

## *Supporting Information*

### **Selective 1,1- and 1,2-Dibromination of the Phenylethanes in the Presence of NaBr/NaBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> as the Bromination Reagent**

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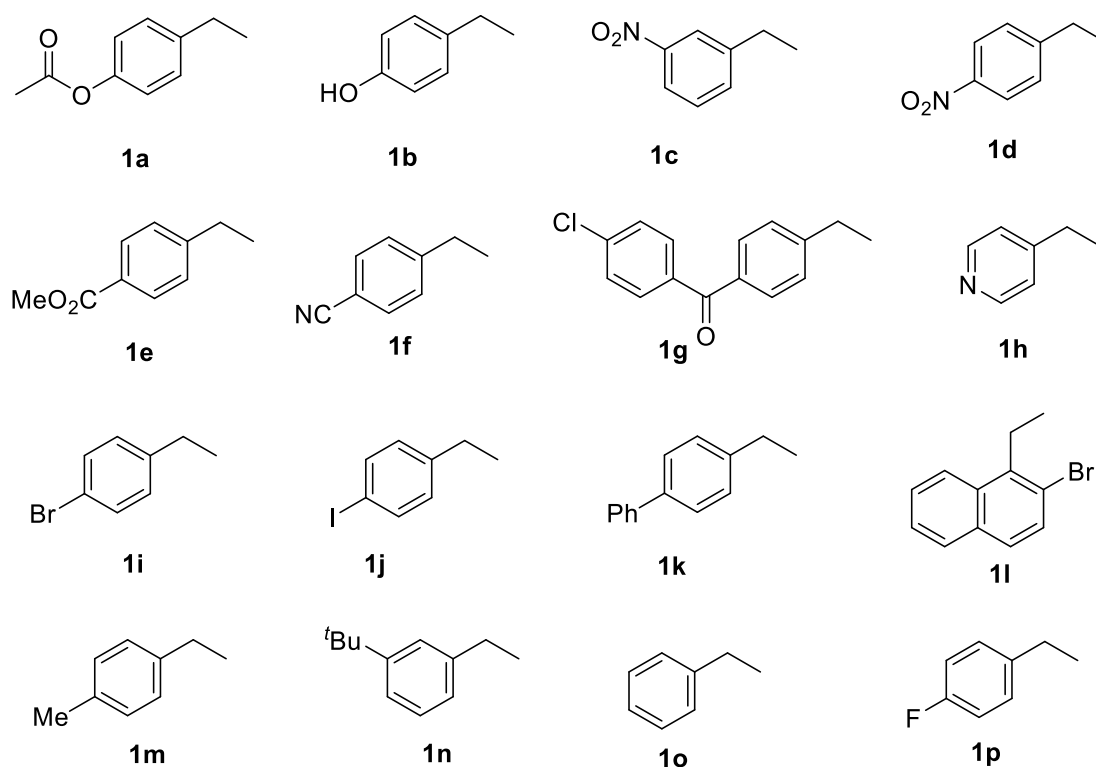
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## I. General remarks

NMR spectra were obtained on Bruker AV-400 MHz and AV-600 MHz spectrometers. The  $^1\text{H}$  NMR chemical shifts were measured relative to  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as the internal reference ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm;  $\text{DMSO-}d_6$ :  $\delta = 2.50$  ppm). The  $^{13}\text{C}$  NMR chemical shifts were given using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as the internal standard ( $\text{CDCl}_3$ :  $\delta = 77.16$  ppm;  $\text{DMSO-}d_6$ :  $\delta = 39.52$  ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). GC-MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC-MS instrument with Agilent J & W GC column DB-5MS-UI. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

Phenylethanes were purchased from Alfa Aesar, J&K Scientific, and Adamas-beta Ltd. The numbers of phenylethanes are shown in Figure S1.

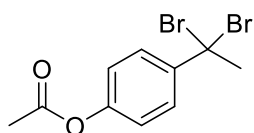


**Figure 1.** The numbers of phenylethanes.

## II. General procedure for 1,1-dibromination of phenylethanes

A 50-mL boiling flask-3-neck with a magnetic stir bar was charged with **1** (3 mmol, 1

equiv), DCE (10 mL), 75% H<sub>2</sub>SO<sub>4</sub> (0.52 mL, 6 mmol, 2.0 eq.), NaBr (772 mg, 7.5 mmol, 2.5 eq.). The reaction mixture was heated to 50 °C, and 0.5 mL of AIBN solution (0.8 M in DCE) was added. By Using the automatic injection pump, NaBrO<sub>3</sub> solution (588 mg of NaBrO<sub>3</sub> in 1 mL of H<sub>2</sub>O, 1.3 eq.) and AIBN solution (1.0 mL, 0.8 M in DCE) were injected simultaneously slowly to the flask at an injection rate of 0.167 mL/h. After the injection is completed, the reaction continued for 14 h. Upon completion, the reaction mixture was cooled to rt and then quenched with 10 mL of saturated aqueous NaHSO<sub>3</sub>. The resulting mixture was extracted with DCE (3x), and the combined organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product.



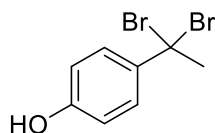
#### 4-(1,1-Dibromoethyl)phenyl acetate (2a)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 (v/v), R<sub>f</sub> = 0.25) afforded the product as colorless oil (792 mg, 82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.01 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 2.56 (s, 3H), 2.33 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 166.1, 142.6, 130.5, 130.1, 129.1, 61.2, 32.4, 14.4 ppm.

HRMS (ESI): calcd for C<sub>10</sub>H<sub>11</sub>Br<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 320.9126 u, found 320.9122 u.



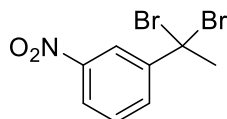
#### 4-(1,1-Dibromoethyl)phenol (2b)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 (v/v), R<sub>f</sub> = 0.35) afforded the product as colorless oil (756 mg, 90%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.90 (d,  $J$  = 9.0 Hz, 2H), 7.14-7.12 (m, 2H), 6.37 (s, 1H), 2.31 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.9, 151.6, 130.2, 121.3, 54.6, 21.3 ppm.

HRMS (ESI): calcd for  $\text{C}_8\text{H}_9\text{Br}_2\text{O}$   $[\text{M}+\text{H}]^+$  278.9020 u, found 278.9012 u.



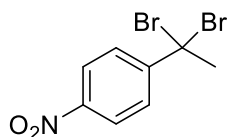
### 1- (1,1-Dibromoethyl) -3-nitrobenzene (2c)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f$  = 0.3) afforded the product as a yellow solid (750 mg, 81%). M.p.: 83-85 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.59-8.58 (m, 1H), 8.19-8.16 (m, 2H), 7.58 (t,  $J$  = 8.4 Hz, 1H), 3.02 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.3, 147.8, 132.9, 129.6, 124.0, 120.6, 58.6, 40.9 ppm.

HRMS (ESI): calcd for  $\text{C}_8\text{H}_8\text{Br}_2\text{NO}$   $[\text{M}+\text{H}]^+$  307.8922 u, found 307.8930 u.



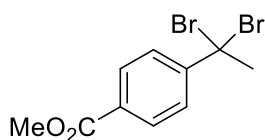
### 1- (1,1-Dibromoethyl) -4-nitrobenzene (2d)<sup>1</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f$  = 0.3) afforded the product as colorless oil (798 mg, 86%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.22-8.20 (m, 2H), 7.96-7.94 (m, 2H), 3.00 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.3, 147.8, 127.4, 123.6, 58.9, 41.0 ppm.

HRMS (ESI): calcd for  $\text{C}_8\text{H}_8\text{Br}_2\text{NO}$   $[\text{M}+\text{H}]^+$  307.8922 u, found 307.8928 u.



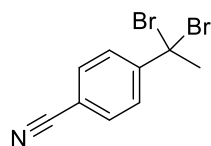
### Methyl 4-(1,1-dibromoethyl)benzoate (2e)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 (v/v),  $R_f = 0.2$ ) afforded the product as colorless oil (822 mg, 85%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 8.02$  (d,  $J = 8.4$  Hz, 2H), 7.84 (d,  $J = 8.4$  Hz, 2H), 3.93 (s, 3H), 2.99 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta = 166.3, 150.5, 130.7, 129.6, 126.3, 60.8, 52.5, 41.0$  ppm.

HRMS (ESI): calcd for  $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  320.9126 u, found 320.9132 u.



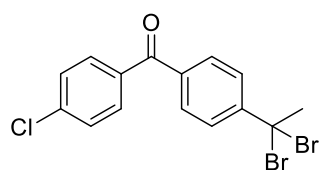
#### 4-(1,1-Dibromoethyl)benzonitrile (2f)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.3$ ) afforded the product as colorless oil (708 mg, 82%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.89$ -7.87 (m, 2H), 7.67-7.65 (m, 2H), 2.97 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 150.6, 132.2, 127.0, 118.1, 113.0, 59.4, 40.8$  ppm.

HRMS (ESI): calcd for  $\text{C}_9\text{H}_7\text{Br}_2\text{NNa}$   $[\text{M}+\text{Na}]^+$  309.8843 u, found 309.8851 u.



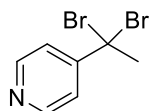
#### (4-Chlorophenyl)(4-(1,1-dibromoethyl)phenyl)methanone (2g)

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 (v/v),  $R_f = 0.3$ ) afforded the product as a white solid (1.06 g, 88%). M.p.: 124-127 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.90$ -7.88 (m, 2H), 7.78-7.75 (m, 4H), 7.49-7.47 (m, 2H), 3.02 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 194.5, 150.2, 139.4, 137.7, 135.5, 131.6, 129.9, 128.9, 126.3, 60.6, 41.0$  ppm.

HRMS (ESI): calcd for  $C_{15}H_{11}Br_2ClNaO$  ( $M+Na$ )<sup>+</sup> 422.8763 u, found 422.8757 u.



#### 4-(1,1-Dibromoethyl)pyridine (2h)<sup>2</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.5$ ) afforded the product as colorless oil (588 mg, 74%).

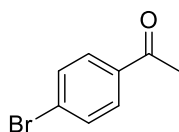
<sup>1</sup>H NMR (600 MHz,  $CDCl_3$ ):  $\delta = 8.64$ - $8.63$  (m, 2H),  $7.63$ - $7.62$  (m, 2H),  $2.92$  (s, 3H) ppm.

<sup>13</sup>C NMR (151 MHz,  $CDCl_3$ ):  $\delta = 154.1$ ,  $150.3$ ,  $120.4$ ,  $58.9$ ,  $41.6$  ppm.

HRMS (ESI): calcd for  $C_7H_8Br_2N$  ( $M+H$ )<sup>+</sup> 263.9023 u, found 263.9018 u.

### III. General procedure for direct synthesis of ketones from phenylethanes

A 50-mL boiling flask-3-neck with a magnetic stir bar was charged with **1** (3 mmol, 1 equiv), DCE (10 mL), 75%  $H_2SO_4$  (0.52 mL, 6 mmol, 2.0 eq.), NaBr (772 mg, 7.5 mmol, 2.5 eq.). The reaction mixture was heated to 50 °C, and 0.5 mL of AIBN solution (0.8 M in DCE) was added. By Using the automatic injection pump,  $NaBrO_3$  solution (588 mg of  $NaBrO_3$  in 1 mL of  $H_2O$ , 1.3 eq.) and AIBN solution (1.0 mL, 0.8 M in DCE) were injected simultaneously slowly to the flask at an injection rate of 0.167 mL/h. After the injection is completed, the reaction continued for 14 h. Upon completion, the reaction mixture was cooled to rt and then quenched with 10 mL of saturated aqueous  $NaHSO_3$ . The resulting mixture was extracted with DCE (3x), and the combined organic phase was dried with  $Na_2SO_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product.



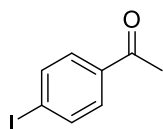
#### 1-(4-Bromophenyl)ethan-1-one (3a)<sup>3</sup>

Following the general procedure, purification via column chromatography on silica

gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.3$ ) afforded the product as a white solid (510 mg, 85%). M.p.: 51-53 °C (lit.: 50-51 °C).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.84\text{-}7.80$  (m, 2H), 7.62-7.59 (m, 2H), 2.59 (s, 3H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.2, 136.0, 132.0, 130.0, 128.5, 26.7$  ppm.



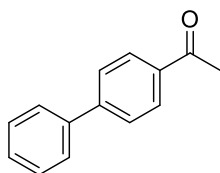
### 1-(4-Iodophenyl)ethan-1-one (3b)<sup>3</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.3$ ) afforded the product as a white solid (642 mg, 87%). M.p.: 85-87 °C (lit.: 86 °C).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.85\text{-}7.82$  (m, 2H), 7.68-7.65 (m, 2H), 2.58 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.5, 138.1, 136.5, 129.9, 101.2, 26.6$  ppm.

HRMS (ESI): calcd for  $\text{C}_8\text{H}_8\text{IO}$   $[\text{M}+\text{H}]^+$  246.9620 u, found 246.9610 u.



### 1-([1,1'-Biphenyl]-4-yl)ethan-1-one (3c)<sup>4</sup>

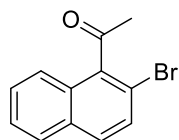
Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.25$ ) afforded the product as a white solid (492 mg, 84%). M.p.: 120-122 °C (lit.: 119-120 °C).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.05\text{-}8.03$  (m, 2H), 7.70-7.68 (m, 2H), 7.65-7.62 (m, 2H), 7.50-7.46 (m, 2H), 7.41-7.39 (m, 1H), 2.64 (s, 3H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.9, 145.9, 140.0, 136.0, 129.1, 129.0, 128.4, 127.4, 127.3, 26.8$  ppm.

HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{13}\text{O}$   $[\text{M}+\text{H}]^+$  197.0966 u, found 197.0960 u.





### 1-(2-Bromonaphthalen-1-yl)ethan-1-one (3d)<sup>5</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1 (v/v),  $R_f = 0.35$ ) afforded the product as a white solid (618 mg, 83%). M.p.: 63-65 °C (lit.: 59-61 °C).

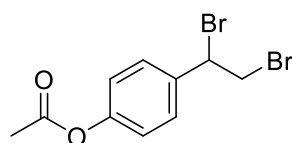
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.74$ -8.69 (m, 1H), 8.35-8.31 (m, 1H), 7.83 (d,  $J = 7.6$  Hz, 1H), 7.74 (d,  $J = 7.6$  Hz, 1H), 7.67-7.63 (m, 2H), 2.73 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 201.4, 135.6, 132.5, 131.4, 128.9, 128.8, 128.5, 128.4, 128.0, 127.7, 126.6, 30.3$  ppm.

HRMS (ESI): calcd for C<sub>12</sub>H<sub>10</sub>BrO [M+H]<sup>+</sup> 248.9915 u, found 248.9909 u.

### IV. General procedure for 1,2-dibromination of phenylethanes

A 50-mL boiling flask-3-neck with a magnetic stir bar was charged with **1** (3 mmol, 1 equiv), DCE (10 mL), 75% H<sub>2</sub>SO<sub>4</sub> (0.27 mL, 3 mmol, 1 eq.), NaBr (850 mg, 8.22 mmol, 2.74 eq.). The reaction mixture was heated to 105 °C, and 0.5 mL of AIBN solution (0.8 M in DCE) was added. By Using the automatic injection pump, NaBrO<sub>3</sub> solution (308 mg of NaBrO<sub>3</sub> in 1 mL of H<sub>2</sub>O, 0.68 eq.) and AIBN solution (1.0 mL, 0.8 M in DCE) were injected simultaneously slowly to the flask at an injection rate of 0.167 mL/h. After the injection is completed, the reaction continued for 14 h. Upon completion, the reaction mixture was cooled to rt and then quenched with 10 mL of saturated aqueous NaHSO<sub>3</sub>. The resulting mixture was extracted with DCE (3x), and the combined organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product.



### 4-(1,2-Dibromoethyl)phenyl acetate (4f)<sup>6</sup>

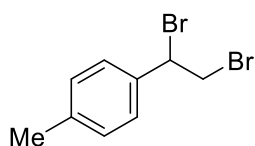
Following the general procedure, purification via column chromatography on silica

gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.25$ ) afforded the product as colorless oil (600 mg, 62%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.42\text{-}7.41$  (m, 2H), 7.13-7.11 (m, 2H), 5.14 (dd,  $J = 10.8, 5.4$  Hz, 1H), 4.08-4.05 (m, 1H), 3.98 (t,  $J = 10.2$  Hz, 1H), 2.31 (s, 3H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta = 169.2, 151.1, 136.2, 129.0, 122.0, 50.2, 35.1, 21.3$  ppm.

HRMS (ESI): calcd for  $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  320.9126 u, found 320.9122 u.



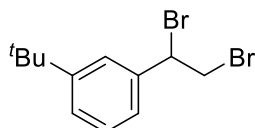
#### 1-(1,2-Dibromoethyl)-4-methylbenzene (4d)<sup>7</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.42$ ) afforded the product as colorless oil (540 mg, 65%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31\text{-}7.29$  (m, 2H), 7.20 (d,  $J = 7.6$  Hz, 2H), 5.15 (dd,  $J = 10.4, 5.6$  Hz, 1H), 4.10-4.00 (m, 2H), 2.37 (s, 3H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 139.4, 135.8, 129.7, 127.7, 51.2, 35.2, 21.4$  ppm.

GC-MS (EI): calcd for  $\text{C}_9\text{H}_{10}\text{Br}_2$  278.0 u, found 278.1 u.



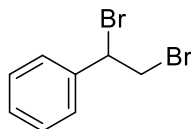
#### 1-(tert-Butyl)-3-(1,2-dibromoethyl)benzene (4e)<sup>8</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.45$ ) afforded the product as colorless oil (643 mg, 67%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.40\text{-}7.38$  (m, 2H), 7.33-7.31 (m, 1H), 7.26-7.23 (m, 1H), 5.17 (dd,  $J = 10.0, 5.6$  Hz, 1H), 4.11-4.01 (m, 2H), 1.351-1.345 (m, 9H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 151.9, 138.3, 128.7, 126.4, 125.0, 124.7, 51.9, 35.5, 34.9, 31.4$  ppm.

GC-MS (EI): calcd for  $\text{C}_{12}\text{H}_{16}\text{Br}_2$  320.1 u, found 320.0 u.



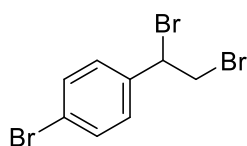
### **(1,2-Dibromoethyl)benzene (4c)**<sup>9</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.42$ ) afforded the product as colorless oil (515 mg, 65%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.42\text{-}7.34$  (m, 5H), 5.17-5.13 (m, 1H), 4.11-4.01 (m, 2H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 138.7, 129.3, 129.0, 127.8, 60.0, 35.2$  ppm.

GC-MS (EI): calcd for  $\text{C}_8\text{H}_8\text{Br}_2$  264.0 u, found 264.1 u.



### **1-Bromo-4-(1,2-dibromoethyl)benzene (4a)**<sup>9</sup>

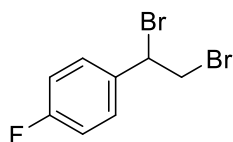
Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.5$ ) afforded the product as a white solid (636 mg, 62%).

M.p.: 60-62 °C (lit.: 60-61 °C).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.54\text{-}7.50$  (m, 2H), 7.30-7.26 (m, 2H), 5.09 (dd,  $J = 11.2, 5.2$  Hz, 1H), 4.08-4.04 (m, 1H), 3.97 (t,  $J = 10.8$  Hz, 1H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 137.8, 132.2, 129.5, 123.3, 49.7, 34.7$  ppm.

GC-MS (EI): calcd for  $\text{C}_8\text{H}_7\text{Br}_3$  342.9 u, found 342.9 u.



### **1-(1,2-Dibromoethyl)-4-fluorobenzene (4b)**<sup>9</sup>

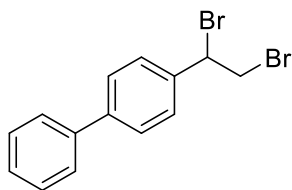
Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.5$ ) afforded the product as colorless oil (468 mg, 55%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.40\text{-}7.38$  (m, 2H), 7.07 (t,  $J = 8.4$  Hz, 2H), 5.13 (dd,  $J = 10.8, 4.8$  Hz, 1H), 4.08 (dd,  $J = 10.2, 4.8$  Hz, 1H), 3.98 (t,  $J = 10.8$  Hz, 1H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.0 (d,  $J_{\text{C-F}} = 249.15$  Hz), 134.7, 129.7 (d,  $J_{\text{C-F}} = 45.6$  Hz), 116.0 (d,  $J_{\text{C-F}} = 21.9$  Hz), 49.9, 35.1 ppm.

$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta -111.7$  ppm.

GC-MS (EI): calcd for  $\text{C}_8\text{H}_7\text{Br}_2\text{F}$  282.0 u, found 282.0 u.



#### 4-(1,2-Dibromoethyl)-1,1'-biphenyl (**4g**)<sup>10</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether,  $R_f = 0.45$ ) afforded the product as colorless oil (612 mg, 60%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.62$ -7.59 (m, 4H), 7.49-7.44 (m, 4H), 7.37 (t,  $J = 7.2$  Hz, 1H), 5.23 (dd,  $J = 10.4, 5.6$  Hz, 1H), 4.14-4.05 (m, 2H) ppm.

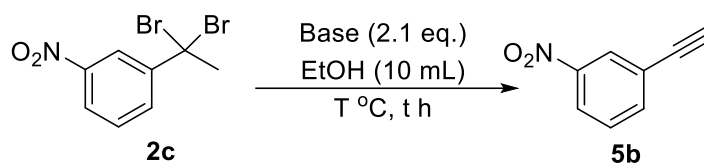
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 142.2, 140.4, 137.6, 129.0, 128.2, 127.8, 127.7, 127.2, 50.8, 35.0$  ppm.

GC-MS (EI): calcd for C<sub>14</sub>H<sub>12</sub>Br<sub>2</sub> 340.1 u, found 340.1 u.

#### V. Optimization of elimination of **2c** for the synthesis of phenylacetylenes

A 50-mL boiling flask-2-neck with a magnetic stir bar was charged with base (10.5 mmol, 2.1 equiv) and EtOH (10 mL). 1-(1,1-Dibromoethyl)-3-nitrobenzene **2c** (5 mmol, 1 equiv) was added and the resulting mixture was stirred at T °C for t hours. Upon completion, the mixture was filtered through a celite pad and washed with 5-10 mL of DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give 1-ethynyl-3-nitrobenzene **5b**.

**Table S1.** Optimization of the elimination of **2c**<sup>a</sup>



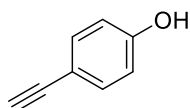
Entry	Base	T (°C)	t (h)	Yield (%) <sup>b</sup>
1	Na <sub>2</sub> CO <sub>3</sub>	reflux	10	64
2	K <sub>2</sub> CO <sub>3</sub>	reflux	10	88
3	NaOH	reflux	10	95
4	KOH	reflux	10	94
5	NaO <sup>t</sup> Bu	reflux	10	92
6	KO <sup>t</sup> Bu	reflux	10	95
7	NaOH	10	10	72
8	NaOH	20	10	88

9	NaOH	30	10	95
10	NaOH	40	10	94
11	NaOH	60	10	95
12	NaOH	30	4	94
13	NaOH	30	2	94
14	NaOH	30	1	91

<sup>a</sup> Reaction conditions: **2c** (3 mmol), base (2.1 eq.) in EtOH (10 mL) at T °C for t h. <sup>b</sup> Isolated yields.

## VI. General procedure for the synthesis of phenylacetylenes from **2**

A 50-mL boiling flask-2-neck with a magnetic stir bar was charged with NaOH (6.3 mmol, 2.1 equiv) and EtOH (10 mL). 1,1-Dibromoethyl arene **2** (3 mmol, 1 equiv) was added and the resulting mixture was stirred at 30 °C for 2 hours. Upon completion, the mixture was filtered through a celite pad and washed with 5-10 mL of DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give the alkyne **5**.

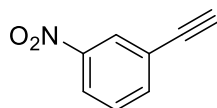


### 4-Ethynylphenol (**5a**)<sup>11</sup>

When **2a** was used as starting material, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 (v/v),  $R_f = 0.3$ ) afforded **5a** in 93% yield (330 mg). When **2b** was used as starting material, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 (v/v),  $R_f = 0.3$ ) afforded **5a** in 92% yield (324 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.90$  (s, 1H), 7.29 (d,  $J = 8.8$  Hz, 2H), 6.76-6.74 (m, 2H), 3.92 (s, 1H) ppm.

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta = 158.1, 133.3, 115.7, 112.0, 84.0, 78.4$  ppm.



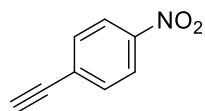
### 1-Ethynyl-3-nitrobenzene (**5b**)<sup>12</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f = 0.3$ ) afforded **5b** as yellow oil

(414 mg, 91%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.29-8.27 (m, 1H), 8.19-8.16 (m, 1H), 7.77 (d,  $J$  = 7.7 Hz, 1H), 7.52-7.49 (m, 1H), 3.22 (s, 1H). ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.1, 129.5, 127.0, 124.6, 123.6, 81.0, 79.8 ppm.

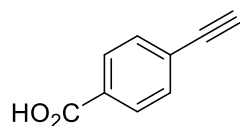


#### 1-Ethynyl-4-nitrobenzene (**5c**)<sup>12</sup>

Following the general procedure, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f$  = 0.3) afforded **5c** as yellow oil (396 mg, 90%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.20-8.18 (m, 2H), 7.64-7.62 (m, 2H), 3.36 (s, 1H) ppm.

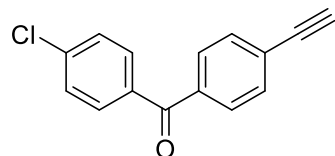
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.7, 133.1, 129.0, 123.7, 82.5, 81.7 ppm.



#### 4-Ethynylbenzoic acid (**5d**)<sup>13</sup>

When **2e** was used as starting material, purification via column chromatography on silica gel (petroleum ether/ethyl acetate/AcOH = 300/100/1 (v/v/v),  $R_f$  = 0.3) afforded **5d** in 85% yield (372 mg). When **2f** was used as starting material, **5d** was obtained in 90% yield (395 mg). M.p.: 225 °C (decomp) (lit.: 224 °C decomp).

$^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 13.16 (s, 1H), 7.93 (d,  $J$  = 8.3 Hz, 2H), 7.59 (d,  $J$  = 8.3 Hz, 2H), 4.44 (s, 1H) ppm.



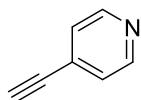
#### (4-Chlorophenyl)(4-ethynylphenyl)methanone (**5e**)<sup>14</sup>

KO<sup>t</sup>Bu (2.1 eq.) and HO<sup>t</sup>Bu (10 mL) were used, purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 (v/v),  $R_f$  = 0.4) afforded **5e** in 95% yield (684 mg).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.73 (d,  $J$  = 8.3 Hz, 4H), 7.60 (d,  $J$  = 8.2 Hz, 2H), 7.47 (d,  $J$  = 8.4 Hz, 2H), 3.26 (s, 1H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 194.5, 139.1, 136.9, 135.4, 132.0, 131.3, 129.7, 128.7, 126.4, 82.6, 80.3 ppm.

HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_9\text{ClNaO}$  ( $\text{M}+\text{Na}$ ) $^+$  263.0228 u, found 265.0234 u.



#### 4-Ethynylpyridine (5f)

KO $^t$ Bu (2.1 eq.) and HO $^t$ Bu (10 mL) were used, purification via column chromatography on silica gel (petroleum ether,  $R_f$  = 0.32) afforded **5b** as colorless oil (270 mg, 87%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.60-8.59 (m, 2H), 7.35-7.34 (m, 2H), 3.29 (s, 1H) ppm.

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.0, 130.5, 126.2, 82.0, 81.1 ppm.

HRMS (ESI) calcd for  $\text{C}_7\text{H}_6\text{N}$  ( $\text{M}+\text{H}$ ) $^+$  104.0510 u, found 104.0595 u.

### VII. General procedure for the synthesis of phenylacetylenes from **4**

A 50-mL boiling flask-2-neck with a magnetic stir bar was charged with NaOH (10.5 mmol, 2.1 equiv) and EtOH (10 mL). 1,2-Dibromoethyl arene **4** (5 mmol, 1 equiv) was added and the resulting mixture was stirred at 30 °C for 2 hours. Upon completion, the mixture was filtered through a celite pad and washed with 5-10 mL of DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give the alkyne **5**.

### VIII. References

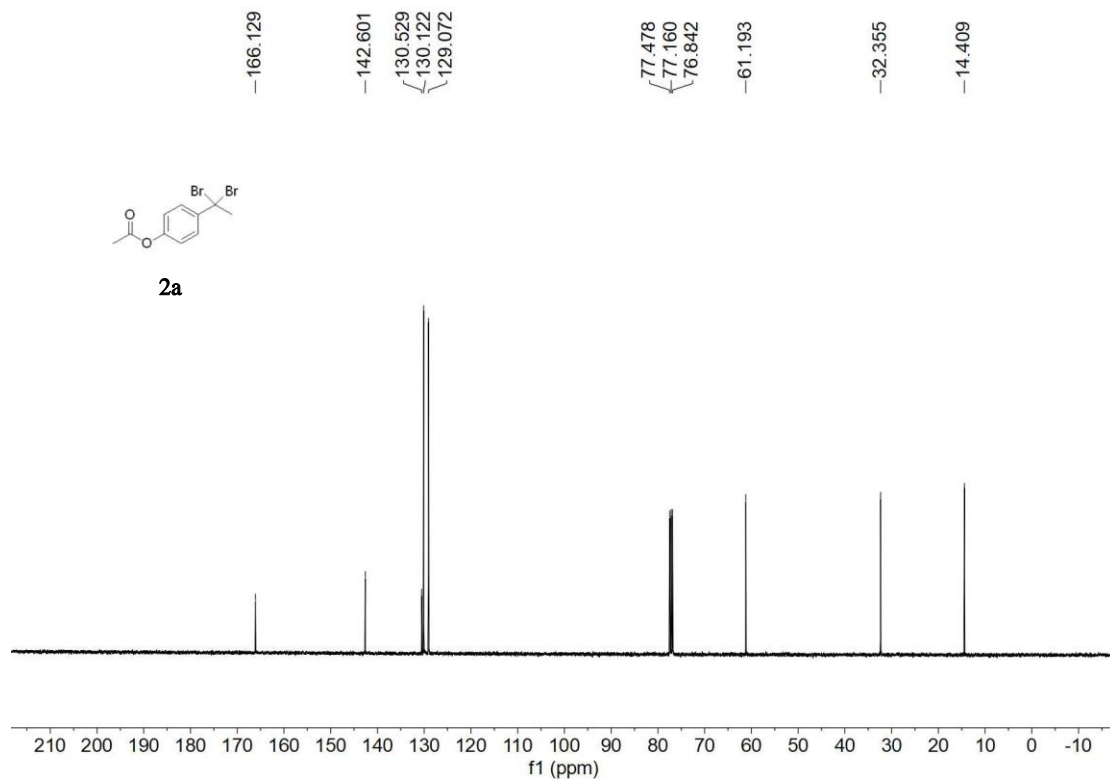
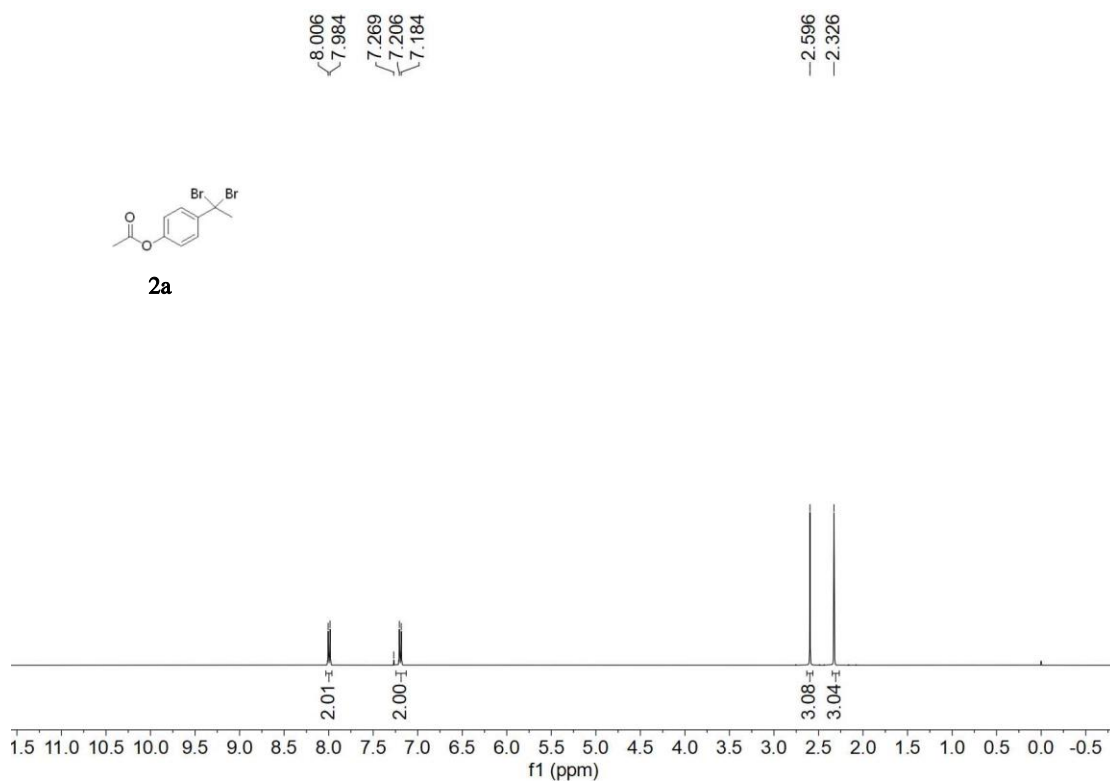
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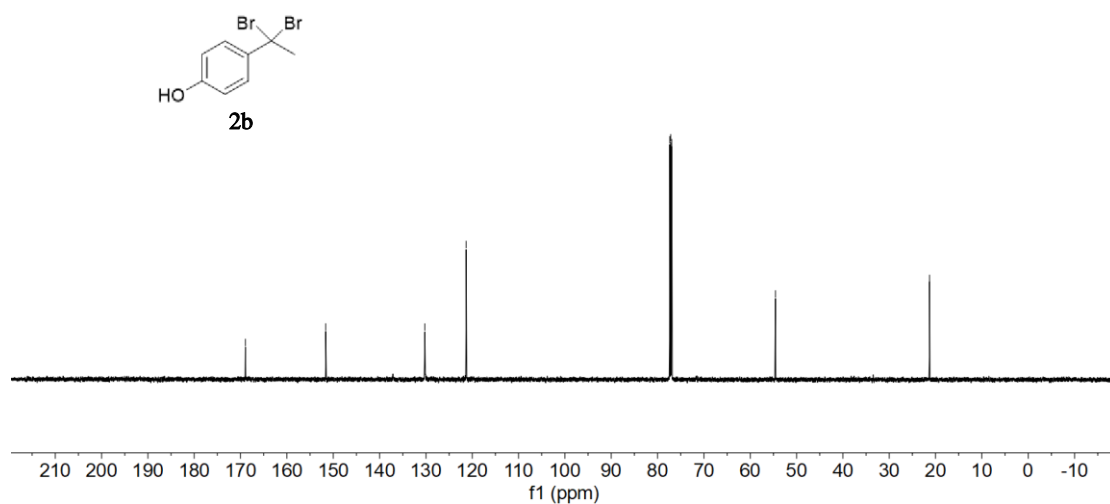
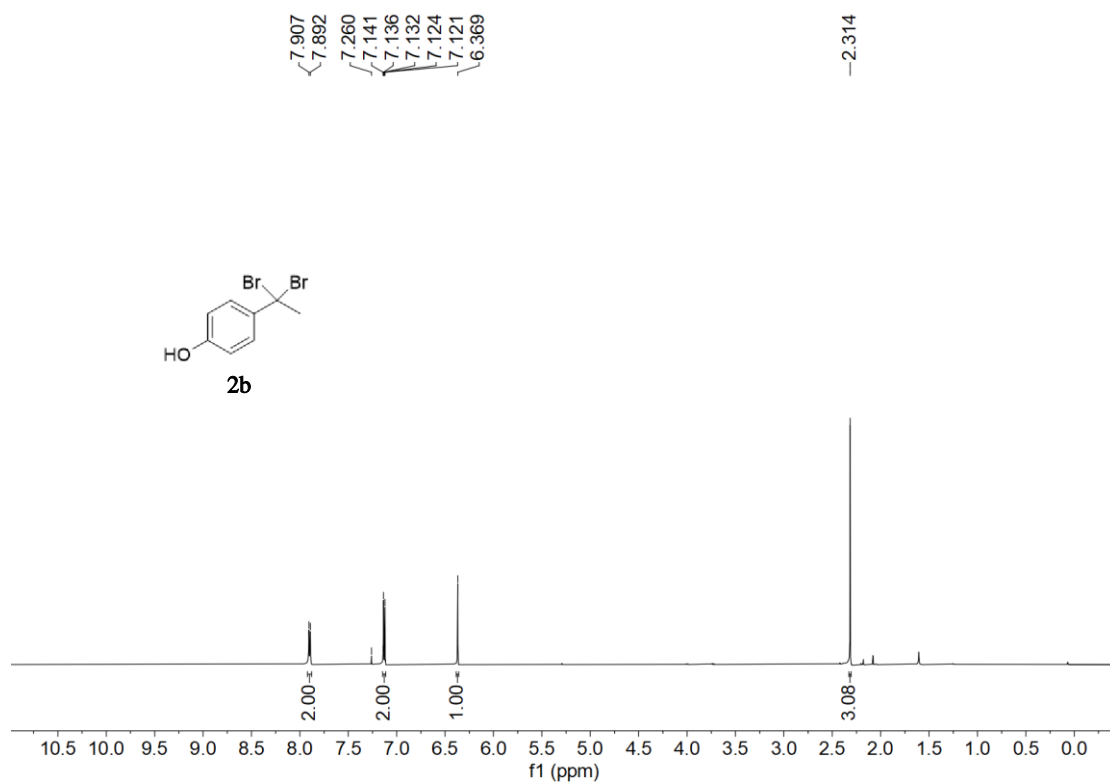
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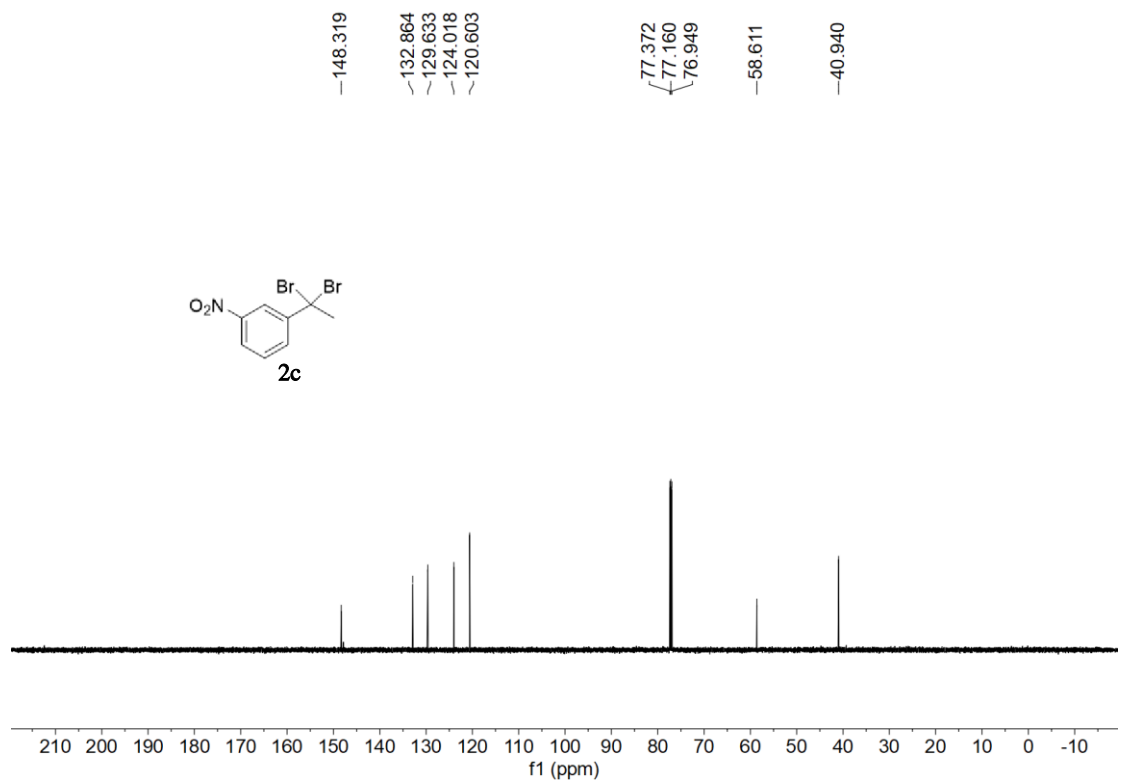
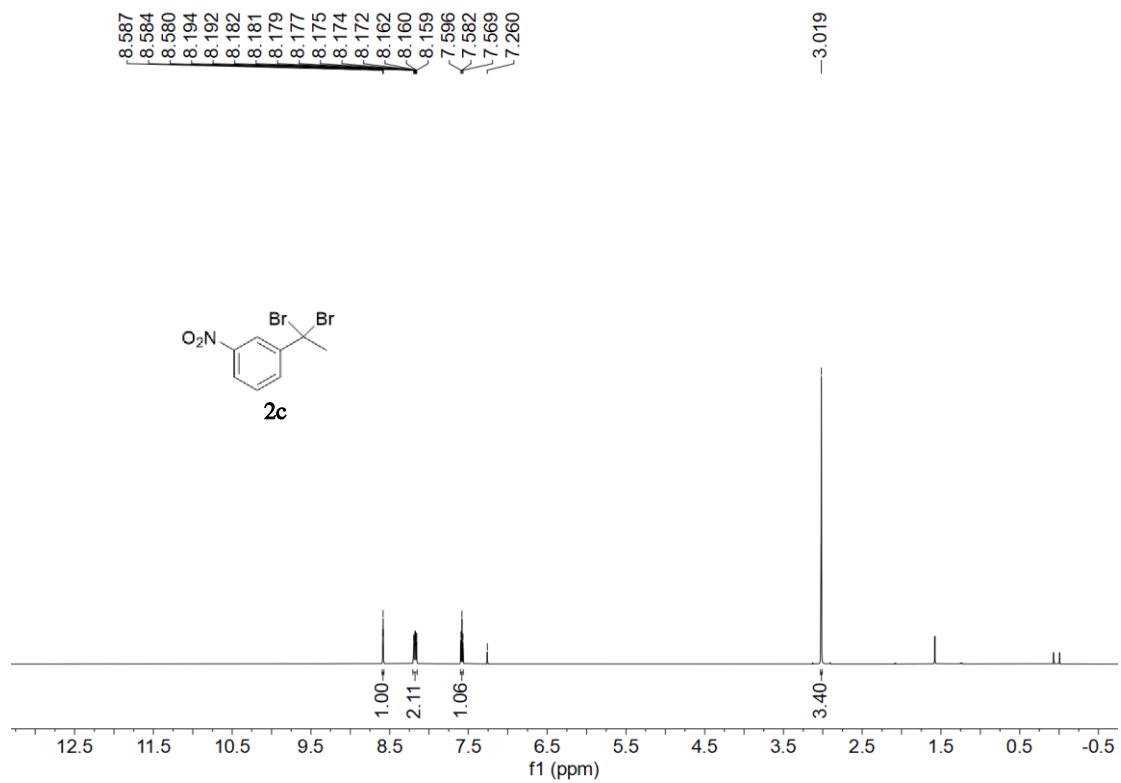
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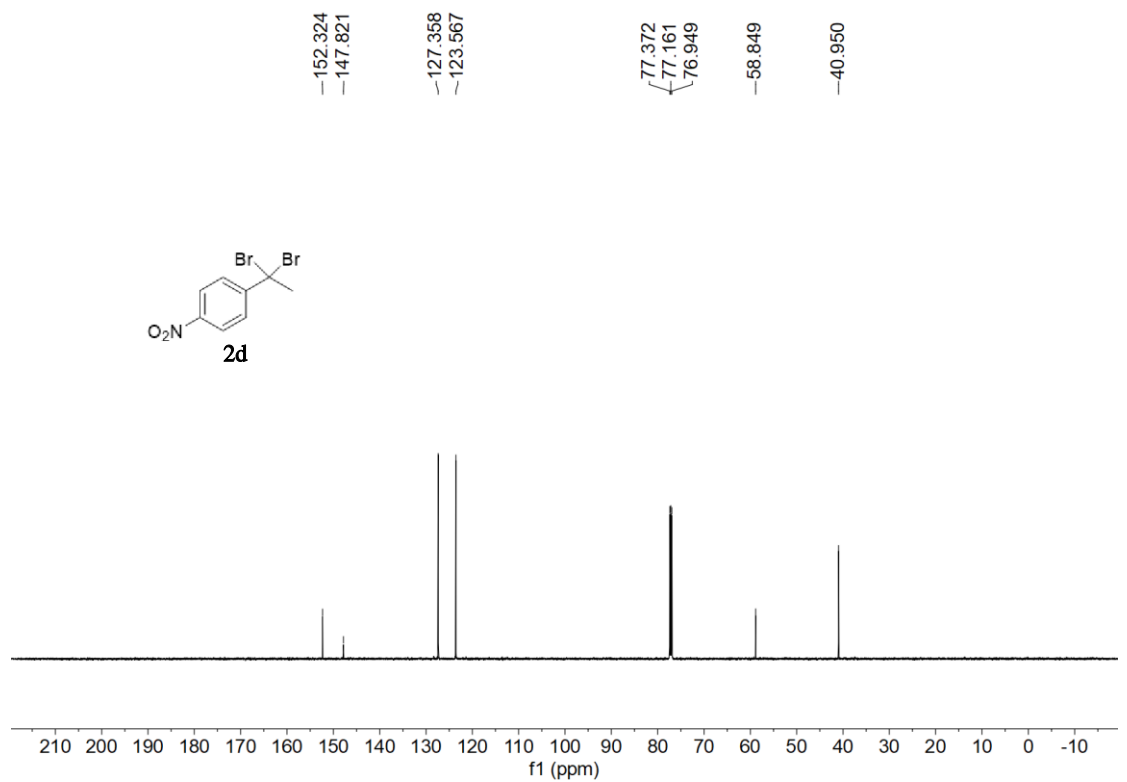
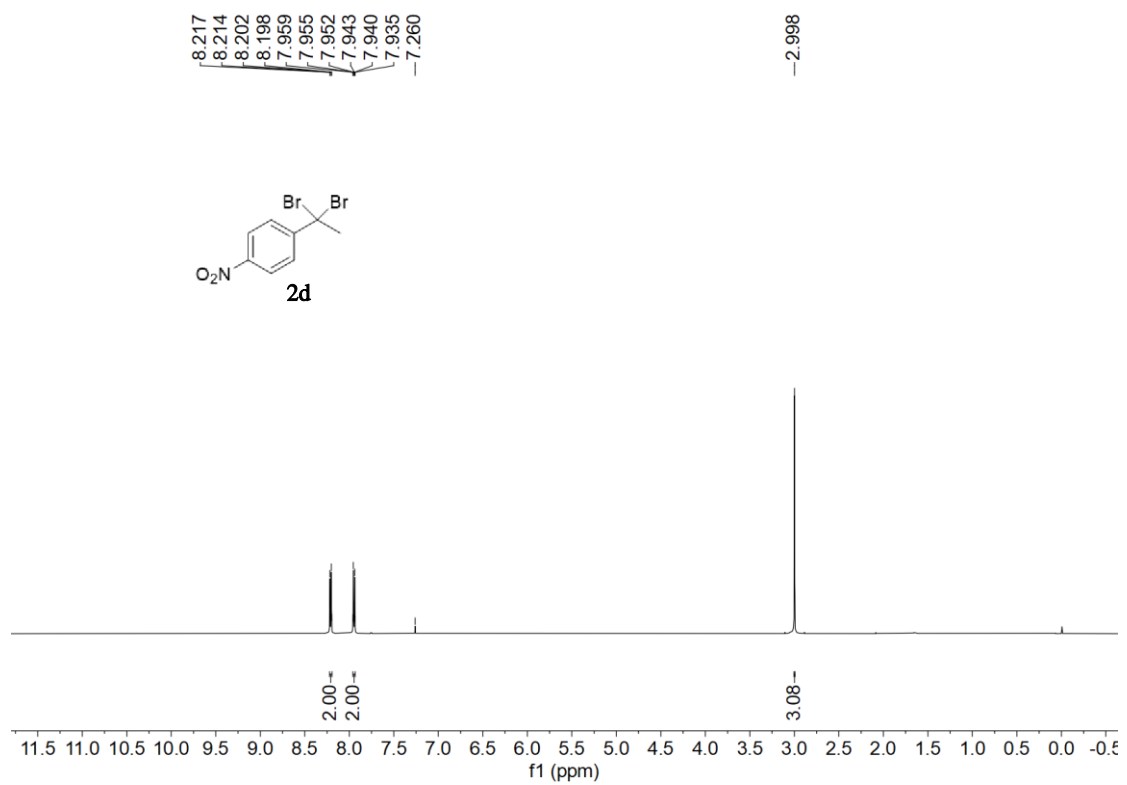


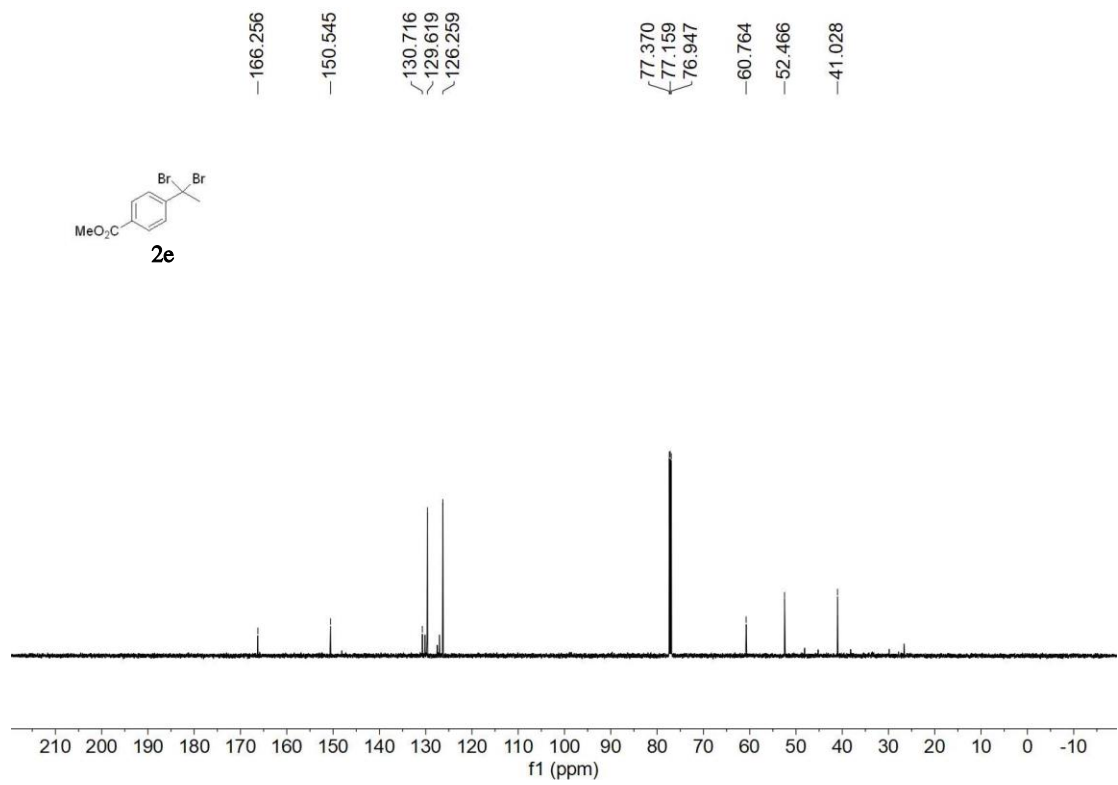
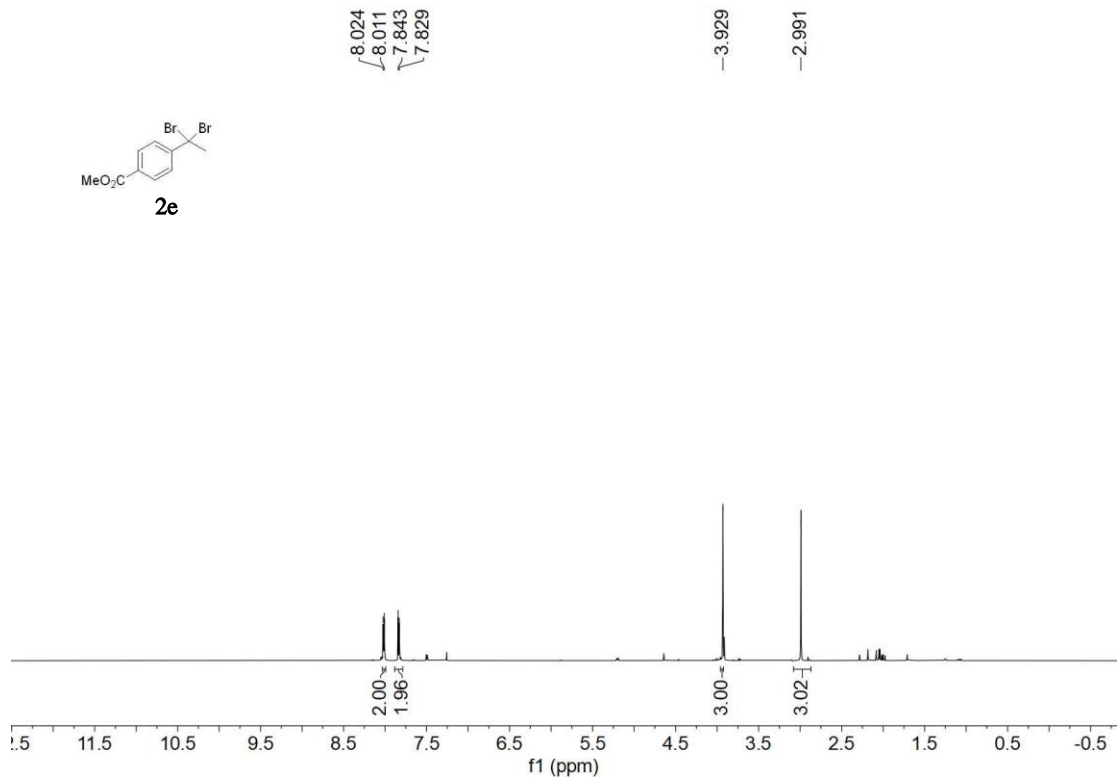
# IX. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

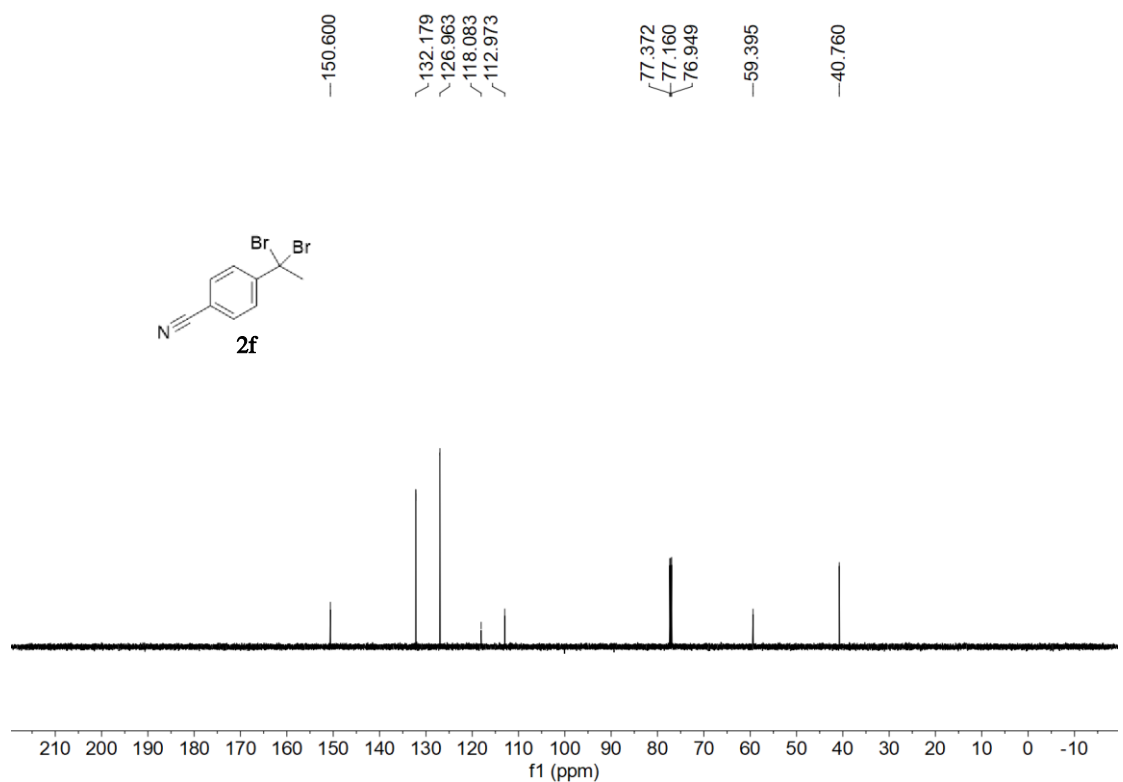
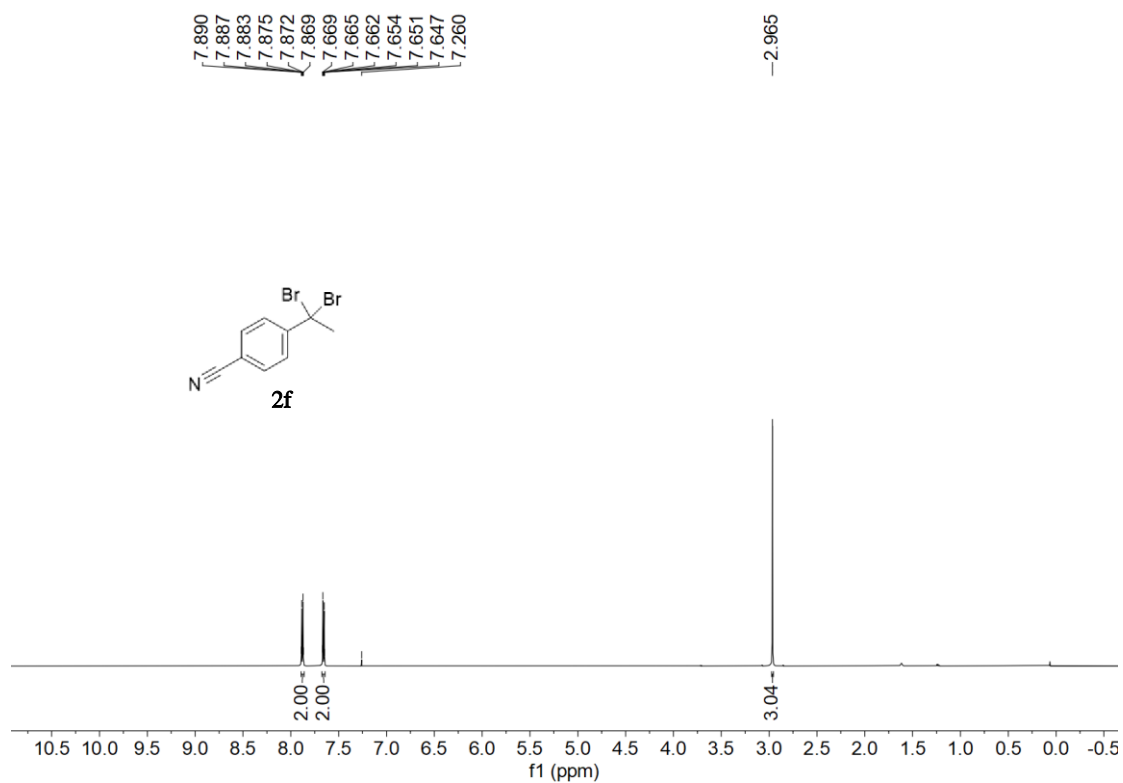


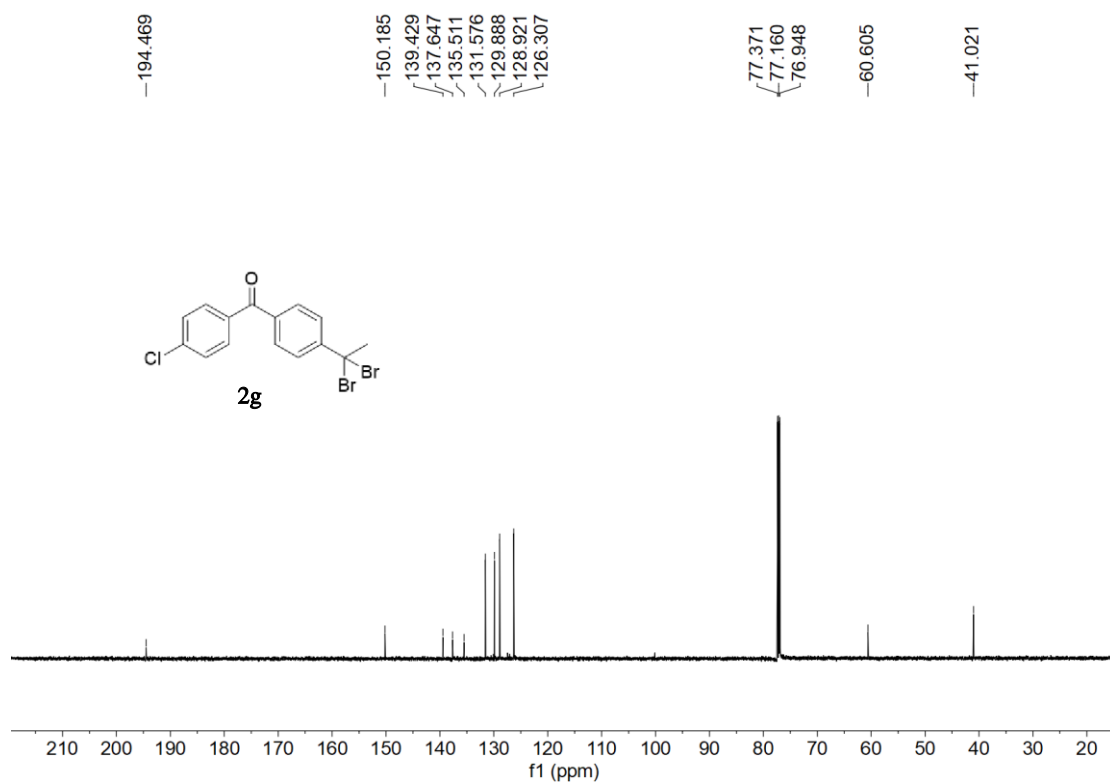
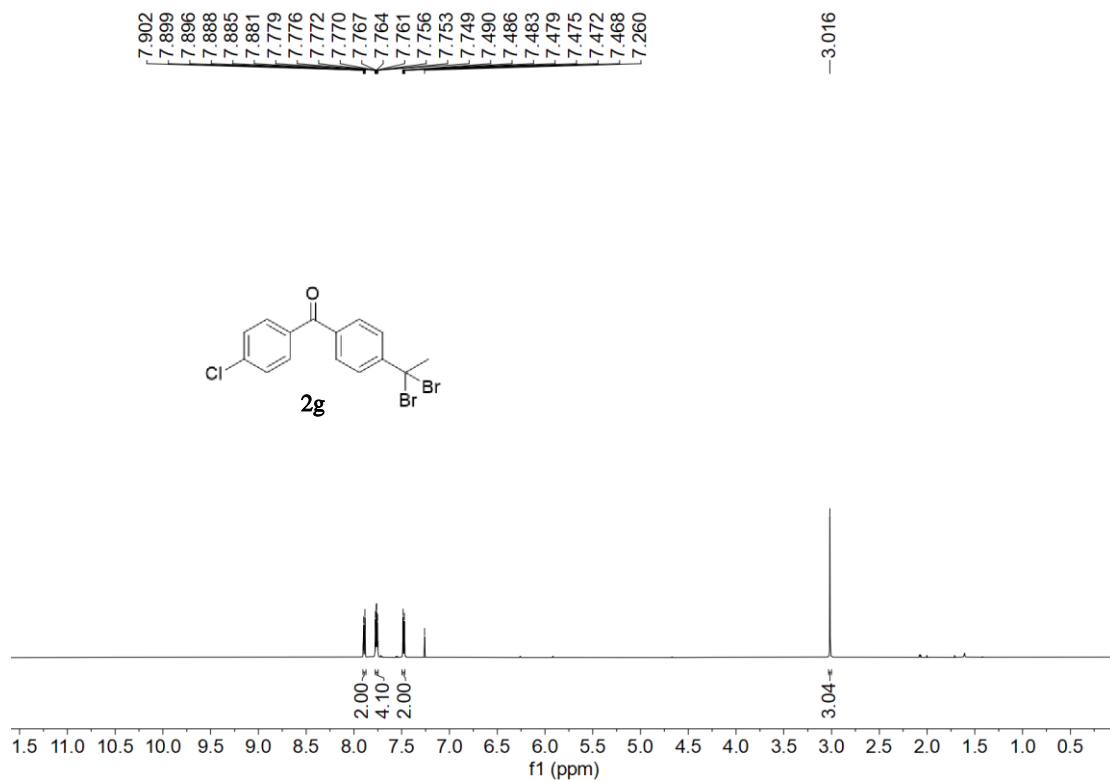


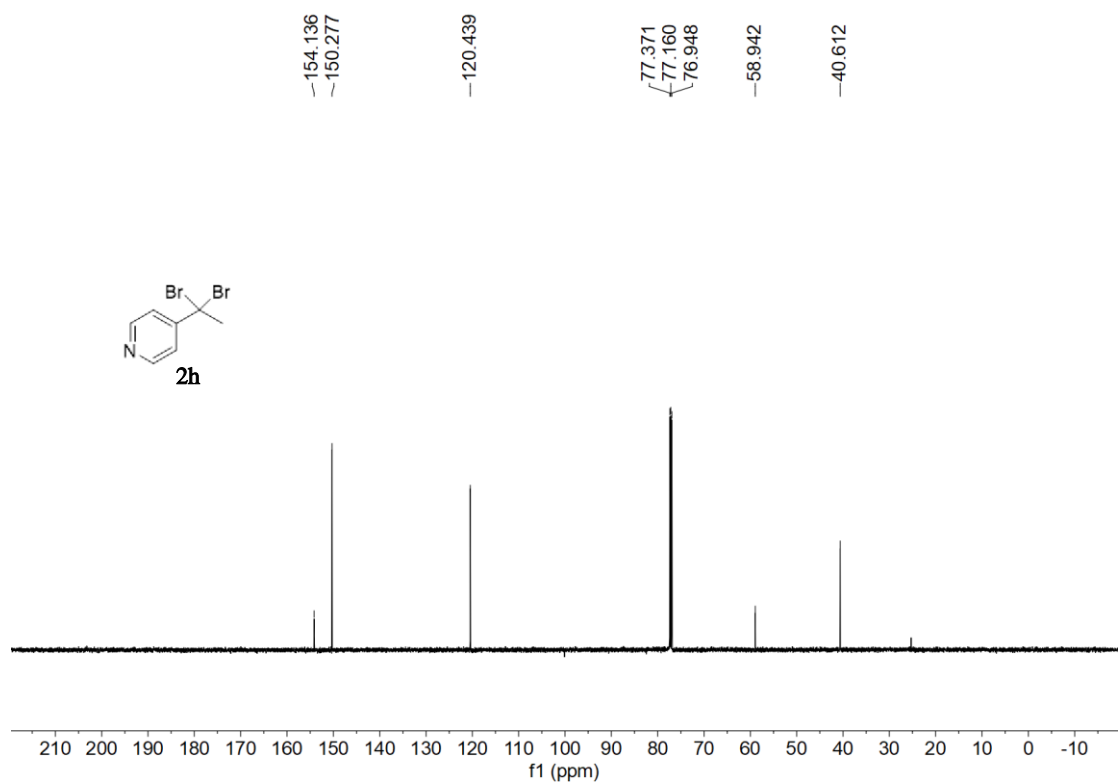
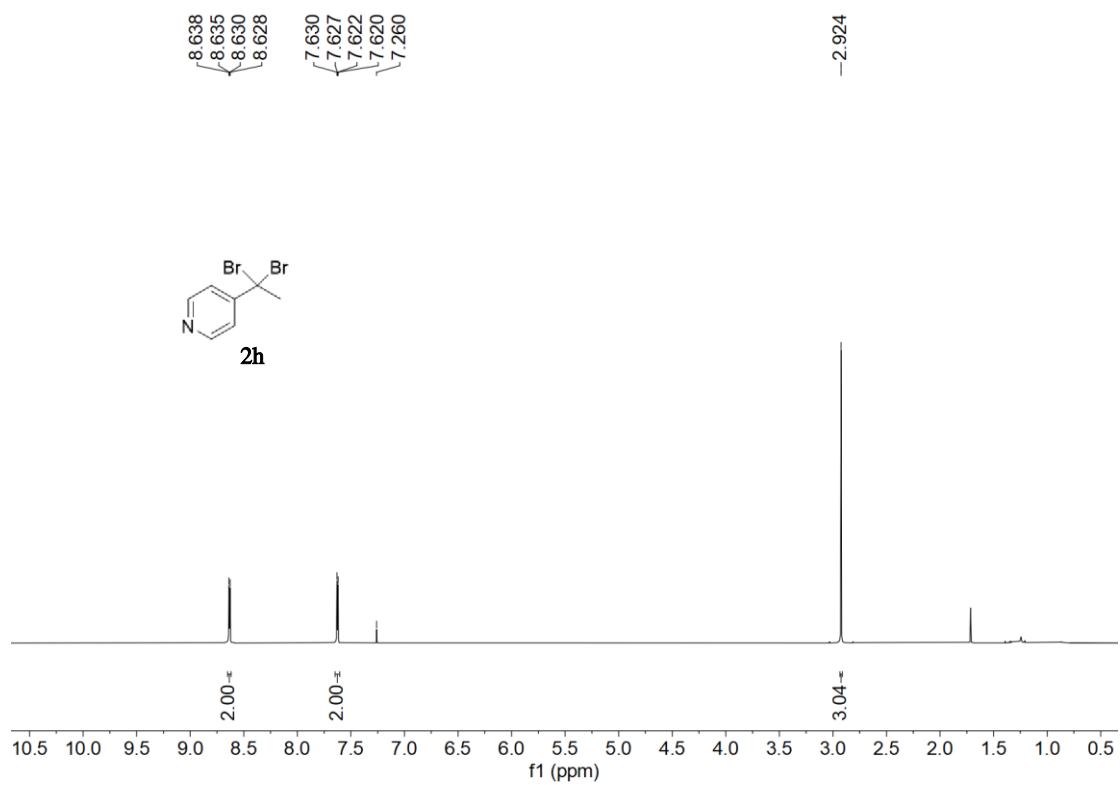




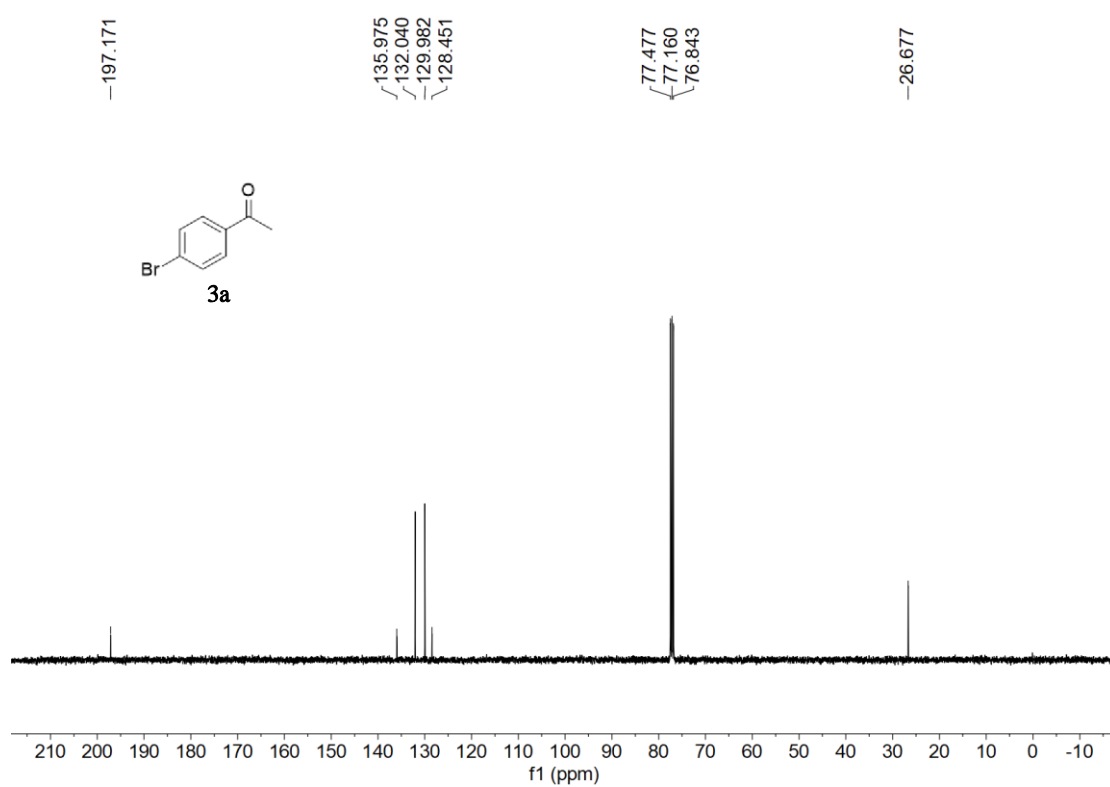
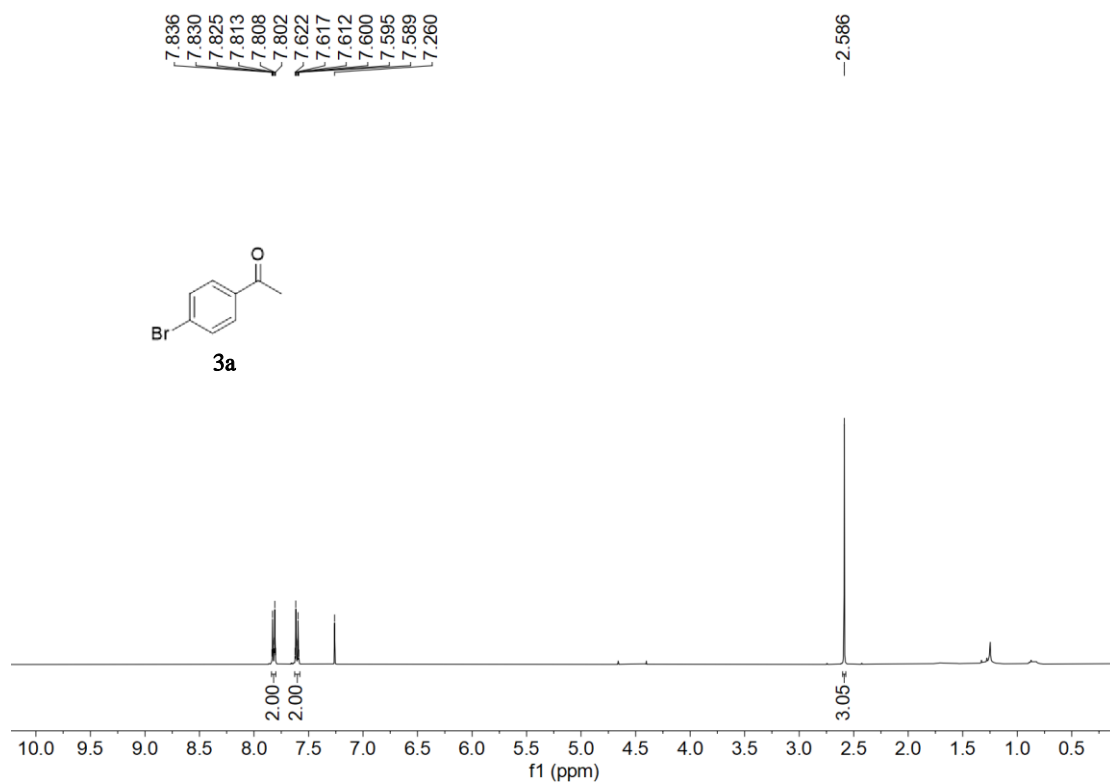


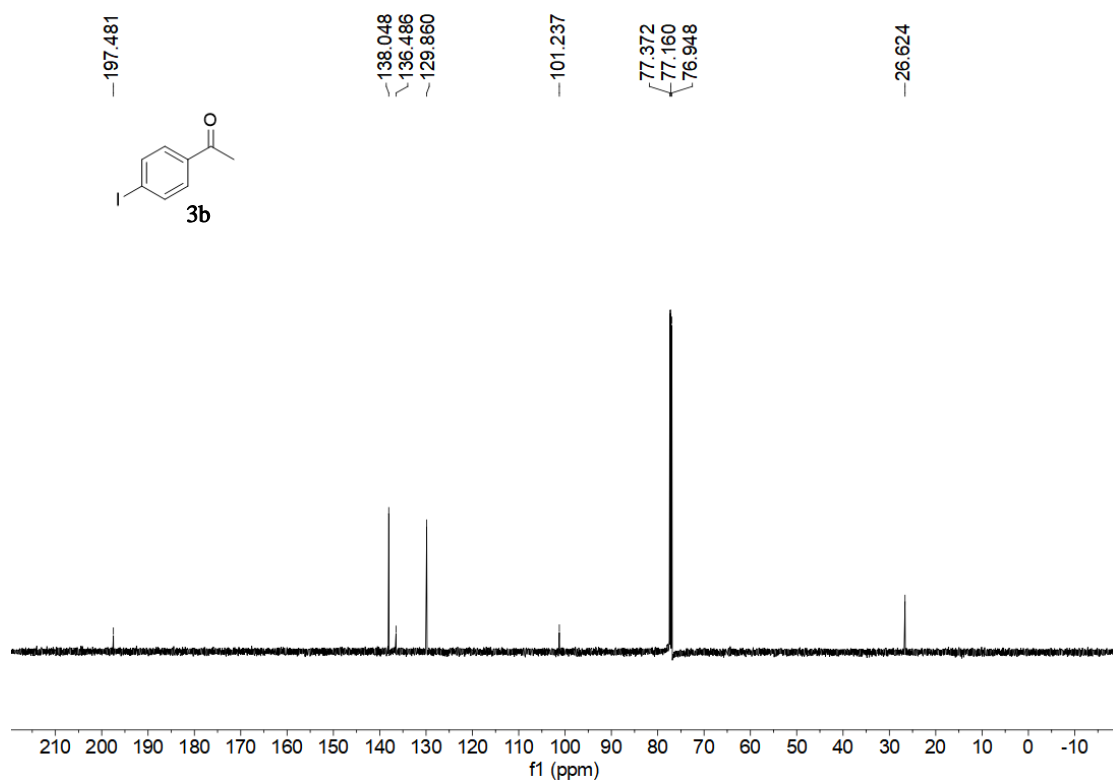
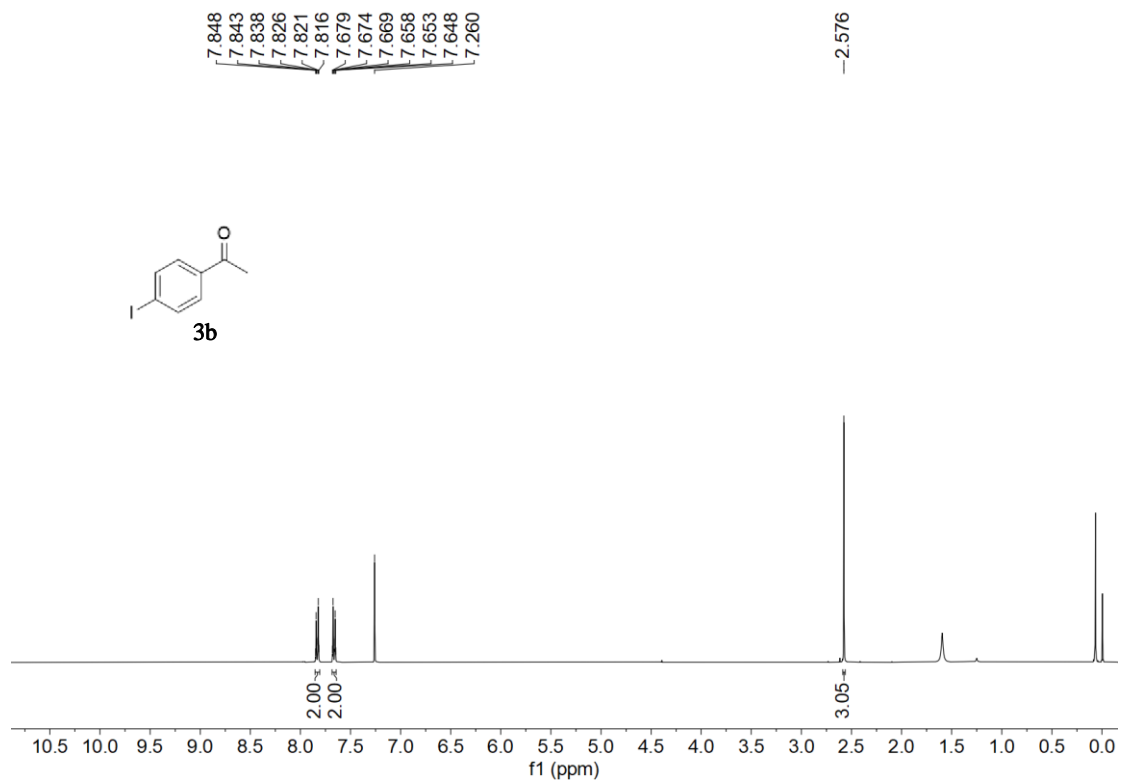


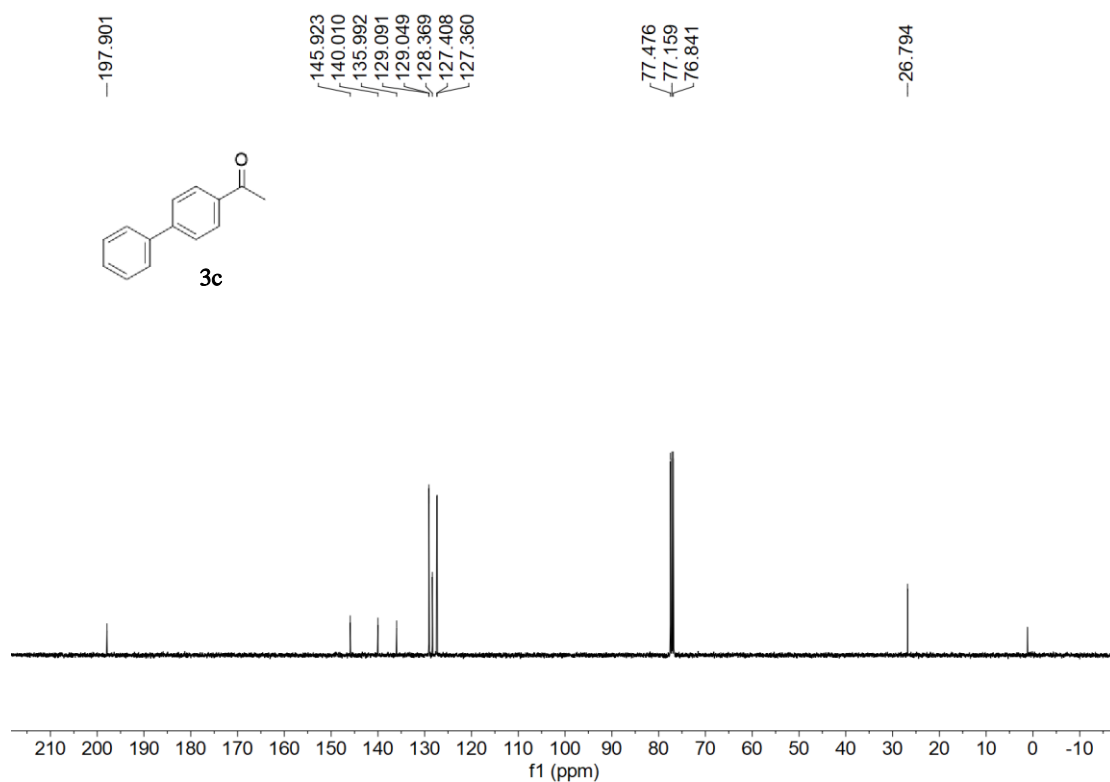
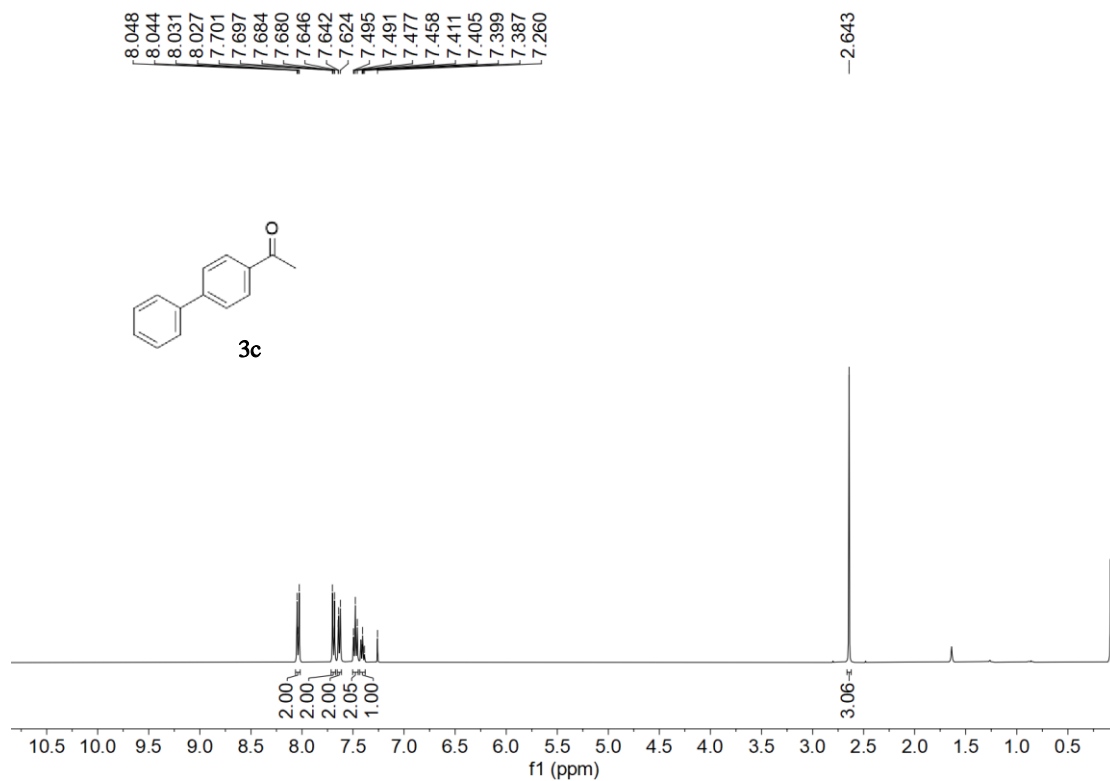


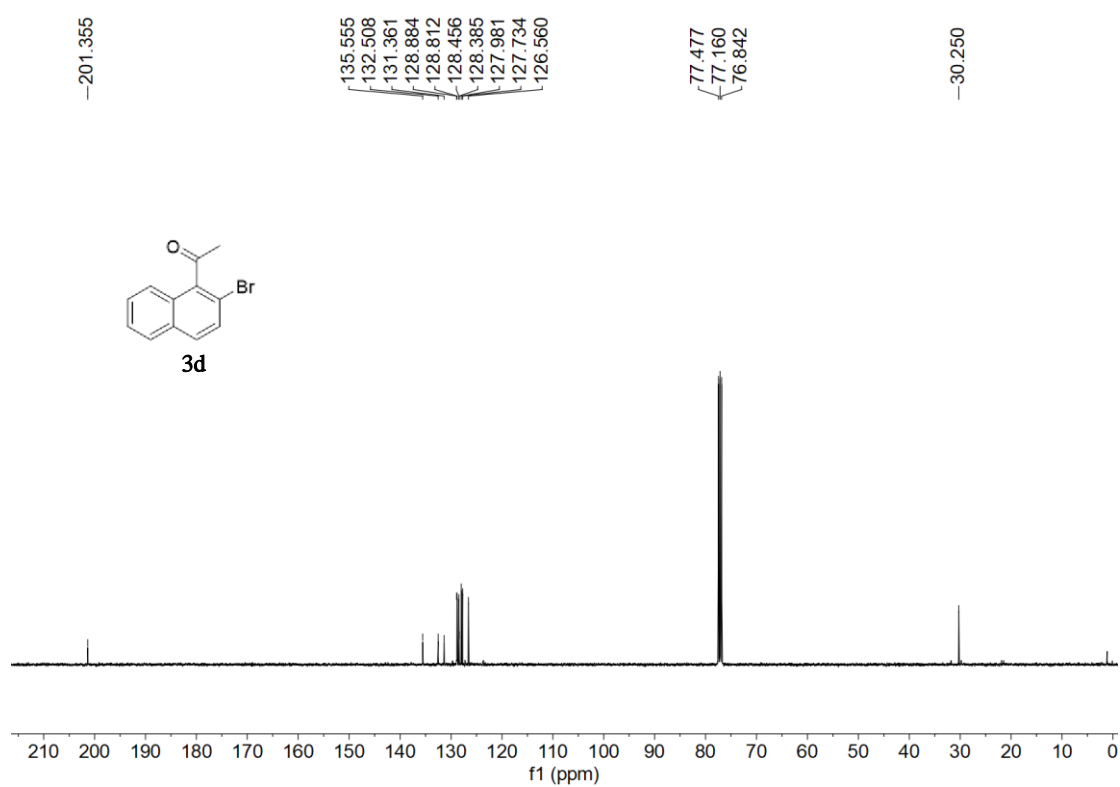
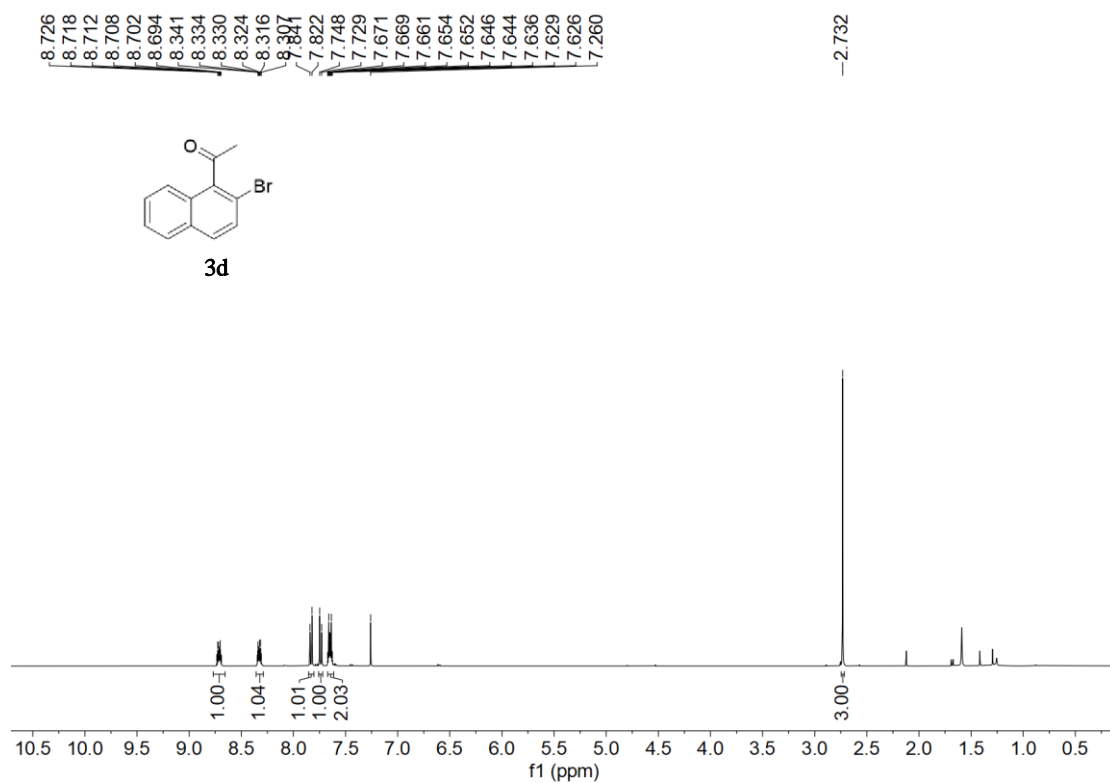


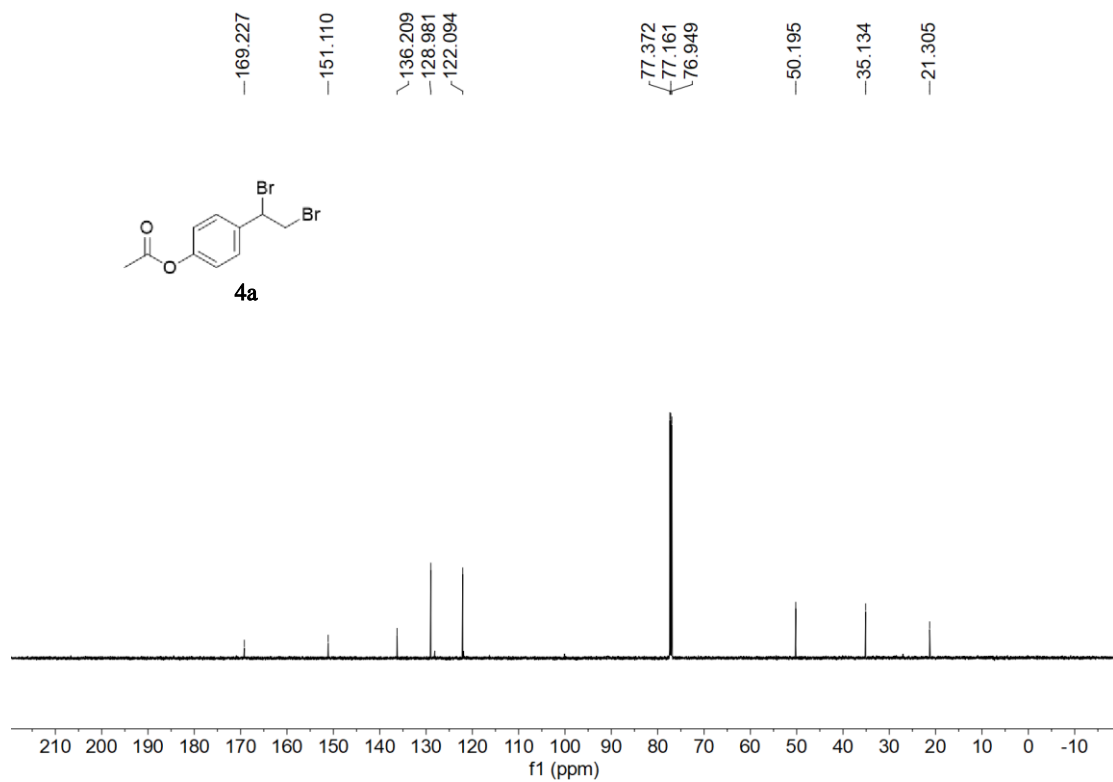
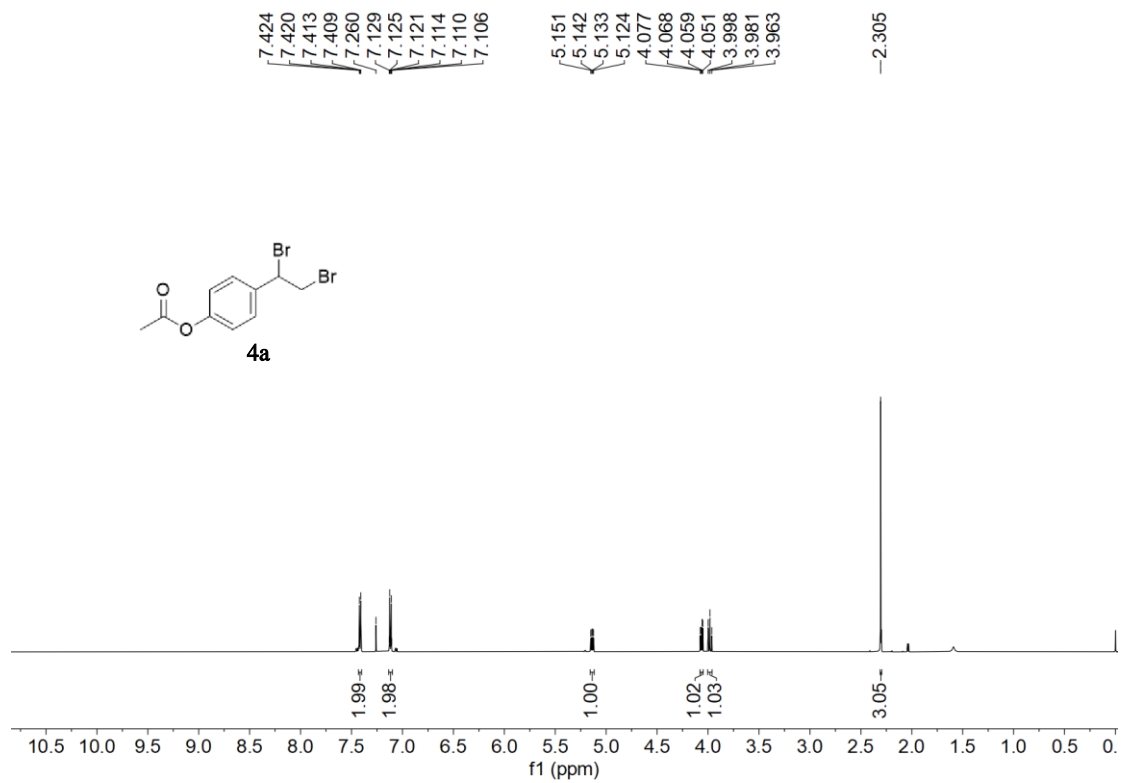


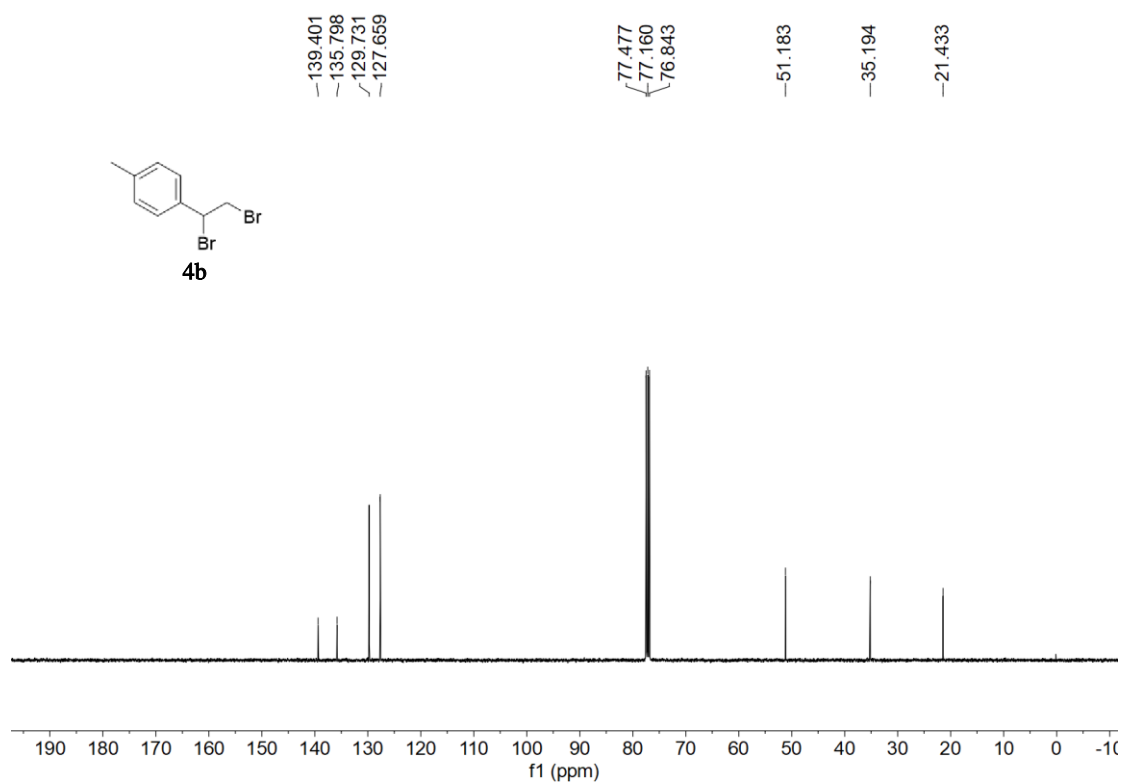
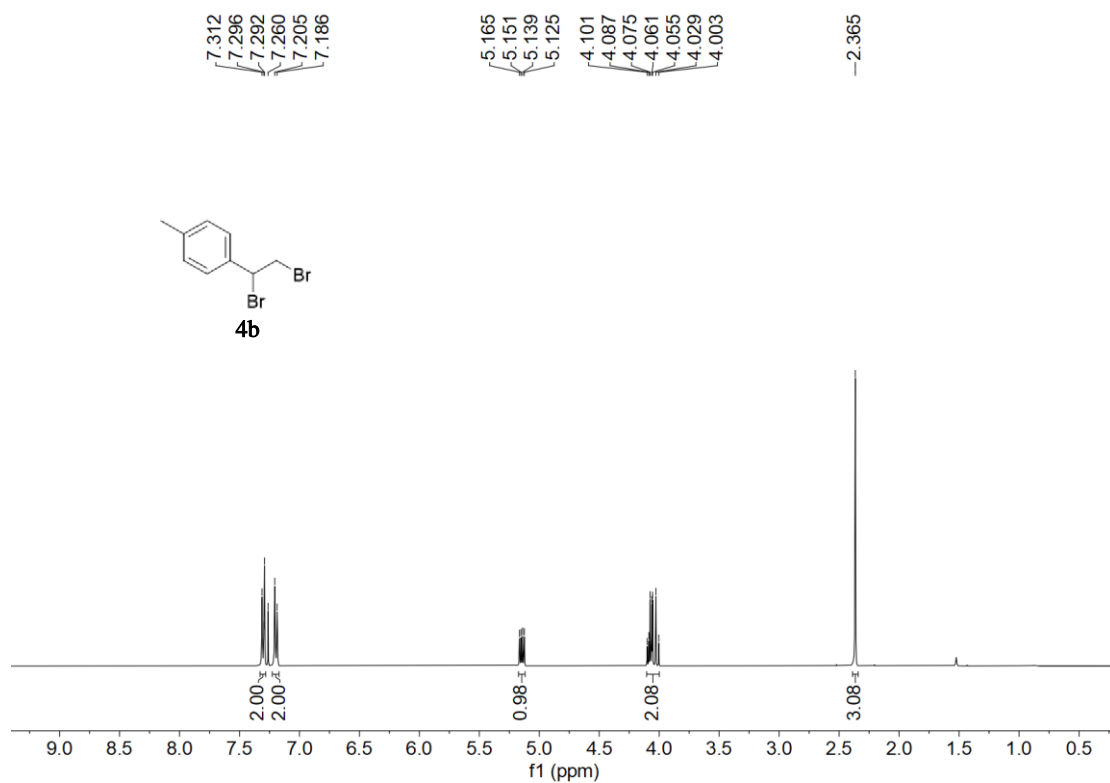


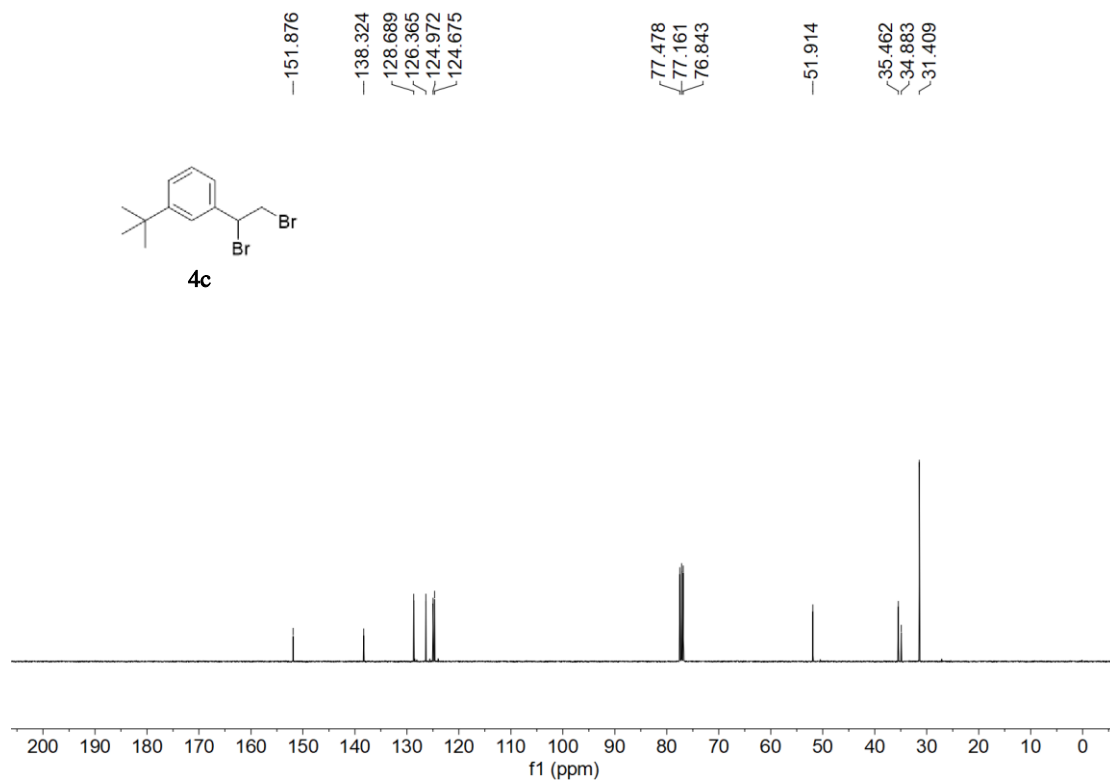
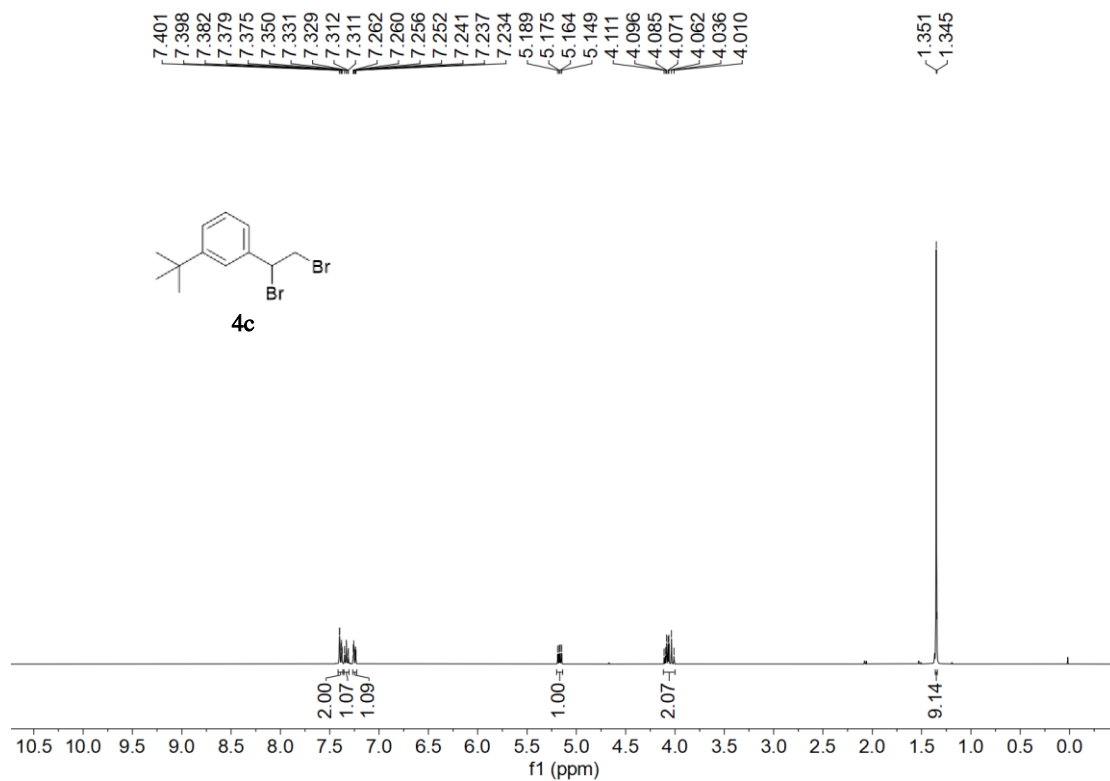


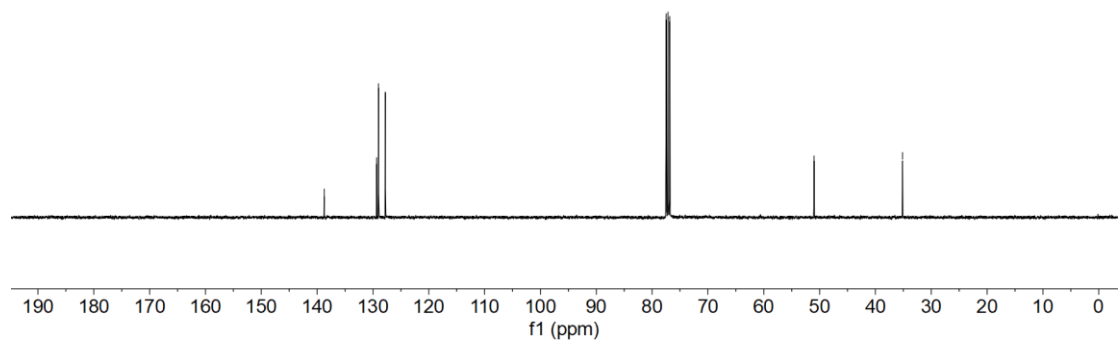
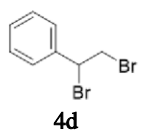
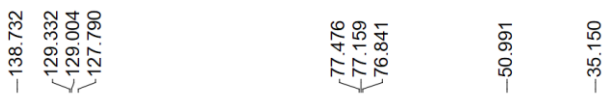
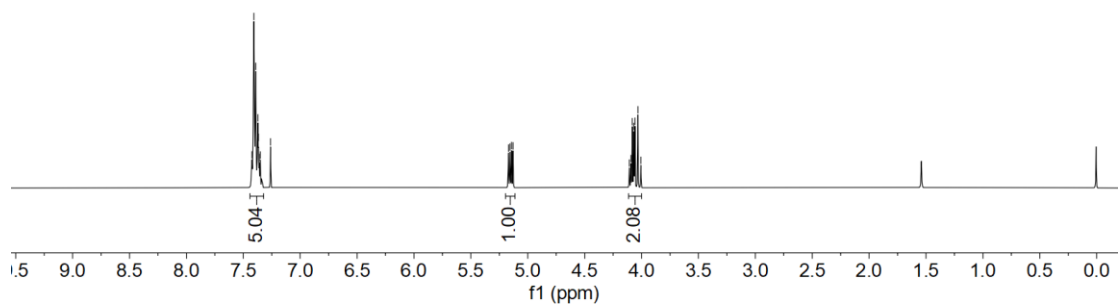
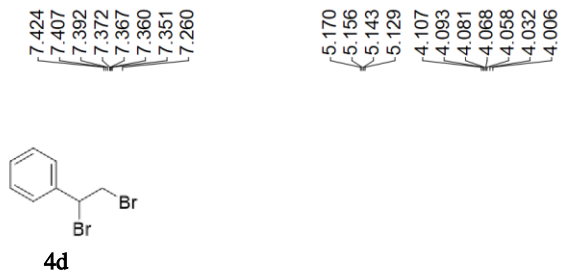








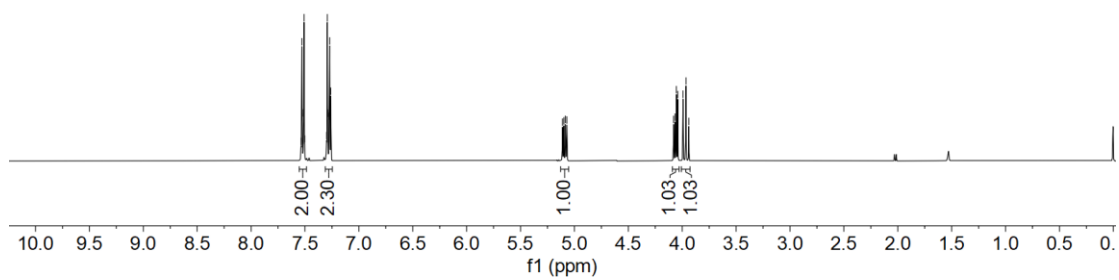
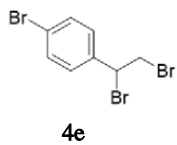






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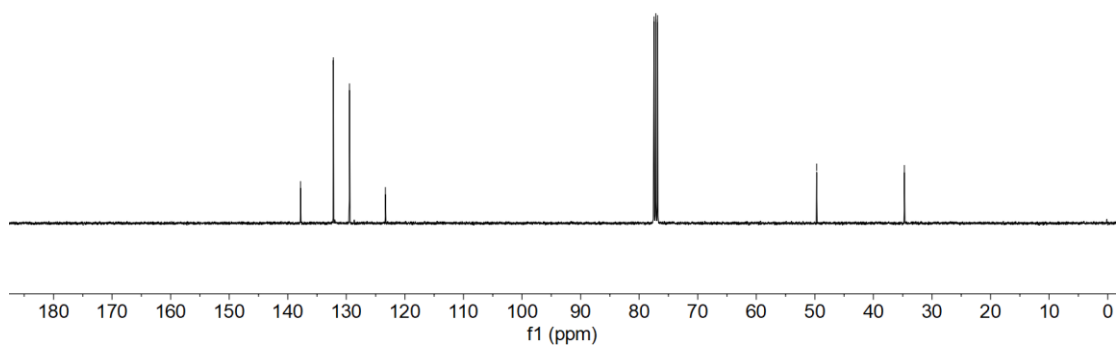
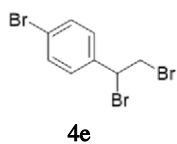


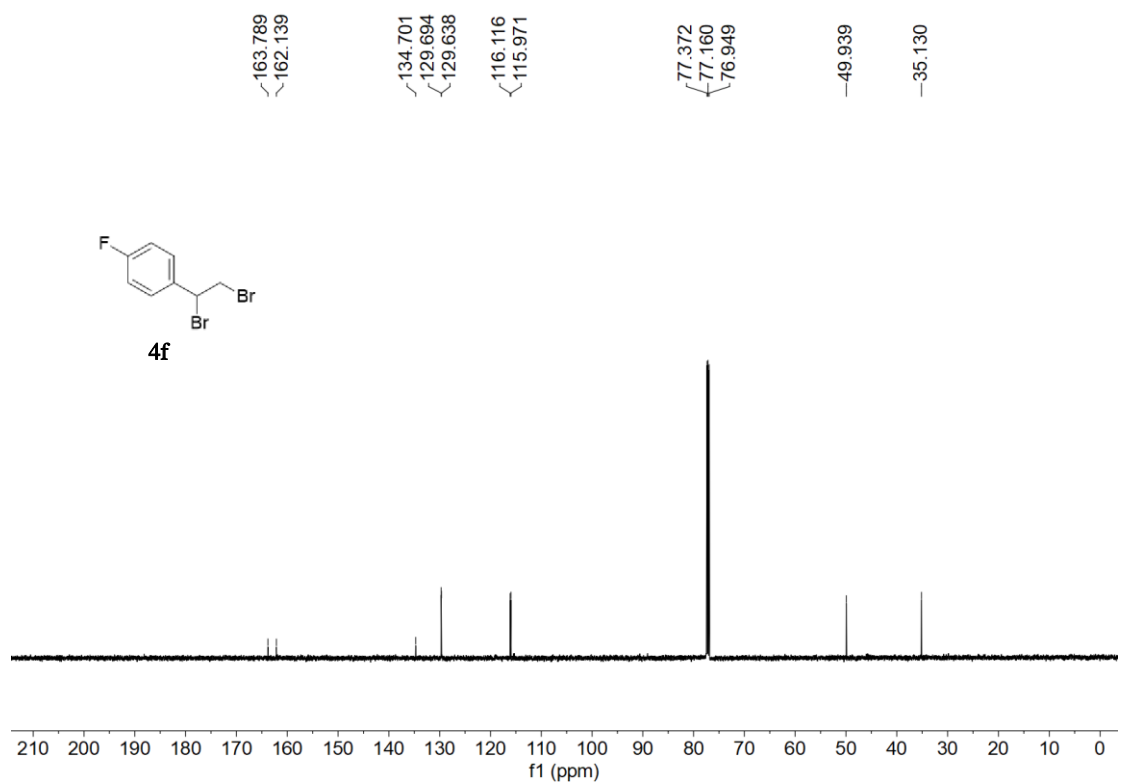
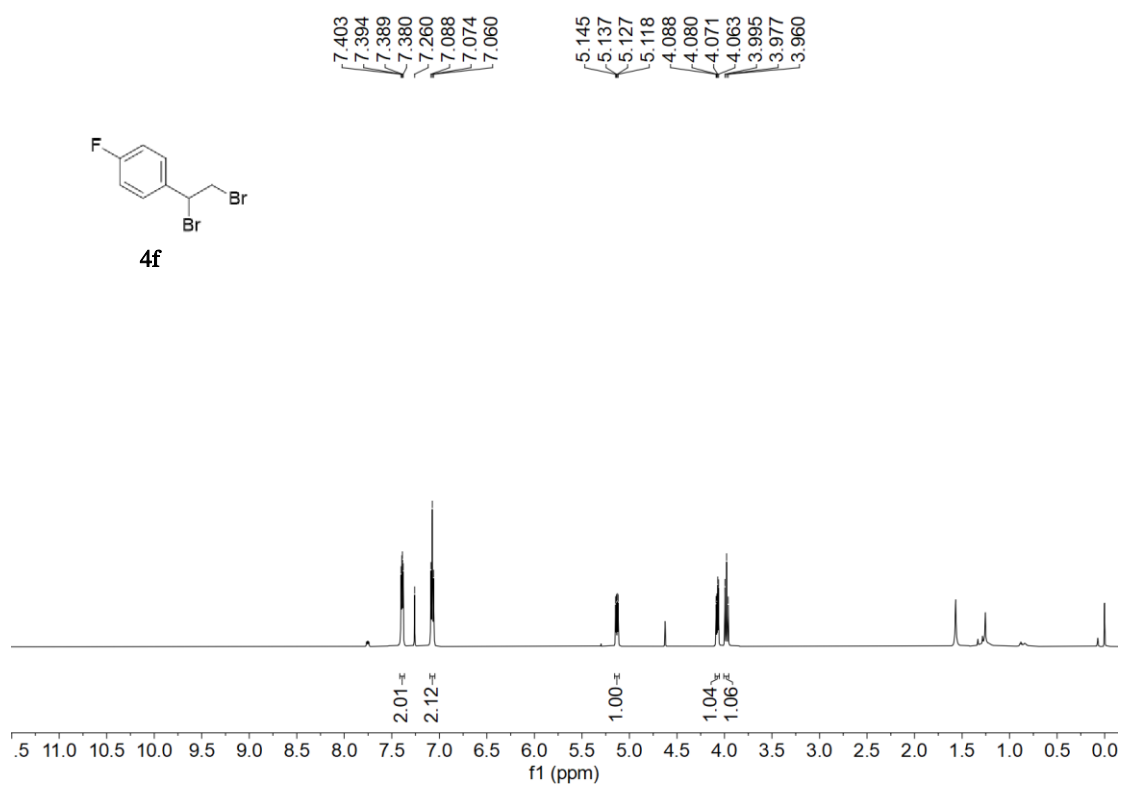
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123.328

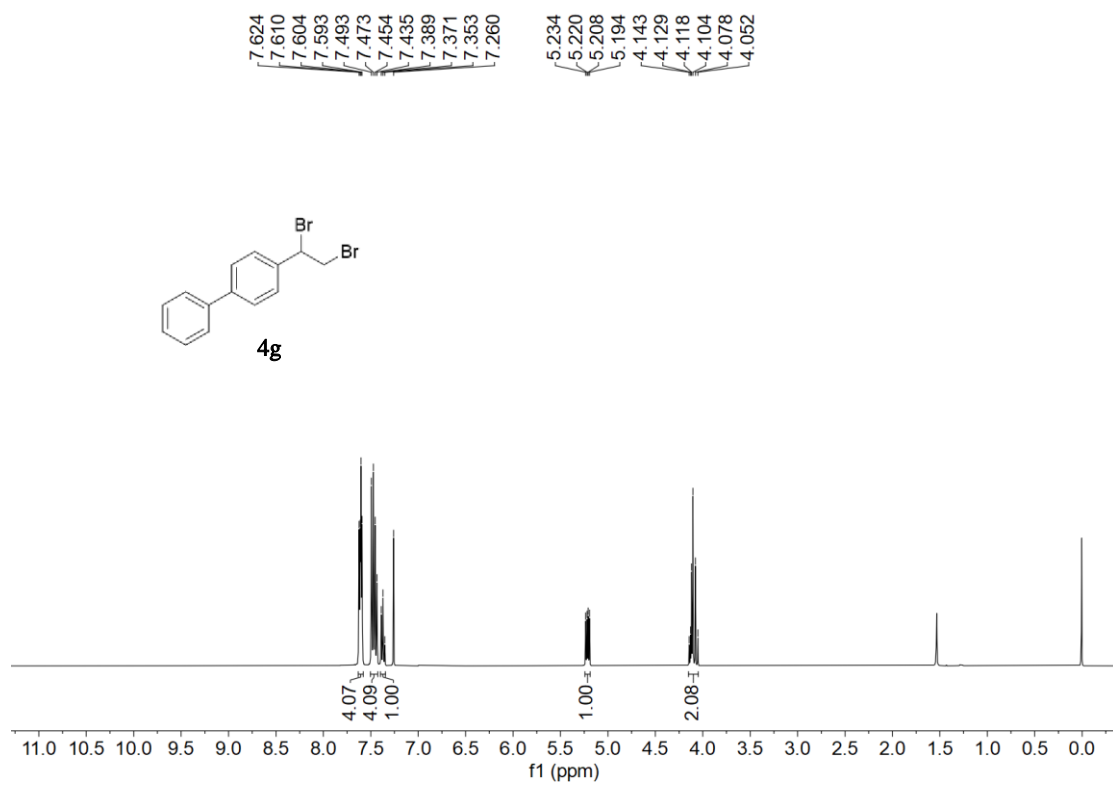
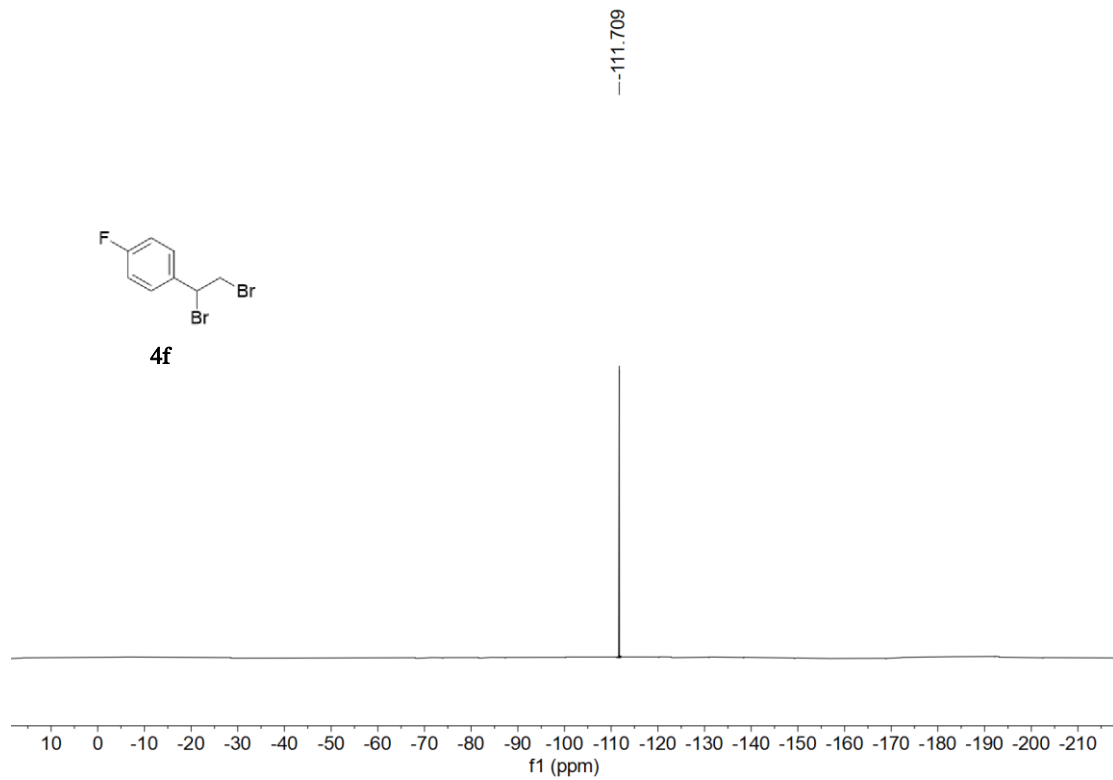
77.479  
77.163  
76.846

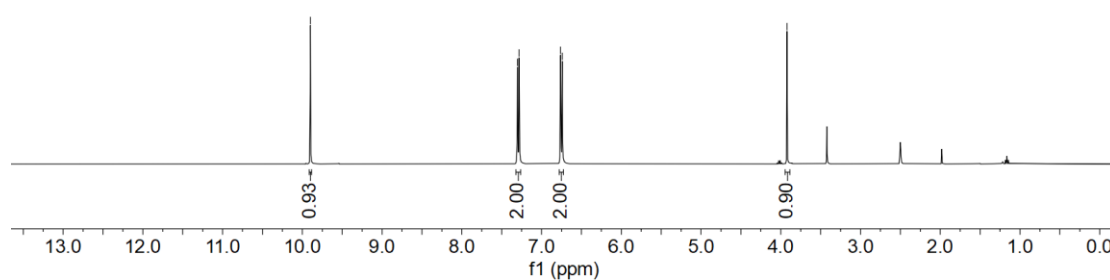
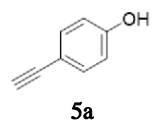
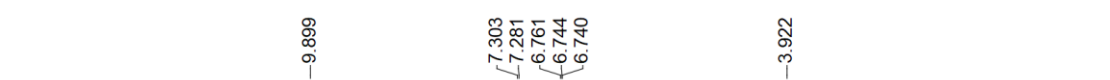
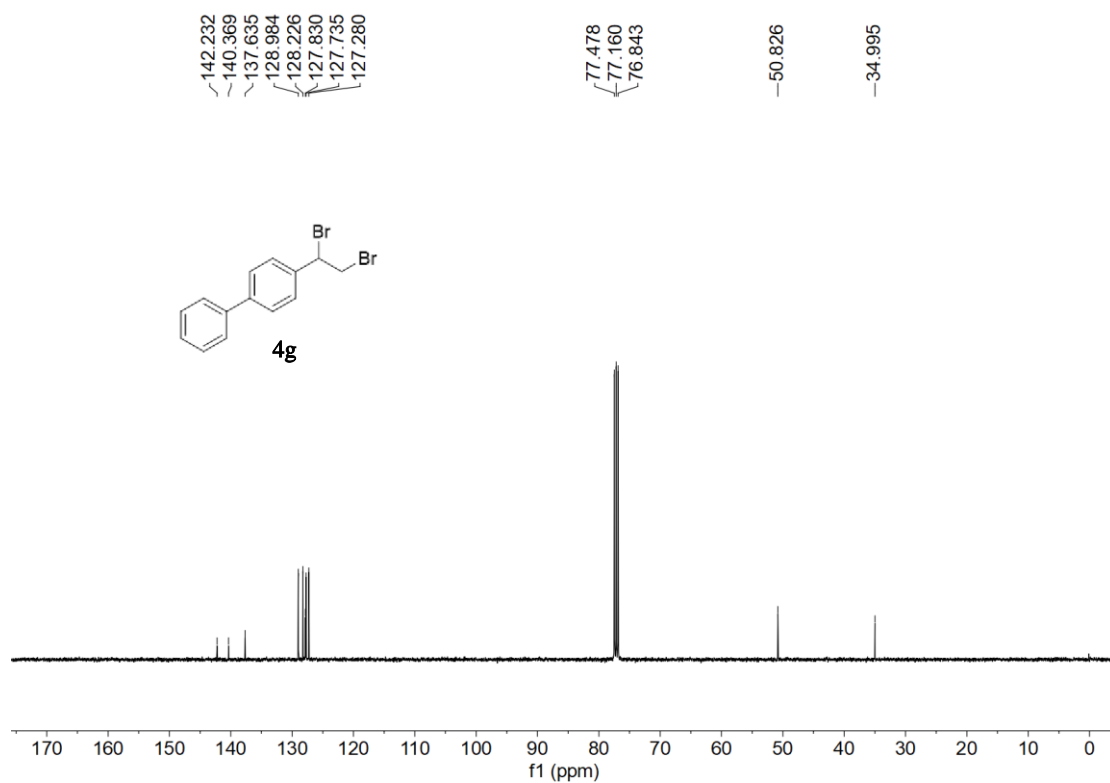
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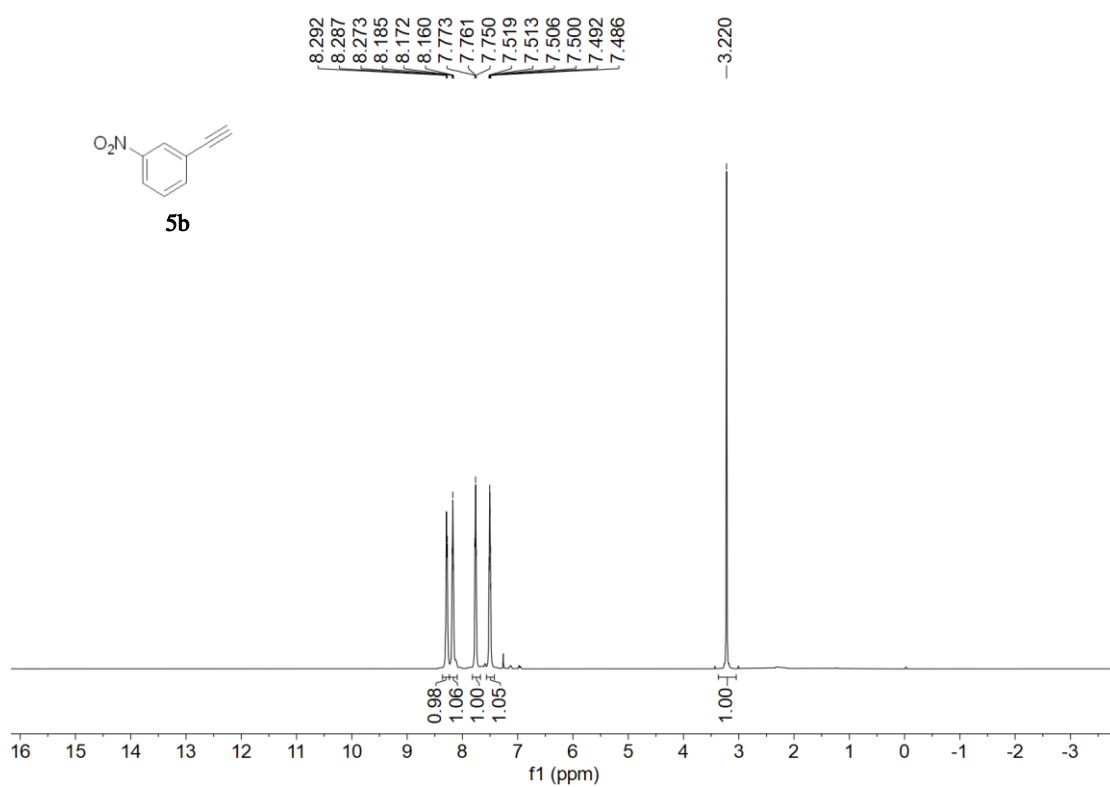
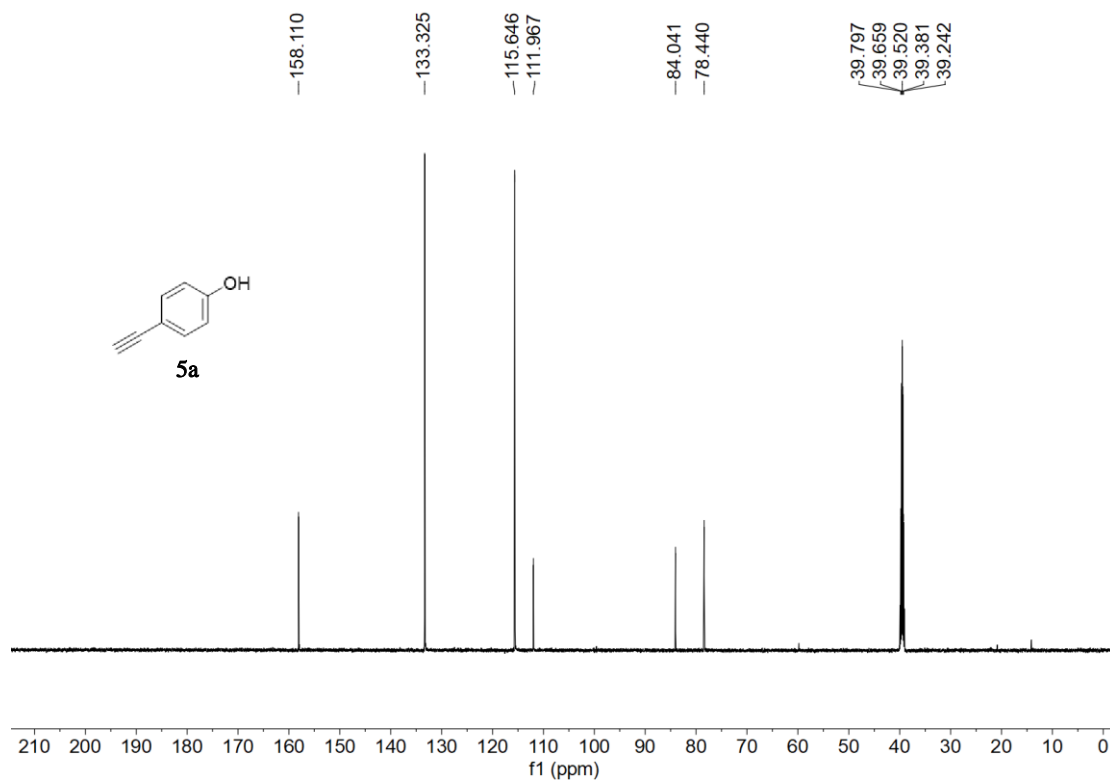
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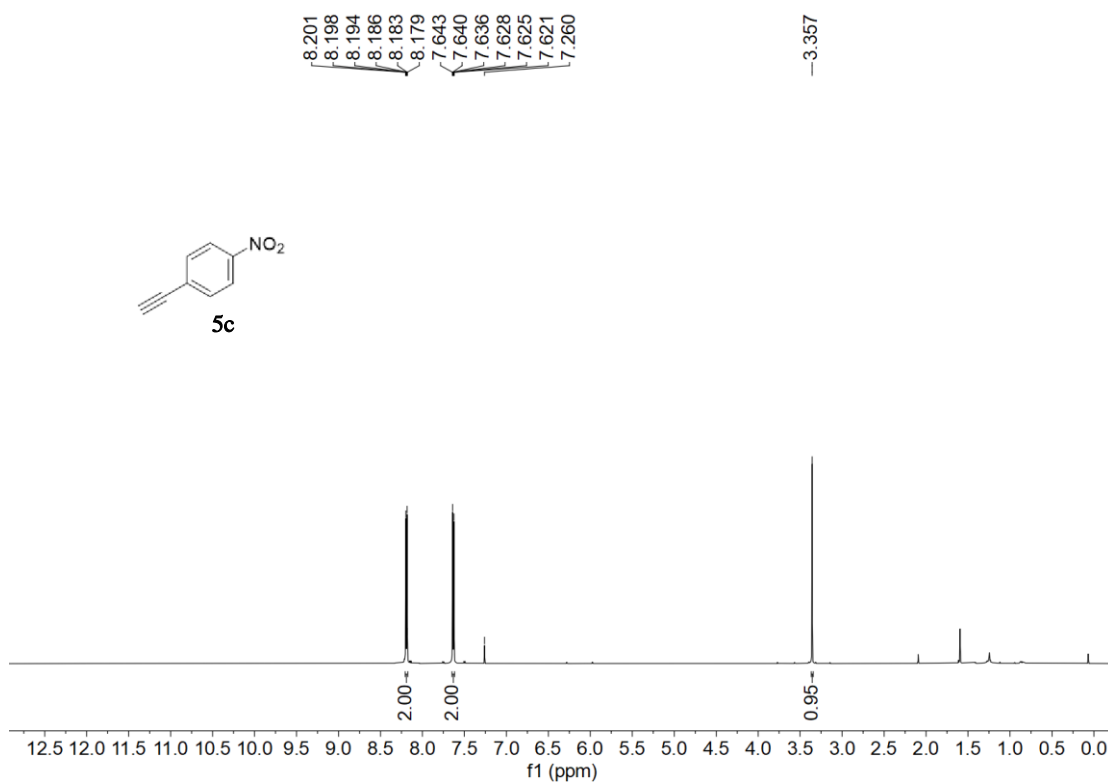
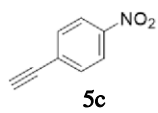
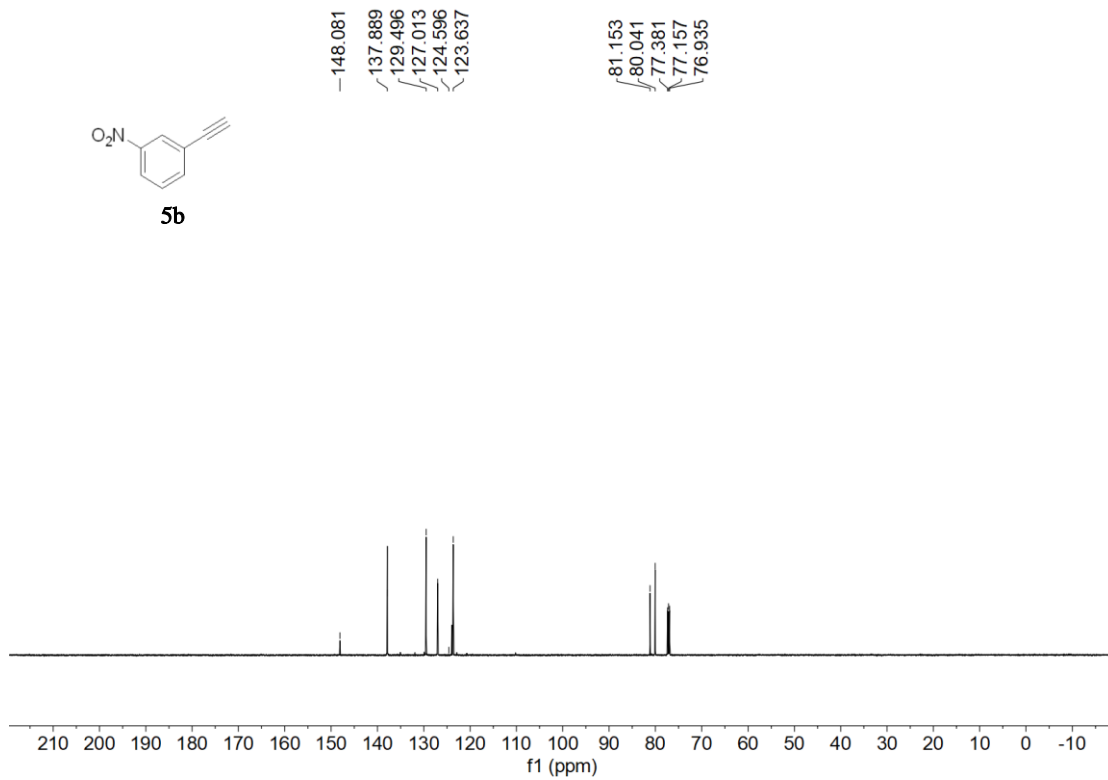
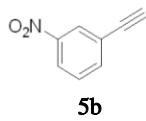


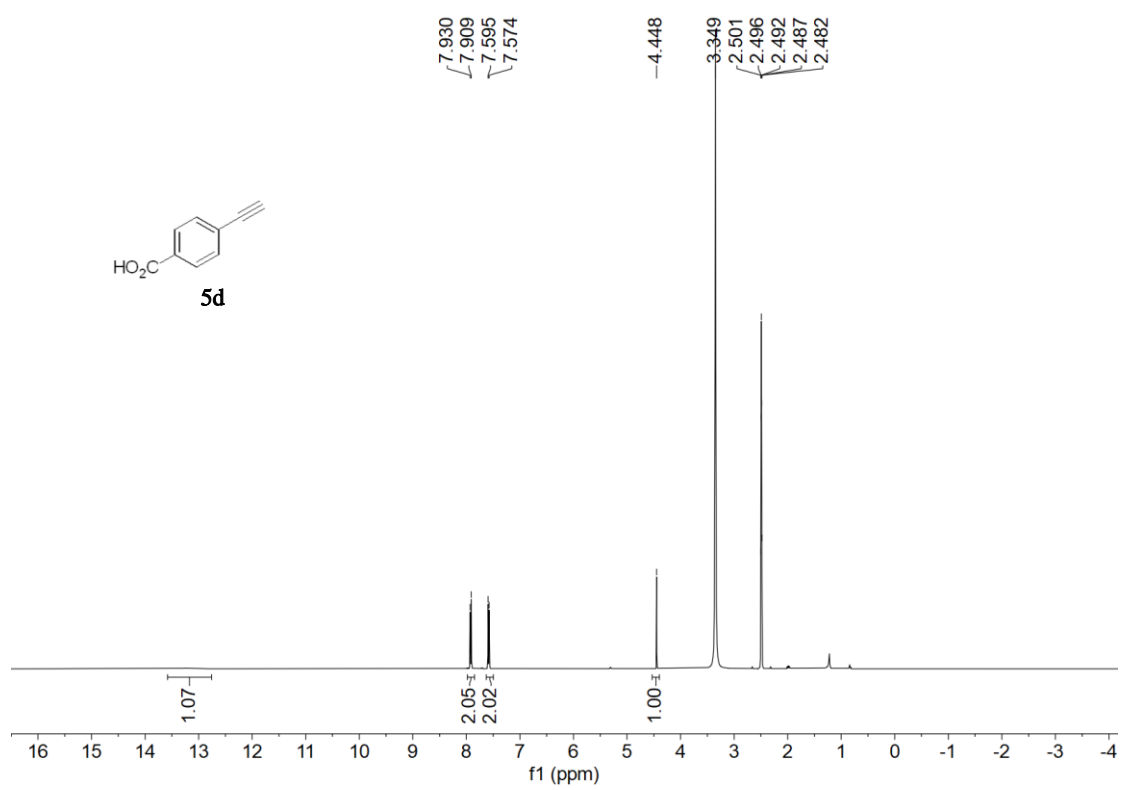
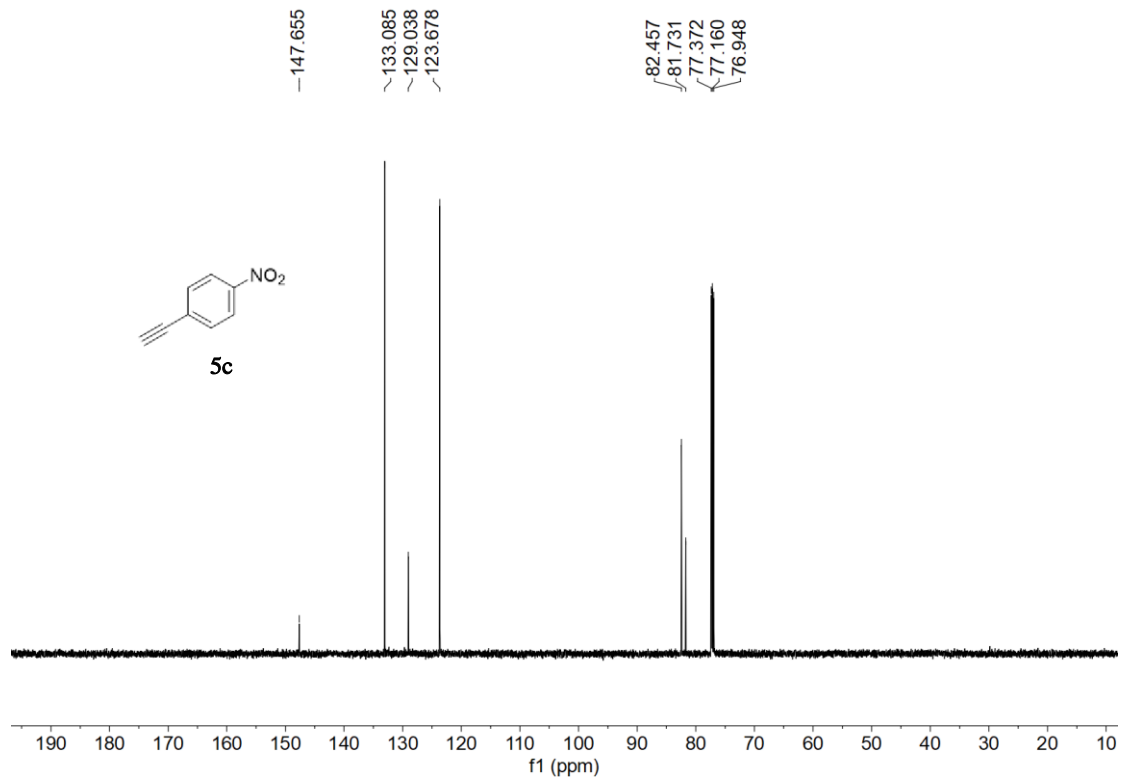


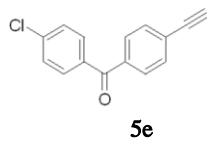




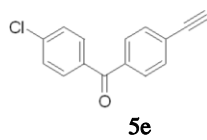
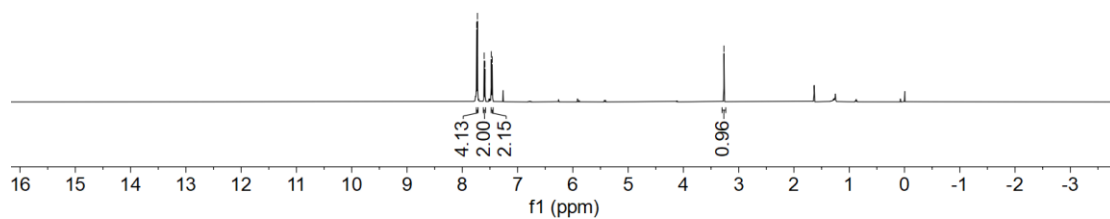








7.739  
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 7.590  
 7.473  
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 7.462  
 7.459  
 -3.264



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 76.949

