

## Supporting Information

### Thermal Induced [3+2] Cyclization of Aniline-tethered Alkylidenecyclopropanes: A Facile Synthetic Protocol of Pyrrolo[1,2-a]indoles

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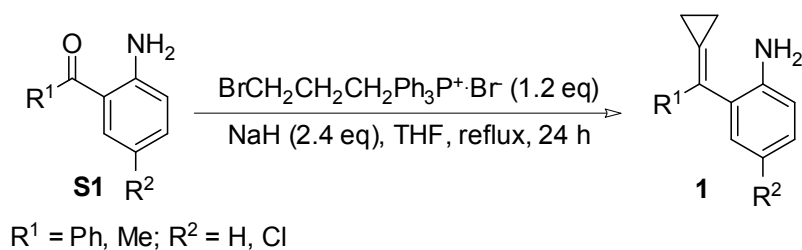
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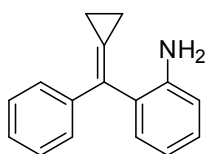
**General remarks.** Dichloromethane was freshly distilled from calcium hydride; THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in  $\text{cm}^{-1}$ . Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF<sub>254</sub>) were used. Mass spectra were recorded by EI, and HRMS were measured on a HP-5989 instrument.

### General procedure for the synthesis of MCPs 1a, 1b and 1c

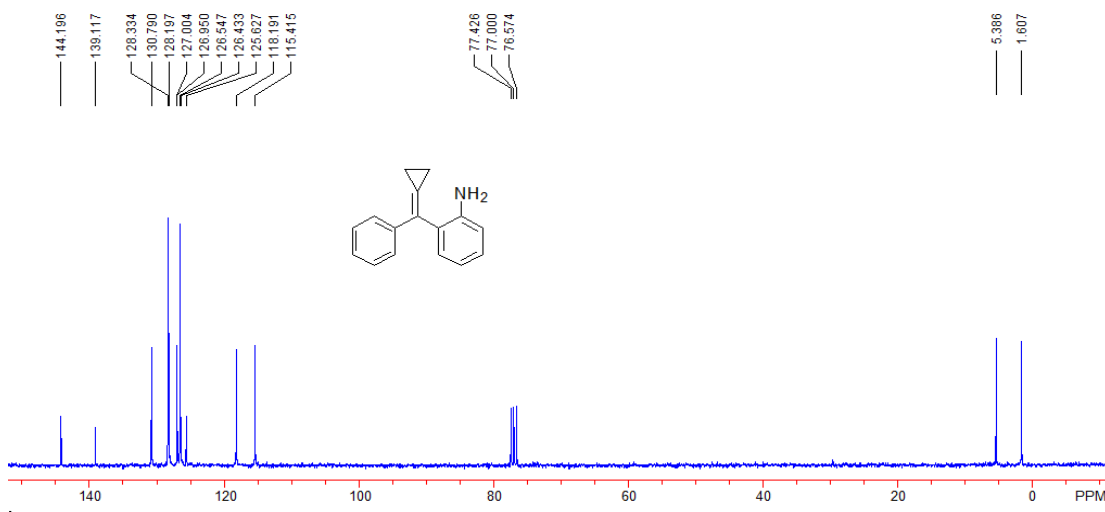
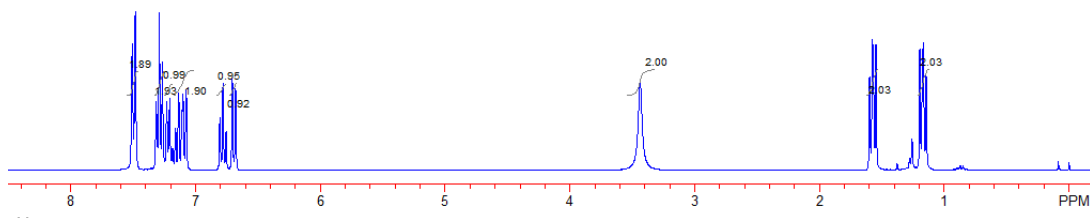
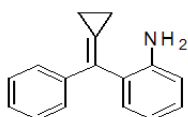
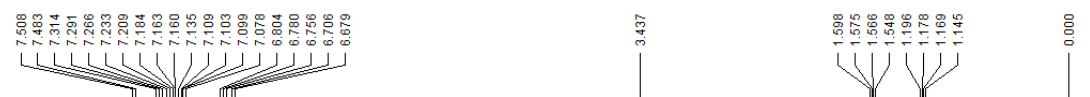


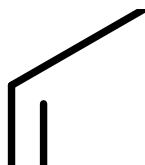
To a solution of 3-bromopropyltriphenylphosphonium bromide (5.5 g, 12 mmol) NaH (576 mg, 24 mmol) in THF (10 mL) was added, then the resulting reaction mixture was stirred at 70 °C for 12 h. Afterwards compound **S1** (10 mmol) in THF (5 mL) was added and the reaction solution was stirred at 70 °C for another 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in moderate yield.<sup>[1]</sup>

## Spectroscopic data for MCPs 1a and 1b

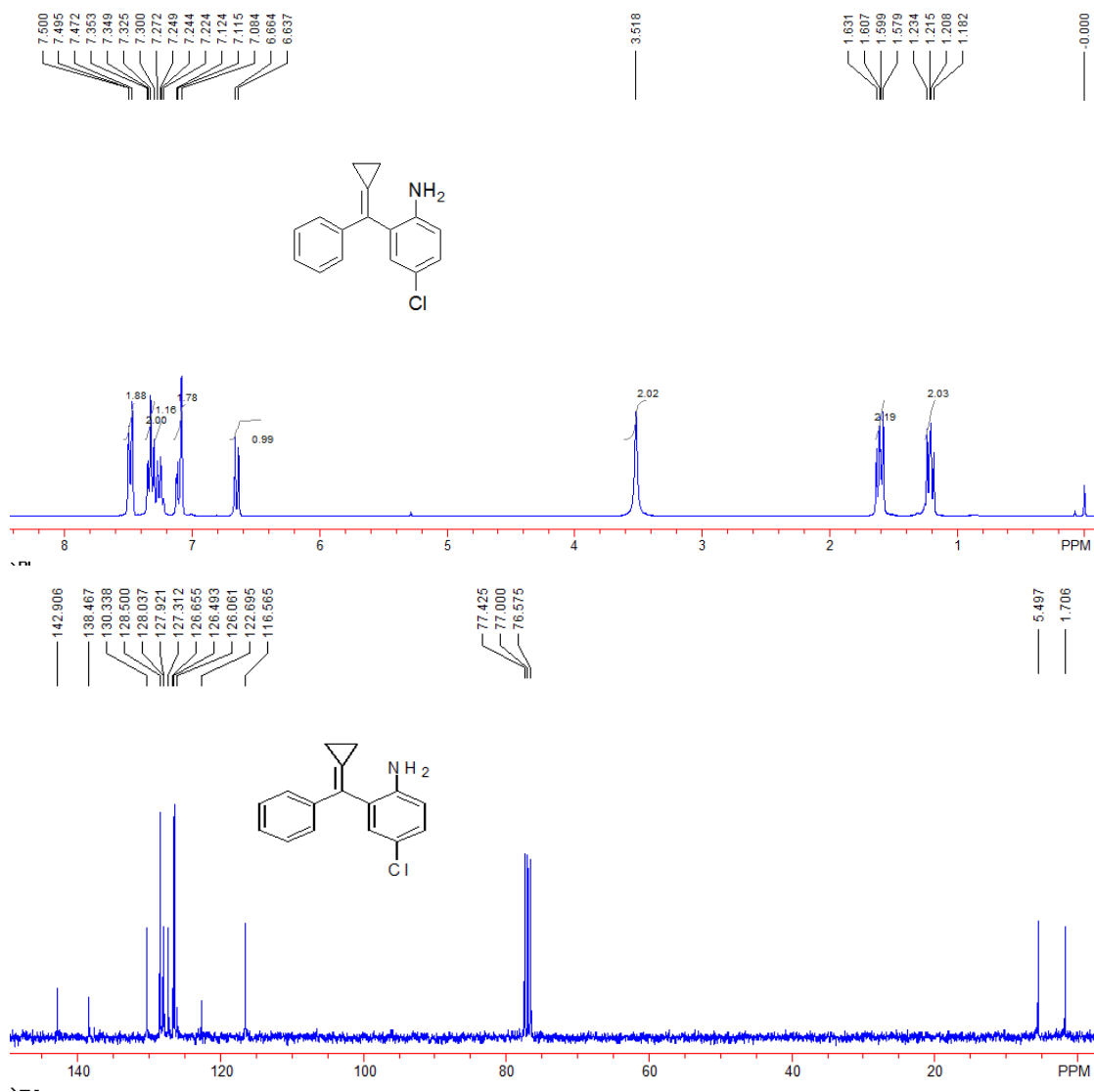


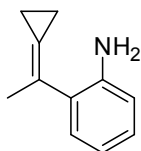
**Compound 1a:** 884 mg, 40%, A yellow solid, m.p. 86-88 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3467, 3372, 3021, 2969, 1611, 1491, 1444, 1298, 766, 693 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.15-1.20 (m, 2H), 1.55-1.60 (m, 2H), 3.44 (s, 2H), 6.69 (d,  $J$  = 8.1 Hz, 1H), 6.78 (t,  $J$  = 7.2 Hz, 1H), 7.08-7.14 (m, 2H), 7.16-7.23 (m, 1H), 7.27-7.31 (m, 2H), 7.50 (d,  $J$  = 7.5 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.6, 5.4, 115.4, 118.2, 125.6, 126.4, 126.5, 126.95, 127.00, 128.2, 128.3, 130.8, 139.1, 144.2; MS (EI)  $m/z$  (%): 221 (75.4) [M<sup>+</sup>], 220 (46.0), 206 (100.0), 204 (29.7), 193 (7.8), 178 (12.7), 144 (12.9), 130 (6.8); HRMS (EI) Calcd. for C<sub>16</sub>H<sub>15</sub>N (M<sup>+</sup>) requires 221.1204, Found: 221.1201.



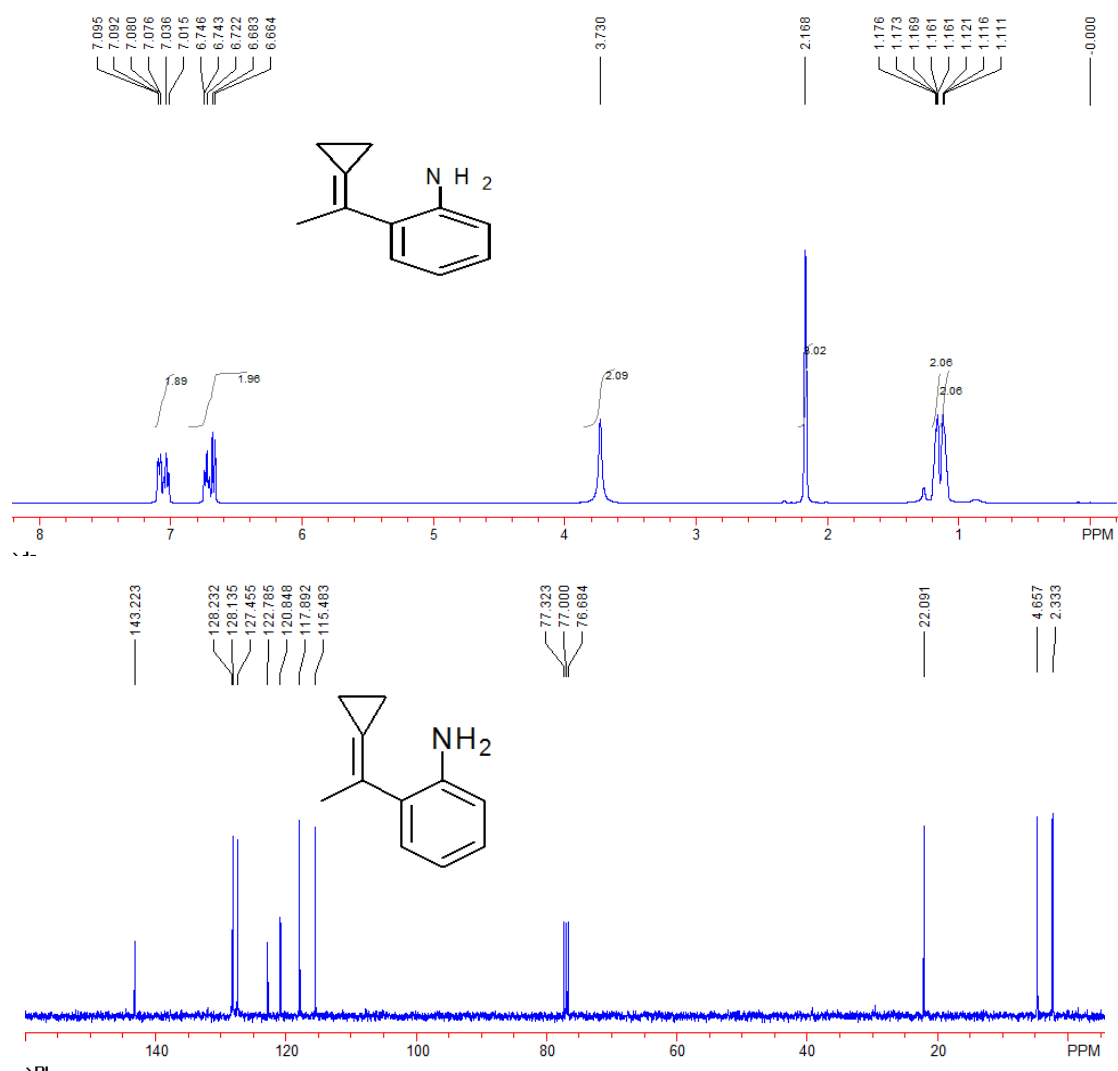


**Compound 1b:** 765 mg, 30%, A yellow solid, m.p. 140-142 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3458, 3371, 3052, 2972, 1611, 1484, 1406, 1146, 768, 693 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.18-1.23 (m, 2H), 1.58-1.63 (m, 2H), 3.52 (s, 2H), 6.65 (d,  $J$  = 8.1 Hz, 1H), 7.08-7.12 (m, 2H), 7.22-7.30 (m, 1H), 7.33-7.35 (m, 2H), 7.47-7.50 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.7, 5.5, 116.6, 122.7, 126.1, 126.5, 126.7, 127.3, 127.9, 128.0, 128.5, 130.4, 138.5, 142.9; MS (EI)  $m/z$  (%): 255 (81.5) [M<sup>+</sup>], 240 (48.0), 220 (100.0), 204 (67.8), 178 (15.9), 165 (9.6), 108 (11.9), 101 (10.6); HRMS (EI) Calcd. for C<sub>16</sub>H<sub>14</sub>NCl (M<sup>+</sup>) requires 255.0815, Found: 255.0808.

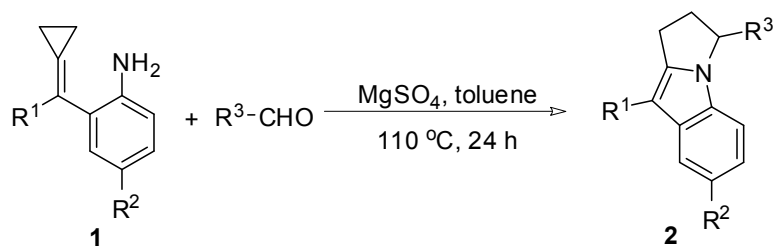




**Compound 1c:** 159 mg, 10%, A yellow liquid; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3461, 3373, 2963, 2915, 1609, 1494, 1452, 1297, 795, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.11-1.12 (m, 2H), 1.16-1.18 (m, 2H), 2.17 (s, 3H), 3.73 (s, 2H), 6.66-6.75 (m, 2H), 7.02-7.10 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.3, 4.7, 22.1, 115.5, 117.9, 120.8, 122.8, 127.5, 128.1, 128.2, 143.2; MS (EI) *m/z* (%): 159 (42.3) [M<sup>+</sup>], 158 (30.9), 144 (100.0), 130 (36.2), 128 (15.2), 115 (11.9), 91 (9.00), 77 (6.4); HRMS (EI) Calcd. for C<sub>11</sub>H<sub>13</sub>N (M<sup>+</sup>) requires 159.1048, Found: 159.1050.



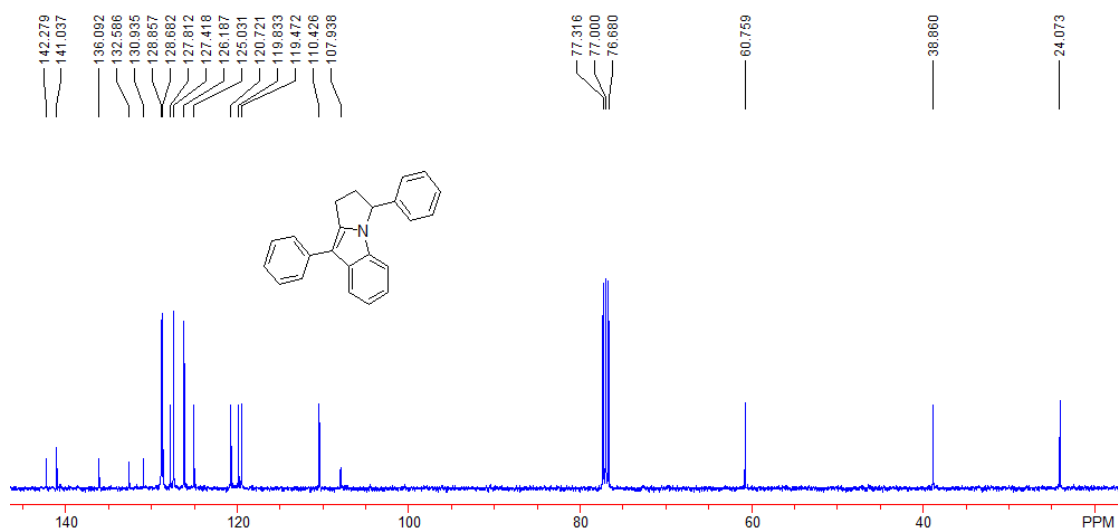
### General Procedure for the Preparation of Compound 2



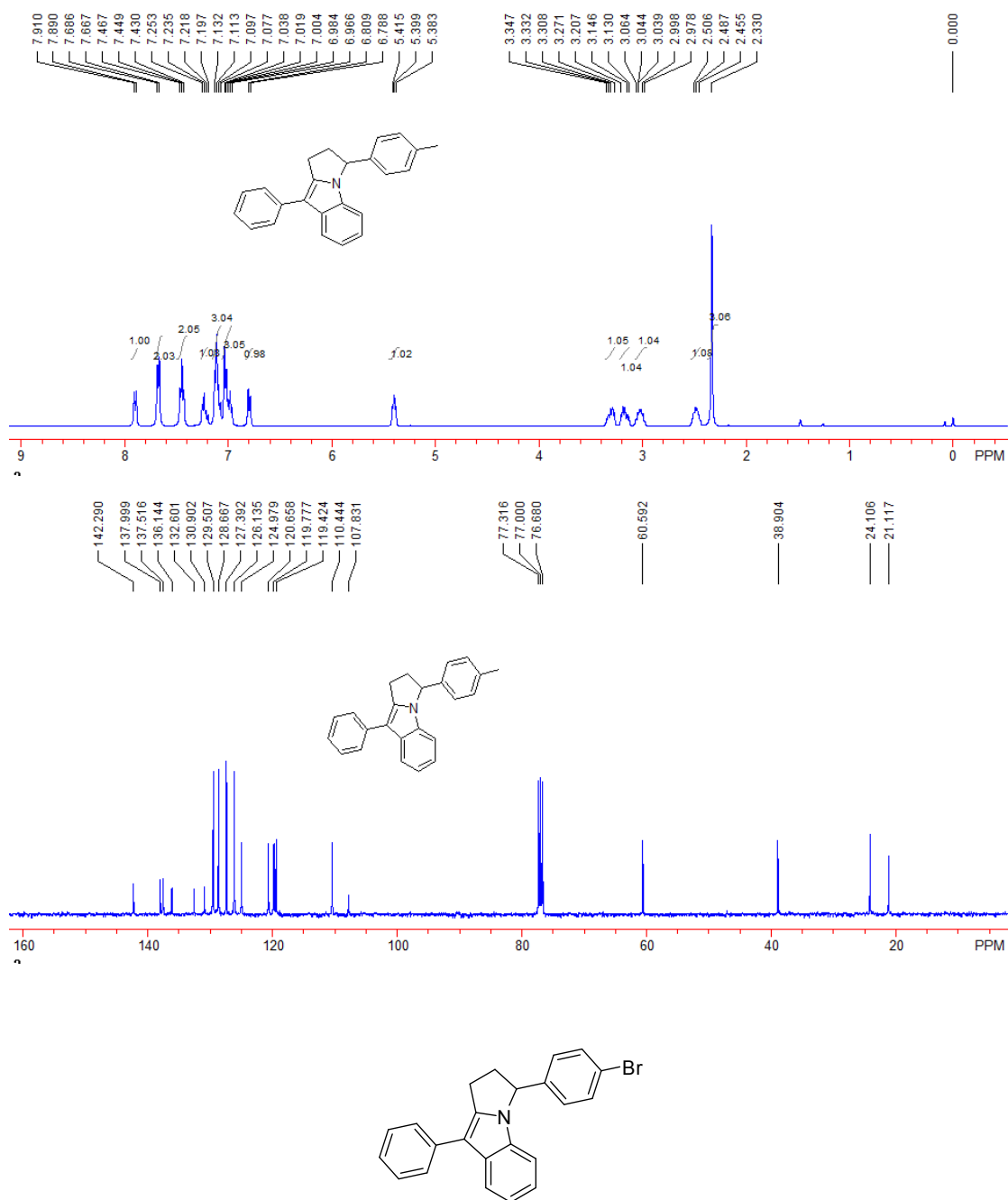
To a solution of **1** (0.2 mmol), PhCHO (42 mg, 0.4 mmol) and MgSO<sub>4</sub> (240 mg, 2.0 mmol) in dry toluene (2.0 mL) were added, then the resulting reaction mixture was stirred at 110 °C for 24 h. Afterwards the reaction was stopped and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using neutral silica gel (the silica gel was treated by 10% Et<sub>3</sub>N in petroleum ether for 24 h. eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in high yield.





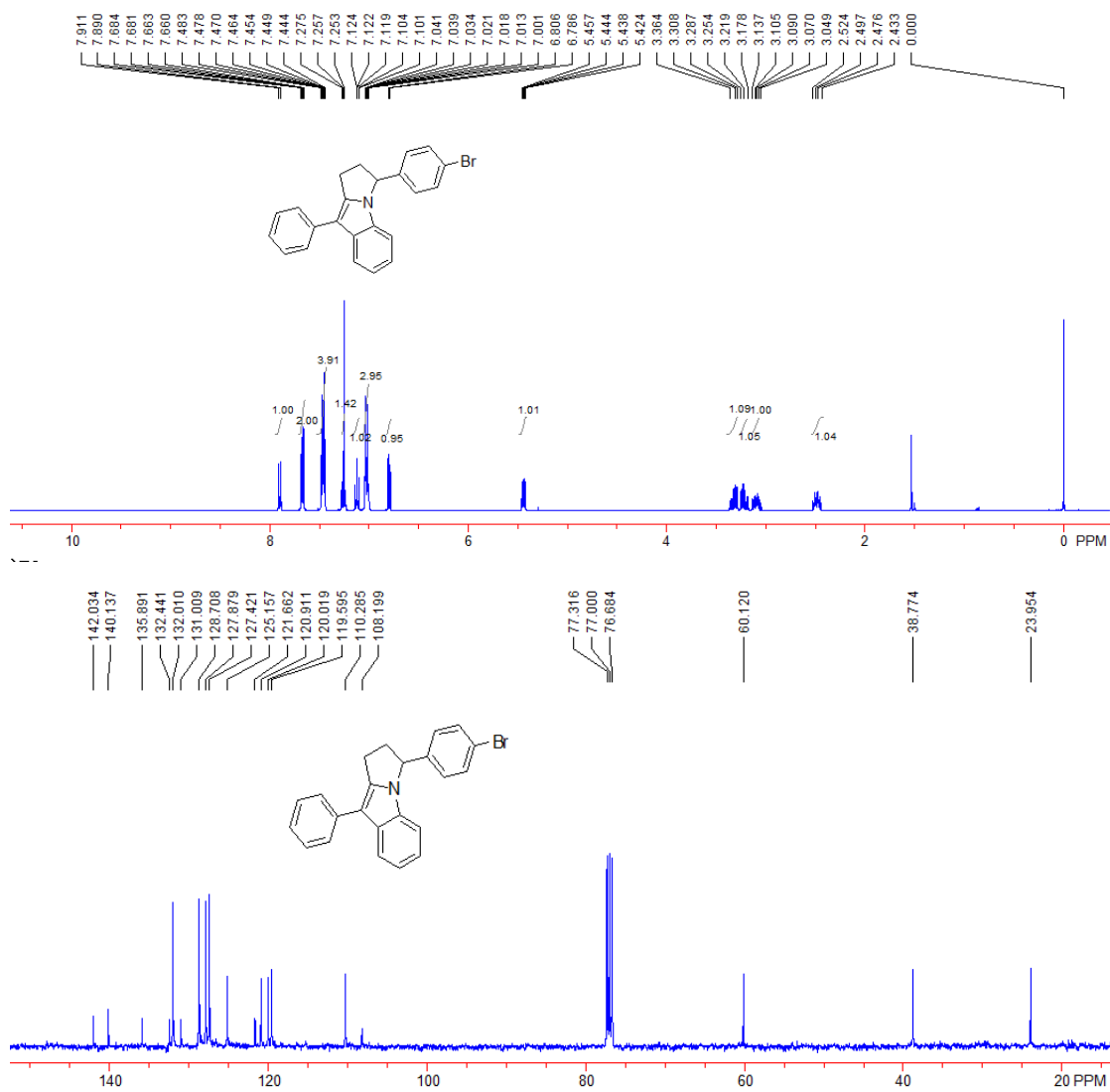


**Compound 2b:** 60 mg, 93%, A white solid, m.p. 154-156 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3084, 3054, 3020, 2844, 2303, 1880, 1611, 1601, 1455, 1076, 736, 679 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.33 (s, 3H), 2.46-2.51 (m, 1H), 2.98-3.06 (m, 1H), 3.13-3.21 (m, 1H), 3.27-3.35 (m, 1H), 5.40 (t,  $J$  = 6.4 Hz, 1H), 6.80 (d,  $J$  = 8.0 Hz, 1H), 6.97-7.04 (m, 3H), 7.08-7.13 (m, 3H), 7.20-7.25 (m, 1H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.68 (d,  $J$  = 7.6 Hz, 2H), 7.90 (d,  $J$  = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  21.1, 24.1, 38.9, 60.6, 107.8, 110.4, 119.4, 119.8, 120.7, 125.0, 126.1, 127.4, 128.7, 129.5, 130.9, 132.6, 136.1, 137.5, 138.0, 142.3; MS (EI)  $m/z$  (%): 323 (100.0) [M<sup>+</sup>], 324 (18.6), 246 (3.8), 230 (4.1), 218 (13.2), 217 (20.7), 206 (9.5), 204 (14.9); HRMS (EI) Calcd. for C<sub>24</sub>H<sub>21</sub>N (M<sup>+</sup>) requires 323.1674, Found: 323.1669.



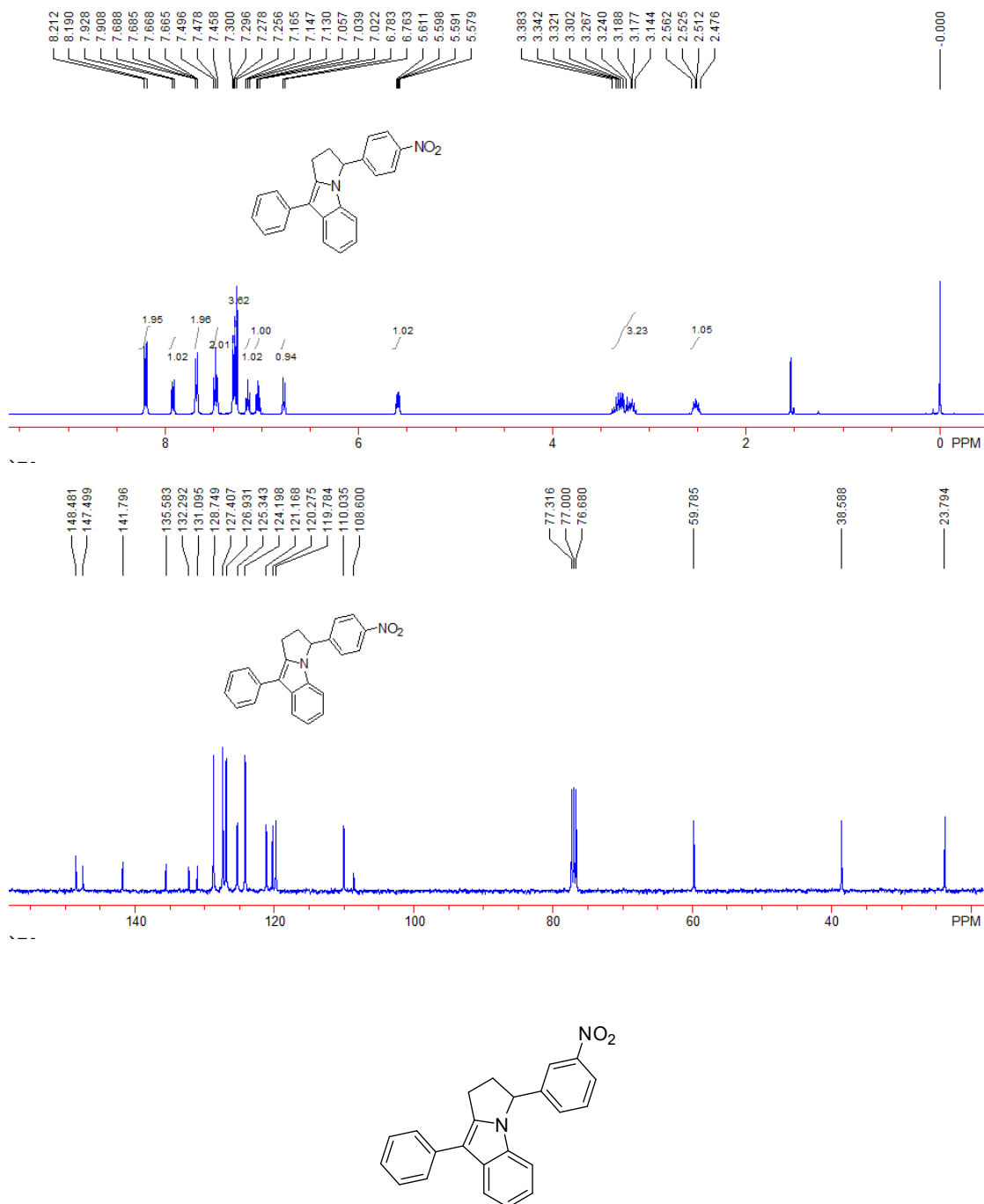
**Compound 2c:** 67 mg, 86%, A white solid, m.p. 194-196 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3084, 3054, 3020, 2851, 1612, 1488, 1456, 1398, 1072, 1010, 740, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.43-2.53 (m, 1H), 3.04-3.14 (m, 1H), 3.18-3.26 (m, 1H), 3.29-3.37 (m, 1H), 5.44 (dd,  $J$  = 5.6, 7.6 Hz, 1H), 6.80 (d,  $J$  = 8.0 Hz, 1H), 7.00-7.04 (m, 3H), 7.10-7.14 (m, 1H), 7.24-7.28 (m, 1H), 7.45-7.48 (m, 4H), 7.66-7.68 (m, 2H), 7.90 (d,  $J$  = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  24.0, 38.8, 60.1, 108.2, 110.3, 119.6, 120.0, 120.9, 121.7, 125.2, 127.4, 127.9, 128.7, 131.0, 132.0, 132.4, 135.9, 140.1, 142.0; MS (EI)  $m/z$  (%): 387 (100.0)

$[M^+]$ , 389 (93.5), 308 (3.3), 232 (5.8), 218 (26.5), 204 (26.6), 193 (2.5), 178 (3.1); HRMS (EI)  
Calcd. for  $C_{23}H_{18}BrN$  ( $M^+$ ) requires 387.0623, Found: 387.0620.



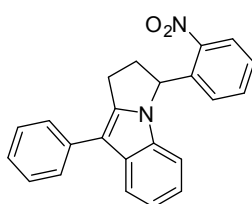
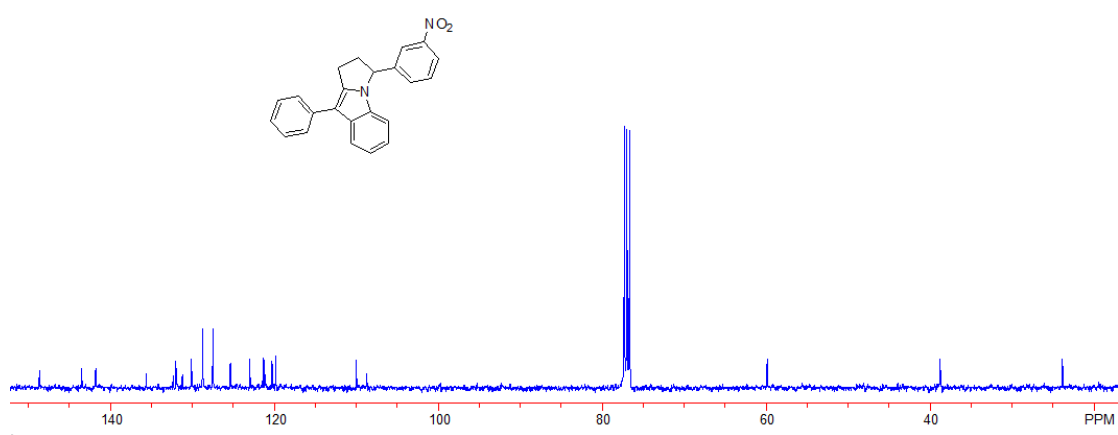
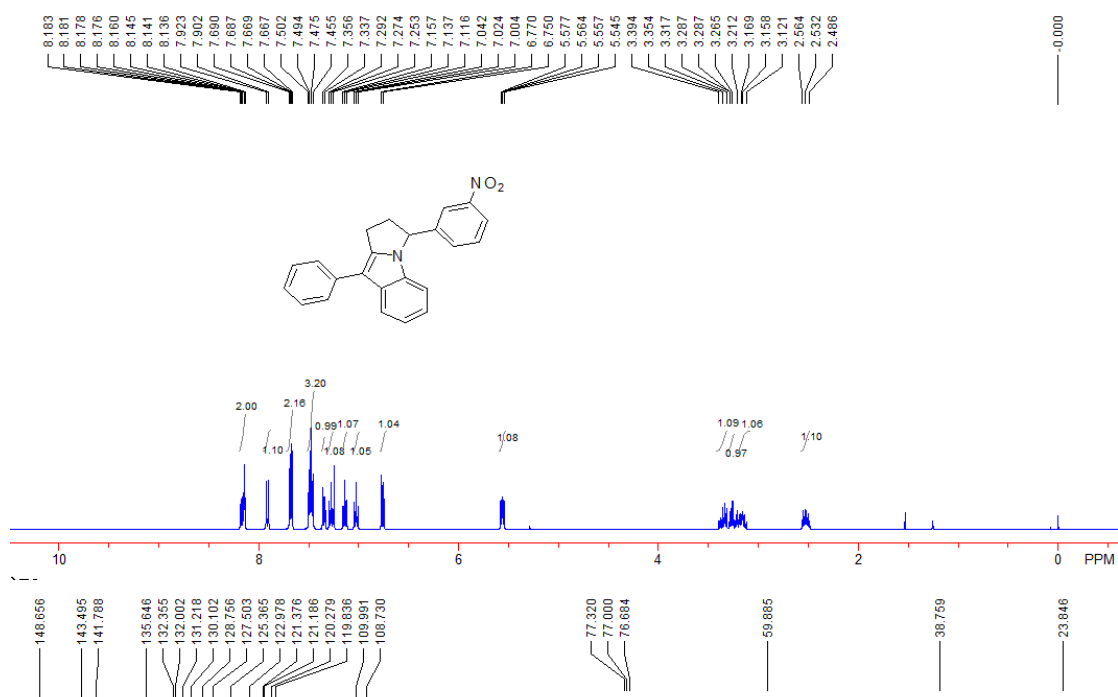
**Compound 2d:** 64 mg, 91%, A yellow solid, m.p. 164-166 °C; IR ( $CH_2Cl_2$ ):  $\nu$  3080, 3043, 3020, 2859, 2435, 1600, 1519, 1343, 738, 698  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ , TMS):  $\delta$  2.48-2.56 (m, 1H), 3.14-3.38 (m, 3H), 5.59 (dd,  $J = 4.8, 7.6$  Hz, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 7.04 (t,  $J = 6.8$  Hz, 1H), 7.15 (t,  $J = 6.8$  Hz, 1H), 7.26-7.30 (m, 3H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.67-7.69 (m, 2H), 7.92 (d,  $J = 8.0$  Hz, 1H), 8.20 (d,  $J = 8.8$  Hz, 2H);  $^{13}C$  NMR (100 MHz,

CDCl<sub>3</sub>, TMS): δ 23.8, 38.6, 59.8, 108.6, 110.0, 119.8, 120.3, 121.2, 124.2, 125.3, 126.9, 127.4, 128.7, 131.1, 132.3, 135.6, 141.8, 147.5, 148.5; MS (EI) *m/z* (%): 354 (100.0) [M<sup>+</sup>], 355 (14.0), 324 (2.8), 308 (5.6), 232 (3.8), 218 (4.9), 205 (5.4), 204 (10.0); HRMS (EI) Calcd. for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>) requires 354.1368, Found: 354.1363.

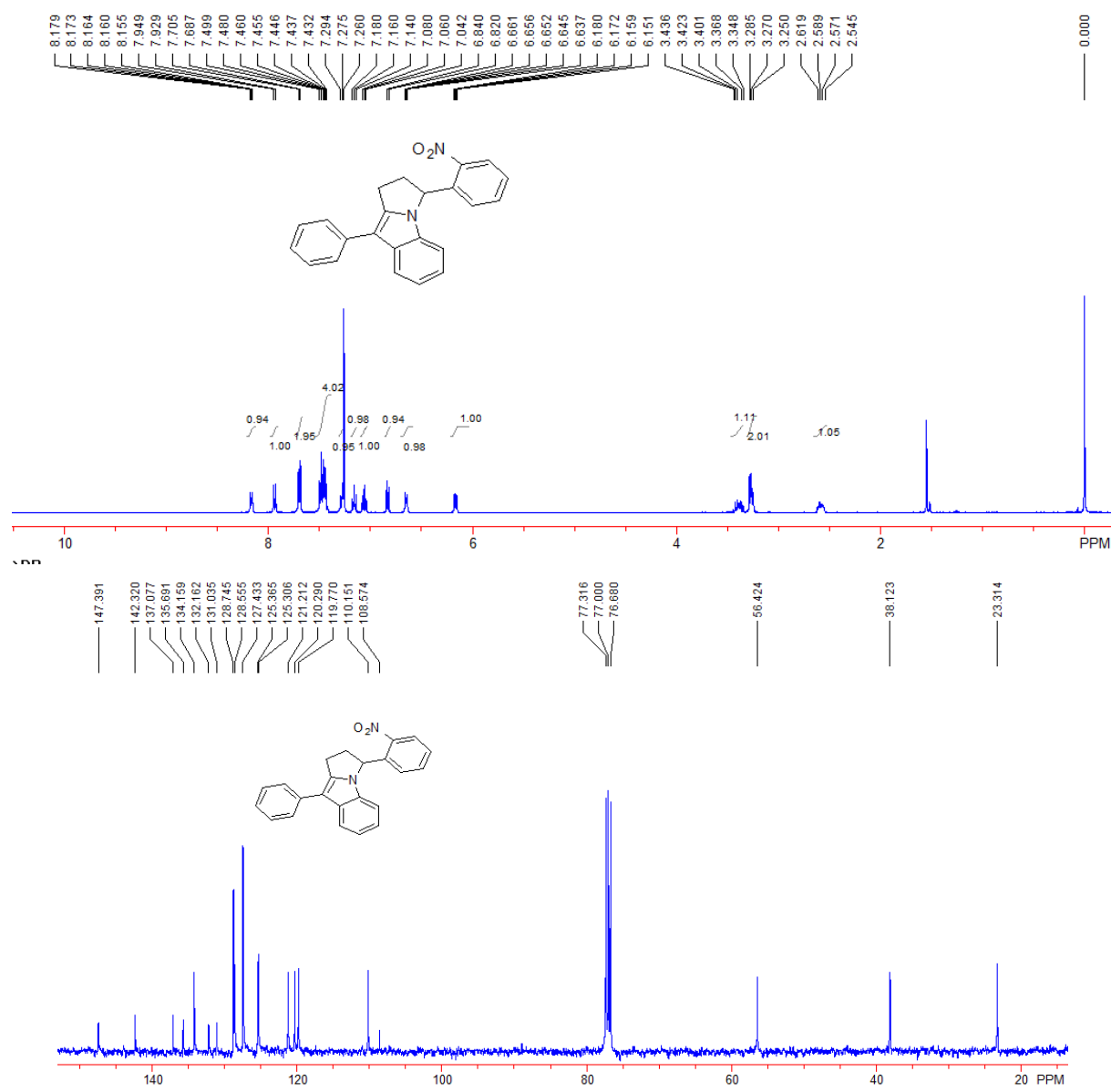


**Compound 2e:** 63 mg, 89%, A yellow solid, m.p. 187-189 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3080, 3051, 2953, 2848, 1612, 1601, 1528, 1456, 1347, 737, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.49-2.56 (m, 1H), 3.12-3.21 (m, 1H), 3.27-3.29 (m, 1H), 3.32-3.39 (m, 1H), 5.56

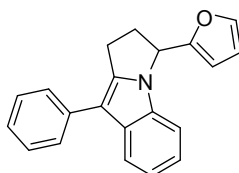
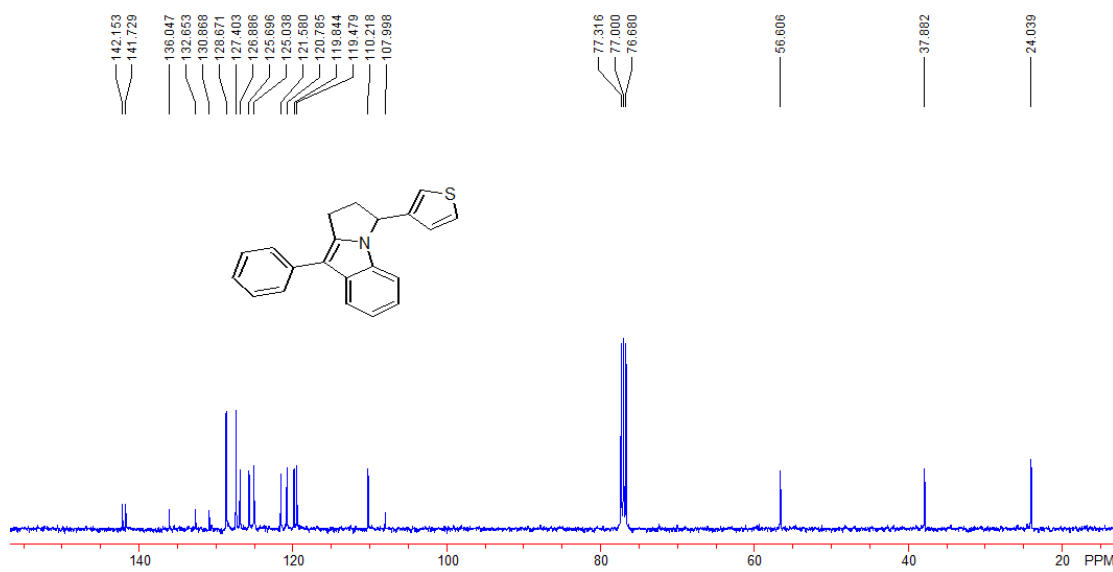
(dd,  $J = 4.8, 7.6$  Hz, 1H), 6.76 (d,  $J = 8.0$  Hz, 1H), 7.02 (t,  $J = 7.6$  Hz, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.25-7.29 (m, 1H), 7.35 (d,  $J = 8.0$  Hz, 1H), 7.46-7.50 (m, 3H), 7.67-7.69 (m, 2H), 7.91 (d,  $J = 8.0$  Hz, 1H), 8.14-8.18 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  23.8, 38.8, 59.9, 108.7, 110.0, 119.8, 120.3, 121.2, 121.4, 123.0, 125.4, 127.5, 128.8, 130.1, 131.2, 132.0, 132.4, 135.7, 141.8, 143.5, 148.7; MS (EI)  $m/z$  (%): 354 (100.0) [ $\text{M}^+$ ], 355 (13.6), 308 (1.8), 232 (11.9), 218 (3.3), 205 (4.5), 204 (8.6), 177 (1.6); HRMS (EI) Calcd. for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$  ( $\text{M}^+$ ) requires 354.1368, Found: 354.1367.



**Compound 2f:** 65 mg, 92%, A yellow solid, m.p. 178-180 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3080, 3051, 2955, 2859, 1602, 1525, 1496, 1344, 787, 739, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.55-2.62 (m, 1H), 3.25-3.29 (m, 2H), 3.35-3.44 (m, 1H), 6.17 (dd,  $J$  = 3.2, 8.4 Hz, 1H), 6.64-6.66 (m, 1H), 6.83 (d,  $J$  = 8.0 Hz, 1H), 7.06 (t,  $J$  = 7.2 Hz, 1H), 7.16 (t,  $J$  = 8.0 Hz, 1H), 7.26-7.29 (m, 1H), 7.43-7.50 (m, 4H), 7.70 (d,  $J$  = 7.2 Hz, 1H), 7.94 (d,  $J$  = 8.0 Hz, 1H), 8.16-8.18 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  23.3, 38.1, 56.4, 108.6, 110.2, 119.8, 120.3, 121.2, 125.3, 125.4, 127.4, 128.6, 128.7, 131.0, 132.2, 134.2, 135.7, 137.1, 142.3, 147.4; MS (EI)  $m/z$  (%): 354 (100.0) [M<sup>+</sup>], 355 (14.7), 337 (14.0), 306 (22.8), 295 (11.7), 218 (21.2), 204 (11.4), 193 (5.6); HRMS (EI) Calcd. for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>) requires 354.1368, Found: 354.1367.

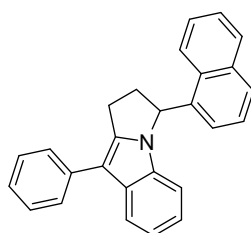
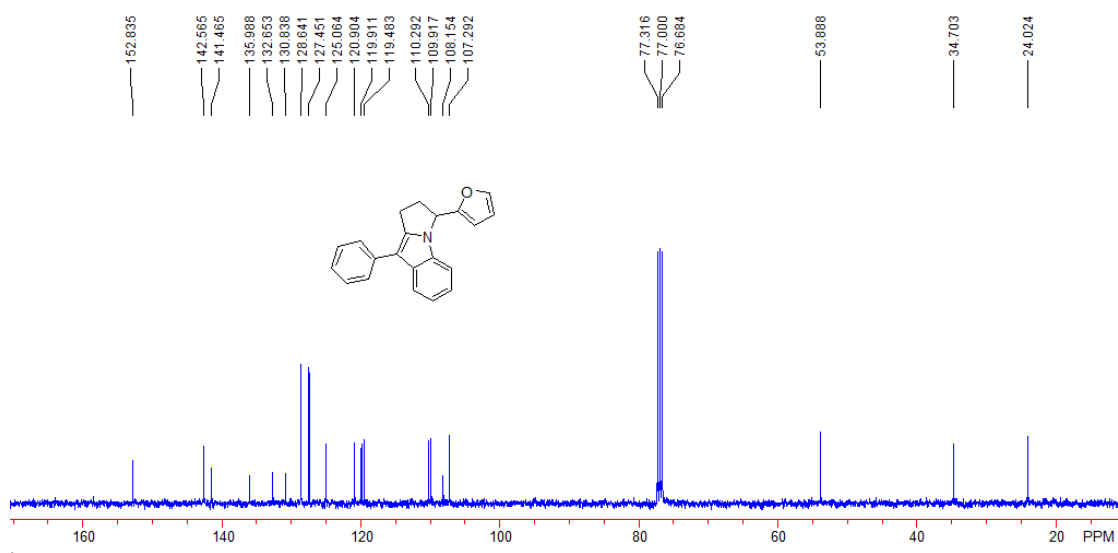
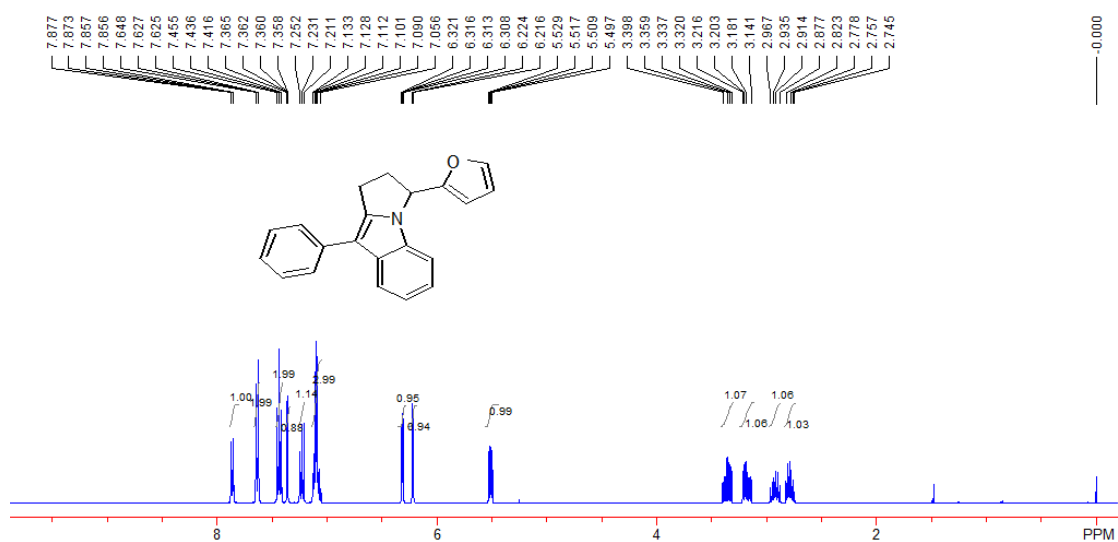






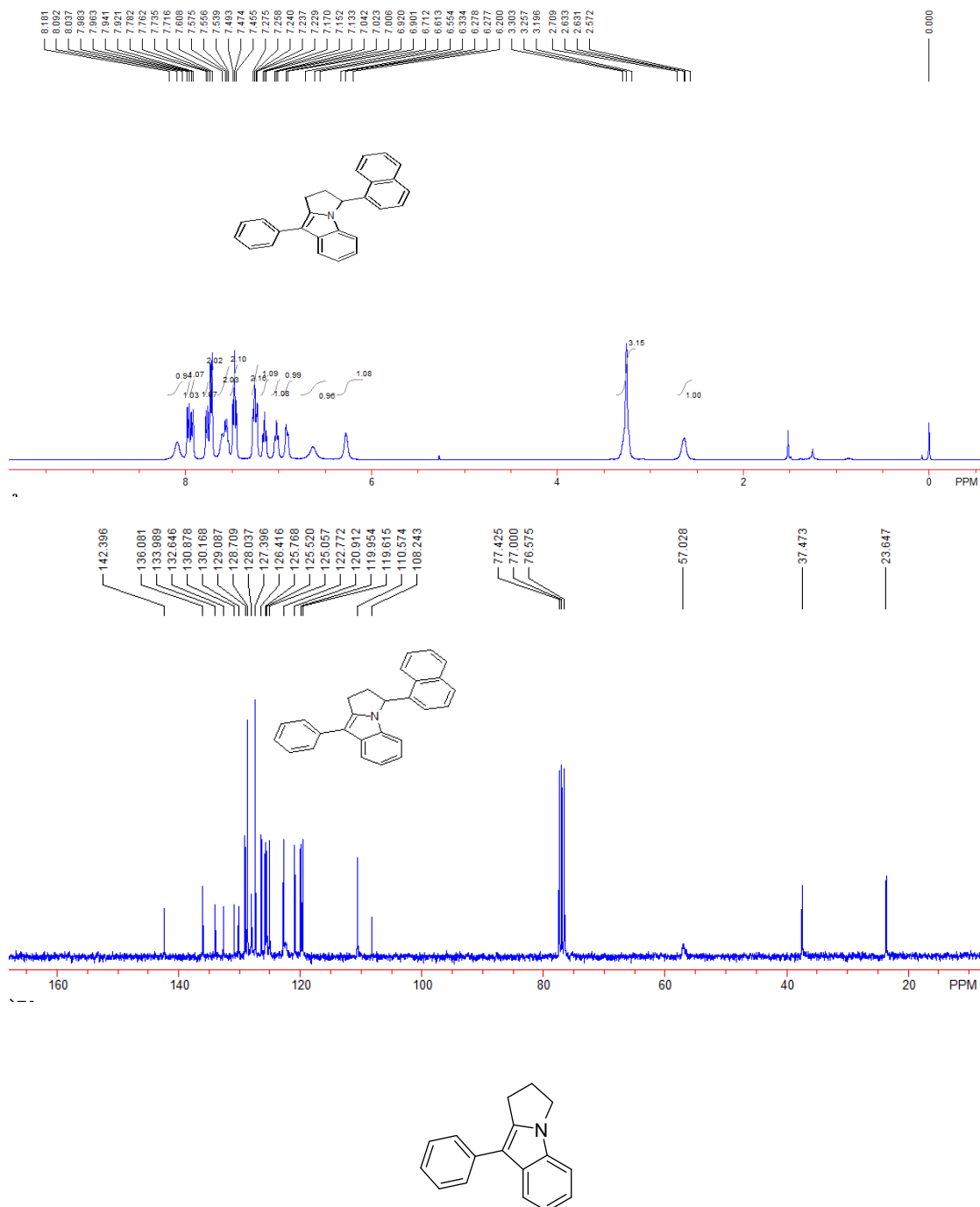
**Compound 2h:** 54 mg, 91%, A white solid, m.p. 116-118 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3125, 3031, 2953, 2855, 1613, 1601, 1455, 1362, 738, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.75-2.82 (m, 1H), 2.88-2.97 (m, 1H), 3.14-3.22 (m, 1H), 3.32-3.40 (m, 1H), 5.51 (dd,  $J$  = 4.8, 8.0 Hz, 1H), 6.22 (d,  $J$  = 3.2 Hz, 1H), 6.31 (dd,  $J$  = 2.0, 3.2 Hz, 1H), 7.06-7.13 (m, 3H), 7.31 (t,  $J$  = 8.0 Hz, 1H), 7.36-7.37 (m, 1H), 7.44 (t,  $J$  = 8.0 Hz, 2H), 7.63-7.65 (m, 2H), 7.86-7.87 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  24.0, 34.7, 53.9, 107.3, 108.2, 109.9, 110.3, 119.5, 119.9, 120.9, 125.1, 127.5, 128.6, 130.8, 132.7, 136.0, 141.5, 142.6, 152.8; MS (EI)  $m/z$  (%): 299 (100.0) [M<sup>+</sup>], 282 (2.6), 270 (11.8), 256 (2.6), 230 (5.9), 218 (28.2), 204 (22.2), 176 (2.7); HRMS (EI) Calcd. for C<sub>21</sub>H<sub>17</sub>NO (M<sup>+</sup>) requires 299.1310, Found: 299.1312.





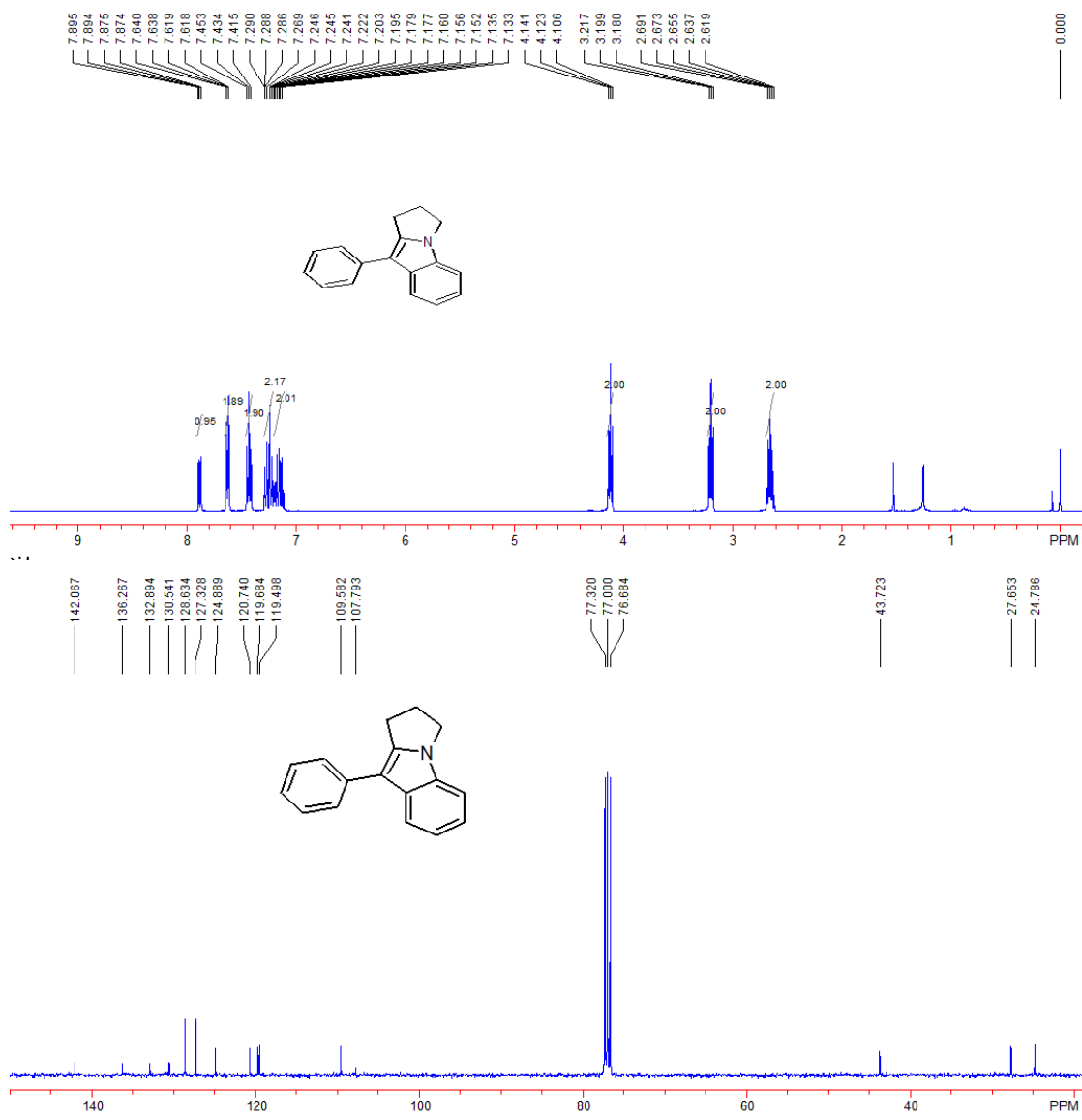
**Compound 2i:** 58 mg, 81%, A white solid, m.p. 172-174 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3048, 2950, 2851, 1612, 1600, 1456, 1077, 737, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.57-2.71 (m, 1H), 3.20-3.30 (m, 3H), 6.20-6.33 (m, 1H), 6.55-6.71 (m, 1H), 6.90-6.92 (m, 1H), 7.02 (t,  $J$  = 7.6 Hz, 1H), 7.15 (t,  $J$  = 7.6 Hz, 1H), 7.23-7.28 (m, 2H), 7.47 (t,  $J$  = 7.6 Hz, 2H), 7.54-7.61 (m, 2H), 7.73 (d,  $J$  = 7.6 Hz, 2H), 7.77 (d,  $J$  = 8.0 Hz, 1H), 7.93 (d,  $J$  = 8.0 Hz, 1H), 7.97 (d,  $J$  = 8.0 Hz, 1H), 8.04-8.18 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  23.6, 37.5,

57.0, 108.2, 110.6, 119.6, 120.0, 120.9, 122.8, 125.1, 125.5, 125.8, 126.4, 127.4, 128.0, 128.7, 129.1, 130.2, 130.9, 132.6, 134.0, 136.1, 142.4; MS (EI)  $m/z$  (%): 359 (100.0) [ $M^+$ ], 282 (3.7), 218 (15.0), 204 (13.5), 193 (3.2), 165 (5.9), 153 (3.6), 141 (2.5); HRMS (EI) Calcd. for  $C_{27}H_{21}N$  ( $M^+$ ) requires 359.1674, Found: 359.1669.



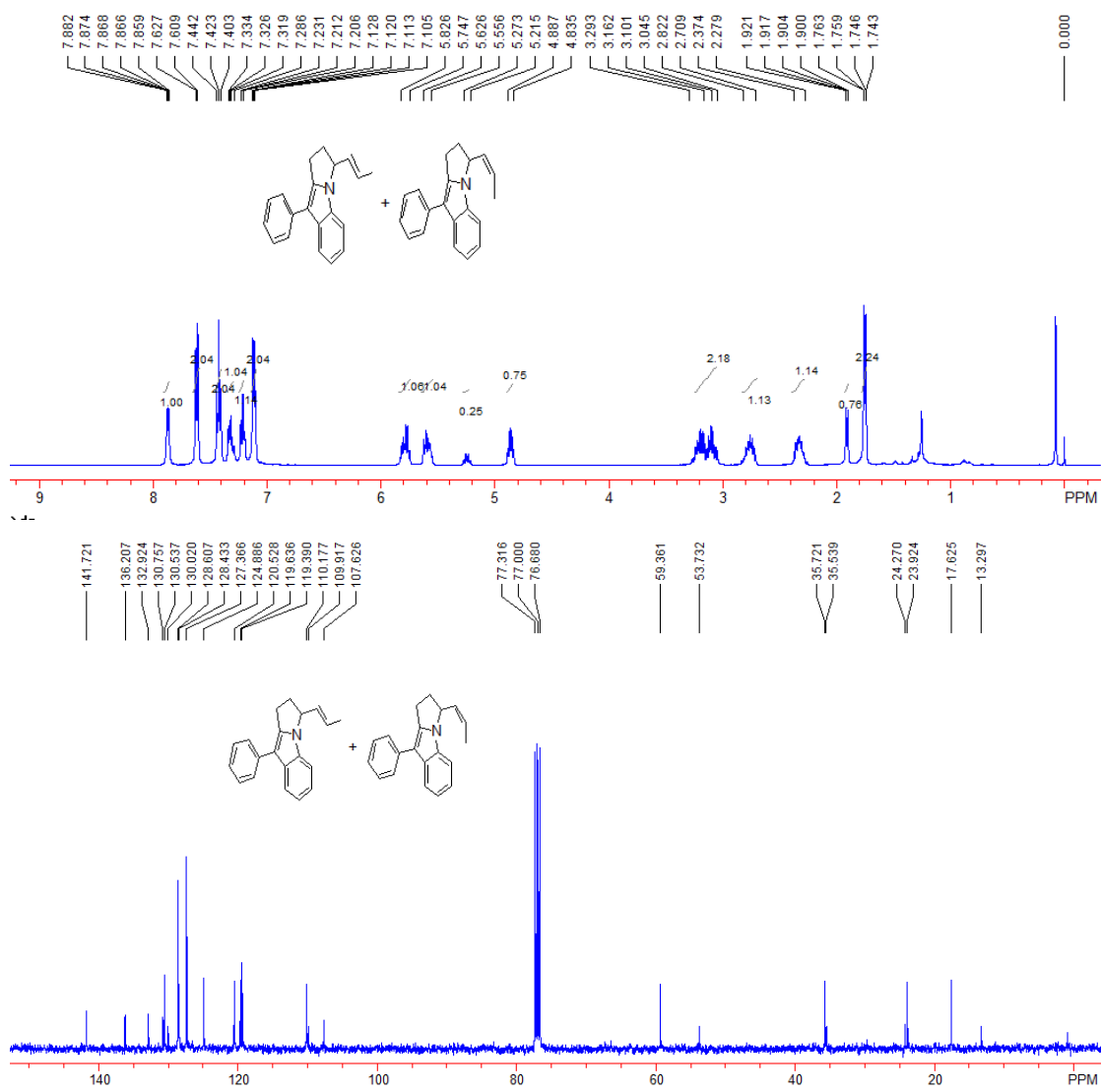
**Compound 2j:** 43 mg, 92%, A white solid, m.p. 121-123 °C; IR ( $CH_2Cl_2$ ):  $\nu$  3080, 3049, 2923, 2850, 1742, 1602, 1456, 1411, 739, 698  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ , TMS):  $\delta$  2.62-2.69 (m, 2H), 3.20 (t,  $J = 7.2$  Hz, 2H), 4.12 (t,  $J = 7.2$  Hz, 2H), 7.13-7.18 (m, 2H),

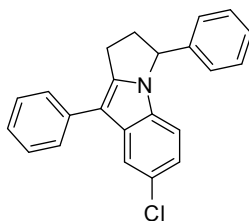
7.20-7.29 (m, 2H), 7.43 (t,  $J = 7.6$  Hz, 2H), 7.62-7.64 (m, 2H), 7.87-7.90 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  24.8, 27.7, 43.7, 107.8, 109.6, 119.5, 119.7, 120.7, 124.9, 127.3, 128.6, 130.5, 132.9, 136.3, 142.1; MS (EI)  $m/z$  (%): 233 (100.0) [ $\text{M}^+$ ], 232 (24.5), 230 (5.8), 217 (5.0), 204 (11.3), 203 (3.1), 154 (3.6), 116 (2.0); HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}$  ( $\text{M}^+$ ) requires 233.1204, Found: 233.1200.



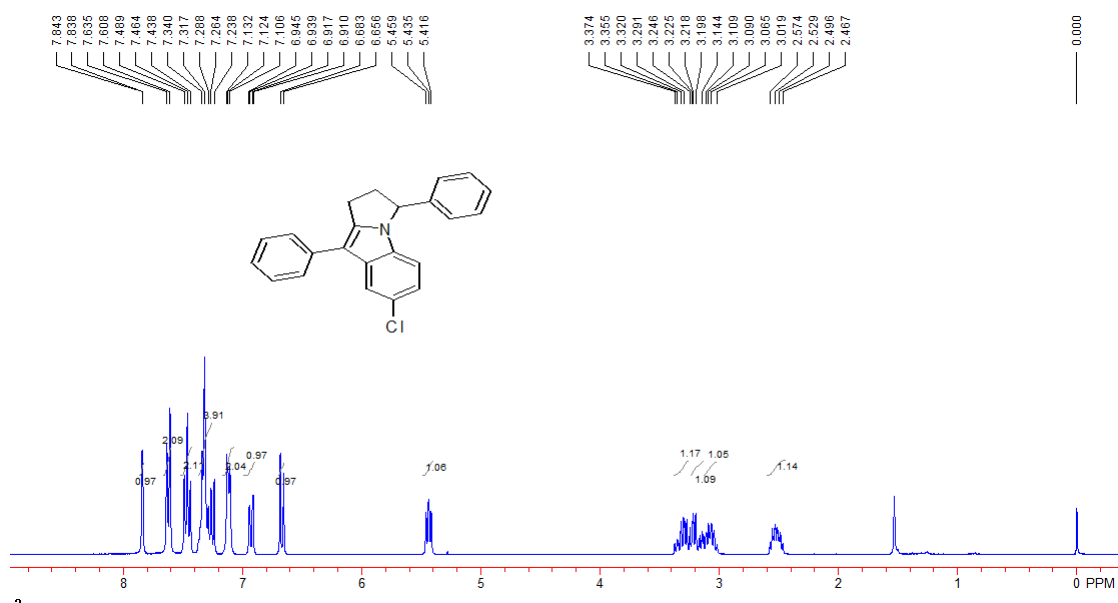
**Compound 2k:** 48 mg, 88%, A white solid, m.p. 84-86 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3088, 3048, 2963, 2852, 1612, 1601, 1455, 1362, 1256, 767, 739, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)

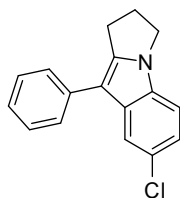
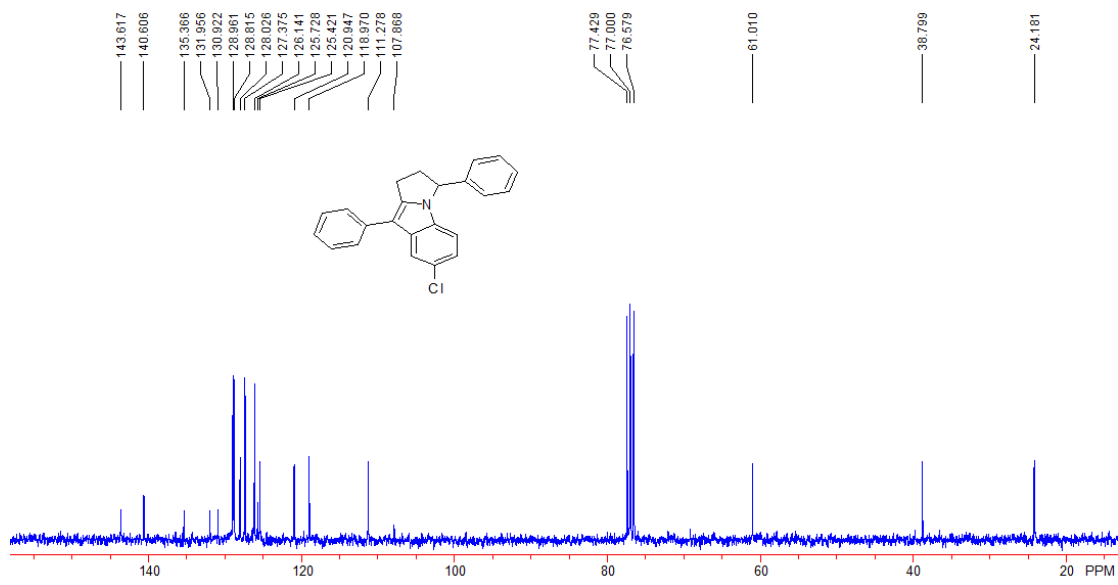
(two isomers):  $\delta$  1.75 (dd,  $J = 1.2, 6.8$  Hz, 2.25H), 1.91 (dd,  $J = 1.2, 6.8$  Hz, 0.75H), 2.28-2.37 (m 1H), 2.71-2.82 (m, 1H), 3.05-3.29 (m, 2H), 4.84-4.89 (m, 0.75H), 5.22-5.27 (m, 0.25H), 5.56-5.63 (m, 1H), 5.75-5.83 (m, 1H), 7.11-7.13 (m, 2H), 7.21-7.23 (m, 1H), 7.29-7.33 (m, 1H), 7.42 (t,  $J = 8.0$  Hz, 2H), 7.62 (d,  $J = 7.2$  Hz, 2H), 7.86-7.88 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS) (two isomers):  $\delta$  13.3, 17.6, 23.9, 24.3, 35.5, 35.7, 53.7, 59.4, 107.6, 109.9, 110.2, 119.4, 119.6, 120.5, 124.9, 127.4, 128.4, 128.6, 130.0, 130.5, 130.7, 132.8, 132.9, 136.2, 141.7; MS (EI)  $m/z$  (%): 273 (100.0) [ $\text{M}^+$ ], 258 (22.5), 230 (11.3), 218 (14.5), 206 (11.1), 204 (22.9), 193 (10.0), 178 (3.8); HRMS (EI) Calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}$  ( $\text{M}^+$ ) requires 273.1517, Found: 273.1509.



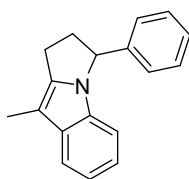
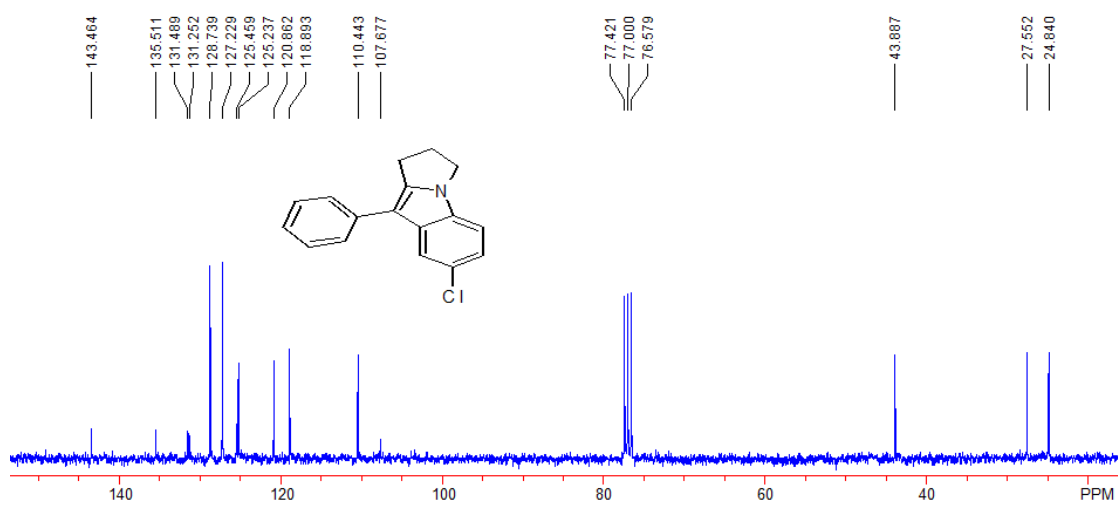
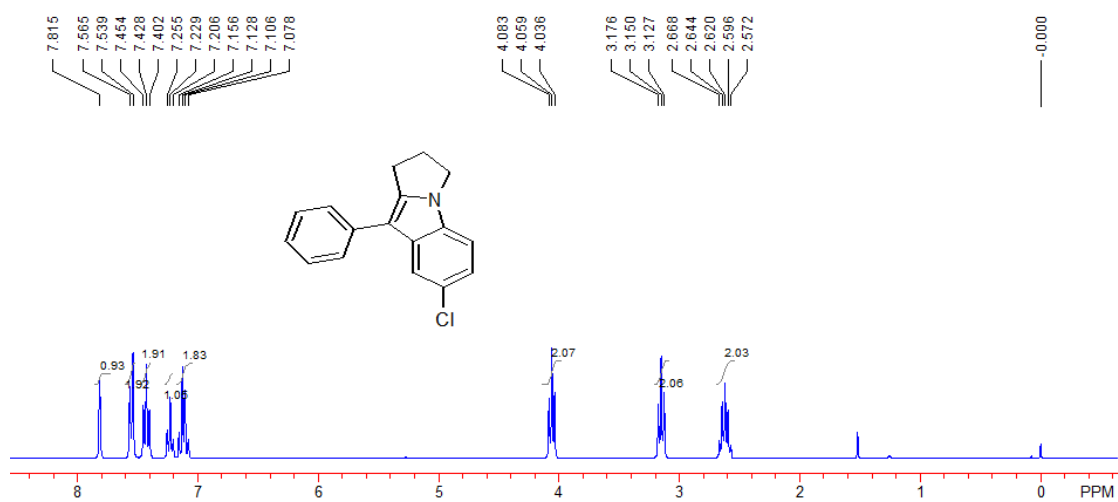


**Compound 2l:** 59 mg, 86%, A white solid, m.p. 158-160 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3099, 3059, 2854, 2438, 1949, 1808, 1601, 1449, 1065, 794, 696, 663 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.47-2.57 (m, 1H), 3.02-3.11 (m, 1H), 3.14-3.25 (m, 1H), 3.29-3.37 (m, 1H), 5.42-5.46 (m, 1H), 6.67 (d,  $J$  = 8.1 Hz, 1H), 6.91-6.95 (m, 1H), 7.11-7.13 (m, 2H), 7.24-7.34 (m, 4H), 7.46 (t,  $J$  = 7.8 Hz, 2H), 7.62 (d,  $J$  = 8.1 Hz, 2H), 7.83-7.84 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  24.2, 38.8, 61.0, 107.9, 111.3, 119.0, 120.9, 125.4, 125.7, 126.1, 127.4, 128.0, 128.8, 129.0, 130.9, 132.0, 135.4, 140.6, 143.6; MS (EI)  $m/z$  (%): 343 (100.0) [M<sup>+</sup>], 345 (31.0), 240 (10.0), 217 (21.4), 204 (21.8), 176 (3.0), 115 (2.6), 91 (2.4); HRMS (EI) Calcd. for C<sub>23</sub>H<sub>18</sub>NCl (M<sup>+</sup>) requires 343.1128, Found: 343.1122.

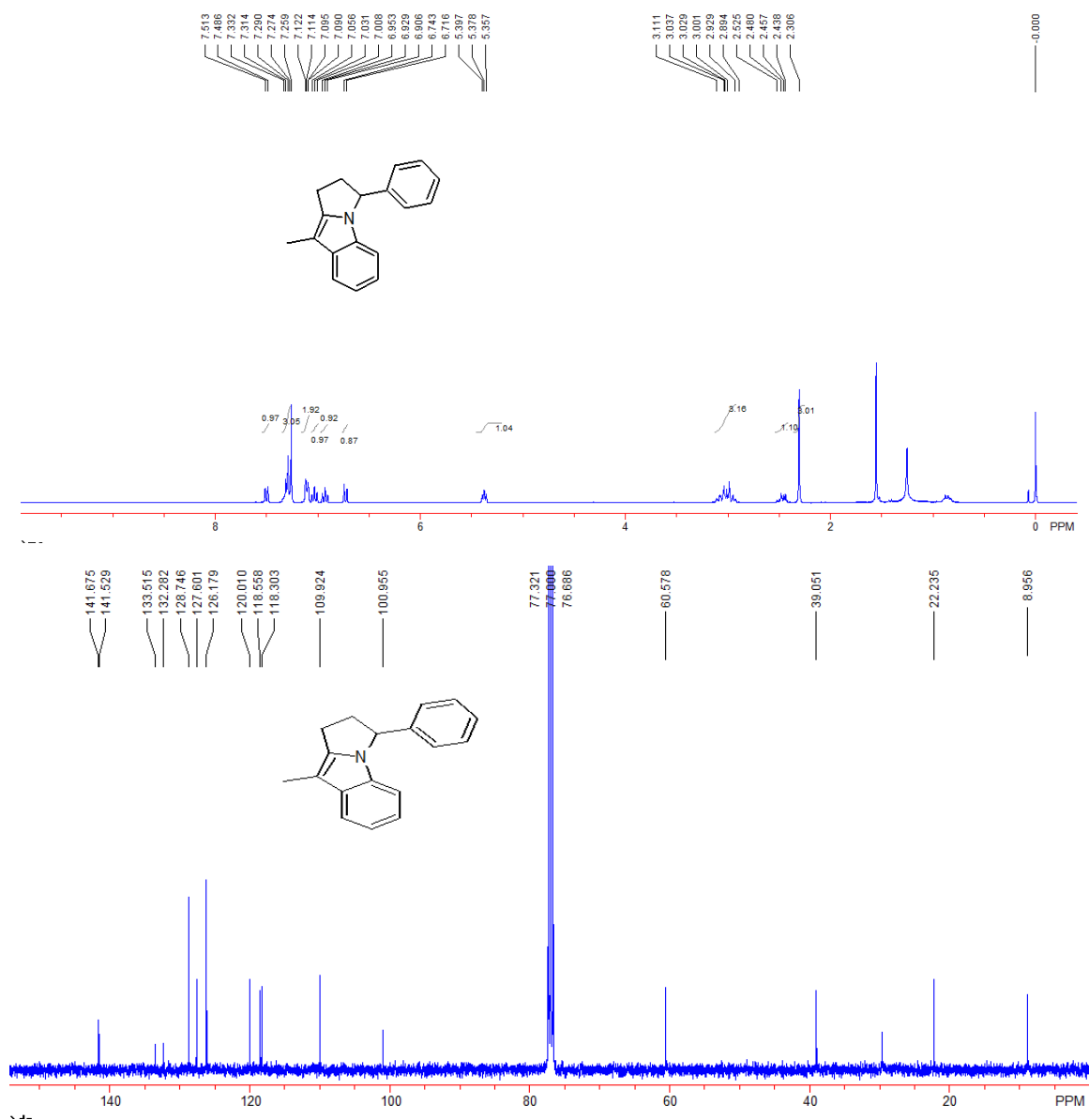




**Compound 2m:** 45 mg, 85%, A white solid, m.p. 129-131 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3053, 2976, 2880, 1601, 1463, 1412, 792, 741, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ 2.57-2.67 (m, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 4.06 (t, *J* = 6.9 Hz, 2H), 7.08-7.16 (m, 2H), 7.21-7.26 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.82 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ 24.8, 27.6, 43.9, 107.7, 110.4, 118.9, 120.9, 125.2, 125.5, 127.2, 128.7, 131.3, 131.5, 135.5, 143.5; MS (EI) *m/z* (%): 267 (100.0) [M<sup>+</sup>], 269 (27.7), 232 (15.0), 230 (10.3), 217 (5.4), 204 (11.0), 190 (3.5), 149 (5.8); HRMS (EI) Calcd. for C<sub>17</sub>H<sub>14</sub>NCl (M<sup>+</sup>) requires 267.0815, Found: 267.0806.



**Compound 2n:** 34 mg, 70%, A yellow solid, m.p. 109-111 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3054, 3025, 2923, 2852, 1619, 1458, 1260, 1016, 737 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.31(s, 3H), 2.44-2.53 (m, 1H), 2.89-3.11 (m, 3H), 5.38 (t,  $J$  = 6.0 Hz, 1H), 6.73 (d,  $J$  = 7.8 Hz, 1H), 6.93 (t,  $J$  = 7.2 Hz, 1H), 7.03 (t,  $J$  = 7.2 Hz, 1H), 7.09-7.12 (m, 2H), 7.26-7.33 (m, 3H), 7.50 (d,  $J$  = 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  9.0, 22.2, 39.0, 60.6, 101.0, 110.0, 118.3, 118.6, 120.0, 126.2, 127.6, 128.7, 132.3, 133.5, 141.5, 141.7; MS (EI)  $m/z$  (%): 247 (100.0) [M<sup>+</sup>], 246 (22.1), 232 (17.8), 170 (7.9), 143 (11.4), 115 (9.2), 91 (2.1), 77 (1.9); HRMS (EI) Calcd. for C<sub>18</sub>H<sub>17</sub>N (M<sup>+</sup>) requires 247.1361, Found: 247.1355.

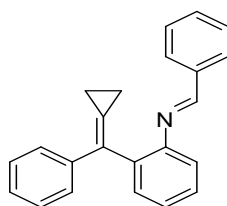




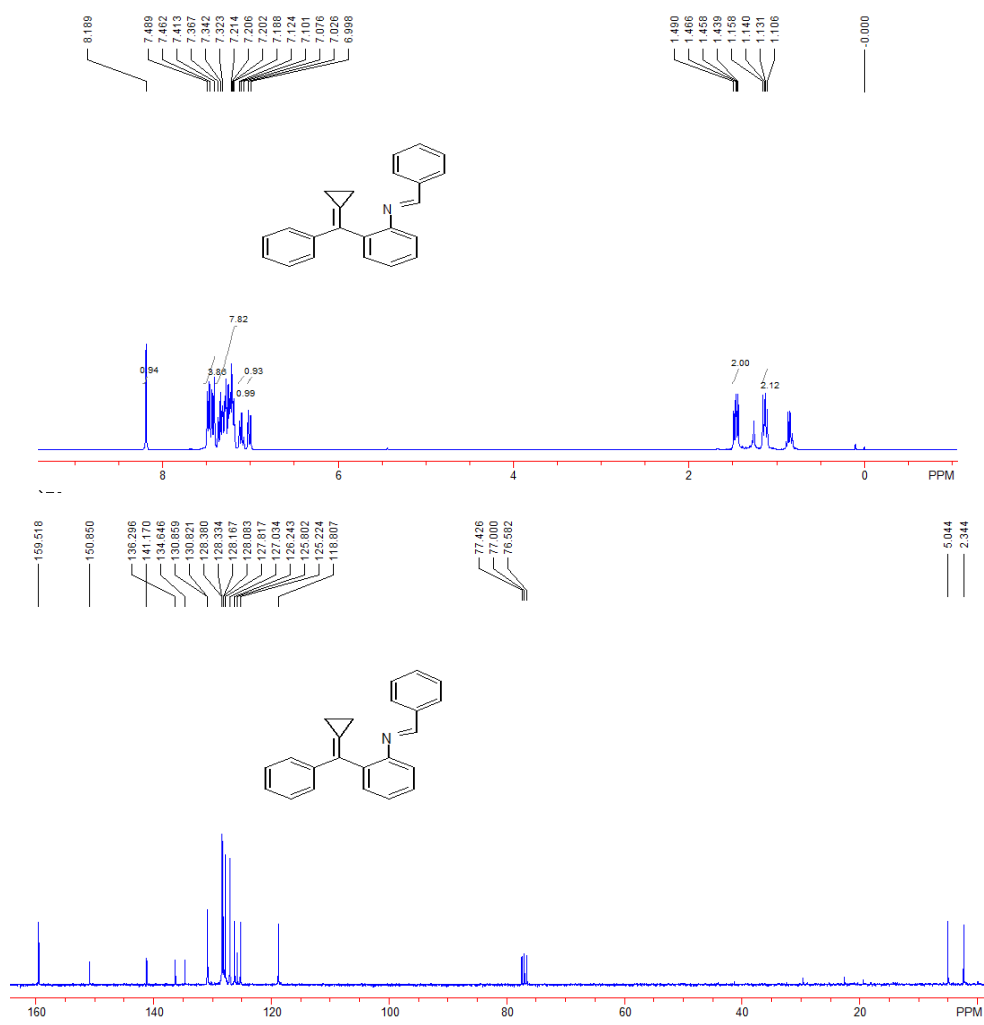
The procedure for the synthesis of **3a**

To a solution of **1a** (44 mg, 0.2 mmol), PhCHO (42 mg, 0.4 mmol) and MgSO<sub>4</sub> (240 mg, 2 mmol) in dry toluene (2.0 mL) were added, then the resulting reaction mixture was stirred at 20 °C for 24 h. Afterwards the reaction was stopped and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using neutral silica gel (the silica gel was treated by 10% Et<sub>3</sub>N in petroleum ether for 24 h. eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in high yield (54 mg, 88%).

### Spectroscopic data for **3a**

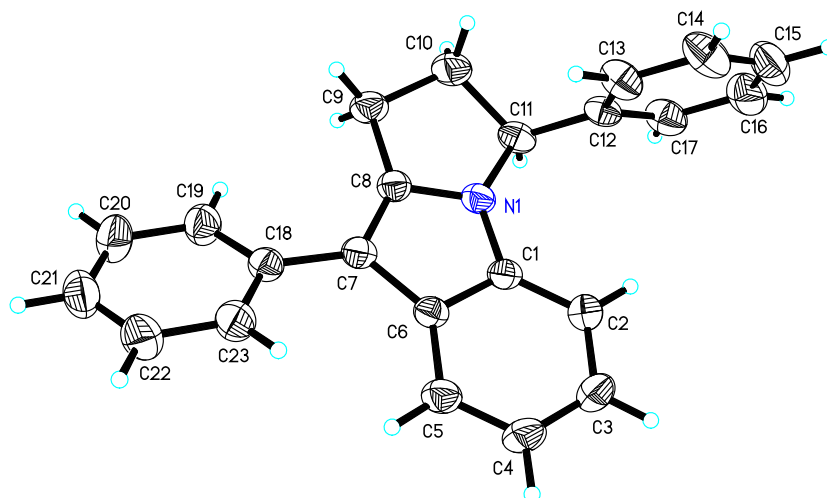


**Compound 3a:** 54 mg, 88%, A yellow liquid; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3057, 3026, 1770 1628, 1492, 1479, 1310, 764, 693 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.11-1.16 (m, 2H), 1.44-1.49 (m, 2H), 7.01 (d,  $J$  = 8.4 Hz, 1H), 7.08-7.12 (m, 1H), 7.19-7.37 (m, 8H), 7.41-7.49 (m, 4H), 8.19 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.3, 5.0, 118.8, 125.2, 125.8, 126.2, 127.0, 127.8, 128.1, 128.2, 128.3, 128.4, 130.8, 130.9, 134.6, 136.3, 141.2, 150.9, 159.5; MS (EI)  $m/z$  (%): 309 (100.0) [M<sup>+</sup>], 308 (43.1), 293 (17.0), 232 (28.5), 204 (40.1), 193 (29.9), 165 (17.6), 77 (17.1); HRMS (EI) Calcd. for C<sub>23</sub>H<sub>19</sub>N (M<sup>+</sup>) requires 309.1517, Found: 309.1518.

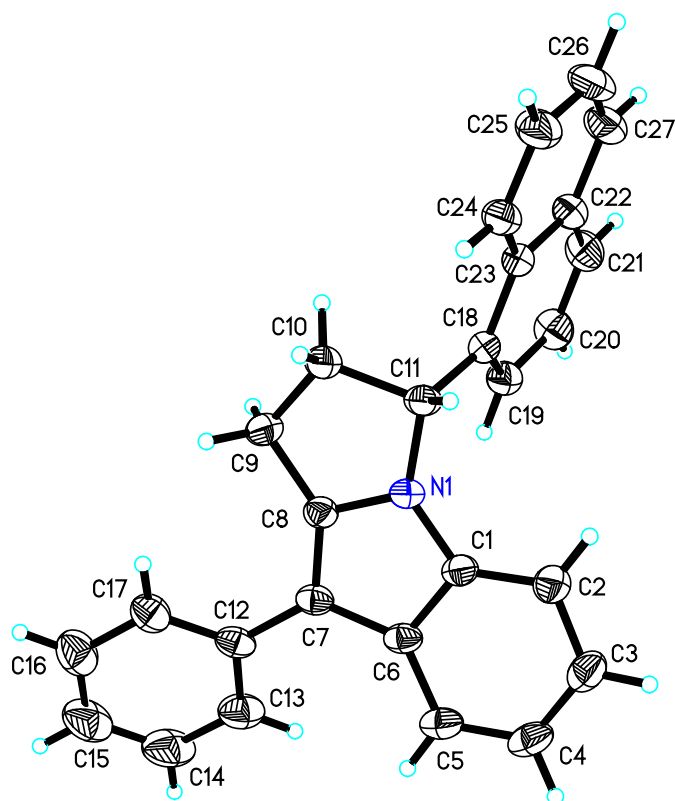




## The crystal data of **2a** and **2i**



The crystal data of **2a** have been deposited in CCDC with number 826603. Empirical Formula:  $C_{23}H_{19}N$ ; Formula Weight: 309.39; Crystal Color, Habit: colorless; Crystal Dimensions: 0.311 x 0.269 x 0.167 mm; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters:  $a = 9.8435(10)\text{\AA}$ ,  $b = 9.9731(10)\text{\AA}$ ,  $c = 10.8542(11)\text{\AA}$ ,  $\alpha = 97.636(2)^\circ$ ,  $\beta = 116.238(2)^\circ$ ,  $\gamma = 111.320(2)^\circ$ ,  $V = 833.58(15)\text{\AA}^3$ ; Space group: P-1;  $Z = 2$ ;  $D_{calc} = 1.233\text{ g/cm}^3$ ;  $F_{000} = 328$ ; Final R indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0453$ ,  $wR2 = 0.1189$ .



The crystal data of **2i** have been deposited in CCDC with number 869056. Empirical Formula:  $C_{27}H_{21}N$ ; Formula Weight: 359.45; Crystal Color, Habit: colorless; Crystal Dimensions: 0.311 x 0.256 x 0.127 mm; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters:  $a = 16.2578(8)\text{\AA}$ ,  $b = 8.2615(4)\text{\AA}$ ,  $c = 28.7208(15)\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3857.6(3)\text{\AA}^3$ ; Space group:  $Pbc_a$ ;  $Z = 8$ ;  $D_{calc} = 1.238\text{ g/cm}^3$ ;  $F_{000} = 1520$ ; Final R indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0433$ ,  $wR2 = 0.1080$ .

## Reference

- [1] (a) J. A. Stafford, J. E. McMurry, *Tetrahedron Lett.* **1988**, *29*, 2531–2534; (b) K. Utimoto, M. Tamura, K. Sisido, *Tetrahedron* **1973**, *29*, 1169–1171.