

Supporting Information for:

Stereocontrolled and time-honored access to piperidine- and pyrrolidine-fused 3-  
methylenetetrahydropyrans using lactam-tethered alkenols

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## 2. Experimental Section

All experiments involving air and moisture-sensitive reagents were carried out under an inert atmosphere of nitrogen and using freshly distilled solvents. Freshly purchased toluene and DMF were stored under 4 Å molecular sieves for several days prior to use. THF and 2-MeTHF were distilled from sodium benzophenone ketyl. Other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. All amines, enals, Grignard reagents, *N*-bromosuccinimide, and potassium carbonate were newly purchased and used without further purification. Column chromatography was performed on silica gel (230-400 mesh). Thin-layer chromatography (TLC) was performed using Silicycle Siliplate™ glass backed plates (250 µm thickness, 60 Å porosity, F-254 indicator) and visualized using UV (254 nm). Unless otherwise indicated, <sup>1</sup>H NMR spectral data were acquired using CDCl<sub>3</sub> as solvent, at room temperature. Chemical shifts are quoted in parts per million (ppm) referenced to 0.00 ppm for TMS. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). <sup>13</sup>C NMR spectra were recorded on Bruker DRX-400 was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of CDCl<sub>3</sub>. HRMS-EI<sup>+</sup> data were obtained using either electron spray ionization (ESI) or electron impact (EI) techniques. High-resolution ESI was obtained on an LTQ-FT (ion trap; analyzed using Excalibur). High resolution EI was obtained on an Autospec (magnetic sector; analyzed using MassLynx). The alkenols were prepared using reported procedures.<sup>1,2</sup>

**General Procedure A: Bromoetherification of lactam-tethered alkenol 1 and concomitant elimination for the synthesis of lactam-fused 3-MeTHP:** An oven-dried vial was equipped with a stir bar and a solution of **1** (1.00 mmol) in dry 1,4-dioxane (5.0 mL), was added to the vial followed by TBAB (1.1 mmol, 1.1 equiv) and a solution of PPO (1.1 mmol, 1.1 equiv) in dry 1,4-dioxane (5.0 mL) at room temperature under an air atmosphere. After stirring for 30 minutes at room temperature, the vial was transferred to an oil bath thermostatted at 100 °C and the contents were heated for the indicated duration (18 to 36 h). Upon completion, the reaction mixture was diluted by the addition of EtOAc (20 mL) and quenched by the addition of saturated sodium bicarbonate solution (10 mL). The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine (20 mL), dried over anhydrous

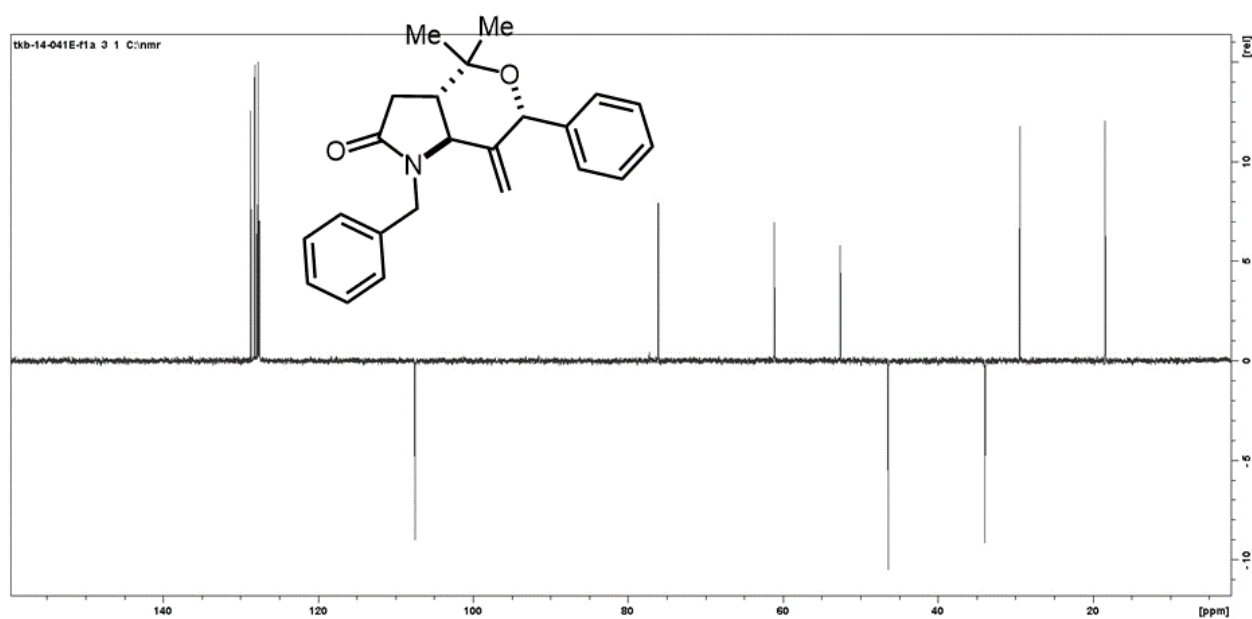
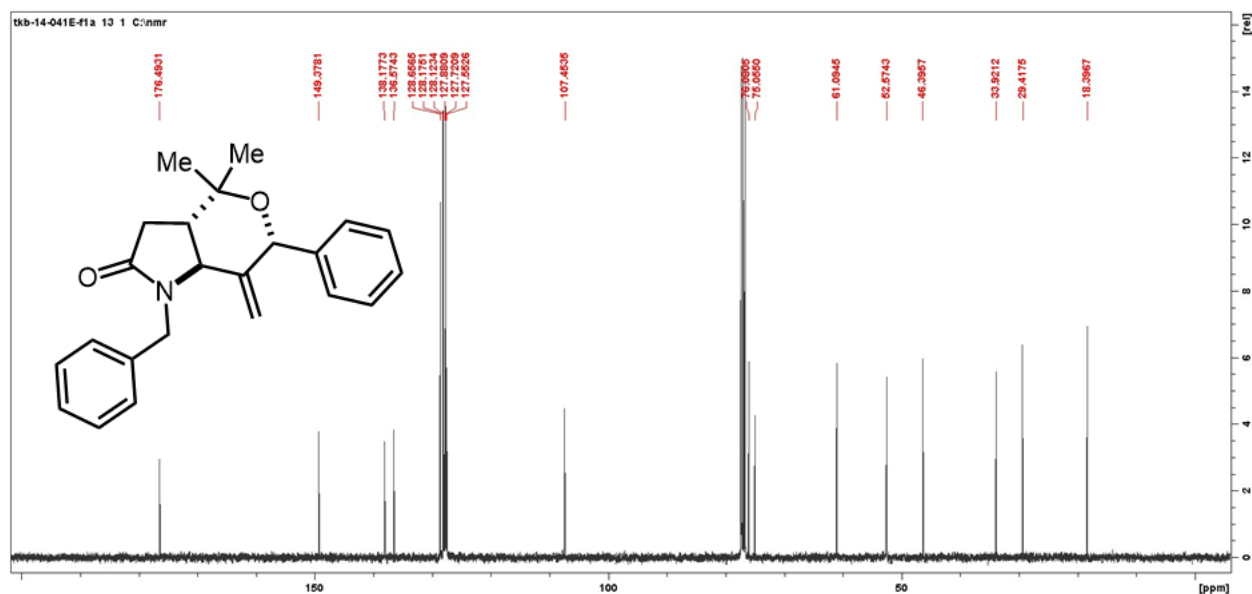
sodium sulfate, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the lactam-fused 3-methylenetetrahydropyran.

**General Procedure B: Dehydrogenative alkoxylation of lactam-tethered alkenol 1 and concomitant isomerization for the synthesis of lactam-fused 3-MeTHP:** To an oven dried vial equipped with a stir bar was added the lactam-tethered alkenol **1** (1.0 mmol) in 2-MeTHF (5 mL) at room temperature and atmospheric pressure. Pd(OAc)<sub>2</sub> (5 mol%) and Cu(OAc)<sub>2</sub> (2 mmol, 2 equiv) were then added to the vial. The vial was sealed with a Teflon-lined cap and the contents were stirred at room temperature for 12 h. K<sub>2</sub>CO<sub>3</sub> (1.2 equiv) was then added to the vial and it was placed in an oil bath thermostatted at 100 °C. The contents were stirred for the indicated length of time (usually 2 h). After complete consumption of the starting material (TLC and GC-MS monitoring), the mixture was cooled to room temperature. It was then diluted with EtOAc:H<sub>2</sub>O (50:10) and the contents were transferred to a separatory funnel. A few drops of 1M HCl(aq) were added to the mixture and the layers were separated. The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was subjected to flash column chromatography on silica gel.

**General Procedure C: LAH reduction:** To a 10 mL round-bottomed flask equipped with a magnetic stir bar under a N<sub>2</sub> atmosphere, in a 0 °C ice/water bath, was added the lactam-fused 3-MeTHP (1.0 mmol) and THF (50 mL). LiAlH<sub>4</sub> (220 mg, 5.6 mmol) was then added portion-wise. The reaction mixture was allowed to warm to room temperature overnight (judged complete by GC-MS analysis). After this time, the reaction mixture was cooled to 0 °C and quenched by slow addition of a solution of 2 N NaOH(aq) (1 mL). The organic layer was decanted into a clean beaker and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated *in vacuo* to yield the crude tertiary amine as an oil, which was purified by flash column chromatography on silica gel.

**General Procedure D: Catalytic hydrogenation:** To a 25 mL-round-bottomed flask equipped with a magnetic stir bar was added EtOAc (10 mL) and 10% Pd/C (200 mg) at room temperature. A solution of the lactam-fused 3-MeTHP (0.50 mmol) in EtOAc (10 mL) was added. The flask was degassed and placed under an inert atmosphere of nitrogen. After complete addition of the lactam, the nitrogen line was cut off. A balloon of H<sub>2</sub> was attached and the reaction mixture was stirred at room temperature. After complete consumption (based on GC-MS and TLC monitoring), the

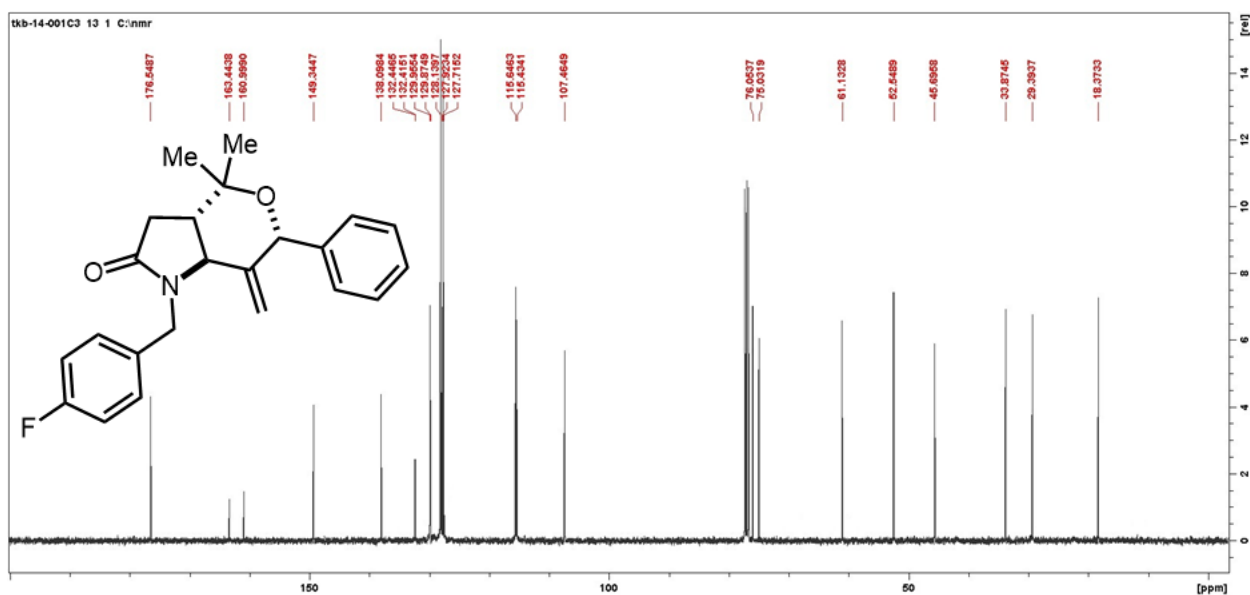
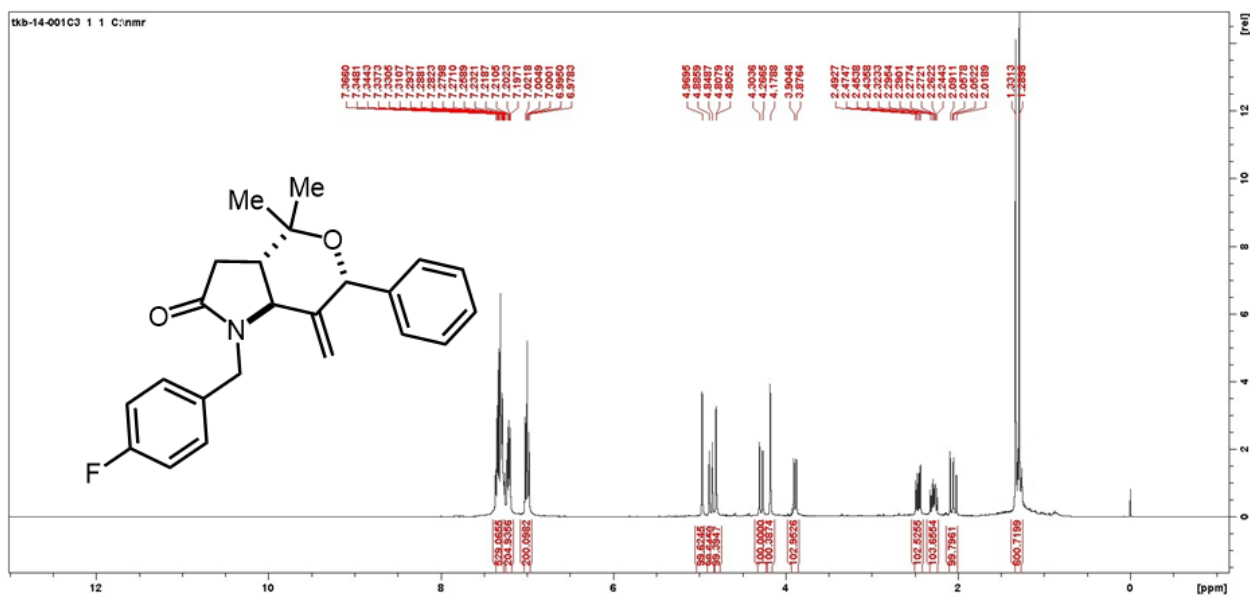




### Compound 4b

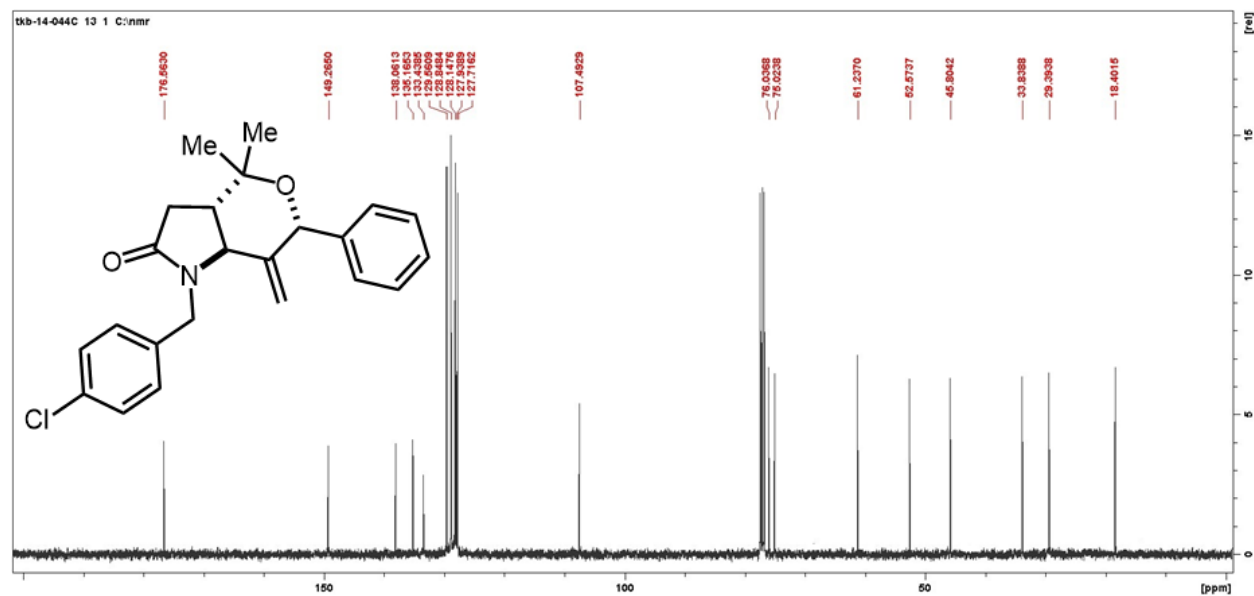
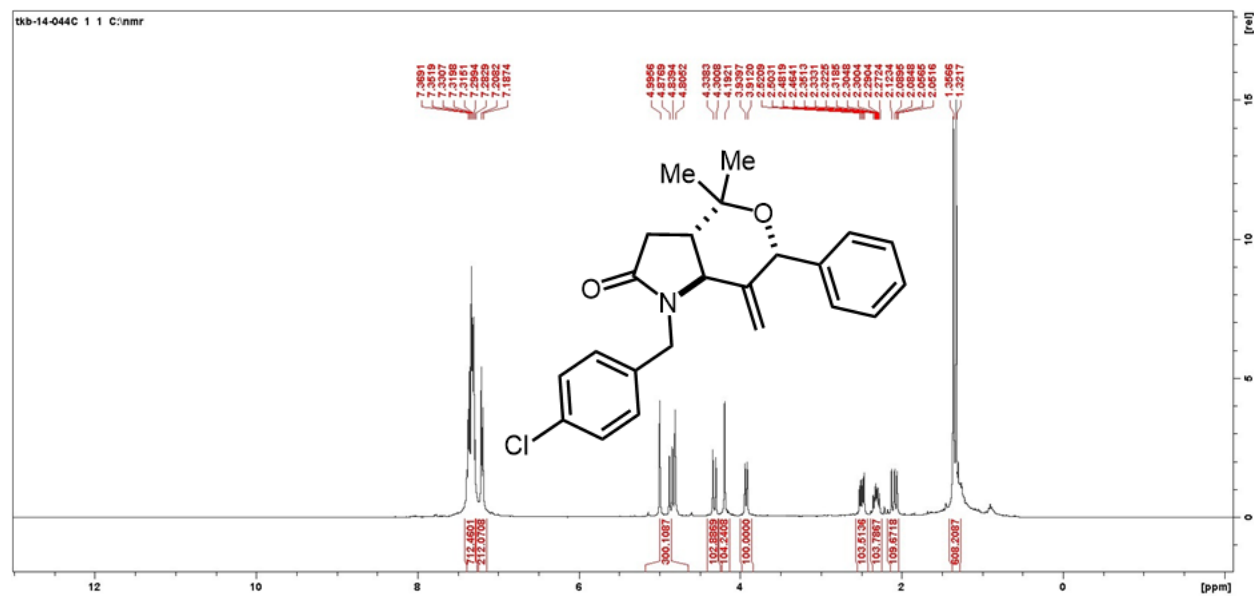
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Greenish-yellow oil. Yield = 328.9 mg, 90%, 95:5 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.20 (m, 7H), 7.02 – 6.98 (m, 2H), 4.97 (s, 1H), 4.87 (d, J = 14.9 Hz, 1H), 4.81 (d, J = 1.6 Hz, 1H), 4.29 (d, J = 14.9 Hz, 1H), 4.18 (q, J = 1.9 Hz, 1H), 3.95 – 3.84 (m, 1H), 2.46 (dd, J = 15.6, 7.2 Hz, 1H), 2.28 (ddd, J = 13.4, 11.1, 7.2 Hz, 1H), 2.06 (dd, J = 15.6, 13.3 Hz, 1H), 1.35 (s, 3H), 1.29 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.5, 163.4 and 161.0 (C-F, d, <sup>1</sup>J<sub>C-F</sub> = 246.7 Hz), 149.3, 138.1, 132.5, 132.4, 130.0, 129.9, 128.1, 127.9, 127.7,

115.6, 115.4, 107.5, 76.0, 75.0, 61.1, 52.5, 45.7, 33.9, 29.4, 18.4. FTIR (KBr): 2976.0, 1721.7, 1650.1, 1492.0, 1438.4, 1362.2, 1320.5, 1290.1, 1206.3, 1180.3, 1146.7, 1132.1, 995.8, 918.8, 700.1. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>23</sub>H<sub>24</sub>FNO<sub>2</sub> [M]<sup>+</sup> 365.1791, found 365.1794.

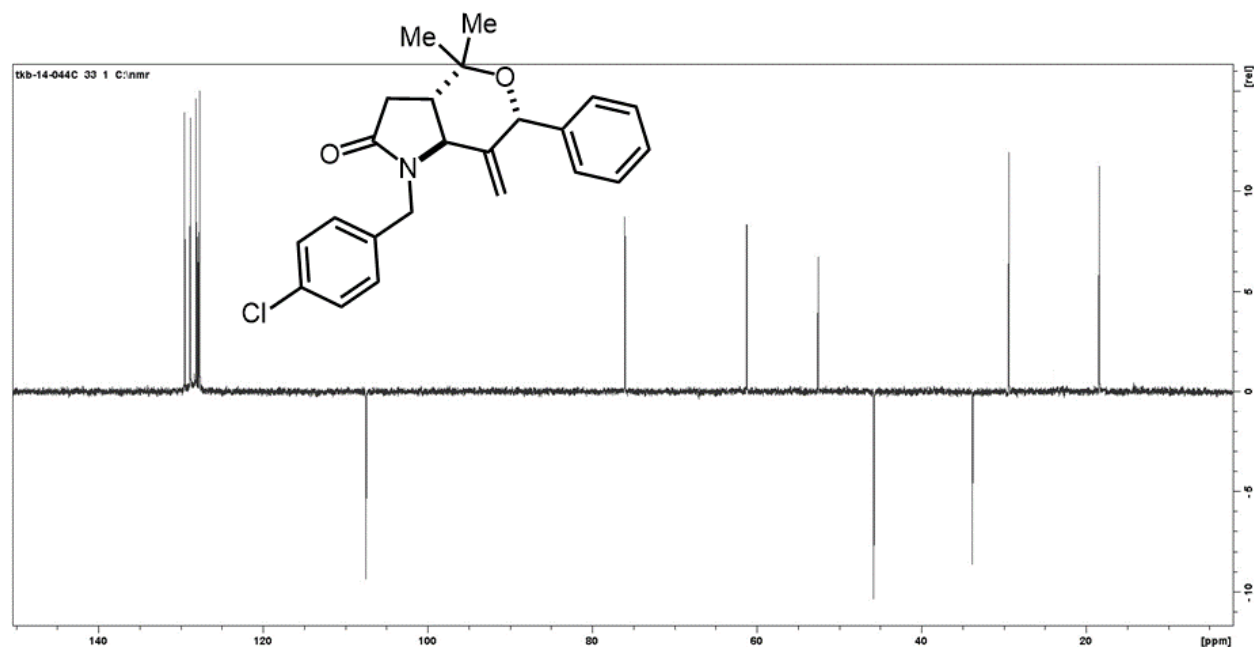




133.4, 129.6, 128.8, 128.1, 127.9, 127.7, 107.5, 76.0, 75.0, 61.2, 52.6, 45.8, 33.8, 29.4, 18.4. FTIR (KBr): 2932.4, 1721.5, 1666.3, 1606.9, 1511.0, 1448.5, 1414.7, 1384.9, 1357.4, 1298.7, 1247.5, 1179.3, 1135.9, 1031.8, 995.8, 831.0, 750.2, 694.7. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>23</sub>H<sub>24</sub>ClNO<sub>2</sub> [M]<sup>+</sup> 381.1496, found 381.1493.

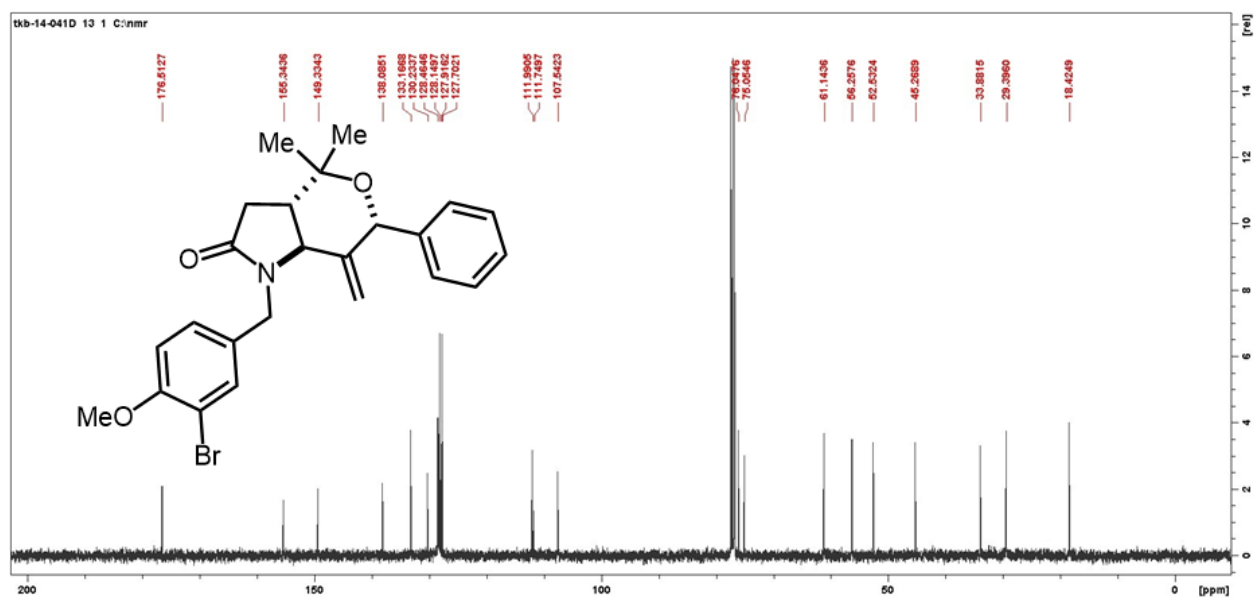
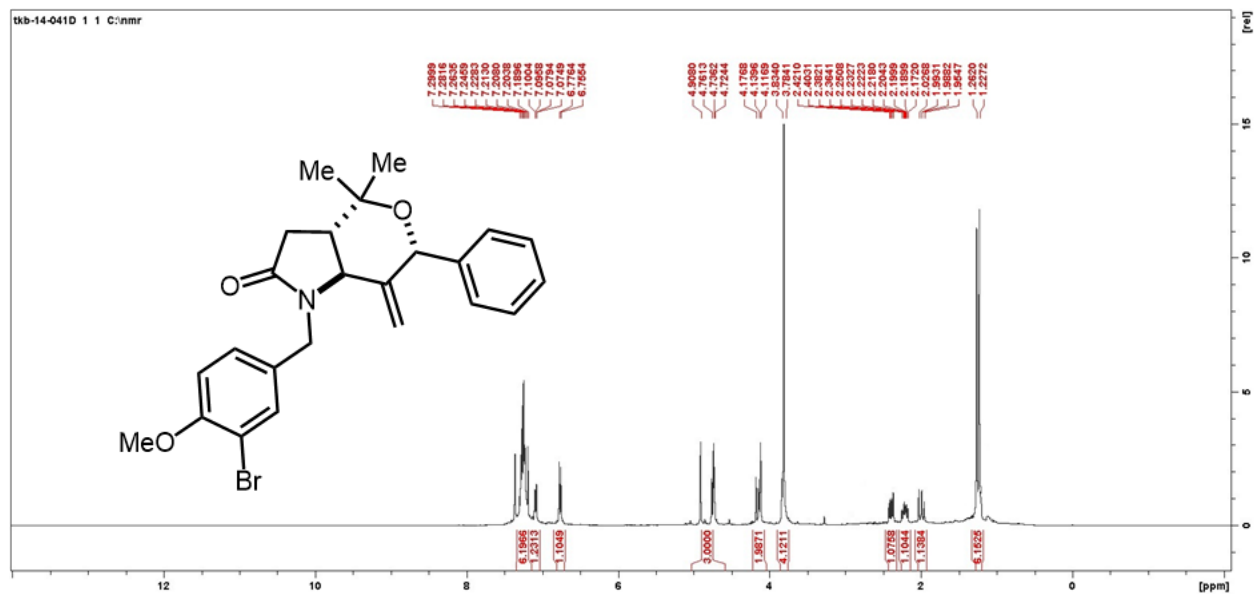


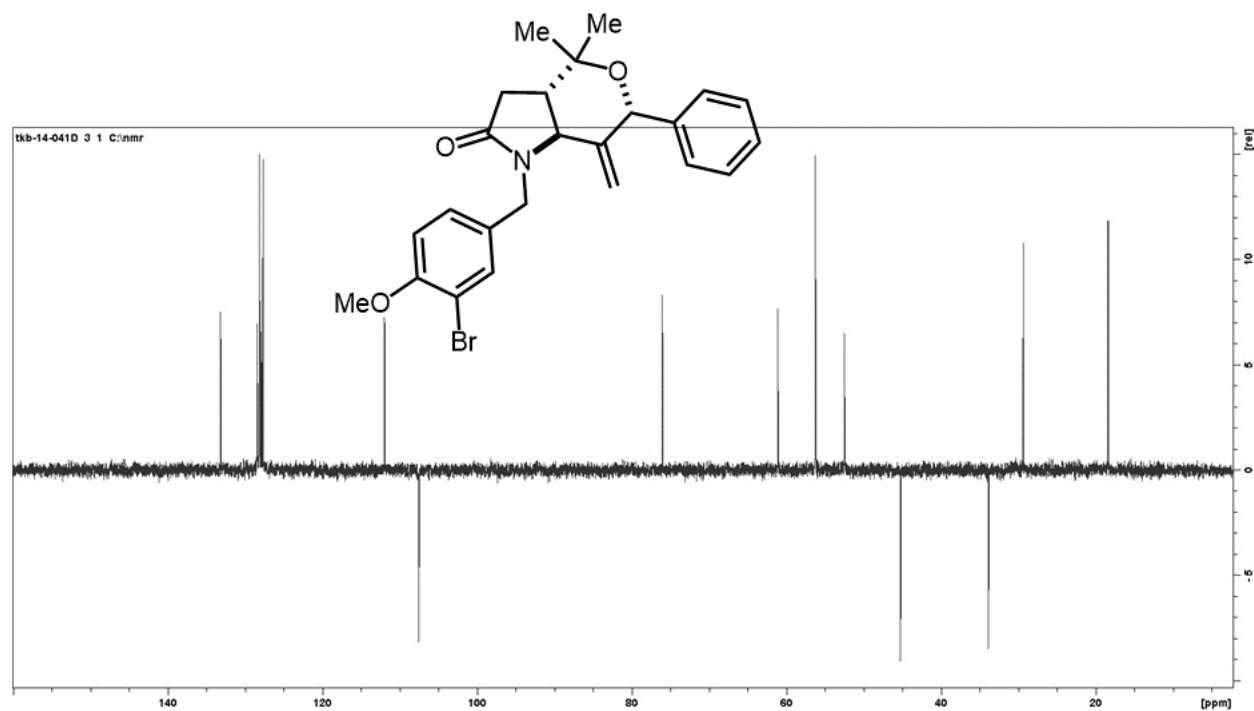




### Compound 4d

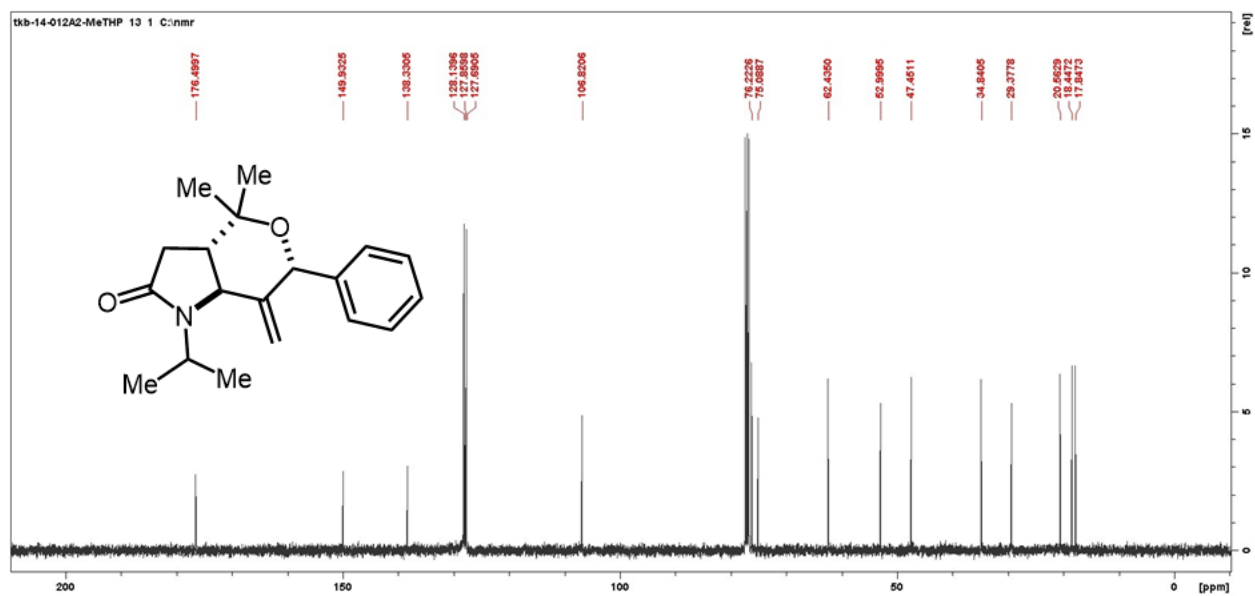
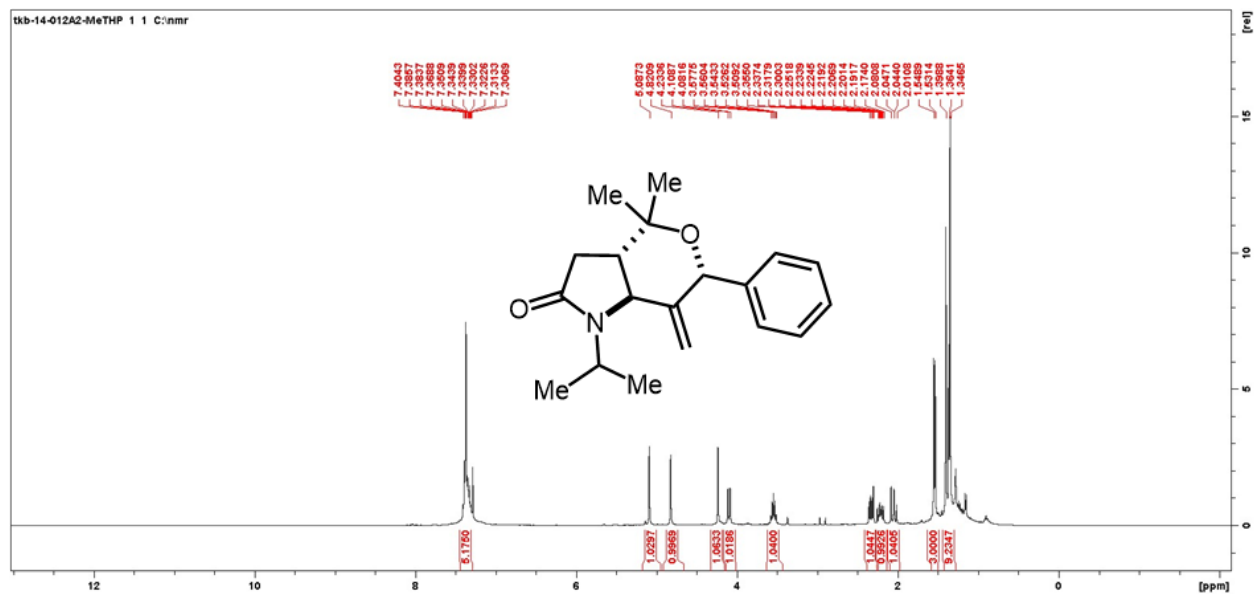
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Amorphous solid. Yield = 378.8 mg, 83%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.19 (m, 6H), 7.09 (dd,  $J = 8.4, 2.2$  Hz, 1H), 6.77 (d,  $J = 8.4$  Hz, 1H), 4.91 (s, 1H), 4.78 – 4.68 (m, 2H), 4.20 – 4.09 (m, 2H), 3.83 (s, 1H), 3.81 (s, 3H), 2.39 (dd,  $J = 15.6, 7.2$  Hz, 1H), 2.21 (ddd,  $J = 13.3, 11.1, 7.2$  Hz, 1H), 1.99 (dd,  $J = 15.6, 13.3$  Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 155.4, 149.3, 138.1, 133.2, 130.2, 128.5, 128.4, 128.1, 127.9, 127.7, 112.0, 111.7, 107.5, 76.0, 75.1, 61.1, 56.3, 52.5, 45.3, 33.9, 29.4, 18.4. FTIR (KBr): 2930.9, 1721.7, 1664.2, 1606.9, 1576.9, 1511.8, 1422.4, 1359.3, 1300.0, 1250.9, 1175.8, 1113.2, 1031.2, 996.3, 970.3, 923.7, 826.6, 764.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{24}\text{H}_{26}\text{BrNO}_3$   $[\text{M}]^+$  455.1096, found 455.1092.

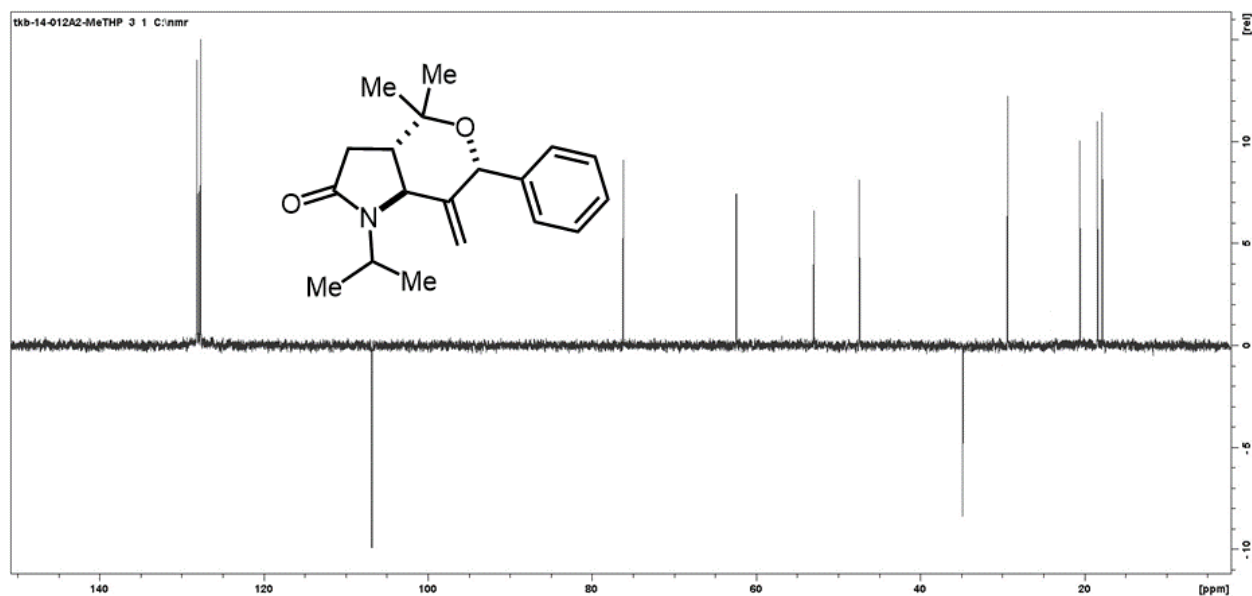




### Compound 4e

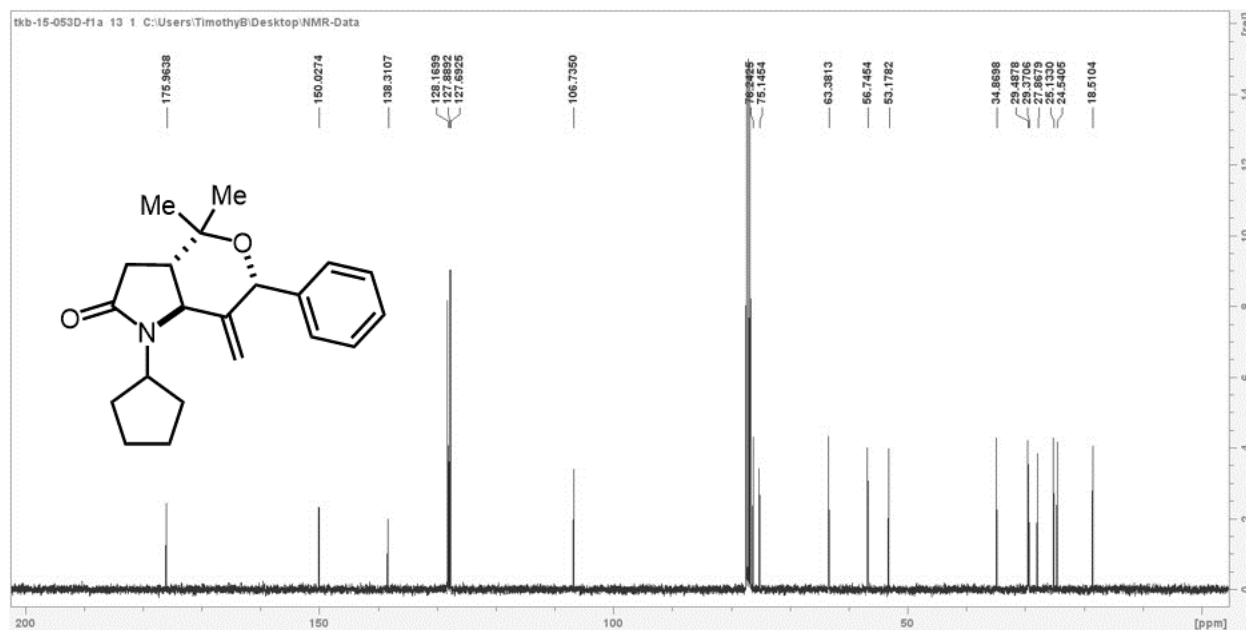
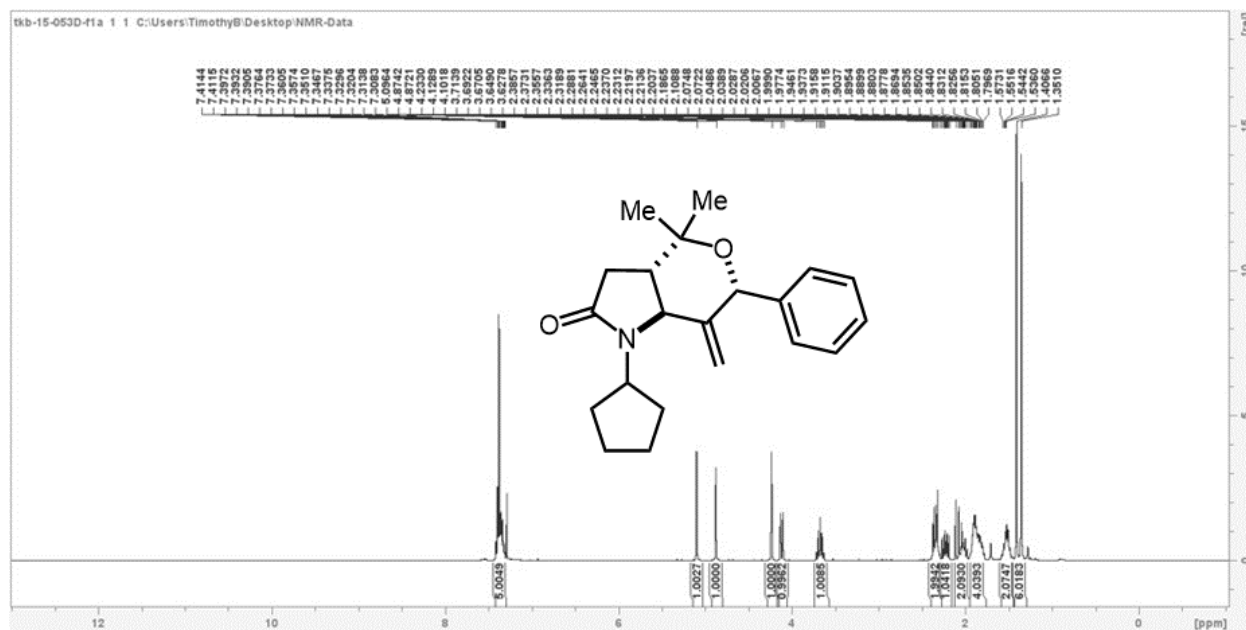
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Pale yellowish oil. Yield = 254.5 mg, 85%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.31 (m, 5H), 5.09 (s, 1H), 4.82 (d,  $J = 1.6$  Hz, 1H), 4.23 (s, 1H), 4.10 (d,  $J = 10.8$  Hz, 1H), 3.54 (hept,  $J = 6.8$  Hz, 1H), 2.33 (dd,  $J = 14.8, 7.0$  Hz, 1H), 2.21 (ddd,  $J = 13.3, 10.9, 7.1$  Hz, 1H), 2.05 (dd,  $J = 14.8, 13.2$  Hz, 1H), 1.55 (d,  $J = 8.6$  Hz 3H), 1.40 – 1.35 (m, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 149.9, 138.3, 128.1, 127.8, 127.7, 106.8, 76.2, 75.1, 62.4, 53.0, 47.4, 34.8, 29.4, 20.6, 18.4, 17.8. FTIR (KBr): 2934.6, 1721.8, 1669.4, 1608.2, 1511.1, 1431.8, 1414.7, 1344.9, 1298.4, 1245.6, 1179.4, 1135.3, 1031.8, 996.7, 921.8, 832.1, 701.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{19}\text{H}_{25}\text{NO}_2$   $[\text{M}]^+$  299.1885, found 299.1892.

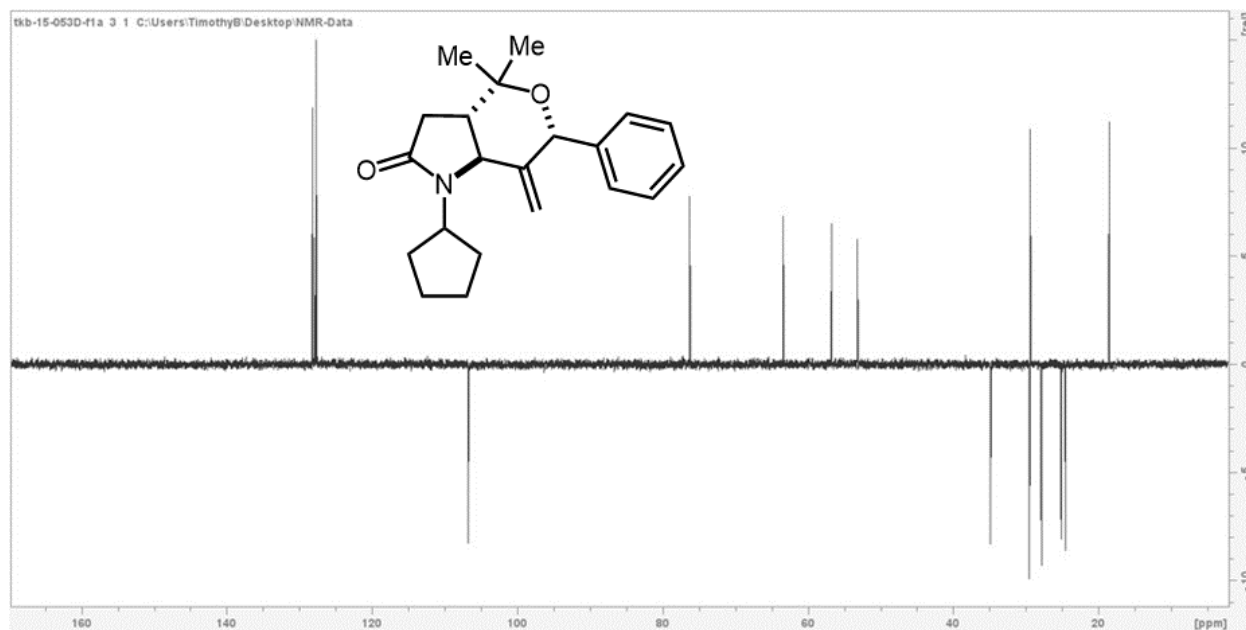




### Compound 4f

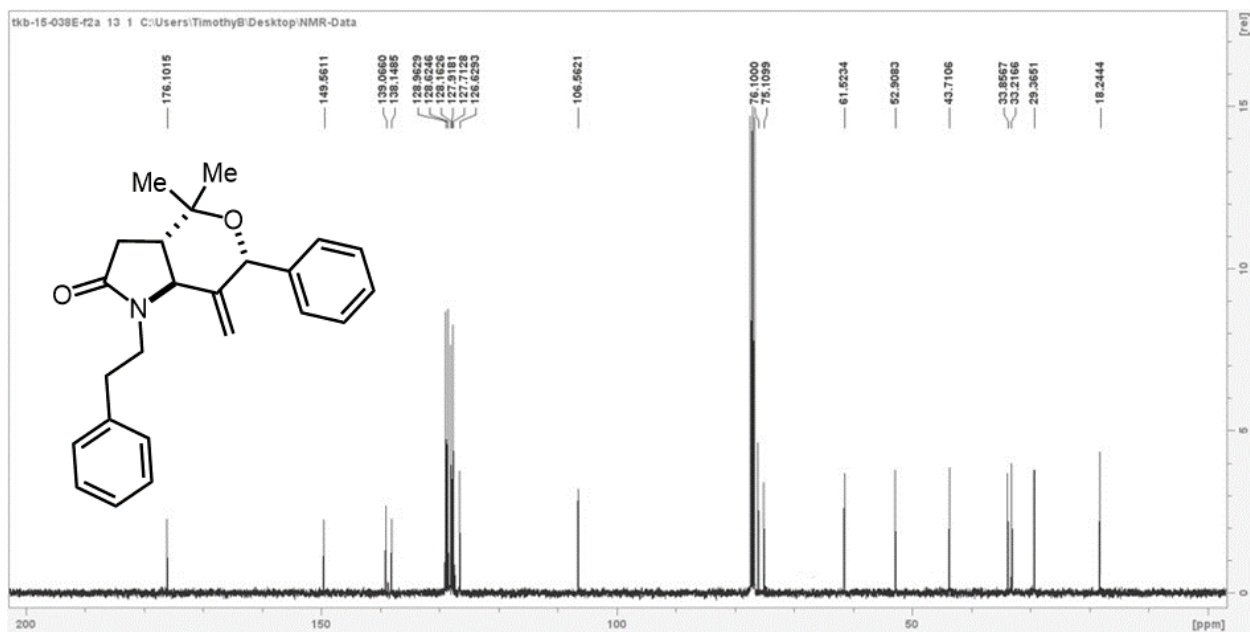
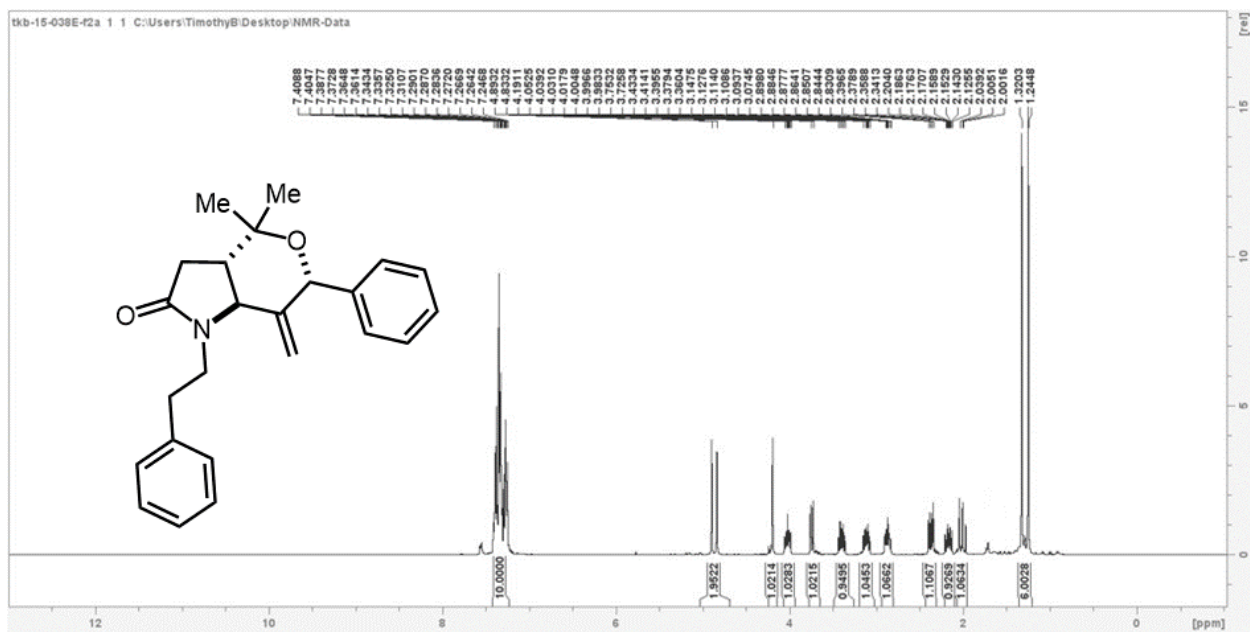
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Pale yellowish oil. Yield = 260.4 mg, 80%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.19 (m, 5H), 5.10 (s, 1H), 4.78 (s, 1H), 4.14 (s, 1H), 4.02 (d,  $J = 10.9$  Hz, 1H), 3.58 (p,  $J = 8.3$  Hz, 1H), 2.27-2.21 (m, 3H), 2.03 – 1.86 (m, 2H), 1.86 – 1.66 (m, 4H), 1.61 – 1.43 (m, 2H), 1.41 (s, 3H), 1.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 150.0, 138.3, 128.2, 127.9, 127.7, 106.7, 76.2, 75.1, 63.4, 56.7, 53.2, 34.9, 29.5, 29.4, 27.9, 25.1, 24.5, 18.5. FTIR (KBr): 2984.1, 1723.4, 1669.4, 1608.2, 1511.1, 1431.8, 1414.7, 1344.9, 1298.4, 1135.3, 1031.8, 996.7, 702.4. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{21}\text{H}_{27}\text{NO}_2$  [ $\text{M}$ ]<sup>+</sup> 325.2042, found 325.2047.



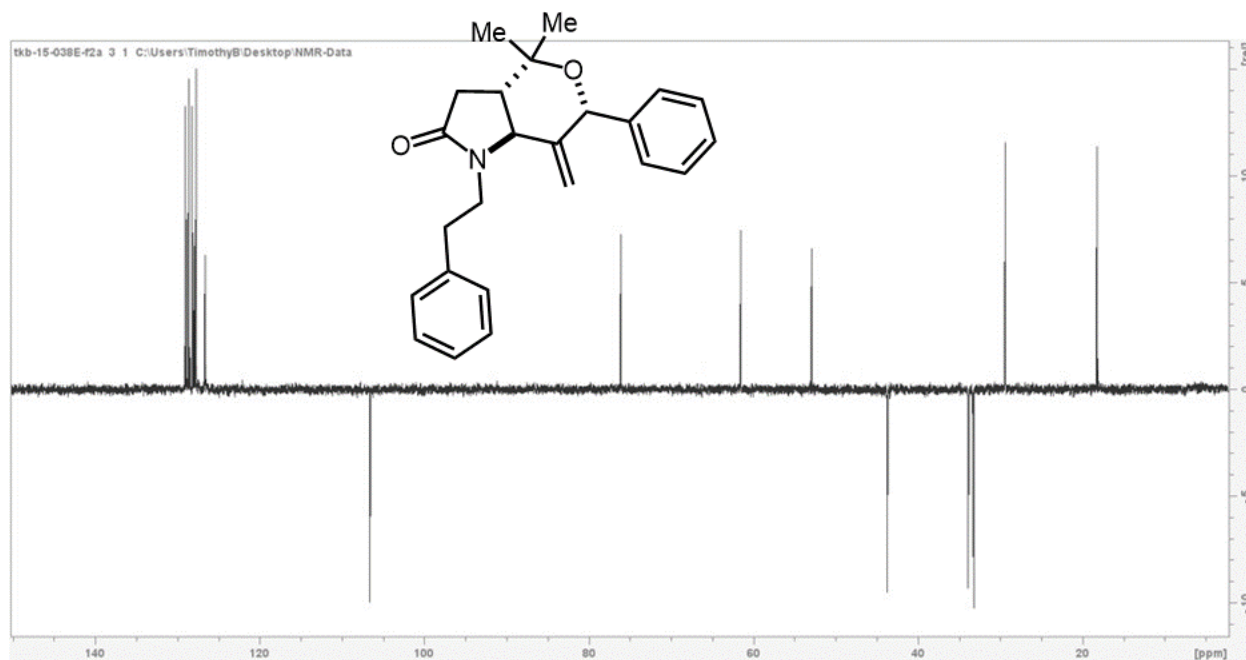


### Compound 4g

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 300.0 mg, 83%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.18 (m, 10H), 4.89 (s, 1H), 4.83 (d,  $J = 1.5$  Hz, 1H), 4.26 – 4.17 (m, 1H), 4.02 (ddd,  $J = 13.8, 8.6, 5.3$  Hz, 1H), 3.74 (d,  $J = 11.0$  Hz, 1H), 3.40 (dt,  $J = 13.9, 7.7$  Hz, 1H), 3.11 (ddd,  $J = 13.4, 8.5, 7.0$  Hz, 1H), 2.86 (ddd,  $J = 13.3, 8.1, 5.3$  Hz, 1H), 2.42 – 2.30 (m, 1H), 2.16 (ddd,  $J = 13.4, 10.9, 7.0$  Hz, 1H), 2.10 – 1.95 (m, 1H), 1.32 (s, 3H), 1.24 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 149.6, 139.1, 138.1, 129.0, 128.6, 128.2, 127.9, 127.7, 126.6, 106.6, 76.1, 75.1, 61.5, 52.9, 43.7, 33.9, 33.2, 29.4, 18.2. FTIR (KBr): 2972.8, 1728.5, 1669.3, 1606.9, 1511.0, 1448.5, 1414.7, 1384.9, 1357.4, 1298.7, 1247.5, 1179.3, 1135.9, 1031.8, 992.8, 833.0, 755.2. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{24}\text{H}_{27}\text{NO}_2$   $[\text{M}]^+$  361.2042, found 361.2048.

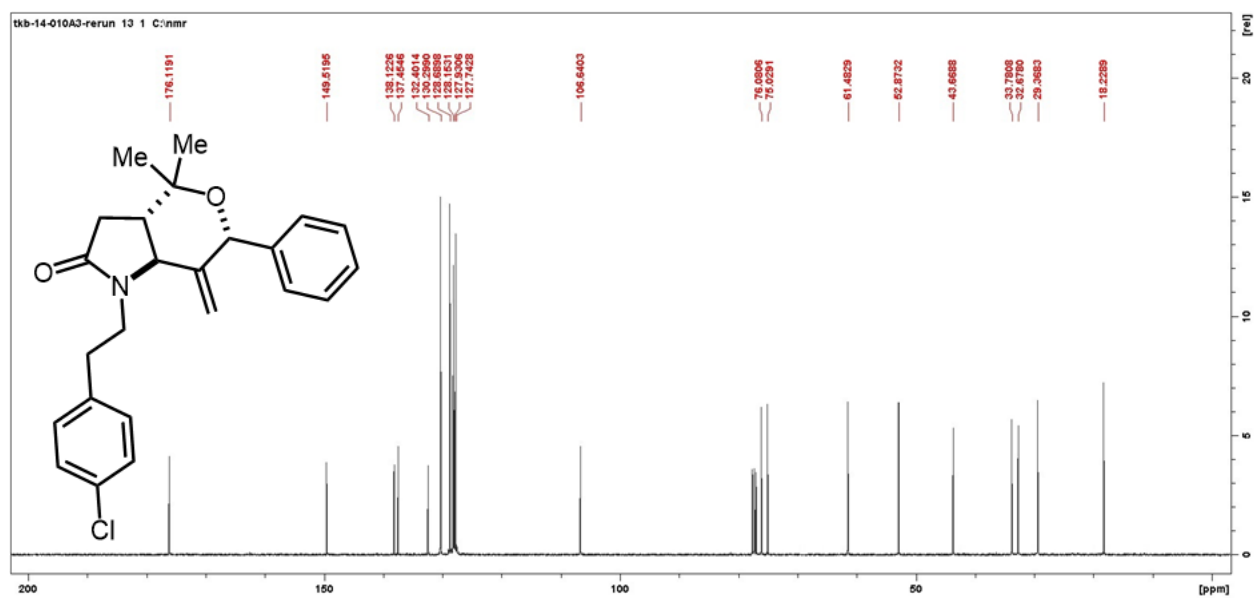
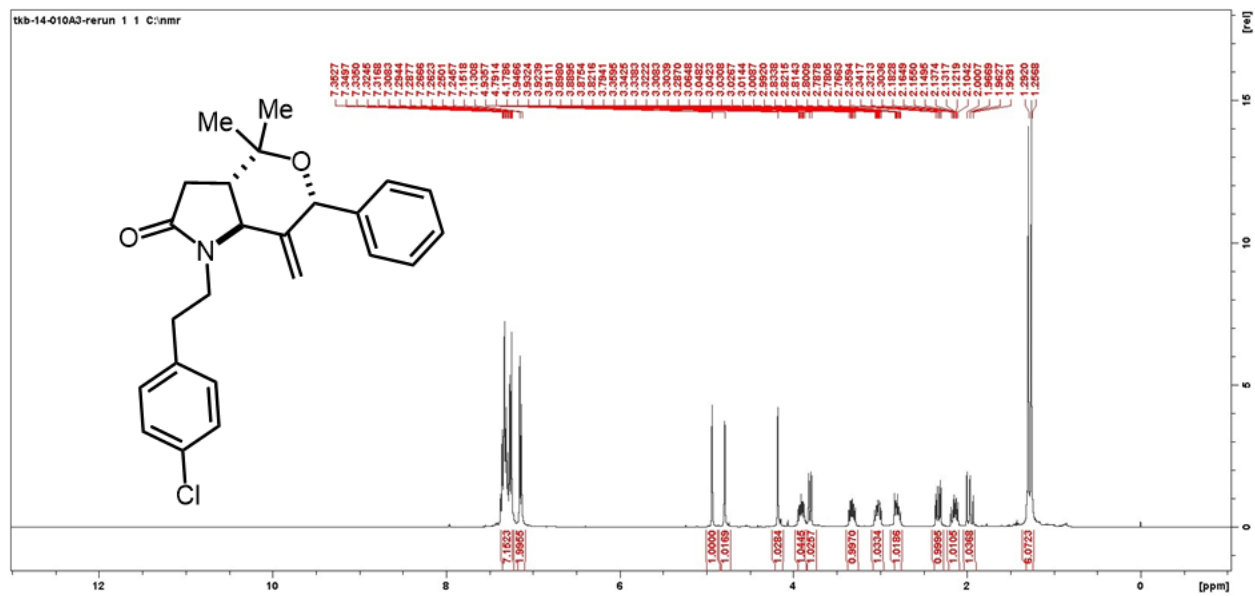


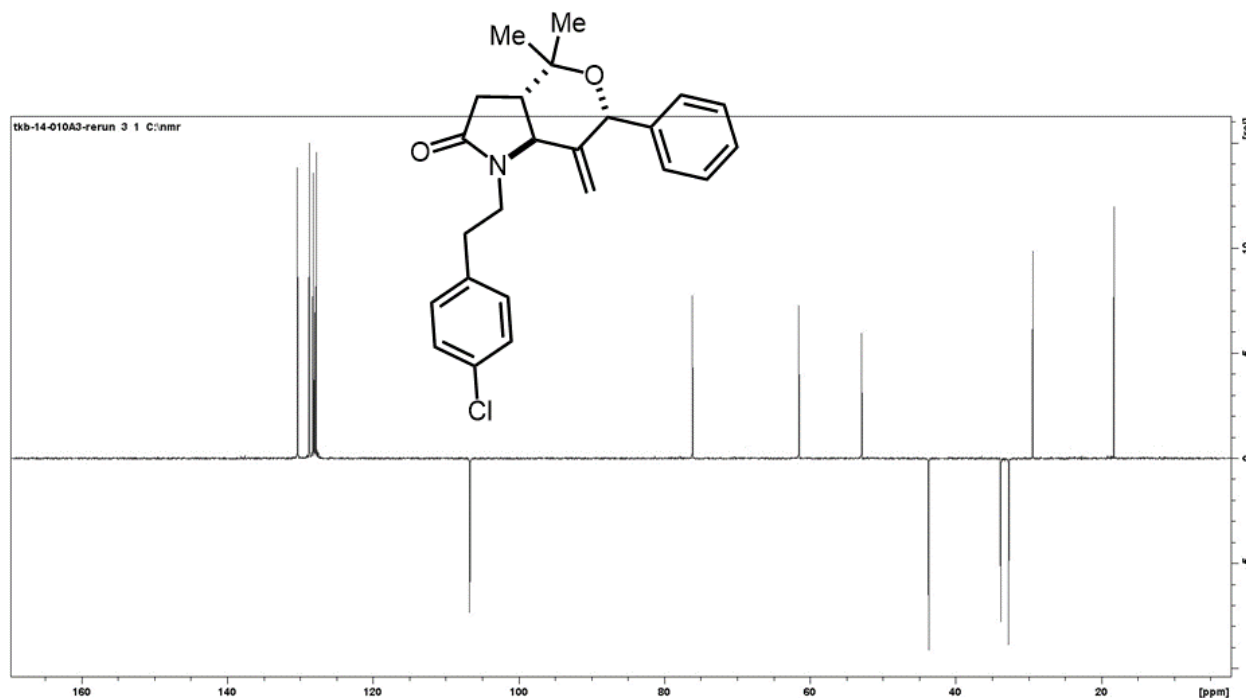




### Compound 4h

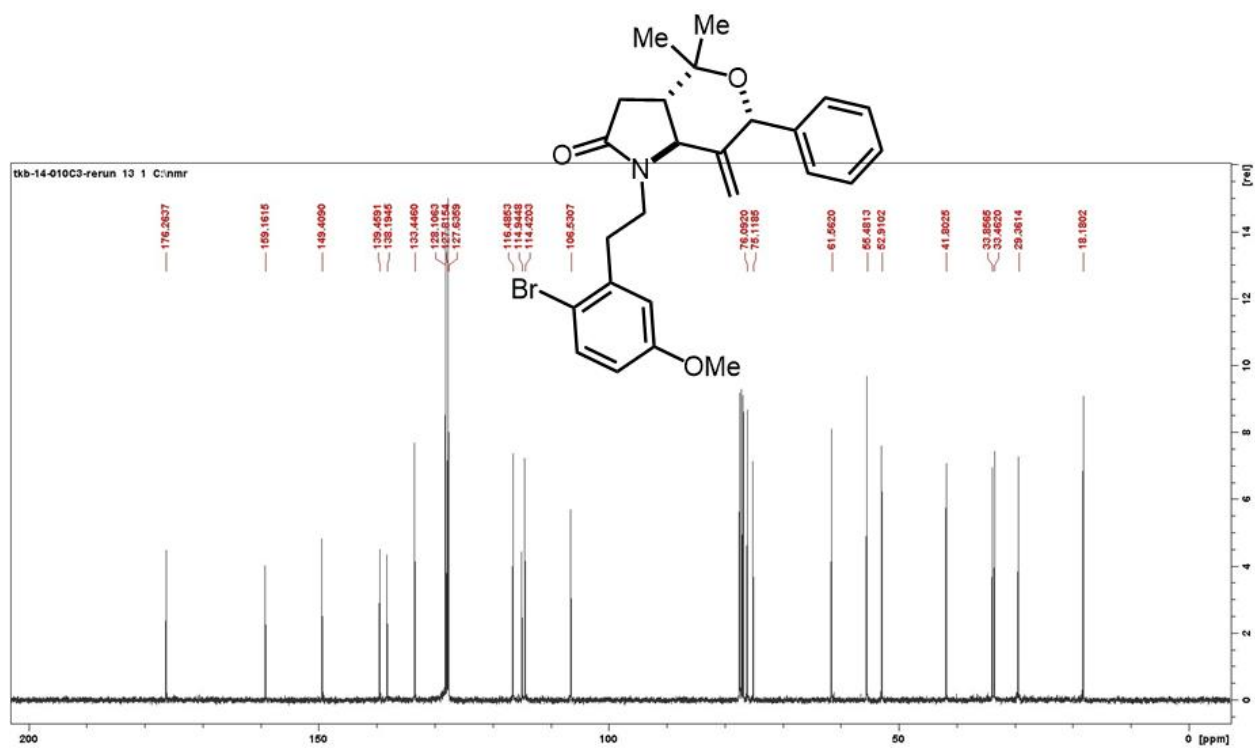
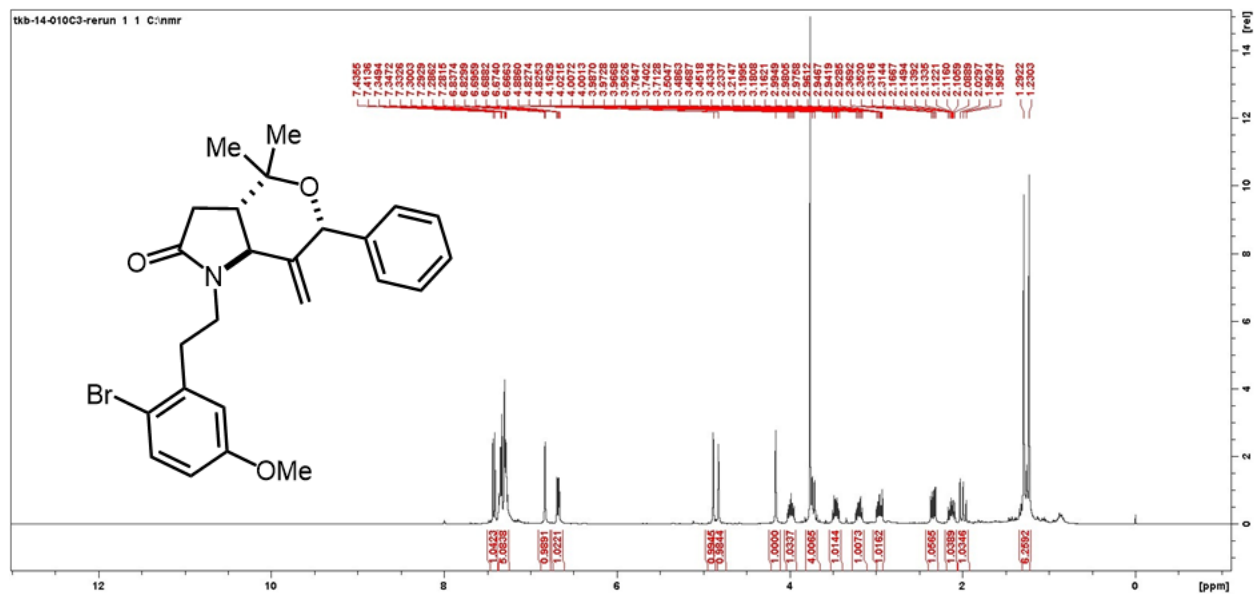
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 344.4 mg, 87%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.18 (m, 7H), 7.17 – 7.11 (m, 2H), 4.94 (s, 1H), 4.79 (d,  $J$  = 1.6 Hz, 1H), 4.20 (s, 1H), 3.91 (ddd,  $J$  = 14.3, 9.1, 5.6 Hz, 1H), 3.81 (d,  $J$  = 11.0 Hz, 1H), 3.32 (ddd,  $J$  = 13.7, 8.7, 6.6 Hz, 1H), 3.03 (ddd,  $J$  = 13.4, 9.1, 6.5 Hz, 1H), 2.80 (ddd,  $J$  = 13.9, 8.2, 5.1 Hz, 1H), 2.33 (dd,  $J$  = 15.3, 7.1 Hz, 1H), 2.14 (ddd,  $J$  = 13.4, 11.0, 7.1 Hz, 1H), 1.97 (dd,  $J$  = 15.3, 13.3 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 149.5, 138.1, 137.5, 132.4, 130.3, 128.7, 128.2, 127.9, 127.7, 106.6, 76.1, 75.0, 61.5, 52.9, 43.7, 33.8, 32.7, 29.4, 18.2. FTIR (KBr): 2935.4, 1727.5, 1696.3, 1604.9, 1511.0, 1448.5, 1414.7, 1384.9, 1357.4, 1298.7, 1247.5, 1179.3, 1135.9, 1031.8, 995.8, 831.0. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{24}\text{H}_{26}\text{ClNO}_2$  [ $\text{M}$ ]<sup>+</sup> 395.1652, found 395.1655.

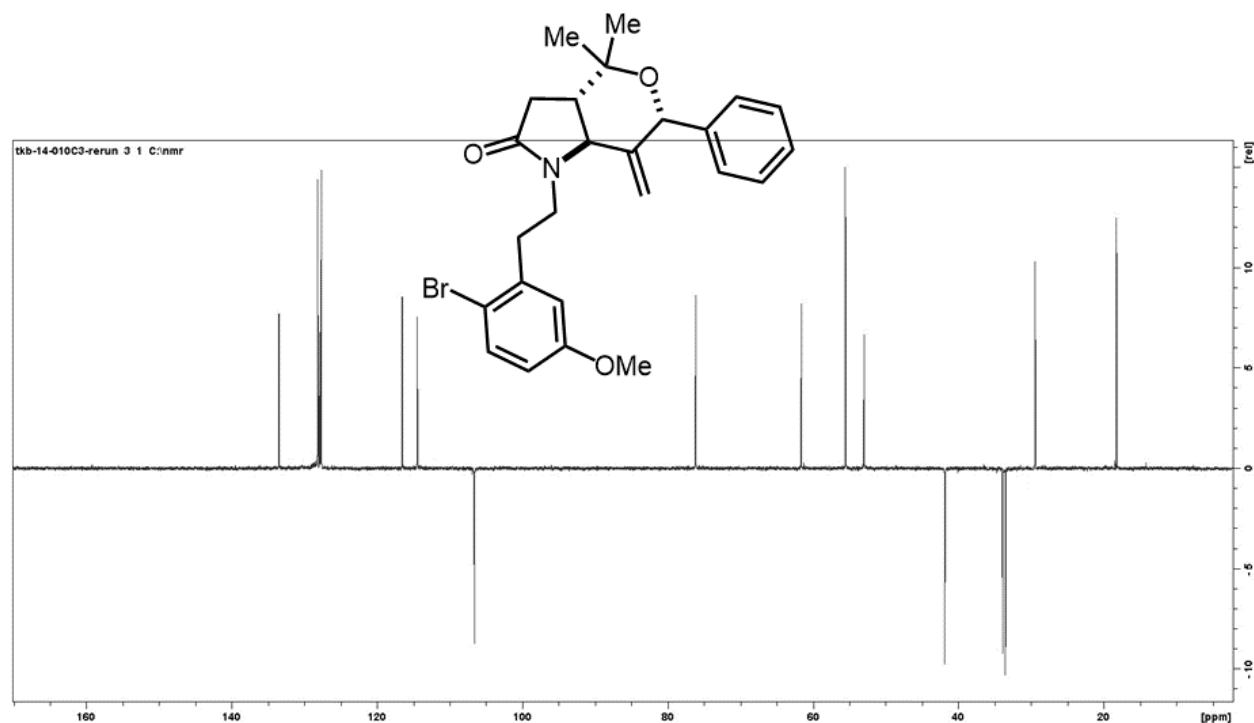




### Compound 4i

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Amorphous solid. Yield = 399.8 mg, 85%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.8$  Hz, 1H), 7.34 – 7.28 (m, 5H), 6.83 (d,  $J = 3.1$  Hz, 1H), 6.68 (dd,  $J = 8.8, 3.1$  Hz, 1H), 4.89 (s, 1H), 4.83 (d,  $J = 1.6$  Hz, 1H), 4.16 (d,  $J = 1.3$  Hz, 1H), 3.99 (ddd,  $J = 13.8, 8.1, 5.7$  Hz, 1H), 3.76 – 3.71 (m, 4H), 3.47 (dt,  $J = 14.1, 7.4$  Hz, 1H), 3.20 (ddd,  $J = 13.4, 8.1, 7.0$  Hz, 1H), 2.96 (ddd,  $J = 13.1, 7.5, 5.4$  Hz, 1H), 2.34 (dd,  $J = 15.0, 6.9$  Hz, 1H), 2.13 (ddd,  $J = 13.4, 10.9, 6.9$  Hz, 1H), 1.99 (dd,  $J = 15.0, 13.4$  Hz, 1H), 1.29 – 1.23 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 159.2, 149.4, 139.5, 138.2, 133.4, 128.1, 127.8, 127.8, 127.6, 127.5, 116.5, 114.9, 114.4, 106.5, 76.0, 75.1, 61.6, 55.5, 52.9, 41.8, 33.9, 33.5, 29.4, 18.2. FTIR (KBr): 2932.5, 1721.4, 1665.4, 1607.2, 1511.1, 1431.8, 1414.7, 1344.9, 1298.4, 1245.6, 1179.4, 1135.3, 1031.8, 996.7, 921.8, 832.1, 701.6. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{25}\text{H}_{28}\text{BrNO}_3$  [ $\text{M}$ ]<sup>+</sup> 469.1253, found 469.1258.

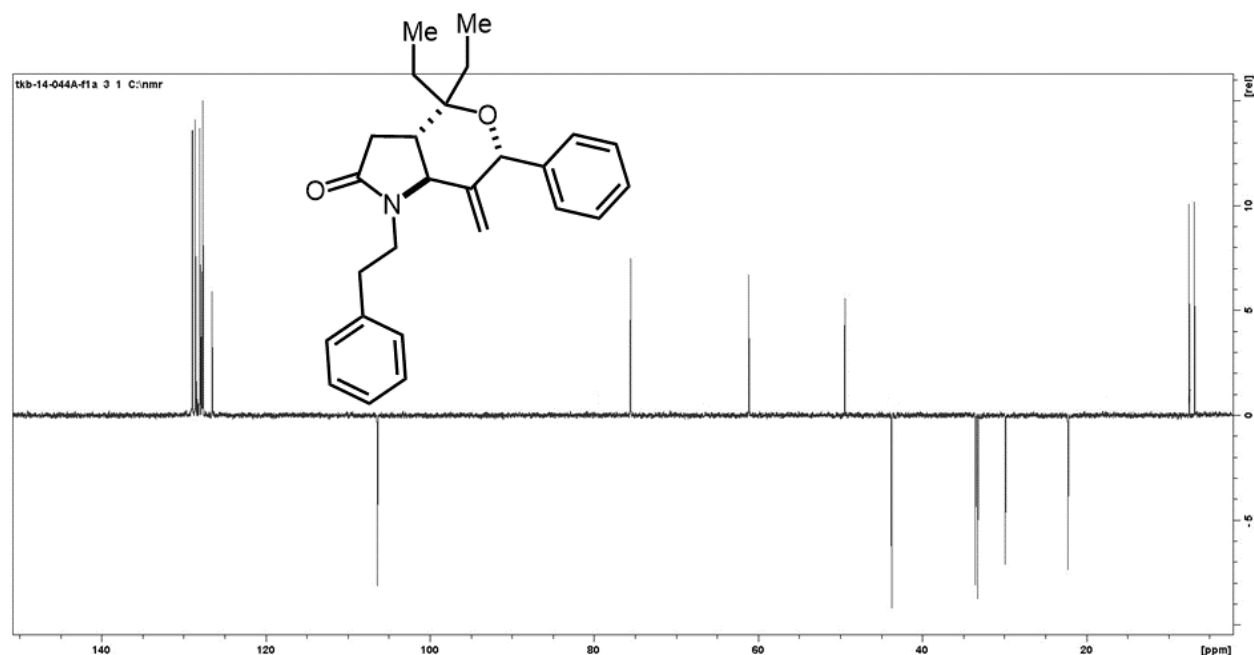




### Compound 4j

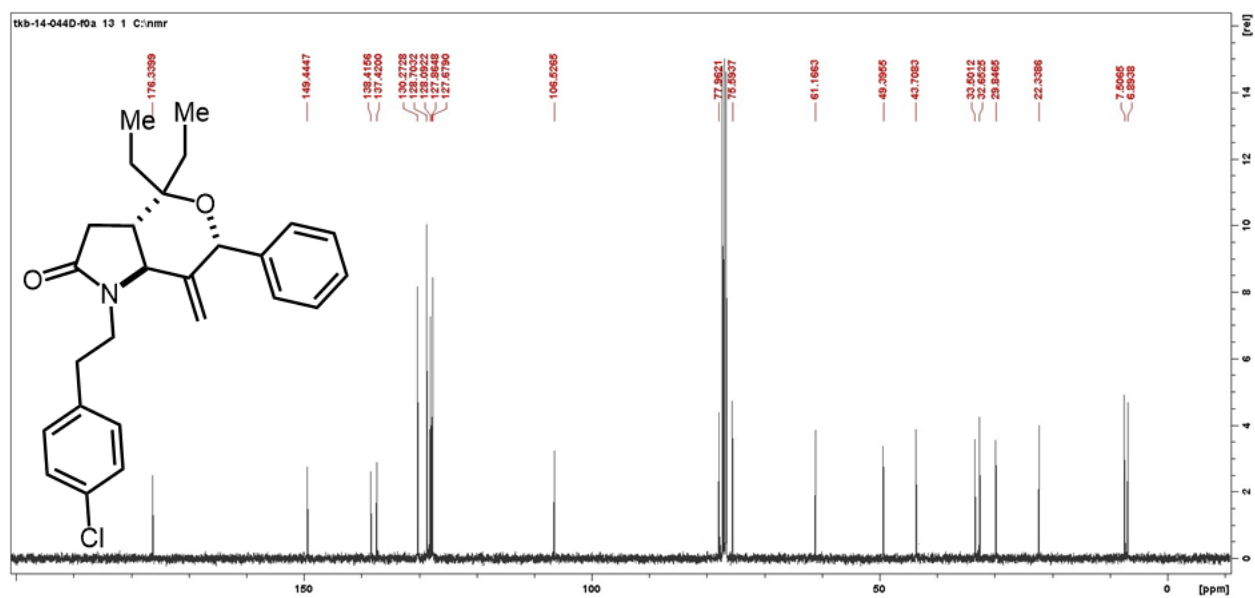
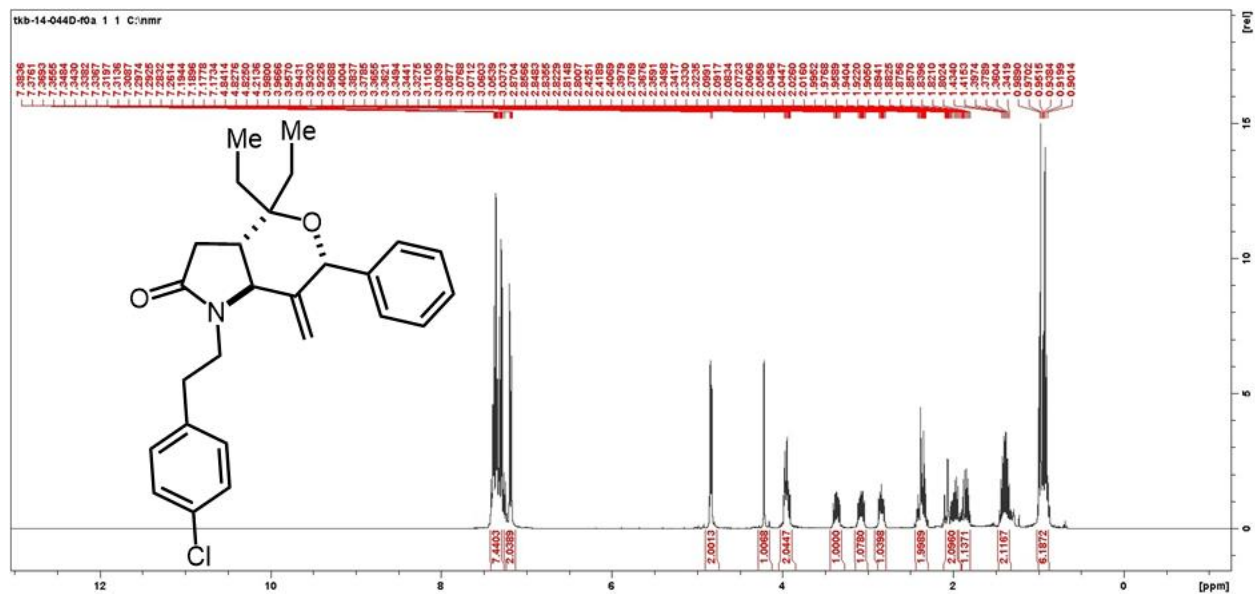
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Amorphous solid. Yield = 342.8 mg, 88%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.25 (m, 10H), 4.85 (s, 1H), 4.80 (s, 1H), 4.21 (d,  $J = 1.3$  Hz, 1H), 4.02 (ddd,  $J = 14.0, 8.9, 5.4$  Hz, 1H), 3.92 (d,  $J = 10.4$  Hz, 1H), 3.41 (ddd,  $J = 13.7, 8.5, 7.0$  Hz, 1H), 3.12 (ddd,  $J = 13.3, 8.9, 6.9$  Hz, 1H), 2.87 (ddd,  $J = 13.7, 8.5, 5.4$  Hz, 1H), 2.43 – 2.27 (m, 2H), 2.15 – 2.00 (m, 1H), 1.89 (ddq,  $J = 36.6, 14.9, 7.5$  Hz, 2H), 1.38 (ddq,  $J = 24.0, 14.8, 7.5$  Hz, 2H), 0.96 (d,  $J = 7.5$  Hz, 3H), 0.90 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 149.6, 139.1, 138.5, 129.7, 129.1, 128.9, 128.6, 128.4, 128.3, 128.0, 127.9, 127.7, 127.3, 126.5, 106.4, 78.0, 75.6, 61.2, 49.5, 43.8, 33.5, 33.3, 29.9, 22.3, 7.5, 6.9. FTIR (KBr): 2924.8, 1642.2, 1494.9, 1448.8, 1427.0, 1393.4, 1361.6, 1328.7, 1289.7, 1223.6, 1198.9, 1130.1, 1074.1, 1030.4, 988.5, 966.1, 925.5, 741.6, 693.4. **HRMS-EI $^+$**  ( $m/z$ ): calc for  $\text{C}_{26}\text{H}_{31}\text{NO}_2$   $[\text{M}]^+$  389.2355, found 389.2358.



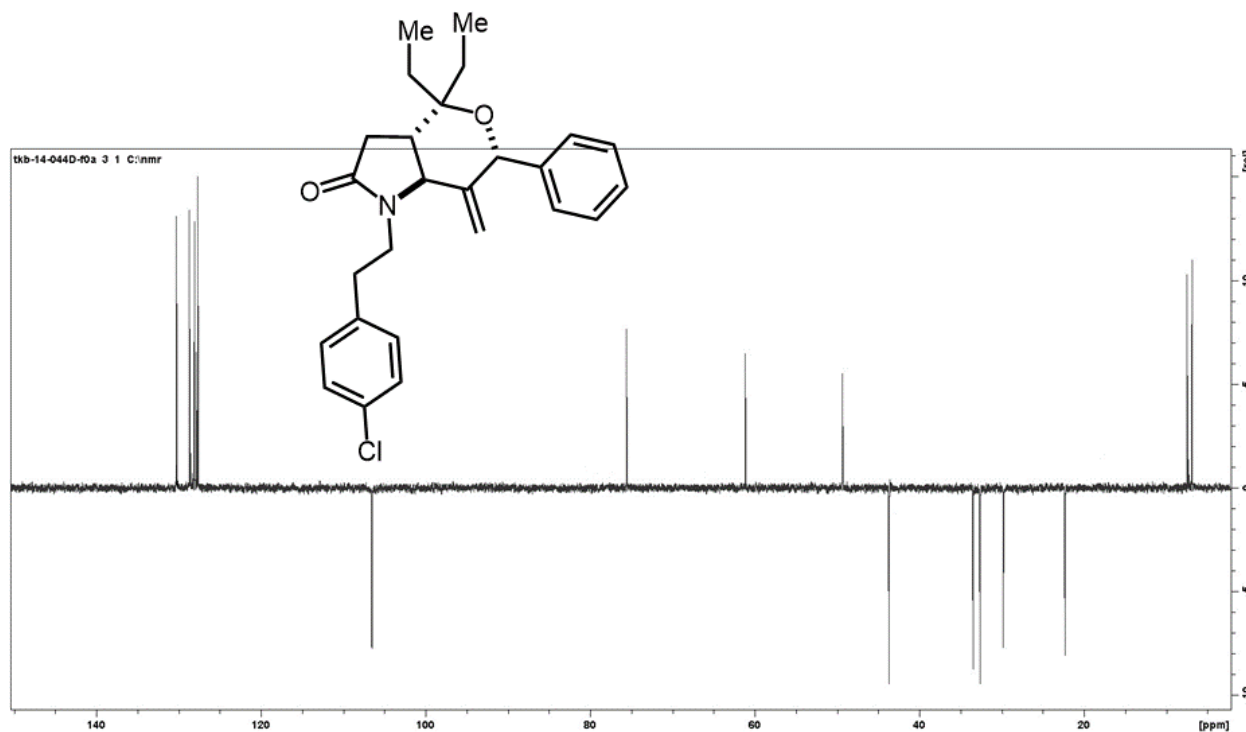


### Compound 4k

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 368.9 mg, 87%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.26 (m, 7H), 7.19 – 7.16 (m, 2H), 4.88 – 4.77 (m, 2H), 4.22 (d,  $J = 1.3$  Hz, 1H), 3.95 (ddt,  $J = 13.6, 9.2, 4.9$  Hz, 2H), 3.36 (ddd,  $J = 13.6, 8.8, 6.6$  Hz, 1H), 3.15 – 3.02 (m, 1H), 2.84 (ddd,  $J = 13.9, 8.9, 5.5$  Hz, 1H), 2.47 – 2.27 (m, 2H), 2.23 – 1.76 (m, 3H), 1.43 (dd,  $J = 14.8, 7.3$  Hz, 1H), 1.40 – 1.26 (m, 1H), 0.99 – 0.90 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 149.4, 138.4, 137.4, 132.5, 130.4, 130.3, 129.7, 128.7, 128.6, 128.1, 127.9, 127.7, 127.3, 106.5, 78.0, 75.6, 61.2, 49.4, 43.7, 33.5, 32.7, 29.8, 22.3, 7.5, 6.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{26}\text{H}_{30}\text{ClNO}_2$   $[\text{M}]^+$  423.1965, 423.1969.



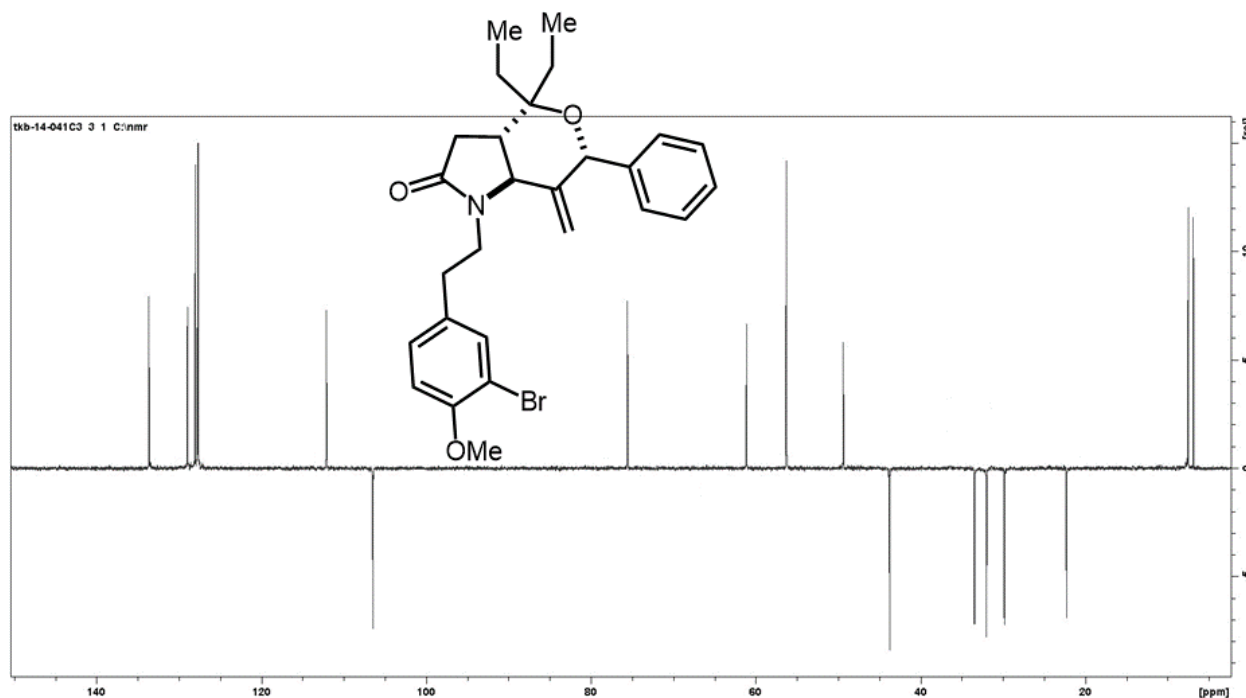




### Compound 4l

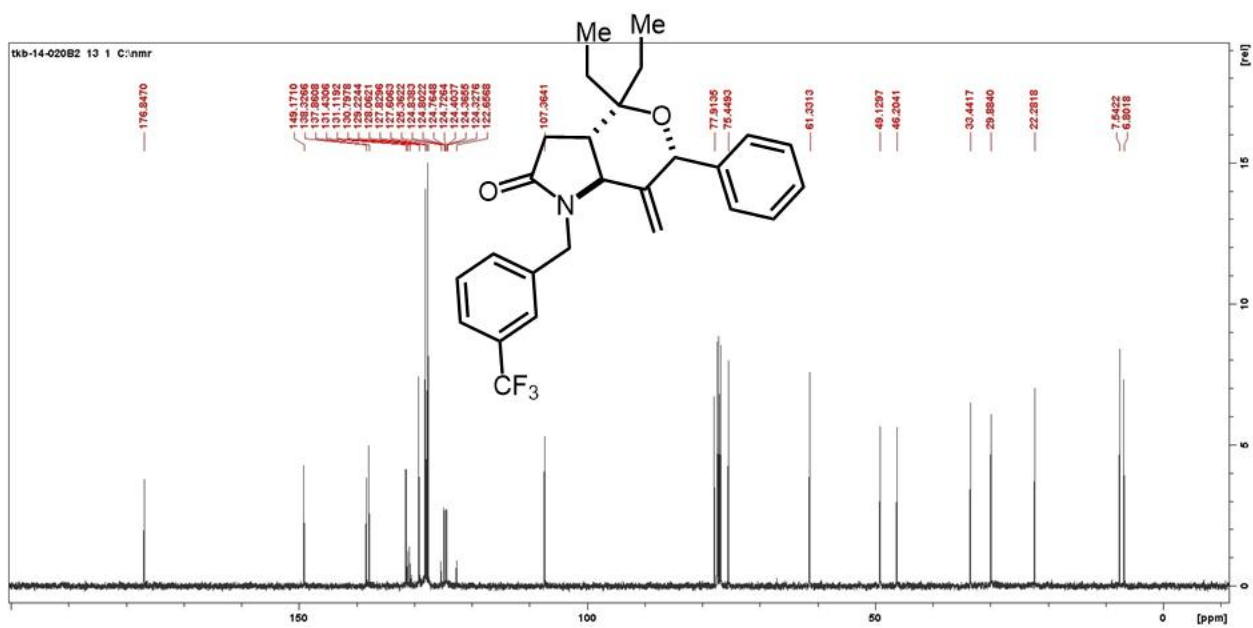
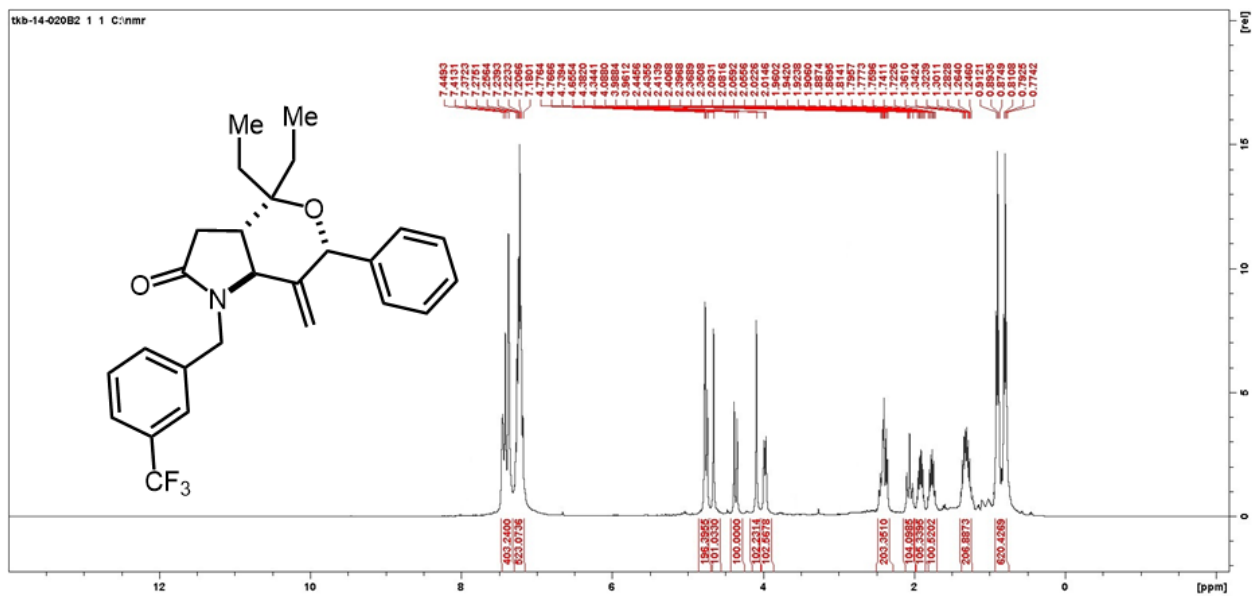
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Yellowish oil. Yield = 408.7 mg, 82%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.20 (m, 6H), 7.04 (dd,  $J$  = 8.4, 2.2 Hz, 1H), 6.75 (d,  $J$  = 8.4 Hz, 1H), 4.74 – 4.68 (m, 2H), 4.09 (s, 1H), 3.88 – 3.74 (m, 5H), 3.28 – 3.16 (m, 1H), 2.91 (ddd,  $J$  = 13.5, 8.8, 6.8 Hz, 1H), 2.66 (ddd,  $J$  = 13.5, 8.3, 5.3 Hz, 1H), 2.31 – 2.16 (m, 2H), 2.01 – 1.65 (m, 2H), 1.35 – 1.23 (m, 1H), 1.27 – 1.10 (m, 1H), 0.87 – 0.77 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 162.4, 154.7, 149.4, 138.4, 133.6, 132.6, 128.9, 128.0, 127.8, 127.7, 127.6, 112.1, 111.6, 106.4, 77.9, 75.5, 67.0, 61.1, 60.3, 56.3, 53.5, 49.4, 43.7, 36.4, 33.4, 32.0, 31.3, 29.8, 22.3, 14.2, 7.5, 6.9. FTIR (KBr): 2965.2, 2872.3, 1716.4, 1650.8, 1612.9, 1585.9, 1513.1, 1455.3, 1359.3, 1304.1, 1251.3, 1177.4, 1135.5, 1033.8, 996.7, 896.0, 833.6, 804.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{27}\text{H}_{32}\text{BrNO}_3$   $[\text{M}]^+$  497.1566, found 497.1569.

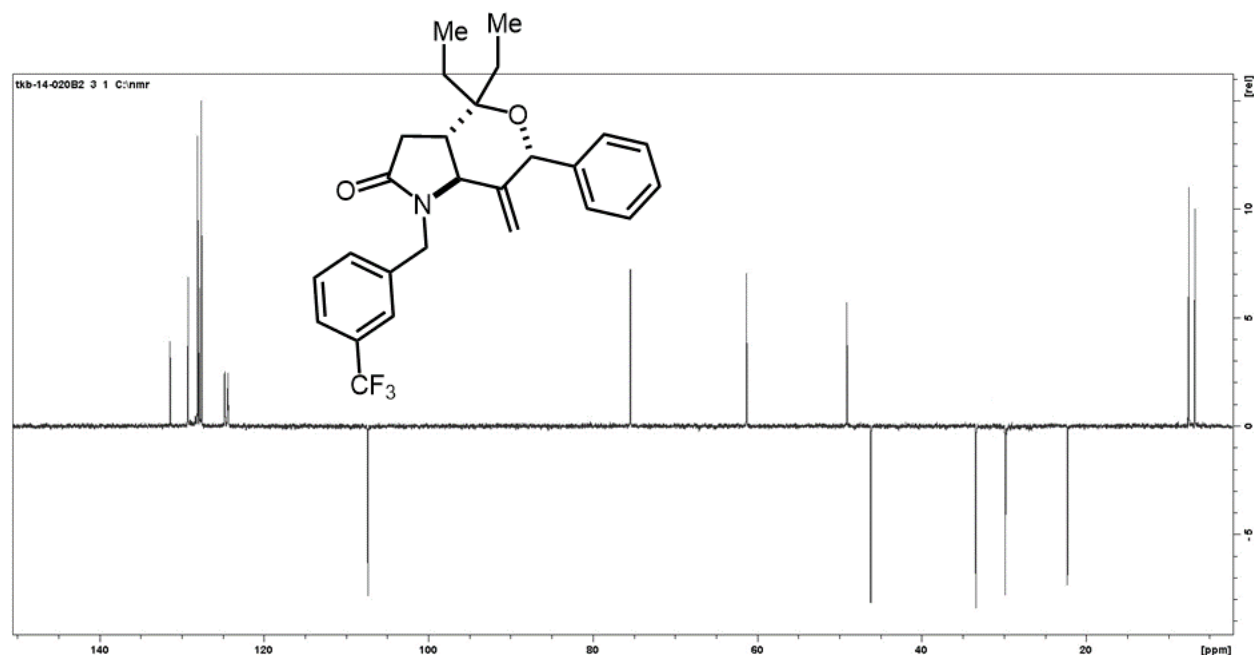




### Compound 4m

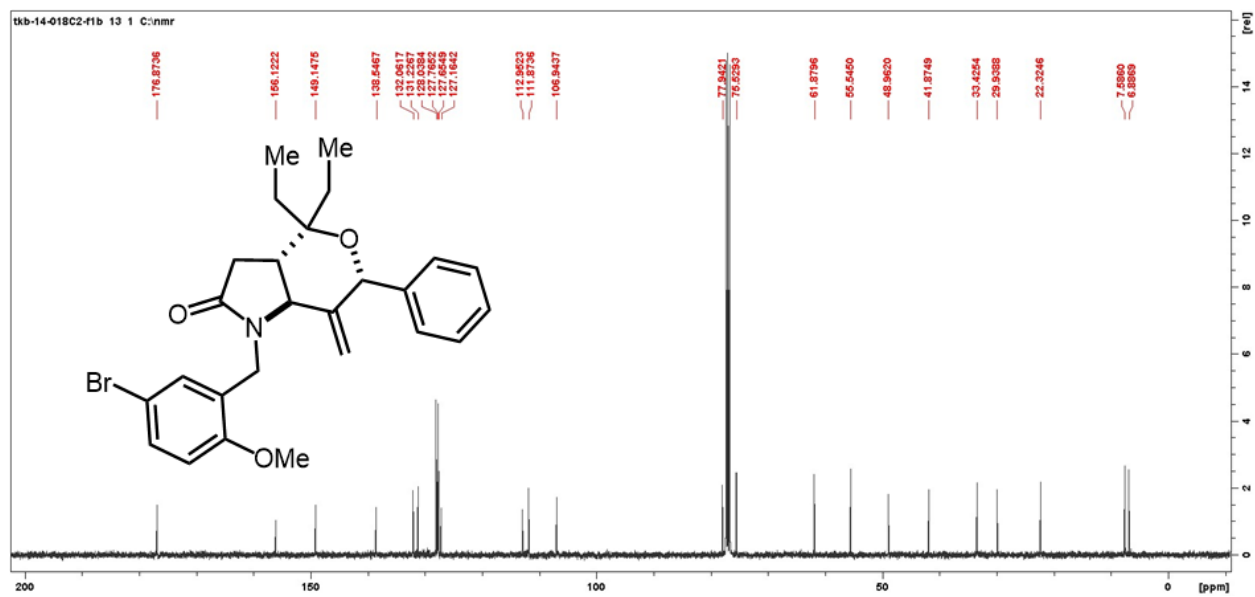
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Greenish-yellow oil. Yield = 381.4 mg, 86%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.18 (m, 9H), 4.80 – 4.72 (m, 2H), 4.68 – 4.63 (m, 1H), 4.36 (d,  $J = 15.2$  Hz, 1H), 4.09 (s, 1H), 3.97 (d,  $J = 10.9$  Hz, 1H), 2.50 – 2.33 (m, 2H), 2.14 – 1.99 (m, 1H), 1.92 (dq,  $J = 14.8, 7.4$  Hz, 1H), 1.84 – 1.68 (m, 1H), 1.40 – 1.23 (m, 2H), 0.89 (t,  $J = 7.5$  Hz, 3H), 0.78 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 149.4, 138.4, 137.4, 132.5, 130.4, 130.3, 129.7, 128.7, 128.6, 128.1, 127.9, 127.7, 127.3, 106.5, 77.9, 75.6, 61.2, 49.4, 43.7, 33.5, 32.7, 29.8, 22.3, 7.5, 6.9. FTIR (KBr): 2933.4, 1721.5, 1666.3, 1606.9, 1511.0, 1448.5, 1414.7, 1384.9, 1357.4, 1298.7, 1247.5, 1179.3, 1137.9, 1033.8, 995.8, 831.7. **HRMS- $\text{EI}^+$**  ( $m/z$ ): calc for  $\text{C}_{26}\text{H}_{28}\text{F}_3\text{NO}_2$  [ $\text{M}$ ] $^+$  443.2072, found 443.2077.

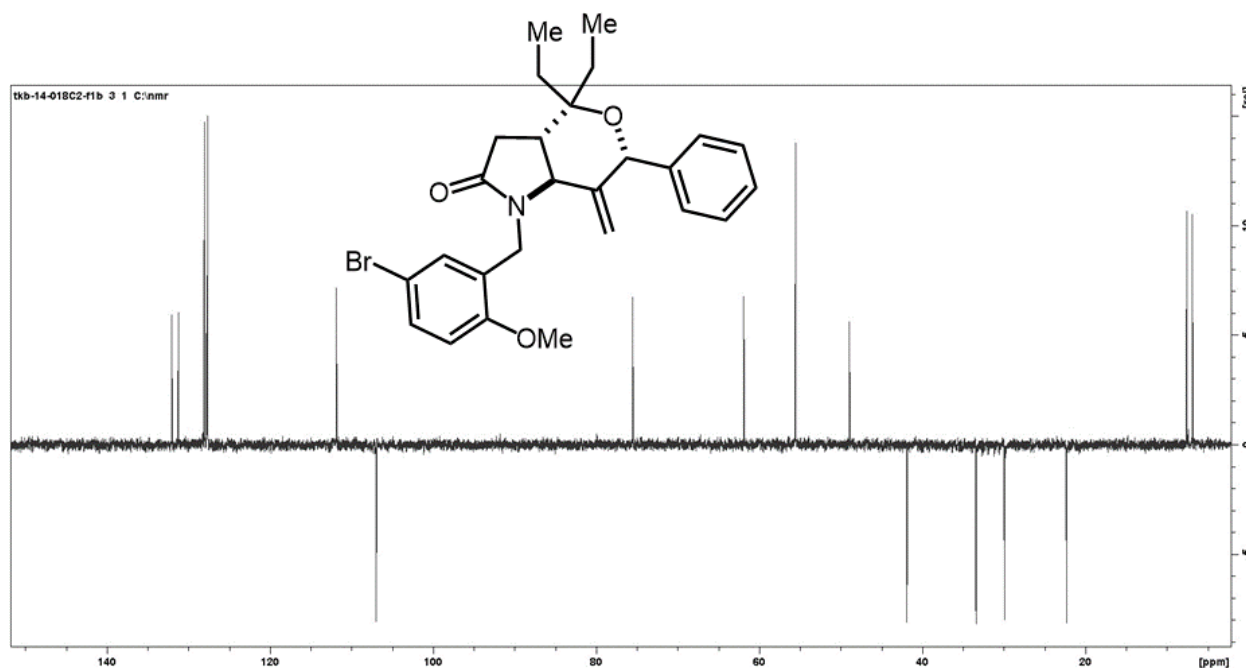




### Compound 4n

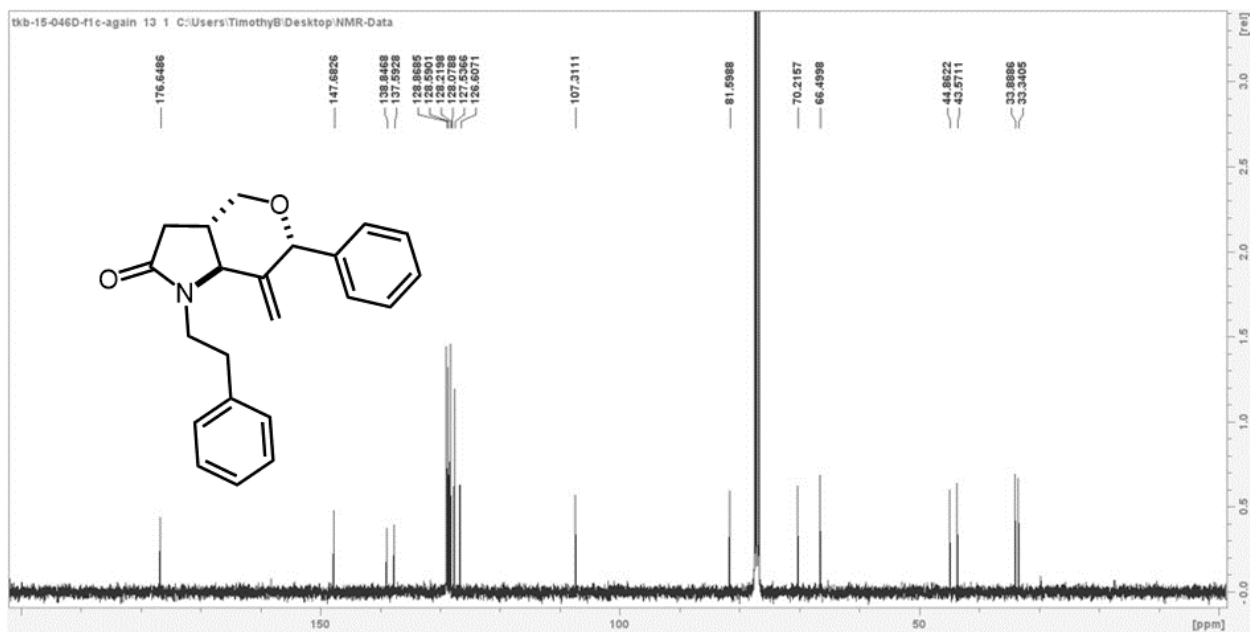
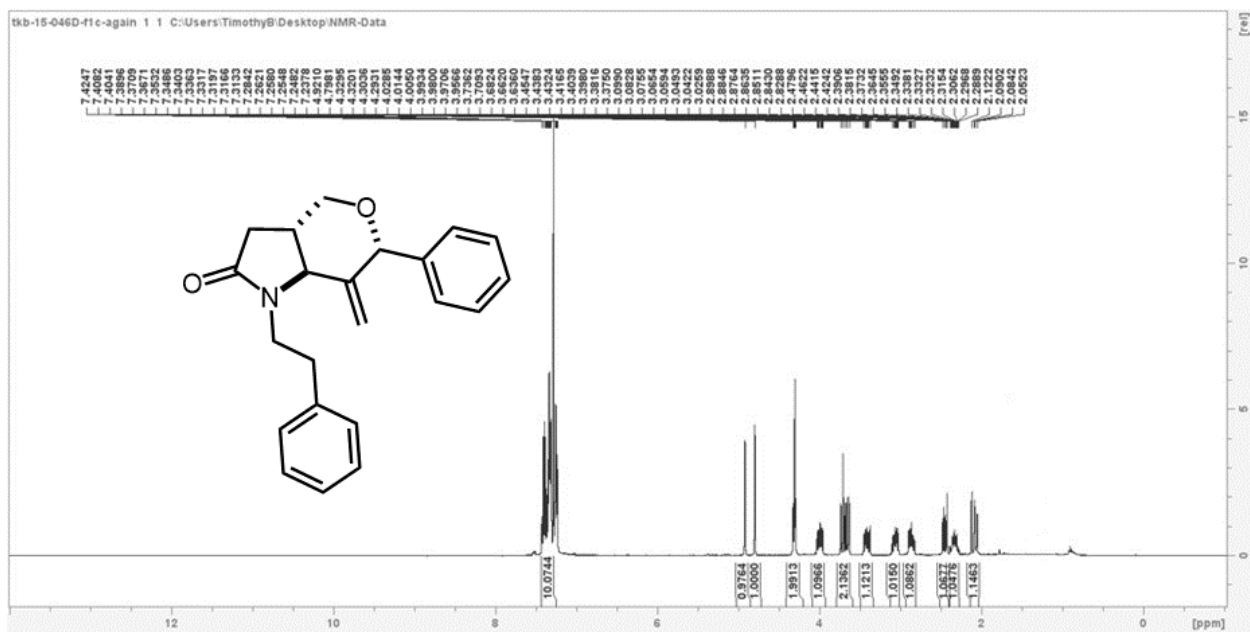
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Amorphous solid. Yield = 392.4 mg, 81%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.31 (m, 7H), 6.74 (d,  $J = 8.3$  Hz, 1H), 4.87 (s, 1H), 4.74 (d,  $J = 1.5$  Hz, 1H), 4.71 (d,  $J = 15.8$  Hz, 1H), 4.42 (d,  $J = 15.8$  Hz, 1H), 4.17 – 4.09 (m, 2H), 3.80 (s, 3H), 2.60 – 2.41 (m, 2H), 2.26 – 2.01 (m, 2H), 1.89 (dq,  $J = 14.9, 7.5$  Hz, 1H), 1.63 (s, 1H), 1.44 (tq,  $J = 15.4, 7.9$  Hz, 2H), 1.02 (t,  $J = 7.5$  Hz, 3H), 0.92 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.87, 156.12, 149.15, 138.54, 132.06, 131.22, 128.07, 127.76, 127.65, 127.17, 112.95, 111.87, 106.94, 77.94, 75.52, 61.88, 55.54, 48.96, 41.87, 34.42, 29.94, 22.32, 7.59, 6.89. FTIR (KBr): 3027.4, 2924.0, 1724.2, 1646.3, 1474.3, 1452.8, 1361.9, 1342.0, 1205.6, 1140.2, 1071.7, 1028.3, 996.4, 735.4. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{26}\text{H}_{30}\text{BrNO}_3$   $[\text{M}]^+$  483.1409, found 483.1412.



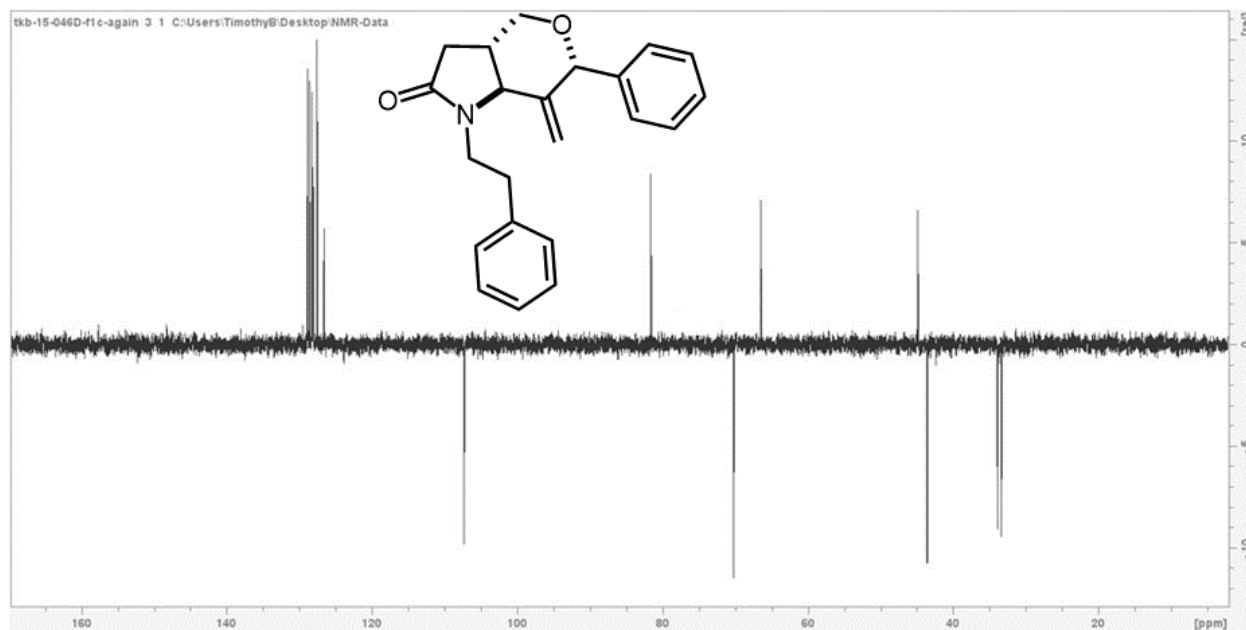


### Compound 4o

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Pale-yellowish oil. Yield = 296.8 mg, 89%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.21 (m, 10H), 4.92 (d,  $J = 1.5$  Hz, 1H), 4.80 (s, 1H), 4.35 – 4.26 (m, 2H), 3.99 (ddd,  $J = 13.7, 9.4, 5.6$  Hz, 1H), 3.77 – 3.61 (m, 2H), 3.48 – 3.35 (m, 1H), 3.06 (ddd,  $J = 13.3, 9.4, 6.5$  Hz, 1H), 2.86 (ddd,  $J = 13.9, 9.0, 5.6$  Hz, 1H), 2.45 (dd,  $J = 15.2, 6.9$  Hz, 1H), 2.33 (dddq,  $J = 17.5, 10.6, 6.9, 3.7$  Hz, 1H), 2.09 (dd,  $J = 15.3, 12.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 147.7, 138.8, 137.6, 128.9, 128.6, 128.2, 128.1, 127.5, 126.6, 107.3, 81.6, 70.2, 66.5, 44.9, 43.6, 33.9, 33.3. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{22}\text{H}_{23}\text{NO}_2$  [ $\text{M}$ ]<sup>+</sup> 333.1729, found 333.1723.

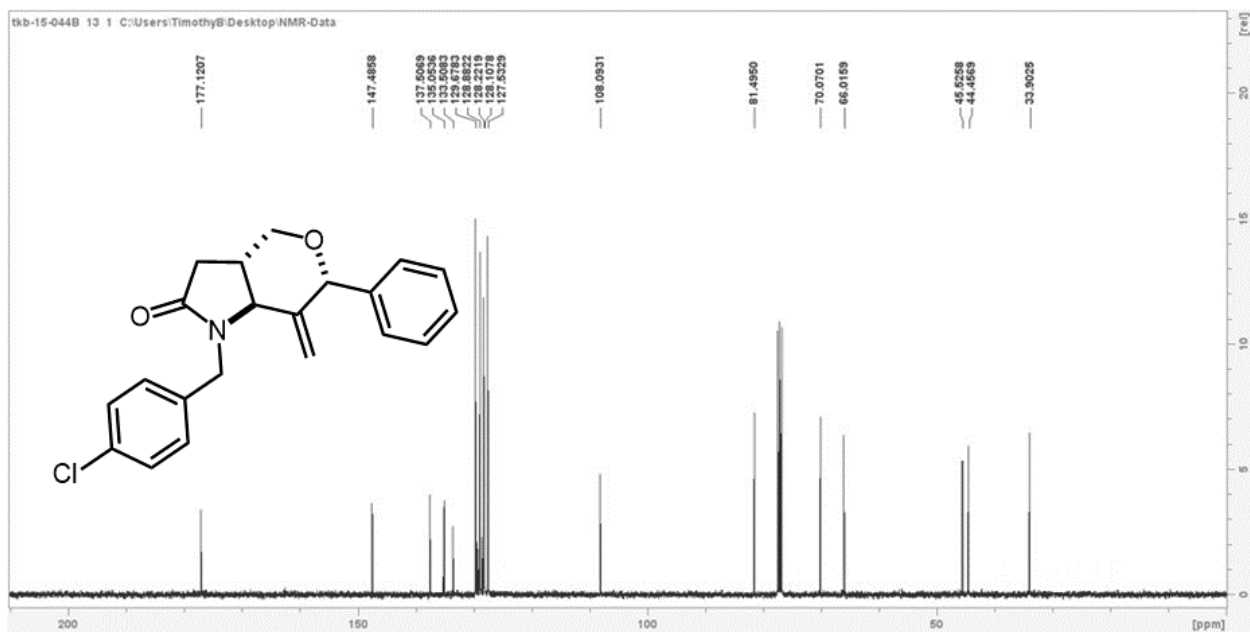
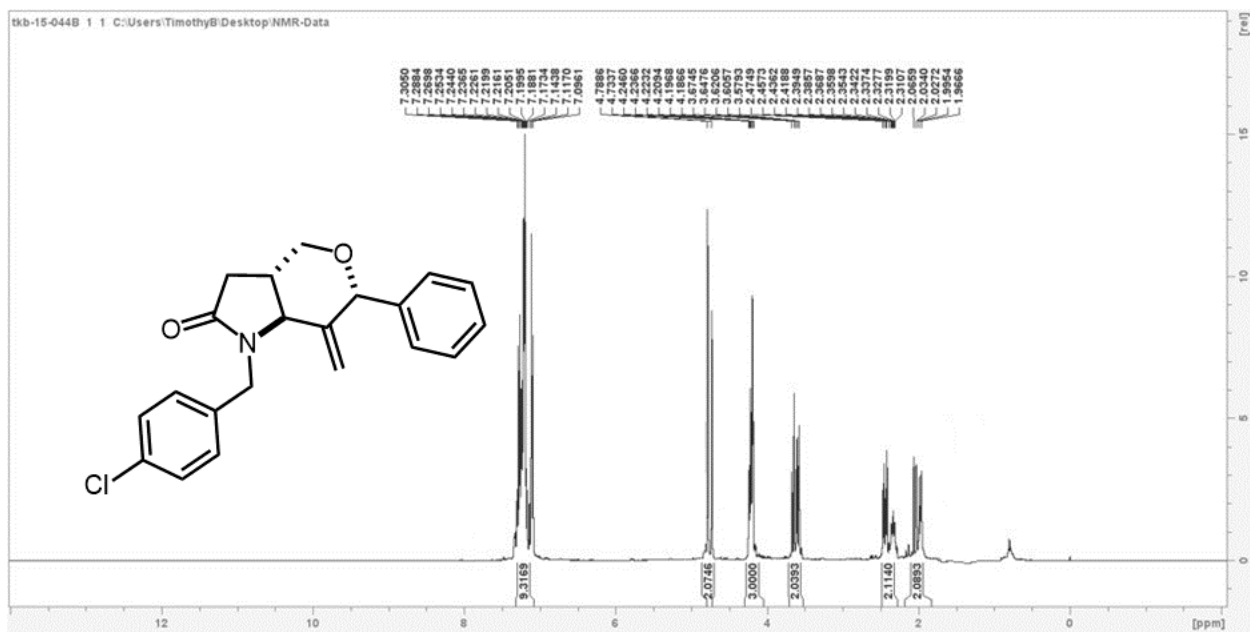


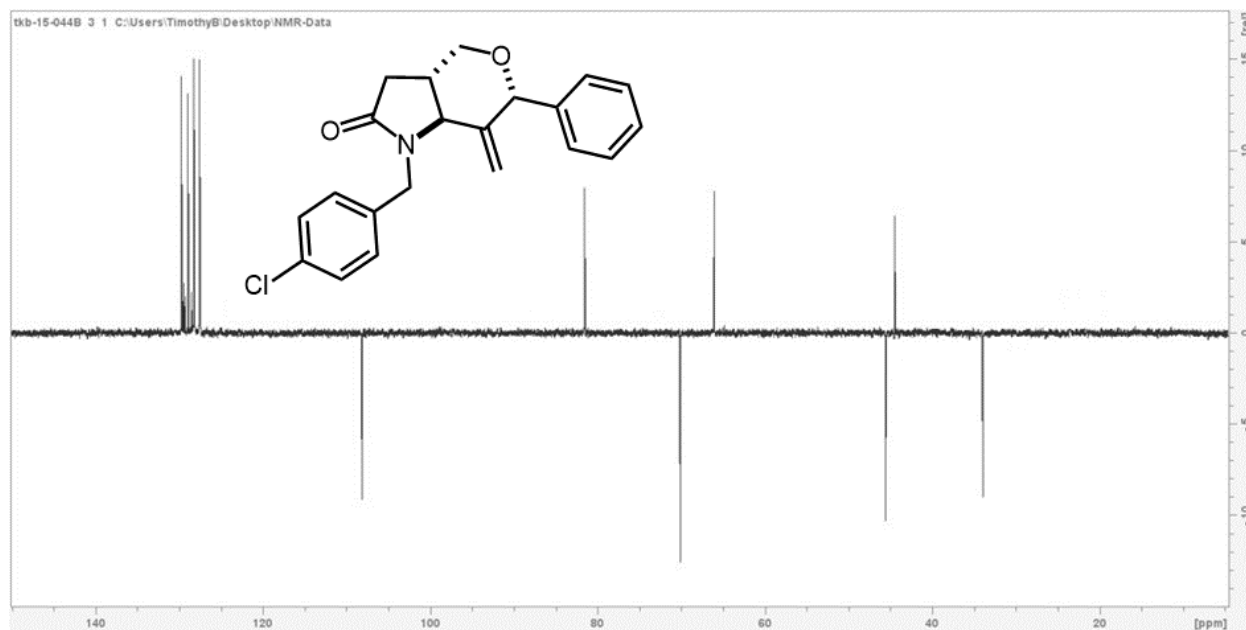




### Compound 4p

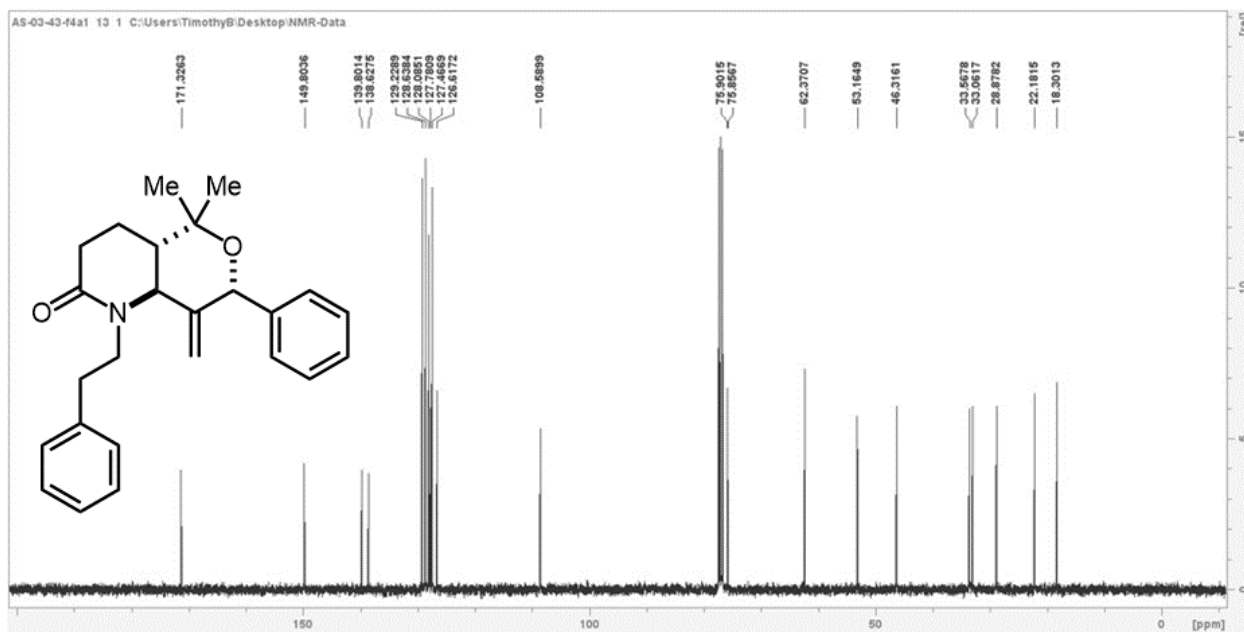
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Pale-yellowish oil. Yield = 304.3 mg, 86%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.10 (m, 9H), 4.78 – 4.74 (m, 2H), 4.25 – 4.19 (m, 3H), 3.67 – 3.58 (m, 2H), 2.52 – 2.26 (m, 2H), 2.07 – 1.97 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.1, 147.5, 137.5, 129.7, 128.8, 128.2, 127.5, 108.1, 81.5, 77.4, 77.1, 76.8, 70.1, 66.0, 45.5, 44.5, 33.9. FTIR (KBr): 2972.9, 2932.8, 1638.2, 1449.1, 1364.7, 1290.2, 1270.3, 1247.8, 1206.5, 1179.9, 1131.1, 1071.4, 994.4, 924.8, 881.7. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{21}\text{H}_{20}\text{ClNO}_2$  [ $\text{M}$ ]<sup>+</sup> 353.1183, found 353.1188.

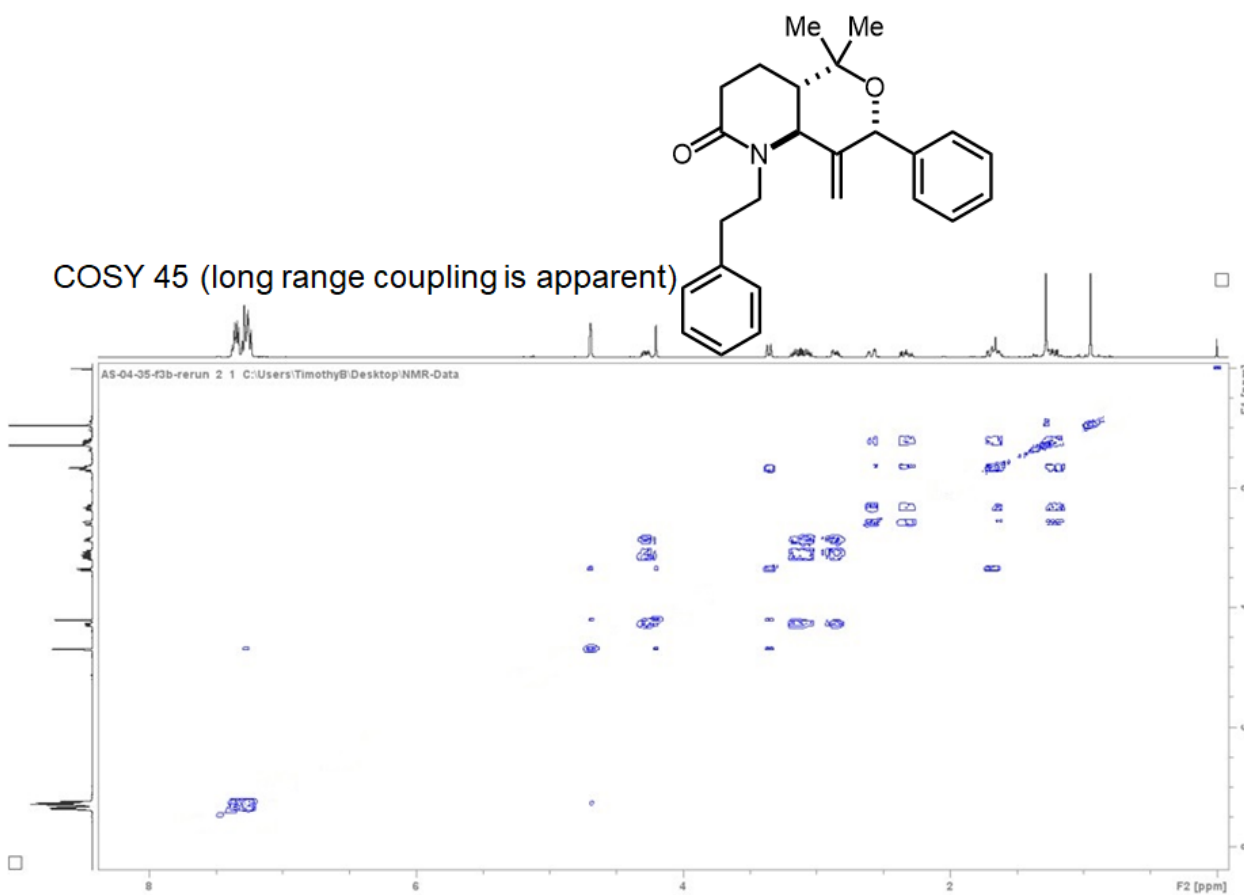
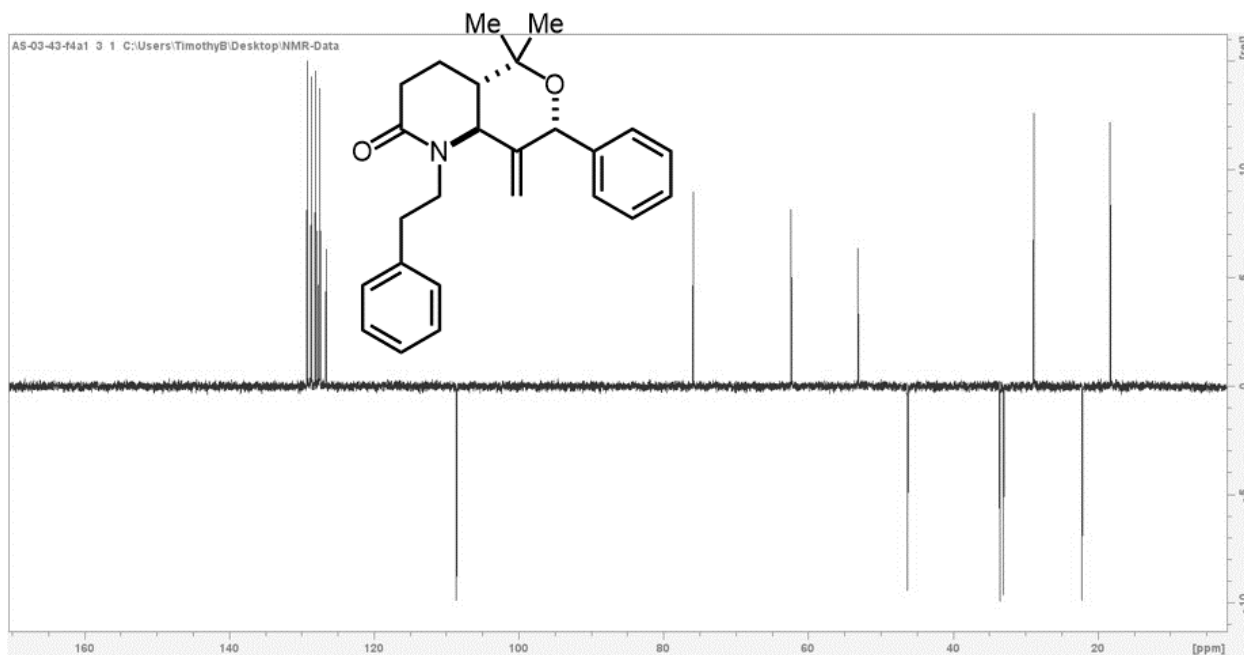


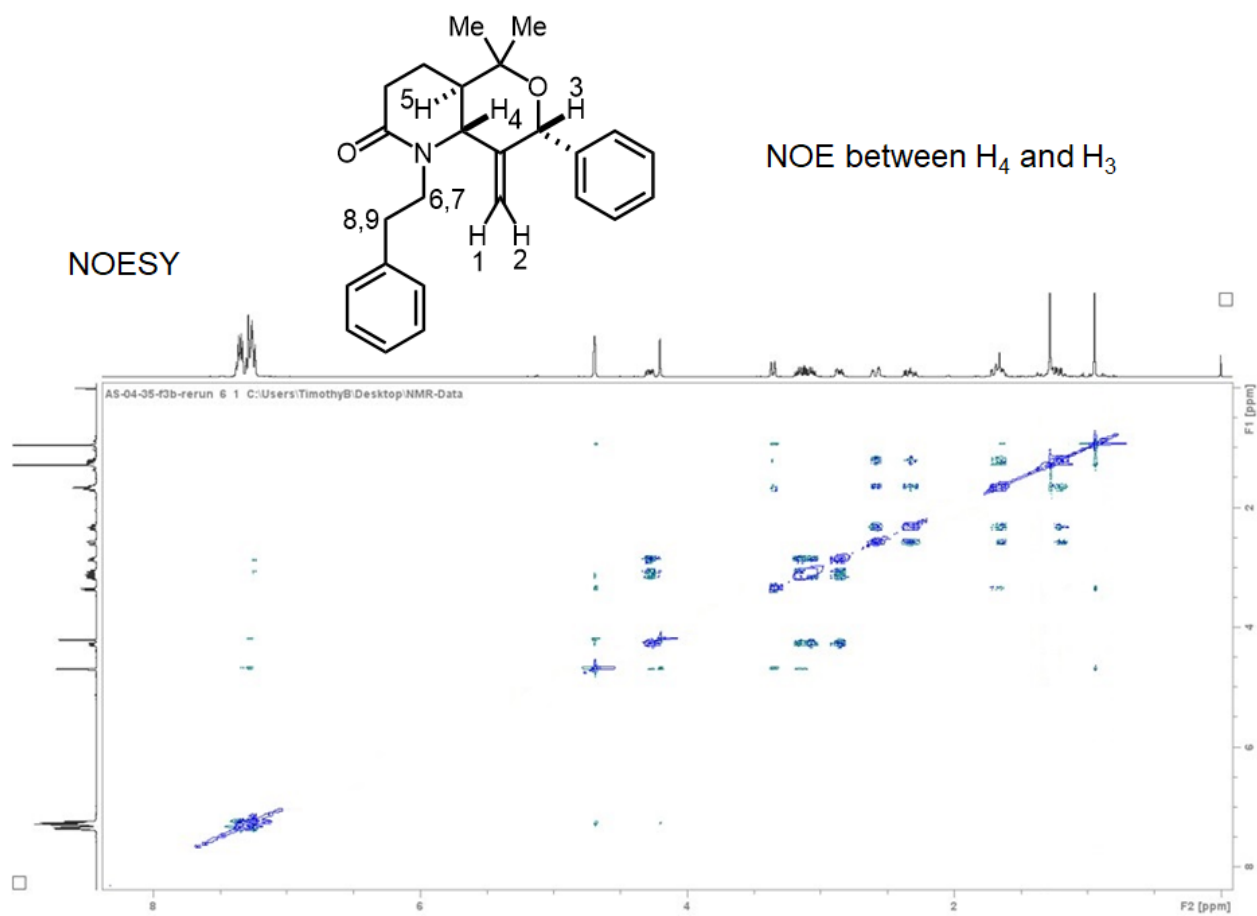
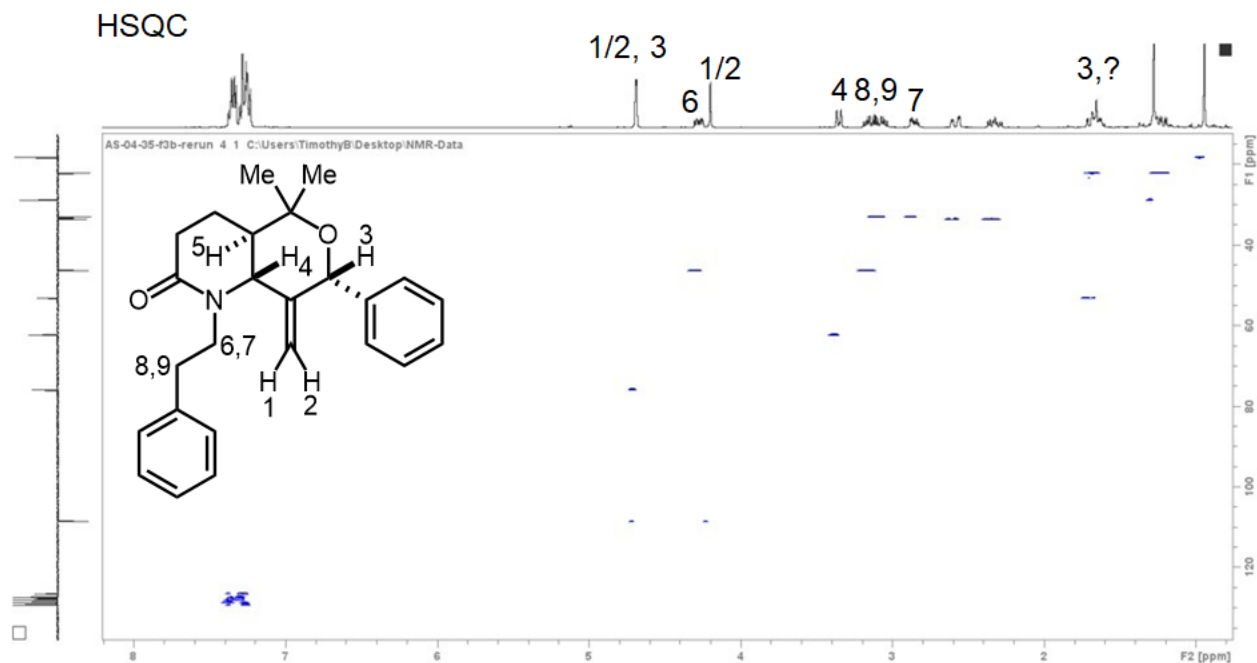


### Compound 4q

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Pale-yellowish oil. Yield = 337.9 mg, 90%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.23 (m, 10H), 4.74 – 4.69 (m, 2H), 4.30 (ddd,  $J = 12.6, 5.8, 3.8$  Hz, 1H), 4.23 (s, 1H), 3.38 (d,  $J = 11.2$  Hz, 1H), 3.14 (dddd,  $J = 32.6, 13.3, 9.9, 5.9$  Hz, 2H), 2.93 – 2.83 (m, 1H), 2.61 (ddd,  $J = 17.5, 4.3, 2.1$  Hz, 1H), 2.35 (ddd,  $J = 17.9, 13.2, 5.3$  Hz, 1H), 1.76 – 1.61 (m, 2H), 1.30 (s, 3H), 1.22 (td,  $J = 12.9, 4.1$  Hz, 1H), 0.97 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 149.8, 139.8, 138.6, 129.2, 128.6, 128.1, 127.8, 127.5, 126.6, 108.6, 75.9, 75.9, 62.4, 53.4, 46.3, 33.6, 33.1, 28.9, 22.2, 18.3. FTIR (KBr): 3009.7, 2933.6, 1647.4, 1607.2, 1577.1, 1512.0, 1454.2, 1427.6, 1359.8, 1299.2, 1250.9, 1176.0, 1151.5, 1119.6, 1031.3, 990.3, 927.8, 825.4, 765.0. **HRMS-EI $^+$**  ( $m/z$ ): calc for  $\text{C}_{25}\text{H}_{29}\text{NO}_2$  [ $\text{M}$ ] $^+$  375.2198, found 373.2195.

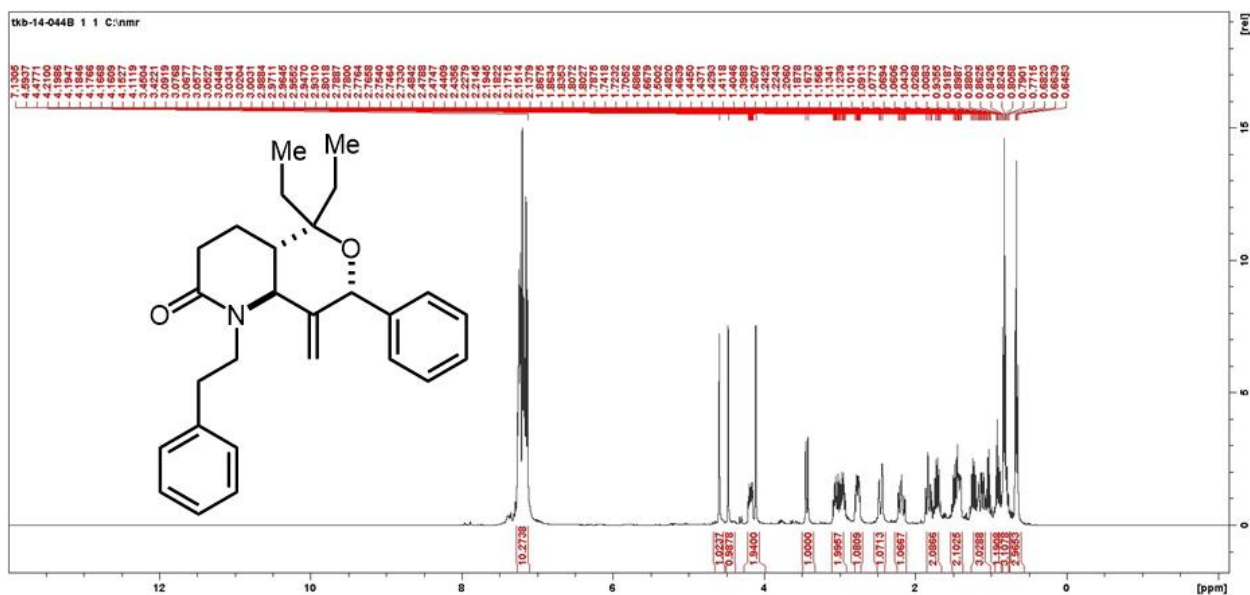


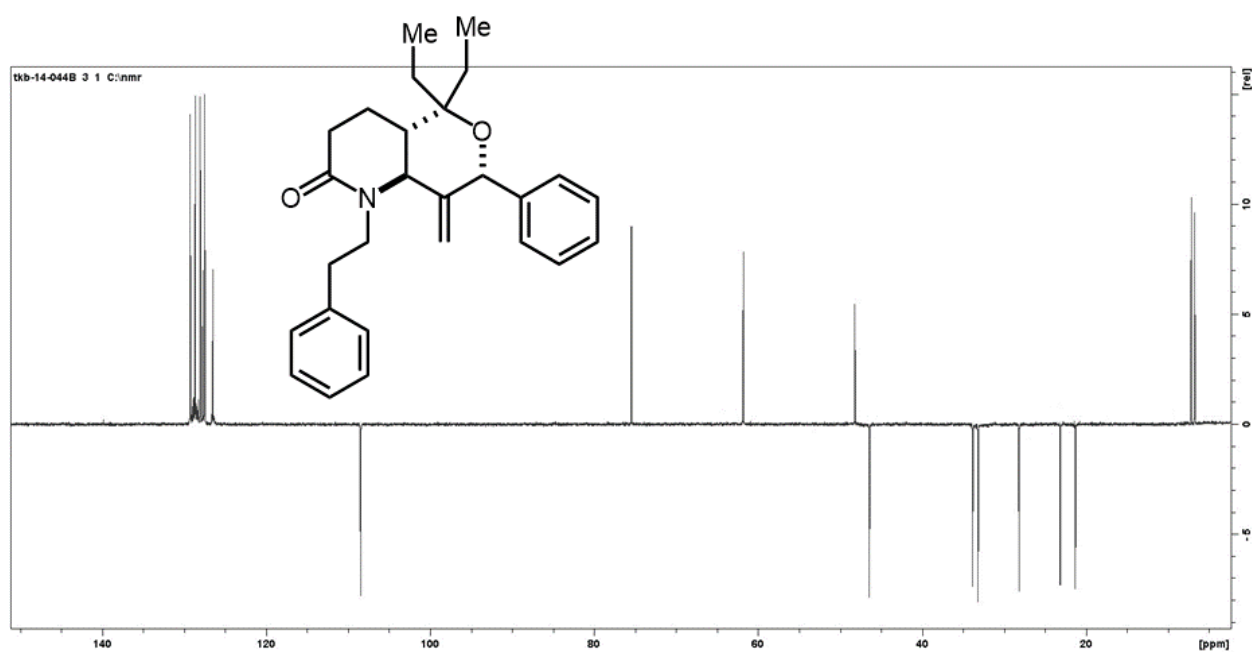
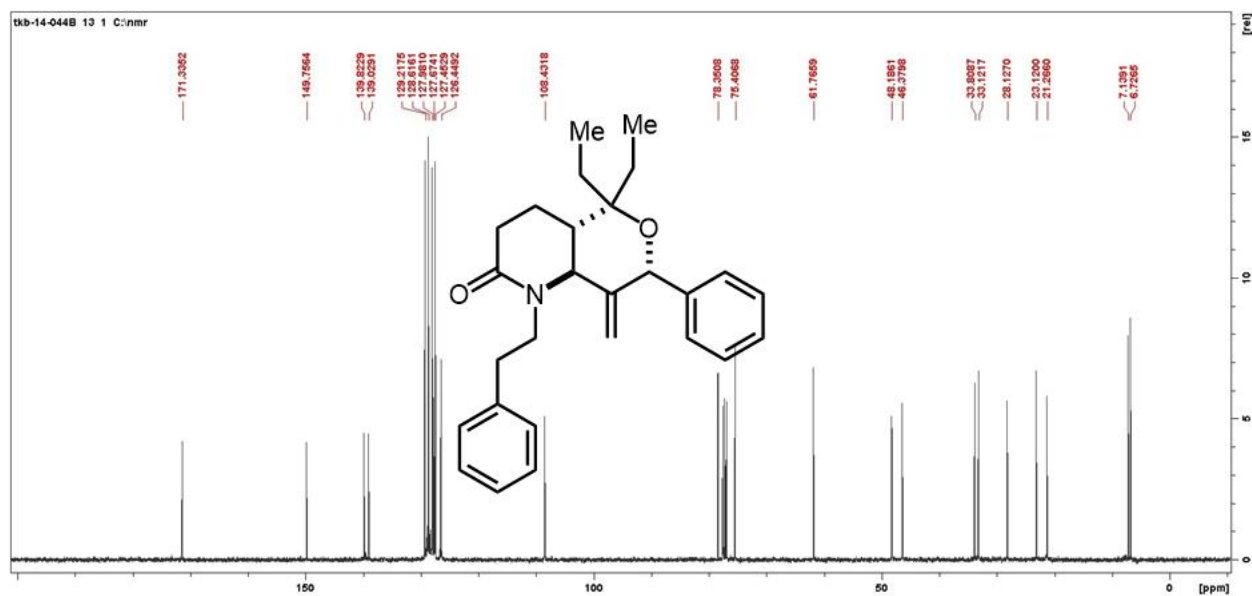




**Compound 4r**

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Pale-yellowish oil. Yield = 367.2 mg, 91%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.06 (m, 10H), 4.59 (s, 1H), 4.48 (s, 1H), 4.18 (ddd,  $J = 12.9, 6.1, 3.8$  Hz, 1H), 4.11 (s, 1H), 3.44 (d,  $J = 11.3$  Hz, 1H), 3.01 (dddd,  $J = 35.8, 13.2, 9.7, 6.1$  Hz, 2H), 2.82 – 2.71 (m, 1H), 2.53 – 2.39 (m, 1H), 2.18 (ddd,  $J = 17.8, 13.4, 5.5$  Hz, 1H), 1.89 – 1.77 (m, 1H), 1.71 (dq,  $J = 14.9, 7.5$  Hz, 1H), 1.56 – 1.37 (m, 2H), 1.30 – 1.07 (m, 2H), 1.10 – 0.70 (m, 5H), 0.66 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 149.7, 139.8, 139.0, 129.2, 128.8, 128.7, 128.6, 128.0, 127.7, 127.5, 126.4, 108.4, 78.3, 75.4, 61.8, 48.2, 46.4, 33.8, 33.1, 28.1, 23.1, 21.4, 7.1, 6.7. FTIR (KBr): 3029.4, 2924.0, 1724.9, 1646.3, 1474.3, 1452.8, 1361.9, 1342.0, 1205.6, 1140.2, 1071.7, 1028.3, 996.4, 775.4. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{27}\text{H}_{33}\text{NO}_2$   $[\text{M}]^+$  403.2511, found 403.2515.



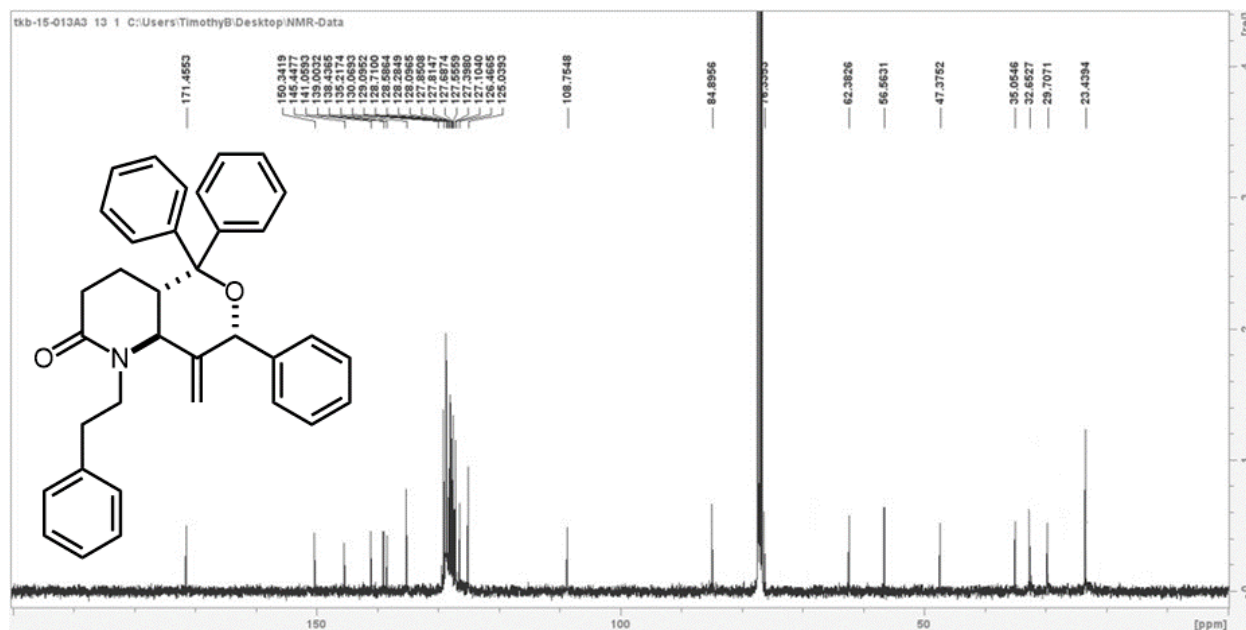


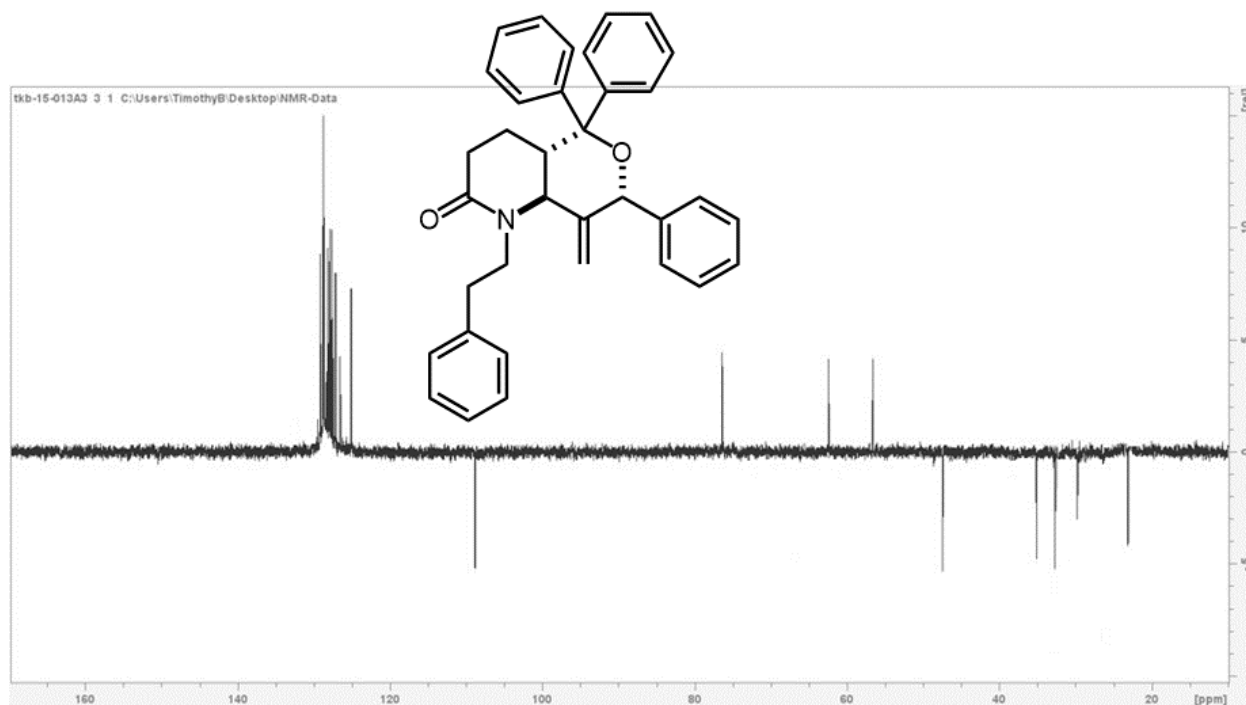
### Compound 4s

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 60:40). Amorphous solid. Yield = 434.7 mg, 87%, 95:5 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.11 (m, 20H), 4.79 (s, 1H), 4.73 (d, *J* = 1.4 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.13 (d, *J* = 11.6 Hz, 1H), 3.63 (s, 2H), 3.05 – 2.72 (m, 3H), 2.48 – 2.35 (m, 1H), 2.29 (ddd, *J* = 13.7, 11.5, 2.5 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.88 (dtd, *J* = 26.0, 12.0, 4.1 Hz, 1H), 1.55 – 1.39 (m, 1H), 1.19 (d, *J* = 2.5 Hz, 1H), 0.85 – 0.73 (m, 1H). <sup>13</sup>C NMR (101 MHz,



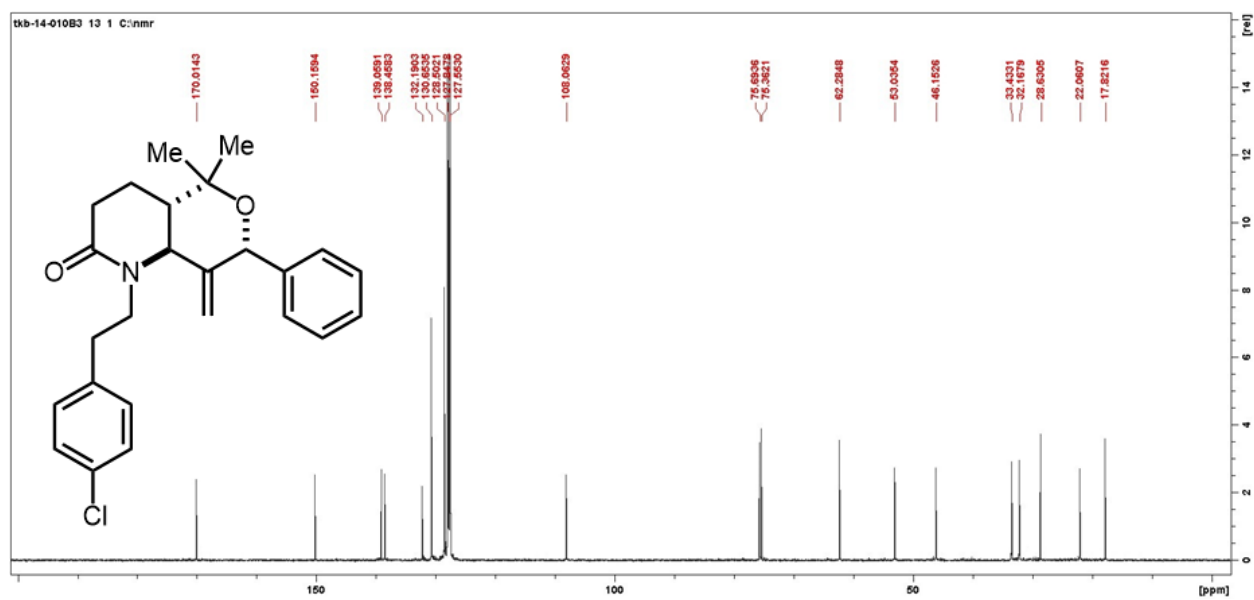
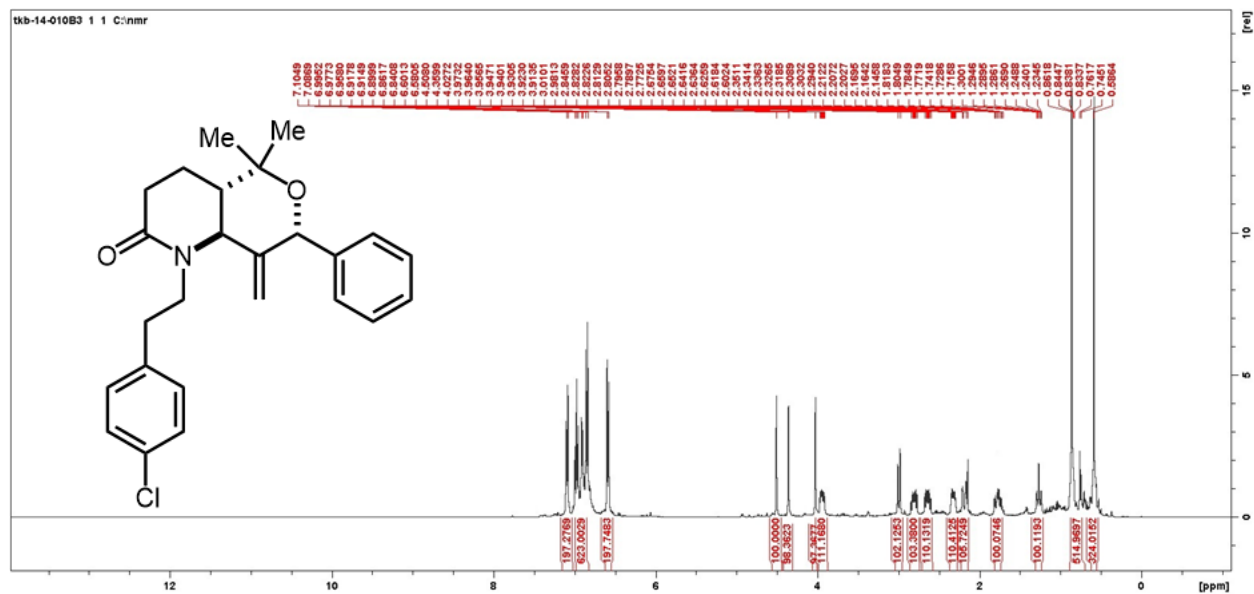
$\text{CDCl}_3$ )  $\delta$  171.5, 150.3, 145.4, 141.1, 139.0, 138.4, 135.2, 129.1, 128.7, 128.6, 128.3, 128.1, 127.8, 127.8, 127.7, 127.6, 127.1, 126.5, 125.0, 108.8, 84.9, 77.3, 77.2, 77.0, 76.7, 76.3, 67.1, 62.4, 56.6, 47.4, 35.1, 32.2, 29.7, 23.4. FTIR (KBr): 2971.4, 2923.9, 1644.4, 1491.4, 1446.8, 1429.3, 1391.6, 1362.4, 1318.9, 1292.6, 1268.8, 1223.0, 1199.5, 1151.3, 993.1, 905.3, 744.2. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{35}\text{H}_{33}\text{NO}_2$   $[\text{M}]^+$  499.2511, found 499.2514.

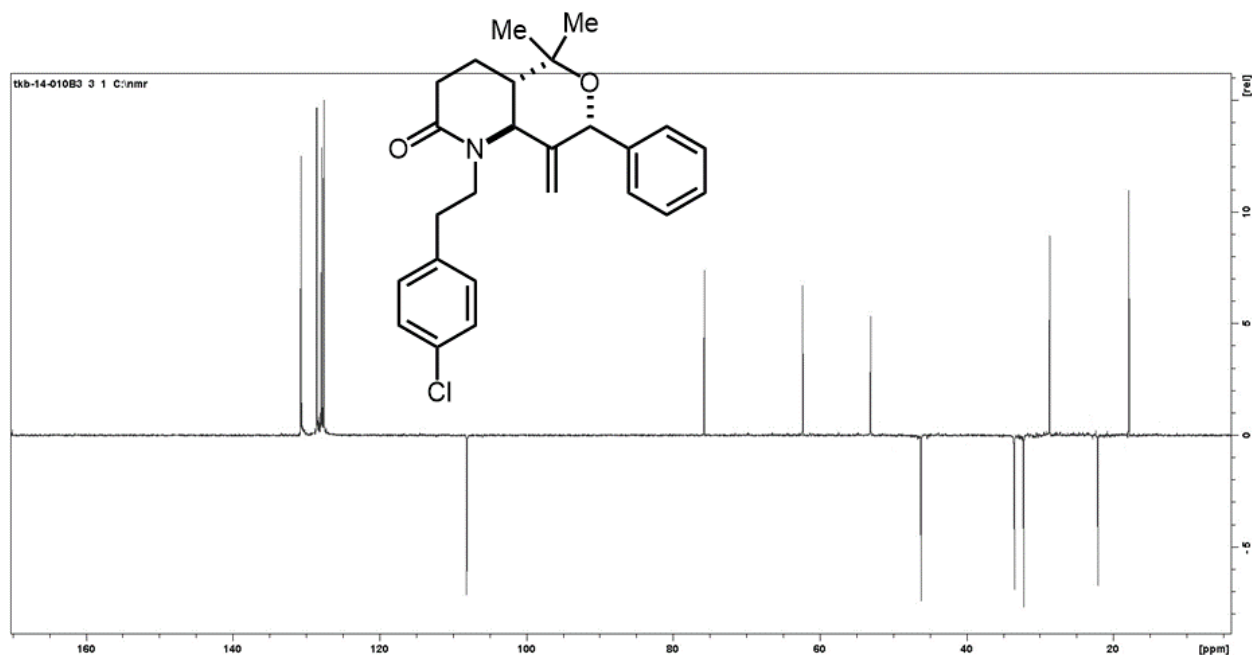




### Compound 4t

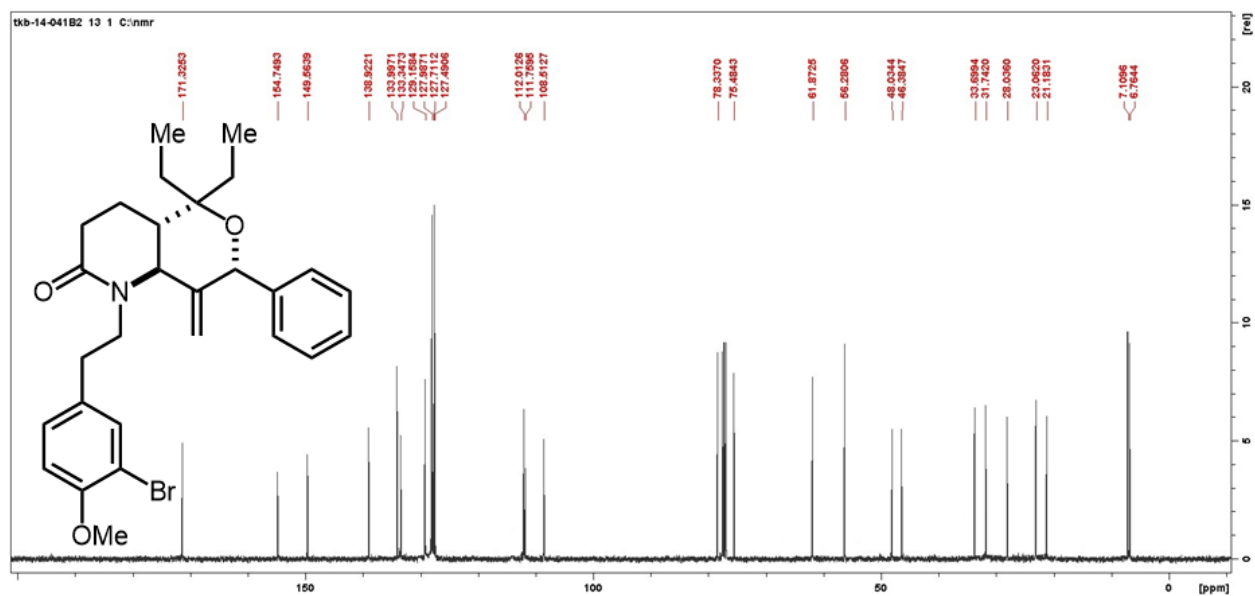
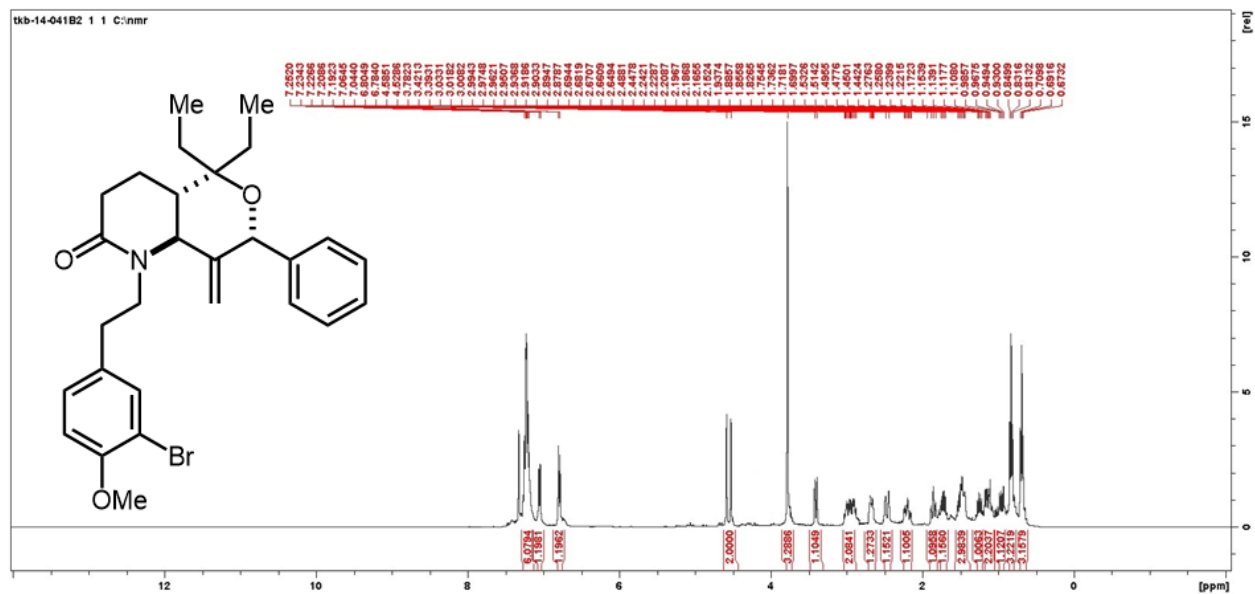
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Yellowish oil. Yield = 360.8 mg, 88%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.10 – 7.08 (m, 2H), 6.99 – 6.84 (m, 6H), 6.60 – 6.58 (m, 2H), 4.51 (s, 1H), 4.36 (d,  $J = 1.3$  Hz, 1H), 4.03 (s, 1H), 3.94 (ddd,  $J = 13.5, 6.9, 3.7$  Hz, 1H), 3.03 – 2.96 (m, 1H), 2.81 (ddd,  $J = 13.1, 9.4, 6.8$  Hz, 1H), 2.64 (ddd,  $J = 13.5, 9.4, 6.3$  Hz, 1H), 2.32 (ddd,  $J = 13.2, 6.2, 3.7$  Hz, 1H), 2.27 – 2.09 (m, 1H), 1.84 – 1.68 (m, 1H), 1.27 (tt,  $J = 11.4, 2.4$  Hz, 1H), 0.91 – 0.48 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  170.0, 150.2, 139.1, 138.5, 132.2, 130.7, 128.5, 127.9, 127.8, 127.7, 127.6, 127.5, 108.1, 75.7, 75.4, 62.3, 53.0, 46.2, 33.4, 32.3, 28.6, 22.1, 17.8. FTIR (KBr): 2934.2, 1721.2, 1652.1, 1511.3, 1448.8, 1414.9, 1341.3, 1298.4, 1245.2, 1139.4, 1075.9, 1032.9, 999.4, 832.0, 734.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{25}\text{H}_{28}\text{ClNO}_2$   $[\text{M}]^+$  409.1809, found 409.1812.

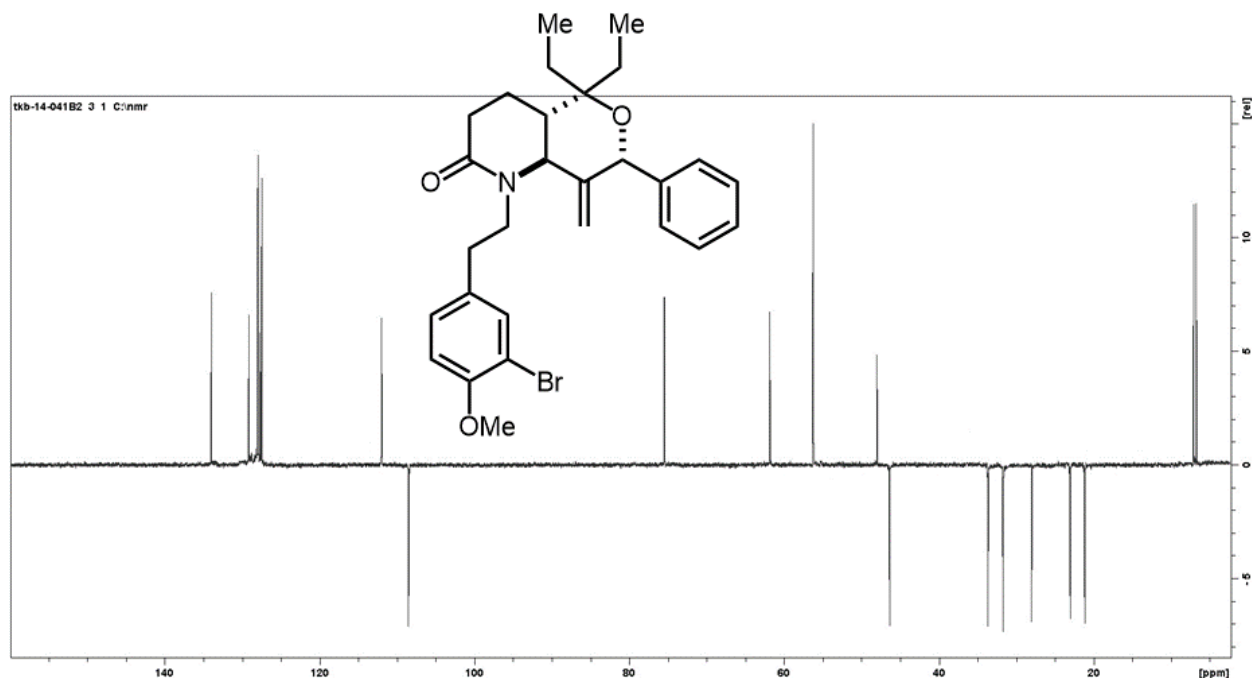




### Compound 4u

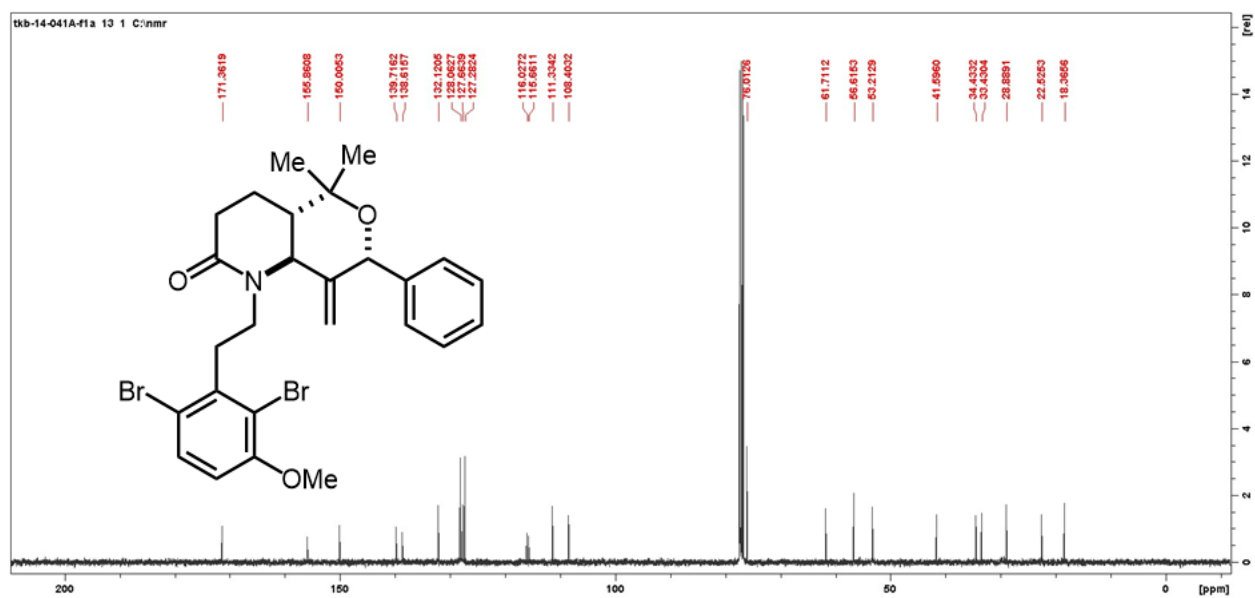
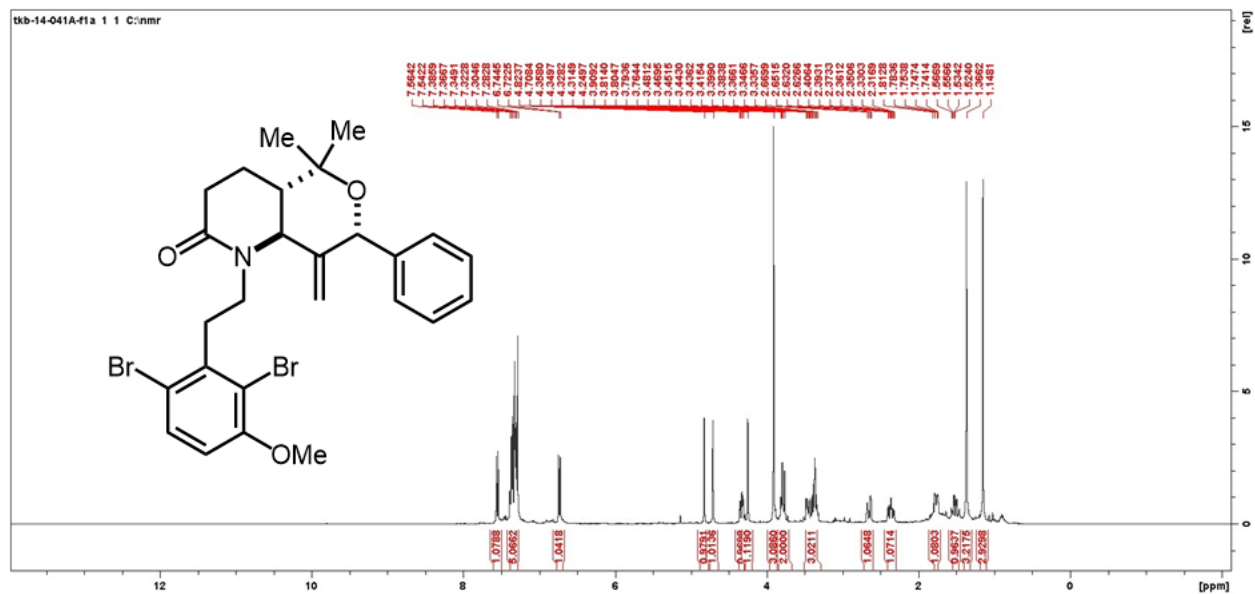
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Yellowish oil. Yield = 456.3 mg, 89%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.19 (m, 6H), 7.05 (dd,  $J = 8.3, 2.1$  Hz, 1H), 6.79 (d,  $J = 8.3$  Hz, 1H), 4.59 (s, 1H), 4.53 (s, 1H), 3.78 (s, 3H), 3.41 (d,  $J = 11.3$  Hz, 1H), 3.06 – 2.85 (m, 2H), 2.75 – 2.61 (m, 1H), 2.54 – 2.42 (m, 1H), 2.20 (ddd,  $J = 17.8, 13.3, 5.5$  Hz, 1H), 1.91 – 1.78 (m, 1H), 1.81 – 1.66 (m, 1H), 1.48 (ddd,  $J = 16.3, 11.6, 6.3$  Hz, 2H), 1.32 – 0.95 (m, 3H), 0.97 – 0.75 (m, 4H), 0.69 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 162.5, 154.7, 149.6, 138.9, 134.0, 133.7, 133.3, 130.1, 130.0, 129.7, 129.2, 129.0, 128.8, 128.2, 128.0, 127.7, 127.7, 127.5, 127.4, 127.3, 114.0, 112.0, 111.8, 108.5, 78.3, 75.5, 61.9, 56.3, 48.0, 46.4, 33.7, 31.7, 28.0, 23.1, 21.2, 7.1, 6.8. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{28}\text{H}_{34}\text{BrNO}_3$   $[\text{M}]^+$  511.1722, found 511.1726.

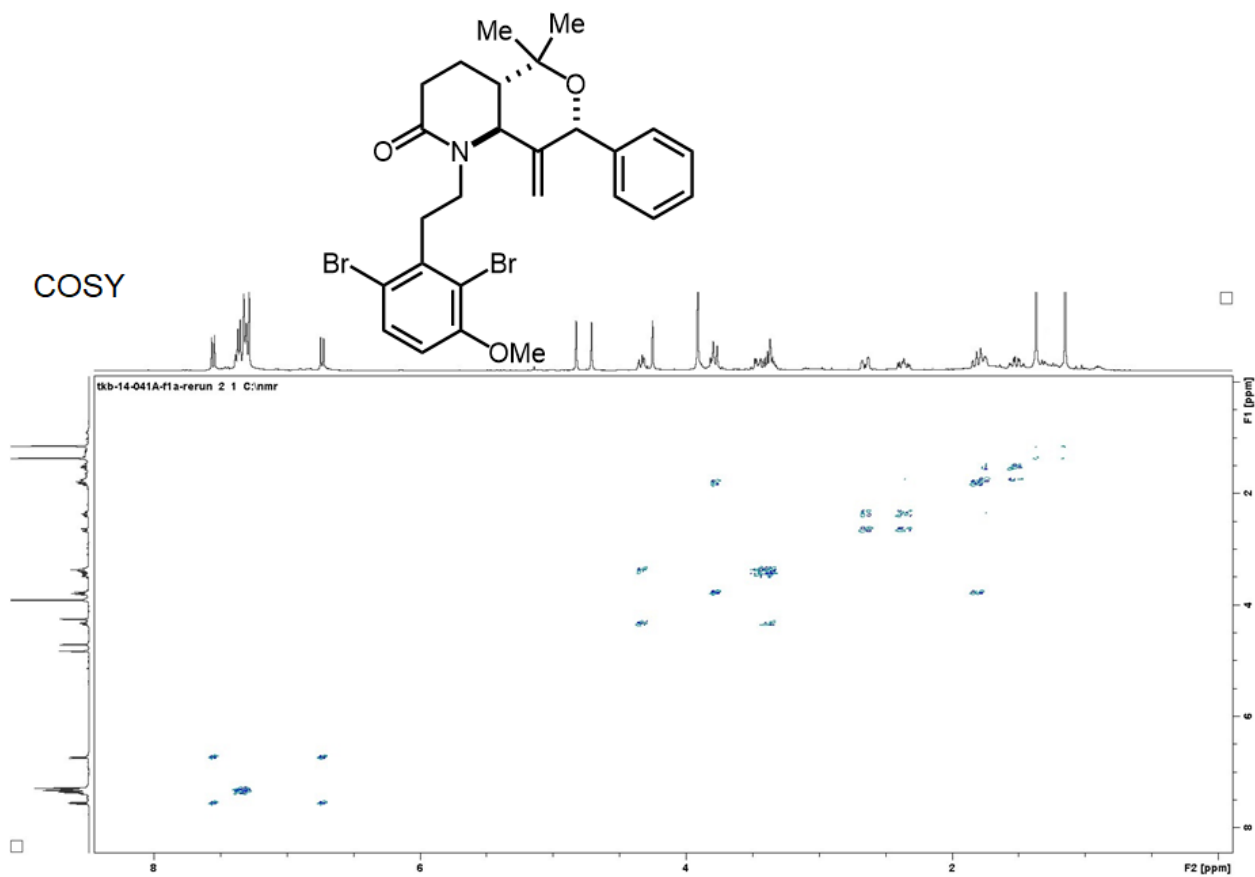
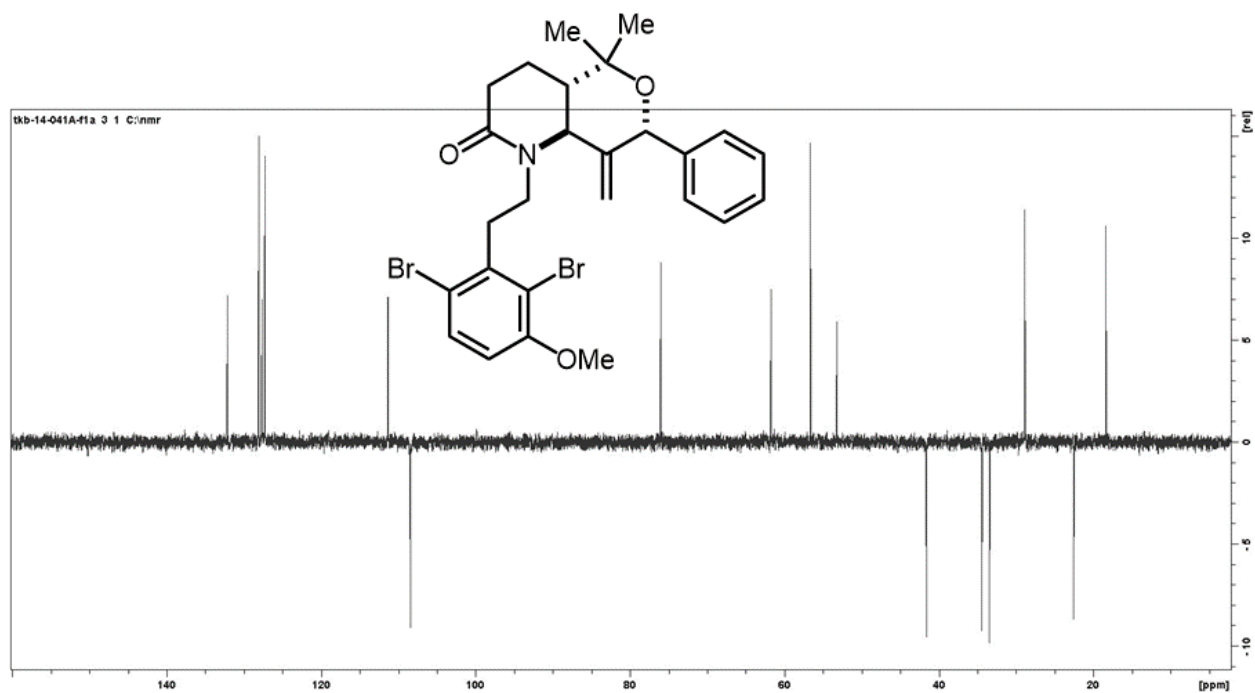




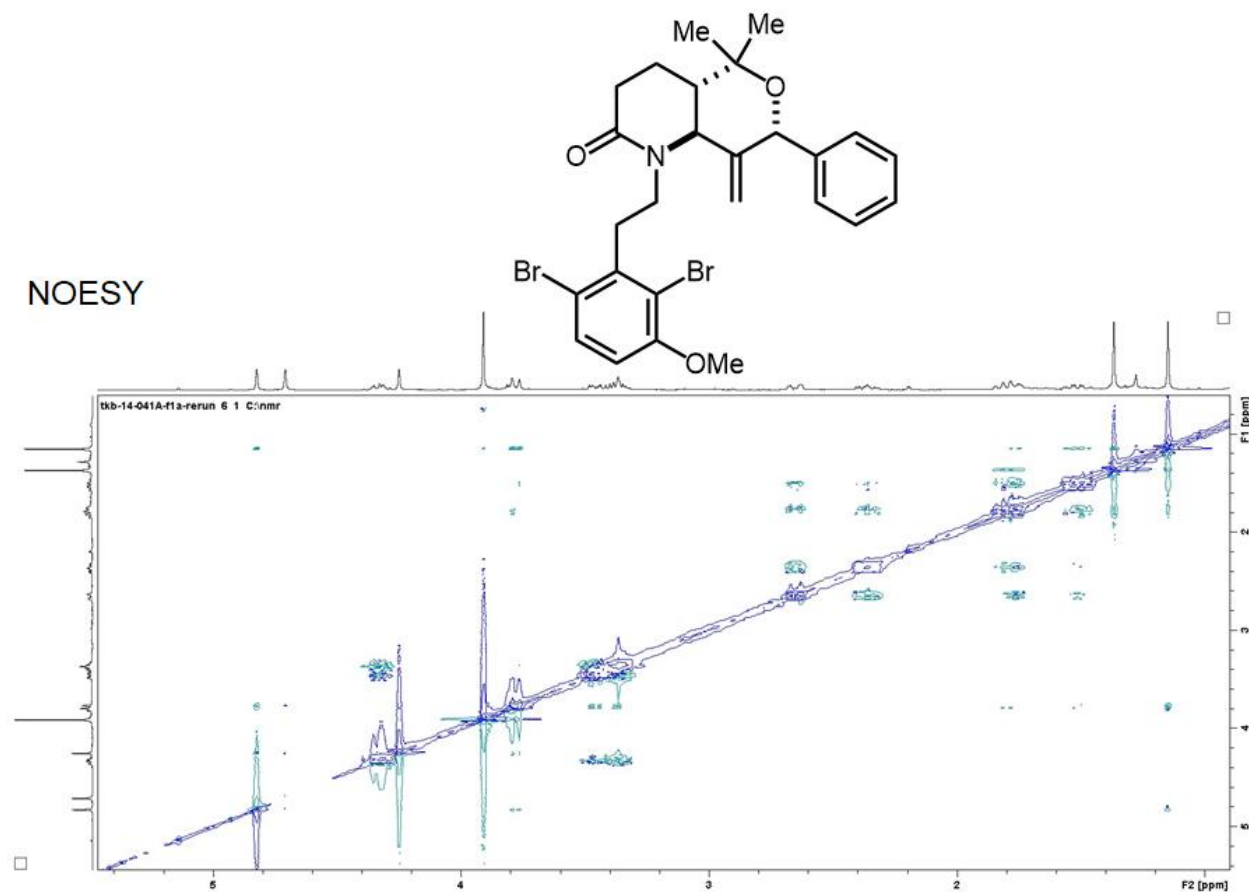
### Compound 4v

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Yellowish oil. Yield = 473.2 mg, 84%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.8$  Hz, 1H), 7.41 – 7.28 (m, 5H), 6.73 (d,  $J = 8.8$  Hz, 1H), 4.82 (s, 1H), 4.71 (s, 1H), 4.32 (td,  $J = 11.7, 6.4$  Hz, 1H), 4.25 (s, 1H), 3.91 (s, 3H), 3.85 – 3.74 (m, 2H), 3.53 – 3.30 (m, 3H), 2.70 – 2.60 (m, 1H), 2.36 (ddd,  $J = 17.8, 13.2, 5.4$  Hz, 1H), 1.87 – 1.71 (m, 1H), 1.51 (qd,  $J = 12.9, 4.3$  Hz, 1H), 1.37 (s, 3H), 1.15 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 155.9, 150.0, 139.7, 138.6, 132.1, 128.1, 127.7, 127.3, 116.0, 115.7, 111.3, 108.4, 76.5, 76.0, 61.7, 56.6, 53.2, 41.6, 34.4, 33.4, 28.9, 22.5, 18.4. **HRMS-EI $^+$**  ( $m/z$ ): calc for  $\text{C}_{26}\text{H}_{29}\text{Br}_2\text{NO}_3$  [ $\text{M}$ ] $^+$  561.0514, found 561.0519.



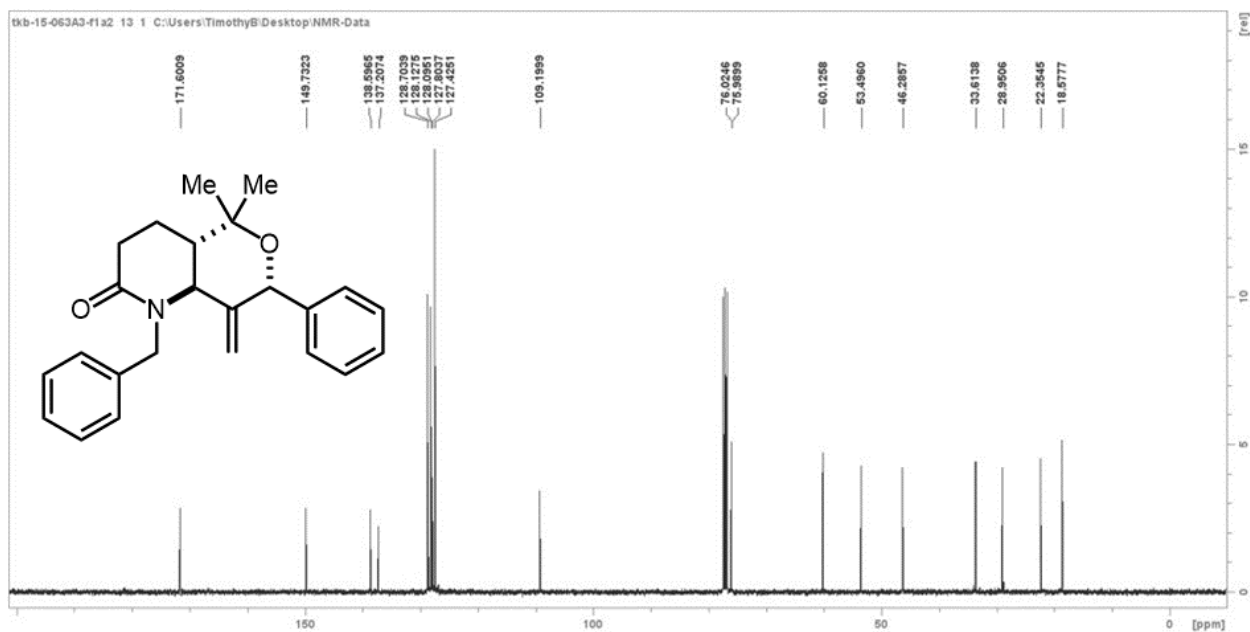
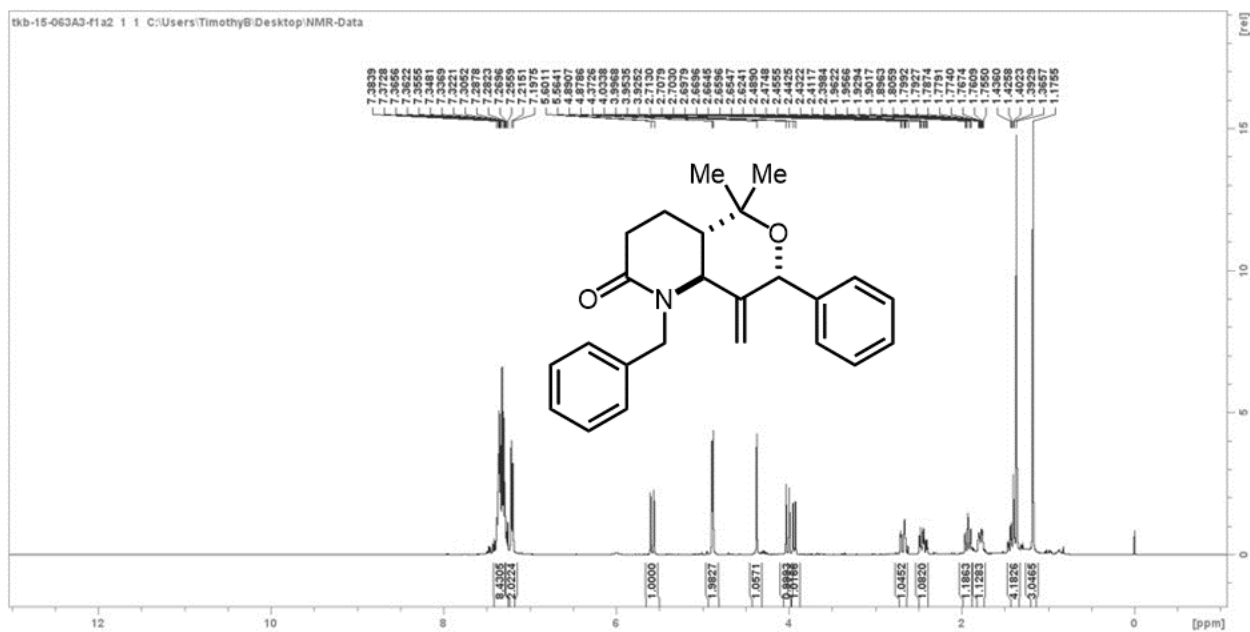


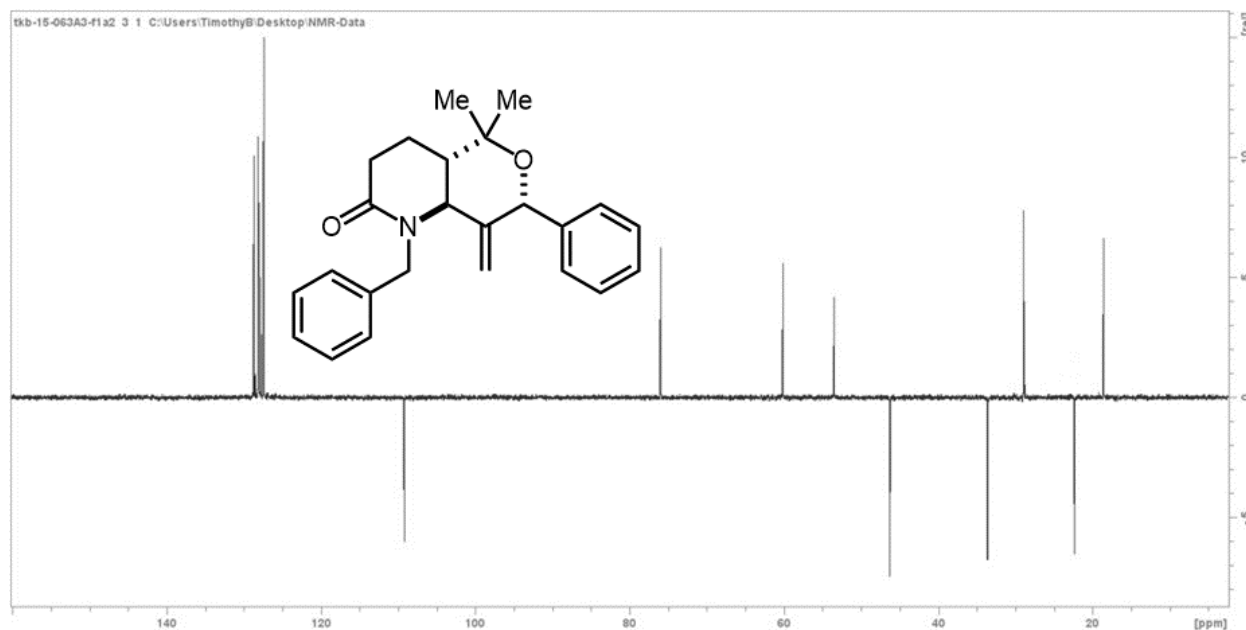




### Compound 4w

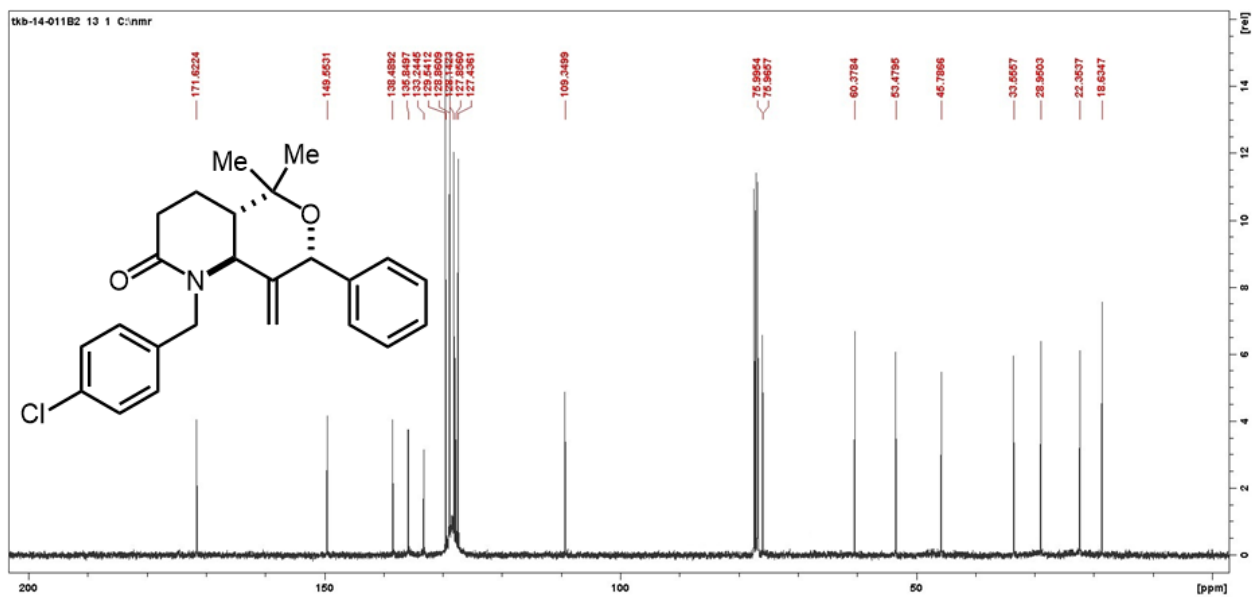
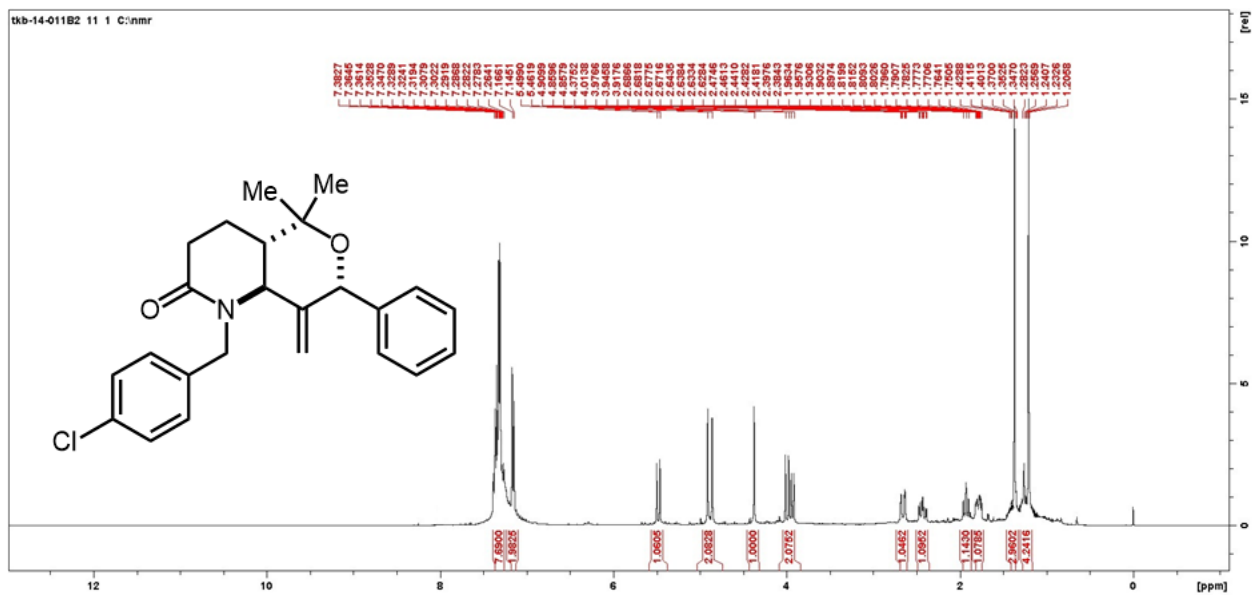
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 310.9 mg, 86%, 95:5 dr. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>24</sub>H<sub>27</sub>NO<sub>2</sub> [M]<sup>+</sup> 361.2042, found 361.2044.

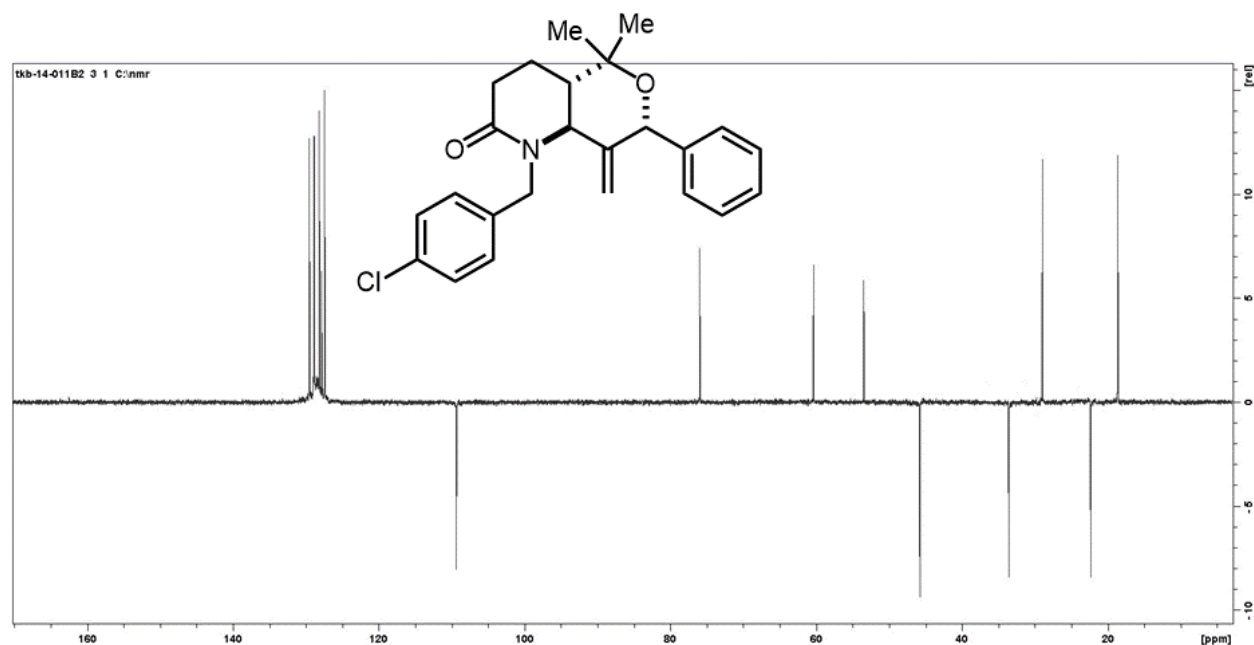




### Compound 4x

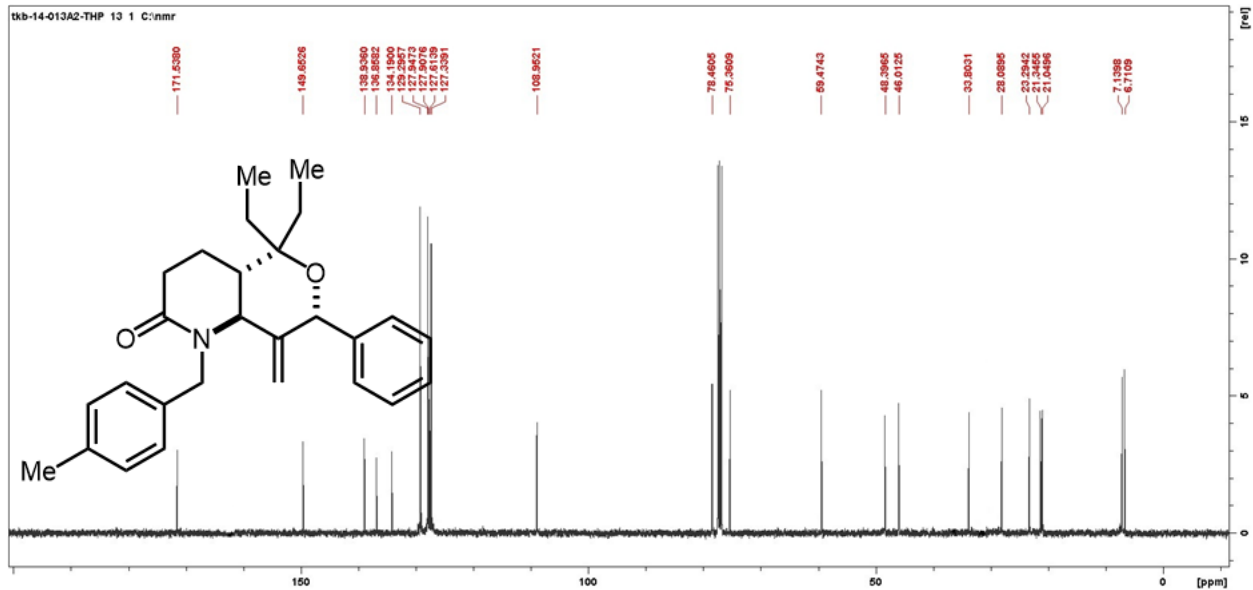
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 348.4 mg, 88%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.26 (m, 7H), 7.16 (d,  $J$  = 8.2 Hz, 2H), 5.48 (d,  $J$  = 14.8 Hz, 1H), 4.91 (s, 1H), 4.88–4.83 (m, 1H), 4.38 (s, 1H), 3.99 (d,  $J$  = 14.9 Hz, 1H), 3.93 (d,  $J$  = 11.3 Hz, 1H), 2.66 (ddd,  $J$  = 17.4, 4.1, 2.1 Hz, 1H), 2.43 (ddd,  $J$  = 17.7, 13.4, 5.3 Hz, 1H), 1.93 (ddd,  $J$  = 13.3, 11.2, 2.4 Hz, 1H), 1.84–1.73 (m, 1H), 1.43–1.21 (m, 7H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 149.5, 138.5, 135.8, 133.2, 129.5, 129.0, 128.9, 128.7, 128.4, 128.1, 127.4, 109.3, 76.0, 75.9, 60.4, 53.5, 45.8, 33.6, 28.9, 22.4, 18.6. FTIR (KBr): 3039.4, 2904.0, 1724.9, 1646.3, 1474.3, 1452.8, 1361.9, 1342.0, 1205.6, 1140.2, 1071.7, 986.4, 765.4. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{24}\text{H}_{26}\text{ClNO}_2$   $[\text{M}]^+$  395.1652, found 395.1657.

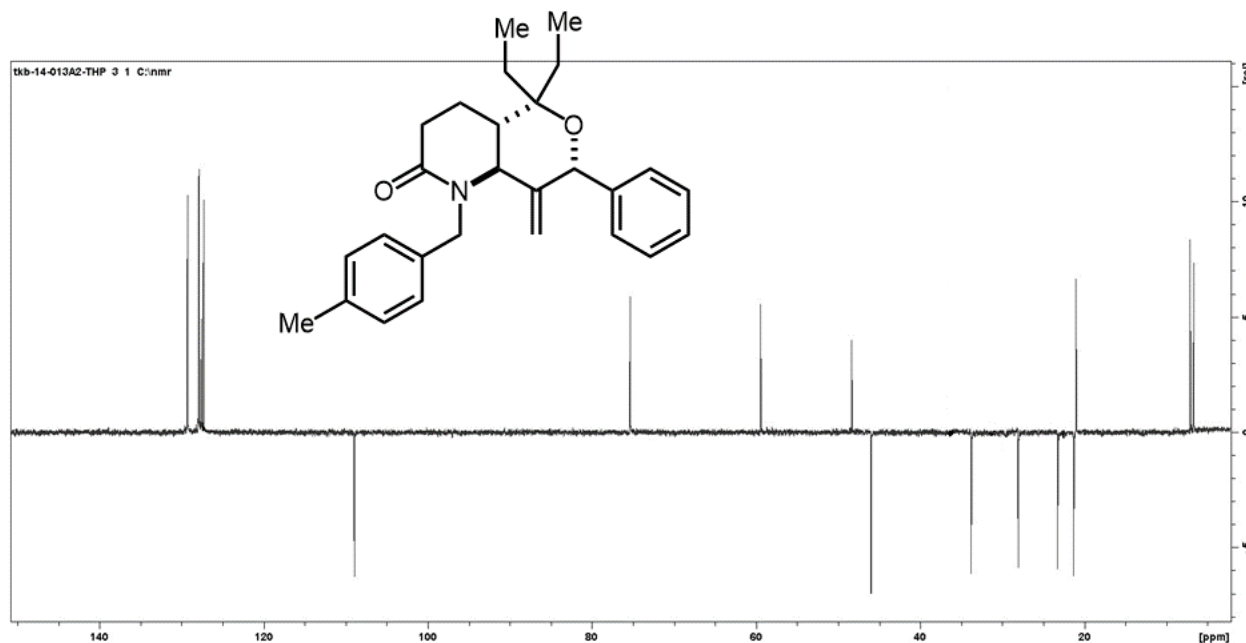




### Compound 4y

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 371.3 mg, 92%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.19 (m, 5H), 7.13 – 7.00 (m, 4H), 5.45 (d,  $J$  = 14.8 Hz, 1H), 4.80 (s, 1H), 4.68 (s, 1H), 4.29 (s, 1H), 4.02 (d,  $J$  = 11.4 Hz, 1H), 3.90 (d,  $J$  = 14.8 Hz, 1H), 2.57 (ddd,  $J$  = 17.2, 4.2, 2.1 Hz, 1H), 2.39 – 2.19 (m, 4H), 2.09 (ddd,  $J$  = 13.4, 11.3, 2.3 Hz, 1H), 1.83 (ddq,  $J$  = 14.7, 11.2, 7.4 Hz, 2H), 1.58 (ddt,  $J$  = 12.7, 5.0, 2.2 Hz, 1H), 1.33 (tdd,  $J$  = 12.5, 7.9, 3.4 Hz, 2H), 1.24 – 1.02 (m, 3H), 0.91 (t,  $J$  = 7.4 Hz, 3H), 0.73 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 149.7, 139.0, 136.9, 134.3, 129.4, 129.0, 128.0, 127.7, 127.4, 109.1, 78.5, 75.5, 59.5, 48.5, 46.1, 33.9, 28.2, 23.4, 21.4, 21.1, 7.2, 6.8. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{27}\text{H}_{33}\text{NO}_2$   $[\text{M}]^+$  403.2511, found 403.2514.



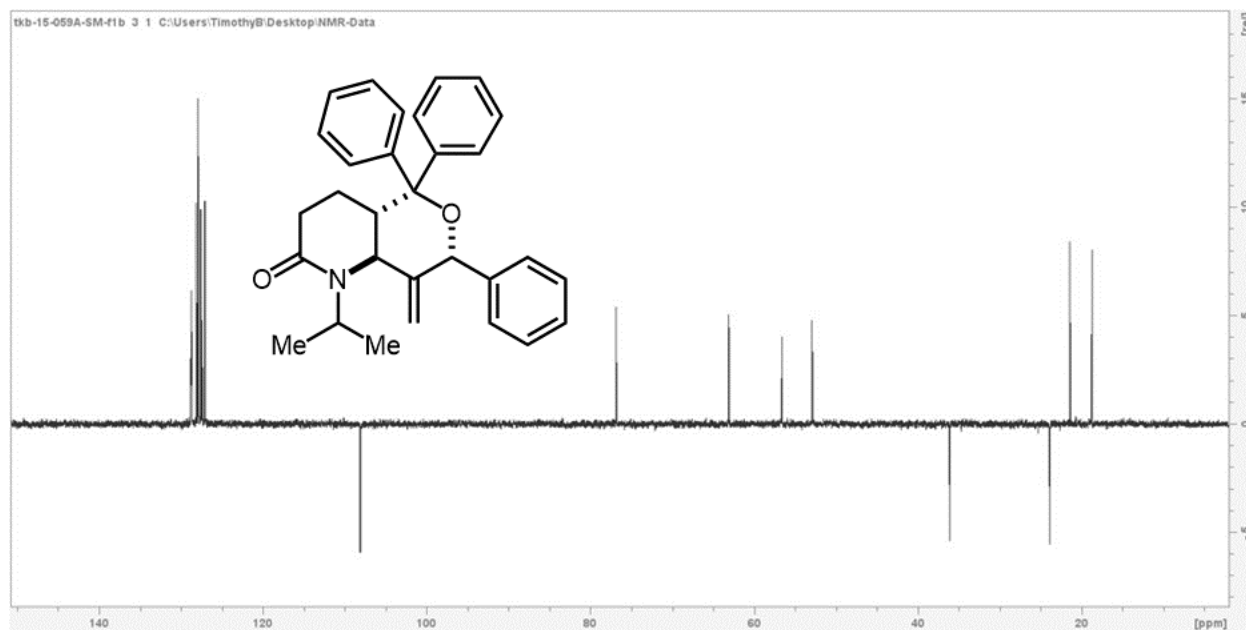


### Compound 4z

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Yellowish oil. Yield = 380.7 mg, 87%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.64 (m, 2H), 7.48 – 7.24 (m, 13H), 5.10 (s, 1H), 5.01 (s, 1H), 4.47 (d,  $J = 11.5$  Hz, 1H), 4.38 (s, 1H), 3.24 (hept,  $J = 6.8$  Hz, 1H), 2.54 (ddd,  $J = 13.4, 11.5, 3.1$  Hz, 1H), 2.40 (dt,  $J = 15.6, 2.9$  Hz, 1H), 2.26 – 2.04 (m, 2H), 1.68 – 1.49 (m, 4H), 1.36 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 151.5, 145.4, 141.4, 138.6, 128.8, 128.7, 128.1, 127.9, 127.6, 127.4, 127.1, 108.1, 85.2, 76.9, 63.1, 56.6, 52.9, 36.1, 23.9, 21.4, 18.8. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{30}\text{H}_{31}\text{NO}_2$   $[\text{M}]^+$  437.2355, found 437.2359.

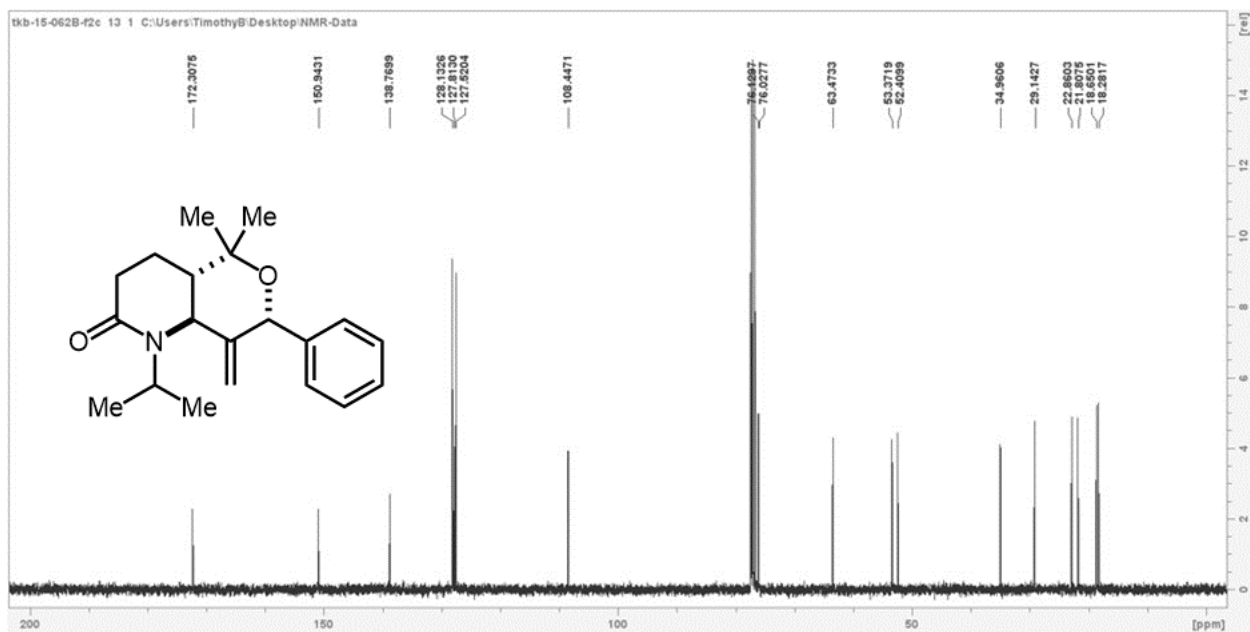
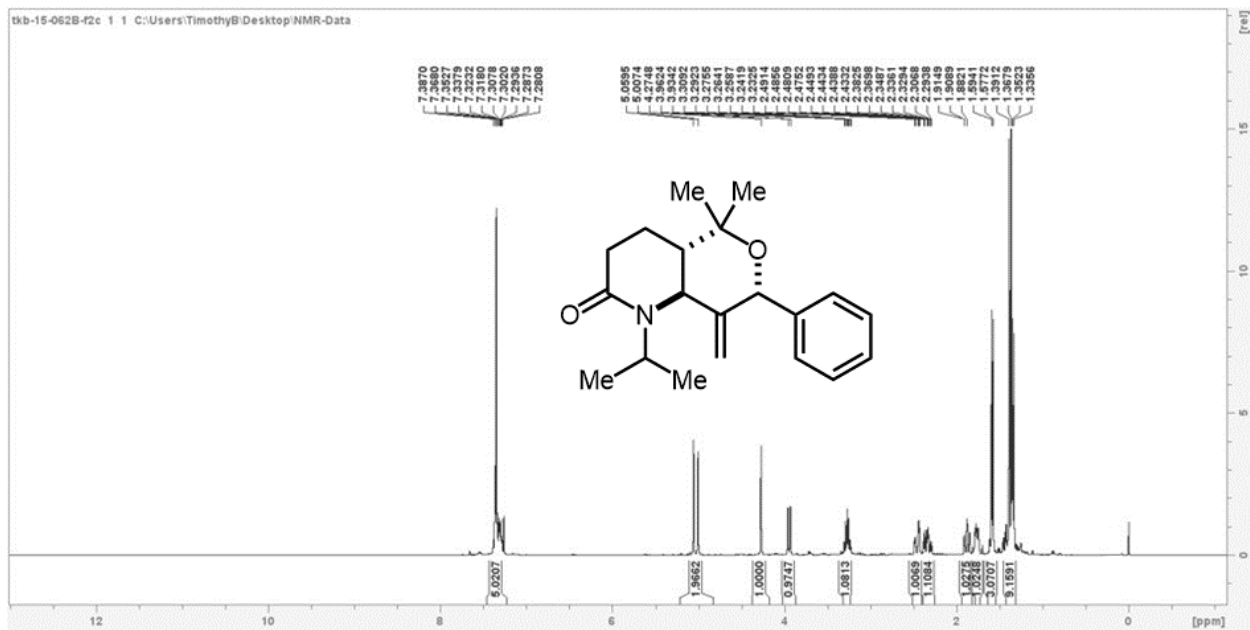


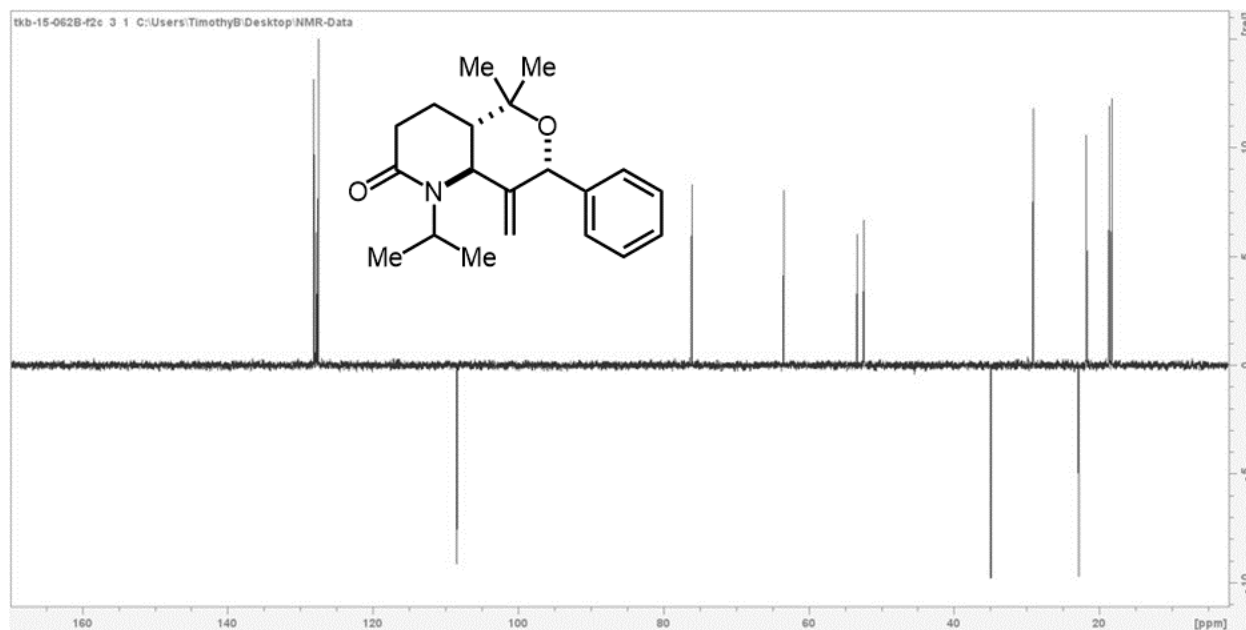




### Compound 4z1

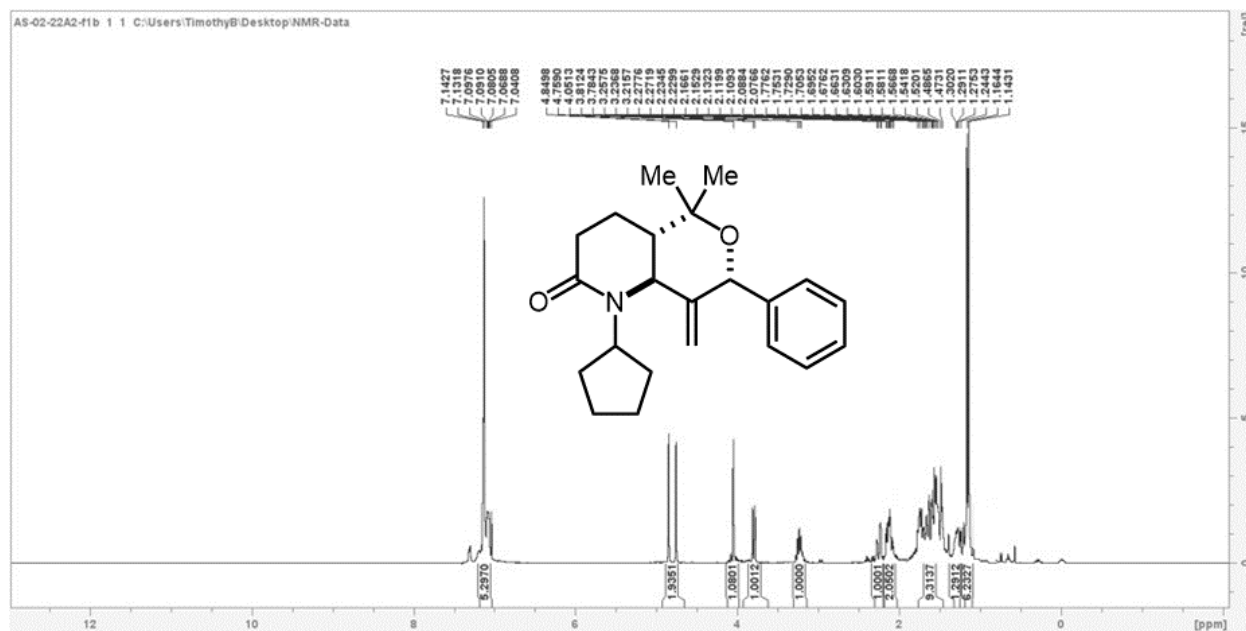
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 282.1 mg, 90%, 95:5 dr.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.31 (m, 5H), 5.06 (s, 1H), 5.01 (d,  $J = 1.4$  Hz, 1H), 4.28 (s, 1H), 3.95 (d,  $J = 11.2$  Hz, 1H), 3.28 (hept,  $J = 6.6$  Hz, 1H), 2.46 (ddd,  $J = 16.8, 4.3, 2.3$  Hz, 1H), 2.34 (ddd,  $J = 16.8, 13.5, 5.2$  Hz, 1H), 1.94 – 1.65 (m, 3H), 1.60 – 1.43 (m, 4H), 1.45 – 1.33 (m, 8H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 150.9, 138.8, 128.1, 127.8, 127.5, 108.4, 76.1, 76.0, 63.5, 53.4, 52.4, 34.9, 29.1, 22.9, 21.8, 18.6, 18.3. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{20}\text{H}_{27}\text{NO}_2$   $[\text{M}]^+$  313.2042, found 313.2047.

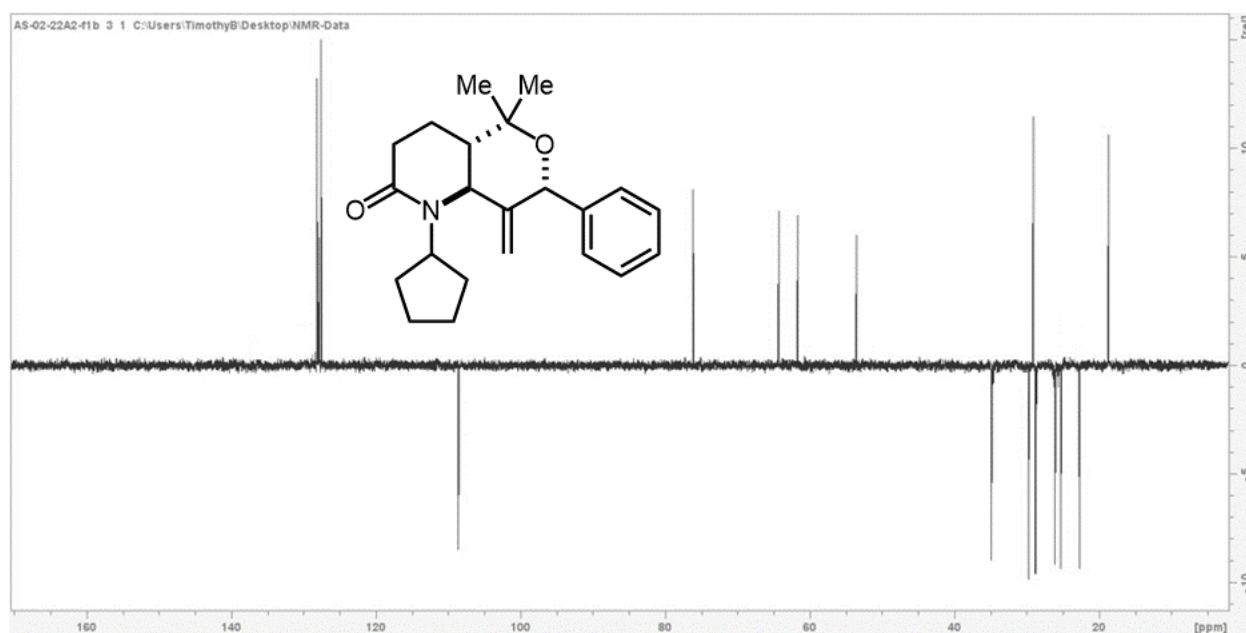
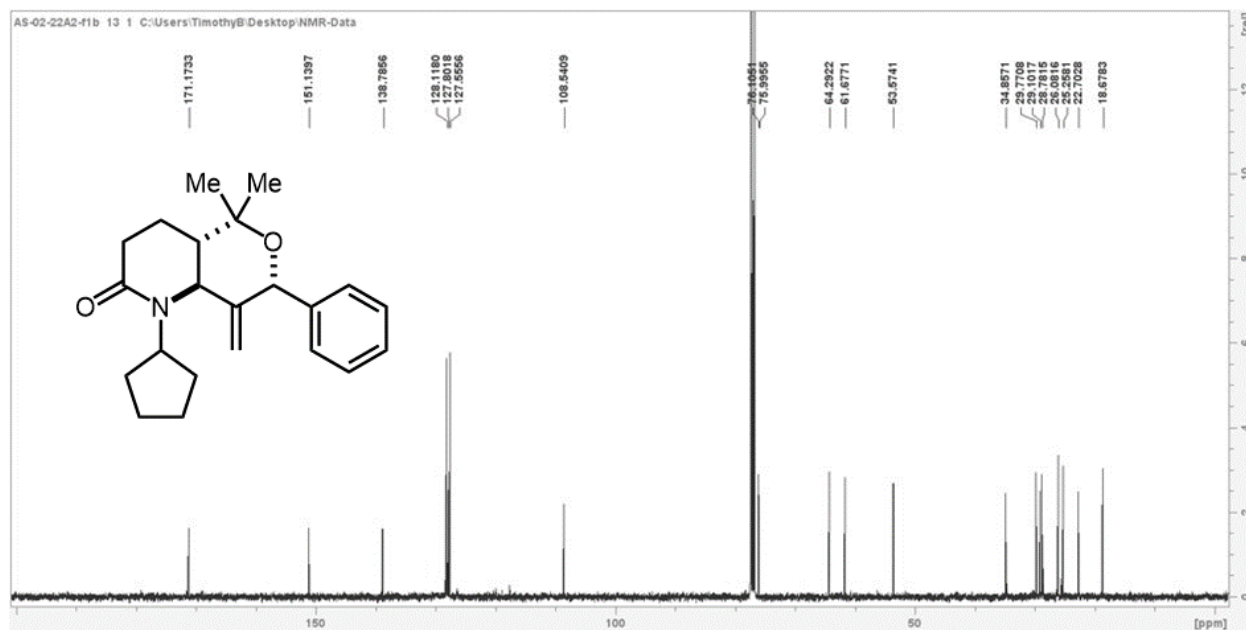




### Compound 4z2

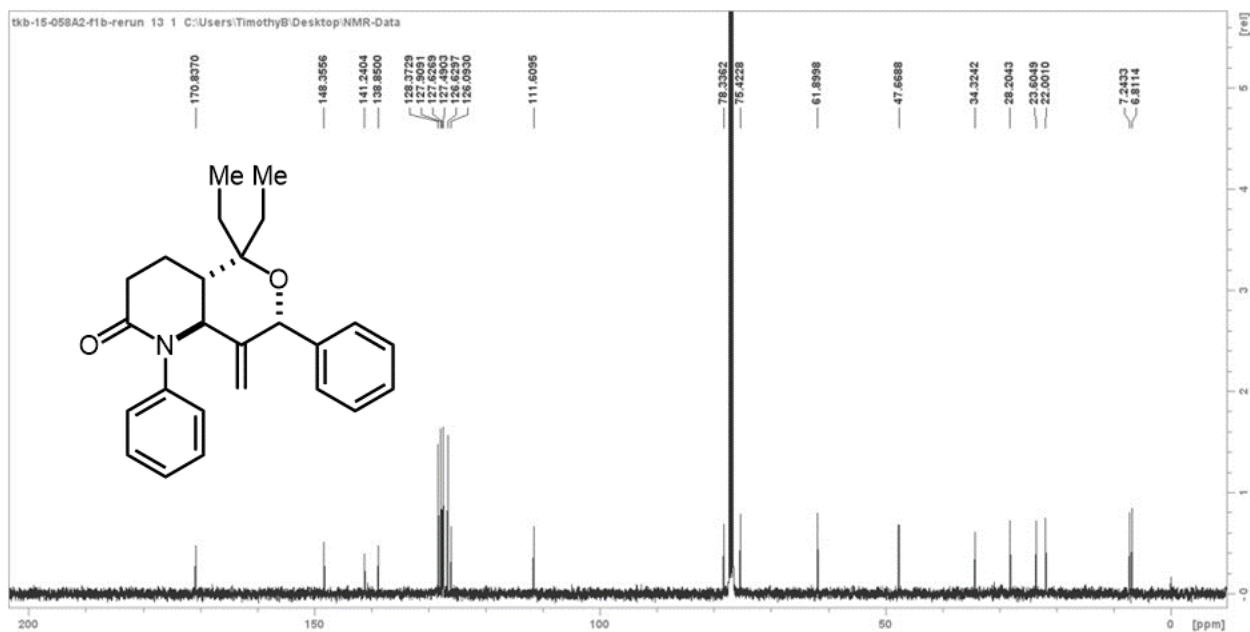
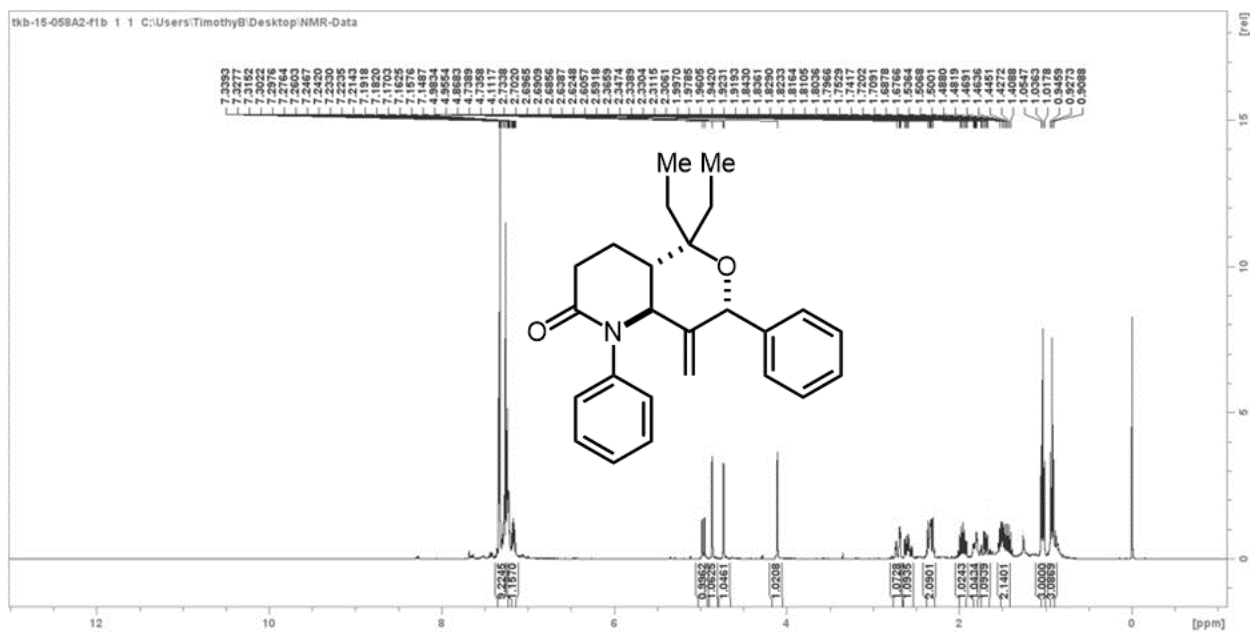
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Yellowish oil. Yield = 288.6 mg, 85%, 95:5 dr. FTIR (KBr): 2984.1, 1733.5, 1654.3, 1606.9, 1511.0, 1448.5, 1414.7, 1384.9, 1357.4, 1299.7, 1242.5, 1179.3, 1031.8, 994.9, 823.7, 735.2. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for C<sub>22</sub>H<sub>29</sub>NO<sub>2</sub> [M]<sup>+</sup> 339.2198, found 339.2195.

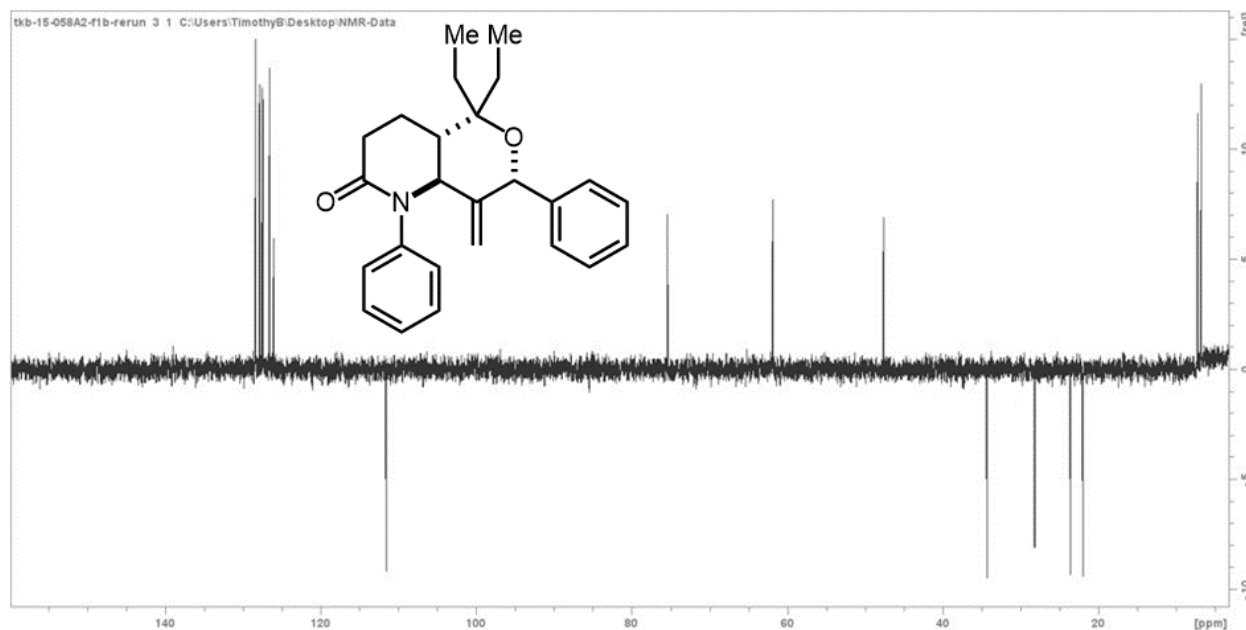




### Compound 4z3

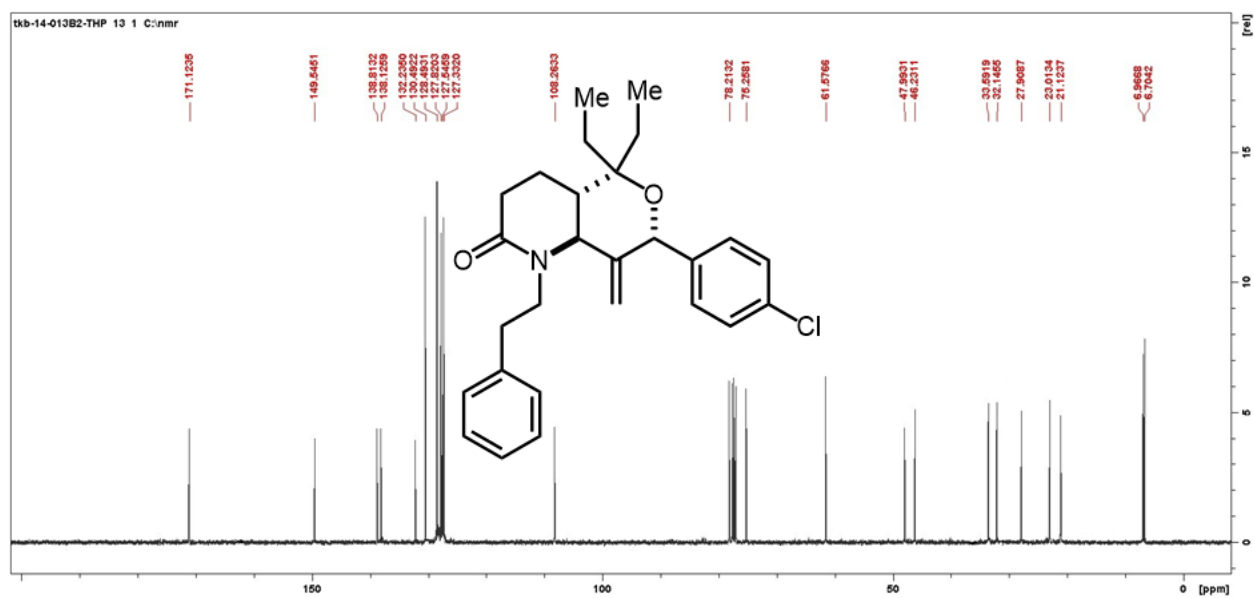
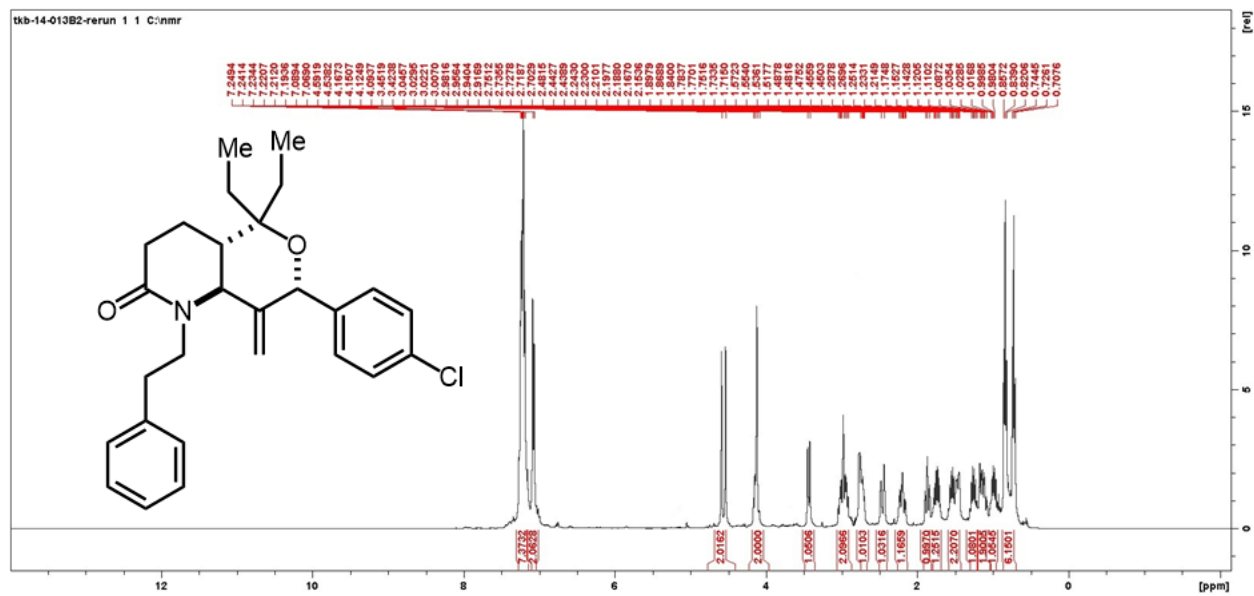
Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Yellowish oil. Yield = 311.7 mg, 83%, 95:5 dr. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>25</sub>H<sub>29</sub>NO<sub>2</sub> [M]<sup>+</sup> 375.2198, found 375.2194.

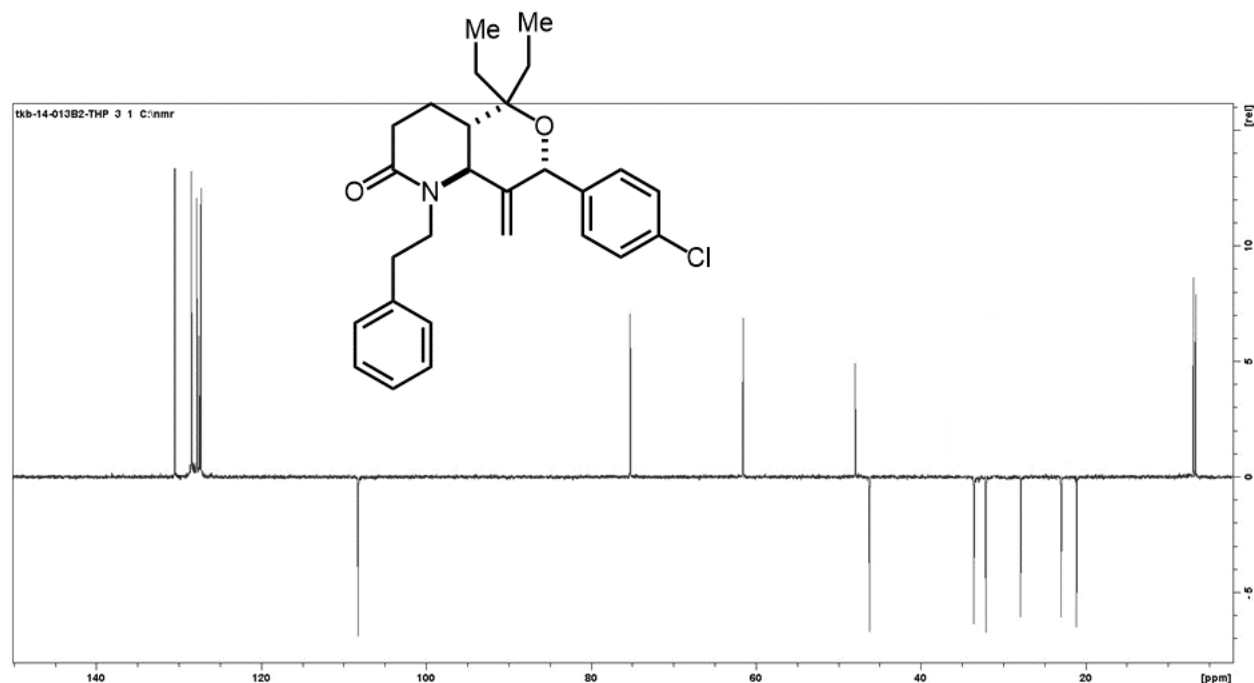




### Compound 4z4

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 75:25). Yellowish oil. Yield = 372.3 mg, 85%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.08 (m, 9H), 4.59 (s, 1H), 4.54 (s, 1H), 4.17 – 4.09 (m, 2H), 3.44 (d,  $J = 11.3$  Hz, 1H), 3.07 – 2.87 (m, 2H), 2.79 – 2.68 (m, 1H), 2.46 (ddd,  $J = 17.3, 4.2, 2.0$  Hz, 1H), 2.20 (ddd,  $J = 17.7, 13.2, 5.5$  Hz, 1H), 1.92 – 1.67 (m, 2H), 1.61 – 1.40 (m, 2H), 1.33 – 0.88 (m, 3H), 0.84 (t,  $J = 7.4$  Hz, 3H), 0.73 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 149.6, 138.9, 138.2, 132.5, 130.9, 128.7, 128.0, 127.7, 127.5, 108.5, 78.4, 75.5, 61.8, 48.2, 46.4, 36.4, 33.7, 32.3, 28.1, 23.2, 21.3, 7.1, 6.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{27}\text{H}_{32}\text{ClNO}_2$  [ $\text{M}$ ]<sup>+</sup> 437.2122, found 437.2126.

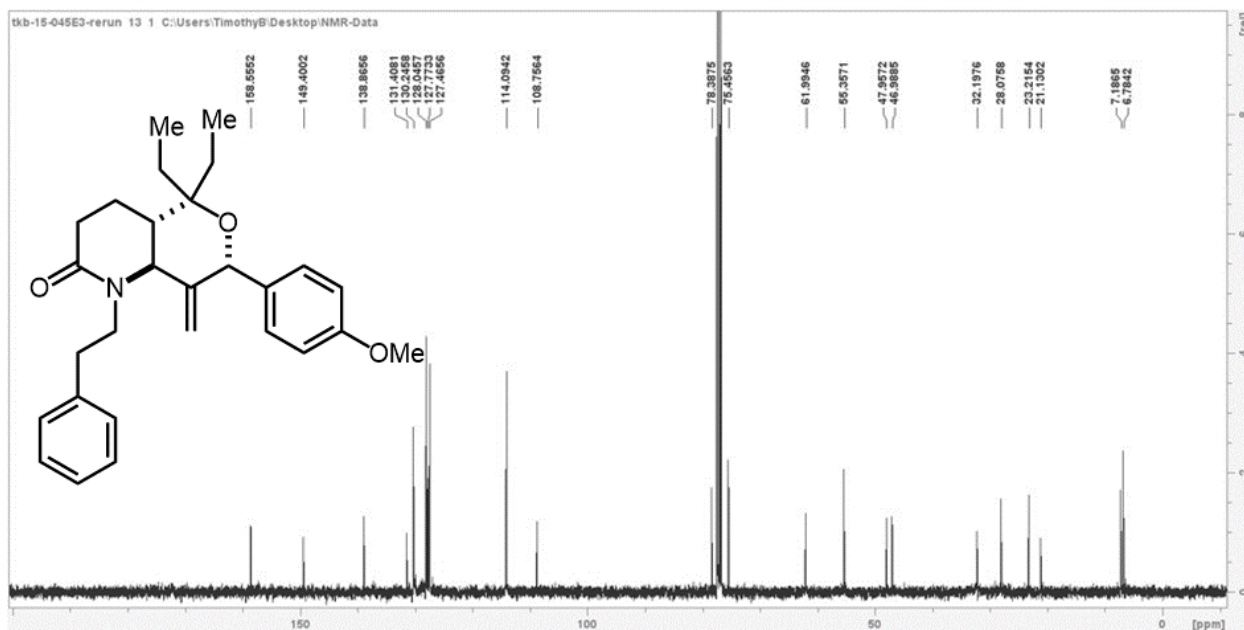
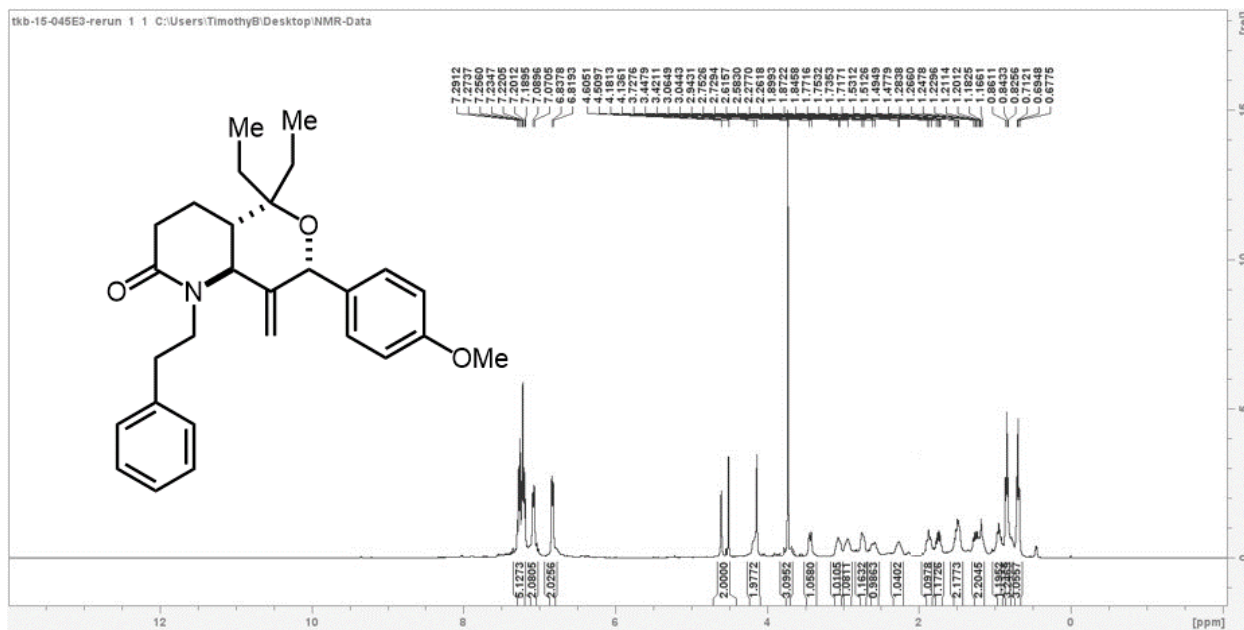


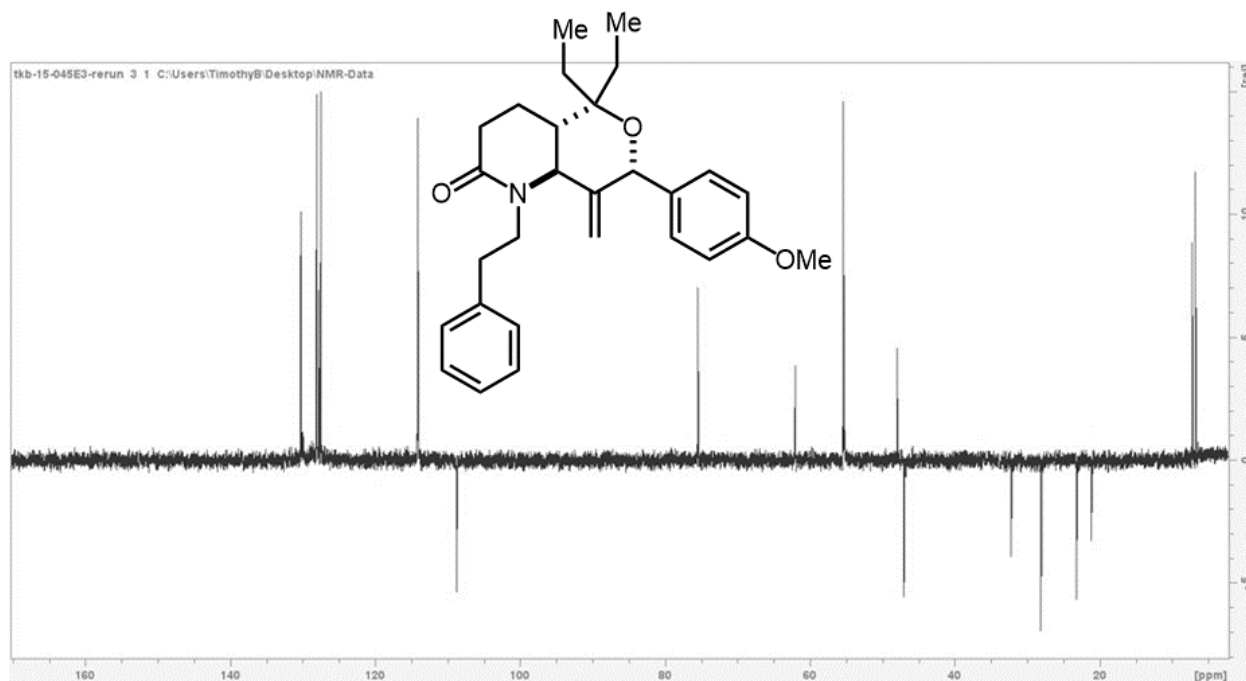


### Compound 4z5

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Yellowish oil. Yield = 368.5 mg, 85%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.18 (m, 5H), 7.18 – 6.99 (m, 2H), 6.83 (d,  $J = 7.4$  Hz, 2H), 4.61 (s, 1H), 4.51 (s, 1H), 4.22 – 4.12 (m, 1H), 4.14 (s, 1H), 3.73 (s, 3H), 3.43 (d,  $J = 11.0$  Hz, 1H), 3.12 – 3.01 (m, 1H), 3.00 – 2.88 (m, 1H), 2.74 (d,  $J = 12.7$  Hz, 1H), 2.66 – 2.54 (m, 1H), 2.32 – 2.22 (m, 1H), 1.93 – 1.81 (m, 1H), 1.74 (dq,  $J = 14.3, 7.2$  Hz, 1H), 1.50 (dt,  $J = 14.5, 7.4$  Hz, 2H), 1.32 – 1.13 (m, 2H), 0.95 (p,  $J = 7.3$  Hz, 1H), 0.84 (t,  $J = 7.2$  Hz, 3H), 0.69 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 149.4, 138.9, 131.4, 130.2, 128.0, 127.8, 127.5, 114.10, 108.8, 78.4, 75.5, 62.0, 55.4, 48.0, 47.0, 32.2, 28.1, 23.2, 21.1, 7.2, 6.8. FTIR (KBr): 2944.8, 1642.2, 1494.9, 1448.8, 1427.0, 1393.4, 1361.6, 1328.7, 1289.7, 1223.6, 1198.9, 1130.1, 1074.1, 1030.4, 988.5, 966.1, 925.5, 741.8, 673.4. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{28}\text{H}_{35}\text{NO}_3$   $[\text{M}]^+$  433.2617, found 433.2613.





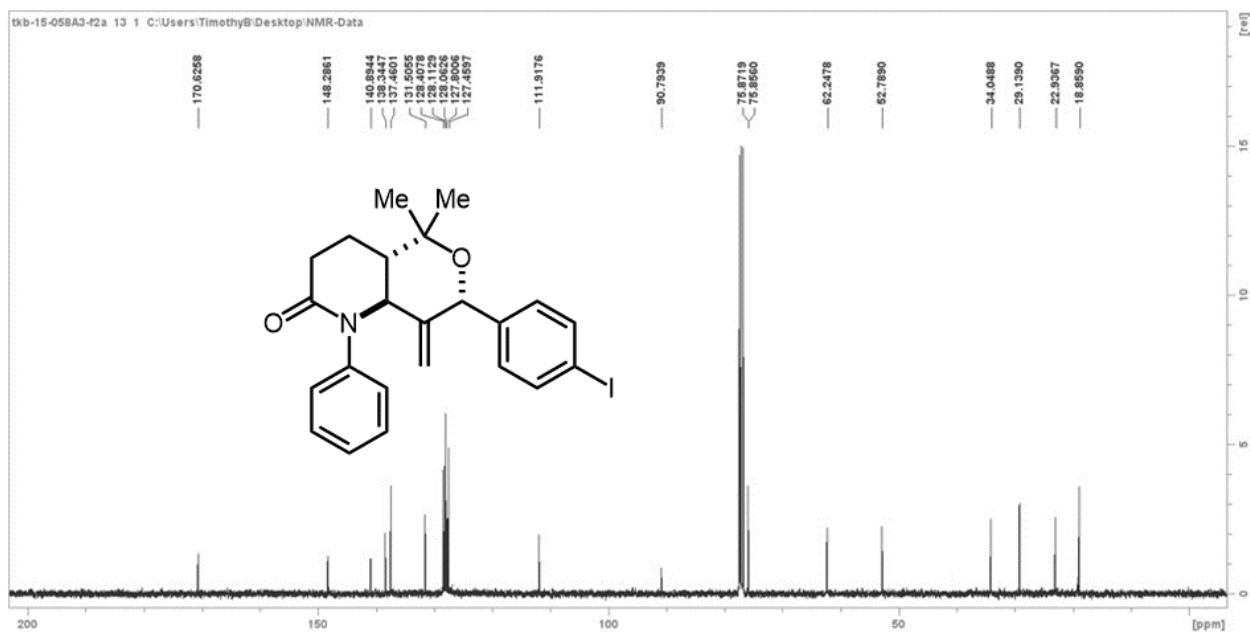
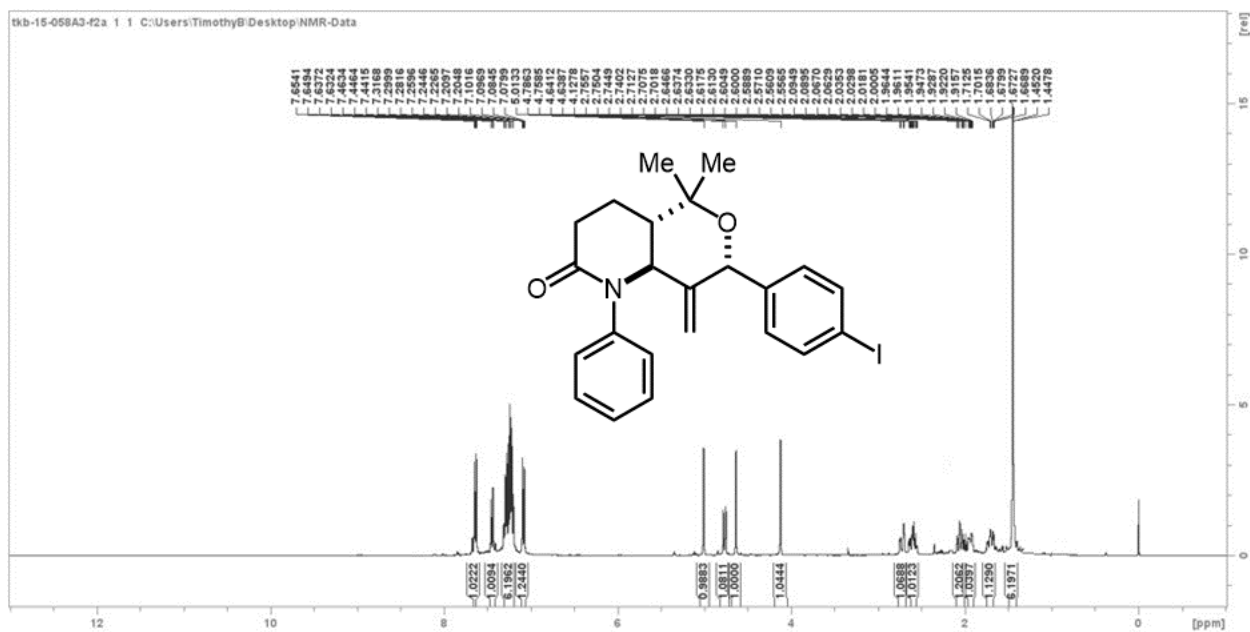


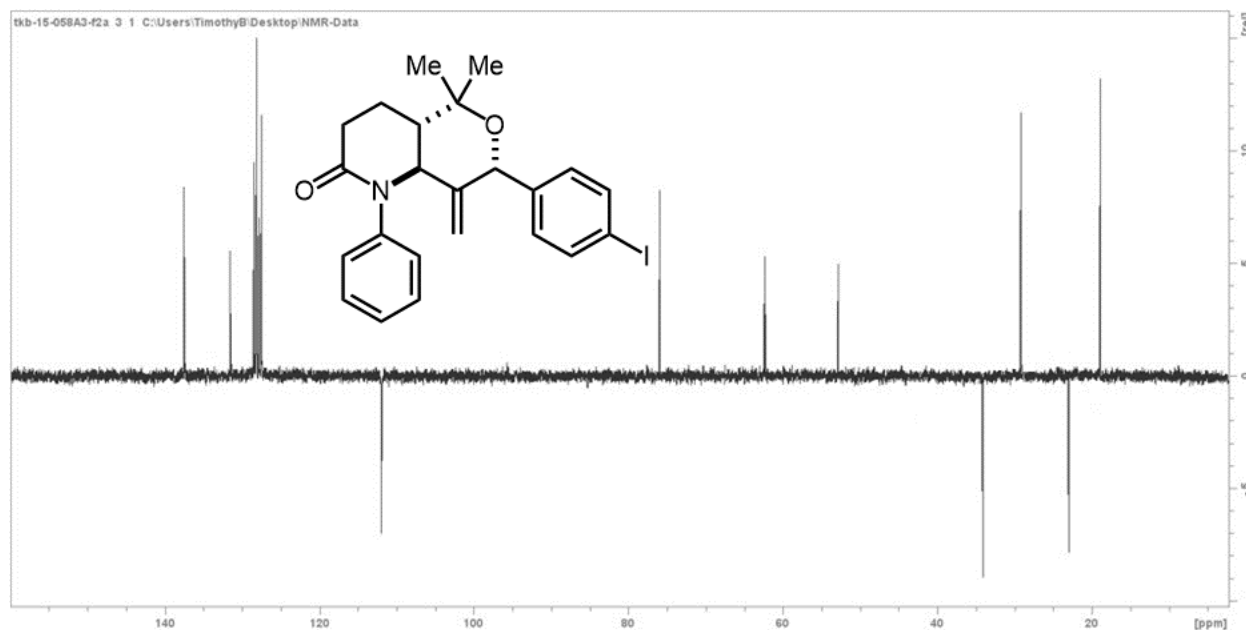
### Compound 4z6

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Amorphous solid. Yield = 348.4 mg, 88%, 95:5 dr. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>24</sub>H<sub>26</sub>ClNO<sub>2</sub> [M]<sup>+</sup> 395.1652, found 395.1657.

### Compound 4z7

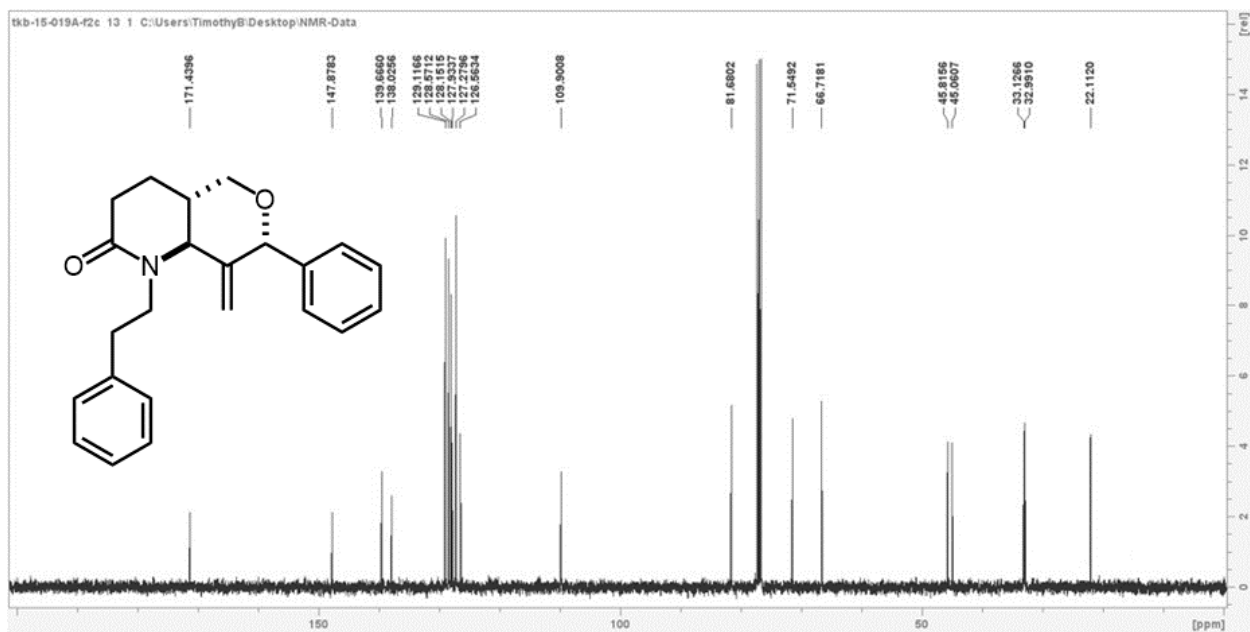
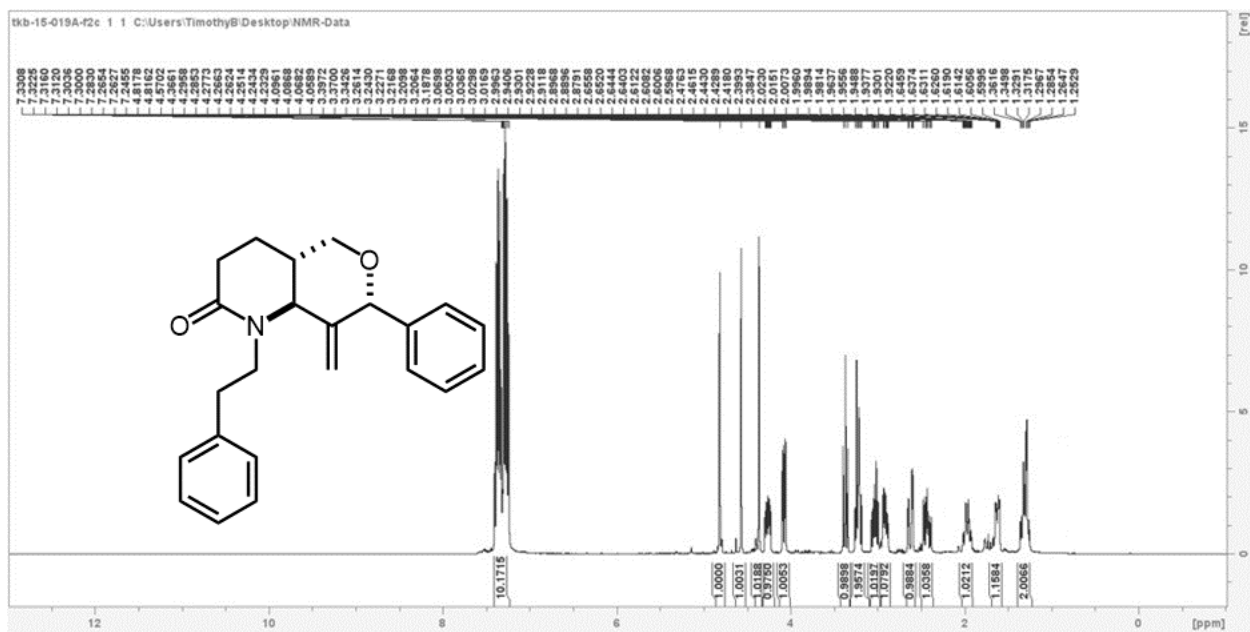
Prepared in 0.5 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 70:30). Amorphous solid. Yield = 203.5 mg, 86%, 95:5 dr. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>23</sub>H<sub>24</sub>INO<sub>2</sub> [M]<sup>+</sup> 473.0852, found 473.0856.

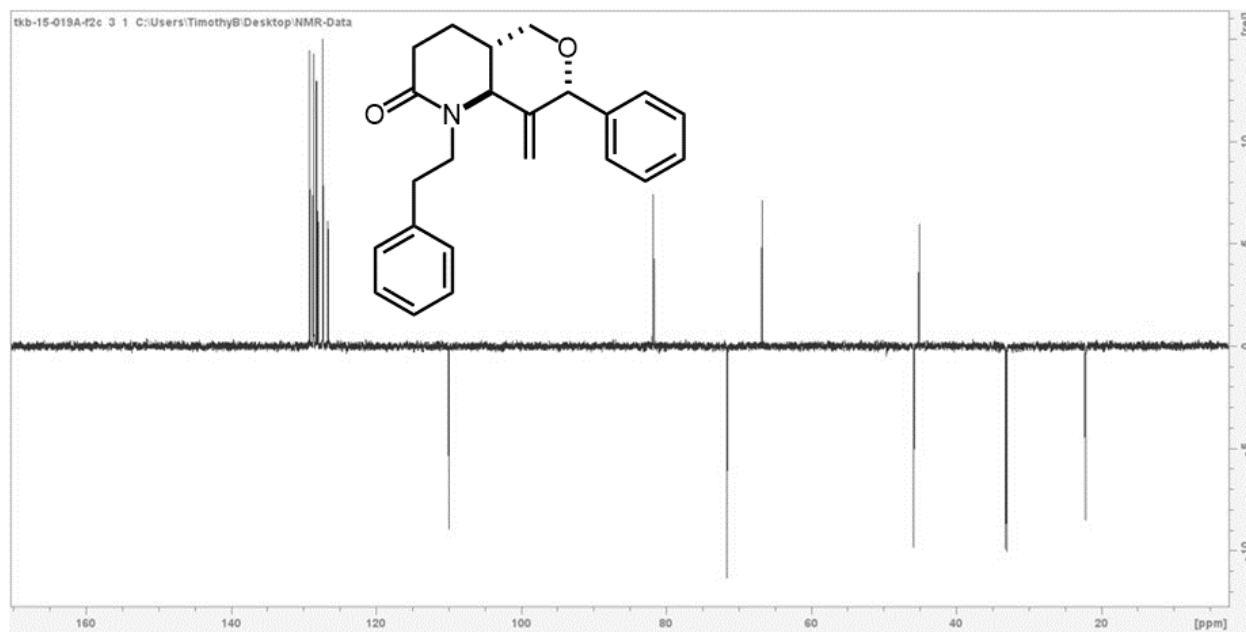




### Compound 4z8

Prepared in 1.0 mmol scale using **General Procedure A**. Purification: Flash chromatography on silica eluting with hexane/acetone (90:10 to 50:50). Yellowish oil. Yield = 309.3 mg, 89%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.22 (m, 10H), 4.82 (d,  $J = 1.3$  Hz, 1H), 4.57 (s, 1H), 4.37 (s, 1H), 4.26 (ddd,  $J = 13.5, 7.5, 4.2$  Hz, 1H), 4.08 (dd,  $J = 11.2, 3.7$  Hz, 1H), 3.37 (t,  $J = 10.9$  Hz, 1H), 3.28 – 3.17 (m, 2H), 3.03 (ddd,  $J = 13.3, 8.6, 7.4$  Hz, 1H), 2.91 (ddd,  $J = 13.3, 7.2, 4.2$  Hz, 1H), 2.63 (ddd,  $J = 17.5, 4.7, 1.8$  Hz, 1H), 2.55 – 2.36 (m, 1H), 2.05 – 1.88 (m, 1H), 1.75 – 1.57 (m, 1H), 1.38 – 1.23 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 147.9, 139.7, 138.0, 129.1, 128.6, 128.1, 127.9, 127.3, 126.6, 109.9, 81.7, 71.5, 66.7, 45.8, 45.1, 33.1, 33.0, 22.1. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{23}\text{H}_{25}\text{NO}_2$  [ $\text{M}$ ]<sup>+</sup> 347.1885, found 347.1889.





**Scheme 2 Results**

**Compound 4c**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 81%, 95:5 dr.

**Compound 4f**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 86%, 95:5 dr.

**Compound 4h**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 79%, 95:5 dr.

**Compound 4q**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 77%, 95:5 dr.

**Compound 4s**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 81%, 95:5 dr.

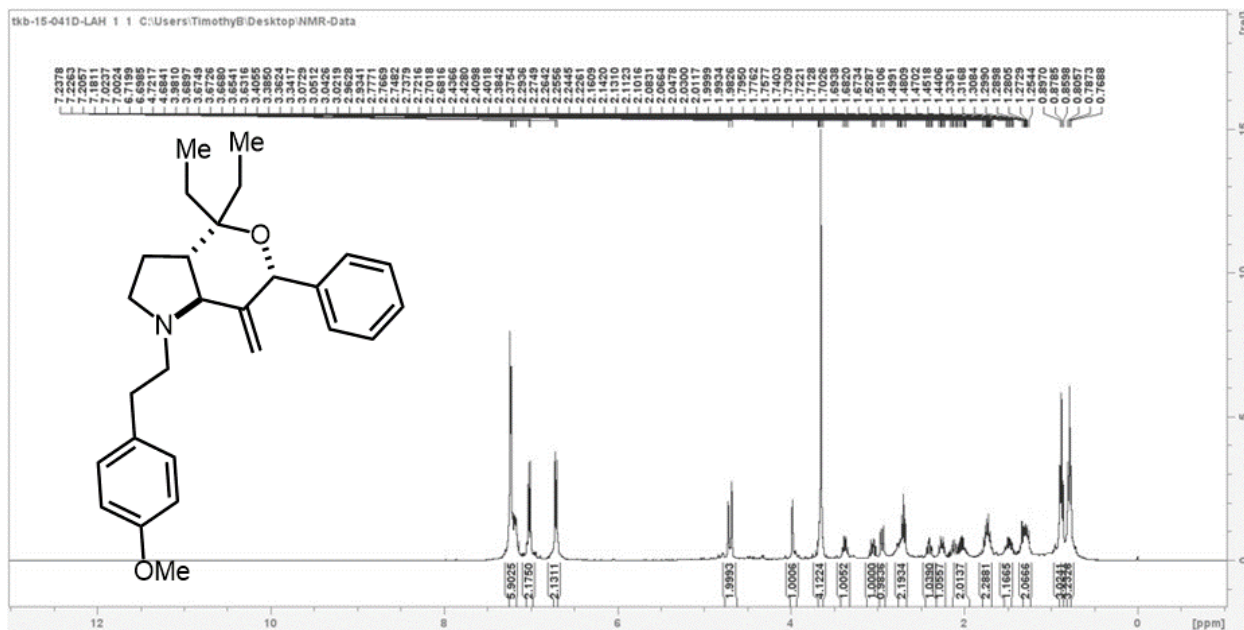
**Compound 4z**

Prepared in 1.0 mmol scale using **General Procedure B**. Yield = 75%, 95:5 dr.

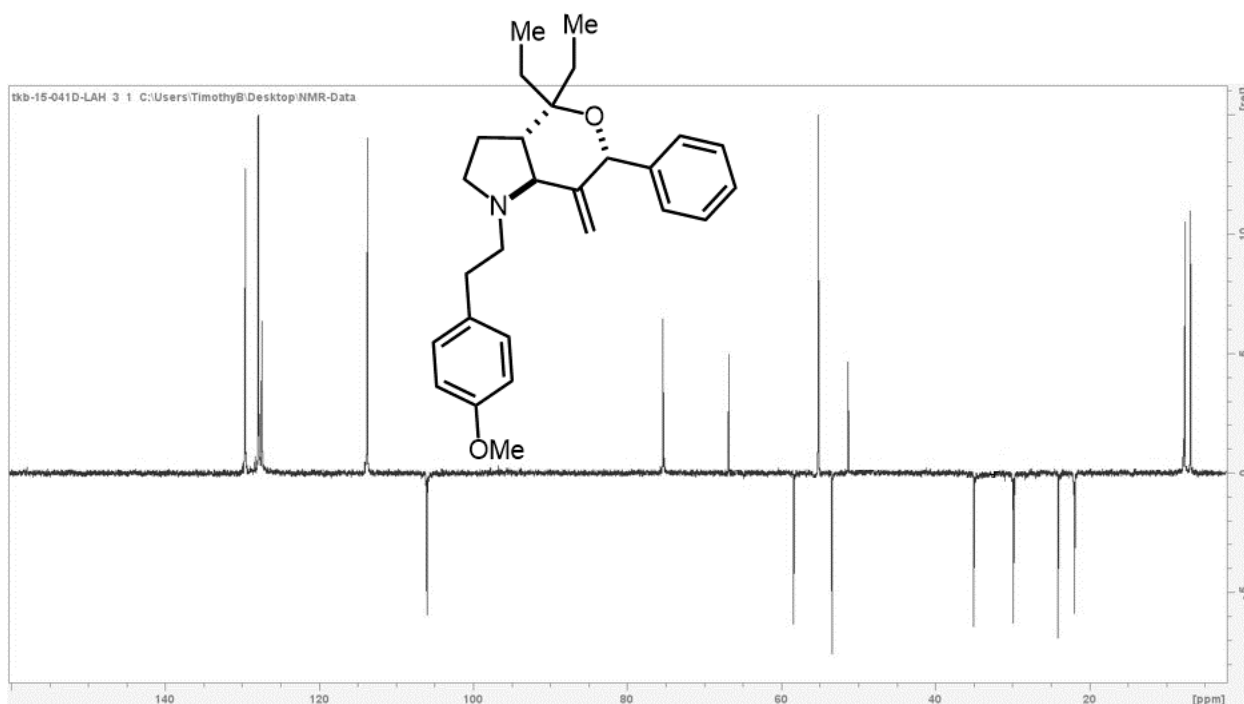
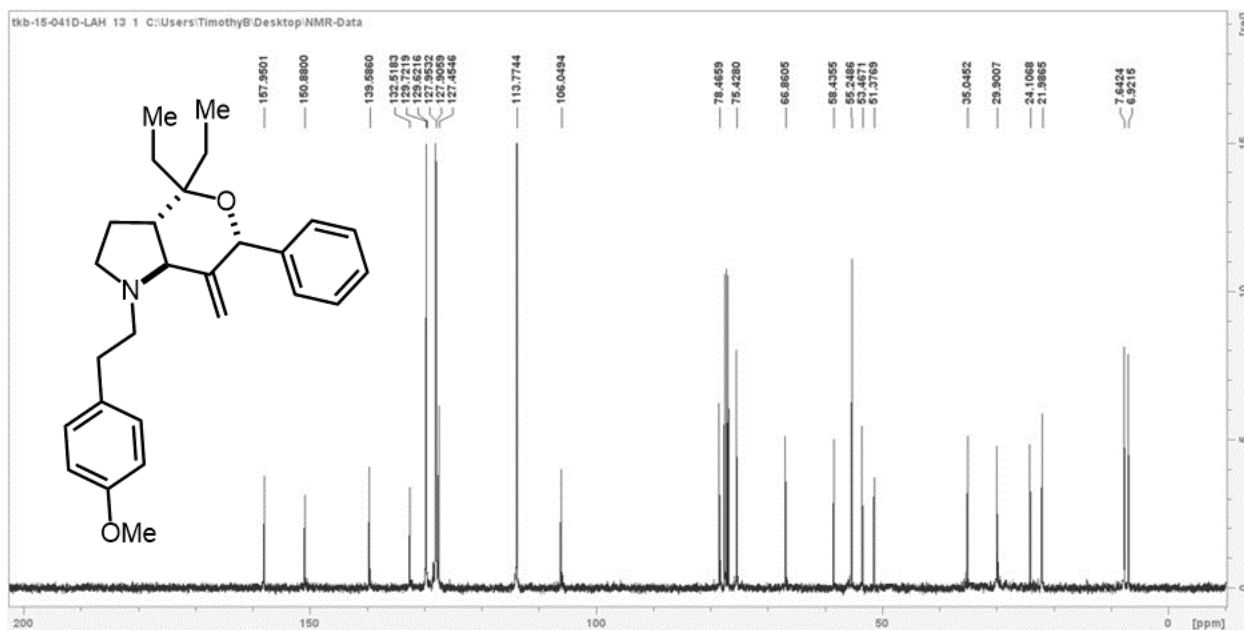
## Scheme 3 Results

## Compound 18a

Prepared in 1.0 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica, pretreated with triethylamine (0.1 mL), eluting with hexane/acetone (90:10 to 20:80). Colorless oil. Yield = 344.7 mg, 85%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.18 (m, 5H), 7.13 – 6.91 (m, 2H), 6.80 – 6.60 (m, 2H), 4.70 (d,  $J = 15.1$  Hz, 2H), 4.01 – 3.89 (m, 1H), 3.79 – 3.60 (m, 4H), 3.43 – 3.32 (m, 1H), 3.06 (dt,  $J = 11.8, 8.4$  Hz, 1H), 2.99 – 2.89 (m, 1H), 2.77 (td,  $J = 13.8, 5.3$  Hz, 1H), 2.69 (d,  $J = 8.1$  Hz, 1H), 2.41 (td,  $J = 10.6, 3.6$  Hz, 1H), 2.26 (dt,  $J = 11.9, 7.5$  Hz, 1H), 2.20 – 1.94 (m, 2H), 1.84 – 1.60 (m, 2H), 1.48 (qd,  $J = 11.8, 7.2$  Hz, 1H), 1.41 – 1.20 (m, 2H), 0.89 (t,  $J = 7.4$  Hz, 3H), 0.78 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9, 150.9, 139.6, 132.5, 129.7, 129.6, 128.0, 127.9, 127.5, 113.8, 106.1, 78.5, 75.4, 66.9, 58.4, 55.2, 53.5, 51.5, 35.0, 29.9, 24.1, 22.0, 7.6, 6.9. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{27}\text{H}_{35}\text{NO}_2$   $[\text{M}]^+$  405.2668, found 405.2666.





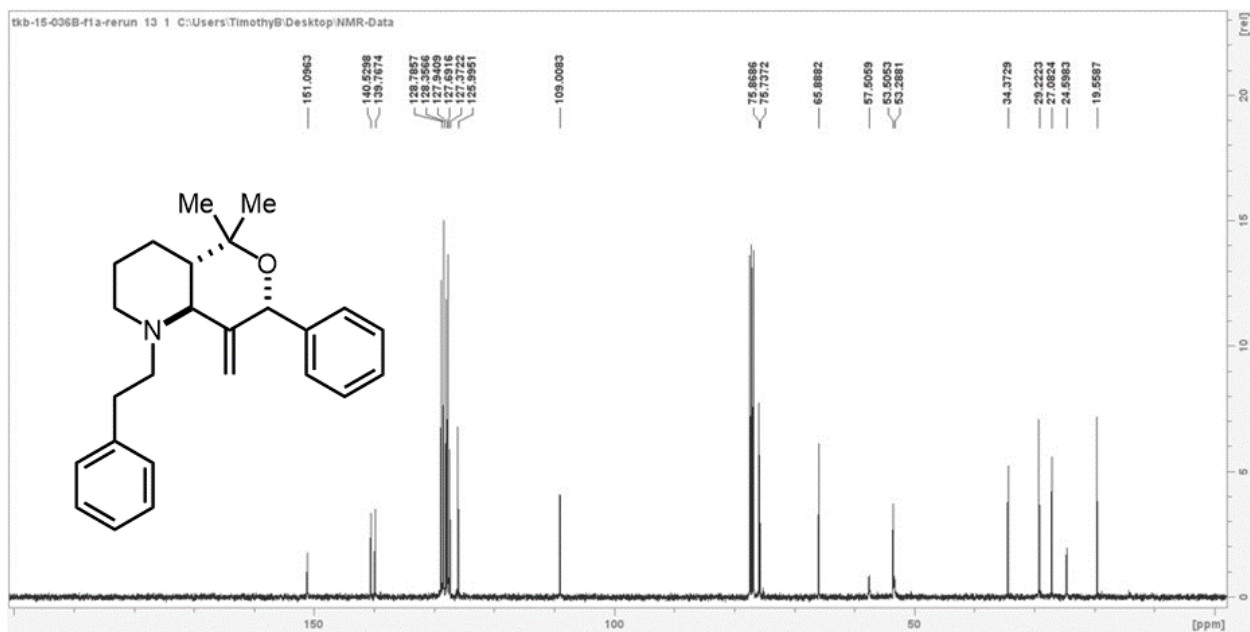
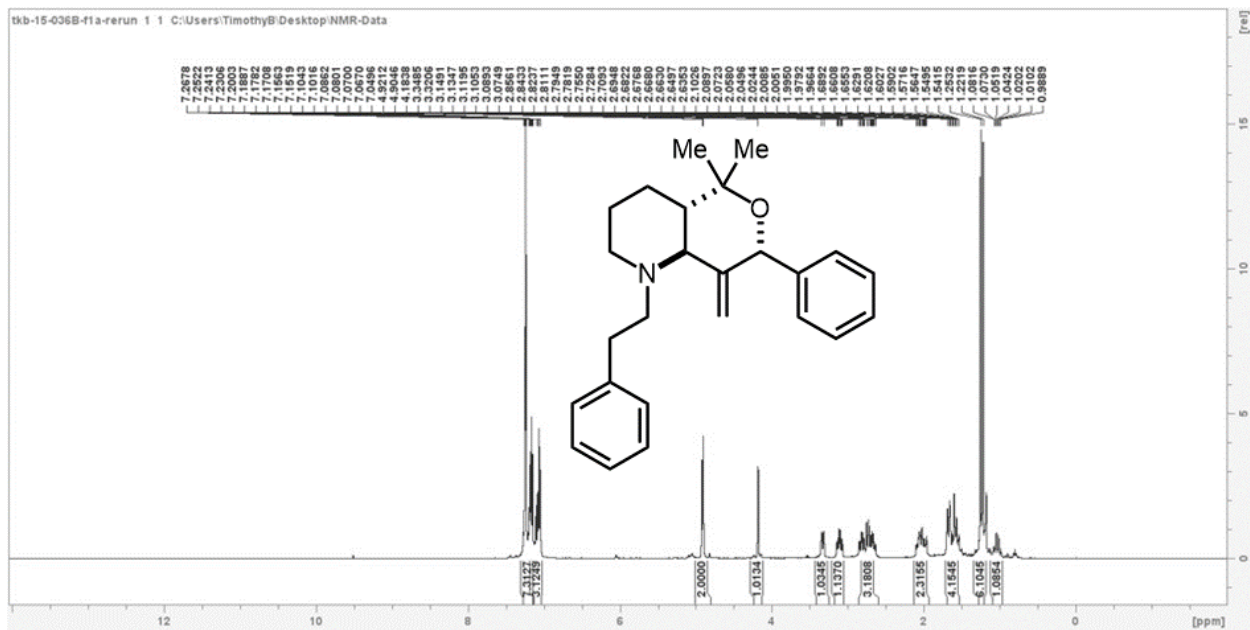


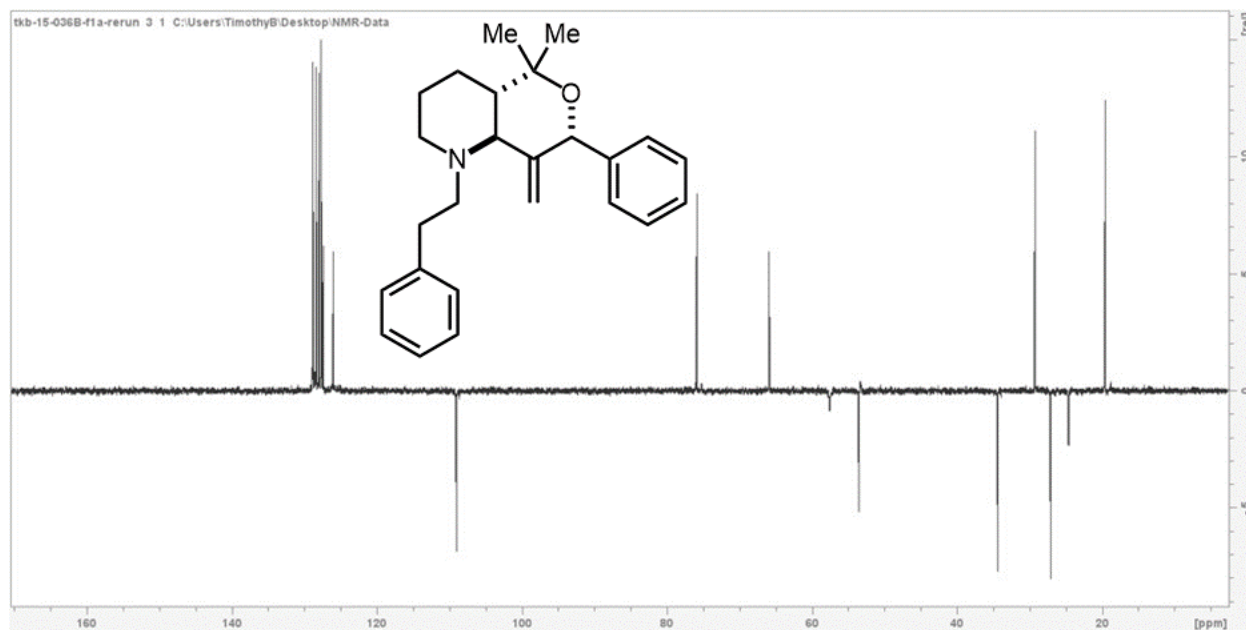
### Compound 18b

Prepared in 1.0 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica, pretreated with triethylamine (0.1 mL), eluting with hexane/acetone (90:10 to 40:60). Colorless oil. Yield = 319.7 mg, 92%, 95:5 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.25 (m,



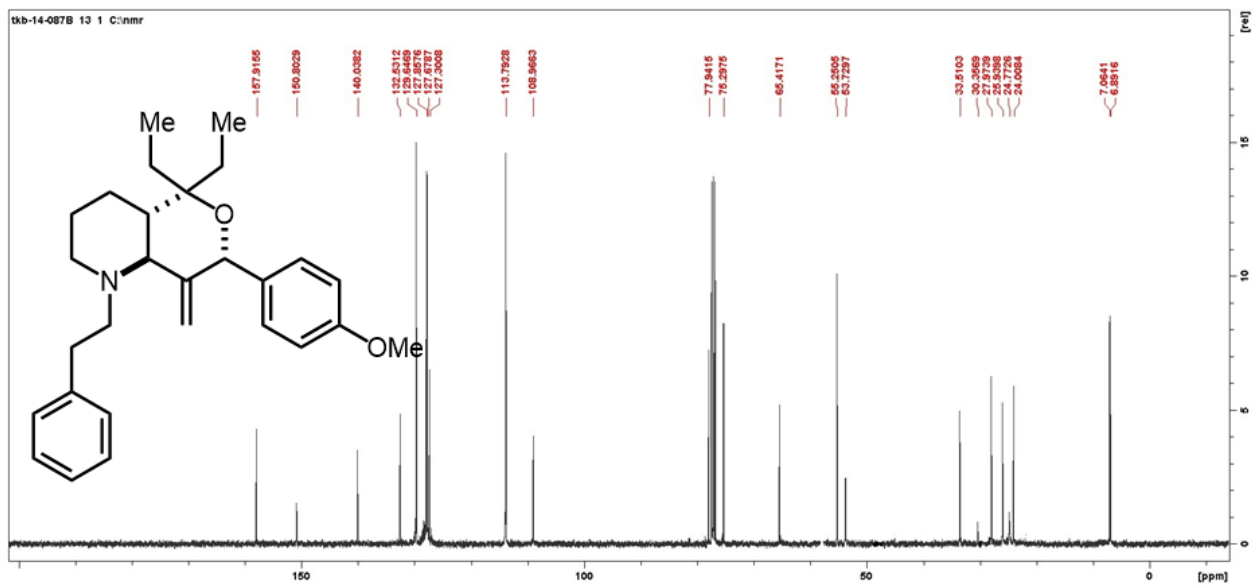
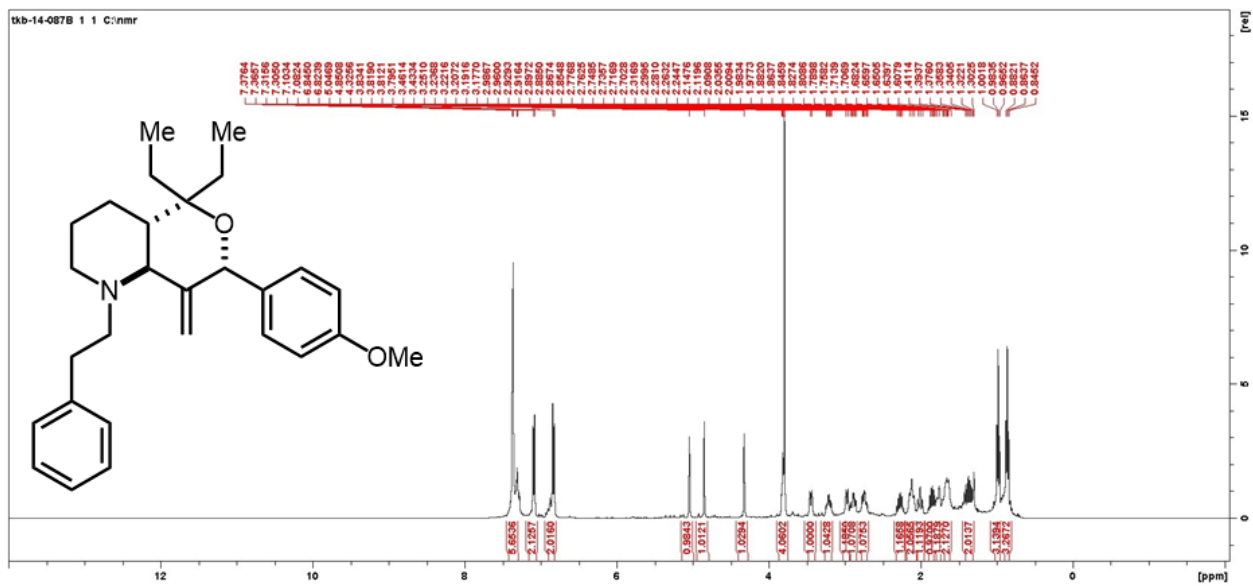


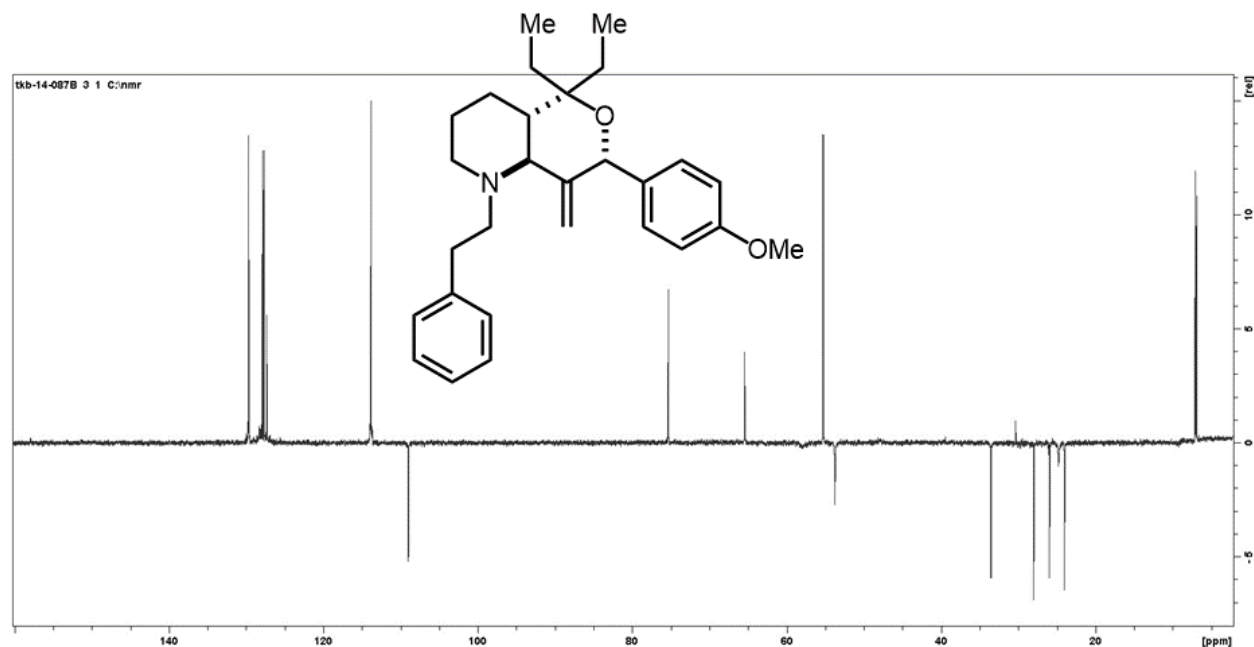




### Compound 18d

Prepared in 1.0 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica, pretreated with triethylamine (0.1 mL), eluting with hexane/acetone (90:10 to 15:85). Colorless oil. Yield = 373.4 mg, 89%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.30 (m, 5H), 7.09 (d,  $J = 8.1$  Hz, 2H), 6.83 (d,  $J = 8.1$  Hz, 2H), 5.05 (s, 1H), 4.85 (s, 1H), 4.33 (s, 1H), 3.82 (d,  $J = 3.1$  Hz, 1H), 3.80 (s, 3H), 3.45 (dd,  $J = 11.3, 3.7$  Hz, 1H), 3.21 (ddt,  $J = 19.0, 12.7, 6.2$  Hz, 1H), 2.97 (d,  $J = 10.8$  Hz, 1H), 2.89 (td,  $J = 12.4, 5.2$  Hz, 1H), 2.74 (ddd,  $J = 13.1, 10.8, 5.7$  Hz, 1H), 2.27 (dq,  $J = 14.8, 7.2$  Hz, 1H), 2.13 (q,  $J = 8.7$  Hz, 2H), 2.01 (ddd,  $J = 13.4, 10.7, 3.1$  Hz, 1H), 1.92 – 1.59 (m, 3H), 1.59 – 1.39 (m, 1H), 1.42 – 1.26 (m, 2H), 1.01 – 0.84 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9, 150.8, 140.0, 132.5, 129.8, 129.6, 129.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 127.3, 127.0, 113.9, 113.8, 113.7, 109.0, 77.9, 75.3, 65.4, 55.3, 53.7, 33.5, 28.0, 25.9, 24.0, 7.1, 6.9. **HRMS-EI $^+$**  ( $m/z$ ): calc for  $\text{C}_{28}\text{H}_{37}\text{NO}_2$   $[\text{M}]^+$  419.2824, found 419.2827.

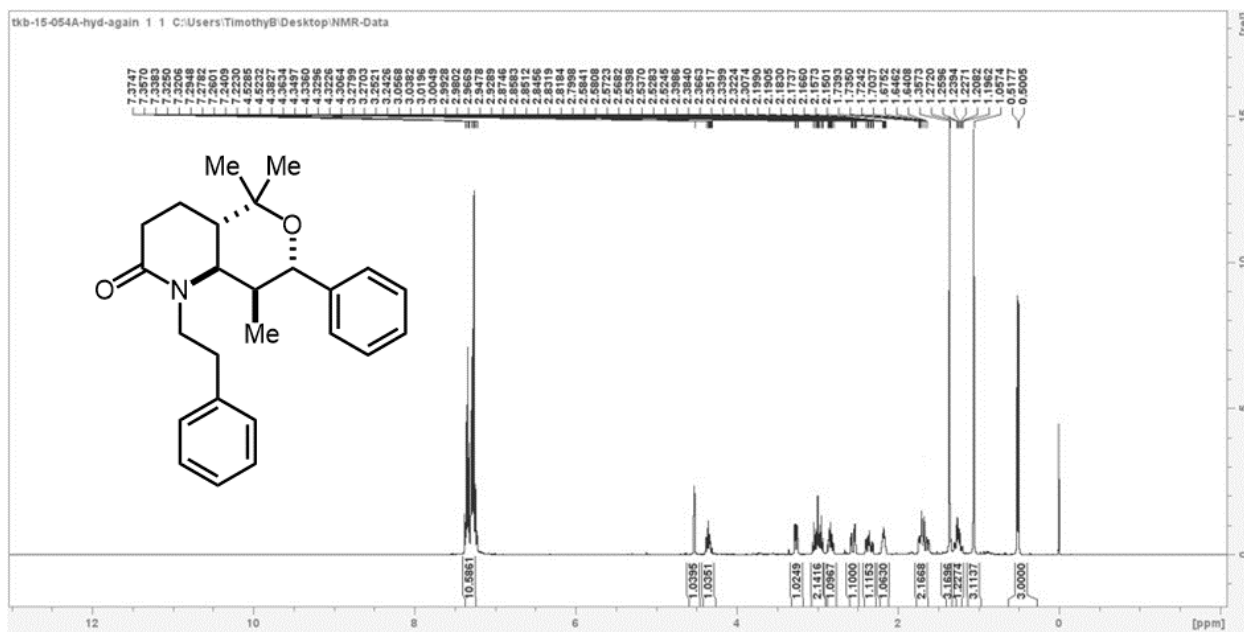




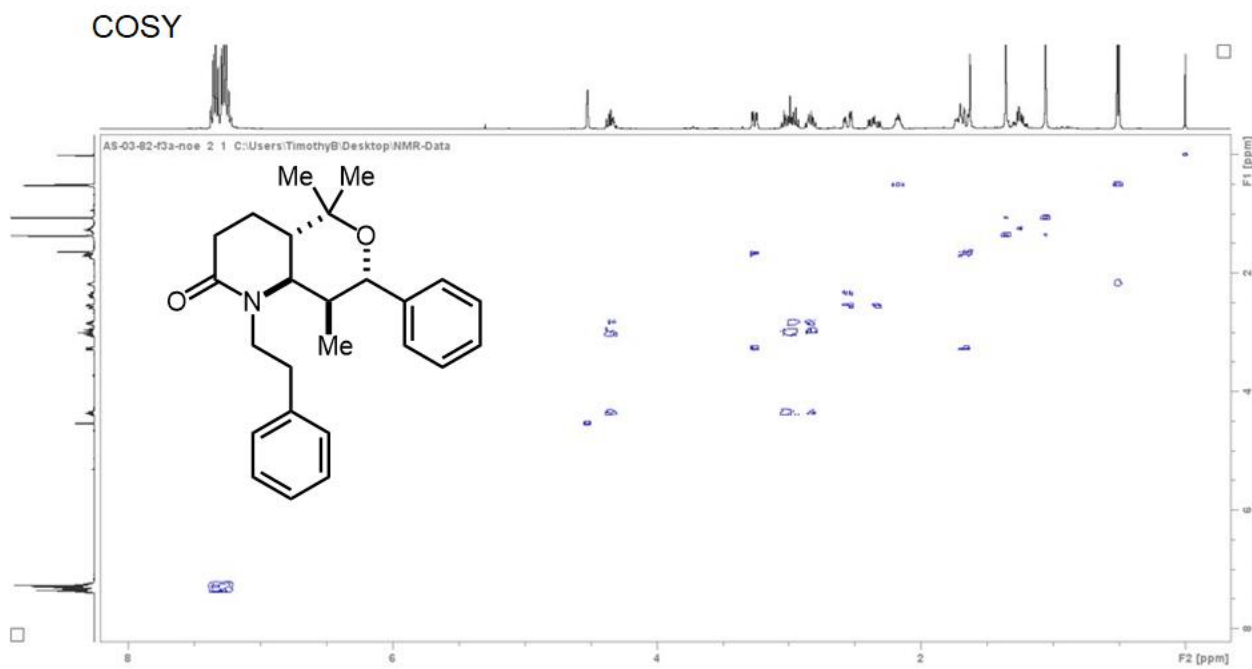
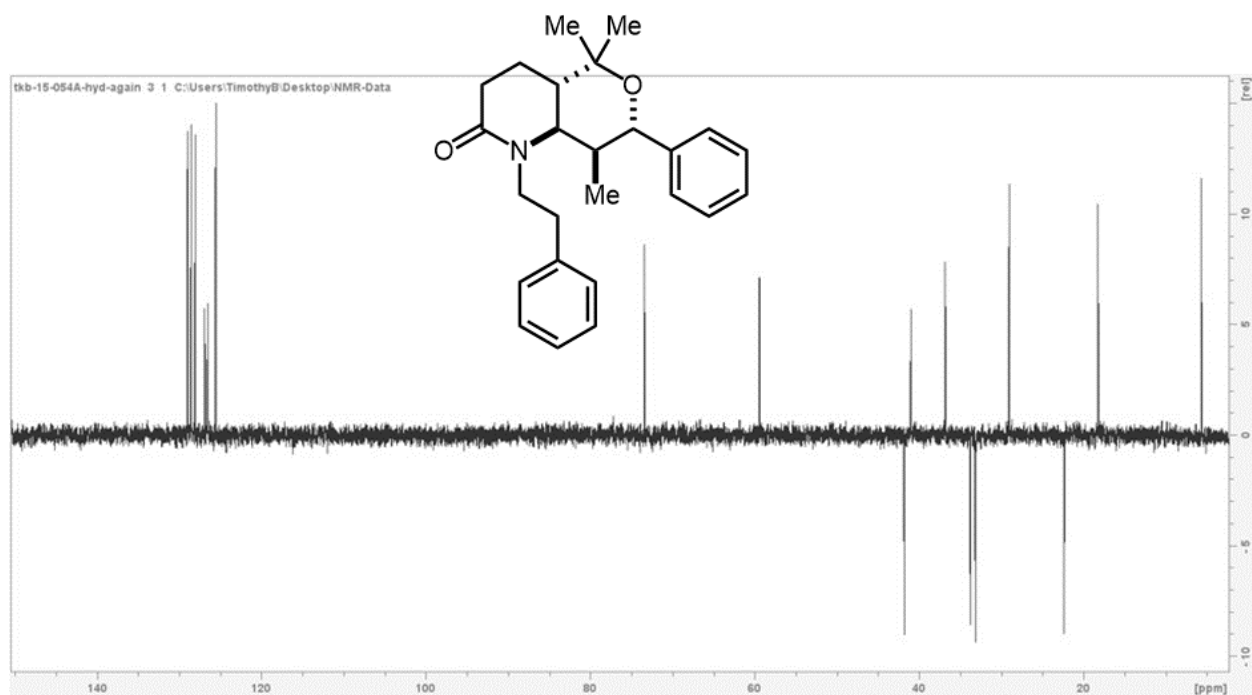
## Scheme 4 Results

### Compound 19a

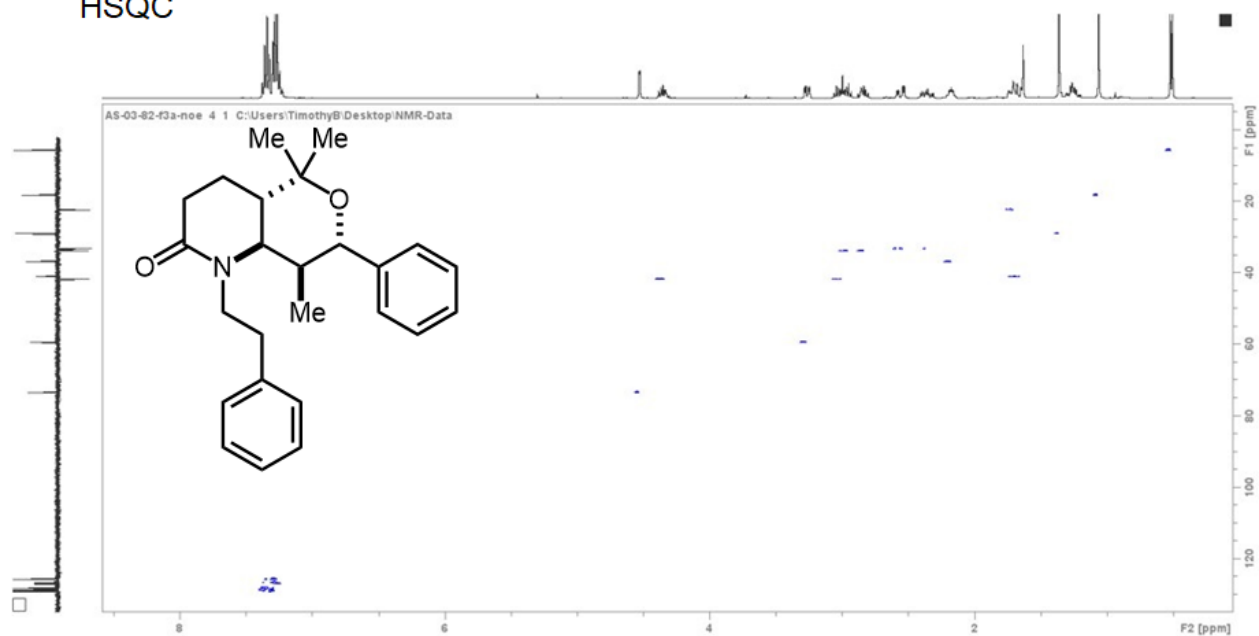
Prepared in 0.5 mmol scale using **General Procedure D**. Purification: Flash chromatography on silica gel eluting with hexane/acetone (90:10 to 50:50). Colorless oil. Yield = 183.1 mg, 97%, >99:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.22 (m, 10H), 4.53 (d, *J* = 2.4 Hz, 1H), 4.41 – 4.27 (m, 1H), 3.26 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.08 – 2.91 (m, 2H), 2.90 – 2.78 (m, 1H), 2.55 (ddd, *J* = 17.6, 5.0, 1.7 Hz, 1H), 2.35 (ddd, *J* = 17.4, 13.0, 5.8 Hz, 1H), 2.17 (dhept, *J* = 10.4, 3.1 Hz, 1H), 1.77 – 1.62 (m, 2H), 1.36 (s, 3H), 1.29 – 1.19 (m, 1H), 1.06 (s, 3H), 0.51 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.69, 141.15, 139.69, 129.02, 128.59, 128.10, 126.92, 126.58, 125.60, 75.17, 73.44, 59.46, 41.82, 41.04, 36.84, 33.80, 33.19, 29.08, 22.40, 18.24, 5.69. **HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>25</sub>H<sub>31</sub>NO<sub>2</sub> [M]<sup>+</sup> 377.2355, found 377.2359.



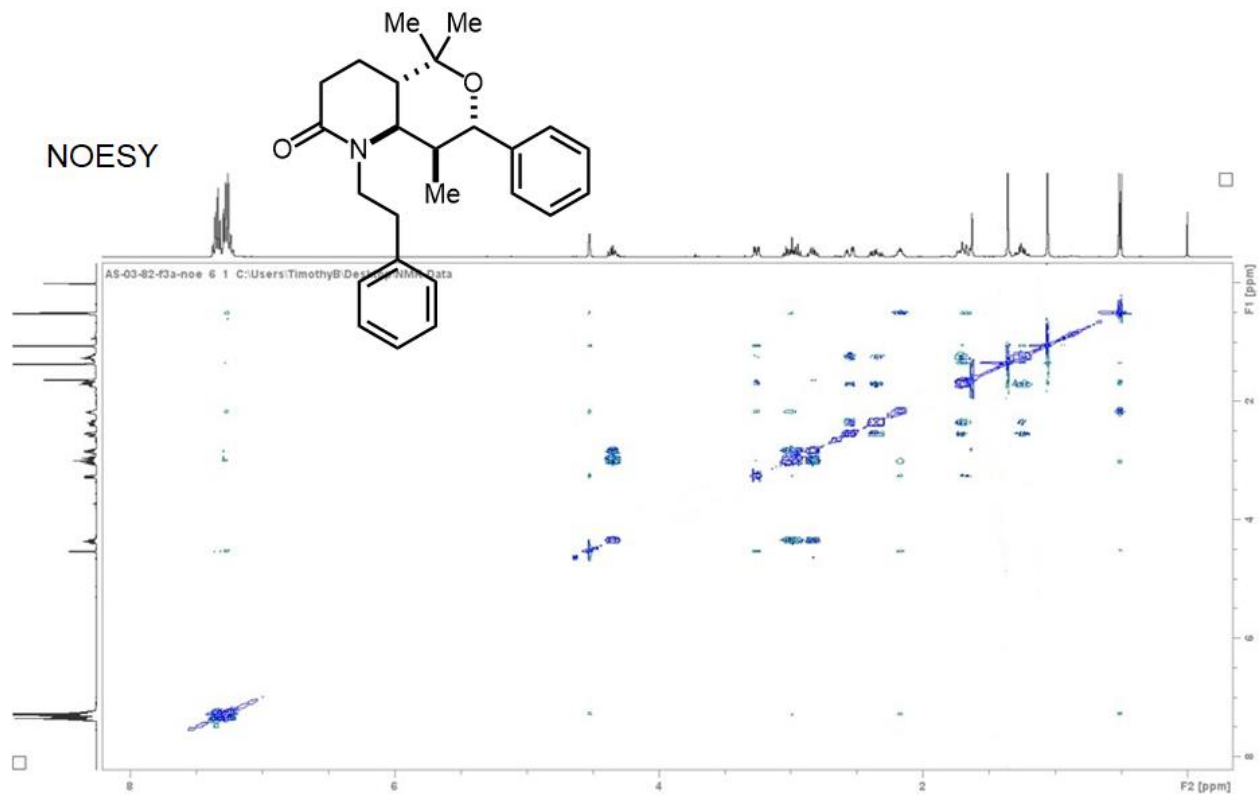




HSQC

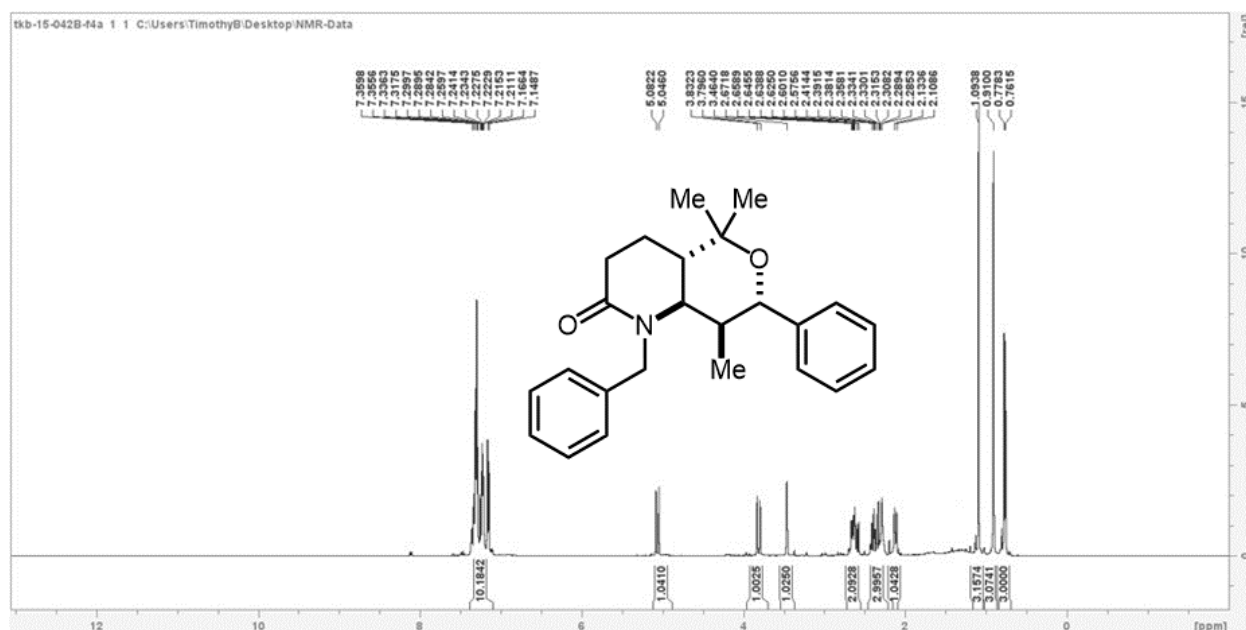


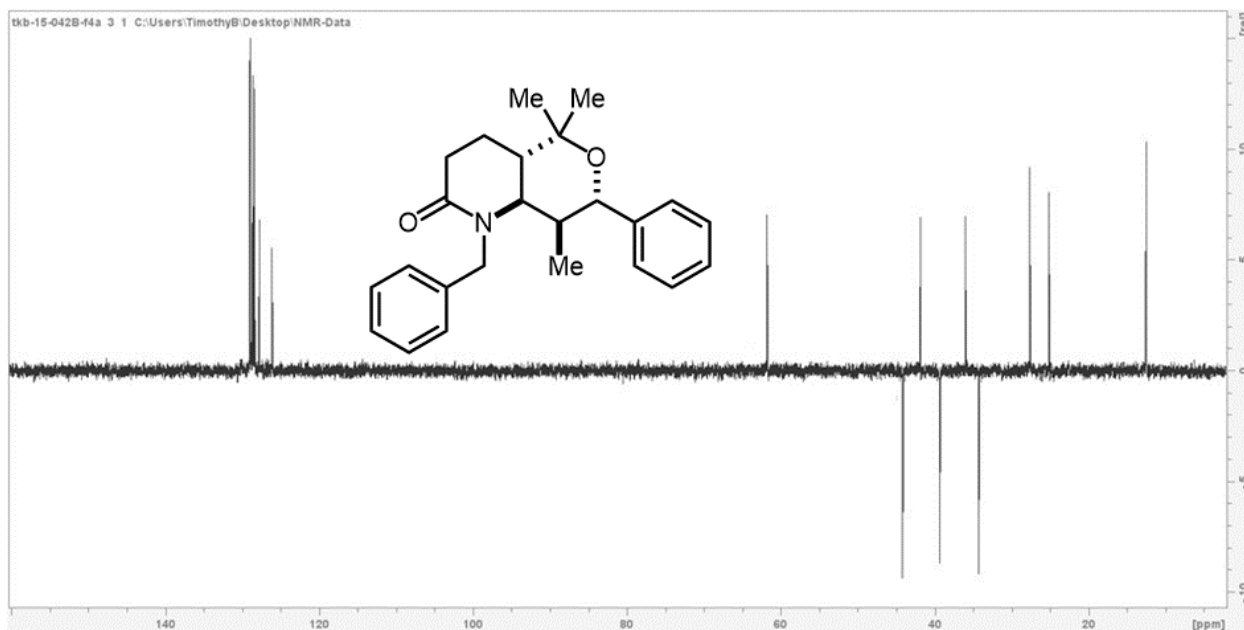
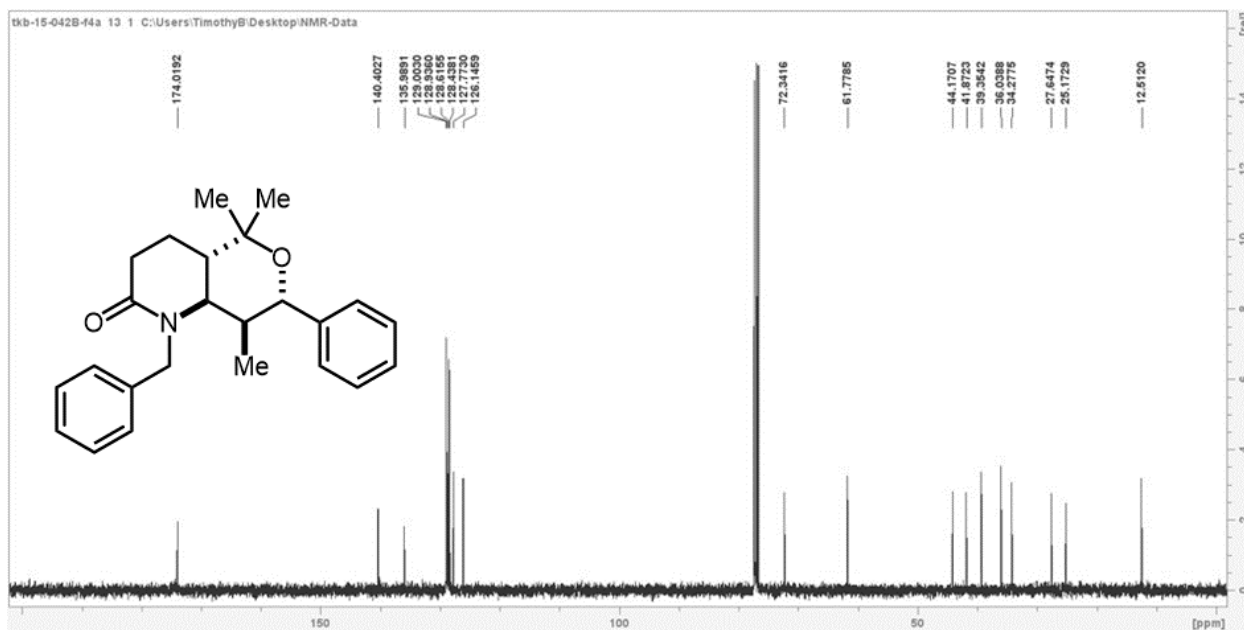
NOESY



**Compound 19b**

Prepared in 0.5 mmol scale using **General Procedure D**. Purification: Flash chromatography on silica gel eluting with hexane/acetone (90:10 to 50:50). Colorless oil. Yield = 174.5 mg, 96%, 95:5 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.14 (m, 10H), 5.06 (d,  $J = 14.5$  Hz, 1H), 3.81 (dd,  $J = 14.5, 1.1$  Hz, 1H), 3.47 (dd,  $J = 2.8, 1.5$  Hz, 1H), 2.72 – 2.55 (m, 2H), 2.46 – 2.24 (m, 3H), 2.22 – 2.06 (m, 1H), 1.09 (s, 3H), 0.91 (s, 3H), 0.76 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.02, 140.41, 135.99, 129.01, 128.94, 128.62, 128.44, 127.78, 126.15, 72.34, 61.78, 44.17, 41.88, 39.36, 36.04, 34.28, 27.65, 25.18, 12.52. **HRMS-EI<sup>+</sup>** ( $m/z$ ): calc for  $\text{C}_{24}\text{H}_{29}\text{NO}_2$  [ $\text{M}$ ]<sup>+</sup> 363.2198, found 363.2195.



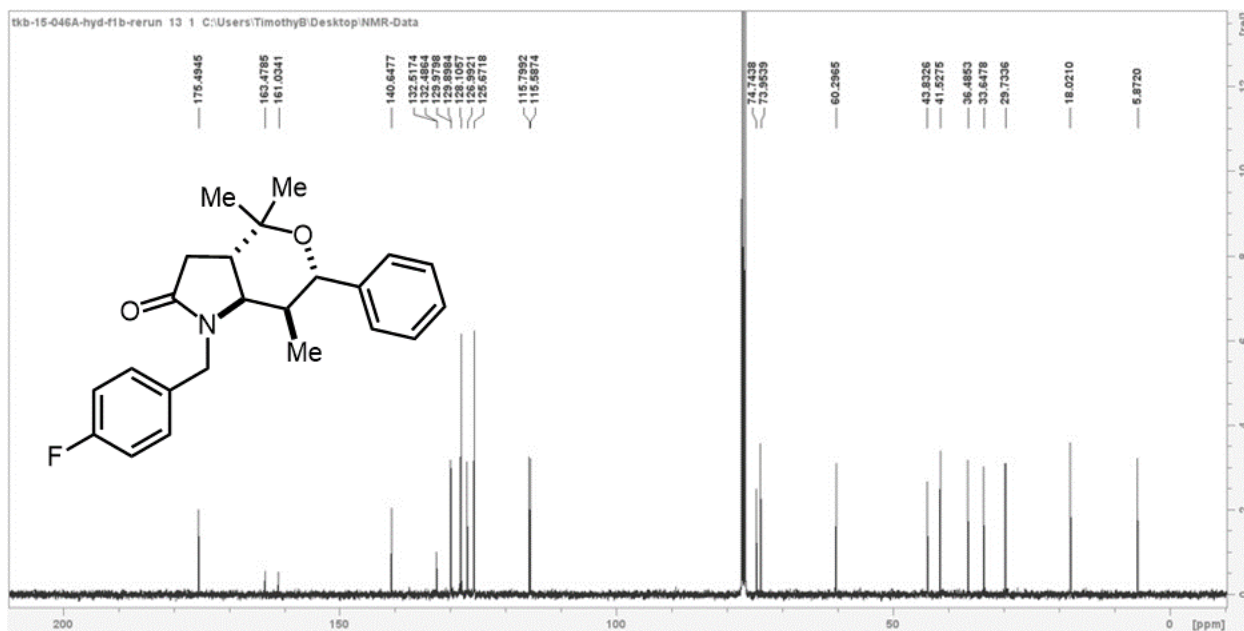
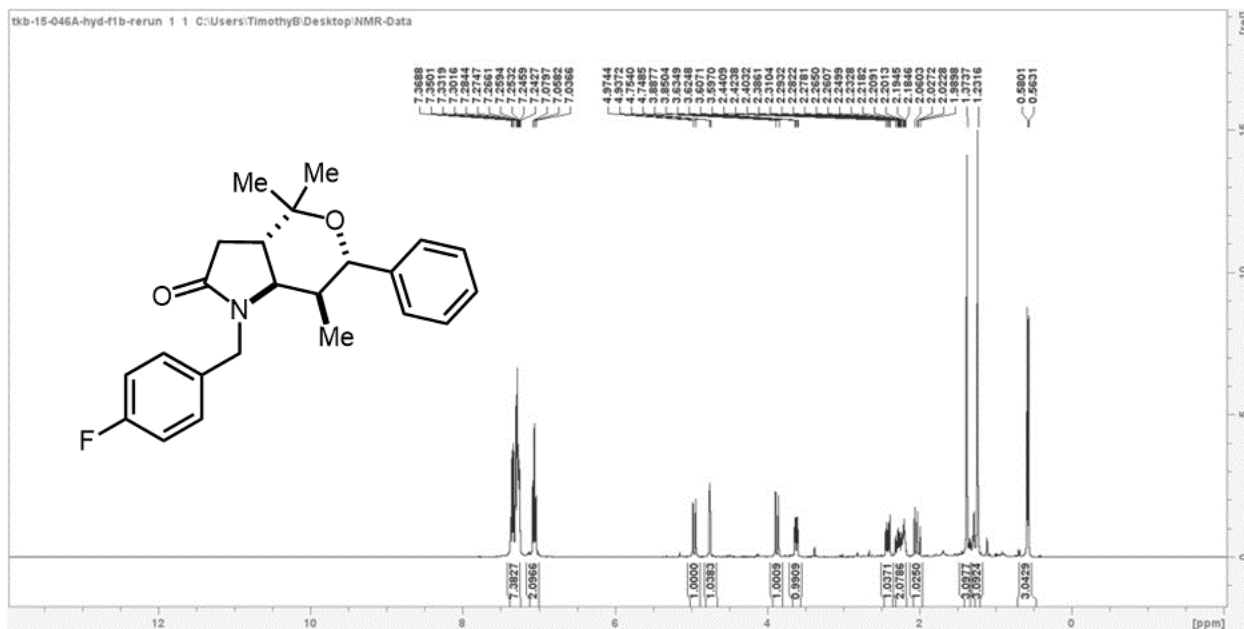


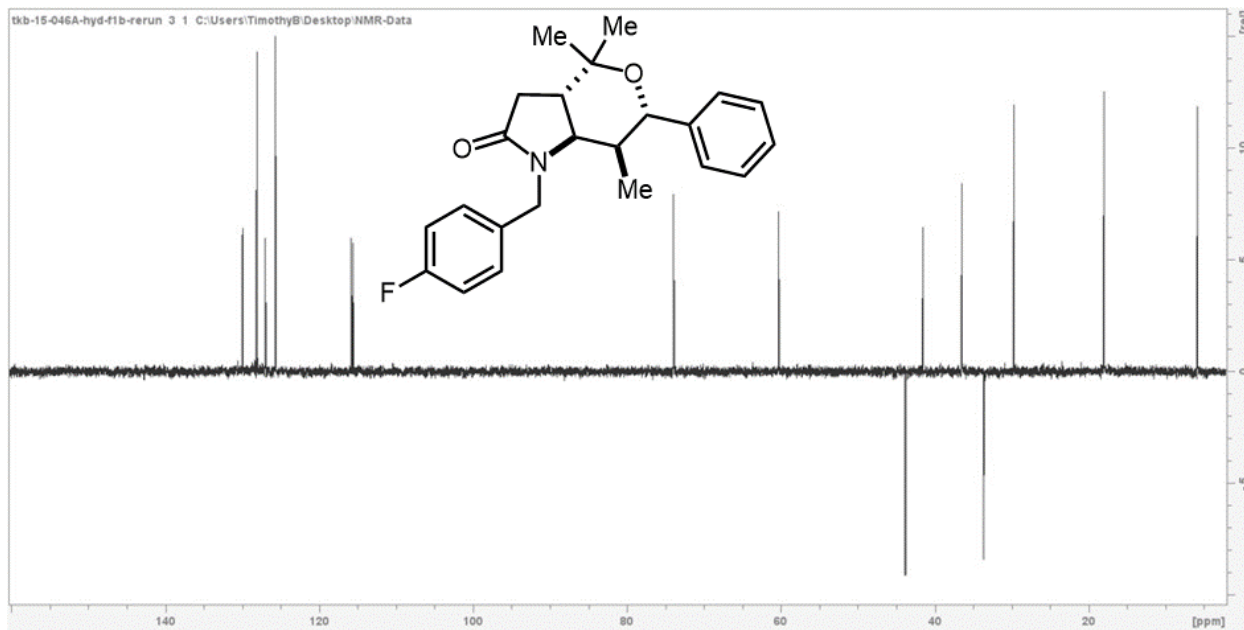
### Compound 19c

Prepared in 0.5 mmol scale using **General Procedure D**. Purification: Flash chromatography on silica gel eluting with hexane/acetone (90:10 to 70:30). Colorless oil. Yield = 170.9 mg, 93%, 94:6 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.22 (m, 7H), 7.11 – 7.01 (m, 2H), 4.96 (d,  $J$  = 14.9 Hz, 1H), 4.75 (d,  $J$  = 2.5 Hz, 1H), 3.87 (d,  $J$  = 14.9 Hz, 1H), 3.62 (dd,  $J$  = 11.1, 4.1 Hz, 1H), 2.41 (dd,  $J$  = 15.1, 6.9 Hz, 1H), 2.27 (ddd,  $J$  = 13.0, 11.1, 6.9 Hz, 1H), 2.20 (tq,  $J$  = 9.4, 3.1 Hz, 1H), 2.03 (dd,  $J$  = 15.1, 13.1 Hz, 1H), 1.37 (s, 3H), 1.23 (s, 3H), 0.57 (d,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (101

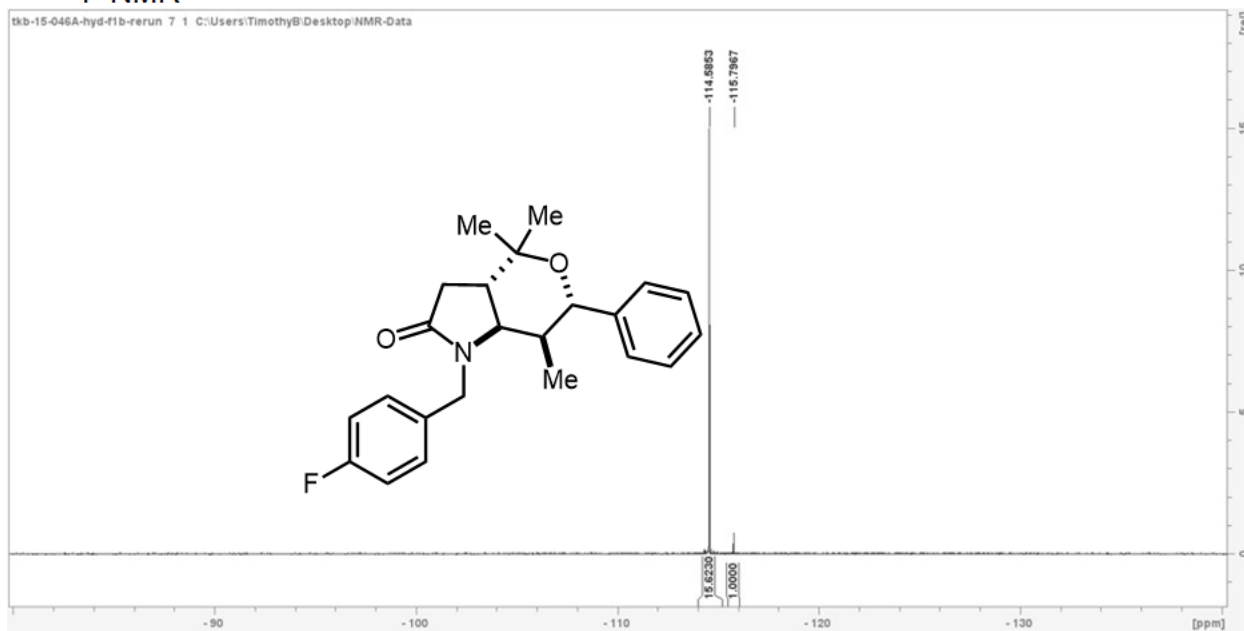
MHz, CDCl<sub>3</sub>) δ 175.5, 163.5 + 161.0 (C-F, d, <sup>1</sup>J<sub>C-F</sub> = 246.6 Hz), 140.7, 132.5, 130.0, 129.9, 128.1, 127.0, 125.9, 115.8, 115.6, 74.75, 73.96, 60.30, 43.84, 41.53, 36.49, 33.65, 29.74, 18.02, 5.87.

**HRMS-EI<sup>+</sup>** (*m/z*): calc for C<sub>24</sub>H<sub>29</sub>NO<sub>2</sub> [M]<sup>+</sup> 363.2198, found 363.2195.

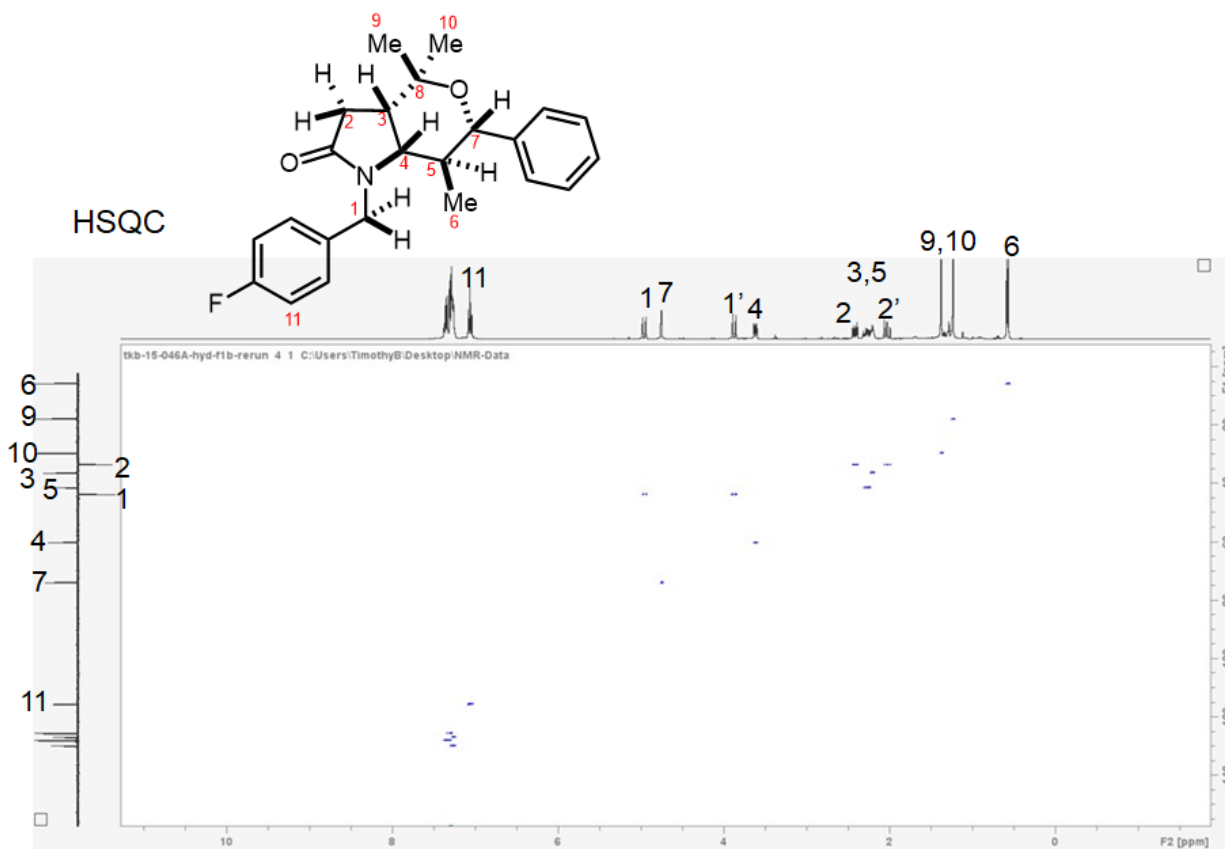




<sup>19</sup>F NMR







## References

- 1 H. Braunstein, S. Langevin, M. Khim, J. Adamson, K. Hovenkotter, L. Kotlarz, B. Mansker and T. K. Beng, *Org. Biomol. Chem.*, 2016, **14**, 8864-8872.
- 2 K. Hovenkotter, H. Braunstein, S. Langevin and T. K. Beng, *Org. Biomol. Chem.*, 2017, **15**, 1217-1221.