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### General Considerations

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Dry solvents were purchased and used as received except THF, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, and toluene. They were rigorously purged with argon for 2 h and then further purified by passing through two packed columns of neutral alumina (for THF and Et<sub>2</sub>O) or through neutral alumina and copper (II) oxide (for toluene and CH<sub>2</sub>Cl<sub>2</sub>) under argon from a solvent purification system. A standard workup protocol consisted of extraction with diethyl ether, washing with brine, drying over Na<sub>2</sub>SO<sub>4</sub>, and removal of the solvent in vacuo. Column chromatography was carried out with silica gel (230-400 mesh). Nuclear magnetic resonance (NMR) spectra were recorded on a BrukerAvance DPX-400. All <sup>1</sup>H NMR experiments were reported in δ units, parts per million (ppm), and measured relative to the signal for residual chloroform (7.26 ppm) in the deuterated solvent. All <sup>13</sup>C NMR experiments were reported in ppm relative to deuteriochloroform (77.23 ppm) and obtained with <sup>1</sup>H decoupling. All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy, high-resolution mass spectroscopy and/or CHN analysis. High-resolution mass spectra were recorded on a BrukerUltraflex II TOF/TOF mass spectrometer. IR spectra were recorded (thin film on NaCl plates) on a PerkinElmer Spectrum 100 series instrument. Melting Points were determined with a capillary melting point apparatus, Stuart SMP10, and were uncorrected. Gas Chromatographic analyses were performed on a Shimadzu GC-2010 Plus gas chromatography instrument with a FID detector using 15 m x 0.25 mm x 0.25 μm capillary column SHRXI-5MS. Cyclic voltammetry experiments were performed using a CH Instruments electrochemical analyzer.

## Experimental Procedures and Spectroscopic Data

- **General procedure 1 (GP1): Preparation of substituted 2-bromostyrenes:**

**Wittig reaction using potassium tertiary butoxide as base (GP1-A).** Under an argon atmosphere, potassium *tert*-butoxide (1.2 mmol) was added to a stirred mixture of triphenylphosphonium salt (1.2 mmol, pre-dried in vacuo at 60 °C for 3 h) in anhydrous Et<sub>2</sub>O (5 mL) at 0 °C. The resulting yellow mixture was allowed to stir for 1 h at the same temperature, after which a solution of an aldehyde or a ketone (1 mmol) in anhydrous Et<sub>2</sub>O (1 mL) was added drop-wise. The reaction was maintained at 0 °C and monitored by TLC for complete consumption of the starting material. The mixture was then quenched with saturated aqueous NH<sub>4</sub>Cl solution and diluted with diethyl ether. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. Purification of the residual mass by silica gel column chromatography afforded 2-bromostyrene derivatives.

**Wittig reaction using *n*-butyllithium as base (GP1-B).** To a stirred solution of triphenyl phosphonium salt (1.3 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M in hexanes, 1.2 mmol) dropwise at 0 °C. After 1 h, a solution of an aldehyde or a ketone (1.0 mmol) in THF (1 mL) was added dropwise at the same temperature. After complete consumption (as monitored by TLC) of the starting materials, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution. The reaction mixture was extracted with diethyl ether, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. Purification of the residual mass by column chromatography on silica gel afforded the corresponding 2-bromostyrene derivatives.

**Grignard reaction, followed by dehydration (GP1-C).** A solution of alkyl magnesium halide (6.0 mmol) in THF was added slowly to a solution of *o*-bromobenzaldehyde (5.0 mmol) in THF (25 mL) at 0 °C. The mixture was stirred at rt for 2 h and quenched with saturated aqueous NH<sub>4</sub>Cl solution. The standard workup protocol gave crude 1-(2-bromophenyl)-1-alcohol that was used in the next step without further purification. To a stirred solution of the crude alcohol from above in toluene (25 mL) was added *p*-TsOH (0.25 mmol). The mixture was stirred and heated at reflux under a Dean-Stark trap for 12 h to azeotropically remove H<sub>2</sub>O. The standard workup protocol followed by chromatography on silica gel gave 2-bromostyrene derivatives.

- **General procedure 2 (GP2): Synthesis of styrylanilines from 2-bromostyrenes**

**Using XPhos as ligand (GP2-A).**

Typically, 0.0075 mmol (7.0 mg) of Pd<sub>2</sub>(dba)<sub>3</sub>, 0.0225 mmol (10.7 mg) of XPhos<sup>1</sup>, 1.5 mmol (165 mg) of NaO<sup>t</sup>Pent and 1.2 mmol of the appropriate substituted aniline (if solid) were mixed in an oven-dried schlenk tube. The tube was evacuated and then refilled with nitrogen (3 times). 2-Bromostyrene (1.0 mmol), dissolved in degassed dioxane (1 mL), was added under an argon atmosphere (liquid anilines were added with 2-bromostyrene in the same manner). The tube was then placed in a preheated oil bath at 110°C and stirred for 12 h. The reaction mixture was cooled to room temperature, diluted with ether (10 mL), filtered through a short pad of silica gel, and

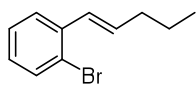
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<sup>1</sup> Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653

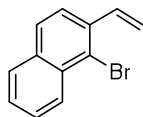
concentrated under vacuum. Purification of the residual mass by column chromatography on silica gel afforded styryl anilines.

**Using BrettPhos as ligand (GP2-B).** A oven-dried Schlenk tube equipped with a magnetic stir bar in a stream of nitrogen was charged with 0.02 mmol (19.0 mg) of Pd<sub>2</sub>(dba)<sub>3</sub>, 0.08 mmol (43.0 mg) of BrettPhos<sup>2</sup>, 1.5 mmol (165 mg) of NaO<sup>t</sup>Pent, 1.5 mmol of the appropriate substituted 2-vinylaniline (if solid). The tube was evacuated and then refilled with nitrogen (3 times). 1.0 mmol of 4-Bromoanisole and toluene (5 mL) were added (liquid 2-vinylanilines were added with 2-bromostyrene in the same manner). The resulting mixture was heated to 80 °C for 1 h. The mixture was cooled to room temperature, diluted with ether (10 mL), filtered through a short pad of silica gel, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired styrylanilines.

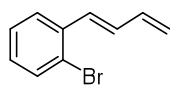
**(E)-1-bromo-2-(pent-1-enyl)benzene.** Following **GP1-C**, 2-bromo benzaldehyde (586 μL, 5.0 mmol) and *n*-butyl magnesium chloride (3.5 mL, 6.0 mmol, 20 wt% in THF/toluene) provided the title compound (720 mg, 64%) as liquid after column chromatography on silica gel (0.5% Et<sub>2</sub>O/hexane). IR ν<sub>max</sub> (film) 2959, 2929, 2870, 1647, 1588, 1465, 1435 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.06 (dt, *J* = 7.2, 1.6 Hz, 1H), 6.73 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.18 (td, *J* = 15.6, 7.2 Hz, 1H), 2.28-2.22 (m, 2H), 1.54 (dt, *J* = 14.6, 7.2 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.7, 134.1, 132.8, 128.8, 128.1, 127.4, 126.8, 123.2, 35.2, 22.4, 13.7; Anal. calcd. for C<sub>11</sub>H<sub>13</sub>Br: C, 58.69; H, 5.82. Found: C, 58.94; H, 5.91.



**1-bromo-2-vinylnaphthalene.** Following **GP1-A**, 1-bromo-2-naphthaldehyde (705 mg, 3.0 mmol) and methyltriphenylphosphonium bromide (1.4 g, 3.9 mmol) provided the title compound (540 mg, 77%) as white solid after column chromatography on silica gel (1.0% Et<sub>2</sub>O/hexane): mp 62–64 °C. IR ν<sub>max</sub> (plate) 3043, 2982, 1627, 1573, 1552, 1448, 1425, 1379 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 17.2, 10.8 Hz, 1H), 5.84 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.49 (dd, *J* = 11.2, 0.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.9, 135.0, 134.1, 132.6, 128.1, 127.8, 127.6, 126.7, 123.9, 117.5; Anal. calcd. for C<sub>12</sub>H<sub>9</sub>Br: C, 61.83; H, 3.89. Found: C, 62.05; H, 3.99.



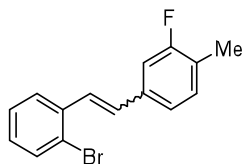
**(E)-1-bromo-2-(buta-1,3-dienyl)benzene.** Following **GP1-C**, 2-bromobenzaldehyde (1.2 mL, 10.0 mmol) and allyl magnesium chloride (7.1 mL, 12.0 mmol, 1.7 M in THF) provided the title compound (900 mg, 43%) as liquid after column chromatography on silica gel (0.5% Et<sub>2</sub>O/hexane). IR ν<sub>max</sub> (film) 3020, 2965, 2925, 1642, 1587, 1513, 1465, 1436 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59–7.54 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 15.6 Hz, 1H), 6.78–6.71 (m, 1H), 6.64–6.54 (m, 1H), 5.40 (d, *J* = 16.8 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.0,



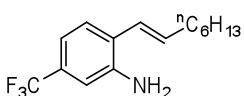
<sup>2</sup> Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 13552.

136.8, 133.1, 132.2, 131.3, 128.8, 127.5, 126.6, 124.0, 118.9; Anal. calcd. for C<sub>10</sub>H<sub>9</sub>Br: C, 57.44; H, 4.34. Found: C, 57.67; H, 4.43.

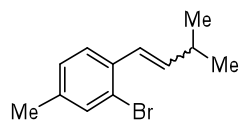
**4-(2-bromostyryl)-2-fluoro-1-methylbenzene.** Following **GP1-B**, 3-fluoro-4-methylbenzaldehyde (489  $\mu$ L, 4.0 mmol) and 2-bromobenzyl triphenylphosphonium bromide (2.66 g, 5.2 mmol) provided the title compound (1.06 g, 91%) as inseparable E/Z mixtures and liquid after column chromatography on silica gel (0.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\max}$  (film) 3057, 2925, 1622, 1466, 1571, 1509, 1421 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66–7.51 (m, 1H), 7.42 (d, *J* = 16.4 Hz) and 7.33–7.29 (m, total 1H) 7.24–7.14 (m, 2H), 7.13–7.06 (m, 2H), 6.98–6.94 (m, 1H), 6.82–6.75 (m, 1H), 6.61 (s, 1H), 2.29 (d, *J* = 2.0 Hz) and 2.21 (d, *J* = 2.0 Hz, total 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.6 (d, *J* = 243.0 Hz), 161.0 (d, *J* = 243.0 Hz), 137.7, 136.9, 136.8, 135.8 (d, *J* = 8.0 Hz), 133.2, 132.8, 132.4, 131.6 (d, *J* = 5.0 Hz), 131.1 (d, *J* = 6.0 Hz), 130.8, 130.3, 129.9, 128.9, 127.6 (d, *J* = 11.0 Hz), 127.3 (d, *J* = 8.0 Hz), 127.2, 126.7, 124.8, 124.6 (d, *J* = 3.0 Hz), 124.2, 123.9, 123.8, 122.5 (d, *J* = 3.0 Hz), 115.2 (d, *J* = 22.0 Hz), 112.8 (d, *J* = 23.0 Hz), 14.5 (d, *J* = 3.0 Hz), 14.4 (d, *J* = 3.0 Hz); Anal. calcd. for C<sub>15</sub>H<sub>12</sub>BrF: C, 61.88; H, 4.15. Found: C, 61.98; H, 4.19.



**(E)-2-(oct-1-enyl)-5-(trifluoromethyl)aniline.** Following a literature<sup>3</sup> procedure, to a solution of *trans*-1-octen-1-ylboronic acid (470 mg, 3.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (230 mg, 0.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.1 g, 8.0 mmol) in a mixture of solvents (32 mL, 5/2/1 toluene/EtOH/H<sub>2</sub>O) was added 2-bromo-5-(trifluoromethyl)aniline (288  $\mu$ L, 2.0 mmol). The resultant mixture was then purged with N<sub>2</sub> and refluxed for 20 h. The mixture was cooled to room temperature and diluted with water (25 mL) and CH<sub>2</sub>Cl<sub>2</sub> (25 mL). The organic phase was extracted with diethyl ether, washed with brine and concentrated in vacuo. Purification of the crude residue with silica gel column chromatography (5.0% EtOAc/hexane) provided the title compound (510 mg, 94%) as liquid. IR  $\nu_{\max}$  (film) 3410, 3056, 2950, 2913, 1642, 1602, 1484, 1462, 1372 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.19–6.12 (m, 1H), 4.05 (br s, 2H), 2.24 (q, *J* = 6.8 Hz, 2H), 1.48 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.39–1.26 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 135.6, 129.7 (q, *J* = 32.0 Hz), 127.6, 127.5, 124.3 (q, *J* = 270.0 Hz), 124.2, 115.2 (q, *J* = 3.5 Hz), 112.1 (q, *J* = 4.0 Hz), 33.4, 31.7, 29.3, 28.9, 22.6, 14.1; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>15</sub>H<sub>21</sub>F<sub>3</sub>N 272.1621; found 272.1617.



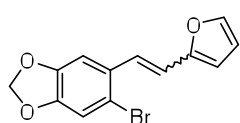
**2-bromo-4-methyl-1-(3-methylbut-1-enyl)benzene.** Following **GP1-B**, 2-bromo-4-methylbenzaldehyde (497 mg, 2.5 mmol) and isobutyltriphenylphosphonium bromide (2.0 g, 5.0 mmol) provided the title compound (585 mg, 98%) as inseparable E/Z mixtures and liquid after silica gel column chromatography (0.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\max}$  (film) 2960, 2867, 1604, 1486, 1463, 1381 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42–7.36 (m) and 7.16 (d, *J* = 7.6 Hz, total 2H), 7.09–7.01 (m, 1H), 6.65 (d, *J* = 16.0 Hz) and 6.30 (d, *J* = 11.2 Hz, total 1H), 6.10 (dd, *J*



<sup>3</sup> Shen, M.; Leslie, B. E.; Driver, T. G. *Angew. Chem. Int. Ed.* **2008**, *47*, 5056.

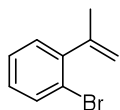
= 16.0, 6.8 Hz) and 5.55 (t,  $J = 10.0$  Hz, total 1H), 2.71–2.62 (m) and 2.56–2.46 (m, total 1H), 2.33 (s) and 2.30 (s, total 3H), 1.12 (d,  $J = 6.8$  Hz) and 1.02 (d,  $J = 8.8$  Hz, total 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.0, 138.3, 138.2, 135.0, 134.7, 133.2, 132.9, 130.1, 128.3, 127.7, 126.4, 125.9, 125.7, 123.7, 123.1, 31.7, 27.2, 23.0, 22.4, 20.8, 20.7; Anal. calcd. for  $\text{C}_{12}\text{H}_{15}\text{Br}$ : C, 60.27; H, 6.32. Found: C, 60.93; H, 6.42.

**5-bromo-6-(2-(furan-2-yl)vinyl)benzo[*d*][1,3]dioxole.** Following **GPI-B**, furan-2-carbaldehyde (248  $\mu\text{L}$ , 3.0 mmol) and 5-bromo-1,3-benzodioxole-6-methyltriphenylphosphonium bromide (2.5 g, 4.5 mmol) provided the title compound (660 mg, 75%) as inseparable *E/Z* mixtures and liquid



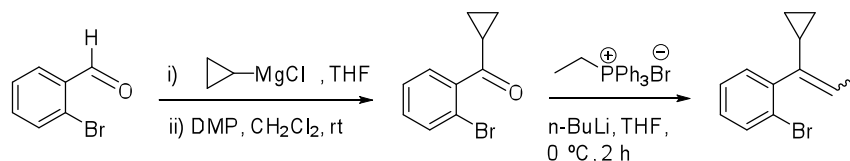
after silica gel column chromatography (1.0%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 2980, 2895, 1502, 1474, 1412, 1427, 1242  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.26 (m, 1H), 7.07–6.97 (m) and 6.68 (d,  $J = 16.0$  Hz, total 2H), 6.43–6.31 (m, 3H), 6.19 (d,  $J = 3.6$  Hz, 1H), 5.98 (br s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 151.7, 148.0, 147.9, 147.8, 147.0, 142.4, 142.0, 130.9, 130.2, 126.7, 125.6, 118.7, 117.4, 115.3, 114.7, 112.9, 112.4, 111.8, 111.4, 110.6, 110.2, 109.1, 105.3, 101.9, 101.8.

**1-bromo-2-(prop-1-en-2-yl)benzene.** Following **GPI-C**, methyl-2-bromo benzoate (1.07 g, 5.0 mmol) and methyl magnesium chloride (4.25 mL, 12.5 mmol, 22 wt% in THF),



provided the title compound (520 mg, 53%) as liquid after silica gel column chromatography (0.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 2980, 1631, 1482, 1440, 1379  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.25 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.20 (dd,  $J = 7.6, 2.0$  Hz, 1H), 7.11 (ddd,  $J = 8.0, 7.6, 2.0$  Hz, 1H), 5.24–5.23 (m, 1H), 4.95–4.94 (m, 1H), 2.10 (dd,  $J = 1.6, 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 144.8, 132.7, 129.7, 128.4, 127.2, 121.6, 116.0, 23.5; Anal. calcd. for  $\text{C}_9\text{H}_9\text{Br}$ : C, 54.85; H, 4.60. Found: C, 54.94; H, 4.64.

**1-bromo-2-(1-cyclopropylprop-1-enyl)benzene.**



To a solution of 2-bromobenzaldehyde (740 mg, 4.0 mmol) in THF (20 mL) was added cyclopropylmagnesium bromide (9.6 mL, 4.8 mmol, 0.5 M in THF) at 0 °C. The mixture was stirred at that temperature for 1 h, and quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution. After stirring it for 15 min at rt, the mixture was extracted with ether (2x25 mL). The combined organic layer was washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent under reduced pressure provided the crude alcohol, which was used directly for the next step.

To a solution of the alcohol (4.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL) at rt was added DMP (2.3 g, 5.2 mmol) portion wise and the reaction mixture was allowed to stir for 1 h. The reaction mixture was quenched with a premixed  $\text{Na}_2\text{S}_2\text{O}_3$ - $\text{NaHCO}_3$  solution (20 mL, 1:1 ratio) at 0 °C and stirred

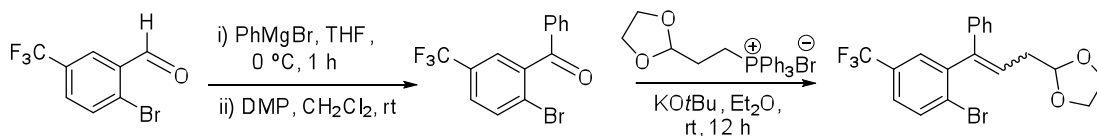
vigorously for 2 h. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel (2% EtOAc/hexane) gave (2-bromophenyl)(cyclopropyl)methanone (750 mg, 83%) as colorless oil. IR  $\nu_{\text{max}}$  (film) 3060, 3009, 1732, 1683, 1587, 1563, 1466, 1429, 1380 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.46 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.37 (dt,  $J = 7.6, 1.2$  Hz, 1H), 7.29 (dt,  $J = 8.0, 2.0$  Hz, 1H), 2.44 (sept,  $J = 4.4$  Hz, 1H), 1.33 (dt,  $J = 7.6, 4.4$  Hz, 2H), 1.12 (dt,  $J = 7.2, 4.4$  Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  204.3, 142.2, 133.5, 131.5, 129.0, 127.4, 119.1, 21.9, 13.4; Anal. calcd. for C<sub>10</sub>H<sub>9</sub>BrO: C, 53.36; H, 4.03. Found: C, 53.35; H, 4.13.

Following **GP1-B**, (2-bromophenyl)(cyclopropyl)methanone (650 mg, 2.89 mmol) and methyltriphenylphosphonium bromide (2.14 g, 5.77 mmol) provided the title compound (550 mg, 85%) as inseparable E/Z mixtures and liquid after silica gel column chromatography (0.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3008, 2913, 1560, 1469, 1430 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (dd,  $J = 8.0, 0.8$  Hz) and 7.51 (dd,  $J = 8.0, 1.2$  Hz, total 1H), 7.27 (dt,  $J = 7.2, 1.2$  Hz) and 7.19 (dt,  $J = 7.6, 1.2$  Hz, total 1H), 7.11 (dt,  $J = 7.6, 1.6$  Hz) and 7.07 (dt,  $J = 7.6, 2.0$  Hz, total 1H), 7.02 (dd,  $J = 7.2, 1.8$  Hz) and 7.00 (dd,  $J = 7.2, 1.6$  Hz, total 1H), 5.64 (q,  $J = 6.8$  Hz) and 5.45 (q,  $J = 7.2$  Hz, total 1H), 1.89 (d,  $J = 6.8$  Hz) and 1.38 (d,  $J = 6.8$  Hz, total 3H), 1.66-1.59 (m, 1H), 0.71-0.66 (m) and 0.59-0.54 (m, total 2H), 0.48-0.25 (m) and 0.20-0.16 (m, total 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.5, 141.8, 141.5, 140.3, 132.5, 132.3, 131.3, 131.0, 128.2, 128.0, 127.0, 126.5, 125.7, 124.2, 123.8, 121.5, 17.6, 14.4, 13.5, 11.7, 5.3, 4.9, 4.3; Anal. calcd. for C<sub>12</sub>H<sub>13</sub>Br: C, 60.78; H, 5.53. Found: C, 60.70; H, 5.52.

### 1-bromo-2-(1-phenylprop-1-enyl)benzene.

Following **GP1-B**, 2-bromobenzophenone (364  $\mu$ L, 2.0 mmol) and methyltriphenylphosphonium bromide (1.5 g, 4.0 mmol) provided the title compound (440 mg, 80%) as inseparable E/Z mixtures and liquid after silica gel column chromatography (0.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3051, 2934, 1492, 1463, 1433, 1352 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (d,  $J = 7.6$  Hz) and 7.54 (d,  $J = 7.6$  Hz, total 1H), 7.38–7.09 (m, 8H), 6.38–6.31 (m) and 5.89–5.82 (m, total 1H), 1.93 (dd,  $J = 7.2, 3.6$  Hz) and 1.63 (dd,  $J = 6.8, 3.6$  Hz, total 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.0, 141.7, 141.3, 140.7, 140.5, 139.1, 133.1, 133.0, 131.8, 131.7, 129.7, 128.7, 128.4, 128.3, 127.9, 127.8, 127.5, 127.1, 126.9, 126.8, 126.2, 125.3, 124.4, 123.7, 15.6, 15.4; Anal. calcd. for C<sub>15</sub>H<sub>13</sub>Br: C, 65.95; H, 4.80. Found: C, 66.03; H, 4.85.

### 2-(3-(2-bromo-5-(trifluoromethyl)phenyl)-3-phenylallyl)-1,3-dioxolane.



Following the above described protocol for the synthesis of (2-bromophenyl)(cyclopropyl)methanone, a solution of 2-bromo-5-(trifluoromethyl)benzaldehyde (2.02 g, 8.0 mmol) in THF (50 mL) was treated with phenylmagnesium bromide (4.3 mL, 12.0 mmol, 2.8 M in Et<sub>2</sub>O) to afford the crude alcohol, which was treated with DMP to provide (2-

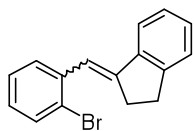
bromo-5-(trifluoromethyl)phenyl)(phenyl)methanone (2.05 g, 78%) as yellow oil after silica gel column chromatography (1.0% EtOAc/hexane). IR  $\nu_{\max}$  (film) 3066, 2926, 1680, 1605, 1598, 1582, 1450, 1333,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81–7.79 (m, 3H), 7.67–7.60 (m, 3H), 7.52–7.48 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.3, 141.5, 135.4, 135.0, 134.2, 134.0, 130.2, 129.8, 128.9, 127.7 (q,  $J = 3.5$  Hz), 125.7 (q,  $J = 3.5$  Hz), 123.5; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{14}\text{H}_9\text{BrF}_3\text{O}$  328.9783; found 328.9777.

Following **GP1-A**, (2-bromo-5-(trifluoromethyl)phenyl)(phenyl)methanone (658 mg, 2.0 mmol) and 2-(1,3-dioxolan-2-yl)ethyltriphenylphosphonium bromide (1.15 g, 2.6 mmol) provided the title compound (350 mg, 42%) as inseparable E/Z mixtures and colorless oil after silica gel column chromatography (2.0% EtOAc/hexane). IR  $\nu_{\max}$  (film) 2958, 2887, 1602, 1495, 1411, 1323  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.4$  Hz) and 7.65 (d,  $J = 8.4$  Hz, total 1H), 7.56–7.54 (m, 1H), 7.48–7.44 (m, 1H), 7.39–7.18 (m, 5H), 6.38 (t,  $J = 8.0$  Hz) and 5.87 (t,  $J = 7.6$  Hz, total 1H), 5.05 (t,  $J = 8.4$  Hz) and 4.98 (t,  $J = 4.8$  Hz, total 1H), 4.03–3.94 (m, 2H), 3.92–3.83 (m, 2H), 2.73 (dd,  $J = 7.2, 4.4$  Hz) and 2.42–2.21 (m, total 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 142.6, 142.0, 141.3, 139.2, 138.0, 133.7, 133.6, 130.1, 129.8, 129.5, 128.6 (q,  $J = 3.5$  Hz), 128.4, 128.2 (q,  $J = 3.5$  Hz), 128.1, 127.8, 127.6, 127.5, 127.4, 126.3, 125.6 (q,  $J = 3.5$  Hz), 125.2 (q,  $J = 3.5$  Hz), 124.7, 122.5, 122.4, 103.6, 103.3, 65.1, 65.0, 64.9, 34.9, 34.3; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{19}\text{H}_{17}\text{BrF}_3\text{O}_2$  413.0359; found 413.0362.

**(2-(2-bromophenyl)ethene-1,1-diyl)dibenzene.** Following **GP1-B**, 2-bromobenzaldehyde (409  $\mu\text{L}$ , 3.5 mmol) was added to the ylid generated by treatment of (diphenylmethyl)triphenylphosphonium bromide (2.32 g, 4.55 mmol) with *n*BuLi (2.4 mL, 3.85 mmol, 1.6 M in  $\text{Et}_2\text{O}$ ) and then refluxed for 12 h. The title compound (650 mg, 55%) was obtained as colorless liquid after silica gel column chromatography (0.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\max}$  (film) 3056, 3025, 1599, 1557, 1491, 1462, 1443  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.39–7.31 (m, 5H), 7.28–7.22 (m, 3H), 7.17–7.12 (m, 2H), 7.04 (s, 1H), 6.98 (dt,  $J = 7.2, 1.6$  Hz, 1H), 6.93 (dd,  $J = 7.6, 1.2$  Hz, 1H), 6.84 (dd,  $J = 7.2, 1.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 142.8, 139.7, 138.1, 132.4, 131.4, 130.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 126.6, 125.2; Anal. calcd. for  $\text{C}_{20}\text{H}_{15}\text{Br}$ : C, 71.65; H, 4.51. Found: C, 71.88; H, 4.36.

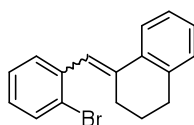
**1-bromo-2-(2-phenylprop-1-enyl)benzene.** Following **GP1-B**, 2-bromobenzaldehyde (702  $\mu\text{L}$ , 6.0 mmol) and (1-phenylethyl)triphenylphosphonium bromide (3.7 g, 8.4 mmol) provided the title compound (1.6 g, 98%) as inseparable E/Z mixtures and colorless liquid after silica gel column chromatography (0.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\max}$  (film) 3055, 2972, 1599, 1494, 1433  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64–7.57 (m) and 7.53–7.50 (m, total 2H), 7.42–7.30 (m, 2H), 7.24–7.11 (m, 3H), 6.97–6.86 (m) and 6.77–6.74 (m, total 2H), 6.56 (s, 1H), 2.27 (d,  $J = 1.6$  Hz) and 2.17 (d,  $J = 1.6$  Hz, total 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 141.1, 140.2, 138.5, 138.4, 132.7, 132.4, 131.8, 131.0, 128.6, 128.5, 128.4, 128.3, 127.8, 127.6, 127.2, 127.1, 127.0, 126.6, 126.4, 126.2, 124.8, 124.4, 26.1, 17.3; Anal. calcd. for  $\text{C}_{15}\text{H}_{13}\text{Br}$ : C, 65.95; H, 4.80. Found: C, 65.88; H, 4.76.

**1-(2-bromobenzylidene)-2,3-dihydro-1H-indene.** Following **GPI-B**, 2-



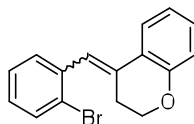
bromobenzaldehyde (878  $\mu\text{L}$ , 7.5 mmol) and the corresponding phosphonium salt (4.5 g, 9.75 mmol) provided the title compound (980 mg, 46%) as inseparable E/Z mixtures and colorless liquid after silica gel column chromatography (0.3% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3059, 2951, 2868, 1649, 1586, 1559, 1463, 1431  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ( ) 7.70–7.46 (m, 2H), 7.34–7.20 (m, 2H), 7.17–7.07 (m, 2H), 6.99–6.90 (m, 2H), 6.50 (s, 1H), 3.07–2.95 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.9, 146.1, 146.0, 144.4, 142.1, 139.3, 138.7, 137.8, 132.9, 132.7, 130.8, 129.2, 128.6, 128.5, 128.4, 127.8, 127.2, 127.1, 126.8, 125.9, 125.4, 125.3, 124.3, 124.0, 120.7, 118.2, 33.6, 30.7, 30.4, 30.1; Anal. calcd. for C<sub>16</sub>H<sub>13</sub>Br: C, 67.39; H, 4.59. Found: C, 67.36; H, 4.60.

**1-(2-bromobenzylidene)-1,2,3,4-tetrahydronaphthalene.** Following **GPI-B**, 2-



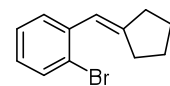
bromobenzaldehyde (820  $\mu\text{L}$ , 7.0 mmol) and the corresponding phosphonium salt (4.3 g, 9.1 mmol) provided the title compound (1.27 g, 60%) as inseparable E/Z mixtures and colorless liquid after silica gel column chromatography (0.3% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3061, 2932, 2861, 1629, 1558, 1484, 1462, 1432  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78–7.76 (m) and 7.63–7.56 (m, total 1H), 7.35–7.03 (m, 5H), 6.93 (d,  $J$  = 7.6 Hz, 1H), 6.79 (dt,  $J$  = 8.0, 1.6 Hz, 1H), 6.40 (s, 1H), 2.93–2.86 (m, 2H), 2.64–2.59 (m, 2H), 2.07–2.01 (m) and 1.89–1.83 (m, total 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 138.8, 138.5, 138.4, 137.9, 135.7, 134.5, 132.7, 131.6, 131.1, 129.3, 129.1, 128.9, 128.2, 127.8, 127.6, 127.1, 127.0, 126.3, 125.1, 124.8, 124.7, 124.2, 124.0, 123.0, 34.7, 30.4, 29.8, 28.0, 24.2, 23.8; Anal. calcd. for C<sub>17</sub>H<sub>15</sub>Br: C, 68.24; H, 5.05. Found: C, 68.27; H, 5.07.

**4-(2-bromobenzylidene)chroman.** Following **GPI-B**, 2-bromobenzaldehyde (820  $\mu\text{L}$ , 7.0



mmol) and the corresponding phosphonium salt (4.3 g, 9.1 mmol) provided the title compound (1.6 g, 76%) as inseparable E/Z mixtures and colorless liquid after silica gel column chromatography (0.3% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3065, 2970, 2894, 1604, 1571, 1483, 1450, 1304  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (dd,  $J$  = 8.0, 1.6 Hz) and 7.66–7.60 (m, total 2H), 7.38–7.06 (m, 4H), 7.00–6.81 (m, 2H), 6.53 (t,  $J$  = 7.6 Hz) and 6.31 (s, total 1H), 4.44 (t,  $J$  = 5.6 Hz, 1H), 4.20 (t,  $J$  = 6.0 Hz, 1H), 2.79–2.72 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.0, 154.9, 138.5, 137.2, 132.9, 132.8, 132.2, 132.1, 131.4, 131.1, 129.7, 129.6, 128.7, 128.6, 128.5, 127.3, 126.9, 125.0, 124.8, 124.0, 123.9, 122.2, 121.2, 120.9, 120.4, 119.4, 117.6, 117.1, 67.3, 66.2, 33.1, 26.8; Anal. calcd. for C<sub>16</sub>H<sub>13</sub>BrO: C, 63.81; H, 4.35. Found: C, 63.76; H, 4.39.

**1-bromo-2-(cyclopentylidenemethyl)benzene.** Following **GPI-B**, 2-bromobenzaldehyde (586

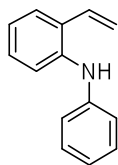


$\mu\text{L}$ , 5.0 mmol) and cyclopentyltriphenylphosphonium bromide (2.7 g, 6.5 mmol) provided the title compound (1.06 g, 89%) as colorless liquid after silica gel column chromatography (0.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 2924, 2852, 1615, 1468, 1426, 1164  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.39 (dd,  $J$  = 7.6, 1.6 Hz, 1H), 7.27–7.23 (m, 1H), 7.02 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 6.50 (quint,  $J$  = 2.4 Hz, 1H),



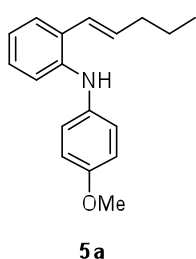
2.55–2.50 (m, 2H), 2.45–2.42 (m, 2H), 1.77–1.66 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 138.5, 132.6, 129.5, 127.3, 126.9, 124.0, 120.0, 35.2, 31.0, 27.0, 25.6; Anal. calcd. for  $\text{C}_{12}\text{H}_{13}\text{Br}$ : C, 60.78; H, 5.53. Found: C, 60.78; H, 5.71.

***N*-phenyl-2-vinylaniline.**



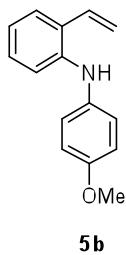
Following **GP2-A**, 2-bromostyrene (130  $\mu\text{L}$ , 1 mmol) and aniline (110  $\mu\text{L}$ , 1.2 mmol) provided the title compound as a colorless liquid after column chromatography on silica gel (2% EtOAc/hexane) (190 mg, 97%). IR  $\nu_{\text{max}}$  (film) 3046, 1624, 1573, 1498, 1423, 1310  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 7.6$  Hz, 1H), 7.28–7.19 (m, 4H), 7.02 (t,  $J = 6.8$  Hz, 1H), 6.96–6.86 (m, 4H), 5.69 (d,  $J = 17.6$  Hz, 1H), 5.53 (br s, 1H), 5.33 (d,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 140.1, 132.9, 130.1, 129.3, 128.6, 127.2, 122.6, 120.5, 120.0, 117.2, 116.3; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{14}\text{H}_{14}\text{N}$  196.1121; found 196.1129.

**(*E*)-*N*-(4-methoxyphenyl)-2-(pent-1-enyl)aniline (5a).**



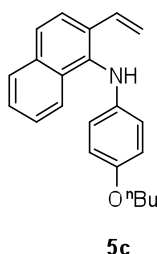
Following **GP2-A**, (*E*)-1-bromo-2-(pent-1-enyl)benzene (450 mg, 2 mmol) and 4-methoxyaniline (296 mg, 2.4 mmol) provided the title compound as a colorless liquid (453 mg, 85%) after column chromatography on silica gel (2% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3394, 2957, 2833, 1598, 1576, 1510, 1456, 1240  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 7.6$  Hz, 1H), 7.10 (t,  $J = 5.6$  Hz, 1H), 7.05–6.99 (m, 3H), 6.90–6.84 (m, 3H), 6.51 (d,  $J = 16.0$  Hz, 1H), 6.13 (dt,  $J = 16.0, 14.0$  Hz, 1H), 5.45 (br s, 1H), 3.80 (s, 3H), 2.22 (ddd,  $J = 14.4, 7.2, 1.2$  Hz, 2H), 1.51 (dt,  $J = 14.6, 7.2$  Hz, 2H), 0.97 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 141.7, 136.6, 133.9, 127.8, 127.7, 127.5, 125.5, 121.6, 120.5, 116.3, 114.7, 55.6, 35.5, 22.6, 13.7; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{18}\text{H}_{22}\text{NO}$  268.1696; found 268.1695.

***N*-(4-methoxyphenyl)-2-vinylaniline (5b).**



Following **GP2-A**, 2-bromostyrene (388  $\mu\text{L}$ , 3 mmol) and 4-methoxyaniline (445 mg, 3.6 mmol) provided the title compound as a colorless liquid (650 mg, 96%) after column chromatography on silica gel (2% EtOAc/hexane). IR  $\nu_{\text{max}}$  (film) 3393, 2948, 2833, 1623, 1598, 1573, 1510, 1455, 1240  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 7.6$  Hz, 1H), 7.15 (t,  $J = 8.0$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H), 6.99 (d,  $J = 8.4$  Hz, 2H), 6.93–6.87 (m, 2H), 6.86 (d,  $J = 7.6$  Hz, 2H), 5.69 (d,  $J = 17.6$  Hz, 1H), 5.44 (br s, 1H), 5.34 (d,  $J = 11.2$  Hz, 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.02, 142.1, 136.44, 132.9, 128.6, 127.6, 127.4, 121.6, 120.7, 116.7, 116.3, 114.7, 55.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{15}\text{H}_{16}\text{NO}$  226.1226; found 226.1231.

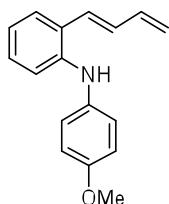
***N*-(4-butoxyphenyl)-2-vinylnaphthalen-1-amine (5c).**



Following **GP2-A**, 1-bromo-2-vinylnaphthalene (233 mg, 1.0 mmol) and 4-butoxyaniline (200  $\mu\text{L}$ , 1.2 mmol) provided the title compound as yellow solid (250 mg, 79%) after column chromatography on silica gel (1% Et<sub>2</sub>O/hexane). mp 65–67  $^{\circ}\text{C}$ . IR  $\nu_{\text{max}}$  (film) 3389, 3058, 2958, 2871, 1620, 1564, 1474, 1418, 1383  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 8.4$  Hz, 1H), 7.74 (dd,  $J = 14.0, 8.4$  Hz, 2H), 7.48–7.39 (m, 2H), 7.12 (dd,  $J = 17.6, 10.8$  Hz, 1H), 6.74 (dd,  $J = 9.2,$

3.2 Hz, 2H), 6.55 (br s, 2H), 5.84 (d,  $J = 17.6$  Hz, 1H), 5.50 (br s, 1H), 5.35 (d,  $J = 12.4$  Hz, 1H), 3.88 (br s, 2H), 1.72 (dt,  $J = 14.8, 6.8$  Hz, 2H), 1.47 (dt,  $J = 14.4, 7.2$  Hz, 2H), 0.97 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 141.2, 135.0, 134.4, 133.2, 131.3, 128.2, 126.4, 126.1, 125.9, 124.0, 123.7, 115.8, 115.5, 68.2, 31.5, 19.3, 13.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{24}\text{NO}$  318.1852; found 318.1852.

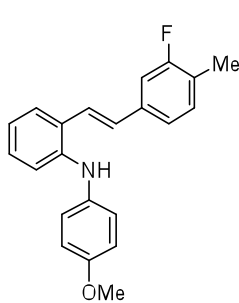
**(E)-2-(buta-1,3-dienyl)-N-(4-methoxyphenyl)aniline (5d).**



**5d**

Following **GP2-A**, (*E*)-1-bromo-2-(buta-1,3-dienyl)benzene (418 mg, 2 mmol) and 4-methoxyaniline (296 mg, 2.4 mmol) provided the title compound as a colorless liquid (260 mg, 52%) after column chromatography on silica gel (2% EtOAc/hexane). IR  $\nu_{\text{max}}$  (film) 3400, 3018, 2958, 1625, 1430, 1310  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 7.6$  Hz, 1H), 7.19–7.14 (m, 1H), 7.10 (d,  $J = 8.4$  Hz, 1H), 7.02 (d,  $J = 8.4$  Hz, 2H), 6.95 (t,  $J = 6.8$  Hz, 1H), 6.90 (d,  $J = 8.8$  Hz, 2H), 6.78 (d,  $J = 7.2$  Hz, 2H), 6.62–6.53 (m, 1H), 5.44 (br s, 1H), 5.38 (dt,  $J = 16.8, 1.6$  Hz, 1H), 5.22 (dt,  $J = 10.0, 1.6$  Hz, 1H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 142.3, 137.5, 136.5, 131.6, 128.6, 128.3, 127.1, 127.0, 121.5, 120.9, 117.6, 117.1, 114.8, 55.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{17}\text{H}_{18}\text{NO}$  252.138; found 252.142.

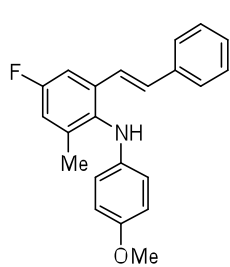
**(E)-2-(3-fluoro-4-methylstyryl)-N-(4-methoxyphenyl)aniline (5e).**



**5e**

Following **GP2-A**, 4-(2-bromostyryl)-2-fluoro-1-methylbenzene (291 mg, 1 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound as a colorless liquid (270 mg, 81%) after column chromatography on silica gel (1.5% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3394, 3016, 2943, 1597, 1573, 1510, 1454, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21–7.14 (m, 2H), 7.09 (d,  $J = 7.6$  Hz, 1H), 7.03 (t,  $J = 8.0$  Hz, 1H), 6.99–6.91 (m, 4H), 6.86 (dd,  $J = 6.8, 2.0$  Hz, 2H), 6.80 (t,  $J = 7.2$  Hz, 1H), 6.65 (d,  $J = 12.4$  Hz, 1H), 6.59 (d,  $J = 12.4$  Hz, 1H), 5.54 (br s, 1H), 3.81 (s, 3H), 2.24 (d,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 159.8, 155.4, 142.4, 136.1 (d,  $J = 8.0$  Hz), 135.5, 131.1 (d,  $J = 6.0$  Hz), 131.0 (d,  $J = 2.0$  Hz), 129.7, 128.5, 126.9, 124.6, 124.3 (d,  $J = 3.0$  Hz), 124.3, 124.1, 122.7, 119.3, 114.9 (d,  $J = 22.0$  Hz), 114.6, 114.4, 55.6, 14.4 (d,  $J = 4.0$  Hz); HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{21}\text{FNO}$  334.1602; found 334.1604.

**(E)-4-fluoro-N-(4-methoxyphenyl)-2-methyl-6-styrylaniline (5f).**

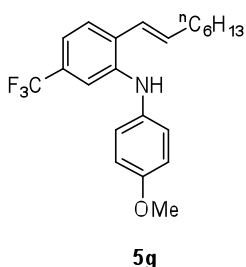


**5f**

Following **GP2-B**, (*E*)-4-fluoro-2-methyl-6-styrylaniline<sup>3</sup> (341 mg, 1.5 mmol) and 1-bromo-4-methoxybenzene (126  $\mu\text{L}$ , 1.0 mmol) provided the title compound as a yellow liquid (304 mg, 91%) after column chromatography on silica gel (2% EtOAc/hexane). IR  $\nu_{\text{max}}$  (film) 3389, 3053, 2910, 2853, 1597, 1560, 1494, 1432, 1351  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 7.2$  Hz, 2H), 7.34–7.23 (m, 5H), 7.03 (d,  $J = 16.4$  Hz, 1H), 6.93 (dd,  $J = 8.8, 2.8$  Hz, 1H), 6.78 (d,  $J = 8.8$  Hz, 2H), 6.53 (d,  $J = 8.8$  Hz, 2H), 5.03 (s, 1H), 3.75 (s, 3H), 2.21 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 159.2, 152.8, 140.6,

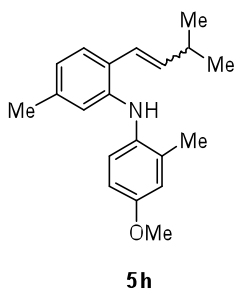
138.4 (d,  $J = 9.0$  Hz), 137.1 (d,  $J = 8.0$  Hz), 134.4 (d,  $J = 2.0$  Hz), 131.1, 128.7, 127.9, 126.7, 124.5 (d,  $J = 2.0$  Hz), 116.8 (d,  $J = 22.0$  Hz), 115.1, 114.9, 109.9 (d,  $J = 22.0$  Hz), 55.7, 18.6; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{22}H_{21}FNO$  334.1602; found 334.1603.

**(E)-N-(4-methoxyphenyl)-2-(oct-1-enyl)-5-(trifluoromethyl)aniline (5g).** Following



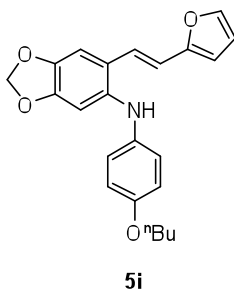
**GP2-B**, (*E*)-2-(oct-1-enyl)-5-(trifluoromethyl)aniline (210 mg, 0.77 mmol) and 1-bromo-4-methoxybenzene (66  $\mu$ L, 0.52 mmol) provided the title compound as a yellowish liquid (175 mg, 90%) after column chromatography on silica gel (1% EtOAc/hexane). IR  $\nu_{max}$  (film) 3387, 2955, 2930, 2858, 1607, 1511, 1435, 1335  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.38 (d,  $J = 8.0$  Hz, 1H), 7.19 (d,  $J = 1.2$  Hz, 1H), 7.07–7.02 (m, 3H), 6.90 (dd,  $J = 6.8, 2.4$  Hz, 2H), 6.48 (d,  $J = 15.6$  Hz, 1H), 6.24–6.17 (m, 1H), 5.51 (br s, 1H), 3.82 (s, 3H), 2.26 (q,  $J = 7.2$  Hz, 2H), 1.50 (dt,  $J = 13.6, 6.4$  Hz, 2H), 1.40–1.27 (m, 6H), 0.91 (t,  $J = 6.8$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.8, 142.5, 136.5, 134.9, 129.7 (q,  $J = 32.0$  Hz), 129.6, 127.9, 125.6, 124.3, 122.9, 116.1 (q,  $J = 4.0$  Hz), 114.9, 111.3 (q,  $J = 4.0$  Hz), 55.6, 33.4, 31.7, 29.2, 28.9, 22.6, 14.1; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{22}H_{27}F_3NO$  378.2039; found 378.2045.

**4-methoxy-2-methyl-N-(5-methyl-2-(3-methylbut-1-enyl)phenyl)aniline (5h).** Following



**GP2-A**, 2-bromo-4-methyl-1-(3-methylbut-1-enyl)benzene (239 mg, 1.0 mmol) and 4-methoxy-2-methylaniline (155  $\mu$ L, 1.2 mmol) provided the title compound as inseparable *E/Z* mixtures and colorless liquid (290 mg, 98%) after column chromatography on silica gel (2%  $Et_2O$ /hexane). IR  $\nu_{max}$  (film) 3397, 2957, 2866, 1612, 1570, 1500, 1464, 1379  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.30–7.17 (m, 1H), 7.16–7.09 (m, 1H), 6.88–6.84 (m, 1H), 6.82–6.77 (m, 1H), 6.71 (d,  $J = 7.6$  Hz) and 6.67 (d,  $J = 7.6$  Hz, total 1H), 6.61–6.51 (m, 2H), 6.18–6.12 (m) and 5.75–5.69 (m, total 1H), 5.25 (br s, 1H), 3.87 (s) and 3.86 (s, total 3H), 2.81–2.76 (m) and 2.60–2.52 (m, total 1H), 2.28 (s) and 2.27 (s, total 6H), 1.19–1.15 (m) and 1.11–1.07 (m, total 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  156.3, 156.0, 143.6, 142.9, 142.7, 140.1, 137.7, 134.5, 134.2, 133.7, 133.0, 129.6, 127.4, 125.5, 124.2, 123.8, 122.6, 122.4, 121.7, 120.6, 118.9, 116.5, 116.4, 115.9, 113.6, 111.9, 55.5, 55.4, 32.0, 27.7, 23.3, 22.7, 21.6, 21.5, 18.3, 18.2; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{20}H_{26}NO$  296.2009; found 296.2001.

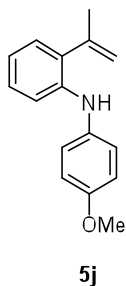
**(E)-N-(4-butoxyphenyl)-6-(2-(furan-2-yl)vinyl)benzo[d][1,3]dioxol-5-amine (5i).** Following



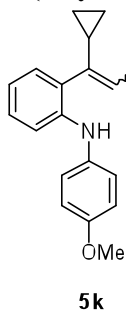
**GP2-A**, 5-bromo-6-(2-(furan-2-yl)vinyl)benzo[d][1,3]dioxole (246 mg, 0.84 mmol) and 4-butoxyaniline (168  $\mu$ L, 1.0 mmol) provided the title compound as a colorless liquid (174 mg, 54%) after column chromatography on silica gel (2%  $Et_2O$ /hexane). IR  $\nu_{max}$  (film) 3408, 2958, 2932, 2873, 1618, 1511, 1473, 1443, 1232  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (s, 1H), 7.16 (d,  $J = 16.4$  Hz, 1H), 7.00 (s, 1H), 6.88–6.81 (m, 4H), 6.69 (d,  $J = 13.6$  Hz, 2H), 6.40 (dd,  $J = 3.6, 2.0$  Hz, 1H), 6.29 (d,  $J = 2.8$  Hz, 1H), 5.91 (s, 2H), 5.26 (br s, 1H), 3.93 (t,  $J = 6.8$  Hz, 2H),

1.75(dt,  $J = 14.4, 6.4$  Hz, 2H), 1.48 (dt,  $J = 14.8, 7.6$  Hz, 2H), 0.98 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 153.7, 148.0, 143.2, 141.9, 137.8, 137.1, 122.4, 121.9, 119.5, 116.1, 115.6, 111.7, 108.0, 105.1, 101.6, 101.1, 68.2, 31.5, 19.3, 14.0; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{23}\text{H}_{24}\text{NO}_4$  378.1700; found 378.1694.

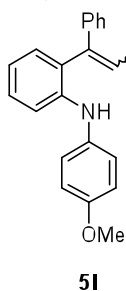
***N*-(4-methoxyphenyl)-2-(prop-1-en-2-yl)aniline (5j).** Following **GP2-A**, 1-bromo-2-(prop-1-en-2-yl)benzene (167 mg, 0.85 mmol) and 4-methoxyaniline (125 mg, 1.01 mmol) provided the title compound as a colorless liquid (120 mg, 59%) after column chromatography on silica gel (1%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3394, 2953, 2833, 1622, 1597, 1510, 1440, 1238  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.07 (m, 5H); 6.89–6.81 (m, 3H); 5.33–5.31 (m, 1H), 5.11–5.10 (m, 1H), 3.81 (s, 3H); 2.09 (dd,  $J = 1.2, 0.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 143.7, 141.3, 136.0, 131.7, 128.5, 127.8, 122.5, 119.3, 116.1, 114.8, 114.6, 55.6, 24.0; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{16}\text{H}_{18}\text{NO}$  240.1383; found 240.1380.



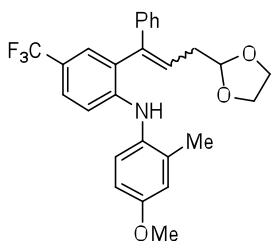
**2-(1-cyclopropylprop-1-enyl)-*N*-(4-methoxyphenyl)aniline (5k).** Following **GP2-A**, 1-bromo-2-(1-cyclopropylprop-1-enyl)benzene (237 mg, 1.0 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound as inseparable E/Z mixtures and colorless liquid (270 mg, 96%) after column chromatography on silica gel (1.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3397, 2953, 2833, 1577, 1510, 1449, 1292  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–6.97 (m, 4H), 6.90–6.83 (m, 3H), 6.77 (dt,  $J = 7.6, 1.2$  Hz) and 6.71 (dt,  $J = 7.6, 1.2$  Hz, total 1H), 5.78 (q,  $J = 6.8$  Hz) and 5.56 (q,  $J = 6.8$  Hz, total 1H), 3.80 (s, 3H), 1.91 (d,  $J = 6.8$  Hz) and 1.48 (d,  $J = 6.8$  Hz, total 3H), 1.89–1.83 (m) and 1.66–1.59 (m, total 1H), 0.67–0.53 (m) and 0.45–0.27 (m, total 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 155.3, 143.0, 142.5, 139.6, 139.5, 136.0, 135.9, 130.9, 130.2, 128.1, 127.7, 127.6, 125.5, 125.2, 122.9, 122.8, 122.6, 118.4, 118.2, 114.6, 113.3, 113.2, 55.6, 17.5, 14.6, 13.6, 11.0, 4.9, 4.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{19}\text{H}_{22}\text{NO}$  280.1696; found 280.1682.



***N*-(4-methoxyphenyl)-2-(1-phenylprop-1-enyl)aniline (5l).** Following **GP2-A**, 1-bromo-2-(1-phenylprop-1-enyl)benzene (273 mg, 1.0 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound as inseparable E/Z mixtures and colorless liquid (310 mg, 98%) after column chromatography on silica gel (2%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3405, 3027, 2932, 2833, 1598, 1508, 1452, 1293  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.17 (m, 6H), 7.16–7.08 (m, 1H), 7.06–6.95 (m, 2H), 6.88–6.75 (m, 4H), 6.44 (q,  $J = 6.8$  Hz) and 6.02 (d,  $J = 7.2$  Hz, total 1H), 3.77 (s) and 3.76 (s, total 3H), 1.94 (d,  $J = 7.2$  Hz) and 1.74 (d,  $J = 6.8$  Hz, total 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 143.1, 140.9, 138.7, 135.7, 131.2, 131.0, 129.2, 128.5, 128.1, 128.0, 127.7, 126.5, 126.4, 126.2, 123.2, 122.8, 119.0, 114.5, 114.4, 113.9, 55.5, 15.7, 15.5; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{22}\text{NO}$  316.1696; found 316.1689.



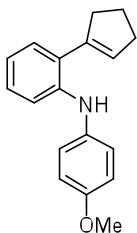
**2-(3-(1,3-dioxolan-2-yl)-1-phenylprop-1-enyl)-*N*-(4-methoxy-2-methylphenyl)-4-(trifluoromethyl)aniline (5m).** Following **GP2-A**, 2-(3-(2-bromo-5-(trifluoromethyl)phenyl)-3-



**5m**

phenylallyl)-1,3-dioxolane (180 mg, 0.44 mmol) and 4-methoxy-2-methylaniline (85  $\mu$ L, 0.65 mmol) provided the title compound as inseparable E/Z mixtures and yellowish liquid (170 mg, 83%) after column chromatography on silica gel (7% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3403, 3052, 3022, 2908, 1594, 1577, 1454, 1311  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39–7.25 (m, 7H), 7.02 (d,  $J$  = 8.8 Hz) and 6.987 (d,  $J$  = 8.4 Hz, total 1H), 6.77–6.70 (m, 2H), 6.54–6.48 (m) and 6.07 (t,  $J$  = 7.6 Hz, total 2H), 5.77 (br s) and 5.67 (br s, total 1H), 5.04 (t,  $J$  = 4.0 Hz, 1H), 3.98–3.91 (m, 2H), 3.90–3.84 (m, 2H), 3.79 (s) and 3.78 (s, total 3H), 2.798 (dd,  $J$  = 7.6, 4.4 Hz, 1H), 2.58–2.52 (m, 1H), 1.97 (s) and 1.87 (s, total 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.5, 157.3, 147.1, 147.0, 140.8, 139.7, 138.5, 136.3, 136.0, 131.8, 131.7, 129.2, 129.1, 128.6, 128.5, 128.0(q,  $J$  = 3.5 Hz), 127.7 (q,  $J$  = 3.5 Hz), 127.6, 127.4, 127.2, 126.4, 126.3, 125.8 (q,  $J$  = 3.5 Hz), 125.7, 125.5 (q,  $J$  = 3.5 Hz), 124.4, 123.6, 119.4, 119.0 (q,  $J$  = 33 Hz), 118.9 (q,  $J$  = 33.0 Hz), 116.2, 116.1, 112.1, 112.0, 111.5, 111.4, 103.5, 103.4, 65.1, 65.0, 55.4, 34.9, 34.0, 17.9, 17.7; HRMS (ESI)  $m/z$  [M+H]<sup>+</sup>, calc'd for C<sub>27</sub>H<sub>27</sub>F<sub>3</sub>NO<sub>3</sub> 470.1938; found 470.1950.

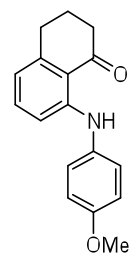
**2-cyclopentenyl-N-(4-methoxyphenyl)aniline (5n).** Following **GP2-A**, 1-bromo-2-



**5n**

cyclopentenylbenzene<sup>4</sup> (223 mg, 1.0 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound as a colorless liquid (242 mg, 91%) after column chromatography on silica gel (1% Et<sub>2</sub>O/hexane). IR  $\nu_{\text{max}}$  (film) 3399, 3034, 2952, 2840, 1594, 1574, 1511, 1450, 1292, 1244  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 7.10 (d,  $J$  = 8.8 Hz, 4H), 6.86 (d,  $J$  = 8.4 Hz, 3H), 6.03 (dt,  $J$  = 4.4, 2.0 Hz, 1H), 3.80 (s, 3H), 2.70–2.65 (m, 2H), 2.58–2.53 (m, 2H), 1.98 (dt,  $J$  = 14.8, 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 142.5, 141.3, 136.0, 129.2, 128.5, 127.6, 126.1, 122.8, 119.2, 114.8, 114.7, 55.6, 36.5, 33.8, 23.3; HRMS (ESI)  $m/z$  [M+H]<sup>+</sup>, calc'd for C<sub>18</sub>H<sub>20</sub>NO 266.1539; found 266.1535.

**8-(4-methoxyphenylamino)-3,4-dihydronaphthalen-1(2H)-one.** An oven-dried Schlenk



tube containing a stir bar was charged with Pd(OAc)<sub>2</sub> (14.0 mg, 0.06 mmol), 2-dicyclohexylphosphino-2',4',6' triisopropylbiphenyl, XPhos<sup>5</sup> (72.0 mg, 0.15 mmol), phenylboronic acid (18.0 mg, 0.15 mmol), 8-amino-3,4-dihydronaphthalen-1(2H)-one<sup>6</sup> (725 mg, 4.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.5 mmol). The tube was capped, evacuated and backfilled with argon. Then 4-bromoanisole (377 mL, 3.0 mmol) and *t*BuOH (5 mL) were added through the septum via syringe and put into a pre-heated oil bath at 110 °C for 24 h. The resulting mixture was allowed to cool down to room temperature and then filtered through celite with ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column

<sup>4</sup> Morrow, G. W.; Marks, T. M.; Sear, D. L.; *Tetrahedron* **1995**, *51*, 10115.

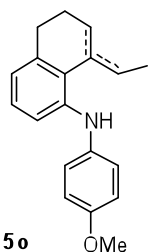
<sup>5</sup> Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L.; *J. Am. Chem. Soc.* **2003**, *125*, 6653.

<sup>6</sup> Nguyen, P.; Corpuz, E.; Heidelbaugh, T. M.; Chow, K.; Garst, M. E. *J. Org. Chem.* **2003**, *68*, 10195.

chromatography (2% EtOAc/hexane) to afford the title compound as yellowish solid. mp 91–93 °C; IR  $\nu_{\max}$  (plate) 3406, 3252, 2935, 1632, 1595, 1576, 1463, 1437, 1394  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (dd,  $J = 8.8, 1.2$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 1H), 6.91 (dd,  $J = 8.8, 1.2$  Hz, 2H), 6.82 (d,  $J = 8.8$  Hz, 1H), 6.47 (dt,  $J = 7.6, 1.2$  Hz, 1H), 3.81 (s, 3H), 2.91 (t,  $J = 6.0$  Hz, 2H), 2.69 (t,  $J = 6.4$  Hz, 1H), 2.07 (dt,  $J = 12.4, 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.5, 156.9, 150.4, 146.4, 134.5, 133.0, 126.4, 116.0, 115.3, 114.6, 111.2, 55.5, 40.5, 31.2, 23.0; HRMS (ESI)  $m/z$   $[\text{M}+\text{Na}]^+$ , calc'd for  $\text{C}_{17}\text{H}_{17}\text{NO}_2\text{Na}$  290.1152; found 290.1148.

**8-ethylidene-N-(4-methoxyphenyl)-5,6,7,8-tetrahydronaphthalen-1-amine** and **8-ethyl-N-(4-methoxyphenyl)-5,6-dihydronaphthalen-1-amine (5o)**.

Following **GP1-A**, 8-(4-methoxyphenylamino)-3,4-dihydronaphthalen-1(2H)-one (535 mg, 2.0 mmol) and ethyltriphenylphosphonium bromide (1.48 g, 4 mmol) provided the title compound (297 mg, 58%) as inseparable mixtures and colorless oil after silica gel column chromatography (0.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\max}$  (film) 3393, 2937, 2833, 1579, 1511, 1463, 1240  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15–7.09 (m, 2H), 7.07–6.94 (m, 2H), 6.88–6.79 (m, 2H), 6.67–6.63 (m, 1H),



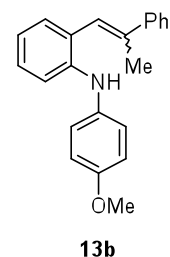
**5o**

6.12(dq,  $J = 6.8, 2.4$  Hz), 6.00 (dt,  $J = 5.2, 1.2$  Hz) and 5.63 (dq,  $J = 6.8, 1.2$  Hz, total 1H), 3.80 (s) and 3.77 (s, total 3H), 2.66–2.38 (m, 4H), 1.78 (d,  $J = 12.0$  Hz), 1.77 (d,  $J = 12.4$  Hz) and 0.99 (dt,  $J = 6.8, 1.6$  Hz, total 3H), 1.63 (dd,  $J = 6.8, 1.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 155.2, 153.7, 141.9, 141.5, 141.2, 141.0, 140.6, 139.5, 139.2, 138.2, 136.4, 135.9, 133.7, 133.6, 128.7, 127.5, 127.4, 126.9, 126.8, 126.5, 126.0, 124.4, 122.9, 122.3, 122.2, 122.1, 121.5, 119.7, 119.0, 118.4, 117.7, 114.7, 114.6, 113.3, 111.3, 55.5, 55.6, 55.7, 32.2, 30.6, 30.5, 29.4, 28.0, 26.2, 22.8, 22.7, 22.0, 16.2, 14.3, 13.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{19}\text{H}_{22}\text{NO}$  280.1696; found 280.1695.

**2-(2,2-diphenylvinyl)-N-(4-methoxyphenyl)aniline (13a)**.

Following **GP2-A**, (2-(2-bromophenyl)ethene-1,1-diyl)dibenzene (335 mg, 1.0 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound after column chromatography on silica gel (1.5%  $\text{Et}_2\text{O}$ /hexane) as a colorless liquid (190 mg, 50%) after column chromatography on silica gel (1.5%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\max}$  (film) 3399, 3027, 2947, 2833, 1597, 1574, 1507, 1454, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.30 (m, 5H), 7.28–7.24 (m, 3H), 7.21–7.18 (m, 2H), 7.02 (d,  $J = 4.0$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 6.91 (s, 1H), 6.89 (d,  $J = 8.4$  Hz, 1H), 6.84 (dd,  $J = 6.4, 2.0$  Hz, 2H), 6.61 (sept,  $J = 4.4$ , 1H), 5.54 (br s, 1H), 3.80 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 144.6, 143.3, 143.0, 139.9, 135.7, 130.7, 130.5, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 125.8, 124.4, 122.2, 119.1, 114.7, 114.6, 55.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{27}\text{H}_{24}\text{NO}$  378.1852; found 378.1850.

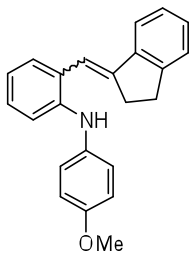
**N-(4-methoxyphenyl)-2-(2-phenylprop-1-enyl)aniline (13b)**. Following **GP2-A**, 1-bromo-2-(2-phenylprop-1-enyl)benzene (546 mg, 2.0 mmol) and 4-methoxyaniline (296 mg, 2.4 mmol) provided the title compound as inseparable E/Z mixtures and colorless liquid (610 mg, 97%) after column chromatography on silica gel (1%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\max}$  (film) 3399, 2933, 2832, 1590, 1572,



**13b**

1453, 1376, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61–7.31 (m, 2H), 7.27–7.20 (m, 4H), 7.18–6.64 (m, 7H), 6.64 (br s, 1H), 6.52 (br s, 1H), 3.81 (s, 3H), 2.31 (d,  $J = 1.2$  Hz) and 2.22 (d,  $J = 1.2$  Hz, total 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 155.2, 143.2, 142.7, 142.5, 141.0, 140.1, 139.6, 135.9, 135.7, 130.8, 130.2, 128.4, 128.2, 128.0, 127.9, 127.5, 127.3, 127.2, 125.9, 123.3, 123.1, 122.6, 122.5, 119.1, 119.0, 114.7, 114.6, 114.1, 55.6, 25.7, 17.2; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{22}\text{NO}$  316.1696; found 316.1690.

**2-((2,3-dihydro-1H-inden-1-ylidene)methyl)-N-(4-methoxyphenyl)aniline (13c)**

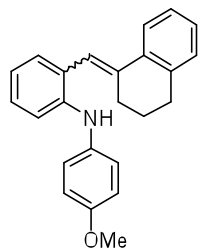


**13c**

Following **GP2-B**, 1-(2-bromobenzylidene)-2,3-dihydro-1H-indene (143 mg, 0.5 mmol) and 4-methoxyaniline (92 mg, 0.75 mmol) provided the title compound as inseparable E/Z mixtures and colorless liquid (134 mg, 82%) after column chromatography on silica gel (2%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3390, 2936, 2834, 1596, 1575, 1510, 1453, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65–7.61 (m) and 7.32–7.21 (m, total 3H), 7.40–7.38 (m) and 7.19–7.12 (m, total 3H), 7.07 (d,  $J = 8.4$  Hz, 1H), 7.01–6.95 (m, 2H), 6.92–6.80 (m, 3H), 6.48 (s, 1H), 5.59 (br s, 1H), 3.80 (s) and 3.78 (s, total 3H), 3.06–2.96 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 155.2, 148.6, 146.2,

145.8, 143.0, 142.1, 139.5, 136.0, 135.5, 129.9, 129.1, 128.5, 128.4, 128.0, 127.7, 126.7, 125.5, 125.3, 125.2, 124.6, 123.3, 122.2, 120.5, 119.5, 119.0, 117.2, 114.7, 114.6, 114.1, 113.4, 55.7, 55.6, 33.3, 30.6, 30.3, 30.1; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{23}\text{H}_{22}\text{NO}$  328.1696; found 328.1696.

**2-((3,4-dihydronaphthalen-1(2H)-ylidene)methyl)-N-(4-methoxyphenyl)aniline (13d)**



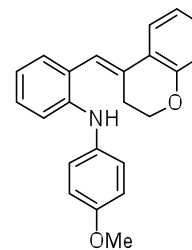
**13d**

Following **GP2-A**, 1-(2-bromobenzylidene)-1,2,3,4-tetrahydronaphthalene (100 mg, 0.33 mmol) and 4-methoxyaniline (50 mg, 0.40 mmol) provided the title compound as inseparable E/Z mixtures and yellowish oil (100 mg, 87%) after column chromatography on silica gel (1%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3397, 2935, 2834, 1596, 1575, 1510, 1452, 1293  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78–7.74 (m) and 7.24–7.19 (m, 2H), 7.17–7.06 (m, 5H), 7.01–6.93 (m, 1H), 6.89–6.71 (m, 4H), 6.38 (s, 1H), 5.52 (br s, 1H), 3.80 (s) and 3.78 (s, total 3H), 2.90 (quint,  $J = 6.0$  Hz, 2H),

2.67–2.60 (m, 2H), 2.06–1.99 (m, 1H), 1.85 (quint,  $J = 6.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 143.3, 142.5, 139.8, 139.6, 138.3, 137.7, 135.8, 135.7, 135.6, 134.5, 130.4, 130.3, 129.3, 129.0, 128.3, 127.8, 127.7, 127.6, 127.5, 126.2, 126.1, 125.7, 124.4, 122.8, 122.5, 120.9, 119.2, 119.0, 118.9, 114.7, 114.6, 114.0, 113.9, 55.6, 35.2, 30.3, 30.0, 28.1, 24.5, 23.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{24}\text{H}_{24}\text{NO}$  342.1852; found 342.1858.

**(E)-2-(chroman-4-ylidenemethyl)-N-(4-methoxyphenyl)aniline (13e)**

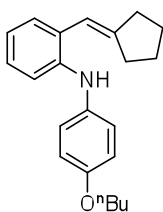
Following **GP2-A**, 4-(2-bromobenzylidene)chroman (301 mg, 1.0 mmol) and 4-methoxyaniline (148 mg, 1.2 mmol) provided the title compound as a yellowish oil (172 mg, 50%) after column chromatography on silica gel (2%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3401, 3033, 2955, 2833, 1598, 1575, 1509, 1451, 1402  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 6.8$  Hz, 1H),



**13e**

7.16–7.05 (m, 4H), 6.98–6.87 (m, 2H), 6.86–6.76 (m, 4H), 6.60 (dt,  $J = 8.4, 1.2$  Hz, 1H), 6.28 (s, 1H), 5.59 (br s, 1H), 4.41 (t,  $J = 5.2$  Hz, 2H), 3.79 (s, 3H), 2.75 (t,  $J = 5.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 154.7, 143.4, 135.4, 132.9, 130.5, 129.4, 128.1, 124.5, 124.4, 122.5, 122.4, 120.8, 119.0, 117.5, 117.3, 114.7, 114.3, 66.4, 55.6, 26.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{23}\text{H}_{22}\text{NO}_2$  344.1645; found 344.1656.

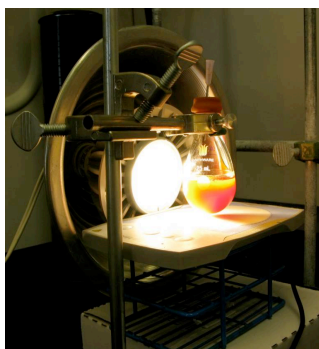
***N*-(4-butoxyphenyl)-2-(cyclopentylidenemethyl)aniline (13f)**. Following **GP2-A**, 1-bromo-2-(cyclopentylidenemethyl)benzene (237 mg, 1.0 mmol) and 4-butoxyaniline (200  $\mu\text{L}$ , 1.2 mmol) provided the title compound as a colorless liquid (298 mg, 93%) after column chromatography on silica gel (2%  $\text{Et}_2\text{O}$ /hexane). IR  $\nu_{\text{max}}$  (film) 3396, 2956, 2869, 1599, 1510, 1454, 1238  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (a few extra peaks for rotamers) 7.22–6.80 (m, 4H), 6.94 (dd,  $J = 6.8, 2.4$  Hz, 1H), 6.87–6.79 (m, 3H), 6.28 (t,  $J = 2.0$  Hz) and 5.41 (t,  $J = 2.0$  Hz, 1H), 3.94 (dt,  $J =$



**13f**

6.4, 2.0 Hz, 2H), 3.41 (br s, 1H), 2.48 (br s, 1H), 2.38–2.33 (m, 2H), 2.25 (t,  $J = 6.8$  Hz, 1H), 1.90 (dt,  $J = 15.2, 7.2$  Hz, 1H), 1.80–1.69 (m, 4H), 1.50 (dt,  $J = 14.8, 7.2$  Hz, 2H), 0.98 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (few extra peaks in carbon for rotamers) 154.7, 154.5, 149.4, 143.8, 142.7, 142.4, 136.3, 136.0, 130.7, 129.3, 127.2, 127.1, 127.0, 126.9, 125.8, 122.3, 121.7, 120.0, 119.1, 115.8, 115.6, 115.4, 115.3, 114.4, 68.2, 68.1, 35.0, 34.9, 34.5, 32.5, 31.5, 30.7, 26.7, 25.8, 23.6, 19.3, 13.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{28}\text{NO}$  322.2165; found 322.2153.

#### *Experimental set-up for the photo-catalyzed synthesis of indoles.*



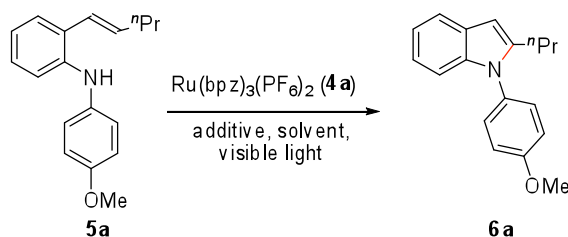
#### **Optimization of the catalyst system.**

**General Procedure (GP-cat):** An oven-dried flask equipped with a stir bar was charged with  $[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$  (3.6 mg, 2 mol%), a styryl aniline derivative **5a** (0.2 mmol), and dry solvent (12 mL). The flask was capped with a rubber septum and a needle (16G, 1.5 inch) was pierced through the septum so that the reaction mixture was exposed to air. The orange reaction mixture was irradiated at room temperature with a LED white light (Sylvania PAR38 18W LED Bulb) at a distance of app. 8 cm for specific time. *n*-Dodecane (45.2  $\mu\text{L}$ ) was added as an internal standard and the reaction mixture was diluted with  $\text{Et}_2\text{O}$  (2 mL). An aliquot of that mixture was filtered through a plug of cotton and analyzed by GC. Some of this data is presented in Table 1 of the manuscript.



- For entry 5, an oxygen balloon was placed on top of the flask using a needle (16G, 1.5 inch).
- For entries 6-9, HCl (0.2 mL, 0.2 mmol, 1 M in Et<sub>2</sub>O), *p*-TsOH (38 mg, 0.2 mmol), PPTS (50 mg, 0.2 mmol) and AcOH (12 μL, 0.2 mmol) were added respectively.
- For entries 10 and 16, no [Ru(bpz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O **4a** was added.
- For entries 10-15, silica gel (500 mg) was added.
- For entry 11, the reaction was conducted inside a dark cabinet.
- For entry 12, the reaction mixture was degassed by three freeze-pump-thaw cycles.
- For entry 14, Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (3.4 mg, 2 mol%) was added in place of [Ru(bpz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O.
- For entry 15, [Ru(bpz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O (7.2 mg, 4 mol%) was added
- For entry 16, a mixture of styrylaniline **5a** (0.2 mmol, 54 mg), TPP (5 mg, 4 mol%) and silica gel (500 mg) were dissolved in CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> (12 mL, 3:1). Because TPP was not very soluble in CH<sub>3</sub>CN, we had to switch the solvent to the 3:1 mixture of CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>.

**Table1.**



Entry	Conditions <sup>[a]</sup>	t [h]	Conv. of <b>5a</b> [%]	Yield of <b>6a</b> [%]
1	<b>4a</b> (2 mol%), CH <sub>3</sub> CN	24	44	31
2	<b>4a</b> (2 mol%), CH <sub>3</sub> NO <sub>2</sub>	24	69	39
3	<b>4a</b> (2 mol%), DMF	24	32	15
4	<b>4a</b> (2 mol%), TFE	24	42	21
5	<b>4a</b> (2 mol%), CH <sub>3</sub> CN, O <sub>2</sub> balloon	24	49	33
6 <sup>[b]</sup>	<b>4a</b> (2 mol%), HCl (1 M in Et <sub>2</sub> O), CH <sub>3</sub> CN	24	77	0
7 <sup>[b]</sup>	<b>4a</b> (2 mol%), <i>p</i> -TsOH, CH <sub>3</sub> CN	24	55	0
8 <sup>[b]</sup>	<b>4a</b> (2 mol%), PPTS, CH <sub>3</sub> CN	24	49	15
9 <sup>[b]</sup>	<b>4a</b> (2 mol%), AcOH, CH <sub>3</sub> CN	12	100	60
10	silica gel, CH <sub>3</sub> CN, no <b>4a</b> , light	24	8	4
11	<b>4a</b> (2 mol%), silica gel, CH <sub>3</sub> CN, no light	24	4	2
12	<b>4a</b> (2 mol%), silica gel, degassed, CH <sub>3</sub> CN	24	8	0
13	<b>4a</b> (2 mol%), silica gel, CH <sub>3</sub> CN	12	100	68
14	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub> (2 mol%), silica gel, CH <sub>3</sub> CN	24	100	19

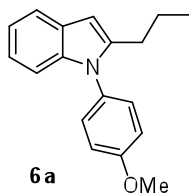
<b>15</b>	<b>4a (4 mol%), silica gel, CH<sub>3</sub>CN</b>	<b>5</b>	<b>100</b>	<b>88</b>
16	TPP (4 mol%), silica gel, CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (3:1)	24	9	2

Conditions: [a] **5a** (0.2 mmol), solvent, open air, irradiation with a white LED light. [b] 1 equivalent of acids were used. PPTS= pyridinium-*p*-toluenesulfonate, *p*-TsOH= *p*-toluenesulfonic acid, TPP= tetraphenylporphyrin.

- General procedure 3 (GP3): Visible light mediated synthesis of indoles from styryl anilines**

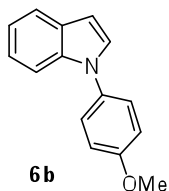
An oven-dried flask equipped with a stir bar was charged with [Ru(bpz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O (7.2 mg, 4 mol%), a styryl aniline derivative (0.2 mmol), dry CH<sub>3</sub>CN (12 mL) and silica gel (500 mg). The flask was capped with a rubber septum and a needle (16G, 1.5 inch) was pierced through the septum so that the reaction mixture was exposed to air. The orange reaction mixture was irradiated at room temperature with a LED white light (Sylvania PAR38 18W LED Bulb) at a distance of app. 8 cm. After the reaction was complete as shown by TLC, the mixture was filtered through a short silica pad and eluted with Et<sub>2</sub>O (20 mL). The solution was concentrated and the residue was purified by silica gel flash chromatography to afford the corresponding indoles.

**1-(4-methoxyphenyl)-2-propyl-1*H*-indole (6a).** Following **GP3** with styrylaniline **5a** (54 mg,

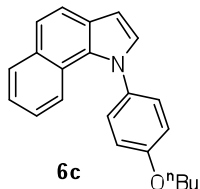


0.20 mmol) in the photo-condition after 5 h, indole **6a** (39 mg, 73%) was obtained after silica gel column chromatography (2% Et<sub>2</sub>O/hexane) as yellowish solid: mp 73–75 °C; IR  $\nu_{\text{max}}$  (plate) 2927, 2860, 1510, 1457, 1296, 1242 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.13–7.08 (m, 2H), 7.06–7.02 (m, 3H), 6.41 (br s, 1H), 3.91 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.63 (dt, *J* = 15.0, 7.6 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 142.1, 138.6, 130.7, 129.4, 128.0, 120.9, 119.8, 119.6, 114.6, 110.0, 99.7, 55.5, 29.1, 21.9, 13.9; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>18</sub>H<sub>20</sub>NO 266.1539; found 266.1542.

**1-(4-methoxyphenyl)-1*H*-indole (6b).**<sup>7</sup> Following **GP3** with styrylaniline **5b** (52 mg, 0.23



mmol) in the photo-condition after 18 h (after 12 h, an extra amount of the catalyst, 3.6 mg, and 500 mg of silica gel were added), indole **6b** (41 mg, 80%) was obtained after silica gel column chromatography (2% Et<sub>2</sub>O/hexane) as solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.26–7.17 (m, 2H), 7.05 (d, *J* = 9.2 Hz, 2H), 6.70–6.68 (m, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.3, 136.3, 132.8, 129.0, 128.3, 126.0, 122.2, 121.0, 120.1, 114.7, 110.4, 102.9, 55.6.

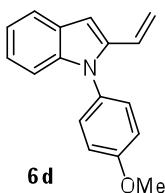


**1-(4-butoxyphenyl)-1*H*-benzo[*g*]indole (6c).** Following **GP3** with styrylaniline **5c** (64 mg, 0.20 mmol) in the photo-condition after 17 h (after 12 h, an extra amount of the catalyst, 3.6 mg, and 500 mg of silica gel were

<sup>7</sup> Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575.

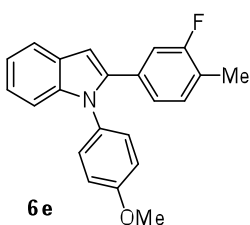
added), indole **6c** (47 mg, 74%) was obtained after silica gel column chromatography (1% EtOAc/hexane) as white solid: mp 78–80 °C; IR  $\nu_{\max}$  (plate) 2957, 2933, 2869, 1513, 1400, 1350, 1244  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.0$  Hz, 1H), 7.77 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.56 (d,  $J = 8.8$  Hz, 1H), 7.45–7.39 (m, 3H), 7.35 (t,  $J = 7.2$  Hz, 1H), 7.23–7.17 (m, 2H), 7.06 (d,  $J = 8.4$  Hz, 2H), 6.76 (dd,  $J = 3.2, 0.8$  Hz, 1H), 4.09 (t,  $J = 6.4$  Hz, 2H), 1.87 (dt,  $J = 14.8, 6.8$  Hz, 2H), 1.58 (dt,  $J = 14.4, 7.2$  Hz, 2H), 1.05 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 134.6, 131.4, 130.6, 129.5, 129.0, 128.6, 125.5, 124.8, 123.4, 122.7, 121.5, 120.9, 120.8, 115.1, 103.6, 68.1, 31.4, 19.3, 13.9; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{22}\text{NO}$  316.1696; found 316.1698.

**1-(4-methoxyphenyl)-2-vinyl-1H-indole (6d).** Following **GP3** with styrylaniline **5d** (52 mg,



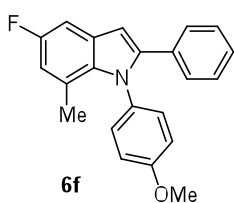
0.207 mmol) in the photo-condition after 4 h, indole **6d** (35 mg, 68%) was obtained after silica gel column chromatography (2%  $\text{Et}_2\text{O}$ /hexane) as white solid: mp 75–77 °C; IR  $\nu_{\max}$  (plate) 3056, 2932, 1612, 1514, 1454, 1214  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63–7.61 (m, 1H), 7.28 (dd,  $J = 6.4, 2.0$  Hz, 2H), 7.13 (d,  $J = 6.0$  Hz, 2H), 7.12 (d,  $J = 5.6$  Hz, 1H), 7.10–7.07 (m, 1H), 7.04 (dd,  $J = 6.8, 2.0$  Hz, 2H), 6.83 (s, 1H), 6.47 (ddd,  $J = 17.4, 11.4, 0.8$  Hz, 1H), 5.69 (dd,  $J = 17.6, 1.2$  Hz, 1H), 5.19 (dd,  $J = 11.6, 1.2$  Hz, 1H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 138.9, 138.8, 130.3, 129.5, 127.8, 126.6, 122.1, 120.4, 115.5, 114.6, 110.4, 99.7, 55.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{17}\text{H}_{16}\text{NO}$  250.1226; found 250.1213.

**2-(3-fluoro-4-methylphenyl)-1-(4-methoxyphenyl)-1H-indole (6e).** Following **GP3** with



styrylaniline **5e** (67 mg, 0.20 mmol) in the photo-condition after 4 h, indole **6e** (55 mg, 83%) was obtained after silica gel column chromatography (2%  $\text{Et}_2\text{O}$ /hexane) as white solid: mp 110–112 °C; IR  $\nu_{\max}$  (plate) 2933, 1513, 1455, 1293, 1249  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70–7.66 (m, 1H), 7.25–7.16 (m, 5H), 7.05 (t,  $J = 7.6$  Hz, 1H), 6.98–6.93 (m, 4H), 6.78 (s, 1H), 3.87 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 159.7, 158.7, 139.6 (d,  $J = 2.0$  Hz), 139.4, 132.0 (d,  $J = 8.0$  Hz), 131.1 (d,  $J = 6.0$  Hz), 129.1, 127.9, 124.2 (d,  $J = 3.0$  Hz), 123.9 (d,  $J = 17.0$  Hz), 122.4, 120.5 (d,  $J = 13.0$  Hz), 115.3, 115.1, 114.6, 110.7, 103.3, 55.5, 14.3 (d,  $J = 3.0$  Hz); HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{22}\text{H}_{19}\text{FNO}$  332.1445; found 332.1449.

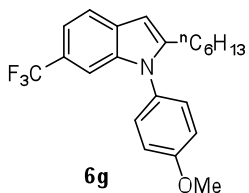
**5-fluoro-1-(4-methoxyphenyl)-7-methyl-2-phenyl-1H-indole (6f).** Following **GP3** with



styrylaniline **5f** (66 mg, 0.20 mmol) in the photo-condition after 3.5 h, indole **6f** (46 mg, 70%) was obtained after silica gel column chromatography (1% EtOAc/hexane) as white solid: mp 138–140 °C; IR  $\nu_{\max}$  (plate) 2931, 2916, 2908, 1582, 1510, 1441, 1301, 1249  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26–7.19 (m, 7H), 7.17 (dd,  $J = 8.8, 6.4$  Hz, 1H), 6.85 (dd,  $J = 6.8, 2.4$  Hz, 2H), 6.69–6.66 (m, 1H), 6.66 (s, 1H), 3.83 (s, 3H), 1.92 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 158.9, 156.6, 143.7, 134.3, 132.7, 131.3, 129.3, 128.8 (d,  $J = 12.0$  Hz), 128.0, 127.4, 123.5 (d,  $J = 10.0$  Hz), 113.5, 113.0 (d,  $J = 26.0$  Hz),

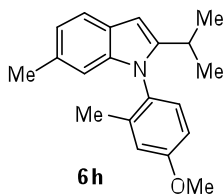
103.2 (d,  $J = 5.0$  Hz), 102.7 (d,  $J = 22.0$  Hz), 55.4, 19.4; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{22}H_{19}FNO$  332.1445; found 332.1449.

**2-hexyl-1-(4-methoxyphenyl)-6-(trifluoromethyl)-1H-indole (6g).** Following **GP3** with



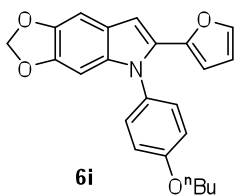
styrylaniline **5g** (76 mg, 0.20 mmol) in the photo-condition after 18 h (during reaction after 12 h, an extra 3.6 mg catalyst and 500 mg silica gel was added), indole **6g** (55 mg, 73%) was obtained after silica gel column chromatography (1% EtOAc/hexane) as yellowish oil. IR  $\nu_{max}$  (film) 2930, 2858, 1514, 1455, 1321, 1251  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.63 (d,  $J = 8.4$  Hz, 1H), 7.32 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.25–7.21 (m, 3H), 7.06 (dd,  $J = 6.8, 2.4$  Hz, 2H), 6.44 (dd,  $J = 0.8$  Hz, 1H), 3.91 (s, 3H), 2.59 (t,  $J = 7.6$  Hz, 2H), 1.59 (dt,  $J = 15.2, 7.6$  Hz, 2H), 1.33–1.17 (m, 6H), 0.85 (t,  $J = 6.8$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.5, 145.4, 137.6, 130.4, 129.7, 129.4, 125.4 (q,  $J = 269.0$  Hz), 123.0 (q,  $J = 32.0$  Hz), 119.7, 116.4 (q,  $J = 3.6$  Hz), 114.8, 107.4 (q,  $J = 4.6$  Hz), 100.0, 55.6, 31.5, 28.9, 28.4, 27.1, 22.5, 14.0; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{22}H_{25}F_3NO$  376.1883; found 376.1868.

**2-isopropyl-1-(4-methoxy-2-methylphenyl)-6-methyl-1H-indole (6h).** Following **GP3** with

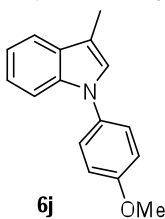


styrylaniline **5h** (60 mg, 0.20 mmol) in the photo-condition after 2 h, indole **6h** (48 mg, 81%) was obtained after silica gel column chromatography (1%  $Et_2O$ /hexane) as colorless oil. IR  $\nu_{max}$  (film) 2937, 2833, 1579, 1511, 1463, 1240  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.48 (d,  $J = 8.0$  Hz, 1H), 7.19 (d,  $J = 8.4$  Hz, 1H), 6.93 (d,  $J = 7.2$  Hz, 2H), 6.88 (dd,  $J = 8.8, 7.2$  Hz, 1H), 6.59 (d,  $J = 0.8$  Hz, 1H), 6.36 (br s, 1H), 3.89 (s, 3H), 2.69 (sept,  $J = 6.8$  Hz, 1H), 2.38 (s, 3H), 1.87 (s, 3H), 1.21 (dd,  $J = 6.8, 2.0$  Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.4, 148.0, 138.9, 138.4, 130.7, 130.5, 129.7, 125.7, 121.3, 119.4, 116.1, 111.9, 109.9, 96.7, 55.4, 26.1, 23.5, 22.4, 21.7, 17.6; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{20}H_{24}NO$  294.1852; found 294.1845.

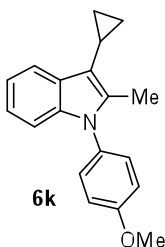
**5-(4-butoxyphenyl)-6-(furan-2-yl)-5H-[1,3]dioxolo[4,5-f]indole (6i).** Following **GP3** with



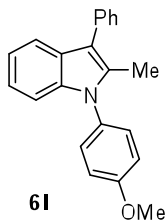
styrylaniline **5i** (77 mg, 0.20 mmol) in the photo-condition after 3 h, indole **6i** (46 mg, 60%) was obtained after silica gel column chromatography (1%  $Et_2O$ /hexane) as white solid: mp 112–114  $^{\circ}C$ ; IR  $\nu_{max}$  (plate) 2958, 2932, 2873, 1612, 1512, 1470, 1439, 1340, 1246  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.34 (dd,  $J = 1.2, 0.4$  Hz, 1H), 7.24 (dd,  $J = 6.8, 2.4$  Hz, 2H), 7.03–7.00 (m, 3H), 6.83 (br s, 1H), 6.48 (s, 1H), 6.23 (dd,  $J = 3.2, 1.6$  Hz, 1H), 5.91 (s, 2H), 5.47 (dd,  $J = 3.2, 0.4$  Hz, 1H), 4.04 (t,  $J = 6.4$  Hz, 2H), 1.84 (dt,  $J = 14.4, 6.8$  Hz, 2H), 1.55 (dt,  $J = 14.8, 8.4$  Hz, 2H), 1.02 (t,  $J = 7.6$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.1, 147.4, 145.3, 143.5, 141.3, 135.1, 130.7, 129.6, 121.6, 115.2, 111.0, 106.0, 101.1, 100.6, 98.9, 91.5, 68.0, 31.3, 19.3, 13.9; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{23}H_{22}NO_4$  376.1543; found 376.1539.

**1-(4-methoxyphenyl)-3-methyl-1H-indole (6j).**<sup>8</sup>

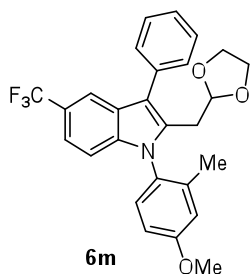
Following **GP3** with styrylaniline **5j** (48 mg, 0.20 mmol) in the photo-condition after 2 h, indole **6j** (26 mg, 55%) was obtained after silica gel column chromatography (1% EtOAc/hexane) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.25-7.17 (m, 2H), 7.09 (d, *J* = 0.8 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.9, 136.4, 133.1, 129.4, 125.9, 125.7, 122.1, 119.5, 119.1, 114.7, 112.1, 110.2, 55.6, 9.6; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>16</sub>H<sub>16</sub>NO 238.1226; found 238.1213.

**3-cyclopropyl-1-(4-methoxyphenyl)-2-methyl-1H-indole (6k).**

Following **GP3** with styrylaniline **5k** (61 mg, 0.21 mmol) in the photo-condition after 4 h, indole **6k** (43 mg, 71%) was obtained after silica gel column chromatography (1.5% EtOAc/hexane) as white solid: mp 78–80 °C; IR ν<sub>max</sub> (plate) 3002, 2954, 1611, 1514, 1461, 1291, 1247 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.14–7.10 (m, 2H), 7.08–7.02 (m, 3H), 3.90 (s, 3H), 2.31 (s, 3H), 1.87 (ddd, *J* = 13.6, 8.8, 5.6 Hz, 1H), 0.99–0.95 (m, 2H), 0.78–0.74 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.9, 137.4, 135.4, 130.9, 129.3, 128.4, 120.8, 119.3, 118.4, 114.6, 113.0, 109.8, 55.5, 11.3, 5.7, 5.1; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>19</sub>H<sub>20</sub>NO 278.1539; found 278.1540.

**1-(4-methoxyphenyl)-2-methyl-3-phenyl-1H-indole (6l).**

Following **GP3** with styrylaniline **5l** (63 mg, 0.20 mmol) in the photo-condition after 3 h, indole **6l** (45 mg, 72%) was obtained after silica gel column chromatography (1.5% Et<sub>2</sub>O/hexane) as yellowish solid: mp 123–125 °C; IR ν<sub>max</sub> (plate) 2957, 2930, 2836, 1514, 1461, 1248 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76–7.71 (m, 1H), 7.59 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.36–7.32 (m, 3H), 7.18–7.06 (m, 5H), 3.92 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.2, 137.9, 135.6, 133.9, 130.6, 129.7, 129.4, 128.5, 127.2, 125.9, 121.6, 120.2, 118.6, 114.9, 114.7, 110.1, 55.6, 11.9; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>22</sub>H<sub>20</sub>NO 314.1539; found 314.1537.

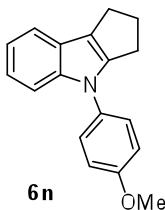
**2-((1,3-dioxolan-2-yl)methyl)-1-(4-methoxy-2-methylphenyl)-3-phenyl-5-(trifluoromethyl)-1H-indole (6m).**

Following **GP3** with styrylaniline **5m** (95 mg, 0.20 mmol) in the photo-condition after 4 h, indole **6m** (68 mg, 72%) was obtained after silica gel column chromatography (7% EtOAc/hexane) as colorless liquid. IR ν<sub>max</sub> (film) 2960, 2888, 1611, 1505, 1441, 1324 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 0.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.40–7.35 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.94–6.88 (m, 3H), 4.84 (dd, *J* = 5.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.79–3.66 (m, 4H), 3.14 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.90 (dd, *J* = 14.4, 5.6 Hz, 1H), 1.94 (s, 3H);

<sup>8</sup> Verma, A. K.; Singh, J.; Larock, R. C. *Tetrahedron* **2009**, *65*, 8434.

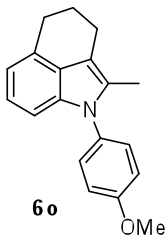
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 139.0, 138.8, 134.4, 134.0, 130.7, 130.0, 128.7, 126.7, 126.6, 124.1, 122.7, 122.3, 118.7 (q,  $J = 3.5$  Hz), 117.8, 116.9 (q,  $J = 4.5$  Hz), 116.2, 112.2, 110.5, 102.6, 64.6, 64.6, 55.5, 30.6, 17.6; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{27}\text{H}_{25}\text{F}_3\text{NO}_3$  468.1781; found 468.1774.

**4-(4-methoxyphenyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (6n).** Following **GP3** with



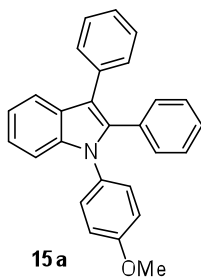
styrylaniline **5n** (59 mg, 0.22 mmol) in the photo-condition after 3 h, indole **6n** (44 mg, 75%) was obtained after silica gel column chromatography (1.5% EtOAc/hexane) as white solid: mp 86–88 °C; IR  $\nu_{\text{max}}$  (plate) 2953, 2932, 2851, 1513, 1451, 1377, 1245  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53–7.50 (m, 1H), 7.38–7.35 (m, 3H), 7.17–7.10 (m, 2H), 7.05–7.02 (m, 2H), 3.89 (s, 3H), 2.94 (dt,  $J = 7.6, 1.2$  Hz, 2H), 2.87 (t,  $J = 7.6$  Hz, 2H), 2.57 (dt,  $J = 14.0, 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 146.0, 141.4, 131.9, 126.4, 124.7, 120.7, 119.8, 119.6, 118.6, 114.6, 110.6, 55.6, 28.4, 25.9, 24.7; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{18}\text{H}_{18}\text{NO}$  264.1383; found 264.1385.

**1-(4-methoxyphenyl)-2-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (6o).** Following **GP3**



with styrylaniline **5o** (59 mg, 0.20 mmol) in the photo-condition after 8 h, indole **6o** (38 mg, 65%) was obtained after silica gel column chromatography (2% EtOAc/hexane) as colorless liquid. IR  $\nu_{\text{max}}$  (film) 2925, 2834, 1513, 1457, 1246  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (dd,  $J = 8.8, 1.2$  Hz, 2H), 7.04–6.99 (m, 3H), 6.89 (d,  $J = 8.0$  Hz, 1H), 6.82 (d,  $J = 6.8$  Hz, 1H), 3.89 (s, 3H), 2.96 (t,  $J = 6.0$  Hz, 2H), 2.82 (t,  $J = 5.6$  Hz, 2H), 2.21 (s, 3H), 2.11 (dt,  $J = 12.0, 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 135.8, 131.5, 131.2, 129.5, 128.7, 127.2, 121.6, 116.0, 114.5, 110.4, 106.9, 55.5, 27.6, 24.5, 21.4, 11.1; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{19}\text{H}_{20}\text{NO}$  278.1539; found 278.1535.

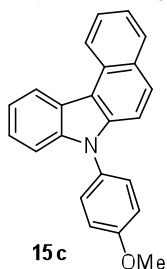
**1-(4-methoxyphenyl)-2,3-diphenyl-1*H*-indole (15a).** Following **GP3** with styrylaniline **13a**



(75 mg, 0.20 mmol) in the photo-condition after 4 h, indole **15a** (45 mg, 60%) was obtained after silica gel column chromatography (1% Et<sub>2</sub>O/hexane) as yellowish solid: mp 153–155 °C; IR  $\nu_{\text{max}}$  (plate) 3045, 1605, 1513, 1457, 1247  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85–7.81 (m, 1H), 7.40 (dd,  $J = 6.8, 1.2$  Hz, 2H), 7.36–7.28 (m, 3H), 7.27–7.23 (m, 3H), 7.20–7.11 (m, 7H), 6.90 (dd,  $J = 6.4, 2.0$  Hz, 2H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.49, 138.3, 137.3, 135.1, 131.7, 131.2, 131.0, 130.2, 129.4, 128.3, 127.9, 127.4, 127.3, 125.9, 122.6, 120.7, 119.5, 116.3, 114.3, 110.7, 55.4; HRMS (ESI)  $m/z$   $[\text{M}+\text{H}]^+$ , calc'd for  $\text{C}_{27}\text{H}_{22}\text{NO}$  376.1696; found 376.1694.

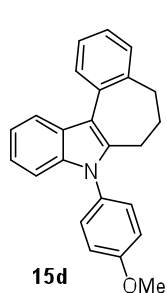
**1-(4-methoxyphenyl)-2-methyl-3-phenyl-1*H*-indole (6l).** Following **GP3** with styrylaniline **13b** (65 mg, 0.20 mmol) in the photo-condition after 4.5 h, indole **6l** (40 mg, 62%) was obtained after silica gel column chromatography (1.5% Et<sub>2</sub>O/hexane) as yellowish solid. Full characterization of **6l** was described early in this SI.

**7-(4-methoxyphenyl)-7H-benzo[c]carbazole (15c).** Following **GP3** with styrylaniline **13c**



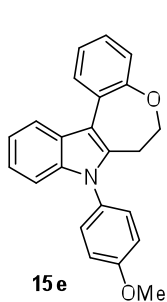
(66 mg, 0.20 mmol) in the photo-condition after 6 h, indole **15c** (34 mg, 52%) was obtained after silica gel column chromatography (1% Et<sub>2</sub>O/hexane) as white solid: mp 150–152 °C; IR  $\nu_{\max}$  (plate) 2921, 2846, 1513, 1465, 1388, 1282 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (d, *J* = 8.4 Hz, 1H), 8.66–8.63 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.74 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.52–7.40 (m, 7H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 140.6, 139.1, 130.0, 129.9, 129.4, 129.2, 129.1, 127.3, 126.9, 124.3, 123.7, 123.3, 123.0, 122.0, 120.4, 115.2, 115.1, 111.7, 110.4, 55.6; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>23</sub>H<sub>18</sub>NO 324.1358; found 324.1360.

**Indole 15d.** Following **GP3** with styrylaniline **13d** (70 mg, 0.20 mmol) in the photo-condition



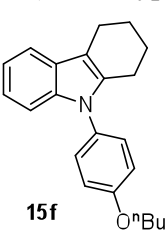
after 6 h, indole **15d** (42 mg, 60%) was obtained after silica gel column chromatography (1.5% EtOAc/hexane) as off-white solid: mp 145–147 °C; IR  $\nu_{\max}$  (plate) 3049, 2934, 2839, 1548, 1514, 1458, 1294, 1247 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.40 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.34–7.31 (m, 3H), 7.26–7.19 (m, 2H), 7.18–7.15 (m, 2H), 7.08 (dd, *J* = 6.8, 2.4 Hz, 2H), 3.92 (s, 3H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.26 (dt, *J* = 13.2, 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 140.7, 139.2, 138.3, 135.8, 130.4, 129.4, 129.2, 128.0, 126.4, 126.3, 125.3, 121.5, 120.4, 118.8, 114.8, 113.4, 110.5, 55.6, 33.2, 32.3, 24.1; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>24</sub>H<sub>22</sub>NO 340.1696; found 340.1695.

**Indole 15e.** Following **GP3** with styrylaniline **13e** (69 mg, 0.20 mmol) in the photo-condition



after 6 h, indole **15e** (40 mg, 58%) was obtained after silica gel column chromatography (1.5% EtOAc/hexane) as white solid: mp 155–157 °C; IR  $\nu_{\max}$  (plate) 2933, 1551, 1512, 1489, 1461, 1244 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.31–7.12 (m, 7H), 7.08–7.03 (m, 3H), 4.38 (t, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 3.12 (t, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.5, 158.8, 139.1, 136.9, 130.1, 129.6, 128.7, 127.3, 126.2, 125.8, 123.7, 122.0, 121.0, 120.6, 119.9, 114.9, 110.3, 109.8, 70.6, 55.6, 31.0; HRMS (ESI) *m/z* [M+H]<sup>+</sup>, calc'd for C<sub>23</sub>H<sub>20</sub>NO<sub>2</sub> 342.1489; found 342.1494.

**9-(4-butoxyphenyl)-2,3,4,9-tetrahydro-1H-carbazole (15f).** Following **GP3** with



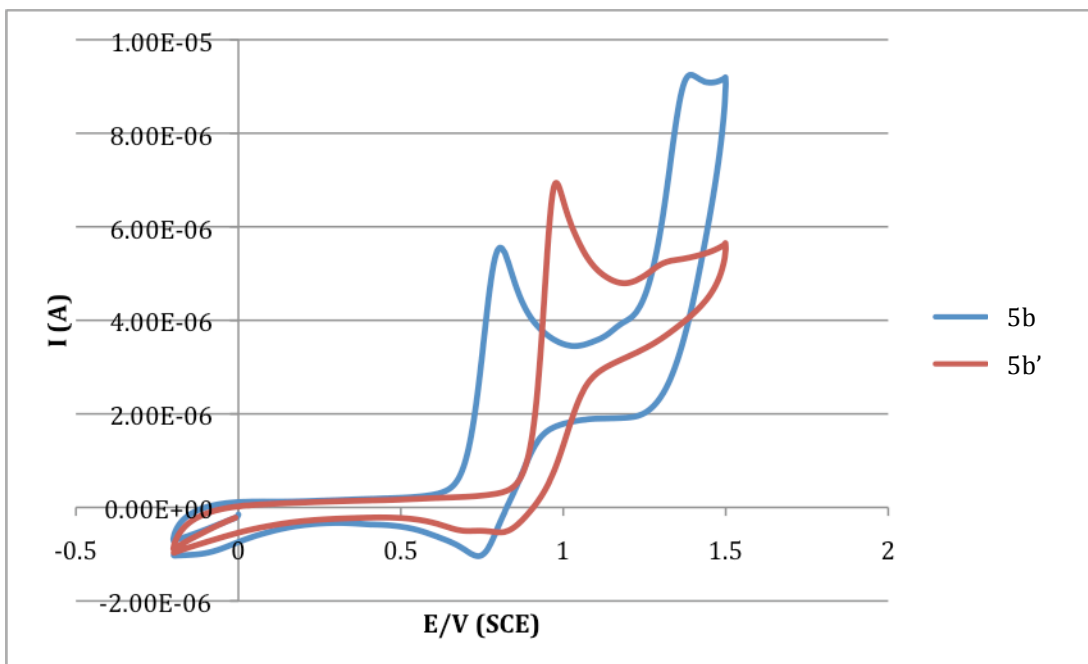
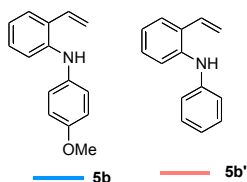
styrylaniline **13f** (63 mg, 0.20 mmol) in the photo-condition after 16 h (after 12 h, an extra amount of the catalyst, 3.6 mg, and 500 mg of silica gel were added), indole **15f** (25 mg, 40%) was obtained after silica gel column chromatography (2% EtOAc/hexane) as off-white solid: mp 84–86 °C; IR  $\nu_{\max}$  (plate) 2925, 2856, 1614, 1516, 1460, 1387 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (a few extra peaks for rotamers) 8.15 (d, *J* = 7.2 Hz) and 7.53–7.25 (m, 3H), 7.18–7.07 (m, 3H), 7.03–6.99 (m, 2H), 4.08 (t, *J* = 6.4 Hz) and 4.03 (t, *J* = 6.4 Hz, 2H), 2.81 (br s, 2H), 2.58 (br s, 2H), 1.90 (br s, 4H), 1.86–1.76 (m, 2H), 1.62–1.50 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (few extra peaks in carbon for rotamers) 158.2, 141.4, 137.6, 136.2, 130.5,

128.6, 128.5, 127.4, 125.8, 123.1, 121.0, 120.2, 119.6, 119.3, 117.6, 115.6, 115.0, 110.3, 109.8, 109.7, 68.0, 31.3, 23.4, 23.2, 23.0, 21.1, 19.3, 13.9; HRMS (ESI)  $m/z$   $[M+H]^+$ , calc'd for  $C_{22}H_{26}NO$  320.2009; found 320.2011.

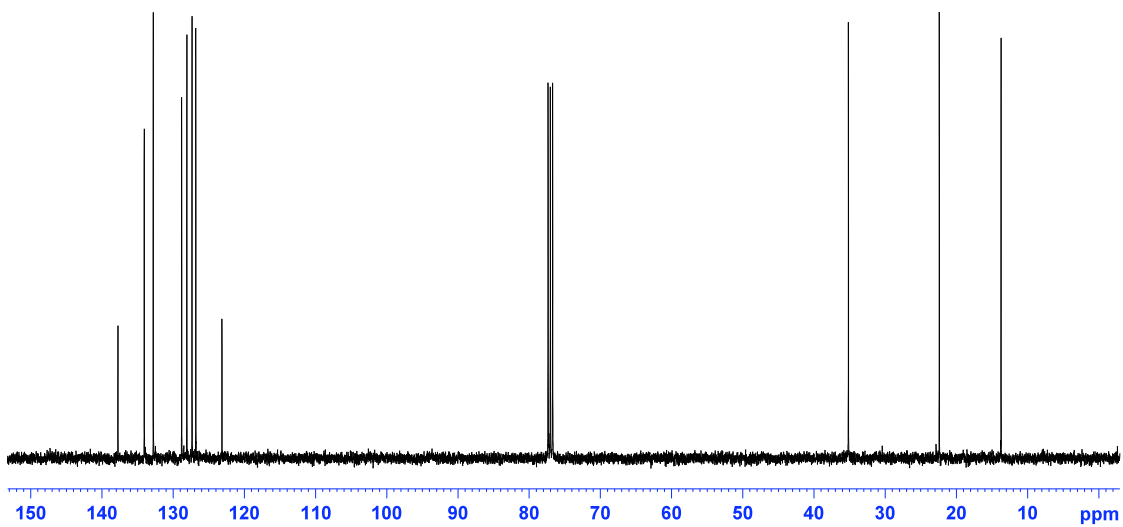
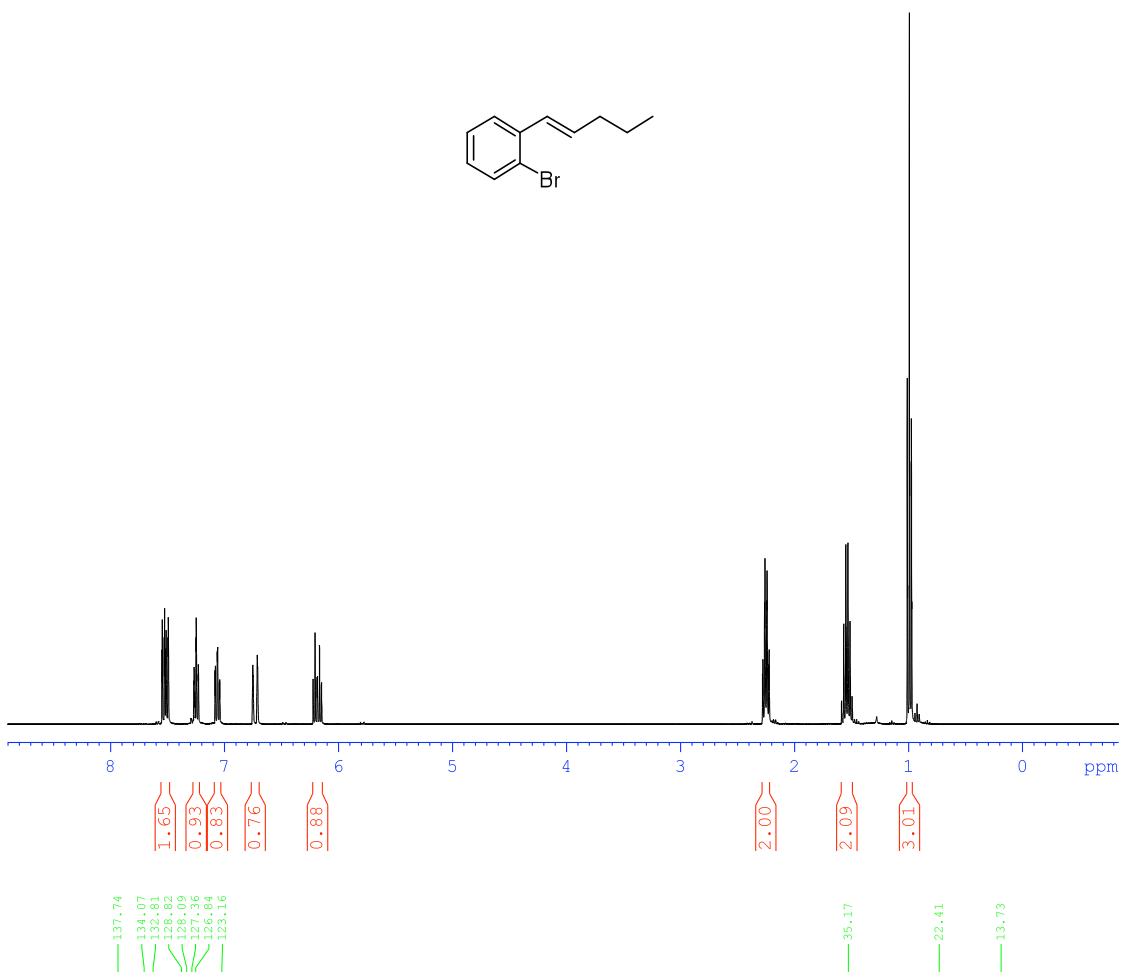
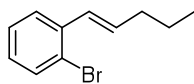
**Gram Scale Experiment (6n).** Following **GP-3** except that the catalyst was added in two batches, a 250 mL round-bottom flask was charged with  $[Ru(bpz)_3](PF_6)_2 \cdot 2H_2O$  (76 mg, 0.084 mmol, 2 mol%), stryryl aniline derivative **5n** (1.12 g, 4.23 mmol), dry  $CH_3CN$  (140 mL) and silica gel (6.0 g). The flask was capped with a rubber septum and a needle (16G, 1.5 inch) was pierced through the septum so that the reaction mixture was exposed to air. The orange reaction mixture was irradiated at room temperature with a LED light. After 4 h of the reaction, another batch of the catalyst (76 mg) and silica gel (6.0 g) were added. Six hours later (10 h total from the beginning), the mixture was filtered through a short silica pad and eluted with  $Et_2O$  (100 mL). The solution was concentrated and the residue was purified by silica gel flash chromatography (1.5 %  $EtOAc$ /hexane) to afford the indole **6n** (786 mg, 71%) as white solid.

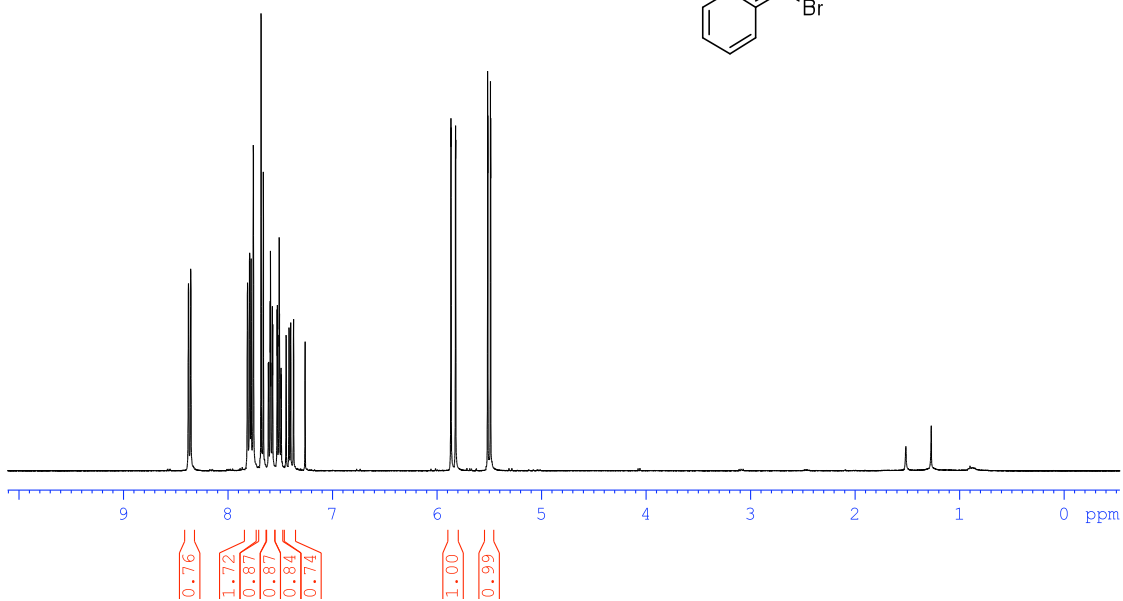
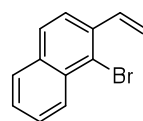


**Cyclic Voltammogram of *N*-(4-methoxyphenyl)-2-vinylaniline (5b) and *N*-phenyl-2-vinylaniline (5b')**

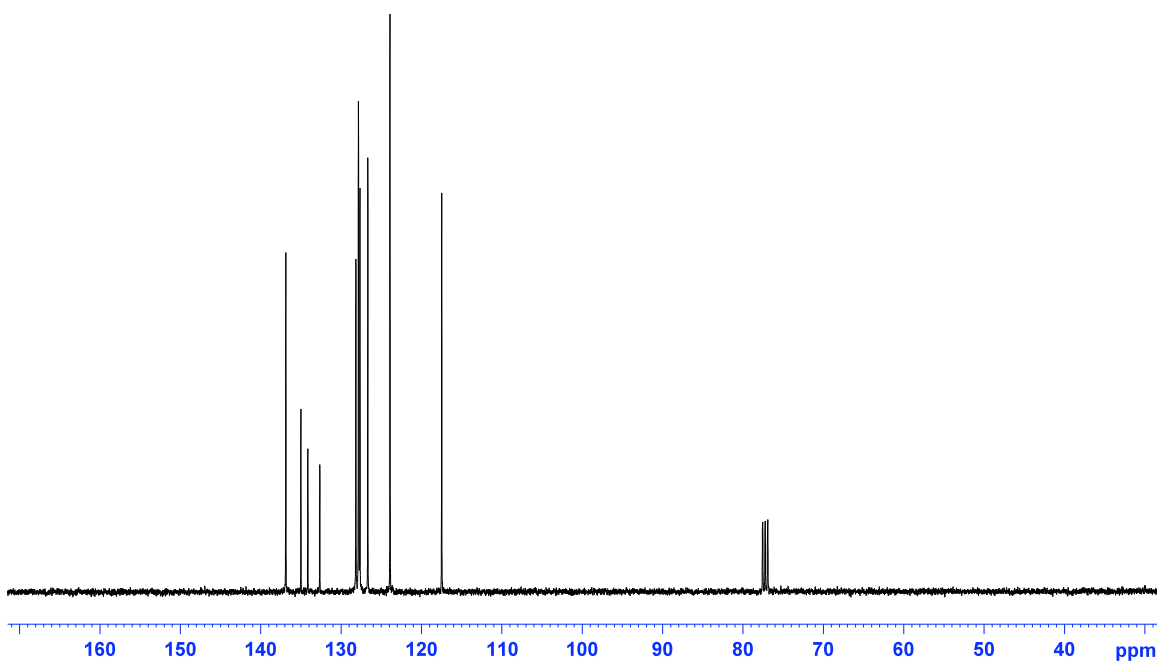


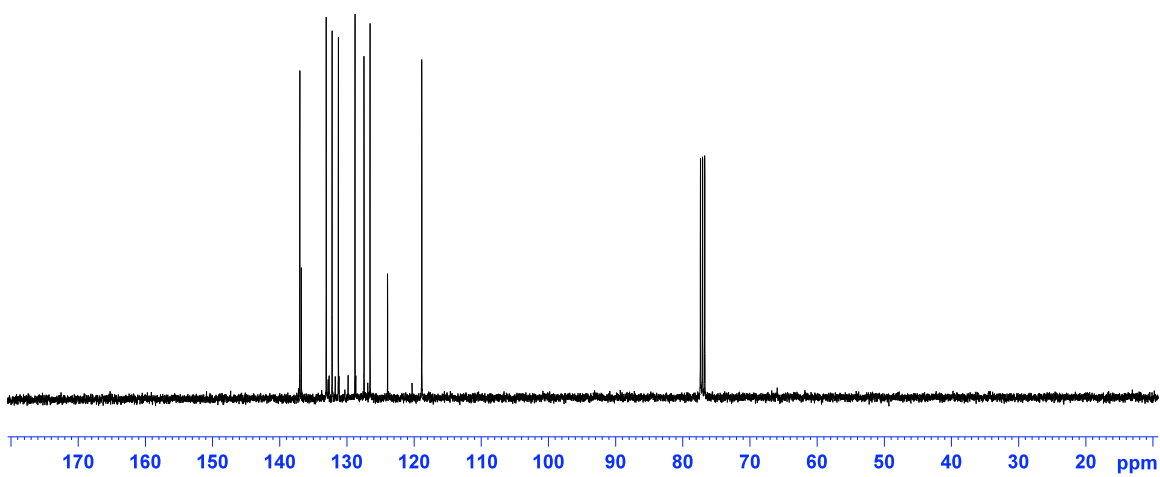
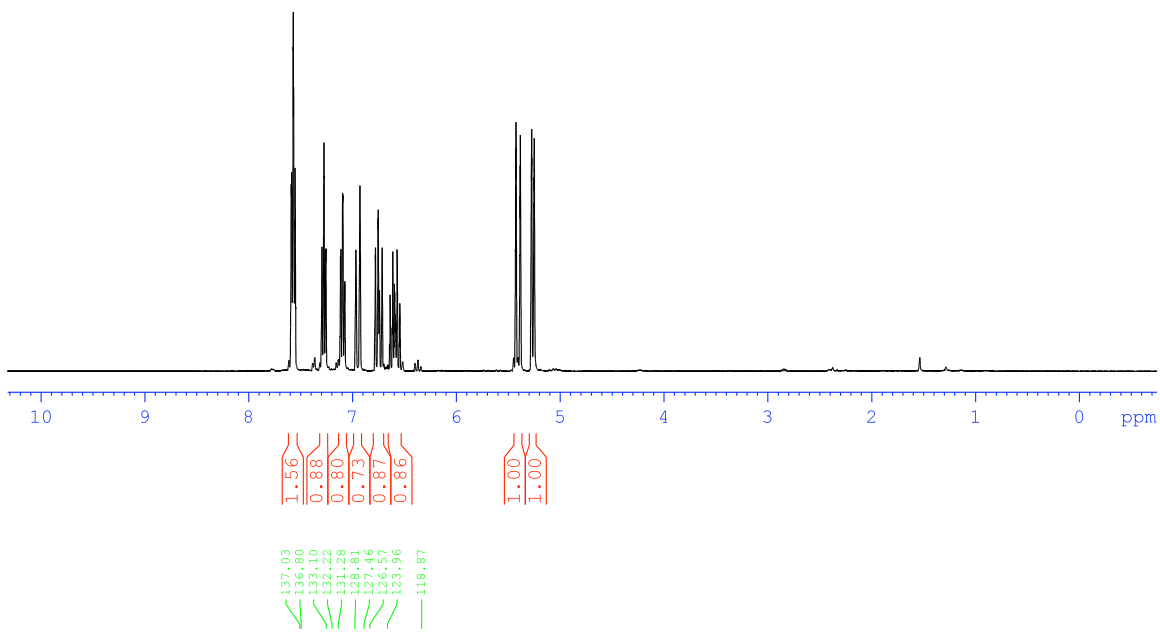
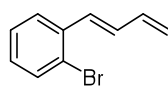
Cyclic voltammetry experiments were performed using a CH Instruments electrochemical analyzer, on solutions of the styryl anilines under study in  $\text{CH}_3\text{CN}$  ( $c \sim 2 \cdot 10^{-3}$  mol/L), contained in a three electrode cell at room temperature in the presence of air. Tetrabutylammonium hexafluorophosphate (0.1 M in  $\text{CH}_3\text{CN}$ ) was used as the supporting electrolyte. The reference electrode was a saturated calomel electrode (SCE), which was separated from the solution by a bridge compartment filled with the same supporting electrolyte solution used in the cell. A platinum disc (2.0 mm diameter) was used as the working electrode and a platinum wire as the auxiliary electrode.

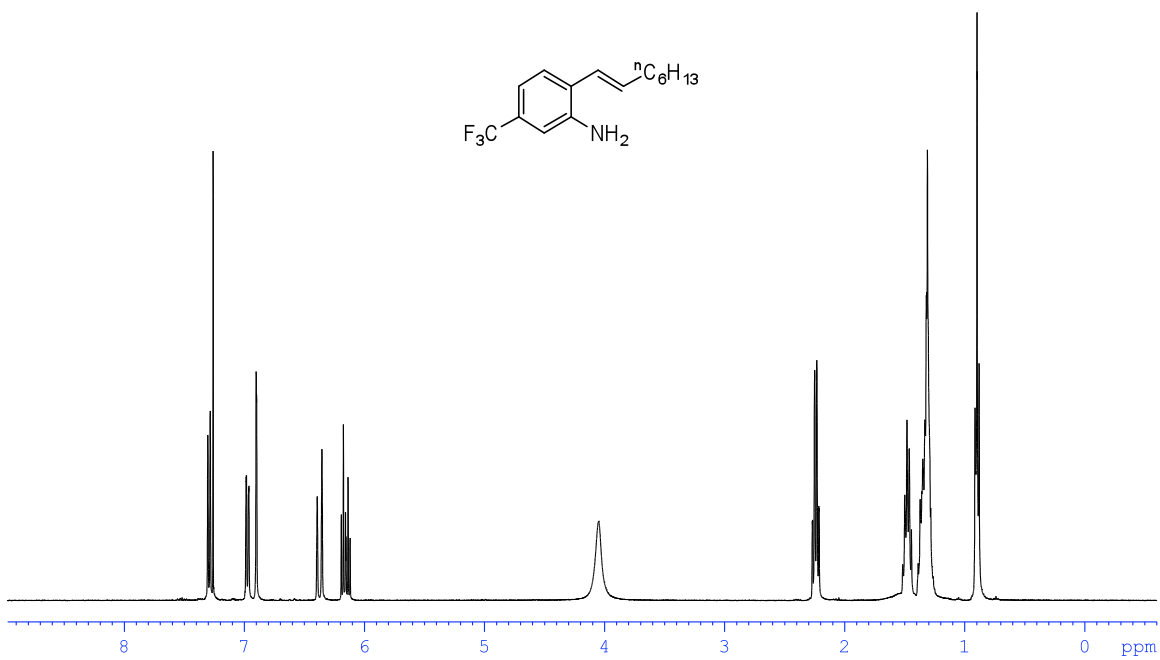
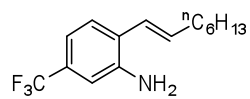




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134.10  
132.64  
128.15  
127.84  
127.65  
126.67  
123.92  
117.46

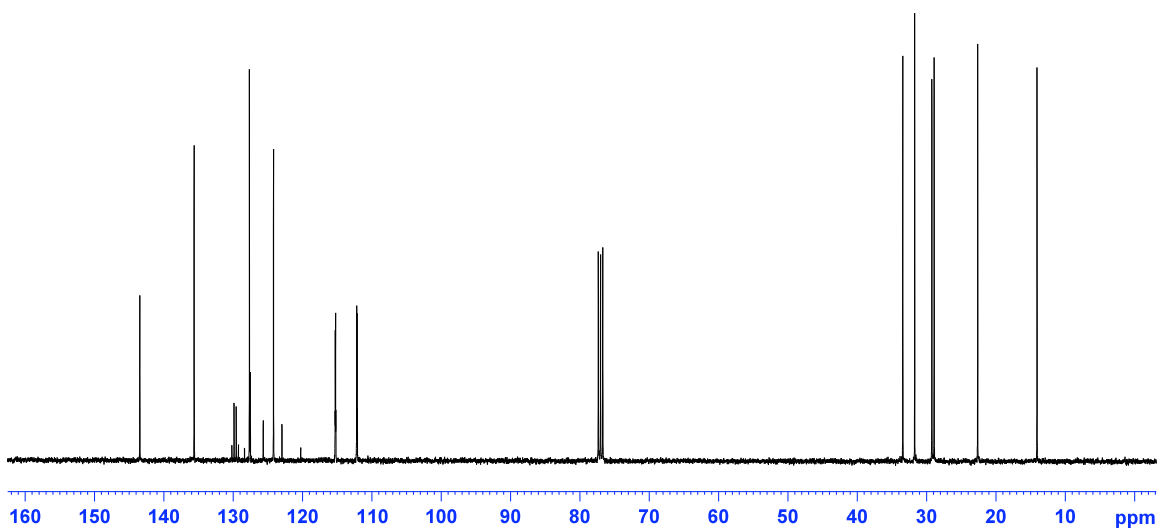


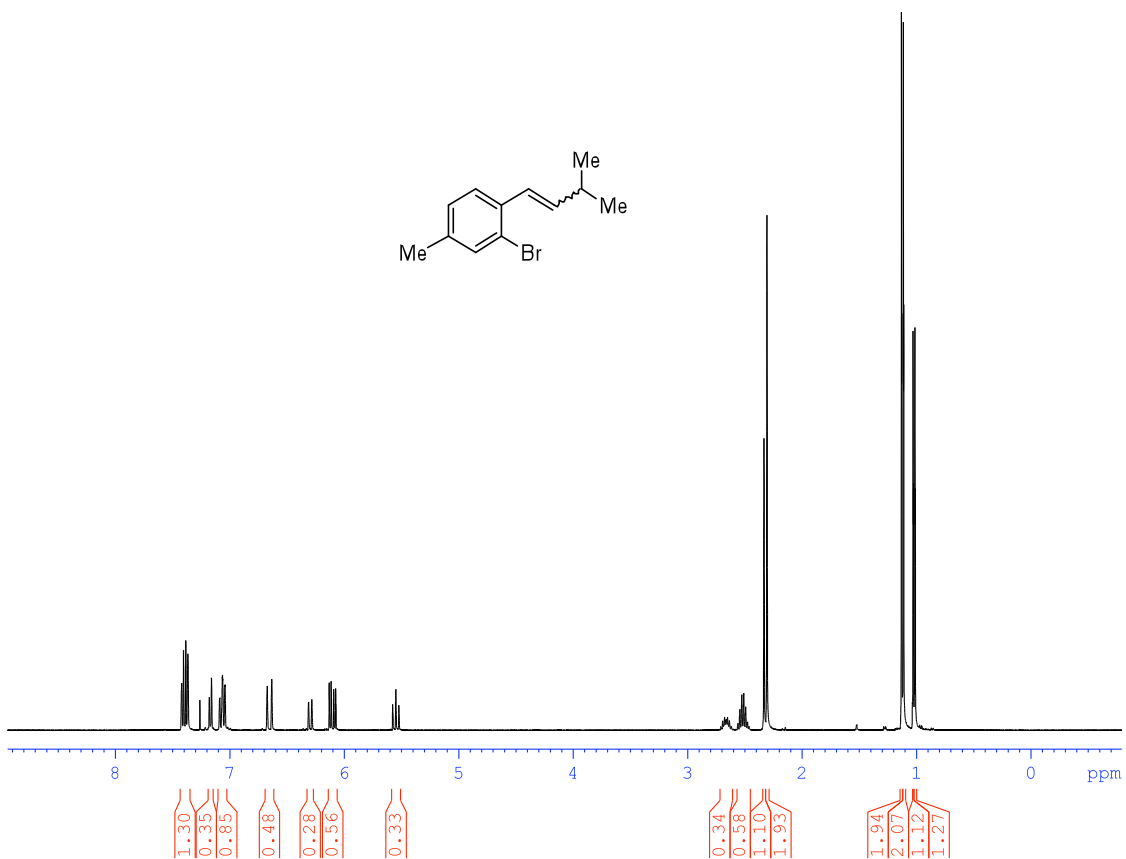
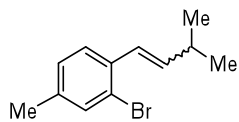




143.46  
135.62  
130.19  
129.57  
129.23  
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127.65  
125.66  
124.18  
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120.25  
115.30  
115.26  
115.22  
115.19  
112.20  
112.15  
111.15  
111.08

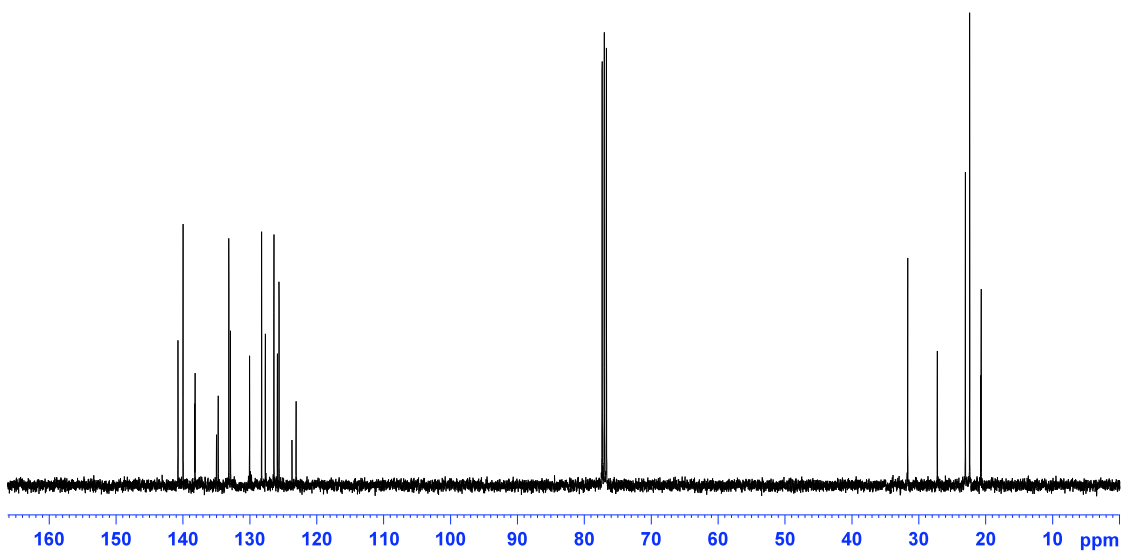
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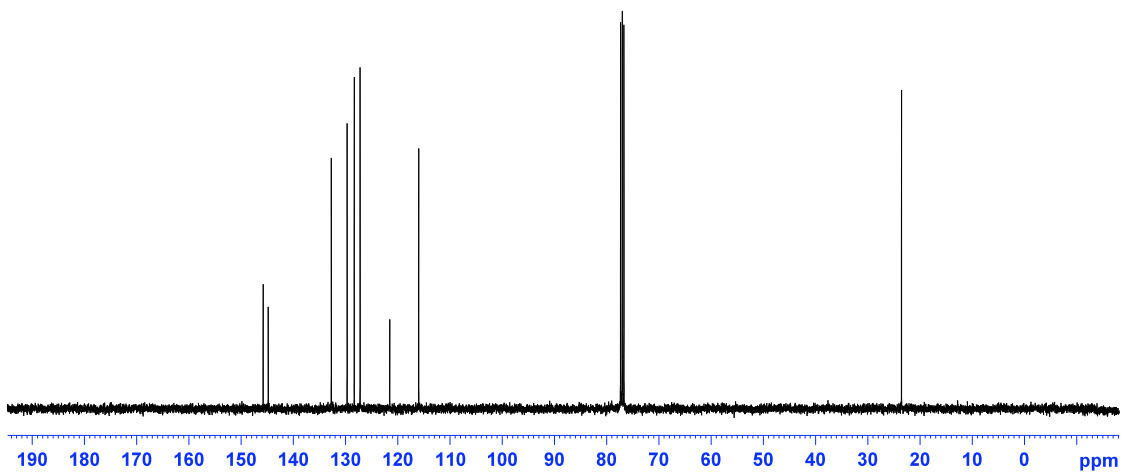
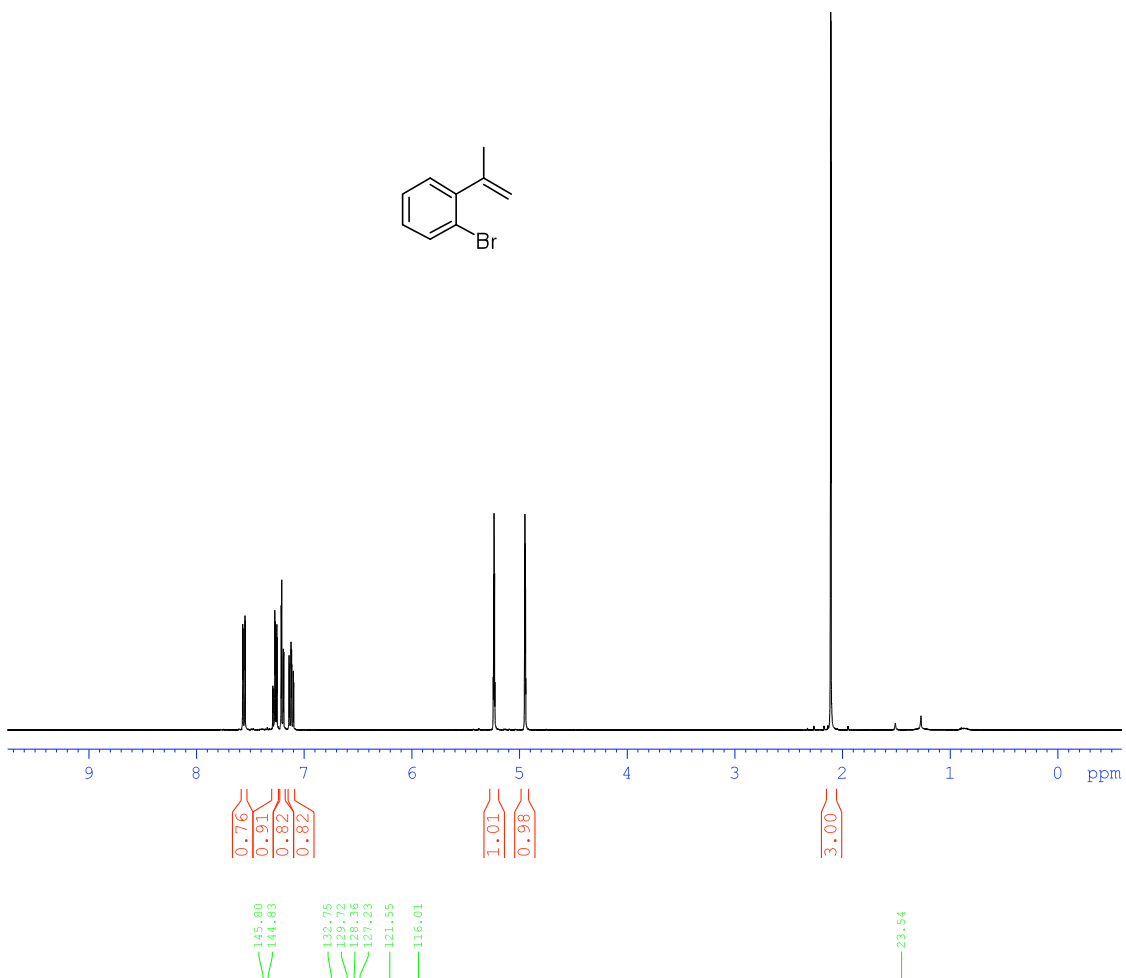
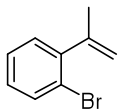


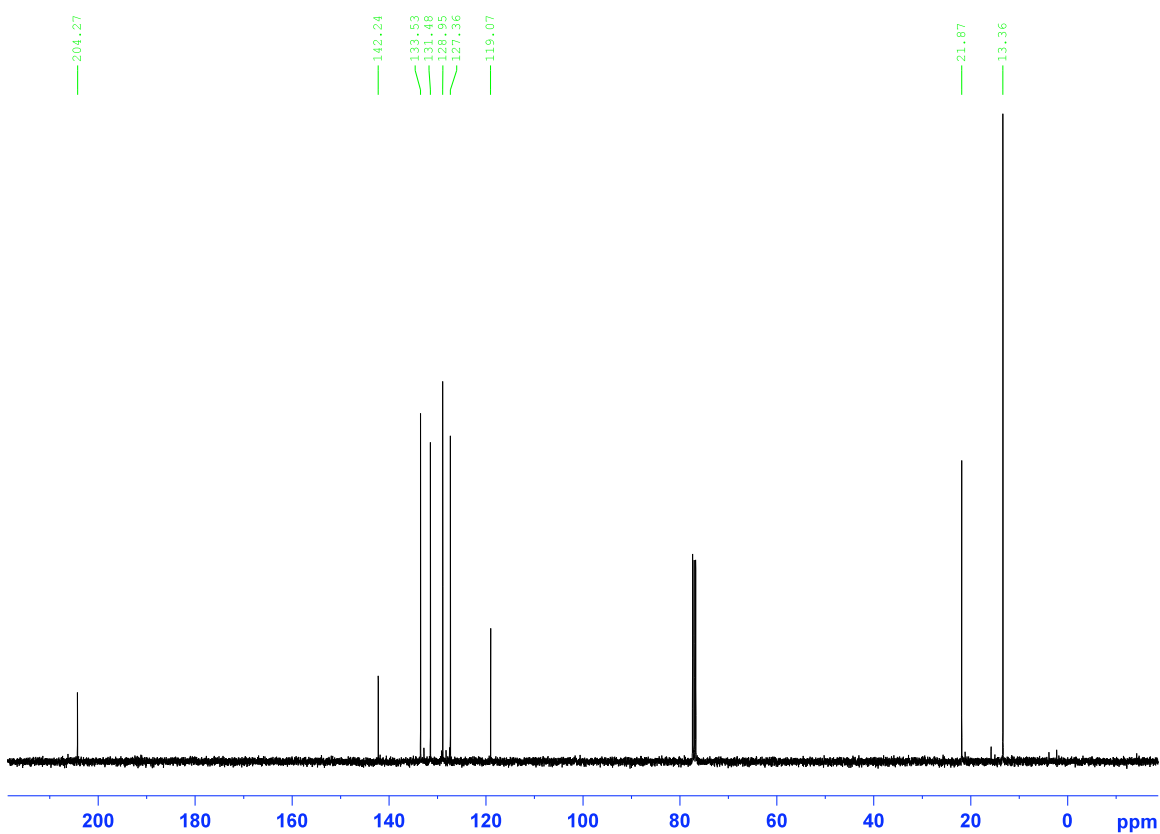
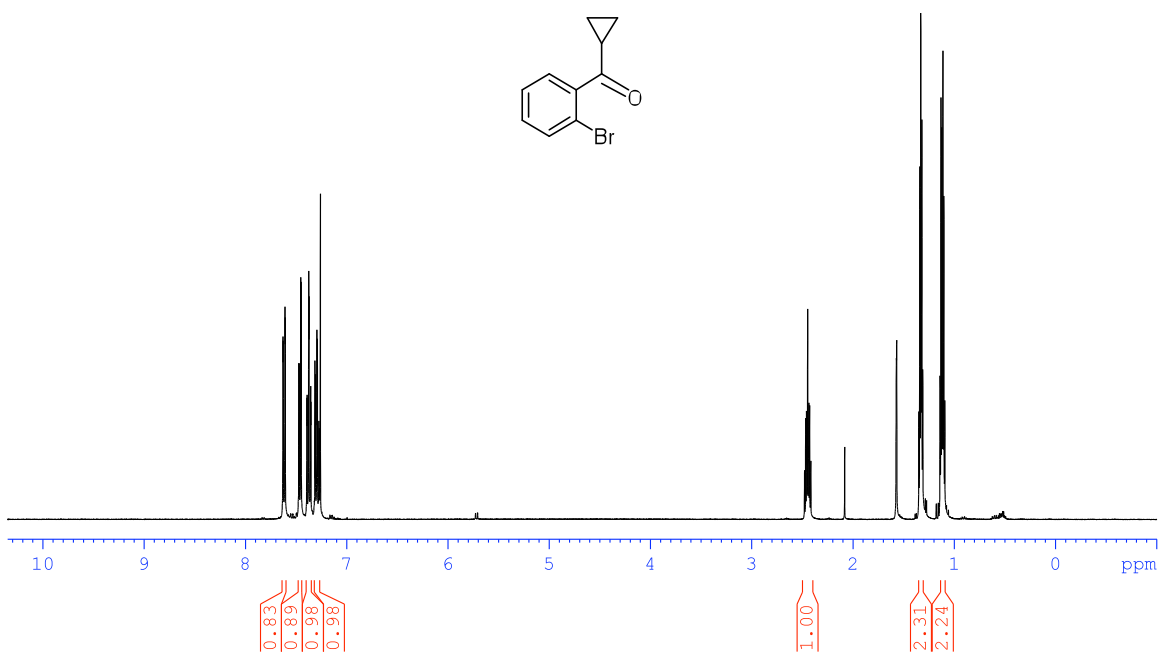
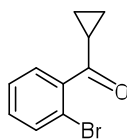


140.77  
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125.90  
125.85  
123.92  
123.10

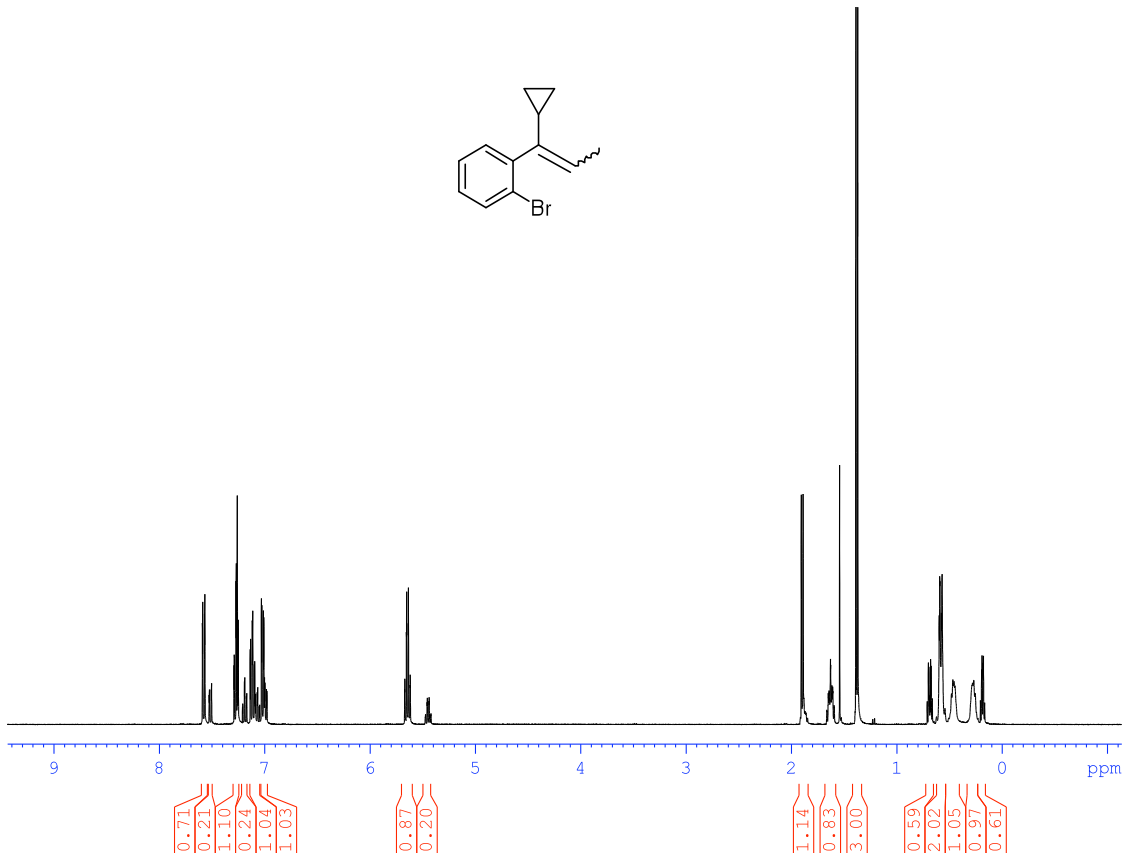
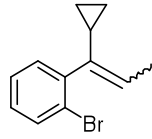
31.67  
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20.68





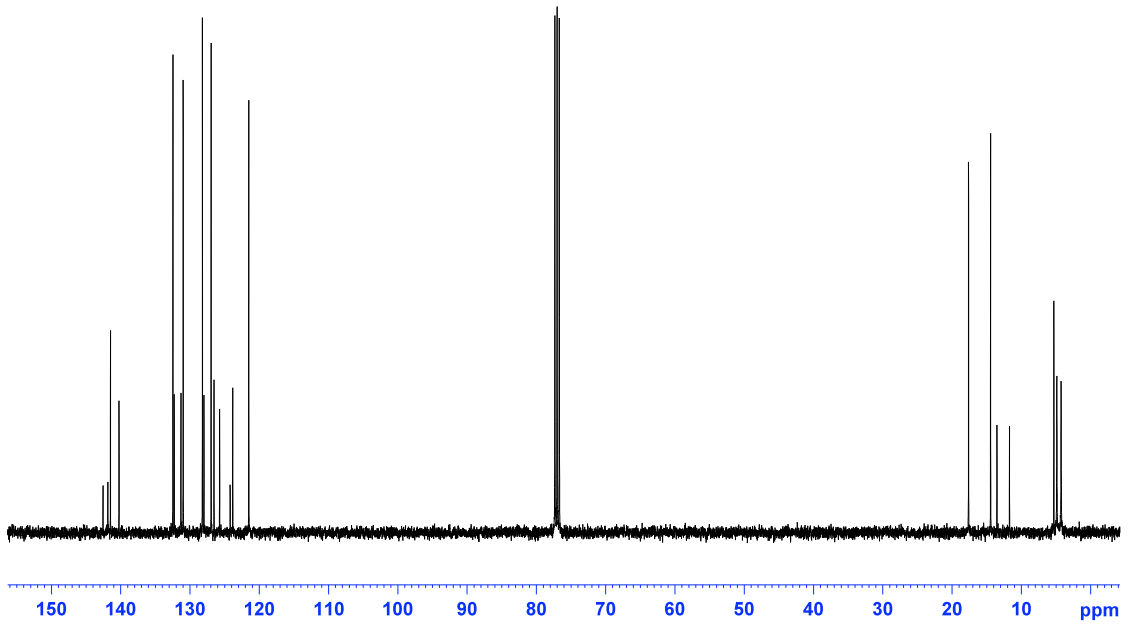


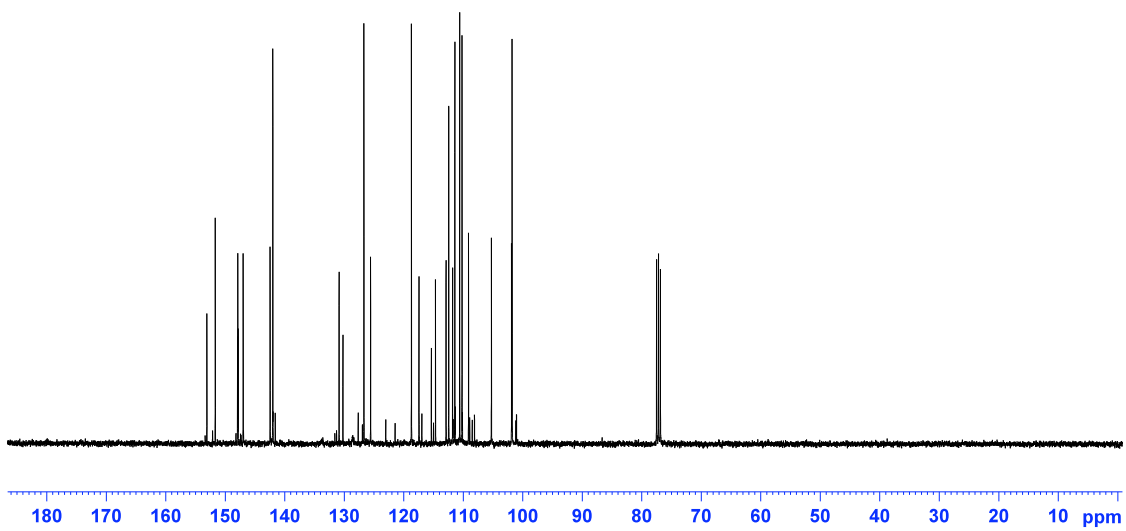
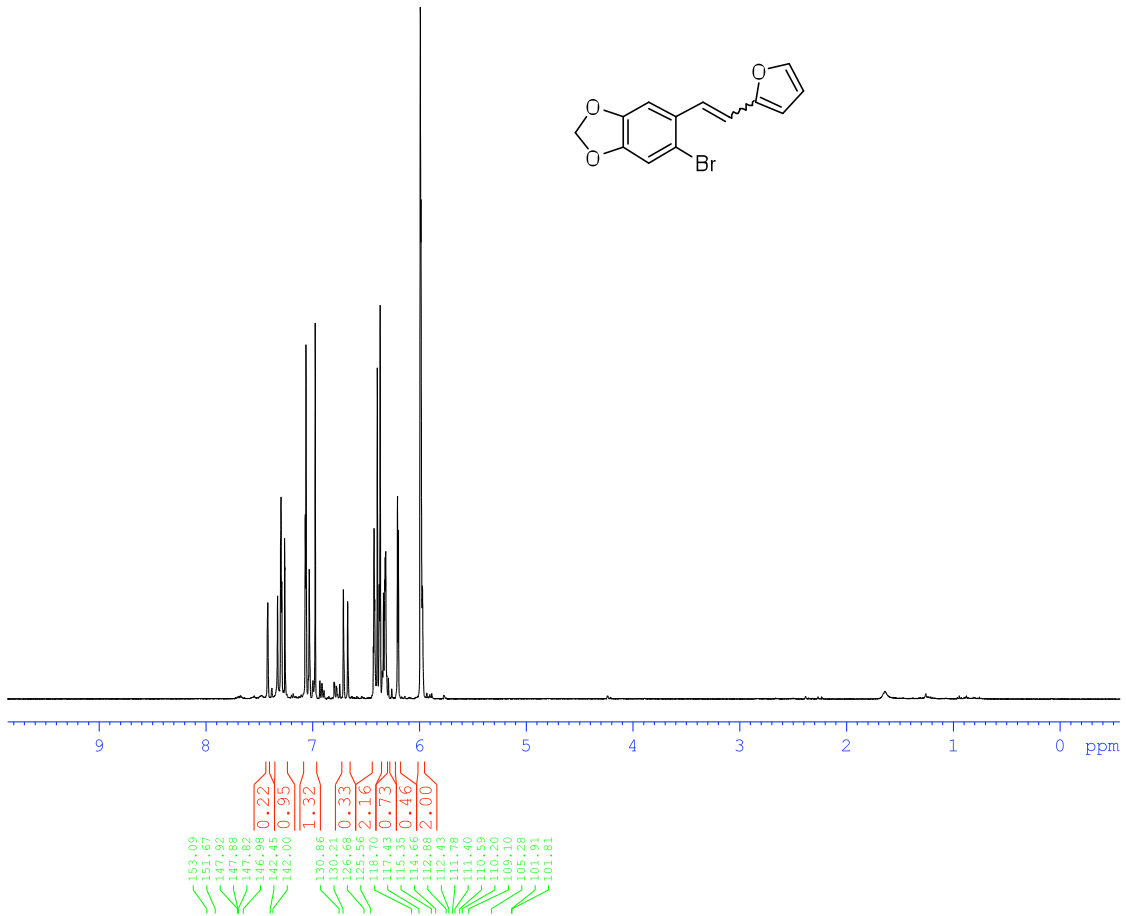
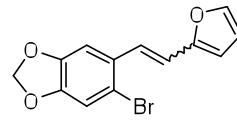


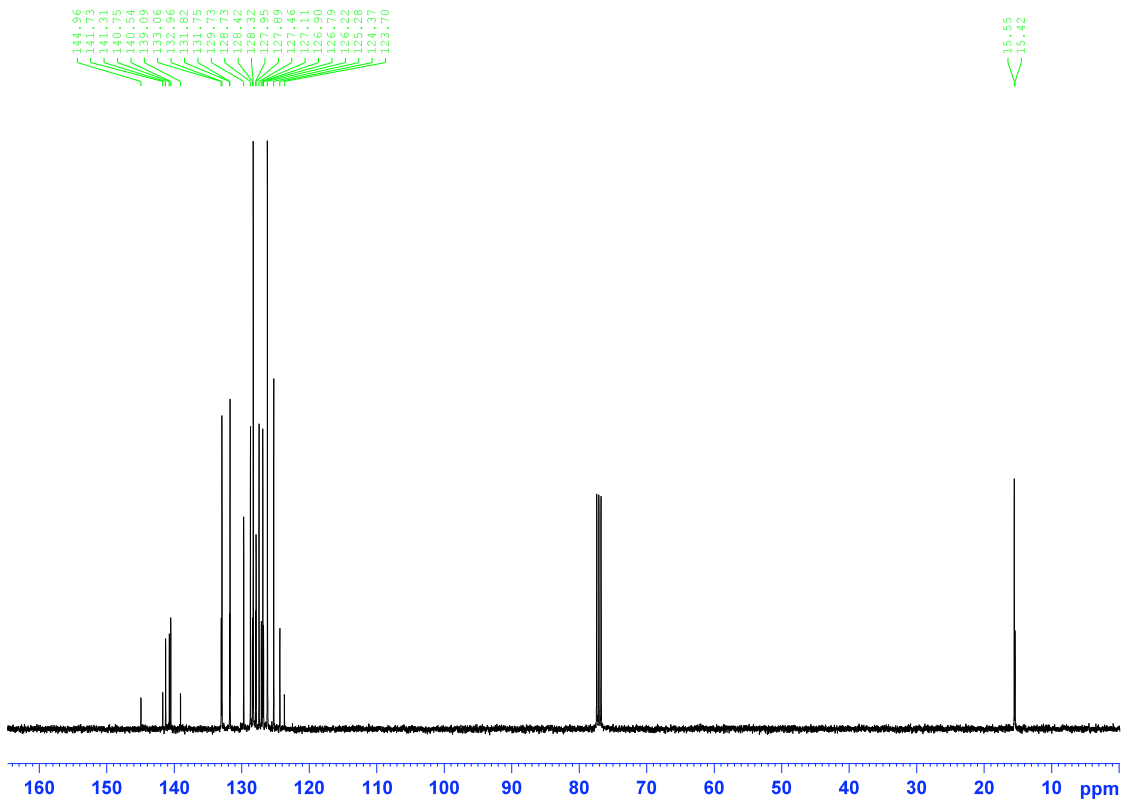
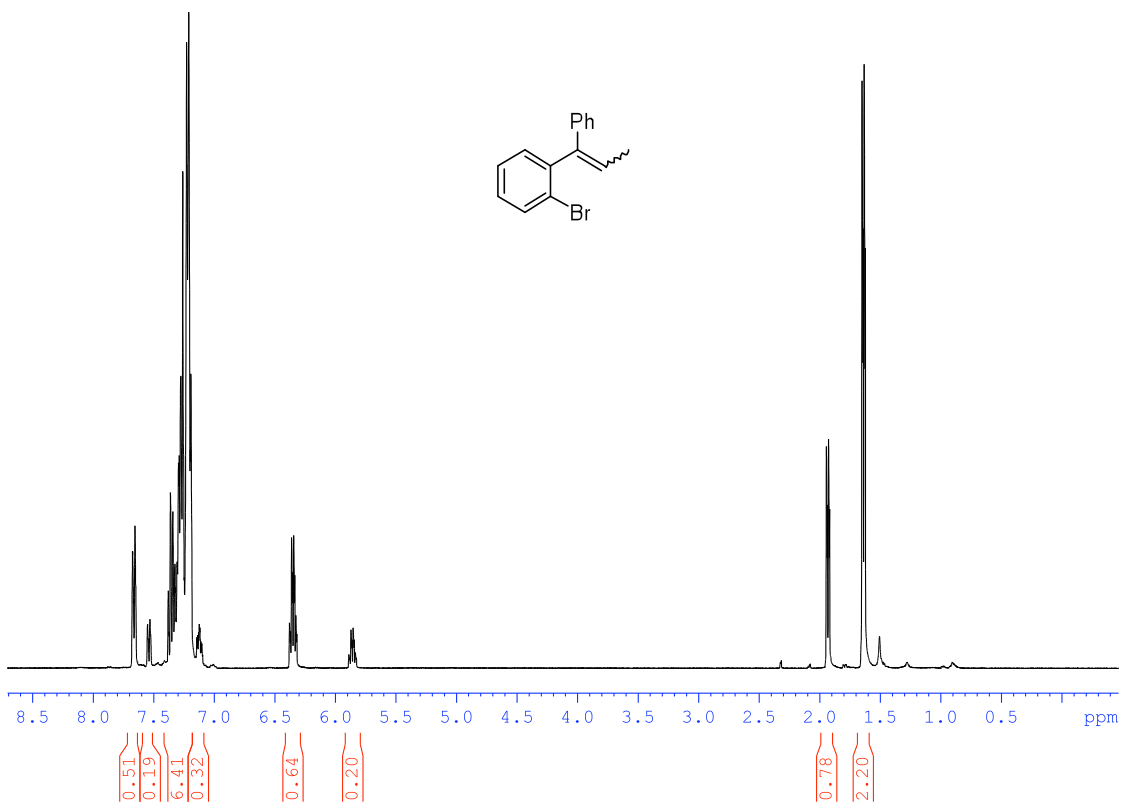


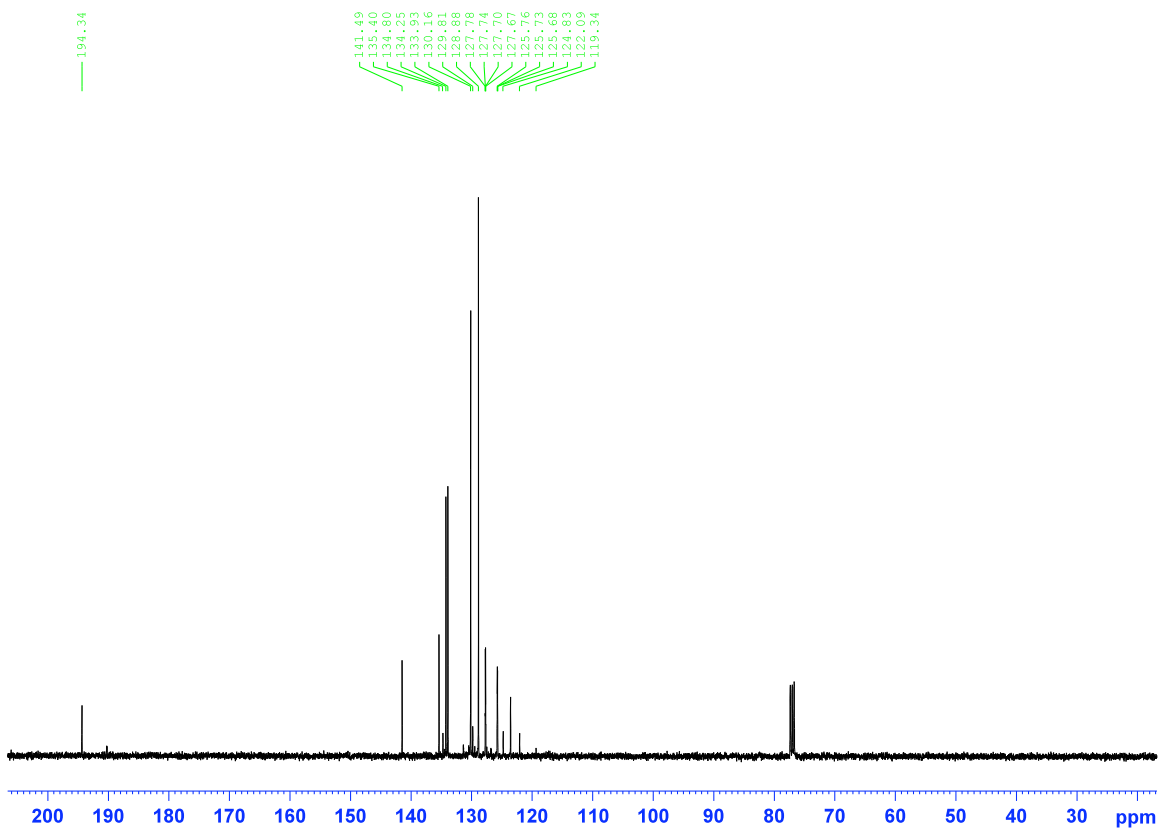
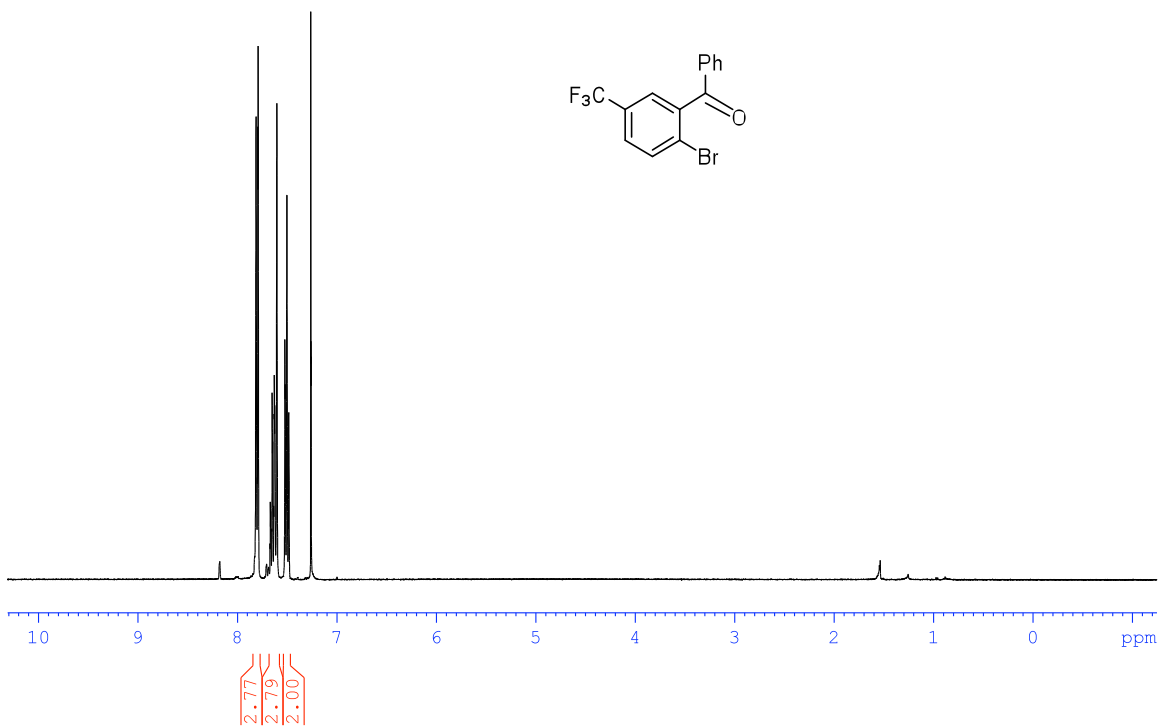
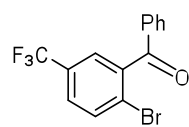
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128.00  
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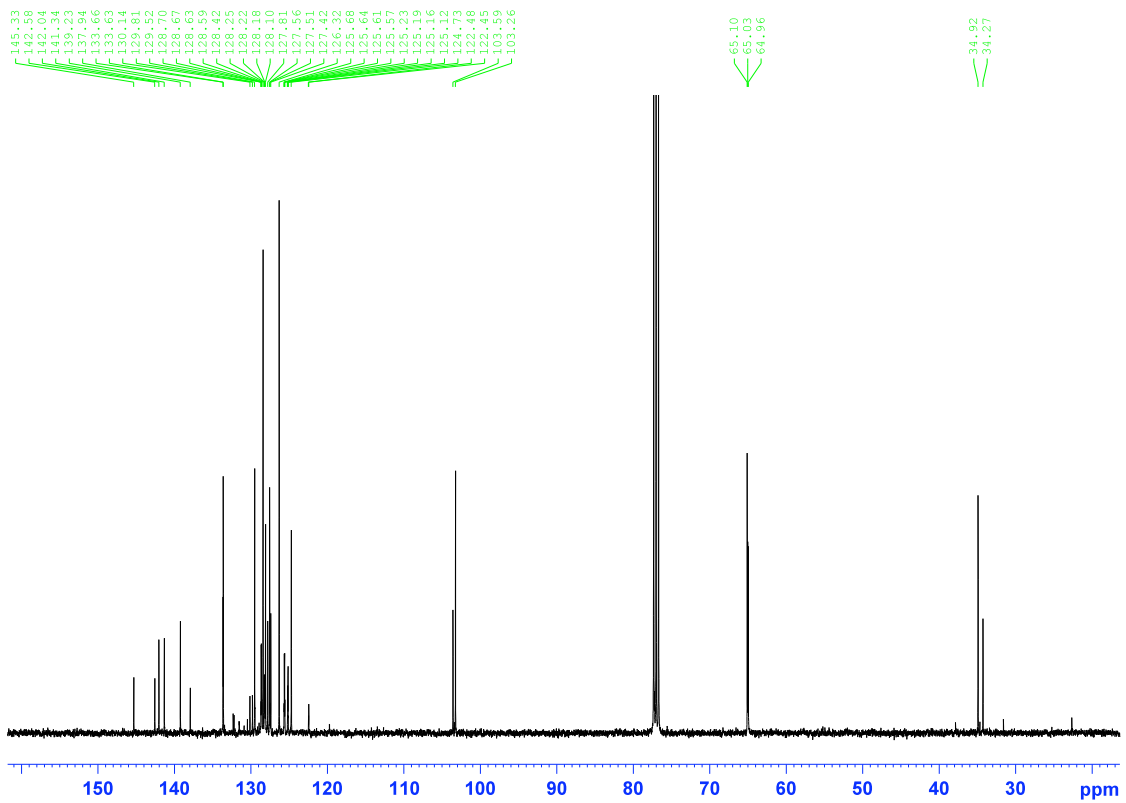
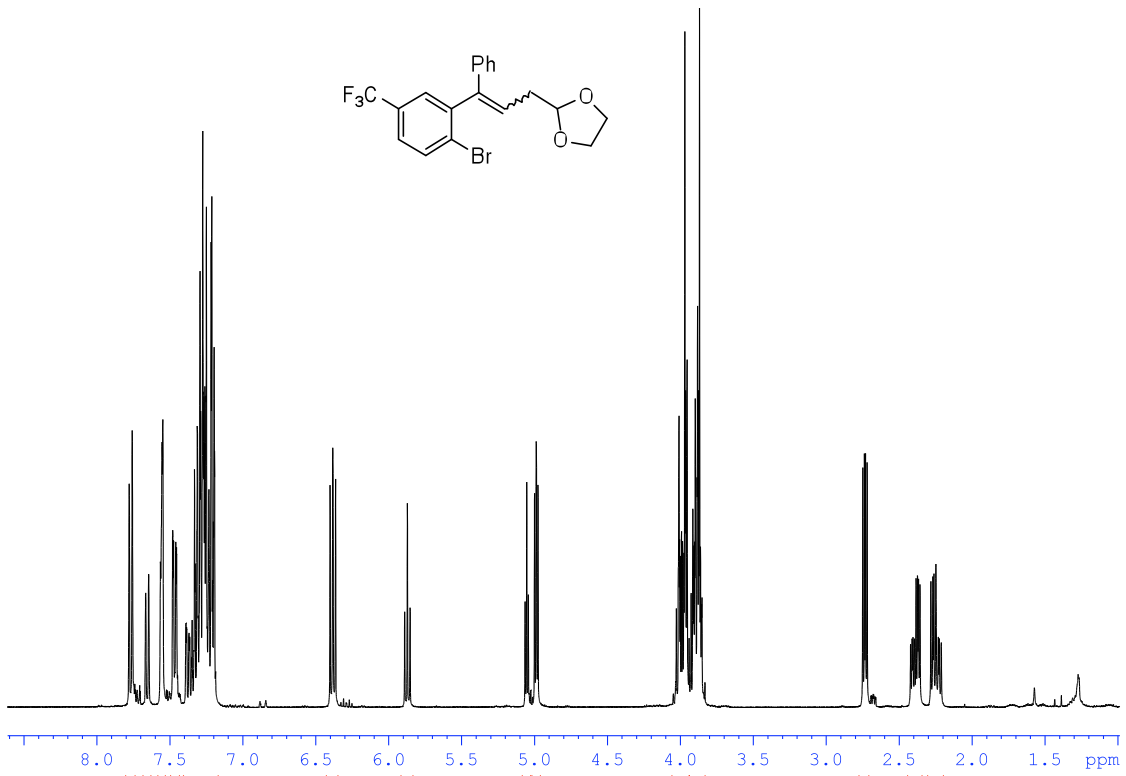
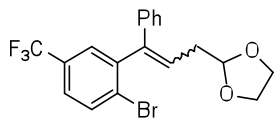
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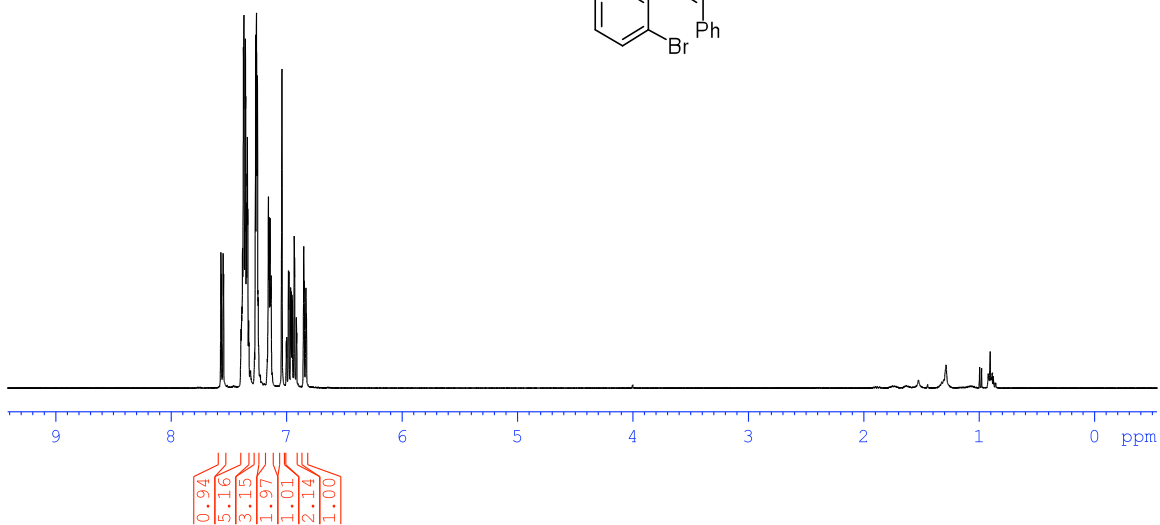
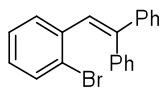


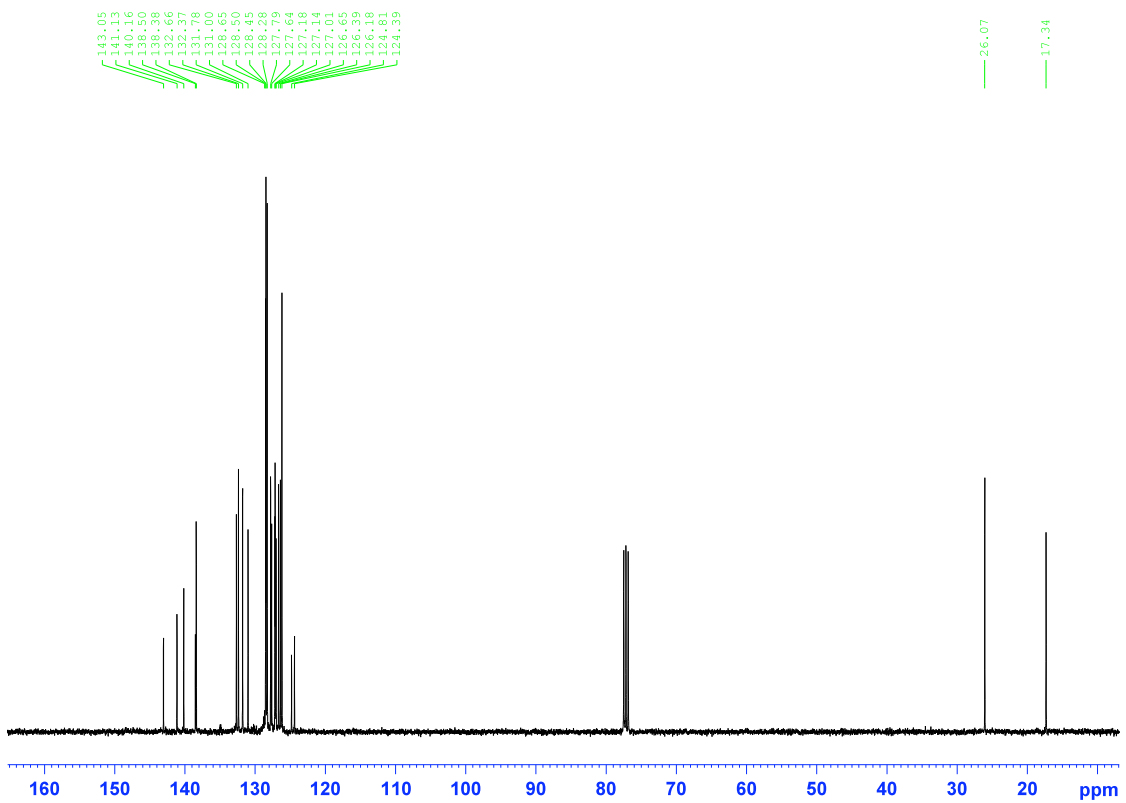
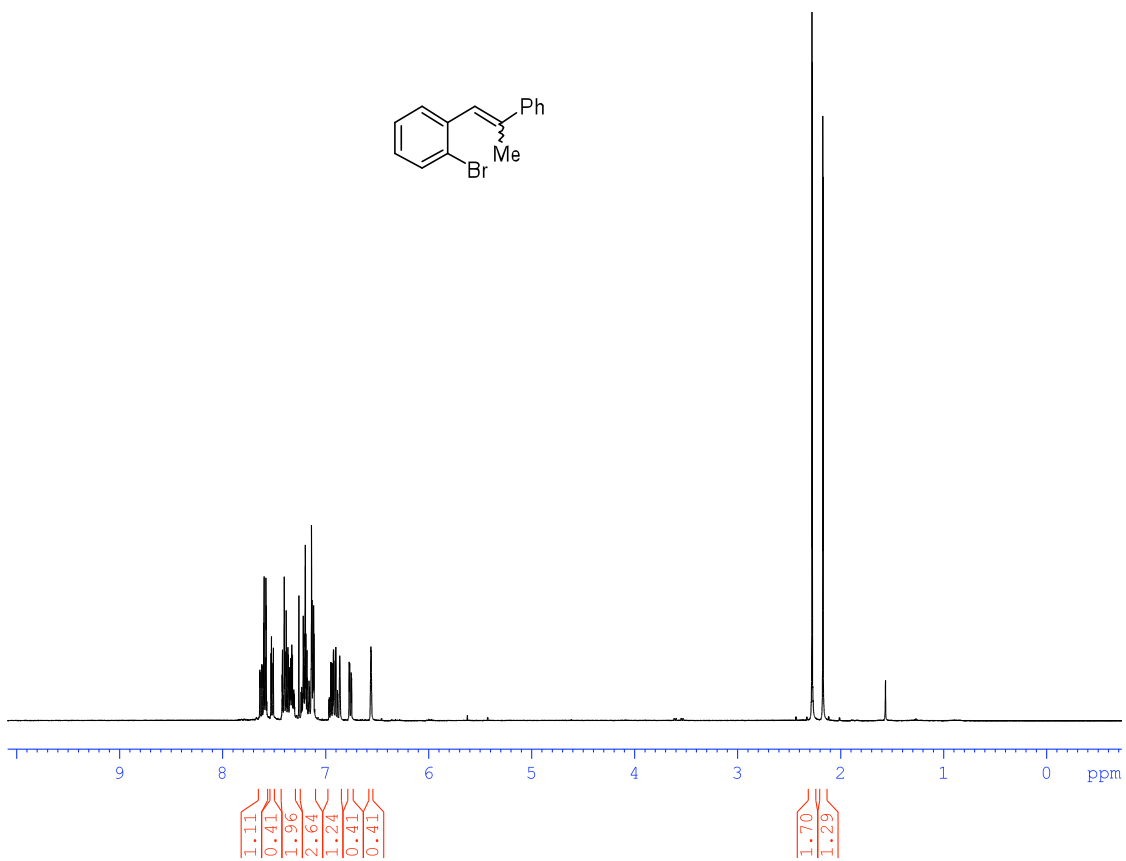
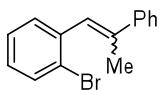




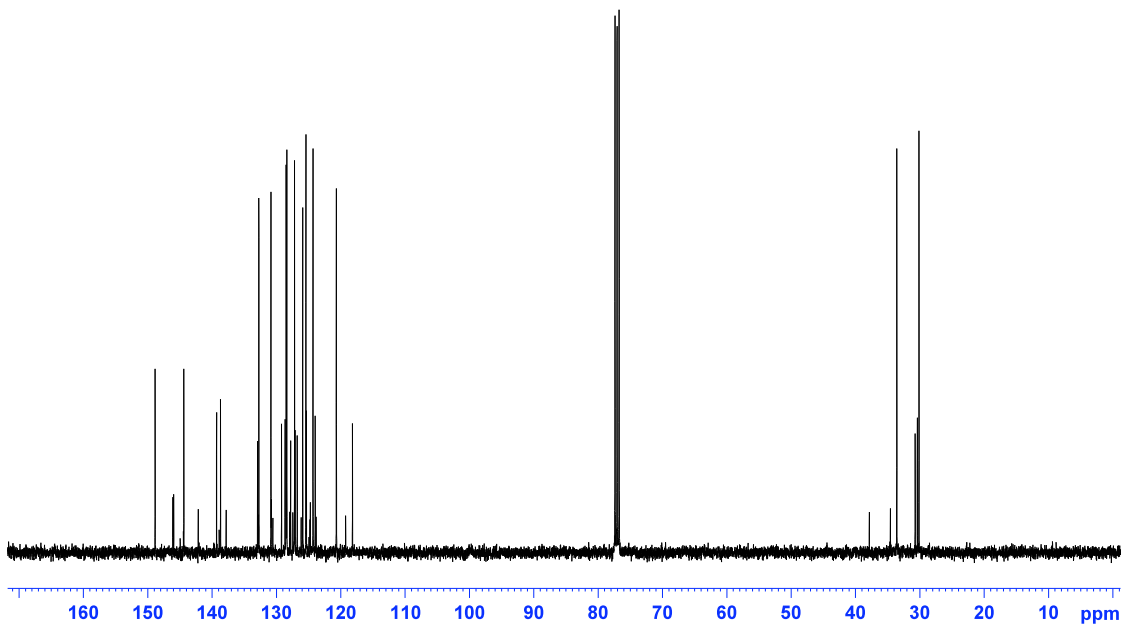
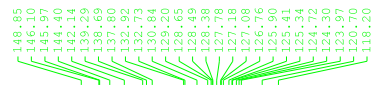
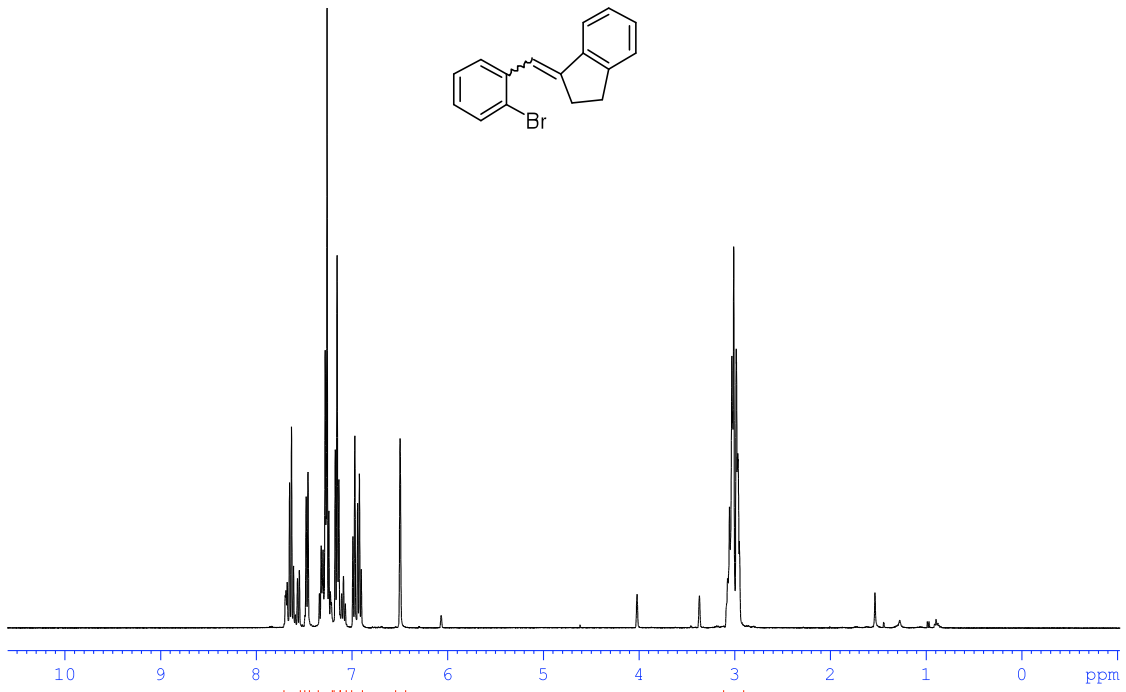
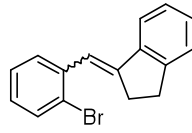


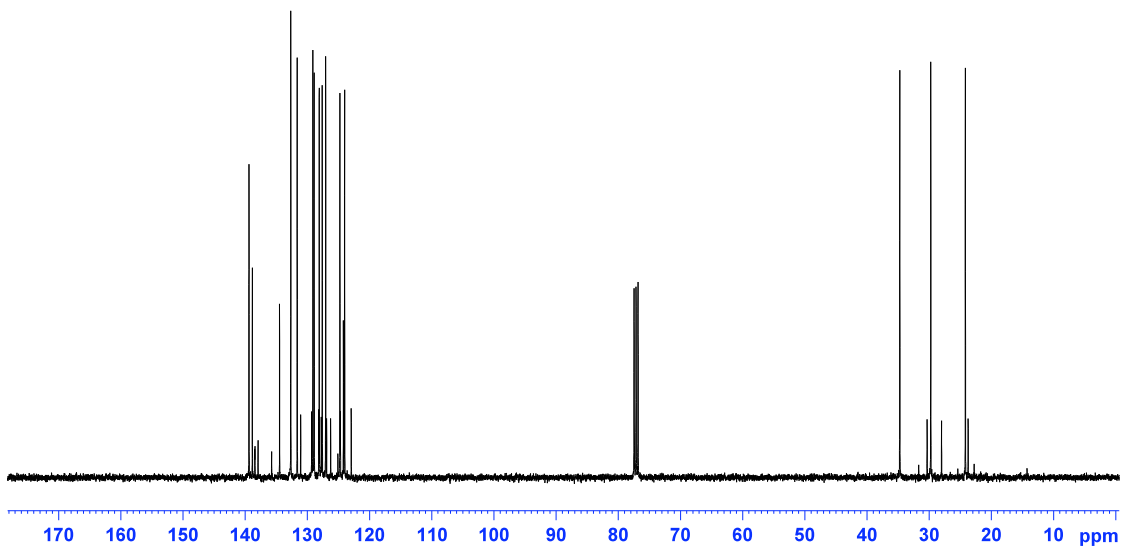
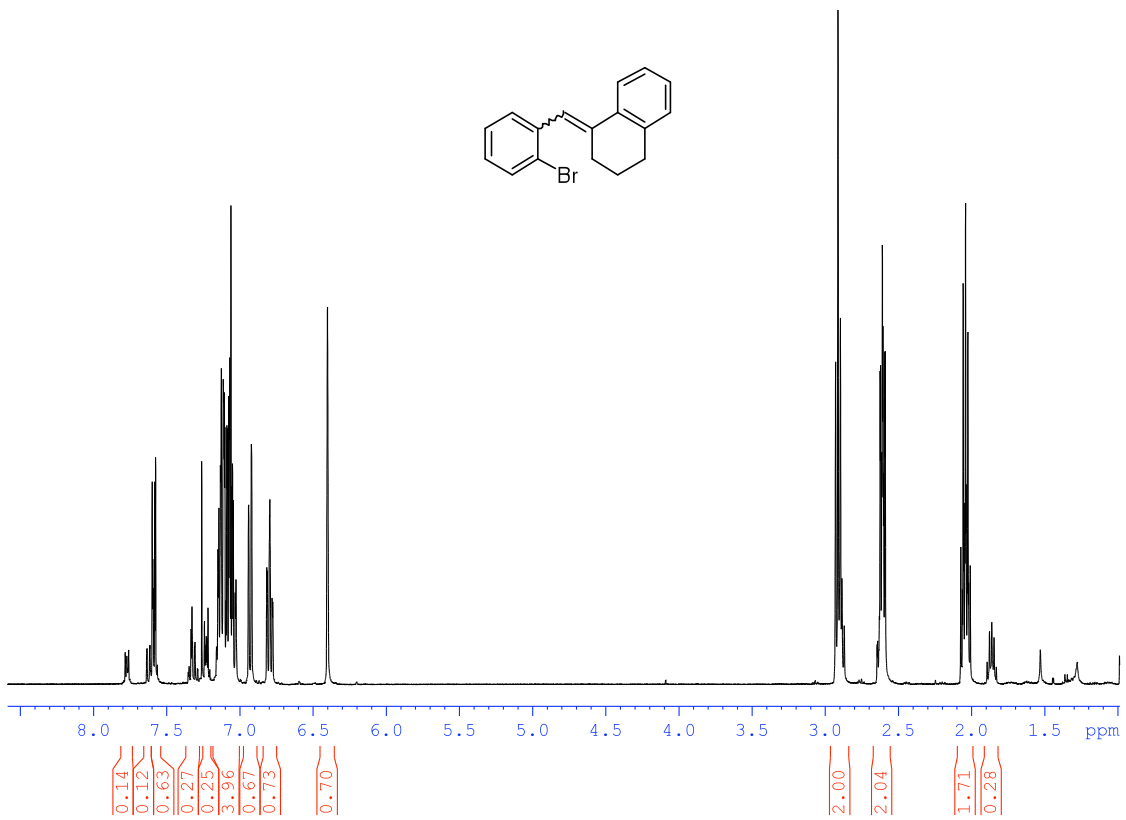
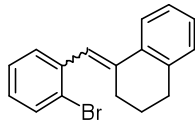


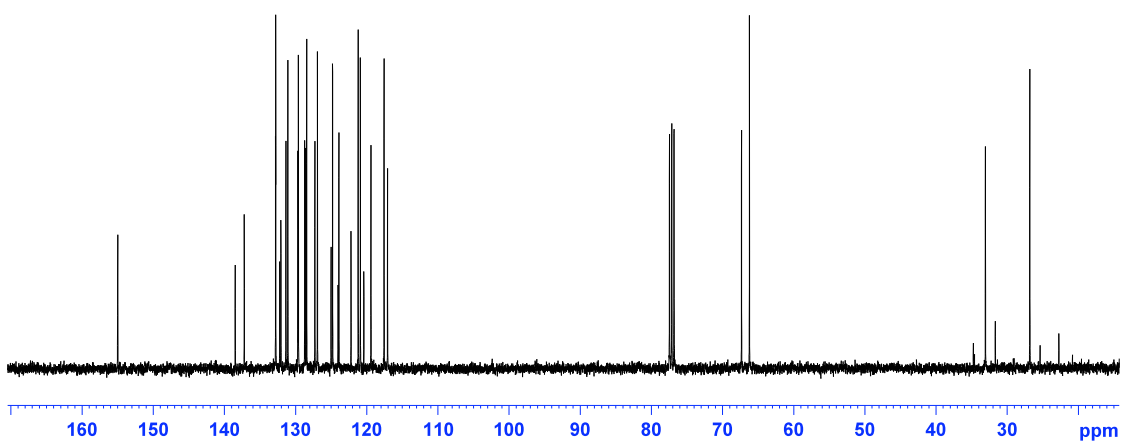
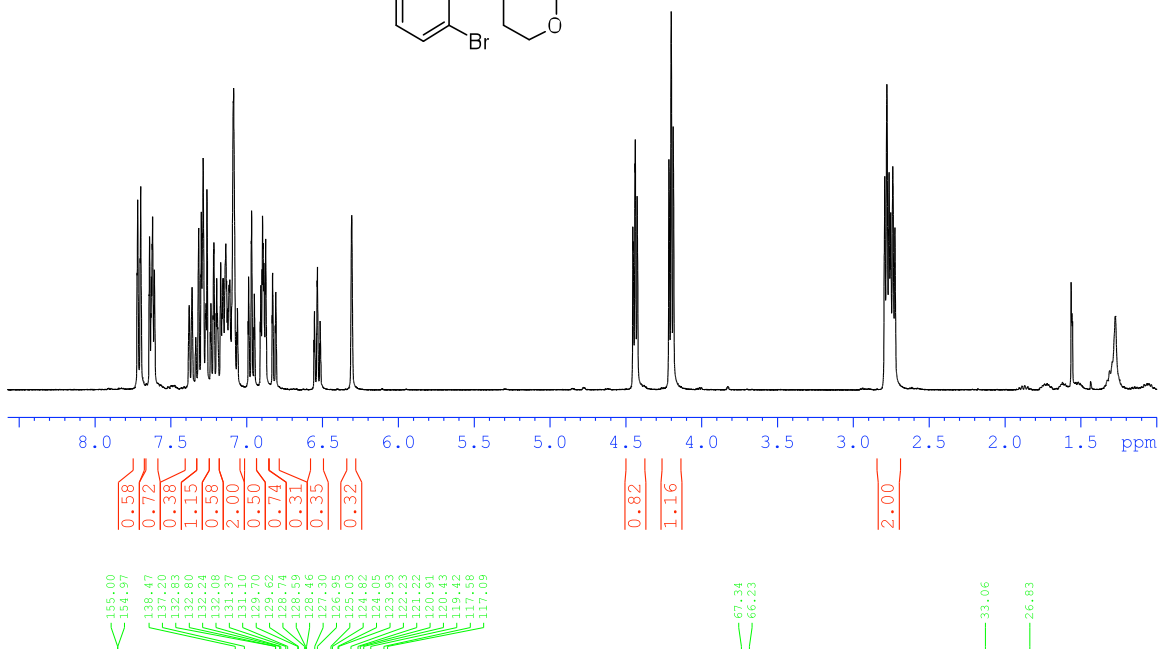
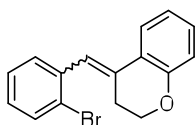


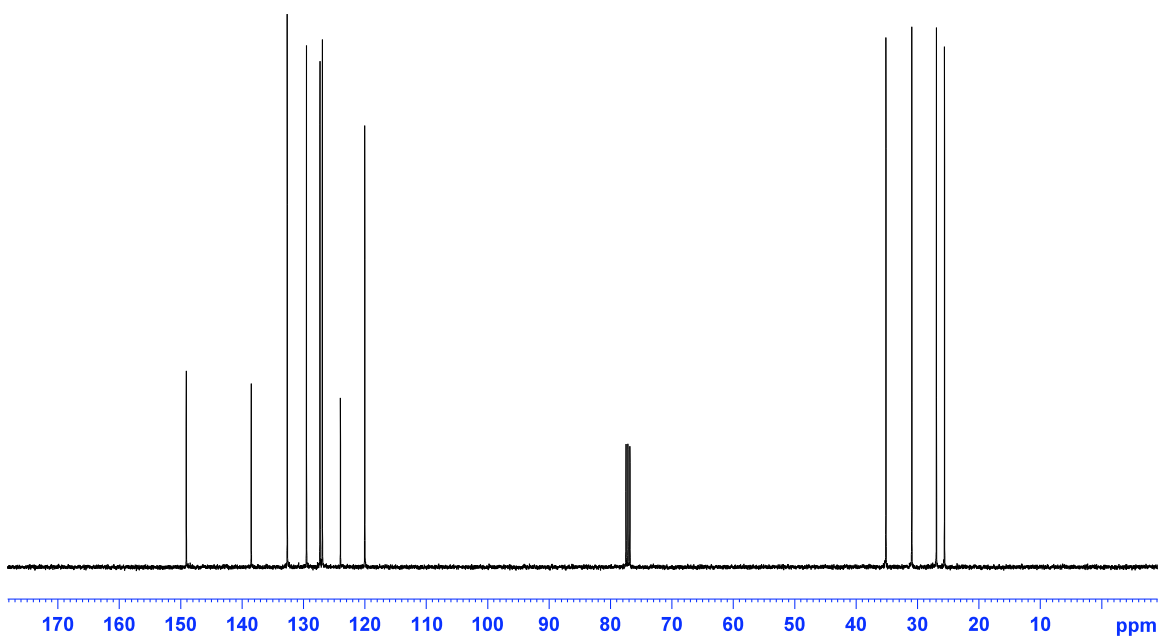
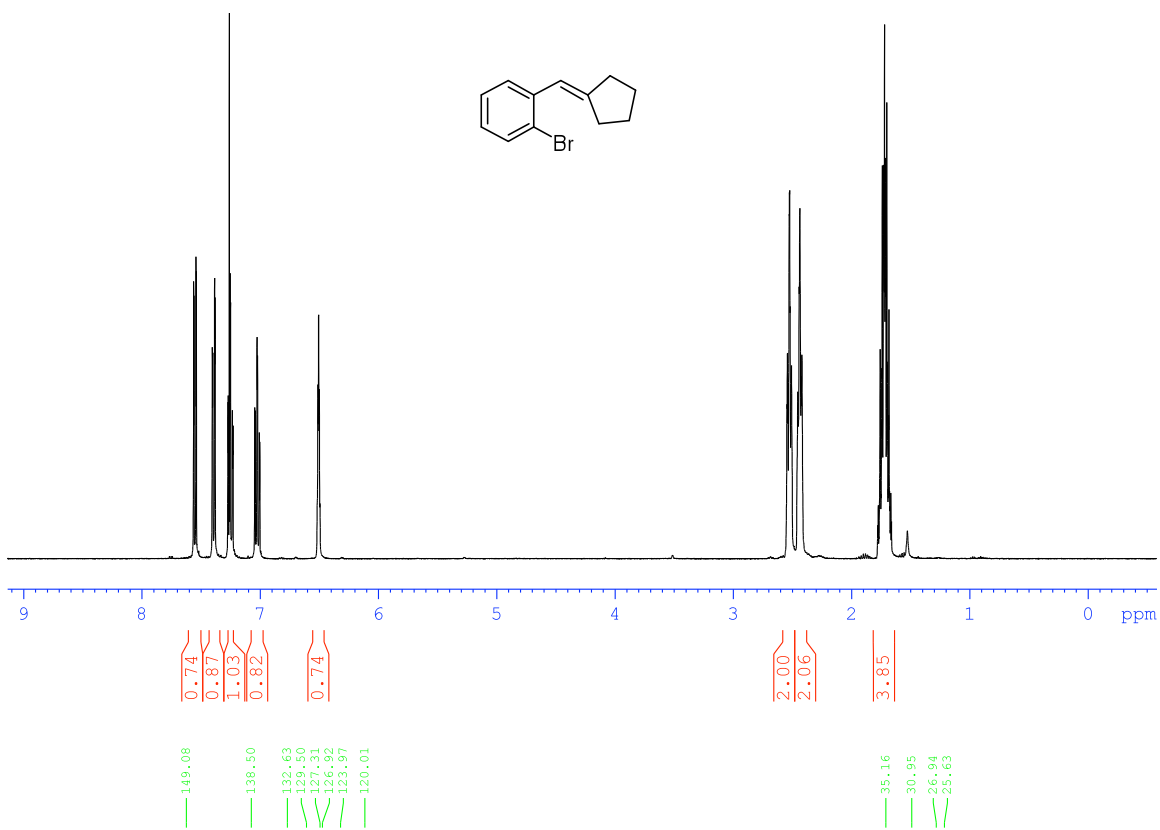
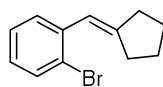


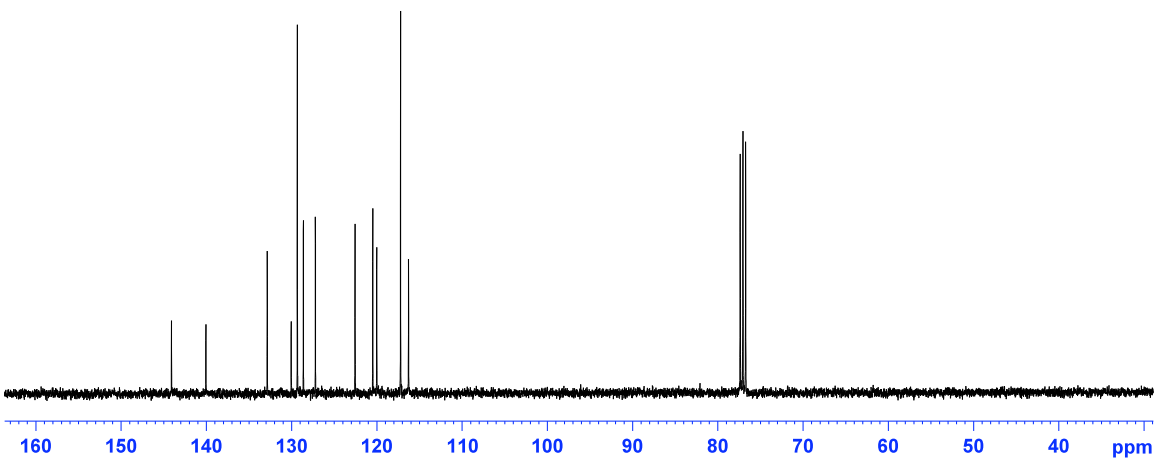
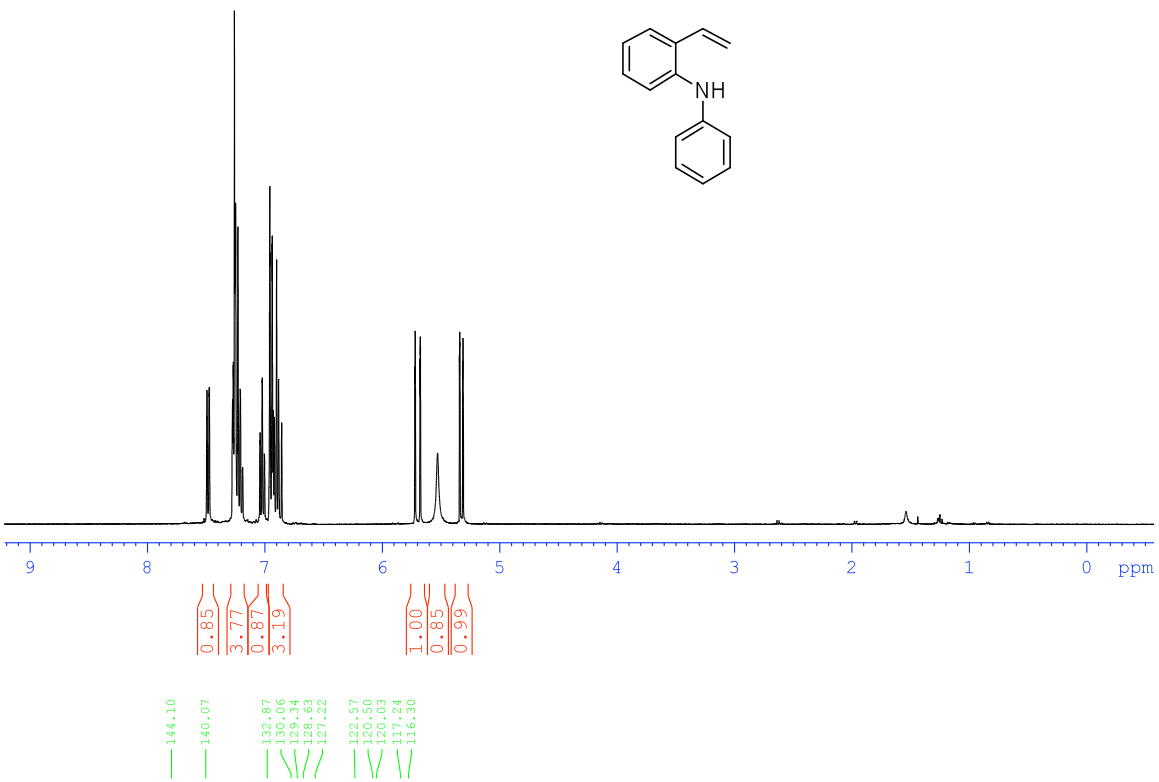
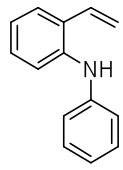


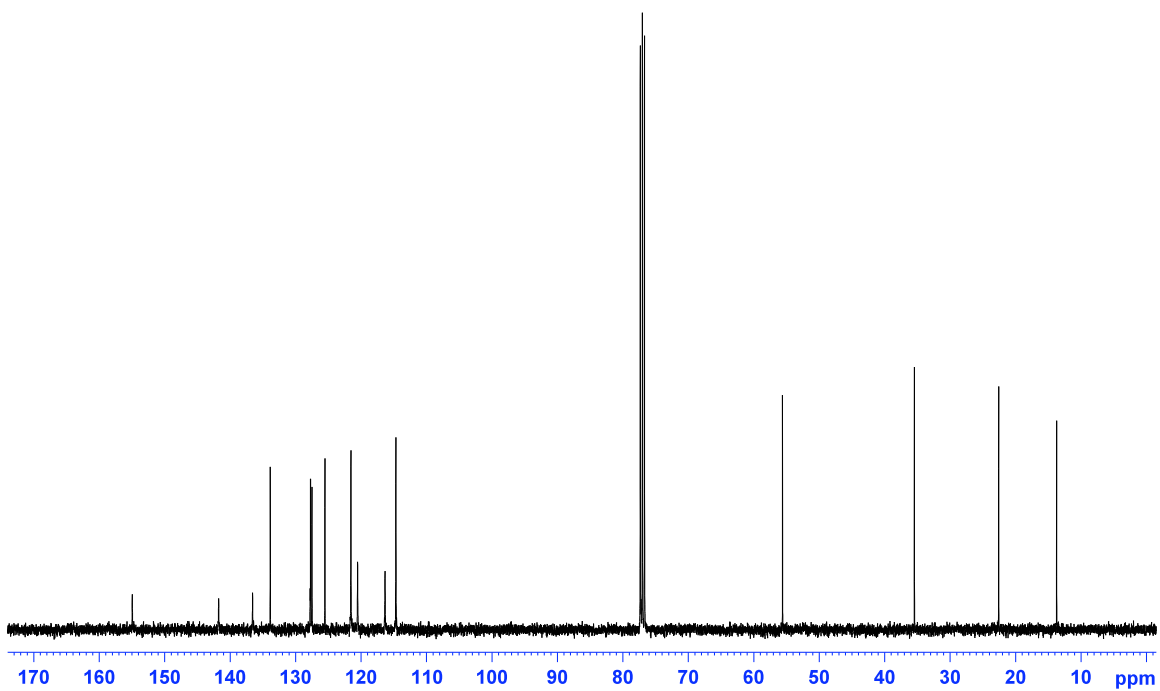
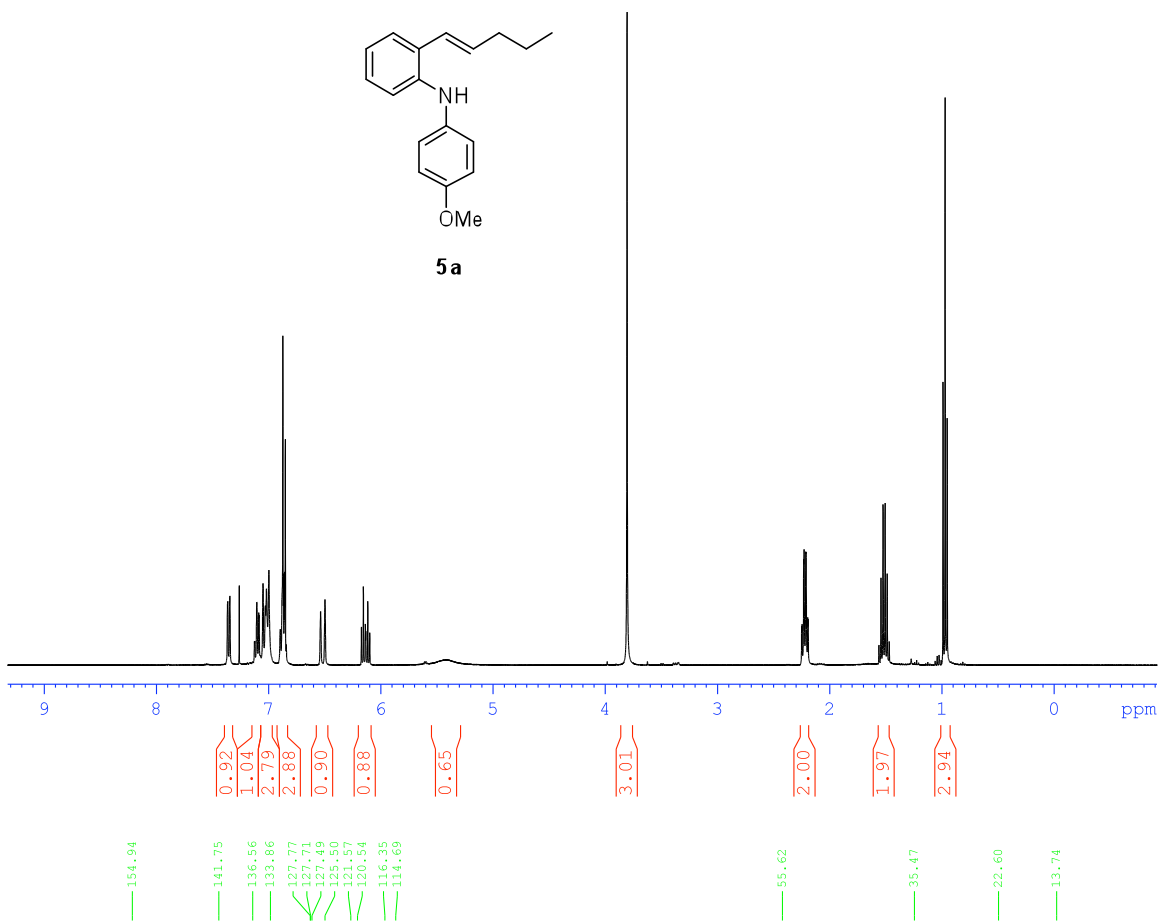
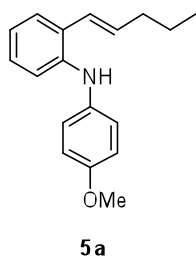


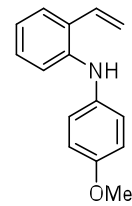




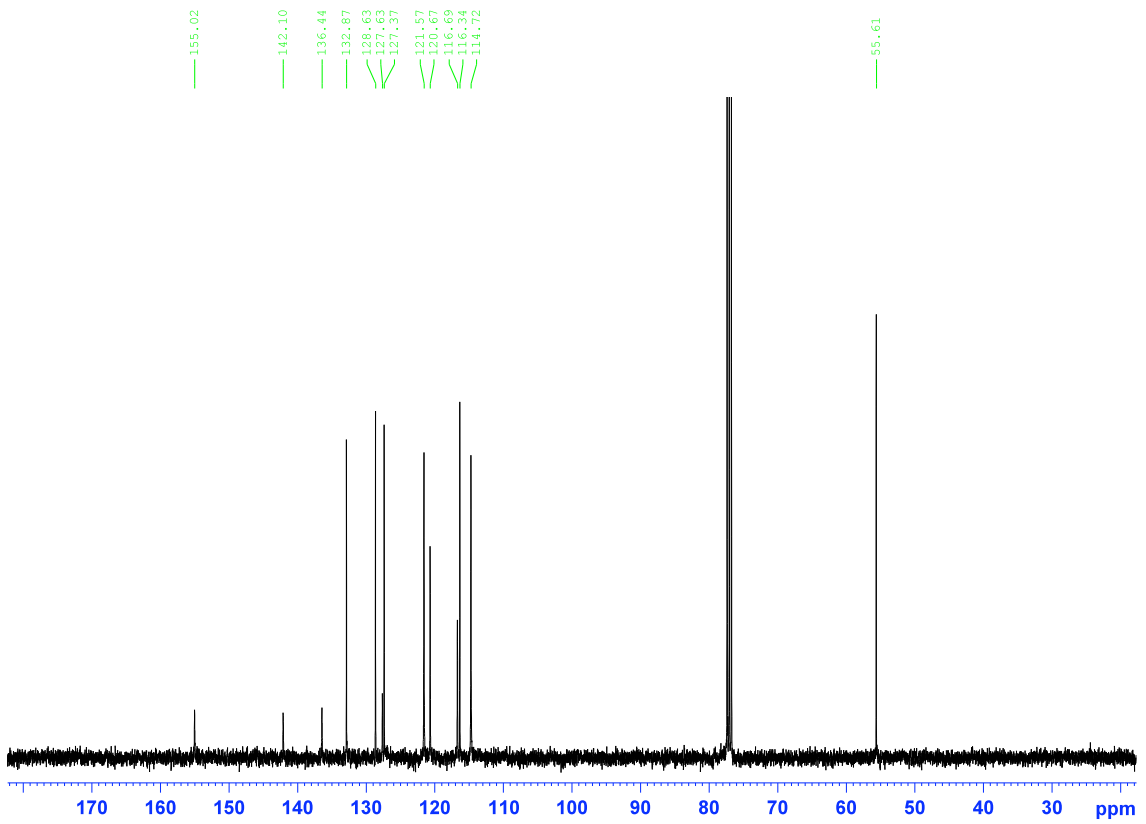
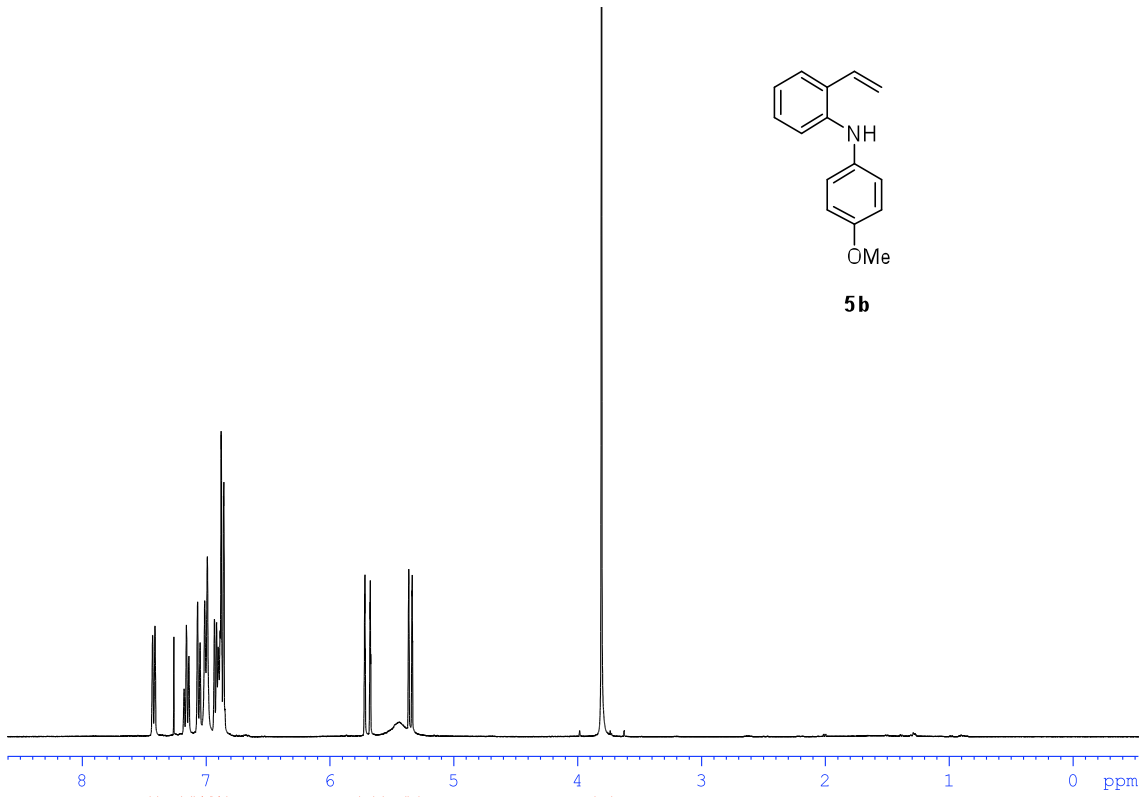






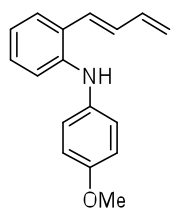


**5b**

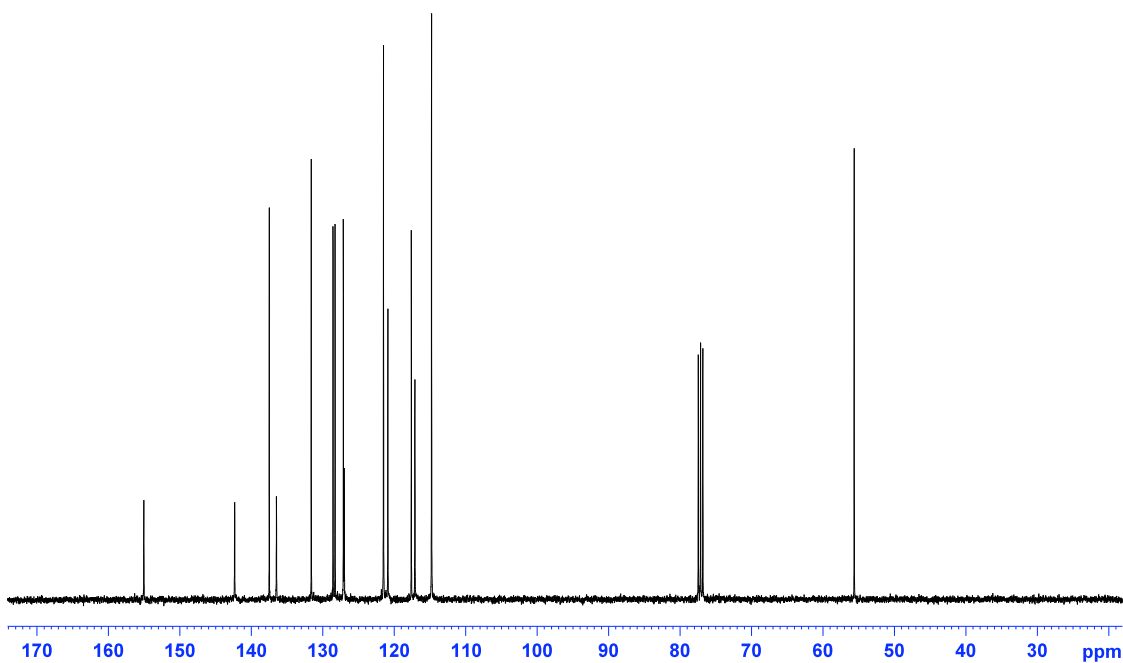
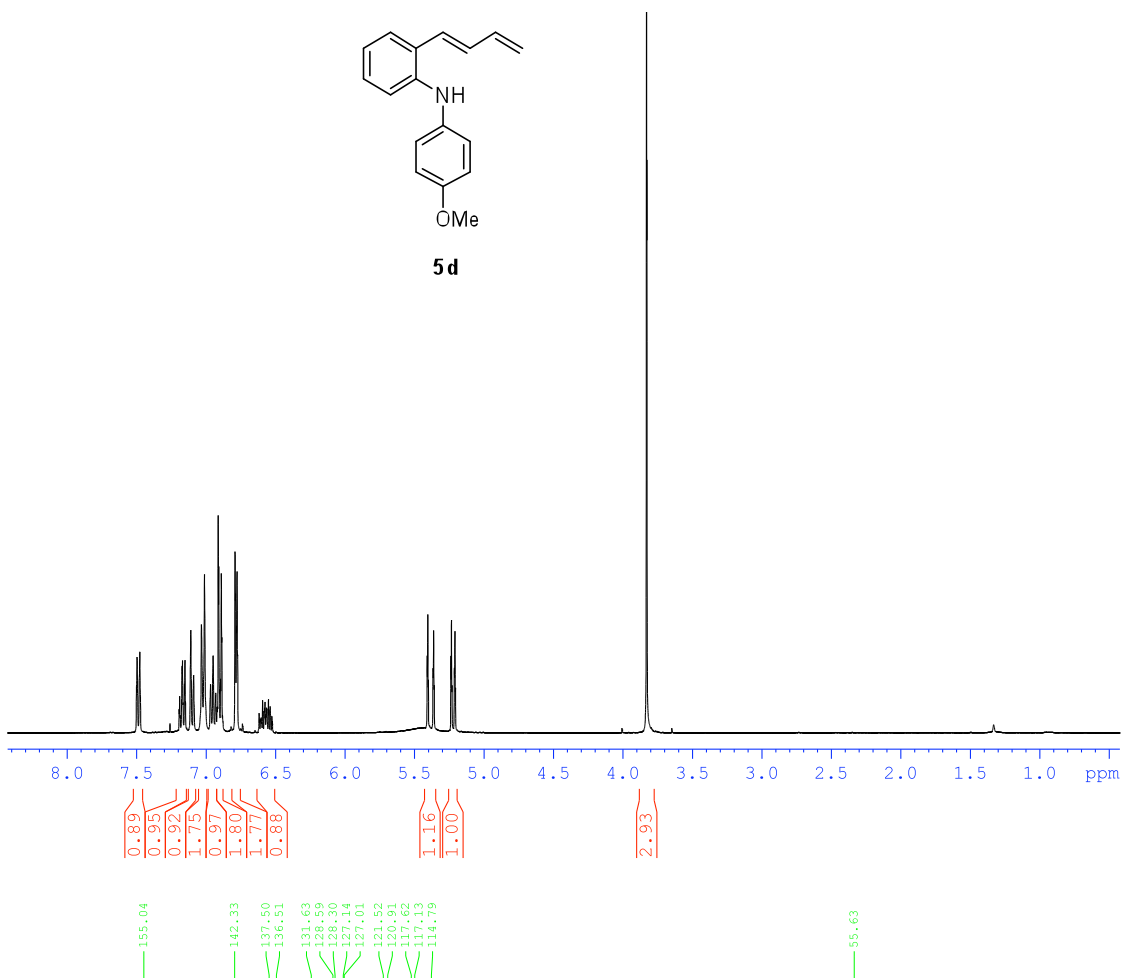


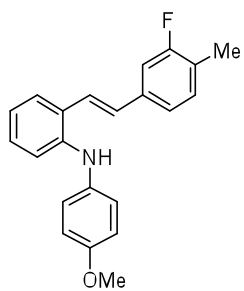




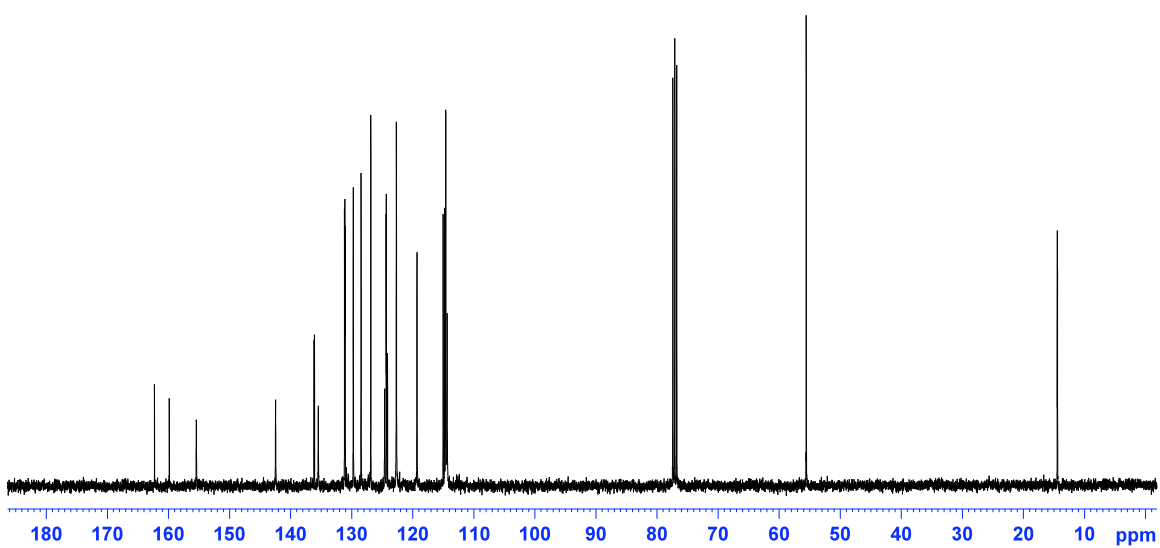
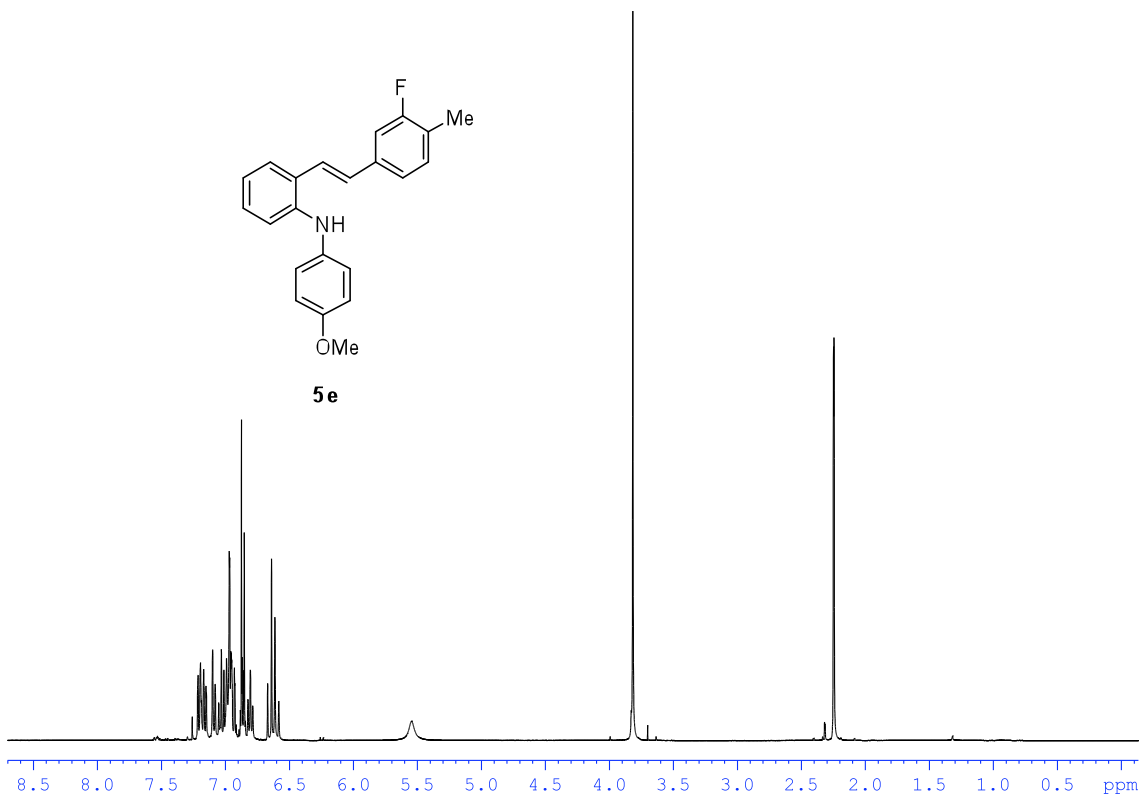


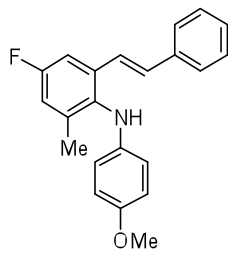
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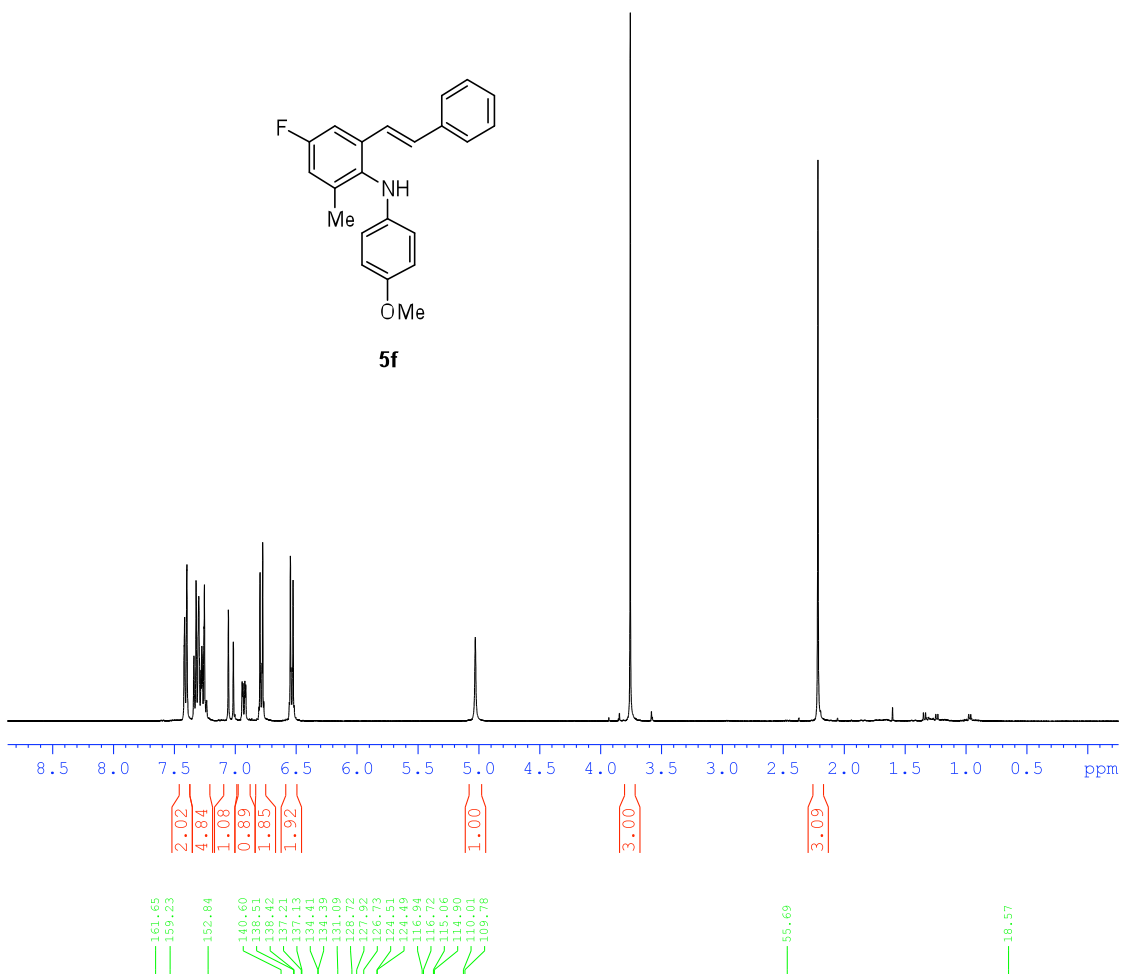


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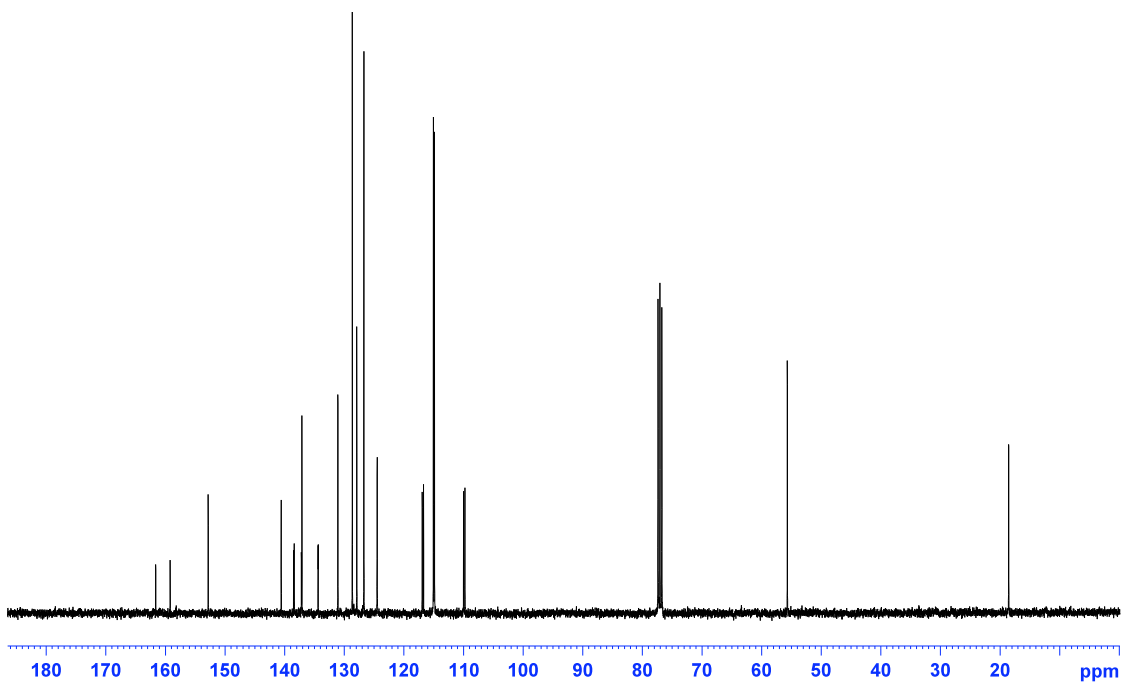


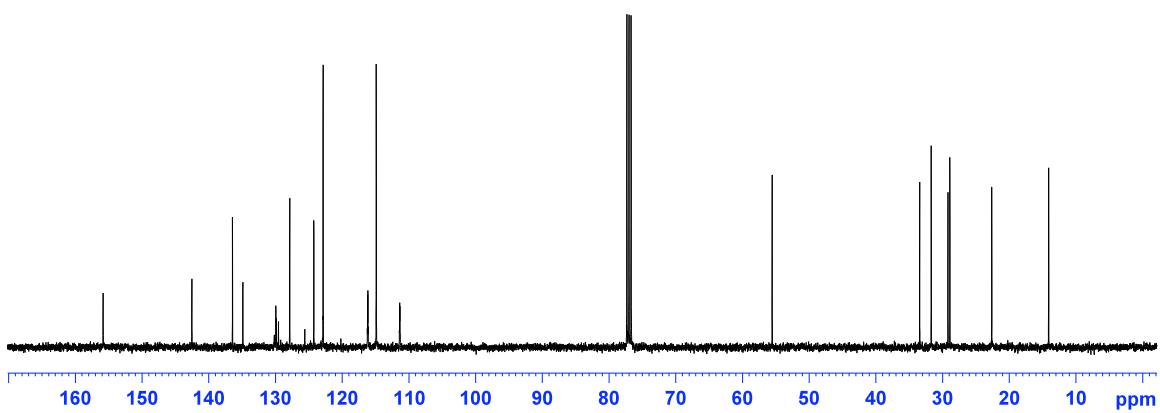
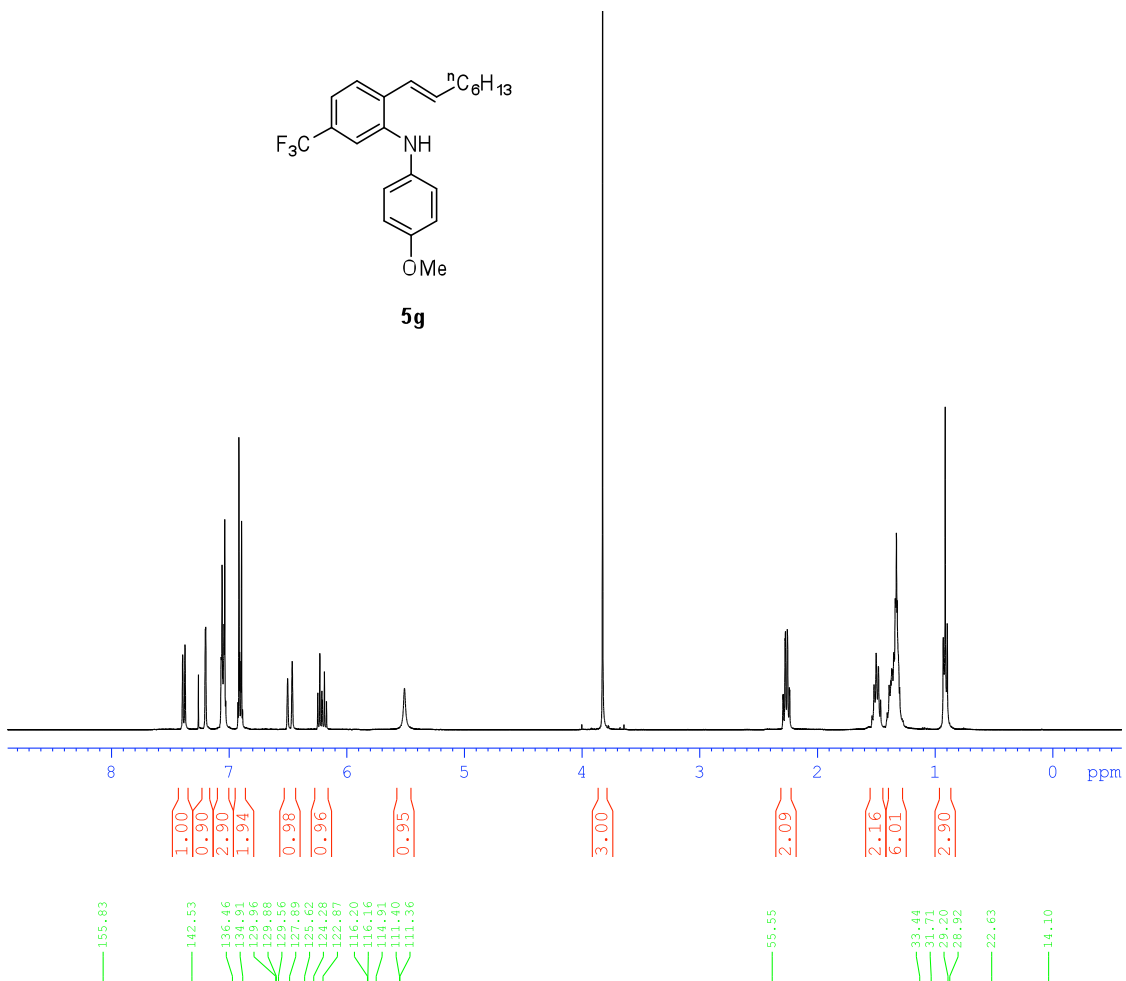
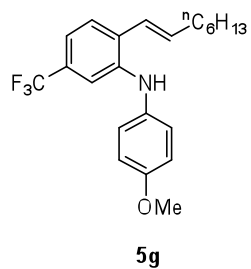


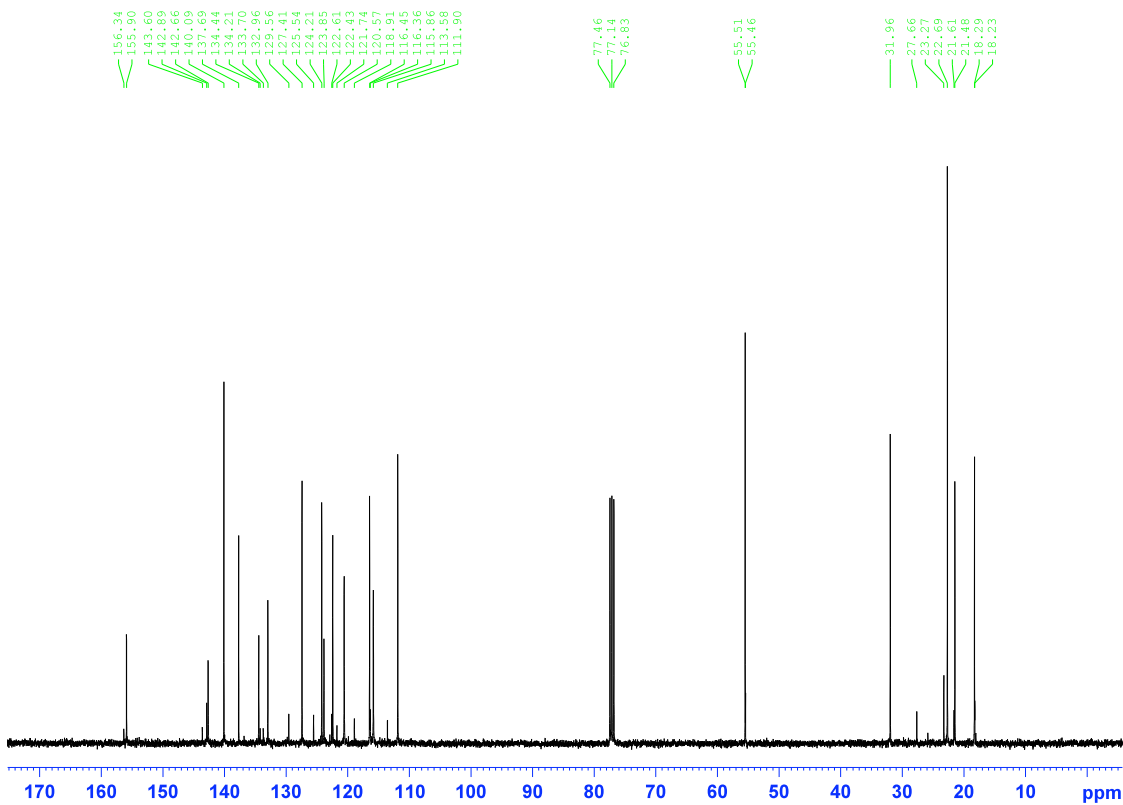
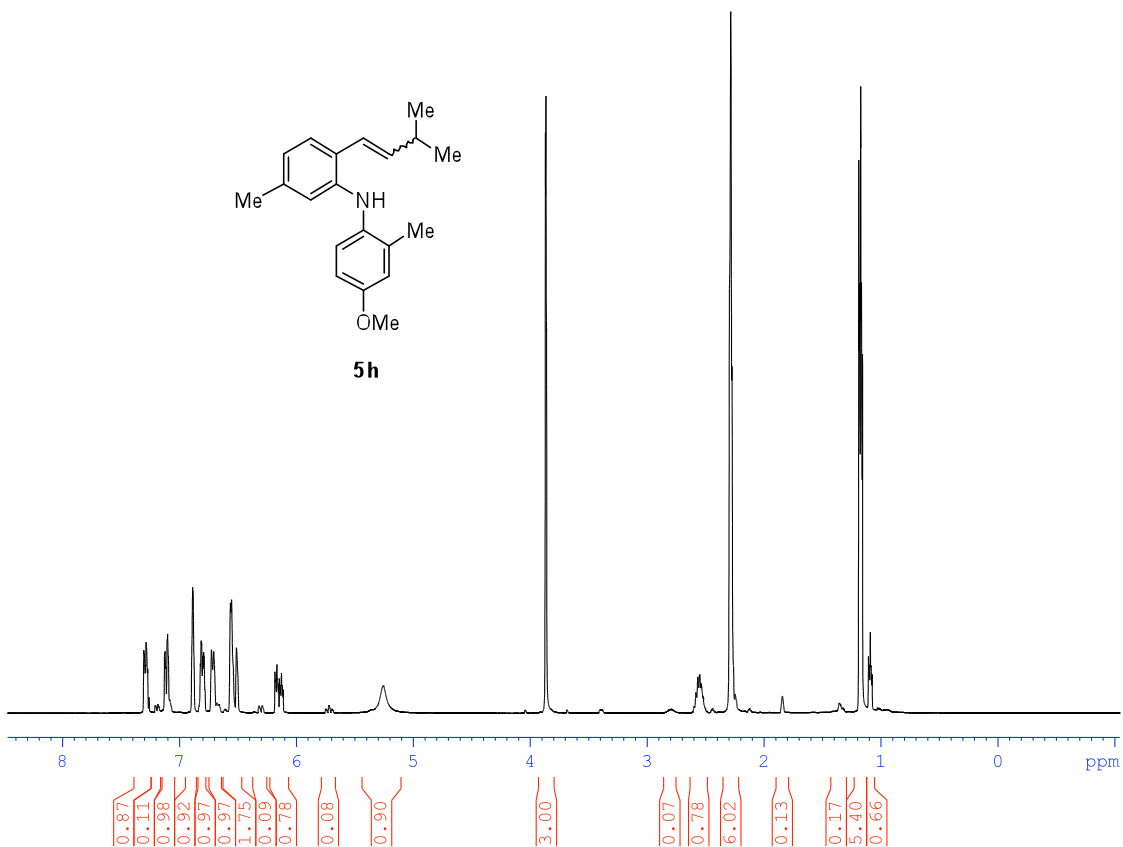
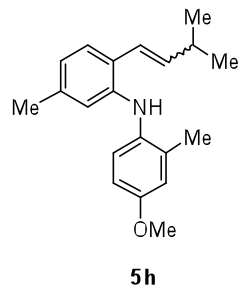
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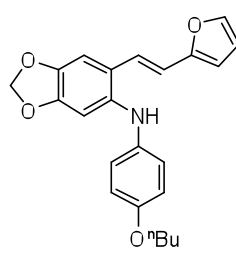


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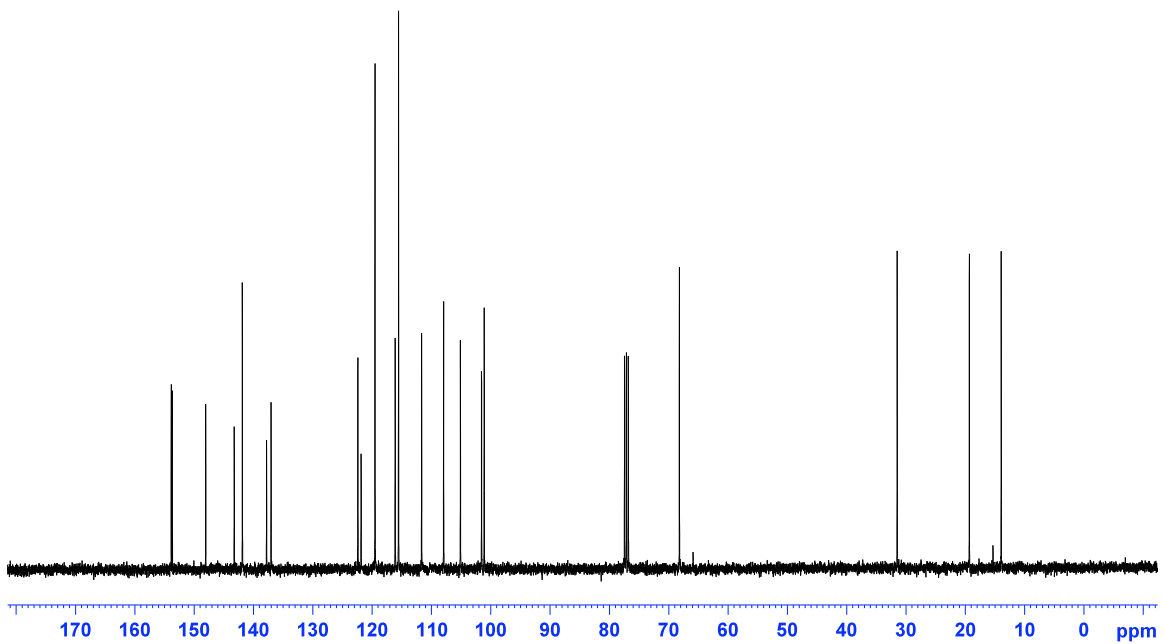
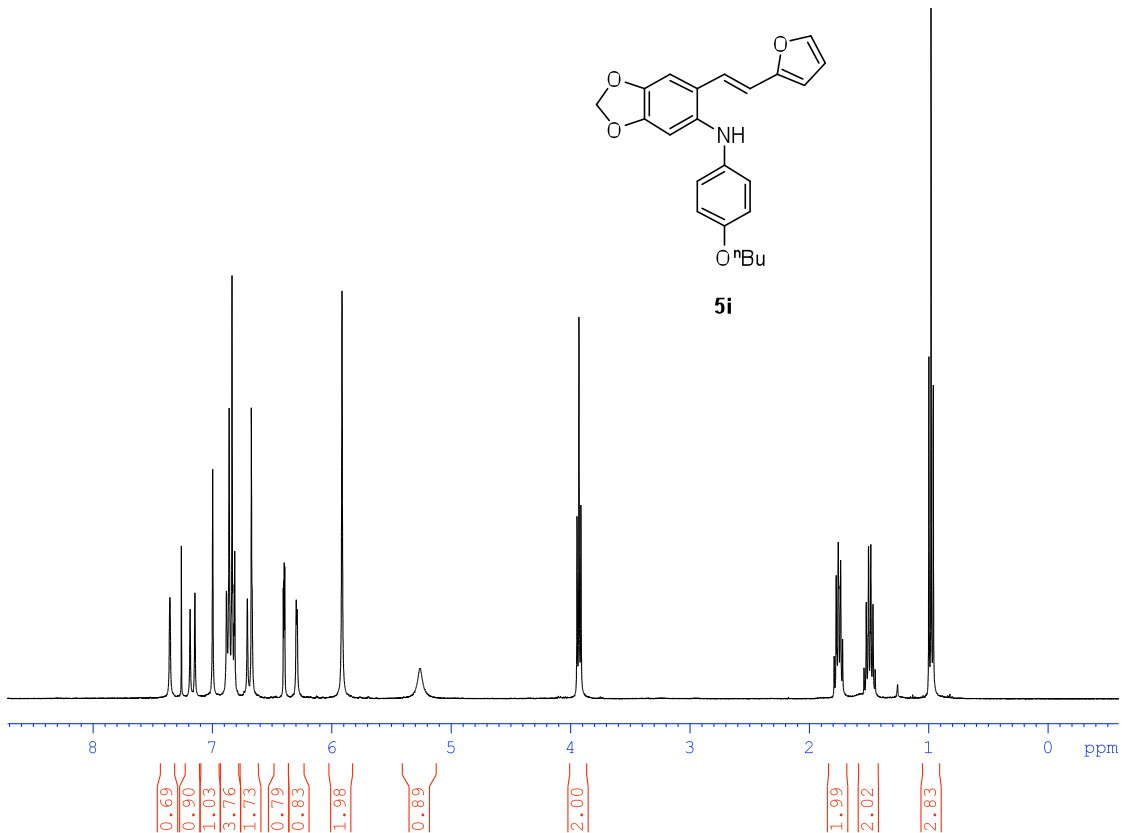


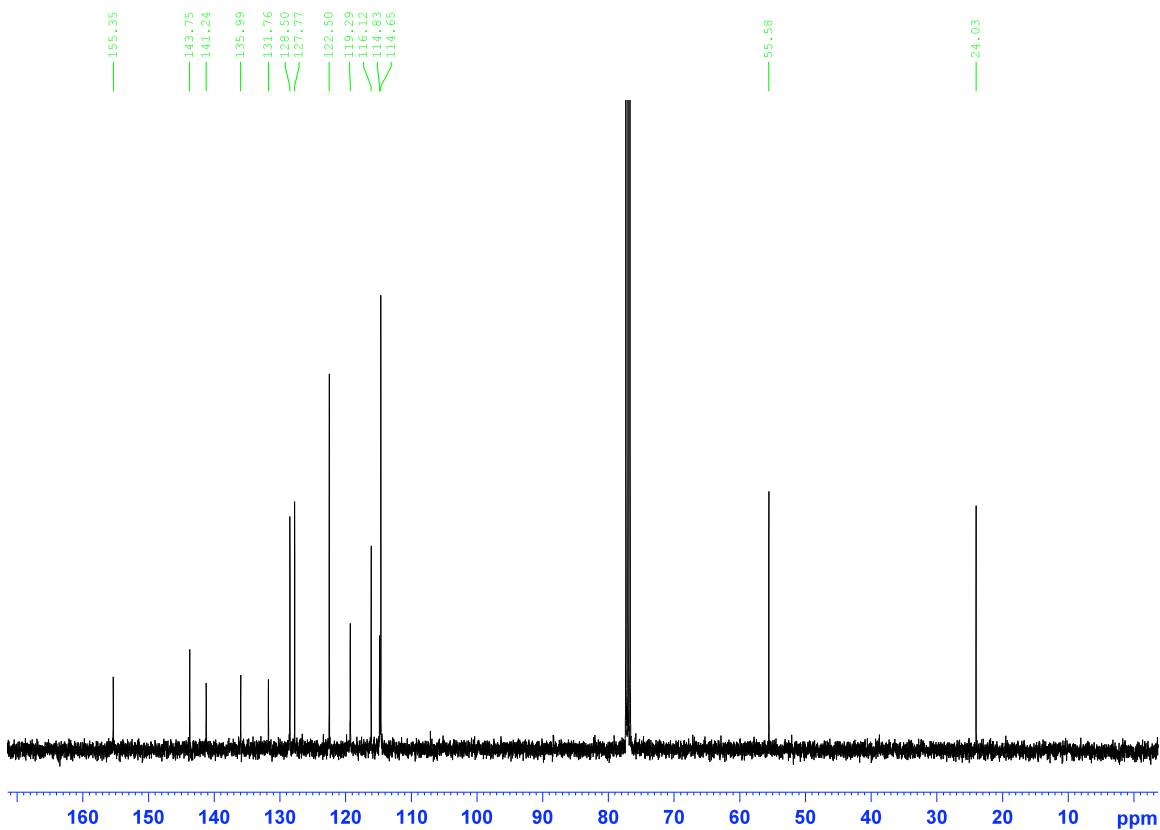
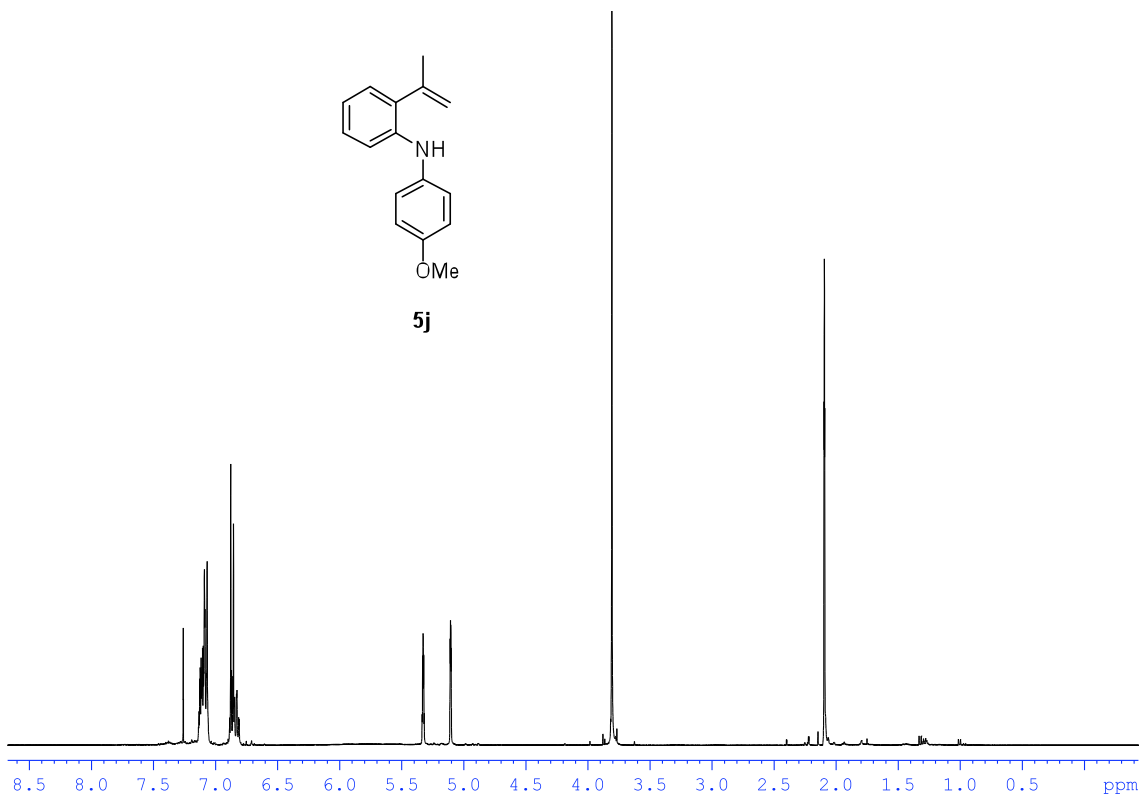
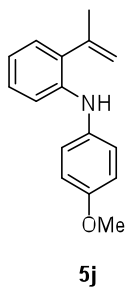


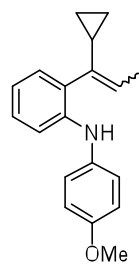




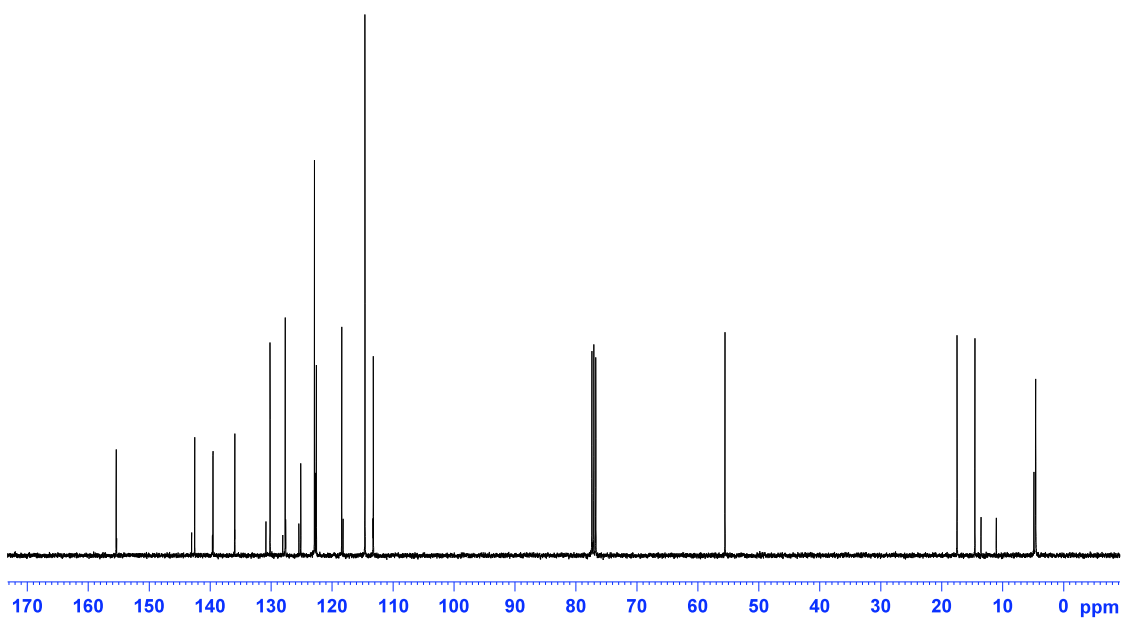
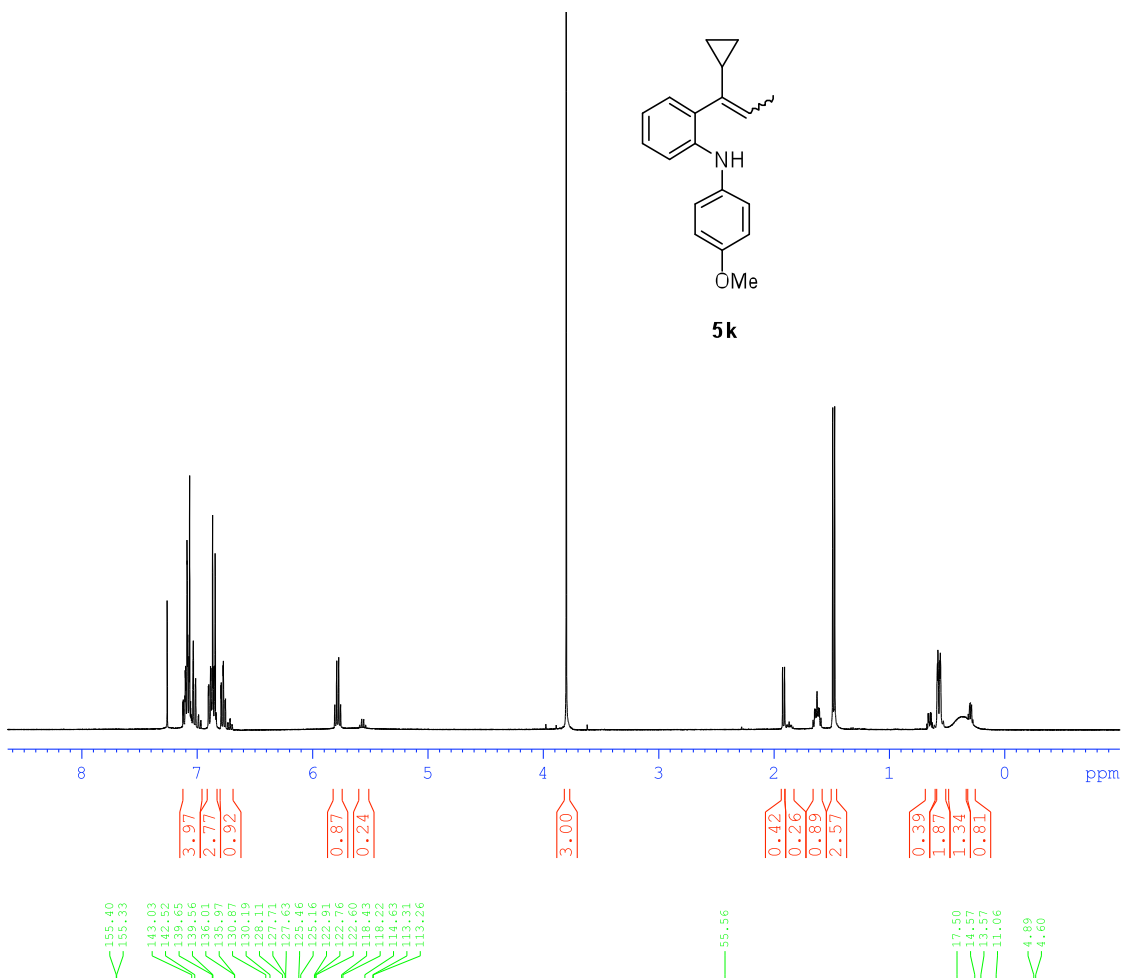
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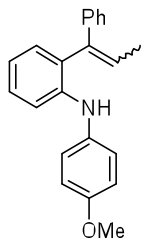




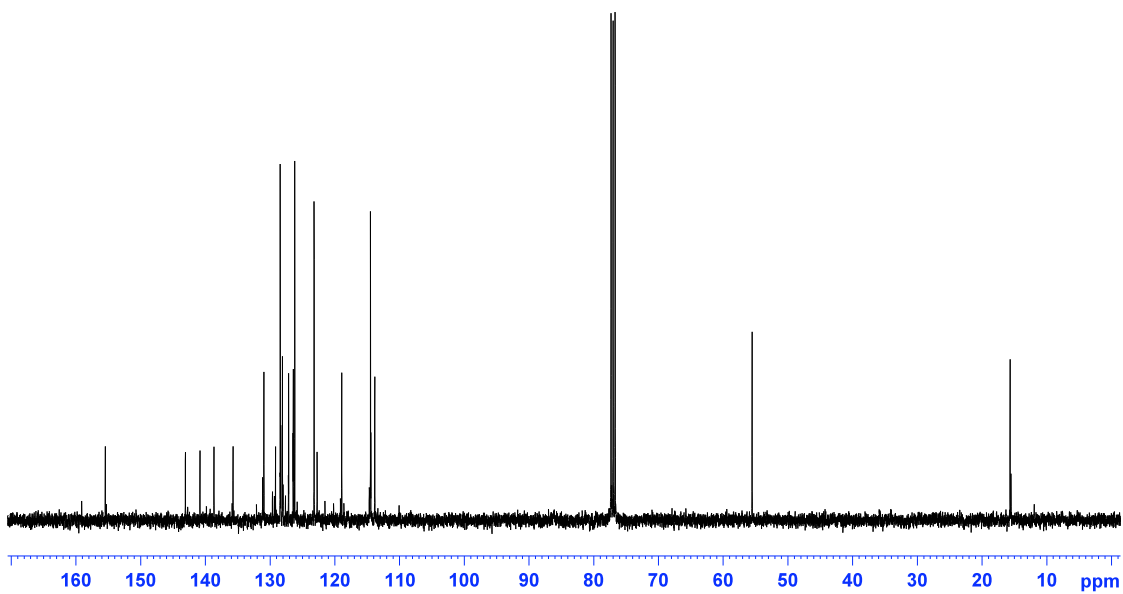
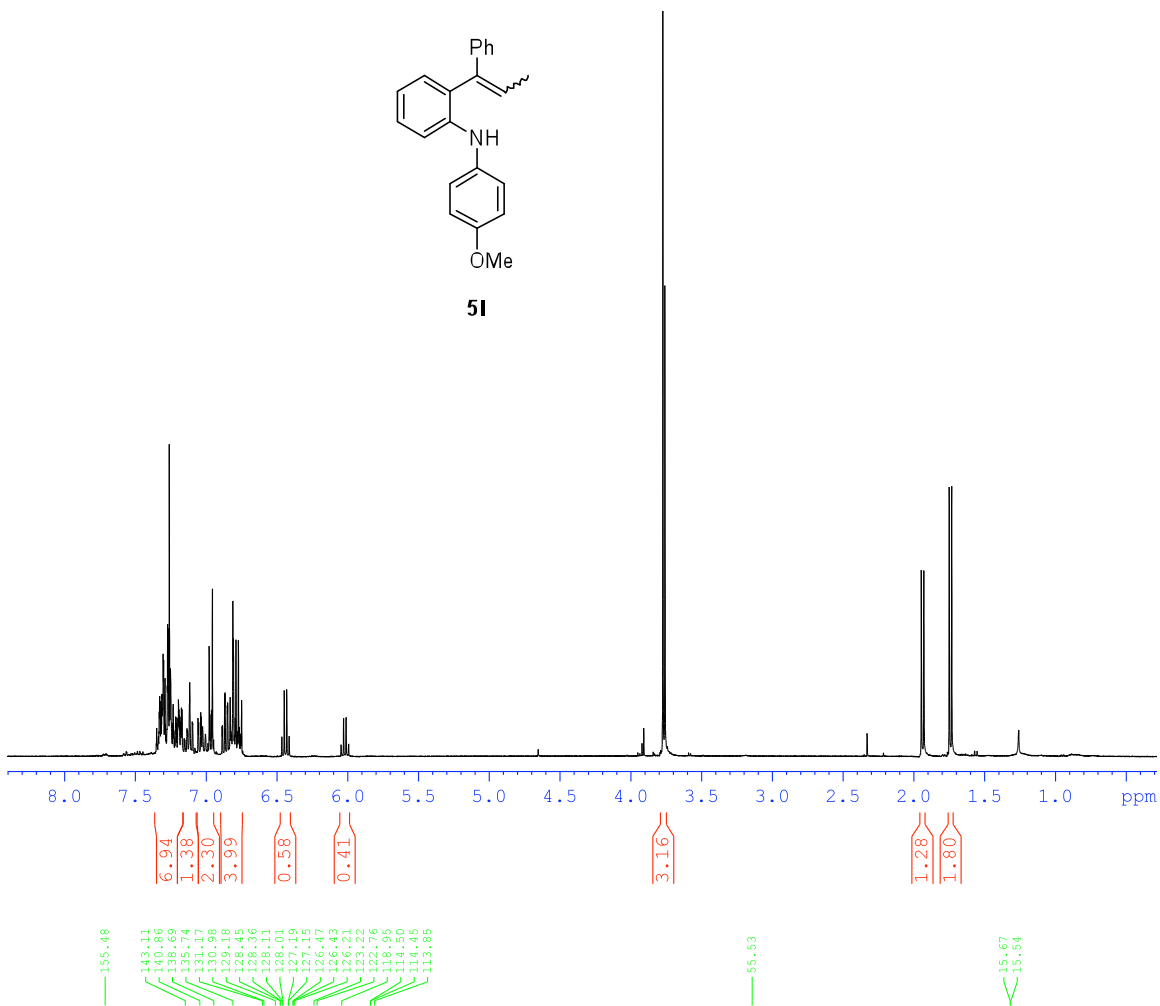
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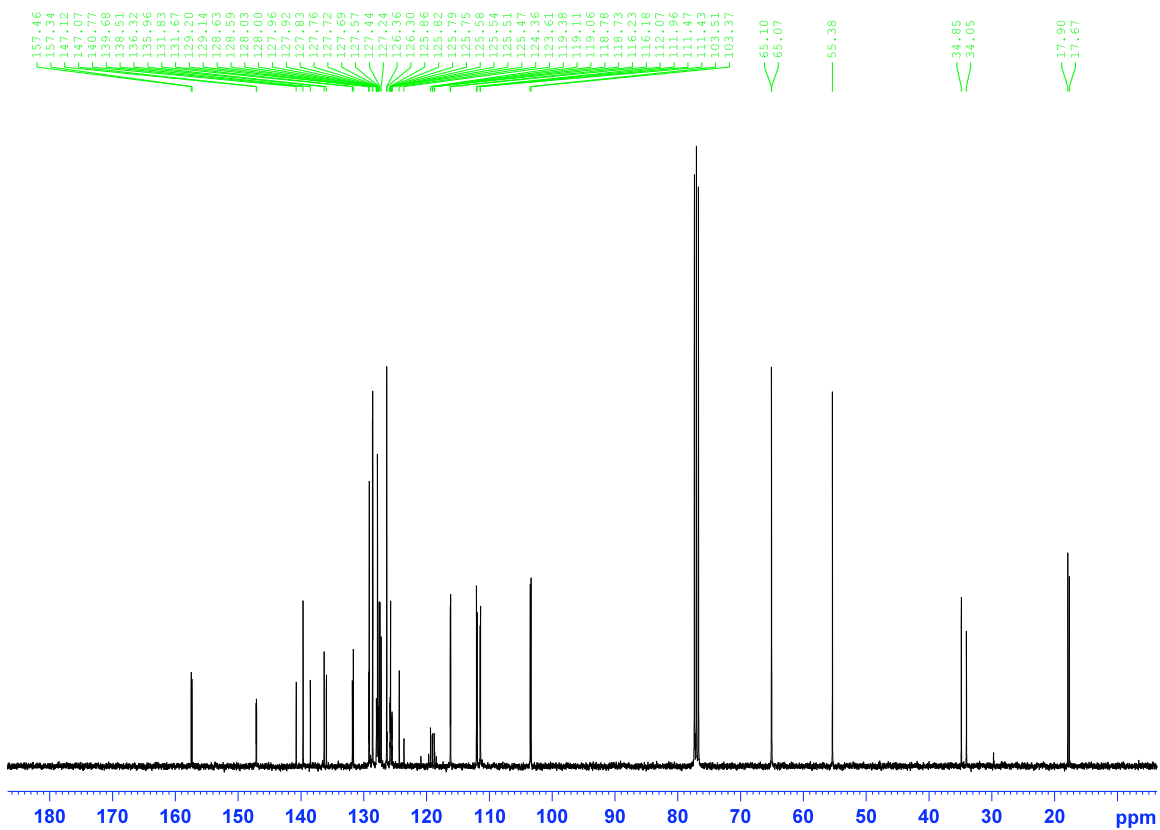
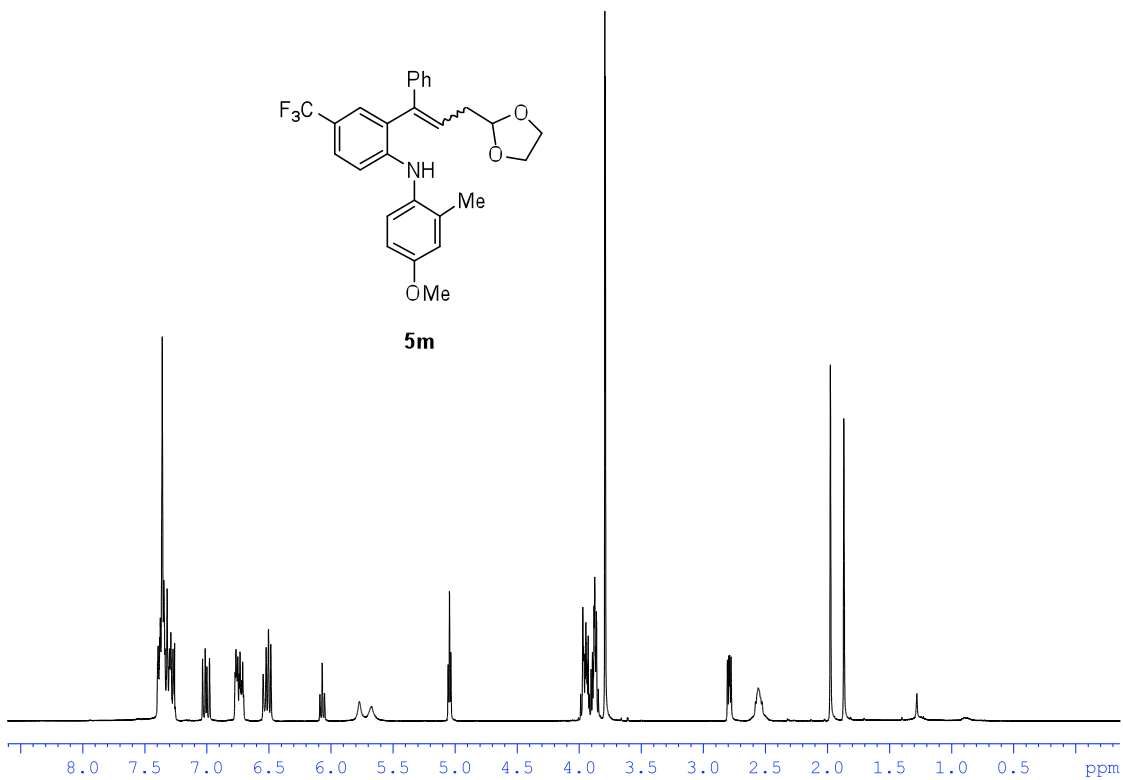
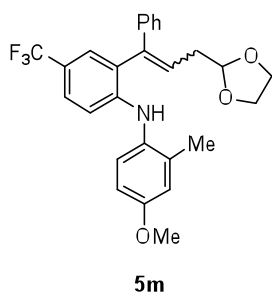


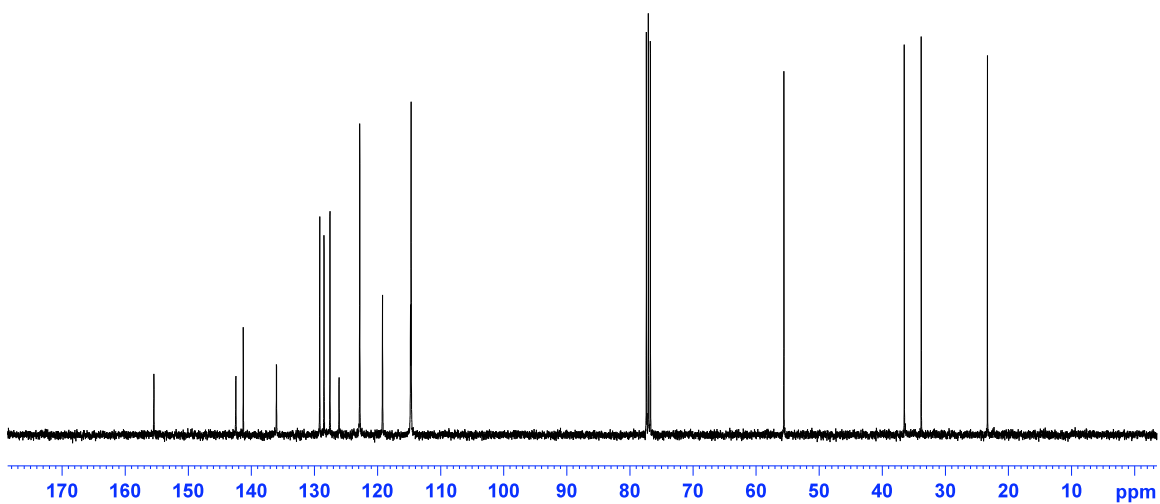
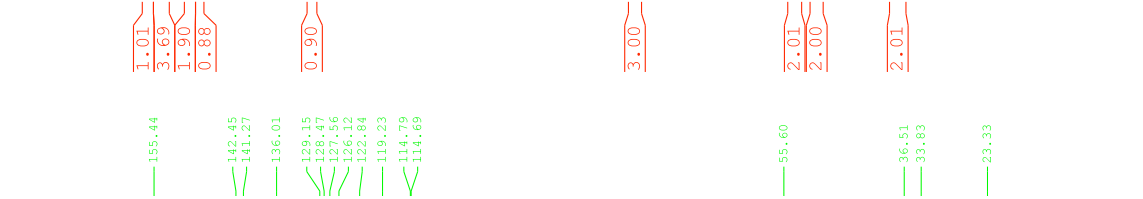
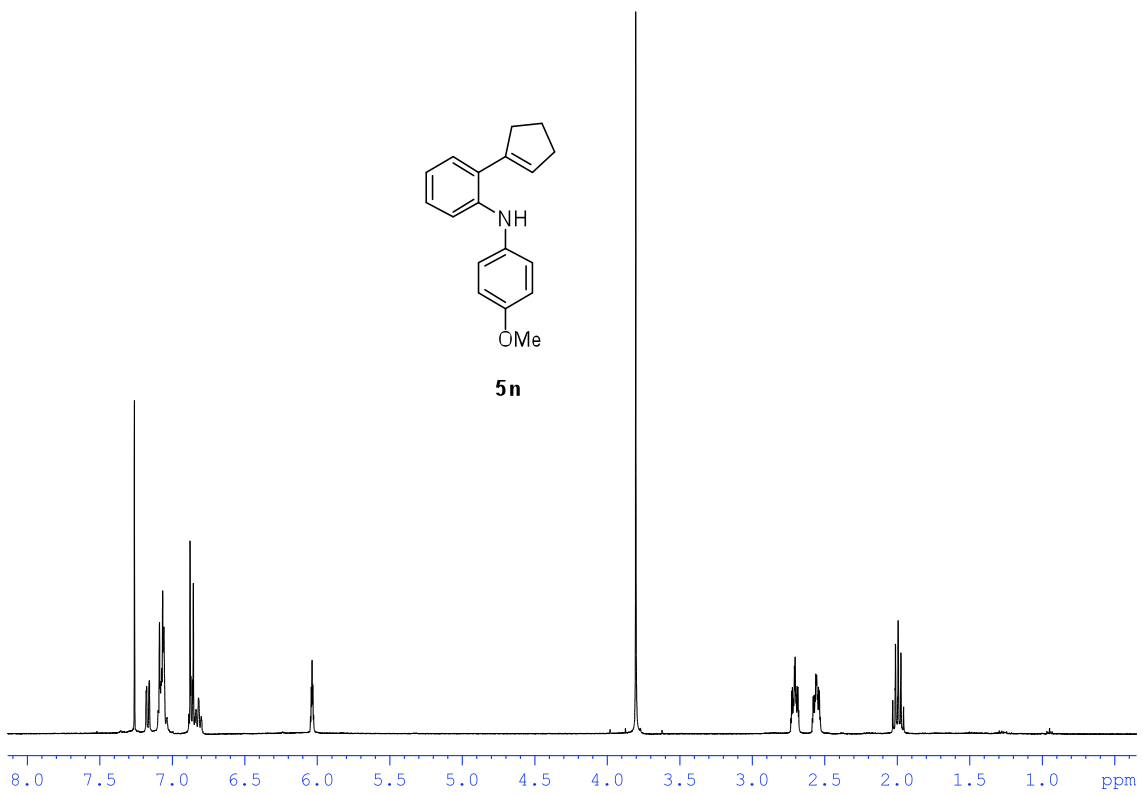


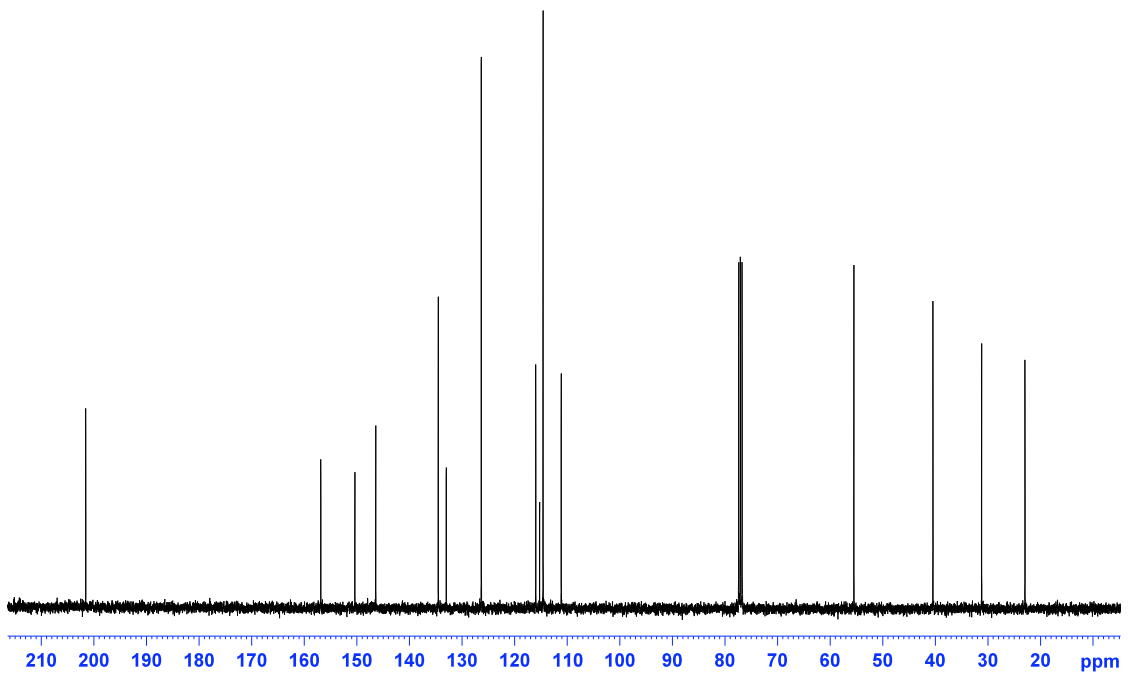
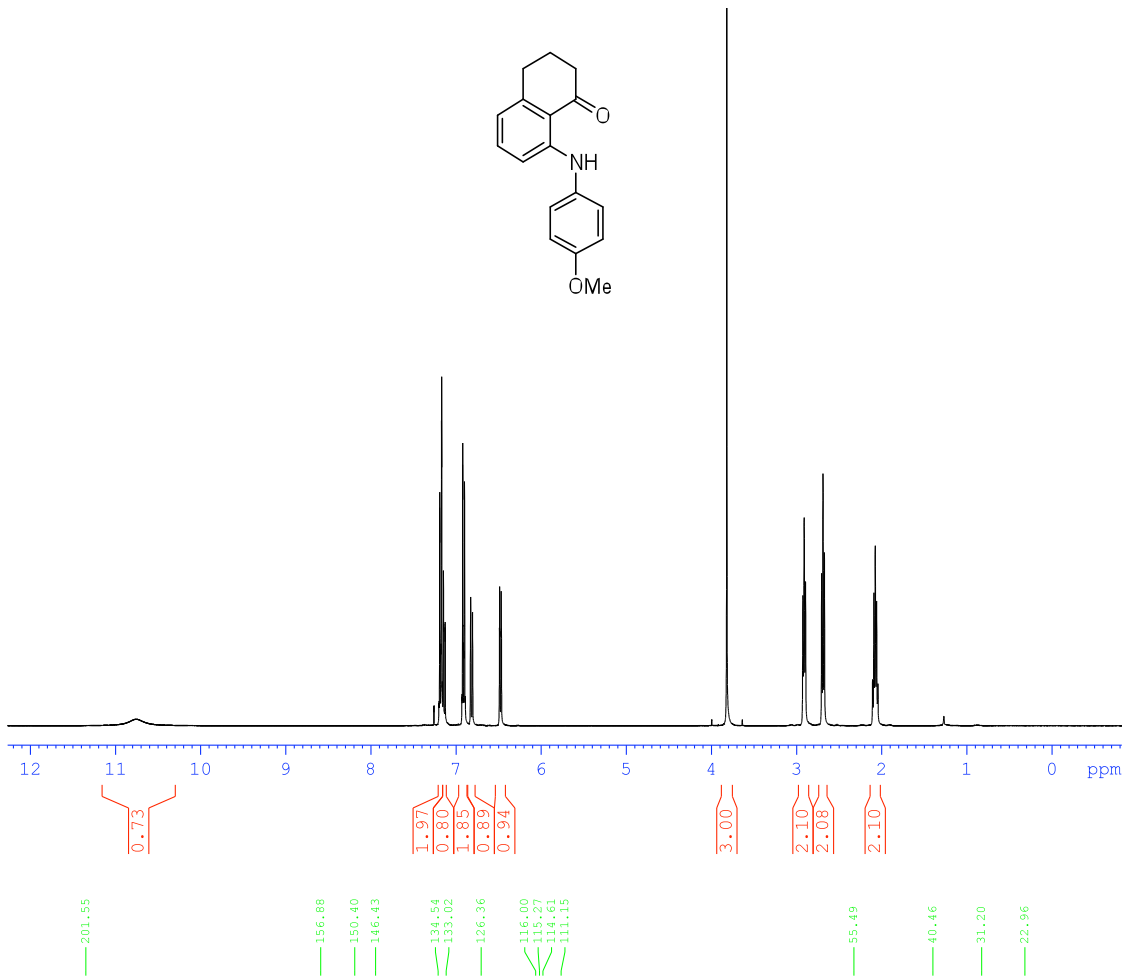
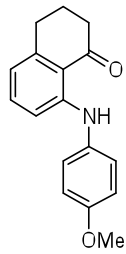


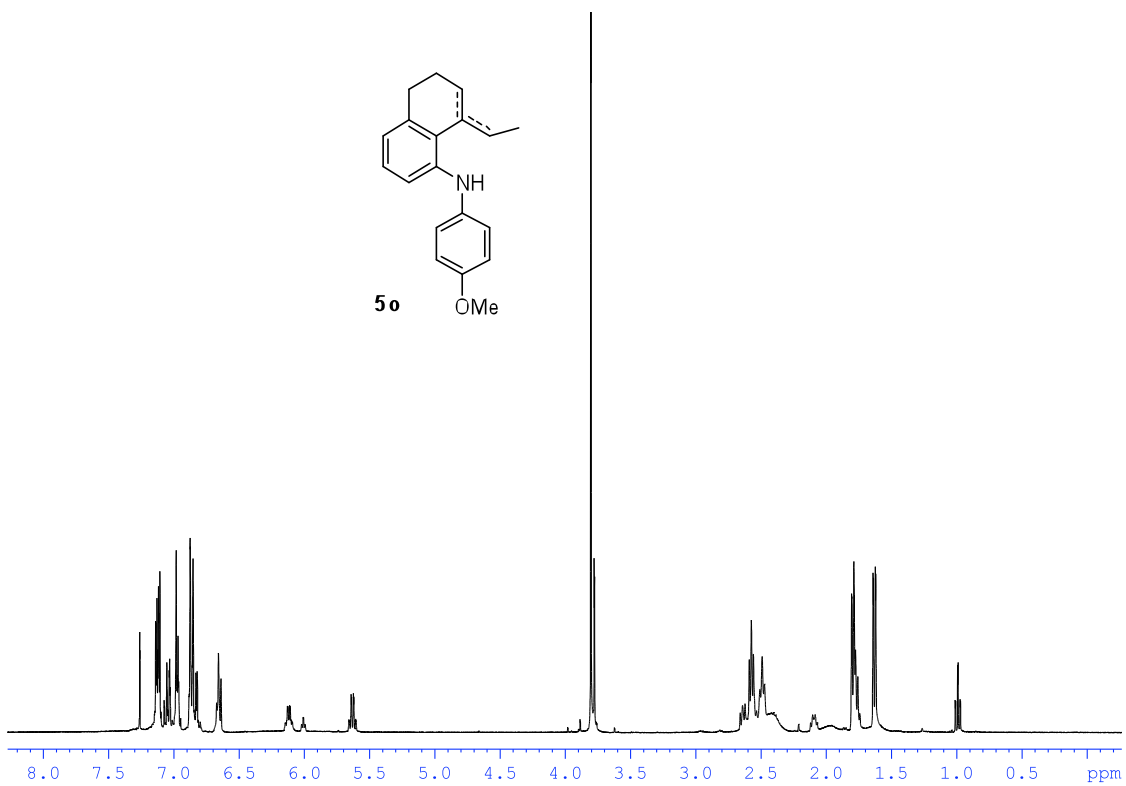
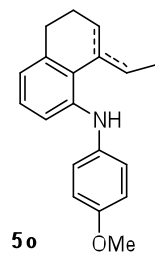
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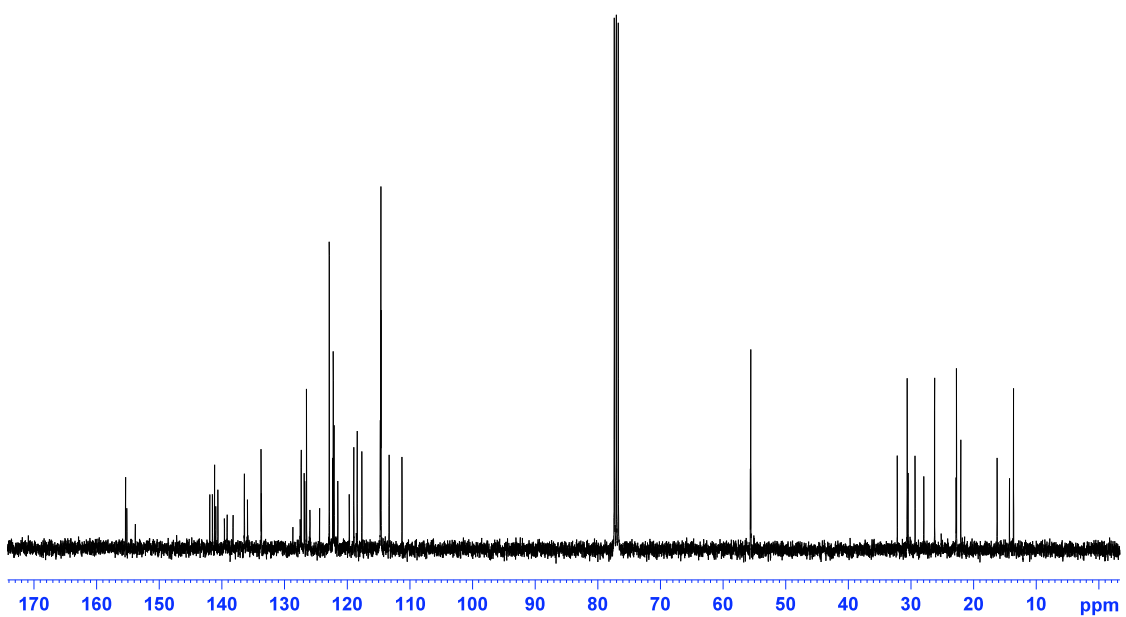


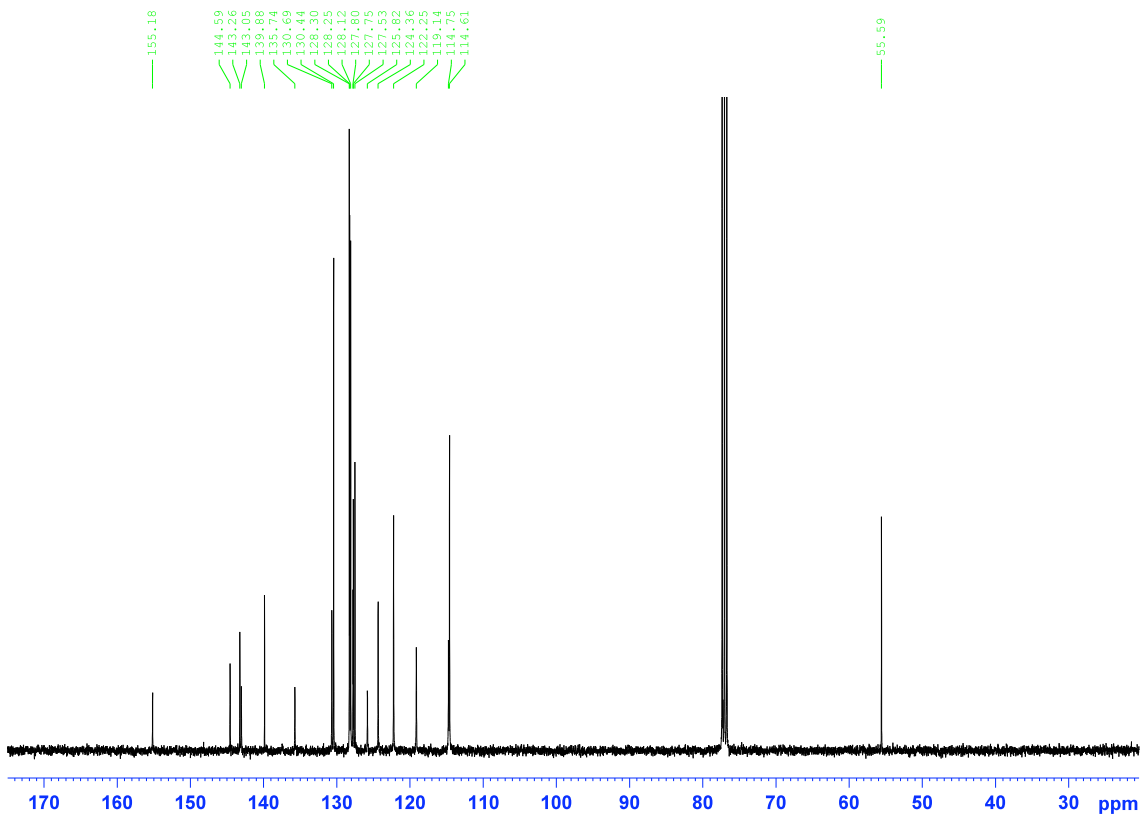
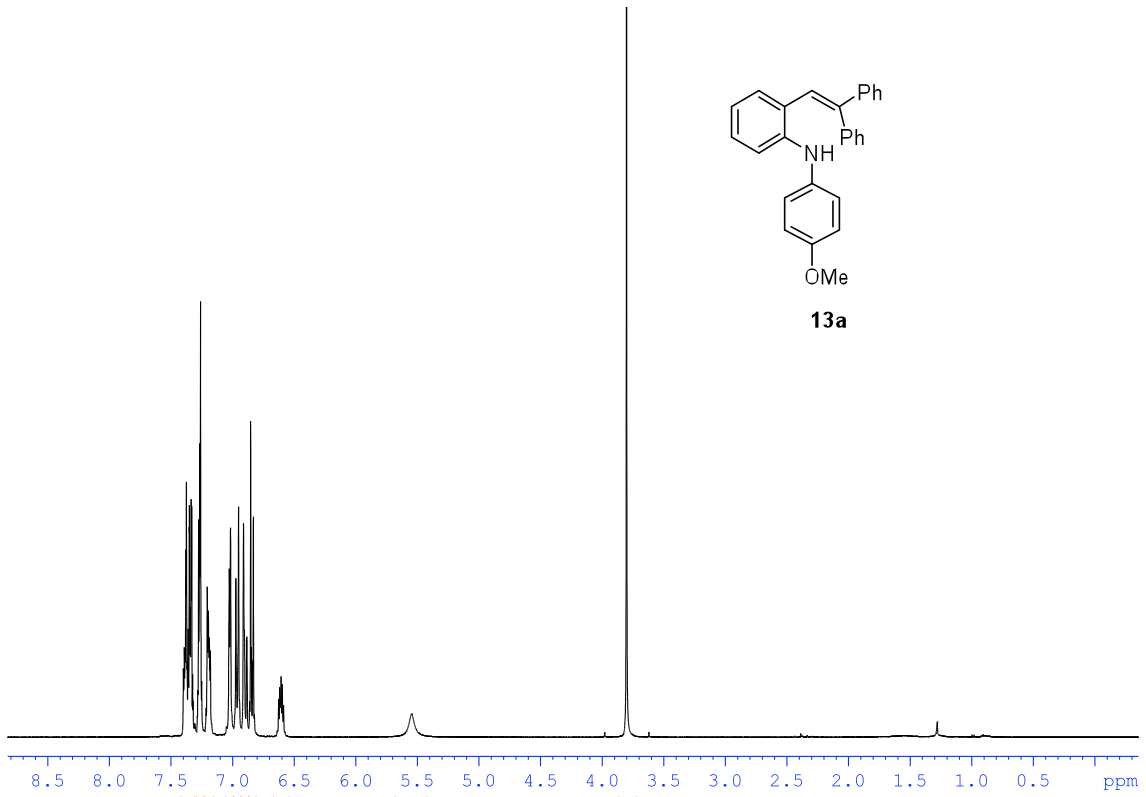
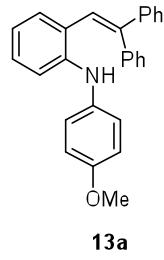


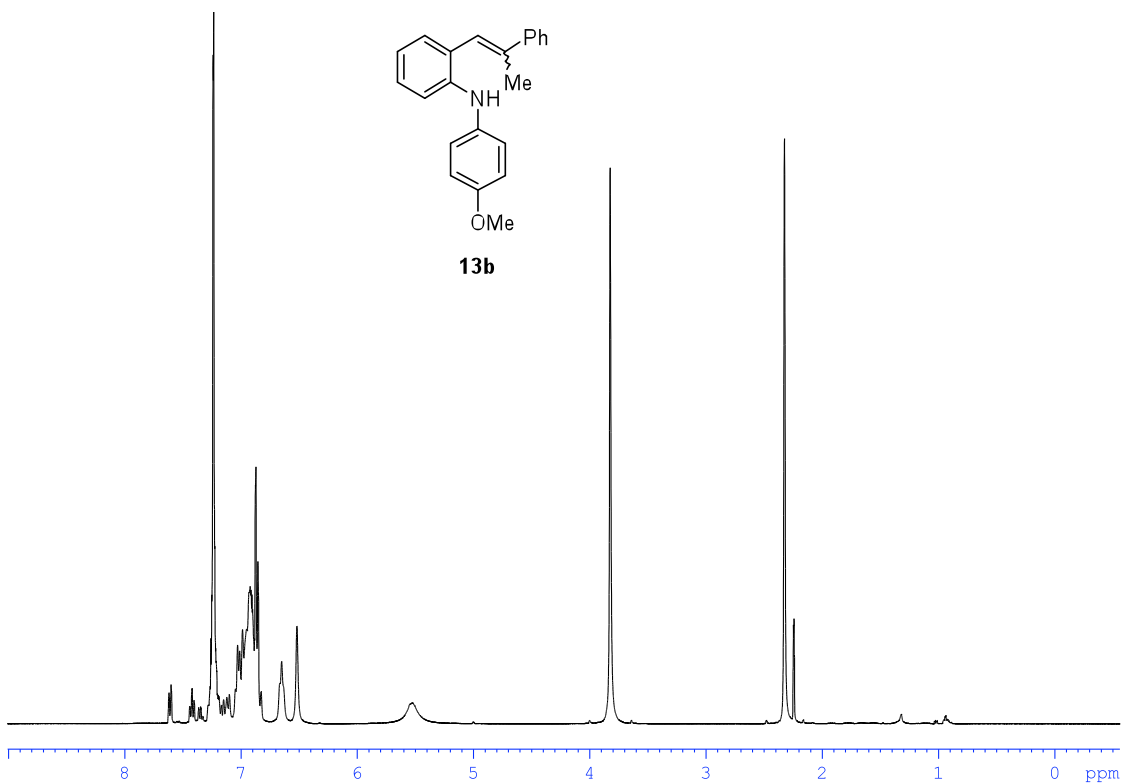
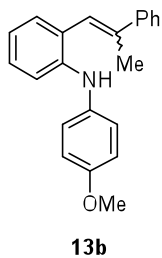
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118.42  
117.82  
114.93  
114.65  
114.61  
113.32  
111.27

55.65  
55.59  
55.57

32.19  
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13.63





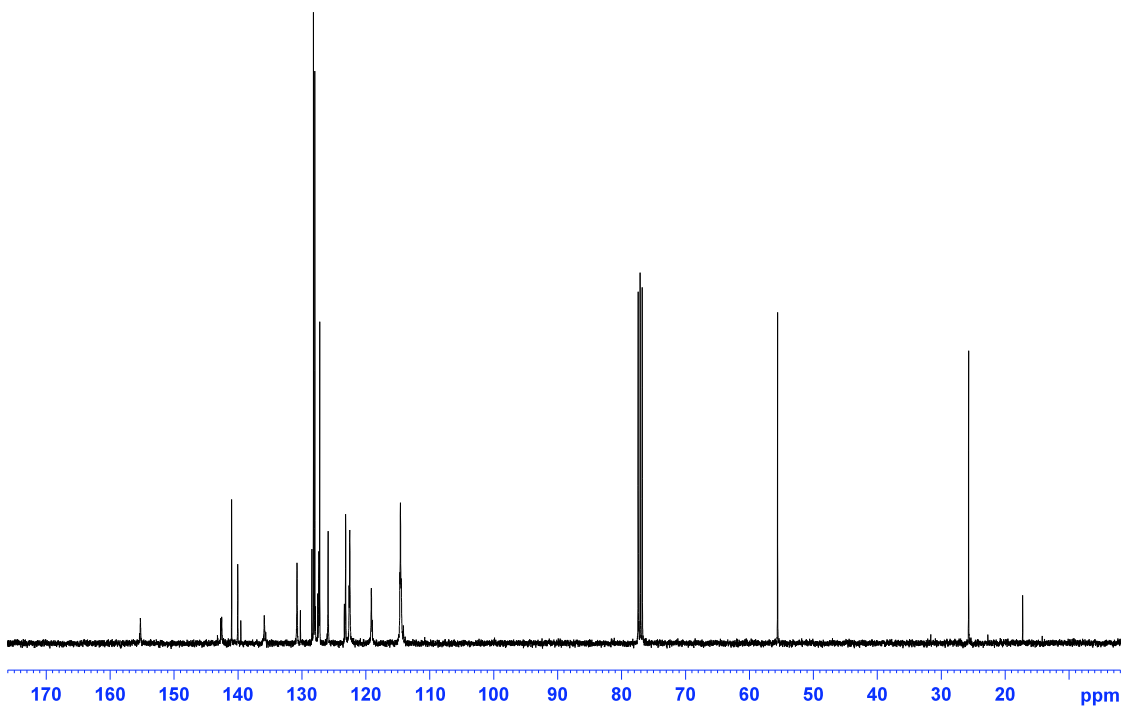


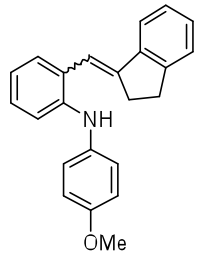
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55.60

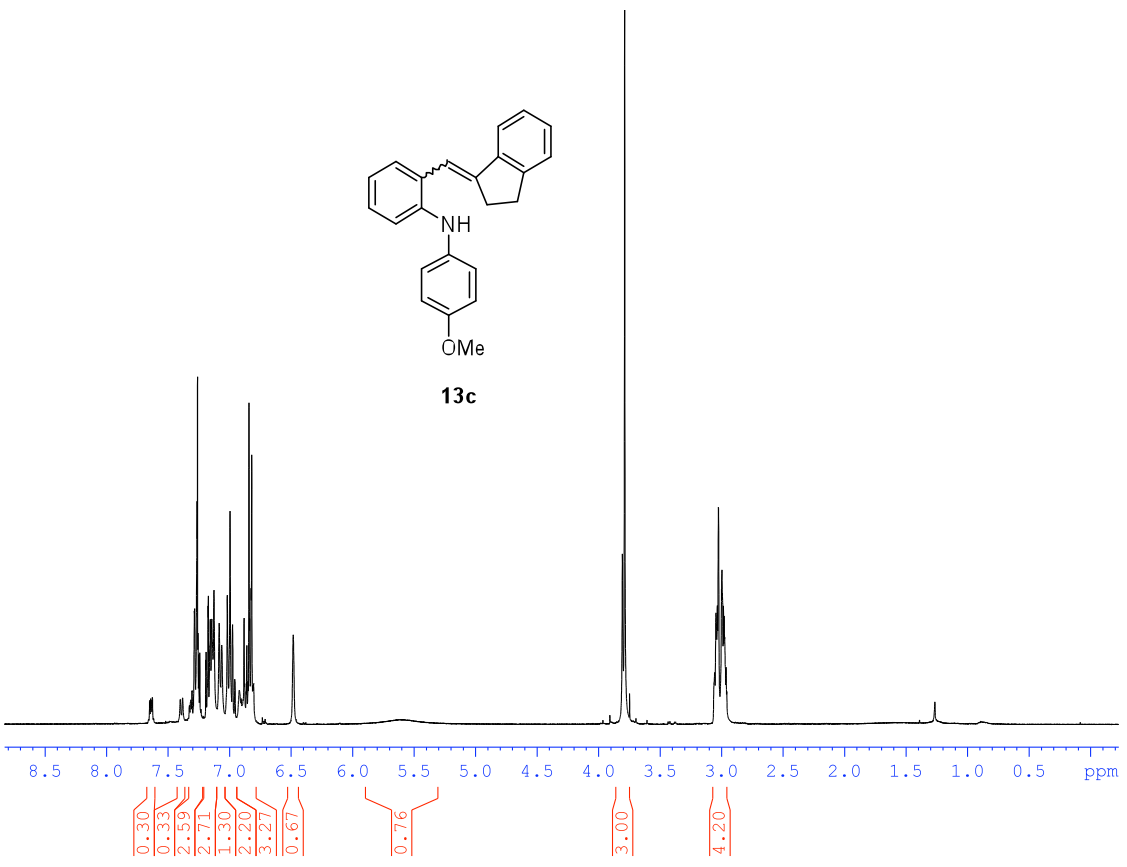
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17.27





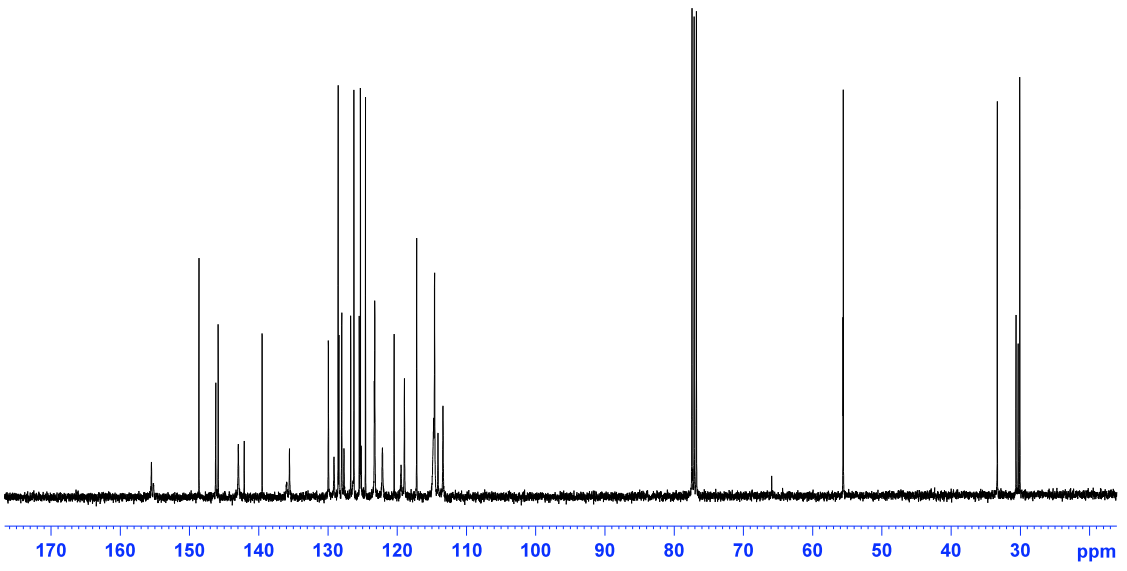
**13c**



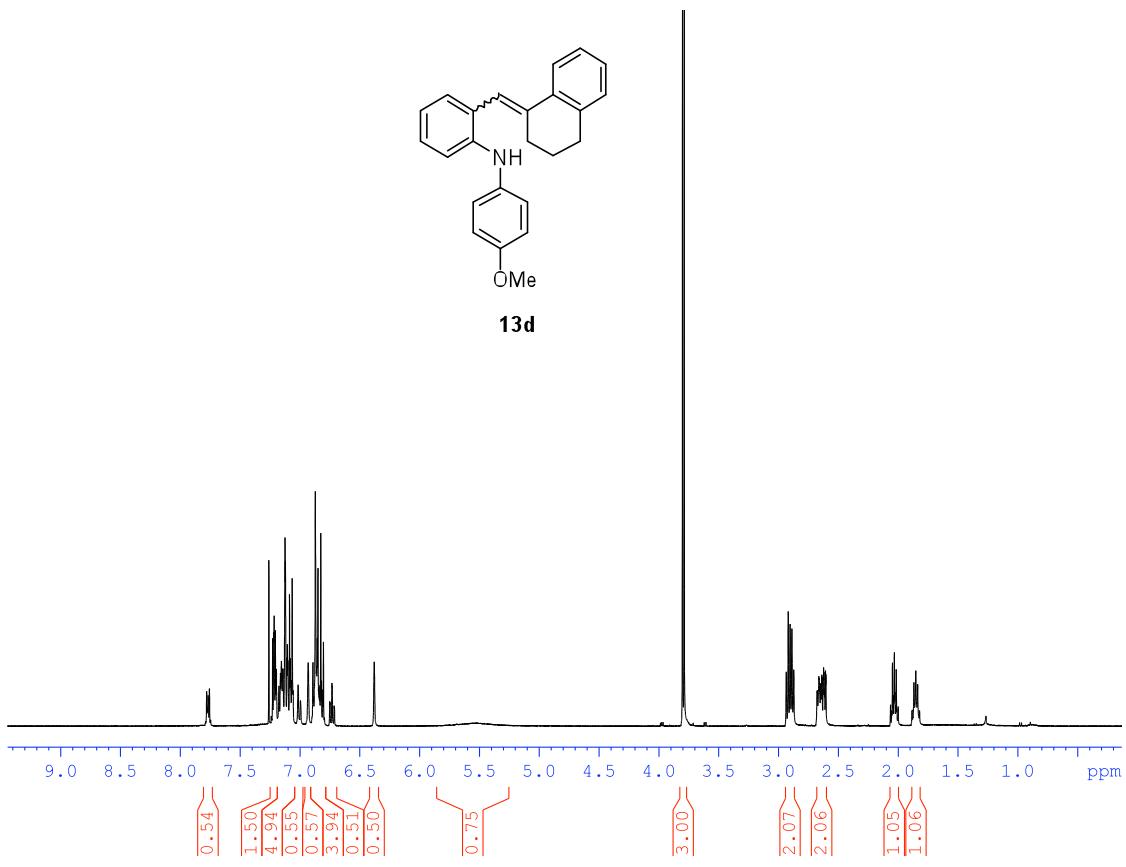
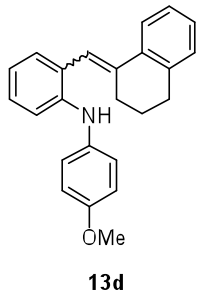
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- 155.22
- 146.19
- 145.85
- 142.94
- 139.51
- 135.55
- 129.93
- 128.52
- 128.41
- 127.68
- 126.71
- 126.25
- 125.47
- 125.31
- 123.57
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- 119.39
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- 114.62
- 113.41

- 55.63
- 55.59

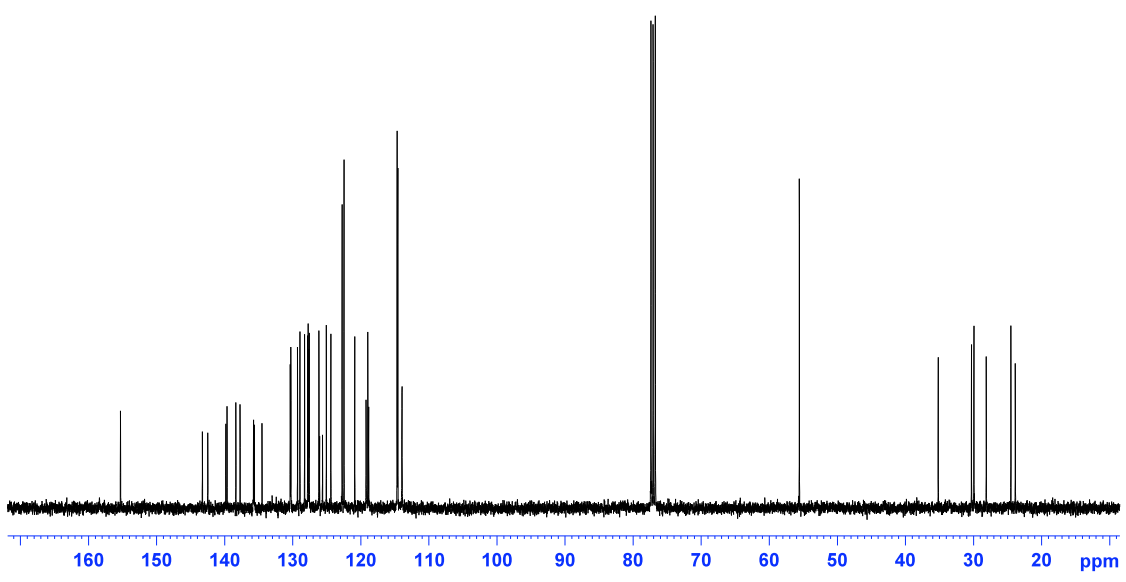
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- 30.63
- 30.33
- 30.09

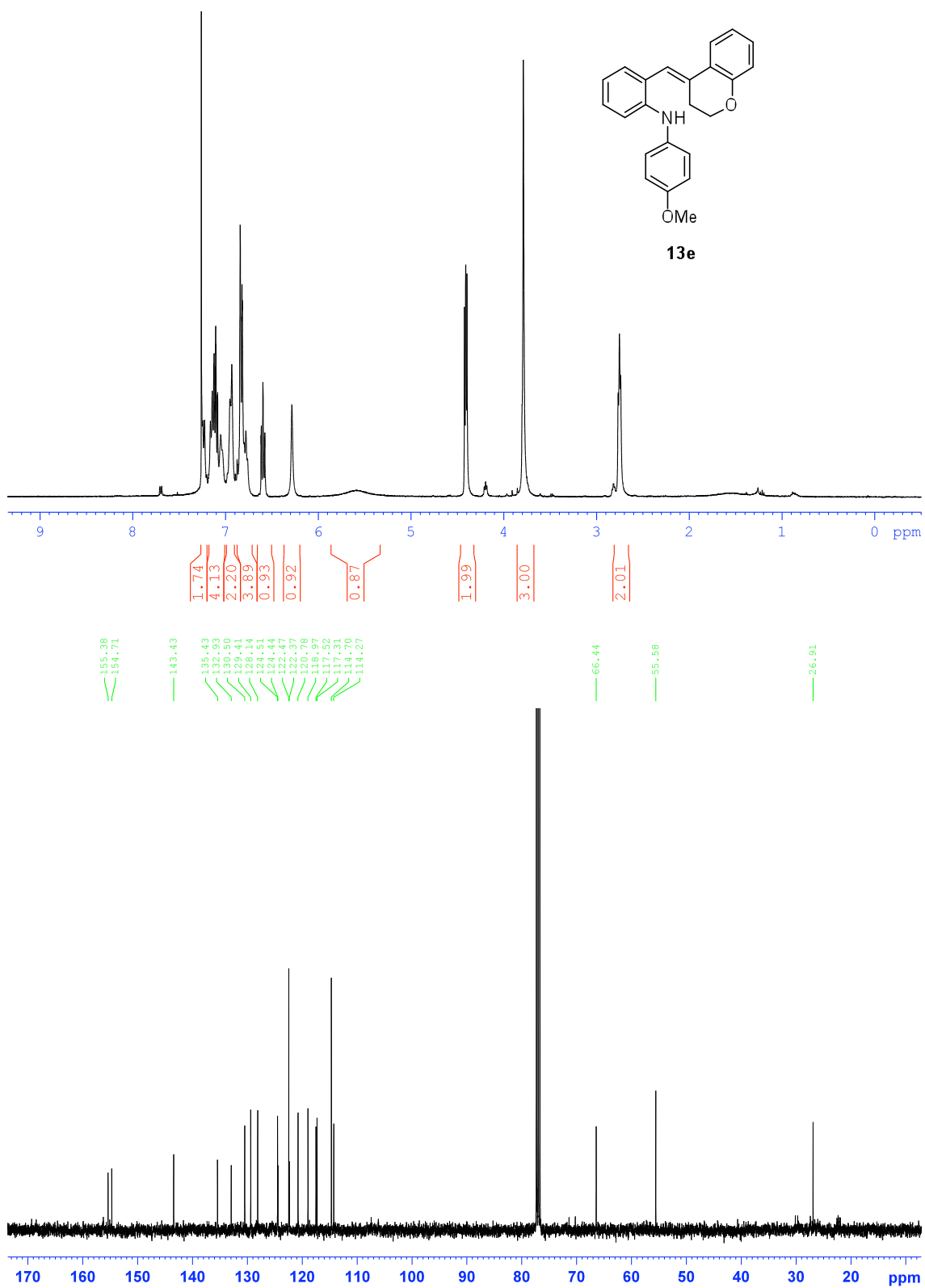


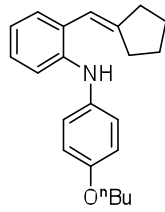




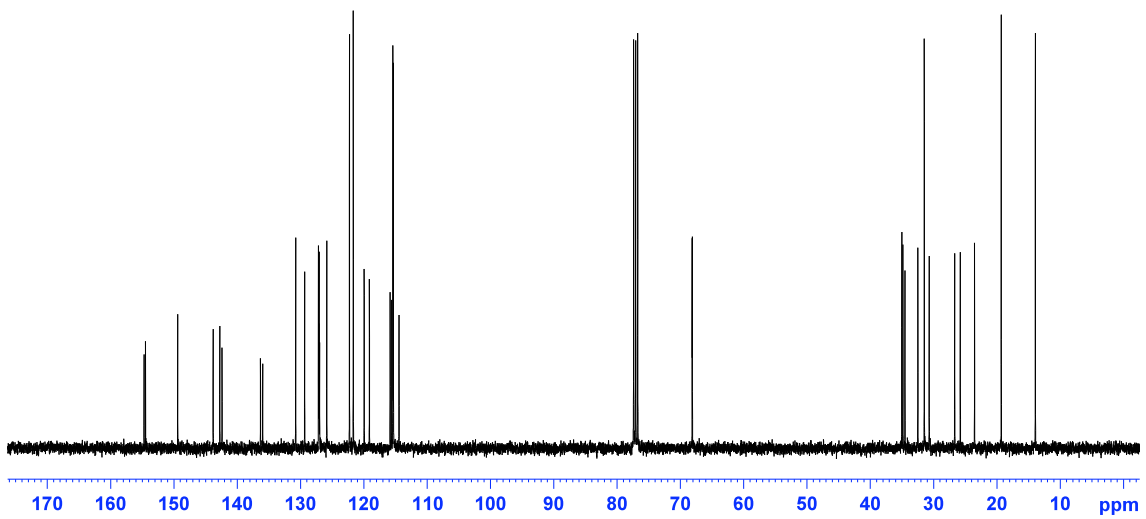
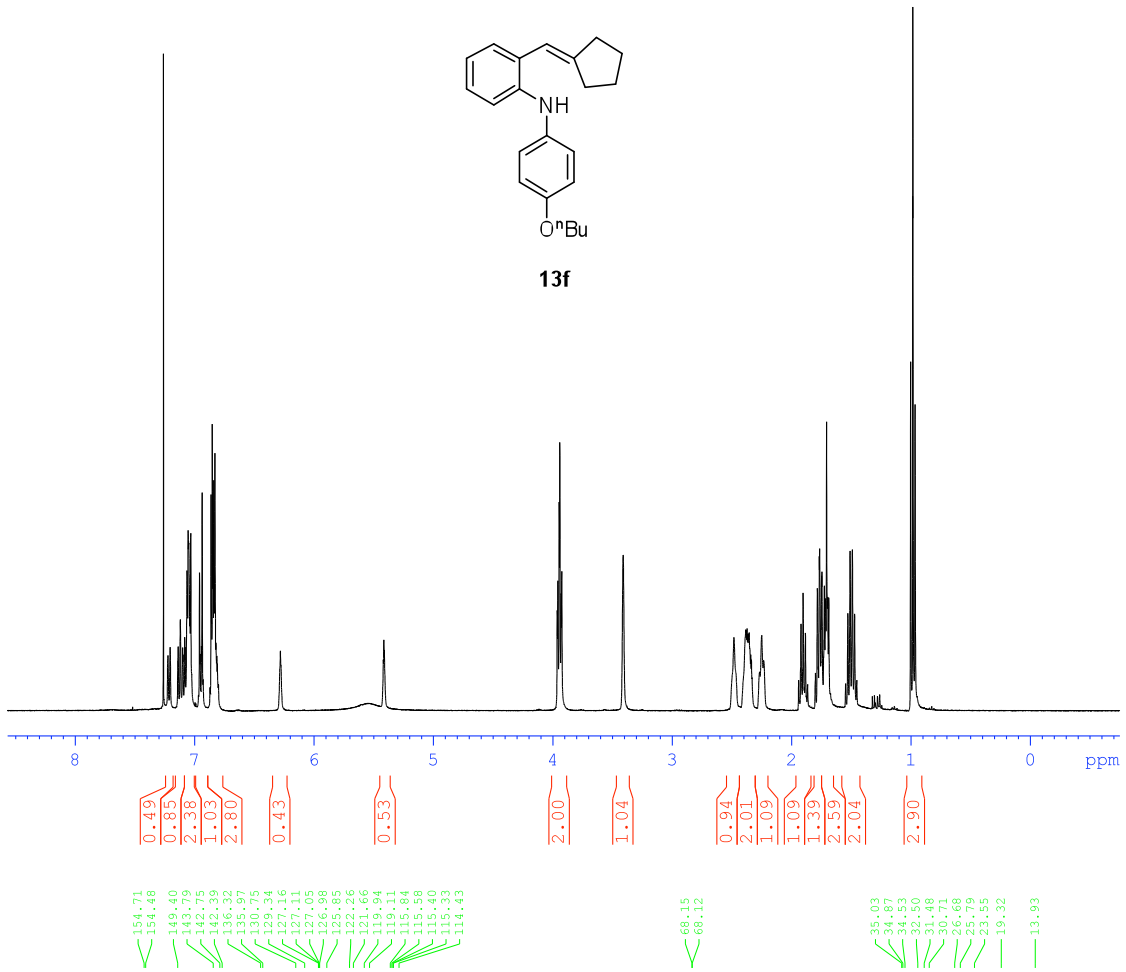
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  - 134.53
  - 130.39
  - 130.29
  - 129.32
  - 128.57
  - 128.58
  - 127.83
  - 127.76
  - 127.64
  - 127.60
  - 126.07
  - 125.65
  - 125.09
  - 124.42
  - 122.77
  - 122.49
  - 119.54
  - 119.54
  - 118.99
  - 118.87
  - 114.68
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  - 113.96
- 55.59
- 35.19
- 30.31
- 29.94
- 28.13
- 24.52
- 23.87

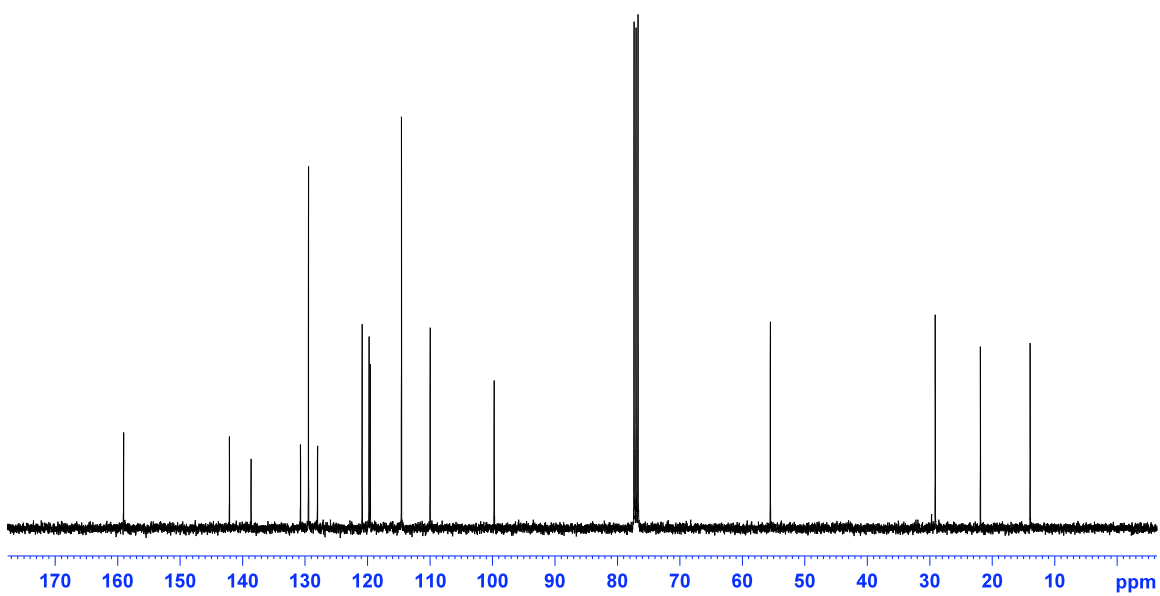
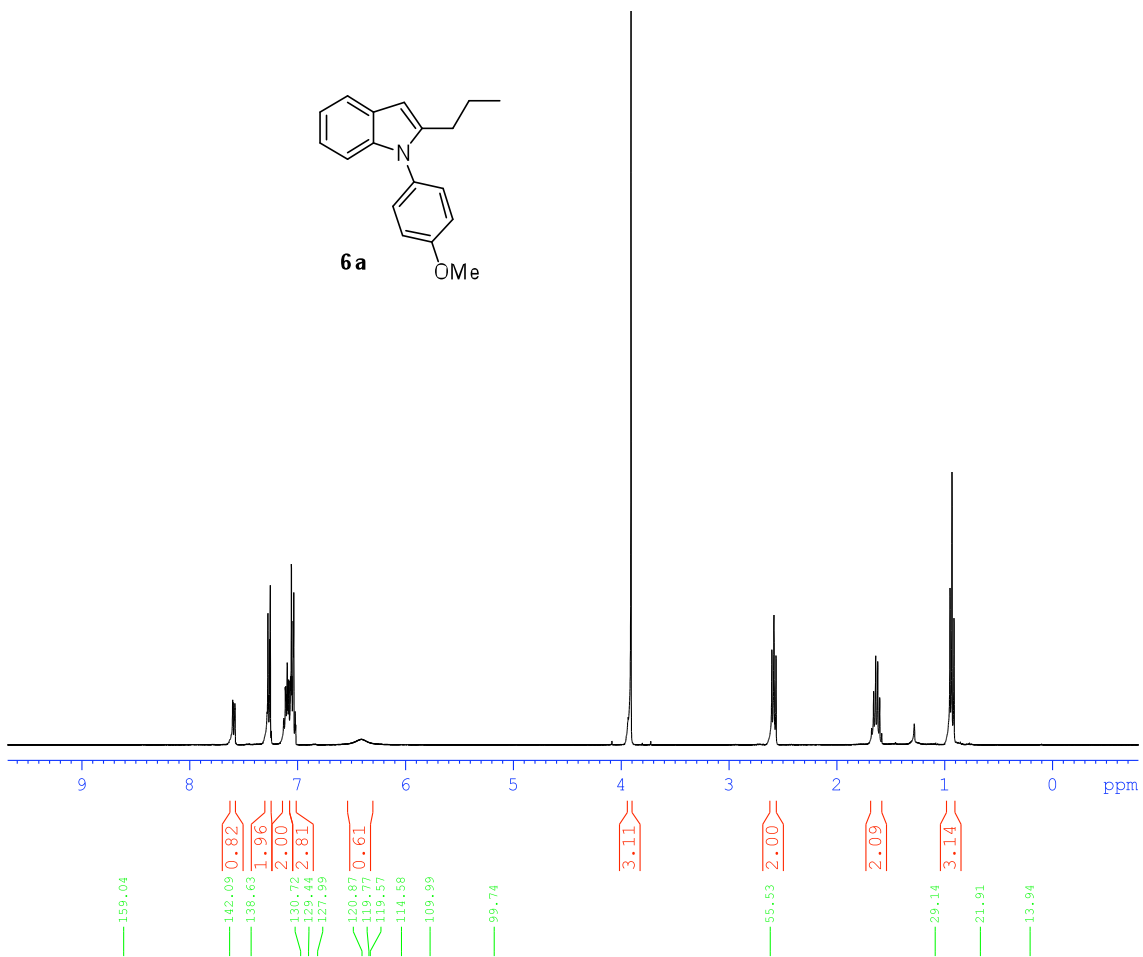
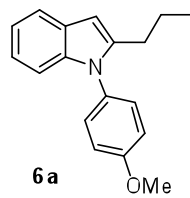


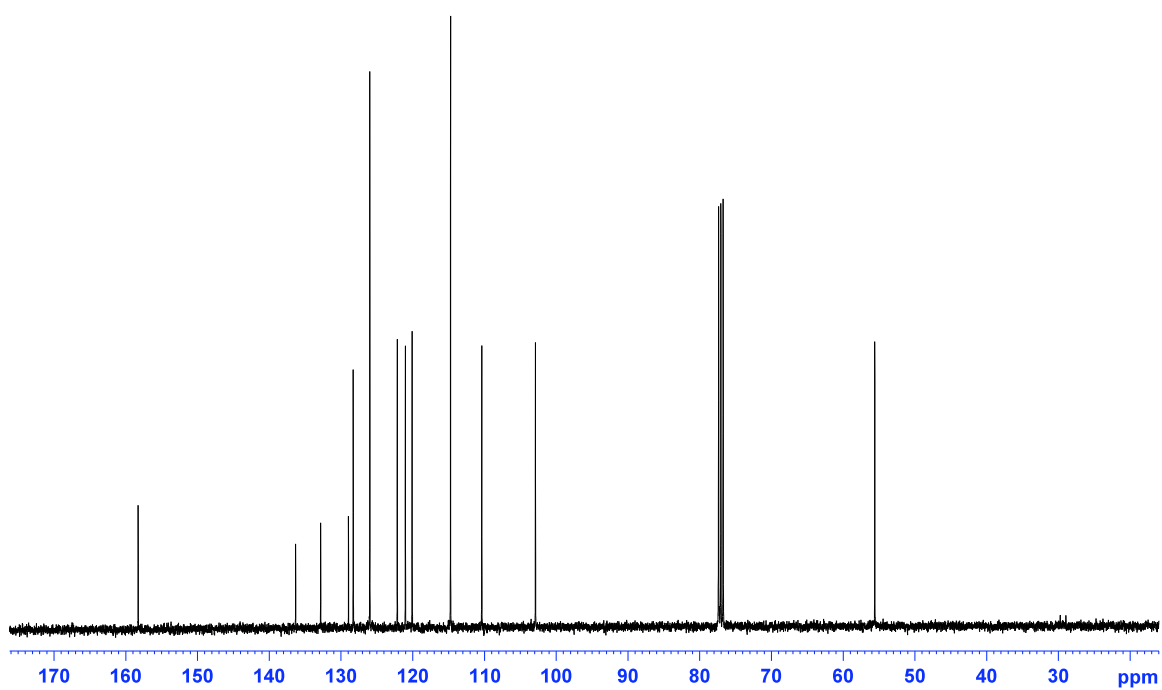
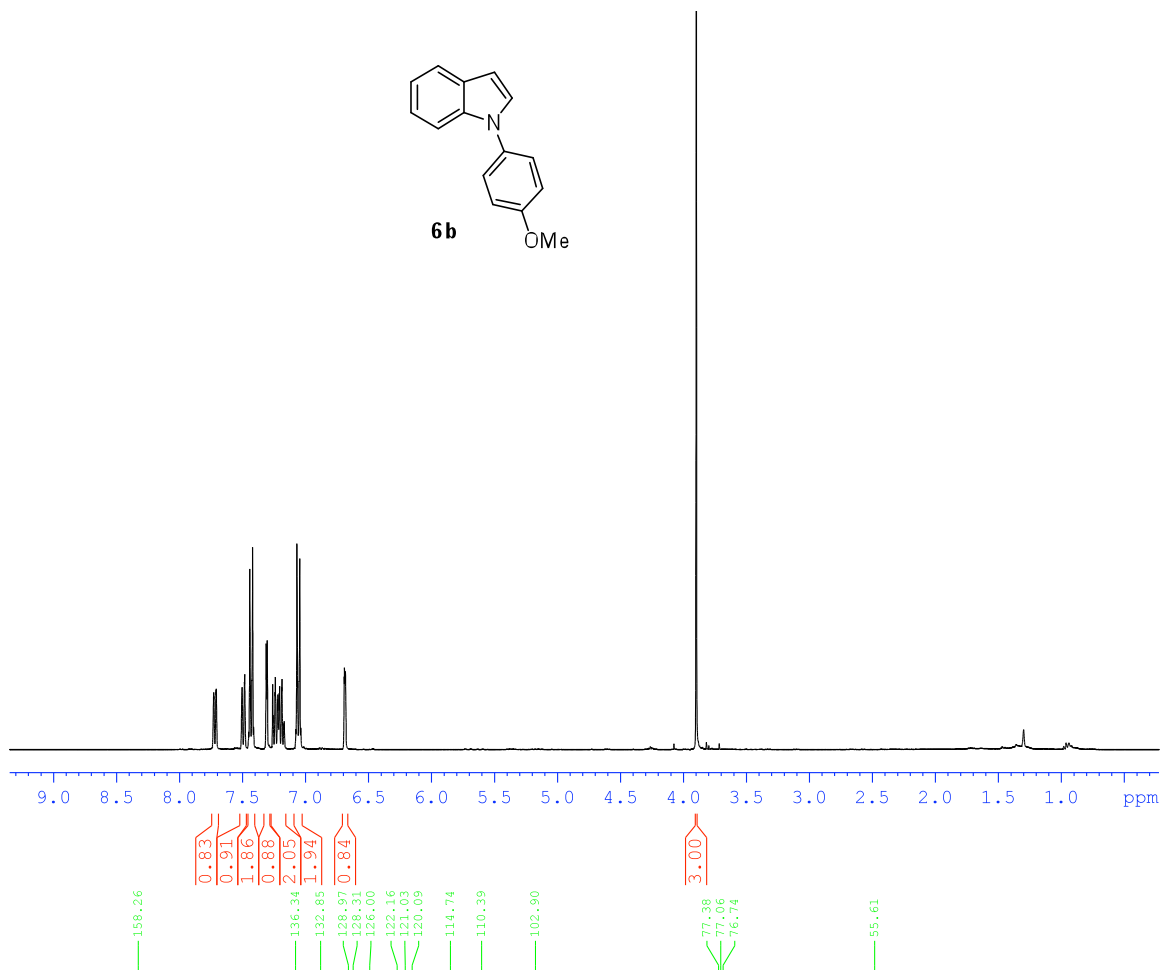
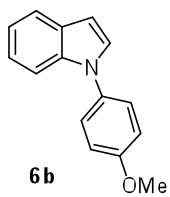


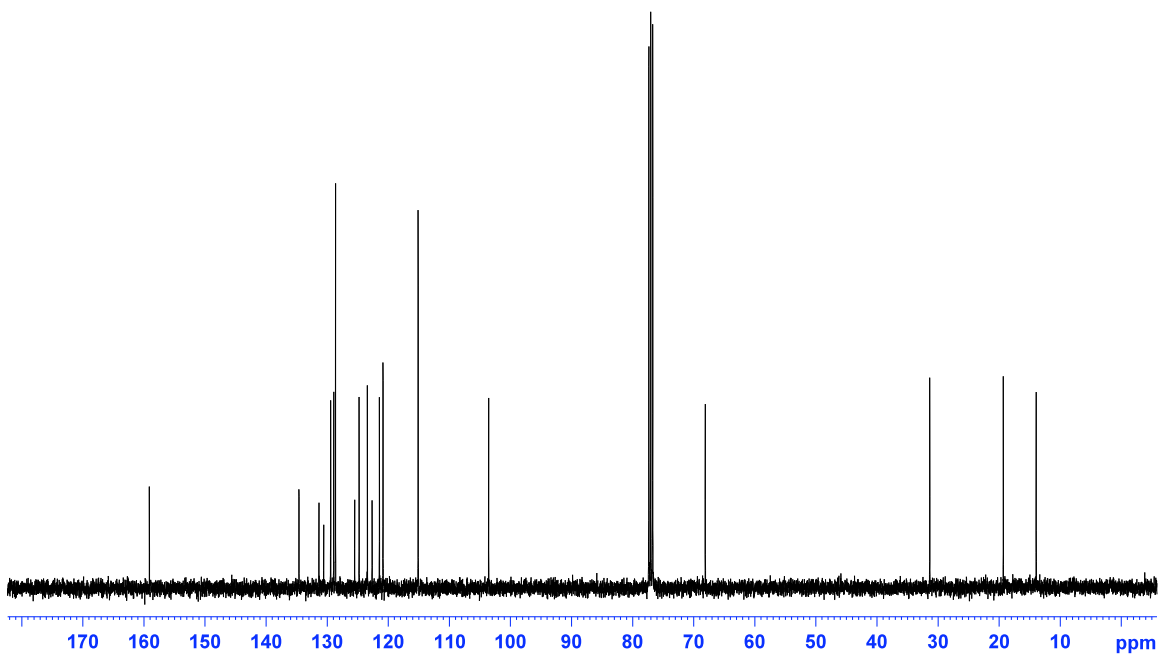
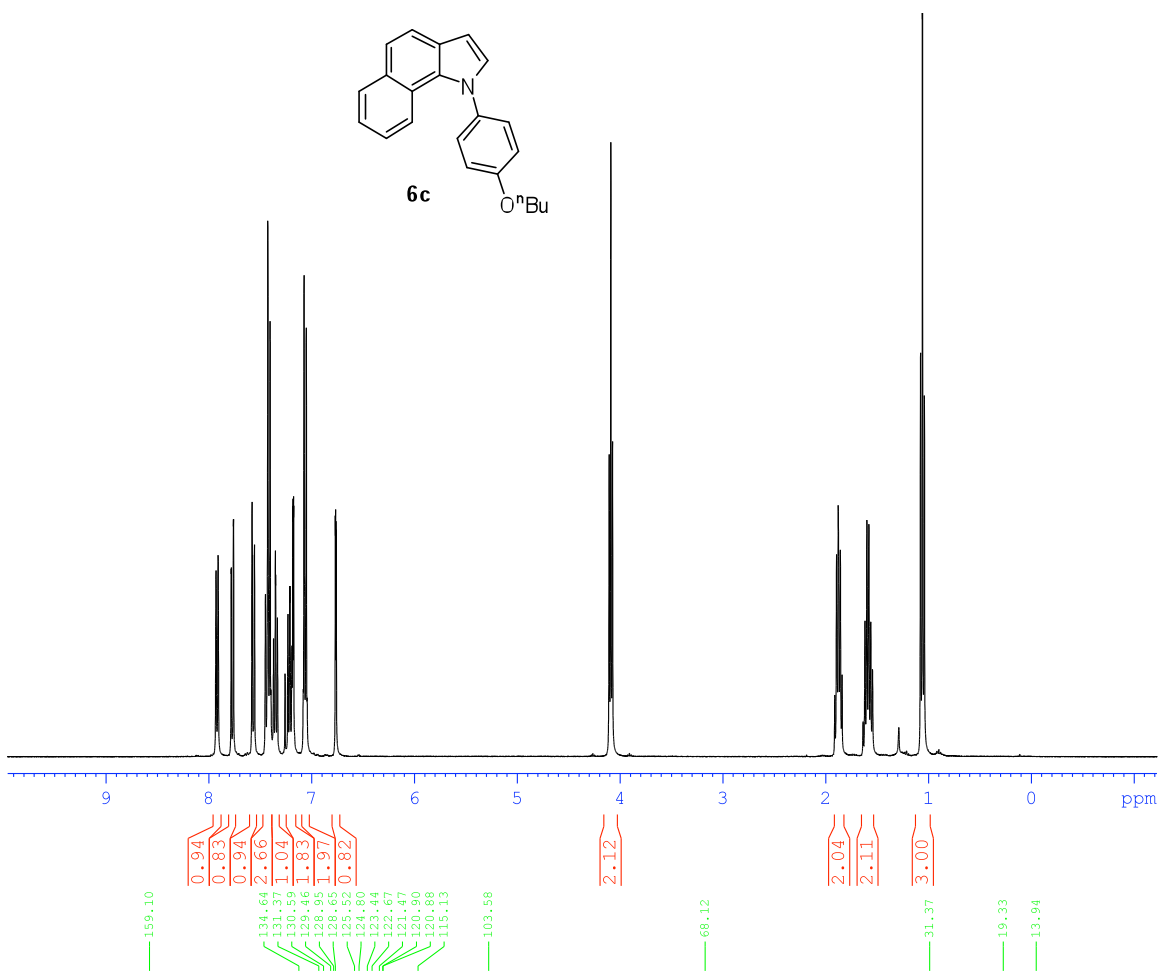
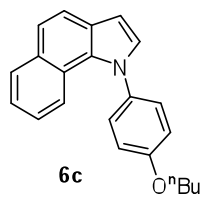


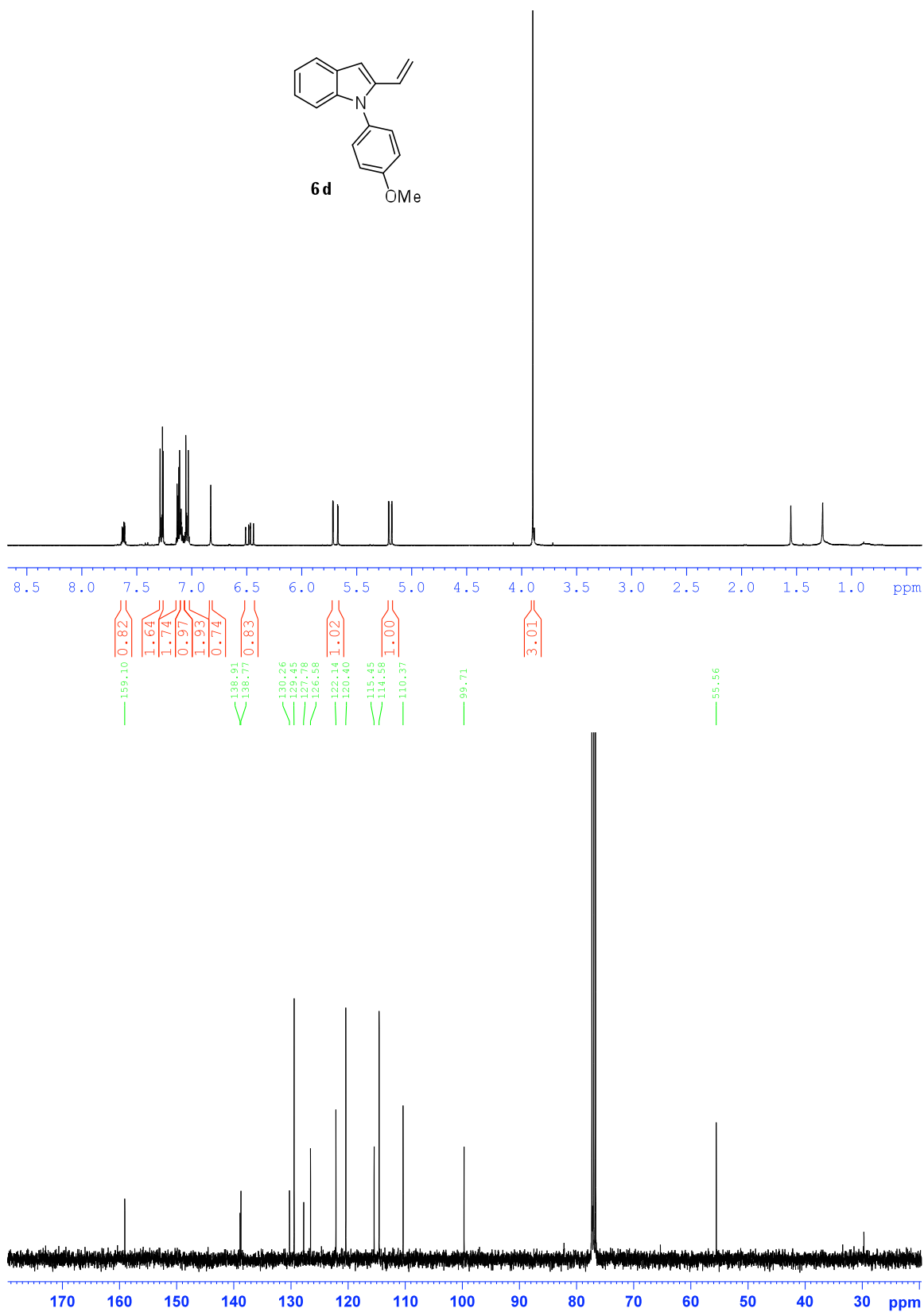
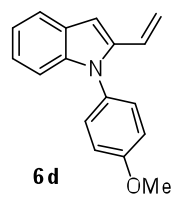
**13f**

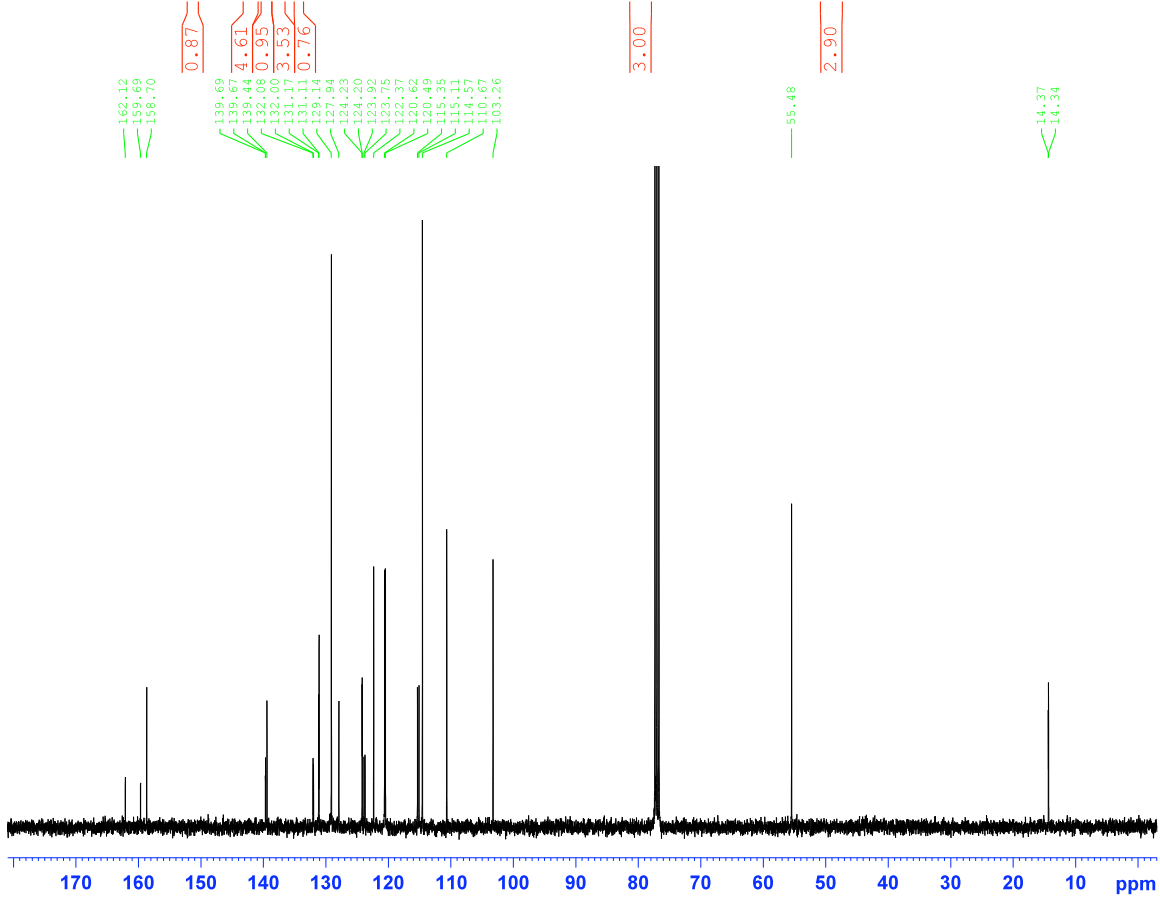
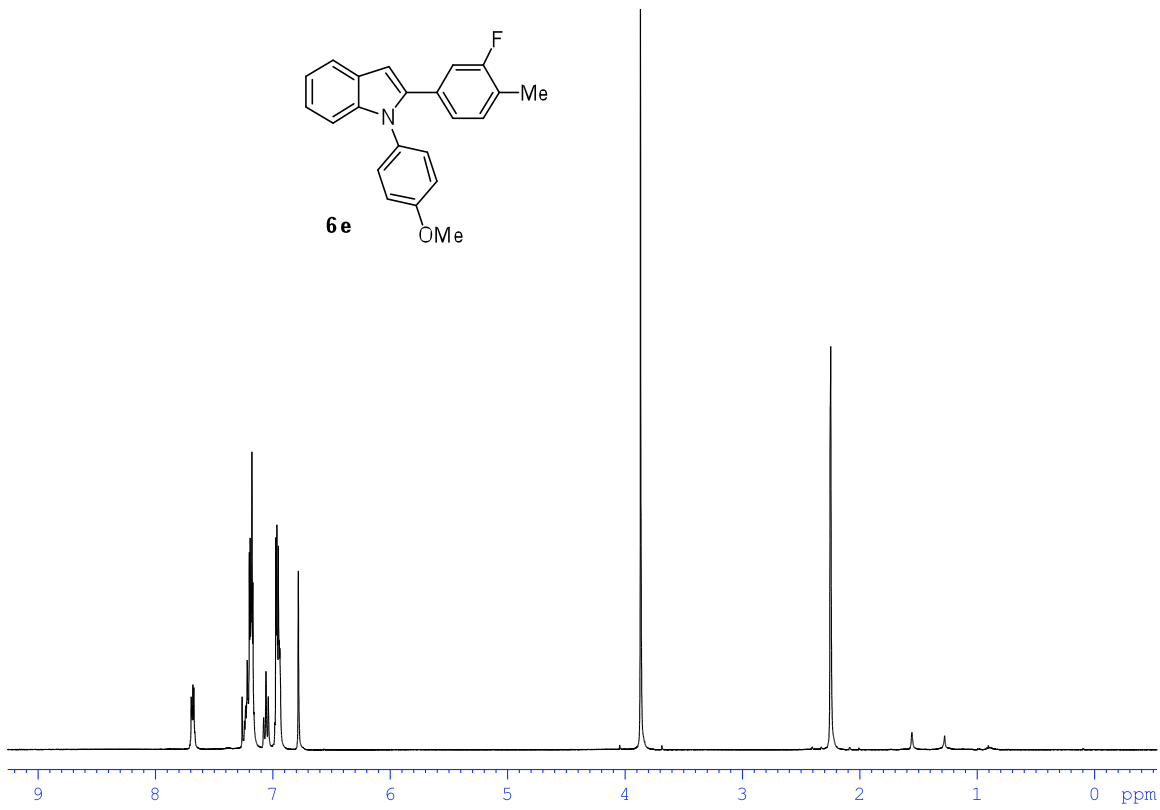
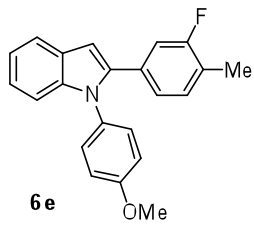




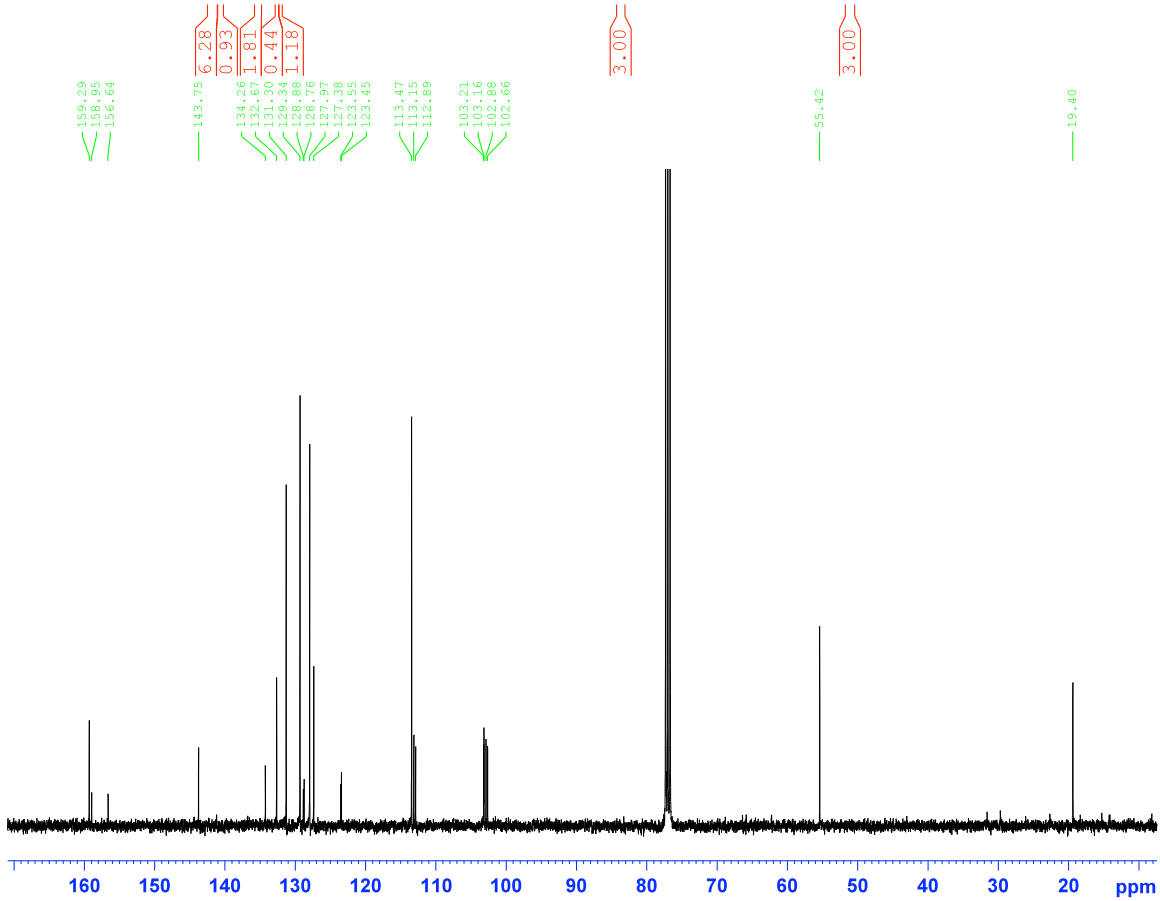
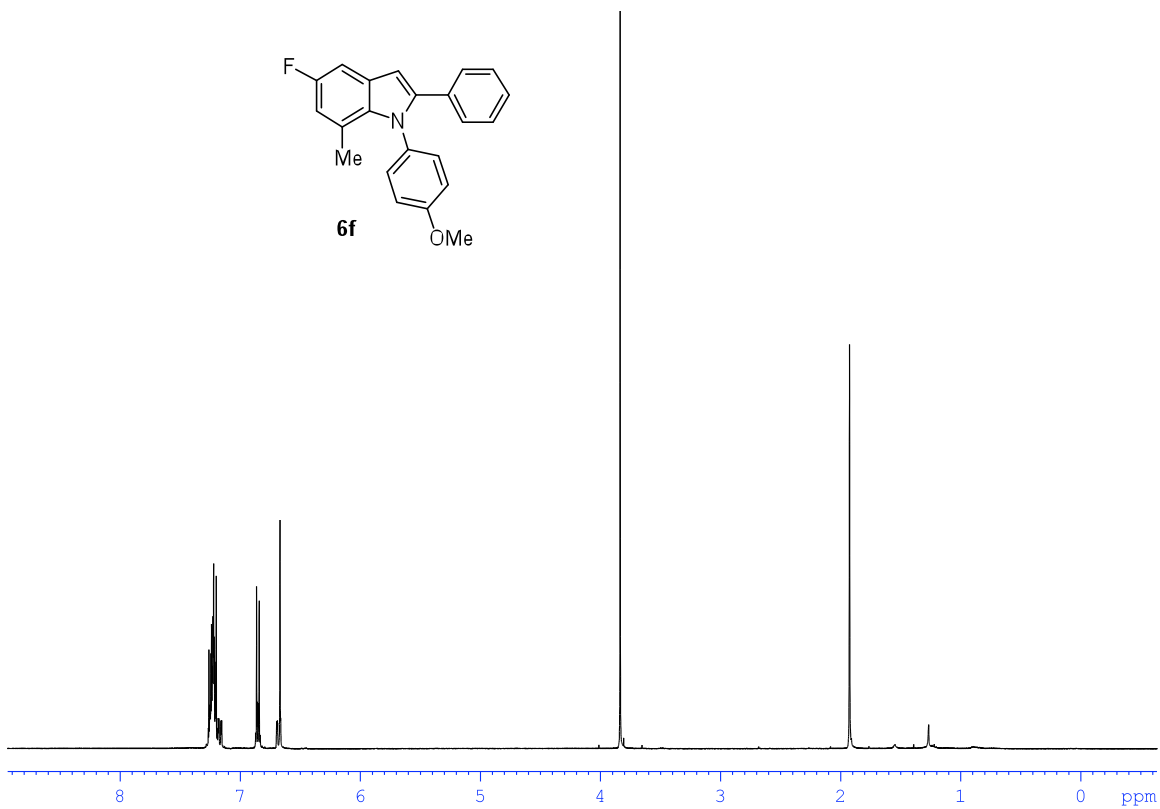
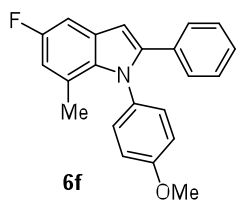


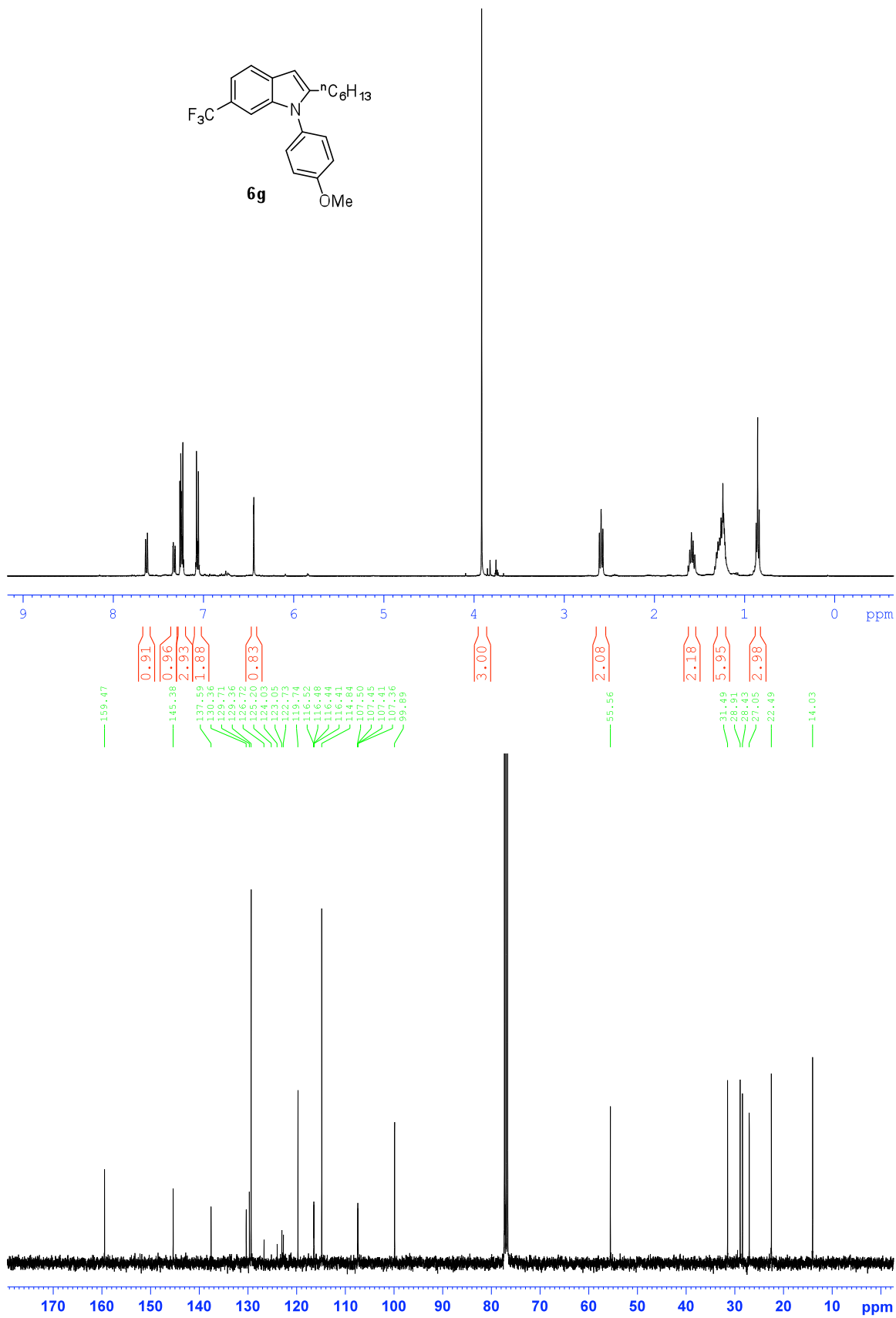
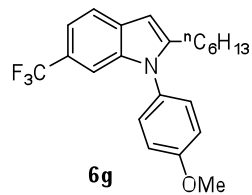


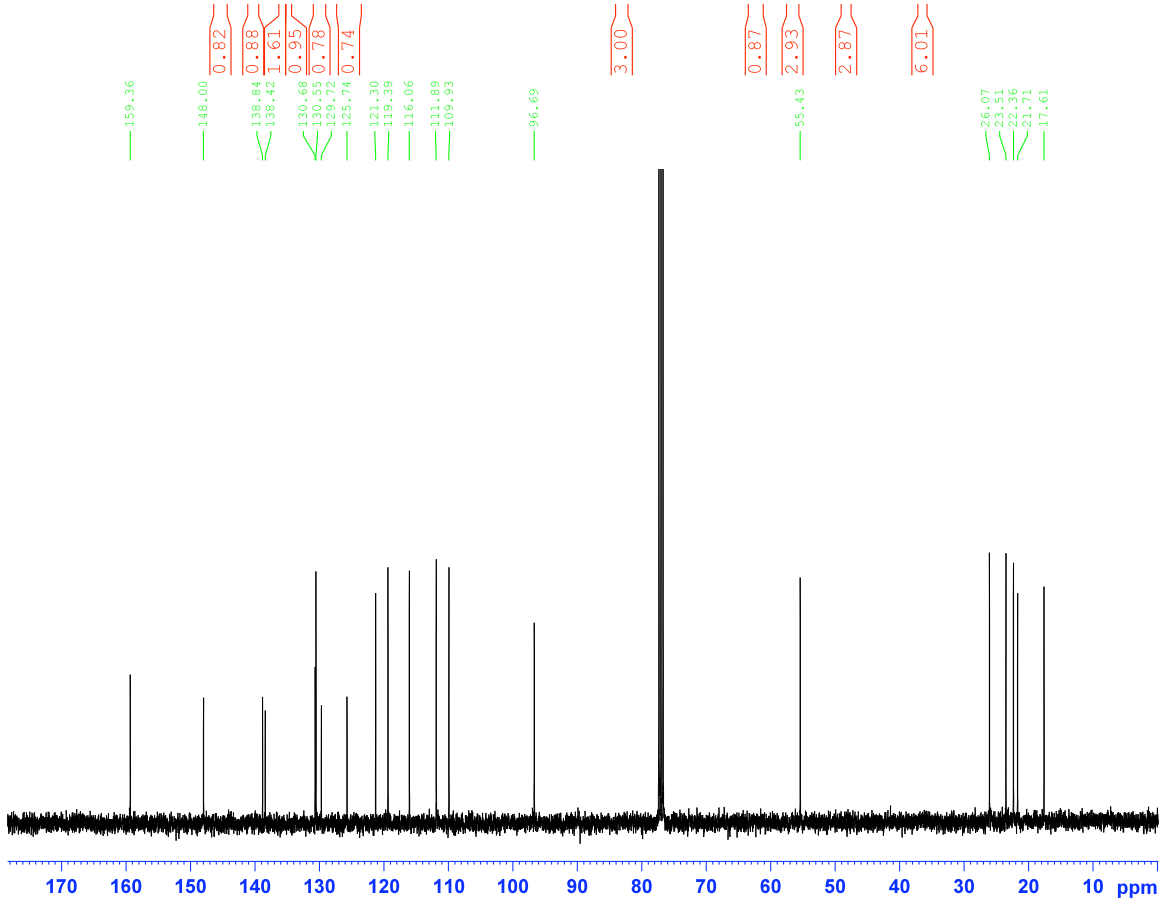
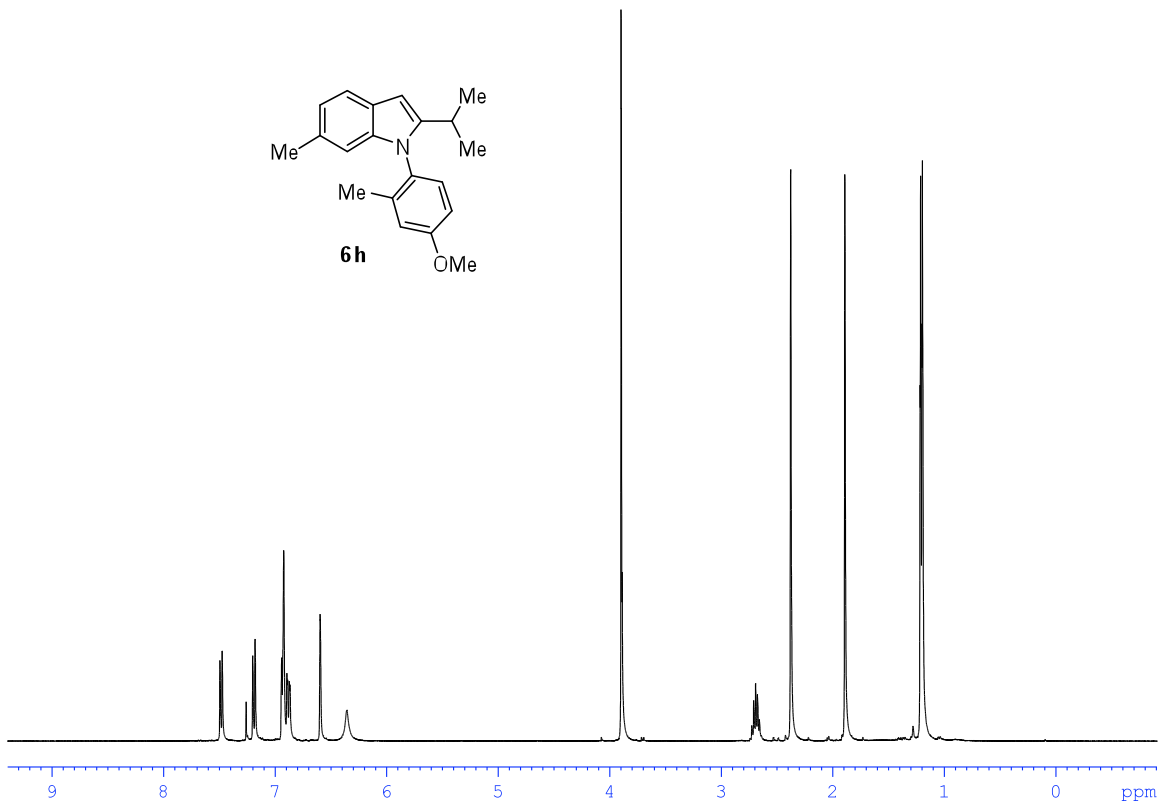
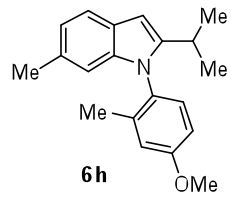


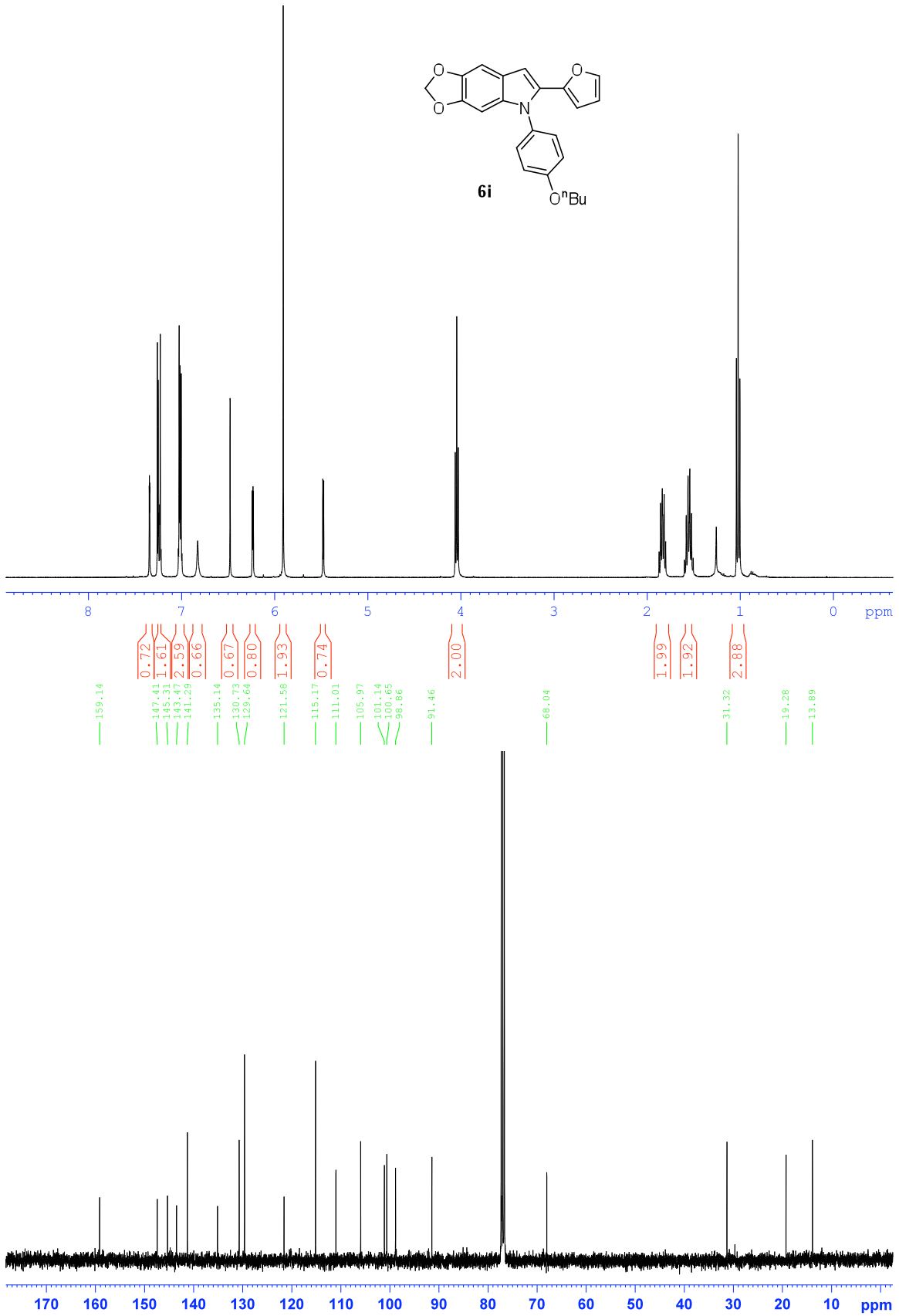
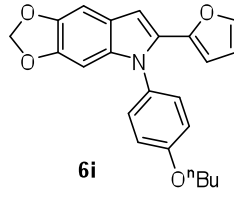


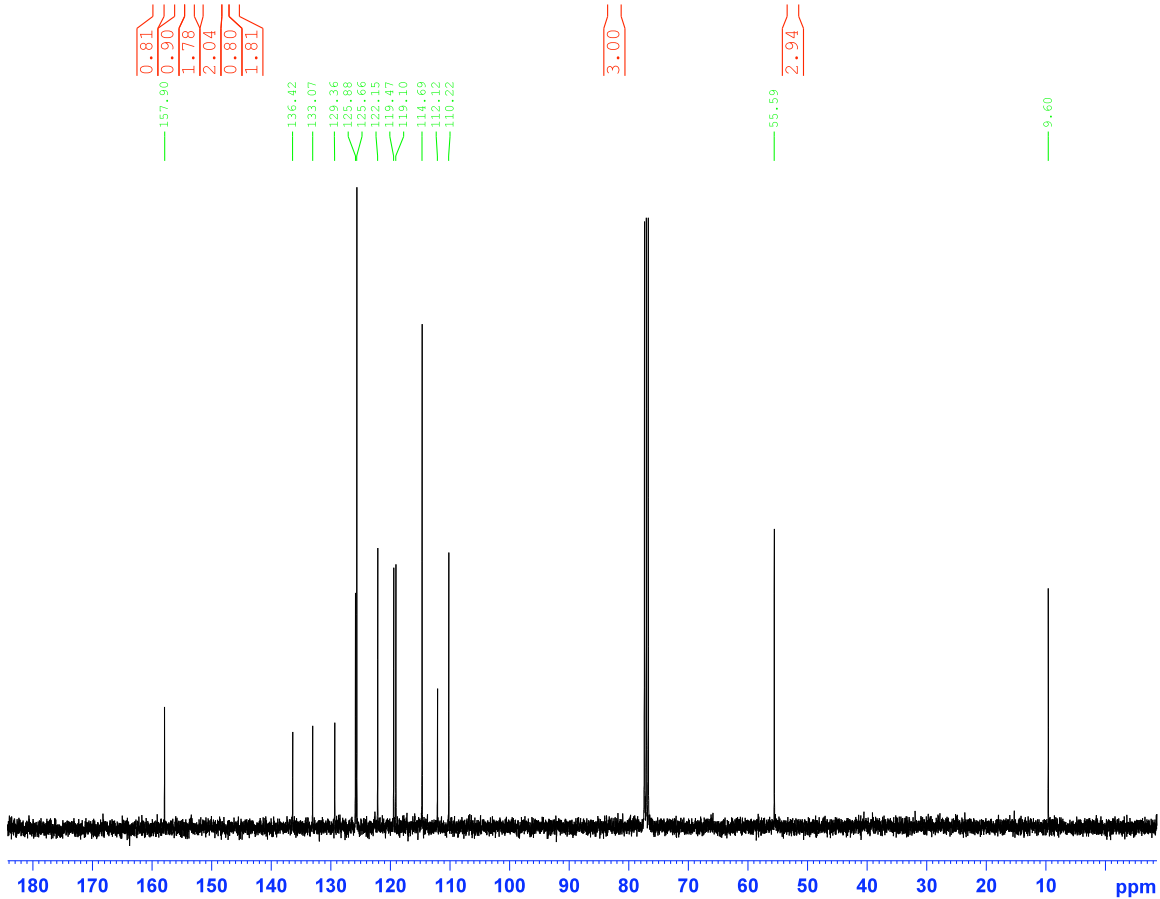
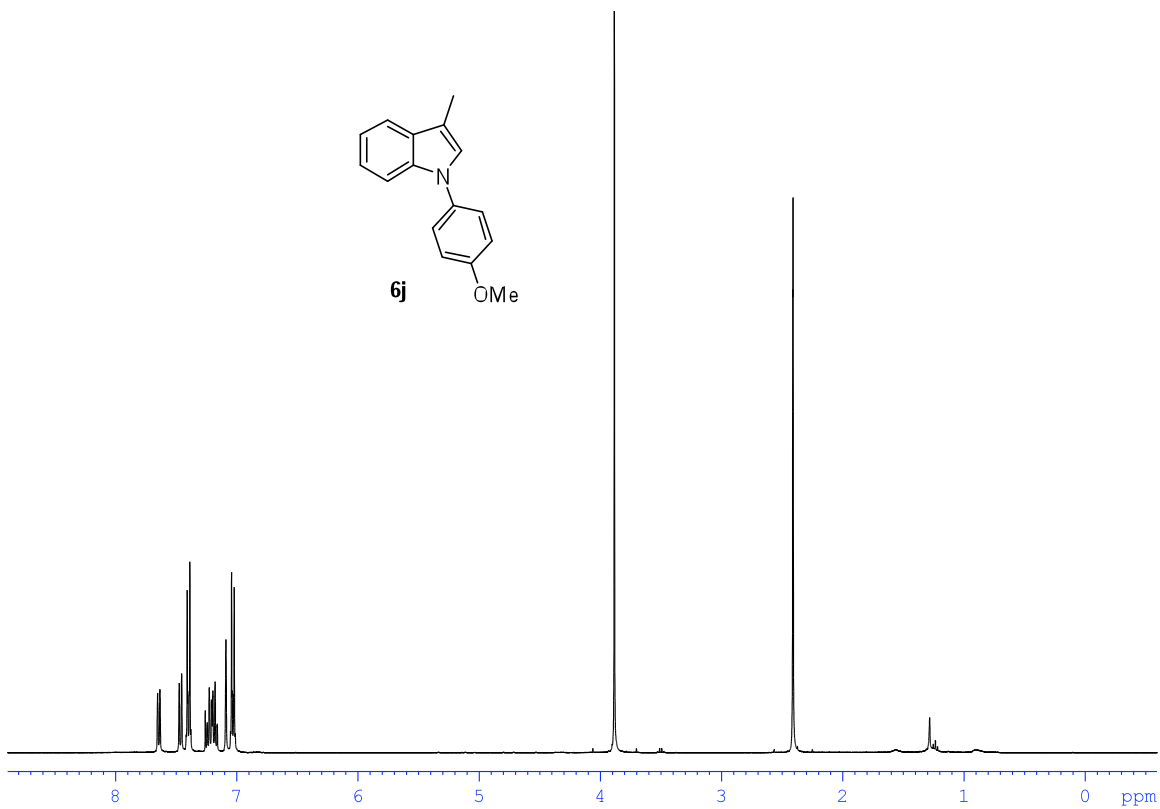
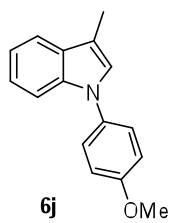


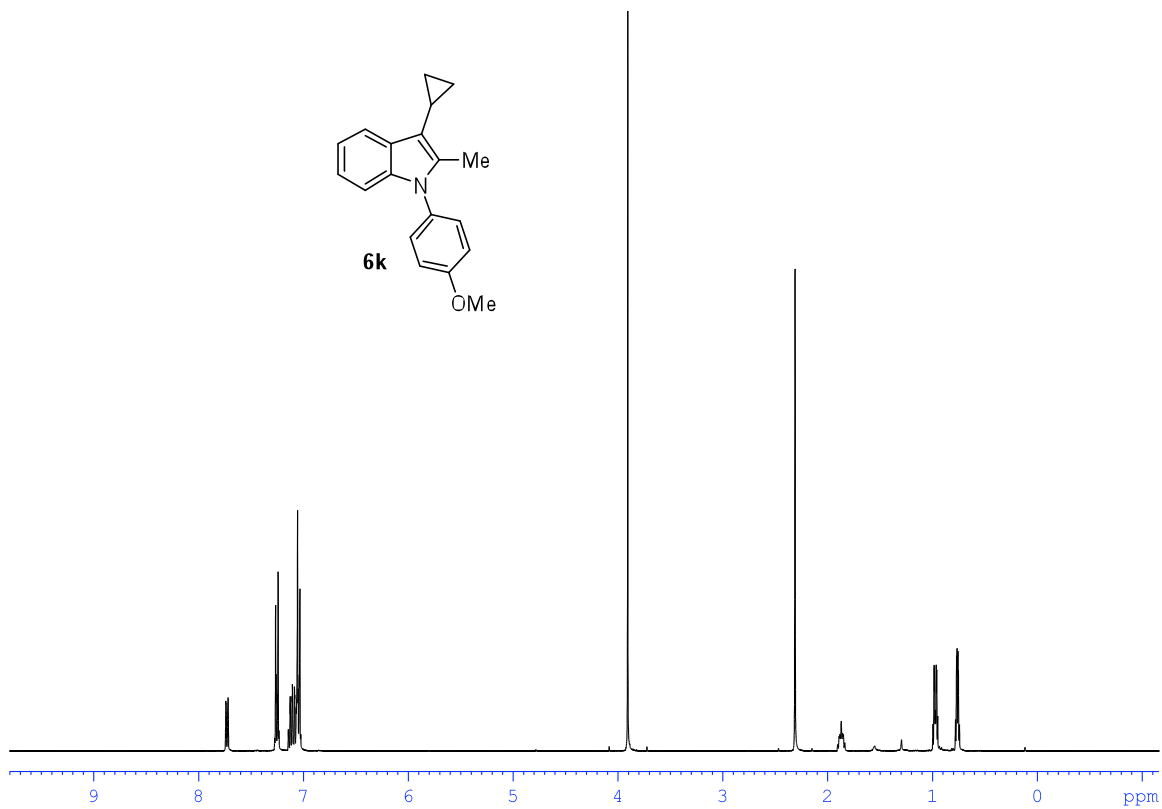
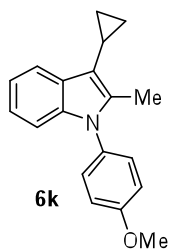




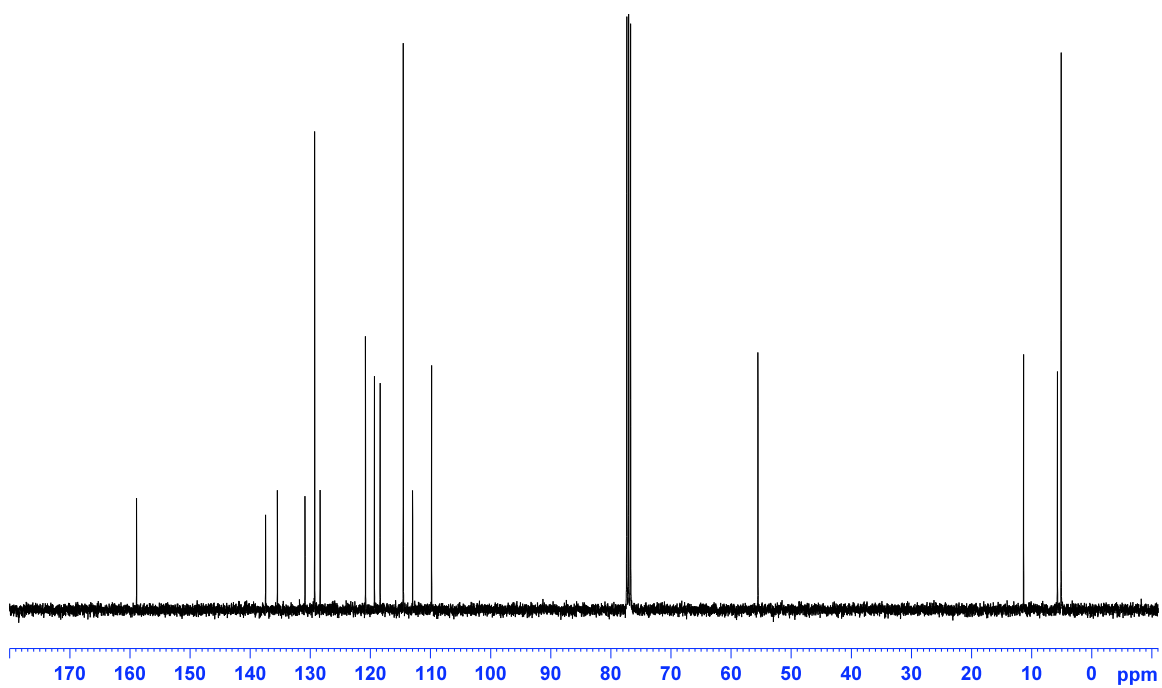


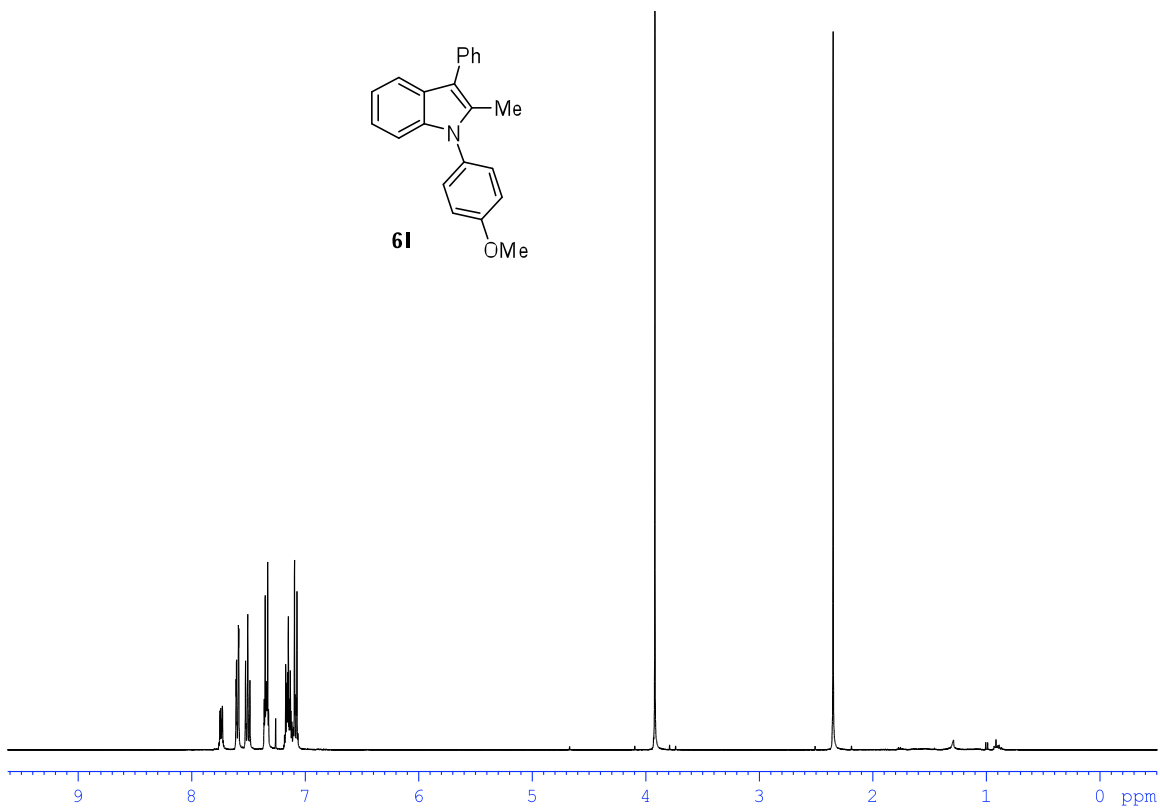
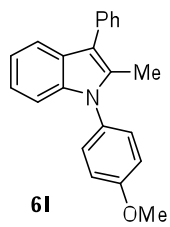






Chemical shifts (ppm) (green): 158.89, 137.42, 135.45, 130.85, 129.88, 128.38, 120.83, 119.35, 118.40, 114.55, 113.00, 109.84, 55.54, 11.35, 5.72, 5.10.





159.15

137.05

136.65

133.91

130.59

129.68

129.37

128.50

127.15

121.58

120.23

118.64

114.90

114.70

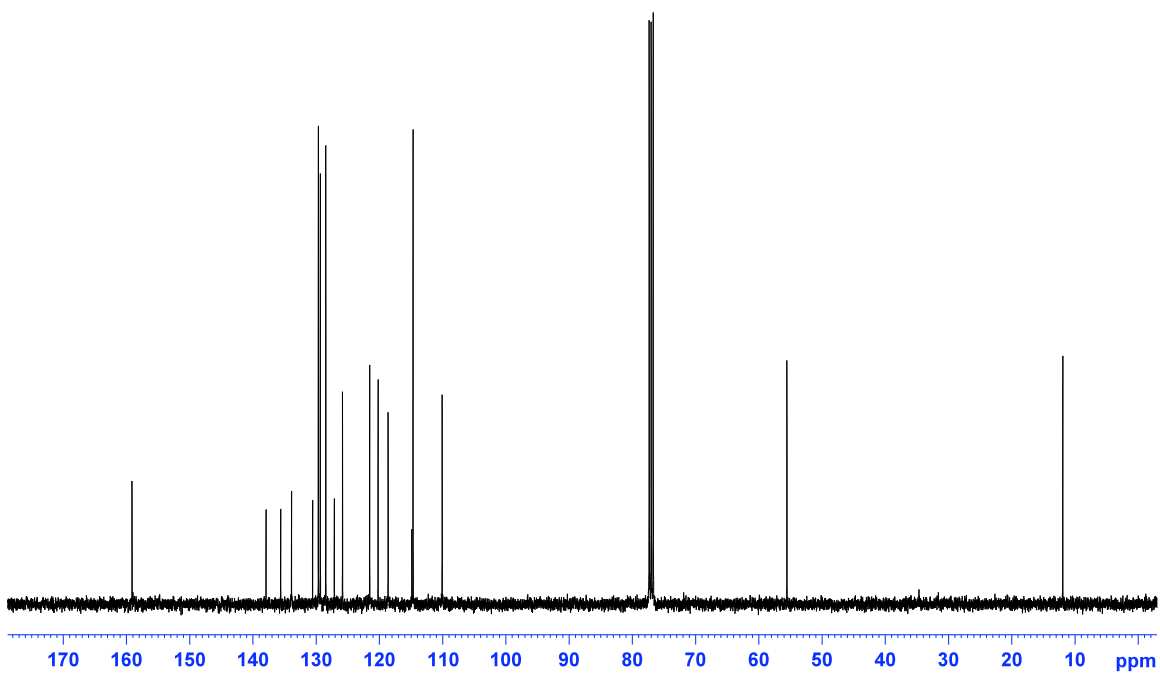
110.10

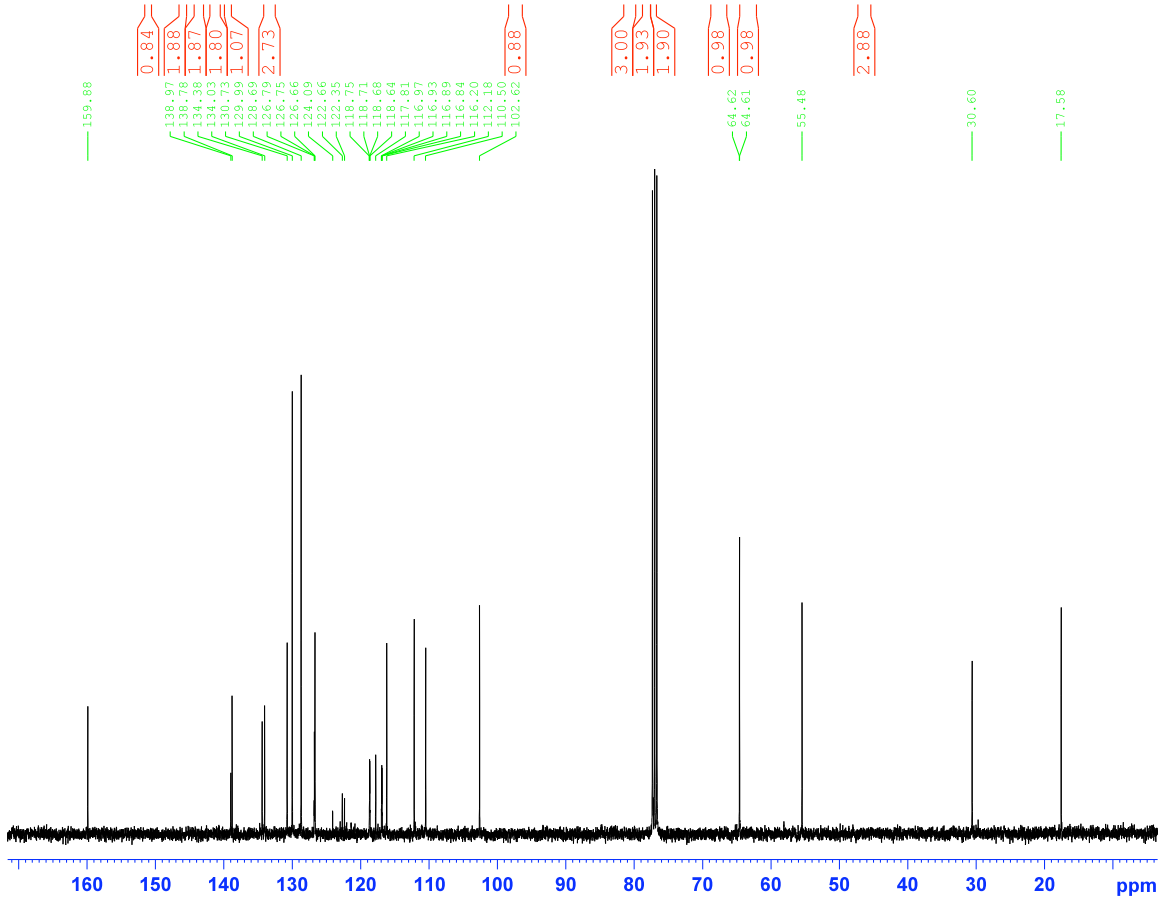
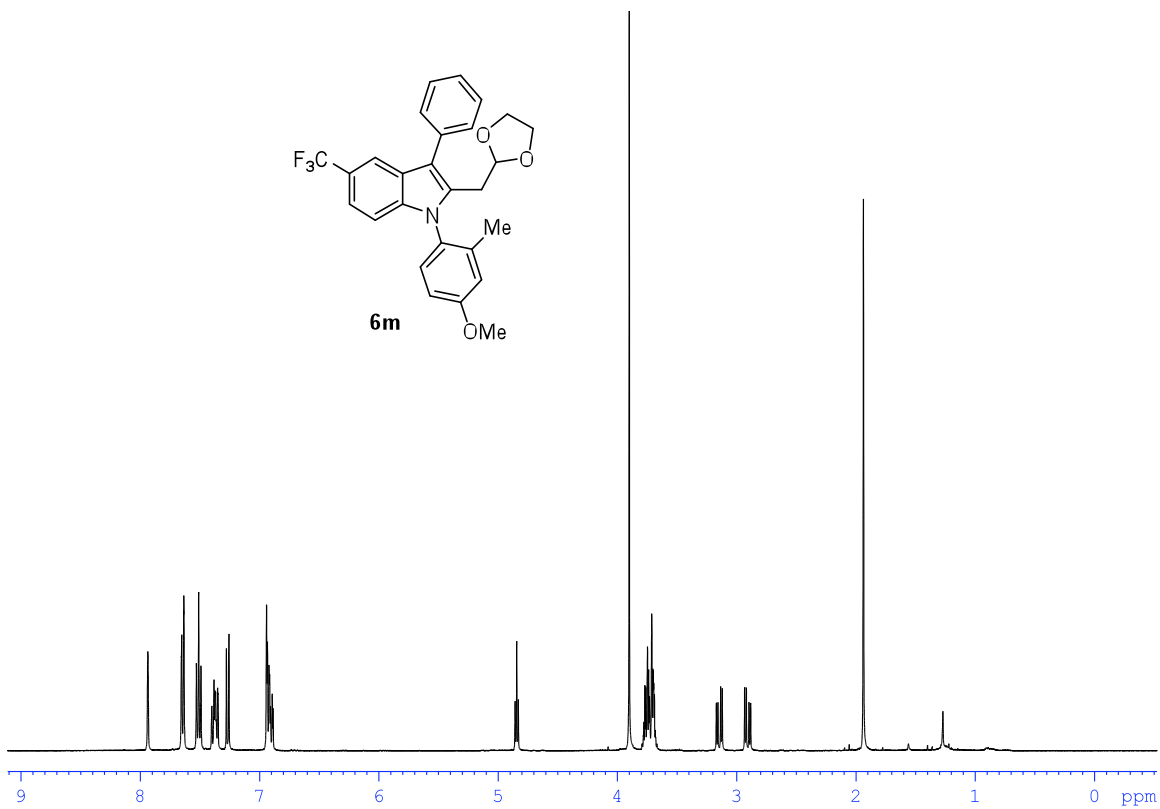
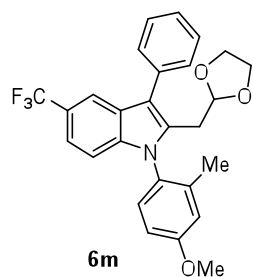
3.00

55.57

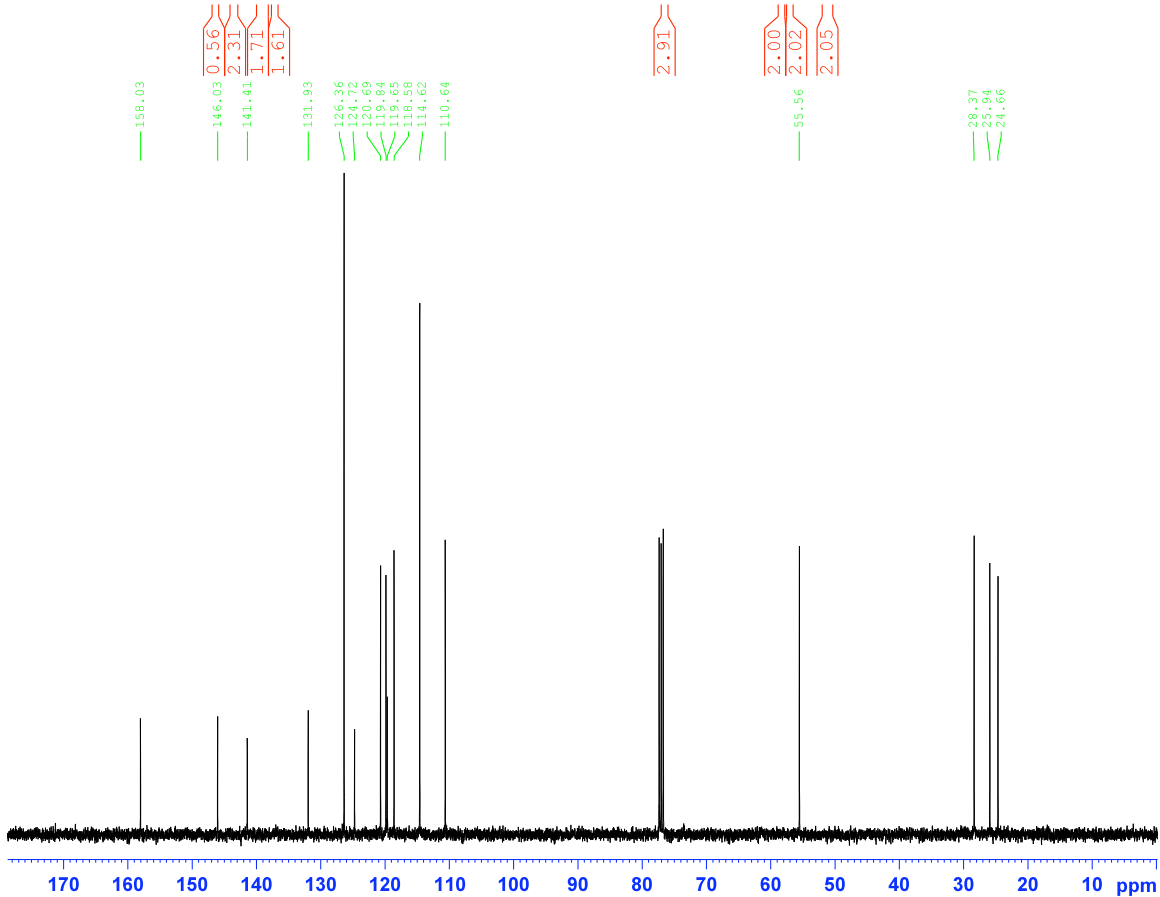
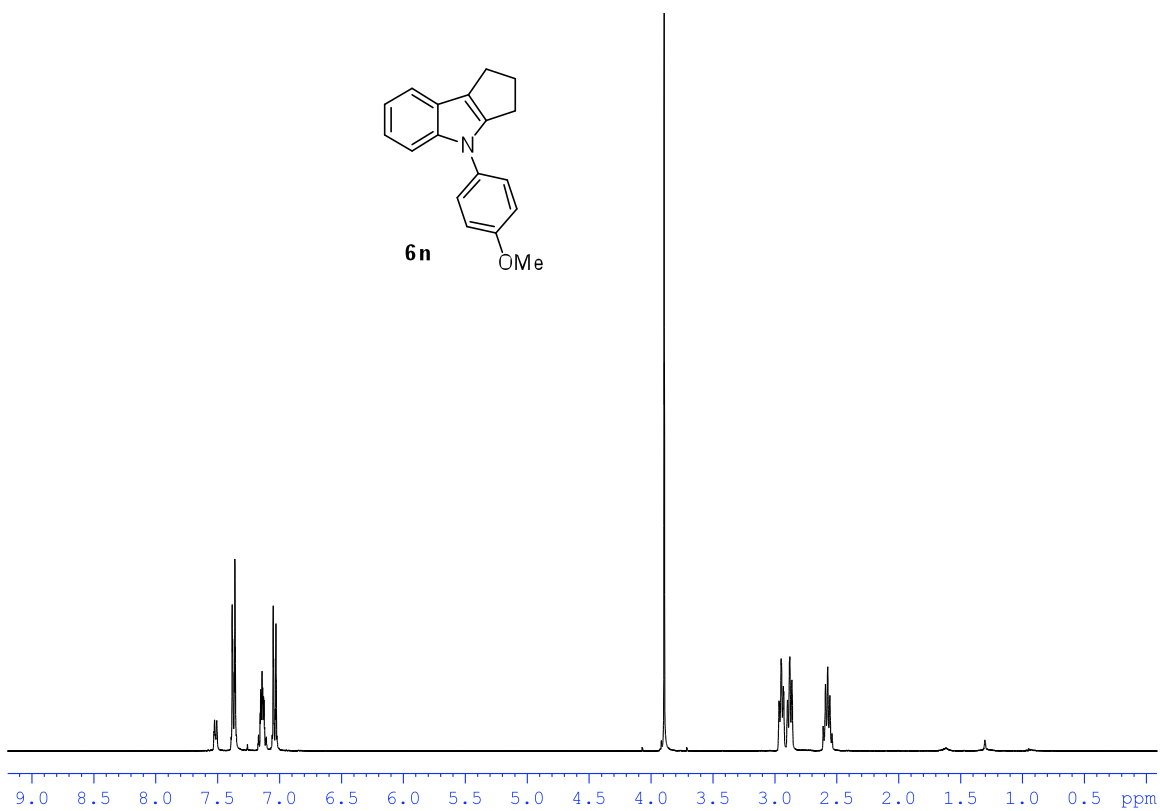
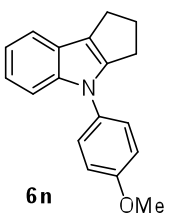
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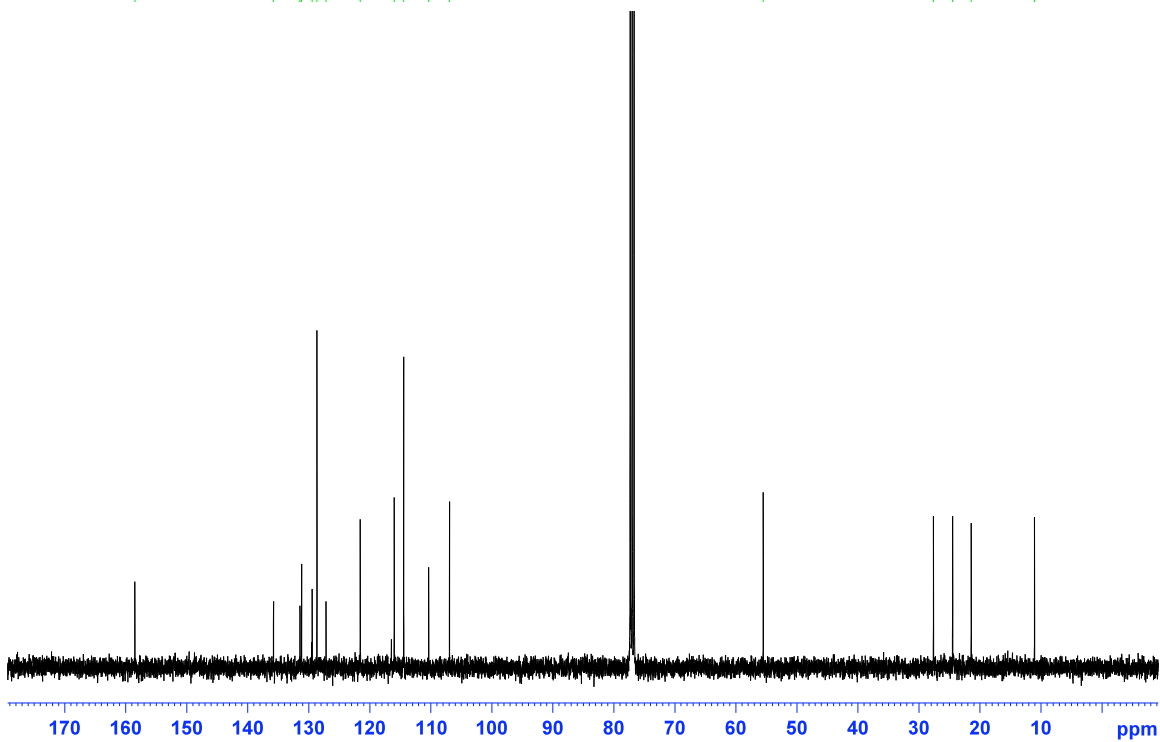
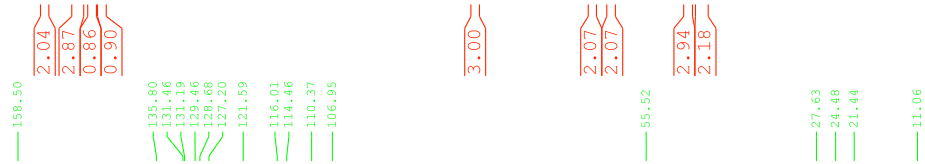
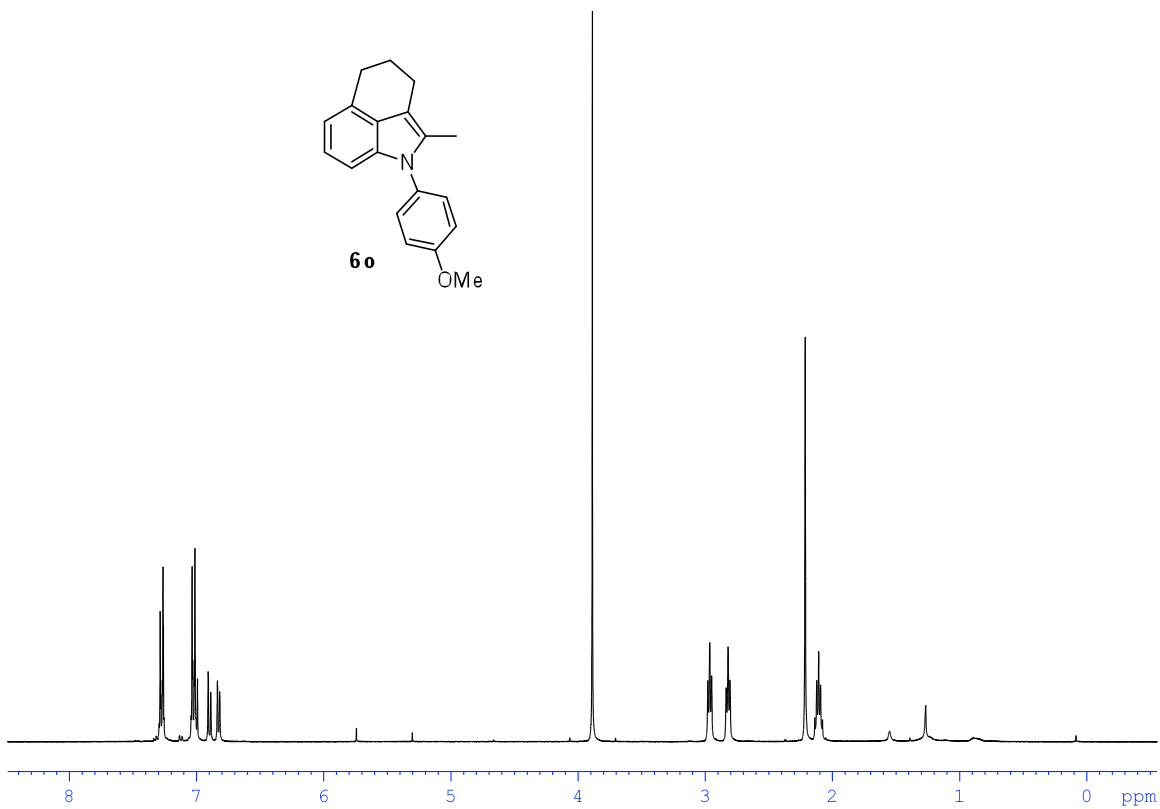
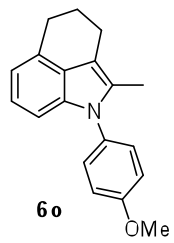
11.94

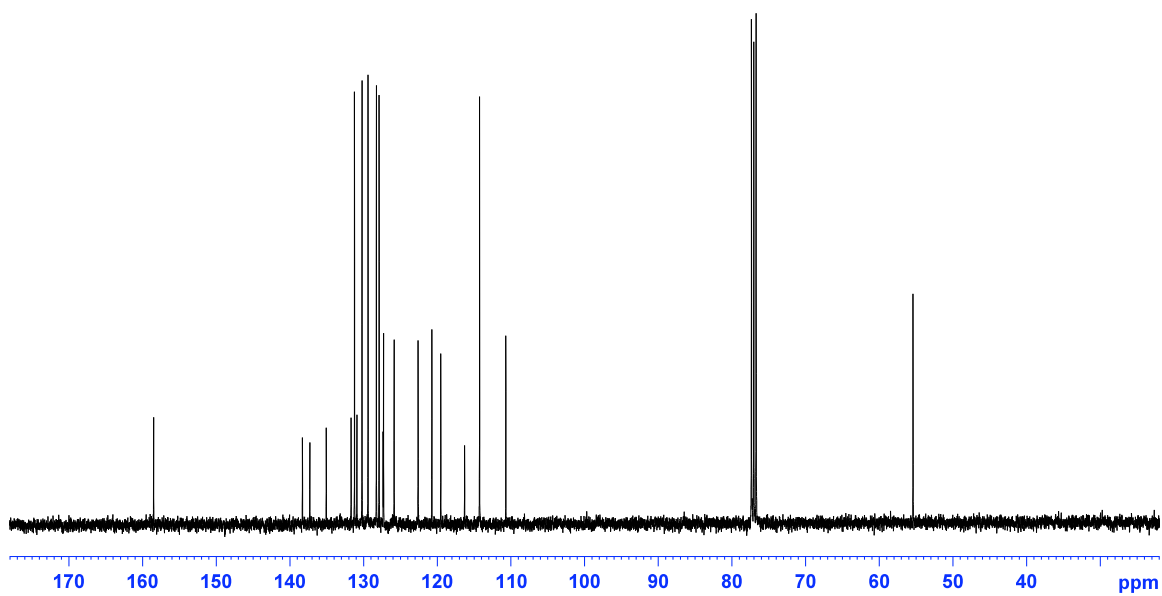
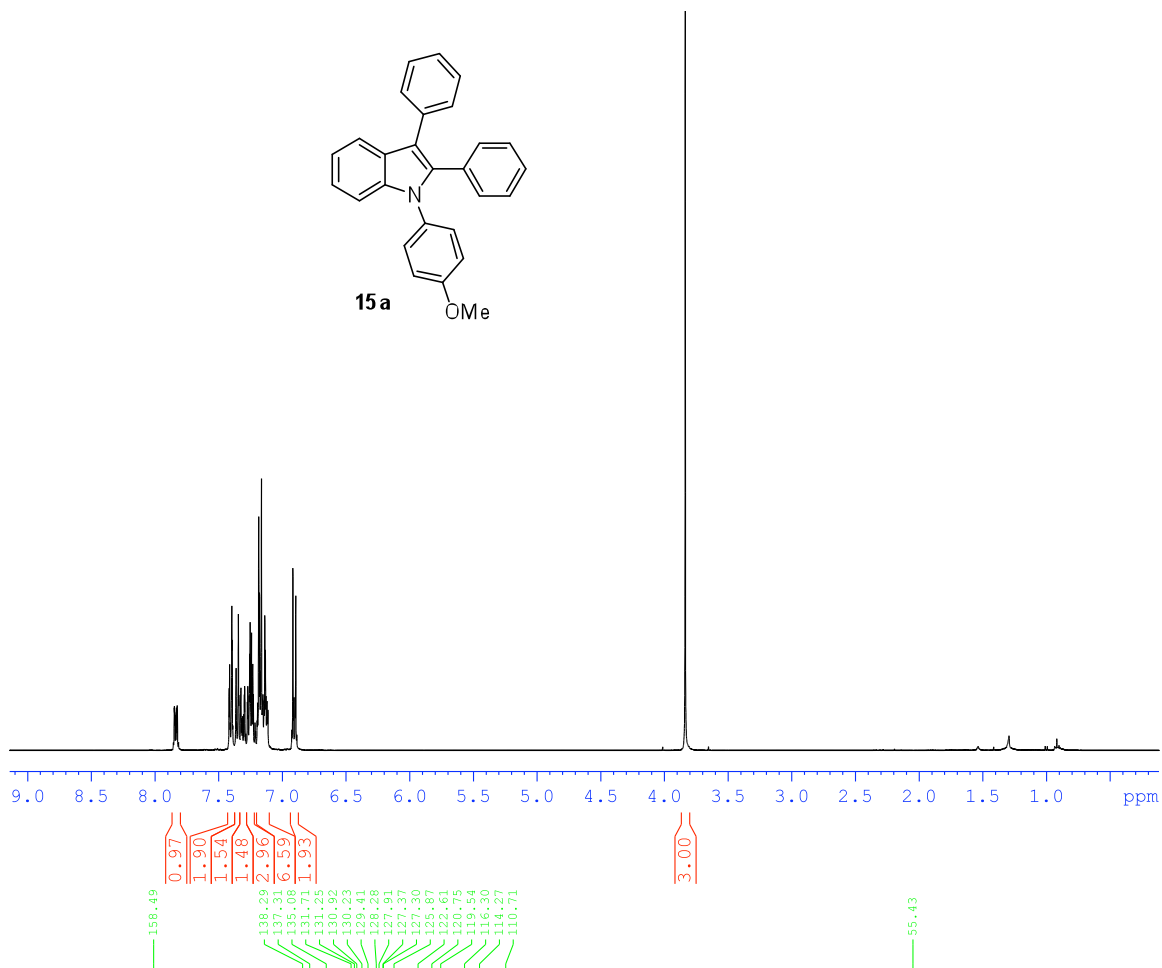
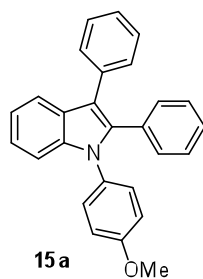


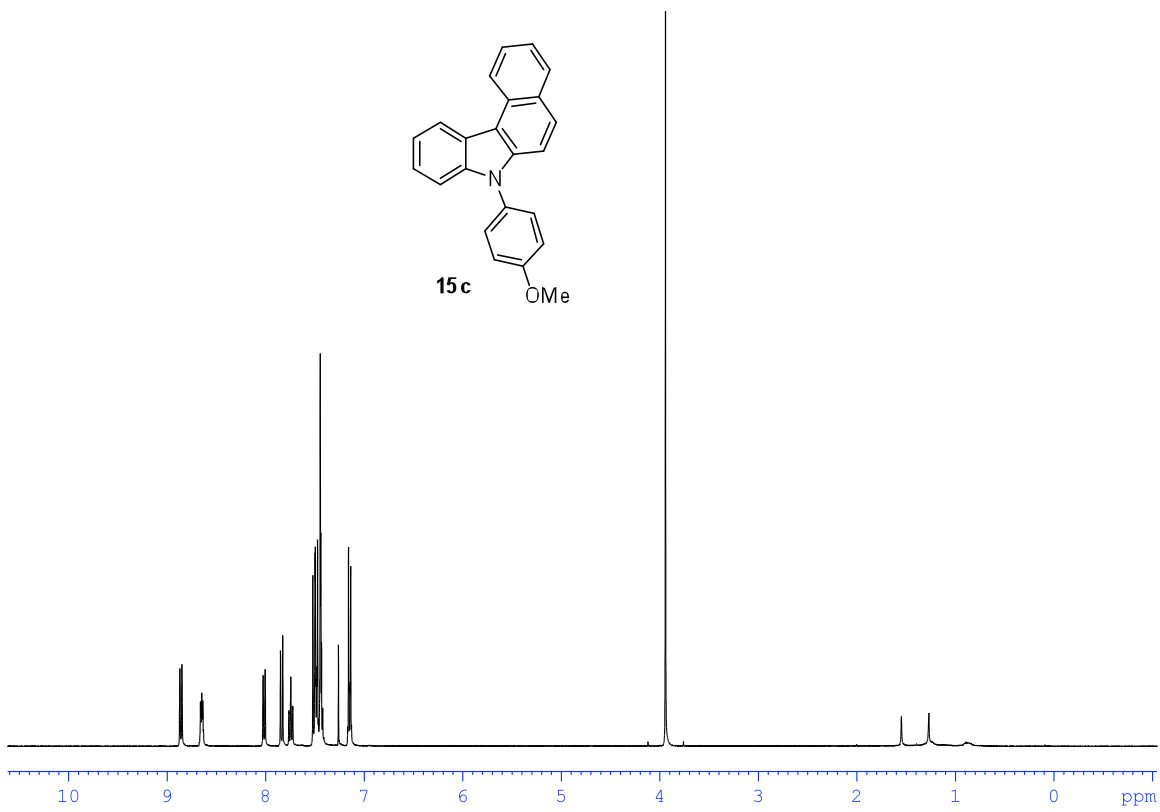
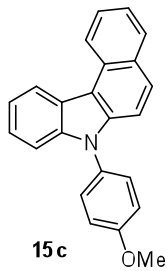












159.20  
 140.59  
 139.05  
 129.92  
 129.88  
 129.20  
 129.10  
 129.08  
 127.29  
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 124.32  
 123.67  
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 111.70  
 110.36  
 55.64  
 3.00  
 1.02  
 1.01  
 0.98  
 0.97  
 0.94  
 6.49  
 1.89

