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Supporting Information

Palladium/Norbornene-Catalyzed Direct Vicinal Di-Carbo-Functionalization of Indoles: Reaction Development and Mechanistic Study

X. Liu, Y. Zhou, X. Qi, R. Li, P. Liu*, G. Dong**

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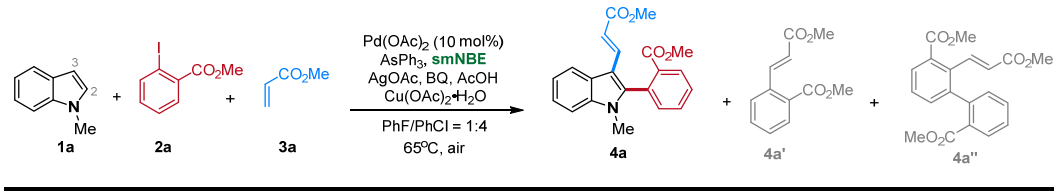
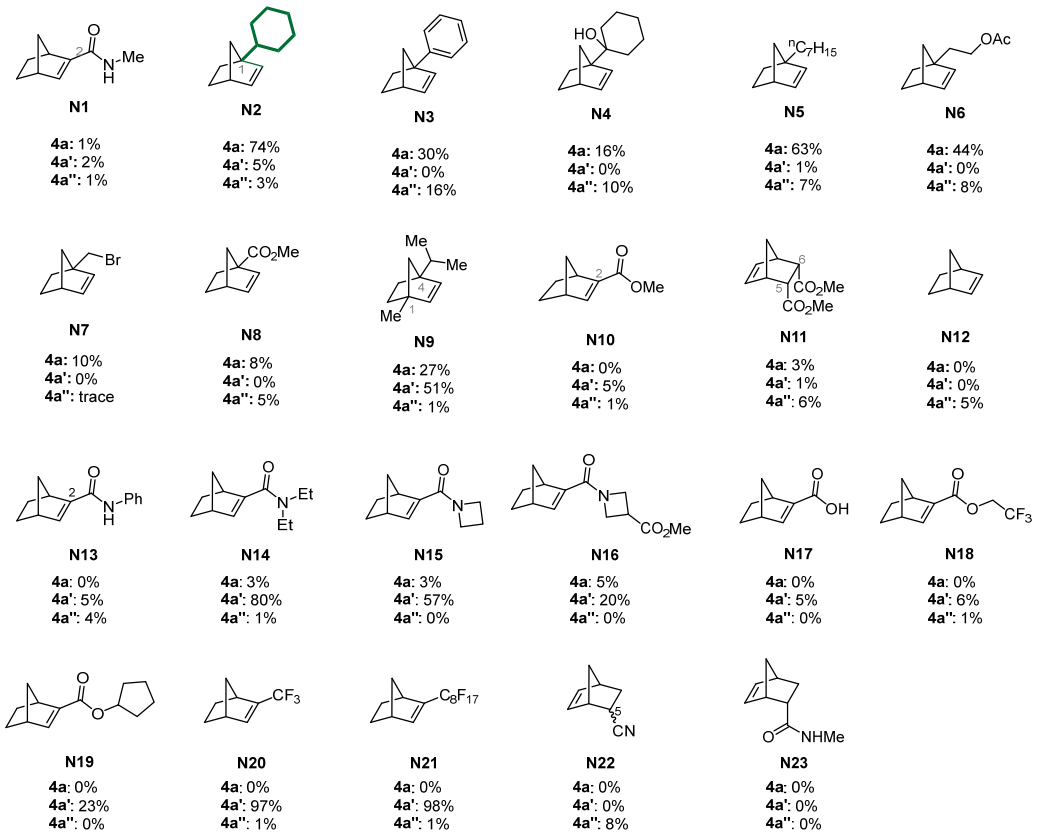
1. General information

Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Ethyl acetate and *t*-butyl methyl ether were used directly without further purification. Reaction temperatures were reported as the temperatures of the bather surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Sodium acetate was purchased from STREM, stored and used directly in the glovebox. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15 x 45 mm 1 dram (4 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried and cooled in a desiccator prior to usage. High resolution mass spectra (HR-MS) were recorded on an Agilent 6530 LC Q-TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V and processed with an Agilent MassHunter Operating System. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with a Bruker DMX 400 (400 MHz, ^{1}H at 400 MHz, ^{13}C at 101 MHz) or Bruker Model DMX 500 (500 MHz, ^{1}H at 500 MHz, ^{13}C at 126 MHz) or Bruker Model DMX 600 (600 MHz, ^{1}H at 600 MHz, ^{13}C at 151 MHz). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00ppm) and were referenced to residual solvent ($CDCl_3$, δ=7.26 ppm (^{1}H) and 77.16 ppm (^{13}C)). All the ^{19}F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Sigma-Aldrich Corporation or Combi-Blocks Inc and were used as received.

2 NBE effect

Table S1: NBE effect of the reaction

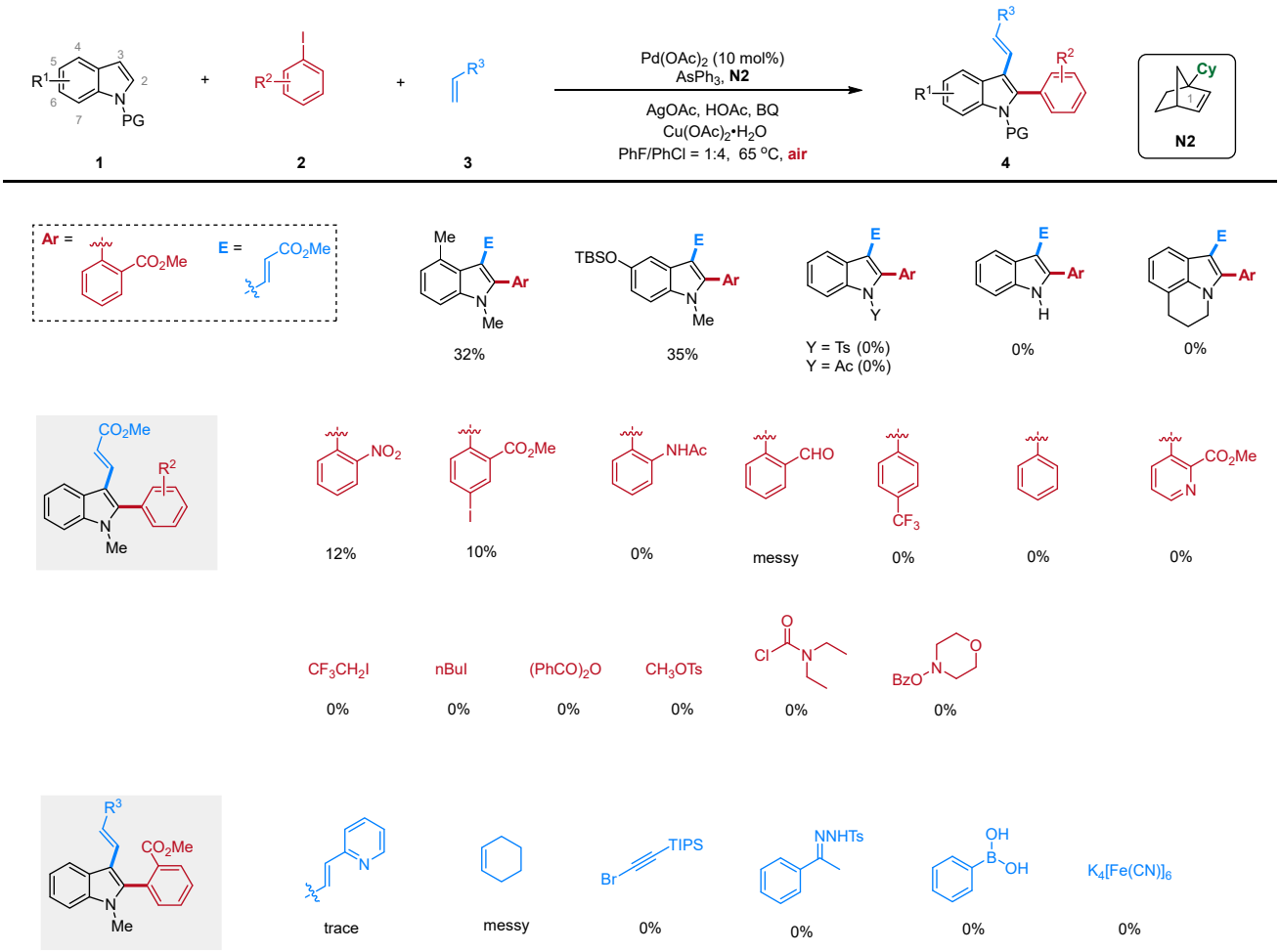




[a] The reaction was run with 0.15 mmol **1a**, 0.1 mmol **2a**, 0.3 mmol **3a**, $Pd(OAc)_2$ (0.01 mmol, 10 mol%), smNBE (0.15 mmol, 1.5 equiv), $AsPh_3$ (0.025 mmol, 25 mol%), BQ (0.06 mmol, 60 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.05 mmol, 50 mol%), AgOAc (0.3 mmol, 3.0 equiv), and HOAc (0.5 mmol, 5.0 equiv) in 0.5 mL solvent (PhF/PhCl = 4:1) for 72 h. Yields were determined by ^1H NMR analysis using dibromomethane as the internal standard. BQ: 1,4-Benzoquinone.

3 Unsuccessful examples

Table S2 unsuccessful examples in the reaction



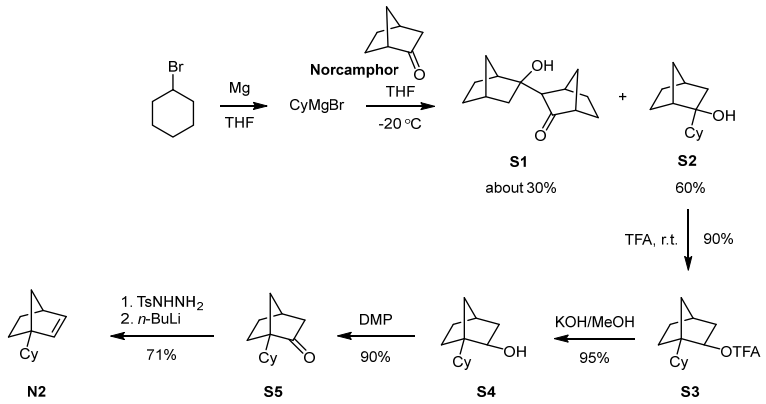
[a] The reaction was run with 0.3 mmol **1**, 0.2 mmol **2**, 0.6 mmol **3**, $Pd(OAc)_2$ (0.02 mmol, 10 mol%), **N2** (0.3 mmol, 1.5 equiv), $AsPh_3$ (0.05 mmol, 25 mol%), BQ (0.12 mmol, 60 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol, 50 mol%), AgOAc (0.6 mmol, 3.0 equiv), and HOAc (1.0 mmol, 5.0 equiv) in 1.0 mL solvent (PhF/PhCl = 4:1) for 72 h.

4. Experimental procedures and characterization data

4.1 Structurally modified norbornenes

SmNBEs **N1**,[1] **N5**,[2] **N9**,[2] **N13**,[3] **N14**,[4] **N10**,[5] **N15**,[1] **N17**,[5] **N19**,[4] **N20**,[5] **N21**,[5] **N23**,[6] **N11**[7] and **N8**[8] are known compounds, which were prepared according to the literature reported procedures. **N22** and **N12** are commercially available and were purchased from Combi-Blocks and Sigma-Aldrich, respectively. **N2**, **N3**, **N4**, **N6**, **N7**, **N8**, **N16** and **N18** were prepared as follows.

Preparation of N2



A dry two-neck round-bottom flask with a reflux condenser under nitrogen atmosphere was charged with magnesium (5.9 g, 245 mmol, 1.5 equiv), anhydrous THF (250 mL, 1.0 M) and a small amount of iodine. Under slightly elevated temperature, 1-bromocyclohexane (30 mL, 245 mmol, 1.5 equiv) was added dropwise over 0.5 h. The reaction was further stirred at room temperature for additional 1.5 h. Then, a solution of norcamphor (18 g, 163 mmol, 1.0 equiv) in dry THF (20 mL) was slowly added to the mixture at -20 °C. The reaction was stirred for 1 h at -20 °C and an additional 1 h at 0 °C. The reaction was quenched by pouring it slowly into a cooled sat. NH_4Cl solution. The water layer was extracted with Et_2O (100 mL × 2) and the combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S2** as a white solid (60% yield, 19 g, 97.5 mmol). The major by-product is **S1** (R_f = 0.3, hexane/ethyl acetate = 10:1).

Trifluoracetic acid (18 mL) was cooled to 0 °C in an open flask. **S2** (18 g, 92.7 mmol) was added in portion, and then the reaction was warmed up to room temperature and stirred for 2 h. The reaction mixture was then slowly

poured into ice water, and the mixture was extracted with diethyl ether (100 mL × 2). The combined organic layers were carefully neutralized with a sodium bicarbonate solution (50 mL), washed with brine (30 mL), dried over $NaSO_4$, and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane = 100%, visualization on TLC with CAN) to yield **S3** as a colorless oil (90%, 24.2 g, 83.4 mmol).

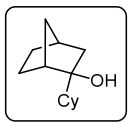
To an open flask charged with KOH (9.2 g, 165 mmol, 2.0 equiv) and methanol (165 mL, 1 M) at 0 °C, **S3** (24 g, 82.7 mmol, 1.0 equiv) was slowly added and the mixture was stirred at room temperature for 2 h. Then, the reaction was quenched by slowly pouring it into ice water, and the mixture was neutralized with a sat. NH_4Cl solution. After removing the methanol under vacuum, the water layer was extracted with Et_2O (100 mL × 2). The combined organic layers were dried over anhydrous $NaSO_4$, and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S4** as a white solid (95%, 15.2 g, 78.5 mmol).

To an ice-cooled solution of **S4** (15.1 g, 78.0 mmol, 1.0 equiv) in 300 mL dichloromethane was slowly added Dess-Martin periodinane (36.3 g, 85.8 mmol, 1.1 equiv), and the mixture was stirred at room temperature for 3 h. After removal of the solvent under reduced pressure, hexane was added to the residue and the mixture was filtered through a pad of silica gel. Then the silica gel pad was rinsed with Et_2O (250 mL), and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S5** as a colorless oil (90%, 9.4 g, 70.1 mmol).

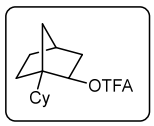
p-Toluenesulfonyl hydrazide (13.0 g, 70.0 mmol, 1.0 equiv) was dissolved in refluxing methanol. (Note: the amount of methanol needs to be minimal to dissolve sulfonyl hydrazine.) Then **S5** (9.4 g, 70.0 mmol, 1.0 equiv) was added to this solution together with a few drops of formic acid. After refluxing for 3 h, white solid precipitated from the solution. The solid was filtered, washed with hexanes, and dried in vacuo. The crude white solid was directly used in the next step.

In a dried Schlenk flask, the white solid from the above reaction (20.1 g, 56 mmol, 1.0 equiv) was dissolved in tetrahydrofuran (200 mL). At 0 °C, *n*-butyl lithium (67 mL, 168 mmol, 2.5 M, 3.0 equiv) was slowly added into the reaction mixture. Afterwards, the mixture was warmed to 75 °C slowly, during which the mixture started to bubble, and the reaction mixture became dark red in the end. The reaction was stirred at 75 °C for 30 min before cooled to 0 °C, which was then slowly poured into an ice-cooled NH_4Cl solution. After extraction with diethyl ether, the residue

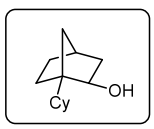
was purified by flash column chromatography (hexane) on silica gel to yield **N2** as a colorless oil (71% for two steps, 9.7 g, 49.7 mmol).



S2: White solid. R_f = 0.35 (hexane/ethyl acetate = 10:1). Mp = 57 – 59 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.34 – 2.32 (m, 1H), 2.20 (t, *J* = 4.8 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.86 – 1.77 (m, 4H), 1.75 – 1.66 (m, 2H), 1.61 – 1.54 (m, 1H), 1.46 (dt, *J* = 10.0, 2.1 Hz, 1H), 1.37 – 1.28 (m, 2H), 1.25 (tt, *J* = 6.8, 2.1 Hz, 3H), 1.22 – 1.16 (m, 2H), 1.13 – 1.05 (m, 2H), 1.00 (dd, *J* = 12.9, 3.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 81.3, 46.7, 44.9, 43.6, 38.5, 37.1, 28.2, 27.4, 26.9, 26.7, 26.7, 25.8, 22.6. **IR** (KBr): υ 3480, 2929, 2851, 1448, 1307, 1166, 1012, 976 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{23}O$ ($M+H^+$): 195.1742, found: 195.1732.

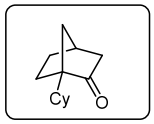


S3: Colorless oil (dr = 9:1). R_f = 0.55 (hexane = 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.93 (dd, *J* = 7.1, 1.9 Hz, 1H), 2.27 (t, *J* = 3.8 Hz, 1H), 1.97 (ddd, *J* = 13.8, 7.0, 2.5 Hz, 1H), 1.77 (ddt, *J* = 13.1, 6.3, 2.4 Hz, 1H), 1.73 – 1.64 (m, 3H), 1.61 – 1.49 (m, 5H), 1.39 (dq, *J* = 10.1, 2.0 Hz, 1H), 1.33 – 1.26 (m, 2H), 1.25 – 1.20 (m, 1H), 1.19 – 1.09 (m, 3H), 0.99 (ddt, *J* = 12.0, 7.8, 2.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9 (d, *J* = 41.9 Hz), 114.65 (dd, *J* = 286.1 Hz), 82.0, 54.4, 40.5, 37.8, 37.1, 35.1, 29.4, 29.2, 28.4, 26.7, 26.7, 26.5, 25.0. **IR** (KBr): υ 2928, 2854, 1779, 1450, 1387, 1345, 1222, 1163, 1055, 989, 724 cm^{-1}. **HRMS** (EI): Calculated for $C_{15}H_{21}F_3O_2$ (M^+): 290.1488, found: 290.1508.

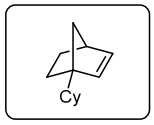


S4: White solid. R_f = 0.25 (hexane/ethyl acetate = 10:1). Mp = 58 – 60 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.71 – 3.67 (m, 1H), 2.14 (dq, *J* = 4.4, 1.9 Hz, 1H), 1.80 – 1.64 (m, 6H), 1.56 (dtd, *J* = 10.8, 3.7, 2.0 Hz, 1H), 1.47 – 1.41 (m, 3H), 1.34 (ddt, *J* = 13.4, 5.1, 2.6 Hz, 1H), 1.29 (dt, *J* = 12.6, 3.4 Hz, 1H), 1.26 – 1.17 (m, 3H), 1.16 – 1.08 (m,

3H), 1.04 – 0.93 (m, 1H), 0.80 (ddd, J = 9.4, 7.2, 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 74.8, 54.7, 42.7, 36.7, 36.6, 34.9, 29.8, 29.1, 28.6, 26.8, 26.8, 26.7, 25.0. **IR** (KBr): υ 3371, 2925, 2850, 1448, 1297, 1074, 1062, 1026, 1010, 945 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{23}O$ ($M+H^+$): 195.1743, found: 195.1738.

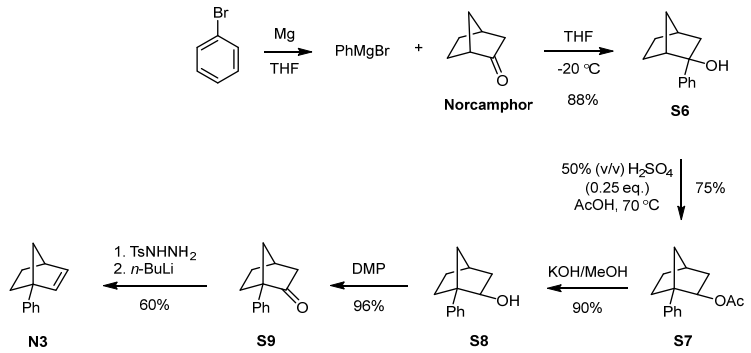


S5: Colorless oil. R_f = 0.4 (hexane/ethyl acetate = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.52 (q, J = 3.2 Hz, 1H), 2.05 (ddd, J = 17.6, 4.6, 2.1 Hz, 1H), 1.93 (dd, J = 17.6, 4.3 Hz, 1H), 1.84 – 1.57 (m, 9H), 1.49 – 1.40 (m, 2H), 1.26 (dddd, J = 16.3, 12.8, 9.8, 1.7 Hz, 3H), 1.18 – 1.08 (m, 2H), 0.99 (qd, J = 12.5, 3.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.9, 61.2, 47.0, 39.1, 36.6, 33.6, 29.4, 28.6, 28.1, 26.7, 26.7, 26.5, 26.5. **IR** (KBr): υ 2924, 2851, 1738, 1449, 1407, 1293, 1169, 1062, 964 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{21}O$ ($M+H^+$): 193.1587, found: 193.1575.



N2: Colorless oil. R_f = 0.85 (hexane = 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.99 (dd, J = 5.8, 3.0 Hz, 1H), 5.94 (d, J = 5.8 Hz, 1H), 2.80 – 2.77 (m, 1H), 1.78 (tddd, J = 12.8, 11.4, 6.3, 1.6 Hz, 4H), 1.74 – 1.66 (m, 2H), 1.56 – 1.51 (m, 1H), 1.50 – 1.46 (m, 1H), 1.29 – 1.24 (m, 3H), 1.20 – 1.12 (m, 2H), 1.10 – 1.02 (m, 2H), 0.99 – 0.94 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.8, 135.3, 58.4, 49.9, 42.0, 40.6, 30.3, 29.9, 27.6, 26.9, 26.9, 26.8. **IR** (KBr): υ 3055, 2926, 2852, 1448, 1345, 1265, 907, 715, 704 cm^{-1}. **HRMS** (EI): Calculated for $C_{13}H_{20}$ (M^+): 176.1560, found: 176.1570. Spectral data are in accordance with the literature.[2]

Preparation of N3



A dry two-neck round-bottom flask with a reflux condenser under nitrogen atmosphere was charged with magnesium (1.8 g, 75 mmol, 1.5 equiv), anhydrous THF (75 mL, 1.0 M) and a small amount of iodine. Under a slightly elevated temperature, bromobenzene (30 mL, 75 mmol, 1.5 equiv) was added dropwise over 0.5 h. The reaction was further stirred at room temperature for additional 1.5 h. Then, a solution of norcamphor (5.5 g, 50 mmol, 1.0 equiv) in dry THF (10 mL) was slowly added to the mixture at -20 °C. The mixture was stirred for 1 h at -20 °C and an additional 1 h at 0 °C. The reaction was quenched by pouring it slowly into a cooled sat. NH_4Cl solution. The water layer was extracted with Et_2O (50 mL × 2) and the combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S6** as a white solid (88% yield, 8.3 g, 44 mmol).

Acetic acid (18 mL) was added to a flask charged with **S6** (8.3 g, 44 mmol, 1.0 equiv) at room temperature. Then, sulfuric acid (50% v/v, 1.2 mL, 11.0 mmol, 0.25 equiv) was added slowly to the reaction before it was warmed up to 70 °C and stirred for 2 h. The reaction mixture was cooled to room temperature before it was quenched by slowly pouring into ice water, and the mixture was extracted with diethyl ether (50 mL × 2). The combined organic layers were carefully neutralized with a sodium bicarbonate solution (30 mL), washed with brine (30 mL), dried over $NaSO_4$, and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 15:1, visualization on TLC with CAN) to yield **S7** as a colorless oil (75%, 7.6 g, 33 mmol).

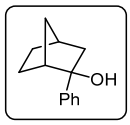
To an open flask charged with KOH (3.4 g, 60 mmol, 2.0 equiv) and methanol (165 mL, 1 M) at 0 °C, **S7** (6.9 g, 30 mmol, 1.0 equiv) was slowly added and stirred at room temperature for 2 h. Then, the reaction was quenched by slowly pouring it into ice water and neutralizing it with sat. NH_4Cl solution. After removing the methanol under vacuum, the water layer was extracted with Et_2O (50 mL × 2). The combined organic layers were dried over

anhydrous $NaSO_4$, and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S8** as a white solid (90%, 5.1 g, 27 mmol).

To an ice-cooled solution of **S8** (5.0 g, 26.6 mmol, 1.0 equiv) in 100 mL dichloromethane was slowly added Dess-Martin periodinane (12.4 g, 29.3 mmol, 1.1 equiv) and stirred at room temperature for 3 h. After removal of the solvent under reduced pressure, hexane was added to the residue and filtered through a pad of silica gel. Then the silica gel pad was rinsed with Et_2O (100 mL), and the crude was concentrated under reduced pressure The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1, visualization on TLC with CAN) to yield **S9** as a colorless oil (96%, 4.7 g, 25.5 mmol).

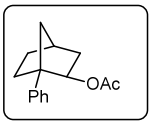
p-Toluenesulfonyl hydrazide (4.7 g, 25.0 mmol, 1.0 equiv) was dissolved in refluxing methanol. (Note: the amount of methanol needs to be minimal to dissolve sulfonyl hydrazine.) Then **S9** (4.7 g, 25 mmol, 1.0 equiv) was added to the reaction mixture with a few drops of formic acid. After refluxing for 3 h, white solid precipitated from the solution. The solid was filtered, washed with hexanes, and dried in vacuo. The crude white solid was directly used in the next step.

In a dried Schlenk flask, the white solid from the above reaction (7.4 g, 21.0 mmol, 1.0 equiv) was dissolved in tetrahydrofuran (50 mL). At 0 ºC, *n*-butyl lithium (25.2 mL, 63 mmol, 2.5 M, 3.0 equiv) was slowly added into the reaction mixture, during which the mixture started to bubble. Afterwards, the mixture was warmed to 75 ºC, and the reaction mixture became dark red in the end. The reaction was stirred at 75 ºC for 30 min before cooled to 0 ºC and was then slowly poured into an ice-cooled NH_4Cl solution. After extraction with diethyl ether, the residue was purified by flash column chromatography (hexane) on silica gel to yield **N3** as a colorless oil (60% for two steps, 2.1 g, 12.6 mmol).

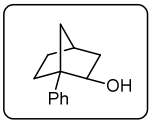


S6: White solid. R_f = 0.3 (hexane/ethyl acetate = 10:1). Mp = 44 – 46 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.35 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.24 (dd, *J* = 8.2, 6.6 Hz, 1H), 2.61 (d, *J* = 3.9 Hz, 1H), 2.35 – 2.29 (m, 2H), 2.23 – 2.16 (m, 1H), 1.71 (d, *J* = 4.0 Hz, 1H), 1.65 (d, *J* = 3.5 Hz, 1H), 1.58 – 1.44 (m, 4H), 1.35 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.0, 128.3, 126.9, 125.9, 80.8, 47.2, 46.6, 38.8, 37.6, 29.1, 22.3. **IR** (KBr): υ 3396,

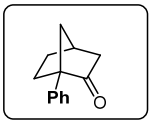
2953, 2869, 1493, 1446, 1307, 1143, 1072, 1015, 699 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{15}$ ($M-H_2O^+$): 171.1168, found: 171.1171.



S7: White solid. R_f = 0.5 (hexane/ethyl acetate = 10:1). Mp = 41 – 43 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.19 (tt, *J* = 6.0, 2.1 Hz, 1H), 5.00 (dt, *J* = 7.1, 2.1 Hz, 1H), 2.38 (t, *J* = 4.0 Hz, 1H), 2.08 – 2.03 (m, 1H), 2.00 (ddd, *J* = 13.6, 6.9, 2.4 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 6H), 1.63 (ddd, *J* = 13.5, 4.8, 2.4 Hz, 1H), 1.59 – 1.55 (m, 1H), 1.40 – 1.33 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.2, 141.9, 127.7, 127.5, 126.1, 78.7, 55.0, 40.9, 38.7, 35.5, 32.8, 30.0, 21.0. **IR** (KBr): υ 2957, 2872, 1731, 1497, 1448, 1372, 1246, 1074, 699 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{15}$ ($M-AcOH^+$): 171.1168, found: 171.1170.

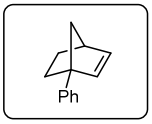


S8: White solid. R_f = 0.25 (hexane/ethyl acetate = 10:1). Mp = 68 – 70 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 3.82 (dq, *J* = 6.8, 1.8 Hz, 1H), 2.34 (td, *J* = 3.4, 1.7 Hz, 1H), 2.04 (dd, *J* = 9.5, 2.0 Hz, 1H), 1.86 (ddd, *J* = 13.2, 6.9, 2.4 Hz, 1H), 1.73 – 1.65 (m, 2H), 1.61 (dddd, *J* = 13.3, 9.0, 6.5, 4.1 Hz, 2H), 1.47 – 1.42 (m, 1H), 1.35 – 1.31 (m, 1H), 1.29 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.2, 128.4, 127.7, 126.5, 77.5, 56.5, 41.3, 36.9, 35.4, 32.2, 30.3. **IR** (KBr): υ 3420, 2956, 2869, 1495, 1302, 1081, 1040, 1011, 761, 700 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{15}$ ($M-H_2O^+$): 171.1168, found: 171.1169.



S9: White solid. R_f = 0.4 (hexane/ethyl acetate = 10:1). Mp = 42 – 43 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.31 – 7.26 (m, 3H), 2.74 (dt, *J* = 4.8, 2.3 Hz, 1H), 2.33 (ddd, *J* = 17.8, 4.7, 2.2 Hz, 1H), 2.21 (dq, *J* = 10.2, 1.8 Hz, 1H), 2.14 (dd, *J* = 17.8, 4.4 Hz, 1H), 2.09 – 1.96 (m, 4H), 1.69 – 1.62 (m, 1H). **^{13}C NMR** (126

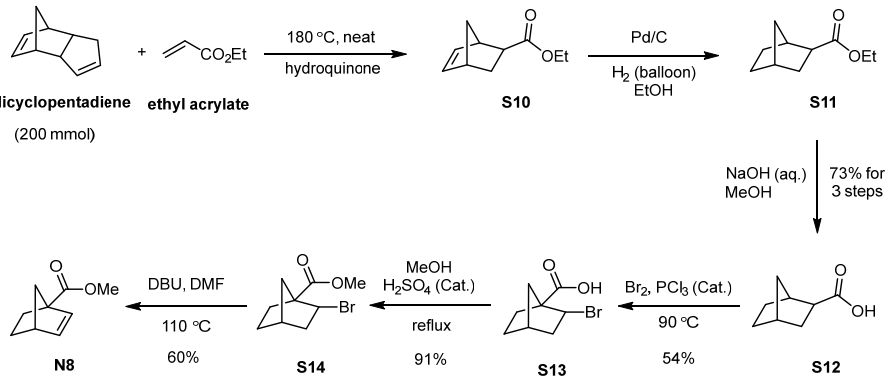
MHz, $CDCl_3$) δ 215.5, 138.1, 128.2, 127.6, 126.9, 61.7, 46.0, 42.2, 33.8, 31.0, 28.8. **IR** (KBr): υ 2957, 2877, 2360, 1745, 1499, 1297, 1082, 933, 697 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{15}O$ ($M+H^+$): 187.1117, found: 187.1122.



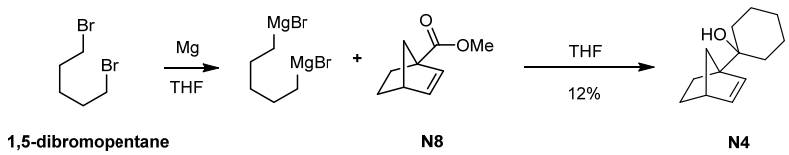
N2: Colorless oil. R_f = 0.85 (hexane = 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.20 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.16 (d, *J* = 5.6 Hz, 1H), 3.04 (dd, *J* = 3.0, 1.5 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.75 – 1.69 (m, 1H), 1.58 – 1.53 (m, 1H), 1.52 – 1.45 (m, 1H), 1.31 – 1.24 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 138.8, 135.8, 128.3, 126.8, 126.1, 57.7, 53.7, 42.9, 31.7, 27.5. **IR** (KBr): υ 3058, 2962, 2868, 1603, 1496, 1446, 1340, 1032, 903, 697 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{15}$ ($M+H^+$): 171.1168, found: 171.1167. Spectral data are in accordance with the literature.[2]

Preparation of N8

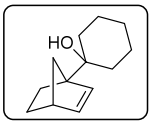
Compound **N8** is a known compound and was prepared according to the reported synthetic route shown below.[8]



Preparation of N4

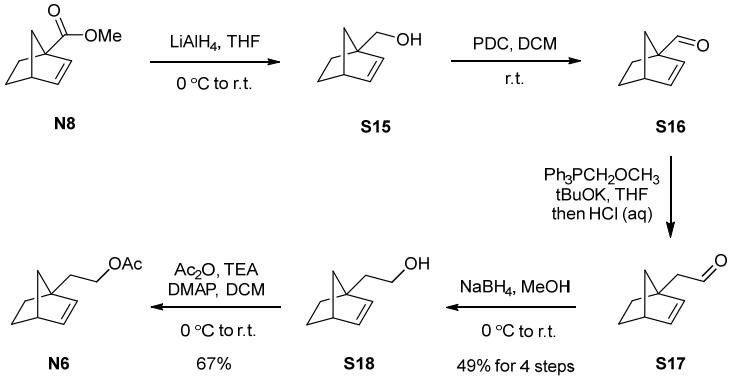


A dry two-neck round-bottom flask under nitrogen atmosphere was charged with magnesium (1.2 g, 50 mmol, 10 equiv), anhydrous THF (50 mL, 0.4 M) and a small amount of iodine. Under slightly elevated temperature, 1,5-dibromopentane (2.7 mL, 20 mmol, 4.0 equiv) was added dropwise over 0.5 h. The reaction was further stirred at room temperature for additional 1.5 h. Then, about 31 mL of the Grignard reagent (about 12.5 mmol, 2.5 equiv) was added to a solution of **N8** (760 mg, 5 mmol, 1.0 equiv) in dry THF (10 mL) slowly at 0 °C. The resulting mixture was stirred for 1 h at the same temperature before the reaction was quenched by adding a sat. NH_4Cl solution. The water layer was extracted with Et_2O (30 mL × 2) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and then concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 8:1) to yield **N4** as a white solid (12% yield, 115 mg, 0.6 mmol).



N4: White solid. R_f = 0.2 (hexane/ethyl acetate = 10:1). Mp = 73 – 75 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.01 – 5.97 (m, 1H), 2.85 (s, 1H), 1.75 – 1.70 (m, 3H), 1.64 (dt, *J* = 13.4, 3.5 Hz, 2H), 1.60 – 1.56 (m, 2H), 1.53 – 1.35 (m, 3H), 1.32 – 1.29 (m, 1H), 1.27 – 1.24 (m, 1H), 1.19 – 1.11 (m, 2H), 1.11 – 1.06 (m, 1H), 0.96 (ddd, *J* = 10.1, 6.9, 2.6 Hz, 1H), 0.92 – 0.80 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.9, 135.3, 71.6, 64.1, 47.2, 42.0, 34.5, 33.8, 27.1, 25.9, 24.6, 21.6, 21.6. **IR** (KBr): υ 3473, 2932, 2859, 1447, 1339, 1285, 1127, 1035, 956, 709 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{19}$ ($M-H_2O^+$): 175.1481, found: 175.1486.

Preparation of N6



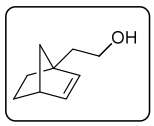
To a suspension of $LiAlH_4$ (570 mg, 15 mmol, 1.5 equiv) in anhydrous THF (30 mL) was slowly added a solution of **N8** (1.5 g, 10 mmol, 1.0 equiv) in THF (5 mL) at 0 °C. The reaction was stirred at room temperature until TLC indicated full conversion of **N8**. The reaction was carefully quenched with a saturated NaCl solution followed by addition of a 3 N HCl solution to reach an acidic solution (pH ~ 1). The layers were separated, and the aqueous phase was extracted with ether (10 mL × 3). The combined organic extracts were washed sequentially with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated under vacuum to give crude **S15**, which was directly used in the next step (>90% yield).

To a stirred solution of crude **S15** (about 10.0 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was added Celite@ (2 g) and pyridinium dichromate (4.5 g, 12 mmol, 1.2 equiv) sequentially at room temperature. The reaction was stirred at room temperature for an additional 5h. The reaction was filtered through a pad of silica gel, washed with DCM, and concentrated carefully under vacuum to give the crude aldehyde **S16** (volatile), which was directly used in the next step.

To a suspension of (methoxymethyl)triphenylphosphonium chloride (4.6 g, 13.5 mmol, 1.5 equiv) in anhydrous THF (50 mL) was added *t*-BuOK (1.5 g, 13.5 mmol, 1.5 equiv) at 0 °C. The mixture was stirred at 0 °C for 1 h, and then a solution of **S16** (1.1 g, 9.0 mmol, 1.0 equiv) in anhydrous THF (15 mL) was added. The reaction was allowed to warm up to room temperature over 3 h, and then hexane (50 mL) was added. The resulting mixture was filtered through a pad of Celite@ and thoroughly washed with hexane. The filtrate was concentrated in vacuo and the residue was diluted with hexane (50 mL). The resulting mixture was filtered through a pad of Celite@ again to remove the remaining triphenylphosphine oxide. After evaporation, the crude methyl ether product was taken up in THF (50 mL) and 3 M HCl (5 mL) at 0 °C. The reaction was allowed to warm up to room temperature over 1 h, and then quenched with saturated aqueous Na_2CO_3 at 0 °C. The aqueous layer was extracted with ether twice. The combined organic layers were washed with water, and then brine, dried over Na_2SO_4, and concentrated carefully under vacuum to give the crude aldehyde **S17** (volatile), which was directly used in the next step.

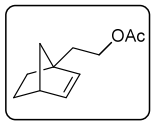
To a stirred solution of crude **S17** (1.1 g, 5.3 mmol, 1.0 equiv) in MeOH (50 mL) was added sodium borohydride (0.3 g, 8.0 mmol, 1.5 equiv) at 0 °C. The reaction was allowed to warm up to room temperature and stirred for an additional 1h before the reaction was quenched with water. After removal of the solvent under reduced pressure, the aqueous layer was extracted with ether twice, washed with brine, dried over Na_2SO_4, and concentrated carefully

under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 8:1) to yield **S18** as a colorless oil (49% yield for 4 steps, 676 mg, 4.9 mmol).



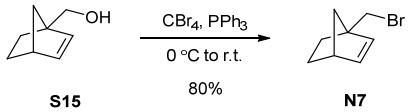
S18: Colorless oil. R_f = 0.2 (hexane/ethyl acetate = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.02 (dd, *J* = 5.7, 3.0 Hz, 1H), 5.87 (d, *J* = 5.7 Hz, 1H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.81 (d, *J* = 3.6 Hz, 1H), 2.04 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.94 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.52 – 1.45 (m, 1H), 1.30 (dd, *J* = 7.9, 2.2 Hz, 1H), 1.05 (td, *J* = 7.1, 4.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.7, 136.1, 61.4, 52.2, 51.8, 42.3, 36.3, 30.7, 26.6. **IR** (KBr): υ 3332, 2951, 2866, 1446, 1344, 1271, 1045, 1011, 711 cm^{-1}. **HRMS** (EI): Calculated for C_9H_{13} ($M\text{-}H_2O^+$): 121.1012, found: 121.1012.

To a stirred solution of **S18** (138 mg, 2.0 mmol, 1.0 equiv) in DCM (10 mL) were added DMAP (122 mg, 1.0 mmol, 0.5 equiv), TEA (0.33 mL, 2.4 mmol, 1.2 equiv), and acetic anhydride (245 mg, 8.0 mmol, 1.2 equiv) at 0 °C. The reaction was allowed to warm up to room temperature and stirred for an additional 1h before the reaction was quenched with saturated NH_4Cl. The aqueous layer was extracted with ether twice, washed with brine, dried over Na_2SO_4, and concentrated carefully under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 8:1) to yield **N6** as a colorless oil (67% yield, 241 mg, 1.3 mmol).

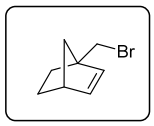


N6: Colorless oil. R_f = 0.6 (hexane/ethyl acetate = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.02 (dd, *J* = 5.7, 3.1 Hz, 1H), 5.85 (d, *J* = 5.7 Hz, 1H), 4.24 – 4.16 (m, 2H), 2.81 (s, 1H), 2.09 – 2.00 (m, 5H), 1.77 – 1.71 (m, 1H), 1.52 – 1.45 (m, 1H), 1.32 – 1.28 (m, 1H), 1.05 (td, *J* = 8.5, 3.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 137.4, 136.1, 63.0, 52.3, 51.8, 42.3, 32.0, 30.4, 26.7, 21.1. **IR** (KBr): υ 2957, 2866, 1742, 1446, 1345, 1366, 1239, 1044, 713 cm^{-1}. **HRMS** (EI): Calculated for $C_{11}H_{17}O_2$ ($M+H^+$): 181.1223, found: 181.1233.

Preparation of N7

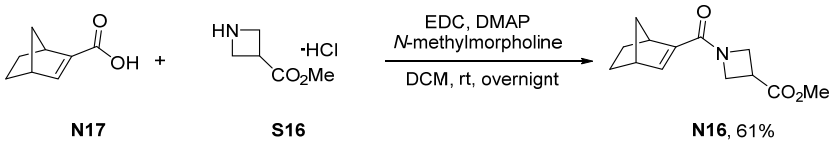


To a stirred solution of **S15** (250 mg, 2.0 mmol, 1.0 equiv) and triphenylphosphine (550 mg, 2.1 mmol, 1.05 equiv) in dry CH_2Cl_2 (10 mL) under N_2 was slowly added carbon tetrabromide (728 mg, 2.2 mmol, 1.1 equiv) at 0 °C. The cooling bath was then removed, and the reaction was stirred at room temperature for an additional 2h. The reaction was quenched with the addition of ethyl acetate (5 mL) and washed with 5% aq. Na_2SO_3, brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane = 100%) to yield **N7** as a colorless oil (80% yield, 297 mg, 1.6 mmol).



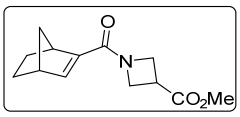
N7: Colorless oil. R_f = 0.7 (hexane = 100%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.10 (dd, *J* = 5.8, 3.1 Hz, 1H), 5.93 (d, *J* = 5.6 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.90 (s, 1H), 1.85 (ddd, *J* = 10.0, 7.1, 3.6 Hz, 1H), 1.65 – 1.59 (m, 1H), 1.43 (dt, *J* = 8.1, 2.4 Hz, 1H), 1.18 (dd, *J* = 6.6, 3.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.6, 136.0, 55.4, 52.0, 42.7, 37.4, 29.8, 27.9. **IR** (KBr): υ 3059, 2964, 2869, 2359, 1446, 1434, 1345, 1241, 907, 711 cm^{-1}. **HRMS** (EI): Calculated for $C_8H_{11}Br$ (M^+): 186.0039, found: 186.0037.

Preparation of N16



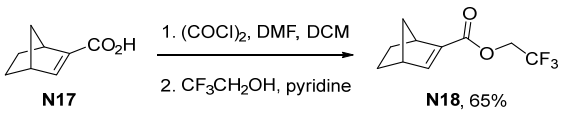
N16 was prepared according to the literature reported procedures.[7] **N17** (2.79 g, 20.2 mmol, 1.0 equiv), **S16** (3.4 g, 22.2 mmol, 1.1 equiv), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (4.65 g, 24.2 mmol, 1.2 equiv), 4-dimethylaminopyridine (246 mg, 2.02 mmol, 10 mol%) and *N*-methylmorpholine (2.04 g, 20.2 mmol, 1.0 equiv) were dissolved in dichloromethane (60 mL). Then, the reaction mixture was stirred at room temperature.

After 12 h, it was diluted with diethyl ether, washed with 1 M HCl, water and brine, dried over $MgSO_4$, and then purified on silica gel (hexanes/acetone = 2:1) to afford **N16** as a white solid (2.87 g, 61%).

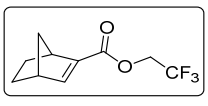


N16: White solid. m. p. = 53.5 – 55.2 °C. R_f = 0.4 (hexane/acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.40 (d, *J* = 3.2 Hz, 1H), 4.53 – 4.05 (m, 4H), 3.75 (s, 3H), 3.43 (p, *J* = 7.6 Hz, 1H), 3.25 (s, 1H), 3.03 – 2.95 (m, 1H), 1.72 (pt, *J* = 5.9, 2.9 Hz, 2H), 1.46 – 1.34 (m, 1H), 1.14 (dd, *J* = 9.0, 4.8 Hz, 2H), 1.10 – 0.98 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 166.6, 142.4, 141.6, 52.3, 47.8, 43.8, 43.0, 33.1, 24.9, 24.8. **IR** (KBr): 2955, 2873, 1737, 1625, 1578, 1432, 1361, 1206, 742 cm^{-1}. **HRMS** (ESI): Calculated for $C_{13}H_{17}NO_3Na$ ($M+Na^+$): 258.1101, found: 258.1095.

Preparation of N18



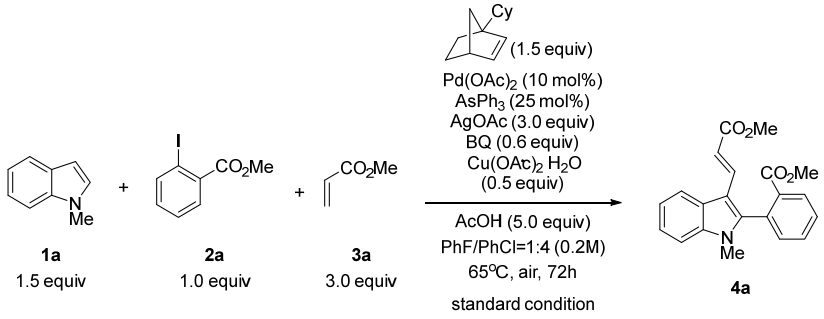
To a solution of **N17** (1.29 g, 9.3 mmol, 1.0 equiv) in DCM (10 mL) with 3 drops of DMF was added oxalyl chloride (1.19 g, 9.3 mmol, 1.0 equiv) dropwise at 0 °C. The reaction mixture was stirred at room temperature for another 1 h until the bubbling stopped. Then a mixture of 2,2,2-trifluoroethanol (1.86 g, 18.6 mmol, 2.0 equiv) and pyridine (2.94 g, 37.2 mmol, 4.0 equiv) was added dropwise. The reaction mixture was stirred at room temperature for another 3 h until the reaction was completed. The organic layer was washed with 1 M hydrochloric acid and then concentrated under vacuum. The corresponding ester-substituted NBE was isolated after silica gel chromatography (hexane/Et_2O = 20:1) as a colorless oil (1.30 g, 65%).



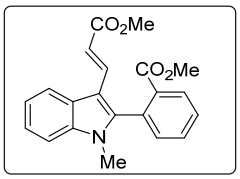
N18: Colorless oil. R_f = 0.3 (hexane/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 3.1 Hz, 1H), 4.50 (qd, *J* = 8.5, 3.9 Hz, 2H), 3.29 (s, 1H), 3.06 (s, 1H), 1.85 – 1.70 (m, 2H), 1.55 – 1.47 (m, 1H), 1.27 – 1.20 (m, 1H), 1.09 (qd, *J* = 8.1, 2.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 150.0, 139.2, 123.3 (q, *J* = 277.1 Hz),

60.2 (q, J = 36.4 Hz), 48.3, 43.9, 42.0, 24.6, 24.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.78. **IR** (KBr): υ 2974, 2884, 1749, 1413, 1287, 1260, 1171, 1095, 975 cm^{-1}. **HRMS** (ESI): Calculated for $C_{10}H_{12}F_3O_2$ ($M+H^+$): 221.0784, found: 221.0774.

4.2 General Procedure of Vicinal Difunctionalization of Indoles

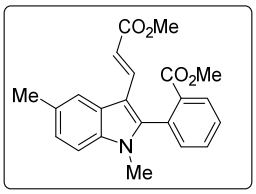


A flame-dried 4.0 mL vial was charged with $Pd(OAc)_2$ (4.6 mg, 0.02 mmol, 10 mol%), $AsPh_3$ (15.2 mg, 0.05 mmol, 25 mol%), BQ (13.0 mg, 0.12 mmol, 0.6 equiv.), $Cu(OAc)_2.H_2O$ (20.0 mg, 0.1 mmol, 0.5 equiv.), NBE-Cy (53.0 mg, 0.3 mmol, 1.5 equiv.), AgOAc (100 mg, 0.6 mmol, 3.0 equiv.), indole **1a** (39.4 mg, 0.2 mmol, 1.5 equiv.) and aryl iodide **2a** (52.4 mg, 0.2 mmol, 1.0 equiv.). Then, 1.0 mL chlorobenzene /fluorobenzene = 4:1 was added. After acrylate **3a** (51.6 mg/60 µL, 0.6 mmol, 3.0 equiv.) and AcOH (60 mg/56 µL, 1.0 mmol, 5.0 equiv.) were added, the vial was tightly sealed and stirred on a pie-block preheated to 65 ºC for 72 hours. After completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate and the combined filtrate was concentrated. The residue was loaded to a small amount of silica gel and subjected to flash column chromatography to give the desired difunctionalization product **4a**.

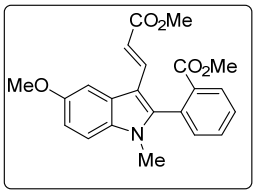


4a: Light yellow solid (71%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 123.1– 123.6 ºC. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (dd, J = 7.7, 1.4 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.48 (d, J = 15.9 Hz,

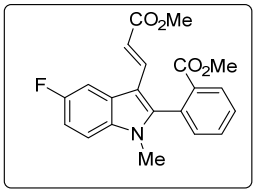
1H), 7.41 – 7.27 (m, 4H), 6.33 (d, *J* = 15.9 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 166.4, 144.7, 138.6, 137.8, 133.0, 132.5, 131.7, 131.4, 131.1, 129.9, 125.8, 123.0, 121.7, 120.8, 111.9, 110.3, 110.0, 52.5, 51.3, 30.9. **IR** (KBr): 2949, 1727, 1620, 1470, 1429, 1434, 1408, 1373, 1286, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{19}NO_4Na$ ($M+Na^+$): 372.1206, found: 372.1206.



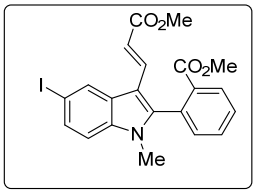
4b: Light yellow oil (65%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.16 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.52 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.46 – 7.34 (m, 2H), 7.20 – 7.15 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 3.62 (s, 3H), 3.61 (s, 3H), 3.51 (s, 3H), 2.52 (s, 3H). **^{13}C NMR** (101 MHz, Acetone) δ 168.6, 166.9, 145.8, 139.0, 137.3, 133.7, 133.2, 133.1, 132.0, 131.6, 131.3, 130.8, 126.8, 125.0, 120.9, 111.7, 110.8, 110.2, 52.6, 51.1, 31.1, 21.7. **IR** (KBr): 2948, 1727, 1615, 1478, 1434, 1407, 1372, 1286, 1260, 1159 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{21}NO_4Na$ ($M+Na^+$): 386.1363, found: 386.1367.



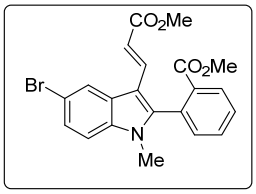
4c: Light yellow solid (52%). R_f = 0.3 (hexane/ ethyl acetate = 2:1). Mp = 153.1– 153.5 ºC. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.48 (d, *J* = 15.9 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.28 (d, *J* = 8.9 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 3.92 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 166.4, 155.8, 145.0, 138.7, 133.0, 132.9, 132.5, 131.7, 131.5, 131.0, 129.9, 126.3, 112.6, 111.2, 110.7, 109.9, 103.2, 56.2, 52.5, 51.3, 31.0. **IR** (KBr): 2948, 1726, 1614, 1484, 1432, 1409, 1292, 1261, 1160, 1046 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{21}NO_5Na$ ($M+Na^+$): 402.1312, found: 402.1312.



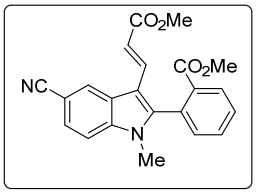
4d: Light yellow solid (65%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 155.4– 155.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 – 7.59 (m, 3H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.37 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.30 (dd, *J* = 8.9, 4.4 Hz, 1H), 7.07 (td, *J* = 9.0, 2.4 Hz, 1H), 6.21 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.46 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.8, 166.2, 160.4, 158.0, 145.9, 138.1, 134.3, 132.9, 132.6, 131.6, 131.1, 130.1, 126.1 (d, *J* = 10.0 Hz), 112.0, 111.1 (d, *J* = 26.0 Hz), 110.7 (d, *J* = 9.7 Hz), 110.1 (d, *J* = 4.4 Hz), 106.2 (d, *J* = 24.6 Hz), 52.6, 51.4, 31.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.1. **IR** (KBr): 2950, 1726, 1618, 1481, 1434, 1409, 1373, 1289, 1194, 1161 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}FNO_4Na$ ($M+Na^+$): 390.1112, found: 390.1113.



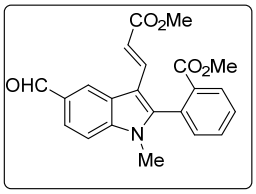
4e: Light yellow oil (50%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 1.4 Hz, 1H), 8.18 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.58 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.40 (d, *J* = 16.0 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 166.2, 145.1, 137.8, 136.9, 132.8, 132.6, 131.6, 131.3, 131.2, 130.9, 130.2, 129.4, 128.0, 112.6, 111.9, 109.4, 85.4, 52.6, 51.4, 30.9. **IR** (KBr): 2948, 1726, 1621, 1467, 1433, 1367, 1284, 1262, 1167, 1092 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}BrNO_4Na$ ($M+Na^+$): 498.0173, found: 498.0173.



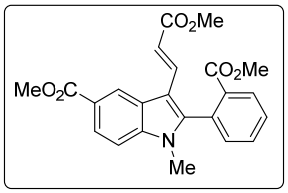
4f: White solid (64%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 161.7– 162.1 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.08 (d, *J* = 1.7 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.44 – 7.35 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 166.2, 145.5, 137.8, 136.4, 132.8, 132.6, 131.5, 131.2, 130.9, 130.2, 127.3, 125.8, 123.3, 115.0, 112.6, 111.4, 109.7, 52.6, 51.4, 31.0. **IR** (KBr): 2949, 1726, 1622, 1467, 1433, 1405, 1366, 1285, 1168, 1092 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}BrNO_4Na$ ($M+Na^+$): 450.0311, found: 450.0310.



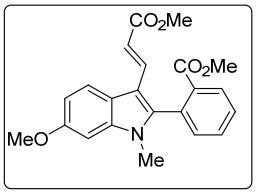
4g: White solid (36%). R_f = 0.3 (hexane/ ethyl acetate = 2:1). Mp = 181.6 – 182.0 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.49 – 8.44 (m, 1H), 8.25 – 8.20 (m, 1H), 7.88 (td, *J* = 7.5, 1.5 Hz, 1H), 7.81 (td, *J* = 7.7, 1.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.40 (d, *J* = 16.1 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (101 MHz, Acetone) δ 168.2, 166.6, 147.7, 140.2, 137.2, 133.6, 133.6, 132.6, 131.7, 131.4, 131.2, 126.4, 126.2, 126.0, 120.7, 114.3, 112.4, 110.9, 105.2, 52.7, 51.3, 31.5. **IR** (KBr): 2950, 2221, 1724, 1626, 1478, 1434, 1406, 1376, 1287, 1264 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{18}N_2O_4Na$ ($M+Na^+$): 397.1159, found: 397.1162.



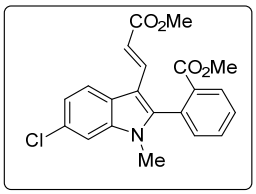
4h: Light yellow oil (52%). R_f = 0.2 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.47 – 8.44 (m, 1H), 8.21 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.90 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.50 – 7.43 (m, 2H), 7.39 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 168.5, 166.1, 146.2, 141.0, 137.3, 132.9, 132.8, 131.4, 131.3, 130.9, 130.8, 130.4, 125.7, 125.4, 123.5, 113.9, 111.5, 110.6, 52.6, 51.5, 31.2. **IR** (KBr): 2949, 2359, 1724, 1685, 1623, 1574, 1457, 1435, 1405, 1288 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{19}NO_5Na$ ($M+Na^+$): 400.1155, found: 400.1158.



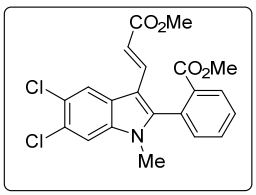
4i: Light yellow solid (51%). R_f = 0.2 (hexane/ ethyl acetate = 2:1). Mp = 163.2 – 163.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.15 (s, 1H), 7.97 (s, 2H), 7.73 – 7.63 (m, 2H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.38 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.97 (s, 3H), 3.71 (s, 3H), 3.65 (s, 3H), 3.53 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 167.9, 166.1, 147.3, 137.8, 137.2, 132.7, 132.7, 131.4, 131.3, 130.9, 130.3, 129.3, 124.4, 122.6, 120.2, 113.0, 112.3, 110.4, 52.6, 52.2, 51.4, 31.1. **IR** (KBr): 2950, 1715, 1623, 1464, 1433, 1379, 1289, 1264, 1242, 1171 cm^{-1}. **HRMS** (ESI): Calculated for $C_{23}H_{21}NO_6Na$ ($M+Na^+$): 430.1261, found: 4301263.



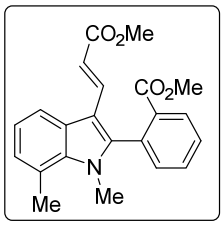
4j: Light yellow oil (51%). R_f = 0.3 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.64 (dtd, *J* = 21.8, 7.5, 1.4 Hz, 2H), 7.43 (d, *J* = 15.9 Hz, 1H), 7.37 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 166.4, 157.0, 143.9, 138.8, 138.6, 133.1, 132.4, 131.8, 131.4, 131.0, 129.8, 121.5, 119.9, 111.6, 110.7, 110.3, 94.0, 55.9, 52.5, 51.3, 30.9. **IR** (KBr): 2949, 1727, 1617, 1575, 1472, 1433, 1381, 1350, 1290, 1169 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{21}NO_5Na$ ($M+Na^+$): 402.1312, found: 402.1310.



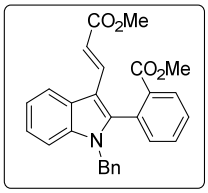
4k: Light yellow oil (61%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.20 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 3.55 (s, 3H). **^{13}C NMR** (101 MHz, Acetone) δ 168.4, 166.7, 146.6, 139.3, 138.1, 136.2, 133.6, 133.4, 132.8, 131.5, 131.1, 129.0, 125.1, 122.5, 122.2, 112.9, 111.3, 110.5, 52.7, 51.2, 31.3. **IR** (KBr): 2949, 1726, 1621, 1473, 1433, 1407, 1287, 1289, 1170, 1091 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}ClNO_4Na$ ($M+Na^+$): 406.0817, found: 406.0817.



4l: Light yellow solid (55%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 182.9 – 183.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.01 (s, 1H), 7.73 – 7.63 (m, 2H), 7.48 (s, 1H), 7.40 – 7.34 (m, 2H), 6.22 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.0, 146.2, 137.4, 136.6, 132.8, 132.7, 131.4, 131.3, 130.6, 130.4, 126.8, 125.7, 125.2, 121.7, 113.1, 111.6, 109.7, 52.6, 51.5, 31.1. **IR** (KBr): 2949, 1726, 1623, 1469, 1435, 1406, 1324, 1291, 1169, 1092 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}Cl_2NO_4$ ($M+H^+$): 418.0607, found: 418.0611.

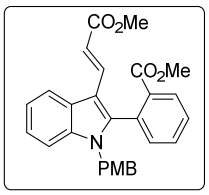


4m: Light yellow solid (62 %). R_f = 0.2 (hexane / ethyl acetate = 5:1). Mp = 167.5 – 168.0 °C. **^{1}H NMR** (400 MHz, Benzene-d_6) δ 8.01 (d, *J* = 16.0 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.03 – 6.96 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 3.43 (s, 3H), 3.22 (s, 3H), 3.12 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.34, 166.26, 145.05, 138.26, 137.07, 132.85, 132.63, 132.08, 131.95, 130.76, 129.54, 127.57, 126.28, 122.04, 121.64, 119.11, 113.03, 110.72, 51.81, 50.78, 33.99, 20.22. **IR** (KBr): 2950, 2923, 1728, 1618, 1540, 1475, 1456, 1434, 1286, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{22}NO_4$ ($M+H^+$): 364.1543, found: 364.1544.

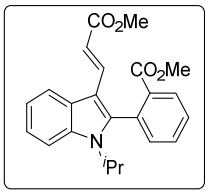


4n: Light yellow oil (41%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 – 8.09 (m, 1H), 8.02 – 7.97 (m, 1H), 7.60 – 7.52 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.26 (td, *J* = 4.3, 3.5, 2.0 Hz, 4H), 7.21 – 7.17 (m, 3H), 6.92 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 5.24 – 4.95 (m, 2H), 3.71 (s, 3H), 3.61 (s,

3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 166.3, 144.5, 138.4, 137.5, 136.9, 133.1, 132.3, 131.8, 131.1, 131.0, 129.9, 128.7, 127.6, 126.6, 126.1, 123.2, 121.8, 120.8, 112.5, 111.0, 110.9, 52.5, 51.4, 48.2. **IR** (KBr): 2949, 1727, 1621, 1574, 1462, 1419, 1365, 1292, 1263, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{27}H_{23}NO_4Na$ ($M+Na^+$): 448.1519, found: 448.1522.

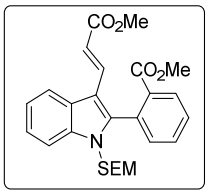


4o: Light yellow oil (44%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.14 – 8.10 (m, 1H), 8.01 – 7.96 (m, 1H), 7.60 – 7.53 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.31 – 7.24 (m, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.74 – 6.70 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.13 (d, *J* = 16.3 Hz, 1H), 4.93 (d, *J* = 16.3 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 166.3, 159.0, 144.5, 138.4, 137.5, 133.1, 132.3, 131.8, 131.2, 131.0, 129.9, 129.0, 127.9, 126.1, 123.1, 121.7, 120.8, 114.1, 112.4, 111.0, 110.8, 55.4, 52.5, 51.3, 47.7. **IR** (KBr): 2949, 2837, 1727, 1620, 1513, 1461, 1288, 1173, 1038, 741 cm^{-1}. **HRMS** (ESI): Calculated for $C_{28}H_{26}NO_5$ ($M+Na^+$): 456.1805, found: 456.1809.

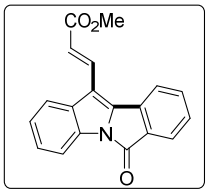


4p: Light yellow oil (50%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.16 – 8.11 (m, 1H), 7.99 – 7.94 (m, 1H), 7.64 (dddd, *J* = 15.3, 7.9, 4.4, 2.0 Hz, 3H), 7.39 (dd, *J* = 15.9, 1.0 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.27 – 7.25 (m, 2H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.20 (p, *J* = 7.0 Hz, 1H), 3.69 (d, *J* = 1.0 Hz, 3H), 3.62 (d, *J* = 1.0 Hz, 3H), 1.59 (d, *J* = 7.0 Hz, 3H), 1.50 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 166.5, 144.3, 138.5, 135.4, 132.4, 132.3, 132.1, 132.1, 131.0, 129.9, 127.1, 122.3, 121.2, 121.0, 112.8, 111.8, 110.0, 52.4, 51.3,

49.3, 21.6, 20.9. **IR** (KBr): 2984, 2948, 1728, 1619, 1418, 1356, 1280, 1172, 1138, 1089, 731 cm^{-1}. **HRMS** (ESI): Calculated for $C_{23}H_{24}NO_4$ ($M+H^+$): 378.1700, found: 378.1709.

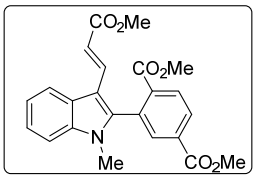


4q: Light yellow oil (47%). R_f = 0.4 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 15.9, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.36 – 7.28 (m, 2H), 6.38 (dd, *J* = 16.0, 1.5 Hz, 1H), 5.40 (dd, *J* = 11.2, 1.5 Hz, 1H), 5.04 (dd, *J* = 11.2, 1.6 Hz, 1H), 3.71 (d, *J* = 1.5 Hz, 3H), 3.63 (d, *J* = 1.5 Hz, 3H), 3.36 (q, *J* = 8.7 Hz, 1H), 3.23 (q, *J* = 8.3 Hz, 1H), 0.75 (t, *J* = 8.3 Hz, 2H), -0.10 (d, *J* = 1.5 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 166.3, 144.0, 138.2, 137.6, 133.5, 132.2, 132.0, 131.1, 131.0, 130.0, 126.1, 123.4, 122.1, 120.7, 113.3, 111.4, 111.1, 73.7, 66.0, 52.5, 51.4, 17.8, -1.3. **IR** (KBr): 2950, 2859, 1727, 1622, 1574, 1459, 1277, 1172, 1086, 836 cm^{-1}. **HRMS** (ESI): Calculated for $C_{26}H_{32}NO_5Si$ ($M+H^+$): 466.2044, found: 466.2053.

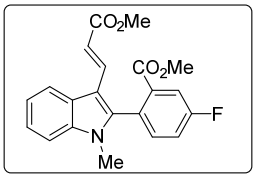


4r: Yellow solid (36%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 172– 174 °C, The reaction was set up according to the standard condition at 90 °C; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 16.1 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60 (td, *J* = 7.6, 1.1 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.35 (m, 1H), 7.25 (d, *J* = 1.1 Hz, 1H), 6.69 (d, *J* = 16.1 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 162.5, 139.7, 134.7, 134.3, 134.1, 133.9, 133.7, 132.0, 129.8, 127.4, 125.9, 124.8,

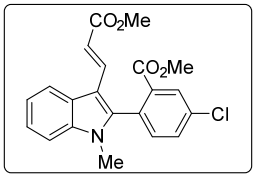
122.7, 122.1, 120.4, 114.5, 113.8, 52.1. **IR** (KBr): 2923, 2851, 1733, 1718, 1635, 1456, 1362, 1307, 1172, 1130, 740 cm^{-1}. **HRMS** (ESI): Calculated for $C_{19}H_{14}NO_3$ ($M+H^+$): 304.0968, found: 304.0963.



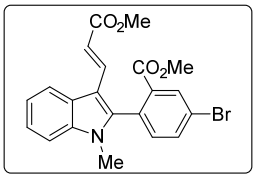
4u: Light yellow oil (50%). R_f = 0.2 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 1.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.30 (td, *J* = 7.5, 7.0, 1.4 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 3.95 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 165.8, 165.7, 143.1, 138.0, 137.9, 135.7, 133.7, 133.5, 131.7, 131.0, 130.9, 125.7, 123.2, 121.8, 120.8, 112.5, 110.7, 110.1, 52.9, 52.8, 51.4, 31.0. **IR** (KBr): 2949, 1727, 1621, 1574, 1462, 1419, 1365, 1292, 1263, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{23}H_{21}NO_6Na$ ($M+Na^+$): 430.1261, found: 430.1265.



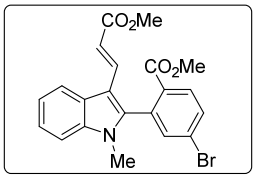
4v: Light yellow oil (50%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.87 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.44 (d, *J* = 16.0 Hz, 1H), 7.41 – 7.26 (m, 5H), 6.34 (d, *J* = 15.9 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.9, 165.2 (d, *J* = 2.5 Hz), 163.1 (d, *J* = 251.7 Hz), 143.3, 138.2, 137.8, 134.9 (d, *J* = 8.0 Hz), 133.8 (d, *J* = 7.7 Hz), 127.4 (d, *J* = 3.7 Hz), 125.7, 123.1, 121.7, 120.8, 119.7 (d, *J* = 21.3 Hz), 118.3 (d, *J* = 23.7 Hz), 112.3, 110.6, 110.0, 52.8, 51.4, 30.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.7. **IR** (KBr): 2950, 1732, 1710, 1621, 1575, 1470, 1435, 1411, 1287, 1195 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}FNO_4Na$ ($M+Na^+$): 390.1112, found: 390.1117.



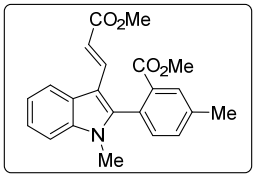
4w: Light yellow oil (51%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.3 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.65 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (td, *J* = 12.3, 7.2 Hz, 3H), 6.35 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 165.2, 143.1, 138.1, 137.9, 136.3, 134.3, 133.2, 132.5, 131.2, 129.8, 125.7, 123.2, 121.8, 120.8, 112.5, 110.6, 110.0, 52.8, 51.4, 30.9. **IR** (KBr): 2949, 1731, 1621, 1469, 1434, 1287, 1253, 1172, 1133, 748 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{19}ClNO_4$ ($M+H^+$): 384.0997, found: 384.1005.



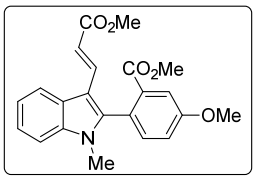
4x: Light yellow oil (51%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.43 (d, *J* = 15.9 Hz, 1H), 7.40 – 7.24 (m, 4H), 6.36 (d, *J* = 15.9 Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 165.0, 143.1, 138.1, 137.9, 135.5, 134.4, 134.1, 133.3, 130.2, 125.6, 124.3, 123.2, 121.8, 120.8, 112.5, 110.5, 110.0, 52.8, 51.4, 30.9. **IR** (KBr): 2949, 1732, 1708, 1621, 1470, 1434, 1411, 1287, 1253, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{18}BrNO_4Na$ ($M+Na^+$): 450.0311, found: 450.0312.



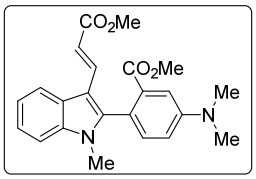
4y: Light yellow solid (63%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 200 – 202 °C **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.77 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.54 (t, *J* = 1.6 Hz, 1H), 7.44 (dd, *J* = 16.0, 1.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 (tt, *J* = 8.2, 1.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.36 (dd, *J* = 15.9, 1.2 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 165.6, 142.6, 137.9, 137.8, 135.7, 133.4, 133.2, 132.4, 130.7, 127.2, 125.6, 123.3, 121.8, 120.9, 112.7, 110.6, 110.0, 52.7, 51.4, 31.0. **IR** (KBr): 2948, 1728, 1621, 1470, 1433, 1369, 1286, 1172, 1100, 1039, 747 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{19}BrNO_4$ ($M+H^+$): 428.0492, found: 428.0501.



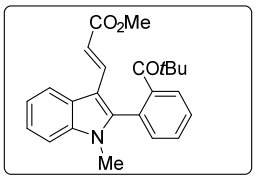
4z: Light yellow oil (75%). R_f = 0.35 (hexane/ ethyl acetate = 3:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.53 – 7.47 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 7.28 (s, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.49 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 166.6, 145.0, 140.2, 138.7, 137.8, 133.2, 132.9, 131.6, 131.5, 128.3, 125.8, 122.9, 121.6, 120.7, 111.7, 110.3, 109.9, 52.5, 51.3, 30.8, 21.4. **IR** (KBr): 2949, 1726, 1620, 1469, 1434, 1287, 1208, 1171, 1092, 844 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{22}NO_4$ ($M+H^+$): 364.1543, found: 364.1551.



4aa: White solid (72%). R_f = 0.35 (hexane/ ethyl acetate = 3:1). Mp = 129 – 131 °C **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.98 – 7.94 (m, 1H), 7.67 (d, *J* = 2.7 Hz, 1H), 7.49 (d, *J* = 15.9 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.32 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.19 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 3.95 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H), 3.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 166.2, 160.5, 144.8, 138.8, 137.8, 134.2, 132.9, 125.8, 123.2, 122.8, 121.6, 120.7, 118.3, 116.1, 111.6, 110.4, 109.9, 55.8, 52.6, 51.3, 30.8. **IR** (KBr): 2948, 2849, 1727, 1619, 1469, 1287, 1172, 1063, 1043, 842 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{22}NO_5$ ($M+H^+$): 380.1492, found: 380.1497.

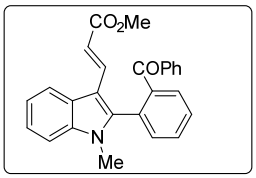


4ab: Light yellow oil (51%). R_f = 0.4 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.56 (d, *J* = 15.9 Hz, 1H), 7.43 (d, *J* = 2.8 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.30 (ddd, *J* = 8.0, 7.1, 1.4 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 3.71 (s, 3H), 3.60 (s, 3H), 3.47 (s, 3H), 3.10 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 167.3, 150.9, 146.3, 139.4, 137.7, 133.7, 132.2, 125.9, 122.6, 121.4, 120.6, 117.5, 115.1, 113.9, 111.0, 110.3, 109.9, 52.4, 51.2, 40.4, 30.7. **IR** (KBr): 2948, 1722, 1607 1469, 1433, 1366, 1248, 1171, 1059, 829 cm^{-1}. **HRMS** (ESI): Calculated for $C_{23}H_{25}N_2O_4$ ($M+H^+$): 393.1809, found: 393.1807.

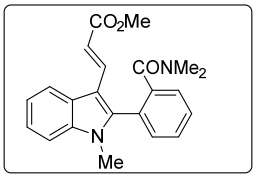


4ac: Light yellow solid (65%). R_f = 0.3 (hexane/ ethyl acetate = 3:1). Mp = 127 – 129 °C **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.11 – 8.06 (m, 1H), 7.99 – 7.95 (m, 1H), 7.65 – 7.58 (m, 2H), 7.53 (d, *J* = 16.0 Hz, 1H), 7.38 –

7.28 (m, 4H), 6.34 (d, J = 15.9 Hz, 1H), 3.71 (s, 3H), 3.47 (s, 3H), 1.06 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 166.0, 145.2, 138.6, 137.7, 134.5, 132.3, 131.7, 130.8, 130.3, 129.9, 125.8, 123.0, 121.7, 120.6, 112.0, 110.3, 109.8, 81.6, 51.3, 30.8, 27.6. **IR** (KBr): 2977, 2947, 1714, 1621, 1470, 1433, 1369, 1288, 1172, 1042 cm^{-1}. **HRMS** (ESI): Calculated for $C_{24}H_{26}NO_4$ ($M+H^+$): 392.1856, found: 392.1859.

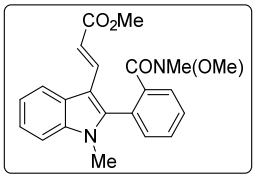


4ad: Light yellow oil (61%). R_f = 0.3 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 7.9 Hz, 1H), 7.72 – 7.62 (m, 3H), 7.61 – 7.57 (m, 2H), 7.52 (d, J = 15.9 Hz, 1H), 7.47 (d, J = 7.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.29 (d, J = 3.5 Hz, 1H), 7.26 – 7.17 (m, 4H), 6.22 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 168.7, 143.4, 141.4, 138.4, 137.9, 136.6, 133.1, 132.3, 130.9, 129.8, 129.8, 129.4, 129.4, 128.1, 125.5, 123.1, 121.7, 120.5, 112.4, 111.2, 110.1, 51.3, 31.4. **IR** (KBr): 3056, 2947, 1706, 1663, 1621, 1597, 1469, 1433, 1288, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{26}H_{21}NO_3Na$ ($M+Na^+$): 418.1414, found: 418.1414.

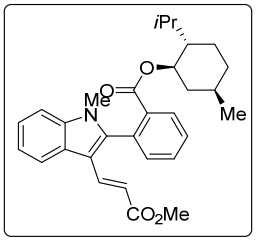


4ae: Light yellow oil (60%). R_f = 0.3 (toluene/ ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, J = 7.6 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.49 – 7.43 (m, 1H), 7.41 – 7.26 (m, 4H), 6.42 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H), 3.57 (s, 3H), 2.79 (d, J = 1.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 168.9, 143.9, 138.7, 138.6, 138.2, 132.2, 129.9, 129.2, 128.2, 127.1, 125.5, 123.2, 121.7, 120.7, 111.8, 110.7, 110.6, 51.3, 39.3, 34.8, 31.7. **IR** (KBr):

3056, 2947, 1706, 1663, 1621, 1597, 1469, 1433, 1288, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{22}N_2O_3Na$ ($M+Na^+$): 385.1523, found: 385.1526.

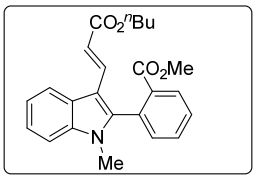


4af: Light yellow oil (60%). R_f = 0.35 (hexane/ ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.24 (m, 3H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.55 (s, 3H), 3.34 (s, 3H), 3.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 143.5, 138.9, 138.4, 137.6, 132.1, 129.7, 129.6, 129.1, 127.5, 125.9, 123.2, 121.8, 120.7, 112.3, 111.2, 110.4, 61.0, 51.1, 34.4, 31.6. **IR** (KBr): 2946, 1706, 1651, 1621, 1469, 1288, 1172, 1134, 1041, 983 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{23}N_2O_4$ ($M+H^+$): 379.1652, found: 379.1658.

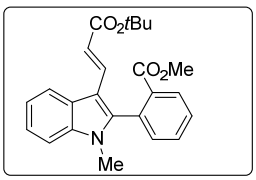


4ag: Light yellow oil (60%, dr =1:1). R_f = 0.3 (hexane / ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.66 (tt, *J* = 6.6, 3.6 Hz, 2H), 7.51 (d, *J* = 15.9 Hz, 1H), 7.39 – 7.28 (m, 4H), 6.33 (d, *J* = 15.9 Hz, 1H), 4.63 (td, *J* = 10.9, 4.3 Hz, 1H), 3.70 (s, 3H), 3.43 (s, 3H), 1.78 – 1.71 (m, 1H), 1.52 – 1.24 (m, 6H), 0.83 (dd, *J* = 13.0, 3.2 Hz, 1H), 0.73 (d, *J* = 6.5 Hz, 3H), 0.58 – 0.52 (m, 6H), 0.41 – 0.33 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.92, 165.84, 145.16, 138.58, 137.69, 132.69, 132.66, 132.30, 131.44, 130.84, 129.97, 125.77, 122.98, 121.70, 120.79, 111.88, 110.43, 109.82, 75.03, 51.32, 46.66, 40.47, 34.08, 31.24, 30.83, 25.66, 22.76, 22.04, 20.80, 15.83. **IR** (KBr): 2953, 1711, 1621, 1470, 1433, 1409, 1288, 1254, 1171, 1090 cm^{-1}. **HRMS** (ESI): Calculated for $C_{30}H_{35}NO_4Na$ ($M+Na^+$): 496.2458, found: 496.2466.

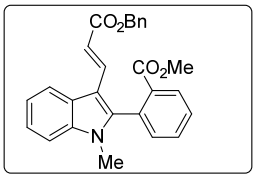
4ag': **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 – 8.05 (m, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.46 – 7.28 (m, 5H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.61 (td, *J* = 10.7, 4.4 Hz, 1H), 3.69 (s, 3H), 3.48 (s, 3H), 1.68 – 1.64 (m, 1H), 1.56 – 1.46 (m, 3H), 1.27 (dd, *J* = 9.7, 2.5 Hz, 2H), 0.90 – 0.85 (m, 2H), 0.68 (dd, *J* = 13.7, 6.8 Hz, 6H), 0.55 (d, *J* = 6.9 Hz, 3H), 0.35 (q, *J* = 12.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.71, 166.11, 138.23, 137.56, 133.48, 132.11, 131.77, 130.62, 129.82, 129.01, 126.02, 125.80, 122.86, 121.57, 120.50, 111.84, 110.62, 109.83, 75.05, 51.18, 46.71, 40.14, 33.98, 31.09, 30.77, 25.81, 22.82, 21.87, 20.73, 15.75. **IR** (KBr): 2952, 1714, 1620, 1470, 1433, 1373, 1287, 1255, 1170, 1132 cm^{-1}. **HRMS** (ESI): Calculated for $C_{30}H_{35}NO_4Na$ ($M+Na^+$): 496.2458, found: 496.2465.



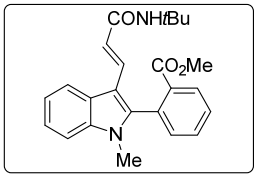
4ah: Light yellow oil (61%). R_f = 0.3 (hexane / ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.99 (d, *J* = 7.3 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.46 (d, *J* = 15.9 Hz, 1H), 7.40 – 7.27 (m, 4H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.65 (s, 3H), 3.48 (s, 3H), 1.65 – 1.60 (m, 2H), 1.43 – 1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 166.4, 144.7, 138.4, 137.8, 133.1, 132.4, 131.8, 131.4, 131.0, 129.9, 125.7, 122.9, 121.6, 120.8, 112.4, 110.3, 110.0, 63.9, 52.5, 31.0, 30.9, 19.4, 13.9. **IR** (KBr): 2956, 1728, 1704, 1619, 1574, 1470, 1433, 1373, 1284, 1172 cm^{-1}. **HRMS** (ESI): Calculated for $C_{24}H_{25}NO_4Na$ ($M+Na^+$): 414.1676, found: 414.1677.



4ai: Light yellow oil (65%). R_f = 0.3 (hexane / ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.63 (dtd, *J* = 24.0, 7.5, 1.4 Hz, 2H), 7.42 – 7.27 (m, 5H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.64 (s, 3H), 3.47 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.4, 144.5, 137.8, 137.4, 133.1, 132.4, 131.8, 131.5, 131.0, 129.8, 125.8, 122.8, 121.5, 120.9, 114.2, 110.3, 109.9, 79.6, 52.5, 30.9, 28.5. **IR** (KBr): 2919, 1728, 1699, 1617, 1471, 1470, 1434, 1368, 1288, 1149 cm^{-1}. **HRMS** (ESI): Calculated for $C_{24}H_{25}NO_4Na$ ($M+Na^+$): 414.1676, found: 414.1680.

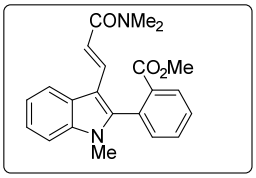


4aj: Light yellow oil (62%). R_f = 0.3 (hexane / ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.52 (d, *J* = 15.9 Hz, 1H), 7.41 – 7.27 (m, 9H), 6.40 (d, *J* = 15.9 Hz, 1H), 5.17 (s, 2H), 3.64 (s, 3H), 3.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 166.4, 145.0, 139.1, 137.8, 136.8, 133.0, 132.4, 131.8, 131.3, 131.1, 129.9, 128.6, 128.2, 128.1, 125.7, 123.0, 121.7, 120.9, 111.7, 110.4, 110.0, 65.8, 52.5, 30.9. **IR** (KBr): 2950, 1727, 1618, 1574, 1470, 1434, 1409, 1377, 1284, 1168 cm^{-1}. **HRMS** (ESI): Calculated for $C_{27}H_{23}NO_4Na$ ($M+Na^+$): 448.1519, found: 448.1522.

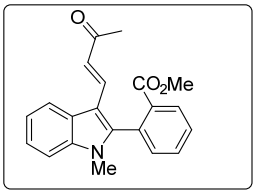


4ak: Light yellow oil (45%). R_f = 0.3 (toluene / ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.43 – 7.36 (m, 3H), 7.33 – 7.29 (m, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 6.28 (d, *J* = 15.5 Hz, 1H), 5.29 (s, 1H), 3.63 (s, 3H), 3.45 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 166.4, 143.9, 137.7, 134.0, 133.2, 132.5, 131.7, 131.6, 131.0, 129.7, 125.8, 122.6, 121.1, 120.7,

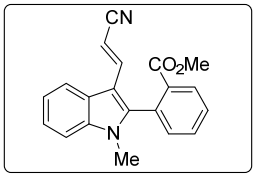
116.4, 110.1, 109.9, 52.4, 51.3, 30.8, 29.2. **IR** (KBr): 3290, 2964, 1727, 1651, 1607, 1552, 1470, 1453, 1290, 1261 cm^{-1}. **HRMS** (ESI): Calculated for $C_{24}H_{26}N_2O_3Na$ ($M+Na^+$): 413.1836, found: 413.1838.



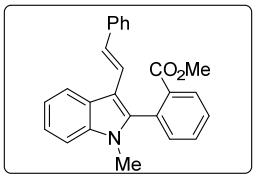
4al: Light yellow oil (61%). R_f = 0.3 (hexane / ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 – 8.12 (m, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.66 (td, *J* = 7.4, 1.3 Hz, 1H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 7.53 (d, *J* = 15.4 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 2H), 6.69 (d, *J* = 15.4 Hz, 1H), 3.64 (s, 3H), 3.48 (s, 3H), 3.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 166.4, 143.5, 137.7, 136.0, 133.1, 132.6, 132.0, 131.7, 131.0, 129.7, 126.0, 122.6, 121.2, 120.4, 111.9, 110.6, 110.0, 52.5, 30.8, 29.8. **IR** (KBr): 2924, 1727, 1643, 1593, 1470, 1434, 1386, 1275, 1129, 1091 cm^{-1}. **HRMS** (ESI): Calculated for $C_{22}H_{22}N_2O_3Na$ ($M+Na^+$): 385.1523, found: 385.1527.



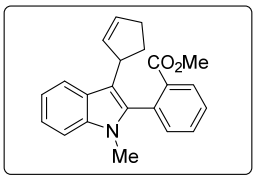
4am: Light yellow oil (52%). R_f = 0.2 (hexane/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.41 – 7.29 (m, 5H), 6.70 (d, *J* = 16.1 Hz, 1H), 3.65 (s, 3H), 3.50 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 166.4, 145.4, 138.0, 137.5, 132.9, 132.4, 131.9, 131.2, 131.0, 130.0, 125.7, 123.2, 122.5, 121.9, 120.9, 110.4, 110.1, 52.6, 31.0, 27.4. **IR** (KBr): 2924, 1727, 1676, 1585, 1572, 1470, 1408, 1374, 1357, 1284 cm^{-1}. **HRMS** (ESI): Calculated for $C_{21}H_{19}NO_3Na$($M+Na^+$): 356.1257, found: 356.1260.



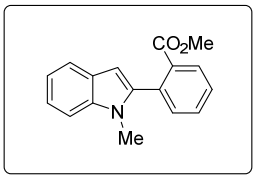
4an: Light yellow oil (45%). R_f = 0.30 (hexane/ ethyl acetate = 4:1). 15 mol% $Pd(OAc)_2$ was used. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.22 – 8.17 (m, 1H), 7.80 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.75 – 7.63 (m, 2H), 7.41 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.07 (d, *J* = 16.5 Hz, 1H), 5.61 (d, *J* = 16.5 Hz, 1H), 3.69 (s, 3H), 3.49 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 144.7, 143.9, 137.8, 132.8, 132.6, 131.8, 131.1, 130.8, 130.3, 125.2, 123.4, 122.1, 120.8, 120.2, 110.3, 110.2, 88.9, 52.6, 31.0. **IR** (KBr): 3062, 2949, 2359, 2205, 1726, 1608, 1470, 1406, 1274, 1091, 960 cm^{-1}. **HRMS** (ESI): Calculated for $C_{20}H_{17}N_2O_2$ ($M+H^+$): 317.1285, found: 317.1294.



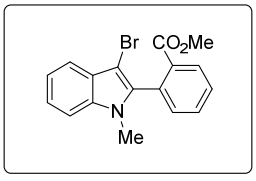
4ao: Light yellow oil (45%). R_f = 0.35 (hexane/ ethyl acetate = 4:1). 15 mol% $Pd(OAc)_2$ was used. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.12 (ddd, *J* = 17.5, 7.8, 1.3 Hz, 2H), 7.67 (td, *J* = 7.5, 1.5 Hz, 1H), 7.61 (td, *J* = 7.7, 1.4 Hz, 1H), 7.44 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.32 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 3H), 7.27 (dt, *J* = 8.1, 5.7 Hz, 3H), 7.16 – 7.11 (m, 1H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.88 (d, *J* = 16.4 Hz, 1H), 3.62 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 139.9, 139.1, 137.7, 133.3, 132.6, 132.3, 132.0, 130.6, 129.3, 128.6, 126.3, 125.7, 125.7, 125.2, 122.3, 122.3, 120.7, 120.5, 111.9, 109.7, 52.5, 30.8. **IR** (KBr): 3046, 2948, 1728, 1630, 1469, 1293, 1255, 1128, 1089, 955 cm^{-1}. **HRMS** (ESI): Calculated for $C_{25}H_{22}NO_2$ ($M+H^+$): 368.1645, found: 368.1651.



4ap: White solid (44%, dr = 1:1). R_f = 0.35 (hexane/ ethyl acetate = 4:1). Mp = 116 – 118 °C; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.60 (tdd, *J* = 6.3, 5.5, 2.7 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.32 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.79 (dt, *J* = 5.6, 2.9 Hz, 1H), 5.76 – 5.64 (m, 1H), 3.75 (dt, *J* = 8.8, 2.7 Hz, 1H), 3.59 (s, 3H), 3.45 (s, 3H), 2.52 (q, *J* = 13.5 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.23 – 2.09 (m, 1H), 2.05 – 1.91 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 167.7, 137.4, 137.3, 136.1, 136.1, 135.3, 135.1, 133.3, 133.2, 133.1, 133.1, 133.0, 131.5, 131.5, 130.5, 130.2, 130.1, 130.0, 128.8, 128.8, 126.7, 126.7, 121.3, 120.2, 120.1, 118.7, 116.0, 109.2, 52.3, 52.3, 42.9, 42.8, 32.9, 32.9, 31.8, 31.7, 30.5. **IR** (KBr): 3049, 2947, 2847, 1731, 1601, 1467, 1430, 1366, 1293, 1125, 1088, 740 cm^{-1}. **HRMS** (ESI): Calculated for $C_{25}H_{22}NO_2$ ($M+H^+$): 368.1645, found: 368.1651.



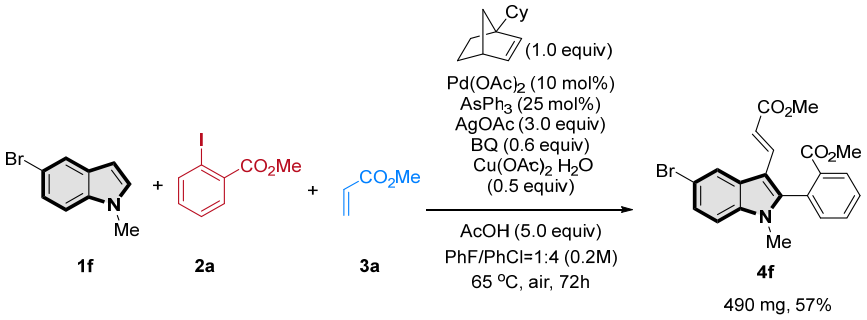
4aq: White solid (56%). R_f = 0.5 (hexane/ ethyl acetate = 4:1). Mp = 73 – 75 °C. The reaction was set up according to the standard condition except 10.0 equiv. of acetic acid was used; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.00 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.63 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.53 (td, *J* = 7.7, 1.4 Hz, 1H), 7.46 (ddd, *J* = 7.6, 1.4, 0.6 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.26 – 7.23 (m, 1H), 7.14 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.45 (d, *J* = 0.8 Hz, 1H), 3.65 (s, 3H), 3.53 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.8, 140.1, 137.5, 133.5, 132.6, 132.0, 131.7, 130.1, 128.7, 128.0, 121.6, 120.6, 119.7, 109.4, 101.5, 52.4, 30.6. **IR** (KBr): 2926, 2851, 1732, 1600, 1574, 1463, 1430, 1257, 1127, 1085, 1006 cm^{-1}. **HRMS** (ESI): Calculated for $C_{17}H_{16}NO_2$ ($M+H^+$): 266.1176, found: 266.1177.



4ar: white solid (53%). R_f = 0.45 (hexane/ ethyl acetate = 8:1). Mp = 97 – 99 °C. The reaction was set up according to the standard condition except 10.0 equiv. of acetic acid was used. After stirred at 65 °C for 72h, the mixture was cooled to room temperature before 3.0 equiv. of NBS was added. The reaction was stirred at the room temperature for 24 h and then was quenched and worked up according to the standard condition; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.67 (td, *J* = 7.6, 1.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.43 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.23 – 7.20 (m, 1H), 3.66 (s, 3H), 3.54 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 137.5, 136.5, 133.0, 132.2, 132.1, 131.6, 130.7, 129.5, 127.0, 122.7, 120.4, 119.3, 109.6, 89.9, 52.5, 31.4. **IR** (KBr): 2947, 2850, 1731 1575, 1464, 1292, 1261, 1089, 741 cm^{-1}. **HRMS** (ESI): Calculated for $C_{17}H_{15}BrNO_2$ ($M+H^+$): 344.0281, found: 344.0279.

4.3 Synthetic utility

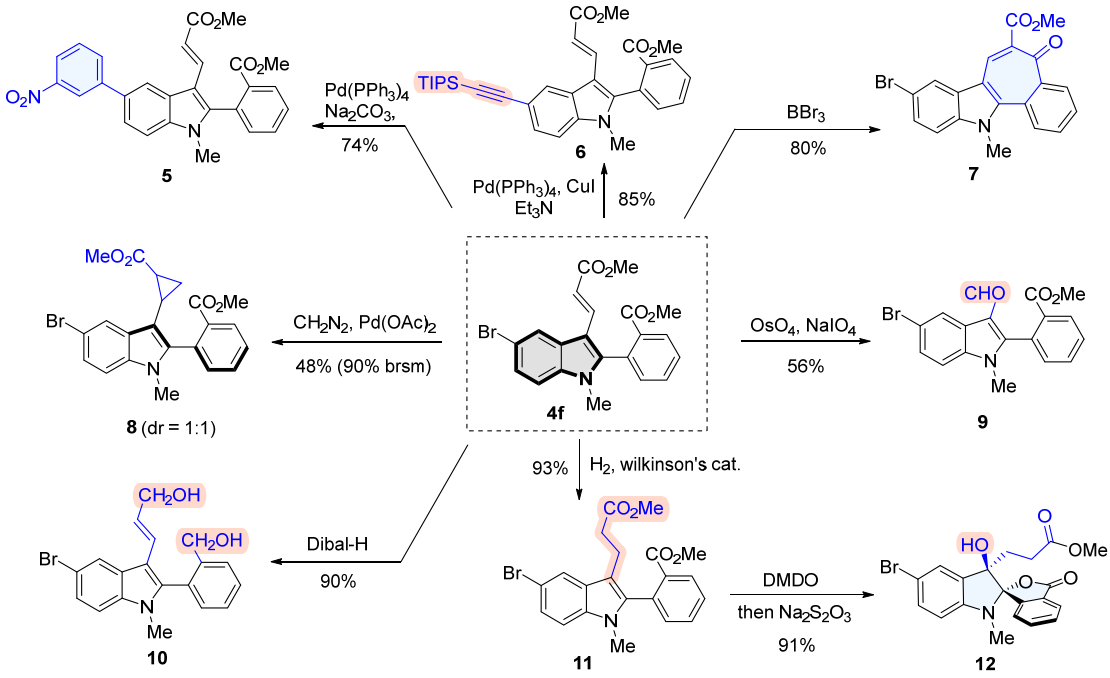
Large-scale preparation of 4f



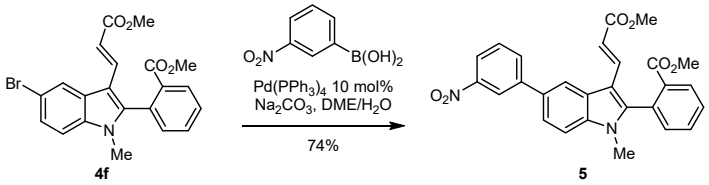
A flame-dried 40 mL vial was charged with $Pd(OAc)_2$ (44.8 mg, 0.2 mmol, 10 mol%), $AsPh_3$ (153 mg, 0.5 mmol, 25 mol%), BQ (130 mg, 1.2 mmol, 0.6 equiv.), $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol, 0.5 equiv.), **N2** (352 mg, 2.0 mmol, 1.0 equiv), AgOAc (1.0 g, 6.0 mmol, 3.0 equiv.), indole **1f** (630 mg, 3.0 mmol, 1.5 equiv.) and aryl iodide **2a** (524 mg, 2.0 mmol, 1.0 equiv.). Then, 2 mL of fluorobenzene and 8 mL of chlorobenzene were added. After acrylate **3a** (516 mg, 6.0 mmol, 3.0 equiv.) and AcOH (0.57 ml, 10.0 mmol, 5.0 equiv.) were added, the vial was tightly sealed and stirred on a pie-block preheated to 65 °C for 72 hours. After completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate and the combined

filtrate was concentrated. The residue was loaded to a small amount of silica gel and subjected to flash column chromatography to give the desired difunctionalization product **4f** (490 mg, 57%) as a white solid.

Derivatizations of compound 4f

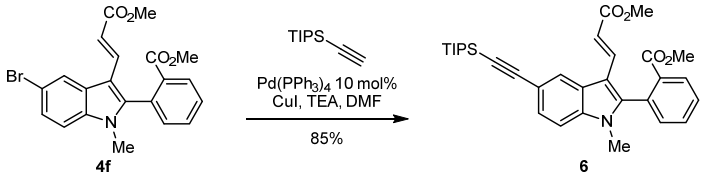


Synthesis of compounds ***5-12***.



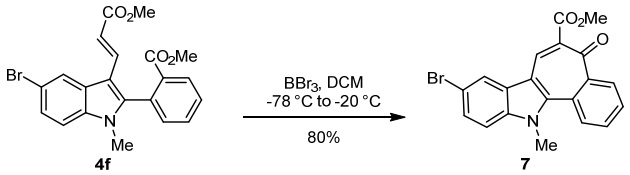
An oven-dried 4 mL vial equipped with a Teflon-coated magnetic stir bar was charged with compound **4f** (43 mg, 0.1 mmol), *m*-nitrophenylboronic acid (33 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol), and Na_2CO_3 (21 mg, 0.2 mmol). Then, DME (1.0 mL) and H_2O (0.2 mL) were added to the mixture under N_2. The reaction mixture was stirred at 85 °C for 18h. Upon completion of the reaction, the mixture was filtered through a thin pad of Celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 3:1) to afford **5** (34.8 mg, 0.074 mmol, 74%).

5: Yellow oil. R_f = 0.2 (hexane:EtOAc = 2:1). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.54 (t, *J* = 2.0 Hz, 1H), 8.22 – 8.16 (m, 3H), 8.06 (ddd, *J* = 7.7, 1.8, 1.1 Hz, 1H), 7.75 (td, *J* = 7.5, 1.5 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.67 (d, *J* = 0.7 Hz, 6H), 3.51 (s, 3H); **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 168.2, 166.0, 148.8, 145.7, 143.9, 137.7, 137.5, 133.5, 132.6, 132.5, 132.4, 131.7, 131.0, 130.9, 130.1, 129.7, 126.2, 122.3, 122.1, 121.3, 119.1, 112.3, 110.6, 110.1, 52.3, 51.0, 30.8. **IR** (KBr, cm^{-1}): ν 2949, 2853, 1726, 1621, 1529, 1433, 1348, 1165, 1090. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}N_2O_6^+$ 471.1551; found 471.1551.



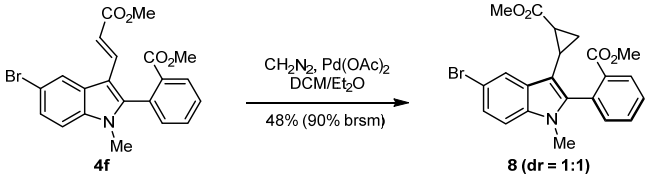
$Pd(PPh_3)_4$ (5.7 mg, 0.005 mol) and CuI (1.9 mg, 0.01 mmol) were degassed in a flame-dried round-bottom flask, and then Et_3N (0.4 mL), DMF (2.0 mL) and compound **4f** (43 mg, 0.1 mmol) were added. The solution was degassed again before (triisopropylsilyl)acetylene (27.3 mg, 0.15 mmol) was added. The reaction mixture was heated at 110 °C for 6h and then allowed to cool to room temperature. The black solution was washed with water (3 x 10 mL) and extracted with CH_2Cl_2 (2 x 10 mL). All organic phases were combined, dried over sodium sulfate, filtered and concentrated in vacuo to obtain the crude product. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 3:1) to afford **6** (45 mg, 0.085 mmol, 85%).

6: Colorless oil. R_f = 0.35 (hexane:EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.08 (d, *J* = 1.5 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.62 (s, 3H), 3.45 (s, 3H), 1.18 (s, 22H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 166.3, 145.3, 138.0, 137.3, 132.9, 132.6, 131.8, 131.2, 131.1, 130.1, 127.3, 125.6, 124.6, 116.7, 112.6, 110.3, 109.8, 108.6, 88.6, 52.6, 51.4, 31.0, 18.9, 11.6. **IR** (KBr, cm^{-1}): ν 2944, 2864, 2144, 1728, 1622, 1475, 1283, 1161, 1089, 924. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{40}NO_4Si^+$ 530.2721; found 530.2725.



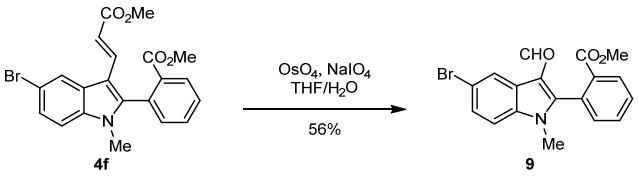
To a solution of compound **4f** (43 mg, 0.1 mmol) in DCM (5 mL) was added BBr_3 (0.096 mL, 1.0 mmol, 10.0 equiv.) at -78 °C. Then, the mixture was warmed to -20 °C and stirred at the same temperature for 10h. The reaction mixture was quenched by adding aqueous $NaHCO_3$ and extracted with DCM (5 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 2:1) to afford **7** (32.7 mg, 0.083 mmol, 83%)

7: Yellow solid. Melting point = 233−235 °C; R_f = 0.5 (hexane:EtOAc = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (d, *J* = 1.8 Hz, 1H), 8.03 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.70 (tt, *J* = 7.3, 5.5 Hz, 2H), 7.54 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 4.01 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 166.1, 143.0, 142.5, 138.1, 133.9, 130.1, 130.1, 129.7, 128.0, 127.9, 127.8, 126.8, 125.8, 122.0, 115.6, 112.3, 112.0, 52.7, 34.7. **IR** (KBr, cm^{-1}): ν 2923, 2860, 1717, 1651, 1469, 1287, 1217, 1120, 803. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_3^+$ 396.0230; found 396.0230.



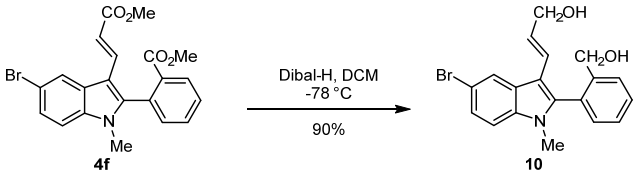
To a stirred solution of compound **4f** (43 mg, 0.1 mmol) in dichloromethane (2.0 mL) was added palladium (II) acetate (1.2 mg, 0.005 mmol). The reaction mixture was cooled to -10 °C before a cold solution of diazomethane (2.0 mL, 10 mmol, 0.5 M) in ether (generated from aqueous KOH and 1-methyl-1-nitrosourea at 0 °C.) was added. The reaction mixture was stirred at room temperature for 12 h. It was then filtered through celite, diluted with diethyl ether, and washed with water and saturated NaCl solution. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 5:1) to afford **8** (21 mg, 0.048 mmol, 48%; dr = 1:1, inseparable) and **4f** (20 mg, 0.046 mmol).

8: Light yellow oil. R_f = 0.5 (hexane:EtOAc = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.74 (t, *J* = 1.7 Hz, 1H), 7.67 – 7.53 (m, 2H), 7.40 – 7.34 (m, 1H), 7.31 (dt, *J* = 8.6, 1.8 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 3.67 – 3.57 (m, 6H), 3.42 (s, 3H), 2.29 (dddd, *J* = 9.3, 6.8, 4.2, 2.7 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.37 – 1.28 (m, 1H), 1.07 – 0.93 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 174.5, 167.1, 139.6, 139.4, 135.4, 135.3, 132.8, 132.7, 132.3, 132.2, 132.2, 132.0, 132.0, 130.6, 130.5, 129.3, 129.2, 129.1, 124.6, 124.6, 121.5, 121.5, 112.9, 110.9, 110.3, 52.5, 51.9, 51.8, 30.6, 21.2, 21.0, 18.1, 18.0, 15.3, 15.2. **IR** (KBr, cm^{-1}): ν 2997, 2950, 2852, 2254, 1731, 1469, 1366, 1173, 1091, 911. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}BrNO_4^+$ 442.0648; found 442.0649.



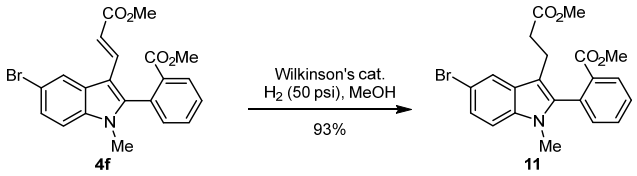
To a solution of **4f** (43 mg, 0.1 mmol, 1.0 equiv.) in THF/ water (15 mL, 3:1 v/v) were added an aqueous OsO_4 solution (0.025 mL, 0.079 M, 0.02 equiv.), and $NaIO_4$ (64 mg, 0.3 mmol, 3.0 equiv.) in a sequence. The suspension was stirred at room temperature for 2 h, before the reaction was quenched by saturated aqueous $Na_2S_2O_3$ (10 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (hexane:EtOAc = 4:1) to afford **9** (20.5 mg, 0.056 mmol, 56%).

9: White solid. Melting point = 179−181 °C; R_f = 0.23 (hexane:EtOAc = 3:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.42 (s, 1H), 8.45 (d, *J* = 2.0 Hz, 1H), 8.23 – 8.14 (m, 1H), 7.69 (pd, *J* = 7.5, 1.7 Hz, 2H), 7.46 (ddd, *J* = 8.6, 4.8, 2.0 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 1H), 3.66 (s, 3H), 3.46 (s, 3H); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 185.2, 166.2, 152.1, 136.3, 133.0, 132.6, 131.9, 131.3, 130.9, 129.7, 127.0, 126.9, 124.5, 116.7, 115.5, 111.8, 52.8, 31.1. **IR** (KBr, cm^{-1}): ν 2949, 2856, 1752, 1650, 1453, 1266, 1133, 1042, 963. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}BrNO_3^+$ 372.0230; found 372.0236.



To a solution of **4f** (43 mg, 0.1 mmol, 1.0 equiv.) in DCM (5 mL) were added diisobutylaluminum hydride solution (0.5 mL, 1.0 M, 5.0 equiv.) dropwise at -78 °C. The suspension was stirred at the same temperature for 2 h, before the reaction was quenched by saturated potassium sodium tartrate (10 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (hexane:EtOAc = 2:1) to afford **10** (33.3 mg, 0.09 mmol, 90%).

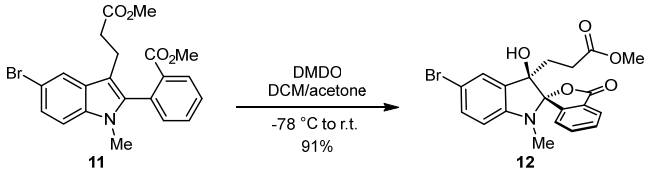
10: White solid. Melting point = 110−112 °C; R_f = 0.35 (hexane:EtOAc = 1:1). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.09 (d, *J* = 1.9 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.59 (td, *J* = 7.6, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.31 (td, *J* = 5.2, 2.9 Hz, 2H), 6.36 (dt, *J* = 16.1, 1.4 Hz, 1H), 6.19 (dt, *J* = 16.2, 6.0 Hz, 1H), 4.47 – 4.37 (m, 2H), 4.16 (dd, *J* = 6.0, 1.3 Hz, 2H), 3.46 (s, 3H); **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 141.9, 139.9, 136.6, 131.6, 130.2, 129.7, 128.5, 128.0, 127.6, 126.4, 125.1, 124.0, 122.8, 113.9, 111.6, 110.9, 64.6, 63.0, 31.0. **IR** (KBr, cm^{-1}): ν 3344, 2921, 2358, 1650, 1462, 1398, 1363, 1042, 963. **HRMS** (ESI) m/z: $[M\text{-}OH]^+$ calcd for $C_{19}H_{17}BrNO^+$ 354.0488; found 354.0496.



To a Q-tube charged with a stir bar, compound **4f** (43 mg, 0.1 mmol, 1.0 equiv.), Wilkinson's catalyst (9.3 mg, 0.01 mmol, 0.1 equiv.) and methanol (5.0 mL) were added successively at room temperature. The Q-tube was then resembled and flushed with nitrogen gas 5 times. The reaction mixture was then flushed with hydrogen gas 10 times and then charged with 50 psi H_2 followed by stirring at room temperature for 48 h. After the reaction was completed, the H_2 pressure was released, and the solvent was removed under vacuum. The resulting crude product was purified

by flash column chromatography on silica gel (hexane:EtOAc = 5:1) to afford **11** (39.8 mg, 0.093 mmol, 93%).

11: Light yellow solid. Melting point = 94−96 °C; R_f = 0.45 (hexane:EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.64 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.30 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 3.40 (s, 3H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.50 – 2.37 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.5, 167.0, 138.3, 135.5, 132.7, 132.3, 132.2, 132.1, 130.6, 129.3, 128.9, 124.3, 121.3, 112.5, 110.8, 110.6, 52.4, 51.6, 35.1, 30.6, 20.1. **IR** (KBr, cm^{-1}): ν 2950, 2842, 1732, 1575, 1343, 1369, 1259, 1090, 763. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}BrNO_4^+$ 430.0648; found 430.0646.

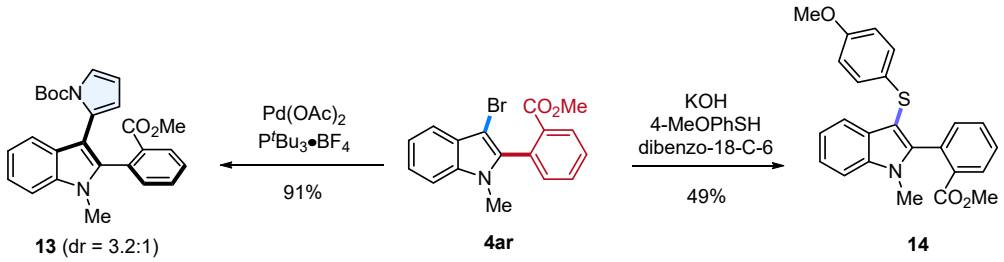


To a solution of **11** (30 mg, 0.07 mmol, 1.0 equiv.) in DCM (5 mL) was added a freshly prepared dimethyldioxirane solution (2.5 mL, 0.057 M in acetone, 2.0 equiv.) at -78 °C. The suspension was stirred at the same temperature for 1 h, before the reaction was quenched by saturated aqueous $Na_2S_2O_3$ (2 mL). The resulting mixture was allowed to warm up to room temperature and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (hexane:EtOAc = 4:1) to afford **12** (39.1 mg, 0.091 mmol, 91%).

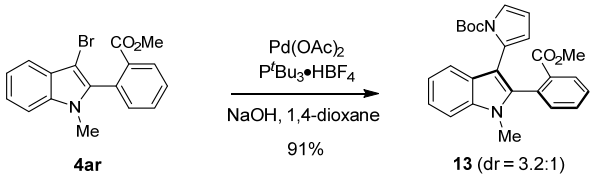
12: Yellow solid. Melting point = 194−196 °C; R_f = 0.3 (hexane:EtOAc = 2:1). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.99 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.85 (td, *J* = 7.5, 1.2 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.46 – 7.40 (m, 2H), 6.62 (d, *J* = 8.3 Hz, 1H), 3.62 (s, 3H), 3.00 (d, *J* = 2.3 Hz, 1H), 2.56 (s, 4H), 2.47 (ddd, *J* = 16.4, 9.6, 5.8 Hz, 1H), 2.30 – 2.22 (m, 1H), 1.98 (ddd, *J* = 13.7, 9.6, 5.9 Hz, 1H); **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 173.8, 168.0, 148.2, 142.0, 134.6, 133.8, 132.8, 131.7, 130.0, 127.3, 126.2, 125.6, 112.6, 112.4, 110.6, 83.0, 52.0, 31.9, 29.5, 28.7. **IR** (KBr, cm^{-1}): ν 3441, 2951, 2850, 1759, 1604, 1477, 1284, 1085, 878. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}BrNO_5^+$ 432.0441;

found 432.0449.

Derivatizations of compound 4ar:



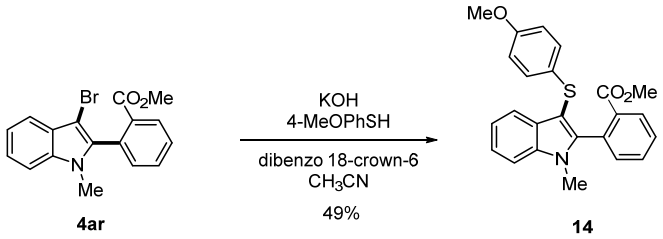
*Synthesis of compounds **13-14***



An oven-dried 4 mL vial equipped with a Teflon-coated magnetic stir bar was charged with compound **4ar** (34.3 mg, 0.1 mmol), *N*-boc-2-pyrroleboronic acid (31.7 mg, 0.15 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), and tri-*tert*-butylphosphinium tetrafluoroborate (3.5 mg, 0.012 mmol). Then, degassed 1,4-dioxane (1.0 mL) and a NaOH solution (0.13 mL, 1.3 M, 0.17 mmol) were added to the mixture under N_2. The reaction mixture was stirred at room temperature for 30 min and then stirred at 50 °C for 2 h. Upon completion of the reaction, the mixture was filtered through a thin pad of Celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 15:1) to afford **13** (39.2 mg, 0.091 mmol, 91%).

13: Light yellow foam. R_f = 0.35 (hexane:EtOAc = 10:1). The major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 1H), 7.46 (td, *J* = 7.0, 1.8 Hz, 2H), 7.40 – 7.38 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.28 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.07 (t, *J* = 3.3 Hz, 1H), 5.84 (dd, *J* = 3.2, 1.8 Hz, 1H), 3.67 (s, 3H), 3.50 (s, 3H), 1.14 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 149.7, 137.7, 136.8, 133.0, 132.6, 132.6, 131.8, 130.1, 128.9, 128.7, 127.5, 121.8, 121.7, 120.0, 119.7,

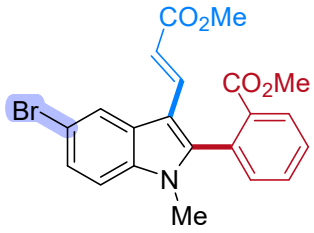
115.4, 110.7, 109.2, 82.8, 52.4, 30.6, 27.5, 27.4. **IR** (KBr, cm^{-1}): ν 3057, 2977, 2930, 1732, 1574, 1469, 1325, 1257, 1088. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_4^+$ 431.1965; found 431.1975.



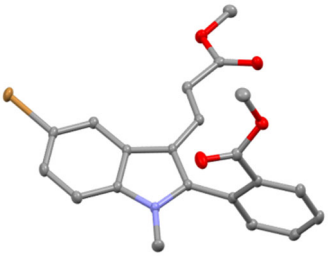
A mixture of powdered potassium hydroxide (11.2 mg, 0.2 mmol), dibenzo 18-crown-6 ether (3.6 mg, 0.01 mmol) and **4ar** (34.3 mg, 0.1 mmol) in acetonitrile (0.5 mL) was stirred at room temperature for 30 min. Then, 4-methoxybenzenethiol was added (28 mg, 0.2 mmol) and the reaction mixture was heated at 60 °C for 6h. Hydrochloric acid (1N, 0.5 mL) was added, and the aqueous solution was extracted with CH_2Cl_2 (2 × 5.0 mL). The combined organic extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 15:1) to afford **14** (19.8 mg, 0.049 mmol, 49%).

14: Colorless oil. R_f = 0.28 (hexane:EtOAc = 10:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.65 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.30 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.18 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H), 3.57 (s, 3H), 3.56 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.8, 157.5, 145.0, 137.3, 133.1, 132.1, 131.9, 131.8, 130.5, 130.2, 129.6, 129.3, 128.4, 122.5, 120.7, 119.7, 114.3, 109.7, 101.0, 55.4, 52.3, 31.3. **IR** (KBr, cm^{-1}): ν 2948, 2835, 1725, 1595, 1492, 1241, 1089, 1031, 745. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NO_3S^+$ 404.1315; found 404.1311.

5. X-ray data



4f

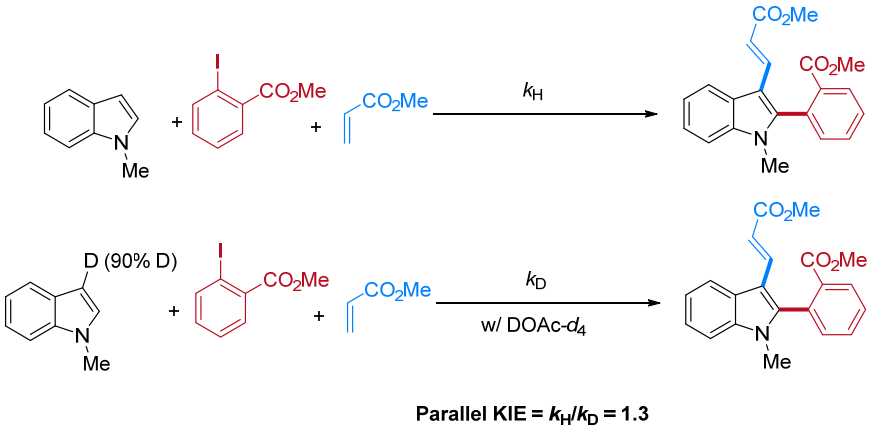


CCDC: 2252608

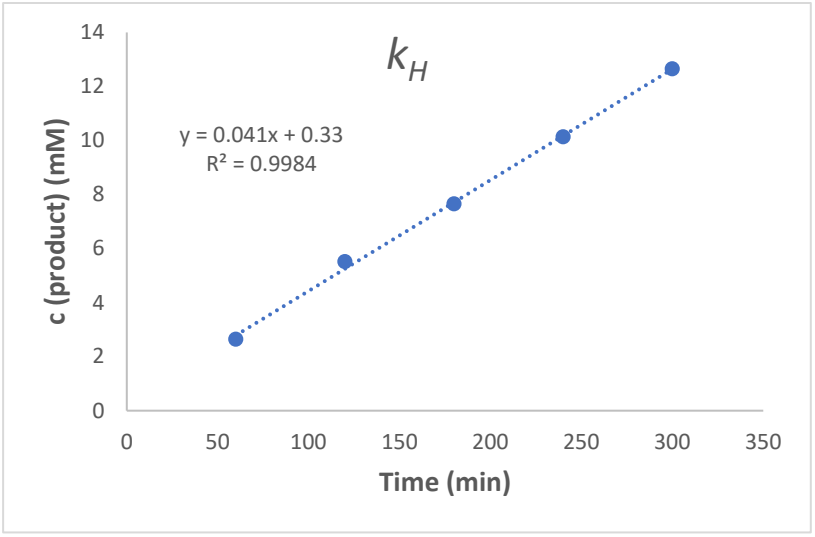
Identification code	ZY-indole
Empirical formula	$C_{21}H_{18}BrNO_4$
Formula weight	428.27
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.6550(8)
b/Å	10.3036(10)
c/Å	11.9510(12)
α/°	94.916(2)
β/°	99.295(2)
γ/°	102.025(2)
Volume/Å^3	902.85(16)
Z	2
ρ_{calc}g/cm^3	1.575
μ/mm^{-1}	2.304
F(000)	436.0
Crystal size/mm^3	0.441 × 0.254 × 0.162
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.02 to 59.268
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	27134
Independent reflections	5085 [R_{int} = 0.0206, R_{sigma} = 0.0143]
Data/restraints/parameters	5085/0/247
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0234, wR_2 = 0.0598
Final R indexes [all data]	R_1 = 0.0255, wR_2 = 0.0609
Largest diff. peak/hole / e Å^{-3}	1.02/-0.21

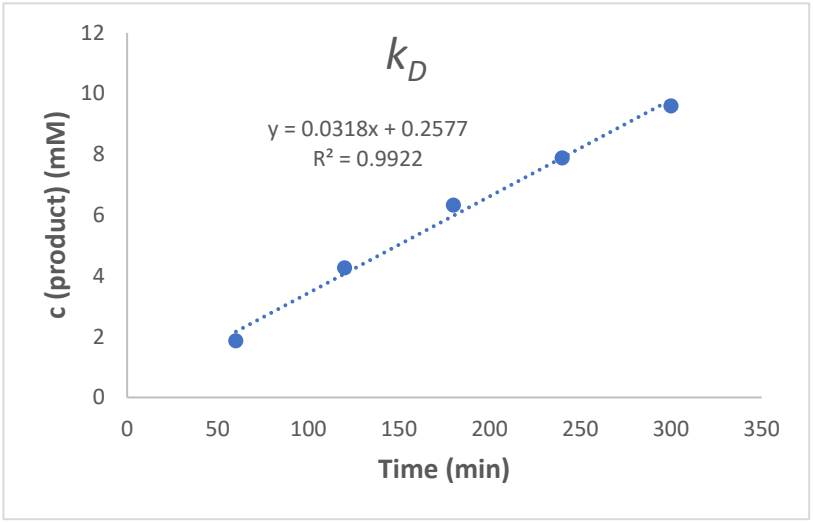
6 Kinetic study

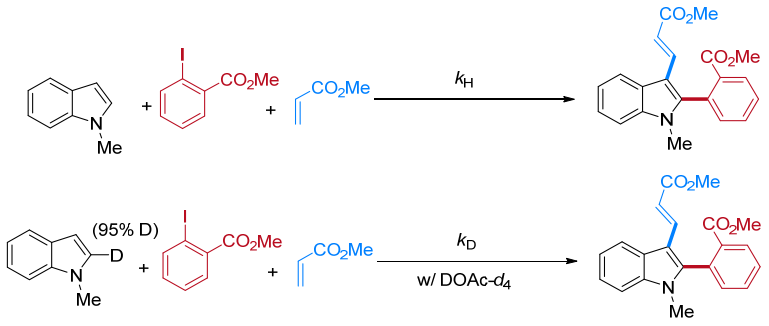
Figure S1. Parallel KIE of Indole



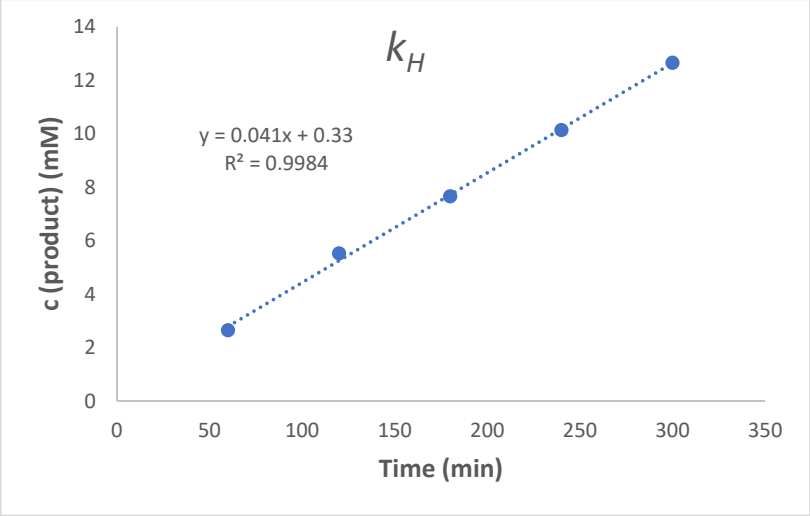
Parallel KIE = k_H/k_D = 1.3







Parallel KIE = k_H/k_D = 1.4



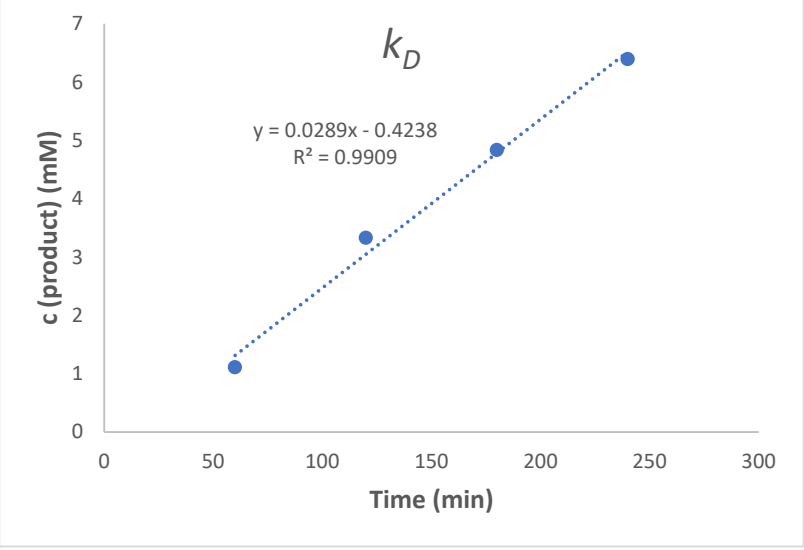
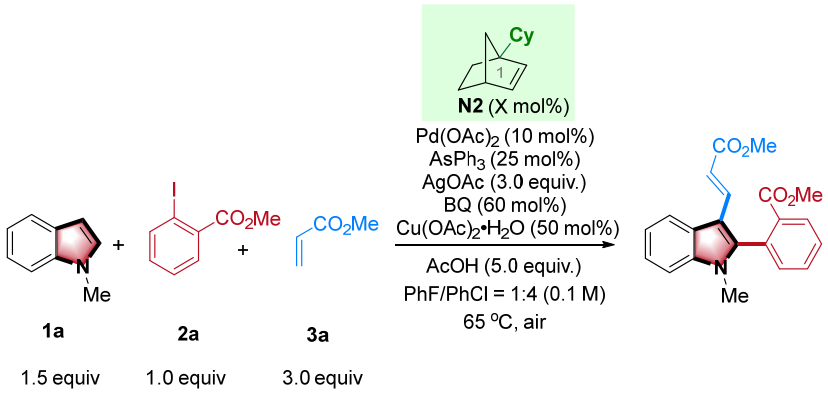
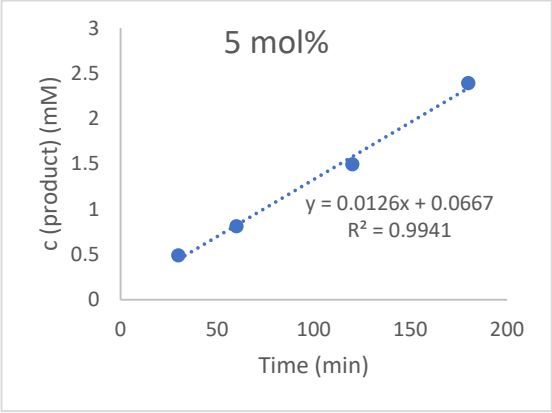
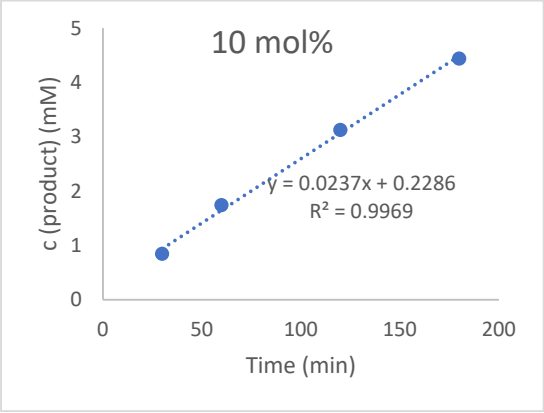


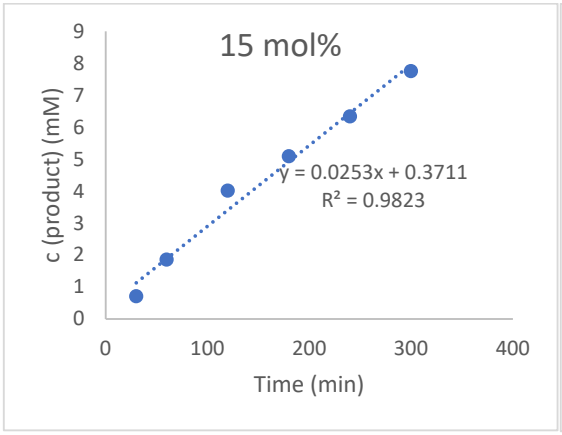
Figure S2. Initial-Rate Dependence on N2

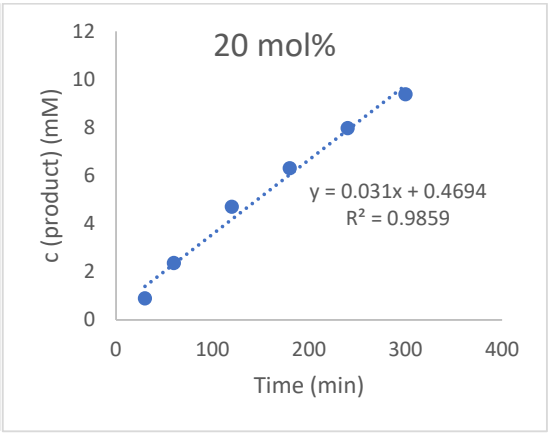


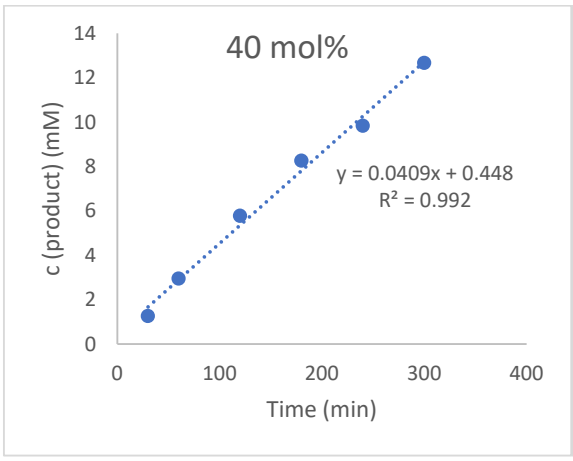
Equivalency of **N2**	0.05	0.1	0.15	0.2	0.4	0.8
[**N2**]/M	0.005	0.01	0.015	0.02	0.04	0.08
[**1a**]/M	0.15	0.15	0.15	0.15	0.15	0.15
[**2a**]/M	0.1	0.1	0.1	0.1	0.1	0.1
[**3a**]/M	0.3	0.3	0.3	0.3	0.3	0.3
[$Pd(OAc)_2$]/M	0.01	0.01	0.01	0.01	0.01	0.01
[$AsPh_3$]/M	0.025	0.025	0.025	0.025	0.025	0.025
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5	0.5
initial rate/mM·min^{-1}	0.0126	0.0195	0.00253	0.031	0.0409	0.0429

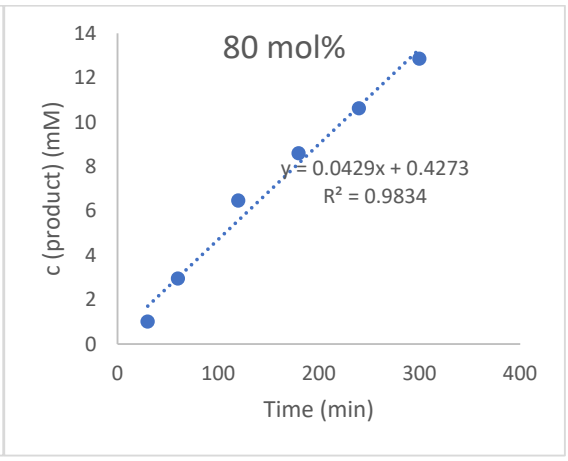












N2: <u>Saturation Dependence</u>

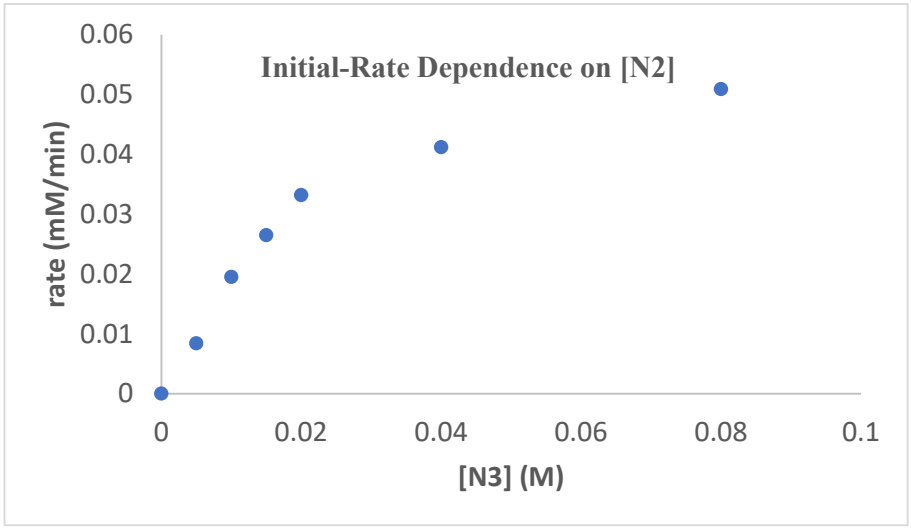
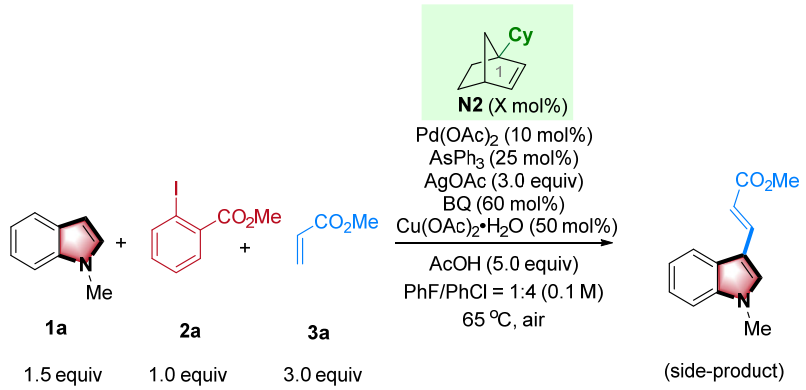
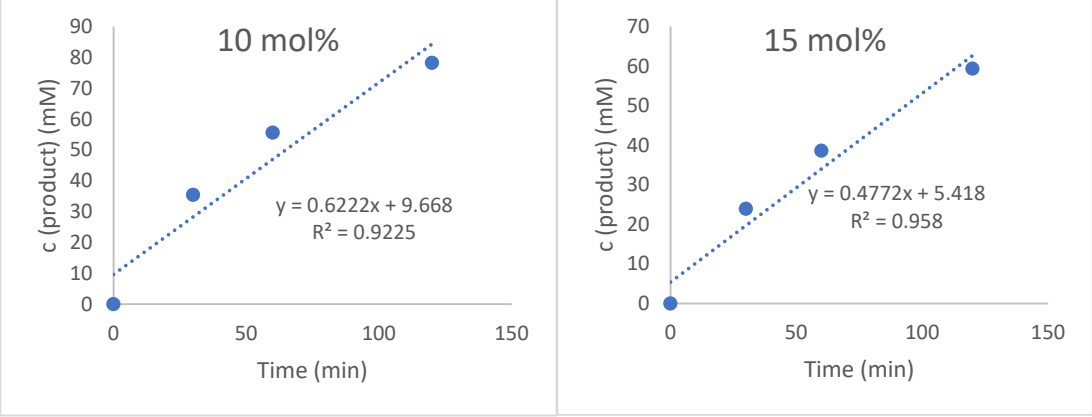
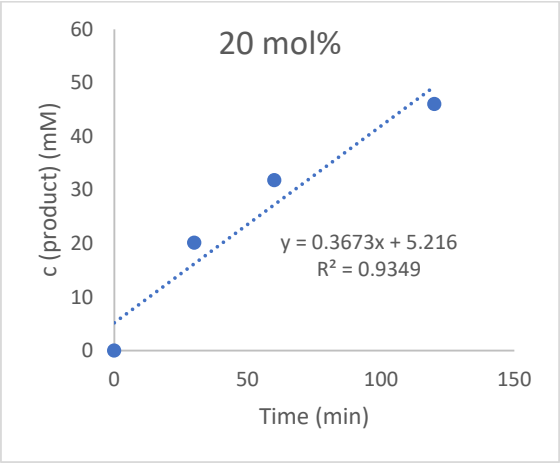


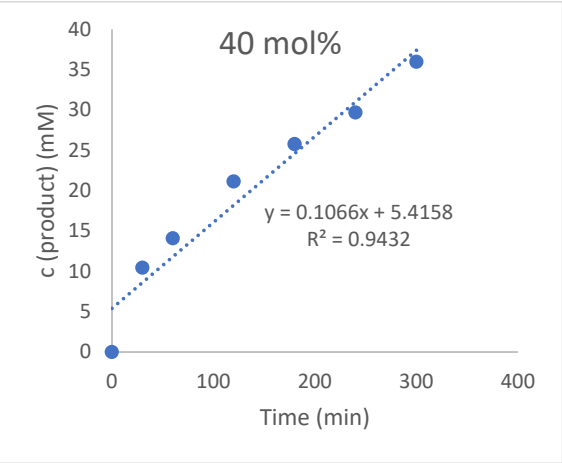
Figure S3. Initial-Rate Dependence on N2 (Formation of Direct Alkenylation Side-Product)

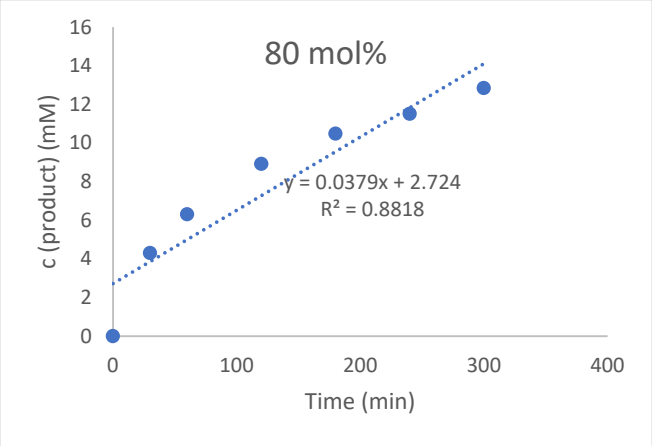


Equivalency of **N2**	0.1	0.15	0.2	0.4	0.8
[**N2**]/M	0.01	0.015	0.02	0.04	0.08
[**1a**]/M	0.15	0.15	0.15	0.15	0.15
[**2a**]/M	0.1	0.1	0.1	0.1	0.1
[**3a**]/M	0.3	0.3	0.3	0.3	0.3
[$Pd(OAc)_2$]/M	0.01	0.01	0.01	0.01	0.01
[$AsPh_3$]/M	0.025	0.025	0.025	0.025	0.025
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5
initial rate/mM·min^{-1}	0.6222	0.4772	0.3673	0.1066	0.0379

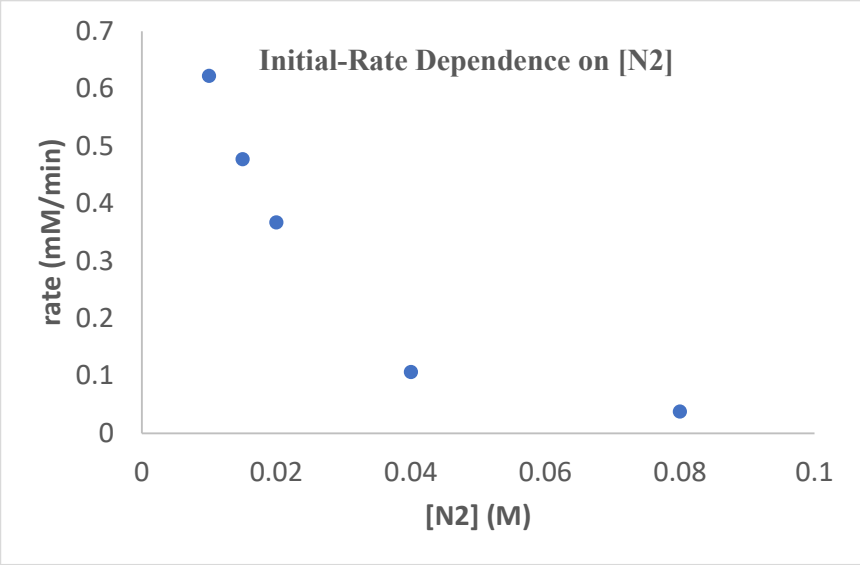



20 mol%
c (product) (mM)
Time (min)
y = 0.3673x + 5.216
R² = 0.9349
0
10
20
30
40
50
60
0
50
100
150


40 mol%
c (product) (mM)
Time (min)
y = 0.1066x + 5.4158
R² = 0.9432
0
5
10
15
20
25
30
35
40
0
100
200
300
400


80 mol%
c (product) (mM)
Time (min)
y = 0.0379x + 2.724
R² = 0.8818
0
2
4
6
8
10
12
14
16
0
100
200
300
400

N2: <u>Reverse First Order</u>



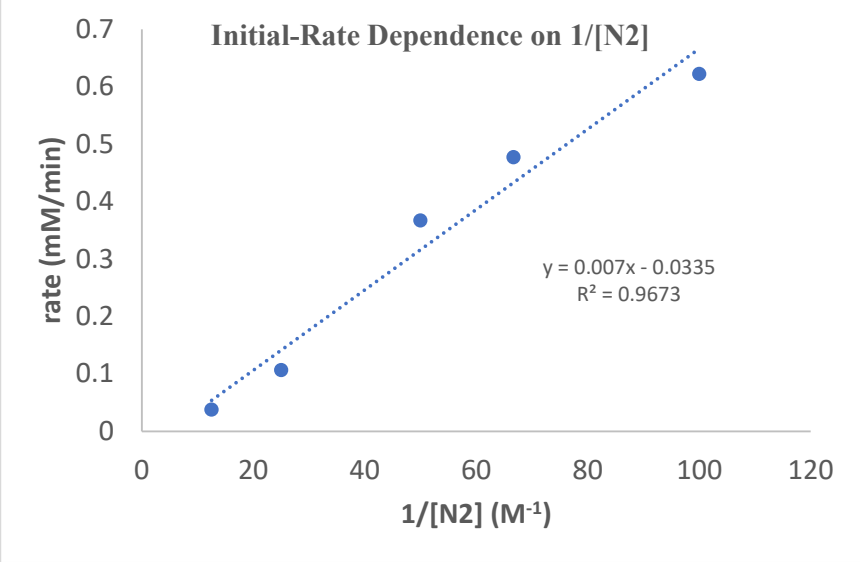
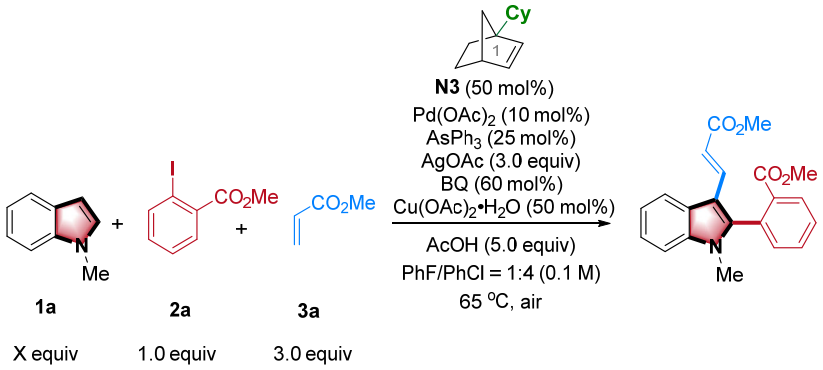
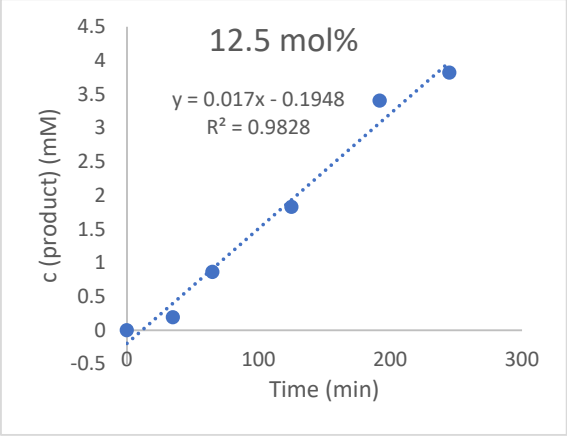
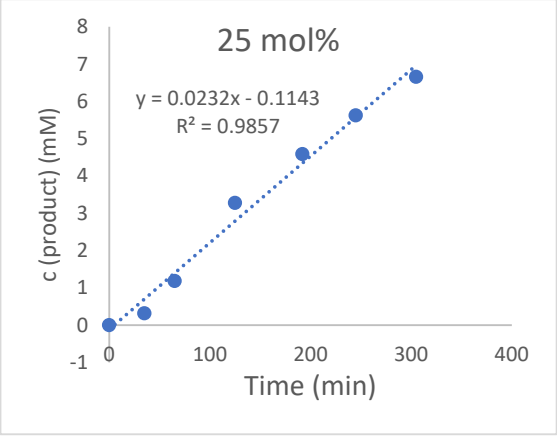


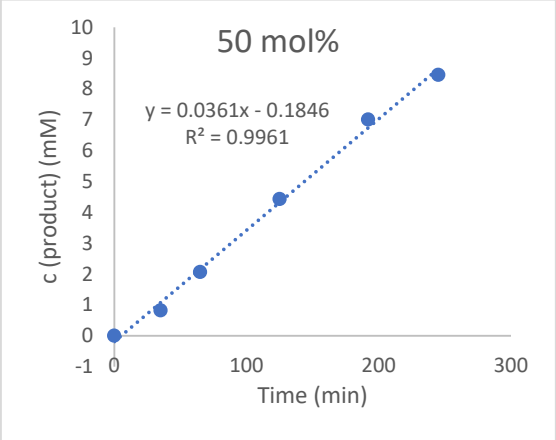
Figure S4. Initial-Rate Dependence on 1a

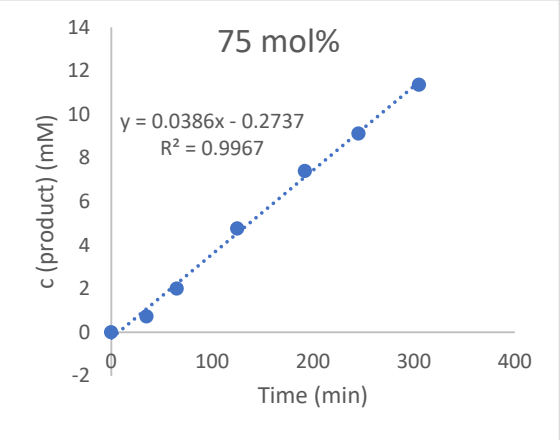


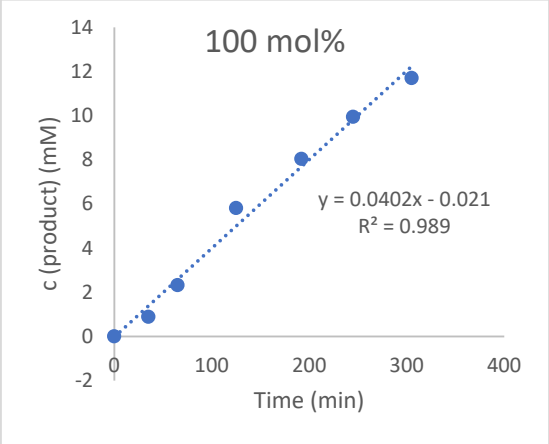
Equivalency of **1a**	0.125	0.25	0.5	0.75	1.0	1.25
[**1a**]/M	0.0125	0.025	0.05	0.075	0.1	0.125
[**2a**]/M	0.1	0.1	0.1	0.1	0.1	0.1
[**3a**]/M	0.3	0.3	0.3	0.3	0.3	0.3
[**N2**]/M	0.05	0.05	0.05	0.05	0.05	0.05
[$Pd(OAc)_2$]/M	0.01	0.01	0.01	0.01	0.01	0.01
[$AsPh_3$]/M	0.025	0.025	0.025	0.025	0.025	0.025
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5	0.5
initial rate/mM·min^{-1}	0.017	0.0232	0.0361	0.0386	0.0402	0.0431

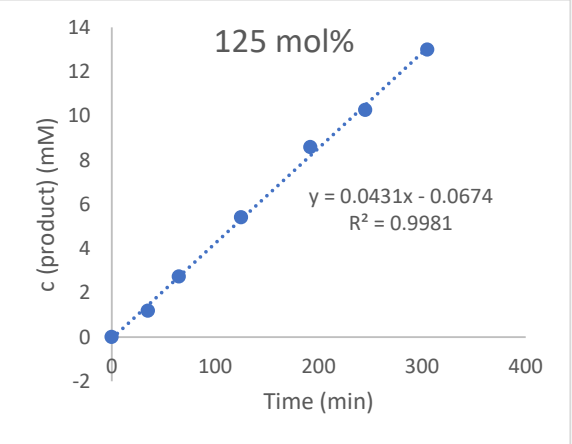












1a: Saturation dependence

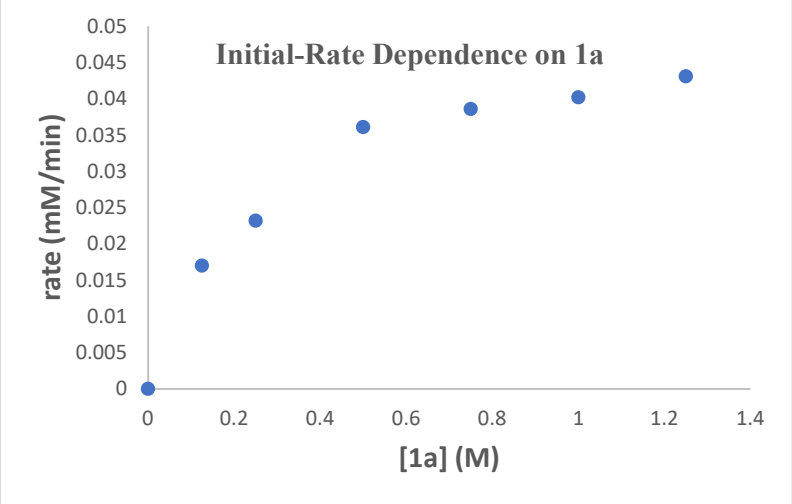
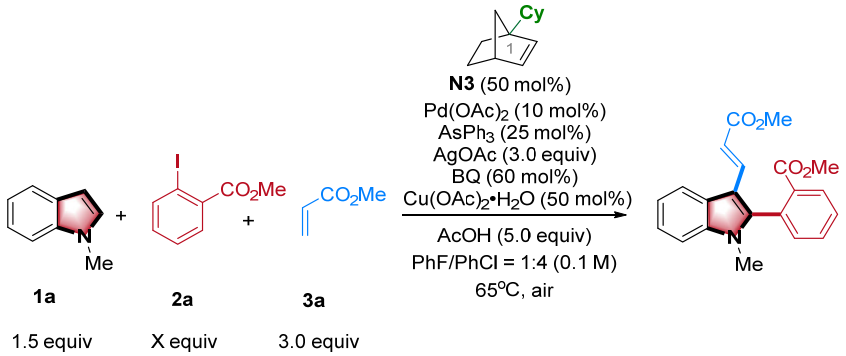
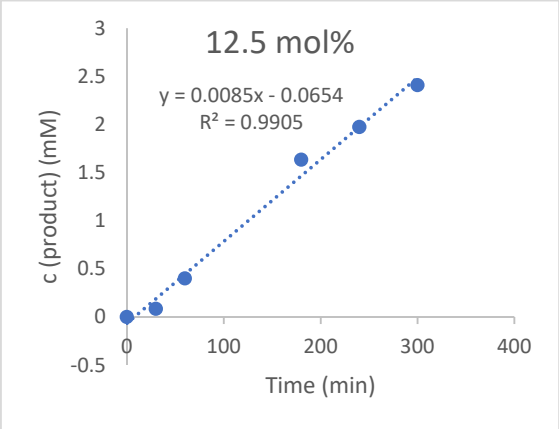
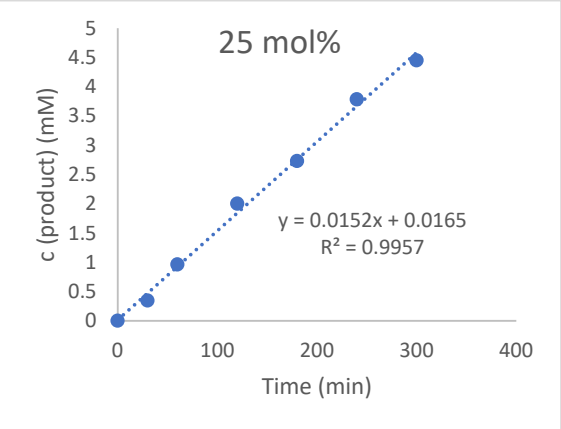


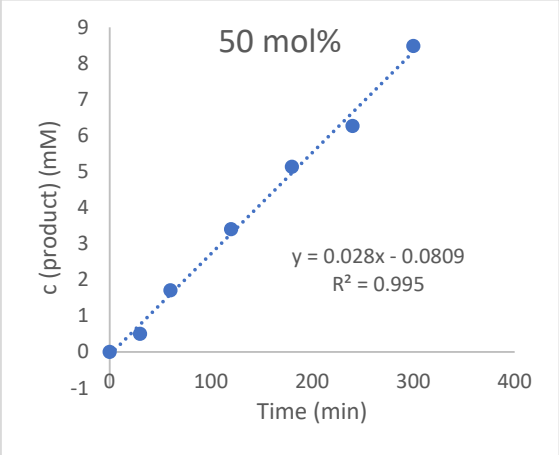
Figure S5. Initial-Rate Dependence on 2a

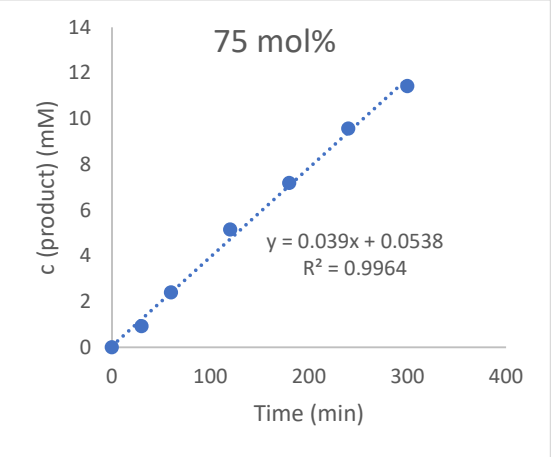


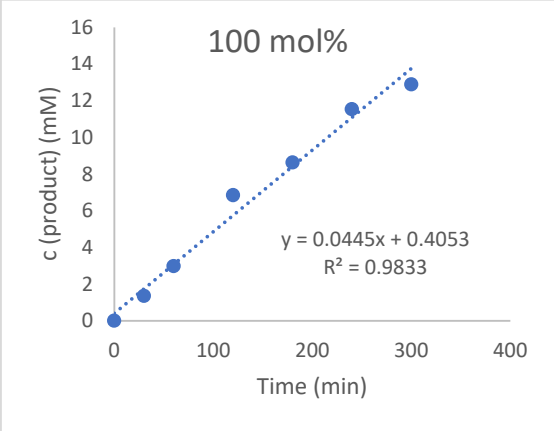
Equivalency of 2**a**	0.125	0.25	0.5	0.75	1.0
[**2a**]/M	0.0125	0.025	0.05	0.075	0.1
[**1a**]/M	0.15	0.15	0.15	0.15	0.15
[**3a**]/M	0.3	0.3	0.3	0.3	0.3
[**N2**]/M	0.05	0.05	0.05	0.05	0.05
[$Pd(OAc)_2$]/M	0.01	0.01	0.01	0.01	0.01
[$AsPh_3$]/M	0.025	0.025	0.025	0.025	0.025
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5
initial rate/mM·min^{-1}	0.0085	0.0152	0.028	0.039	0.0445











2a: First Order

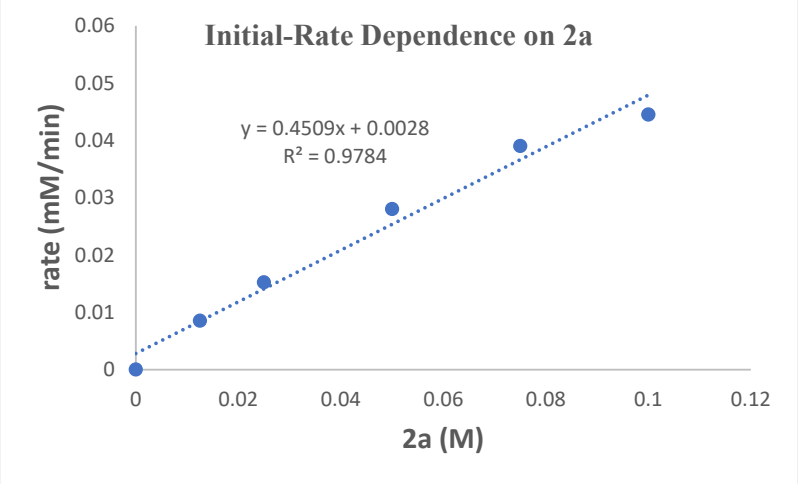
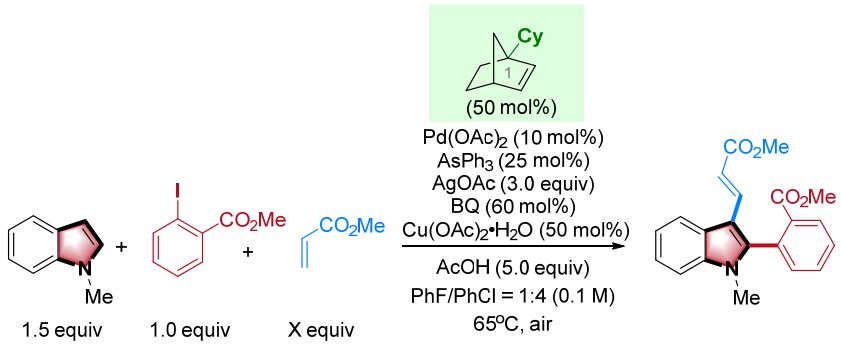
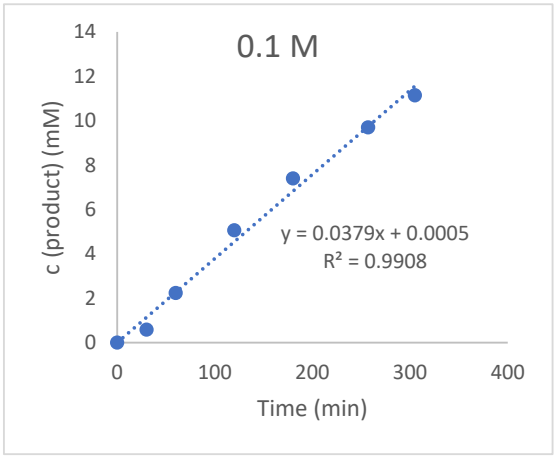
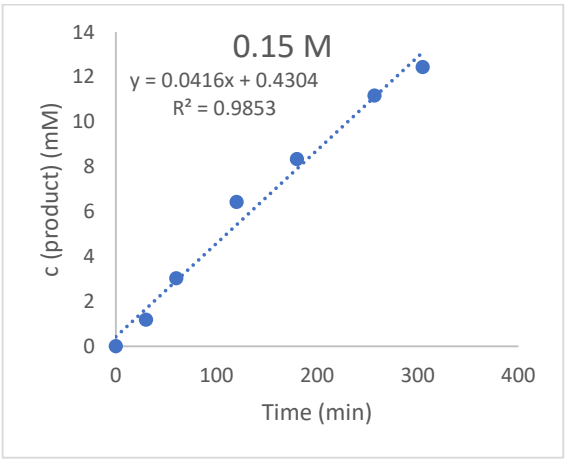


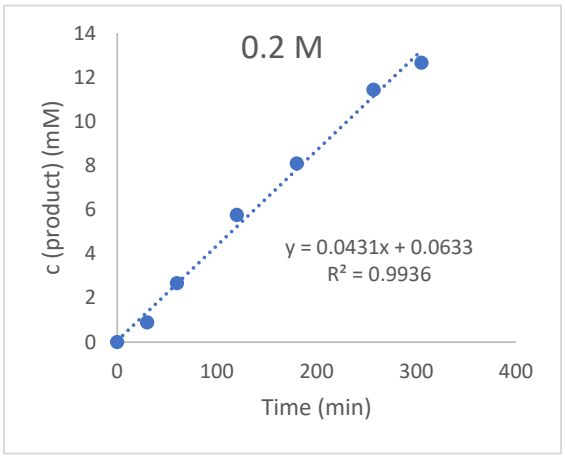
Figure S6. Initial-Rate Dependence on 3a

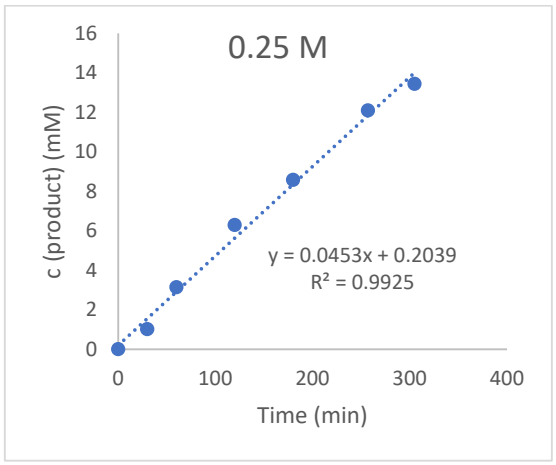


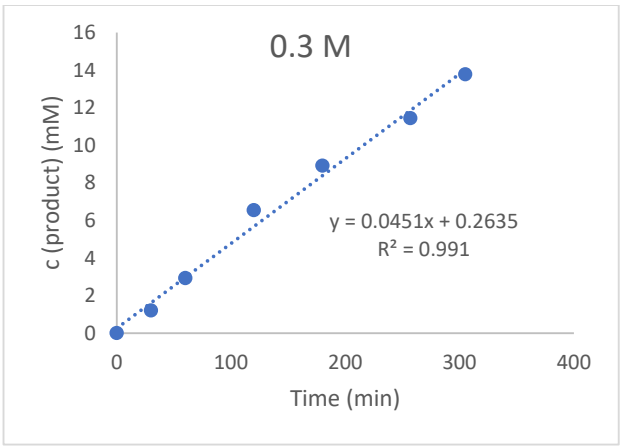
Equivalency of 3**a**	1.0	1.5	2.0	2.5	3.0
[3**a**]/M	0.1	0.15	0.2	0.25	0.3
[**1a**]/M	0.15	0.15	0.15	0.15	0.15
[**2a**]/M	0.1	0.1	0.1	0.1	0.1
[**N2**]/M	0.05	0.05	0.05	0.05	0.05
[$Pd(OAc)_2$]/M	0.01	0.01	0.01	0.01	0.01
[$AsPh_3$]/M	0.025	0.025	0.025	0.025	0.025
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5
Initial rate/mM·min^{-1}	0.0379	0.0416	0.0431	0.0453	0.0451











3a: <u>Zero order</u>

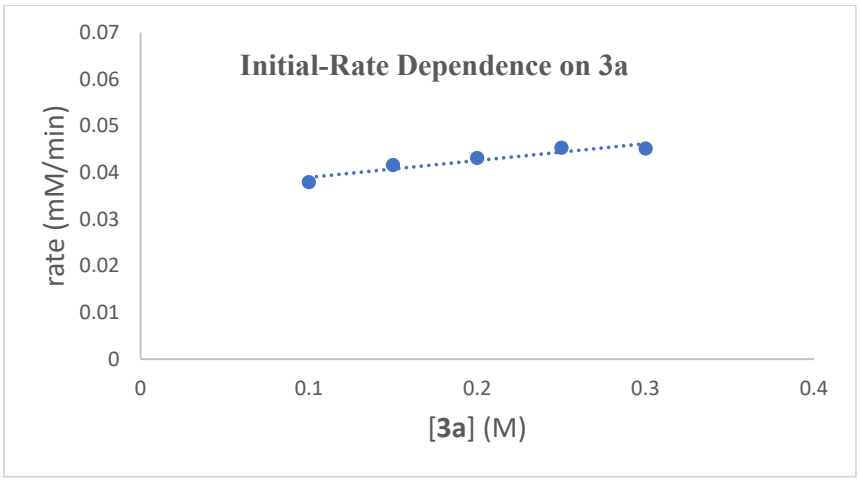
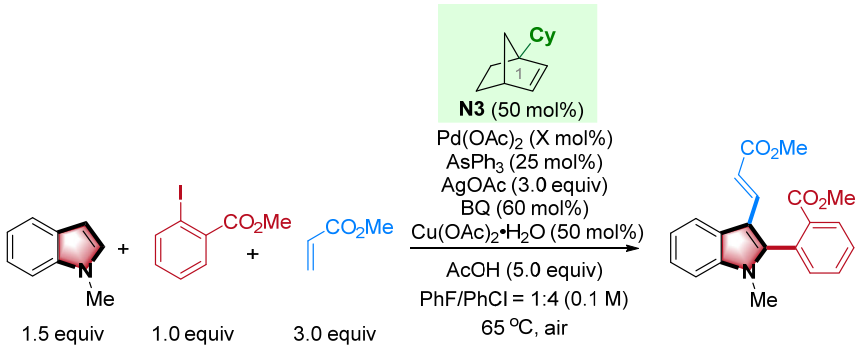
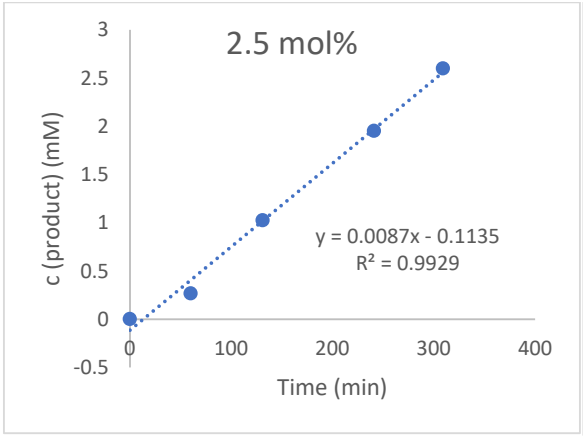
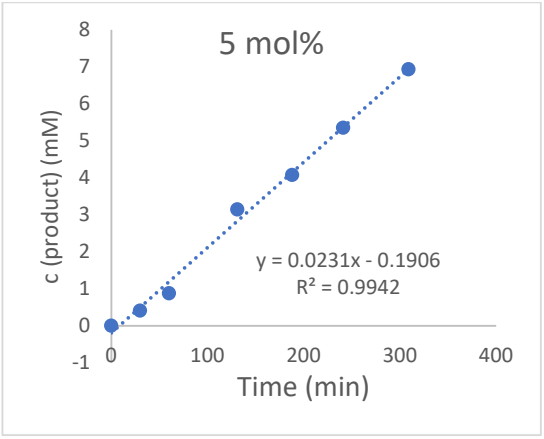


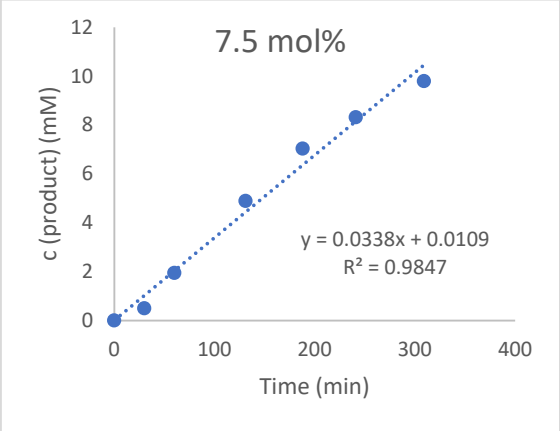
Figure S7. Initial-Rate Dependence on [Pd]

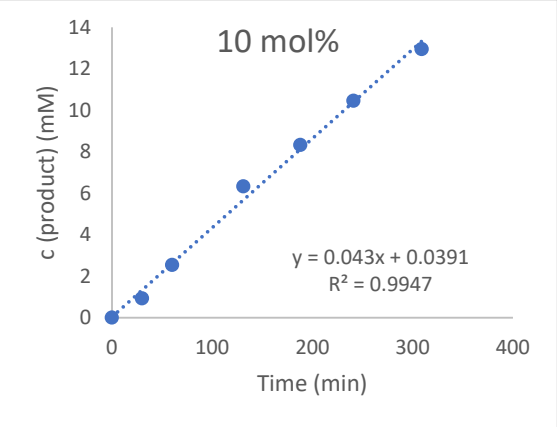


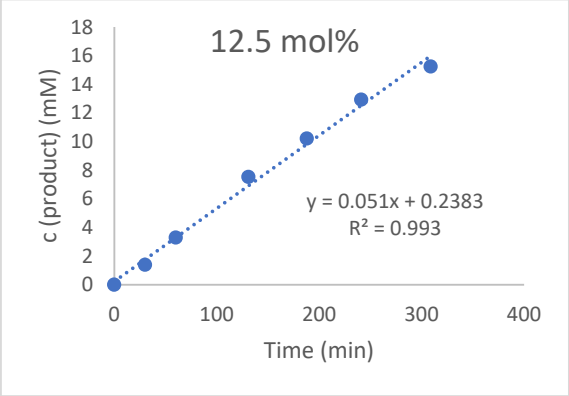
Equivalency of [Pd]	0.025	0.05	0.075	0.1	0.125
Equivalency of [AsPh3]	0.0625	0.125	0.1875	0.25	0.3125
[Pd]/M	0.0025	0.005	0.0075	0.01	0.0125
[AsPh3]/M	0.00625	0.0125	0.01875	0.025	0.03125
[**1a**]/M	0.15	0.15	0.15	0.15	0.15
[**2a**]/M	0.1	0.1	0.1	0.1	0.1
[**3a**]/M	0.3	0.3	0.3	0.3	0.3
[**N2**]/M	0.05	0.05	0.05	0.05	0.05
[AgOAc]/M	0.3	0.3	0.3	0.3	0.3
[BQ]/M	0.06	0.06	0.06	0.06	0.06
[$Cu(OAc)_2•H_2O$]/M	0.05	0.05	0.05	0.05	0.05
[HOAc]/M	0.5	0.5	0.5	0.5	0.5
Initial rate/mM·min^{-1}	0.0087	0.0231	0.0338	0.043	0.051



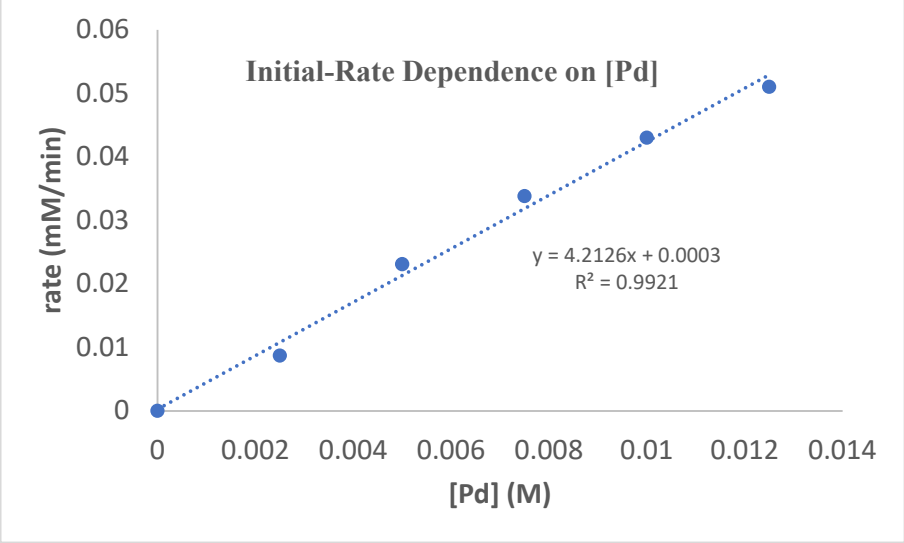








[Pd]: <u>First Order</u>



7. DFT data

7.1 Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[9] Geometries were optimized using the (U)B3LYP[10] functional and Grimme's D3(BJ) dispersion correction[11] with a mixed basis set of LANL2DZ for Pd and I and 6-31G(d) for other atoms. Vibrational frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy corrections were calculated in chlorobenzene solvent with the SMD continuum solvation model[12] based on the gas phase optimized geometries. The M06[13] functional with a mixed basis set of SDD for Pd and I and 6-311+G(d, p) for other atoms were used for single-point energy calculations. The optimized transition state structures were plotted using CYLview.[14]

7.2 Detailed computational results

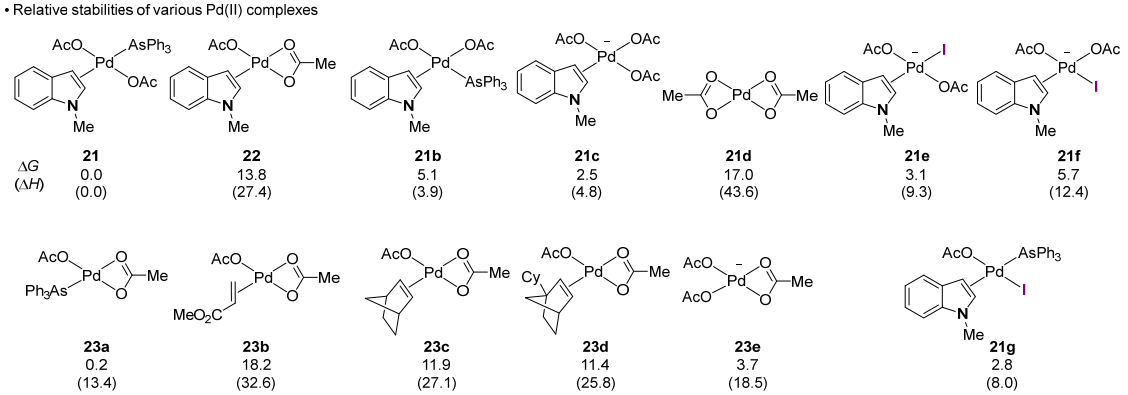


Figure S1. The relative stabilities of various Pd(II) complexes. All energies are in kcal/mol. Computational results suggest that neutral Pd(II) species **21** has the lowest relative free energy among these Pd(II) complexes. Thus, **21** is selected as the relative zero point of the following free energy profiles.

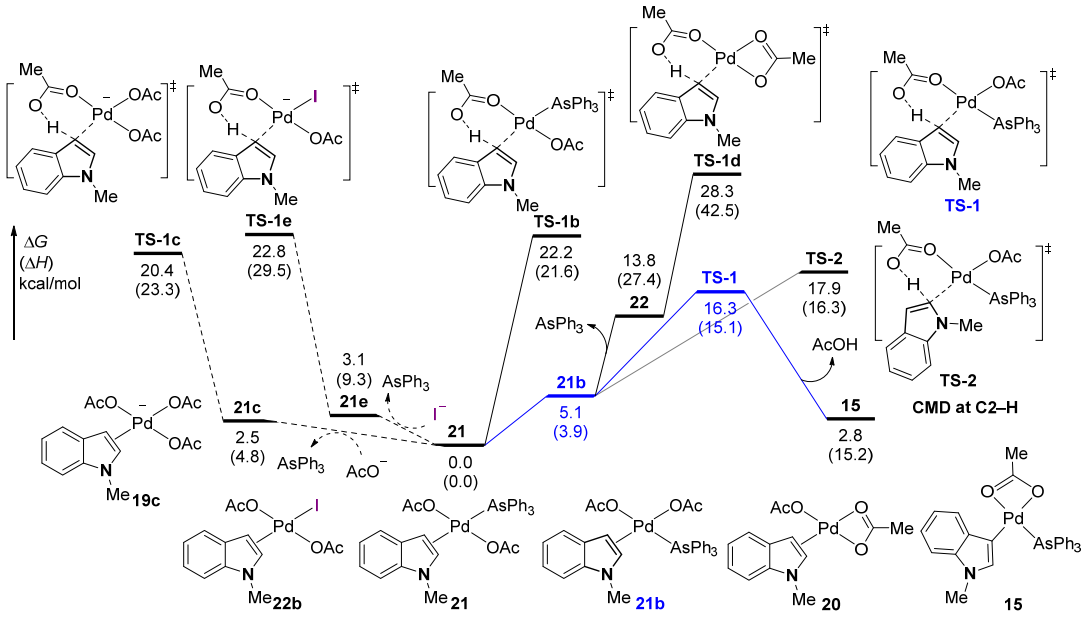


Figure S2. Free energy profiles of the first C−H palladation of indole. Different reaction pathways have been considered in the DFT studies, including neutral and anionic Pd(II) species mediated CMD pathways. The site-selectivity of C−H palladation was also investigated.

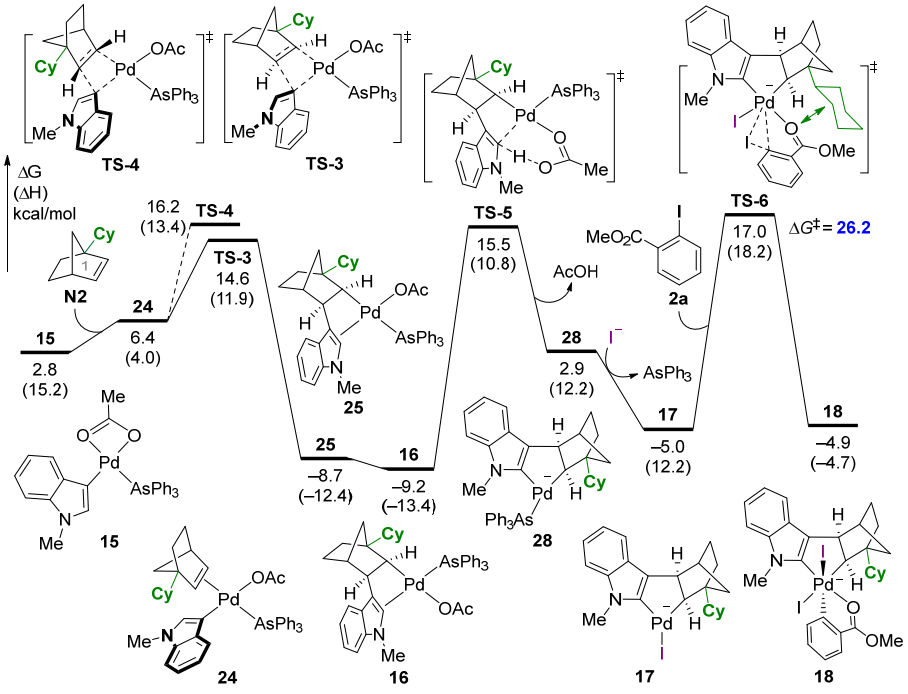


Figure S3. Free energy profile of the NBE (**N2**) insertion, the second C−H palladation at the C2 position of indole (via **TS-5**), and the oxidative addition of **2a** with ANP (via **TS-6**).

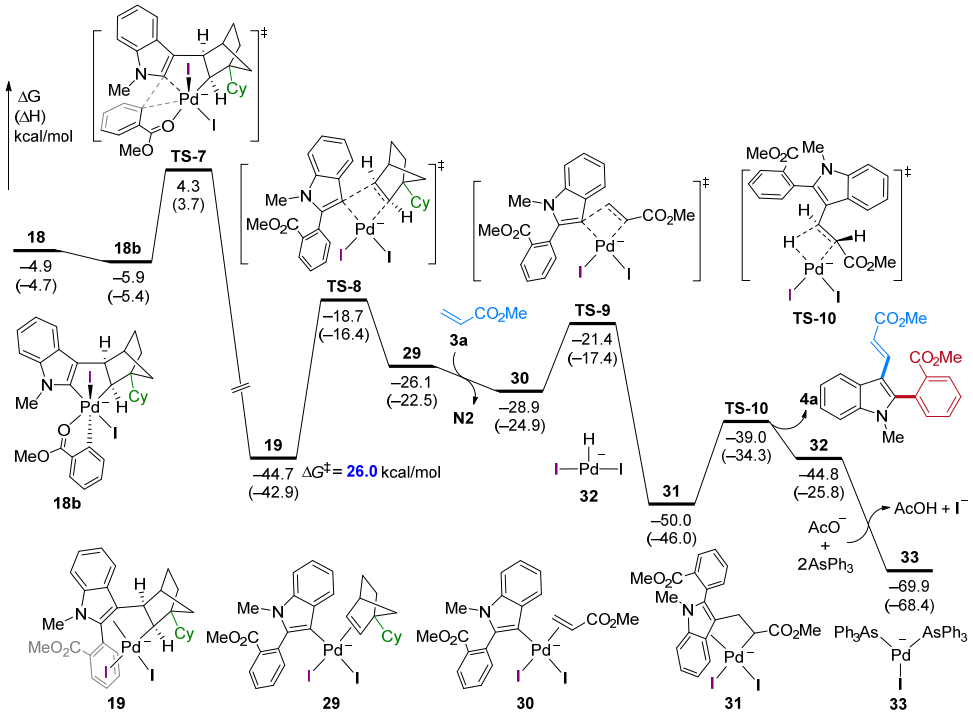


Figure S4. Free energy profile of the C–C reductive elimination from Pd(IV) intermediate (via **TS-7**), β-C elimination (via **TS-8**), alkene insertion (via **TS-9**), and β-H elimination (via **TS-10**).

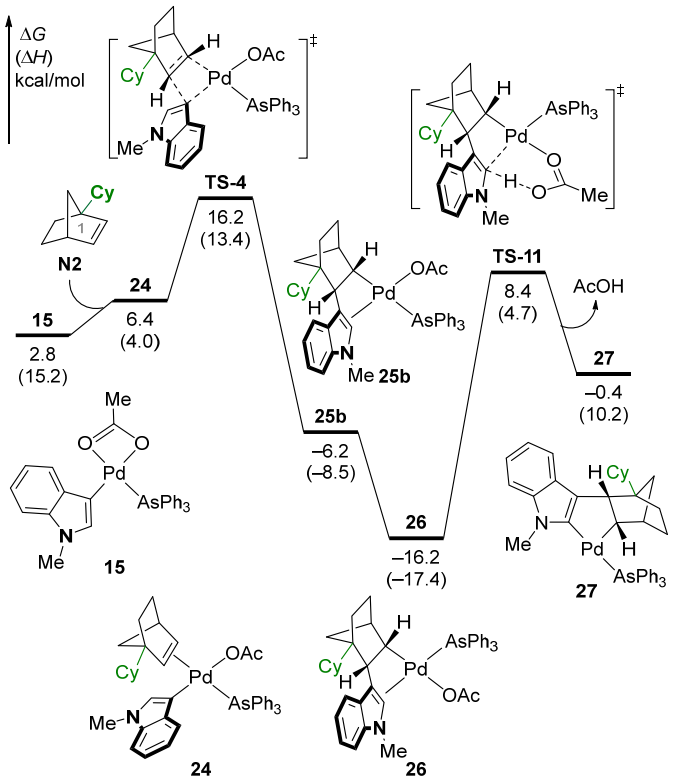


Figure S5. Free energy profile of the NBE (**N2**) insertion through **TS-4** followed by the second C–H palladation at the C2 position of indole (via **TS-11**).

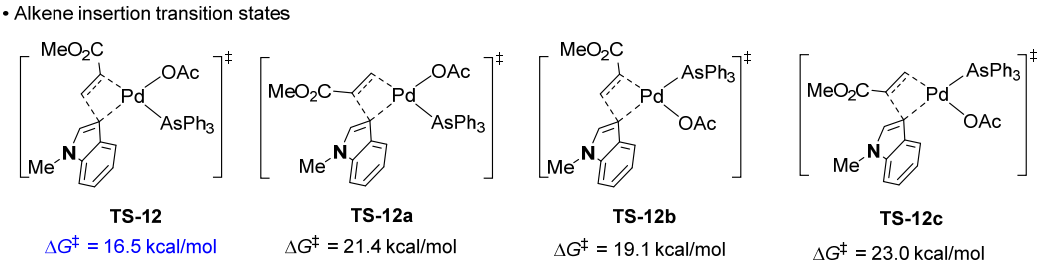


Figure S6. Located transition states for the competing acrylate **3a** migratory insertion into the Pd–C bond of intermediate **15**. The activation free energy of **TS-12** is 1.9 kcal/mol higher than that of **TS-3**, which indicates that acrylate **3a** may compete with **N2** for migratory insertion under the circumstance of low [**N2**].

7.3 Cartesian coordinates (Å) and energies of optimized structures

1a
B3LYP SCF energy: -403.15644481 a.u.
B3LYP enthalpy: -402.989296 a.u.
B3LYP free energy: -403.031112 a.u.
M06 SCF energy in solution: -402.92844590 a.u.
M06 enthalpy in solution: -402.761297 a.u.
M06 free energy in solution: -402.803113 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.151286	-0.332275	-0.000085
C	0.388097	0.986763	0.000033
C	1.783862	1.145189	0.000112
C	2.592580	0.015273	0.000074
C	2.036249	-1.280245	-0.000044
C	0.658773	-1.472459	-0.000139
C	-1.864075	1.120502	-0.000062
C	-0.729365	1.889449	-0.000055
H	2.222965	2.139278	0.000171
H	3.673027	0.128205	0.000130
H	2.695045	-2.143932	-0.000055
H	0.231968	-2.471230	-0.000221
H	-2.905278	1.413021	-0.000142
H	-0.692635	2.969786	-0.000081
C	-2.451716	-1.337148	0.000178
H	-2.312972	-1.962433	-0.889919
H	-2.313025	-1.961988	0.890597
H	-3.473922	-0.952904	0.000043
N	-1.529126	-0.224014	-0.000084

2a
B3LYP SCF energy: -470.92395408 a.u.
B3LYP enthalpy: -470.779102 a.u.
B3LYP free energy: -470.829250 a.u.
M06 SCF energy in solution: -470.72827571 a.u.

M06 enthalpy in solution: -470.583424 a.u.
M06 free energy in solution: -470.633572 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.013589	1.718110	-0.132977
O	-1.745642	2.525586	-0.671537
O	0.132944	2.049763	0.477256
C	0.502185	3.433581	0.387400
H	-0.244384	4.059413	0.883179
H	1.466106	3.508017	0.890339
H	0.585558	3.739183	-0.658516
C	-1.340715	0.260385	-0.029259
C	-2.717107	-0.027065	-0.031423
C	-0.440040	-0.813190	0.058931
C	-3.190700	-1.327195	0.087300
H	-3.399672	0.809966	-0.128308
C	-0.911266	-2.124052	0.166683
C	-2.281427	-2.379381	0.192723
H	-4.259232	-1.518279	0.093638
H	-0.207342	-2.946091	0.223686
H	-2.630746	-3.403760	0.284433
I	1.697118	-0.628272	-0.079820

3a

B3LYP SCF energy: -306.47612303 a.u.
B3LYP enthalpy: -306.372638 a.u.
B3LYP free energy: -306.410550 a.u.
M06 SCF energy in solution: -306.37047836 a.u.
M06 enthalpy in solution: -306.266993 a.u.
M06 free energy in solution: -306.304905 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.316131	-0.647864	0.000134
H	-1.239990	-1.730862	0.000282
C	-2.488382	-0.010098	-0.000071
H	-2.519760	1.075696	-0.000251
H	-3.431766	-0.547174	-0.000028
C	-0.043406	0.114977	0.000044
O	0.060824	1.325446	0.000028
O	1.016649	-0.726931	-0.000172
C	2.299447	-0.085839	0.000046
H	2.415147	0.540309	0.888915
H	3.031933	-0.893352	0.000183
H	2.415491	0.540210	-0.888861

4a

B3LYP SCF energy: -1167.42270581 a.u.
B3LYP enthalpy: -1167.038003 a.u.
B3LYP free energy: -1167.120073 a.u.
M06 SCF energy in solution: -1166.87870619 a.u.
M06 enthalpy in solution: -1166.494003 a.u.

M06 free energy in solution: -1166.576073 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.830263	0.526721	-0.534468
C	-1.928047	1.584839	-0.257150
C	-2.441547	2.856166	0.035784
C	-3.820428	3.037074	0.050834
C	-4.698913	1.970045	-0.220768
C	-4.216763	0.698519	-0.517120
C	-0.740043	-0.309300	-0.660869
C	-0.588851	1.038237	-0.343671
H	-1.774863	3.685986	0.252166
H	-4.229665	4.017034	0.278387
H	-5.771167	2.140828	-0.196022
H	-4.894829	-0.124540	-0.720776
C	-2.637442	-1.927235	-1.013283
H	-3.007999	-2.350691	-0.072751
H	-3.459759	-1.869665	-1.732210
H	-1.864809	-2.583882	-1.414762
N	-2.079149	-0.608570	-0.801273
C	0.309498	-1.326974	-0.885097
C	0.947067	-1.329781	-2.133935
C	0.731209	-2.254475	0.093814
C	1.976148	-2.224916	-2.418280
H	0.632280	-0.602884	-2.875829
C	1.772829	-3.144776	-0.201287
C	2.391689	-3.136668	-1.446681
H	2.455317	-2.204482	-3.392629
H	2.084716	-3.833295	0.575958
H	3.197324	-3.833559	-1.656626
C	0.618294	1.785633	-0.102932
H	0.480994	2.852655	0.066860
C	1.897147	1.351283	-0.044850
H	2.183669	0.316451	-0.180124
C	2.973965	2.311683	0.221903
O	2.850846	3.511499	0.402745
O	4.182729	1.685575	0.247233
C	5.297933	2.542590	0.507278
H	5.194199	3.029587	1.481333
H	6.176709	1.896244	0.494998
H	5.380326	3.316580	-0.261468
C	0.176079	-2.348754	1.479578
O	-0.920201	-1.590589	1.667995
O	0.657283	-3.045600	2.351724
C	-1.457249	-1.589626	2.999006
H	-0.705028	-1.242211	3.711213
H	-2.303332	-0.903642	2.964920
H	-1.779171	-2.595307	3.281856

16

B3LYP SCF energy: -4193.82679070 a.u.
B3LYP enthalpy: -4192.995906 a.u.
B3LYP free energy: -4193.120039 a.u.
M06 SCF energy in solution: -4196.25620603 a.u.

M06 enthalpy in solution: -4195.425321 a.u.
M06 free energy in solution: -4195.549454 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.965147	-0.455658	-0.084311
C	-2.581968	1.872117	0.140664
O	-2.207673	1.701630	1.311931
O	-2.184985	1.165452	-0.870410
C	-3.536179	3.005551	-0.212599
H	-3.977662	3.428241	0.692203
H	-2.977167	3.787429	-0.738881
H	-4.326692	2.649715	-0.880562
C	-4.435658	-0.841559	-0.414243
C	-3.650777	-1.488260	0.572011
C	-4.029419	-1.406917	1.917142
C	-5.163182	-0.674190	2.247312
C	-5.917805	-0.017816	1.256512
C	-5.565896	-0.090019	-0.088024
C	-2.719214	-1.823067	-1.475926
C	-2.526186	-2.104615	-0.115880
H	-3.431459	-1.884226	2.687893
H	-5.464402	-0.590085	3.287108
H	-6.789348	0.561348	1.546916
H	-6.144713	0.426297	-0.847023
H	-2.142911	-2.147382	-2.329282
C	-4.160072	-0.332101	-2.857445
H	-5.242073	-0.293243	-3.010067
H	-3.750138	0.677405	-2.759353
H	-3.705999	-0.832652	-3.716079
N	-3.858929	-1.090211	-1.656156
C	2.160068	0.948587	-1.357511
C	3.870594	0.681306	-3.561318
C	1.748176	0.240540	-2.493171
C	3.437112	1.515879	-1.330886
C	4.289605	1.379915	-2.427434
C	2.597863	0.108337	-3.591734
H	0.761638	-0.217067	-2.500697
H	3.781006	2.052742	-0.455117
H	5.283563	1.817006	-2.393566
H	2.268473	-0.445620	-4.466277
H	4.536904	0.574867	-4.412473
C	1.771115	1.418382	1.724258
C	3.060827	1.726511	4.189020
C	2.707191	2.444838	1.907671
C	1.449397	0.583336	2.797483
C	2.094929	0.733416	4.025842
C	3.358149	2.589942	3.131697
H	2.902608	3.152934	1.109449
H	0.680664	-0.170233	2.670268
H	1.838528	0.078325	4.853375
H	4.087683	3.383866	3.264318
H	3.566991	1.842048	5.143214
C	0.301674	3.003155	-0.324429
C	-0.499824	5.630165	-0.854120
C	-0.128768	3.829506	0.718894
C	0.317299	3.491705	-1.633561

C	-0.083596	4.801873	-1.897767
C	-0.522792	5.140565	0.453405
H	-0.177788	3.444186	1.729973
H	0.642084	2.854234	-2.449052
H	-0.067793	5.174115	-2.918413
H	-0.856660	5.775615	1.269027
H	-0.809451	6.651276	-1.059204
As	0.823152	1.163952	0.052771
C	-0.210997	-2.207907	0.764579
C	0.919605	-3.040075	0.125564
C	-0.989766	-4.165643	-0.437215
C	-1.493347	-3.039241	0.494559
H	-0.047630	-1.984923	1.823126
C	0.211164	-3.522231	-1.164328
H	0.788896	-4.261892	-1.728402
H	-0.041148	-2.689664	-1.828025
C	0.984198	-4.380203	0.936465
H	1.911768	-4.919438	0.716056
H	0.970867	-4.192682	2.014639
C	-0.260366	-5.182571	0.459356
H	0.037466	-6.061722	-0.123056
H	-0.887918	-5.532975	1.285842
H	-1.773406	-4.596819	-1.067682
H	-1.926880	-3.462732	1.409049
C	2.273652	-2.336061	-0.008982
C	2.985865	-2.175653	1.346681
C	3.227796	-2.997864	-1.018327
H	2.068366	-1.331579	-0.386929
C	4.272515	-1.354522	1.214514
H	3.237446	-3.168431	1.745619
H	2.316812	-1.707323	2.073371
C	4.545505	-2.219583	-1.147127
H	3.440974	-4.031208	-0.706332
H	2.748506	-3.058129	-2.002535
C	5.230013	-2.006134	0.209195
H	4.755277	-1.246741	2.194031
H	4.019956	-0.340818	0.877349
H	5.222383	-2.742090	-1.835829
H	4.334566	-1.243274	-1.596837
H	6.132267	-1.393550	0.083973
H	5.561084	-2.976826	0.607836

16b

B3LYP SCF energy: -3959.11713499 a.u.
B3LYP enthalpy: -3958.443864 a.u.
B3LYP free energy: -3958.557556 a.u.
M06 SCF energy in solution: -3961.70289638 a.u.
M06 enthalpy in solution: -3961.029625 a.u.
M06 free energy in solution: -3961.143317 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.681687	-0.036785	-0.788255
C	0.842789	2.866771	-0.774021
O	0.710170	2.687543	-1.997375

O	0.943291	1.927884	0.105382
C	0.863627	4.278787	-0.196815
H	1.039688	5.016080	-0.983727
H	-0.110896	4.480857	0.262795
H	1.622462	4.367799	0.586879
C	4.026428	0.880530	-0.132083
C	3.556183	-0.424250	0.184143
C	3.851592	-0.952622	1.451832
C	4.587888	-0.189970	2.350652
C	5.038895	1.100345	2.014625
C	4.764624	1.652007	0.769022
C	2.873704	0.159404	-1.909013
C	2.806198	-0.889628	-0.975972
H	3.502698	-1.936104	1.739178
H	4.817081	-0.596059	3.331618
H	5.610452	1.673822	2.738626
H	5.110517	2.646723	0.507080
H	2.522711	0.179895	-2.930910
C	3.817158	2.477669	-2.071375
H	3.728634	3.281268	-1.335791
H	4.806599	2.527945	-2.541110
H	3.027420	2.622647	-2.807611
N	3.614629	1.199711	-1.414093
C	-1.396250	-0.398679	1.870271
C	-0.876747	-1.204243	4.493760
C	-0.373256	0.222897	2.604556
C	-2.151294	-1.421070	2.448507
C	-1.888891	-1.823741	3.760766
C	-0.121904	-0.179409	3.914693
H	0.225558	1.000890	2.136922
H	-2.934969	-1.910109	1.878894
H	-2.474713	-2.623180	4.206118
H	0.672476	0.300298	4.479448
H	-0.671964	-1.521154	5.512649
C	-3.092846	-0.864313	-0.646273
C	-5.292791	-2.284799	-1.628422
C	-4.359812	-0.681188	-0.077775
C	-2.937784	-1.746142	-1.719693
C	-4.035738	-2.456374	-2.208817
C	-5.454829	-1.393841	-0.564133
H	-4.491584	0.025035	0.736626
H	-1.960821	-1.872077	-2.172456
H	-3.907955	-3.140031	-3.043257
H	-6.434775	-1.249874	-0.117823
H	-6.147387	-2.837521	-2.008272
C	-2.302482	1.921552	0.127238
C	-3.387319	4.493636	0.197161
C	-2.308819	2.708730	-1.029436
C	-2.833674	2.423371	1.318641
C	-3.375618	3.709577	1.352027
C	-2.851890	3.992485	-0.991776
H	-1.847258	2.340528	-1.939070
H	-2.811636	1.820035	2.220582
H	-3.783391	4.098895	2.280860
H	-2.841823	4.605466	-1.888262
H	-3.804625	5.496374	0.225383
As	-1.565216	0.133600	0.013622

C	0.659084	-1.995522	-1.404809
C	0.065774	-2.998702	-0.406913
C	2.295881	-3.347778	-0.243263
C	2.193417	-2.247561	-1.321991
H	0.245945	-2.064356	-2.416382
C	1.129128	-3.002867	0.708945
H	0.954637	-3.777580	1.464220
H	1.222263	-2.034477	1.206457
C	0.241079	-4.416759	-1.007506
H	-0.324386	-5.155995	-0.428114
H	-0.115594	-4.469723	-2.041866
C	1.779383	-4.656902	-0.886288
H	1.994737	-5.510358	-0.234594
H	2.256617	-4.854906	-1.852171
H	3.289720	-3.445450	0.199066
H	2.627791	-2.605085	-2.264118
H	-0.955155	-2.786987	-0.085846

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B3LYP SCF energy: -1047.73871251 a.u.
B3LYP enthalpy: -1047.269578 a.u.
B3LYP free energy: -1047.349767 a.u.
M06 SCF energy in solution: -1048.38384393 a.u.
M06 enthalpy in solution: -1047.914709 a.u.
M06 free energy in solution: -1047.994898 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.189491	-0.747723	-0.441170
C	-3.906039	-0.854524	0.394115
C	-3.778055	0.487394	-0.101745
C	-4.928268	1.291509	-0.154106
C	-6.150717	0.772674	0.269078
C	-6.253599	-0.546355	0.748690
C	-5.130794	-1.374059	0.814949
C	-1.736676	-0.528552	-0.149971
C	-2.395001	0.653684	-0.435549
H	-4.862942	2.312214	-0.524570
H	-7.041631	1.395851	0.228223
H	-7.219269	-0.927646	1.072418
H	-5.209445	-2.393238	1.184910
C	-2.366294	-2.803051	0.759621
H	-2.632554	-2.965329	1.812442
H	-2.920393	-3.525188	0.145008
H	-1.295949	-2.981086	0.634382
N	-2.655773	-1.446534	0.356418
C	-0.078171	1.226673	-1.015748
C	0.715315	2.204490	-0.109038
C	-1.428102	2.988604	-0.012610
C	-1.553602	1.762995	-0.958122
H	0.315918	1.196143	-2.039066
C	-0.343564	2.527273	0.973937
H	-0.033941	3.323721	1.661270
H	-0.630576	1.640686	1.546132
C	0.760789	3.557419	-0.888568

H	1.478336	4.248306	-0.430340
H	1.073830	3.411556	-1.927803
C	-0.693426	4.107625	-0.775739
H	-0.714279	5.047198	-0.209342
H	-1.148577	4.304818	-1.753904
H	-2.382354	3.294711	0.427595
H	-1.893802	2.099591	-1.950905
C	2.075796	1.683241	0.381400
C	3.052411	1.406214	-0.777094
C	2.750964	2.581406	1.433582
H	1.877504	0.718477	0.872761
C	4.370611	0.799504	-0.281928
H	3.257016	2.347018	-1.311199
H	2.589627	0.722932	-1.497932
C	4.062676	1.963679	1.938939
H	2.966563	3.570662	1.002264
H	2.071633	2.748156	2.277827
C	5.031062	1.683770	0.782853
H	5.055242	0.645134	-1.126757
H	4.160386	-0.192968	0.137182
H	4.531965	2.624001	2.681740
H	3.836815	1.018204	2.452120
H	5.948620	1.211455	1.159380
H	5.332059	2.641161	0.328502
I	2.092456	-2.765382	-0.114625

17b

B3LYP SCF energy: -813.02574104 a.u.
B3LYP enthalpy: -812.714075 a.u.
B3LYP free energy: -812.780963 a.u.
M06 SCF energy in solution: -813.82780790 a.u.
M06 enthalpy in solution: -813.516142 a.u.
M06 free energy in solution: -813.583030 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.894878	-0.606396	-0.107500
C	-3.274071	-1.353018	0.074306
C	-3.238600	0.037719	-0.280687
C	-4.458576	0.713706	-0.445634
C	-5.657717	0.025532	-0.265693
C	-5.668569	-1.338574	0.078766
C	-4.473924	-2.042297	0.251146
C	-1.092794	-0.738830	-0.091970
C	-1.852305	0.383928	-0.377811
H	-4.465311	1.767937	-0.713972
H	-6.602275	0.550221	-0.393911
H	-6.617375	-1.852992	0.212807
H	-4.481586	-3.096789	0.516558
C	-1.578433	-3.141649	0.512070
H	-1.986889	-3.448923	1.484508
H	-1.921718	-3.857190	-0.248273
H	-0.487942	-3.180639	0.562416
N	-1.966919	-1.793395	0.184002
C	0.422767	1.332702	-0.568496

C	0.918908	2.278529	0.533551
C	-1.290836	2.761177	0.404022
C	-1.113220	1.643445	-0.667022
H	0.960021	1.451904	-1.514706
C	-0.288727	2.325846	1.490833
H	-0.176876	3.066530	2.293328
H	-0.523241	1.348920	1.920541
C	0.894308	3.716792	-0.057012
H	1.419493	4.411337	0.610718
H	1.389509	3.765300	-1.033088
C	-0.630077	4.048907	-0.132625
H	-0.878175	4.911394	0.498599
H	-0.961281	4.282966	-1.151726
H	-2.329882	2.885912	0.724122
H	-1.366995	2.045184	-1.661407
I	3.661195	-0.764597	-0.040670
H	1.882400	1.997053	0.959513

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B3LYP SCF energy: -3915.43612741 a.u.
B3LYP enthalpy: -3914.856980 a.u.
B3LYP free energy: -3914.972263 a.u.
M06 SCF energy in solution: -3918.12882205 a.u.
M06 enthalpy in solution: -3917.549675 a.u.
M06 free energy in solution: -3917.664958 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.821477	-3.234454	0.164425
O	0.044311	-2.697368	-0.731933
O	1.116086	-2.716497	1.247308
C	1.418425	-4.567180	-0.260576
H	1.638744	-5.174821	0.620000
H	0.757460	-5.105820	-0.943574
H	2.360149	-4.365195	-0.785599
Pd	-0.726862	-0.883340	-0.201561
C	-2.052004	1.636277	-0.582453
O	-2.142371	1.301814	-1.766694
O	-1.497129	0.924301	0.358578
C	-2.564253	2.975619	-0.081614
H	-3.175514	3.454743	-0.848568
H	-3.144009	2.840969	0.835623
H	-1.705767	3.616986	0.149190
C	-4.344688	-0.580072	-0.294500
C	-3.662018	-1.122046	0.822633
C	-3.980060	-0.670062	2.107693
C	-4.954059	0.313222	2.247467
C	-5.605817	0.855575	1.123053
C	-5.309152	0.420449	-0.165935
C	-2.838917	-2.035234	-1.096997
C	-2.672164	-2.040821	0.298673
H	-3.458743	-1.066507	2.974009
H	-5.210822	0.678697	3.237368
H	-6.352319	1.631978	1.262828
H	-5.797537	0.853418	-1.032549

H	-2.330781	-2.634983	-1.838178
H	-2.145481	-2.801354	0.858849
C	-4.133192	-0.731702	-2.795853
H	-5.214679	-0.736533	-2.962494
H	-3.723265	0.272273	-2.934838
H	-3.663636	-1.418633	-3.502670
N	-3.843288	-1.183027	-1.445902
C	1.783373	0.620900	1.851792
C	2.253748	1.257743	4.528696
C	0.708858	0.937986	2.692346
C	3.090073	0.630936	2.347875
C	3.322856	0.948029	3.687419
C	0.949508	1.255194	4.028468
H	-0.300496	0.948126	2.293697
H	3.923032	0.386899	1.697292
H	4.339260	0.950676	4.071156
H	0.115419	1.499087	4.680522
H	2.436031	1.500902	5.571798
C	1.388847	1.995648	-0.809300
C	1.365134	4.514099	-2.018509
C	2.022111	3.077033	-0.187197
C	0.742980	2.177145	-2.036692
C	0.733161	3.435721	-2.639420
C	2.008366	4.333987	-0.791715
H	2.515243	2.940591	0.769734
H	0.211551	1.352248	-2.497047
H	0.216574	3.572899	-3.584726
H	2.496602	5.172508	-0.302910
H	1.350386	5.495265	-2.484948
C	3.039900	-0.533339	-0.706952
C	5.385500	-1.639383	-1.761412
C	3.618522	0.009250	-1.860113
C	3.641090	-1.634220	-0.080990
C	4.812630	-2.178510	-0.607533
C	4.785286	-0.546302	-2.386956
H	3.165176	0.866878	-2.345320
H	3.183775	-2.069272	0.800275
H	5.276343	-3.027837	-0.113437
H	5.225942	-0.119102	-3.283355
H	6.295661	-2.069069	-2.170443
As	1.401032	0.232784	-0.002170

21b

B3LYP SCF energy: -3915.42350786 a.u.
B3LYP enthalpy: -3914.844752 a.u.
B3LYP free energy: -3914.958185 a.u.
M06 SCF energy in solution: -3918.12221266 a.u.
M06 enthalpy in solution: -3917.543457 a.u.
M06 free energy in solution: -3917.656890 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.061391	2.638410	1.406111
O	0.062133	2.554830	0.592507
O	1.628782	1.678941	1.954984

C	1.587530	4.051833	1.595899
H	2.083394	4.140854	2.564846
H	2.327510	4.241644	0.808784
H	0.787748	4.789244	1.500895
Pd	-0.769325	0.682015	0.314252
C	-3.086985	2.168366	-0.368937
O	-2.642553	2.081553	-1.522267
O	-2.575952	1.603222	0.679386
C	-4.357104	2.954161	-0.064367
H	-4.752477	3.403666	-0.977800
H	-5.103717	2.286000	0.378001
H	-4.141644	3.736529	0.670342
C	-3.929372	-0.975042	-0.254426
C	-3.068731	-1.269343	0.827595
C	-3.596796	-1.366544	2.115688
C	-4.961680	-1.153837	2.295189
C	-5.796979	-0.840244	1.209038
C	-5.292654	-0.742726	-0.087016
C	-1.867062	-1.178964	-1.116229
C	-1.718210	-1.354886	0.283071
H	-2.950737	-1.581567	2.961712
H	-5.388327	-1.219599	3.291530
H	-6.855191	-0.668106	1.381736
H	-5.935159	-0.486958	-0.923045
H	-1.126102	-1.260916	-1.896309
H	-0.929193	-1.942335	0.734031
C	-3.641850	-0.492858	-2.720250
H	-4.595985	-0.977059	-2.944797
H	-3.740267	0.596249	-2.702834
H	-2.911746	-0.776454	-3.480961
N	-3.161366	-0.949736	-1.425115
C	2.239245	-1.280515	1.429229
C	3.335840	-2.830503	3.477519
C	1.758917	-1.150997	2.736141
C	3.268505	-2.188077	1.148690
C	3.820809	-2.955958	2.174248
C	2.304623	-1.931071	3.755626
H	0.989209	-0.418383	2.946990
H	3.629827	-2.305687	0.131754
H	4.623953	-3.653392	1.953766
H	1.929296	-1.828834	4.769748
H	3.761986	-3.432680	4.275047
C	2.738907	1.000535	-0.677111
C	4.566751	2.823118	-1.738584
C	4.092961	0.897629	-0.351910
C	2.293410	2.023135	-1.523258
C	3.211638	2.930105	-2.055851
C	5.004740	1.809254	-0.883717
H	4.433104	0.125201	0.329613
H	1.234453	2.132914	-1.733926
H	2.862929	3.725342	-2.708402
H	6.056782	1.731600	-0.624166
H	5.278979	3.533502	-2.148705
C	1.372206	-1.569290	-1.420053
C	0.945642	-3.399743	-3.506961
C	1.468679	-1.158857	-2.755911
C	1.062755	-2.907303	-1.141977

C	0.853316	-3.818000	-2.178732
C	1.256992	-2.068400	-3.792956
H	1.710903	-0.126766	-2.988513
H	0.992989	-3.245404	-0.112927
H	0.615936	-4.852486	-1.947028
H	1.338728	-1.736793	-4.824317
H	0.779802	-4.106875	-4.314605
As	1.429322	-0.238657	0.018731

21c

B3LYP SCF energy: -1215.52317394 a.u.
B3LYP enthalpy: -1215.182132 a.u.
B3LYP free energy: -1215.269486 a.u.
M06 SCF energy in solution: -1216.31990614 a.u.
M06 enthalpy in solution: -1215.978864 a.u.
M06 free energy in solution: -1216.066218 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.648769	2.180215	-0.415447
O	-2.211968	1.406927	0.531533
O	-2.305248	2.179194	-1.597872
C	-3.706115	3.169446	0.094298
H	-4.044616	3.812361	-0.722262
H	-4.558785	2.622584	0.512242
H	-3.286978	3.782255	0.900033
Pd	-0.796805	0.059566	-0.111902
C	1.142434	1.631719	1.370779
O	0.886894	0.992314	2.396261
O	0.640815	1.456442	0.190625
C	2.189825	2.748365	1.382767
H	2.513423	2.951561	2.406906
H	3.050283	2.437036	0.779678
H	1.781141	3.657018	0.929466
C	2.647320	-0.922470	-0.051077
C	1.981328	-0.766651	-1.294888
C	2.632101	-0.109795	-2.341102
C	3.918098	0.385063	-2.132304
C	4.554657	0.239251	-0.886940
C	3.927177	-0.412721	0.173895
C	0.612880	-1.854118	0.176284
C	0.660305	-1.344984	-1.135494
H	2.128865	0.033795	-3.293178
H	4.431521	0.906175	-2.936033
H	5.552035	0.647956	-0.744969
H	4.409959	-0.505994	1.141750
H	-0.170825	-2.434965	0.653900
H	-0.013073	-1.625810	-1.933334
C	2.033802	-1.788775	2.231546
H	3.022937	-2.230863	2.397796
H	1.940538	-0.823164	2.737440
H	1.270792	-2.467364	2.618067
N	1.808163	-1.615717	0.808387
C	-2.720379	-2.196014	0.044148
O	-2.316407	-1.201028	-0.678244

O	-2.143981	-2.721146	1.005220
C	-4.084695	-2.723426	-0.411813
H	-4.295075	-3.689083	0.055053
H	-4.858753	-2.004219	-0.119573
H	-4.118142	-2.811549	-1.502300

21d

B3LYP SCF energy: -583.75057548 a.u.
B3LYP enthalpy: -583.635236 a.u.
B3LYP free energy: -583.686278 a.u.
M06 SCF energy in solution: -584.77877388 a.u.
M06 enthalpy in solution: -584.663434 a.u.
M06 free energy in solution: -584.714476 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.444749	0.000006	-0.004783
O	1.772684	-1.088451	-0.009758
O	1.772652	1.088452	-0.009661
C	3.939086	0.000028	0.036862
H	4.327056	0.899650	-0.446193
H	4.266980	-0.000612	1.082972
H	4.327084	-0.899018	-0.447246
Pd	-0.000006	-0.000009	-0.009688
C	-2.444740	-0.000001	-0.004818
O	-1.772655	1.088454	-0.010184
O	-1.772676	-1.088460	-0.010293
C	-3.939067	0.000023	0.036964
H	-4.327112	-0.899301	-0.446587
H	-4.266855	0.000017	1.083108
H	-4.327087	0.899371	-0.446564

21e

B3LYP SCF energy: -998.46585073 a.u.
B3LYP enthalpy: -998.178627 a.u.
B3LYP free energy: -998.258381 a.u.
M06 SCF energy in solution: -999.32322009 a.u.
M06 enthalpy in solution: -999.035996 a.u.
M06 free energy in solution: -999.115750 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.162644	2.607487	-0.222468
O	1.823520	1.678828	0.621005
O	1.656211	2.837289	-1.324227
C	3.333319	3.449628	0.289155
H	3.434283	4.360222	-0.306832
H	3.200758	3.698476	1.346849
H	4.252301	2.858099	0.205369
Pd	0.570337	0.177460	0.017981
C	-1.278548	-2.016546	0.306851
O	-1.189690	-1.906233	1.533912
O	-0.676665	-1.296125	-0.585889

C	-2.188486	-3.068014	-0.328256
H	-2.664270	-3.671790	0.448580
H	-2.954255	-2.568697	-0.931156
H	-1.604691	-3.710763	-0.995292
C	-3.003557	0.706249	0.416728
C	-2.351411	1.173667	-0.754738
C	-2.952068	0.967920	-2.000197
C	-4.172768	0.300673	-2.058252
C	-4.793858	-0.173955	-0.887592
C	-4.216503	0.016406	0.366109
C	-1.066297	1.635870	1.061508
C	-1.098869	1.763259	-0.335957
H	-2.456053	1.304338	-2.906031
H	-4.646501	0.126549	-3.020703
H	-5.737774	-0.707980	-0.962456
H	-4.682639	-0.374403	1.265046
H	-0.354543	2.049646	1.760332
H	-0.425677	2.371080	-0.930299
C	-2.408456	0.503106	2.847398
H	-3.430501	0.704163	3.187794
H	-2.200074	-0.571063	2.836553
H	-1.709023	1.002184	3.522192
N	-2.221876	1.039728	1.512503
I	2.690537	-1.509734	-0.190467

21f

B3LYP SCF energy: -998.45694203 a.u.
B3LYP enthalpy: -998.170012 a.u.
B3LYP free energy: -998.250517 a.u.
M06 SCF energy in solution: -999.31797575 a.u.
M06 enthalpy in solution: -999.031046 a.u.
M06 free energy in solution: -999.111551 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.061945	2.485142	0.496356
O	1.699079	1.782136	-0.536172
O	1.797545	2.261012	1.676137
C	2.921245	3.687786	0.089810
H	3.111583	4.320989	0.960045
H	3.873843	3.333162	-0.319849
H	2.421626	4.266102	-0.694413
Pd	0.539384	0.180468	-0.038825
C	-1.656776	1.747933	-1.122382
O	-1.436389	1.258310	-2.236246
O	-1.061586	1.468626	-0.009773
C	-2.767155	2.785250	-0.929620
H	-3.221268	3.036352	-1.891690
H	-3.527753	2.377259	-0.255131
H	-2.359958	3.686895	-0.460733
C	-2.795800	-1.083540	-0.024103
C	-2.062634	-1.011632	1.188149
C	-2.683936	-0.517805	2.336678
C	-4.010733	-0.099994	2.258039
C	-4.715938	-0.159111	1.042728

C	-4.117814	-0.646029	-0.118524
C	-0.721710	-1.823603	-0.466271
C	-0.717801	-1.470173	0.894429
H	-2.128202	-0.436845	3.266354
H	-4.504060	0.294995	3.142021
H	-5.745212	0.188636	1.004585
H	-4.654707	-0.667220	-1.061630
H	0.034134	-2.349883	-1.029462
H	0.015350	-1.797366	1.617705
C	-2.270677	-1.626355	-2.423057
H	-3.246536	-2.096127	-2.589289
H	-2.253883	-0.600865	-2.804911
H	-1.505277	-2.214929	-2.934195
N	-1.970058	-1.617326	-1.003420
I	2.752954	-1.435647	0.044821

21g

B3LYP SCF energy: -3698.36037429 a.u.
B3LYP enthalpy: -3697.835982 a.u.
B3LYP free energy: -3697.945661 a.u.
M06 SCF energy in solution: -3701.12556512 a.u.
M06 enthalpy in solution: -3700.601173 a.u.
M06 free energy in solution: -3700.710852 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.732629	3.140143	0.037765
O	-0.103918	2.518503	-0.919499
O	-0.911780	2.686574	1.173067
C	-1.297831	4.489659	-0.376936
H	-1.452781	5.115142	0.504735
H	-0.643622	4.991829	-1.093938
H	-2.266576	4.319946	-0.860885
Pd	0.694689	0.710727	-0.301915
C	4.399158	0.512798	-0.600166
C	3.839248	1.384368	0.366983
C	4.415281	1.462312	1.641388
C	5.520932	0.669479	1.921585
C	6.054873	-0.201482	0.950834
C	5.501608	-0.297700	-0.321006
C	2.634279	1.520048	-1.562570
C	2.698702	2.015667	-0.251157
H	3.993706	2.120633	2.395345
H	5.979489	0.713159	2.904899
H	6.913323	-0.816744	1.203833
H	5.904261	-0.985385	-1.057340
H	2.013051	1.853295	-2.381909
H	2.170133	2.884066	0.112352
C	3.729944	-0.297370	-2.882264
H	4.769216	-0.424255	-3.198138
H	3.312485	-1.267851	-2.588989
H	3.155743	0.105337	-3.719614
N	3.660907	0.633427	-1.773264
C	-2.005998	-0.500386	1.888671
C	-2.712707	-0.968523	4.548101

C	-1.020114	-0.520306	2.878337
C	-3.349312	-0.699374	2.232301
C	-3.699799	-0.937752	3.561103
C	-1.376155	-0.756411	4.206059
H	0.016795	-0.354252	2.609418
H	-4.120647	-0.653365	1.470104
H	-4.742274	-1.093012	3.824157
H	-0.606966	-0.770929	4.972529
H	-2.986647	-1.150739	5.583453
C	-1.795149	-1.871319	-0.875737
C	-2.232382	-4.209280	-2.343138
C	-2.669059	-2.846865	-0.391586
C	-1.129927	-2.074434	-2.089545
C	-1.354964	-3.236314	-2.826203
C	-2.883119	-4.015663	-1.123983
H	-3.169926	-2.708209	0.560333
H	-0.419818	-1.331957	-2.442202
H	-0.834400	-3.388645	-3.767389
H	-3.556400	-4.776053	-0.738409
H	-2.400522	-5.120038	-2.910841
C	-2.969823	0.866551	-0.653701
C	-5.062499	2.395270	-1.708607
C	-3.386535	0.673160	-1.974865
C	-3.604786	1.829281	0.139725
C	-4.651447	2.585988	-0.387754
C	-4.426413	1.439167	-2.501825
H	-2.908582	-0.080271	-2.592187
H	-3.264716	2.004212	1.152800
H	-5.141955	3.328479	0.235392
H	-4.742040	1.283299	-3.529513
H	-5.875339	2.988809	-2.117549
As	-1.501204	-0.192007	0.053760
I	1.743170	-1.670238	0.357679

22

B3LYP SCF energy: -986.94150959 a.u.
B3LYP enthalpy: -986.656576 a.u.
B3LYP free energy: -986.728833 a.u.
M06 SCF energy in solution: -987.73545944 a.u.
M06 enthalpy in solution: -987.450526 a.u.
M06 free energy in solution: -987.522783 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.662812	0.038753	-0.109227
O	3.158957	-1.118225	-0.064172
O	2.881248	1.056997	-0.256107
C	5.146899	0.260315	-0.027856
H	5.362702	1.183624	0.516027
H	5.628093	-0.592587	0.455077
H	5.549739	0.363052	-1.042282
Pd	1.172686	-0.122010	-0.315499
C	-0.806280	-1.873395	0.685288
O	-0.561065	-1.360935	1.779182
O	-0.234408	-1.541424	-0.441866

C	-1.857788	-2.956822	0.509416
H	-2.223381	-3.281448	1.485443
H	-2.688659	-2.556095	-0.080837
H	-1.440815	-3.807036	-0.038378
C	-2.197496	0.968653	0.300788
C	-1.610897	0.991105	-0.984026
C	-2.344880	0.541355	-2.082408
C	-3.639227	0.070405	-1.871578
C	-4.196510	0.033576	-0.581713
C	-3.480874	0.478399	0.529552
C	-0.121002	1.769244	0.571149
C	-0.242088	1.466344	-0.815626
H	-1.905887	0.538292	-3.075284
H	-4.223878	-0.286937	-2.713715
H	-5.202539	-0.351693	-0.445543
H	-3.904593	0.432600	1.526915
H	0.702586	2.243397	1.086342
H	0.340174	1.954880	-1.588908
C	-1.422281	1.385967	2.661973
H	-2.369624	1.844410	2.959026
H	-1.387430	0.332222	2.951669
H	-0.600526	1.924787	3.136885
N	-1.268528	1.476609	1.218546

23a

B3LYP SCF energy: -3512.24339084 a.u.
B3LYP enthalpy: -3511.833669 a.u.
B3LYP free energy: -3511.928165 a.u.
M06 SCF energy in solution: -3515.17673520 a.u.
M06 enthalpy in solution: -3514.767013 a.u.
M06 free energy in solution: -3514.861509 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.007921	0.629601	-0.084172
O	-3.669329	1.817957	-0.333871
O	-3.091829	-0.267071	0.085896
C	-5.448399	0.211795	0.023342
H	-5.634533	-0.208690	1.017091
H	-6.105095	1.065463	-0.150700
H	-5.656899	-0.575997	-0.708444
Pd	-1.528868	1.089479	-0.229823
C	0.541869	3.012279	0.249221
O	0.760731	2.419446	1.308332
O	-0.324892	2.647727	-0.655570
C	1.349787	4.233659	-0.154150
H	1.684937	4.765951	0.738463
H	2.232659	3.886016	-0.703671
H	0.776468	4.895916	-0.806205
C	2.046011	0.378927	-0.563214
C	4.481355	1.409348	-1.443864
C	2.133920	0.973295	-1.826520
C	3.170033	0.303632	0.261707
C	4.388353	0.819066	-0.182100
C	3.354060	1.486311	-2.265734

H	1.251603	1.050349	-2.453595
H	3.089842	-0.140232	1.248253
H	5.262228	0.764493	0.460566
H	3.422241	1.950265	-3.245409
H	5.430047	1.813396	-1.785470
C	0.144261	-1.901180	-1.103687
C	-0.161200	-4.211946	-2.640306
C	1.263652	-2.507547	-1.685827
C	-1.130870	-2.448621	-1.293748
C	-1.277457	-3.604204	-2.061922
C	1.108733	-3.663241	-2.452165
H	2.250198	-2.078329	-1.544107
H	-1.998664	-1.969977	-0.851077
H	-2.266626	-4.027628	-2.211068
H	1.978837	-4.131697	-2.903344
H	-0.280702	-5.110062	-3.239720
C	0.601707	-1.046595	1.777483
C	0.965733	-2.082617	4.340937
C	0.537135	-0.194054	2.886601
C	0.842750	-2.414709	1.949043
C	1.026319	-2.929249	3.232711
C	0.722466	-0.718745	4.165758
H	0.361687	0.864097	2.732594
H	0.882939	-3.075931	1.090294
H	1.213428	-3.991132	3.364785
H	0.674364	-0.058186	5.026679
H	1.105290	-2.486141	5.339976
As	0.343710	-0.323445	0.004282

23b

B3LYP SCF energy: -890.24775744 a.u.
B3LYP enthalpy: -890.026797 a.u.
B3LYP free energy: -890.096471 a.u.
M06 SCF energy in solution: -891.16890089 a.u.
M06 enthalpy in solution: -890.947940 a.u.
M06 free energy in solution: -891.017614 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.139193	-0.177620	-0.374362
O	-2.437292	0.626253	-1.065526
O	-2.545904	-0.875717	0.530502
C	-4.609029	-0.339539	-0.613202
H	-5.095210	-0.752822	0.272985
H	-5.049542	0.623491	-0.882754
H	-4.759878	-1.029047	-1.452042
Pd	-0.708287	-0.007519	0.072869
C	1.246558	2.008165	-0.061309
O	0.718292	2.416745	0.965983
O	0.848265	0.942980	-0.733540
C	2.477677	2.644704	-0.677779
H	2.596883	3.660094	-0.295680
H	3.347112	2.043622	-0.388483
H	2.415162	2.650712	-1.769173
C	0.724103	-1.380488	1.063120

H	0.230694	-2.338823	0.923644
C	0.286320	-0.469069	2.004413
H	0.882982	0.404551	2.242821
H	-0.572412	-0.688115	2.631398
C	2.063176	-1.209036	0.410949
O	2.947187	-0.494478	0.830626
O	2.144214	-1.967593	-0.692652
C	3.338135	-1.777569	-1.470873
H	4.224780	-2.000186	-0.872352
H	3.252142	-2.466896	-2.310123
H	3.383907	-0.743516	-1.821091

23c

B3LYP SCF energy: -856.53254546 a.u.
B3LYP enthalpy: -856.254518 a.u.
B3LYP free energy: -856.322145 a.u.
M06 SCF energy in solution: -857.39237857 a.u.
M06 enthalpy in solution: -857.114351 a.u.
M06 free energy in solution: -857.181978 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.047648	-2.110424	-0.101557
O	2.584144	-0.996895	0.190079
O	0.769798	-2.155281	-0.225846
C	2.867851	-3.354799	-0.270013
H	2.335033	-4.080537	-0.888160
H	3.835386	-3.106199	-0.712630
H	3.048210	-3.799199	0.715839
Pd	0.610605	-0.098561	0.206520
C	1.213572	2.626076	-0.258344
O	1.016209	2.376137	-1.443053
O	0.993257	1.794704	0.739943
C	1.763606	3.960927	0.221084
H	1.720141	4.687658	-0.592056
H	1.204809	4.323517	1.088513
H	2.805537	3.827755	0.532409
C	-1.481472	0.485028	0.781098
C	-2.501469	-0.584617	1.113901
C	-2.297480	-0.551312	-1.141954
C	-1.365497	0.517366	-0.608257
H	-1.243095	1.313274	1.438581
C	-2.283946	-1.609235	-0.017489
H	-3.118485	-2.312888	-0.103847
H	-1.349654	-2.162057	0.055783
C	-3.854202	0.061921	0.648365
H	-4.689459	-0.568988	0.968055
H	-4.008175	1.057552	1.074740
C	-3.715068	0.082289	-0.906222
H	-4.476843	-0.540885	-1.384795
H	-3.796025	1.088318	-1.327726
H	-2.499085	-0.951805	2.140767
H	-2.109645	-0.889337	-2.161115
H	-1.015004	1.358991	-1.196914

23d

B3LYP SCF energy: -1091.24857214 a.u.
B3LYP enthalpy: -1090.813015 a.u.
B3LYP free energy: -1090.893032 a.u.
M06 SCF energy in solution: -1091.95266883 a.u.
M06 enthalpy in solution: -1091.517112 a.u.
M06 free energy in solution: -1091.597129 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.685994	-2.609348	-0.803507
O	2.231788	-2.209276	0.270694
O	0.900501	-1.804257	-1.424208
C	1.963686	-3.971987	-1.365627
H	2.798682	-3.901118	-2.072504
H	2.245685	-4.658691	-0.564628
H	1.089265	-4.343629	-1.905229
Pd	1.222524	-0.301784	0.026206
C	2.873788	1.415528	1.542032
O	3.447113	1.642068	0.481596
O	1.772463	0.703512	1.670408
C	3.380735	1.931239	2.880335
H	4.146370	2.690988	2.713465
H	2.560093	2.339889	3.476769
H	3.814701	1.097818	3.443718
C	-0.376653	1.250640	-0.029304
C	-1.640004	0.980261	-0.829641
C	-0.007679	1.599562	-2.303180
C	0.621415	1.625762	-0.926504
H	-0.381937	1.513963	1.021984
C	-1.055888	0.479535	-2.174599
H	-1.802742	0.516159	-2.975314
H	-0.624142	-0.516960	-2.131990
C	-2.057621	2.437311	-1.265965
H	-3.043111	2.395788	-1.742778
H	-2.131880	3.120563	-0.415697
C	-0.947772	2.855424	-2.276332
H	-1.358166	3.023188	-3.277000
H	-0.420742	3.766186	-1.977103
H	0.681178	1.559774	-3.147289
H	1.510723	2.197740	-0.684240
C	-2.733116	0.141647	-0.166694
C	-2.236886	-1.267207	0.211035
C	-3.345552	0.830768	1.067499
H	-3.537862	0.025167	-0.910667
C	-3.348623	-2.116101	0.840098
H	-1.409168	-1.169528	0.929388
H	-1.820282	-1.774401	-0.665354
C	-4.459108	-0.015393	1.699640
H	-2.556927	0.998468	1.815597
H	-3.736838	1.818378	0.796117
C	-3.959932	-1.419504	2.061893
H	-2.954134	-3.100942	1.118974
H	-4.135901	-2.292977	0.092421
H	-4.856559	0.491368	2.587650

H	-5.292699	-0.100950	0.987170
H	-4.778758	-2.020317	2.476531
H	-3.196567	-1.339019	2.849514

23e

B3LYP SCF energy: -812.33088155 a.u.
B3LYP enthalpy: -812.160086 a.u.
B3LYP free energy: -812.225574 a.u.
M06 SCF energy in solution: -813.36655111 a.u.
M06 enthalpy in solution: -813.195756 a.u.
M06 free energy in solution: -813.261244 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.803577	-0.014625	-0.001450
O	2.166160	-1.005749	-0.480245
O	2.173197	0.981431	0.478756
C	4.315504	-0.011441	0.000517
H	4.680379	0.088847	1.028399
H	4.700004	-0.933481	-0.440829
H	4.680966	0.852491	-0.565026
Pd	0.294234	-0.003092	-0.000374
C	-1.560200	-2.161218	0.114457
O	-1.126751	-2.421276	1.234030
O	-1.162796	-1.217729	-0.692009
C	-2.707981	-2.973397	-0.499619
H	-2.940469	-3.831128	0.136596
H	-3.596107	-2.338230	-0.595717
H	-2.440491	-3.313264	-1.505719
C	-1.535881	2.175316	-0.114112
O	-1.098725	2.431862	-1.233032
O	-1.149967	1.226257	0.691428
C	-2.674573	2.999907	0.500356
H	-2.896369	3.861358	-0.134645
H	-3.570207	2.375075	0.594543
H	-2.404085	3.334927	1.507273

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B3LYP SCF energy: -3686.30393007 a.u.
B3LYP enthalpy: -3685.794833 a.u.
B3LYP free energy: -3685.897139 a.u.
M06 SCF energy in solution: -3689.06349892 a.u.
M06 enthalpy in solution: -3688.554402 a.u.
M06 free energy in solution: -3688.656708 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.760075	-1.708319	0.086747
C	2.590697	-3.456979	0.349633
O	1.381677	-3.816688	0.184582
O	2.899970	-2.218625	0.393322
C	3.666968	-4.500086	0.529840
H	3.346070	-5.458343	0.116076

H	4.595553	-4.168624	0.057656
H	3.862173	-4.629898	1.600937
C	-3.450523	-1.162158	-0.029880
C	-2.213692	-1.141760	0.684000
C	-2.191845	-0.601476	1.978945
C	-3.364478	-0.088737	2.522557
C	-4.572713	-0.114521	1.797189
C	-4.633169	-0.655720	0.516046
C	-1.845895	-1.989434	-1.370857
C	-1.205100	-1.674793	-0.196630
H	-1.263387	-0.576818	2.541638
H	-3.353308	0.335489	3.522833
H	-5.475028	0.290063	2.247421
H	-5.565494	-0.670786	-0.041276
H	-1.450772	-2.391197	-2.293717
C	-4.184556	-1.830726	-2.329731
H	-5.034344	-2.443882	-2.007117
H	-4.558139	-0.845750	-2.638156
H	-3.717228	-2.313583	-3.190761
N	-3.206979	-1.701761	-1.275190
C	1.935812	1.321360	-1.322012
C	3.936967	2.291766	-3.007737
C	3.130966	0.605670	-1.468073
C	1.740419	2.516077	-2.023298
C	2.742158	2.999983	-2.865236
C	4.128910	1.097096	-2.310551
H	3.276473	-0.328231	-0.931535
H	0.805520	3.058855	-1.924673
H	2.587759	3.926620	-3.410997
H	5.055691	0.542064	-2.424226
H	4.715486	2.668350	-3.665303
C	1.005694	1.544916	1.561787
C	1.614209	2.810041	3.974626
C	1.077605	2.941228	1.620828
C	1.250821	0.783853	2.708082
C	1.554987	1.417239	3.914245
C	1.377323	3.571945	2.827235
H	0.901231	3.534508	0.728602
H	1.211447	-0.300288	2.648436
H	1.746040	0.822425	4.802597
H	1.429193	4.656048	2.872076
H	1.848975	3.303465	4.913453
C	-1.045366	1.444982	-0.713714
C	-3.532741	2.347929	-1.602812
C	-1.894470	2.127110	0.160938
C	-1.438830	1.221843	-2.038105
C	-2.678828	1.677225	-2.482105
C	-3.138556	2.574293	-0.284113
H	-1.604817	2.279295	1.193622
H	-0.783772	0.682251	-2.715099
H	-2.980704	1.502300	-3.511048
H	-3.804071	3.082135	0.406780
H	-4.504796	2.690866	-1.945859
As	0.599086	0.638217	-0.098370

24
B3LYP SCF energy: -4193.80512273 a.u.
B3LYP enthalpy: -4192.975346 a.u.
B3LYP free energy: -4193.102517 a.u.
M06 SCF energy in solution: -4196.22728507 a.u.
M06 enthalpy in solution: -4195.397508 a.u.
M06 free energy in solution: -4195.524679 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.595588	-0.398902	0.924478
C	0.585691	-3.147360	1.759236
O	0.208462	-2.567733	2.789695
O	0.909646	-2.546049	0.658063
C	0.639042	-4.667473	1.692739
H	0.670032	-5.094455	2.697470
H	-0.267937	-5.023646	1.188422
H	1.498872	-5.005437	1.107310
C	-1.527356	3.197792	1.622721
C	-1.251834	1.815932	1.849142
C	-2.162670	1.055487	2.599652
C	-3.311574	1.666852	3.088903
C	-3.563481	3.034192	2.853942
C	-2.674061	3.819167	2.126000
C	0.364522	2.659971	0.532263
C	-0.036209	1.493545	1.140417
H	-1.962393	0.004892	2.789445
H	-4.025393	1.086603	3.667014
H	-4.467783	3.485982	3.252458
H	-2.875104	4.871060	1.944028
H	1.197749	2.851858	-0.130102
C	-0.434287	5.057243	0.346175
H	-1.339569	5.324131	-0.212396
H	-0.307145	5.769523	1.171114
H	0.424851	5.144018	-0.323178
N	-0.518956	3.699442	0.827332
C	-2.523483	-1.970484	-0.195769
C	-4.428384	-3.909667	0.429542
C	-2.572189	-2.505314	1.094214
C	-3.422790	-2.407714	-1.175283
C	-4.376023	-3.374510	-0.860736
C	-3.526357	-3.477946	1.402473
H	-1.853189	-2.193255	1.844555
H	-3.373411	-2.000301	-2.180890
H	-5.073561	-3.713741	-1.621437
H	-3.555969	-3.898451	2.403461
H	-5.169194	-4.666542	0.672042
C	-0.554139	-1.176021	-2.364442
C	0.481410	-2.039569	-4.813723
C	-1.034583	-0.631659	-3.560040
C	0.435615	-2.168506	-2.395293
C	0.948675	-2.594553	-3.619813
C	-0.513459	-1.061918	-4.782382
H	-1.805568	0.130730	-3.543216
H	0.794799	-2.593940	-1.462877
H	1.719190	-3.360262	-3.640171
H	-0.886995	-0.631757	-5.707536

H	0.889670	-2.369849	-5.764817
C	-2.301040	0.941406	-1.021755
C	-3.774871	3.283025	-1.413845
C	-1.746070	2.009032	-1.736968
C	-3.594780	1.050612	-0.504219
C	-4.326147	2.222704	-0.693977
C	-2.486484	3.172113	-1.941540
H	-0.735111	1.935564	-2.124437
H	-4.020516	0.234650	0.068303
H	-5.321504	2.308899	-0.269334
H	-2.053516	3.994180	-2.504957
H	-4.345896	4.195420	-1.561300
As	-1.216854	-0.611662	-0.628142
C	2.796952	0.558457	1.538714
C	3.971663	0.043973	0.712868
C	3.580683	-1.446781	2.394565
C	2.544853	-0.347225	2.531717
H	2.457500	1.584546	1.536314
C	3.795280	-1.487609	0.869407
H	4.702123	-2.034275	0.584000
H	2.934028	-1.897715	0.346438
C	5.192138	0.257573	1.684203
H	6.124100	0.028407	1.154397
H	5.261501	1.288632	2.042692
C	4.923709	-0.762442	2.834632
H	5.718185	-1.513758	2.892824
H	4.846645	-0.284800	3.815884
H	3.352292	-2.384993	2.900439
H	1.939106	-0.180107	3.415671
C	4.121878	0.598140	-0.707674
C	2.932263	0.193413	-1.598914
C	4.316236	2.126651	-0.724902
H	5.031484	0.147786	-1.137623
C	3.010488	0.772182	-3.014580
H	2.001230	0.533375	-1.124000
H	2.856442	-0.896270	-1.649983
C	4.402100	2.689343	-2.150119
H	3.471034	2.604129	-0.209741
H	5.215345	2.397643	-0.158163
C	3.174622	2.295683	-2.981952
H	2.112857	0.487114	-3.576745
H	3.867439	0.331615	-3.545501
H	4.511535	3.780839	-2.115915
H	5.305827	2.298899	-2.640434
H	3.255301	2.699196	-3.999129
H	2.274289	2.745952	-2.534711

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B3LYP SCF energy: -4193.82785518 a.u.
B3LYP enthalpy: -4192.997270 a.u.
B3LYP free energy: -4193.122312 a.u.
M06 SCF energy in solution: -4196.25427548 a.u.
M06 enthalpy in solution: -4195.423690 a.u.
M06 free energy in solution: -4195.548732 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.725555	-0.510236	-0.241599
C	-0.838250	1.319751	-2.399469
O	0.111377	0.617891	-2.779502
O	-1.497272	1.147611	-1.297295
C	-1.284685	2.522969	-3.218712
H	-1.086227	2.347555	-4.278845
H	-2.343005	2.744032	-3.059949
H	-0.701209	3.393435	-2.898356
C	1.865575	-2.991477	0.191108
C	0.700135	-3.084927	-0.607855
C	0.814318	-3.487632	-1.944252
C	2.076572	-3.790750	-2.442172
C	3.222579	-3.691587	-1.629864
C	3.136823	-3.288477	-0.301885
C	0.118531	-2.408413	1.485277
C	-0.432497	-2.713912	0.231943
H	-0.063914	-3.542663	-2.579930
H	2.184350	-4.098192	-3.478009
H	4.196764	-3.917726	-2.051710
H	4.025017	-3.182195	0.310585
H	-0.384328	-2.187891	2.413979
C	2.399982	-2.333470	2.557433
H	2.940742	-3.251892	2.811317
H	3.120526	-1.557328	2.284694
H	1.839736	-1.992015	3.427959
N	1.480793	-2.580165	1.463608
C	1.801505	1.243947	2.085790
C	2.267092	1.863667	4.781182
C	0.978261	0.719717	3.087413
C	2.841304	2.111984	2.444191
C	3.079818	2.411813	3.784982
C	1.208357	1.025094	4.430809
H	0.144333	0.083568	2.805921
H	3.454666	2.565351	1.671224
H	3.891617	3.082345	4.053062
H	0.557704	0.616921	5.199629
H	2.450105	2.103081	5.824902
C	1.320115	2.653722	-0.441240
C	1.107096	5.303509	-1.311769
C	2.307518	3.202462	-1.261415
C	0.219228	3.432353	-0.064228
C	0.116371	4.754339	-0.493264
C	2.198716	4.524885	-1.697867
H	3.153528	2.598398	-1.571382
H	-0.566294	2.996960	0.544807
H	-0.742591	5.351204	-0.199536
H	2.968143	4.944507	-2.340183
H	1.023394	6.331834	-1.652342
C	3.071354	0.191739	-0.505460
C	5.401833	-0.768030	-1.721233
C	3.063752	-0.151195	-1.865335
C	4.243250	0.039330	0.242443
C	5.404511	-0.445326	-0.363652
C	4.230968	-0.618918	-2.467698
H	2.144460	-0.048387	-2.434751

H	4.260005	0.303980	1.294543
H	6.311838	-0.559593	0.223828
H	4.219523	-0.880175	-3.521979
H	6.307256	-1.138671	-2.194218
As	1.385790	0.826200	0.225047
C	-2.422253	-1.591037	-0.639138
C	-3.634514	-1.252710	0.247991
C	-2.846943	-3.246316	1.052863
C	-1.900704	-2.943476	-0.126949
H	-2.591668	-1.513414	-1.714270
C	-3.181134	-1.846051	1.605813
H	-3.985430	-1.881624	2.347985
H	-2.335435	-1.297492	2.031603
C	-4.733194	-2.287908	-0.154179
H	-5.700769	-2.013756	0.280350
H	-4.866730	-2.331552	-1.239187
C	-4.210574	-3.634361	0.437232
H	-4.884074	-4.010419	1.215005
H	-4.111626	-4.421708	-0.317831
H	-2.449971	-3.977484	1.764264
H	-1.938130	-3.744343	-0.875259
C	-4.056388	0.221432	0.237263
C	-4.569636	0.674491	-1.140697
C	-5.081021	0.591441	1.323996
H	-3.147060	0.802116	0.438508
C	-4.846029	2.181897	-1.157493
H	-5.494754	0.130315	-1.384128
H	-3.829448	0.431039	-1.906248
C	-5.373507	2.099481	1.316005
H	-6.019631	0.041619	1.160674
H	-4.712401	0.296094	2.314061
C	-5.844969	2.578807	-0.063107
H	-5.220029	2.489961	-2.142717
H	-3.893367	2.705296	-0.999569
H	-6.120238	2.345093	2.082306
H	-4.454184	2.639247	1.587479
H	-5.998291	3.665795	-0.055357
H	-6.822434	2.125026	-0.285617

25b

B3LYP SCF energy: -4193.81980035 a.u.
B3LYP enthalpy: -4192.988741 a.u.
B3LYP free energy: -4193.116053 a.u.
M06 SCF energy in solution: -4196.24855531 a.u.
M06 enthalpy in solution: -4195.417496 a.u.
M06 free energy in solution: -4195.544808 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.211982	-1.136639	-0.079918
C	-1.101017	-3.320760	1.201545
O	-0.744413	-2.710259	2.214110
O	-0.815376	-2.984103	-0.024259
C	-1.976911	-4.566369	1.295248
H	-2.066901	-4.891025	2.333562

H	-2.974020	-4.331804	0.903229
H	-1.566345	-5.373854	0.680985
C	0.832550	2.273613	0.944940
C	1.384993	1.107310	1.534156
C	1.324065	0.940446	2.923913
C	0.711442	1.927774	3.687645
C	0.159510	3.075065	3.084943
C	0.214794	3.268501	1.707904
C	1.645686	0.999467	-0.720047
C	1.919545	0.286273	0.456524
H	1.720852	0.042807	3.387822
H	0.645912	1.809756	4.764986
H	-0.320538	3.824431	3.707146
H	-0.212319	4.152168	1.246387
H	1.946765	0.792310	-1.734505
C	0.790971	3.259960	-1.377416
H	-0.143272	3.771299	-1.148391
H	1.616719	3.982023	-1.352418
H	0.708611	2.838806	-2.379847
N	1.017890	2.186619	-0.428628
C	-2.926843	0.255581	1.307824
C	-4.069051	0.602931	3.835633
C	-2.144717	0.110886	2.456602
C	-4.288756	0.559982	1.428123
C	-4.857827	0.733102	2.688281
C	-2.715788	0.289518	3.718006
H	-1.102471	-0.166616	2.368845
H	-4.906607	0.654782	0.540888
H	-5.915646	0.965774	2.776716
H	-2.098488	0.173295	4.603798
H	-4.514499	0.736932	4.817794
C	-3.423059	-0.830505	-1.478325
C	-5.384326	-2.209709	-2.928514
C	-4.525229	-0.145563	-2.007357
C	-3.303169	-2.210558	-1.686785
C	-4.284336	-2.893359	-2.408863
C	-5.502401	-0.833188	-2.727434
H	-4.619334	0.926624	-1.870404
H	-2.447475	-2.740700	-1.277927
H	-4.183879	-3.963893	-2.566514
H	-6.353901	-0.292717	-3.132327
H	-6.144617	-2.744749	-3.491117
C	-2.296307	1.885712	-1.118921
C	-2.636178	4.455834	-2.198802
C	-2.159309	2.103944	-2.496739
C	-2.596605	2.968623	-0.286513
C	-2.763355	4.248165	-0.823962
C	-2.333437	3.378146	-3.035748
H	-1.937095	1.267271	-3.154286
H	-2.705663	2.812439	0.780900
H	-3.003391	5.080081	-0.167078
H	-2.237038	3.529964	-4.107366
H	-2.775124	5.448908	-2.616640
As	-2.052537	0.076225	-0.420609
C	2.816020	-0.936288	0.664615
C	3.982256	-1.162216	-0.347025
C	2.575710	-2.945436	-0.670827

C	1.904215	-2.144835	0.434717
H	3.199617	-0.881807	1.688596
C	3.243295	-1.853834	-1.526925
H	3.935549	-2.265987	-2.268799
H	2.521681	-1.215279	-2.044038
C	4.764868	-2.379847	0.233175
H	5.716814	-2.509047	-0.289614
H	4.995783	-2.241589	1.294223
C	3.823646	-3.598475	-0.018631
H	4.283754	-4.317366	-0.706817
H	3.571360	-4.136950	0.900098
H	1.917797	-3.647174	-1.186959
H	1.604134	-2.707165	1.317994
C	4.822167	0.084150	-0.657317
C	5.442204	0.704669	0.608991
C	5.908153	-0.144804	-1.724316
H	4.140776	0.841377	-1.070648
C	6.207737	1.996383	0.293351
H	6.127752	-0.020468	1.070282
H	4.658588	0.912365	1.347068
C	6.664467	1.151916	-2.045214
H	6.627888	-0.894241	-1.367854
H	5.459222	-0.551398	-2.638296
C	7.277583	1.768312	-0.781602
H	6.662515	2.398811	1.207105
H	5.495457	2.755731	-0.062368
H	7.443444	0.958741	-2.793395
H	5.967880	1.874074	-2.496741
H	7.785537	2.710542	-1.022777
H	8.046283	1.087950	-0.386511

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B3LYP SCF energy: -4193.83475849 a.u.
B3LYP enthalpy: -4193.003281 a.u.
B3LYP free energy: -4193.132221 a.u.
M06 SCF energy in solution: -4196.26320250 a.u.
M06 enthalpy in solution: -4195.431725 a.u.
M06 free energy in solution: -4195.560665 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.057712	0.506296	-0.001298
C	0.513706	2.364248	2.240114
O	-0.169427	1.513726	2.844665
O	0.763466	2.363955	0.976867
C	1.156864	3.509764	3.018837
H	0.676535	3.634332	3.992093
H	2.215095	3.270447	3.181597
H	1.116246	4.443681	2.450187
C	-2.543900	2.991624	-0.633524
C	-2.409961	1.819539	-1.422266
C	-2.427958	1.927565	-2.819245
C	-2.565097	3.187516	-3.392232
C	-2.681108	4.340911	-2.591946
C	-2.673817	4.260568	-1.202213

C	-2.351774	1.252860	0.776649
C	-2.282821	0.697722	-0.507271
H	-2.326169	1.043468	-3.442334
H	-2.578343	3.287469	-4.473632
H	-2.780614	5.312040	-3.068038
H	-2.767944	5.149946	-0.587028
H	-2.292360	0.782717	1.743796
C	-2.496355	3.526182	1.826303
H	-1.747586	4.306232	1.656753
H	-3.477769	3.993490	1.966575
H	-2.210682	2.968857	2.718057
N	-2.513479	2.613281	0.698916
C	3.073941	-0.654046	1.619984
C	4.170174	-1.149704	4.137504
C	2.261634	-0.592266	2.756384
C	4.436917	-0.951583	1.743309
C	4.982395	-1.203744	3.000682
C	2.815787	-0.839285	4.014918
H	1.216231	-0.312436	2.666862
H	5.071141	-0.976840	0.861903
H	6.039728	-1.435132	3.095413
H	2.184778	-0.777693	4.896752
H	4.598254	-1.340765	5.117751
C	3.570088	0.879545	-0.952423
C	5.408155	2.656100	-2.072655
C	4.650202	0.391393	-1.695832
C	3.403635	2.258824	-0.770943
C	4.327675	3.140925	-1.332131
C	5.568457	1.281434	-2.254917
H	4.770548	-0.676634	-1.847811
H	2.558232	2.625496	-0.193478
H	4.199148	4.210833	-1.193348
H	6.405791	0.900594	-2.833279
H	6.122225	3.348258	-2.510430
C	2.548350	-1.971825	-1.073975
C	2.685900	-4.374786	-2.503578
C	2.276851	-1.993283	-2.448497
C	2.889769	-3.159545	-0.420920
C	2.955980	-4.357860	-1.134893
C	2.350162	-3.188676	-3.161613
H	2.008942	-1.072431	-2.959938
H	3.098553	-3.150937	0.643835
H	3.218674	-5.277339	-0.619460
H	2.140693	-3.195709	-4.227506
H	2.735852	-5.308063	-3.057096
As	2.288468	-0.308412	-0.114500
C	-2.210153	-0.761993	-0.941187
C	-2.935291	-1.821236	-0.052658
C	-0.726783	-2.419755	0.034808
C	-0.723200	-1.179170	-0.861958
H	-2.592951	-0.809251	-1.966182
C	-1.859130	-2.109115	1.028940
H	-2.113753	-2.970680	1.655485
H	-1.636487	-1.259320	1.680375
C	-2.861066	-3.142666	-0.876001
H	-3.503661	-3.908746	-0.432609
H	-3.199553	-2.995459	-1.906706

C	-1.361057	-3.563307	-0.793384
H	-1.247412	-4.521907	-0.273452
H	-0.887142	-3.665898	-1.774927
H	0.239548	-2.679525	0.470161
H	-0.245868	-1.336930	-1.831603
C	-4.333401	-1.408017	0.425671
C	-5.279777	-1.080943	-0.744957
C	-4.993375	-2.423818	1.375639
H	-4.214550	-0.478972	1.000462
C	-6.646526	-0.588710	-0.251409
H	-5.418940	-1.980799	-1.361544
H	-4.826648	-0.320515	-1.391600
C	-6.355785	-1.923384	1.875652
H	-5.138026	-3.381174	0.856048
H	-4.334458	-2.625566	2.228385
C	-7.294027	-1.595497	0.707302
H	-7.308105	-0.392080	-1.104452
H	-6.513006	0.370902	0.269288
H	-6.813324	-2.671499	2.535313
H	-6.206674	-1.018437	2.482922
H	-8.250234	-1.208282	1.081307
H	-7.521802	-2.521246	0.158281

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B3LYP SCF energy: -3964.67905332 a.u.
B3LYP enthalpy: -3963.917833 a.u.
B3LYP free energy: -3964.032998 a.u.
M06 SCF energy in solution: -3967.17786933 a.u.
M06 enthalpy in solution: -3966.416649 a.u.
M06 free energy in solution: -3966.531814 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.329956	1.144196	0.134196
C	-3.429874	3.066450	0.108257
C	-3.745132	1.825804	-0.533279
C	-5.034290	1.674676	-1.073056
C	-5.962806	2.703218	-0.944290
C	-5.635133	3.901785	-0.284018
C	-4.361756	4.098055	0.245453
C	-1.562983	1.790027	0.144425
C	-2.546105	1.028324	-0.468241
H	-5.305209	0.768193	-1.600742
H	-6.957002	2.580557	-1.365786
H	-6.379164	4.688664	-0.195786
H	-4.099991	5.029879	0.739102
C	-1.395168	4.103422	1.136123
H	-1.239080	4.940307	0.441933
H	-1.939725	4.475545	2.012248
H	-0.420252	3.734824	1.466632
N	-2.107426	3.015539	0.511930
C	3.206981	-0.664461	1.685345
C	3.939507	-1.894270	4.087686
C	2.244861	-0.911357	2.671762
C	4.540259	-1.024723	1.911924

C	4.904502	-1.639086	3.109805
C	2.610485	-1.528585	3.869275
H	1.213400	-0.615279	2.498901
H	5.293939	-0.817874	1.158145
H	5.940846	-1.916041	3.281858
H	1.858818	-1.718476	4.630054
H	4.225562	-2.371796	5.020546
C	4.171632	1.239190	-0.446899
C	6.382667	2.849557	-1.036971
C	5.238951	0.723089	-1.189841
C	4.213693	2.567963	-0.009660
C	5.316821	3.370202	-0.299877
C	6.341393	1.527482	-1.483015
H	5.204899	-0.301419	-1.546729
H	3.380372	2.977149	0.556516
H	5.341719	4.400601	0.042964
H	7.166423	1.121489	-2.061634
H	7.240121	3.475012	-1.268109
C	2.758062	-1.297555	-1.244726
C	2.752265	-3.358957	-3.138100
C	2.463446	-1.023495	-2.586745
C	3.050818	-2.607439	-0.856999
C	3.043953	-3.635702	-1.802260
C	2.465923	-2.048826	-3.531036
H	2.225340	-0.007476	-2.891234
H	3.272936	-2.829190	0.181470
H	3.265063	-4.652949	-1.491821
H	2.236283	-1.827348	-4.569323
H	2.744345	-4.160286	-3.871264
As	2.623307	0.165379	0.027569
C	-2.148256	-0.325420	-0.964647
C	-2.674736	-1.585702	-0.163742
C	-0.405488	-1.714278	0.047832
C	-0.597831	-0.462642	-0.804085
H	-2.416516	-0.439847	-2.025607
C	-1.629477	-1.669501	0.973645
H	-1.729602	-2.575489	1.580230
H	-1.642432	-0.790115	1.624751
C	-2.282716	-2.830077	-1.010089
H	-2.766667	-3.730231	-0.615768
H	-2.598528	-2.724455	-2.052941
C	-0.738118	-2.923166	-0.863768
H	-0.435489	-3.854011	-0.370164
H	-0.205196	-2.874951	-1.818651
H	0.567351	-1.809785	0.529600
H	-0.052488	-0.469478	-1.750683
C	-4.154431	-1.524706	0.244265
C	-5.097930	-1.837034	-0.933759
C	-4.509948	-2.440392	1.430890
H	-4.356388	-0.496753	0.571201
C	-6.570445	-1.658833	-0.544835
H	-4.941903	-2.876925	-1.253168
H	-4.848287	-1.213189	-1.799878
C	-5.985328	-2.292794	1.831426
H	-4.306848	-3.489511	1.167356
H	-3.874940	-2.203670	2.291926
C	-6.928174	-2.552178	0.649782

H	-7.220188	-1.887087	-1.399679
H	-6.749602	-0.607656	-0.280290
H	-6.220309	-2.970025	2.662775
H	-6.149767	-1.270664	2.201861
H	-7.970851	-2.390956	0.951771
H	-6.846671	-3.607005	0.347355

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B3LYP SCF energy: -3964.67912504 a.u.
B3LYP enthalpy: -3963.918526 a.u.
B3LYP free energy: -3964.031619 a.u.
M06 SCF energy in solution: -3967.17398343 a.u.
M06 enthalpy in solution: -3966.413384 a.u.
M06 free energy in solution: -3966.526477 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.420909	0.513388	-0.938216
C	-3.713634	-2.020393	-0.219178
C	-4.326918	-0.729122	-0.199622
C	-5.694087	-0.633887	0.105247
C	-6.412851	-1.793241	0.379702
C	-5.790349	-3.055876	0.353157
C	-4.435432	-3.185247	0.052855
C	-2.120189	-0.498249	-0.726974
C	-3.293169	0.209642	-0.532454
H	-6.183152	0.336671	0.125596
H	-7.470917	-1.726556	0.618458
H	-6.373775	-3.945333	0.574863
H	-3.958412	-4.161176	0.042235
C	-1.470747	-2.954014	-0.831228
H	-0.996190	-3.349307	0.075843
H	-2.016647	-3.766492	-1.321169
H	-0.692847	-2.606617	-1.511453
N	-2.373938	-1.861452	-0.548133
C	2.035758	-2.536789	-1.047671
C	2.930313	-4.653702	-2.646914
C	2.116529	-2.388363	-2.438513
C	2.387438	-3.757512	-0.464318
C	2.830930	-4.812408	-1.263240
C	2.572222	-3.439482	-3.235265
H	1.806417	-1.452650	-2.897984
H	2.303467	-3.892991	0.608490
H	3.097543	-5.760165	-0.803820
H	2.634312	-3.313934	-4.312447
H	3.275810	-5.476929	-3.265607
C	0.961190	-1.700534	1.717516
C	0.298377	-2.680857	4.253617
C	1.957044	-2.222191	2.555204
C	-0.363645	-1.651093	2.166571
C	-0.692757	-2.145103	3.430733
C	1.625330	-2.714954	3.816623
H	2.992708	-2.225961	2.229060
H	-1.133325	-1.224798	1.532352
H	-1.724239	-2.105363	3.768356

H	2.401803	-3.119353	4.459983
H	0.041237	-3.063331	5.237376
C	3.052913	-0.072239	0.369422
C	5.326255	1.482110	0.888742
C	3.104700	0.750353	1.502633
C	4.147851	-0.113015	-0.499195
C	5.278614	0.663890	-0.241239
C	4.238792	1.518704	1.764198
H	2.259641	0.787614	2.183710
H	4.120714	-0.751886	-1.376672
H	6.123826	0.626386	-0.922747
H	4.269703	2.150270	2.647397
H	6.206711	2.085936	1.088165
As	1.387005	-0.998944	-0.044474
C	-1.797718	2.048967	-1.162414
C	-1.368938	3.129938	-0.136993
C	-3.510814	2.599822	0.457983
C	-3.260619	1.678191	-0.769191
H	-1.699670	2.377696	-2.202845
C	-2.128482	2.650921	1.125872
H	-2.079587	3.366103	1.955780
H	-1.778439	1.672687	1.469774
C	-2.190793	4.403964	-0.506519
H	-1.834634	5.277632	0.047293
H	-2.113805	4.641823	-1.572934
C	-3.646204	4.042341	-0.071917
H	-3.992448	4.717273	0.718852
H	-4.363268	4.109660	-0.897452
H	-4.341684	2.271629	1.088760
H	-3.969544	1.949300	-1.566505
C	0.159365	3.297973	0.034192
C	0.940146	3.192418	-1.292502
C	0.570592	4.580778	0.776485
H	0.493817	2.457505	0.665607
C	2.457958	3.315217	-1.107525
H	0.574246	3.959351	-1.990277
H	0.730228	2.228018	-1.802089
C	2.084436	4.636156	1.014967
H	0.280306	5.457619	0.182348
H	0.027980	4.650768	1.727389
C	2.846563	4.568388	-0.314060
H	2.952870	3.313788	-2.086861
H	2.821310	2.433005	-0.572315
H	2.348093	5.551545	1.559628
H	2.386685	3.790720	1.648158
H	3.929283	4.573448	-0.137147
H	2.616297	5.466848	-0.905355

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B3LYP SCF energy: -1518.71811370 a.u.
B3LYP enthalpy: -1518.100318 a.u.
B3LYP free energy: -1518.203531 a.u.
M06 SCF energy in solution: -1519.14289743 a.u.
M06 enthalpy in solution: -1518.525102 a.u.
M06 free energy in solution: -1518.628315 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.003340	-0.453110	-0.084015
C	4.042491	0.587397	-0.403154
C	3.606088	1.416669	0.678705
C	4.546434	2.232029	1.328866
C	5.872572	2.215260	0.904997
C	6.281448	1.395484	-0.164197
C	5.372604	0.572671	-0.828926
C	1.846663	0.231554	-0.118961
C	2.203180	1.165214	0.830544
H	4.239553	2.867408	2.156221
H	6.605276	2.843917	1.405794
H	7.323108	1.399441	-0.475681
H	5.693152	-0.065993	-1.646695
C	2.997134	-0.984470	-2.046080
H	3.672262	-0.540178	-2.784827
H	3.342155	-1.990144	-1.785298
H	2.000726	-1.059050	-2.475176
N	2.949844	-0.122318	-0.879676
C	-0.231390	1.168367	1.367735
C	-1.063893	2.404280	0.969534
C	0.979880	3.267295	1.520338
C	1.173333	1.738966	1.736599
H	-0.702148	0.612913	2.177771
C	0.018700	3.303115	0.320648
H	-0.341022	4.315479	0.105096
H	0.435272	2.867186	-0.588739
C	-1.286809	3.172495	2.322886
H	-2.048195	3.947456	2.175509
H	-1.652689	2.508304	3.112563
C	0.094014	3.799903	2.657346
H	0.045734	4.895446	2.637603
H	0.466334	3.505057	3.645864
H	1.927241	3.798119	1.392139
H	1.411616	1.530634	2.791413
C	-2.376109	2.135372	0.214070
C	-3.507961	1.631639	1.128230
C	-2.862915	3.338875	-0.609207
H	-2.174668	1.340344	-0.506535
C	-4.741025	1.245208	0.302669
H	-3.792921	2.414631	1.846057
H	-3.164084	0.772693	1.713369
C	-4.115377	2.981867	-1.421515
H	-3.080357	4.192712	0.052785
H	-2.070035	3.652398	-1.295122
C	-5.238102	2.431936	-0.532778
H	-5.544602	0.880562	0.959389
H	-4.468318	0.419558	-0.367522
H	-4.468678	3.858548	-1.981594
H	-3.836131	2.221464	-2.163337
H	-6.101207	2.136364	-1.144912
H	-5.588834	3.225985	0.145057
C	0.318915	-1.538567	1.611027
C	1.524079	-1.737038	2.284681
C	-0.848147	-2.139654	2.123119

C	1.556331	-2.519052	3.440957
C	-0.810972	-2.932856	3.280064
C	0.395052	-3.118423	3.943994
H	2.503248	-2.665143	3.956361
H	-1.725075	-3.396003	3.637707
H	0.436914	-3.727622	4.842702
I	0.172519	-3.139964	-1.313073
I	-0.403952	0.790095	-2.607552
C	-2.077556	-1.920237	1.357913
O	-2.138964	-1.155378	0.389069
O	-3.147213	-2.613514	1.767649
C	-4.317956	-2.490755	0.943263
H	-5.027808	-3.216256	1.342550
H	-4.725318	-1.479351	1.004400
H	-4.069267	-2.717047	-0.095972
H	2.434632	-1.283649	1.912582

18b

B3LYP SCF energy: -1518.71702793 a.u.
B3LYP enthalpy: -1518.099326 a.u.
B3LYP free energy: -1518.203003 a.u.
M06 SCF energy in solution: -1519.14382508 a.u.
M06 enthalpy in solution: -1518.526123 a.u.
M06 free energy in solution: -1518.629800 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.109095	0.487031	-0.026857
C	-3.674048	-1.662565	-0.761874
C	-3.098241	-2.382365	0.334293
C	-3.804291	-3.471059	0.869634
C	-5.037595	-3.821053	0.324493
C	-5.584413	-3.101779	-0.754318
C	-4.908949	-2.013716	-1.308673
C	-1.703327	-0.699482	-0.271095
C	-1.851032	-1.734288	0.621149
H	-3.391867	-4.032928	1.704204
H	-5.587976	-4.663223	0.737583
H	-6.549196	-3.394507	-1.161272
H	-5.336195	-1.455116	-2.136814
C	-2.999061	0.241895	-2.243427
H	-3.392591	-0.331166	-3.089675
H	-3.705674	1.048622	-2.003018
H	-2.039868	0.670793	-2.526279
N	-2.802145	-0.642119	-1.114801
C	0.465640	-1.074012	1.334176
C	1.626009	-2.017812	0.947640
C	-0.133724	-3.439646	1.297549
C	-0.751406	-2.039040	1.573791
H	0.727730	-0.435331	2.175192
C	0.873105	-3.133879	0.179483
H	1.511279	-3.993195	-0.051369
H	0.412188	-2.770419	-0.740660
C	1.943478	-2.780997	2.291942
H	2.899451	-3.301633	2.175906

H	2.053345	-2.093394	3.136098
C	0.781573	-3.790050	2.476834
H	1.139939	-4.824196	2.404998
H	0.272890	-3.684621	3.442893
H	-0.895507	-4.189333	1.067389
H	-1.096279	-1.984714	2.617905
C	2.894415	-1.397359	0.323796
C	3.854188	-0.789593	1.364861
C	3.654321	-2.384815	-0.577962
H	2.572575	-0.579080	-0.322503
C	5.043410	-0.100051	0.685778
H	4.238992	-1.576156	2.030307
H	3.319215	-0.064541	1.986328
C	4.855892	-1.707763	-1.250416
H	3.999917	-3.251297	0.010155
H	2.980190	-2.763887	-1.352049
C	5.802322	-1.072885	-0.224643
H	5.718110	0.319740	1.444764
H	4.666669	0.743662	0.094872
H	5.397068	-2.432144	-1.875377
H	4.475071	-0.927771	-1.923349
H	6.628772	-0.558210	-0.734413
H	6.256828	-1.867397	0.389193
C	-1.227274	1.395992	1.437332
C	-1.398482	1.001499	2.764168
C	-1.901862	2.559536	1.008675
C	-2.203695	1.736173	3.635212
C	-2.709257	3.300876	1.886349
C	-2.865249	2.889164	3.202683
H	-2.315282	1.401911	4.664461
H	-3.201344	4.195652	1.519952
H	-3.490010	3.457183	3.886314
I	1.925926	2.324351	0.668107
I	0.852148	-0.384040	-2.582908
C	-1.708676	2.984494	-0.382552
O	-1.051250	2.349314	-1.202739
O	-2.308618	4.143604	-0.716383
C	-2.071896	4.578920	-2.062800
H	-2.581762	5.539349	-2.150729
H	-0.999895	4.686875	-2.244074
H	-2.480419	3.858424	-2.776689
H	-0.903199	0.117580	3.143746

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B3LYP SCF energy: -1518.76170338 a.u.
B3LYP enthalpy: -1518.142848 a.u.
B3LYP free energy: -1518.248701 a.u.
M06 SCF energy in solution: -1519.20474952 a.u.
M06 enthalpy in solution: -1518.585894 a.u.
M06 free energy in solution: -1518.691747 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.380252	-0.664576	-0.011236
C	-3.046528	-0.925208	1.592124

C	-2.023046	-0.066070	2.077441
C	-1.769304	-0.066517	3.461171
C	-2.510979	-0.896595	4.293480
C	-3.507688	-1.747139	3.781060
C	-3.782418	-1.774764	2.419727
C	-2.208063	0.155764	-0.187090
C	-1.467429	0.616609	0.919025
H	-0.994467	0.557626	3.885866
H	-2.307083	-0.896265	5.361210
H	-4.058291	-2.399414	4.453525
H	-4.528514	-2.447992	2.010642
C	-3.981428	-1.573356	-0.631926
H	-4.987690	-1.638974	-0.206560
H	-3.541641	-2.573190	-0.723779
H	-4.045053	-1.111188	-1.617273
N	-3.150226	-0.752432	0.223965
C	-0.515055	1.811100	0.821744
C	-0.050355	2.379625	2.175560
C	1.905568	1.713733	1.196911
C	0.811934	1.340746	0.164963
H	-0.997655	2.604354	0.240154
C	1.144984	1.475277	2.525873
H	1.691364	1.830619	3.406956
H	0.884915	0.422055	2.667059
C	0.659373	3.717825	1.887629
H	0.870755	4.247075	2.824718
H	0.044831	4.381972	1.267933
C	1.973644	3.275953	1.183633
H	2.854055	3.626925	1.735626
H	2.055803	3.663868	0.163972
H	0.990364	1.738005	-0.835569
C	-2.116039	0.599065	-1.599766
C	-1.568532	-0.261028	-2.560827
C	-2.484910	1.905126	-1.984267
C	-1.371242	0.170710	-3.870658
C	-2.259263	2.338945	-3.298035
C	-1.709649	1.473802	-4.239630
H	-0.914877	-0.505008	-4.586907
H	-2.525976	3.354358	-3.569478
H	-1.536399	1.818880	-5.255290
I	-0.614881	-3.350054	0.108388
C	-3.145525	2.813519	-1.010215
O	-2.844058	4.118646	-1.252545
O	-3.876930	2.473606	-0.102715
C	-3.430903	5.044056	-0.332687
H	-4.522626	4.978203	-0.355200
H	-3.097676	6.031110	-0.656613
H	-3.087980	4.837807	0.685197
H	-1.249176	-1.251893	-2.253604
I	2.214922	-1.084290	-1.996546
C	3.266985	1.019518	1.032956
C	4.070785	1.594475	-0.147479
C	4.128809	1.039990	2.308596
H	3.059479	-0.032395	0.800174
C	5.384135	0.834600	-0.361584
H	4.297955	2.653552	0.047945
H	3.467212	1.547175	-1.058218

C	5.450826	0.285828	2.103027
H	4.346363	2.079528	2.601583
H	3.580177	0.586347	3.142209
C	6.241213	0.837875	0.910193
H	5.943393	1.273880	-1.198927
H	5.145472	-0.197694	-0.648004
H	6.057722	0.327399	3.018388
H	5.225279	-0.774435	1.920645
H	7.160000	0.254376	0.759786
H	6.556050	1.869508	1.134413
H	-0.849821	2.462737	2.915243

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B3LYP SCF energy: -1518.72647860 a.u.
B3LYP enthalpy: -1518.109571 a.u.
B3LYP free energy: -1518.218126 a.u.
M06 SCF energy in solution: -1519.17036966 a.u.
M06 enthalpy in solution: -1518.553462 a.u.
M06 free energy in solution: -1518.662017 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.053722	0.442720	-0.127498
C	-2.926231	-2.365560	-1.431289
C	-1.680349	-1.690428	-1.562788
C	-0.839556	-2.033275	-2.633480
C	-1.251719	-3.002700	-3.541276
C	-2.504664	-3.632899	-3.410948
C	-3.362532	-3.314604	-2.360988
C	-2.732477	-0.876378	0.262340
C	-1.574817	-0.736663	-0.480852
H	0.102341	-1.510812	-2.762326
H	-0.607846	-3.263567	-4.377310
H	-2.810901	-4.376169	-4.143389
H	-4.332721	-3.795295	-2.267118
C	-4.998033	-1.939450	-0.145288
H	-5.348494	-2.975823	-0.208750
H	-5.501884	-1.348216	-0.922620
H	-5.276572	-1.541225	0.831212
N	-3.555593	-1.894968	-0.292007
C	0.070369	-0.988601	1.766828
C	0.067607	-2.474111	1.455403
C	2.204470	-1.740361	1.140478
C	1.362912	-0.557733	1.603574
H	-0.663394	-0.506923	2.398089
C	1.148758	-2.563978	0.365094
H	1.469170	-3.594924	0.178460
H	0.853589	-2.096695	-0.573923
C	0.839411	-3.120394	2.653469
H	0.786935	-4.213542	2.589166
H	0.419471	-2.825004	3.620628
C	2.301858	-2.612806	2.447448
H	2.993666	-3.447990	2.290983
H	2.672805	-2.034423	3.298814
H	1.786908	0.321931	2.064605

C	-3.029121	-0.392987	1.613704
C	-3.352586	-1.335742	2.609927
C	-2.856859	0.949317	2.009333
C	-3.467084	-0.973790	3.948758
C	-2.929081	1.298197	3.363379
C	-3.237418	0.348560	4.335167
H	-3.703576	-1.729718	4.693585
H	-2.754293	2.332112	3.642167
H	-3.299626	0.637797	5.380671
I	-0.612202	1.637115	-2.482005
C	-2.706934	2.051077	1.006836
O	-1.721508	2.894674	1.366138
O	-3.442804	2.208554	0.057123
C	-1.503324	4.018037	0.492109
H	-1.408071	3.674345	-0.538197
H	-0.566112	4.460045	0.826098
H	-2.336345	4.724086	0.582668
H	-3.455688	-2.376156	2.317235
I	2.147655	2.376306	0.167792
C	3.505647	-1.387862	0.418058
C	4.509792	-0.663228	1.331297
C	4.177908	-2.595100	-0.257551
H	3.226274	-0.678783	-0.374082
C	5.760958	-0.233686	0.556370
H	4.801642	-1.330839	2.156888
H	4.037570	0.220869	1.770824
C	5.432777	-2.172134	-1.034618
H	4.458677	-3.340652	0.502421
H	3.472649	-3.087912	-0.937113
C	6.429235	-1.428606	-0.135641
H	6.472152	0.263125	1.229680
H	5.464482	0.510738	-0.194793
H	5.910072	-3.049511	-1.492136
H	5.131668	-1.510094	-1.858853
H	7.297907	-1.098719	-0.721422
H	6.810216	-2.123355	0.629272
H	-0.902736	-2.918832	1.235582

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B3LYP SCF energy: -1317.74274914 a.u.
B3LYP enthalpy: -1317.340004 a.u.
B3LYP free energy: -1317.438920 a.u.
M06 SCF energy in solution: -1318.40158918 a.u.
M06 enthalpy in solution: -1317.998844 a.u.
M06 free energy in solution: -1318.097760 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.972126	-0.393547	0.391622
C	2.782193	-2.450113	0.538272
C	1.398430	-2.375584	0.892317
C	0.876400	-3.322747	1.786740
C	1.721004	-4.287045	2.327364
C	3.087275	-4.329412	1.982823
C	3.633765	-3.416753	1.083417

C	1.850240	-0.724668	-0.576239
C	0.831378	-1.271491	0.170424
H	-0.182773	-3.302626	2.028634
H	1.323419	-5.024326	3.020371
H	3.727331	-5.089975	2.423798
H	4.687752	-3.455439	0.820458
C	4.343760	-1.120164	-0.888445
H	4.941095	-0.579569	-0.143797
H	4.874289	-2.031662	-1.186528
H	4.230845	-0.484323	-1.769248
N	3.037786	-1.454759	-0.378327
C	-0.608380	-0.028044	2.587244
C	0.150498	0.912706	1.928126
H	-1.574735	0.241452	2.999732
H	-0.169463	-0.975298	2.880096
H	1.175246	0.700461	1.647416
C	-0.261616	2.334766	1.814455
O	-0.965248	2.950754	2.584767
O	0.330451	2.894617	0.727249
C	-0.097370	4.219196	0.409318
H	0.480433	4.504361	-0.470266
H	-1.168387	4.216607	0.188674
H	0.098936	4.902963	1.241242
I	-1.857081	-2.145045	-1.478534
C	1.755570	0.382686	-1.552026
C	2.322934	1.669021	-1.386568
C	0.993816	0.140030	-2.706318
C	2.152374	2.642566	-2.384238
C	0.820350	1.116356	-3.682679
H	0.513859	-0.826753	-2.805497
C	1.416004	2.369693	-3.530738
H	2.590894	3.622183	-2.237505
H	0.214787	0.896873	-4.557485
H	1.290822	3.136455	-4.290516
C	2.998518	2.042187	-0.119448
O	3.313580	1.286178	0.781252
O	3.226488	3.380813	-0.035005
C	3.704667	3.821747	1.236901
H	2.963455	3.604282	2.011149
H	4.645033	3.327902	1.496873
H	3.848901	4.898964	1.138971
I	-3.379362	1.049864	0.500171

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B3LYP SCF energy: -1317.77497558 a.u.
B3LYP enthalpy: -1317.370290 a.u.
B3LYP free energy: -1317.469296 a.u.
M06 SCF energy in solution: -1318.43711927 a.u.
M06 enthalpy in solution: -1318.032434 a.u.
M06 free energy in solution: -1318.131440 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.981271	-0.100932	0.016698
C	-1.679852	2.253902	1.149115

C	-1.101743	1.188307	1.882248
C	-0.593423	1.427324	3.166434
C	-0.679260	2.716957	3.680370
C	-1.248462	3.767616	2.933970
C	-1.750763	3.553131	1.653913
C	-1.812713	0.417691	-0.141635
C	-1.179971	0.007763	1.043054
H	-0.105202	0.624259	3.707420
H	-0.281942	2.924726	4.670630
H	-1.283069	4.767942	3.357984
H	-2.164309	4.367621	1.067636
C	-2.650126	2.569250	-1.138734
H	-3.435353	3.220400	-0.741212
H	-1.849720	3.167448	-1.586449
H	-3.082975	1.919311	-1.900088
N	-2.115107	1.752582	-0.069649
C	-0.938114	-1.435780	1.459713
C	0.503425	-1.815956	1.128747
H	-1.142513	-1.533593	2.531687
H	-1.629141	-2.092673	0.921746
H	0.631005	-2.668226	0.464819
C	1.400523	-1.864268	2.296969
O	1.270205	-1.222584	3.333959
O	2.420587	-2.744116	2.126052
C	3.465638	-2.655600	3.090089
H	3.088165	-2.829362	4.103027
H	4.189201	-3.424292	2.812216
H	3.936430	-1.668409	3.049235
I	1.203274	2.368915	-1.357067
C	-2.186814	-0.425876	-1.301444
C	-3.261250	-1.337661	-1.228863
C	-1.405263	-0.389897	-2.463885
C	-3.513702	-2.209799	-2.297256
C	-1.681295	-1.243223	-3.530990
H	-0.563666	0.295921	-2.501900
C	-2.731822	-2.158891	-3.447296
H	-4.330236	-2.918291	-2.215586
H	-1.056015	-1.204116	-4.418159
H	-2.937769	-2.835685	-4.272093
C	-4.148294	-1.356808	-0.033965
O	-4.388857	-0.411441	0.688120
O	-4.696011	-2.585422	0.167008
C	-5.566357	-2.669855	1.300103
H	-5.027858	-2.411283	2.215820
H	-6.415897	-1.989428	1.189513
H	-5.905427	-3.706236	1.332947
I	3.301331	-1.122739	-0.903213

31

B3LYP SCF energy: -150.30863844 a.u.
B3LYP enthalpy: -150.294598 a.u.
B3LYP free energy: -150.335355 a.u.
M06 SCF energy in solution: -151.52033230 a.u.
M06 enthalpy in solution: -151.506292 a.u.
M06 free energy in solution: -151.547049 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.000100	-0.026630	-0.000008
I	2.675698	-0.002402	0.000004
H	0.001451	1.478809	-0.000006
I	-2.675639	-0.002386	0.000004

33

B3LYP SCF energy: -5995.21201995 a.u.
B3LYP enthalpy: -5994.622404 a.u.
B3LYP free energy: -5994.745743 a.u.
M06 SCF energy in solution: -6000.23955173 a.u.
M06 enthalpy in solution: -5999.649936 a.u.
M06 free energy in solution: -5999.773275 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.000023	1.074243	0.000084
C	-2.307981	-1.447231	1.449850
C	-2.422167	-3.389195	3.475430
C	-1.168774	-2.184844	1.798336
C	-3.504277	-1.686289	2.134029
C	-3.560094	-2.651750	3.143230
C	-1.222295	-3.153514	2.798918
H	-0.230358	-1.976059	1.296578
H	-4.393212	-1.115889	1.883972
H	-4.494934	-2.825142	3.671792
H	-0.321733	-3.703227	3.057803
H	-2.467514	-4.136655	4.264098
C	-2.342933	-1.275142	-1.523258
C	-2.534550	-2.861033	-3.833440
C	-2.820034	-2.587758	-1.444551
C	-1.953780	-0.767497	-2.770694
C	-2.054912	-1.550520	-3.918958
C	-2.912953	-3.378595	-2.593718
H	-3.105944	-2.999845	-0.481546
H	-1.539453	0.236234	-2.824496
H	-1.742093	-1.145622	-4.877948
H	-3.279417	-4.399952	-2.518153
H	-2.602787	-3.476923	-4.726955
C	-3.828142	0.773816	0.060259
C	-6.239564	2.197454	0.127662
C	-3.844170	2.112986	0.467210
C	-5.022575	0.159589	-0.335109
C	-6.225582	0.866338	-0.297993
C	-5.048176	2.820013	0.504791
H	-2.905831	2.603395	0.720294
H	-5.010968	-0.870338	-0.682038
H	-7.149695	0.382341	-0.606597
H	-5.049718	3.861247	0.816715
H	-7.175828	2.750414	0.152014
C	2.343027	-1.275314	1.523255
C	2.534670	-2.861360	3.833336
C	1.954323	-0.767599	2.770801

C	2.819709	-2.588074	1.444393
C	2.912642	-3.378983	2.593507
C	2.055470	-1.550699	3.919013
H	1.540330	0.236260	2.824749
H	3.105279	-3.000214	0.481310
H	3.278776	-4.400450	2.517818
H	1.743001	-1.145733	4.878089
H	2.602912	-3.477312	4.726808
C	3.828207	0.773631	-0.060264
C	6.239752	2.197036	-0.127802
C	3.844276	2.112905	-0.466860
C	5.022659	0.159173	0.334690
C	6.225730	0.865806	0.297499
C	5.048349	2.819820	-0.504507
H	2.905931	2.603463	-0.719645
H	5.011014	-0.870849	0.681337
H	7.149863	0.381634	0.605768
H	5.049935	3.861135	-0.816162
H	7.176070	2.749903	-0.152215
C	2.307763	-1.447226	-1.449861
C	2.421598	-3.389006	-3.475646
C	1.168598	-2.185106	-1.797934
C	3.503834	-1.685937	-2.134551
C	3.559471	-2.651295	-3.143862
C	1.221950	-3.153688	-2.798609
H	0.230333	-1.976611	-1.295771
H	4.392731	-1.115341	-1.884821
H	4.494135	-2.824403	-3.672828
H	0.321422	-3.703611	-3.057164
H	2.466806	-4.136393	-4.264391
As	2.071673	-0.106677	-0.033822
As	-2.071670	-0.106616	0.033922
I	0.000101	3.911558	0.000054

$AsPh_3$

B3LYP SCF energy: -2928.42962418 a.u.
B3LYP enthalpy: -2928.138161 a.u.
B3LYP free energy: -2928.202842 a.u.
M06 SCF energy in solution: -2930.34698647 a.u.
M06 enthalpy in solution: -2930.055523 a.u.
M06 free energy in solution: -2930.120204 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.706905	-1.565657	-0.315742
C	-1.838479	-3.810234	0.935684
C	-1.860214	-2.167413	-0.836271
C	-0.120390	-2.107922	0.833377
C	-0.682939	-3.224490	1.455069
C	-2.428493	-3.278145	-0.212584
H	-2.318986	-1.762110	-1.734993
H	0.774813	-1.655160	1.246591
H	-0.217948	-3.635291	2.347344
H	-3.326055	-3.730648	-0.625339
H	-2.275158	-4.679032	1.420390

C	-1.002285	1.395043	-0.314782
C	-2.381135	3.496050	0.937899
C	-1.761457	1.158138	0.836758
C	-0.950756	2.694188	-0.837001
C	-1.628987	3.741091	-0.212739
C	-2.447521	2.202958	1.459106
H	-1.813757	0.156890	1.251352
H	-0.373291	2.888884	-1.737592
H	-1.575281	4.744247	-0.626906
H	-3.032863	2.005588	2.353281
H	-2.915525	4.308135	1.423061
C	1.709635	0.170691	-0.315192
C	4.218772	0.313717	0.937134
C	2.809117	-0.522430	-0.838531
C	1.883984	0.945208	0.837293
C	3.131945	1.016663	1.459475
C	4.054984	-0.458798	-0.214445
H	2.689042	-1.118837	-1.739818
H	1.042800	1.490107	1.252774
H	3.253640	1.621194	2.354382
H	4.897024	-1.006036	-0.629465
H	5.189341	0.370257	1.422147
As	0.000271	0.000299	-1.258917

N2

B3LYP SCF energy: -272.75118801 a.u.
B3LYP enthalpy: -272.591172 a.u.
B3LYP free energy: -272.625837 a.u.
M06 SCF energy in solution: -507.14274891 a.u.
M06 enthalpy in solution: -506.982733 a.u.
M06 free energy in solution: -507.017398 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.278321	-0.670117	-0.505731
C	-0.087185	-1.127879	0.323559
C	-0.087036	1.127876	0.323598
C	-1.278193	0.670291	-0.505766
H	-1.917612	-1.328531	-1.085136
C	-0.038278	-0.000025	1.380557
H	0.883130	-0.000101	1.975587
H	-0.908415	0.000019	2.043723
C	1.188176	-0.780119	-0.517940
H	2.086312	-1.176522	-0.031454
H	1.139256	-1.205079	-1.524364
C	1.188299	0.779998	-0.517877
H	2.086480	1.176231	-0.031334
H	1.139469	1.205043	-1.524270
H	-0.118146	-2.156392	0.689984
H	-0.117883	2.156379	0.690060
H	-1.917367	1.328800	-1.085193

N12

B3LYP SCF energy: -272.75118801 a.u.
B3LYP enthalpy: -272.591172 a.u.
B3LYP free energy: -272.625837 a.u.
M06 SCF energy in solution: -272.58471347 a.u.
M06 enthalpy in solution: -272.424697 a.u.
M06 free energy in solution: -272.459362 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.278321	-0.670117	-0.505731
C	-0.087185	-1.127879	0.323559
C	-0.087036	1.127876	0.323598
C	-1.278193	0.670291	-0.505766
H	-1.917612	-1.328531	-1.085136
C	-0.038278	-0.000025	1.380557
H	0.883130	-0.000101	1.975587
H	-0.908415	0.000019	2.043723
C	1.188176	-0.780119	-0.517940
H	2.086312	-1.176522	-0.031454
H	1.139256	-1.205079	-1.524364
C	1.188299	0.779998	-0.517877
H	2.086480	1.176231	-0.031334
H	1.139469	1.205043	-1.524270
H	-0.118146	-2.156392	0.689984
H	-0.117883	2.156379	0.690060
H	-1.917367	1.328800	-1.085193

TS-1
B3LYP SCF energy: -3915.40490672 a.u.
B3LYP enthalpy: -3914.831516 a.u.
B3LYP free energy: -3914.944950 a.u.
M06 SCF energy in solution: -3918.09900533 a.u.
M06 enthalpy in solution: -3917.525615 a.u.
M06 free energy in solution: -3917.639049 a.u.
Imaginary frequency: -1355.9798 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.573789	4.169108	0.822283
O	0.473080	3.804928	0.329372
O	2.550313	3.389718	1.097013
C	1.771703	5.638662	1.127968
H	2.716551	5.982865	0.697470
H	0.938082	6.226055	0.741419
H	1.838595	5.769020	2.213659
Pd	-0.063197	1.724332	0.201948
C	-2.552516	2.129748	-1.088268
O	-1.965660	1.525662	-2.001300
O	-2.072696	2.343464	0.097468
C	-3.976100	2.626987	-1.289201
H	-4.130709	2.901864	-2.335374
H	-4.660789	1.806465	-1.044535
H	-4.200649	3.471464	-0.633849
C	3.376218	-0.695765	-0.519896
C	2.651400	-0.091531	0.539985

C	2.748790	-0.661692	1.815566
C	3.504039	-1.817354	1.990642
C	4.199399	-2.403764	0.915849
C	4.157256	-1.840349	-0.356859
C	2.309987	1.087674	-1.352394
C	1.960350	1.082981	0.006646
H	2.232110	-0.211286	2.653764
H	3.562105	-2.273194	2.974676
H	4.786584	-3.302012	1.083563
H	4.699584	-2.282469	-1.187043
H	1.998287	1.779338	-2.124636
H	2.261627	2.264409	0.631739
C	3.690581	-0.237740	-2.977793
H	4.785037	-0.197360	-2.951885
H	3.369409	-1.230872	-3.303955
H	3.322365	0.502374	-3.690228
N	3.138841	0.056146	-1.669676
C	-0.519499	-1.539137	1.704041
C	-0.307560	-2.915078	4.127676
C	-0.272689	-0.840943	2.888903
C	-0.694766	-2.926665	1.740441
C	-0.574244	-3.613820	2.947758
C	-0.169478	-1.526650	4.099752
H	-0.156171	0.239203	2.855690
H	-0.932052	-3.470253	0.831226
H	-0.698440	-4.692803	2.969212
H	0.023253	-0.977572	5.017018
H	-0.218946	-3.451749	5.067986
C	0.019223	-1.517917	-1.368204
C	1.156549	-2.852563	-3.540805
C	0.901476	-2.578205	-1.149950
C	-0.263797	-1.091876	-2.675406
C	0.300254	-1.767802	-3.756578
C	1.464729	-3.247648	-2.238692
H	1.169495	-2.873162	-0.142062
H	-0.915146	-0.235324	-2.825874
H	0.071649	-1.446043	-4.768779
H	2.151953	-4.070083	-2.062348
H	1.588180	-3.381438	-4.386507
C	-2.693372	-0.825519	-0.114733
C	-5.448646	-1.269026	-0.225379
C	-3.233005	-1.606319	-1.137666
C	-3.532050	-0.266716	0.856173
C	-4.906782	-0.489580	0.799718
C	-4.610682	-1.825704	-1.192051
H	-2.588270	-2.036549	-1.895703
H	-3.114905	0.355100	1.640646
H	-5.554286	-0.049535	1.552729
H	-5.026893	-2.431058	-1.992399
H	-6.520613	-1.439466	-0.270484
As	-0.785620	-0.520703	0.075921

TS-2

B3LYP SCF energy: -3918.09900533 a.u.
B3LYP enthalpy: -3914.835638 a.u.

B3LYP free energy: -3914.948454 a.u.
M06 SCF energy in solution: -3918.09695428 a.u.
M06 enthalpy in solution: -3917.63649 a.u.
M06 free energy in solution: -3917.523674 a.u.
Imaginary frequency: -825.02 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.573788	4.169108	0.822283
O	0.473079	3.804928	0.329372
O	2.550312	3.389718	1.097013
C	1.771702	5.638662	1.127968
H	2.716550	5.982865	0.697470
H	0.938081	6.226055	0.741419
H	1.838594	5.769020	2.213659
Pd	-0.063197	1.724332	0.201948
C	-2.552516	2.129748	-1.088268
O	-1.965660	1.525662	-2.001300
O	-2.072696	2.343464	0.097468
C	-3.976100	2.626986	-1.289201
H	-4.130709	2.901863	-2.335374
H	-4.660789	1.806464	-1.044535
H	-4.200650	3.471463	-0.633849
C	3.376218	-0.695764	-0.519896
C	2.651400	-0.091531	0.539985
C	2.748790	-0.661691	1.815566
C	3.504039	-1.817353	1.990642
C	4.199399	-2.403763	0.915849
C	4.157256	-1.840348	-0.356859
C	2.309987	1.087674	-1.352394
C	1.960350	1.082981	0.006646
H	2.232110	-0.211286	2.653764
H	3.562105	-2.273193	2.974676
H	4.786585	-3.302011	1.083563
H	4.699584	-2.282468	-1.187043
H	1.998287	1.779338	-2.124636
H	2.261627	2.264409	0.631739
C	3.690581	-0.237739	-2.977793
H	4.785037	-0.197359	-2.951885
H	3.369409	-1.230871	-3.303955
H	3.322365	0.502375	-3.690228
N	3.138841	0.056147	-1.669676
C	-0.519499	-1.539137	1.704041
C	-0.307560	-2.915078	4.127676
C	-0.272689	-0.840943	2.888903
C	-0.694766	-2.926665	1.740441
C	-0.574243	-3.613820	2.947758
C	-0.169478	-1.526650	4.099752
H	-0.156171	0.239203	2.855690
H	-0.932051	-3.470253	0.831226
H	-0.698439	-4.692803	2.969212
H	0.023253	-0.977572	5.017018
H	-0.218945	-3.451749	5.067986
C	0.019223	-1.517917	-1.368204
C	1.156549	-2.852563	-3.540805
C	0.901476	-2.578205	-1.149950
C	-0.263797	-1.091876	-2.675406

C	0.300254	-1.767802	-3.756578
C	1.464730	-3.247648	-2.238692
H	1.169495	-2.873162	-0.142062
H	-0.915146	-0.235324	-2.825874
H	0.071649	-1.446043	-4.768779
H	2.151954	-4.070083	-2.062348
H	1.588181	-3.381438	-4.386507
C	-2.693372	-0.825519	-0.114733
C	-5.448646	-1.269027	-0.225379
C	-3.233005	-1.606319	-1.137666
C	-3.532050	-0.266717	0.856173
C	-4.906782	-0.489581	0.799718
C	-4.610682	-1.825705	-1.192051
H	-2.588270	-2.036549	-1.895703
H	-3.114905	0.355100	1.640646
H	-5.554286	-0.049536	1.552729
H	-5.026893	-2.431059	-1.992399
H	-6.520613	-1.439467	-0.270484
As	-0.785620	-0.520703	0.075921

TS-3

B3LYP SCF energy: -4193.78649966 a.u.
B3LYP enthalpy: -4192.958474 a.u.
B3LYP free energy: -4193.084970 a.u.
M06 SCF energy in solution: -4196.21305067 a.u.
M06 enthalpy in solution: -4195.385025 a.u.
M06 free energy in solution: -4195.511521 a.u.
Imaginary frequency: -284.3710 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.638494	-0.385253	-0.495433
C	-1.744386	1.096964	-2.601087
O	-1.114347	0.213088	-3.201170
O	-1.841843	1.190375	-1.309771
C	-2.457149	2.205046	-3.368131
H	-2.570975	1.928608	-4.418337
H	-3.433155	2.422550	-2.924747
H	-1.854209	3.119508	-3.310027
C	2.625810	-3.018289	-0.105492
C	1.569073	-2.446994	-0.864364
C	1.667605	-2.407132	-2.262590
C	2.803630	-2.940625	-2.864974
C	3.839403	-3.506478	-2.094908
C	3.768552	-3.551106	-0.704774
C	1.042113	-2.304730	1.324317
C	0.553172	-1.992339	0.065978
H	0.880441	-1.938580	-2.848241
H	2.899430	-2.915337	-3.946735
H	4.715326	-3.910768	-2.594619
H	4.578408	-3.969771	-0.115035
H	0.602223	-2.137987	2.297827
C	3.130735	-3.294331	2.340451
H	3.428952	-4.345893	2.260891
H	4.030740	-2.669292	2.360847

H	2.582413	-3.156607	3.274878
N	2.277451	-2.921760	1.234246
C	0.922644	1.706184	2.026960
C	0.566794	2.407726	4.713642
C	-0.012768	1.029467	2.815475
C	1.671657	2.746865	2.588458
C	1.496724	3.093672	3.927837
C	-0.191088	1.377368	4.155548
H	-0.608692	0.240850	2.366936
H	2.383758	3.291923	1.976069
H	2.080413	3.903264	4.357185
H	-0.924943	0.849698	4.758600
H	0.428129	2.682723	5.755504
C	1.340689	2.920265	-0.675470
C	1.509222	5.463951	-1.821862
C	2.590447	3.510007	-0.891737
C	0.172405	3.603337	-1.038908
C	0.261327	4.873675	-1.608101
C	2.672569	4.780408	-1.465344
H	3.497473	2.978626	-0.622110
H	-0.791631	3.124231	-0.897755
H	-0.646260	5.400665	-1.889822
H	3.645549	5.234033	-1.633722
H	1.574810	6.451781	-2.269547
C	2.958050	0.500703	0.142467
C	5.547427	-0.549239	-0.012436
C	3.519743	0.184064	-1.101365
C	3.694796	0.276236	1.308084
C	4.987624	-0.248215	1.229471
C	4.811046	-0.331635	-1.178929
H	2.942081	0.329773	-2.008911
H	3.265883	0.514677	2.275480
H	5.559673	-0.409508	2.139714
H	5.231284	-0.584428	-2.146892
H	6.552245	-0.957974	-0.072381
As	1.140985	1.181124	0.166757
C	-2.195618	-1.799739	-0.819766
C	-3.292622	-1.744468	0.254679
C	-1.868517	-3.437829	0.828791
C	-1.301797	-2.841216	-0.439617
H	-2.422943	-1.617248	-1.866038
C	-2.494766	-2.206639	1.502653
H	-3.139524	-2.473236	2.345714
H	-1.757511	-1.466611	1.826925
C	-4.138204	-3.033486	-0.010658
H	-5.026493	-3.050245	0.630026
H	-4.479491	-3.088491	-1.048030
C	-3.157485	-4.187800	0.358702
H	-3.544929	-4.795072	1.183552
H	-2.957805	-4.864146	-0.478577
H	-1.175264	-4.044635	1.413387
H	-0.808781	-3.466412	-1.175501
C	-4.044636	-0.415739	0.356563
C	-4.839289	-0.089569	-0.919395
C	-4.961486	-0.309190	1.587011
H	-3.276189	0.362064	0.449809
C	-5.457571	1.310575	-0.836443

H	-5.637211	-0.834808	-1.056561
H	-4.185000	-0.152269	-1.793407
C	-5.598164	1.085444	1.680794
H	-5.757046	-1.066776	1.530165
H	-4.395111	-0.515915	2.503679
C	-6.357945	1.448521	0.398067
H	-6.026294	1.531094	-1.748964
H	-4.640790	2.043102	-0.781871
H	-6.267169	1.138956	2.549347
H	-4.803066	1.826477	1.848253
H	-6.758965	2.467579	0.470304
H	-7.222767	0.776839	0.289904

TS-3b

B3LYP SCF energy: -3959.06877863 a.u.
B3LYP enthalpy: -3958.398508 a.u.
B3LYP free energy: -3958.512502 a.u.
M06 SCF energy in solution: -3961.65331621 a.u.
M06 enthalpy in solution: -3960.983046 a.u.
M06 free energy in solution: -3961.097040 a.u.
Imaginary frequency: -285.9068 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.950188	-1.036179	-0.219099
C	0.333261	-3.087268	-2.017244
O	0.747769	-2.194920	-2.772780
O	0.286063	-3.001863	-0.722953
C	-0.219425	-4.389137	-2.587476
H	0.201117	-4.578054	-3.577795
H	-0.019445	-5.231566	-1.919738
H	-1.307338	-4.290657	-2.689941
C	1.620083	3.120863	-0.443966
C	1.699714	1.814302	-0.997010
C	1.734783	1.656568	-2.389831
C	1.695800	2.794791	-3.190159
C	1.616930	4.082187	-2.622370
C	1.574152	4.265202	-1.242511
C	1.658785	1.642158	1.251418
C	1.722266	0.869727	0.103495
H	1.758846	0.659229	-2.821920
H	1.717675	2.691765	-4.271317
H	1.581820	4.950880	-3.273936
H	1.493904	5.258250	-0.810751
H	1.650116	1.338791	2.289223
C	1.407021	4.077404	1.869251
H	2.169824	4.850570	1.723475
H	0.415621	4.526231	1.738326
H	1.490228	3.692702	2.888032
N	1.600730	2.989250	0.937129
C	-1.808429	-0.270441	2.073079
C	-2.441151	-0.360660	4.798960
C	-0.815027	-0.535813	3.020168
C	-3.125942	-0.063124	2.498049
C	-3.440265	-0.105294	3.856112

C	-1.128262	-0.579888	4.379741
H	0.199625	-0.722251	2.683235
H	-3.907106	0.121454	1.766769
H	-4.465301	0.054964	4.178746
H	-0.350346	-0.792677	5.107912
H	-2.688413	-0.397521	5.856236
C	-2.866133	-1.049660	-0.620670
C	-5.065386	-2.387210	-1.709157
C	-3.983363	-0.326299	-1.050866
C	-2.846990	-2.445355	-0.741469
C	-3.948009	-3.109041	-1.282894
C	-5.080957	-0.996272	-1.594816
H	-3.994720	0.756055	-0.971263
H	-1.961388	-2.995367	-0.437861
H	-3.929706	-4.191406	-1.376943
H	-5.946062	-0.430675	-1.930234
H	-5.919394	-2.907006	-2.134640
C	-1.619872	1.675541	-0.227868
C	-1.957810	4.358995	-0.945842
C	-1.510432	2.068234	-1.568211
C	-1.887132	2.635397	0.751478
C	-2.055395	3.975193	0.391805
C	-1.685985	3.402529	-1.926376
H	-1.275402	1.331326	-2.330028
H	-1.969813	2.340811	1.792158
H	-2.273610	4.715231	1.157665
H	-1.586386	3.697253	-2.965918
H	-2.086758	5.401159	-1.224352
As	-1.322789	-0.195803	0.190970
C	2.957330	-1.698876	-0.408672
C	3.362256	-2.593119	0.758609
C	4.057610	-0.501855	1.288605
C	3.398519	-0.385352	-0.070754
H	2.975272	-2.061267	-1.432985
C	3.228774	-1.620422	1.952051
H	3.689596	-2.001141	2.869899
H	2.193702	-1.329711	2.151860
C	4.912112	-2.718229	0.668706
H	5.285255	-3.437962	1.406110
H	5.239326	-3.054982	-0.319423
C	5.390858	-1.269280	1.000328
H	6.023691	-1.249591	1.893660
H	5.960728	-0.810661	0.186054
H	4.180476	0.435686	1.833132
H	3.795842	0.293648	-0.816342
H	2.820409	-3.537247	0.823263

TS-4

B3LYP SCF energy: -4193.78475943 a.u.
B3LYP enthalpy: -4192.956393 a.u.
B3LYP free energy: -4193.082850 a.u.
M06 SCF energy in solution: -4196.21095947 a.u.
M06 enthalpy in solution: -4195.382593 a.u.
M06 free energy in solution: -4195.509050 a.u.
Imaginary frequency: -270.8063 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.157588	1.358995	-0.062831
C	1.745633	3.591743	0.880034
O	1.364479	3.199060	1.993553
O	1.415438	3.064922	-0.256860
C	2.709127	4.768418	0.758473
H	2.813777	5.279112	1.717733
H	3.691046	4.394734	0.442998
H	2.365904	5.469786	-0.008396
C	-1.682992	-2.408319	0.652172
C	-1.198960	-1.176937	1.174720
C	-0.787645	-1.121757	2.513567
C	-0.880635	-2.270635	3.294493
C	-1.385395	-3.473471	2.761719
C	-1.796242	-3.559739	1.433446
C	-1.656392	-0.902711	-1.013836
C	-1.205700	-0.202737	0.097417
H	-0.375969	-0.202278	2.918899
H	-0.552665	-2.243596	4.329363
H	-1.450082	-4.352433	3.396630
H	-2.168363	-4.492270	1.019932
H	-1.783838	-0.565883	-2.032515
C	-2.460660	-3.218398	-1.601300
H	-1.836019	-4.114913	-1.564322
H	-3.494991	-3.482938	-1.349152
H	-2.435002	-2.822833	-2.618468
N	-1.944725	-2.214166	-0.696390
C	2.888446	-0.583267	1.389946
C	4.078801	-1.009126	3.882987
C	2.591593	0.267333	2.460486
C	3.792441	-1.637791	1.566799
C	4.382165	-1.853147	2.811092
C	3.190675	0.051366	3.703998
H	1.920235	1.111564	2.321554
H	4.030023	-2.298856	0.739197
H	5.078710	-2.676530	2.944250
H	2.960779	0.719660	4.529043
H	4.539610	-1.177217	4.852695
C	3.539271	0.217095	-1.466545
C	5.714803	0.964745	-3.055022
C	4.445283	-0.750126	-1.918436
C	3.720488	1.560975	-1.815898
C	4.810629	1.929000	-2.608050
C	5.530044	-0.376633	-2.710664
H	4.299190	-1.795565	-1.665447
H	3.011428	2.305894	-1.463045
H	4.949159	2.972523	-2.877696
H	6.229937	-1.131206	-3.059552
H	6.560314	1.254815	-3.672927
C	1.602666	-2.026541	-0.943816
C	0.896038	-4.563713	-1.903746
C	1.486809	-2.257060	-2.321711
C	1.335888	-3.068895	-0.051353
C	0.990282	-4.333884	-0.531074
C	1.136919	-3.518403	-2.800584

H	1.689633	-1.451323	-3.021735
H	1.392948	-2.898387	1.017891
H	0.787569	-5.134164	0.174553
H	1.062229	-3.688741	-3.871183
H	0.636116	-5.551237	-2.275829
As	2.034111	-0.236379	-0.320165
C	-2.308631	1.493590	0.698338
C	-3.508565	1.700172	-0.222783
C	-2.084671	3.461041	-0.578693
C	-1.438525	2.609147	0.502666
H	-2.446661	1.061645	1.682651
C	-2.820300	2.401694	-1.422561
H	-3.535250	2.840546	-2.125756
H	-2.139363	1.738262	-1.964513
C	-4.211979	2.940189	0.460241
H	-5.206486	3.076622	0.028711
H	-4.344703	2.787041	1.535522
C	-3.285783	4.145602	0.130304
H	-3.783836	4.849307	-0.546713
H	-2.975929	4.701270	1.020110
H	-1.409907	4.137463	-1.105016
H	-0.945045	3.078835	1.351724
C	-4.420503	0.499610	-0.495505
C	-4.856476	-0.228190	0.789433
C	-5.648598	0.826878	-1.363361
H	-3.825930	-0.218004	-1.070550
C	-5.665209	-1.492438	0.470853
H	-5.464754	0.449533	1.406367
H	-3.979442	-0.503889	1.383414
C	-6.435380	-0.447191	-1.702341
H	-6.315887	1.517993	-0.830856
H	-5.338986	1.334659	-2.284957
C	-6.868329	-1.186945	-0.429726
H	-5.993689	-1.973897	1.400037
H	-5.005810	-2.212531	-0.035532
H	-7.310114	-0.199475	-2.316371
H	-5.802663	-1.111442	-2.309982
H	-7.399325	-2.112193	-0.686777
H	-7.581443	-0.558681	0.123821

TS-5

B3LYP SCF energy: -4193.78882023 a.u.
B3LYP enthalpy: -4192.963240 a.u.
B3LYP free energy: -4193.086629 a.u.
M06 SCF energy in solution: -4196.21235503 a.u.
M06 enthalpy in solution: -4195.386775 a.u.
M06 free energy in solution: -4195.510164 a.u.
Imaginary frequency: -1328.3123 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.470020	0.470672	-0.371028
C	-0.214537	3.328330	-1.118829
O	-1.152101	3.391233	-0.243162
O	0.192967	2.264241	-1.657801

C	0.461828	4.631522	-1.484414
H	0.824996	4.593213	-2.513880
H	-0.214316	5.477058	-1.341925
H	1.324524	4.761404	-0.820671
C	-4.720977	1.251427	-0.687867
C	-4.579687	0.553088	0.553077
C	-5.748104	0.157443	1.237054
C	-6.989078	0.458320	0.698071
C	-7.101991	1.154651	-0.525951
C	-5.977671	1.564661	-1.227770
C	-2.502067	1.100696	-0.243266
C	-3.172015	0.440300	0.797323
H	-5.680936	-0.352867	2.192073
H	-7.891215	0.164286	1.226874
H	-8.088785	1.381449	-0.920077
H	-6.069335	2.113436	-2.159988
H	-1.692762	2.213950	-0.097755
C	-3.193958	2.321235	-2.352242
H	-3.337925	3.392812	-2.166021
H	-2.160917	2.146658	-2.655370
H	-3.855822	2.008668	-3.165843
N	-3.468802	1.528916	-1.171793
C	2.415997	2.113234	0.819661
C	3.037686	4.691403	1.714470
C	1.484141	2.845618	1.565442
C	3.655040	2.682388	0.512811
C	3.963200	3.968843	0.957976
C	1.796593	4.128138	2.017144
H	0.500179	2.429859	1.758532
H	4.375010	2.130585	-0.082422
H	4.926055	4.407522	0.711086
H	1.062368	4.690783	2.586086
H	3.279140	5.693535	2.057342
C	3.200844	-0.068853	-1.157176
C	4.962274	-0.608914	-3.259079
C	4.525085	-0.433838	-0.886804
C	2.763943	0.033866	-2.483300
C	3.645176	-0.233797	-3.531031
C	5.402569	-0.705897	-1.937384
H	4.869841	-0.511034	0.139575
H	1.740435	0.334158	-2.686742
H	3.301326	-0.153960	-4.558223
H	6.428141	-0.993436	-1.723450
H	5.645566	-0.824560	-4.075584
C	2.451608	-0.751069	1.750161
C	2.942486	-2.364758	3.992324
C	3.042593	-2.011407	1.600712
C	2.112697	-0.305591	3.034059
C	2.355467	-1.107857	4.148489
C	3.289042	-2.812091	2.716805
H	3.307067	-2.376655	0.614926
H	1.658569	0.671278	3.167104
H	2.084687	-0.750202	5.137798
H	3.748762	-3.787635	2.586014
H	3.128966	-2.991305	4.859721
As	1.905433	0.329862	0.223162
C	-1.091816	-0.925499	1.000484

C	-1.406096	-2.372173	0.473319
C	-3.120373	-1.843482	1.878732
C	-2.405827	-0.473601	1.719291
H	-0.266835	-0.969814	1.714559
C	-2.952328	-2.418302	0.467427
H	-3.335080	-3.440335	0.381870
H	-3.407723	-1.805233	-0.314077
C	-1.131873	-3.264051	1.716722
H	-1.257931	-4.325010	1.467509
H	-0.118063	-3.135010	2.108204
C	-2.231263	-2.793441	2.720381
H	-2.817044	-3.639964	3.094179
H	-1.806600	-2.282429	3.592084
H	-4.144183	-1.768813	2.247472
H	-2.203202	-0.013689	2.696359
C	-0.735532	-2.795964	-0.845492
C	0.776878	-3.009886	-0.708276
C	-1.368934	-4.043687	-1.490101
H	-0.884800	-1.958848	-1.546929
C	1.446657	-3.332414	-2.046733
H	0.969079	-3.824589	0.003764
H	1.222830	-2.113679	-0.279929
C	-0.704962	-4.388435	-2.831662
H	-1.271229	-4.900347	-0.806859
H	-2.441263	-3.886804	-1.646873
C	0.811769	-4.569085	-2.692153
H	2.526428	-3.476418	-1.908606
H	1.335297	-2.470722	-2.719252
H	-1.160256	-5.292860	-3.254913
H	-0.903406	-3.574439	-3.544566
H	1.265091	-4.770231	-3.671185
H	1.014682	-5.448733	-2.063257

TS-11

B3LYP SCF energy: -4193.79644145 a.u.
B3LYP enthalpy: -4192.970986 a.u.
B3LYP free energy: -4193.096077 a.u.
M06 SCF energy in solution: -4196.22191337 a.u.
M06 enthalpy in solution: -4195.396458 a.u.
M06 free energy in solution: -4195.521549 a.u.
Imaginary frequency: -1525.7513 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.238124	0.805500	-0.146005
C	0.385637	2.119026	2.496473
O	-0.794734	1.600084	2.549678
O	1.028410	2.321767	1.435861
C	1.027819	2.453968	3.823849
H	1.599592	1.577318	4.152162
H	1.724045	3.287111	3.706183
H	0.273336	2.679783	4.580007
C	-3.390579	2.814729	-0.871572
C	-3.586649	1.481546	-1.346294
C	-4.620933	1.235322	-2.269793

C	-5.456058	2.275467	-2.648442
C	-5.275521	3.575973	-2.127602
C	-4.248106	3.862770	-1.238950
C	-1.776255	1.510871	0.064815
C	-2.570821	0.679478	-0.733575
H	-4.760566	0.242514	-2.686342
H	-6.260567	2.092153	-3.354891
H	-5.950415	4.370214	-2.434695
H	-4.113267	4.867266	-0.849747
H	-1.220437	1.408629	1.412767
C	-1.770853	3.983625	0.631800
H	-2.244326	4.113655	1.613373
H	-0.693861	3.875222	0.764165
H	-1.957919	4.876330	0.028730
N	-2.279448	2.819314	-0.064223
C	3.057362	-0.705056	1.465031
C	3.835094	-1.525250	4.023320
C	2.092077	-0.956405	2.446776
C	4.413931	-0.857062	1.771766
C	4.801053	-1.269220	3.047305
C	2.480563	-1.367522	3.722878
H	1.040617	-0.818729	2.214478
H	5.166620	-0.639874	1.019634
H	5.855775	-1.383886	3.281123
H	1.725456	-1.560910	4.479579
H	4.138313	-1.841772	5.017300
C	3.900781	1.105631	-0.779499
C	5.937295	2.914030	-1.397182
C	4.960432	0.710857	-1.601876
C	3.857144	2.408994	-0.266278
C	4.877875	3.307351	-0.575516
C	5.977344	1.616877	-1.910121
H	4.990965	-0.296582	-2.004514
H	3.031708	2.708428	0.373161
H	4.843905	4.317547	-0.177086
H	6.798794	1.307988	-2.550678
H	6.728288	3.618396	-1.639082
C	2.784404	-1.638772	-1.430630
C	3.059343	-3.830615	-3.146973
C	2.399140	-1.535995	-2.773613
C	3.308237	-2.842868	-0.951990
C	3.442205	-3.936765	-1.809284
C	2.541089	-2.626620	-3.630303
H	1.983326	-0.603576	-3.146256
H	3.601331	-2.931014	0.089051
H	3.844631	-4.871856	-1.430059
H	2.240027	-2.539512	-4.670307
H	3.161199	-4.683794	-3.811467
As	2.469935	-0.106802	-0.286284
C	-2.183154	-0.734880	-1.028962
C	-2.647617	-1.846873	-0.010324
C	-0.379845	-2.089265	-0.140995
C	-0.628251	-0.859850	-1.025007
H	-2.567310	-0.987543	-2.025585
C	-1.439723	-1.907271	0.957258
H	-1.492626	-2.763493	1.638527
H	-1.312234	-0.993460	1.545314

C	-2.464909	-3.193817	-0.758522
H	-2.883683	-4.018559	-0.170879
H	-2.973312	-3.196261	-1.727860
C	-0.918702	-3.334933	-0.892261
H	-0.557655	-4.252414	-0.413268
H	-0.576910	-3.356803	-1.932386
H	0.647126	-2.223159	0.199295
H	-0.203439	-0.935976	-2.028733
C	-4.026697	-1.600505	0.613936
C	-5.175599	-1.856744	-0.377783
C	-4.281644	-2.395783	1.907067
H	-4.060207	-0.535536	0.886354
C	-6.534713	-1.476836	0.220110
H	-5.187527	-2.922611	-0.647315
H	-5.006675	-1.301184	-1.304213
C	-5.644639	-2.041722	2.520589
H	-4.246989	-3.474719	1.693488
H	-3.490367	-2.193182	2.637553
C	-6.792610	-2.244212	1.523218
H	-7.336836	-1.672742	-0.502968
H	-6.547468	-0.395910	0.419620
H	-5.817294	-2.637124	3.426427
H	-5.626172	-0.988386	2.836122
H	-7.745364	-1.934155	1.971110
H	-6.886123	-3.316444	1.294585

TS-6

B3LYP SCF energy: -1518.66907287 a.u.
B3LYP enthalpy: -1518.054323 a.u.
B3LYP free energy: -1518.159141 a.u.
M06 SCF energy in solution: -1519.10329746 a.u.
M06 enthalpy in solution: -1518.488548 a.u.
M06 free energy in solution: -1518.593366 a.u.
Imaginary frequency: -124.3190 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.150833	-0.164295	-0.287249
C	3.821444	0.845987	-1.172867
C	3.549959	1.704572	-0.056443
C	4.596663	2.487688	0.457794
C	5.861313	2.408060	-0.121593
C	6.106579	1.557332	-1.216196
C	5.088569	0.766998	-1.752849
C	1.649913	0.572866	-0.614379
C	2.170617	1.503398	0.268717
H	4.418466	3.148671	1.303213
H	6.673894	3.012245	0.276359
H	7.102910	1.512436	-1.649667
H	5.278937	0.107263	-2.595125
C	2.543960	-0.785822	-2.572333
H	2.951676	-0.362697	-3.498204
H	3.090152	-1.707238	-2.331733
H	1.491265	-1.022064	-2.729470
N	2.651818	0.179596	-1.499446

C	-0.149456	1.417115	1.104996
C	-1.084578	2.585084	0.687845
C	0.939288	3.589992	1.008396
C	1.253419	2.093011	1.280520
H	-0.496158	0.919438	2.014532
C	-0.112068	3.489329	-0.107745
H	-0.547114	4.461778	-0.366216
H	0.262927	3.006142	-1.013711
C	-1.278897	3.447560	1.974376
H	-2.069884	4.191889	1.815797
H	-1.578442	2.835409	2.831724
C	0.103221	4.135184	2.182467
H	0.013110	5.227279	2.128695
H	0.554263	3.891623	3.152281
H	1.832785	4.178760	0.778357
H	1.635048	1.964679	2.304546
C	-2.386396	2.162157	-0.008947
C	-3.414342	1.564111	0.967437
C	-3.058500	3.264921	-0.844028
H	-2.117420	1.372932	-0.722677
C	-4.610012	0.974840	0.210294
H	-3.768966	2.348784	1.653256
H	-2.941193	0.793345	1.581754
C	-4.266128	2.701224	-1.608585
H	-3.381828	4.094301	-0.194253
H	-2.341529	3.681001	-1.559914
C	-5.281495	2.040809	-0.666311
H	-5.343414	0.553328	0.914221
H	-4.252627	0.150041	-0.419560
H	-4.752561	3.494691	-2.193004
H	-3.901416	1.951620	-2.323631
H	-6.104917	1.599369	-1.244024
H	-5.727663	2.810817	-0.016798
C	0.777154	-1.614193	1.644490
C	2.008422	-1.198011	2.180409
C	-0.368001	-1.629274	2.477685
C	2.084105	-0.785819	3.503820
C	-0.255735	-1.257429	3.827046
C	0.961838	-0.836081	4.346734
H	3.037370	-0.433060	3.889300
H	-1.153079	-1.257287	4.438367
H	1.039014	-0.531240	5.385909
I	0.935801	-3.177009	0.044255
I	-1.377834	-0.802466	-2.880176
C	-1.695648	-1.750598	1.860995
O	-1.969925	-1.294602	0.752056
O	-2.625894	-2.339835	2.633259
C	-3.952265	-2.358703	2.077993
H	-4.562516	-2.891226	2.808600
H	-4.321462	-1.341249	1.930724
H	-3.953508	-2.876801	1.116311
H	2.886155	-1.174751	1.546493

TS-6b

B3LYP SCF energy: -1283.95137953 a.u.

B3LYP enthalpy: -1283.494484 a.u.
B3LYP free energy: -1283.587913 a.u.
M06 SCF energy in solution: -1284.54595321 a.u.
M06 enthalpy in solution: -1284.089058 a.u.
M06 free energy in solution: -1284.182487 a.u.
Imaginary frequency: -112.0905 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.373126	-0.084617	0.615803
C	-3.463574	-1.351427	-0.560926
C	-3.684006	0.044678	-0.318731
C	-4.956946	0.578058	-0.579308
C	-5.962979	-0.253763	-1.067055
C	-5.724536	-1.621310	-1.300884
C	-4.471149	-2.183699	-1.051130
C	-1.519058	-0.474715	0.189528
C	-2.435617	0.564638	0.149815
H	-5.152359	1.633577	-0.402237
H	-6.949389	0.157873	-1.270707
H	-6.526028	-2.249588	-1.682537
H	-4.286139	-3.238635	-1.235400
C	-1.554180	-2.953432	-0.388340
H	-2.191573	-3.711032	0.082951
H	-1.425011	-3.208900	-1.448696
H	-0.582808	-2.959549	0.106119
N	-2.149309	-1.643295	-0.235807
C	-0.439307	1.818152	0.864714
C	-0.325035	2.215221	2.342952
C	-2.542778	2.399079	1.933865
C	-1.973678	1.915626	0.566218
H	0.161211	2.456818	0.213914
C	-1.634714	1.657960	2.934825
H	-1.802584	1.962207	3.975960
H	-1.702313	0.570556	2.854907
C	-0.577673	3.745591	2.430903
H	-0.332202	4.122259	3.432568
H	0.033548	4.302698	1.711226
C	-2.108856	3.866909	2.142517
H	-2.635407	4.316461	2.993512
H	-2.323188	4.483935	1.261324
H	-3.618849	2.228404	2.036908
H	-2.181189	2.669899	-0.208616
C	0.879647	0.738157	-1.820611
C	-0.257785	1.072834	-2.575312
C	1.823820	1.748062	-1.511300
C	-0.448853	2.380326	-3.001133
C	1.639840	3.049302	-2.005799
C	0.513087	3.372610	-2.751928
H	-1.353125	2.626619	-3.551899
H	2.369055	3.809013	-1.740980
H	0.366527	4.385696	-3.113830
I	1.623967	-1.341332	-2.111247
I	1.403058	-2.371714	2.083353
C	2.795326	1.516635	-0.431949
O	2.552600	0.843024	0.567122
O	3.962784	2.173173	-0.574274

C	4.860267	2.054264	0.540818
H	5.744784	2.629249	0.263232
H	4.401805	2.460202	1.446846
H	5.114400	1.006156	0.714858
H	-0.993898	0.309178	-2.795416
H	0.603103	1.895671	2.824799

TS-7

B3LYP SCF energy: -1518.69331605 a.u.
B3LYP enthalpy: -1518.077212 a.u.
B3LYP free energy: -1518.179119 a.u.
M06 SCF energy in solution: -1519.12782049 a.u.
M06 enthalpy in solution: -1518.511716 a.u.
M06 free energy in solution: -1518.613623 a.u.
Imaginary frequency: -378.4233 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.006634	0.487462	-0.005131
C	3.642794	-1.618980	0.550196
C	2.946136	-2.393498	-0.431876
C	3.480499	-3.638810	-0.816320
C	4.656474	-4.087353	-0.229141
C	5.319999	-3.314724	0.745306
C	4.824726	-2.075548	1.142147
C	1.841475	-0.434608	-0.101997
C	1.803084	-1.631961	-0.810815
H	2.982065	-4.237165	-1.573188
H	5.073896	-5.046709	-0.524349
H	6.238421	-3.687999	1.191050
H	5.351566	-1.481088	1.882395
C	3.203734	0.484591	1.833749
H	3.677329	1.406708	1.475278
H	3.871145	0.004435	2.551669
H	2.261807	0.718356	2.332971
N	2.950250	-0.440682	0.747779
C	0.639028	-1.965206	-1.680728
C	0.036538	-3.361262	-1.344468
C	-1.712771	-1.939648	-0.963678
C	-0.564298	-0.998204	-1.394958
H	0.919347	-1.953928	-2.746364
C	-0.931377	-3.039829	-0.201831
H	-1.559000	-3.898012	0.060304
H	-0.446762	-2.661934	0.699668
C	-0.921839	-3.732607	-2.485254
H	-1.270630	-4.766624	-2.376007
H	-0.450704	-3.647268	-3.472171
C	-2.083024	-2.725246	-2.277145
H	-3.032156	-3.248009	-2.120052
H	-2.223708	-2.052473	-3.128586
H	-0.828868	-0.354801	-2.234194
C	1.648226	1.162471	-1.186264
C	1.894410	0.874265	-2.543241
C	2.122997	2.415080	-0.704012
C	2.605983	1.743146	-3.354837

C	2.875703	3.272762	-1.526941
C	3.128242	2.943182	-2.847200
H	2.766181	1.480184	-4.397905
H	3.217419	4.215601	-1.113882
H	3.698901	3.612267	-3.484502
I	-0.716468	-0.522870	2.672039
C	1.678261	2.868542	0.613143
O	2.264982	3.997330	1.063313
O	0.822665	2.289719	1.278494
C	1.736351	4.491699	2.303420
H	0.662290	4.670812	2.213802
H	2.273691	5.421429	2.496341
H	1.907017	3.771296	3.107672
H	1.536250	-0.054120	-2.964381
I	-1.887564	2.382856	-0.928057
C	-2.944190	-1.303784	-0.285261
C	-3.944187	-0.697711	-1.287710
C	-3.674357	-2.274023	0.658891
H	-2.581453	-0.485124	0.341517
C	-5.084798	0.023412	-0.560775
H	-4.373566	-1.492150	-1.916376
H	-3.430779	0.006031	-1.949608
C	-4.830137	-1.570456	1.382709
H	-4.062219	-3.137750	0.093186
H	-2.970897	-2.656833	1.403992
C	-5.814216	-0.923332	0.400395
H	-5.789652	0.445914	-1.290324
H	-4.662416	0.868380	-0.002980
H	-5.354016	-2.280706	2.037894
H	-4.401492	-0.795582	2.032284
H	-6.601908	-0.386037	0.947072
H	-6.317332	-1.713153	-0.180808
H	0.799055	-4.112239	-1.128382

TS-8

B3LYP SCF energy: -1518.71227098 a.u.
B3LYP enthalpy: -1518.096460 a.u.
B3LYP free energy: -1518.203084 a.u.
M06 SCF energy in solution: -1519.15941633 a.u.
M06 enthalpy in solution: -1518.543605 a.u.
M06 free energy in solution: -1518.650229 a.u.
Imaginary frequency: -257.2982 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.152258	-0.121599	0.259771
C	-3.552637	2.080290	0.133438
C	-2.160101	2.079741	0.428334
C	-1.667052	3.033684	1.328900
C	-2.541752	3.956855	1.892439
C	-3.916806	3.931082	1.594516
C	-4.442405	2.982960	0.720566
C	-2.600508	0.386406	-1.005026
C	-1.560778	0.974850	-0.296464
H	-0.622040	3.020222	1.612798

H	-2.162776	4.690641	2.598931
H	-4.582642	4.650500	2.064840
H	-5.507728	2.946656	0.510208
C	-5.108457	0.470073	-0.986744
H	-5.851136	1.260921	-1.129489
H	-5.396959	-0.160643	-0.137453
H	-5.080517	-0.148011	-1.886183
N	-3.801635	1.059892	-0.775009
C	-0.020002	1.353378	-1.690670
C	0.340775	2.810340	-1.482056
C	2.278068	1.640054	-1.161167
C	1.177214	0.603927	-1.469006
H	-0.679955	1.080090	-2.502039
C	1.448343	2.717369	-0.420139
H	1.985299	3.664185	-0.299283
H	1.097338	2.366650	0.553571
C	1.182933	3.172897	-2.741793
H	1.377455	4.251595	-2.758062
H	0.663909	2.920658	-3.673419
C	2.496113	2.361791	-2.537269
H	3.366356	3.025909	-2.486636
H	2.678316	1.645773	-3.344064
H	1.406170	-0.261009	-2.084271
C	-2.507816	-0.646943	-2.053874
C	-2.606848	-0.263238	-3.400059
C	-2.205495	-1.987683	-1.755921
C	-2.364282	-1.174146	-4.428198
C	-1.922393	-2.888458	-2.787958
C	-1.999239	-2.485707	-4.120180
H	-2.438086	-0.854220	-5.464371
H	-1.655800	-3.907826	-2.531675
H	-1.783445	-3.195213	-4.914429
I	-0.770022	-0.331086	2.889523
C	-2.346003	-2.479643	-0.349263
O	-1.451602	-3.431179	-0.066010
O	-3.228621	-2.103721	0.396856
C	-1.448175	-3.907378	1.293218
H	-1.310336	-3.065061	1.974199
H	-0.597091	-4.584013	1.351443
H	-2.388208	-4.425203	1.510882
H	-2.848559	0.771464	-3.629061
I	2.020558	-2.161845	0.526559
C	3.545763	1.130199	-0.471481
C	4.357307	0.185689	-1.375615
C	4.450359	2.253780	0.065465
H	3.213386	0.539938	0.390720
C	5.572039	-0.390508	-0.639570
H	4.698208	0.733461	-2.268114
H	3.716705	-0.634800	-1.713011
C	5.667124	1.680013	0.806014
H	4.800961	2.889738	-0.762519
H	3.883949	2.902670	0.743841
C	6.469418	0.722302	-0.084082
H	6.146654	-1.044076	-1.309974
H	5.208158	-1.019820	0.182913
H	6.309024	2.494556	1.169380
H	5.314883	1.133839	1.692150

H	7.310814	0.294868	0.478351
H	6.905864	1.290482	-0.920951
H	-0.495441	3.480073	-1.280906

TS-9

B3LYP SCF energy: -1317.72443653 a.u.
B3LYP enthalpy: -1317.322884 a.u.
B3LYP free energy: -1317.421722 a.u.
M06 SCF energy in solution: -1318.38850317 a.u.
M06 enthalpy in solution: -1317.986951 a.u.
M06 free energy in solution: -1318.085789 a.u.
Imaginary frequency: -251.1680 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-1.104749	0.059301	0.039811
C	2.401250	-2.371838	-0.309178
C	1.081113	-2.171039	0.179975
C	0.331446	-3.273413	0.609298
C	0.900421	-4.541099	0.526549
C	2.201260	-4.724368	0.017759
C	2.971579	-3.643770	-0.407249
C	1.971412	-0.155446	-0.347737
C	0.809384	-0.756443	0.116740
H	-0.666196	-3.120038	1.007895
H	0.331490	-5.406945	0.855043
H	2.617302	-5.727500	-0.038606
H	3.978929	-3.788272	-0.788389
C	4.228079	-0.944987	-1.228363
H	5.032498	-1.103059	-0.497325
H	4.364868	-1.646825	-2.058981
H	4.304477	0.070688	-1.619423
N	2.928594	-1.134527	-0.632650
C	0.330401	0.066843	2.032246
C	-1.005693	0.485221	2.192990
H	0.614986	-0.895181	2.440086
H	1.113647	0.811238	1.975876
H	-1.254738	1.538683	2.244113
C	-1.971477	-0.460006	2.789185
O	-1.853013	-1.675488	2.819500
O	-3.020333	0.192516	3.340728
C	-4.124483	-0.637464	3.701810
H	-4.856728	0.029451	4.159987
H	-4.547400	-1.100254	2.805282
H	-3.818297	-1.418177	4.404436
I	-1.182808	-0.685931	-2.607577
C	2.226326	1.282657	-0.489969
C	3.330615	1.946213	0.103744
C	1.313311	2.050459	-1.232950
C	3.521023	3.321010	-0.103809
C	1.492755	3.421797	-1.397747
H	0.473151	1.546956	-1.698198
C	2.605663	4.060224	-0.846531
H	4.376593	3.804978	0.353542
H	0.762797	3.985497	-1.971613

H	2.754514	5.127711	-0.984367
C	4.223126	1.241068	1.059783
O	3.918166	0.296810	1.761064
O	5.465528	1.800799	1.107069
C	6.344845	1.214343	2.070629
H	5.928404	1.296176	3.078801
H	6.510713	0.156066	1.848832
H	7.279203	1.772729	1.994337
I	-3.574906	1.287876	-0.059669

TS-10

B3LYP SCF energy: -1317.74203819 a.u.
B3LYP enthalpy: -1317.343118 a.u.
B3LYP free energy: -1317.443162 a.u.
M06 SCF energy in solution: -1318.41281070 a.u.
M06 enthalpy in solution: -1318.013891 a.u.
M06 free energy in solution: -1318.113935 a.u.
Imaginary frequency: -661.7176 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-1.317546	-0.239186	0.318544
C	2.263015	1.523646	-2.584933
C	1.054765	1.448997	-1.839925
C	-0.172209	1.587038	-2.508913
C	-0.160768	1.808828	-3.882230
C	1.046465	1.891551	-4.601129
C	2.275728	1.743227	-3.964447
C	2.808985	1.081083	-0.448669
C	1.431041	1.178839	-0.470190
H	-1.114265	1.481434	-1.979898
H	-1.105384	1.902551	-4.409980
H	1.020372	2.056732	-5.675209
H	3.205516	1.780279	-4.524667
C	4.677576	1.024193	-2.123308
H	4.749791	-0.007026	-2.486189
H	4.988635	1.718981	-2.909046
H	5.346474	1.142970	-1.268300
N	3.324579	1.328848	-1.710746
C	0.586132	1.032219	0.712050
C	-0.649607	1.725584	0.867129
H	0.193738	-0.607725	0.702088
H	1.104360	0.806890	1.641635
H	-1.004029	2.402134	0.099571
C	-1.142472	1.967219	2.236295
O	-0.716517	1.445253	3.254478
O	-2.145960	2.876933	2.237707
C	-2.830474	3.015787	3.481380
H	-2.145145	3.324533	4.277211
H	-3.594104	3.776911	3.313481
H	-3.298878	2.067783	3.762088
I	-1.495452	-2.901862	-0.265118
C	3.662583	0.767282	0.717680
C	3.861761	-0.564934	1.130912
C	4.194832	1.802277	1.495781

C	4.557247	-0.834553	2.314240
C	4.916934	1.527189	2.657172
H	4.014622	2.828339	1.189798
C	5.093701	0.206068	3.069902
H	4.672509	-1.864984	2.631868
H	5.321210	2.343845	3.248839
H	5.638880	-0.013552	3.983535
C	3.358406	-1.686955	0.277756
O	3.364122	-1.671615	-0.937786
O	2.935698	-2.719952	1.020353
C	2.369121	-3.825447	0.283297
H	1.411896	-3.525121	-0.151670
H	3.060358	-4.150961	-0.498179
H	2.213763	-4.610237	1.023657
I	-3.864182	0.616712	-0.304044

TS-12

B3LYP SCF energy: -3992.79227308 a.u.
B3LYP enthalpy: -3992.178049 a.u.
B3LYP free energy: -3992.296864 a.u.
M06 SCF energy in solution: -3995.43529112 a.u.
M06 enthalpy in solution: -3994.821067 a.u.
M06 free energy in solution: -3994.939882 a.u.
Imaginary frequency: -255.9212 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.352067	-1.334805	-0.412386
C	3.141184	-1.158435	-0.821390
O	2.746636	-0.572177	-1.843046
O	2.370050	-1.647775	0.095910
C	4.630878	-1.300144	-0.545842
H	5.176158	-1.409857	-1.486622
H	4.977826	-0.383864	-0.054588
H	4.836190	-2.145181	0.115347
C	-3.787443	-0.337694	-0.339944
C	-2.757185	-1.240690	0.048311
C	-2.943437	-2.045737	1.182570
C	-4.120239	-1.905505	1.913493
C	-5.115944	-0.985173	1.528715
C	-4.968084	-0.193328	0.392138
C	-2.099879	-0.141330	-1.811808
C	-1.663379	-1.073545	-0.886154
H	-2.176519	-2.758917	1.470172
H	-4.277258	-2.517762	2.796881
H	-6.021187	-0.897973	2.122861
H	-5.740953	0.508646	0.092952
H	-1.585239	0.272595	-2.667240
C	-4.095554	1.351913	-2.182392
H	-5.024005	0.959081	-2.613560
H	-4.343770	2.168519	-1.494908
H	-3.468155	1.753785	-2.979458
N	-3.362479	0.314677	-1.488885
C	2.336336	1.587564	0.721930
C	4.890650	2.365522	1.544258

C	2.965784	0.920627	1.779504
C	2.989888	2.637402	0.072533
C	4.267429	3.023471	0.483137
C	4.237940	1.313477	2.192182
H	2.472196	0.082823	2.260599
H	2.510643	3.145512	-0.757492
H	4.774101	3.837448	-0.027714
H	4.723734	0.791397	3.011563
H	5.884892	2.666472	1.862353
C	-0.499975	1.811757	1.644122
C	-2.065907	3.000668	3.631948
C	-0.168111	3.082366	2.133717
C	-1.605675	1.135237	2.164473
C	-2.390287	1.731139	3.153893
C	-0.951003	3.674254	3.123691
H	0.701793	3.603711	1.745619
H	-1.858844	0.148774	1.801477
H	-3.251494	1.195366	3.541958
H	-0.690001	4.659185	3.500957
H	-2.674339	3.464994	4.403201
C	0.111682	2.105969	-1.306993
C	-0.618963	3.476115	-3.631182
C	-0.905114	3.063380	-1.263752
C	0.767502	1.830561	-2.516199
C	0.401703	2.521241	-3.671938
C	-1.269673	3.747173	-2.426214
H	-1.420175	3.268352	-0.331292
H	1.539928	1.065750	-2.540666
H	0.911396	2.308118	-4.607485
H	-2.060932	4.491203	-2.388111
H	-0.903629	4.007945	-4.534993
As	0.555552	1.007258	0.228025
C	-1.033861	-2.987049	-1.668681
C	0.254145	-3.353078	-1.240013
H	-1.888519	-3.412664	-1.157281
H	-1.179809	-2.691858	-2.699722
H	1.093445	-3.318726	-1.927226
C	0.405285	-4.178220	-0.023094
O	-0.458916	-4.359326	0.821443
O	1.638367	-4.717271	0.047410
C	1.923190	-5.431426	1.255905
H	1.226876	-6.264023	1.388206
H	2.944232	-5.797052	1.145280
H	1.848079	-4.761492	2.116796

TS-12a

B3LYP SCF energy: -3992.78164618 a.u.
B3LYP enthalpy: -3992.168189 a.u.
B3LYP free energy: -3992.285726 a.u.
M06 SCF energy in solution: -3995.42800406 a.u.
M06 enthalpy in solution: -3994.814547 a.u.
M06 free energy in solution: -3994.932084 a.u.
Imaginary frequency: -313.3319 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.265226	-1.683078	-0.235327
C	-2.120715	-2.708312	-1.384736
O	-1.961943	-1.715314	-2.114755
O	-1.333878	-3.047583	-0.415377
C	-3.343965	-3.597927	-1.558307
H	-3.155435	-4.613063	-1.200891
H	-4.163254	-3.170955	-0.967695
H	-3.652113	-3.612311	-2.606636
C	2.759951	1.718893	-0.388049
C	2.133237	0.650486	-1.084630
C	1.815698	0.810403	-2.439617
C	2.139913	2.008093	-3.066476
C	2.761087	3.054803	-2.358464
C	3.072746	2.931149	-1.006760
C	2.477987	0.023473	1.060816
C	1.931127	-0.426763	-0.134178
H	1.296125	0.020489	-2.973850
H	1.886521	2.151750	-4.112026
H	2.989363	3.983794	-2.872809
H	3.537865	3.747212	-0.461697
H	2.572667	-0.492065	2.004549
C	3.408183	2.148641	2.013265
H	4.287735	2.723275	1.707535
H	2.614804	2.838848	2.324392
H	3.677436	1.520752	2.865187
N	2.964103	1.301606	0.925546
C	-0.812222	1.158256	1.912884
C	-0.193011	2.378302	4.361093
C	-0.066865	0.473540	2.878640
C	-1.276052	2.447774	2.198132
C	-0.960471	3.058615	3.412166
C	0.243351	1.078812	4.098029
H	0.262591	-0.539932	2.672066
H	-1.883308	2.978479	1.472058
H	-1.320941	4.062118	3.621107
H	0.820454	0.534831	4.841024
H	0.050357	2.854459	5.306899
C	-3.113666	-0.133627	0.559299
C	-5.794506	-0.665097	1.148008
C	-4.105092	0.784155	0.201017
C	-3.465713	-1.318576	1.215143
C	-4.804499	-1.581256	1.508773
C	-5.443006	0.516395	0.492596
H	-3.837031	1.699321	-0.316733
H	-2.700214	-2.047754	1.458475
H	-5.072994	-2.505882	2.012189
H	-6.210426	1.230427	0.206310
H	-6.836884	-0.873183	1.372921
C	-1.240471	1.617106	-1.085626
C	-1.208586	3.529827	-3.126864
C	-1.898123	1.360981	-2.297591
C	-0.545439	2.818104	-0.914249
C	-0.533575	3.772617	-1.930983
C	-1.883818	2.320899	-3.308941
H	-2.388541	0.405327	-2.448948
H	0.005826	3.006834	-0.000979

H	0.017701	4.697568	-1.790577
H	-2.397059	2.118448	-4.244996
H	-1.198163	4.273601	-3.919064
As	-1.227885	0.216501	0.254871
C	2.663251	-2.274535	-0.790593
C	1.618699	-3.227126	-0.802153
H	1.566601	-3.948149	0.009353
H	2.997848	-1.842255	-1.727032
H	1.192225	-3.525617	-1.755866
C	3.714695	-2.358090	0.269216
O	3.584836	-2.898317	1.348780
O	4.851149	-1.758514	-0.144249
C	5.901794	-1.714541	0.829035
H	6.747356	-1.243893	0.327432
H	5.590376	-1.120200	1.693633
H	6.160741	-2.721464	1.165581

TS-12b

B3LYP SCF energy: -3992.78490365 a.u.
B3LYP enthalpy: -3992.170465 a.u.
B3LYP free energy: -3992.288318 a.u.
M06 SCF energy in solution: -3995.43225562 a.u.
M06 enthalpy in solution: -3994.817817 a.u.
M06 free energy in solution: -3994.935670 a.u.
Imaginary frequency: -158.2703 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.856868	-0.073624	-0.734480
C	-1.216363	1.869395	1.279460
O	-0.866016	0.918538	1.992437
O	-1.282533	1.842128	-0.014808
C	-1.548545	3.218676	1.897233
H	-1.953765	3.076607	2.901648
H	-0.622076	3.799498	1.975647
H	-2.252738	3.777388	1.276468
C	-5.077363	0.064171	-0.306369
C	-3.807887	-0.479722	0.044725
C	-3.671435	-1.184309	1.249856
C	-4.785737	-1.325990	2.069287
C	-6.032351	-0.774708	1.709877
C	-6.197468	-0.072608	0.519233
C	-3.626422	0.560890	-1.953289
C	-2.900439	-0.136084	-1.019191
H	-2.709808	-1.604719	1.524849
H	-4.695592	-1.866319	3.007289
H	-6.882224	-0.898332	2.375469
H	-7.159256	0.353099	0.247353
H	-3.316421	1.001877	-2.890805
C	-5.994999	1.408545	-2.219329
H	-6.863878	0.761152	-2.388135
H	-6.319434	2.284135	-1.643215
H	-5.620933	1.747844	-3.187829
N	-4.945256	0.690660	-1.533784
C	2.239970	-0.795715	1.331882

C	3.217614	-2.285024	3.484503
C	1.401895	-1.087419	2.415763
C	3.564178	-1.247901	1.326670
C	4.049819	-1.994633	2.401078
C	1.897630	-1.828865	3.490227
H	0.385098	-0.710812	2.417739
H	4.213881	-1.022158	0.487796
H	5.078915	-2.343429	2.393468
H	1.246831	-2.049772	4.331420
H	3.597825	-2.864089	4.321631
C	1.873913	2.094443	0.492374
C	2.355247	4.727650	1.297914
C	2.610514	2.348041	1.651996
C	1.369161	3.162343	-0.259888
C	1.618017	4.475606	0.138608
C	2.846473	3.663152	2.055412
H	2.990431	1.523330	2.245038
H	0.762892	2.966935	-1.136994
H	1.222180	5.299963	-0.447606
H	3.414018	3.854198	2.961782
H	2.539693	5.750791	1.613322
C	2.882701	0.079856	-1.502157
C	4.762707	-0.252990	-3.558409
C	3.613412	1.174309	-1.976994
C	3.106159	-1.187259	-2.061385
C	4.043546	-1.350724	-3.081168
C	4.545607	1.008026	-3.003231
H	3.459308	2.157916	-1.547779
H	2.567296	-2.048907	-1.683342
H	4.212350	-2.338410	-3.501596
H	5.105773	1.866706	-3.362925
H	5.489899	-0.381083	-4.355259
As	1.527503	0.286331	-0.112410
C	-1.779715	-1.896750	-1.883343
C	-0.426665	-2.050627	-1.544754
H	-2.518503	-2.450473	-1.318378
H	-2.049773	-1.600728	-2.888303
H	0.343106	-1.893568	-2.293197
C	-0.086862	-2.930141	-0.397770
O	-0.853968	-3.288606	0.473415
O	1.210131	-3.314510	-0.453952
C	1.651329	-4.169971	0.614445
H	1.150027	-5.139240	0.547916
H	2.725816	-4.277960	0.473204
H	1.437413	-3.710663	1.579095

TS-12c

B3LYP SCF energy: -3992.77165142 a.u.
B3LYP enthalpy: -3992.157977 a.u.
B3LYP free energy: -3992.278216 a.u.
M06 SCF energy in solution: -3995.42301038 a.u.
M06 enthalpy in solution: -3994.809336 a.u.
M06 free energy in solution: -3994.929575 a.u.
Imaginary frequency: -200.9964 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.501883	0.069857	-0.139828
C	-0.746379	-2.730616	0.128454
O	-0.731461	-2.624158	-1.107621
O	-0.581918	-1.751764	0.962026
C	-1.017610	-4.077834	0.783963
H	-0.745706	-4.889320	0.105289
H	-0.478749	-4.174102	1.730370
H	-2.091105	-4.149222	0.996895
C	-4.680453	-0.699158	0.412921
C	-3.559327	-0.737944	-0.464098
C	-3.604110	-1.574186	-1.588327
C	-4.750229	-2.328314	-1.817123
C	-5.849419	-2.274174	-0.937854
C	-5.828224	-1.464796	0.194884
C	-3.121053	0.699475	1.228902
C	-2.568100	0.155869	0.084713
H	-2.734603	-1.663178	-2.229351
H	-4.794011	-2.985775	-2.680595
H	-6.725995	-2.883319	-1.139776
H	-6.669855	-1.436361	0.880954
H	-2.718215	1.444339	1.900049
C	-5.248697	0.474860	2.564264
H	-6.224831	0.834071	2.217678
H	-5.403994	-0.416537	3.183818
H	-4.786381	1.251478	3.177170
N	-4.385364	0.186260	1.440752
C	2.930452	-1.417858	-0.807041
C	4.354906	-3.491229	-2.015372
C	2.285448	-2.271592	-1.706432
C	4.284669	-1.607701	-0.502480
C	4.995564	-2.641434	-1.108499
C	3.003719	-3.308492	-2.308221
H	1.222216	-2.159416	-1.894147
H	4.779806	-0.956289	0.211340
H	6.045518	-2.787935	-0.870458
H	2.497726	-3.977551	-2.998315
H	4.909356	-4.299702	-2.484103
C	2.555815	0.017337	1.835680
C	3.403986	-0.129070	4.493896
C	3.710668	0.695316	2.241732
C	1.820328	-0.733041	2.762821
C	2.250183	-0.803371	4.088624
C	4.133244	0.620999	3.569756
H	4.273685	1.289304	1.528907
H	0.922249	-1.253069	2.440075
H	1.678738	-1.385036	4.806728
H	5.029677	1.150300	3.881088
H	3.732500	-0.184794	5.528108
C	2.857204	1.605075	-0.714684
C	4.027980	3.926225	-1.757782
C	2.593635	2.853939	-0.134483
C	3.705655	1.528134	-1.822637
C	4.287215	2.686956	-2.343066
C	3.180117	4.008335	-0.649850
H	1.933756	2.921769	0.726648

H	3.916502	0.565761	-2.277189
H	4.945433	2.617605	-3.204628
H	2.973069	4.970312	-0.189750
H	4.482318	4.825998	-2.162700
As	1.943502	0.044280	-0.006023
C	-1.878089	1.667642	-1.355481
C	-0.476730	1.798450	-1.399032
H	-0.027165	2.633031	-0.870850
H	-2.401425	1.138481	-2.143029
H	0.055554	1.438716	-2.275579
C	-2.677454	2.710495	-0.642713
O	-2.233277	3.497566	0.169333
O	-3.957612	2.697309	-1.065416
C	-4.832022	3.599462	-0.378196
H	-5.807192	3.478954	-0.849853
H	-4.884300	3.335161	0.682357
H	-4.479194	4.629697	-0.471607

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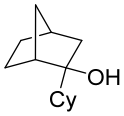
9. NMR spectra



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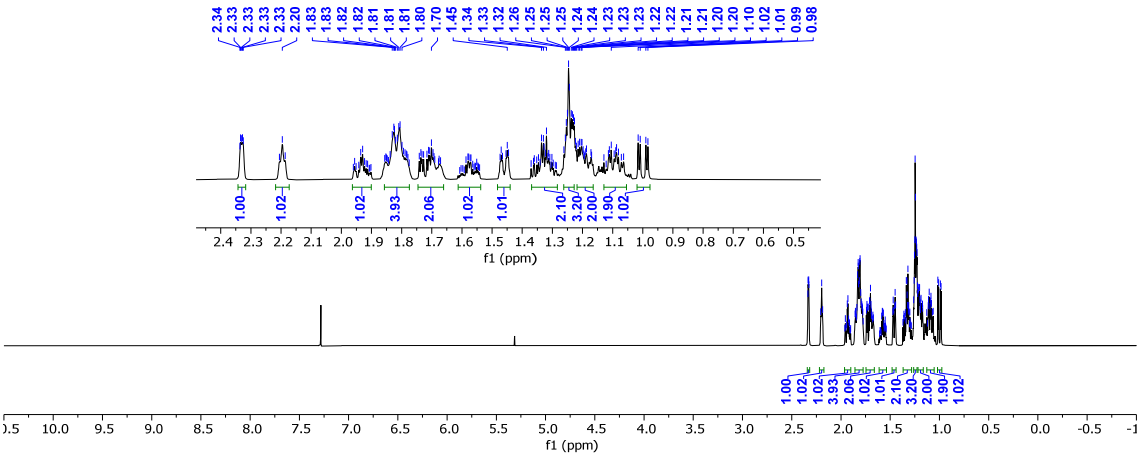

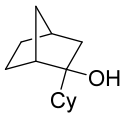

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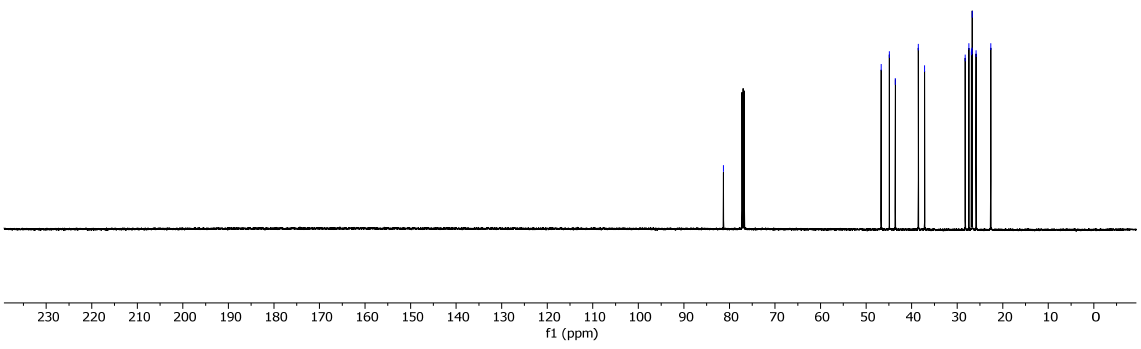

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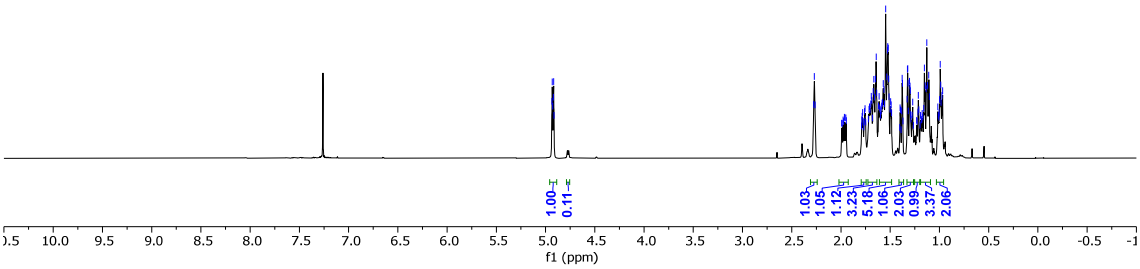

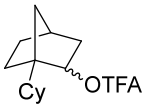

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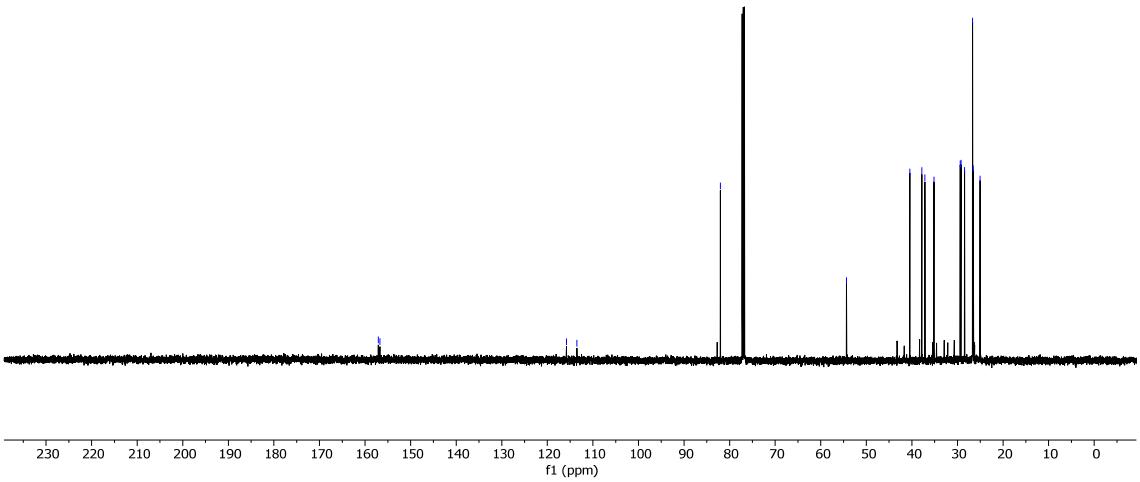
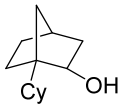
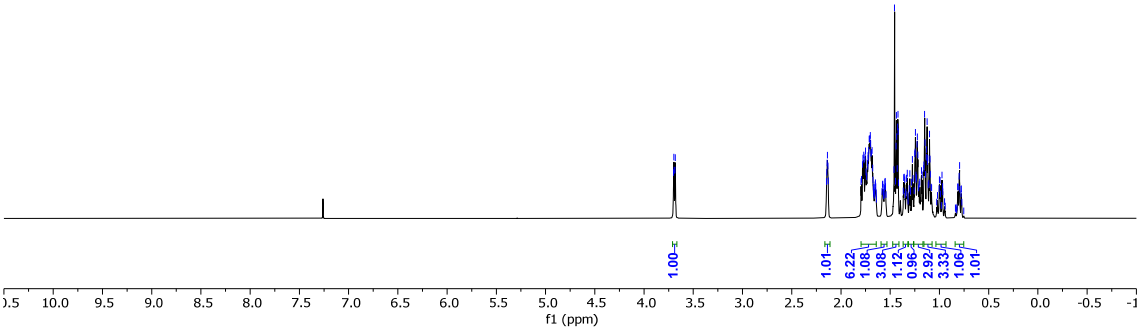



Cy
OH

S4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3.08
1.12
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2.92
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1.06
1.01
f1 (ppm)


74.82
54.69
42.73
36.72
36.57
34.94
29.82
29.08
28.58
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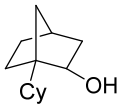
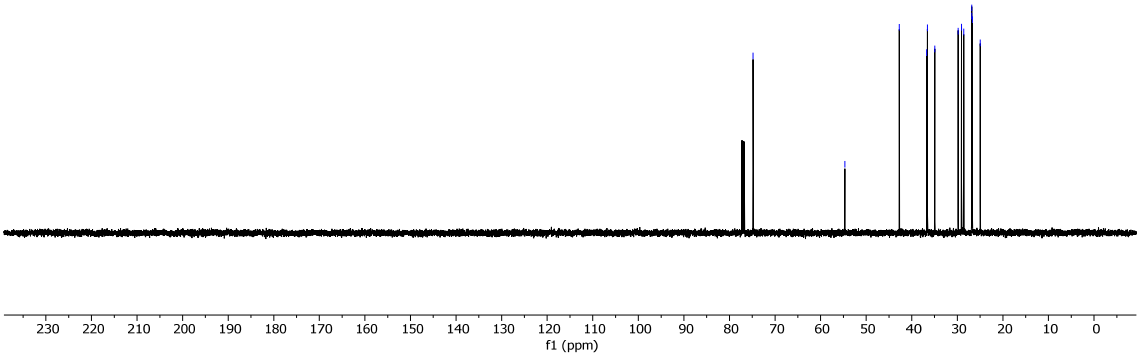
26.83
26.71
24.97


Cy
OH

S4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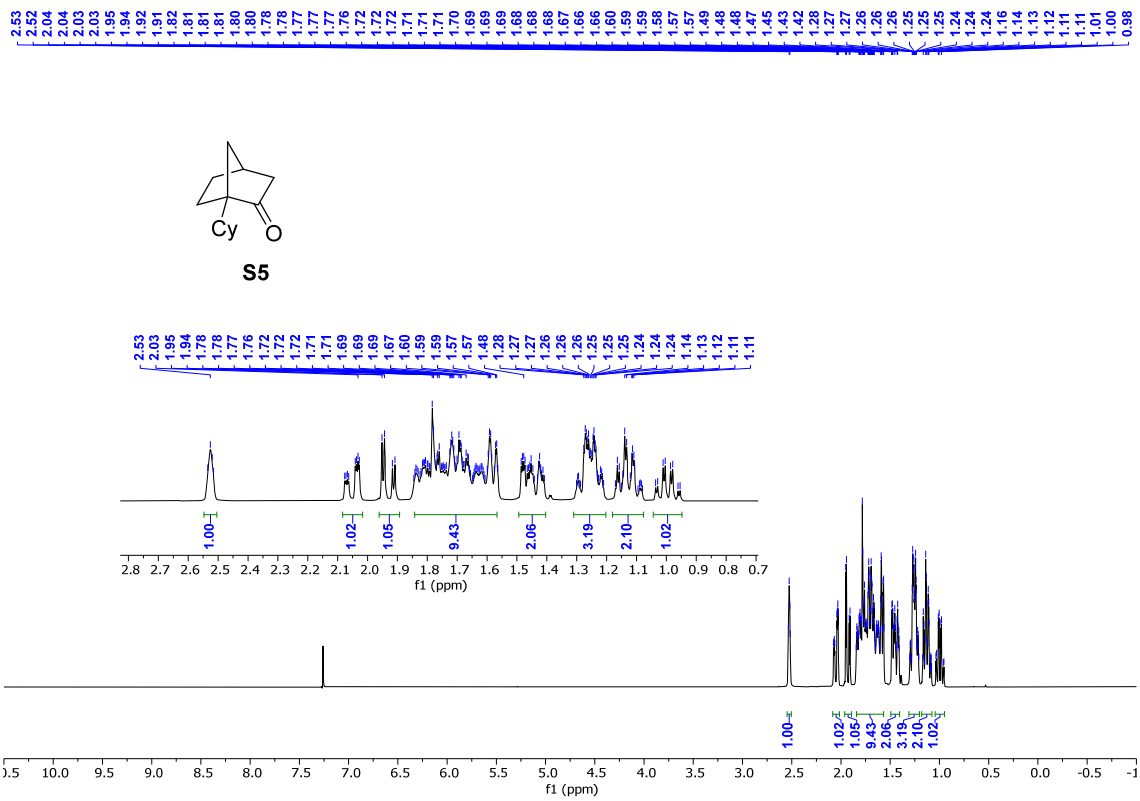
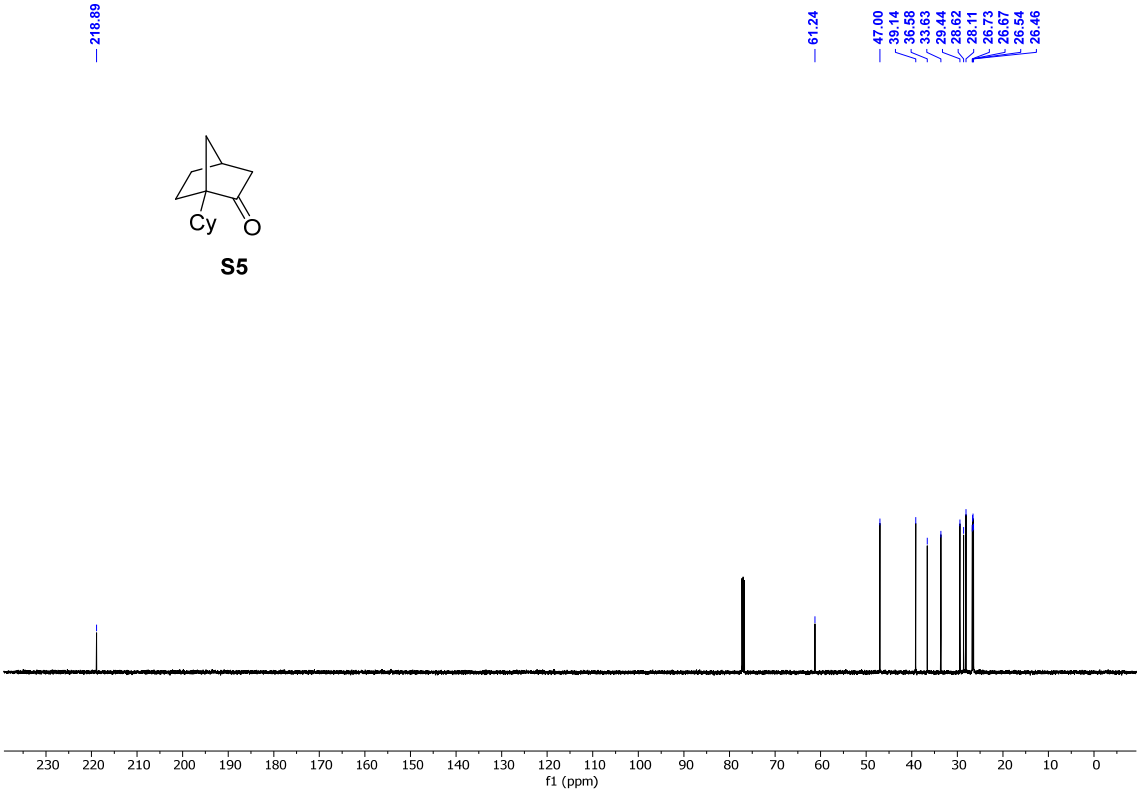

Cy
O
S5
f1 (ppm)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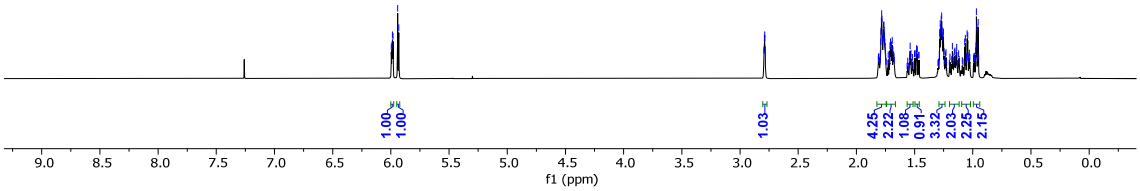
26.73
26.67
26.54
26.46
Cy
O
S5
f1 (ppm)


Cy

N2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3.32
2.03
2.25
2.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.85
135.27
58.44
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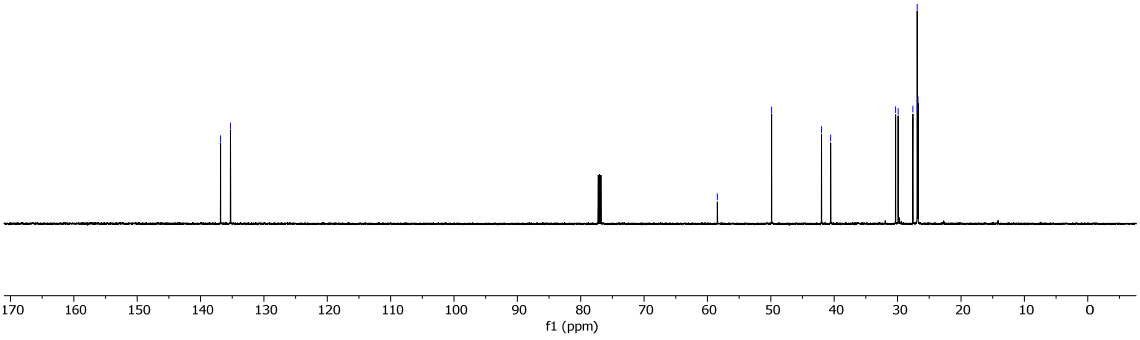
42.00
40.56
30.32
29.90
27.59
26.91
26.87
26.78


Cy

N2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110
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70
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50
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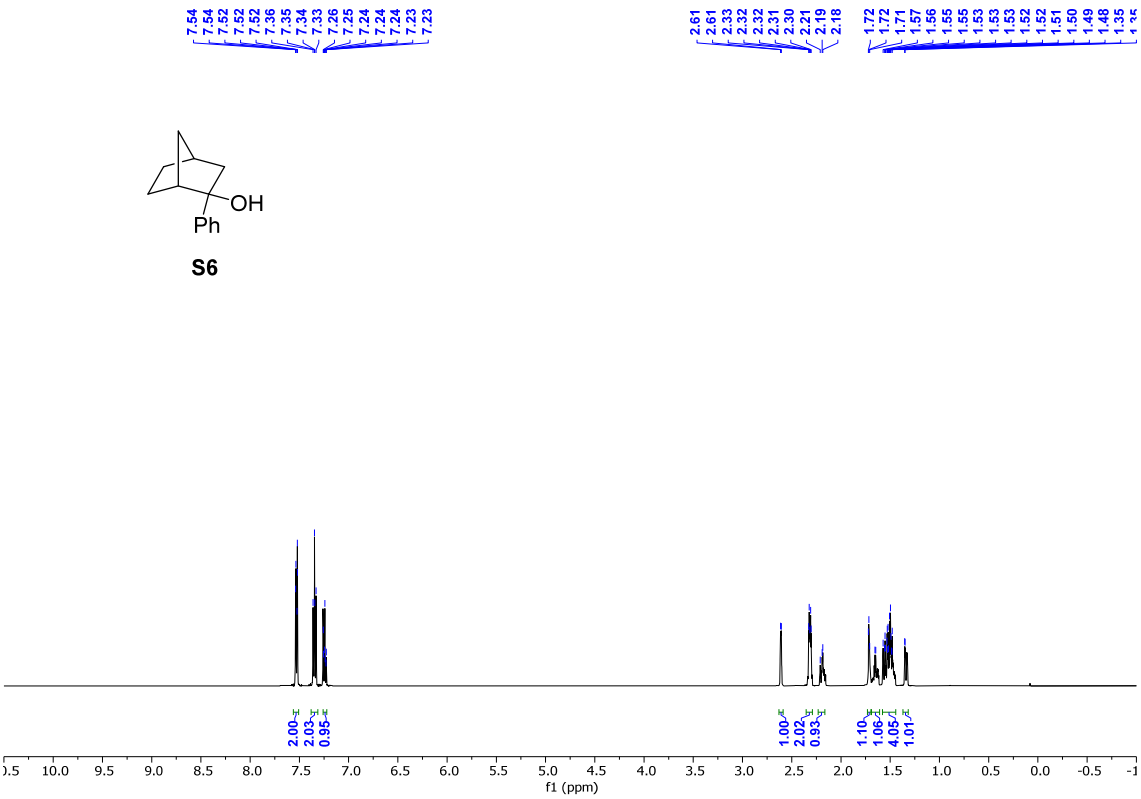
30
20
10
0
f1 (ppm)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7.34
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7.24
7.24
7.23
7.23
2.61
2.61
2.33
2.32
2.32
2.31
2.30
2.21
2.19
2.18
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1.72
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1.53
1.53
1.52
1.52
1.51
1.50
1.49
1.48
1.35
OH
Ph
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1.06
4.05
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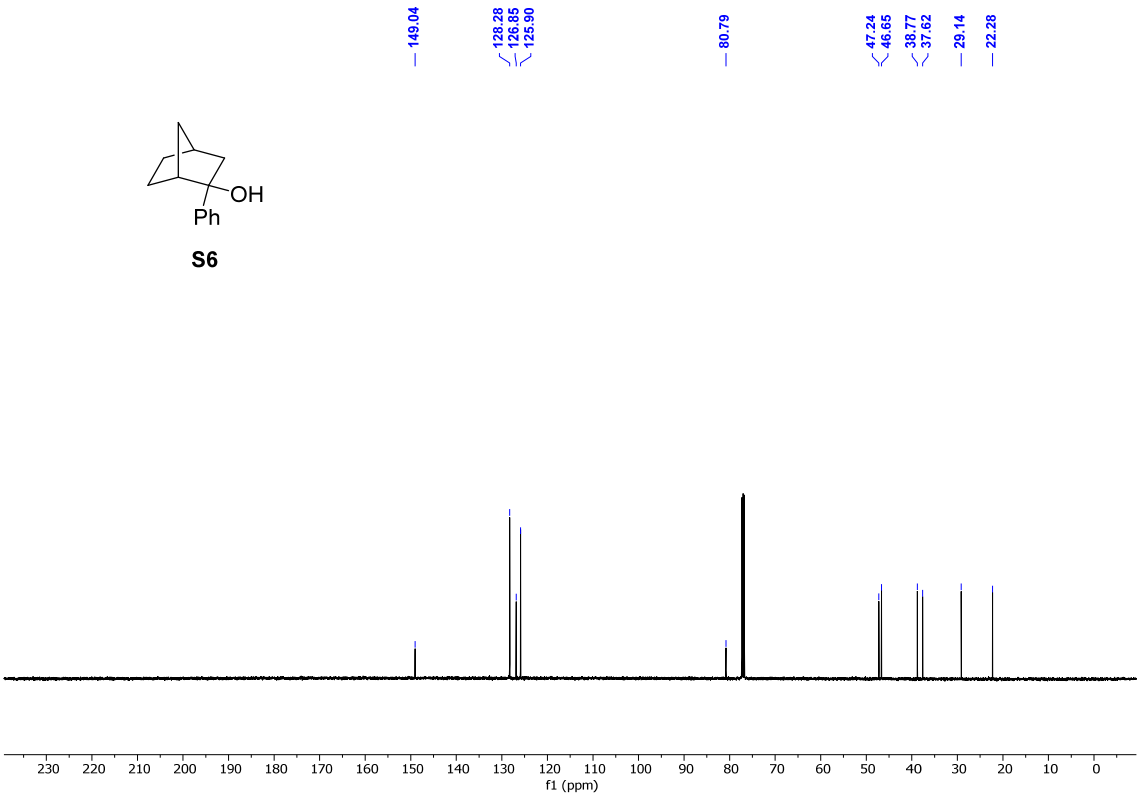
f1 (ppm)

S6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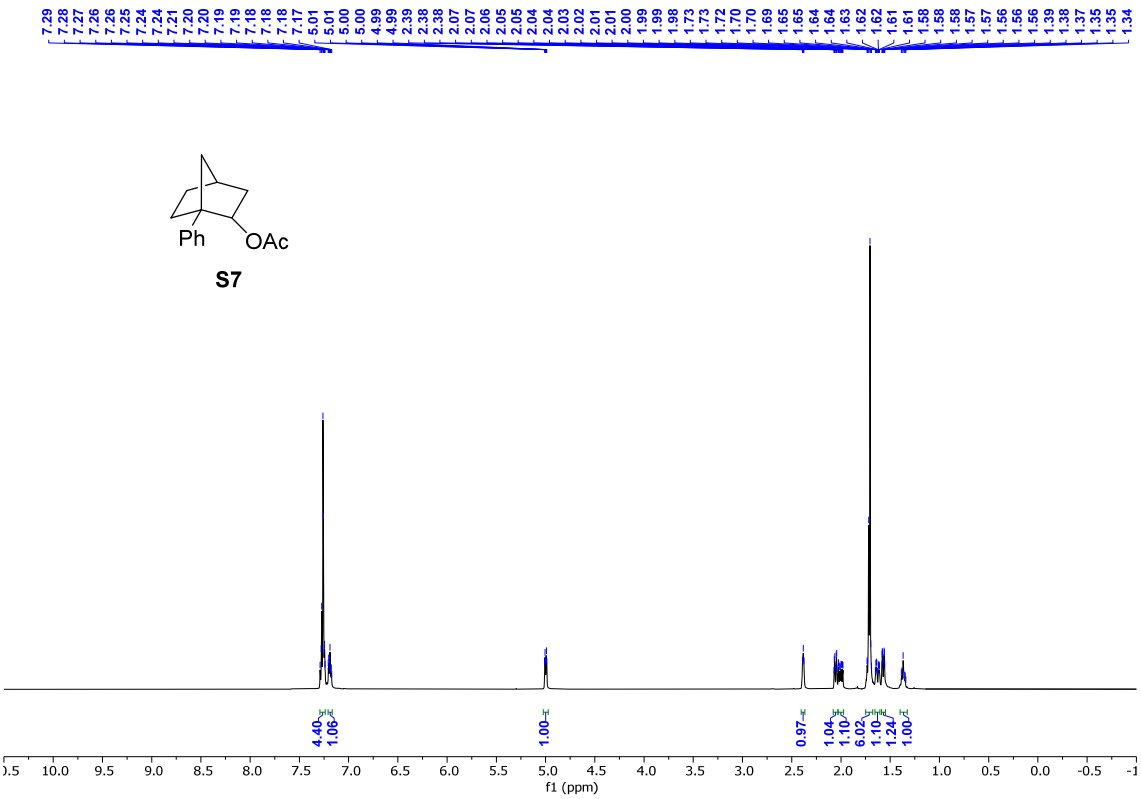
OH
Ph
f1 (ppm)

S6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Ph
OAc
S7
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1.00
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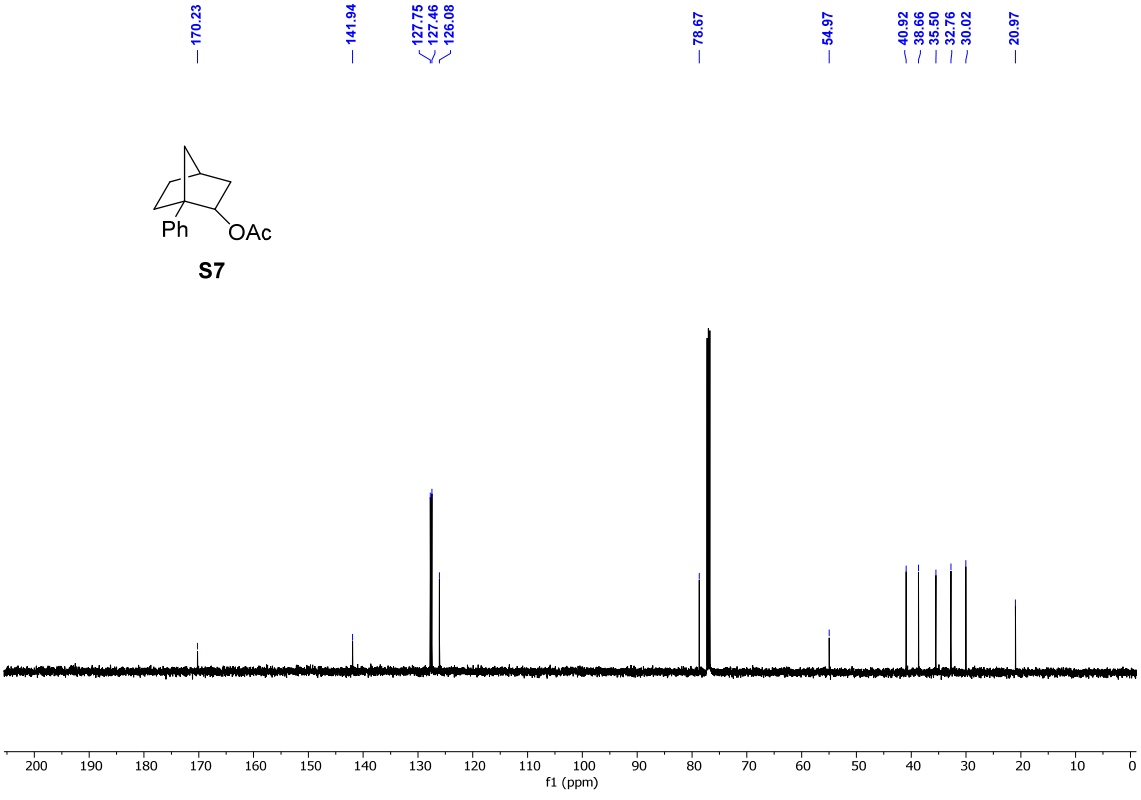
1.04
1.10
6.02
1.10
1.24
1.00
f1 (ppm)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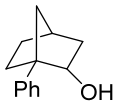
54.97
40.92
38.66
35.50
32.76
30.02
20.97
Ph
OAc
S7
f1 (ppm)


7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.31 7.31 7.30 7.30 7.30 7.29 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.24 7.23 3.83 3.82 3.81 3.81 2.35 2.35 2.34 2.34 2.34 2.05 2.05 2.04 2.03 1.85 1.85 1.84 1.84 1.70 1.70 1.69 1.69 1.69 1.69 1.68 1.68 1.68 1.68 1.67 1.63 1.62 1.62 1.62 1.61 1.61 1.60 1.60 1.60 1.58 1.45 1.45 1.45 1.44 1.44 1.43 1.32 1.32 1.29 1.29


Ph
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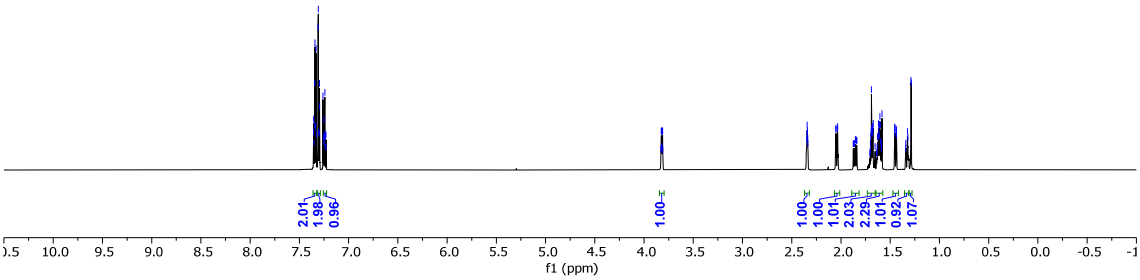
S8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1.00
1.00
1.00
1.01
2.03
2.29
1.01
0.92
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


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127.65
126.47
77.52
56.53
41.30
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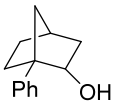
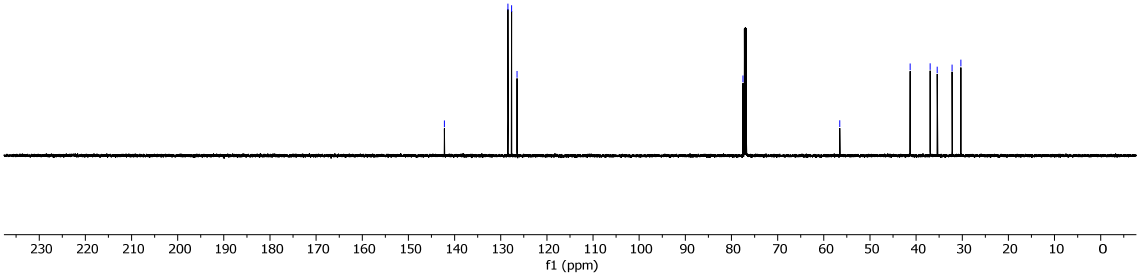
35.43
32.20
30.31


Ph
OH

S8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f1 (ppm)


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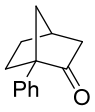
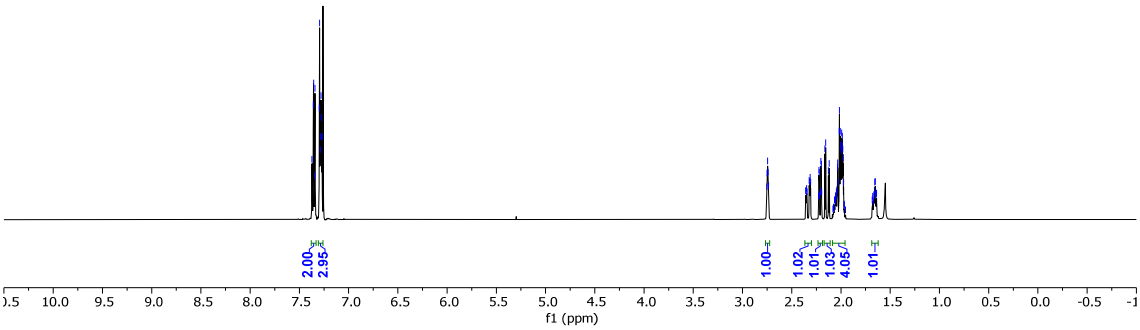

Ph
O

S9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1.02
1.01
1.03
4.05
1.01
f1 (ppm)


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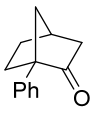
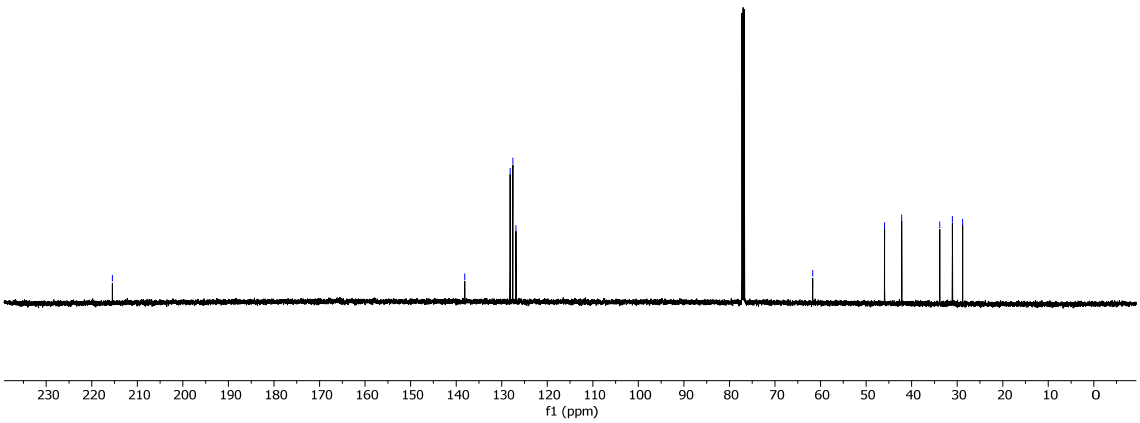
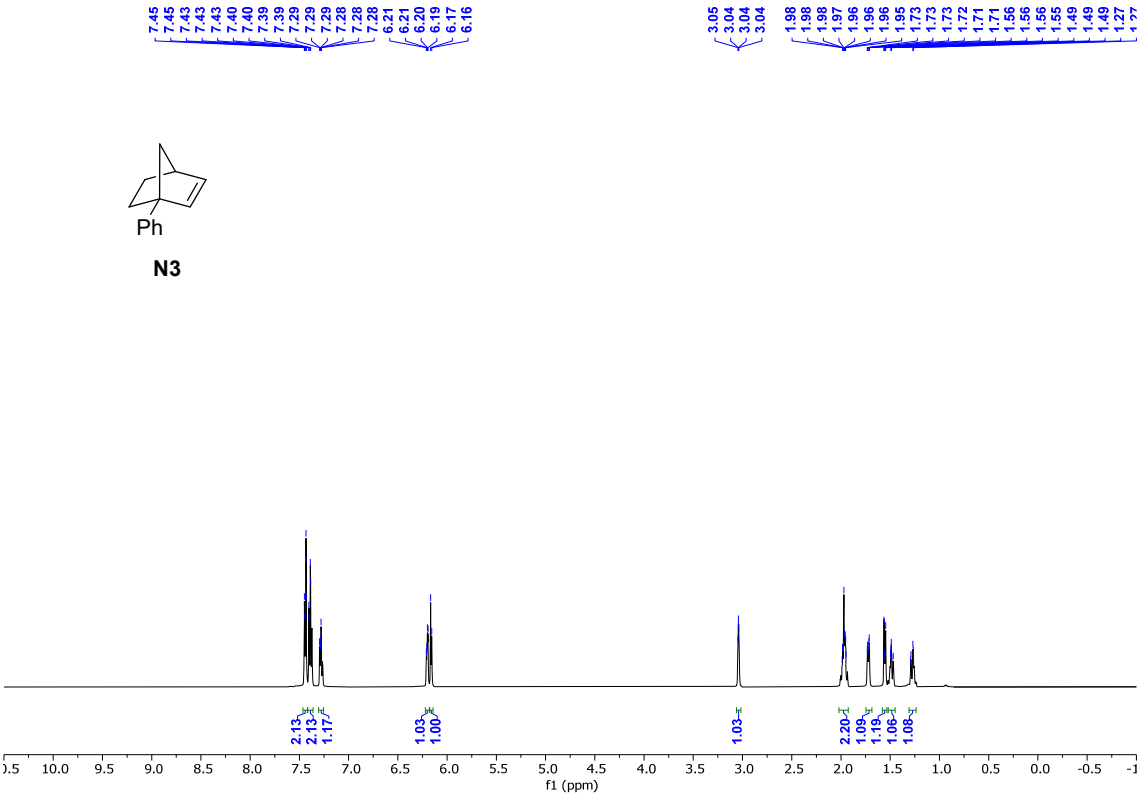
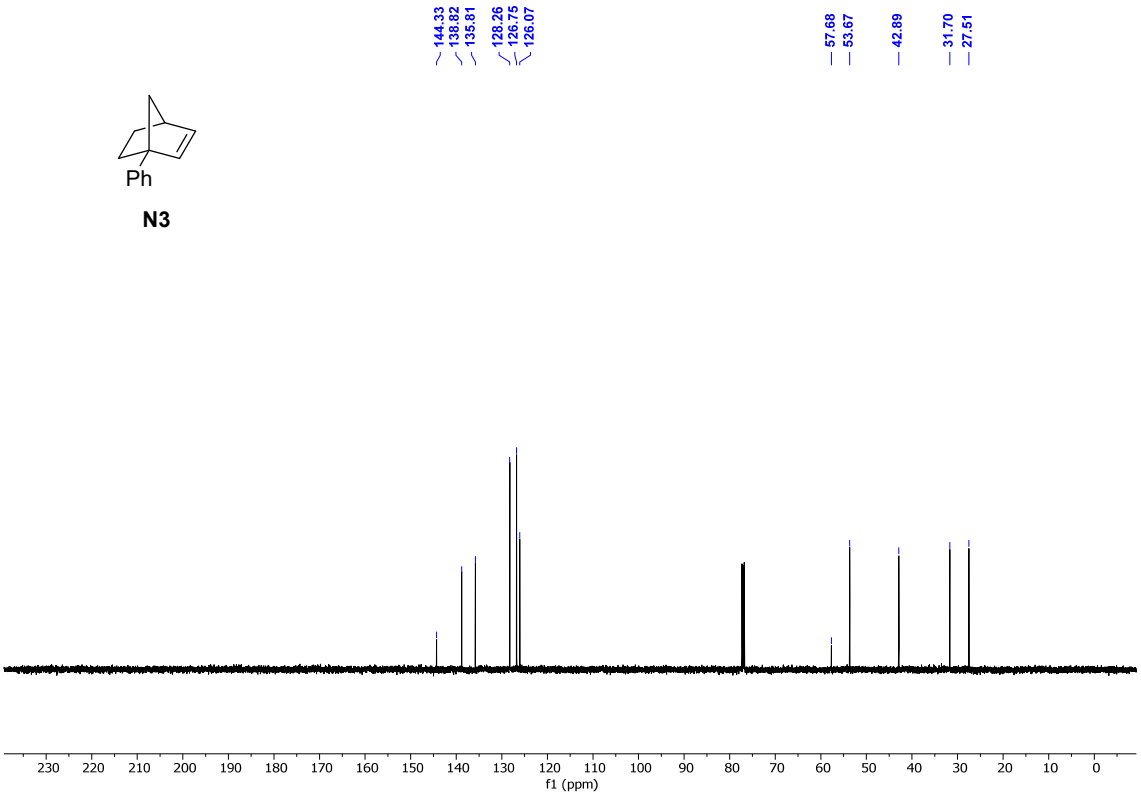
138.13
128.16
127.57
126.88
61.73
45.95
42.19
33.83
31.05
28.82


Ph
O

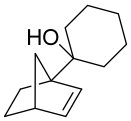
S9


f1 (ppm)

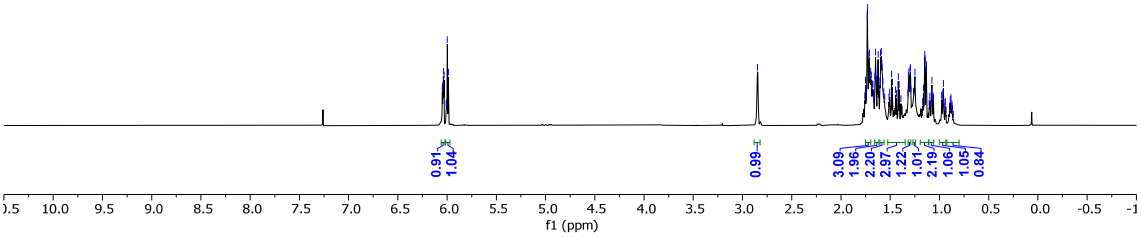

7.45
7.45
7.43
7.43
7.43
7.40
7.40
7.39
7.39
7.29
7.29
7.29
7.28
7.28
7.28
6.21
6.21
6.20
6.19
6.17
6.16
3.05
3.04
3.04
3.04
3.04
1.98
1.98
1.98
1.97
1.96
1.96
1.96
1.95
1.73
1.73
1.73
1.72
1.71
1.71
1.56
1.56
1.56
1.55
1.49
1.49
1.49
1.27
Ph
N3
2.13
2.13
1.17
1.03
1.00
1.03
2.20
1.05
1.19
1.06
1.08
f1 (ppm)


144.33
138.82
135.81
128.26
126.75
126.07
57.68
53.67
42.89
31.70
27.51
Ph
N3
f1 (ppm)

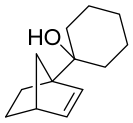

6.05
6.04
6.04
6.03
6.00
5.99
2.85
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.68
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.62
1.62
1.60
1.60
1.59
1.58
1.58
1.57
1.57
1.56
1.51
1.51
1.49
1.48
1.44
1.44
1.42
1.41
1.39
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.26
1.25
1.25
1.16
1.15
1.15
1.14
1.13
1.10
1.08
1.08
1.07
1.06
1.06
0.98
0.97
0.96
0.96
0.89
0.88


HO

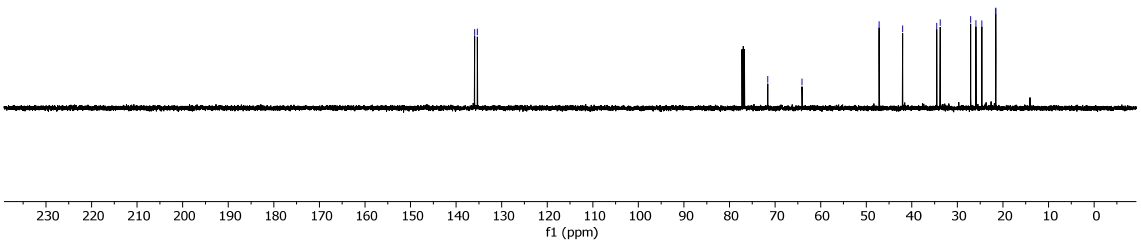
N4

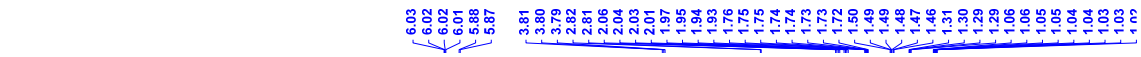

0.91
1.04
0.99
3.09
1.96
2.20
2.97
1.22
1.01
2.19
1.06
1.05
0.84
f1 (ppm)

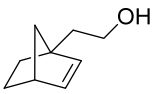

135.94
135.34
71.60
64.09
47.16
42.01
34.53
33.78
27.08
25.93
24.64
21.59
21.57


HO

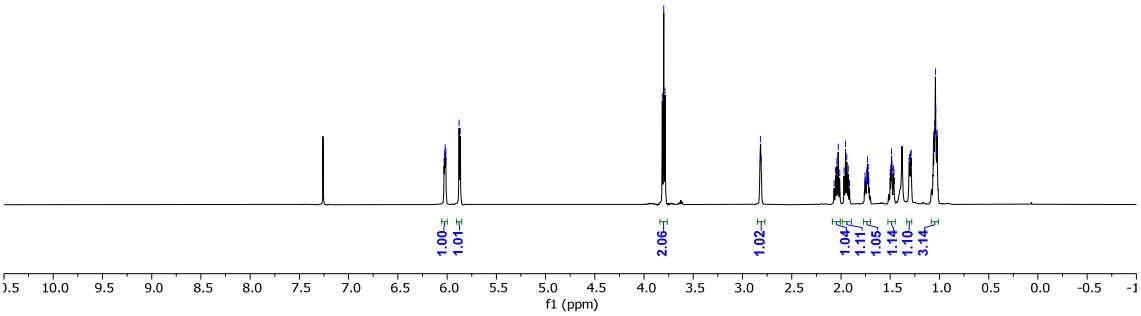
N4


f1 (ppm)

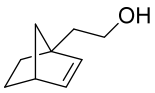

6.03
6.02
6.02
6.01
5.88
5.87
3.81
3.80
3.79
2.82
2.81
2.06
2.04
2.03
2.01
1.97
1.95
1.94
1.93
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.50
1.49
1.49
1.48
1.47
1.46
1.31
1.30
1.29
1.29
1.06
1.06
1.05
1.05
1.04
1.04
1.03
1.03


OH

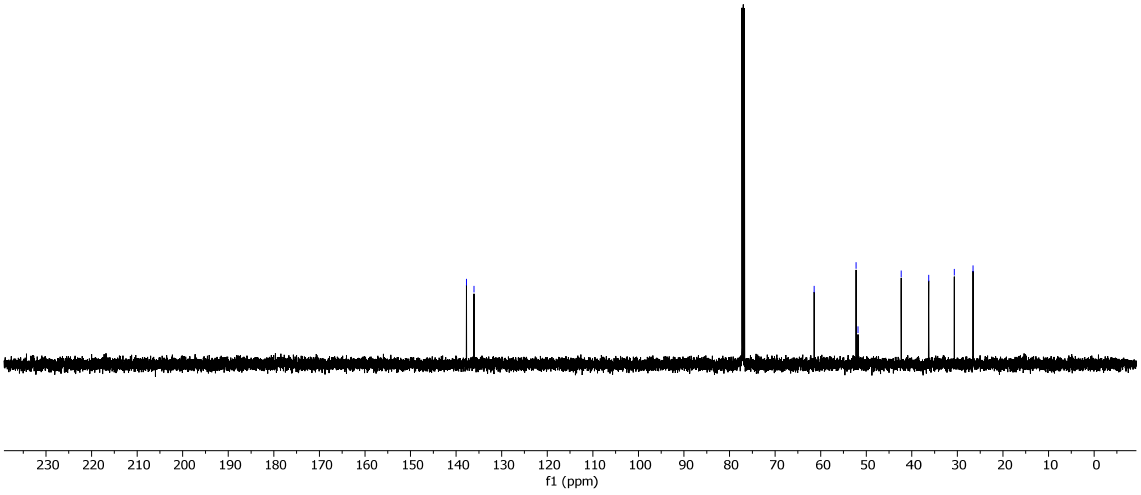
S18

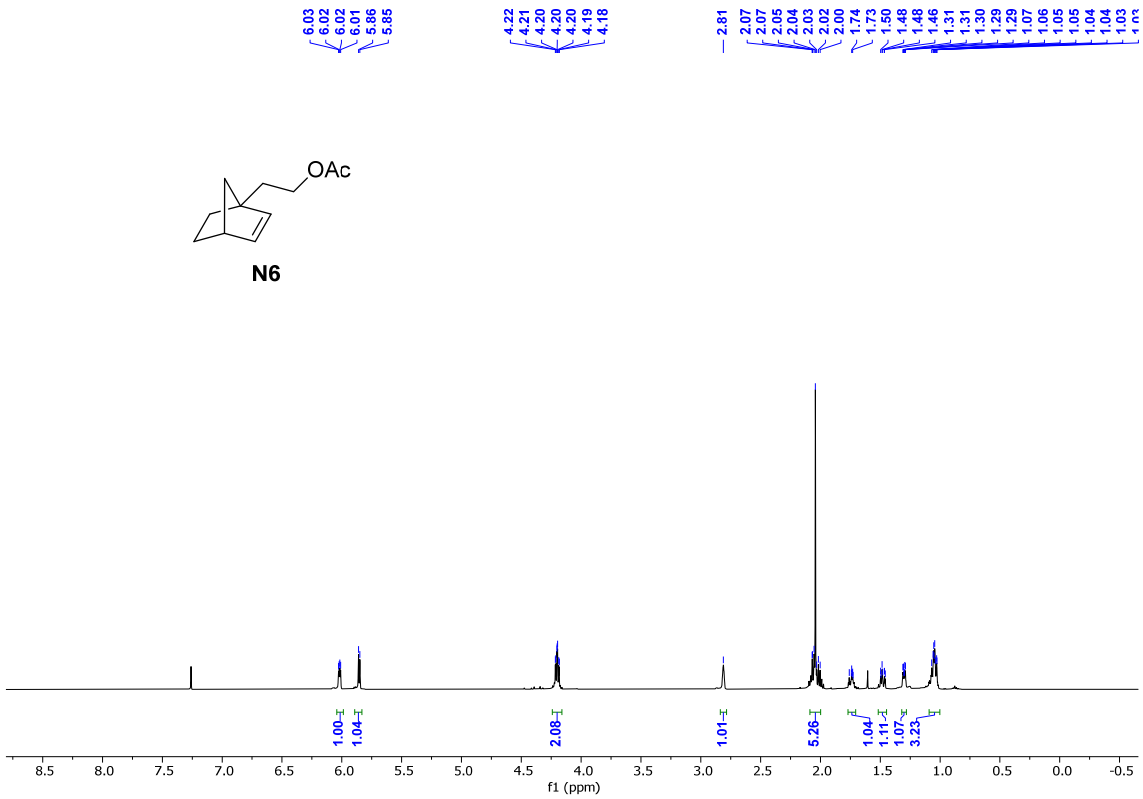

1.00
1.01
2.06
1.02
1.04
1.11
1.05
1.14
1.10
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

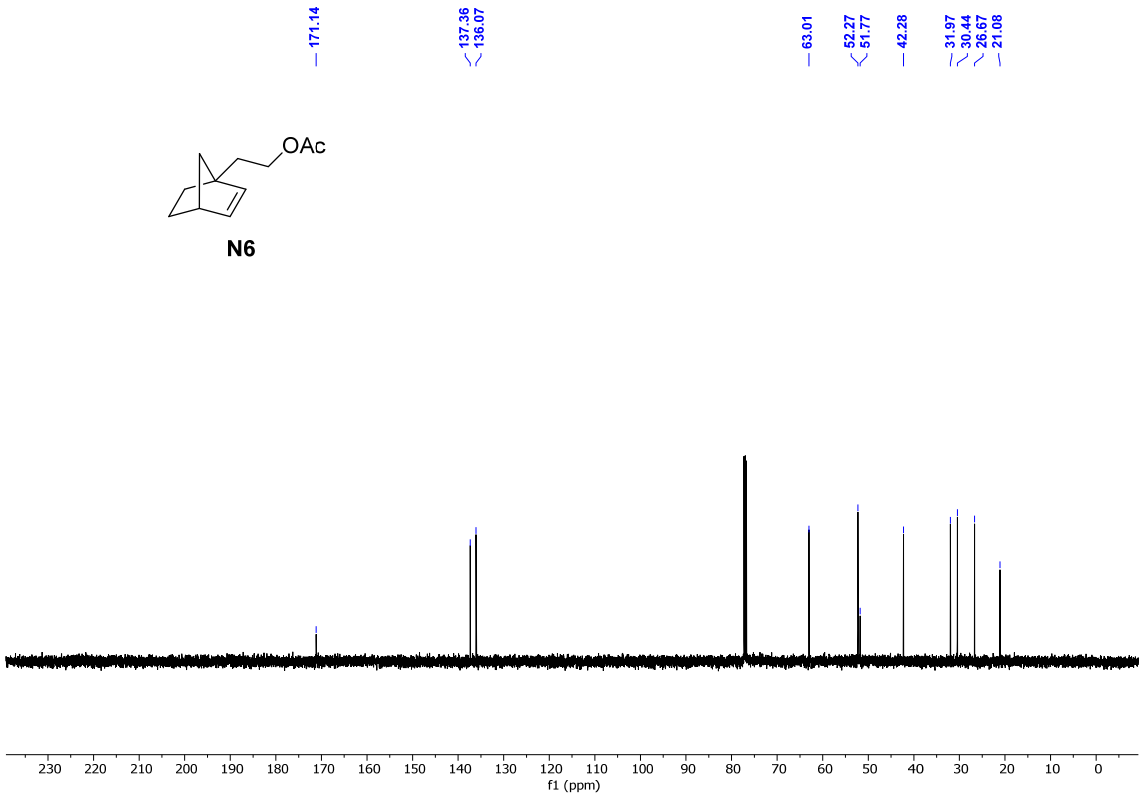

137.74
136.07
61.45
52.22
51.82
42.32
36.30
30.68
26.56

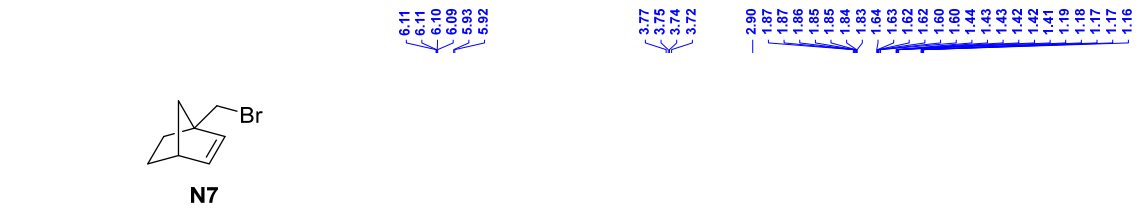

OH

S18


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

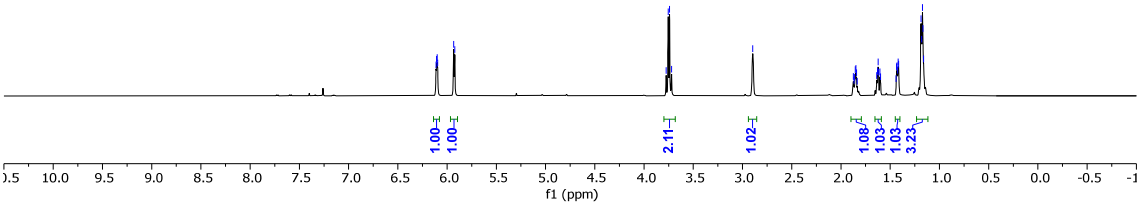

6.03
6.02
6.02
6.01
5.86
5.85
4.22
4.21
4.20
4.20
4.20
4.19
4.18
2.81
2.07
2.07
2.05
2.04
2.03
2.02
2.00
1.74
1.73
1.50
1.48
1.48
1.46
1.31
1.31
1.30
1.29
1.29
1.07
1.06
1.05
1.05
1.04
1.04
1.03
OAc
N6
1.00
1.04
2.08
1.01
5.26
1.04
1.11
1.07
3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.14
137.36
136.07
63.01
52.27
51.77
42.28
31.97
30.44
26.67
21.08
OAc
N6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

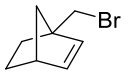

6.11
6.11
6.10
6.09
5.93
5.92
3.77
3.75
3.74
3.72
2.90
1.87
1.87
1.86
1.85
1.85
1.84
1.83
1.64
1.63
1.62
1.62
1.60
1.60
1.44
1.43
1.43
1.42
1.42
1.41
1.19
1.18
1.17
1.17
1.16

Br

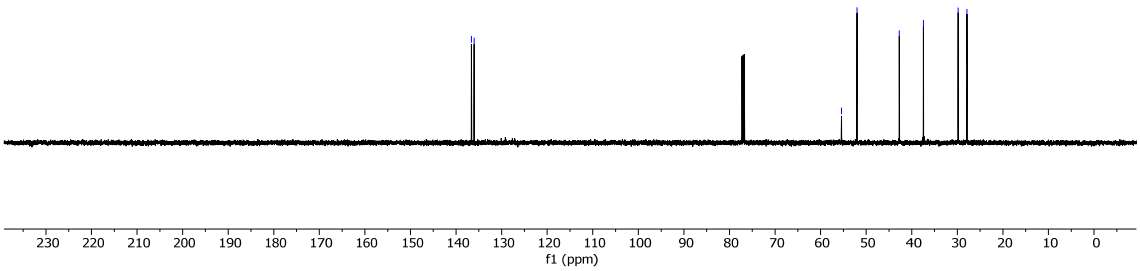
N7

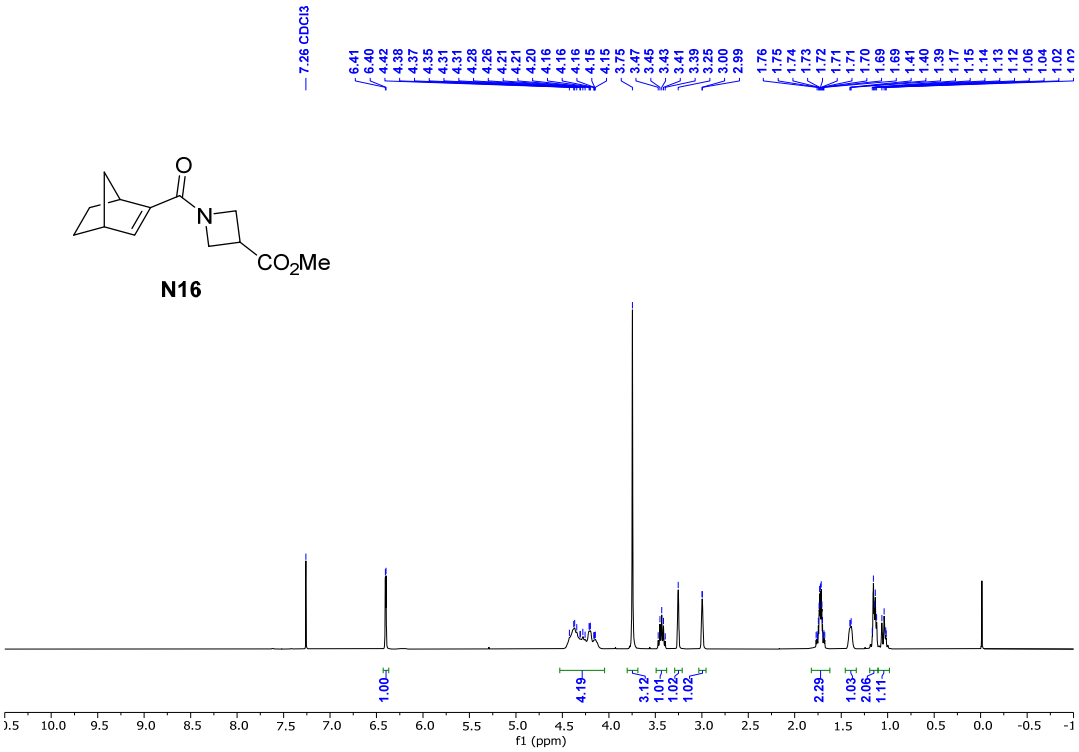

1.00
1.00
2.11
1.02
1.08
1.03
1.03
3.23
f1 (ppm)

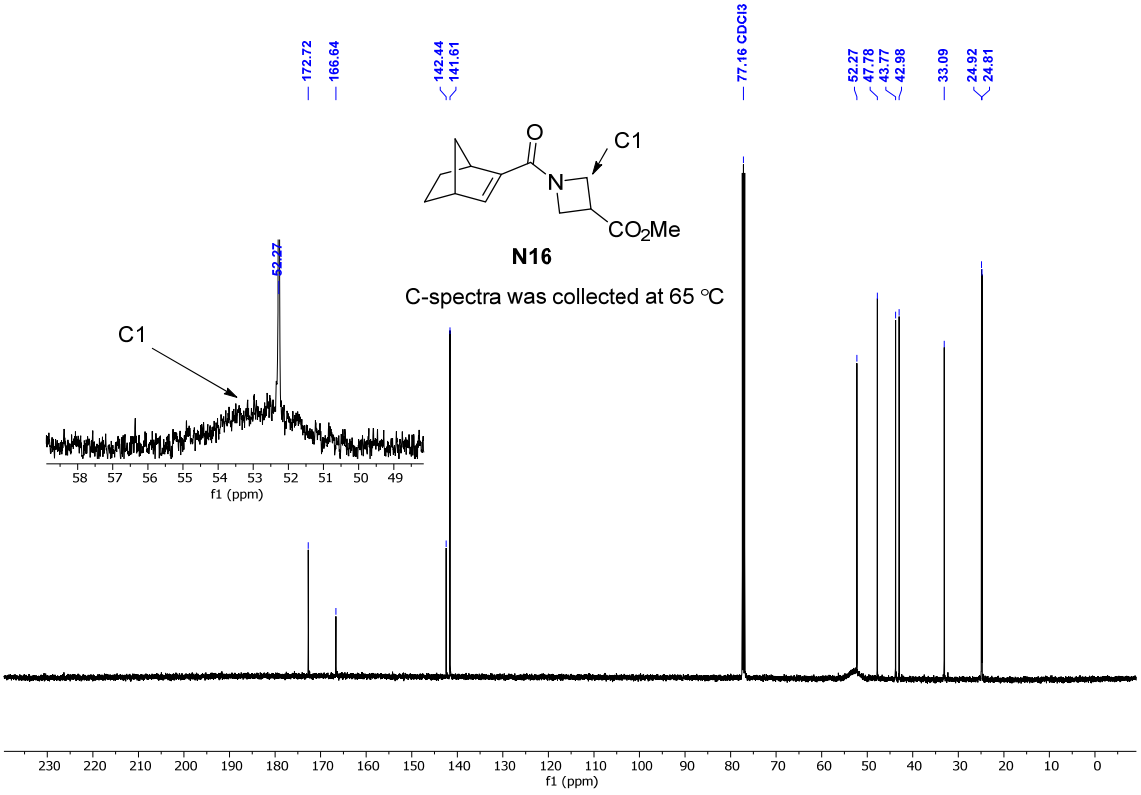

136.63
136.02
55.42
52.02
42.73
37.45
29.81
27.88

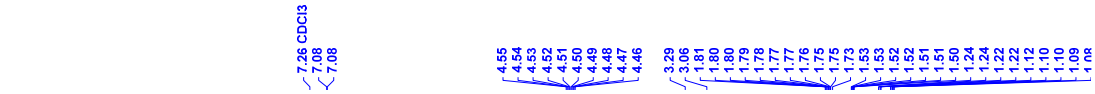

Br

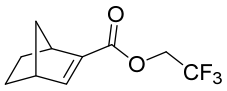
N7


f1 (ppm)

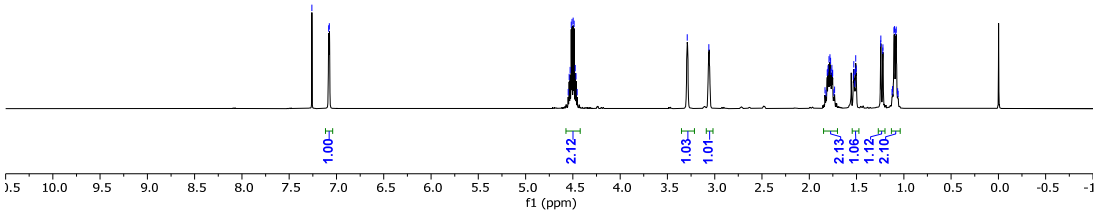

7.26 CDCl3
6.41
6.40
4.42
4.38
4.37
4.35
4.31
4.31
4.28
4.26
4.21
4.21
4.20
4.16
4.16
4.16
4.15
4.15
3.75
3.47
3.45
3.43
3.41
3.39
3.25
3.00
2.99
1.76
1.75
1.74
1.73
1.72
1.71
1.71
1.70
1.69
1.69
1.41
1.40
1.39
1.17
1.15
1.14
1.13
1.12
1.06
1.04
1.02
O
N
CO2Me
N16
1.00
4.19
3.12
1.01
1.02
1.02
2.29
1.03
2.06
1.11
f1 (ppm)

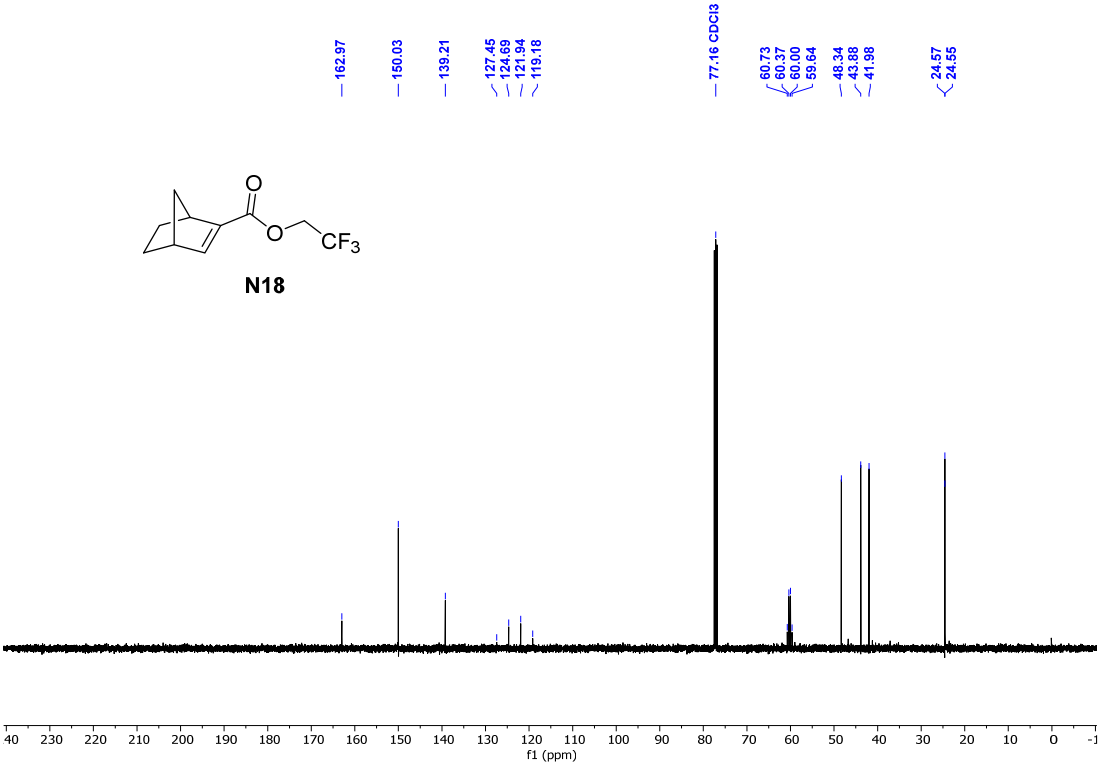

172.72
166.64
142.44
141.61
77.16 CDCl3
52.27
47.78
43.77
42.98
33.09
24.92
24.81
O
C1
N
CO2Me
N16
C-spectra was collected at 65 °C
C1
52.27
f1 (ppm)


7.26 CDCl3
7.08
7.08
4.55
4.54
4.53
4.52
4.51
4.50
4.49
4.48
4.47
4.46
3.29
3.06
1.81
1.80
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.73
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.24
1.24
1.22
1.22
1.12
1.10
1.10
1.09


O
O
CF3

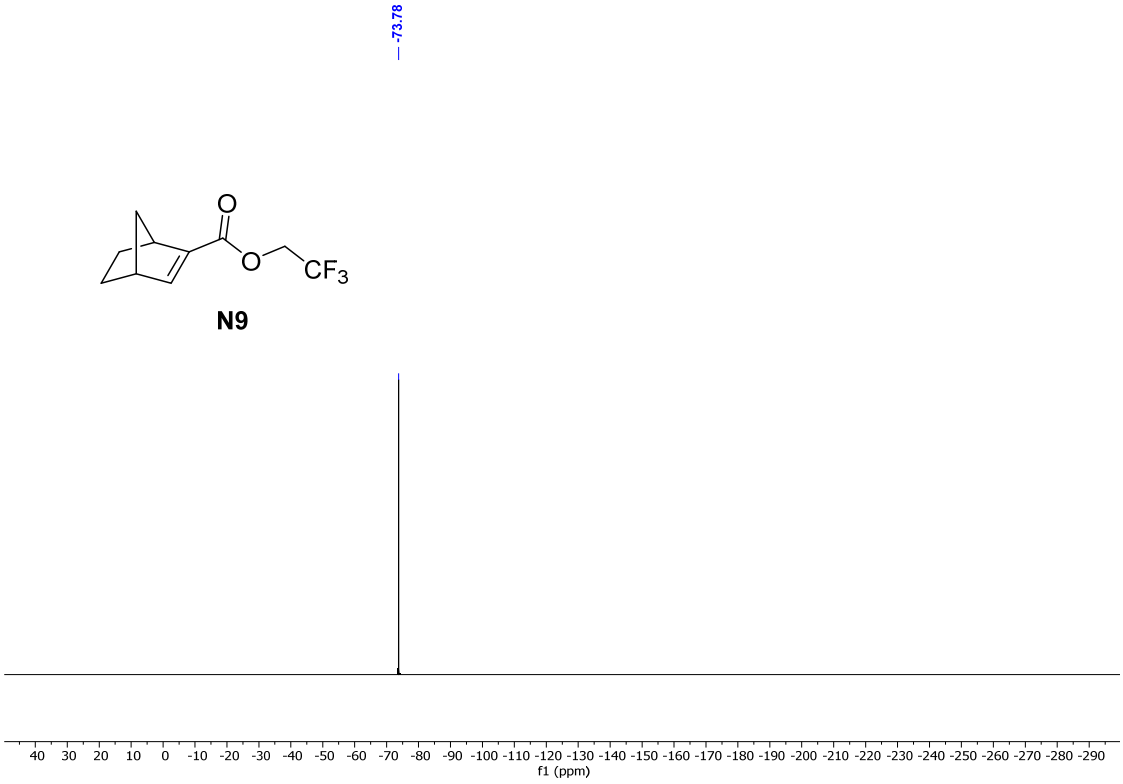
N18


1.00
2.12
1.03
1.01
2.13
1.06
1.12
2.10
f1 (ppm)

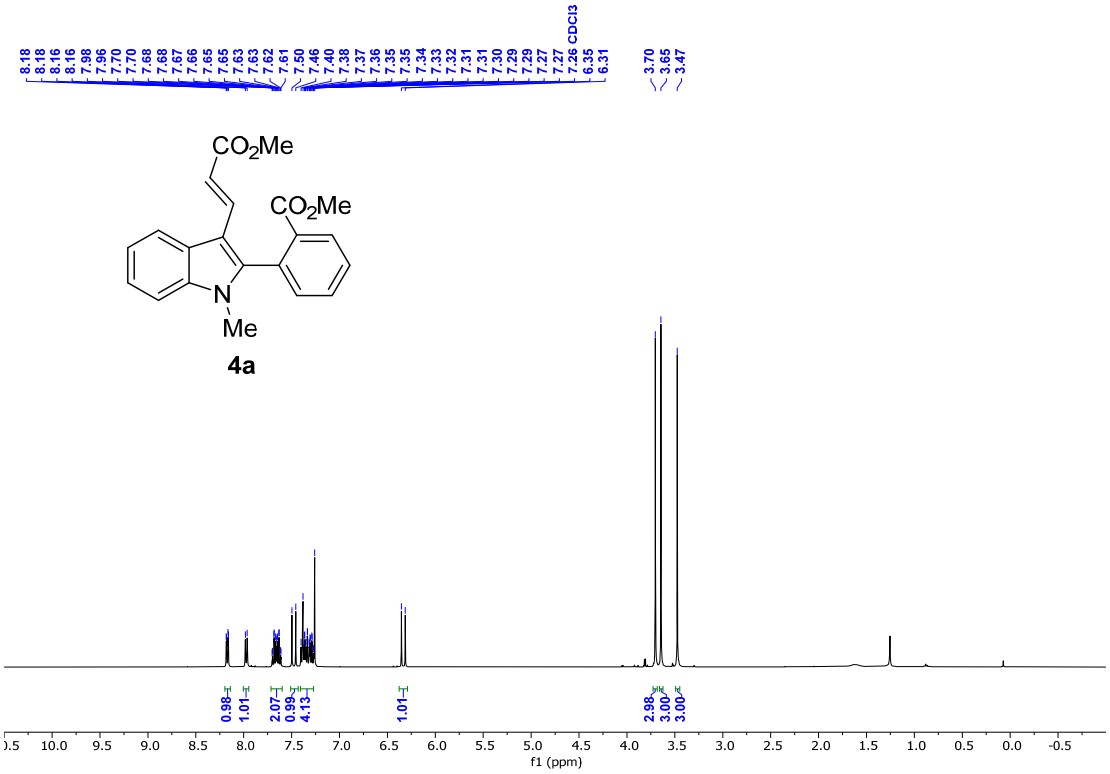

162.97
150.03
139.21
127.45
124.69
121.94
119.18
77.16 CDCl3
60.73
60.37
60.00
59.64
48.34
43.88
41.98
24.57
24.55
f1 (ppm)

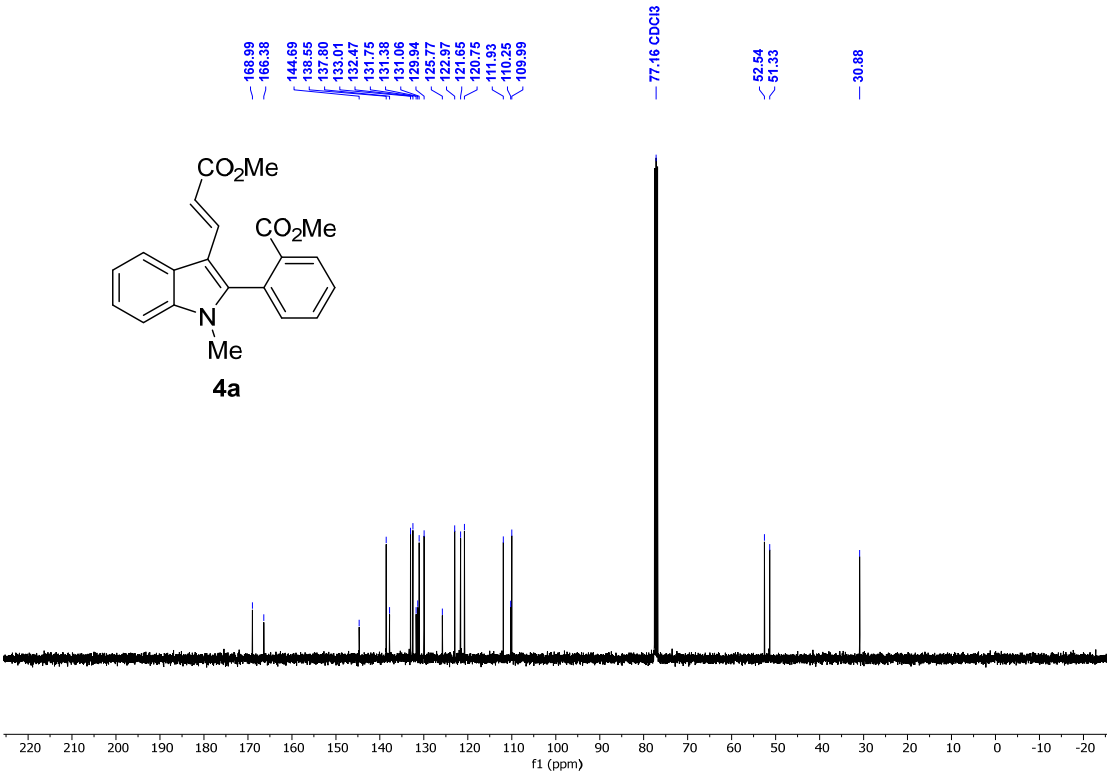
O
O
CF3

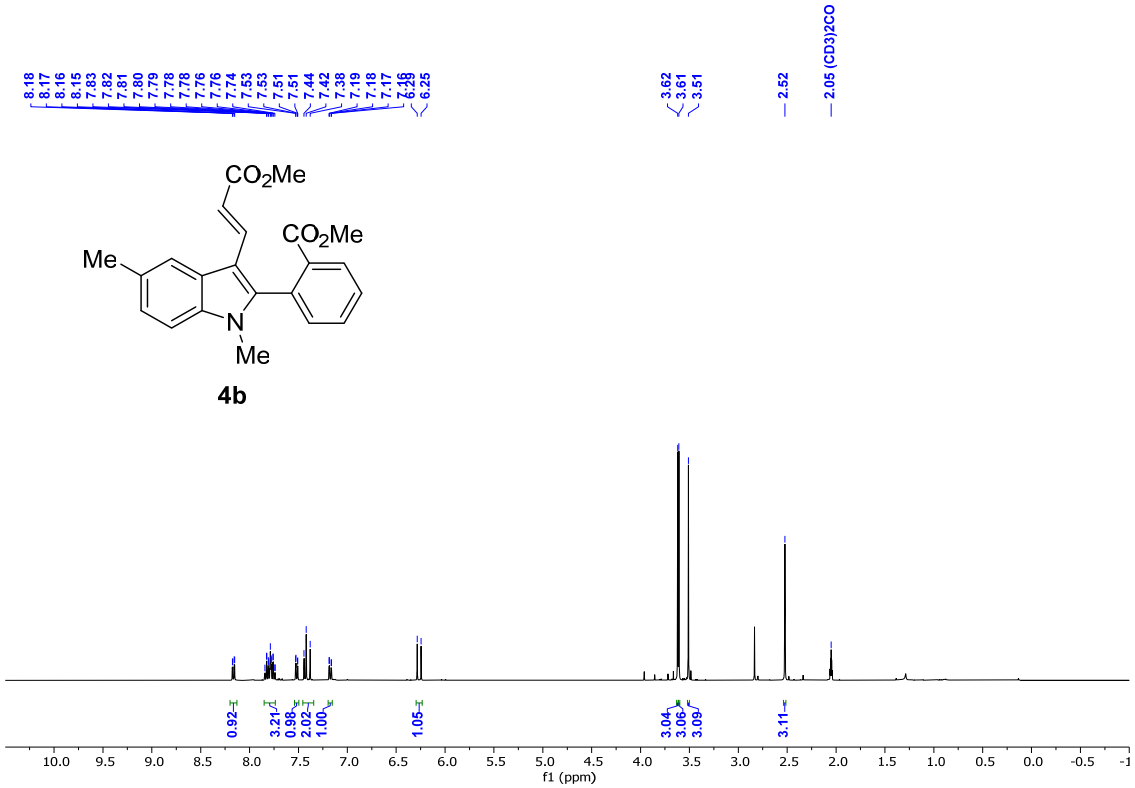
N18

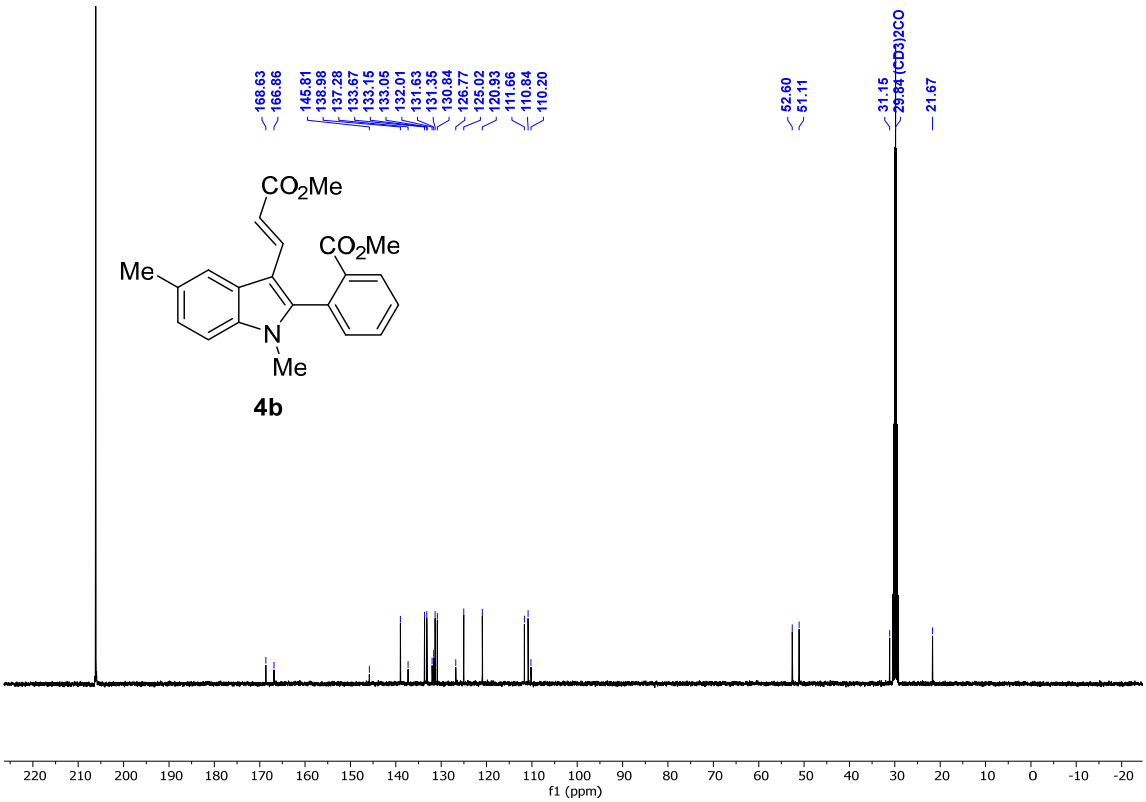

-73.78
O
O
CF3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)

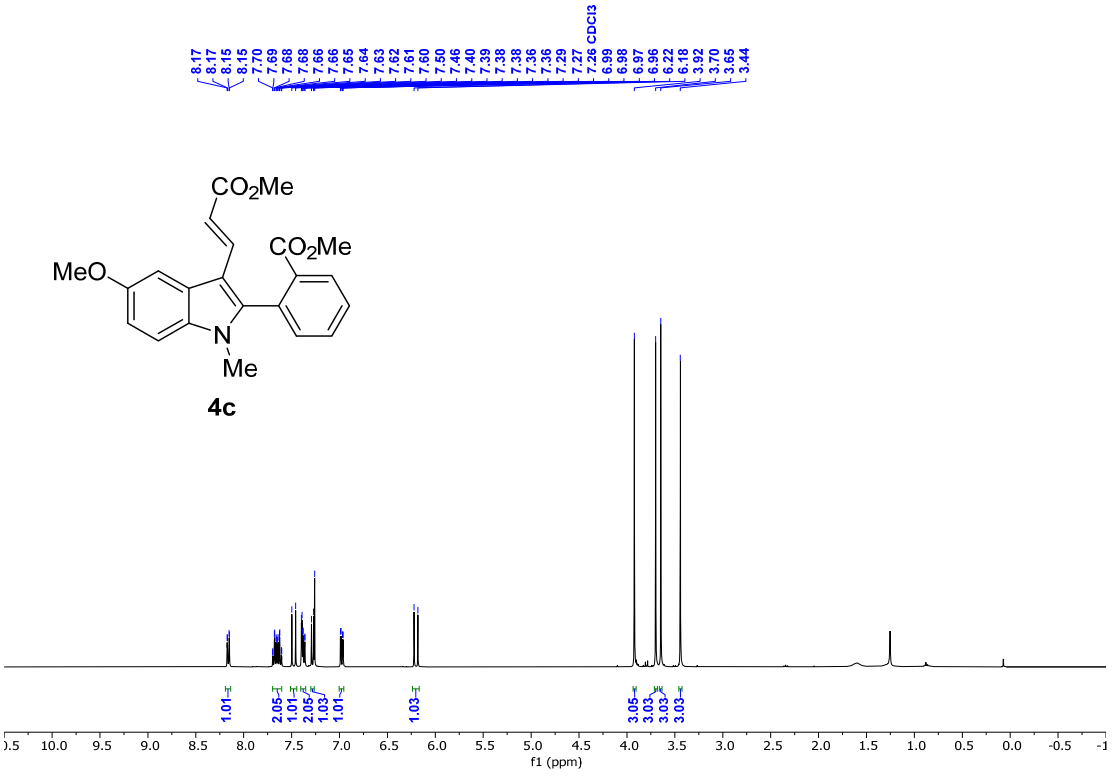
N9

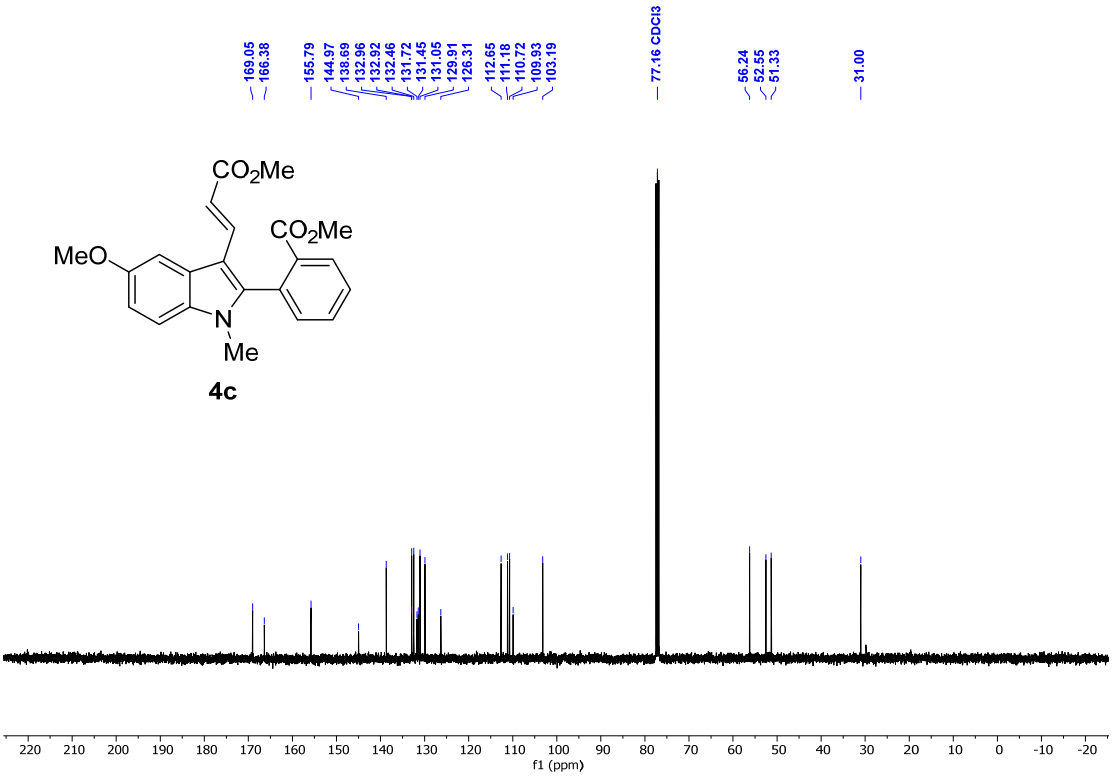

8.18
8.18
8.16
8.16
7.98
7.96
7.70
7.70
7.68
7.68
7.67
7.66
7.65
7.65
7.63
7.63
7.62
7.61
7.60
7.46
7.40
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.27
7.27
7.26 CDCl3
6.35
6.31
3.70
3.65
3.47
CO2Me
CO2Me
N
Me
4a
0.98
1.01
2.07
0.99
4.13
1.01
2.98
3.00
3.00
f1 (ppm)


168.99
166.38
144.69
138.55
137.80
133.01
132.47
131.75
131.38
131.06
129.94
125.77
122.97
121.65
120.75
111.93
110.25
109.99
77.16 CDCl3
52.54
51.33
30.88
CO2Me
CO2Me
N
Me
4a
f1 (ppm)


8.18
8.17
8.16
8.15
7.83
7.82
7.81
7.80
7.79
7.78
7.78
7.76
7.76
7.74
7.53
7.53
7.51
7.51
7.44
7.42
7.38
7.19
7.18
7.17
7.16
6.29
6.25
3.62
3.61
3.51
2.52
2.05 (CD3)2CO
CO2Me
CO2Me
Me
N
Me
4b
0.92
3.21
0.98
2.02
1.00
1.05
3.04
3.06
3.09
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


168.63
166.86
145.81
138.98
137.28
133.67
133.15
133.05
132.01
131.63
131.35
130.84
126.77
125.02
120.93
111.66
110.84
110.20
52.60
51.11
31.15
29.84
(CD3)2CO
21.67
CO2Me
CO2Me
Me
N
Me
4b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.17
8.17
8.15
8.15
7.70
7.69
7.68
7.68
7.66
7.66
7.65
7.64
7.63
7.62
7.61
7.60
7.50
7.46
7.40
7.39
7.38
7.38
7.36
7.36
7.29
7.27
7.26 CDCl3
6.99
6.98
6.97
6.96
6.22
6.18
3.92
3.70
3.65
3.44
CO2Me
CO2Me
MeO
N
Me
4c
1.01
2.05
1.01
2.05
1.03
1.01
1.03
3.05
3.03
3.03
3.03
f1 (ppm)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132.96
132.92
132.46
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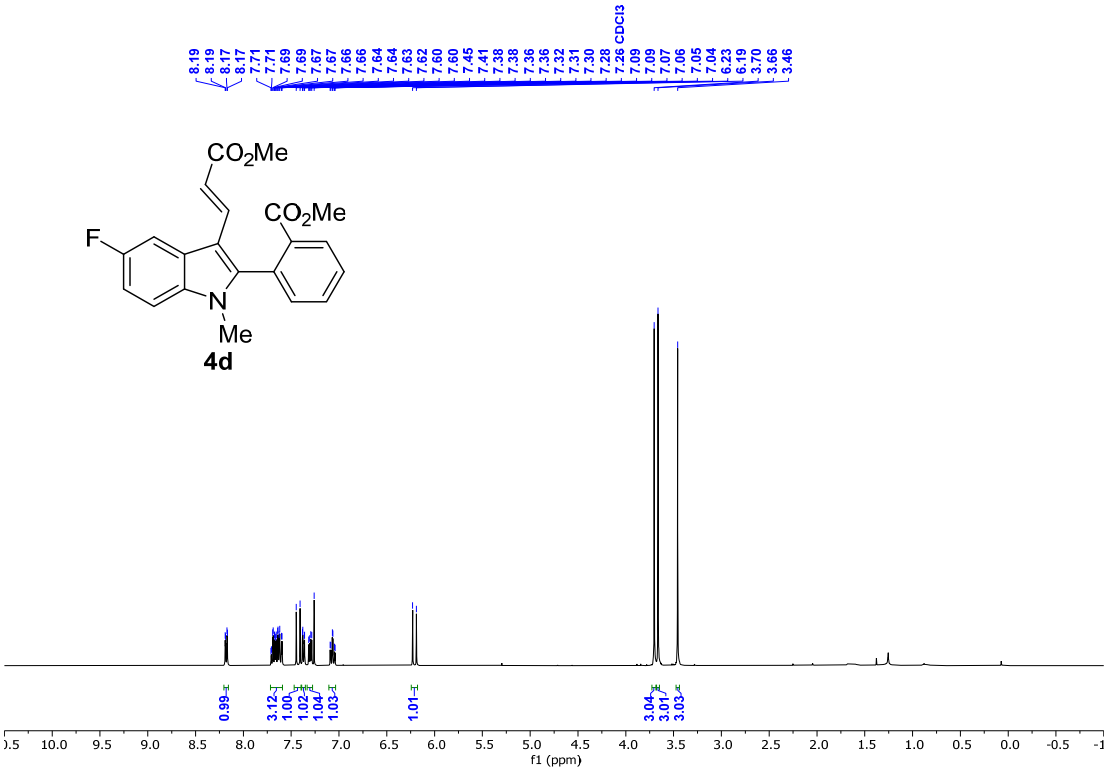
131.45
131.05
129.91
126.31
112.65
111.18
110.72
109.93
103.19
77.16 CDCl3
56.24
52.55
51.33
31.00
CO2Me
CO2Me
MeO
N
Me
4c
f1 (ppm)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7.64
7.64
7.63
7.62
7.60
7.60
7.45
7.41
7.38
7.38
7.36
7.36
7.32
7.31
7.30
7.28
7.26 CDCl3
7.09
7.09
7.07
7.06
7.05
7.04
6.23
6.19
3.70
3.66
3.46
CO2Me
CO2Me
F
N
Me
4d
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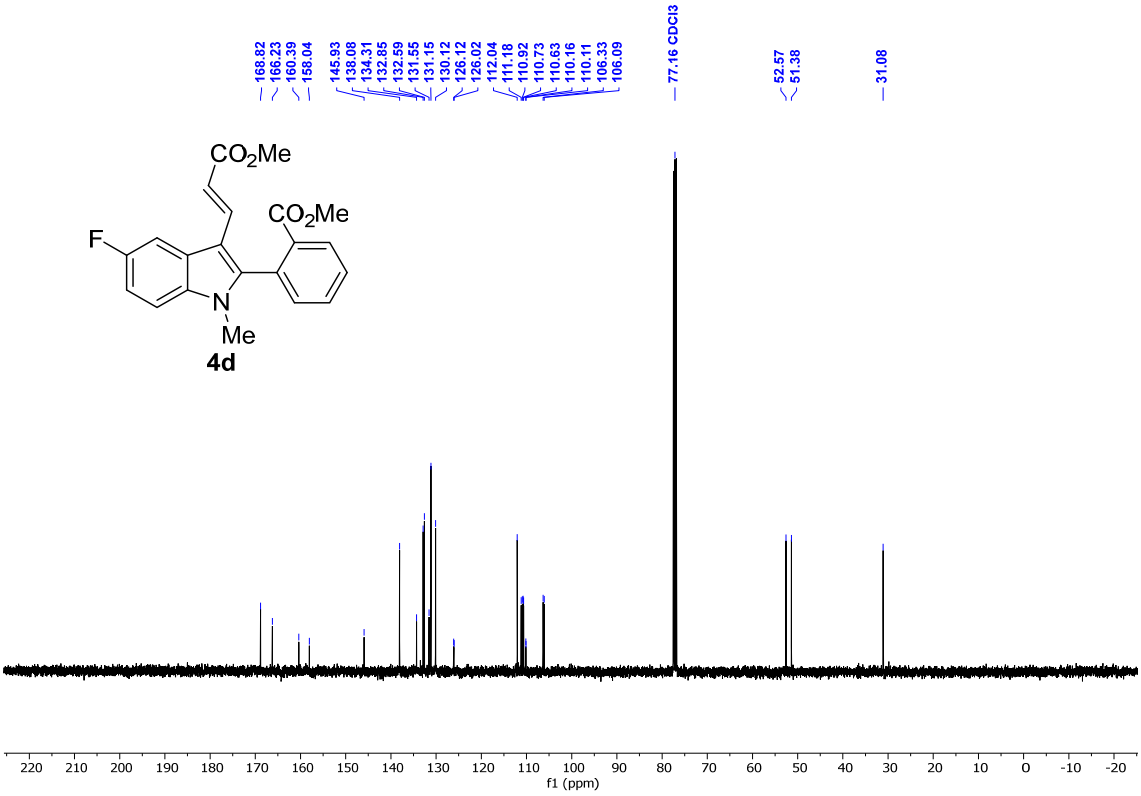
1.00
1.02
1.04
1.03
1.01
3.04
3.01
3.03
f1 (ppm)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132.85
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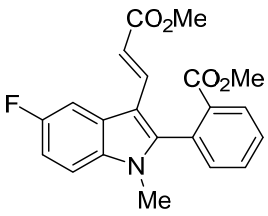
131.15
130.12
126.12
126.02
112.04
111.18
110.92
110.73
110.63
110.16
110.11
106.33
106.09
77.16 CDCl3
52.57
51.38
31.08
CO2Me
CO2Me
F
N
Me
4d
f1 (ppm)


CO2Me
CO2Me
F
N
Me

4d

-122.13
10
0
-10
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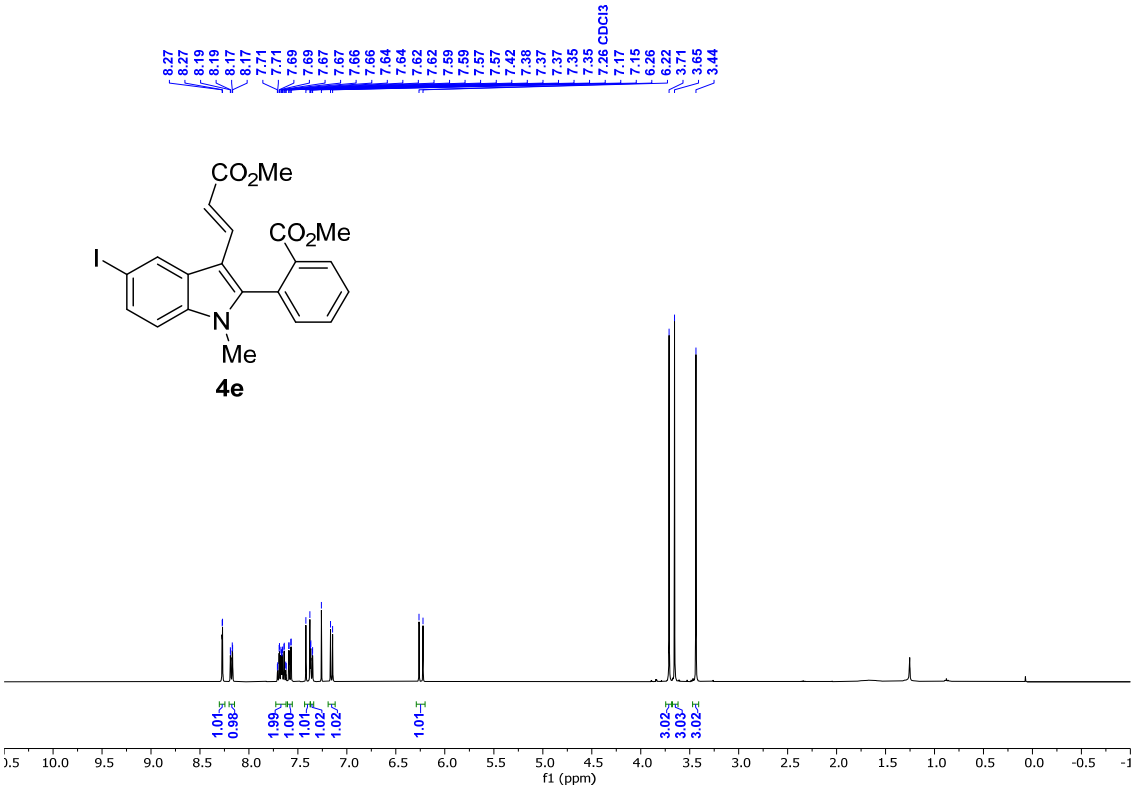
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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7.66
7.64
7.64
7.62
7.62
7.59
7.59
7.57
7.57
7.42
7.38
7.37
7.37
7.35
7.35
7.26 CDCl3
7.17
7.15
6.26
6.22
3.71
3.65
3.44
CO2Me
CO2Me
I
N
Me
4e
1.01
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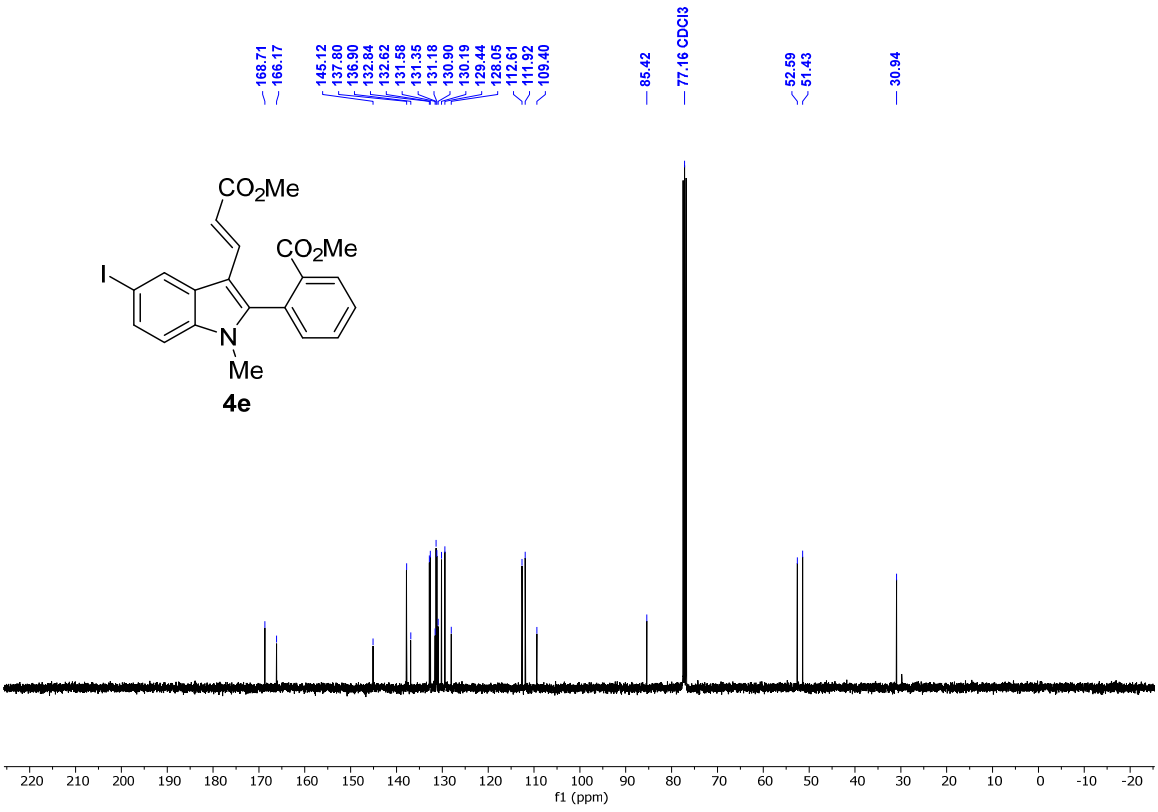
1.99
1.00
1.01
1.02
1.02
1.01
3.02
3.03
3.02
f1 (ppm)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130.19
129.44
128.05
112.61
111.92
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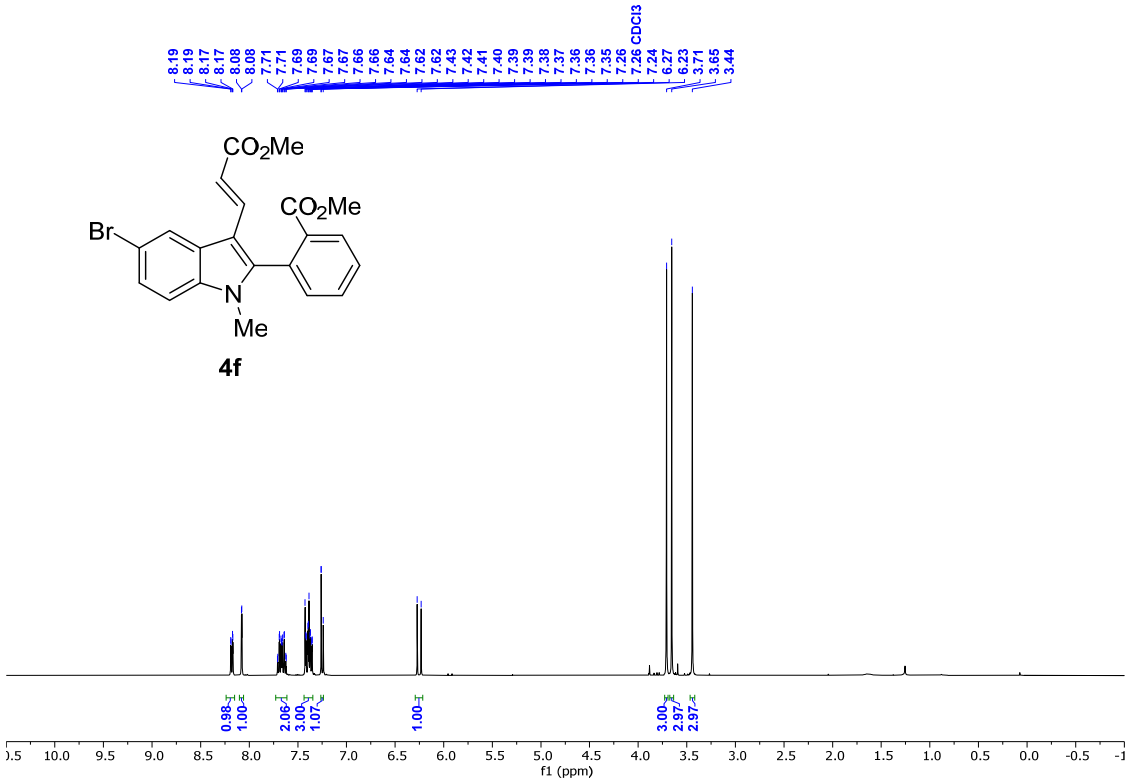
52.59
51.43
30.94
CO2Me
CO2Me
I
N
Me
4e
f1 (ppm)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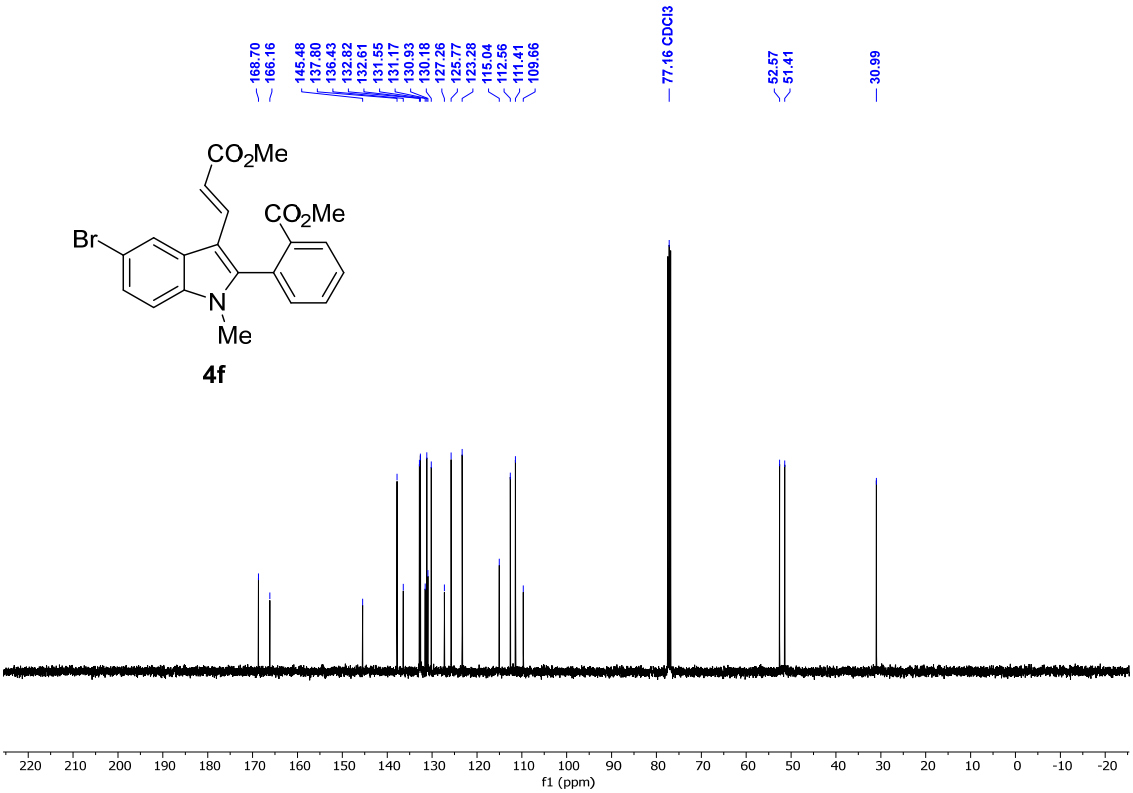
7.66
7.64
7.64
7.62
7.62
7.43
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.26
7.26 CDCl3
7.24
6.27
6.23
3.71
3.65
3.44
CO2Me
CO2Me
Br
N
Me
4f
0.98
1.00
2.06
3.00
1.07
1.00
3.00
2.97
2.97
f1 (ppm)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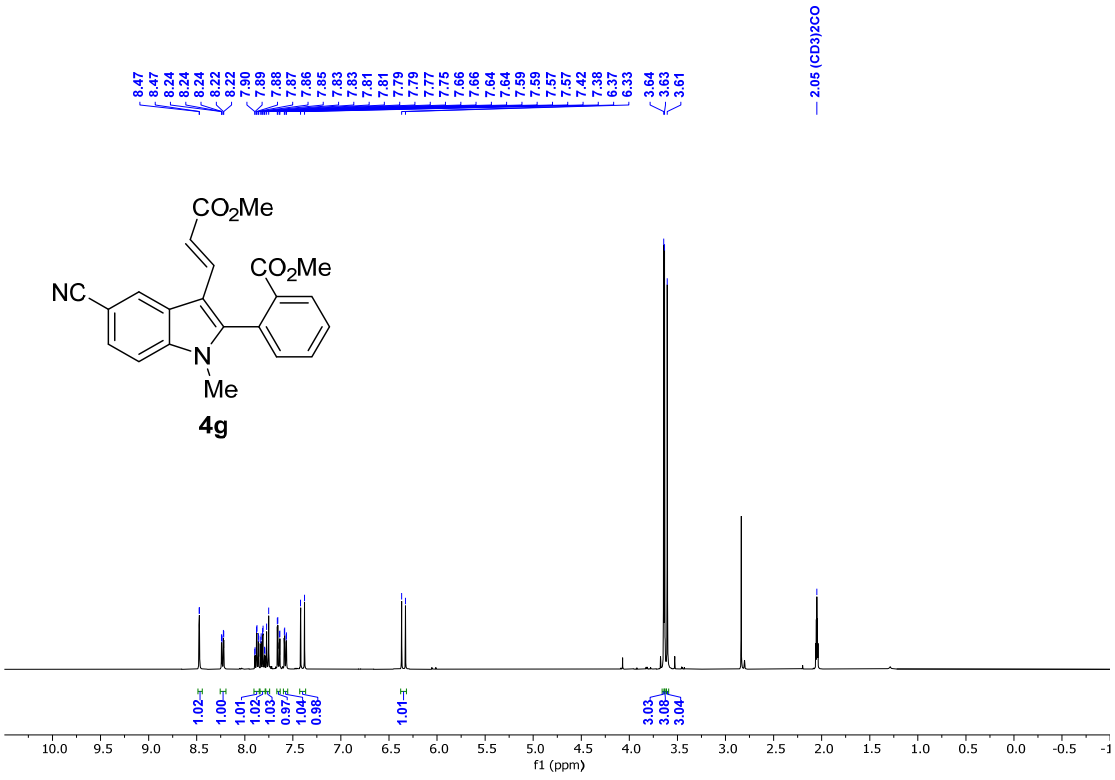
130.18
127.26
125.77
123.28
115.04
112.56
111.41
109.66
77.16 CDCl3
52.57
51.41
30.99
CO2Me
CO2Me
Br
N
Me
4f
f1 (ppm)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8.22
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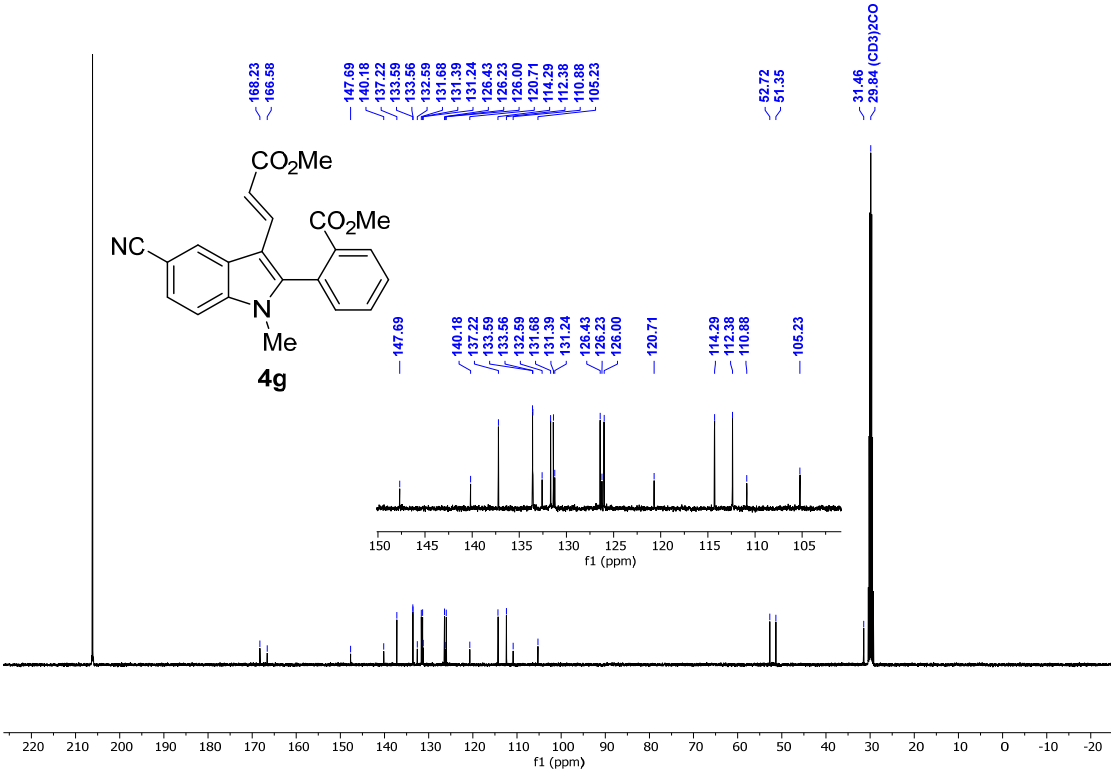
7.87
7.86
7.85
7.83
7.83
7.81
7.81
7.79
7.79
7.77
7.75
7.66
7.66
7.64
7.64
7.59
7.59
7.57
7.57
7.42
7.38
6.37
6.33
3.64
3.63
3.61
2.05 (CD3)2CO
CO2Me
CO2Me
NC
N
Me
4g
1.02
1.00
1.01
1.02
1.03
0.97
1.04
0.98
1.01
3.03
3.08
3.04
f1 (ppm)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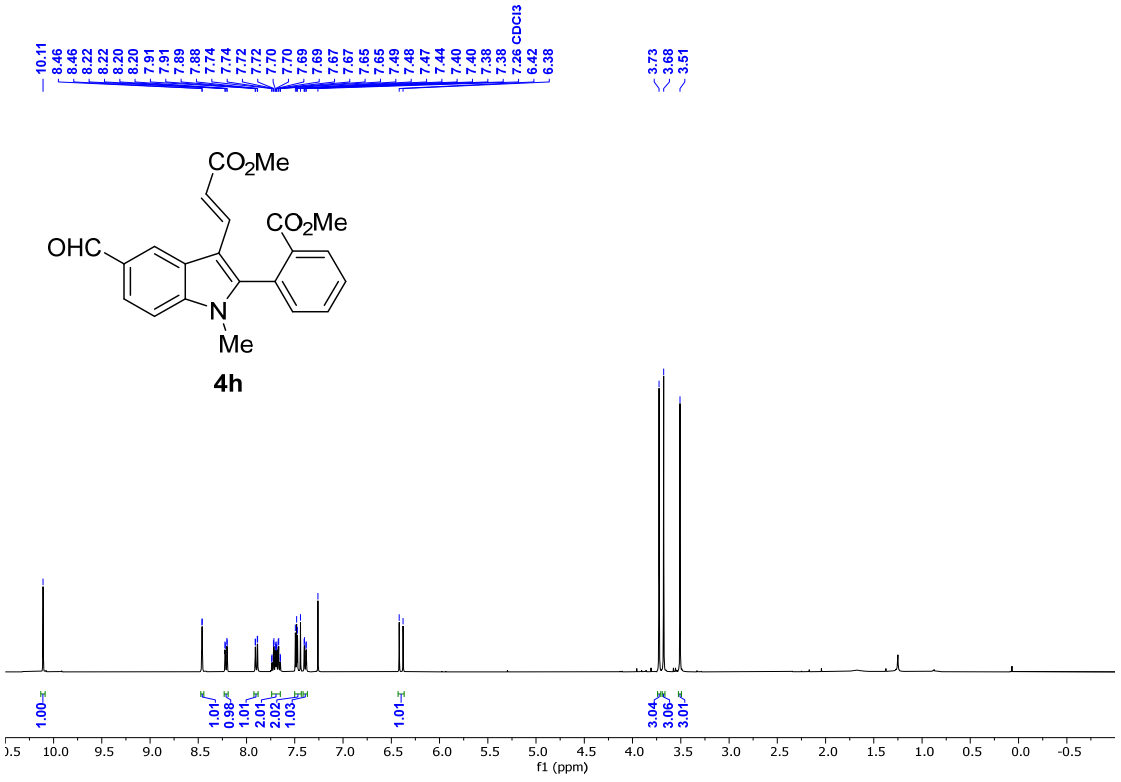
133.59
133.56
132.59
131.68
131.39
131.24
126.43
126.23
126.00
120.71
114.29
112.38
110.88
105.23
52.72
51.35
31.46
29.84 (CD3)2CO
CO2Me
CO2Me
NC
N
Me
4g
f1 (ppm)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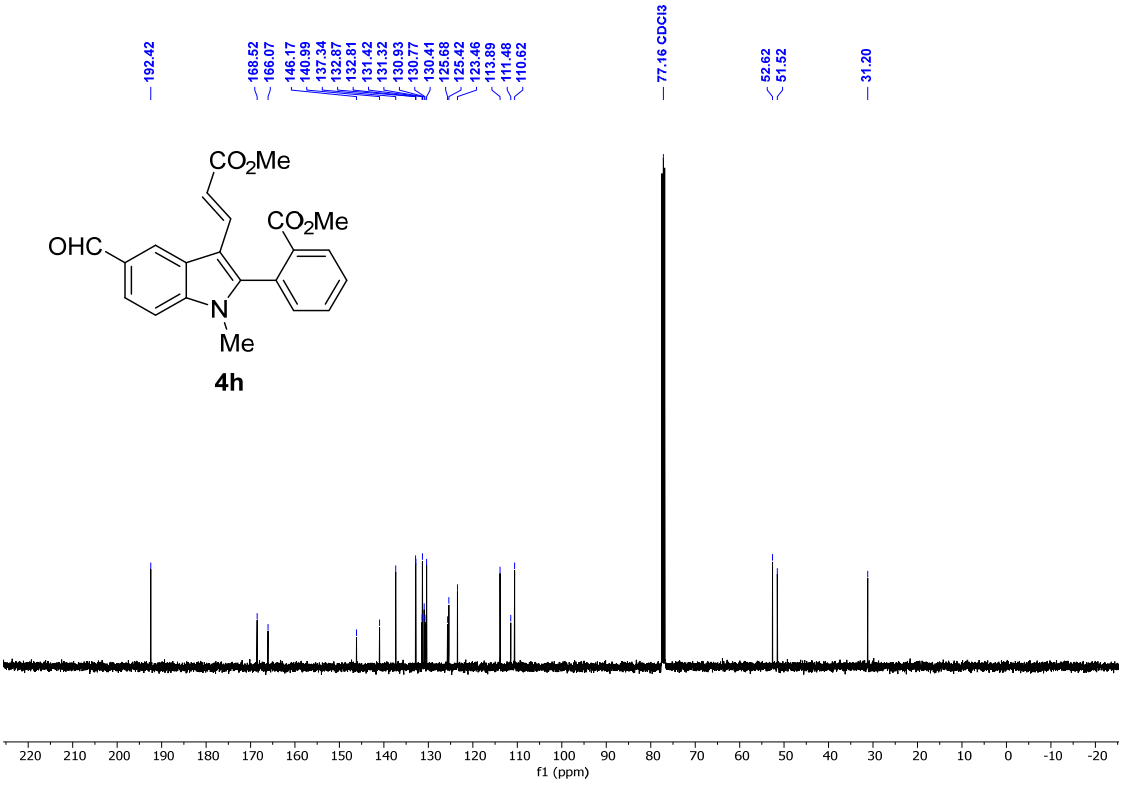
8.20
8.20
7.91
7.91
7.89
7.88
7.74
7.74
7.72
7.72
7.70
7.70
7.69
7.69
7.67
7.67
7.65
7.65
7.49
7.48
7.47
7.44
7.40
7.40
7.38
7.26 CDCl3
6.42
6.38
3.73
3.68
3.51
CO2Me
CO2Me
OHC
N
Me
4h
1.00
1.01
0.98
1.01
2.01
2.02
1.03
1.01
3.04
3.06
3.01
f1 (ppm)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132.81
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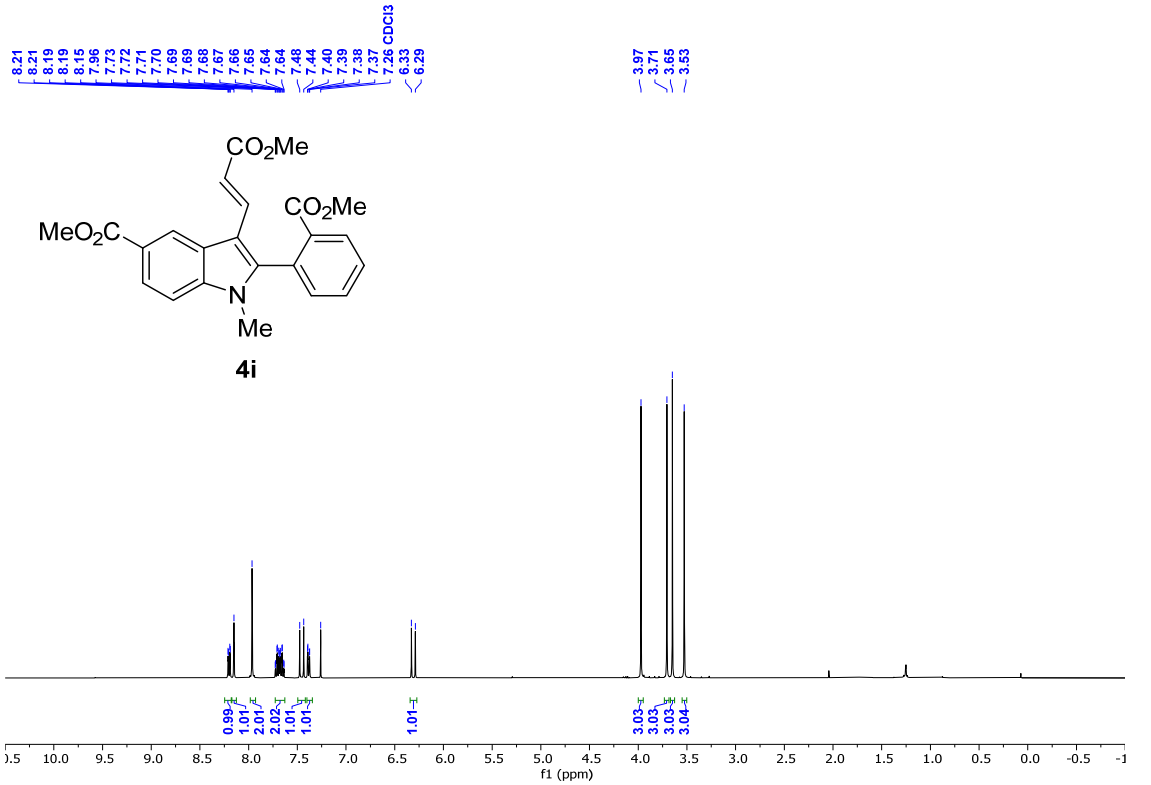
131.32
130.93
130.77
130.41
125.68
125.42
123.46
113.89
111.48
110.62
77.16 CDCl3
52.62
51.52
31.20
CO2Me
CO2Me
OHC
N
Me
4h
f1 (ppm)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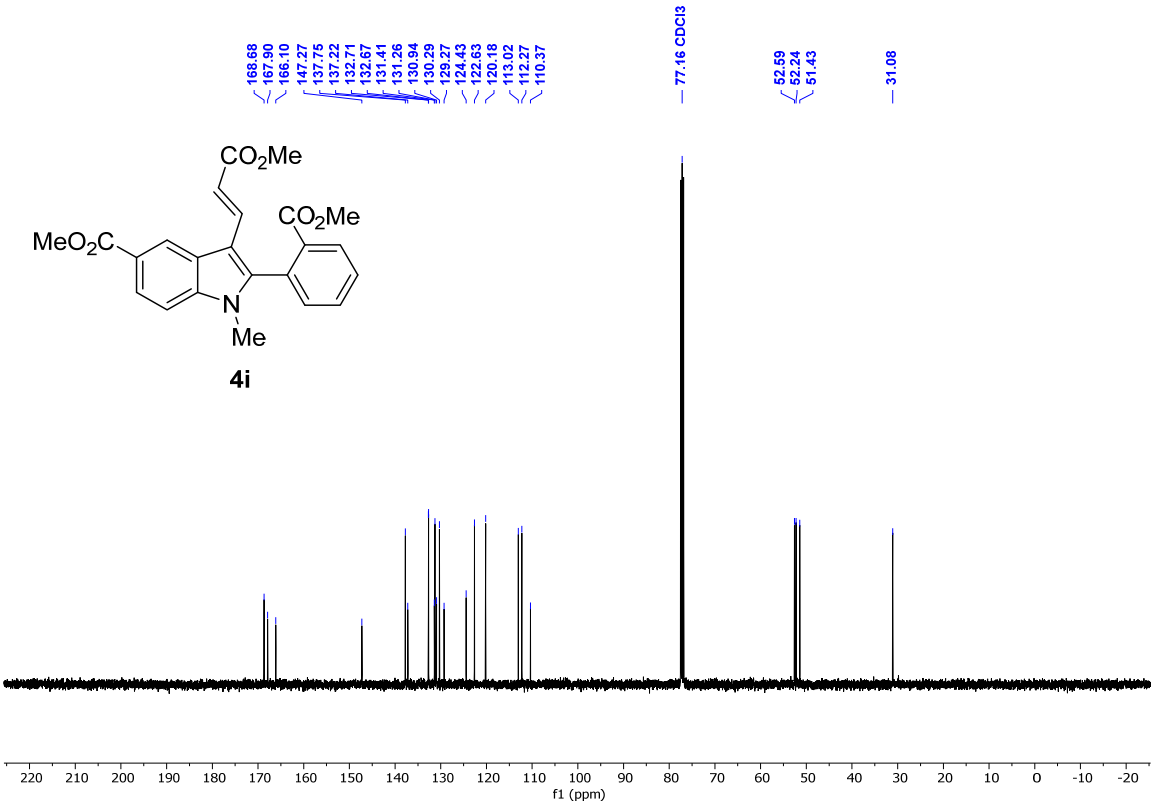
7.70
7.69
7.69
7.68
7.67
7.66
7.65
7.64
7.64
7.48
7.44
7.40
7.39
7.38
7.37
7.26 CDCl3
6.33
6.29
3.97
3.71
3.65
3.53
CO2Me
CO2Me
MeO2C
N
Me
4i
0.99
1.01
2.01
2.02
1.01
1.01
1.01
3.03
3.03
3.03
3.04
f1 (ppm)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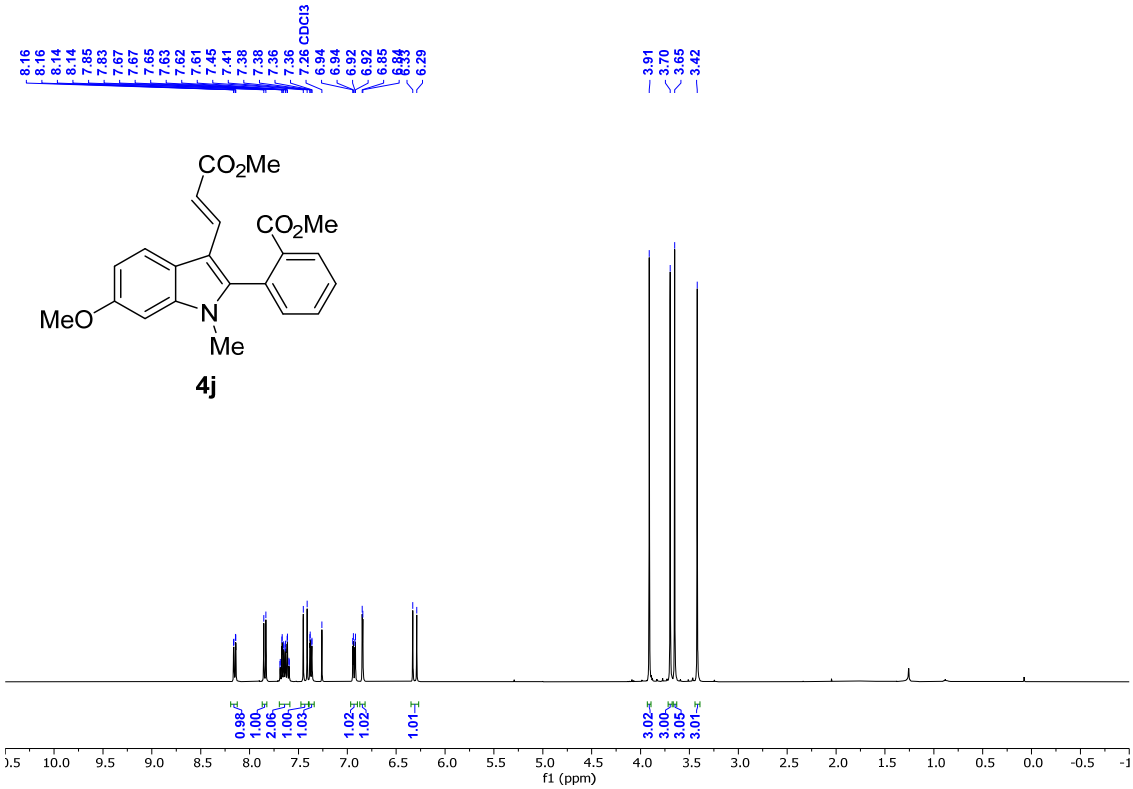
132.67
131.41
131.26
130.94
130.29
129.27
124.43
122.63
120.18
113.02
112.27
110.37
77.16 CDCl3
52.59
52.24
51.43
31.08
CO2Me
CO2Me
MeO2C
N
Me
4i
f1 (ppm)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7.67
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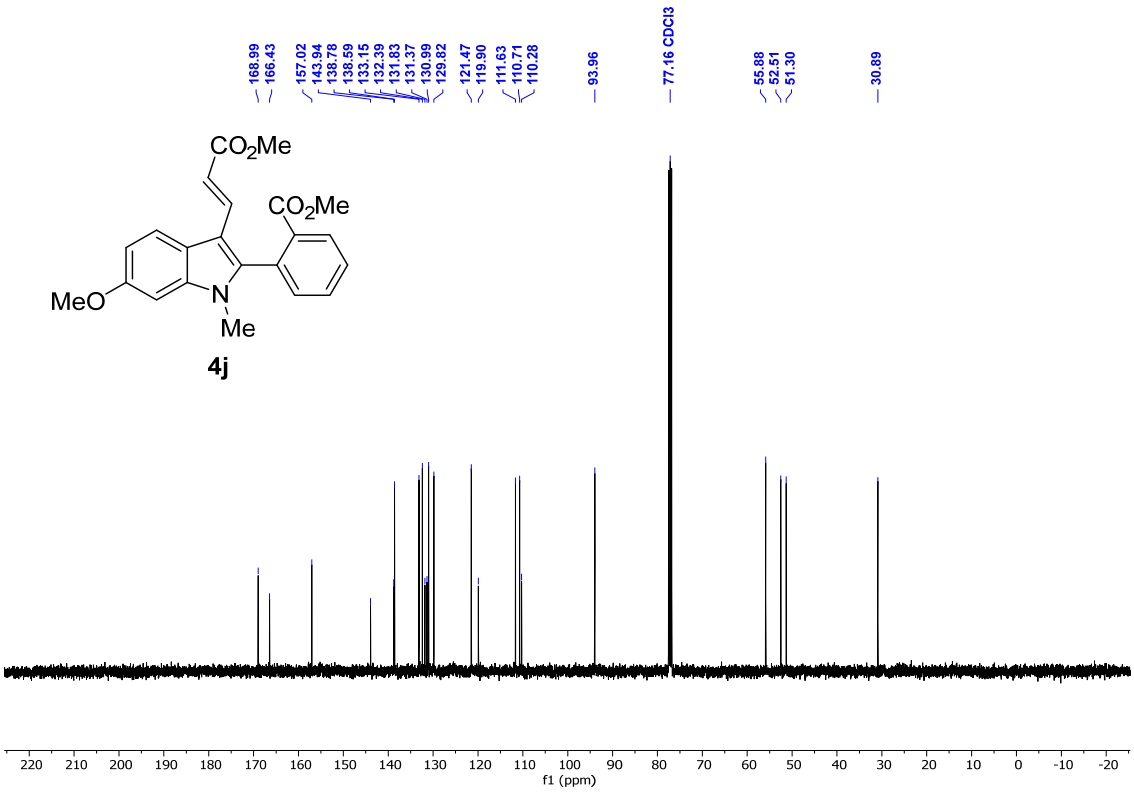
7.63
7.62
7.61
7.45
7.41
7.38
7.38
7.36
7.36
7.26 CDCl3
6.94
6.94
6.92
6.92
6.85
6.84
6.83
6.29
3.91
3.70
3.65
3.42
CO2Me
CO2Me
MeO
N
Me
4j
0.98
1.00
2.06
1.00
1.03
1.02
1.02
1.01
3.02
3.00
3.05
3.01
f1 (ppm)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131.37
130.99
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121.47
119.90
111.63
110.71
110.28
93.96
77.16 CDCl3
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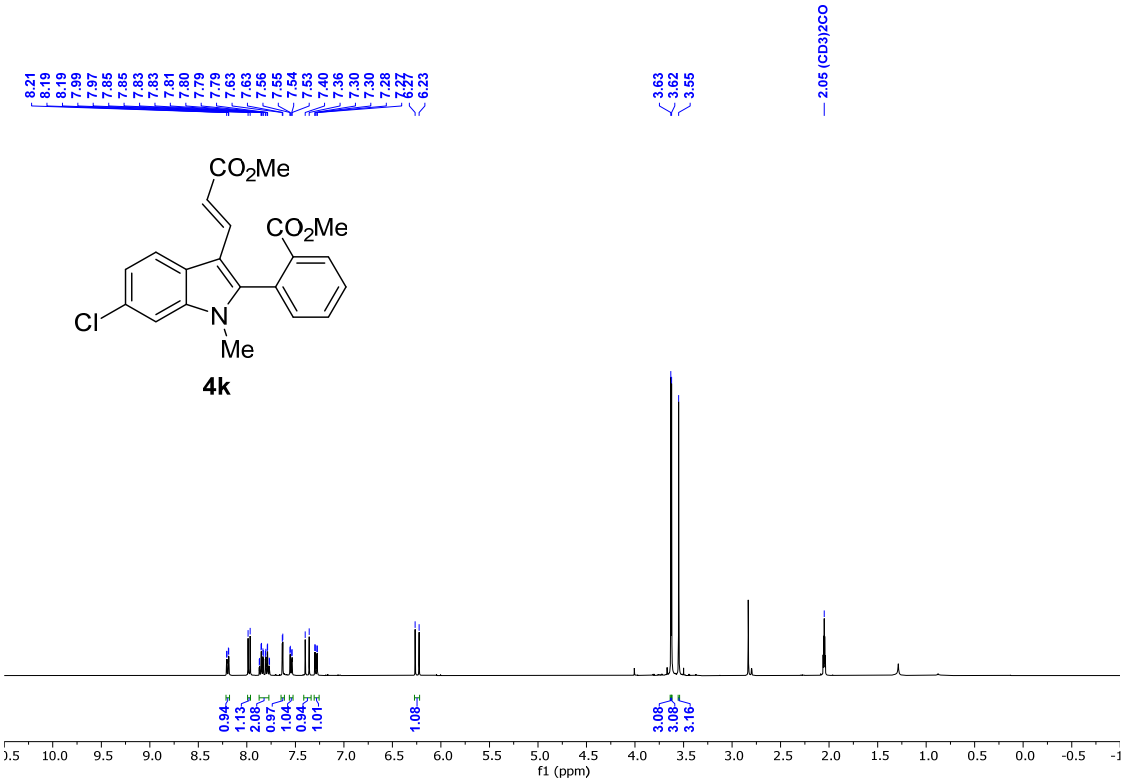
52.51
51.30
30.89
CO2Me
CO2Me
MeO
N
Me
4j
f1 (ppm)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7.85
7.83
7.83
7.81
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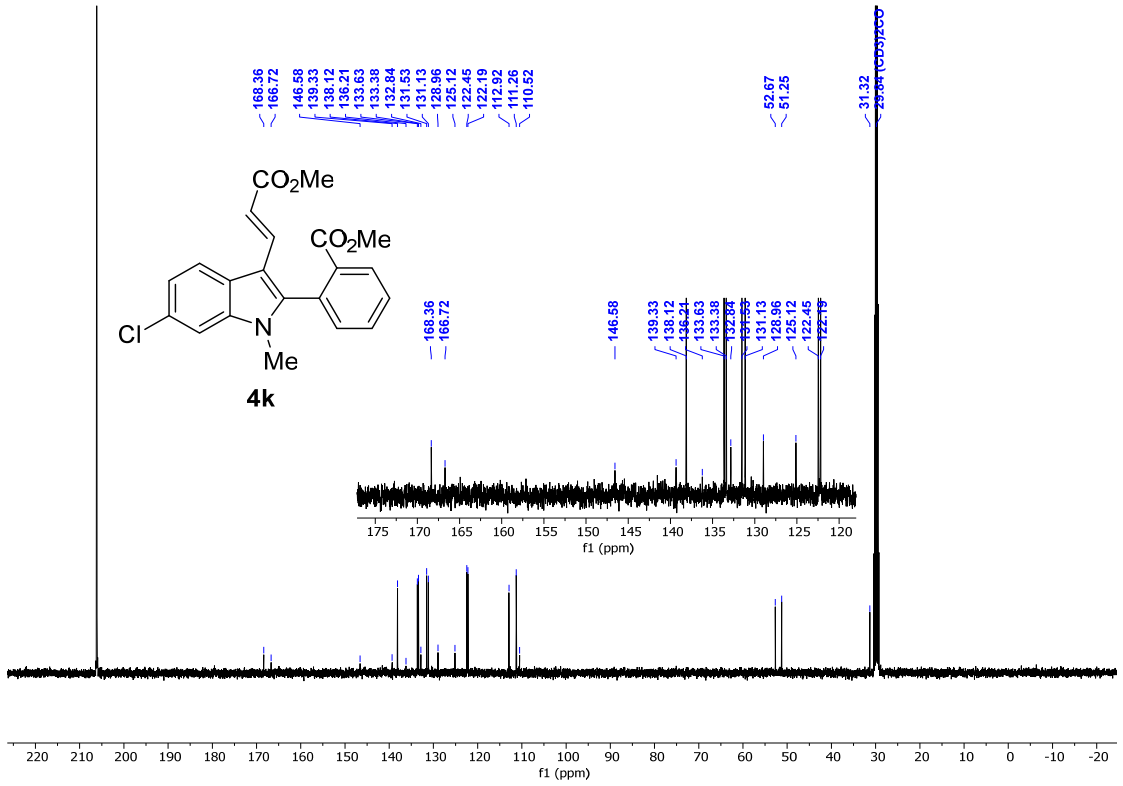
7.79
7.79
7.63
7.63
7.56
7.55
7.54
7.53
7.40
7.36
7.30
7.30
7.28
7.27
6.23
3.63
3.62
3.55
2.05 (CD3)2CO
CO2Me
CO2Me
Cl
N
Me
4k
0.94
1.13
2.08
0.97
1.04
0.94
1.01
1.08
3.08
3.08
3.16
f1 (ppm)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133.38
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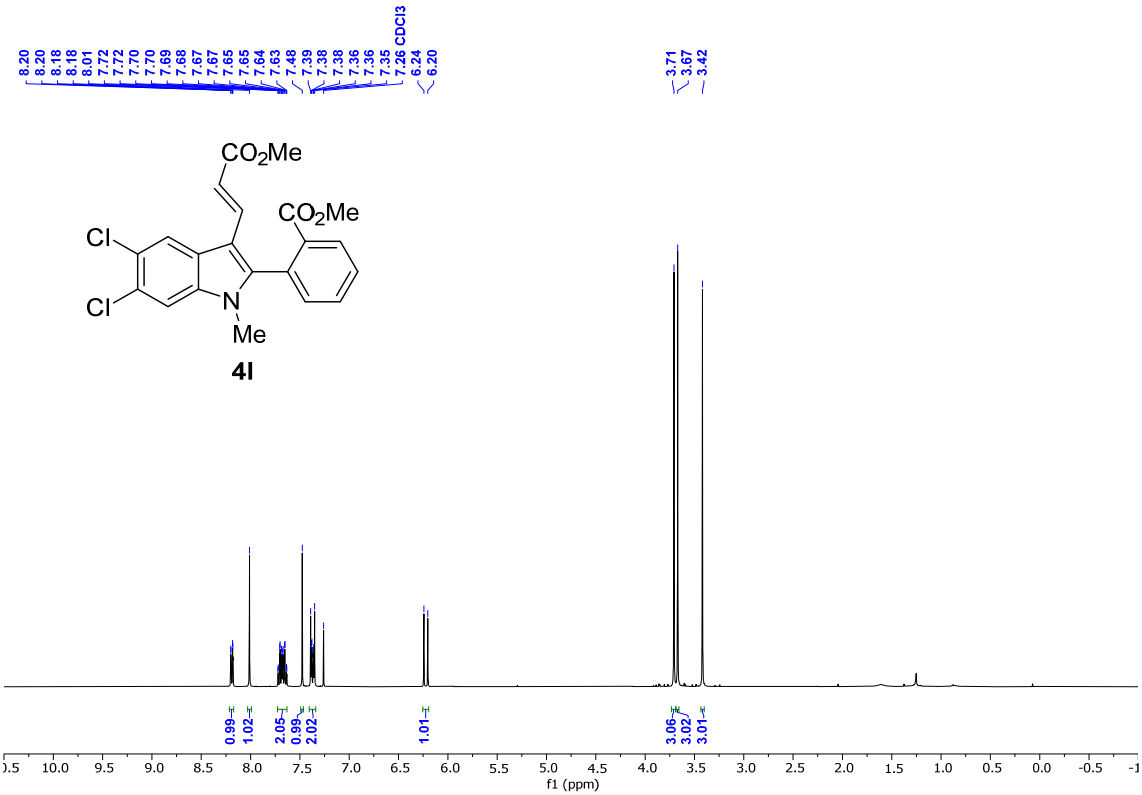
131.53
131.13
128.96
125.12
122.45
122.19
112.92
111.26
110.52
52.67
51.25
31.32
29.84 (CD3)2CO
CO2Me
CO2Me
Cl
N
Me
4k
f1 (ppm)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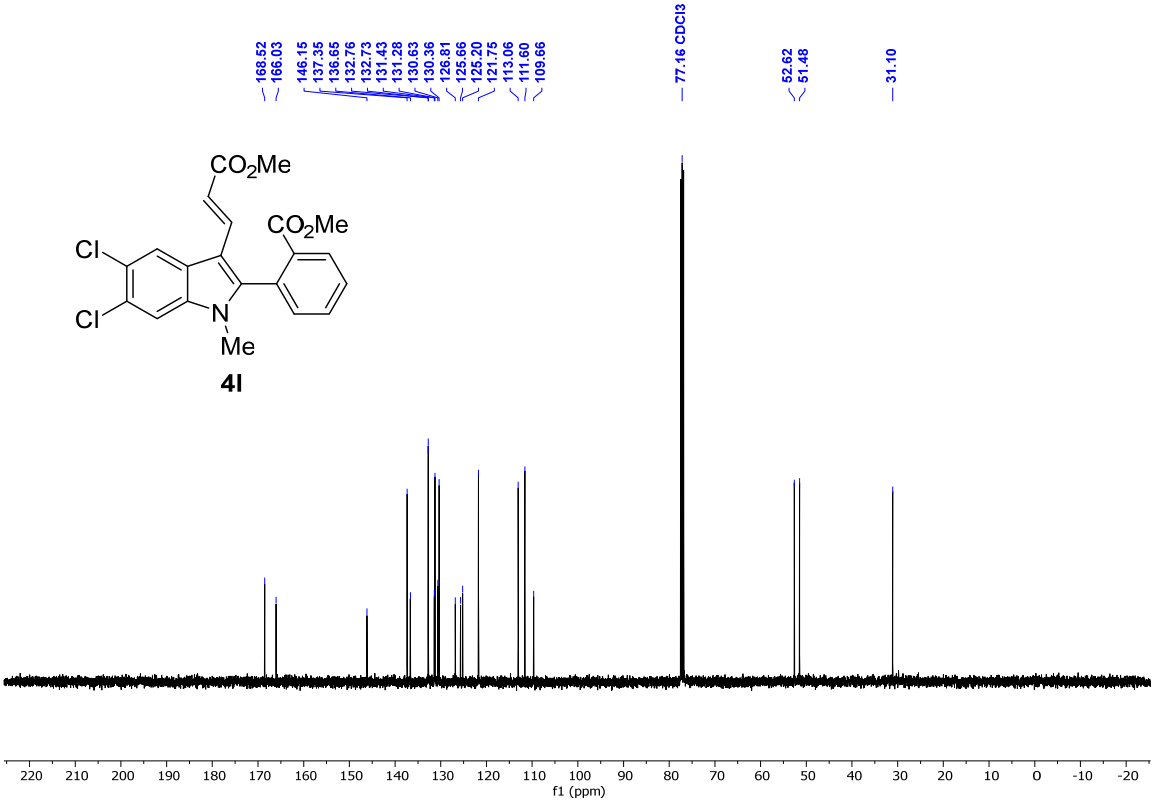
7.72
7.70
7.70
7.69
7.68
7.67
7.67
7.65
7.65
7.64
7.63
7.48
7.39
7.38
7.38
7.36
7.36
7.35
7.26 CDCl3
6.24
6.20
3.71
3.67
3.42
CO2Me
CO2Me
Cl
Cl
N
Me
4l
0.99
1.02
2.05
0.99
2.02
1.01
3.06
3.02
3.01
f1 (ppm)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130.63
130.36
126.81
125.66
125.20
121.75
113.06
111.60
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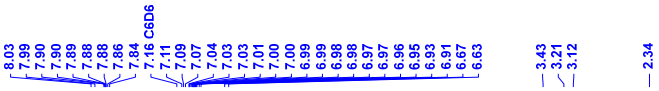
CO2Me
CO2Me
Cl
Cl
N
Me
4l
f1 (ppm)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7.16 C6D6
7.11
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7.07
7.04
7.03
7.03
7.01
7.00
7.00
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6.99
6.98
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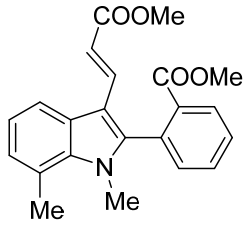
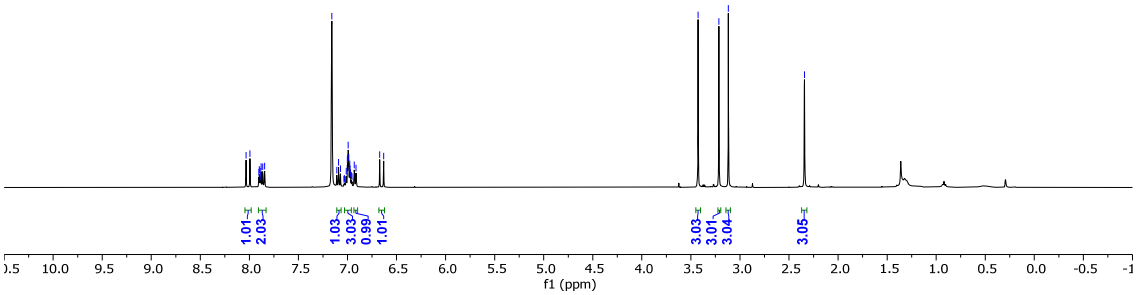
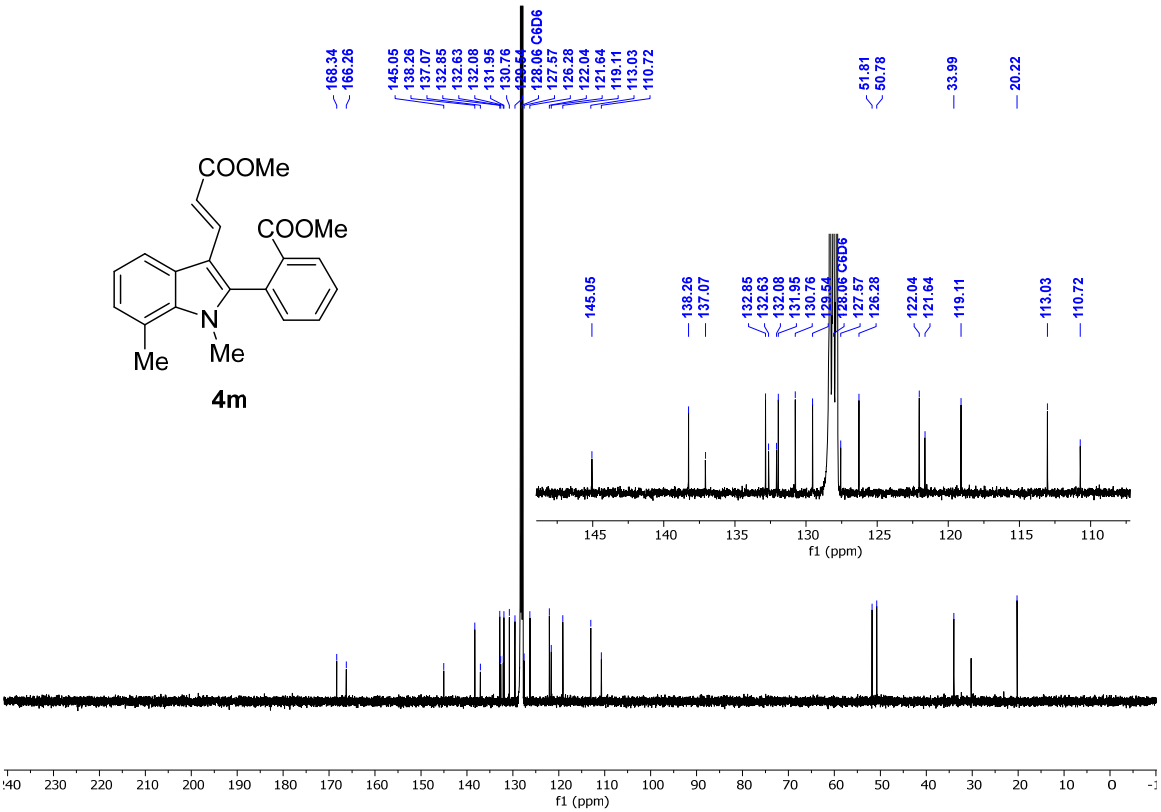
6.67
6.63
3.43
3.21
3.12
2.34


COOMe
COOMe
N
Me
Me

4m


1.01
2.03
1.03
3.03
0.99
1.01
3.03
3.01
3.04
3.05
f1 (ppm)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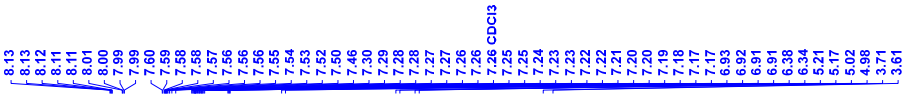
138.26
137.07
132.85
132.63
132.08
131.95
130.76
130.54
128.06 C6D6
127.57
126.28
122.04
121.64
119.11
113.03
110.72
51.81
50.78
33.99
20.22
f1 (ppm)

COOMe
COOMe
N
Me
Me

4m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8.13
8.12
8.11
8.11
8.01
8.00
7.99
7.99
7.60
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7.58
7.58
7.57
7.56
7.56
7.56
7.55
7.54
7.53
7.52
7.50
7.46
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
CDCl3
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.17
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6.34
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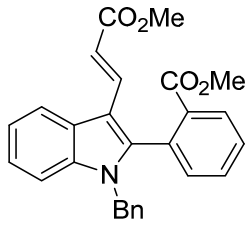
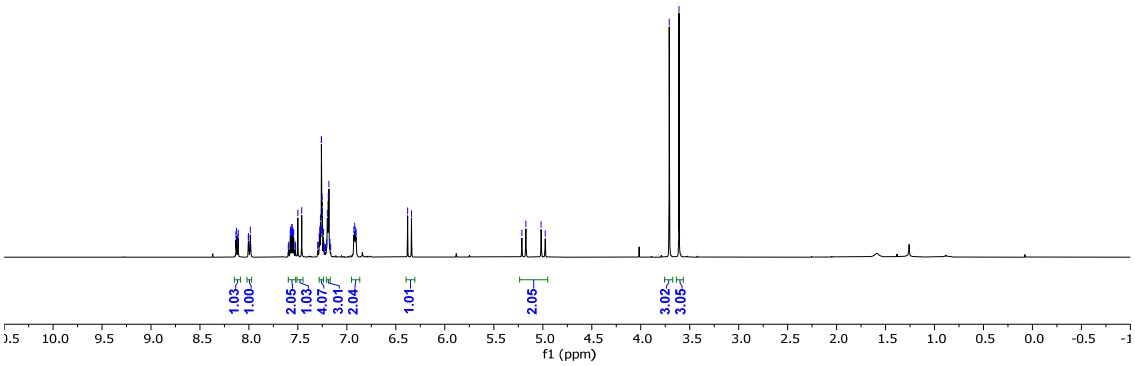
3.61


CO2Me
CO2Me
N
Bn

4n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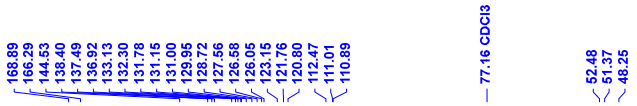
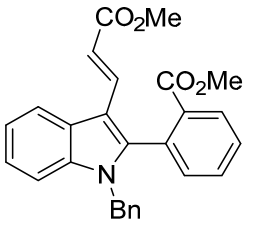
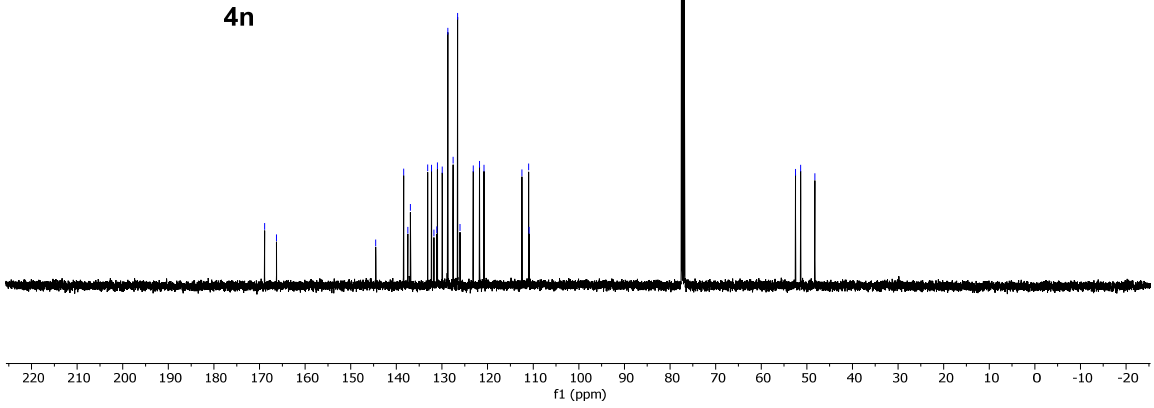
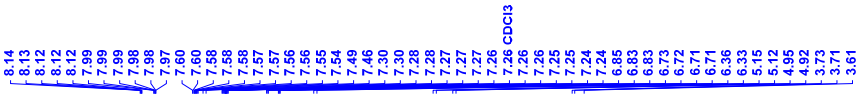
1.00
2.05
1.03
4.07
3.01
2.04
1.01
2.05
3.02
3.05
f1 (ppm)

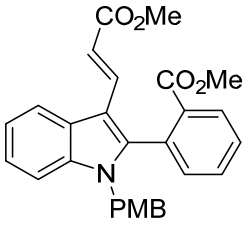

168.89
166.29
144.53
138.40
137.49
136.92
133.13
132.30
131.78
131.15
131.00
129.95
128.72
127.56
126.58
126.05
123.15
121.76
120.80
112.47
111.01
110.89
77.16 CDCl3
52.48
51.37
48.25


CO2Me
CO2Me
N
Bn

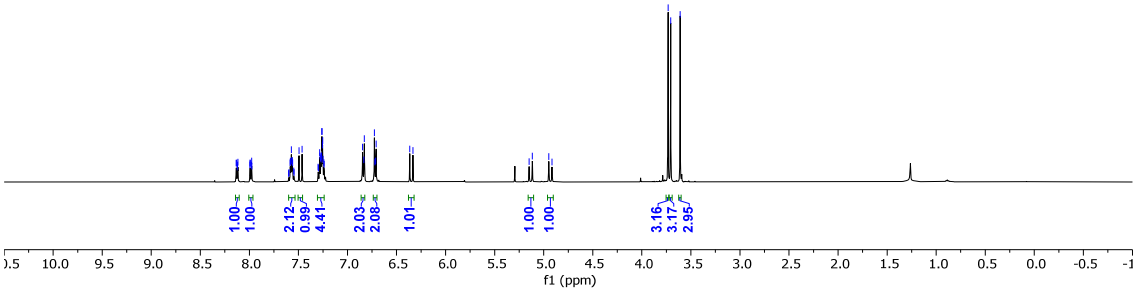
4n


f1 (ppm)

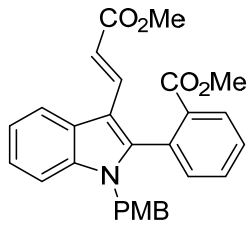

8.14
8.13
8.12
8.12
8.12
7.99
7.99
7.99
7.98
7.98
7.97
7.60
7.60
7.58
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.54
7.49
7.46
7.30
7.30
7.28
7.28
7.27
7.27
7.27
7.26
7.26 CDCl3
7.26
7.26
7.25
7.25
7.24
7.24
6.85
6.83
6.83
6.73
6.72
6.71
6.71
6.36
6.33
5.15
5.12
4.95
4.92
3.73
3.71
3.61


CO2Me
CO2Me
N
PMB

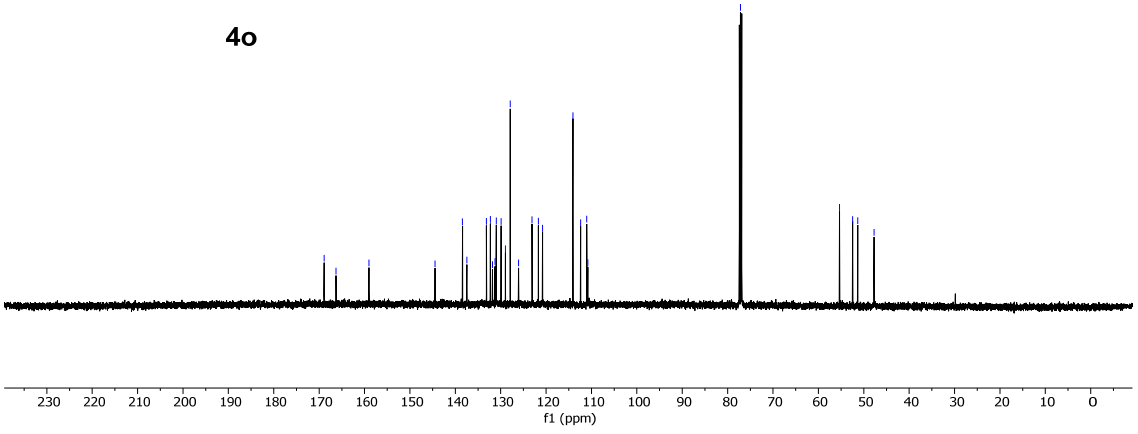
4o

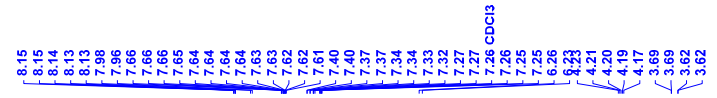

1.00
1.00
2.12
0.99
4.41
2.03
2.08
1.01
1.00
1.00
3.16
3.17
2.95
f1 (ppm)

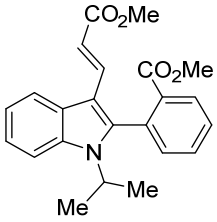

168.89
166.29
159.03
144.47
138.42
137.46
133.14
132.27
131.80
131.25
130.98
129.91
128.96
127.90
126.07
123.09
121.70
120.77
114.07
112.38
111.03
110.82
77.16 CDCl3
55.36
52.45
51.34
47.74


CO2Me
CO2Me
N
PMB

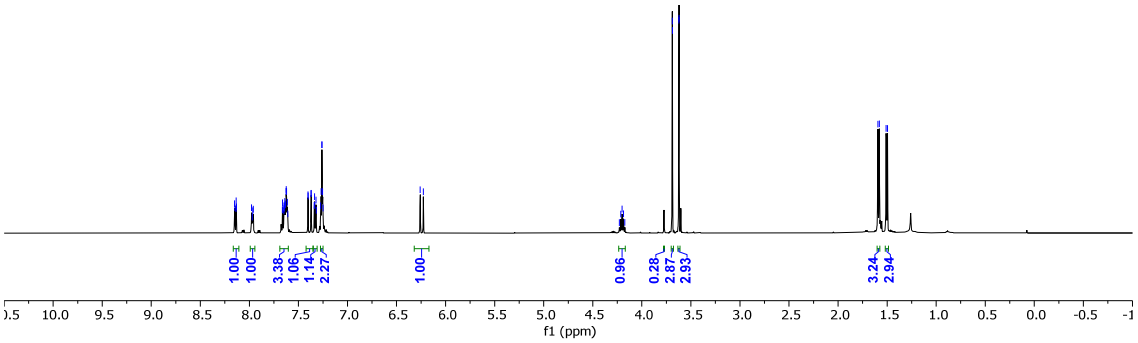
4o


f1 (ppm)

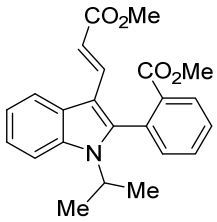

8.15
8.15
8.14
8.13
8.13
7.98
7.96
7.66
7.66
7.66
7.65
7.64
7.64
7.64
7.64
7.63
7.63
7.62
7.62
7.61
7.40
7.40
7.37
7.37
7.34
7.34
7.33
7.32
7.27
7.27
7.26 CDCl3
7.26
7.25
7.25
6.26
4.23
4.21
4.20
4.19
4.17
3.69
3.69
3.62
3.62
1.59
1.58
1.51
1.50


CO2Me
CO2Me
N
Me
Me

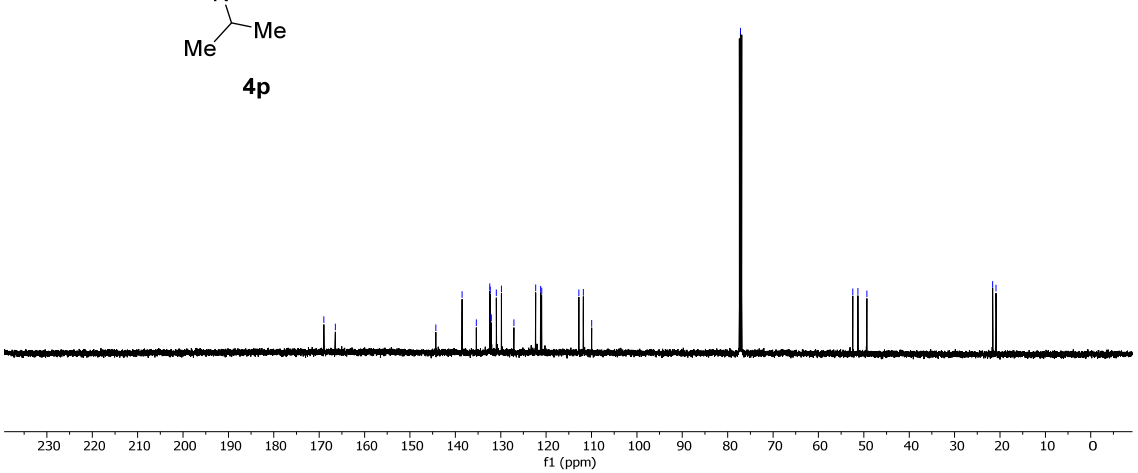
4p

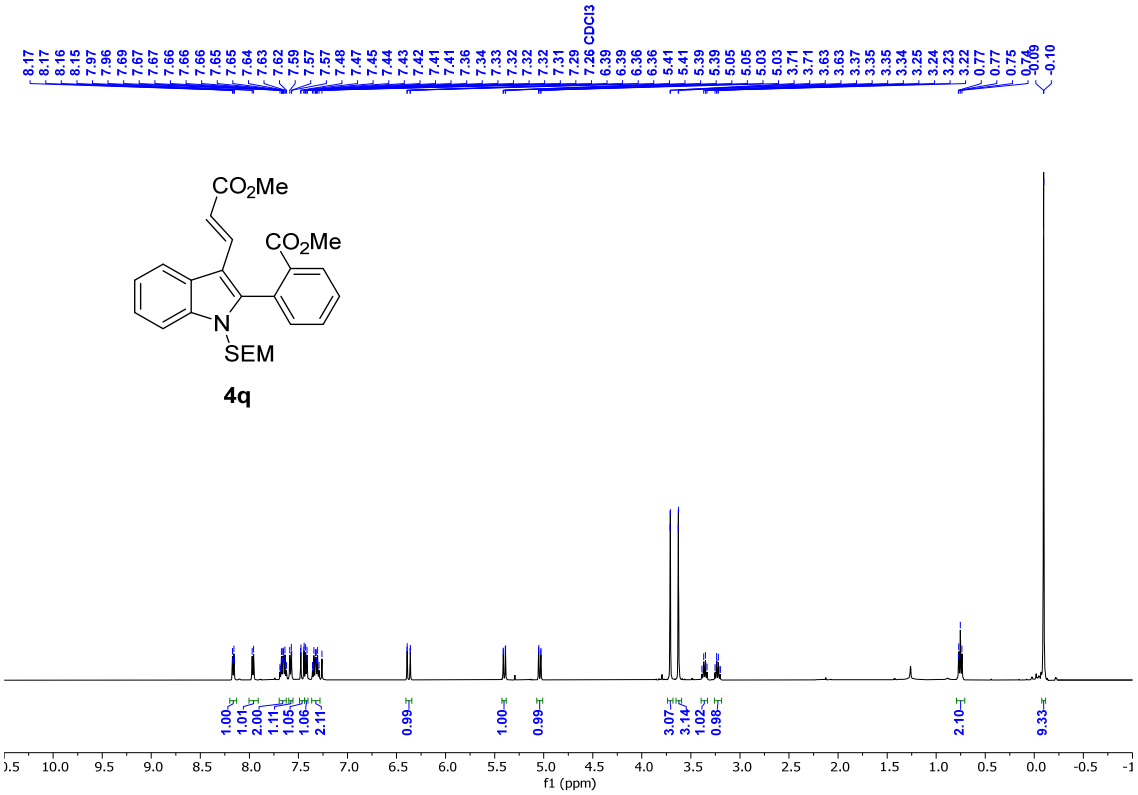

1.00
1.00
3.38
1.06
1.14
2.27
1.00
0.96
0.28
2.87
2.93
3.24
2.94
f1 (ppm)

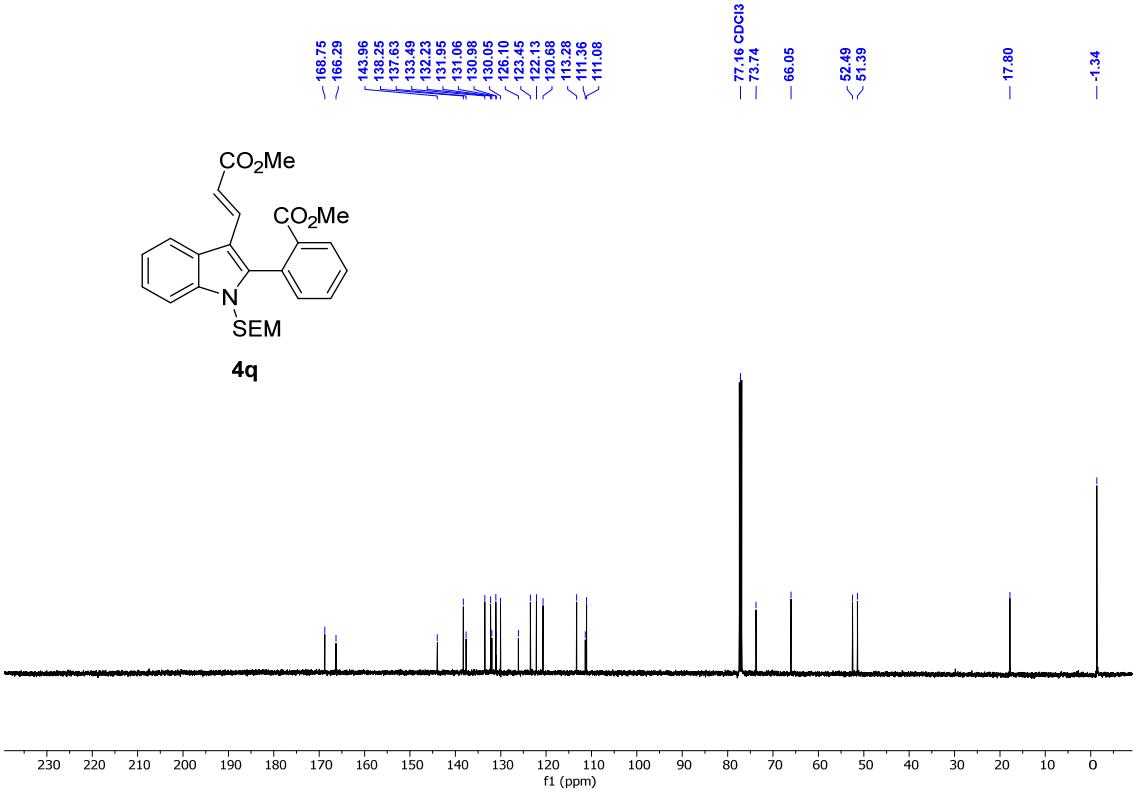

168.96
166.45
144.29
138.51
135.37
132.43
132.31
132.12
132.09
130.96
129.86
127.11
122.31
121.20
120.98
112.77
111.79
109.97
77.16 CDCl3
52.43
51.29
49.32
21.60
20.87

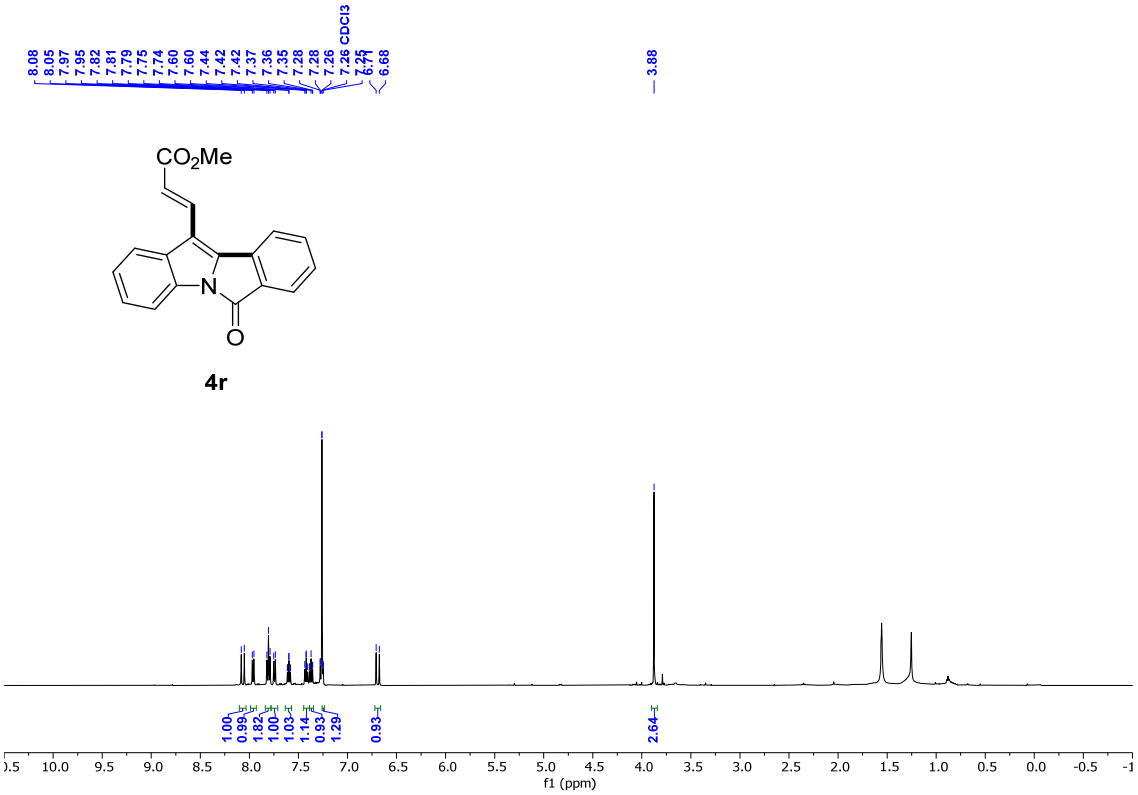

CO2Me
CO2Me
N
Me
Me

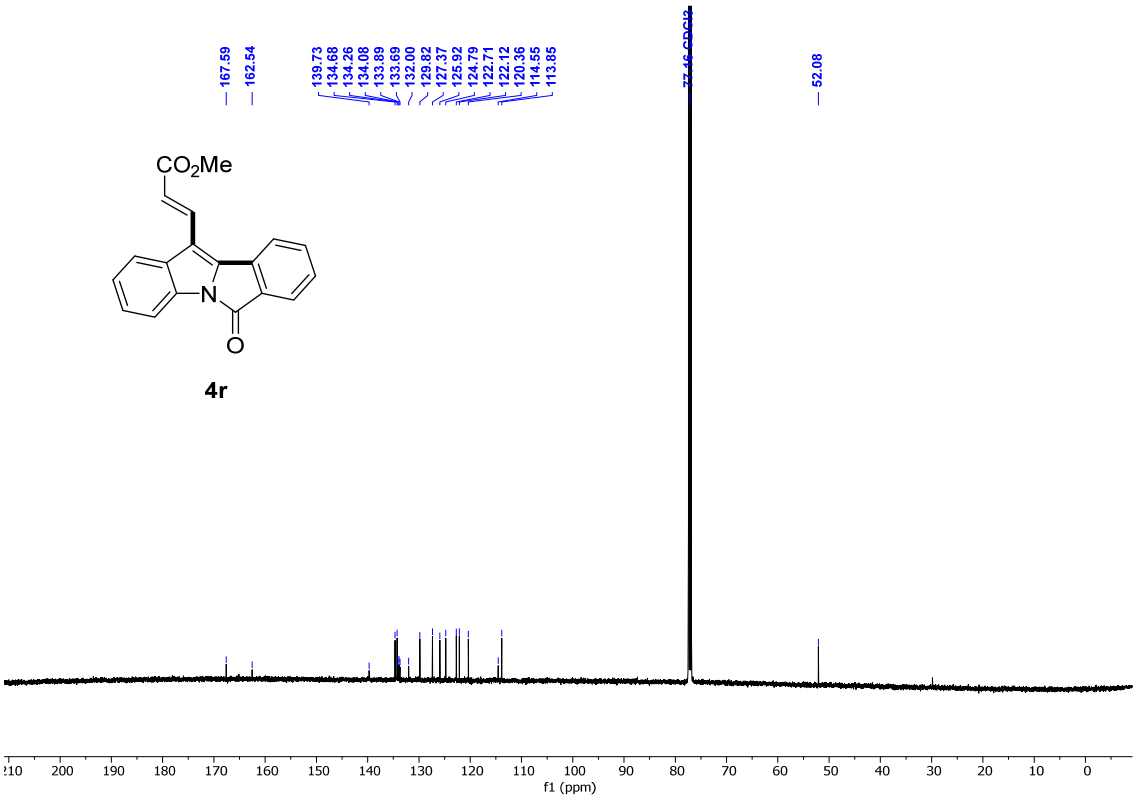
4p

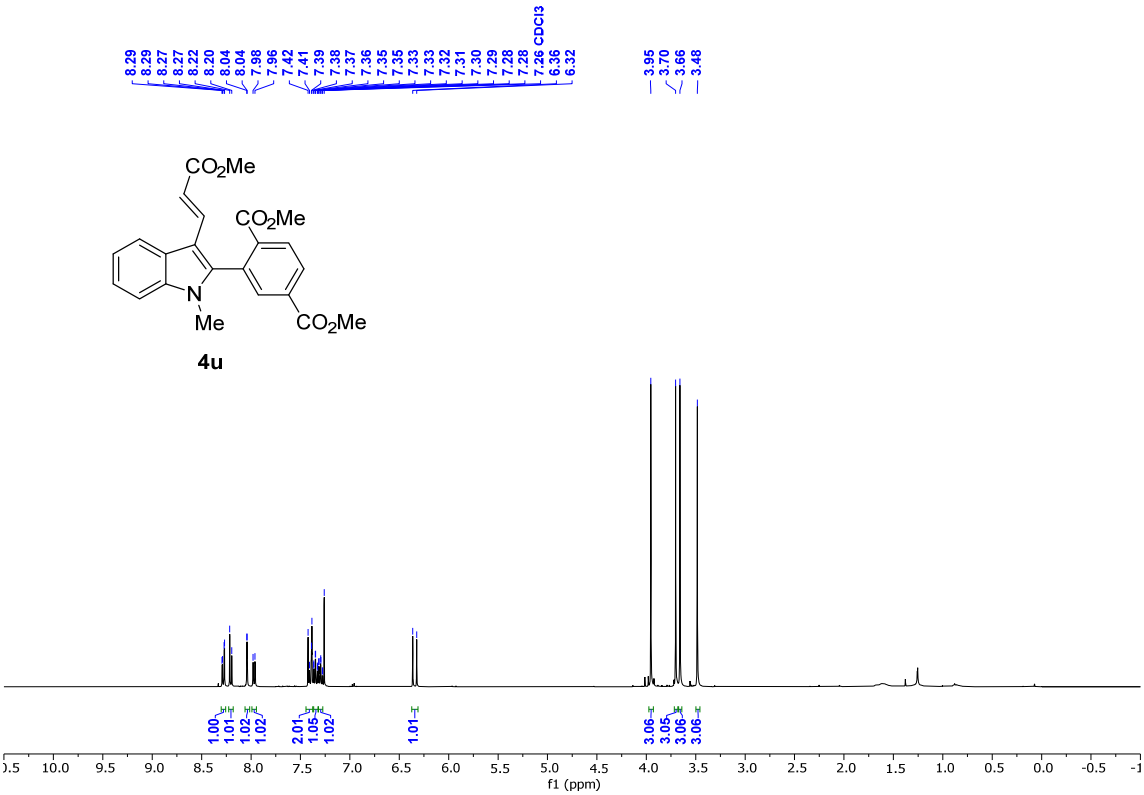

f1 (ppm)


8.17
8.17
8.16
8.15
7.97
7.96
7.69
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.64
7.63
7.62
7.59
7.57
7.57
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.41
7.36
7.34
7.33
7.32
7.32
7.31
7.29
7.26 CDCl3
6.39
6.39
6.36
6.36
5.41
5.41
5.39
5.39
5.05
5.05
5.03
5.03
3.71
3.71
3.63
3.63
3.37
3.35
3.35
3.34
3.25
3.24
3.23
3.22
0.77
0.77
0.75
0.74
0.09
-0.10
CO2Me
CO2Me
N
SEM
4q
1.00
1.01
2.00
1.11
1.05
1.06
2.11
0.99
1.00
0.99
3.07
3.14
1.02
0.98
2.10
9.33
f1 (ppm)

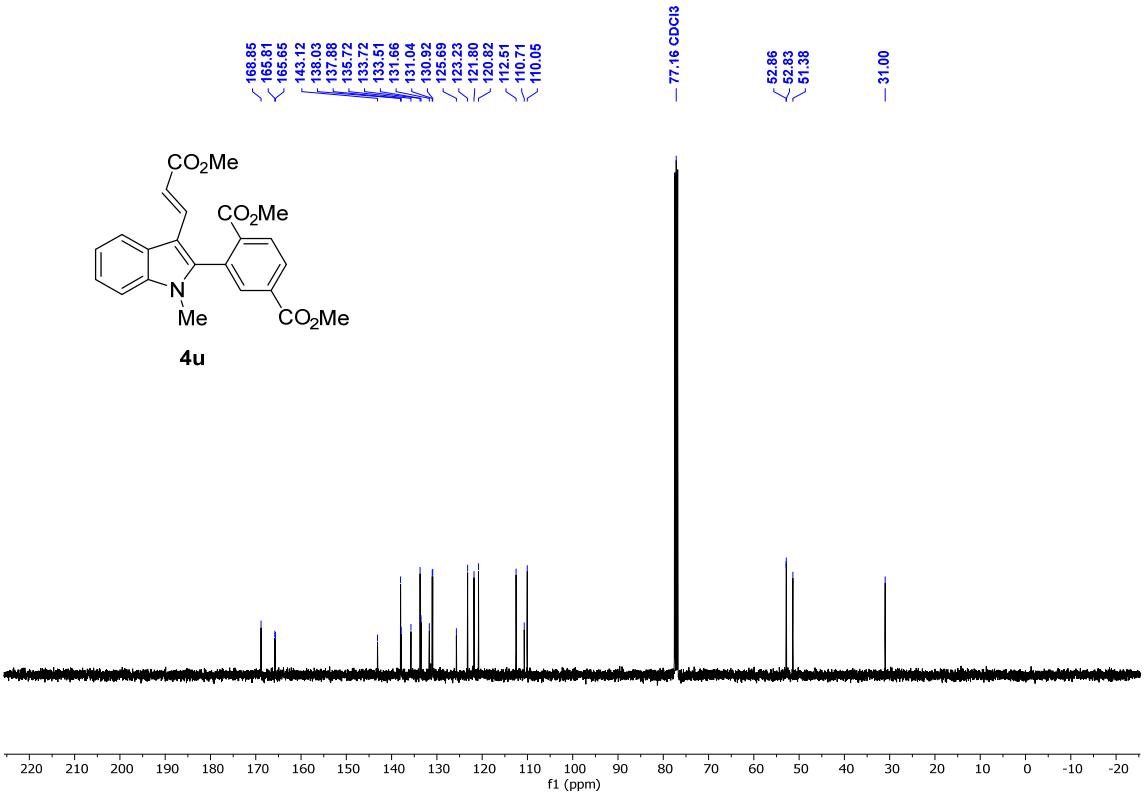

168.75
166.29
143.96
138.25
137.63
133.49
132.23
131.95
131.06
130.98
130.05
126.10
123.45
122.13
120.68
113.28
111.36
111.08
77.16 CDCl3
73.74
66.05
52.49
51.39
17.80
-1.34
CO2Me
CO2Me
N
SEM
4q
f1 (ppm)


8.08
8.05
7.97
7.95
7.82
7.81
7.79
7.75
7.74
7.60
7.60
7.44
7.42
7.42
7.37
7.36
7.35
7.28
7.28
7.26
7.26 CDCl3
6.71
6.68
3.88
CO2Me
N
O
4r
1.00
0.99
1.82
1.00
1.03
1.14
0.93
1.29
0.93
2.64
f1 (ppm)

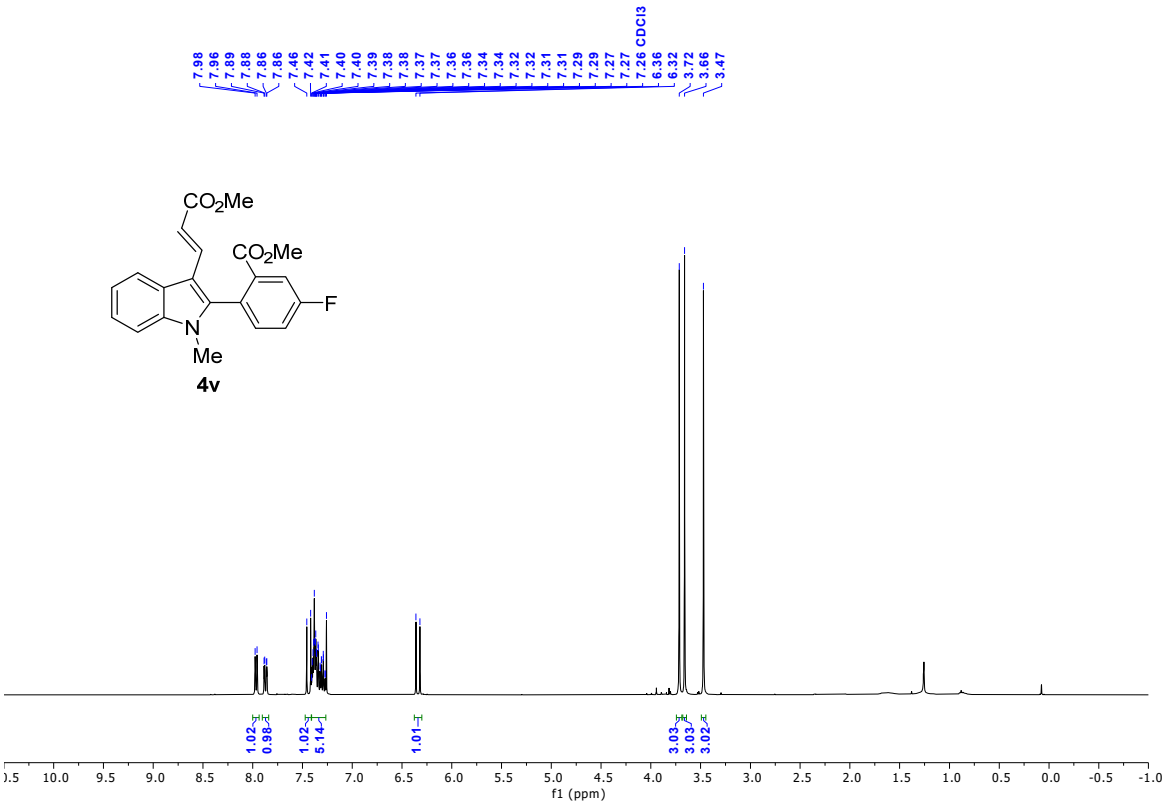

167.59
162.54
139.73
134.68
134.26
134.08
133.89
133.69
132.00
129.82
127.37
125.92
124.79
122.71
122.12
120.36
114.55
113.85
77.46 CDCl3
52.08
CO2Me
N
O
4r
f1 (ppm)

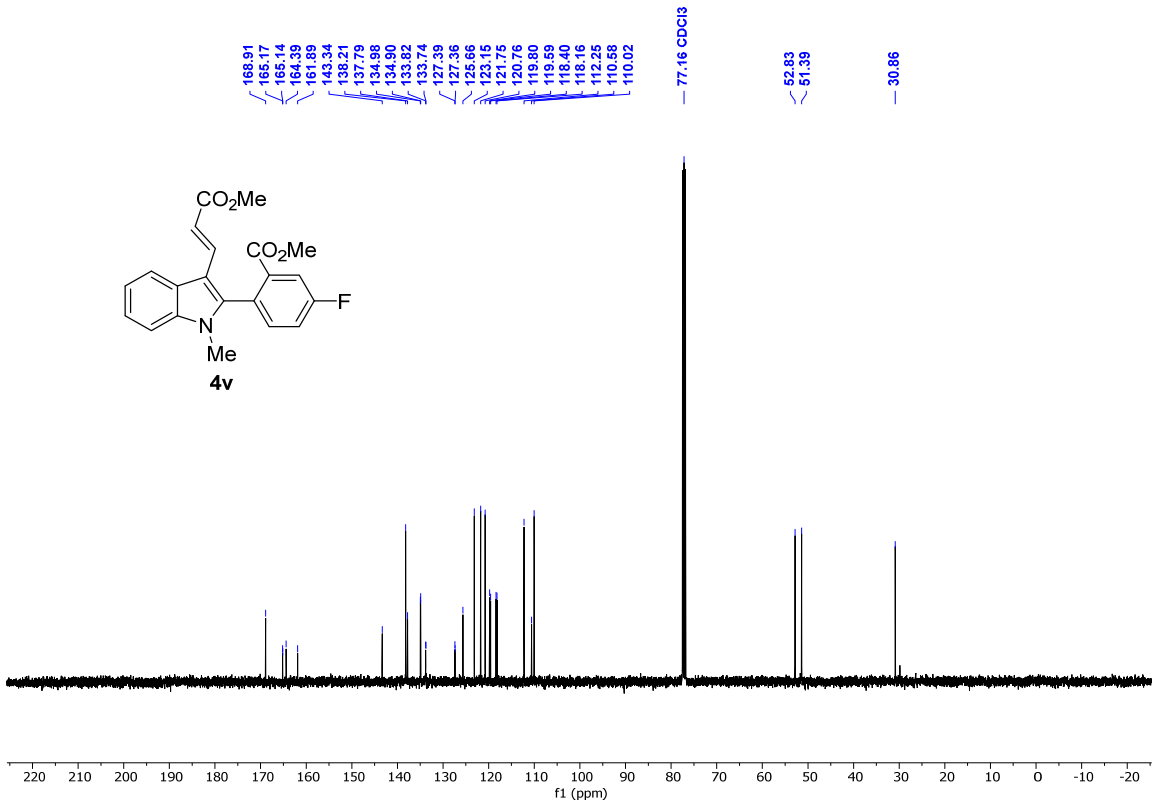

8.29
8.29
8.27
8.27
8.22
8.20
8.04
8.04
7.98
7.96
7.42
7.41
7.39
7.38
7.37
7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.28
CDCl3
7.26
6.36
6.32
3.95
3.70
3.66
3.48
CO2Me
CO2Me
N
Me
CO2Me
1.00
1.01
1.02
1.02
2.01
1.05
1.02
1.01
3.06
3.05
3.06
3.06
f1 (ppm)

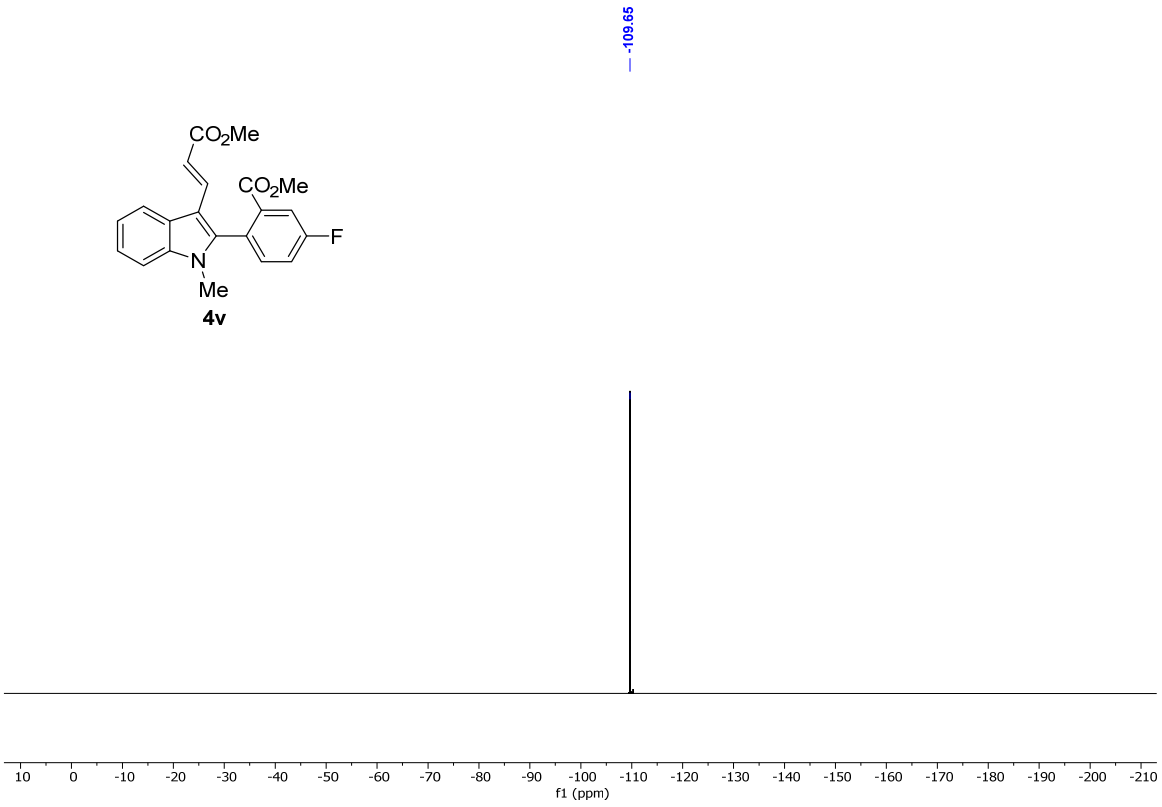
4u

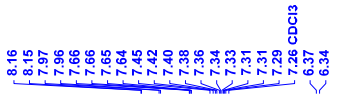

168.85
165.81
165.65
143.12
138.03
137.88
135.72
133.72
133.51
131.66
131.04
130.92
129.69
123.23
121.80
120.82
112.51
110.71
110.05
77.16 CDCl3
52.86
52.83
51.38
31.00
CO2Me
CO2Me
N
Me
CO2Me
f1 (ppm)

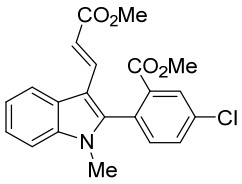
4u


7.98
7.96
7.89
7.88
7.86
7.86
7.46
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.31
7.29
7.29
7.27
7.27
7.26 CDCl3
6.36
6.32
3.72
3.66
3.47
CO2Me
CO2Me
F
N
Me
4v
1.02
0.98
1.02
5.14
1.01
3.03
3.03
3.02
f1 (ppm)

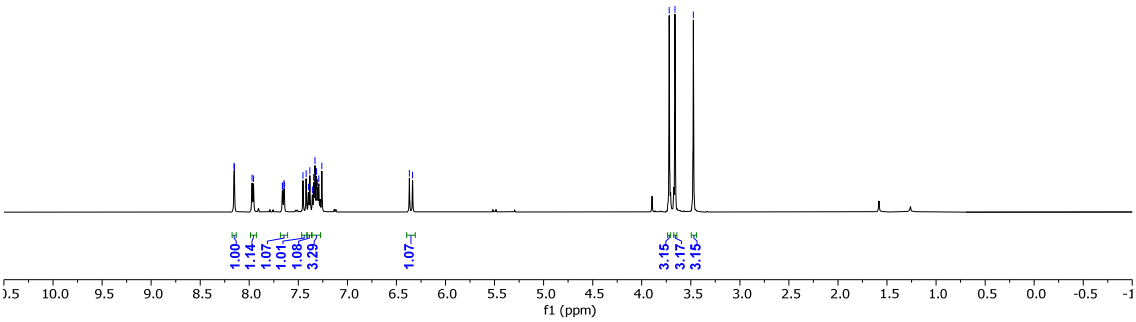

168.91
165.17
165.14
164.39
161.89
143.34
138.21
137.79
134.98
134.90
133.82
133.74
127.39
127.36
125.66
123.15
121.75
120.76
119.80
119.59
118.40
118.16
112.25
110.58
110.02
77.16 CDCl3
52.83
51.39
30.86
CO2Me
CO2Me
F
N
Me
4v
f1 (ppm)


-109.65
CO2Me
CO2Me
F
N
Me
4v
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

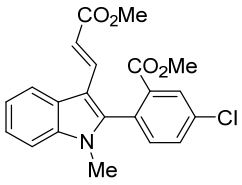

8.16
8.15
7.97
7.96
7.66
7.66
7.65
7.64
7.45
7.42
7.40
7.38
7.36
7.34
7.33
7.31
7.29
7.26 CDCl3
6.37
6.34
3.72
3.66
3.47


CO2Me
CO2Me
Cl
N
Me

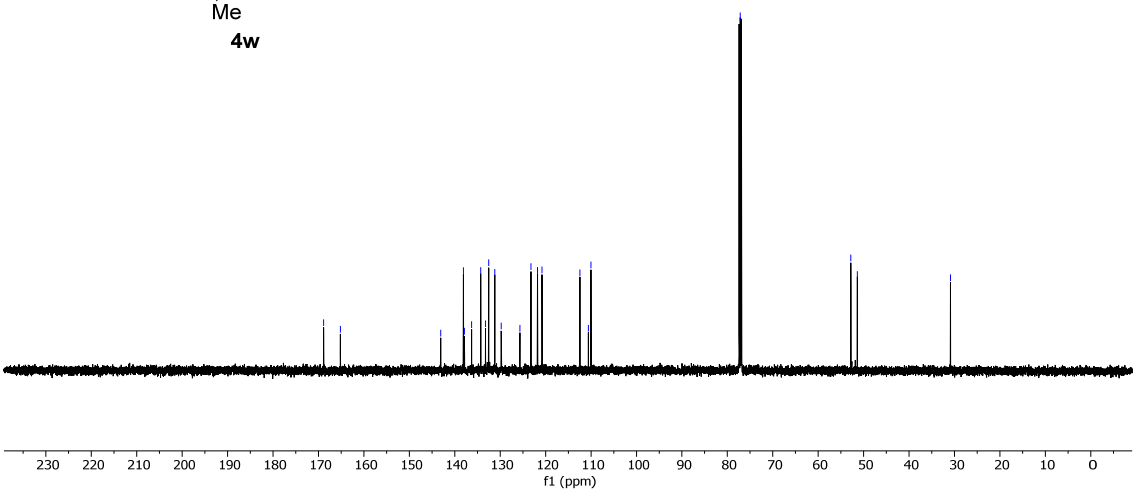
4w

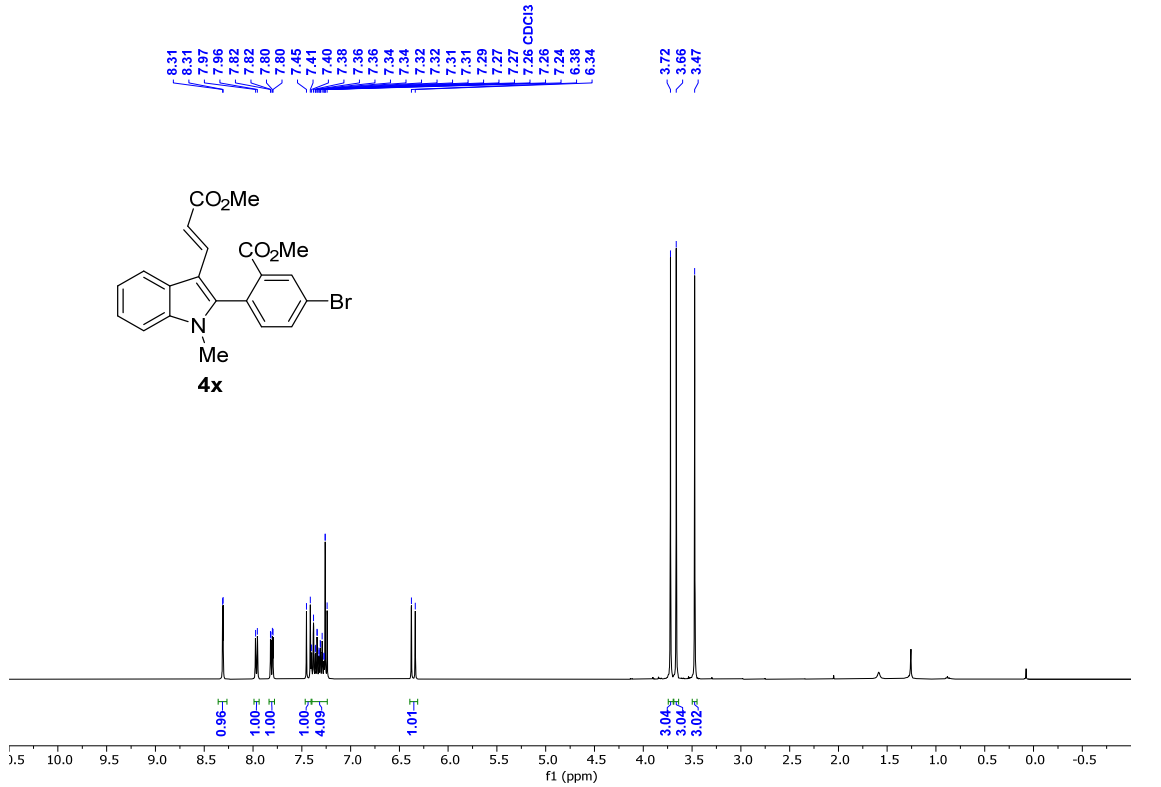

1.00
1.14
1.07
1.01
1.08
3.29
1.07
3.15
3.17
3.15
f1 (ppm)

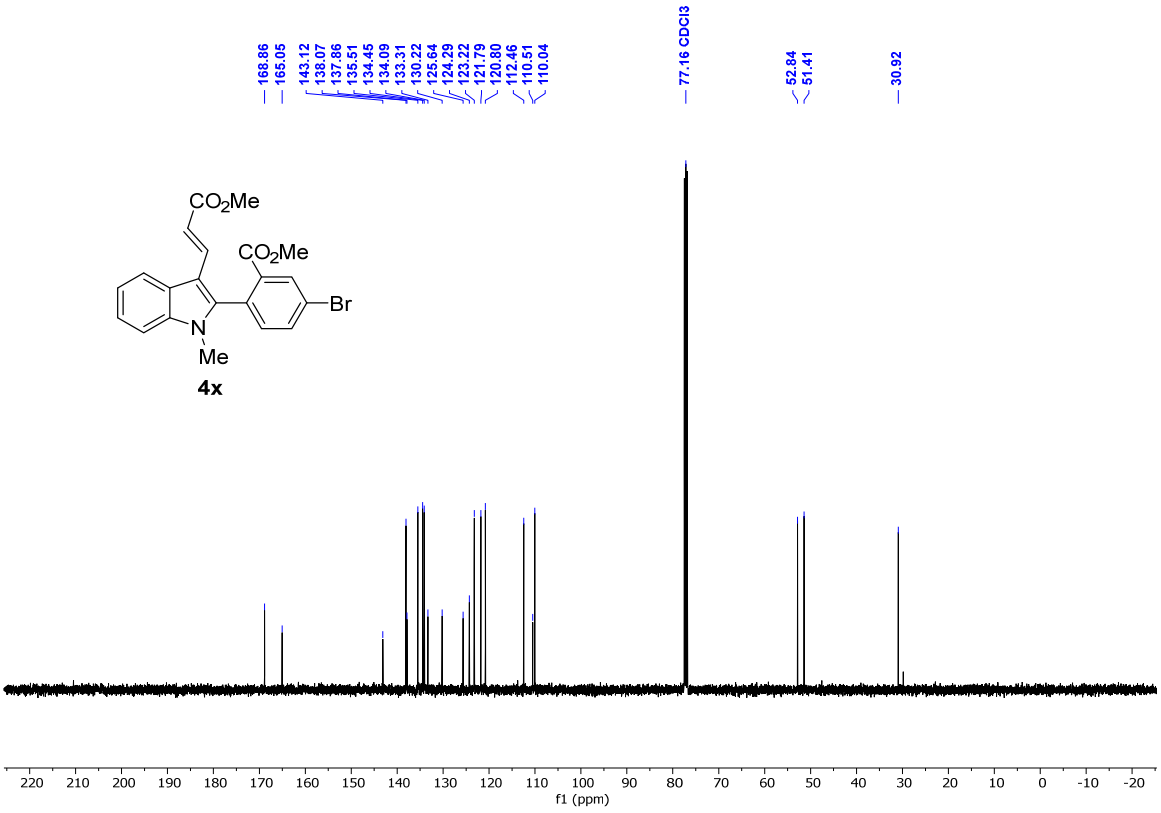

168.85
165.17
143.08
138.07
137.87
136.29
134.28
133.23
132.53
131.19
129.76
125.67
123.21
121.78
120.79
112.46
110.57
110.03
77.16 CDCl3
52.82
51.38
30.90


CO2Me
CO2Me
Cl
N
Me

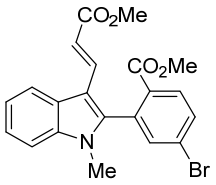
4w


f1 (ppm)

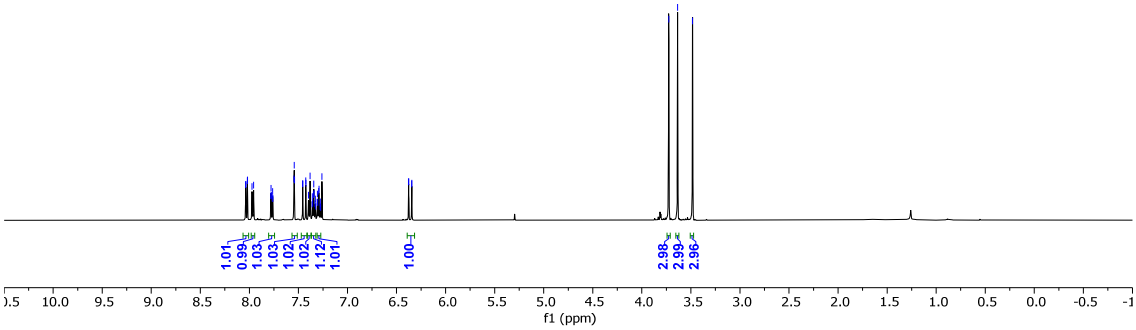

8.31
8.31
7.97
7.96
7.82
7.82
7.80
7.80
7.45
7.41
7.40
7.38
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.31
7.29
7.27
7.27
7.26 CDCl3
7.24
6.38
6.34
3.72
3.66
3.47
CO2Me
CO2Me
Br
N
Me
4x
0.96
1.00
1.00
1.00
4.09
1.01
3.04
3.04
3.02
f1 (ppm)


168.86
165.05
143.12
138.07
137.86
135.51
134.45
134.09
133.31
130.22
125.64
124.29
123.22
121.79
120.80
112.46
110.51
110.04
77.16 CDCl3
52.84
51.41
30.92
CO2Me
CO2Me
Br
N
Me
4x
f1 (ppm)


8.04
8.04
8.02
8.02
7.97
7.96
7.78
7.78
7.78
7.77
7.76
7.76
7.55
7.54
7.54
7.46
7.46
7.43
7.42
7.40
7.38
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26 CDCl3
6.38
6.38
6.35
6.34
3.72
3.64
3.48


CO2Me
CO2Me
N
Me
Br

4y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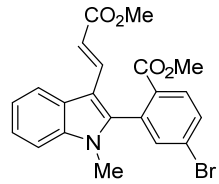
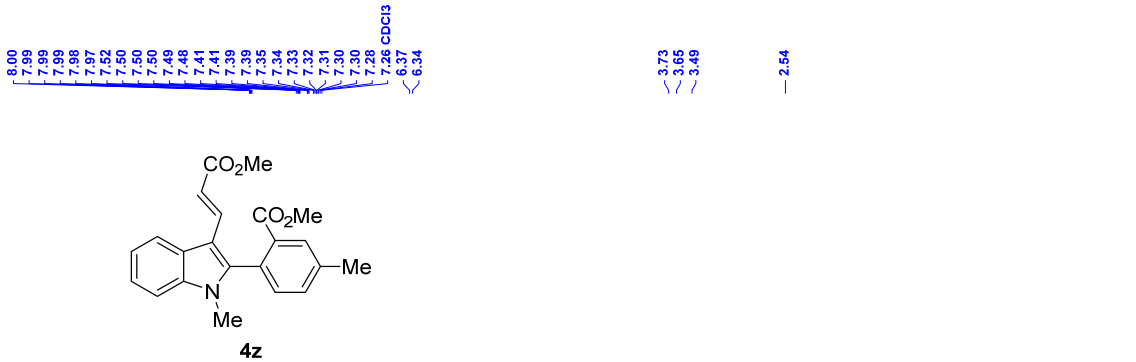
1.03
1.03
1.02
1.02
1.12
1.01
1.00
2.98
2.99
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.83
165.64
142.63
137.94
137.85
135.68
133.38
133.24
132.42
130.73
127.23
125.63
123.26
121.81
120.85
112.67
110.58
110.04
77.16 CDCl3
52.70
51.40
30.97


CO2Me
CO2Me
N
Me
Br

4y

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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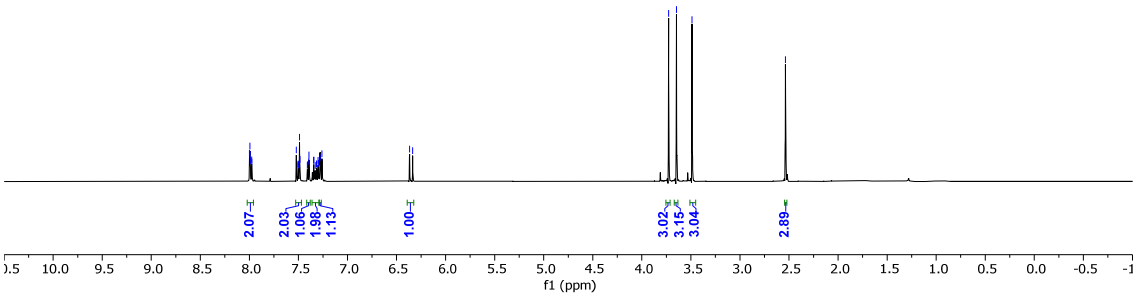
7.49
7.48
7.41
7.41
7.39
7.39
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.28
7.26 CDCl3
6.37
6.34
3.73
3.65
3.49
2.54
CO2Me
CO2Me
Me
N
Me

4z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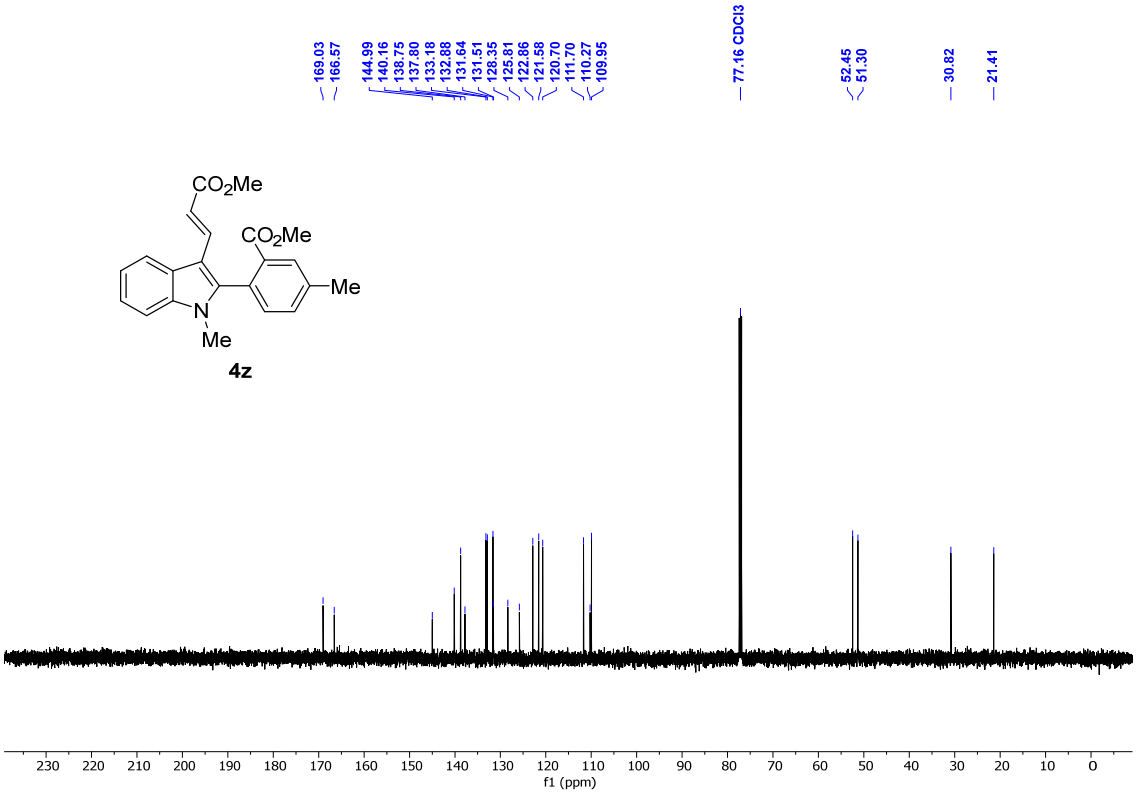
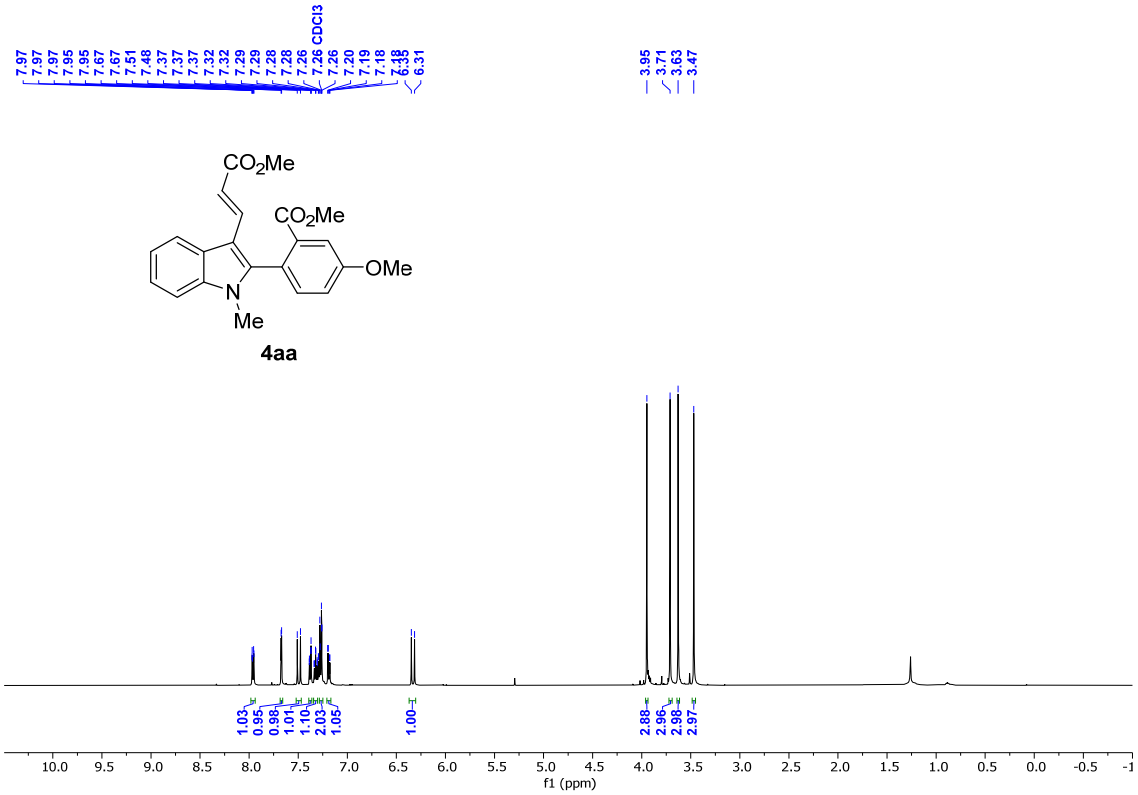
2.03
1.06
1.98
1.13
1.00
3.02
3.15
3.04
2.89
f1 (ppm)


169.03
166.57
144.99
140.16
138.75
137.80
133.18
132.88
131.64
131.51
128.35
125.81
122.86
121.58
120.70
111.70
110.27
109.95
77.16 CDCl3
52.45
51.30
30.82
21.41
CO2Me
CO2Me
Me
N
Me
f1 (ppm)

4z


7.97
7.97
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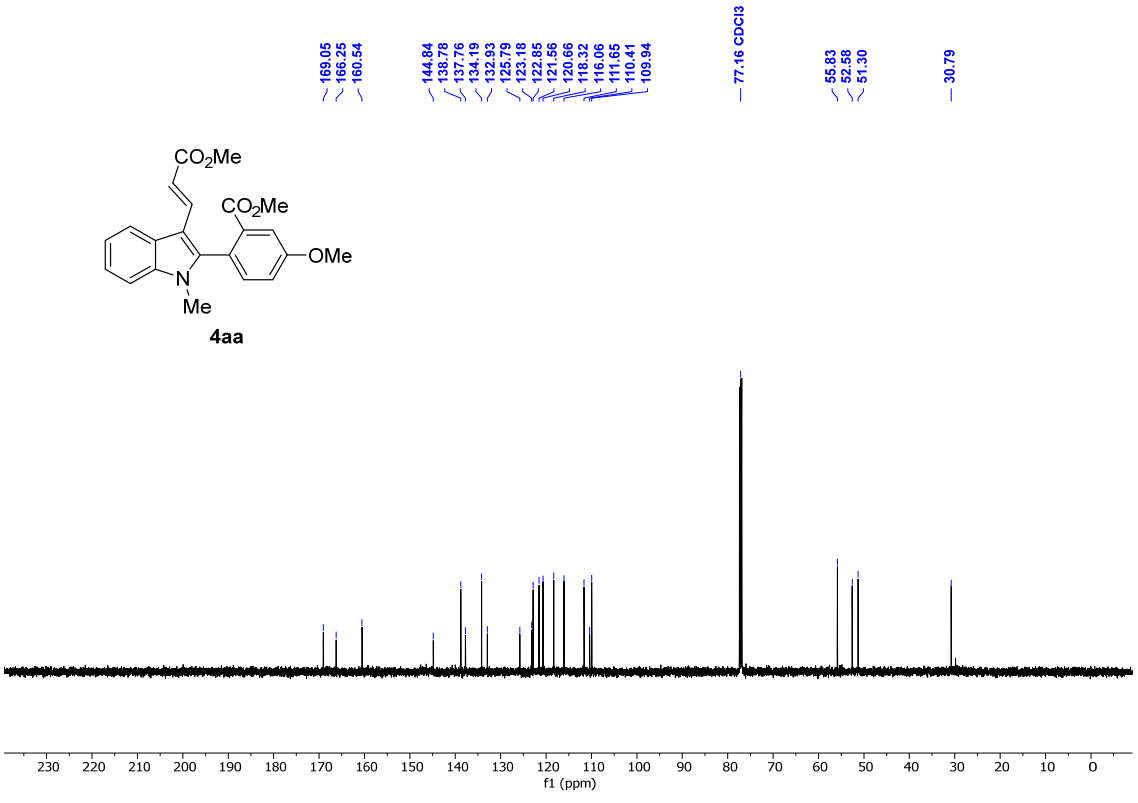
7.48
7.37
7.37
7.37
7.32
7.32
7.29
7.29
7.28
7.28
7.26
7.26
CDCl3
7.26
7.20
7.19
7.18
7.18
6.33
6.31
3.95
3.71
3.63
3.47
CO2Me
CO2Me
OMe
N
Me
1.03
0.95
0.98
1.01
1.10
2.03
1.05
1.00
2.88
2.96
2.98
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

4aa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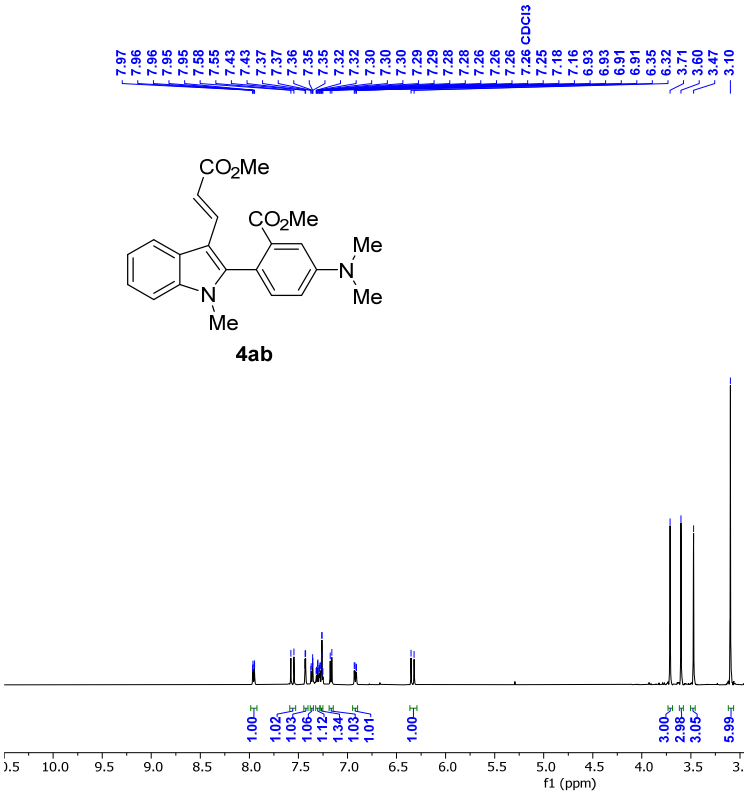
166.25
160.54
144.84
138.78
137.76
134.19
132.93
125.79
123.18
122.85
121.56
120.66
118.32
116.06
111.65
110.41
109.94
77.16 CDCl3
55.83
52.58
51.30
30.79
CO2Me
CO2Me
OMe
N
Me
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4aa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7.96
7.95
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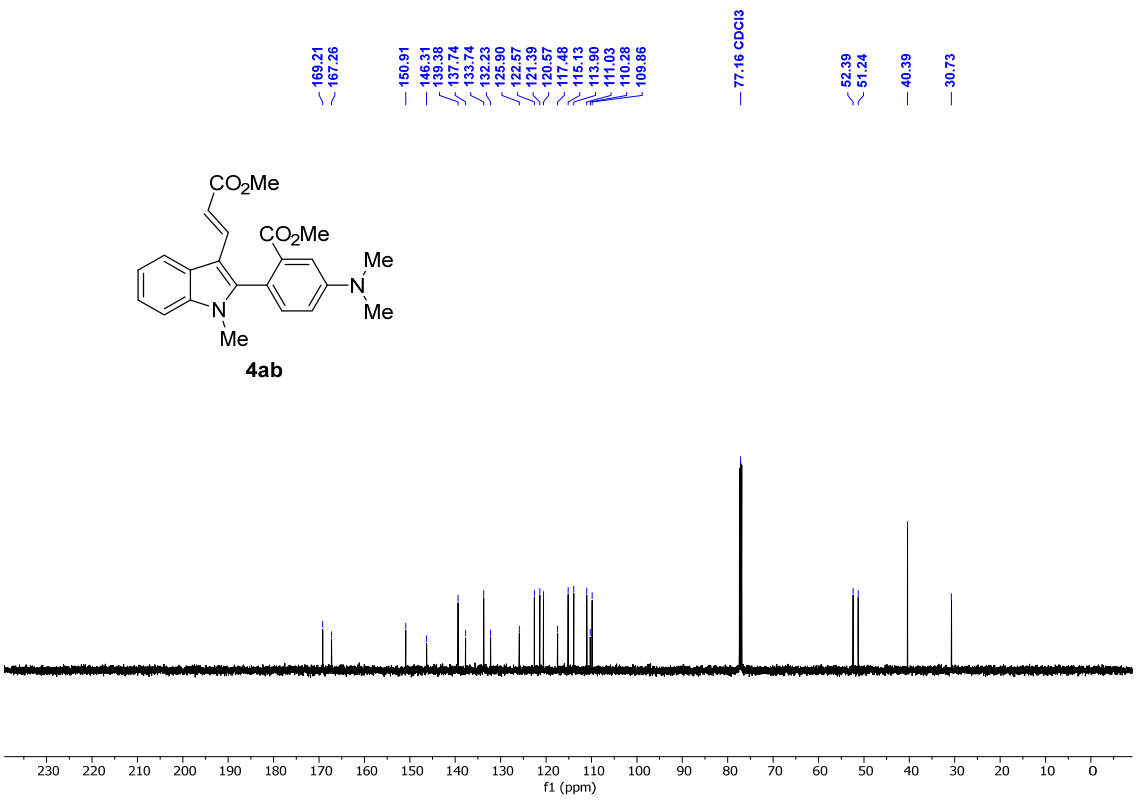
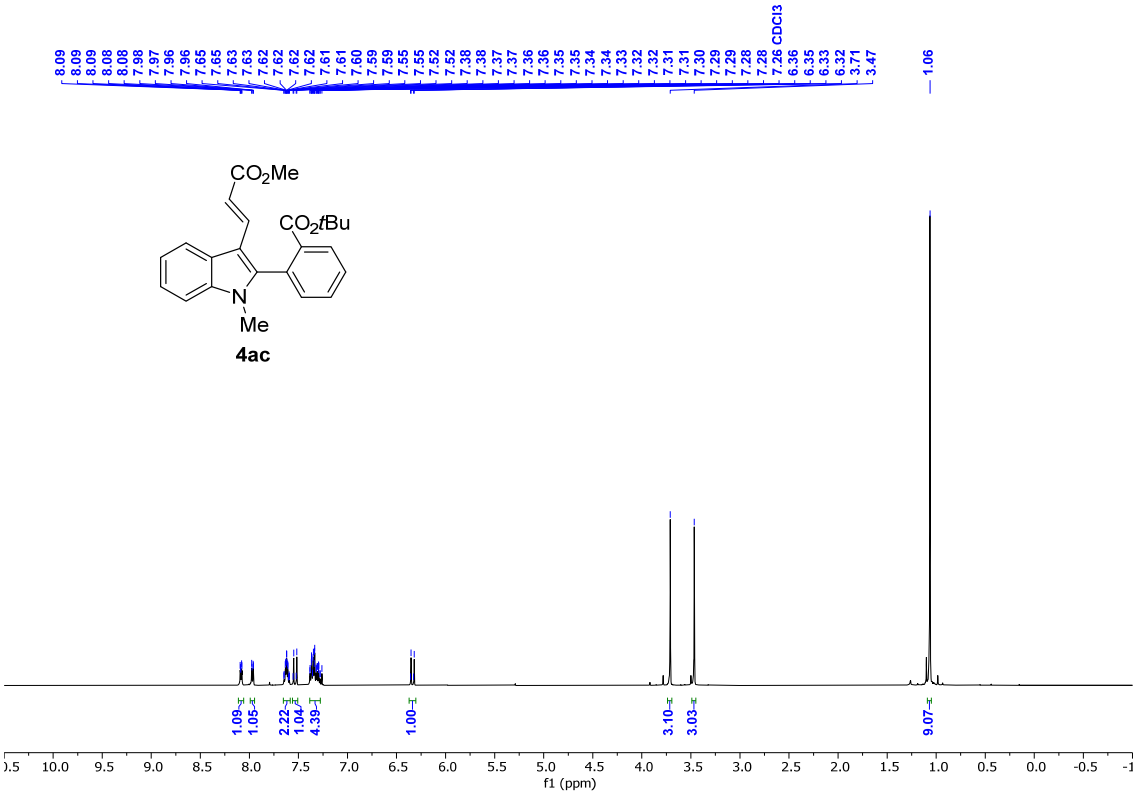
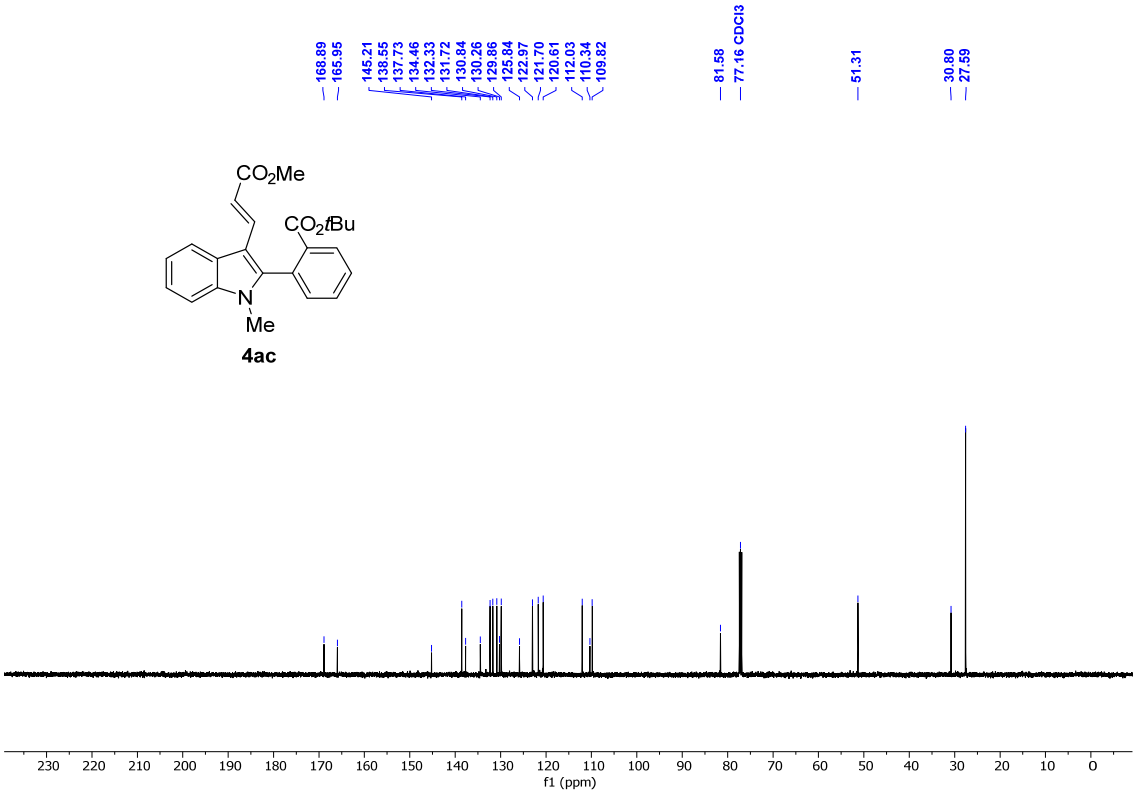
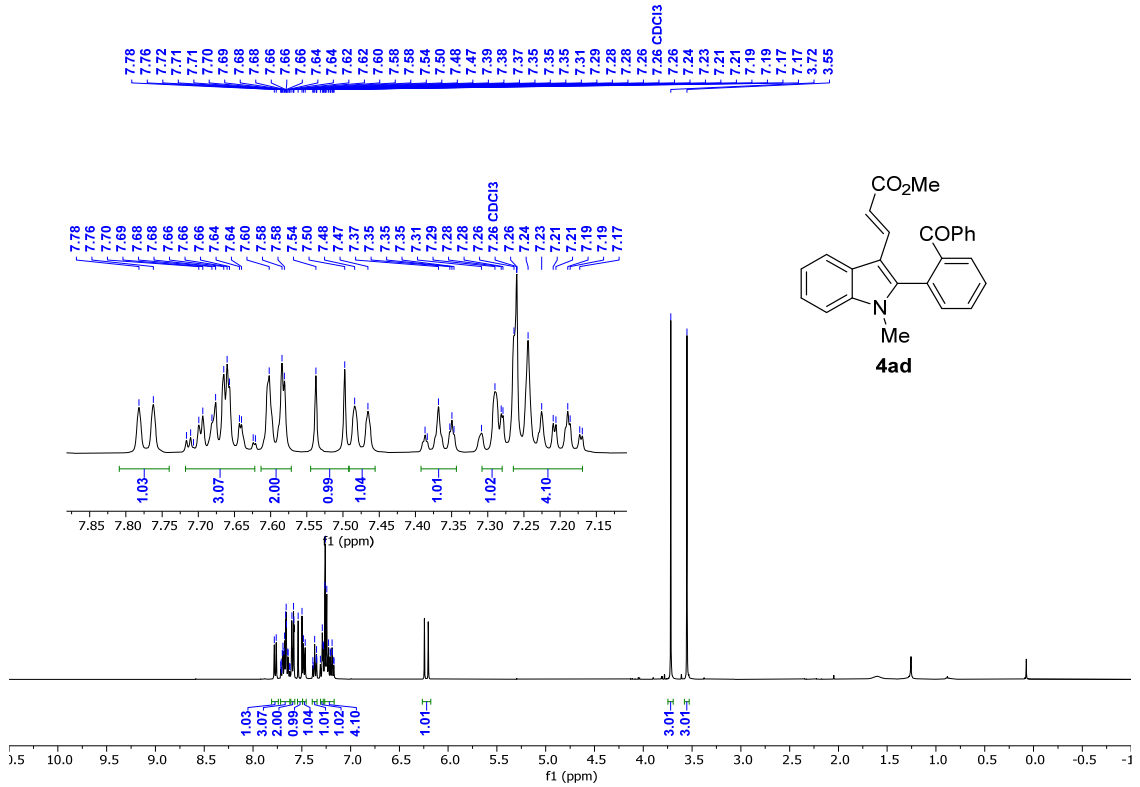
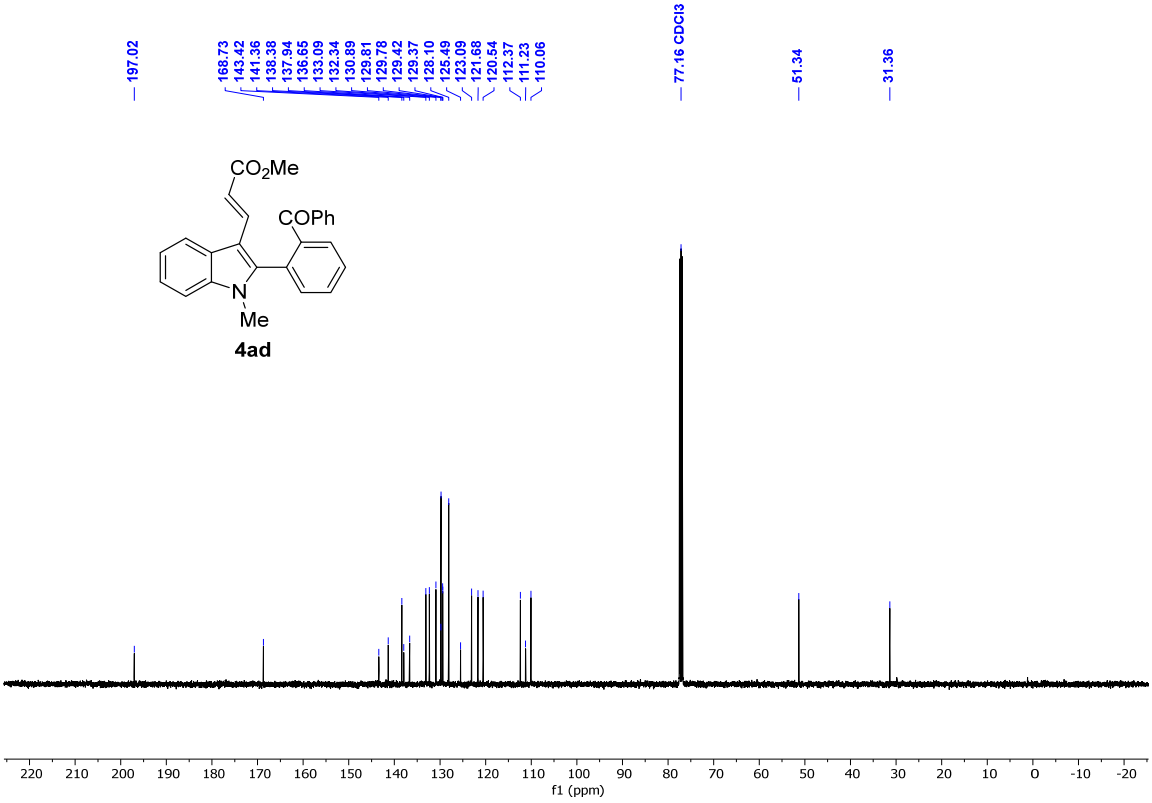
7.55
7.43
7.43
7.37
7.37
7.36
7.35
7.35
7.32
7.32
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.26
7.26 CDCl3
7.25
7.18
7.16
6.93
6.93
6.91
6.91
6.35
6.32
3.71
3.60
3.47
3.10
CO2Me
CO2Me
Me
N
Me
N
Me
4ab
1.00
1.02
1.03
1.06
1.12
1.34
1.03
1.01
1.00
3.00
2.98
3.05
5.99
f1 (ppm)

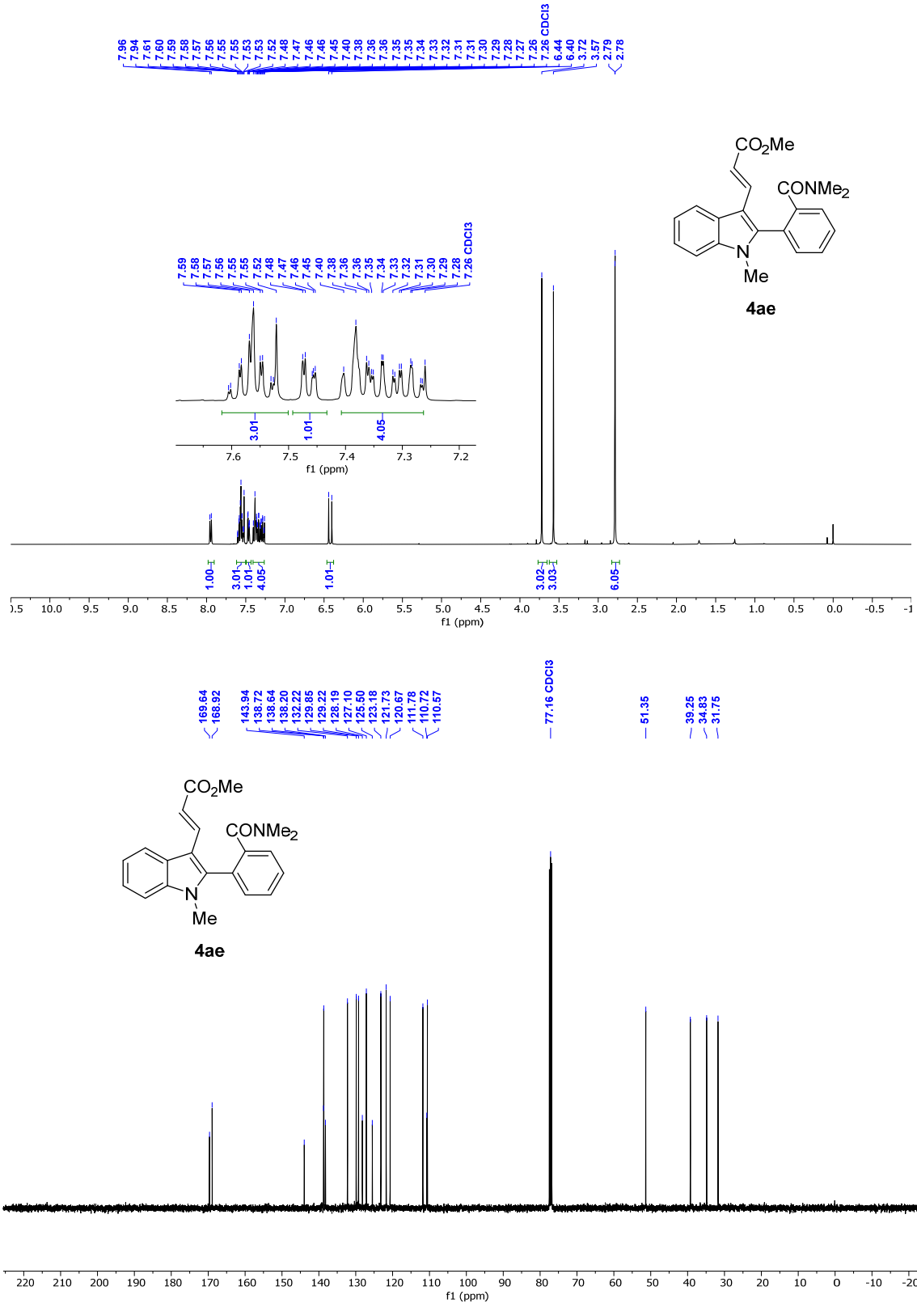

169.21
167.26
150.91
146.31
139.38
137.74
133.74
132.23
125.90
122.57
121.39
120.57
117.48
115.13
113.90
111.03
110.28
109.86
77.16 CDCl3
52.39
51.24
40.39
30.73
CO2Me
CO2Me
Me
N
Me
N
Me
4ab
f1 (ppm)

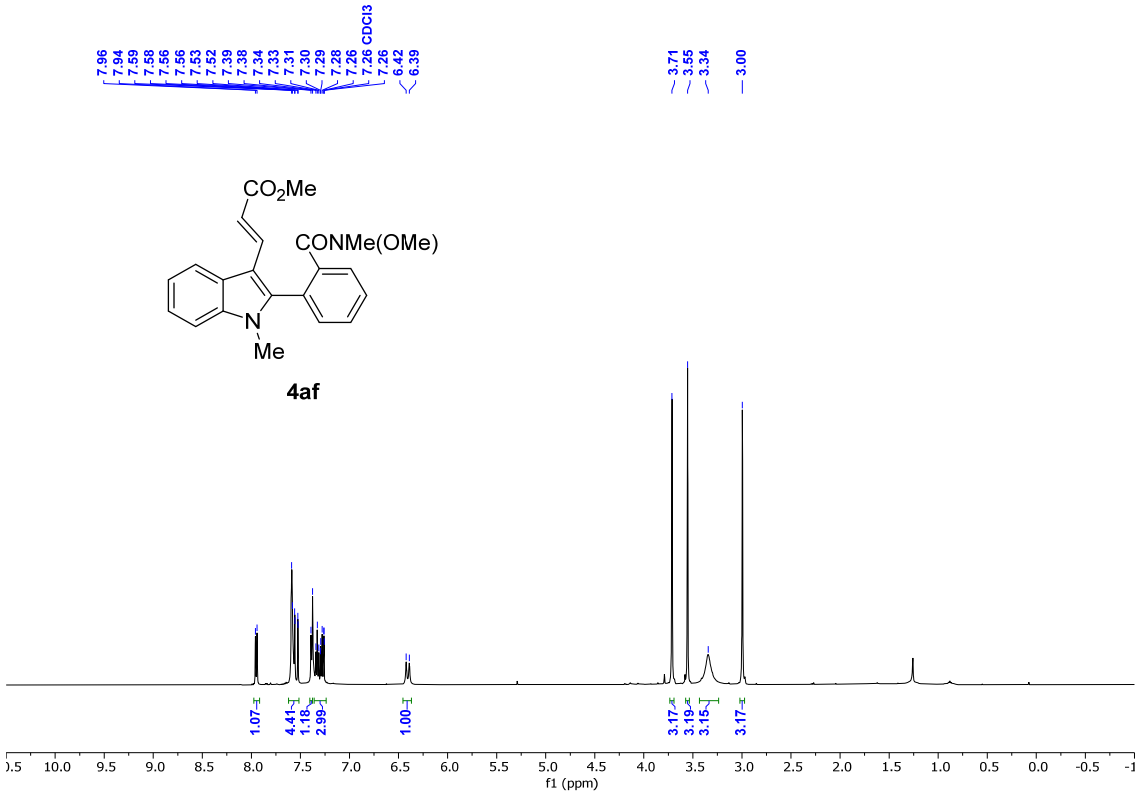

8.09 8.09 8.09 8.08 8.08 8.08 7.98 7.97 7.96 7.96 7.65 7.65 7.63 7.63 7.62 7.62 7.62 7.62 7.61 7.61 7.60 7.59 7.59 7.55 7.55 7.52 7.52 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.26 CDCl3 6.36 6.35 6.33 6.32 3.71 3.47 1.06
CO2Me
CO2tBu
N
Me
4ac
1.09 1.05 2.22 1.04 4.39 1.00 3.10 3.03 9.07
f1 (ppm)


168.89 165.95 145.21 138.55 137.73 134.46 132.33 131.72 130.84 130.26 129.86 125.84 122.97 121.70 120.61 112.03 110.34 109.82 81.58 77.16 CDCl3 51.31 30.80 27.59
CO2Me
CO2tBu
N
Me
4ac
f1 (ppm)


CO2Me
COPh
N
Me
4ad
f1 (ppm)


CO2Me
COPh
N
Me
4ad
f1 (ppm)


7.96 7.94 7.61 7.60 7.59 7.58 7.57 7.56 7.55 7.53 7.52 7.48 7.47 7.46 7.46 7.45 7.40 7.38 7.36 7.36 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.26 CDCl3 6.44 6.40 3.72 3.57 2.79 2.78
CO2Me
CONMe2
N
Me
4ae
7.59 7.58 7.57 7.56 7.55 7.55 7.52 7.48 7.47 7.46 7.45 7.40 7.38 7.36 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.26 CDCl3
3.01 1.01 4.05
7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.00 3.01 1.01 4.05 1.01 3.02 3.03 6.05
f1 (ppm)
169.64 168.92 143.94 138.72 138.64 138.20 132.22 129.85 129.22 128.19 127.10 125.50 123.18 121.73 120.67 111.78 110.72 110.57 77.16 CDCl3 51.35 39.25 34.83 31.75
CO2Me
CONMe2
N
Me
4ae
f1 (ppm)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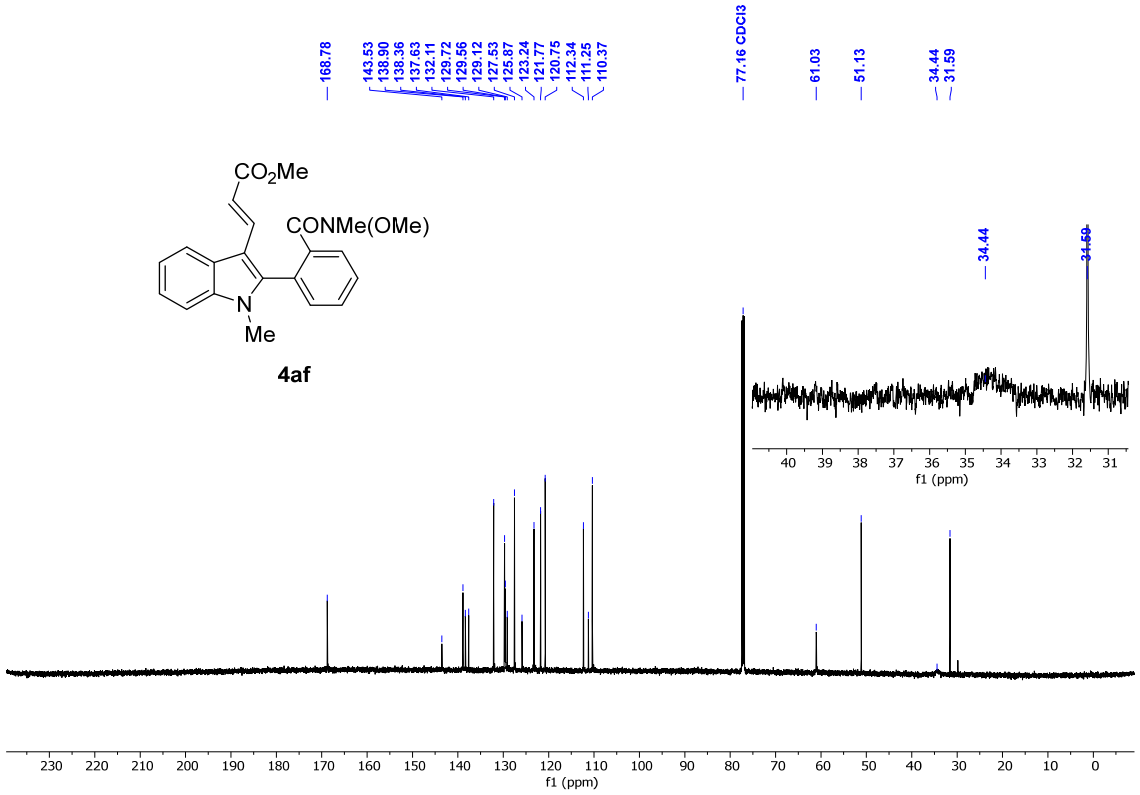
7.59
7.58
7.56
7.56
7.53
7.52
7.39
7.38
7.34
7.33
7.31
7.30
7.29
7.28
7.26
7.26 CDCl3
7.26
6.42
6.39
3.71
3.55
3.34
3.00
CO2Me
CONMe(OMe)
N
Me
1.07
4.41
1.18
2.99
1.00
3.17
3.19
3.15
3.17
f1 (ppm)

4af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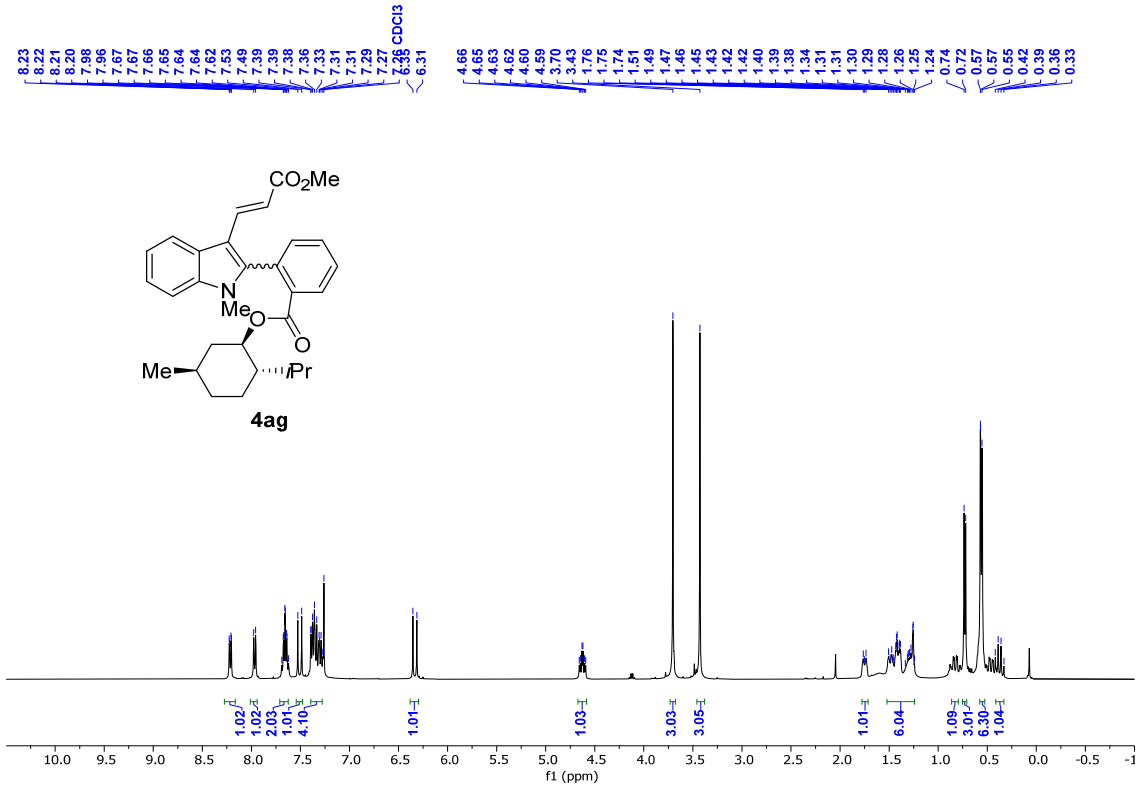
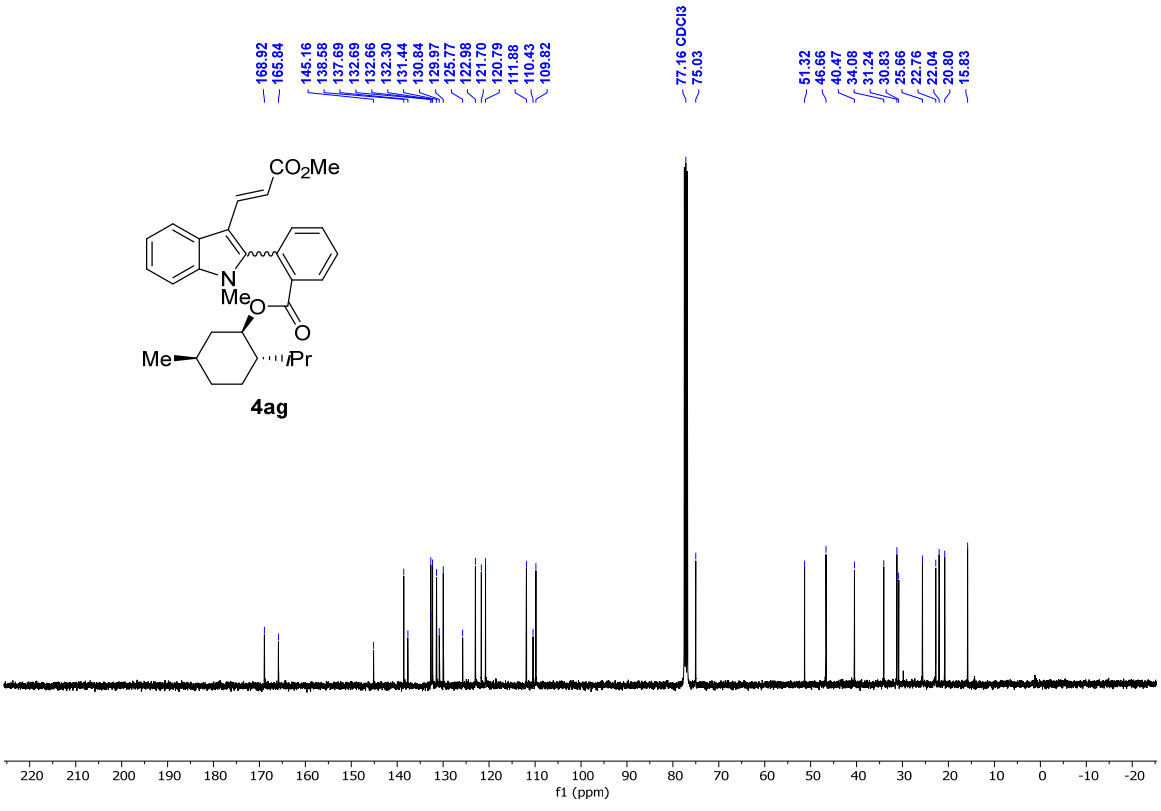
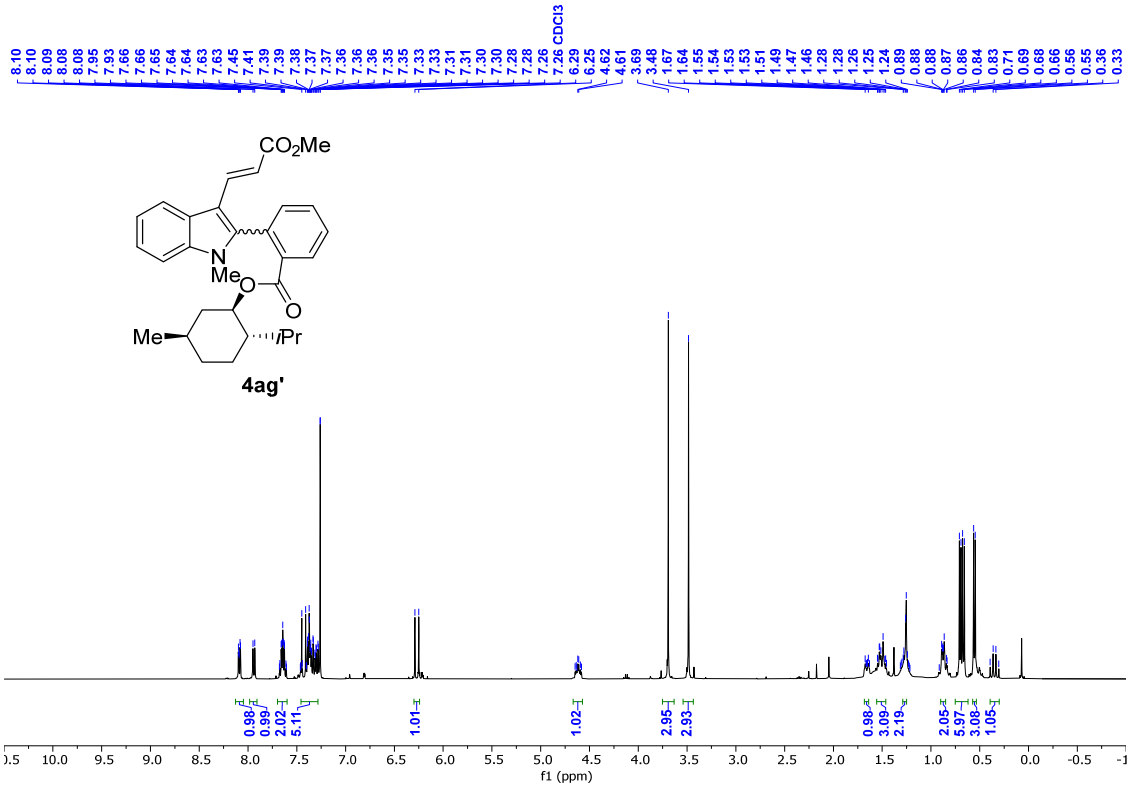
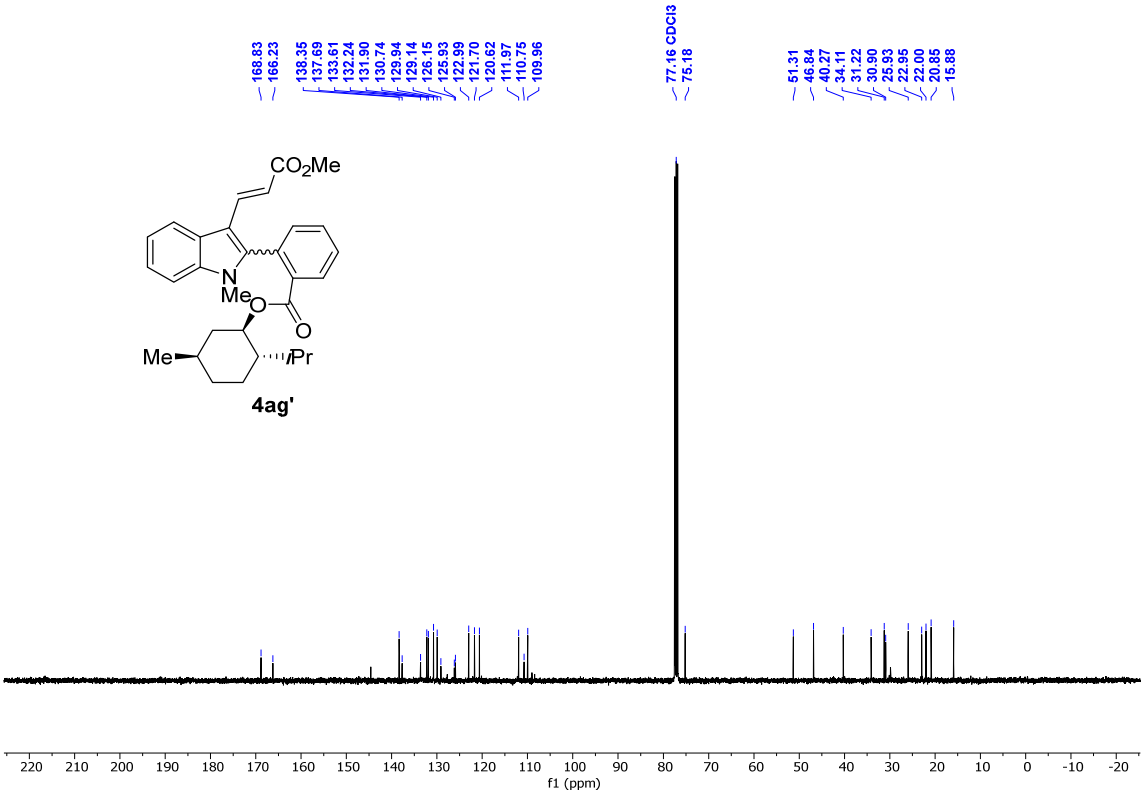
129.56
129.12
127.53
125.87
123.24
121.77
120.75
112.34
111.25
110.37
77.16 CDCl3
61.03
51.13
34.44
31.59
CO2Me
CONMe(OMe)
N
Me
34.44
31.59
f1 (ppm)
f1 (ppm)

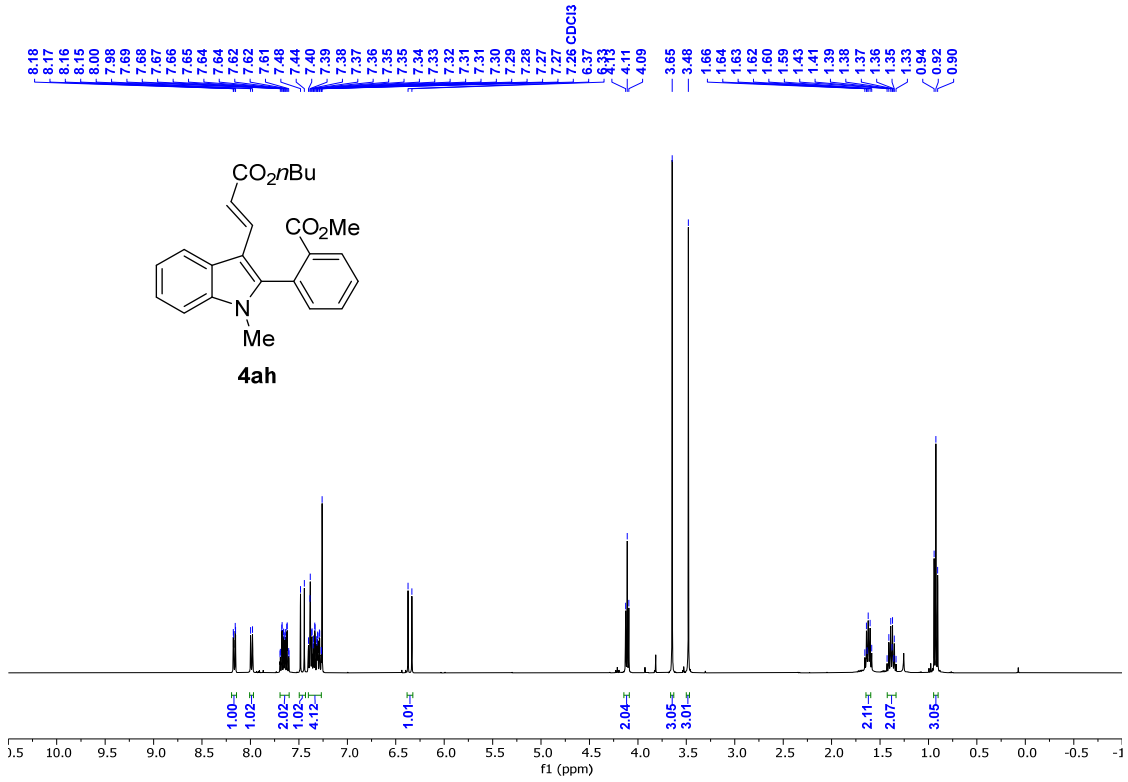
4af

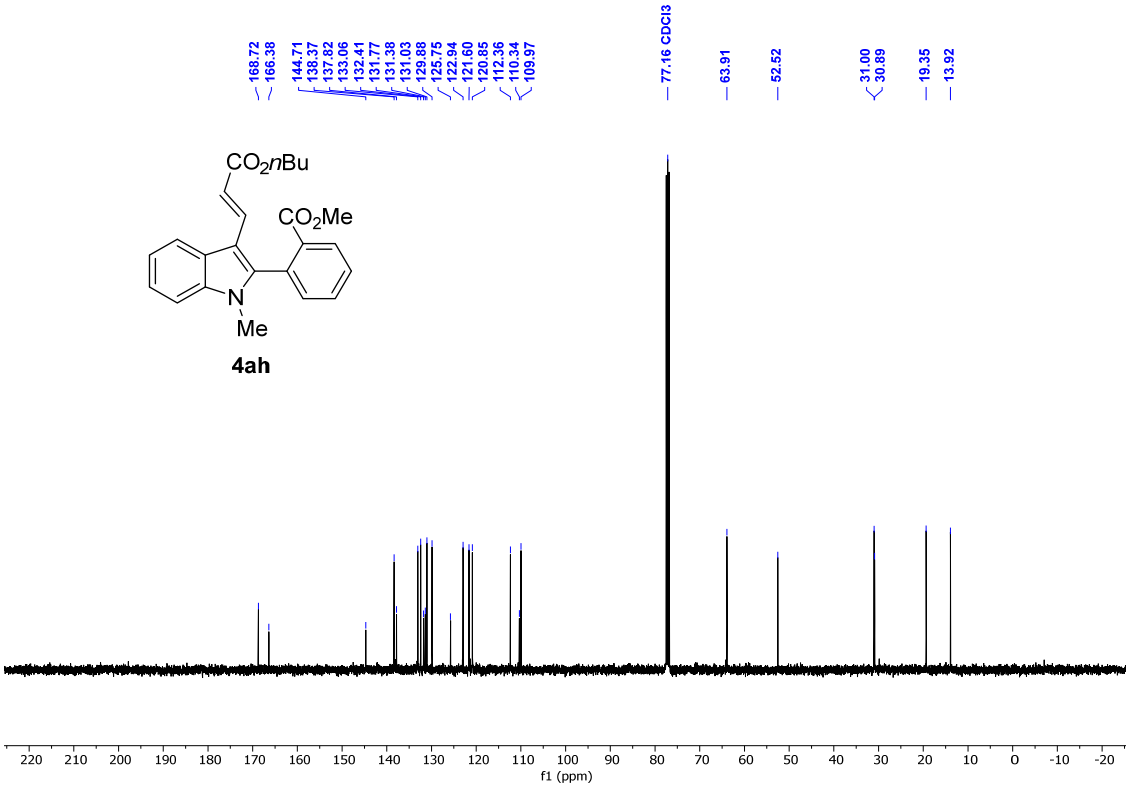

8.23 8.22 8.21 8.20 7.98 7.96 7.67 7.67 7.66 7.65 7.64 7.64 7.62 7.53 7.49 7.39 7.39 7.38 7.36 7.33 7.31 7.31 7.29 7.27 7.26 CDCl3 6.35 6.31
4.66 4.65 4.63 4.62 4.60 4.59 3.70 3.43 1.76 1.75 1.74 1.51 1.49 1.47 1.46 1.45 1.43 1.42 1.42 1.40 1.39 1.38 1.34 1.31 1.31 1.30 1.29 1.28 1.26 1.25 1.24 0.74 0.72 0.57 0.57 0.55 0.42 0.39 0.36 0.33
CO2Me
N
Me
O
O
Me
iPr
4ag
1.02 1.02 2.03 1.01 4.10 1.01 1.03 3.03 3.05 1.01 6.04 1.09 3.01 6.30 1.04
f1 (ppm)

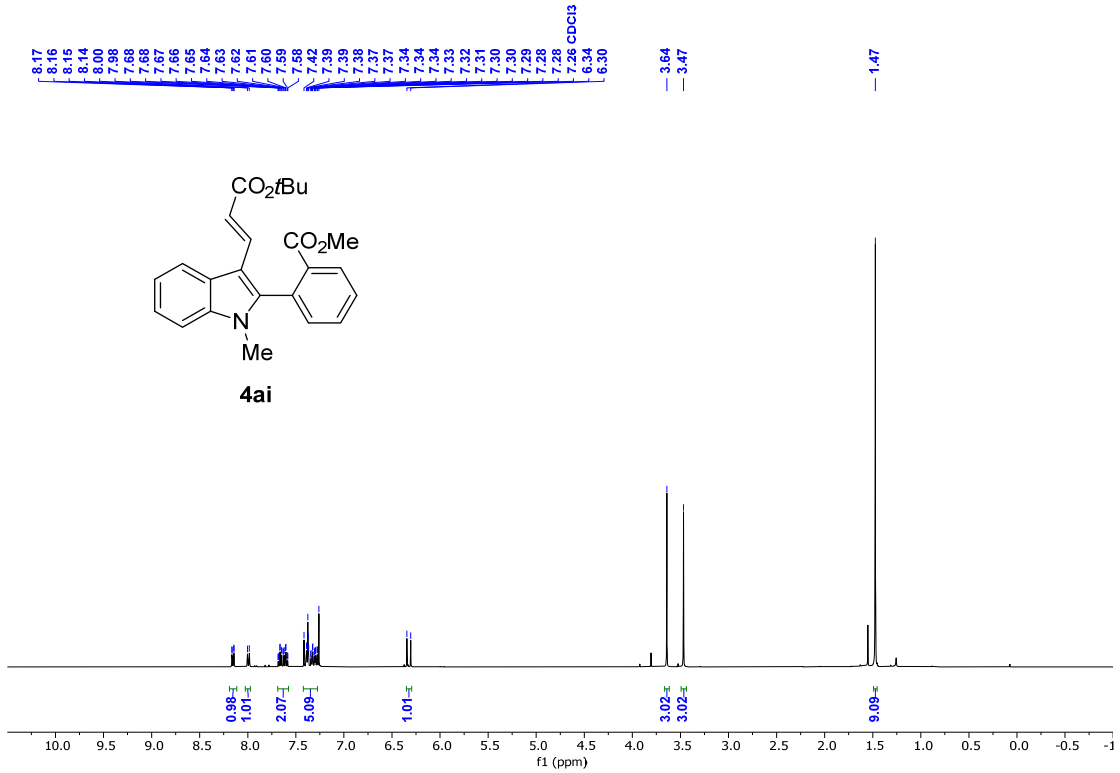

168.92 165.84 145.16 138.58 137.69 132.69 132.66 132.30 131.44 130.84 129.97 125.77 122.98 121.70 120.79 111.88 110.43 109.82
77.16 CDCl3 75.03
51.32 46.66 40.47 34.08 31.24 30.83 25.66 22.76 22.04 20.80 15.83
CO2Me
N
Me
O
O
Me
iPr
4ag
f1 (ppm)


8.10 8.10 8.09 8.08 8.08 7.95 7.93 7.66 7.66 7.65 7.64 7.64 7.63 7.63 7.45 7.41 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.33 7.33 7.31 7.31 7.30 7.30 7.28 7.28 7.26 7.26 CDCl3 6.29 6.25 4.62 4.61 3.69 3.48 1.67 1.64 1.55 1.54 1.53 1.53 1.51 1.49 1.47 1.46 1.28 1.28 1.26 1.25 1.24 0.89 0.88 0.88 0.87 0.86 0.84 0.83 0.71 0.69 0.68 0.66 0.56 0.55 0.36 0.33
CO2Me
N
Me
O
O
Me
iPr
4ag'
0.98 0.99 2.02 5.11 1.01 1.02 2.95 2.93 0.98 3.09 2.19 2.05 5.97 3.08 1.05
f1 (ppm)


168.83 166.23 138.35 137.69 133.61 132.24 131.90 130.74 129.94 129.14 126.15 125.93 122.99 121.70 120.62 111.97 110.75 109.96 77.16 CDCl3 75.18 51.31 46.84 40.27 34.11 31.22 30.90 25.93 22.95 22.00 20.85 15.88
CO2Me
N
Me
O
O
Me
iPr
4ag'
f1 (ppm)


8.18 8.17 8.16 8.15 8.00 7.98 7.69 7.68 7.67 7.66 7.65 7.64 7.64 7.62 7.62 7.61 7.48 7.44 7.40 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.27 7.26 CDCl3 6.37 6.33 4.13 4.11 4.09 3.65 3.48 1.66 1.64 1.63 1.62 1.60 1.59 1.43 1.41 1.39 1.38 1.37 1.36 1.35 1.33 0.94 0.92 0.90
CO2nBu
CO2Me
N
Me
4ah
1.00 1.02 2.02 1.02 4.12 1.01 2.04 3.05 3.01 2.11 2.07 3.05
f1 (ppm)


168.72 166.38 144.71 138.37 137.82 133.06 132.41 131.77 131.38 131.03 129.88 125.75 122.94 121.60 120.85 112.36 110.34 109.97 77.16 CDCl3 63.91 52.52 31.00 30.89 19.35 13.92
CO2nBu
CO2Me
N
Me
4ah
f1 (ppm)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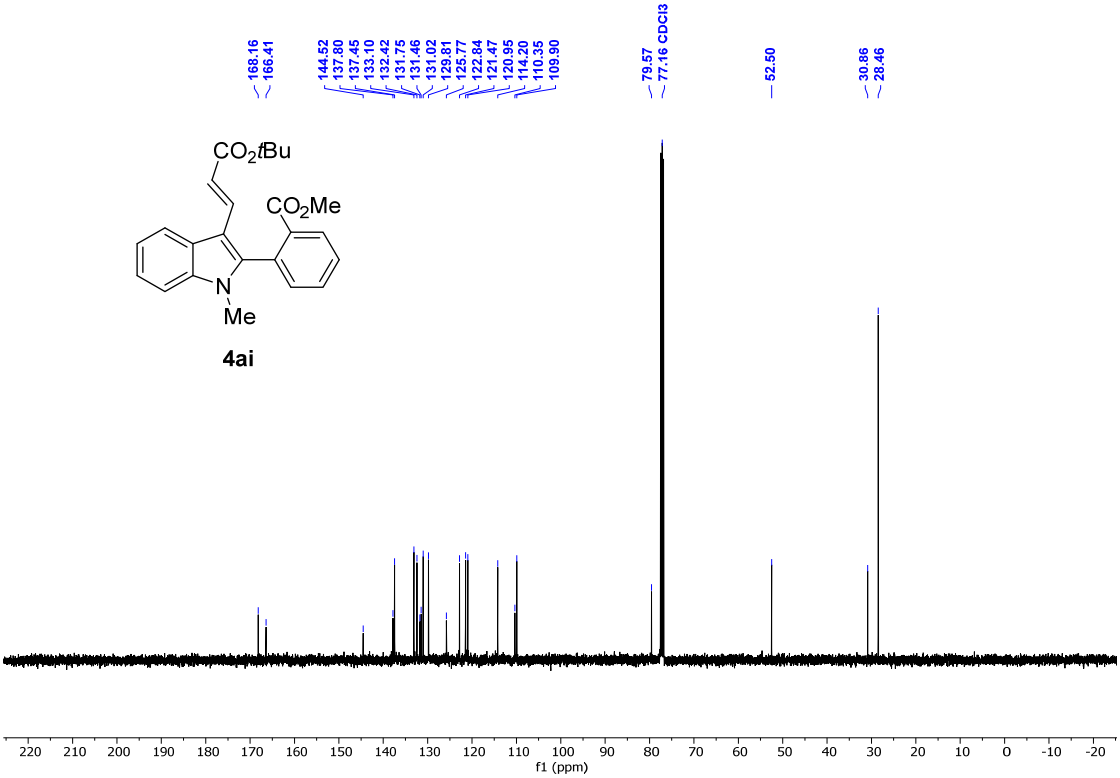
7.30
7.30
7.29
7.28
7.28
CDCl3
7.26
6.34
6.30
3.64
3.47
1.47
CO2tBu
CO2Me
N
Me
4ai
0.98
1.01
2.07
5.09
1.01
3.02
3.02
9.09
f1 (ppm)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137.45
133.10
132.42
131.75
131.46
131.02
129.81
125.77
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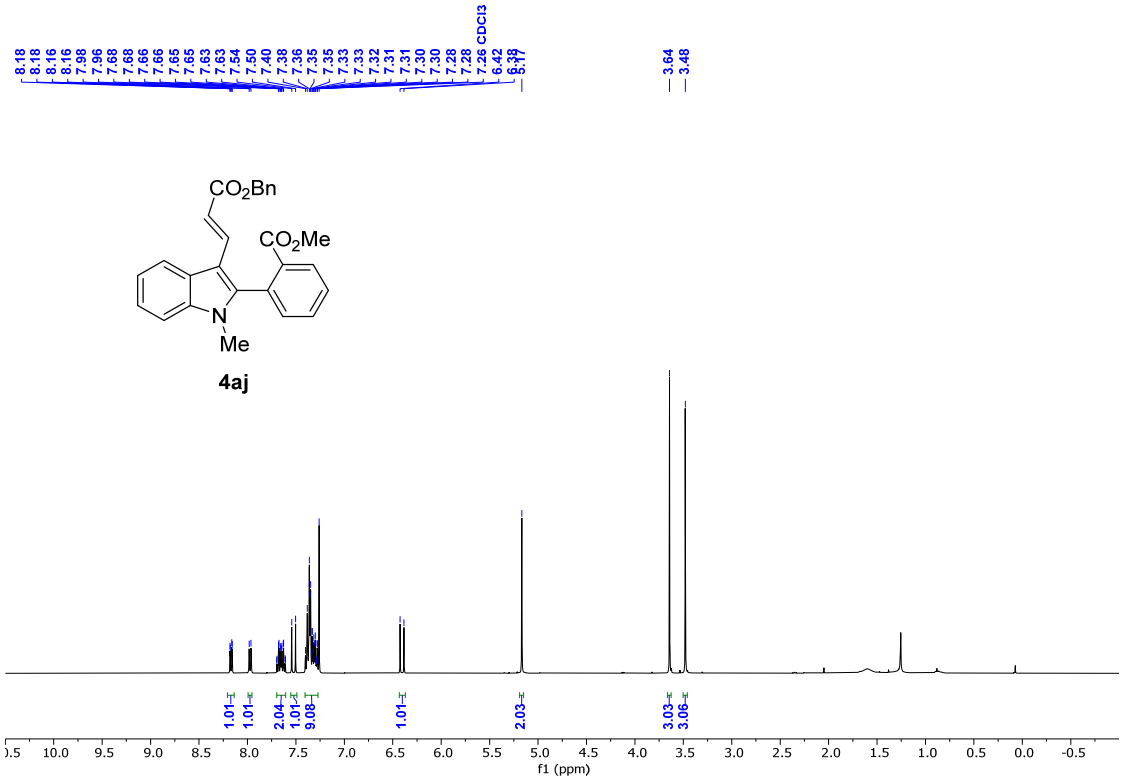
121.47
120.95
114.20
110.35
109.90
79.57
77.16
CDCl3
52.50
30.86
28.46
CO2tBu
CO2Me
N
Me
4ai
f1 (ppm)


8.18
8.18
8.16
8.16
7.98
7.96
7.68
7.68
7.66
7.66
7.65
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7.63
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7.35
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7.32
7.31
7.31
7.30
7.30
7.28
7.28
7.26 CDCl3
6.42
6.38
6.17
3.64
3.48
CO2Bn
CO2Me
N
Me
4aj
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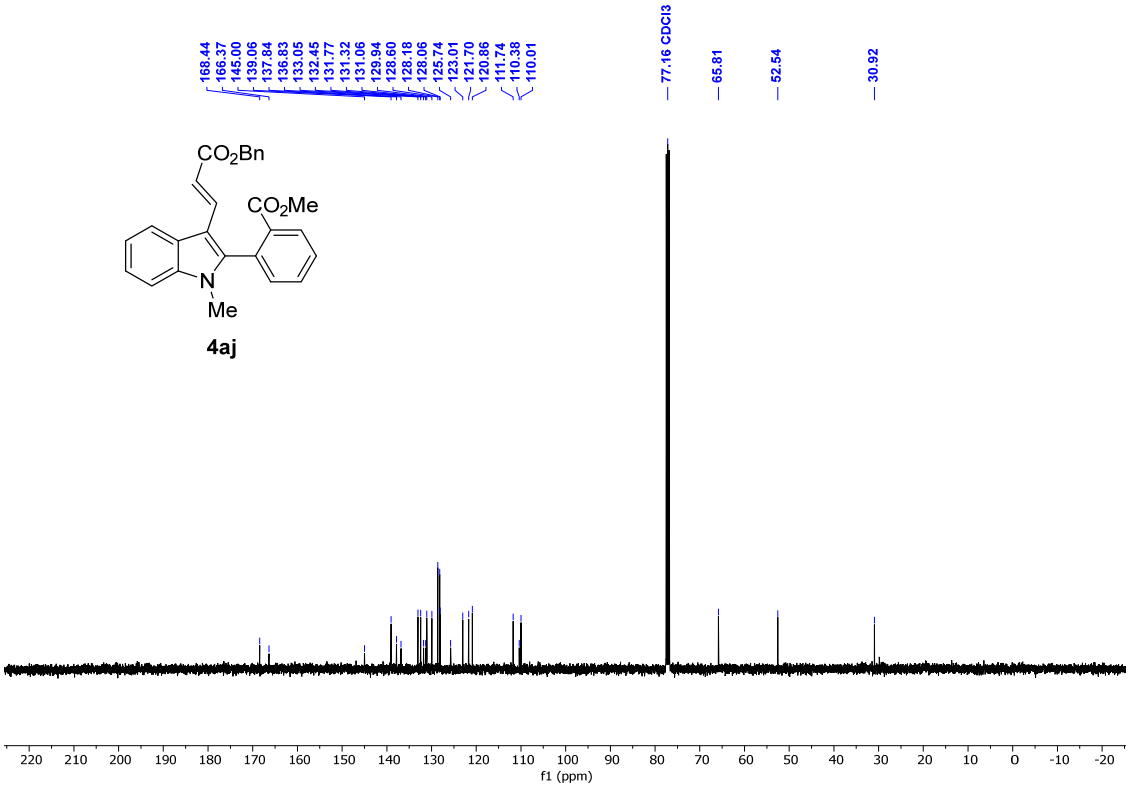
1.01
2.04
1.01
9.08
1.01
2.03
3.03
3.06
f1 (ppm)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133.05
132.45
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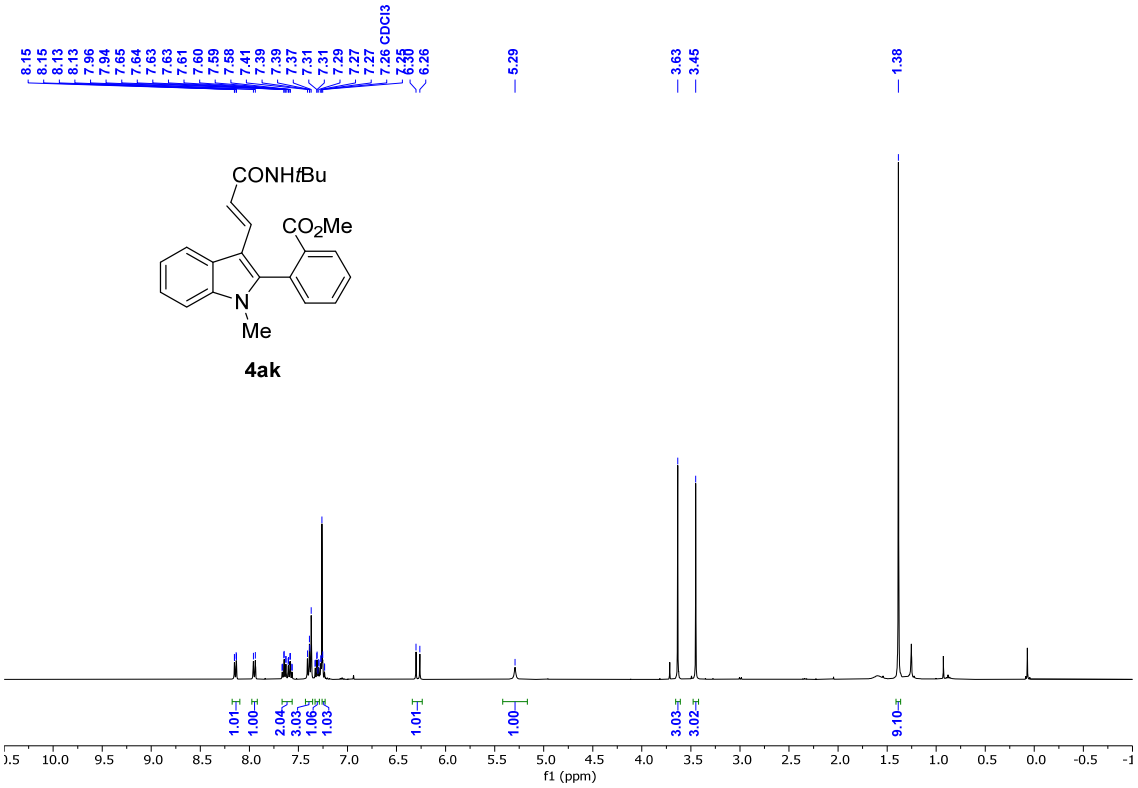
131.32
131.06
129.94
128.60
128.18
128.06
125.74
123.01
121.70
120.86
111.74
110.38
110.01
77.16 CDCl3
65.81
52.54
30.92
CO2Bn
CO2Me
N
Me
4aj
f1 (ppm)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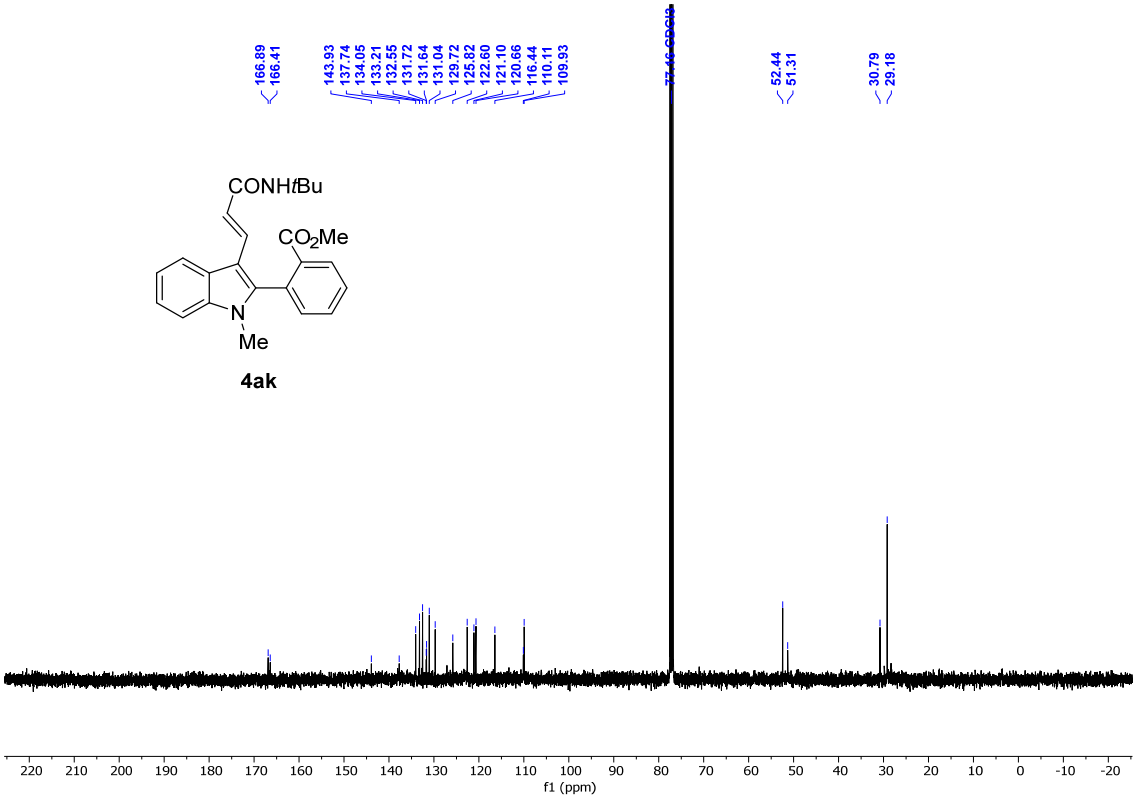
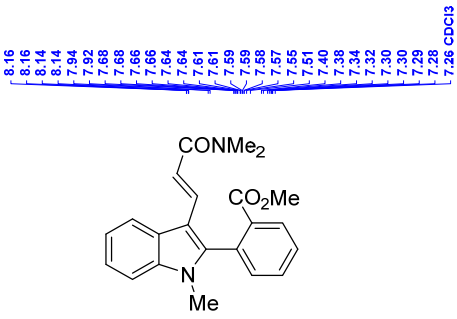
7.61
7.60
7.59
7.58
7.41
7.39
7.39
7.37
7.31
7.31
7.29
7.27
7.27
7.26 CDCl3
6.35
6.26
5.29
3.63
3.45
1.38
CONHtBu
CO2Me
N
Me
4ak
1.01
1.00
2.04
3.03
1.06
1.03
1.01
1.00
3.03
3.02
9.10
f1 (ppm)


166.89
166.41
143.93
137.74
134.05
133.21
132.55
131.72
131.64
131.04
129.72
125.82
122.60
121.10
120.66
116.44
110.11
109.93
77.48 CDCl3
52.44
51.31
30.79
29.18
CONHtBu
CO2Me
N
Me
4ak
f1 (ppm)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7.68
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7.66
7.64
7.64
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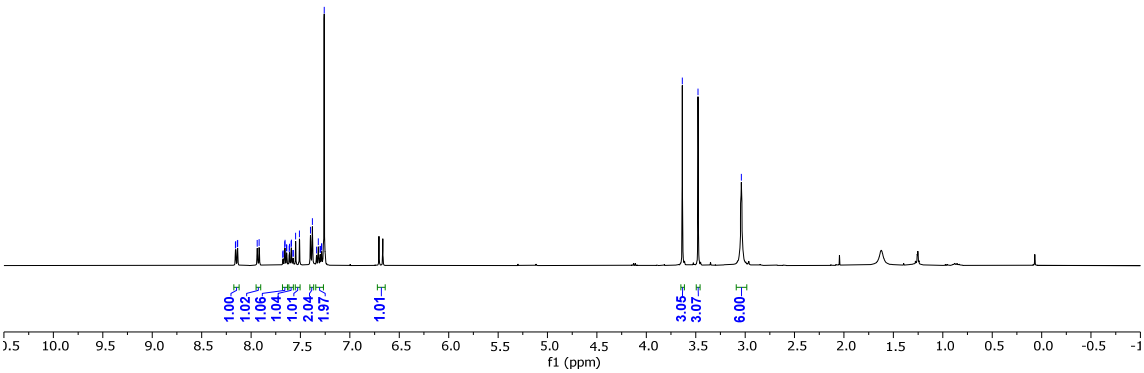
7.61
7.59
7.59
7.58
7.57
7.55
7.51
7.40
7.38
7.34
7.32
7.30
7.30
7.29
7.28
7.26 CDCl3
3.64
3.48
3.04
CONMe2
CO2Me
N
Me

4al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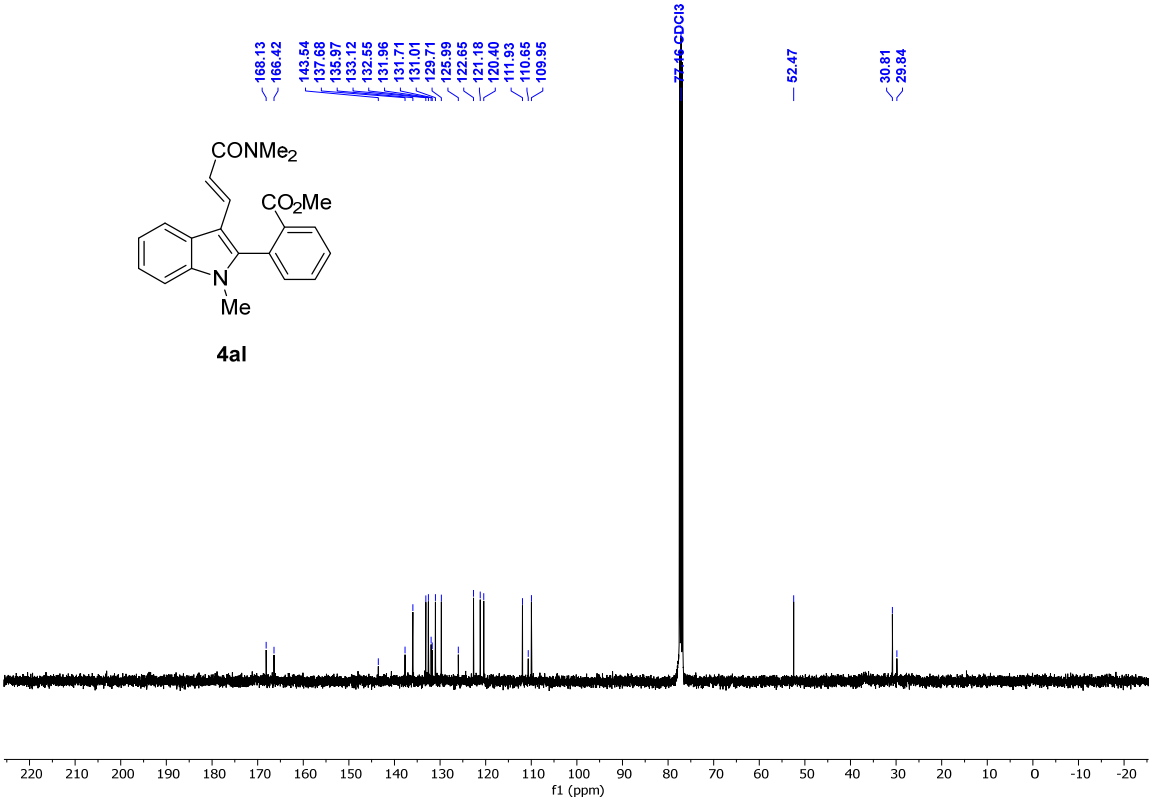
1.04
1.01
2.04
1.97
1.01
3.05
3.07
6.00
f1 (ppm)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131.96
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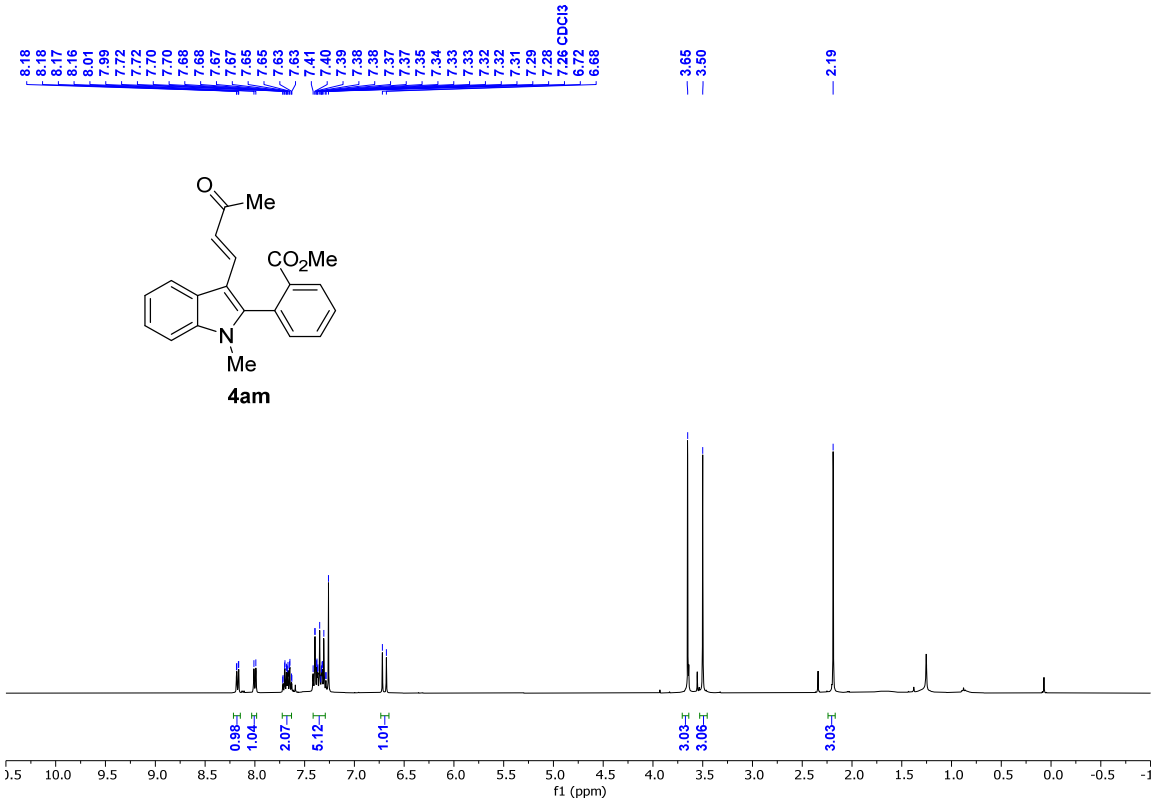
131.01
129.71
125.99
122.65
121.18
120.40
111.93
110.65
109.95
77.46 CDCl3
52.47
30.81
29.84
CONMe2
CO2Me
N
Me
f1 (ppm)

4al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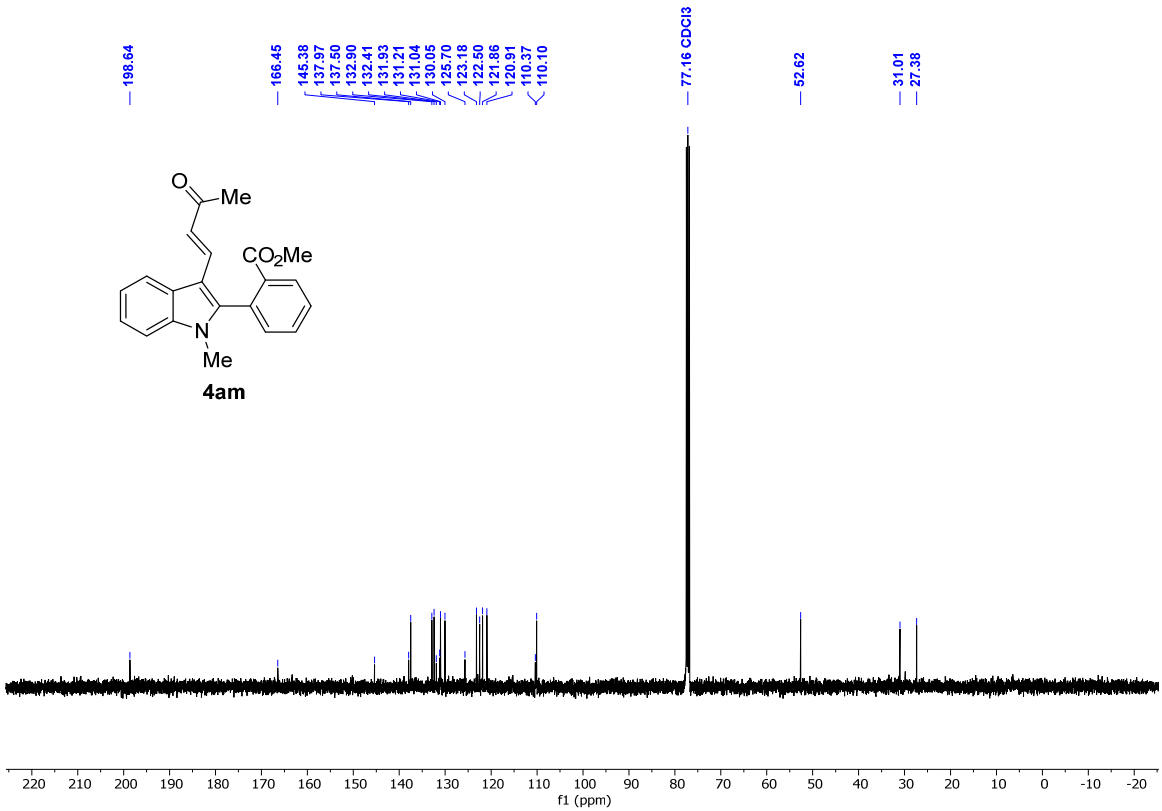
8.18
8.17
8.16
8.01
7.99
7.72
7.72
7.70
7.70
7.68
7.68
7.67
7.67
7.65
7.65
7.63
7.63
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.29
7.28
7.26 CDCl3
6.72
6.68
3.65
3.50
2.19
O
Me
CO2Me
N
Me
4am
0.98
1.04
2.07
5.12
1.01
3.03
3.06
3.03
f1 (ppm)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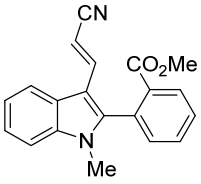
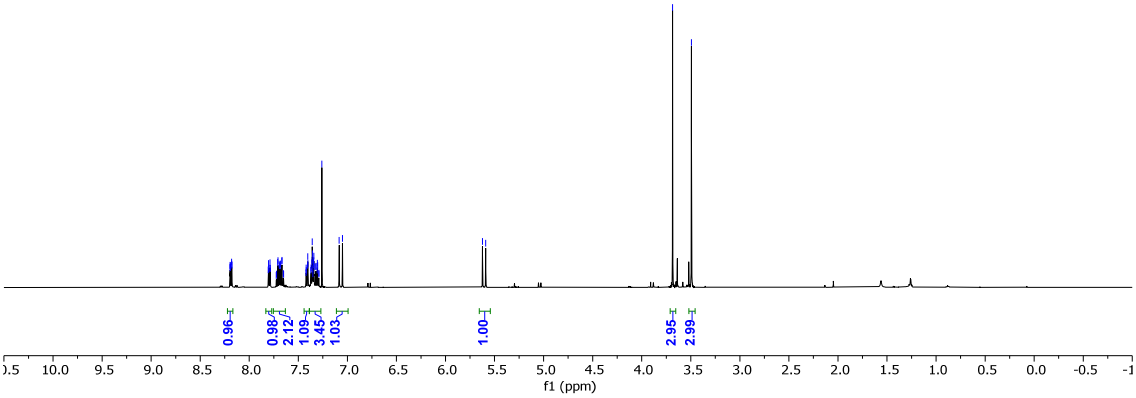
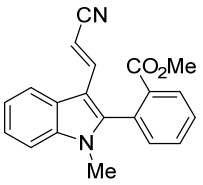
166.45
145.38
137.97
137.50
132.90
132.41
131.93
131.21
131.04
130.05
125.70
123.18
122.50
121.86
120.91
110.37
110.10
77.16 CDCl3
52.62
31.01
27.38
O
Me
CO2Me
N
Me
4am
f1 (ppm)

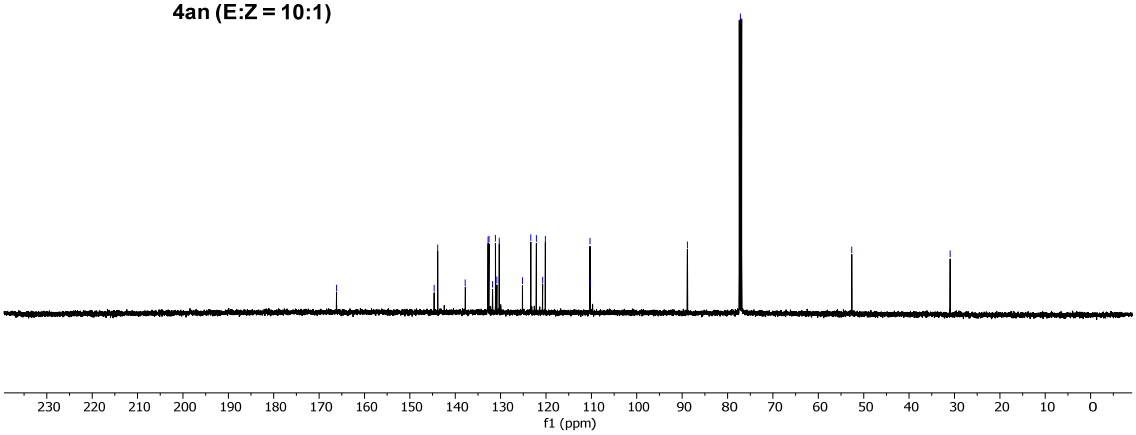


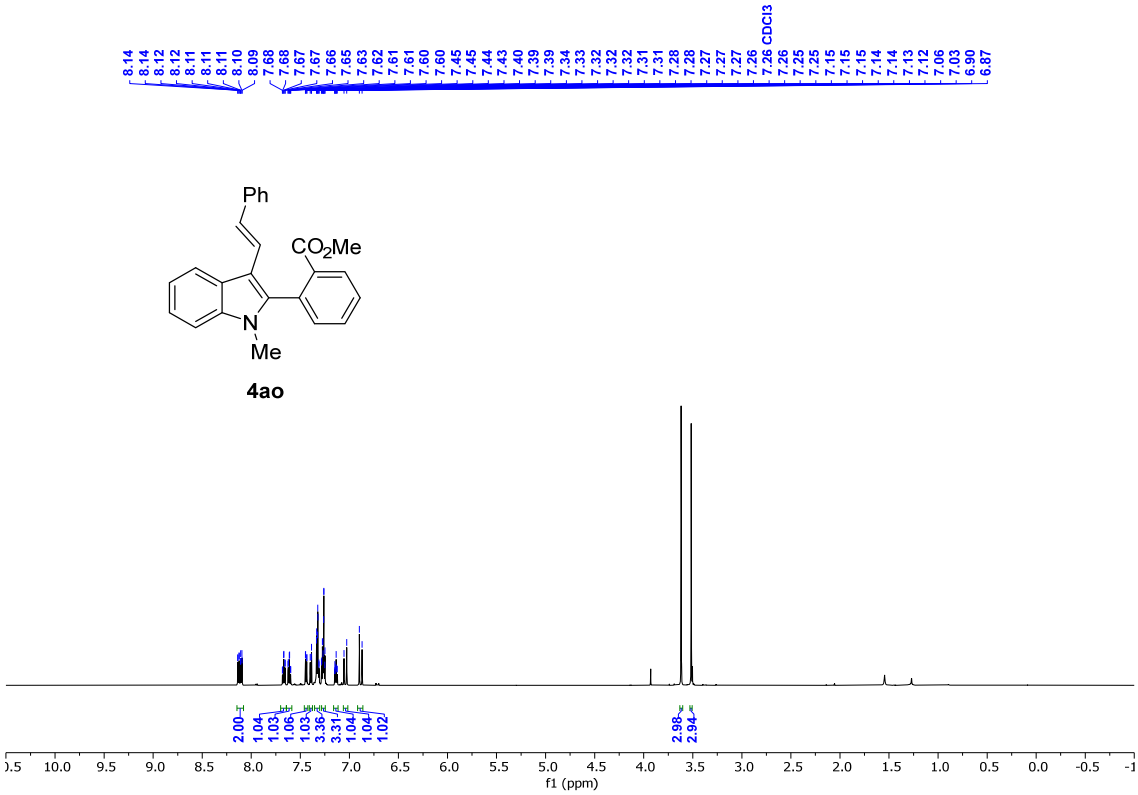
4an (E:Z = 10:1)

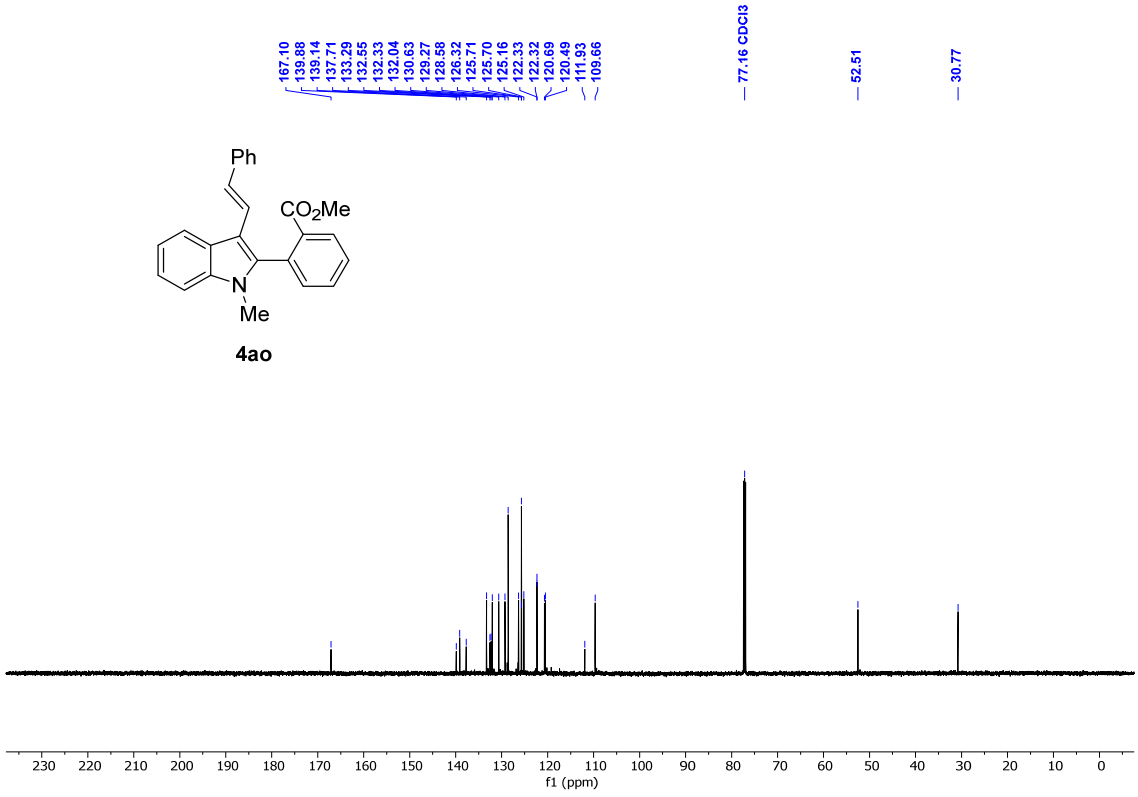


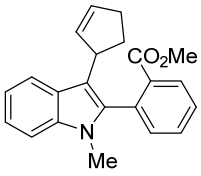


4an (E:Z = 10:1)

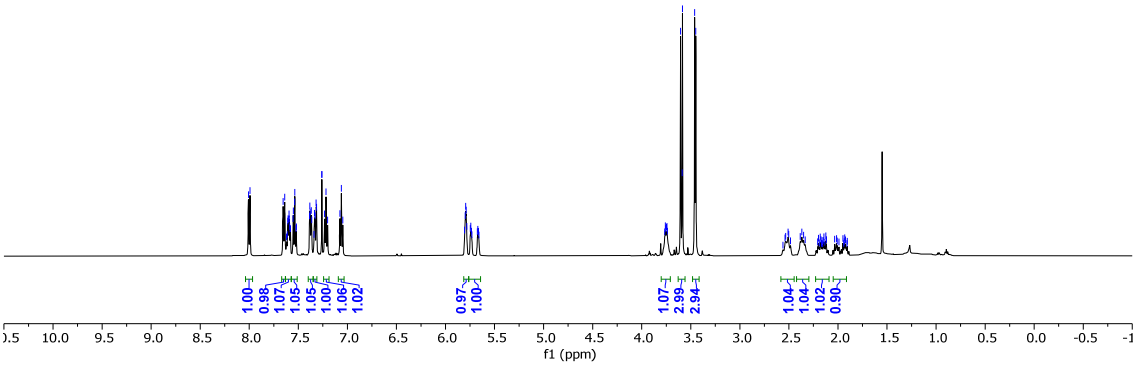


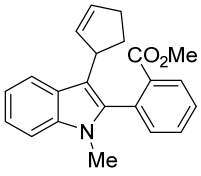

8.14 8.14 8.12 8.12 8.11 8.11 8.11 8.10 8.09 7.68 7.68 7.67 7.67 7.67 7.66 7.65 7.63 7.62 7.61 7.61 7.60 7.60 7.45 7.45 7.44 7.43 7.40 7.39 7.39 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.28 7.28 7.27 7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.15 7.15 7.15 7.14 7.14 7.13 7.12 7.06 7.03 6.90 6.87
Ph
CO2Me
N
Me
4ao
2.00 1.04 1.03 1.06 1.03 3.36 3.31 1.04 1.04 1.02 2.98 2.94
f1 (ppm)


167.10 139.88 139.14 137.71 133.29 132.55 132.33 132.04 130.63 129.27 128.58 126.32 125.71 125.70 125.16 122.33 122.32 120.69 120.49 111.93 109.66
77.16 CDCl3
52.51
30.77
Ph
CO2Me
N
Me
4ao
f1 (ppm)

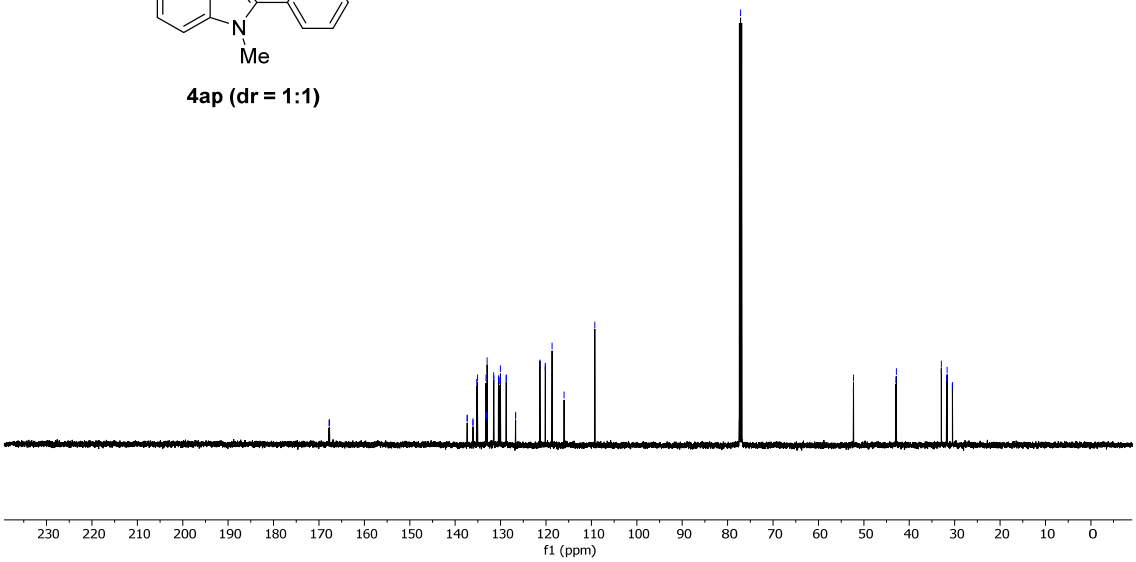


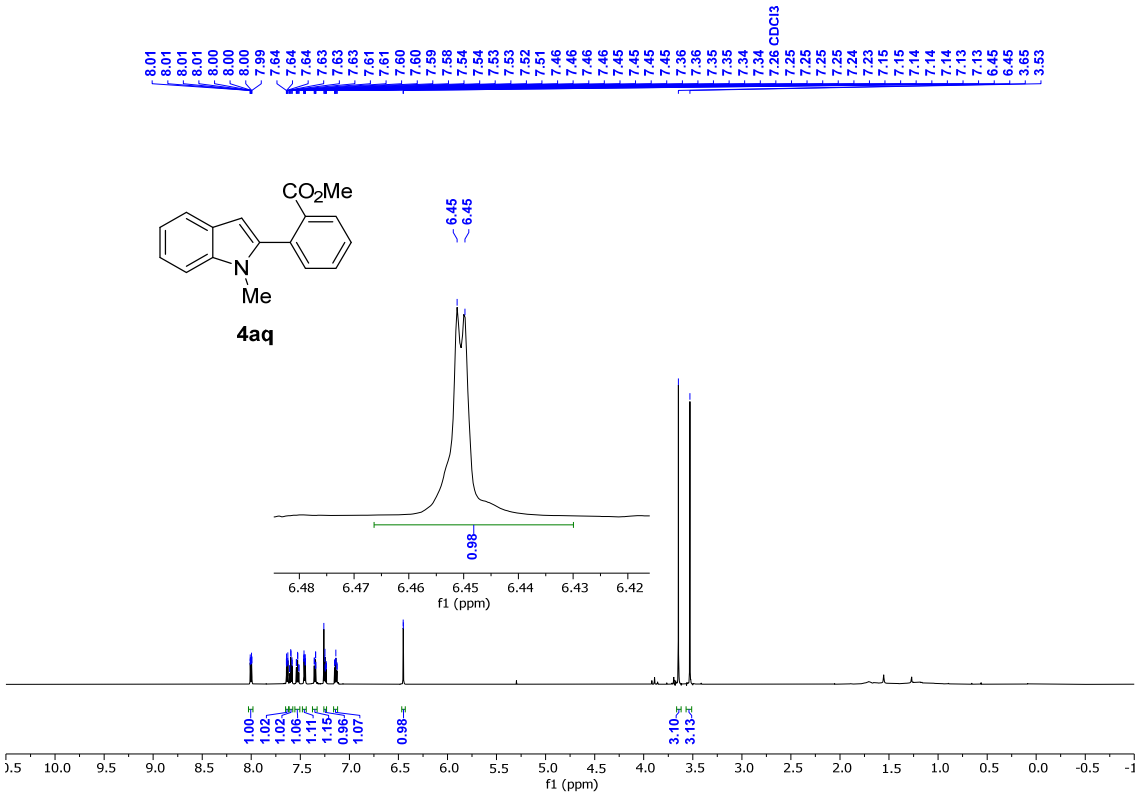
4ap (dr = 1:1)





4ap (dr = 1:1)

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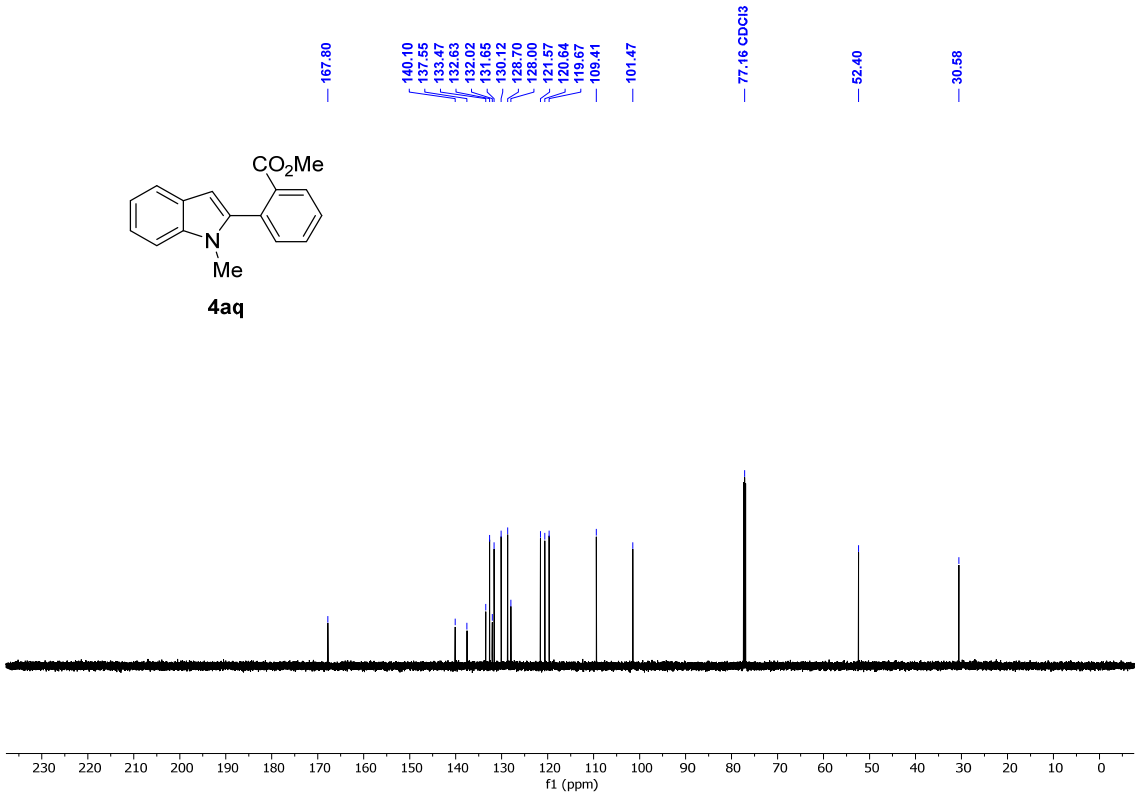
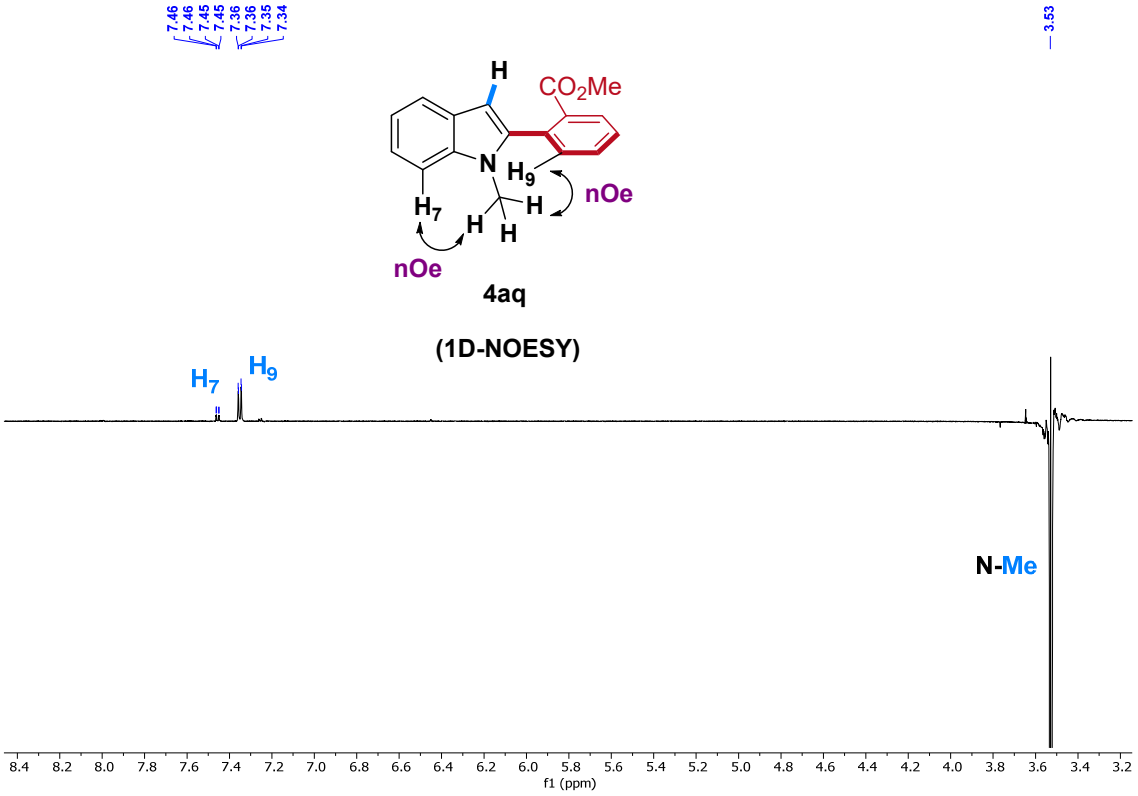
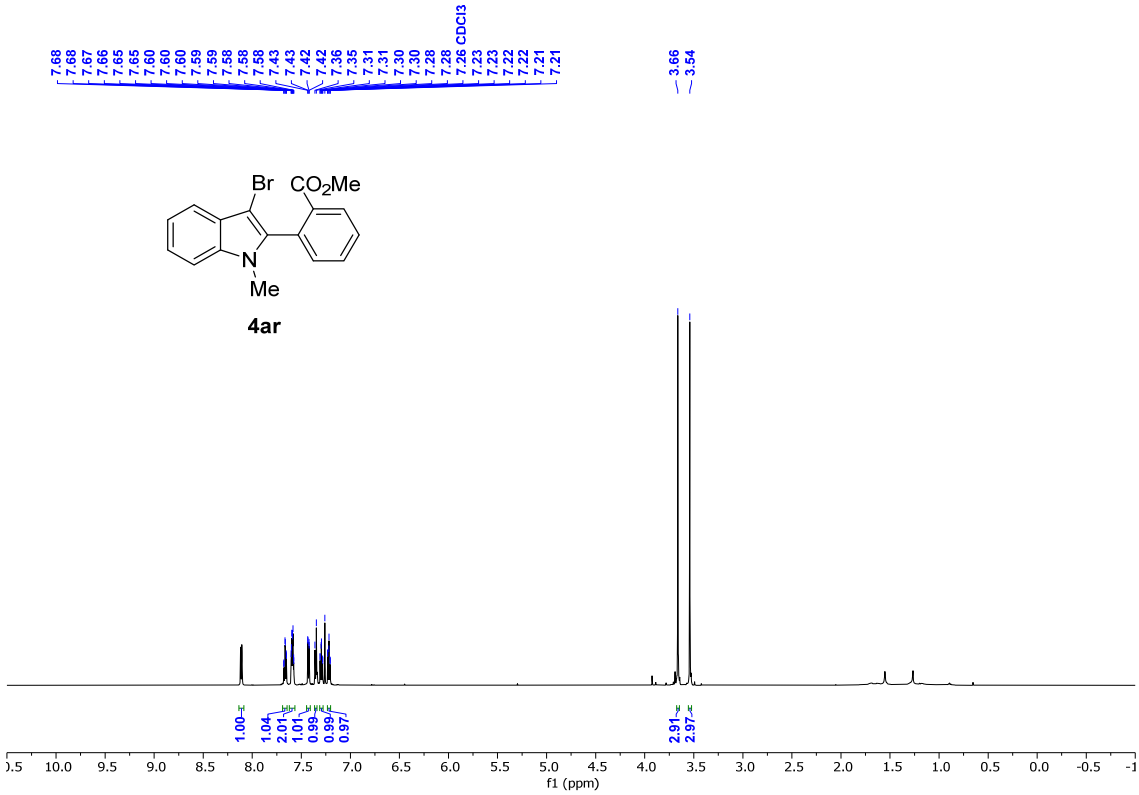
CO2Me
N
Me
4aq
6.45
6.45
0.98
6.48 6.47 6.46 6.45 6.44 6.43 6.42
f1 (ppm)
1.00 1.02 1.02 1.06 1.11 1.15 0.96 1.07 0.98 3.10 3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


167.80
140.10 137.55 133.47 132.63 132.02 131.65 130.12 128.70 128.00 121.57 120.64 119.67 109.41
101.47
77.16 CDCl3
52.40
30.58
CO2Me
N
Me
4aq
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.46
7.46
7.45
7.45
7.36
7.36
7.35
7.34
3.53
H
CO2Me
N
H9
nOe
H7
H
H
H
nOe
4aq
(1D-NOESY)
H7
H9
N-Me
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
f1 (ppm)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7.68
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7.66
7.65
7.65
7.60
7.60
7.60
7.59
7.59
7.58
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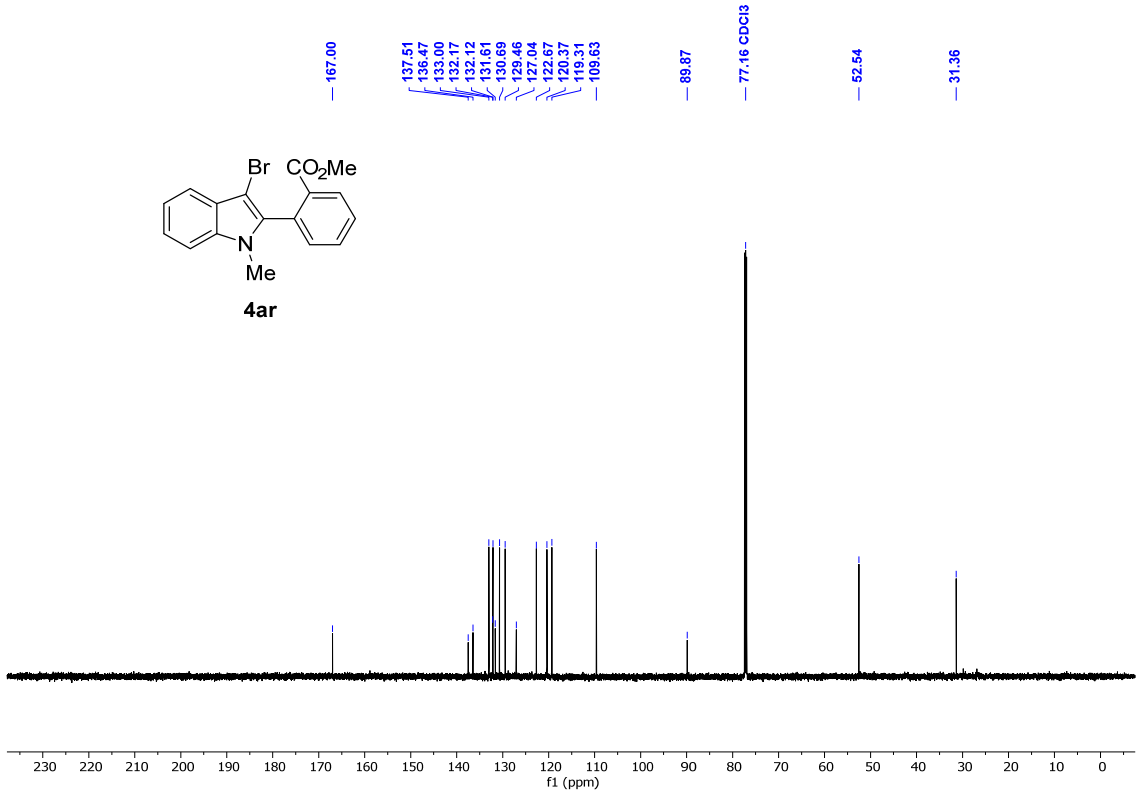
7.58
7.43
7.43
7.42
7.42
7.36
7.35
7.31
7.31
7.30
7.30
7.28
7.28
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
7.21
3.66
3.54
Br
CO2Me
N
Me
4ar
1.00
1.04
2.01
1.01
0.99
0.99
0.97
2.91
2.97
f1 (ppm)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132.12
131.61
130.69
129.46
127.04
122.67
120.37
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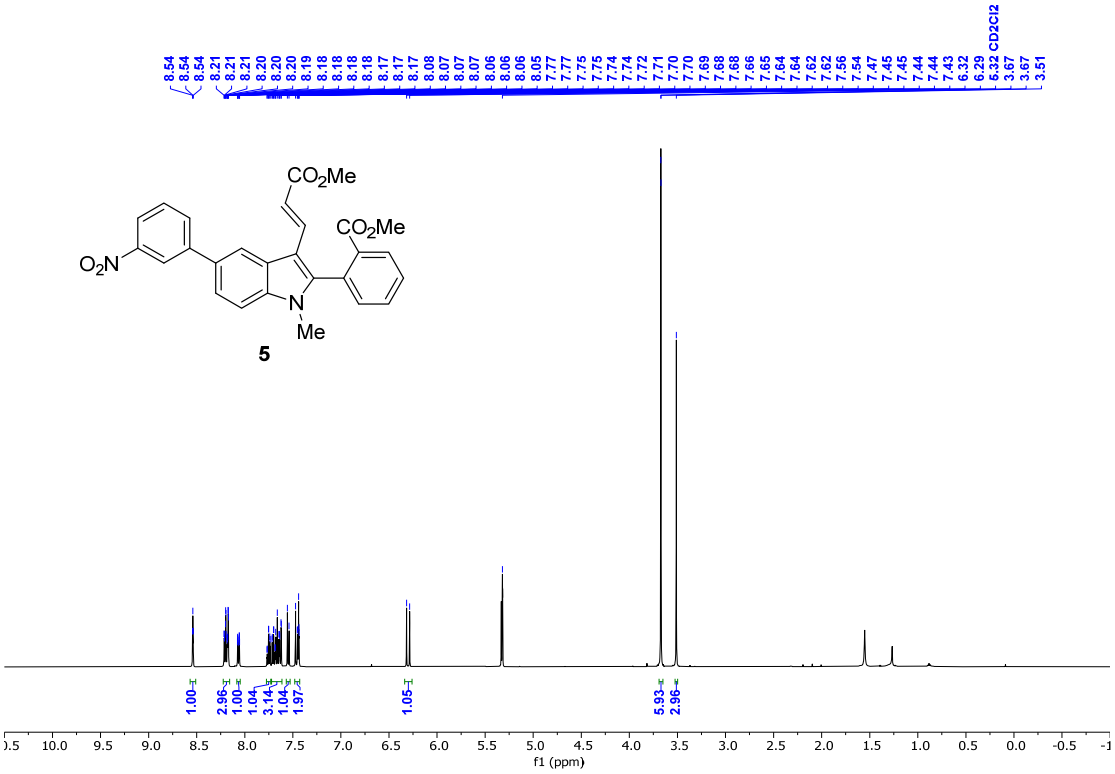
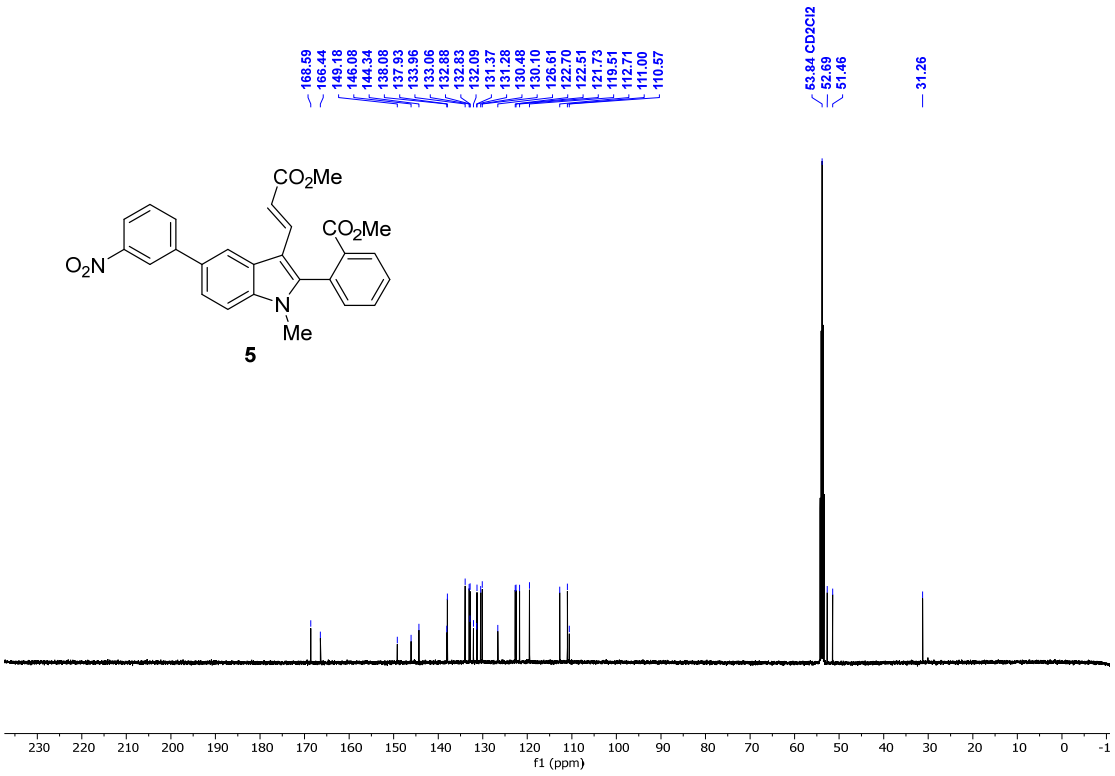
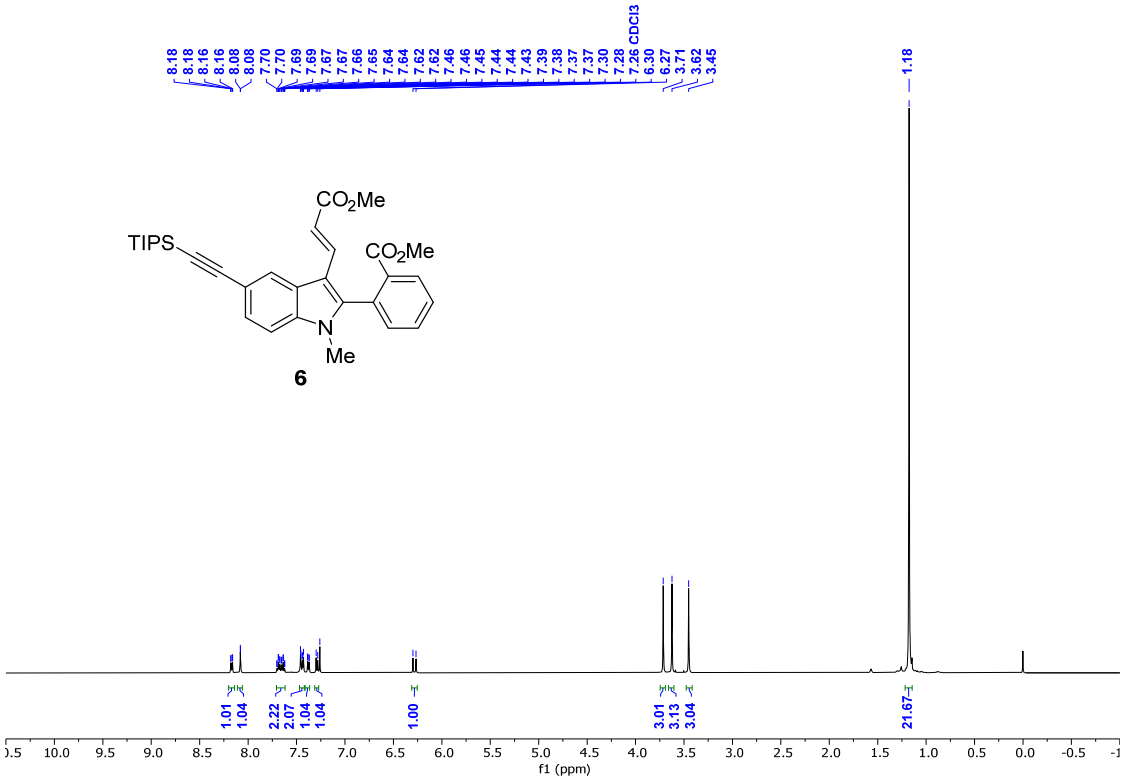
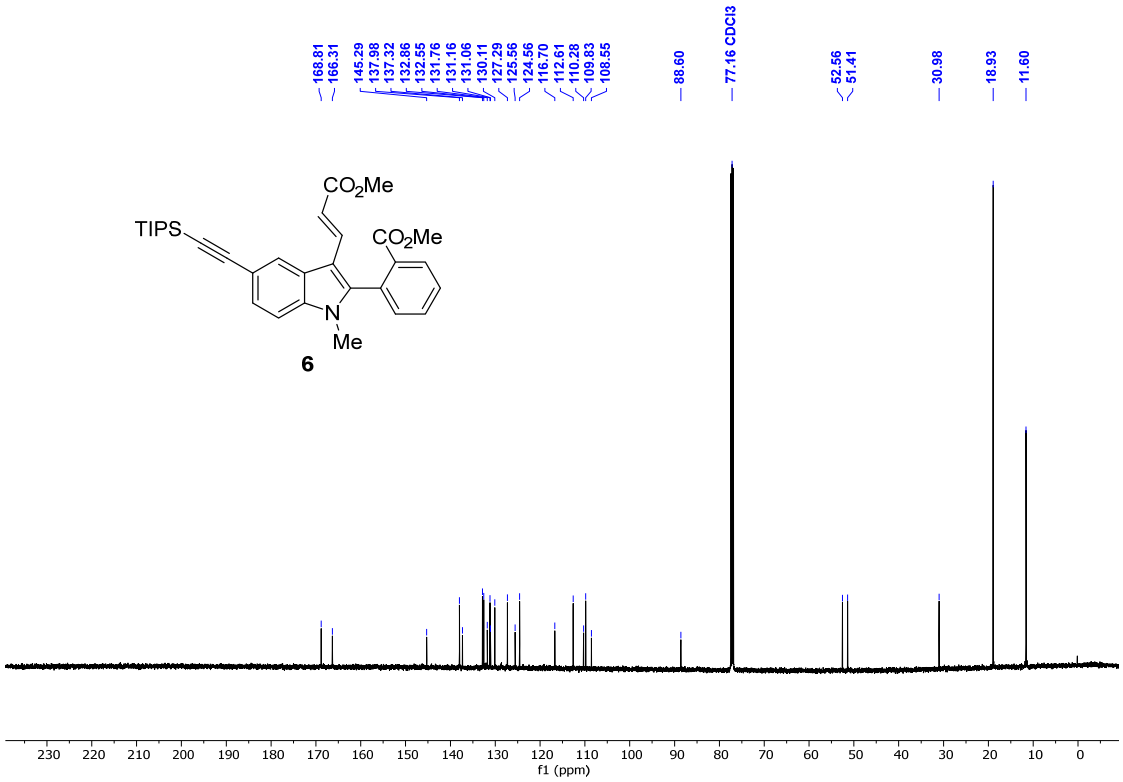
109.63
89.87
77.16 CDCl3
52.54
31.36
Br
CO2Me
N
Me
4ar
f1 (ppm)


8.54 8.54 8.54 8.21 8.21 8.21 8.20 8.20 8.20 8.19 8.18 8.18 8.18 8.18 8.17 8.17 8.17 8.08 8.07 8.07 8.07 8.06 8.06 8.06 8.05 7.77 7.77 7.75 7.75 7.74 7.74 7.72 7.71 7.70 7.70 7.69 7.68 7.68 7.66 7.65 7.64 7.64 7.62 7.62 7.56 7.54 7.47 7.45 7.45 7.44 7.44 7.43 6.32 6.29 6.32 CD2Cl2 3.67 3.67 3.51
CO2Me
CO2Me
O2N
N
Me
5
1.00 2.96 1.00 1.04 3.14 1.04 1.97 1.05 5.93 2.96
f1 (ppm)


168.59 166.44 149.18 146.08 144.34 138.08 137.93 133.96 133.06 132.88 132.83 132.09 131.37 131.28 130.48 130.10 126.61 122.70 122.51 121.73 119.51 112.71 111.00 110.57 63.84 CD2Cl2 52.69 51.46 31.26
CO2Me
CO2Me
O2N
N
Me
5
f1 (ppm)


8.18
8.18
8.16
8.16
8.08
8.08
7.70
7.70
7.69
7.69
7.67
7.67
7.66
7.65
7.64
7.64
7.62
7.62
7.46
7.46
7.45
7.44
7.44
7.43
7.39
7.38
7.37
7.37
7.30
7.28
7.26 CDCl3
6.30
6.27
3.71
3.62
3.45
1.18
CO2Me
TIPS
CO2Me
N
Me
6
1.01
1.04
2.22
2.07
1.04
1.04
1.00
3.01
3.13
3.04
21.67
f1 (ppm)


168.81
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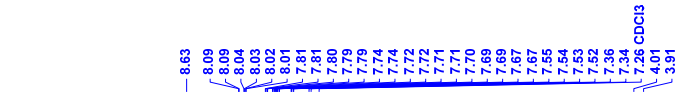
137.32
132.86
132.55
131.76
131.16
131.06
130.11
127.29
125.56
124.56
116.70
112.61
110.28
109.83
108.55
88.60
77.16 CDCl3
52.56
51.41
30.98
18.93
11.60
CO2Me
TIPS
CO2Me
N
Me
6
f1 (ppm)


8.63
8.09
8.09
8.04
8.03
8.02
8.01
7.81
7.81
7.80
7.79
7.79
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7.74
7.72
7.72
7.71
7.71
7.70
7.69
7.69
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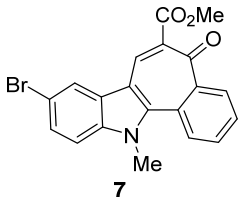
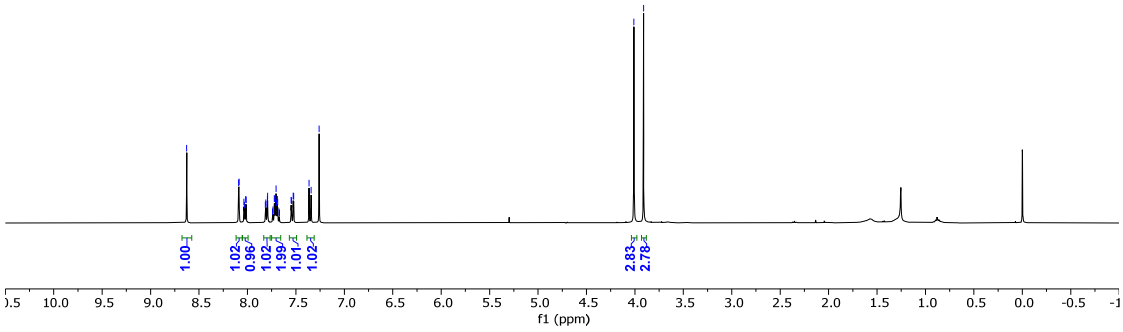
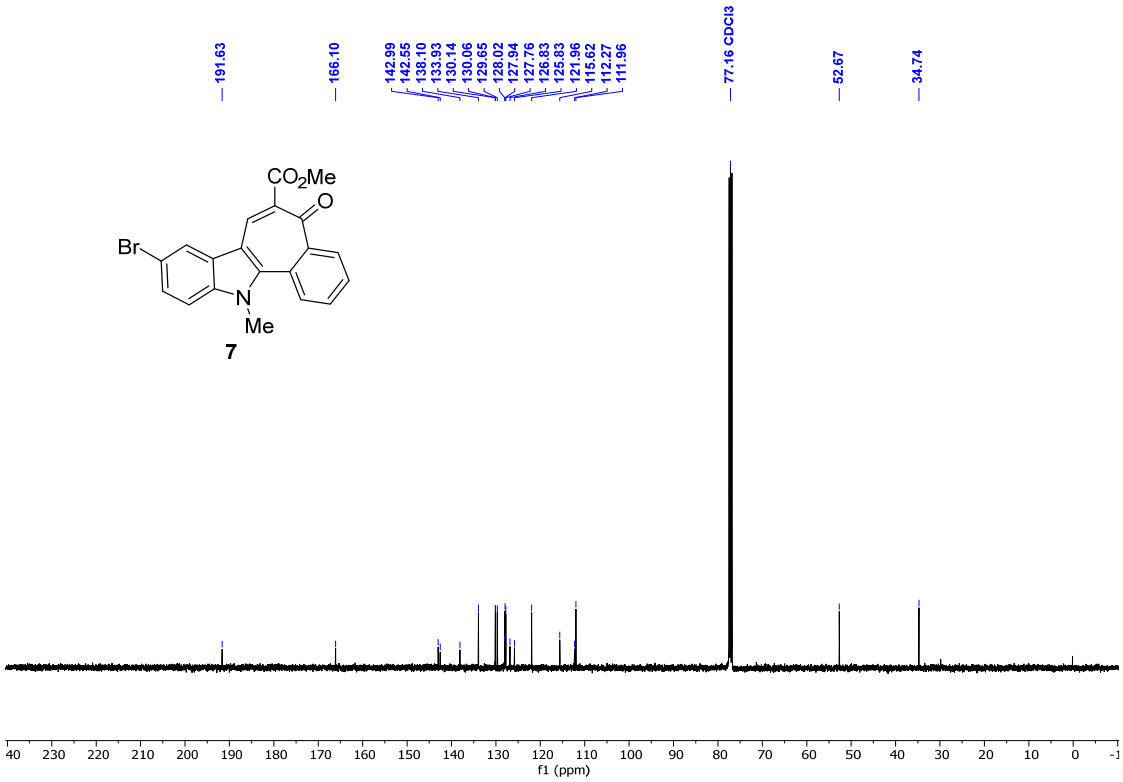
7.67
7.55
7.54
7.53
7.52
7.36
7.34
7.26 CDCl3
4.01
3.91

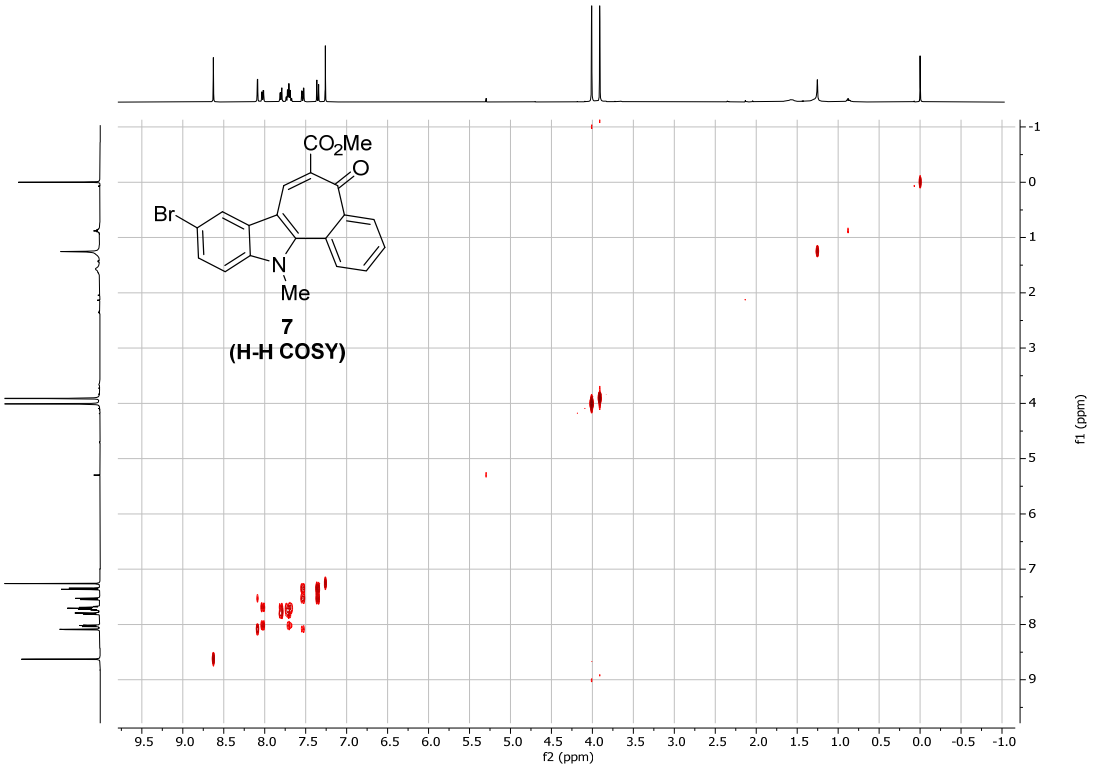

CO2Me
O
Br
N
Me

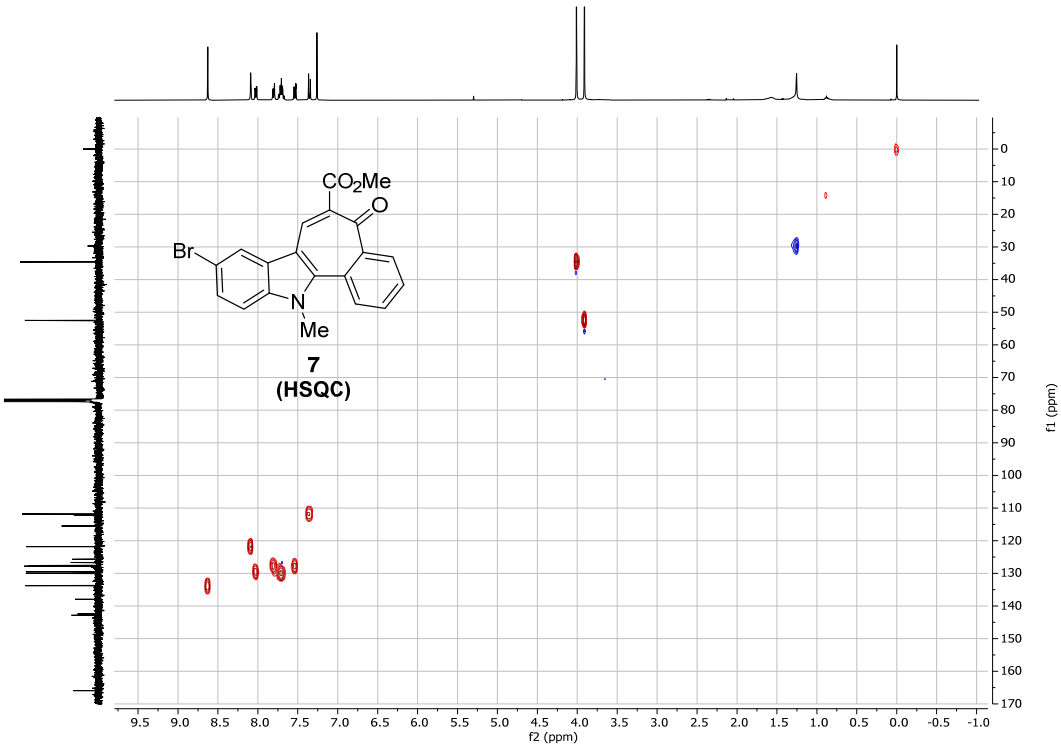
7

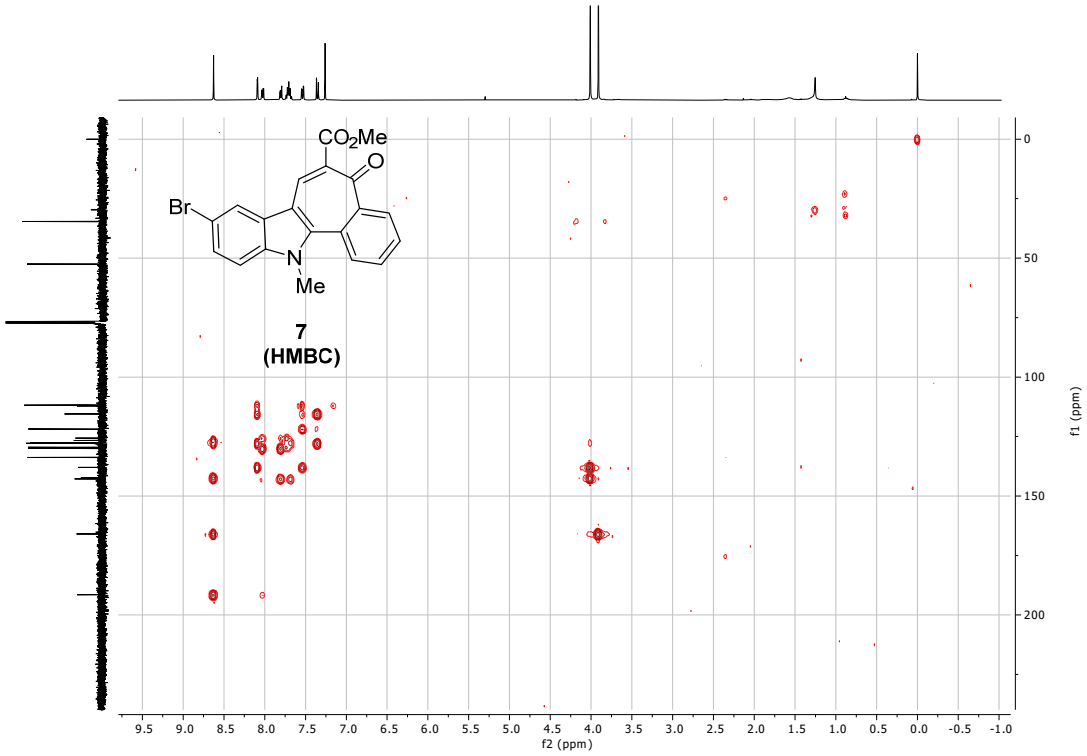

1.00
1.02
0.96
1.02
1.99
1.01
1.02
2.83
2.78
f1 (ppm)

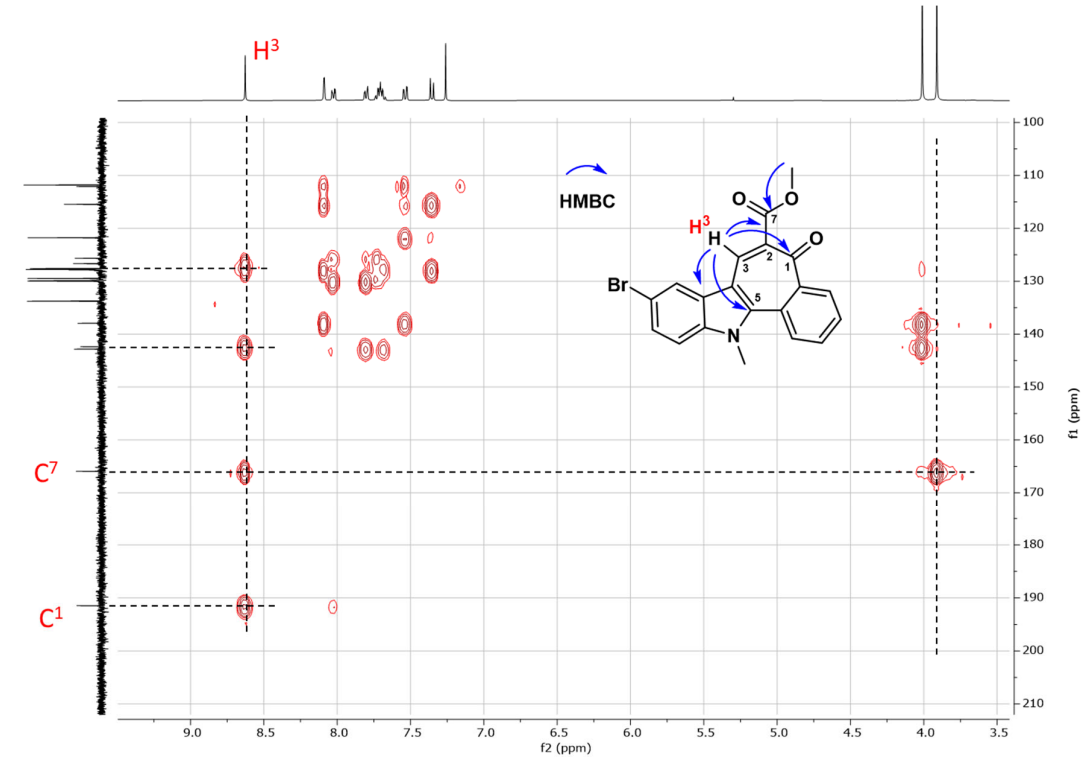

191.63
166.10
142.99
142.55
138.10
133.93
130.14
130.06
129.65
128.02
127.94
127.76
126.83
125.83
121.96
115.62
112.27
111.96
77.16 CDCl3
52.67
34.74
CO2Me
O
Br
N
Me
f1 (ppm)

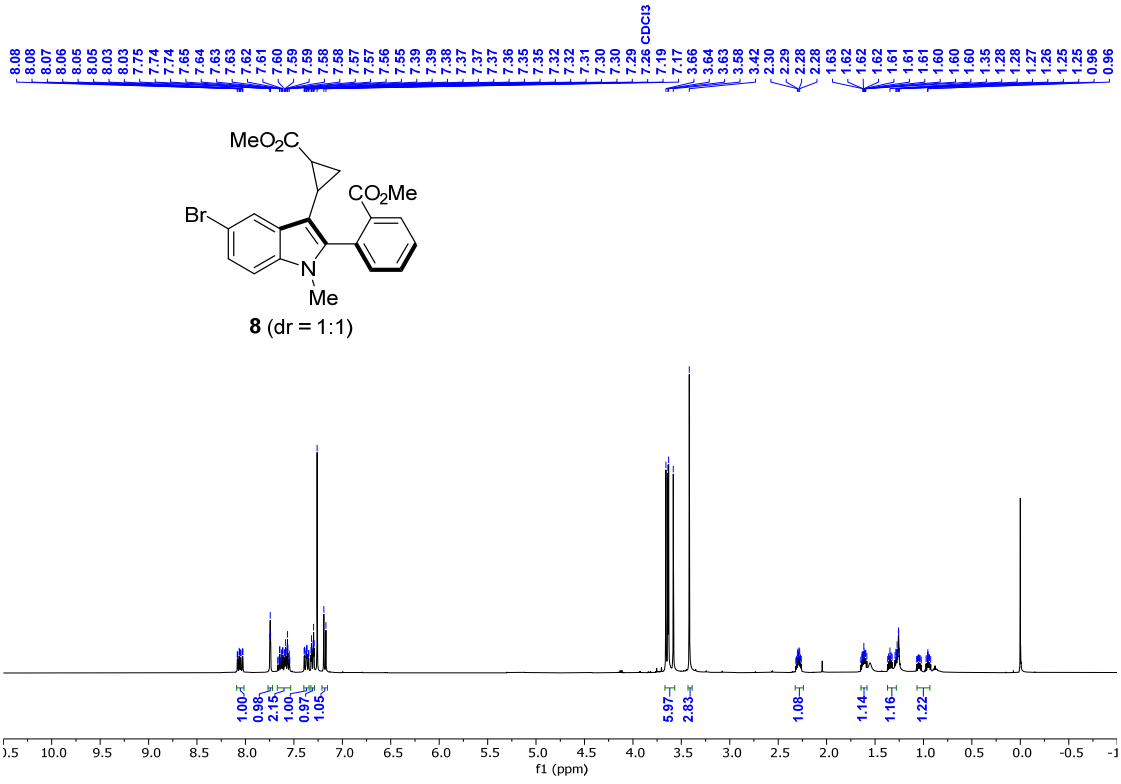
7

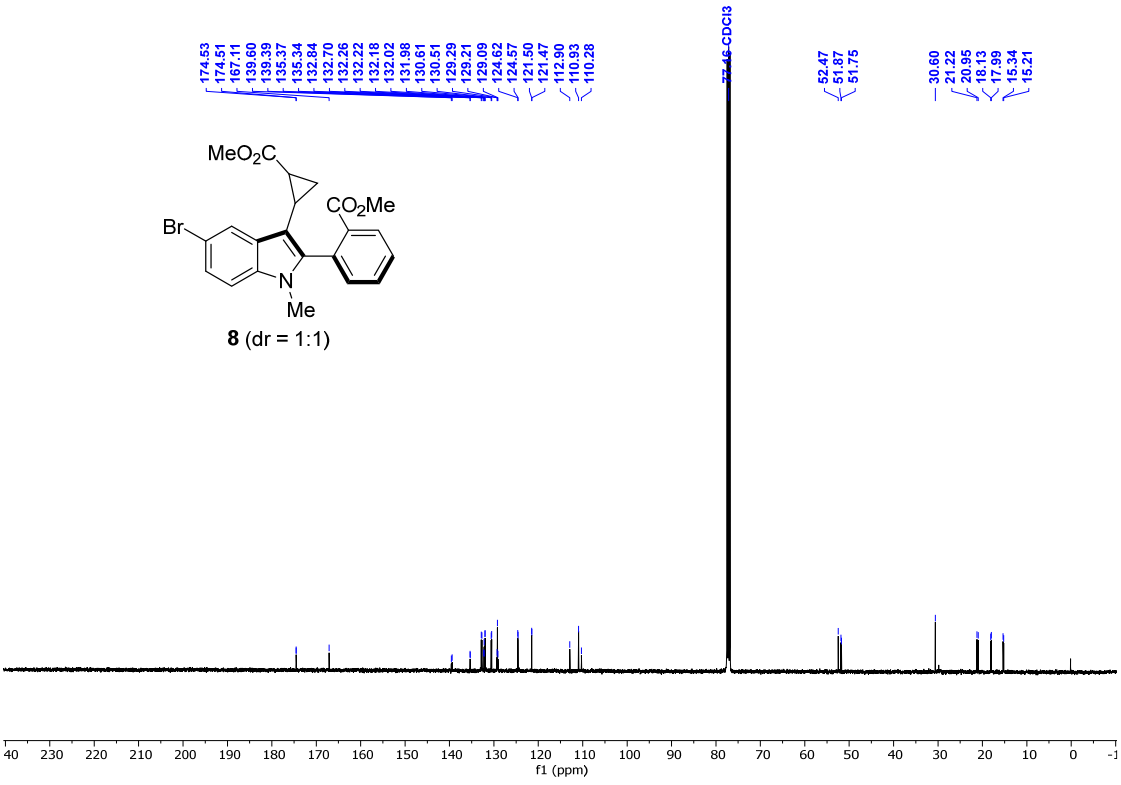

CO2Me
O
Br
N
Me
7
(H-H COSY)
f2 (ppm)
f1 (ppm)

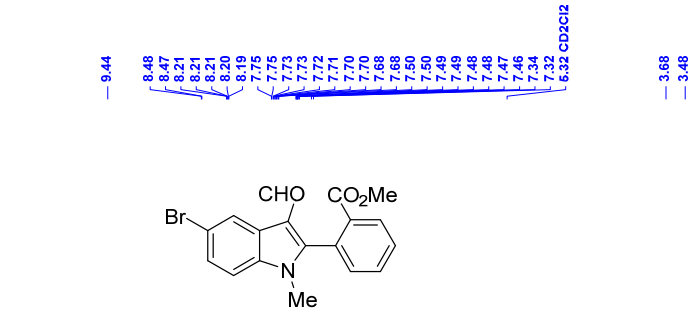

CO2Me
O
Br
N
Me
7
(HSQC)
f2 (ppm)
f1 (ppm)


CO2Me
O
Br
N
Me
7
(HMBC)
f2 (ppm)
f1 (ppm)

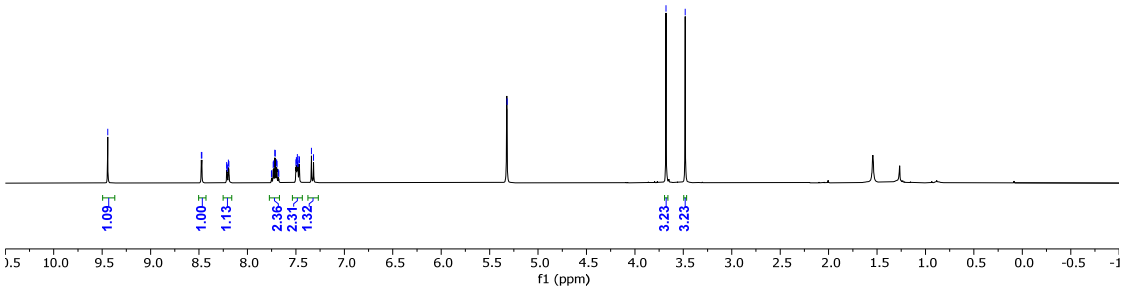

H3
HMBC
C7
C1
f2 (ppm)
f1 (ppm)

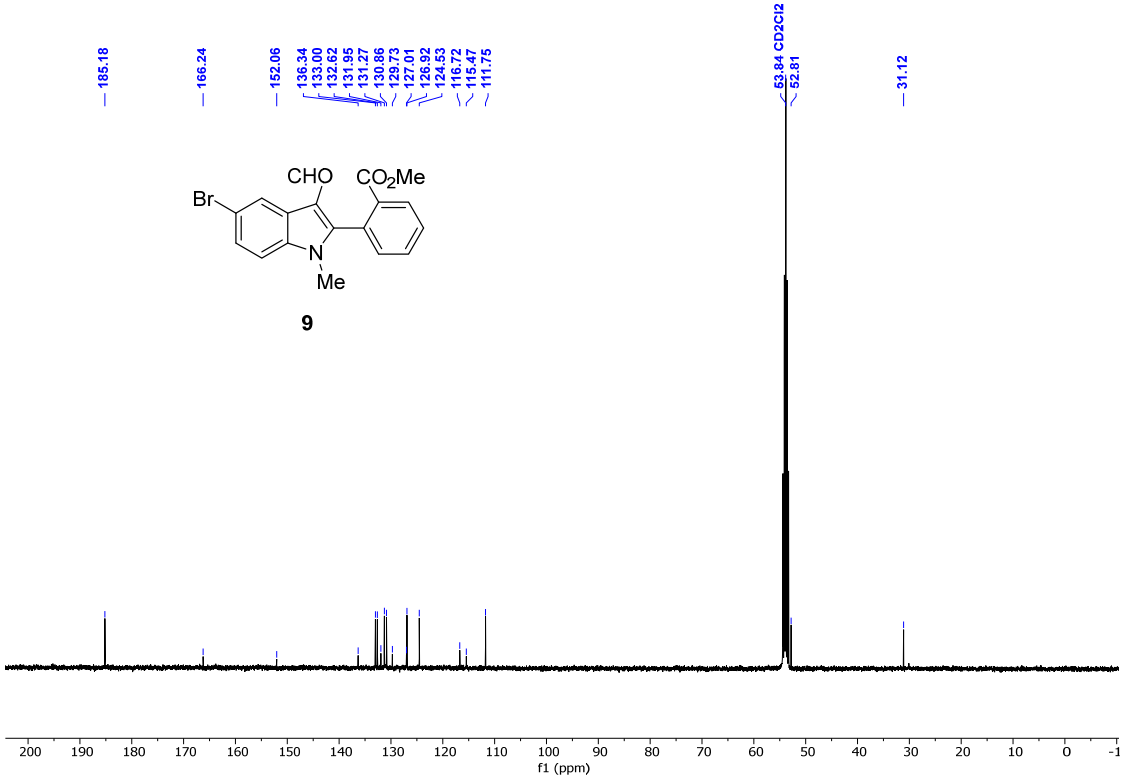

MeO2C
CO2Me
Br
N
Me
8 (dr = 1:1)
f1 (ppm)


MeO2C
CO2Me
Br
N
Me
8 (dr = 1:1)
f1 (ppm)


9.44
8.48
8.47
8.21
8.21
8.21
8.20
8.19
7.75
7.75
7.73
7.73
7.72
7.71
7.70
7.70
7.68
7.68
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.34
7.32
6.32 CD2Cl2
3.68
3.48
CHO
CO2Me
Br
N
Me

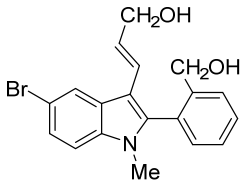
9


1.09
1.00
1.13
2.36
2.31
1.32
3.23
3.23
f1 (ppm)

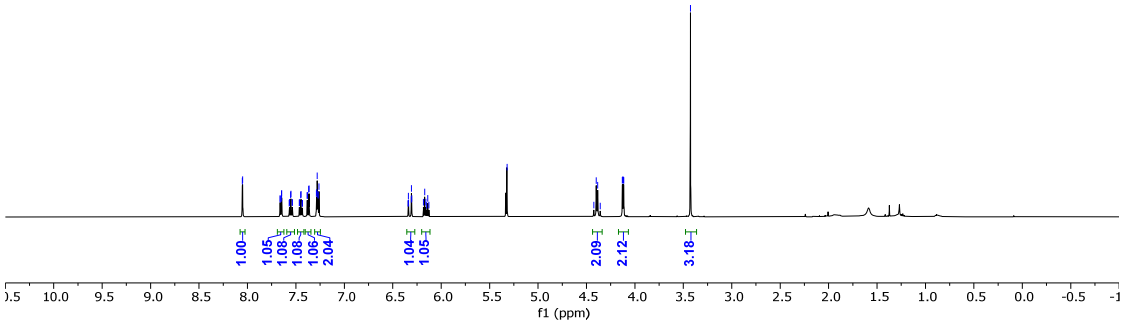

185.18
166.24
152.06
136.34
133.00
132.62
131.95
131.27
130.86
129.73
127.01
126.92
124.53
116.72
115.47
111.75
53.84 CD2Cl2
52.81
31.12
CHO
CO2Me
Br
N
Me
f1 (ppm)

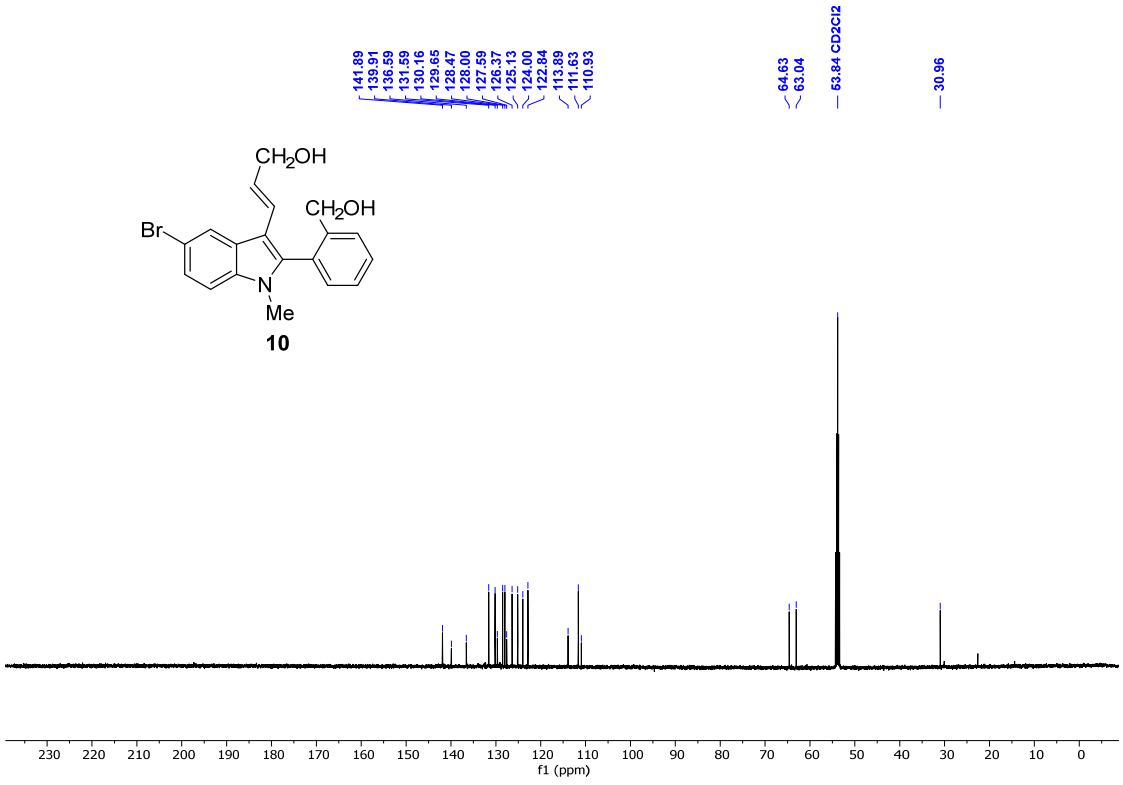
9


8.05
8.05
7.66
7.66
7.65
7.65
7.65
7.57
7.57
7.55
7.55
7.54
7.54
7.47
7.46
7.45
7.45
7.44
7.43
7.38
7.38
7.37
7.36
7.29
7.29
7.28
7.27
7.27
7.26
6.34
6.34
6.34
6.31
6.31
6.30
6.18
6.17
6.16
6.15
6.14
6.13
5.32 CD2Cl2
4.42
4.40
4.38
4.36
4.13
4.13
4.12
4.12
3.43


CH2OH
CH2OH
Br
N
Me

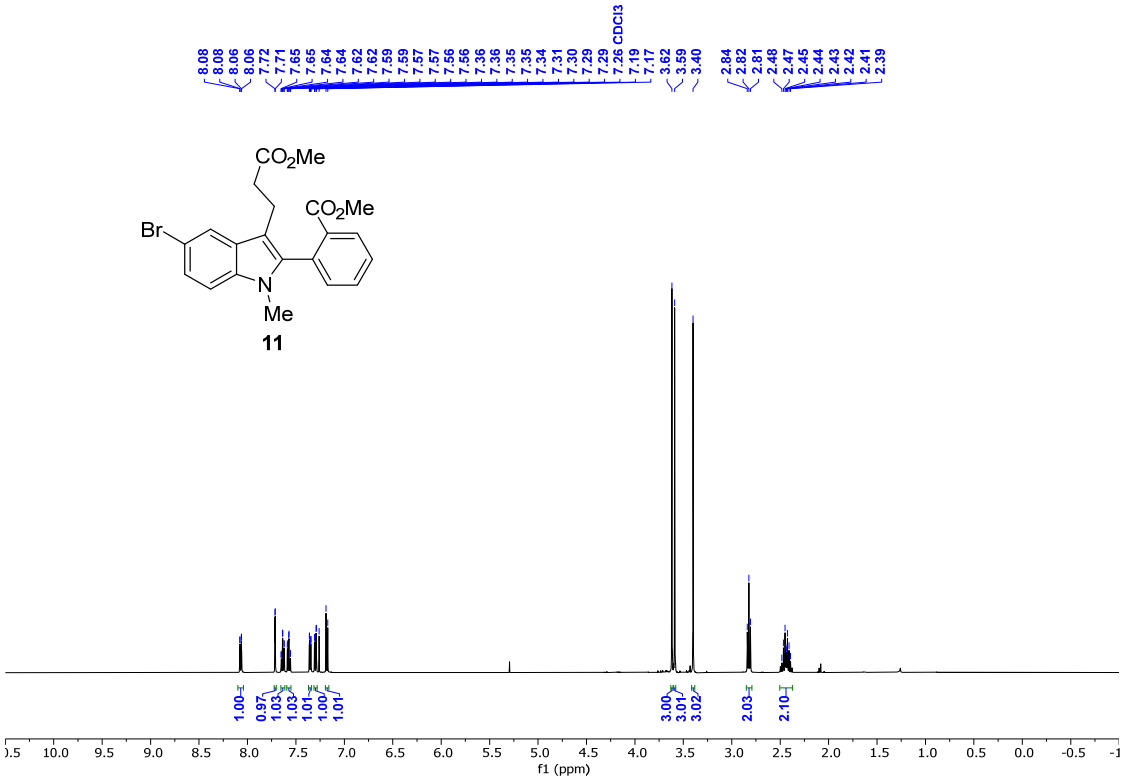
10

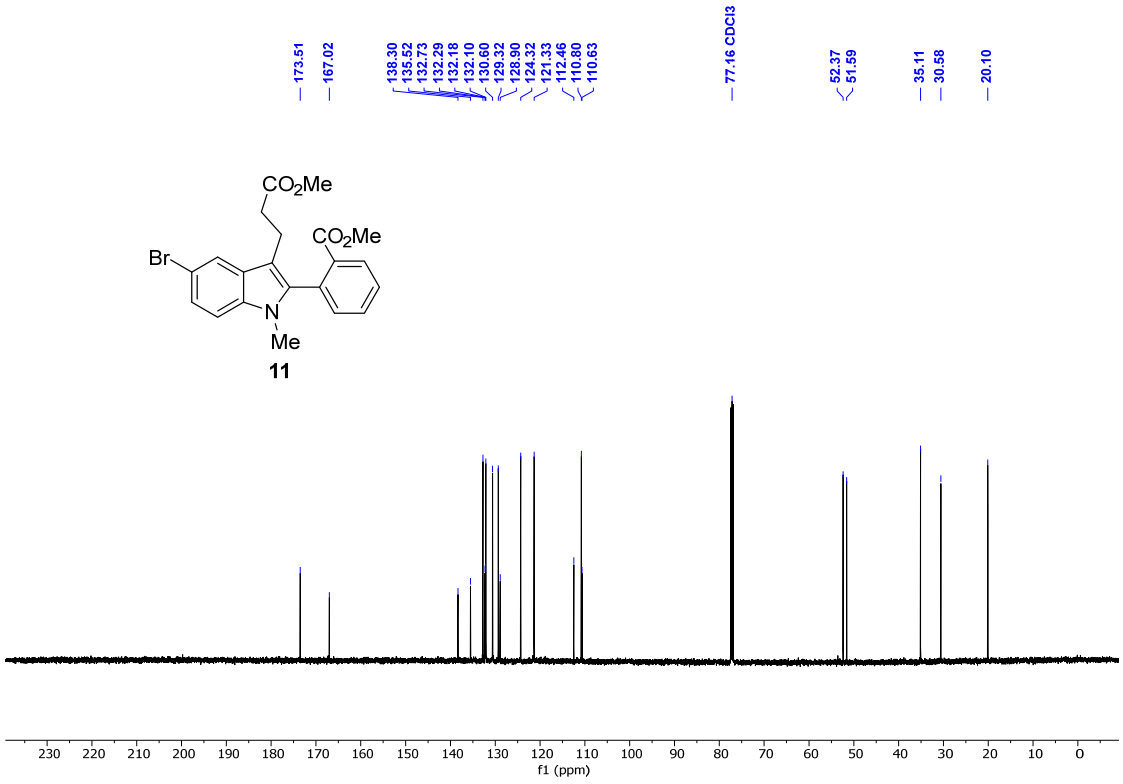

1.00
1.05
1.08
1.08
1.06
2.04
1.04
1.05
2.09
2.12
3.18
f1 (ppm)

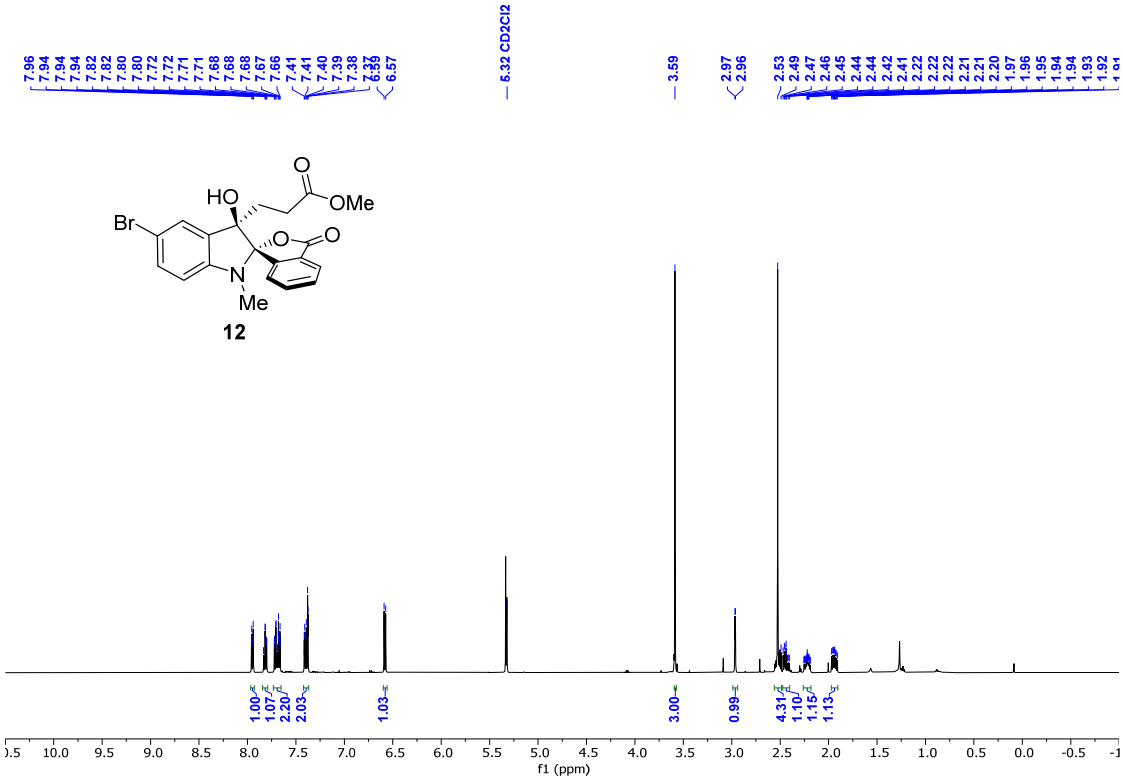

141.89
139.91
136.59
131.59
130.16
129.65
128.47
128.00
127.59
126.37
125.13
124.00
122.84
113.89
111.63
110.93
64.63
63.04
53.84 CD2Cl2
30.96
f1 (ppm)

CH2OH
CH2OH
Br
N
Me

10

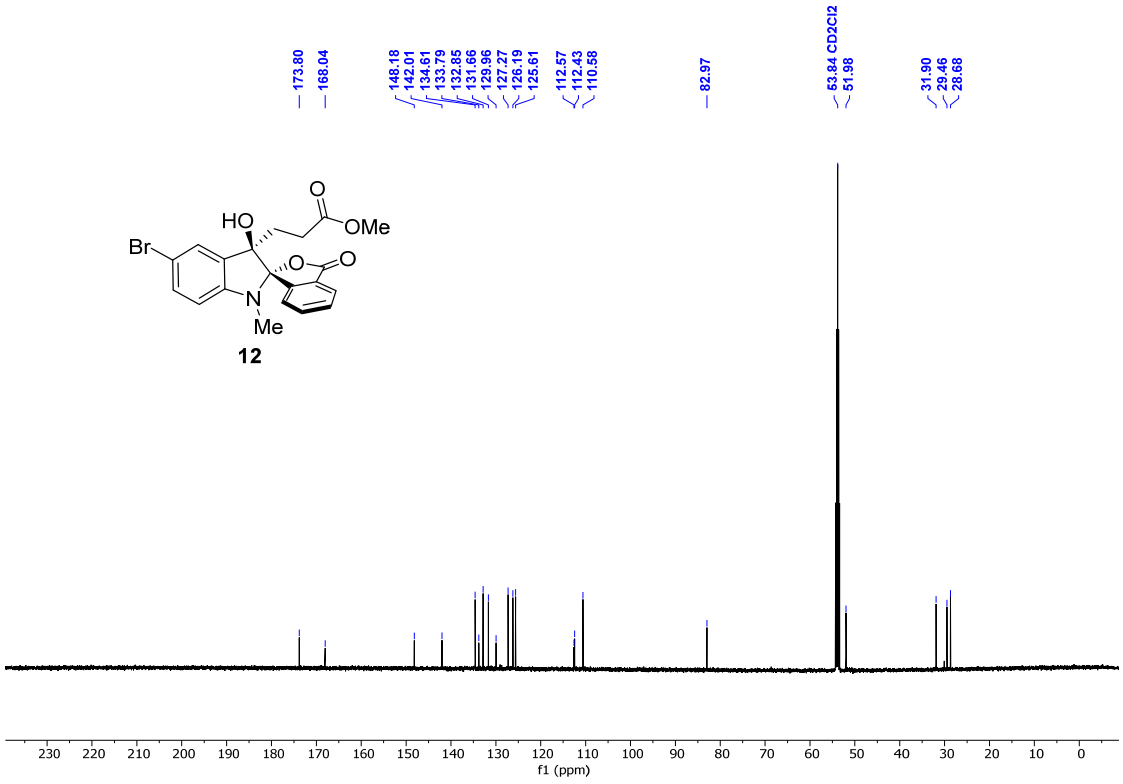

8.08
8.08
8.06
8.06
7.72
7.71
7.65
7.65
7.64
7.64
7.62
7.62
7.59
7.59
7.57
7.57
7.56
7.56
7.36
7.36
7.35
7.35
7.34
7.31
7.30
7.29
7.29
7.26 CDCl3
7.19
7.17
3.62
3.59
3.40
2.84
2.82
2.81
2.48
2.47
2.45
2.44
2.43
2.42
2.41
2.39
CO2Me
CO2Me
Br
N
Me
11
1.00
0.97
1.03
1.03
1.01
1.00
1.01
3.00
3.01
3.02
2.03
2.10
f1 (ppm)


173.51
167.02
138.30
135.52
132.73
132.29
132.18
132.10
130.60
129.32
128.90
124.32
121.33
112.46
110.80
110.63
77.16 CDCl3
52.37
51.59
35.11
30.58
20.10
CO2Me
CO2Me
Br
N
Me
11
f1 (ppm)


7.96
7.94
7.94
7.94
7.82
7.82
7.80
7.80
7.72
7.72
7.71
7.71
7.68
7.68
7.68
7.67
7.66
7.41
7.41
7.40
7.39
7.38
6.57
5.32 CD2Cl2
3.59
2.97
2.96
2.53
2.49
2.47
2.46
2.45
2.44
2.44
2.42
2.41
2.22
2.22
2.22
2.21
2.21
2.20
1.97
1.96
1.95
1.94
1.94
1.93
1.92
1.00
1.07
2.20
2.03
1.03
3.00
0.99
4.31
1.10
1.15
1.13
f1 (ppm)

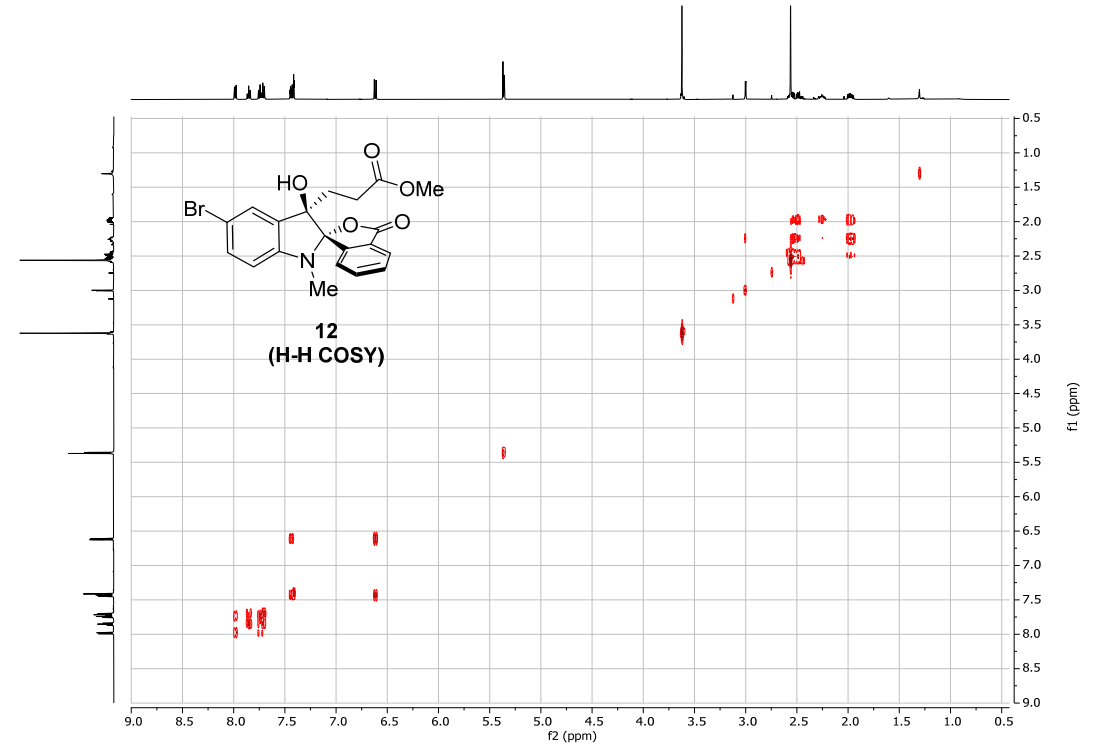
HO
OMe
Br
O
O
N
Me

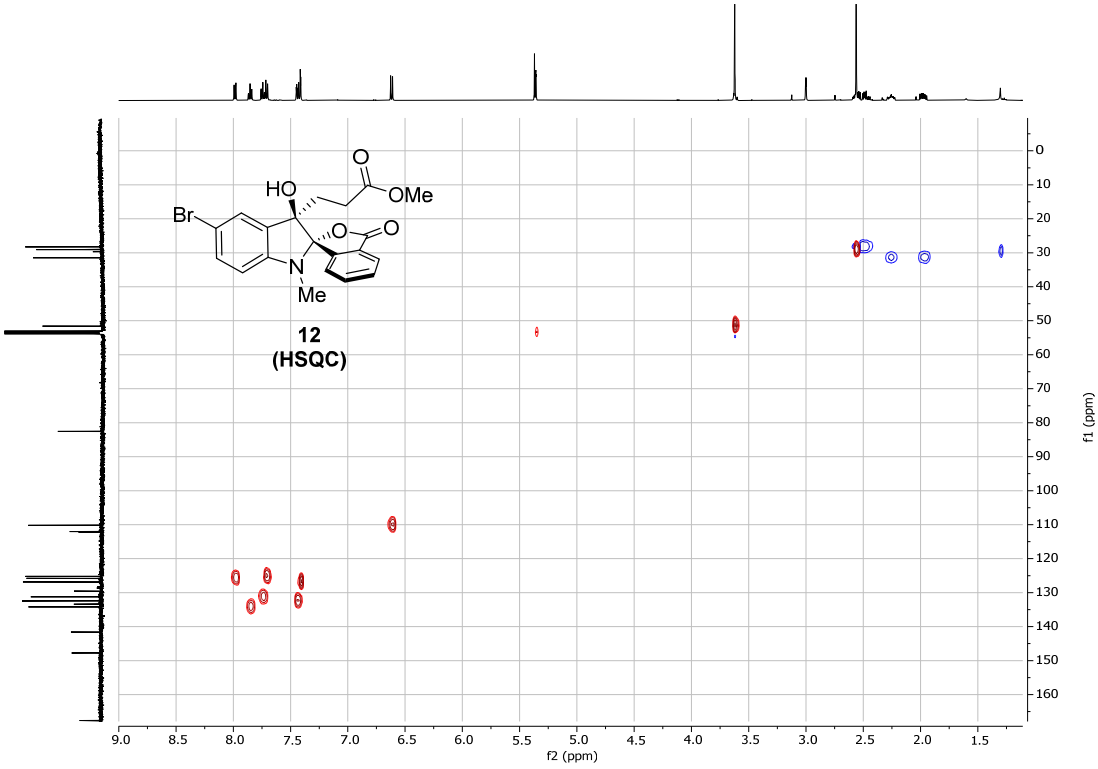
12

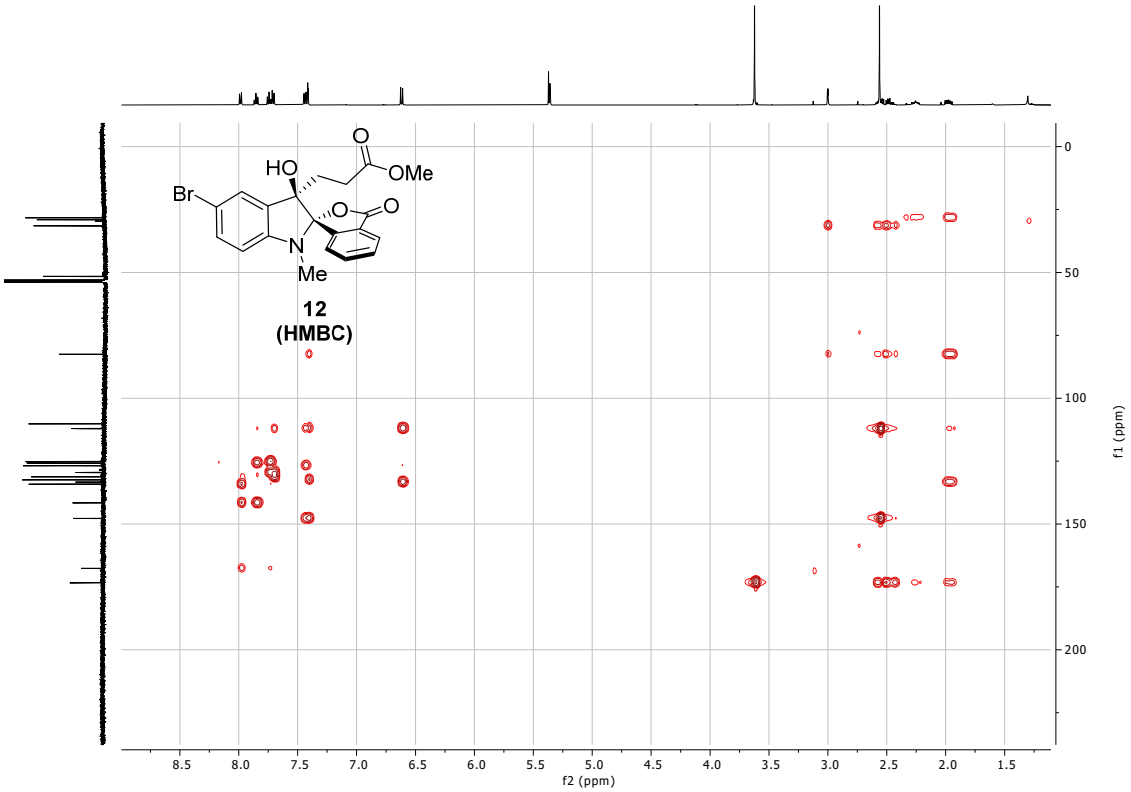

173.80
168.04
148.18
142.01
134.61
133.79
132.85
131.66
129.96
127.27
126.19
125.61
112.57
112.43
110.58
82.97
53.84 CD2Cl2
51.98
31.90
29.46
28.68
f1 (ppm)

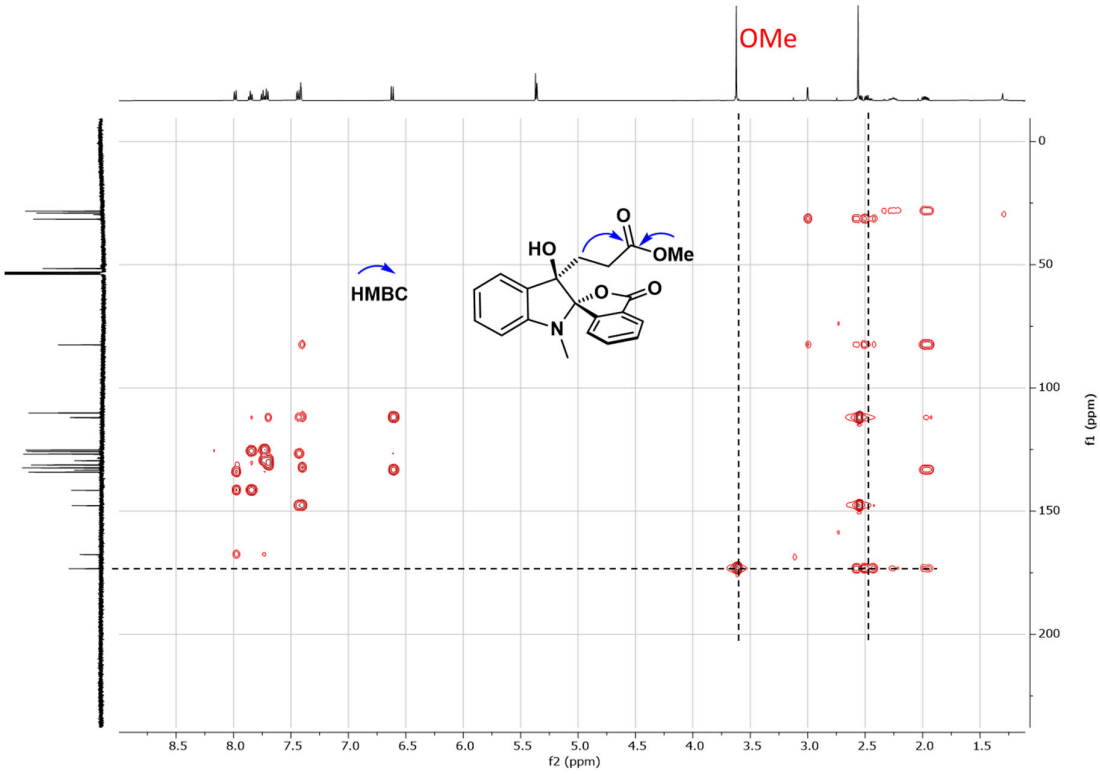
HO
OMe
Br
O
O
N
Me

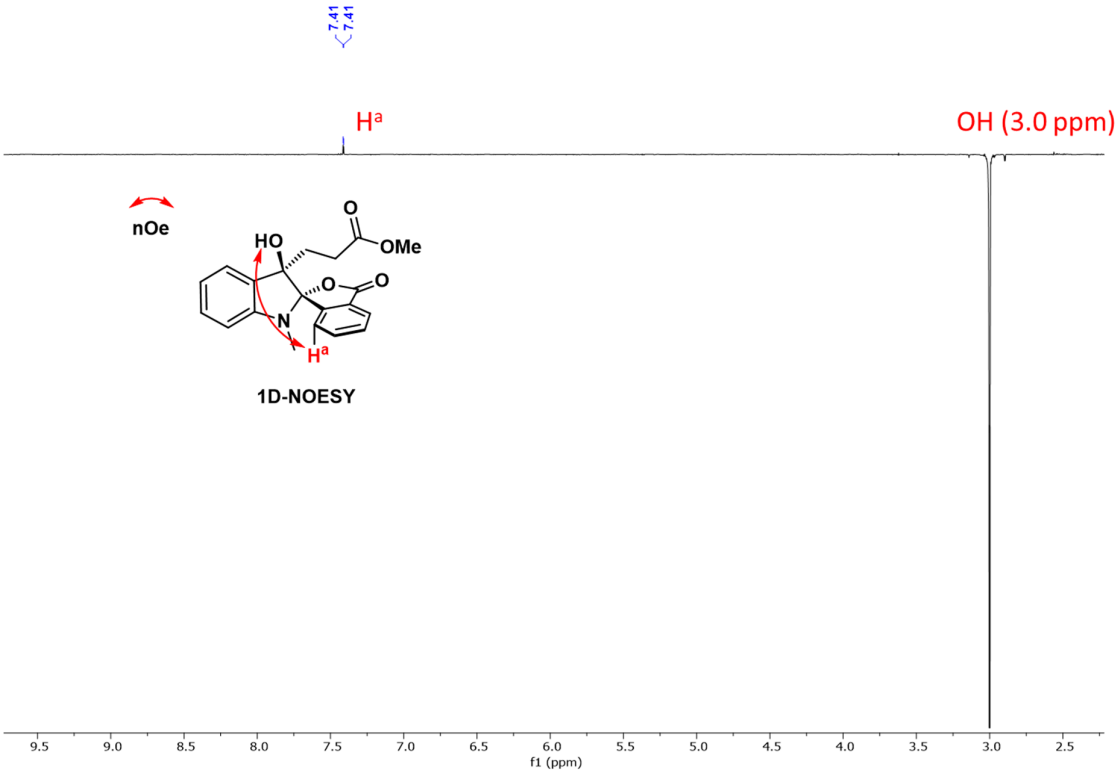
12

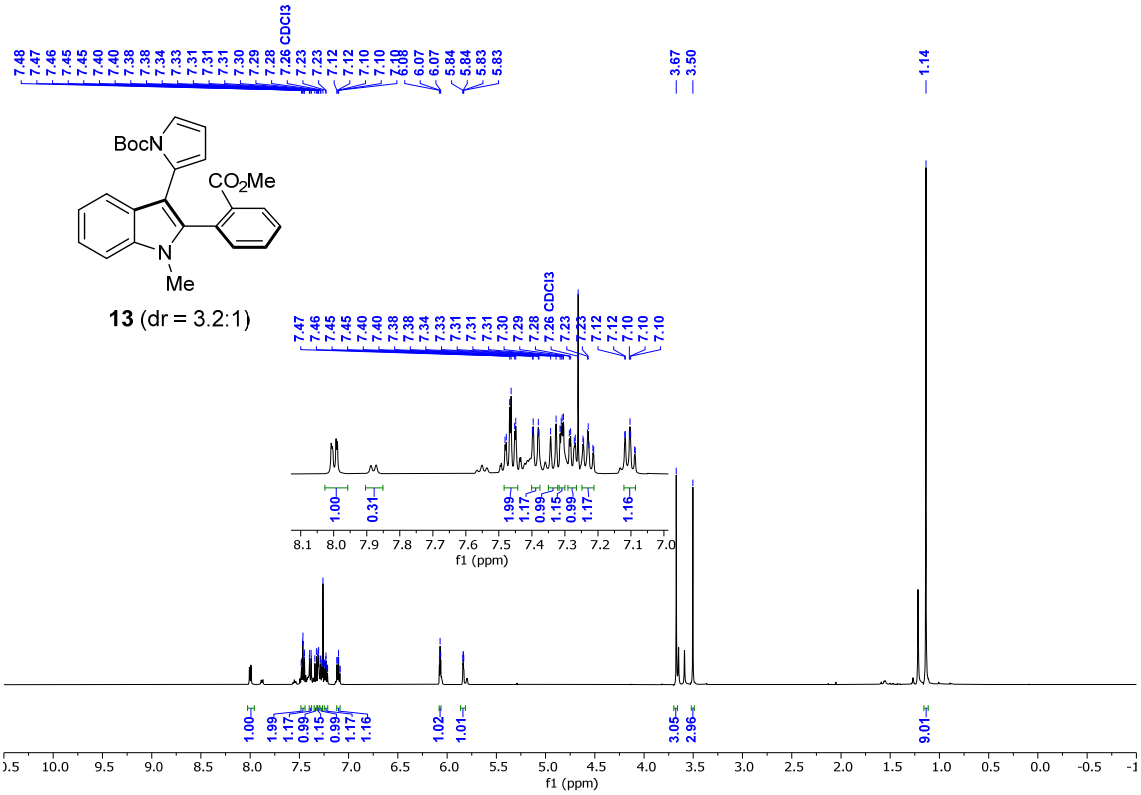

HO
OMe
Br
O
O
N
Me
12
(H-H COSY)
f2 (ppm)
f1 (ppm)

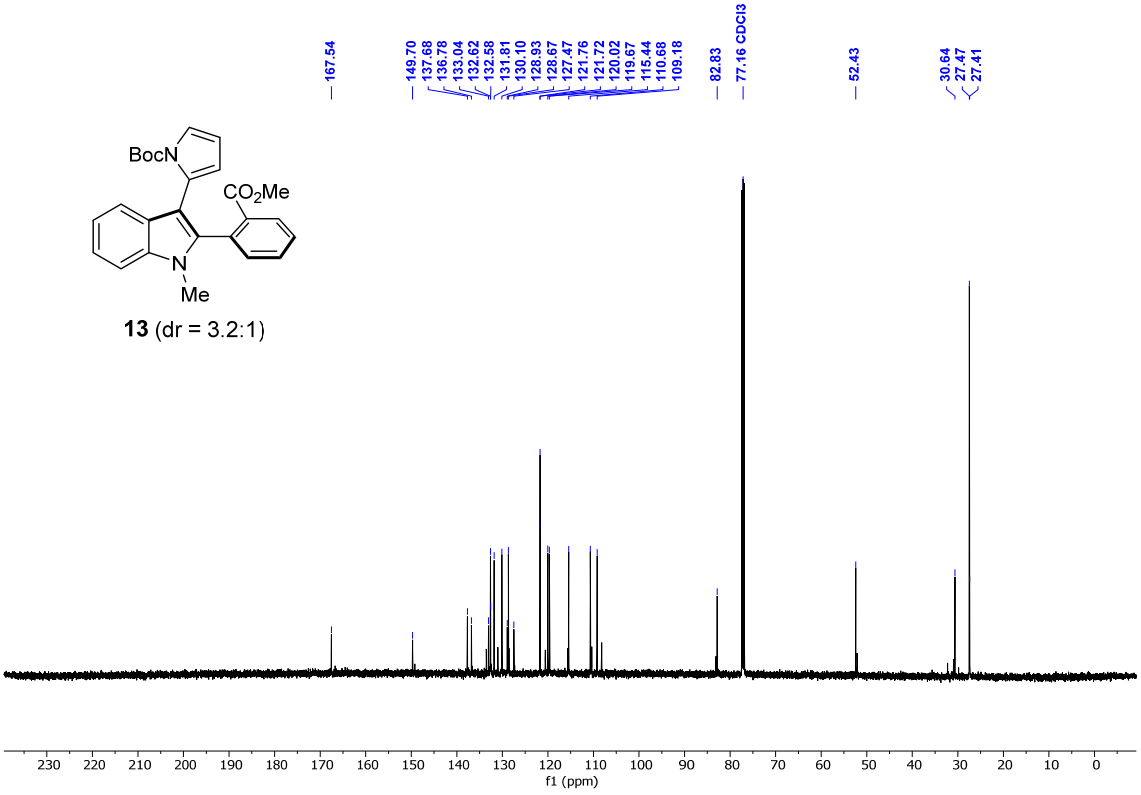

HO
OMe
Br
O
O
N
Me
12
(HSQC)
f2 (ppm)
f1 (ppm)

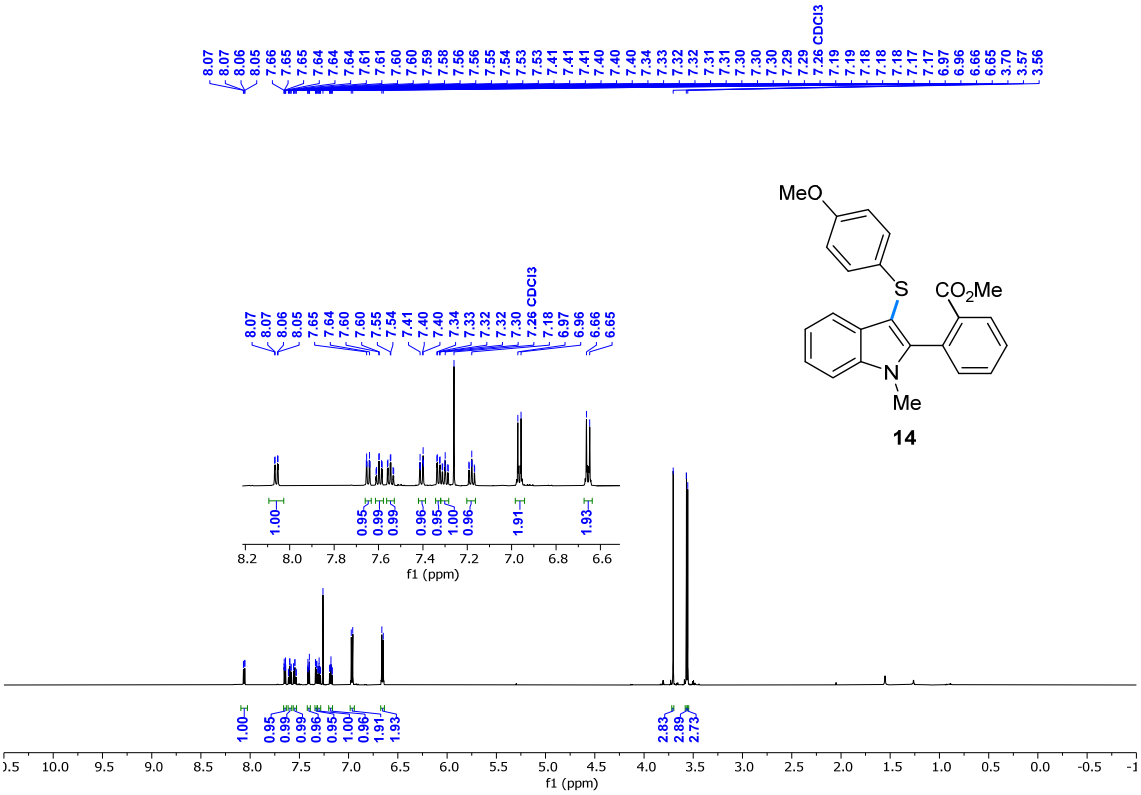

HO
OMe
Br
O
O
N
Me
12
(HMBC)
f2 (ppm)
f1 (ppm)

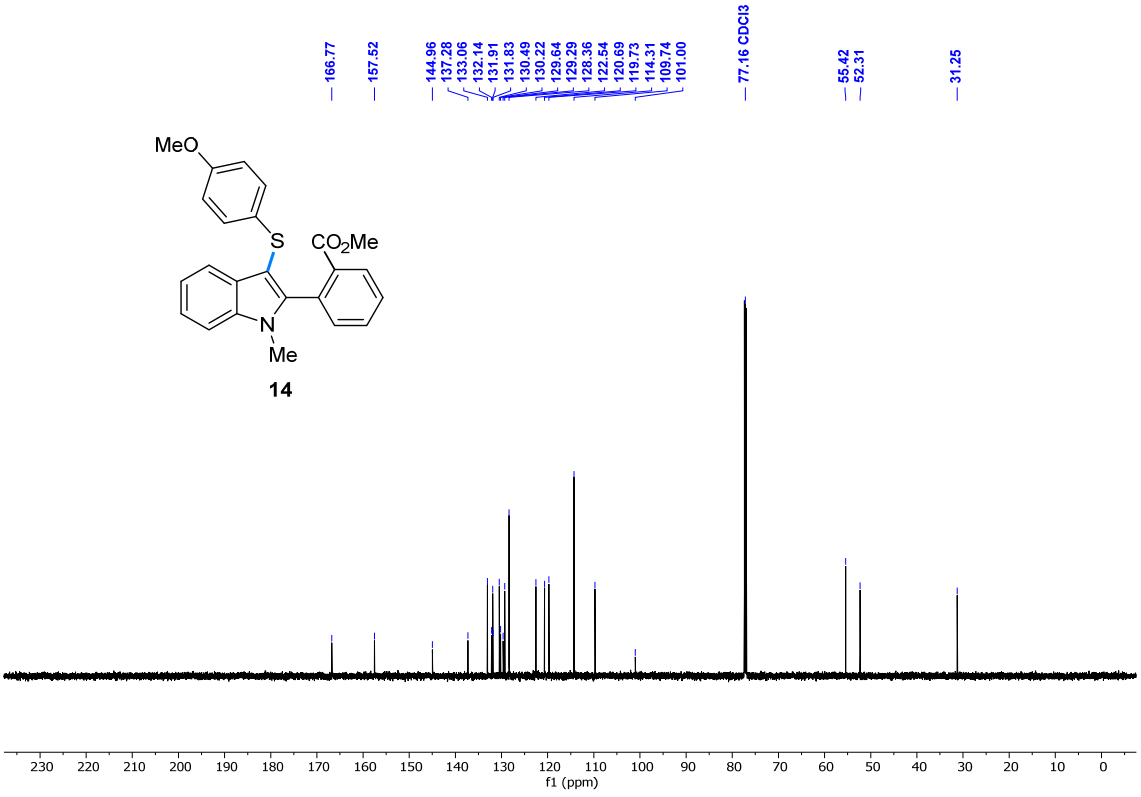

OMe
HMBC
HO
OMe
O
O
N
f2 (ppm)
f1 (ppm)


7.41
7.41
Ha
OH (3.0 ppm)
nOe
HO
O
OMe
O
O
N
Ha
1D-NOESY
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


BocN
CO2Me
N
Me
13 (dr = 3.2:1)
f1 (ppm)


BocN
CO2Me
N
Me
13 (dr = 3.2:1)
f1 (ppm)


MeO
S
CO2Me
N
Me
14
f1 (ppm)


MeO
S
CO2Me
N
Me
14
f1 (ppm)