

## Supporting Information

### Deciphering Substitution Effects on Reductive Hydroalkoxylation of Alkynyl Aminols for Stereoselective Synthesis of Morpholines and 1,4-Oxazepanes: Total Synthesis of Tridemorph and Fenpropimorph

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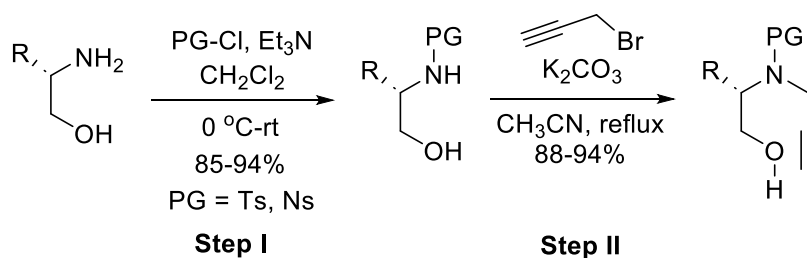
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**General experimental:**

Melting points are recorded using dbk programmable melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer.  $^1\text{H}$  (500 MHz) and  $^{13}\text{C}$  (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts ( $\delta$  ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual  $\text{CHCl}_3$  (7.26 ppm for  $^1\text{H}$ ) or the central line (77.16 ppm) of  $\text{CDCl}_3$  (for  $^{13}\text{C}$ ). In the  $^{13}\text{C}$  NMR spectra, the nature of the carbons (C, CH,  $\text{CH}_2$  or  $\text{CH}_3$ ) was determined by recording the DEPT-135 experiment, and is given in parentheses.

High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates ( $7.5 \times 2.5$  and  $9 \times 5.0$  cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F<sub>245</sub> silica plates and various combinations of ethyl acetate and Petroleum ether were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or  $\text{KMnO}_4$  stain or vanillin strain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane was prepared by refluxing over anhydrous  $\text{P}_2\text{O}_5$  and distillation on to calcium hydride. Dry DMF was prepared by stirring on CaH and distillation on to molecular sieves.  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{Cu}(\text{OTf})_2$ , TMSOTf, TfOH,  $\text{AgOTf}$ ,  $\text{In}(\text{OTf})_3$ ,  $\text{Bi}(\text{OTf})_3$ , and  $\text{Et}_3\text{SiH}$  were obtained from Aldrich. All other Lewis/Bronsted acids, propargyl bromide (80% in toluene), amino alcohol, propylene oxide, cyclohexane carbaldehyde, But-2-en-1-ol are commercial reagents and were used as such without further purification. All the starting material were prepared according to literature established protocol.<sup>1-2</sup>

### General procedure for the synthesis of *N*-Sulfonyl protected alkynyl aminols (6):



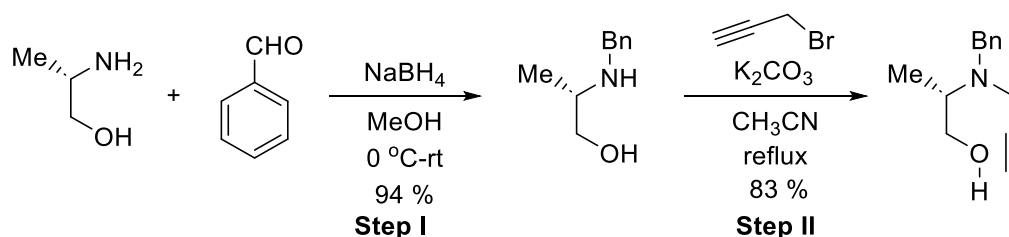
#### Step I:

To the magnetically stirred solution of amino alcohol (1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), was added *p*-Toluene/*p*-Nosylsulfonyl chloride (1.1 equiv) and Et<sub>3</sub>N (1.5 equiv) at 0 °C. The reaction mixture was allowed to stir at room temperature. After the complete consumption of the starting material (TLC control), the reaction mixture was diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo and the crude product was purified by silica gel chromatography using dichloromethane-methanol (98:2) as eluent to furnish *N*-Sulfonyl protected aminols.

#### Step II:

To a magnetically stirred solution of *N*-Sulfonyl protected amino alcohols (1.0 equiv) in CH<sub>3</sub>CN (10 mL), was added K<sub>2</sub>CO<sub>3</sub> (1.5 equiv) and propargyl bromide (1.3 equiv) at room temperature. The reaction mixture was heated at 80 °C. After the complete consumption of the starting material (TLC control), the reaction mixture is cooled to room temperature and filtered through celite. The filtrate was concentrated and purified by silica gel column using ethyl acetate-petroleum ether (20:80) as eluent to furnish terminal alkynols **6**.

### General procedure for the synthesis of *N*-benzylated alkynyl aminol (6d):



#### Step I:

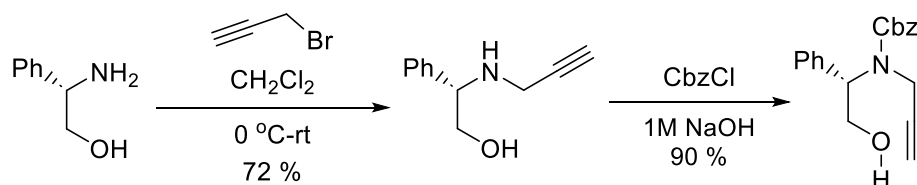
To a magnetically stirred solution of benzaldehyde (1.0 equiv) in dry MeOH (10 mL), was added amino alcohol (1.1 equiv) dropwise. After completion of addition, the reaction mixture was heated to 75 °C. After 1 h, the reaction mixture was cooled down to room temperature and then placed in an ice bath. Then NaBH<sub>4</sub> (1.5 equiv) was added over 20 min at 0 °C. After completion of addition, the reaction mixture continued stirring at room temperature. After complete conversion of the starting material (TLC control), the reaction mixture was

concentrated and the white crude reaction mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic layer was extracted with water. The aqueous layer was acidified with 10% HCl and then extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give benzyl protected amino alcohol.

**Step II:**

To a magnetically stirred solution of *N*-benzylated amino alcohols (1.0 equiv) in CH<sub>3</sub>CN (10 mL), was added K<sub>2</sub>CO<sub>3</sub> (1.5 equiv) and propargyl bromide (1.3 equiv) at room temperature. The reaction mixture was heated at 80 °C. After the complete consumption of the starting material (TLC control), the reaction mixture is cooled to room temperature and filtered through celite. The filtrate was concentrated and purified by silica gel column using ethyl acetate-petroleum ether (20:80) as eluent to furnish terminal alkynols **6d**.

**General procedure for the synthesis of *N*-Cbz protected alkynyl aminol (**6e**):**



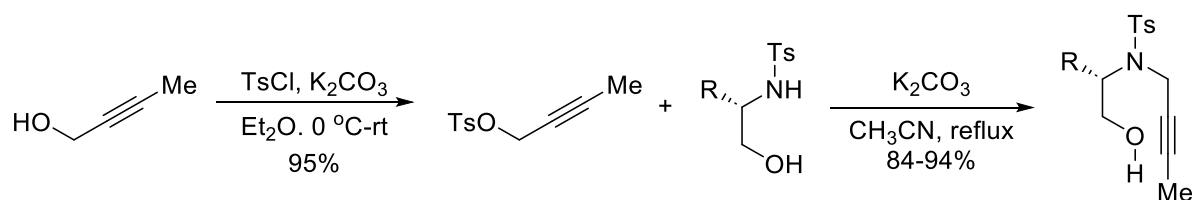
**Step I:**

To a magnetically stirred solution of amino alcohol (1.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), was added propargyl bromide (1.0 equiv, 80% in toluene). The temperature was monitored and if the reaction warmed above ambient temperature it was cooled in an ice bath. After complete consumption of starting material (TLC control), the mixture was poured into a separatory funnel, washed with water. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. Purification was accomplished by silica gel column chromatography using ethyl acetate-petroleum ether (40:80) as eluent to furnish terminal alkynol.

**Step II:**

A solution of benzyl chloroformate (1.1 equiv) in CHCl<sub>3</sub> (10 mL) was dropwise added to a mixture of amino alkynol (1.0 equiv), 4% aq. NaOH (1.5 mL) and CHCl<sub>3</sub> (40 mL). The reaction mixture was stirred in an ice bath. After the complete consumption of starting material (TLC control), the resulting mixture was diluted with water. The aqueous phase was extracted with CHCl<sub>3</sub> (3 x 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column using ethyl acetate-petroleum ether (20:80) as eluent to furnish terminal alkynol **6e**.

### General procedure for the synthesis of internal alkynol (8):



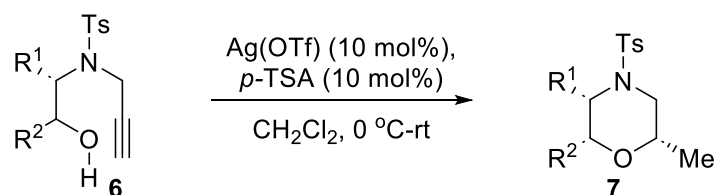
#### Step I:<sup>3</sup>

To a magnetically stirred solution of 2-butyn-1-ol (1.0 equiv) in  $\text{Et}_2\text{O}$  (15 mL), was added *p*-toluenesulfonyl chloride (1.1 equiv). The reaction mixture was allowed to cool at  $0\text{ }^\circ\text{C}$  followed by portion wise addition of powdered  $\text{KOH}$  (6 equiv). After the addition was completed, the reaction mixture was stirred at room temperature. After complete consumption of starting material (TLC control), reaction mixture was poured into water (30 mL). The layers were separated and the aqueous phase was extracted with  $\text{EtOAc}$  ( $3 \times 10\text{ mL}$ ). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, concentrated in vacuo and purified by silica gel column using ethyl acetate-petroleum ether (20:80) as eluent to furnish tosylated alcohol.

#### Step II:

To a solution of  $N$ -tosylated amino alcohols (1.0 equiv) in  $\text{CH}_3\text{CN}$  (15 mL), was added  $\text{K}_2\text{CO}_3$  (1.5 equiv) and but-2-yn-1-yl 4-methylbenzenesulfonate (1.3 equiv) and refluxed for 12 hr. After complete consumption of starting material (TLC control), the crude reaction mixture was filtered through celite, concentrated followed by purification on a silica gel column using ethyl acetate-petroleum ether (15:85) as eluent to furnish the alkynols **6**.

### General procedure for the synthesis of morpholines (7):



To a magnetically stirred solution of alkynol **6** (1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (5 mL) at  $0\text{ }^\circ\text{C}$ , were added  $\text{Ag}(\text{OTf})$  (10 mol%) and *p*-TSA (10 mol%). The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control),  $\text{Et}_3\text{SiH}$  (2.0 equiv) was added. After the complete consumption of the hydroalkoxylated product, the reaction mixture was quenched with saturated  $\text{NaHCO}_3$ , extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5\text{ mL}$ ), washed with brine, and dried. Evaporation of solvent and purification of residue on silica gel column using  $\text{EtOAc}$ -petroleum ether as eluent furnished morpholines **7**.

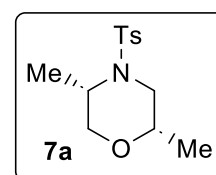
**(2*S*,5*S*)-2-Methyl-5-phenyl-4-tosylmorpholine (7a):**

To a magnetically stirred solution of alkynol **6a** (100 mg, 0.374 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (9.6 mg, 0.037 mmol) and *p*-TSA (6.4 mg, 0.037 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (119.3 μL, 0.748 mmol) was added. After the complete consumption of starting material (TLC control), the reaction mixture was quenched with saturated NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL) dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent and purification of residue on silica gel column using EtOAc-petroleum ether as eluent furnished morpholine **7a** (96 mg, 95%).

**Physical appearance:** Sticky liquid.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sup>23</sup><sub>D</sub>:** 46.4 (*c* 1.3, CHCl<sub>3</sub>).



**IR (neat):** 3058, 2979, 2919, 2865, 1599, 1495, 1451, 1381, 1341, 1299, 1268, 1162, 1120, 1096, 1022, 997, 907, 843, 816, 770, 737, 703 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.66 (dd, *J* = 8.0, 2.8 Hz, 2H), 7.28 (dd, *J* = 8.0, 2.8 Hz, 2H), 3.94-3.92 (m, 1H), 3.58-3.57 (m, 2 H), 3.52-3.48 (m, 1H), 3.46-3.41 (m, 1H), 2.79-2.72 (m, 1H), 2.39 (s, 3H), 1.12 (dd, *J* = 6.0, 3.2 Hz, 3H), 1.06 (dd, *J* = 6.8, 3.4 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.3 (C), 137.5 (C), 129.8 (2 × CH), 127.0 (2 × CH), 71.8 (CH), 71.3 (CH<sub>2</sub>), 48.1 (CH), 45.8 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>), 18.6 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub>S 270.1168, found 270.1168.

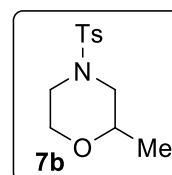
**2-methyl-4-tosylmorpholine (7b):**

To a magnetically stirred solution of alkynol **6b** (100 mg, 0.395 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (10.1 mg, 0.039 mmol) and *p*-TSA (6.8 mg, 0.039 mmol) ) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (125.9 μL, 0.789 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7b** (92 mg, 91%).

**Physical appearance:** Sticky liquid.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2982, 2920, 2899, 2861, 1595, 1489, 1447, 1387, 1377, 1340, 1296, 1280, 1184, 1162, 1112, 1053, 1001, 903, 861, 823, 769, 709 cm<sup>-1</sup>.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.63 (d, *J* = 6.4 Hz, 2H), 7.34 (d, *J* = 6.4 Hz, 2H), 3.89-3.86 (m, 1H), 3.70-3.64 (m, 2H), 3.55-3.49 (m, 2H), 2.44 (s, 3H), 2.36 (ddd, *J* = 11.6, 3.2 Hz, 1H), 2.01 (t, *J* = 8.4 Hz, 1H), 1.12 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 144.0 (C), 132.3 (C), 129.9 (2 × CH), 128.0 (2 × CH), 71.5 (CH), 66.0 (CH<sub>2</sub>), 51.7 (CH<sub>2</sub>), 45.4 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. for C<sub>12</sub>H<sub>18</sub>NO<sub>3</sub>S 256.1005, found 256.1005.

**(2*S*,5*S*)-2,5-dimethyl-4-((4-nitrophenyl) sulfonyl) morpholine (7c):**

To a magnetically stirred solution of alkynol **6c** (100 mg, 0.335 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (8.71 mg, 0.034 mmol) and *p*-TSA (6.44 mg, 0.034) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (119.5 μL, 0.748 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7c** (91 mg, 90%).

**Physical Appearance:** White solid.

**m.p.:** 105-107°C.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sup>23</sup><sub>D</sub>:** 48.9 (*c* 0.3, CHCl<sub>3</sub>).

**IR (neat):** 2876, 2363, 1535, 1354, 1039, 741, 554 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.37-8.34 (m, 2H), 8.00-7.97 (m, 2H), 4.02-3.97 (m, 1H), 3.63 (d, *J* = 2.0 Hz, 2H), 3.56 (ddd, *J* = 12.8, 2.8, 0.8 Hz, 3H), 3.51-3.43 (m, 1H), 2.82 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 150.1 (C), 146.6 (C), 128.8 (2 × CH), 124.5 (2 × CH), 72.1 (CH), 71.5 (CH<sub>2</sub>), 48.7 (CH), 46.1 (CH<sub>2</sub>), 18.6 (CH<sub>3</sub>), 14.2 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>S 301.0809, found 301.0809.

**(2*S*,5*S*)-5-Isopropyl-2-methyl-4-tosylmorpholine (7f):**

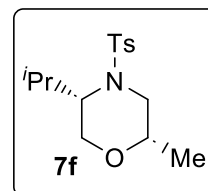
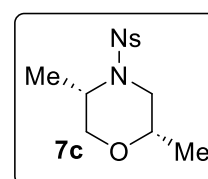
To a magnetically stirred solution of alkynol **6f** (77.0 mg, 0.251 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (6.4 mg, 0.025 mmol) and *p*-TSA (4.3 mg, 0.025 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (119.3 μL, 0.748 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7f** (68 mg, 91%).

**Physical appearance:** Sticky liquid.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sup>23</sup><sub>D</sub>:** 23.6 (*c* 1.5, CHCl<sub>3</sub>).

**IR (neat):** 2965, 2364, 1458, 1340, 1277, 1160, 1096, 1021, 995, 905, 815, 782, 679, 560 cm<sup>-1</sup>.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.83 (d, *J* = 11.6 Hz, 1H), 3.61 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.30-3.23 (m, 2H), 3.21-3.15 (m, 1H), 2.83 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.41 (s, 3H), 2.27-2.18 (m, 1H), 1.03 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3 H), 0.93 (d, *J* = 6.8 Hz, 3 H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.3 (C), 138.8 (C), 129.9 (2 × CH), 127.0 (2 × CH), 70.5 (CH), 66.3 (CH<sub>2</sub>), 59.0 (CH), 47.0 (CH<sub>2</sub>), 25.4 (CH<sub>3</sub>), 21.6 (CH), 20.0 (CH<sub>3</sub>), 19.8 (CH<sub>3</sub>), 18.6 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>15</sub>H<sub>24</sub>NO<sub>3</sub>S 298.1478, found 298.1478.

**(2*S*)-5-isobutyl-2-methyl-4-tosylmorpholine (7g):**

To a magnetically stirred solution of alkynol **6g** (100 mg, 0.323 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (8.31 mg, 0.032 mmol) and *p*-TSA (5.57 mg, 0.032 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (103.3 μL, 0.647 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7g** (93 mg, 92%).

**Physical appearance:** Yellow oil.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>23</sup>:** 30.3 (*c* 0.2, CHCl<sub>3</sub>).

**IR (neat):** 2932, 1343, 1159, 1018, 993, 679, 559 cm<sup>-1</sup>.

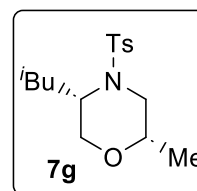
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.84 (d, *J* = 12.0 Hz, 1H), 3.59 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.36 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.24 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.21-3.14 (m, 1H), 2.82 (dd, *J* = 14.8, 11.2 Hz, 1H), 2.42 (s, 3H), 2.03-1.92 (m, 1H), 1.65-1.57 (m, 2H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.92-0.87 (m, 6H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 138.9 (C), 130.0 (2 × CH), 127.1 (2 × CH), 70.4 (CH), 66.4 (CH<sub>2</sub>), 57.8 (CH), 47.2 (CH<sub>2</sub>), 31.7 (CH), 25.4 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 19.0 (CH<sub>3</sub>), 16.0 (CH<sub>3</sub>), 11.3 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>16</sub>H<sub>26</sub>NO<sub>3</sub>S 312.1628, found 312.1628.

**(2*S*,5*S*)-2-Methyl-5-phenyl-4-tosylmorpholine (7h):**

To a magnetically stirred solution of alkynol **6h** (100 mg, 0.302 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (8.17 mg, 0.030 mmol) and *p*-TSA (5.50 mg, 0.030 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (96.5 μL, 0.604 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7h** (94 mg, 94%).





**Physical appearance:** Yellow oil.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sup>23</sup><sub>D</sub>:** -104.7 (*c* 0.6, CHCl<sub>3</sub>).

**IR (neat):** 2917, 2363, 1340, 1163, 770, 688, 558 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.49-7.47 (m, 2H), 7.33-7.27 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.93 (s, *J* = 3.2 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.82 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.61 (dd, *J* = 13.6, 2.8 Hz, 1H), 3.56-3.50 (m, 1H), 2.84 (dd, *J* = 13.6, 10.4 Hz, 1H), 2.42 (s, 3H), 1.13 (d, *J* = 6.0 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 138.1 (C), 137.7 (C), 129.8 (2 × CH), 128.53 (2 × CH), 128.46 (2 × CH), 127.7 (CH), 127.2 (2 × CH), 71.4 (CH), 69.0 (CH<sub>2</sub>), 54.4 (CH), 47.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub>S 332.1308, found 332.1308.

**(2*S*,5*S*)-5-benzyl-2-methyl-4-tosylmorpholine (7i):**

To a magnetically stirred solution of alkynol **6i** (100 mg, 0.291 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (7.5 mg, 0.029 mmol) and *p*-TSA (5.0 mg, 0.029 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (93.0 μL, 0.582 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7i** (97 mg, 96%).

**Physical appearance:** Yellow oil.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sup>23</sup><sub>D</sub>:** -42.6 (*c* 0.3, CHCl<sub>3</sub>).

**IR (neat):** 3301, 2340, 1661, 1406, 1045, 772, 558 cm<sup>-1</sup>.

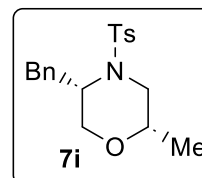
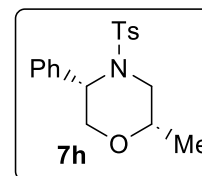
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.30-7.18 (m, 7H), 3.99-3.96 (m, 1H), 3.65 (d, *J* = 11.8 Hz, 1H), 3.59 (dd, *J* = 13.2, 2.0 Hz, 1H), 3.52-3.47 (m, 1H), 3.43 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.03 (dd, *J* = 12.8, 10.8 Hz, 1H), 2.91 (dd, *J* = 12.8, 11.2 Hz, 1H), 2.69 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.40 (s, 3H), 1.19 (d, *J* = 6.0 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.5 (C), 138.0 (C), 137.7 (C), 129.9 (2 × CH), 129.5 (2 × CH), 128.7 (2 × CH), 127.1 (2 × CH), 126.6 (CH), 71.8 (CH), 67.3 (CH<sub>2</sub>), 54.1 (CH), 46.6 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. for C<sub>19</sub>H<sub>24</sub>NO<sub>3</sub>S 346.1461, found 346.1461.

**(2*S*\*,6*R*\*)-2,6-Dimethyl-4-tosylmorpholine (7j):**

To a magnetically stirred solution of alkynol **6j** (100 mg, 0.374 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (9.61 mg, 0.037 mmol) and *p*-TSA (6.44 mg, 0.037) at 0 °C. The



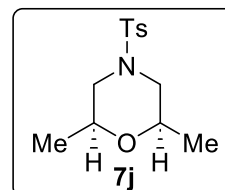
reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (119.5 μL, 0.748 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7j** (89 mg, 88%).

**Physical Appearance:** White solid.

**m.p.:** 100-102 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2931, 2363, 1716, 1339, 1159, 1090, 816, 760, 657, 551 cm<sup>-1</sup>.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.71-3.63 (m, 2H), 3.53-3.51 (m, 2H), 2.41 (s, 3H), 1.90 (t, *J* = 10.4 Hz, 2H), 1.10 (d, *J* = 6.4 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.9 (C), 132.3 (C), 129.8 (2 × CH), 127.8 (2 × CH), 71.4 (2 × CH), 50.9 (2 × CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 18.7 (2 × CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub>S 270.1182, found 270.1182.

**(2S\*,6R\*)-2-Cyclohexyl-6-methyl-4-tosylmorpholine (7k):**

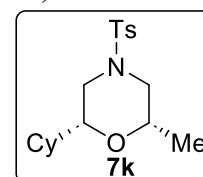
To a magnetically stirred solution of alkynol **6k** (100 mg, 0.298 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (7.6 mg, 0.029 mmol) and *p*-TSA (5.1 mg, 0.0269) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (95.2 μL, 0.596 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7k** (85 mg, 85%).

**Physical Appearance:** White solid.

**m.p.:** 126-128 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2929, 2849, 1595, 1449, 1343, 1161, 1095, 1064, 994, 932, 816, 774 cm<sup>-1</sup>.



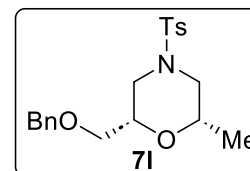
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.64-3.59 (m, 2H), 3.54-3.29 (m, 1H), 3.29-3.24 (m, 1H), 2.42 (s, 3H), 1.99-1.84 (m, 3H), 1.69-1.57 (m, 4H), 1.32-1.24 (m, 1H), 1.20-1.09 (m, 6H), 1.03-0.92 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.8 (C), 132.4 (C), 129.8 (2 × CH), 127.8 (2 × CH), 79.5 (CH), 71.3 (CH), 51.3 (CH<sub>2</sub>), 47.7 (CH<sub>2</sub>), 40.9 (CH), 29.0 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>18</sub>H<sub>28</sub>NO<sub>3</sub>S 338.1801, found 338.1801.

**(2R\*,6R\*)-2-(Benzyloxymethyl)-6-methyl-4-tosylmorpholine (7l):**

To a magnetically stirred solution of alkynol **6l** (100 mg, 0.268 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (6.9 mg, 0.027 mmol) and *p*-TSA (4.6 mg, 0.027 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (85.5 μL, 0.536 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **7l** (91 mg, 90%).



**Physical Appearance:** Pale yellow liquid.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 3062, 3032, 2978, 2869, 2251, 1724, 1599, 1495, 1453, 1347, 1235, 1166, 1089, 1001, 912, 812, 783, 734, 703 cm<sup>-1</sup>.

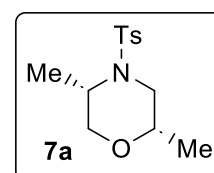
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.36-7.28 (m, 7H), 4.52 (s, 2H), 3.83-3.78 (m, 1H), 3.76-3.68 (m, 1H), 3.56 (dt, *J* = 11.2, 1.6 Hz, 1H), 3.56 (dt, *J* = 11.2, 2.0 Hz, 1H), 3.44 (qd, *J* = 10.0, 4.8 Hz, 2H), 2.44 (s, 3H), 2.11 (t, *J* = 10.8 Hz, 1H), 1.96 (t, *J* = 10.4 Hz, 1H), 1.15 (d, *J* = 6 Hz, 3H);

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 144.0 (C), 137.8 (C), 132.3 (C), 129.8 (2×CH), 128.5 (CH), 127.91 (2 × CH), 127.88 (2 × CH), 127.82 (2 × CH), 74.4 (CH), 73.5 (CH<sub>2</sub>), 71.6 (CH), 70.5 (CH<sub>2</sub>), 51.2 (CH<sub>2</sub>), 47.3 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub>NaS 376.1598, found 376.1598.

**Gram scale procedure for the synthesis of (2*S*,5*S*)-2-Methyl-5-phenyl-4-tosylmorpholine (7a):**

To a magnetically stirred solution of alkynol **6a** (1.0 g, 3.74 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), were added Ag(OTf) (96 mg, 0.37 mmol) and *p*-TSA (64 mg, 0.37 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (1.19 mL, 7.48 mmol) was added. After the complete consumption of starting material (TLC control), the reaction mixture was quenched with saturated NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL) dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent and purification of residue on silica gel column using EtOAc-petroleum ether as eluent furnished morpholine **7a** (836 mg, 83%).



**Physical appearance:** Sticky liquid.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>23</sup>:** 46.4 (*c* 1.3, CHCl<sub>3</sub>).

**IR (neat):** 3058, 2979, 2919, 2865, 1599, 1495, 1451, 1381, 1341, 1299, 1268, 1162, 1120,

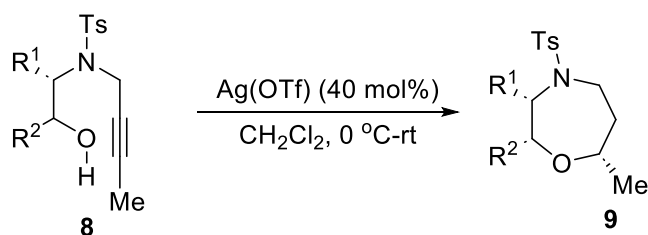
1096, 1022, 997, 907, 843, 816, 770, 737, 703  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.66 (dd,  $J = 8.0, 2.8$  Hz, 2H), 7.28 (dd,  $J = 8.0, 2.8$  Hz, 2H), 3.94-3.92 (m, 1H), 3.58-3.57 (m, 2 H), 3.52-3.48 (m, 1H), 3.46-3.41 (m, 1H), 2.79-2.72 (m, 1H), 2.39 (s, 3H), 1.12 (dd,  $J = 6.0, 3.2$  Hz, 3H), 1.06 (dd,  $J = 6.8, 3.4$  Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , DEPT):**  $\delta$  143.3 (C), 137.5 (C), 129.8 ( $2 \times \text{CH}$ ), 127.0 ( $2 \times \text{CH}$ ), 71.8 (CH), 71.3 ( $\text{CH}_2$ ), 48.1 (CH), 45.8 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_3$ ), 18.6 ( $\text{CH}_3$ ), 13.7 ( $\text{CH}_3$ ).

**HRMS (ESI,  $\text{M}+\text{H}^+$ ):**  $m/z$  calcd. For  $\text{C}_{13}\text{H}_{20}\text{NO}_3\text{S}$  270.1168, found 270.1168.

### General procedure for the synthesis of oxazepanes (**9**):



To a magnetically stirred solution of alkyne **8** (1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (5 mL), was added  $\text{Ag(OTf)}$  (40 mol%) at  $0\text{ }^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control),  $\text{Et}_3\text{SiH}$  (1.088 mmol) was added. After the complete consumption of the hydrated product, the reaction mixture was quenched with saturated  $\text{NaHCO}_3$ , extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL), washed with brine, and dried. Evaporation of solvent and purification of residue on silica gel column using  $\text{EtOAc}$ -petroleum ether as eluent furnished oxazepanes **9**.

### (*3S,7S*)-3,7-dimethyl-4-tosyl-1,4-oxazepane (**9a**):

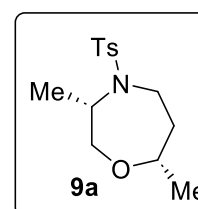
To a magnetically stirred solution of alkyne **8a** (70 mg, 0.213 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL), was added  $\text{Ag(OTf)}$  (21.9mg, 0.085 mmol) at  $0\text{ }^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control),  $\text{Et}_3\text{SiH}$  (68.1  $\mu\text{L}$ , 0.426 mmol) was added. After the complete consumption of the starting material (TLC control), the reaction mixture was quenched with saturated  $\text{NaHCO}_3$ , extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent and purification of residue on silica gel column using  $\text{EtOAc}$ - petroleum ether as eluent furnished oxazepane **9a** (56 mg, 92%).

**Physical Appearance:** Yellow oil.

**$R_f$ :** 0.7 (20:80,  $\text{EtOAc}$ :Petroleum ether).

**$[\alpha]_{\text{D}}^{25}$ :** 60.4 ( $c$  0.5,  $\text{CHCl}_3$ )

**IR (neat):** 2932, 1336, 1158, 1085, 944, 851, 673, 550  $\text{cm}^{-1}$ .



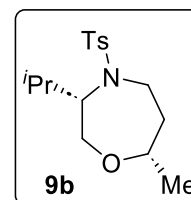
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.09-4.03 (m, 1H), 3.73-3.65 (m, 2H), 3.58-3.47 (m, 2H), 3.33-3.26 (m, 1H), 2.40 (s, 3H), 2.07-1.99 (m, 1H), 1.68-1.60 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.2 (C), 137.7 (C), 129.8 (2 × CH), 126.9 (2 × CH), 76.3 (CH), 74.2 (CH<sub>2</sub>), 54.2 (CH), 40.5 (CH<sub>2</sub>), 37.4 (CH<sub>2</sub>), 22.4 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 16.5 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>14</sub>H<sub>21</sub>NNaO<sub>3</sub>S 306.1143, found 306.1143.

**(3*S*,7*S*)-3-isopropyl-7-methyl-4-tosyl-1,4-oxazepane (9b):**

To a magnetically stirred solution of alkynol **8b** (50 mg, 0.179 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (18.7 mg, 0.072 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (57.2 μL, 0.358 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9b** (49 mg, 87%).



**Physical Appearance:** White solid.

**m.p.:** 67-69 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>25</sup>:** 29.8 (*c* 0.9, CHCl<sub>3</sub>)

**IR (neat):** 2957, 1462, 1337, 1157, 755, 672, 551 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.67-3.58 (m, 2H), 3.44-3.38 (m, 2H), 3.22-3.15 (m, 1H), 2.41 (s, 3H), 2.10-2.02 (m, 2H), 1.62-1.54 (m, 1H), 1.14 (dd, *J* = 6.4, 0.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.65 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.1 (C), 138.3 (C), 129.6 (2×CH), 127.2 (2×CH), 76.3 (CH), 71.3 (CH<sub>2</sub>), 65.1 (CH), 40.5 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 26.7 (CH), 22.6 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 20.2 (CH<sub>3</sub>), 20.1 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>16</sub>H<sub>26</sub>NO<sub>3</sub>S 312.1667, found 312.1667.

**(3*S*,7*S*)-3-isobutyl-7-methyl-4-tosyl-1,4-oxazepane (9c):**

To a magnetically stirred solution of alkynol **8c** (50 mg, 0.154 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (15.9 mg, 0.062 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (49.3 μL, 0.309 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the

oxazepane derivative **9c** (43 mg, 85%).

**Physical Appearances:** Colorless oil.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>25</sup>:** 39.5 (*c* 0.2, CHCl<sub>3</sub>)

**IR (neat):** 2957, 1462, 1337, 1157, 755, 672, 551 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.4 Hz, 2H), 4.05 (dd, *J* = 13.2, 1.6 Hz, 1H), 3.64-3.56 (m, 2H), 3.52 (d, *J* = 10.8 Hz, 1H), 3.39 (dd, *J* = 13.2, 2.4 Hz, 1H), 3.19-3.12 (m, 1H), 2.41 (s, 3H), 2.06-1.98 (m, 1H), 1.85-1.79 (m, 1H), 1.62-1.53 (m, 1H), 1.33-1.24 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 4.8 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.1 (C), 138.3 (C), 129.6 (2 × CH), 127.2 (2 × CH), 76.1 (CH), 71.2 (CH<sub>2</sub>), 63.8 (CH), 40.6 (CH<sub>2</sub>), 36.7 (CH<sub>2</sub>), 33.1 (CH), 25.4 (CH<sub>2</sub>), 22.6 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 16.0 (CH<sub>3</sub>), 11.5 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>17</sub>H<sub>27</sub>NNaO<sub>3</sub>S 348.1616, found 348.1616.

**(3*S*,7*S*)-7-methyl-3-phenyl-4-tosyl-1,4-oxazepane (9d):**

To a magnetically stirred solution of alkynol **8d** (50 mg, 0.213 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (21.9 mg, 0.085 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (68.1 μL, 0.426 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9d** (62 mg, 83%).

**Physical Appearance:** White solid.

**m.p.:** 72-74 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

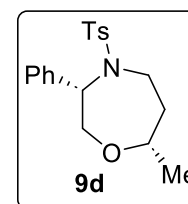
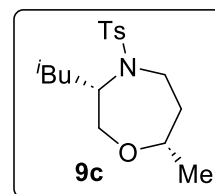
**[α]<sub>D</sub><sup>25</sup>:** -92.8 (*c* 1.1, CHCl<sub>3</sub>).

**IR (neat):** 2931, 2341, 1339, 1160, 684, 554 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28-7.25 (m, 5H), 5.13 (s, 1H), 4.50 (dd, *J* = 13.5, 1.5 Hz, 1H), 3.85 (dd, *J* = 13.5, 3.5 Hz, 1H), 3.80-3.73 (m, 1H), 3.57-3.51 (m, 1H), 3.24-3.18 (m, 1H), 2.47 (s, 3H), 2.12-2.06 (m, 1H), 1.60-1.53 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 138.6 (C), 138.1 (C), 129.8 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 127.5 (CH), 127.2 (2 × CH), 76.9 (CH), 73.1 (CH<sub>2</sub>), 61.0 (CH), 41.8 (CH<sub>2</sub>), 37.5 (CH<sub>2</sub>), 22.4 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>19</sub>H<sub>23</sub>NNaO<sub>3</sub>S 368.1301, found 368.1301.



**(3*S*,7*S*)-7-methyl-4-((4-nitrophenyl) sulfonyl)-3-phenyl-1,4-oxazepane (9e):**

To a magnetically stirred solution of alkynol **8e** (60 mg, 0.160 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (16.5 mg, 0.064 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (51.2 μL, 0.321 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9e** (49 mg, 81%).

**Physical Appearance:** White solid.

**m.p.:** 108-110 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>25</sup>:** -98.9 (*c* 0.5, CHCl<sub>3</sub>).

**IR (neat):** 2931, 2339, 1531, 1350, 1308, 1166, 856, 738 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 8.31 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.24-7.18 (m, 5H), 5.13 (s, 1H), 4.44 (dd, *J* = 13.5, 2.0 Hz, 1H), 3.86 (dd, *J* = 13.5, 3.5 Hz, 1H), 3.83-3.77 (m, 1H), 3.59-3.54 (m, 1H), 3.34-3.29 (m, 1H), 2.16-2.09 (m, 1H), 1.66-1.60 (m, 2H), 1.21 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, DEPT):** δ 149.9 (C), 146.8 (C), 137.8 (C), 128.7 (CH), 128.3 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 124.4 (2 × CH), 76.8 (CH), 73.1 (CH<sub>2</sub>), 61.8 (CH), 42.3 (CH<sub>2</sub>), 37.6 (CH<sub>2</sub>), 22.2 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>S 377.1175, found 377.1175.

**(3*S*,7*S*)-7-methyl-3-phenyl-4-tosyl-1,4-oxazepane (9f):**

To a magnetically stirred solution of alkynol **8f** (60 mg, 0.168 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (17.2 mg, 0.067 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (53.6 μL, 0.336 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9f** (53 mg, 88%).

**Physical Appearance:** White solid.

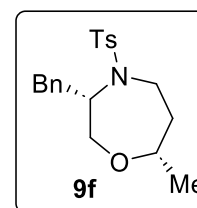
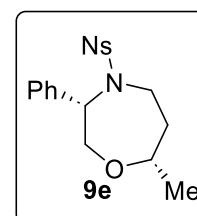
**m.p.:** 74-76 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>25</sup>:** 15.9 (*c* 0.9, CHCl<sub>3</sub>).

**IR (neat):** 2932, 2308, 1590, 1590, 1457, 1336, 1155, 752, 550 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.26-7.18 (m, 5H), 7.15-7.13 (m, 2H), 4.07-4.04 (m, 1H), 3.77-3.70 (m, 2H), 3.53-3.41 (m, 3H), 3.05 (dd, *J*



= 13.2, 10.0 Hz, 1H), 2.76 (dd,  $J = 13.2, 5.2$  Hz, 1H), 2.40 (s, 3H), 2.16-2.08 (m, 1H), 1.78-1.70 (m, 1H), 1.23 (d,  $J = 6.4$  Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , DEPT):**  $\delta$  143.2 (C), 138.3 (C), 137.4 (C), 129.8 (2  $\times$  CH), 129.5 (2  $\times$  CH), 128.6 (2  $\times$  CH), 127.1 (2  $\times$  CH), 126.5 (CH), 76.5 (CH), 70.4 ( $\text{CH}_2$ ), 60.8 (CH), 41.4 ( $\text{CH}_2$ ), 37.5 ( $\text{CH}_2$ ), 37.2 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ).

**HRMS (ESI,  $\text{M}+\text{Na}^+$ ):**  $m/z$  calcd. For  $\text{C}_{20}\text{H}_{25}\text{NNaO}_3\text{S}$  382.1459, found 382.1459.

***7-methyl-4-tosyl-1,4-oxazepane (9g):***

To a magnetically stirred solution of alkynol **8g** (50 mg, 0.187 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL), was added  $\text{Ag}(\text{OTf})$  (19.2 mg, 0.075 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control),  $\text{Et}_3\text{SiH}$  (59.7  $\mu\text{L}$ , 0.374 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9g** (42 mg, 84%).

**Physical Appearance:** Colorless oil.

**$R_f$ :** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2931, 1338, 1161, 714, 549  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.69-7.66 (m, 2H), 7.33-7.28 (m, 2H), 3.97-3.93 (m, 1H), 3.81-3.77 (m, 1H), 3.64-3.58 (m, 2H), 3.50-3.46 (m, 1H), 3.24-3.20 (m, 1H), 3.15-3.09 (m, 1H), 2.43 (s, 3H), 2.05-2.00 (m, 1H), 1.71-1.67 (m, 1H), 1.19-1.17 (m, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , DEPT):**  $\delta$  143.4 (C), 135.9 (C), 129.8 (2  $\times$  CH), 127.1 (2  $\times$  CH), 75.8 (CH), 69.2 ( $\text{CH}_2$ ), 51.6 ( $\text{CH}_2$ ), 46.0 ( $\text{CH}_2$ ), 37.4 ( $\text{CH}_2$ ), 22.4 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ).

**HRMS (ESI,  $\text{M}+\text{Na}^+$ ):**  $m/z$  calcd. For  $\text{C}_{13}\text{H}_{19}\text{NNaO}_3\text{S}$  292.0958, found 292.0958.

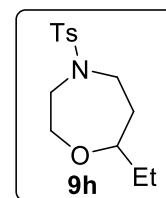
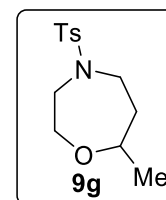
***7-ethyl-4-tosyl-1,4-oxazepane (9h):***

To a magnetically stirred solution of alkynol **8h** (50 mg, 0.178 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL), was added  $\text{Ag}(\text{OTf})$  (18.3 mg, 0.071 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control),  $\text{Et}_3\text{SiH}$  (56.7  $\mu\text{L}$ , 0.355 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9h** (43 mg, 85%).

**Physical Appearance:** Colorless liquid.

**$R_f$ :** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2939, 2340, 1338, 1163, 1039, 769, 549  $\text{cm}^{-1}$ .





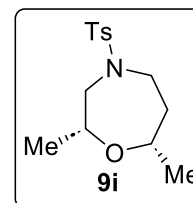
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.68 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.33-7.28 (m, 2H), 4.01-3.97 (m, 1H), 3.63-3.57 (m, 2H), 3.54-3.48 (m, 2H), 3.20-3.16 (m, 1H), 3.15-3.06 (m, 1H), 2.44 (s, 3H), 2.08-2.00 (m, 1H), 1.74-1.62 (m, 2H), 1.55-1.40 (m, 2H), 0.94-0.89 (m, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 136.0 (C), 129.8 (2 × CH), 127.1 (2 × CH), 81.4 (CH), 69.9 (CH<sub>2</sub>), 51.8 (CH<sub>2</sub>), 46.4 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 10.4 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>14</sub>H<sub>21</sub>NNaO<sub>3</sub>S 306.1120, found 306.1120.

**(2*R*\*, 7*S*\*)-2,7-dimethyl-4-tosyl-1,4-oxazepane (9i):**

To a magnetically stirred solution of alkynol **8i** (50 mg, 0.178 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (18.3 mg, 0.071 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (56.7 μL, 0.355 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9i** (46 mg, 92%).



**Physical Appearance:** Colorless oil.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2932, 1336, 1158, 1085, 944, 851, 673, 550 cm<sup>-1</sup>.

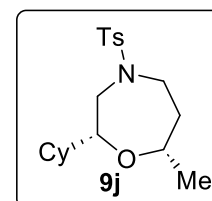
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.90-3.82 (m, 1H), 3.78-3.69 (m, 2H), 3.67-3.61 (m, 1H), 3.01-2.96 (m, 1H), 2.58 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.41 (s, 3H), 2.09-2.01 (m, 1H), 1.68-1.59 (m, 1H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.12 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.3 (C), 136.4 (C), 129.8 (2 × CH), 127.0 (2 × CH), 76.8 (CH), 74.9 (CH<sub>2</sub>), 57.6 (CH), 46.5 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 22.8 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 19.6 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>14</sub>H<sub>22</sub>NO<sub>3</sub>S 284.1346, found 284.1346.

**(2*R*\*, 7*S*\*)-2-cyclohexyl-7-methyl-4-tosyl-1,4-oxazepane (9j):**

To a magnetically stirred solution of alkynol **8j** (50 mg, 0.143 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (14.7 mg, 0.057 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (45.6 μL, 0.286 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9j** (43 mg, 86%).



**Physical Appearance:** Colorless solid.

**m.p.:** 70-72 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2966, 2924, 2850, 1598, 1494, 1446, 1371, 1337, 1306, 1266, 1205, 1154, 1086, 1044, 1022, 957, 883, 868, 817, 747, 732, 706 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.80-3.72 (m, 2H), 3.64-3.58 (m, 1H), 3.25-3.20 (m, 1H), 3.01-2.94 (m, 1H), 2.66 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.40 (s, 3H), 2.07-2.00 (m, 1H), 1.88 (d, *J* = 11 Hz, 1H), 1.71-1.68 (m, 2H), 1.62-1.54 (m, 3H), 1.31-1.23 (m, 2H), 1.15 (d, *J* = 6.5 Hz, 4H), 1.09-0.94 (m, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** 143.2 (C), 136.5 (C), 129.8 (2 × CH), 127.0 (2 × CH), 85.1 (CH), 75.7 (CH), 54.7 (CH<sub>2</sub>), 46.3 (CH<sub>2</sub>), 41.5 (CH), 37.9 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 22.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>19</sub>H<sub>30</sub>NO<sub>3</sub>S 352.1965, found 352.1965.

**Gram scale synthesis of (3*S*,7*S*)-7-methyl-3-phenyl-4-tosyl-1,4-oxazepane (9d):**

**(3*S*,7*S*)-7-methyl-3-phenyl-4-tosyl-1,4-oxazepane (9d):**

To a magnetically stirred solution of alkynol **8d** (1 g, 2.890 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), was added Ag(OTf) (288 mg, 1.16 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (926 μL, 5.800 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **9d** (792 mg, 79%).

**Physical Appearance:** White solid.

**m.p.:** 72-74 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**[α]<sub>D</sub><sup>25</sup>:** -92.8 (*c* 1.1, CHCl<sub>3</sub>).

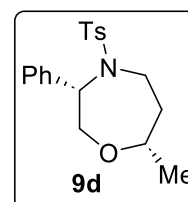
**IR (neat):** 2931, 2341, 1339, 1160, 684, 554 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28-7.25 (m, 5H), 5.13 (s, 1H), 4.50 (dd, *J* = 13.5, 1.5 Hz, 1H), 3.85 (dd, *J* = 13.5, 3.5 Hz, 1H), 3.80-3.73 (m, 1H), 3.57-3.51 (m, 1H), 3.24-3.18 (m, 1H), 2.47 (s, 3H), 2.12-2.06 (m, 1H), 1.60-1.53 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H).

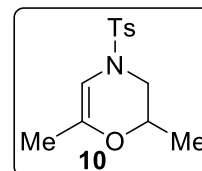
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 138.6 (C), 138.1 (C), 129.8 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 127.5 (CH), 127.2 (2 × CH), 76.9 (CH), 73.1 (CH<sub>2</sub>), 61.0 (CH), 41.8 (CH<sub>2</sub>), 37.5 (CH<sub>2</sub>), 22.4 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>19</sub>H<sub>23</sub>NNaO<sub>3</sub>S 368.1301, found 368.1301.

**2,6-dimethyl-4-tosyl-3,4-dihydro-2*H*-1,4-oxazine (10):**



To a magnetically stirred solution of alkynol **6j** (100 mg, 0.374 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (9.61 mg, 0.037 mmol) and *p*-TSA (6.44 mg, 0.037) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), the reaction mixture was quenched with saturated NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, and dried. Evaporation of solvent and purification of residue on silica gel column using EtOAc-petroleum ether as eluent furnished the morphine derivative **10** (90 mg, 90 %).



**Physical Appearance:** Colourless oil.

**R<sub>f</sub>:** 0.5 (10:90, EtOAc:Petroleum ether).

**IR (neat):** 3067, 2820, 2352, 1686, 1596, 1183, 1081, 1005, 917 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.81 (s, 1H), 3.68 (ddd, *J* = 13.1, 2.2, 1.4 Hz, 1H), 3.38-3.30 (m, 1H), 2.74 (d, *J* = 13.1, 9.0 Hz, 1H), 2.42 (s, 3H), 1.72 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.9 (C), 140.0 (C), 134.1 (C), 129.9 (2 × CH), 127.5 (2 × CH), 99.5 (CH), 68.5 (CH), 48.3 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>), 18.1 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>13</sub>H<sub>17</sub>NNaO<sub>3</sub>S 290.0823, found 290.0823.

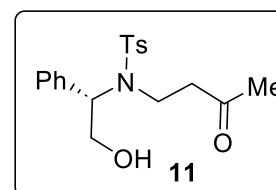
**(*S*)-*N*-(2-hydroxy-1-phenylethyl)-4-methyl-*N*-(3-oxobutyl) benzenesulfonamide (**11**):**

To a magnetically stirred solution of alkynol **8d** (50 mg, 0.213 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (21.9 mg, 0.085 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), the reaction mixture was quenched with saturated NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL), washed with brine, and dried. Evaporation of solvent and purification of residue on silica gel column using EtOAc-petroleum ether as eluent furnished methyl ketone **11** (69 mg, 90%).

**Physical Appearance:** Yellow oil.

**R<sub>f</sub>:** 0.3 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 3110, 2931, 2363, 1715, 1264, 1212, 1159, 1090, 816, 760, 657, 551 cm<sup>-1</sup>.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.24-7.22 (m, 4H), 7.13-7.04 (m, 2H), 5.09 (t, *J* = 8.4 Hz, 1H), 4.00 (d, *J* = 6.8 Hz, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 2.91-2.83 (m, 1H), 2.54-2.46 (m, 1H), 2.40 (s, 3H), 1.97 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 207.7 (C), 143.7 (C), 137.6 (C), 136.2 (C), 129.8 (2 × CH), 128.8 (2 × CH), 128.3 (CH), 128.0 (2 × CH), 127.4 (2 × CH), 62.3 (CH), 62.0 (CH<sub>2</sub>), 44.3 (CH<sub>2</sub>), 39.4 (CH<sub>2</sub>), 30.1 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>).

**HRMS (ESI, M+Na<sup>+</sup>):** *m/z* calcd. For C<sub>19</sub>H<sub>23</sub>NNaO<sub>4</sub>S 384.1239, found 384.1239.

**(5*S*\*)-5-methyl-3-tosyl-6,8-dioxa-3-azabicyclo [3.2.1] octane (14):**

To a magnetically stirred solution of alkynol **12** (100 mg, 0.353 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), were added Ag(OTf) (9.1 mg, 0.035 mmol) and *p*-TSA (6.1 mg, 0.035 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (112.7 μL, 0.706 mmol) was added as described for the morpholine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the morpholine derivative **14** (85 mg, 85%).

**Physical Appearance:** White solid.

**m.p.:** 156-158 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 3013, 2341, 1346, 1166, 1002, 767, 549 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.52 (d, *J* = 4.8 Hz, 1H), 4.03 (d, *J* = 6.8 Hz, 1H), 3.80 (t, *J* = 6.0 Hz, 1H), 3.48 (dd, *J* = 11.2, 1.3 Hz, 2H), 2.74 (d, *J* = 11.2 Hz, 1H), 2.44 (d, *J* = 10.8 Hz, 1H), 2.39 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.9 (C), 132.8 (C), 129.8 (2 × CH), 127.5 (2 × CH), 104.1 (C), 72.8 (CH), 68.2 (CH<sub>2</sub>), 52.6 (CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>13</sub>H<sub>18</sub>NO<sub>4</sub>S 284.0942, found 284.0942.

**(1*S*\*,6*R*\*)-6-methyl-3-tosyl-7,9-dioxa-3-azabicyclo [4.2.1] nonane (15):**

To a magnetically stirred solution of alkynol **13** (70 mg, 0.235 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added Ag(OTf) (24.1 mg, 0.094 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After complete consumption of starting material (TLC control), Et<sub>3</sub>SiH (74.9 μL, 0.469 mmol) was added as described for the oxazepane derivative **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the oxazepane derivative **15** (65 mg, 93%).

**Physical Appearance:** White solid.

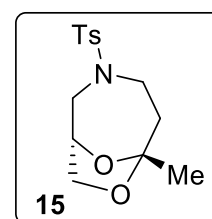
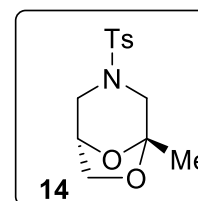
**m.p.:** 181-183 °C.

**R<sub>f</sub>:** 0.7 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2957, 1462, 1337, 1157, 755, 672, 551 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.50-4.48 (m, 1H), 4.02-4.00 (m, 1H), 3.95 (t, *J* = 6.8 Hz, 1H), 3.67-3.60 (m, 2H), 2.86 (dd, *J* = 13.2, 1.6 Hz, 1H), 2.77-2.70 (m, 1H), 2.40 (s, 3H), 2.20-2.12 (m, 1H), 1.89-1.84 (m, 1H), 1.41 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 143.4 (C), 136.1 (C), 129.8 (2 × CH), 127.0 (2 ×



CH), 110.4 (C), 76.1 (CH), 66.3 (CH<sub>2</sub>), 53.6 (CH<sub>2</sub>), 45.7 (CH<sub>2</sub>), 41.8 (CH<sub>2</sub>), 27.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>).

**HRMS (ESI, M+H<sup>+</sup>):** *m/z* calcd. For C<sub>14</sub>H<sub>20</sub>NO<sub>4</sub>S 298.3130, found 298.3130.

**(2*S*\*,6*R*\*)-2,6-Dimethyl-morpholine (16):**

To a cold (−78 °C) solution of compound **7j** (10 g, 39.469 mmol) in dry THF (100 mL) was added sodium naphthalide solution prepared by adding naphthalene (29.9 g, 236.817 mmol) to sodium (11.8 g, 296.018 mmol) in dry THF (50 mL) at rt and stirred for 2h and the resulting solution is stirred for 1 h. The reaction mixture was quenched by addition of saturated NH<sub>4</sub>Cl at −78 °C and warmed to rt. The reaction mixture was extracted with EtOAc (3 × 5 mL), and the combined organic layer was washed with dilute HCl (3 × 5 mL). The aqueous layer was neutralized with saturated aq NaHCO<sub>3</sub> and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to furnish **16** (2.65 g, 62%).

**Physical Appearance:** Colourless liquid.

**R<sub>f</sub>:** 0.5 (50:50, EtOAc:Petroleum ether).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 3.56-3.49 (m, 2H), 2.77 (d, *J* = 13.7 Hz, 2H), 2.37 (t, *J* = 11.2 Hz, 2H), 1.79 (brs, 1H), 1.72 (s, 3H), 1.08 (d, *J* = 4.8 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, DEPT):** δ 73.1 (2 × CH), 52.1 (2 × CH<sub>2</sub>), 19.2 (2 × CH<sub>3</sub>).

*Data is matching with the reported one*<sup>4,5</sup>

**(2*S*\*, 6*R*\*)-4-(3-(4-(*tert*-butyl) phenyl)-2-methylpropyl)-2,6-dimethylmorpholine (2):**

A magnetically stirred solution of 3-(4-(*tert*-butyl) phenyl)-2-methylpropanal (**18**) (100 mg, 0.489 mmol) and (2*S*\*, 6*R*\*)-2,6-dimethylmorpholine **16** (68 mg, 0.587 mmol) in acetic acid (3 mL), was heated at 80°C for 10 minutes. NaBH<sub>4</sub> (22 mg, 0.362 mmol) was added to the solution portion wise and the resulting mixture was refluxed until complete consumption of starting material. The solvent was removed under reduced pressure. After completion of reaction (TLC control), the residue was washed with 20% NaOH solution and was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL). The organic layer was washed with water (2 × 5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent and purification of residue on silica gel column using EtOAc-petroleum ether as eluent furnished morpholine (**2**) (137 mg, 92%).

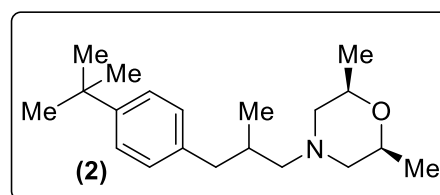
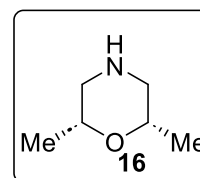
**Physical Appearance:** Yellow oil.

**R<sub>f</sub>:** 0.5 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 2965, 1682, 1373, 1145, 1084, 575 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.29 (d, *J* = 8.0 Hz, 2H),

7.09 (d, *J* = 8.0 Hz, 2H), 3.72-3.66 (m, 2H), 2.77 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.70 (dd, *J* =



20.5, 11.5 Hz, 2H), 2.29 (dd,  $J = 13.5, 8.5$ , Hz, 1H), 2.22-2.18 (m, 1H), 2.13-2.09 (m, 1H), 2.03-1.93 (m, 1H), 1.73-1.65 (m, 2H), 1.32 (s, 9H), 1.16 (dd,  $J = 6.0, 1.0$  Hz, 6H), 0.86 (d,  $J = 7.0$  Hz, 3H).

**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , DEPT):**  $\delta$  148.5 (C), 138.0 (C), 129.0 ( $2 \times \text{CH}$ ), 125.1 ( $2 \times \text{CH}$ ), 71.84 (CH), 71.81 (CH), 65.1 ( $\text{CH}_2$ ), 60.2 ( $\text{CH}_2$ ), 59.9 ( $\text{CH}_2$ ), 40.9 ( $\text{CH}_2$ ), 34.5 (C), 32.1 ( $2 \times \text{CH}_3$ ), 31.6 ( $3 \times \text{CH}_3$ ), 19.3 ( $\text{CH}_3$ ), 18.2 (CH).

**HRMS (ESI,  $\text{M}+\text{H}^+$ ):**  $m/z$  calcd. For  $\text{C}_{20}\text{H}_{34}\text{NO}$  304.2640, found 304.2640.

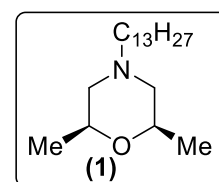
**(2*S*\*, 6*R*\*)-2,6-dimethyl-4-tridecylmorpholine (1):**

A magnetically stirred solution of tridecanal (**17**) (100 mg, 0.504 mmol) and (2*S*\*,6*R*\*)-2,6-dimethylmorpholine **16** (70 mg, 0.605 mmol) in acetic acid (3 mL) was heated at 80 °C for 10 minutes.  $\text{NaBH}_4$  (23 mg, 0.605 mmol) was added to the solution portion wise and the resulting mixture was refluxed until complete consumption of starting material. The solvent was removed under reduced pressure. After completion of reaction (TLC control), the residue was washed with 20% NaOH solution and was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL). The organic layer was washed with water ( $2 \times 5$  mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent and purification of residue on silica gel column using EtOAc- petroleum ether as eluent furnished morpholine (**1**) (132 mg, 88%).

**Physical Appearance:** Yellow oil.

**$R_f$ :** 0.5 (20:80, EtOAc:Petroleum ether).

**IR (neat):** 3324, 2855, 1467, 1144, 1081, 716  $\text{cm}^{-1}$ .

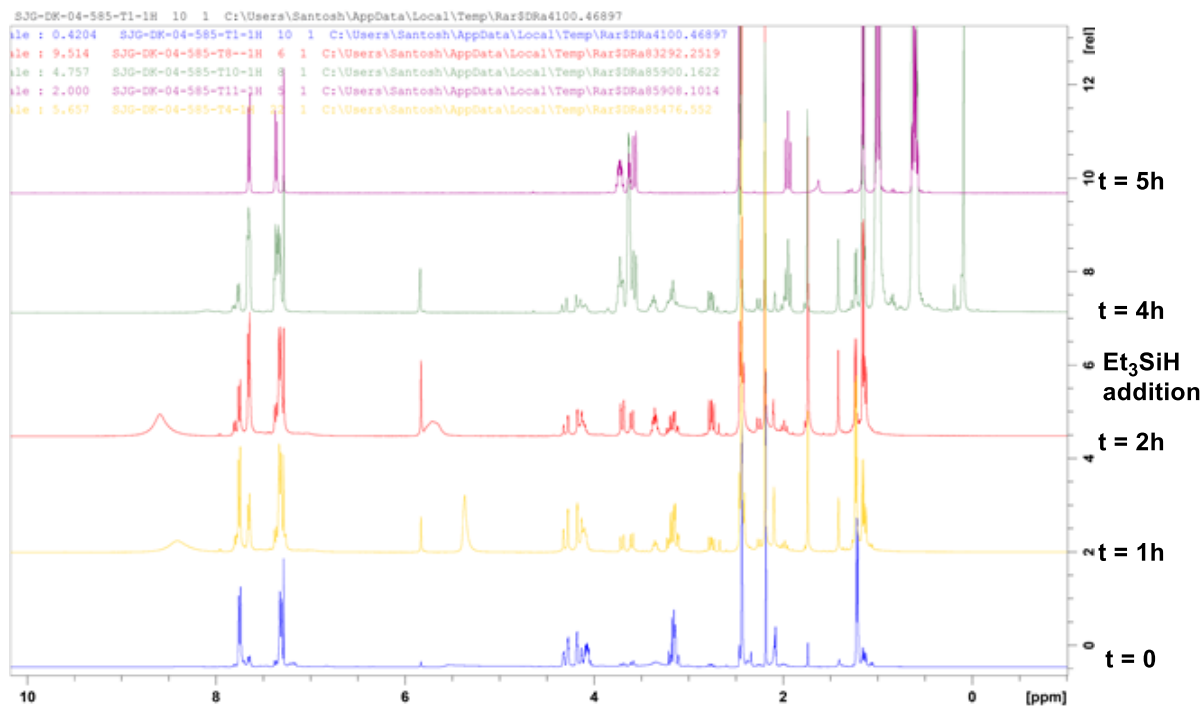
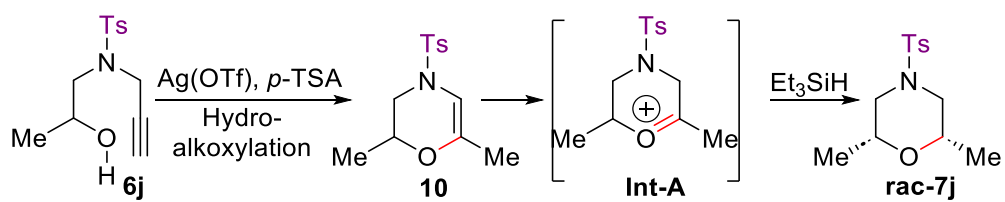


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  3.70-3.62 (m, 2H), 2.72 (d,  $J = 10.8$  Hz, 2H), 2.26 (t,  $J = 8.8$  Hz, 2H), 1.65 (t,  $J = 10.8$  Hz, 2H), 1.45-1.44 (m, 2H), 1.25-1.23 (m, 20H), 1.13 (d,  $J = 6.0$  Hz, 6H), 0.87-0.84 (t,  $J = 6.4$  Hz, 3H).

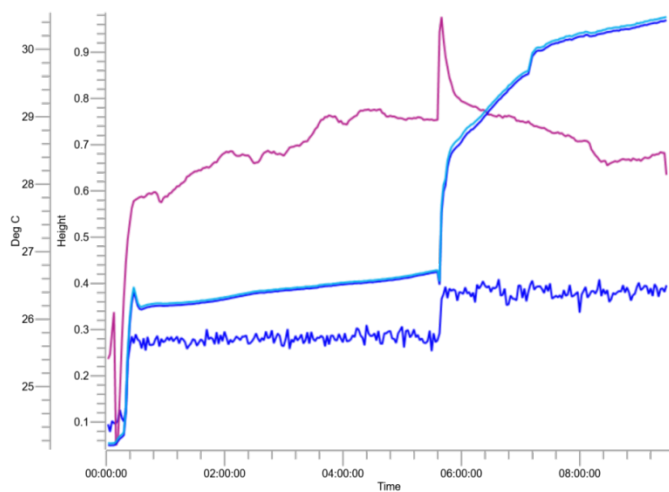
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , DEPT):**  $\delta$  71.8 ( $2 \times \text{CH}$ ), 59.8 ( $3 \times \text{CH}_2$ ), 59.0 ( $2 \times \text{CH}_2$ ), 32.0 ( $\text{CH}_2$ ), 29.8 ( $\text{CH}_2$ ), 29.77 ( $\text{CH}_2$ ), 29.74 ( $\text{CH}_2$ ), 29.71 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 27.7 ( $\text{CH}_2$ ), 26.7 ( $\text{CH}_2$ ), 22.8 ( $\text{CH}_2$ ), 19.3 ( $2 \times \text{CH}_3$ ), 14.2 ( $\text{CH}_3$ ).





**HRMS (ESI,  $\text{M}+\text{H}^+$ ):**  $m/z$  calcd. For  $\text{C}_{19}\text{H}_{40}\text{NO}$  298.3126, found 298.3126.

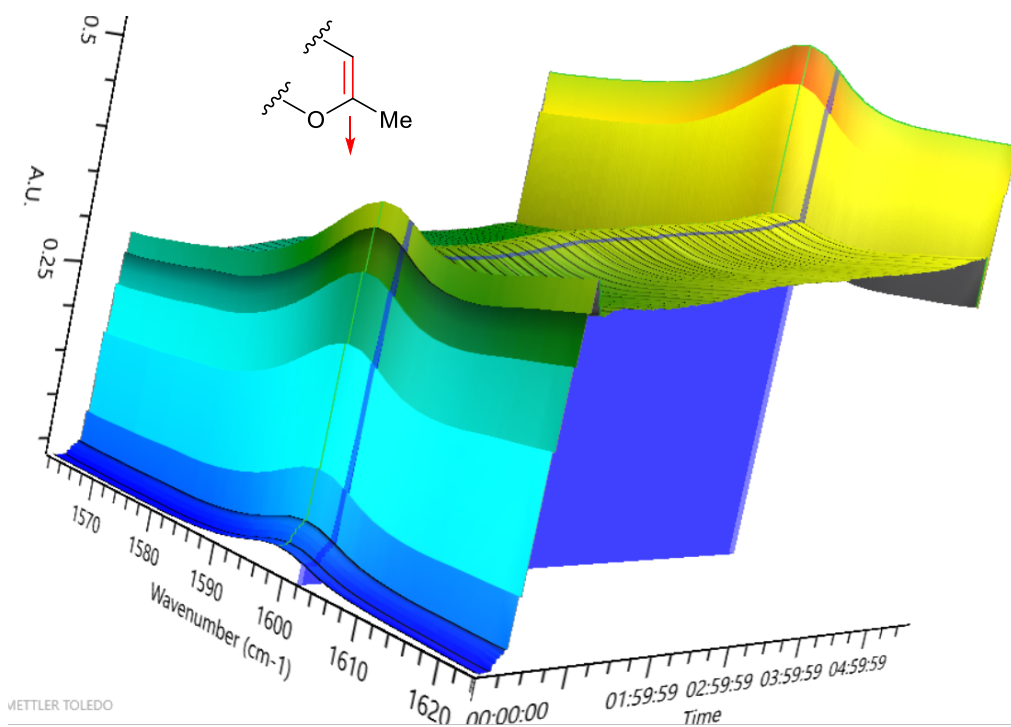
## Mechanistic study for the formation of morpholine: NMR experiment



## Mechanistic study for the formation of morpholine: React IR experiment

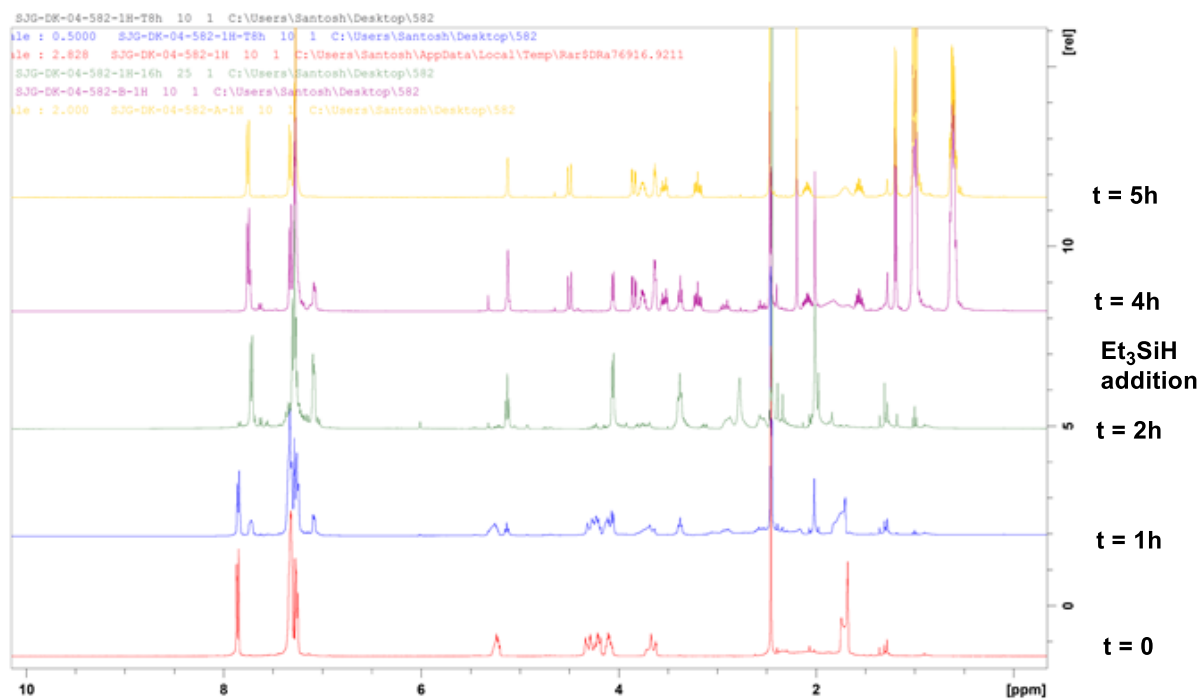
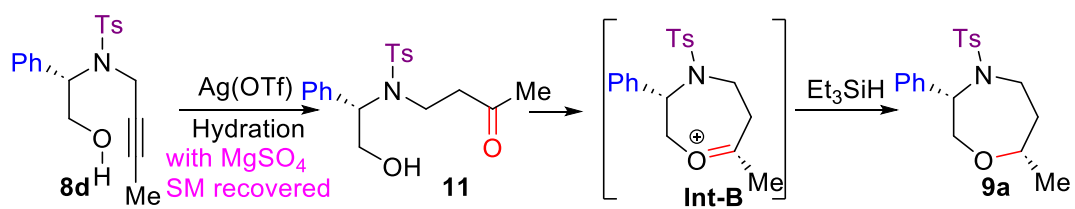


Trend	Color	Units
Peak at 3310 cm <sup>-1</sup>		Height
Probe Temp		Deg C
Peak at 1602 cm <sup>-1</sup>		Height
Peak at 1600 cm <sup>-1</sup>		Height

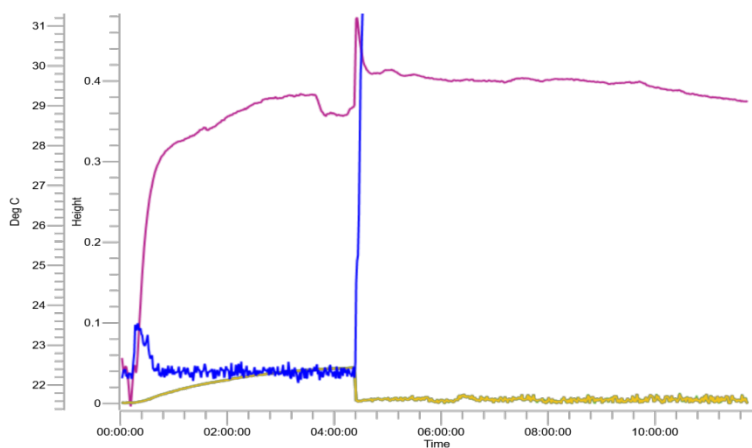







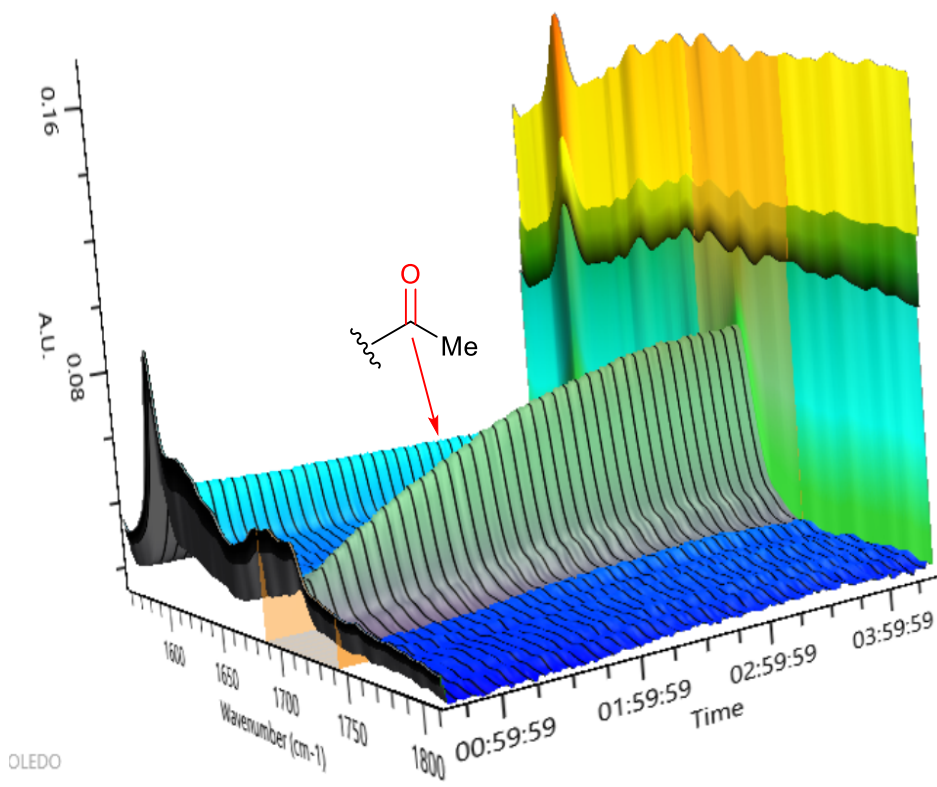
## Mechanistic study for the formation of oxazepane: NMR experiment



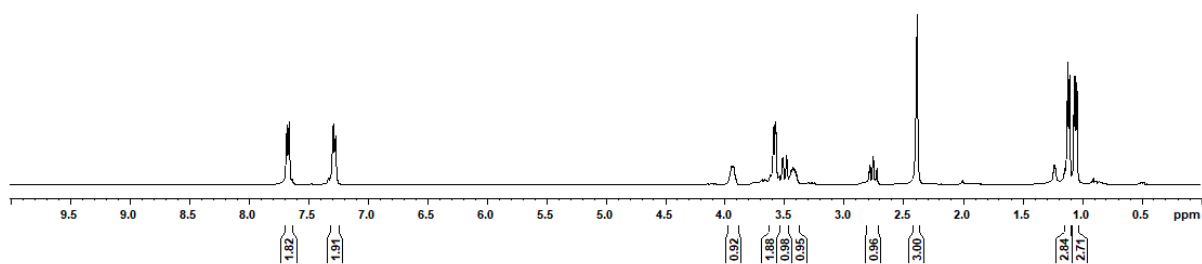
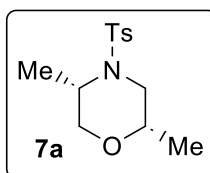
## Mechanistic study for the formation of oxazepane: React IR experiment



Trend	Color	Units
Probe Temp		Deg C
Peak at 1715 cm-1		Height
Peak at 3110 cm-1		Height

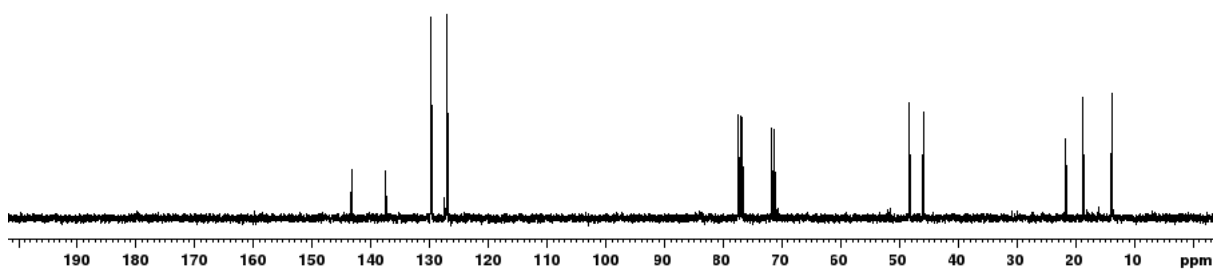
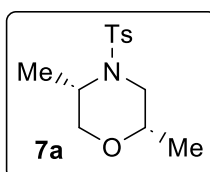


7.677, 7.670, 7.657, 7.650, 7.287, 7.280, 7.267, 7.266, 7.260, 3.937, 3.931, 3.921, 3.582, 3.578, 3.573, 3.518, 3.511, 3.486, 3.479, 3.464, 3.458, 3.449, 3.442, 3.433, 3.426, 3.423, 3.416, 3.407, 3.368, 2.790, 2.783, 2.763, 2.757, 2.751, 2.732, 2.724, 2.396, 1.129, 1.121, 1.114, 1.105, 1.072, 1.064, 1.055, 1.047



<sup>1</sup>H NMR spectrum of **7a** (400 MHz, CDCl<sub>3</sub>)

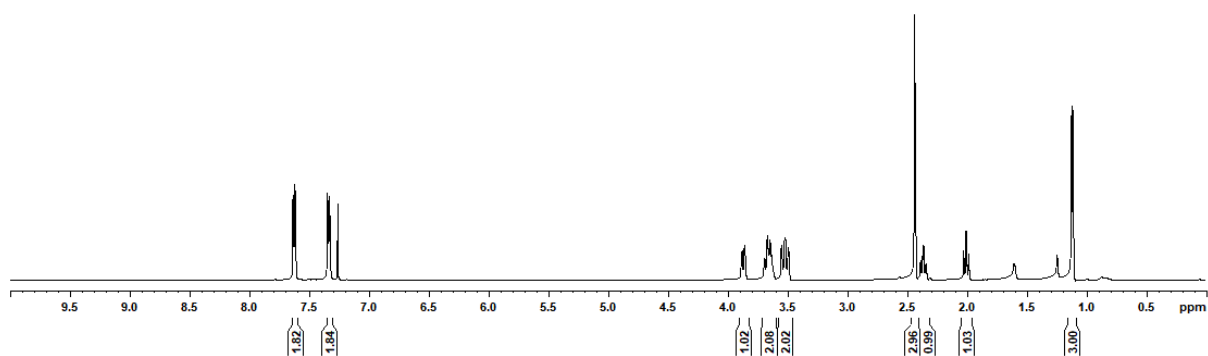
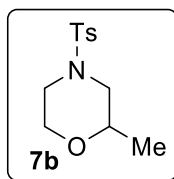
143.32, 137.54, 129.77, 127.04, 77.48, 77.16, 76.84, 71.78, 71.33, 48.09, 45.78, 21.47, 18.57, 13.69



<sup>13</sup>C NMR spectrum of **7a** (100 MHz, CDCl<sub>3</sub>)

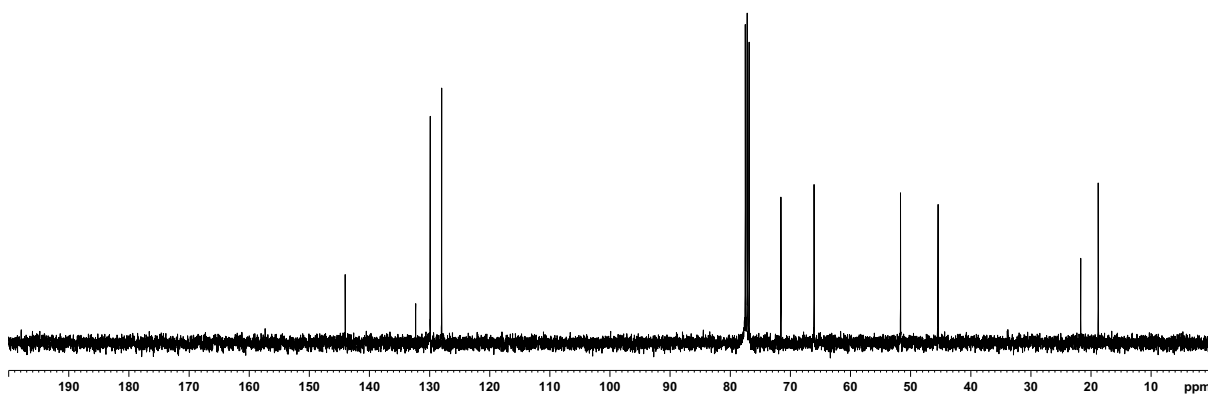
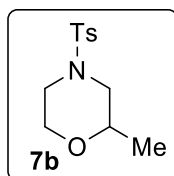
7.636  
7.620  
7.347  
7.331  
7.260

3.887  
3.881  
3.874  
3.858  
3.699  
3.696  
3.694  
3.691  
3.676  
3.673  
3.670  
3.668  
3.664  
3.661  
3.653  
3.648  
3.645  
3.636  
3.552  
3.520  
3.494  
2.440  
2.393  
2.388  
2.387  
2.370  
2.365  
2.364  
2.349  
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2.344  
2.030  
2.009  
1.987  
1.131  
1.129  
1.119  
1.117

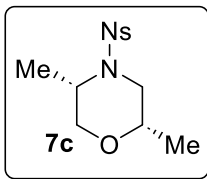
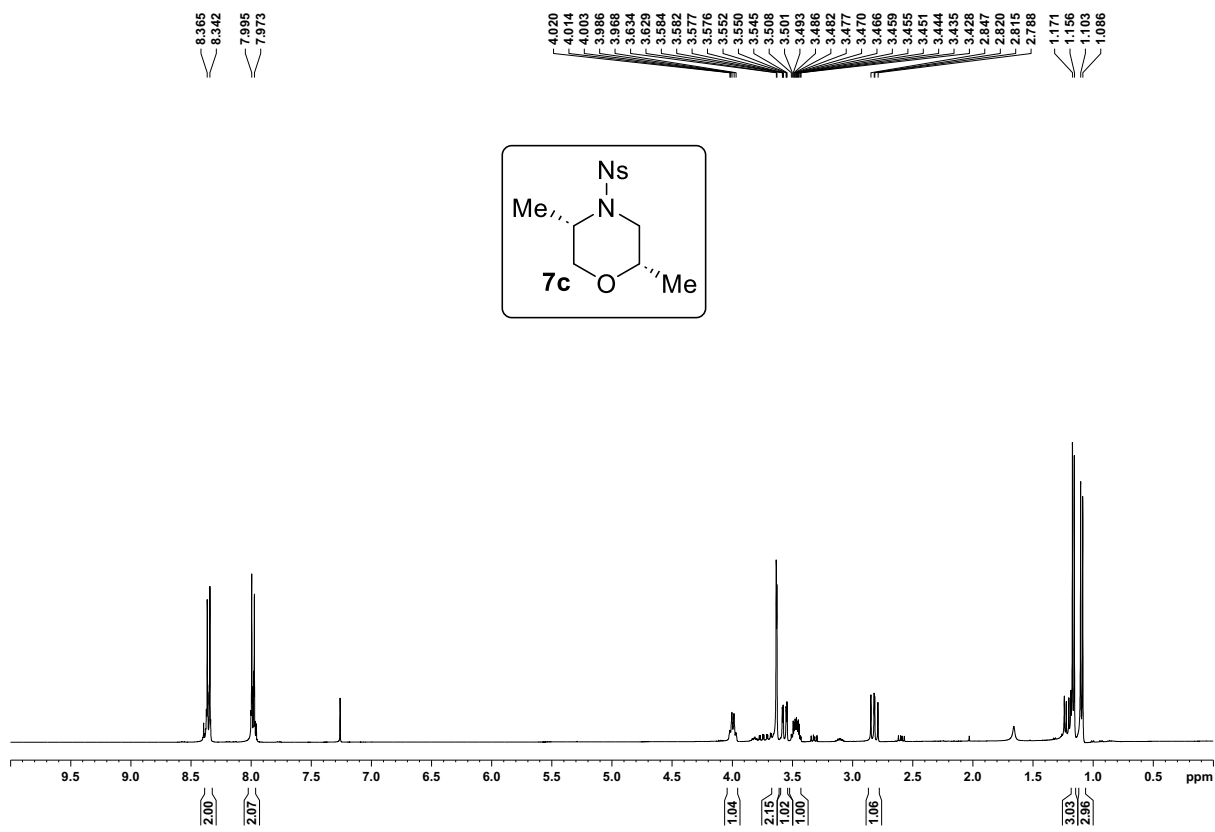


<sup>1</sup>H NMR spectrum of **7b** (400 MHz, CDCl<sub>3</sub>)

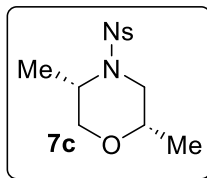
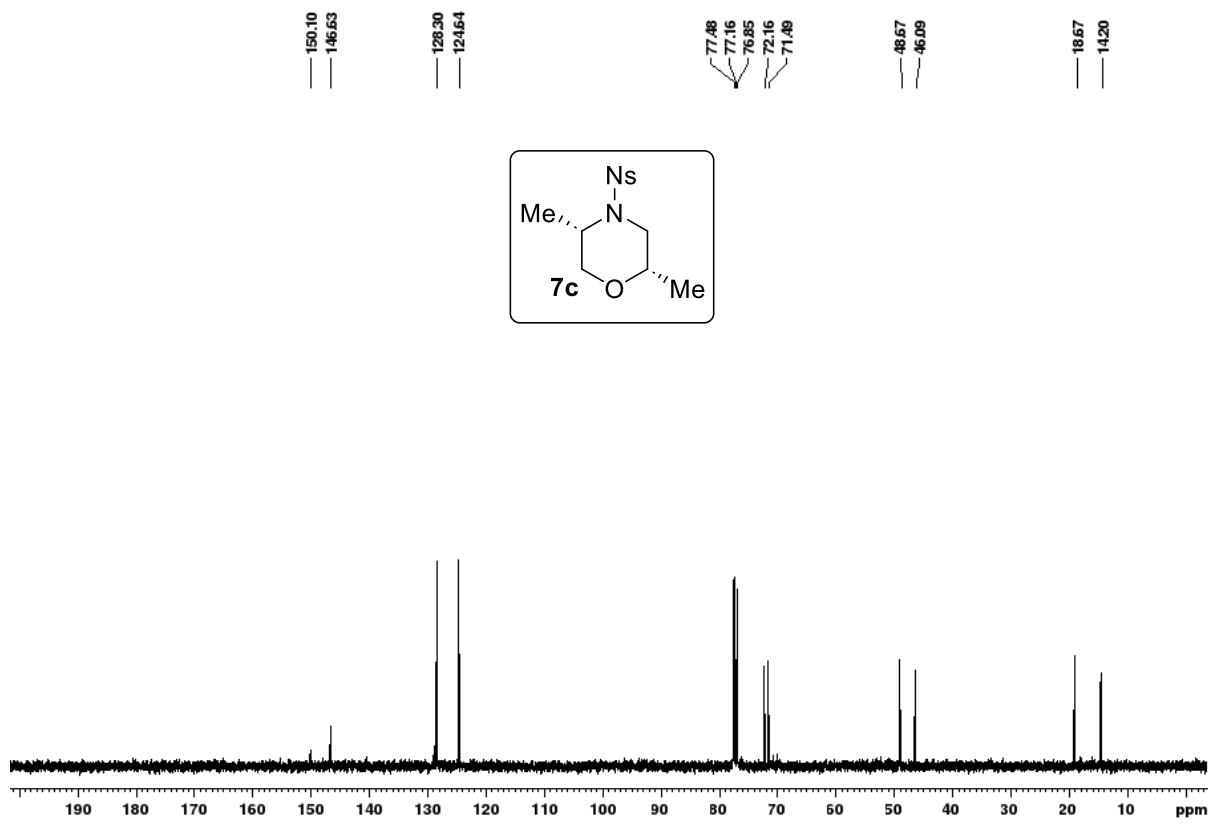
144.02 132.30 129.88 127.97 77.48 77.16 76.84 71.54 66.03 51.65 45.42 21.67 18.77



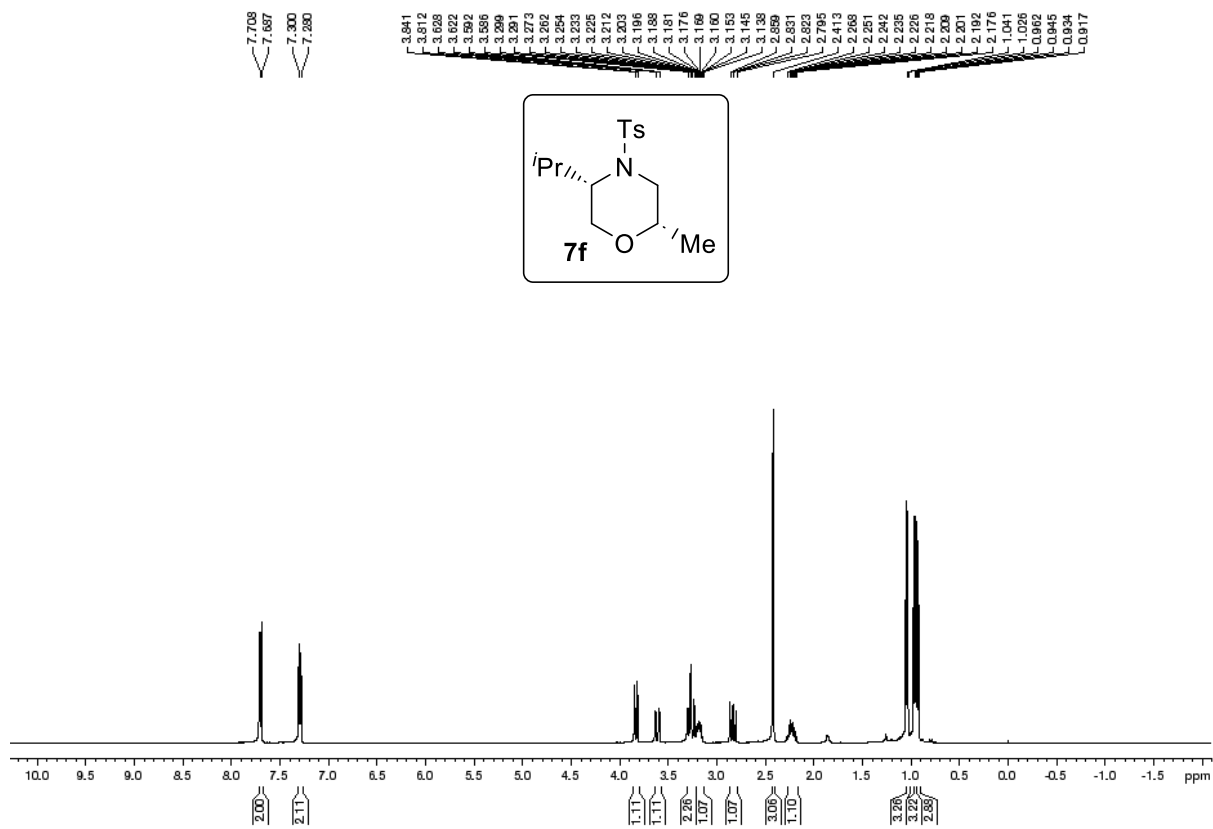
<sup>13</sup>C NMR spectrum of **7b** (100 MHz, CDCl<sub>3</sub>)



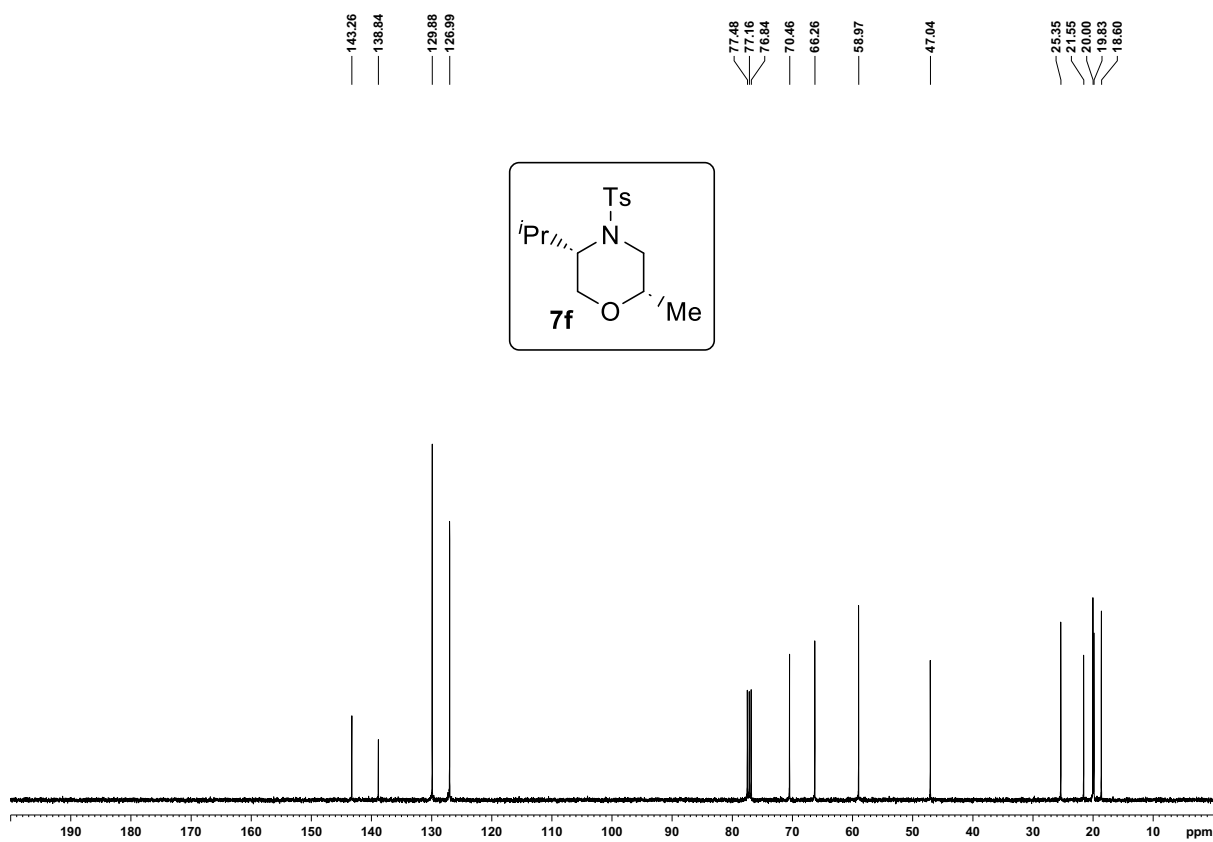
<sup>1</sup>H NMR spectrum of 7c (400 MHz, CDCl<sub>3</sub>)



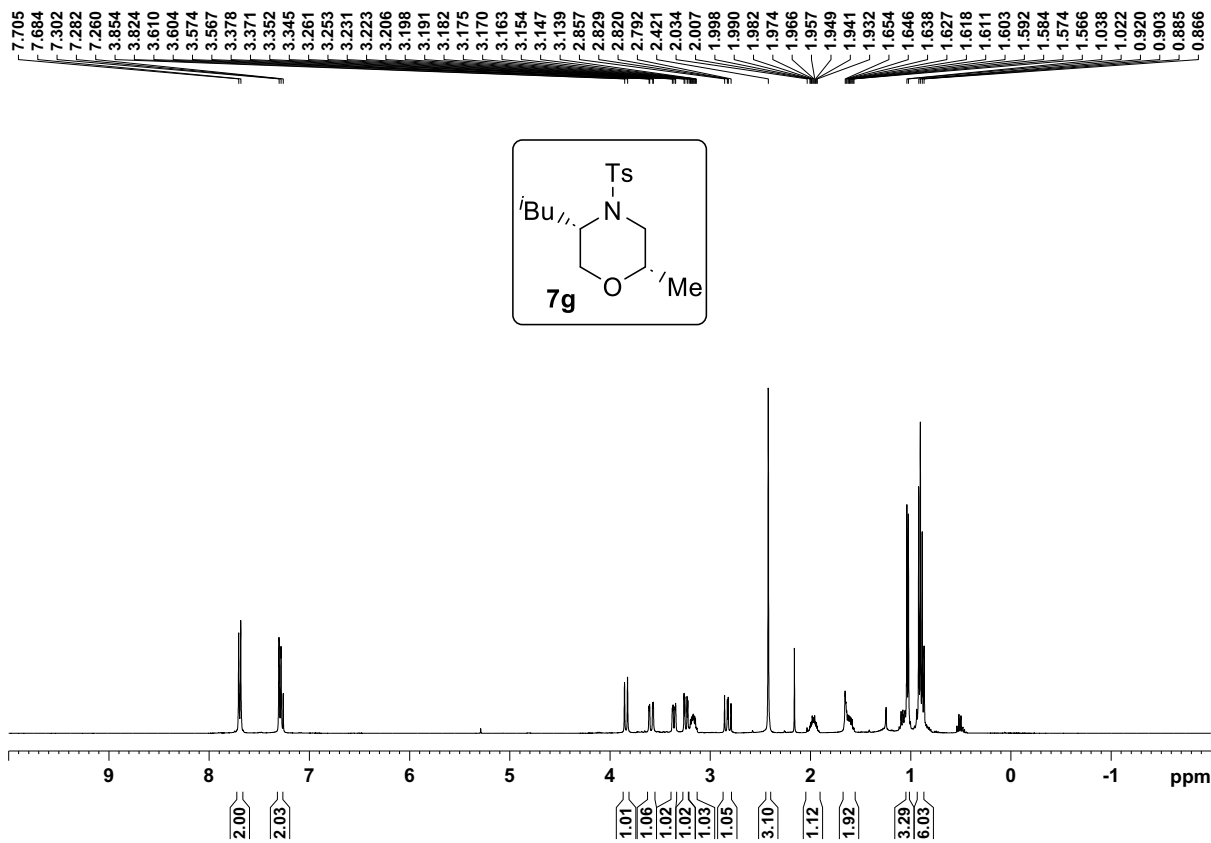
<sup>13</sup>C NMR spectrum of 7c (100 MHz, CDCl<sub>3</sub>)



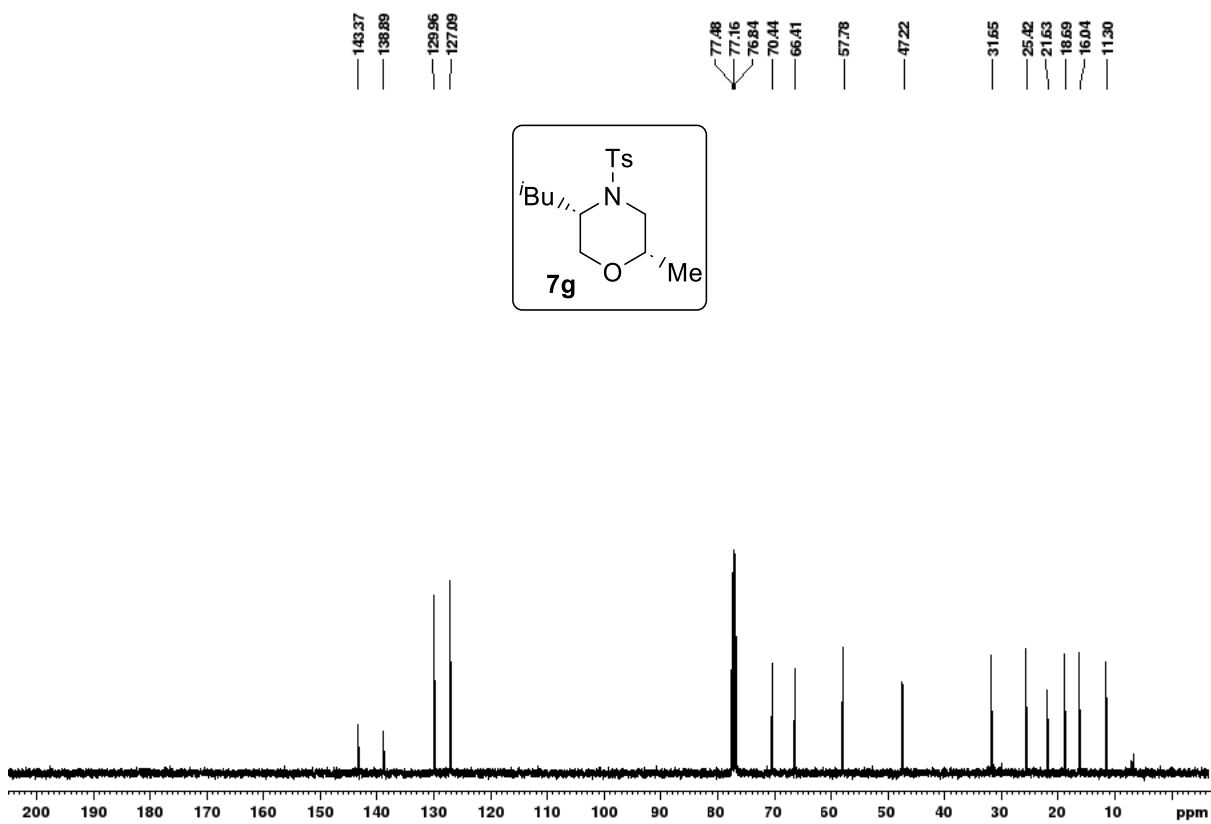
<sup>1</sup>H NMR spectrum of **7f** (400 MHz, CDCl<sub>3</sub>)



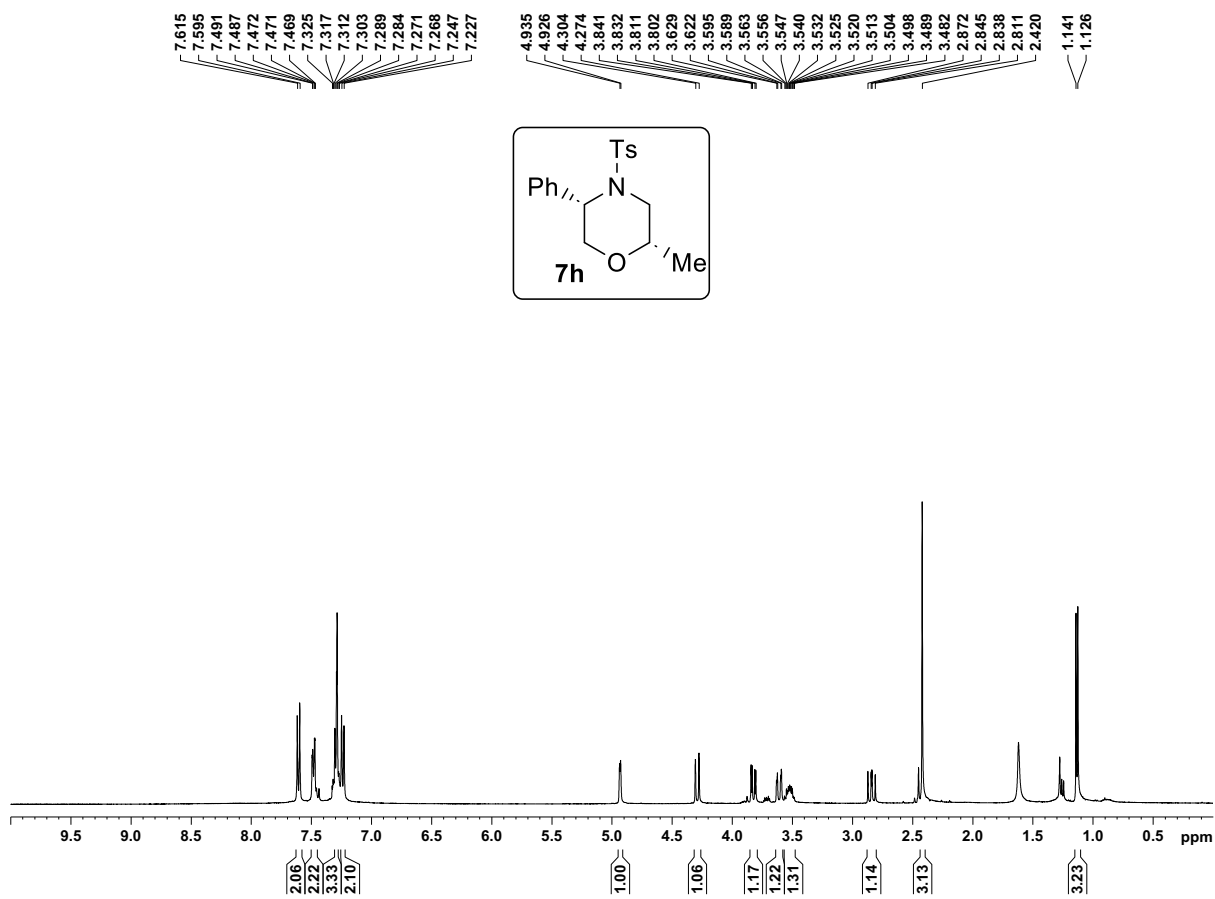
<sup>13</sup>C NMR spectrum of **7f** (100 MHz, CDCl<sub>3</sub>)



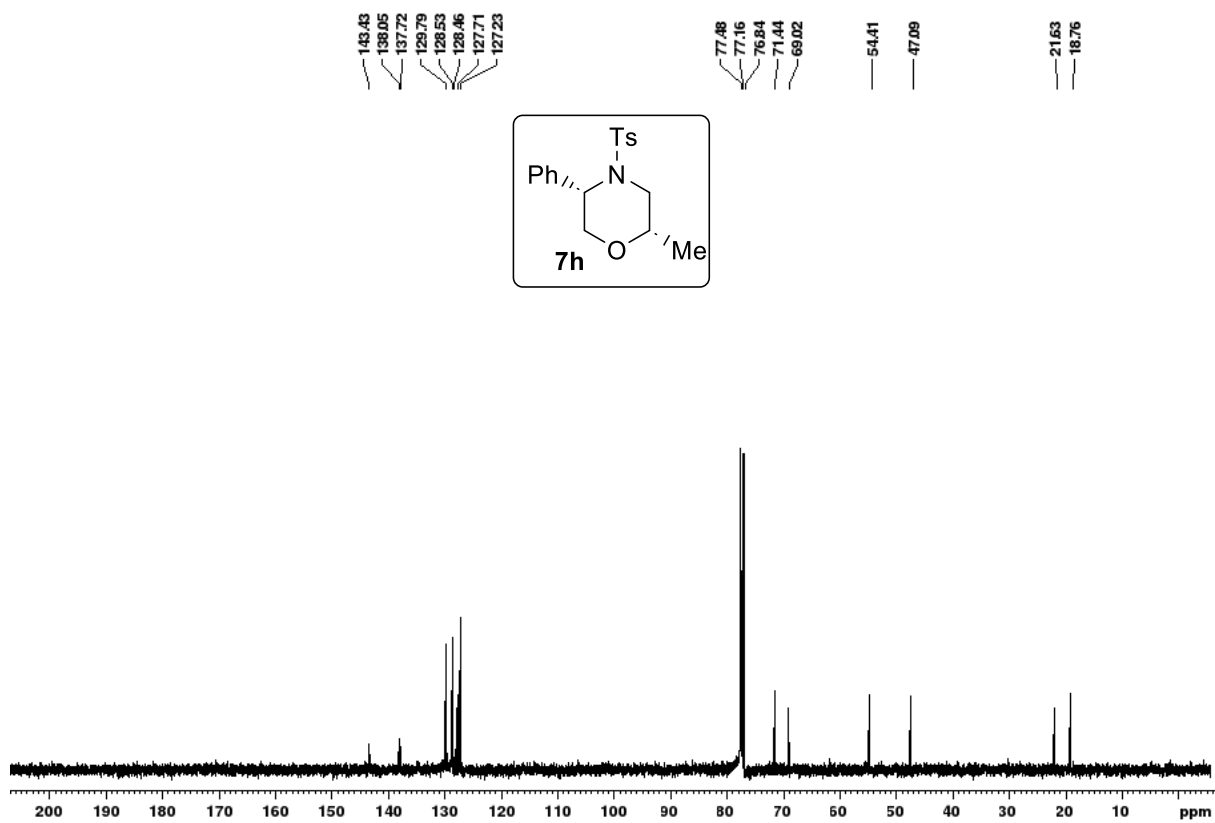
<sup>1</sup>H NMR spectrum of **7g** (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of **7g** (100 MHz, CDCl<sub>3</sub>)

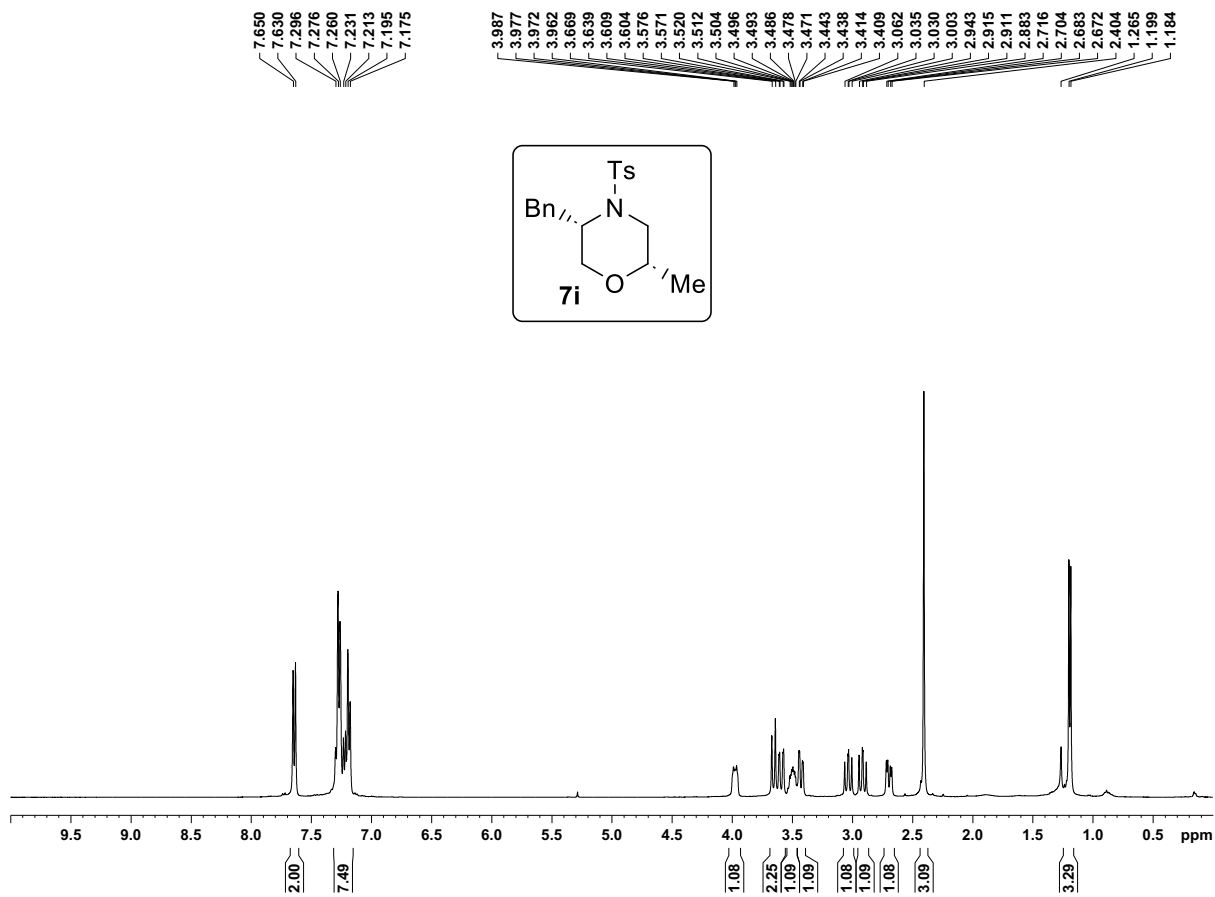


<sup>1</sup>H NMR spectrum of **7h** (400 MHz, CDCl<sub>3</sub>)

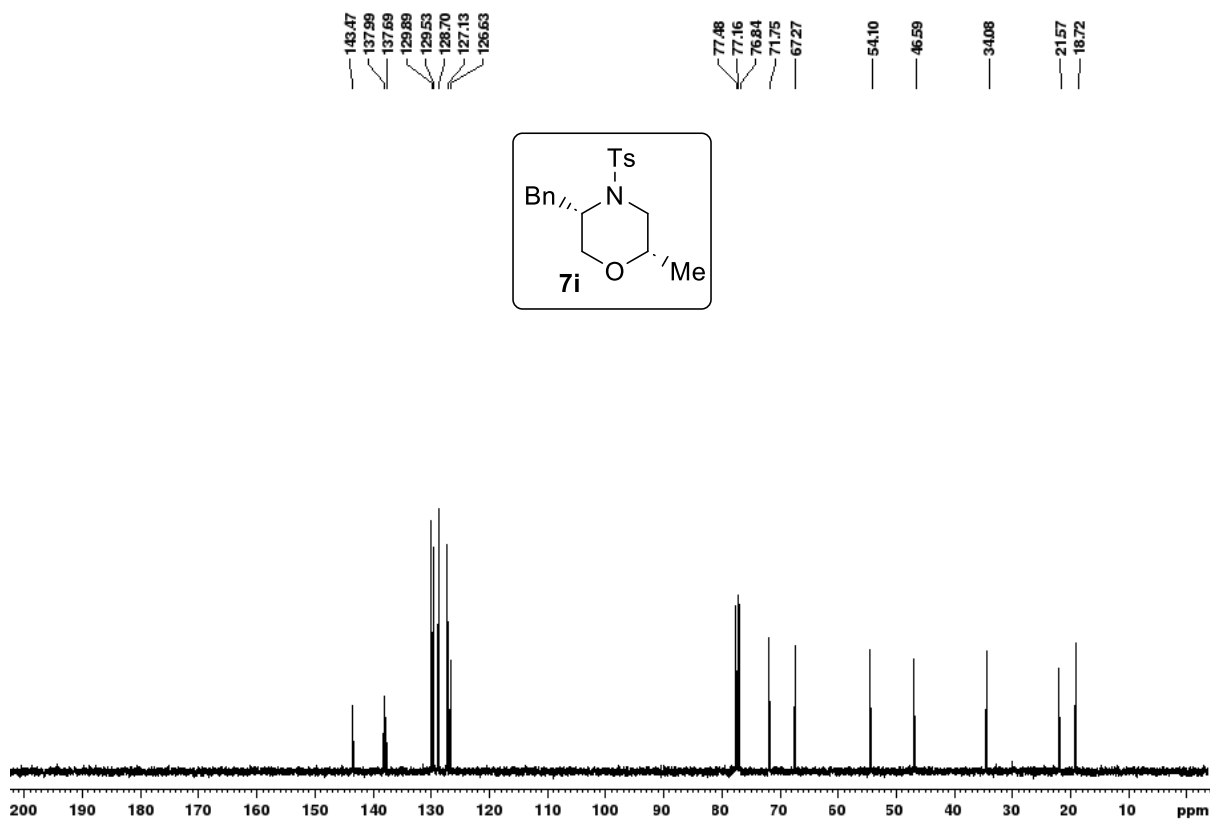


<sup>13</sup>C NMR spectrum of **7h** (100 MHz, CDCl<sub>3</sub>)

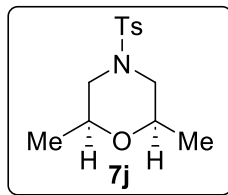
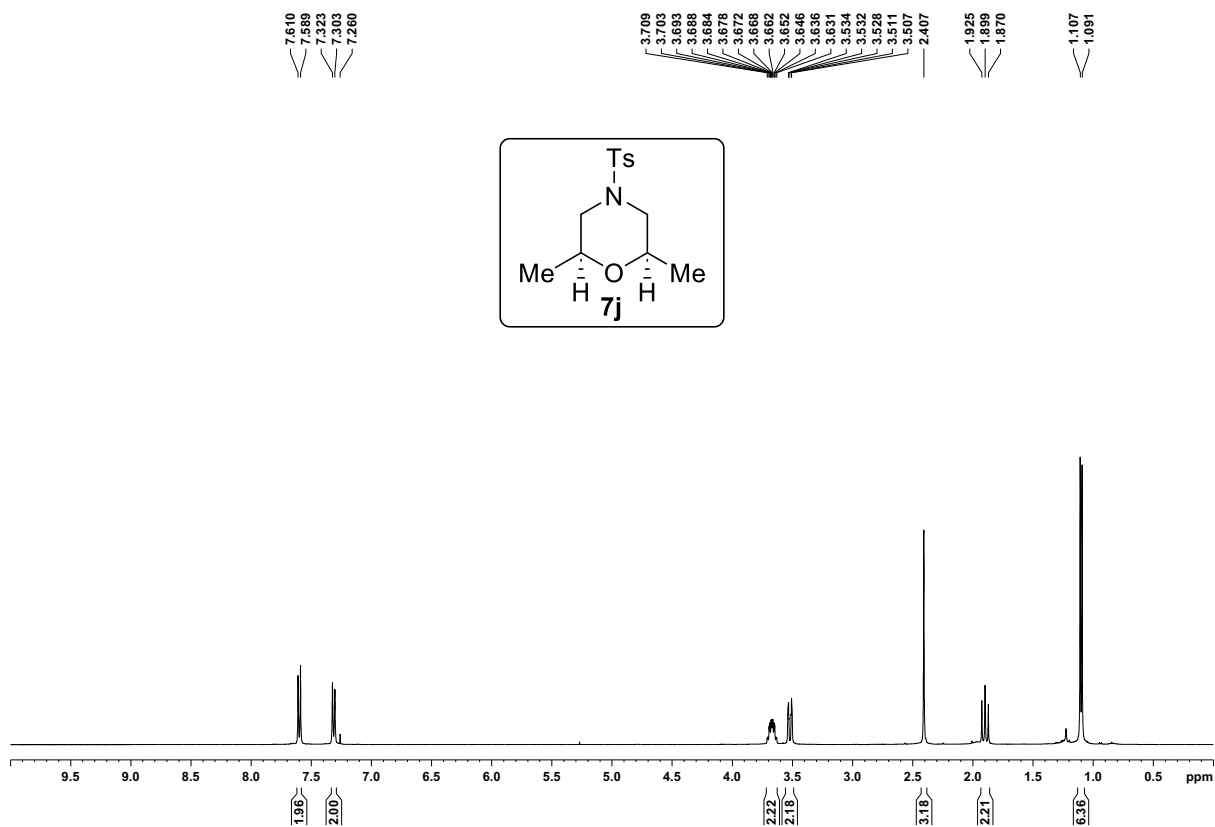




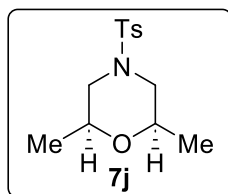
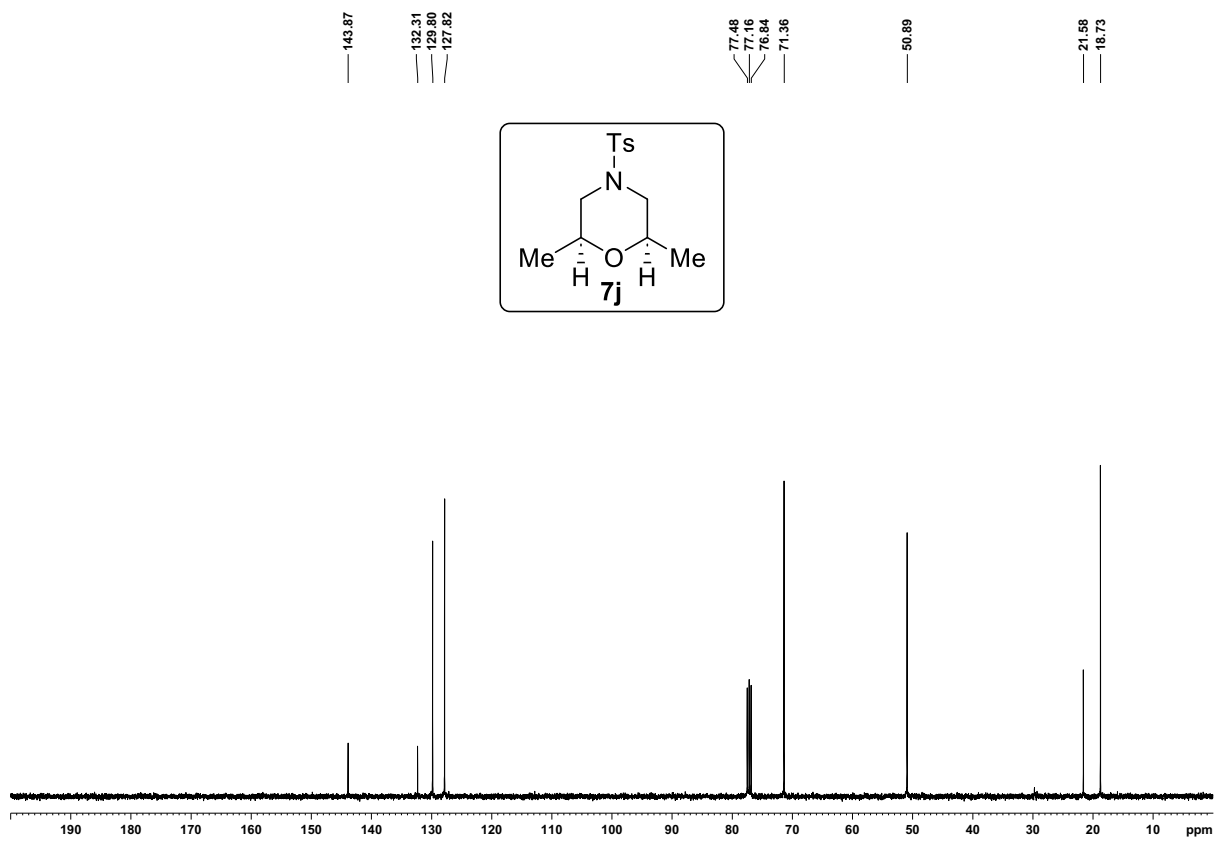
<sup>1</sup>H NMR spectrum of **7i** (400 MHz, CDCl<sub>3</sub>)



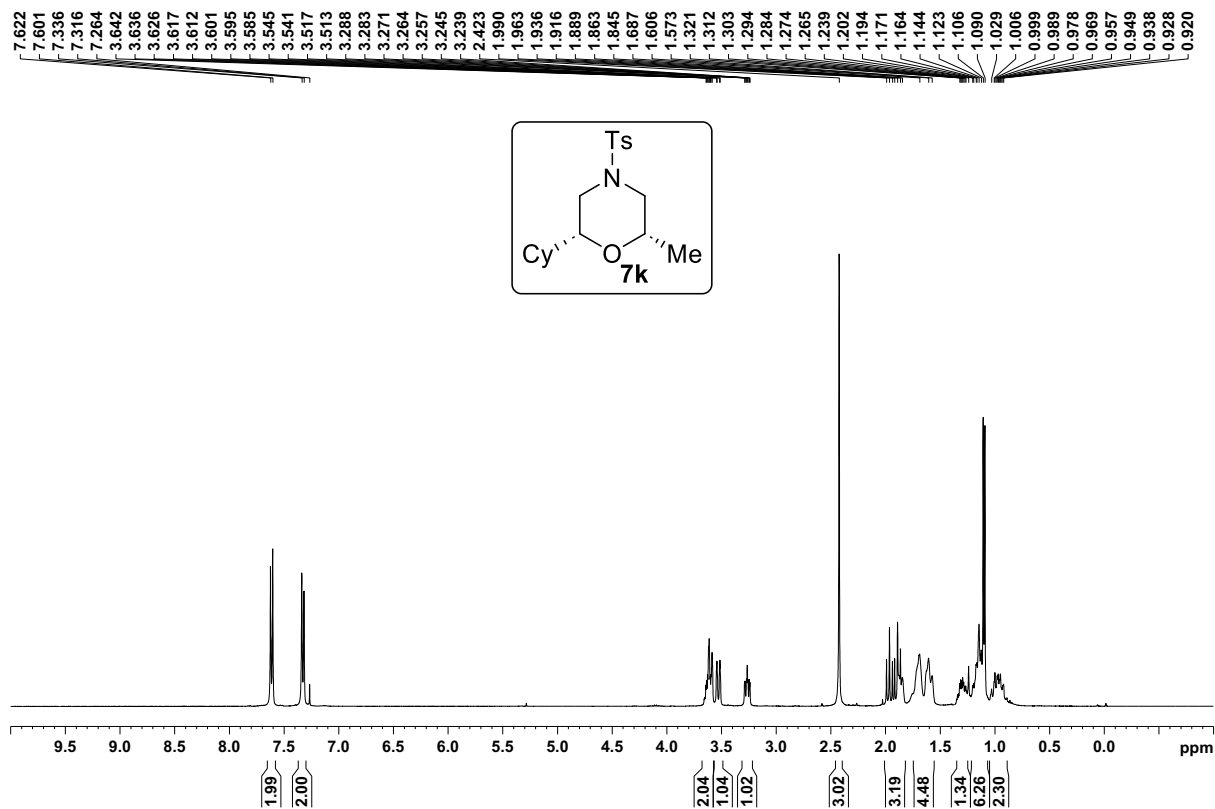
<sup>13</sup>C NMR spectrum of **7i** (100 MHz, CDCl<sub>3</sub>)



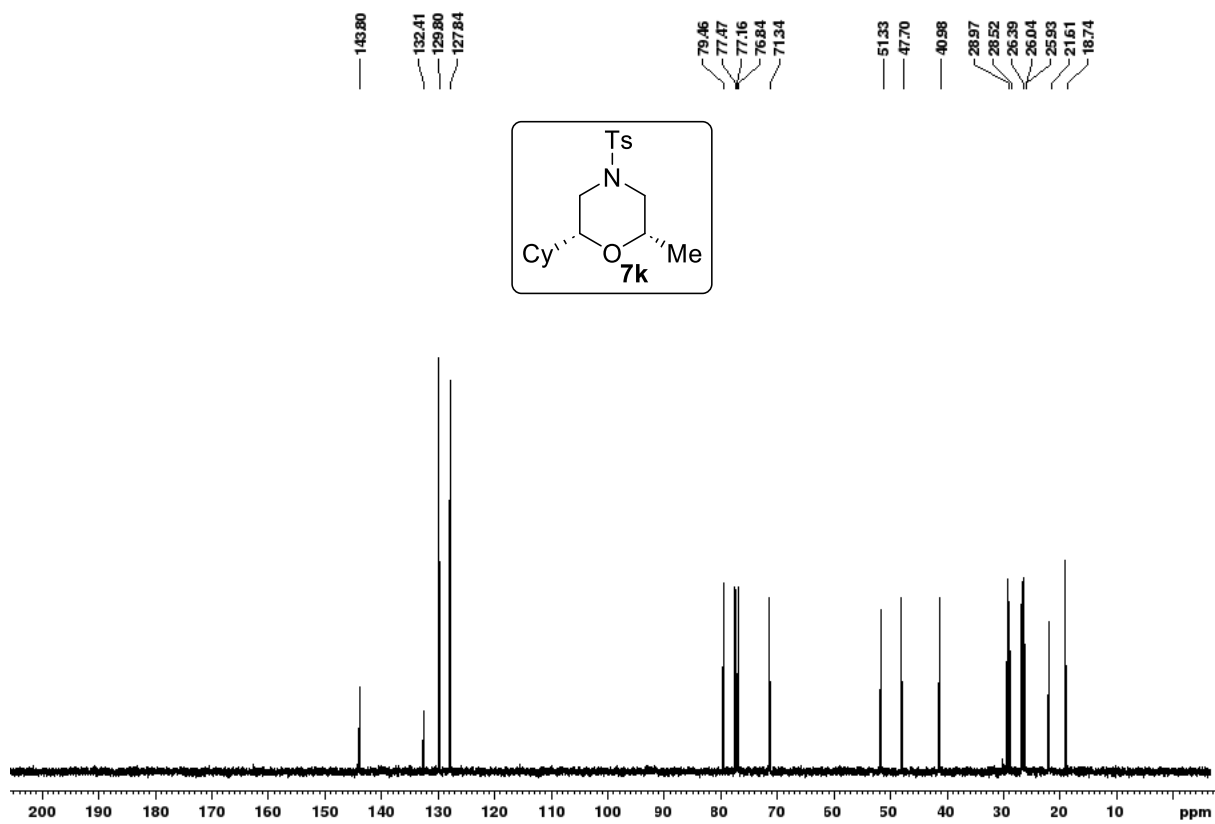
$^1\text{H}$  NMR spectrum of **7j** (400 MHz,  $\text{CDCl}_3$ )



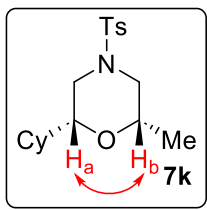
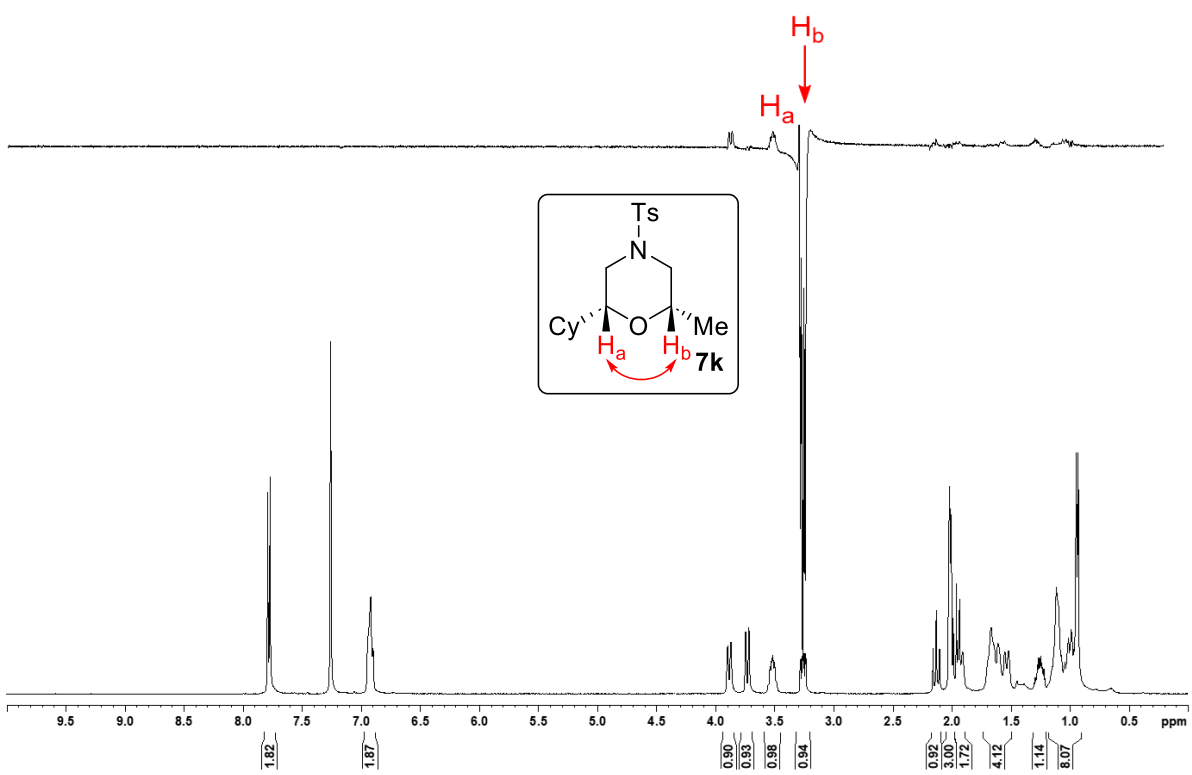
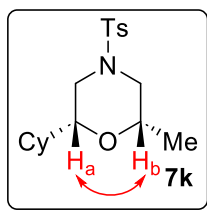
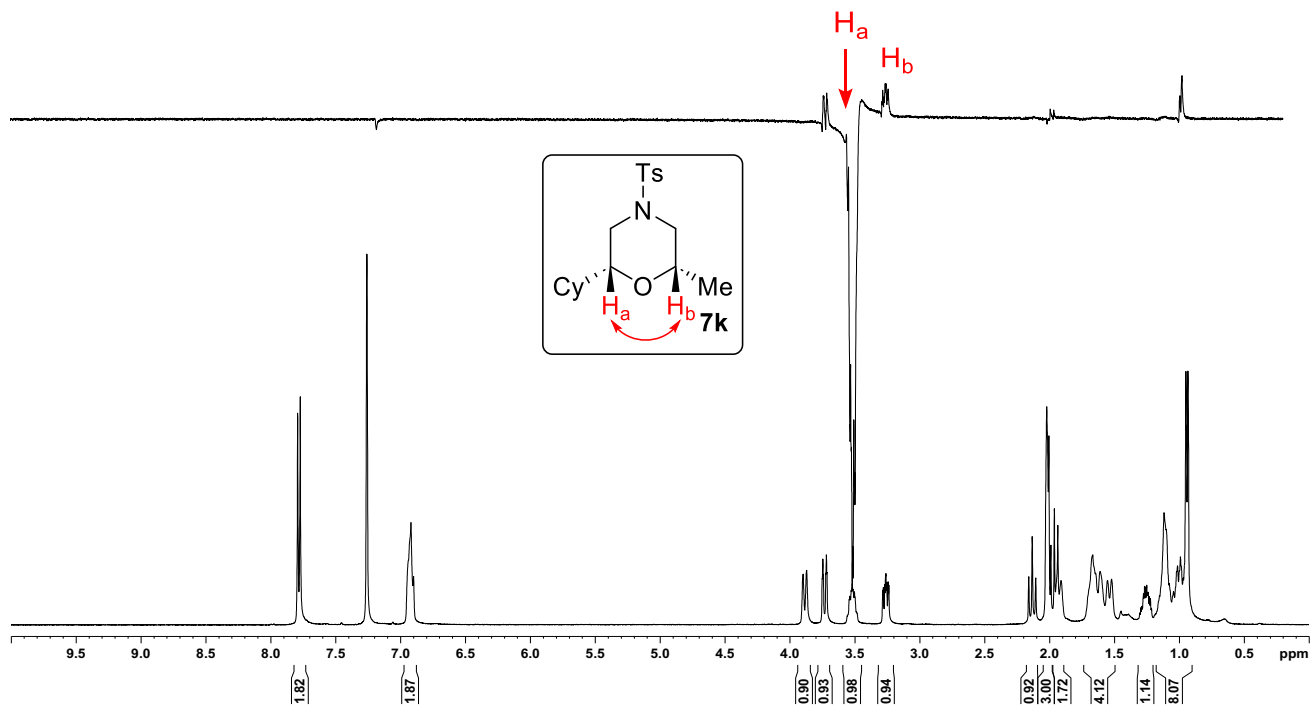
$^{13}\text{C}$  NMR spectrum of **7j** (100 MHz,  $\text{CDCl}_3$ )



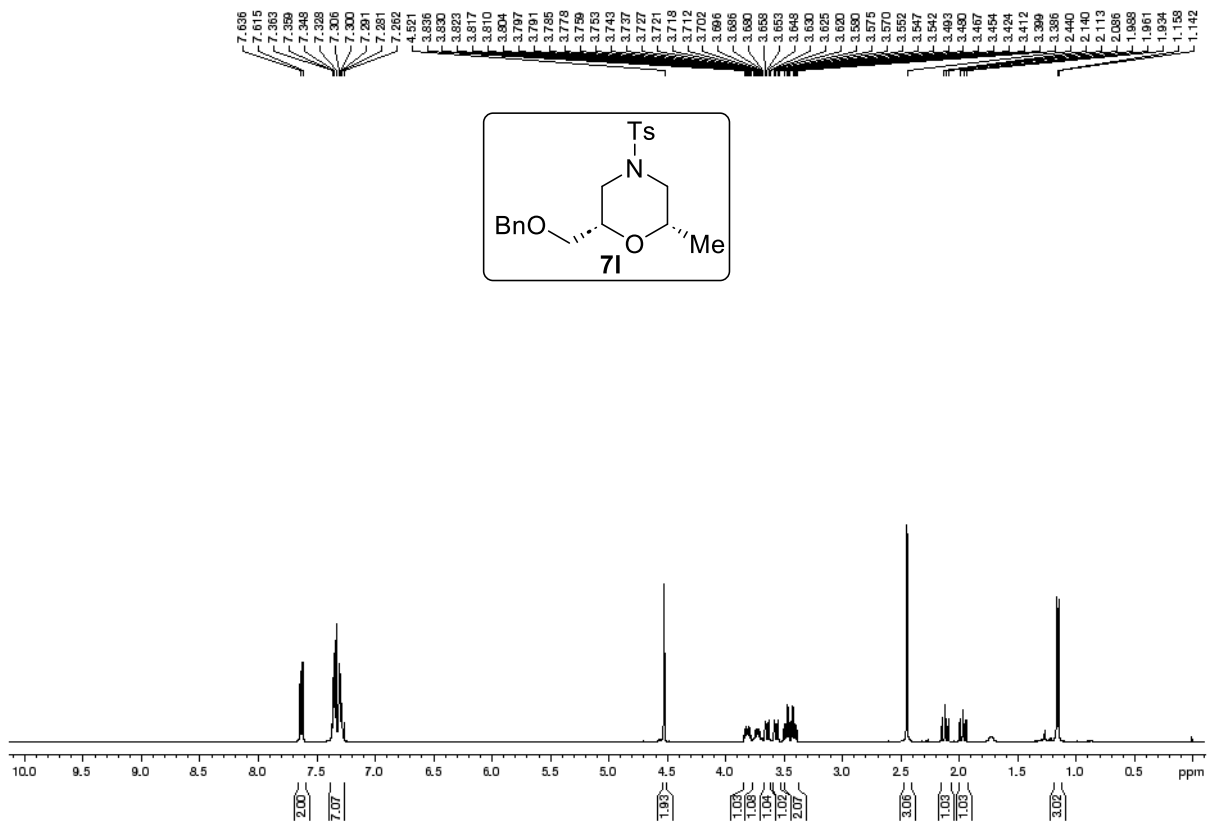
$^1\text{H}$  NMR spectrum of **7k** (400 MHz,  $\text{CDCl}_3$ )



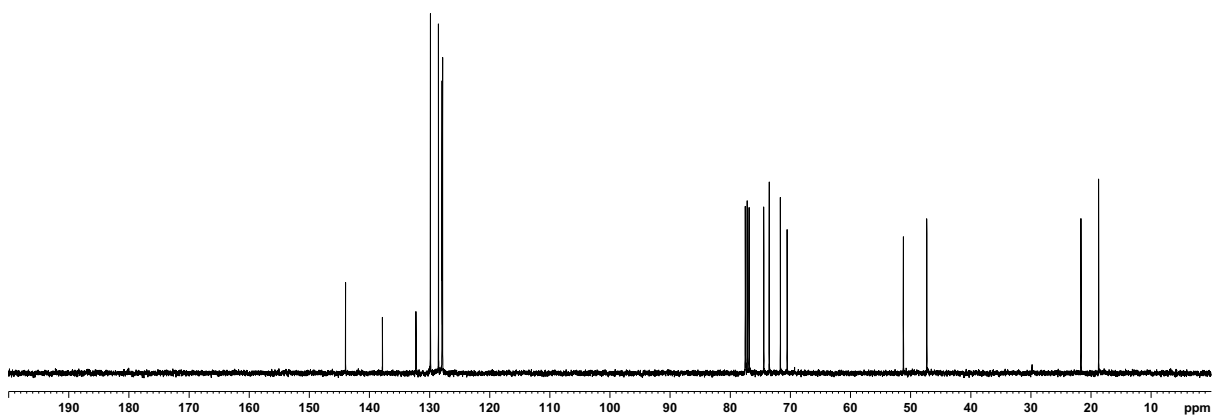
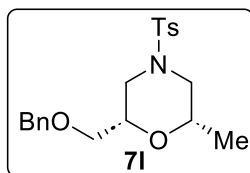
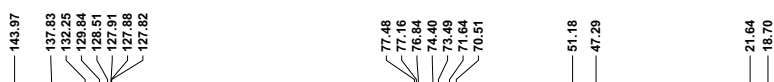
$^{13}\text{C}$  NMR spectrum of **7k** (100 MHz,  $\text{CDCl}_3$ )



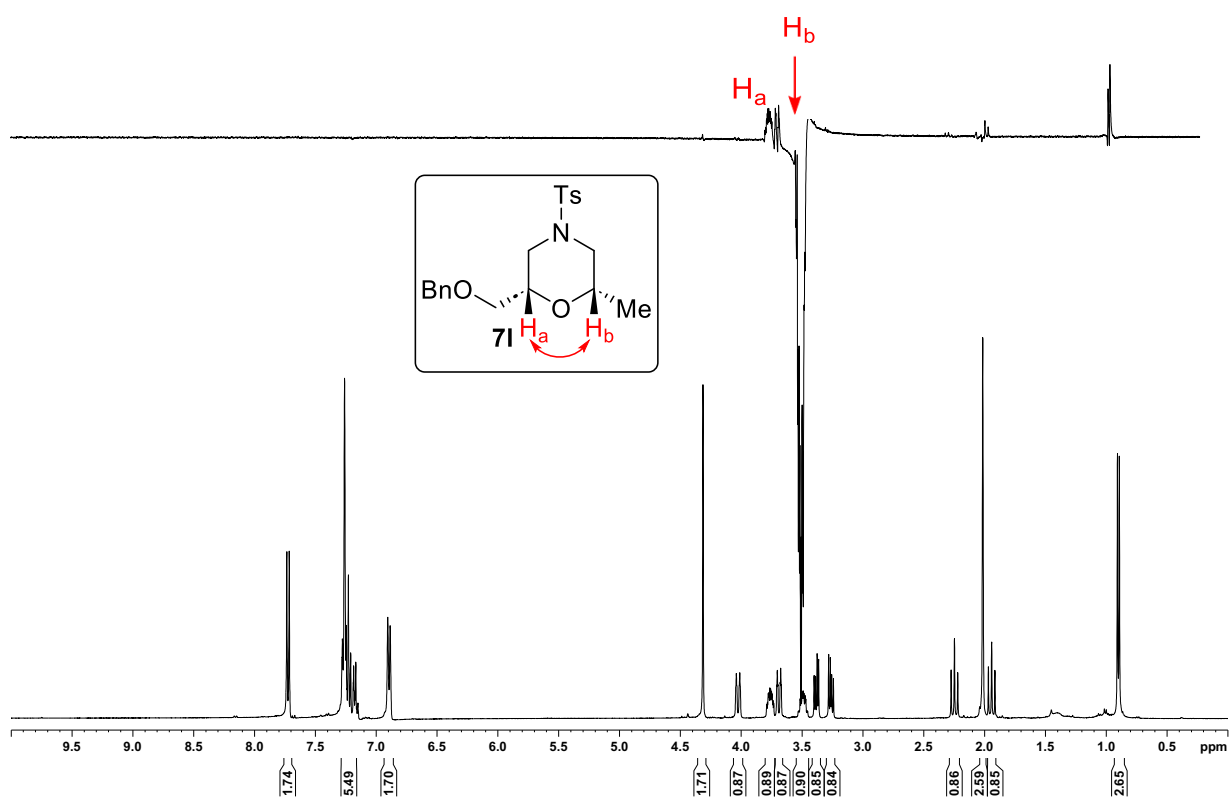
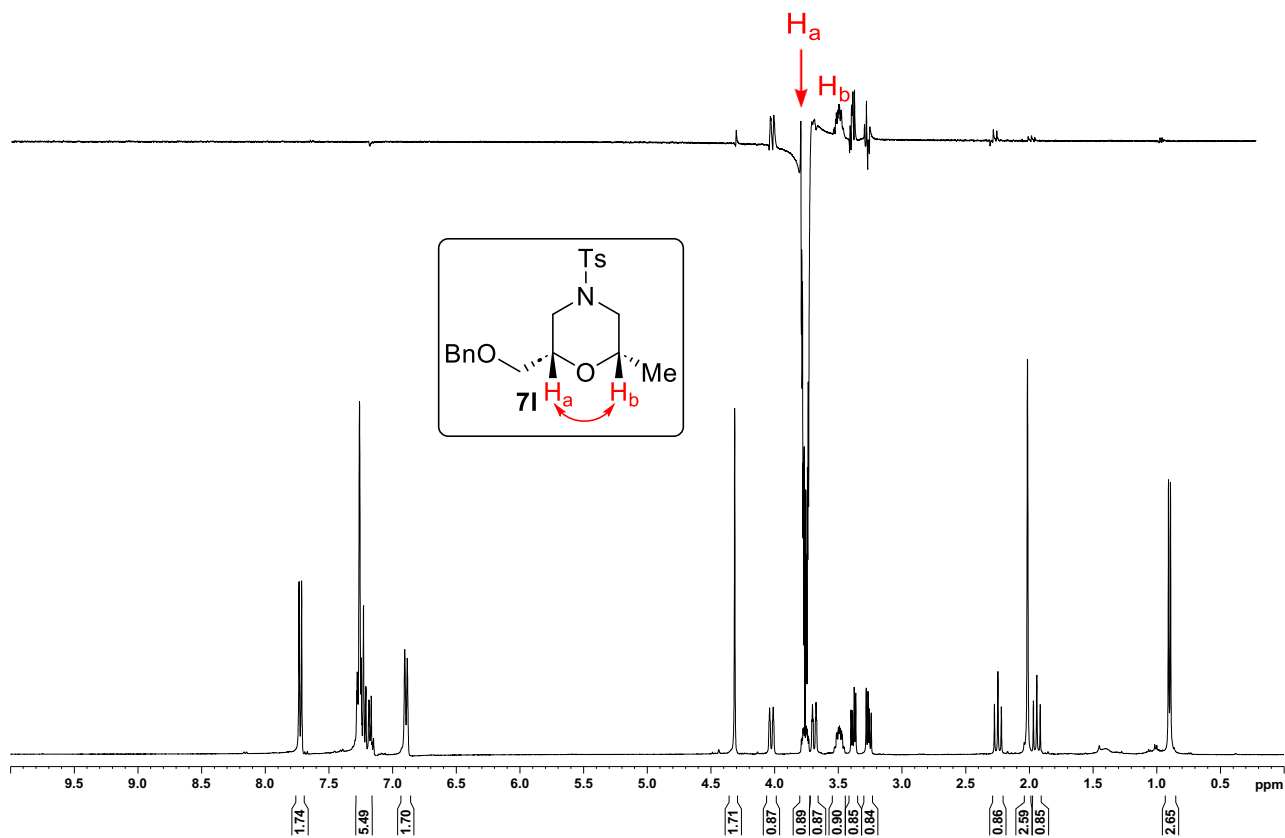
NOE spectrum of 7k (400 MHz,  $C_6D_6$ )



<sup>1</sup>H NMR spectrum of **7I** (400 MHz, CDCl<sub>3</sub>)

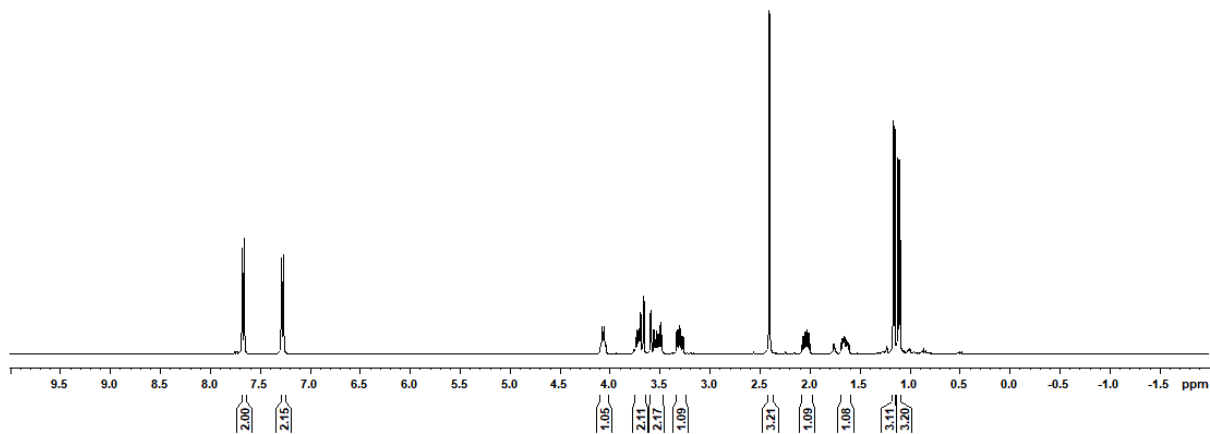
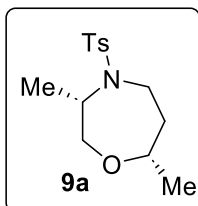


<sup>13</sup>C NMR spectrum of **7I** (100 MHz, CDCl<sub>3</sub>)



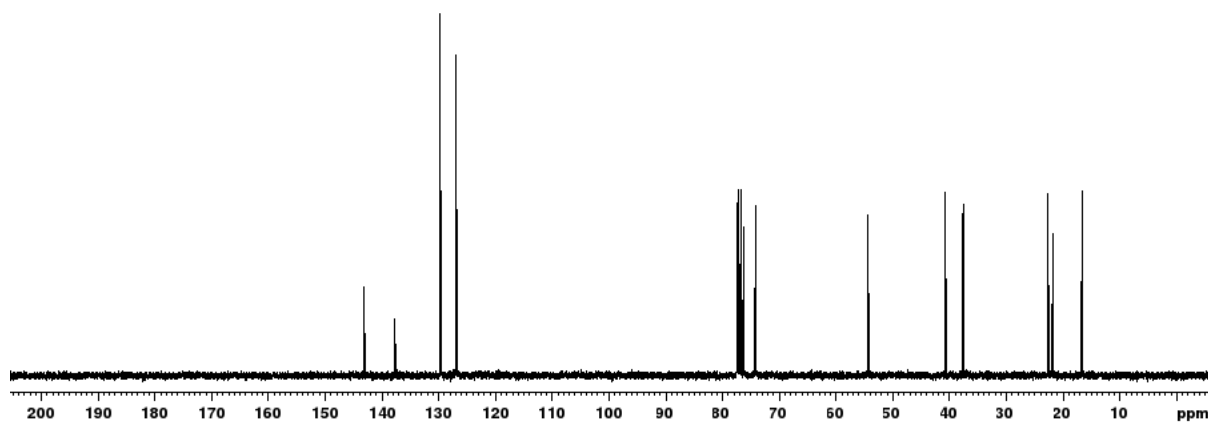
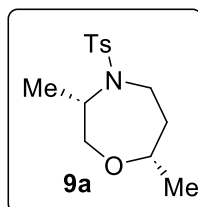
NOE spectrum of **71** (400 MHz, C<sub>6</sub>D<sub>6</sub>)

7.671, 7.650, 7.278, 7.258, 6.086, 6.065, 6.051, 6.051, 4.034, 3.732, 3.720, 3.717, 3.713, 3.704, 3.701, 3.697, 3.689, 3.684, 3.670, 3.657, 3.651, 3.584, 3.579, 3.552, 3.547, 3.535, 3.521, 3.508, 3.499, 3.486, 3.472, 3.472, 3.326, 3.316, 3.303, 3.283, 3.280, 3.267, 3.257, 2.397, 2.073, 2.061, 2.049, 2.038, 2.024, 2.013, 2.001, 1.990, 1.681, 1.671, 1.666, 1.662, 1.656, 1.652, 1.647, 1.636, 1.630, 1.625, 1.619, 1.615, 1.610, 1.600, 1.169, 1.153, 1.120, 1.103

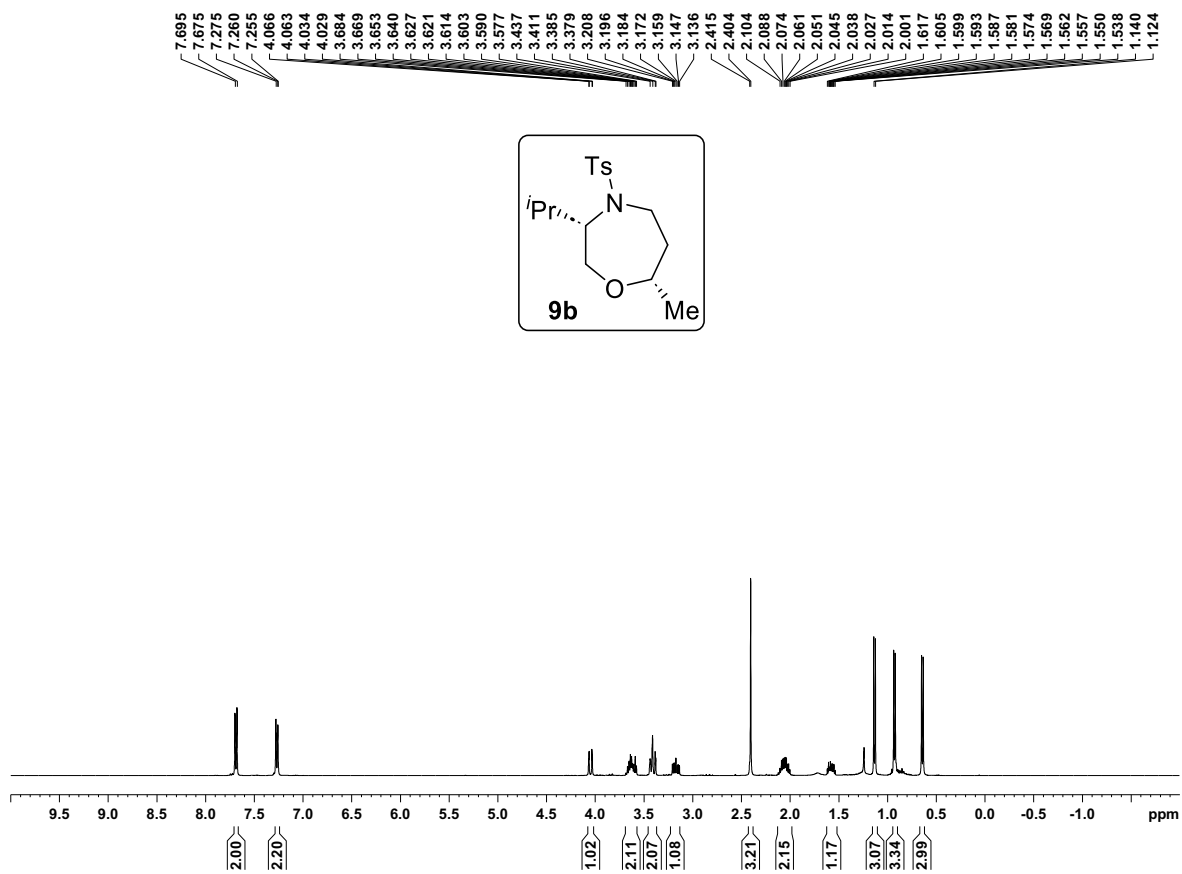


$^1\text{H}$  NMR spectrum of **9a** (400 MHz,  $\text{CDCl}_3$ )

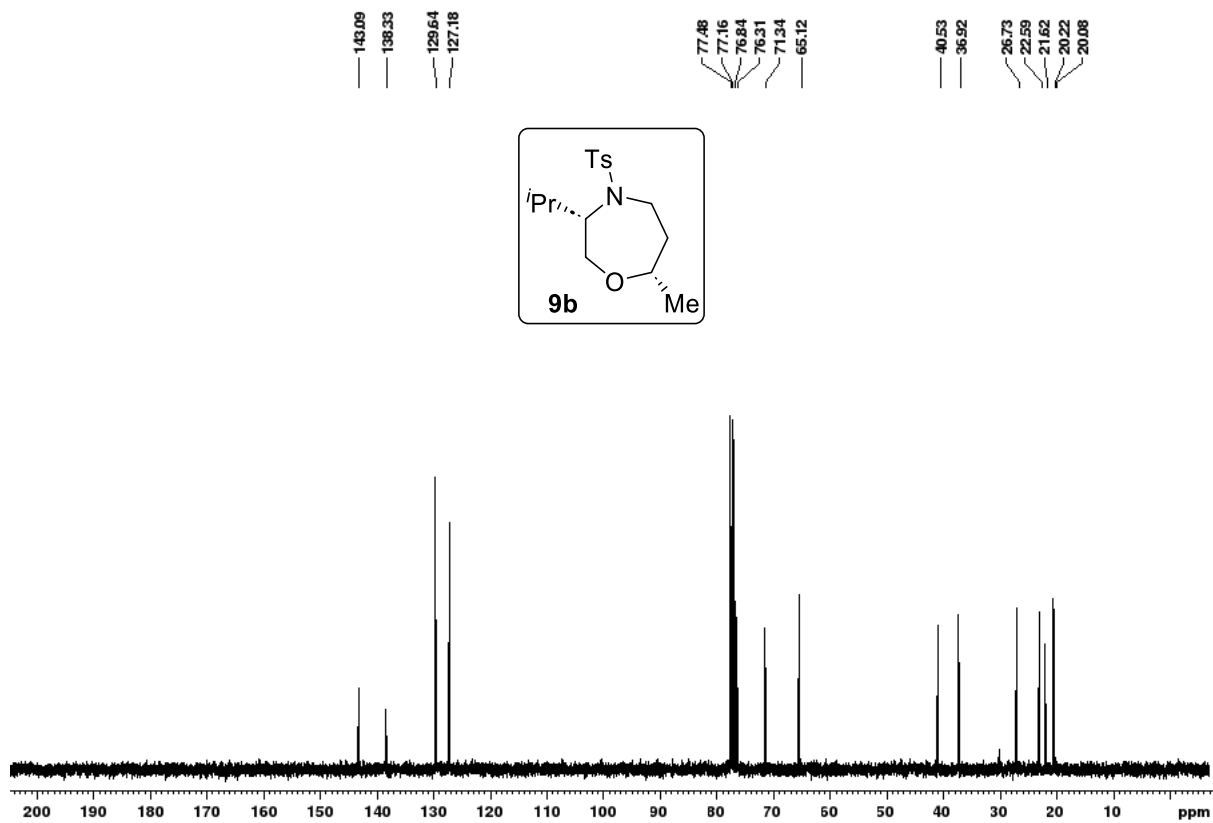
143.16, 137.69, 129.77, 126.92, 77.48, 77.16, 76.84, 76.26, 74.23, 54.20, 40.49, 37.41, 22.45, 21.58, 16.47



$^{13}\text{C}$  NMR spectrum of **9a** (100 MHz,  $\text{CDCl}_3$ )

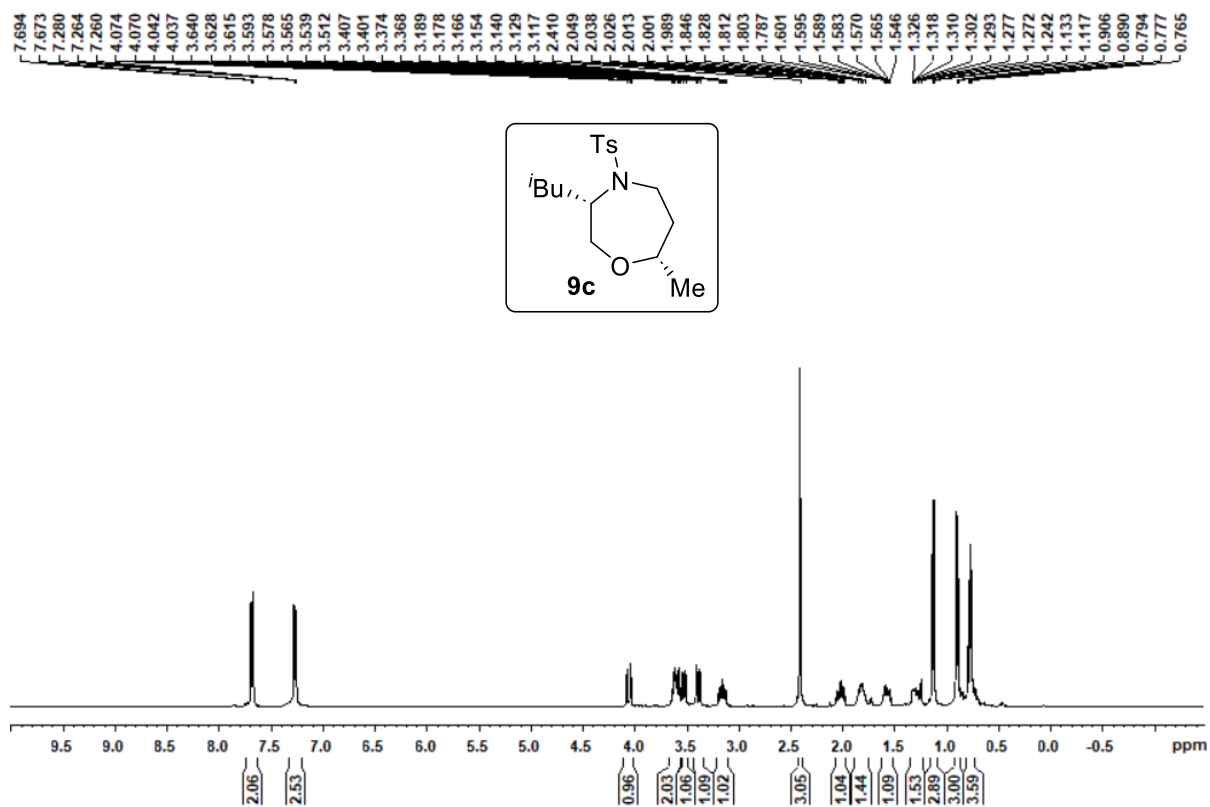


$^1\text{H}$  NMR spectrum of **9b** (400 MHz,  $\text{CDCl}_3$ )

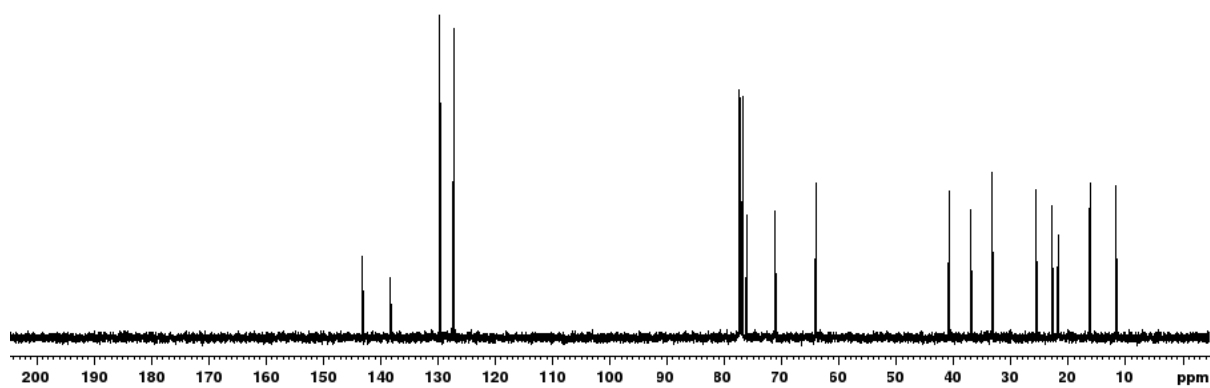
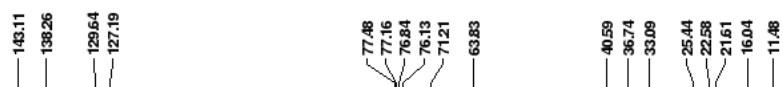


$^{13}\text{C}$  NMR spectrum of **9b** (100 MHz,  $\text{CDCl}_3$ )

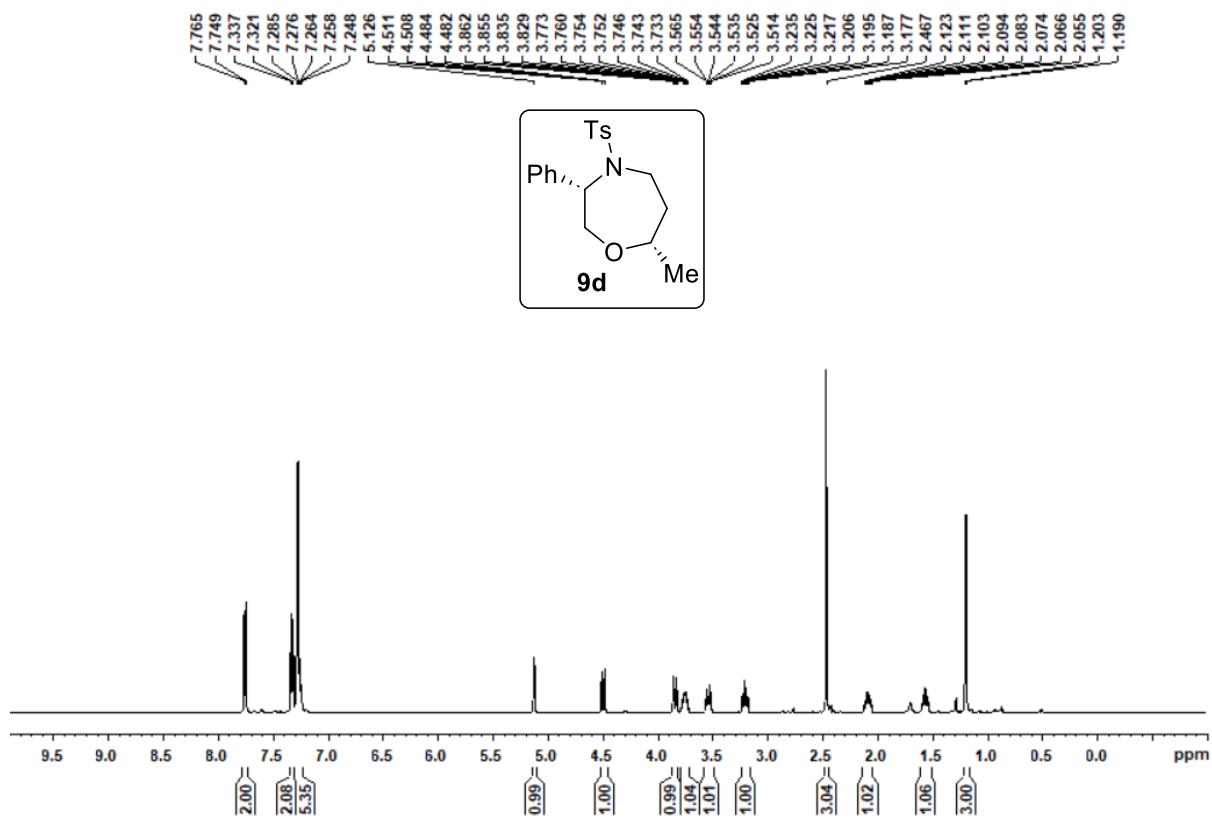




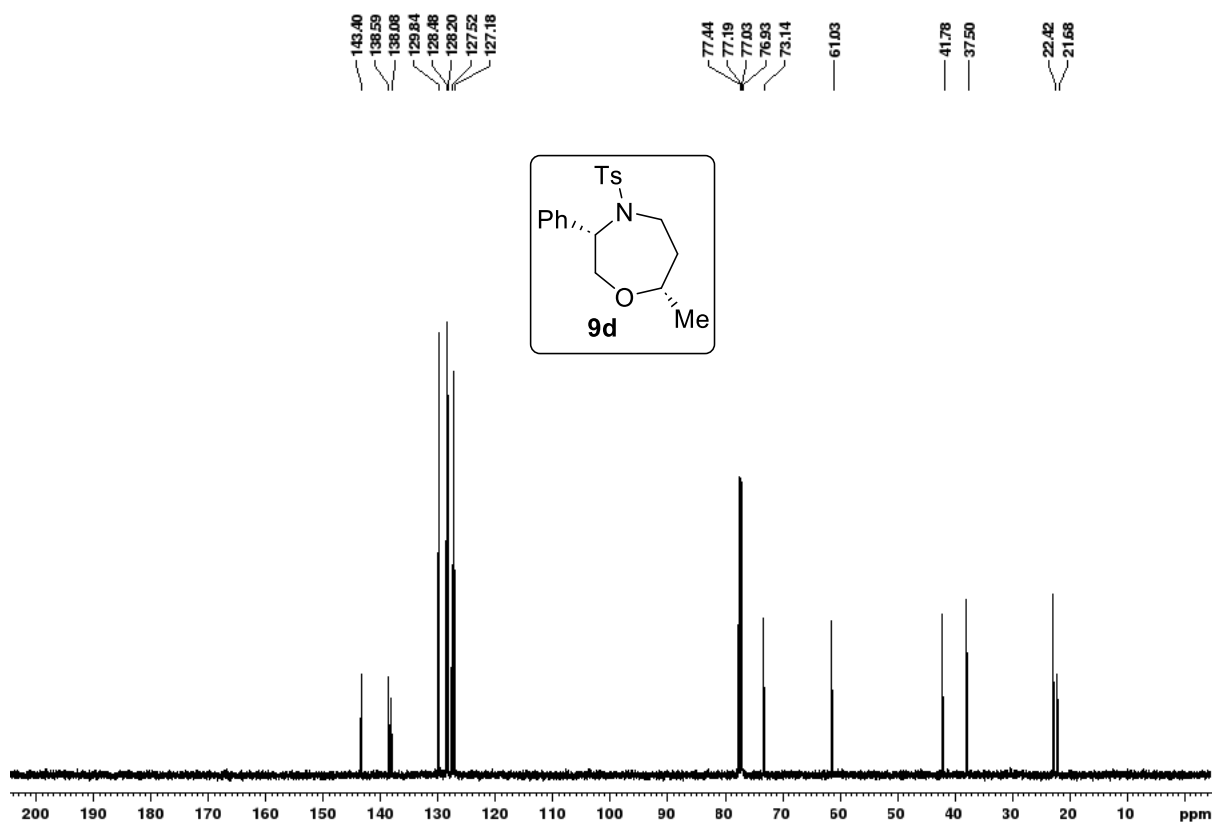
<sup>1</sup>H NMR spectrum of **9c** (400 MHz, CDCl<sub>3</sub>)



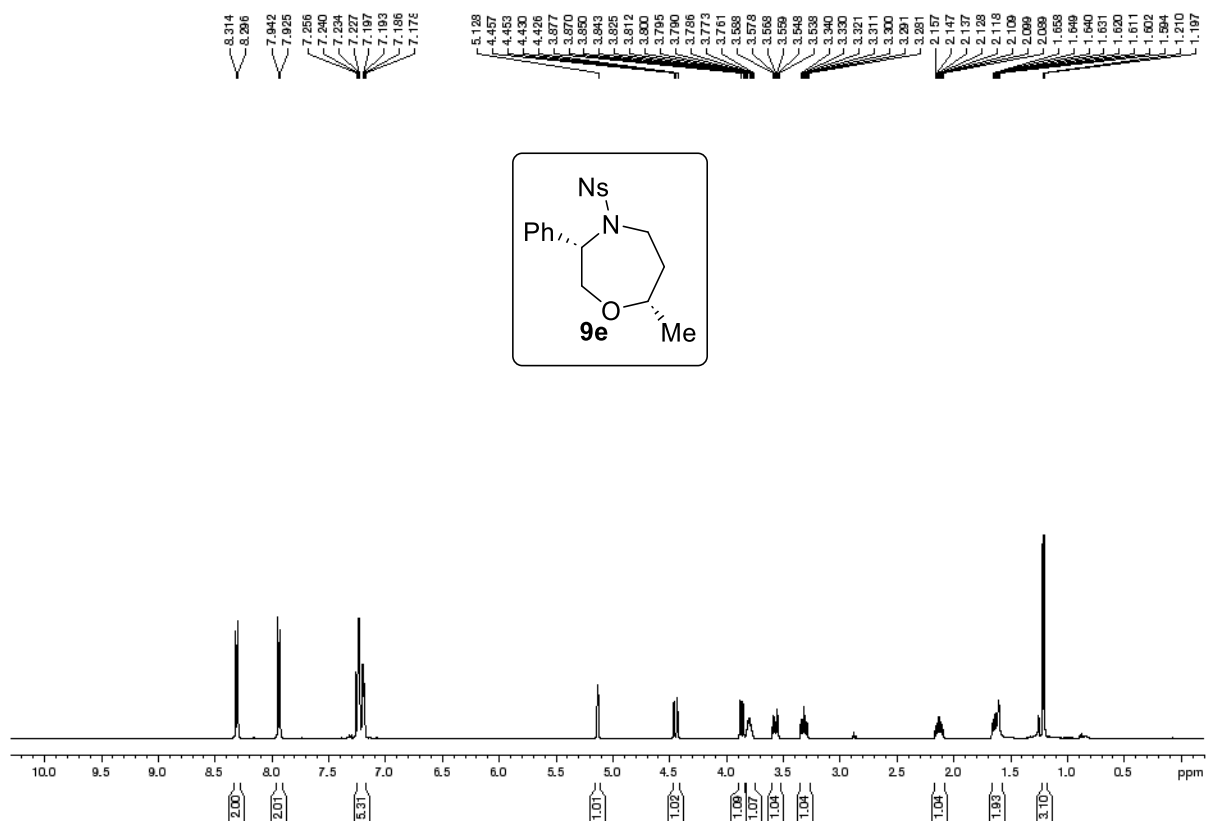
<sup>13</sup>C NMR spectrum of **9c** (100 MHz, CDCl<sub>3</sub>)



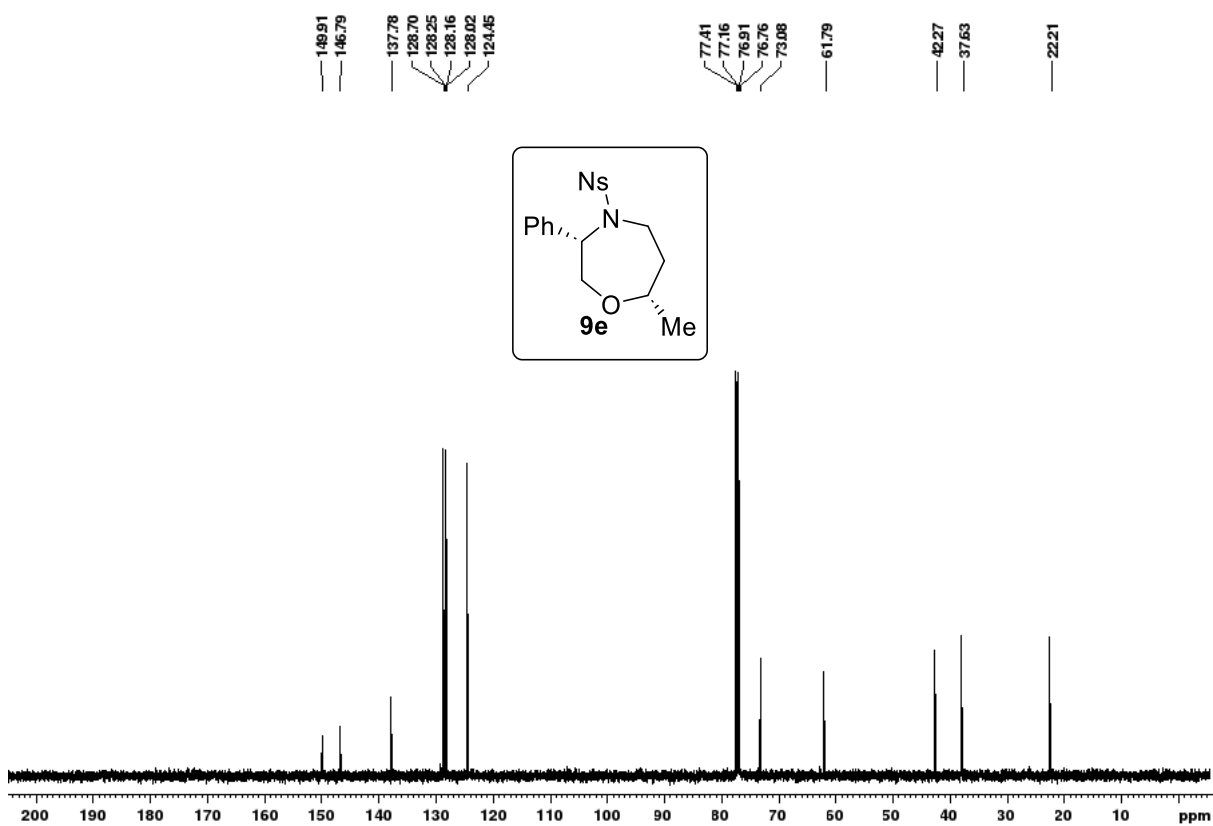
$^1\text{H}$  NMR spectrum of **9d** (500 MHz,  $\text{CDCl}_3$ )



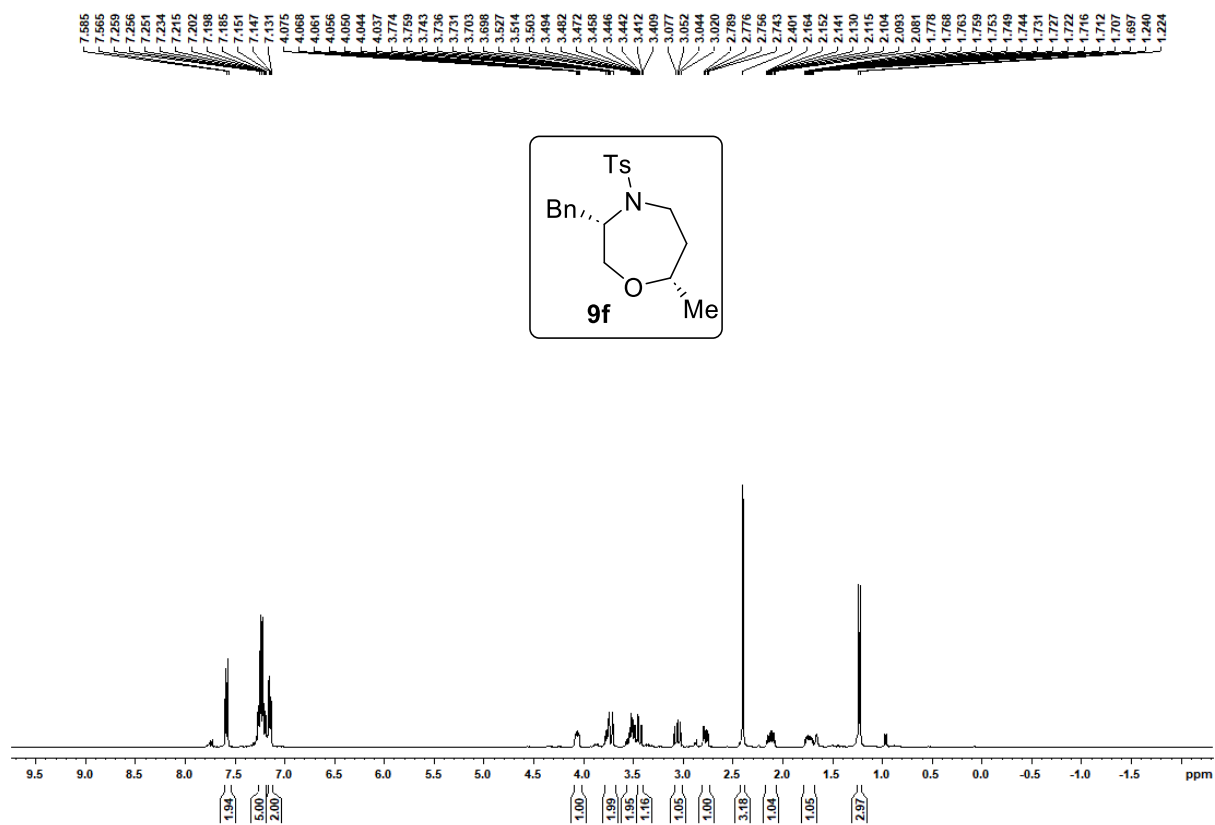
$^{13}\text{C}$  NMR spectrum of **9d** (125 MHz,  $\text{CDCl}_3$ )



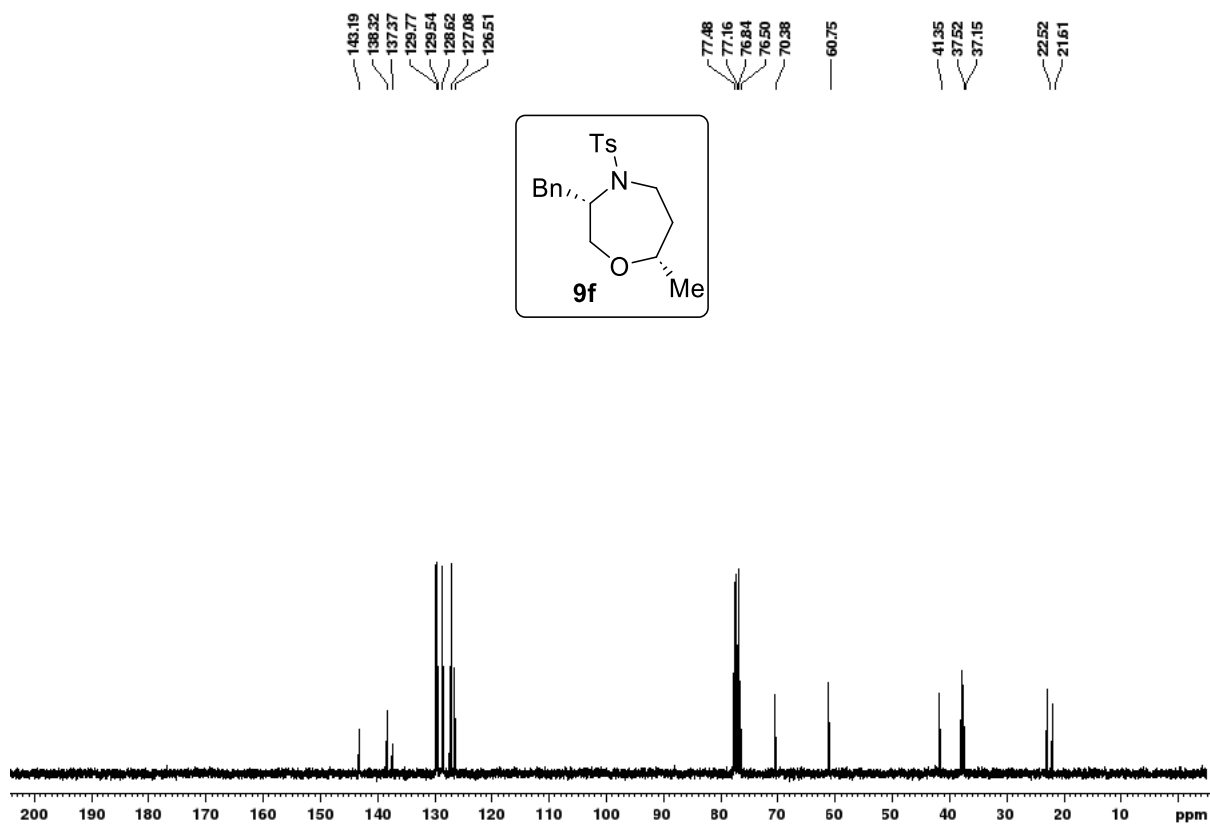
<sup>1</sup>H NMR spectrum of **9e** (500 MHz, CDCl<sub>3</sub>)



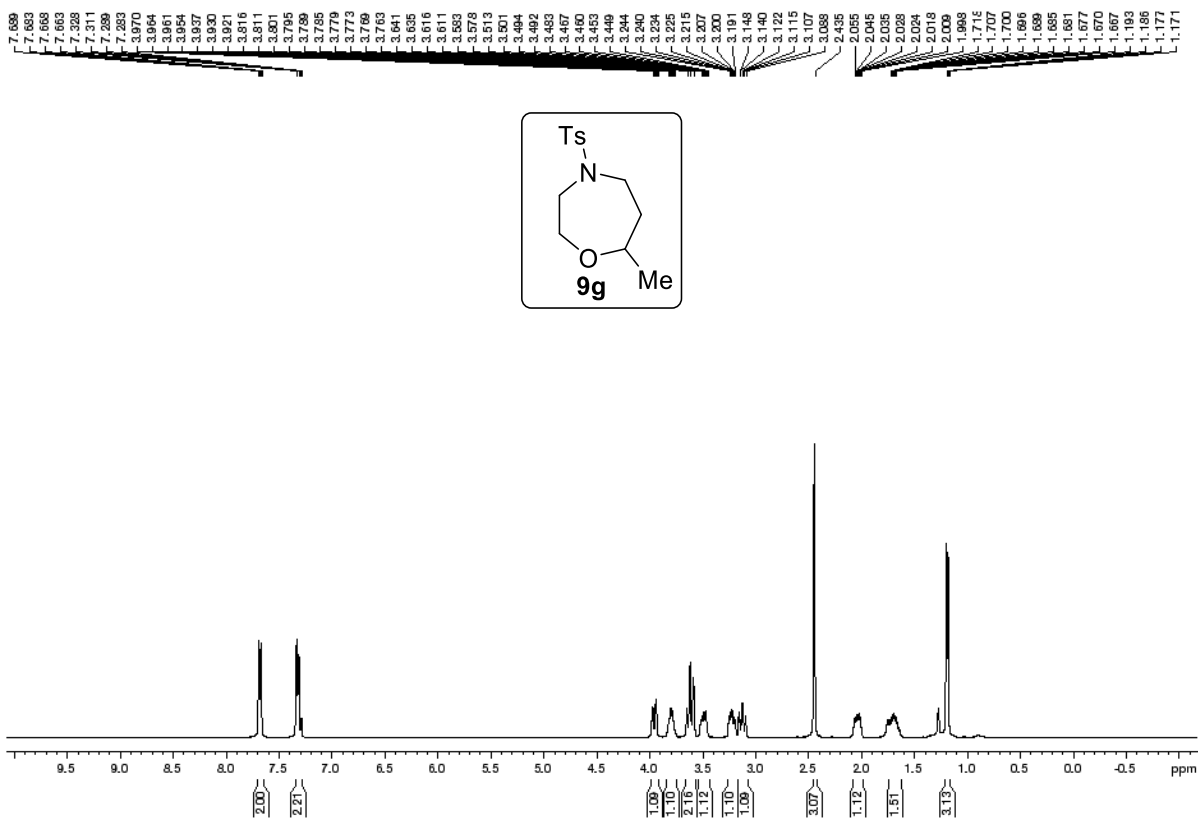
<sup>13</sup>C NMR spectrum of **9e** (125 MHz, CDCl<sub>3</sub>)



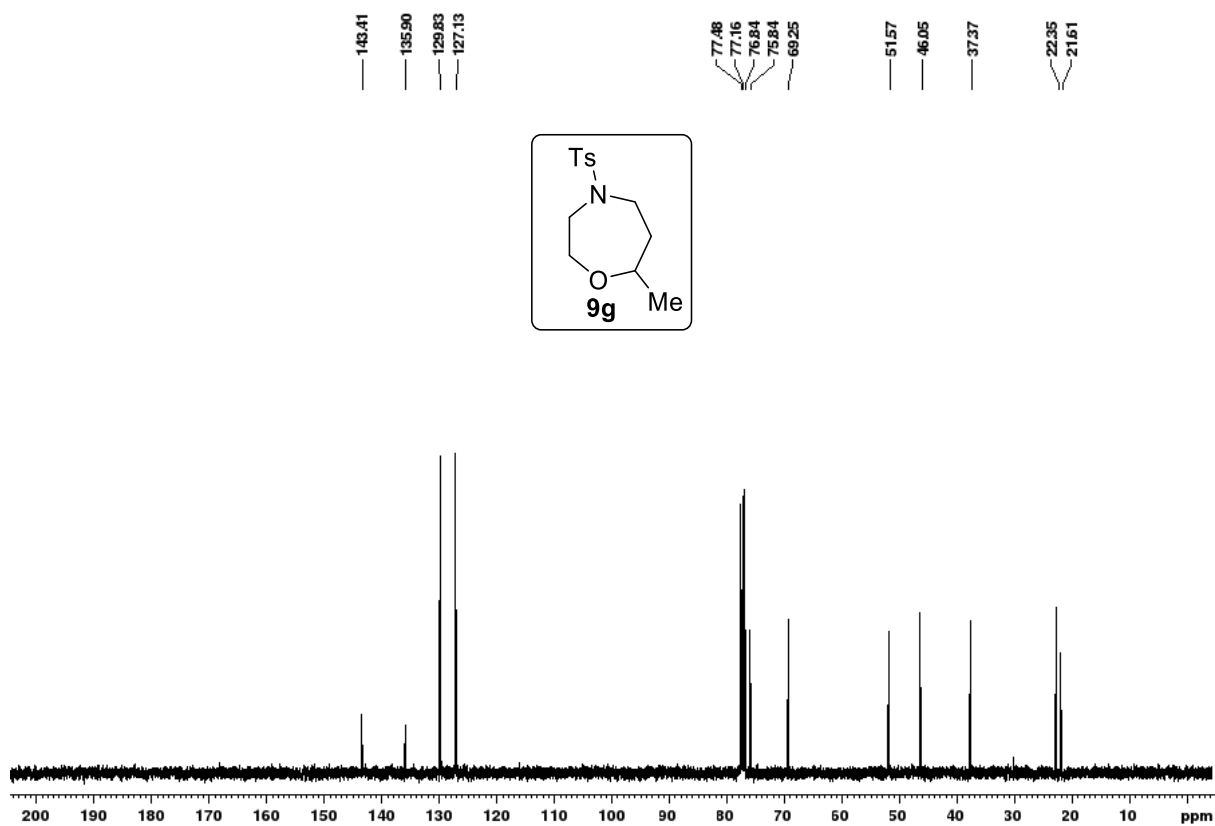
$^1\text{H}$  NMR spectrum of **9f** (400 MHz,  $\text{CDCl}_3$ )



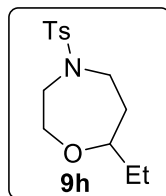
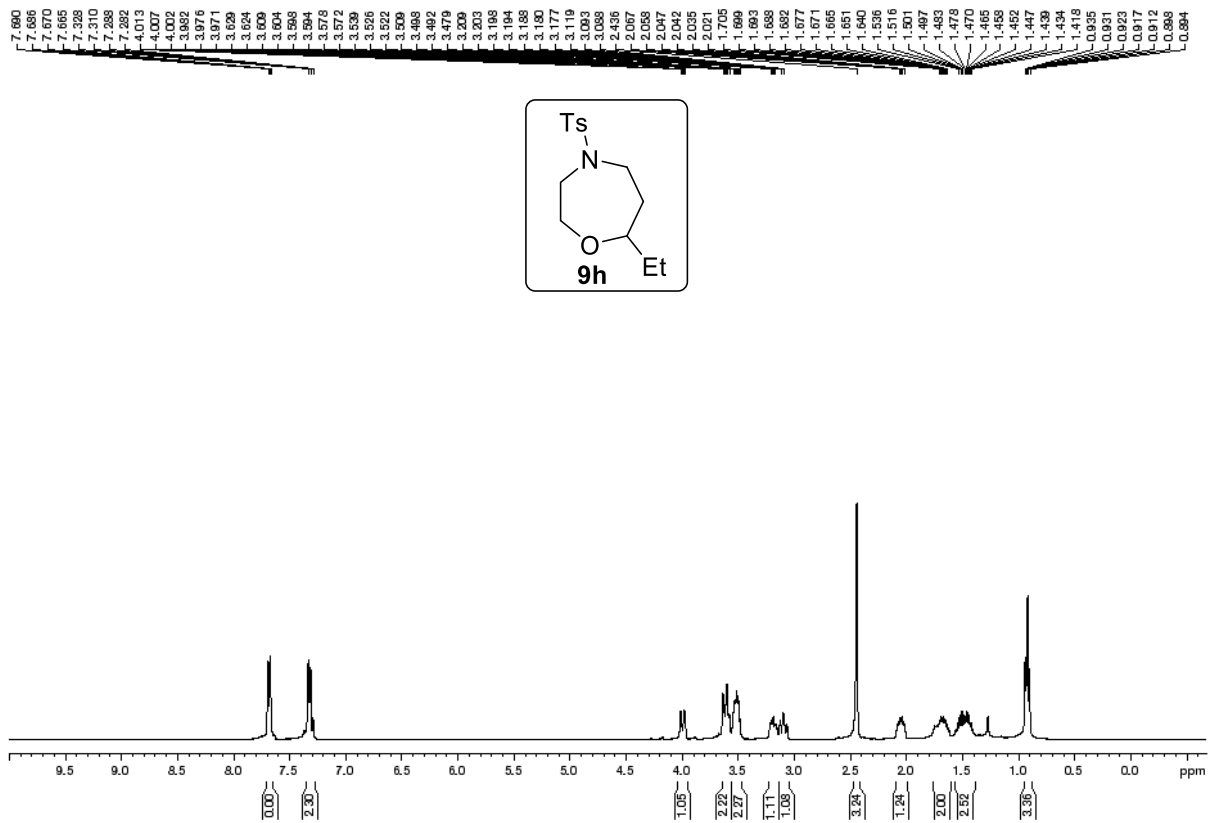
$^{13}\text{C}$  NMR spectrum of **9f** (100 MHz,  $\text{CDCl}_3$ )



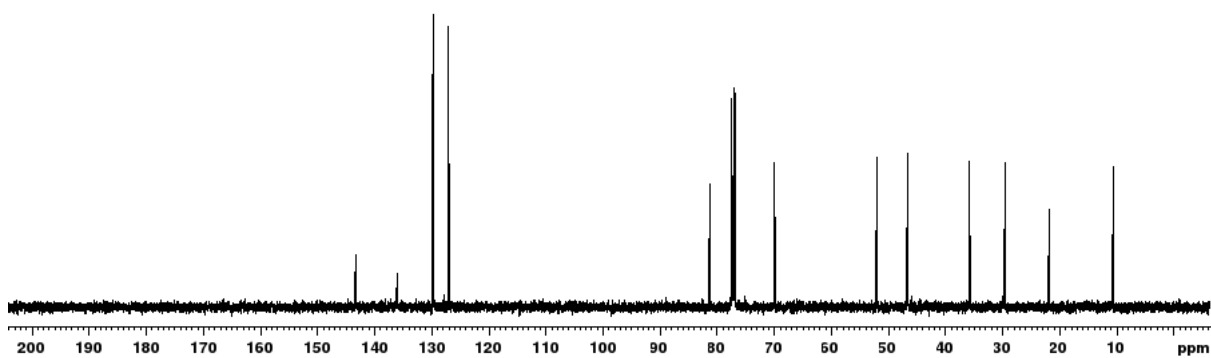
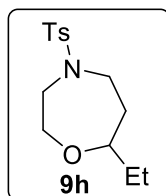
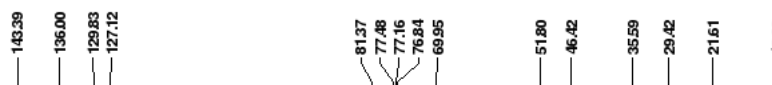
<sup>1</sup>H NMR spectrum of **9g** (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of **9g** (100 MHz, CDCl<sub>3</sub>)

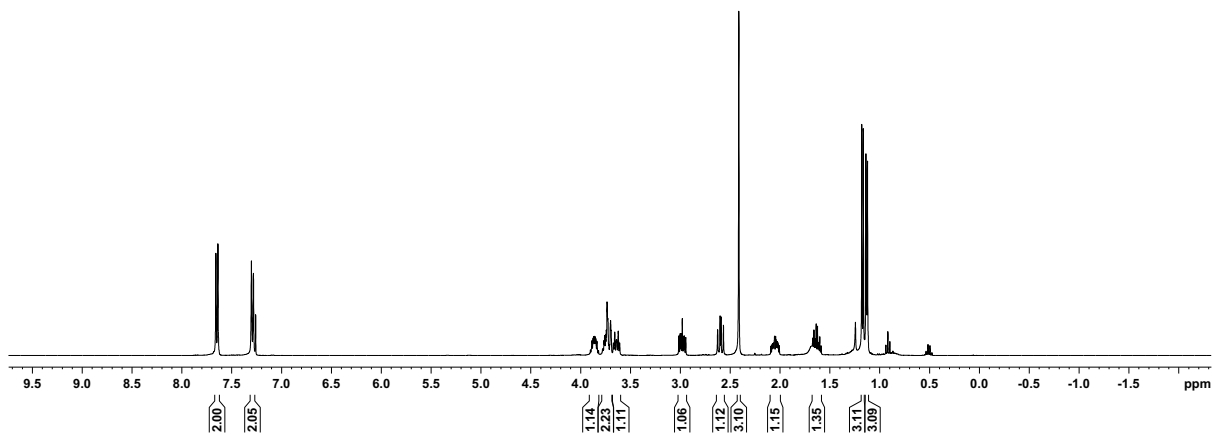
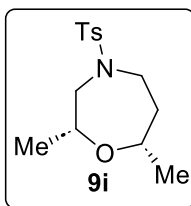


$^1\text{H}$  NMR spectrum of **9h** (400 MHz,  $\text{CDCl}_3$ )



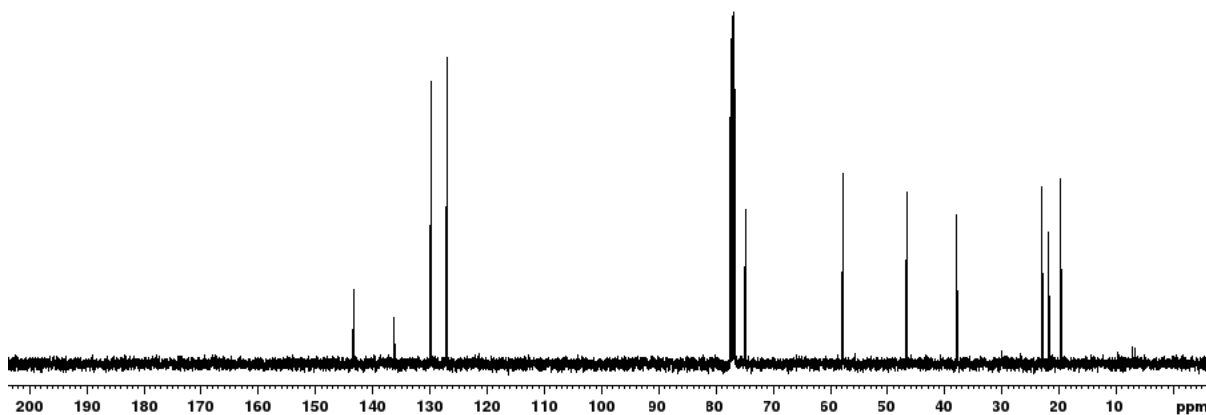
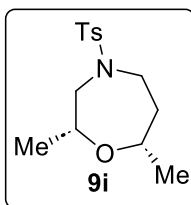
$^{13}\text{C}$  NMR spectrum of **9h** (100 MHz,  $\text{CDCl}_3$ )

7.659  
7.638  
7.302  
7.282  
7.260  
3.901  
3.885  
3.875  
3.869  
3.862  
3.859  
3.852  
3.847  
3.836  
3.820  
3.781  
3.774  
3.765  
3.758  
3.749  
3.743  
3.735  
3.727  
3.717  
3.708  
3.701  
3.699  
3.693  
3.670  
3.657  
3.639  
3.622  
3.608  
3.014  
3.001  
2.992  
2.979  
2.968  
2.958  
2.945  
2.626  
2.600  
2.591  
2.567  
2.413  
2.091  
2.080  
2.075  
2.069  
2.065  
2.054  
2.043  
2.040  
2.033  
2.029  
2.022  
2.018  
2.007  
1.683  
1.672  
1.659  
1.649  
1.646  
1.636  
1.623  
1.613  
1.610  
1.600  
1.587  
1.179  
1.163

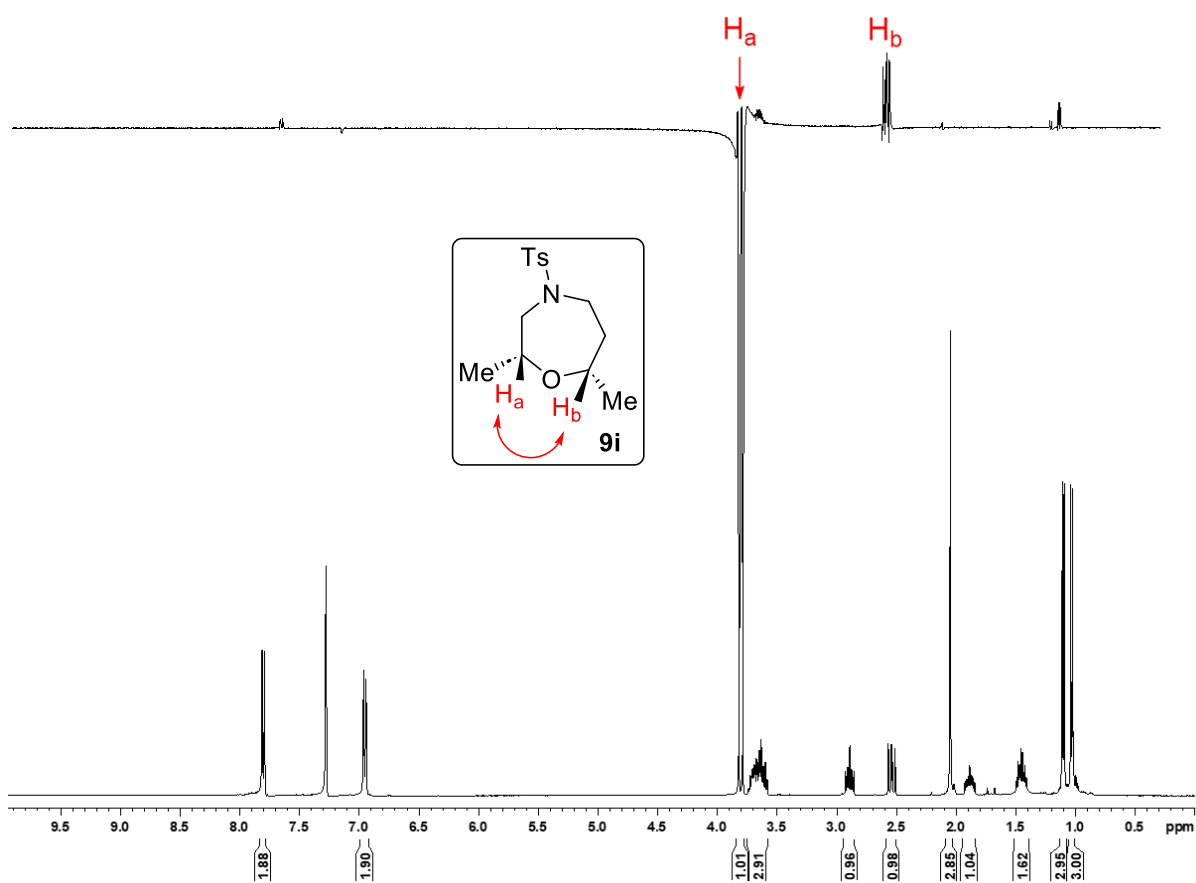
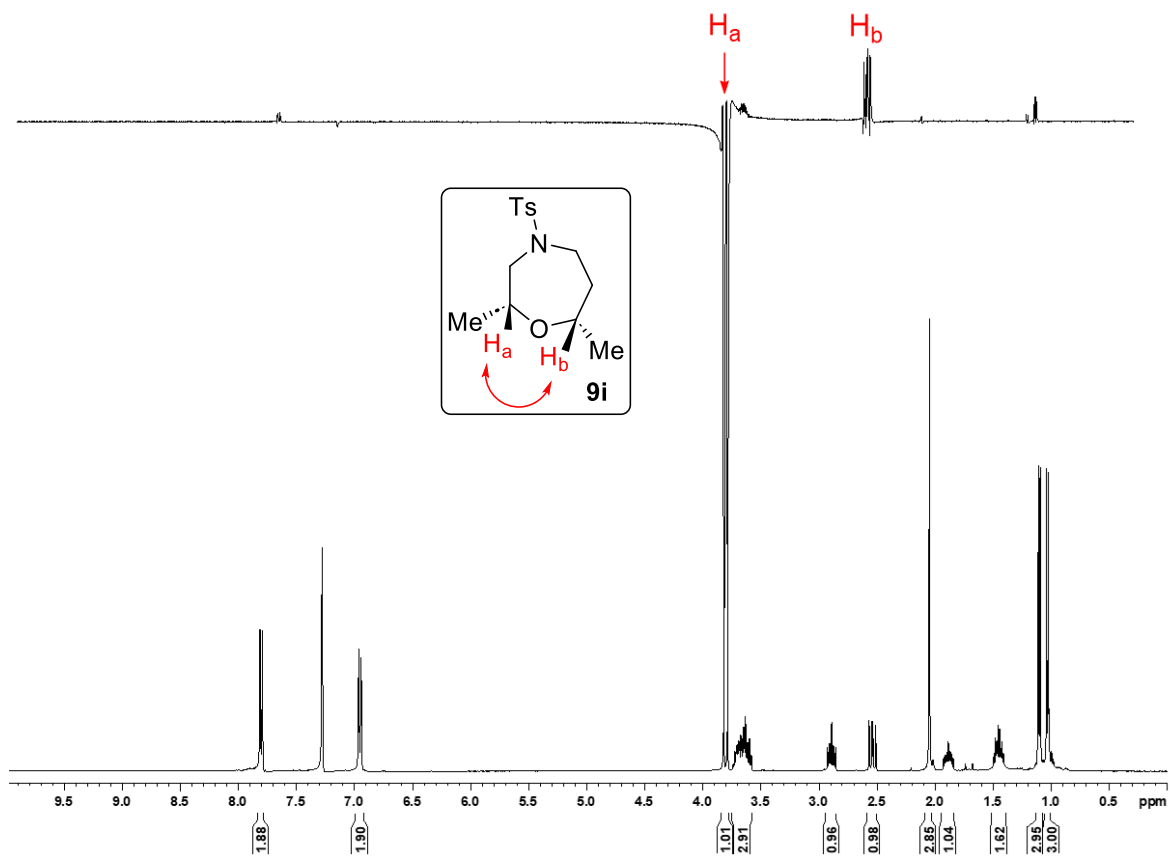


$^1\text{H}$  NMR spectrum of **9i** (400 MHz,  $\text{CDCl}_3$ )

143.33  
136.35  
129.84  
127.02  
77.48  
77.16  
76.84  
76.77  
74.91  
57.62  
46.48  
37.76  
22.81  
21.61  
19.57



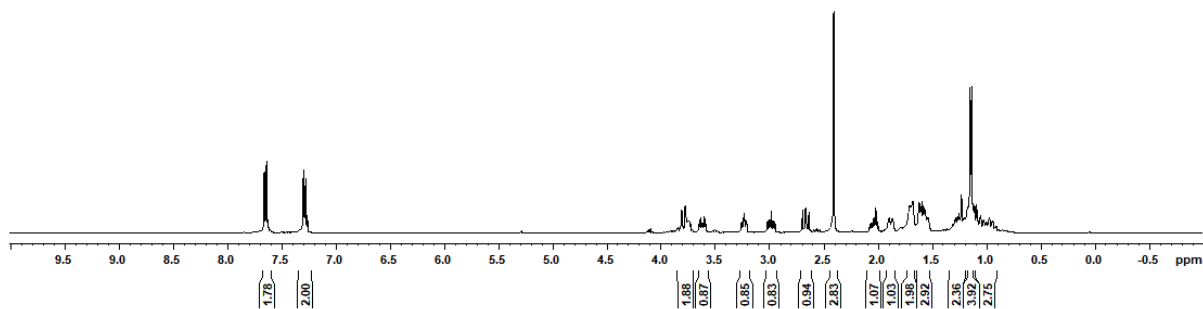
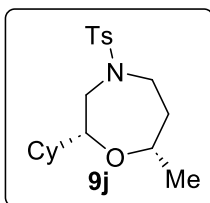
$^{13}\text{C}$  NMR spectrum of **9i** (100 MHz,  $\text{CDCl}_3$ )



NOE spectrum of **9i** (400 MHz,  $C_6D_6$ )

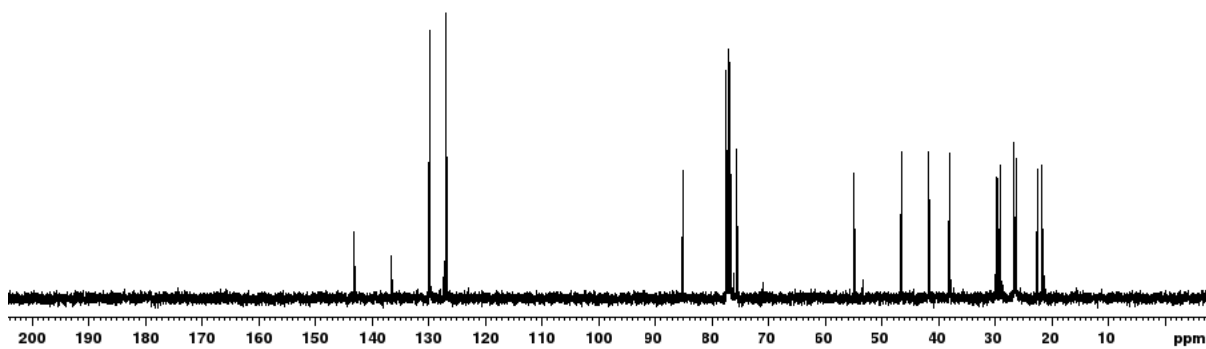
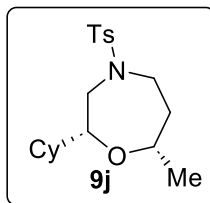


7.650  
7.629  
7.288  
7.268  
3.802  
3.799  
3.769  
3.754  
3.747  
3.742  
3.735  
3.731  
3.719  
3.640  
3.627  
3.613  
3.605  
3.593  
3.579  
3.251  
3.245  
3.234  
3.227  
3.220  
3.206  
3.072  
3.042  
3.000  
2.989  
2.977  
2.965  
2.954  
2.942  
2.687  
2.661  
2.654  
2.629  
2.400  
2.067  
2.056  
2.046  
2.032  
2.022  
2.009  
2.009  
1.997  
1.897  
1.868  
1.709  
1.702  
1.680  
1.621  
1.609  
1.586  
1.575  
1.573  
1.553  
1.550  
1.540  
1.309  
1.300  
1.290  
1.281  
1.272  
1.263  
1.253  
1.235  
1.231  
1.155  
1.139  
1.094  
1.064  
1.053  
1.031  
1.023  
1.003  
0.973  
0.943

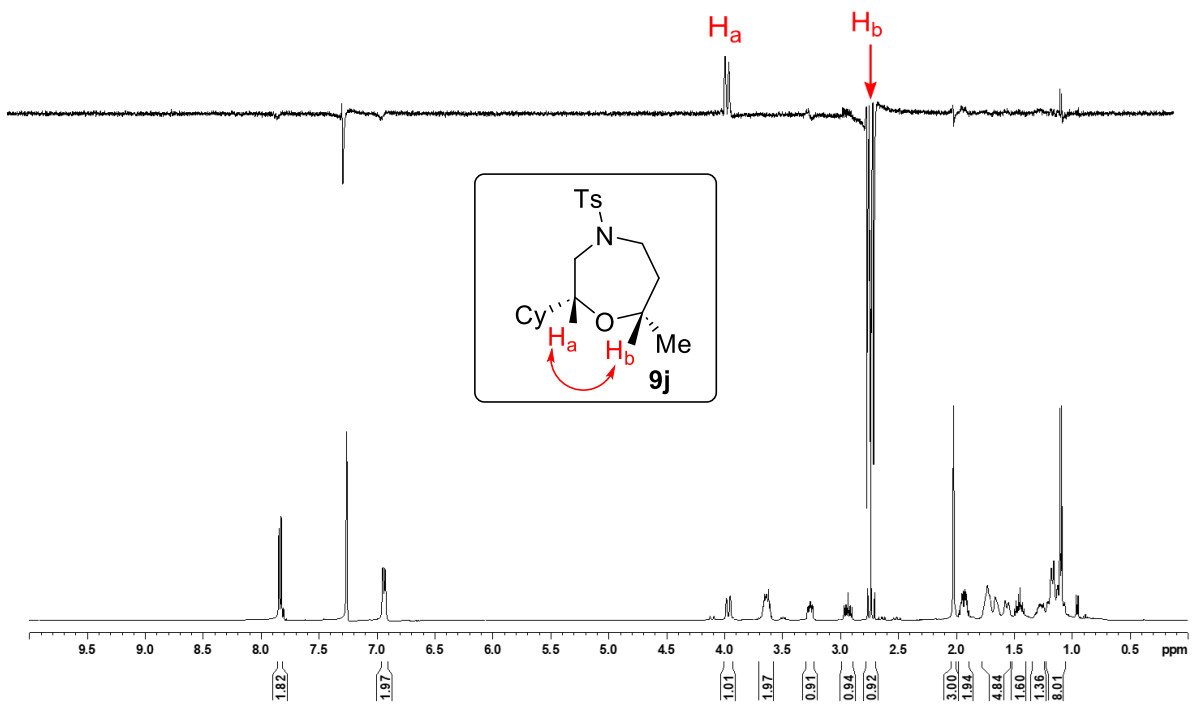
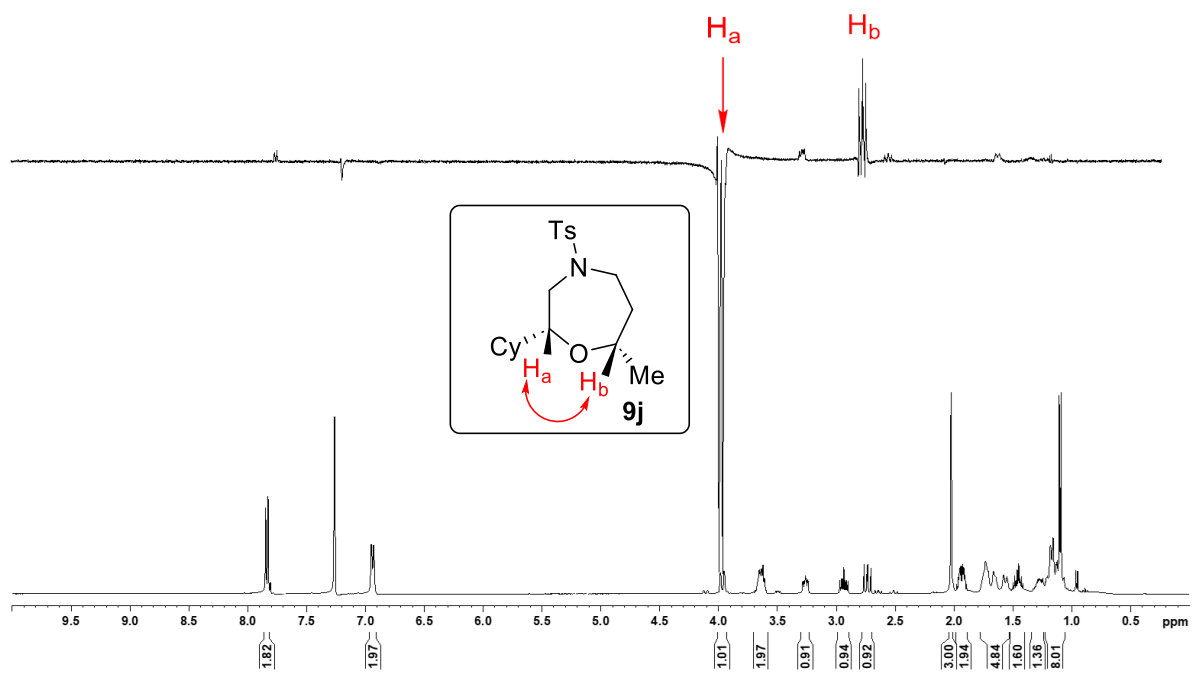


$^1\text{H}$  NMR spectrum of **9j** (400 MHz,  $\text{CDCl}_3$ )

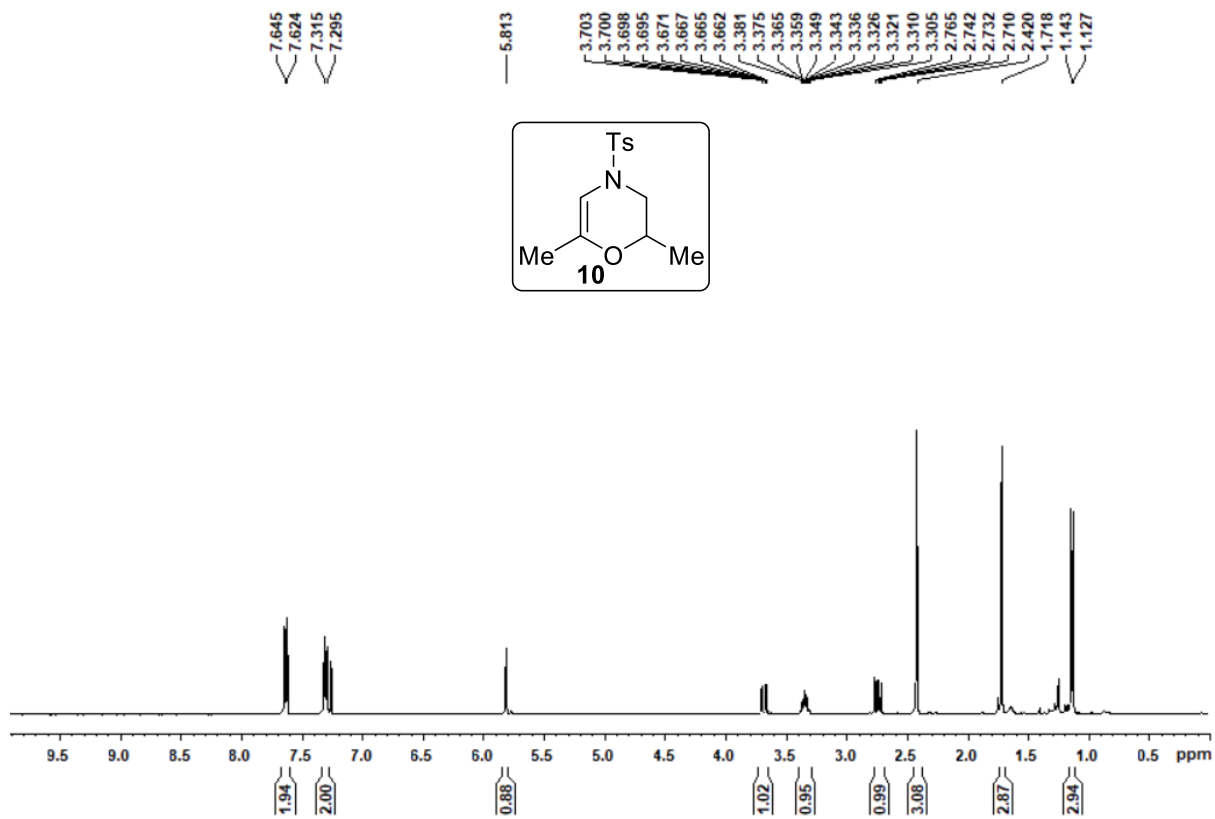
143.20  
136.54  
129.79  
126.99  
85.14  
77.48  
77.16  
76.84  
75.71  
54.66  
46.31  
41.47  
37.88  
29.46  
28.89  
26.43  
26.14  
26.00  
22.28  
21.60



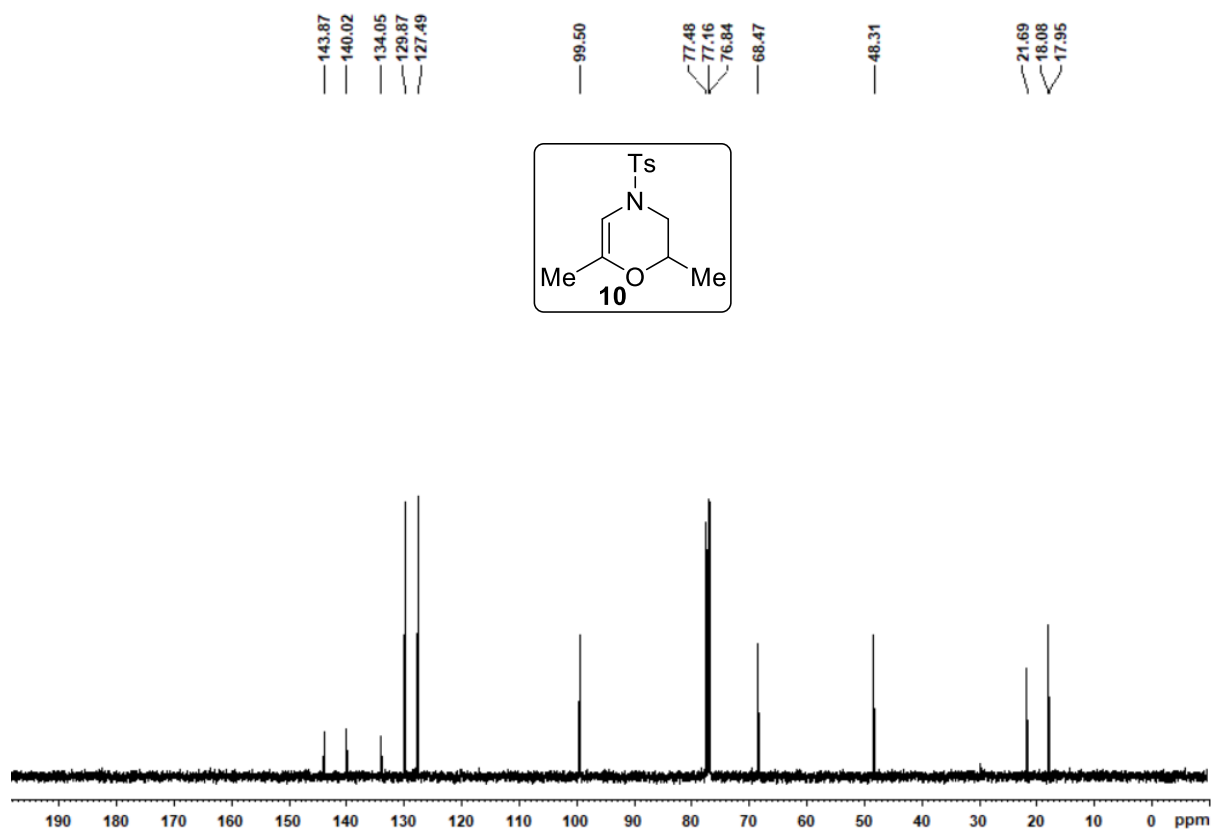
$^{13}\text{C}$  NMR spectrum of **9j** (100 MHz,  $\text{CDCl}_3$ )



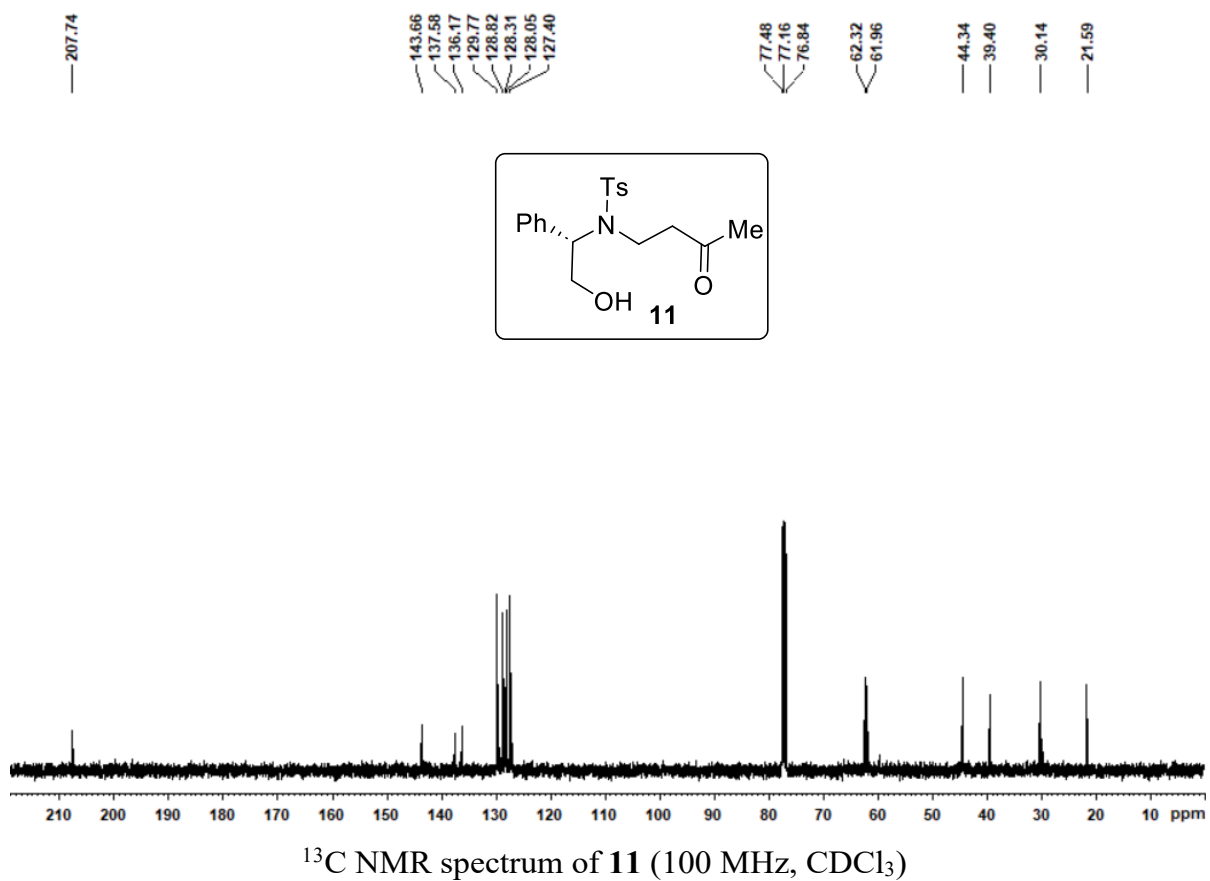
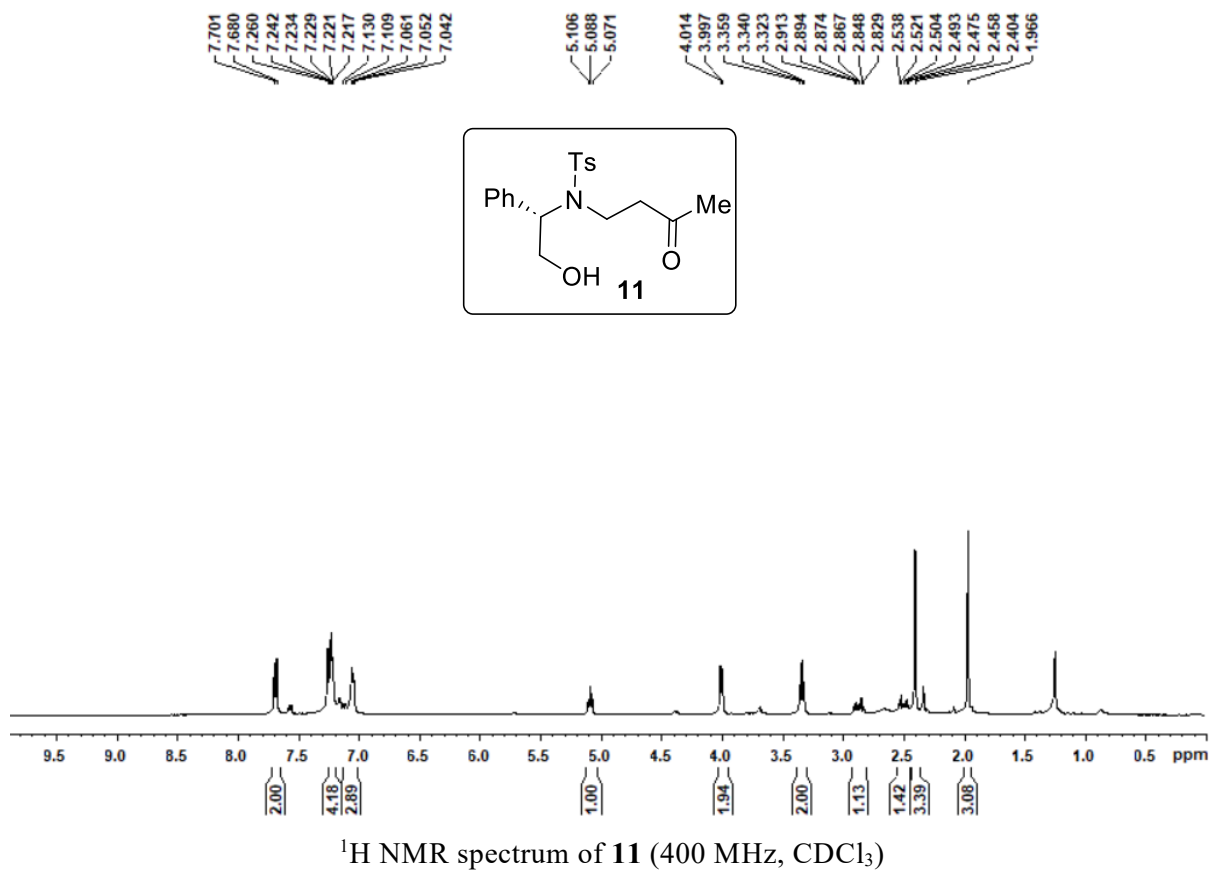
NOE spectrum of **9j** (400 MHz,  $C_6D_6$ )

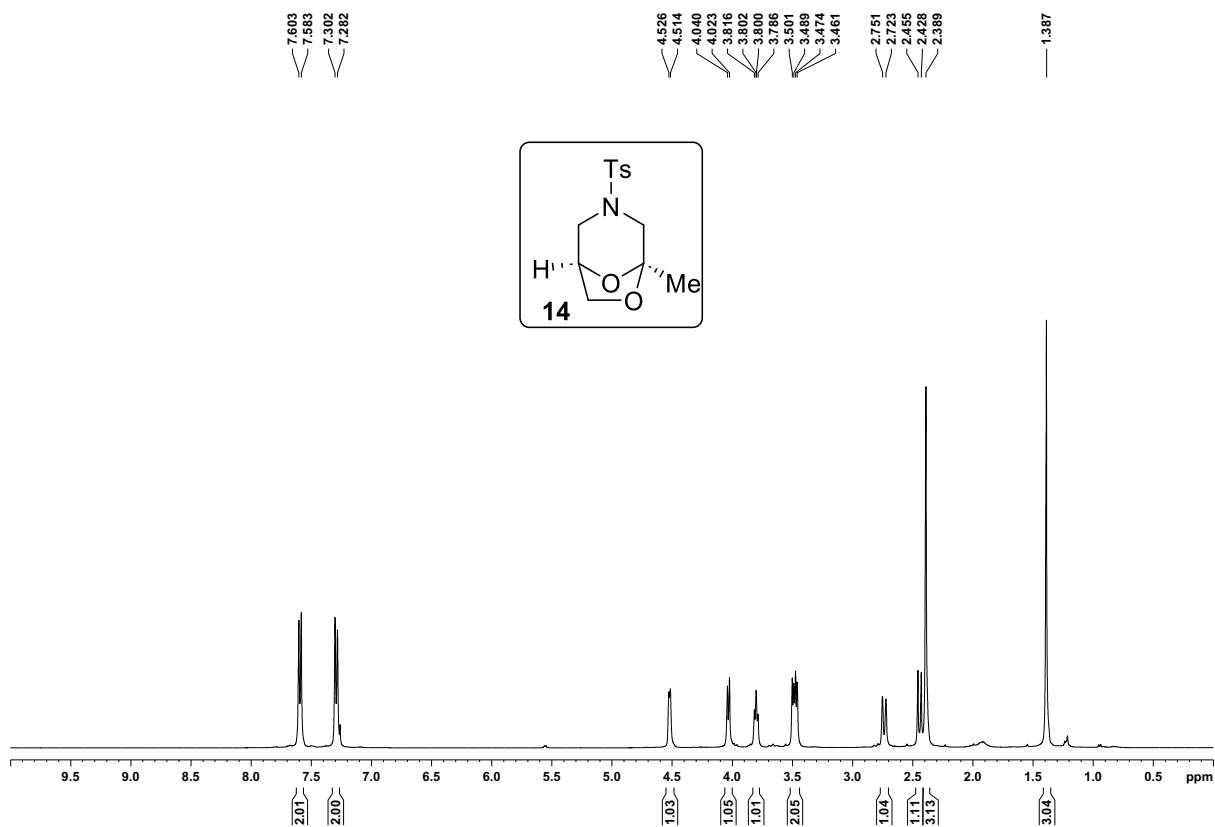


<sup>1</sup>H NMR spectrum of **10** (400 MHz, CDCl<sub>3</sub>)

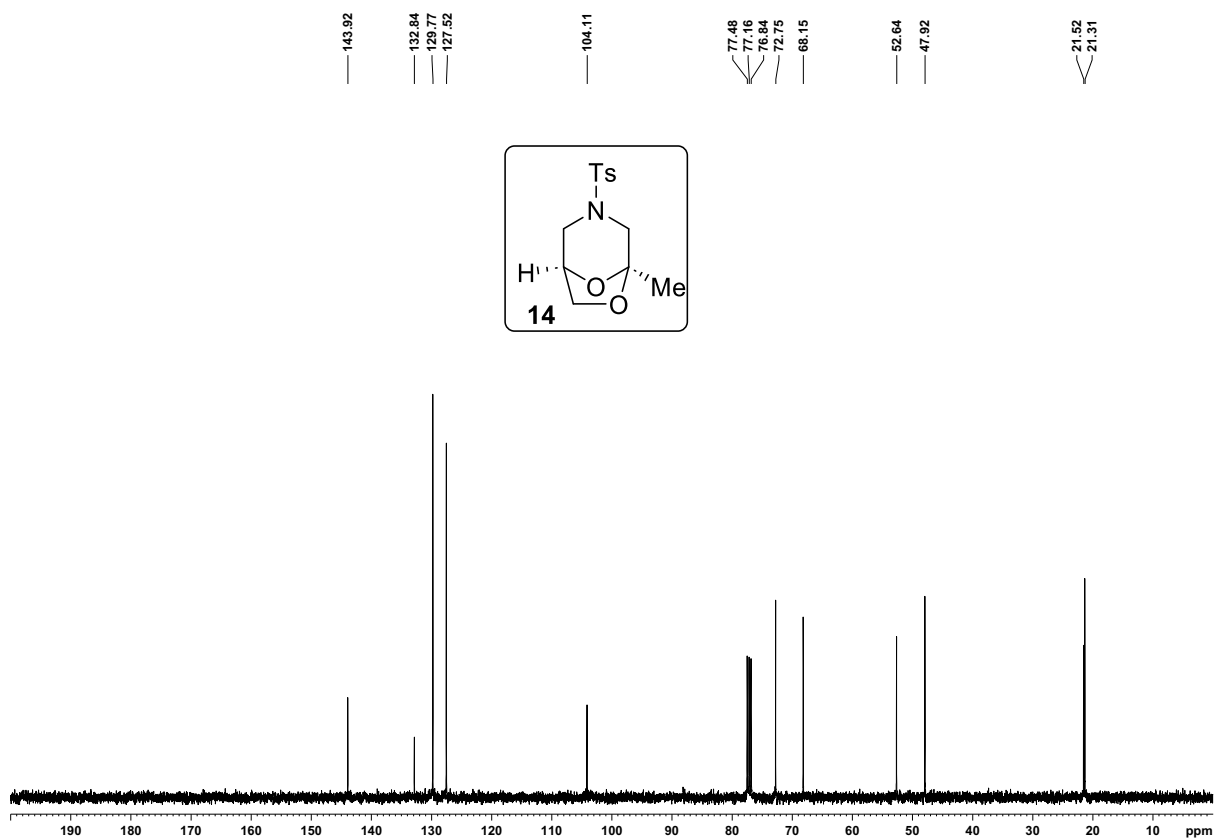


<sup>13</sup>C NMR spectrum of **10** (100 MHz, CDCl<sub>3</sub>)

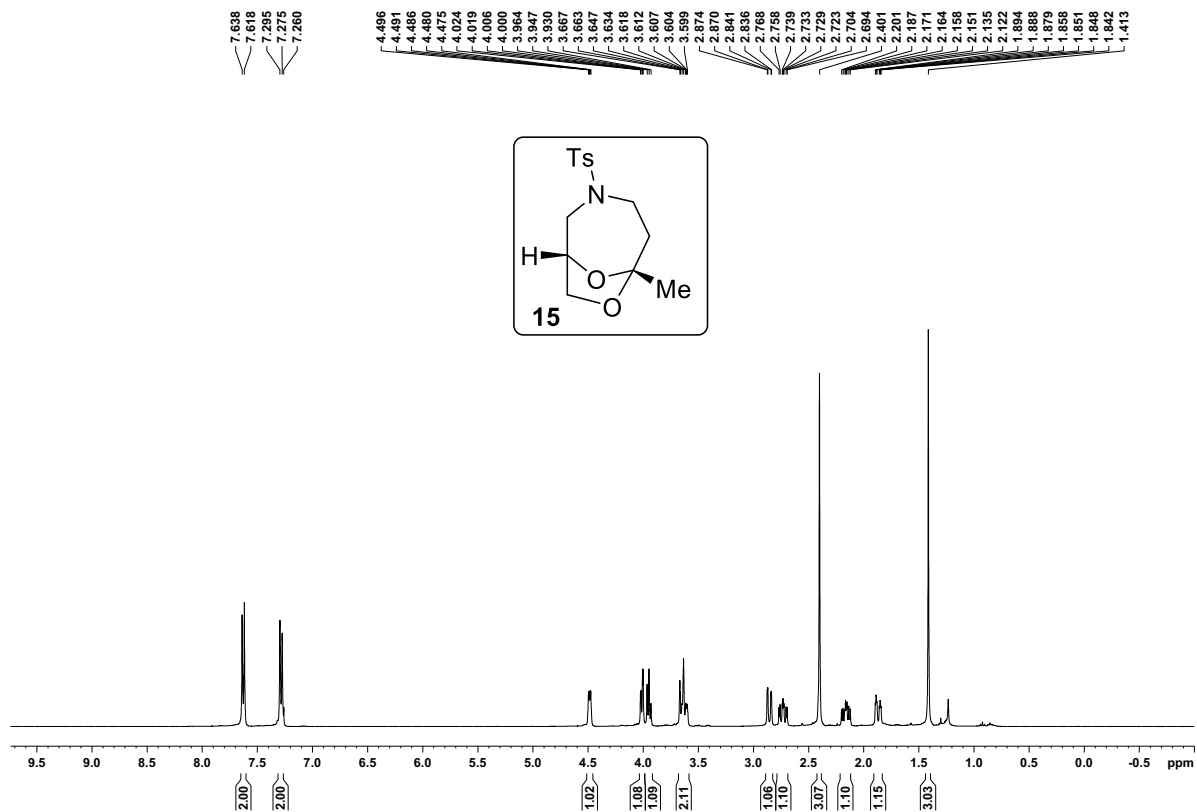




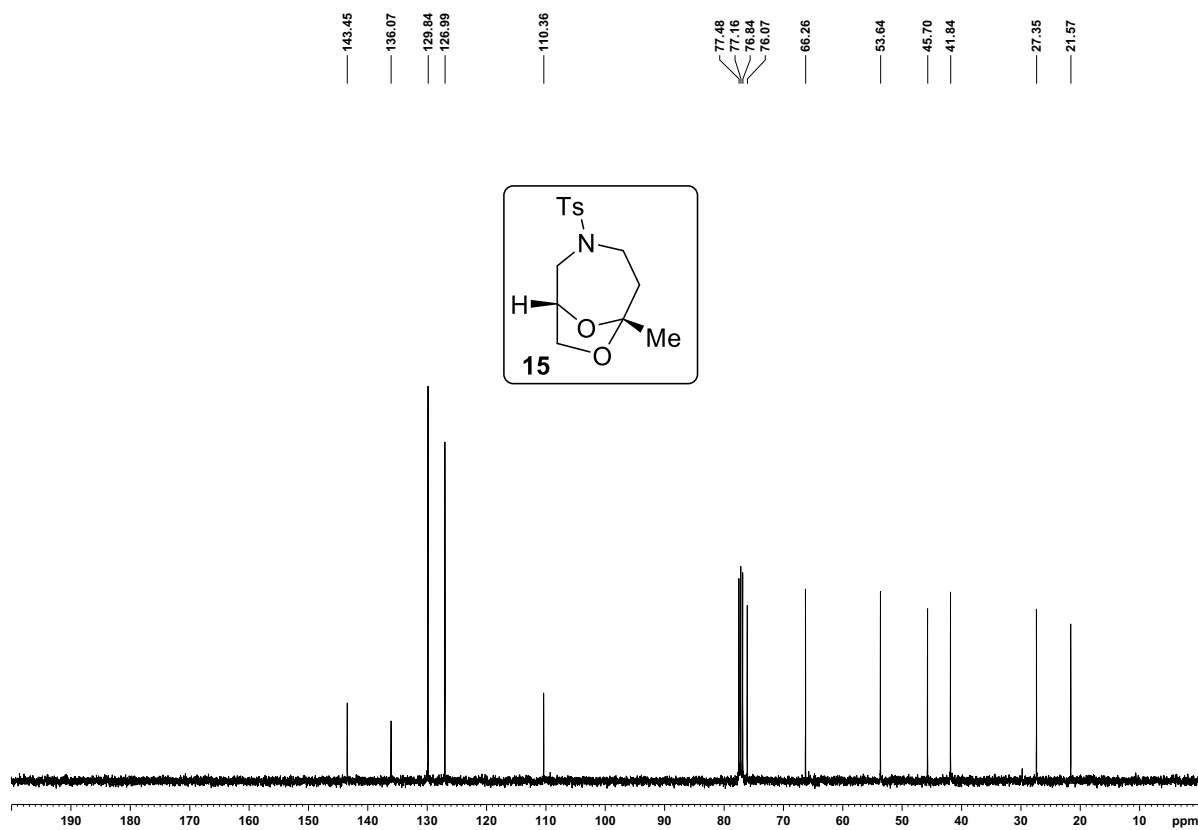
<sup>1</sup>H NMR spectrum of **14** (400 MHz, CDCl<sub>3</sub>)



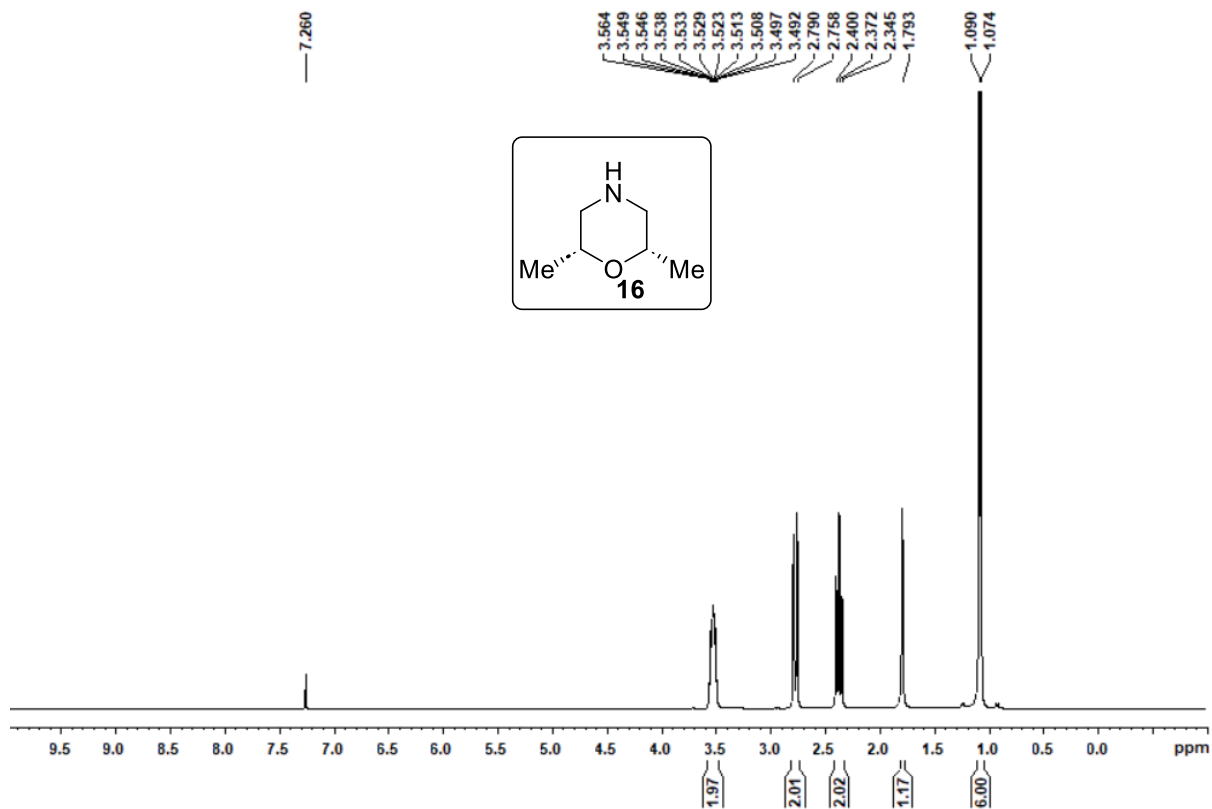
<sup>13</sup>C NMR spectrum of **14** (100 MHz, CDCl<sub>3</sub>)



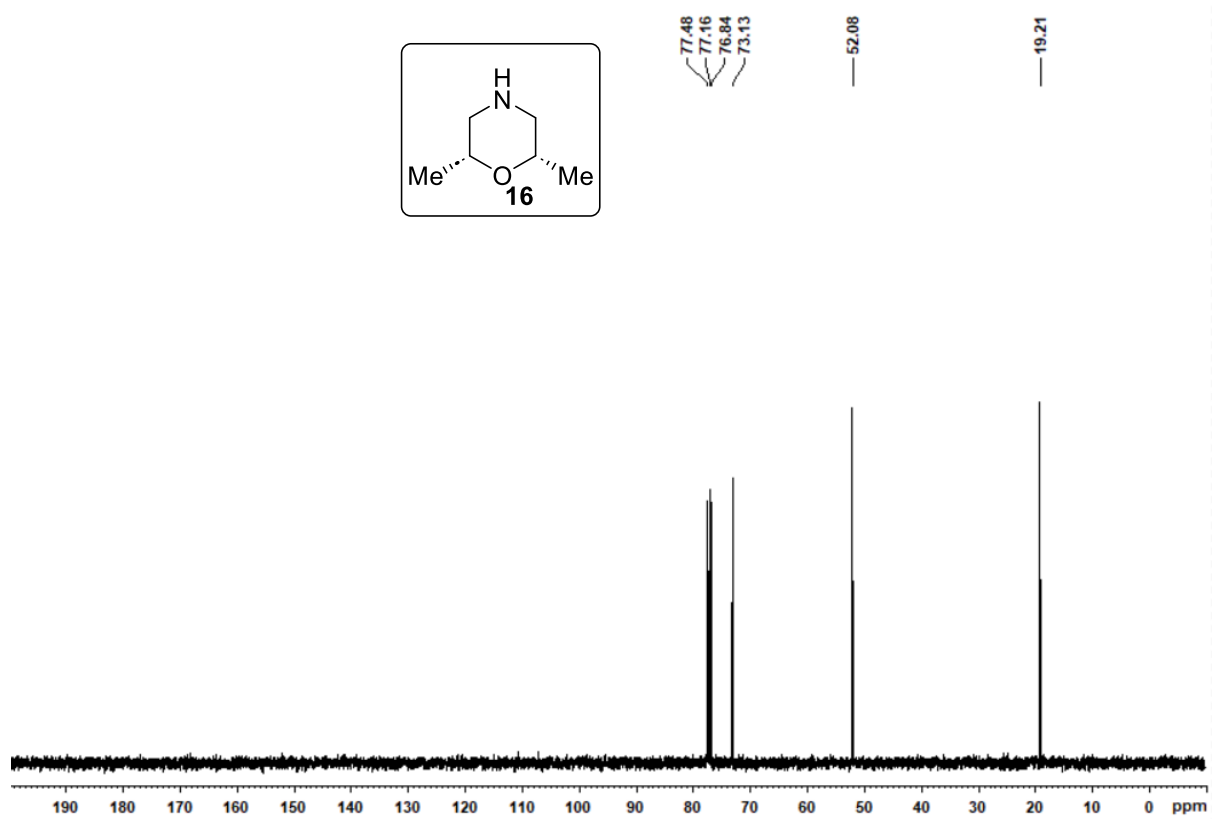
<sup>1</sup>H NMR spectrum of **15** (400 MHz, CDCl<sub>3</sub>)



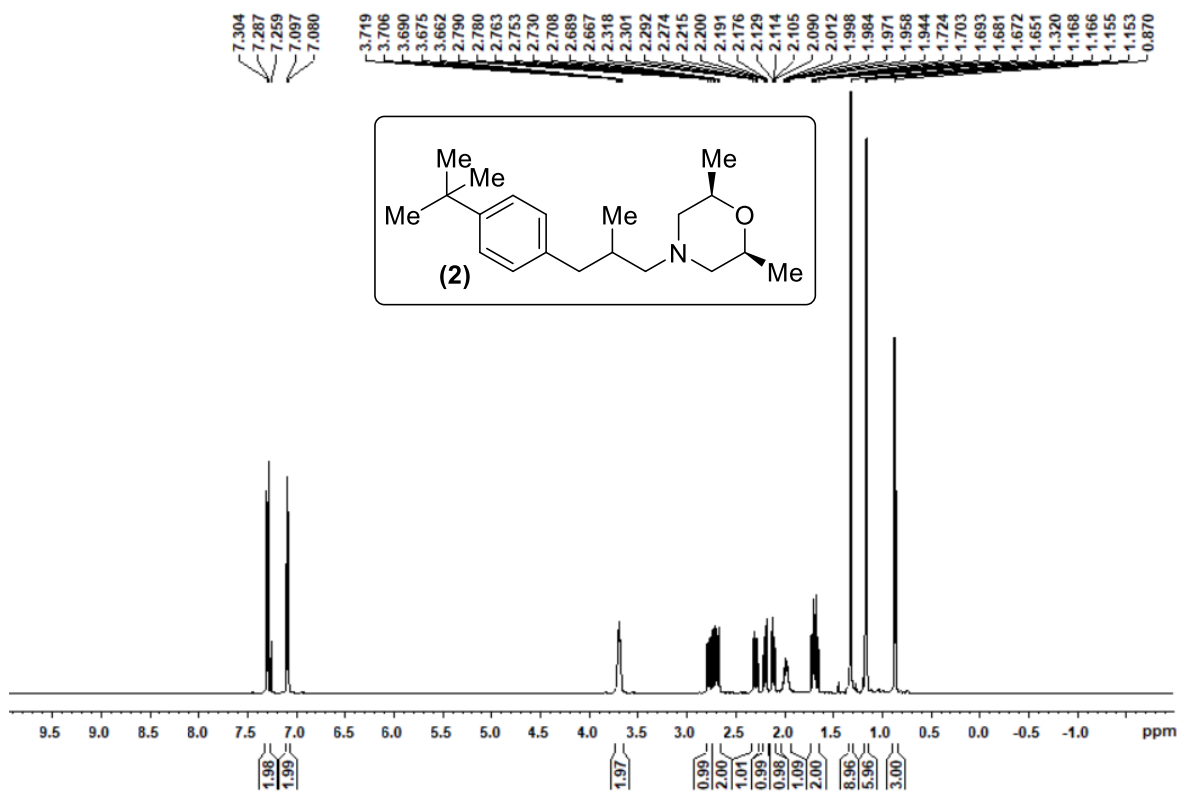
<sup>13</sup>C NMR spectrum of **15** (100 MHz, CDCl<sub>3</sub>)



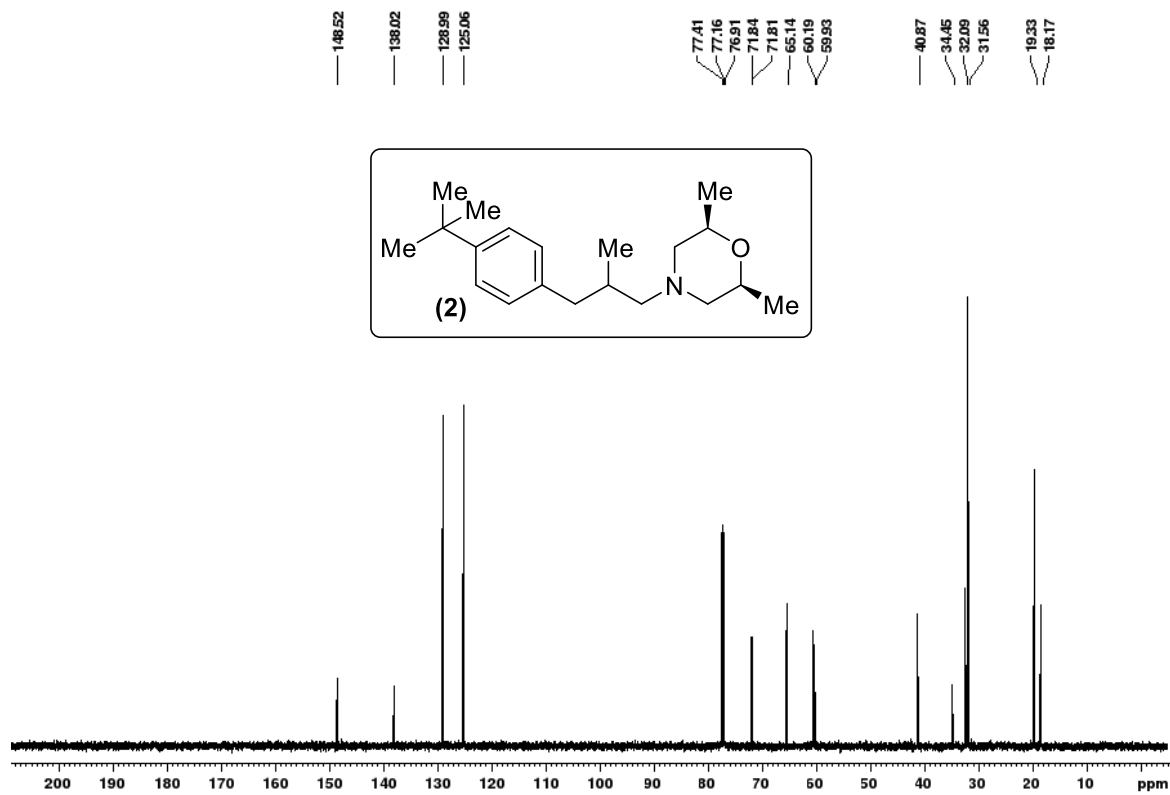
$^1\text{H}$  NMR spectrum of **16** (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR spectrum of **16** (100 MHz,  $\text{CDCl}_3$ )

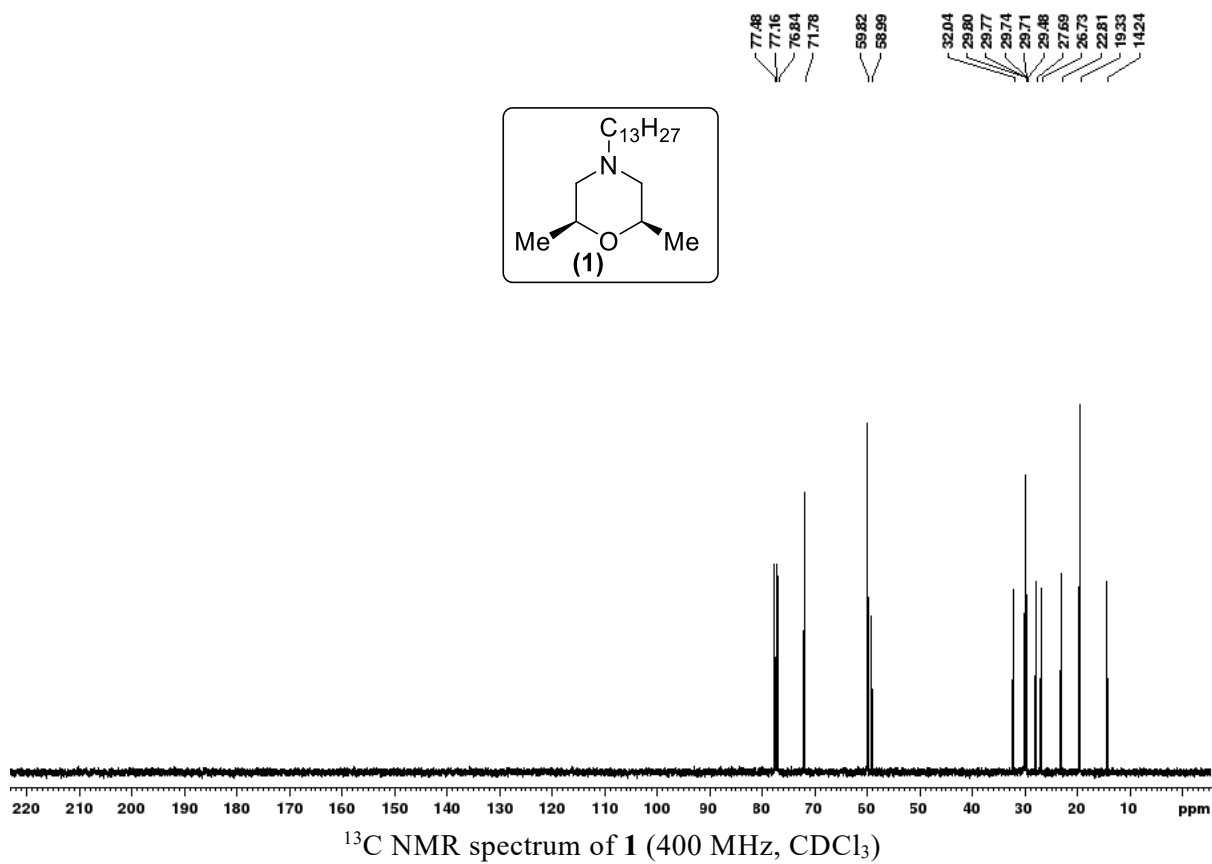
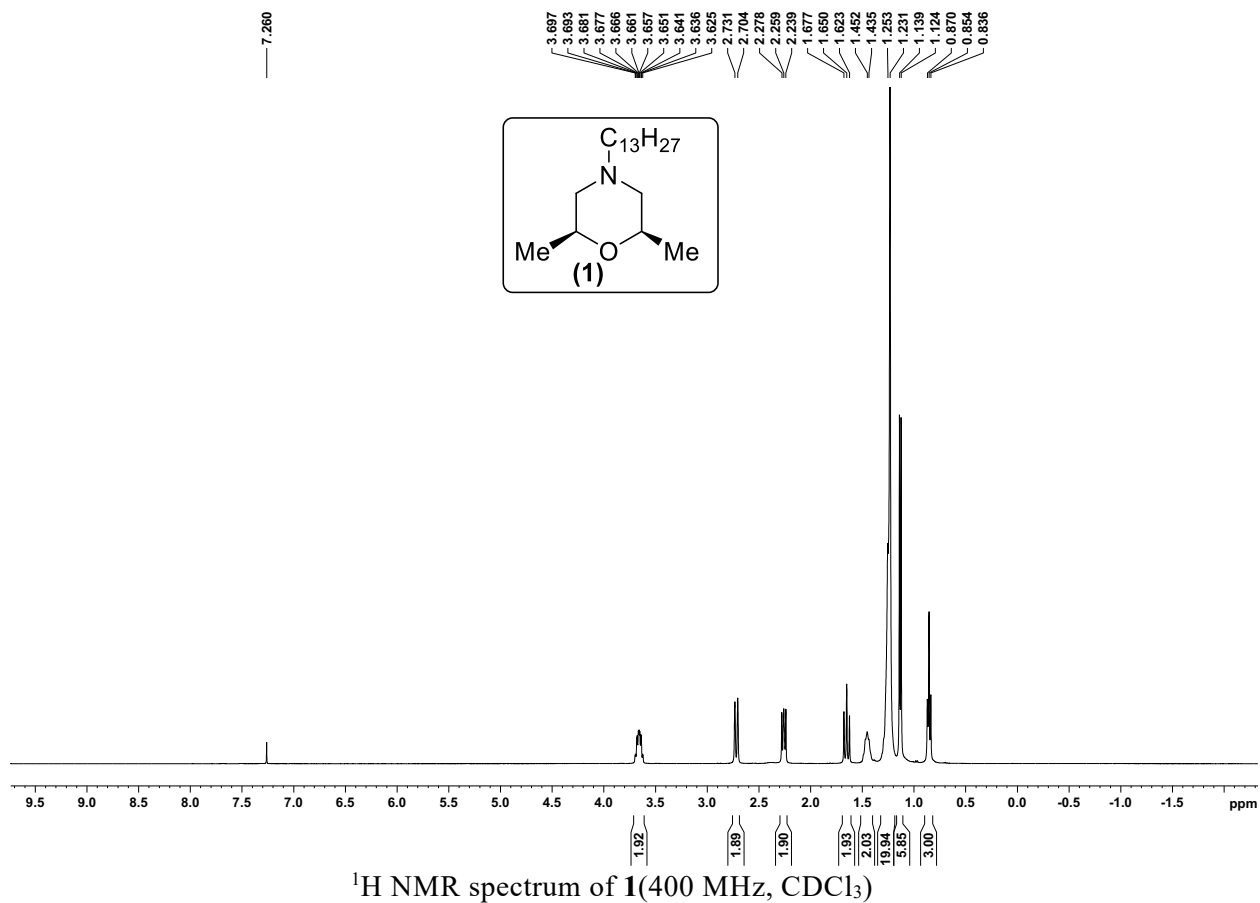


<sup>1</sup>H NMR spectrum of **2** (500 MHz, CDCl<sub>3</sub>)

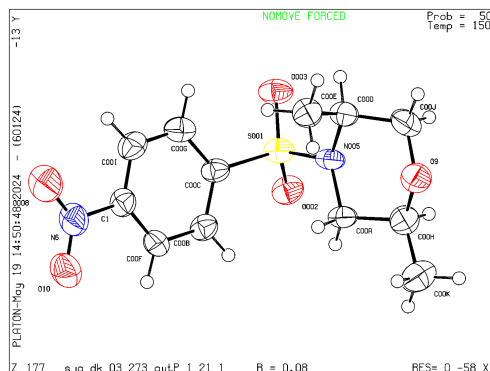


<sup>13</sup>C NMR spectrum of **16** (125 MHz, CDCl<sub>3</sub>)





**Crystal data and structure refinement for 7c (ellipsoid is drawn at the 50% probability level)**



Identification code

**7c**

Solvent

CH<sub>2</sub>Cl<sub>2</sub> : Petroleum ether (1:1)

CCDC

2356421

Bond precision:

C-C = 0.0107 Å

Wavelength=0.71073

Cell:

a=10.2670(15)

b=5.7556(6)

c=11.9973(14)

alpha=90

beta=98.887(12)

gamma=90

Temperature:

150 K

Volume

Calculated

Reported

Space group

700.44(15)

700.44(15)

Hall group

P 21

P 1 21 1

Moiety formula

P 2yb

P 2yb

Sum formula

C<sub>12</sub> H<sub>16</sub> N<sub>2</sub> O<sub>5</sub> S

C<sub>12</sub> H<sub>16</sub> N<sub>2</sub> O<sub>5</sub> S

Mr

C<sub>12</sub> H<sub>16</sub> N<sub>2</sub> O<sub>5</sub> S

C<sub>12</sub> H<sub>16</sub> N<sub>2</sub> O<sub>5</sub> S

Dx,g cm<sup>-3</sup>

300.33

300.33

Z

1.424

1.424

Mu (mm<sup>-1</sup>)

2

2

F000

0.252

0.252

F000'

316.0

316.0

h,k,lmax

316.41

12,6,14

Nref

12,6,14

2458

Tmin,Tmax

2461[ 1367]

0.661,1.000

Tmin'

0.908,0.923

Correction method= # Reported T Limits: Tmin=0.661 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.80/1.00

Theta(max)= 24.994

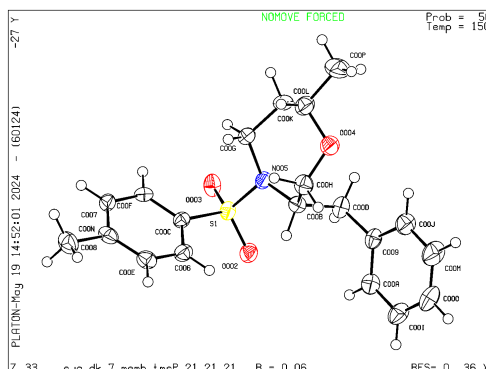
R(reflections)= 0.0842( 1971)

wR2(reflections)=  
0.2311( 2458)

S = 1.024

Npar= 183

**Crystal data and structure refinement for 9f (ellipsoid is drawn at the 50% probability level)**



Identification code

**9f**

Solvent

CH<sub>2</sub>Cl<sub>2</sub> : Petroleum ether (1:1)

CCDC

2356420

Bond precision:

C-C = 0.0079 Å

Wavelength=0.71073

Cell:

a=7.8103(7)

b=13.6493(13)

c=17.9317(14)

alpha=90

beta=90

gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	1911.6(3)	1911.6(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C <sub>20</sub> H <sub>25</sub> N O <sub>3</sub> S	C <sub>20</sub> H <sub>25</sub> N O <sub>3</sub> S
Sum formula	C <sub>20</sub> H <sub>25</sub> N O <sub>3</sub> S	C <sub>20</sub> H <sub>25</sub> N O <sub>3</sub> S
Mr	359.47	359.47
D <sub>x</sub> , g cm <sup>-3</sup>	1.249	1.249
Z	4	4
Mu (mm <sup>-1</sup> )	0.187	0.187
F <sub>000</sub>	768.0	768.0
F <sub>000</sub> '	768.82	
h,k,l <sub>max</sub>	9,16,21	9,16,21
N <sub>ref</sub>	3371[ 1947]	3368
T <sub>min</sub> ,T <sub>max</sub>	0.931,0.949	0.242,1.000
T <sub>min</sub> '	0.886	
Correction method= # Reported T Limits:	T <sub>min</sub> =0.242 T <sub>max</sub> =1.000	
AbsCorr = MULTI-SCAN		
Data completeness= 1.73/1.00		Theta(max)= 24.988
R(reflections)= 0.0573( 2491)		wR2(reflections)= 0.1367( 3368)
S = 0.987	Npar= 228	

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