

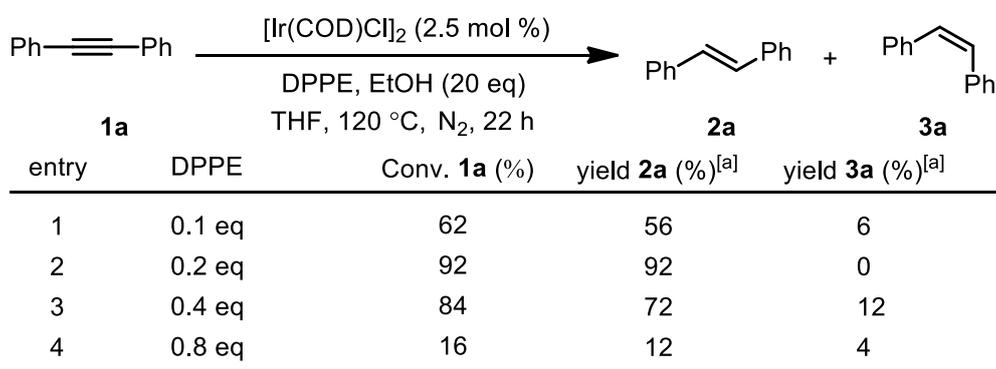
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## 1. General Information

Unless stated otherwise, all reactions were conducted in pressure tubes under N<sub>2</sub>. All solvents were received from commercial sources without further purification. Commercially available reagents were used as received. Non-commercially available substrates were synthesized following reported protocols. Thin-layer chromatography (TLC) was visualized using a combination of UV and potassium permanganate staining techniques. Silica gel (particle size 40 – 63 μm) was used for flash column chromatography. NMR spectra were recorded on Bruker AV 400 spectrometer at 400 MHz (<sup>1</sup>H NMR), 100 MHz (<sup>13</sup>C NMR). Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI resource.

## 2. Reaction Optimization

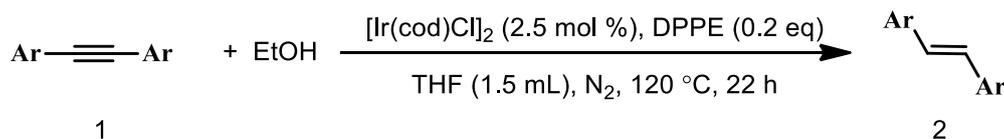


**Table 1** Effect of DPPE amount on the stereoselectivity. 1,2-Diphenylethyne (0.2 mmol), ethanol (4 mmol), [Ir(COD)Cl]<sub>2</sub> (10 μmol), THF (1.5 mL), at 120 °C under N<sub>2</sub> for 22 h. [a] Yields were determined by GC analysis.

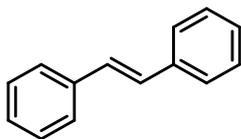
entry	ligand	Conv. <b>1a</b> (%)	yield <b>2a</b> (%) <sup>[a]</sup>	yield <b>3a</b> (%) <sup>[a]</sup>
1	COD (0.5 eq)	40	6	34
2	COD (1.0 eq)	50	8	42
3	COD (1.5 eq)	76	9	67
4	COD (2.0 eq)	91	7	84
5	COE (2.0 eq) <sup>[b]</sup>	59	16	43
6	Norbornylene (2.0 eq)	37	8	29

**Table 2** Effects of COD amount and other ligand on the stereoselectivity. 1,2-Diphenylethyne (0.2 mmol), ethanol (4 mmol), [Ir(COD)Cl]<sub>2</sub> (10 μmol), DPPE (0.04 mmol), THF (1.5 mL), at 120 °C under N<sub>2</sub> for 40 h. [a] Yields were determined by GC analysis. [b] COE = cyclooctene.

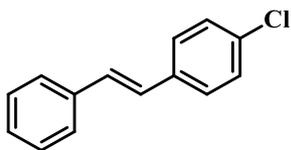
### 3. Typical Procedure for Synthesis of (*E*)-1,2-diphenylethene



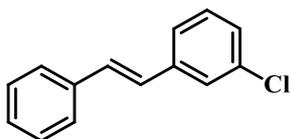
To a 15 mL pressure tube were added diarylacetylene **1** (0.20 mmol), [Ir(cod)Cl]<sub>2</sub> (5 μmol, 3.6 mg), DPPE (0.04 mmol, 15.9 mg) under N<sub>2</sub>, and then EtOH (4 mmol, 232 μL) and THF (1.5 mL) were added. The resulting solution was stirred at 120 °C for 22 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in *vacuo*. The crude product was purified by column chromatography (*n*-Hexane or *n*-Hex/EtOAc = 100:1 to 40:1) to afford the desired product.



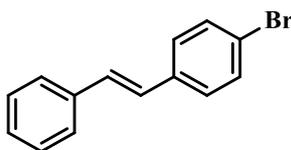
**2a: (*E*)-1,2-diphenylethene,**<sup>[1]</sup> White solid (33 mg, 92% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.49 (m, 4H), 7.34 (m, 4H), 7.26 – 7.22 (m, 2H), 7.09 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.4, 128.8, 127.7, 126.6.



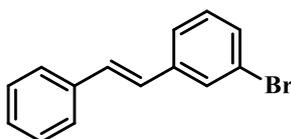
**2b: (*E*)-1-chloro-4-styrylbenzene,**<sup>[1]</sup> White solid (36 mg, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 – 7.49 (m, 2H), 7.45 – 7.43 (m, 2H), 7.38 – 7.25 (m, 5H), 7.11 – 7.02 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.1, 136.0, 133.3, 129.5, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7.



**2c: (*E*)-1-chloro-3-styrylbenzene,**<sup>[1]</sup> White solid (36 mg, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 – 7.49 (m, 3H), 7.38 – 7.34 (m, 3H), 7.29 – 7.21 (m, 3H), 7.11 (d,  $J$  = 16.3 Hz, 1H), 7.02 (d,  $J$  = 16.3 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 137.0, 134.8, 130.3, 130.0, 128.9, 128.2, 127.6, 127.4, 126.8, 126.4, 124.9.

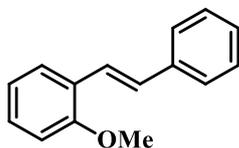


**2d: (*E*)-1-bromo-4-styrylbenzene,**<sup>[2]</sup> White solid (44 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 – 7.43 (m, 4H), 7.35 – 7.31 (m, 4H), 7.23 (t,  $J$  = 7.2 Hz, 1H), 7.02 (d,  $J$  = 16.0 Hz, 1H), 6.95 (d,  $J$  = 16.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.1, 136.4, 131.9, 129.6, 128.9, 128.1, 128.1, 127.6, 126.7, 121.5.

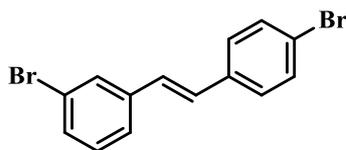


**2e: (*E*)-1-bromo-3-styrylbenzene,**<sup>[3]</sup> White solid (47 mg, 91% yield). <sup>1</sup>H NMR (400

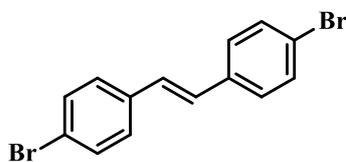
MHz, CDCl<sub>3</sub>):  $\delta$  7.66 (t,  $J$  = 4.0 Hz, 1H), 7.50 (d,  $J$  = 8.0 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.28 (t,  $J$  = 8.0 Hz, 1H), 7.22 (t,  $J$  = 8.0 Hz, 1H), 7.10 (d,  $J$  = 16.4 Hz, 1H), 7.01 (d,  $J$  = 16.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.7, 136.9, 130.5, 130.3, 130.3, 129.4, 128.9, 128.2, 127.2, 126.8, 125.3, 123.0.



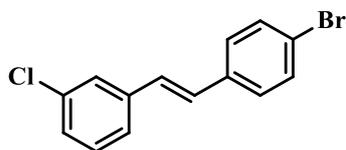
**2f: (E)-1-methoxy-2-styrylbenzene,**<sup>[2]</sup> White solid (56 mg, 83% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 – 7.59 (m, 1H), 7.55 – 7.53 (m, 2H), 7.49 (d,  $J$  = 16.4 Hz, 1H), 7.35 (t,  $J$  = 7.6 Hz, 2H), 7.27-7.22 (m, 2H), 7.12 (d,  $J$  = 16.4 Hz, 1H), 6.97 (t,  $J$  = 7.6 Hz, 1H), 6.91 (m, d,  $J$  = 8.0 Hz, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.1, 138.1, 129.3, 128.8, 128.7, 127.5, 126.7, 126.6, 126.6, 123.7, 120.9, 111.1, 55.7.



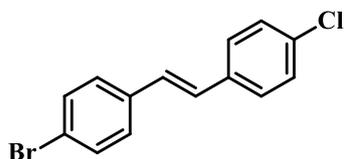
**2g: (E)-2-(3-bromophenyl)-1-(4-bromophenyl)ethene,**<sup>[2]</sup> White solid (56 mg, 83% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (s, 1H), 7.49 (d,  $J$  = 8.0 Hz, 2H), 7.41 – 7.35 (m, 4H), 7.22 (t,  $J$  = 7.6 Hz, 1H), 7.03 (d,  $J$  = 16.8 Hz, 1H), 6.99 (d,  $J$  = 16.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.3, 135.9, 132.0, 130.8, 130.4, 129.4, 129.0, 128.2, 128.0, 125.4, 123.1, 122.0.



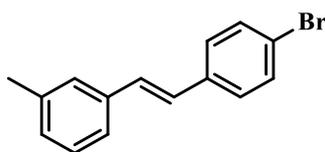
**2h: (E)-1,2-bis(4-bromophenyl)ethene,**<sup>[4]</sup> White solid (58 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d,  $J$  = 8.4 Hz, 4H), 7.08 (d,  $J$  = 8.4 Hz, 4H), 6.54 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.8, 131.7, 130.6, 129.9, 121.4.



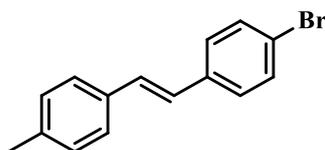
**2i: (E)-1-(4-bromostyryl)-3-chlorobenzene**, White solid (48 mg, 82% yield).  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 – 7.48 (m, 3H), 7.38 – 7.35 (m, 3H), 7.29 (t,  $J$  = 8.0 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.02 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.0, 135.9, 134.9, 132.0, 130.1, 129.0, 128.2, 128.1, 127.9, 126.5, 124.9, 122.0; HRMS(ESI)  $m/z$  Calcd for  $\text{C}_{14}\text{H}_{10}\text{BrCl}$  291.9654, Found 291.9644.



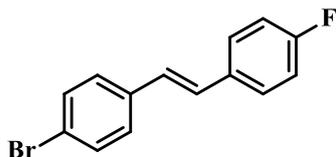
**2j: (E)-1-(4-bromostyryl)-4-chlorobenzene**,<sup>[5]</sup> White solid (47 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.37 – 7.34 (m, 2H), 7.22 – 7.08 (m, 6H), 6.59 – 6.51 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.9, 135.4, 133.2, 131.7, 130.6, 130.3, 129.8, 129.8, 128.7, 121.4.



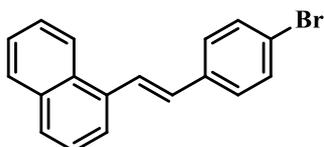
**2k: (E)-1-(4-bromostyryl)-3-methylbenzene**, White solid (49 mg, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 – 7.46 (m, 2H), 7.38 – 7.35 (m, 2H), 7.31 – 7.29 (m, 2H), 7.24 – 7.21 (m, 1H), 7.09 (d,  $J$  = 7.2 Hz, 1H), 7.06 (d,  $J$  = 16.4 Hz, 1H), 7.00 (d,  $J$  = 16.4 Hz, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 137.0, 136.5, 131.9, 129.7, 128.9, 128.8, 128.1, 127.4, 127.3, 123.9, 121.3, 21.6; HRMS(ESI)  $m/z$  Calcd for  $\text{C}_{15}\text{H}_{13}\text{Br}$   $[\text{M}+\text{H}]^+$  273.0279, Found 273.0281.



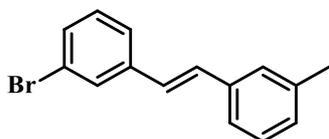
**2l: (E)-1-(4-bromostyryl)-4-methylbenzene**,<sup>[5]</sup> White solid (41 mg, 75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 – 7.45 (m, 2H), 7.41 – 7.35 (m, 4H), 7.18 – 7.16 (m, 2H), 7.07 (d,  $J$  = 16.4 Hz, 1H), 6.98 (d,  $J$  = 16.4 Hz, 1H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.0, 136.6, 134.3, 131.9, 129.6, 129.5, 128.0, 126.6, 126.5, 121.2, 21.4.



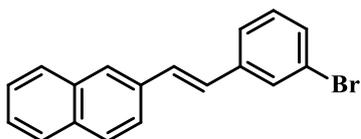
**2m:** (*E*)-1-(4-bromostyryl)-4-fluorobenzene,<sup>[6]</sup> White solid (50 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 – 7.45 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.07 – 7.03 (m, 3H), 6.94 (d, *J* = 16.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.6 (d, *J*<sub>C-F</sub> = 240 Hz), 136.3, 133.3, 132.0, 128.3 (d, *J*<sub>C-F</sub> = 10 Hz), 128.0, 127.3 (d, *J*<sub>C-F</sub> = 2.0 Hz), 121.5, 116.0, 115.9 (d, *J*<sub>C-F</sub> = 20.0 Hz).



**2n:** (*E*)-1-(4-bromostyryl)naphthalene,<sup>[7]</sup> White solid (53 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.81 (m, 3H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.57 – 7.46 (m, 7H), 7.08 (d, *J* = 16.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.7, 134.8, 133.9, 132.0, 131.5, 130.6, 128.8, 128.5, 128.3, 126.7, 126.4, 126.1, 125.8, 123.8, 121.7.

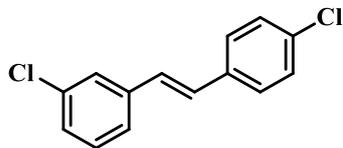


**2o:** (*E*)-1-(3-bromostyryl)-3-methylbenzene,<sup>[8]</sup> White solid (50 mg, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 (t, *J* = 4.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.98 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.7, 138.4, 136.8, 130.4, 130.4, 130.3, 129.3, 129.0, 128.8, 127.5, 127.0, 125.3, 124.0, 123.0, 21.6.

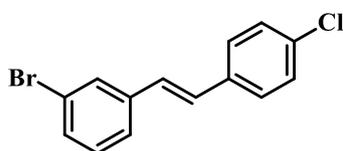


**2p:** (*E*)-2-(3-bromostyryl)naphthalene,<sup>[9]</sup> White solid (54 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.85 – 7.71 (m, 6H), 7.51 – 7.39 (m, 4H), 7.29 – 7.23 (m, 2H),

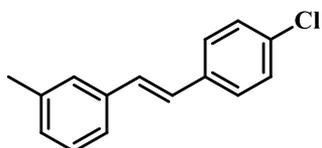
7.15 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 134.4, 133.8, 133.3, 130.6, 130.4, 129.4, 128.6, 128.2, 127.9, 127.5, 127.2, 126.6, 125.4, 123.5, 123.1.



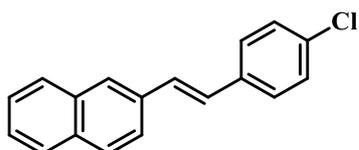
**2q:** (*E*)-2-(3-chlorophenyl)-1-(4-chlorophenyl)ethene,<sup>[8]</sup> White solid (39 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (s, 1H), 7.43 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 7.28 – 7.22 (m, 2H), 7.05 (d,  $J = 16.4$  Hz, 1H), 6.98 (d,  $J = 16.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.0, 135.5, 134.9, 133.8, 130.1, 129.1, 128.9, 128.0, 127.9, 127.9, 126.5, 124.9.



**2r:** (*E*)-1-(4-chlorostyryl)-3-bromobenzene,<sup>[8]</sup> White solid (49 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 (s, 1H), 7.44 – 7.32 (m, 6H), 7.24 – 7.20 (m, 1H), 7.05 (d,  $J = 16.0$  Hz, 1H), 6.98 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 135.4, 133.8, 130.8, 130.4, 129.4, 129.1, 129.0, 127.9, 127.8, 125.4, 123.1.

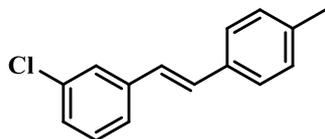


**2s:** (*E*)-1-(4-chlorostyryl)-3-methylbenzene,<sup>[10]</sup> White solid (42 mg, 92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 – 7.40 (m, 2H), 7.32 – 7.29 (m, 4H), 7.24 – 7.22 (m, 1H), 7.09 (d,  $J = 7.6$  Hz, 1H), 7.04 (s, 2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 137.0, 136.1, 133.5, 129.5, 129.0, 128.8, 128.8, 127.8, 127.4, 127.3, 123.9, 21.6.

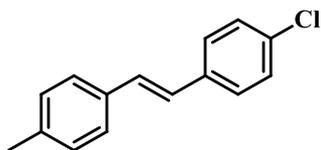


**2t:** (*E*)-2-(4-chlorostyryl)naphthalene,<sup>[11]</sup> White solid (47mg, 89% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 – 7.71 (m, 5H), 7.51 – 7.44 (m, 4H), 7.37 – 7.33 (m, 2H),

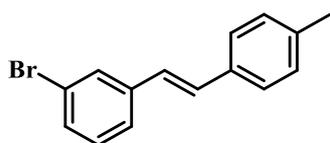
7.25 (d,  $J = 16.0$  Hz, 1H), 7.18 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.0, 134.6, 133.8, 133.4, 133.3, 129.6, 129.0, 128.5, 128.2, 127.9, 127.8, 127.0, 126.6, 126.2, 123.5.



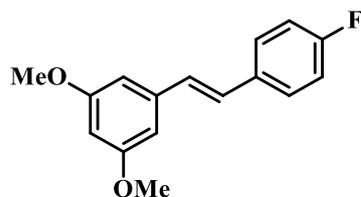
**2u:** (*E*)-1-(3-chlorostyryl)-4-methylbenzene,<sup>[5]</sup> White solid (38 mg, 84% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.27 (t,  $J = 8.0$  Hz, 1H), 7.22 – 7.17 (m, 3H), 7.09 (d,  $J = 16.0$  Hz, 1H), 6.98 (d,  $J = 16.0$  Hz, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.6, 139.2, 134.7, 134.2, 130.2, 130.0, 129.6, 127.4, 126.7, 126.3, 126.3, 124.8, 21.4.



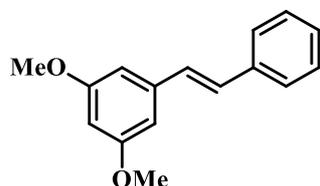
**2v:** (*E*)-1-(4-chlorostyryl)-4-methylbenzene,<sup>[5]</sup> White solid (35 mg, 77% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 – 7.40 (m, 4H), 7.33 (d,  $J = 8.4$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 16.0$  Hz, 1H), 7.00 (d,  $J = 16.0$  Hz, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.0, 136.2, 134.3, 133.0, 129.6, 129.4, 128.9, 127.7, 126.6, 126.5, 21.4.



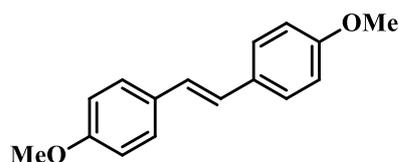
**2w:** (*E*)-1-(3-bromostyryl)-4-methylbenzene,<sup>[12]</sup> White solid (49 mg, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (s, 1H), 7.40 – 7.36 (m, 4H), 7.23 – 7.17 (m, 3H), 7.08 (d,  $J = 16.0$  Hz, 1H), 6.97 (d,  $J = 16.0$  Hz, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.9, 138.2, 134.1, 130.3, 130.3, 130.2, 129.6, 129.2, 126.7, 126.2, 125.2, 123.0, 21.4.



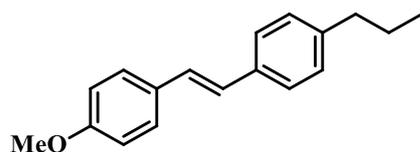
**2x:** (*E*)-1-(3,5-dimethoxystyryl)-4-fluorobenzene,<sup>[13]</sup> White solid (44 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 – 7.45 (m, 2H), 7.06 – 6.92 (m, 3H), 6.94 (d,  $J$  = 16.4 Hz, 1H), 6.66 (d,  $J$  = 2.0 Hz, 2H), 6.40 (t,  $J$  = 2.4 Hz, 1H), 3.83 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.6 (d,  $J_{C-F}$  = 246.0 Hz), 161.2, 139.3, 133.5, 128.6 (d,  $J_{C-F}$  = 2.0 Hz), 128.2 (d,  $J_{C-F}$  = 5.0 Hz), 128.1, 115.8 (d,  $J_{C-F}$  = 21.0 Hz), 104.7, 100.5, 55.5.



**2y:** (*E*)-1-(3,5-dimethoxystyryl)benzene,<sup>[3]</sup> White solid (38 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 – 7.49 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.24 (m, 1H), 7.09 (d,  $J$  = 16.4 Hz, 1H), 7.03 (d,  $J$  = 16.4 Hz, 1H), 6.7 (d,  $J$  = 2.4 Hz, 2H), 6.40 (t,  $J$  = 2.0 Hz, 1H), 3.82 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.1, 139.5, 137.3, 129.3, 128.8, 128.8, 127.9, 126.7, 104.7, 100.1, 55.5.

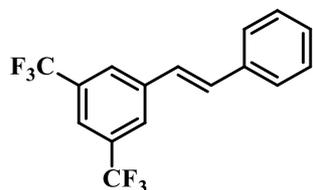


**2z:** (*E*)-1,2-bis(4-methoxyphenyl)ethene,<sup>[11]</sup> White solid (35 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 – 7.41 (m, 4H), 6.93 (s, 2H), 6.90 – 6.87 (m, 4H), 3.82 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 130.6, 127.6, 126.3, 114.3, 55.5.

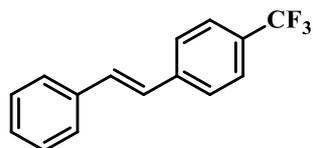


**2 $\alpha$ :** (*E*)-1-(4-propylstyryl)-4-methoxybenzene, White solid (35 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 – 7.41 (m, 4H), 7.17 (d,  $J$  = 8.0 Hz, 2H), 7.04 (d,  $J$  = 16.0 Hz, 1H), 6.96 (d,  $J$  = 16.0 Hz, 1H), 6.92 – 6.89 (m, 2H), 3.83 (s, 3H), 2.59 (t,  $J$  =

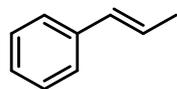
8.0 Hz, 2H), 1.70 – 1.61 (m, 2H), 0.96 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.3, 142.1, 135.2, 130.5, 128.9, 127.7, 127.4, 126.7, 126.3, 114.2, 55.5, 37.9, 24.7, 14.0; HRMS(ESI)  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}$   $[\text{M}+\text{H}]^+$  253.1592, Found 253.1581.



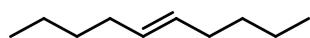
**2 $\beta$** : (*E*)-1-styryl-3,5-bis(trifluoromethyl)benzene,<sup>[14]</sup> White solid (46 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 2H), 7.74 (s, 1H), 7.55 (d,  $J = 7.2$  Hz, 2H), 7.40 (t,  $J = 7.2$  Hz, 2H), 7.35 – 7.32 (m, 1H), 7.20 (d,  $J = 16.4$  Hz, 1H), 7.20 (d,  $J = 16.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.6, 136.2, 132.7, 132.2 (d,  $J_{\text{C-F}} = 33.0$  Hz), 129.1, 128.9, 127.1, 126.3 (d,  $J_{\text{C-F}} = 3.4$  Hz), 125.7, 123.5 (d,  $J_{\text{C-F}} = 271.1$  Hz), 121.0-120.9 (m).



**2 $\gamma$** : (*E*)-1-styryl-4-(trifluoromethyl)benzene,<sup>[1]</sup> White solid (41 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 4H), 7.54 (m, 2H), 7.38 (t,  $J = 8.0$  Hz, 2H), 7.35 – 7.32 (m, 1H), 7.25 (d,  $J = 16.4$  Hz, 1H), 7.14 (d,  $J = 16.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.0, 136.8, 131.4, 129.6, 129.3, 129.0, 128.4, 127.3, 126.9, 126.7, 125.8 (q,  $J_{\text{C-F}} = 3.8$  Hz).



**2 $\epsilon$** : (*E*)-prop-1-en-1-ylbenzene,<sup>[15]</sup> Colorless liquid (20 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 – 7.26 (m, 4H), 7.20 – 7.16 (m, 1H), 6.40 (dd,  $J = 16.0, 1.2$  Hz, 1H), 6.28 – 6.19 (m, 1H), 1.88 (dd,  $J = 6.4, 1.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.1, 131.2, 128.6, 126.9, 126.0, 125.8, 18.6.

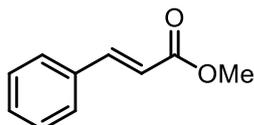


**2 $\phi$** : (*E*)-dec-5-ene,<sup>[16]</sup> Colorless liquid (20 mg, 70% yield).  $^1\text{H}$  NMR (400 MHz,

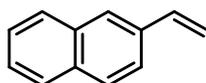
CDCl<sub>3</sub>):  $\delta$  5.40 – 5.36 (m, 2H), 1.98 – 1.97 (m, 4H), 1.34 – 1.27 (m, 8H), 0.89 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  130.5, 32.5, 32.0, 22.4, 14.1.



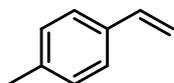
**2η: (E)-tetradec-7-ene,**<sup>[17]</sup> Colorless liquid (28 mg, 72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.40 – 5.34 (m, 2H), 2.03 – 1.95 (m, 4H), 1.30 – 1.27 (m, 16H), 0.88 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  130.5, 32.8, 32.0, 29.8, 29.0, 22.8, 14.3..



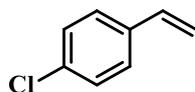
**2A: Methyl cinnamate,**<sup>[18]</sup> White solid (25 mg, 76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.70 (d,  $J$  = 16.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.40-7.38 (m, 3H), 6.45 (d,  $J$  = 16.0 Hz, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.7, 145.1, 134.5, 130.5, 129.0, 128.2, 117.9, 51.9.



**2B: 2-vinylnaphthalene,**<sup>[15]</sup> White solid (24 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 – 7.76 (m, 4H), 7.64 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 6.89 (dd,  $J$  = 17.6, 11.2 Hz, 1H), 5.88 (d,  $J$  = 17.6 Hz, 1H), 5.35 (d,  $J$  = 14.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.1, 135.2, 133.7, 133.3, 128.3, 128.2, 127.8, 126.5, 126.4, 126.1, 123.3, 114.3.



**2C: 1-methyl-4-vinylbenzene,**<sup>[15]</sup> Colorless liquid (22 mg, 93% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d,  $J$  = 8.0 Hz, 2H), 7.18 (d,  $J$  = 8.0 Hz, 2H), 6.74 (dd,  $J$  = 17.6, 11.2 Hz, 1H), 5.75 (d,  $J$  = 17.6 Hz, 1H), 5.23 (d,  $J$  = 10.8 Hz, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.7, 136.8, 134.9, 129.3, 126.2, 112.8, 21.3.



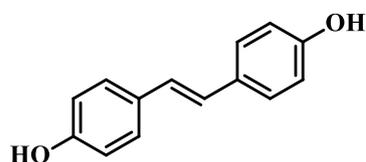
**2D: 1-chloro-4-vinylbenzene,**<sup>[15]</sup> Colorless liquid (25 mg, 91% yield). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>):  $\delta$  7.34-7.25 (m, 4H), 6.66 (dd,  $J = 17.6, 11.2$  Hz, 1H), 5.72 (d,  $J = 17.6$  Hz, 1H), 5.26 (d,  $J = 11.2$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  136.2, 135.8, 133.6, 128.8, 127.6, 114.6.

#### 4, Deprotection of (*E*)-1,2-bis(4-methoxyphenyl)ethene



To a solution of (*E*)-1,2-bis(4-methoxyphenyl)ethene (0.2 mmol) in anhydrous DCM (6 mL) maintained under nitrogen at  $-20$  °C with stirring was added BBr<sub>3</sub> dropwise (0.34 g, 1.34 mmol, 30% in DCM). The mixture, maintained under nitrogen with stirring, was allowed to warm up to room temperature for 4 – 5 h, and then it was poured into water (10 mL) and extracted with DCM (3×10 mL). The collected organic phases were washed with brine (10 mL) and then dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was evaporated and the residue purified by column chromatography on silica gel using 6:4 hexane–acetone.



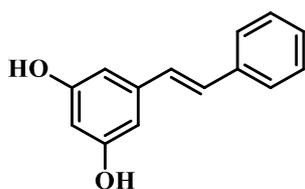
**Pinosylvin**,<sup>[19]</sup> White solid (33mg, 77.8% yield). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  8.04 (s, 2H), 7.40 (d,  $J = 8.8$  Hz, 4H), 6.96 (s, 2H), 6.83 (d,  $J = 8.8$  Hz, 4H); <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  157.7, 130.5, 128.3, 126.5, 116.4.

#### 5, Deprotection of 3-Mesityl-2'-methoxy-[1,1'-binaphthalene]-2-ol



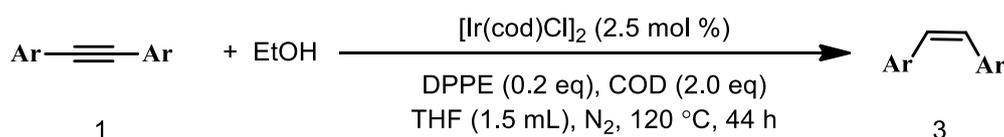
To a solution of (*E*)-1,3-dimethoxy-5-styrylbenzene (0.2 mmol) in anhydrous DCM (6

mL) maintained under nitrogen at  $-20\text{ }^{\circ}\text{C}$  with stirring was added  $\text{BBr}_3$  dropwise (0.34 g, 1.34 mmol, 30% in DCM). The mixture, maintained under nitrogen with stirring, was allowed to warm up to room temperature for 4 – 5 h, and then it was poured into water (10 mL) and extracted with DCM ( $3\times 10$  mL). The collected organic phases were washed with brine (10 mL) and then dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the solvent was evaporated and the residue purified by column chromatography on silica gel using 6:4 hexane–acetone.



**4,4'-dihydroxystilbene (DHS),**<sup>[13]</sup> White solid (35mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  7.57 (d,  $J = 7.2$  Hz, 2H), 7.35 (t,  $J = 7.2$  Hz, 2H), 7.25 (t,  $J = 7.2$  Hz, 1H), 7.10 (s, 2H), 6.60 (d,  $J = 2.0$  Hz, 2H), 6.32 (t,  $J = 2.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  159.6, 140.4, 138.4, 129.8, 129.5, 129.2, 128.3, 127.3, 105.9, 103.1.

## 6. Typical Procedure for Synthesis of (Z)-1,2-diarylethene



To a 15 mL pressure tube were added diphenylacetylene **1** (0.20 mmol),  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (5  $\mu\text{mol}$ , 3.6 mg), DPPE (0.04 mmol, 15.9 mg) under  $\text{N}_2$ , and then EtOH (4 mmol, 232  $\mu\text{L}$ ), COD (0.4 mmol, 49  $\mu\text{L}$ ) and THF (1.5 mL) were added. The resulting solution was stirred at  $120\text{ }^{\circ}\text{C}$  for 44 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in *vacuo*. The crude product was purified by column chromatography (*n*-Hexane or *n*-Hex/EtOAc = 100:1 to 40:1) to afford the desired

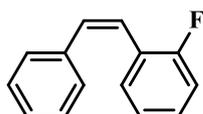
product.



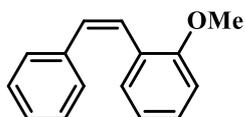
**3a: (Z)-1,2-diphenylethene,**<sup>[1]</sup> Colorless liquid (30 mg, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.27 – 7.21 (m, 10H), 6.63 – 6.60 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.4, 130.4, 130.4, 129.0, 129.0, 128.4, 128.3, 127.2, 127.2.



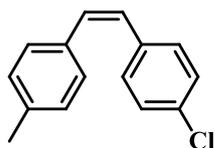
**3b: (Z)-1-chloro-2-styrylbenzene,**<sup>[20]</sup> Colorless liquid (37 mg, 81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 – 7.40 (m, 1H), 7.21 – 7.15 (m, 7H), 7.06 – 7.02 (m, 1H), 6.73 (d,  $J$  = 12.4 Hz 1H), 6.68 (d,  $J$  = 12.4 Hz 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  136.6, 136.2, 133.8, 131.8, 130.9, 129.7, 129.1, 128.6, 128.3, 127.5, 127.4, 126.5.



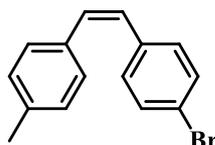
**3c: (Z)-1-fluoro-2-styrylbenzene,**<sup>[20]</sup> Colorless liquid (44 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 – 7.17 (m, 7H), 7.07 – 7.02 (m, 1H), 7.95 – 7.91 (m, 1H), 6.73 (d,  $J$  = 12.4 Hz 1H), 6.63 (d,  $J$  = 12.4 Hz 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.5 (d,  $J_{C-F}$  = 246.2 Hz), 136.9, 132.4, 130.6 (d,  $J_{C-F}$  = 3.5 Hz); 129.1 (d,  $J_{C-F}$  = 8.2 Hz), 128.9, 128.4, 127.5, 125.2 (d,  $J_{C-F}$  = 14.4 Hz), 123.7 (d,  $J_{C-F}$  = 3.5 Hz), 122.8 (d,  $J_{C-F}$  = 3.3 Hz), 115.7 (d,  $J_{C-F}$  = 21.8 Hz).



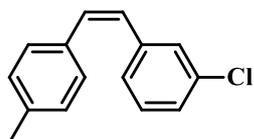
**3d: (Z)-1-methoxy-2-styrylbenzene,**<sup>[21]</sup> Colorless liquid (36 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 – 7.12 (m, 7H), 6.89 (d,  $J$  = 8.0 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.69 (d,  $J$  = 12.4 Hz, 1H), 6.62 (d,  $J$  = 12.4 Hz, 1H), 3.82 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.2, 137.3, 130.2, 130.1, 128.9, 128.6, 128.0, 126.9, 126.2, 125.8, 120.2, 110.7, 55.5.



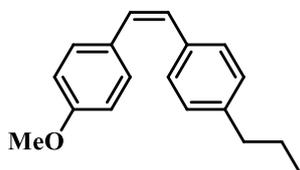
**3e: (Z)-1-(4-chlorostyryl)-4-methylbenzene**, Colorless liquid (37 mg, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (s, 4H), 7.13 – 7.03 (m, 4H), 6.59 (d,  $J = 12.4$  Hz, 1H), 6.48 (d,  $J = 12.4$  Hz, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.3, 136.0, 134.0, 132.7, 131.0, 130.3, 129.2, 128.9, 128.5, 128.4, 21.4; HRMS(ESI)  $m/z$  Calcd for  $\text{C}_{15}\text{H}_{13}\text{Cl}$   $[\text{M}+\text{H}]^+$  229.0784, Found 229.0789.



**3f: (Z)-1-(4-bromostyryl)-4-methylbenzene**,<sup>[22]</sup> Colorless liquid (44 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 – 7.33 (m, 2H), 7.13 – 7.03 (m, 6H), 6.60 (d,  $J = 12.0$  Hz, 1H), 6.46 (d,  $J = 12.0$  Hz, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.3, 136.5, 134.0, 131.5, 131.1, 130.7, 129.2, 128.8, 128.4, 120.9, 21.4.

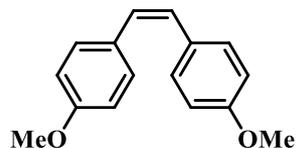


**3g: (Z)-1-(3-chlorostyryl)-4-methylbenzene**,<sup>[81]</sup> Colorless liquid (36 mg, 79% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 (s, 1H), 7.17 – 7.11 (m, 5H), 7.06 – 7.04 (m, 2H), 6.61 (d,  $J = 12.4$  Hz, 1H), 6.47 (d,  $J = 12.4$  Hz, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.5, 137.4, 134.2, 133.8, 131.7, 129.6, 129.2, 129.0, 128.9, 128.1, 127.2, 127.1, 21.4.

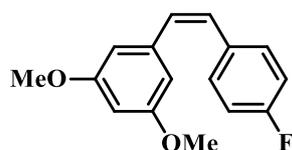


**3h: (Z)-1-(4-propylstyryl)-4-methoxybenzene**, Colorless liquid (39 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23 – 7.19 (m, 4H), 7.05 (d,  $J = 8.0$  Hz, 2H), 6.79 – 6.75 (m, 2H), 6.49 (s, 2H), 3.80 (s, 3H), 2.56 (t,  $J = 8.0$  Hz, 2H), 1.68 – 1.59 (m, 2H), 0.95 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.7, 141.6, 135.0, 130.2,

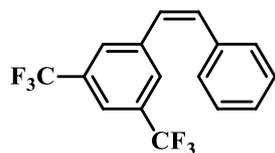
130.1, 129.2, 128.9, 128.8, 128.4, 113.7, 55.3, 37.9, 24.6, 14.0; HRMS(ESI)  $m/z$   
Calcd for  $C_{18}H_{20}O$   $[M+H]^+$  253.1514, Found 253.1582.



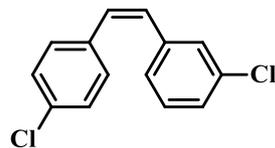
**3i: (Z)-1,2-bis(4-methoxyphenyl)ethene,**<sup>[23]</sup> Colorless liquid (34 mg, 71% yield).  $^1H$   
NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.22 – 7.20 (m, 4H), 6.79 – 6.77 (m, 4H), 6.46 (s, 2H),  
3.80 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  158.7, 130.2, 130.1, 128.5, 113.7, 55.3.



**3j: (Z)-1,2-bis(4-methoxyphenyl)ethene,**<sup>[24]</sup> Colorless liquid (39 mg, 75% yield).  $^1H$   
NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.25 – 7.22 (m, 2H), 6.93 (t,  $J = 8.4$  Hz, 2H), 6.57 – 6.50  
(m, 2H), 6.39 – 6.38 (m, 2H), 6.33 – 6.32 (m, 1H), 3.66 (s, 6H);  $^{13}C$  NMR (100  
MHz,  $CDCl_3$ ):  $\delta$  163.2, 160.8, 139.0, 133.3 (d,  $J_{C-F} = 3.4$  Hz), 130.8 (d,  $J_{C-F} = 7.9$  Hz),  
130.7, 130.4 (d,  $J_{C-F} = 1.2$  Hz), 129.6, 115.2 (d,  $J_{C-F} = 21.3$  Hz), 106.8, 100.0, 55.3.

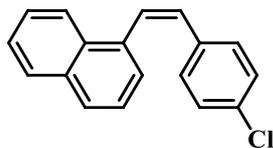


**3k: (Z)-1-styryl-3,5-bis(trifluoromethyl)benzene,**<sup>[25]</sup> Colorless liquid (47 mg, 75%  
yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.67 – 7.64 (m, 3H), 7.28 – 7.26 (m, 3H), 7.19  
– 7.17 (m, 2H), 6.84 (d,  $J = 12.4$  Hz, 1H), 6.59 (d,  $J = 12.4$  Hz, 1H);  $^{13}C$  NMR (100  
MHz,  $CDCl_3$ ):  $\delta$  139.3, 135.8, 134.1, 131.6 (q,  $J_{C-F} = 33.4$  Hz), 129.2 (m), 128.8 (d,  
 $J_{C-F} = 8.8$  Hz), 128.3, 127.2, 124.7, 122.0, 120.8-120.7 (m).



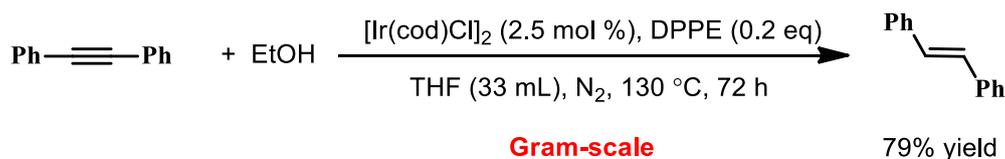
**3l: (Z)-2-(3-chlorophenyl)-1-(4-chlorophenyl)ethene,** Colorless liquid (35 mg, 70%  
yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.22 – 7.13 (m, 7H), 7.10 – 7.07 (m, 1H), 6.58  
(d,  $J = 12.0$  Hz, 1H), 6.54 (d,  $J = 12.0$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  138.9,

135.1, 134.4, 133.3, 130.4, 130.3, 129.7, 129.5, 128.9, 128.7, 127.5, 127.0;  
HRMS(ESI)  $m/z$  Calcd for  $C_{14}H_{10}Cl_2$  248.0160, Found 248.0165.



**3m: (Z)-1-(4-chlorostyryl)naphthalene**, Colorless liquid (41 mg, 78% yield).  
 $^1H$ NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.06 – 8.04 (m, 1H), 7.90 – 7.88 (m, 1H), 7.79(d,  $J$  = 8.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 7.10 – 6.99 (m, 5H), 6.79 (d,  $J$  = 12.0 Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  135.3, 135.0, 133.8, 132.8, 131.6, 130.9, 130.4, 129.4, 128.6, 128.4, 127.9, 126.5, 126.3, 126.2, 125.7, 124.9;  
HRMS(ESI)  $m/z$  Calcd for  $C_{18}H_{13}Cl$   $[M+H]^+$  265.0784, Found 265.0788.

## 7. Gram-scale Synthesis

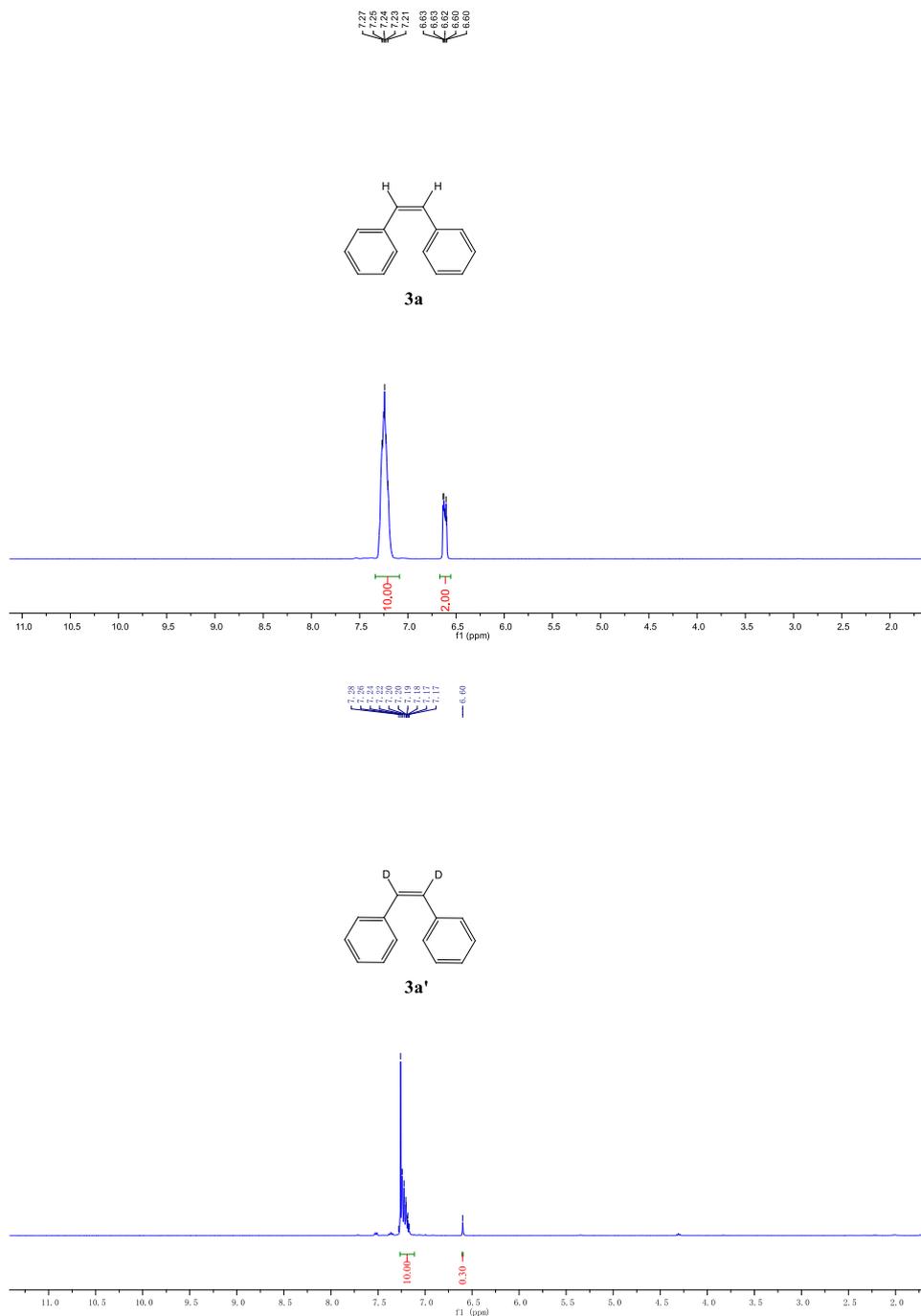


According to the typical procedure: To a 250 mL pressure tube were added diphenylacetylene **1** (5.62 mmol, 1.0 g),  $[Ir(cod)Cl]_2$  (141  $\mu$ mol, 94 mg), DPPE (1.12 mmol, 447 mg) under  $N_2$ , and then EtOH (56.2 mmol, 3.26 mL), and THF (33 mL) were added. The resulting solution was stirred at 130  $^{\circ}C$  for 72 h. After column purification (*n*-Hexane), coupling product was obtained (0.8 g, 79% yield).

## 8. Deuterium Labeling Experiments

To a 15 mL pressure tube were added diphenylacetylene **1** (0.20 mmol),  $[Ir(cod)Cl]_2$  (5  $\mu$ mol, 3.6mg), DPPE (0.04 mmol, 15.9mg) under  $N_2$ , and then  $C_2D_5OH$  or  $C_2H_5OD$  (4 mmol, 232  $\mu$ L), COD (0.4 mmol, 49  $\mu$ L), THF or tetrahydrofuran- $d_8$  (1.5 mL) were added. The resulting solution was stirred at 120  $^{\circ}C$  for 44 h. After the reaction was completed, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried

over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in *vacuo*. The crude product was purified by column chromatography (*n*-Hexane) to afford the desired cis-stilbene **3a** or di-deuterated product **3a'**.

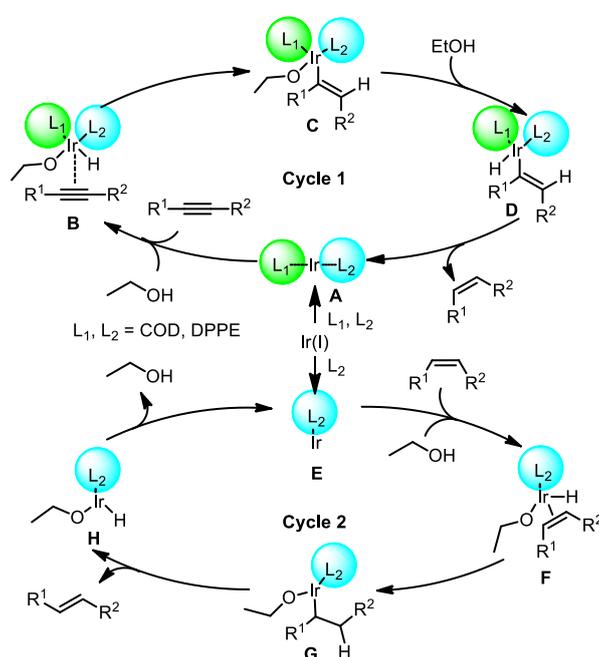


## 9. Zebrafish Experiments

At 6 hpf, embryos were screened under anatomical microscope to remove the morphologically abnormal individuals. Around 10 healthy embryos were loaded into

each well of 96-well plate in E3 solution. At the setting time, E3 solutions were replaced with different pinosylvin or DHS treatment solutions. The control and treated groups were analyzed at different intervals. At 55 hpf, the *Tg(fli1a:nEGFP)* zebrafish embryos were collected for imaging. At 55 hpf, for confocal imaging embryos were anesthetized with E3/0.16 mg/mL tricaine/1% 1-phenyl-2-thiourea (Sigma) and embedded in 0.8% low melt agarose. Confocal imaging was performed with a Leica TCS-SP8 LSM. Analysis was performed using Imaris software.

## 10. Possible Mechanism



**Figure 1** Possible mechanism

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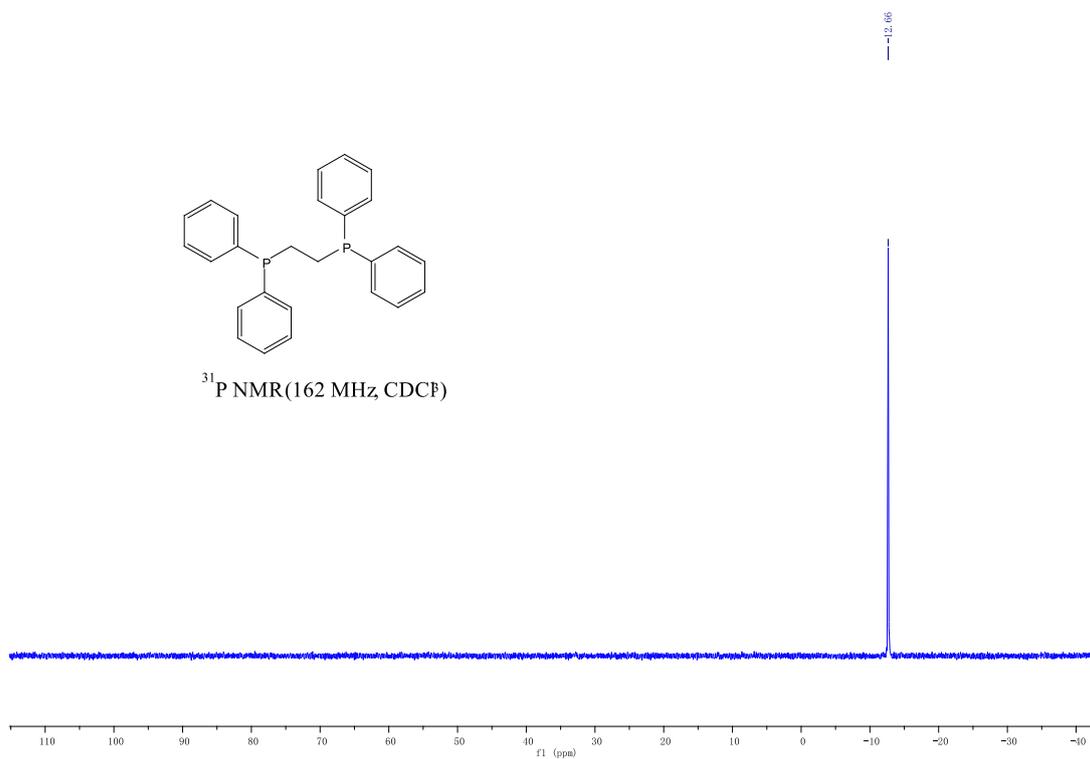
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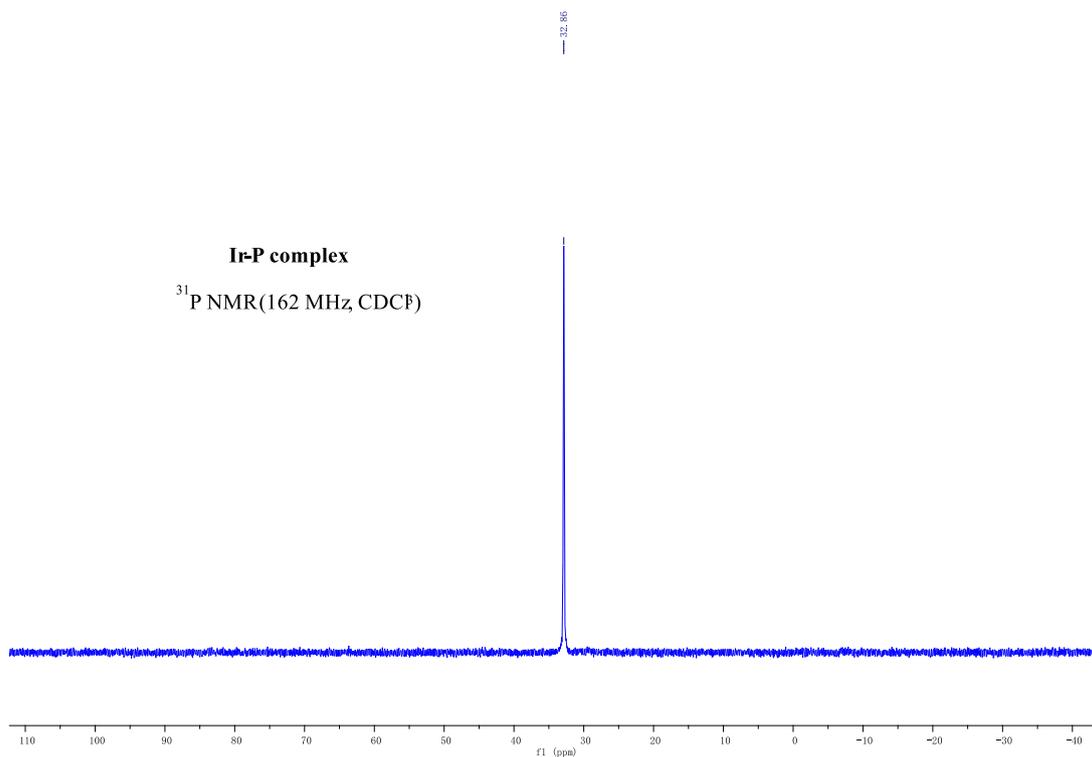
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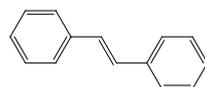
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## 11. NMR Spectra

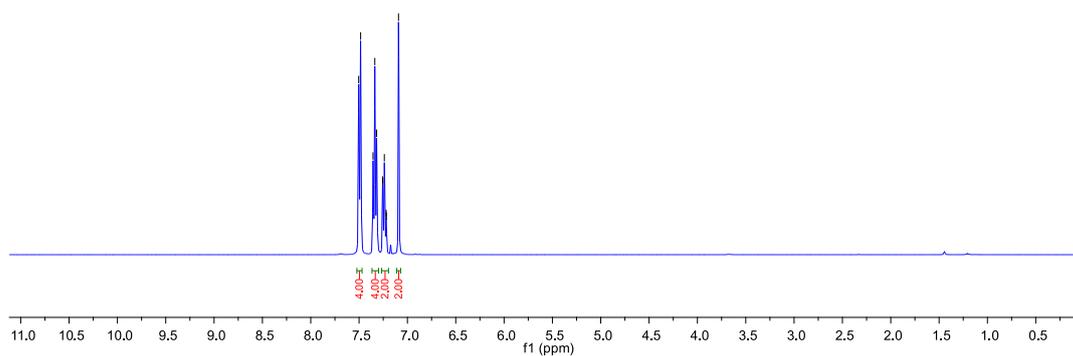




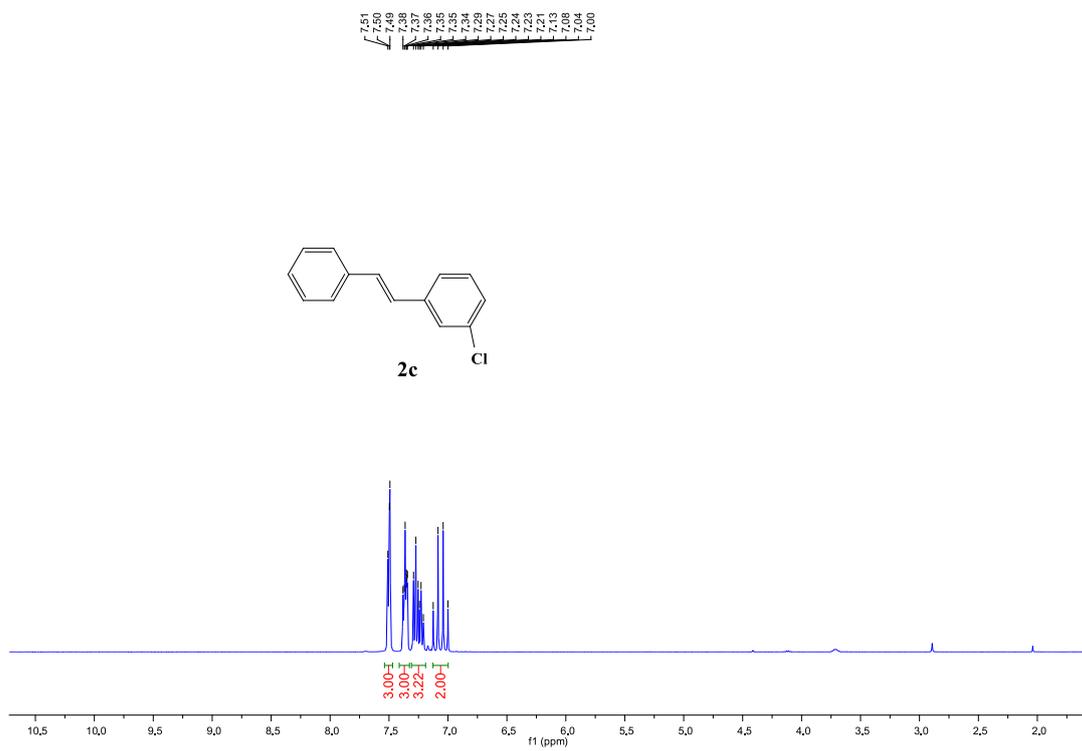
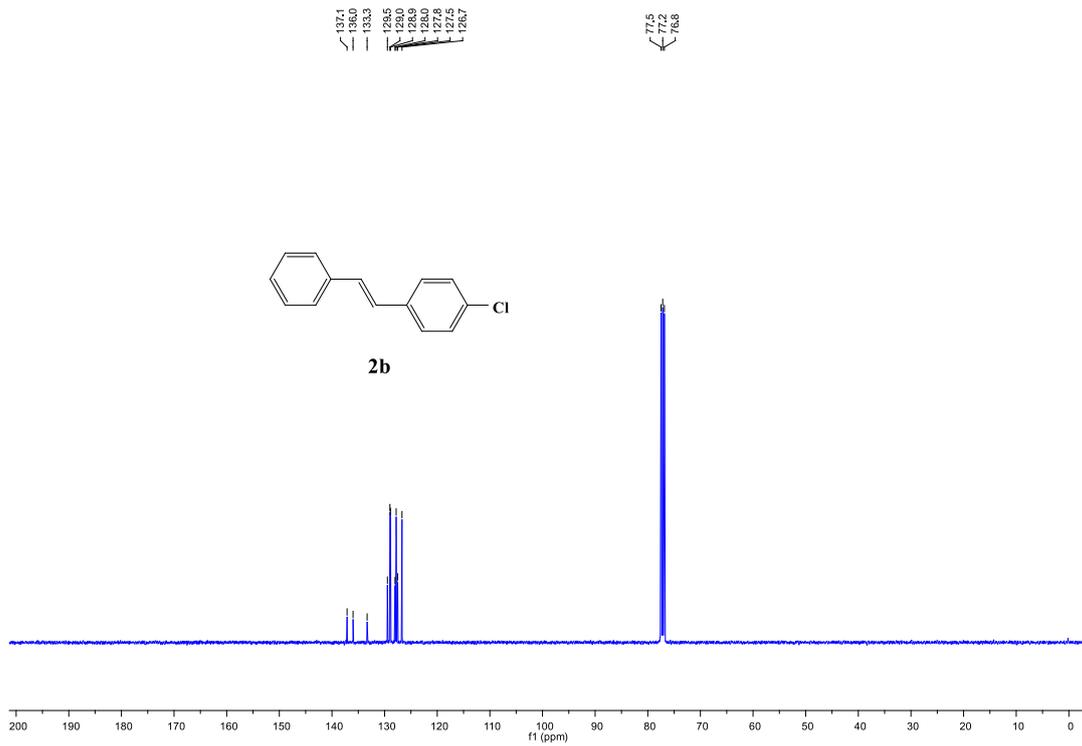
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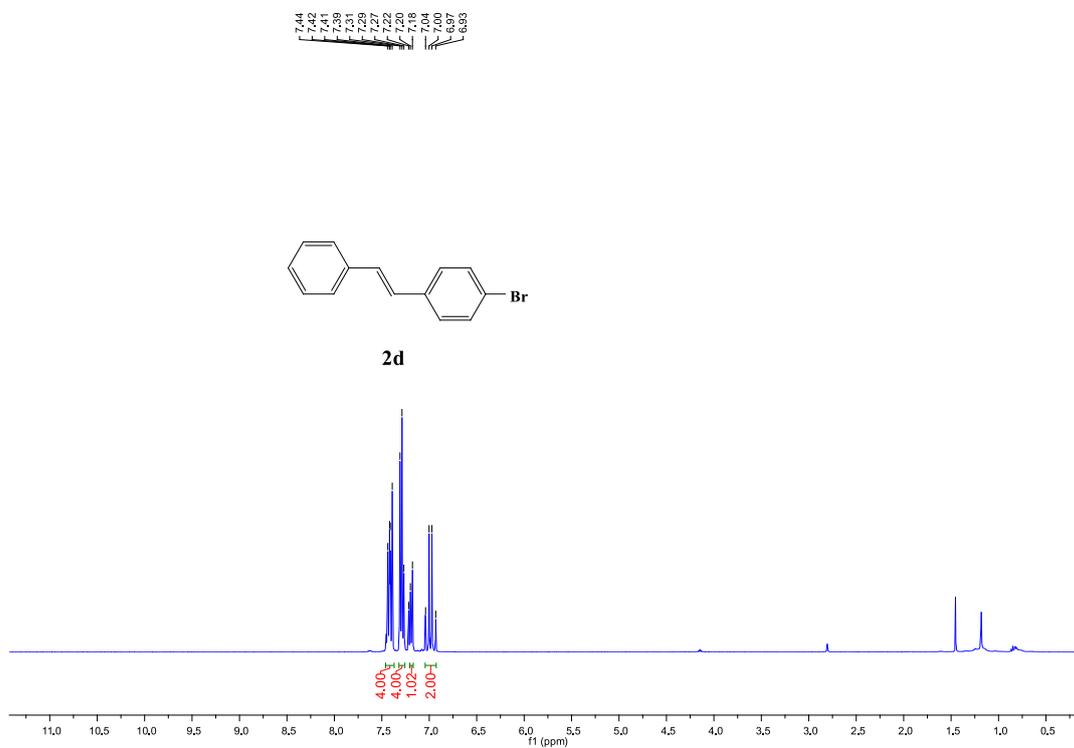
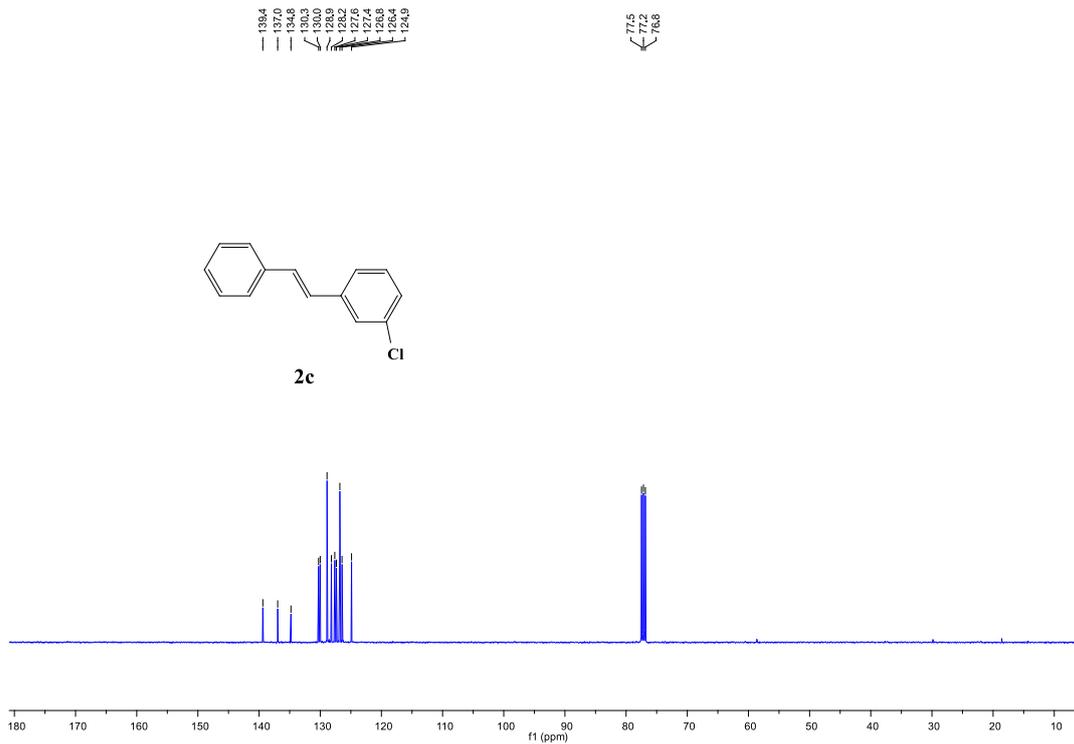


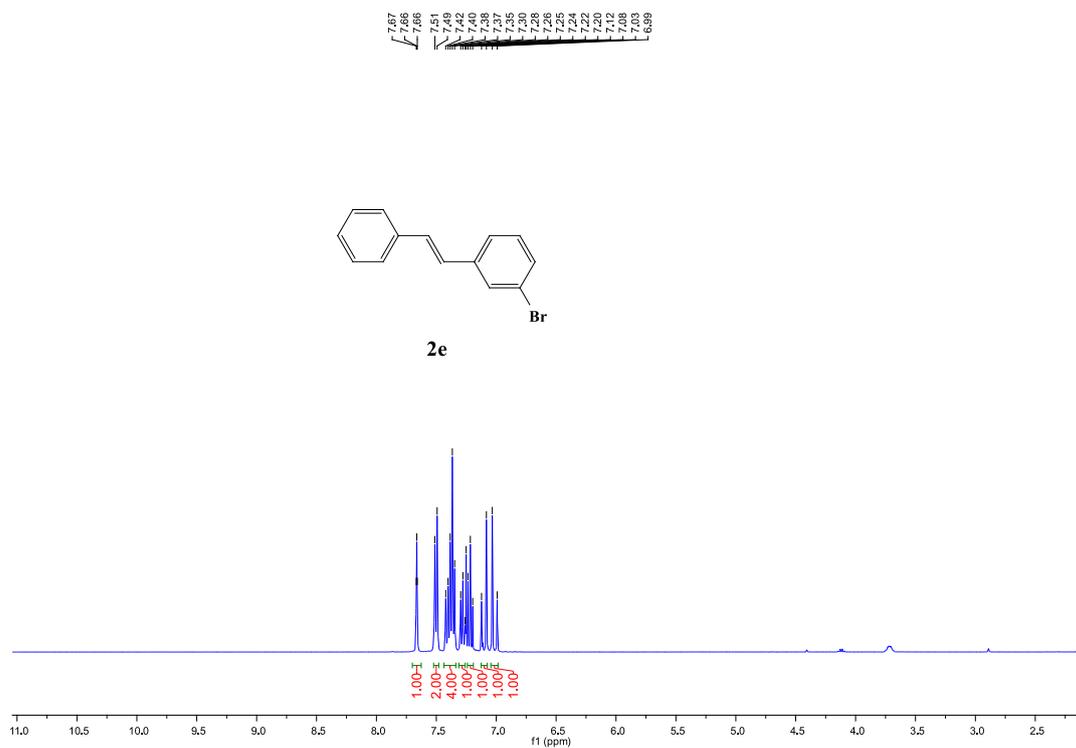
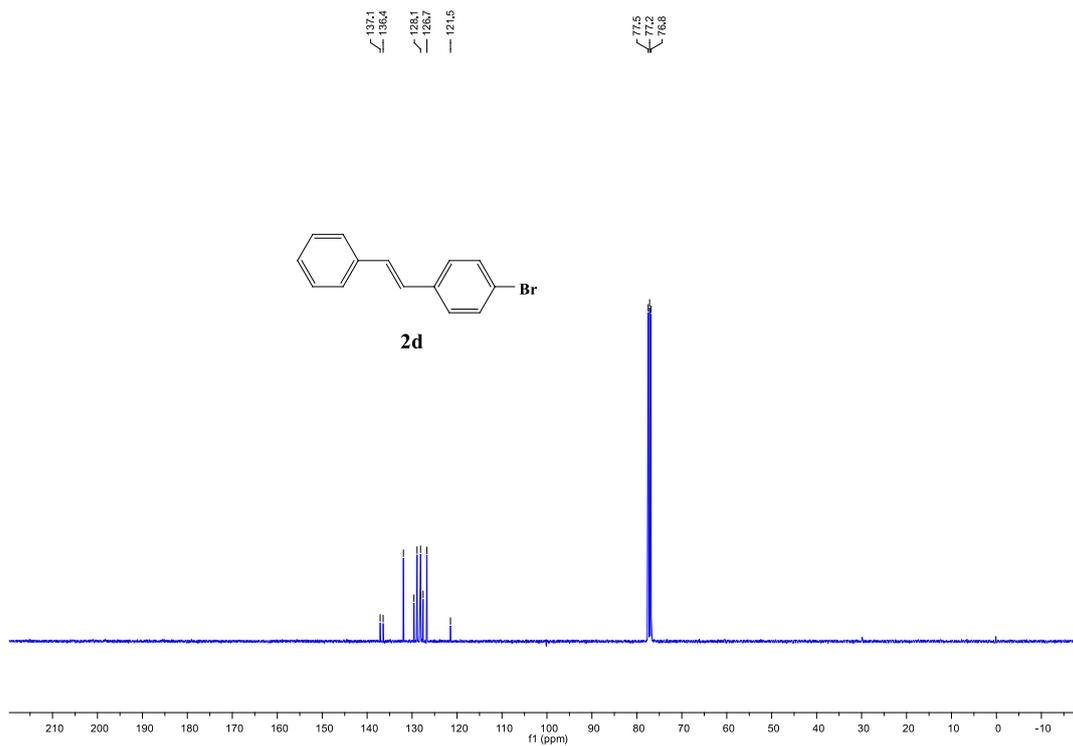
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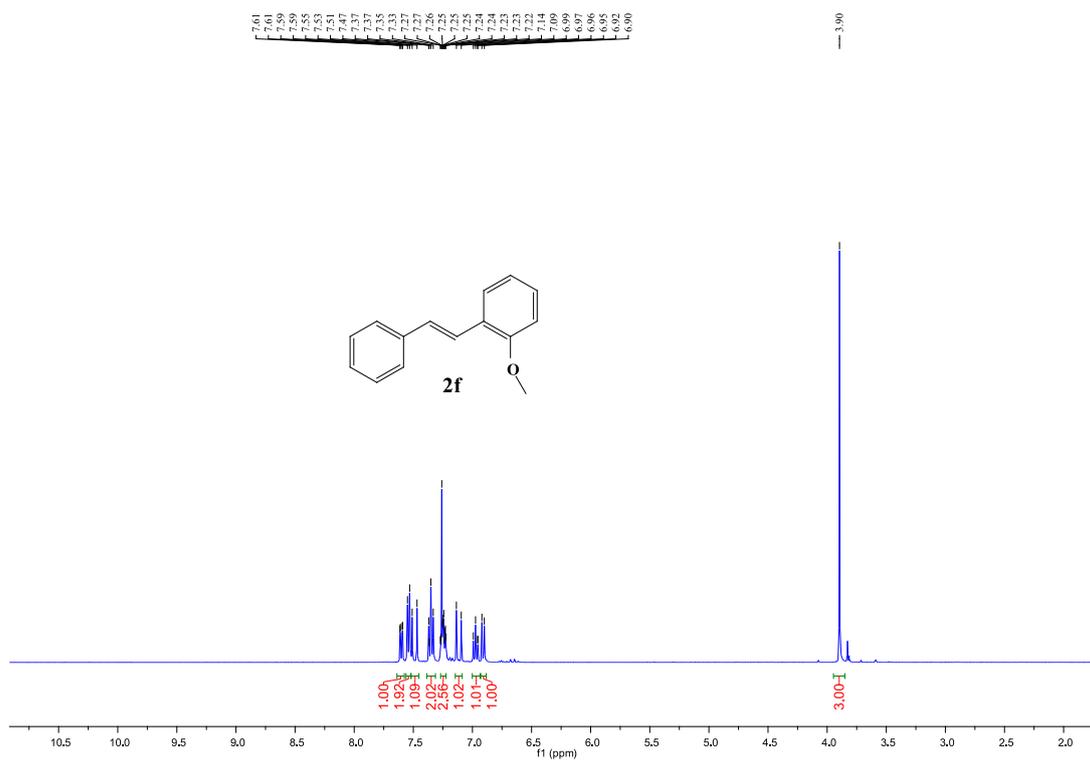
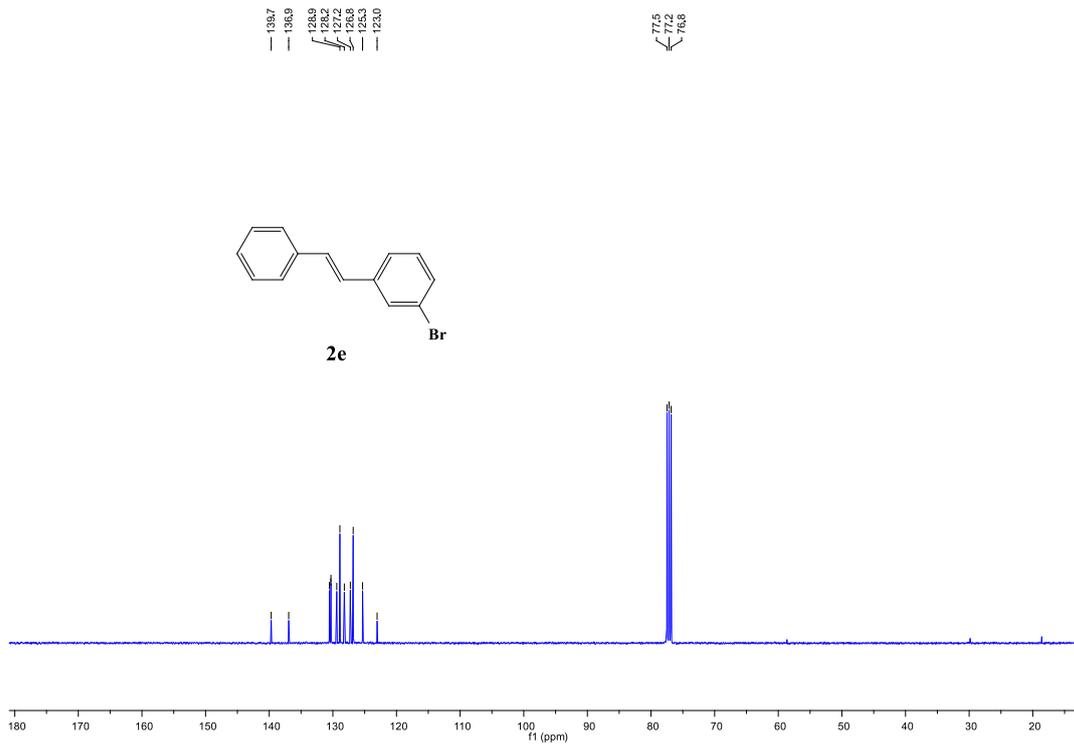


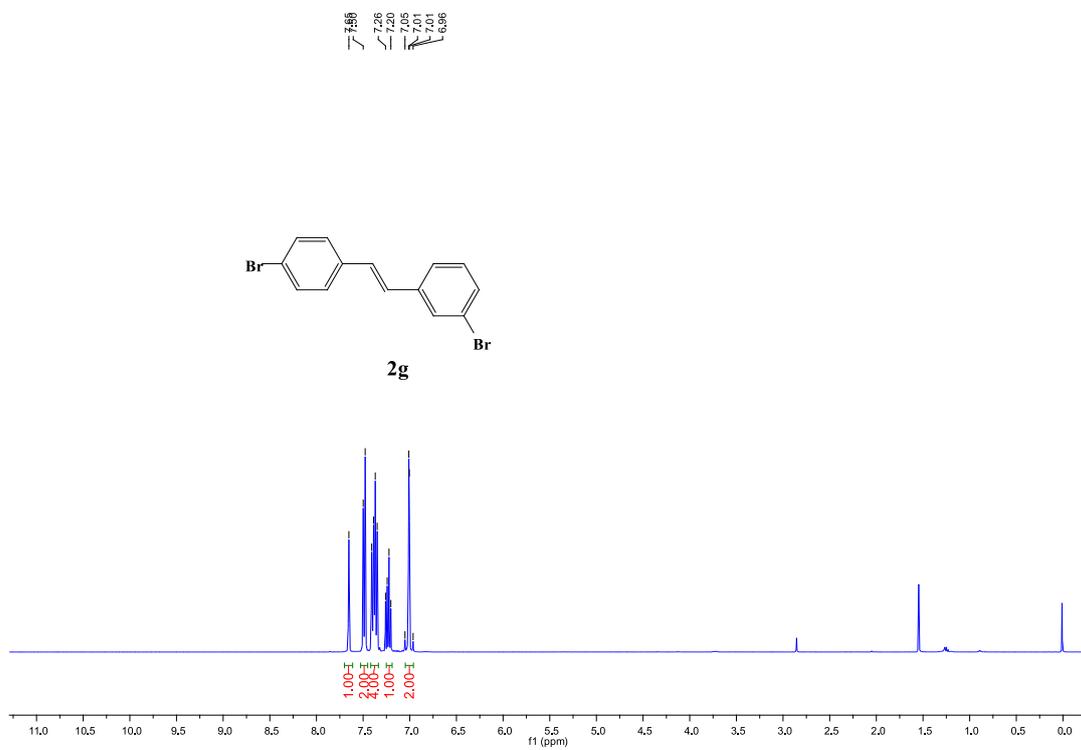
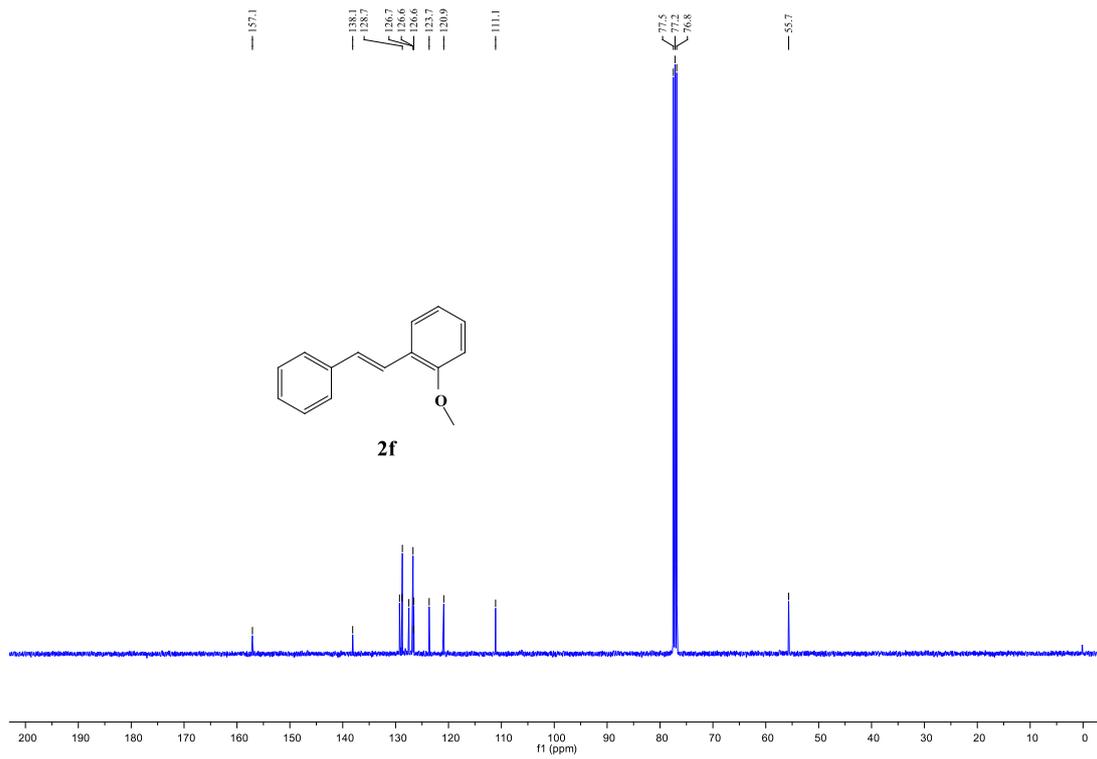


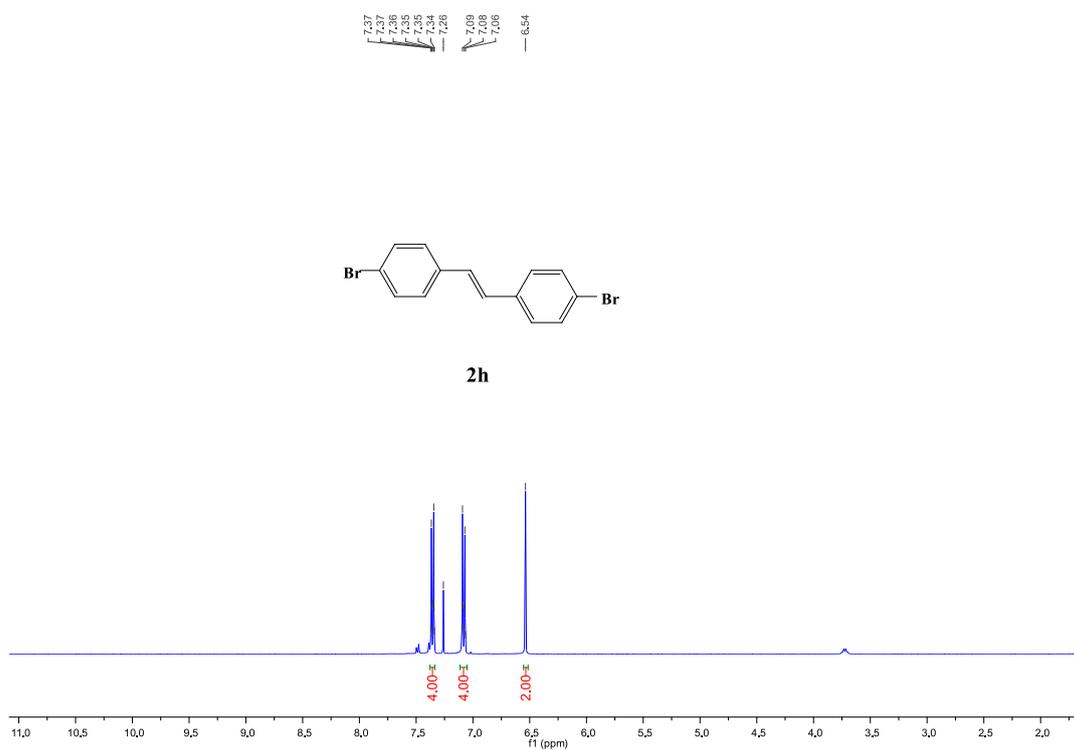
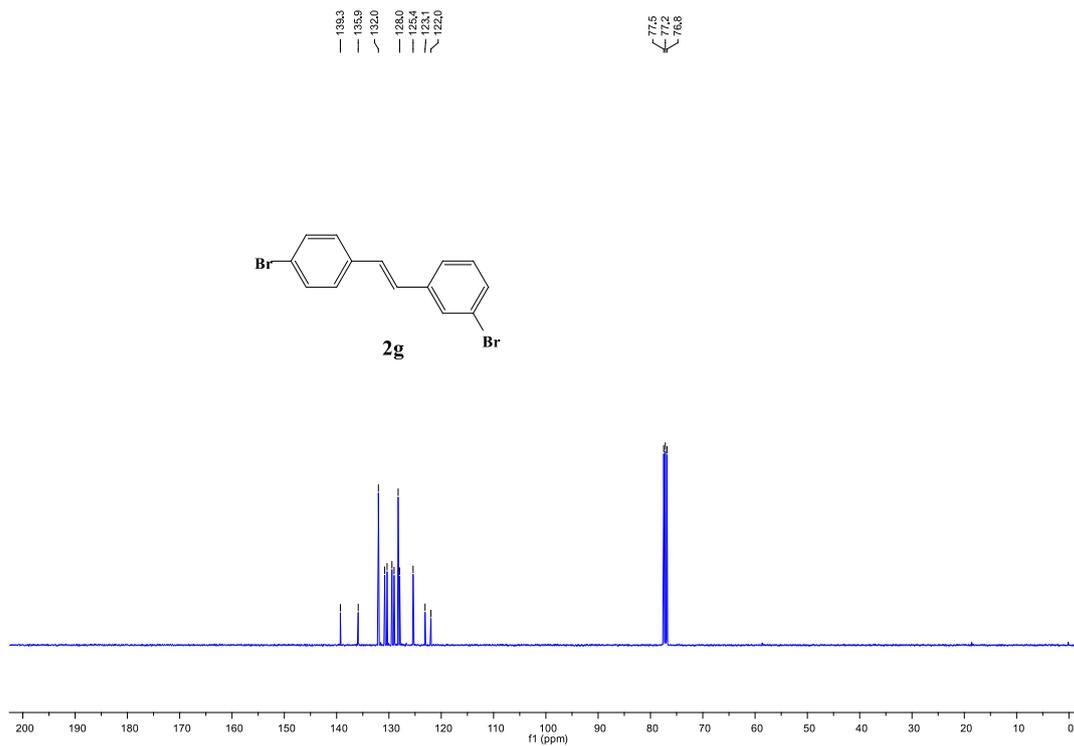


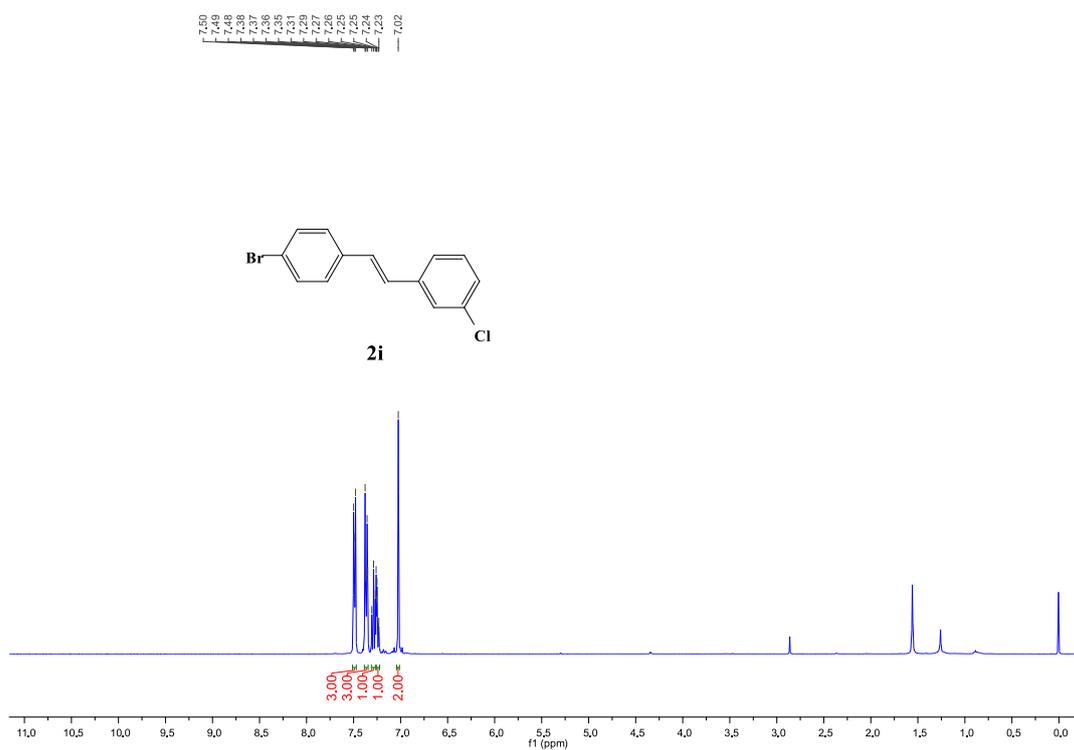
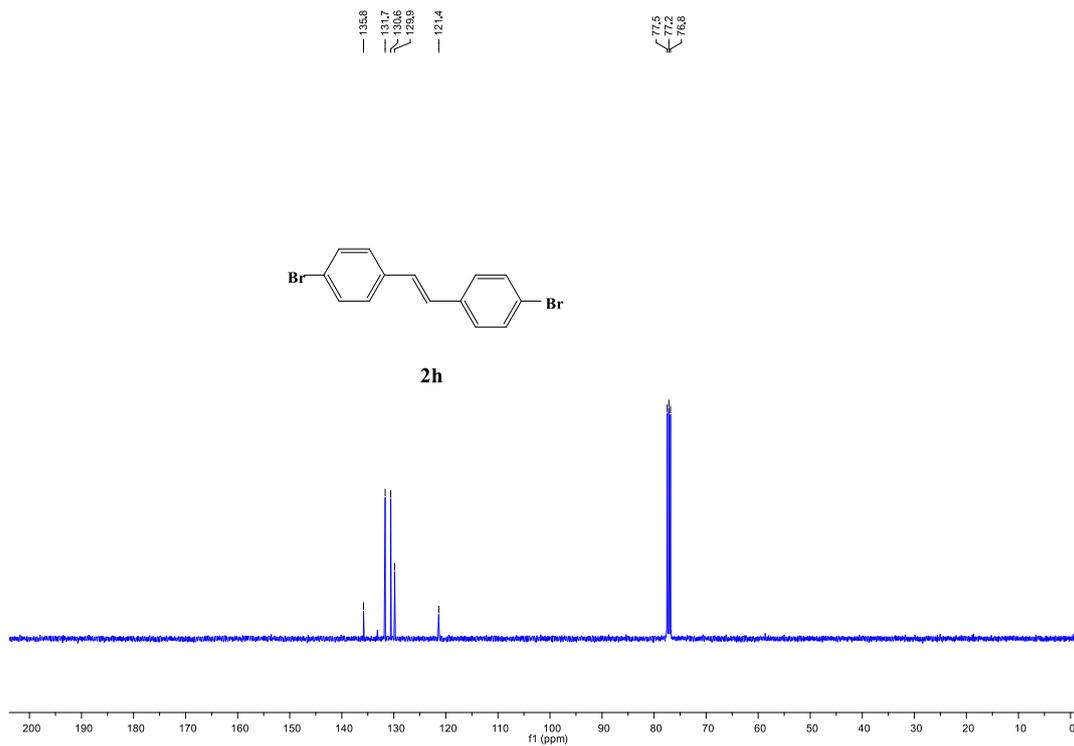


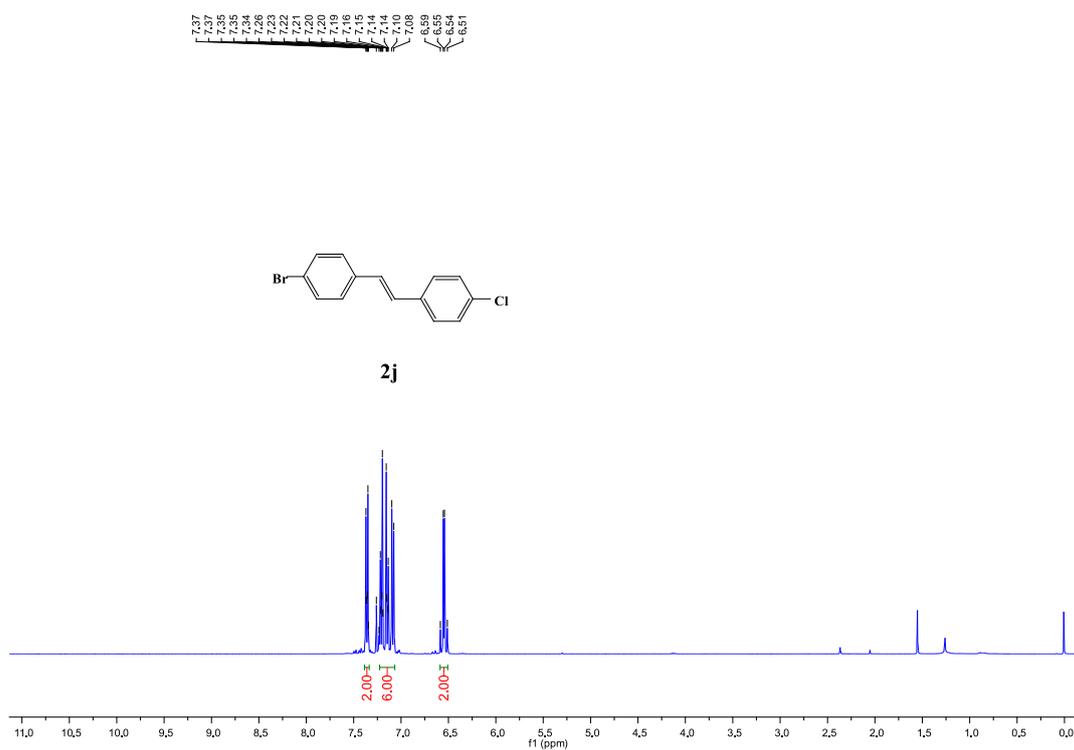
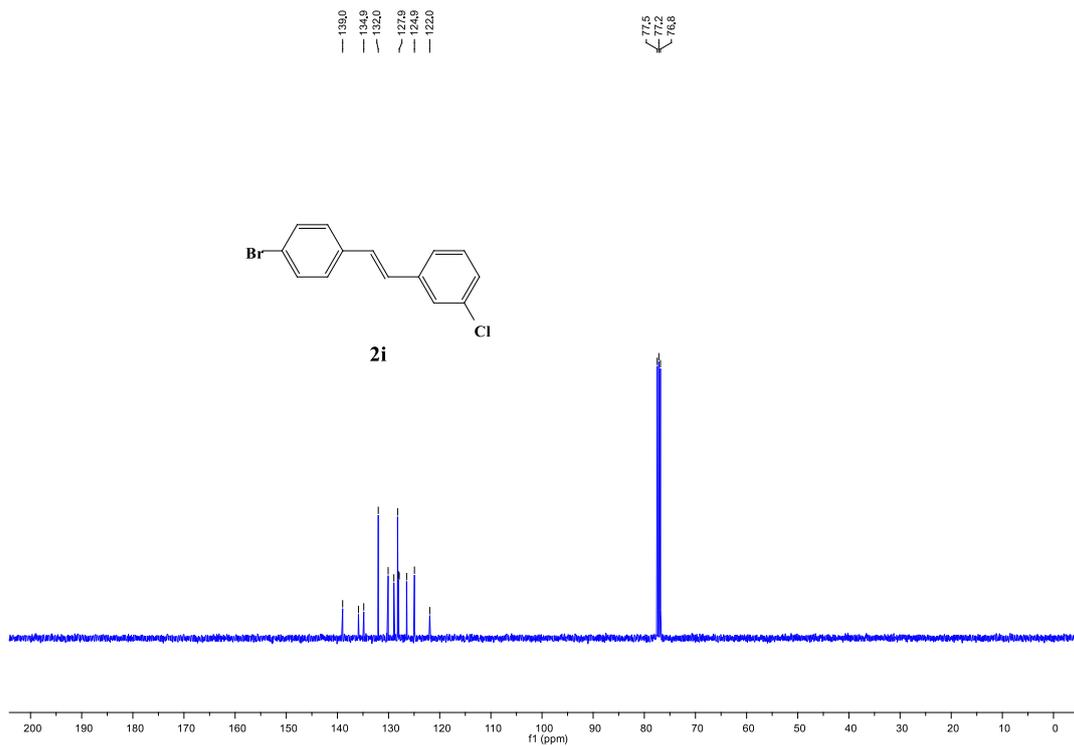


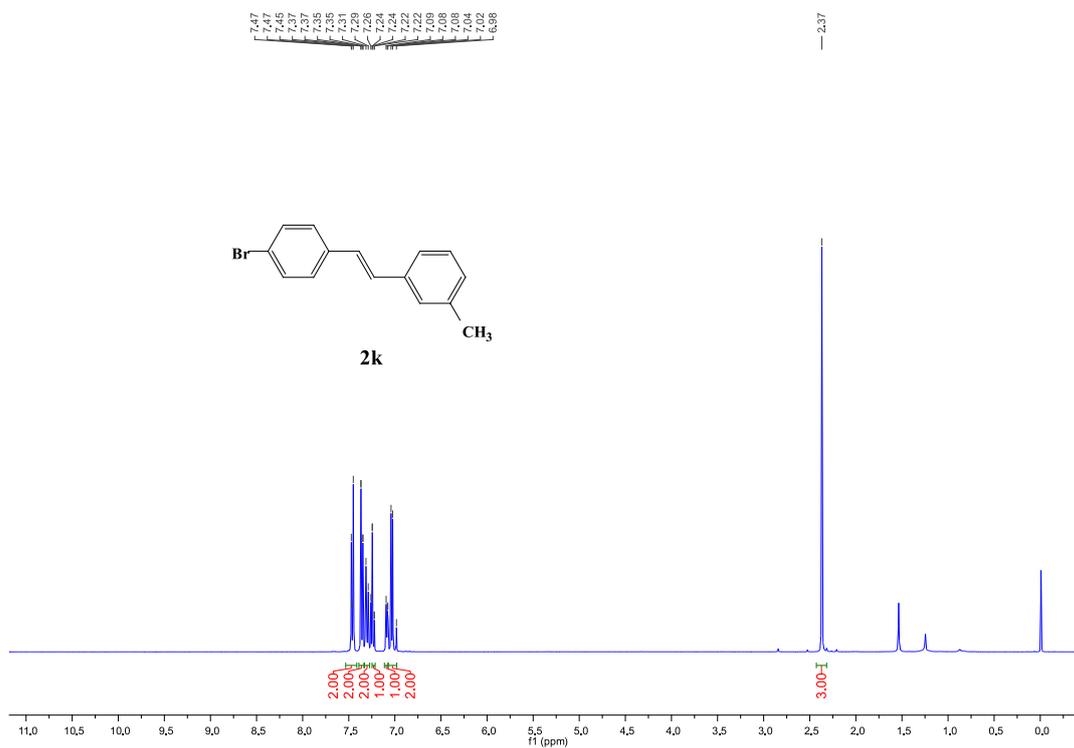
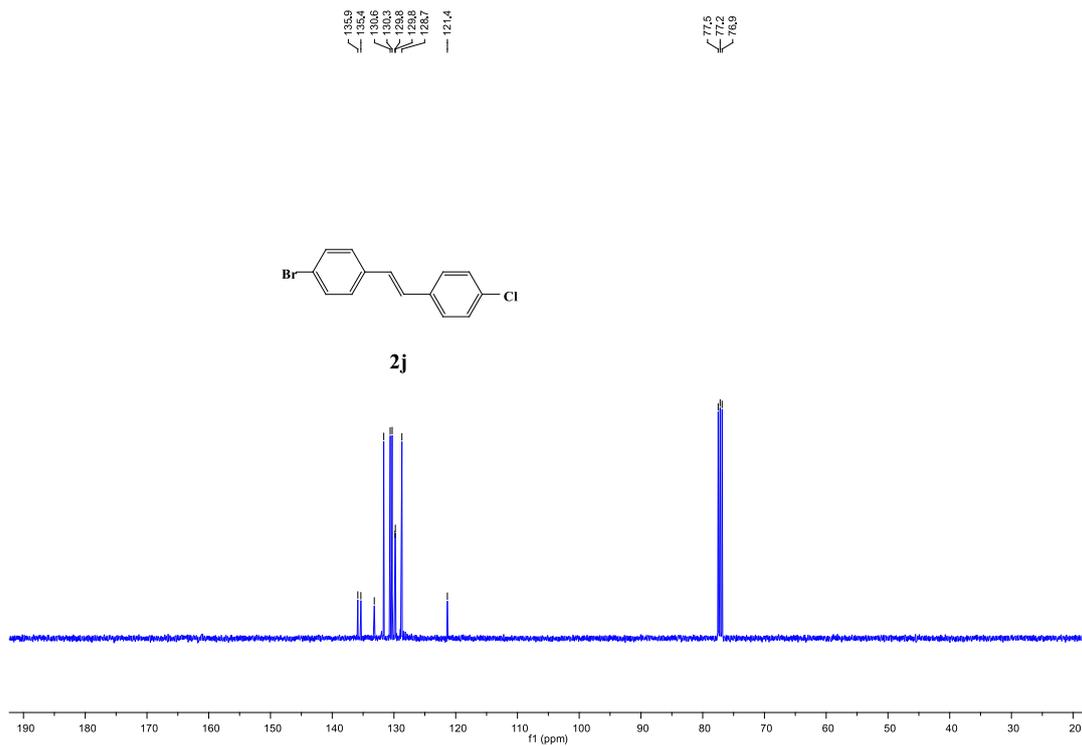


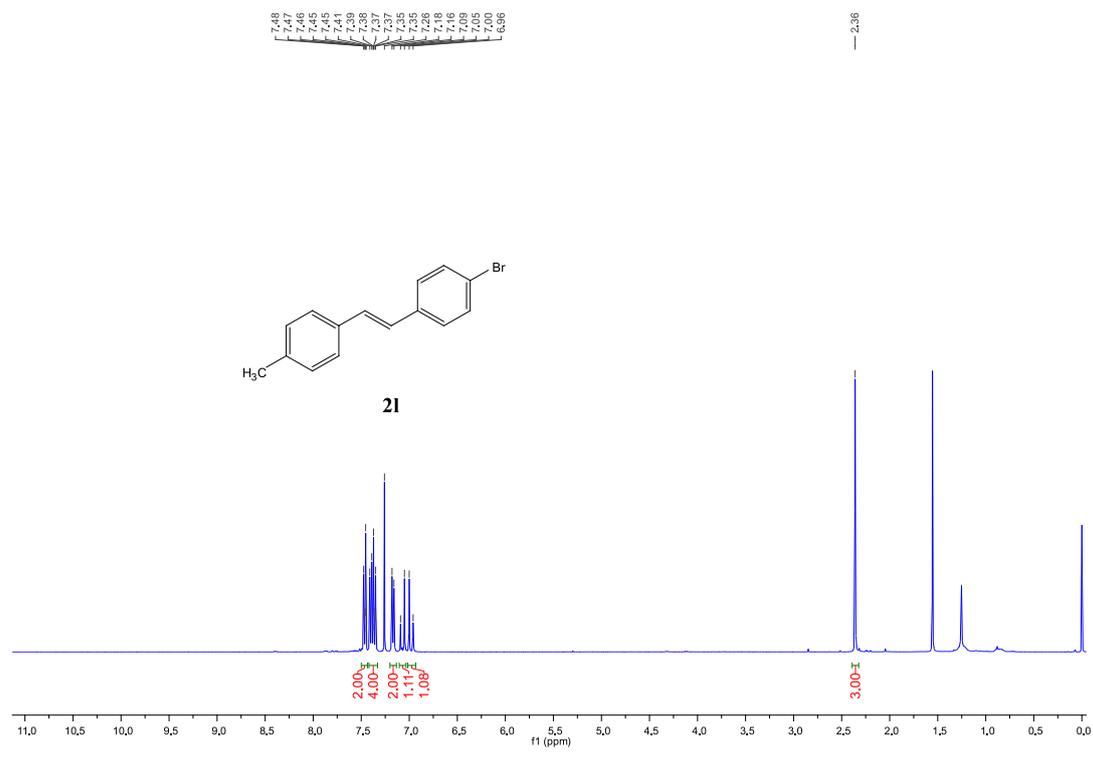
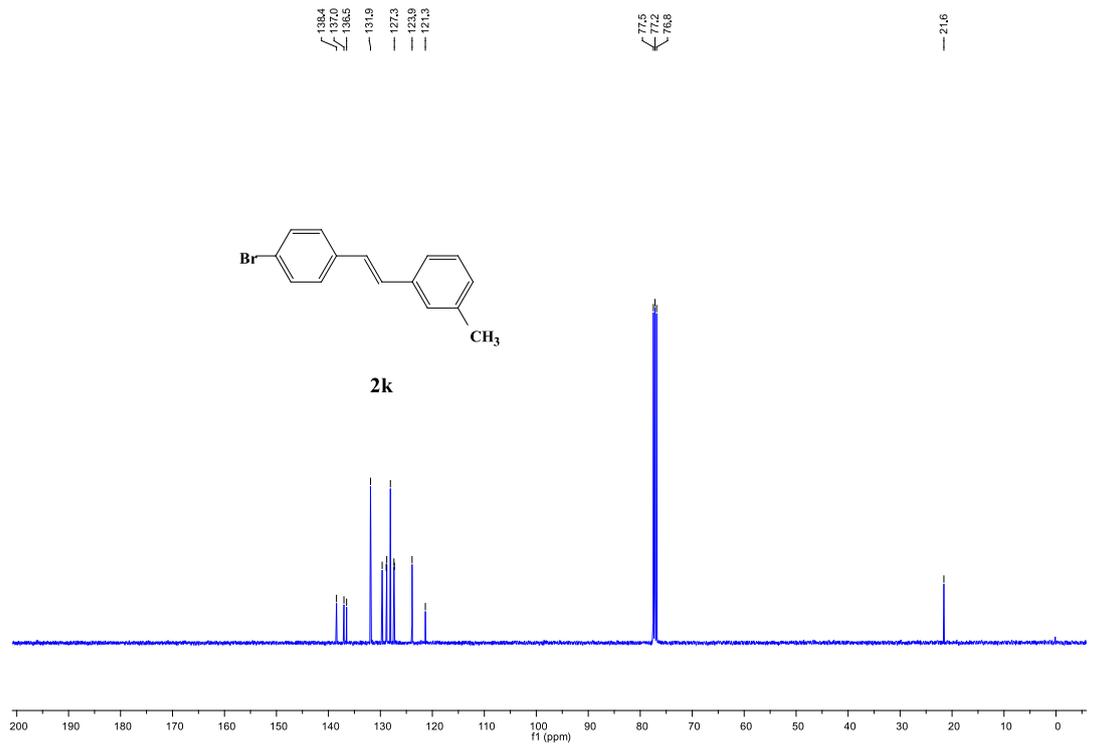


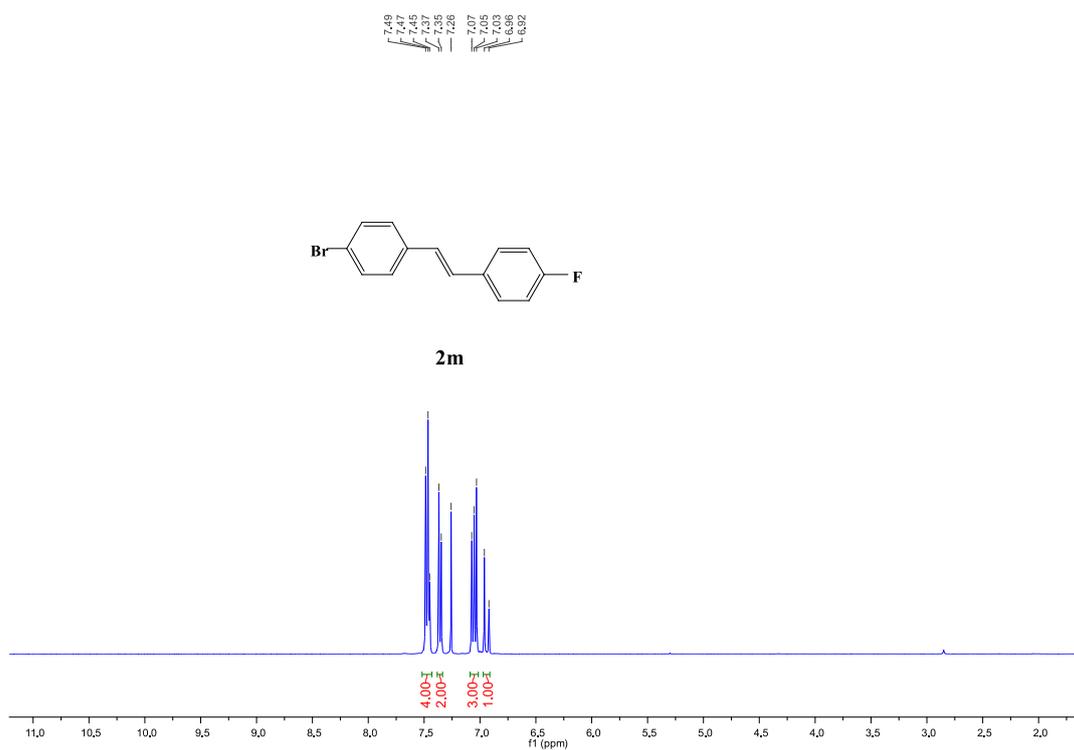
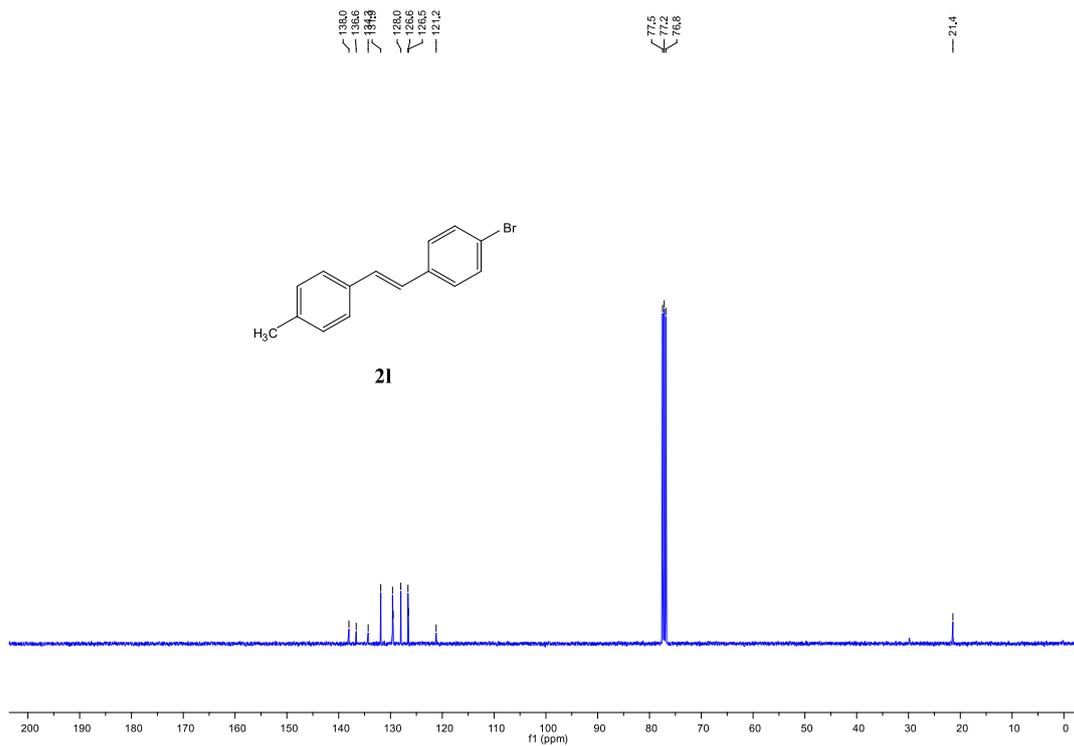


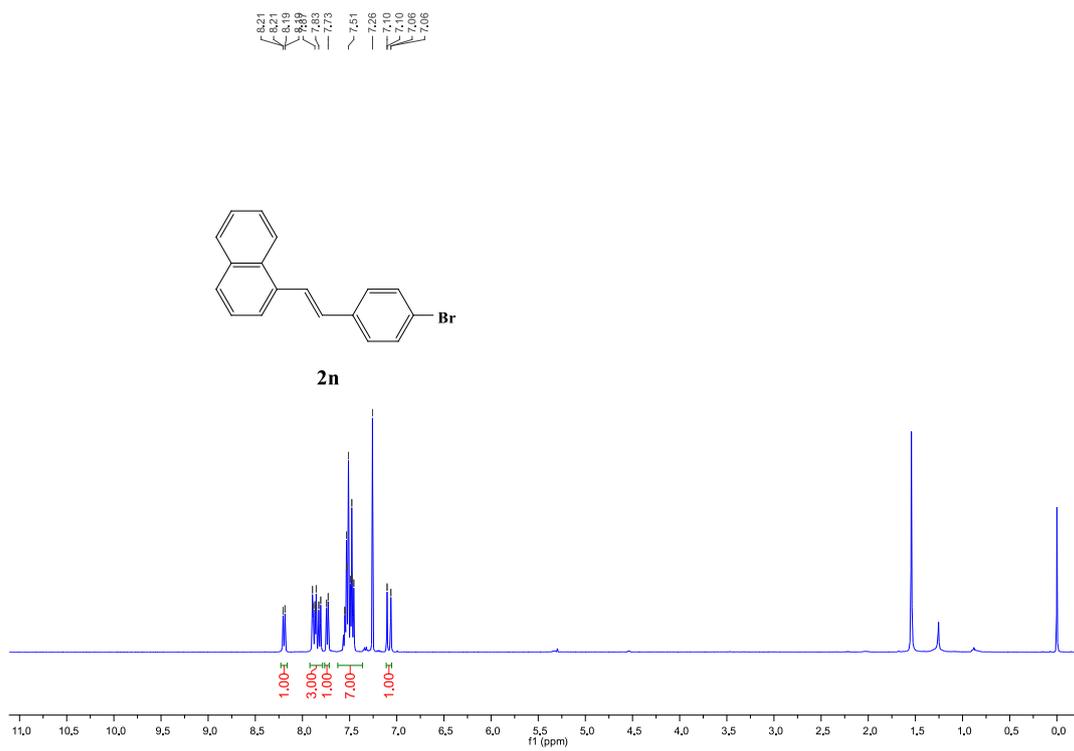
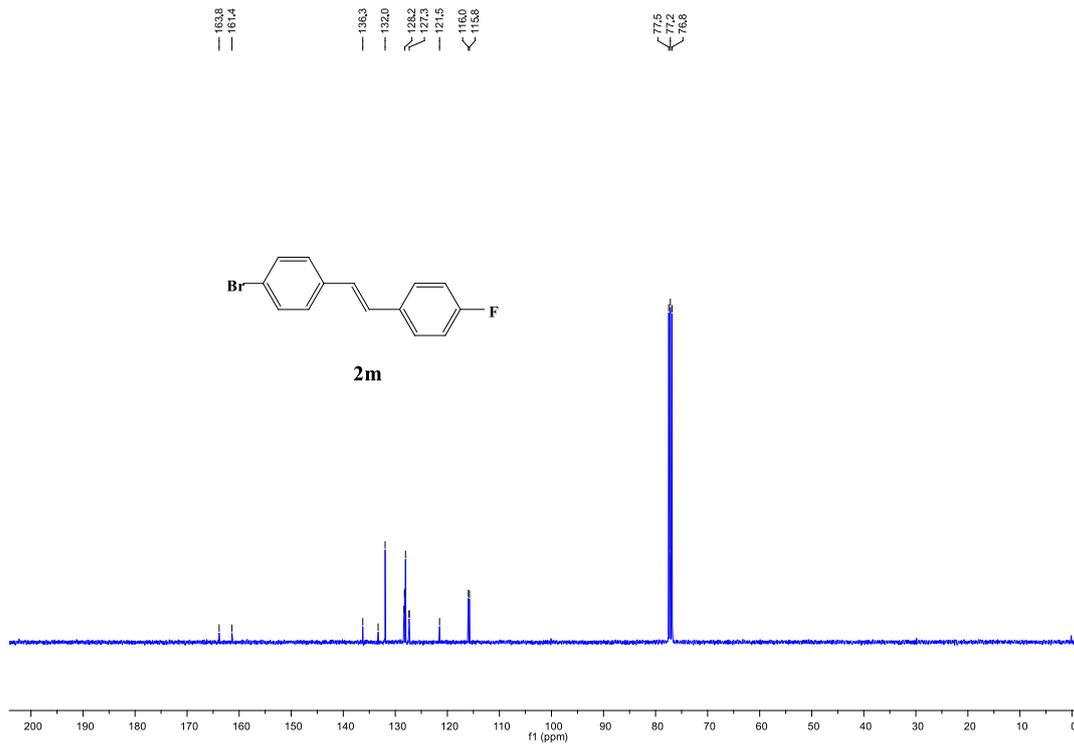


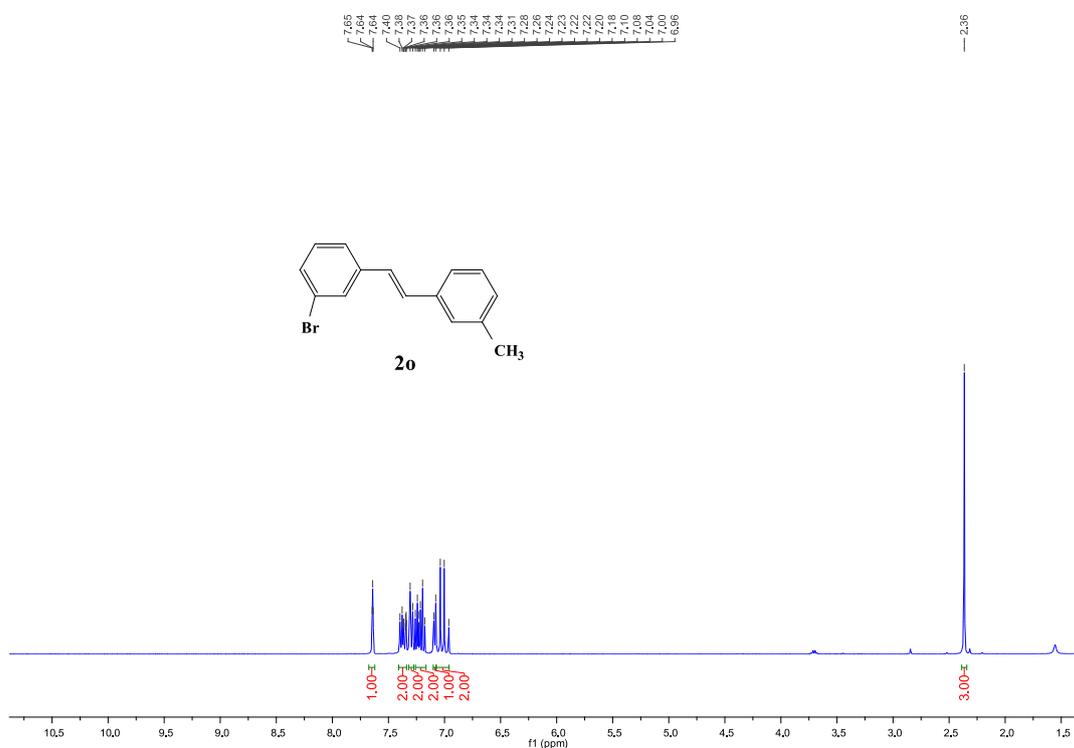
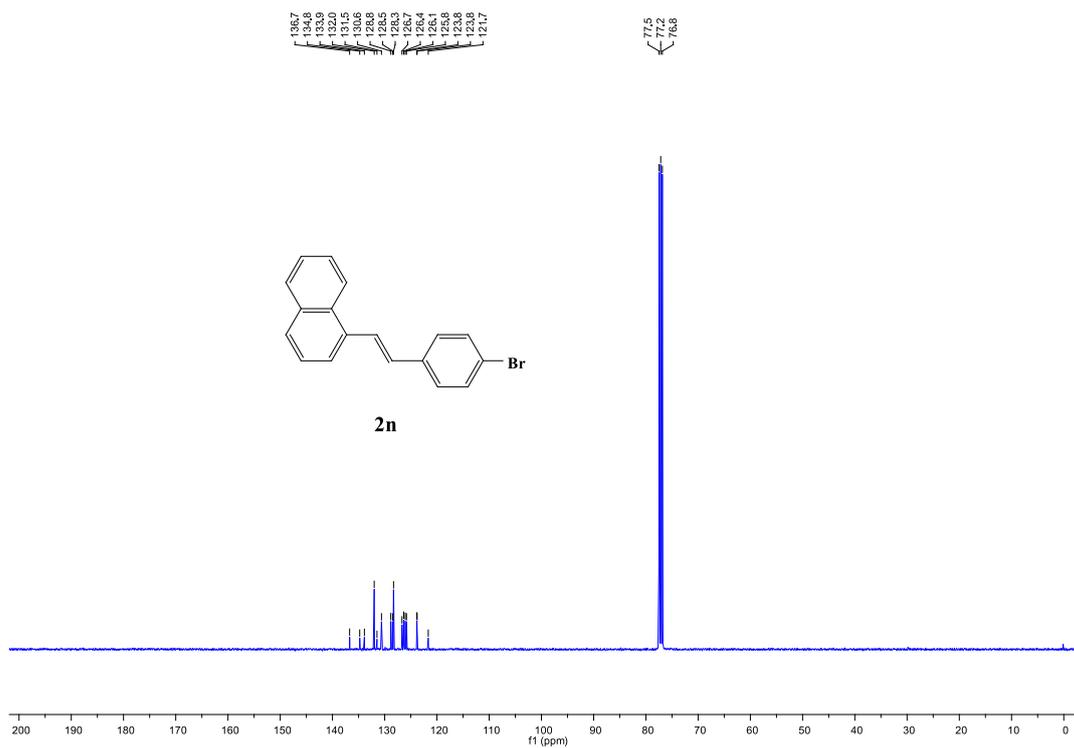


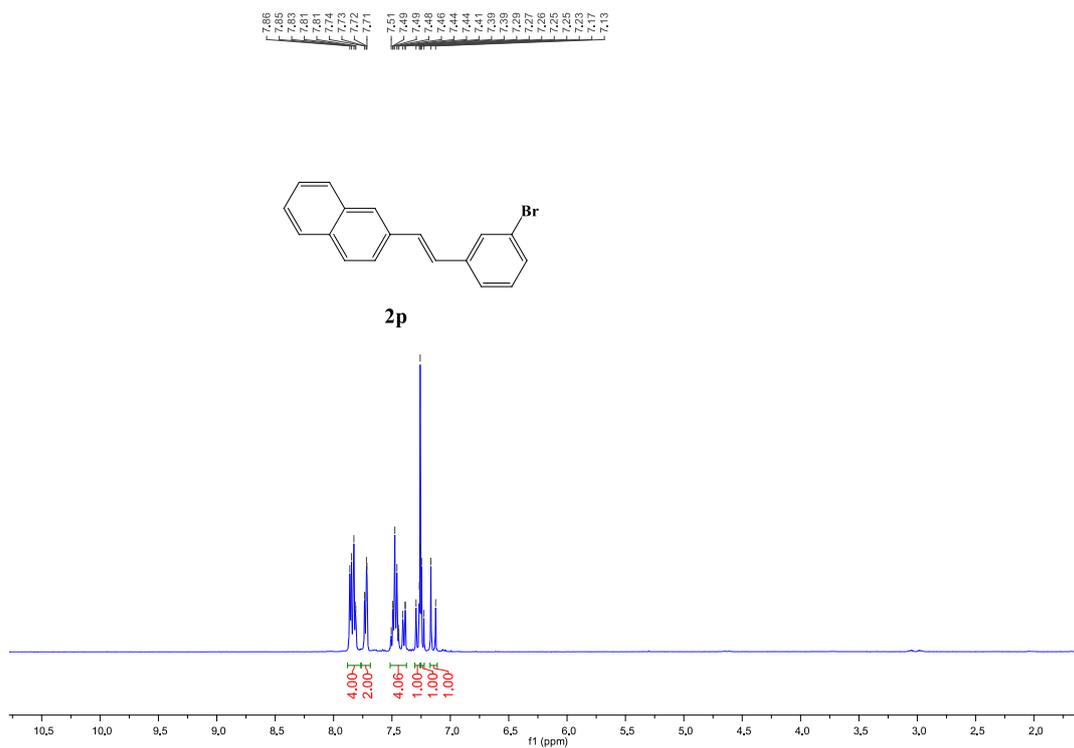
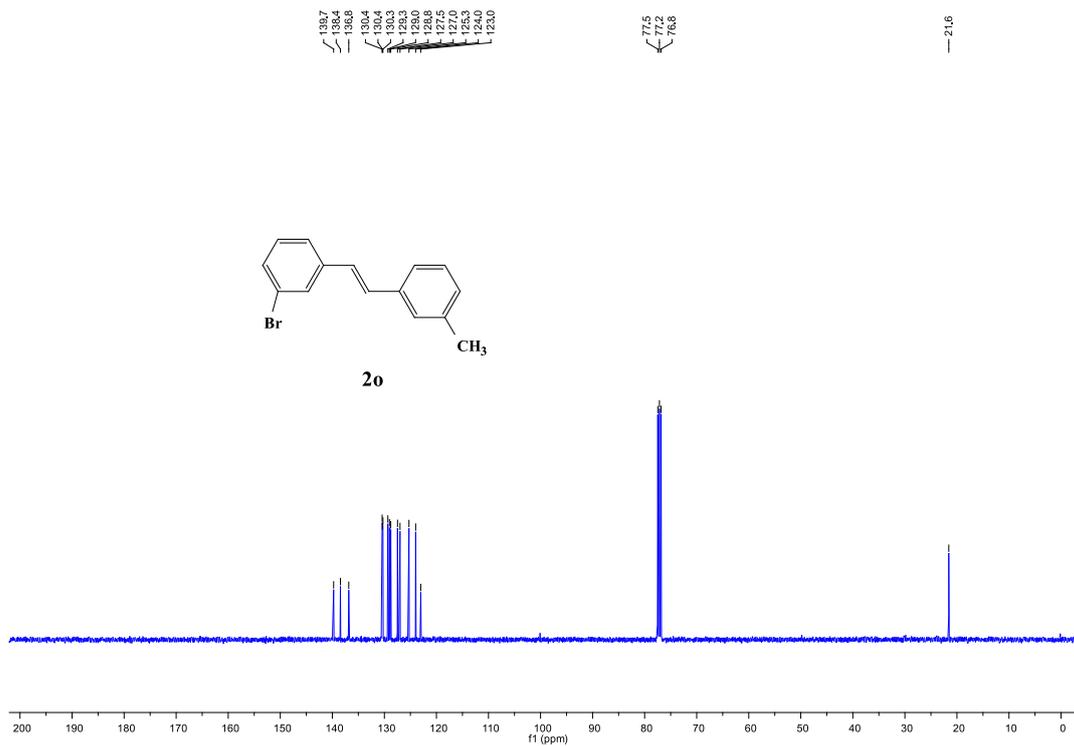


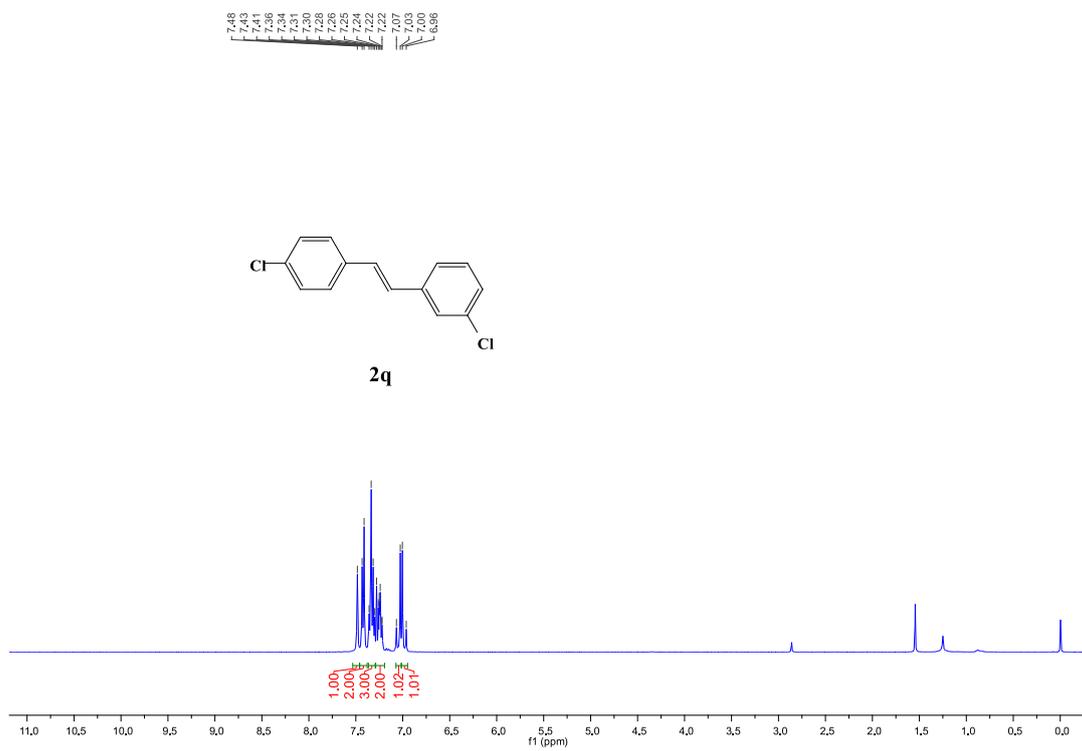
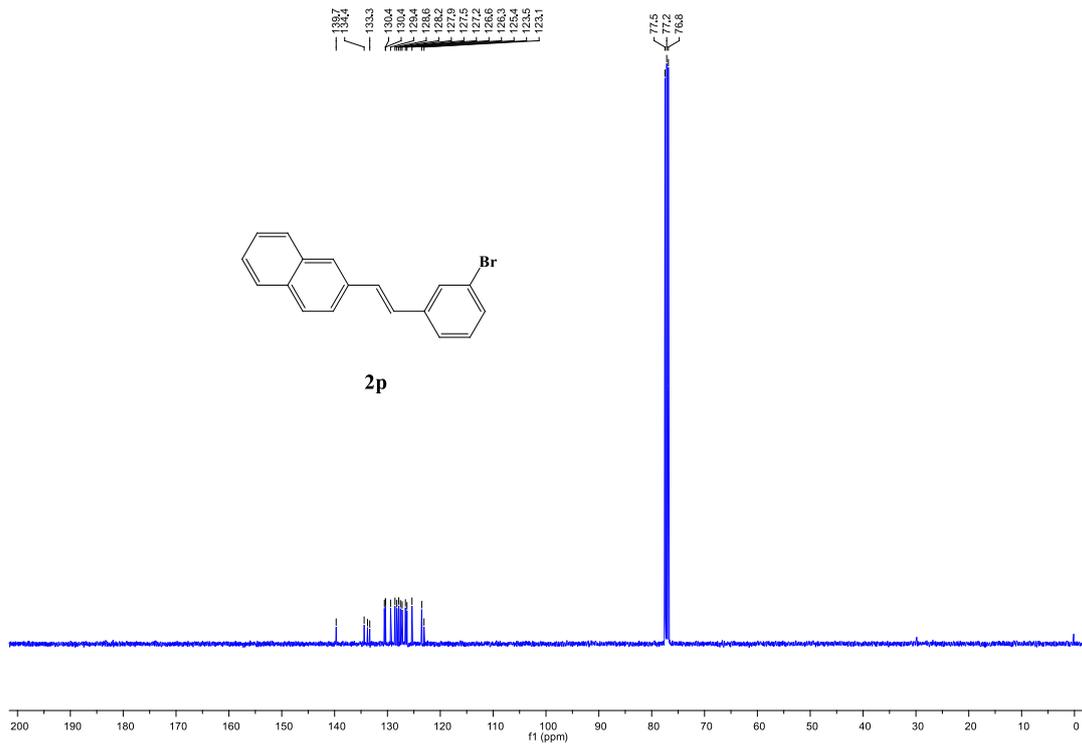


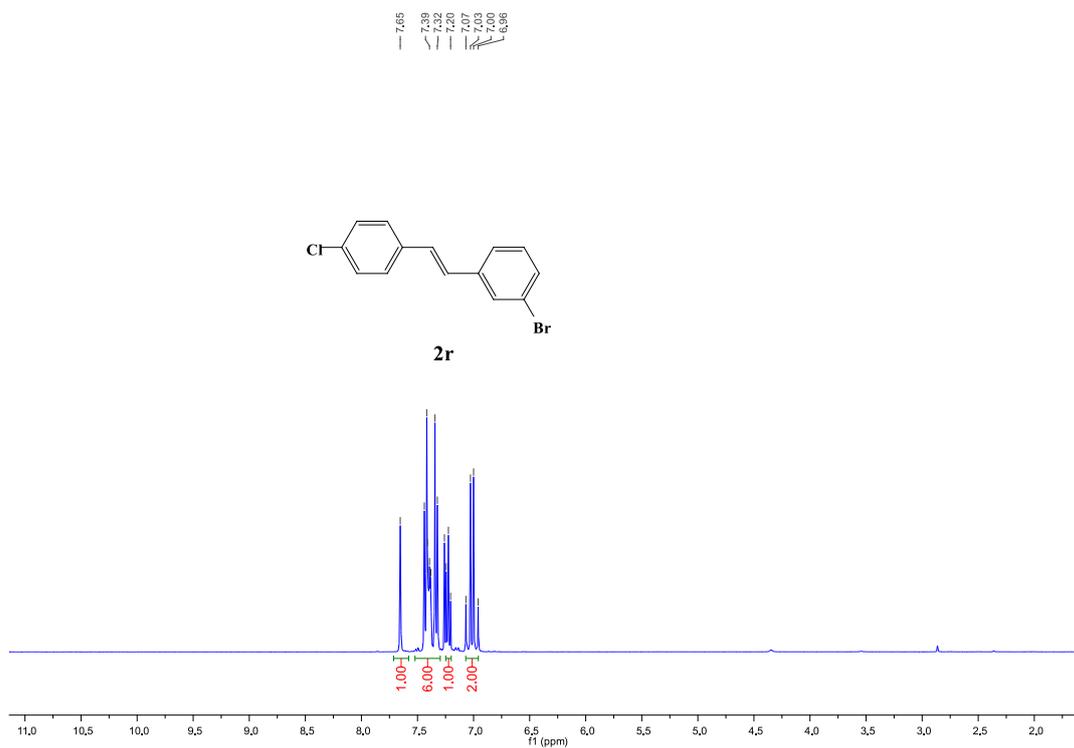
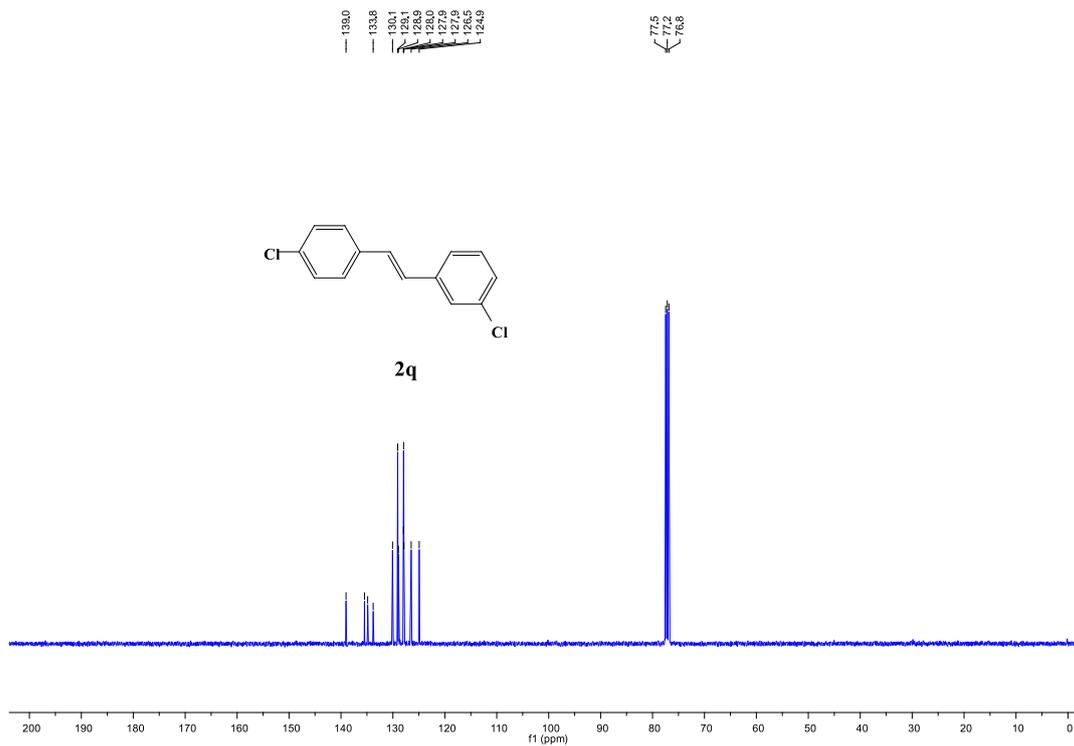


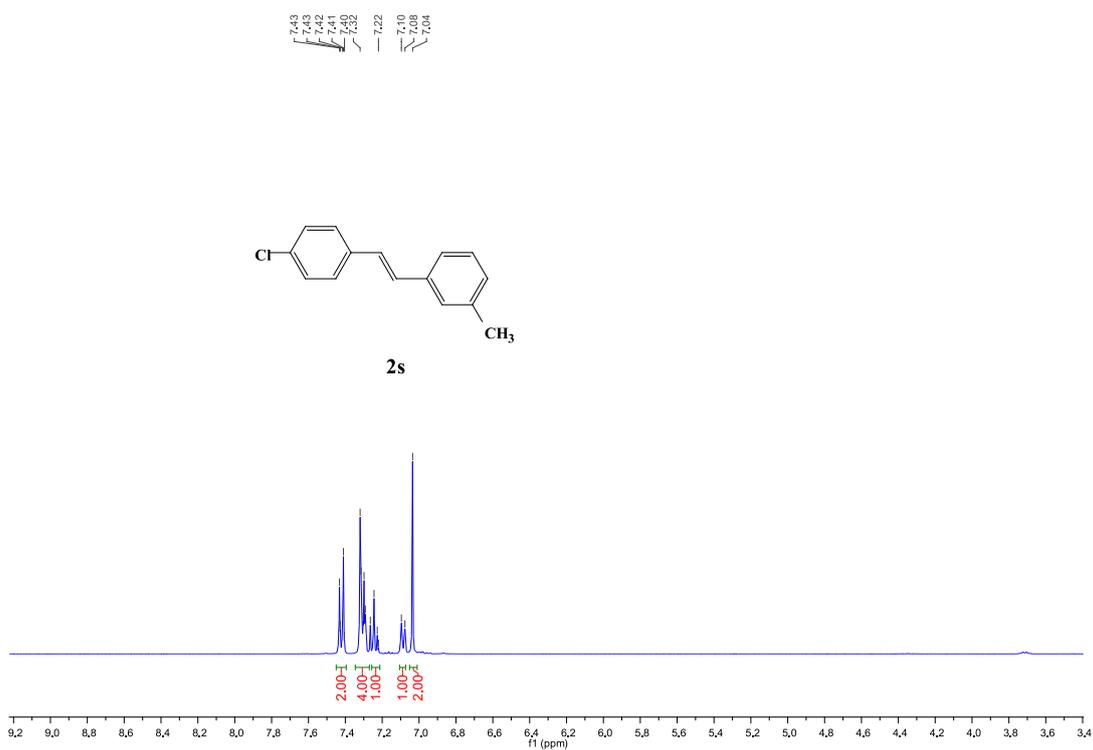
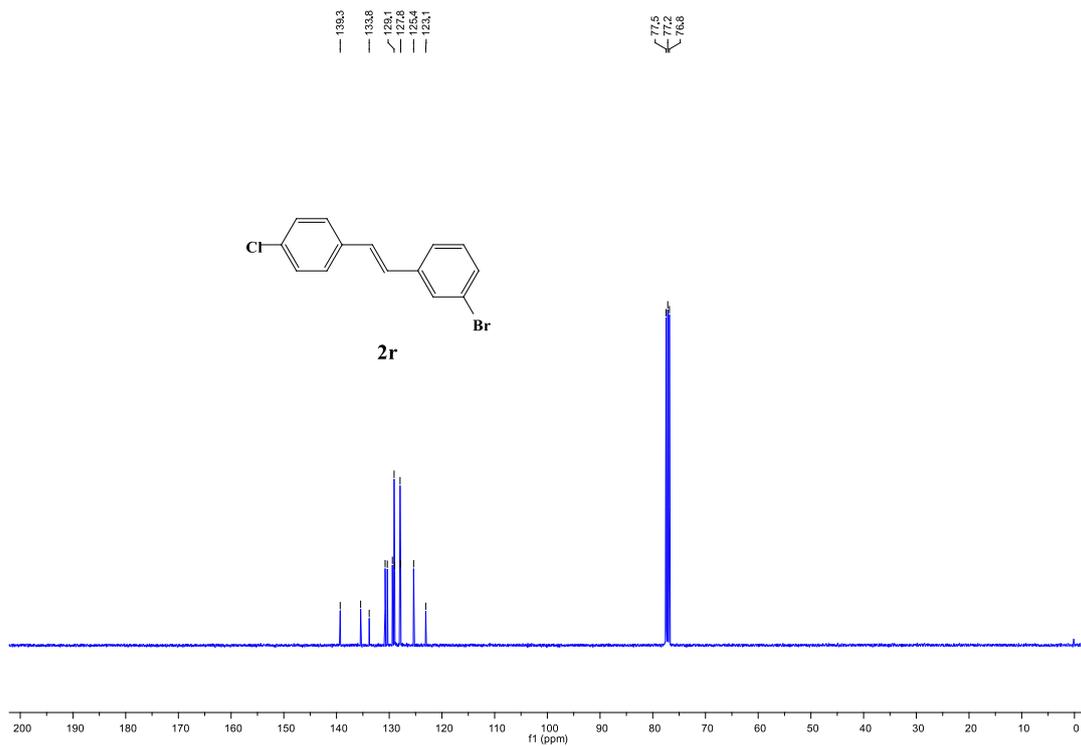


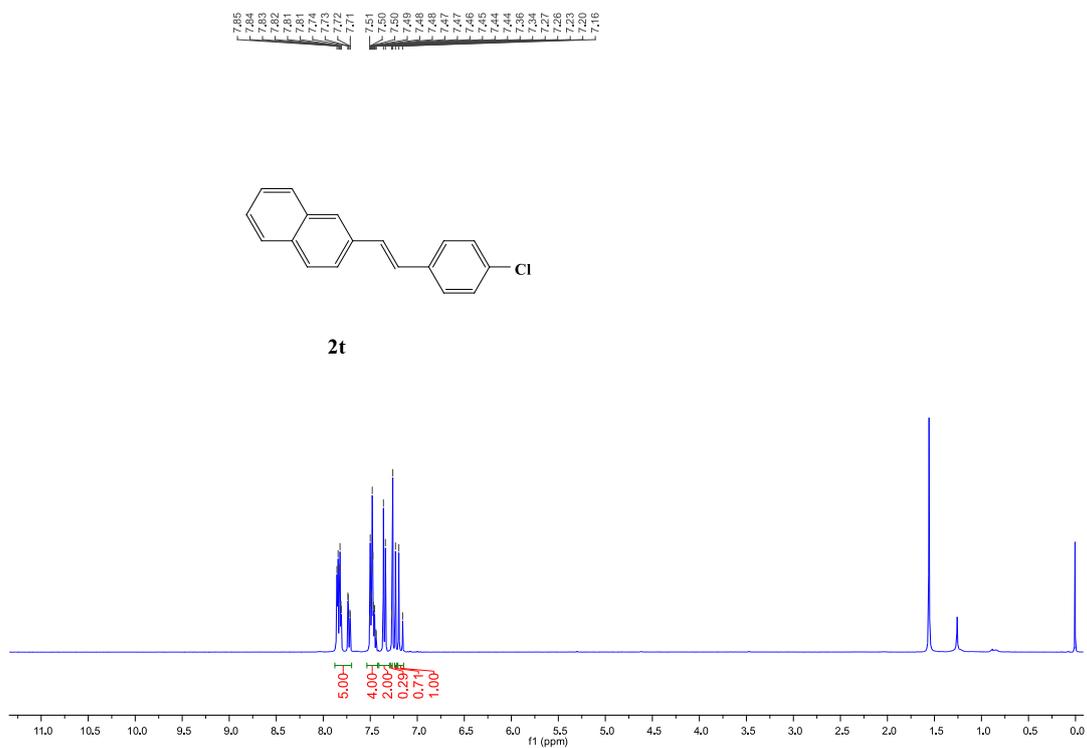
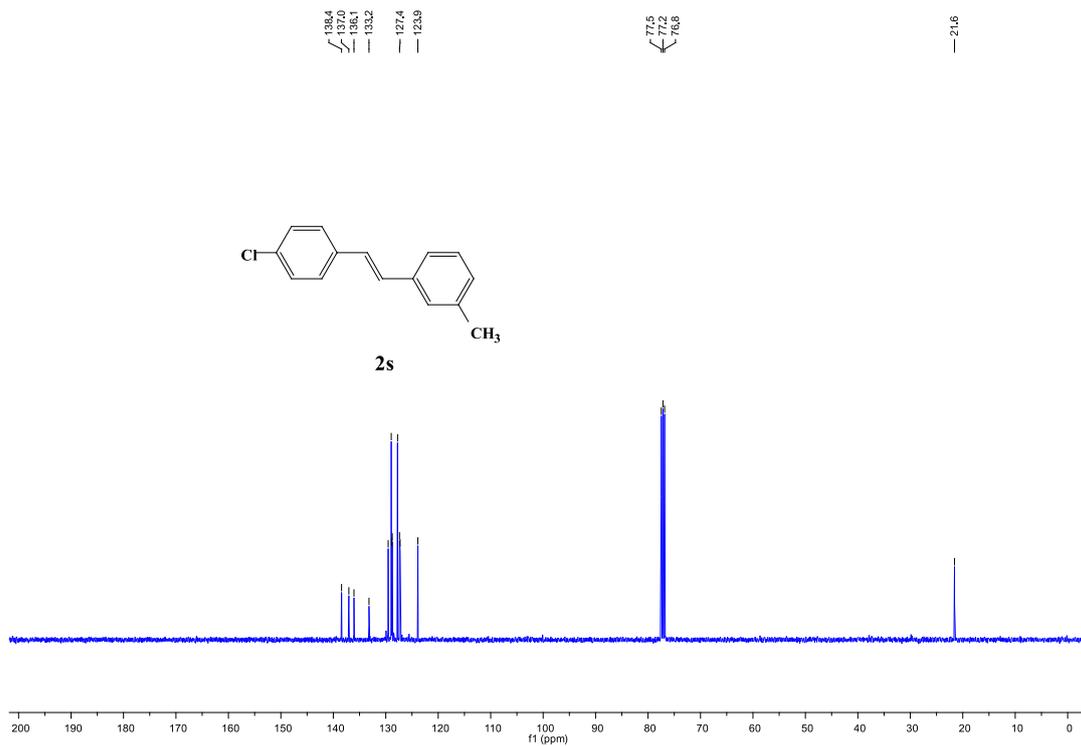


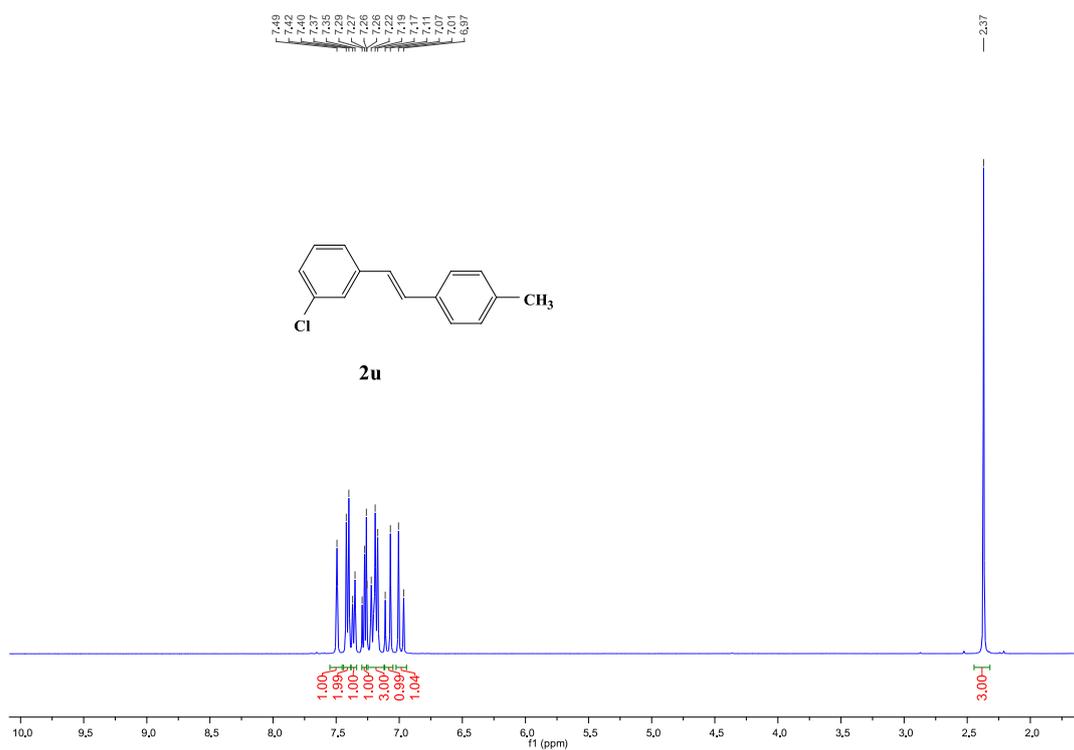
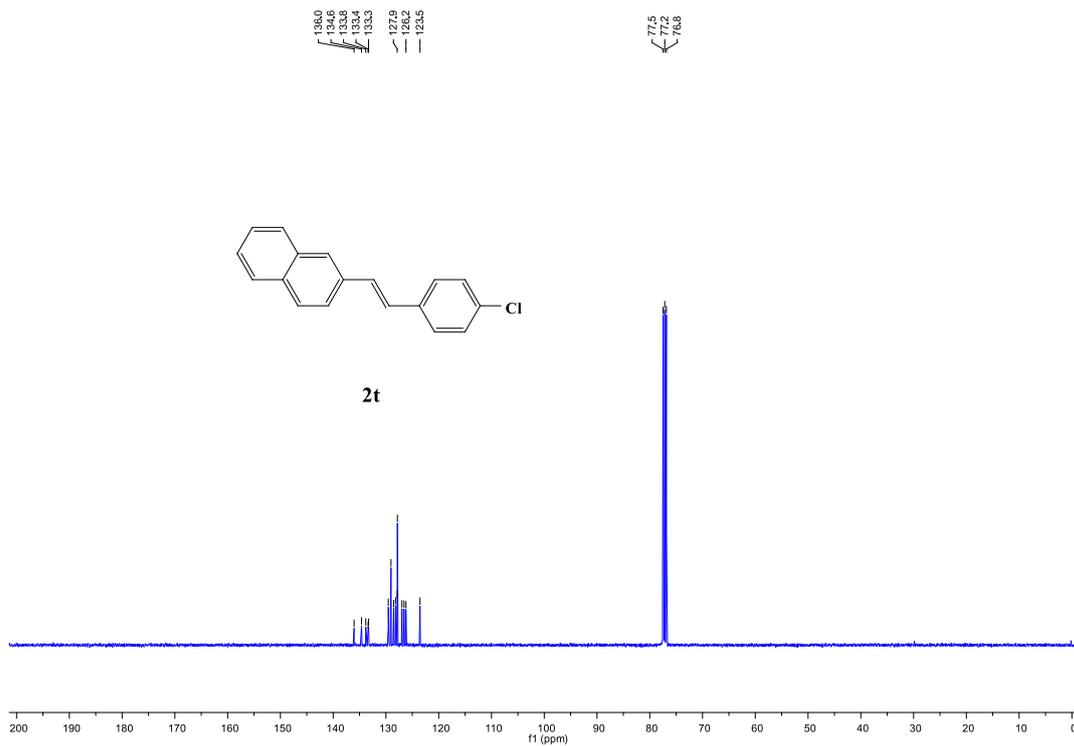


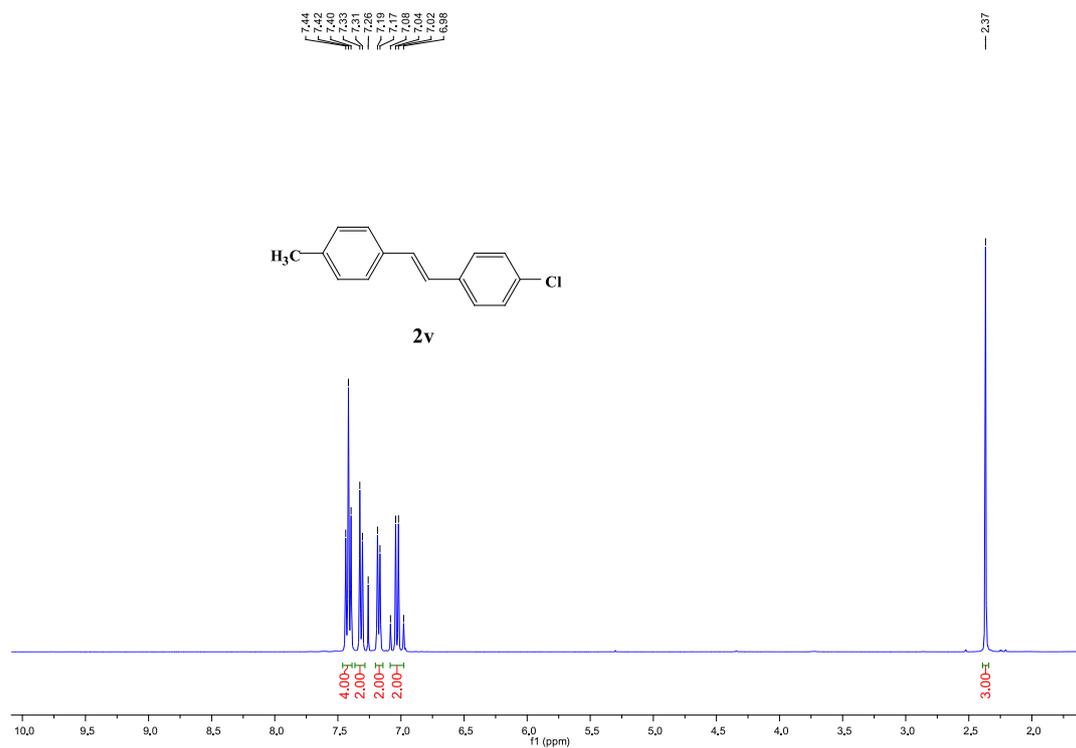
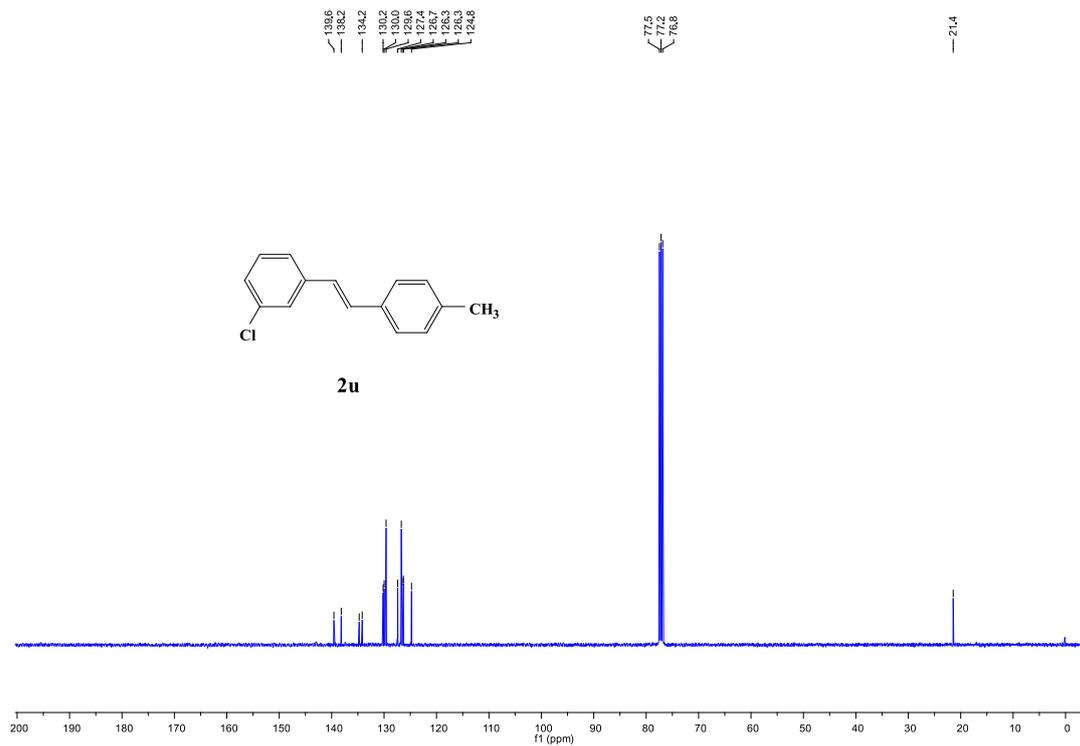


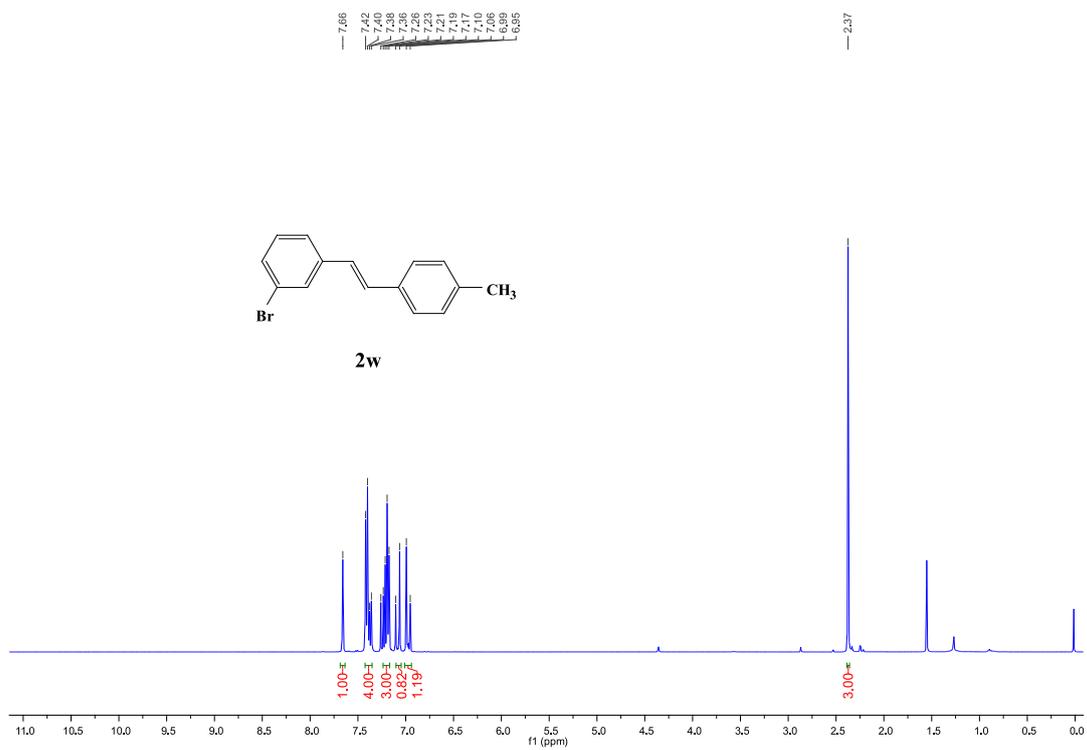
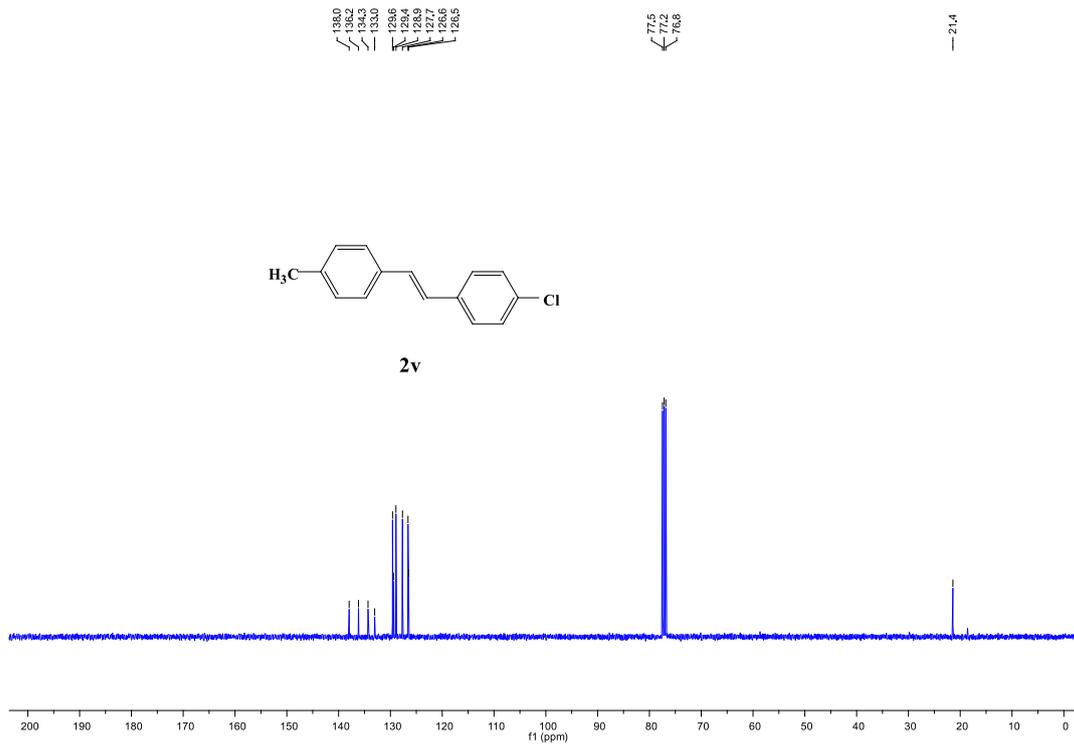


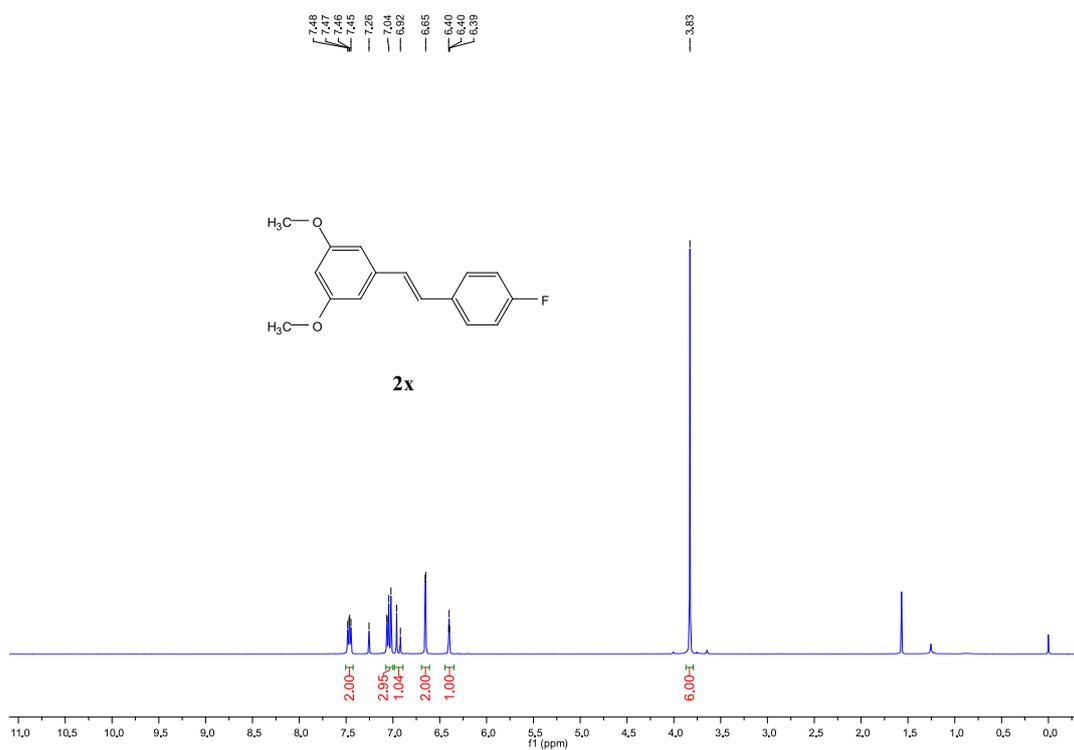
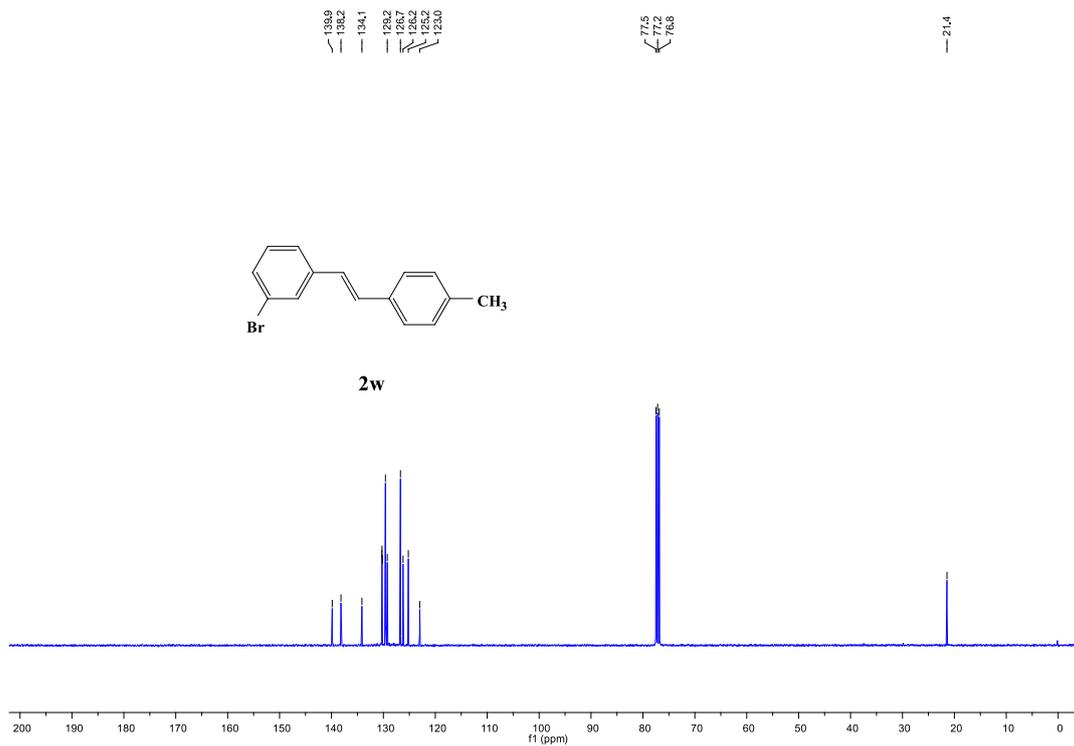












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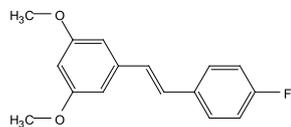
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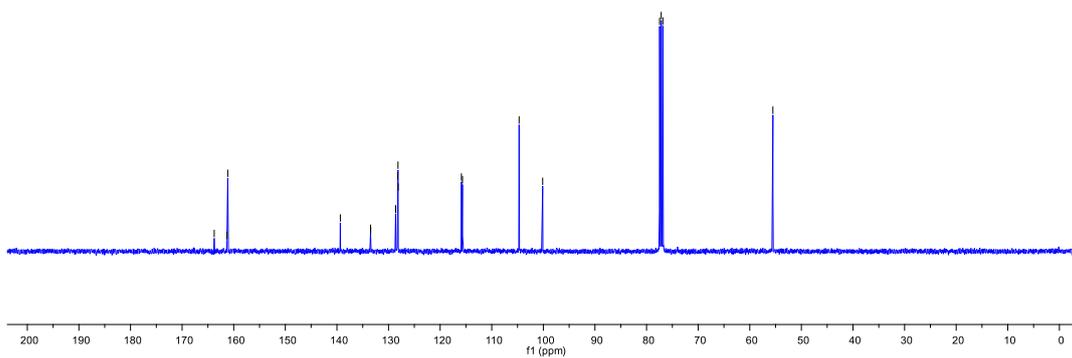
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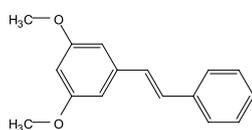
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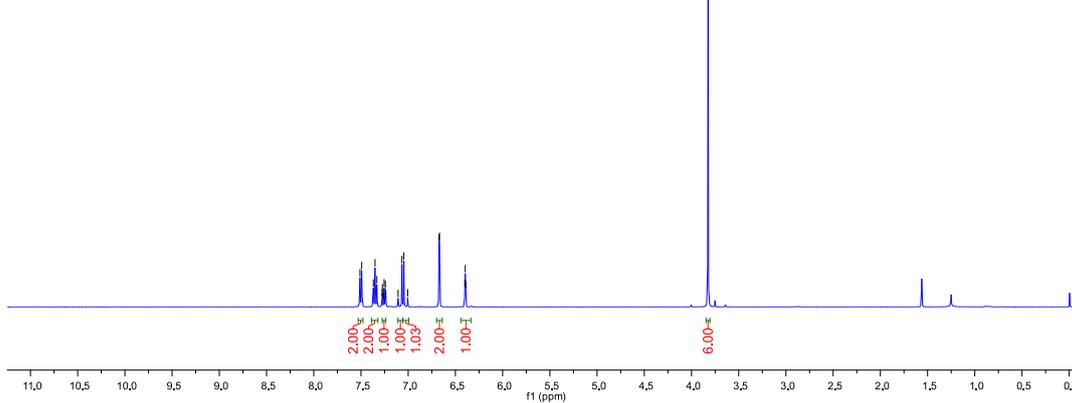
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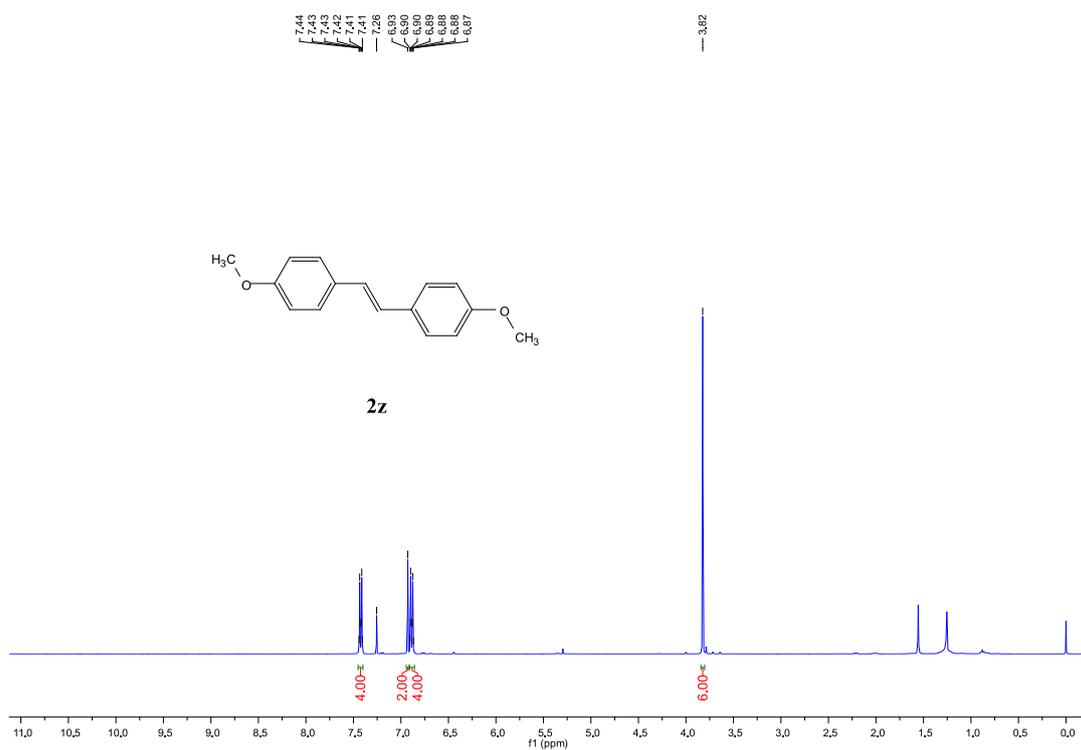
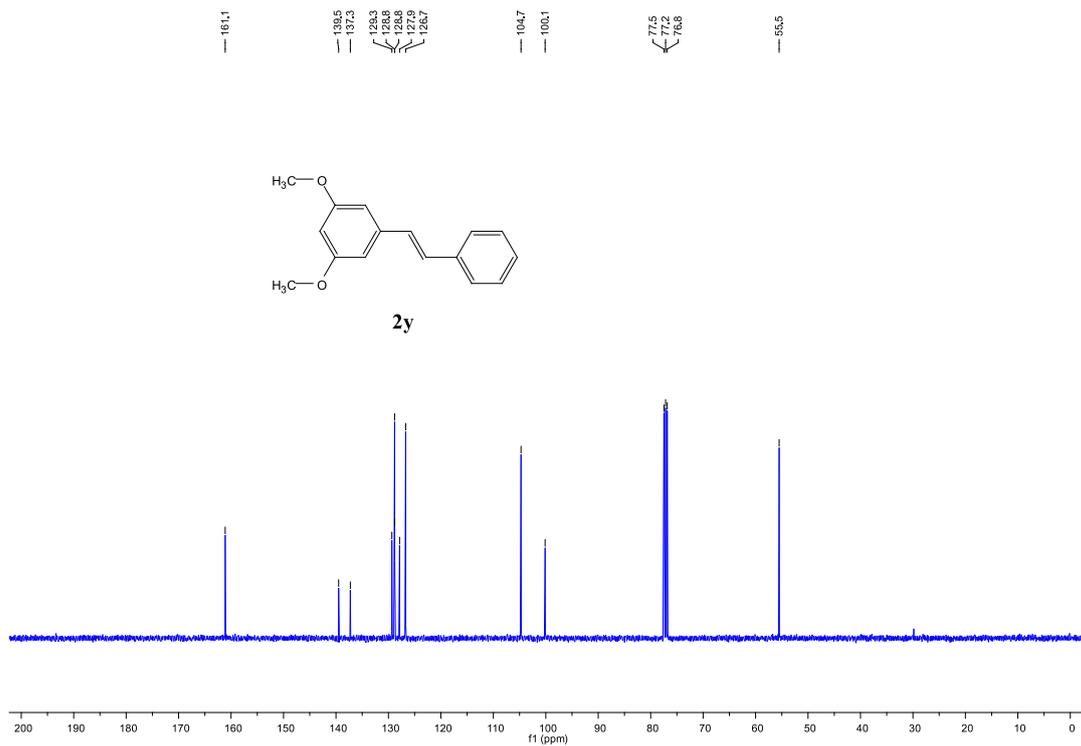
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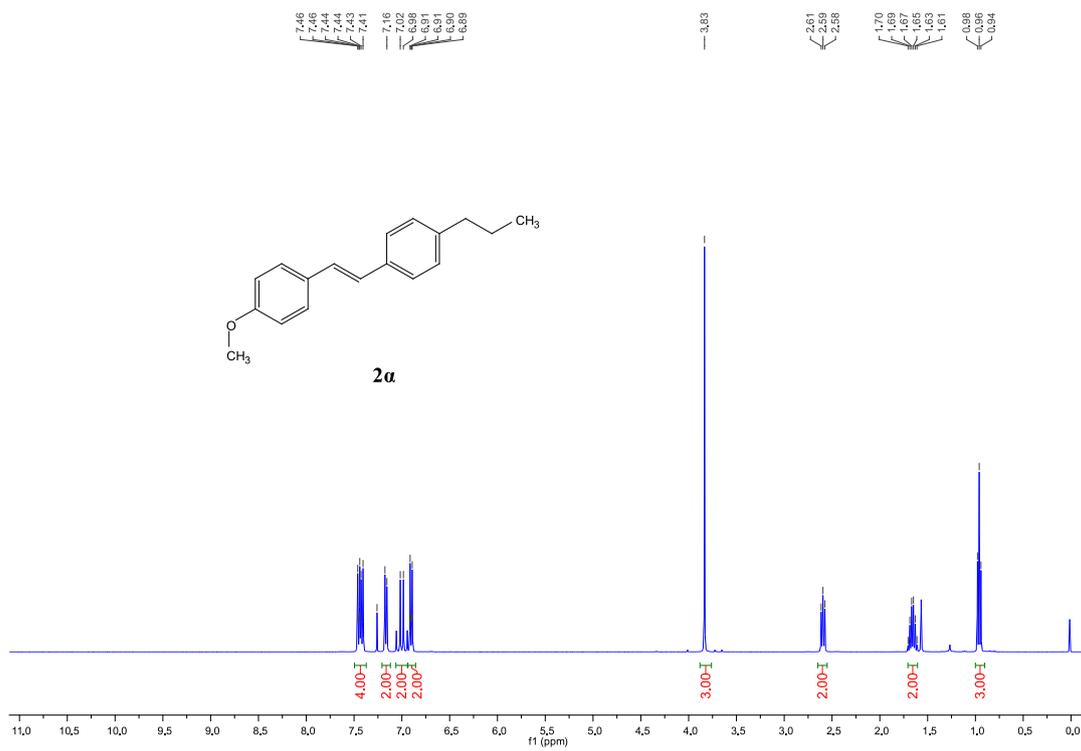
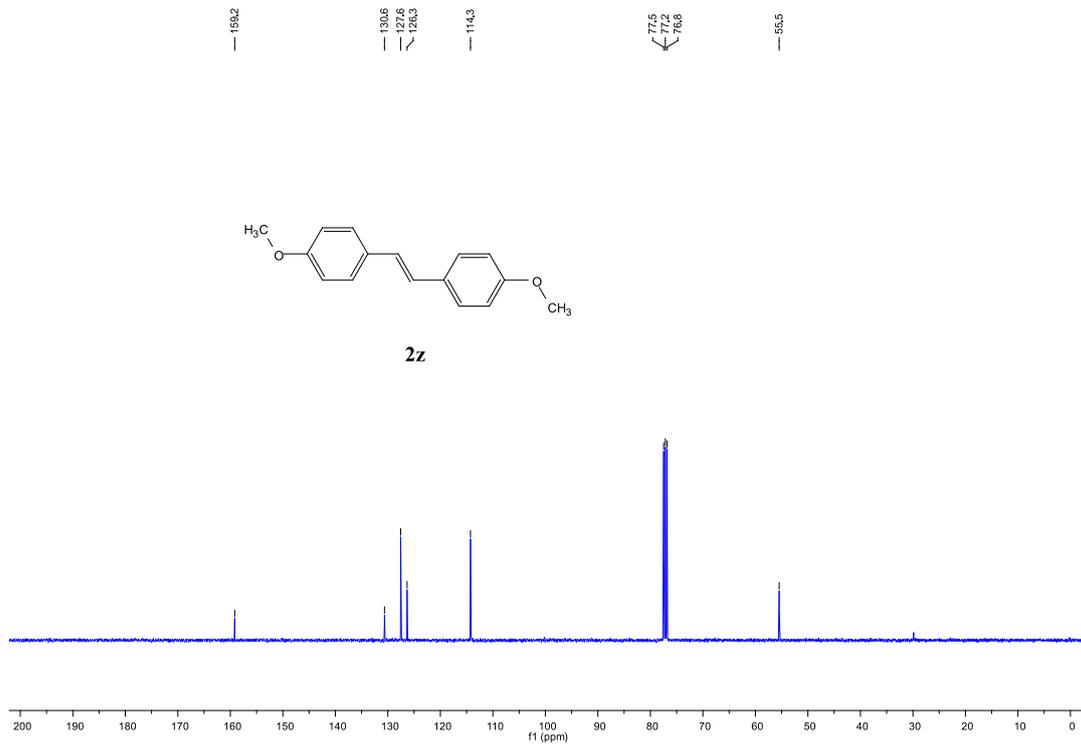
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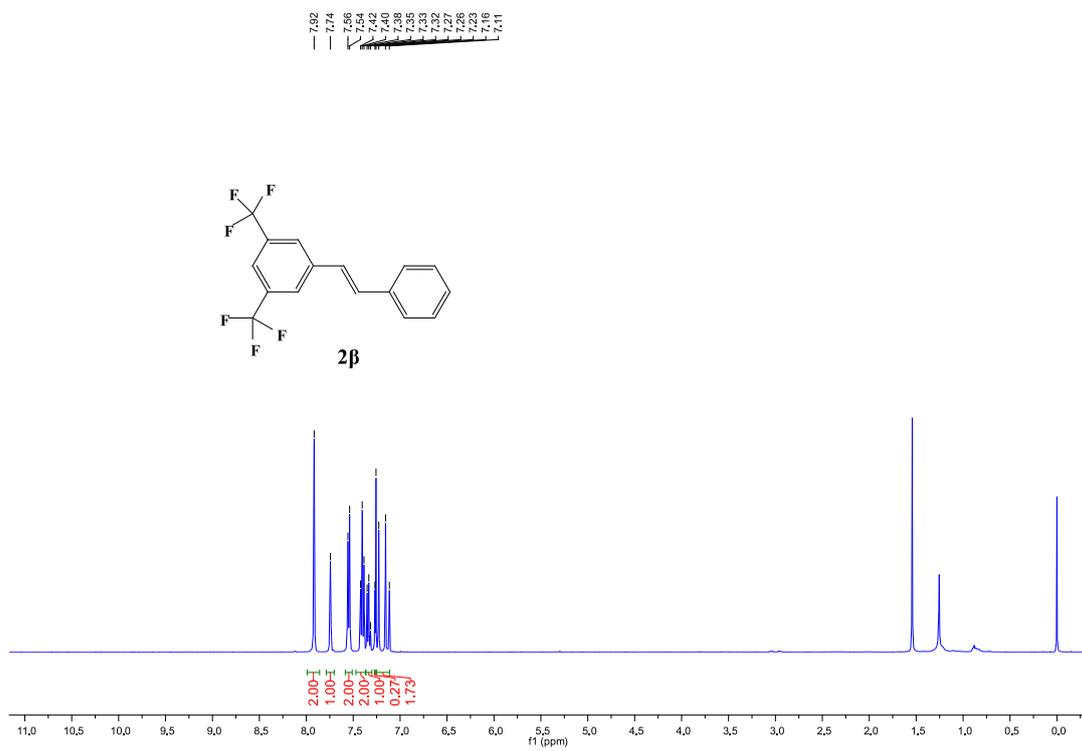
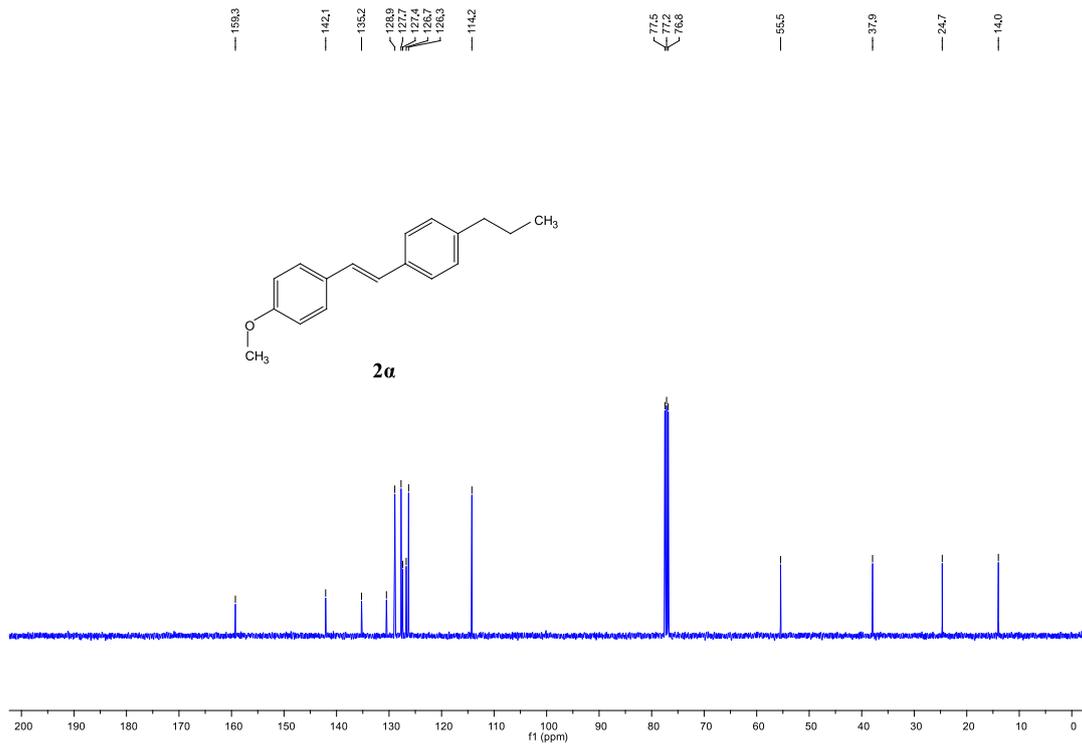


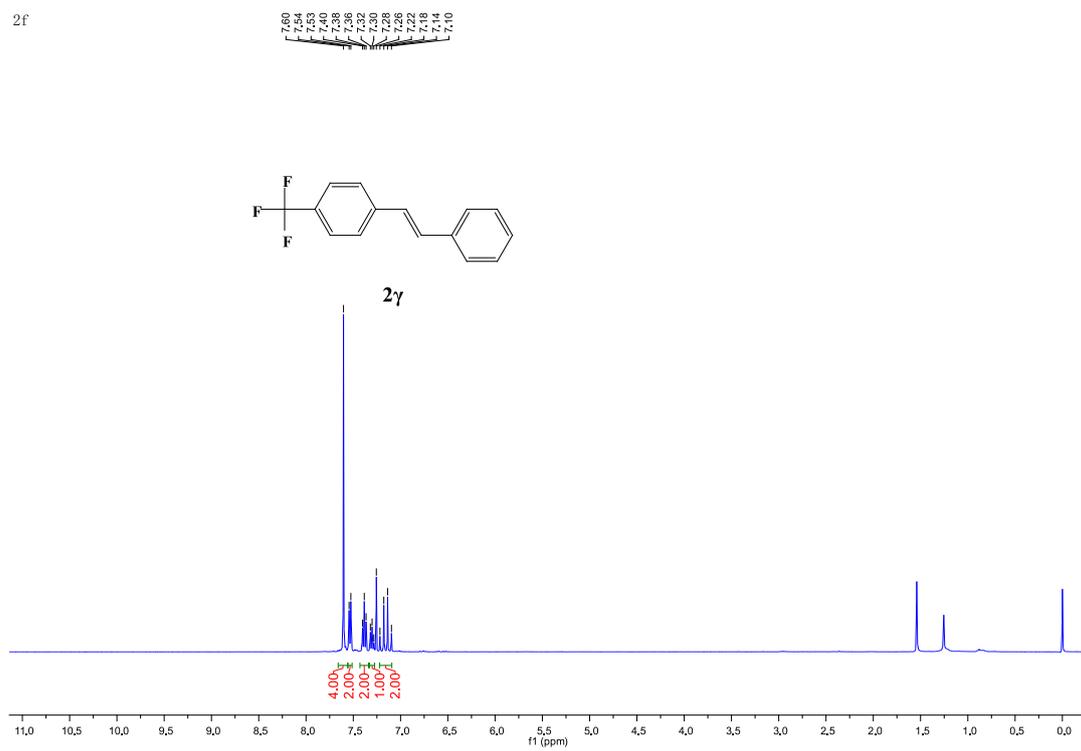
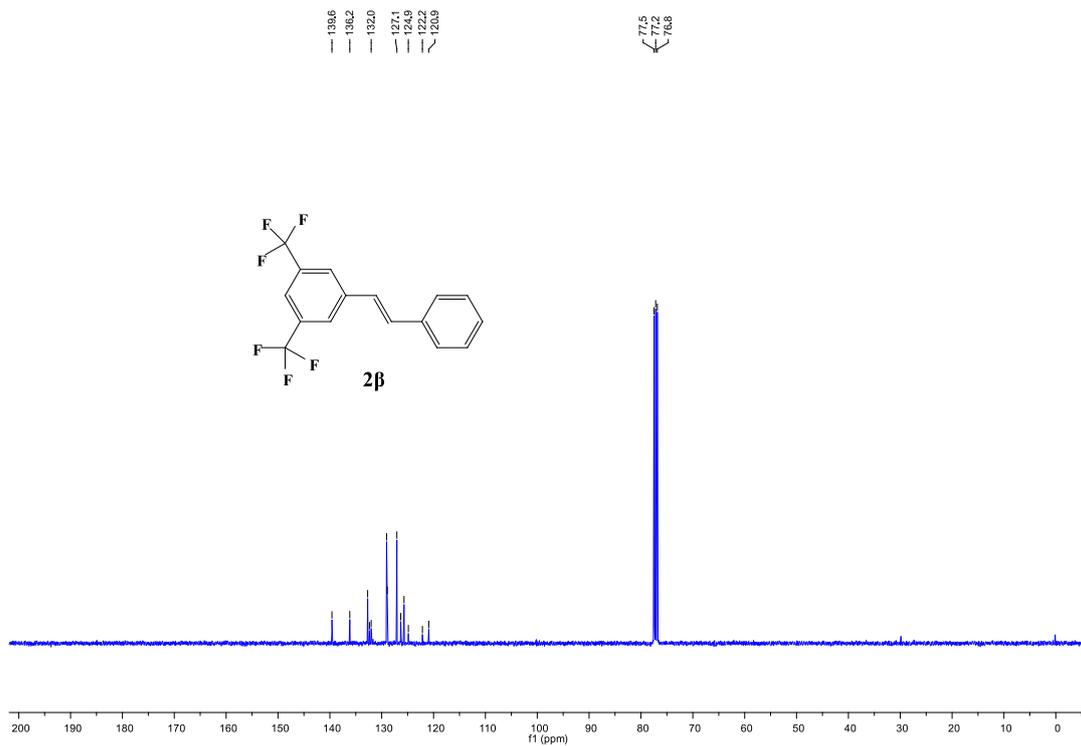
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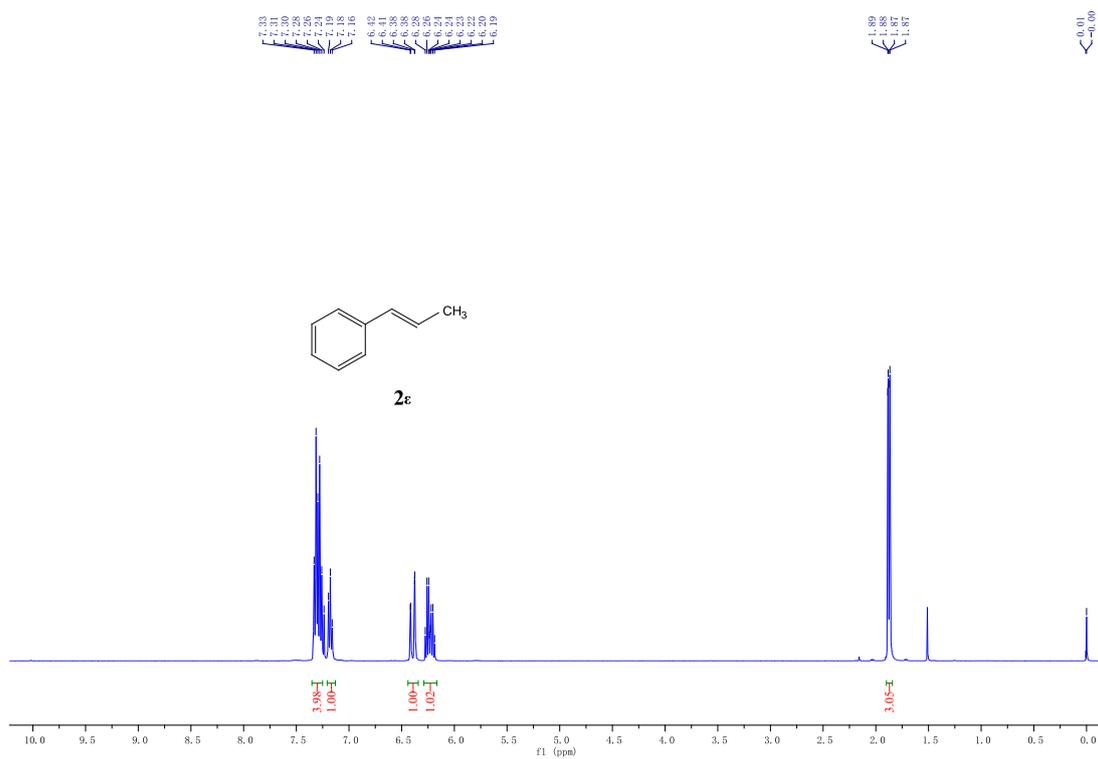
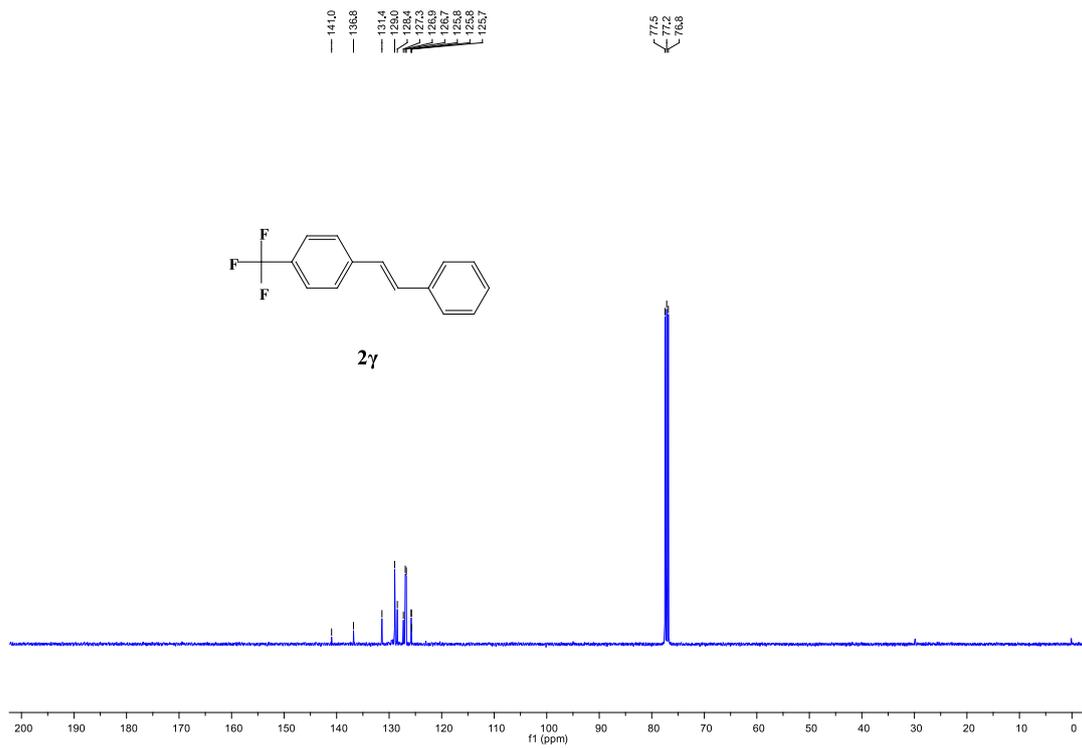


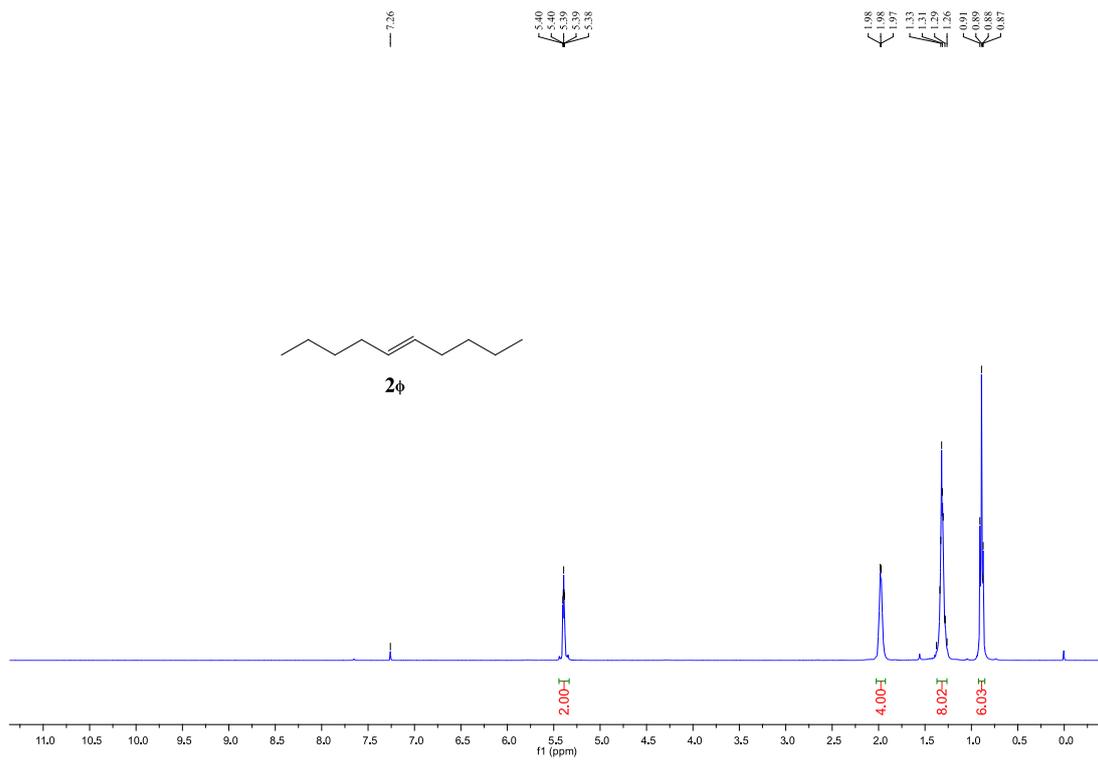
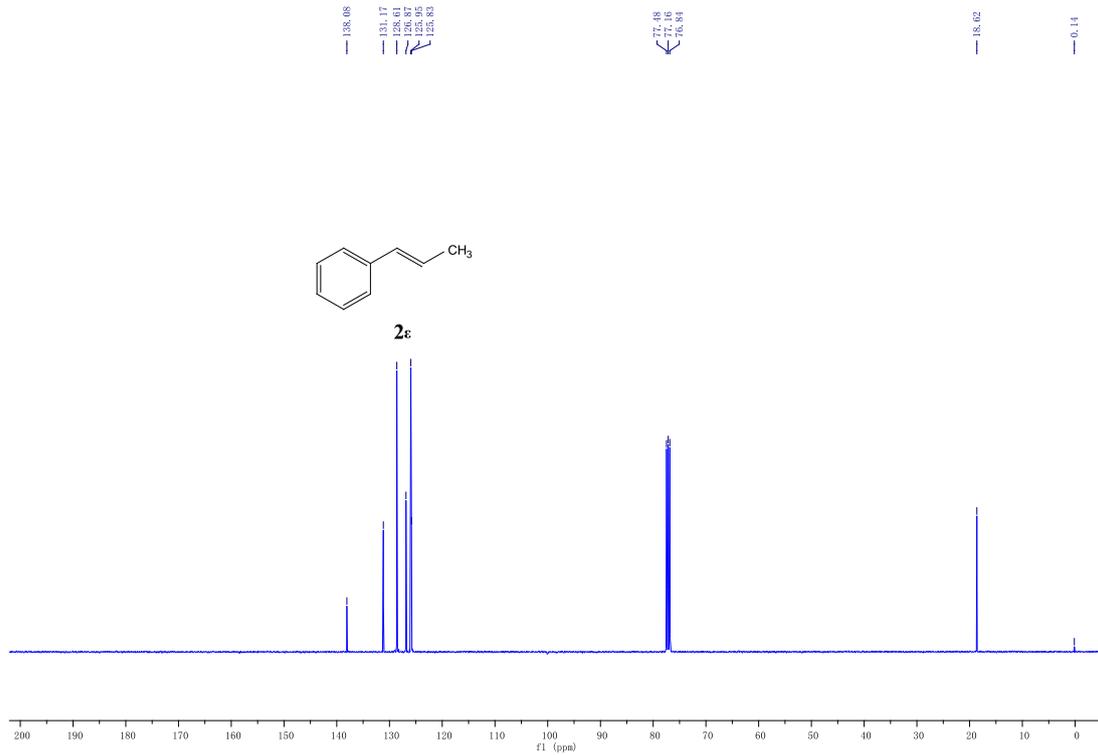


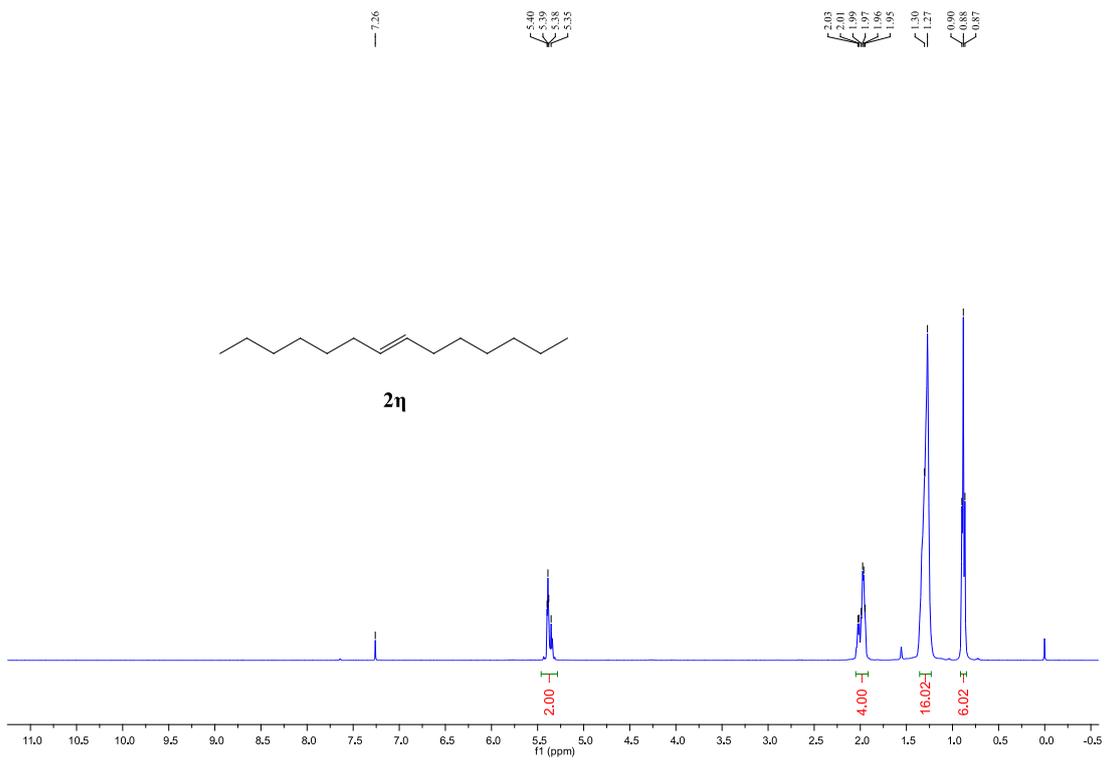
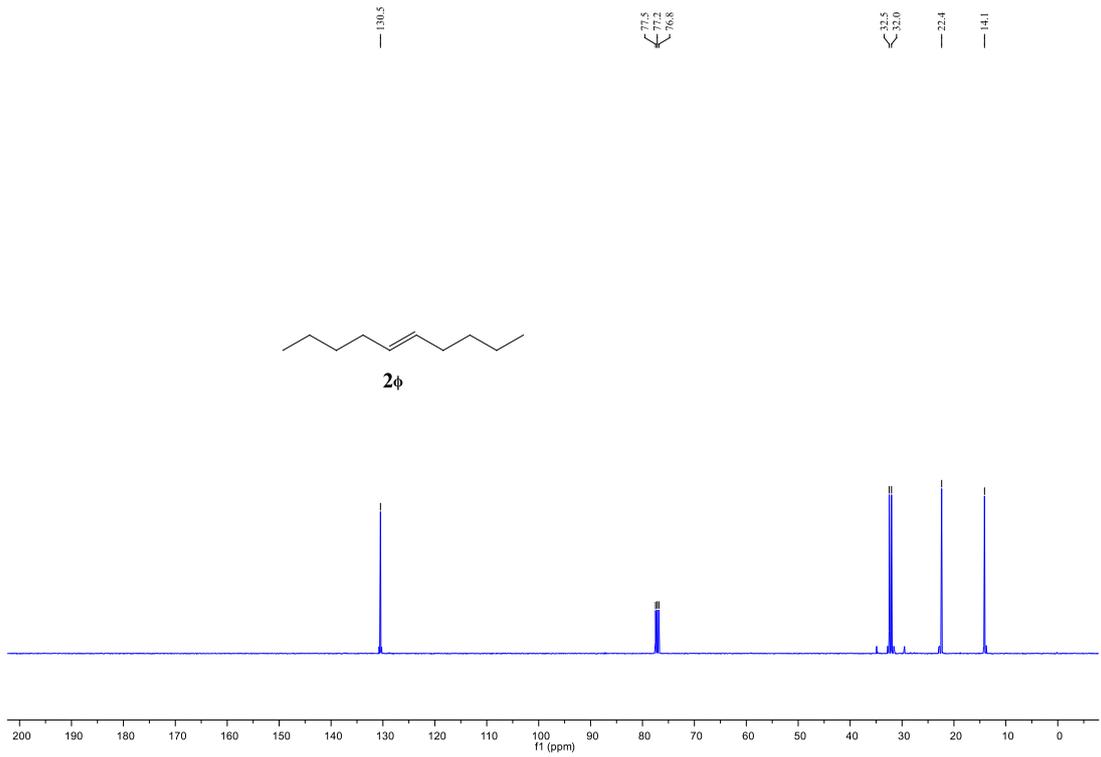


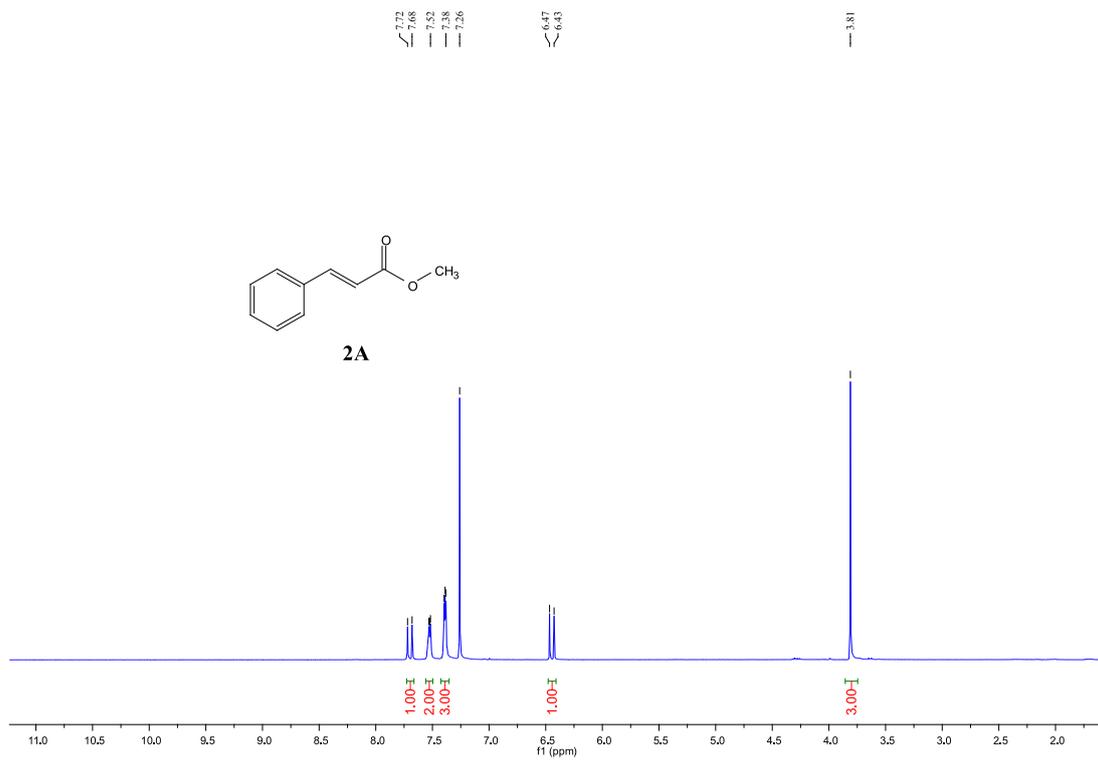
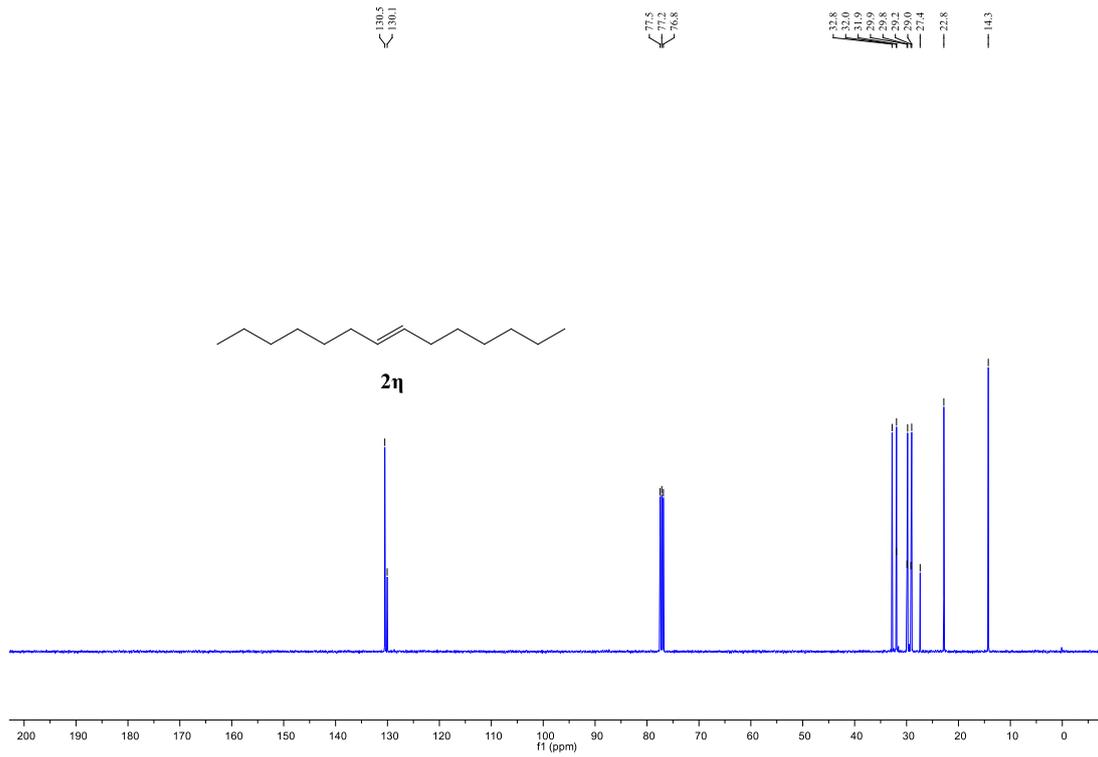


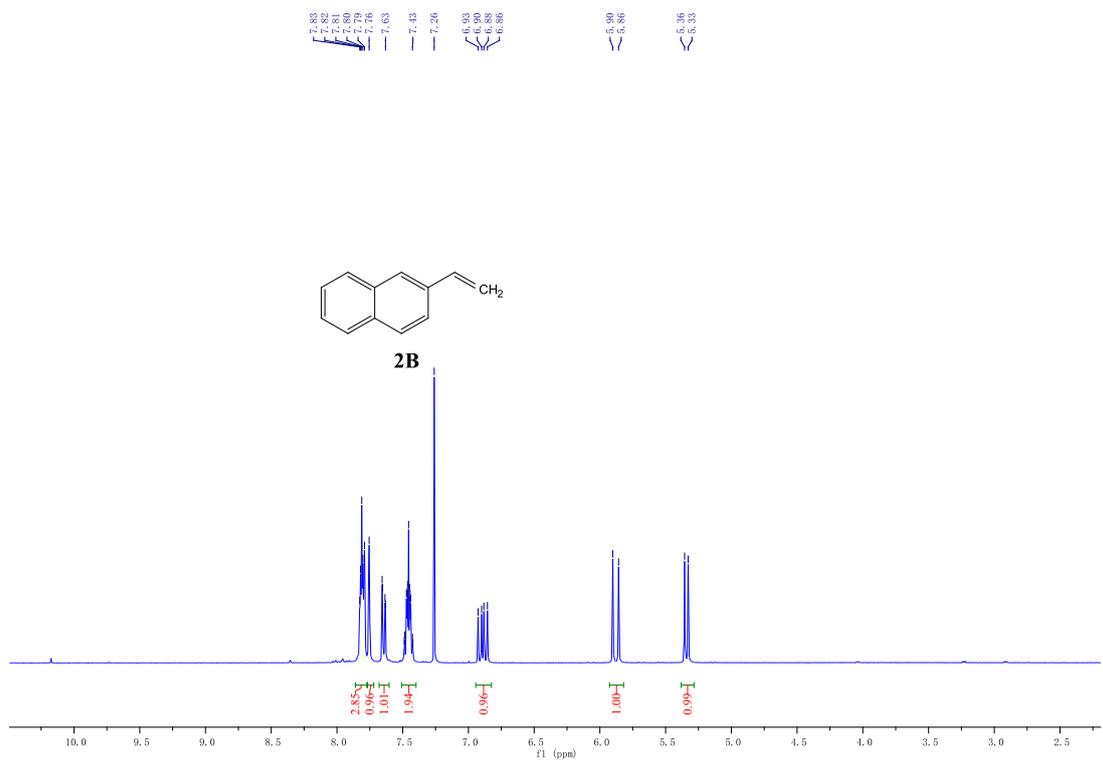
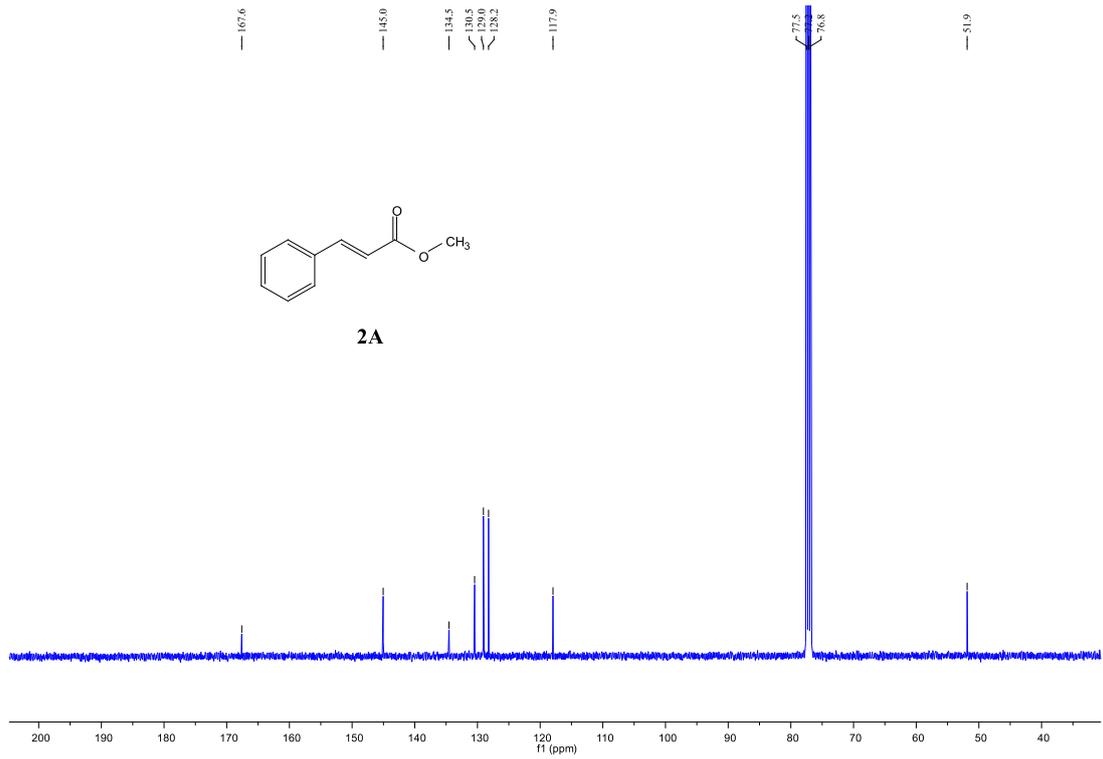


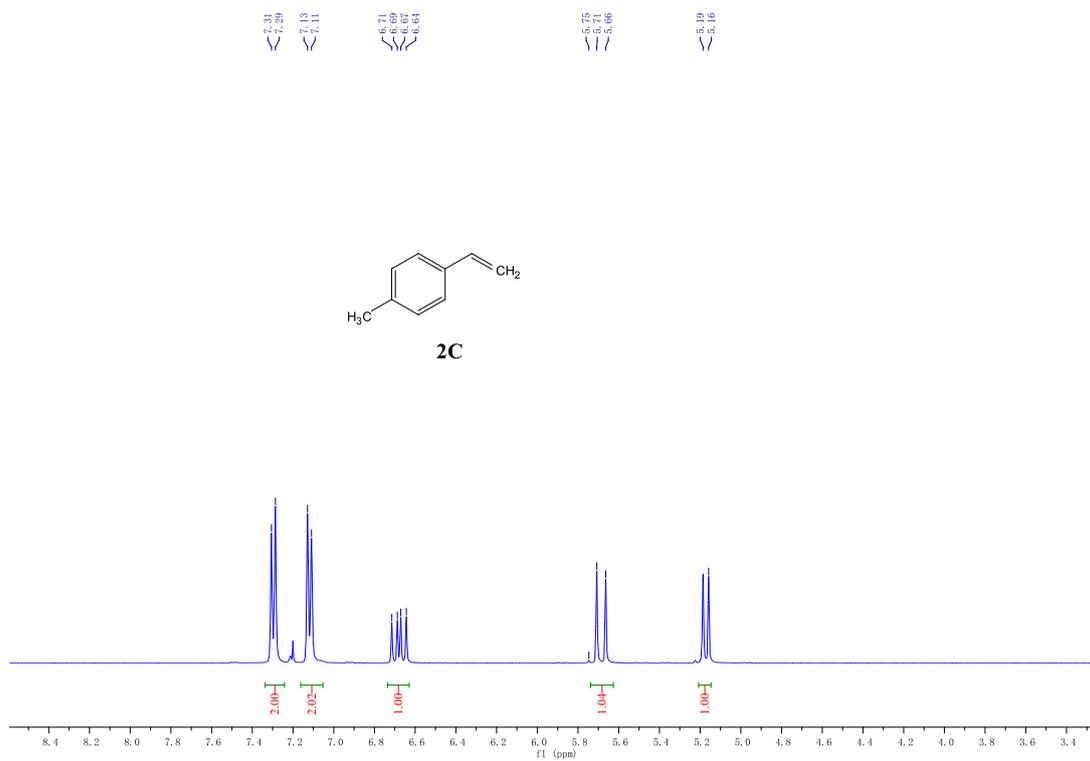
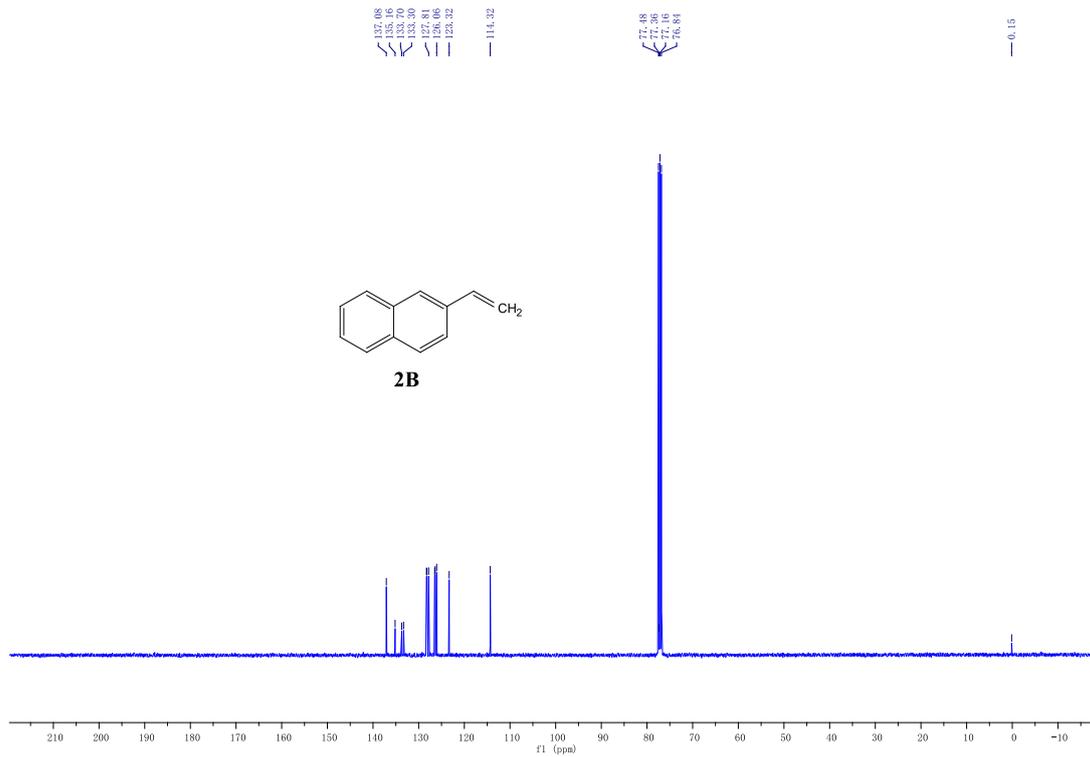


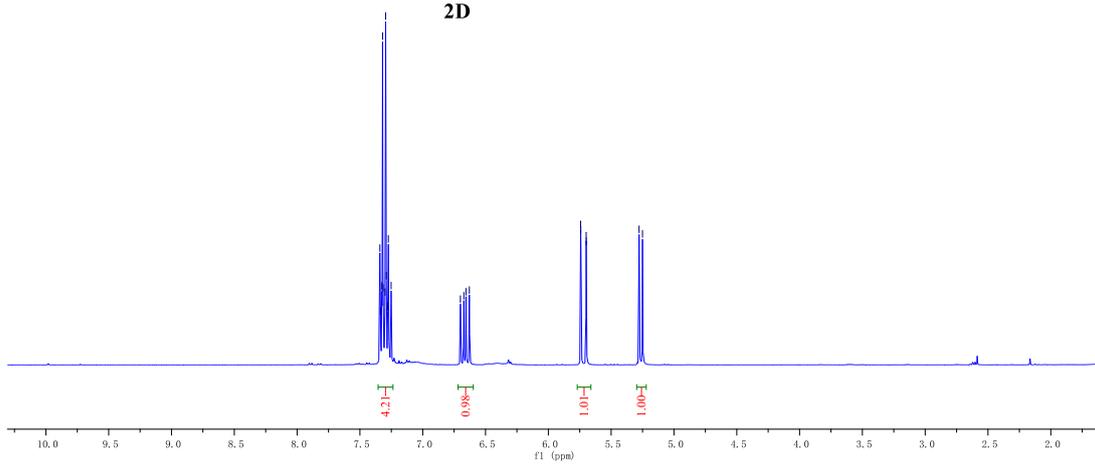
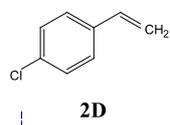
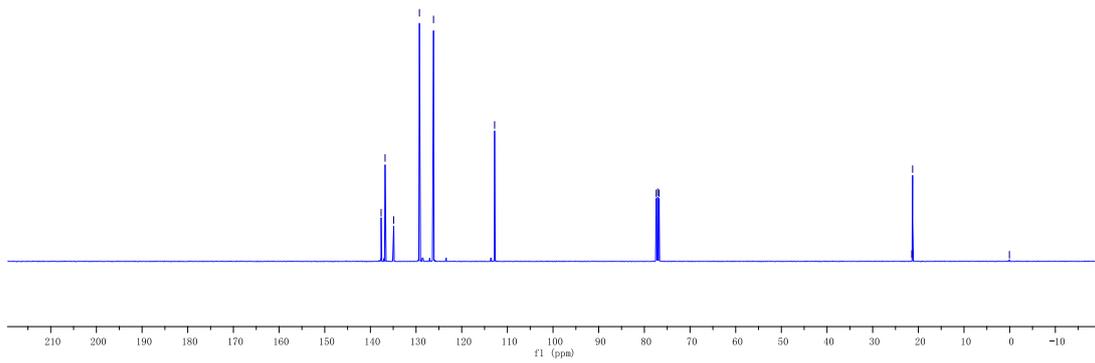
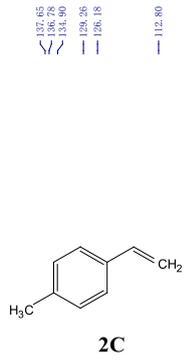


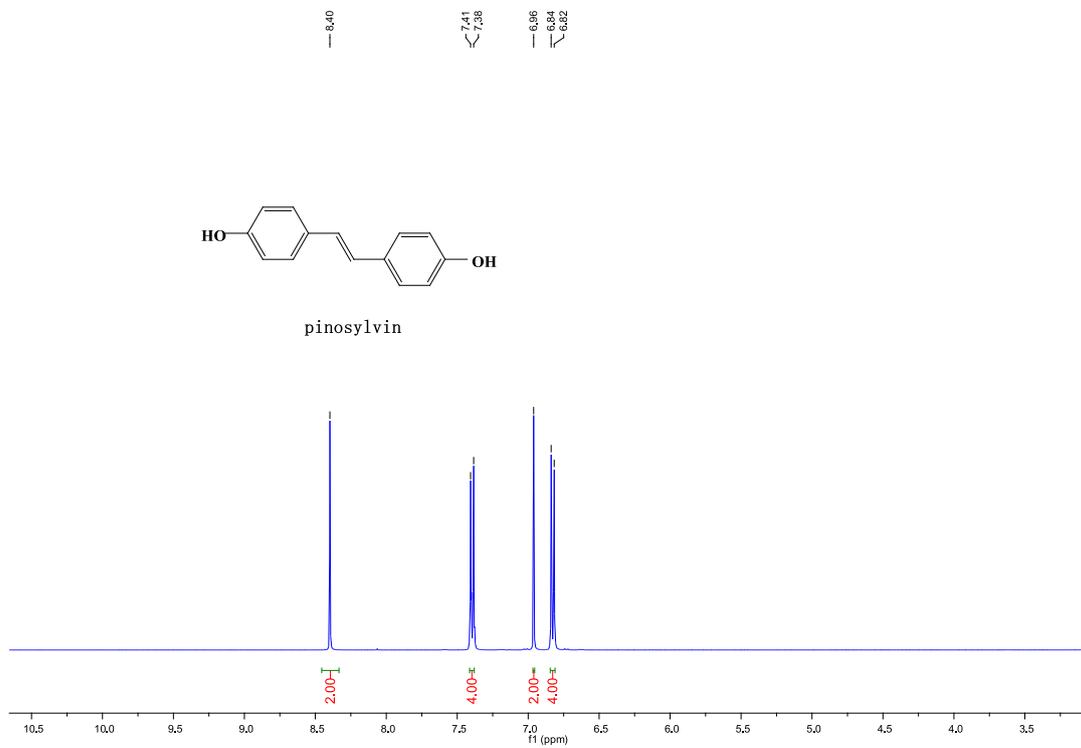
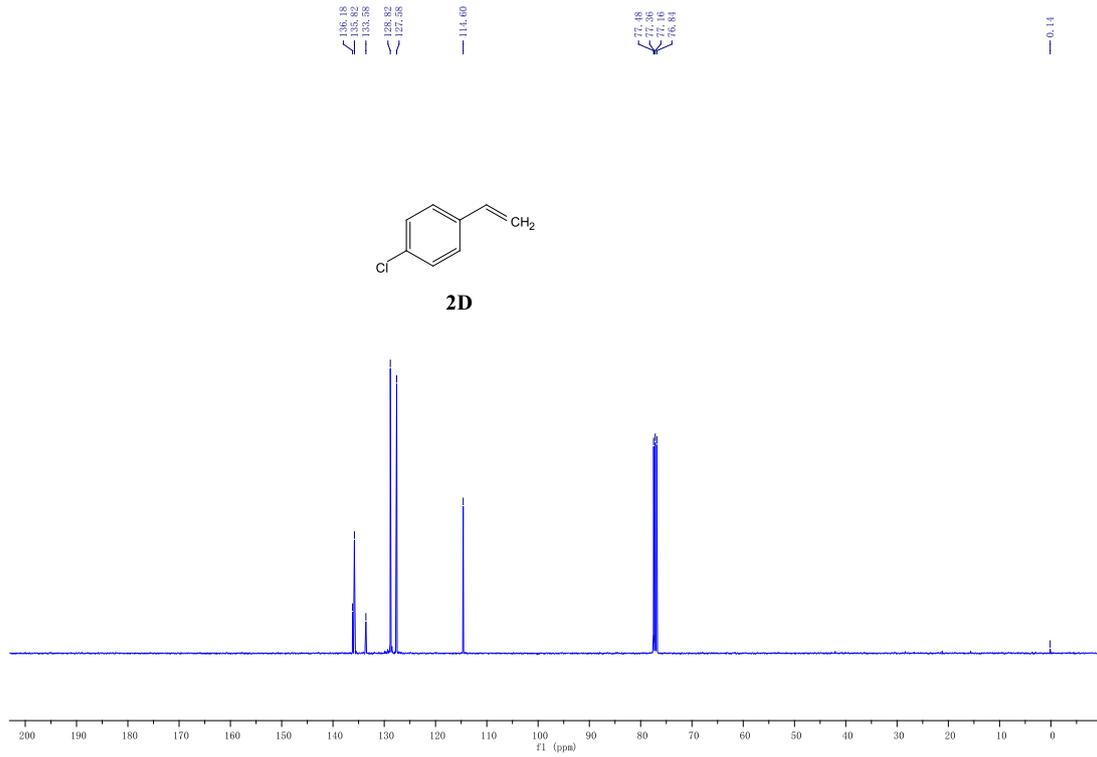


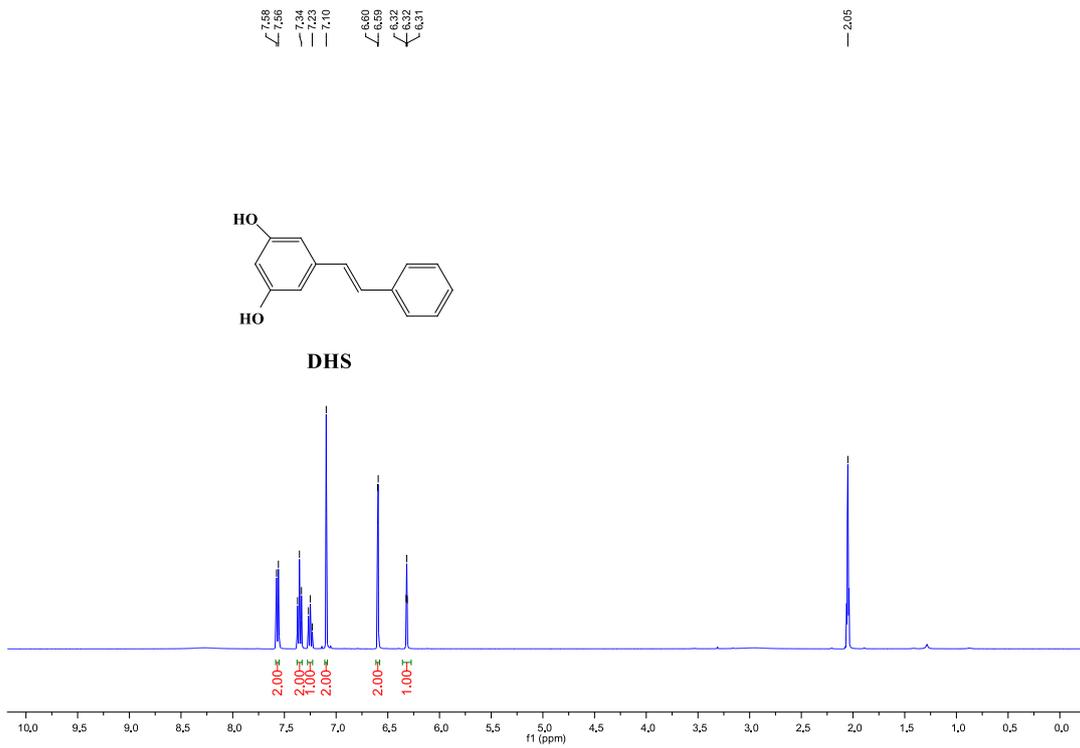
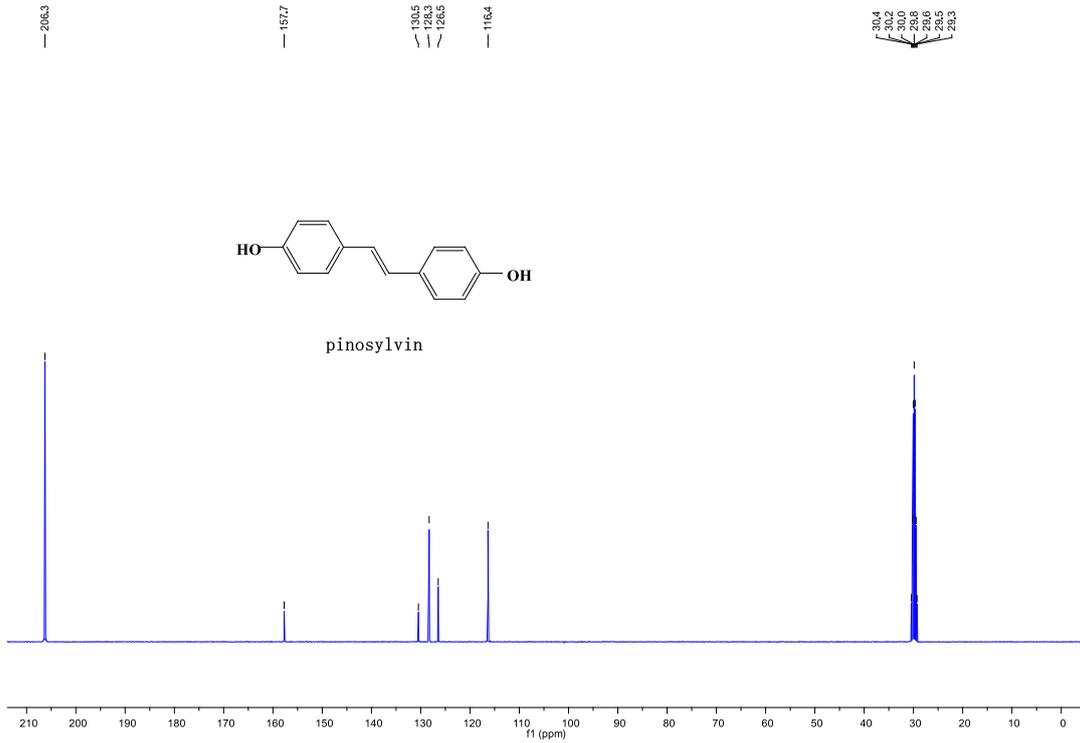


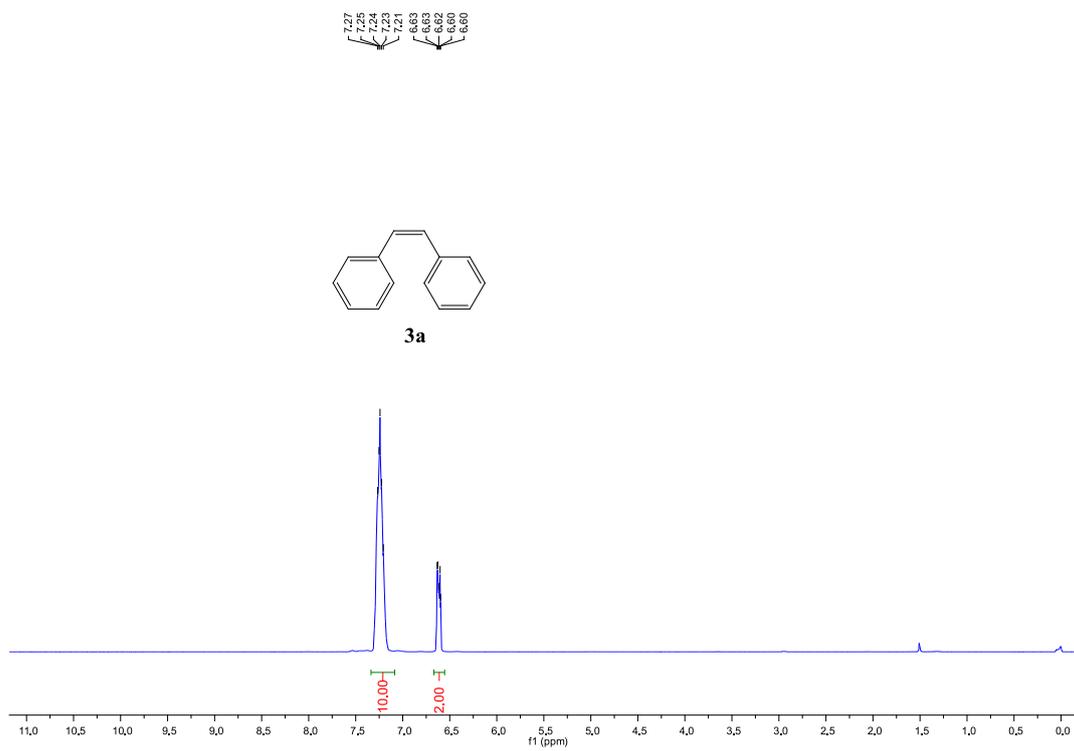
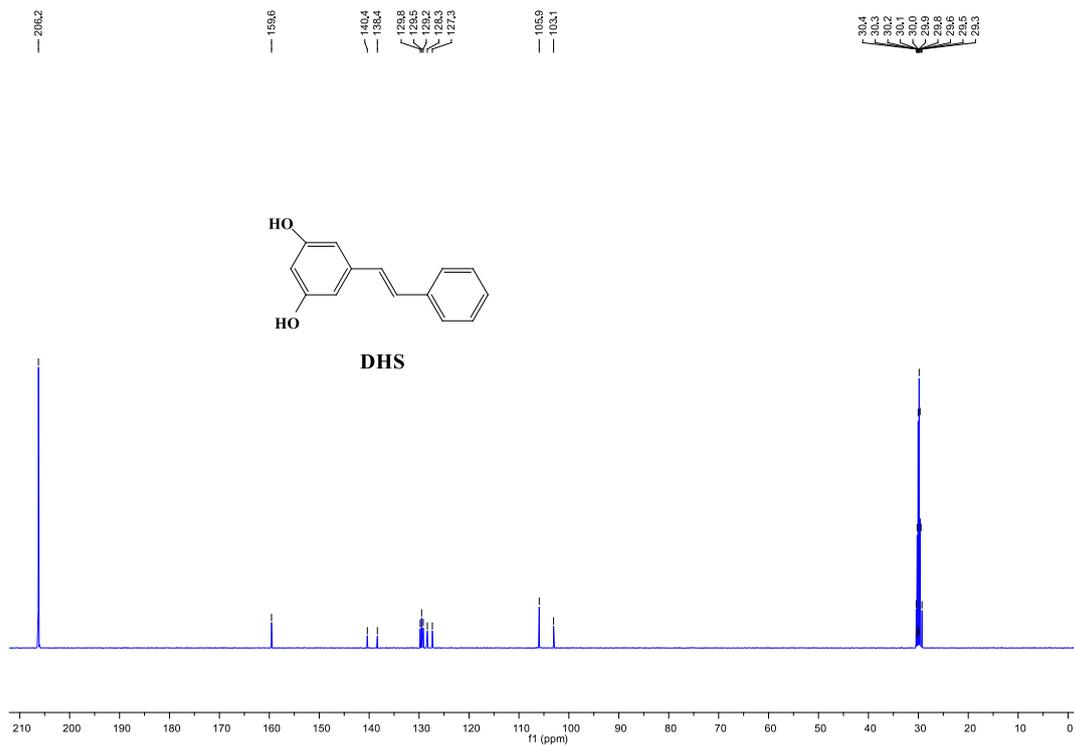


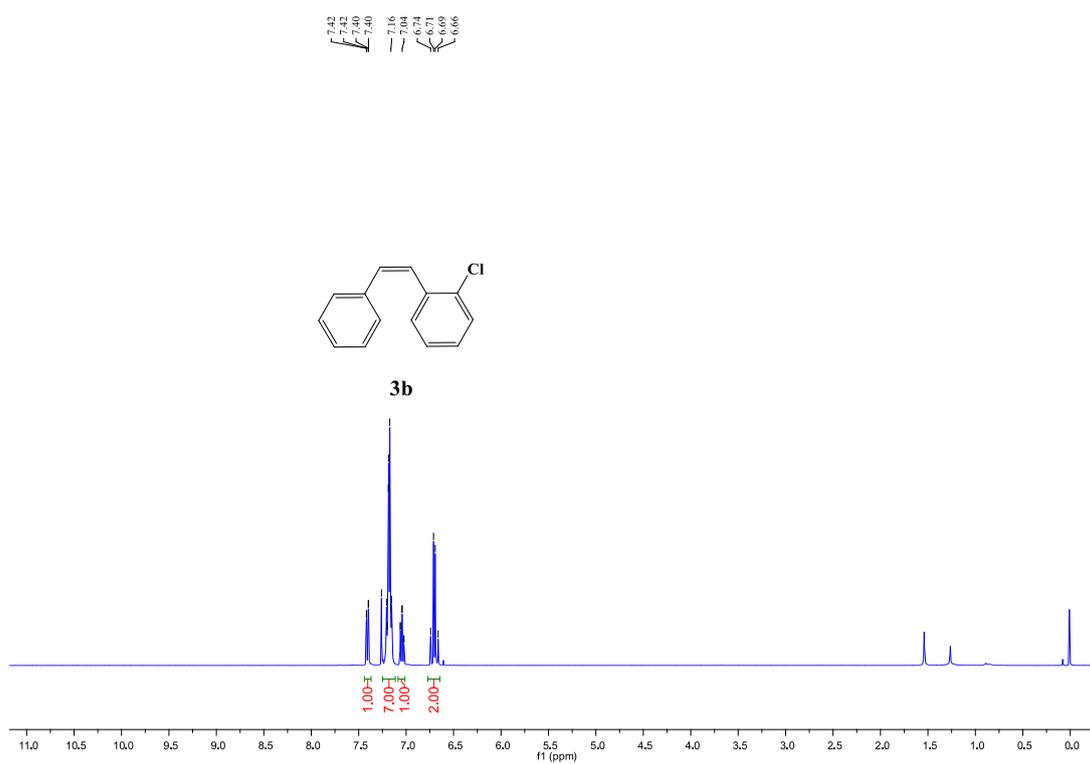
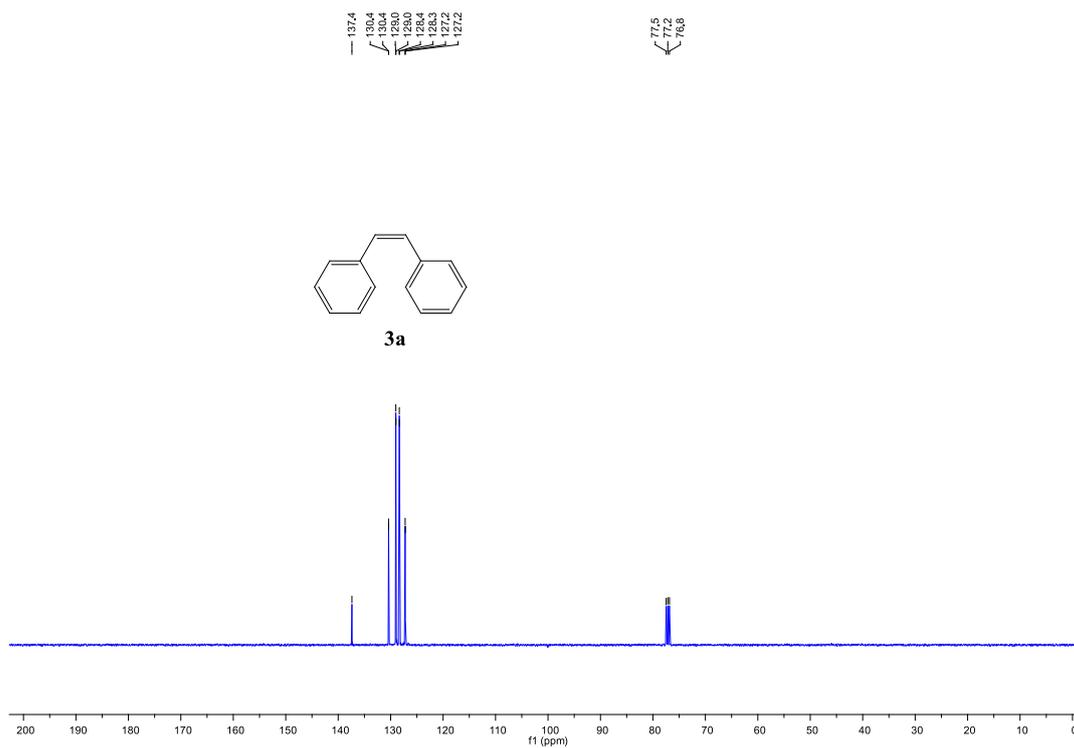


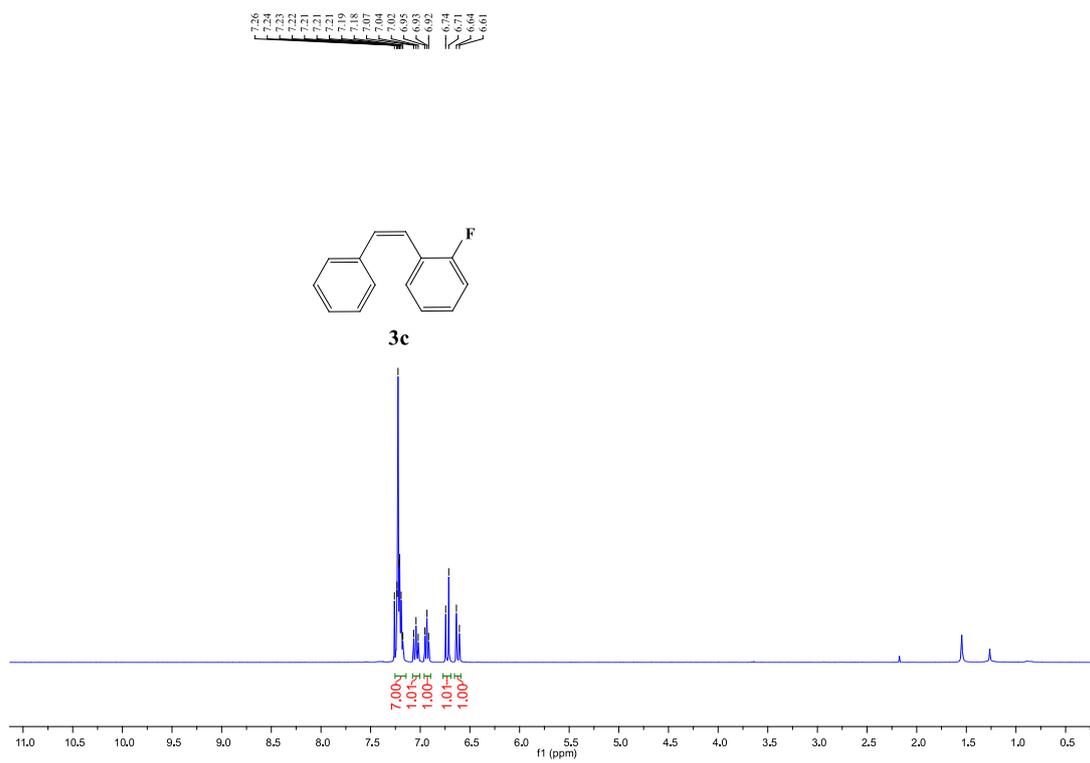
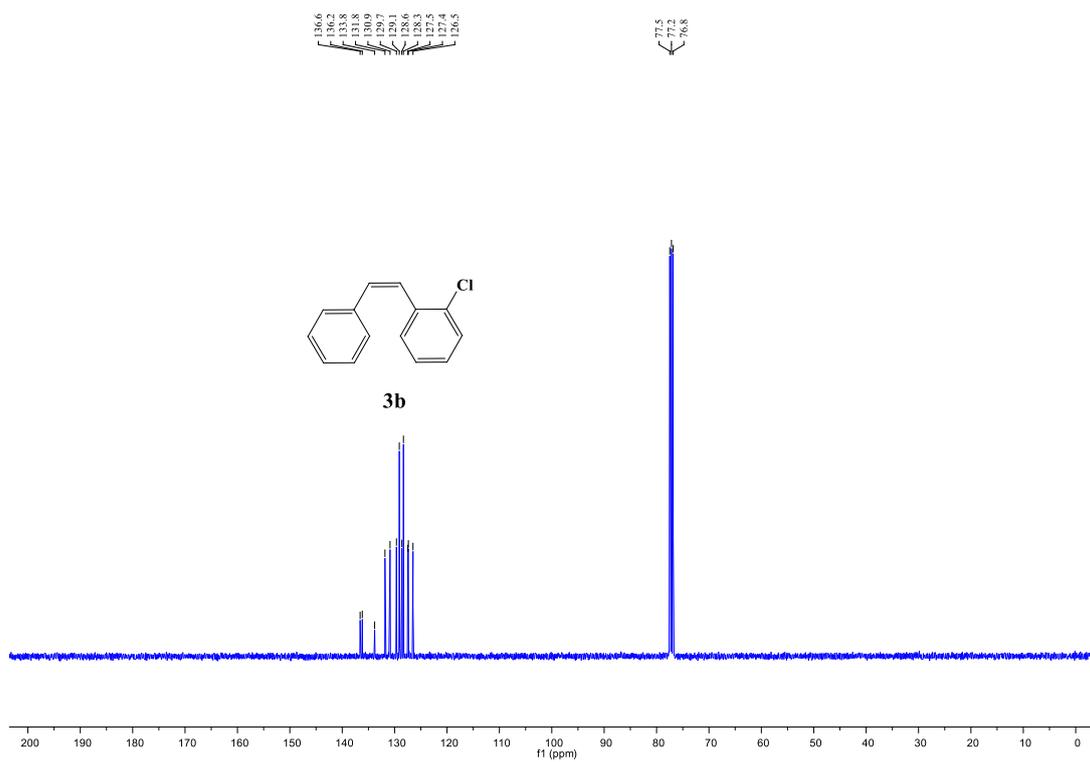


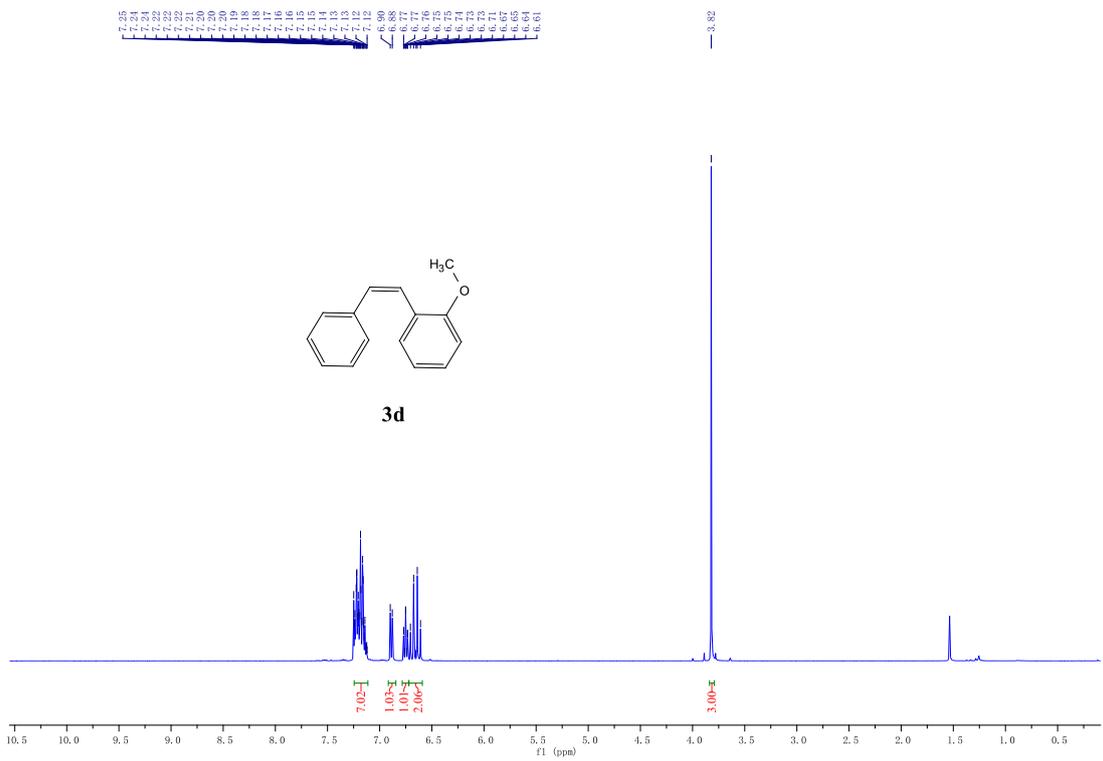
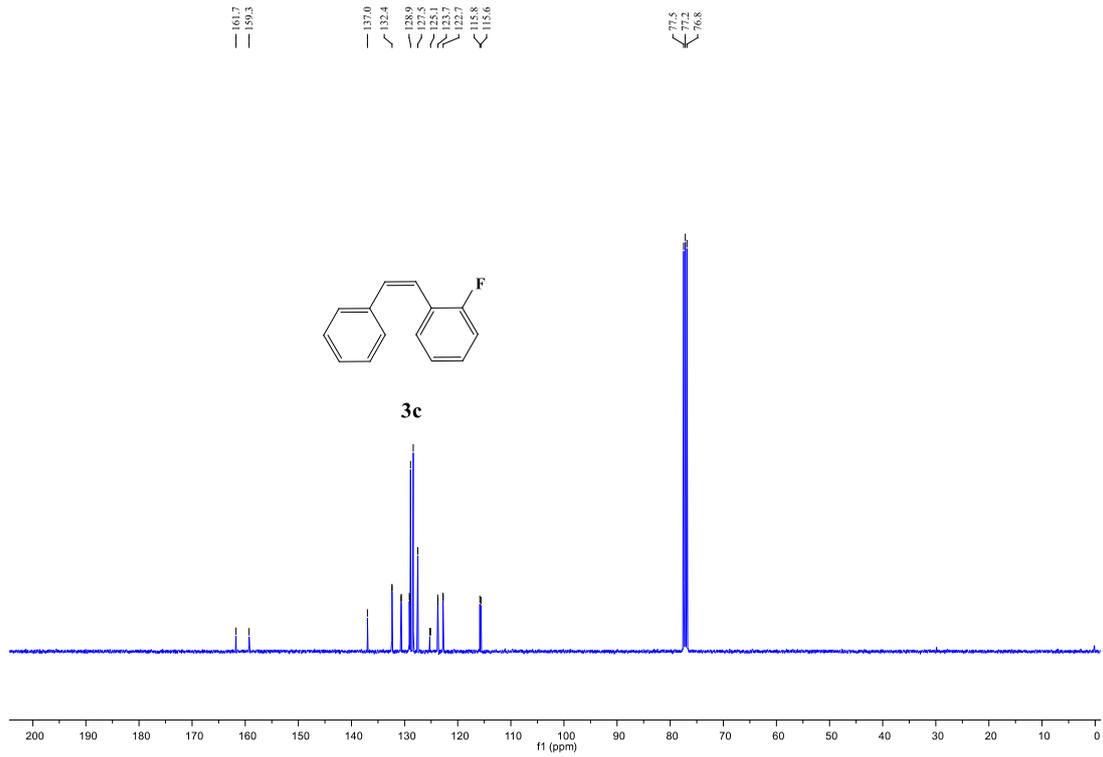


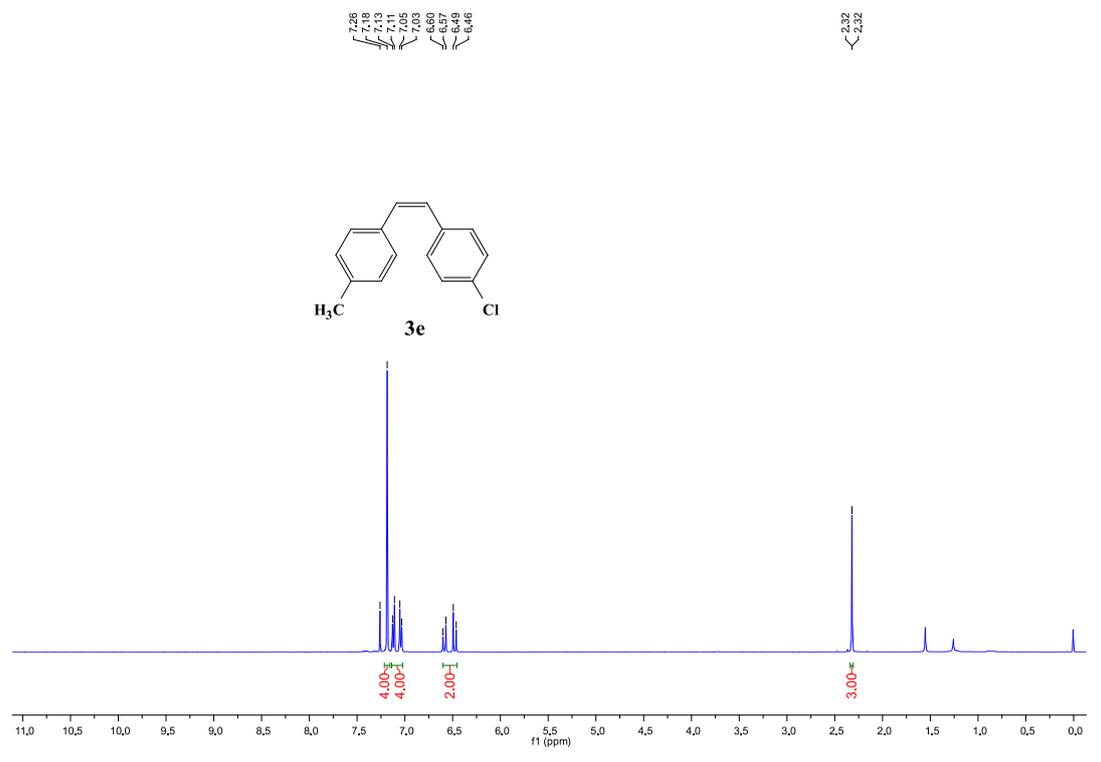
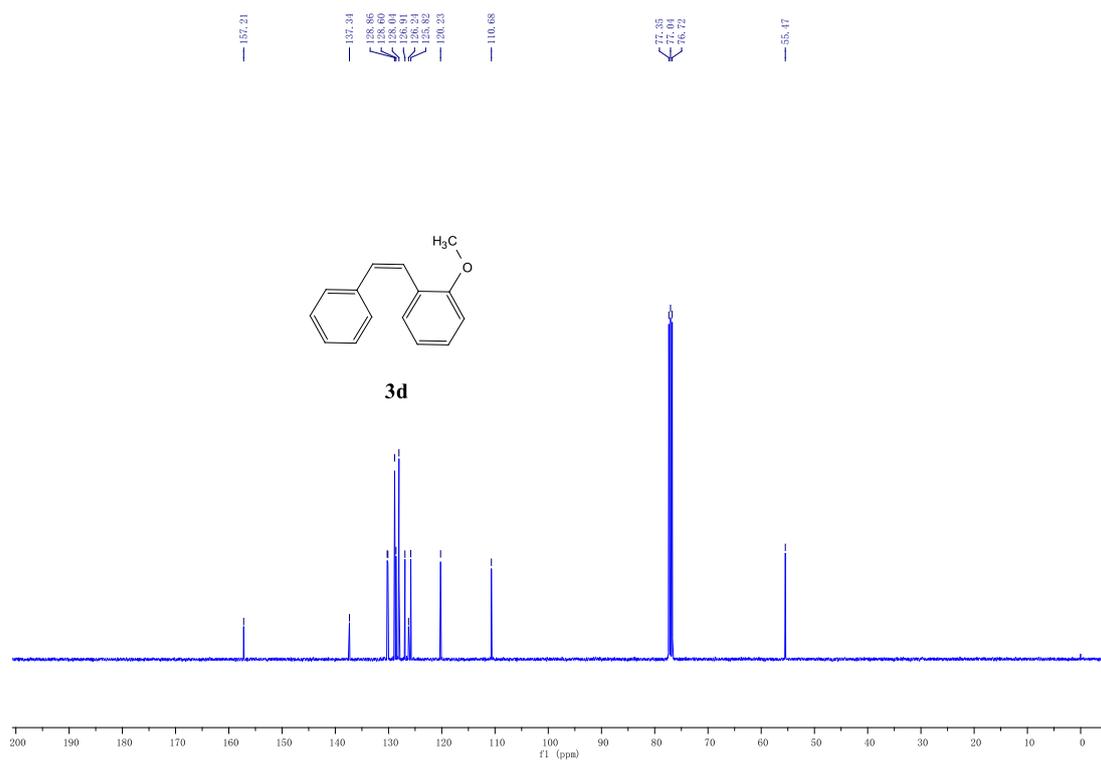


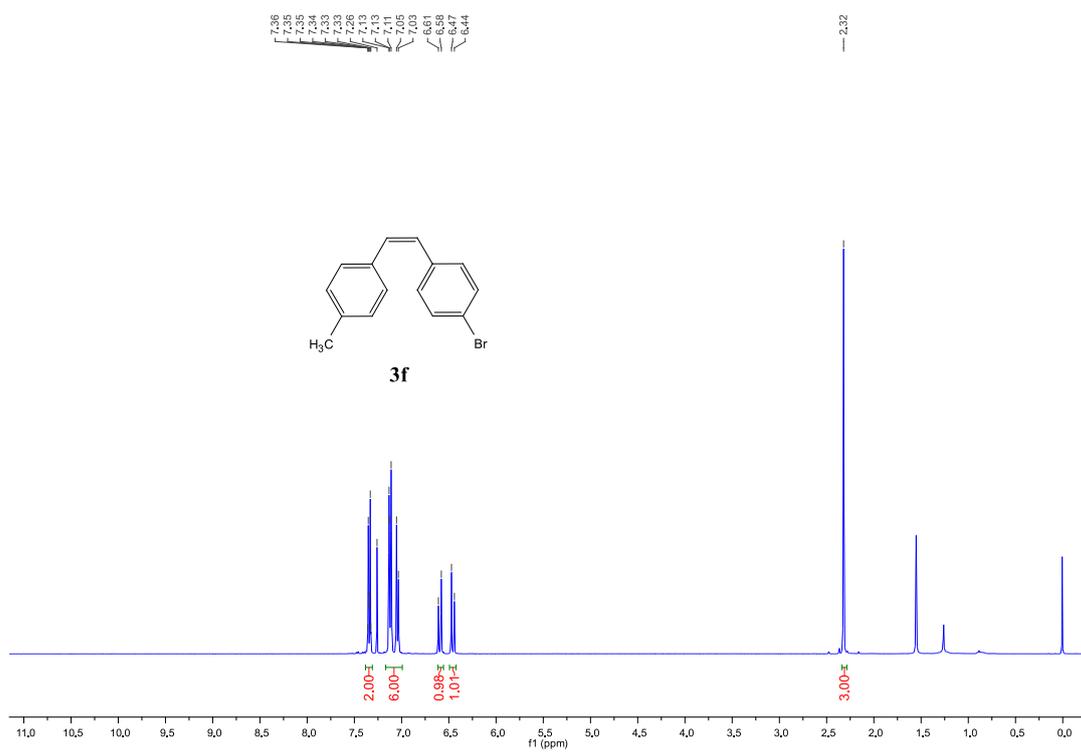
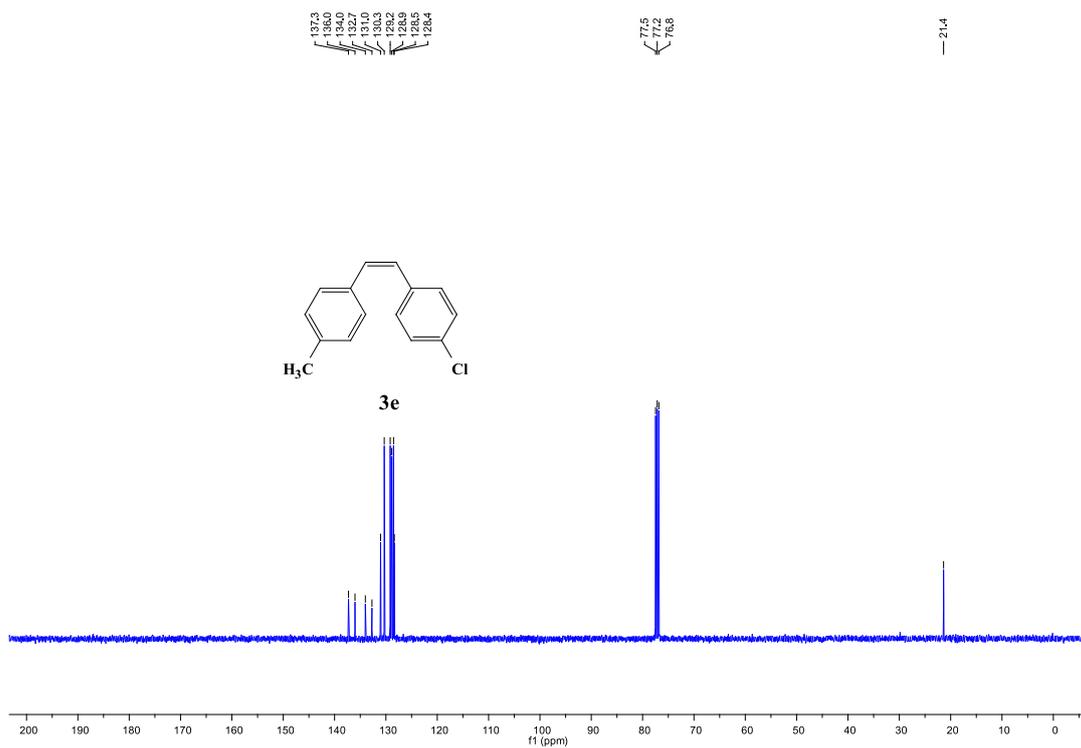


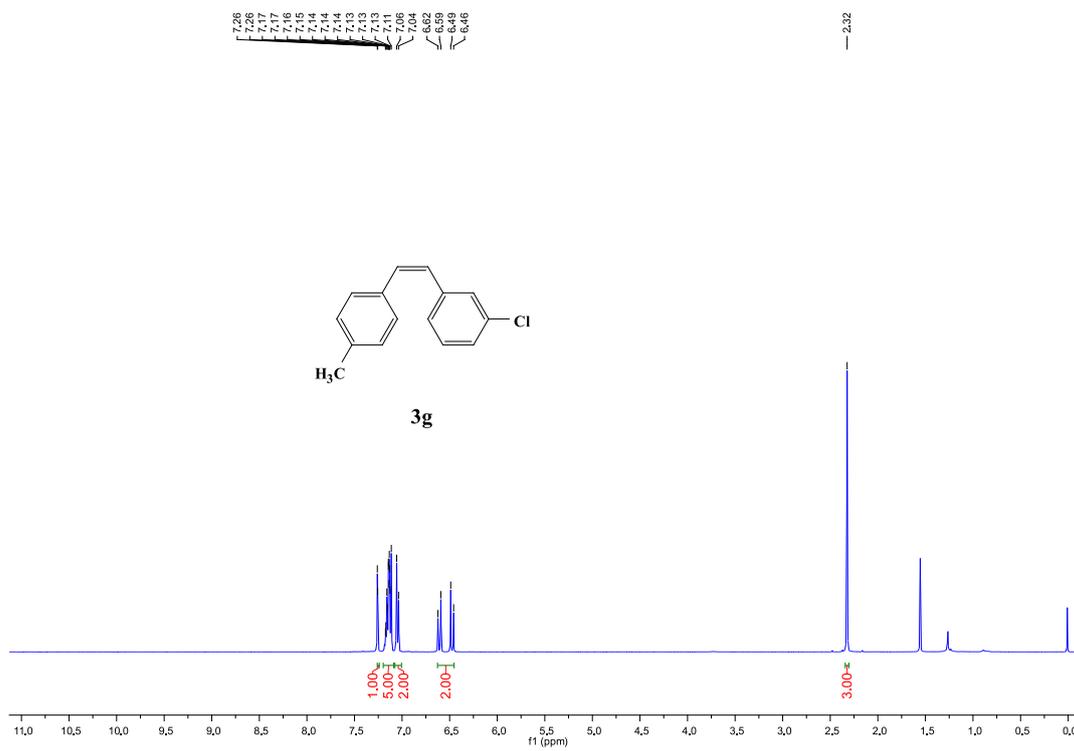
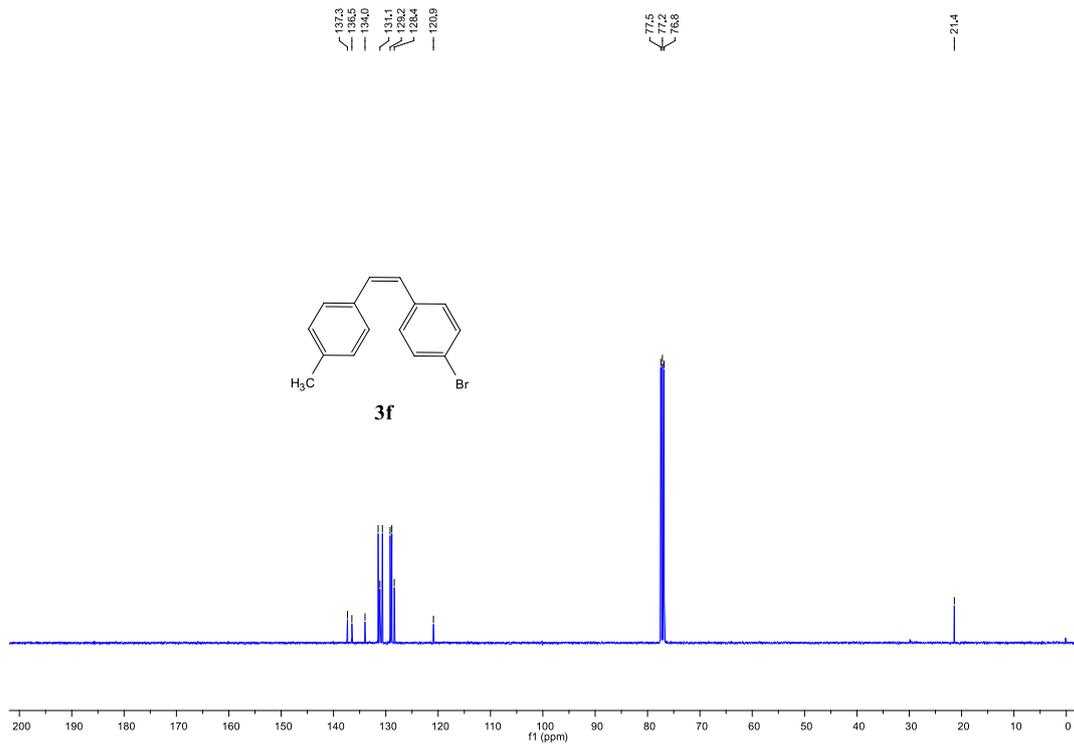


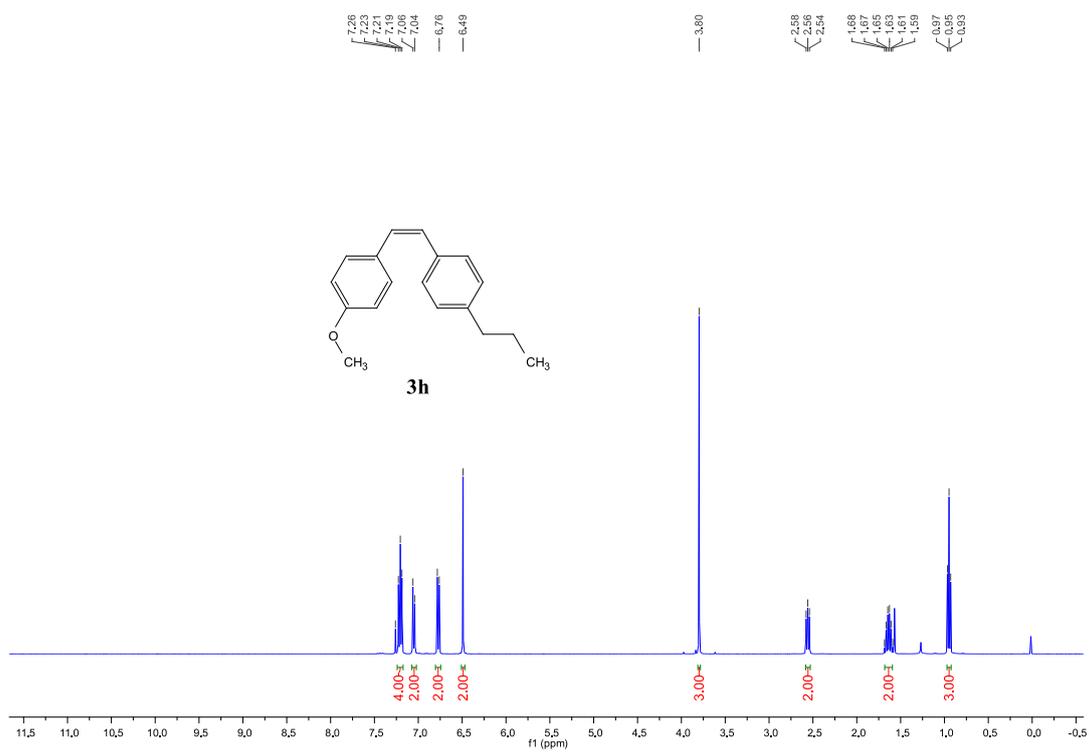
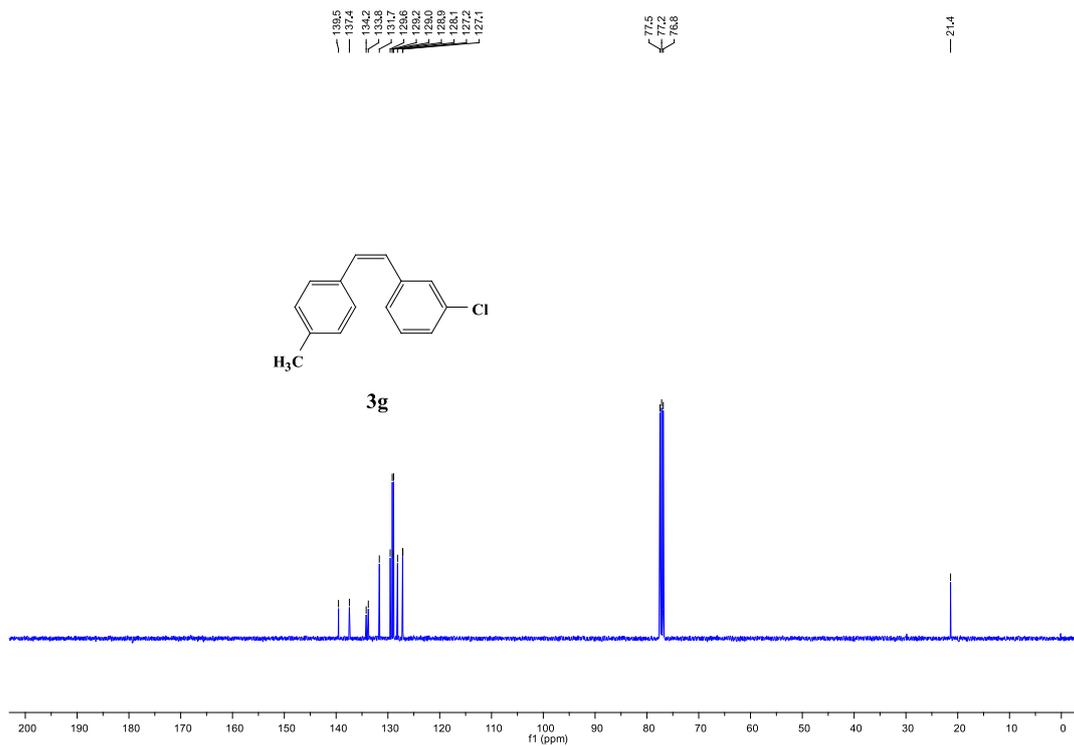


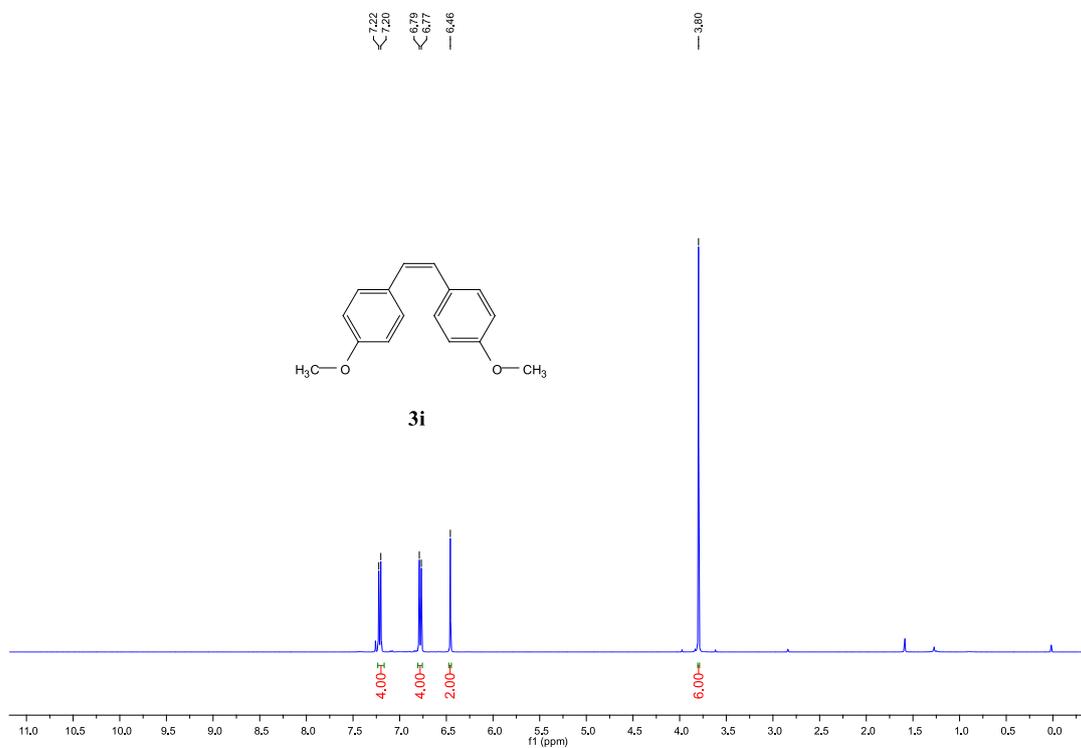
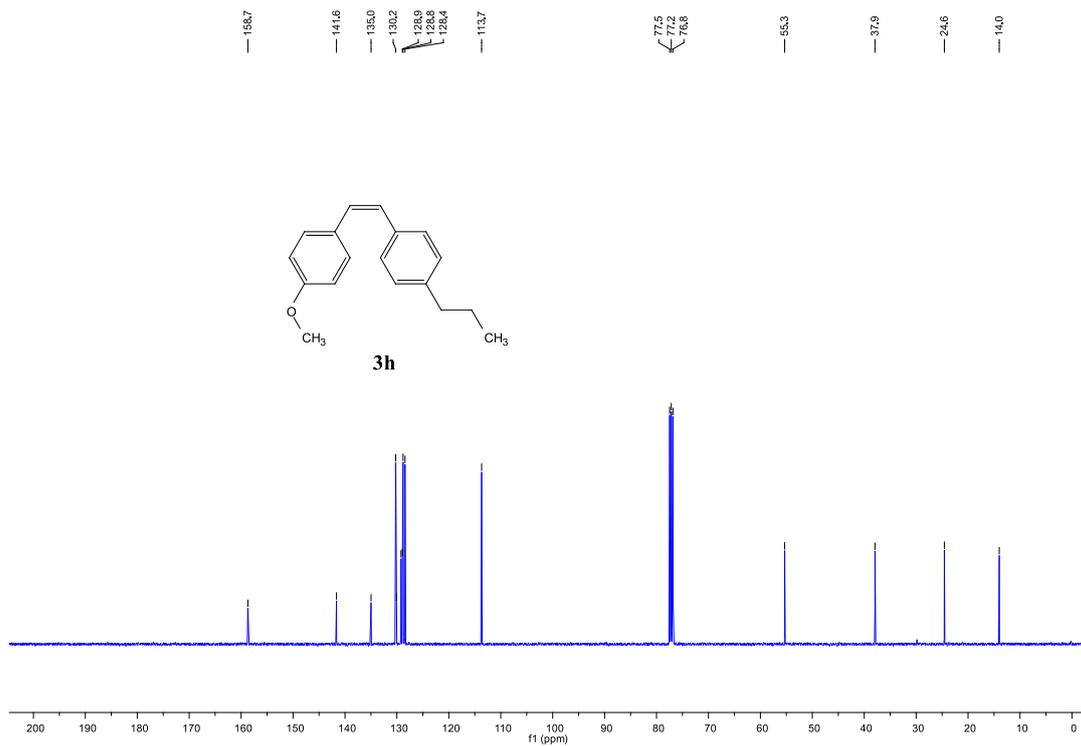


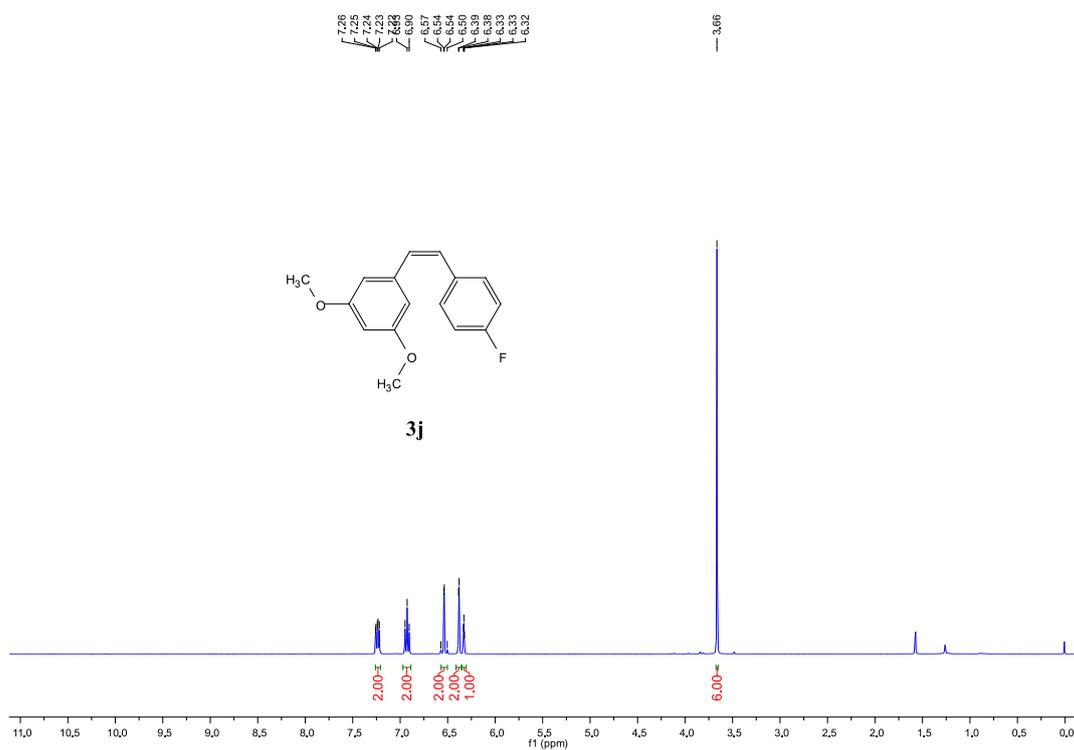
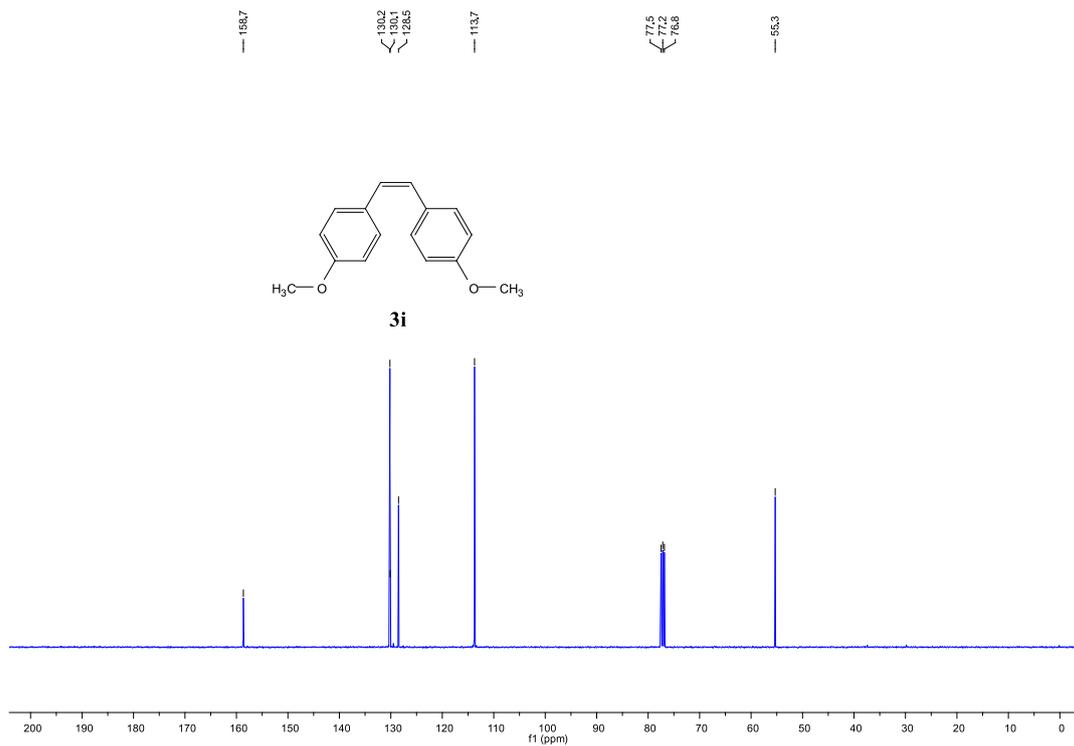




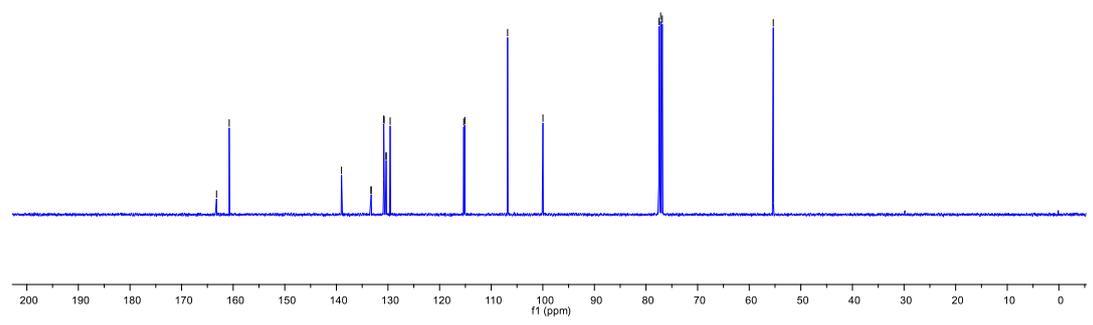
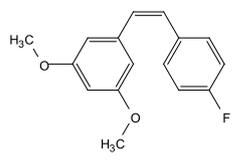




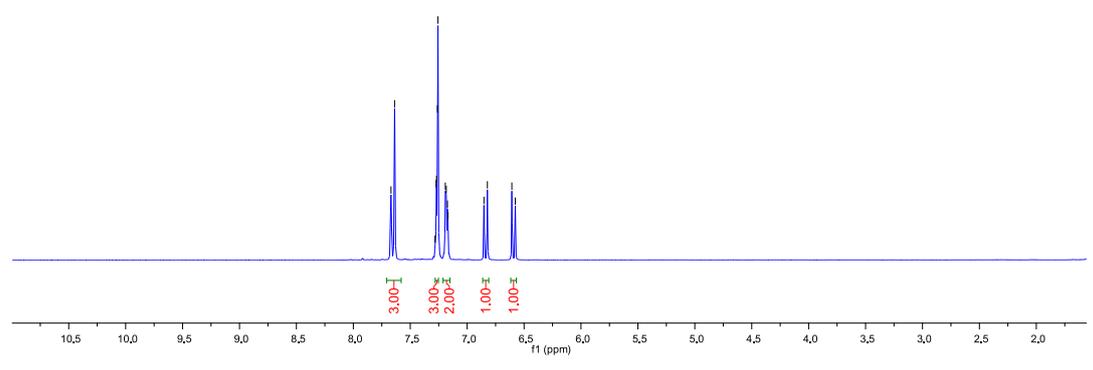
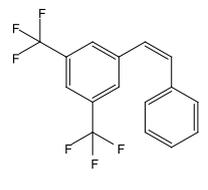




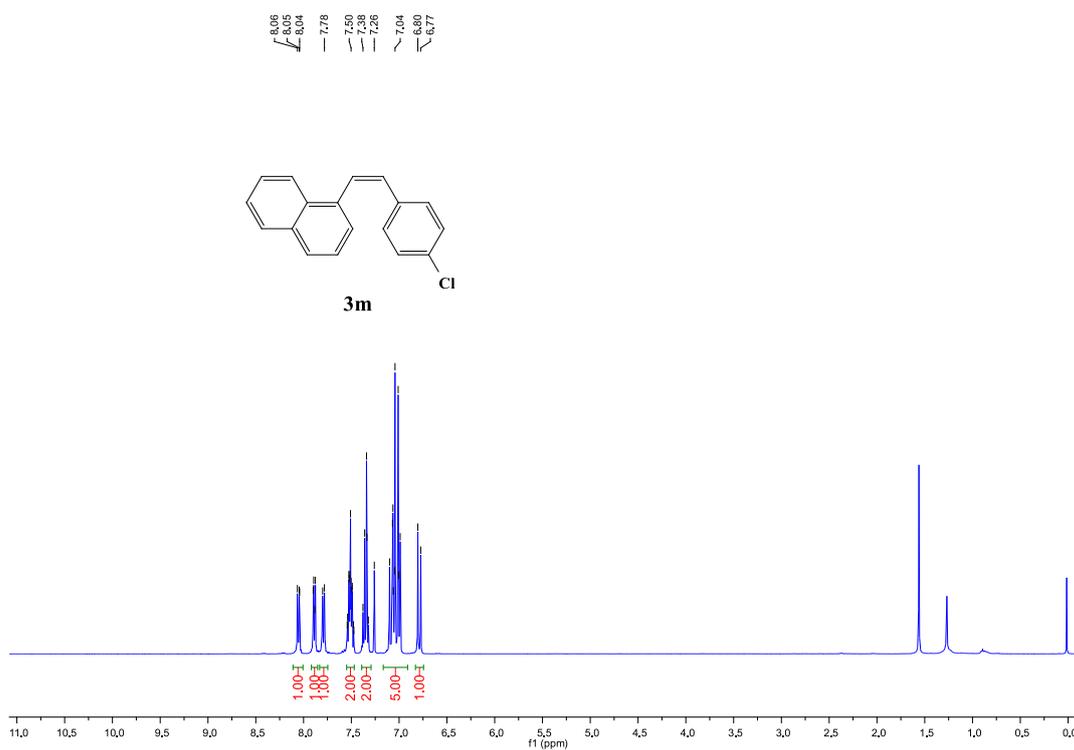
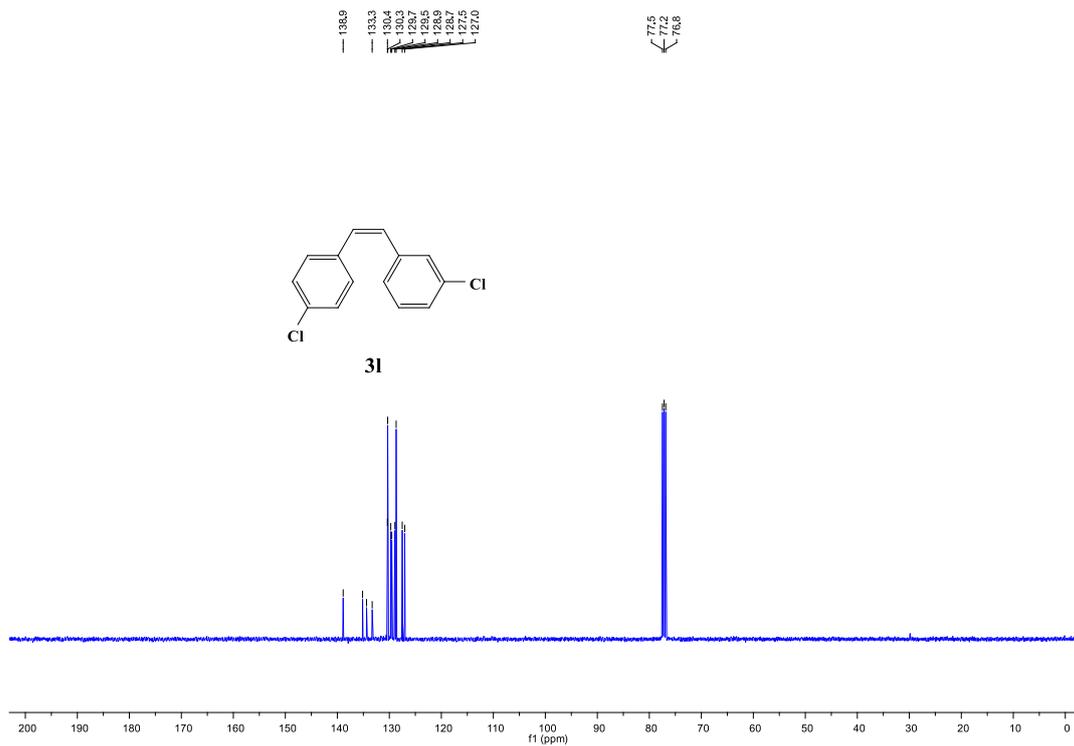
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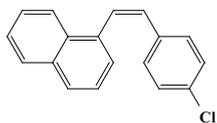






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