

# Supporting Information

## Diastereoselective Synthesis of 3,3-Dimethylazetidines via Intramolecular Iodine-Mediated Cyclization Reaction

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## 1 General Methods

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at 400 MHz and 100 MHz in CDCl<sub>3</sub> with chemical shift ( $\delta$ ) given in ppm relative to TMS as internal standard. High resolution mass spectra (HRMS) were recorded using atmospheric pressure chemical ionization (APCI) and time-of-flight (TOF) mass analysis.

## 2 General Procedure for the Synthesis of 2a-t

Sodium bicarbonate (1.5 mmol) and iodine (1.5 mmol) were added to  $\gamma$ -prenylated amine (0.5 mmol) in anhydrous acetonitrile (15 ml). After the mixture was stirred at room temperature for 6 hours under nitrogen, the solvent was removed under reduced pressure. To the residue was added a solution of sodium sulfite. The mixture was extracted with dichloromethane for three times and dried over anhydrous magnesium sulfate. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 100/1) to afford the products **2a-t**.

**2a:** White solid; 92% yield; mp 132-134 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.47 (d,  $J$  = 8.0 Hz, 2H), 7.19-7.23 (m, 3H), 6.88 (t,  $J$  = 7.2 Hz, 1H), 6.53 (d,  $J$  = 7.6 Hz, 2H), 4.43 (s, 1H), 4.07 (dd,  $J$  = 3.2 Hz,  $J$  = 12.0 Hz, 1H), 3.63 (dd,  $J$  = 2.8 Hz,  $J$  = 10.0 Hz, 1H), 3.28 (dd,  $J$  = 10.0 Hz,  $J$  = 11.2 Hz, 1H), 1.46 (s, 3H), 0.88 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 150.1, 139.9, 132.8, 131.4, 130.5, 129.2, 128.3, 125.8, 119.9, 113.0, 75.1, 71.2, 40.7, 29.3, 17.3, 3.6. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>19</sub>Cl<sub>2</sub>IN [M + H]<sup>+</sup>: 445.9939; Found: 445.9925.

**2b:** Yellow solid; 86% yield; mp 61-63 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.37-7.41 (m, 2H), 7.30-7.34 (m, 3H), 7.10 (d,  $J$  = 9.2 Hz, 2H), 6.46 (d,  $J$  = 8.8 Hz, 2H), 4.45 (s, 1H), 4.02 (dd,  $J$  = 3.2 Hz,  $J$  = 12.0 Hz, 1H), 3.56 (dd,  $J$  = 3.6 Hz,  $J$  = 10.0 Hz, 1H), 3.28 (dd,  $J$  = 10.0 Hz,  $J$  = 11.6 Hz, 1H), 1.45 (s, 3H), 0.84 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.7, 135.5,

125.5, 125.1, 124.1, 122.9, 120.9, 110.8, 67.9, 37.4, 26.0, 13.8. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>20</sub>ClIN [M + H]<sup>+</sup>: 412.0329; Found: 412.0322.

**2c:** Yellow solid; 69% yield; mp 106-108 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.36-7.40 (m, 2H), 7.28-7.33 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 8.8 Hz, 2H), 4.44 (s, 1H), 4.01 (dd, *J* = 3.2 Hz, *J* = 11.6 Hz, 1H), 3.55 (dd, *J* = 3.2 Hz, *J* = 10.0 Hz, 1H), 3.26 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 1.44 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.5, 138.8, 131.8, 128.4, 127.5, 126.3, 114.7, 111.5, 76.3, 71.3, 40.8, 29.4, 17.1, 3.5. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>20</sub>BrIN [M + H]<sup>+</sup>: 455.9824; Found: 455.9828.

**2d:** Yellow solid; 70% yield; mp 82-84 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.32 (d, *J* = 8.8 Hz, 2H), 7.22-7.26 (m, 2H), 7.13-7.16 (m, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.47-6.50 (m, 2H), 4.41 (s, 1H), 4.02 (dd, *J* = 3.2 Hz, *J* = 11.6 Hz, 1H), 3.58 (dd, *J* = 3.2 Hz, *J* = 10.4 Hz, 1H), 3.22 (dd, *J* = 10.0 Hz, *J* = 12.0 Hz, 1H), 1.40 (s, 3H), 0.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 151.3, 137.9, 133.1, 129.1, 128.6, 127.8, 119.6, 113.0, 75.6, 71.2, 40.6, 29.3, 17.3, 3.8. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>20</sub>ClIN [M + H]<sup>+</sup>: 412.0329; Found: 412.0326.

**2e:** Yellow solid; 89% yield; mp 67-69 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.33-7.38 (m, 1H), 7.26 (d, *J* = 9.2 Hz, 2H), 7.00-7.09 (m, 3H), 6.40 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 1H), 4.01 (dd, *J* = 3.2 Hz, *J* = 11.6 Hz, 1H), 3.56 (dd, *J* = 2.8 Hz, *J* = 10.0 Hz, 1H), 3.27 (dd, *J* = 10.4 Hz, *J* = 11.6 Hz, 1H), 1.45 (s, 3H), 0.86 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 164.6, 162.2, 150.4, 141.9, 132.0, 122.0, 114.8, 114.5, 113.5, 112.0, 75.9, 71.6, 40.0, 29.5, 17.2, 3.3. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>19</sub>ClBrIN [M + H]<sup>+</sup>: 489.9434; Found: 489.9424.

**2f:** Yellow oil; 80% yield; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.48 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.94-6.99 (m, 1H), 6.86-6.90 (m, 1H), 6.72-6.78 (m, 1H), 6.39-6.44 (m, 1H),

4.51 (s, 1H), 4.17-4.21 (m, 1H), 3.79 (dd,  $J = 2.8$  Hz,  $J = 9.6$  Hz, 1H), 3.20-3.25 (m, 1H), 1.43 (s, 3H), 0.82 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.5 ( $J = 239.9$ ), 138.6 ( $J = 6.6$  Hz), 131.8, 128.3, 124.8, 121.5, 120.6 ( $J = 7.3$  Hz), 116.8 ( $J = 2.9$  Hz), 116.6, 75.9, 72.4, 40.1, 30.2, 17.7, 4.4 ( $J = 13.1$  Hz). HRMS (APCI): m/z cacled for  $\text{C}_{18}\text{H}_{19}\text{BrFIN}$  [M + H] $^+$ : 473.9730; Found: 473.9761.

**2g:** Yellow solid; 73% yield; mp 89-91 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.50 (d,  $J = 8.8$  Hz, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 7.09-7.11 (m, 2H), 6.42 (d,  $J = 9.2$  Hz, 2H), 4.38 (s, 1H), 4.00 (dd,  $J = 3.2$  Hz,  $J = 11.6$  Hz, 1H), 3.54 (dd,  $J = 3.2$  Hz,  $J = 10.0$  Hz, 1H), 3.24 (dd,  $J = 10.0$  Hz,  $J = 11.6$  Hz, 1H), 1.42 (s, 3H), 0.82 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.4, 138.5, 132.2, 129.5, 128.6, 125.1, 121.9, 114.7, 76.3, 71.8, 41.2, 29.8, 17.7, 3.8. HRMS (APCI): m/z cacled for  $\text{C}_{18}\text{H}_{19}\text{ClBrNI}$  [M + H] $^+$ : 489.9434; Found: 489.9435.

**2h:** Yellow solid; 72% yield; mp 98-100 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.50 (d,  $J = 8.4$  Hz, 2H), 7.17-7.25 (m, 4H), 6.37 (d,  $J = 8.8$  Hz, 2H), 4.38 (s, 1H), 4.00 (dd,  $J = 3.2$  Hz,  $J = 11.6$  Hz, 1H), 3.54 (dd,  $J = 3.2$  Hz,  $J = 10.4$  Hz, 1H), 3.24 (t,  $J = 10.8$  Hz, 1H), 1.43 (s, 3H), 0.82 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.6, 138.2, 132.2, 132.0, 128.4, 121.8, 115.0, 112.2, 76.1, 71.6, 41.1, 29.6, 17.5, 3.6. HRMS (APCI): m/z cacled for  $\text{C}_{18}\text{H}_{19}\text{Br}_2\text{IN}$  [M + H] $^+$ : 533.8929; Found: 533.8912.

**2i:** Yellow solid; 69% yield; mp 85-87 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.22-7.29 (m, 4H), 7.07 (t,  $J = 8.8$  Hz, 2H), 6.38 (d,  $J = 8.8$  Hz, 2H), 4.40 (s, 1H), 4.00 (dd,  $J = 3.2$  Hz,  $J = 11.6$  Hz, 1H), 3.55 (dd,  $J = 1.6$  Hz,  $J = 10.0$  Hz, 1H), 3.25 (dd,  $J = 1.6$  Hz,  $J = 11.6$  Hz, 1H), 1.42 (s, 3H), 0.82 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.3 ( $J = 244.3$  Hz), 150.4, 134.5, 131.9, 127.8 ( $J = 8.0$  Hz), 115.4 ( $J = 21.2$  Hz), 114.7, 111.7, 75.7, 40.7, 29.7, 17.1, 3.3.

HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>19</sub>BrFIN [M + H]<sup>+</sup>: 473.9730; Found: 473.9758.

**2j:** Yellow solid; 92% yield; mp 74-77 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.63 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23-7.25 (m, 2H), 6.37 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 1H), 4.03 (dd, *J* = 3.2 Hz, *J* = 11.2 Hz, 1H), 3.56 (dd, *J* = 3.2 Hz, *J* = 10.0 Hz, 1H), 3.25 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 1.46 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.1, 143.0, 131.9, 130.0, 129.7, 126.6, 125.6, 125.5, 114.7, 112.0, 75.7, 71.4, 40.9, 29.3, 17.2, 3.0.

HRMS (APCI): m/z caclcd for C<sub>19</sub>H<sub>19</sub>BrF<sub>3</sub>IN [M + H]<sup>+</sup>: 523.9698; Found: 523.9704.

**2k:** Yellow oil; 91% yield; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.36 (d, *J* = 9.2 Hz, 2H), 4.36 (s, 1H), 3.99 (dd, *J* = 3.2 Hz, *J* = 11.6 Hz, 1H), 3.54 (dd, *J* = 3.2 Hz, *J* = 10.4 Hz, 1H), 3.24 (dd, *J* = 10.4 Hz, *J* = 12.0 Hz, 1H), 1.43 (s, 3H), 0.86 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.2, 139.5, 133.1, 132.1, 131.7, 130.8, 128.3, 125.8, 114.9, 112.3, 75.3, 71.5, 41.0, 29.4, 17.4, 3.2. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>BrIN [M + H]<sup>+</sup>: 525.9024; Found: 525.9051.

**2l:** Yellow solid; 85% yield; mp 58-60 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.51 (d, *J* = 8.8 Hz, 2H), 7.16 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 3H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.32 (dd, *J* = 2.8 Hz, *J* = 8.8 Hz, 1H), 4.39 (s, 1H), 4.00 (dd, *J* = 3.2 Hz, *J* = 11.6 Hz, 1H), 3.51 (dd, *J* = 3.6 Hz, *J* = 10.4 Hz, 1H), 3.23 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 1.46 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.7, 137.4, 132.8, 131.7, 130.6, 127.9, 122.6, 121.6, 114.5, 112.7, 75.8, 71.4, 40.8, 29.3, 17.1, 2.8. HRMS (APCI): m/z caclcd for C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>BrIN [M + H]<sup>+</sup>: 523.9044; Found: 523.9055.

**2m:** Yellow oil; 95% yield; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.39 (dd, *J* = 1.2 Hz, *J* = 7.6 Hz,

1H), 7.31 (dd,  $J = 1.2$  Hz,  $J = 8.0$  Hz, 1H), 7.17-7.21 (m, 2H), 6.46 (d,  $J = 3.2$  Hz, 1H), 6.20 (dd,  $J = 1.2$  Hz,  $J = 8.0$  Hz, 1H), 5.21 (s, 1H), 4.13 (dd,  $J = 4.4$  Hz,  $J = 10.8$  Hz, 1H), 3.51-3.58 (m, 2H), 1.61 (s, 3H), 1.12 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 135.5, 132.8, 129.8, 129.5, 83.1, 73.6, 42.1, 32.2, 30.6, 27.1, 24.9, 14.0. HRMS (APCI): m/z caclcd for  $\text{C}_{18}\text{H}_{17}\text{Cl}_4\text{IN} [\text{M} + \text{H}]^+$ : 513.9160; Found: 513.9153.

**2n:** Yellow oil; 65% yield;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.31 (dd,  $J = 5.6$  Hz,  $J = 8.4$  Hz, 2H), 7.08 (t,  $J = 8.4$  Hz, 2H), 7.00 (d,  $J = 7.6$  Hz, 2H), 6.45 (d,  $J = 8.4$  Hz, 2H), 4.41 (s, 1H), 4.01 (dd,  $J = 3.2$  Hz,  $J = 12.0$  Hz, 1H), 3.61 (dd,  $J = 3.2$  Hz,  $J = 10.0$  Hz, 1H), 3.27 (dd,  $J = 10.0$  Hz,  $J = 11.6$  Hz, 1H), 2.26 (s, 3H), 1.43 (s, 3H), 0.84 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.1 ( $J = 143.6$  Hz), 161.0, 149.2, 135.1 ( $J = 2.9$  Hz), 129.6, 128.9, 127.8 ( $J = 8.0$  Hz), 115.2 ( $J = 21.1$  Hz), 113.1, 75.6, 71.2, 40.6, 29.2, 20.5, 17.2, 4.0. HRMS (APCI): m/z caclcd for  $\text{C}_{19}\text{H}_{22}\text{FIN} [\text{M} + \text{H}]^+$ : 410.0781; Found: 410.0781.

**2o:** Yellow solid; 65% yield; mp 86-88 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.56-7.61 (m, 2H), 7.29-7.33 (m, 1H), 7.14-7.18 (m, 1H), 6.98 (d,  $J = 8.4$  Hz, 2H), 6.37 (d,  $J = 8.4$  Hz, 2H), 4.82 (s, 1H), 4.04 (dd,  $J = 2.8$  Hz,  $J = 11.6$  Hz, 1H), 3.56 (dd,  $J = 2.8$  Hz,  $J = 10.0$  Hz, 1H), 3.24 (dd,  $J = 10.0$  Hz,  $J = 11.6$  Hz, 1H), 2.24 (s, 3H), 1.64 (s, 3H), 1.55 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.5, 139.1, 132.8, 129.8, 129.7, 128.9, 128.8, 127.6, 122.5, 112.7, 75.2, 71.1, 41.0, 30.4, 20.6, 17.1, 3.9. HRMS (APCI): m/z caclcd for  $\text{C}_{19}\text{H}_{21}\text{BrINNa} [\text{M} + \text{Na}]^+$ : 491.9633; Found: 491.9633.

**2p:** Yellow solid; 76% yield; mp 78-80 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.63 (d,  $J = 8.0$  Hz, 2H), 7.45 (d,  $J = 8.0$  Hz, 2H), 6.99 (d,  $J = 8.0$  Hz, 2H), 6.43 (d,  $J = 8.4$  Hz, 2H), 4.47 (s, 1H), 4.03 (dd,  $J = 2.8$  Hz,  $J = 11.6$  Hz, 1H), 3.61 (dd,  $J = 3.2$  Hz,  $J = 10.0$  Hz, 1H), 3.26 (dd,

*J* = 10.0 Hz, *J* = 11.6 Hz), 2.25 (s, 3H), 1.45 (s, 3H), 0.83 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.3, 144.0 (*J* = 1.5 Hz), 130.0, 129.5, 127.0, 125.7 (*J* = 4.4 Hz), 124.5 (*J* = 270.5 Hz) 113.4, 76.0, 71.6, 41.1, 29.6, 20.8, 17.6, 4.1. HRMS (APCI): m/z caclcd for  $\text{C}_{20}\text{H}_{22}\text{F}_3\text{IN}$  [M + H]<sup>+</sup>: 460.0749; Found: 460.0757.

**2q:** Yellow solid; 66% yield; mp 92-93 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.18 (q, *J* = 8.0 Hz, 4H), 6.94-6.99 (m, 1H), 6.83-6.87 (m, 1H), 6.70-6.75 (m, 1H), 6.42-6.47 (m, 1H), 4.53 (s, 1H), 4.18-4.22 (m, 1H), 3.83 (dd, *J* = 3.2 Hz, *J* = 10.0 Hz, 1H), 3.25 (t, *J* = 10.0 Hz, 1H), 2.36 (s, 3H), 1.43 (s, 3H), 0.83 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.1 (*J* = 239.1 Hz), 138.7 (*J* = 10.2 Hz), 137.1, 136.3, 129.2, 126.3, 124.6, 124.5, 119.8 (*J* = 7.2 Hz), 116.7 (*J* = 4.4 Hz), 116.4, 116.2, 76.2, 72.2 (*J* = 1.5 Hz), 39.9, 30.0, 21.3, 17.5, 4.8, 4.6. HRMS (APCI): m/z caclcd for  $\text{C}_{19}\text{H}_{22}\text{FIN}$  [M + H]<sup>+</sup>: 410.0781; Found: 410.0753.

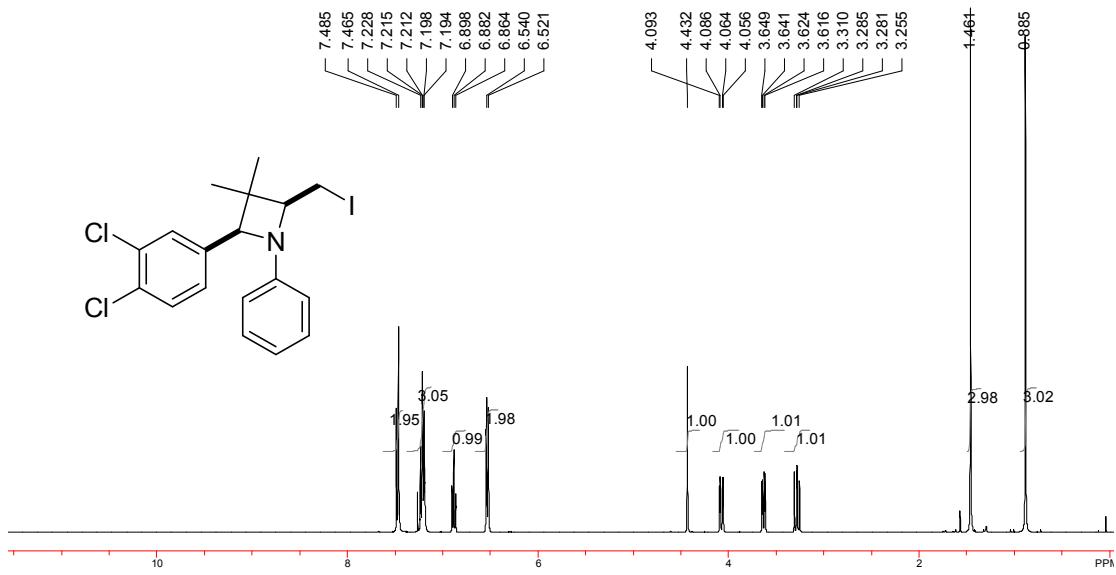
**2r:** Yellow solid; 86% yield; mp 84-86 °C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.22 (d, *J* = 8.0 Hz, 2H), 7.14-7.29 (m, 4H), 6.81 (t, *J* = 6.4 Hz, 2H), 6.54 (dd, *J* = 1.2 Hz, *J* = 8.8 Hz, 2H), 4.45 (s, 1H), 4.04 (dd, *J* = 2.8 Hz, *J* = 11.6 Hz, 1H), 3.60 (dd, *J* = 3.2 Hz, *J* = 10.0 Hz, 1H), 3.27 (dd, *J* = 10.0 Hz, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 1.42 (s, 3H), 0.84 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 151.8, 139.5, 137.1, 136.5, 129.2, 126.5, 119.4, 113.11, 76.3, 71.3, 40.7, 29.5, 21.4, 17.4, 4.2. HRMS (APCI): m/z caclcd for  $\text{C}_{19}\text{H}_{23}\text{IN}$  [M + H]<sup>+</sup>: 392.0885; Found: 392.0886.

**2s:** Yellow oil; 77% yield;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.23 (d, *J* = 8.4 Hz, 2H), 7.07-7.10 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.38 (s, 1H), 3.98 (dd, *J* = 3.2 Hz, *J* = 12.0 Hz, 1H), 3.83 (s, 3H), 3.55 (dd, *J* = 2.8 Hz, *J* = 10.0 Hz, 1H), 3.26 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 1.41 (s, 3H), 0.83 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.1, 150.2,

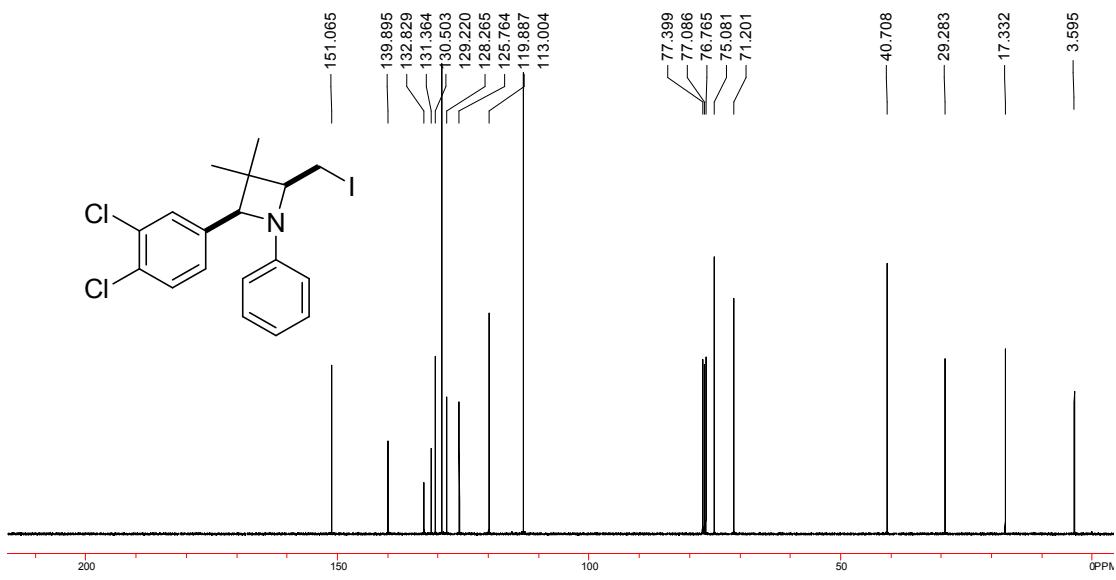
130.9, 128.9, 127.5, 124.2, 114.2, 113.8, 76.0, 71.2, 55.3, 40.8, 29.2, 17.1, 3.6. HRMS

(APCI): m/z cacled for C<sub>19</sub>H<sub>22</sub>ClINO [M + H]<sup>+</sup>: 442.0435; Found: 442.0421.

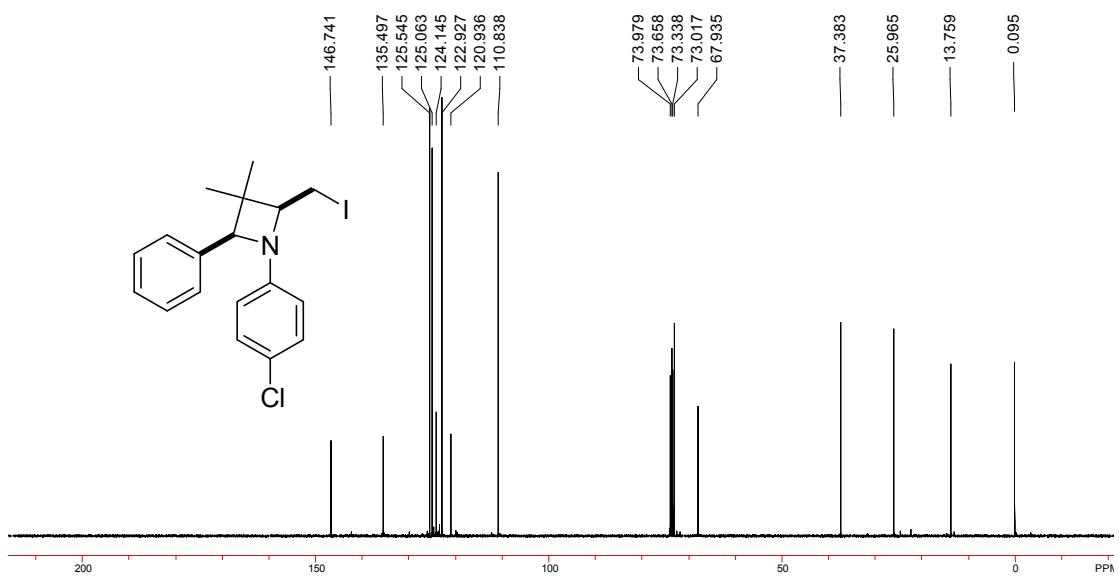
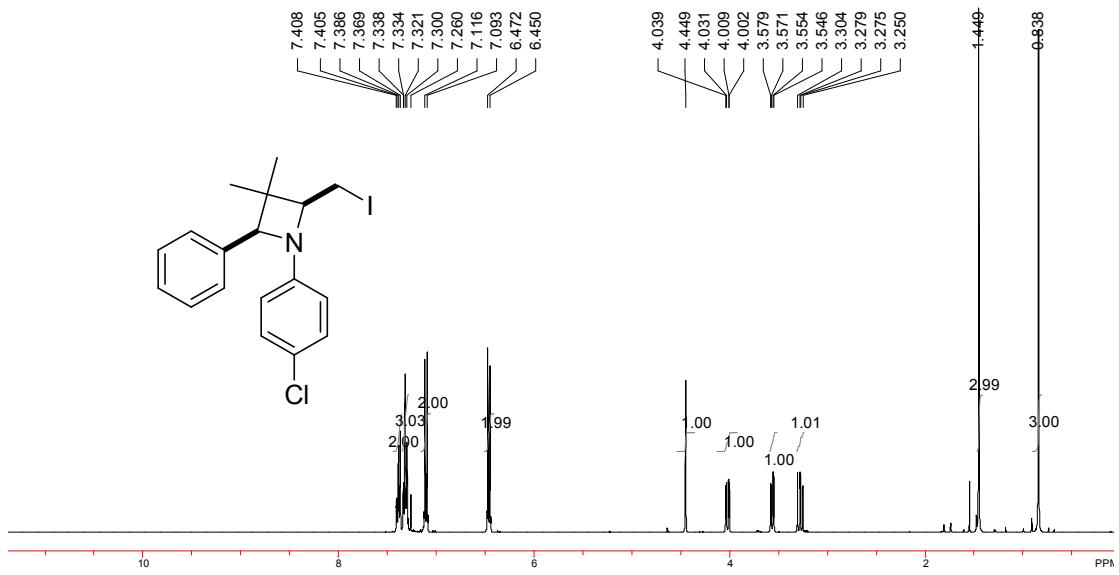
**2t:** Yellow solid; 84% yield; mp 84-86 °C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.19 (q, *J* = 8.0 Hz, 4H), 6.96 (d, *J* = 11.6 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 4.39 (s, 1H), 3.98 (dd, *J* = 2.8 Hz, *J* = 11.6 Hz, 1H), 3.58 (dd, *J* = 2.8 Hz, *J* = 9.6 Hz, 1H), 3.26 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 3H), 1.40 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 149.8, 137.2, 136.8, 129.9, 129.3, 128.9, 126.7, 113.3, 77.0, 76.5, 71.5, 40.9, 29.6, 21.5, 20.8, 17.5, 4.6. HRMS (APCI): m/z cacled for C<sub>20</sub>H<sub>25</sub>IN [M + H]<sup>+</sup>: 406.1032; Found: 406.1031.

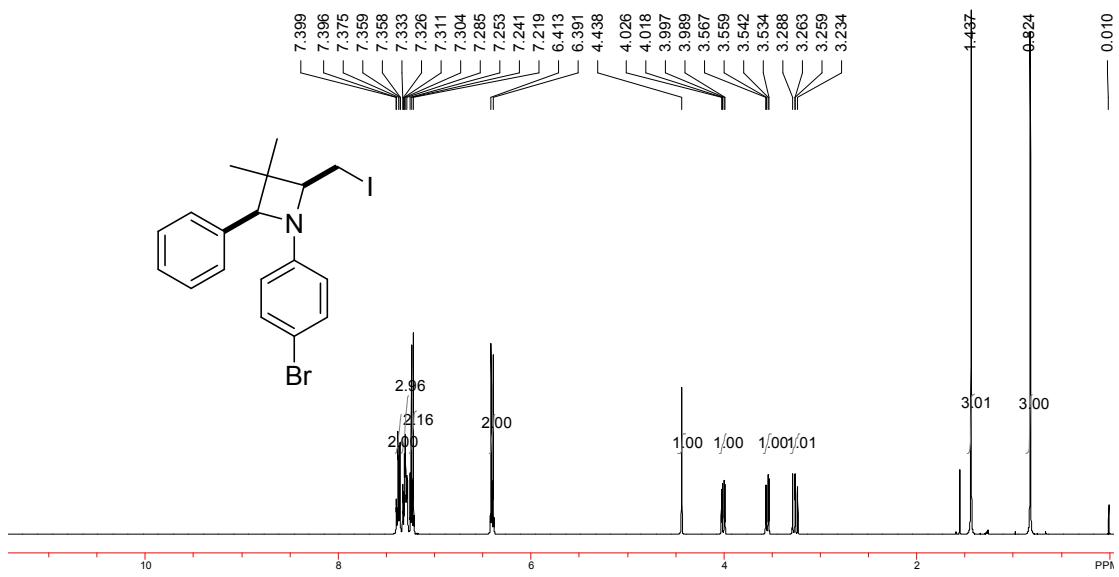


<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound **2a**

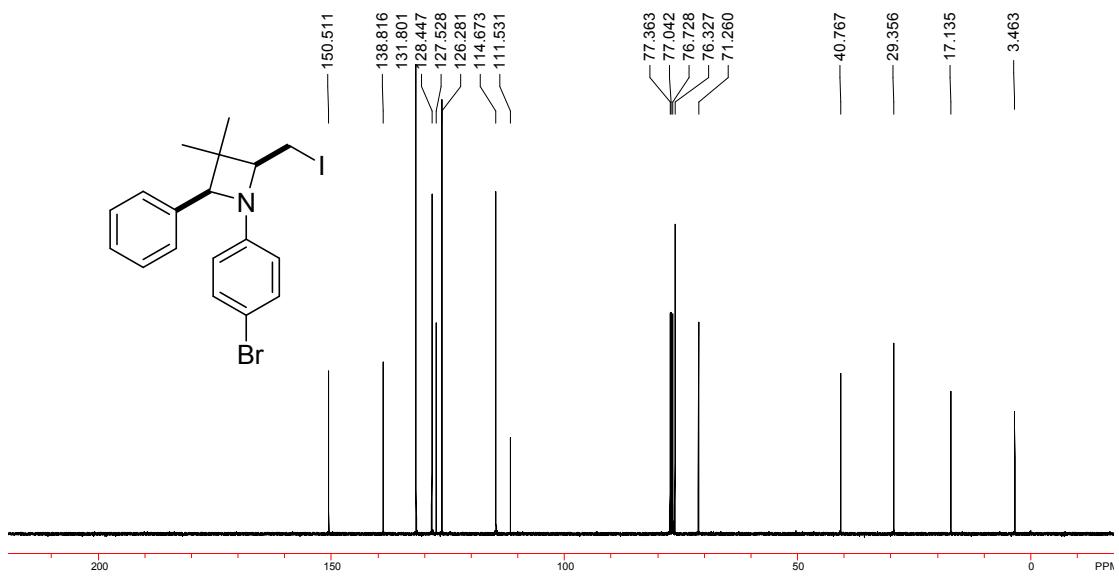


<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound **2a**

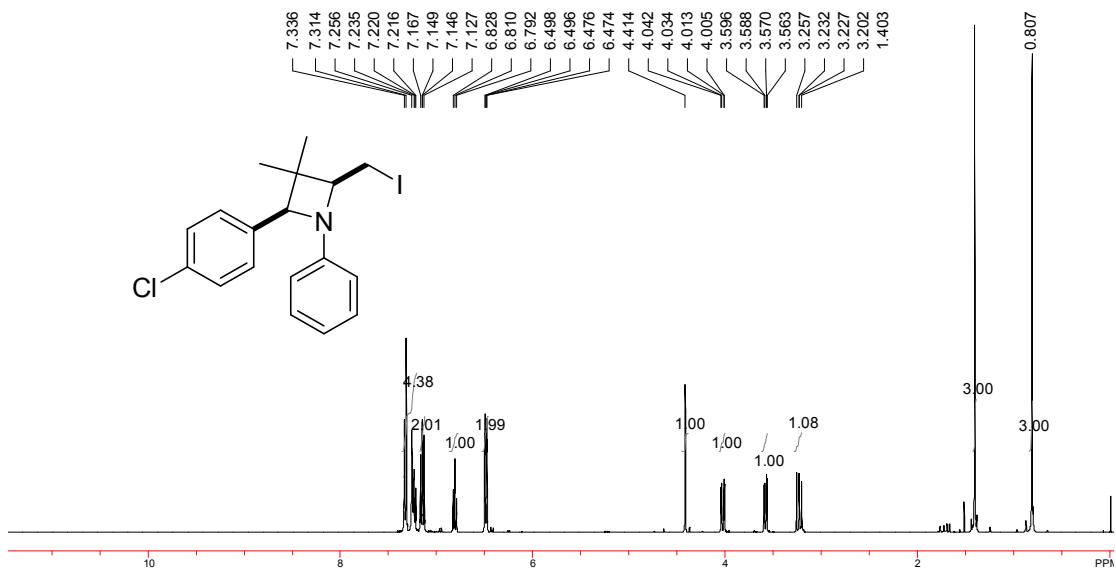




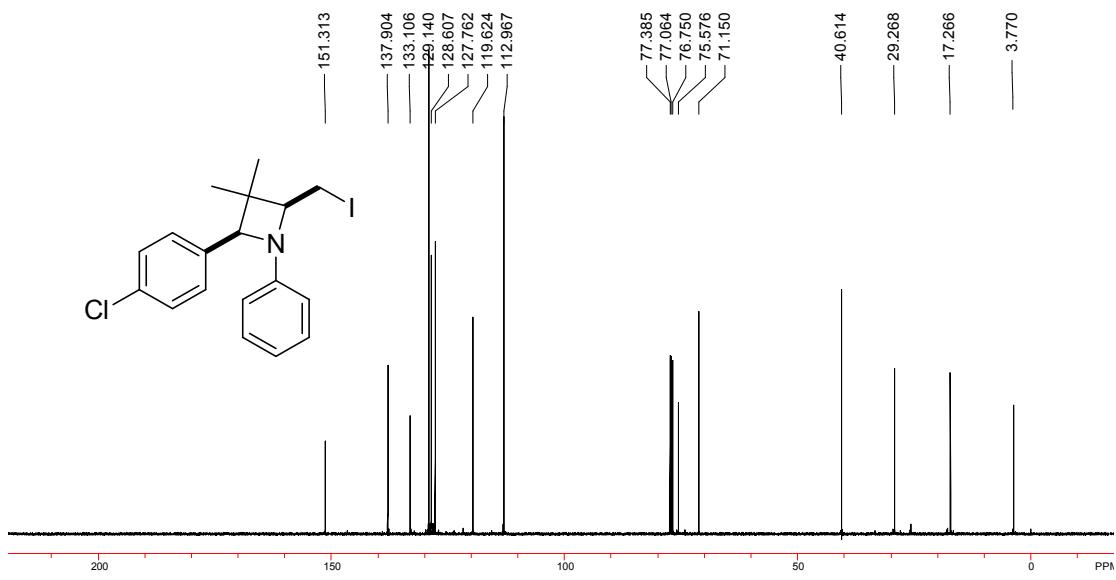
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2c



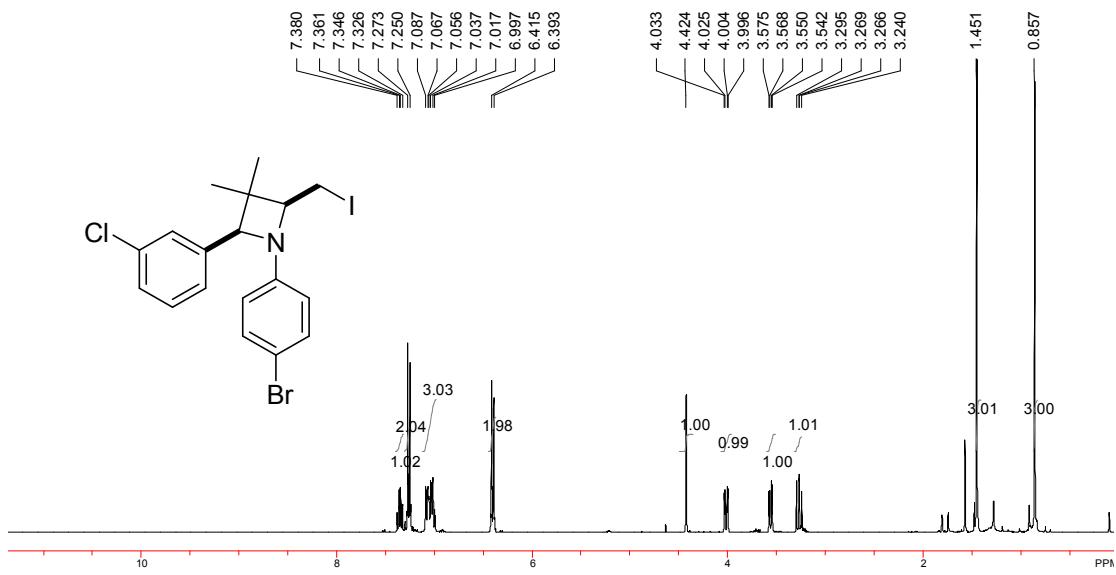
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2c



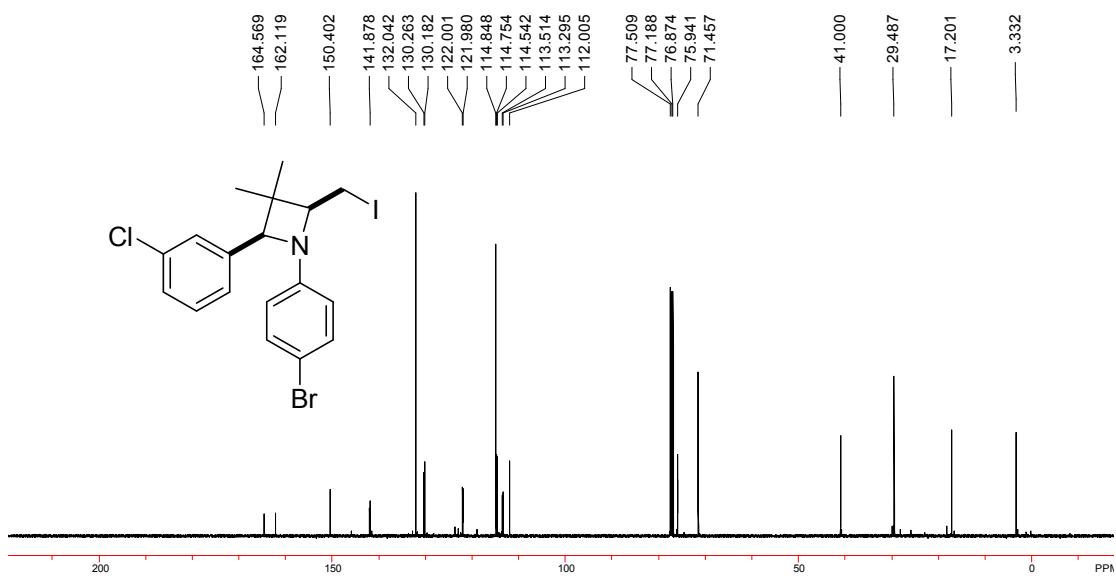
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2d



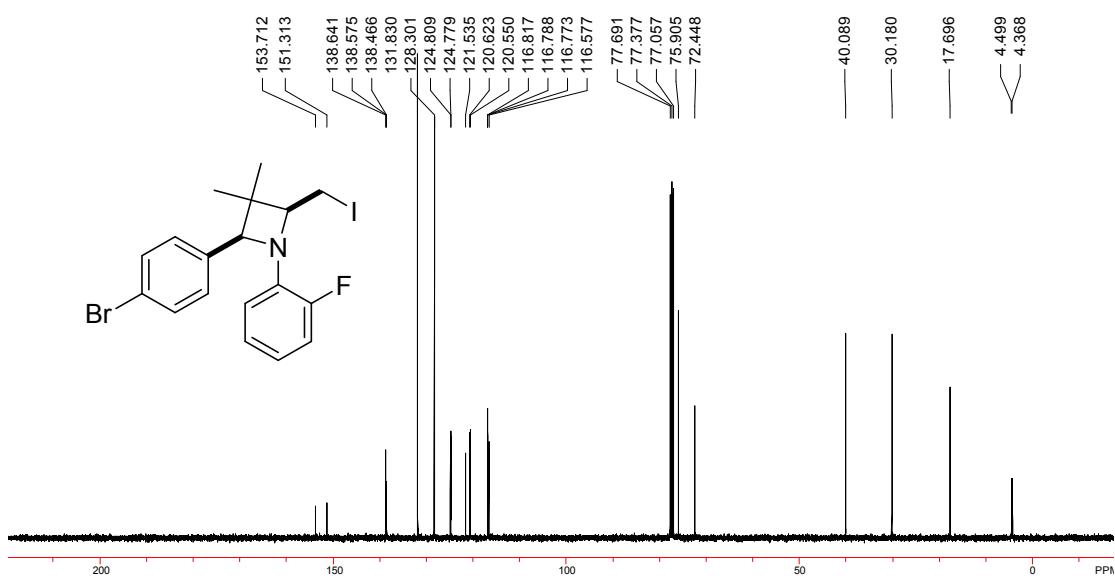
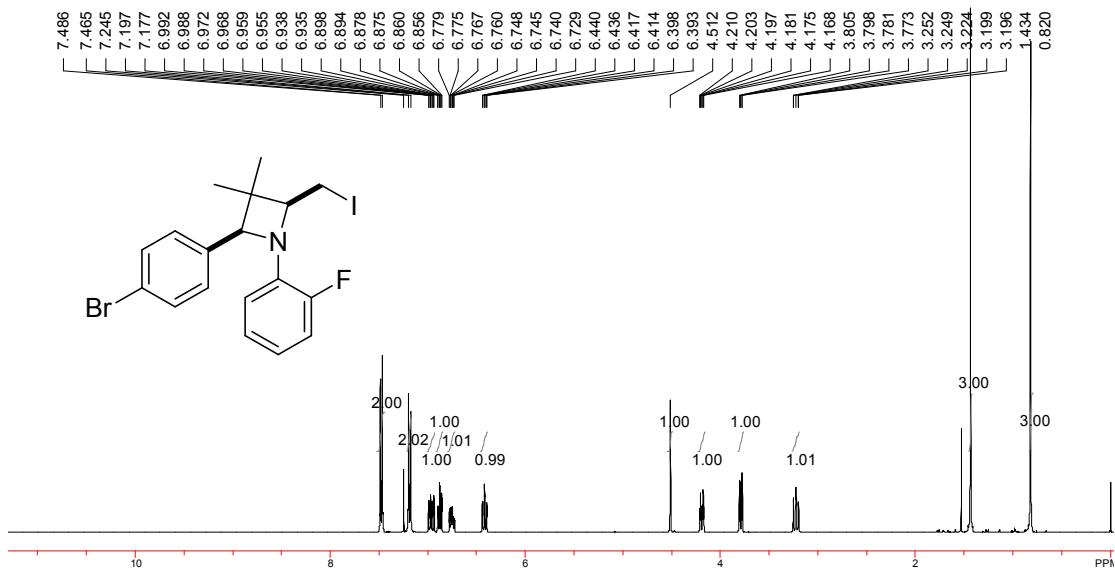
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2d



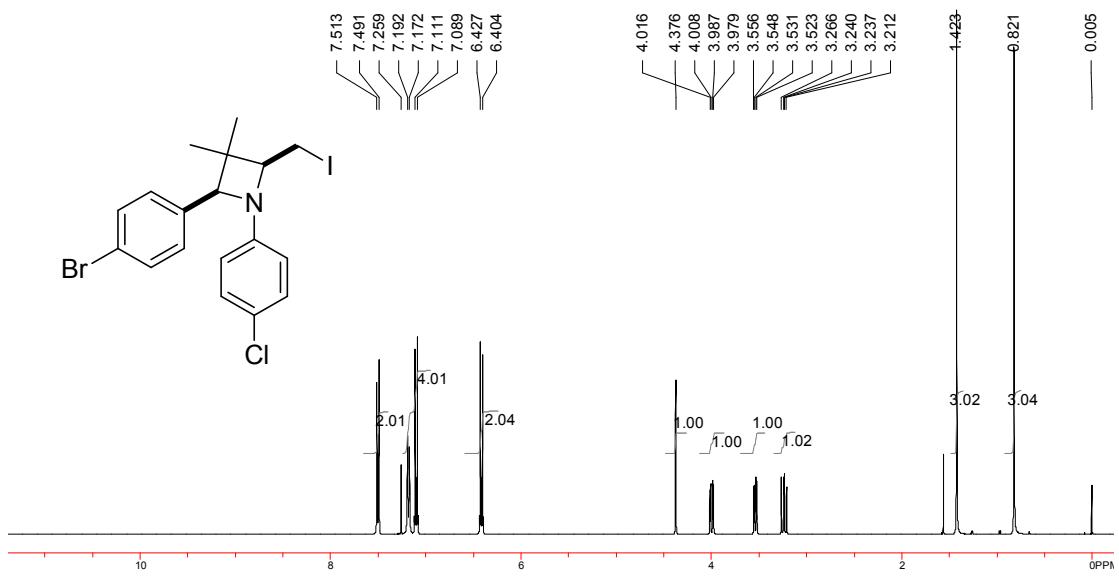
$^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ ) of Compound **2e**



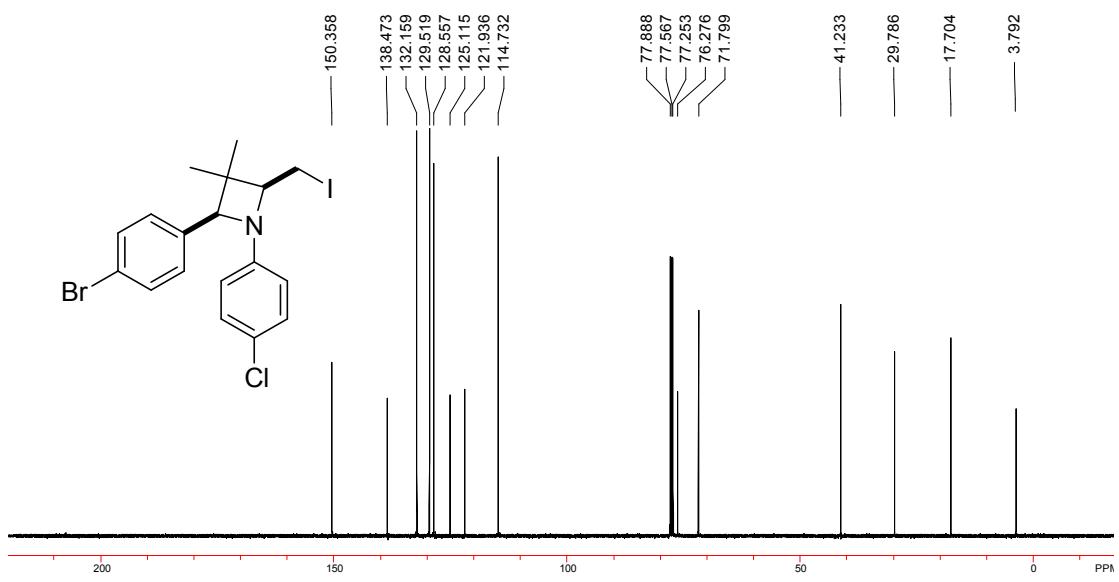
$^{13}\text{C}$  NMR Spectrum (100 MHz,  $\text{CDCl}_3$ ) of Compound **2e**



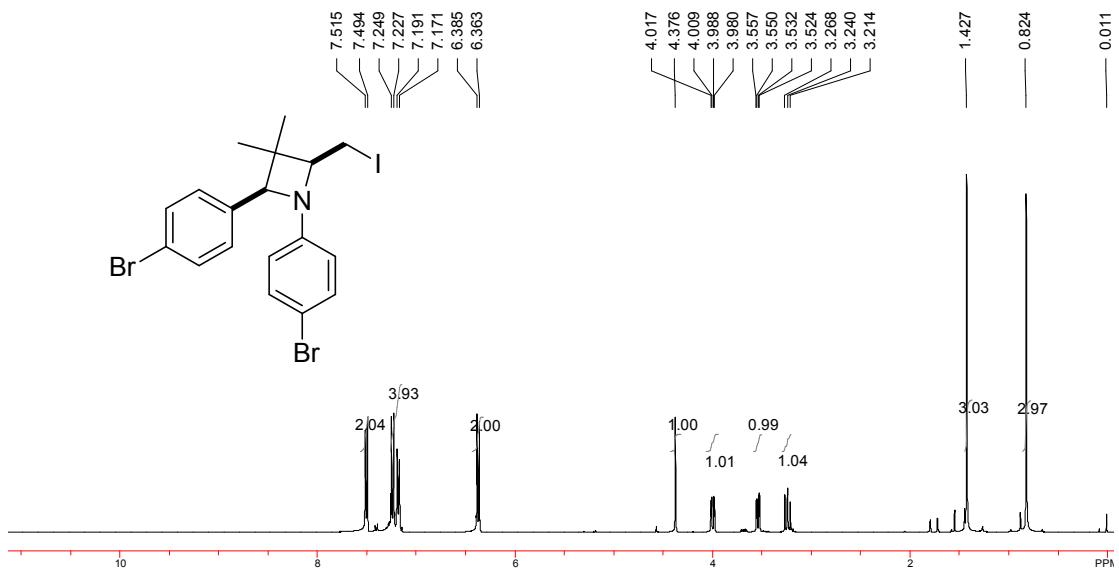
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2f



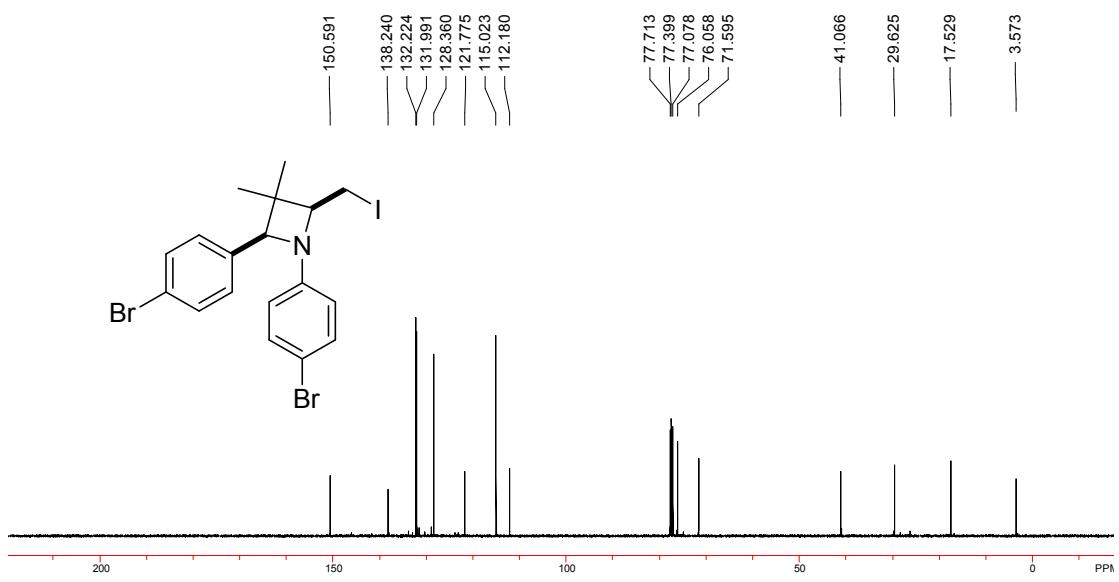
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound **2g**



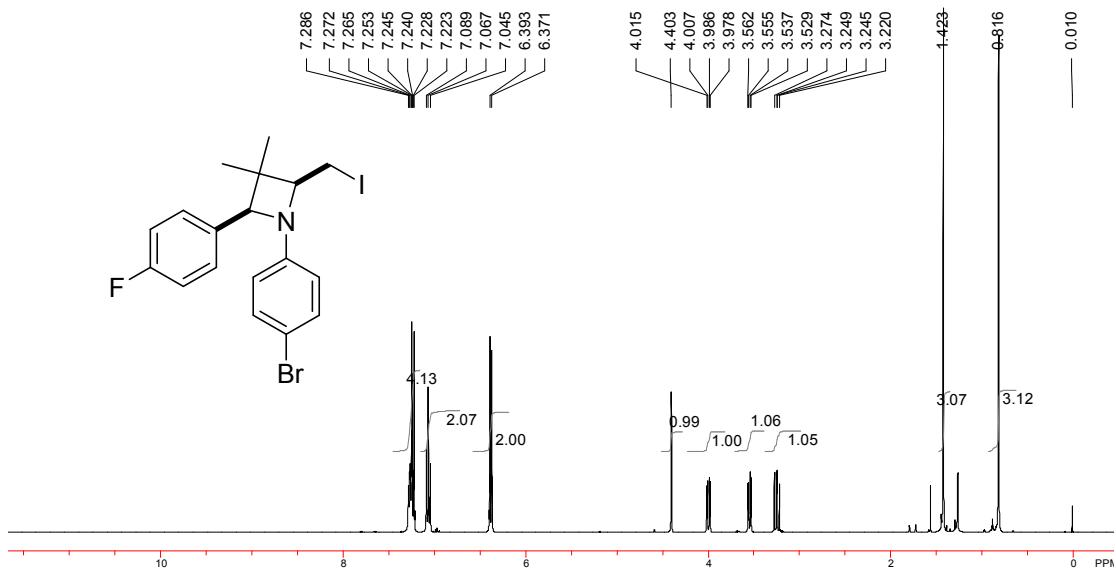
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound **2g**



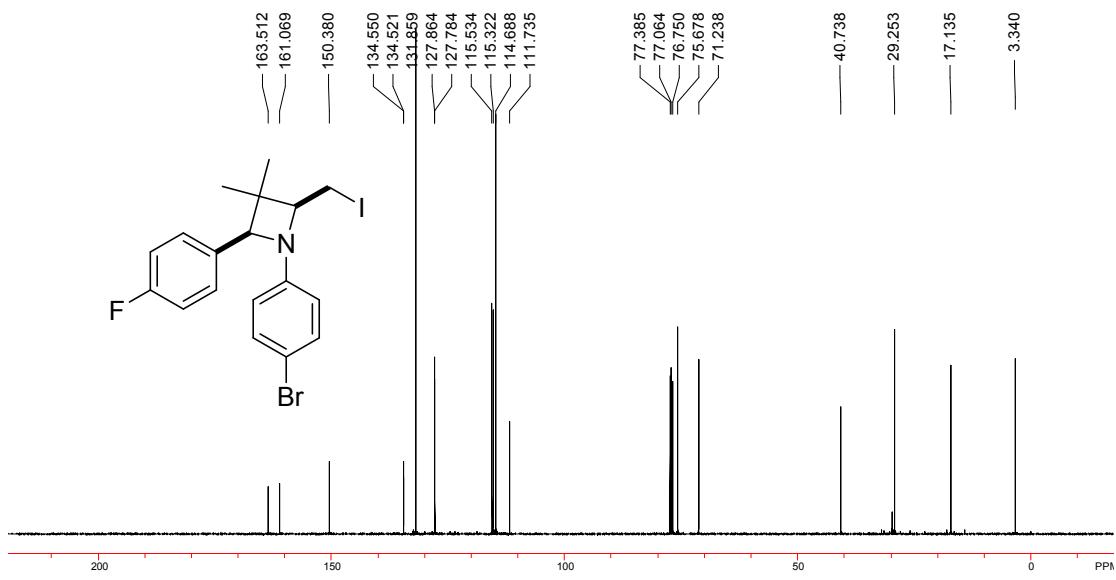
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2h



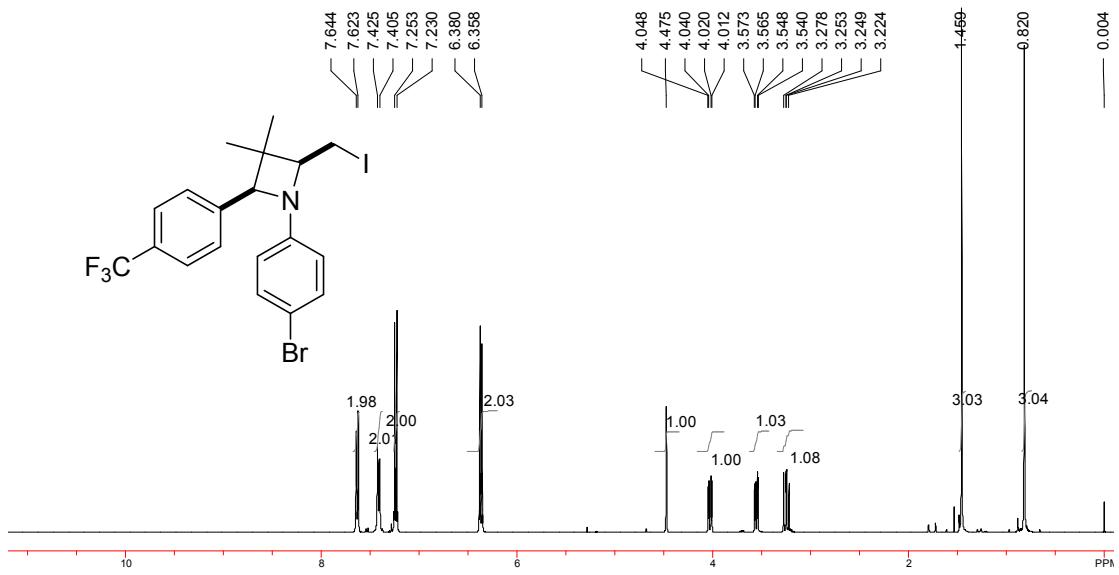
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2h



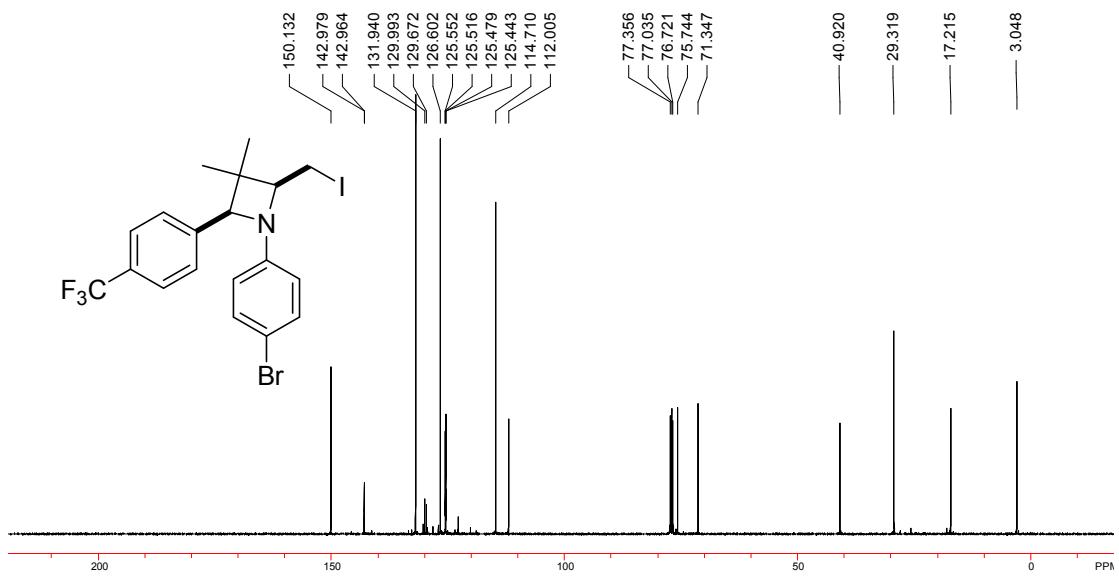
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2i



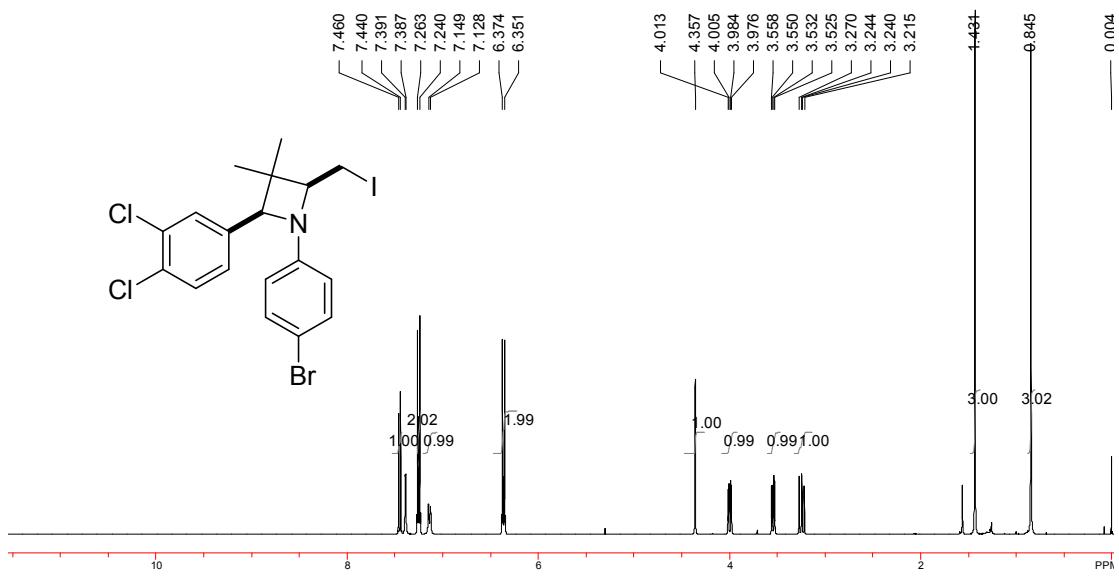
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2i



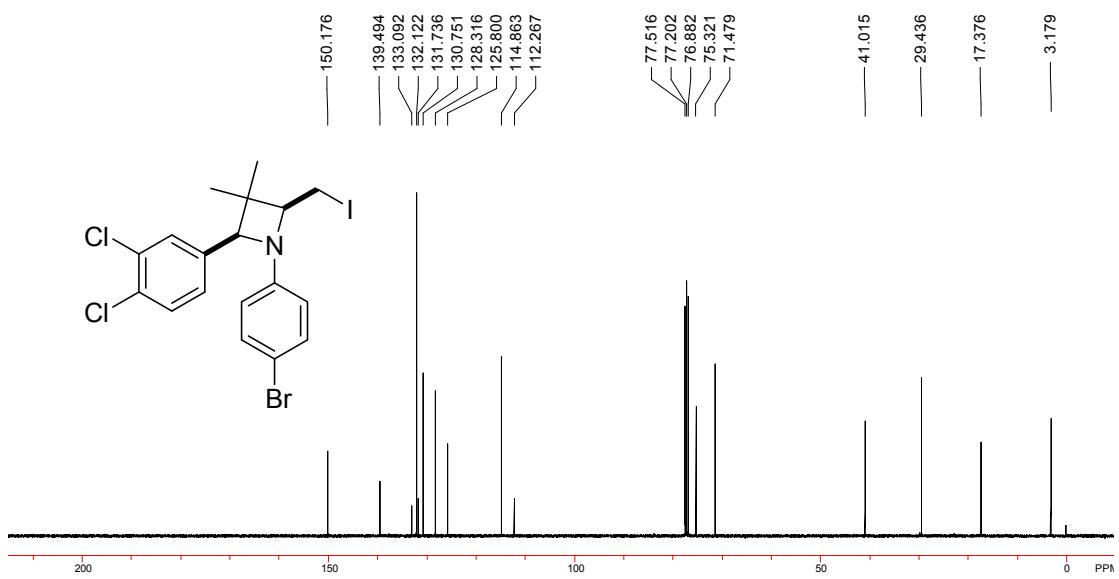
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2j



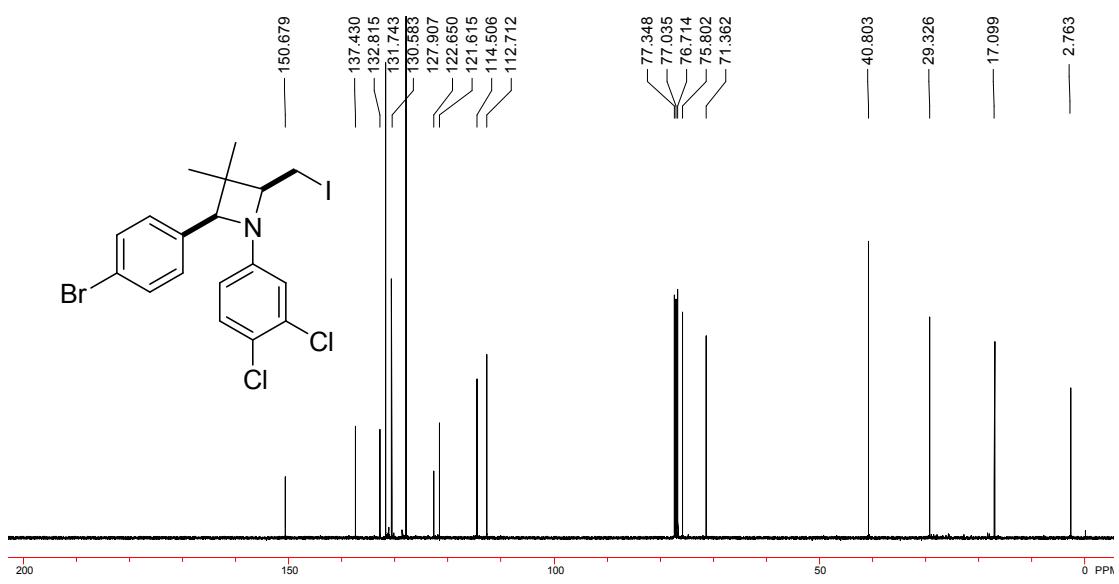
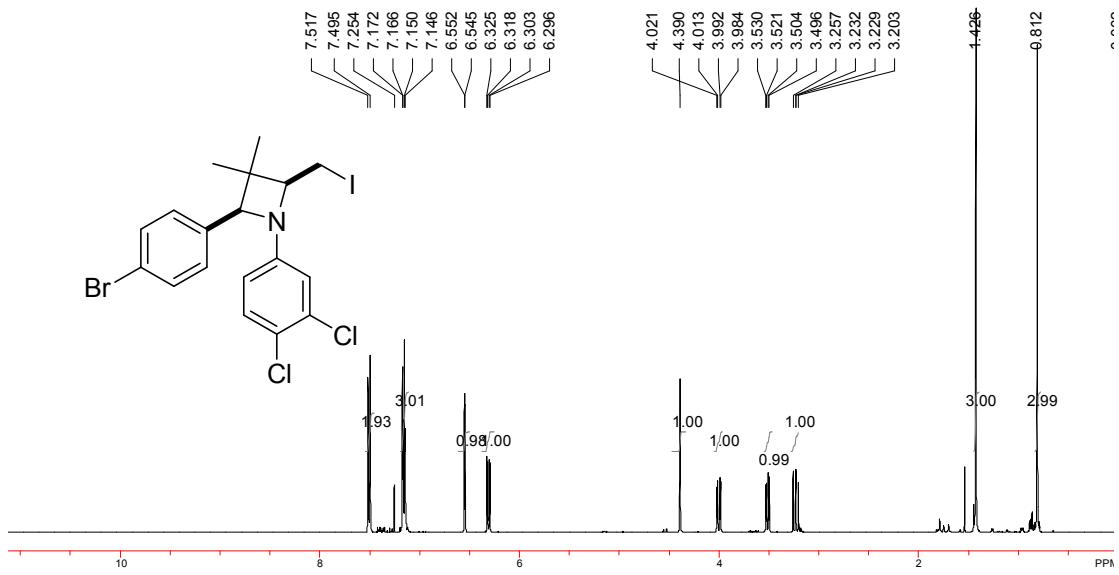
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2j

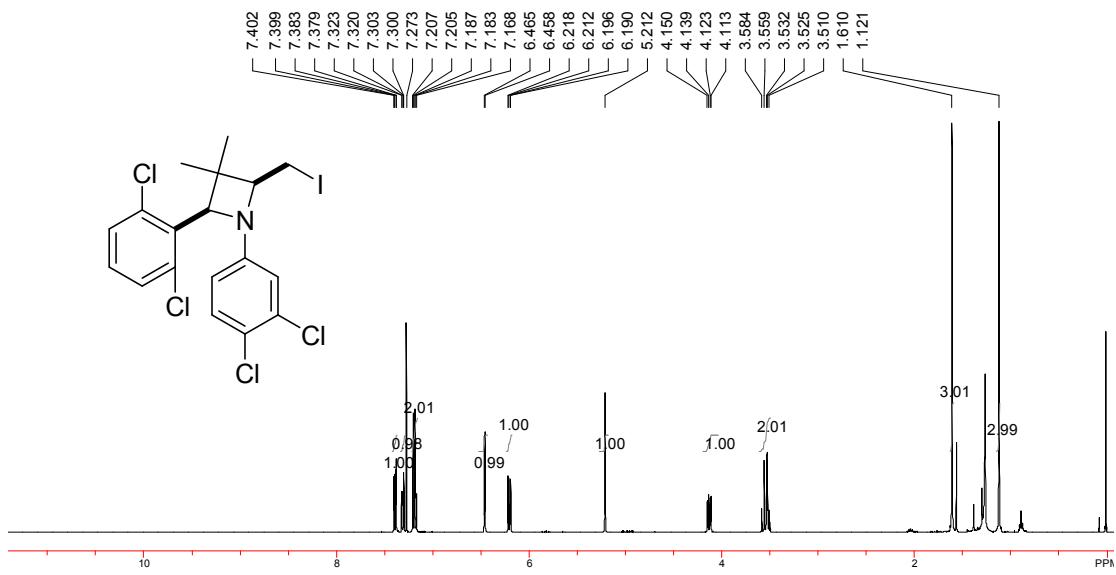


$^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ ) of Compound **2k**

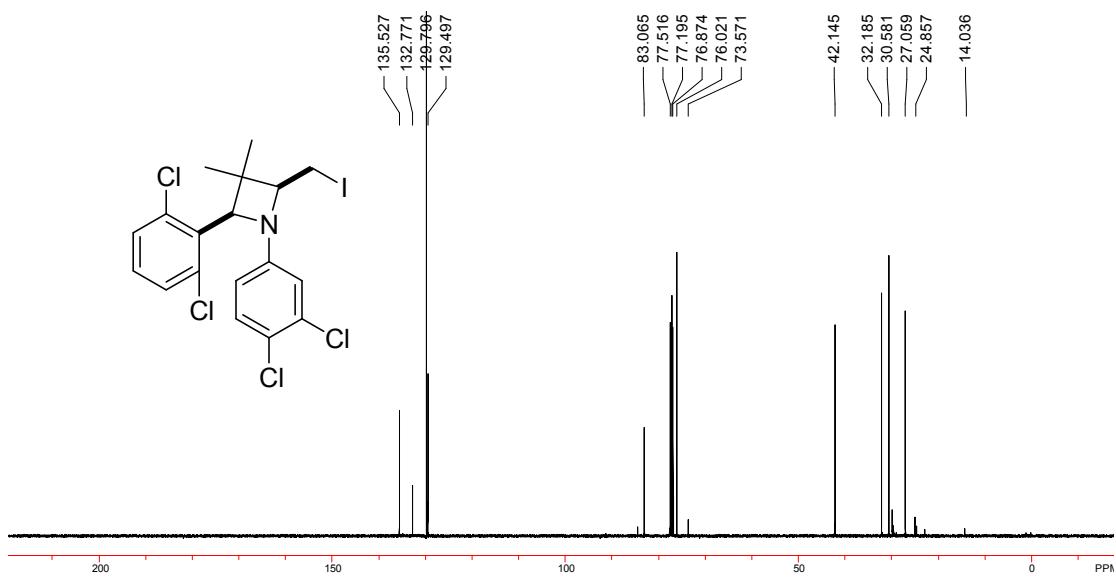


$^{13}\text{C}$  NMR Spectrum (100 MHz,  $\text{CDCl}_3$ ) of Compound **2k**

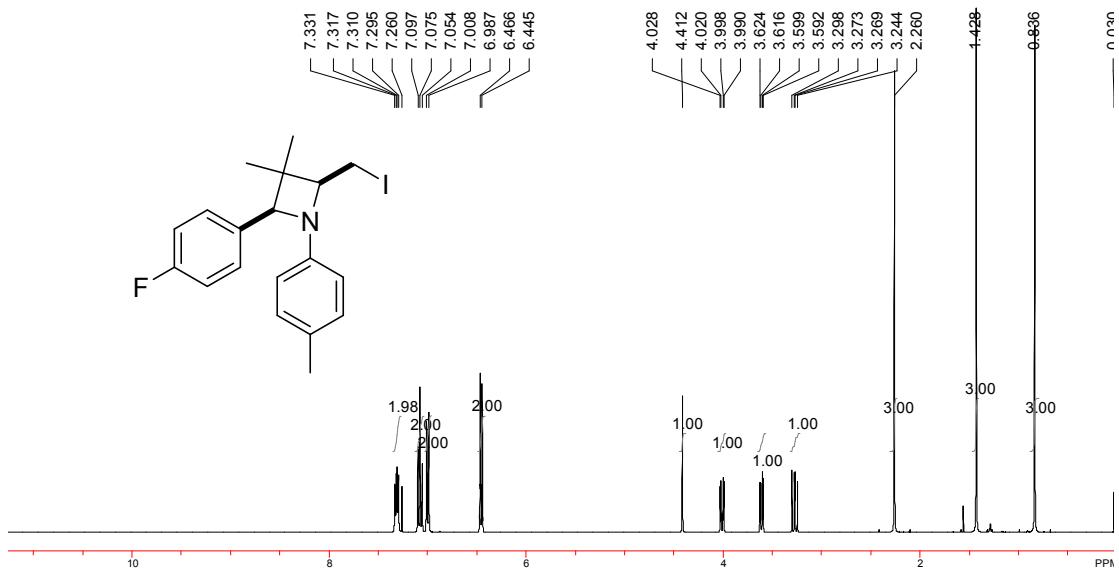




<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2m



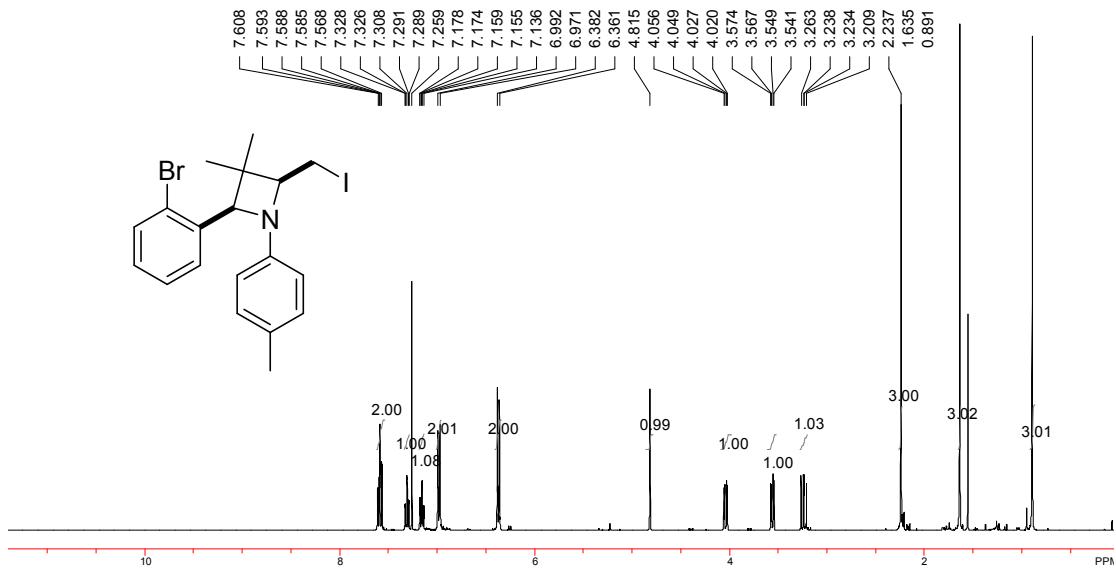
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2m



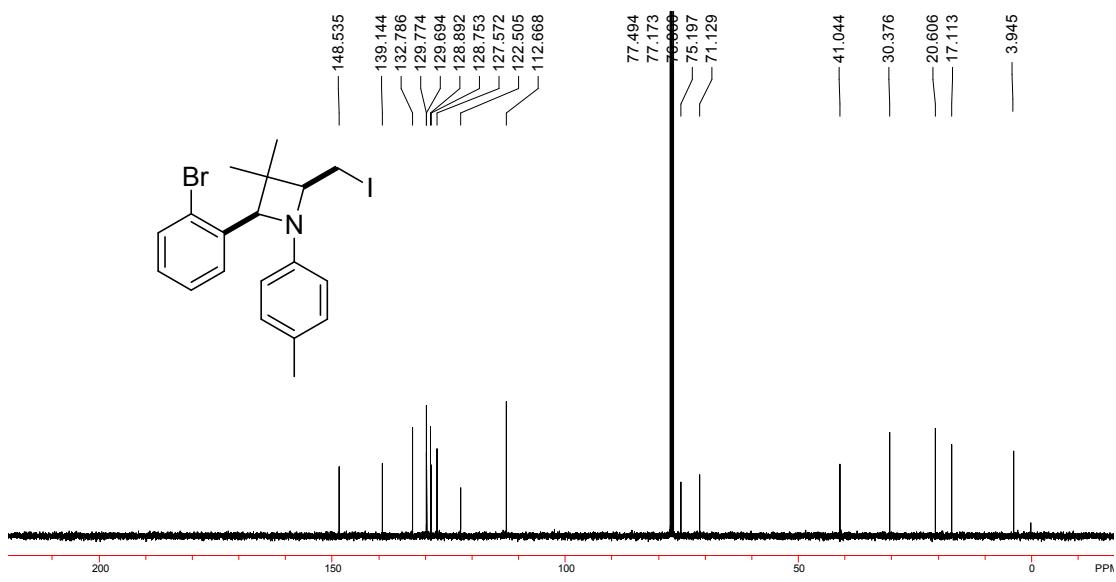
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound **2n**



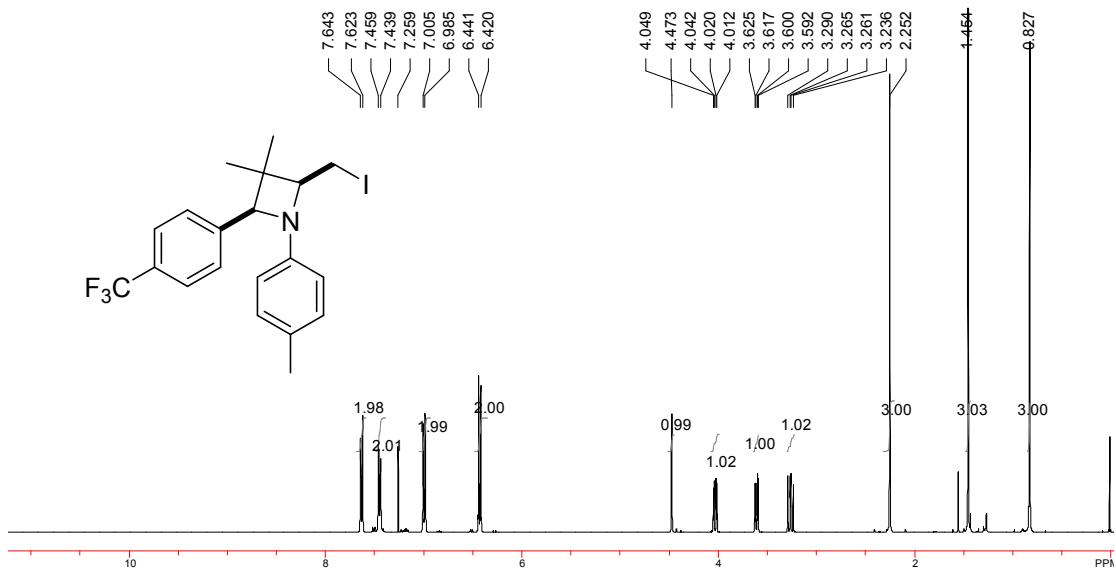
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound **2n**



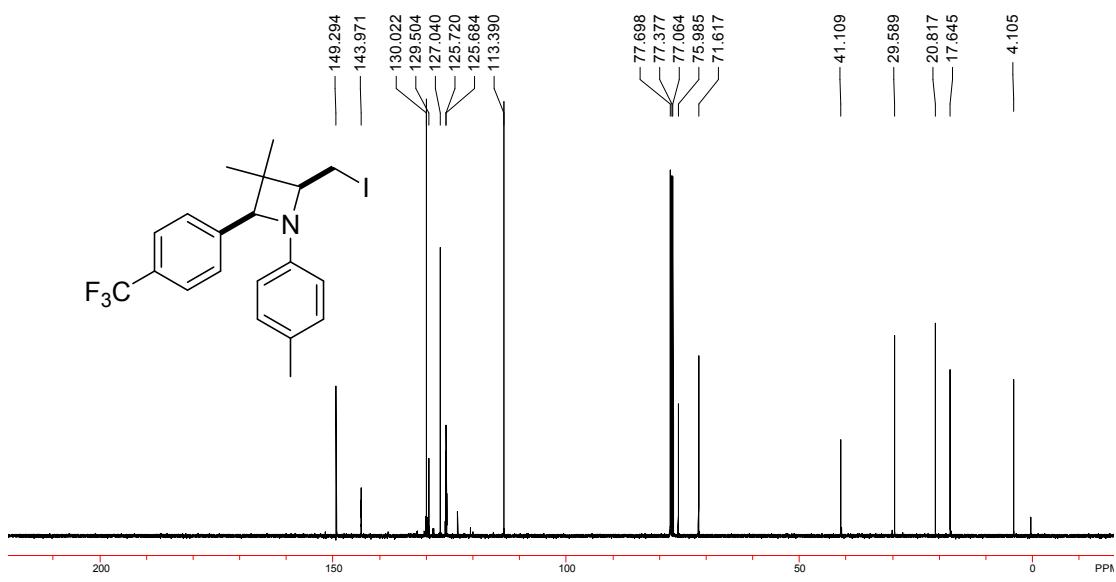
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2o



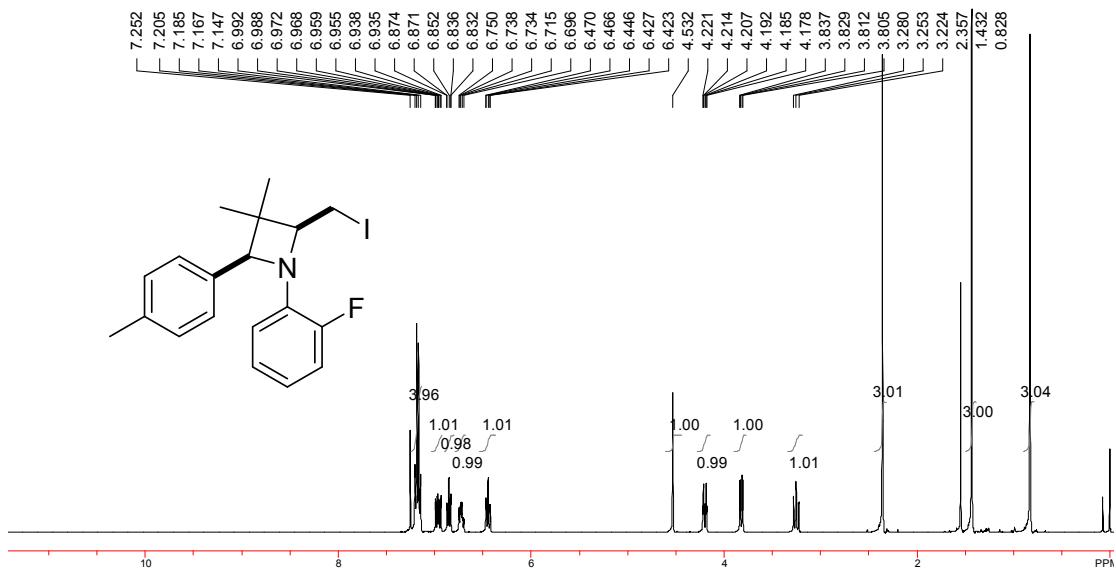
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2o



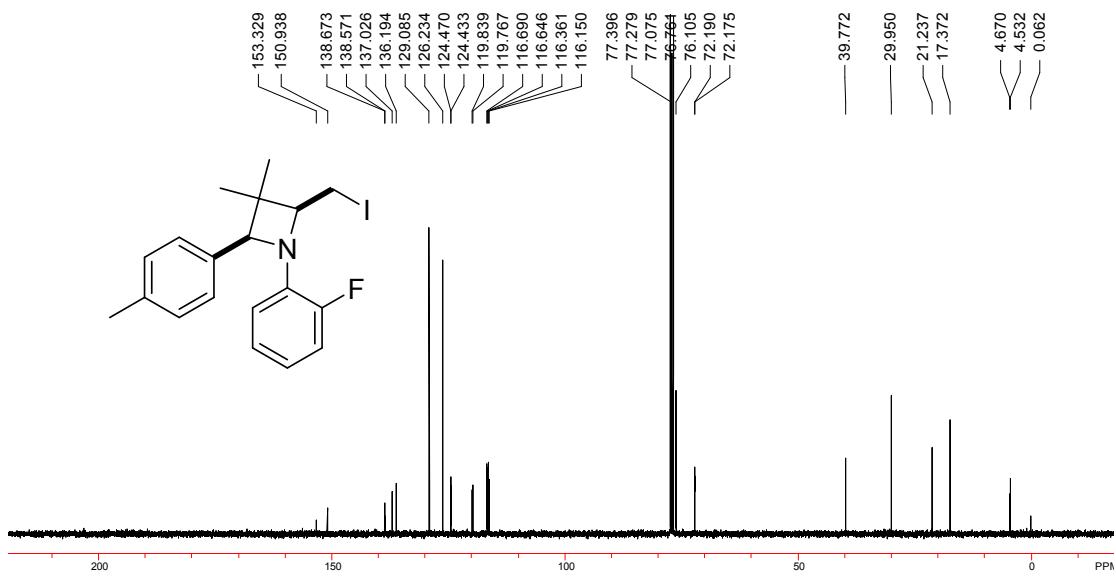
$^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ ) of Compound **2p**



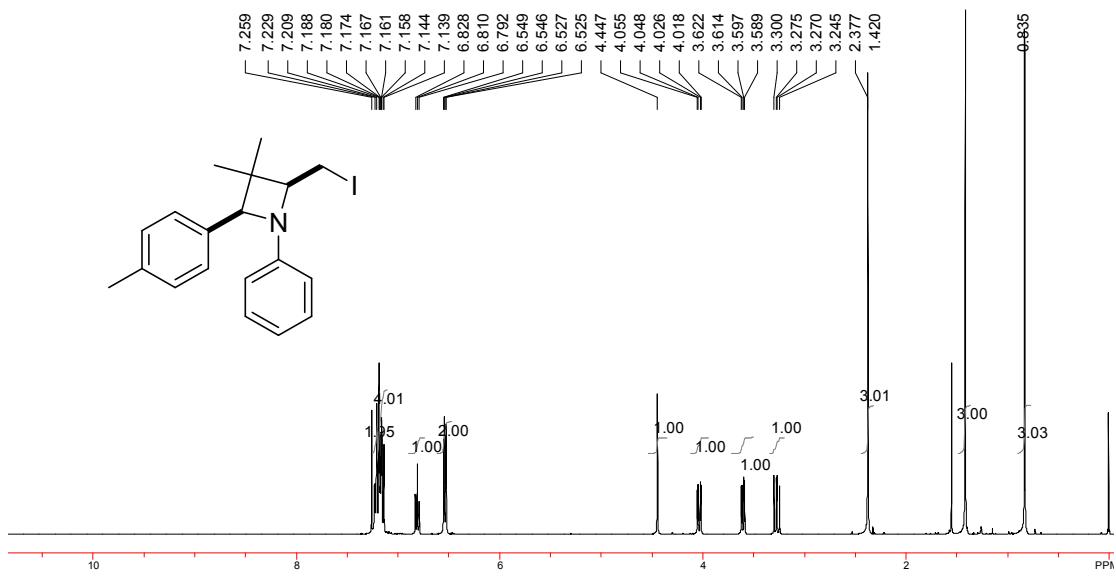
$^{13}\text{C}$  NMR Spectrum (100 MHz,  $\text{CDCl}_3$ ) of Compound **2p**



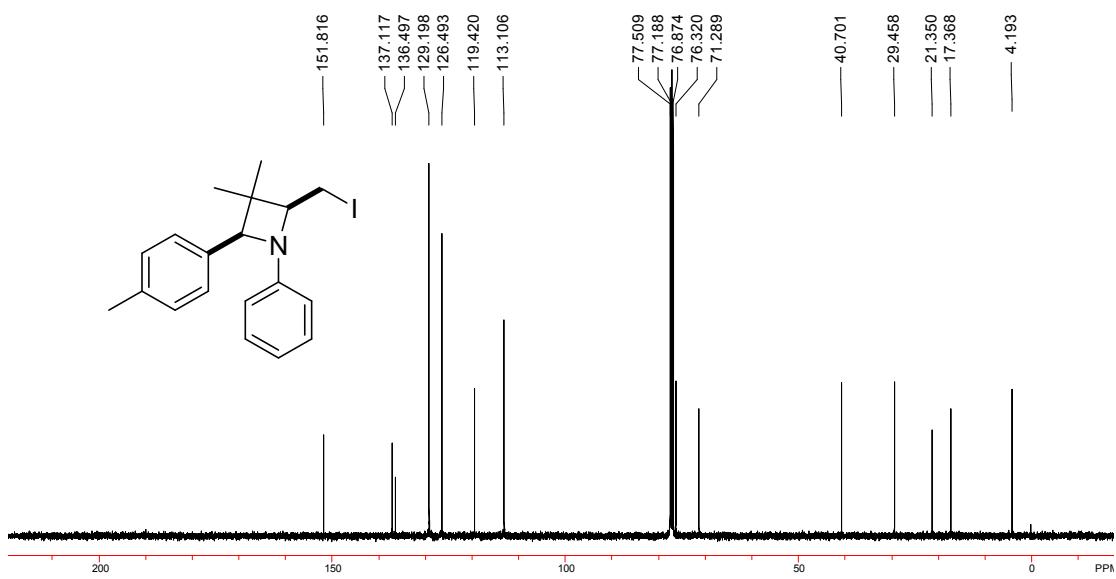
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2q



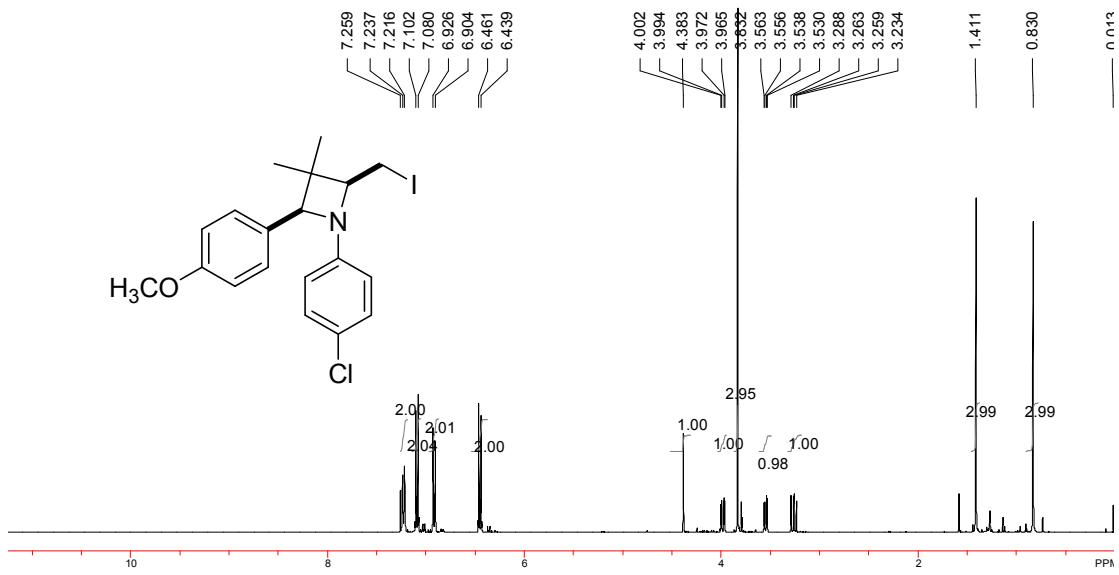
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2q



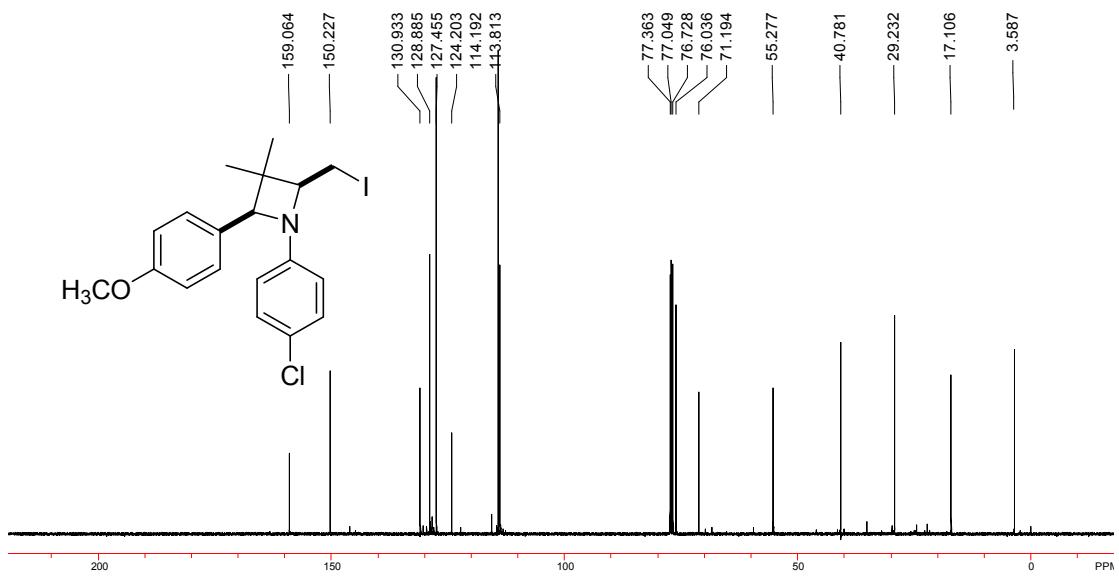
<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound **2r**



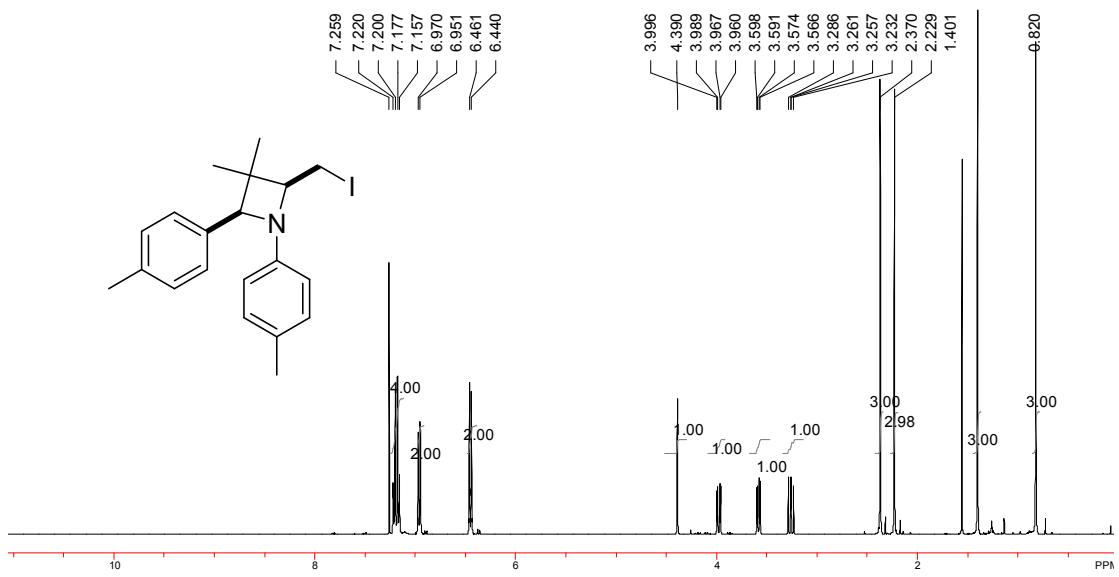
<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound **2r**



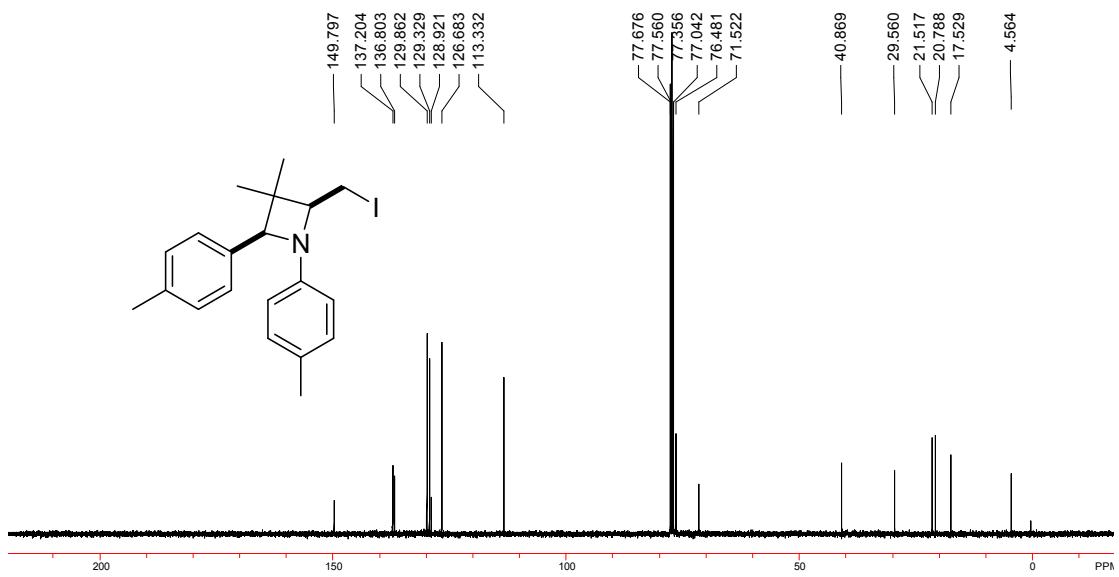
$^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ ) of Compound **2s**



$^{13}\text{C}$  NMR Spectrum (100 MHz,  $\text{CDCl}_3$ ) of Compound **2s**



<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of Compound 2t



<sup>13</sup>C NMR Spectrum (100 MHz, CDCl<sub>3</sub>) of Compound 2t

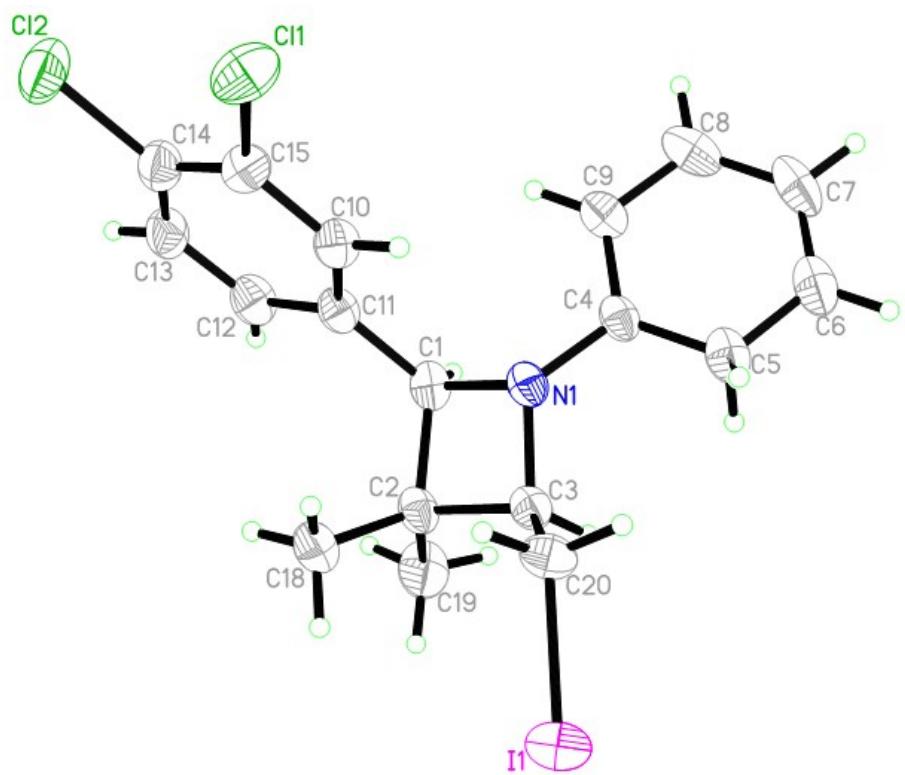


Figure S1. X-ray Crystal Structure of **2a**