

## Supporting Information

# $\beta$ -Aminoethyltrifluoroborates: Efficient Aminoethylations via Suzuki-Miyaura Cross-Coupling

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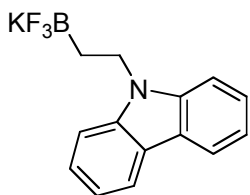
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**General Considerations:** Commercially available reagents were used without further purification. *N*-Boc Vinyl carbamate<sup>1</sup> and *N*-Cbz Vinyl carbamate<sup>2</sup> were prepared

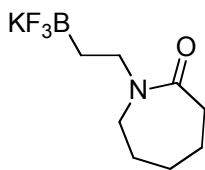
according to the procedures described in the literature. THF was distilled from Na/benzophenone ketyl. Toluene was dried by passing through a column of activated alumina. All other solvents were HPLC grade and used as received. Melting points ( $^{\circ}\text{C}$ ) were determined using a Thomas-Hoover melting point apparatus and are uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR spectra were recorded at 500, 125.8, 128.4 and 470.8 MHz, respectively. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (0.25mm) precoated with a fluorescent indicator. Visualization was effected with ultraviolet light or  $\text{KMnO}_4$  (in aq  $\text{K}_2\text{CO}_3/\text{NaOH}$ ). Standard flash chromatography procedures<sup>3</sup> were performed using 40-63  $\mu\text{m}$  silica gel (200 X 400 mesh). Mass spectra were performed at the mass spectrometry facilities at the University of Pennsylvania.

#### General Method for the Preparation of Potassium $\beta$ -Aminoethyltrifluoroborates.<sup>4</sup>



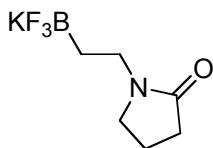
**Potassium 2-(9H-Carbazol-9-yl)ethyltrifluoroborate (1a):** A solution of 2,5-dimethylhexa-2,4-diene (1.81 g, 16.5 mmol) in THF (20 mL) was treated with  $\text{BH}_3$ .THF solution (7.5 mL, 7.5 mmol) at  $0^{\circ}\text{C}$ . The mixture was stirred for 3 h at  $0^{\circ}\text{C}$ , and treated with a solution of 9-vinylcarbazole (0.58 g, 3 mmol) in THF (3 mL) while maintaining the temperature at  $0^{\circ}\text{C}$ . The reaction mixture was allowed to warm to room temperature, stirred for 3 h, cooled in an ice bath, and  $\text{H}_2\text{O}$  (1 mL) was carefully added. After an additional 1.5 h at room temperature, a 37 % aqueous solution of  $\text{CH}_2\text{O}$  (2.5 mL) was added. The mixture was stirred overnight, quenched with brine, and the resulting mixture was extracted with EtOAc. The organic layers were combined, dried ( $\text{MgSO}_4$ ) and then filtered. The solvent was removed under vacuum, and to the residue was added  $\text{KHF}_2$  (0.94 g, 12 mmol),

acetone (10 mL) and H<sub>2</sub>O (4 mL). The mixture was stirred for 4 h at room temperature, evaporated, and the residue was extracted with hot acetone. The organic phases were evaporated and the resulting solids were dried under high vacuum. The crude compound was purified by dissolving in acetone and precipitating in Et<sub>2</sub>O to obtain the title compound **1a** as a white solid (0.85 g, 94% yield). mp = > 210 °C; <sup>1</sup>H NMR (500 MHz, Acetone-*d*<sub>6</sub>) δ 8.08 (d, 2H, *J* = 7.1 Hz), 7.47 (d, 2H, *J* = 8.1 Hz), 7.40-7.37 (m, 2H), 7.13-7.10 (m, 2H), 4.35-4.32 (m, 2H), 0.77-0.73 (m, 2H); <sup>13</sup>C NMR (125.8 MHz, Acetone-*d*<sub>6</sub>) δ 141.1, 126.0, 123.4, 120.7, 118.7, 109.9, 42.0; <sup>11</sup>B NMR (128.4 MHz, Acetone-*d*<sub>6</sub>) δ 5.40 (br s); <sup>19</sup>F NMR (470.8 MHz, Acetone-*d*<sub>6</sub>) δ -141.8 (m); IR (neat) 3053, 2909, 1698, 1595, 1484, 1453, 1255, 752, 725 cm<sup>-1</sup>; HRMS (ES-) *m/z* calcd. for C<sub>14</sub>H<sub>12</sub>BF<sub>3</sub>N (M-K<sup>+</sup>) 262.1014, found 262.1012.



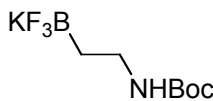
**Potassium 2-(2-Oxazepan-1-yl)ethyltrifluoroborate (1b):** This compound was obtained by the general method for the preparation of potassium β-aminoethyltrifluoroborates using *N*-vinylcaprolactam

(0.41 g, 3 mmol) as the starting material. The title compound was obtained as a white solid (0.56 g, 76% yield). mp = > 210 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 3.20-3.18 (m, 2H), 3.12-3.08 (m, 2H), 2.31-2.29 (m, 2H), 1.60-1.56 (m, 2H), 1.51-1.45 (m, 4H), 0.16-0.12 (m, 2H); <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 172.9, 47.3, 45.7, 36.9, 29.3, 28.5, 23.1; <sup>11</sup>B NMR (128.4 MHz, DMSO-*d*<sub>6</sub>) δ 3.93 (br s); <sup>19</sup>F NMR (470.8 MHz, DMSO-*d*<sub>6</sub>) δ -141.2 (m); IR (neat) 2921, 1620, 1494, 1454, 1249, 1229, 1006, 962, 869 cm<sup>-1</sup>; HRMS (ES-) *m/z* calcd. for C<sub>8</sub>H<sub>14</sub>BF<sub>3</sub>NO (M-K<sup>+</sup>) 208.1120, found 208.1114.



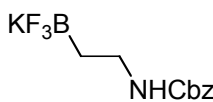
**Potassium 2-(2-Oxopyrrolidin-1-yl)ethyltrifluoroborate (1c):** This compound was obtained by the general method for the preparation of potassium  $\beta$ -aminoethyltrifluoroborates using *N*-vinyl-2-pyrrolidone

(0.330 g, 3 mmol) as the starting material. The title compound was obtained as a white solid (0.440 g, 68% yield). mp = > 195 °C;  $^1\text{H}$  NMR (500 MHz, DMSO-*d*6)  $\delta$  3.25 (t, 2H,  $J$  = 7.1 Hz), 3.04-3.01 (m, 2H), 2.12 (t, 2H,  $J$  = 7.8 Hz), 1.87-1.81 (m, 2H), 0.17-0.12 (m, 2H);  $^{13}\text{C}$  NMR (125.8 MHz, DMSO-*d*6)  $\delta$  172.3, 45.5, 40.4, 31.0, 17.2;  $^{11}\text{B}$  NMR (128.4 MHz, DMSO-*d*6)  $\delta$  4.93 (br s);  $^{19}\text{F}$  NMR (470.8 MHz, DMSO-*d*6)  $\delta$  -142.3 (m); IR (neat) 2913, 2359, 1658, 1495, 1450, 1293, 1246, 1024, 967, 860  $\text{cm}^{-1}$ ; HRMS (ES-)  $m/z$  calcd. for  $\text{C}_6\text{H}_{10}\text{BF}_3\text{NO}$  (M-K $^+$ ) 180.0807, found 180.0816.



**Potassium 2-(*tert*-Butoxycarbonylamino)ethyltrifluoroborate (1d):**

This compound was obtained on a 1 mmol scale by the general method for the preparation of potassium  $\beta$ -aminoethyltrifluoroborates using *N*-Boc vinylcarbamate<sup>1</sup> (143 mg, 1 mmol) as the starting material. The title compound was obtained as a white solid (130 mg, 52% yield). mp = > 185 °C;  $^1\text{H}$  NMR (500 MHz, DMSO-*d*6)  $\delta$  5.79 (s, 1H), 2.85-2.81 (m, 2H), 1.34 (s, 9H), 0.14-0.12 (m, 2H);  $^{13}\text{C}$  NMR (125.8 MHz, DMSO-*d*6)  $\delta$  155.1, 76.6, 38.5, 28.3;  $^{11}\text{B}$  NMR (128.4 MHz, DMSO-*d*6)  $\delta$  3.93 (br s);  $^{19}\text{F}$  NMR (470.8 MHz, DMSO-*d*6)  $\delta$  -136.6 (m); IR (neat) 3411, 2975, 2360, 1676, 1522, 1364, 1034  $\text{cm}^{-1}$ ; HRMS (ES-)  $m/z$  calcd. for  $\text{C}_7\text{H}_{14}\text{BF}_3\text{NO}_2$  (M-K $^+$ ) 212.1069, found 212.1078.

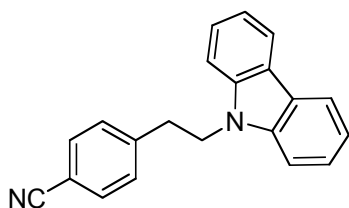


**Potassium 2-(Benzyloxycarbonylamino)ethyltrifluoroborate (1e):**

This compound was obtained on a 1 mmol scale by the general

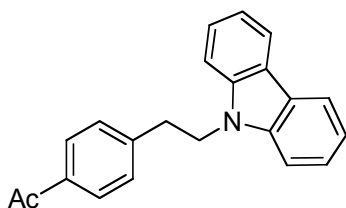
method for the preparation of potassium  $\beta$ -aminoethyltrifluoroborates using *N*-Cbz vinylcarbamate<sup>2</sup> (177 mg, 1 mmol) as the starting material. The title compound was obtained as a white solid (133 mg, 50% yield). mp = > 195 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*6)  $\delta$  7.34-7.25 (m, 5H), 6.36 (br s, 1H), 4.93 (s, 2H), 2.90-2.86 (m, 2H), 0.16-0.13 (m, 2H); <sup>13</sup>C NMR (125.8 MHz, CD<sub>3</sub>CN)  $\delta$  156.1, 137.9, 128.4, 127.7 (2C), 65.3, 39.1; <sup>11</sup>B NMR (128.4 MHz, DMSO-*d*6)  $\delta$  4.17 (br s); <sup>19</sup>F NMR (470.8 MHz, DMSO-*d*6)  $\delta$  -136.9 (m); IR (neat) 3411, 2975, 2360, 1686, 1522, 1272 cm<sup>-1</sup>; HRMS (ES-) *m/z* calcd. for C<sub>10</sub>H<sub>12</sub>BF<sub>3</sub>NO<sub>2</sub> (M-K<sup>+</sup>) 246.0913, found 246.0923.

#### Representative Procedure for the Cross-coupling Reaction of Potassium $\beta$ -Aminoethyltrifluoroborates and Aryl Electrophiles.



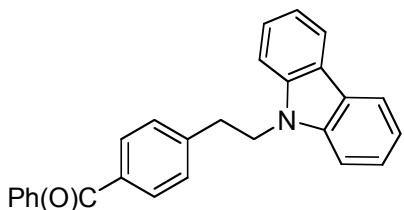
**4-(2-(9H-Carbazol-9-yl)ethyl)benzonitrile (2a).** To a mixture of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), 4-bromobenzonitrile (91 mg, 0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (487 mg, 1.5 mmol), and PdCl<sub>2</sub>(dppf)<sub>CH<sub>2</sub>Cl<sub>2</sub></sub> (20.4 mg, 0.025 mmol) was added toluene/H<sub>2</sub>O (3:1, 3.2 mL). The reaction was heated at 80 °C with stirring under a nitrogen atmosphere for 12 h, and then cooled to room temperature. A saturated solution of NH<sub>4</sub>Cl was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, dried (MgSO<sub>4</sub>) and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with hexane/ethyl acetate) to afford a white solid (133 mg, 90% yield). mp = 155-157 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, 2H, *J* = 7.7

Hz), 7.46 (d, 2H,  $J = 7.6$  Hz), 7.41-7.38 (m, 2H), 7.23-7.19 (m, 4H), 7.14 (d, 2H,  $J = 7.8$  Hz), 4.53 (t, 2H,  $J = 7.0$  Hz), 3.19 (t, 2H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 139.9, 132.2, 129.6, 125.7, 122.8, 120.4, 119.1, 118.7, 110.5, 108.2, 44.1, 35.2; IR (neat) 2360, 2228, 1995, 1454, 1347, 751, 722  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{16}\text{N}_2$  ( $\text{M}^+$ ) 296.1313, found 296.1319.



**1-(4-(2-(9H-Carbazol-9-yl)ethyl)phenyl)ethanone (2b).**

This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromoacetophenone (99 mg, 0.5 mmol) to afford the title compound as a white solid (127 mg, 82%). mp = 124-126  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.81 (d, 2H,  $J = 8.1$  Hz), 7.42-7.39 (m, 2H), 7.28-7.20 (m, 6H), 4.52 (t, 2H,  $J = 7.4$  Hz), 3.17 (t, 2H,  $J = 7.4$  Hz), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 144.2, 140.0, 135.6, 129.0, 128.6, 125.6, 122.8, 120.3, 119.0, 108.3, 44.3, 35.1, 26.5; IR (neat) 1995, 1678, 1605, 1452, 1266, 749, 722  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{19}\text{NO}$  ( $\text{M}^+$ ) 313.1466, found 313.1464.

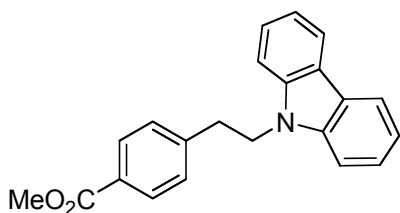


**(4-(2-(9H-Carbazol-9-**

**yl)ethyl)phenyl)(phenyl)methanone (2c).**

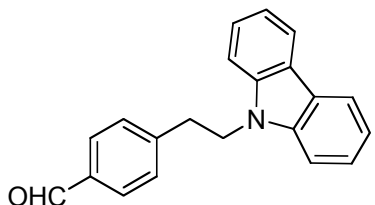
This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromobenzophenone (130 mg, 0.5 mmol) to afford the title compound as a pale yellow solid (147 mg, 79% yield). mp = 87-89  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J$

= 7.7 Hz), 7.67 (d, 2H,  $J = 8.2$  Hz), 7.61 (d, 2H,  $J = 8.0$  Hz), 7.57-7.55 (m, 1H), 7.45-7.39 (m, 4H), 7.27-7.21 (m, 4H), 7.15 (d, 2H,  $J = 7.9$  Hz), 4.57 (t, 2H,  $J = 7.2$  Hz), 3.21 (t, 2H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 143.3, 140.0, 137.5, 135.9, 132.2, 130.2, 129.9, 128.6, 128.1, 125.5, 122.8, 120.3, 118.9, 108.4, 44.3, 35.1; IR (neat) 3053, 1711, 1658, 1605, 1484, 1453, 1278, 750, 724  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{21}\text{NO}$  ( $\text{M}^+$ ) 375.1623, found 375.1614.



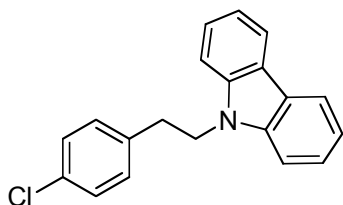
**Methyl 4-(2-(9H-Carbazol-9-yl)ethyl)benzoate (2d).**

This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and methyl 4-bromobenzoate (107 mg, 0.5 mmol) to afford the title compound as a white solid (137 mg, 84% yield). mp = 113-115  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.91 (d, 2H,  $J = 8.2$  Hz), 7.43-7.39 (m, 2H), 7.29-7.20 (m, 6H), 4.53 (t, 2H,  $J = 7.7$  Hz), 3.89 (s, 3H), 3.18 (t, 2H,  $J = 7.7$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 144.0, 140.0, 129.8, 128.8, 128.5, 125.6, 122.8, 120.3, 119.0, 108.3, 51.9, 44.3, 35.1; IR (neat) 1995, 1718, 1484, 1452, 1278, 749, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{19}\text{NO}_2$  ( $\text{M}^+$ ) 329.1415, found 329.1411.

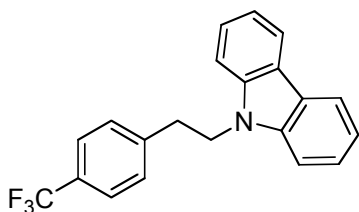


**4-(2-(9H-Carbazol-9-yl)ethyl)benzaldehyde (2e).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromobenzaldehyde (92 mg, 0.5 mmol) to afford the title compound as a white solid (125 mg, 84% yield). mp = 130-132  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,

CDCl<sub>3</sub>)  $\delta$  9.89 (s, 1H), 8.07 (d, 2H,  $J = 7.7$  Hz), 7.68 (d, 2H,  $J = 7.8$  Hz), 7.40-7.36 (m, 2H), 7.23-7.19 (m, 6H), 4.49 (t, 2H,  $J = 7.2$  Hz), 3.16 (t, 2H,  $J = 7.2$  Hz); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  191.7, 145.8, 139.9, 134.9, 129.9, 129.4, 125.6, 122.8, 120.3, 119.0, 108.3, 44.1, 35.2; IR (neat) 1995, 1697, 1604, 1484, 1452, 748, 721 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>)  $m/z$  calcd. for C<sub>21</sub>H<sub>17</sub>NO (M<sup>+</sup>) 299.1310, found 299.1305.



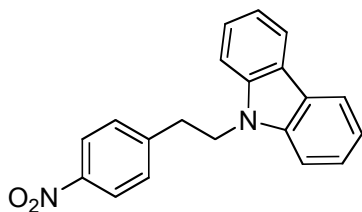
**9-(4-Chlorophenethyl)-9H-carbazole (2f):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromochlorobenzene (95 mg, 0.5 mmol) to afford the title compound as a white solid (110 mg, 73% yield). mp = 143-145 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.43-7.40 (m, 2H), 7.28-7.18 (m, 6H), 7.04 (d, 2H,  $J = 8.2$  Hz), 4.48 (t, 2H,  $J = 7.5$  Hz), 3.08 (t, 2H,  $J = 7.5$  Hz); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  140.0, 137.1, 132.4, 130.1, 128.7, 125.6, 122.8, 120.3, 119.0, 108.4, 44.6, 34.5; IR (neat) 1995, 1595, 1487, 1453, 1235, 753, 723 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>)  $m/z$  calcd. for C<sub>20</sub>H<sub>16</sub>ClN (M<sup>+</sup>) 305.0971, found 305.0974.



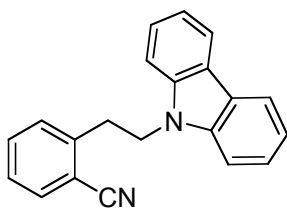
**9-(4-(Trifluoromethyl)phenethyl)-9H-carbazole (2g).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromobenzotrifluoride (112 mg, 0.5 mmol) to afford the title compound as a white solid (125 mg, 74% yield). mp = 101-103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.47 (d, 2H,  $J = 7.9$  Hz), 7.42-7.39 (m, 2H), 7.26-7.21



(m, 6H), 4.52 (t, 2H,  $J = 7.4$  Hz), 3.17 (t, 2H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 140.0, 129.1, 129.0 (q,  $^2J_{\text{CF}} = 32.6$  Hz), 125.6, 125.4 (q,  $^3J_{\text{CF}} = 3.8$  Hz), 124.1 (q,  $^1J_{\text{CF}} = 271.6$  Hz), 122.9, 120.4, 119.0, 108.3, 44.4, 35.0;  $^{19}\text{F}$  NMR (470.8 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.8 (s); IR (neat) 2360, 1995, 1484, 1452, 1325, 1121, 1067, 749, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{16}\text{F}_3\text{N}$  ( $\text{M}^+$ ) 339.1234, found 339.1229.

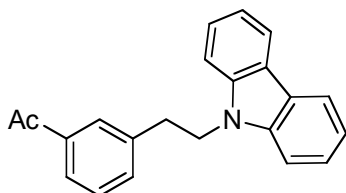


**9-(4-Nitrophenethyl)-9H-carbazole (2h):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol) to afford the title compound as a yellow solid (124 mg, 79% yield). mp = 137-139  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d, 2H,  $J = 8.1$  Hz), 8.01 (d, 2H,  $J = 8.6$  Hz), 7.40-7.36 (m, 2H), 7.23-7.16 (m, 6H), 4.53 (t, 2H,  $J = 7.1$  Hz), 3.22 (t, 2H,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 146.3, 139.9, 129.6, 125.7, 123.7, 122.9, 120.4, 119.2, 108.2, 44.0, 35.0; IR (neat) 1995, 1598, 1515, 1484, 1452, 1343, 749, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$  ( $\text{M}^+$ ) 316.1211, found 316.1197.



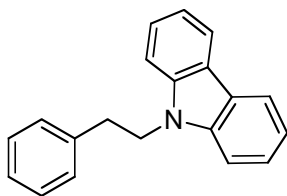
**2-(2-(9H-Carbazol-9-yl)ethyl)benzonitrile (2i):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 2-bromobenzonitrile (91 mg, 0.5 mmol) to afford the title compound as a white solid (125 mg, 85% yield). mp = 133-135 $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d, 2H,  $J = 7.4$  Hz), 7.64 (d, 1H,  $J = 7.4$  Hz), 7.43-7.20 (m, 8H), 7.02 (d, 1H,  $J = 7.6$  Hz), 4.59 (t,

2H,  $J = 7.4$  Hz), 3.35 (t, 2H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 140.0, 132.9, 132.8, 130.4, 127.3, 125.8, 122.9, 120.3, 119.1, 117.9, 112.4, 108.4, 43.4, 33.9; IR (neat) 2360, 2221, 1595, 1484, 1453, 1325, 749, 723  $\text{cm}^{-1}$ ; HRMS (ES+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 319.1211, found 319.1208.



**1-(3-(2-(9H-Carbazol-9-yl)ethyl)phenyl)ethanone (2j).**

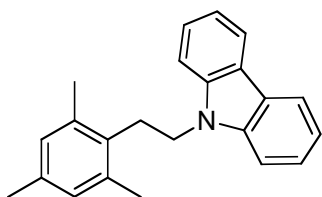
This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 2-bromoacetophenone (99 mg, 0.5 mmol) to afford the title compound as a white solid (123 mg, 79% yield). mp = 121-123  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d, 2H,  $J = 7.5$  Hz), 7.75-7.73 (m, 1H), 7.57 (br s, 1H), 7.42-7.37 (m, 2H), 7.31-7.19 (m, 6H), 4.53 (t, 2H,  $J = 7.2$  Hz), 3.18 (t, 2H,  $J = 7.2$  Hz), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 140.0, 139.2, 137.3, 133.5, 128.7, 128.6, 126.6, 125.6, 122.8, 120.3, 119.0, 108.5, 44.4, 34.9, 26.4; IR (neat) 3048, 2929, 1676, 1584, 1486, 1455, 1350, 1294, 750, 723  $\text{cm}^{-1}$ ; HRMS (ES+)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{19}\text{NONa}$  ( $\text{M}+\text{Na}^+$ ) 336.1364, found 336.1361.



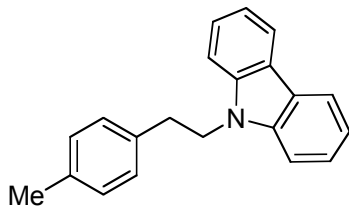
**9-Phenethyl-9H-carbazole (2k):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and

bromobenzene (78 mg, 0.5 mmol) to afford the title compound as a white solid (120 mg, 89% yield). mp = 109-111  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.44-7.41 (m, 2H), 7.32 (d, 2H,  $J = 8.1$  Hz), 7.26-7.17 (m, 7H), 4.51 (t, 2H,  $J = 7.7$  Hz),

3.11 (t, 2H,  $J = 7.7$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 138.6, 128.7, 128.5, 126.5, 125.5, 122.8, 120.3, 118.8, 108.4, 44.7, 35.1. IR (neat) 1995, 1596, 1483, 1452, 1325, 747, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}$  ( $\text{M}^+$ ) 271.1361, found 271.1359.

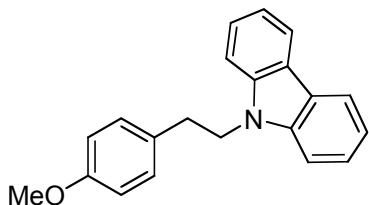


**9-(2,4,6-Trimethylphenethyl)-9H-carbazole (2l):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 2-bromomesitylene (99 mg, 0.5 mmol) to afford the title compound as a white solid (137 mg, 88% yield). mp = 134-136  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d, 2H,  $J = 7.8$  Hz), 7.46-7.44 (m, 2H), 7.40 (d, 2H,  $J = 8.1$  Hz), 7.25-7.22 (m, 2H), 6.88 (s, 2H), 4.37 (t, 2H,  $J = 8.1$  Hz), 3.12 (t, 2H,  $J = 8.1$  Hz), 2.40 (s, 6H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 136.3, 135.9, 131.9, 129.2, 125.7, 122.9, 120.4, 118.9, 108.3, 41.9, 28.6, 20.7, 19.9; IR (neat) 1995, 1483, 1460, 1450, 1343, 747, 719  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{23}\text{N}$  ( $\text{M}^+$ ) 313.1830, found 313.1821.



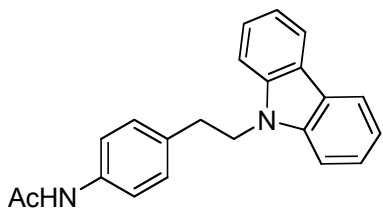
**9-(4-Methylphenethyl)-9H-carbazole (2m):** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromotoluene (85 mg, 0.5 mmol) to afford the title compound as a white solid (115 mg, 81% yield). mp = 117-119  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.43 (t, 2H,  $J = 7.2$  Hz), 7.34 (d, 2H,  $J = 8.1$  Hz), 7.21 (t, 2H,  $J = 7.7$  Hz),

7.08 (s, 4H), 4.46 (t, 2H,  $J = 7.8$  Hz), 3.06 (t, 2H,  $J = 7.8$  Hz), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 136.1, 135.5, 129.3, 128.6, 125.6, 122.8, 120.3, 118.8, 108.5, 44.9, 34.7, 21.0; IR (neat) 1995, 1697, 1514, 1487, 1463, 1455, 1345, 745, 718  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{19}\text{N}$  ( $\text{M}^+$ ) 285.1517, found 285.1502.



**9-(4-Methoxyphenethyl)-9H-carbazole (2n).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165

mg, 0.55 mmol), and 4-bromoanisole (93 mg, 0.5 mmol) to afford the title compound as a white solid (105 mg, 70% yield). mp = 85-87  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.44-7.41 (m, 2H), 7.32 (d, 2H,  $J = 8.2$  Hz), 7.24-7.20 (m, 2H), 7.08 (d, 2H,  $J = 8.6$  Hz), 6.80 (d, 2H,  $J = 8.6$  Hz), 4.46 (t, 2H,  $J = 7.6$  Hz), 3.76 (s, 3H), 3.05 (t, 2H,  $J = 7.6$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 140.1, 130.7, 129.7, 125.6, 122.8, 120.3, 118.8, 114.0, 108.5, 55.2, 45.0, 34.2. IR (neat) 3049, 1995, 1511, 1484, 1462, 1452, 1247, 749, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{19}\text{NO}$  ( $\text{M}^+$ ) 301.1466, found 301.1458.

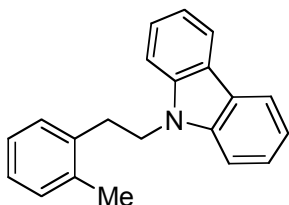


**N-(4-(2-(9H-Carbazol-9-yl)ethyl)phenyl)acetamide**

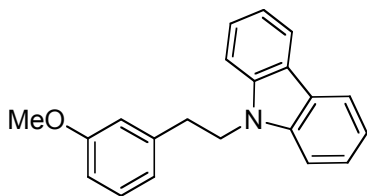
**(2o):** This product was obtained by the general method from the reaction of potassium  $\beta$ -

aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 4-bromoacetanilide (107 mg, 0.5 mmol) to afford the title compound as a white solid (119 mg, 73% yield). mp = 179-181  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.42-7.41 (m, 2H), 7.37 (d,

2H,  $J = 8.1$  Hz), 7.31 (d, 2H,  $J = 8.1$  Hz), 7.23-7.20 (m, 2H), 7.11-7.09 (m, 3H), 4.48 (t, 2H,  $J = 7.4$  Hz), 3.08 (t, 2H,  $J = 7.4$  Hz), 2.15 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 140.1, 136.4, 134.6, 129.3, 125.6, 122.8, 120.3, 120.1, 118.8, 108.5, 44.8, 34.5, 24.5; IR (neat) 1995, 1656, 1513, 1452, 1324, 749, 722  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}$  ( $\text{M}^+$ ) 328.1575, found 328.1587.

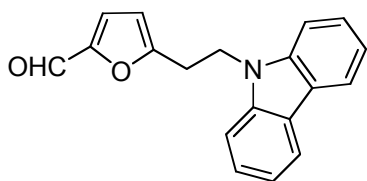


**9-(2-Methylphenethyl)-9H-carbazole (2p).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 2-bromotoluene (85 mg, 0.5 mmol) to afford the title compound as a white solid (112 mg, 79% yield). mp = 97-99  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.45-7.41 (m, 2H), 7.33 (d, 2H,  $J = 8.2$  Hz), 7.23-7.20 (m, 2H), 7.14-7.11 (m, 4H), 4.47 (t, 2H,  $J = 7.8$  Hz), 3.11 (t, 2H,  $J = 7.8$  Hz), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 136.9, 136.1, 130.4, 129.4, 126.8, 126.3, 125.6, 122.9, 120.3, 118.9, 108.3, 43.6, 32.4, 19.3; IR (neat) 2939, 1627, 1490, 1461, 1346, 743, 722  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{19}\text{N}$  ( $\text{M}^+$ ) 285.1517, found 285.1509.



**9-(3-Methoxyphenethyl)-9H-carbazole (2q).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 2-bromoanisole (93 mg, 0.5 mmol) to afford the title compound as a white solid (102 mg, 68% yield). mp = 81-83  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.7$  Hz), 7.44-7.41 (m, 2H), 7.31 (d, 2H,  $J = 8.1$  Hz), 7.23-7.17 (m, 3H), 6.79 (d,

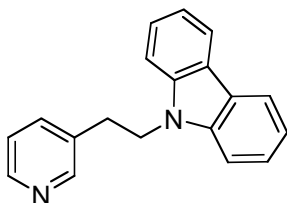
1H,  $J = 7.4$  Hz), 6.75 (d, 1H,  $J = 8.1$  Hz), 6.62 (br s, 1H), 4.50 (t, 2H,  $J = 7.7$  Hz), 3.66 (s, 3H), 3.08 (t, 2H,  $J = 7.7$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 140.2, 140.1, 129.6, 125.6, 122.8, 121.0, 120.3, 118.8, 114.5, 112.1, 108.5, 55.1, 44.7, 35.1; IR (neat) 3050, 2937, 1599, 1486, 1454, 1325, 1259, 1152, 749, 723  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{19}\text{NO}$  ( $\text{M}^+$ ) 324.1364, found 324.1359.



**5-(2-(9H-Carbazol-9-yl)ethyl)furan-2-carbaldehyde**

**(2r)**. This product was obtained by the general method from the reaction of potassium  $\beta$ -

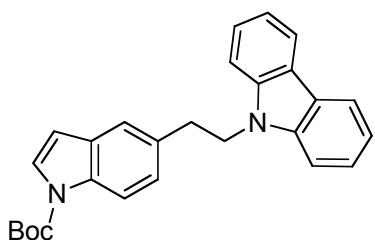
aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 5-bromo-2-furaldehyde (87 mg, 0.5 mmol) to afford the title compound as a yellow oil (89 mg, 62% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.51 (s, 1H), 8.06 (d, 2H,  $J = 7.6$  Hz), 7.43-7.39 (m, 2H), 7.29 (d, 2H,  $J = 8.1$  Hz), 7.24-7.20 (m, 2H), 6.98 (d, 1H,  $J = 3.5$  Hz), 5.98 (d, 1H,  $J = 3.5$  Hz), 4.65 (t, 2H,  $J = 6.9$  Hz), 3.24 (t, 2H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 159.1, 152.2, 139.8, 125.7, 123.2, 122.9, 120.3, 119.2, 110.6, 108.2, 41.1, 27.8; IR (neat) 3050, 2819, 1674, 1519, 1485, 1454, 751, 725  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{NO}_2$  ( $\text{M}^+$ ) 289.1102, found 289.1101.



**9-(2-(pyridin-3-yl)ethyl)-9H-carbazole (2s)**. This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and 3-

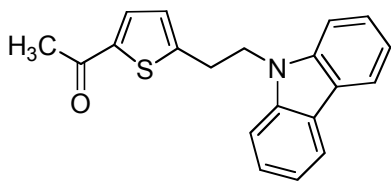
bromopyridine (79 mg, 0.5 mmol) to afford the title compound as a white solid (93 mg, 69% yield). mp = 104-106  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d, 1H,  $J = 1.8$  Hz),

8.43 (dd, 1H,  $J = 4.7, 1.4$  Hz), 8.08 (d, 2H,  $J = 7.7$  Hz), 7.42-7.39 (m, 2H), 7.26-7.20 (m, 5H), 7.06-7.04 (m, 1H), 4.53 (t, 2H,  $J = 7.2$  Hz), 3.14 (t, 2H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 148.1, 140.0, 136.3, 134.0, 125.7, 123.3, 122.9, 120.4, 119.0, 108.3, 44.3, 32.3; IR (neat) 3049, 1594, 1484, 1455, 1350, 749, 726  $\text{cm}^{-1}$ ; HRMS (ES+)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2$  ( $\text{M}+\text{H}^+$ ) 273.1391, found 273.1390.



**tert-Butyl 5-(2-(9H-Carbazol-9-yl)ethyl)-1H-indole-1-carboxylate (2t).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), and

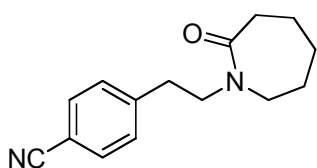
*N*-Boc-4-bromoisouquinoline<sup>5</sup> (147 mg, 0.5 mmol) to afford the title compound as a white solid (129 mg, 63% yield). mp = 128-130  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13-8.11 (m, 3H), 7.59 (br s, 1H), 7.47-7.40 (m, 5H), 7.25-7.21 (m, 3H), 6.51 (d, 1H,  $J = 3.5$  Hz), 4.54 (t, 2H,  $J = 7.8$  Hz), 3.21 (t, 2H,  $J = 7.8$  Hz), 1.69 (s, 9H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 140.1, 134.1, 132.9, 130.9, 126.2, 125.6, 125.0, 122.9, 120.8, 120.3, 118.8, 115.3, 108.5, 107.0, 83.6, 45.3, 35.0, 28.2; IR (neat) 3052, 2978, 1731, 1455, 1372, 1348, 1131, 750, 722  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_2$  ( $\text{M}^+$ ) 410.1094, found 410.1097.



**1-(5-(2-(9H-Carbazol-9-yl)ethyl)thiophen-2-yl)ethanone (2u).** To a mixture of potassium  $\beta$ -aminoethyltrifluoroborate **1a** (165 mg, 0.55 mmol), 2-

acetyl-5-bromo-thiophene (102 mg, 0.5 mmol),  $\text{Cs}_2\text{CO}_3$  (487 mg, 1.5 mmol),  $\text{Pd}(\text{OAc})_2$

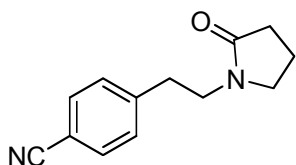
(2.3 mg, 0.01 mmol), and RuPhos (9.3 mg, 0.02 mmol) was added toluene/H<sub>2</sub>O (3:1, 3.2 mL). The reaction was heated at 80 °C with stirring under a nitrogen atmosphere for 12 h, and then cooled to room temperature. A saturated solution of NH<sub>4</sub>Cl was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, dried (MgSO<sub>4</sub>) and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with hexane/ethyl acetate) to afford a yellow solid (112 mg, 71% yield). mp = 94-96 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.08 (d, 2H, *J* = 7.7 Hz), 7.43-7.39 (m, 3H), 7.29 (d, 2H, *J* = 8.1 Hz), 7.24-7.21 (m, 2H), 6.62 (d, 1H, *J* = 3.7 Hz), 4.55 (t, 2H, *J* = 7.3 Hz), 3.33 (t, 2H, *J* = 7.3 Hz), 2.47 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 190.3, 150.0, 143.2, 139.9, 132.8, 127.1, 125.7, 122.9, 120.4, 119.2, 108.3, 44.3, 29.8, 26.4; IR (neat) 3051, 2925, 2360, 1659, 1454, 1326, 1277, 750, 724 cm<sup>-1</sup>; HRMS (CI+) *m/z* calcd. for C<sub>20</sub>H<sub>17</sub>NOSNa (M+Na<sup>+</sup>) 342.0928, found 342.0927.



**4-(2-(2-Oxoazepan-1-yl)ethyl)benzonitrile (3a).** To a mixture of potassium β-aminoethyltrifluoroborate **1b** (54.3 mg, 0.22 mmol), 4-bromobenzonitrile (36.4 mg, 0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol), and RuPhos (9.3 mg, 0.02 mmol) was added toluene/H<sub>2</sub>O (3:1, 1.2 mL). The reaction was heated at 80 °C with stirring under a nitrogen atmosphere for 12 h, and then cooled to room temperature. A saturated solution of NH<sub>4</sub>Cl was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, dried (MgSO<sub>4</sub>) and then filtered. The solvent was removed under vacuum, and the crude product was purified by preparative TLC

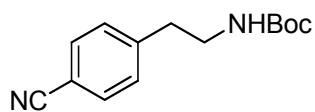


(basic alumina; eluting with hexane/ethyl acetate) to afford a white solid (37.7 mg, 78% yield). mp = 72-74 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (d, 2H, *J* = 8.1 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 3.61 (t, 2H, *J* = 7.4 Hz), 3.26-3.24 (m, 2H), 2.90 (t, 2H, *J* = 7.3 Hz), 2.51-2.49 (m, 2H), 1.70-1.62 (m, 4H), 1.57-1.53 (m, 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 175.7, 144.8, 132.2, 129.6, 118.8, 110.2, 50.4, 49.8, 37.2, 34.6, 29.8, 28.5, 23.3; IR (neat) 3436, 2930, 2226, 1637, 1445, 1367, 1196, 824 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) *m/z* calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O (M+H<sup>+</sup>) 243.1497, found 243.1496.

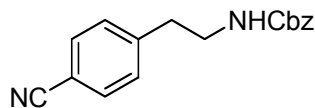


**4-(2-(2-Oxopyrrolidin-1-yl)ethyl)benzonitrile (3b).** To a mixture of potassium β-aminoethyltrifluoroborate **1c** (48.1 mg, 0.22 mmol), 4-bromobenzonitrile (36.4 mg, 0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol), and RuPhos (9.3 mg, 0.02 mmol) was added toluene/H<sub>2</sub>O (3:1, 1.2 mL). The reaction was heated at 80 °C with stirring under a nitrogen atmosphere for 12 h, and then cooled to room temperature. A saturated solution of NH<sub>4</sub>Cl was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, dried (MgSO<sub>4</sub>) and then filtered. The solvent was removed under vacuum, and the crude product was purified by preparative TLC (basic alumina; eluting with hexane/ethyl acetate) to afford a white solid (30.3 mg, 71% yield). mp = 88-90 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 3.55 (t, 2H, *J* = 7.3 Hz), 3.27 (t, 2H, *J* = 7.1 Hz), 2.91 (t, 2H, *J* = 7.5 Hz), 2.34 (t, 2H, *J* = 8.0 Hz), 2.00-1.94 (m, 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 174.9, 144.3, 132.3, 129.4, 118.8, 110.5, 47.5, 43.3, 33.8, 30.8, 17.9; IR (neat) 3459, 2930, 2227, 1667, 1463, 1426, 1289, 825 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) *m/z* calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O (M+H<sup>+</sup>) 215.1184,

found 215.1194.



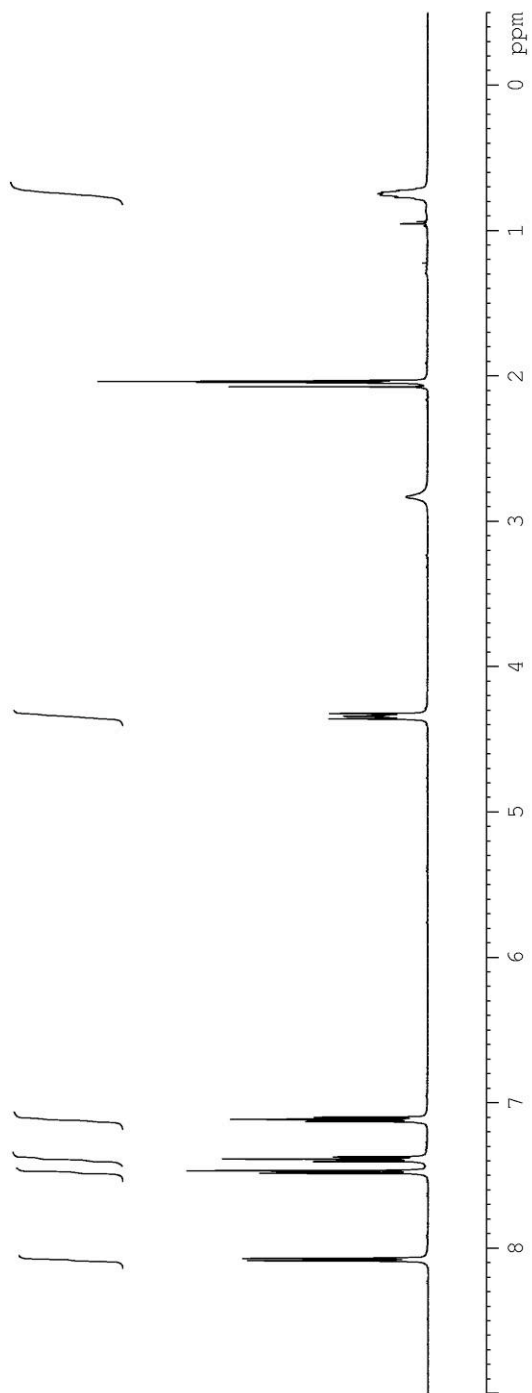
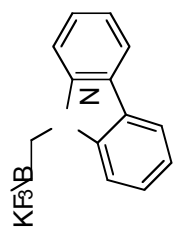
**tert-Butyl 4-Cyanophenethylcarbamate (4a).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1d** (55.2 mg, 0.22 mmol), and 4-bromobenzonitrile (36.4 mg, 0.2 mmol) to afford the title compound as a white solid (35.9 mg, 73% yield). mp = 76-78 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d, 2H,  $J = 8.1$  Hz), 7.30 (d, 2H,  $J = 7.9$  Hz), 4.57 (br s, 1H), 3.39-3.38 (m, 2H), 2.86 (app t, 2H,  $J = 7.0$  Hz), 1.42 (s, 9H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 144.7, 132.3, 129.6, 118.8, 110.3, 79.5, 41.2, 36.4, 28.3; IR (neat) 3357, 2977, 2228, 1697, 1505, 1251, 1170, 823  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}^+$ ) 247.1446, found 247.1445.



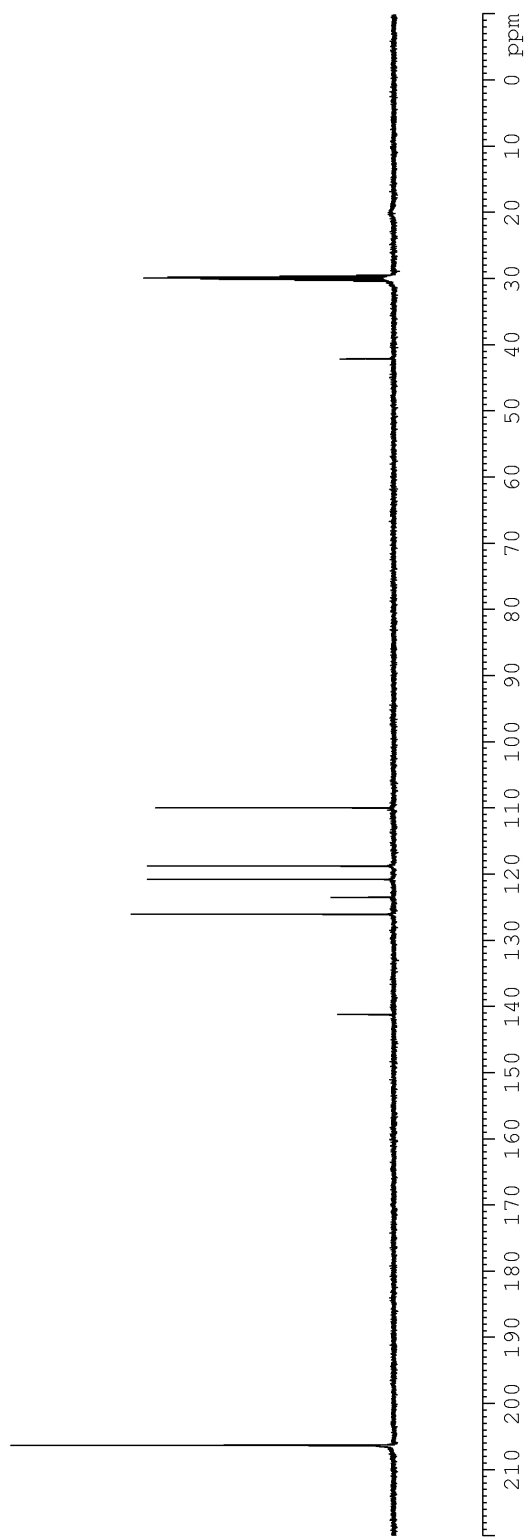
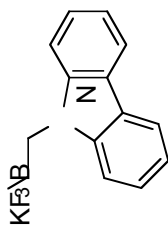
**Benzyl 4-Cyanophenethylcarbamate (4b).** This product was obtained by the general method from the reaction of potassium  $\beta$ -aminoethyltrifluoroborate **1e** (62.7 mg, 0.22 mmol), and 4-bromobenzonitrile (36.4 mg, 0.2 mmol) to afford the title compound as a white solid (39.7 mg, 71% yield). mp = 81-83 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d, 2H,  $J = 7.9$  Hz), 7.37-7.31 (m, 5H), 7.27 (d, 2H,  $J = 7.7$  Hz), 5.08 (s, 2H), 4.78 (br s, 1H), 3.48-3.44 (m, 2H), 2.88 (app t, 2H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 144.3, 136.3, 132.3, 129.5, 128.5, 128.2, 128.1, 118.7, 110.4, 66.7, 41.6, 36.2; IR (neat) 3341, 2938, 2359, 2227, 1703, 1529, 1248, 1136, 823  $\text{cm}^{-1}$ ; HRMS (CI+)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}^+$ ) 281.1290, found 281.1284.

## References

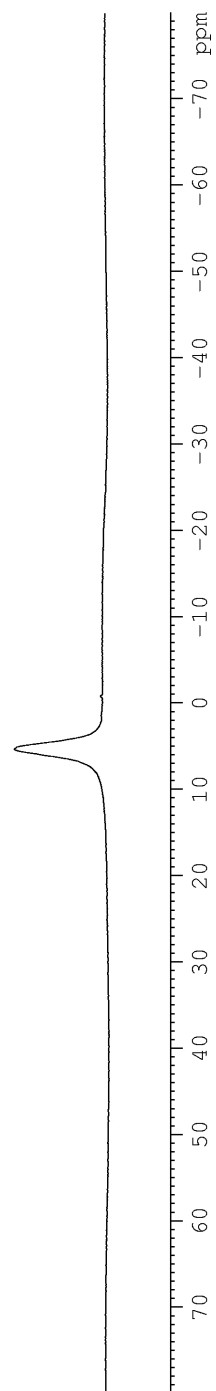
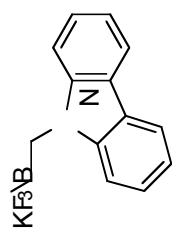
- (1) *N*-Boc Vinyl carbamate was prepared according to the procedure described for the Cbz analogue (Reference 2); using *tert*-butanol instead of benzyl alcohol.
- (2) Wieber, G. M.; Hegedus, L. S.; Åkermark, B.; Michalson, E. T. *J. Org. Chem.* **1989**, *54*, 4649-4653.
- (3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
- (4) Kalinin, A. V.; Scherer, S.; Snieckus, V. *Angew. Chem. Int. Ed.* **2003**, *42*, 3399-3404.
- (5) Prieto, M.; Zurita, E.; Rosa, E.; Munoz, L.; Lloyd-Williams, P.; Giralt, E. *J. Org. Chem.* **2004**, *69*, 6812-6820.



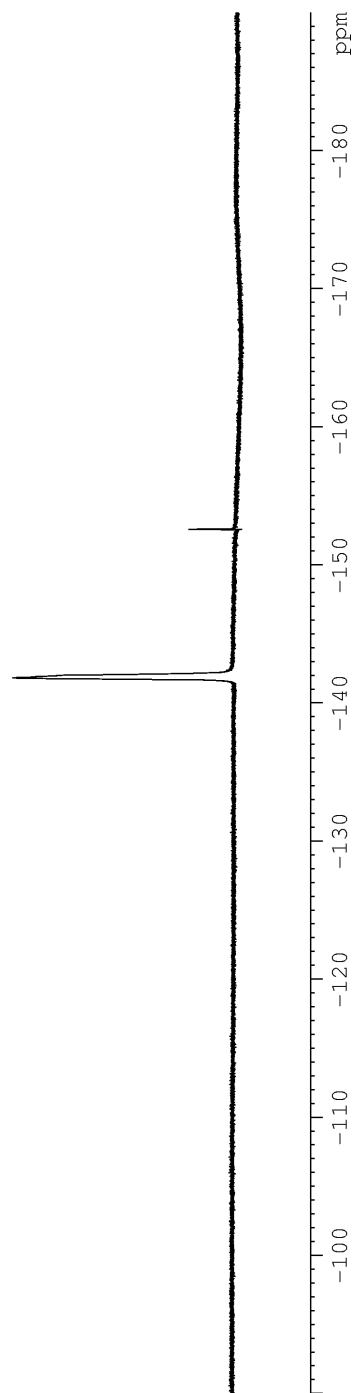
$^1\text{H}$  NMR (500 MHz,  $\text{Acetone-}d_6$ ) Spectrum of **1a**



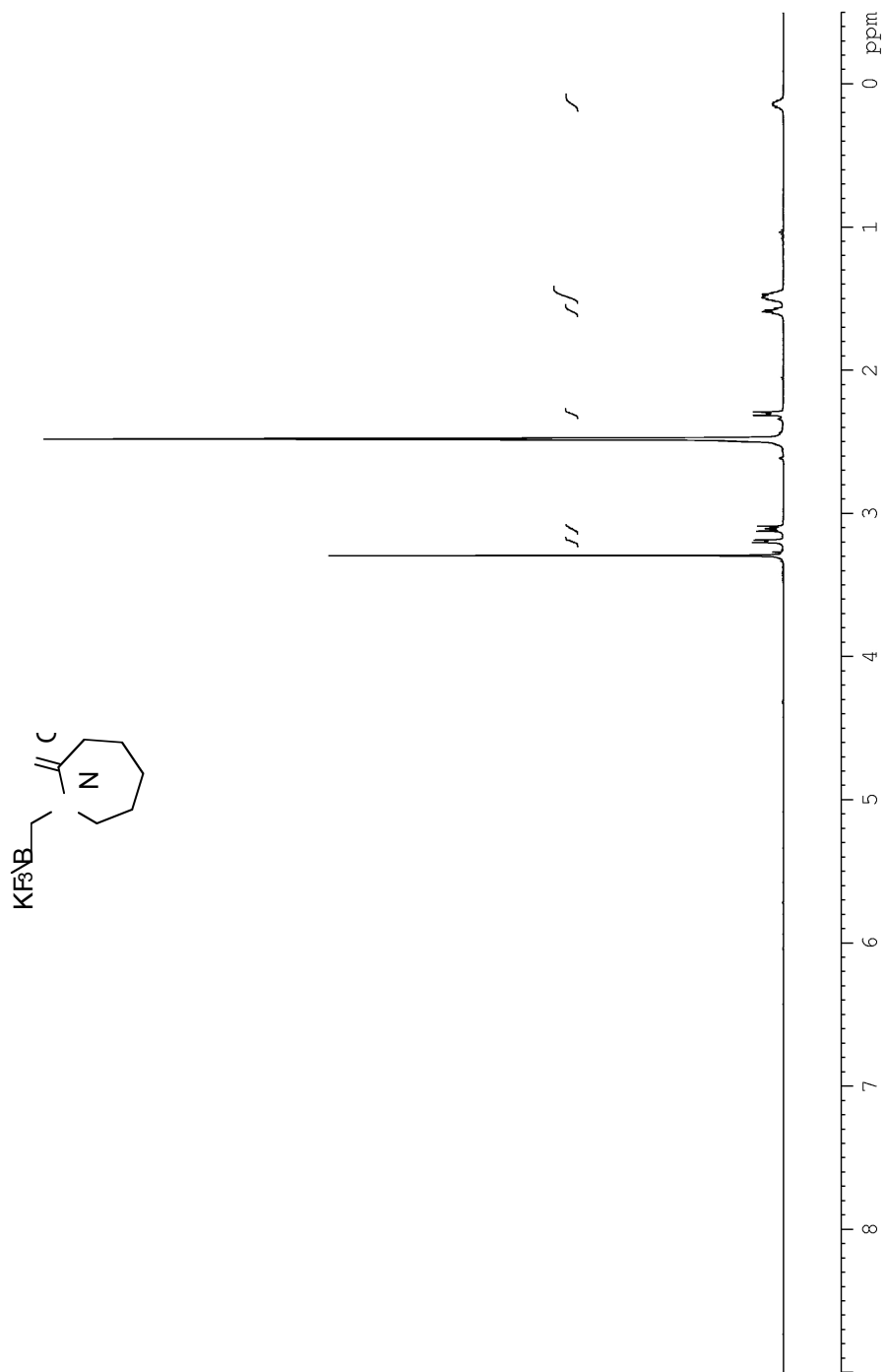
$^{13}\text{C}$  NMR (125.8 MHz, Acetone- $d_6$ ) Spectrum of **1a**



<sup>11</sup>B NMR (128.4 MHz, Acetone-*d*<sub>6</sub>) Spectrum of **1a**

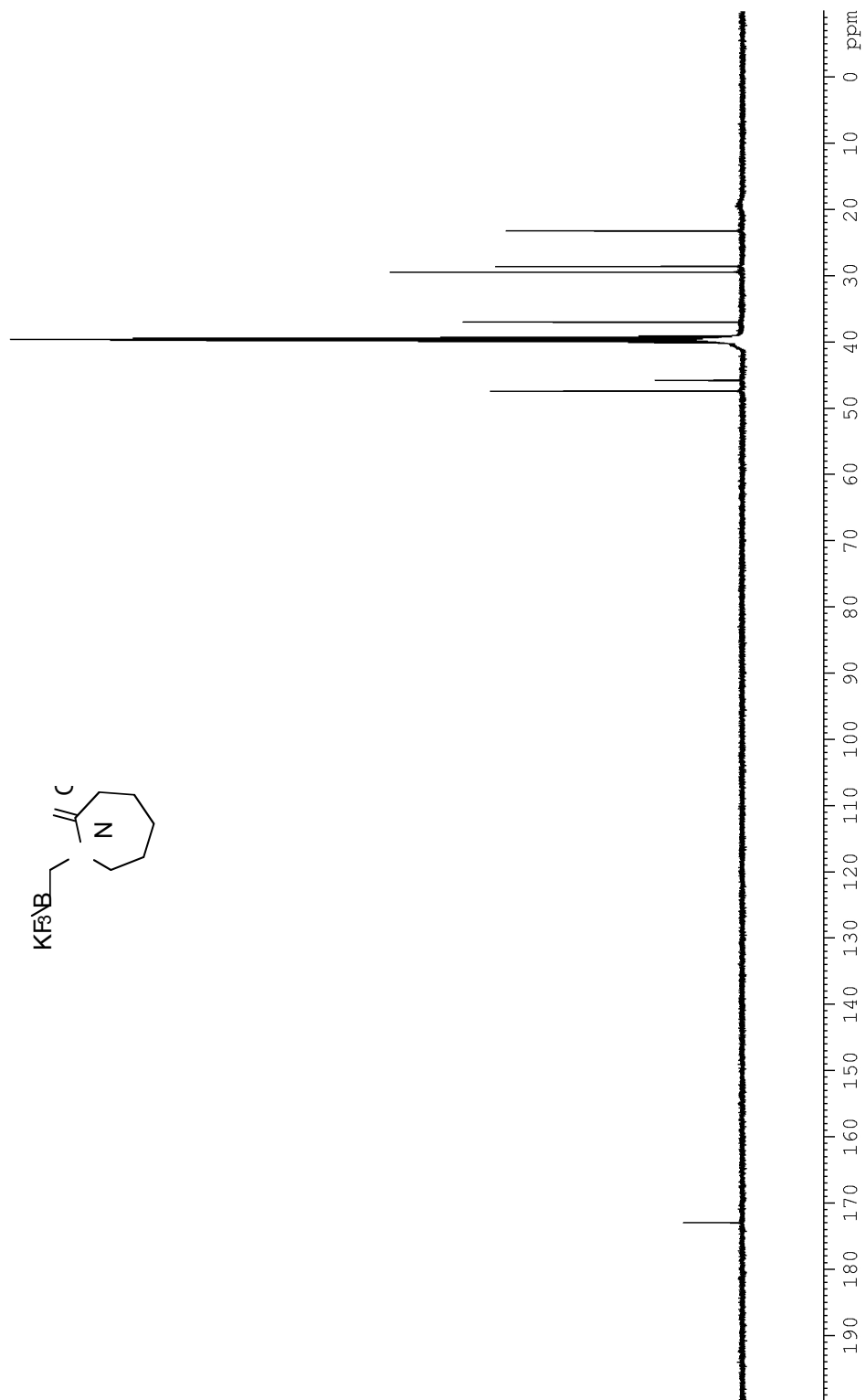


$^{19}\text{F}$  NMR (470.8 MHz, Acetone-*d*<sub>6</sub>) Spectrum of **1a**

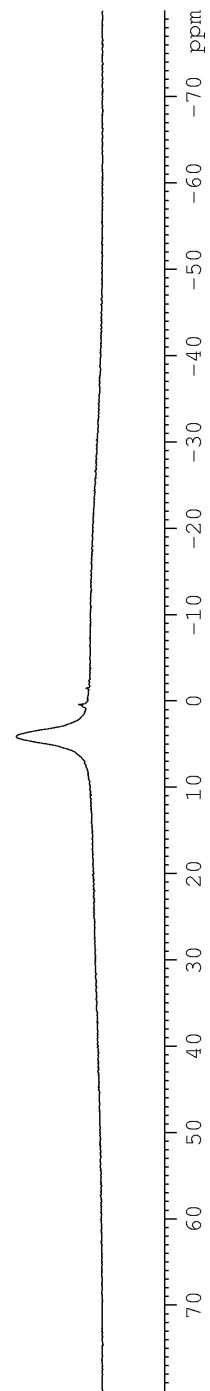
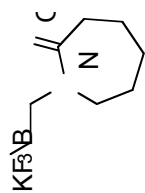


$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) Spectrum of **1b**

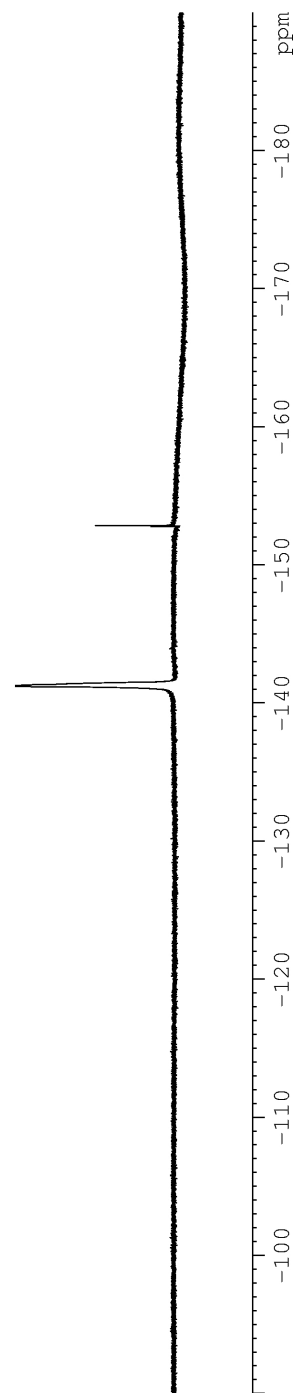
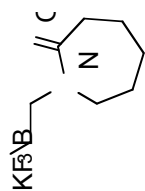




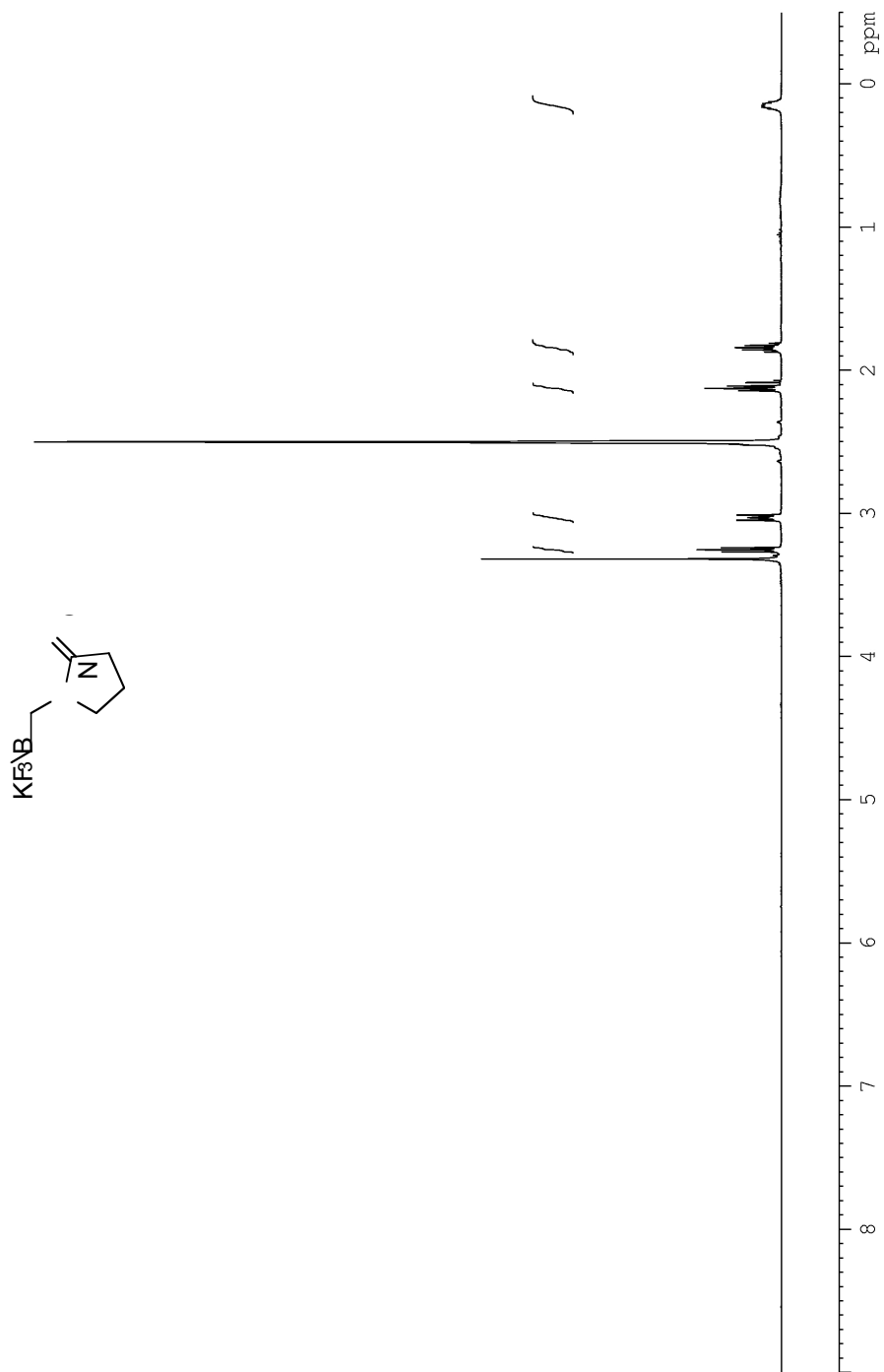
$^{13}\text{C}$  NMR (125.8 MHz, DMSO-*d*6) Spectrum of **1b**



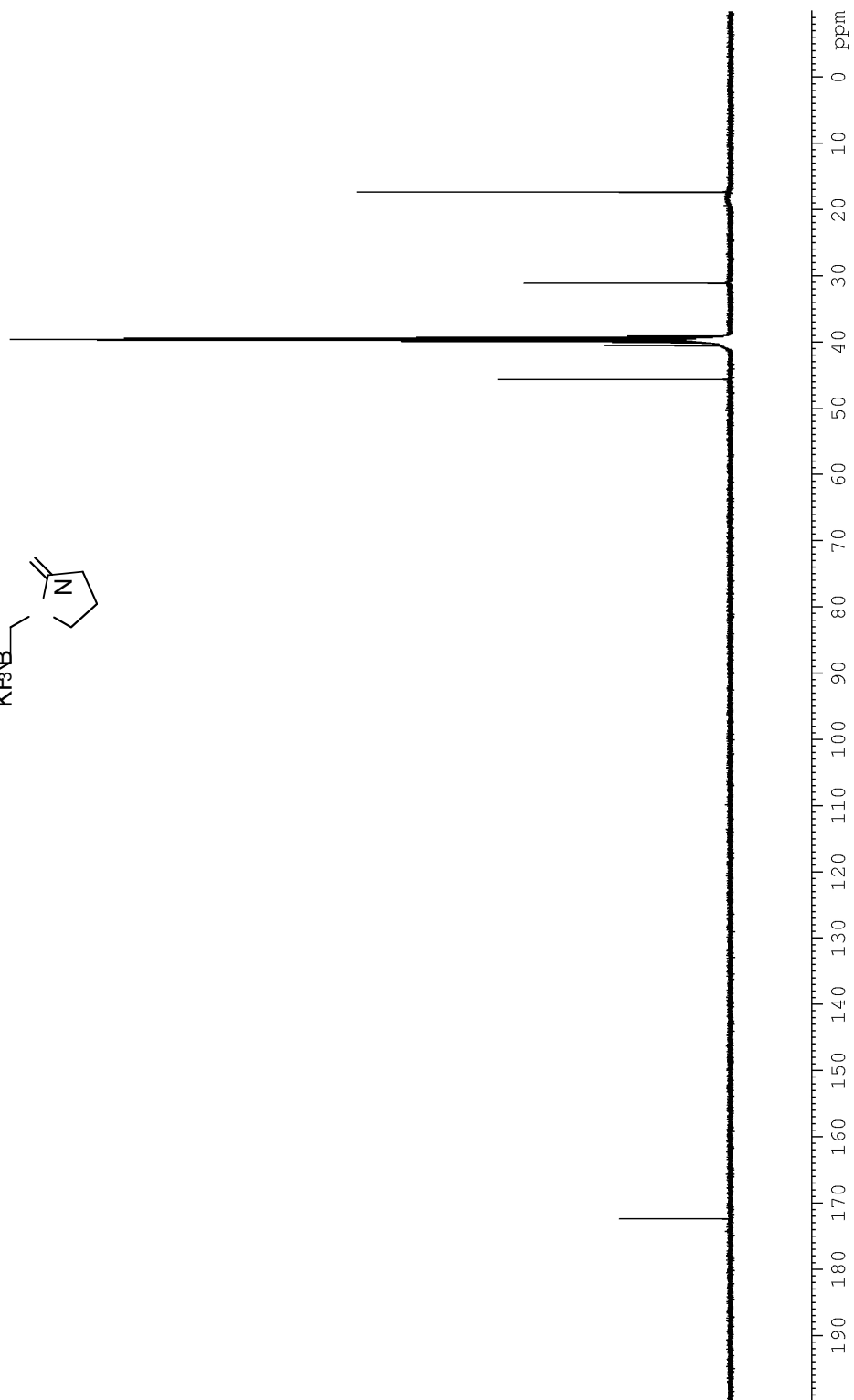
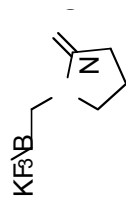
$^{11}\text{B}$  NMR (128.4 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1b**



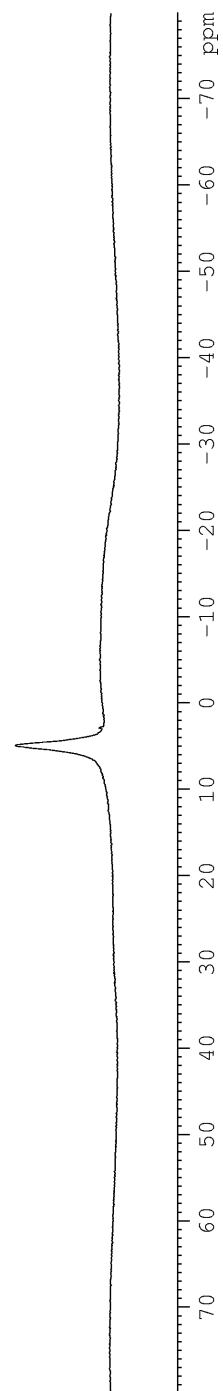
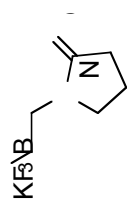
$^{19}\text{F}$  NMR (470.8 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1b**



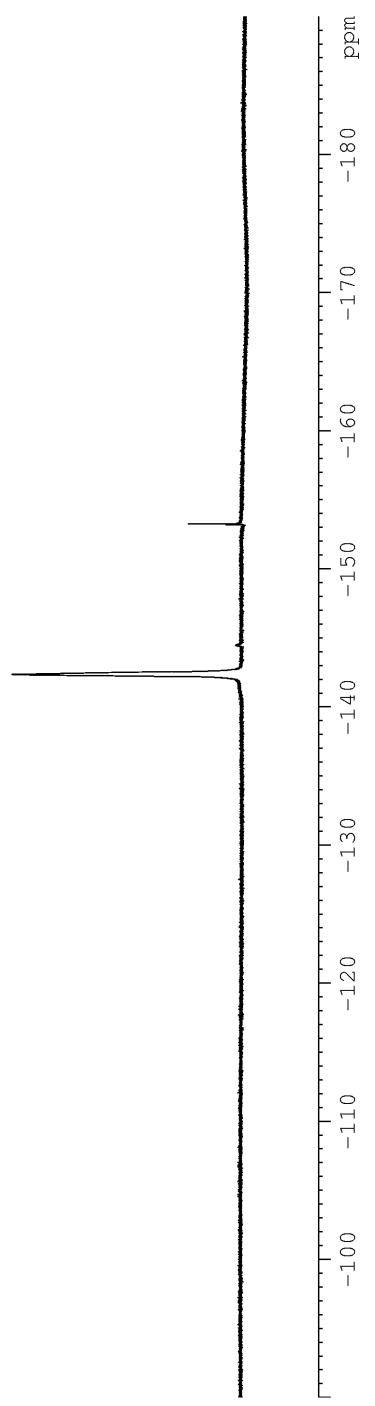
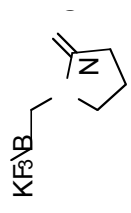
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1c**



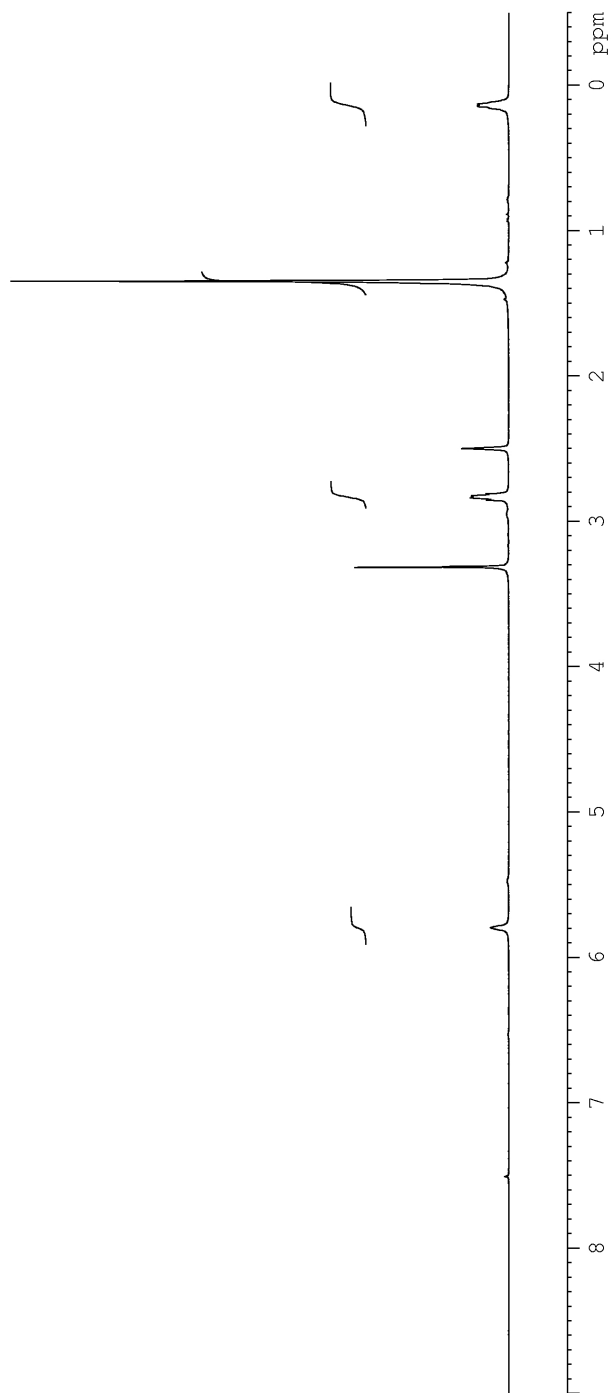
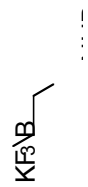
<sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1c**



$^{11}\text{B}$  NMR (128.4 MHz,  $\text{DMSO-}d_6$ ) Spectrum of **1c**

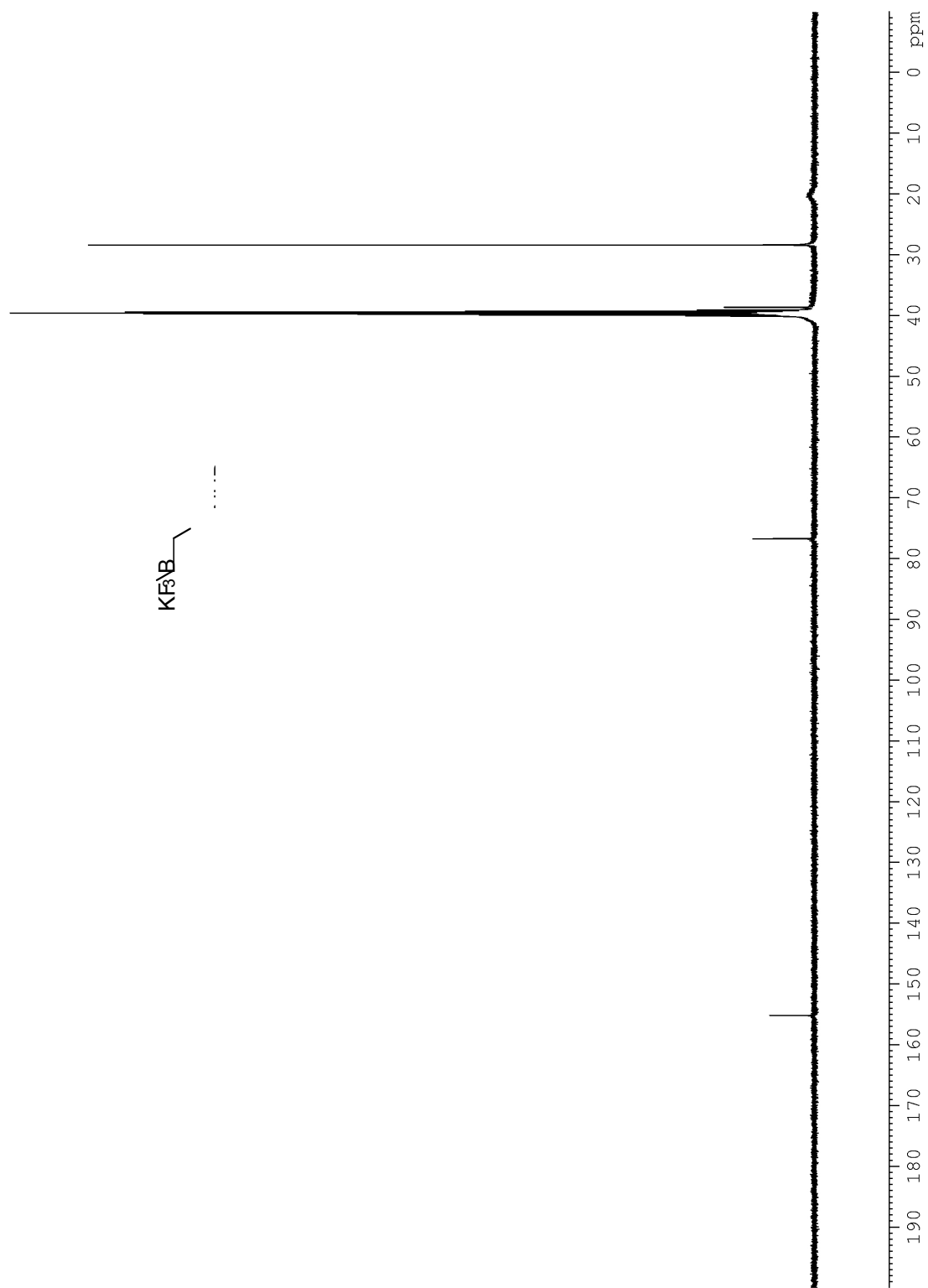


$^{19}\text{F}$  NMR (470.8 MHz,  $\text{DMSO-}d_6$ ) Spectrum of **1c**

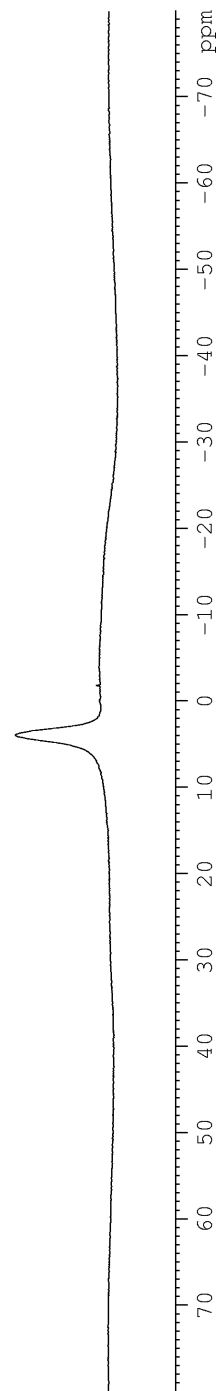
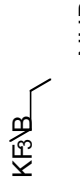


$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) Spectrum of **1d**

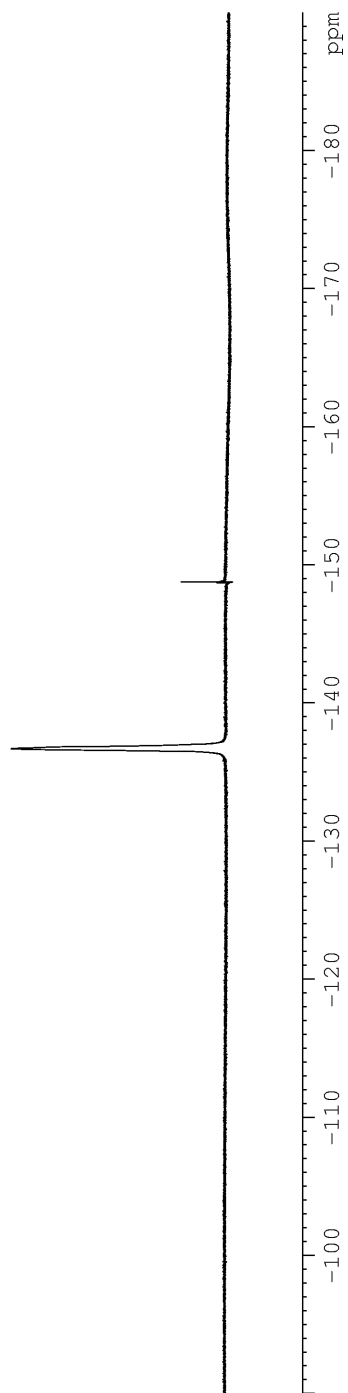
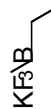




$^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO-}d_6$ ) Spectrum of **1d**



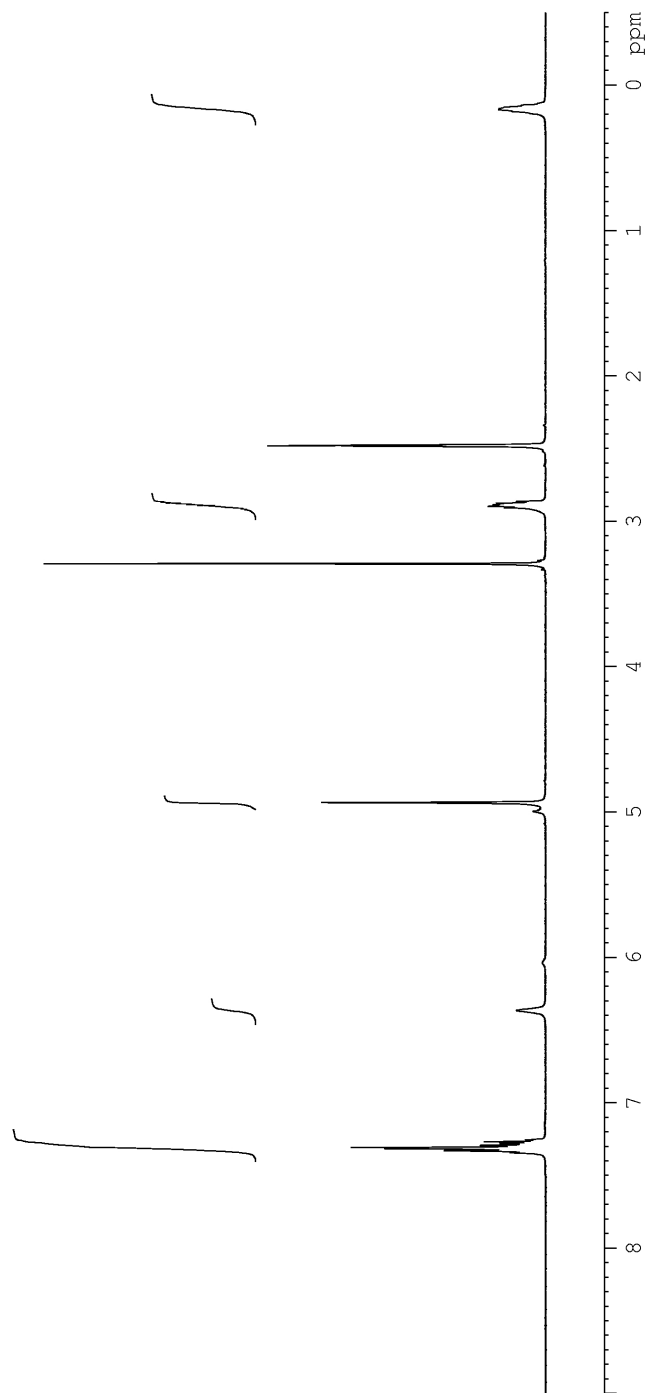
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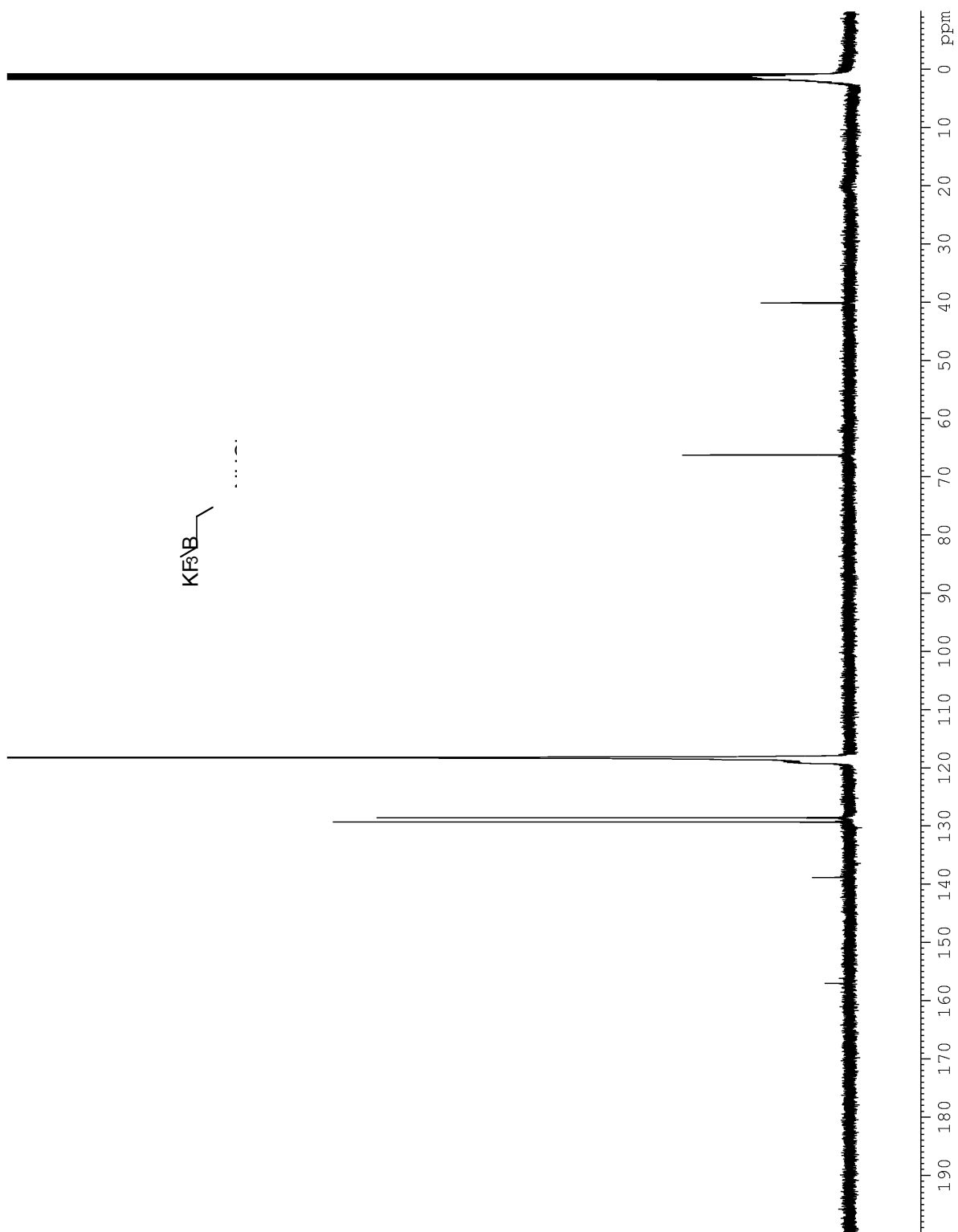
$^{19}\text{F}$  NMR (470.8 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1d**

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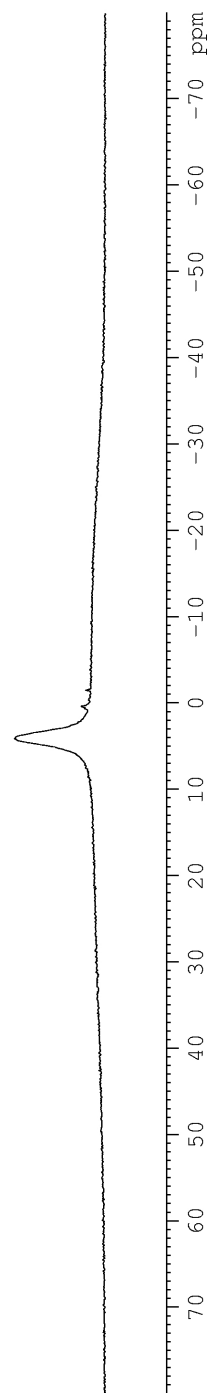


$^1\text{H}$  NMR (500 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1e**

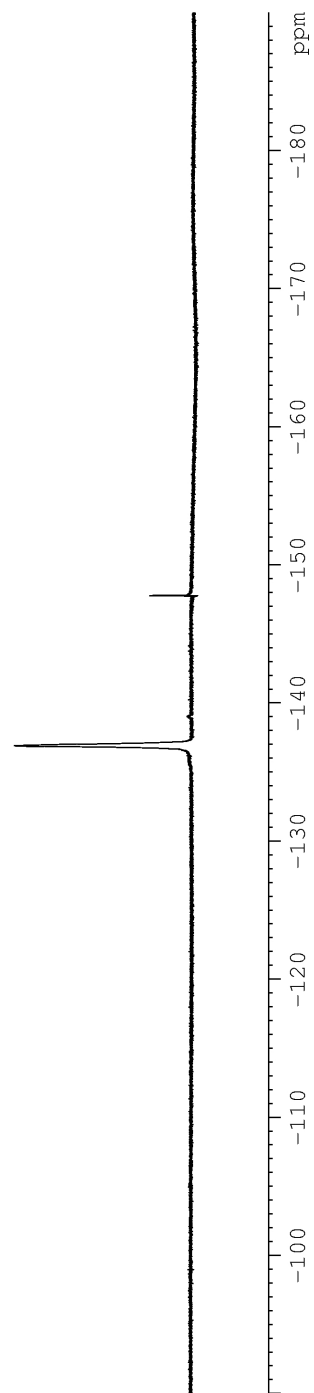
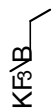


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CD}_3\text{CN}$ ) Spectrum of **1e**

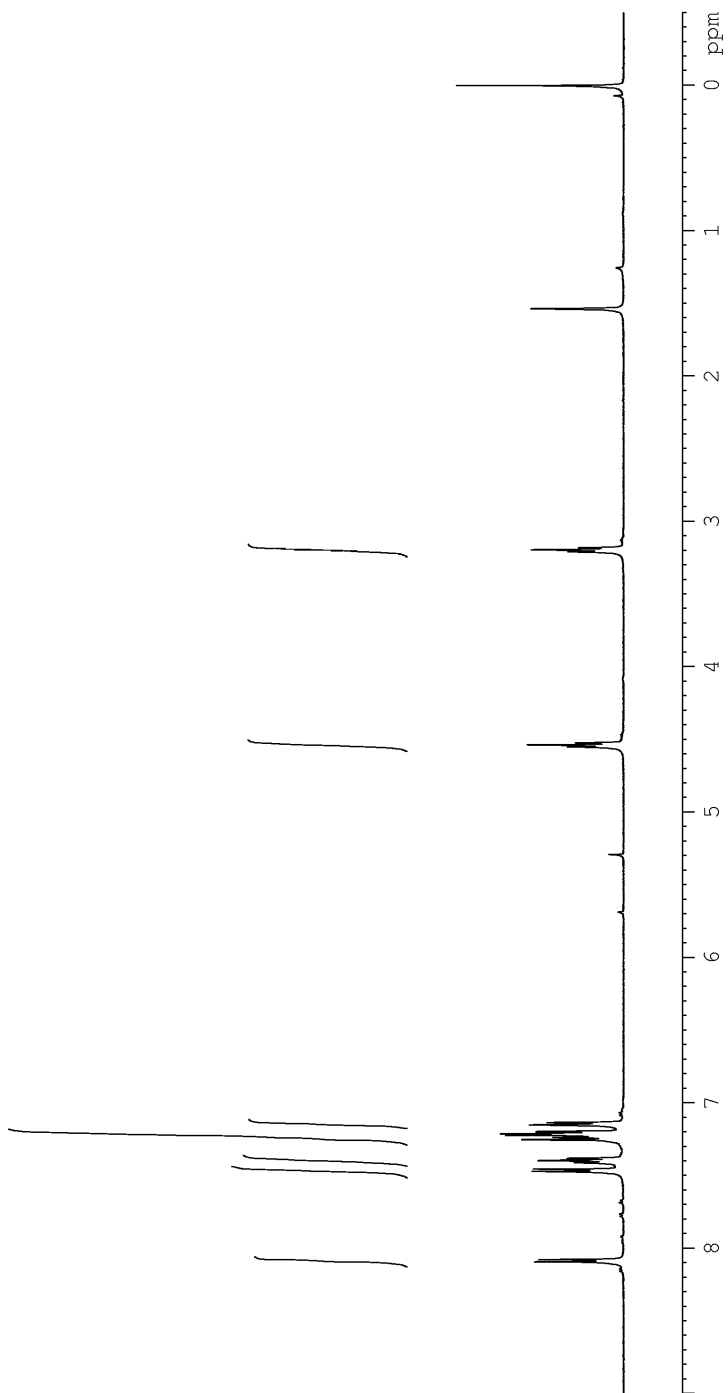
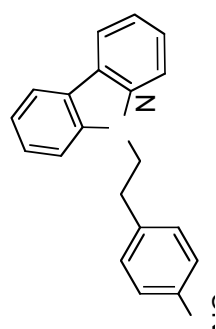
$^{11}\text{B}$



$^{11}\text{B}$  NMR (128.4 MHz, DMSO-*d*<sub>6</sub>) Spectrum of **1e**

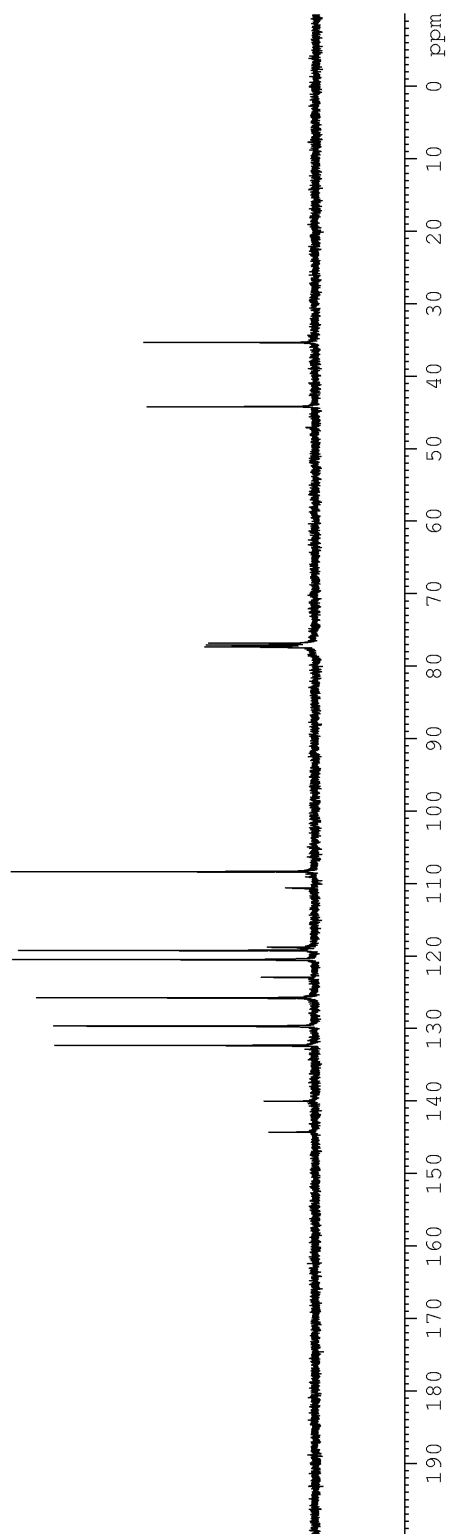
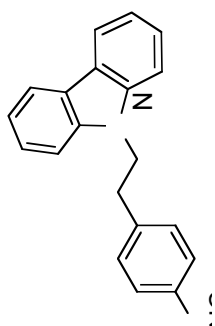


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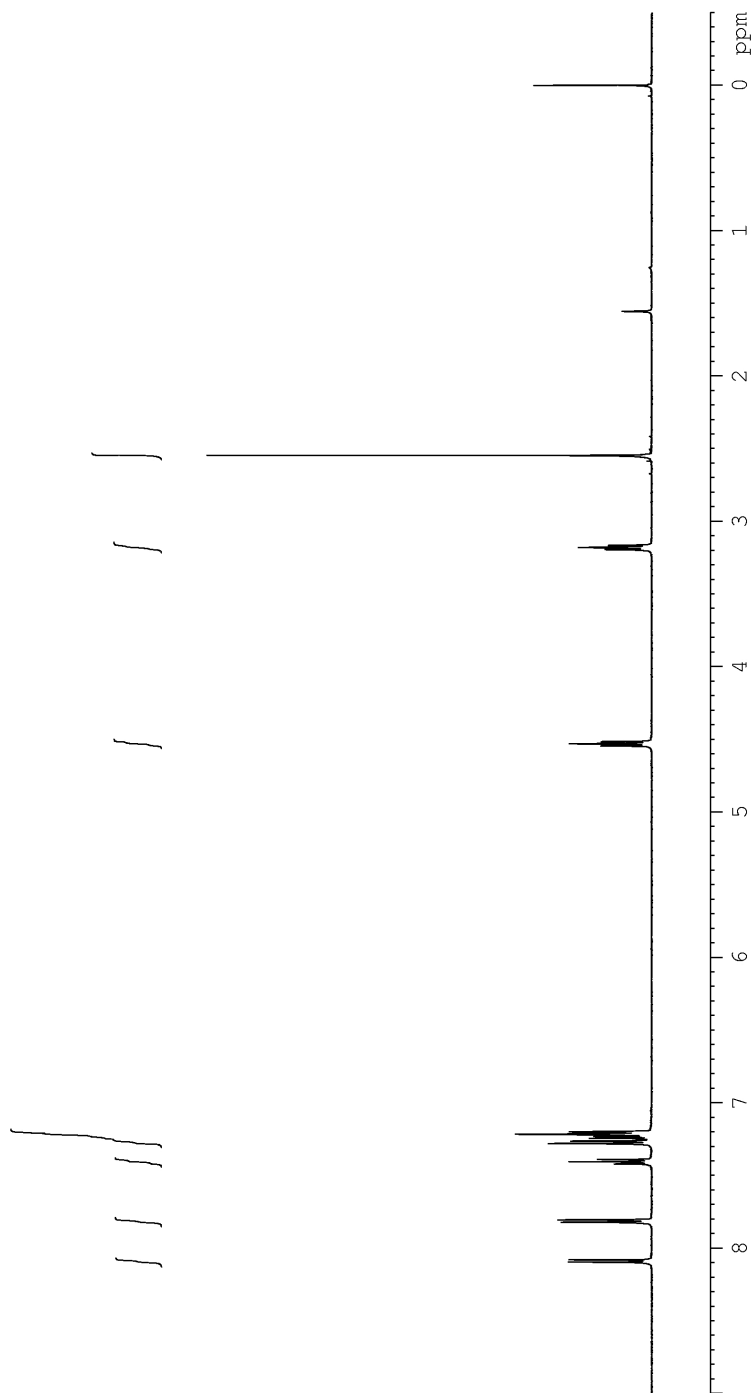
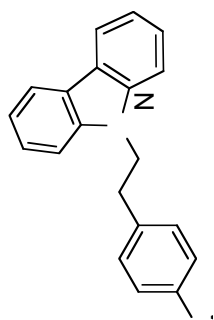


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2a**

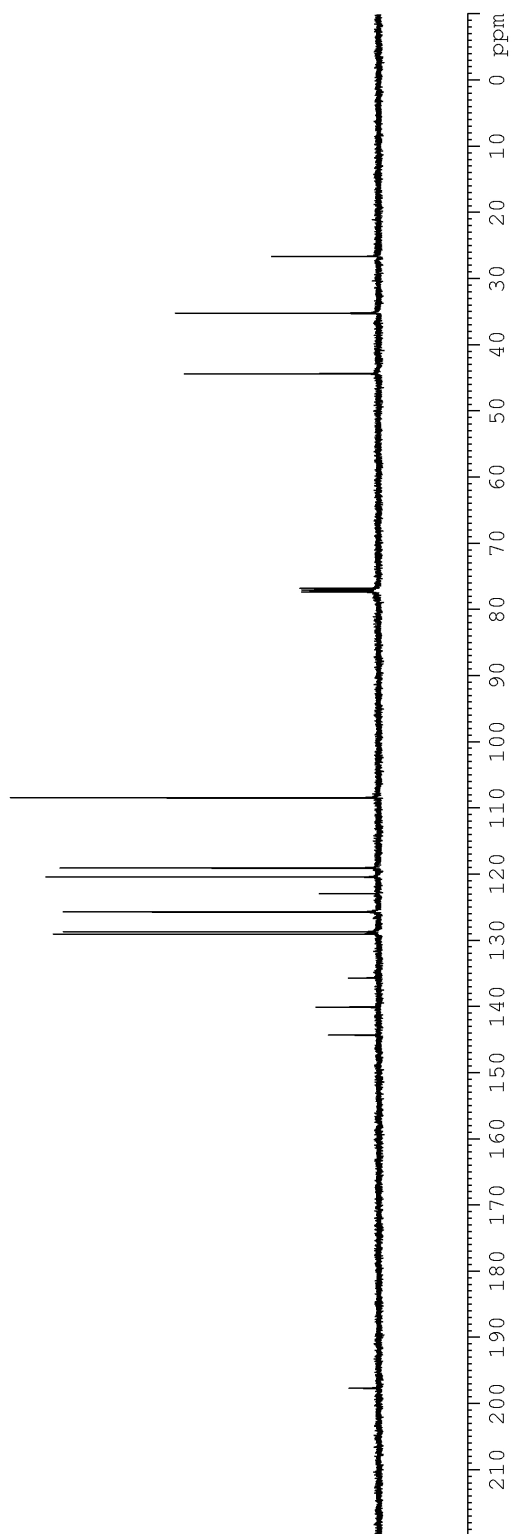
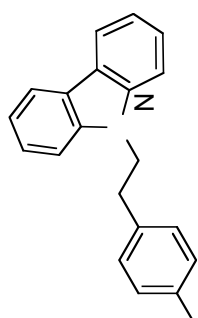




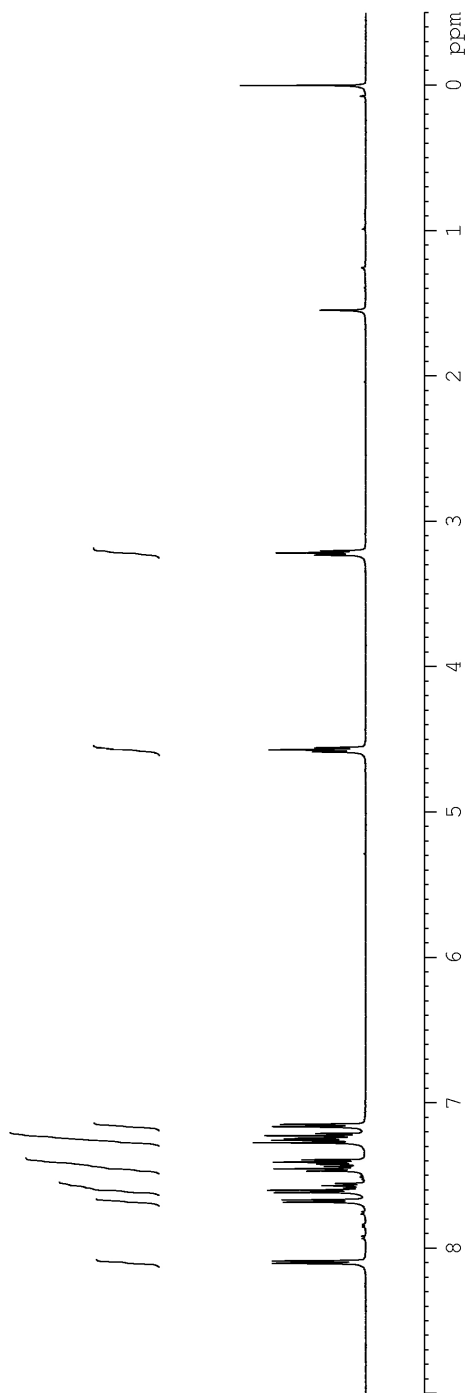
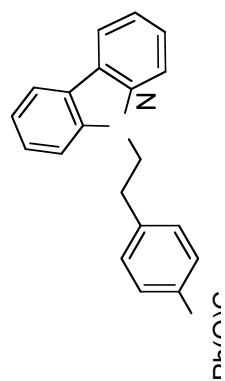
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2a**



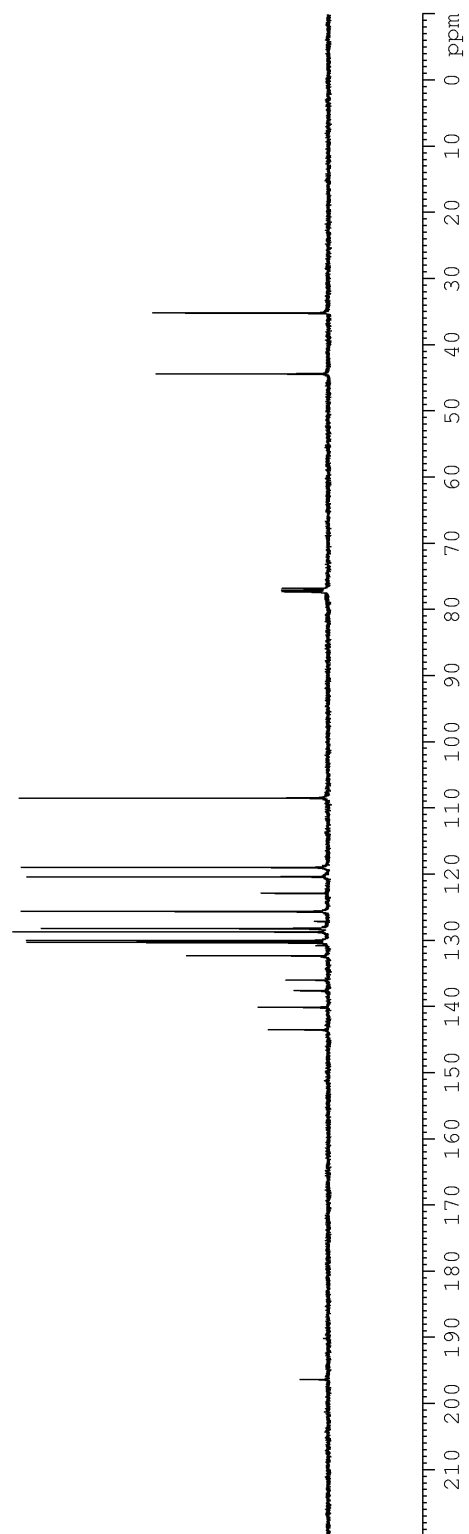
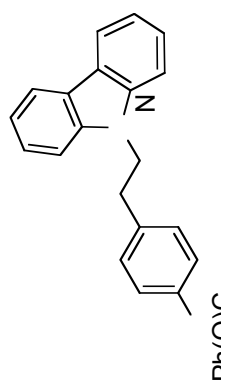
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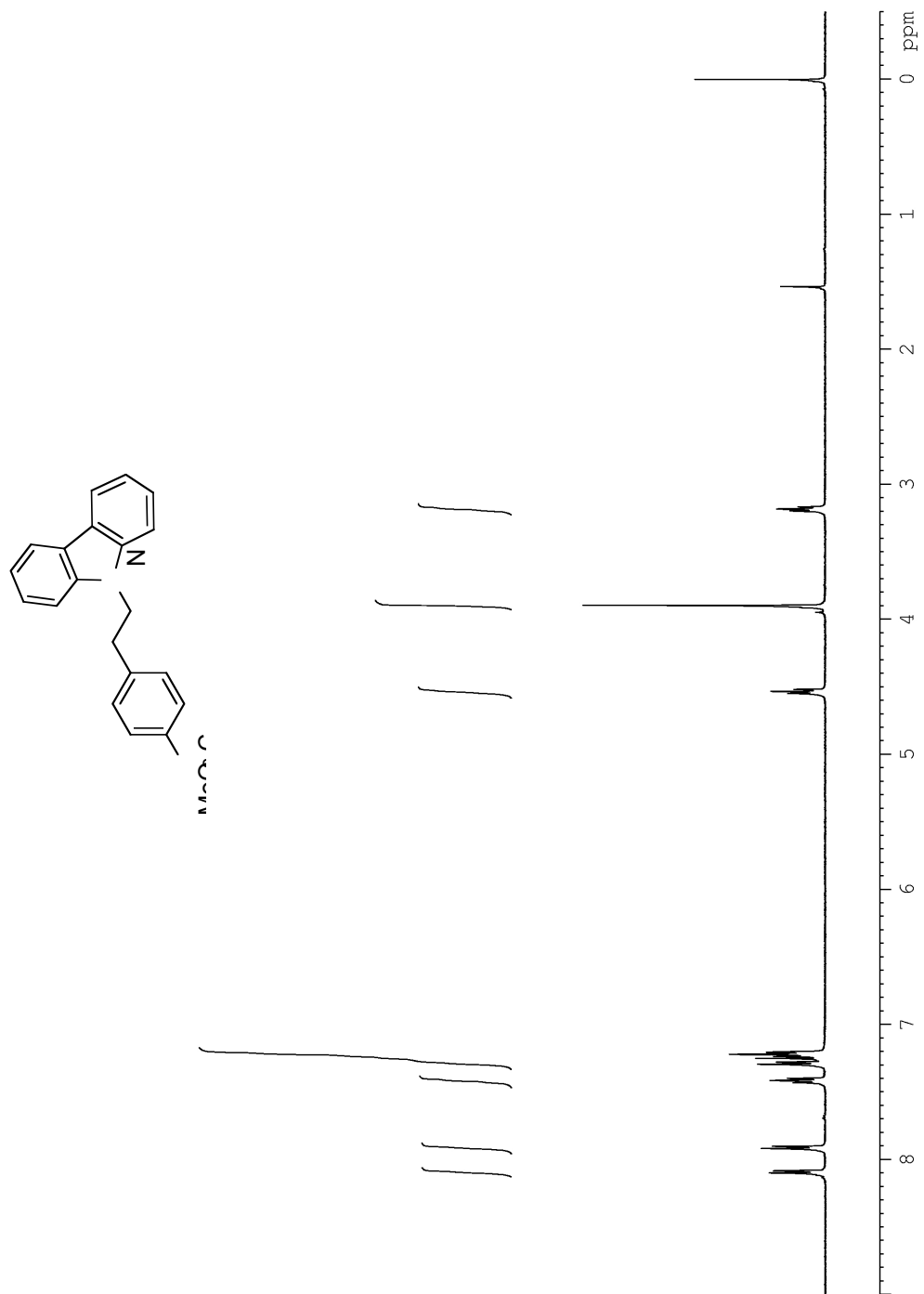
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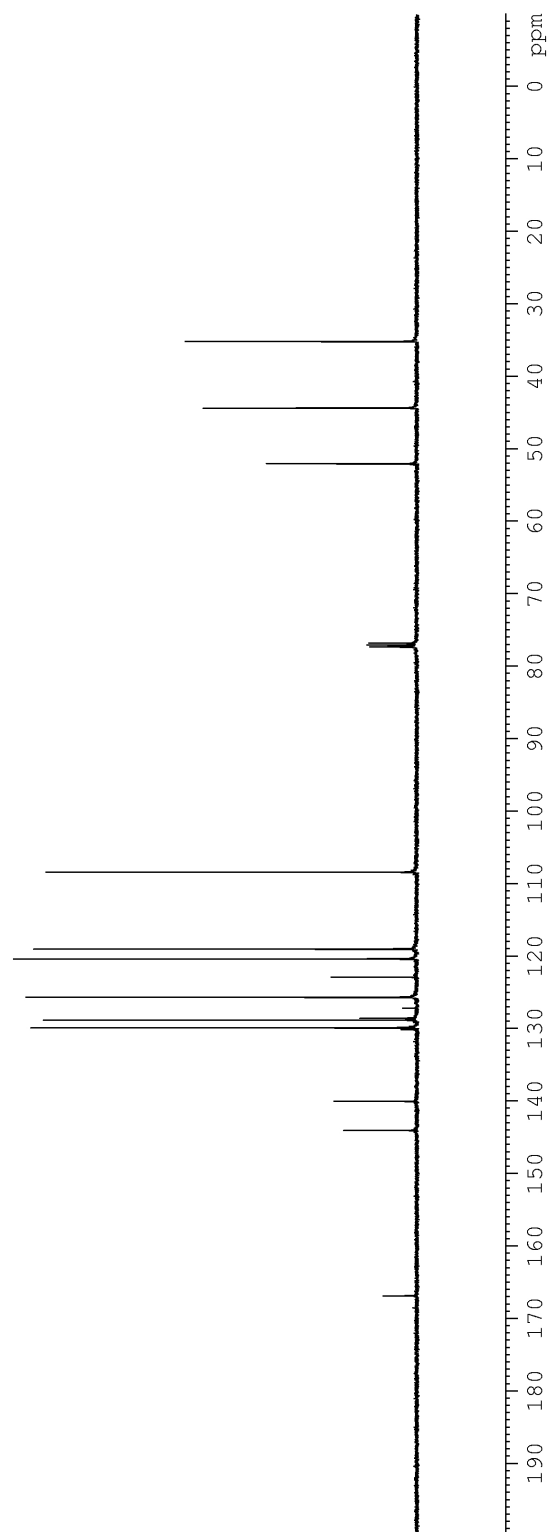
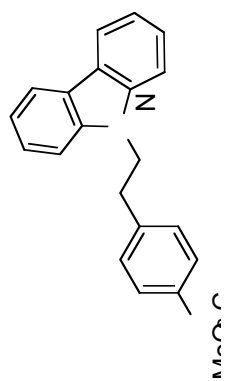
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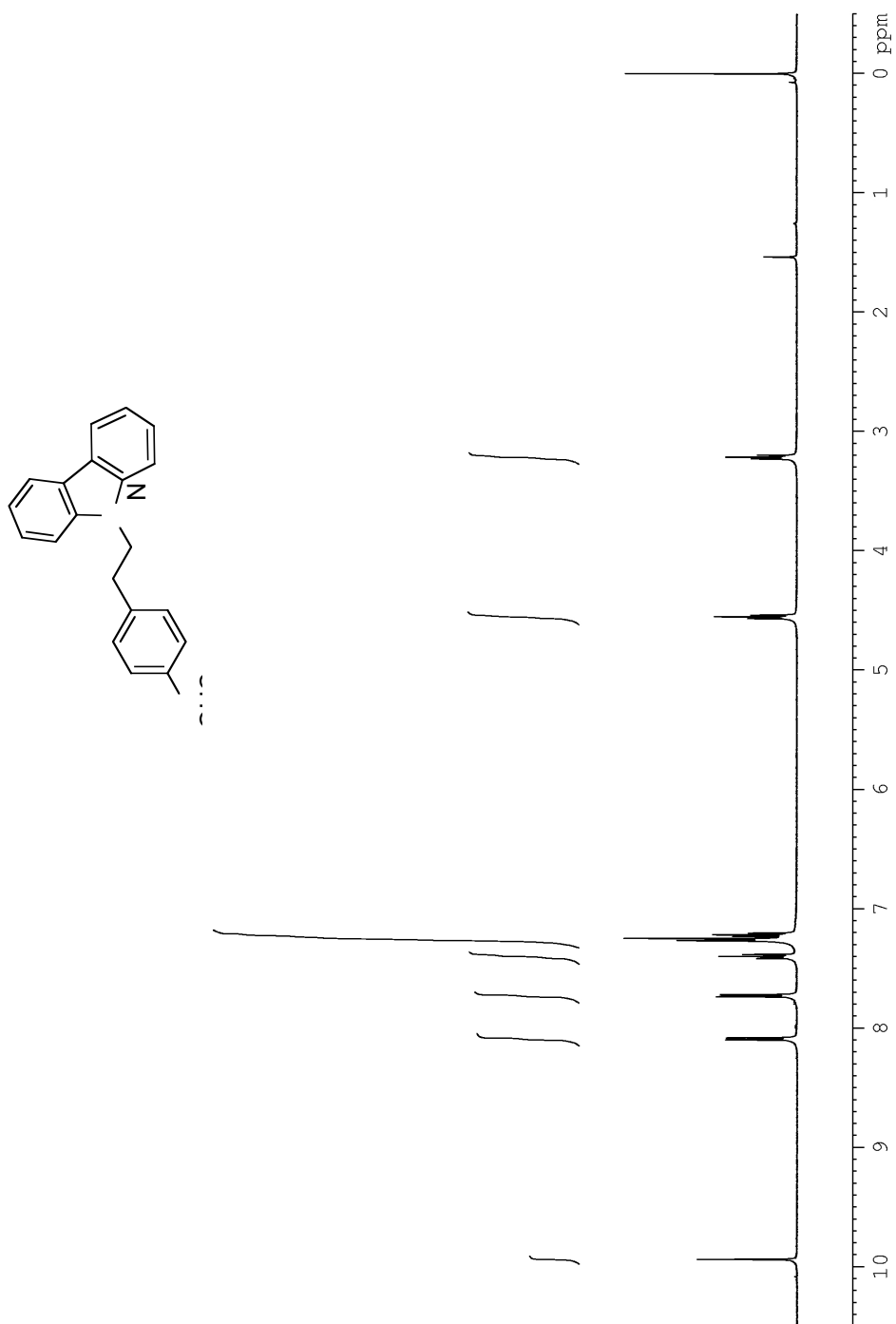
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2c**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2d**

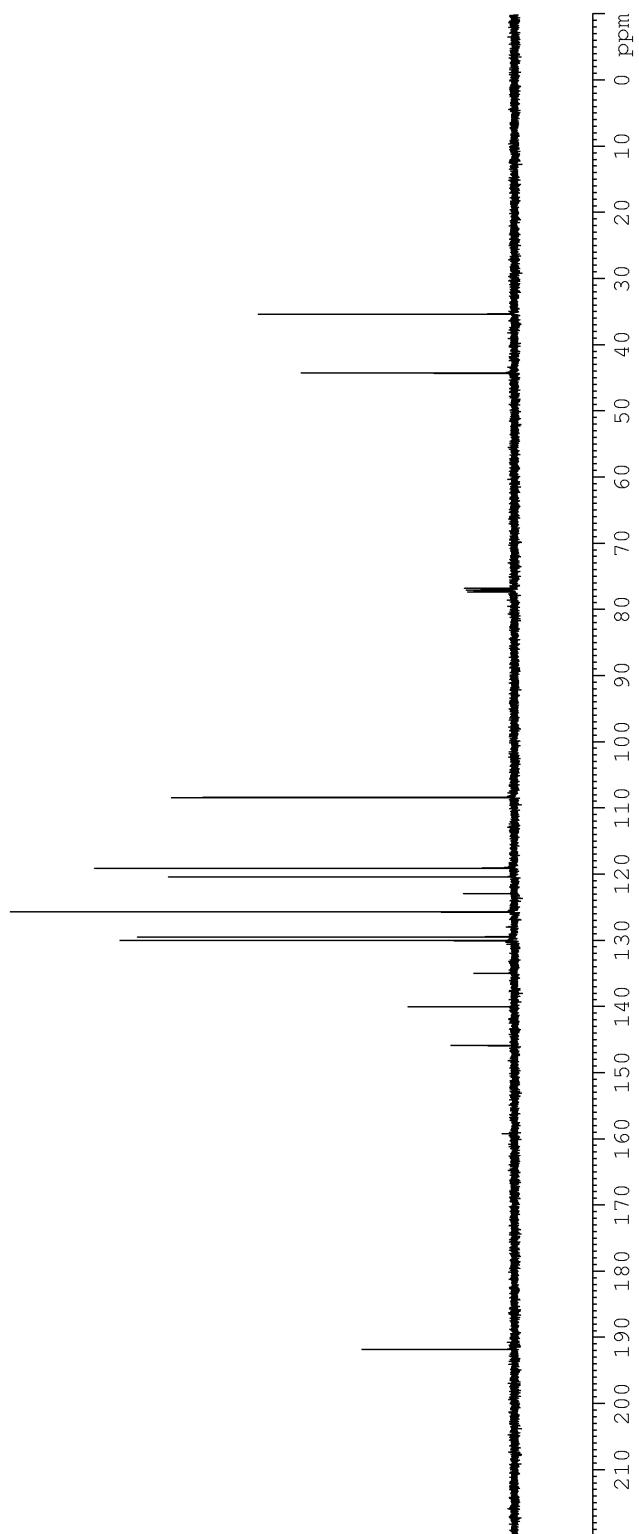
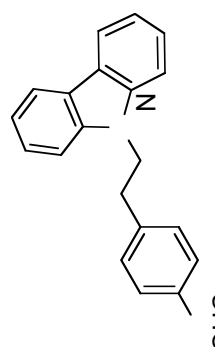


$^{13}C$  NMR (125.8 MHz,  $CDCl_3$ ) Spectrum of **2d**

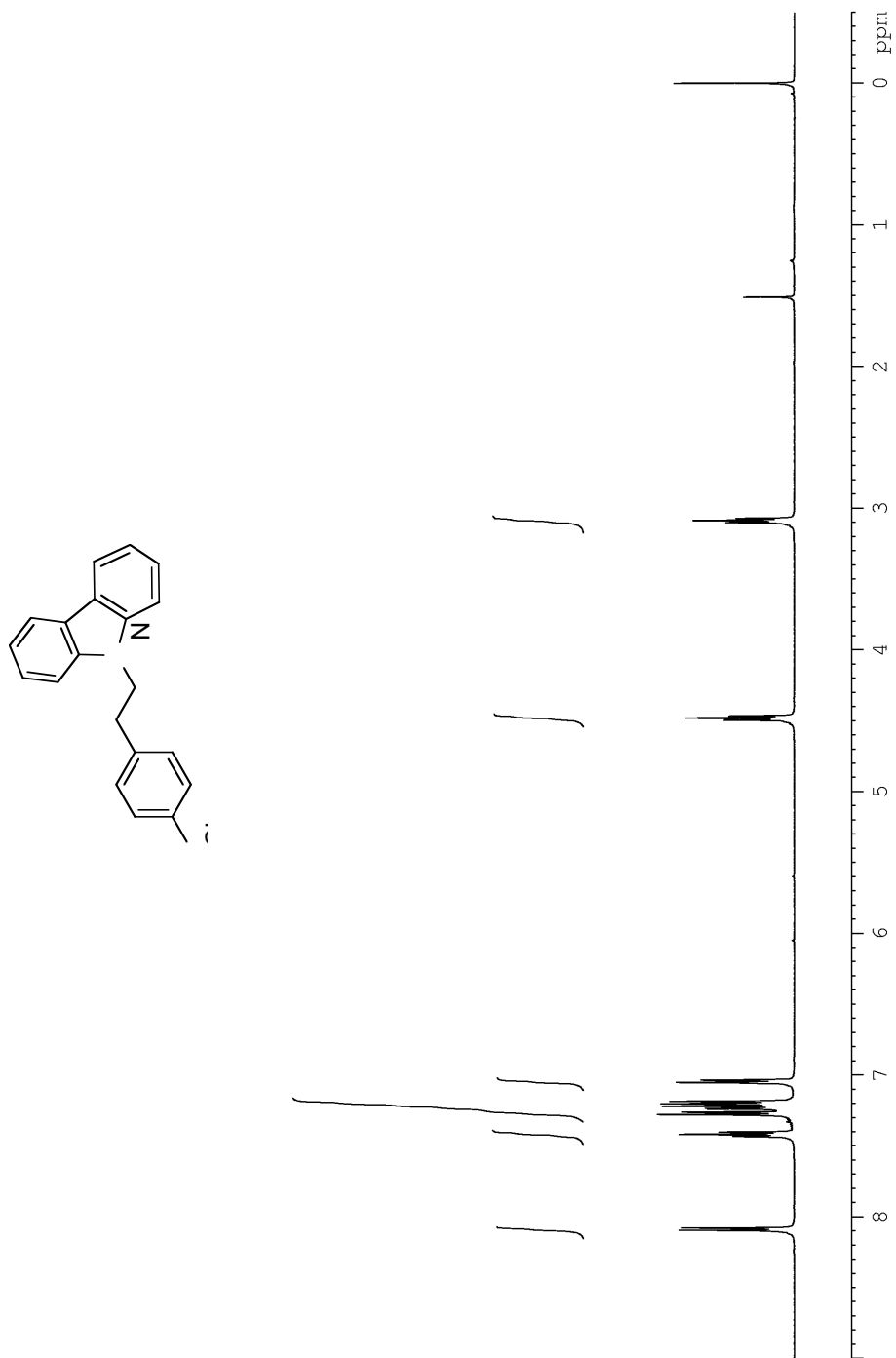


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2e**

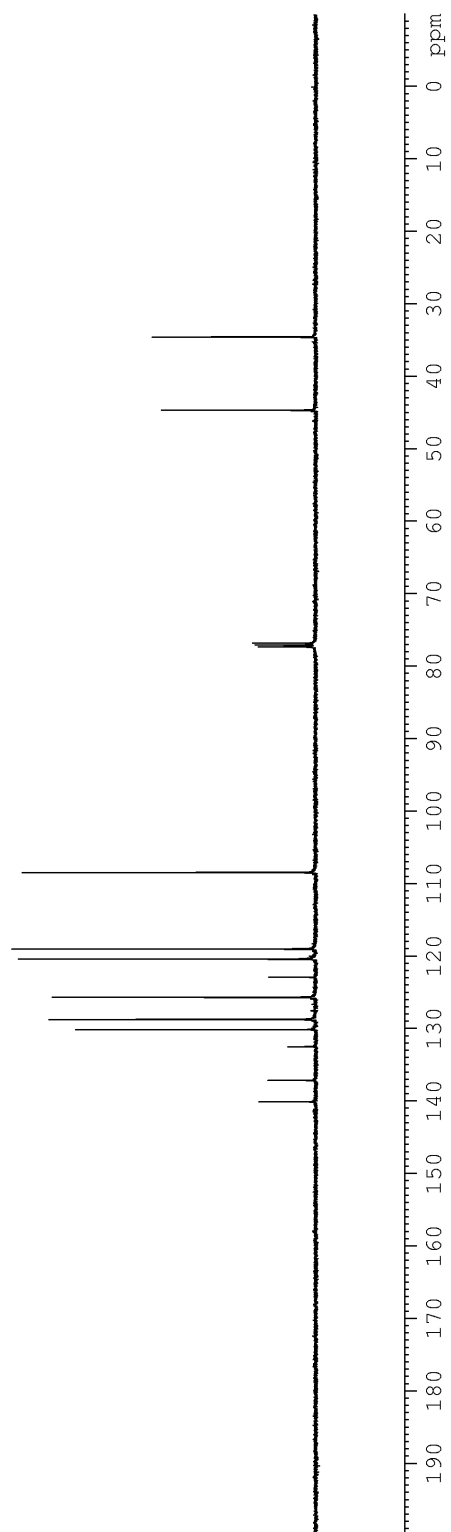
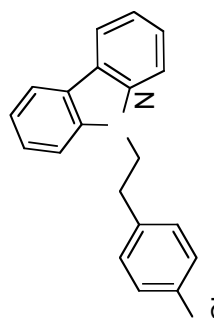




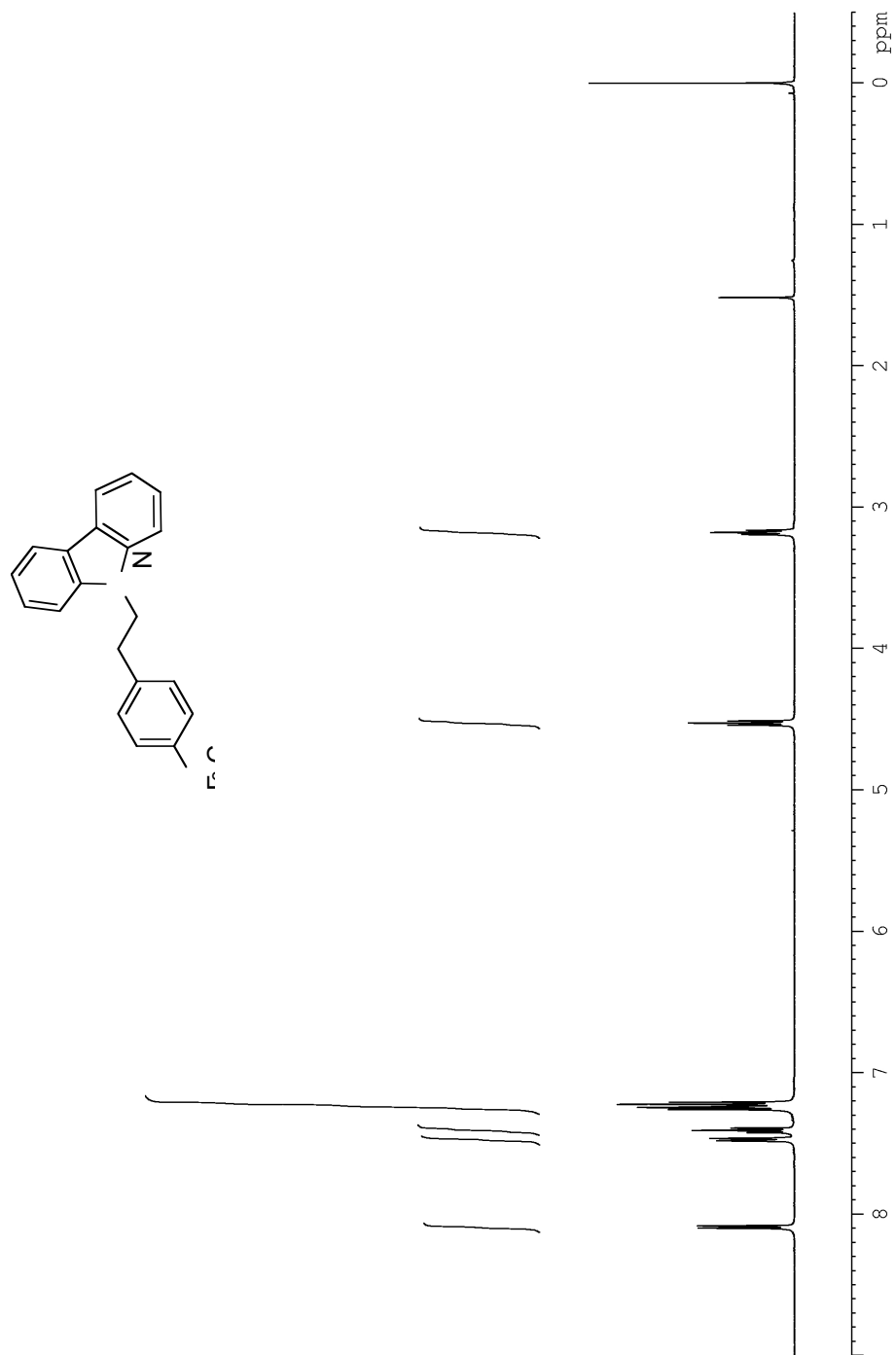
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2e**



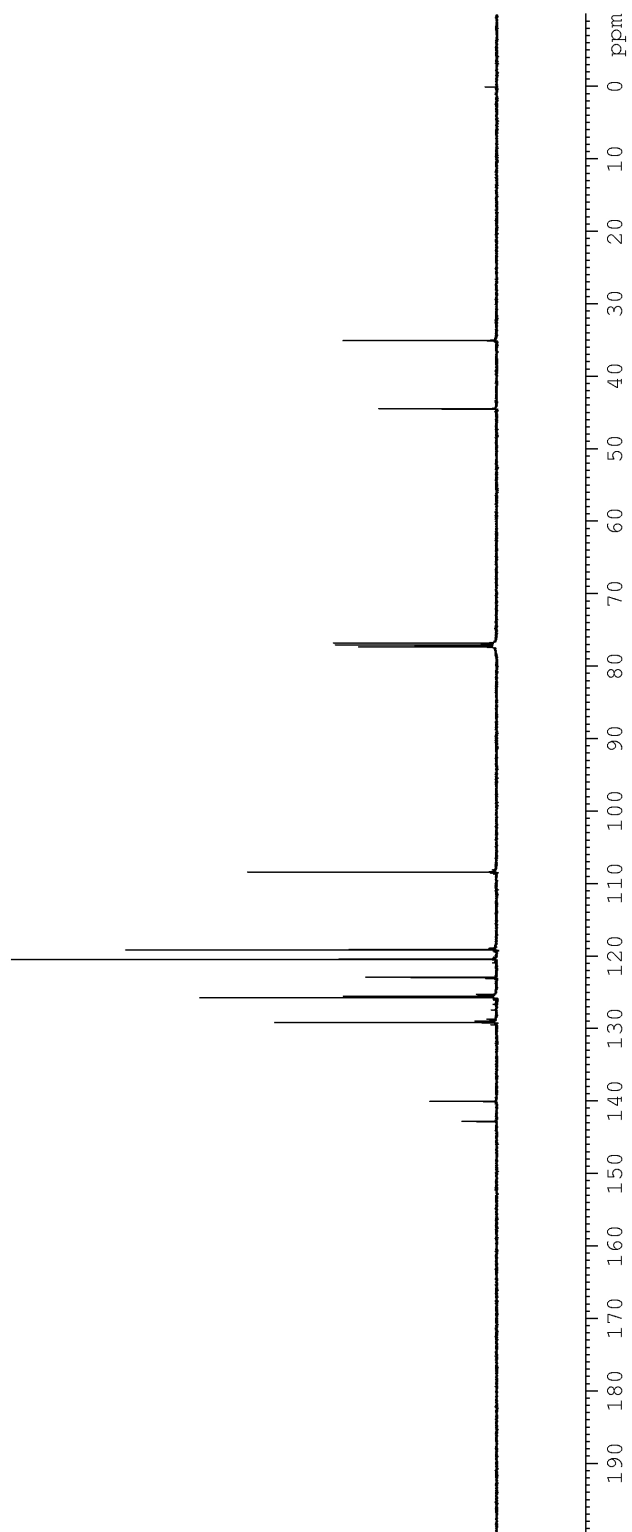
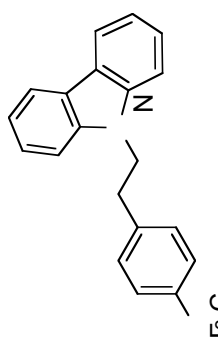
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2f**



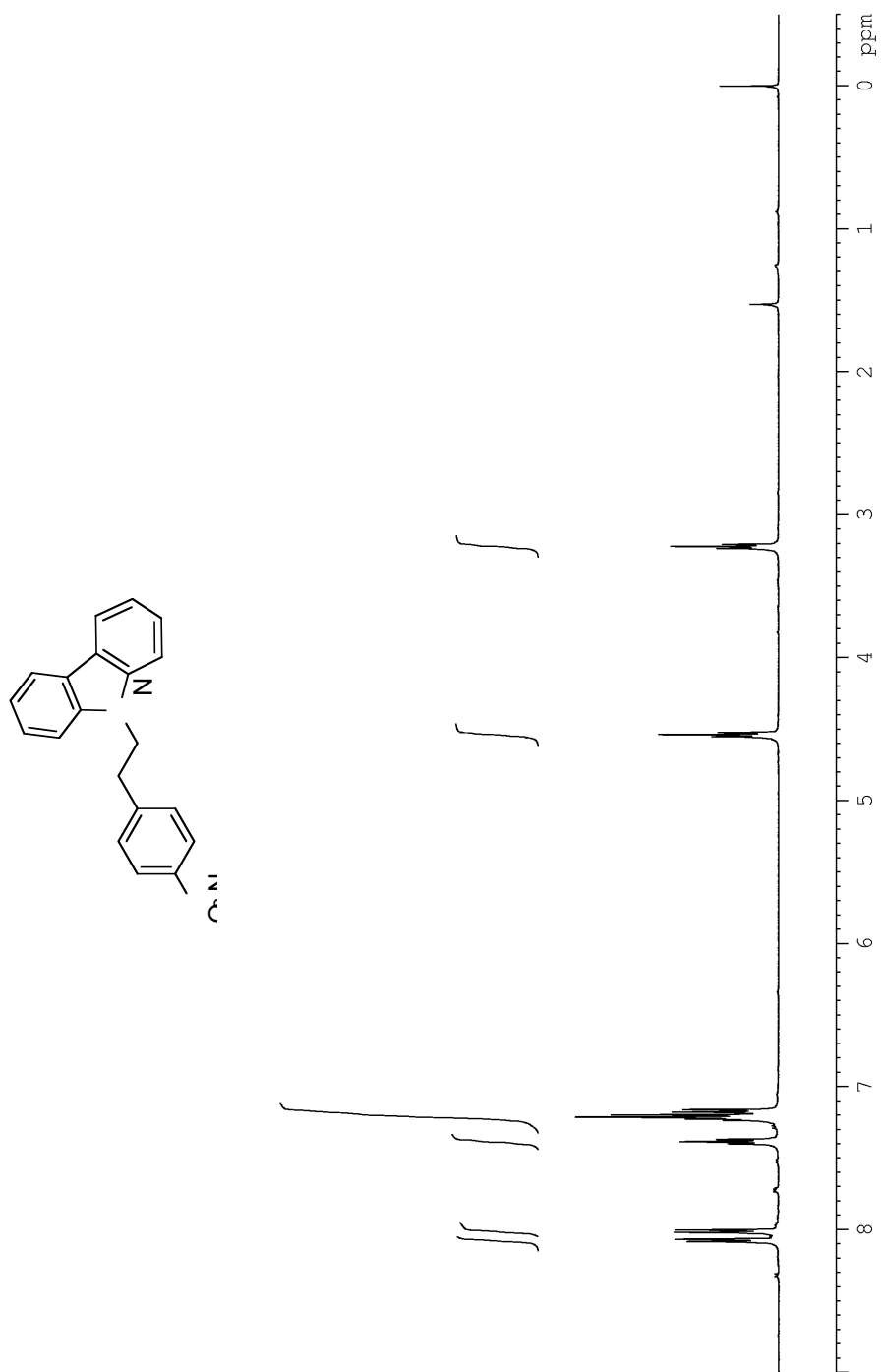
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2f**



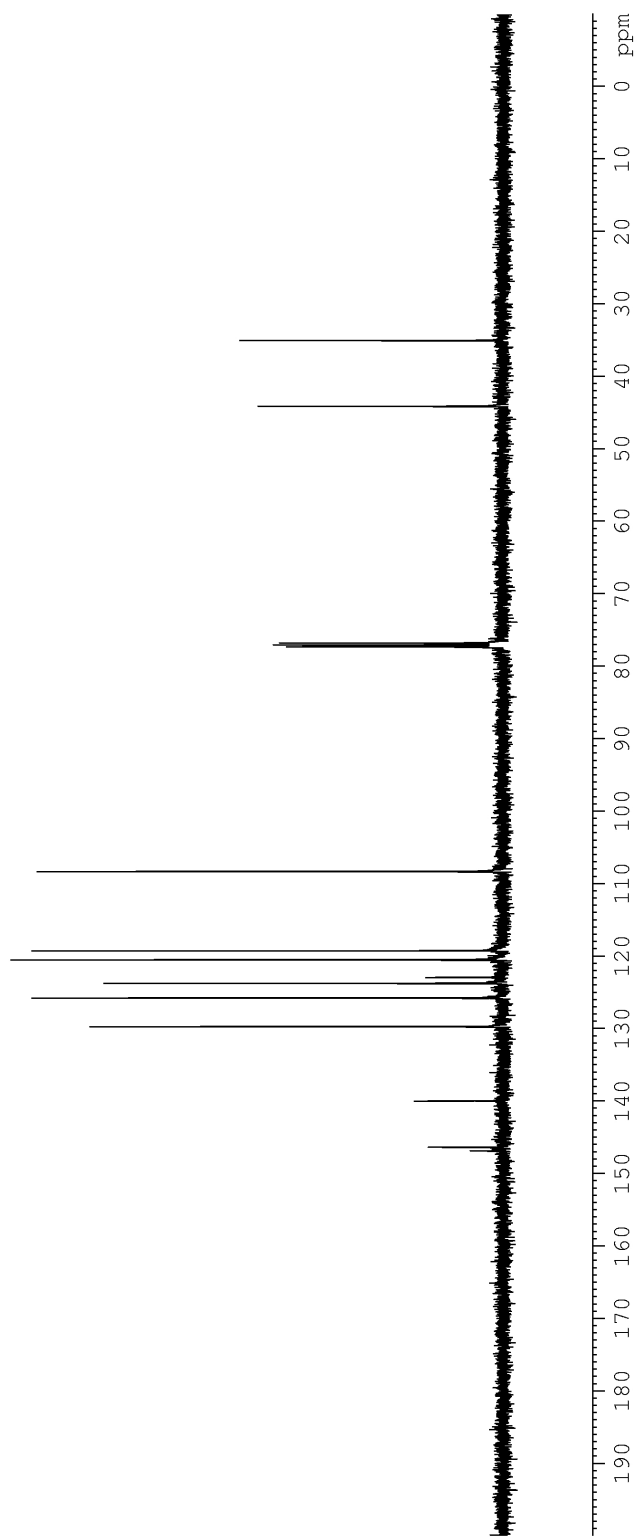
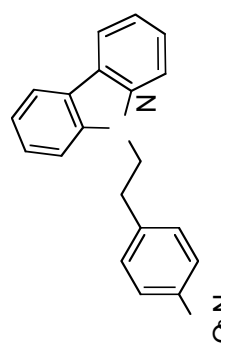
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2g**



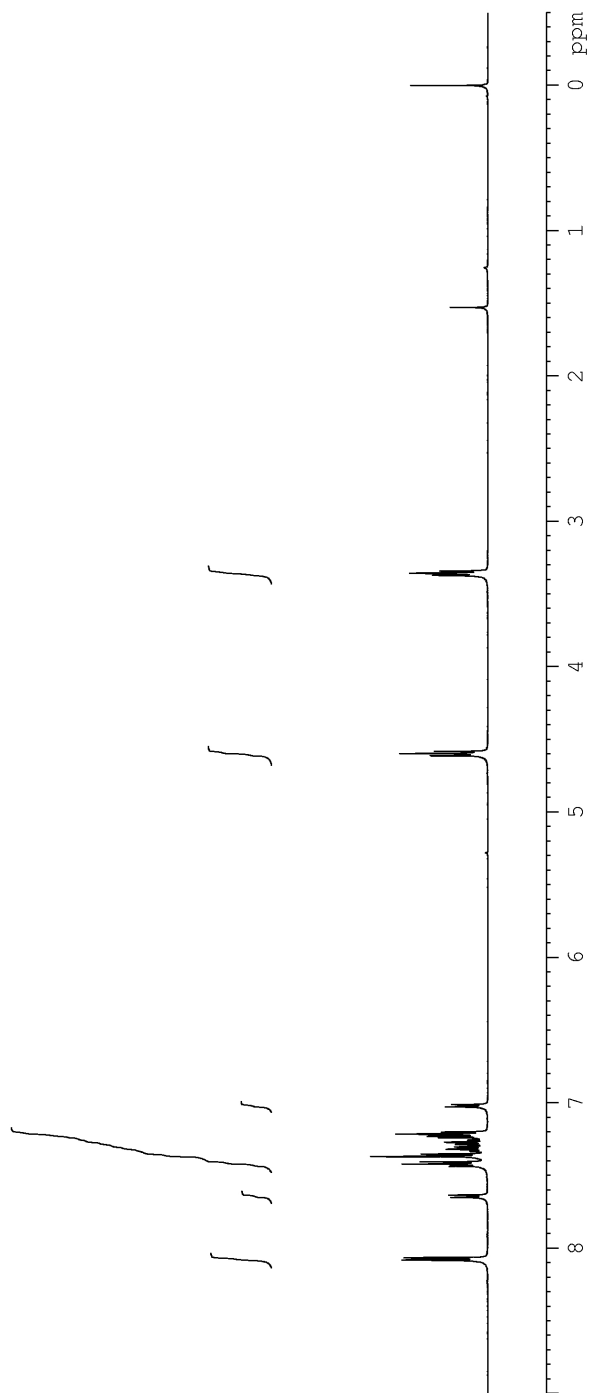
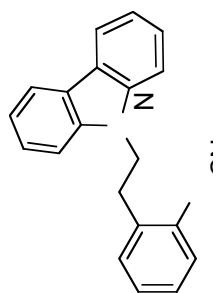
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2g**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2h**

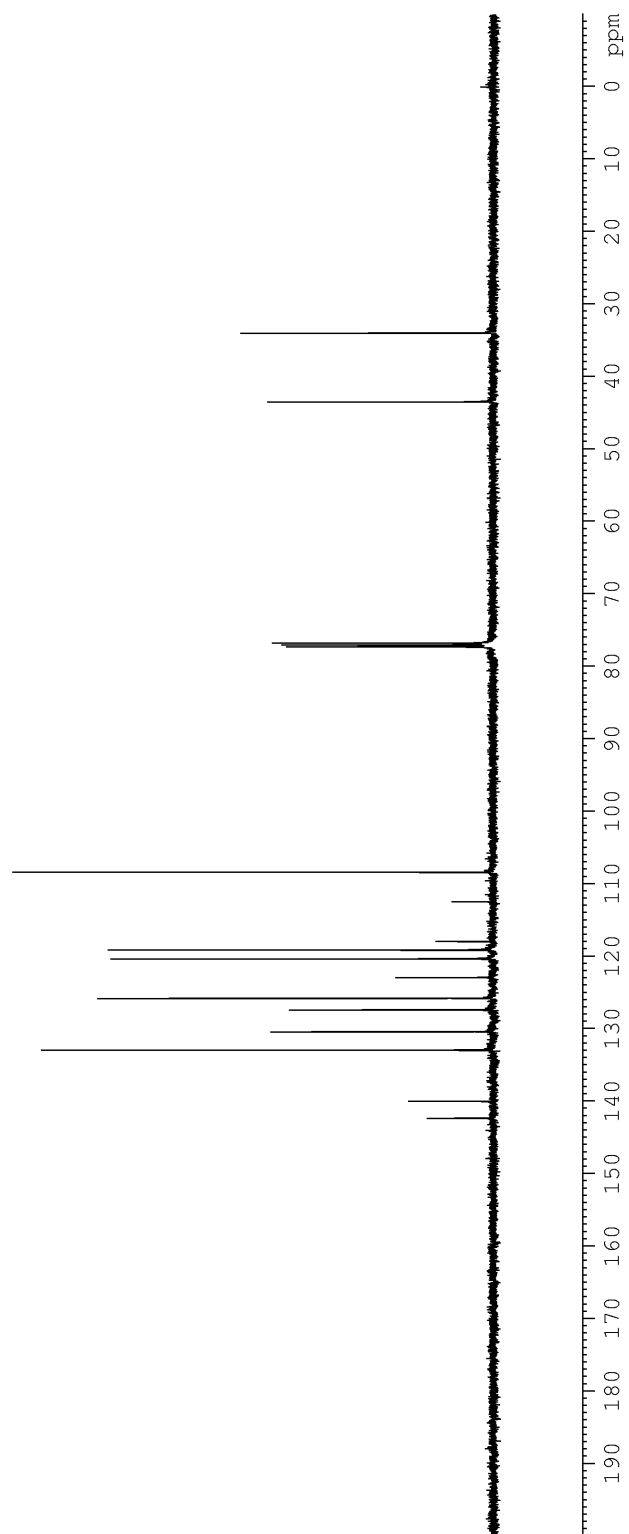
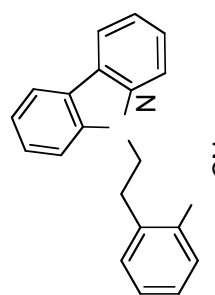


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2h**

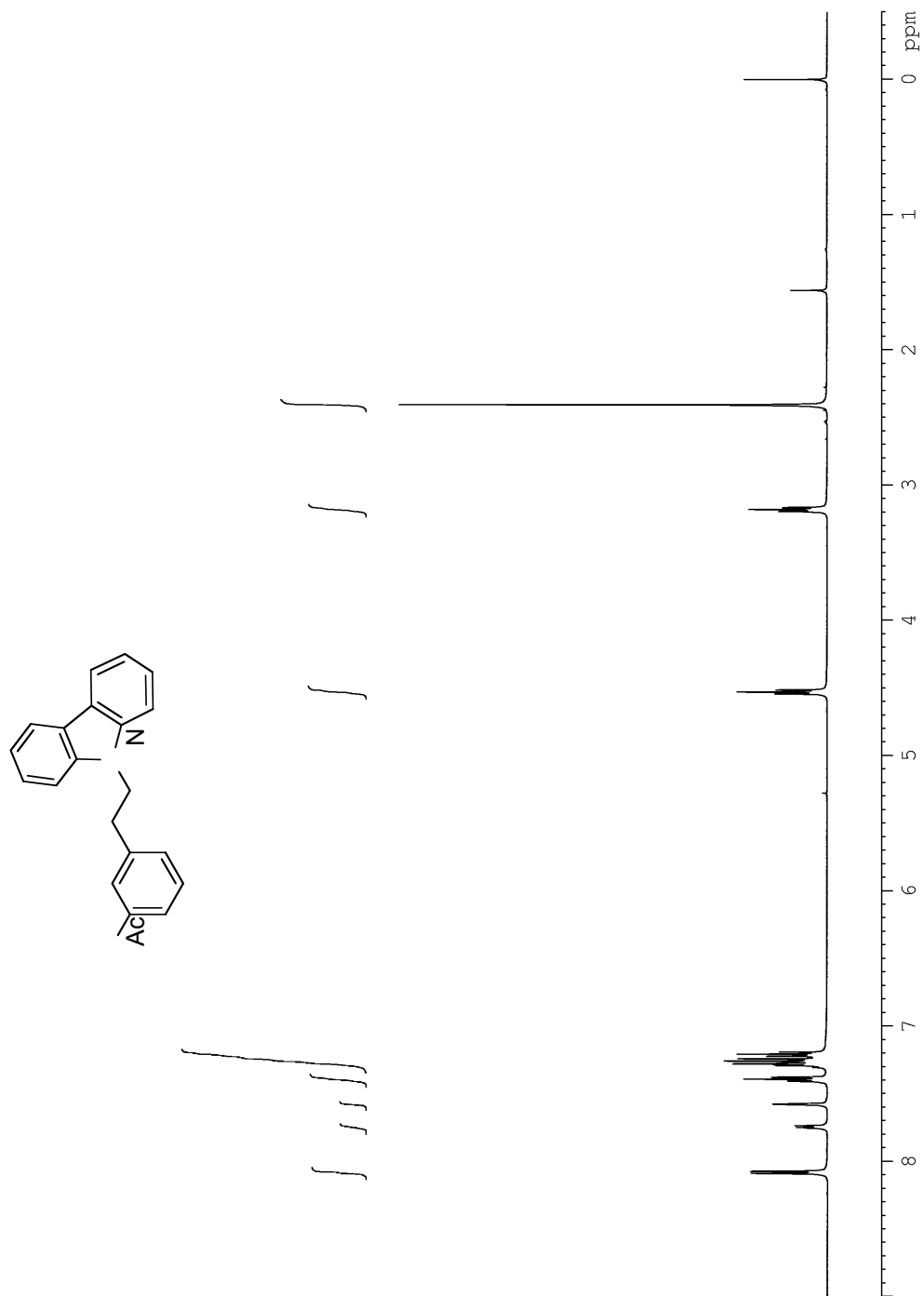


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2i**

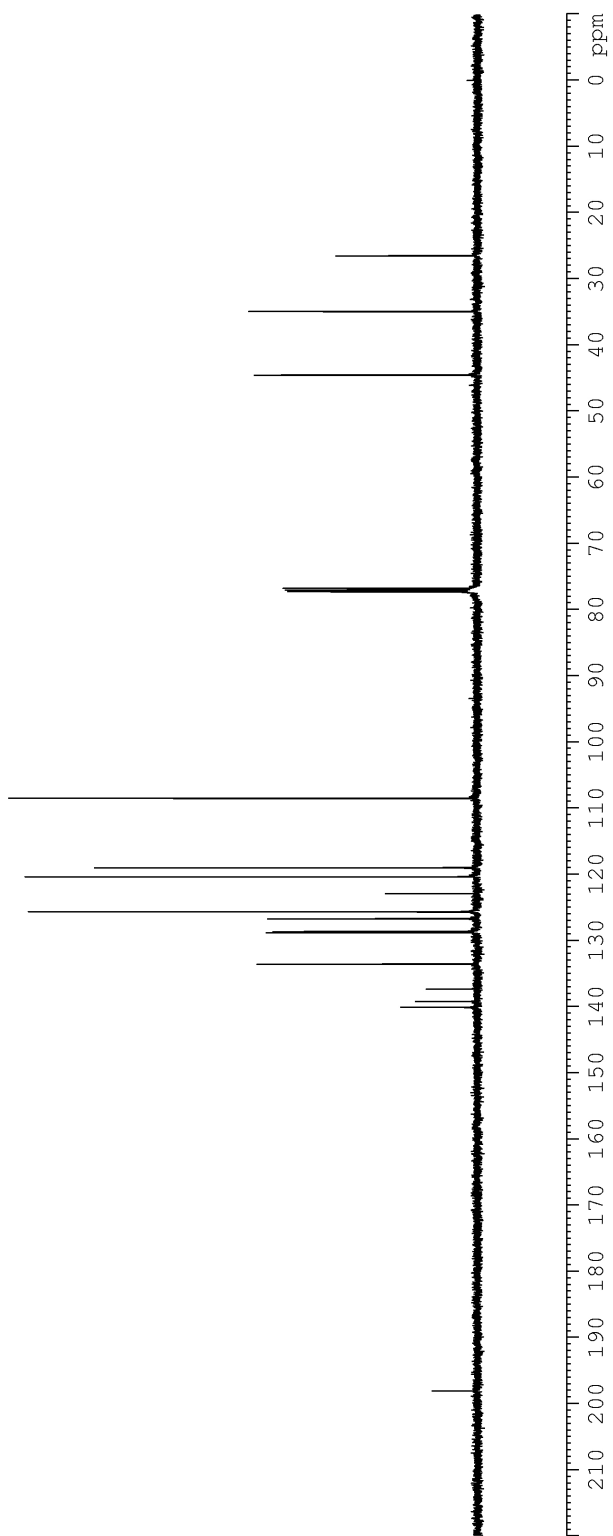
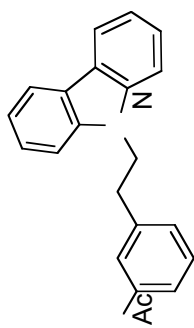




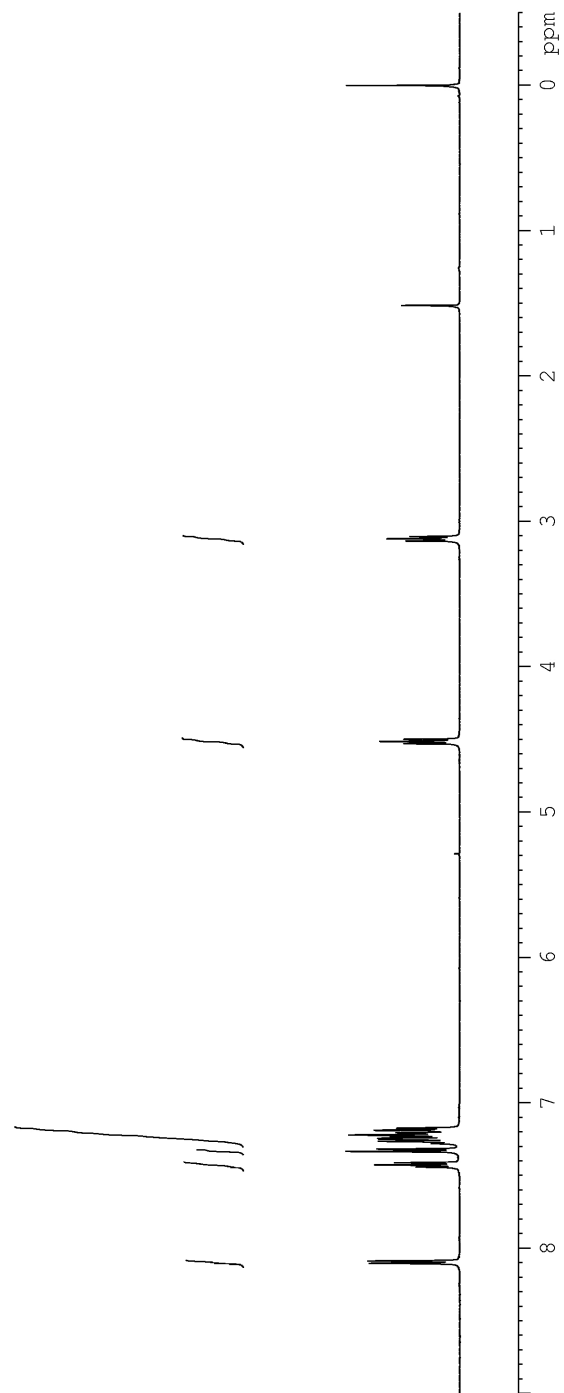
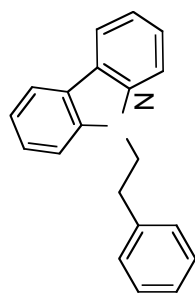
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2i**



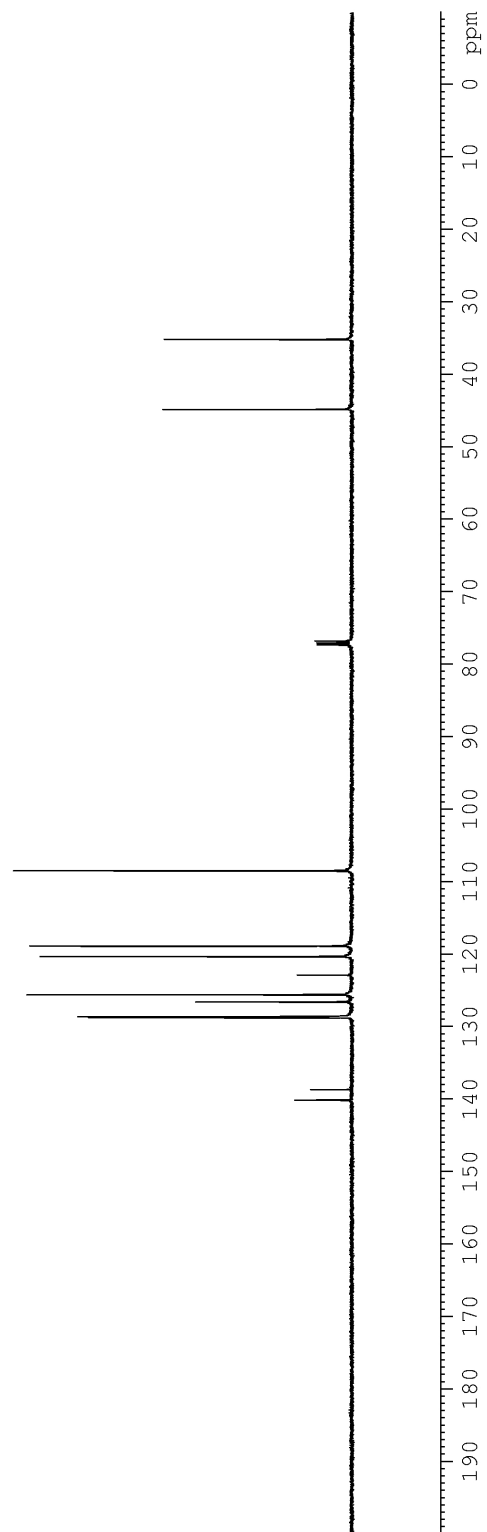
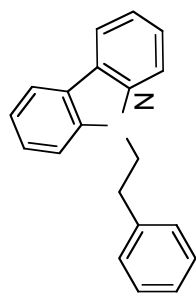
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2j**



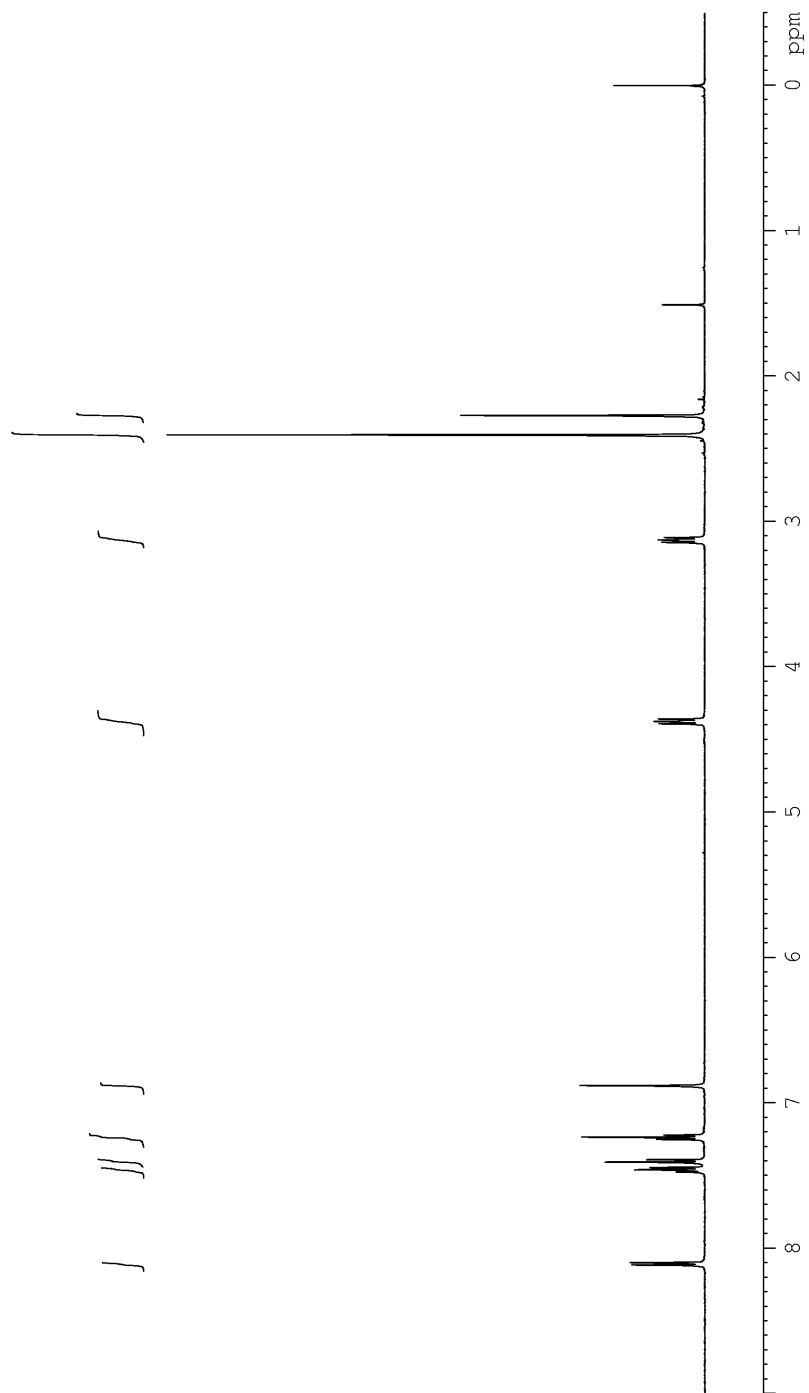
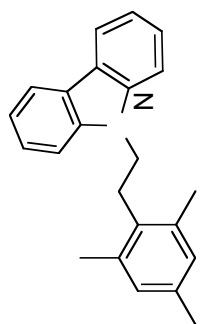
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2j**



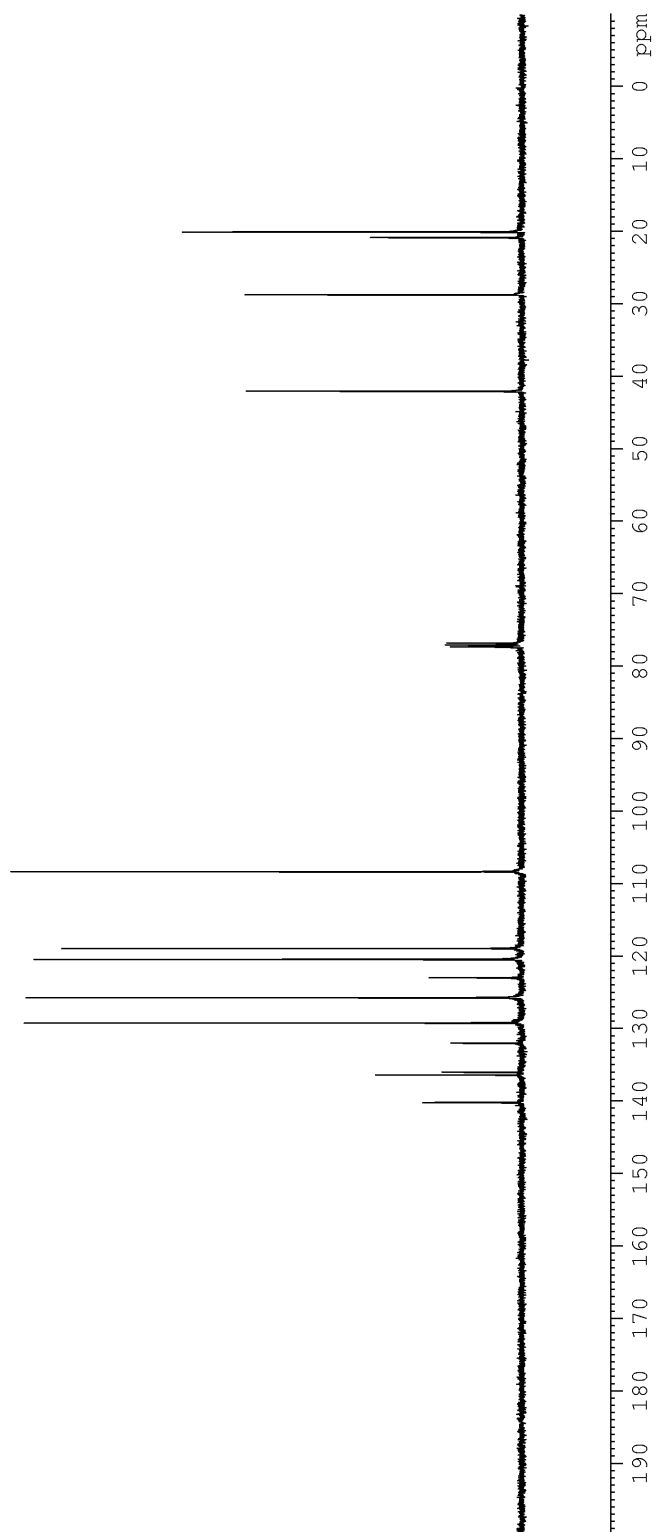
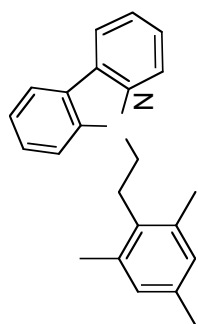
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2k**



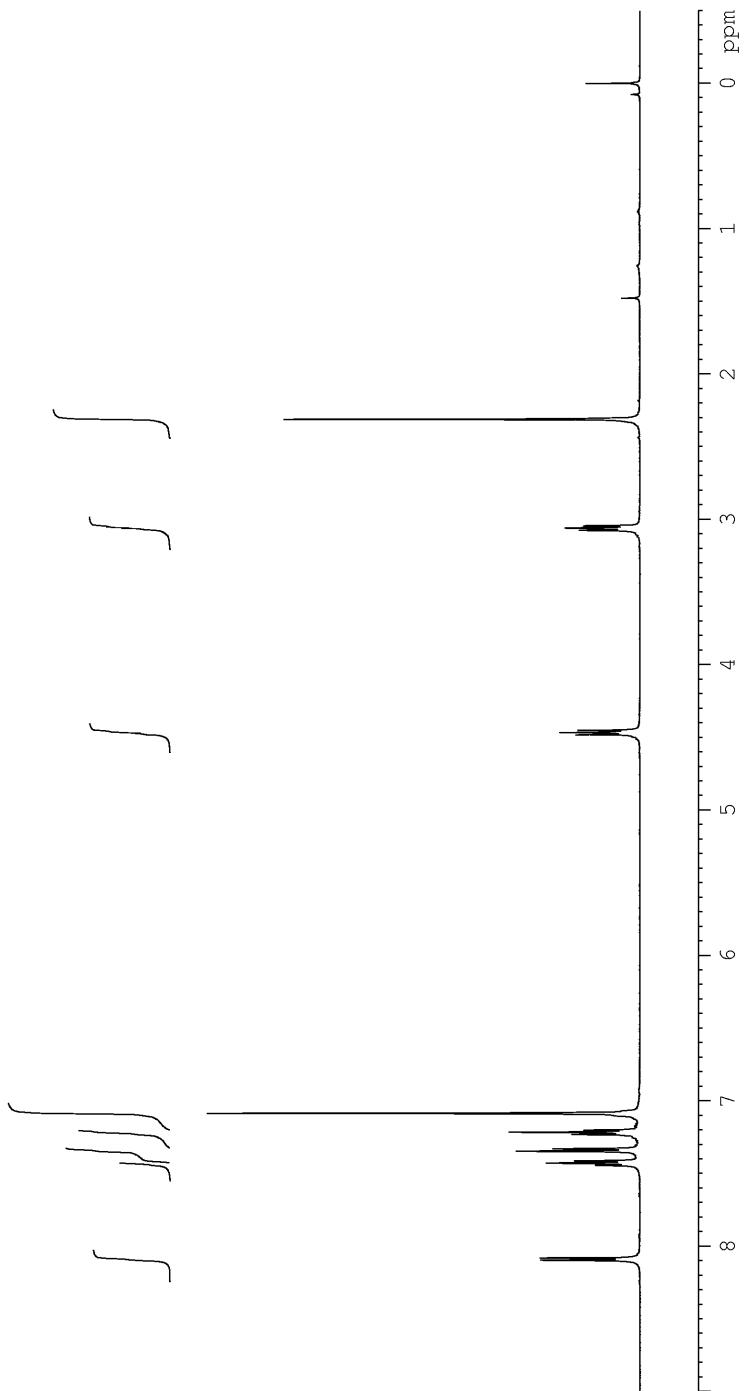
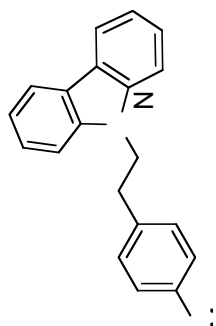
$^{13}\text{C}$  NMR (125.8 MHz, CDCl<sub>3</sub>) Spectrum of **2k**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **21**

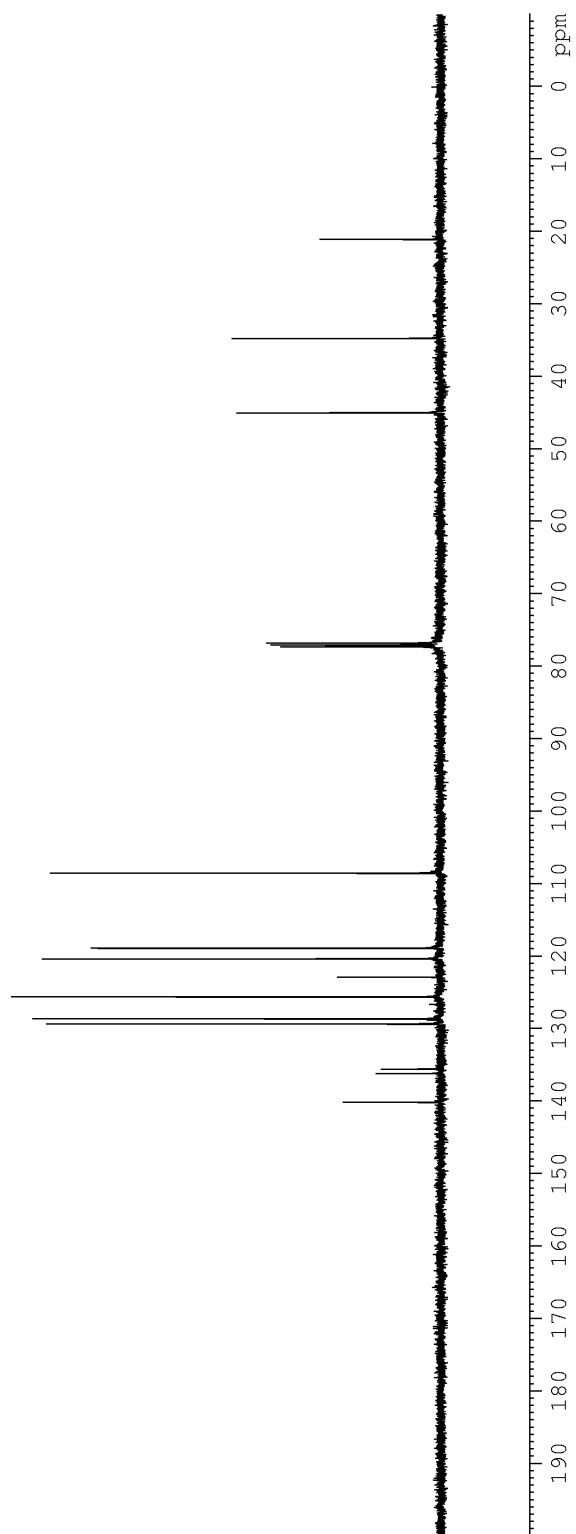
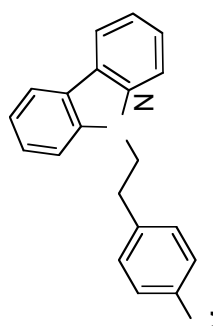


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2I**

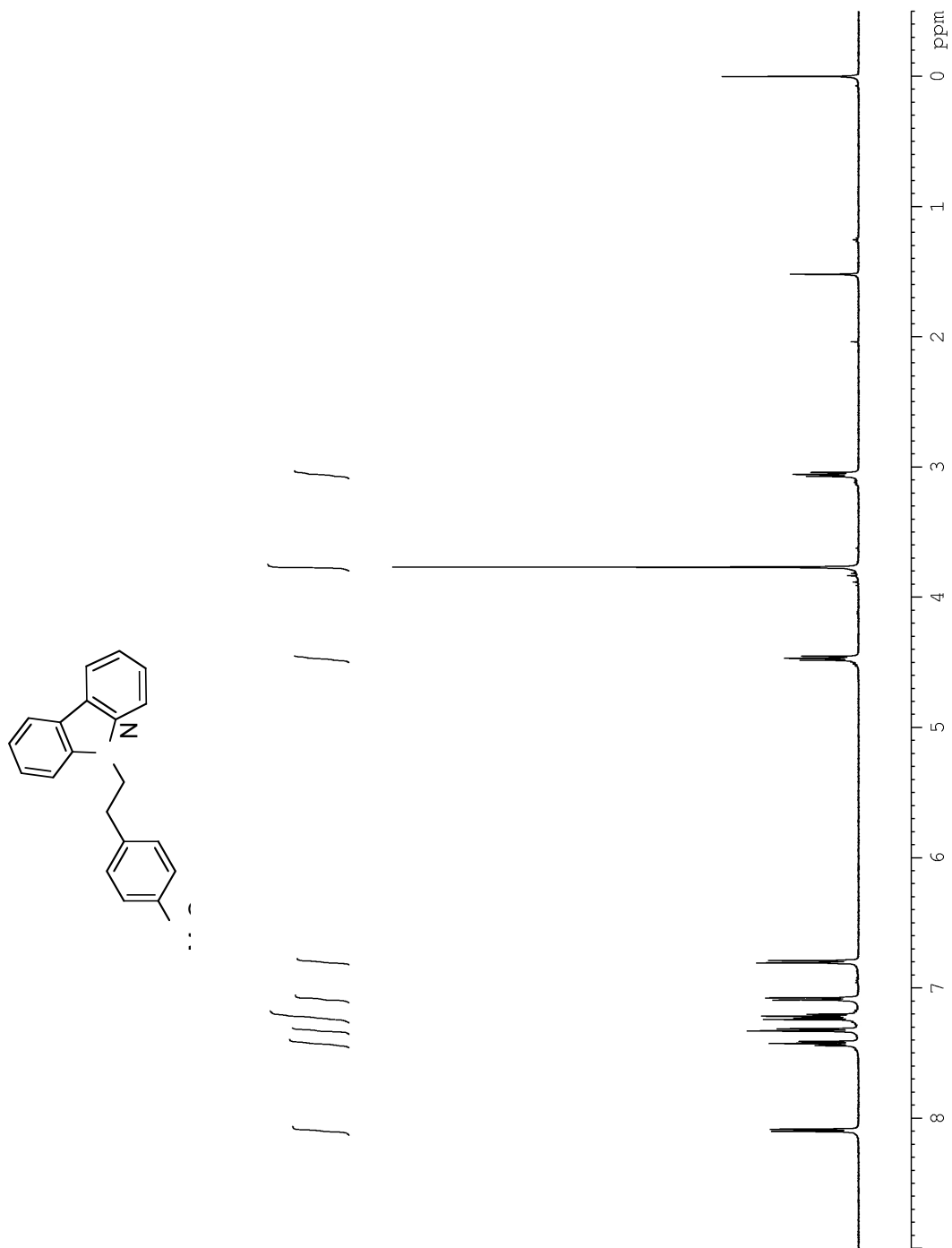


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2m**

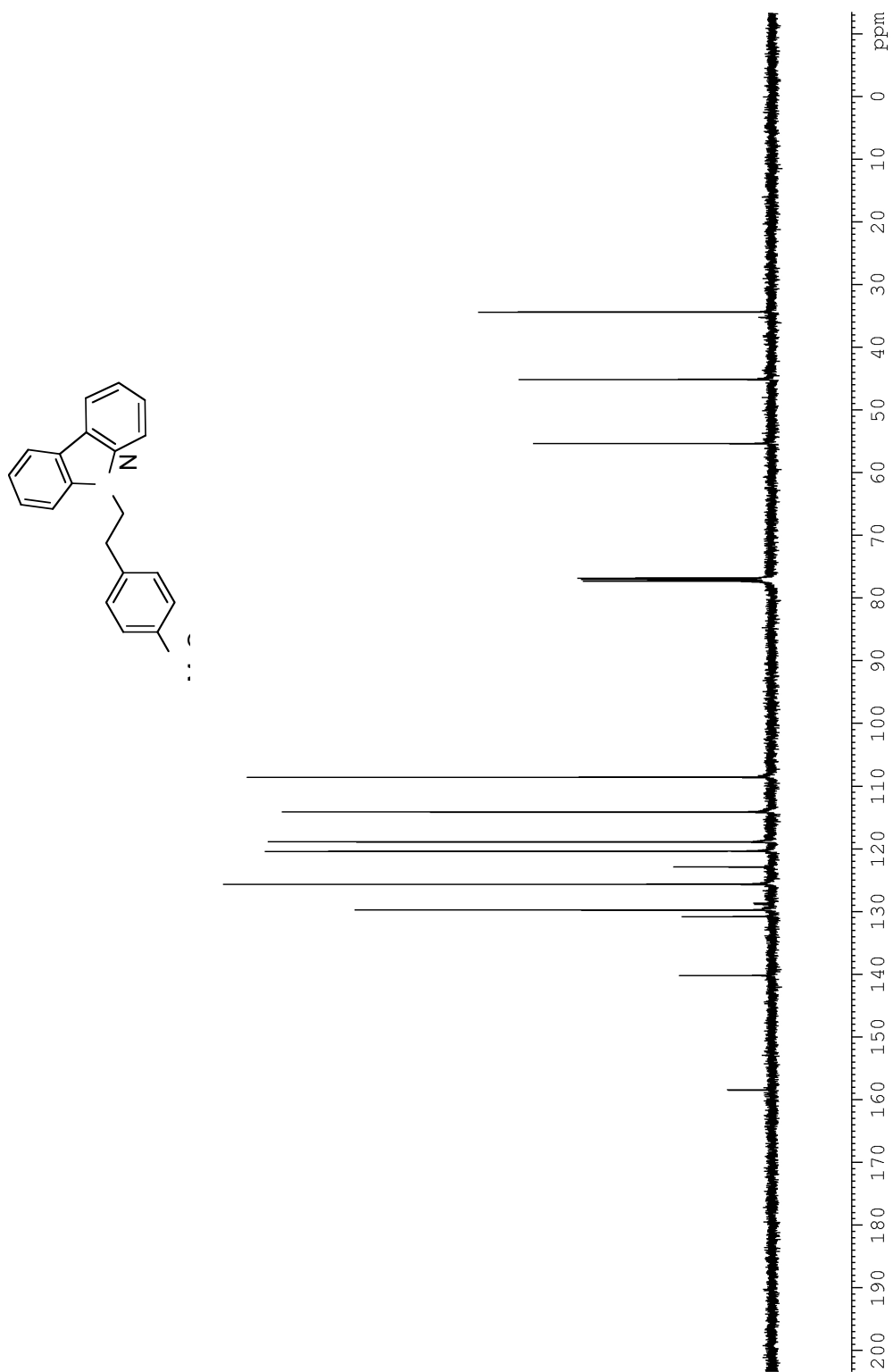




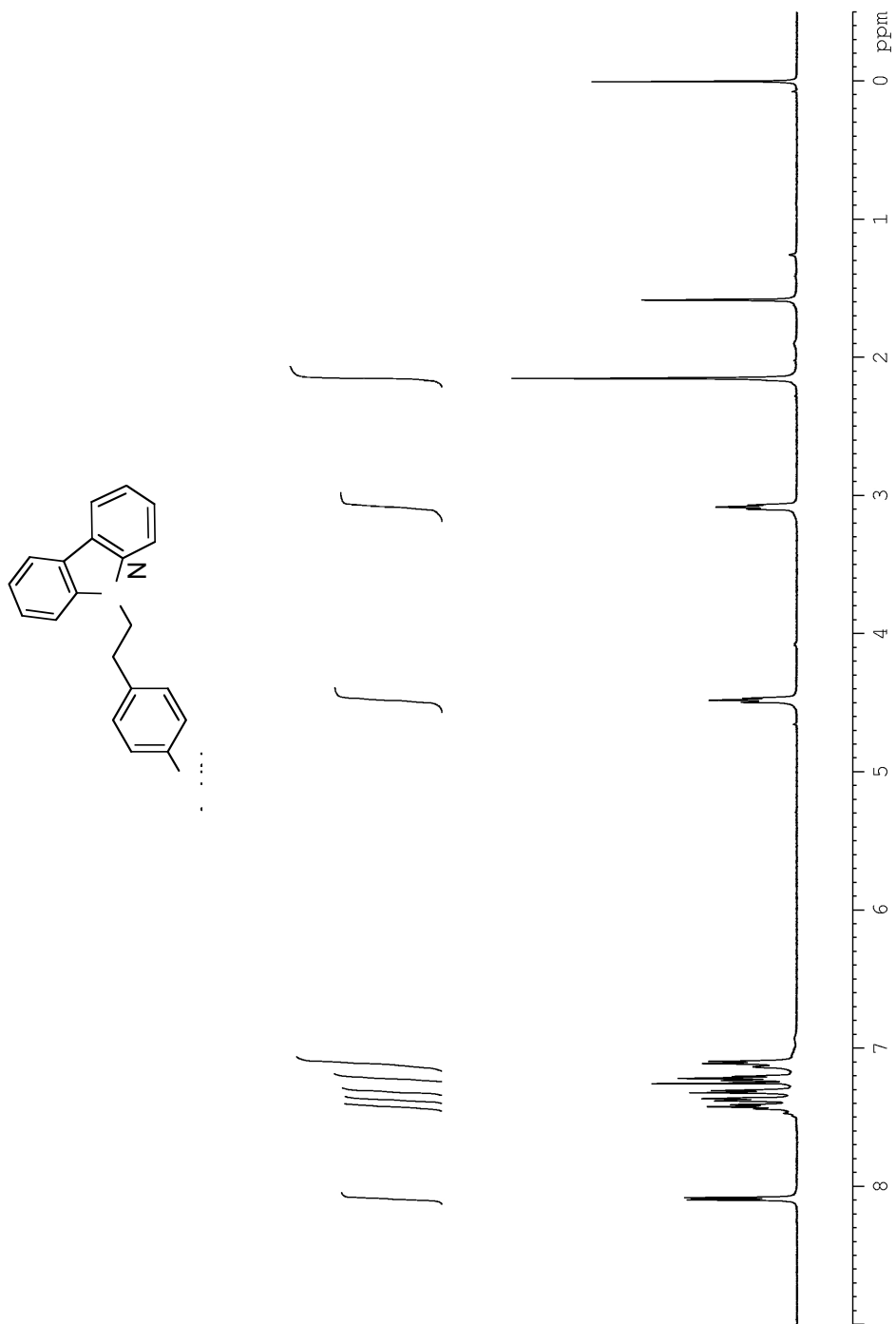
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2m**



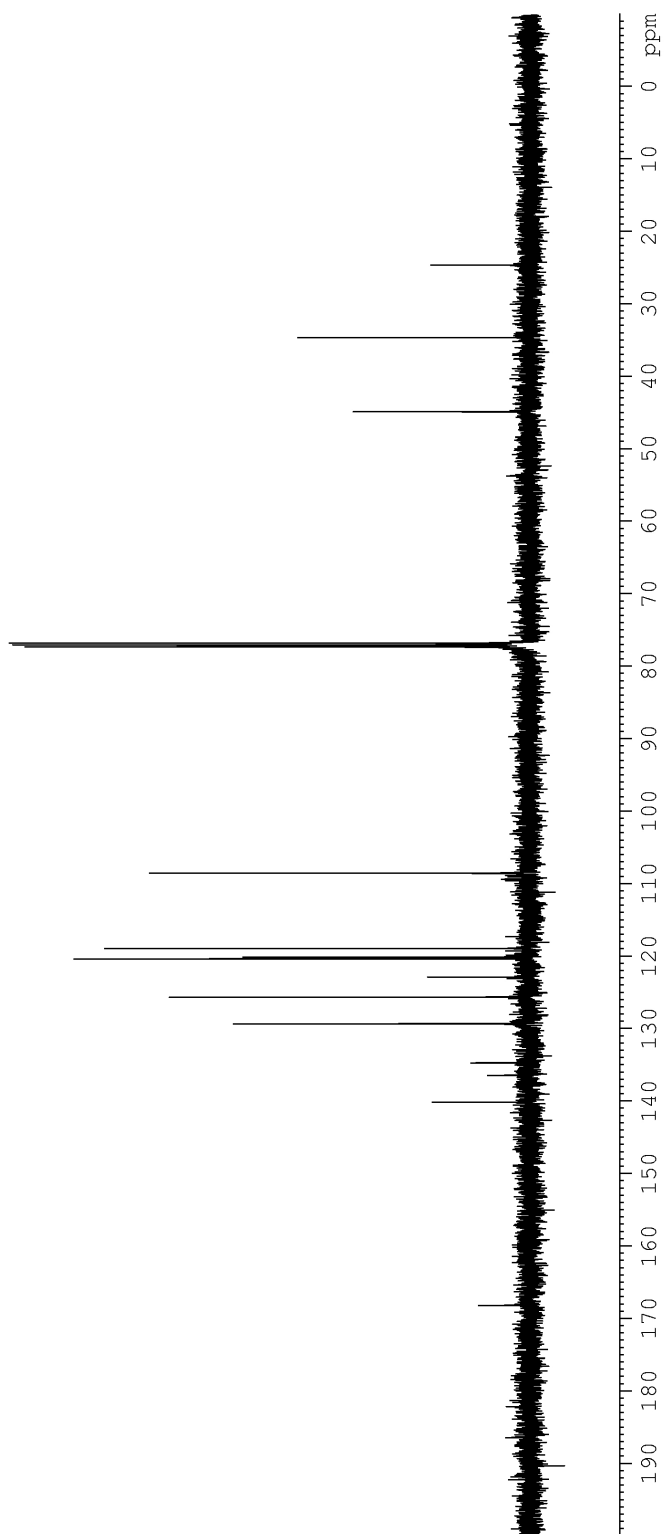
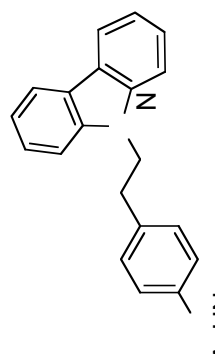
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of **2n**



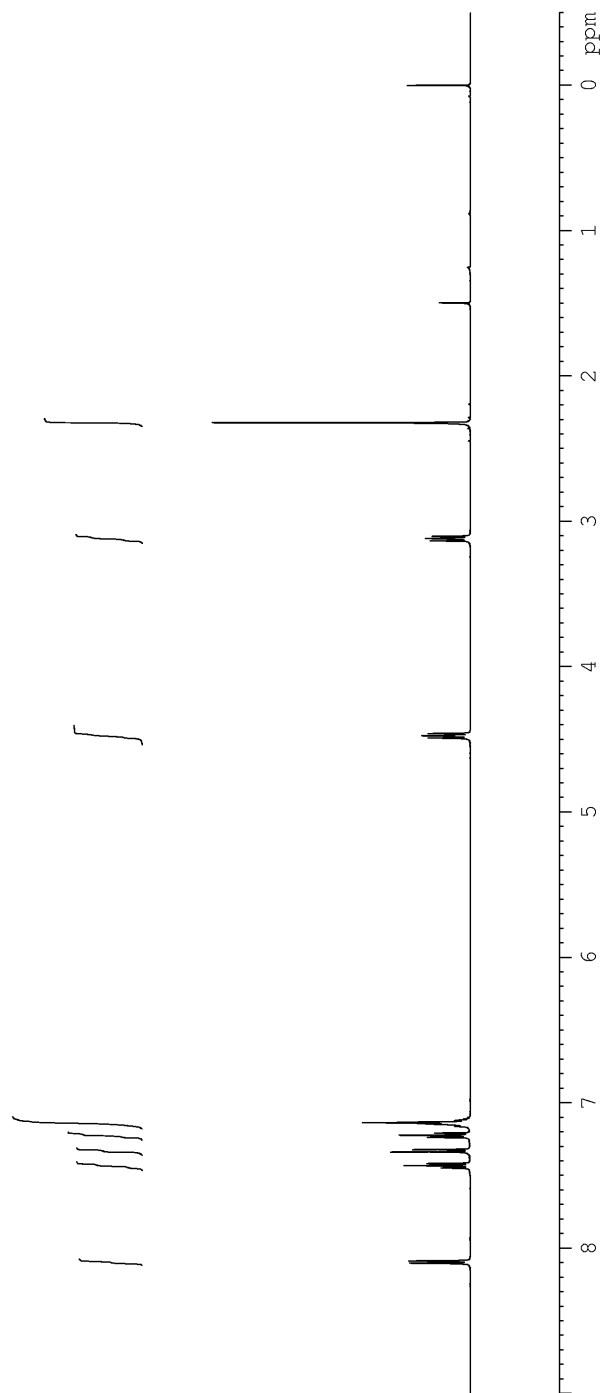
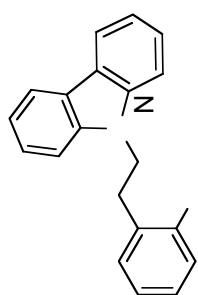
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2n**



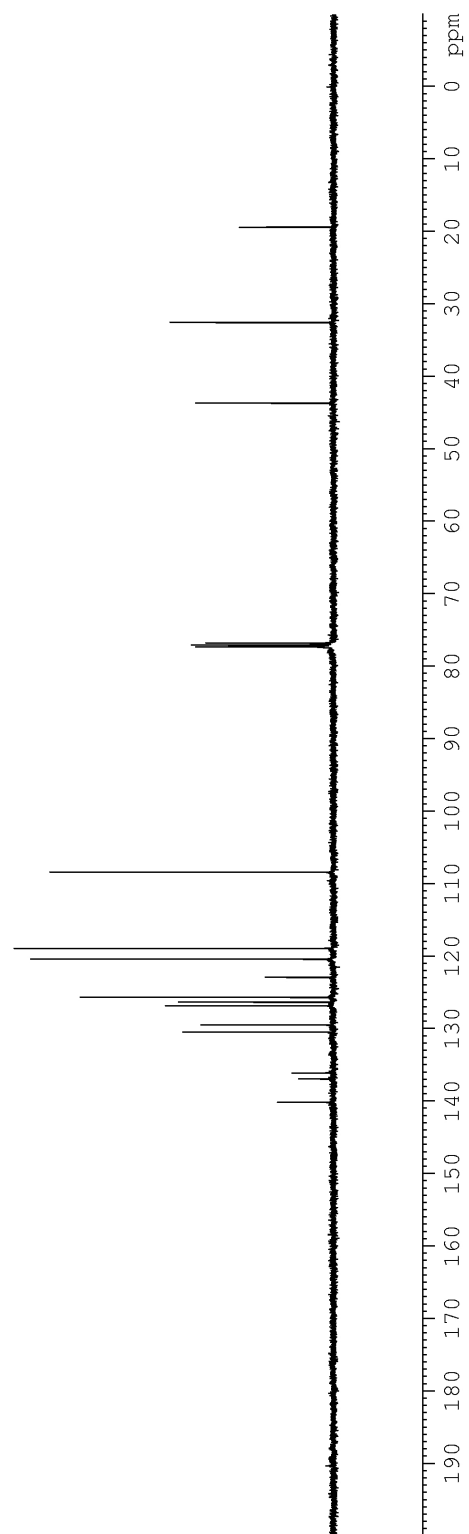
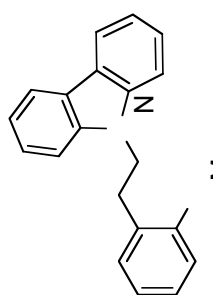
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2o**



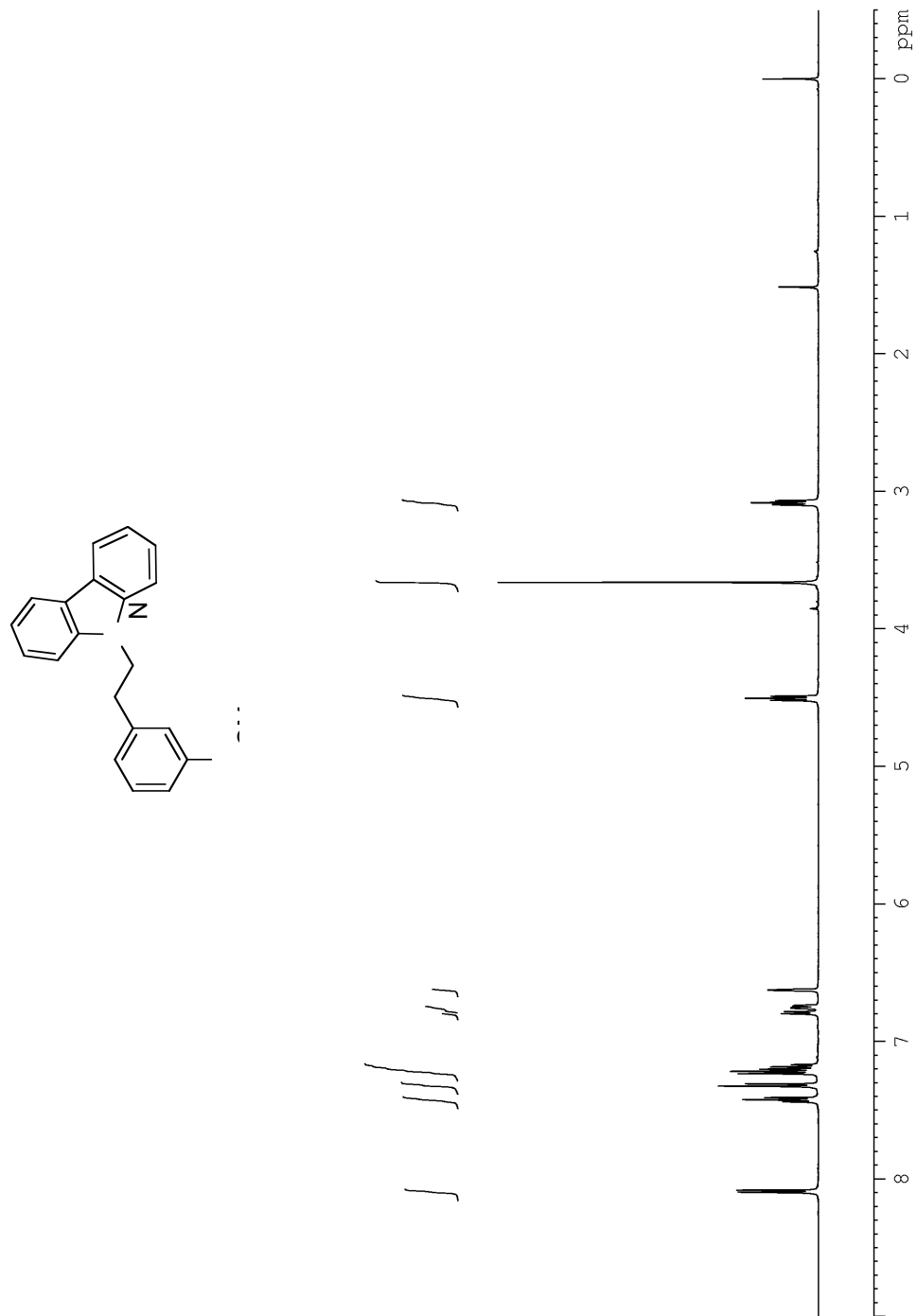
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2o**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2p**

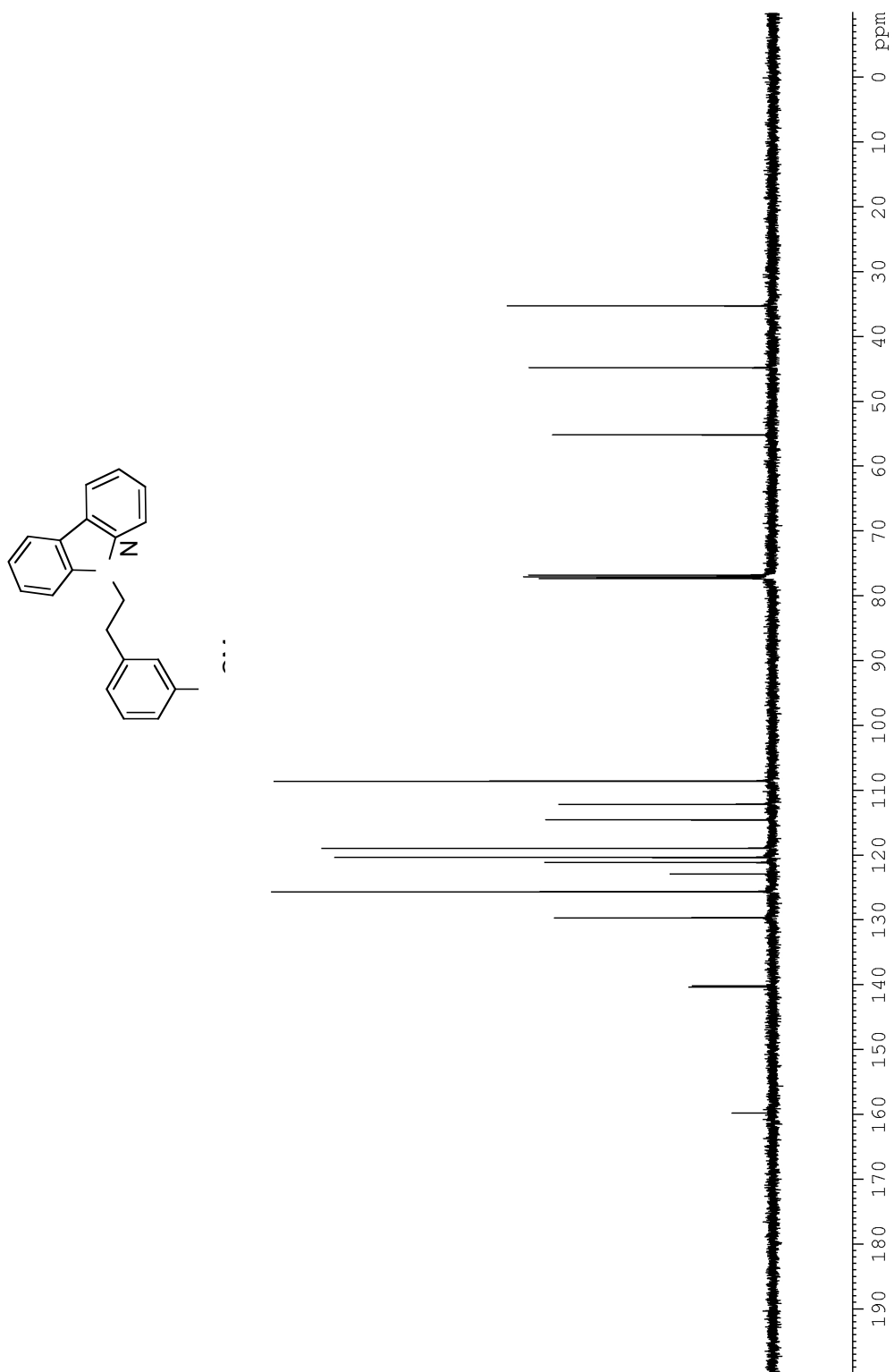


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2p**

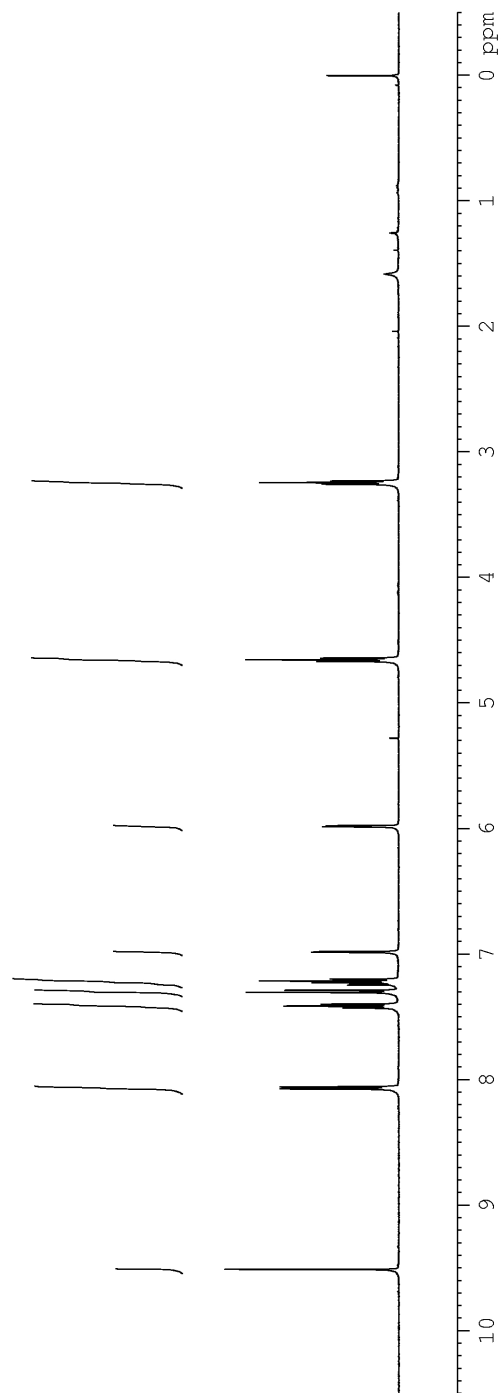
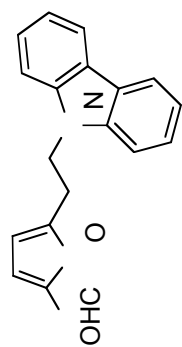


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of **2q**

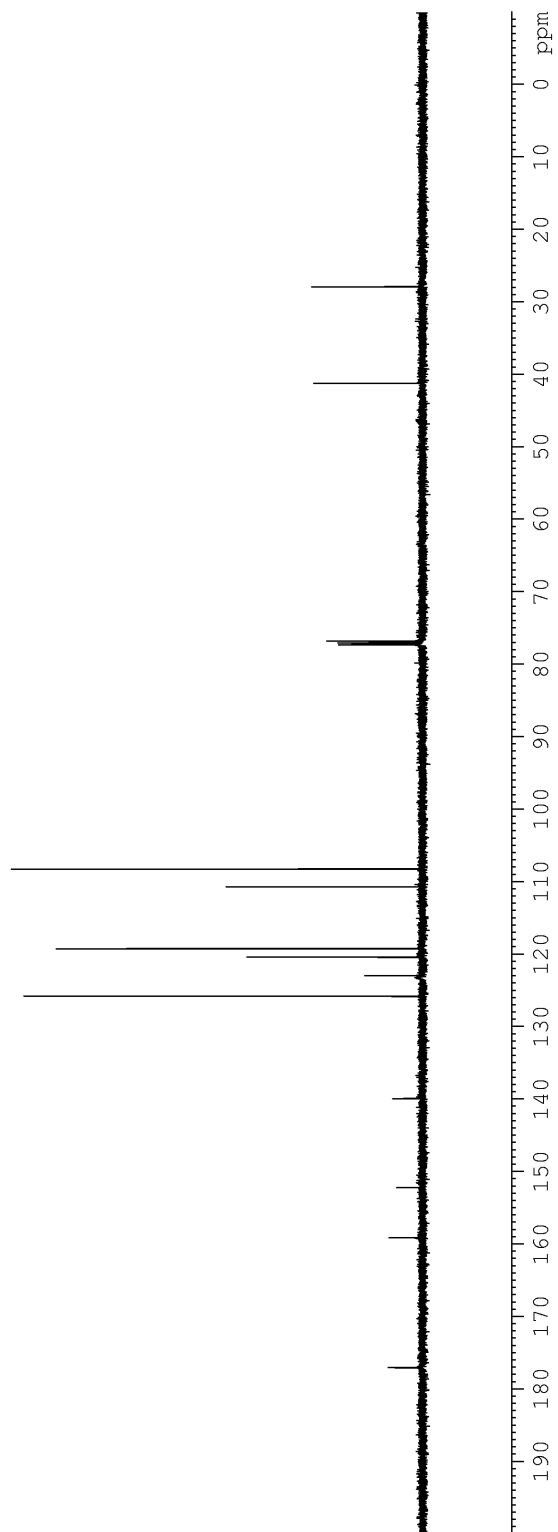
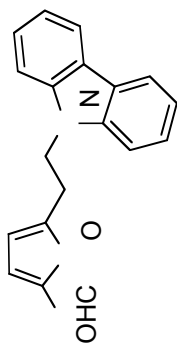




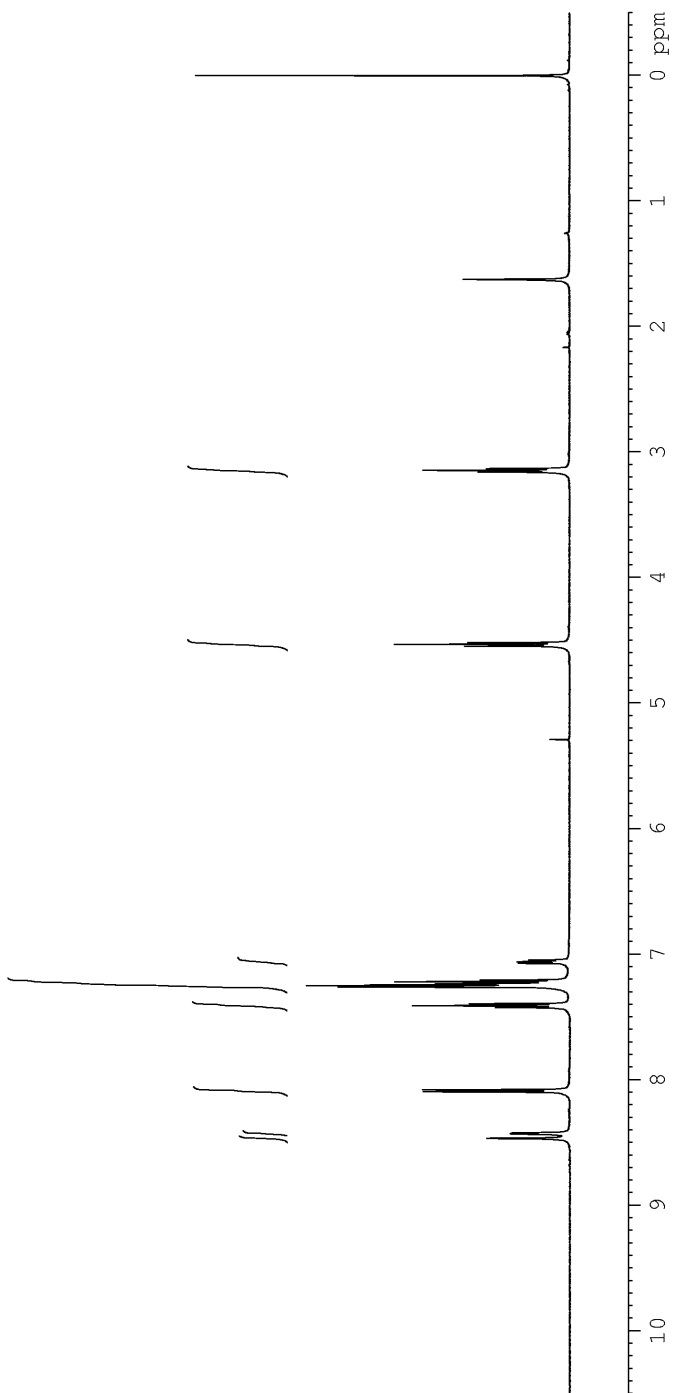
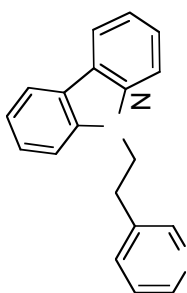
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2q**



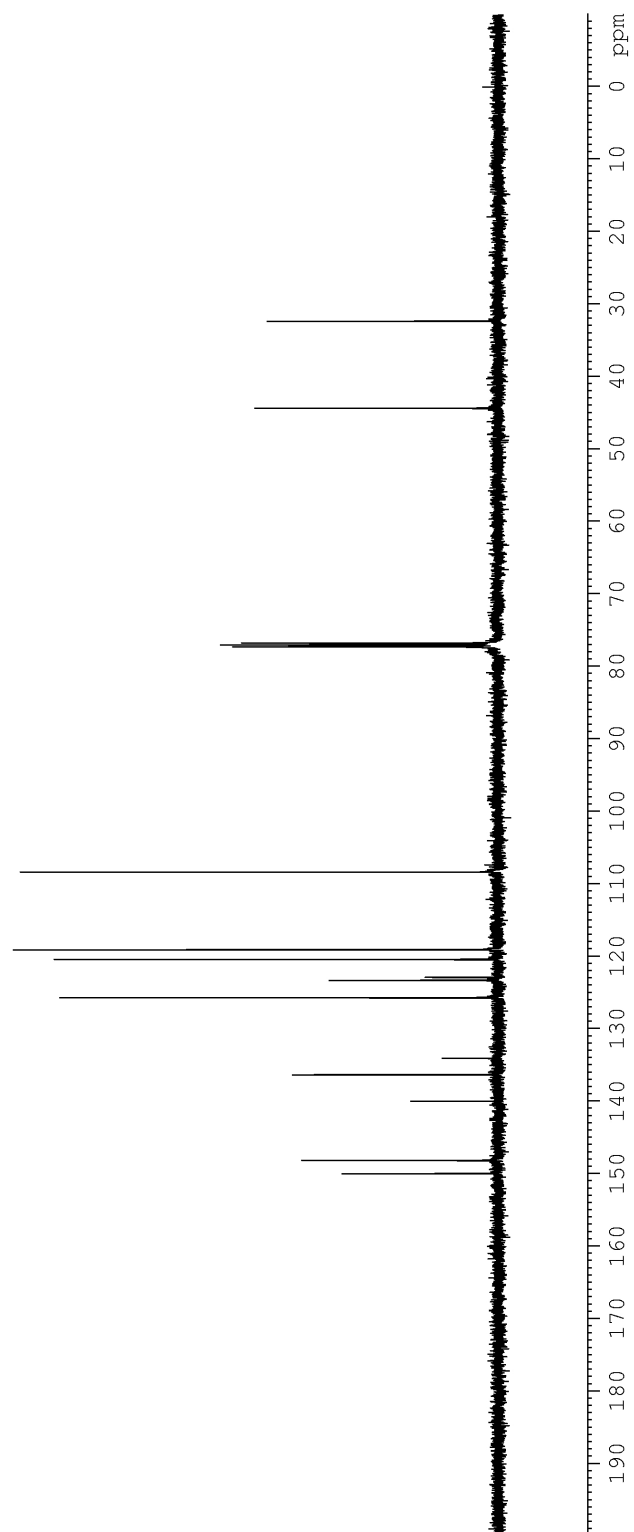
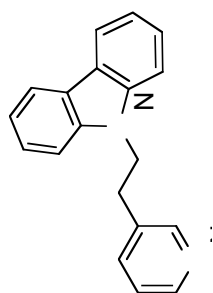
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2r**



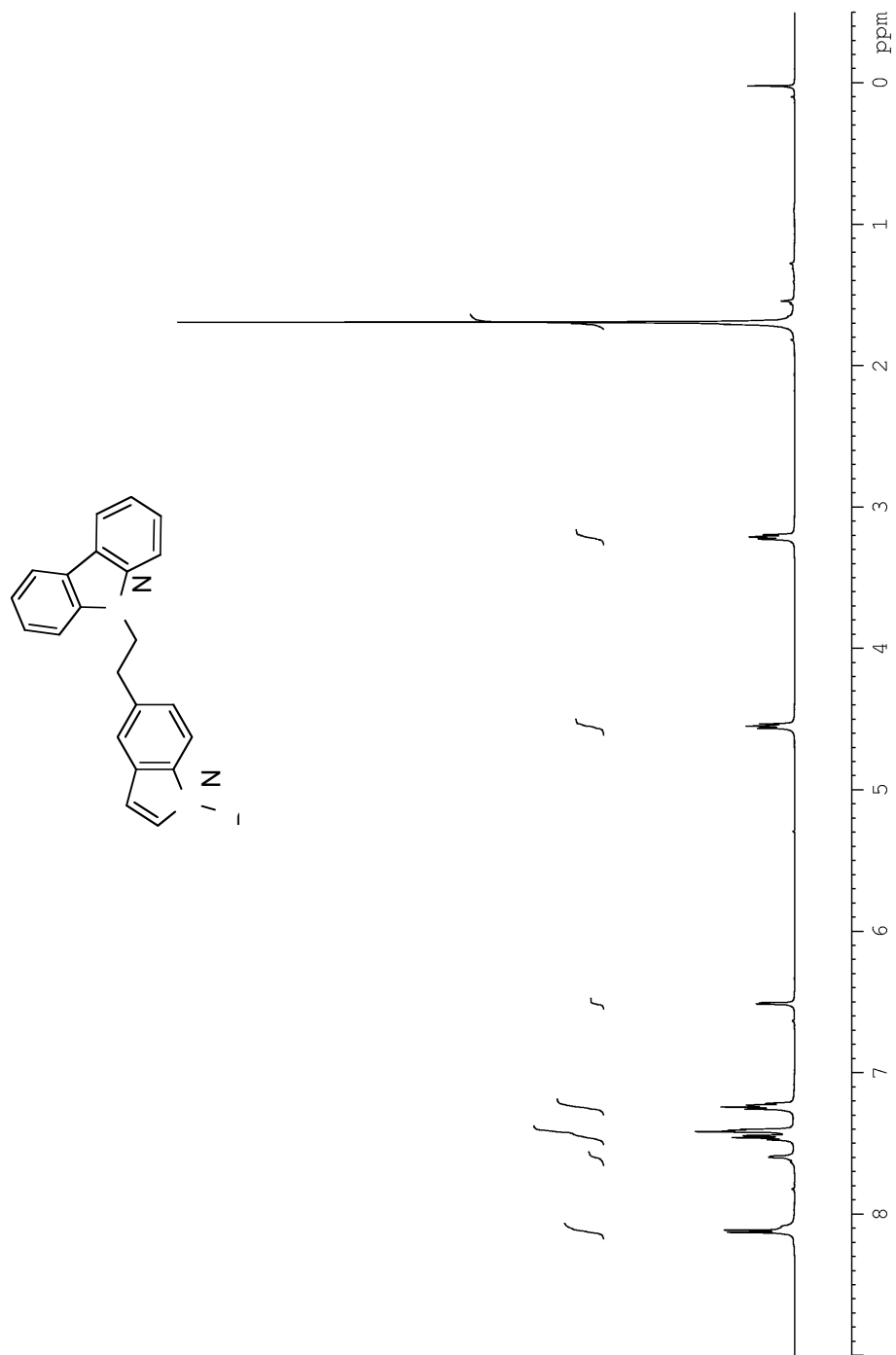
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2r**



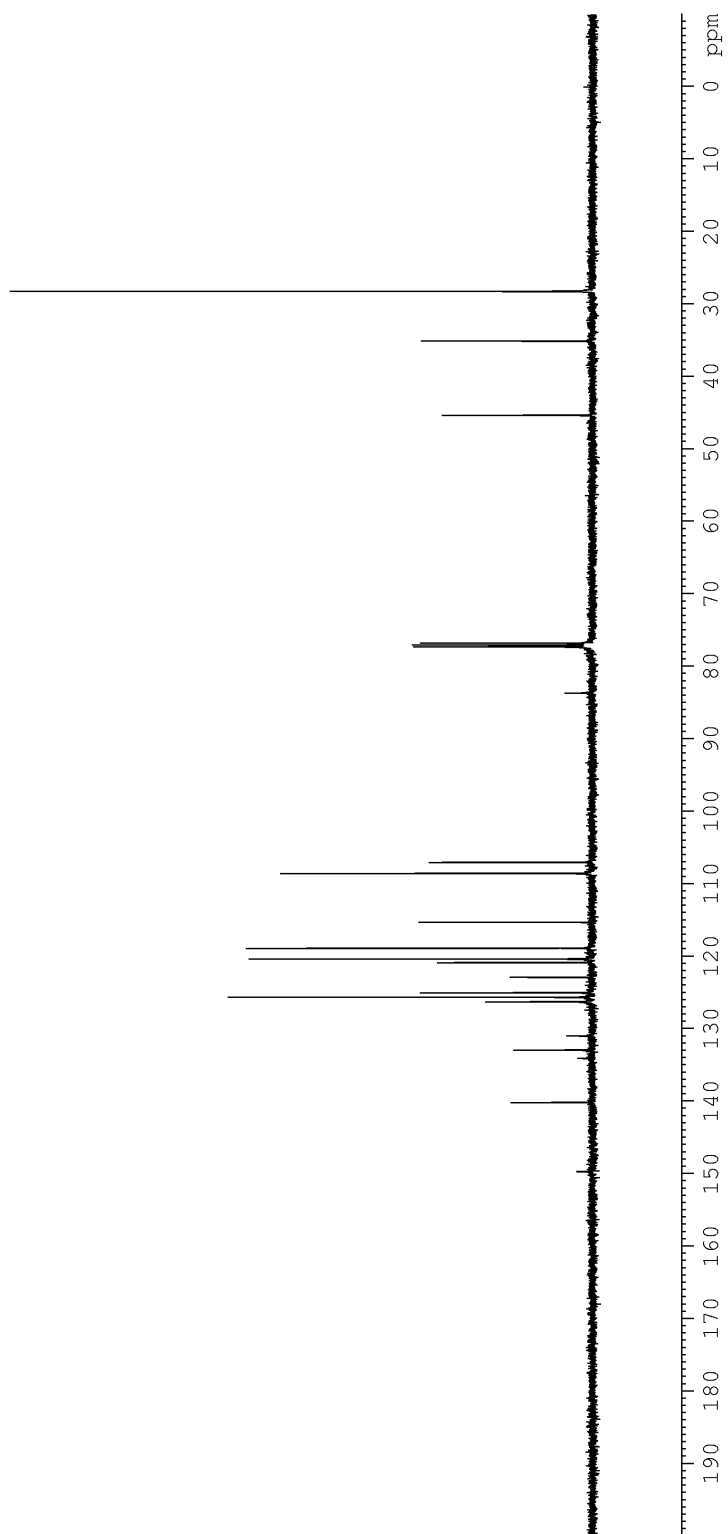
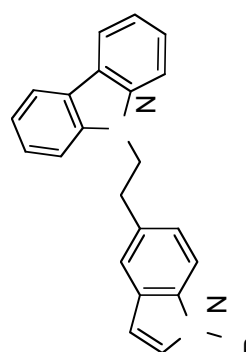
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2s**



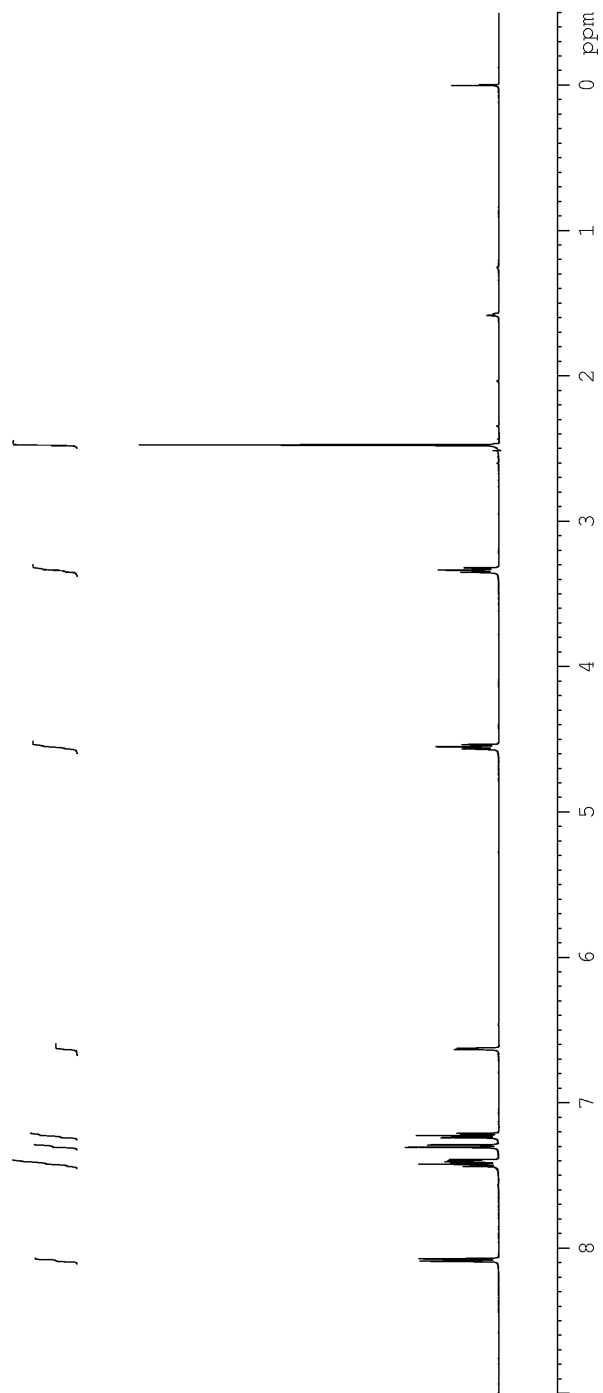
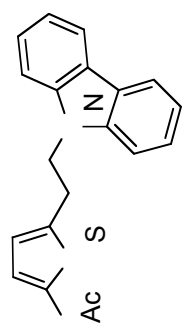
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2s**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of **2t**

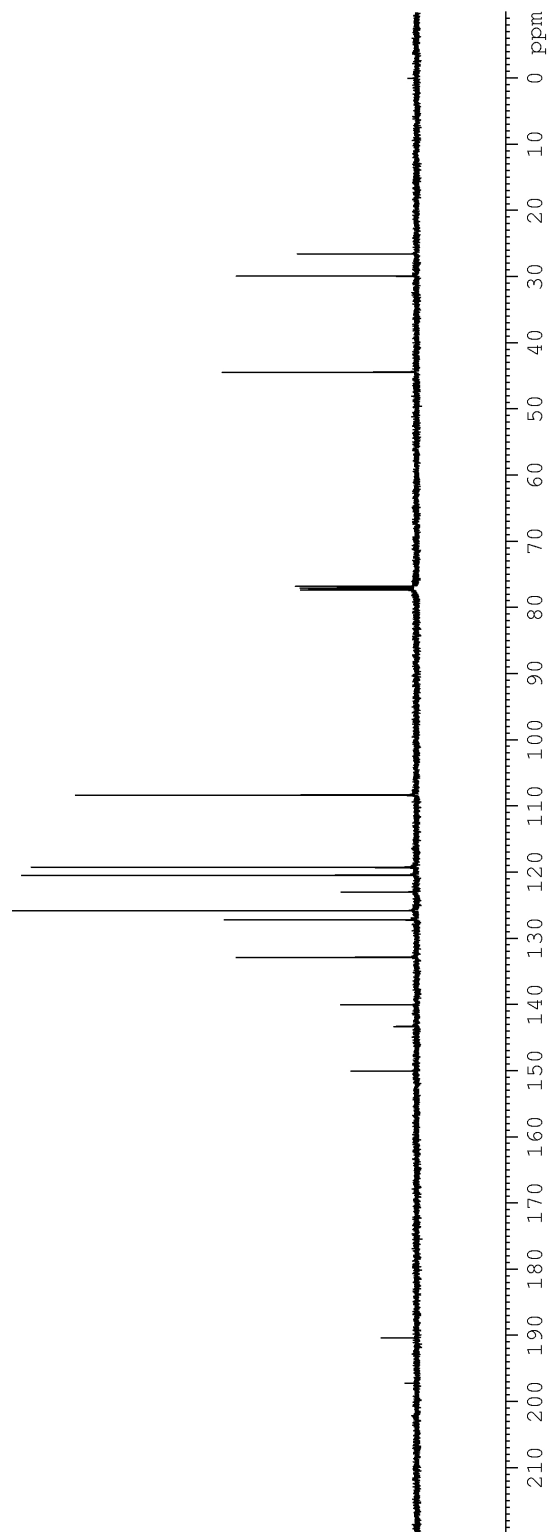
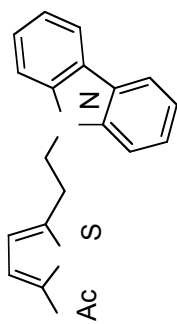


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of 2t

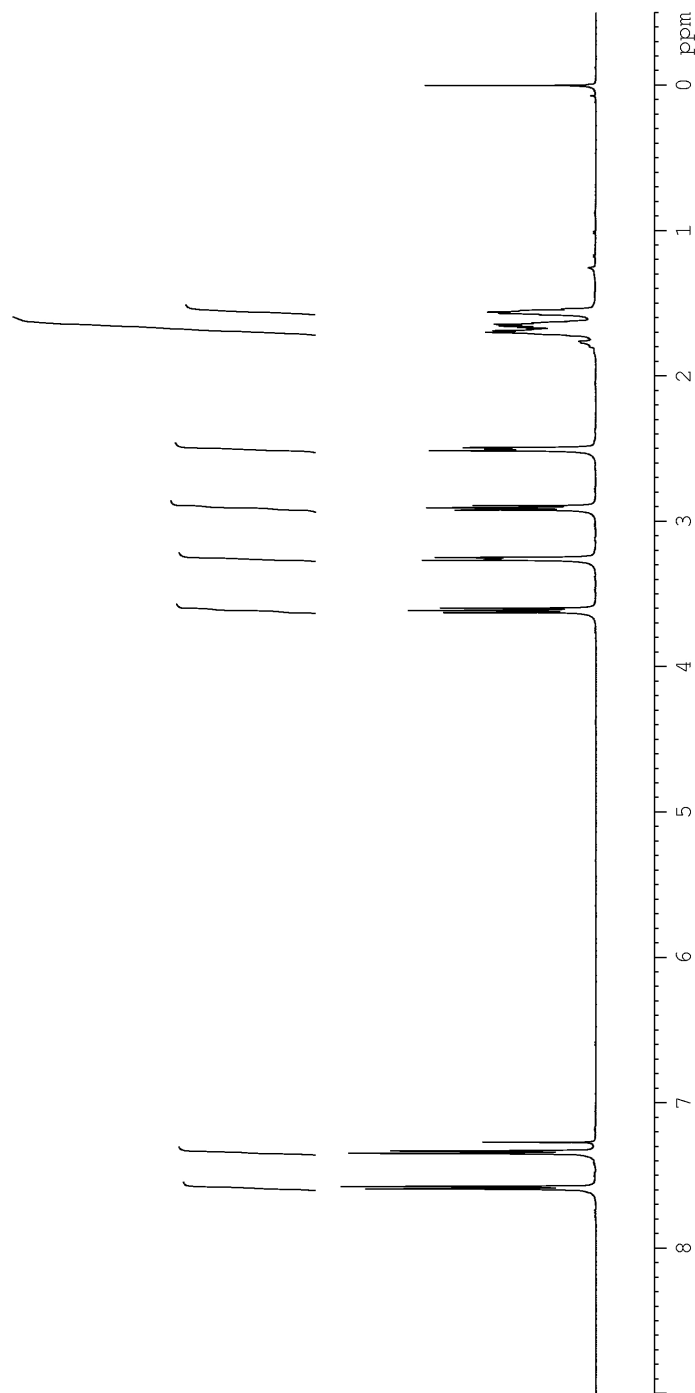
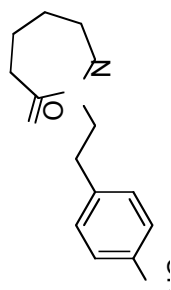


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **2u**

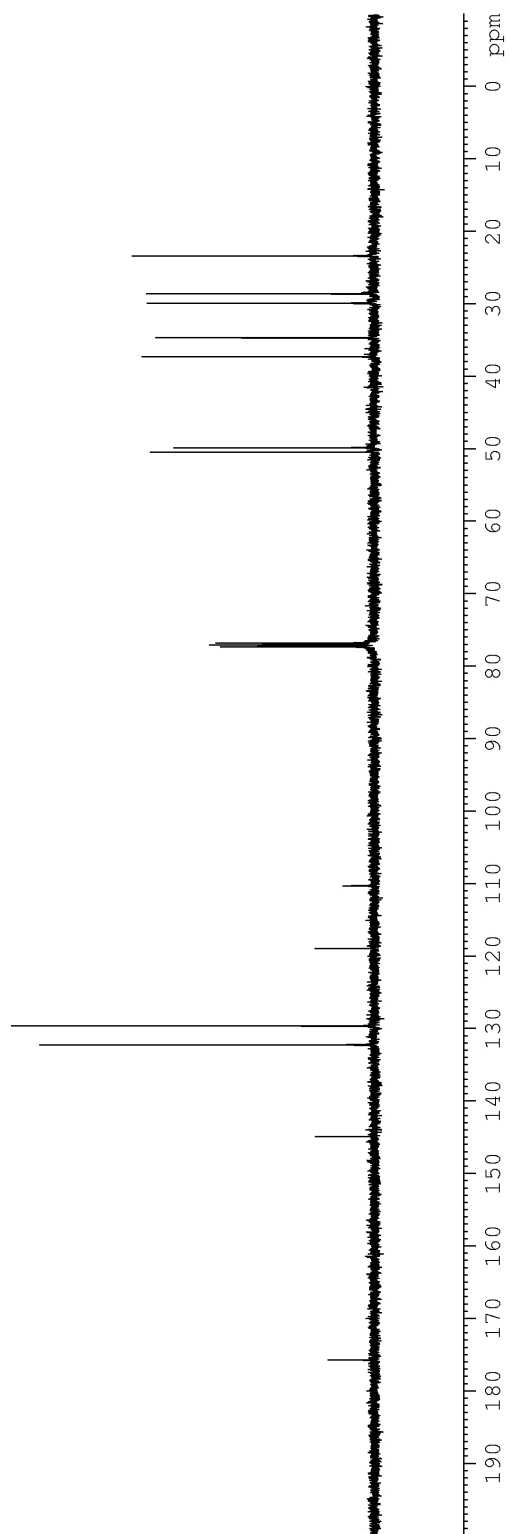
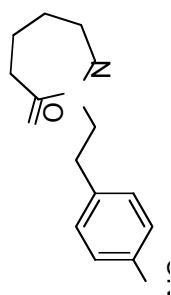




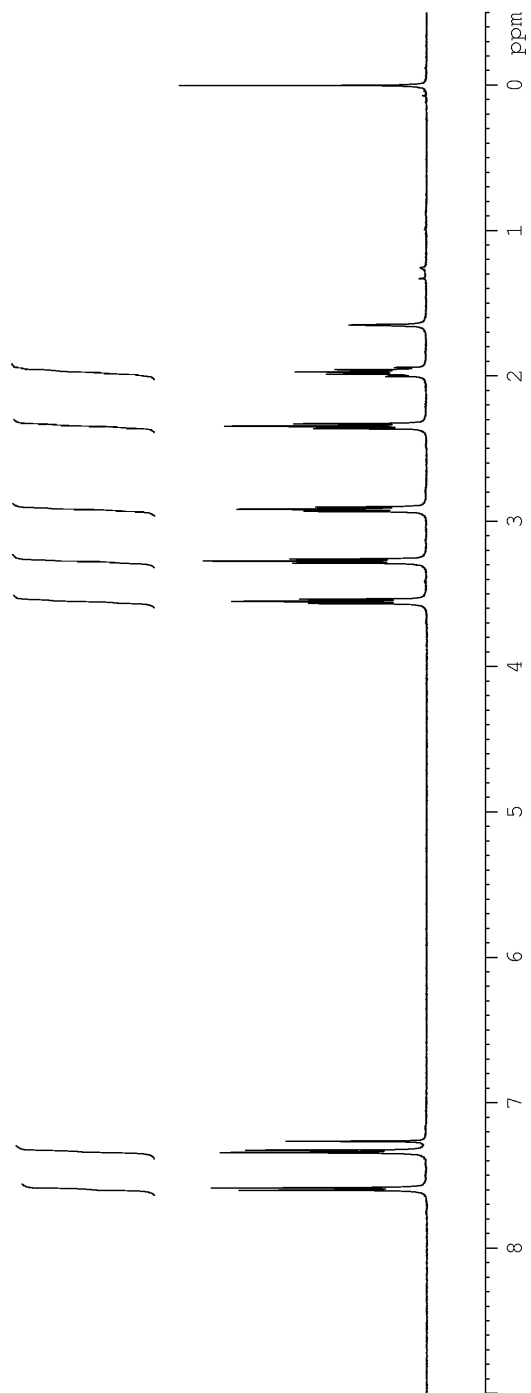
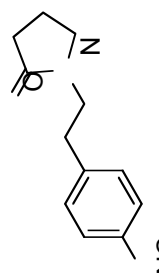
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **2u**



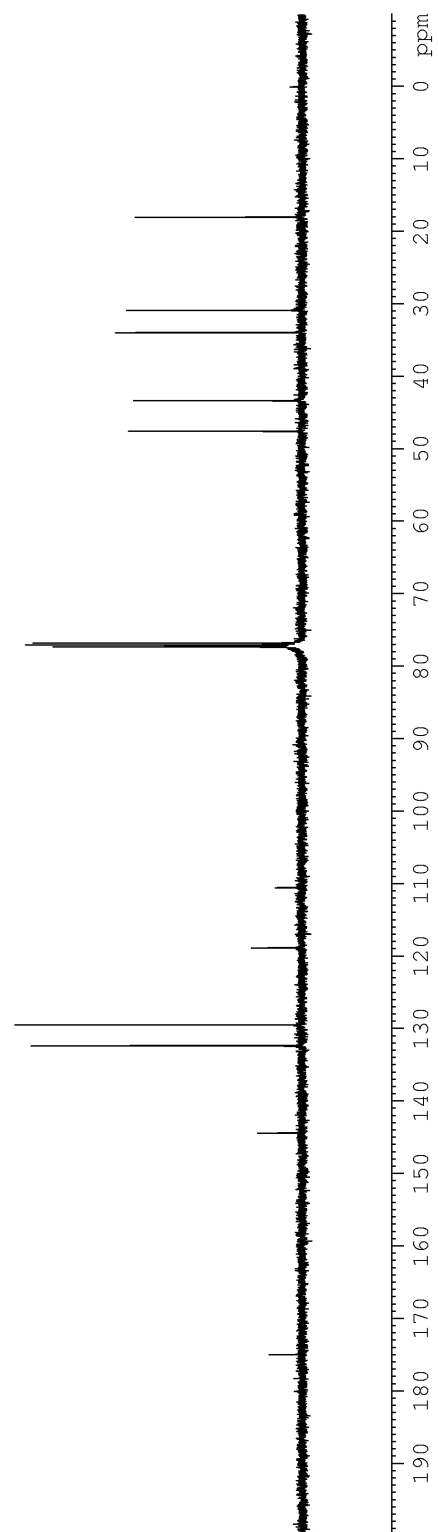
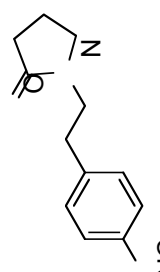
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **3a**



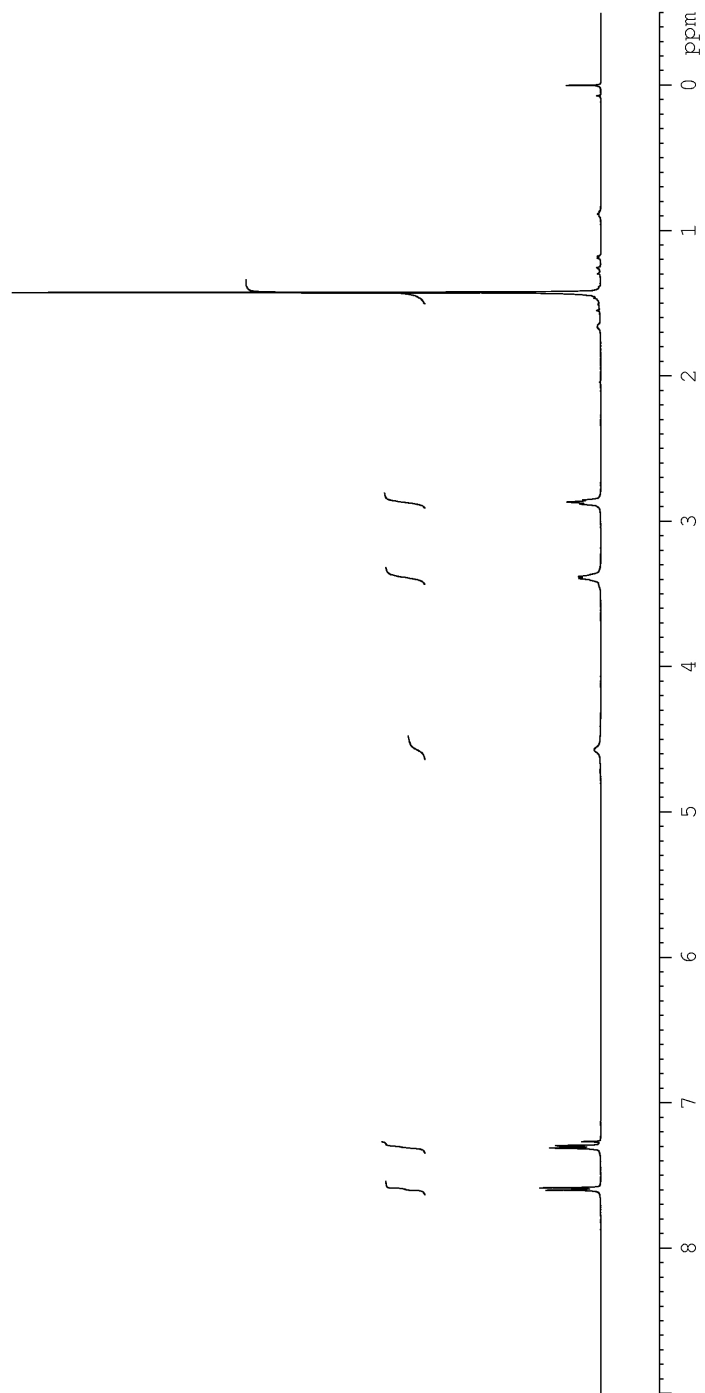
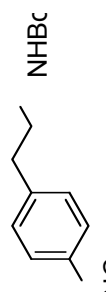
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **3a**



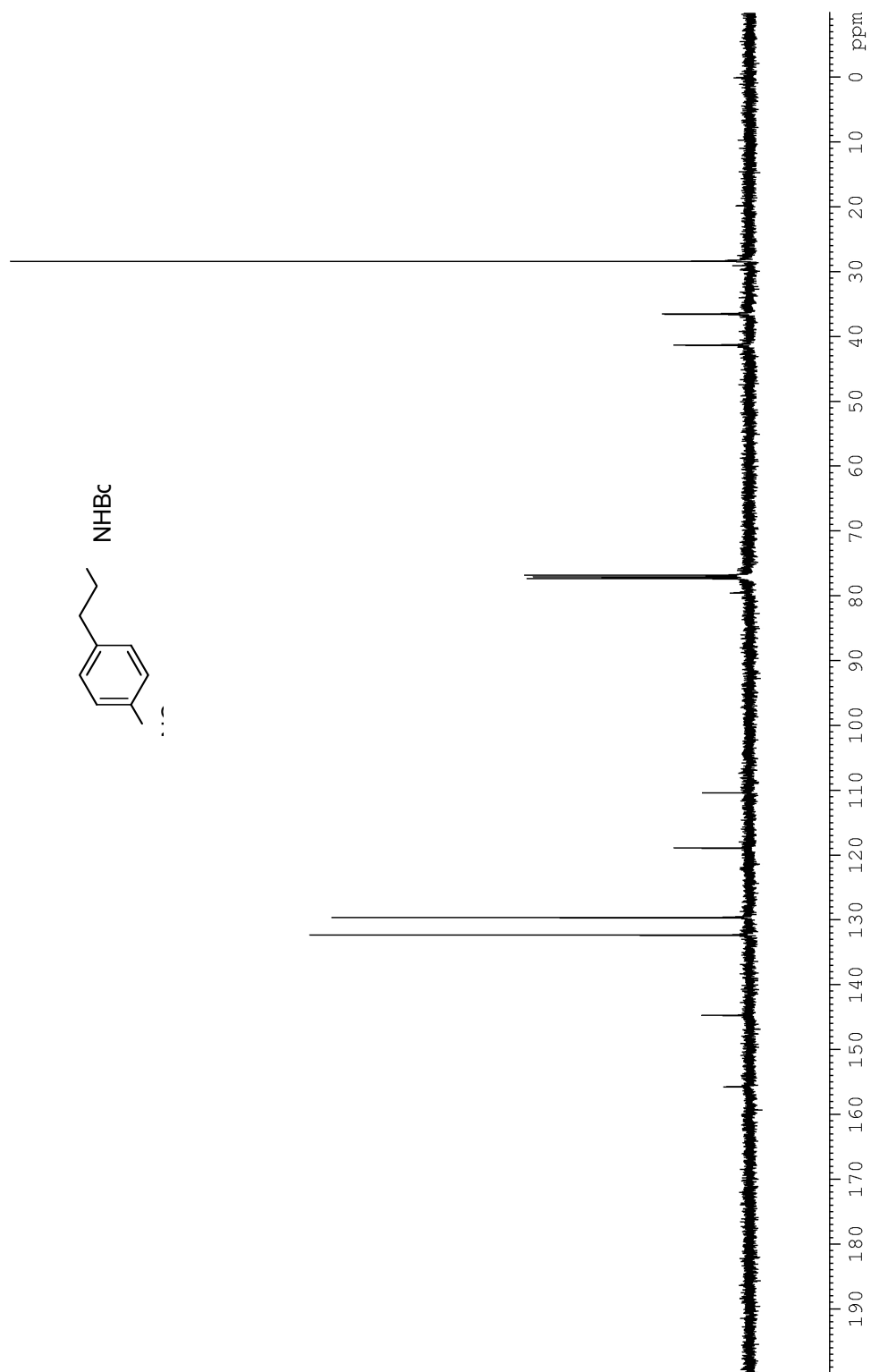
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **3b**



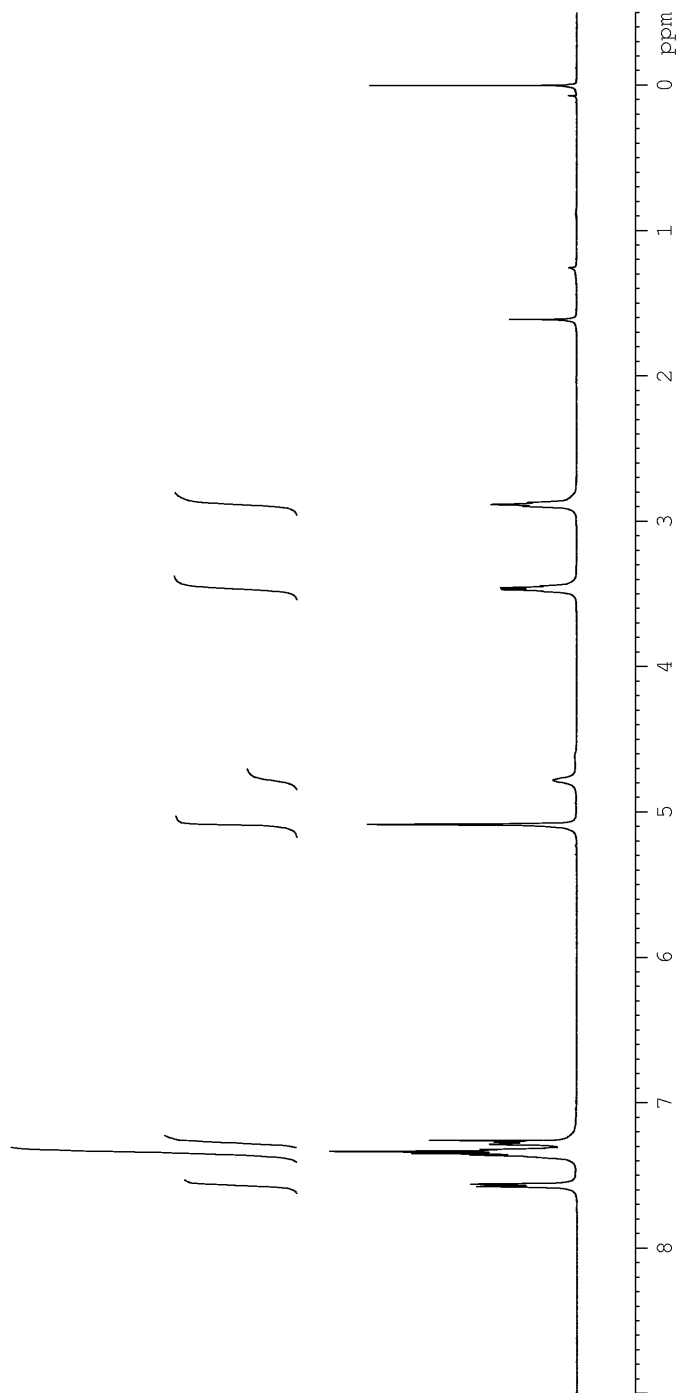
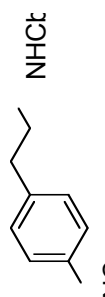
$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **3b**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **4a**

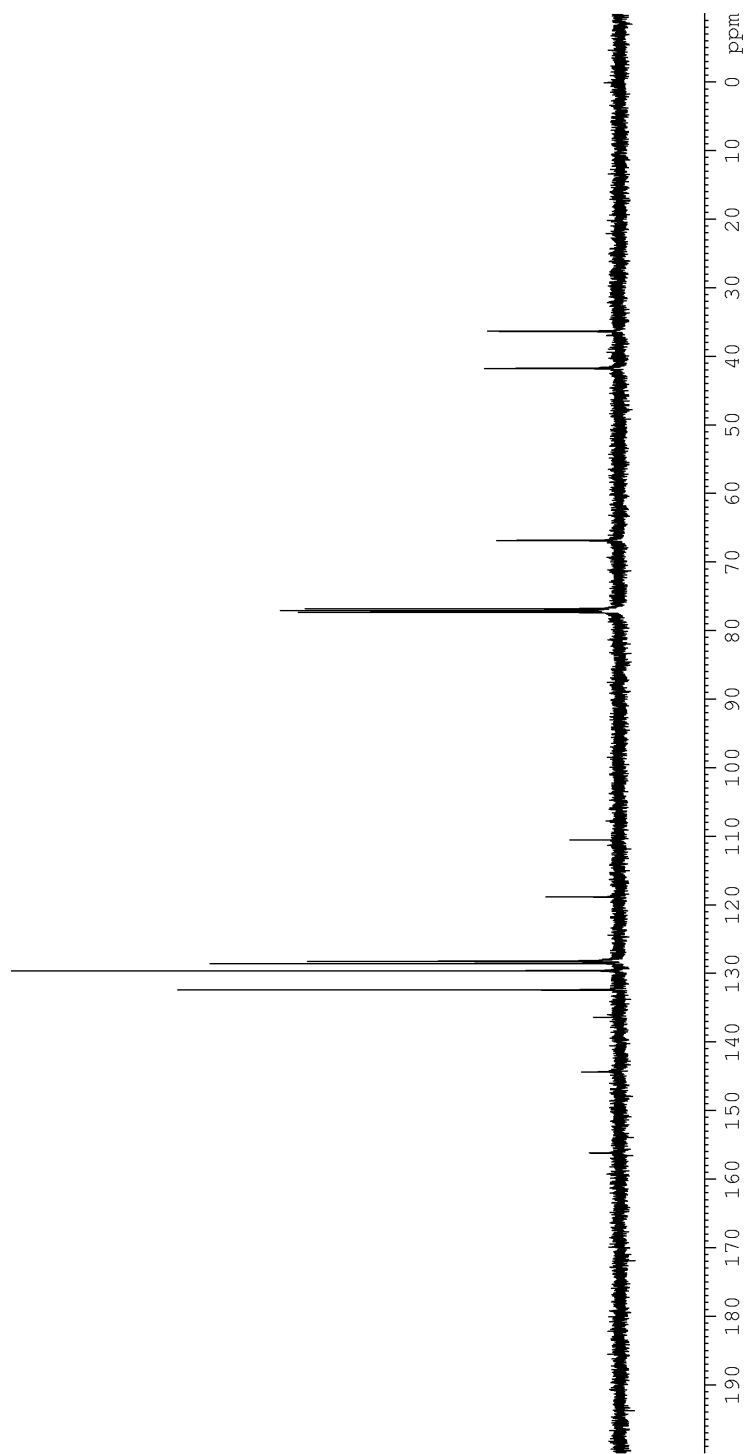
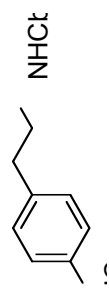


$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **4a**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of **4b**





$^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ) Spectrum of **4b**