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Supporting Information

Rh(I)-Catalyzed [4+3]/[4+1] Cycloaddition of Diene-Vinylcyclopropanes and Carbon Monoxide to Access Angular 5/7/5 Tricycles

Jun Yang, Pan Zhang, Zeyuan Shen, and Zhi-Xiang Yu*

Contents

1. General Information

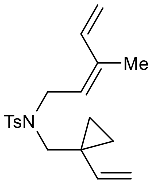
Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Reactions were stirred using Teflon coated magnetic stir bars. Elevated temperatures were maintained using thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a desktop vacuum pump. Tetrahydrofuran (THF) and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane (DCM) was distilled from CaH_2 prior to use. *N*,*N*-dimethylformamide (DMF) and methanol were dried by molecular sieves prior to use. Synthetic reagents were purchased and used without further purification unless otherwise indicated. Super-dried dichloroethane (DCE), super-dried dioxane and super-dried dimethyl sulfoxide (DMSO) were purchased from J&K. $[Rh(CO)_2Cl]_2$ catalysts were purchased from Acros. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating or iodine/silica-gel followed by water washing. Purification of products was accomplished by flash chromatography on silica gel, and the purified compounds showed a single spot by analytical TLC if not special instructions. The diastereomeric ratio was determined by ^{1}H NMR of crude reaction mixtures. NMR spectra were recorded at Bruker AVANCE III 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz), Bruker AVANCE III 500 (^{1}H at 500 MHz, ^{13}C at 126 MHz), and Bruker AVANCE NEO 600 (^{1}H at 600 MHz; ^{13}C at 151 MHz) NMR spectrometers using $CDCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm), CD_2Cl_2 (^{1}H, 5.30 ppm; ^{13}C, 53.5 ppm) or C_6D_6 (^{1}H, 7.15 ppm; ^{13}C, 128.6 ppm) as internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet, hept = heptet, coupling constant (Hz), and integration. HRMS were recorded on Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:

Bn = benzyl
DCM = dichloromethane
DIAD = diisopropyl azodiformate
DIBAL = Diisobutylaluminium hydride
EA = ethyl acetate
Ns = 4-nitrobenzenesulfonyl
TBAF = tetrabutylammonium fluoride
Ts = 4-methylbenzenesulfonyl
THF = tetrahydrofuran
Bs = 4-bromobenzenesulfonyl
DMF = *N*,*N*-dimethylformamide
DCE = dichloroethane
DMSO = dimethyl sulfoxide
MP = melting point
PE = petroleum ether
TBAI = tetrabutylammonium iodide
TBS = tert-butyldimethylsilyl

2. Experimental Procedures and Characterization Data

Table S1. All Substrates Used in the Carbonylative Cycloadditions



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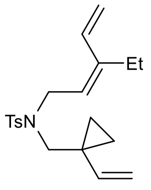

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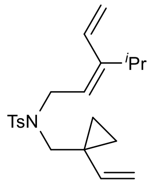

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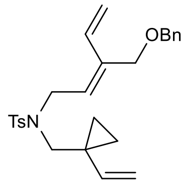

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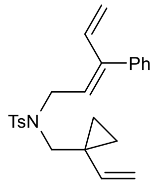

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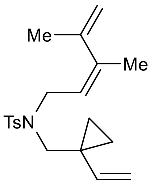

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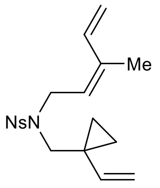

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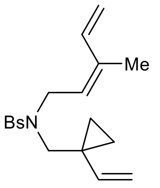

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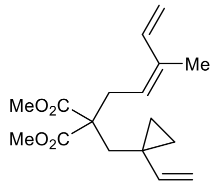

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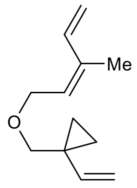

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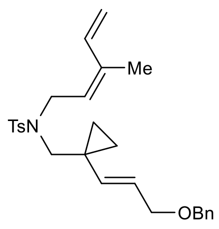
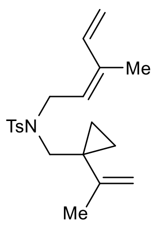


1k



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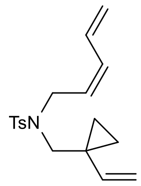

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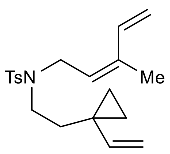

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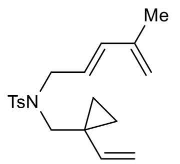

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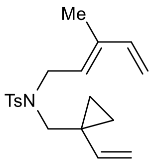
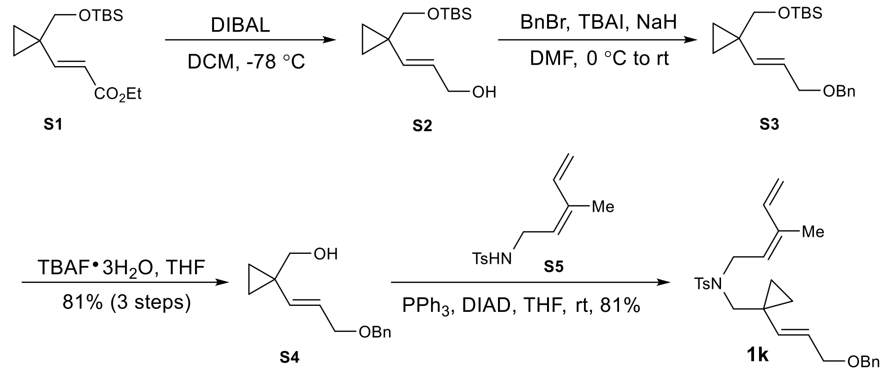


1p

The syntheses and characterizations of **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1l**, **1m**, **1n**, **1o**, **1p** (except for **1k**) have been reported in previous work.[1] Here, we provide the synthesis and characterization of **1k**. The Rh(I)-catalyzed cycloadditions of **1a** – **1k** gave [4+3]/[4+1] products. **1o** and **1p** produced [5+1] cycloaddition products. For **1l** and **1n**, most unreacted starting materials were recovered, but trace impurity was observed in ^{1}H NMR of recycled starting material. For **1m**, only 32% of raw materials were recycled, indicating that reaction was decomposed under the standard conditions.

2.1 Syntheses of 1k



To a solution of **S1** (3.12 g, 11.0 mmol) in DCM (40 mL) was added DIBAL (27 mL, 1.0 M in hexanes, 27 mmol) at -78 °C under an argon atmosphere. After stirred for 1.5 h at the same temperature, the reaction was quenched by saturated aqueous ammonium chloride solution (40 mL) and saturated potassium sodium tartrate tetrahydrate solution (40 mL). It was extracted with diethyl ether (2 × 40 mL). The combined organic layer was washed with water and brine, dried over anhydrous sodium sulphate, filtered, concentrated to give the crude alcohol product **S2**, which was directly used in the next step without further purification.

To a solution of above crude **S2** in DMF (36 mL) was added TBAI (409.3 mg, 1.10 mmol) and NaH (1.33 g, 60% weight in mineral oil, 33.2 mmol) at 0 °C. After stirred for 30 min, BnBr (2.6 mL, 21.9 mmol) was added. The mixture was warmed up naturally and stirred for 12 h. It was quenched by saturated aqueous ammonium chloride solution (20 mL) and water (20 mL), extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with water (2 × 50 mL) and brine (50 mL), dried over anhydrous sodium sulphate, filtered, concentrated to give the crude product **S3**, which was directly used in the next step without further purification.

To a solution of above crude **S3** in THF (37 mL) was added TBAF • $3H_2O$ (5.215 g, 16.5 mmol) at room temperature. After stirred for 4 h, the reaction was quenched by water, extracted with diethyl ether. The combined organic layer was washed with water and brine, dried over anhydrous sodium sulphate, filtered, concentrated. Purification of the residue through column chromatography on silica gel (PE/EA 10:1, 5:1 and 3:1) afforded product **S4** (1.94 g, 81%).

S4: light yellow oil. TLC R_f (PE/EA 5:1) = 0.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (m, 5H), 5.71 (dt, J = 15.8, 6.2 Hz, 1H), 5.56 (d, J = 15.8 Hz, 1H), 4.51 (s, 2H), 4.00 (d, J = 6.2 Hz, 2H), 3.58 (s, 2H), 1.51 (brs, 1H), 0.71 (d, J = 8.0 Hz, 2H), 0.67 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 137.1, 128.5, 128.0, 127.7, 124.4, 72.3, 71.0, 68.3, 24.4, 12.5. HRMS (ESI): calcd for $C_{14}H_{22}NO_2^+$ ($[M + NH_4]^+$) 236.1645, found 236.1641.

To a solution of **S5**[1] (377.1 mg, 1.5 mmol) and PPh_3 (787.1 mg, 3.0 mmol) in THF (15 mL) was added **S4** (459.7 mg, 2.11 mmol) under an argon atmosphere at room temperature, and then DIAD (602.5 mg, 2.98 mmol) was added at 0 °C. The mixture was warmed up naturally and stirred for 26 h, then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (PE/EA 30:1, 20:1 and 10:1) afforded product **1k** (547.9 mg, 81%).

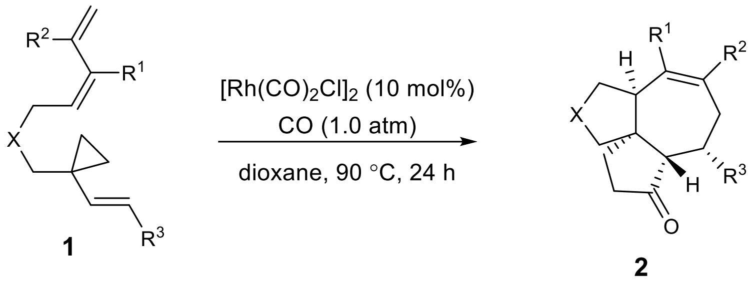
1k: colorless oil. TLC R_f (PE/EA 5:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 2H), 7.38-7.32 (m, 4H), 7.31-7.27 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.63 (dd, J = 17.2, 10.8 Hz, 1H), 5.78 (d, J = 15.6 Hz, 1H), 5.52 (dt, J = 15.6, 6.4 Hz, 1H), 5.25 (d, J = 17.2 Hz, 1H), 5.16 (d, J = 10.8 Hz, 1H), 5.05 (t, J = 6.8 Hz, 1H), 4.48 (s, 2H), 4.10 (d, J = 6.8 Hz, 2H), 3.94 (dd, J = 6.4, 1.2 Hz, 2H), 3.22 (s, 2H), 2.40 (s, 3H), 1.71 (s, 3H), 0.74-0.64 (m, 2H), 0.63-0.52 (m, 2H). ^{13}C

NMR (101 MHz, $CDCl_3$): δ 143.2, 138.5, 137.6, 136.2, 135.5, 132.7, 129.6, 128.5, 128.0, 127.7, 127.5, 124.7, 124.5, 115.8, 72.1, 70.9, 53.3, 44.2, 21.6, 20.0, 19.8, 13.3. HRMS (ESI): calcd for $C_{27}H_{37}N_2O_3S^+$ ($[M + NH_4]^+$) 469.2521, found 469.2519.

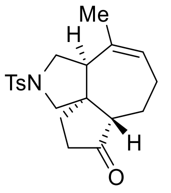
2.2 [4+3]/[4+1] Cycloaddition

General procedure:

A solution of substrate (0.10 mmol) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol, 10 mol%) in super-dried dioxane (2 mL, 0.05 M) was bubbled by CO (1.0 atm) for 5 min. The reaction mixture was stirred at 90 °C under balloon pressure gas of CO (1.0 atm) for 24 h. The reaction mixture was cooled to room temperature and concentrated in vacuo. Purification of the residue through column chromatography on silica gel afforded the corresponding product(s).



Product (2a):



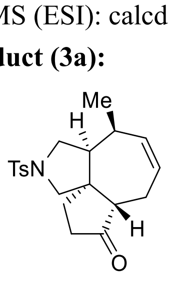
Eluted with PE/EA 5:1, 3:1.

Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1a** (33.3 mg, 0.1 mmol), **2a** (31.9 mg, 88%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1a** (33.3 mg, 0.1 mmol), **2a** (31.7 mg, 88%). So the average yield of two runs was 88%.

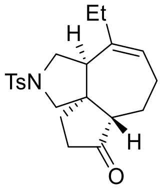
2a: white solid, MP = 161-164 °C. TLC R_f (PE/EA 3:1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 5.47 (dd, J = 5.6, 4.8 Hz, 1H), 3.60 (dd, J = 9.2, 8.8 Hz, 1H), 3.36 (d, J = 9.8 Hz, 1H), 3.31 (d, J = 9.6 Hz, 1H), 3.10 (d, J = 9.7 Hz, 1H), 2.51-2.36 (m, 1H), 2.45 (s, 3H), 2.29 (ddd, J = 18.8, 8.8, 5.2 Hz, 1H), 2.24-2.15 (m, 1H), 2.15-1.97 (m, 3H), 1.97-1.88 (m, 1H), 1.80-1.67 (m, 3H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 218.8, 143.9, 134.1, 132.1, 129.9, 127.7, 127.5, 60.6, 56.0, 51.8, 51.6, 51.5, 36.6, 31.2, 27.1, 25.5, 24.4, 21.7. HRMS (ESI): calcd for $C_{20}H_{29}N_2O_3S^+$ ($[M + NH_4]^+$) 377.1893, found 377.1894.

Product (3a):



3a: white solid, MP = 100-103 °C. TLC R_f (PE/EA 3:1) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 5.75-5.60 (m, 1H), 5.32-5.20 (m, 1H), 3.39 (dd, J = 9.2, 9.2 Hz, 1H), 3.30 (d, J = 9.9 Hz, 1H), 3.24 (d, J = 10.4 Hz, 1H), 3.00 (d, J = 9.7 Hz, 1H), 2.77-2.64 (m, 1H), 2.45 (s, 3H), 2.38-2.27 (m, 1H), 2.27-2.08 (m, 3H), 2.06-1.98 (m, 1H), 1.98-1.86 (m, 2H), 1.77-1.63 (m, 1H), 1.03 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 218.0, 143.8, 135.4, 133.8, 129.9, 128.6, 127.6, 61.4, 53.0, 52.0, 50.0, 48.8, 34.9, 30.5, 30.4, 26.1, 22.0, 21.7. HRMS (ESI): calcd for $C_{20}H_{29}N_2O_3S^+$ ([M + NH$_4$]$^+$) 377.1893, found 377.1892.

Product (2b):



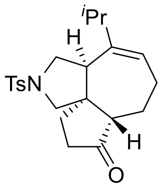
Eluted with PE/EA 10:1, 7:1.

Run 1: [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), **1b** (34.7 mg, 0.1 mmol), **2b** (27.2 mg, 73%).

Run 2: [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), **1b** (34.7 mg, 0.1 mmol), **2b** (26.7 mg, 71%). So the average yield of two runs was 72%.

2b: white solid, MP = 107-110 °C. TLC R$_f$ (PE/EA 3:1) = 0.29. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.72 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.47 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.59 (dd, *J* = 9.6, 9.2 Hz, 1H), 3.38-3.28 (m, 2H), 3.11 (d, *J* = 9.6 Hz, 1H), 2.45 (s, 3H), 2.38 (dd, *J* = 10.8, 8.8 Hz, 1H), 2.30 (ddd, *J* = 18.8, 9.2, 6.0 Hz, 1H), 2.20 (dd, *J* = 8.8, 8.0 Hz, 1H), 2.16-2.11 (m, 1H), 2.08 (dd, *J* = 7.6, 4.8 Hz, 1 H), 2.05-1.99 (m ,1H), 1.99-1.93 (m ,1H), 1.90 (q, *J* = 7.4 Hz , 2H), 1.77-1.70 (m, 1H), 1.70-1.63 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 218.4, 143.9, 137.7, 134.0, 129.9, 127.5, 126.9, 61.2, 56.7, 52.6, 50.8, 50.7, 36.4, 33.9, 31.1, 25.3, 23.8, 21.7, 13.3. HRMS (ESI): calcd for $C_{21}H_{31}N_2O_3S^+$ ([M + NH$_4$]$^+$) 391.2050, found 391.2052.

Product (2c):



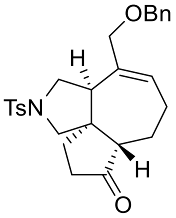
Eluted with PE/EA 10:1, 5:1.

Run 1: [Rh(CO)$_2$Cl]$_2$ (4.1 mg, 0.01 mmol), **1c** (36.1 mg, 0.1 mmol), **2c** (35.5 mg, 91%).

Run 2: [Rh(CO)$_2$Cl]$_2$ (4.1 mg, 0.01 mmol), **1c** (35.9 mg, 0.1 mmol), **2c** (36.0 mg, 93%). So the average yield of two runs was 92%.

2c: light yellow oil. TLC R$_f$ (PE/EA 3:1) = 0.33. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.53 (dd, *J* = 7.6, 4.4 Hz, 1H), 3.54 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.34 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.32 (d, *J* = 9.6, 1H), 3.10 (d, *J* = 9.6 Hz, 1H), 2.45 (s, 3H), 2.36 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.30 (ddd, *J* = 18.8, 9.2, 5.2 Hz, 1H), 2.24-2.10 (m, 3H), 2.07 (dd, *J* = 9.6, 3.6 Hz, 1 H), 2.05-1.93 (m ,2H), 1.75-1.67 (m, 1H), 1.67-1.61 (m, 1H), 1.58-1.46 (m, 1H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 218.2, 143.9, 141.8, 134.0, 129.9, 127.5, 126.4, 61.4, 57.1, 52.9, 50.2, 48.4, 38.1, 36.3, 30.4, 25.4, 23.8, 21.7, 21.6. HRMS (ESI): calcd for $C_{22}H_{33}N_2O_3S^+$ ([M + NH$_4$]$^+$) 405.2206, found 405.2205.

Product (2d):



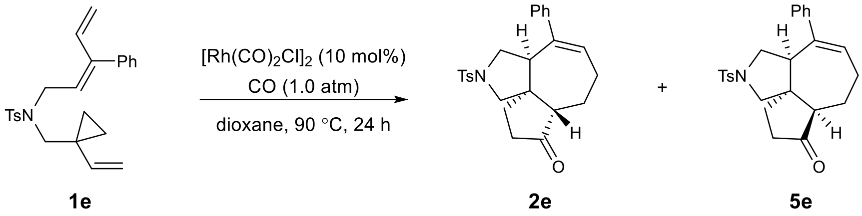
Eluted with PE/EA 7:1, 5:1, 3:1.

Run 1: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1d** (43.6 mg, 0.1 mmol), **2d** (36.2 mg, 78%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1d** (43.7 mg, 0.1 mmol), **2d** (36.3 mg, 78%). So the average yield of two runs was 78%.

2d: colorless oil. TLC R_f (PE/EA 3:1) = 0.2. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65 (d, J = 7.9 Hz, 2H), 7.33-7.16 (m, 7H), 5.73 (dd, J = 5.2, 5.2 Hz, 1H), 4.36 (s, 2H), 3.75 (s, 2H), 3.57 (dd, J = 9.6, 9.2 Hz, 1H), 3.39-3.28 (m, 2H), 3.04 (d, J = 9.6 Hz, 1H), 2.56 (dd, J = 9.6, 9.6 Hz, 1H), 2.41 (s, 3H), 2.36-2.19 (m, 2H), 2.19-2.03 (m, 3H), 1.97-1.82 (m, 1H), 1.79-1.60 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 218.1, 143.9, 138.5, 133.7, 133.6, 131.9, 129.8, 128.4, 127.6, 127.5, 127.4, 77.0, 71.8, 61.1, 56.4, 53.0, 51.2, 48.0, 36.4, 30.9, 25.5, 23.5, 21.3. HRMS (ESI): calcd for $C_{27}H_{32}NO_4S^+$ ($[M + H]^+$) 466.2047, found 466.2051.

Products (2e and 5e):



Eluted with PE/EA 10:1, 5:1, concentrated then purified further by prep. TLC (PE/EA 5:1)

Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1e** (39.5 mg, 0.1 mmol), **2e** (23.8 mg, 56%), **5e** (6.8 mg, 16%).

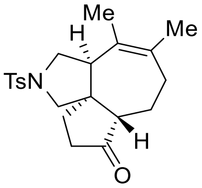
Run 2: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1e** (39.5 mg, 0.1 mmol), **2e** (25.5 mg, 60%), **5e** (8.1 mg, 19%). So the average yield of **2e** was 58% and the average yield of **5e** was 18%.

2e: white solid, MP = 165-167 °C. TLC R_f (PE/EA 3:1) = 0.29. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.69 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.30-7.16 (m, 3H), 7.13-7.06 (m, 2H), 5.86 (dd, J = 7.2, 4.8 Hz, 1H), 3.67 (dd, J = 9.6, 9.2 Hz, 1H), 3.48 (dd, J = 11.2, 10.0 Hz, 1H), 3.41 (d, J = 10.0 Hz, 1H), 3.15 (d, J = 10.0 Hz, 1H), 2.92 (dd, J = 10.8, 9.2 Hz, 1H), 2.43 (s, 3H), 2.42-2.32 (m, 1H), 2.29-2.22 (m, 1H), 2.22-2.10 (m, 3H), 1.98 (ddd, J = 13.2, 9.2, 6.8, 1H) 1.86-1.73 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 217.4, 145.0, 144.1, 137.2, 133.6, 132.6, 129.9, 128.4, 127.5, 127.0, 126.1, 60.9, 56.8, 53.0, 51.1, 50.8, 36.4, 31.5, 25.7, 22.8, 21.4. HRMS (ESI): calcd for $C_{25}H_{31}N_2O_3S^+$ ($[M + NH_4]^+$) 439.2050, found 439.2046.

5e: white solid, MP = 146-149 °C. TLC R_f (PE/EA 3:1) = 0.40. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.33-7.25 (m, 2H), 7.25-7.18 (m, 3H), 5.90 (dd, J = 7.6, 7.6 Hz, 1H), 3.89 (dd, J = 9.2, 9.2 Hz, 1H), 3.35 (dd, J = 9.2, 9.2 Hz, 1H), 3.15 (d, J = 9.6 Hz, 1H), 2.80 (dd, J = 9.6, 9.2 Hz, 1H), 2.76 (dd, J = 9.6, 1.6 Hz, 1H), 2.43 (s, 3H), 2.37-2.22 (m, 3H), 2.21-2.09 (m, 1H), 2.06-1.95 (m, 1H), 1.90-1.79 (m, 1H), 1.79-1.68 (m, 1H), 1.51-1.38 (m, 1H), 1.34-1.25 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 217.2, 144.3, 143.9, 142.8, 130.9, 129.7, 128.4, 128.1, 127.5, 127.1, 126.0, 53.8, 53.7, 51.9, 51.6, 49.5, 37.1, 35.9, 21.9, 21.4, 19.6. HRMS

(ESI): calcd for $C_{25}H_{28}NO_3S^+$ ($[M + H]^+$) 422.1784, found 422.1783.

Product (2f):



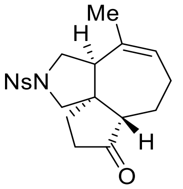
Eluted with PE/EA 10:1, 7:1, 5;1.

Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1f** (34.8 mg, 0.1 mmol), **2f** (33.9 mg, 90%).

Run 2: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1f** (34.6 mg, 0.1 mmol), **2f** (33.8 mg, 90%). So the average yield of two runs was 90%.

2f: white solid, MP = 100-102 °C. TLC R_f (PE/EA 3:1) = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 3.54 (dd, J = 9.2, 9.2 Hz, 1H), 3.36 (dd, J = 9.6, 9.2 Hz, 1H), 3.23 (d, J = 9.7 Hz, 1H), 3.09 (d, J = 9.7 Hz, 1H), 2.48 (dd, J = 9.2, 8.8 Hz, 1H), 2.44 (s, 3H), 2.28-2.10 (m, 2H), 2.10-1.96 (m, 3H), 1.96-1.86 (m, 1H), 1.75-1.61 (m, 3H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 218.1, 143.8, 133.9, 133.5, 129.9, 127.5, 124.1, 59.7, 55.1, 52.7, 51.1, 50.7, 36.2, 31.8, 31.5, 22.9, 22.3, 21.8, 21.7. HRMS (ESI): calcd for $C_{21}H_{31}N_2O_3S^+$ ($[M + NH_4]^+$) 391.2050, found 391.2059.

Product (2g):



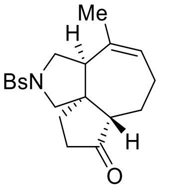
Eluted with PE/EA 5:1, 4:1, reaction time was 48 h.

Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1g** (36.2 mg, 0.1 mmol), **2g** (28.3 mg, 73%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1g** (36.3 mg, 0.1 mmol), **2g** (28.1 mg, 72%). So the average yield of two runs was 73%.

2g: white solid, MP = 156-159 °C. TLC R_f (PE/EA 3:1) = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 5.51 (dd, J = 6.0, 5.6 Hz, 1H), 3.63 (dd, J = 9.2, 9.2 Hz, 1H), 3.45 (d, J = 9.9 Hz, 1H), 3.39 (d, J = 9.9 Hz, 1H), 3.13 (d, J = 9.6 Hz, 1H), 2.50 (dd, J = 9.2, 9.2 Hz, 1H), 2.34 (ddd, J = 19.2, 9.2, 5.2 Hz, 1H), 2.23 (dd, J = 18.6, 9.5 Hz, 1H), 2.19-2.10 (m, 2H), 2.09-1.93 (m, 2H), 1.86-1.70 (m, 3H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 218.2, 150.3, 143.3, 131.6, 128.5, 128.2, 124.6, 60.7, 56.0, 51.8, 51.6, 51.5, 36.4, 30.9, 27.1, 25.5, 24.4. HRMS (ESI): calcd for $C_{19}H_{23}N_2O_5S^+$ ($[M + H]^+$) 391.1322, found 391.1318.

Product (2h):



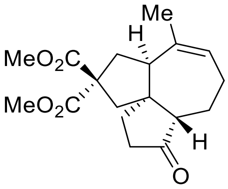
Eluted with PE/EA 5:1, 4:1.

Run 1: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1h** (39.8 mg, 0.1 mmol), **2h** (37.2 mg, 87%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1h** (39.7 mg, 0.1 mmol), **2h** (36.7 mg, 86%). So the average yield of two runs was 87%.

2h: white solid, MP = 138-139 °C. TLC R*f* (PE/EA 3:1) = 0.30. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.69 (s, 4H), 5.47 (dd, *J* = 5.3, 5.3 Hz, 1H), 3.57 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.37 (d, *J* = 9.9 Hz, 1H), 3.32 (d, *J* = 9.4 Hz, 1H), 3.07 (d, *J* = 9.6 Hz, 1H), 2.45 (dd, *J* = 9.2, 9.2 Hz, 1H), 2.30 (ddd, *J* = 18.9, 9.1, 5.5 Hz, 1H), 2.20 (dd, *J* = 18.4, 9.5 Hz, 1H), 2.16-2.07 (m, 2H), 2.07-1.98 (m, 1H), 1.98-1.90 (m, 1H), 1.83-1.68 (m, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 218.5, 136.2, 132.6, 131.8, 128.9, 128.0, 127.9, 60.6, 56.0, 51.8, 51.6, 51.4, 36.5, 31.0, 27.1, 25.5, 24.3. HRMS (ESI): calcd for $C_{19}H_{26}BrN_2O_3S^+$ ([M + NH$_4$]$^+$) 441.0842, found 441.0842.

Product (2i):



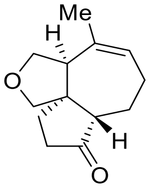
Eluted with PE/EA 20:1, 10:1.

Run 1: [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), **1i** (29.2 mg, 0.1 mmol), **2i** (21.2 mg, 66%).

Run 2: [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), **1i** (29.0 mg, 0.1 mmol), **2i** (21.2 mg, 67%). So the average yield of two runs was 67%.

2i: white solid, MP = 85-88 °C. TLC R*f* (PE/EA 5:1) = 0.35. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 5.48 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.64 (dd, *J* = 19.6, 14.4 Hz, 1H), 2.51 (d, *J* = 14.0 Hz, 1H), 2.39-2.29 (m, 2H), 2.29-2.17 (m, 4H), 2.17-2.00 (m, 3H), 1.89-1.74 (m, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 220.0, 173.1, 172.6, 135.0, 126.5, 57.7, 56.9, 53.5, 53.1, 51.4, 48.1, 40.0, 36.9, 35.2, 27.7, 25.1, 24.5. HRMS (ESI): calcd for $C_{18}H_{28}NO_5^+$ ([M + NH$_4$]$^+$) 338.1962, found 338.1966.

Product (2j):



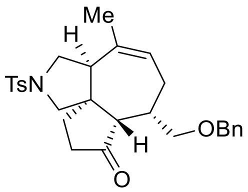
Eluted with PE/EA 15:1, 10:1, reaction time was 31 h.

Run 1: [Rh(CO)$_2$Cl]$_2$ (4.0 mg, 0.01 mmol), **1j** (18.0 mg, 0.1 mmol), **2j** (10.0 mg, 48%).

Run 2: [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 0.01 mmol), **1j** (18.1 mg, 0.1 mmol), **2j** (10.8 mg, 52%). So the average yield of two runs was 50%.

2j: light yellow oil. TLC R*f* (PE/EA 5:1) = 0.23. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 5.46 (dd, *J* = 5.6, 5.4 Hz, 1H), 4.16 (dd, *J* = 8.4, 8.0 Hz, 1H), 3.86 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.79 (d, *J* = 8.4 Hz, 1H), 3.72 (d, *J* = 8.4 Hz, 1H), 2.67 (dd, *J* = 9.2, 8.8 Hz, 1H), 2.42-2.30 (m, 2H), 2.30-2.21 (m, 2H), 2.21-2.12 (m, 1H), 2.10-2.00 (m, 1H), 1.98-1.82 (m, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 219.3, 132.5, 126.6, 80.2, 73.1, 55.9, 53.0, 52.5, 36.8, 31.6, 27.8, 25.4, 23.4. HRMS (ESI): calcd for $C_{13}H_{19}O_2^+$ ([M + H]$^+$) 207.1380, found 207.1376.

Product (2k):



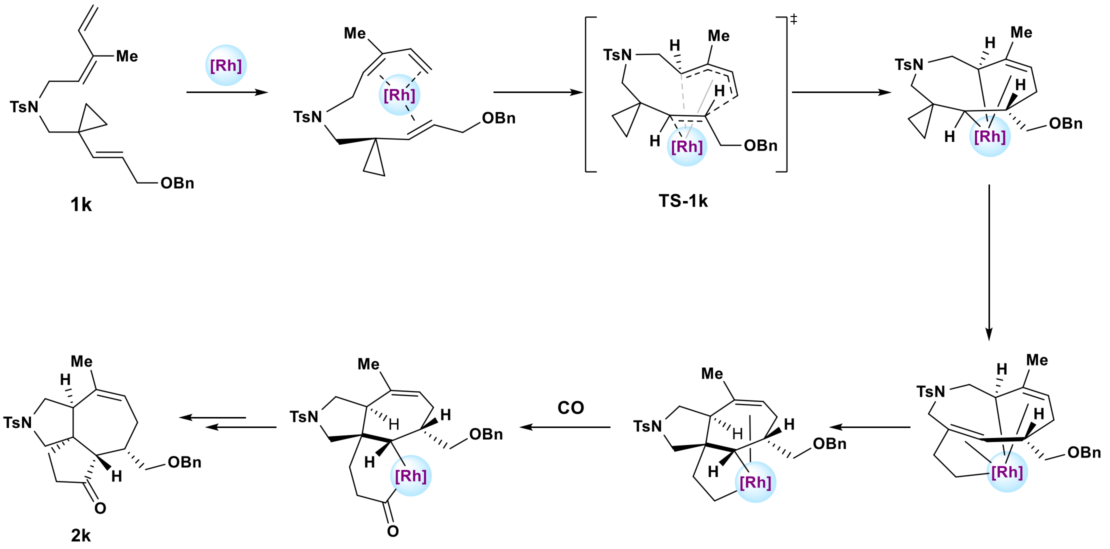
Eluted with PE/EA 7:1, 5:1, reaction was stirred for 36 h and operated at 100 °C.

Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1k** (45.4 mg, 0.1 mmol), **2k** (22.9 mg, 47%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1k** (45.4 mg, 0.1 mmol), **2k** (23.4 mg, 49%). So the average yield of two runs was 48%.

2k: brown oil. TLC R_f (PE/EA 3:1) = 0.30. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (d, J = 8.4 Hz, 2H), 7.38-7.23 (m, 7H), 5.25 (s, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 3.68 (dd, J = 10.0, 9.6 Hz, 1H), 3.55 (dd, J = 9.2, 8.8 Hz, 1H), 3.45 (d, J = 10.0 Hz, 1H), 3.31 (d, J = 10.4 Hz, 1H), 3.26 (dd, J = 9.0, 5.8 Hz, 1H), 3.18 (dd, J = 10.8, 10.4 Hz, 1H), 2.44-2.38 (m, 2H), 2.38 (s, 3H), 2.35-2.27 (m, 1H), 2.23-2.11 (m, 3H), 2.11-1.98 (m, 1H), 1.91 (ddd, J = 12.6, 12.6, 9.2 Hz, 1H), 1.80 (ddd, J = 12.8, 8.0, 2.8 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 215.7, 143.7, 139.9, 135.5, 132.4, 130.4, 129.2, 128.3, 127.0, 74.1, 73.2, 60.8, 57.0, 56.0, 52.7, 52.6, 37.4, 35.3, 33.9, 29.3, 29.0, 21.7. HRMS (ESI): calcd for $C_{28}H_{37}N_2O_4S^+$ ($[M + NH_4]^+$) 497.2469, found 497.2468.

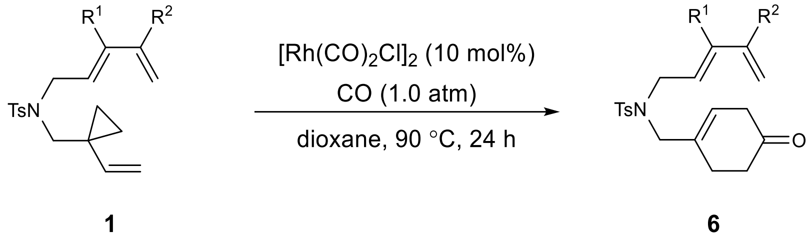
The origin of the stereochemistry of **2k** can be rationalized by the mechanism in the following scheme. As shown in the *endo*-oxidative cyclometalation transition state **TS-1k**, the two hydrogen atoms from alkenes are in a *trans* configuration and will become a *cis* configuration in the final cycloadduct so that the CH_2OBn group becomes *trans* with respect to its adjacent hydrogen atom at the bridgehead position. The stereochemistry is also supported by 2-D NMR attached.



2.3 [5+1] Cycloaddition

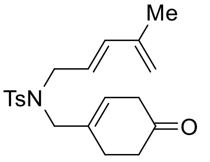
General procedure:

A solution of substrate (0.10 mmol) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol, 10 mol%) in super-dried dioxane (2 mL, 0.05 M) was bubbled by CO (1.0 atm) for 5 min. The reaction mixture was stirred at 90 °C under balloon pressure gas of CO (1.0 atm) for 24 h. The reaction mixture was cooled to room temperature and concentrated in vacuo. Purification of the residue through column chromatography on silica gel afforded the corresponding product.



1 **6**

Product (6o):



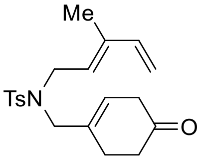
Eluted with PE/EA 10:1, 5:1.

Run 1: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1o** (33.4 mg, 0.1 mmol), **6o** (24.4 mg, 67%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1o** (33.4 mg, 0.1 mmol), **6o** (25.6 mg, 71%). So the average yield of two runs was 69%.

6o: light yellow oil. TLC R_f (PE/EA 3:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.08 (d, J = 15.6 Hz, 1H), 5.63 (t, J = 3.2 Hz, 1H), 5.29 (dt, J = 15.6, 7.2 Hz, 1H), 4.94 (s, 1H), 4.88 (s, 1H), 3.80 (d, J = 6.8 Hz, 2H), 3.73 (s, 2H), 2.85 (s, 2H), 2.45 (s, 4H), 2.42 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 209.8, 143.6, 141.0, 137.2, 137.1, 134.1, 129.8, 127.3, 123.5, 123.0, 117.5, 52.8, 49.7, 39.6, 38.3, 26.3, 21.6, 18.4. HRMS (ESI): calcd for $C_{20}H_{29}N_2O_3S^+$ ($[M + NH_4]^+$) 377.1893, found 377.1891.

Product (6p):



Eluted with PE/EA 10:1, 7:1.

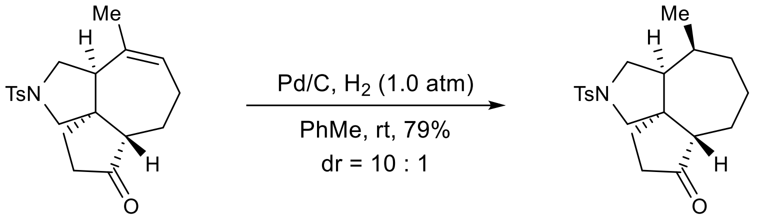
Run 1: $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), **1p** (33.2 mg, 0.1 mmol), **6p** (7.9 mg, 22%).

Run 2: $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), **1p** (33.3 mg, 0.1 mmol), **6p** (7.7 mg, 21%). So the average yield of two runs was 22%.

6p: yellow oil. TLC R_f (PE/EA 3:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.18 (dd, J = 17.6, 10.8 Hz, 1H), 5.62 (t, J = 3.6 Hz, 1H), 5.20 (t, J = 7.2 Hz, 1H), 5.15 (d, J = 17.6 Hz, 1H), 5.01 (d, J = 10.8 Hz, 1H), 3.89 (d, J = 7.2 Hz, 2H), 3.73 (s, 2H), 2.85 (s, 2H), 2.46 (s, 4H), 2.44 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 209.8, 143.6, 140.3, 137.3, 137.1, 134.3, 129.9, 127.4, 126.1, 122.9, 113.5, 53.1, 45.3, 39.6, 38.3, 26.2, 21.7, 11.9. HRMS (ESI): calcd for $C_{20}H_{29}N_2O_3S^+$ ($[M + NH_4]^+$) 377.1893, found 377.1892.

2.4 Transformations of 2a.

Product (7a):



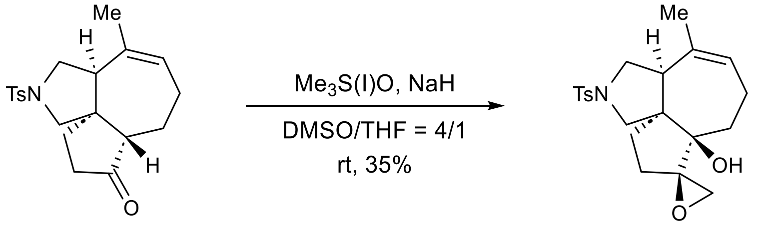
2a **7a**

To a solution of **2a** (18.0 mg, 0.05 mmol) in PhMe (1 mL) was added Pd/C (53.2 mg, 0.05 mmol, 10 mol% on dry basis) and bubbled with H_2 (1 atm) for 10 min. The reaction mixture was stirred under H_2 atmosphere (1 atm) at room temperature for 2.5 h. The reaction mixture was filtered through a short pad of silica gel with ethyl acetate and concentrated. The residue was purified by preparative TLC (PE/EA 3:1) to give product **7a** (14.0 mg, 0.039 mmol, 77%) as a colorless oil.

Run 2: **2a** (18.0 mg, 0.05 mmol) was converted to **7a** (14.4 mg, 0.040 mmol, 80%) using the same procedure as above. The average yield of two runs was 79%.

7a: colorless oil. TLC R_f (PE/EA 3:1) = 0.24. The ratio of diastereomers (10:1) is determined by the ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 3.49 (t, J = 9.3 Hz, 1H), 3.15-3.04 (m, 2H), 2.94 (d, J = 9.6 Hz, 1H), 2.37 (s, 3H), 2.22-2.03 (m, 3H), 2.01-1.94 (d, J = 9.2 Hz, 1H), 1.81-1.66 (m, 2H), 1.66-1.54 (m, 3H), 1.53-1.31 (m, 4H), 0.67 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.1, 143.8, 133.5, 129.8, 127.6, 59.2, 57.8, 53.1, 52.8, 51.9, 36.2, 35.3, 33.6, 28.6, 24.9, 21.7, 17.1. HRMS (ESI): calcd for $C_{20}H_{28}NO_3S^+$ ($[M + H]^+$) 362.1784, found 362.1784.

Product (8a):



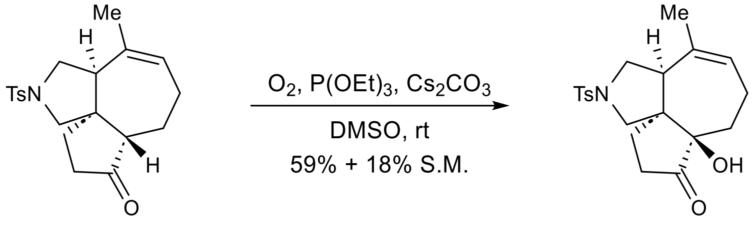
2a **8a**

To a mixture of NaH (12.0 mg, 60 wt % suspension in mineral oil, 0.30 mmol) and trimethylsulfoxonium iodide (66.0 mg, 0.30 mmol) was added super-dried DMSO (1 mL) under nitrogen atmosphere. After stirred at room temperature for 2 h, a solution of **2a** (35.9 mg, 0.10 mmol) in super-dried DMSO (1 mL) was added (0.5 mL THF was used to transfer the residual substrate due to the low solubility of **2a** in DMSO). The reaction mixture was then stirred at room temperature for another 16 h. After quenched by saturated aqueous ammonium chloride solution, the reaction mixture was extracted with EA. The combined organic phase was washed with brine, dried over anhydrous sodium sulphate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA 5:1) to yield **8a** (14.4 mg, 0.037 mmol, 37%) as a white solid. The relative stereochemistry was determined by single crystal XRD analysis (CCDC: 2290933).

Run 2: **2a** (35.9 mg, 0.10 mmol) was converted to **8a** (12.8 mg, 0.033 mmol, 33%) using the same procedure as above. The average yield of two runs was 35%.

8a: white solid, MP = 155.4-157.9 °C, TLC R_f (PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.72 (ddd, J = 8.5, 4.1, 1.7 Hz, 1H), 3.78 (d, J = 10.5 Hz, 1H), 3.61 (dd, J = 8.8, 7.3 Hz, 1H), 3.51 (dd, J = 11.3, 8.7 Hz, 1H), 3.02 (d, *J* = 10.5 Hz, 1H), 2.71 (d, *J* = 4.2 Hz, 1H), 2.58 (d, *J* = 4.2 Hz, 1H), 2.51 (dd, *J* = 11.2, 7.3 Hz, 1H), 2.46-2.35 (m, 1H), 2.42 (s, 3H), 2.13 (ddd, *J* = 15.3, 10.8, 2.3 Hz, 1H), 1.94-1.82 (m, 3H), 1.72-1.62 (m, 1H), 1.68 (s, 3H), 1.61 (m, 1H), 1.47 (ddd, *J* = 12.8, 10.2, 2.3 Hz, 1H), 1.36 (ddd, *J* = 14.0, 6.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 135.2, 132.5, 129.7, 128.6, 127.4, 78.3, 68.6, 55.6, 54.3, 51.1, 50.1, 46.8, 32.7, 30.1, 27.2, 25.8, 21.7, 21.6. HRMS (ESI): calcd for $C_{21}H_{28}NO_4S^+$ ($[M + H]^+$) 390.1734, found 390.1734.

Product (9a):



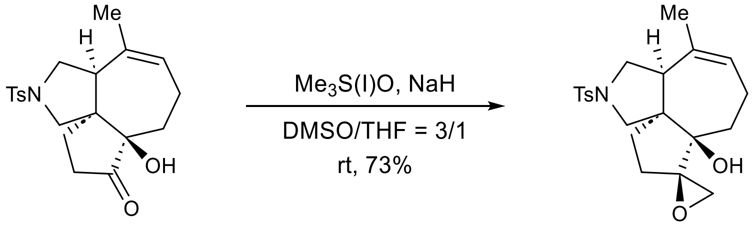
2a **9a**

To a mixture of **2a** (35.9 mg, 0.10 mmol) and Cs_2CO_3 (6.5 mg, 0.02 mmol) was added a solution of triethyl phosphite (66.5 mg, 0.40 mmol) in DMSO (0.4 mL). The reaction system was replaced with O_2 for 3 times, and then stirred under O_2 atmosphere (1 atm) at room temperature for 3 days. The reaction mixture was then added brine (3 mL), extracted with EA, and the combined organic phase was dried over anhydrous sodium sulphate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA 5:1) to yield **9a** (21.5 mg, 0.057 mmol, 57%) as a white solid. **2a** (6.9 mg, 0.019 mmol, 19%) was recovered at the same time.

Run 2: **2a** (35.9 mg, 0.10 mmol) was converted to **9a** (22.4 mg, 0.060 mmol, 60%) using the same procedure as above. **2a** (6.0 mg, 0.017 mmol, 17%) was recovered at the same time. The average yield of two runs was 59%, and the average recovery of S.M. was 18%.

9a: white solid, MP = 161.6-163.0 °C, TLC R_f(PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.73-5.63 (m, 1H), 3.61 (dd, *J* = 9.0, 7.3 Hz, 1H), 3.39 (d, *J* = 9.8 Hz, 1H), 3.34 (dd, *J* = 11.6, 9.0 Hz, 1H), 2.97 (d, *J* = 9.8 Hz, 1H), 2.47-2.32 (m, 3H), 2.41(s, 3H), 2.20-2.04 (m, 3H), 1.90 (dddd, *J* = 16.2, 8.8, 6.4, 2.8 Hz, 1H), 1.68 (s, 3H), 1.66-1.61 (m, 1H), 1.59 (dd, *J* = 12.0, 4.0 Hz, 1H), 1.19-1.10 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 218.0, 143.5, 135.0, 132.4, 129.5, 128.4, 127.4, 83.6, 56.0, 52.0, 51.6, 50.4, 32.0, 31.2, 28.0, 27.2, 21.5, 21.4. HRMS (ESI): calcd for $C_{20}H_{26}NO_4S^+$ ($[M + H]^+$) 376.1577, found 376.1577.

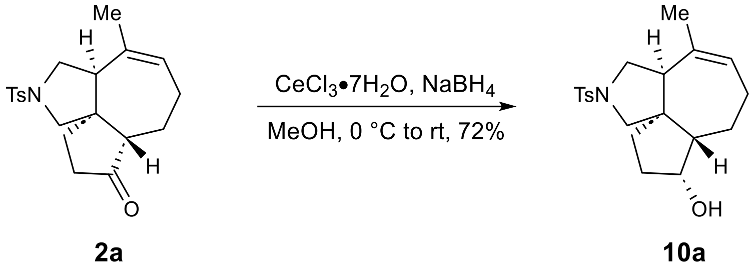
Transformation from 9a to **8a**:



9a **8a**

To a mixture of NaH (3.3 mg, 60 wt % suspension in mineral oil, 0.0831 mmol) and trimethylsulfoxonium iodide (18.3 mg, 0.0831 mmol) was added super-dried DMSO (0.3 mL) under nitrogen atmosphere. After stirred at room temperature for 1 h, a solution of **9a** (10.4 mg, 0.0277 mmol) in super-dried DMSO (0.3 mL) was added (0.2 mL THF was used to transfer the residual substrate). The reaction mixture was then stirred at room temperature for another 18 h. After quenched by saturated aqueous ammonium chloride solution, the reaction mixture was extracted with EA. The combined organic phase was washed with brine, dried over anhydrous sodium sulphate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA 5:1) to yield **8a** (7.9 mg, 0.0203 mmol, 73%) as a white solid. The product **8a** has the same NMR as that from the reaction of **2a** to **8a** shown above.

Product (10a):

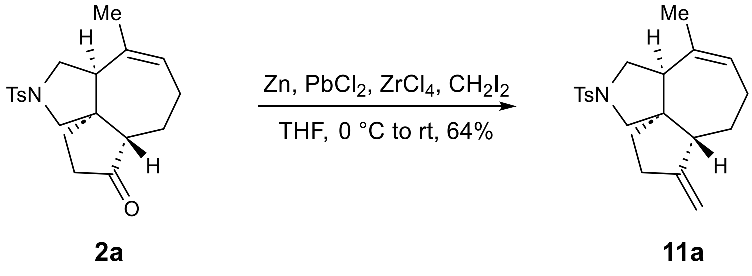


To a solution of **2a** (35.9 mg, 0.10 mmol) in MeOH (1 mL) was added $CeCl_3 \cdot 7H_2O$ (82.0 mg, 0.22 mmol) and sodium borohydride (7.6 mg, 0.20 mmol) under 0 °C. Then the reaction system was allowed to warm to room temperature and stirred for 20 h. After quenched by saturated aqueous ammonium chloride solution, the reaction mixture was extracted with EA. The combined organic phase was dried over anhydrous sodium sulphate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA 3:1) to yield **10a** (26.5 mg, 0.073 mmol, 73%) as a white solid.

Run 2: **2a** (35.9 mg, 0.10 mmol) was converted to **10a** (25.7 mg, 0.071 mmol, 71%) using the same procedure as above. The average yield of two runs was 72%.

10a: white solid, MP = 99.6-102.5 °C, TLC R_f(PE/EA 1:1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.53 (dd, J = 5.8, 5.8 Hz, 1H), 4.23 (ddd, J = 8.2, 8.2, 5.8 Hz, 1H), 3.47 (dd, J = 9.7, 6.0 Hz, 1H), 3.29 (dd, J = 9.7, 6.0 Hz, 1H), 3.16 (d, J = 9.5 Hz, 1H), 3.00 (d, J = 9.4 Hz, 1H), 2.52 (dd, J = 6.4, 6.4 Hz, 1H), 2.43 (s, 3H), 2.28-2.15 (m, 1H), 2.05-1.93 (m, 1H), 1.93-1.83 (m, 1H), 1.82-1.70 (m, 2H), 1.70-1.62 (m, 1H), 1.60 (s, 3H), 1.58 (brs, 1H), 1.55-1.44 (m, 1H), 1.33-1.20 (m, 1H), 1.08 (ddd, J = 13.6, 9.4, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 134.8, 133.2, 129.8, 127.6, 127.4, 74.5, 59.8, 53.5, 50.1, 49.5, 48.5, 31.9, 30.5, 26.3, 25.0, 21.7, 20.8. HRMS (ESI): calcd for $C_{20}H_{28}NO_3S^+$ ($[M + H]^+$) 362.1784, found 362.1784.

Product (11a):

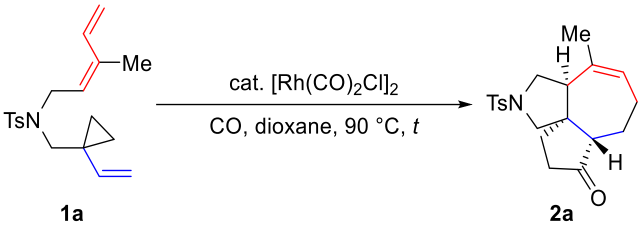


To a suspension of zinc dust (261.5 mg, 4.0 mmol) and lead(II) chloride (55.6 mg, 0.20 mmol) in THF (3 mL) was added diiodomethane (0.12 mL, 1.50 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was then stirred at this temperature for 30 min. During this period, a suspension of $ZrCl_4$ (139.8 mg, 0.60 mmol) in THF (1.5 mL) was prepared by stirring at rt for 20 min. To the first mixture was added the second mixture at 0 °C, and the resultant mixture was stirred at this temperature for another 30 min before a solution of **2a** (35.9 mg, 0.10 mmol) in THF (1.5 mL) was added. The reaction system was allowed to warm to room temperature and stirred for 9 h. After quenched by saturated aqueous sodium bicarbonate solution, the reaction mixture was extracted with EA. The combined organic phase was dried over anhydrous sodium sulphate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA 50:1 and 20:1) to yield **11a** (22.0 mg, 0.061 mmol, 61%) as a white solid.

Run 2: **2a** (35.9 mg, 0.10 mmol) was converted to **11a** (23.7 mg, 0.066 mmol, 66%) using the same procedure as above. The average yield of two runs was 64%.

11a: colorless oil, TLC R_f (PE/EA 5:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.59 (ddd, J = 7.0, 5.4, 1.5 Hz, 1H), 4.79 (s, 1H), 4.71 (s, 1H), 3.52 (dd, J = 9.4, 7.8 Hz, 1H), 3.35 (t, J = 9.7 Hz, 1H), 3.23 (d, J = 9.7 Hz, 1H), 2.90 (d, J = 9.7 Hz, 1H), 2.48-2.41(m, 1H), 2.44 (s, 3H), 2.40-2.30 (m, 1H), 2.20-2.08 (m, 1H), 2.06-1.95 (m, 2H), 1.93-1.77 (m, 2H), 1.65 (s, 3H), 1.50-1.34 (m, 2H), 1.29-1.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 143.4, 134.7, 132.7, 129.7, 128.1, 127.5, 106.9, 60.9, 53.3, 51.7, 50.5, 50.2, 32.3, 31.1, 29.2, 26.7, 26.1, 21.7. HRMS (ESI): calcd for $C_{21}H_{28}NO_2S^+$ ([M + H]$^+$) 358.1835, found 358.1835.

3. Visual Kinetic Analysis



Kinetic Measurements. To a reaction tube was added **1a**, 1,3,5-trimethoxybenzene (internal standard), $[Rh(CO)_2Cl]_2$, and dioxane (5 mL). The reaction mixture was stirred at 90 °C under balloon pressured mix gas of CO and N_2 (1 atm CO or 0.2 atm CO). For each indicated time, about 0.6 mL reaction mixture was taken from the reaction system by a syringe. After cooling, the solvent was removed with a rotary evaporator. The residue was subsequently added to $CDCl_3$, and the solution was measured by a Bruker AVANCE III 400 (^{1}H at 400 MHz) NMR spectrometer.

Table S2. Kinetic Data for Rh Catalyzed [4+3]/[4+1] Cycloaddition of 1a

$[Cat]_T$/mM	[**1a**]$_0$/mM	*p*(CO) (atm)	time/min	[**1a**]/mM	[**2a**]/mM
5	50	1	60	32.37	3.56
5	50	1	120	28.42	6.54
5	50	1	180	24.45	10.51
5	50	1	240	20.44	13.90
5	50	1	300	16.11	17.40
5	50	1	360	12.62	20.19
3.75	50	1	60	37.84	3.21
3.75	50	1	120	31.77	6.43
3.75	50	1	180	26.78	9.28
3.75	50	1	240	22.49	11.78
3.75	50	1	300	18.56	14.99
3.75	50	1	360	14.64	17.49
6.25	50	1	60	29.63	4.28
6.25	50	1	120	26.78	8.21
6.25	50	1	180	21.42	12.14
6.25	50	1	240	16.42	16.07
6.25	50	1	300	12.14	18.92
6.25	50	1	360	10.00	25.70
5	50	0.2	60	30.8	5.0
5	50	0.2	120	25.8	10.6
5	50	0.2	180	19.8	16.3

5	50	0.2	240	14.5	21.2
5	50	0.2	300	9.9	25.1
5	50	0.2	360	6.0	28.0
5	70	1	60	47.88	5.75
5	70	1	120	41.35	11.16
5	70	1	180	36.39	15.65
5	70	1	240	31.92	19.79
5	70	1	300	26.18	23.30
5	70	1	360	22.89	27.92
5	30	1	60	15.82	2.85
5	30	1	120	13.36	5.48
5	30	1	180	11.15	8.03
5	30	1	240	8.22	10.69
5	30	1	300	6.27	12.86
5	30	1	360	3.47	14.97

Order in catalyst. Normalized time scale analysis[2] via plotting the concentration of **1a** against $t[\text{Cat}]_T^l$ ($[\text{Cat}]_\text{T}$ is the total concentration of catalyst added) was performed to determine the order in catalyst (*l*). *l* was adjusted until the curves overlaid (**Figure S1**). For this reaction, *l* equals 0.5.

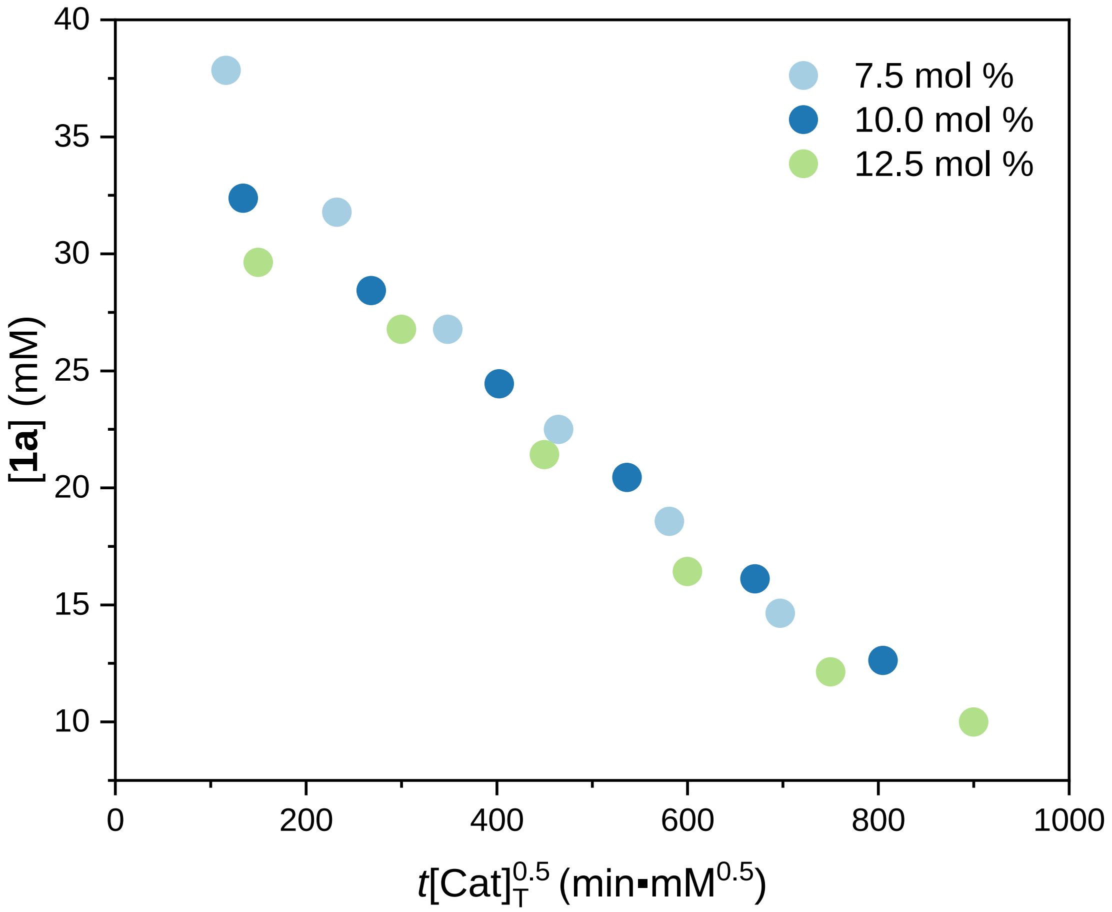


Figure S1. Determination the order in catalyst via normalized time scale analysis. Reaction conditions: **1a** (50 mM), $[Rh(CO)_2Cl]_2$ (7.5 mol %; 10.0 mol %; 12.5 mol %), CO (1 atm), dioxane, 90 °C.

Order in substrate. Variable time normalization analysis[3] via plotting the concentration of cycloadduct **2a** against $[\mathbf{1a}]m\Delta t$ was performed to determine the order in substrate (m). m was adjusted until the curves overlaid and became straight lines (**Figure S2**). For this reaction, m equals 0.5.

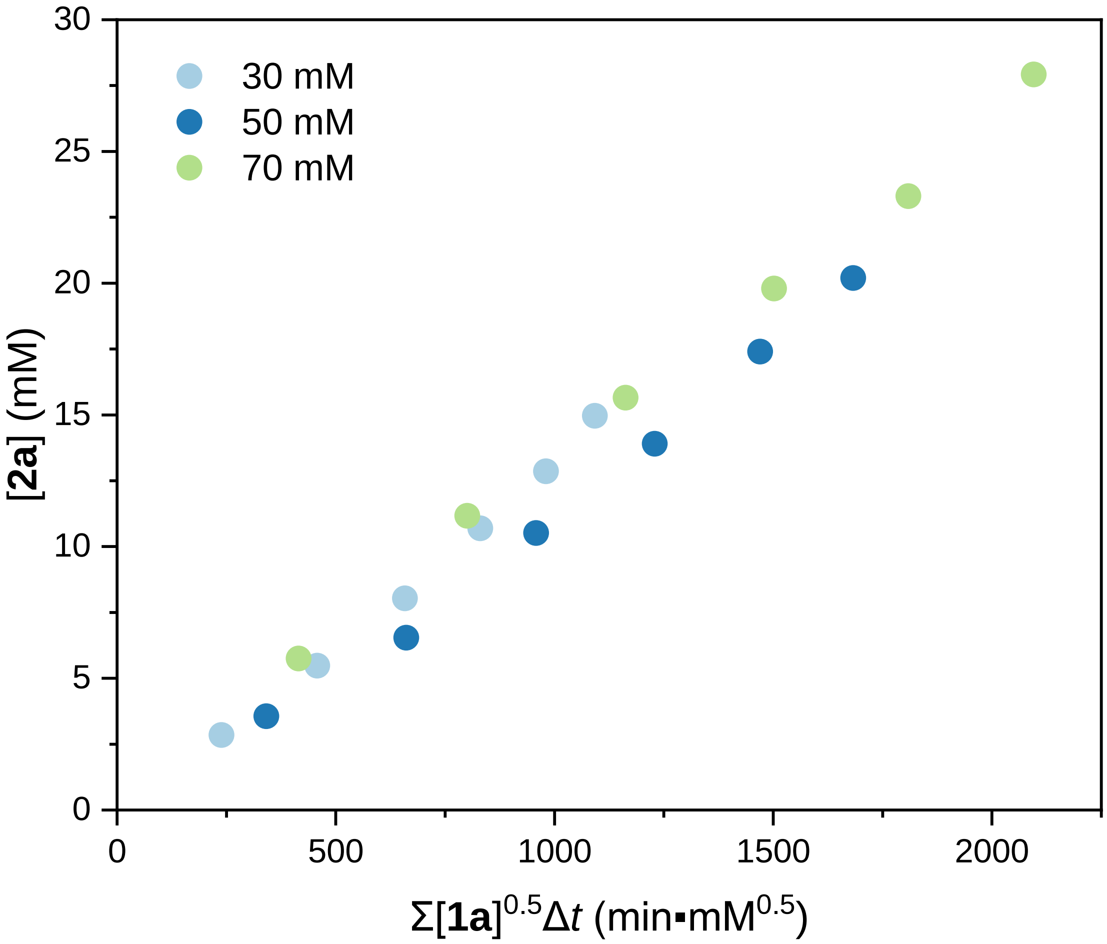


Figure S2. Determination of the order in substrate **1a** via variable time normalization analysis. Reaction conditions: **1a** (30 mM; 50 mM; 70 mM), $[Rh(CO)_2Cl]_2$ (5 mM), CO (1 atm), dioxane, 90 °C.

Order in CO. Normalized time scale analysis[2] via plotting the concentration of cycloadduct **2a** against $t[p(\mathrm{CO})]^n$ was performed to determine the order in CO (n). n was adjusted until the curves overlaid (**Figure S3**). For this reaction, n equals -0.25. While this value may not be the correct one since the side reaction (isomerization of **2a** to **3a**) becomes more distinct under 0.2 atm CO (**Scheme S1**). The side reaction could have influence on the determination of the order in CO, thus this could not be determined precisely.

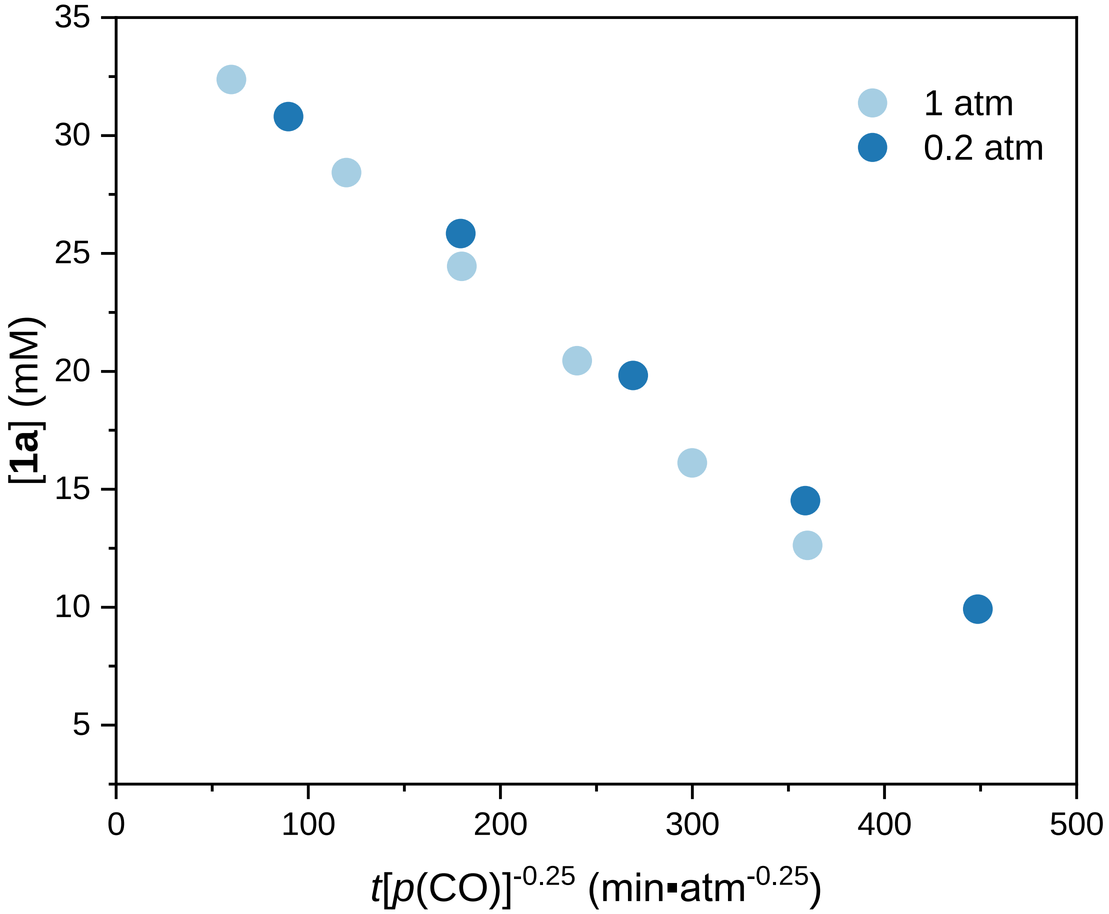
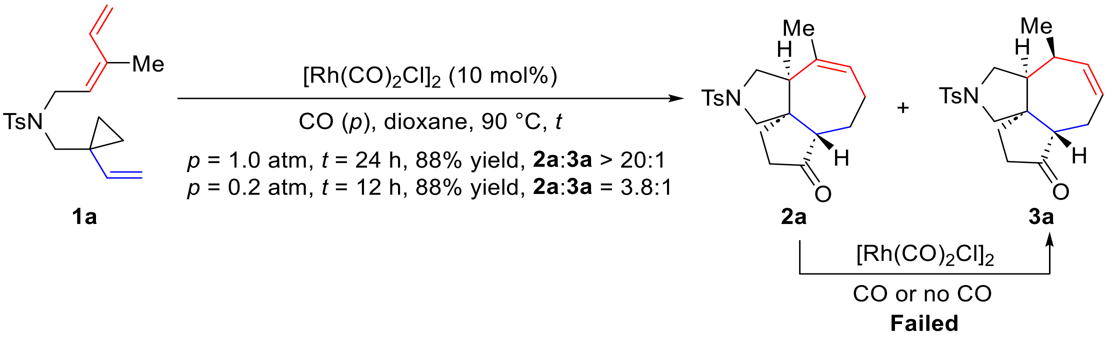


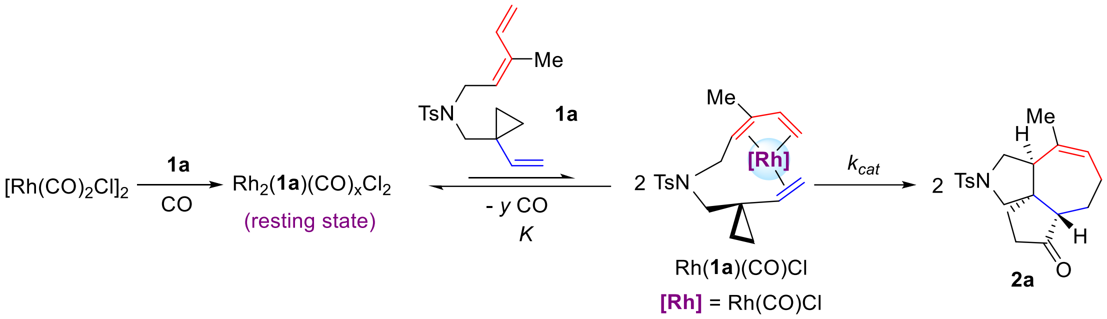
Figure S3. Determination the order in CO via normalized time scale analysis. Reaction conditions: **1a** (50 mM), $[Rh(CO)_2Cl]_2$ (10 mol %), CO (0.2, 1 atm), 1,4-dioxane, 90 °C.

Scheme S1. Reaction Outcomes for Reaction in 1 atm and 0.2 atm CO.



Considering the orders in catalyst and substrate are both 0.5, we proposed a pathway to account for generation of the catalytic active species. As shown in **Scheme S2**, the resting state is proposed to be a Rh dimer complex with one substrate. Considering the uncertainty of the order in CO, we do not know the number (*x*) of CO in the resting state and the number (*y*) of CO releasing when generating the monomeric catalytic species Rh(**1a**)(CO)Cl. With this mechanism, we can derive the rate equation as shown in **Scheme S2**, consistent with the experiment result above, which is also very similar with our previous [5+2+1] reaction.[4]

Scheme S2. Possible Pathway to Generate Active Species and Derivation of the Rate Equation



$$K = \frac{[\mathrm{Rh}(\mathbf{1a})(\mathrm{CO})\mathrm{Cl}]^2[p(\mathrm{CO})]^y}{[\mathrm{Rh}_2(\mathbf{1a})(\mathrm{CO})_x\mathrm{Cl}_2][\mathbf{1a}]}$$

$$[\mathrm{Rh}(\mathbf{1a})(\mathrm{CO})\mathrm{Cl}] \approx K^{0.5}\,\frac{[\mathbf{Cat}]_T^{0.5}[\mathbf{1a}]^{0.5}}{[p(\mathrm{CO})]^{0.5y}}$$

$$\Longrightarrow$$

$$\text{rate} = k_{cat}[\mathrm{Rh}(\mathbf{1a})(\mathrm{CO})\mathrm{Cl}] \approx k_{cat}K^{0.5}[\mathbf{Cat}]_T^{0.5}[\mathbf{1a}]^{0.5}[p(\mathrm{CO})]^{-0.5y}$$

$$\approx k[\mathrm{Cat}]_T^{0.5}[\mathbf{1a}]^{0.5}[p(\mathrm{CO})]^{-0.5y}$$

4. Computational Study

Computational Methods

All the density functional theory computations were carried out by using Gaussian 09[5] software. BMK[6]/6-31G(d)[7]/LANL2DZ[8] level (BMK was selected for its good performance in computing the mechanism of Rh catalyzed reactions[4]) was applied to optimize the stationary points in gas phase. Unscaled harmonic frequency calculations at the same level were applied to confirm each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298.15 K. For each optimized structure, Gibbs energies of solvation in 1,4-dioxane were computed at the SMD[9]/BMK/6-31G(d)/LANL2DZ level. Single point energies at DLPNO-CCSD(T)[10]/def2-TZVPP[11] level were performed on ORCA 4.2.1.[12] Gibbs energy differences discussed in this work are based on energies in 1,4-dioxane at 298.15 K. Standard state concentrations of 7.7 mM[13] and 1.0 M were used for CO and the other species, respectively. CYLview[14] was used to generate all the 3D structures.

More Discussions on the Reaction Mechanism

IN1 can be coordinated by one CO or two CO to undergo further CO migratory insertion steps. As shown in **Figure S4**, **TS1** with one additional CO coordination is much more favored over **TS1’** with two additional CO coordination by 7.6 kcal/mol. Besides, CO migratory insertion is also site selective for [4+3]/[4+1] cycloaddition. Comparing to CO insertion at the secondary C position (via **TS1**), CO insertion at tertiary C position is 14.7 kcal/mol disfavored for **TS1-Iso** and 13.3 kcal/mol for **TS1-Iso’**. As for reductive elimination, **TS2** with two CO coordination is more favored over **TS2’**.

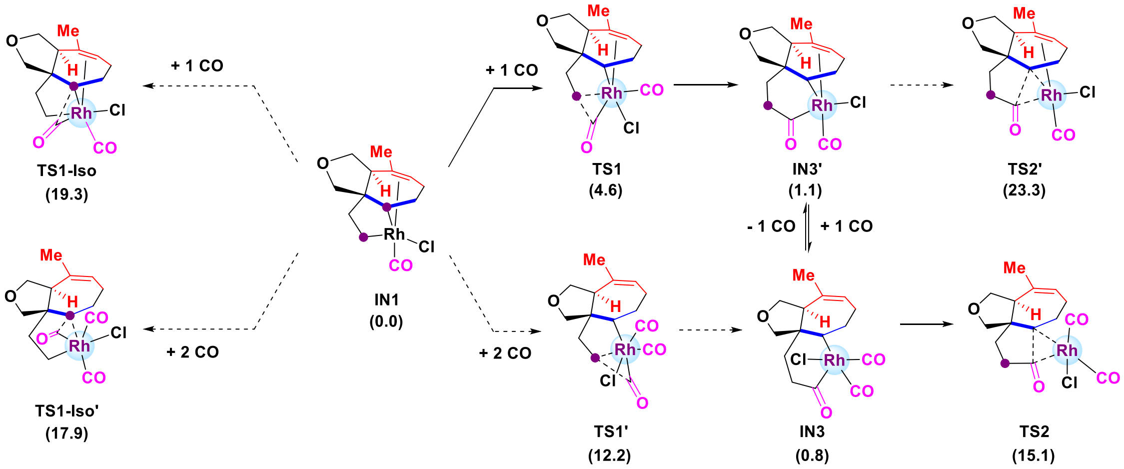


Figure S4. CO migratory insertion and reductive elimination for [4+3]/[4+1] cycloadditions.

Computed Energies of the Stationary Points

Table S3. Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

Stationary point	TCG[a,b]	SPE[a,b]	SPE[c]	SPE[d]
CO	-0.013873	-113.260871	-113.255874	-113.158299
IN1	0.250436	-1225.265966	-1225.280623	-1225.691047
IN2	0.256742	-1338.546374	-1338.559470	-1338.875640
IN3	0.265063	-1451.816955	-1451.833006	-1452.040578
IN3'	0.260586	-1338.548778	-1338.566507	-1338.865087
IN4	0.263718	-1451.867420	-1451.881847	-1452.079775
IN5	0.246173	-1225.241692	-1225.259882	-1225.669631
IN6	0.244569	-1225.232370	-1225.246191	-1225.666560
IN7	0.245217	-1225.288019	-1225.301206	-1225.715630
TS1	0.259926	-1338.535241	-1338.549822	-1338.861995
TS1'	0.259386	-1451.794837	-1451.809597	-1452.017993
TS1-Iso	0.256983	-1338.511568	-1338.526444	-1338.835358
TS1-Iso'	0.260195	-1451.788886	-1451.802385	-1452.010950
TS2	0.263978	-1451.800899	-1451.813937	-1452.019697
TS2’	0.258761	-1338.518766	-1338.534821	-1338.829527
TS3	0.242741	-1225.218978	-1225.234803	-1225.653419
TS4	0.243653	-1225.220320	-1225.233710	-1225.661218

[a] Computed at the BMK/6-31G(d)/LANL2DZ level.

[b] A standard state at 1 atm and 298.15 K was used.

[c] Computed at the SMD(1,4-dioxane)/BMK/6-31G(d)/LANL2DZ//BMK/6-31G(d)/LANL2DZ level.

[d] Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/6-31G(d)/LANL2DZ level.

Cartesian Coordinates of the Stationary Points

The cartesian coordinates for several intermediates and transition states structures (including CO, **IN1**, **IN5**, **TS3**, **IN6**, **TS4**, and **IN7**) have been reported in our previous work.[1] Thus, only the new stationary points are reported below.

IN2

C	-2.082967	0.293383	-0.860072
C	-1.837728	-0.897775	0.126146
C	-3.402288	0.900846	-0.319455
O	-4.148605	-0.225887	0.064811
C	-3.275478	-1.155295	0.682032
C	-0.767313	-0.562859	1.206708
C	-1.062919	0.657779	2.104084
H	-2.331852	-0.137087	-1.839101
C	-0.763682	2.021164	1.408511
C	-0.263306	1.890015	-0.028922
C	-0.875626	1.203679	-1.051900
C	-0.503258	1.547417	-2.483807
H	-3.303918	-1.039833	1.778040
H	-3.639501	-2.160897	0.436720
H	-0.666689	-1.448959	1.849970
H	-0.440599	0.581330	3.005642
H	-2.106239	0.638730	2.455749
H	-0.005958	2.571604	1.979734
H	-1.652973	2.667984	1.406121
H	0.502300	2.605952	-0.335833
H	-0.524620	0.669874	-3.139461
H	0.490822	2.001747	-2.546558
H	-1.252948	2.258321	-2.866820

C	1.818573	-1.820966	0.581534
O	2.306466	-2.802892	0.874640
Rh	0.954127	-0.199580	0.051407
Cl	2.745004	0.437090	-1.537558
C	-1.246834	-2.074815	-0.673062
H	-1.957315	-2.424920	-1.439225
H	-1.062437	-2.919058	0.009818
C	0.074903	-1.585874	-1.290128
H	0.751776	-2.411157	-1.539563
H	-0.072794	-1.026807	-2.217574
H	-3.230182	1.575239	0.533309
H	-3.973871	1.442559	-1.081448
C	2.067850	1.054889	1.334207
O	2.791719	1.688335	1.930595

IN3

C	2.898103	-0.170209	0.671433
C	1.365714	-0.476269	0.419384
C	0.525735	0.725354	-0.066251
C	2.068946	2.802158	-0.012466
C	3.548002	0.712364	-0.412936
C	3.450186	-1.621717	0.706124
O	2.605354	-2.401406	-0.124929
C	1.560521	-1.592029	-0.632676
C	-0.464048	-1.943132	1.557050
C	0.759892	-1.039689	1.741694
H	3.038004	0.306259	1.652069
C	4.670553	0.119052	-1.255594
H	0.716280	0.876200	-1.136894
H	1.627179	3.396420	-0.827360
H	2.494149	3.539455	0.689418
H	3.428599	-2.027769	1.727857
H	4.483928	-1.699515	0.355160
H	0.686509	-2.225220	-0.812411
H	1.839206	-1.137492	-1.597422
H	-0.186882	-2.891101	1.076198
H	-0.901762	-2.209595	2.530521
H	1.501021	-1.631452	2.290407
H	0.502264	-0.194272	2.397149
H	4.360489	-0.826868	-1.722893
H	5.566045	-0.096752	-0.653911
H	4.960711	0.814681	-2.050920
C	-1.640971	-1.392907	0.738649
O	-2.669037	-1.985459	0.614079
C	0.913268	2.030471	0.680309
H	0.070215	2.736531	0.723957
H	1.172226	1.805203	1.725700
Rh	-1.546790	0.404556	-0.163773
C	-3.638420	0.241749	-0.687341
O	-4.687142	0.118016	-1.088143
Cl	-1.256393	-0.474852	-2.357902
C	-1.741648	1.214098	1.583977
O	-1.858080	1.674747	2.616167
C	3.181197	1.983931	-0.638325
H	3.735089	2.526192	-1.408096

IN3’

C	-2.104963	0.399209	-0.739770
C	-1.782313	-0.923544	0.038136
C	-3.407501	0.884463	-0.051215
O	-4.105411	-0.301394	0.221360
C	-3.180693	-1.276202	0.663199
C	-0.666313	-0.723367	1.108449
C	-1.006029	0.334471	2.194208
H	-2.389669	0.127750	-1.765194
C	-0.687360	1.802428	1.754536
C	-0.375262	1.990964	0.273156
C	-0.955965	1.399590	-0.818235
C	-0.611962	1.950878	-2.196012
H	-3.132629	-1.293793	1.762287
H	-3.550434	-2.253354	0.328119
H	-0.516530	-1.694013	1.602625
H	-0.413428	0.115169	3.091574
H	-2.056871	0.265371	2.508164
H	0.187999	2.168017	2.308840
H	-1.508625	2.483925	2.028064
H	0.352865	2.774827	0.056739
H	-0.545632	1.162510	-2.955256
H	0.338504	2.495933	-2.179721
H	-1.412413	2.636072	-2.516027
C	1.069149	-1.409689	-1.109607
O	2.052758	-2.077750	-1.233897
Rh	1.055988	0.081867	0.224145
Cl	2.819975	1.537064	-0.620940
C	-1.386105	-2.036895	-0.964458
H	-2.255796	-2.266890	-1.596788
H	-1.137898	-2.954970	-0.410379
C	-0.215164	-1.673571	-1.901251

H	0.009035	-2.499102	-2.587743
H	-0.464982	-0.789399	-2.498038
H	-3.192597	1.454420	0.867002
H	-4.032150	1.504590	-0.704385
C	2.324503	-0.983485	1.205891
O	3.074912	-1.578691	1.810966

IN4

C	-0.972494	0.695841	-0.776651
C	-2.445729	0.442442	-0.319518
C	-2.667744	-0.467042	0.912492
C	-0.349420	-1.224516	1.742945
C	-0.032492	1.028043	0.400368
C	-1.215800	1.885594	-1.728813
O	-2.259965	2.654502	-1.146048
C	-2.920598	1.903625	-0.143697
C	-4.543212	-0.780699	-0.734270
C	-3.280281	-0.254146	-1.446712
H	-0.583783	-0.170294	-1.318272
C	0.384752	2.490796	0.564379
H	-2.664694	0.085968	1.863164
H	-0.580535	-1.182962	2.819326
H	0.400480	-2.016844	1.617137
H	-1.527084	1.514055	-2.715969
H	-0.343443	2.530938	-1.874058
H	-4.006139	2.024198	-0.265027
H	-2.644707	2.282626	0.856196
H	-5.335158	-0.018093	-0.687331
H	-4.983278	-1.678551	-1.182839
H	-3.513407	0.435643	-2.265491
H	-2.703145	-1.090652	-1.864854
H	-0.505784	3.130940	0.496233
H	1.067507	2.817222	-0.229934
H	0.868159	2.661660	1.532452
C	-4.074943	-1.067462	0.701144
O	-4.685351	-1.686410	1.533772
C	-1.636988	-1.625341	0.995218
H	-2.091270	-2.459518	1.546050
H	-1.388504	-1.990239	-0.009103
Rh	2.169718	-0.177199	0.054484
C	3.797592	-0.849900	-0.752718
O	4.724536	-1.284231	-1.243796
Cl	1.179685	-1.955607	-1.229623
C	3.105558	1.155802	1.057909
O	3.674062	1.932066	1.671390
C	0.257856	0.140280	1.417650
H	0.780251	0.575888	2.273227

TS1

C	-1.916614	-0.005934	1.085944
C	-1.699370	0.983990	-0.123204
C	-3.366228	-0.557093	0.841398
O	-3.749646	-0.123334	-0.441031
C	-3.157729	1.139212	-0.629596
C	-0.746037	0.421537	-1.217767
C	-1.215725	-0.846132	-1.953738
H	-1.932822	0.588381	2.008800
C	-1.224150	-2.120285	-1.056966
C	-0.496711	-1.963770	0.277497
C	-0.830534	-1.070293	1.261480
C	-0.296471	-1.246989	2.673101
H	-3.224198	1.396242	-1.693102
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H	-0.607093	1.215059	-1.967082
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H	0.210063	-2.749001	0.552669
H	-1.115939	-1.606422	3.315637
H	0.063805	-0.300702	3.098012
H	0.531336	-1.961538	2.708948
C	1.555424	1.808504	-0.511449
O	2.004330	2.749778	-1.016846
Rh	1.005983	0.068757	-0.126558
Cl	2.818676	-0.454200	1.456102
C	-1.064720	2.300187	0.378806
H	-1.693535	2.765374	1.153489
H	-0.988060	3.016926	-0.452815
C	0.338299	2.009149	0.942461
H	0.906362	2.899070	1.226584
H	0.319870	1.377145	1.840280
H	-3.431812	-1.649975	0.869980
H	-4.048468	-0.144328	1.603831
C	1.836241	-1.131642	-1.416185
O	2.371665	-1.797907	-2.162121

TS1’

C	2.945886	0.658971	-0.351106
C	1.387207	0.574529	-0.553405
C	0.555292	-0.048437	0.619715
C	2.384960	-1.439698	1.869872
C	3.810514	-0.558283	-0.050260
C	3.068138	1.811922	0.680383
O	1.929869	2.635023	0.477996
C	1.168514	2.114231	-0.584318
C	-0.497622	-0.078963	-2.098411
C	1.027709	-0.083682	-1.899006
H	3.310794	1.063432	-1.307902
C	5.039566	-0.686297	-0.935879
H	0.598163	0.653164	1.465598
H	2.422562	-0.587118	2.567825
H	2.435433	-2.343648	2.491217
H	3.986725	2.396911	0.531540
H	3.060550	1.436478	1.712919
H	1.508896	2.518431	-1.556232
H	0.132342	2.432976	-0.436354
H	-0.909696	0.941029	-2.110350
H	-0.860730	-0.545980	-3.018365
H	1.512601	0.459277	-2.725086
H	1.407096	-1.115446	-1.926898
H	5.661315	-1.541244	-0.645635
H	5.658764	0.222511	-0.883539
H	4.749934	-0.812381	-1.990189
C	-1.053276	-1.557257	-1.115079
O	-0.899490	-2.622885	-1.545446
C	1.019812	-1.429767	1.135348
H	0.267734	-1.800903	1.845523
H	1.058689	-2.165104	0.319791
Rh	-1.492368	-0.098969	-0.006831
C	-2.136254	-0.867579	1.676067
O	-2.539723	-1.375386	2.604619
Cl	-3.811317	-0.001976	-0.849187
C	-1.930091	1.890584	0.600348
O	-2.313805	2.901879	0.928889
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H	4.304765	-2.237988	1.079373

TS1-Iso

C	-2.104664	-0.355653	0.938531
C	-1.720901	0.970518	0.195136
C	-3.463564	-0.770657	0.269708
O	-3.797461	0.249230	-0.648006
C	-3.142197	1.422248	-0.233733
C	-0.812587	0.822472	-1.073765
C	-1.059196	-0.342060	-2.059450
H	-2.328109	-0.055549	1.971267
C	-0.904015	-1.805338	-1.546103
C	-0.497862	-2.021264	-0.096700
C	-1.041686	-1.447721	1.007787
C	-0.747098	-2.006336	2.391931
H	-3.153534	2.133755	-1.067809
H	-3.661324	1.881492	0.628943
H	-1.018767	1.729251	-1.653671
H	-0.370775	-0.202600	-2.902127
H	-2.077789	-0.197184	-2.442937
H	-0.154051	-2.305875	-2.163329
H	-1.851645	-2.342321	-1.706878
H	0.213804	-2.833205	0.059443
H	0.074661	-2.731608	2.368849
H	-1.643206	-2.518362	2.775859
H	-0.500765	-1.216401	3.113705
C	0.896747	1.502664	-0.993865
O	1.246635	2.409846	-1.631592
Rh	1.120352	0.089646	0.198568
Cl	2.310211	-1.286352	-1.488212
C	-1.020008	1.948623	1.161326
H	-1.703343	2.211986	1.983669
H	-0.794102	2.882138	0.622475
C	0.289884	1.320944	1.688969
H	0.988393	2.103597	2.008015
H	0.092173	0.682105	2.560118
H	-3.404679	-1.715538	-0.280425
H	-4.248356	-0.864755	1.037711
C	2.852197	0.249288	1.015769
O	3.888539	0.374251	1.461836

TS1-Iso’

C	-3.027704	-0.322394	-0.465513
C	-1.504497	-0.714993	-0.497612
C	-0.693445	-0.273709	0.760632
C	-2.105483	1.621955	1.797327
C	-3.160950	1.911202	0.747363
C	-3.526045	1.103004	-0.259181
C	-3.605214	-1.349484	0.548501
O	-2.729634	-2.462728	0.520964

C	-1.740585	-2.253520	-0.458655
C	0.632053	-0.789681	-1.870583
C	-0.814928	-0.266026	-1.797553
H	-3.387035	-0.632786	-1.457881
C	-4.579797	1.543942	-1.263081
H	-1.067627	-0.841425	1.621683
H	-2.440022	0.835778	2.494454
H	-1.956974	2.524007	2.404421
H	-3.643647	2.888278	0.807273
H	-4.623989	-1.657941	0.272325
H	-3.634895	-0.942726	1.569198
H	-2.085720	-2.585990	-1.455224
H	-0.870837	-2.856046	-0.184278
H	0.651062	-1.886558	-1.893462
H	1.134889	-0.431609	-2.777924
H	-1.397942	-0.626419	-2.661319
H	-0.827858	0.834144	-1.850038
H	-4.955850	2.548554	-1.037329
H	-5.434655	0.850303	-1.267489
H	-4.170712	1.549412	-2.284772
C	3.304788	-0.778155	-0.707700
O	4.297365	-1.250533	-0.981655
C	0.832091	-1.382643	0.924066
O	0.797451	-2.340872	1.579510
Cl	2.698907	1.018245	1.779984
C	-0.736006	1.216197	1.196765
H	0.045358	1.375518	1.948510
H	-0.518374	1.889141	0.356549
Rh	1.590610	-0.039995	-0.163222
C	1.819896	1.872773	-1.083073
O	2.029933	2.907278	-1.487525

TS2

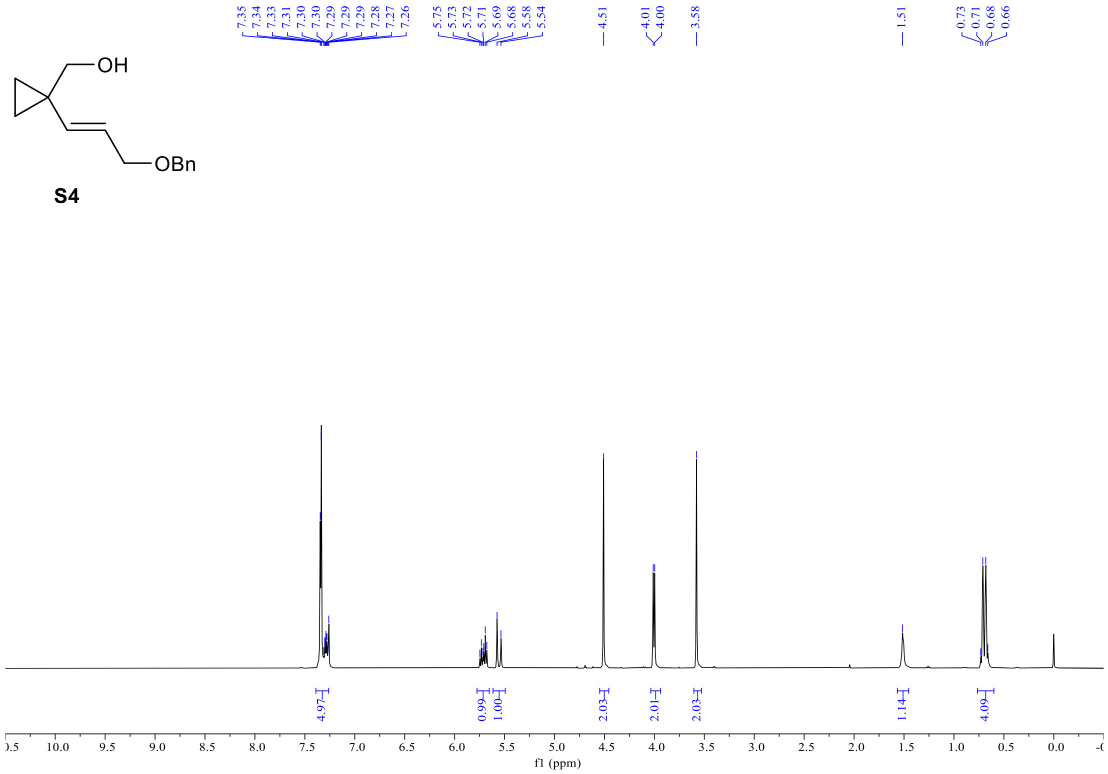
C	3.003807	0.112048	0.492158
C	1.544285	-0.498517	0.533447
C	0.460570	0.532883	0.122311
C	1.556222	2.791220	-0.350311
C	3.307495	0.933766	-0.779253
C	3.812619	-1.196224	0.586714
O	3.097710	-2.149628	-0.172176
C	1.773469	-1.697947	-0.423256
C	-0.275550	-1.332960	2.092086
C	1.234026	-1.038418	1.965521
H	3.191266	0.732100	1.377165
C	4.383766	0.414264	-1.724358
H	0.443136	0.580951	-0.984167
H	0.843377	3.135355	-1.118571
H	1.930287	3.708236	0.134069
H	3.886600	-1.519062	1.637379
H	4.832311	-1.120317	0.195990
H	1.084533	-2.528244	-0.252842
H	1.672975	-1.378560	-1.473269
H	-0.570160	-2.174476	1.460884
H	-0.574856	-1.505167	3.132112
H	1.800153	-1.956503	2.159075
H	1.518776	-0.295701	2.724981
H	4.192154	-0.631352	-2.003428
H	5.381731	0.446855	-1.262409
H	4.418647	1.019766	-2.636949
C	-0.933879	-0.036507	1.625914
O	-1.265512	0.852735	2.354074
C	0.783023	1.938886	0.681007
H	-0.122373	2.473396	0.987739
H	1.364647	1.837653	1.605064
Rh	-1.716893	0.039209	-0.320904
C	-3.574398	-0.497837	-0.754273
O	-4.625589	-0.883081	-0.931911
Cl	-1.385038	-2.234173	-1.028690
C	-2.214117	1.895420	-0.042981
O	-2.555981	2.971805	0.068811
C	2.688030	2.089070	-1.077786
H	3.011424	2.602048	-1.986420

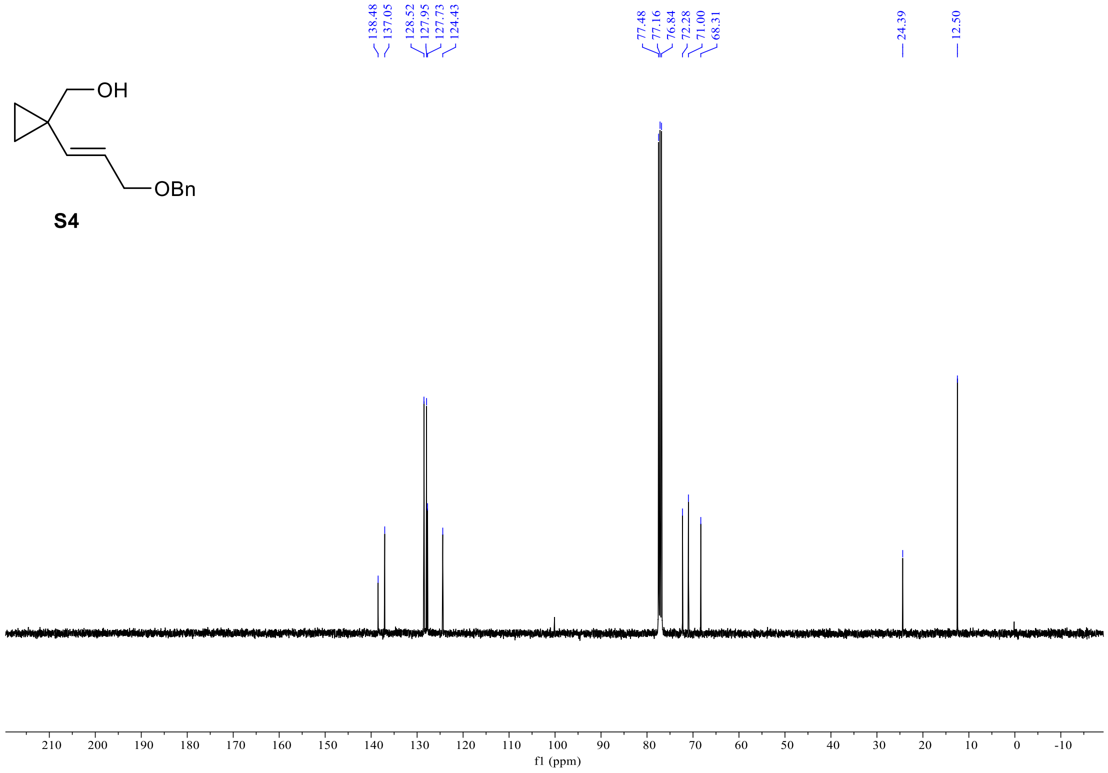
TS2’

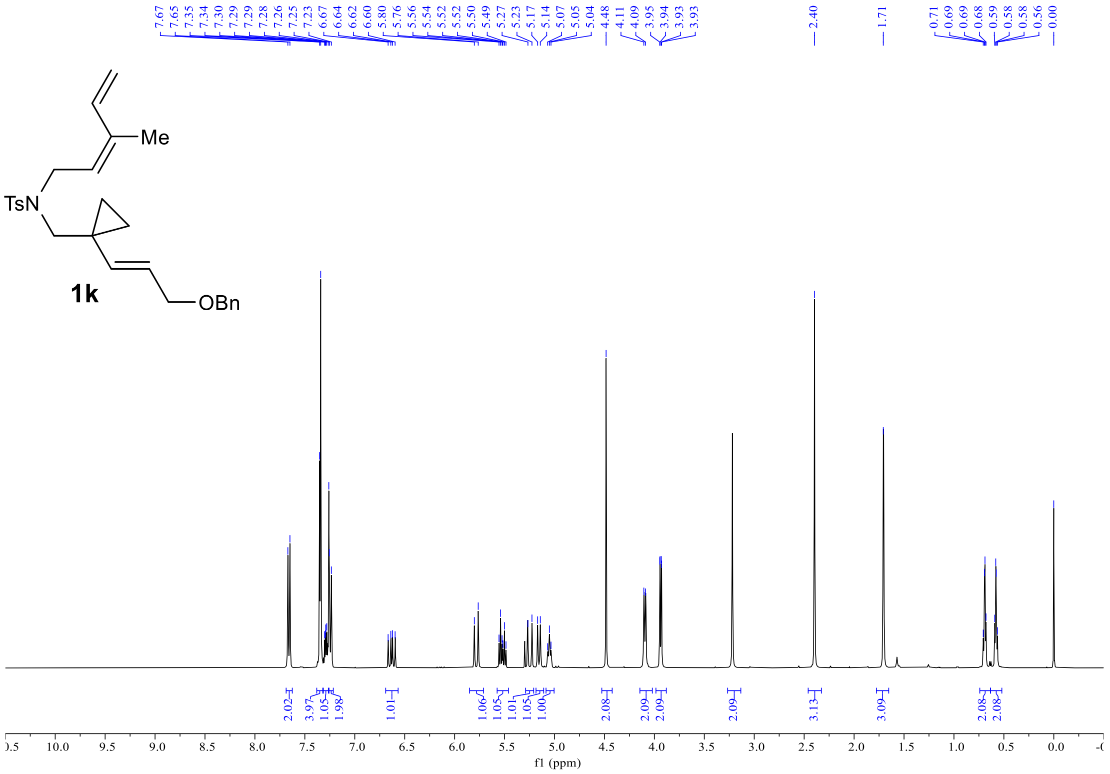
C	1.956473	-0.749149	-0.711161
C	2.007256	0.763628	-0.307261
C	3.221890	-1.341519	0.007798
O	3.598970	-0.399926	0.985733
C	3.378892	0.860543	0.410026
C	0.822808	1.217303	0.591084
C	0.757082	0.592509	2.024660
H	2.112491	-0.816247	-1.795382
C	0.755867	-0.958774	2.115885
C	0.160482	-1.634151	0.887049
C	0.663777	-1.514876	-0.407490
C	0.304566	-2.546780	-1.472069
H	3.414299	1.617719	1.202479
H	4.167513	1.091446	-0.331784

H	0.981701	2.282220	0.813166
H	-0.120061	1.002198	2.538517
H	1.638294	0.969299	2.564989
H	0.178869	-1.259524	2.998015
H	1.785859	-1.306019	2.262564
H	-0.563858	-2.429886	1.065739
H	-0.585707	-3.120226	-1.200626
H	1.151740	-3.239876	-1.603005
H	0.117484	-2.070046	-2.444131
C	-0.326209	1.803697	-0.671461
O	-1.037422	2.750858	-0.436570
Rh	-1.132111	-0.071571	0.022683
Cl	-2.805285	-1.621496	-0.599799
C	1.927414	1.666372	-1.558794
H	2.604258	1.321558	-2.351013
H	2.210067	2.697153	-1.295601
C	0.450046	1.632421	-1.989728
H	0.156343	2.444278	-2.662271
H	0.207210	0.667325	-2.454712
H	3.029110	-2.297819	0.506359
H	4.041507	-1.476905	-0.718852
C	-2.690533	0.943046	0.736594
O	-3.590440	1.437049	1.219663

5. ^{1}H, ^{13}C and NOE NMR Spectra



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5.27
5.23
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5.07
5.05
5.04
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4.11
4.09
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3.94
3.93
3.93
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0.69
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0.58
0.58
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0.00
Me
TsN
OBn
1k
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3.97
1.05
1.98
1.01
1.06
1.05
1.01
1.05
1.00
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2.09
2.09
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3.13
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2.08
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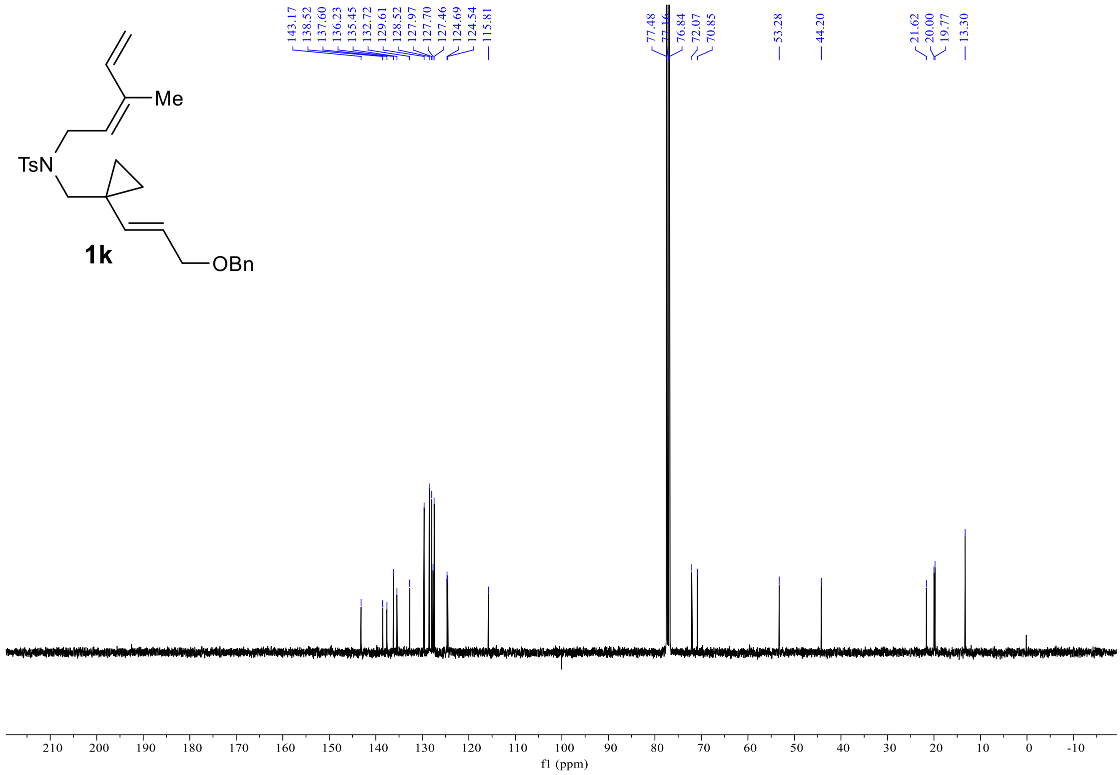
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77.48
77.16
76.84
72.07
70.85
53.28
44.20
21.62
20.00
19.77
13.30
Me
TsN
OBn
1k
210
200
190
180
170
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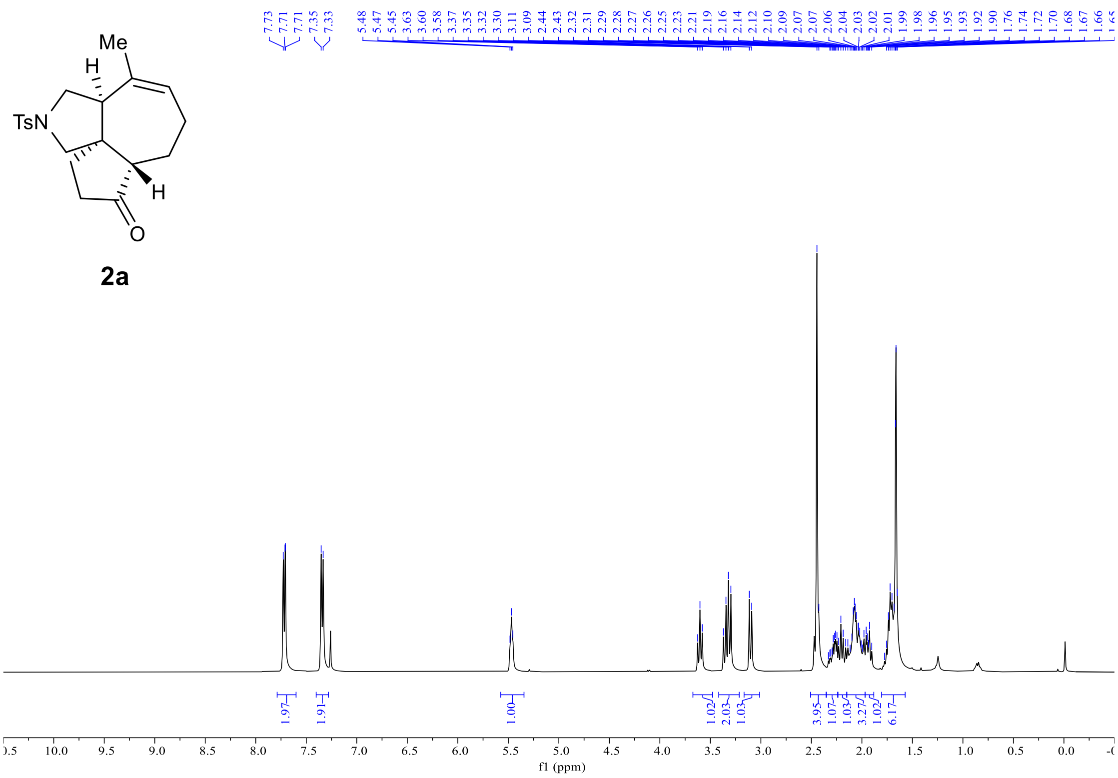
f1 (ppm)



2a

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2.09
2.07
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2.01
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2.03
1.03
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1.03
1.04
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1.02
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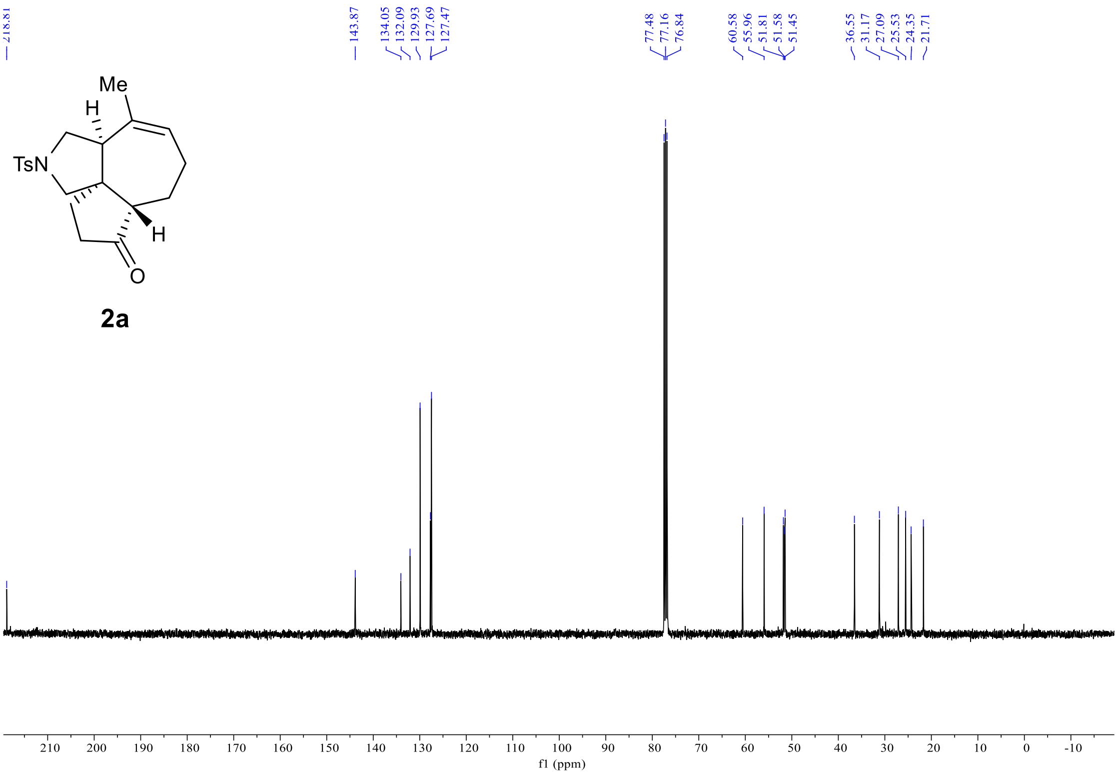

2a

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O
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77.16
76.84
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55.96
51.81
51.58
51.45
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25.53
24.35
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180
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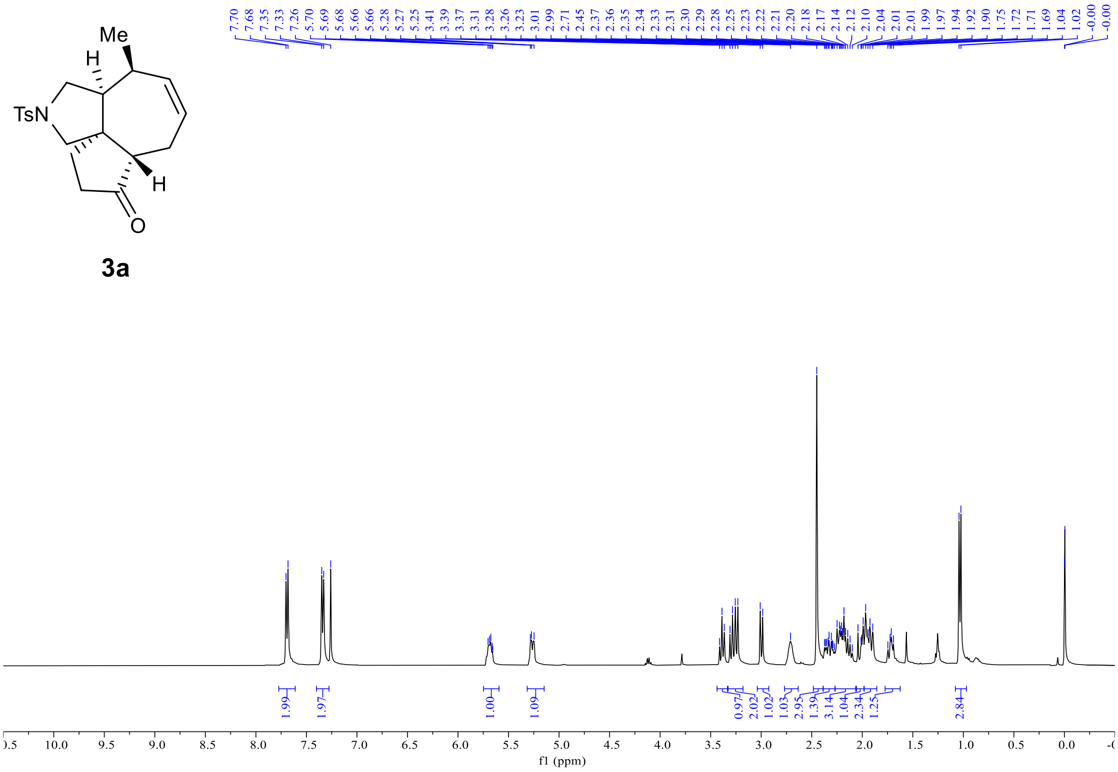
f1 (ppm)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3.39
3.37
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3.28
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3.23
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2.35
2.34
2.33
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2.29
2.28
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2.22
2.21
2.20
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2.14
2.12
2.10
2.04
2.01
2.01
1.99
1.97
1.94
1.92
1.90
1.75
1.72
1.71
1.69
1.04
1.02
-0.00
-0.00
Me
H
TsN
H
O
3a
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1.00
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2.02
1.02
1.03
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0.0
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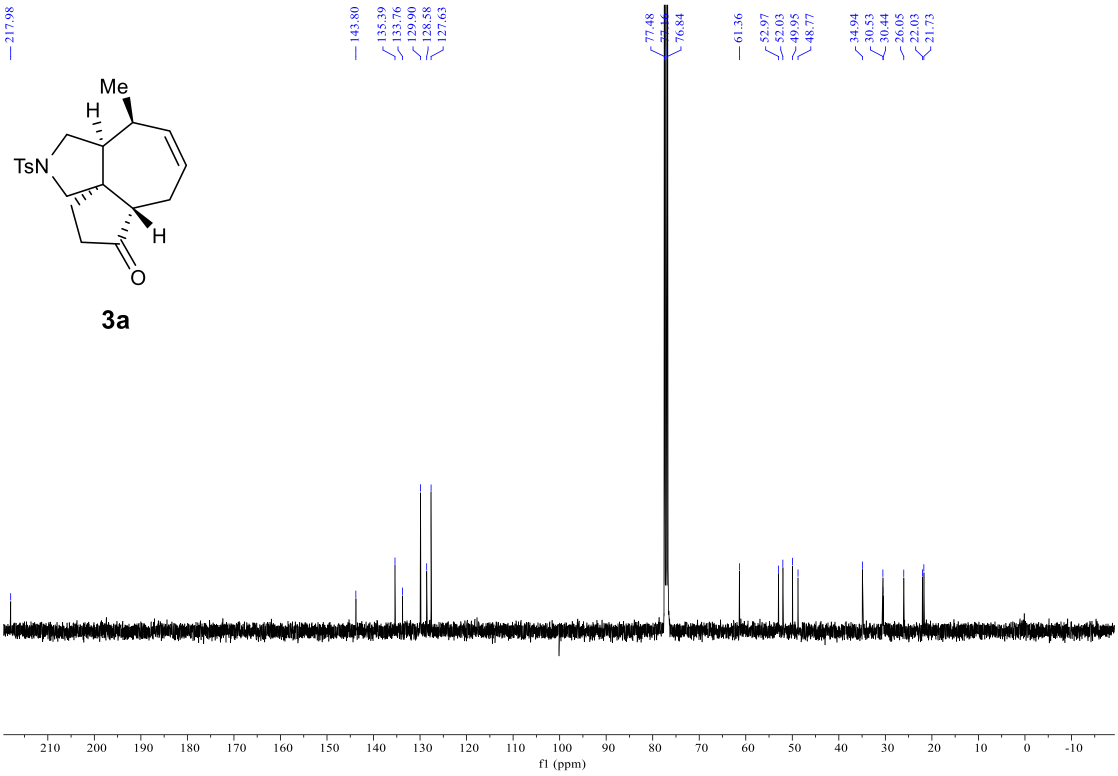
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52.03
49.95
48.77
34.94
30.53
30.44
26.05
22.03
21.73
Me
H
TsN
H
O
3a
210
200
190
180
170
160
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140
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120
110
100
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80
70
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30
20
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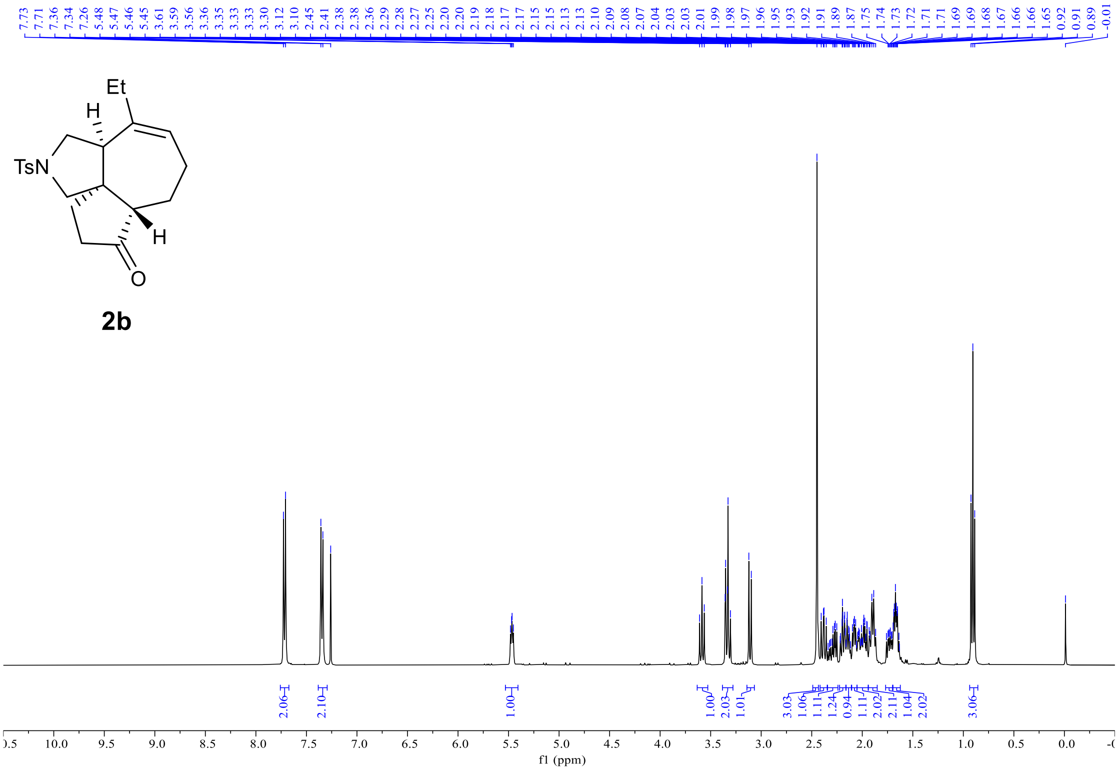
-10
f1 (ppm)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3.36
3.35
3.33
3.33
3.30
3.12
3.10
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2.20
2.19
2.18
2.17
2.17
2.15
2.15
2.13
2.13
2.10
2.09
2.08
2.07
2.04
2.03
2.03
2.01
1.99
1.98
1.97
1.96
1.95
1.93
1.92
1.91
1.89
1.87
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1.74
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1.71
1.69
1.69
1.68
1.67
1.66
1.66
1.65
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0.91
0.89
-0.01
Et
H
TsN
H
O
2.06
2.10
1.00
1.00
2.03
1.01
3.03
1.06
1.11
1.24
0.94
1.11
2.02
2.11
1.04
2.02
3.06
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9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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1.0
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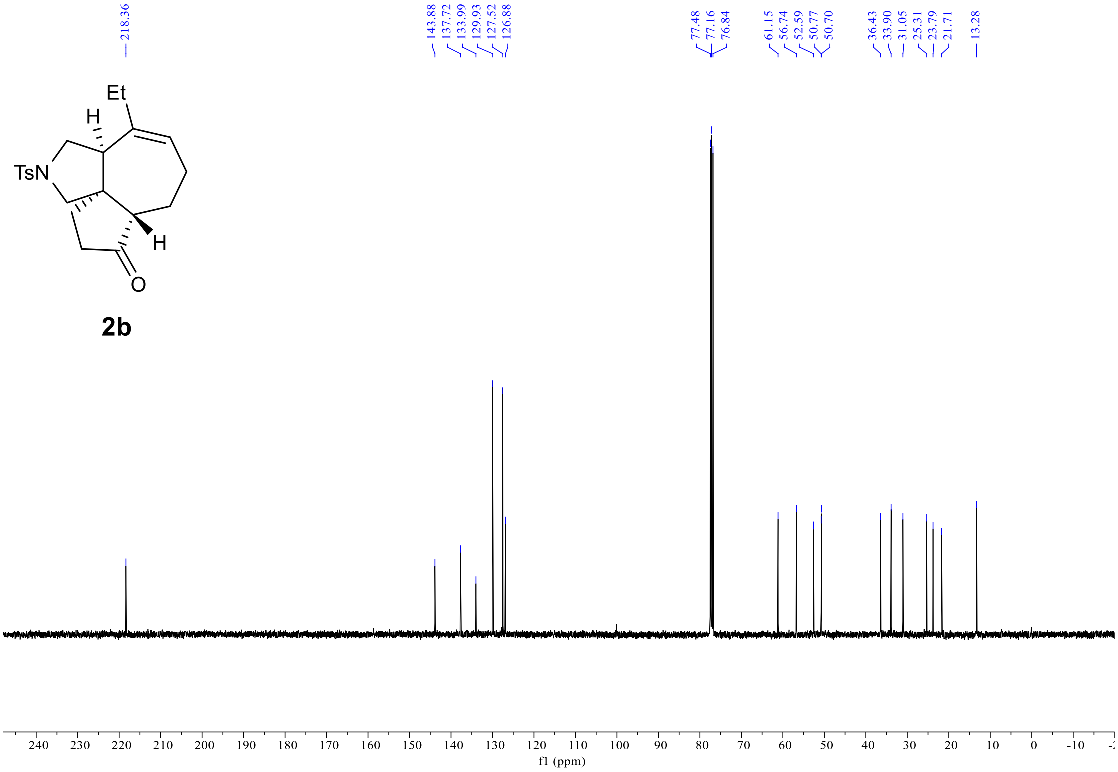
f1 (ppm)

2b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126.88
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77.16
76.84
61.15
56.74
52.59
50.77
50.70
36.43
33.90
31.05
25.31
23.79
21.71
13.28
Et
H
TsN
H
O
240
230
220
210
200
190
180
170
160
150
140
130
120
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100
90
80
70
60
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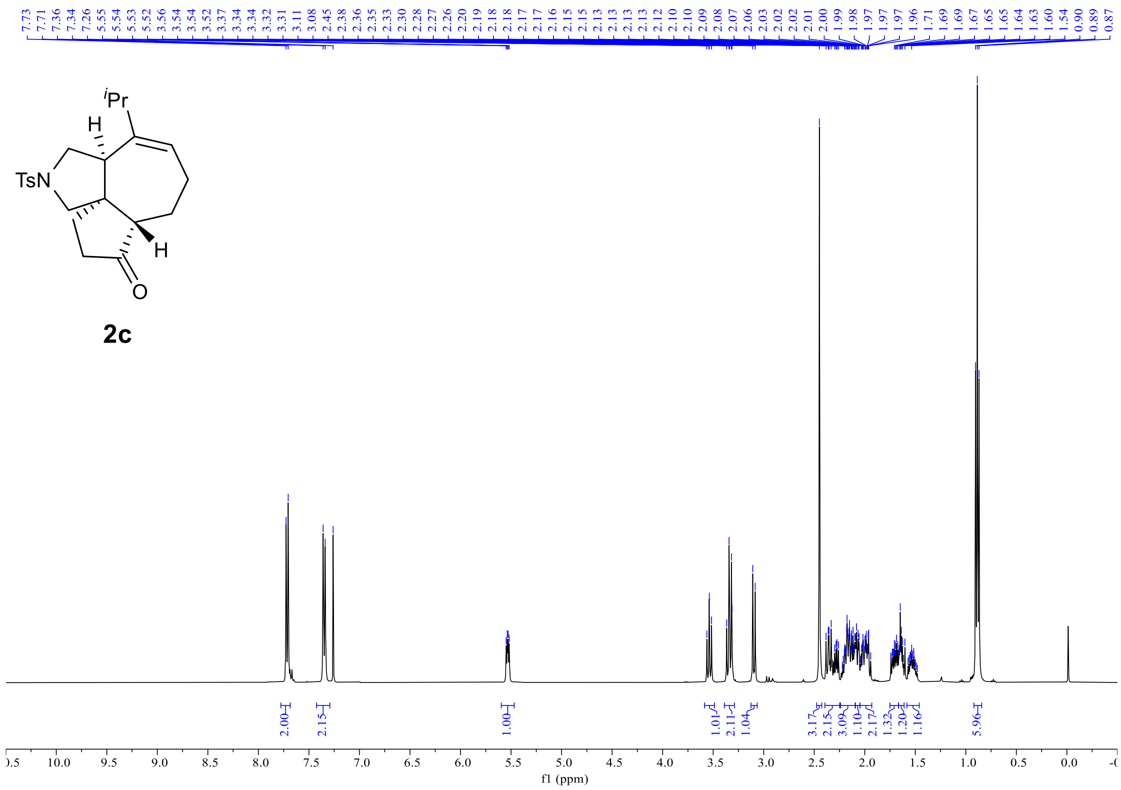
40
30
20
10
0
-10
f1 (ppm)

2b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3.54
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3.37
3.34
3.34
3.32
3.31
3.11
3.08
2.45
2.38
2.36
2.35
2.33
2.30
2.28
2.27
2.26
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.15
2.13
2.13
2.13
2.13
2.12
2.10
2.10
2.09
2.08
2.07
2.06
2.03
2.02
2.02
2.01
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1.97
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1.97
1.96
1.71
1.69
1.69
1.67
1.65
1.65
1.64
1.63
1.60
1.54
0.90
0.89
0.87
iPr
H
TsN
H
O
2c
2.00
2.15
1.00
1.01
2.11
1.04
3.17
2.15
3.09
1.10
2.17
1.32
1.20
1.16
5.96
).5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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1.0
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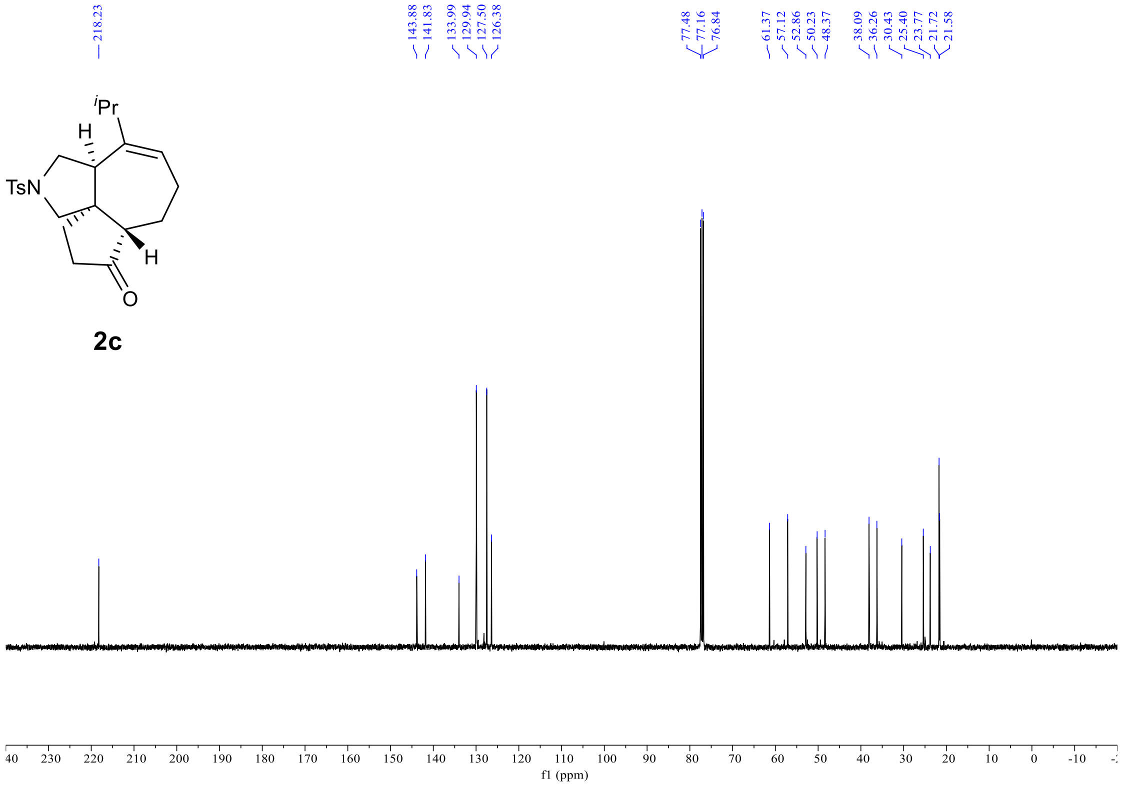
f1 (ppm)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76.84
61.37
57.12
52.86
50.23
48.37
38.09
36.26
30.43
25.40
23.77
21.72
21.58
iPr
H
TsN
H
O
2c
40
230
220
210
200
190
180
170
160
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100
90
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20
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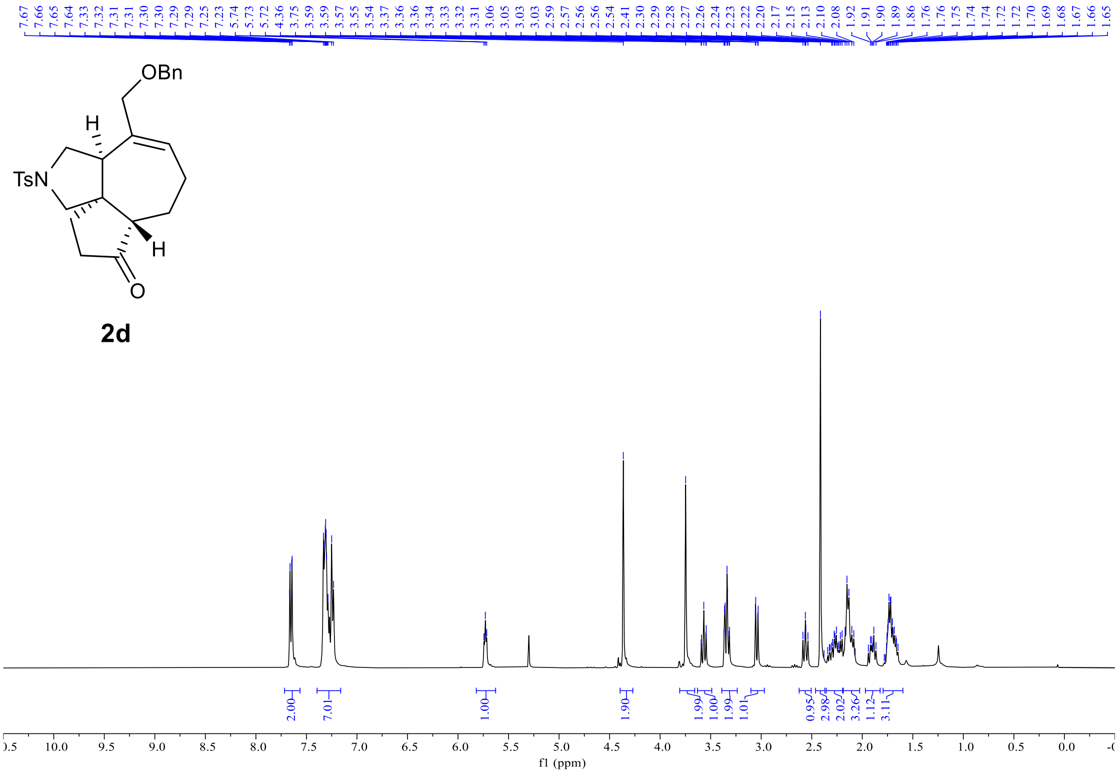
-10
-:
f1 (ppm)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7.23
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5.73
5.72
4.36
3.75
3.59
3.59
3.57
3.55
3.54
3.37
3.36
3.36
3.34
3.33
3.32
3.31
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3.03
3.03
2.59
2.57
2.56
2.56
2.54
2.41
2.30
2.29
2.28
2.27
2.26
2.24
2.23
2.22
2.20
2.17
2.15
2.13
2.10
2.08
1.92
1.91
1.90
1.89
1.86
1.76
1.76
1.75
1.74
1.74
1.72
1.70
1.69
1.68
1.67
1.66
1.65
OBn
H
TsN
H
O
2d
2.00
7.01
1.00
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1.99
1.00
1.99
1.01
0.95
2.98
2.02
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1.12
3.11
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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1.0
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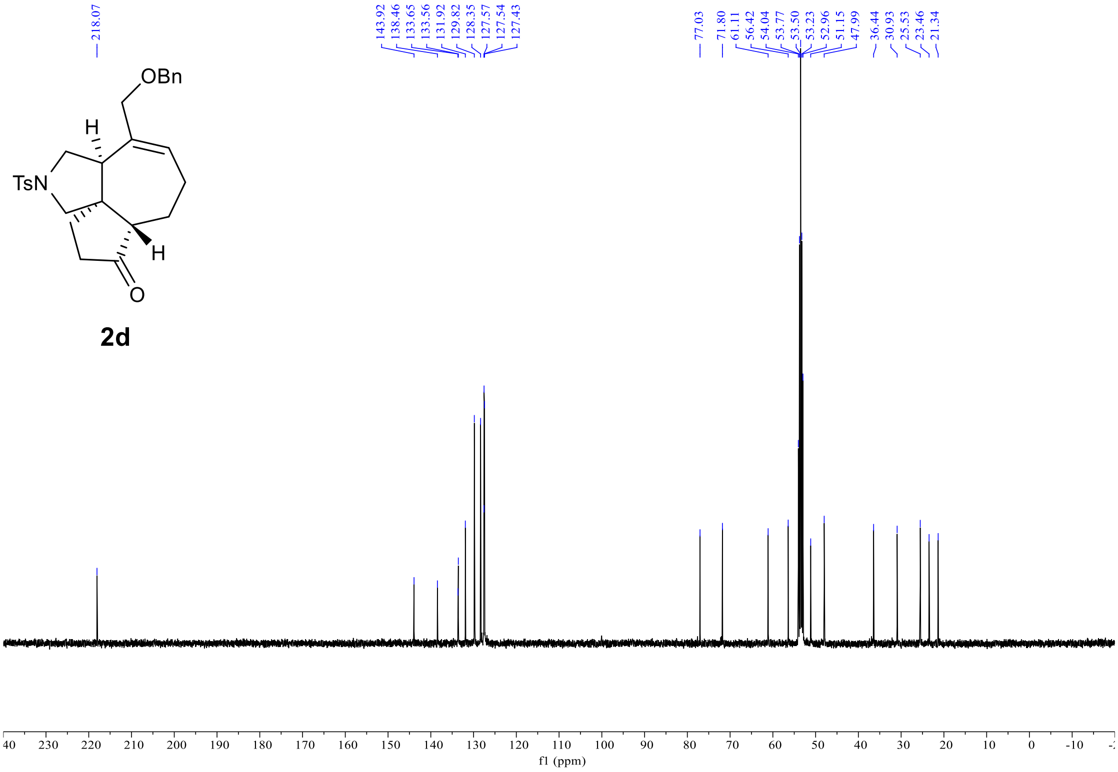
f1 (ppm)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61.11
56.42
54.04
53.77
53.50
53.23
52.96
51.15
47.99
36.44
30.93
25.53
23.46
21.34
OBn
H
TsN
H
O
2d
230
220
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
10
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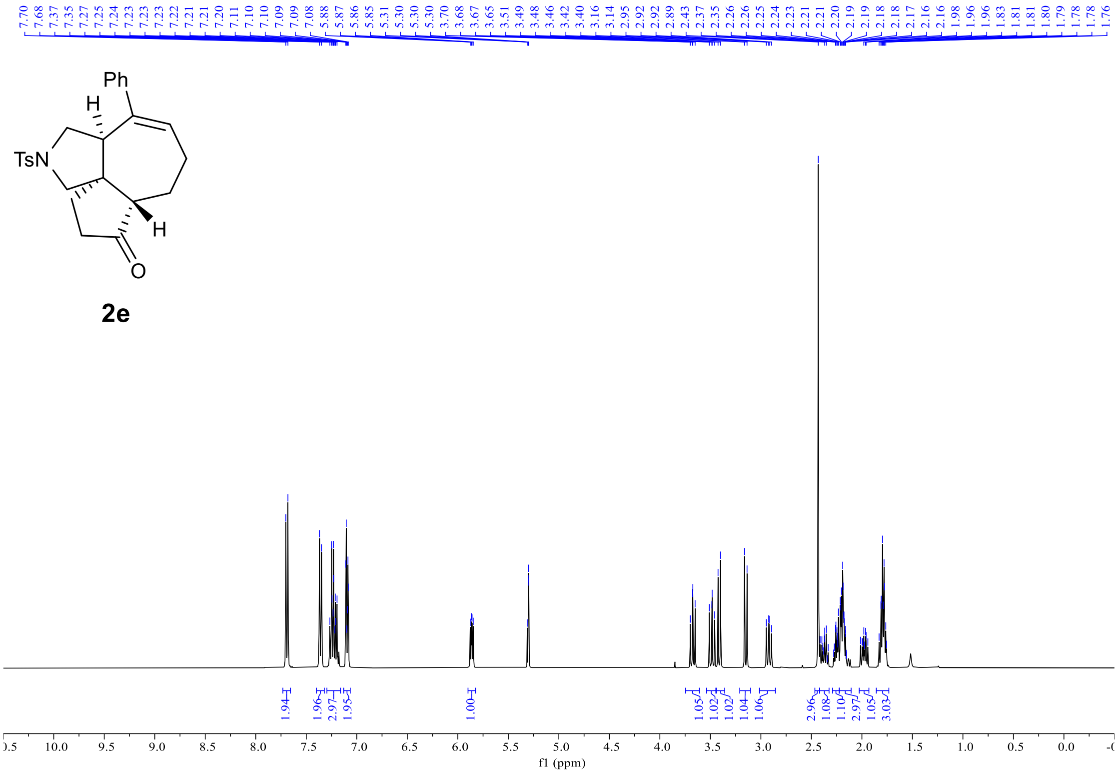
-10
f1 (ppm)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7.20
7.11
7.10
7.10
7.09
7.09
7.08
5.88
5.87
5.86
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5.31
5.30
5.30
5.30
3.70
3.68
3.67
3.65
3.51
3.49
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3.46
3.42
3.40
3.16
3.14
2.95
2.92
2.92
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2.43
2.37
2.35
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2.26
2.25
2.24
2.23
2.21
2.21
2.20
2.19
2.19
2.18
2.18
2.17
2.16
2.16
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1.96
1.96
1.83
1.81
1.81
1.80
1.79
1.78
1.78
1.76
Ph
H
TsN
H
O
2e
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1.00
1.05
1.02
1.02
1.04
1.06
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1.10
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1.0
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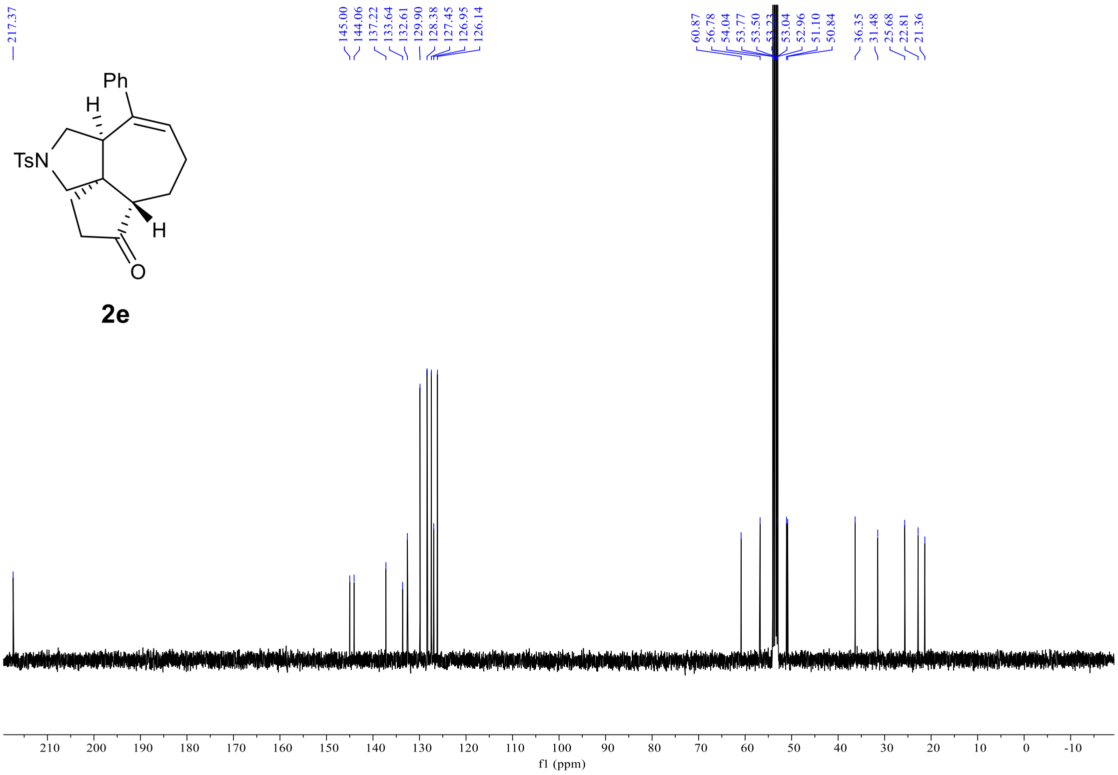
0.0
f1 (ppm)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53.77
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53.23
53.04
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51.10
50.84
36.35
31.48
25.68
22.81
21.36
Ph
H
TsN
H
O
2e
210
200
190
180
170
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100
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80
70
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30
20
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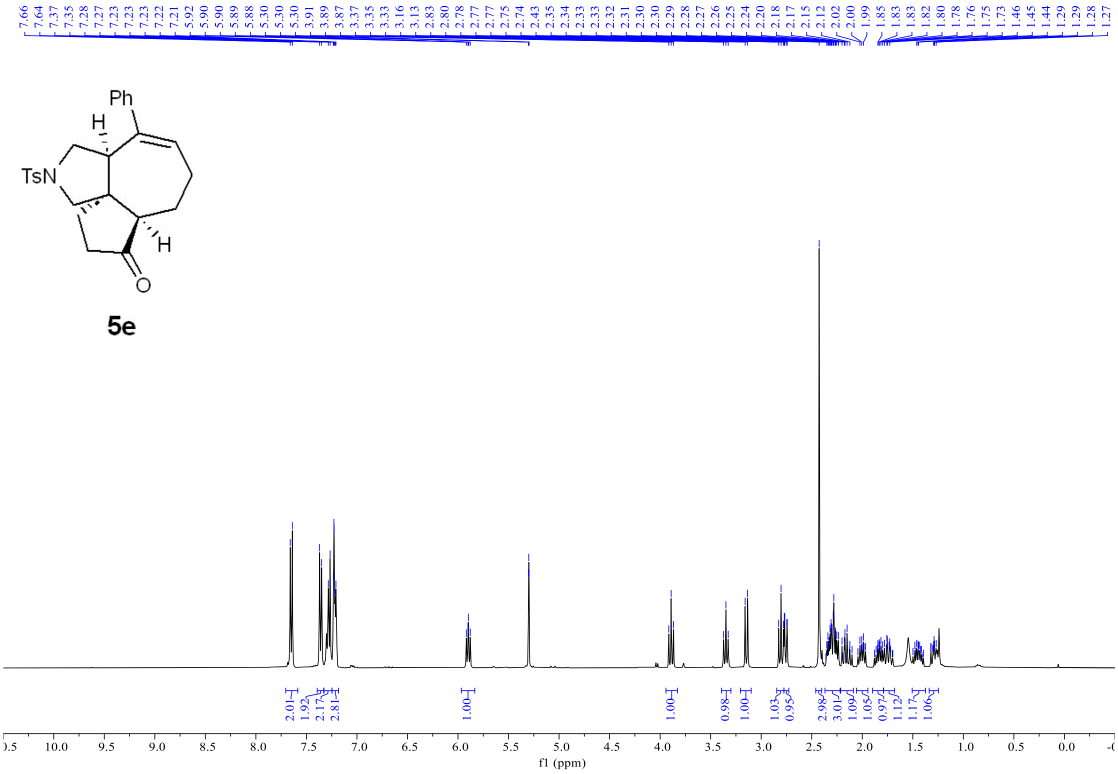
-10
f1 (ppm)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5.30
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3.89
3.87
3.37
3.35
3.33
3.16
3.13
2.83
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2.77
2.77
2.75
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1.83
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1.73
1.46
1.45
1.44
1.29
1.29
1.28
1.27
Ph
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TsN
H
O
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1.00
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3.01
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6.0
5.5
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2.5
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1.0
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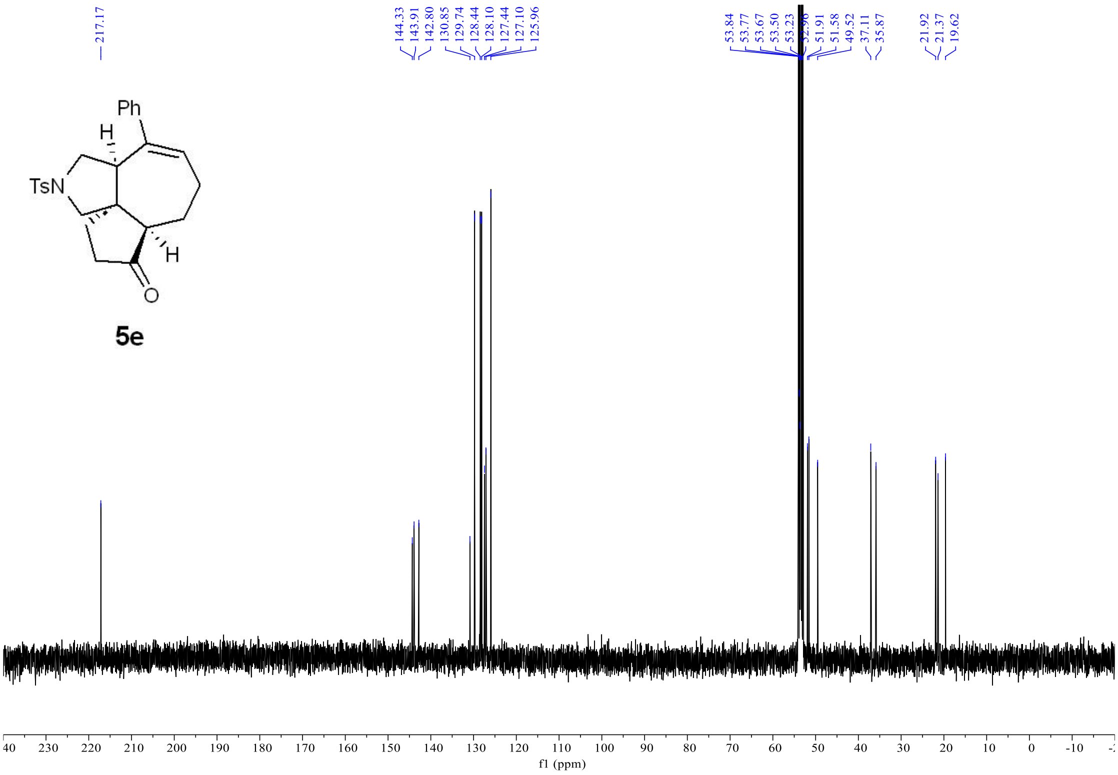
0.0
f1 (ppm)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127.44
127.10
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53.77
53.67
53.50
53.23
52.96
51.91
51.58
49.52
37.11
35.87
21.92
21.37
19.62
Ph
H
TsN
H
O
5e
230
220
210
200
190
180
170
160
150
140
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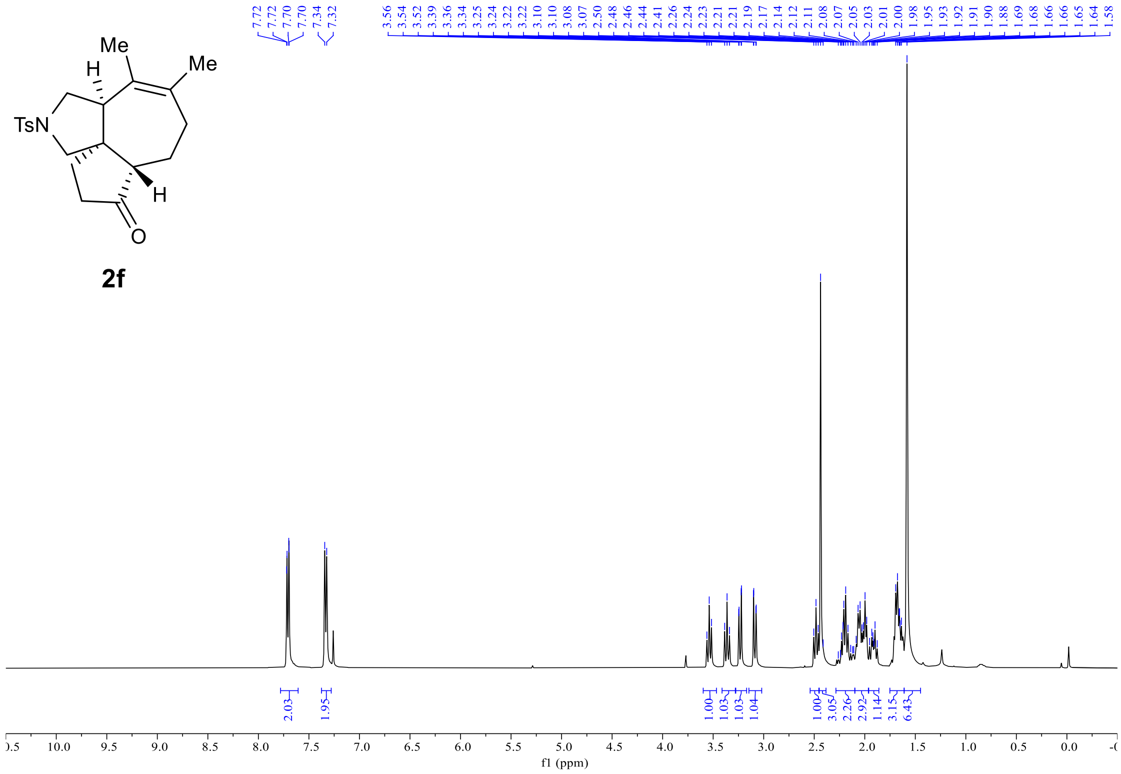
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
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Me
TsN
H
O
2f
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3.54
3.52
3.39
3.36
3.34
3.25
3.24
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3.22
3.10
3.10
3.08
3.07
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2.23
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1.91
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1.65
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1.00
1.03
1.03
1.04
1.00
3.05
2.26
2.92
1.14
3.15
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8.5
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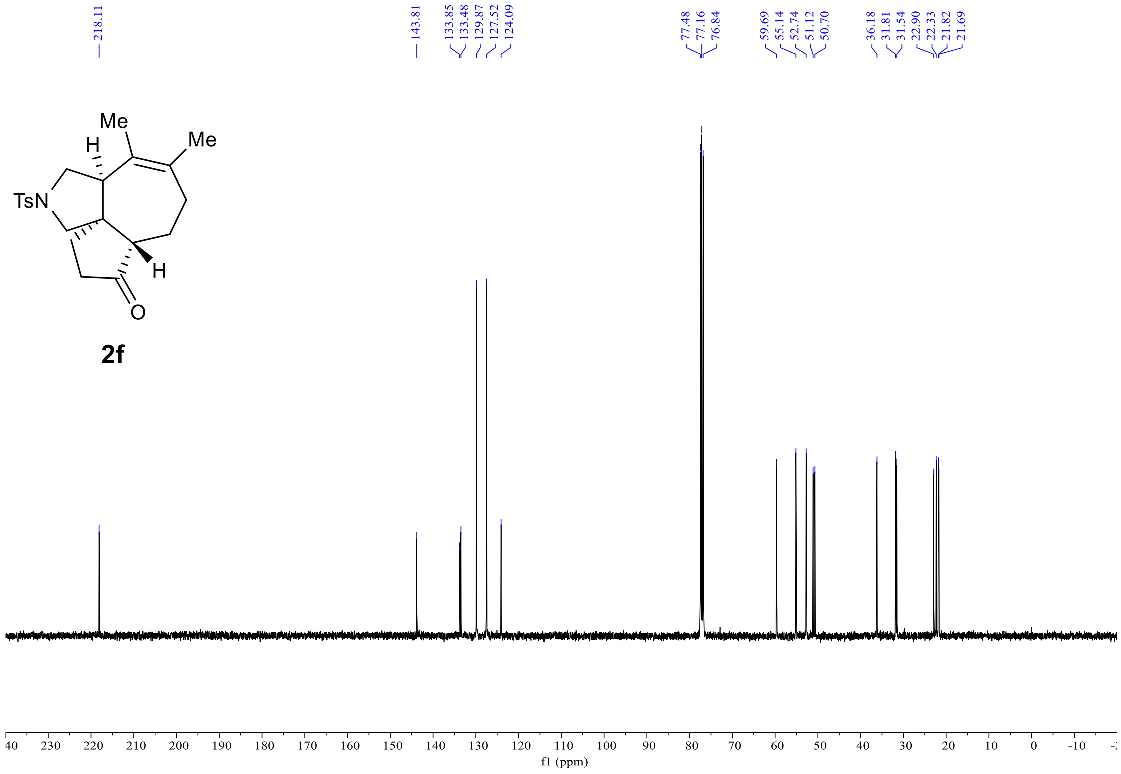
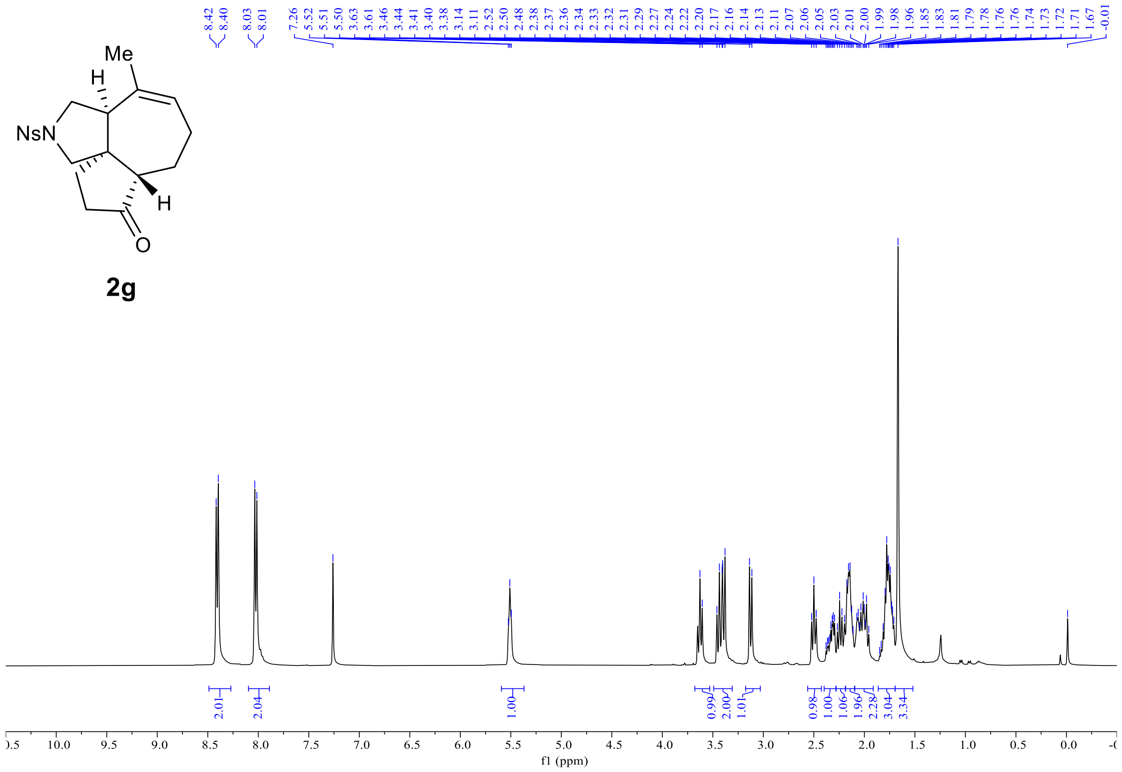
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


218.11
143.81
133.85
133.48
129.87
127.52
124.09
77.48
77.16
76.84
59.69
55.14
52.74
51.12
50.70
36.18
31.81
31.54
22.90
22.33
21.82
21.69
Me
H
Me
TsN
H
O
2f
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2g

Me
H
NsN
H
O
8.42
8.40
8.03
8.01
7.26
5.52
5.51
5.50
3.63
3.61
3.46
3.44
3.41
3.40
3.38
3.14
3.11
2.52
2.50
2.48
2.38
2.37
2.36
2.34
2.33
2.32
2.31
2.29
2.27
2.24
2.22
2.20
2.17
2.16
2.14
2.13
2.11
2.07
2.06
2.05
2.03
2.01
2.00
1.99
1.98
1.96
1.85
1.83
1.81
1.79
1.78
1.76
1.76
1.74
1.73
1.72
1.71
1.67
-0.01
2.01
2.04
1.00
0.99
2.00
1.01
0.98
1.00
1.06
1.96
2.28
3.04
3.34
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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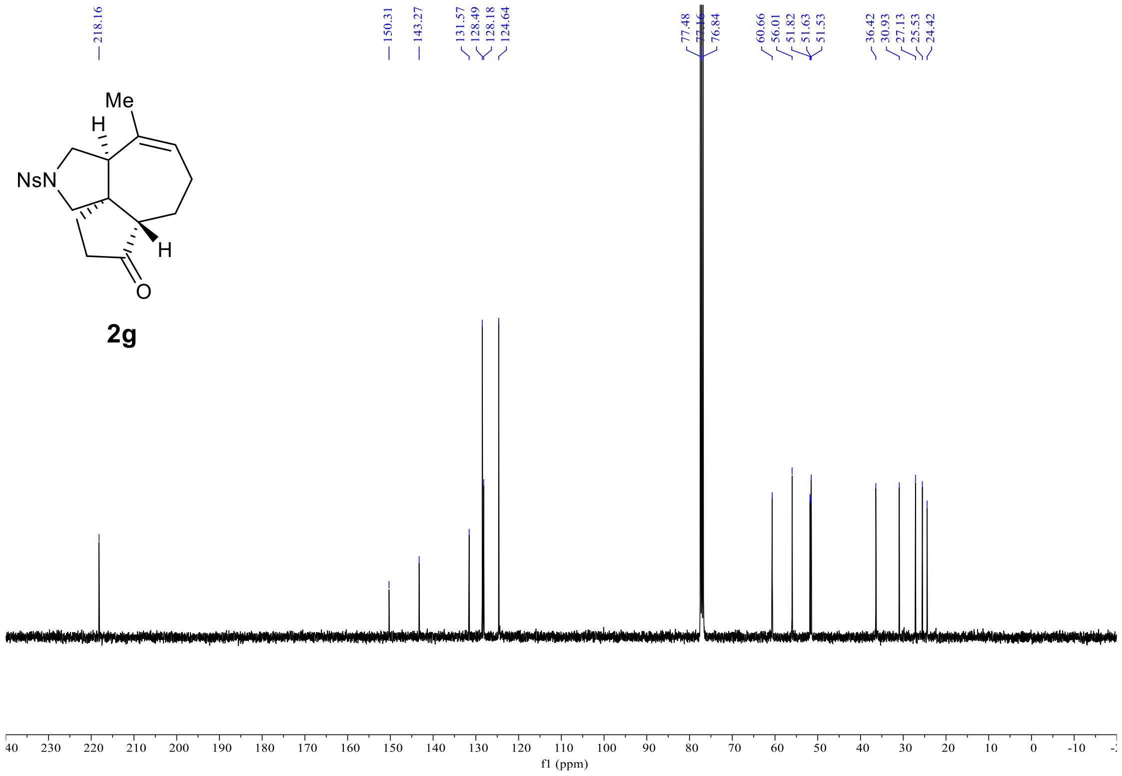
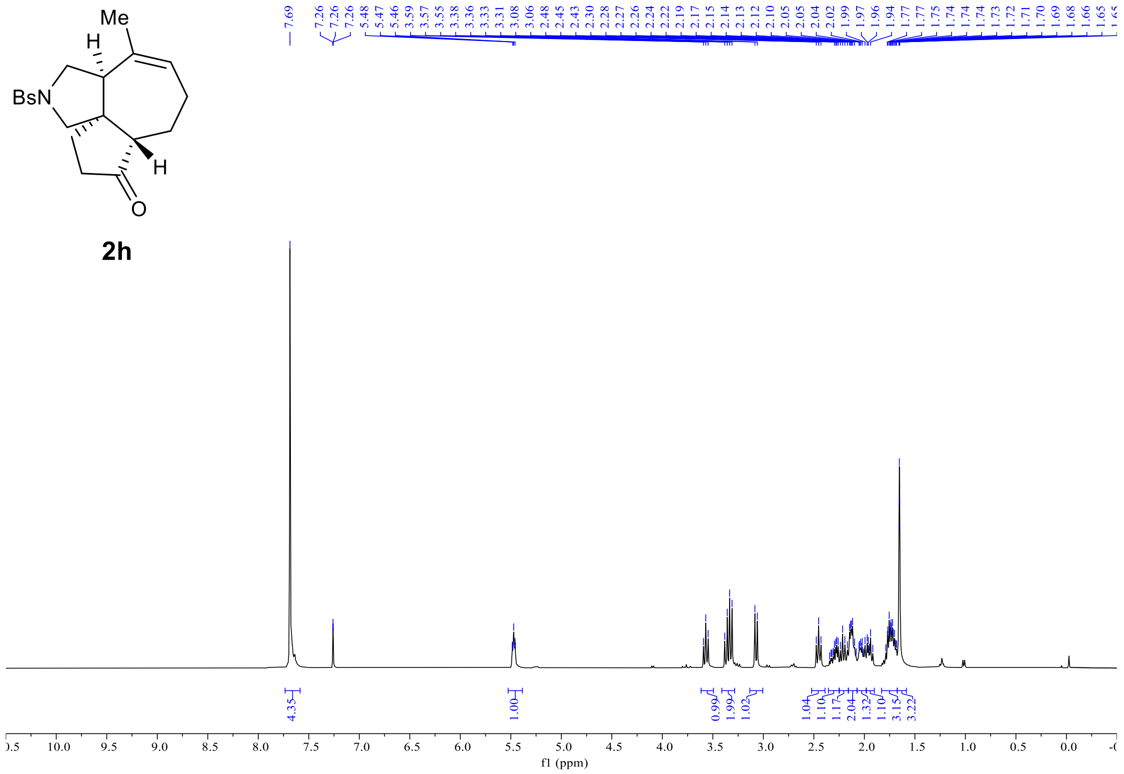
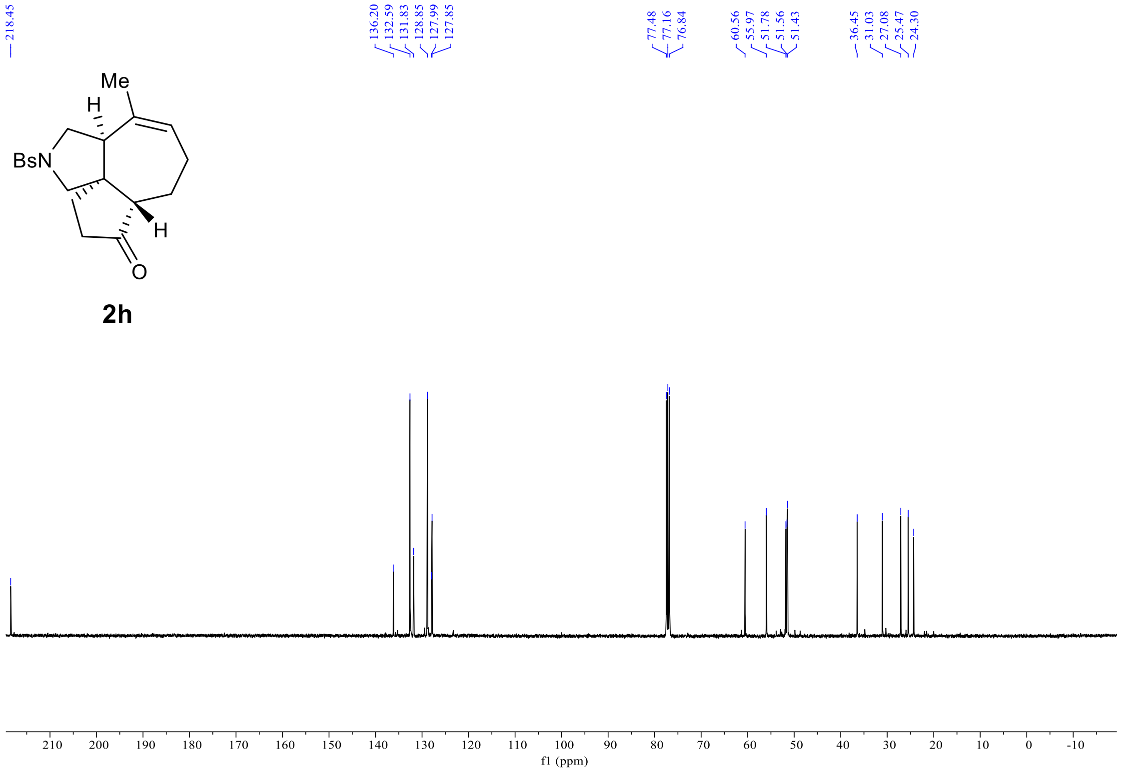
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2g

Me
H
NsN
H
O
218.16
150.31
143.27
131.57
128.49
128.18
124.64
77.48
77.16
76.84
60.66
56.01
51.82
51.63
51.53
36.42
30.93
27.13
25.53
24.42
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
H
BsN
H
O
7.69
7.26
7.26
7.26
5.48
5.47
5.46
3.59
3.57
3.55
3.38
3.36
3.33
3.31
3.08
3.06
2.48
2.45
2.43
2.30
2.28
2.27
2.26
2.24
2.22
2.19
2.17
2.15
2.14
2.13
2.12
2.10
2.05
2.05
2.04
2.02
1.99
1.97
1.96
1.94
1.77
1.77
1.75
1.74
1.74
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.66
1.65
4.35
1.00
0.99
1.99
1.02
1.04
1.10
1.17
2.04
1.32
1.10
3.15
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2h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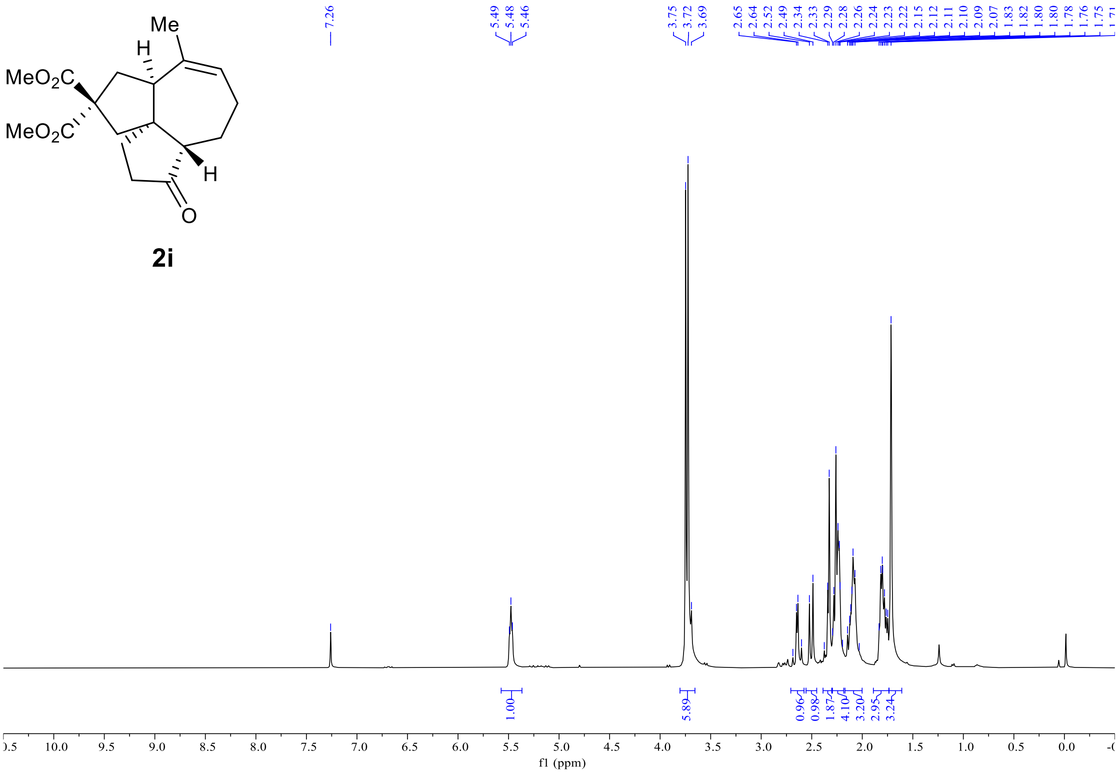
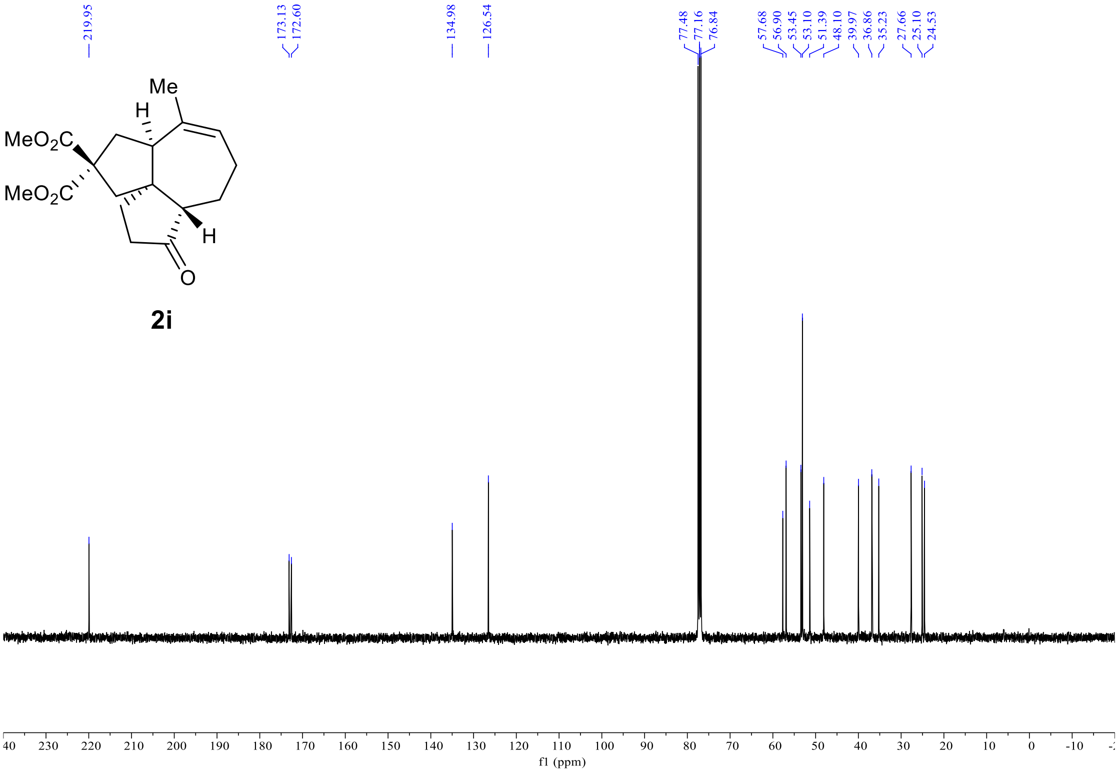
132.59
131.83
128.85
127.99
127.85
77.48
77.16
76.84
60.56
55.97
51.78
51.56
51.43
36.45
31.03
27.08
25.47
24.30
Me
H
BsN
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2h



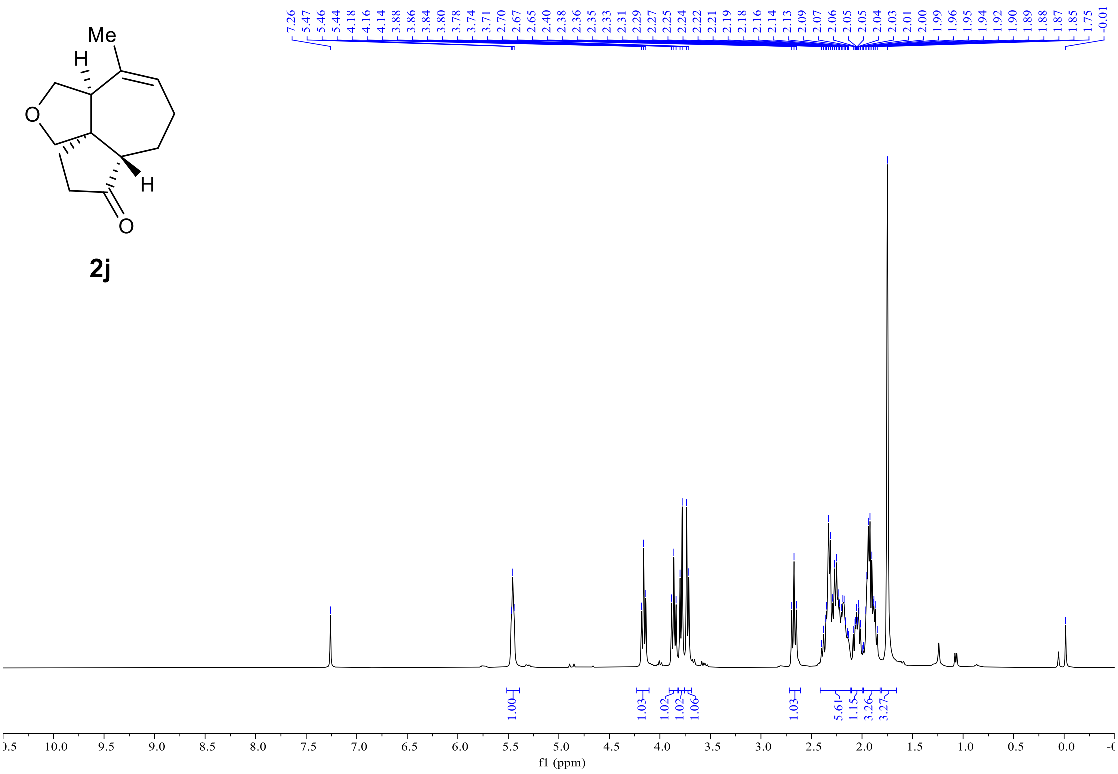
2i

Me
H
MeO2C
MeO2C
H
O
7.26
5.49
5.48
5.46
3.75
3.72
3.69
2.65
2.64
2.52
2.49
2.34
2.33
2.29
2.28
2.26
2.24
2.23
2.22
2.15
2.12
2.11
2.10
2.09
2.07
1.83
1.82
1.80
1.80
1.78
1.76
1.75
1.71
1.00
5.89
0.96
0.98
1.87
4.10
3.20
2.95
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

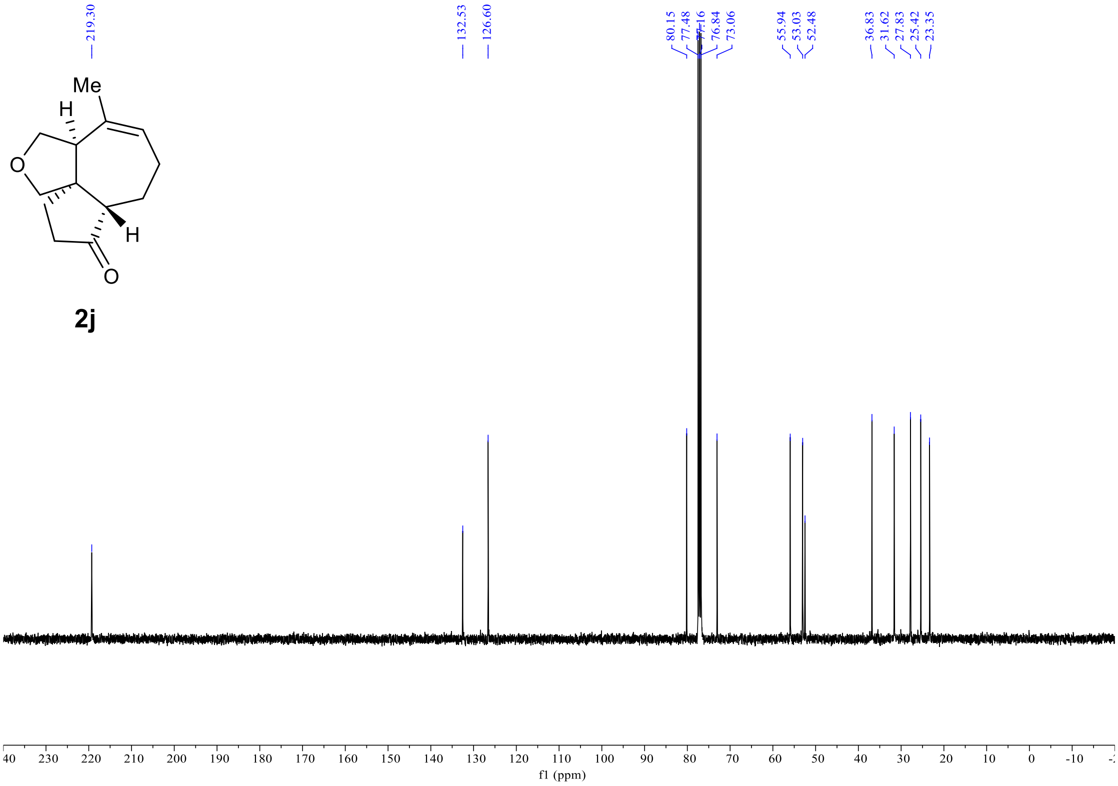


2i

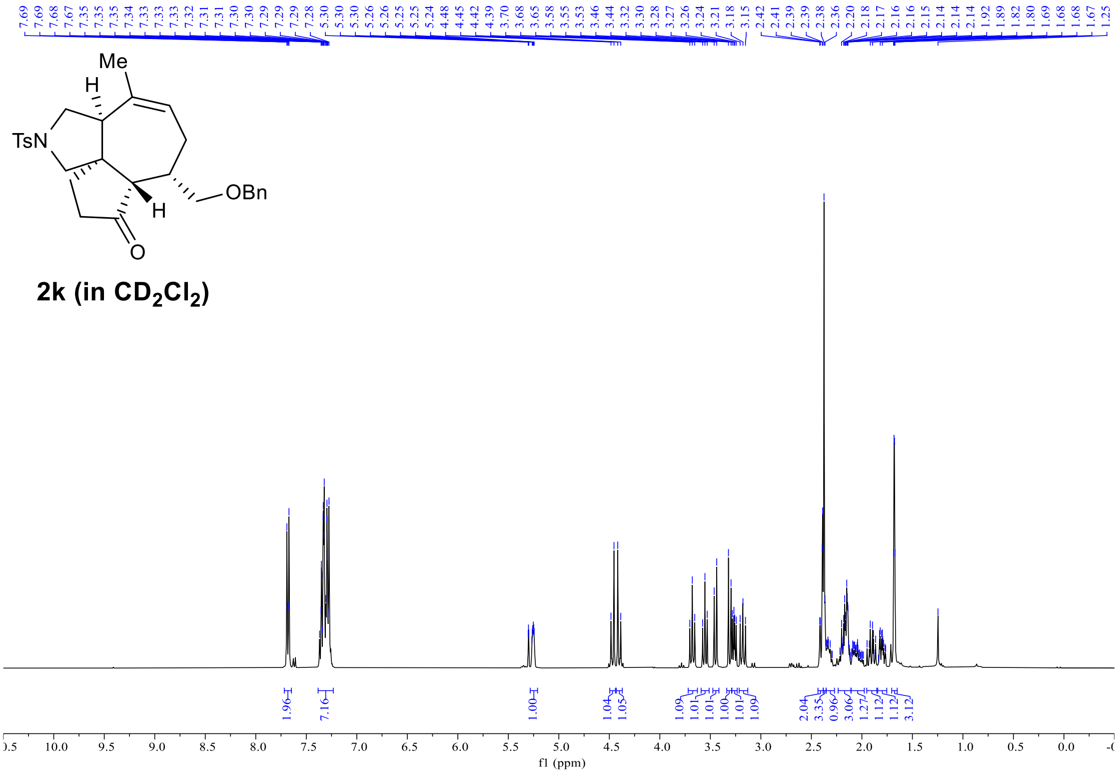
Me
H
MeO2C
MeO2C
H
O
219.95
173.13
172.60
134.98
126.54
77.48
77.16
76.84
57.68
56.90
53.45
53.10
51.39
48.10
39.97
36.86
35.23
27.66
25.10
24.53
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
H
O
H
O
7.26
5.47
5.46
5.44
4.18
4.16
4.14
3.88
3.86
3.84
3.80
3.78
3.74
3.71
2.70
2.67
2.65
2.40
2.38
2.36
2.35
2.33
2.31
2.29
2.27
2.25
2.24
2.22
2.21
2.19
2.18
2.16
2.14
2.13
2.09
2.07
2.06
2.05
2.05
2.04
2.03
2.01
2.00
1.99
1.96
1.95
1.94
1.92
1.90
1.89
1.88
1.87
1.85
1.75
-0.01
1.00
1.03
1.02
1.02
1.06
1.03
5.61
1.15
3.26
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

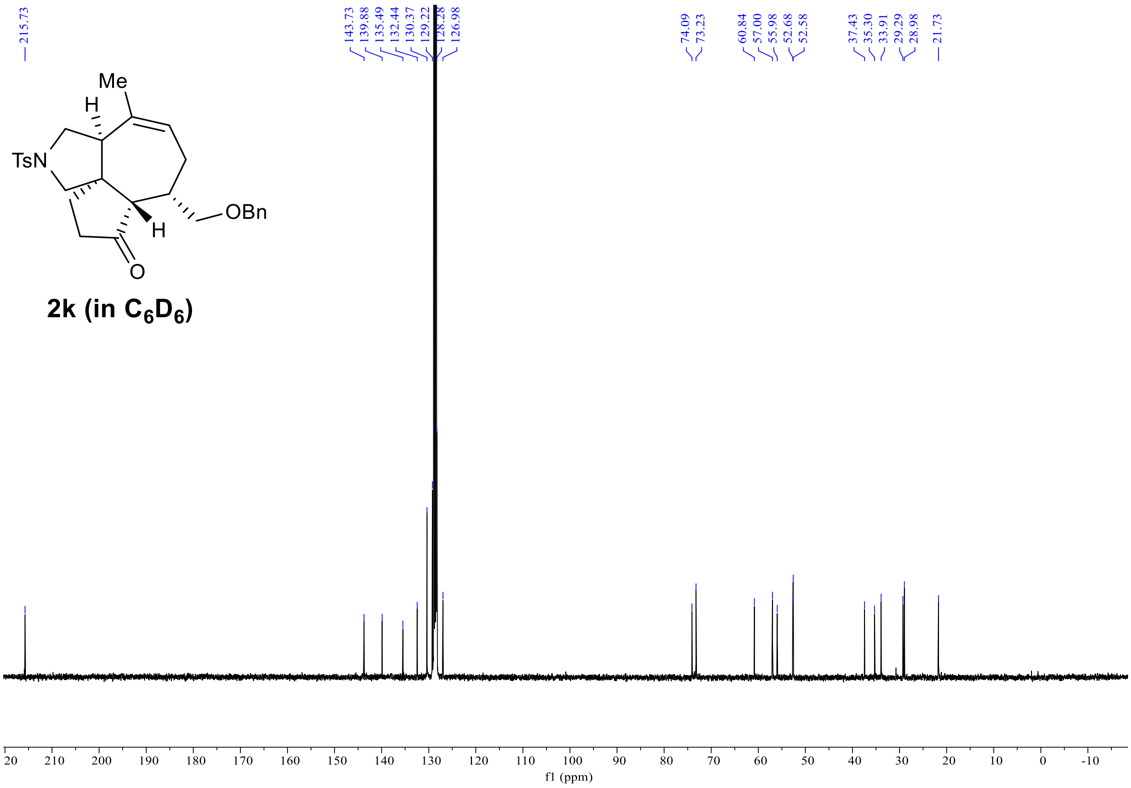
2j


Me
H
O
H
O
219.30
132.53
126.60
80.15
77.48
77.16
76.84
73.06
55.94
53.03
52.48
36.83
31.62
27.83
25.42
23.35
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

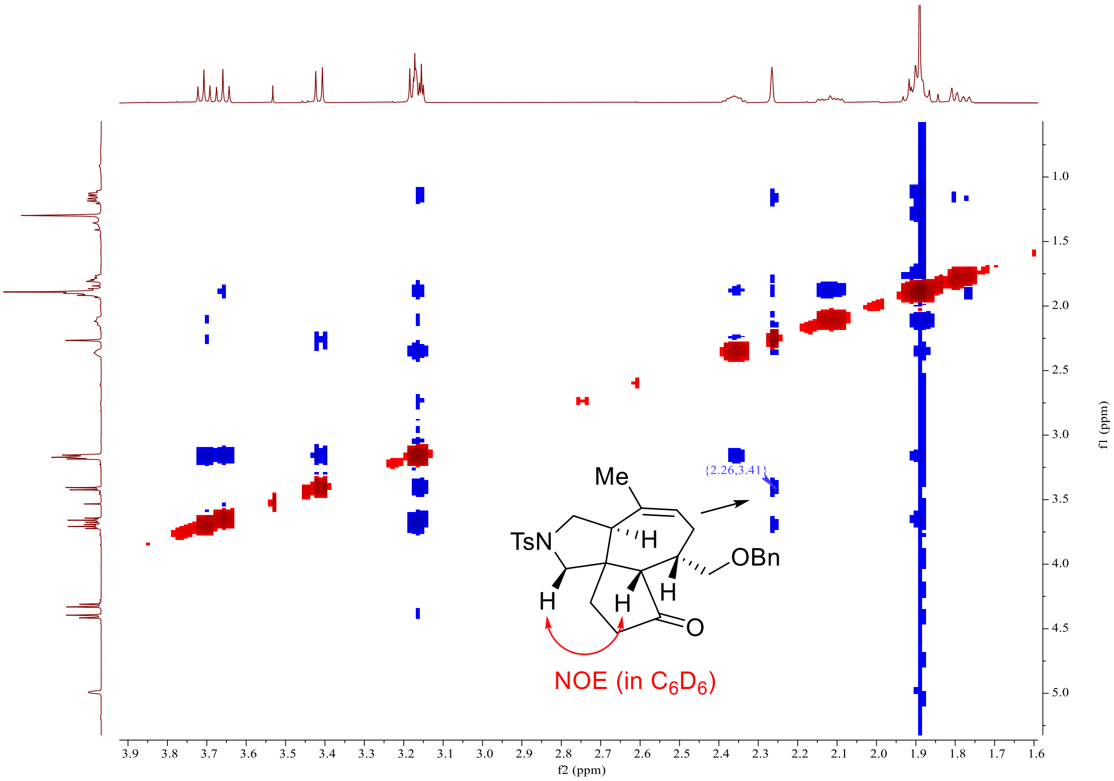
2j

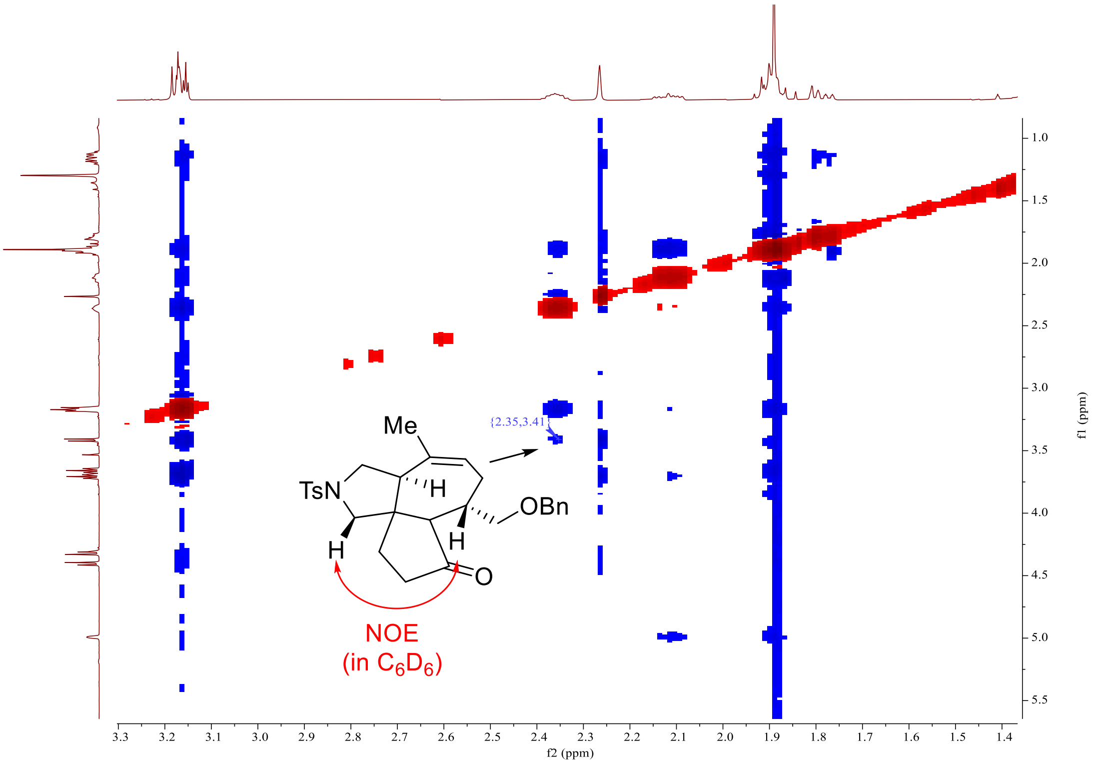


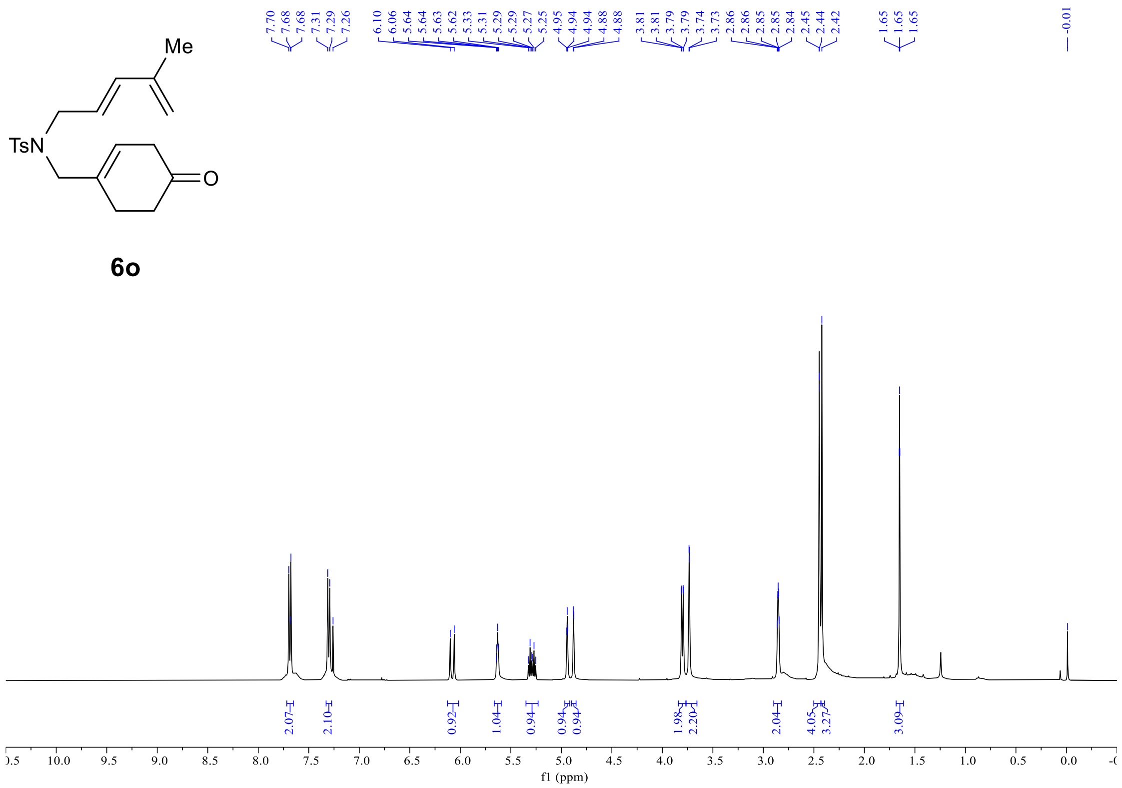
2k (in CD_2Cl_2)

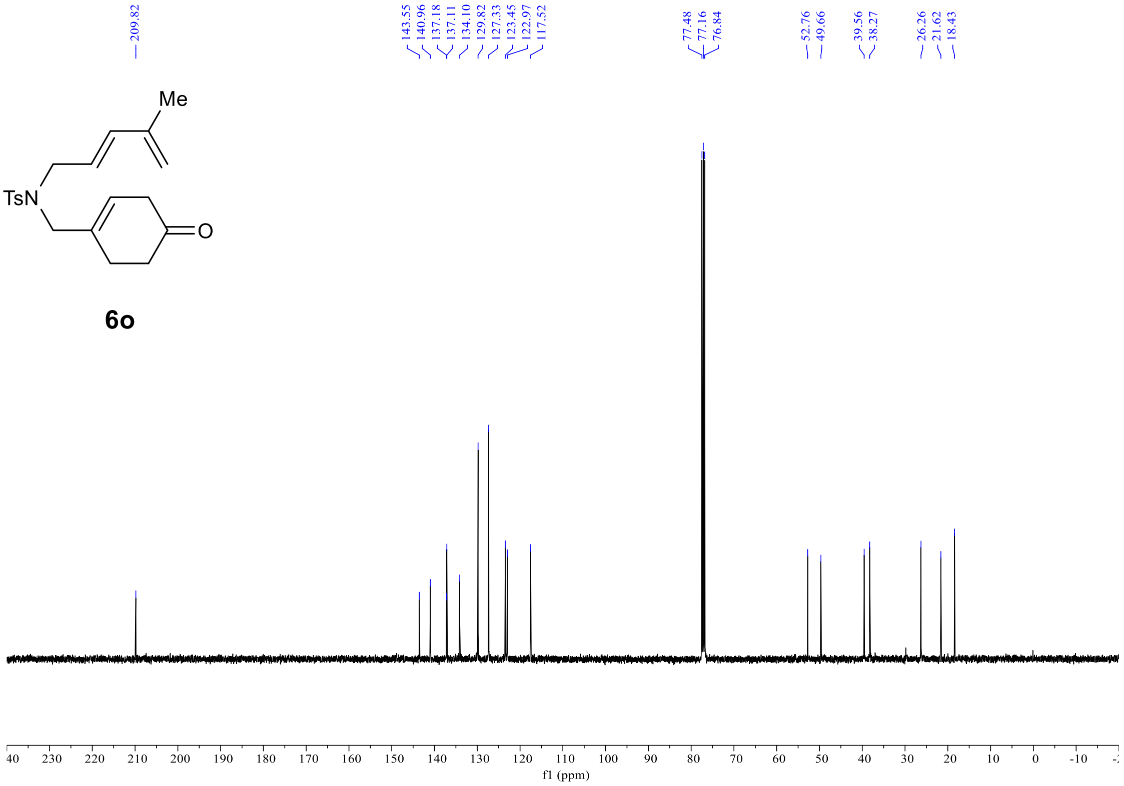


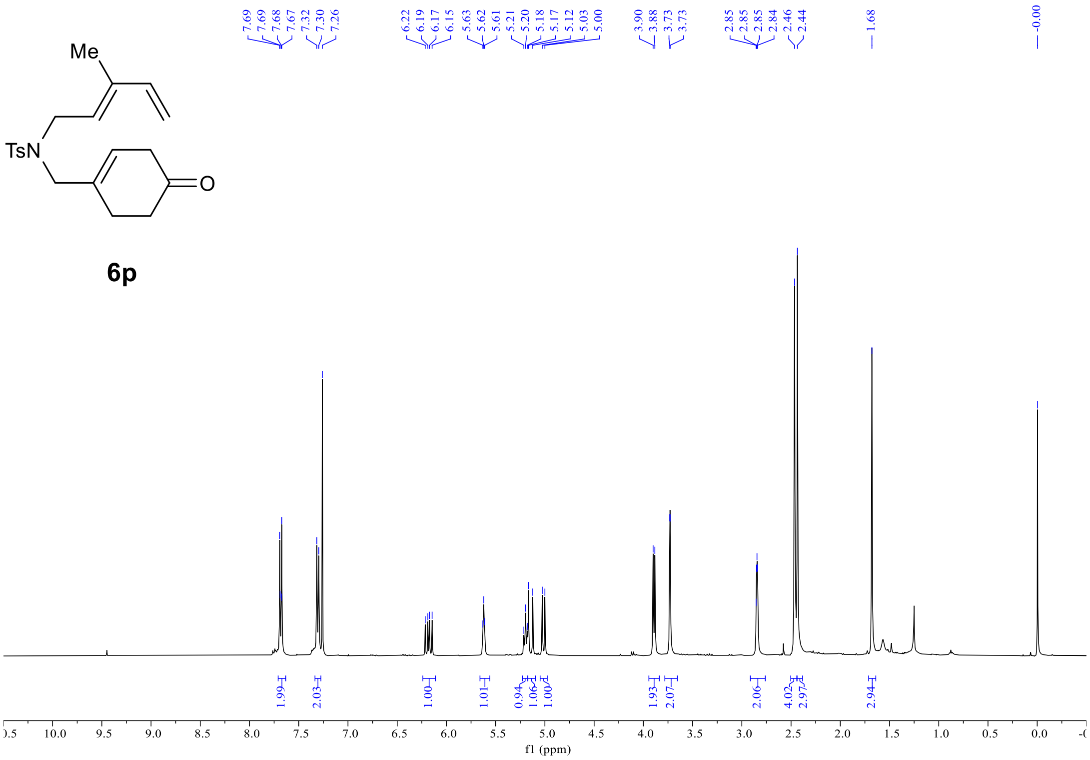
2k (in C_6D_6)


{2.26,3.41}
Me
TsN
H
OBn
O
NOE (in C6D6)
f2 (ppm)
f1 (ppm)

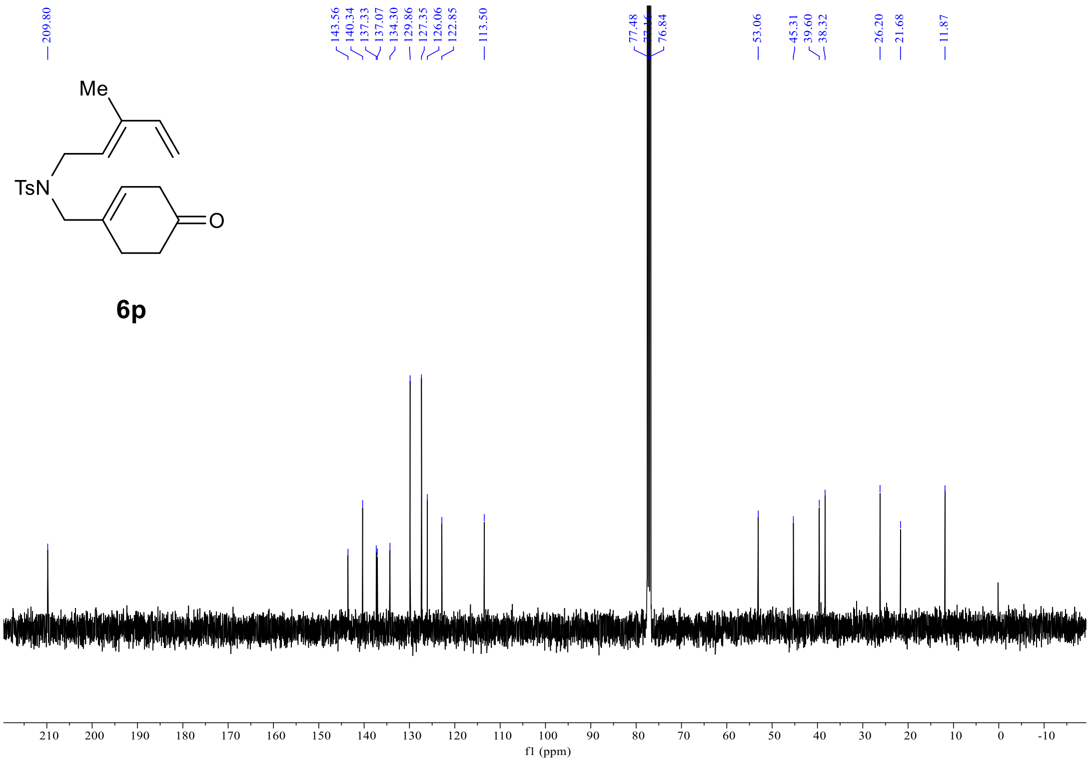

{2.35,3.41}
Me
TsN
H
OBn
O
NOE
(in C6D6)
f2 (ppm)
f1 (ppm)


7.70
7.68
7.68
7.31
7.29
7.26
6.10
6.06
5.64
5.64
5.63
5.62
5.33
5.31
5.29
5.29
5.27
5.25
4.95
4.94
4.94
4.88
4.88
3.81
3.81
3.79
3.79
3.74
3.73
2.86
2.86
2.85
2.85
2.84
2.45
2.44
2.42
1.65
1.65
1.65
-0.01
Me
TsN
O
6o
2.07
2.10
0.92
1.04
0.94
0.94
0.94
1.98
2.20
2.04
4.05
3.27
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

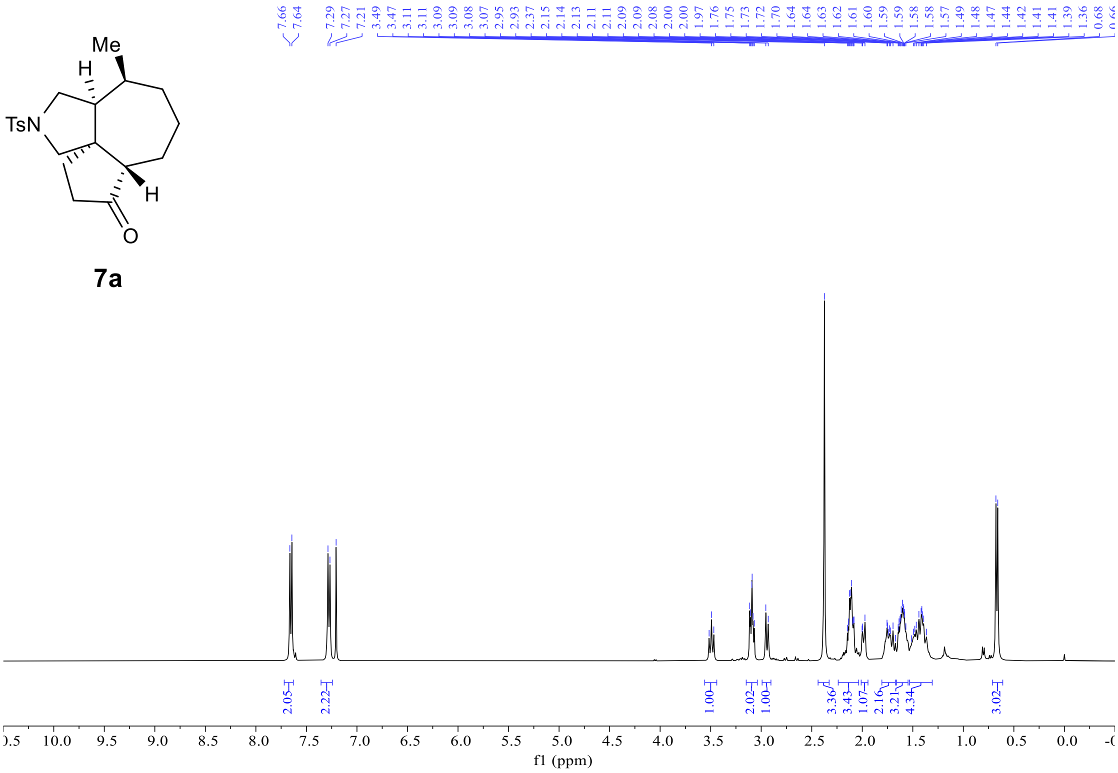

209.82
143.55
140.96
137.18
137.11
134.10
129.82
127.33
123.45
122.97
117.52
77.48
77.16
76.84
52.76
49.66
39.56
38.27
26.26
21.62
18.43
Me
TsN
O
6o
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


6p

Me
TsN
O
7.69
7.69
7.68
7.67
7.32
7.30
7.26
6.22
6.19
6.17
6.15
5.63
5.62
5.61
5.21
5.20
5.18
5.17
5.12
5.03
5.00
3.90
3.88
3.73
3.73
2.85
2.85
2.85
2.84
2.46
2.44
1.68
-0.00
1.99
2.03
1.00
1.01
0.94
1.06
1.00
1.93
2.07
2.06
4.02
2.97
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


6p

Me
TsN
O
209.80
143.56
140.34
137.33
137.07
134.30
129.86
127.35
126.06
122.85
113.50
77.48
77.16
76.84
53.06
45.31
39.60
38.32
26.20
21.68
11.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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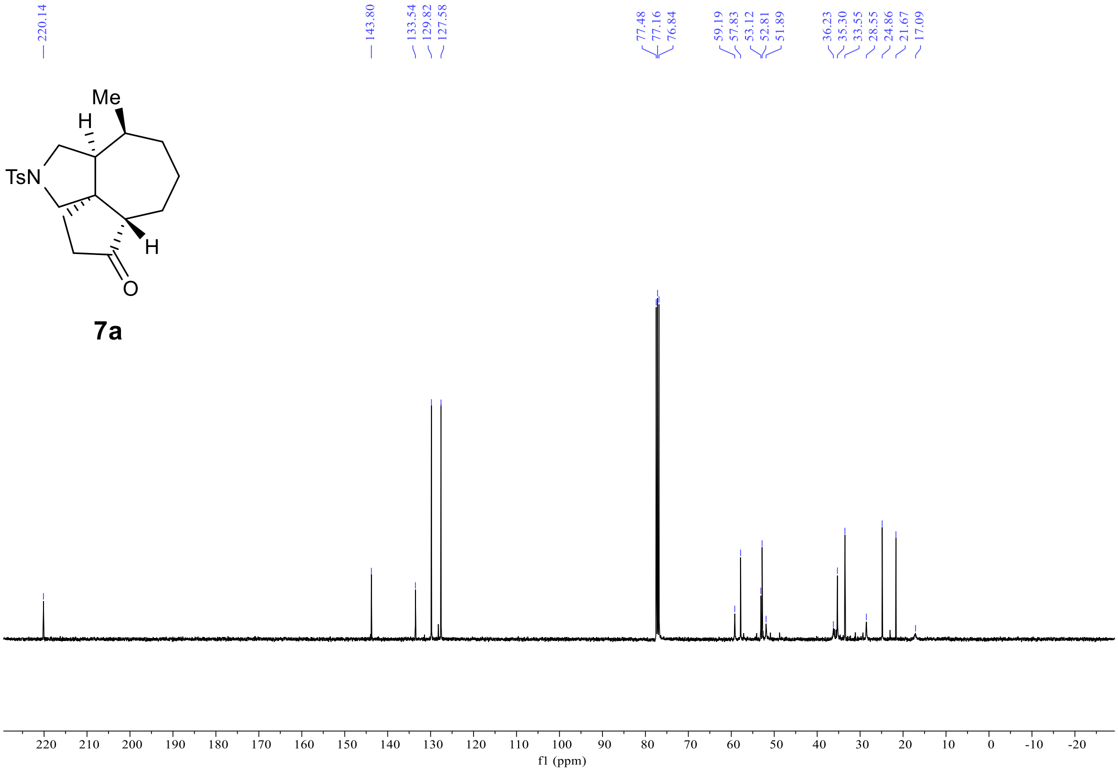
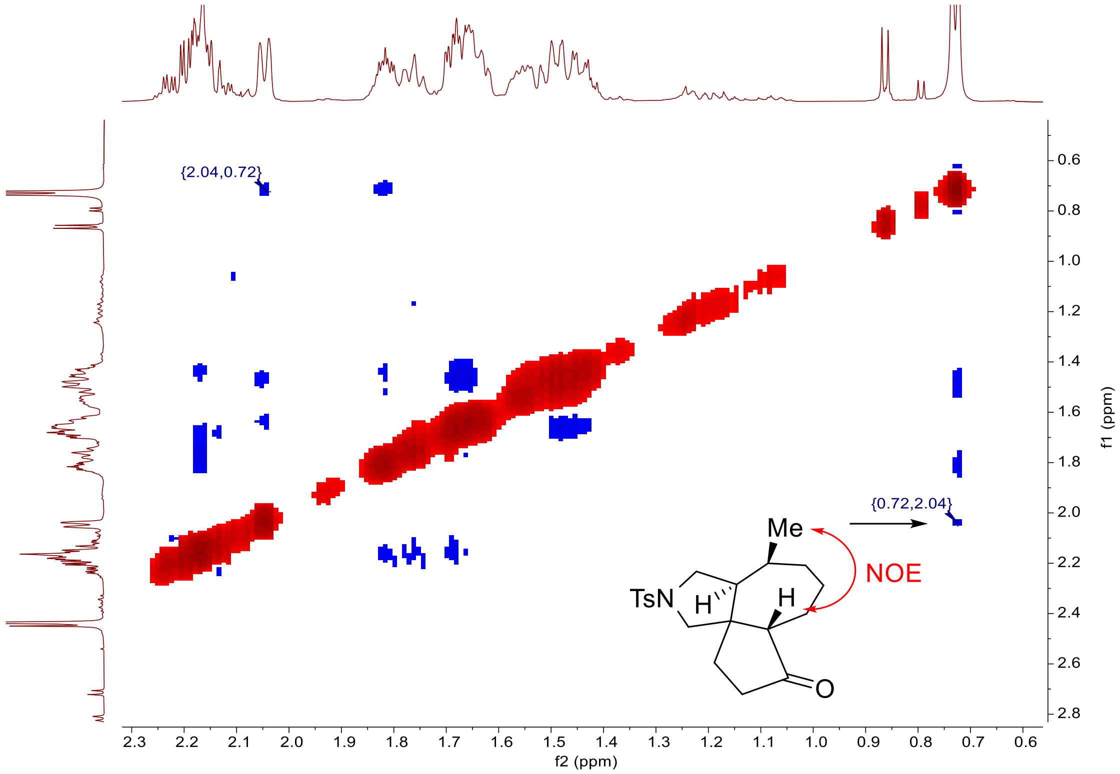
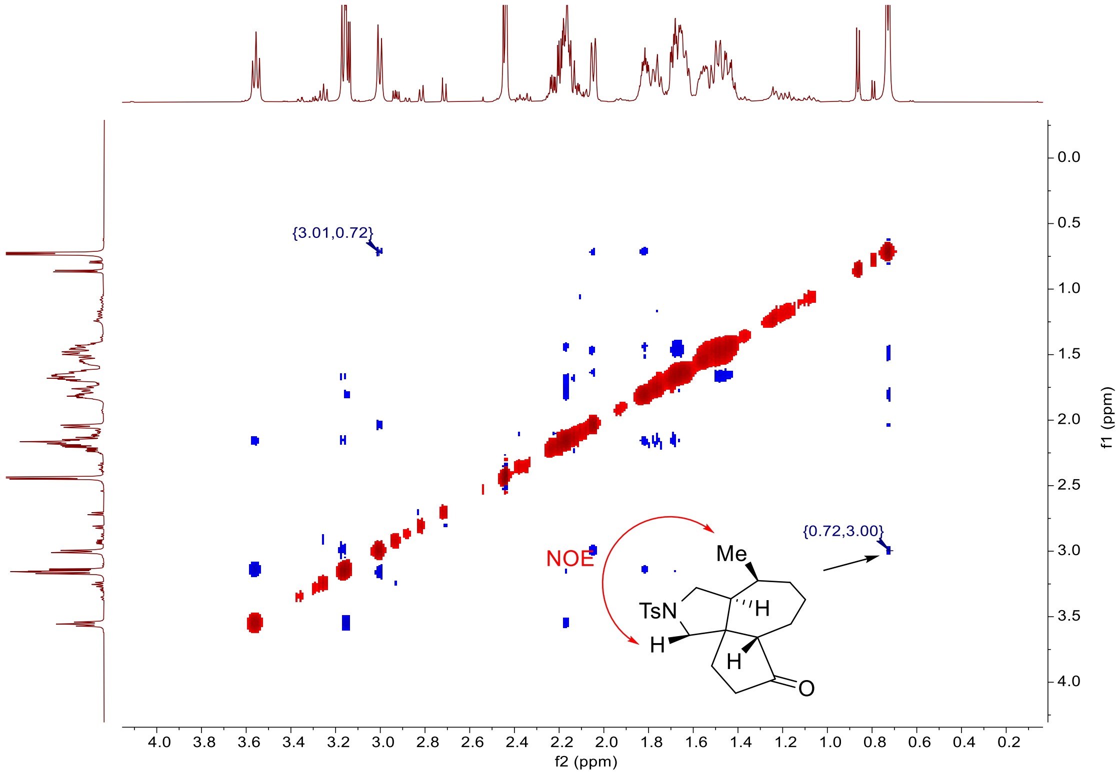
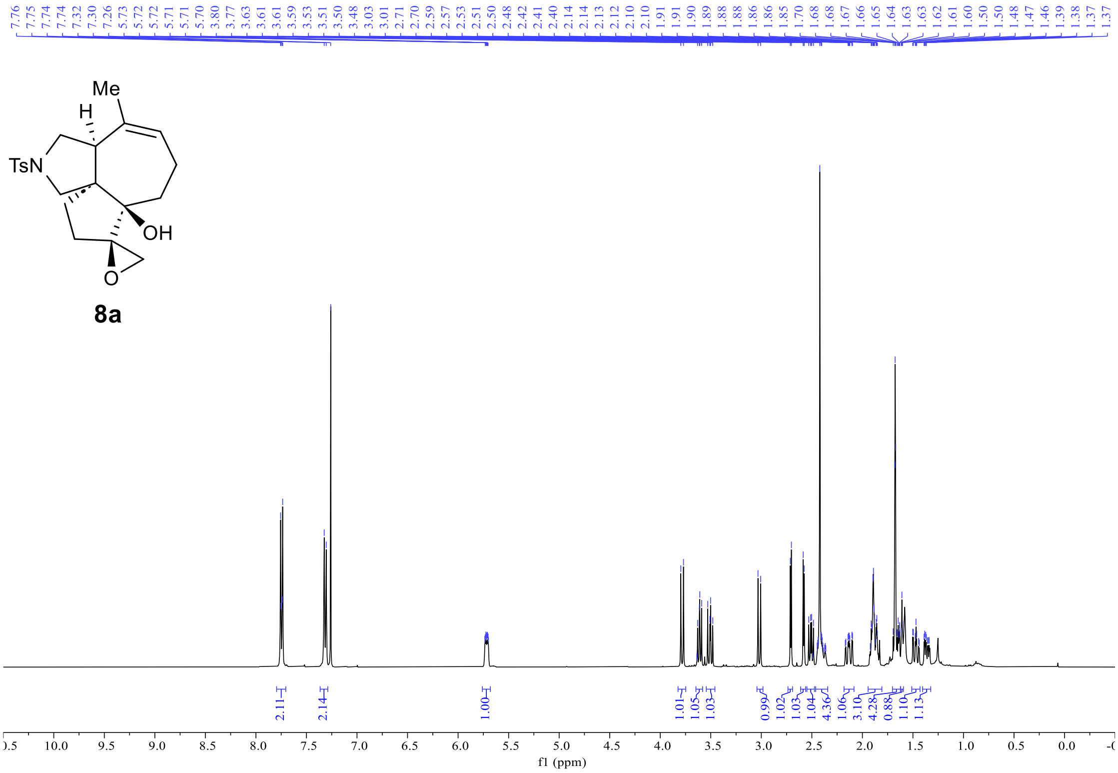
7.27
7.21
3.49
3.47
3.11
3.11
3.09
3.09
3.08
3.07
2.95
2.93
2.37
2.15
2.14
2.13
2.11
2.11
2.09
2.09
2.08
2.00
2.00
1.97
1.76
1.75
1.73
1.72
1.70
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.49
1.48
1.47
1.44
1.42
1.41
1.41
1.39
1.36
0.68
Me
H
TsN
H
O
7a
2.05
2.22
1.00
2.02
1.00
3.36
3.43
1.07
2.16
3.21
4.34
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


220.14
143.80
133.54
129.82
127.58
77.48
77.16
76.84
59.19
57.83
53.12
52.81
51.89
36.23
35.30
33.55
28.55
24.86
21.67
17.09
Me
H
TsN
H
O
7a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


{2.04,0.72}
{0.72,2.04}
Me
NOE
TsN
H
H
O
f2 (ppm)
f1 (ppm)
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8


{3.01,0.72}
{0.72,3.00}
NOE
Me
TsN
H
H
H
O
f2 (ppm)
f1 (ppm)
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0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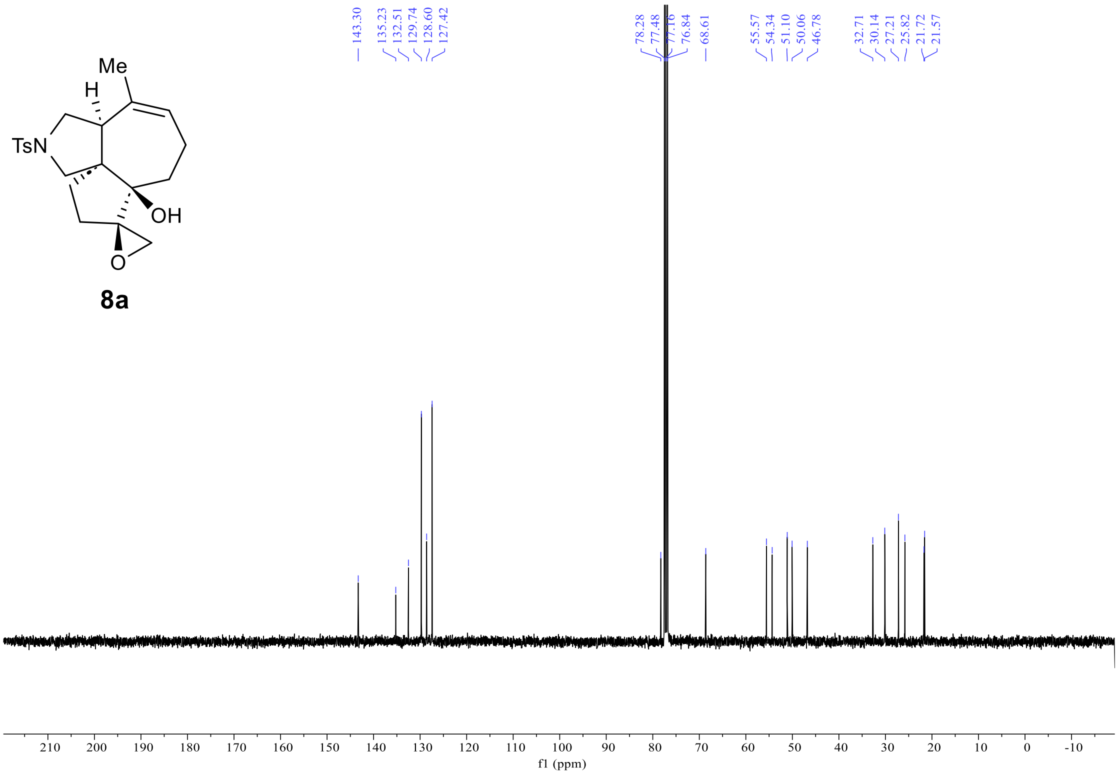
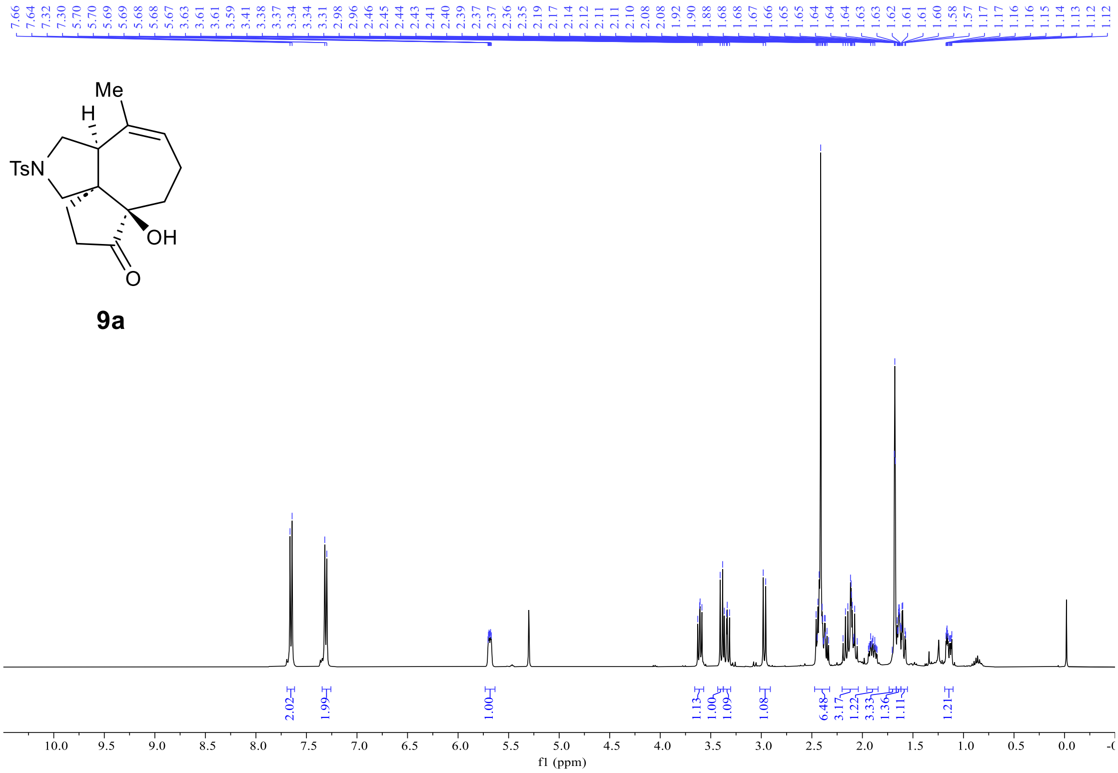
7.74
7.32
7.30
7.26
5.73
5.72
5.72
5.71
5.71
5.70
3.80
3.77
3.63
3.61
3.61
3.59
3.53
3.51
3.50
3.48
3.03
3.01
2.71
2.70
2.59
2.57
2.53
2.51
2.50
2.48
2.42
2.41
2.40
2.14
2.14
2.13
2.12
2.10
2.10
1.91
1.91
1.90
1.89
1.88
1.88
1.86
1.86
1.85
1.70
1.68
1.68
1.67
1.66
1.65
1.64
1.63
1.63
1.62
1.61
1.60
1.50
1.50
1.48
1.47
1.46
1.39
1.38
1.37
1.37
Me
H
TsN
OH
O
8a
2.11
2.14
1.00
1.01
1.05
1.03
0.99
1.02
1.03
1.04
4.36
1.06
3.10
4.28
0.88
1.10
1.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.30
135.23
132.51
129.74
128.60
127.42
78.28
77.48
77.16
76.84
68.61
55.57
54.34
51.10
50.06
46.78
32.71
30.14
27.21
25.82
21.72
21.57
Me
H
TsN
OH
O
8a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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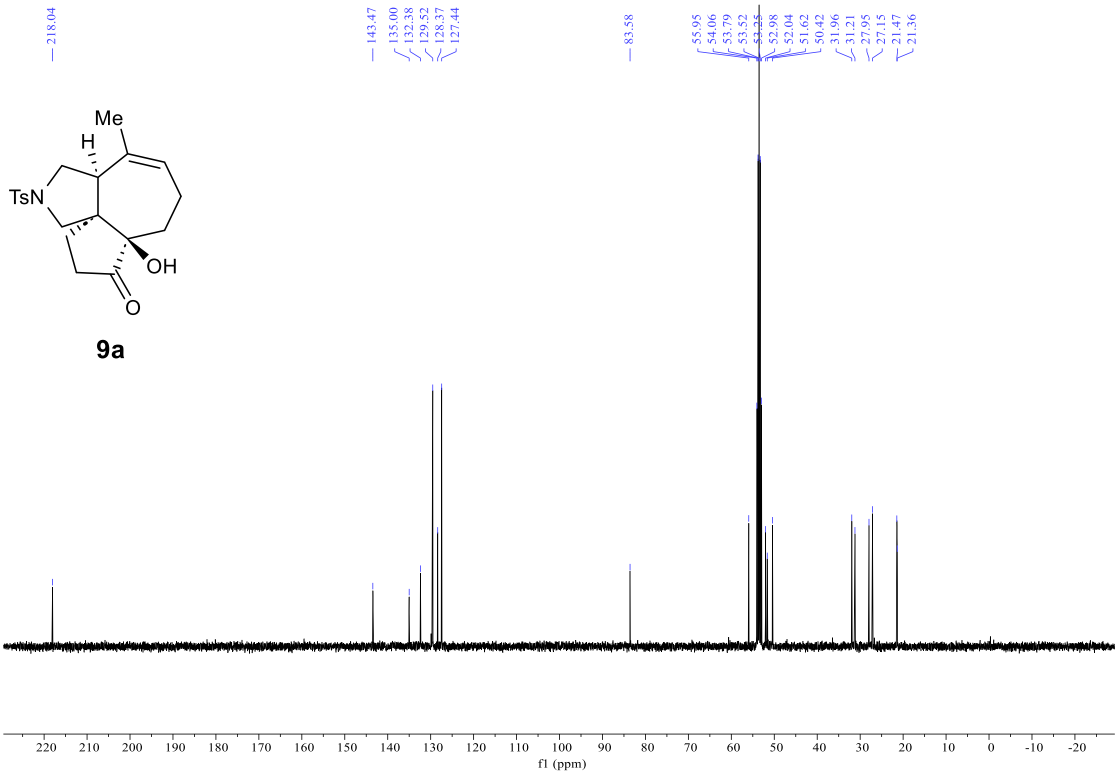
Me
H
TsN
OH
O
9a
2.02
1.99
1.00
1.13
1.00
1.09
1.08
6.48
3.17
1.22
3.33
1.36
1.11
1.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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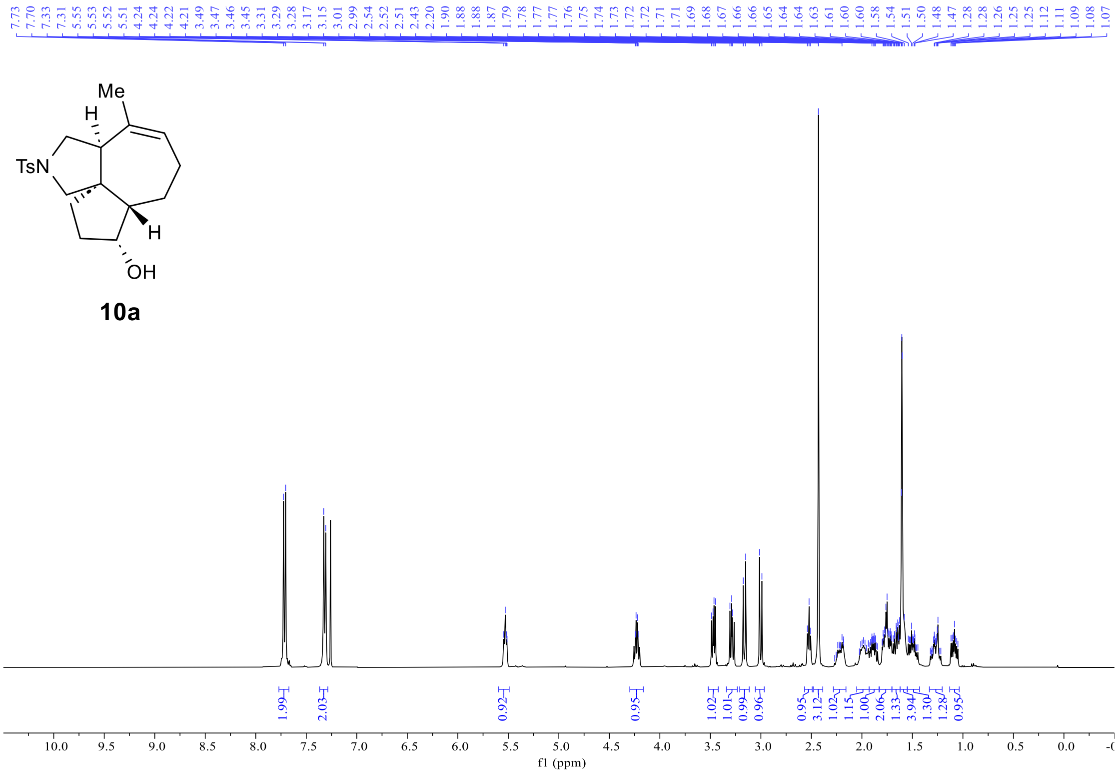
143.47 135.00 132.38 129.52 128.37 127.44
83.58
55.95 54.06 53.79 53.52 53.25 52.98 52.04 51.62 50.42 31.96 31.21 27.95 27.15 21.47 21.36
Me
H
TsN
OH
O
9a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



7.73
7.70
7.33
7.31
5.55
5.53
5.52
5.51
4.24
4.24
4.22
4.21
3.49
3.47
3.46
3.45
3.31
3.29
3.28
3.17
3.15
3.01
2.99
2.54
2.52
2.51
2.43
2.20
1.90
1.88
1.88
1.87
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.72
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1.71
1.69
1.68
1.67
1.66
1.66
1.65
1.64
1.64
1.63
1.61
1.60
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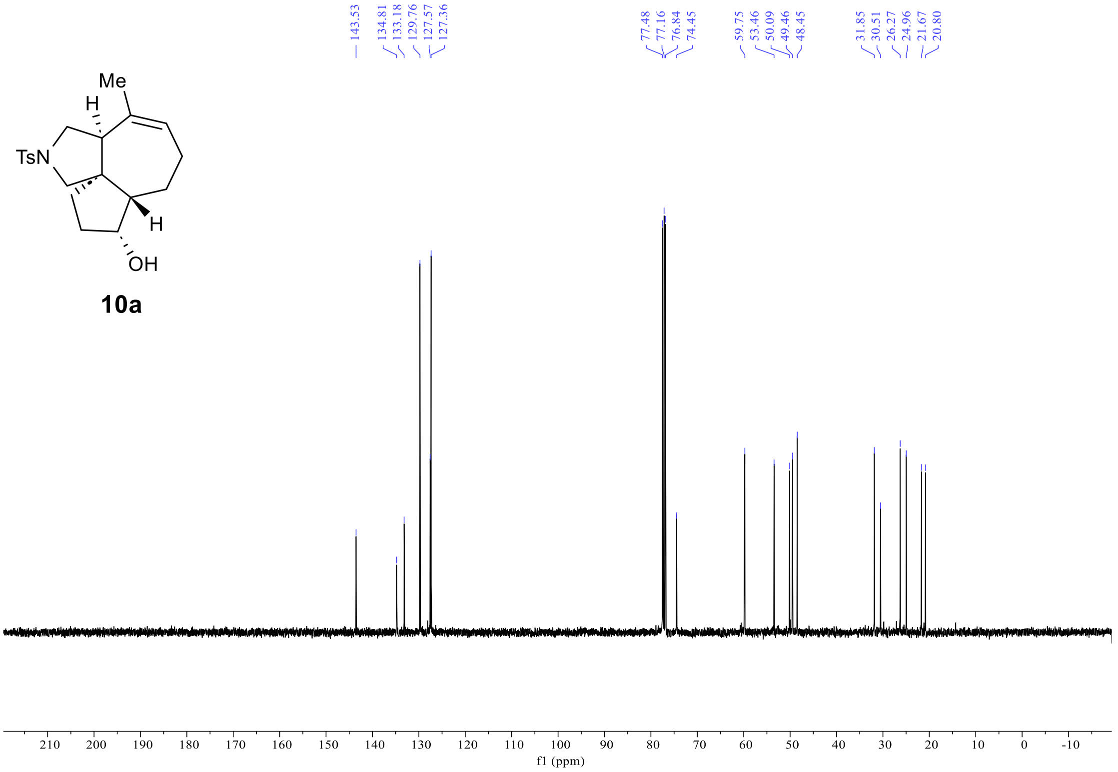
1.50
1.48
1.47
1.28
1.28
1.26
1.25
1.25
1.12
1.11
1.09
1.08
1.07
Me
H
TsN
H
OH
1.99
2.03
0.92
0.95
1.02
1.01
0.99
0.96
0.95
3.12
1.02
1.15
1.00
2.06
1.33
3.94
1.30
1.28
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10a



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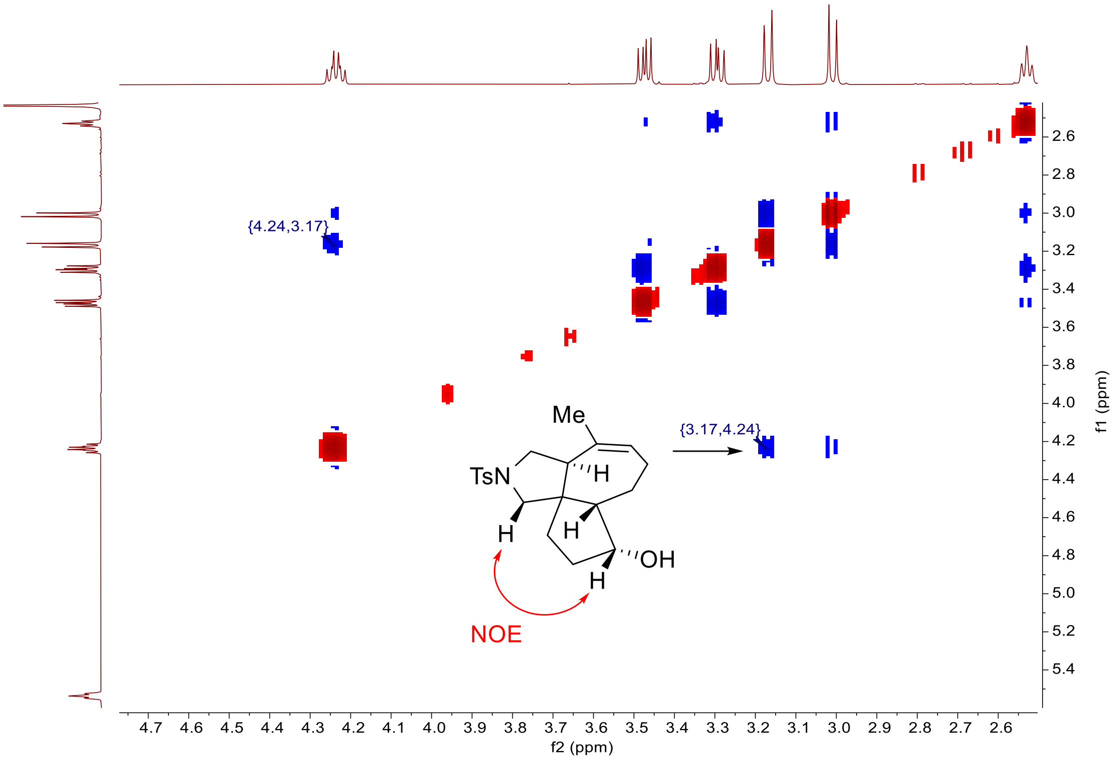
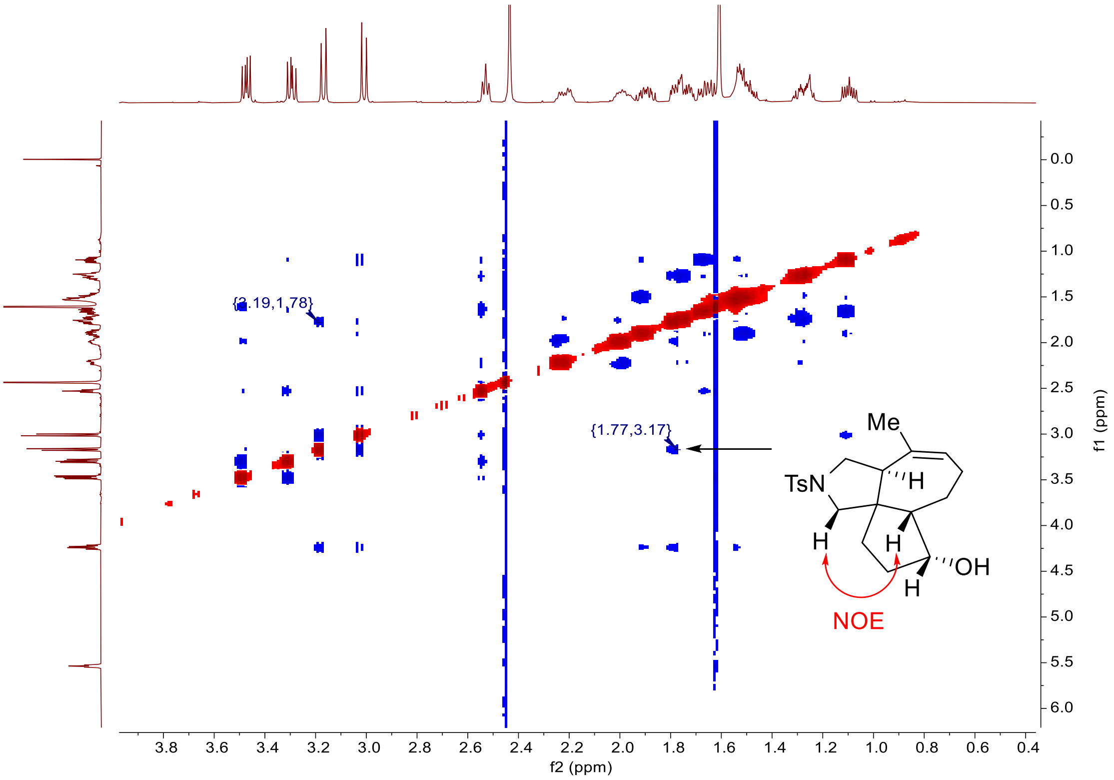
134.81
133.18
129.76
127.57
127.36
77.48
77.16
76.84
74.45
59.75
53.46
50.09
49.46
48.45
31.85
30.51
26.27
24.96
21.67
20.80
Me
H
TsN
H
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10a


{4.24,3.17}
{3.17,4.24}
Me
TsN
H
H
H
H
OH
NOE
4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6
f2 (ppm)
2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4
f1 (ppm)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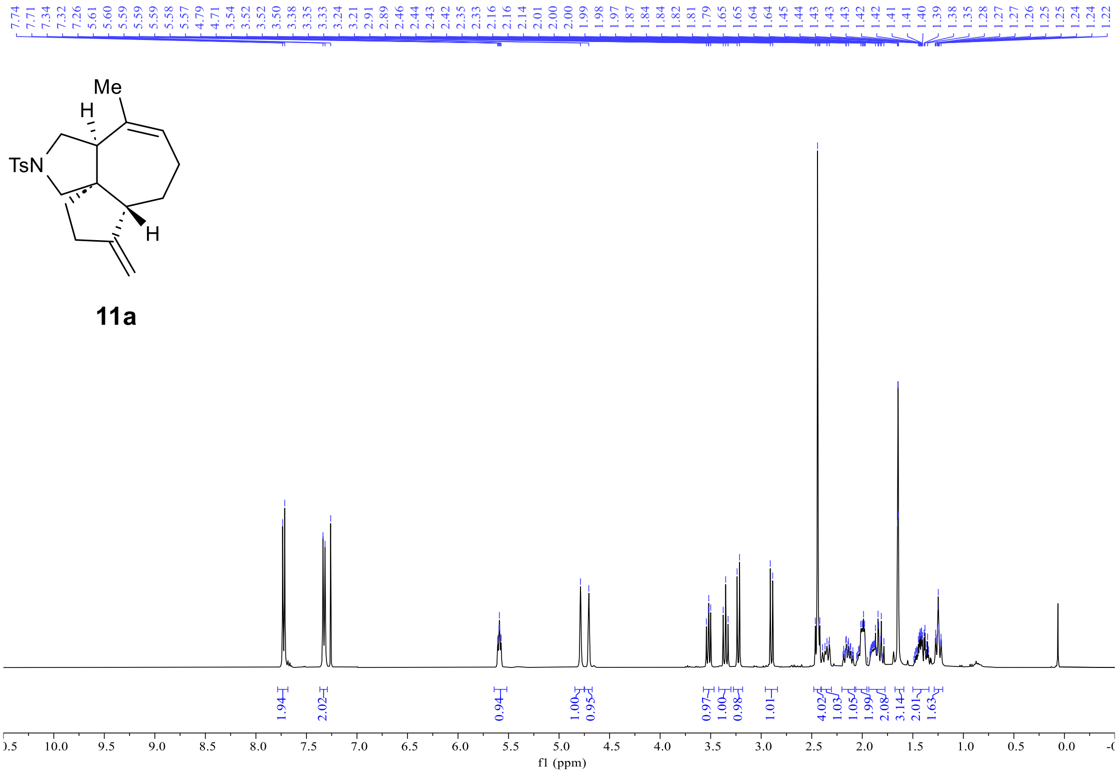
{1.77,3.17}
Me
TsN
H
H
H
H
OH
NOE
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
f1 (ppm)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7.71
7.34
7.32
7.26
5.61
5.60
5.59
5.59
5.59
5.58
5.57
4.79
4.71
3.54
3.52
3.52
3.50
3.38
3.35
3.33
3.24
3.21
2.91
2.89
2.46
2.44
2.43
2.42
2.35
2.33
2.16
2.16
2.14
2.01
2.00
1.99
1.98
1.97
1.87
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1.84
1.82
1.81
1.79
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1.65
1.65
1.64
1.64
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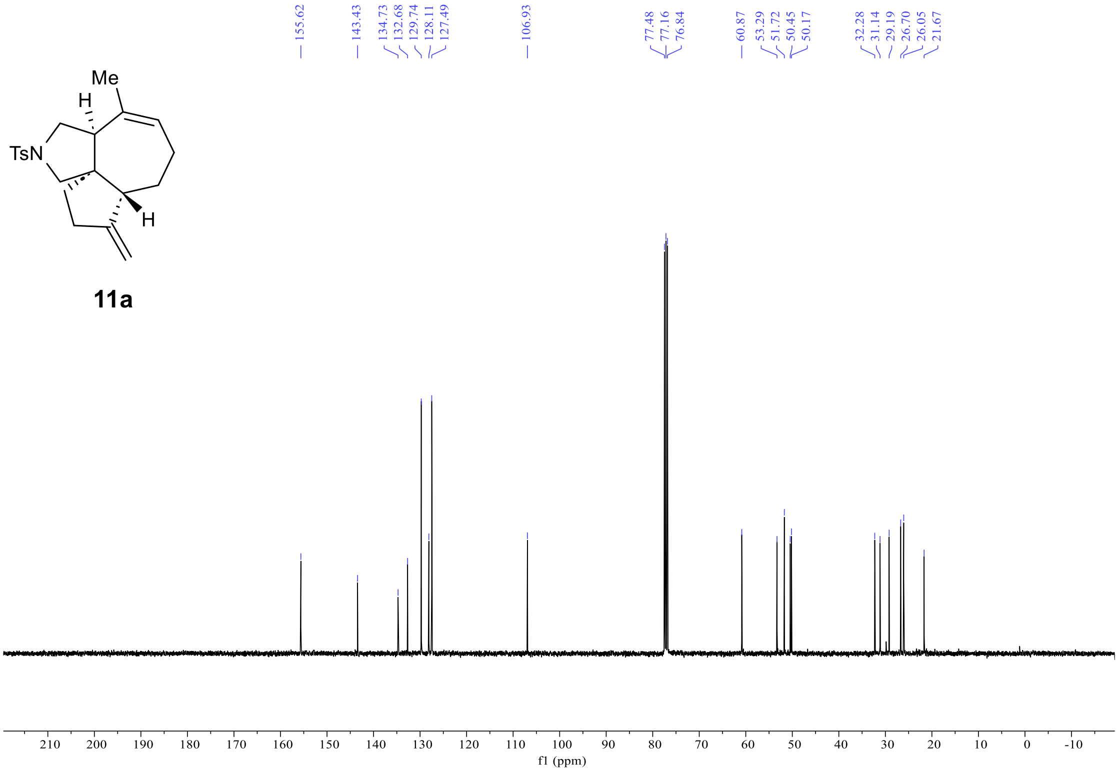
1.43
1.43
1.43
1.42
1.42
1.41
1.41
1.40
1.39
1.38
1.35
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.24
1.22
Me
H
TsN
H
1.94
2.02
0.94
1.00
0.95
0.97
1.00
0.98
1.01
4.02
1.03
1.05
1.99
2.08
3.14
2.01
1.63
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

11a


155.62
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132.68
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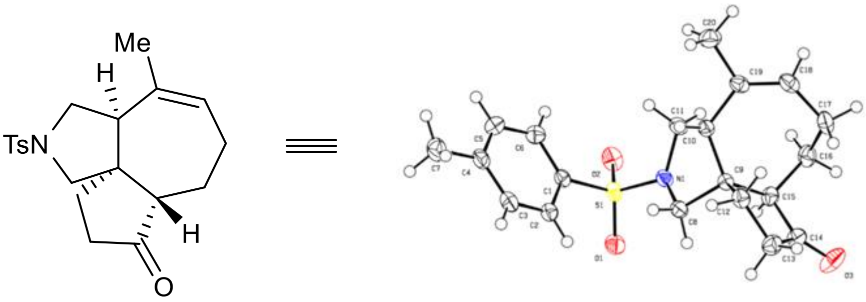
128.11
127.49
106.93
77.48
77.16
76.84
60.87
53.29
51.72
50.45
50.17
32.28
31.14
29.19
26.70
26.05
21.67
Me
H
TsN
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

11a

6. X-ray Data of 2a, 3a, 2e, 5e and 8a

X-ray data of 2a



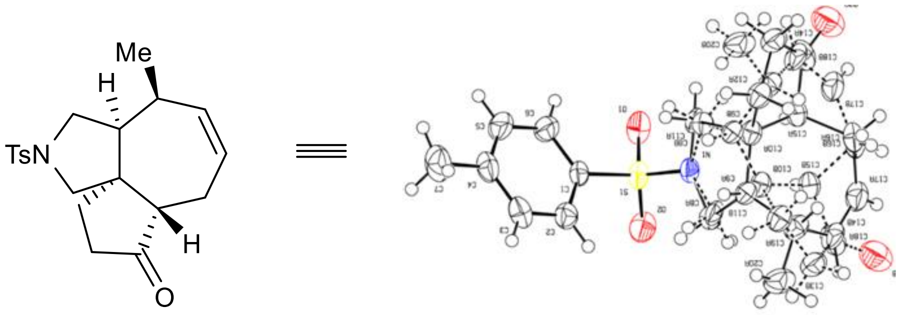
CCDC: 1945730

Chemical formula	$C_{20}H_{25}NO_3S$
M_r	359.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	10.7811 (3), 10.0797 (3), 16.6201 (5)
β (°)	92.559 (2)
V (Å^3)	1804.31 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.25 × 0.2 × 0.17

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.126, 1.06
No. of reflections	4114
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.39

X-ray data of 3a



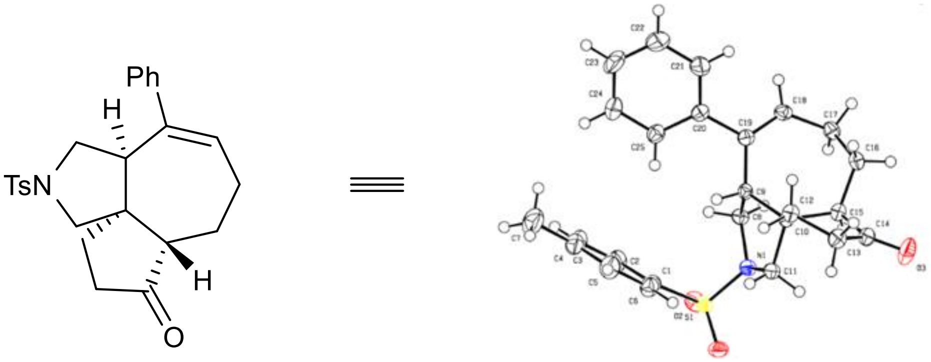
CCDC: 1945733

Chemical formula	$C_{20}H_{25}NO_3S$
M_r	359.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	19.8583 (10), 5.7771 (3), 15.7775 (6)
β (°)	93.647 (4)
V (Å^3)	1806.38 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.25 × 0.23 × 0.05

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.089, 0.222, 1.05
No. of reflections	4148
No. of parameters	272
No. of restraints	16
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.45

X-ray data of 2e



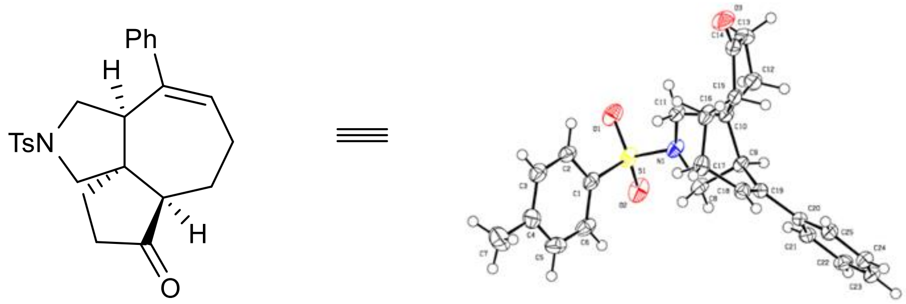
CCDC: 1945734

Chemical formula	$C_{25}H_{27}NO_3S$
M_r	421.53
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, b, c (Å)	9.1858 (2), 10.7454 (3), 12.1281 (3)
α, β, γ (°)	69.337 (3), 81.657 (2), 72.474 (2)
V (Å^3)	1067.09 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.32 × 0.29 × 0.13

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.114, 1.04
No. of reflections	4884
No. of parameters	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.41

X-ray data of 5e



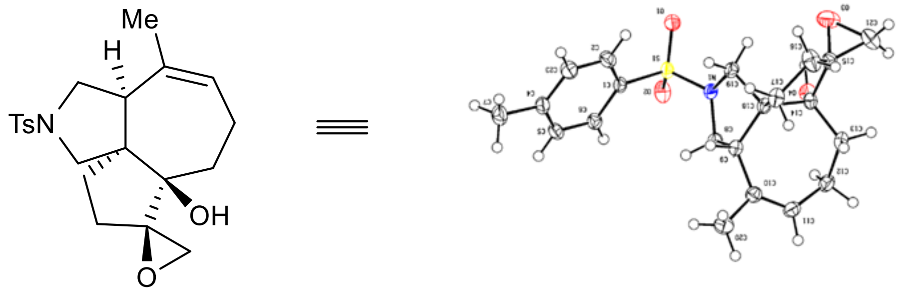
CCDC: 1945736

Chemical formula	$C_{25}H_{27}NO_3S$
M_r	421.53
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	9.2350 (3), 21.4675 (7), 11.5307 (5)
β (°)	108.646 (4)
V (Å^3)	2166.00 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.43 × 0.37 × 0.08

Refinement

$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.116, 1.08
No. of reflections	5442
No. of parameters	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.30, −0.42

X-ray data of 8a



CCDC: 2290933

Chemical formula	$C_{21}H_{27}NO_4S$
M_r	389.49
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	9.9685 (3), 12.4176 (3), 15.6253 (5)
β (°)	102.687 (3)
V (Å^3)	1886.95 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.19 × 0.17 × 0.06

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.106, 1.07
No. of reflections	4761
No. of parameters	247
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.38

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