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Supporting Information

Enhanced Energy Transfer in A π-Conjugated Covalent Organic Framework Facilitates Excited-State Nickel Catalysis

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Supporting Information

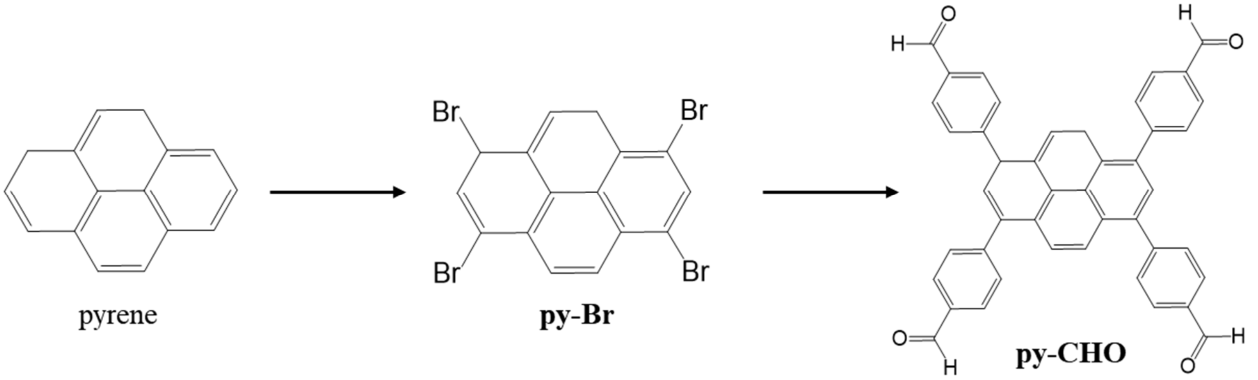
Contents

S1. Materials and Methods

All starting materials were purchased from Sigma-Aldrich and Fisher (USA) unless otherwise noted and used without further purification. Transmission electron microscopy (TEM) was carried out on a TECNAI Spirit microscope. Powder X-ray diffraction (PXRD) data were collected on SAXSLAB's GANESHA using transmission mode. N_2 sorption measurements at 77 K were carried out on a Micromeritics 3FLEX instrument. Inductively coupled plasma-mass spectrometry (ICP-MS) data were obtained with an Agilent 7700x ICP-MS and analyzed using ICP-MS Mass Hunter version B01.03. Samples were diluted in a 2% HNO_3 matrix and analyzed with a ^{159}Tb internal standard against a 12-point standard curve over the range from 0.1 ppb to 500 ppb. The correlation was > 0.9997 for all analyses of interest. Data collection was performed in Spectrum Mode with five replicates per sample and 100 sweeps per replicate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX spectrometer at 400, and 101 MHz, respectively, referenced to the resonances resulting from the solvents. ^{19}F NMR spectra were recorded on a Bruker DRX spectrometer at 376 MHz. ^{1}H NMR Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad peak), coupling constants (Hz), integration and assignment. Emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Mass spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF Mass Spectrometer. Cyclic voltammetry (CV) spectra were recorded on a CHI420 electrochemistry workstation using three electrode systems. Measurements were recorded using a glassy carbon electrode ($S = 0.07$ cm^2) as working electrode and a platinum wire as a counter electrode. AgCl/Ag electrode in 10 mM $AgNO_3$ solution in acetonitrile with 0.1 M NBu_4PF_6 as electrolyte was used as the reference electrode, and its potential was calibrated with the Fc^+/Fc couple.

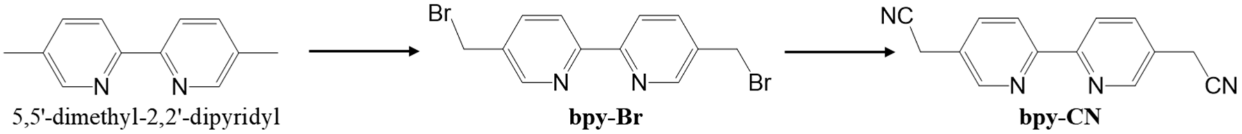
S2. Synthesis of COFs

Synthesis of 1,3,6,8-tetrabromopyrene. 1,3,6,8-tetrabromopyrene (**py-Br**) was synthesized according to reported method with slight modifications.[1] Bromine (16.2 g, 101.3 mmol) was slowly added into a nitrobenzene solution (150 mL) of pyrene (5.0 g, 24.7 mmol) with vigorous stirring at room temperature. After the addition was complete, the reaction temperature was heated at 160 ºC for 6 h. After cooling to room temperature, the mixture was poured into acetone (500 mL) and the precipitate was collected by filtration and thoroughly washed with ethanol. The product was fully dried and used without further purification.



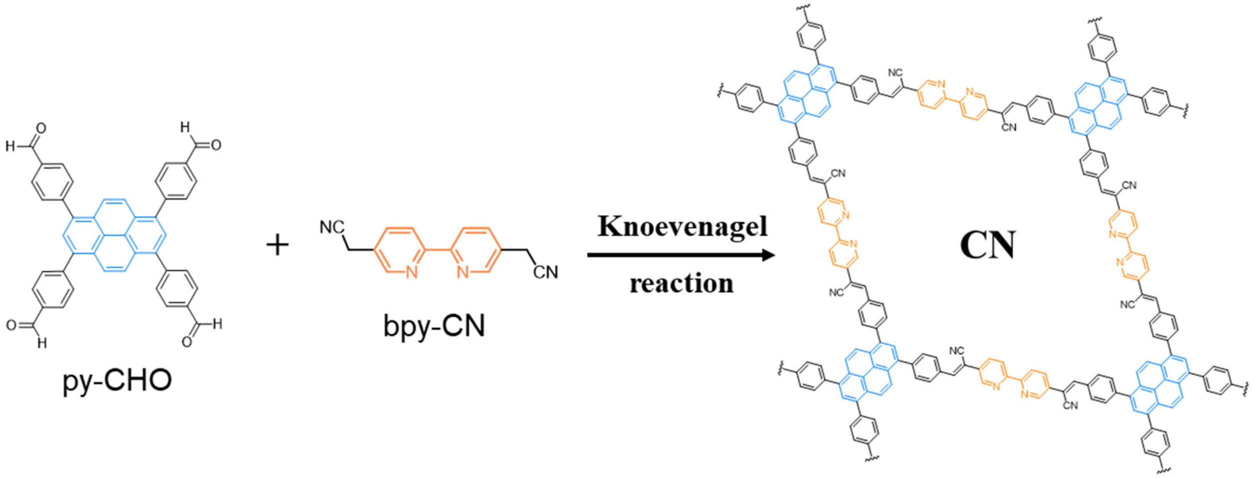
Synthesis of 1,3,6,8-tetrakis(4-formylphenyl)pyrene. 1,3,6,8-tetrakis(4-formylphenyl)pyrene (**py-CHO**) was synthesized according to the reported method with slight modifications.[2] After a 250 mL round bottom flask containing **py-Br** (3.0 g, 5.8 mmol), 4-formylphenylboronic acid (6.0 g, 40.0 mmol), K_2CO_3 (4.0 g, 29.0 mmol), and $Pd(PPh_3)_4$ (600 mg, 0.52 mmol) was dried under vacuum for 3 h, dioxane (80 mL) and H_2O (14 mL) were added into the flask and the mixture was refluxed under N_2 atmosphere for 3 days. Upon cooling to room temperature, the mixture was slowly transferred to a beaker containing 40 mL concentrated hydrochloric acid. The solid was filtered, washed with methanol and water, and dried in a 100 ºC oven overnight. Chloroform (300 mL) was poured into the solid and stirred at 50 ºC for 6 hours. After cooling to room temperature, the solid was separated by filtration and dried under vacuum to obtain **py-CHO** (2.0 g, 3.2 mmol, 55%). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.19 (s, 4H), 8.20 (s, 4H), 8.12 (d, J = 7.9

Hz, 8H), 8.07 (s, 2H), 7.88 (d, J = 7.8 Hz, 8H). HRMS m/z Calc. for $C_{44}H_{26}O_4$ ([M^+]): 618.1831, Found: 618.1829



Synthesis of 5,5'-bis(bromomethyl)-2,2'-bipyridyl. 5,5'-Bis(bromomethyl)-2,2'-bipyridyl (**bpy-Br**) was synthesized according to the reported method with slight modifications.[2] After degassing with N_2 for 30 min, 300 mL CCl_4 was poured into a 500 mL round bottom flask containing 5,5'-dimethyl-2,2'-dipyridyl (5.0 g, 27.2 mmol), *N*-bromosuccinimide (9.8 g, 54.4 mmol), and azobisisobutyronitrile (0.1 g, 0.61 mmol). The mixture was refluxed under N_2 atmosphere for one day and hot filtered. After the filtrate was concentrated under vacuum, the crude solid was purified in methanol by sonication to afford a white powder (4.0 g, 11.7 mmol, 43%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, J = 2.1 Hz, 2H), 8.33 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 8.2, 2.3 Hz, 2H), 4.47 (s, 4H).

Synthesis of 2,2'-([2,2'-bipyridine]-5,5'-diyl)diacetonitrile. After **bpy-Br** (6.0 g, 17.54 mmol) and sodium cyanide (5.40 g, 110.20 mmol) were dissolved in dimethyl sulfoxide (80 mL), the solution was stirred at 45 ºC for 6 hours and then stirred at room temperature for 12 hours. The solution was heated to 80 ºC and poured without cooling into deionized water (500 mL), filtered, and washed with deionized water several times. After the crude product was dried in a 100 ºC oven, it was dissolved in methylene chloride and filtered using celite. The filtrate was concentrated and purified by silica gel column chromatography using methylene chloride/methanol (100/1) as eluent to obtain 2,2'-([2,2'-bipyridine]-5,5'-diyl)diacetonitrile (**bpy-CN**, 2.37 g, 10.12 mmol, 57.68%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 2H), 8.49 (d, J = 8.2 Hz, 2H), 7.88 (dd, J = 8.2, 2.3 Hz, 2H), 3.87 (s, 4H). HRMS m/z Calc. for $C_{14}H_{11}N_4$ ([M+H^+]): 235.0984, Found: 235.0989



Synthesis of pyrene-based COF. A 10 mL Schlenk tube was charged with py-CHO (30 mg, 0.048 mmol), bpy-CN (23.1 mg, 0.099 mmol), 1,2-dichlorobenzene (2 mL), 1-butanol (2 mL) and aqueous KOH solution (0.1 mL, 4 M). The mixture was stirred for 3 min and then degassed through three freeze-pump-thaw cycles using a liquid nitrogen bath. The tube was sealed under vacuum, stirred for 1 min, and then heated at 120 ºC for 3 days. After cooling to room temperature, the precipitate was washed with tetrahydrofuran and water. 300 mL chloroform was then poured into the solid and the mixture was stirred at 60 ºC for 12 hours. After filtration, the resulting powder was dried at 100 ºC to obtain the pyrene-based COF (**CN**). Yield: 37 mg (75%).

Synthesis of Ni-coordinated COF. To 10 mL of **CN** dispersion (10 mg/mL) in 1:1 (V/V) mixture of *N,N*-dimethylformamide (DMF) and toluene was added $NiBr_2$·dme (15.4 mg, 50 μmol). The resulting solution was stirred at 60 ºC for 24 hours. The precipitate was filtered and washed with DMF once and toluene once to yield **NiCN** in quantitative yield. The nickel loading was determined by ICP-MS analysis to be ~100 %.

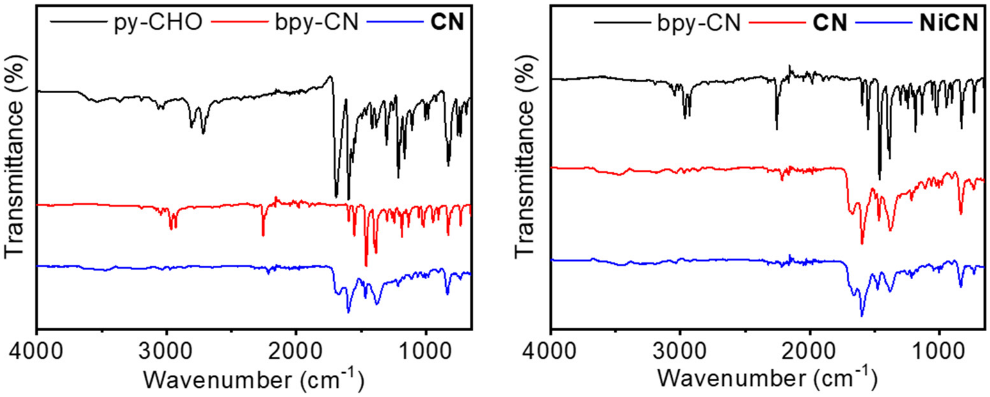


Figure S1. FT-IR spectra for monomers and COFs. From the spectra, several changes in functional groups, particularly near disappearance of formyl C-O stretching vibration, were detected after the Knoevenagel reaction.

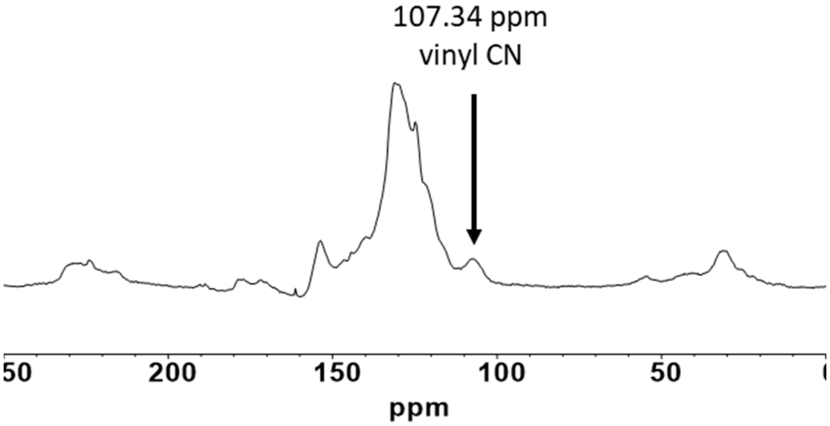


Figure S2. Solid-state NMR spectrum of **CN**. Peak at 107.34 was assigned to vinyl nitrile.[3] The result matches well with the literature report.[2]

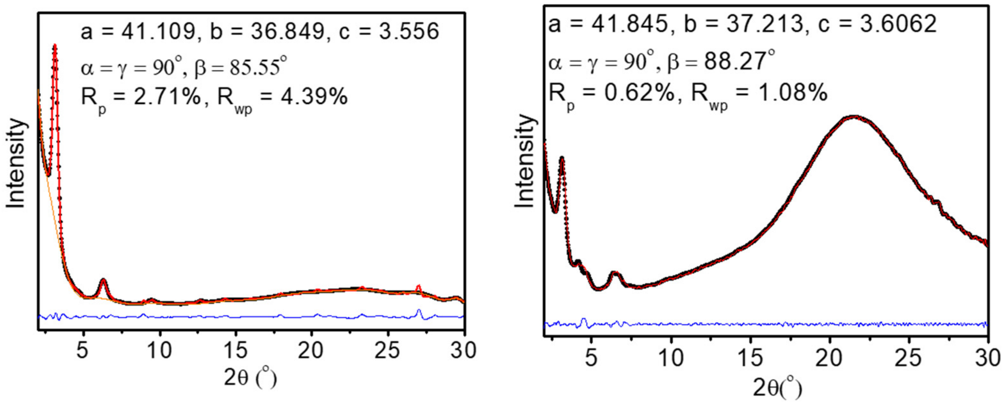


Figure S3. Fitting and Rietveld refinement of the PXRD of **CN** (left) and Fitting and Pawley refinement of the PXRD of **NiCN** (right). Black, red, and blue lines indicate experimental PXRD, simulated PXRD, and their difference, respectively. The detailed Rietveld refinement results for **CN** are shown in Table S1.

Table S1. Fractional atomic coordinates for the structural model of **CN** obtained from Rietveld refinements.

<table>
<tr><th colspan="4">CN</th></tr>
<tr><td colspan="4">Space group: C2/M
a = 41.109 Å, b = 36.849 Å, c = 3.556 Å
α=γ= 90º, β = 88.55º</td></tr>
<tr><td>Atom</td><td>x</td><td>y</td><td>z</td></tr>
<tr><td>C1</td><td>0.52814</td><td>0.57682</td><td>0.38953</td></tr>
<tr><td>C2</td><td>0.52772</td><td>0.53855</td><td>0.36831</td></tr>
<tr><td>C3</td><td>0.55336</td><td>0.51837</td><td>0.20292</td></tr>
<tr><td>C4</td><td>0.55683</td><td>0.59884</td><td>0.31256</td></tr>
<tr><td>C5</td><td>0.55433</td><td>0.63367</td><td>0.15969</td></tr>
<tr><td>C6</td><td>0.58032</td><td>0.6566</td><td>0.12449</td></tr>
<tr><td>C7</td><td>0.61062</td><td>0.64545</td><td>0.24011</td></tr>
<tr><td>C8</td><td>0.6134</td><td>0.61023</td><td>0.38266</td></tr>
<tr><td>C9</td><td>0.58729</td><td>0.58753</td><td>0.41853</td></tr>
<tr><td>C10</td><td>0.63892</td><td>0.6675</td><td>0.24523</td></tr>
<tr><td>C11</td><td>0.6446</td><td>0.70275</td><td>0.15349</td></tr>
<tr><td>C12</td><td>0.67582</td><td>0.71903</td><td>0.22429</td></tr>
<tr><td>C13</td><td>0.67903</td><td>0.75551</td><td>0.31931</td></tr>
<tr><td>C14</td><td>0.7085</td><td>0.76813</td><td>0.42559</td></tr>
<tr><td>C15</td><td>0.73436</td><td>0.74414</td><td>0.43467</td></tr>
<tr><td>N16</td><td>0.73206</td><td>0.70966</td><td>0.32079</td></tr>
<tr><td>C17</td><td>0.7038</td><td>0.69801</td><td>0.21588</td></tr>
<tr><td>C18</td><td>0.621</td><td>0.72605</td><td>0.00889</td></tr>
<tr><td>C19</td><td>0.5</td><td>0.59454</td><td>0.5</td></tr>
<tr><td>C20</td><td>0.5</td><td>0.51932</td><td>0.5</td></tr>
<tr><td>N21</td><td>0.60278</td><td>0.74635</td><td>-0.11509</td></tr>
</table>

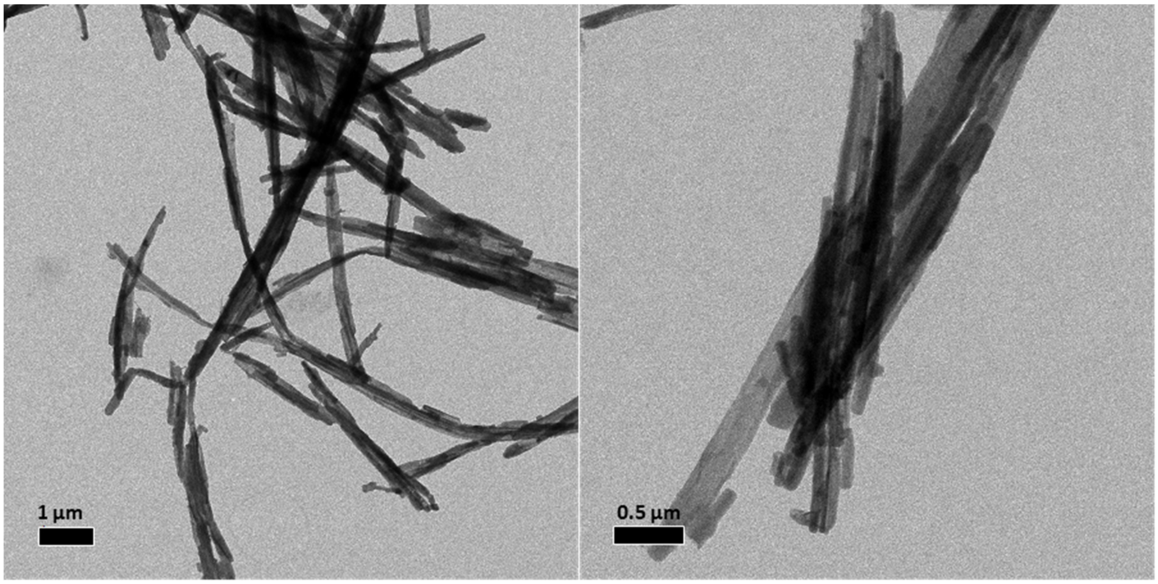


Figure S4. TEM images of **CN** and **NiCN**.

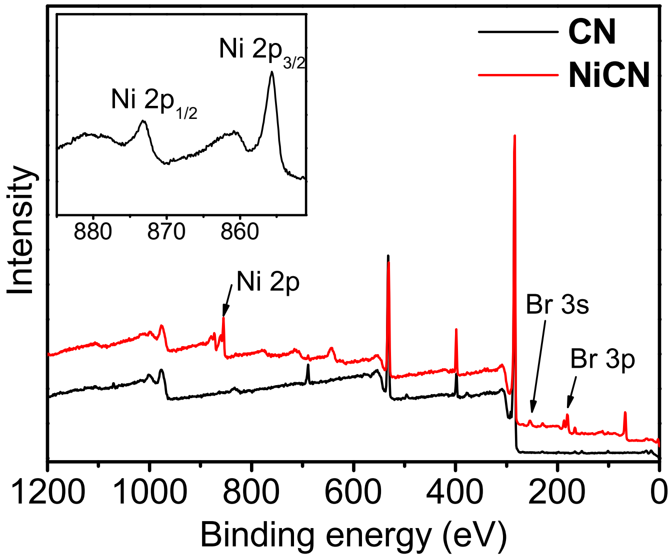


Figure S5. XPS spectra of **CN** and **NiCN**. Ni and Br peaks were observed in the spectrum of **NiCN** but not in the spectrum of **CN**. Inset shows the Ni 2p region XPS spectrum.

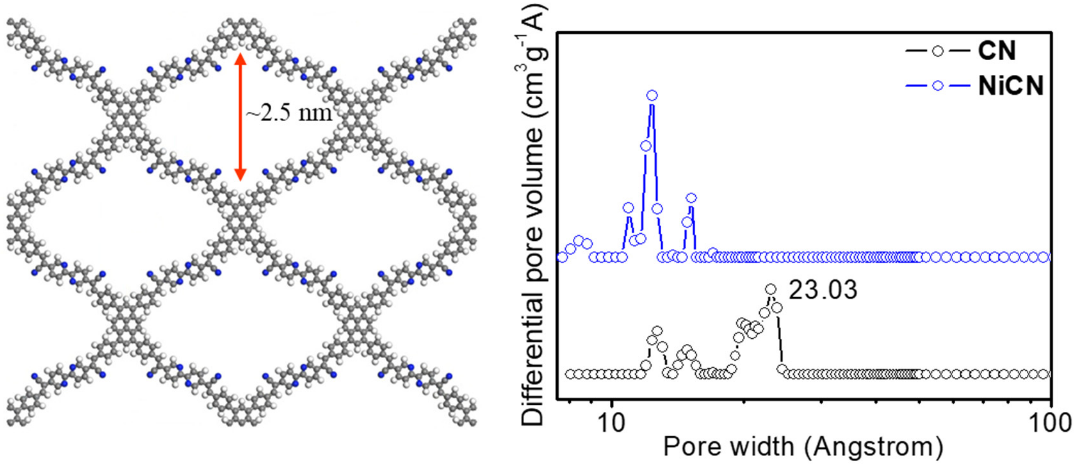
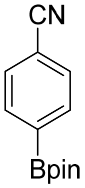


Figure S6. The pore size distributions of **CN** and **NiCN** calculated by DFT method using N_2 cylindrical pores model with regularization (0.00316). The calculated pore sizes matched the expected pore sizes based on the structural models of the COFs.

S3. Catalytic Reactions and Characterization of Products

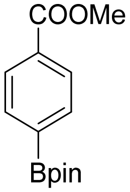
General procedure for borylation of aryl halides. Aryl halide (0.1 mmol, 1 equiv), bis(pinacolato)diboron (B_2pin_2, 0.3 mmol, 3 equiv.), pyridine (0.02 mmol, 1.6 µL, 20 mol%), and N,N-diisopropylethylamine (DIPEA, 3 mmol, 52 µL) were mixed in 4 mL dry acetonitrile (ACN) under nitrogen. **NiCN** (0.5 µmol based on pyrene, dispersion in ACN) was then added and the resulting mixture was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, the solvent was removed under vacuum. The residue was subjected to column chromatography on silica gel using n-hexane and ethyl acetate as eluent to give cross-coupling products **2a-2o**.

General procedure for trifluoromethylation of aryl halides. Copper iodide (0.05 mmol, 9.5 mg, 50 mol%), potassium fluoride (0.15 mmol, 8.7 mg, 1.5 equiv) and trifluoromethyltrimethylsilane ($TMSCF_3$, 0.15 mmol, 22 µL, 1.5 equiv) were added to 1 mL dry ACN under nitrogen. The solution was stirred for 10 mins. Aryl halide (0.1 mmol, 1 equiv) and **NiCN** (0.5 µmol based on pyrene, dispersion in ACN) in 3 mL ACN were then added and the resulting mixture was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, the solvent was removed under vacuum. The residue was subjected to column chromatography on silica gel using n-hexane and ethyl acetate as eluent to give cross-coupling products **3a**-**3o**.



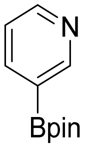
2a

White solid. 87% yield using 4-iodobenzointrile (**1a**) as the starting material. 83% yield using 4-bromobenzointrile (**1a'**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.89-7.86 (d, *J* = 8.3 Hz, 2H,), 7.62-7.60 (d, *J* = 8.3 Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 135.1, 131.1, 118.8, 114.5, 84.5, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{13}H_{17}BNO_2$), 229.1274; observed, 229.1259. Characterization data matched those reported in the literature.[4]



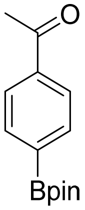
2b

White solid, 78% yield using methyl 4-iodobenzoate (**1b**) as the starting material. 75% yield using methyl 4-bromobenzoate (**1b'**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.00 (dd, J = 8.4, 2.1 Hz, 2H), 7.85 (dd, J = 8.4, 2.0 Hz, 2H), 3.91 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 167.1, 134.6, 132.3, 128.6, 84.1, 52.1, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{14}H_{20}BNO_4$), 263.1455; observed, 263.1450. Characterization data matched those reported in the literature.[4]



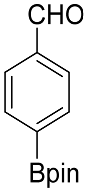
2c

Yellowish oil, 83% yield using 3-iodopyridine (**1c**) as the starting material. 68% yield using 3-bromopyridine (**1c′**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.95 (s, 1H), 8.67 (d, J = 4.7 Hz, 1H), 8.09 – 8.06 (m, 1H), 7.31 (d, J = 7.4 Hz, 1H), 1.35 (s, 13H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 154.9, 151.3, 142.7, 123.3, 84.3, 25.0; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{11}H_{17}BNO_2$), 206.1352; observed, 206.1353. Characterization data matched those reported in the literature.[5]



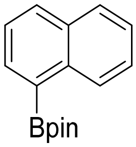
2d

White solid, 85% yield using 4-iodoacetophenone (**1d**) as the starting material. 64% yield using 4-bromoacetophenone (**1d’**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.93 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.3 Hz, 2H), 2.62 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 198.5, 139.0, 134.9, 127.3, 84.2, 26.8, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{14}H_{20}BNO_3$), 247.1505; observed, 247.1505. Characterization data matched those reported in the literature.[4]



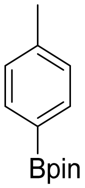
2e

White solid, 78% yield using 4-iodobenzaldehyde (**1e**) as the starting material. 64% yield using 4-bromobenzaldehyde (**1e'**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 10.02 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 1.34 (s, 12H).; ^{13}C NMR (101 MHz, chloroform-*d*): δ 192.6, 138.1, 135.2, 128.7, 84.3, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{13}H_{18}BO_3$), 233.1349; observed, 233.1354. Characterization data matched those reported in the literature.[4]



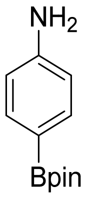
2f

White solid, 80% yield using 1-iodonaphthalene (**1f**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.77 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 6.9, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 8.2, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 1.43 (s, 13H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 136.9, 135.7, 133.2, 131.6, 128.4, 128.4, 126.4, 125.5, 125.0 83.8, 25.0; HRMS (ESI-TOF): calculated m/z for $[M+K]^+$ ($C_{16}H_{19}BO_2K$), 293.1115; observed, 293.1115. Characterization data matched those reported in the literature.[4]



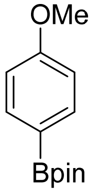
2g

Yellowish oil, 92% yield using 4-iodotoluene (**1g**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.71 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 141.4, 134.8, 128.5, 83.7, 24.9, 21.7; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{13}H_{20}BO_2$), 219.1556; observed, 219.1560.Characterization data matched those reported in the literature.[4]



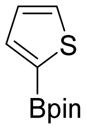
2h

White solid, 73% yield using 4-iodoaniline (**1h**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.55 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 149.0, 136.4, 114.2, 83.3, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{12}H_{19}BNO_2$), 220.1509; observed, 220.1511.Characterization data matched those reported in the literature.[6]



2i

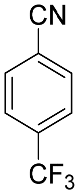
Yellowish oil, 69% yield using 4-iodoanisole (**1i**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.75 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 162.2, 136.5, 113.3, 83.6, 55.1, 24.9; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{13}H_{20}BO_3$), 235.1506; observed, 235.1506. Characterization data matched those reported in the literature.[4]



2j

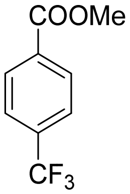
White solid, 86% yield using 2-iodothiophene (**1j**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.68 – 7.59 (m, 2H), 7.19 – 7.17 (m, 1H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, chloroform-*d*): δ 137.1, 132.3, 128.2, 84.0, 24.7; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$

($C_{10}H_{16}BO_2S$), 211.0964; observed, 211.0962.Characterization data matched those reported in the literature.[5]



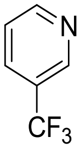
3a

White solid, 82% yield using 4-iodobenzonitrile (**1a**) as the starting material, 76% yield using 4-bromobenzonitirle (**1a'**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.66 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -63.5; ^{13}C NMR (101 MHz, chloroform-*d*): δ 134.6 (q, J^2 = 33.3 Hz), 132.7, 126.2 (q, J^3 = 3.9 Hz), 123.0 (q, J^1 = 274.1 Hz), 117.4, 116.1. HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_8H_5F_3N$), 172.0374; observed, 172.0380. Characterization data matched those reported in the literature.[7]



3b

Colorless oil, 88% yield using methyl 4-iodobenzoate (**1b**) as the starting material, 83% yield using methyl 4-bromobenzoate (**1b'**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.17 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 3.98 (s, 3H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -63.2; ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.9, 134.4 (q, J^2 = 33.3 Hz), 133.4, 130.0, 125.4 (q, J^3 = 4.0 Hz), 123.6 (q, J^1 = 274.7 Hz), 52.5. HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_9H_8F_3O_2$), 205.0476; observed, 205.0480. Characterization data matched those reported in the literature.[7]



3c

76% yield using 3-iodopyridine (**1c**) as the starting material, 60% yield using 3-bromopyridine (**1c'**) as the starting material. The yield was determined by GC-MS using benzotrifluoride as internal standard. HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_6H_5F_3N$), 148.0374; observed, 148.0376.

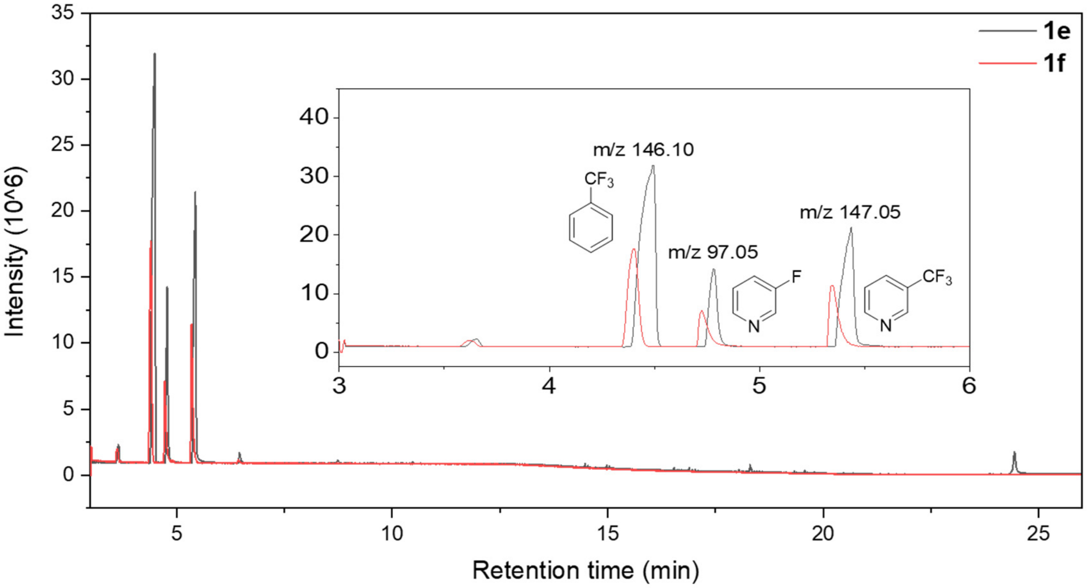
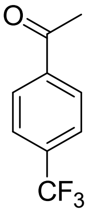
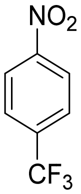


Figure S7. GC-MS results for determination of yield of **3c** from trifluoromethylation reactions of **1e** or **1f** catalyzed by **NiCN**.



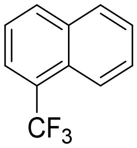
3d

White solid, 85% yield using 4-iodoacetophenone (**1d**) as the starting material, 74% yield using 4-bromoacetophenone (**1d’**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.07 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 2.67 (s, 3H).; ^{19}F NMR (375 MHz, chloroform-*d*): δ -63.2; ^{13}C NMR (101 MHz, chloroform-*d*): δ 197.0, 139.7, 134.4 (q, J^2 = 32.3 Hz), 128.62, 125.7 (q, J^3 = 4.0 Hz), 123.7 (q, J^1 = 274.7 Hz), 26.77; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_9H_8F_3O$), 189.0527; observed, 189.0521. Characterization data matched those reported in the literature.[8]



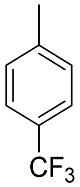
3k

White solid, 63% yield using 4-iodonitrobenzene (**1k**) as the starting material, 74% yield using 4-bromonitrobenzene (**1k’**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.44 – 8.33 (d, J = 8.3 Hz, 2H), 7.92 – 7.80 (d, J = 8.1 Hz, 2H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -63.4; ^{13}C NMR (101 MHz, chloroform-*d*): δ 150.0, 136.1 (q, J^2 = 33.3 Hz), 126.8 (q, J^3 = 4.0 Hz), 124.1, 123.0 (q, J^1 = 274.7 Hz); HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_7H_5F_3NO_2$), 192.0272; observed, 192.0290. Characterization data matched those reported in the literature.[9]



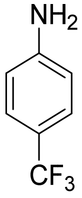
3f

Yellowish oil, 82% yield using using 1-iodonaphthalene (**1f**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.26 (d, J = 8.8, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.1, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.70-7.60 (dt, J = 8.6, 6.8,Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -59.7; ^{13}C NMR (101 MHz, chloroform-*d*): δ 133.9, 132.8, 129.0, 128.8, 127.7, 126.6, 126.1 (q, J^2 = 30.3 Hz), 124.8 (q, J^1 = 273.7 Hz), 124.7 (q, J^3 = 5.8 Hz), 124.3 (q, J^3 = 2.7 Hz), 124.2 ; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{11}H_8F_3$), 197.0578; observed, 197.0580. Characterization data matched those reported in the literature. Characterization data matched those reported in the literature.[10]



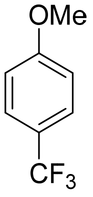
3g

Colorless oil, 81% yield using 4-iodotoluene (**1g**) as the starting material. The product is volatile and was separated by column chromatography using hexane and ethyl ether as eluent. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.53 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.44 (s, J = 3.4 Hz, 3H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -62.3; ^{13}C NMR (101 MHz, chloroform-*d*): δ 142.6, 129.3, 127.8(q, J^2 = 32.5 Hz), 125.1 (q, J^3 = 4.1 Hz), 124.4 (q, J^1 = 272.6 Hz), 21.4; HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_{11}H_8F_3$), 197.0578; observed, 197.0581. Characterization data matched those reported in the literature.[11]

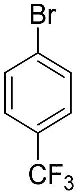


3h

Colorless liquid, 62% yield using 4-iodoaniline (**1h**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.42 (d, J = 8.3 Hz, 2H), 6.71 (d, J = 8.3 Hz, 2H), 3.97 (br, 2H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -62.8; ^{13}C NMR (101 MHz, chloroform-*d*): δ 149.4, 126.7 (q, J^3 = 4.0 Hz), 124.8 (q, J^1 = 271.5 Hz), 120.2 (q, J^2 = 32.9 Hz), 114.2. HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_7H_7F_3N$), 172.0531; observed, 172.0535. Characterization data matched those reported in the literature.[12]


3i

Yellowish liquid, 74% yield using 4-iodoanisole (**1i**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.57 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 3.88 (s, 3H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -61.5; ^{13}C NMR (101 MHz, chloroform-*d*): δ 162.0, 126.9 (q, J^3 = 4.0 Hz), 124.5 (q, J^1 = 271.9 Hz), 122.9 (q, J^2 = 32.9 Hz), 113.9, 55.4. HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_8H_8F_3O$), 177.0527; observed, 177.0527. Characterization data matched those reported in the literature.[7]


3l

Colorless liquid, 62% yield using 4-iodobromobenzene (**1l**) as the starting material. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.66 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H); ^{19}F NMR (375 MHz, chloroform-*d*): δ -62.8; ^{13}C NMR (101 MHz, chloroform-*d*): δ 132.1, 129.6 (q, J^2 = 33.3 Hz) , 126.9 (q, J^3 = 4.0 Hz), 126.4, 123.9 (q, J^1 = 272.7 Hz); HRMS (ESI-TOF): calculated m/z for $[M+H]^+$ ($C_7H_5BrF_3$), 224.9527; observed, 224.9521. Characterization data matched those reported in the literature.[13]

Recycle procedure for borylation reactions. Methyl 4-iodobenzoate (**1b**, 26.2 mg, 0.1 mmol, 1 equiv), bis(pinacolato)diboron (B_2pin_2, 76.2 mg, 0.3 mmol, 3 equiv.), pyridine (1.6 μL, 0.02 mmol, 20 mol%), and N,N-diisopropylethylamine (DIPEA, 52 μL, 3 mmol) were added to 10 mL dry acetonitrile (ACN) under nitrogen. **NiCN** (5 μmol based on pyrene, dispersion in ACN) was added and the resulting mixture was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, the mixture was filtered and the filtrate was analyzed by GC-MS to determine the yield of **2b**. The precipitate was washed with 5 mL acetonitrile three times and directly used in the next run as the COF catalyst.

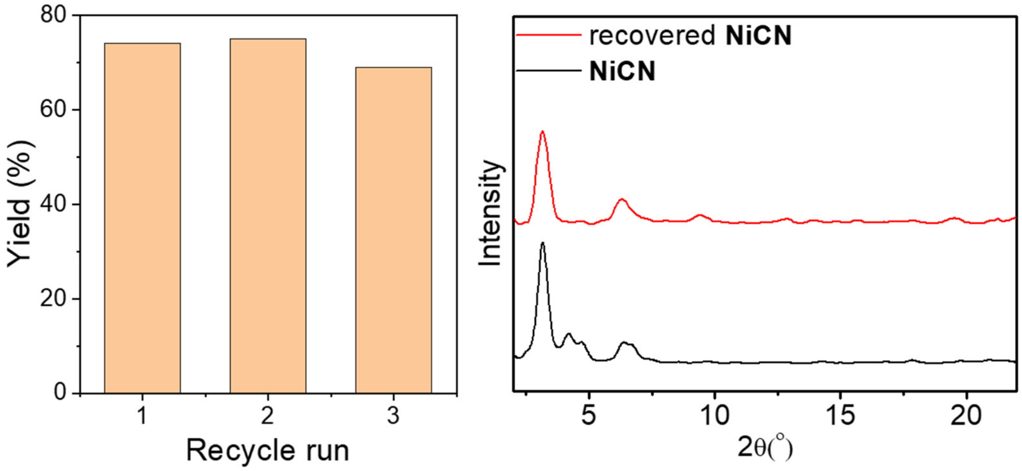
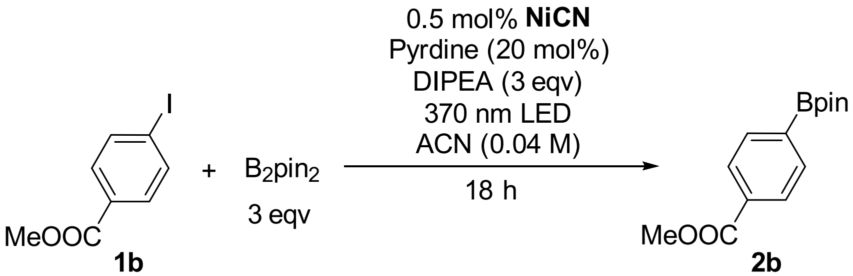


Figure S8. Yields of **2b** in recycle experiments (left) and the PXRD pattern of recovered COF after three cycles of catalytic reactions.

S4. Control Experiments

Table S2. Control experiments of **NiCN**-catalyzed borylation reactions.



1b

2b

Entry	Deviation from the standard condition	Yield[a] (%)

1	No	78
2	Replace COF with 5 mol% pyrene and 5 mol% Ni(dtbpy)	63
3	No light	0
4	Add 1 eqv TEMPO	10

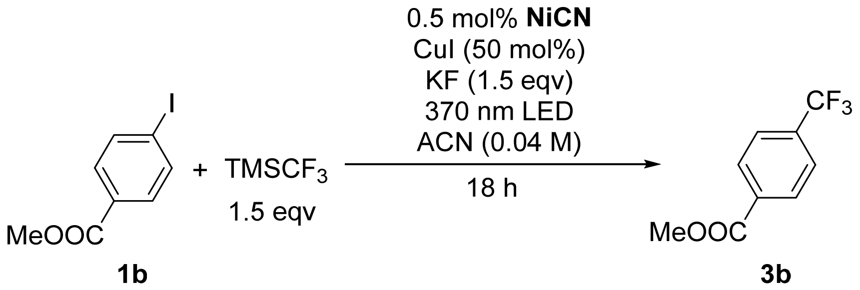
[a] Entry 1 used isolated yield. Entry 2-4 used GC-MS yield.

Homogeneous control reaction. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), B_2pin_2 (0.3 mmol, 3 equiv.), pyridine (0.02 mmol, 1.6 µL, 20 mol%), and DIPEA (3 mmol, 52 µL) were mixed in 4 mL dry acetonitrile (ACN) under nitrogen. Pyrene (0.5 µmol, 0.1 mg, 0.5 mol%), nickel bromide ethylene glycol dimethyl ether complex ($NiBr_2$·dme 1.0 µmol, 0.3 mg, 1 mol%) and di-tertbutyl bipyridine (dtbpy, 1.1 µmol, 0.3 mg, 1.1 mol%) were then added and the resulting solution was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, 50 µL solution was filtered, diluted, and analyzed by GC-MS. The yield of **2b** was 29%.

Control reaction in the absence of light. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), B_2pin_2 (0.3 mmol, 3 equiv.), pyridine (0.02 mmol, 1.6 µL, 20 mol%), and DIPEA (3 mmol, 52 µL) were mixed in 4 mL dry acetonitrile (ACN) under nitrogen. **NiCN** (0.5 µmol based on pyrene, dispersion in ACN) was then added and the resulting solution was stirred in the dark for 18 hours. After the reaction, 50 µL solution was filtered and analyzed by GC-MS. No target product **2b** was detected.

Control reaction inhibited by TEMPO. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), B_2pin_2 (0.3 mmol, 3 equiv.), pyridine (0.02 mmol, 1.6 µL, 20 mol%), 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 0.1 mmol, 15.6 mg) and DIPEA (3 mmol, 52 µL) were mixed in 4 mL dry acetonitrile (ACN) under nitrogen. **NiCN** (0.5 μmol based on pyrene, dispersion in ACN) was then added and the resulting solution was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, 50 μL solution was filtered and analyzed by GC-MS. The yield of **2b** was 10%.

Table S3. Control experiments of **NiCN**-catalyzed trifluoromethylation reactions.



Entry	Deviation from the standard condition	Yield[a] (%)
1	No	88
2	Replace COF with 5 mol% pyrene and 5 mol% Ni(dtbpy).	83
3	No light	0
4	Add 1 eqv TEMPO	11

[a] Entry 1 used isolated yield. Entry 2-4 used GC-MS yield.

Homogeneous control reaction. Copper iodide (0.05 mmol, 9.5 mg, 50 mol%), potassium fluoride (0.15 mmol, 8.7 mg, 1.5 equiv) and $TMSCF_3$ (0.15 mmol, 22 μL, 1.5 equiv) were added in 1 mL dry ACN under nitrogen. The solution was stirred for 10 mins. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), pyrene (0.5 μmol, 0.1 mg, 0.5 mol%), $NiBr_2$·dme (1.0 μmol, 0.3

mg, 1 mol%) and dtbpy (1.1 μmol, 0.3 mg, 1.1 mol%) in 3 mL ACN were then added and the resulting solution was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, 50 μL solution was filtered and analyzed by GC-MS. The yield of **3b** was 21%.

Control reaction in the absence of light. Copper iodide (0.05 mmol, 9.5 mg, 50 mol%), potassium fluoride (0.15 mmol, 8.7 mg, 1.5 equiv) and $TMSCF_3$ (0.15 mmol, 22 μL, 1.5 equiv) were added in 1 mL dry ACN under nitrogen. The solution was stirred for 10 mins. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), and **NiCN** (0.5 μmol based on pyrene, dispersion in ACN) in 3 mL ACN were then added and the resulting solution was stirred in the dark for 18 hours. After the reaction, 50 μL solution was filtered and analyzed by GC-MS. No target product **3b** was detected.

Control reaction inhibited by TEMPO. Copper iodide (0.05 mmol, 9.5 mg, 50 mol%), potassium fluoride (0.15 mmol, 8.7 mg, 1.5 equiv) and $TMSCF_3$ (0.15 mmol, 22 μL, 1.5 equiv) were added in 1 mL dry ACN under nitrogen. The solution was stirred for 10 mins. Methyl 4-iodobenzoate (0.1 mmol, 26.2 mg, 1 equiv), TEMPO (0.1 mmol, 15.6 mg), and **NiCN** (0.5 μmol based on pyrene, dispersion in ACN) in 3 mL ACN were then added and the resulting solution was stirred under 370 nm blue LED irradiation for 18 hours. After the reaction, 50 μL solution was filtered and analyzed by GC-MS. The yield of **3b** was 11%.

S5. Mechanistic study

Synthesis of di-tertbutyl bipyridine 4-cyanophenyl nickel(II) bromide. Di-tertbutyl bipyridine 4-cyanophenyl nickel(II) bromide (**Ni-ArBr**) was synthesized according to a literature report.[14] In a glove box, an oven-dried 10 mL round-bottom bottle was charged with $Ni(cod)_2$ (0.055 g, 0.2 mmol), di-tertbutyl bipyridine (dtbbpy, 0.0536 g, 0.2 mmol), and THF (3 mL). The mixture was stirred for 2 h at room temperature, and the color of the solution turned dark purple. 4-

bromobenzonitrile (0.1092 g, 0.6 mmol) was added and the reaction was stirred for 20 additional minutes and turned dark red. The resulting solution was triturated with hexane (10 mL) and filtered to give the product as an orange solid. After washing with hexane and drying, the solid was directly used without further purification. ^{1}H NMR (400 MHz, dichloromethane-*d*): δ 9.19 (s, 1H), 7.80 (m, 4H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.18 (m, 4H), 1.41 (s, 9H), 1.36 (s, 9H).

Synthesis of NiCN(ArBr). To four different 5 mL THF dispersions of **CN** (1 mg/mL) were added 25, 50, 100, or 150 nmol $Ni(cod)_2$ (0.5, 1.0, 1.5, or 2.0 mol%), respectively. The resulting solutions were stirred overnight. 4-bromobenzonitrile was then added (5 μmol, 182.02 mg) and the solutions were filtrated after 6 extra hours of stirring to yield a dark red powder. The powders were washed by THF several times and the nickel loadings were determined by ICP-MS analysis as 0.40, 0.47, 0.67, and 1.45 mol%, respectively.

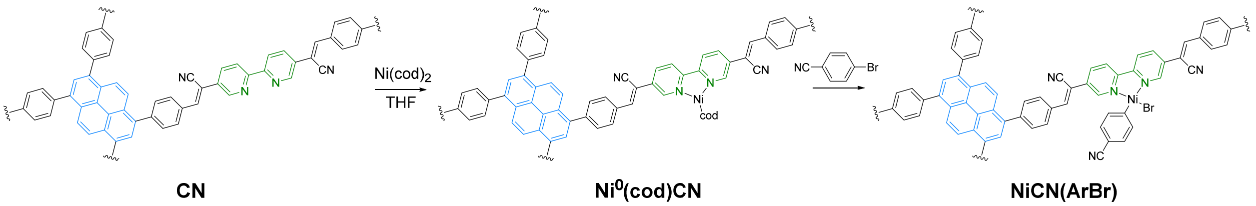


Figure S9. Synthetic procedure for **NiCN(ArBr)**.

Luminescence quenching studies of NiCN(ArBr). CN or **NiCN(ArBr)** COF was separately added to 3 mL ACN to form 20 μM dispersion. After degassing with N_2 for 5 mins, the emission spectrum of each dispersion was collected using 370 nm excitation (excitation slit width: 3 nm, emission slit width: 3 nm).

Luminescence quenching studies of control groups. Quenching of pyrene or **CN** by **Ni-ArBr** was studied to compare with that of **NiCN(ArBr)**. To a 20 uM pyrene solution or **CN** dispersion in 3 mL ACN was added 15, 30, 45, or 60 nmol **Ni-ArBr**, respectively. The emission spectrum of each dispersion were collected using 370 nm excitation (excitation slit width: 3 nm, emission slit width: 3 nm).

Stern-Völmer plots. Emission intensities of **NiCN(ArBr)** at 570 nm (emission intensity of **CN** at 467 nm was used as I_0 because of the shift of emission maximum), pyrene at 392 nm, and **CN** at 467 nm were used to fit the Stern-Völmer equation:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [\mathrm{Q}]$$

Where I_0 is the emission intensity without quencher (amine and enamine), I is the emission intensity with quencher of concentration [Q], τ_0 is the lifetime of photosensitizers (1.30 ns and 308 ns, for **CN** and pyrene, respectively) and k_q is the kinetics constant. Emission spectra and Stern-Völmer plots are shown in Figure S7. k_q, stands for energy transfer efficiency, was calculated to be 2.7 x 10^{15} $M^{-1} \cdot s^{-1}$ for **NiCN(ArBr)**, 1.2 x 10^{13} $M^{-1} \cdot s^{-1}$ for **CN** quenched by **Ni-ArBr**, and 3.7 x 10^{10} $M^{-1} \cdot s^{-1}$ for pyrene quenched by **Ni-ArBr**.

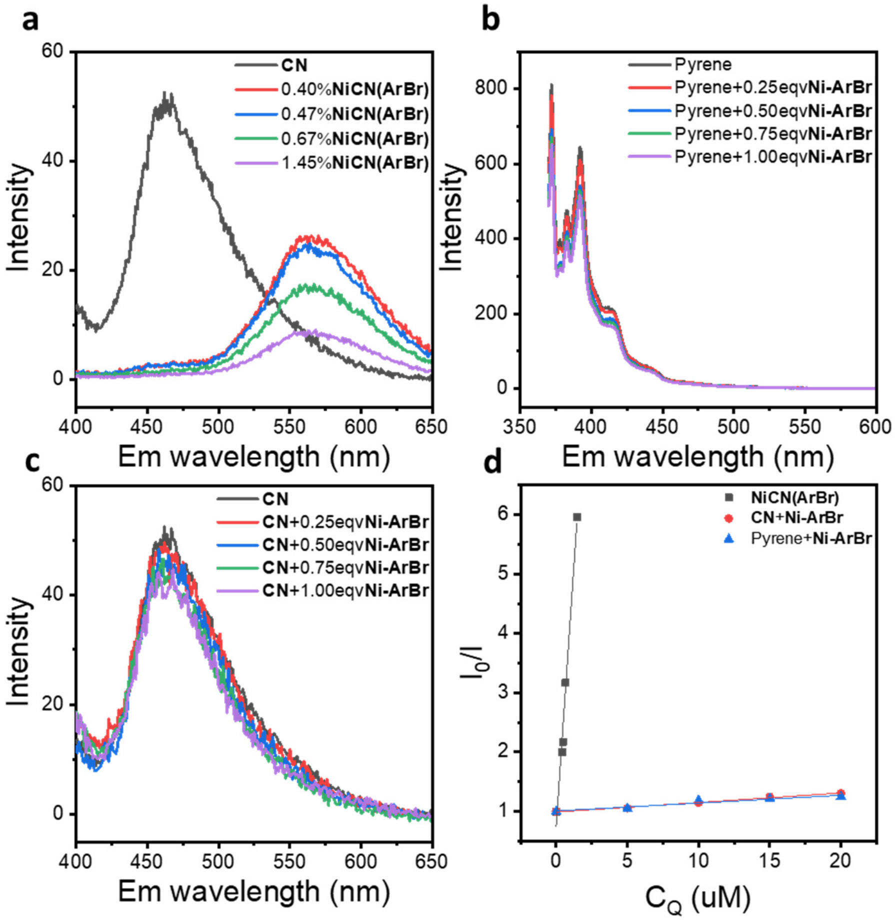


Figure S10. Emission spectra of **NiCN(ArBr)** (**a**), mixture of pyrene and **Ni-ArBr** (**b**), and mixture of **CN** and **Ni-ArBr** (**c**). Stern-Völmer fitting results of quenching experiments (**d**).

Cyclic voltammetry (CV). The working electrode was polished with alpha alumina paste to remove surface absorbates. Subsequent sonication of the working and counter electrodes in H_2O was performed to remove alumina residue and provide additional cleaning. Before each measurement, the solution was degassed with N_2 for 5 min and an N_2 atmosphere was maintained throughout each experiment. 100 mM tetrabutylammonium hexafluorophosphate (NBu_4PF_6) solution was used as the supporting electrolyte and the scan rates were set at 100 mV/s for all measurements.

CV of 15 mM pyrene in 1:1 ACN/benzene mixed solution was scanned from 0 V to -2.7 V. A reversible reductive peak appeared at $E_{1/2}$ = -2.10 V, matching the literature report.[15]

Equal molar amounts of $NiBr_2$·(dme) and 4,4′-Di-tert-butyl-2,2′-dipyridyl (dtbpy) were added to DMF and stirred for 3 mins to synthesize Ni(dtbpy)Br_2. 3 mM of the resulting solution was scanned from 0 V to – 2.3 V. Two reversible reductive peaks appeared at $E_{1/2}$ = -1.20 V and $E_{1/2}$ = -1.90 V, corresponding to oxidation state change from Ni(II) to Ni(0).

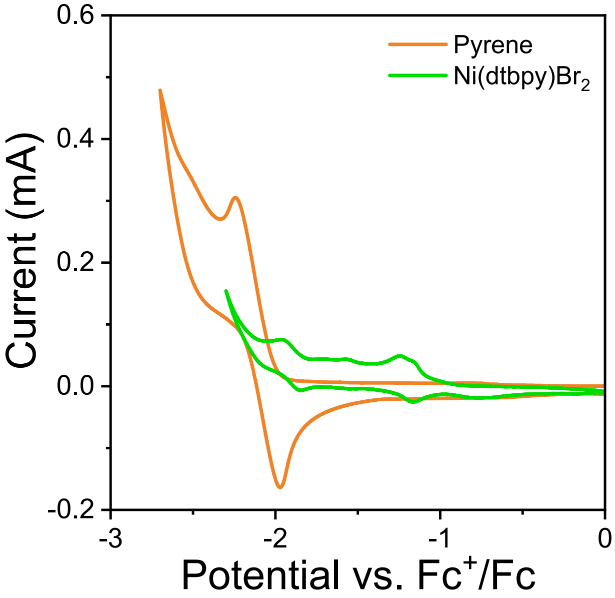


Figure S11. CV spectra of pyrene and Ni(dtbpy)Br_2.

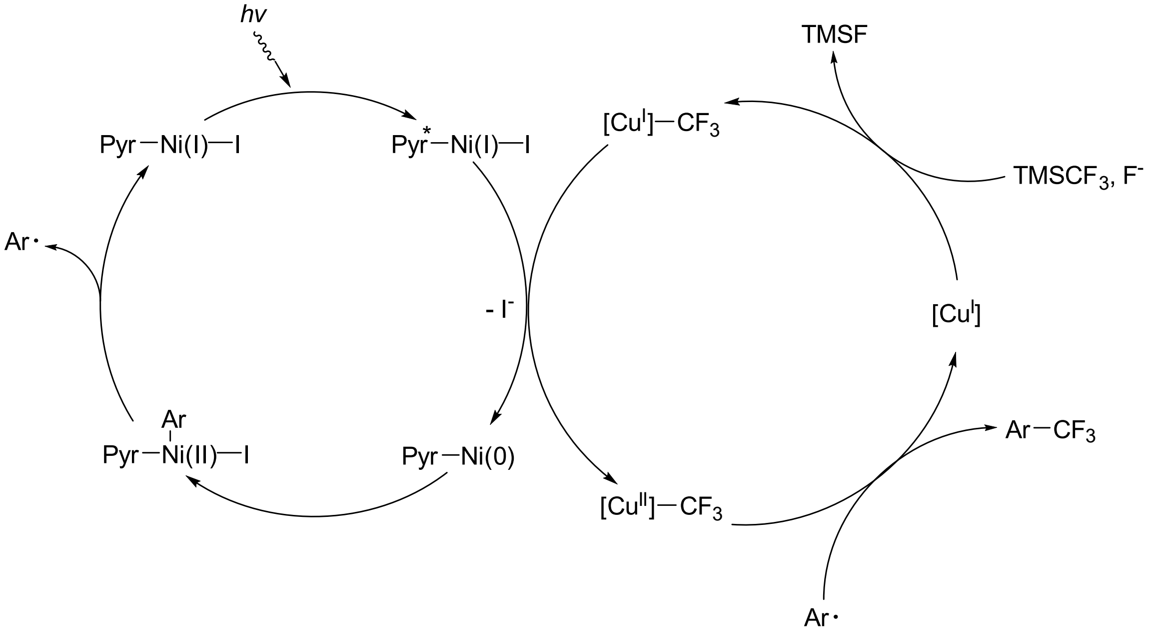


Figure S12. Proposed mechanistic cycles for **NiCN** catalyzed trifluoromethylation reactions.

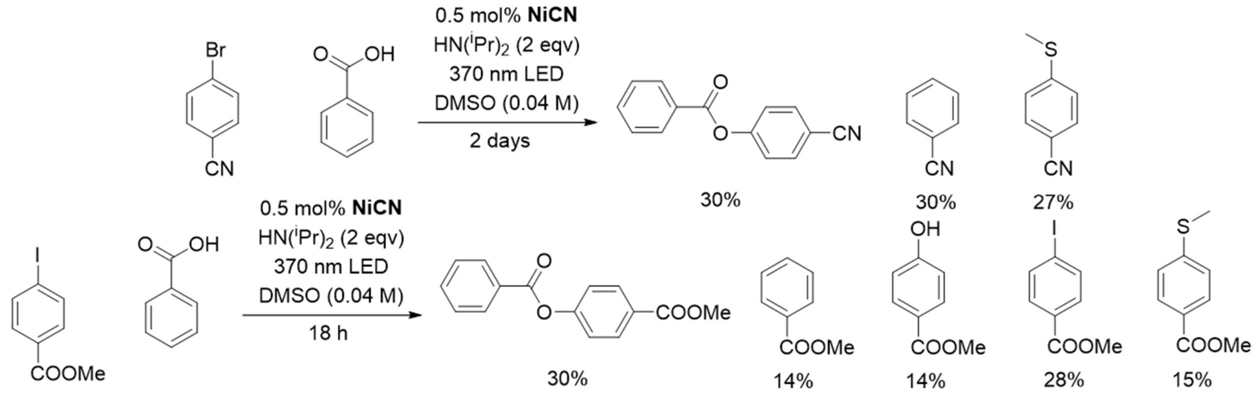
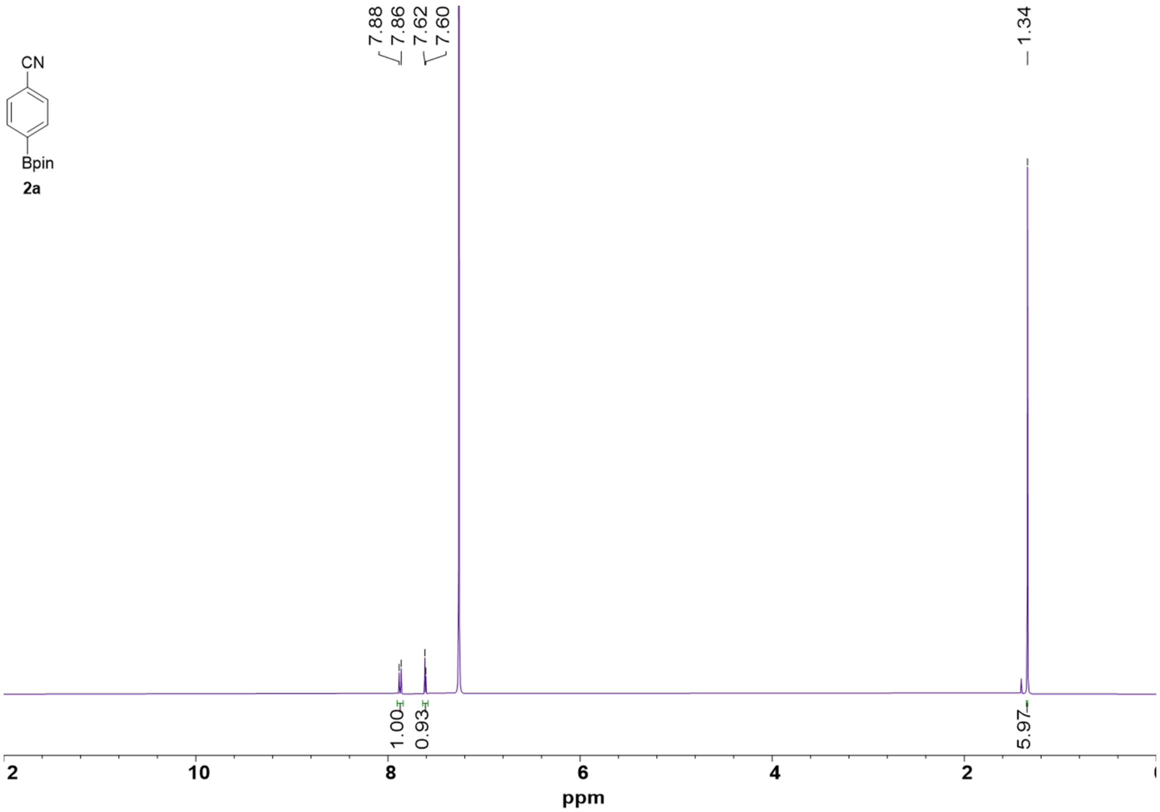
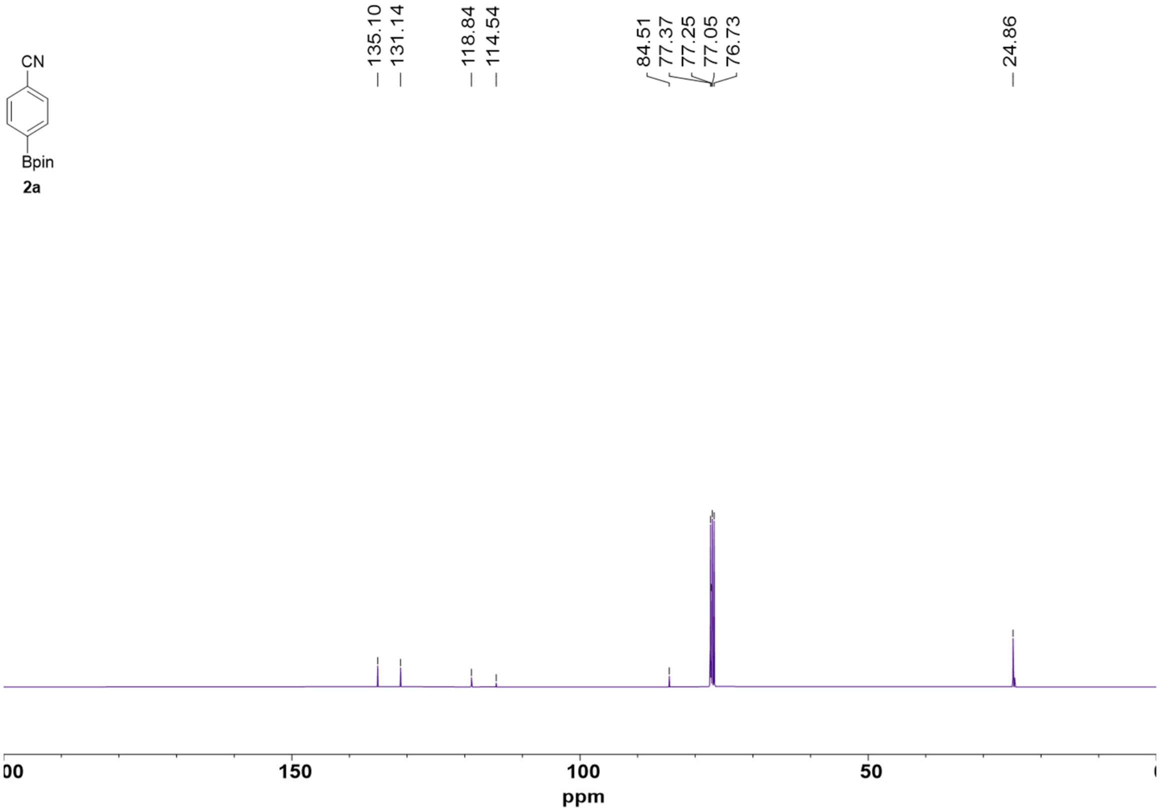
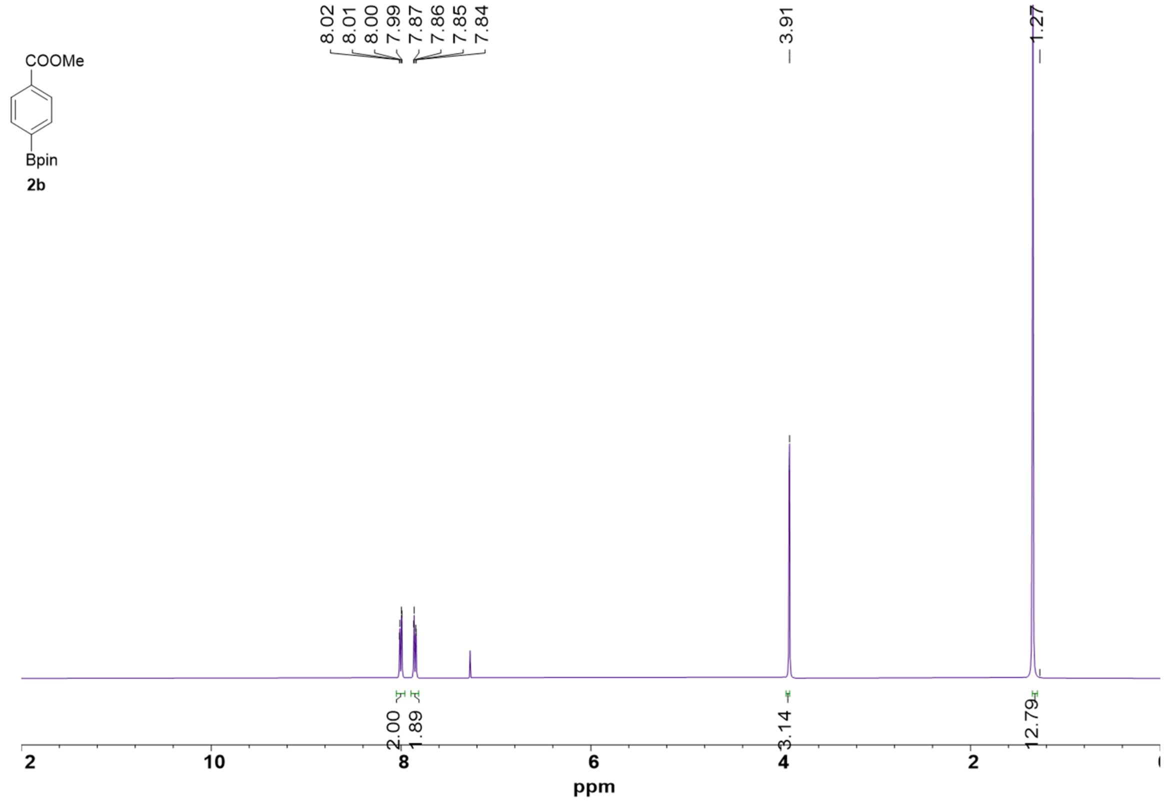


Figure S13. Product distribution detected by GC-MS in **NiCN** catalyzed cross-coupling reactions between aryl halide and benzoic acid.

S6. NMR spectra







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8.01
8.00
7.99
7.87
7.86
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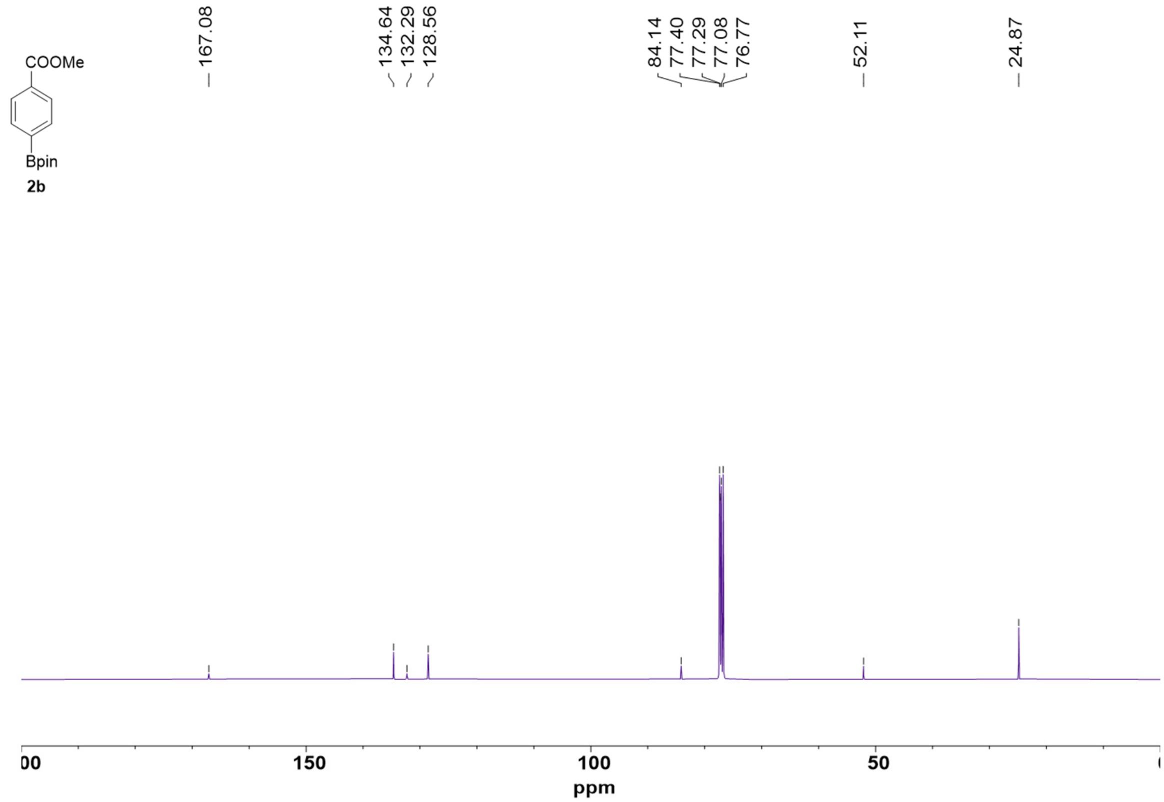

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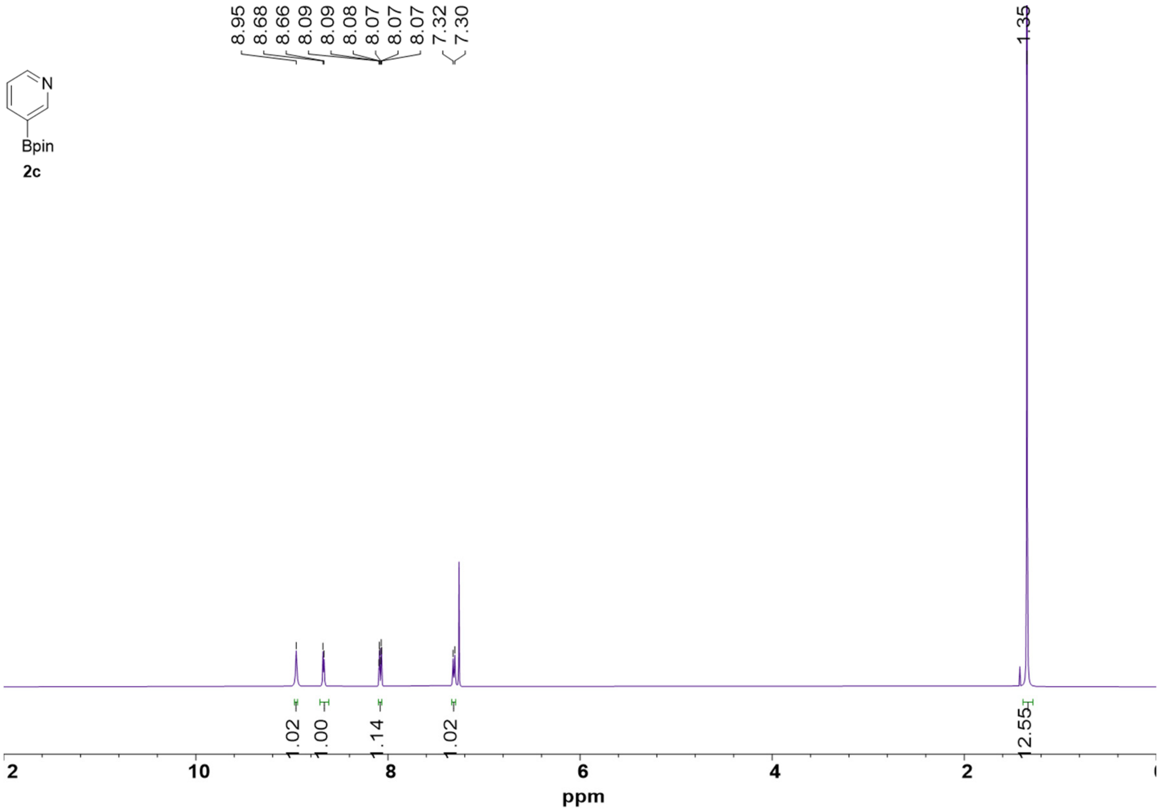
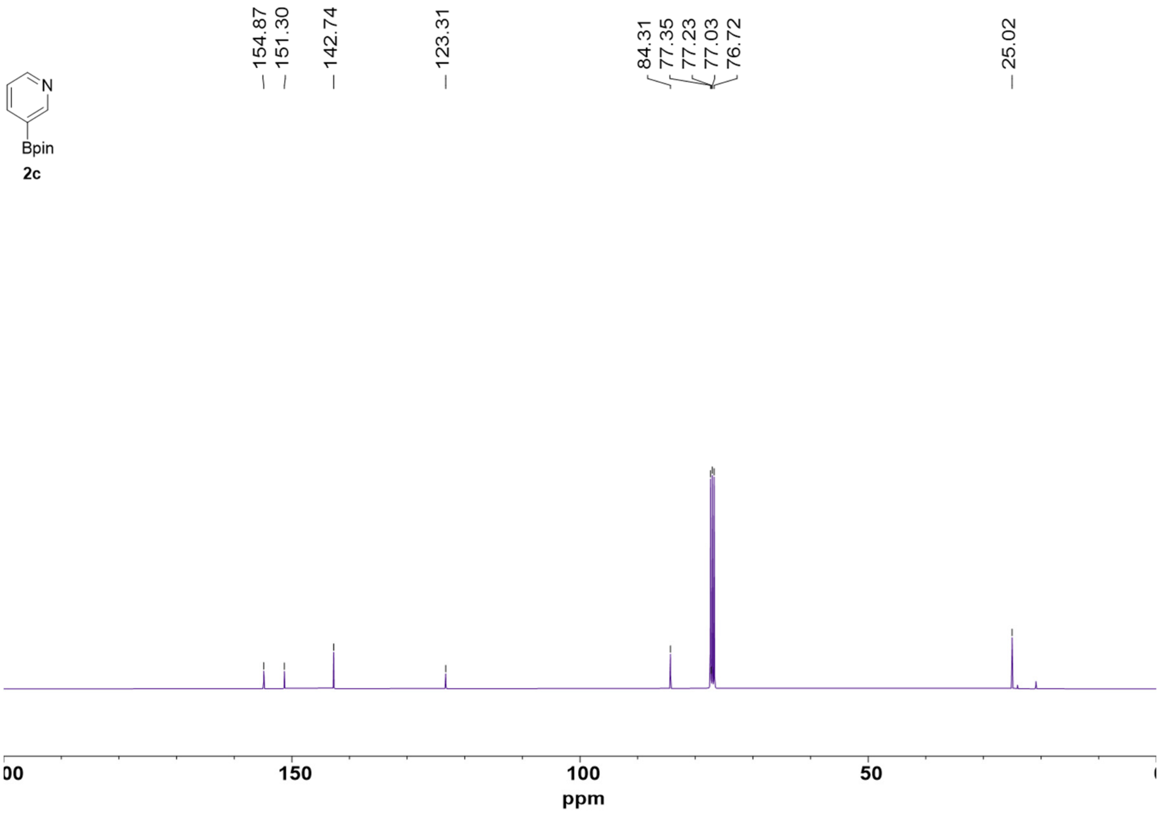
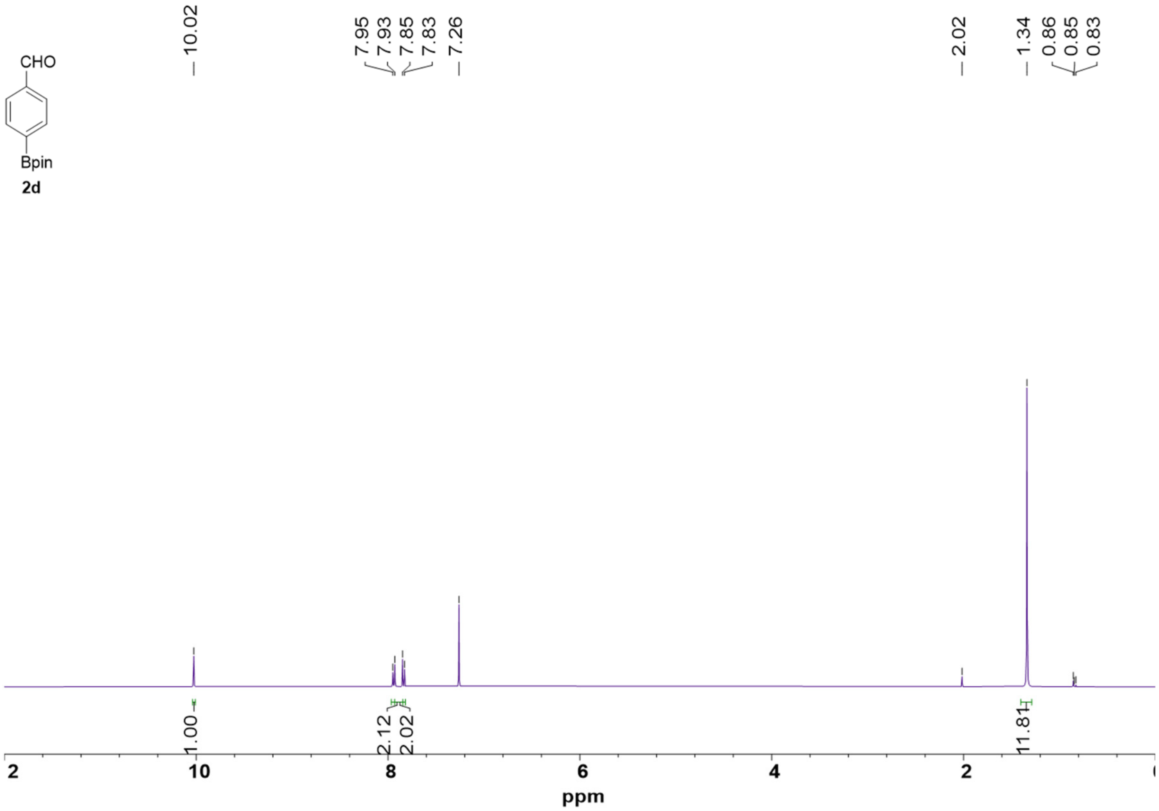
50
ppm

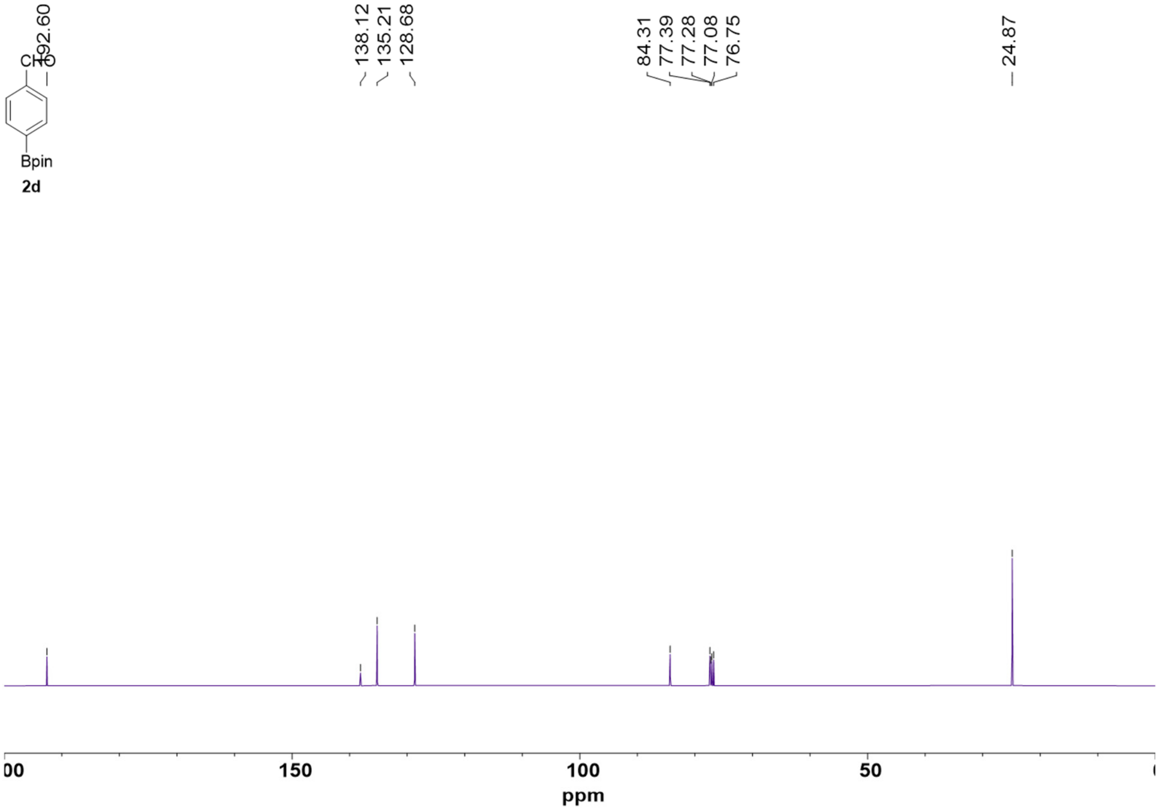

8.95
8.68
8.66
8.09
8.09
8.08
8.07
8.07
8.07
7.32
7.30
1.35
N
Bpin
1.02
1.00
1.14
1.02
12.55
2
10
8
6
4
2
ppm

2c


154.87
151.30
142.74
123.31
84.31
77.35
77.23
77.03
76.72
25.02
N
Bpin
00
150
100
50
ppm

2c


CHO
Bpin
2d
10.02
7.95
7.93
7.85
7.83
7.26
2.02
1.34
0.86
0.85
0.83
1.00
2.12
2.02
11.81
2
10
8
6
4
2
ppm


CHO
Bpin
2d
192.60
138.12
135.21
128.68
84.31
77.39
77.28
77.08
76.75
24.87
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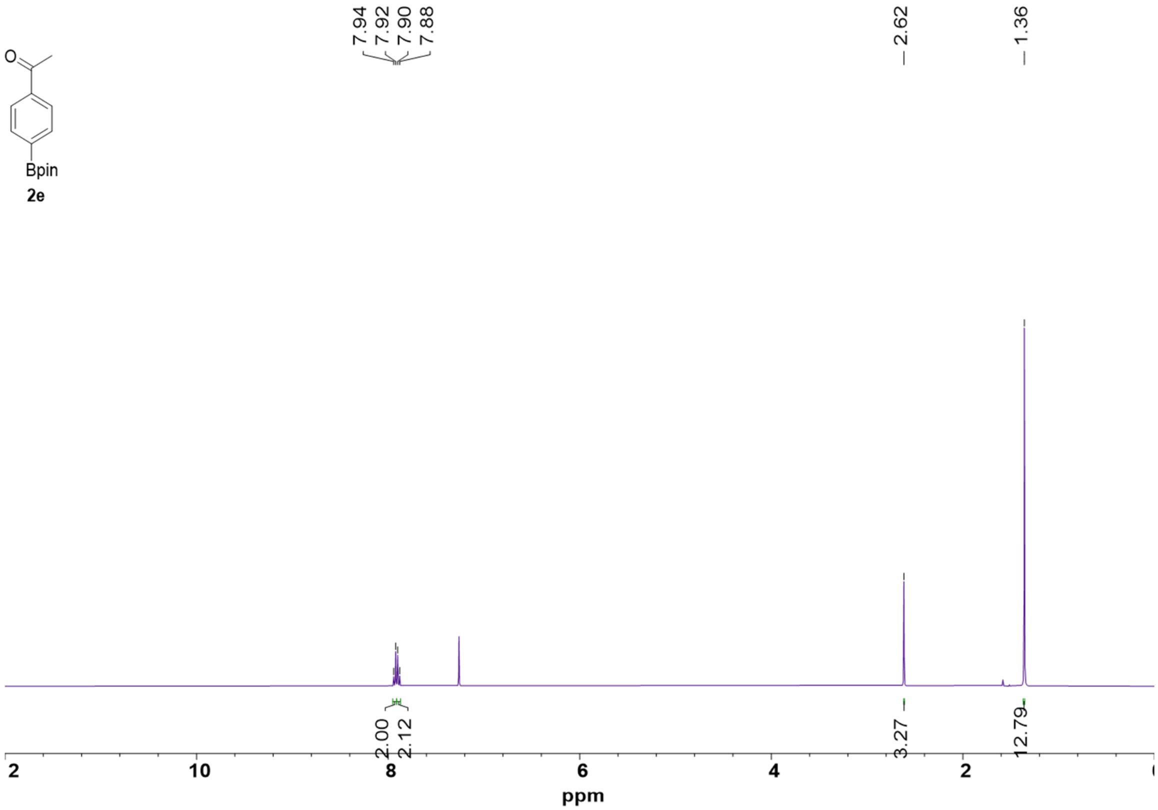
150
100
50
ppm


O
Bpin
2e
7.94
7.92
7.90
7.88
2.62
1.36
2.00
2.12
3.27
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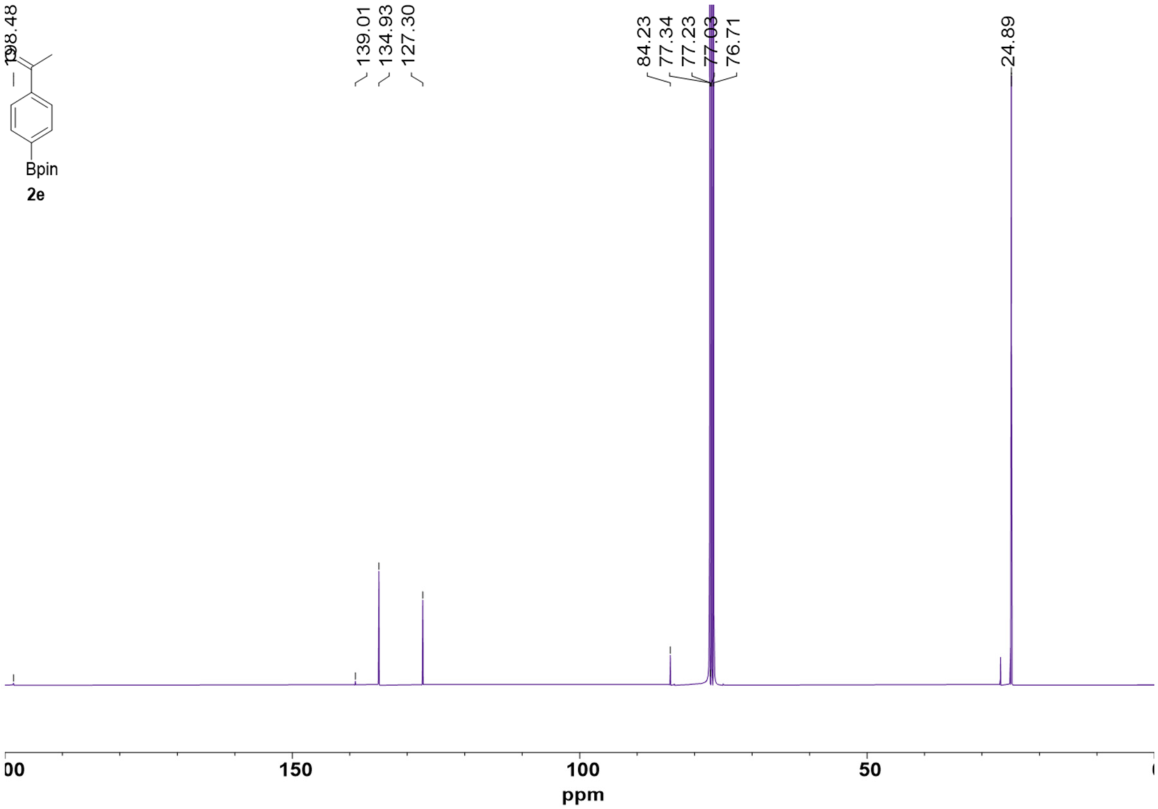
10
8
6
4
2
ppm


O
Bpin
2e
198.48
139.01
134.93
127.30
84.23
77.34
77.23
77.03
76.71
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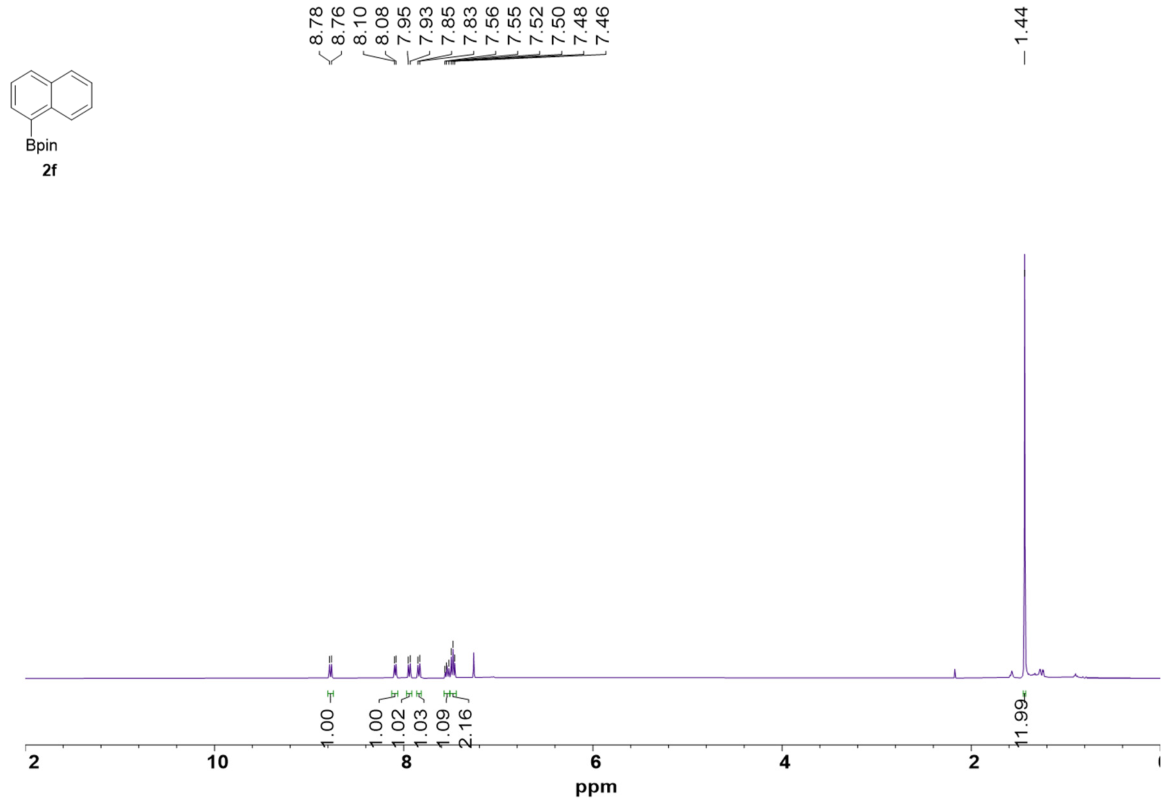
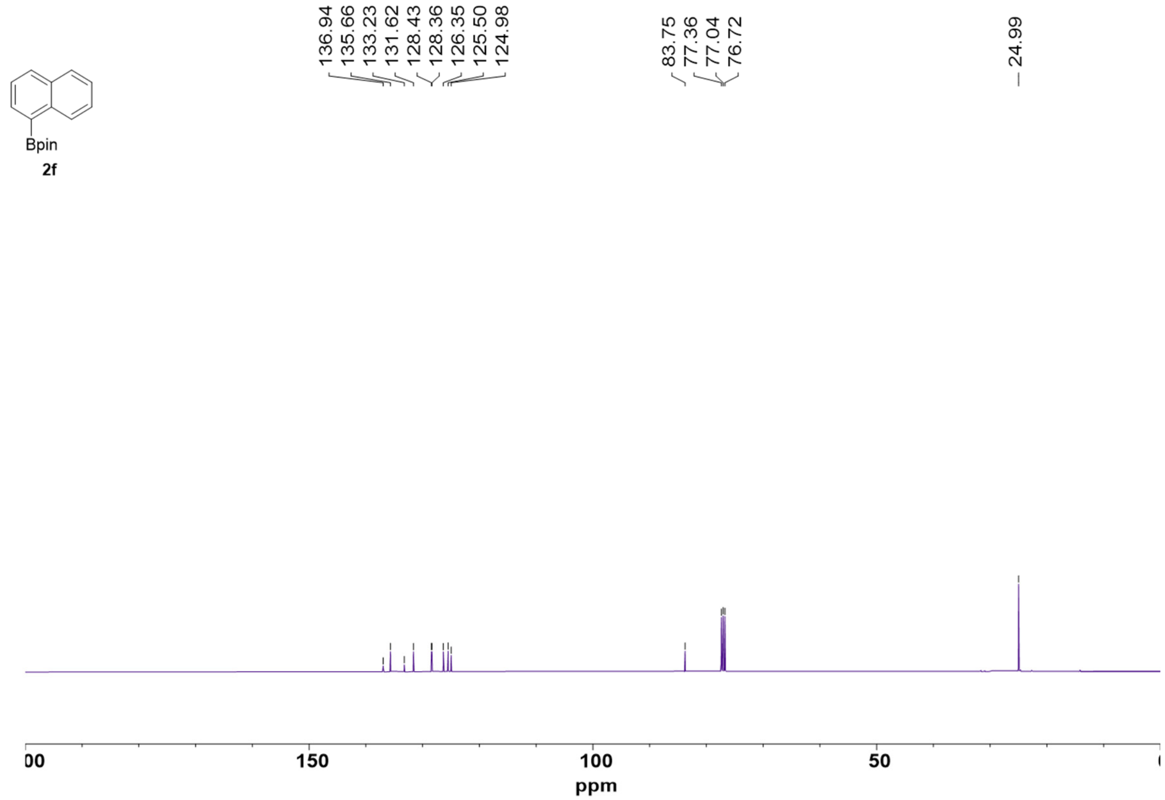
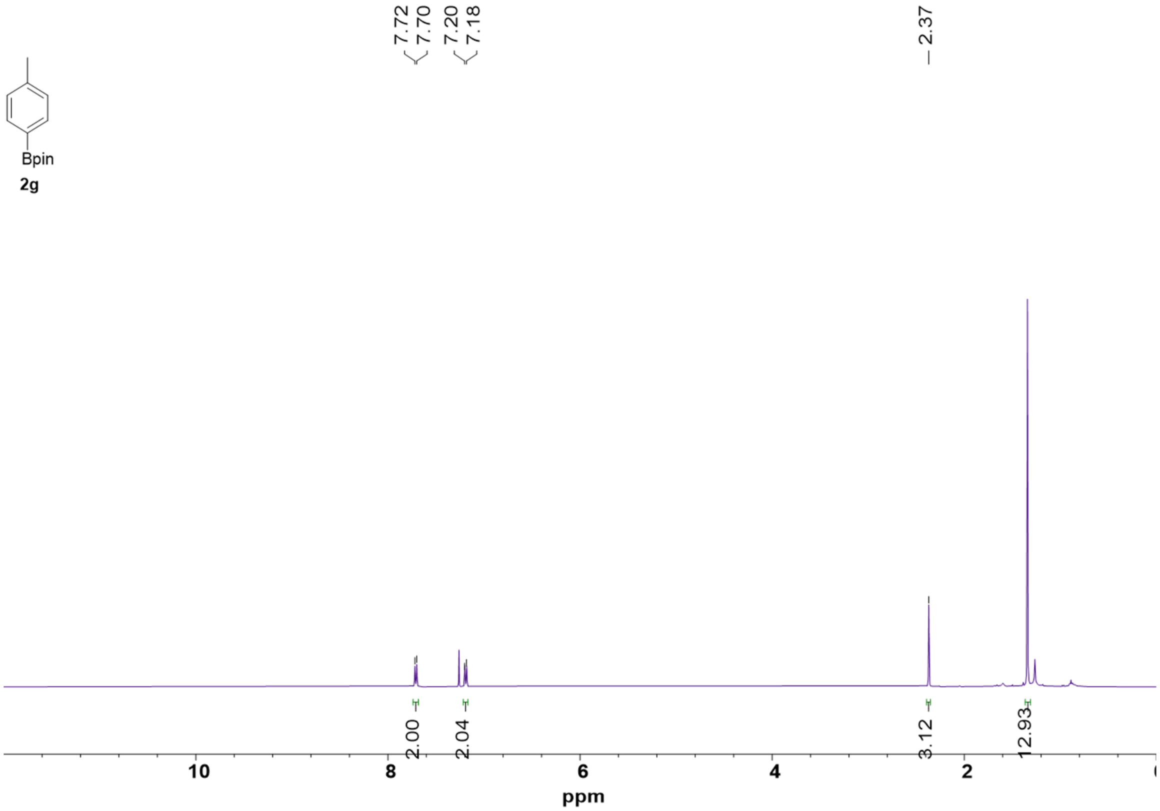
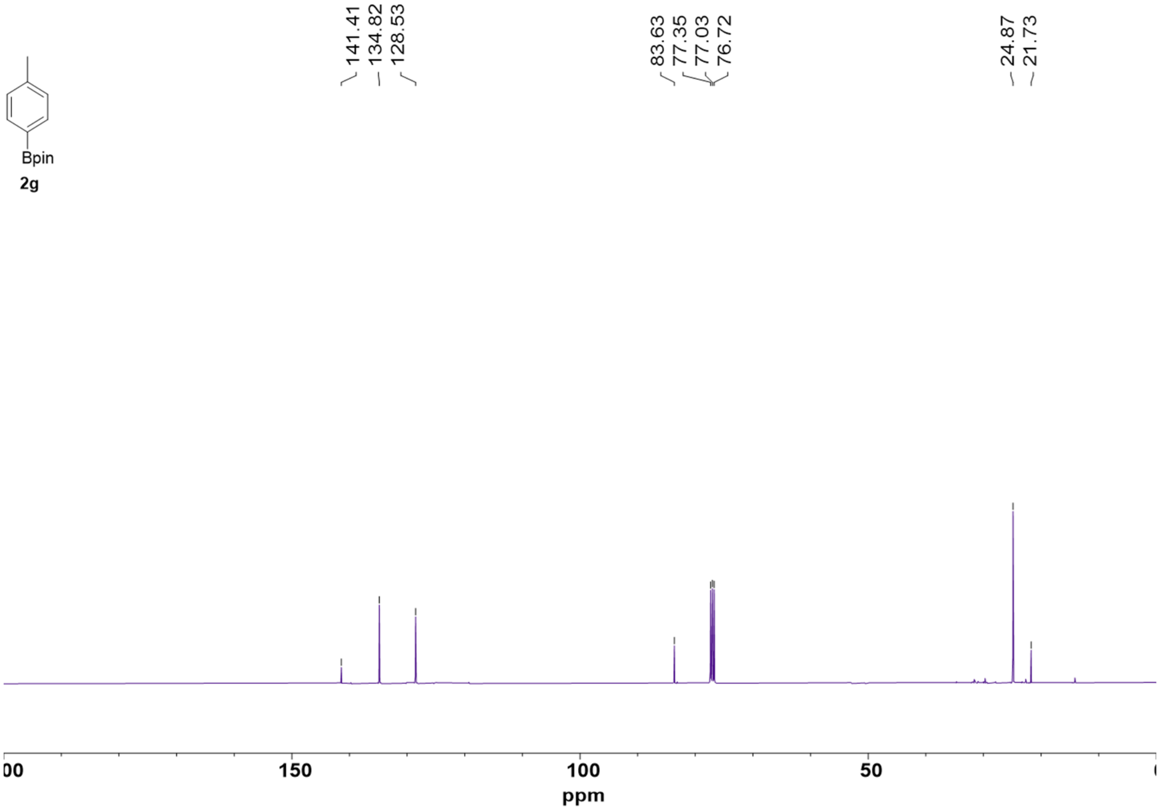
00
150
100
50
ppm


8.78
8.76
8.10
8.08
7.95
7.93
7.85
7.83
7.56
7.55
7.52
7.50
7.48
7.46
1.44
Bpin
2f
1.00
1.00
1.02
1.03
1.09
2.16
11.99
2
10
8
6
4
2
ppm

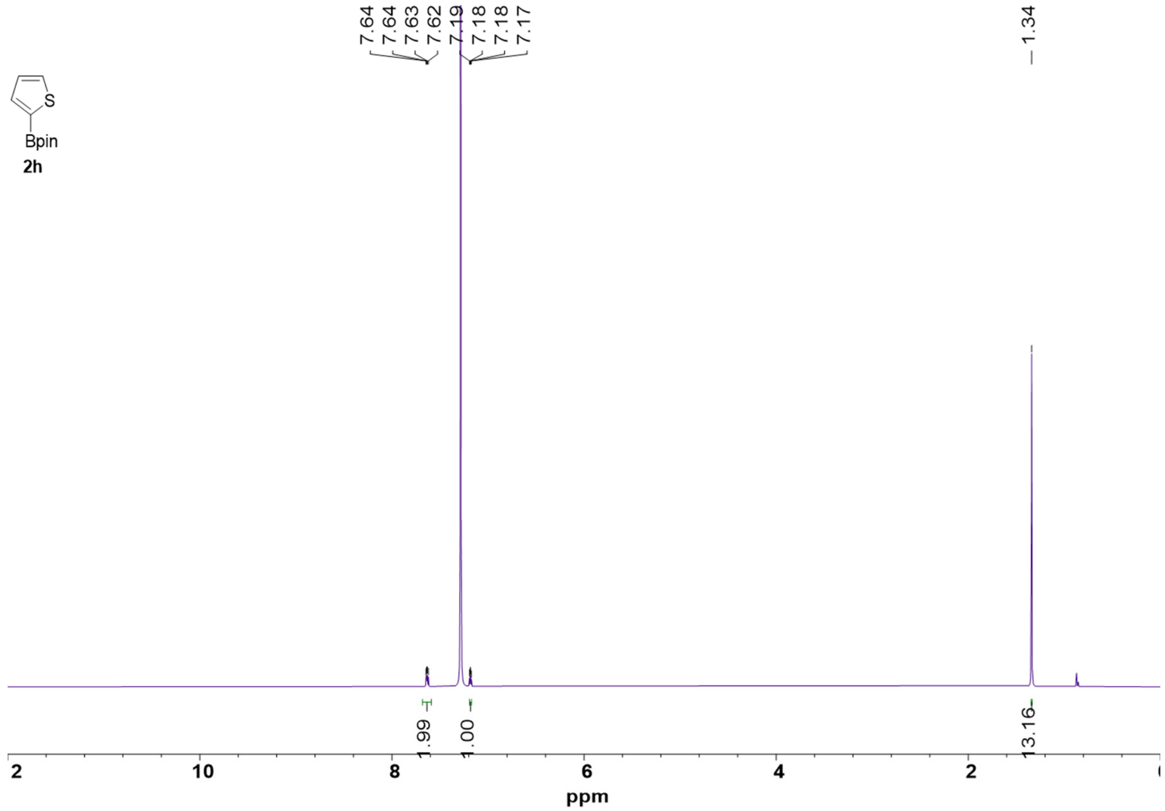

136.94
135.66
133.23
131.62
128.43
128.36
126.35
125.50
124.98
83.75
77.36
77.04
76.72
24.99
Bpin
2f
00
150
100
50
ppm


Bpin
7.72
7.70
7.20
7.18
2.37
2.00
2.04
3.12
12.93
10
8
6
4
2
ppm

2g


Bpin
141.41
134.82
128.53
83.63
77.35
77.03
76.72
24.87
21.73
00
150
100
50
ppm

2g


Bpin
2h
7.64
7.64
7.63
7.62
7.19
7.18
7.18
7.17
1.34
1.99
1.00
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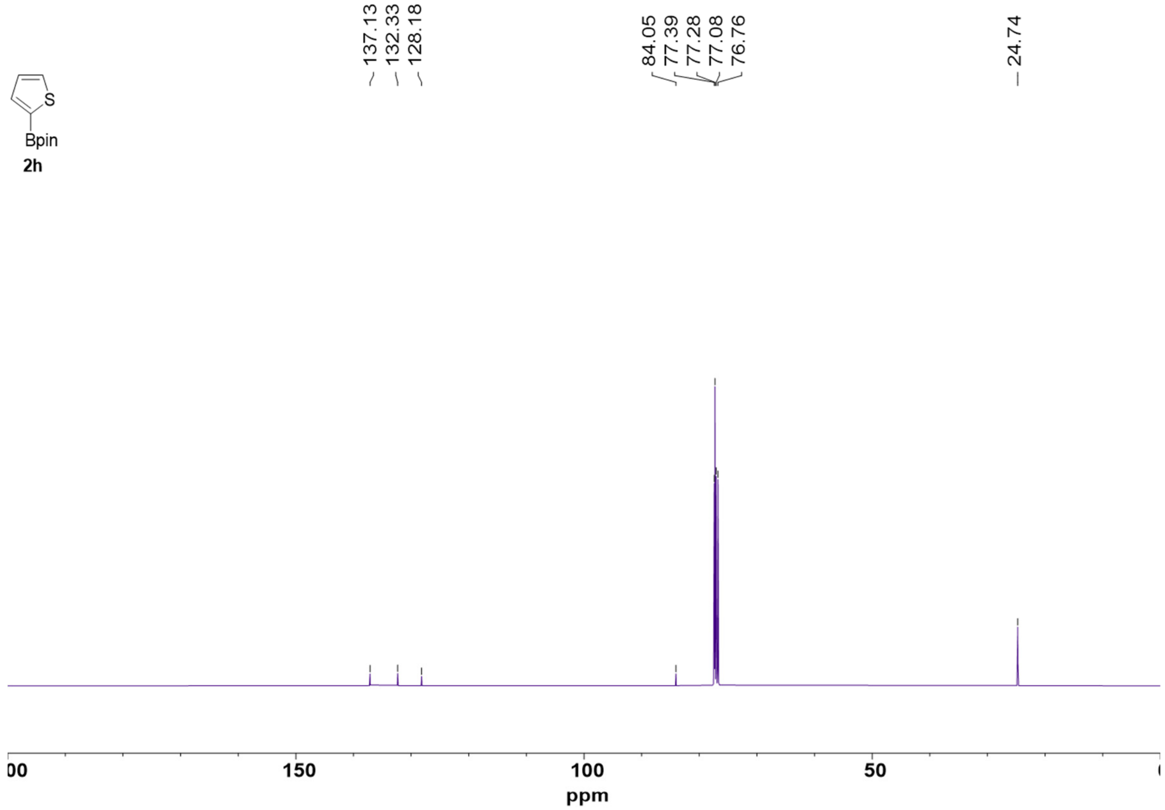
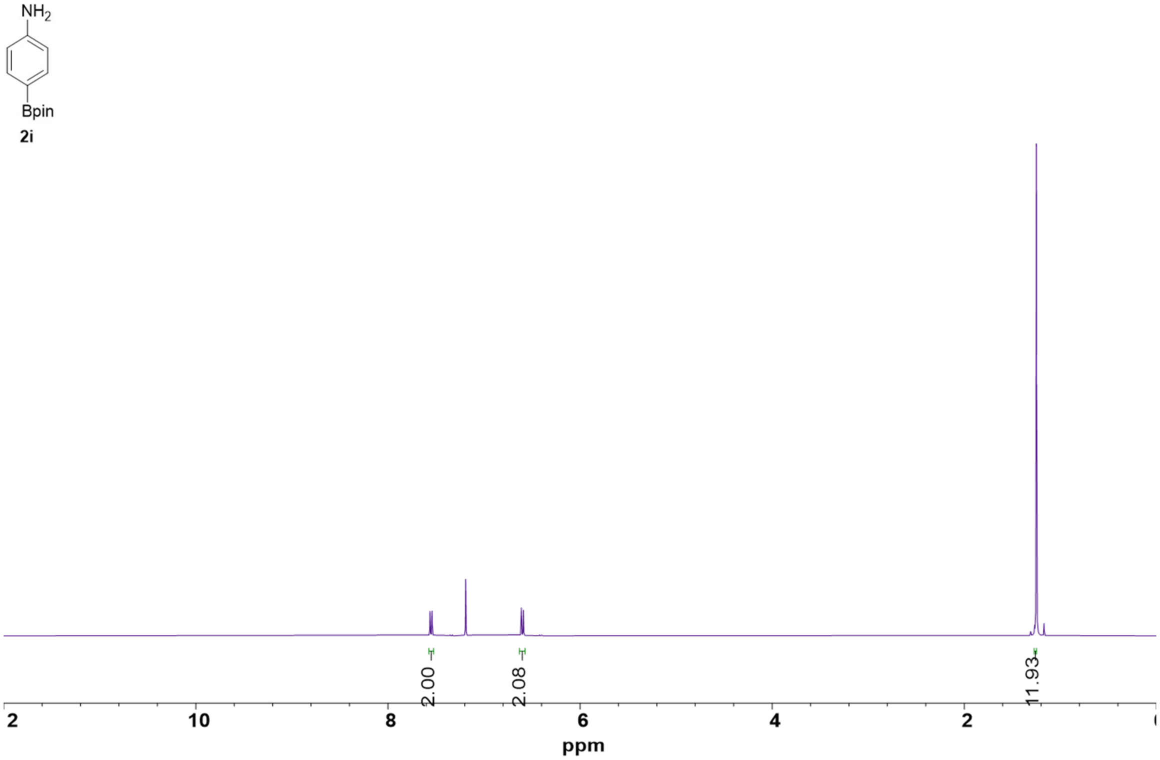
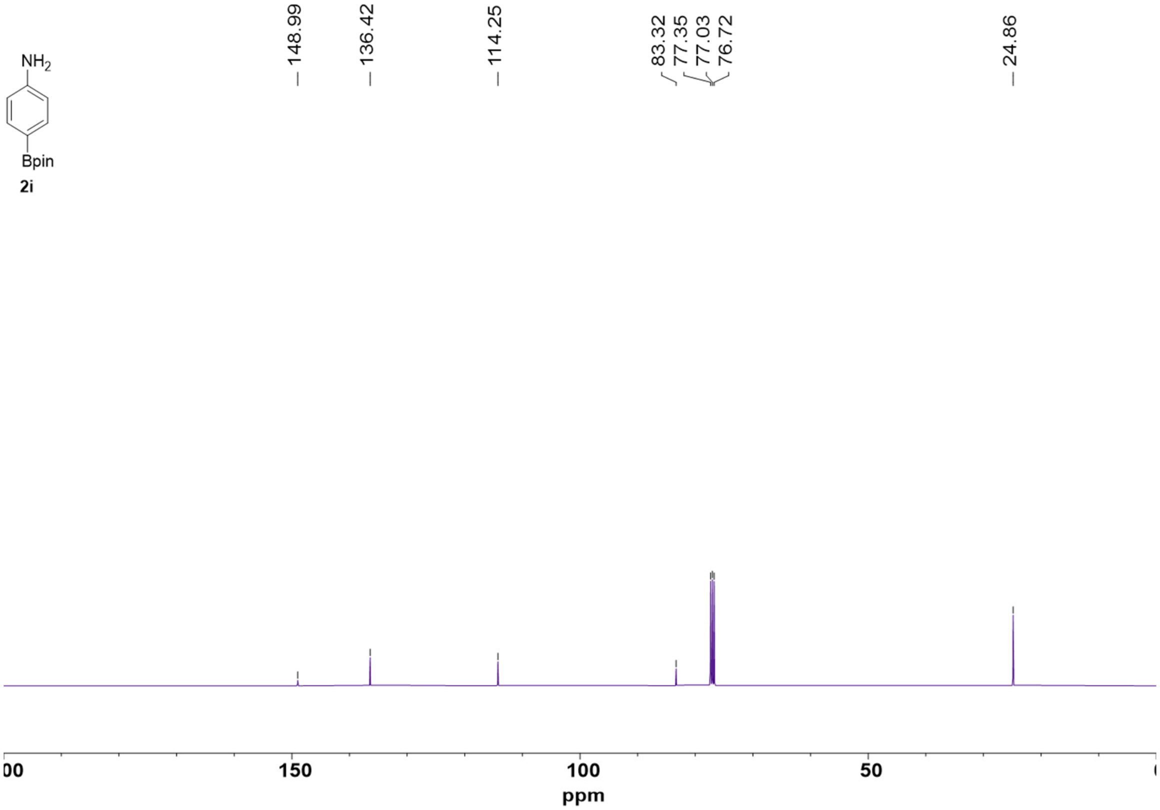
10
8
6
4
2
ppm

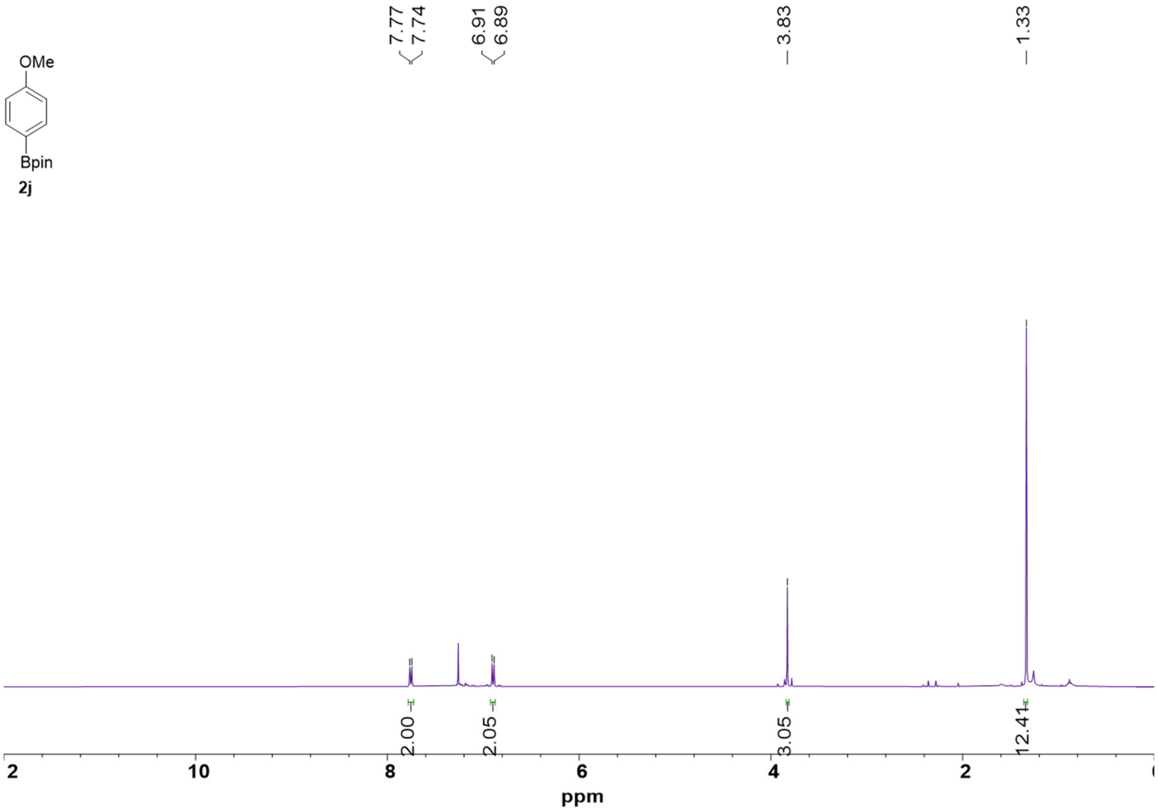

Bpin
2h
137.13
132.33
128.18
84.05
77.39
77.28
77.08
76.76
24.74
00
150
100
50
ppm


NH$_2$
Bpin
2.00
2.08
11.93
2
10
8
6
4
2
ppm

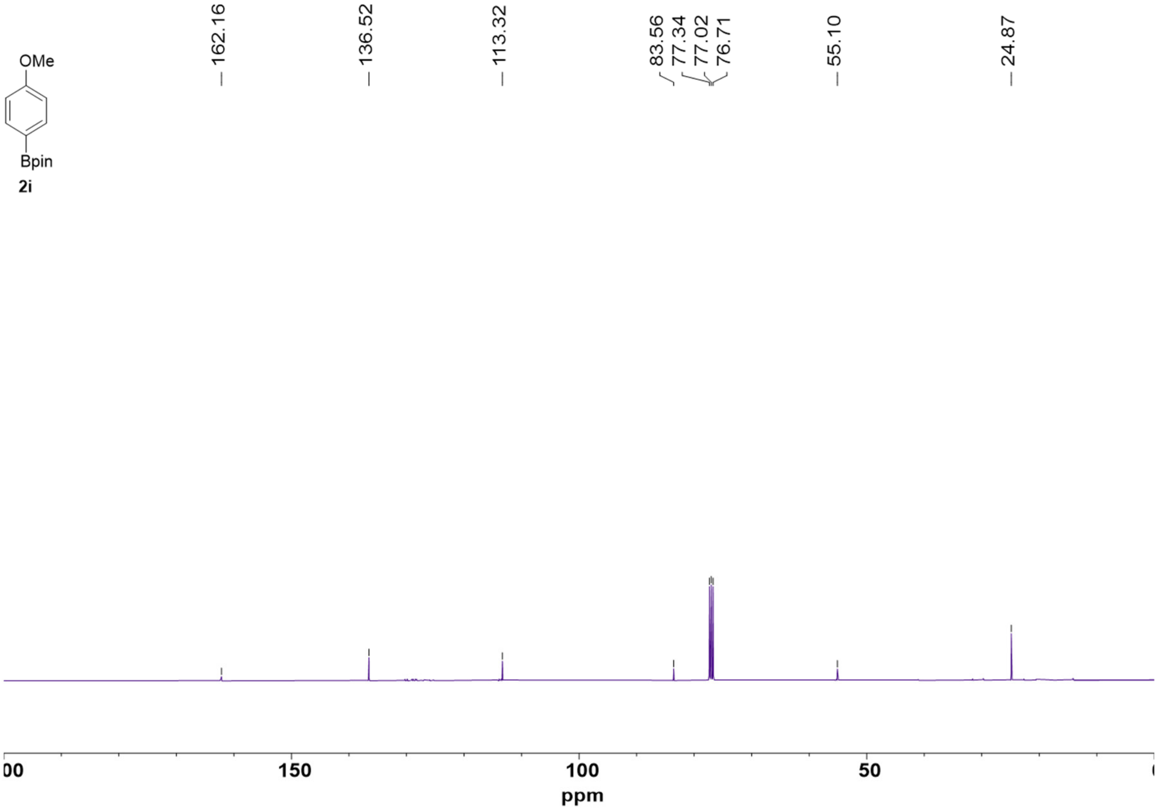
2i


148.99
136.42
114.25
83.32
77.35
77.03
76.72
24.86
NH$_2$
Bpin
00
150
100
50
ppm

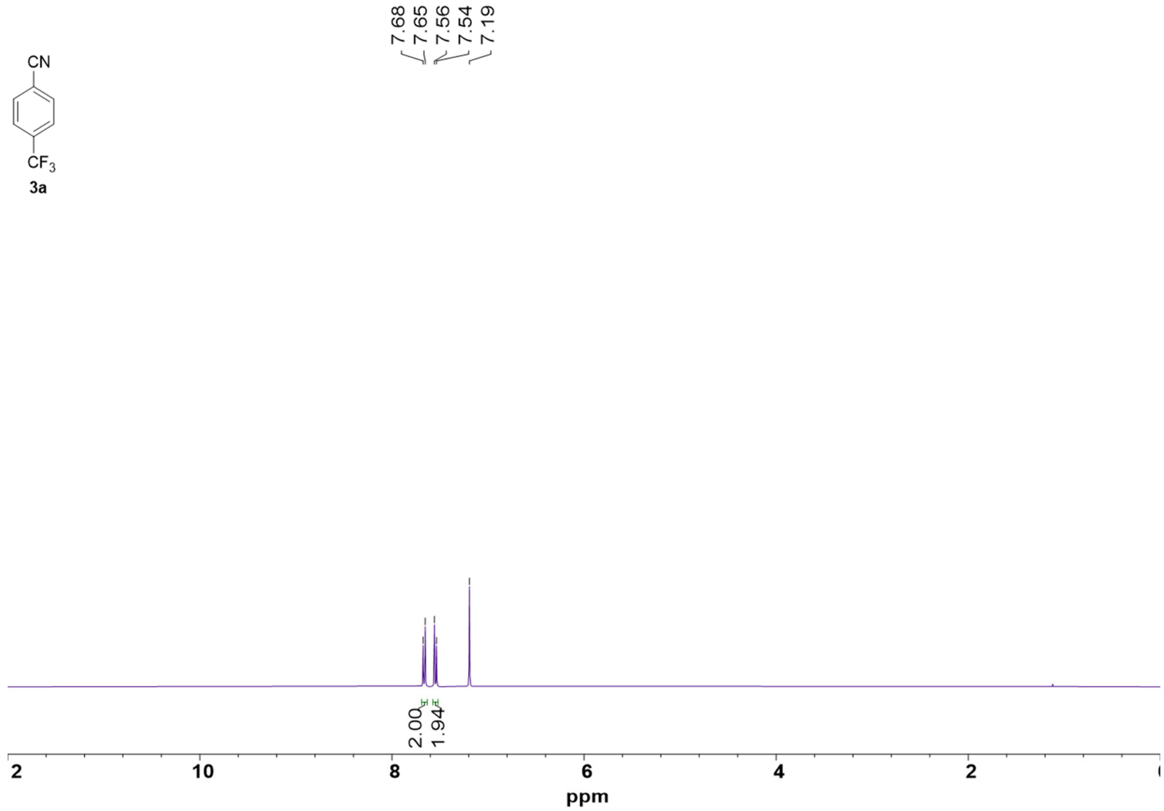
2i


OMe
Bpin
7.77
7.74
6.91
6.89
3.83
1.33
2.00
2.05
3.05
12.41
2
10
8
6
4
2
ppm

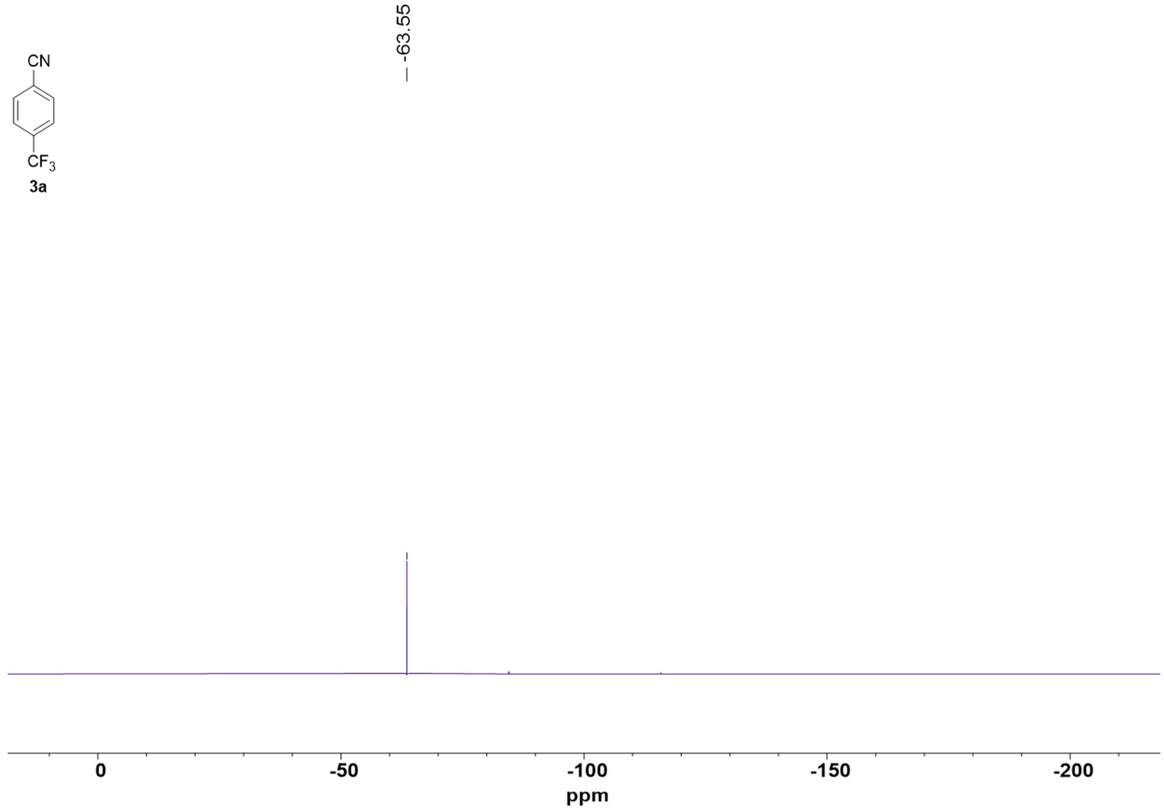
2j


OMe
Bpin
162.16
136.52
113.32
83.56
77.34
77.02
76.71
55.10
24.87
00
150
100
50
ppm

2i


7.68
7.65
7.56
7.54
7.19
CN
CF3
2.00
1.94
2
10
8
6
4
2
ppm

3a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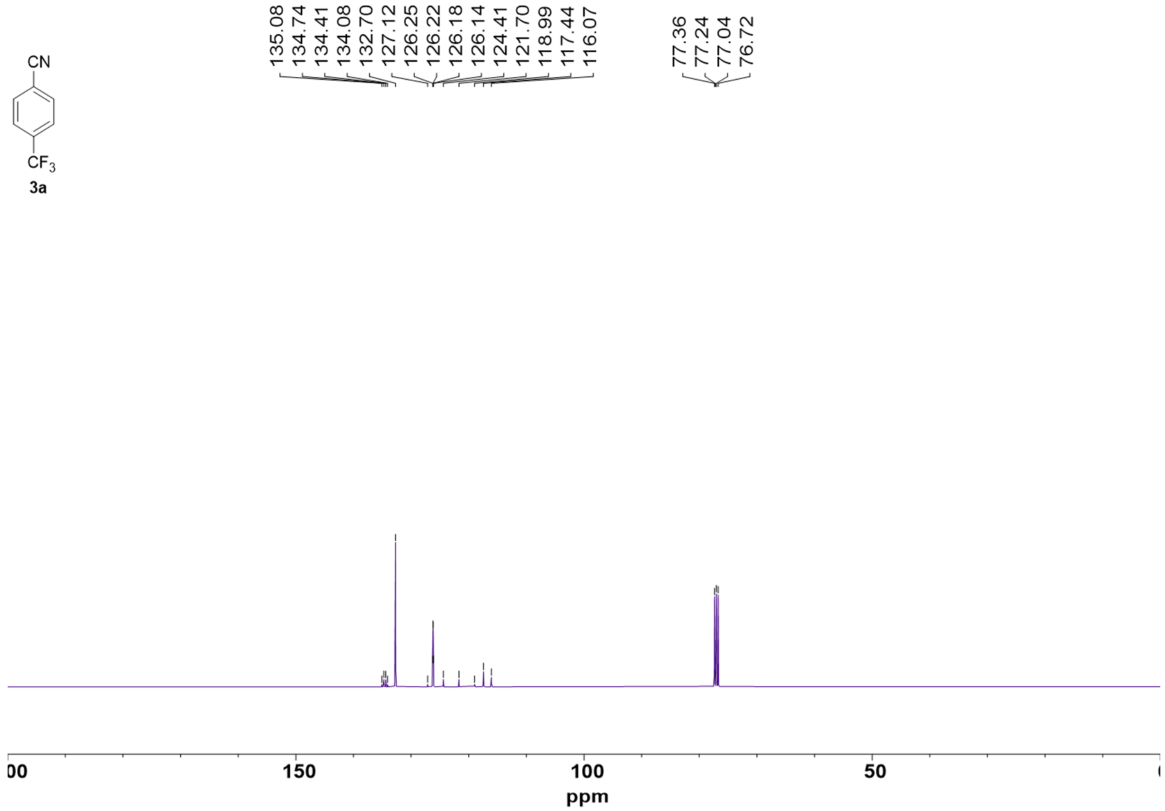
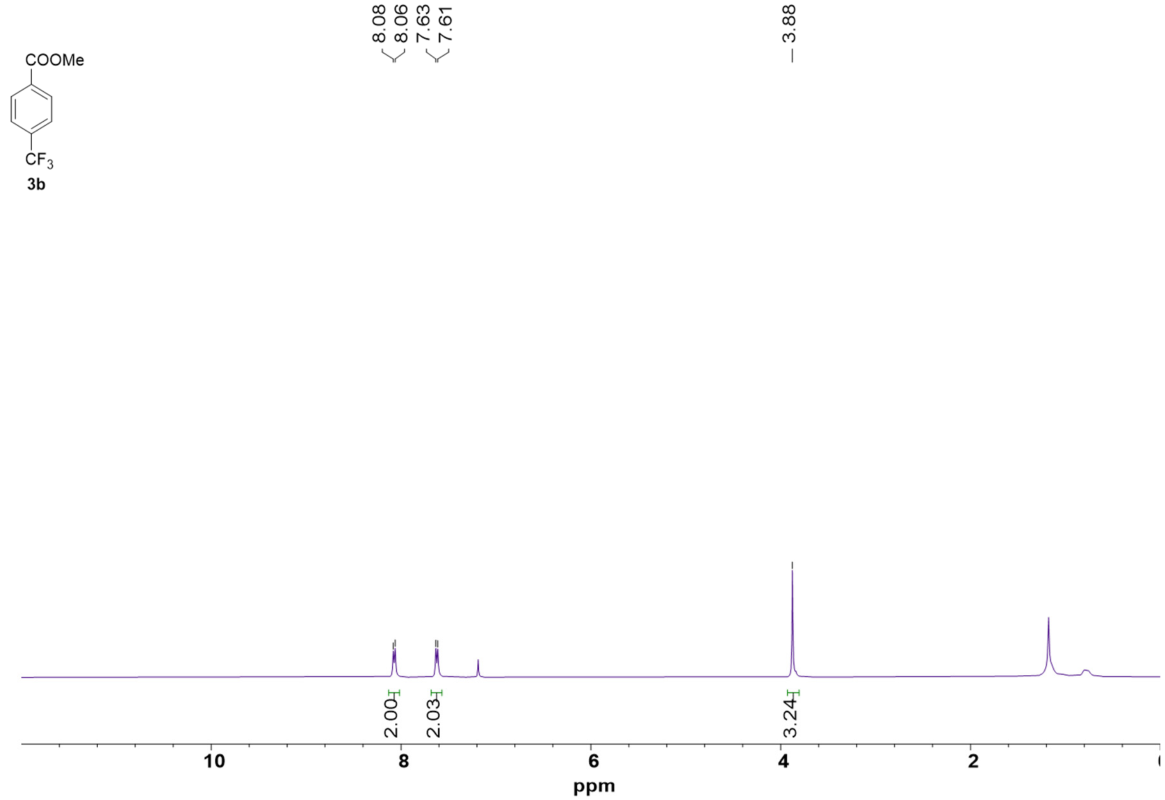
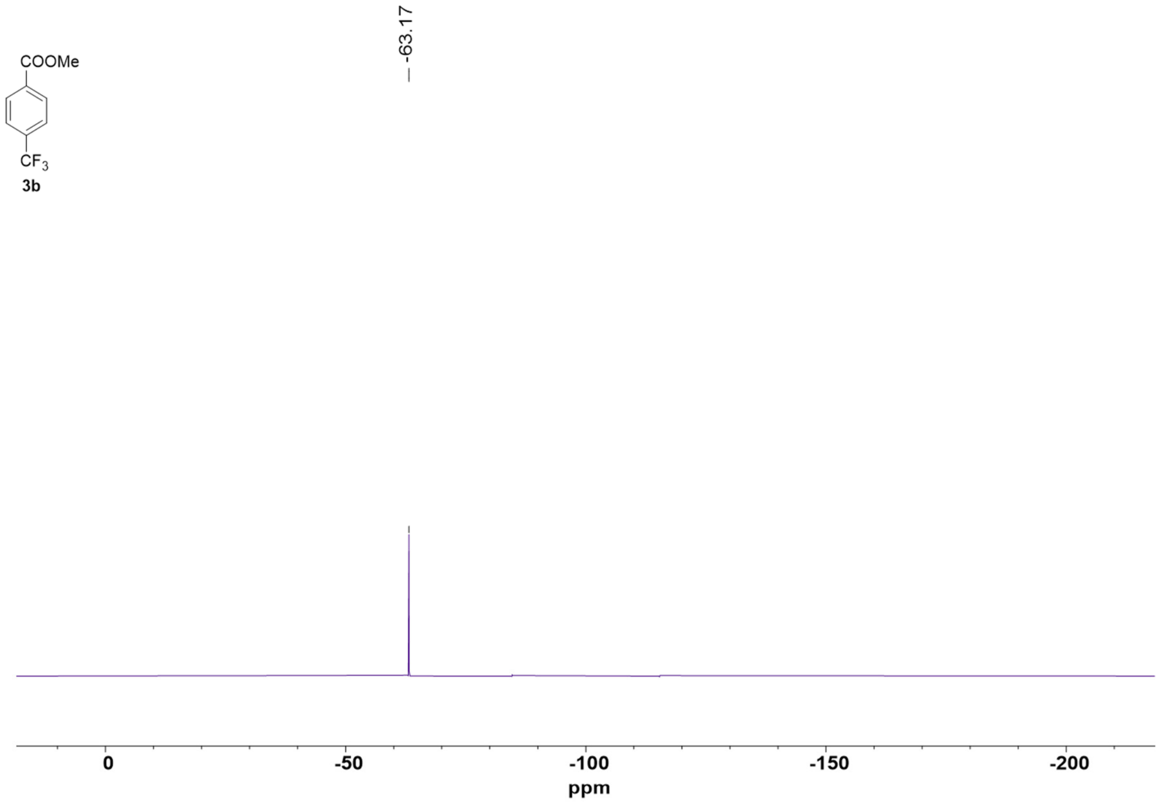
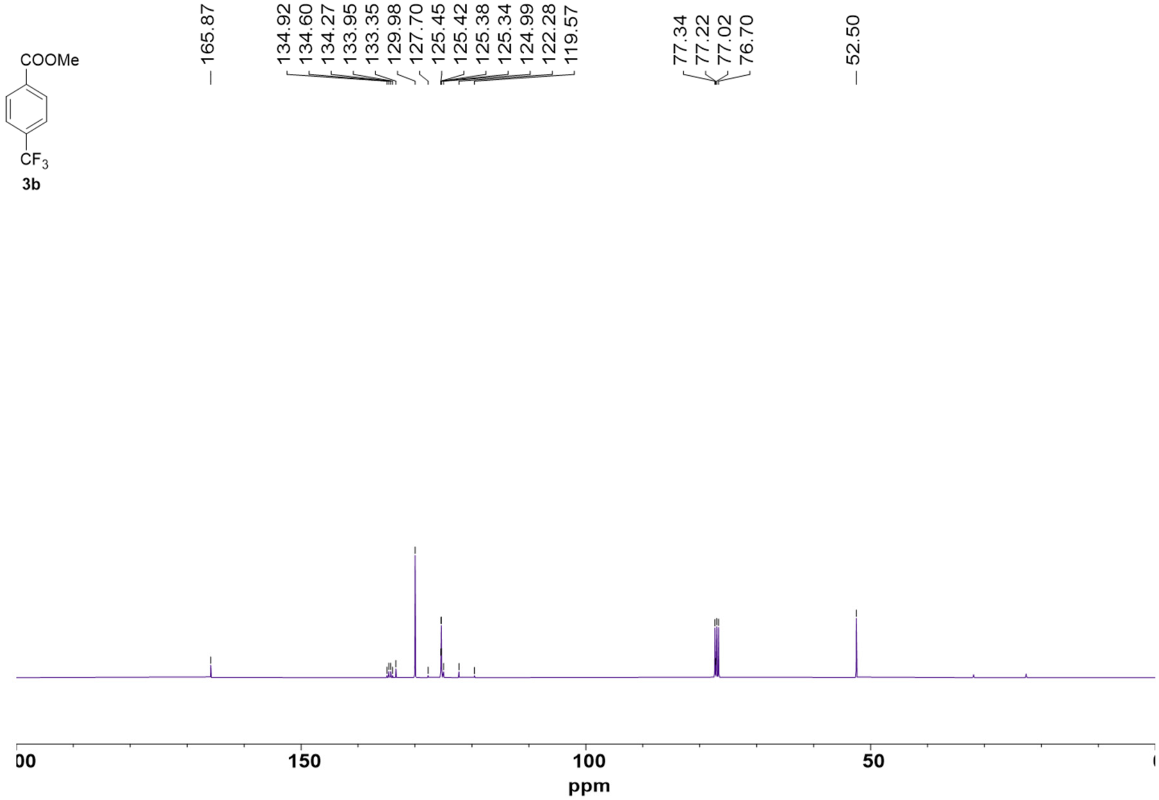
CN
CF3
0
-50
-100
-150
-200
ppm

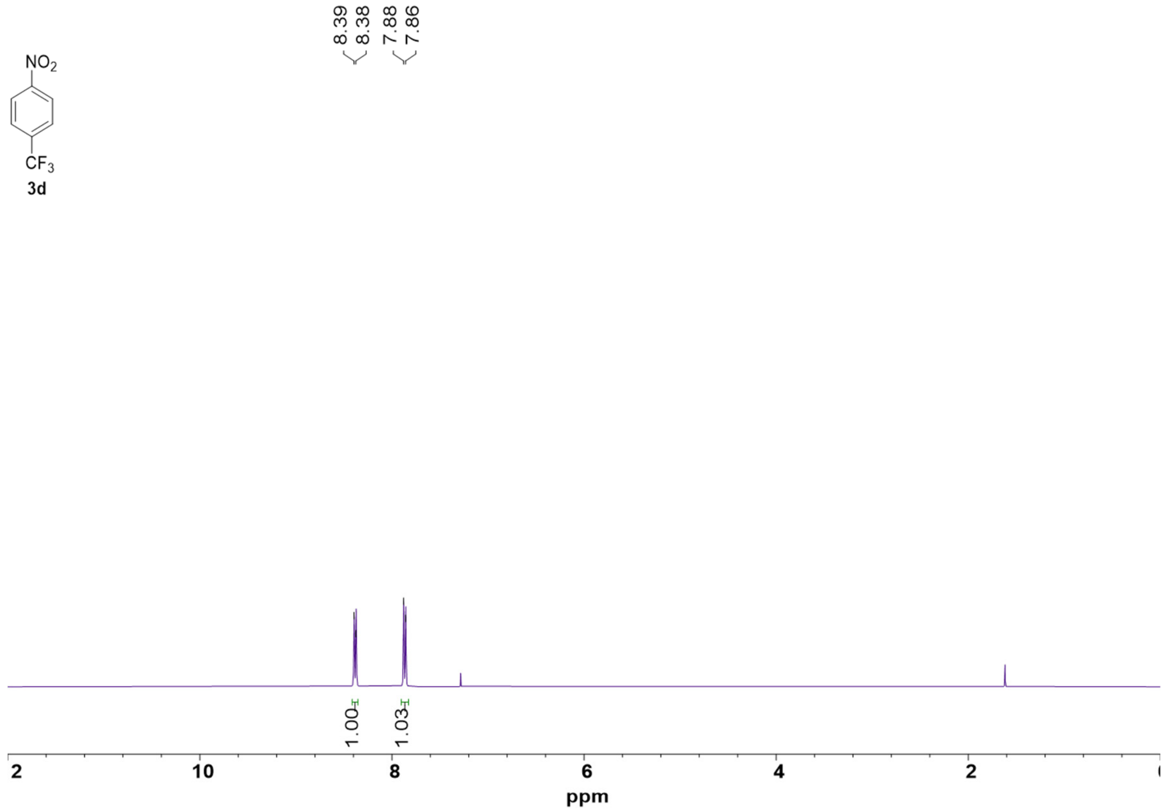
3a


CN
CF3
3a
135.08
134.74
134.41
134.08
132.70
127.12
126.25
126.22
126.18
126.14
124.41
121.70
118.99
117.44
116.07
77.36
77.24
77.04
76.72
00
150
100
50
ppm


COOMe
CF3
3b
8.08
8.06
7.63
7.61
3.88
2.00
2.03
3.24
10
8
6
4
2
ppm


COOMe
CF3
3b
-63.17
0
-50
-100
-150
-200
ppm


COOMe
CF3
3b
165.87
134.92
134.60
134.27
133.95
133.35
129.98
127.70
125.45
125.42
125.38
125.34
124.99
122.28
119.57
77.34
77.22
77.02
76.70
52.50
00
150
100
50
ppm


NO2
CF3
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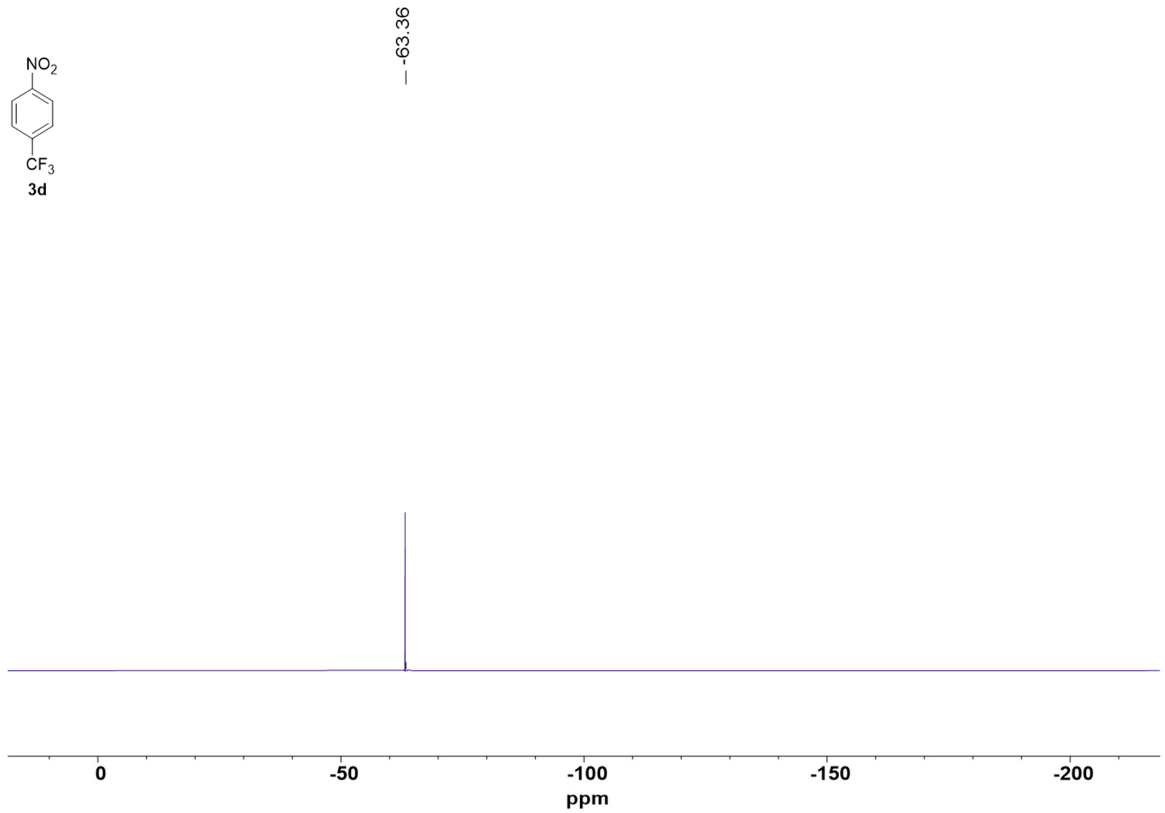
8.38
7.88
7.86
1.00
1.03
2
10
8
6
4
2
ppm

3d


NO2
CF3
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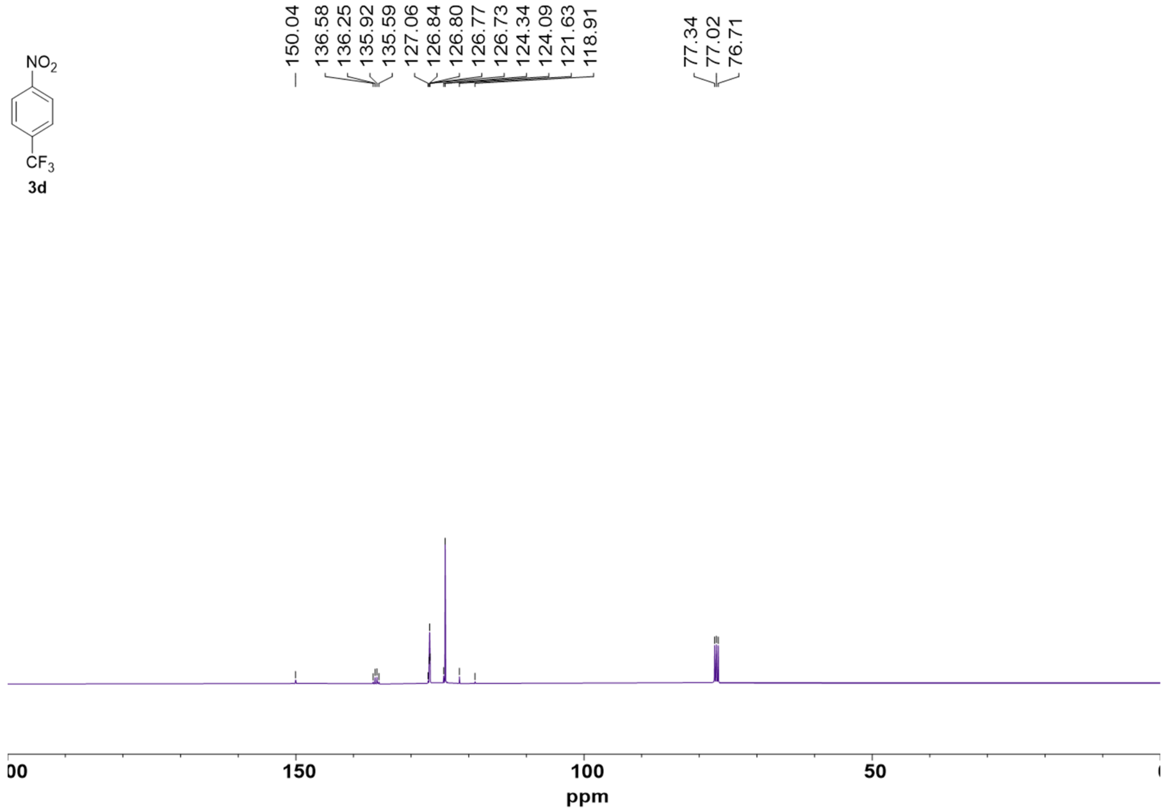
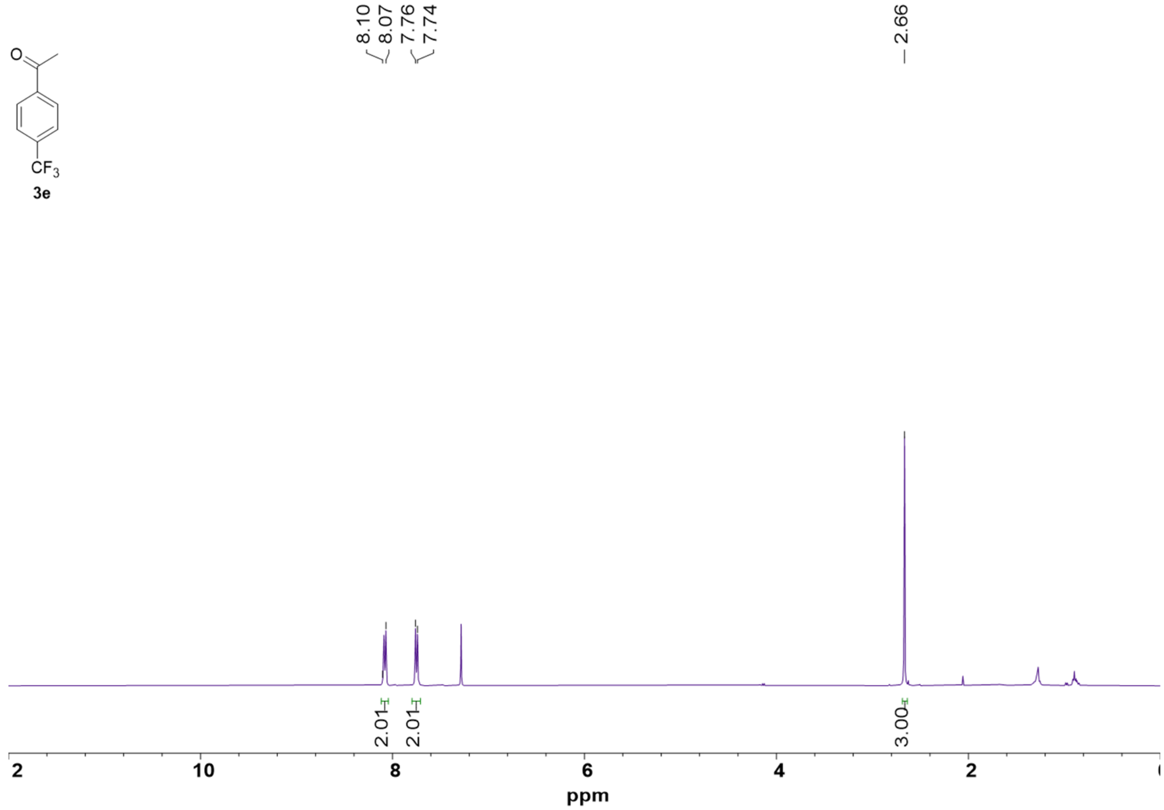
0
-50
-100
-150
-200
ppm

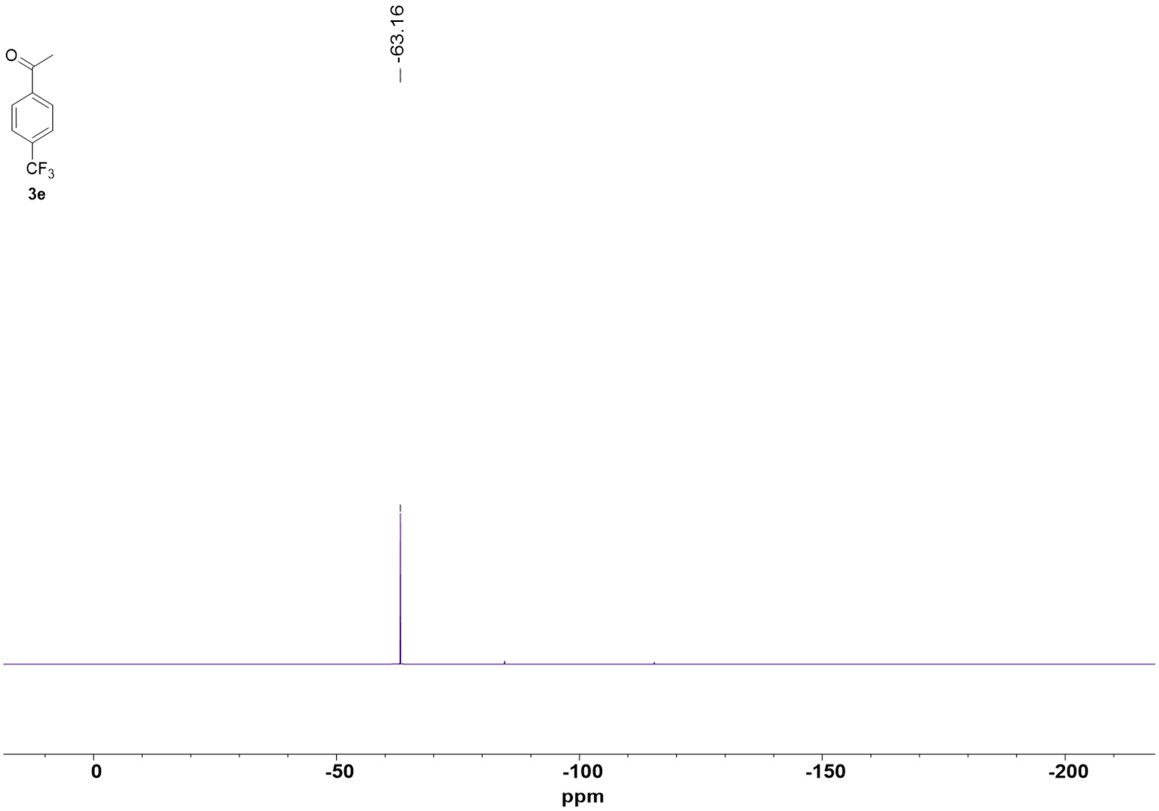
3d


3d

NO2
CF3
150.04
136.58
136.25
135.92
135.59
127.06
126.84
126.80
126.77
126.73
124.34
124.09
121.63
118.91
77.34
77.02
76.71
00
150
100
50
ppm


3e

O
CF3
8.10
8.07
7.76
7.74
2.66
2.01
2.01
3.00
2
10
8
6
4
2
ppm


O
CF3
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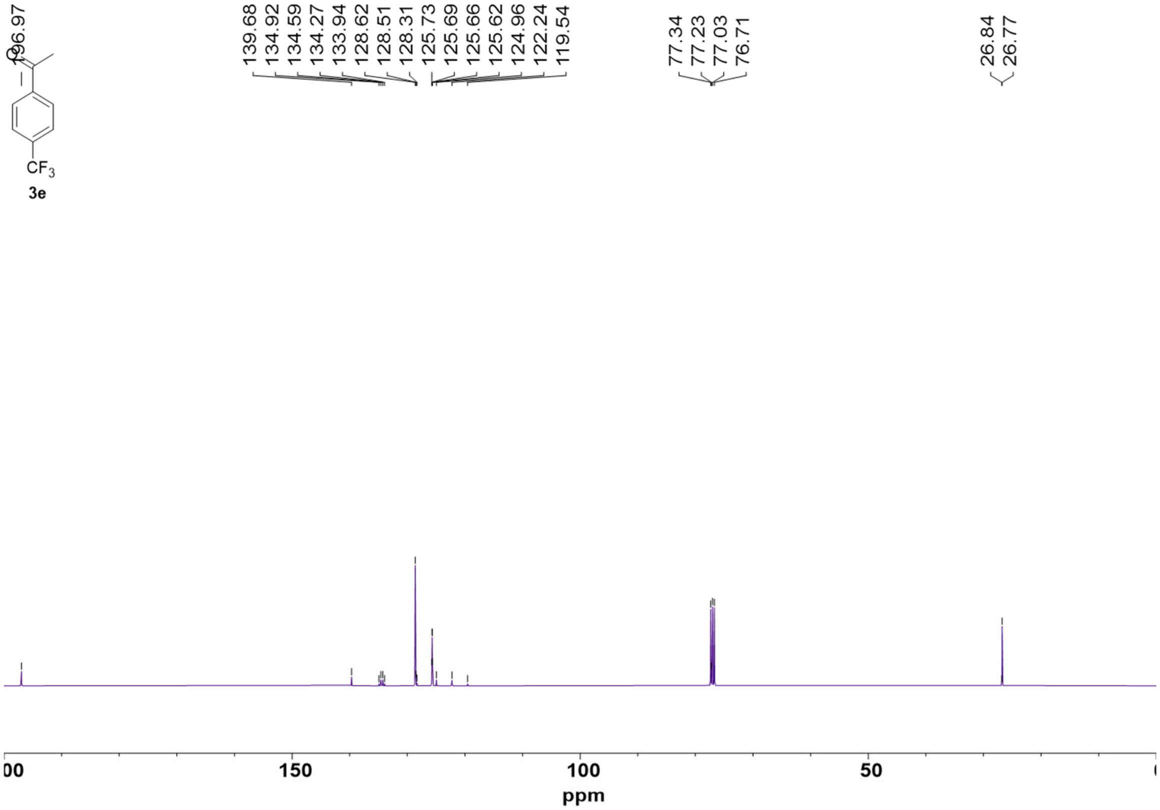
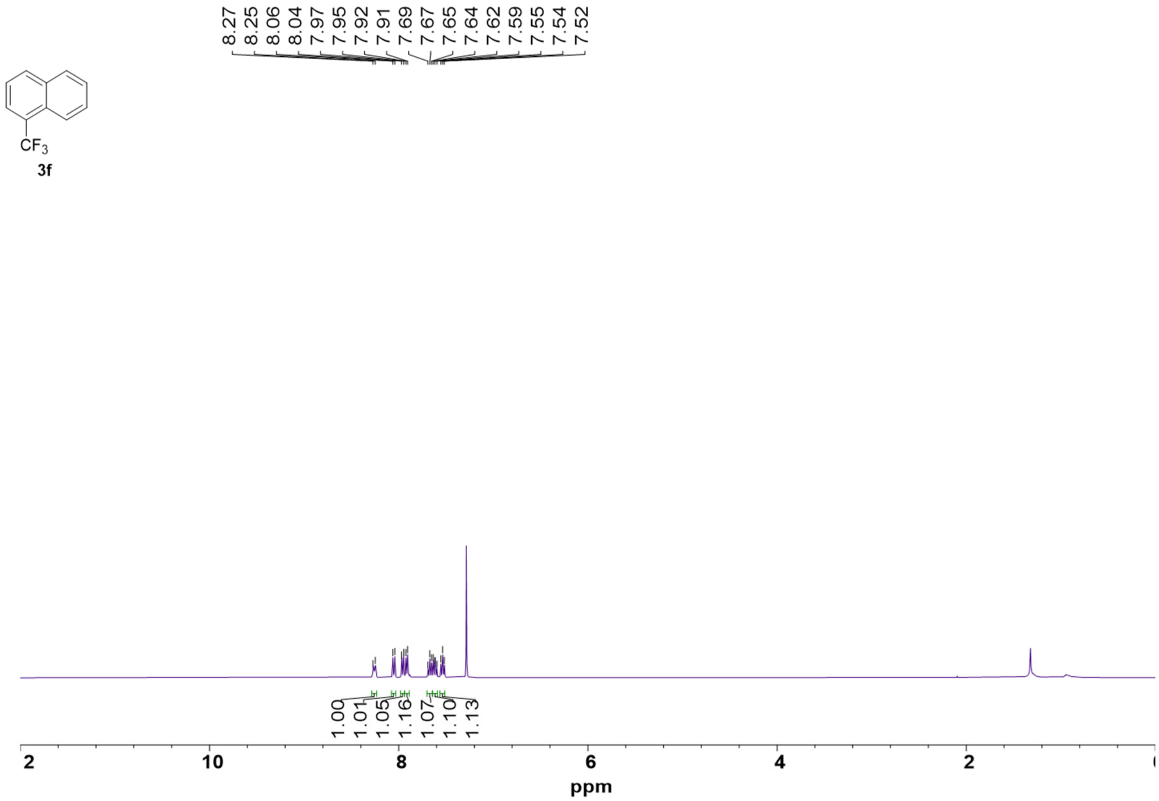
0
-50
-100
-150
-200
ppm

3e

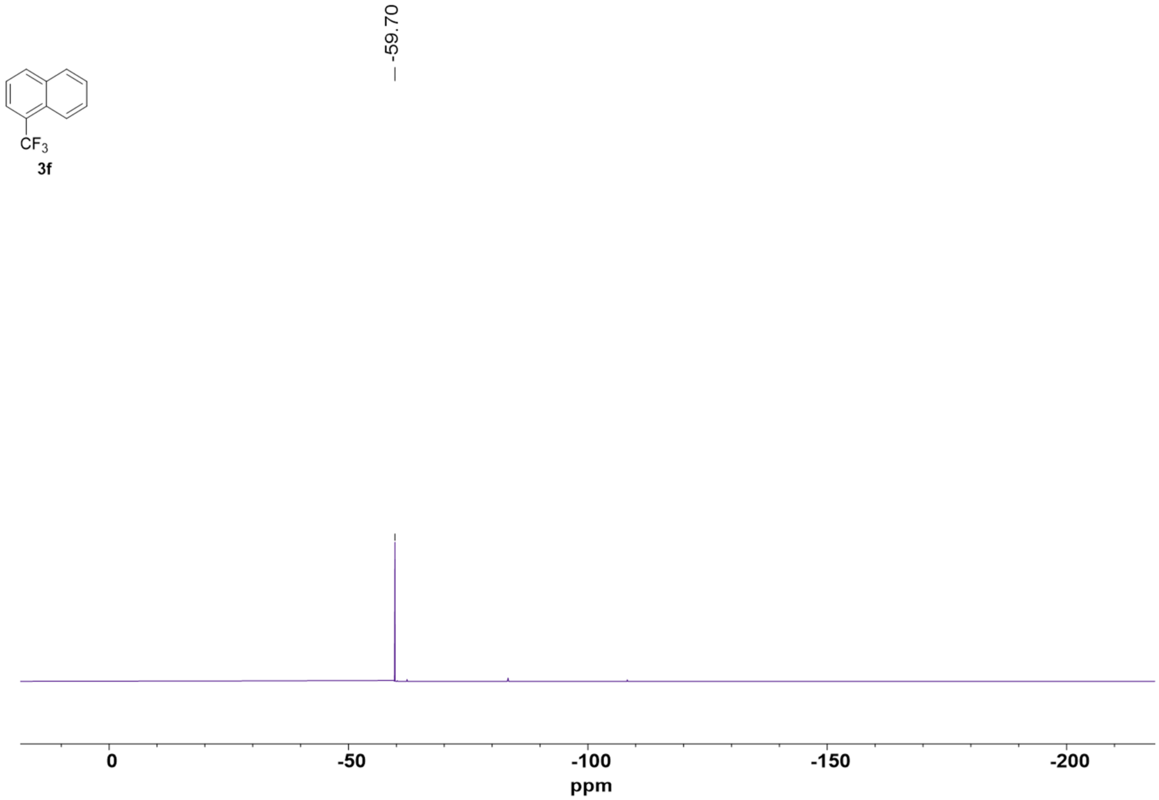

O
CF3
196.97
139.68
134.92
134.59
134.27
133.94
128.62
128.51
128.31
125.73
125.69
125.66
125.62
124.96
122.24
119.54
77.34
77.23
77.03
76.71
26.84
26.77
00
150
100
50
ppm

3e



3f

8.27
8.25
8.06
8.04
7.97
7.95
7.92
7.91
7.69
7.67
7.65
7.64
7.62
7.59
7.55
7.54
7.52
1.00
1.01
1.05
1.16
1.07
1.10
1.13
2
10
8
6
4
2
ppm



3f

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0
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-100
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-200
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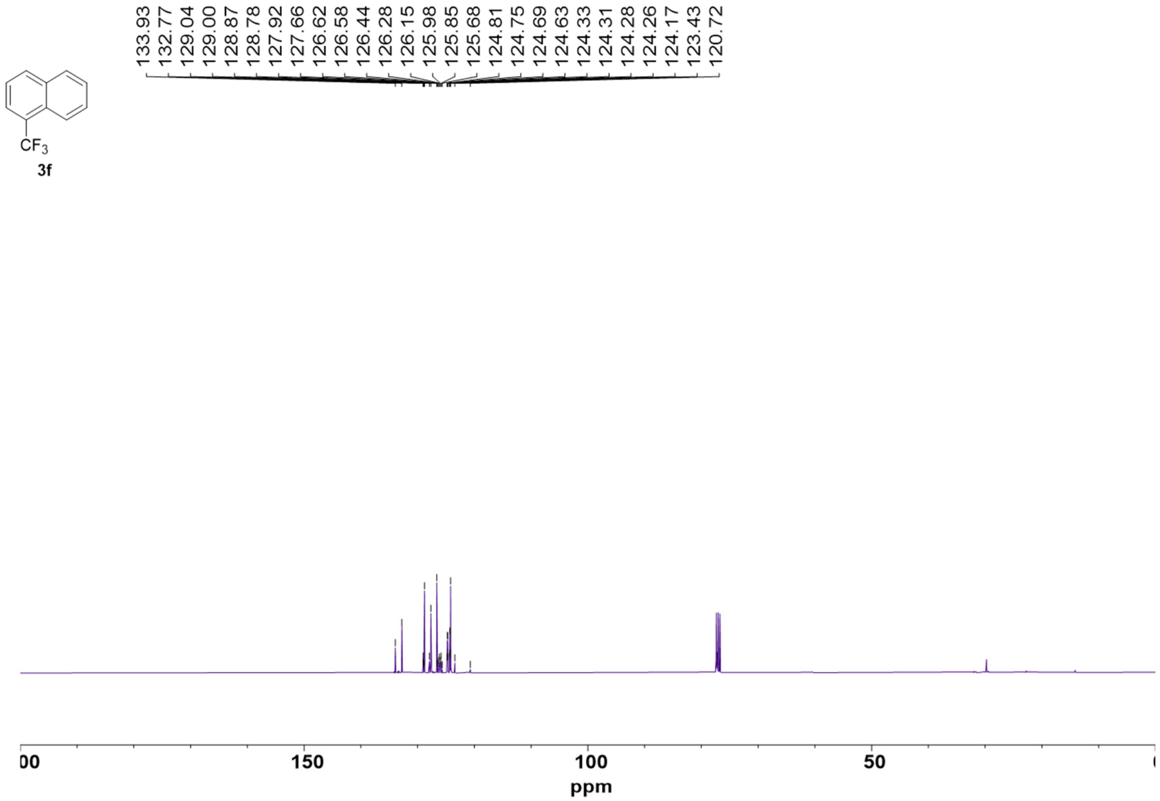
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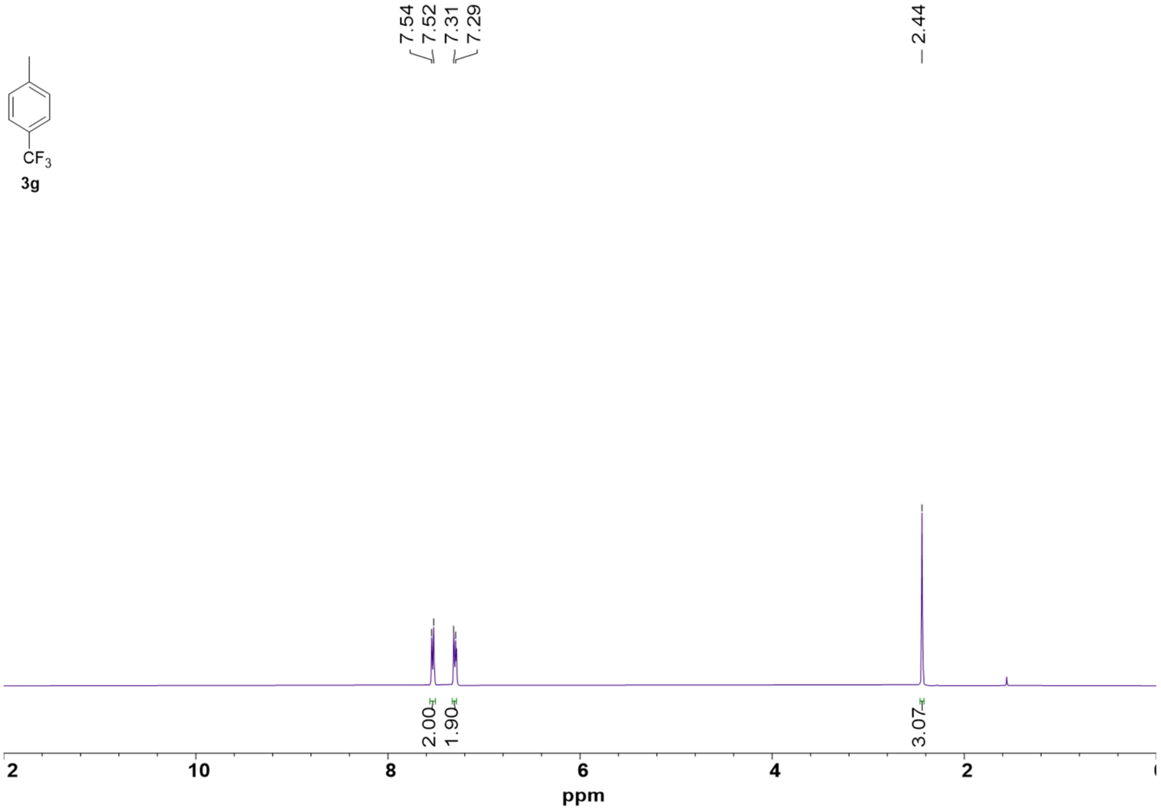
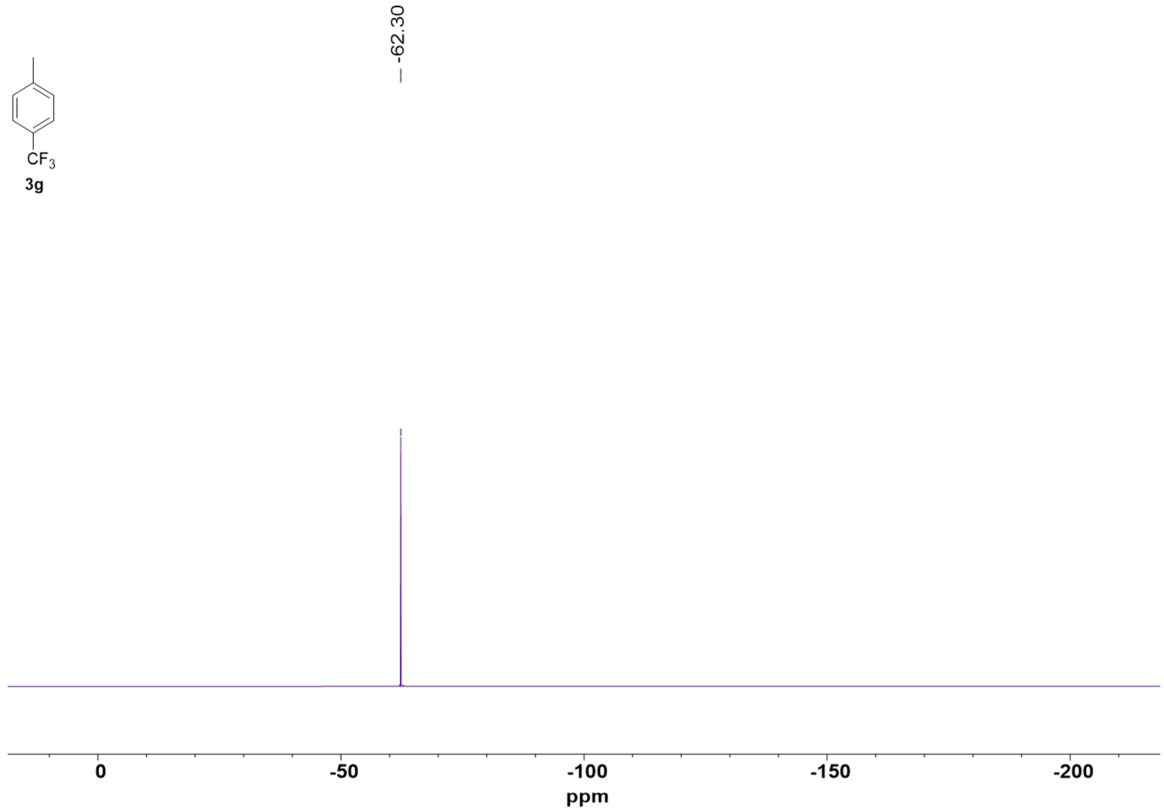
132.77
129.04
129.00
128.87
128.78
127.92
127.66
126.62
126.58
126.44
126.28
126.15
125.98
125.85
125.68
124.81
124.75
124.69
124.63
124.33
124.31
124.28
124.26
124.17
123.43
120.72
CF3
3f
00
150
100
50
ppm


7.54
7.52
7.31
7.29
2.44
CF3
3g
2.00
1.90
3.07
2
10
8
6
4
2
ppm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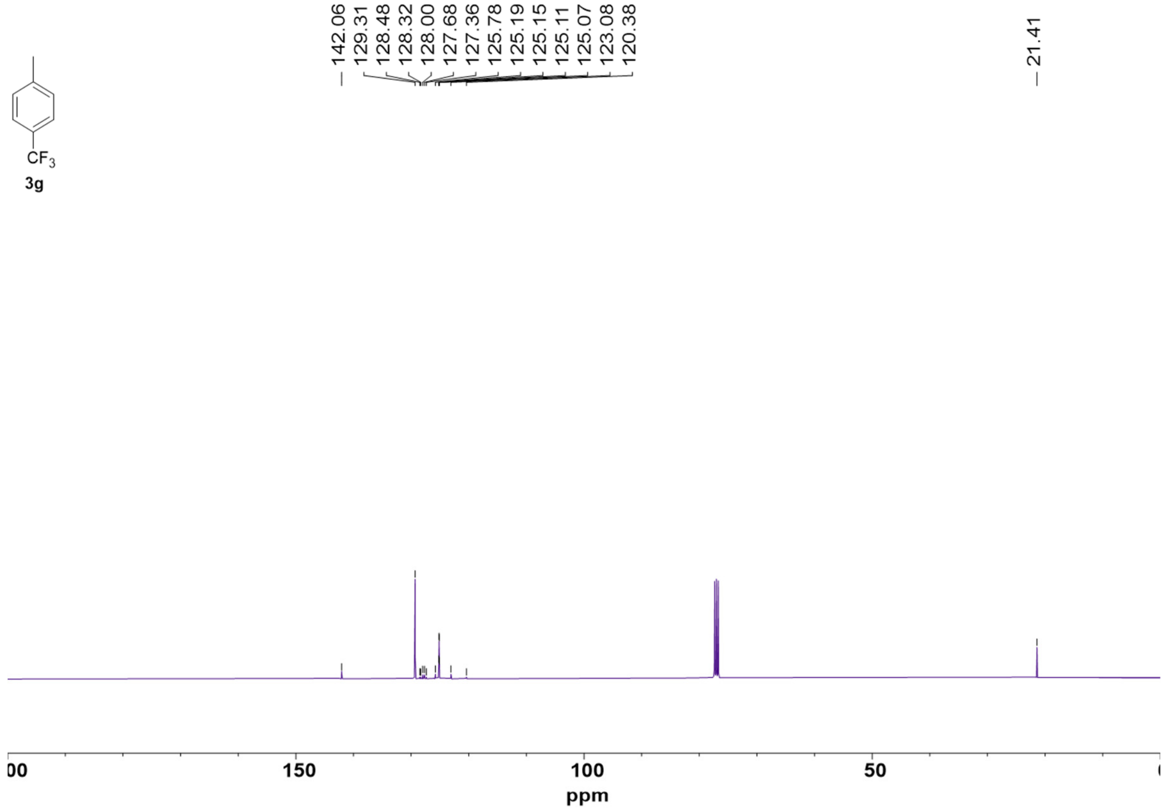
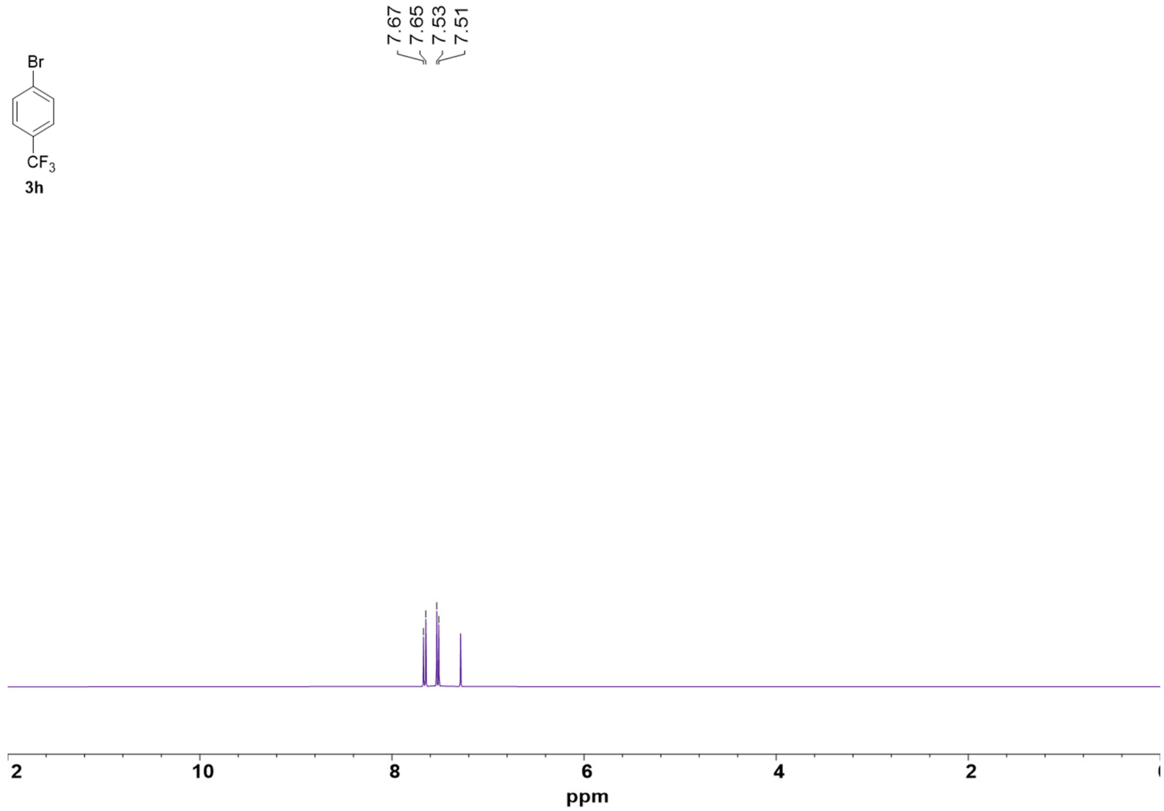
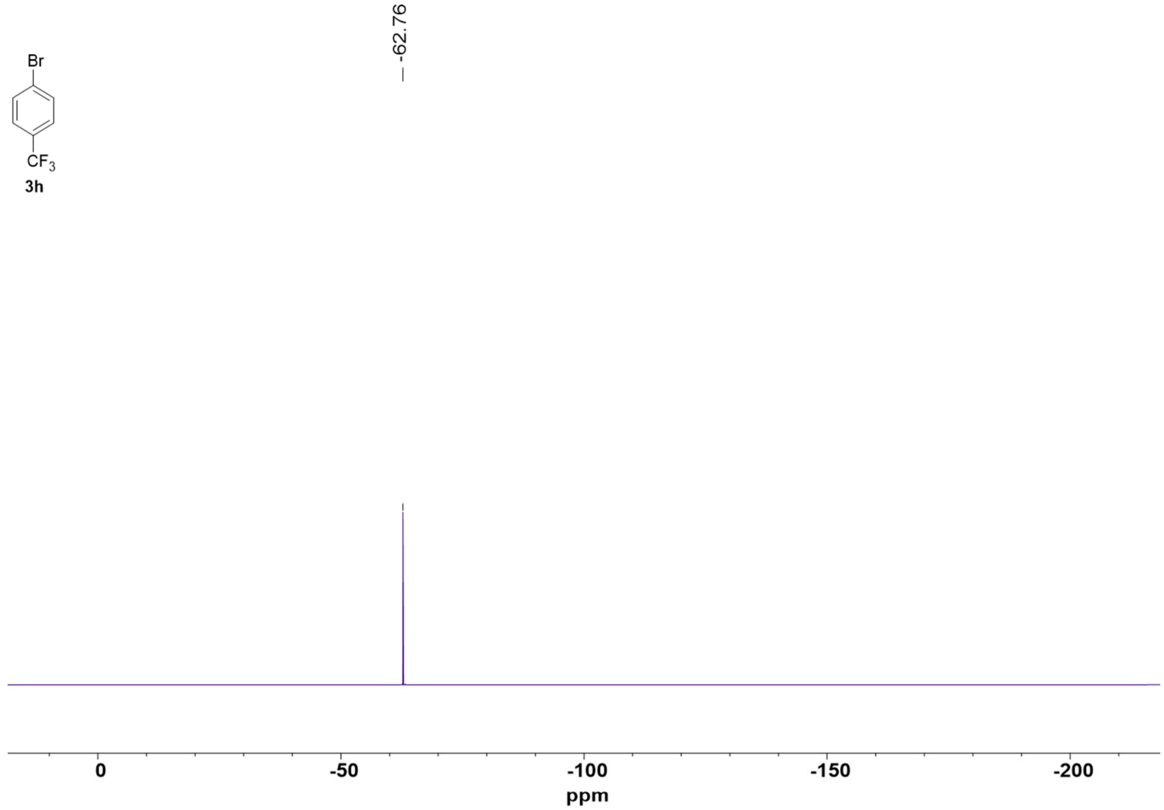
-100
-150
-200
ppm


142.06
129.31
128.48
128.32
128.00
127.68
127.36
125.78
125.19
125.15
125.11
125.07
123.08
120.38
21.41
CF3
3g
00
150
100
50
ppm


7.67
7.65
7.53
7.51
Br
CF3
2
10
8
6
4
2
ppm

3h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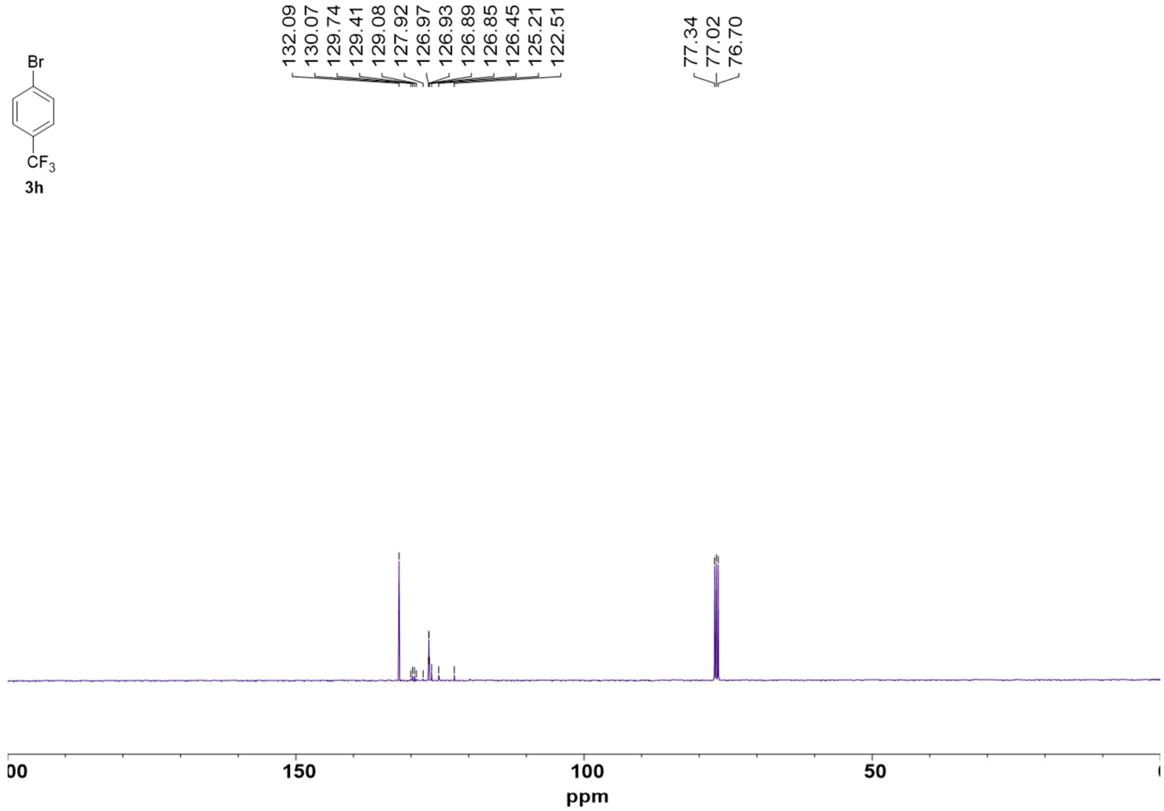
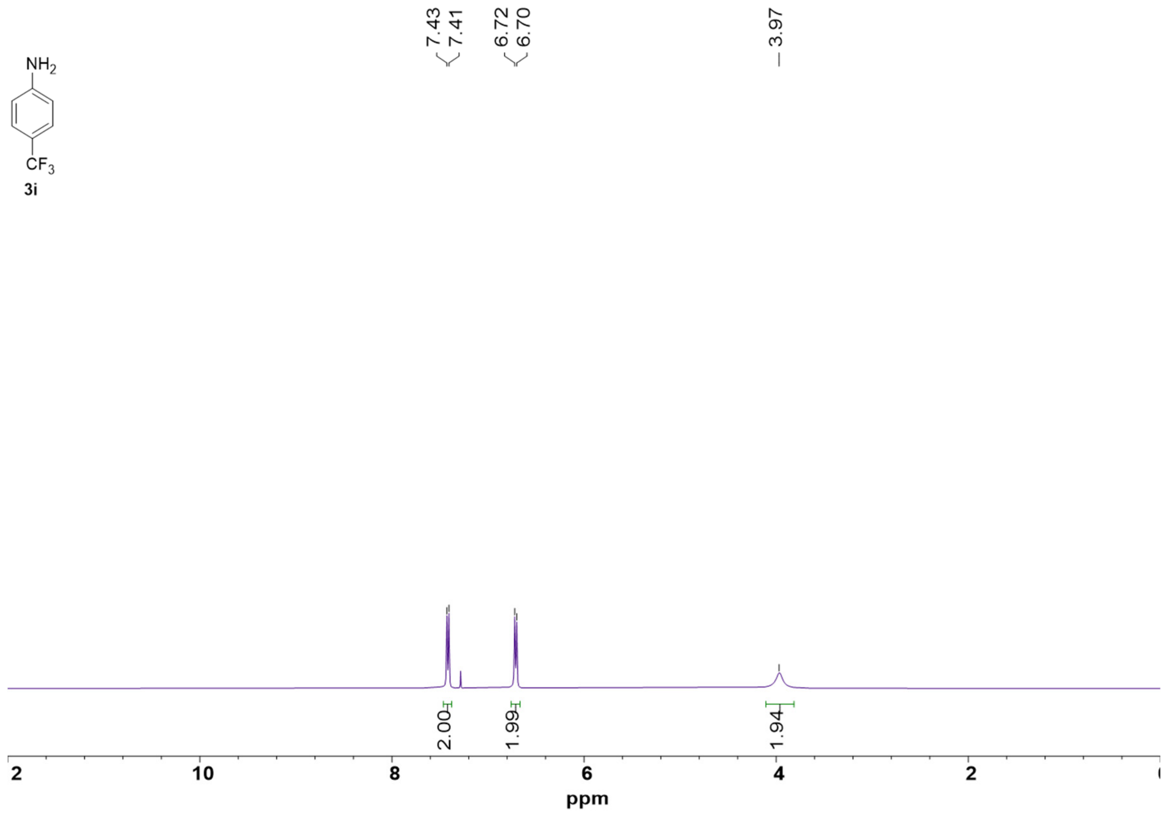
Br
CF3
0
-50
-100
-150
-200
ppm

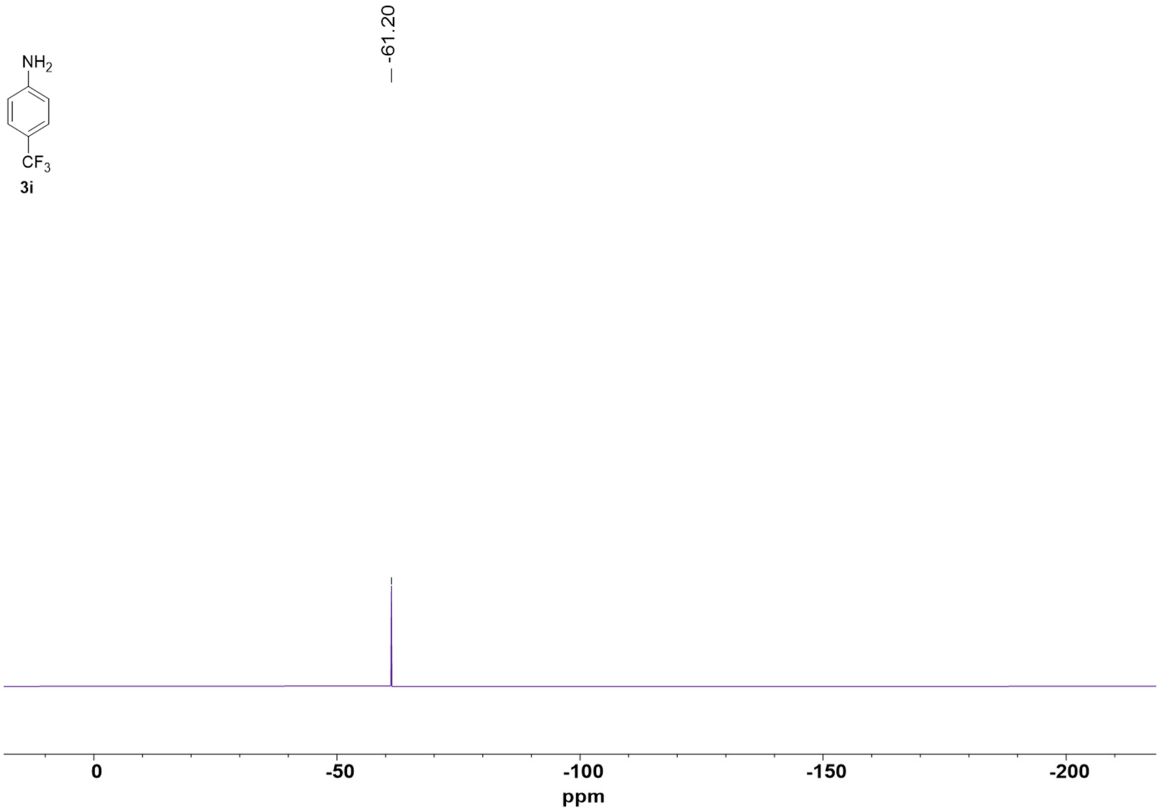
3h


Br
CF3
132.09
130.07
129.74
129.41
129.08
127.92
126.97
126.93
126.89
126.85
126.45
125.21
122.51
77.34
77.02
76.70
00
150
100
50
ppm

3h


NH2
CF3
7.43
7.41
6.72
6.70
3.97
2.00
1.99
1.94
2
10
8
6
4
2
ppm

3i


3i
NH2
CF3
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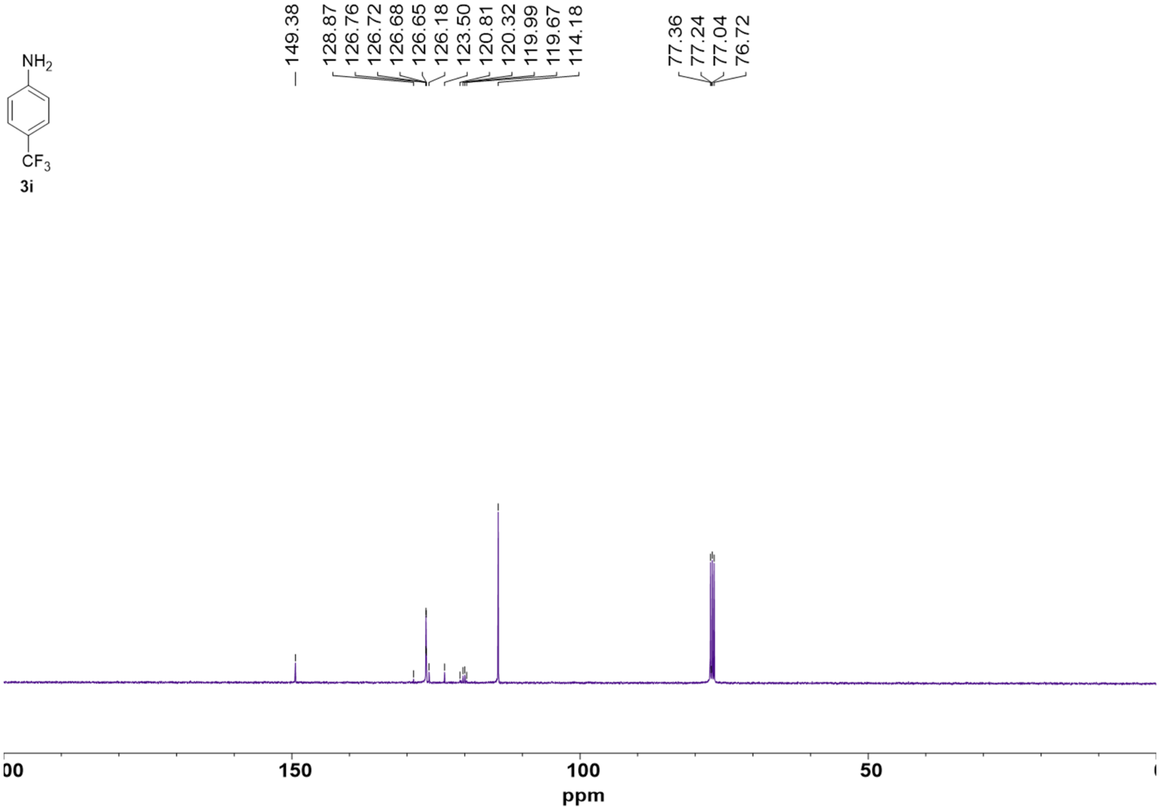
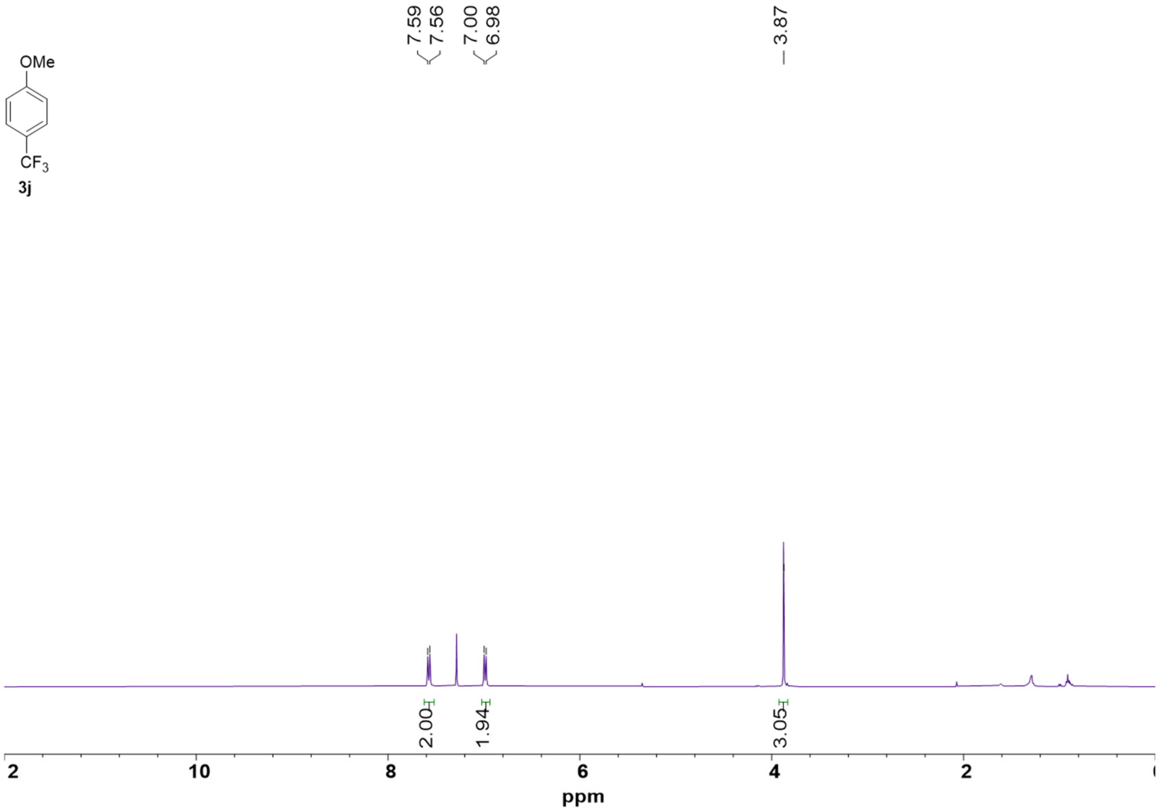
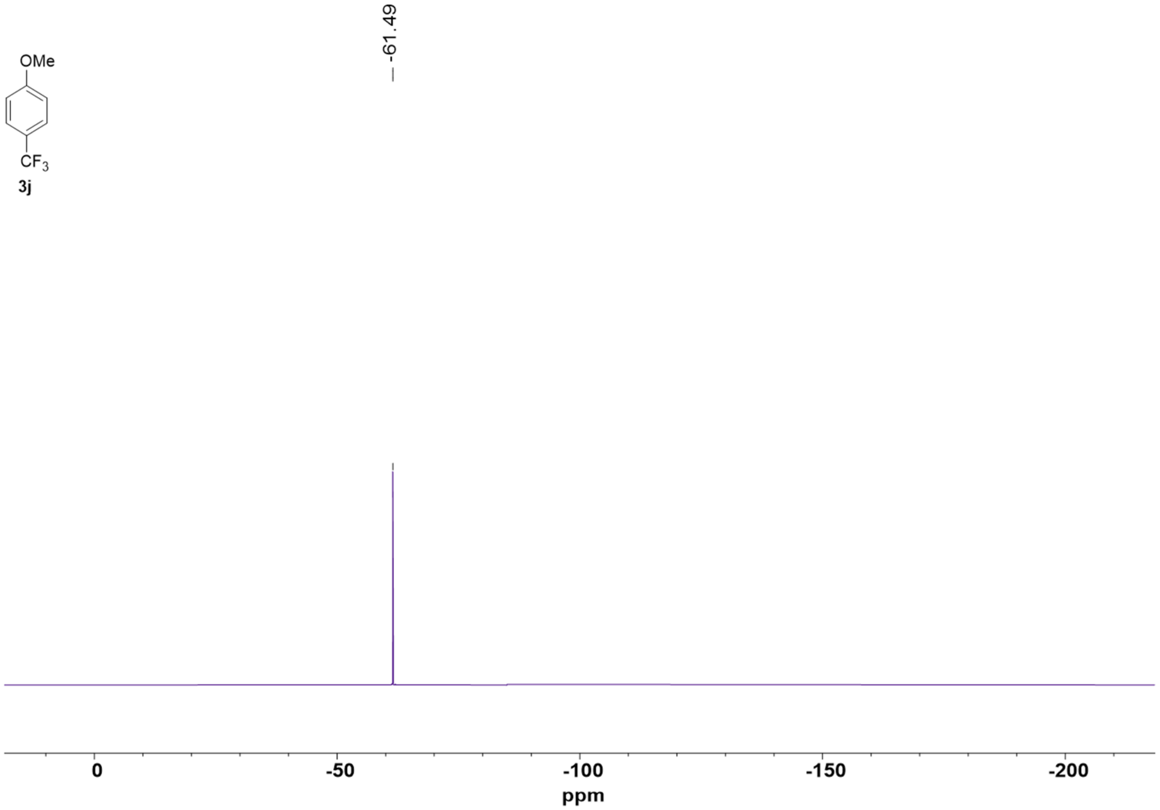
0
-50
-100
-150
-200
ppm


3i
NH2
CF3
149.38
128.87
126.76
126.72
126.68
126.65
126.18
123.50
120.81
120.32
119.99
119.67
114.18
77.36
77.24
77.04
76.72
00
150
100
50
ppm


OMe
CF3
3j
7.59
7.56
7.00
6.98
3.87
2.00
1.94
3.05
12
10
8
6
4
2
0
ppm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CF3
3j
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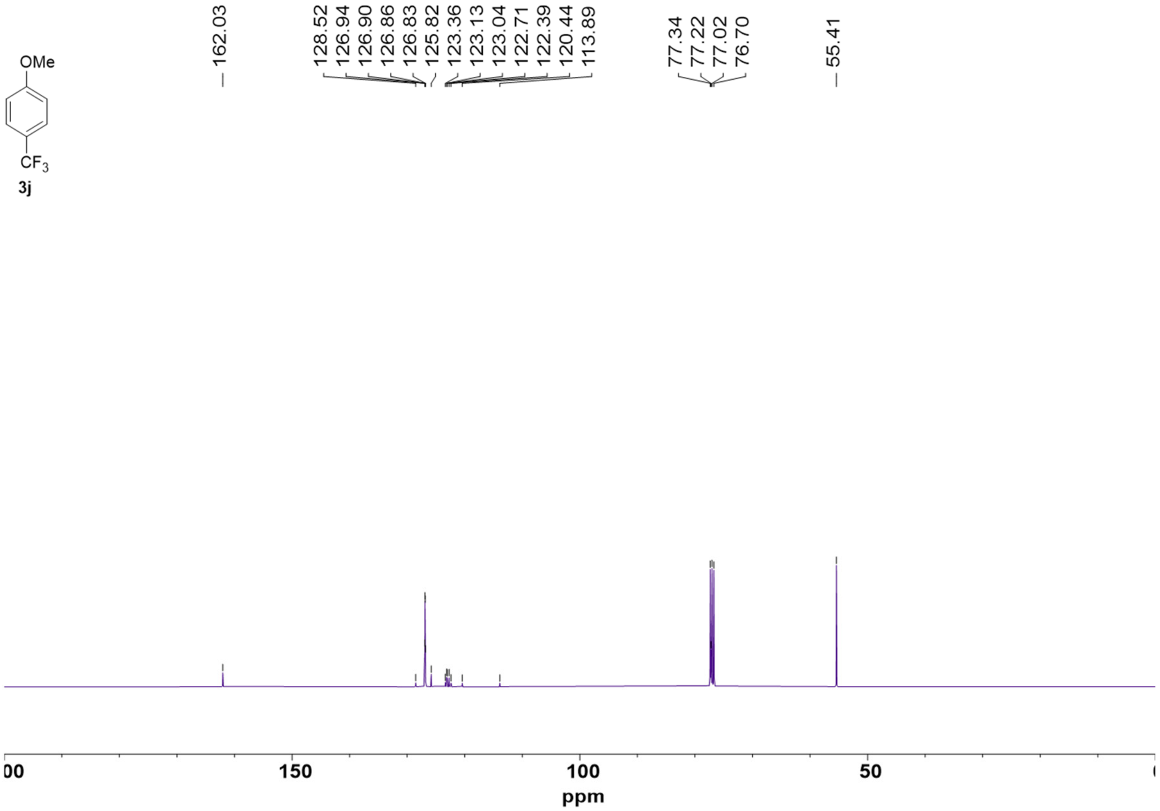
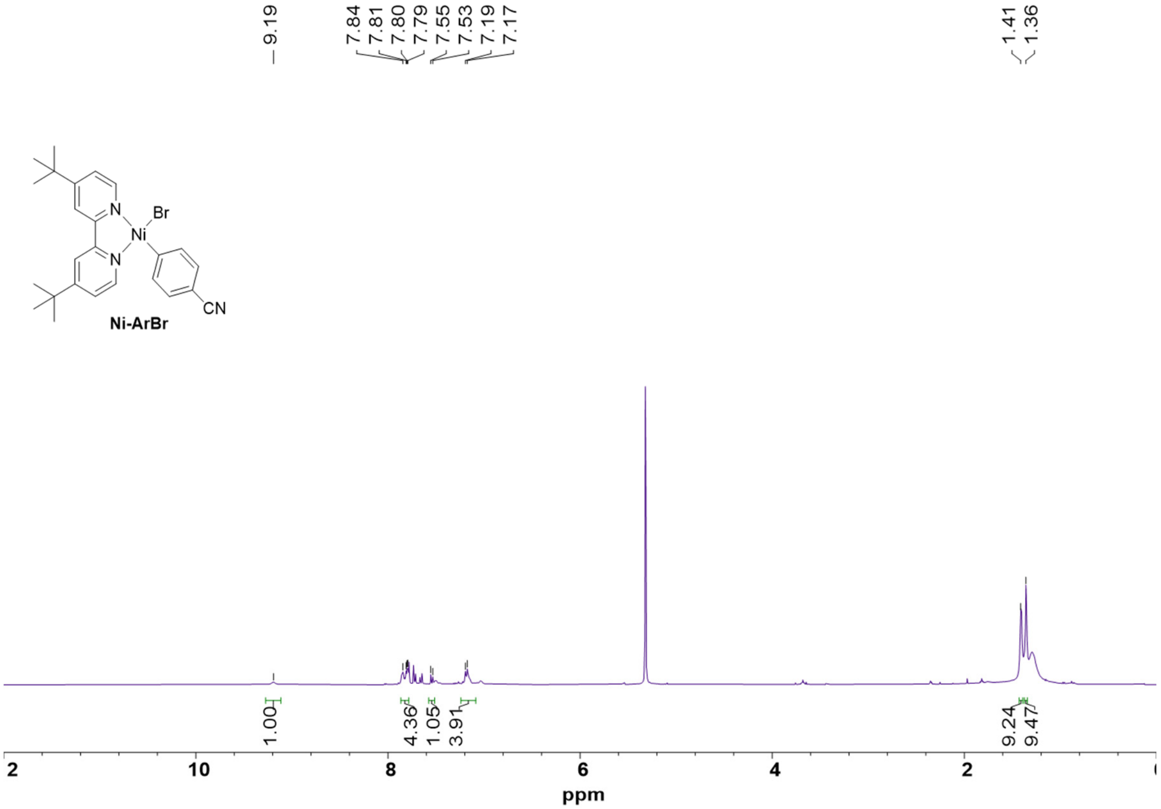
0
-50
-100
-150
-200
ppm


OMe
CF3
162.03
128.52
126.94
126.90
126.86
126.83
125.82
123.36
123.13
123.04
122.71
122.39
120.44
113.89
77.34
77.22
77.02
76.70
55.41
00
150
100
50
ppm

3j


9.19
7.84
7.81
7.80
7.79
7.55
7.53
7.19
7.17
1.41
1.36
N
N
Ni
Br
CN
1.00
4.36
1.05
3.91
9.24
9.47
2
10
8
6
4
2
ppm

Ni-ArBr

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