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Pd-Catalyzed Allylic C-H Activation to Seven-Membered *N*,*O*-Heterocycles

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General Experimental Procedures

All reactions were performed under an inert atmosphere of argon and with anhydrous solvents in glassware oven or flame dried at 80 ºC unless otherwise stated. All chemicals were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Strem Chemicals Inc., Fluorochem Ltd. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise stated. Analytical thin layer chromatography was carried out on silica-coated aluminum plates (silica gel 60 F_{254} Merck) or on aluminum sheets (aluminum oxide 60 F_{254} neutral Merck) using UV light as visualizing agent (254 nm) and $KMnO_4$ (solution of 1.5 g of potassium permanganate, 10 g of potassium bicarbonate and 1.25 mL of 10% sodium hydroxide in 200 mL of water) with heat as developing agents. Flash column chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the indicated eluent. All other reagents and solvents: acetonitrile, dichloromethane, dichloroethane, tetrahydrofuran, toluene and methanol were used dry, unless otherwise indicated.

^{1}H-NMR, ^{13}C-NMR, DEPT and ^{19}F-NMR experiments were carried out using a Varian Inova 500 or Varian Mercury 300 MHz. All NMR experiments were recorded at 298 K otherwise stated. All chemical shifts are reported in parts per million (ppm) and referenced to residual solvent peaks. Coupling constants *J* are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet or as a combination of them.

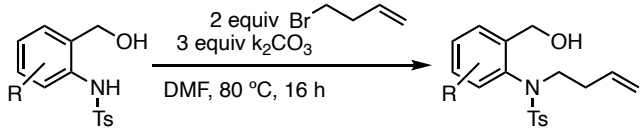
Mass spectrometry analysis was carried out using a Micromass Autospec, a TRACE MS or a HP-5988-A with chemical ionization and a Bruker Microtof APCI using chemical ionization spectrometers at CACTUS Facility (Universidade de Santiago de Compostela).

Enantiomeric ratio (er) values were determined on Jasco SFC 4000 series using commercially available chiral columns.

1a, **1c**, **1d**, **1q** and **1r** were synthesized according to the literature procedure.[1] Compounds **S1** and **S2** were synthesized according to literature.[1,2] **L-SOX** were synthesized according to the literature procedure reported by White and coworkers.[3]

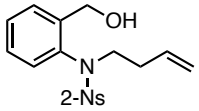
Synthesis of Starting Materials 1

General Procedure A.



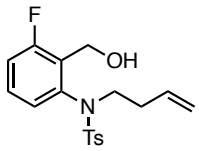
A round-bottomed flask equipped with a stirring magnetic bar was flamed-dried under vacuum and backfilled with argon. Then, it was charged with the corresponding tosylamide **S1** and K_2CO_3 (3 equiv), and it was put under vacuum and backfilled with argon for three times. Afterwards, DMF (0.25M) was added and the mixture was stirred for 30 min at rt. Finally, 4-bromo 1-butene was added and the reaction was heated to 80 ºC in an oil bath for 16 h. The reaction was quenched with a saturated solution of $NH_4Cl_{(aq)}$ and extracted with EtOAc. The organic phase was washed with a saturated solution of $NH_4Cl_{(aq)}$ (3 x 50 mL), dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified in silica gel column chromatography with Hexanes/EtOAc (8:2) as eluent to give the desired product.

***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)phenyl)-2-nitrobenzenesulfonamide (1b)**



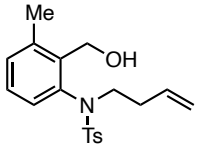
Isolated in an 87% yield (0.9 g, 2.6 mmol) as pale-yellow solid at 4 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.8 – 7.6 (m, 3H), 7.5 – 7.5 (m, 1H), 7.4 (dt, *J* = 12.6, 4.5 Hz, 2H), 7.2 (t, *J* = 7.7 Hz, 1H), 6.8 (d, *J* = 7.9 Hz, 1H), 5.8 – 5.6 (m, 1H), 5.1 – 5.0 (m, 2H), 4.8 (d, *J* = 12.5 Hz, 1H), 4.5 (d, *J* = 12.5 Hz, 1H), 4.1 (dt, *J* = 14.8, 7.9 Hz, 1H), 3.6 (ddd, *J* = 14.0, 7.7, 5.1 Hz, 1H), 2.6 (s, 1H), 2.2 (qq, *J* = 14.1, 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 142.4, 135.7, 134.2, 134.1, 132.2, 131.3, 131.3, 131.2, 129.8, 129.1, 128.8, 123.9, 117.6, 60.8, 52.6, 32.9. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{17}H_{19}N_2O_5S$ $[M\text{-}OH_2]^+$: 345.0904, found 345.0904.

***N*-(but-3-en-1-yl)-*N*-(3-fluoro-2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (1e)**



Isolated in a 77% yield (0.76 g, 2.31 mmol) as brown solid at 4 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.5 (d, *J* = 8.2 Hz, 2H), 7.3 – 7.3 (m, 2H), 7.2 – 7.0 (m, 2H), 6.3 – 6.2 (m, 1H), 5.7 (ddt, *J* = 17.0, 10.5, 6.6 Hz, 1H), 5.1 – 4.8 (m, 3H), 4.7 (d, *J* = 11.8 Hz, 1H), 4.0 (dt, *J* = 12.9, 8.0 Hz, 1H), 3.1 (ddd, *J* = 13.0, 8.2, 5.1 Hz, 1H), 3.0 (bs, 1H), 2.5 (s, 3H), 2.3 – 1.9 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.7 (d, *J* = 250.5 Hz), 144.4, 139.4 (d, *J* = 6.6 Hz), 134.3, 130.7 (d, *J* = 16.6 Hz), 129.8, 129.2 (d, *J* = 9.8 Hz), 128.3, 122.8 (d, *J* = 3.5 Hz), 117.6, 116.3 (d, *J* = 22.5 Hz), 55.0 (d, *J* = 3.9 Hz), 51.5, 32.5, 21.7.**^{19}F NMR** (282 MHz, $CDCl_3$) δ -113.0 (t, *J* = 7.6 Hz). **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{21}FNO_3S$ $[M\text{-}OH_2]^+$: 332.1115, found 332.1118.

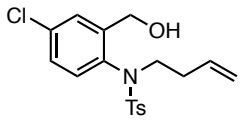
***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-3-methylphenyl)-4-methylbenzenesulfonamide (1f)**



Isolated in a 70% yield (0.69 g, 2.1 mmol) as white solid at 4 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 (s, 2H), 7.2 (d, *J* = 7.5 Hz, 1H), 7.0 (d, *J* = 7.8 Hz, 1H), 6.3 (d, *J* = 7.9 Hz, 1H), 5.7 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.1 (d, *J* = 11.9 Hz, 1H), 5.0 – 4.9 (m, 2H), 4.5 (d, *J* = 11.9 Hz, 1H), 4.0 (ddd, *J* = 12.8, 9.0, 7.2 Hz, 1H), 3.1 (ddd,

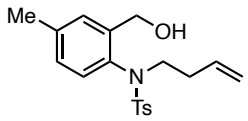
J = 13.3, 8.7, 5.0 Hz, 1H), 2.5 (s, 3H), 2.4 (s, 3H), 2.3 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 140.7, 137.7, 134.5, 134.3, 131.0, 129.6, 128.3, 128.2, 127.3, 124.3, 117.4, 58.0, 51.5, 32.5, 21.7, 19.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_3S$ [M-OH_2]+: 328.1366, found 328.1369.

***N*-(but-3-en-1-yl)-*N*-(4-chloro-2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (1g)**



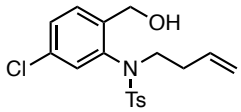
Isolated in a 65% yield (0.68 g, 1.95 mmol) as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.6 (t, *J* = 2.2 Hz, 1H), 7.5 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.3 (d, *J* = 8.2 Hz, 2H), 7.1 (dt, *J* = 8.6, 2.2 Hz, 1H), 6.3 (d, *J* = 8.5 Hz, 1H), 5.6 (ddt, *J* = 17.0, 12.5, 6.7 Hz, 1H), 5.1 – 4.9 (m, 3H), 4.5 (d, *J* = 12.7 Hz, 1H), 3.9 (dt, *J* = 15.1, 7.9 Hz, 1H), 3.1 (ddd, *J* = 13.1, 8.2, 5.2 Hz, 2H), 2.4 (s, 3H), 2.1 (tq, *J* = 15.0, 7.0 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.7, 144.3, 135.6, 134.8, 134.3, 134.1, 130.8, 129.8, 128.5, 128.2, 128.2, 117.5, 60.8, 51.3, 32.4, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{21}ClNO_3S$ [M-OH_2]+: 348.0820, found 348.0820.

***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-4-methylphenyl)-4-methylbenzenesulfonamide (1i)**



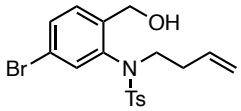
Isolated in an 83% yield (0.82 g, 2.5 mmol) as white-off solid at 4 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.5 (d, *J* = 8.1 Hz, 2H), 7.4 (d, *J* = 2.2 Hz, 1H), 7.3 (s, 2H), 6.9 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.3 (d, *J* = 8.1 Hz, 1H), 5.7 (ddt, *J* = 17.1, 10.7, 6.6 Hz, 1H), 5.0 – 4.9 (m, 3H), 4.4 (d, *J* = 12.0 Hz, 1H), 3.9 (ddd, *J* = 12.8, 8.9, 7.3 Hz, 1H), 3.1 (ddd, *J* = 13.0, 8.5, 5.1 Hz, 2H), 2.4 (s, 3H), 2.3 (s, 3H), 2.3 – 2.0 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9, 142.2, 139.1, 134.6, 134.5, 134.4, 131.9, 129.6, 129.2, 128.2, 126.7, 117.2, 61.2, 51.4, 32.4, 21.6, 21.2. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_3S$ [M-OH_2]+: 328.1366, found 328.1367.

***N*-(but-3-en-1-yl)-*N*-(5-chloro-2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (1k)**



Isolated in a 75% yield (0.78 g, 2.25 mmol) as brown oil at 4 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.3 Hz, 1H), 7.5 – 7.5 (m, 2H), 7.3 (td, *J* = 5.7, 2.7 Hz, 3H), 6.4 (d, *J* = 2.1 Hz, 1H), 5.7 – 5.6 (m, 1H), 5.1 – 4.9 (m, 3H), 4.5 (d, *J* = 12.4 Hz, 1H), 3.9 (dt, *J* = 12.8, 8.0 Hz, 1H), 3.1 (ddd, *J* = 13.2, 8.4, 5.1 Hz, 1H), 3.0 (s, 1H), 2.5 (s, 3H), 2.2 – 2.0 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.5, 141.5, 138.3, 134.3, 133.8, 133.5, 132.3, 129.8, 129.4, 128.3, 127.1, 117.6, 60.7, 51.3, 32.4, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{21}ClNO_3S$ [M-OH_2]+: 348.0820, found 348.0810.

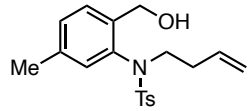
***N*-(5-bromo-2-(hydroxymethyl)phenyl)-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide (1l)**



Isolated in an 80% yield (0.94 g, 2.4 mmol) as brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.5 2– 7.49 (m, 4H), 7.3 (d, *J* = 8.0 Hz, 2H), 6.5 (d, *J* = 1.7 Hz, 1H), 5.7 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.1 – 4.9 (m, 3H), 4.5 (d, *J* = 12.5 Hz, 1H), 3.9 (dt, *J* = 12.9, 8.0 Hz, 1H), 3.1 (ddd, *J* = 13.1, 8.3, 5.0 Hz, 1H), 2.5 (s, 3H), 2.3 – 2.0 (m, 2H). **^{13}C NMR**[1] (126 MHz, $CDCl_3$) δ 144.6, 142.0, 138.5, 134.3, 133.7, 132.6, 132.3, 130.1, 129.8, 128.3,

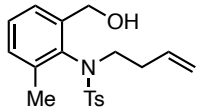
121.2, 117.6, 60.7, 51.3, 32.5, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{21}BrNO_3S$ [M-OH_2]+: 392.0314, found 392.0315.

***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-5-methylphenyl)-4-methylbenzenesulfonamide (1m)**



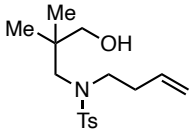
Isolated in a 90% yield (0.88 g, 2.7 mmol) as brown solid at 4 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.5 (d, *J* = 8.1 Hz, 2H), 7.5 (d, *J* = 7.8 Hz, 1H), 7.3 (d, *J* = 8.0 Hz, 2H), 7.2 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.2 (d, *J* = 1.7 Hz, 1H), 5.7 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.1 – 4.9 (m, 3H), 4.5 – 4.4 (m, 1H), 3.9 (ddd, *J* = 12.8, 9.0, 7.2 Hz, 1H), 3.2 – 3.0 (m, 2H), 2.5 (s, 3H), 2.2 (m, 4H), 2.1 (dq, *J* = 13.0, 6.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 139.6, 138.5, 137.1, 134.5, 134.4, 131.2, 129.9, 129.5, 128.3, 127.5, 117.3, 61.0, 51.4, 32.5, 21.7, 21.0. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_3S$ [M-OH_2]+: 328.1366, found 328.1367.

***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-6-methylphenyl)-4-methylbenzenesulfonamide (1o)**



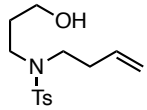
Isolated in a 60% yield in two steps (0.62 g, 1.8 mmol) as yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.6 (m, 2H), 7.5 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.3 – 7.3 (m, 3H), 7.1 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.6 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.1 – 4.9 (m, 2H), 4.8 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.4 (dd, *J* = 12.1, 9.2 Hz, 1H), 3.8 (ddd, *J* = 13.7, 10.6, 5.7 Hz, 1H), 3.3 (ddd, *J* = 13.7, 10.5, 5.3 Hz, 1H), 2.9 (dd, *J* = 9.9, 4.0 Hz, 1H), 2.4 (s, 3H), 2.4 – 2.3 (m, 1H), 2.3 – 2.2 (m, 1H), 1.7 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 142.9, 137.6, 137.3, 135.4, 134.4, 131.3, 129.9, 129.0, 129.0, 127.5, 117.4, 61.9, 51.1, 33.6, 21.7, 18.3. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_3S$ [M-OH_2]+: 328.1366, found 328.1378.

***N*-(but-3-en-1-yl)-*N*-(3-hydroxy-2,2-dimethylpropyl)-4-methylbenzenesulfonamide (1t)**



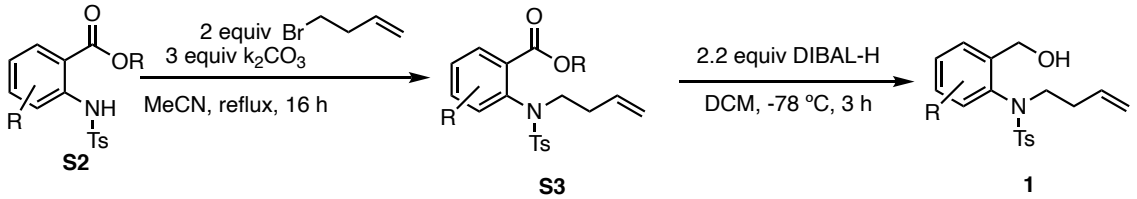
Isolated in a 90% yield (0.79 g, 2.7 mmol) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.3 (d, *J* = 8.0 Hz, 2H), 5.7 – 5.5 (m, 1H), 5.1 – 4.9 (m, 1H), 3.4 (s, 2H), 3.2 – 3.0 (m, 2H), 3.0 (s, 2H), 2.4 (s, 3H), 2.3 (dddd, *J* = 8.4, 6.9, 4.9, 2.1 Hz, 2H), 0.9 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 136.0, 134.6, 129.9, 127.6, 117.1, 67.9, 55.5, 51.1, 38.0, 32.8, 23.3, 21.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{16}H_{26}NO_3S$ [M-OH_2]+: 294.1522, found 294.1522.

***N*-(but-3-en-1-yl)-*N*-(3-hydroxypropyl)-4-methylbenzenesulfonamide (1u)**



Isolated in a 70% yield (0.57 g, 2.1 mmol) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.7 (d, *J* = 7.9 Hz, 1H), 7.4 – 7.3 (m, 1H), 5.7 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.1 – 5.0 (m, 1H), 3.8 (q, *J* = 5.9 Hz, 1H), 3.3 – 3.1 (m, 2H), 2.4 (s, 2H), 2.4 – 2.2 (m, 1H), 1.8 (p, *J* = 5.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.3, 136.4, 134.5, 129.7, 127.0, 117.1, 58.9, 48.2, 45.2, 33.2, 31.3, 21.4. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{14}H_{22}NO_3S$ [M-OH_2]+: 266.1192, found 266.1199.

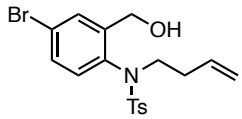
General Procedure B



A round-bottomed flask equipped with a stirring magnetic bar was flamed-dried under vacuum and backfilled with argon. Then, it was charged with the corresponding tosylamide **S2** and K_2CO_3 (2 equiv), and it was put under vacuum and backfilled with argon for three times. Afterward, MeCN (0.1M) was added followed by 4-bromo-1-butene and the reaction was heated to reflux for 16 h in an oil bath. The reaction was quenched with a saturated solution of $NH_4Cl_{(aq)}$ and extracted with EtOAc. The organic phase was washed with a saturated solution of $NH_4Cl_{(aq)}$ (3 x 50 mL), dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was used in the next step without further purification.

DIBAL-H (1M in DCM, 2.2 equiv) was added dropwise to a stirred solution of the ester **S3** (1 equiv) in DCM (0.3 M) at -78ºC. The reaction was then stirred at that temperature for 3 h. Afterward, MeOH (5 mL) was added followed by a saturated solution of the Rochelle Salt at -78ºC. The reaction was then warmed up to rt and stirred for 1 h. The mixture was extracted with DCM (3 x 30 mL) and the combination of organic layers was washed with a saturated solution of NaCl(aq), dried over Na_2SO_4 and concentrated in vacuo. The residue was then purified by silica gel column chromatography with hexanes/EtOAc (8:2) as the eluent to afford the desired product.

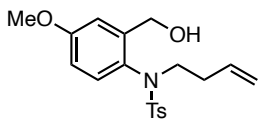
_N_-(4-bromo-2-(hydroxymethyl)phenyl)-_N_-(but-3-en-1-yl)-4-methylbenzenesulfonamide (1h)



Isolated in a 71% yield in two steps (0.83 g, 2.13 mmol) as brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8 (d, *J* = 2.4 Hz, 1H), 7.5 (d, *J* = 8.0 Hz, 2H), 7.3 (t, *J* = 8.4 Hz, 3H), 6.3 (d, *J* = 8.5 Hz, 1H), 5.6 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.0 (ddd, *J* = 16.3, 8.1, 4.5 Hz, 3H), 4.5 (d, *J* = 12.8 Hz, 1H), 3.9 (dt, *J* = 13.0, 8.0 Hz, 1H), 3.1 (ddd, *J* = 13.1, 8.1, 5.2 Hz, 2H), 2.4 (s, 3H), 2.1 (qt, *J* = 15.0, 7.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.9, 144.3, 136.0, 134.3, 133.9, 133.8, 131.4, 129.7, 128.4, 128.1, 122.9, 117.4, 60.6, 51.1, 32.3, 21.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{21}BrNO_3S$ [M-OH_2]+: 392.0314, found 392.0329.

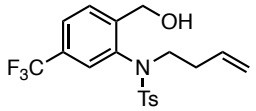
_N_-(but-3-en-1-yl)-_N_-(2-(hydroxymethyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (1j)



Isolated in a 70% yield in two steps (0.72 g, 2.1 mmol) as white-off solid at 4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.4 (d, *J* = 7.9 Hz, 2H), 7.2 (s, 2H), 7.0 (d, *J* = 3.0 Hz, 1H), 6.6 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.3 (d, *J* = 8.7 Hz, 1H), 5.6 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.0 – 4.8 (m, 3H), 4.4 (d, *J* = 12.2 Hz, 1H), 3.9 (dt, *J* = 12.6, 7.9 Hz, 1H), 3.7 (s, 3H), 3.0 (ddd, *J* = 13.3, 8.6, 5.0 Hz, 2H), 2.4 (s, 3H), 2.1 (dq, *J* = 15.1, 7.6 Hz, 1H), 2.0 – 1.9 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 144.0, 144.0, 134.6, 134.4, 129.6, 129.5, 128.2, 128.0, 117.3, 115.0, 114.7, 61.4, 55.5, 51.4, 32.4, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_4S$ [M-OH_2]+: 344.1315, found 344.1312.

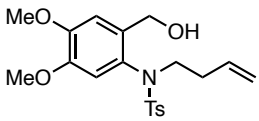
***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (1n)**



Isolated in a 67% yield in two steps (0.8 g, 2.0 mmol) as pale-yellow solid at 4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.8 (d, *J* = 8.0 Hz, 1H), 7.6 (d, *J* = 8.0 Hz, 1H), 7.5 (d, *J* = 7.9 Hz, 2H), 7.3 (d, *J* = 7.9 Hz, 2H), 6.6 (s, 1H), 5.7 (ddt, *J* = 17.1, 10.5, 6.6 Hz, 1H), 5.1 – 4.9 (m, 3H), 4.6 (d, *J* = 12.9 Hz, 1H), 4.0 (dt, *J* = 13.1, 8.0 Hz, 1H), 3.1 (ddd, *J* = 13.2, 8.0, 5.1 Hz, 1H), 2.5 (s, 4H), 2.3 – 2.0 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 144.7, 137.8, 134.3, 133.5, 131.5, 130.6 (q, *J* = 33.1 Hz), 129.8, 128.2, 125.7(d, *J* = 3.7 Hz) 124.1 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.4 Hz), 117.7, 60.8, 51.4, 32.5, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{21}F_3NO_3S$ [M-OH_2]+: 382.1366, found 382.1386.

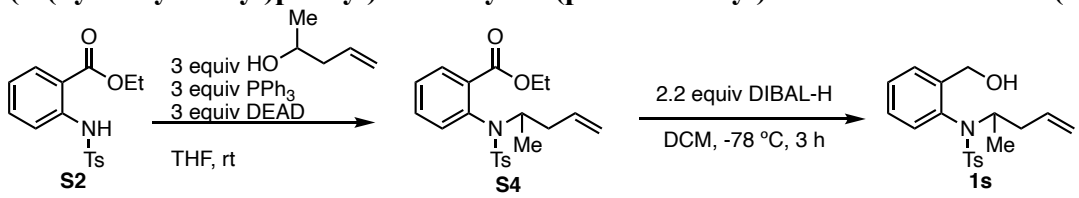
***N*-(but-3-en-1-yl)-*N*-(2-(hydroxymethyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (1p)**



Isolated in a 58% yield in two steps (0.65 g, 1.74 mmol) as white-off solid at 4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 (d, *J* = 8.0 Hz, 2H), 7.1 (s, 1H), 5.8 (s, 1H), 5.7 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.1 – 4.9 (m, 3H), 4.4 (d, *J* = 12.0 Hz, 1H), 4.0 (ddd, *J* = 12.8, 8.8, 7.2 Hz, 1H), 3.9 (s, 3H), 3.5 (s, 3H), 3.1 (ddd, *J* = 13.2, 8.6, 5.0 Hz, 1H), 2.4 (s, 3H), 2.3 – 2.2 (m, 1H), 2.2 – 2.0 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.4, 148.5, 144.1, 135.6, 134.6, 134.6, 129.6, 129.0, 128.4, 117.4, 112.9, 109.6, 61.0, 56.1, 55.7, 51.4, 32.5, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{20}H_{26}NO_5S$ [M-OH_2]+: 374.1421, found 374.1431.

***N*-(2-(hydroxymethyl)phenyl)-4-methyl-*N*-(pent-4-en-2-yl)benzenesulfonamide (1s)**

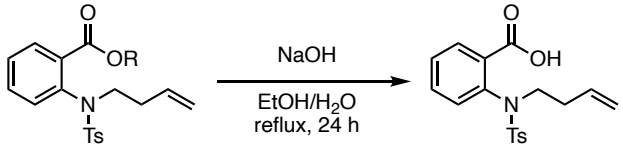


To a solution of **S2** (1 equiv), PPh_3 (3 equiv) and the homoallylic alcohol in THF (0.15 M) at 0 ºC, DEAD was added (40% in toluene, 3 equiv). The reaction was stirred at rt for 4 h. Then the solvent was removed, and the residue was purified by silica gel column chromatography with Hexanes/EtOAc (9:1) to give the desired product **S4**.

DIBAL-H (1M in DCM, 2.2 equiv) was added dropwise to a stirred solution of the ester **S4** (1 equiv) in DCM (0.3 M) at -78ºC. The reaction was then stirred at that temperature for 3 h. Afterward, MeOH (5 mL) was added followed by a saturated solution of the Rochelle Salt at -78ºC. The reaction was then warmed up to rt and stirred for 1 h. The mixture was extracted with DCM (3 x 30 mL) and the combination of organic layers was washed with a saturated solution of NaCl(aq), dried over Na_2SO4 and concentrated in vacuo. The residue was then purified by silica gel column chromatography with hexanes/EtOAc (8:2) as the eluent to afford the desired product **1s** in an 85% yield (837 mg, 2.56 mmol) as white-off solid and as a mixture of isomers. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.6 (dt, *J* = 7.7, 2.0 Hz, 1H), 7.6 – 7.5 (m, 2H), 7.4 – 7.3 (m, 1H), 7.2 (ddd, *J* = 8.6, 1.6, 0.8 Hz, 2H), 7.2 – 7.1 (m, 1H), 6.7 – 6.5 (m, 1H), 5.8 – 5.4 (m, 1H), 5.0 – 4.8 (m, 3H), 4.6 – 4.3 (m, 2H), 3.3 (dd, *J* = 9.5, 3.4 Hz, 1H), 2.4 (s, 3H), 0.9 (dd, *J* = 16.1, 6.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9, 143.9, 143.5, 137.5, 137.2, 134.5,

134.4, 133.2, 131.0, 130.9, 130.9, 130.7, 129.4, 129.3, 129.3, 127.7, 127.5, 127.5, 127.4, 117.7, 117.6, 61.1, 61.0, 56.2, 55.8, 40.1, 40.1, 21.4, 18.7, 18.1. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{24}NO_3S$ [M-OH_2]+: 328.1366, found 328.1378.

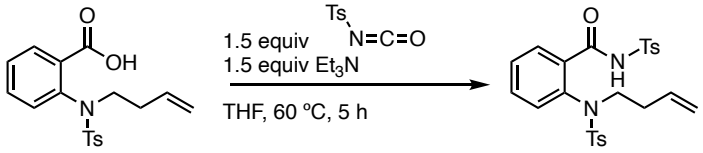
2-((N-(but-3-en-1-yl)-4-methylphenyl)sulfonamido)benzoic acid (1w)



S3 **1w**

To a solution of **S3** (1.4 g, 3.8 mmol) in EtOH (20 mL), an aqueous solution of NaOH (8.5 g, 212 mmol) in water (50 mL) was added. The mixture was heated to reflux for 24 h in an oil bath. Then the reaction was cooled to 0 ºC, and HCl_c was added to reach pH = 3. The solution was extracted with AcOEt (3 x 70 mL) and the combination of organic phases was washed with water (80 mL), brine (80 mL), dried over Na_2SO_4 and the solvent was concentrated in vacuo. The carboxylic acid **1w** was recrystallized in a mixture of Hexanes/AcOEt (1:1) to provide the product in a 68% yield (885 mg, 2.56 mmol) as white-off solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.1 – 7.9 (m, 1H), 7.6 – 7.4 (m, 4H), 7.3 – 7.2 (m, 2H), 7.1 – 6.9 (m, 1H), 5.7 (ddt, *J* = 17.1, 10.5, 6.7 Hz, 1H), 5.1 – 4.9 (m, 2H), 3.8 (s, 1H), 3.6 (s, 1H), 2.4 (s, 5H). **^{13}C NMR** (75 MHz, CD_3OD) δ 169.4, 145.1, 139.3, 137.4, 136.3, 135.1, 133.1, 132.2, 131.3, 130.6, 129.4, 128.7, 117.1, 52.4, 34.3, 21.5. **HRMS** (MM: ESI-APCI-) m/z calc'd for $C_{18}H_{18}NO_4S$ [M -H]: 344.0962, found 344.0950.

2-((*N*-(but-3-en-1-yl)-4-methylphenyl)sulfonamido)-*N*-tosylbenzamide (1x)



1w **1x**

To a solution of **1w** (1.6 mmol, 1 equiv) in THF (8 mL, 0.2 M) were sequentially added TsNCO (365 µL, 2.4 mmol, 1.5 equiv) and NEt_3 (332 µL, 2.4 mmol, 1.5 equiv) at room temperature. After being stirred at 60 °C in an oil bath for 5 hours, the reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was diluted with EtOAc and washed with 1.0 N HCl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography with Hexanes/AcOEt (7:3) to give the desired product **1x** as yellow solid in a 90% yield (0.7 g, 1.4 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.5 (s, 1H), 8.2 – 8.1 (m, 2H), 7.8 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.5 – 7.5 (m, 2H), 7.4 – 7.3 (m, 3H), 7.3 – 7.3 (m, 3H), 6.4 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.4 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 4.9 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.8 (dq, *J* = 17.1, 1.6 Hz, 1H), 3.8 (ddd, *J* = 12.3, 9.9, 6.6 Hz, 1H), 3.0 (ddd, *J* = 12.7, 9.8, 5.0 Hz, 1H), 2.5 (s, 3H), 2.4 (s, 3H), 1.8 (td, *J* = 13.9, 5.4 Hz, 1H), 1.7 – 1.6 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.7, 145.1, 144.9, 136.3, 136.0, 135.8, 133.5, 133.0, 132.2, 131.3, 130.0, 129.5, 129.4, 129.3, 128.6, 127.0, 118.0, 51.6, 32.0, 21.8, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{25}H_{27}N_2O_5S_2$ [M-H]: 499.1361, found 499.1365.

Optimization Data

Experimental Procedure.
A 4 mL flamed-dried vial equipped with a stirring magnetic bar was charged with Pd-catalyst (10 mol%), 1.5 equiv oxidant, additive, **1a** (0.1 mmol) and solvent. The mixture was heated under air and moisture for the indicated time at the indicated temperature.

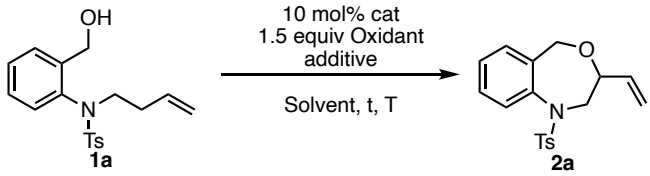


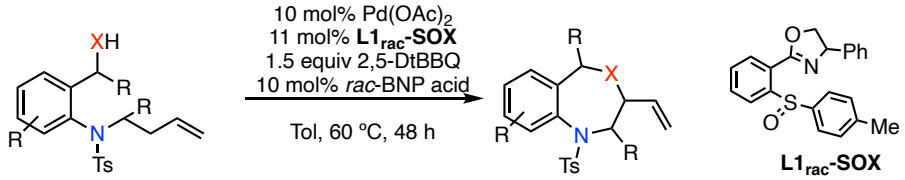
Table S1. Optimization of the cyclization of **1a**

Entry	cat	Oxidant	Adidtive	Solvent (M)	T (ºC)	Time (h)	Yield%
1	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-acid	Tol (0.15)	60	48	88
2	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-acid	Tol (0.15)	60	24	45
3	White's cat	BQ	CrSalenCl	DCE (0.33)	50	48	20
4	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	-	Tol (0.15)	60	48	-
5	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*S*-BNP-Acid	Tol (0.15)	60	48	92
6	$Pd(OAc)_2$ ***rac*-L1-SOX**	BQ	*rac*-BNP-acid	Tol (0.15)	60	48	
7	White's cat	2,5-DtBBQ	*rac*-BNP-acid	Tol (0.15)	60	48	40
8	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-acid	Tol (0.33)	60	48	25
9	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-acid	Tol (0.05)	60	48	30
10	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	1,4-Dioxane (0.15)	60	48	60
11	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	THF (0.15)	60	48	45
12	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	MeCN (0.15)	60	48	Traces

13	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	DCE (0.15)	60	48	Traces
14	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	MeOH (0.15)	60	48	traces
15	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	PPTS	Tol (0.15)	60	48	10%
16	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	Cl_2CO_2H	Tol (0.15)	60	48	-
17	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	4-Clpyr Cl	Tol (0.15)	60	48	-
18	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	25 mol% *rac*-BNP-Acid	Tol (0.15)	60	48	80
19	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	50 mol% *rac*-BNP-Acid	Tol (0.15)	60	48	70
21	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	Tol (0.15)	45	48	45
23	$Pd(OAc)_2$ ***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	Tol (0.15)	rt	10 days	traces
24	***rac*-L1-SOX**	2,5-DtBBQ	*rac*-BNP-Acid	Tol (0.15)	60	48	-
25	$Pd(OAc)_2$	2,5-DtBBQ	*rac*-BNP-Acid	Tol (0.15)	60	48	-

Standard conditions: **1a** (0.1 mmol), 10 mol% $Pd(OAc)_2$, 11 mol% Additive, 11 mol% ***rac*-L1-SOX**, 1.5 equiv 2,5-DtBBQ, isolated yields. Tol= toluene, 2,5-DtBBQ= 2,5-di-*tert*-butyl-1,4-benzoquinone, White's cat = 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate, BNP acid= Binaphthyl Hydrogen Phosphate, 4-Clpyr Cl = 4-Chloropyridinium chloride.

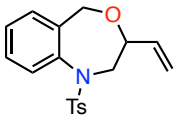
Synthesis and Characterization of Compounds 2



A 4 mL flamed-dried vial equipped with a stirring magnetic bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), ***rac*-L1-SOX** (4 mg, 0.011 mmol, 0.11 equiv), *rac*-BNP acid (3.8 mg, 0.011 mmol, 0.11 equiv), 2,5-di-tert-butyl-1,4-benzoquinone (2,5-DtBBQ) (33 mg, 0.15 mmol, 1.5 equiv), **1** (0.1 mmol, 1 equiv) and toluene (0.67 mL, 0.15 M). The mixture was stirred under air and moisture for 48 h at 60 ºC in an oil bath. After cooling and stripping off the solvent, the residue was purified in a silica gel column

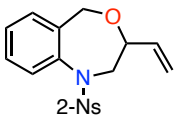
chromatography with a gradient (9.5:0.5 to 8:2) of Hexanes/AcOEt to give the desired product.

1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2a)



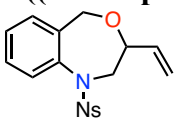
It was isolated in a 91% yield (30 mg, 0.091 mmol) as a white-off foam. The NMR signals matched with the reported in the literature.[4]

1-((2-nitrophenyl)sulfonyl)-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepane (2b)



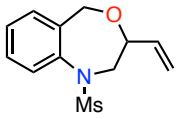
It was isolated in a 50% yield (18 mg, 0.05 mmol) as a yellow foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.8 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.8 – 7.7 (m, 2H), 7.6 (ddd, *J* = 7.8, 7.2, 1.7 Hz, 1H), 7.4 – 7.3 (m, 3H), 7.2 (td, *J* = 7.6, 1.8 Hz, 1H), 7.0 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.8 (ddd, *J* = 17.5, 10.9, 5.3 Hz, 1H), 5.4 (dt, *J* = 17.5, 1.4 Hz, 1H), 5.2 (dt, *J* = 10.9, 1.4 Hz, 1H), 4.8 (d, *J* = 13.4 Hz, 1H), 4.7 (d, *J* = 13.4 Hz, 1H), 4.5 – 4.3 (m, 3H), 3.1 (dd, *J* = 15.3, 10.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 139.5, 139.3, 135.0, 134.3, 134.1, 131.9, 131.6, 130.2, 129.0, 128.9, 128.4, 124.6, 117.6, 82.6, 72.6, 56.2. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{17}H_{17}N_2O_5S$ [M+H]+: 361.0858, found 361.0857.

1-((4-nitrophenyl)sulfonyl)-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepane (2c)



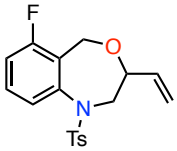
It was isolated in an 83% yield (30 mg, 0.083mmol) as a yellow foam. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.4 (dq, *J* = 9.3, 1.9 Hz, 2H), 8.1 – 7.8 (m, 2H), 7.4 – 7.2 (m, 4H), 5.8 (dddd, *J* = 17.3, 10.7, 5.2, 1.1 Hz, 1H), 5.5 – 5.2 (m, 2H), 4.6 (dd, *J* = 13.6, 1.2 Hz, 1H), 4.4 (dt, *J* = 15.0, 1.5 Hz, 1H), 4.3 – 4.0 (m, 1H), 3.1 (dd, *J* = 15.1, 10.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.2, 147.0, 138.9, 138.4, 134.7, 130.1, 129.3, 128.9, 128.6, 128.5, 124.6, 117.9, 81.2, 72.2, 56.0. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{17}H_{17}N_2O_5S$ [M+H]+: 361.0858, found 361.0841.

1-(methylsulfonyl)-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2d)



It was isolated in an 87% yield (22 mg, 0.087 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.4 (d, *J* = 8.2 Hz, 1H), 7.3 – 7.1 (m, 3H), 5.7 (ddd, *J* = 17.3, 10.8, 5.3 Hz, 1H), 5.3 (dt, *J* = 17.5, 1.5 Hz, 1H), 5.2 (dt, *J* = 10.7, 1.4 Hz, 1H), 4.8 – 4.7 (m, 2H), 4.4 – 4.3 (m, 1H), 4.1 (dd, *J* = 15.0, 2.1 Hz, 1H), 3.1 (s, 3H), 2.9 (dd, *J* = 15.0, 10.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 138.0, 134.9, 129.9, 129.1, 128.0, 127.4, 117.5, 81.6, 72.1, 55.0, 41.5. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{12}H_{16}NO_3S$ [M+H]+: 254.0851, found 254.0849.

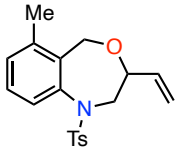
6-fluoro-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2e)



It was isolated in a 58% yield (20 mg, 0.057 mmol) as brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.1 Hz, 2H), 7.3 (s, 2H), 7.2 (td, *J* = 8.2, 6.0 Hz, 1H), 7.2 (d, *J* = 7.9 Hz, 1H), 7.0 (t, *J* = 8.6 Hz, 1H), 5.7 (ddd, *J* = 17.5, 10.8, 5.3 Hz, 1H), 5.4 – 5.3 (m, 1H), 5.2 (dd, *J* = 10.9, 1.5 Hz, 1H), 5.0 (d, *J* = 13.7 Hz, 1H), 4.4 (dd, *J* = 15.1, 2.0 Hz, 1H), 4.3 – 4.2 (m, 1H), 3.9 (dd, *J* = 13.7, 2.5 Hz, 1H), 3.0 (dd, *J* = 15.1, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.1 (d, *J* = 248.5 Hz), 144.1, 141.8 (d, *J* = 4.6 Hz), 138.4, 135.0, 130.1, 129.3 (d, *J* = 9.9 Hz), 127.3, 126.1 (d, *J* = 15.2 Hz), 124.5 (d, *J* = 3.5 Hz), 117.6, 115.3 (d, *J* = 23.1 Hz), 80.9, 63.2, 55.6, 21.7. **^{19}F NMR** (282 MHz, $CDCl_3$) δ

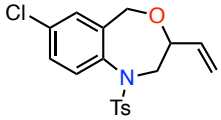
-116.8 (t, J = 7.7 Hz). **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{19}FNO_3S$ [M+H]+: 348.1070, found 348.1064.

6-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2f)



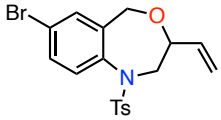
It was synthesized using 15 mol% $Pd(OAc)_2$, 16 mol% *rac*-BNP acid, 16 mol% ***rac*-L1 SOX**. It was isolated in a 60% yield (21 mg, 0.06 mmol) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.3 (d, J = 8.0 Hz, 2H), 7.2 – 7.0 (m, 3H), 5.7 (ddd, J = 17.3, 10.7, 5.4 Hz, 1H), 5.4 (dt, J = 17.4, 1.4 Hz, 1H), 5.2 (dt, J = 10.8, 1.4 Hz, 1H), 4.9 (d, J = 13.6 Hz, 1H), 4.4 – 4.2 (m, 3H), 3.0 (dd, J = 15.2, 10.7 Hz, 1H), 2.4 (s, 3H), 2.4 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.7, 140.7, 138.9, 137.2, 137.1, 135.4, 130.4, 129.9, 128.2, 127.3, 126.2, 117.6, 81.0, 67.0, 55.7, 21.7, 19.8. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1311.

7-chloro-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2g)



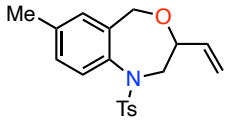
It was isolated in a 55% yield (20 mg, 0.055 mmol) as a white foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 – 7.2 (m, 4H), 7.1 (d, J = 2.4 Hz, 1H), 5.7 (ddd, J = 17.4, 10.8, 5.3 Hz, 1H), 5.3 (dt, J = 17.4, 1.5 Hz, 1H), 5.2 (dt, J = 10.8, 1.4 Hz, 1H), 4.4 – 4.3 (m, 3H), 4.1 (ddq, J = 10.4, 5.2, 1.7 Hz, 1H), 4.0 (d, J = 13.5 Hz, 1H), 2.9 (dd, J = 15.1, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 140.1, 138.4, 138.3, 135.0, 133.6, 130.5, 130.1, 129.8, 129.0, 127.3, 117.6, 80.8, 71.8, 55.6, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{19}ClNO_3S$ [M+H]+: 364.0774, found 364.0772.

7-bromo-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2h)



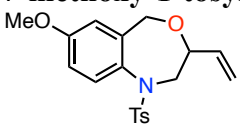
It was isolated in a 75% yield (31 mg, 0.075 mmol) as a brown foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 (dd, J = 8.4, 2.4 Hz, 1H), 7.3 (d, J = 2.4 Hz, 1H), 7.2 – 7.2 (m, 3H), 5.6 (ddd, J = 17.4, 10.8, 5.3 Hz, 1H), 5.3 (dt, J = 17.4, 1.4 Hz, 1H), 5.1 (dt, J = 10.8, 1.4 Hz, 1H), 4.4 – 4.2 (m, 2H), 4.1 (ddq, J = 10.3, 5.1, 1.6 Hz, 1H), 4.0 (d, J = 13.5 Hz, 1H), 2.9 (dd, J = 15.1, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 140.3, 138.9, 138.3, 135.0, 132.7, 132.0, 130.7, 130.1, 127.3, 121.7, 117.6, 80.8, 71.7, 55.6, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{19}BrNO_3S$ [M+H]+: 408.0269, found 408.0272.

7-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2i)



It was isolated in a 45% yield (16 mg, 0.045 mmol) as a white foam. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.7 – 7.5 (m, 2H), 7.4 – 7.2 (m, 3H), 7.2 – 7.0 (m, 2H), 5.8 (ddd, J = 16.9, 10.7, 5.2 Hz, 1H), 5.4 – 5.3 (m, 1H), 5.3 – 5.2 (m, 1H), 4.5 – 4.3 (m, 2H), 4.2 (t, J = 11.4 Hz, 2H), 3.0 (dd, J = 15.0, 10.3 Hz, 1H), 2.4 (s, 3H), 2.3 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.7, 138.8, 138.2, 138.1, 137.2, 135.4, 130.5, 129.9, 129.6, 128.8, 127.3, 117.3, 80.9, 72.4, 55.8, 21.7, 21.1. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1322.

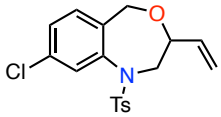
7-methoxy-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2j)



It was isolated in a 75% yield (27 mg, 0.075 mmol) as an amorphous white-off solid at 4 ºC.

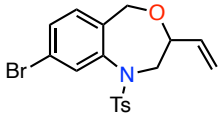
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.5 (d, *J* = 7.8 Hz, 2H), 7.3 – 7.1 (m, 3H), 6.8 – 6.6 (m, 2H), 5.7 (ddd, *J* = 16.6, 10.8, 5.3 Hz, 1H), 5.3 (dd, *J* = 17.6, 2.0 Hz, 1H), 5.1 (d, *J* = 10.8 Hz, 1H), 4.3 (dd, *J* = 14.3, 7.4 Hz, 2H), 4.1 (dd, *J* = 10.6, 5.3 Hz, 1H), 4.0 (d, *J* = 13.4 Hz, 1H), 3.7 (d, *J* = 1.6 Hz, 3H), 2.9 (dd, *J* = 15.0, 10.4 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 142.6, 138.8, 137.5, 134.1, 131.1, 129.3, 128.8, 126.1, 116.1, 114.0, 112.5, 79.9, 71.3, 54.6, 54.5, 20.5. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_4S$ [M+H]+: 360.1270, found 360.1273.

8-chloro-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2k)



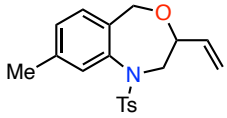
It was isolated in a 70% yield (25 mg, 0.070 mmol) as a white foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 (s, 1H), 7.2 (d, *J* = 8.0 Hz, 2H), 7.2 – 7.1 (m, 1H), 7.1 (d, *J* = 8.1 Hz, 1H), 5.7 (ddd, *J* = 17.4, 10.8, 5.3 Hz, 1H), 5.3 – 5.2 (m, 1H), 5.1 (dt, *J* = 10.7, 1.4 Hz, 1H), 4.4 (d, *J* = 13.5 Hz, 1H), 4.3 (dd, *J* = 15.1, 1.9 Hz, 1H), 4.1 (ddq, *J* = 10.2, 5.1, 1.6 Hz, 1H), 4.1 – 4.0 (m, 1H), 2.9 (dd, *J* = 15.1, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 141.0, 138.3, 136.8, 135.0, 134.2, 130.7, 130.1, 129.2, 128.2, 127.3, 117.6, 80.8, 71.6, 55.6, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{19}ClNO_3S$ [M+H]+: 364.0774, found 364.0771.

8-bromo-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2l)



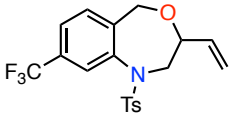
It was isolated in a 37% yield (15 mg, 0.037 mmol) as a brown foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.5 (d, *J* = 1.9 Hz, 1H), 7.3 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.2 (d, *J* = 8.0 Hz, 2H), 7.0 (d, *J* = 8.1 Hz, 1H), 5.7 (ddd, *J* = 17.4, 10.8, 5.3 Hz, 1H), 5.3 (dt, *J* = 17.4, 1.5 Hz, 1H), 5.2 (dt, *J* = 10.8, 1.4 Hz, 1H), 4.4 (d, *J* = 13.5 Hz, 1H), 4.3 (dd, *J* = 15.2, 1.9 Hz, 1H), 4.1 (ddq, *J* = 10.2, 5.1, 1.7 Hz, 1H), 4.0 (d, *J* = 13.5 Hz, 1H), 2.9 (dd, *J* = 15.2, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 141.1, 138.2, 137.3, 135.0, 132.1, 131.1, 130.9, 130.1, 127.3, 121.9, 117.6, 80.8, 71.7, 55.6, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{19}BrNO_3S$ [M+H]+: 408.0269, found 408.0310.

8-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2m)



It was isolated in a 54% yield (19 mg, 0.054mmol) as a white foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.2 – 7.2 (m, 2H), 7.2 – 7.1 (m, 1H), 7.0 – 6.9 (m, 2H), 5.7 (ddd, *J* = 17.4, 10.8, 5.4 Hz, 1H), 5.3 – 5.2 (m, 1H), 5.1 (dt, *J* = 10.8, 1.4 Hz, 1H), 4.4 (d, *J* = 13.3 Hz, 1H), 4.3 (dd, *J* = 15.1, 1.9 Hz, 1H), 4.1 – 4.0 (m, 1H), 4.0 (d, *J* = 13.4 Hz, 1H), 2.9 (dd, *J* = 15.1, 10.3 Hz, 1H), 2.4 (s, 3H), 2.3 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 139.6, 139.1, 138.7, 135.4, 135.3, 129.9, 129.7, 129.6, 128.7, 127.3, 117.3, 80.6, 72.0, 55.8, 21.7, 21.2. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1315.

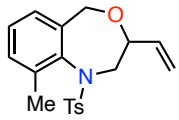
1-tosyl-8-(trifluoromethyl)-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2n)



It was isolated in an 85% yield (34 mg, 0.085mmol) as a yellow foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.0 Hz, 2H), 7.6 (s, 1H), 7.5 (d, *J* = 7.9 Hz, 1H), 7.4 (d, *J* = 7.9 Hz, 1H), 7.3 (d, *J* = 7.9 Hz, 2H), 5.7 (ddd, *J* = 16.8, 10.8, 5.3 Hz, 1H), 5.4 (d, *J* = 17.4 Hz, 1H), 5.2 (d, *J* = 10.8 Hz, 1H), 4.6 (d, *J* = 13.5 Hz, 1H), 4.4 (dd, *J* = 15.1, 1.9 Hz, 1H), 4.3 (d, *J* = 13.5 Hz, 1H), 4.2 (dd, *J* = 10.4, 5.4 Hz, 1H), 3.0 (dd, *J* = 15.2, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 142.2, 140.5, 138.1, 134.9, 131.3 (q, *J* = 33.0 Hz), 130.3, 130.1, 127.4, 126.1 (q, *J* = 3.7 Hz), 124.9 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.5

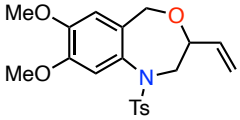
Hz), 117.7, 81.1, 71.8, 55.4, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{19}F_3NO_3S$ [M+H]+: 398.1038, found 398.1062.

9-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2o)



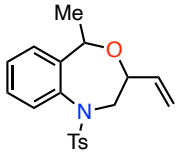
It was isolated in an 87% yield (30 mg, 0.087 mmol) as a pale-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.3 (d, *J* = 8.1 Hz, 2H), 7.2 – 7.1 (m, 2H), 7.0 (dd, *J* = 7.2, 1.9 Hz, 1H), 5.7 (ddd, *J* = 17.4, 10.7, 5.4 Hz, 1H), 5.3 – 5.1 (m, 2H), 4.4 – 4.2 (m, 2H), 4.2 – 4.1 (m, 2H), 3.0 (dd, *J* = 15.3, 10.8 Hz, 1H), 2.4 (s, 3H), 2.4 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.1, 140.3, 139.7, 138.8, 138.5, 135.4, 131.6, 130.0, 128.4, 127.8, 127.4, 117.2, 79.7, 72.5, 54.9, 21.7, 19.4. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1316.

7,8-dimethoxy-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2p)



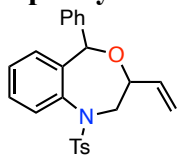
It was isolated in an 80% yield (31 mg, 0.08 mmol) as an amorphous white-off solid at 4 ºC.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 – 7.5 (m, 2H), 7.3 (d, *J* = 8.1 Hz, 2H), 6.9 (s, 1H), 6.7 (s, 1H), 5.7 (ddd, *J* = 17.3, 10.8, 5.3 Hz, 1H), 5.3 (dt, *J* = 17.4, 1.5 Hz, 1H), 5.2 (dt, *J* = 10.8, 1.4 Hz, 1H), 4.5 – 4.3 (m, 2H), 4.1 (ddq, *J* = 10.4, 5.1, 1.6 Hz, 1H), 4.0 (d, *J* = 13.4 Hz, 1H), 3.9 (s, 3H), 3.8 (s, 3H), 3.0 (dd, *J* = 15.1, 10.4 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.6, 148.3, 143.8, 138.6, 135.3, 132.3, 130.9, 129.9, 127.4, 117.3, 112.9, 112.0, 80.8, 72.1, 56.2, 55.8, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{20}H_{24}NO_5S$ [M+H]+: 390.1375, found 390.1374.

5-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2q)



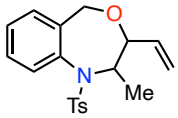
It was isolated in a 70% yield (24 mg, 0.07 mmol) of mixture of isomers (dr = 2:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 (t, *J* = 8.8 Hz, 3H), 7.4 (s, 2H), 7.3 – 7.1 (m, 9H), 5.8 (ddd, *J* = 16.7, 10.7, 5.7 Hz, 1H), 5.7 (ddd, *J* = 16.8, 10.9, 5.5 Hz, 1H), 5.3 (dq, *J* = 17.2, 1.7 Hz, 2H), 5.2 (t, *J* = 11.5 Hz, 2H), 4.5 (q, *J* = 6.7 Hz, 1H), 4.4 (dd, *J* = 10.6, 5.5 Hz, 2H), 4.3 (d, *J* = 14.8 Hz, 1H), 3.9 (d, *J* = 13.8 Hz, 1H), 3.5 (s, 1H), 2.9 (dd, *J* = 14.8, 10.5 Hz, 1H), 2.4 (s, 4H), 2.4 (s, 2H), 1.6 – 1.5 (m, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 143.8, 141.9, 139.9, 138.8, 135.6, 135.5, 129.9, 129.9, 128.7, 128.5, 128.5, 128.2, 127.8, 127.3, 127.2, 126.0, 117.6, 117.3, 80.8, 73.7, 73.1, 54.9, 21.7, 21.7, 19.1, 18.5. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1318.

5-phenyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepane (2r)



It was isolated in a 52% yield (21 mg, 0.052 mmol) of mixture of isomers (dr = 10:1) as a white foam.
^{1}H NMR of the major isomer (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 7.8 Hz, 2H), 7.4 (d, *J* = 7.9 Hz, 1H), 7.3 – 7.2 (m, 6H), 7.2 – 7.2 (m, 2H), 7.1 – 7.0 (m, 3H), 6.4 (d, *J* = 7.8 Hz, 1H), 5.7 (ddd, *J* = 16.3, 10.8, 4.8 Hz, 1H), 5.3 (dd, *J* = 17.5, 1.6 Hz, 1H), 5.2 – 5.1 (m, 2H), 4.4 (dt, *J* = 15.1, 1.6 Hz, 1H), 4.4 (dt, *J* = 10.8, 3.3 Hz, 1H), 3.0 (dd, *J* = 14.9, 10.6 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** of the major isomer (126 MHz, $CDCl_3$) δ 143.9, 142.6, 139.8, 139.6, 138.7, 135.1, 130.0, 129.5, 128.7, 128.6, 128.3, 128.0, 127.7, 127.4, 127.0, 117.1, 80.3, 80.1, 55.0, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{24}H_{24}NO_3S$ [M+H]+: 406.1477, found 406.1480.

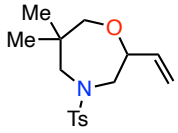
2-methyl-1-tosyl-3-vinyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepine (2s)



It was isolated in an 88% yield (30 mg, 0.088 mmol) of mixture of isomers (dr = 5:1) as an amorphous white solid at 4 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.0 Hz, 2H), 7.5 (d, *J* = 8.0 Hz, 1H), 7.4 – 7.2 (m, 8H), 5.7 (ddd, *J* = 16.9, 10.8, 4.8 Hz, 1H), 5.3 – 5.2 (m, 2H), 4.6 – 4.3 (m, 3H), 4.3 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.1 (d, *J* = 13.4 Hz, 1H), 2.4 (d, *J* = 10.3 Hz, 4H), 1.1 (d, *J* = 6.7 Hz, 1H), 0.8 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.7, 139.1, 138.4, 136.4, 136.1, 135.9, 130.9, 129.9, 129.4, 129.3, 128.8, 128.3, 128.1, 127.8, 127.2, 118.3, 116.3, 84.7, 73.4, 71.1, 57.2, 21.7, 17.4. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{19}H_{22}NO_3S$ [M+H]+: 344.1320, found 344.1328.

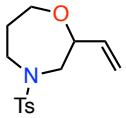
6,6-dimethyl-4-tosyl-2-vinyl-1,4-oxazepane (2t)



It was isolated in a 65% yield (20 mg, 0.065 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.3 – 7.3 (m, 2H), 5.7 (ddd, *J* = 17.3, 10.7, 5.5 Hz, 1H), 5.3 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.2 (dt, *J* = 10.7, 1.4 Hz, 1H), 4.1 (dddt, *J* = 9.2, 5.2, 3.6, 1.4 Hz, 1H), 3.7 (ddd, *J* = 13.3, 3.7, 1.6 Hz, 1H), 3.6 (d, *J* = 12.4 Hz, 1H), 3.5 – 3.4 (m, 1H), 3.4 (dd, *J* = 13.7, 1.6 Hz, 1H), 2.6 – 2.5 (m, 2H), 2.4 (s, 3H), 1.0 (s, 3H), 1.0 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 135.8, 135.6, 129.9, 127.3, 117.1, 82.6, 79.5, 60.4, 57.1, 37.9, 25.5, 23.8, 21.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{16}H_{24}NO_3S$ [M+H]+: 310.1477, found 310.1478.

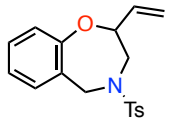
4-tosyl-2-vinyl-1,4-oxazepane (2u)



It was synthesized using 15 mol% $Pd(OAc)_2$, 16 mol% *rac*-BNP acid, 16 mol% ***rac*-L1 SOX**. It was isolated in a 72% yield (26 mg, 0.072 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.3 – 7.3 (m, 2H), 5.8 (ddd, *J* = 17.3, 10.7, 5.4 Hz, 1H), 5.3 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.2 (dt, *J* = 10.7, 1.5 Hz, 1H), 4.2 – 3.9 (m, 2H), 3.8 (ddd, *J* = 13.9, 2.7, 1.4 Hz, 1H), 3.8 – 3.7 (m, 2H), 3.0 (ddd, *J* = 13.8, 8.4, 5.4 Hz, 1H), 2.7 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.4 (s, 3H), 2.1 – 1.9 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 136.4, 135.6, 129.9, 127.1, 116.9, 81.7, 68.0, 55.7, 47.2, 30.7, 21.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{17}H_{17}N_2O_5S$ [M+H]+: 361.0858, found 361.0857.

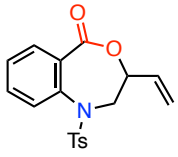
4-tosyl-2-vinyl-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepine (2v)



It was isolated in a 60% yield (20 mg, 0.06 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.0 Hz, 2H), 7.3 – 7.2 (m, 4H), 7.1 (t, *J* = 7.4 Hz, 1H), 7.0 (d, *J* = 7.9 Hz, 1H), 5.9 (dddd, *J* = 17.0, 10.7, 5.2, 0.8 Hz, 1H), 5.4 (dq, *J* = 17.2, 1.3 Hz, 1H), 5.4 – 5.2 (m, 1H), 4.7 (dd, *J* = 14.8, 1.6 Hz, 1H), 4.2 (dd, *J* = 14.8, 8.5 Hz, 2H), 3.9 (dt, *J* = 14.0, 2.0 Hz, 1H), 3.1 (dd, *J* = 14.0, 9.7 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.3, 143.6, 136.3, 134.8, 130.7, 129.8, 129.8, 129.5, 127.3, 124.3, 121.7, 117.6, 81.4, 55.5, 51.4, 21.6. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{20}N_2O_3S$ [M+H]+: 330.1164, found 330.1160.

1-tosyl-3-vinyl-2,3-dihydrobenzo[*e*][1,4]oxazepin-5(1*H*)-one (2w)

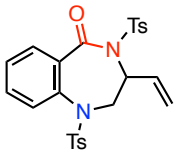


It was isolated in a 75% yield (26 mg, 0.075 mmol) as a white-off solid at 4 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 (dd, *J* = 15.8, 5.9 Hz, 3H), 7.4 (d, *J* = 8.0 Hz, 3H), 7.2 (d, *J* = 8.0 Hz, 2H), 5.8 (ddd, *J* = 16.9, 10.6, 5.9 Hz, 1H),

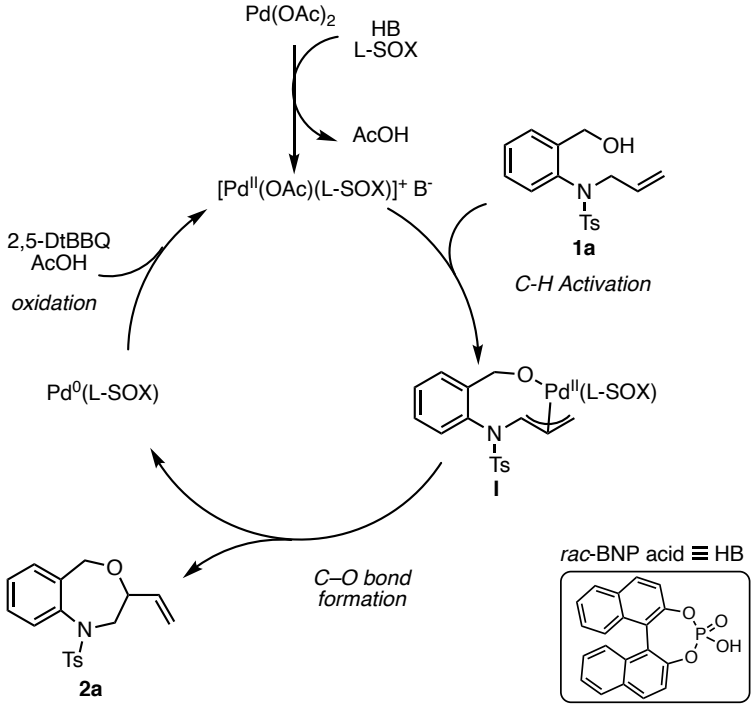
5.4 – 5.3 (m, 2H), 4.5 (t, J = 8.7 Hz, 1H), 4.3 (dd, J = 13.5, 11.9 Hz, 1H), 3.7 (dd, J = 13.5, 3.2 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.2, 144.5, 135.1, 134.7, 133.8, 132.2, 131.4, 130.9, 130.5, 130.0, 129.4, 127.4, 119.9, 76.7, 54.7, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{18}NO_4S$ [M+H]+: 344.0957, found 344.0954.

1,4-ditosyl-3-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (2x)



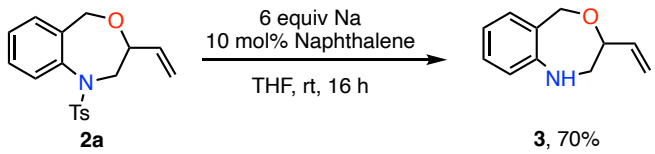
It was isolated in a 55% yield (27 mg, 0.055 mmol) as an amorphous yellow solid at 4 ºC.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 – 7.9 (m, 1H), 7.4 – 7.4 (m, 4H), 7.3 – 7.2 (m, 3H), 7.1 (d, J = 8.2 Hz, 1H), 5.4 (s, 1H), 5.2 – 5.1 (m, 1H), 4.8 – 4.6 (m, 3H), 4.0 – 3.9 (m, 1H), 2.4 (s, 3H), 2.3 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.9, 145.2, 144.3, 136.0, 135.8, 135.6, 133.3, 131.1, 130.4, 130.0, 129.5, 129.3, 128.9, 127.6, 117.5, 55.7, 55.1, 21.8, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{25}H_{25}N_2O_5S_2$ [M+H]+: 497.1205, found 497.1208.

Proposed Mechanism for the Pd-Catalyzed Allylic C-H Activation to Seven Membered *N*,*O*-Heterocycles



Derivatization of 1,4-Benzoxazepine 2a

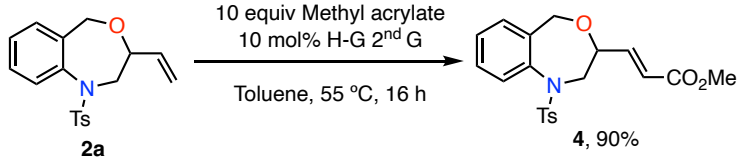
3-vinyl-1,2,3,5-tetrahydrobenzo[e][1,4]oxazepane (3)



2a **3**, 70%

To a solution of naphthalene (7.8 mg, 0.061 mmol, 0.2 equiv) in anhydrous THF (4 mL) in an oven-dried Schlenk flask under a stream of argon, hexane-rinsed sheets of sodium metal were added (44 mg, 1.885 mmol, 6 equiv). The mixture was then sonicated at rt until green color persisted when a solution of **2a** (100 mg, 0.304 mmol, 1 equiv) in THF (4 mL) was then added, resulting in a rapid loss of the green color. The turbid yellow reaction mixture was removed from sonicator and stirred at rt for 15 h. Afterwards, the reaction was cooled to 0 ºC and 10 mL of MeOH was slowly added to quench the Na followed by addition of a saturated solution of $NaHCO_3$ (*NOTE*: *only after consumption*). The reaction was diluted with Et_2O and washed with $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The product was purified by silica gel column chromatography with hexanes/EtOAc (8:2) as the eluent to give the desired product **3** in a 70% yield (37 mg, 0.213 mmol) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.2 (dd, *J* = 9.8, 7.4 Hz, 2H), 6.9 – 6.7 (m, 2H), 5.9 (ddd, *J* = 16.9, 10.7, 5.5 Hz, 1H), 5.4 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.3 – 5.1 (m, 1H), 4.8 (d, *J* = 13.5 Hz, 1H), 4.6 (d, *J* = 13.4 Hz, 1H), 4.3 – 4.0 (m, 1H), 3.3 (dd, *J* = 13.4, 2.0 Hz, 1H), 2.9 (dd, *J* = 13.3, 9.3 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.6, 136.7, 130.3, 129.6, 128.7, 120.9, 118.6, 116.5, 82.7, 73.1, 54.2. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{11}H_{14}NO$ [M +H]+: 176.1075, found 176.1082.

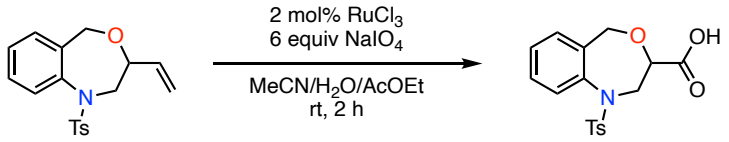
Methyl (*E*)-3-(1-tosyl-1,2,3,5-tetrahydrobenzo[*e*][1,4]oxazepin-3-yl)acrylate (4)



2a **4**, 90%

A flame-dried schlenk charged with the 2nd generation Hoveyda-Grubbs catalyst (6.3 mg, 0.01 mmol, 0.1 equiv) was put under vacuum and backfilled with argon for three times. Afterward, a solution of **2a** (33 mg, 0.1 mmol, 1 equiv) and methyl acrylate (90 µl, 1 mmol, 10 equiv) in 1 mL of dry toluene was added the reaction was heated for 16 h in an oil batgh. The volatiles were removed, and the resulting residue was purified by silica gel column chromatography with a mixture of Hexanes/AcOEt (7:3) as eluent, to give the desired product **4** in a 90% yield (35 mg, 0.09 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 2H), 7.3 – 7.1 (m, 6H), 6.7 (dd, *J* = 15.8, 4.2 Hz, 1H), 6.0 (dd, *J* = 15.8, 1.8 Hz, 1H), 4.5 (d, *J* = 13.4 Hz, 1H), 4.4 – 4.3 (m, 2H), 4.2 (d, *J* = 13.4 Hz, 1H), 3.7 (s, 3H), 2.9 (dd, *J* = 15.2, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 144.1, 143.7, 139.7, 138.4, 138.1, 130.0, 129.8, 129.2, 128.9, 128.3, 127.3, 122.3, 79.3, 72.5, 55.0, 51.9, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{20}H_{22}NO_5S$ [M +H]+: 388.1219, found 388.1215.

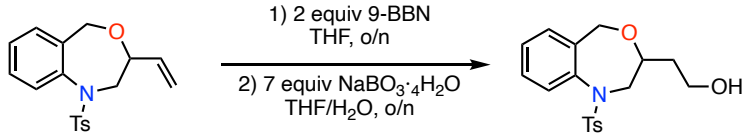
1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,4]oxazepine-3-carboxylic acid (5)



2a **5**, 87%

To a solution of **2a** (33mg, 0.1 mmol, 1 equiv) in MeCN (0.7 mL), H_2O (0.35 mL) and AcOEt (0.7 mL) was added $NaIO_4$ (130 mg, 0.6 mmol, 6 equiv) and $RuCl_3$(0.5 mg, 0.002 mmol, 0.02 equiv). The reaction was stirred at rt for 2 h (*the color of the reaction turns to yellow).* Then, the reaction was washed with brine and extracted with EtOAc. The combination of organic phases was dried over Na_2SO_4 and the solvent was concentrated in vacuo. The residue was then filtrated through a plug of celite®, Fluorisil and SiO_2 to give the desired product **5** in an 87% yield (30 mg, 0.087 mmol) as an amorphous white-off foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.7 (d, *J* = 8.2 Hz, 2H), 7.4 – 7.2 (m, 6H), 6.3 (s, 1H), 4.7 (dd, *J* = 15.2, 2.1 Hz, 1H), 4.7 (d, *J* = 13.5 Hz, 1H), 4.4 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.3 (d, *J* = 13.4 Hz, 1H), 3.2 (dd, *J* = 15.2, 10.3 Hz, 1H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 144.3, 139.7, 138.1, 137.1, 130.2, 130.0, 129.6, 129.0, 128.4, 127.3, 78.7, 72.6, 52.9, 21.7. **HRMS** (MM: ESI-APCI-) m/z calc'd for $C_{17}H_{16}NO_5S$ [M -H]: 346.0755, found 346.0746.

2-(1-tosyl-1,2,3,5-tetrahydrobenzo[e][1,4]oxazepin-3-yl)ethan-1-ol (6)

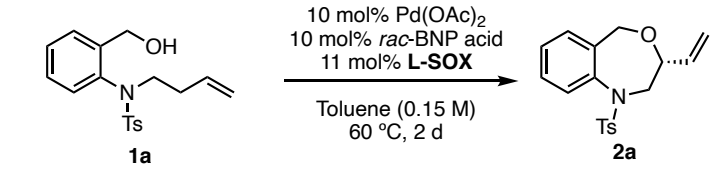


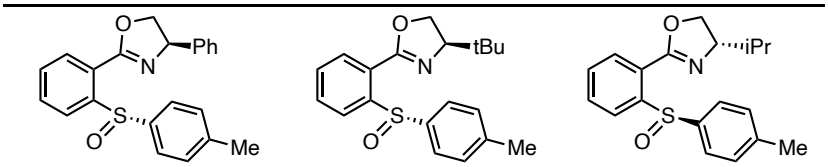
2a **6**, 72%

To a stirred solution of **2a** (33 mg, 0.1 mmol, 1 equiv) in 0.1 mL of THF was added 9-BBN (0.4 mL (0.5 M in THF), 0.2 mmol, 2 equiv) and the resulting mixture was stirred overnight at 60 ºC in an oil bath. The solution was diluted with THF (0.2 mL) and cooled to 0 ºC. Then 0.1 mL of water was added dropwise followed by $NaBO_3{\cdot}4H_2O$ (108 mg, 0.7 mmol, 7 equiv) and the reaction was warmed to rt and stirred overnight. Then the reaction was extracted with AcOEt, washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The resulting product was purified by silica gel column chromatography with Hexanes/EtOAC (1:1) as eluent to give the desired product **6** in a 72% yield (24 mg, 0.072 mmol) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.6 (d, *J* = 7.9 Hz, 2H), 7.4 – 7.1 (m, 6H), 4.5 (d, *J* = 13.4 Hz, 1H), 4.3 (d, *J* = 15.0 Hz, 1H), 4.2 – 4.1 (m, 1H), 4.0 – 3.6 (m, 3H), 3.0 (dd, *J* = 15.1, 10.2 Hz, 1H), 2.4 (s, 3H), 2.2 (s, 1H), 1.6 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9, 140.0, 138.6, 138.2, 129.9, 129.7, 129.1, 128.9, 128.1, 127.3, 80.4, 72.6, 60.6, 55.9, 35.5, 21.7. **HRMS** (MM: ESI-APCI+) m/z calc'd for $C_{18}H_{22}NO_4S$ [M-OH_2]+: 330.1164, found 330.1161.

Pd-Catalyzed Asymmetric Allylic C-H Functionalization

A 4 mL flamed-dried vial equipped with a stirring magnetic bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), **L-SOX** (0.011 mmol, 0.11 equiv), *rac*-BNP acid (3.8 mg, 0.011 mmol, 0.11 equiv), 2,5-di-tert-butyl-1,4-benzoquinone (2,5-DtBBQ) (33 mg, 0.15 mmol, 1.5 equiv), **1a** (0.1 mmol, 1 equiv) and toluene (0.67 mL, 0.15 M). The mixture was heated under air and moisture for 48 h at 60 ºC. After cooling and stripping off the solvent, the residue was purified in a silica gel column chromatography with a gradient (9.5:0.5 to 8:2) of Hexanes/AcOEt to give the desired product.



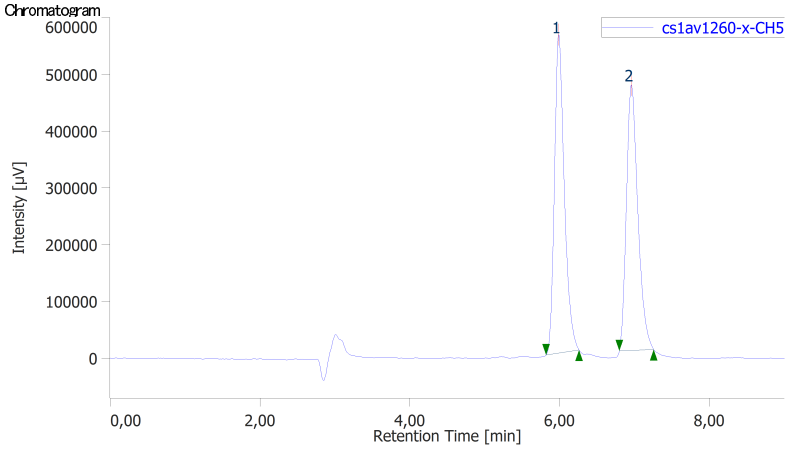


L1-SOX (R,S)
90%
70:30 er

L2-SOX (R,S)
80%
56:44 er

L3-SOX (S,R)
97 %
34:66 er

***rac*-L1-SOX** sample: SFC conditions: 30% MeOH, Phenomenex Amylose 1 at 40 ºC, (CO2/MeOH = 70:30 1mL/min, l= 210 nm, t_R (min): 5.98, 6.93.

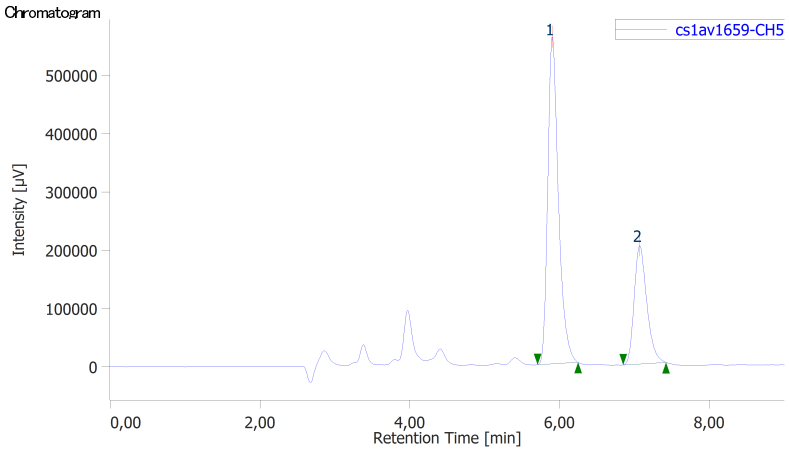


Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	5,983	5130100	560793	50,857	54,539	N/A	10570	3,834	1,340	
2	Unknown	5	6,953	4957209	467447	49,143	45,461	N/A	10262	N/A	1,341	

Signals in the range around 2-4 min are due to the front arriving to the detector.

L1-SOX (R,S) sample: SFC conditions:30% MeOH, Phenomenex Amylose 1 at 40ºC , (CO2/MeOH = 70:30 1mL/min, l= 210 nm, t_R (min): major = 5.90, minor = 7.06.



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
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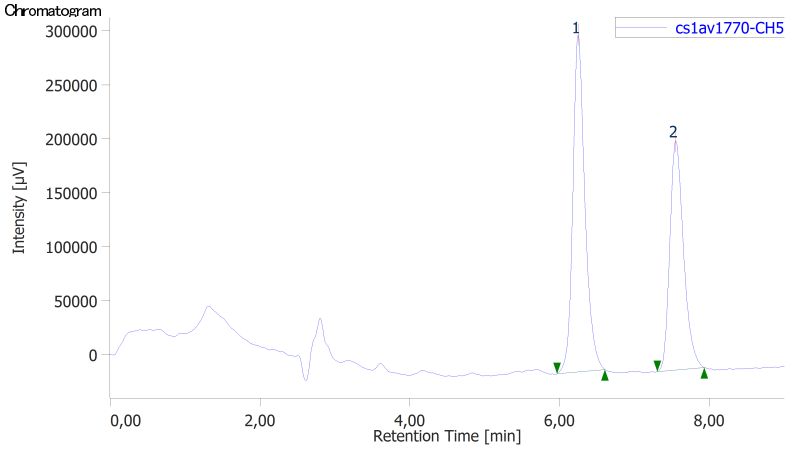
2	Unknown	5	7,067	2374814	202992	29,966	26,564	N/A	8766	N/A	1,292	

Signals in the range around 2-4 min are due to the front arriving to the detector.

L2-SOX (R,S) sample :SFC conditions: 30% MeOH, Phenomenex Amylose 1 at 40ºC , (CO2/MeOH = 70:30 1mL/min, l= 210 nm, t_R (min): major = 6.27, minor = 7.54.

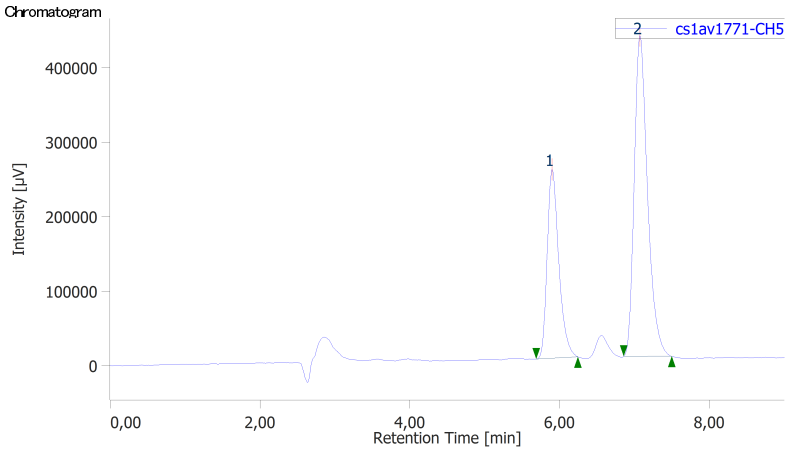


Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	6,247	3498137	312209	56,383	59,533	N/A	8020	4,290	1,222	
2	Unknown	5	7,547	2706096	212224	43,617	40,467	N/A	8439	N/A	1,314	

Signals in the range around 2-4 min are due to the front arriving to the detector.

L3-SOX (S,R) sample: SFC conditions: 30% MeOH, Phenomenex Amylose 1 at 40ºC , (CO2/MeOH = 70:30 1mL/min, l= 210 nm, tR (min): minor = 5.89, minor = 7.07.



Peak Information

#	Peak Name	CH	tR [min]	Area [µV*sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	5,897	2721710	253185	33,918	37,047	N/A	7382	3,990	1,364	
2	Unknown	5	7,070	5302598	430237	66,082	62,953	N/A	8051	N/A	1,344	

Signals in the range around 2-4 min are due to the front arriving to the detector.

X-Ray Crystallographic Data

Crystallographic Data for Compound 2l

Single crystals of compound **2l** (CCDC 2108910) suitable for X-Ray diffraction analysis were grown from solution in DCM in a Hexanes atmosphere (vapor diffusion technique).

Figure S1. ORTEP drawing of **2l** showing ellipsoids at the 30% contour probability level

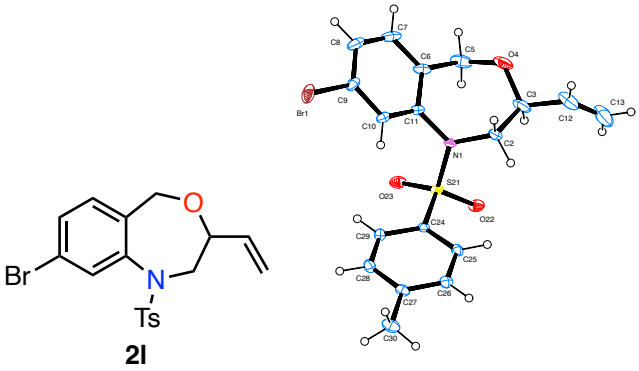


Table S2. Sample and crystal data for 2l (CCDC 2108910).

Identification code	21SRA006	
Chemical formula	$C_{18}H_{18}BrNO_3S$	
Formula weight	408.30 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.081 x 0.125 x 0.256 mm	
Crystal habit	clear colourless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.3536(8) Å	α = 90°
	b = 9.6592(7) Å	β = 107.174(3)°
	c = 16.8001(12) Å	γ = 90°
Volume	1760.3(2) $Å^3$	
Z	4	
Density (calculated)	1.541 g/cm^3	
Absorption coefficient	2.469 mm^{-1}	
F(000)	832	

Table S3. Data collection and structure refinement for 2l.

Diffractometer	Bruker D8 VENTURE PHOTON-III C14 κ-geometry diffractometer
Radiation source	Incoatec IμS 3.0 microfocus sealed tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.46 to 30.54°
Reflections collected	291603
Independent reflections	5431 [R(int) = 0.0866]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2015)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5431 / 181 / 220
Goodness-of-fit on F^2	1.070
Δ/σ_{max}	0.001
Final R indices	4684 data; I>2σ(I) R1 = 0.0615, wR2 = 0.1499
	all data R1 = 0.0724, wR2 = 0.1572
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0579P)^2+4.7000P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.041 and -1.332 eÅ^{-3}
R.M.S. deviation from mean	0.109 eÅ^{-3}

Crystallographic Data for Compound 2p

Single crystals of compound **2p** (CCDC 2108911) suitable for X-Ray diffraction analysis were grown from solution in DCM in a Hexanes atmosphere (vapor diffusion technique).

Figure S2. ORTEP drawing of **2p** showing ellipsoids at the 30% contour probability level

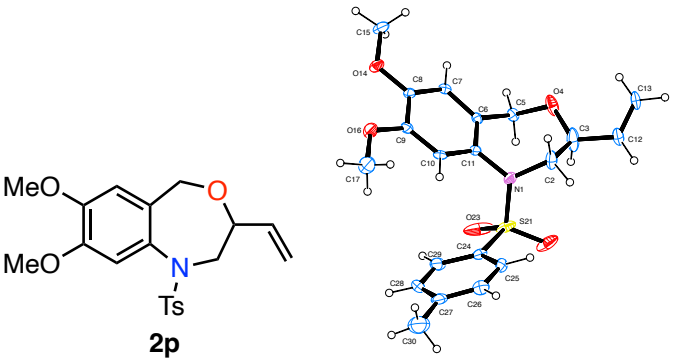


Table S4. Sample and crystal data for 2p (CCDC 2108911).

Identification code	21SRA007	
Chemical formula	$C_{20}H_{23}NO_5S$	
Formula weight	389.45 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.066 x 0.070 x 0.318 mm	
Crystal habit	clear colourless prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.3804(8) Å	α = 90°
	b = 23.7391(19) Å	β = 114.324(3)°
	c = 9.4372(7) Å	γ = 90°
Volume	1914.9(3) $Å^3$	
Z	4	
Density (calculated)	1.351 g/cm^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	824	

Table S5. Data collection and structure refinement for 2p.

Diffractometer	Bruker D8 VENTURE PHOTON-III C14 κ-geometry diffractometer
Radiation source	Incoatec IμS 3.0 microfocus sealed tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.37 to 28.39°
Index ranges	-12<=h<=12, -31<=k<=31, -12<=l<=12
Reflections collected	73538
Independent reflections	4842 [R(int) = 0.0705]
Coverage of independent reflections	99.4%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9870 and 0.9390

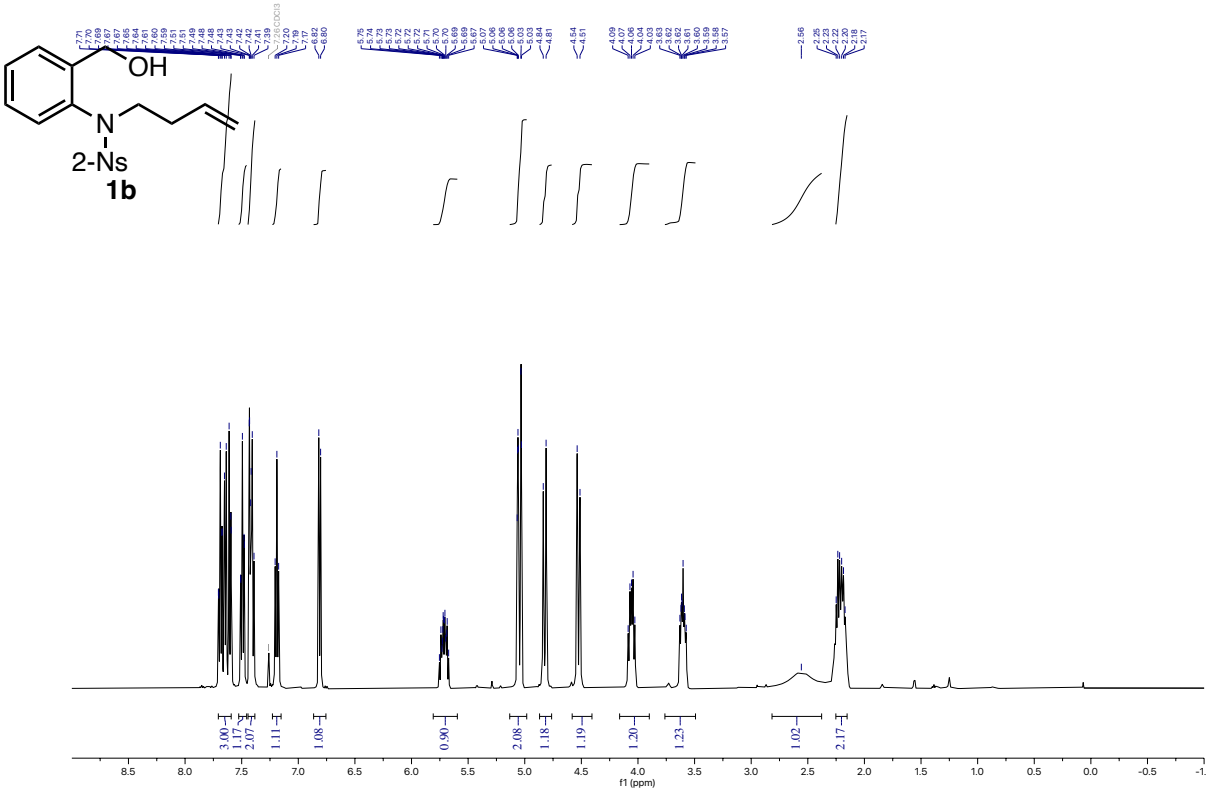
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2015)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4842 / 226 / 267	
Goodness-of-fit on F^2	1.243	
Final R indices	4364 data; $I>2\sigma(I)$	R1 = 0.1292, wR2 = 0.2387
	all data	R1 = 0.1384, wR2 = 0.2431
Weighting scheme	$w=1/[\sigma^2(F_o^2)+12.0839P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.879 and -0.696 eÅ^{-3}	
R.M.S. deviation from mean	0.168 eÅ^{-3}	

References

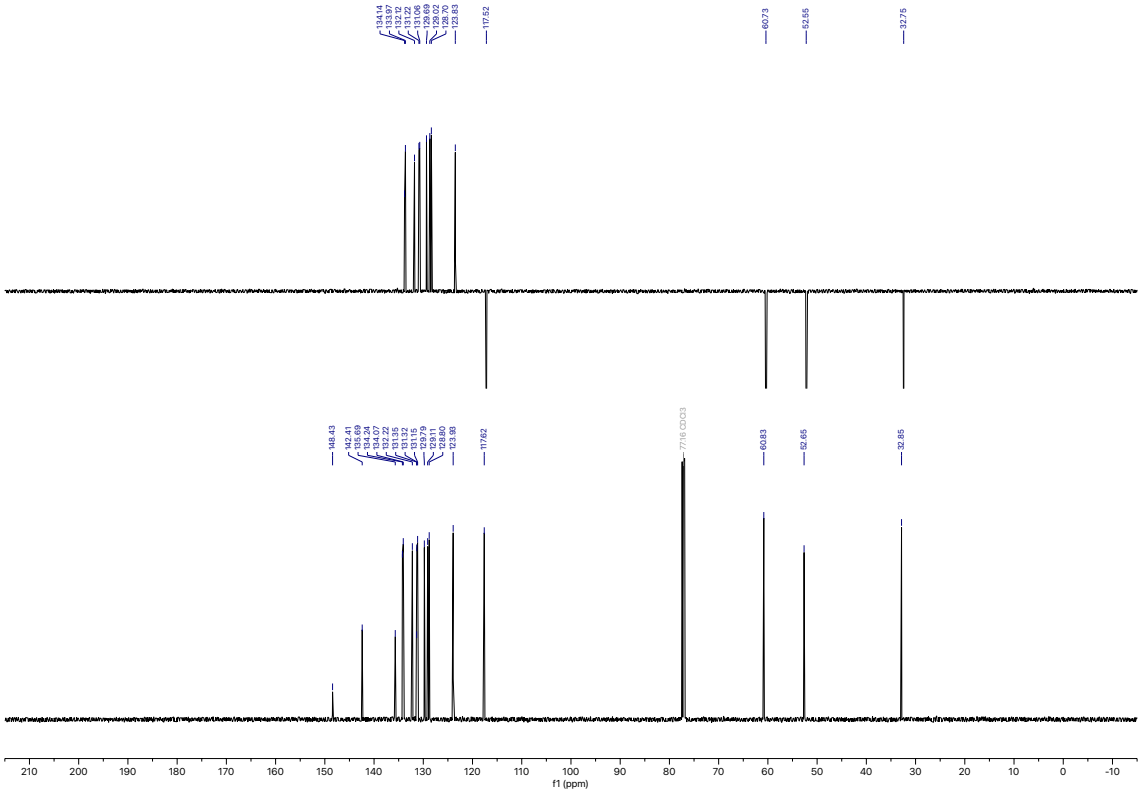
1. Bernárdez, R.; Suárez, J.; Fañanás-Mastral, M.; Varela, J. A.; Saá, C. *Org. Lett.* **2016**, *18*, 642-645.
2. a) Zhao, C.-Y.; Li, K.; Pang, Y.; Li, J.-Q.; Liang, C.; Su, G.-F.; Mo, D.-L. *Adv. Synth. Catal.* **2018**, *360*, 1919-1925. b) Yang, F.; Ding, D.; Wang, C. *Org. Lett.* **2020**, *22*, 9203-9209. c) Theeraladanon, C.; Arisawa, M.; Nishida, A.; Nakagawa, M. *Tetrahedron* **2004**, *60*, 3017-3035. d) Nishiguchi, A.; Ikemoto, T.; Ito, T.; Miura, S.; Tomimatsu, K. *Heterocycles* **2007**, *71*, 1183-1192. e) Iioka, R.; Yorozu, K.; Sakai, Y.; Kawai, R.; Hatae, N.; Takashima, K.; Tanabe, G.; Wasada, H.; Yoshimatsu, M. *Eur. J. Org. Chem.* **2021**, 1553-1558. f) Jia, M.-Q.; You, S.-L. *ACS Catalysis* **2013**, *3*, 622-624. g) Guo, Z.; Jia, H.; Liu, H.; Wang, Q.; Huang, J.; Guo, H. *Org. Lett.* **2018**, *20*, 2939-2943. h) Rogers, M. M.; Wendlandt, J. E.; Guzei, I. A.; Stahl, S. S. *Org. Lett.* **2006**, *8*, 2257.
3. Ammann, S. E.; Liu, W.; White, M. C. *Angew. Chem. Int. Ed.* **2016**, *55*, 9571-9575.
4. M. Bandini, M. Monari, A. Romaniello and M. Tragni, *Chem. Eur. J.*, 2010, **16**, 14272

NMR Spectra

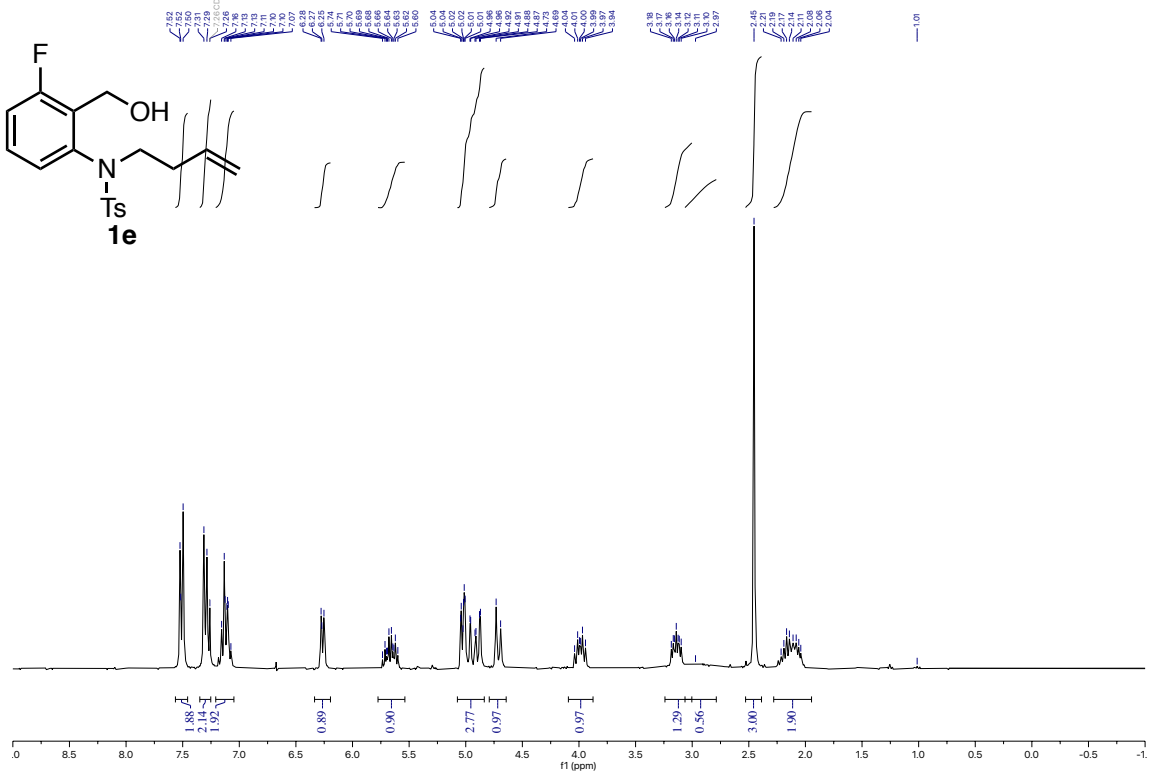
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



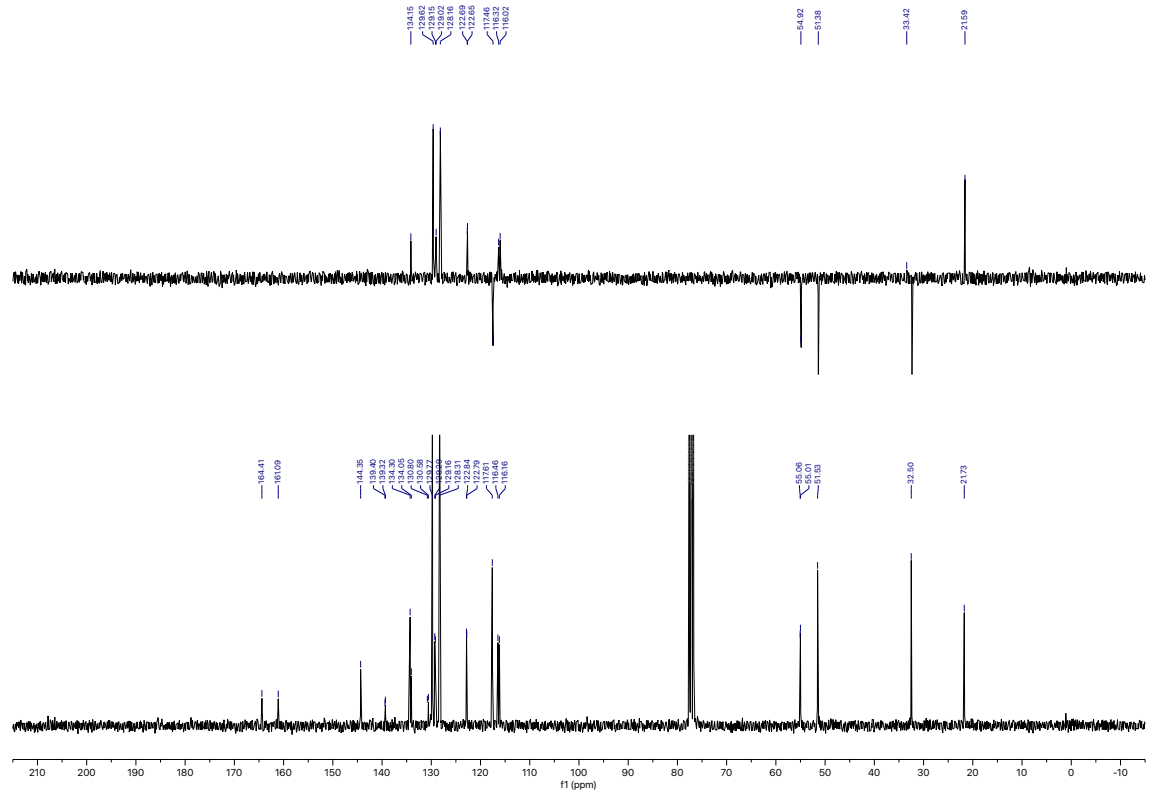
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (300 MHz). Solvent $CDCl_3$



^{13}C-NMR (75 MHz). Solvent $CDCl_3$



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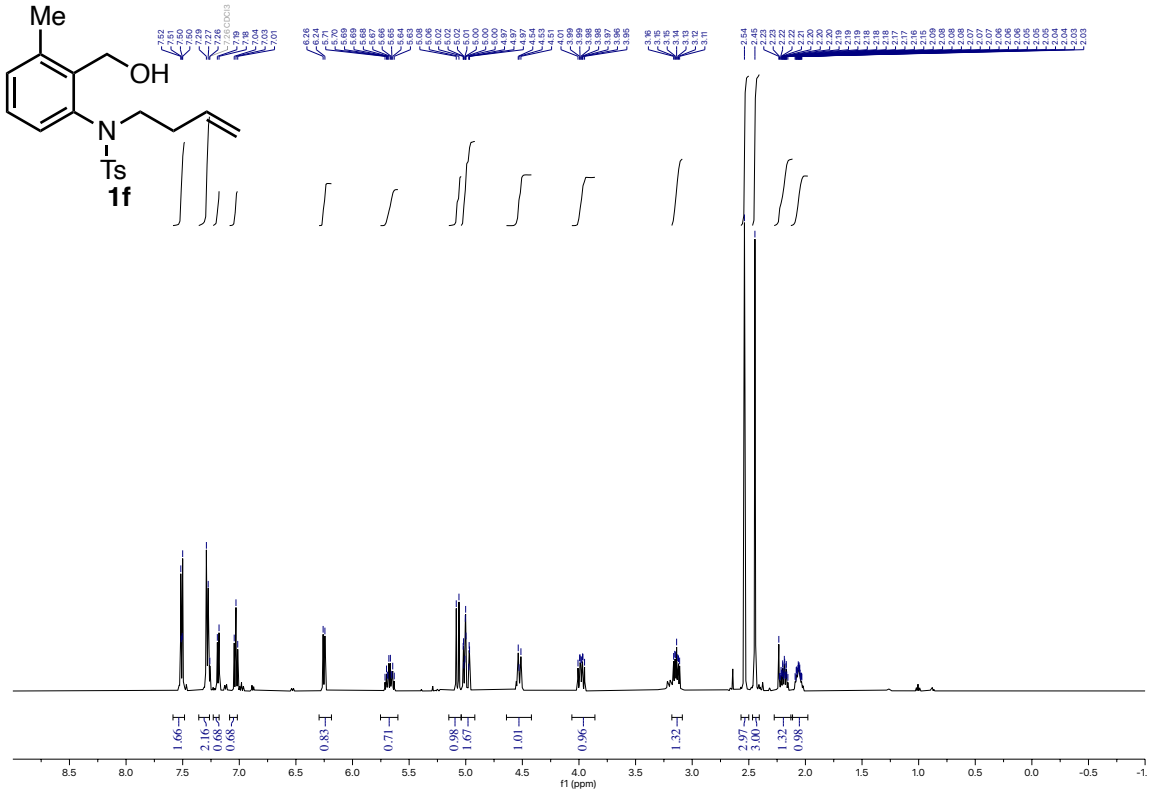

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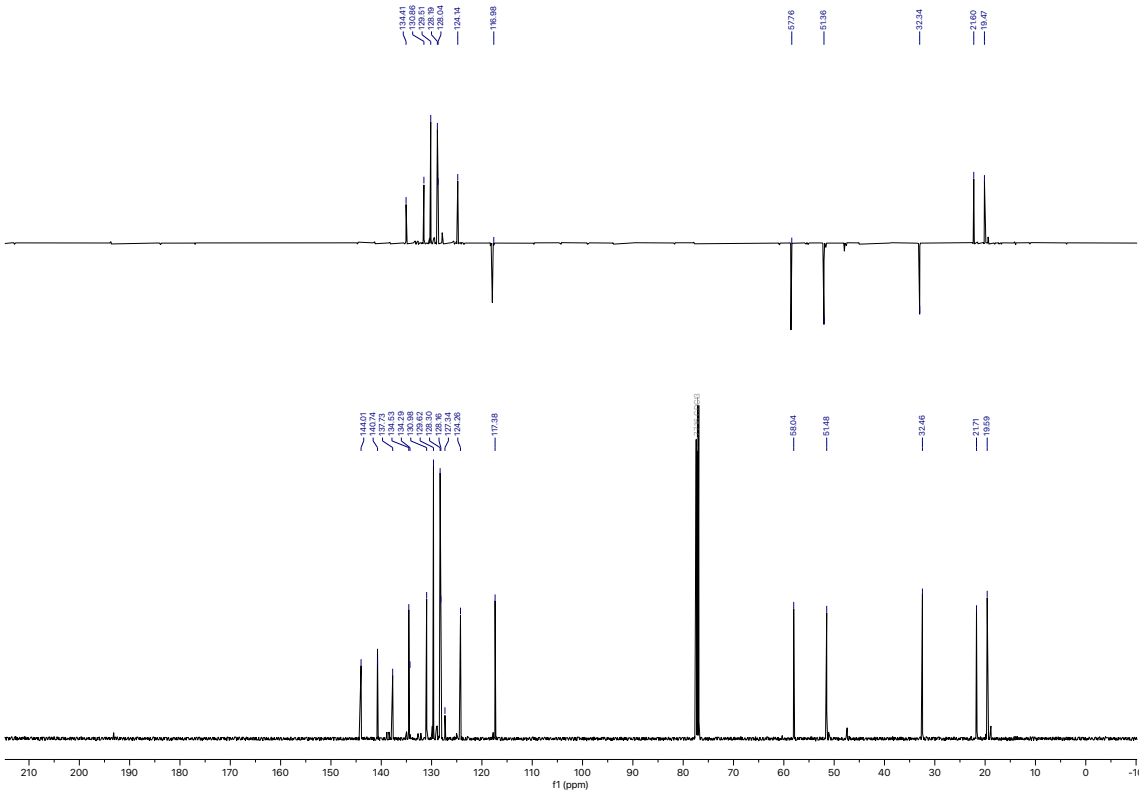

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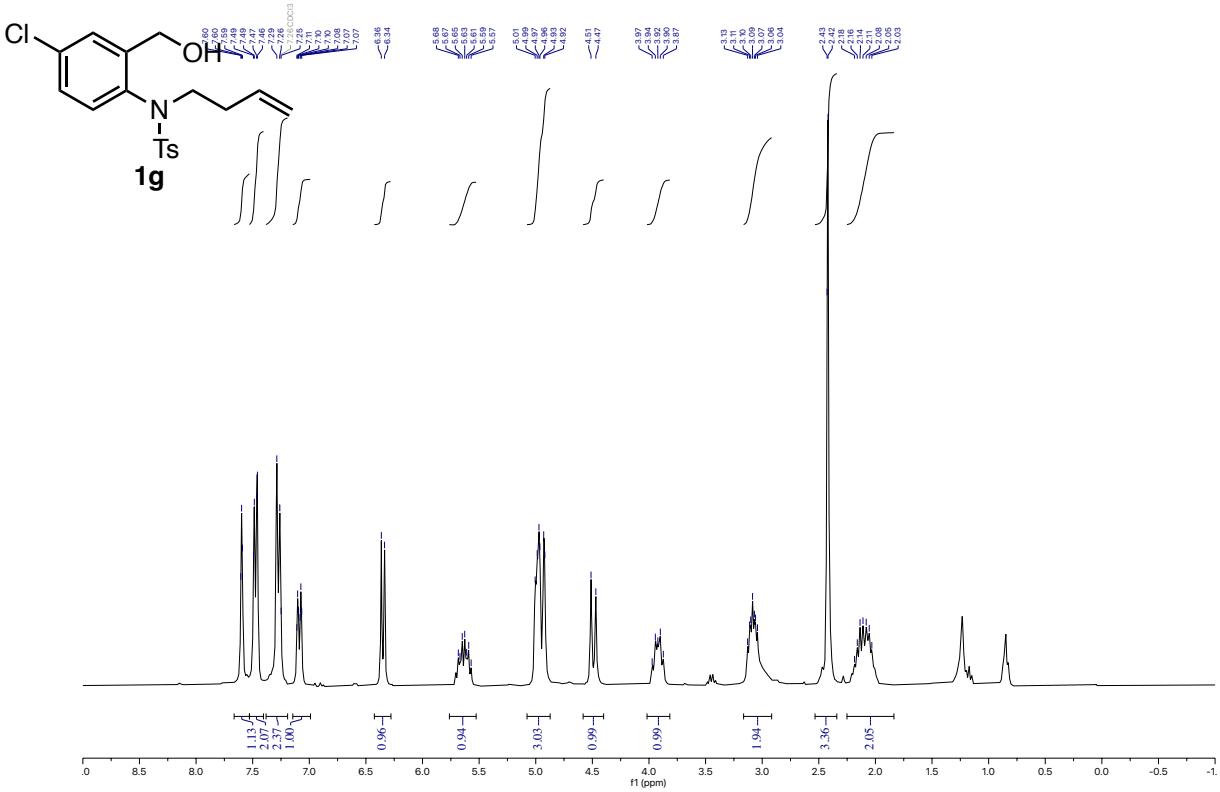
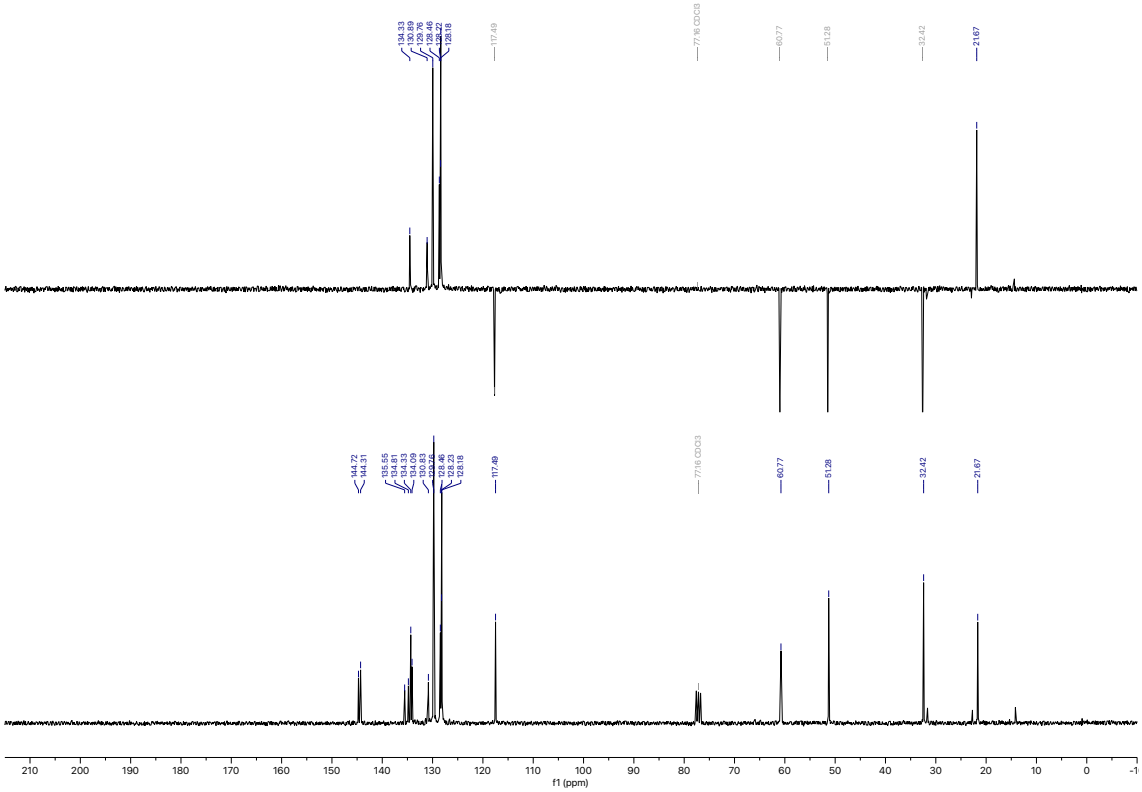
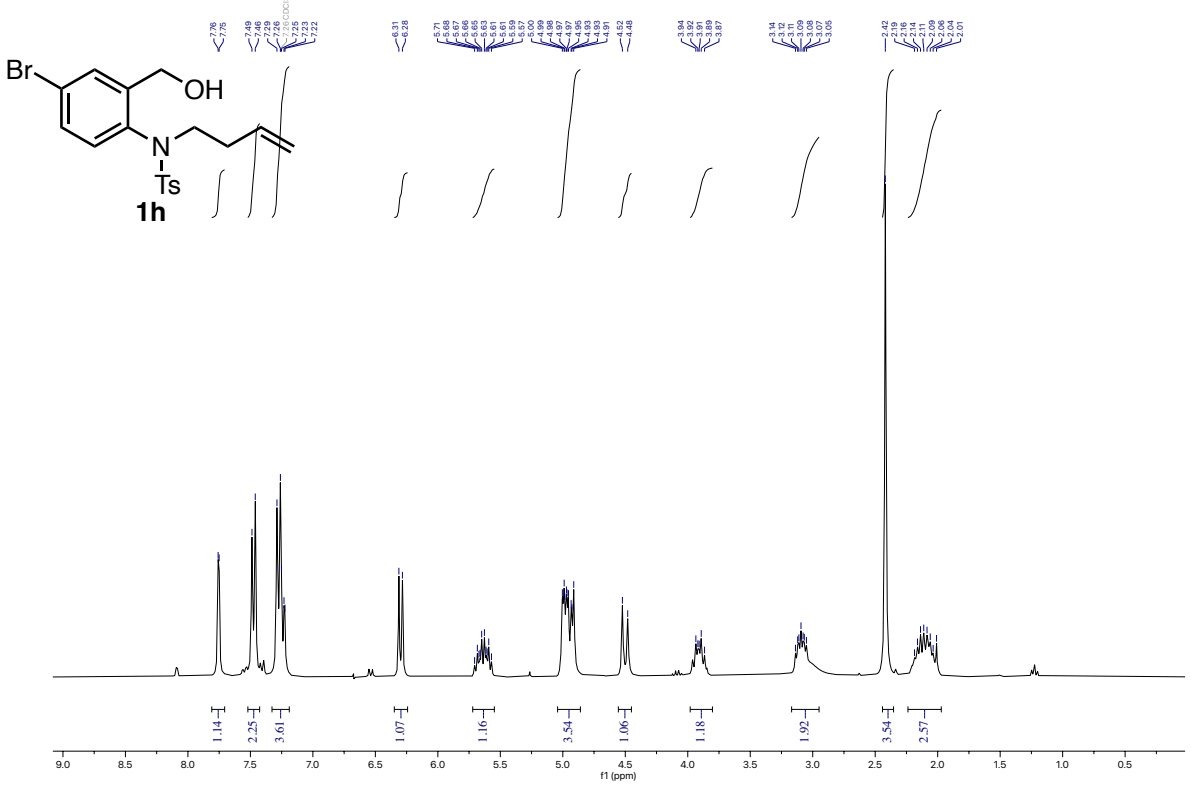


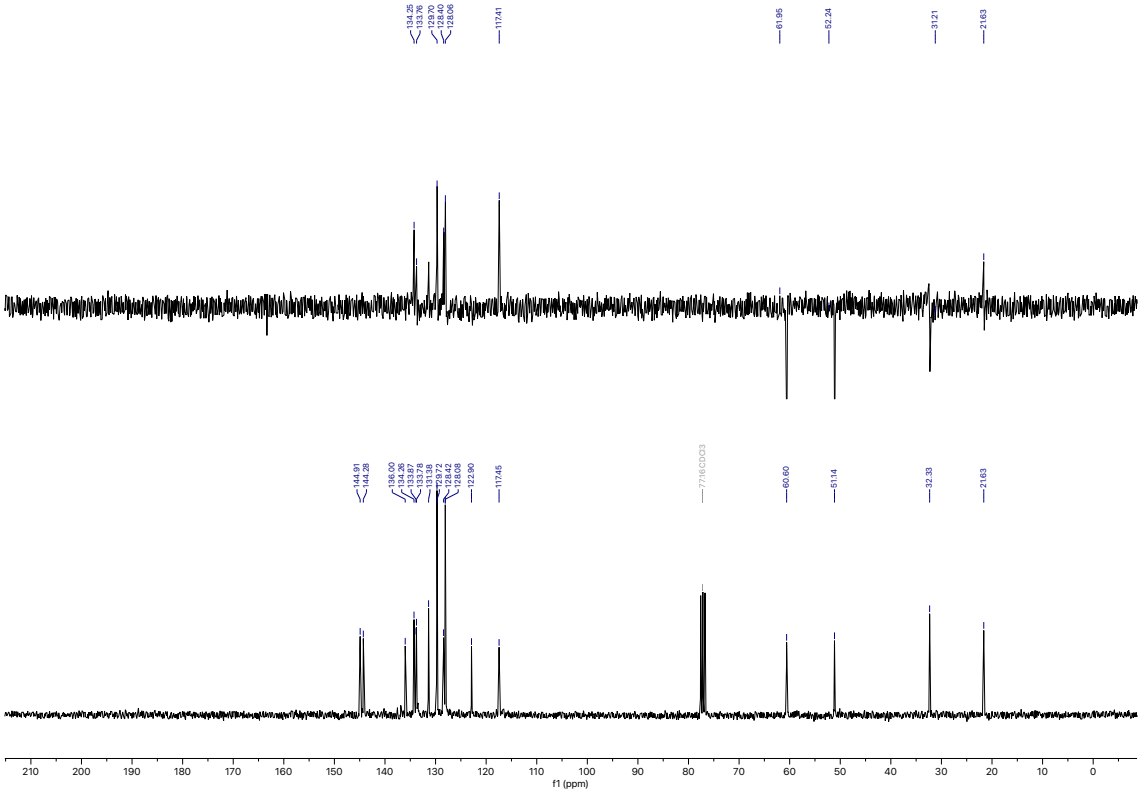
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (300 MHz). Solvent $CDCl_3$



^{13}C-NMR (75 MHz). Solvent $CDCl_3$



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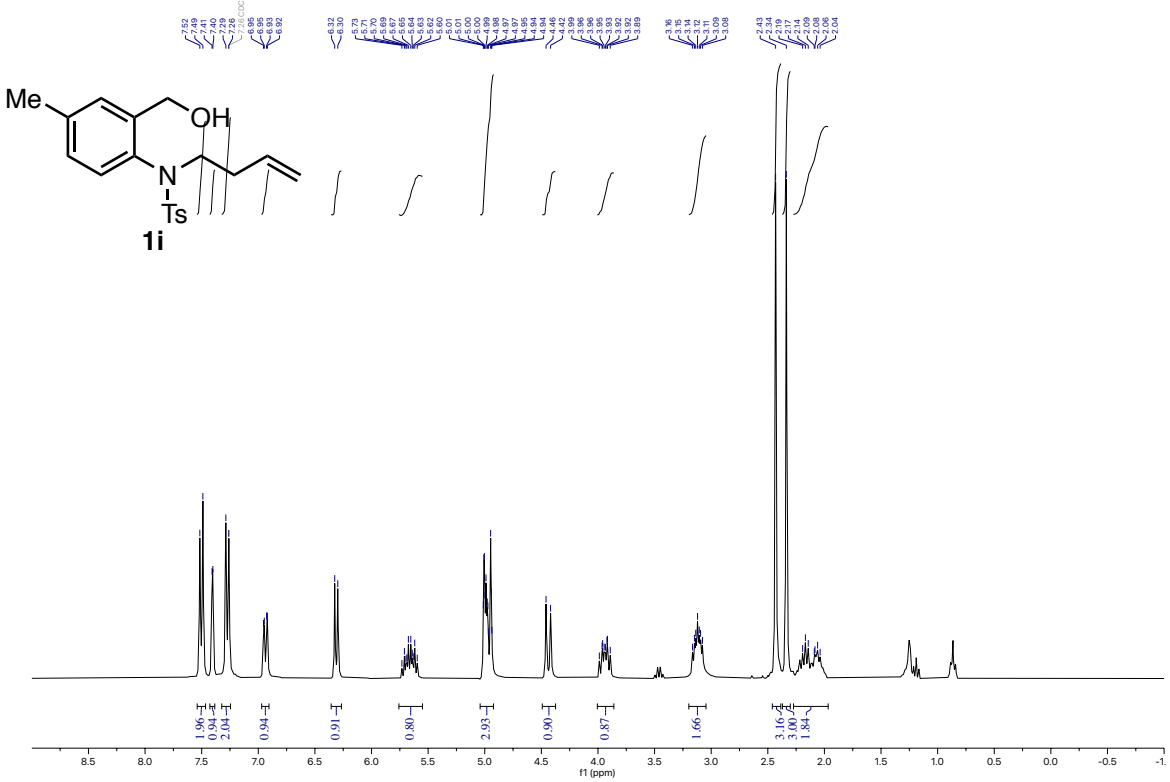
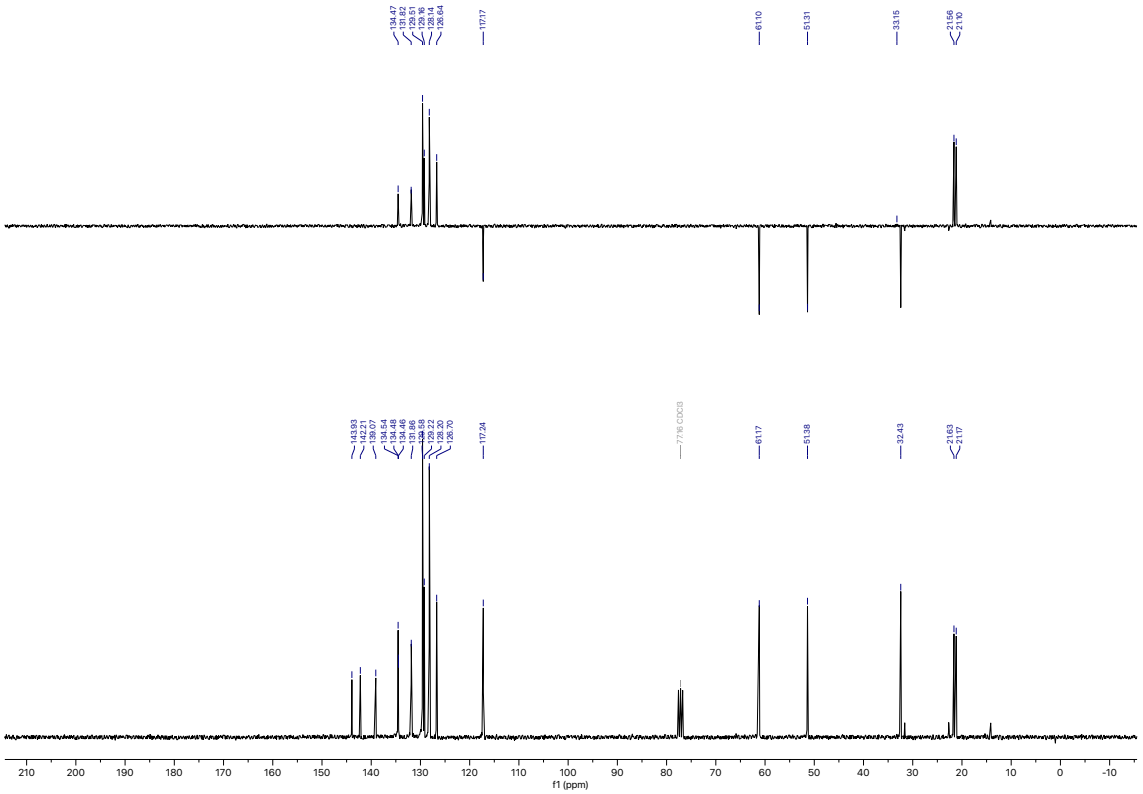
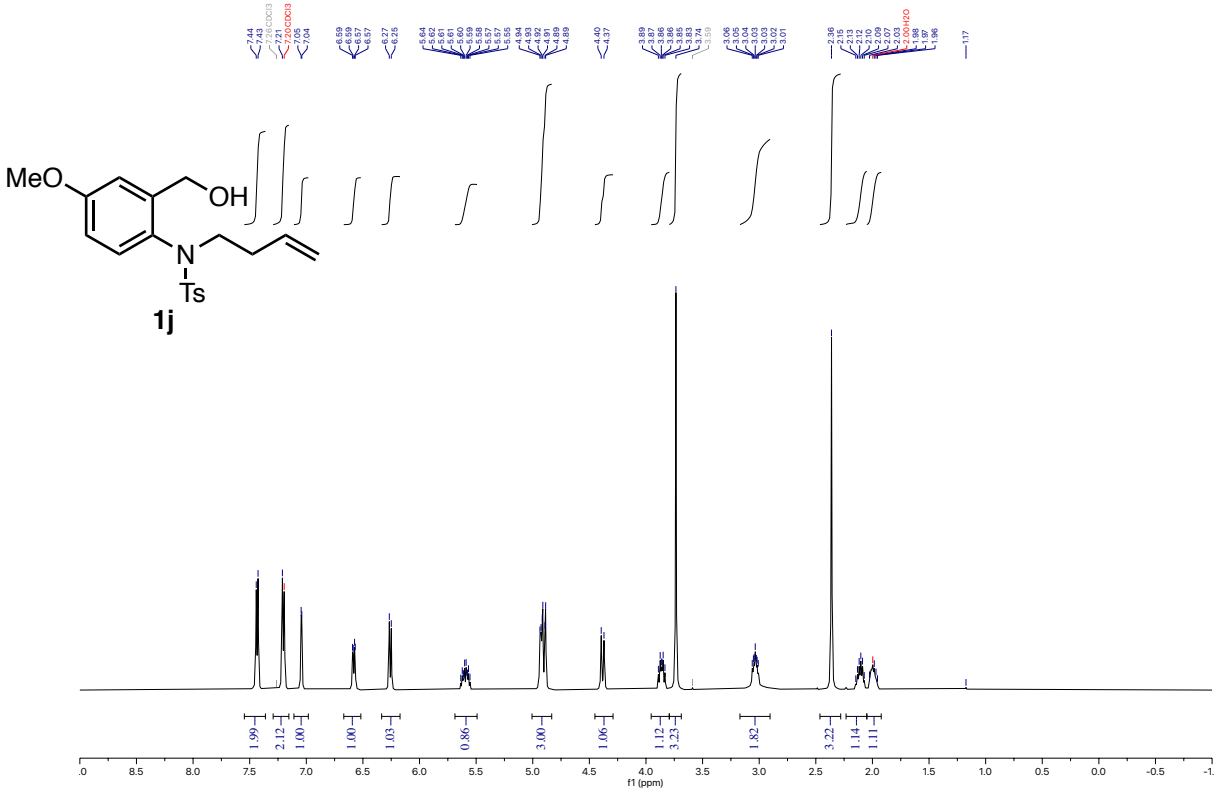


^{13}C-NMR (75 MHz). Solvent $CDCl_3$



^{1}H-NMR (500 MHz). Solvent $CDCl_3$



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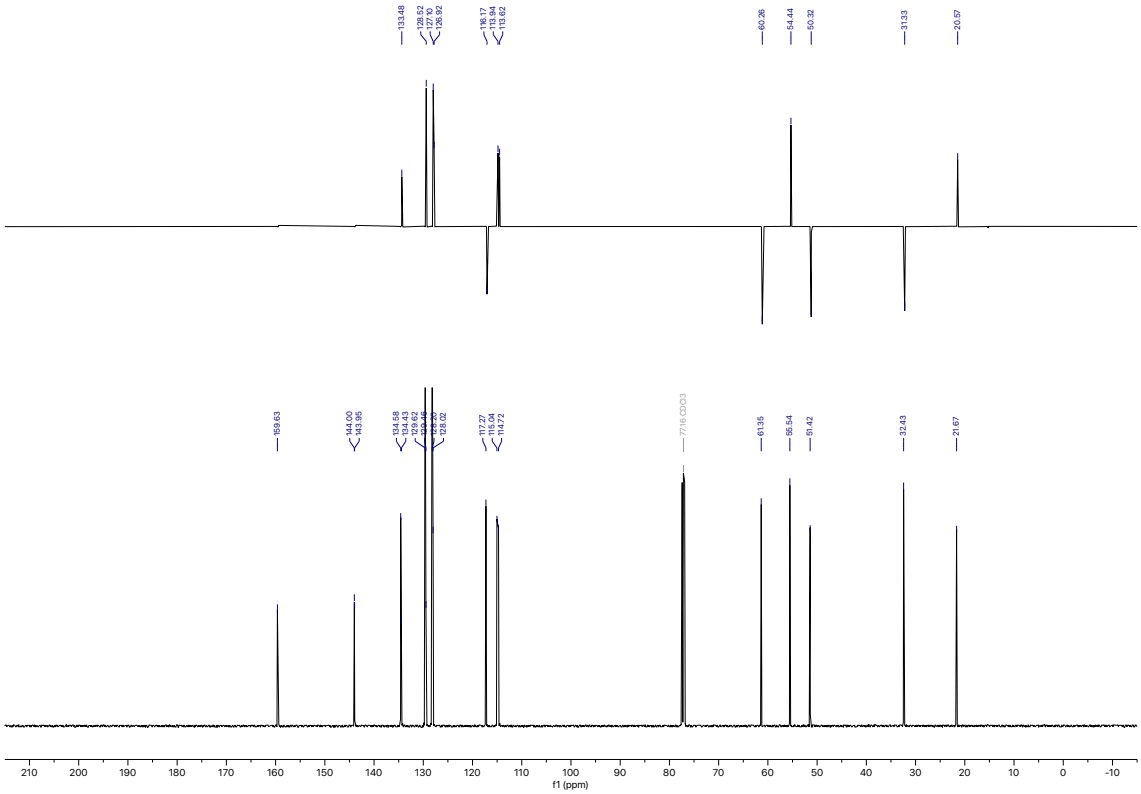

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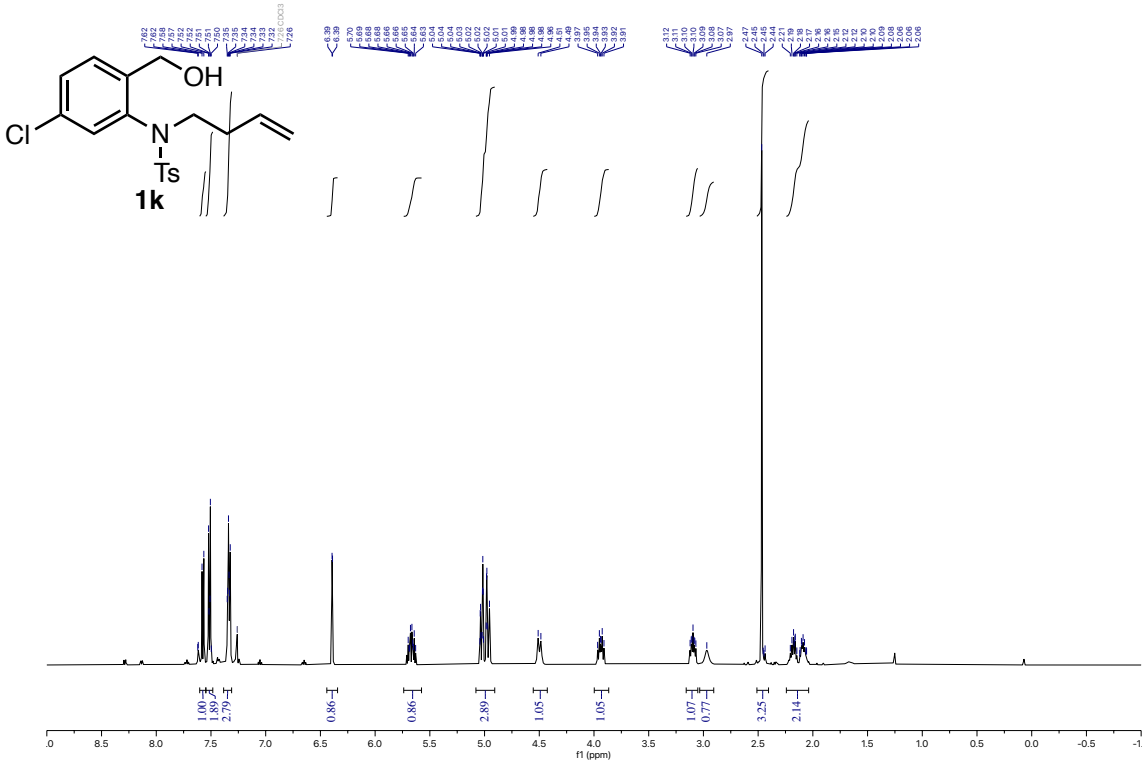
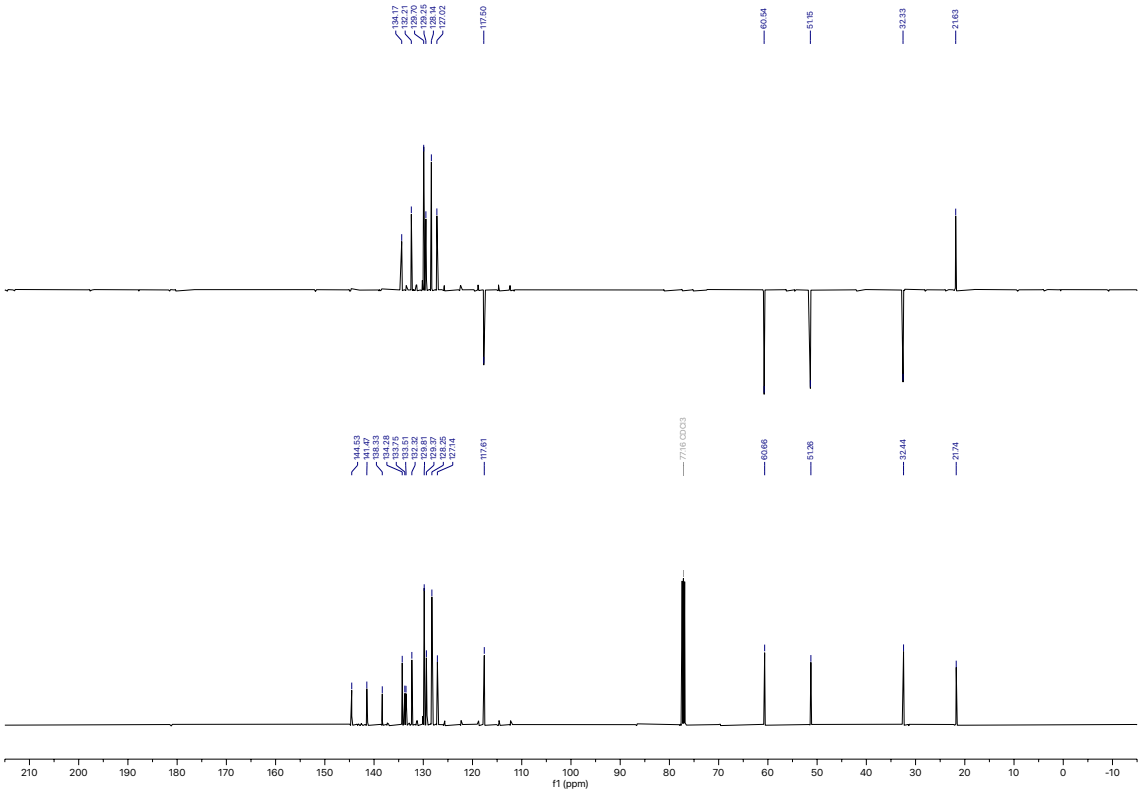


^{13}C-NMR (126 MHz). Solvent $CDCl_3$



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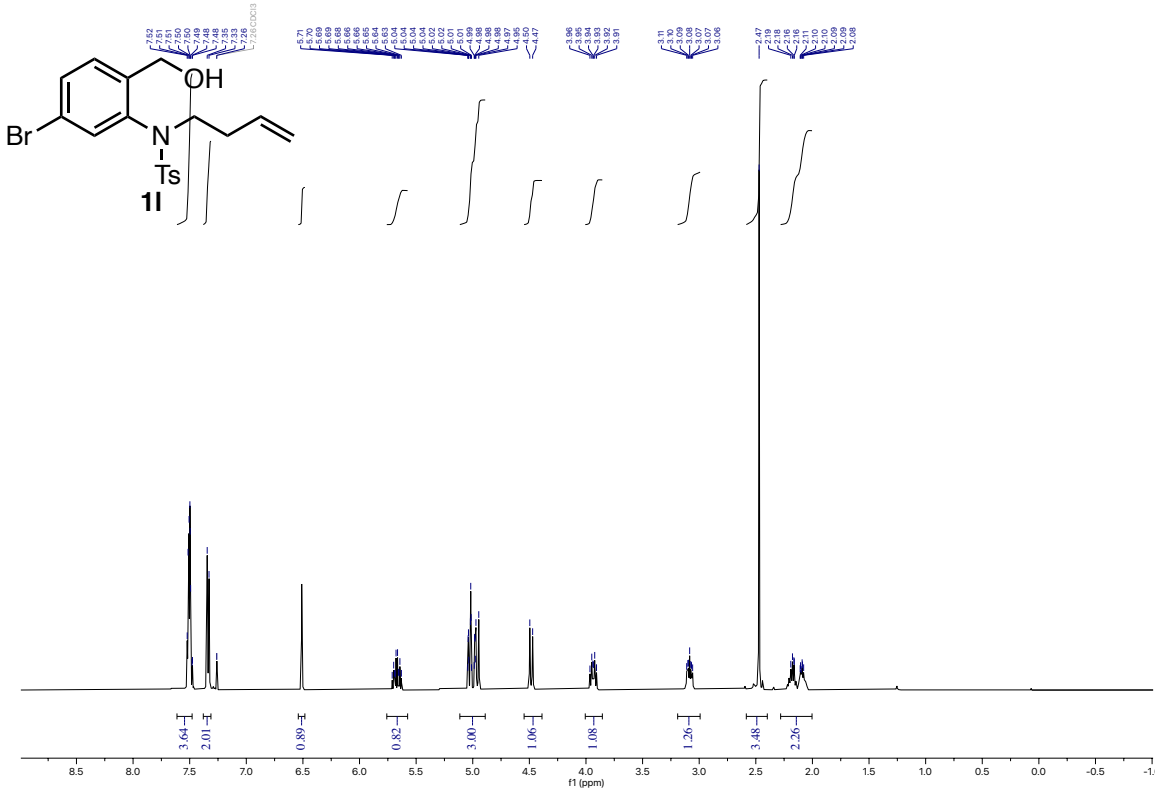
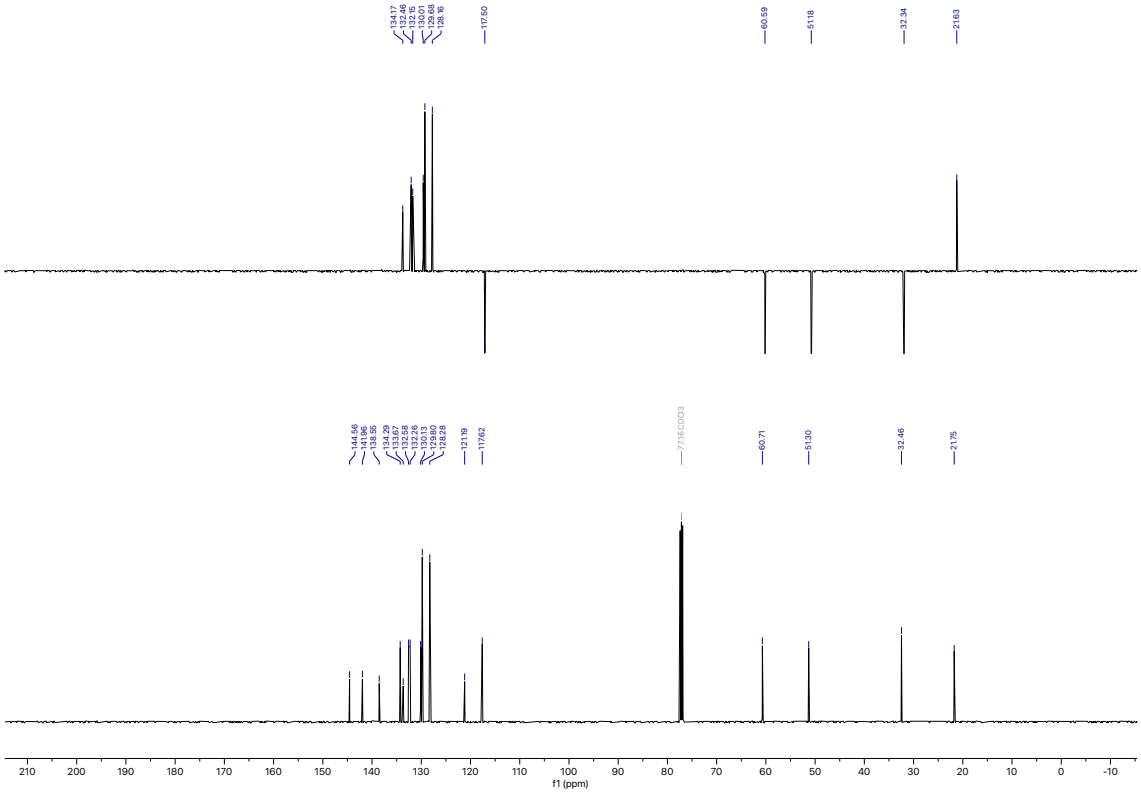
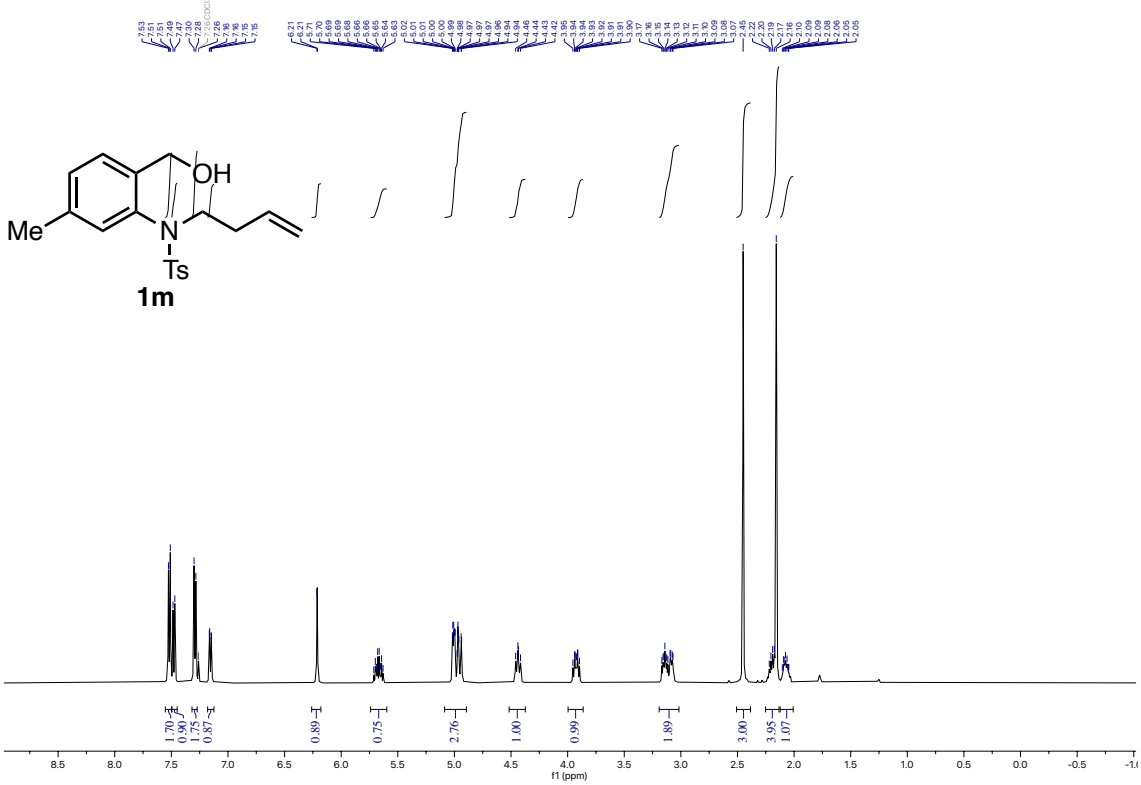


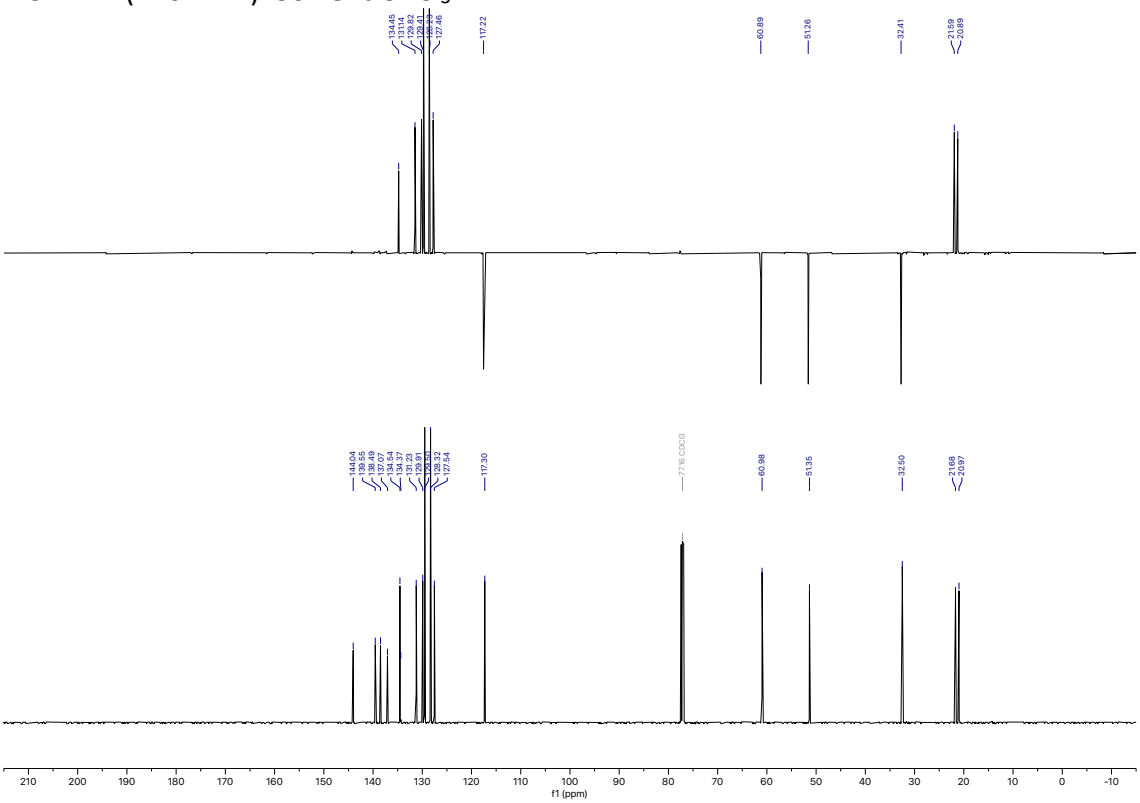
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



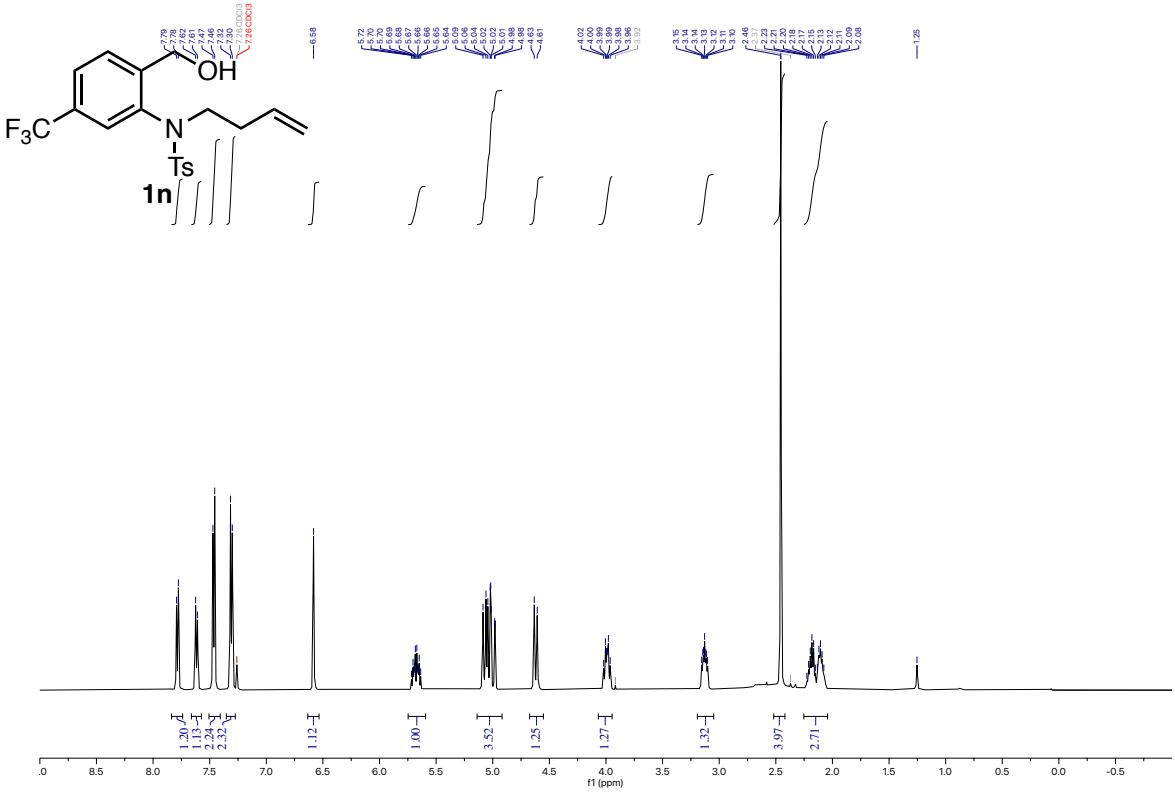
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



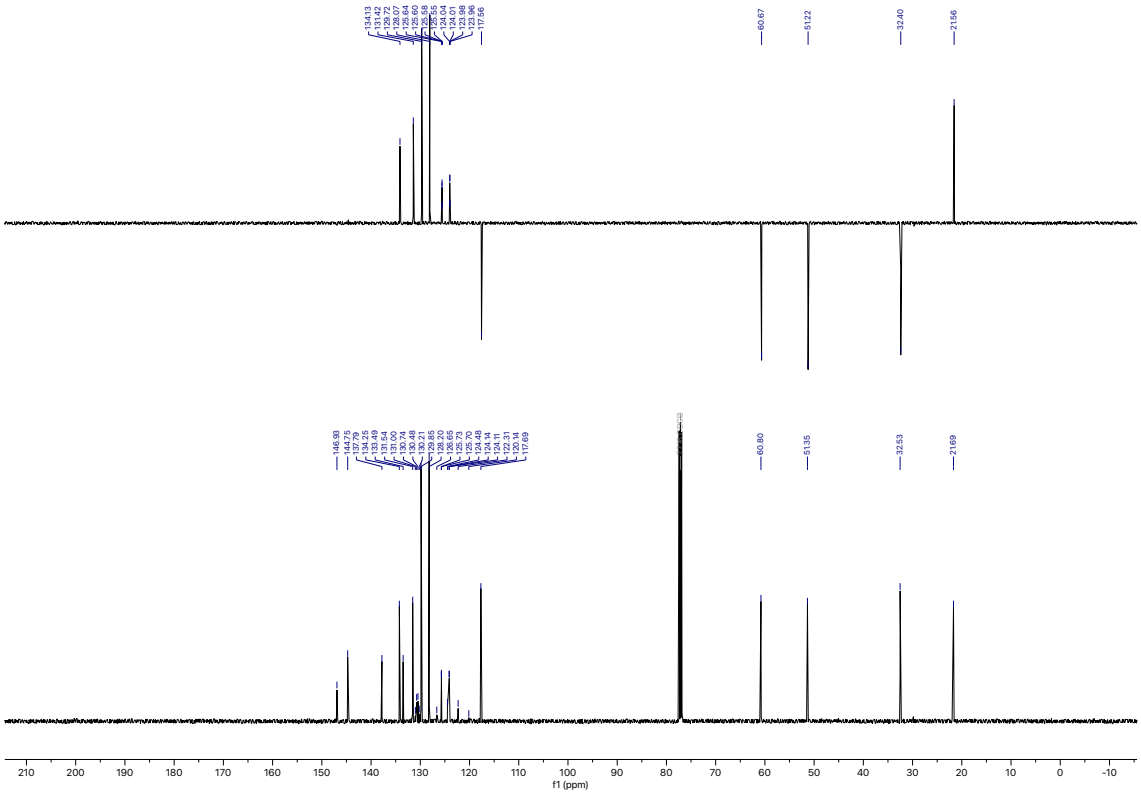
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



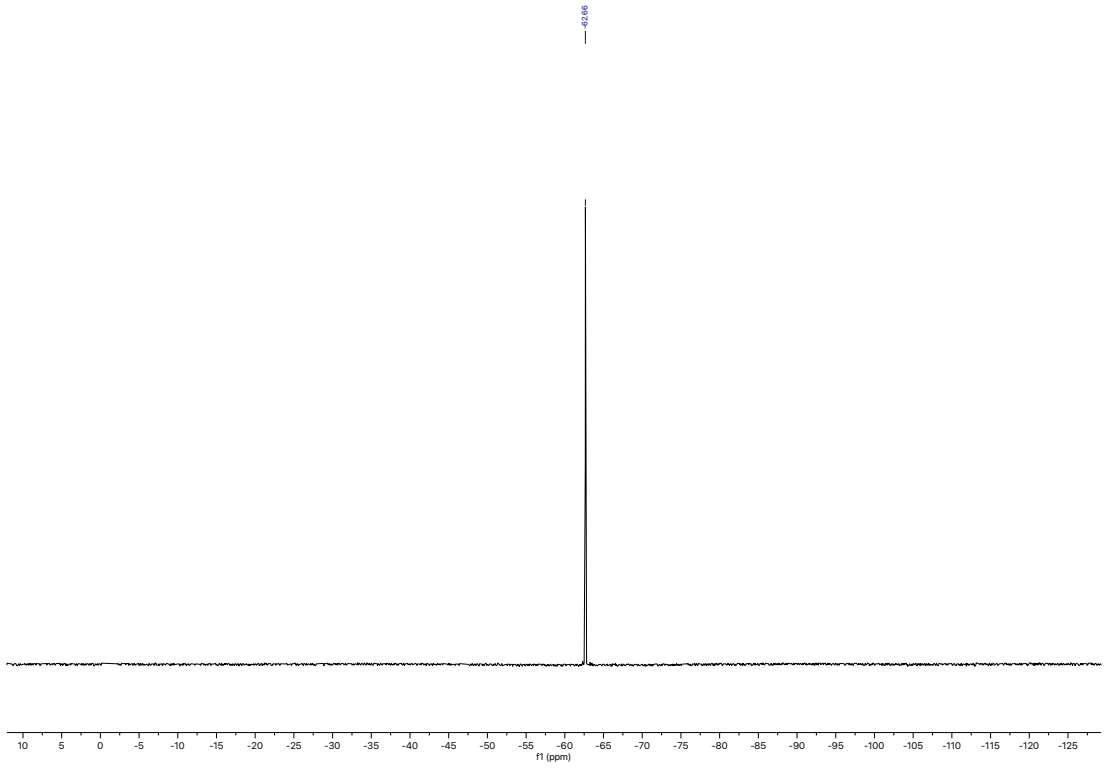
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



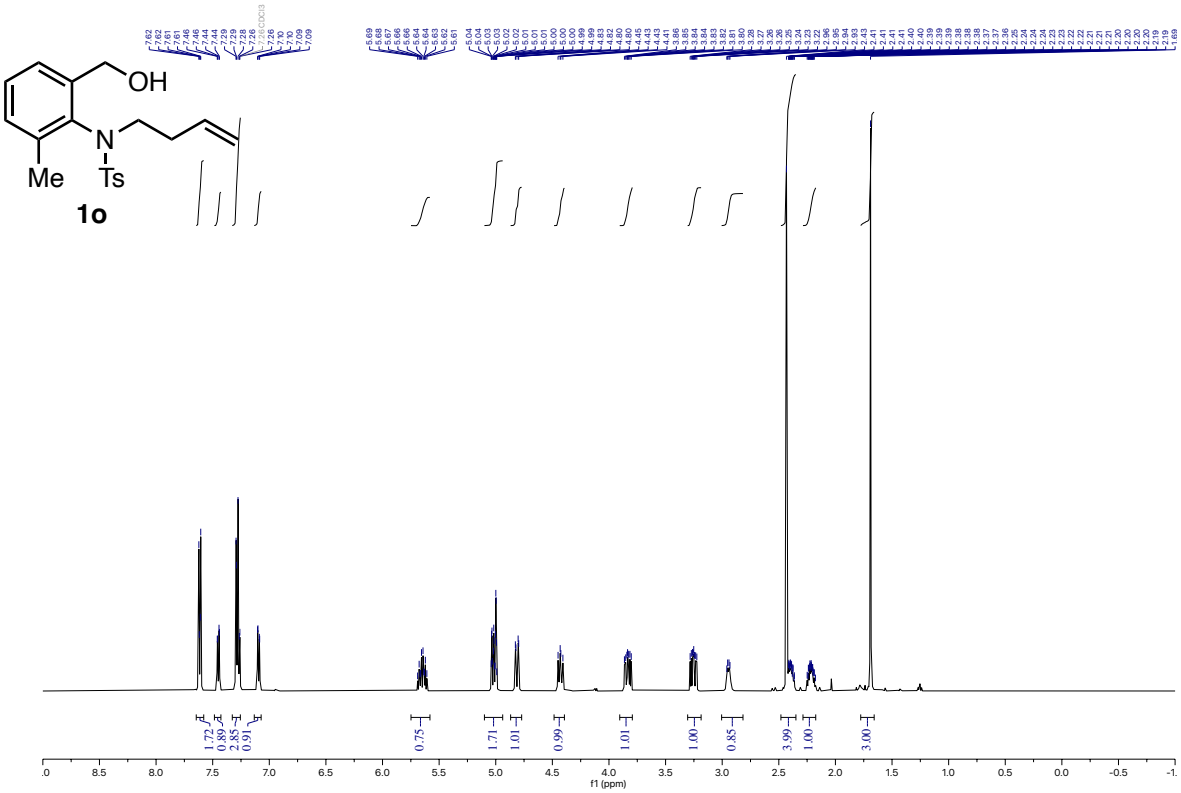
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



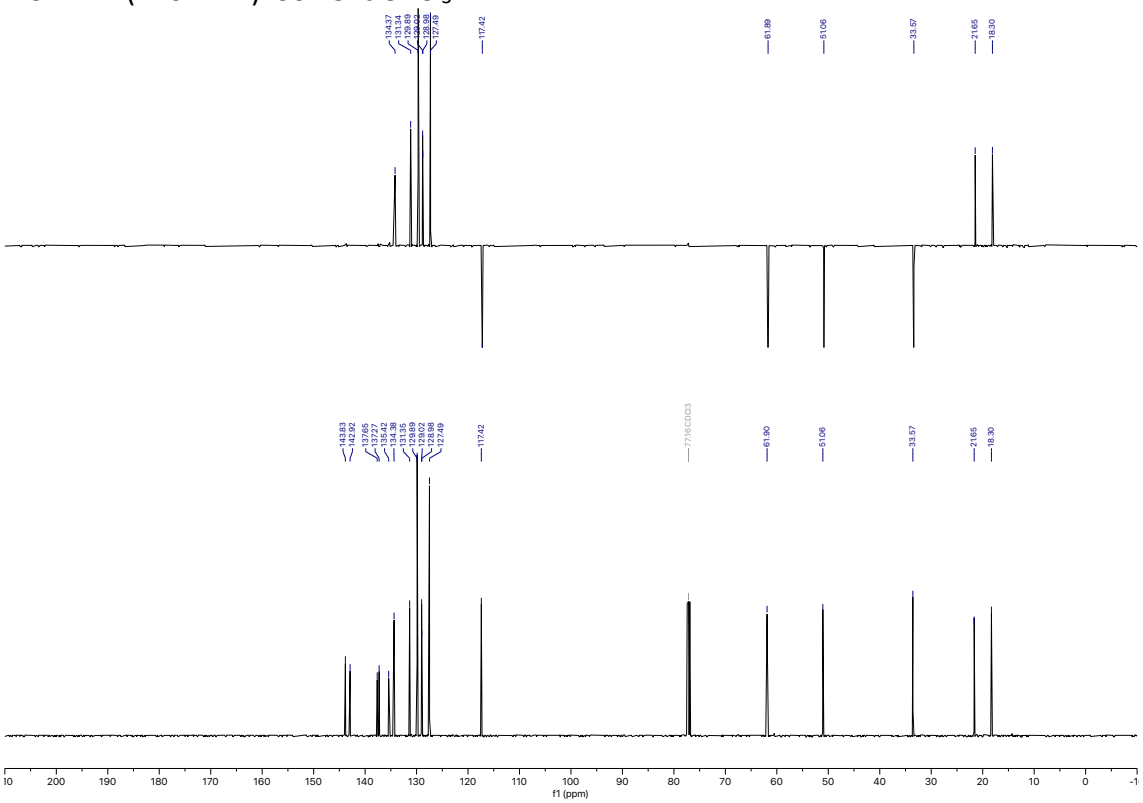
^{19}F-NMR (282 MHz). Solvent $CDCl_3$



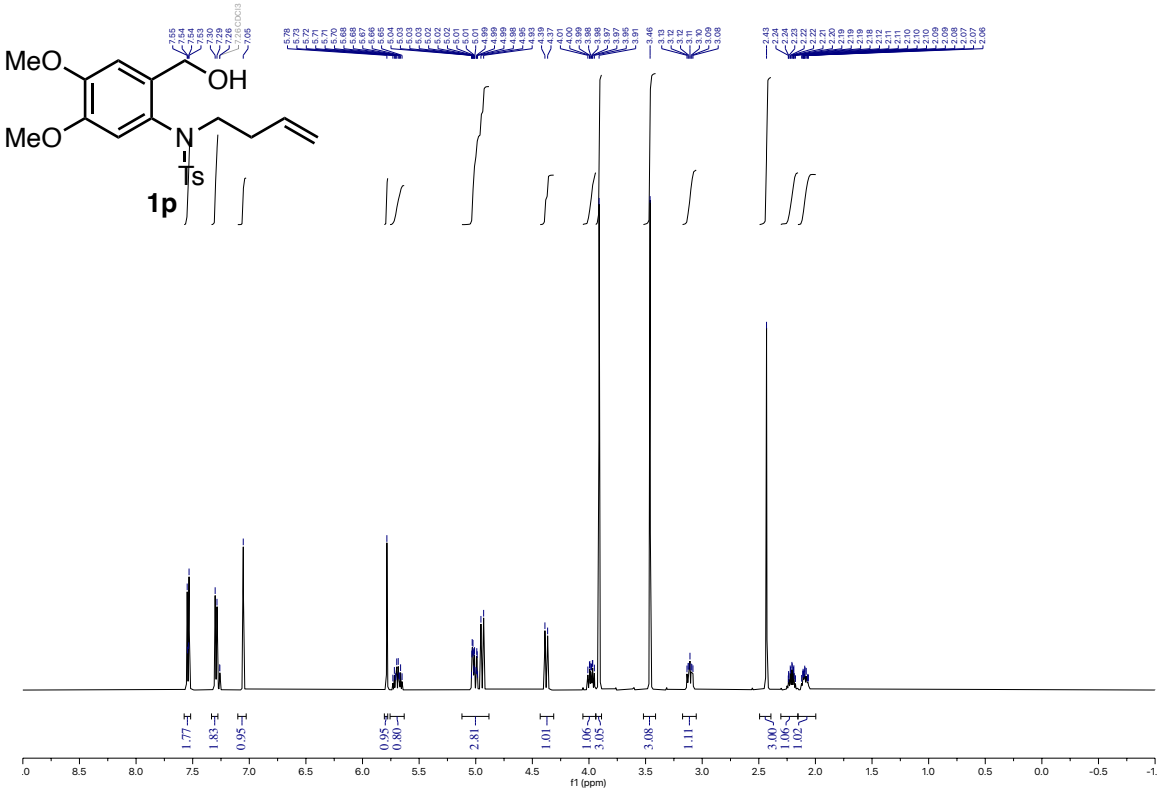
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



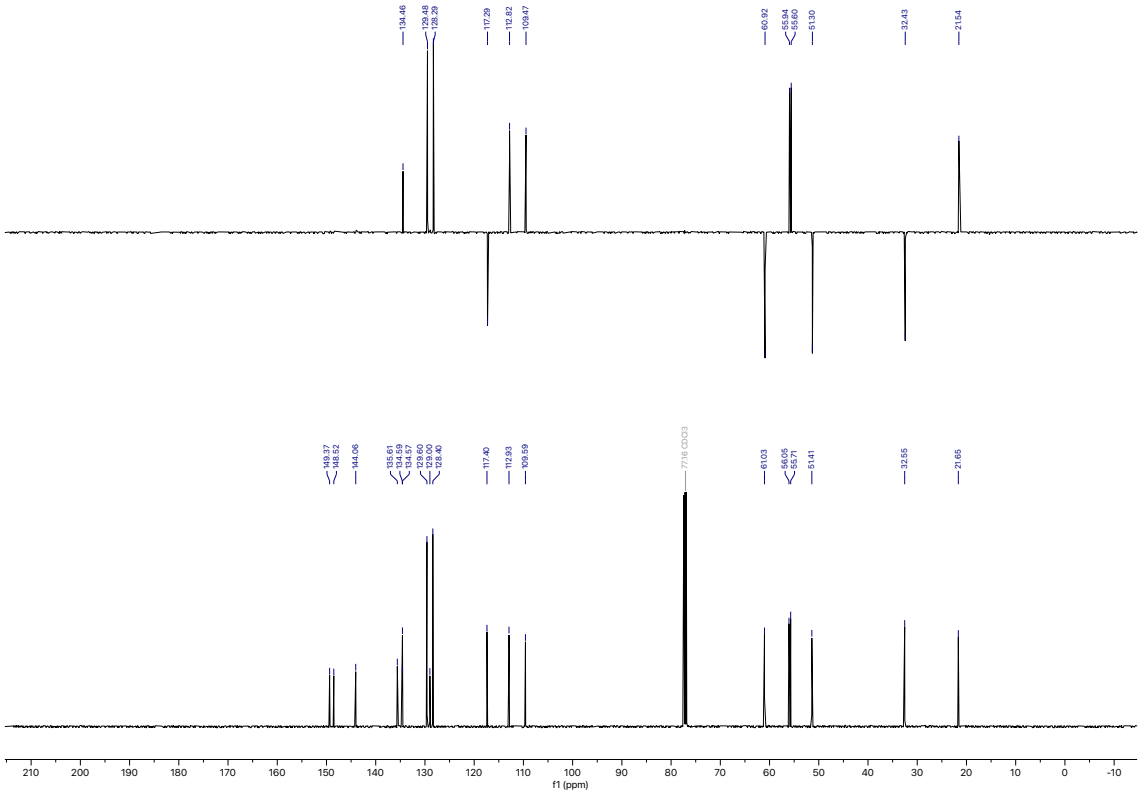
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



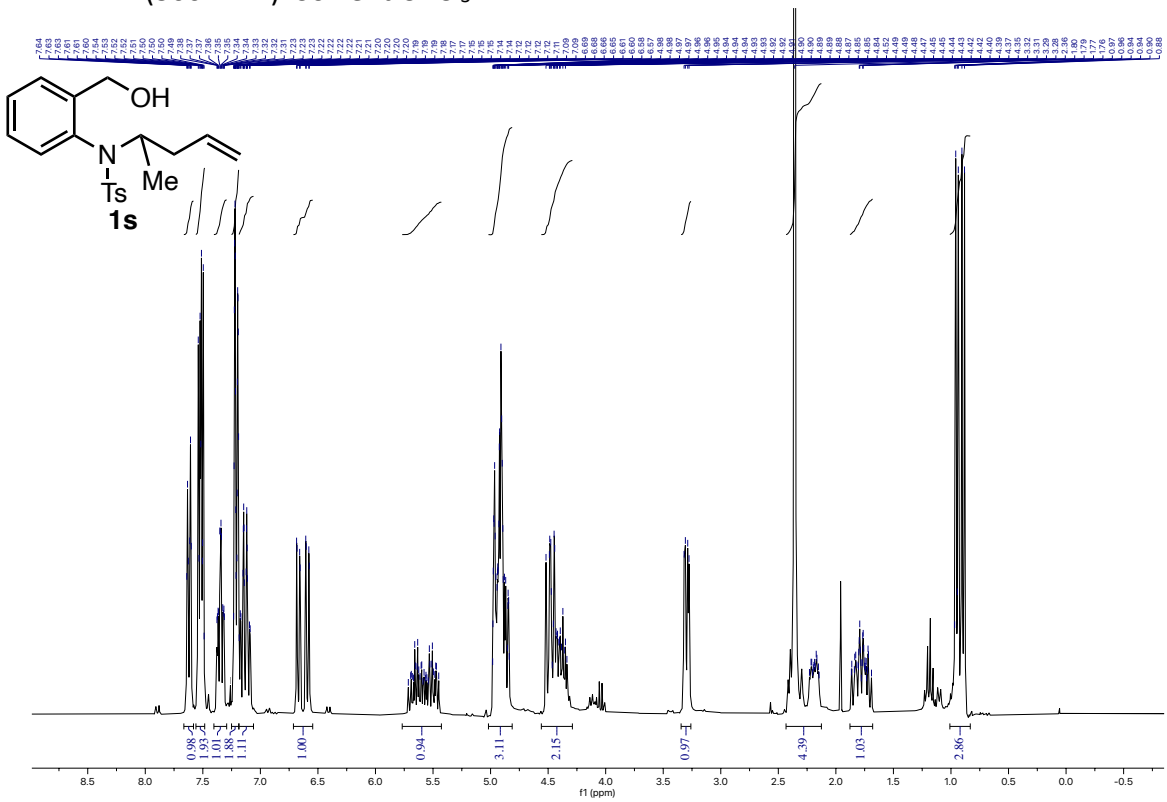
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



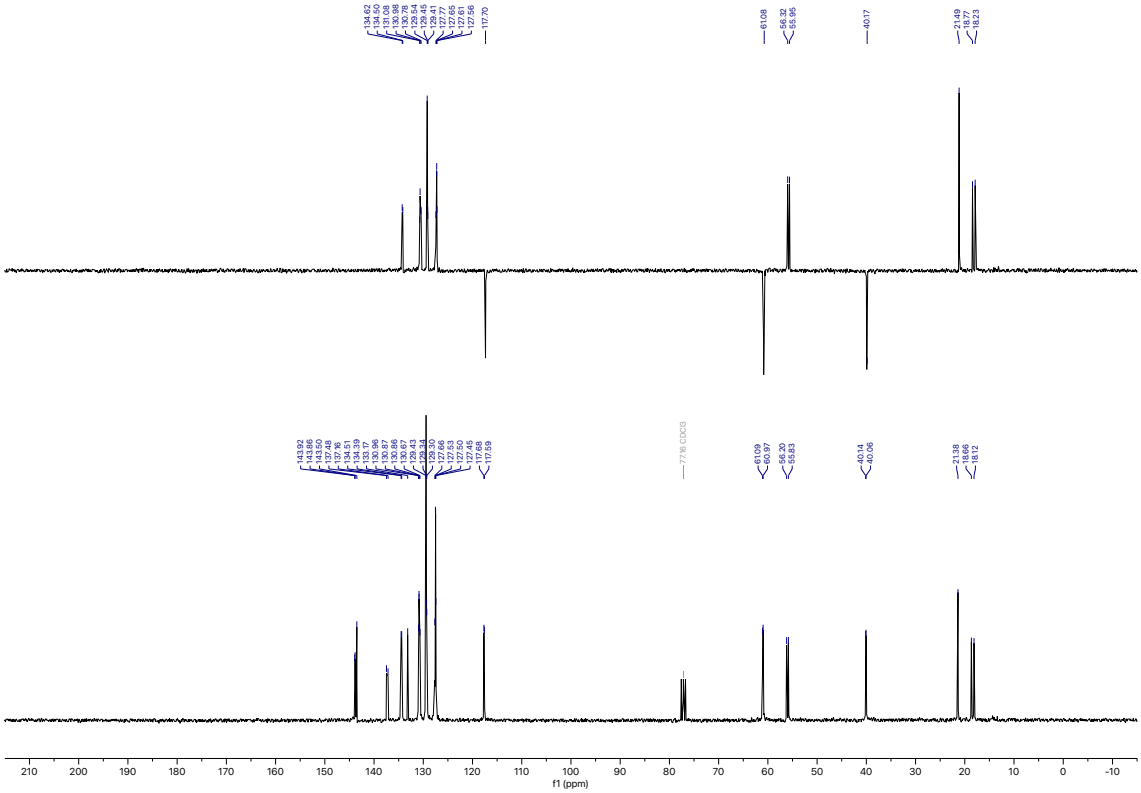
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



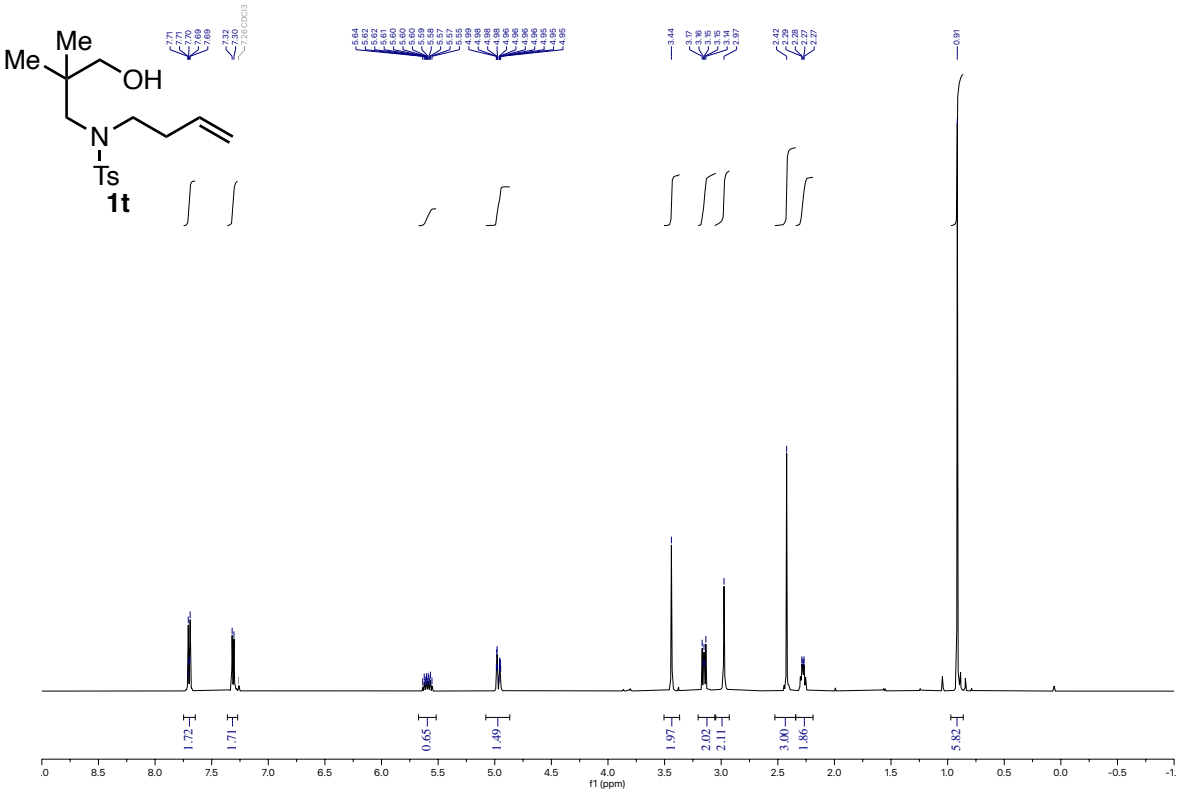
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



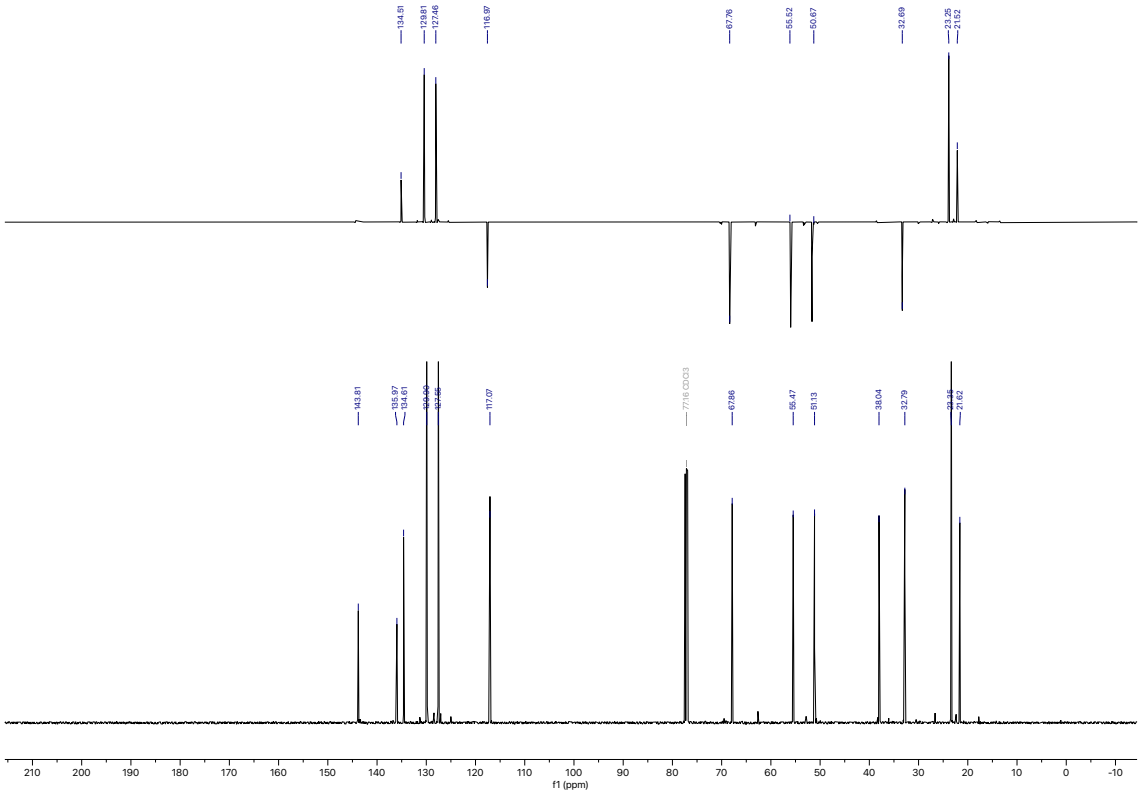
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



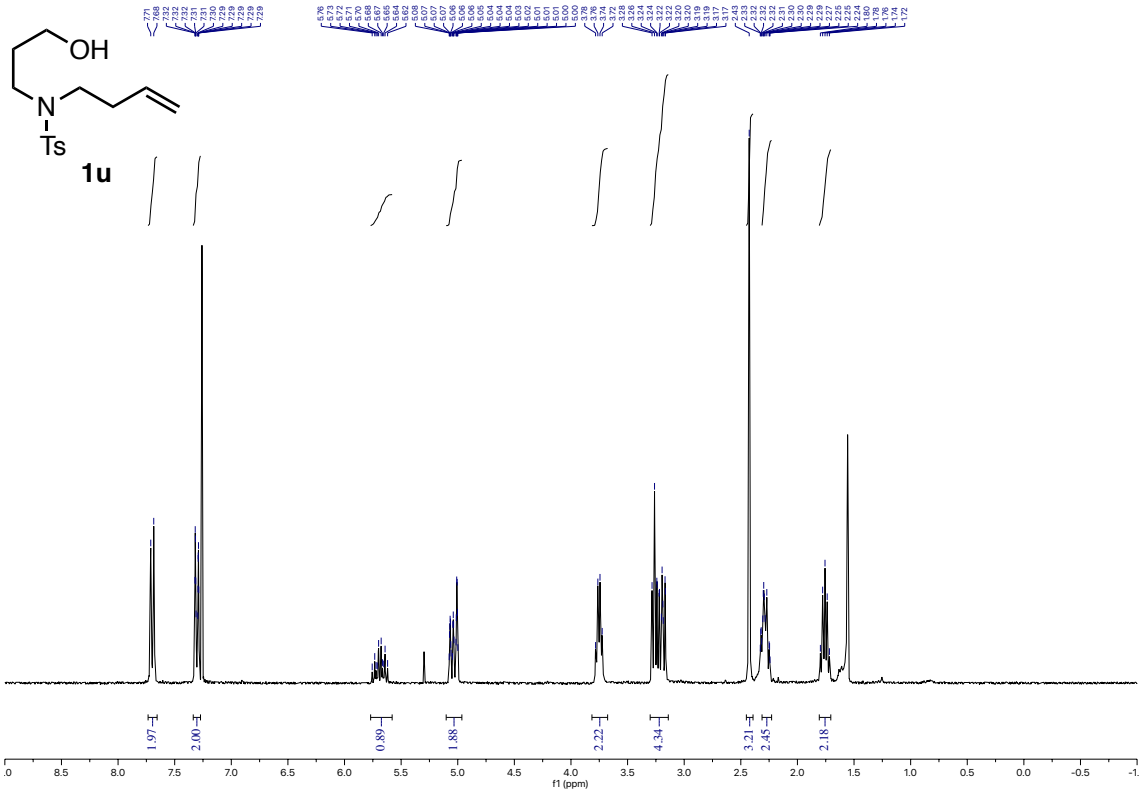
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



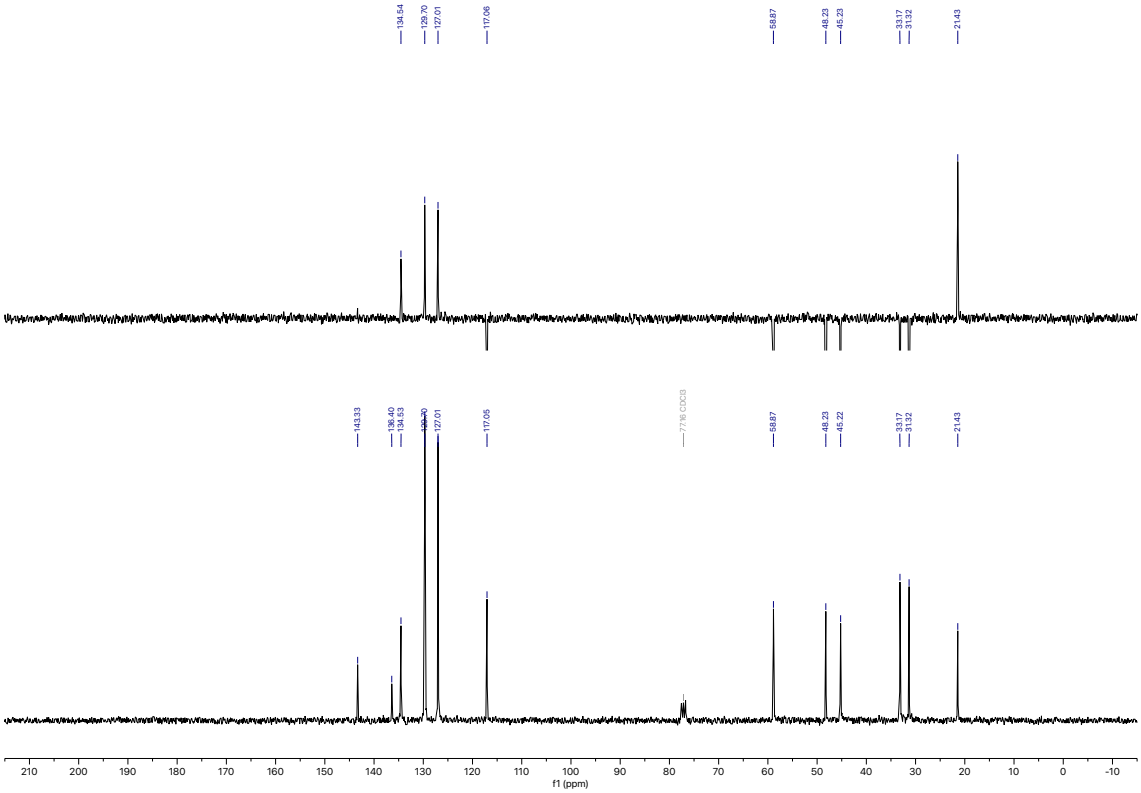
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



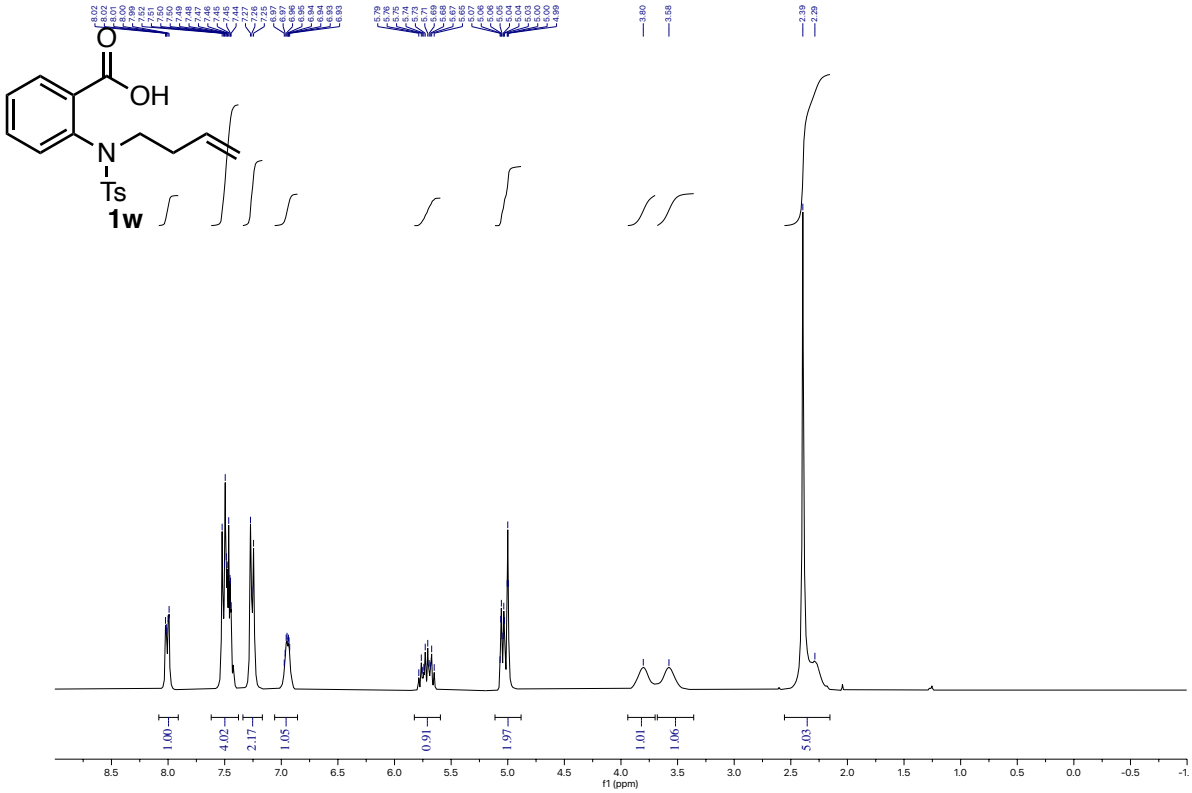
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



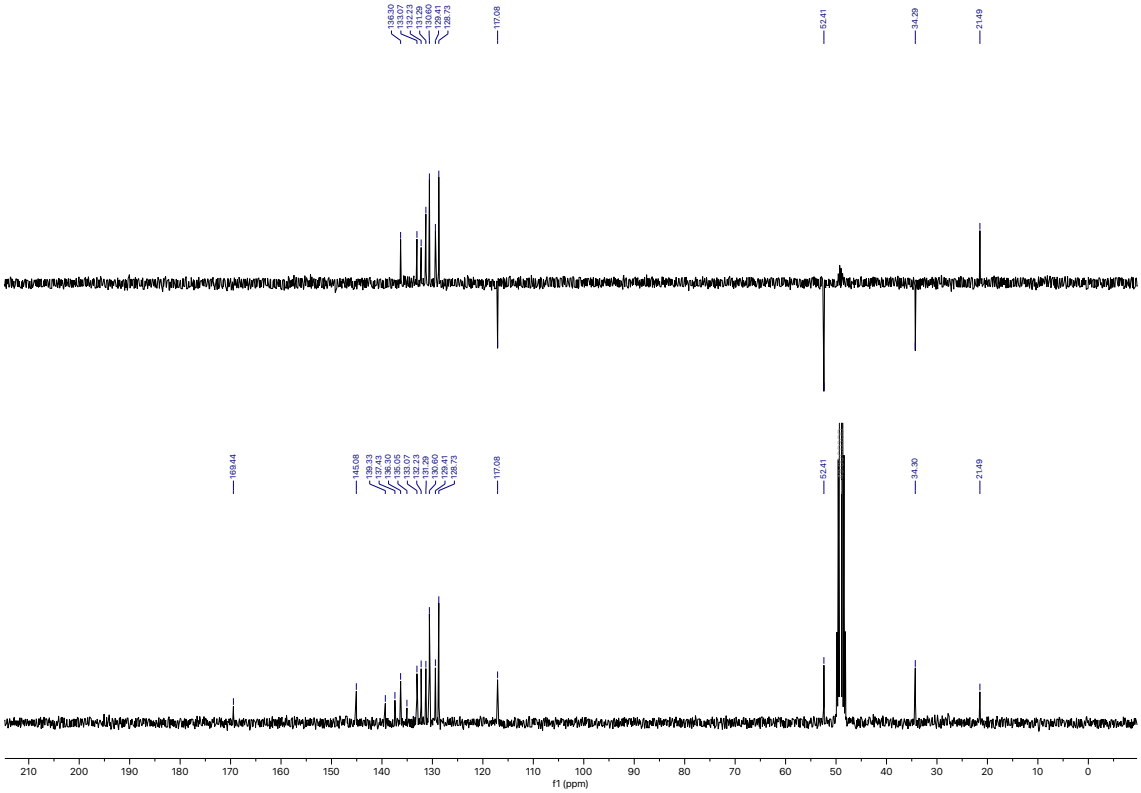
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



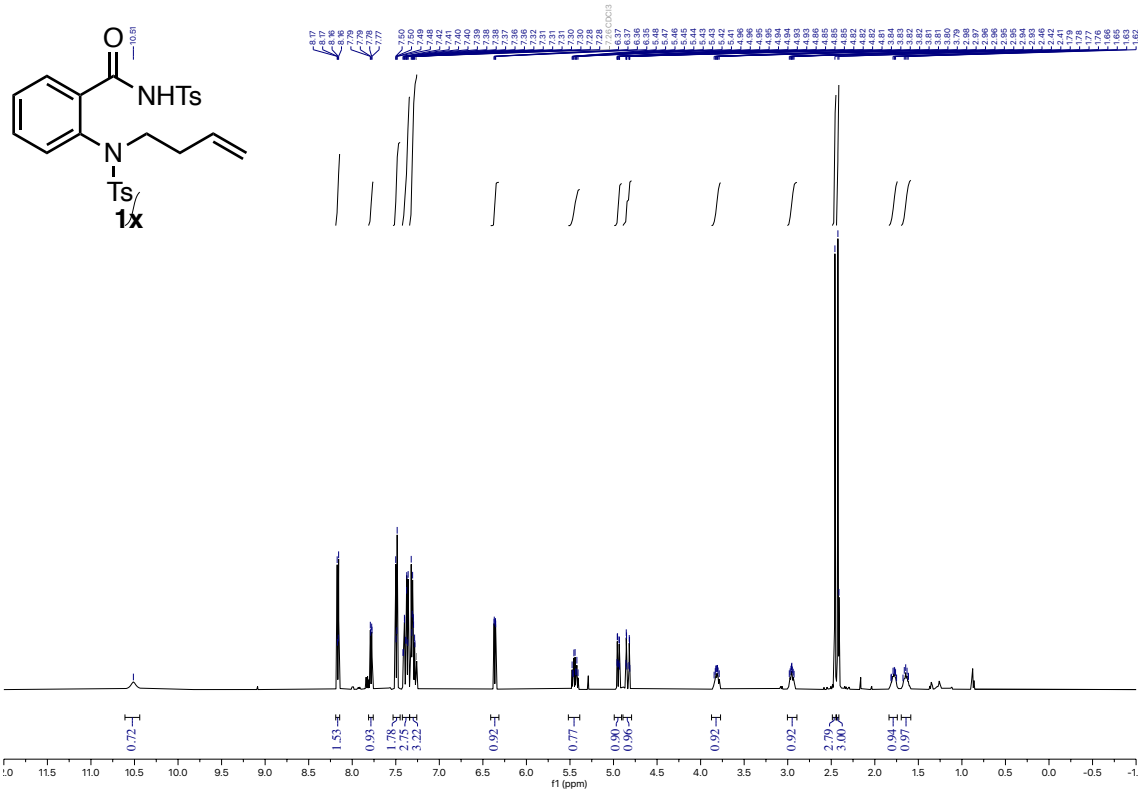
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



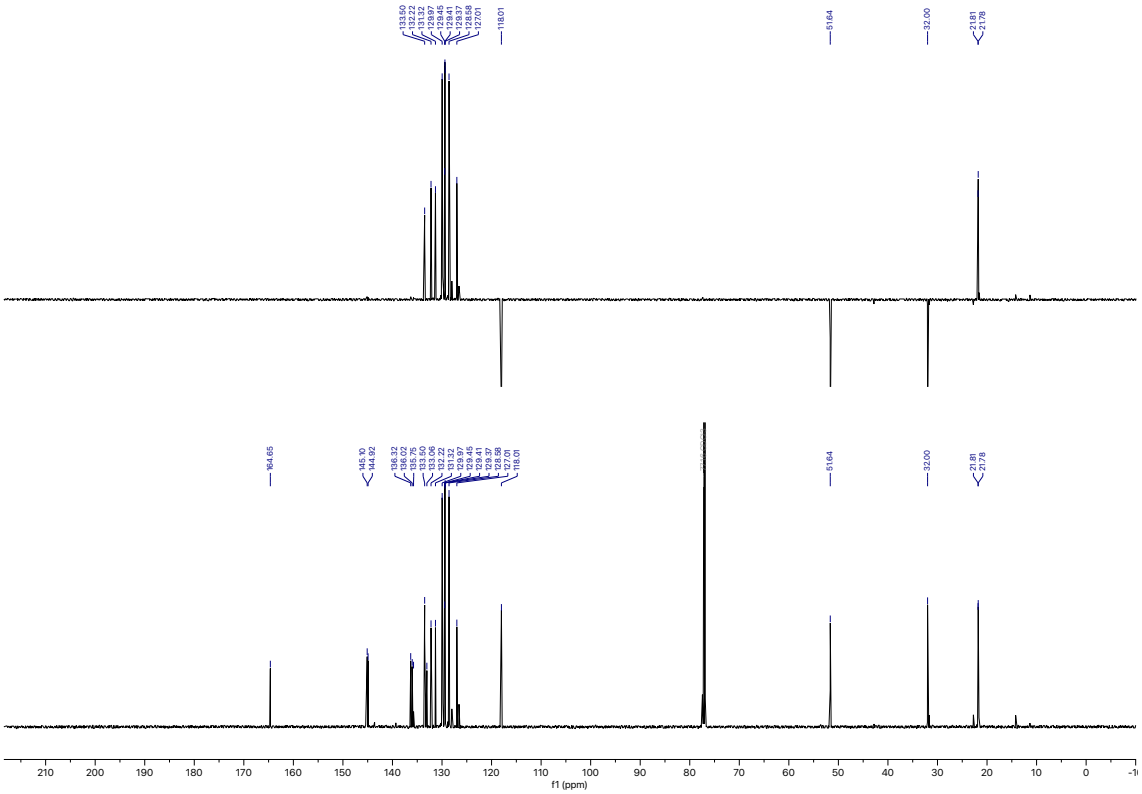
^{13}C-NMR (75 MHz). Solvent CD_3OD



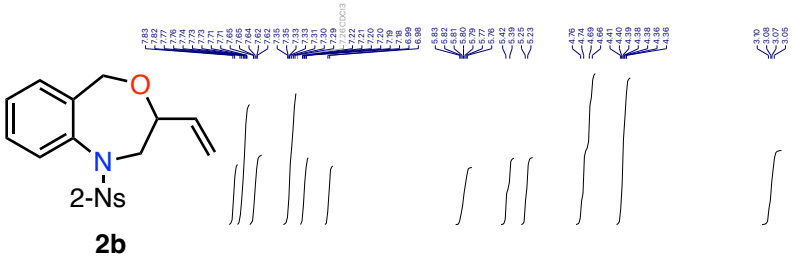
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



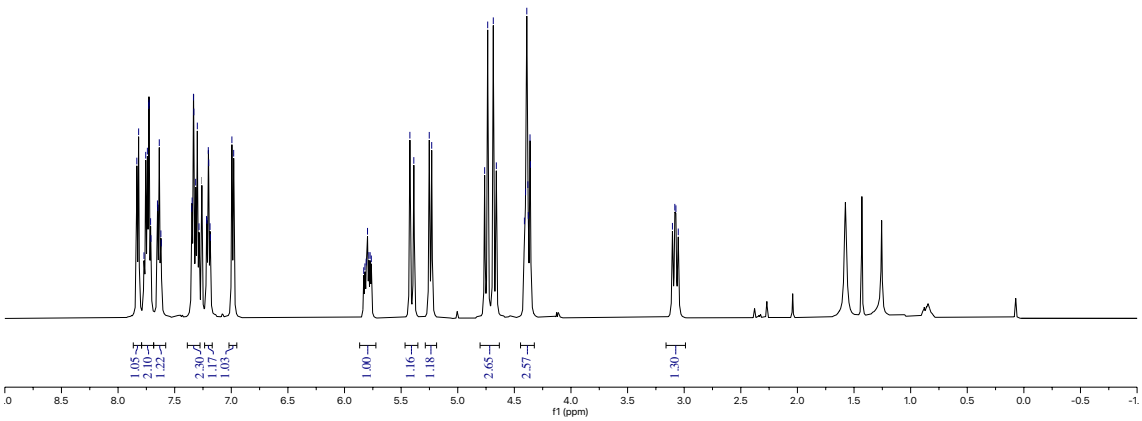
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



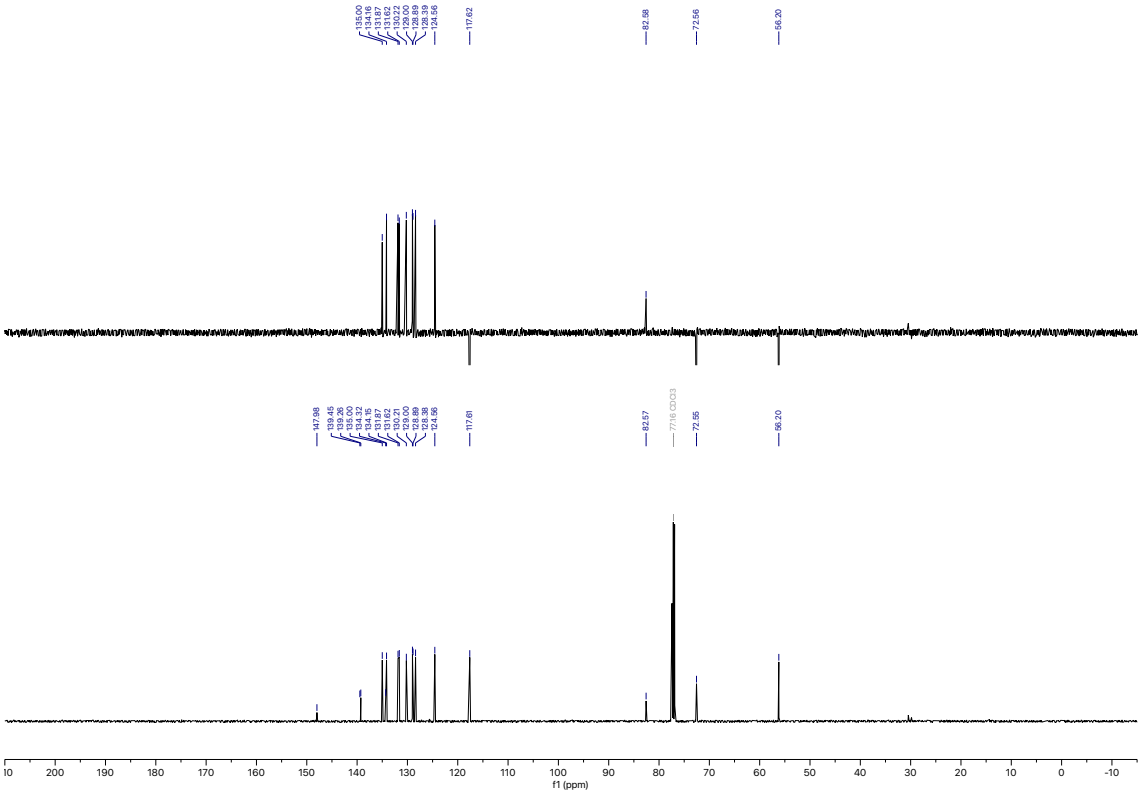
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



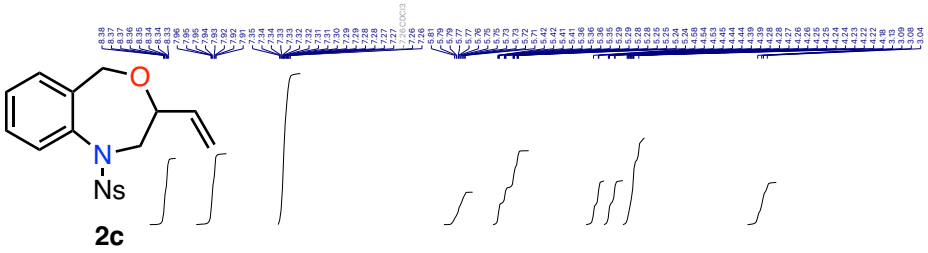
2b



^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (300 MHz). Solvent $CDCl_3$



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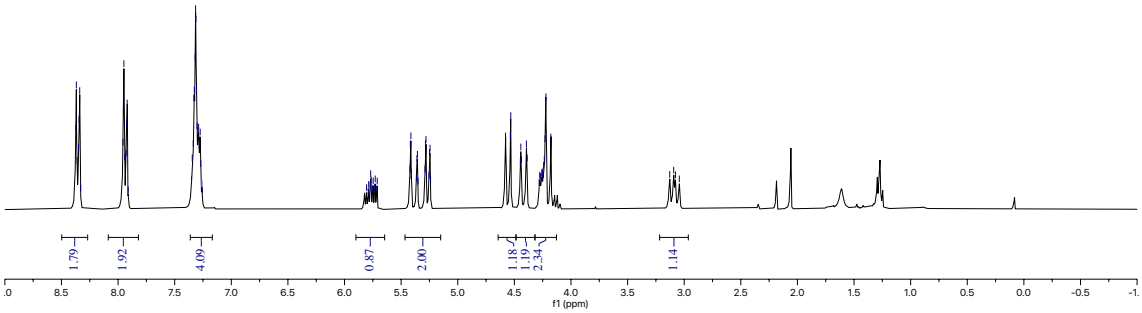
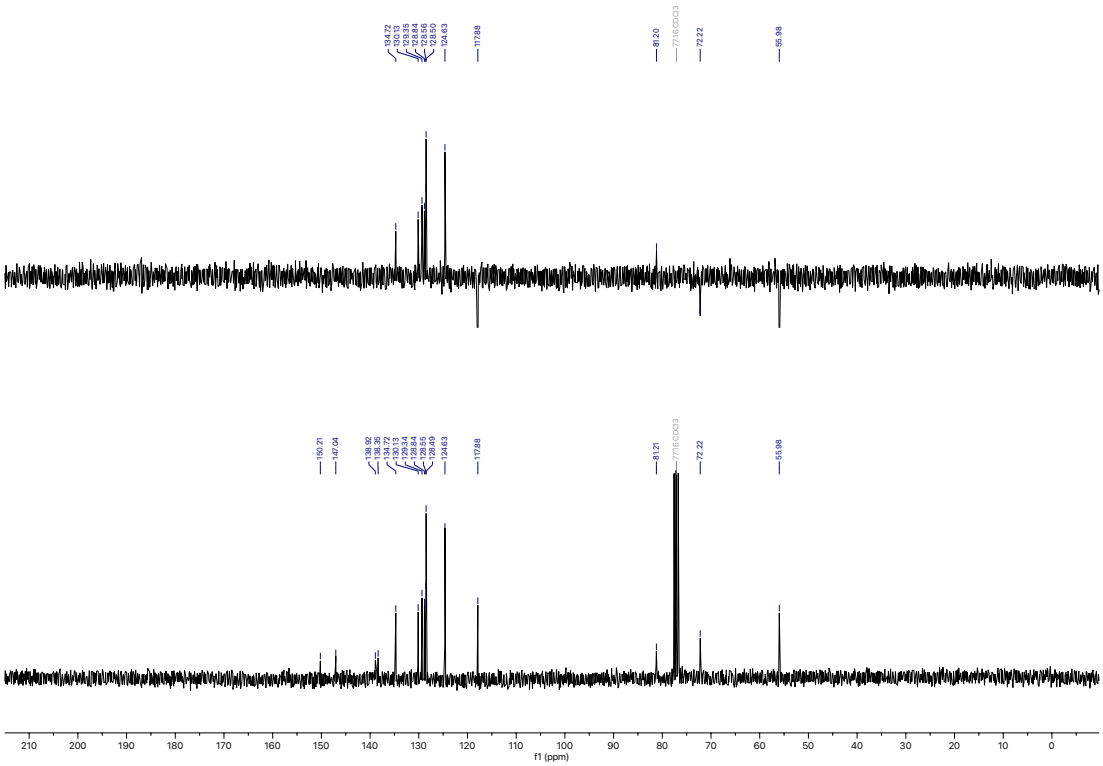
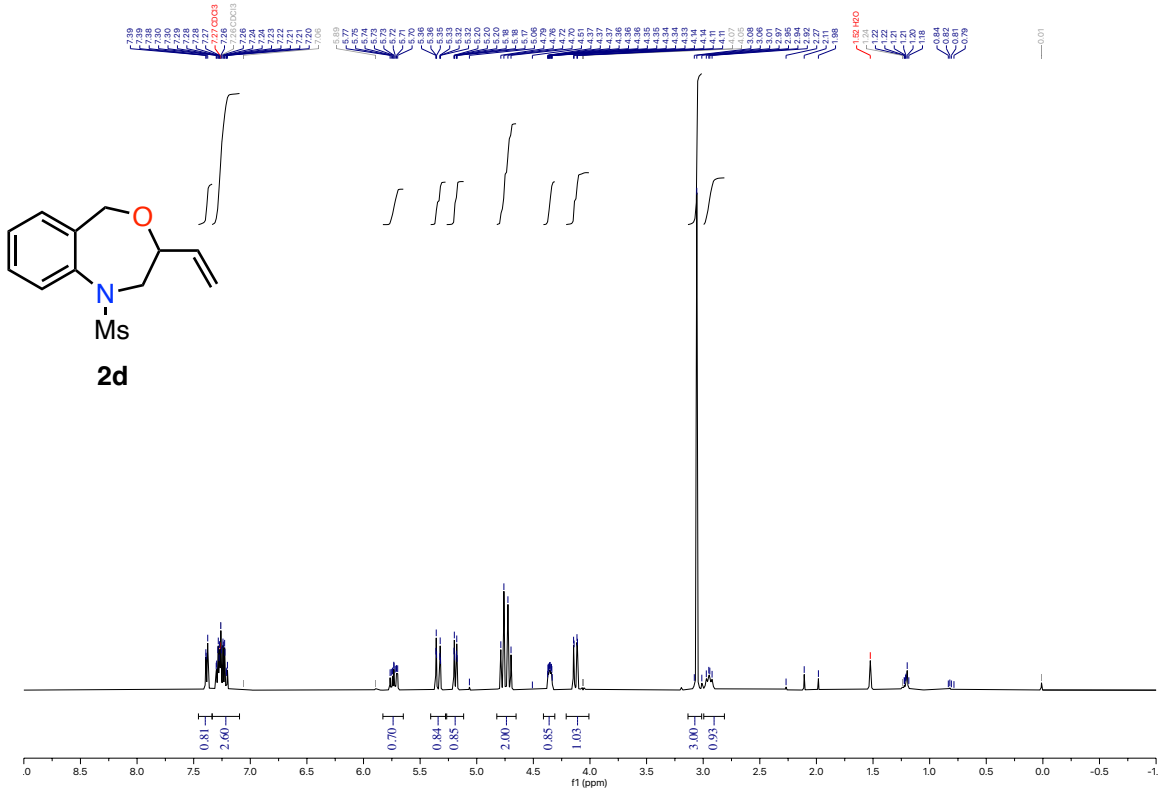


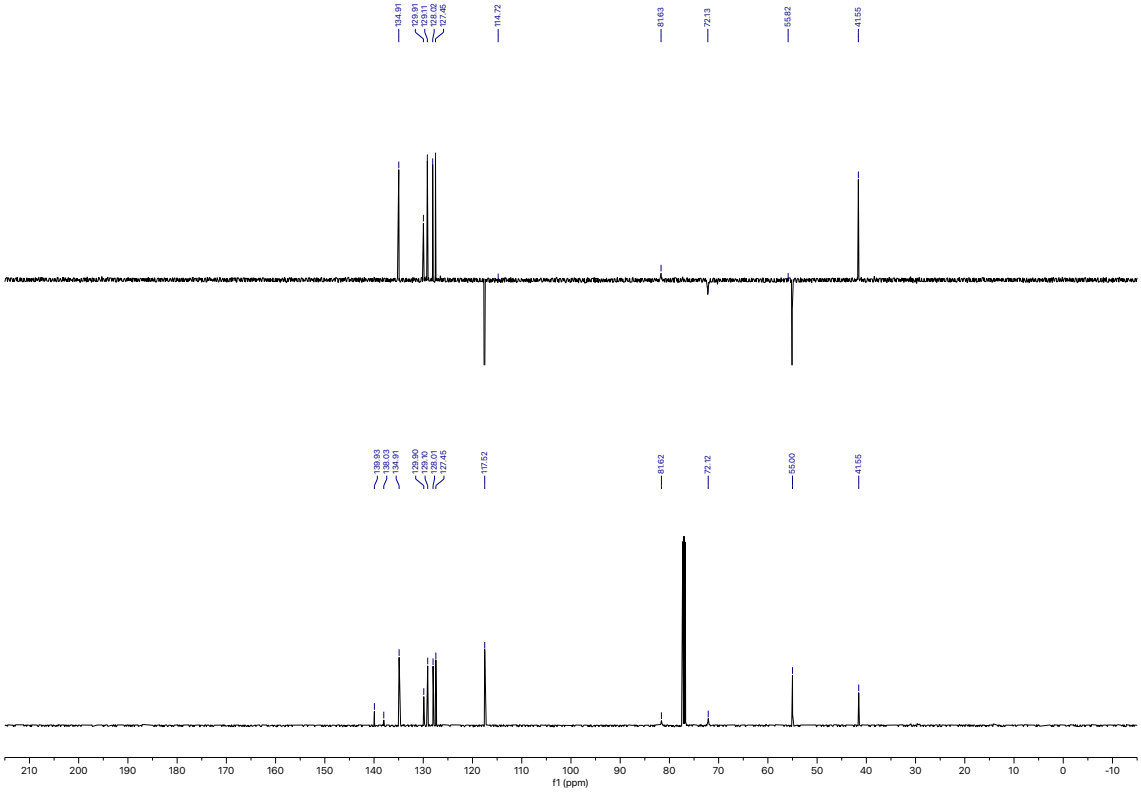
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



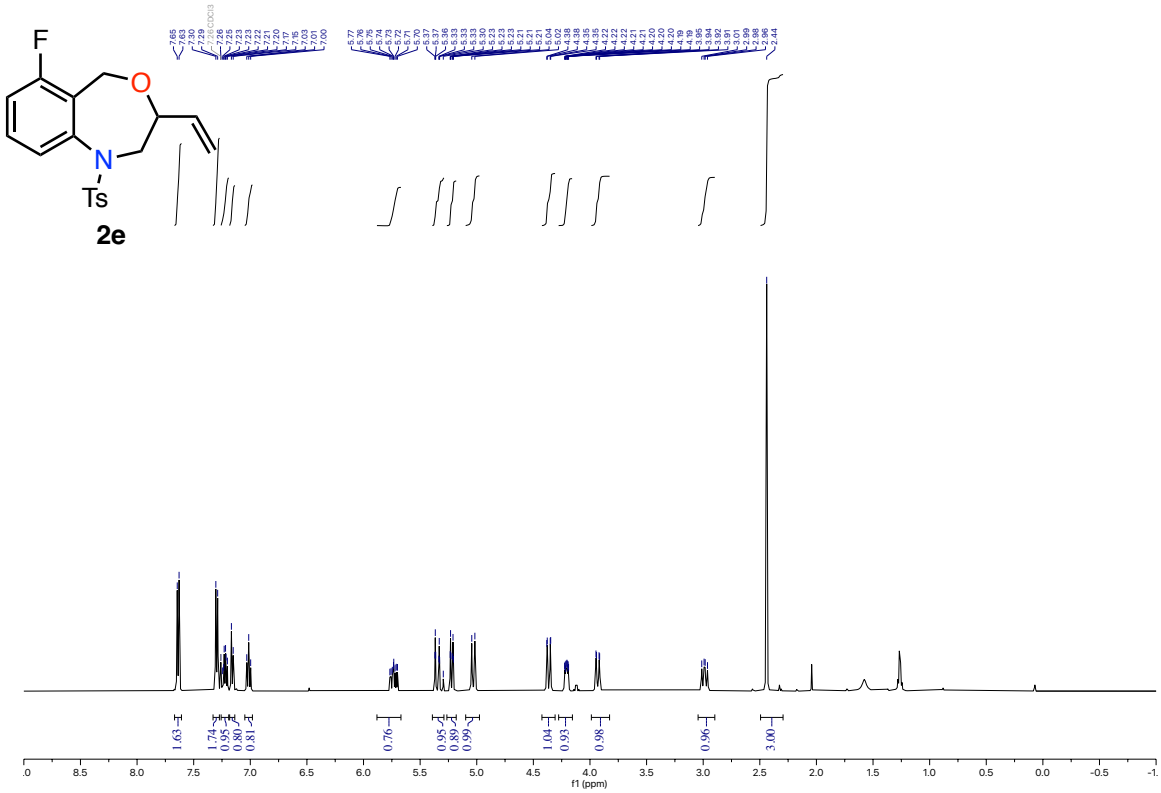
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



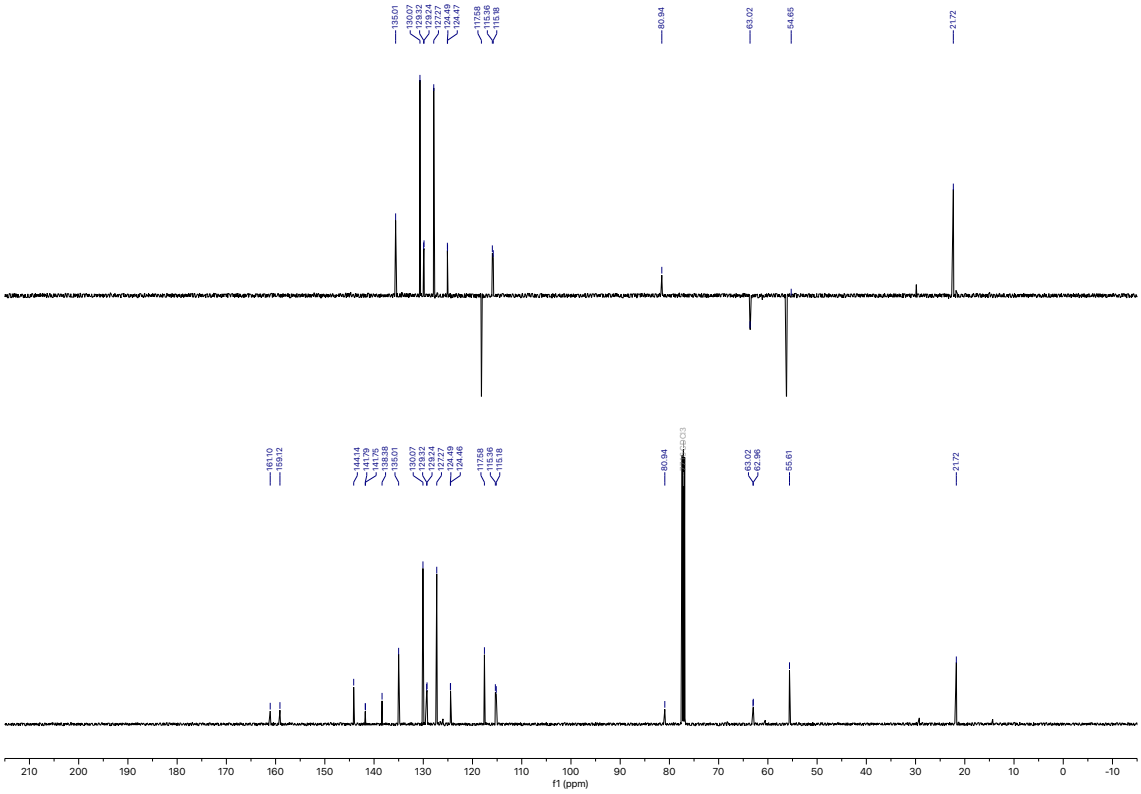
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



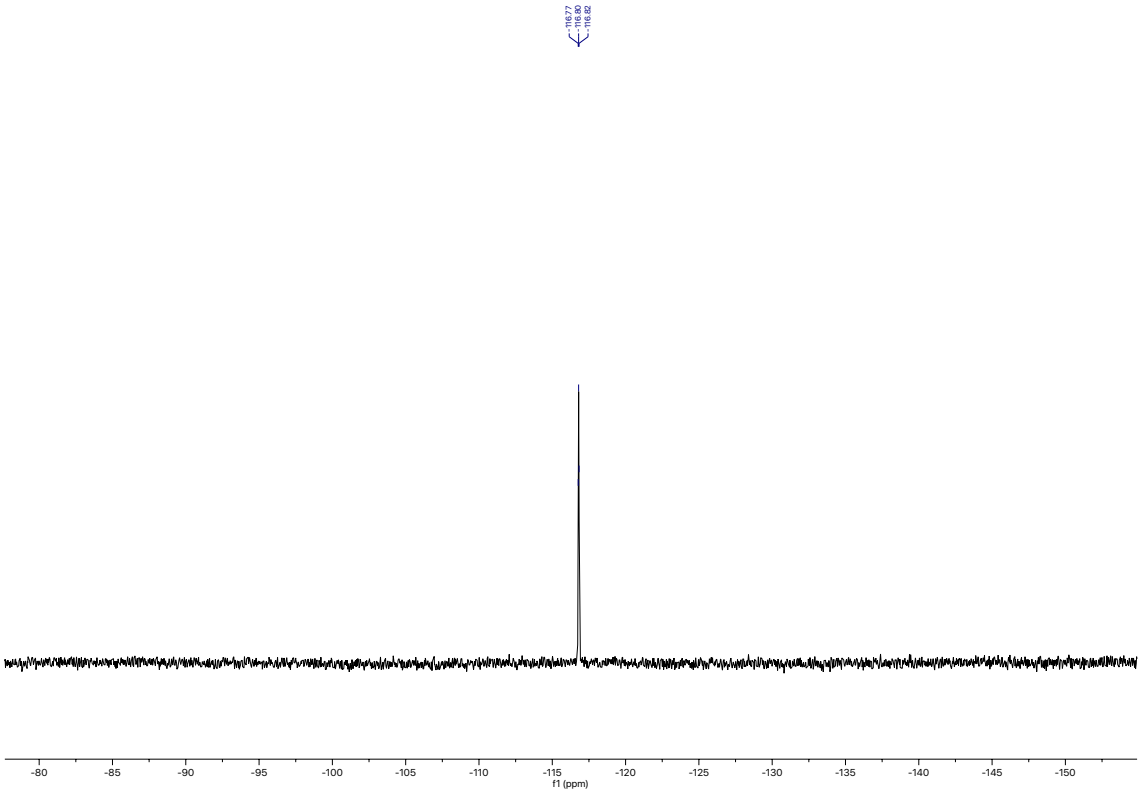
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



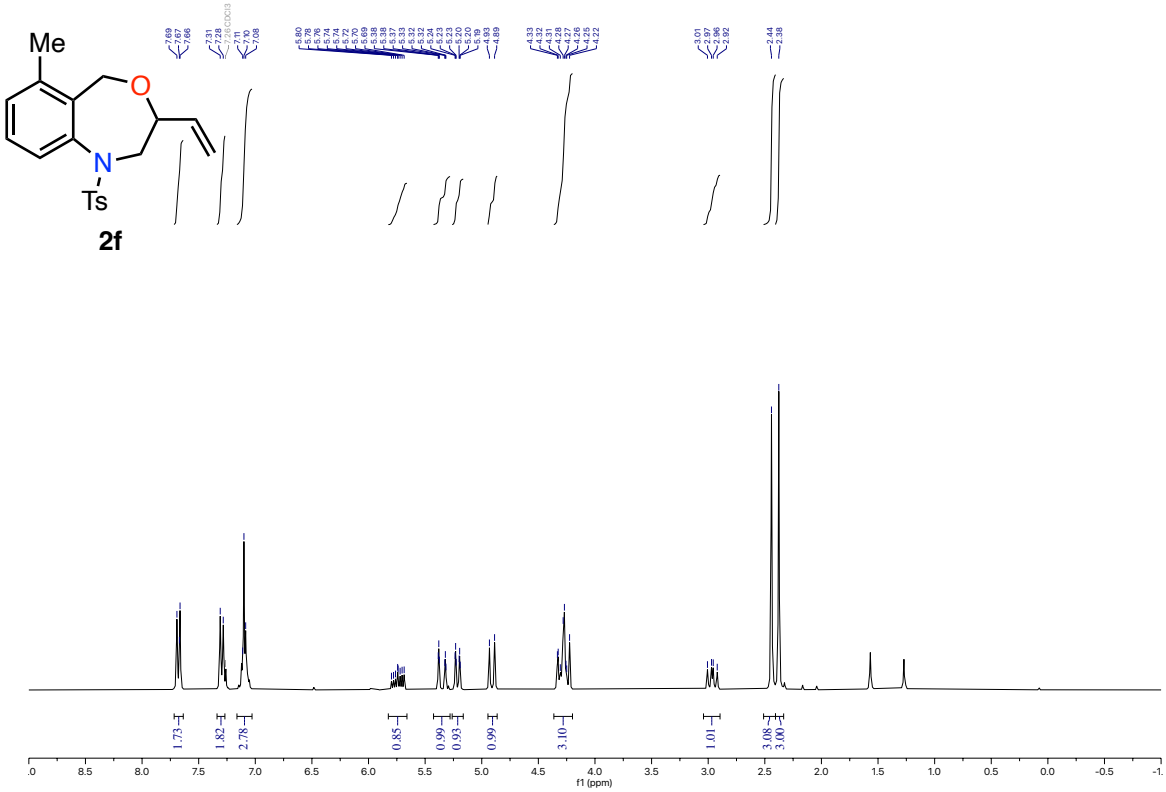
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



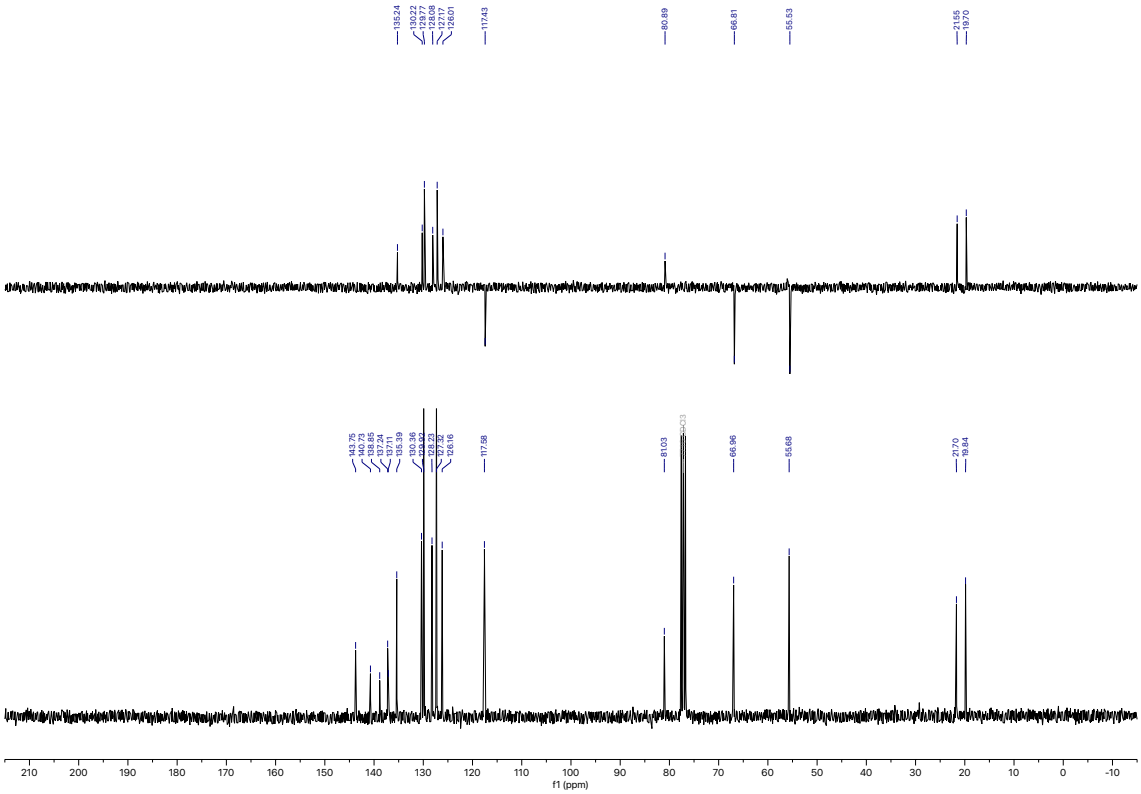
^{19}F-NMR (282 MHz). Solvent $CDCl_3$



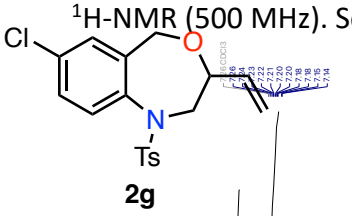
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



^{13}C-NMR (75 MHz). Solvent $CDCl_3$

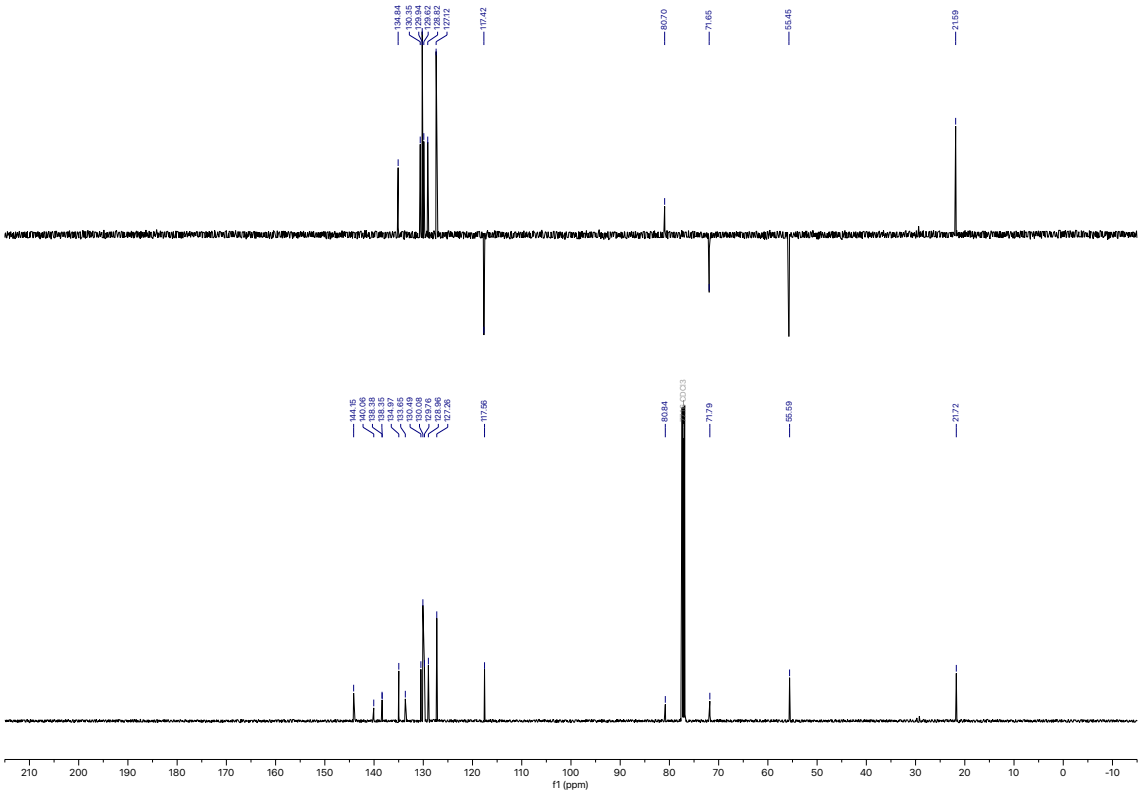


^{1}H-NMR (500 MHz). Solvent $CDCl_3$

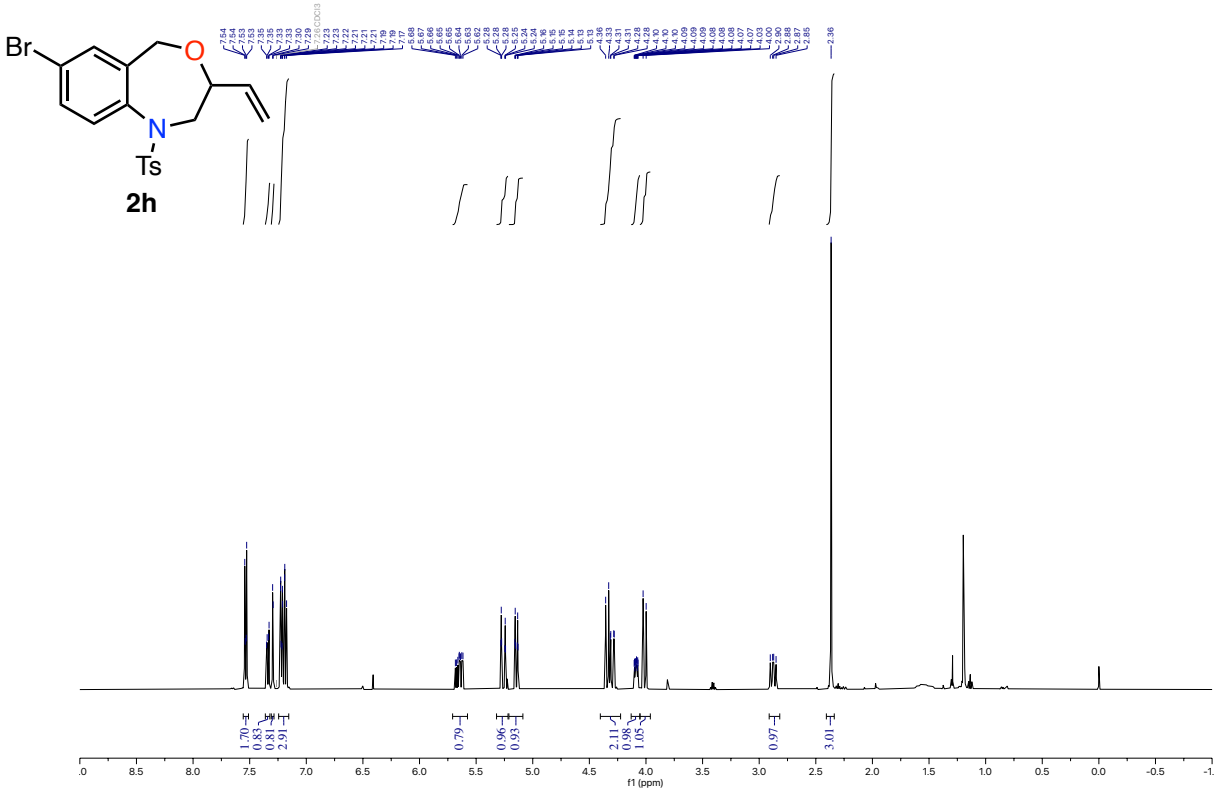


2g

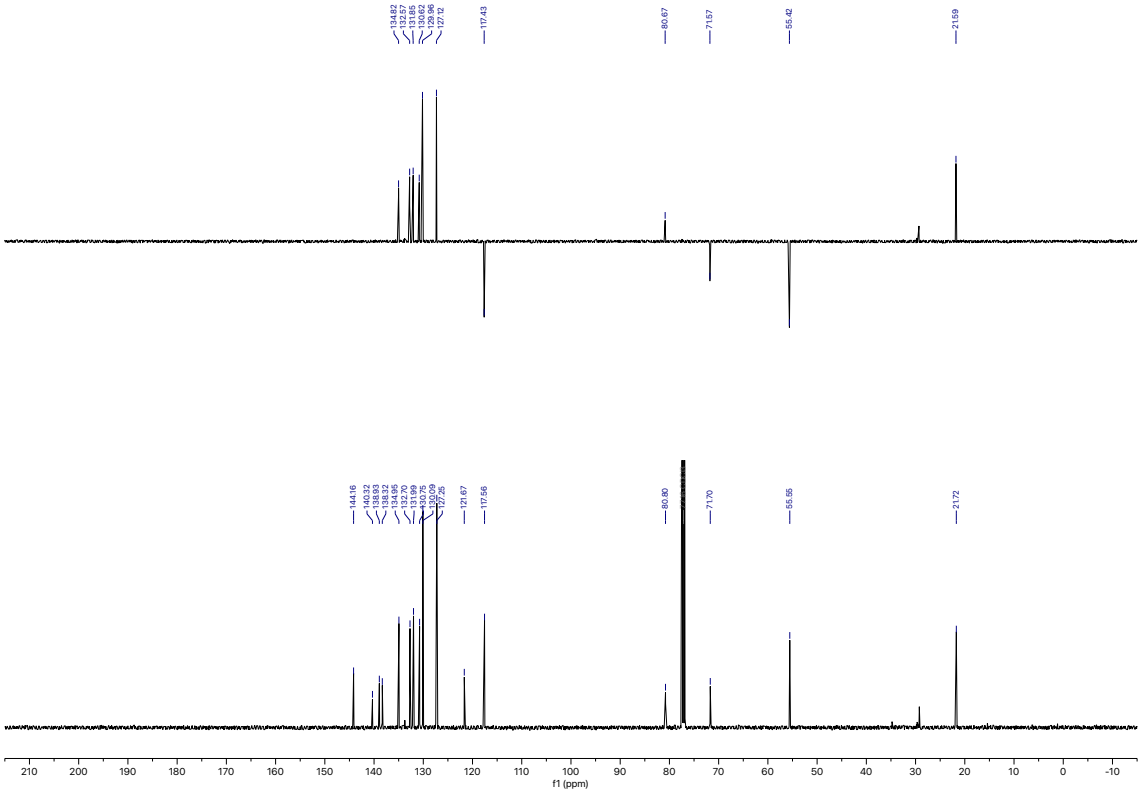
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



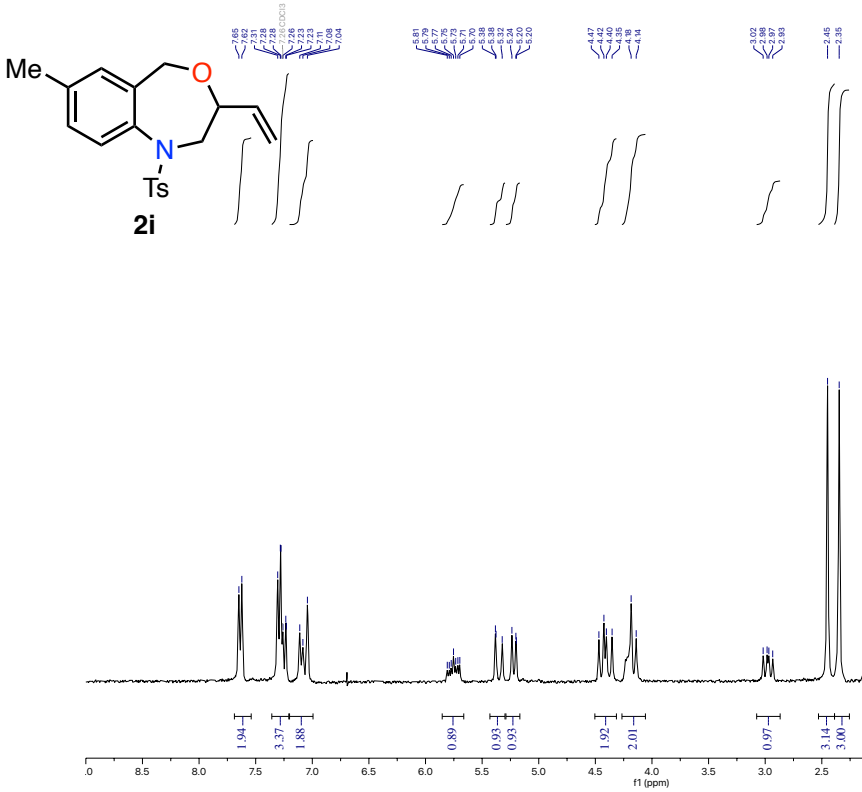
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



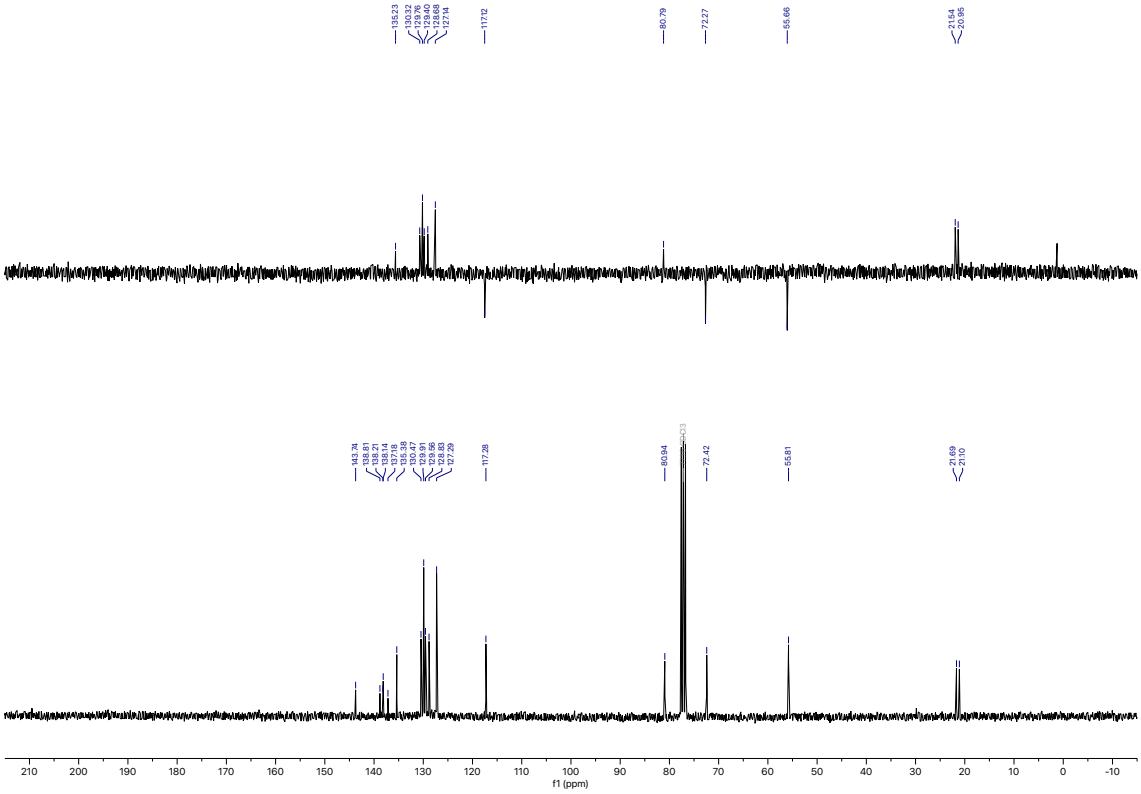
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



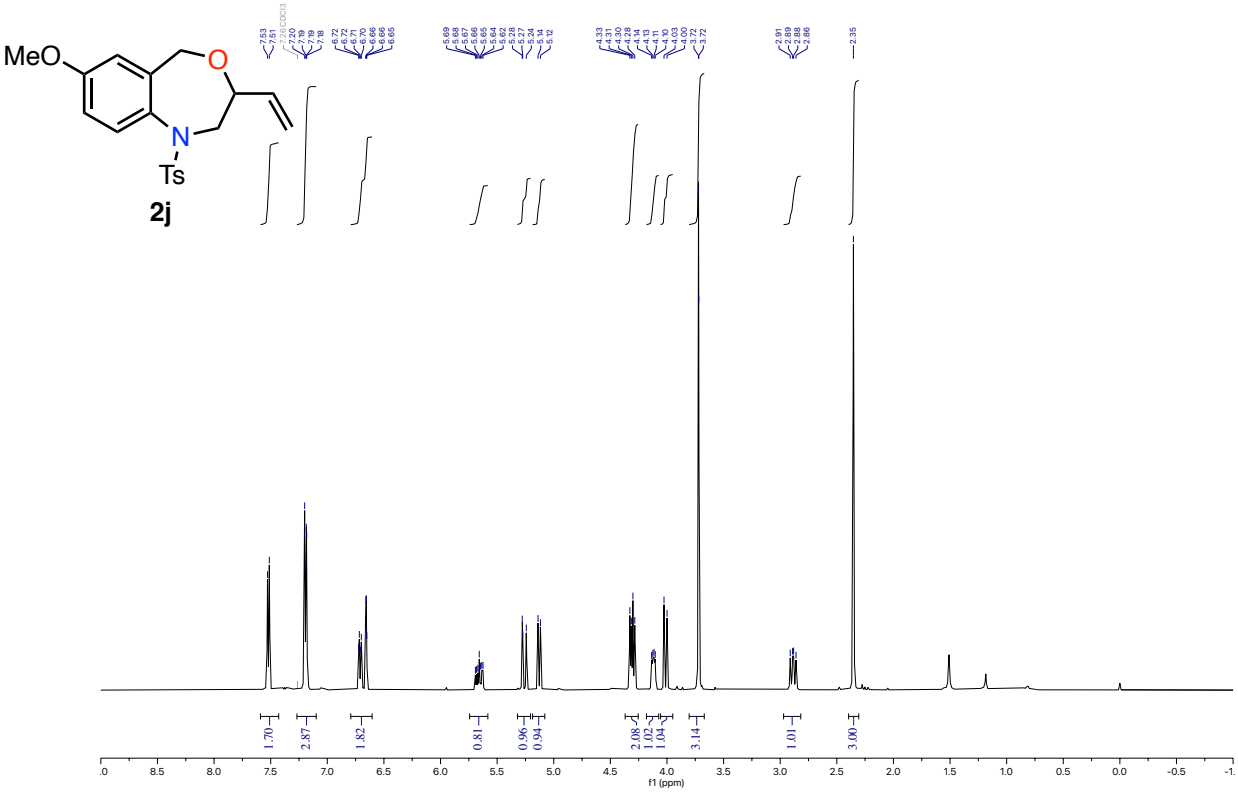
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



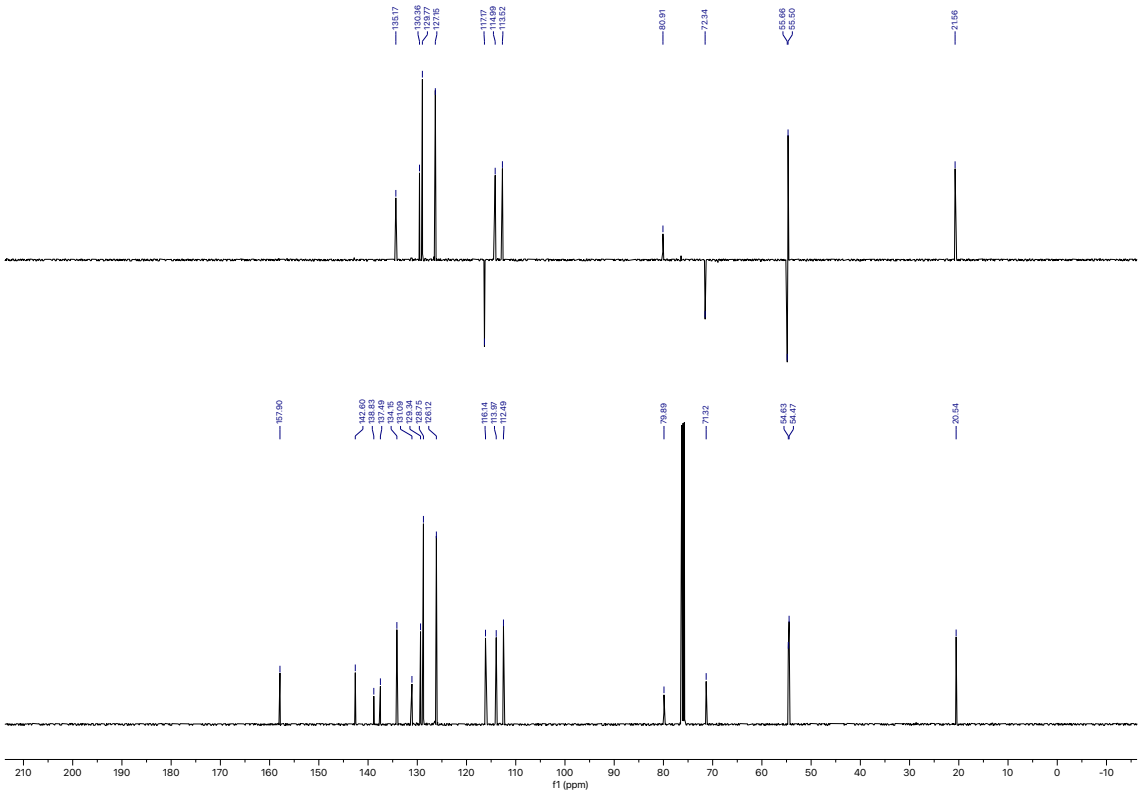
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



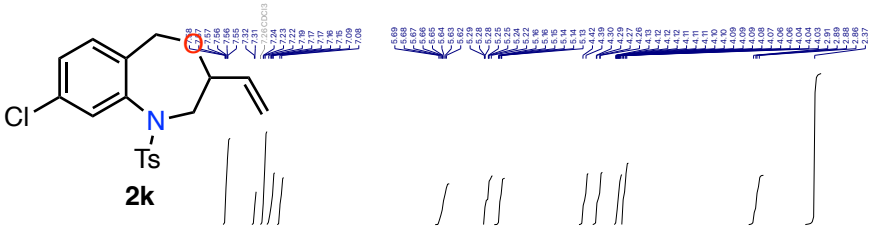
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (500 MHz). Solvent $CDCl_3$



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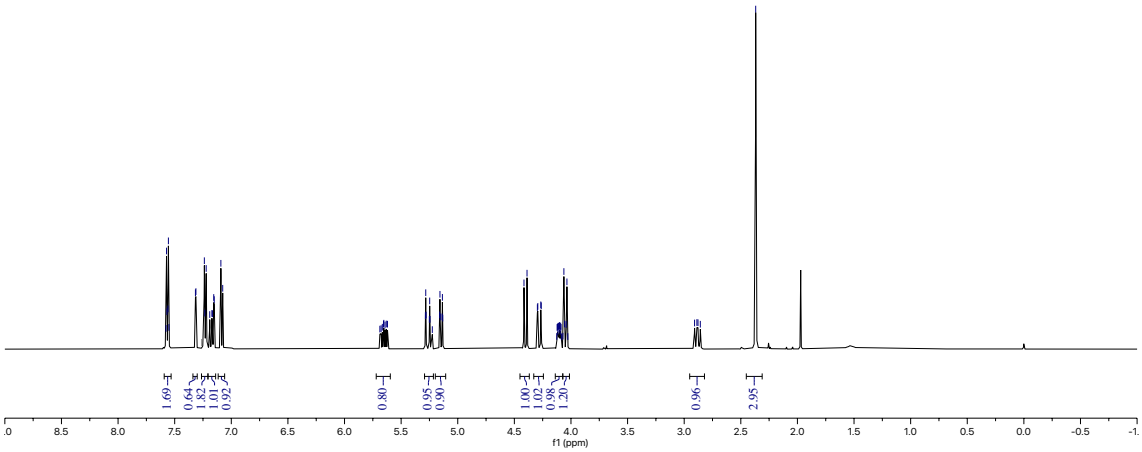
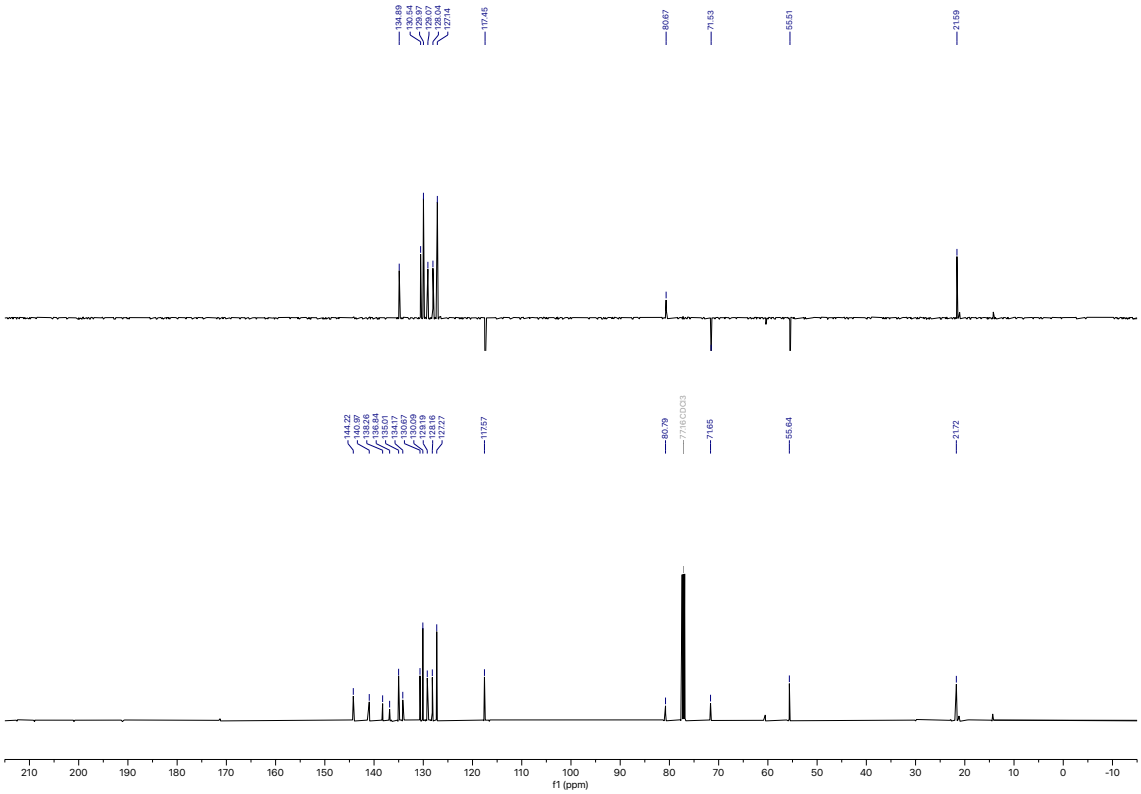


^{13}C-NMR (126 MHz). Solvent $CDCl_3$



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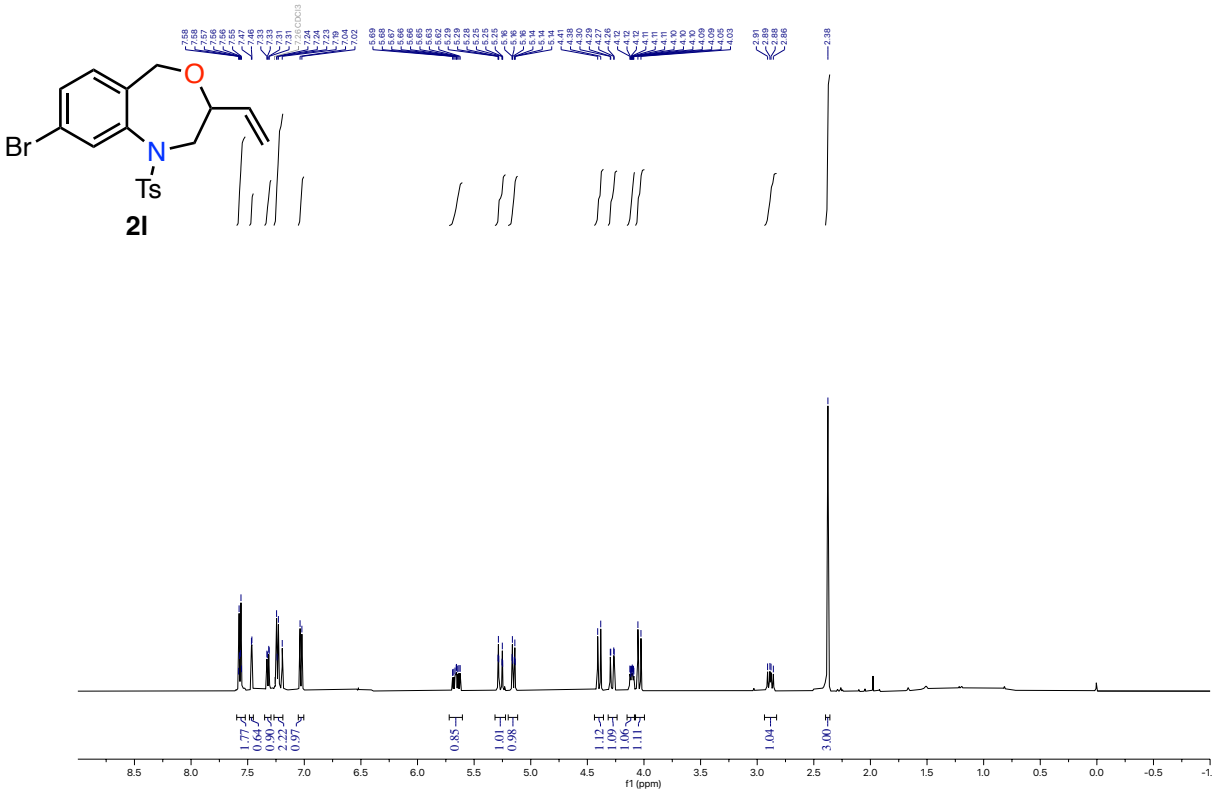
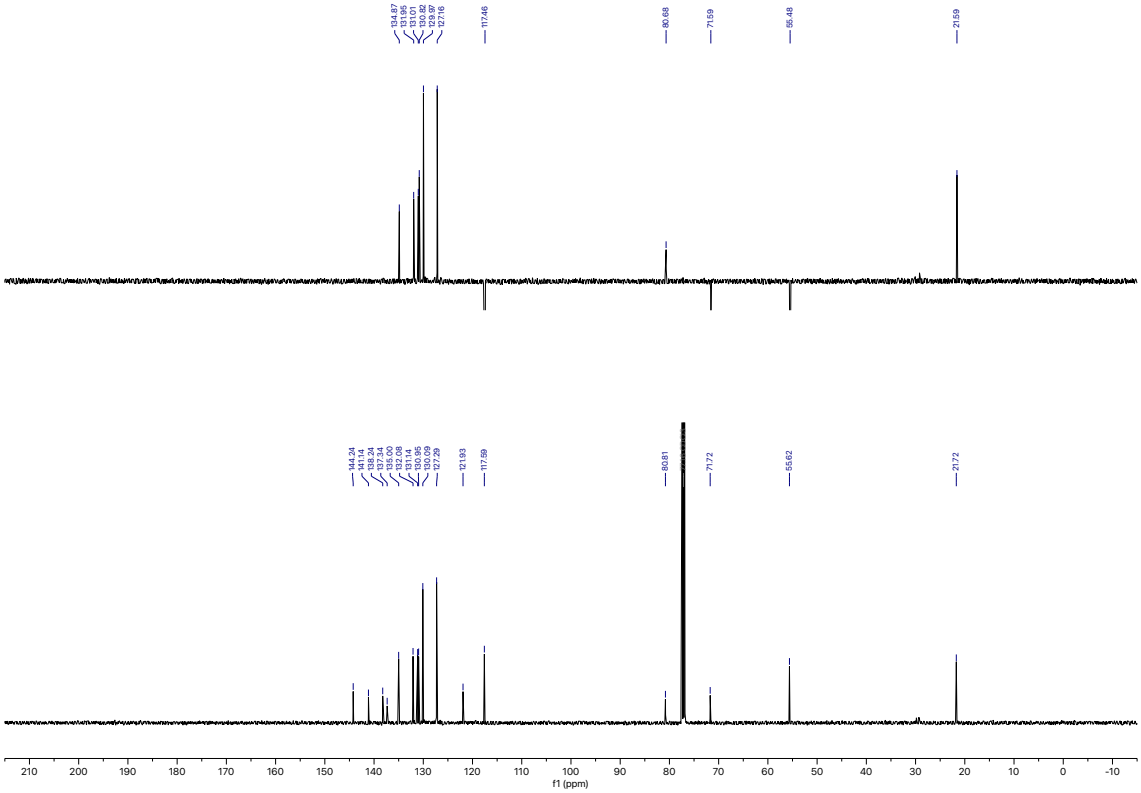
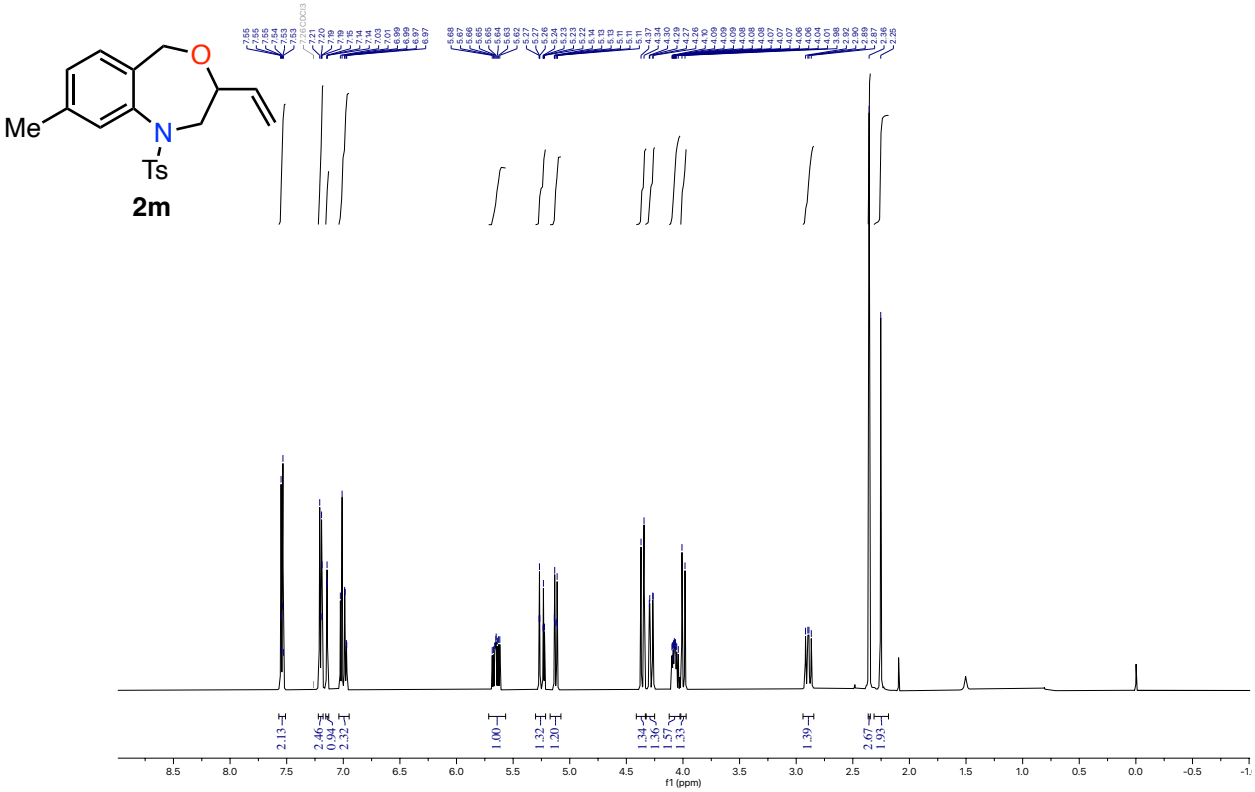


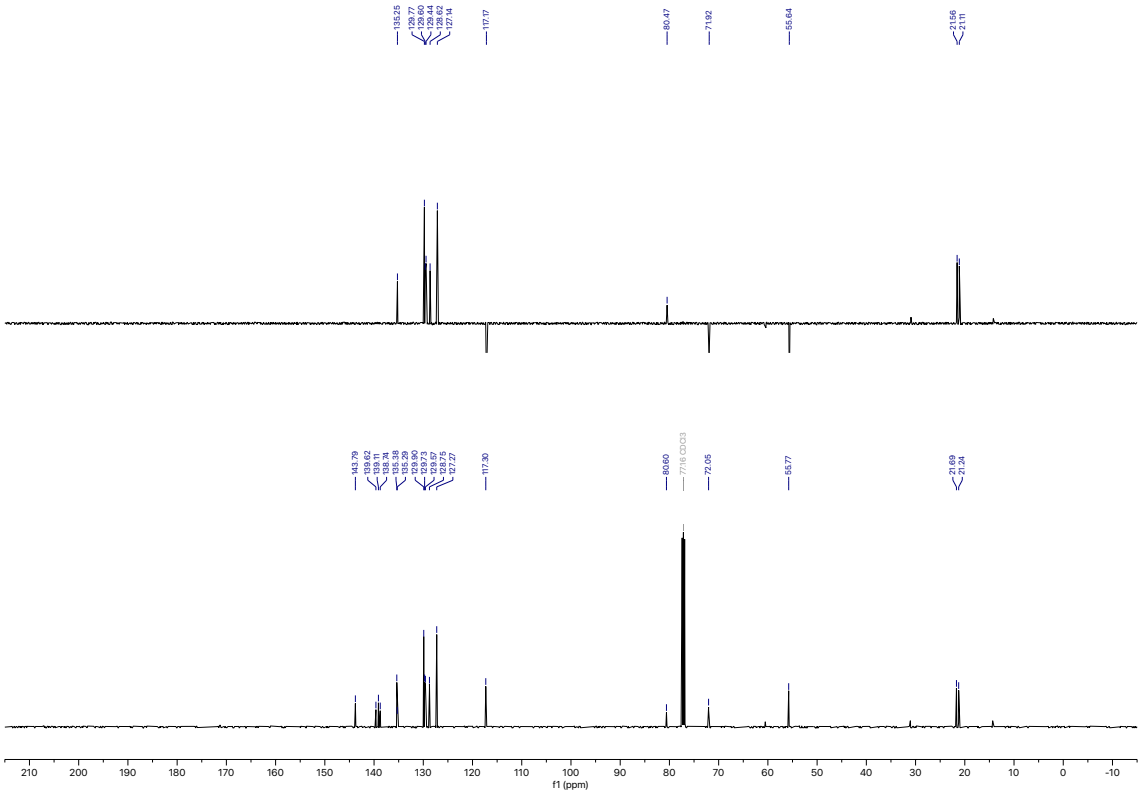
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



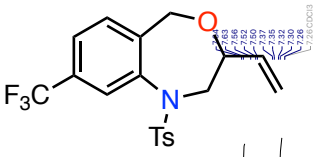
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



^{13}C-NMR (126 MHz). Solvent $CDCl_3$

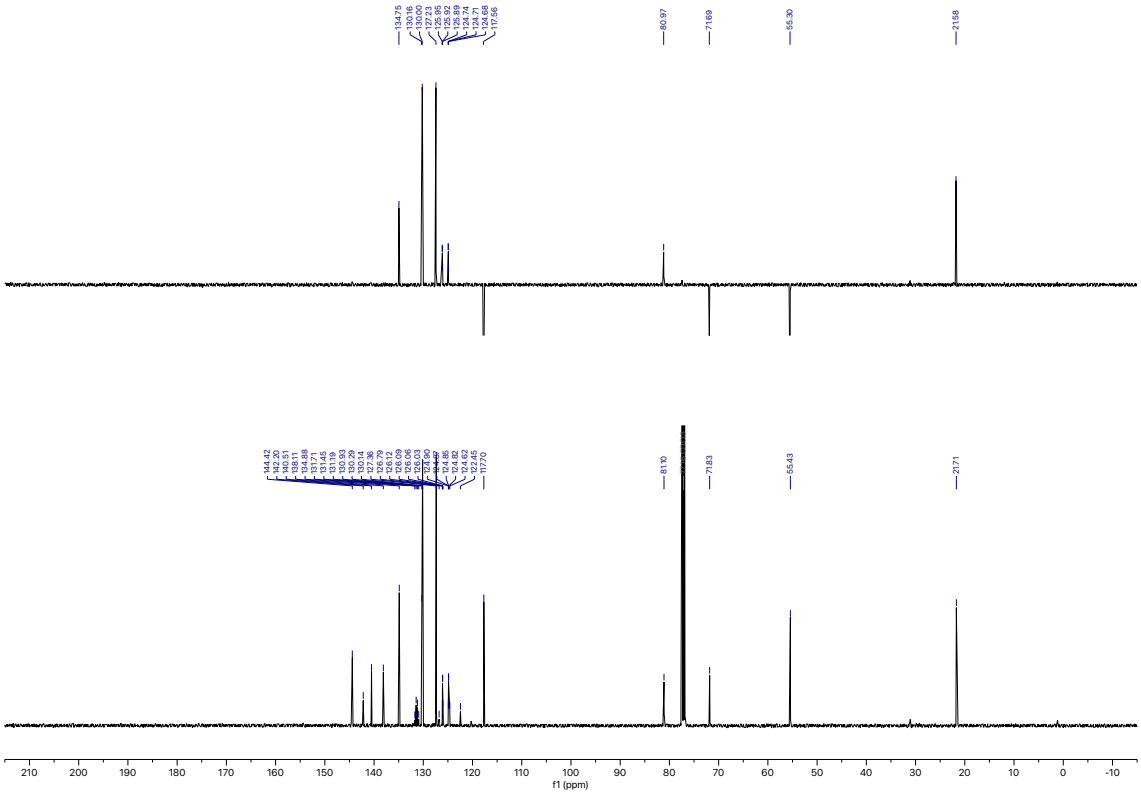


^{1}H-NMR (500 MHz). Solvent $CDCl_3$

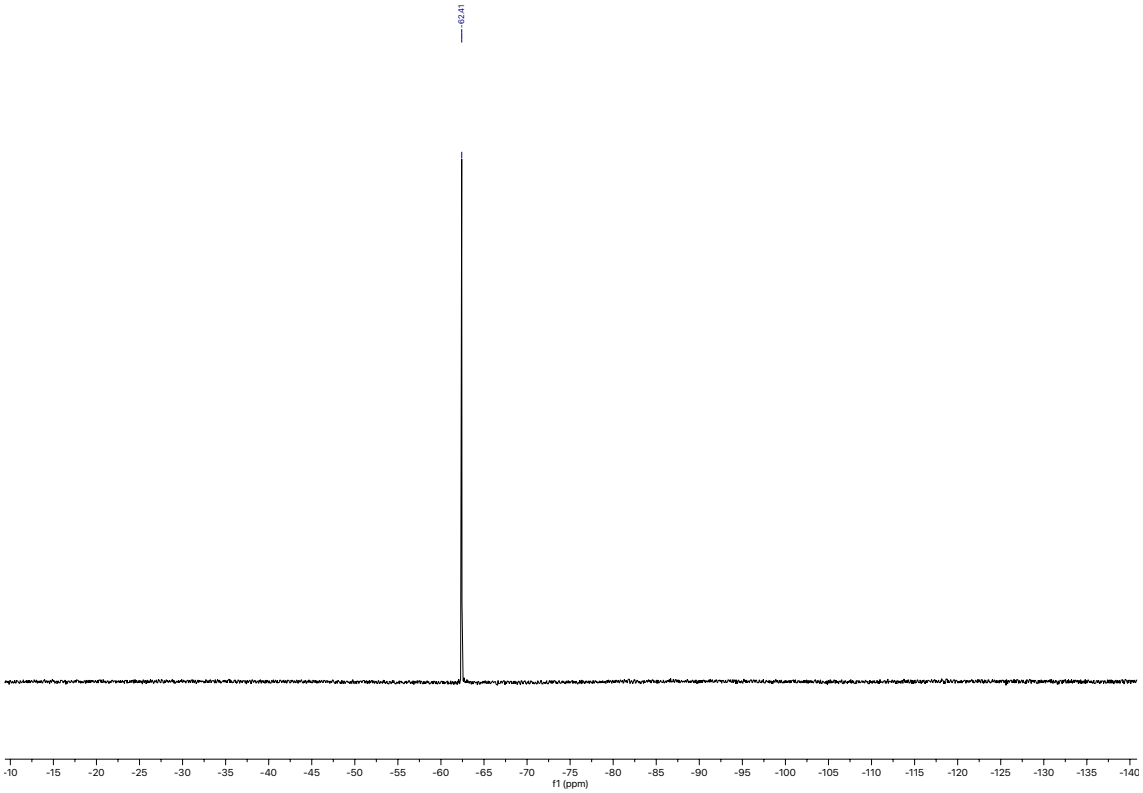


2n

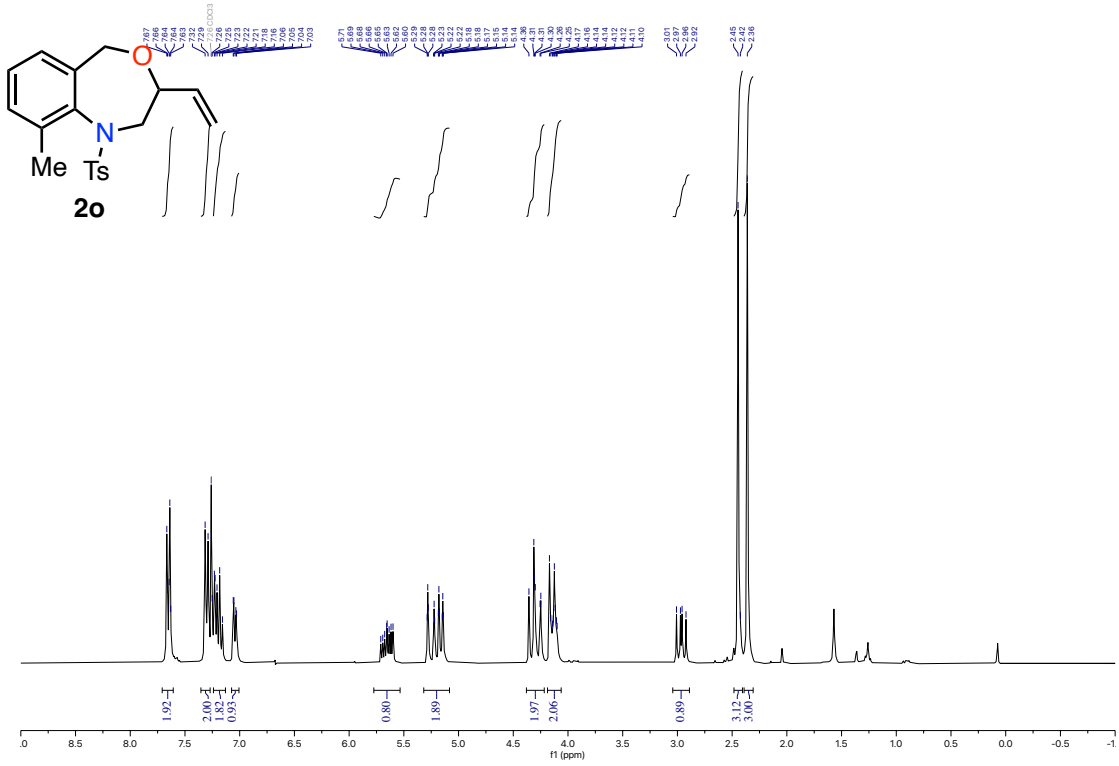
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



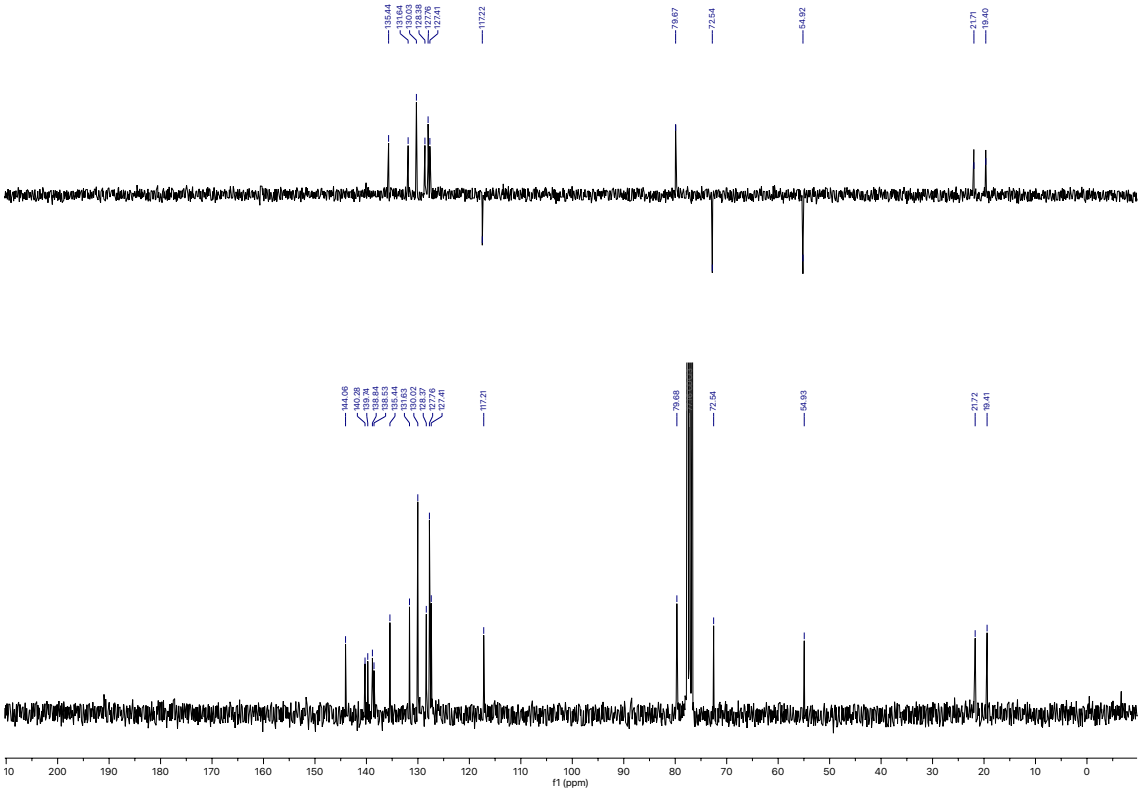
^{19}F-NMR (282 MHz). Solvent $CDCl_3$



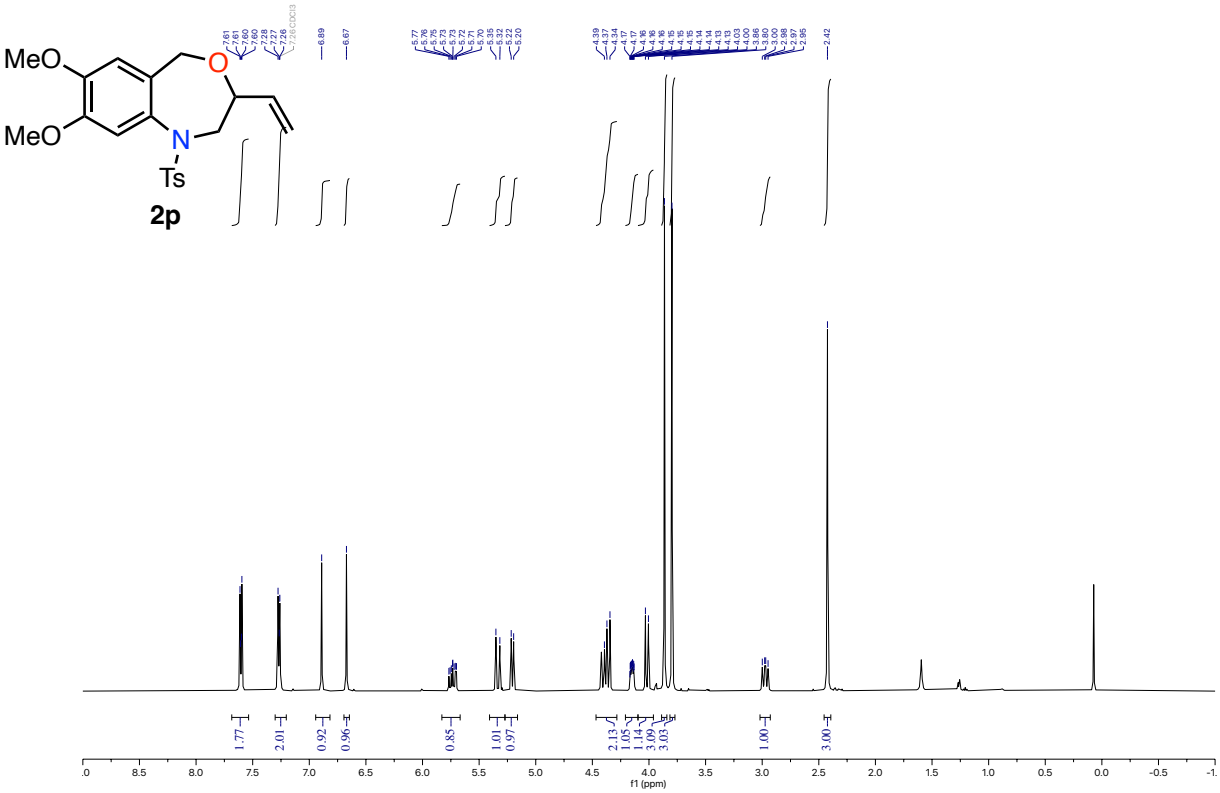
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



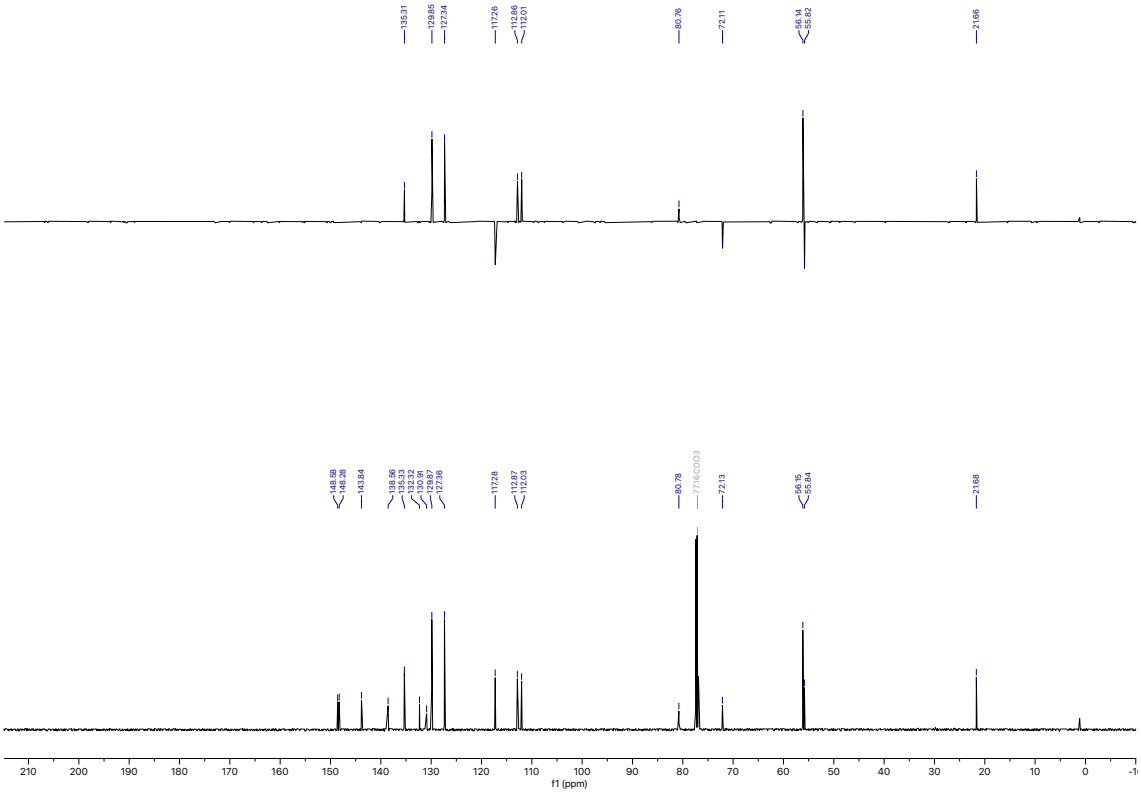
^{13}C-NMR (75MHz). Solvent $CDCl_3$



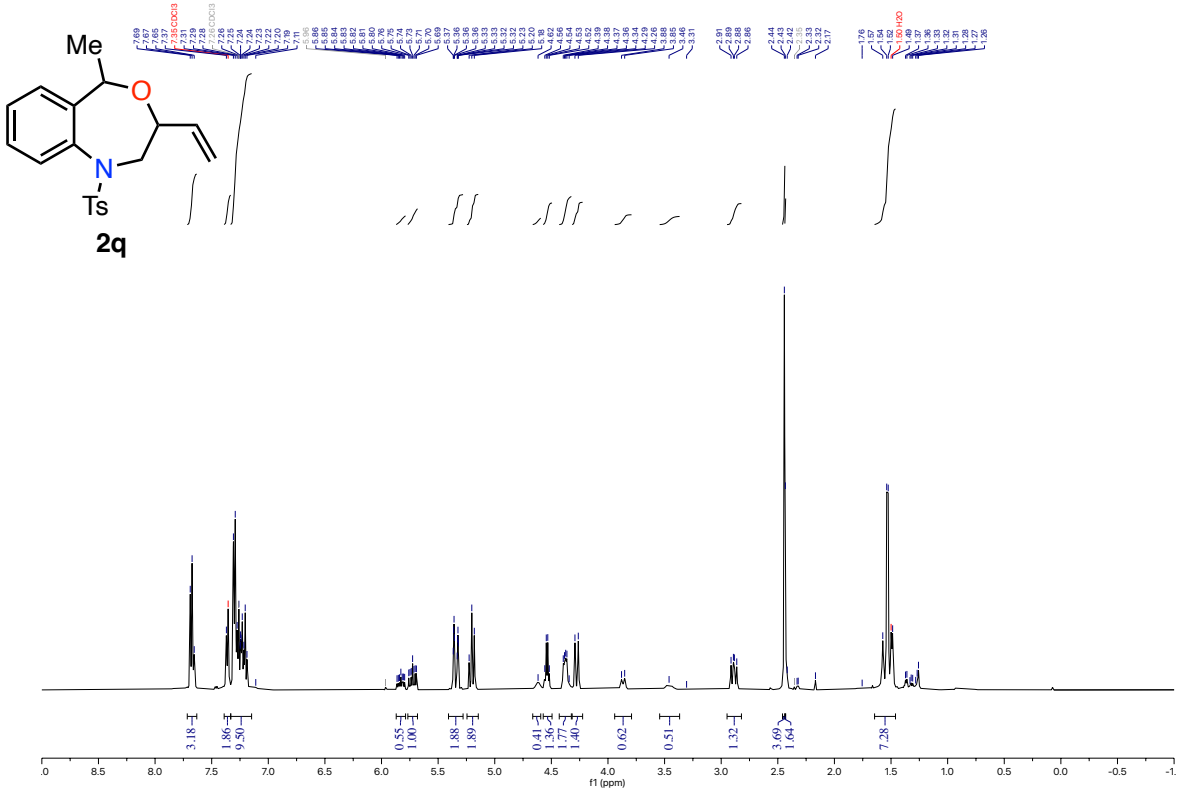
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



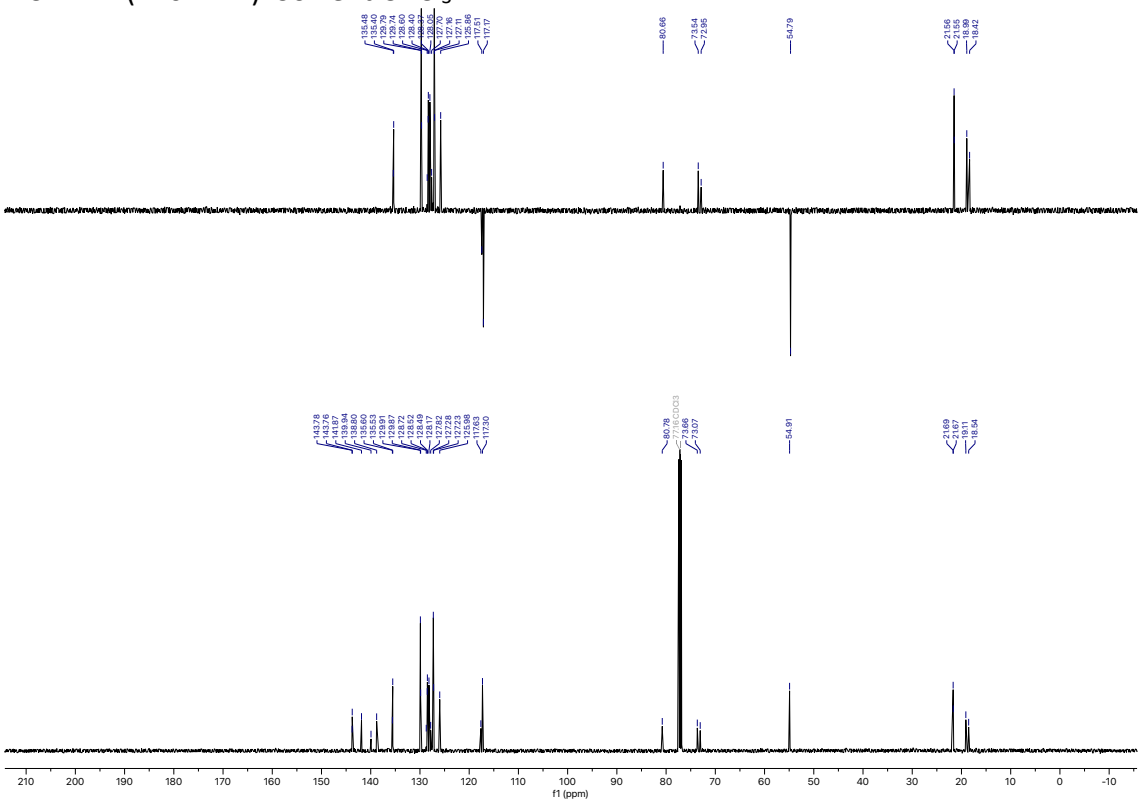
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



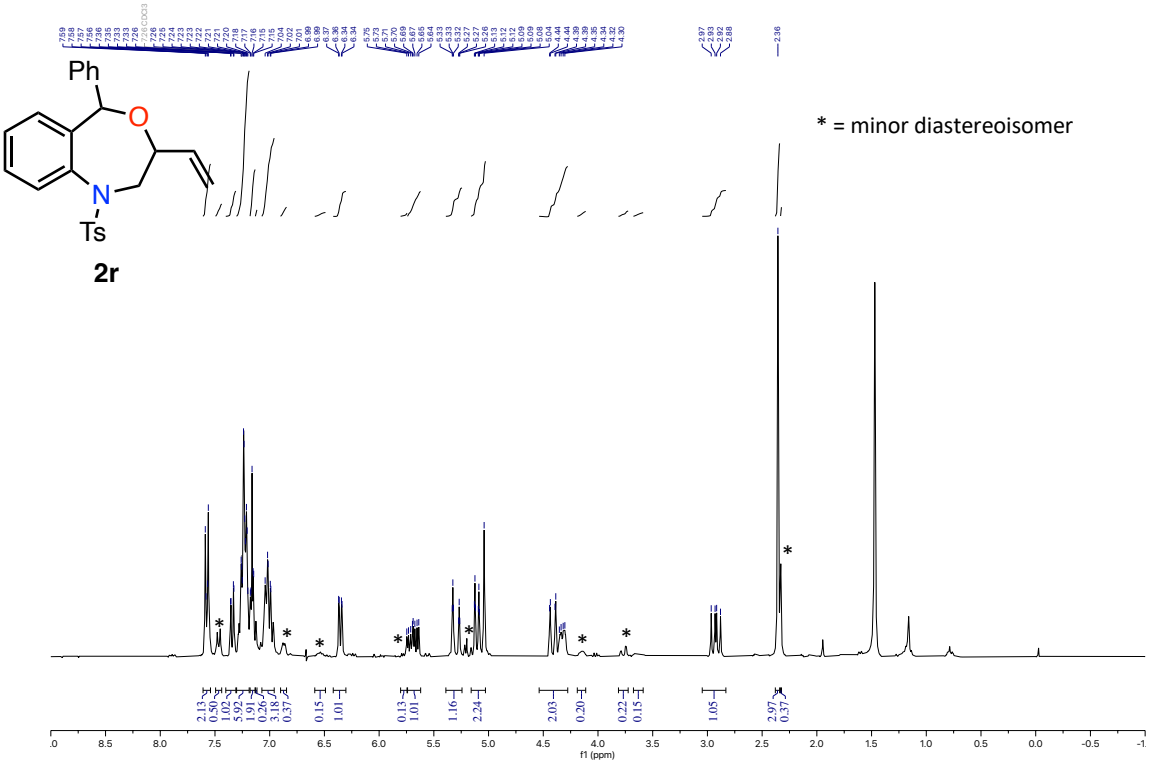
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



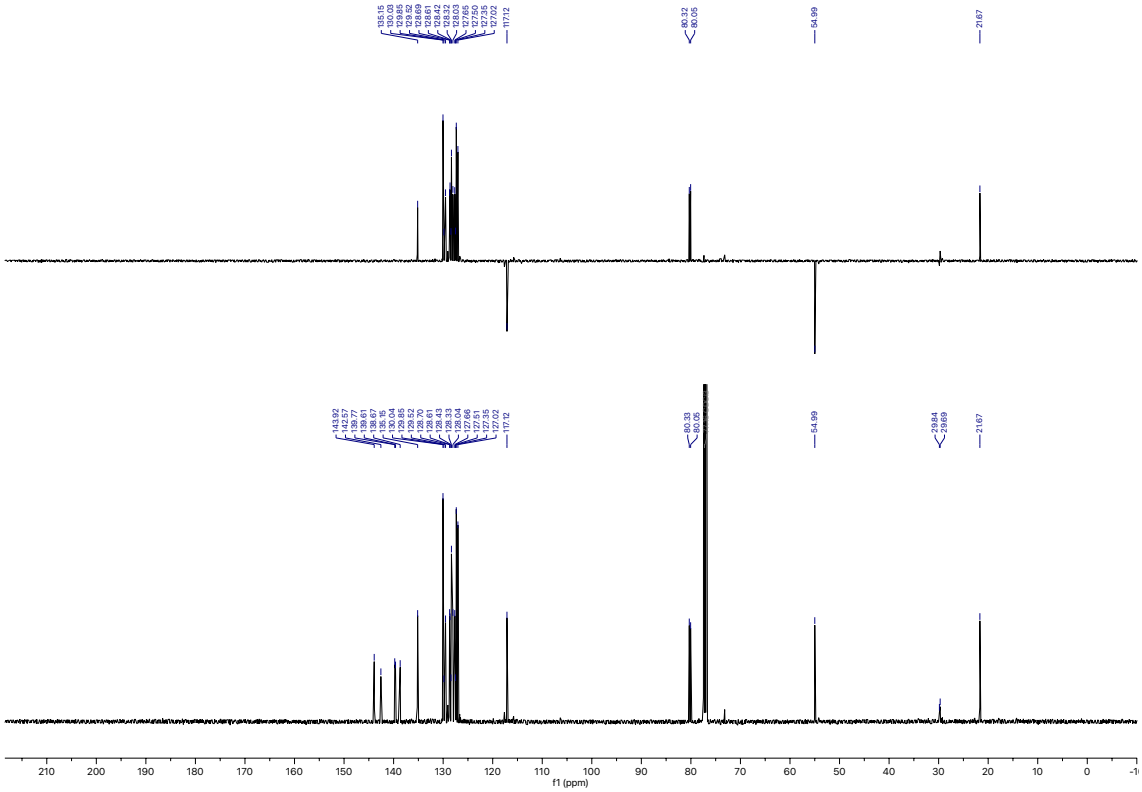
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



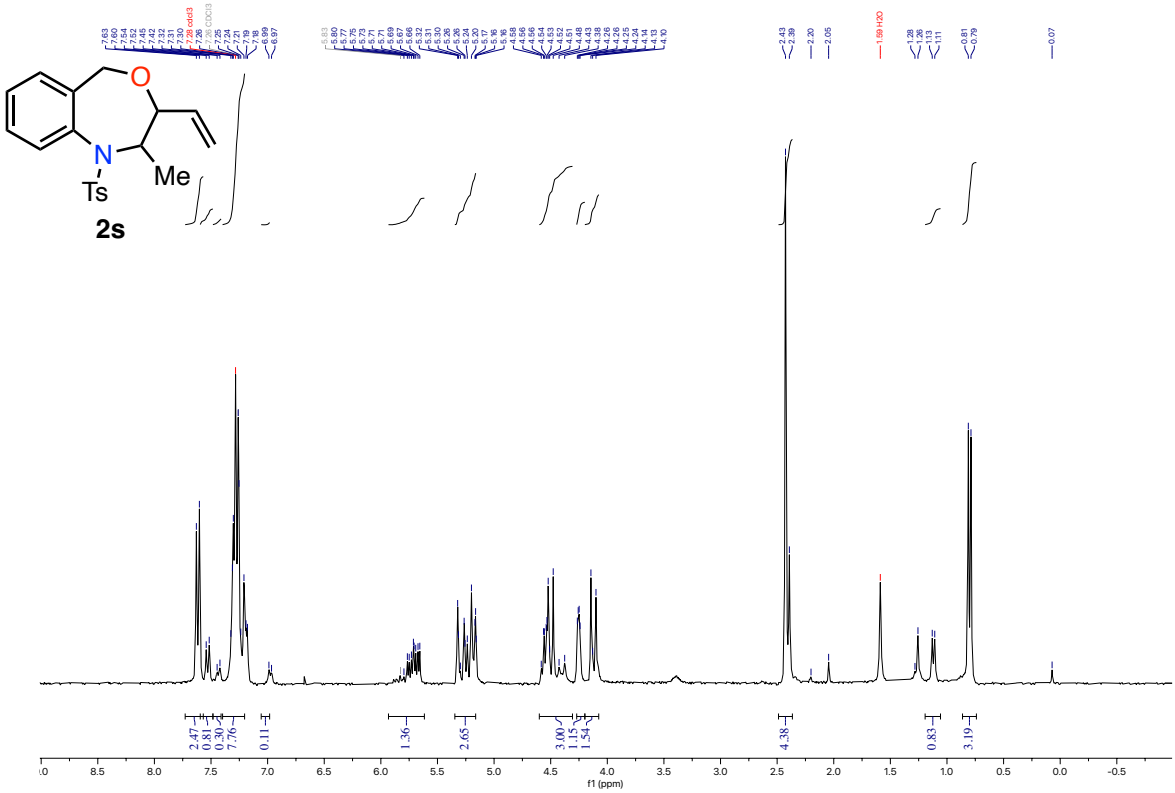
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



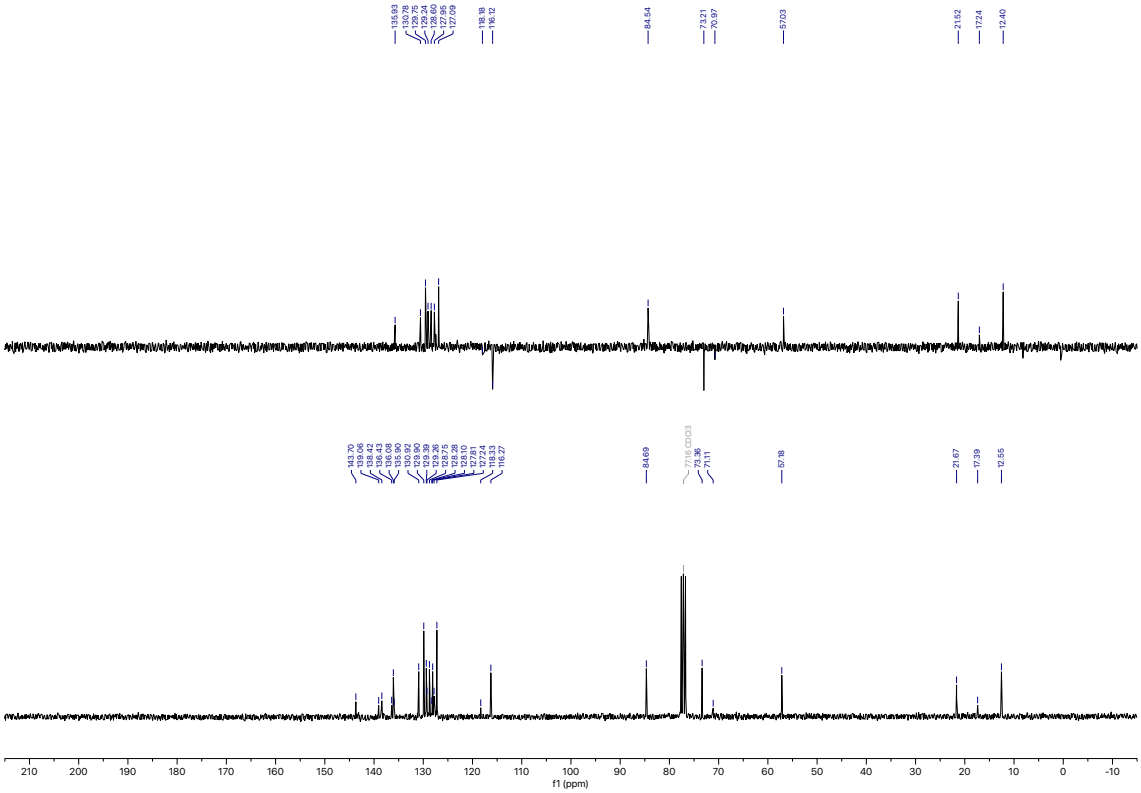
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



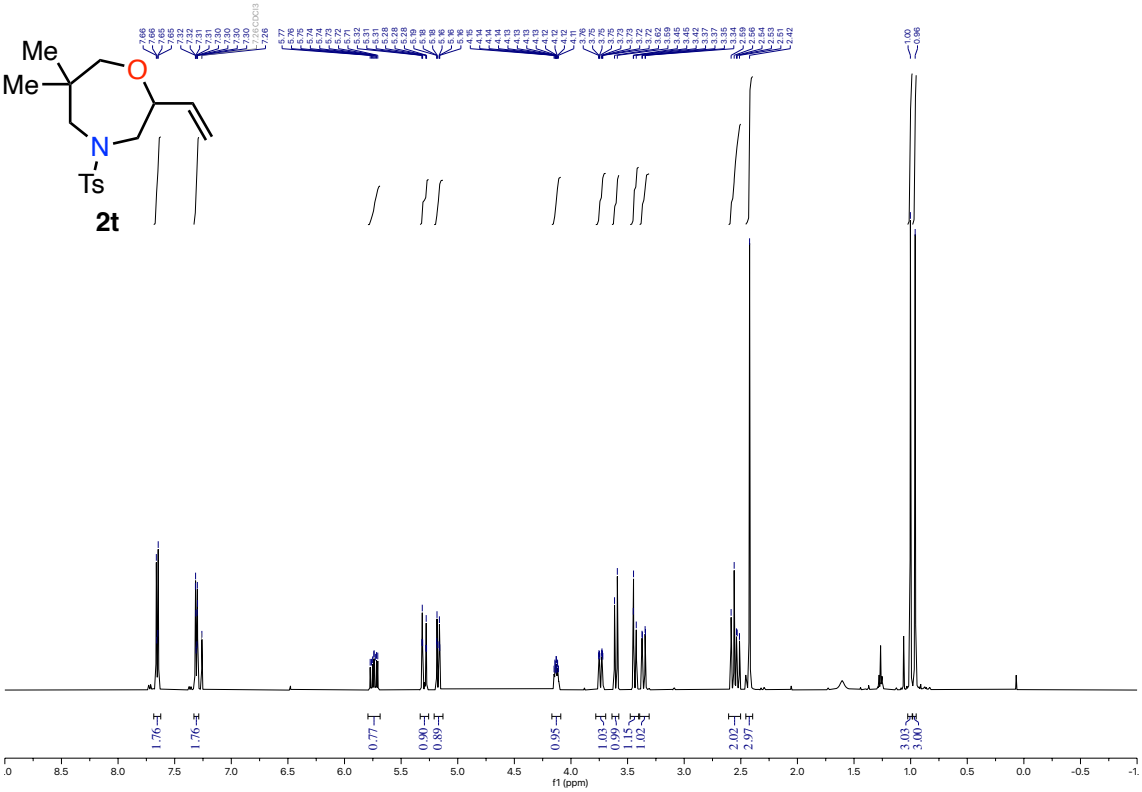
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



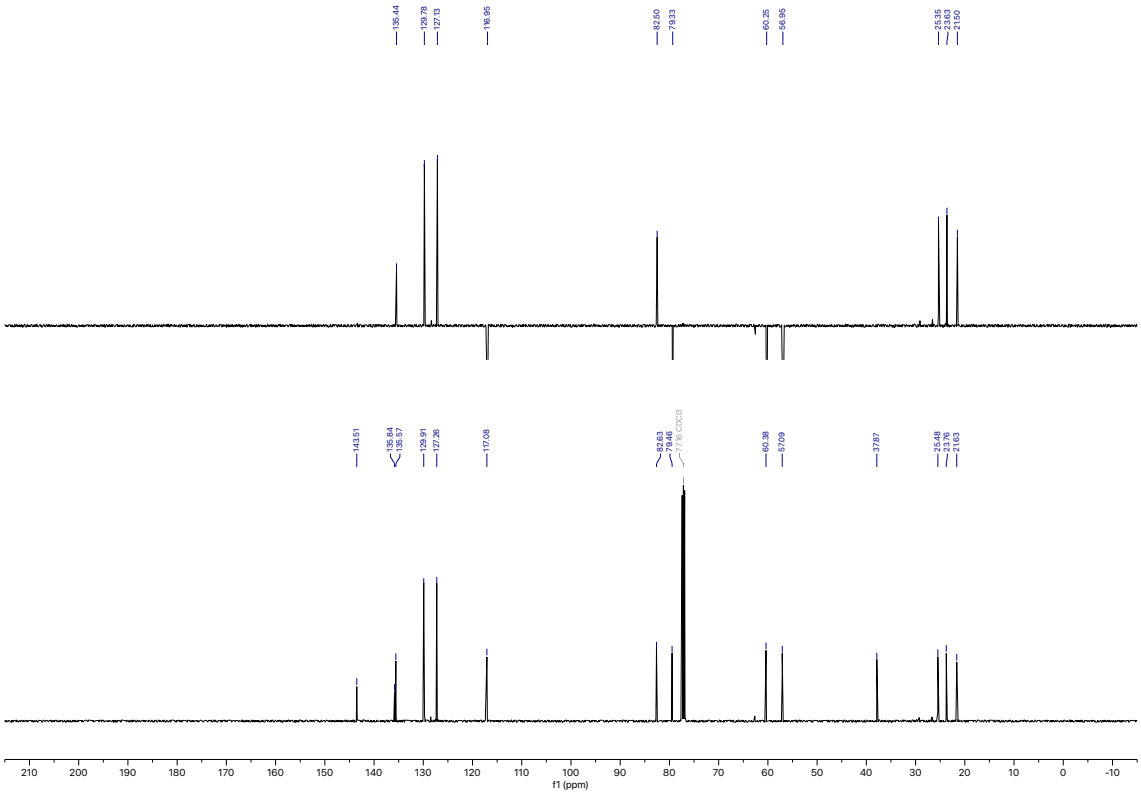
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



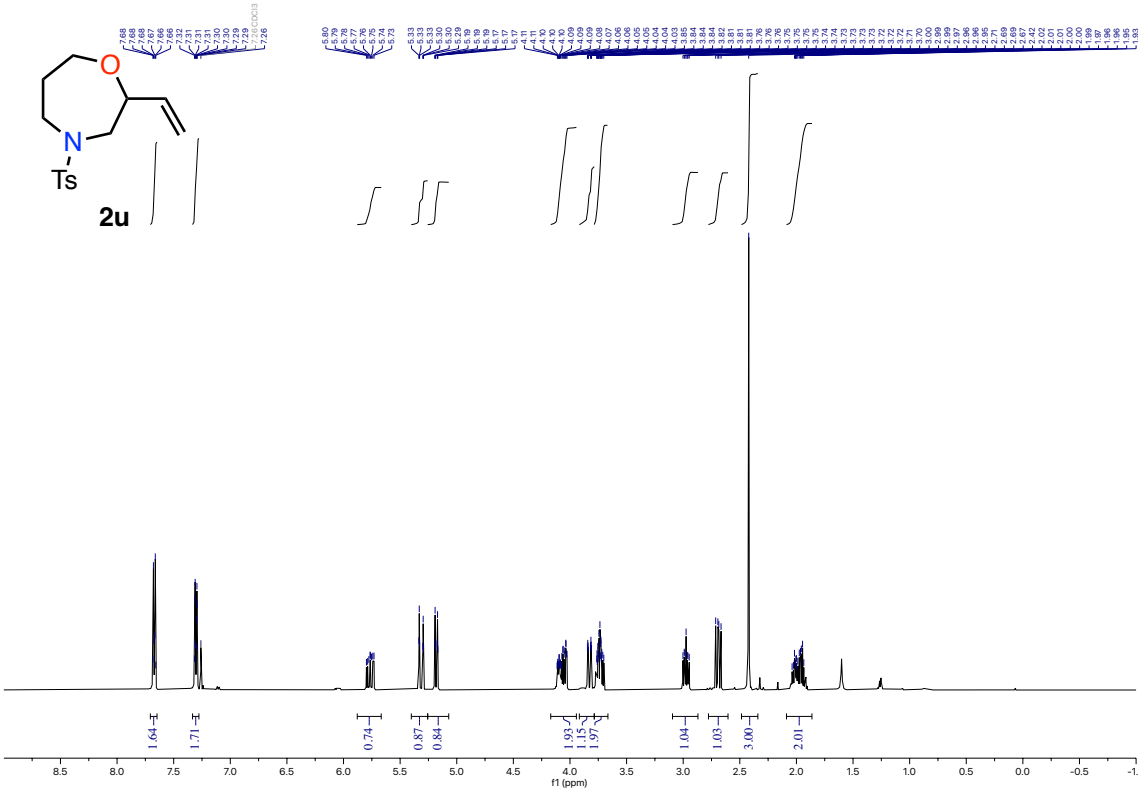
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



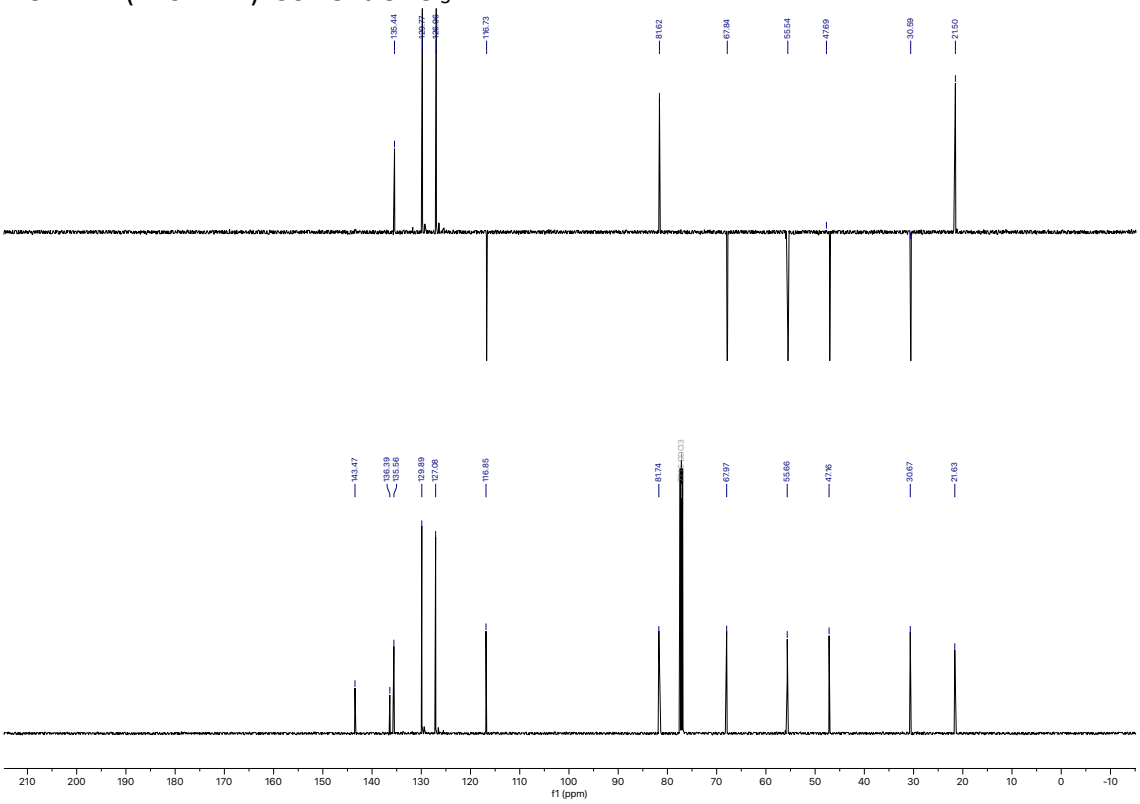
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



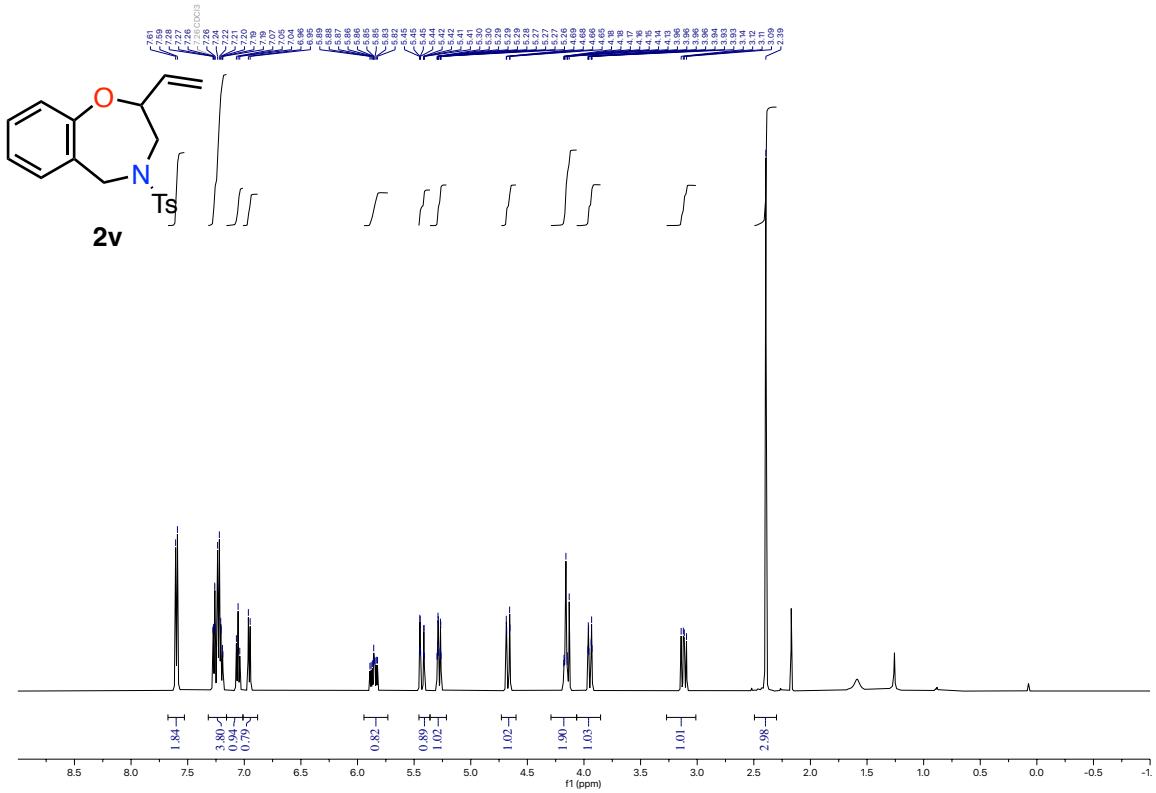
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



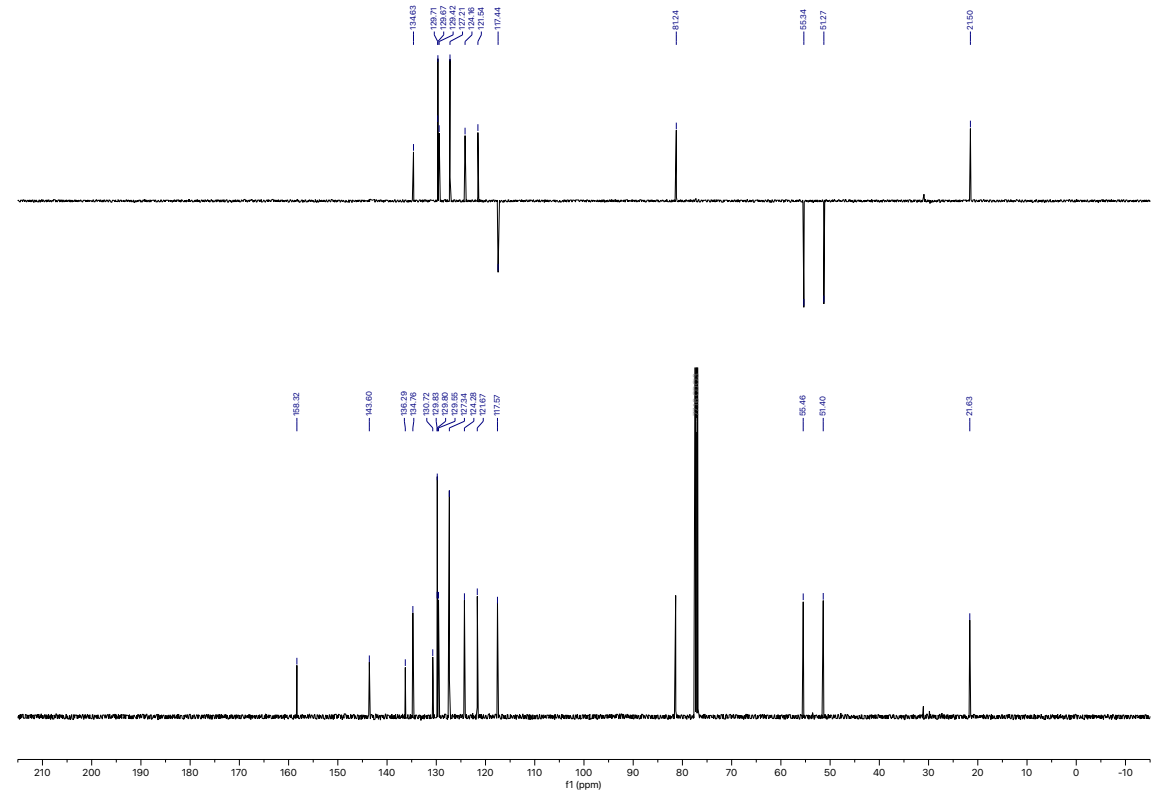
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



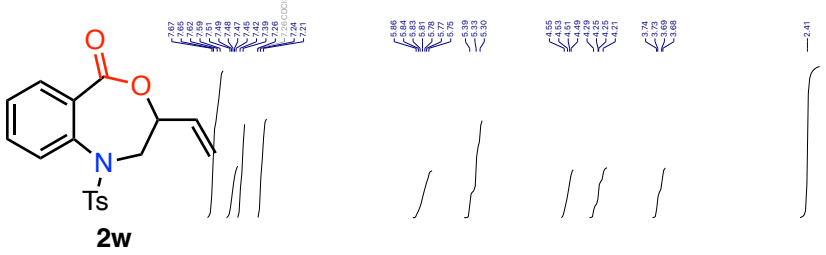
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (300 MHz). Solvent $CDCl_3$



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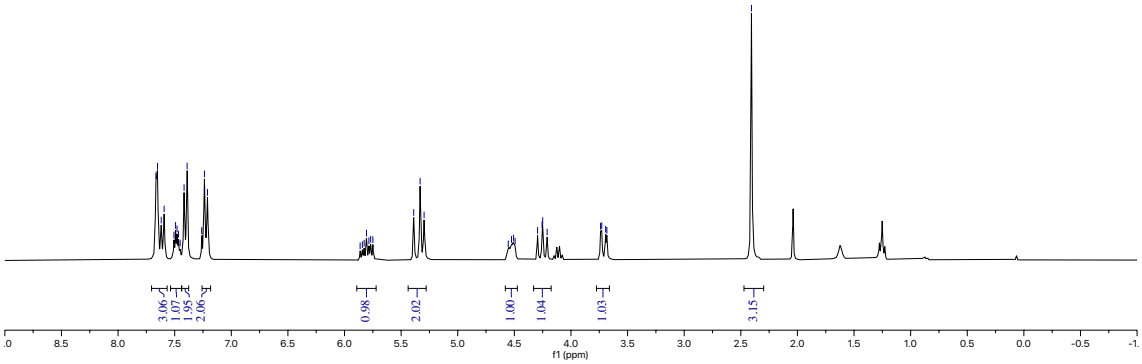
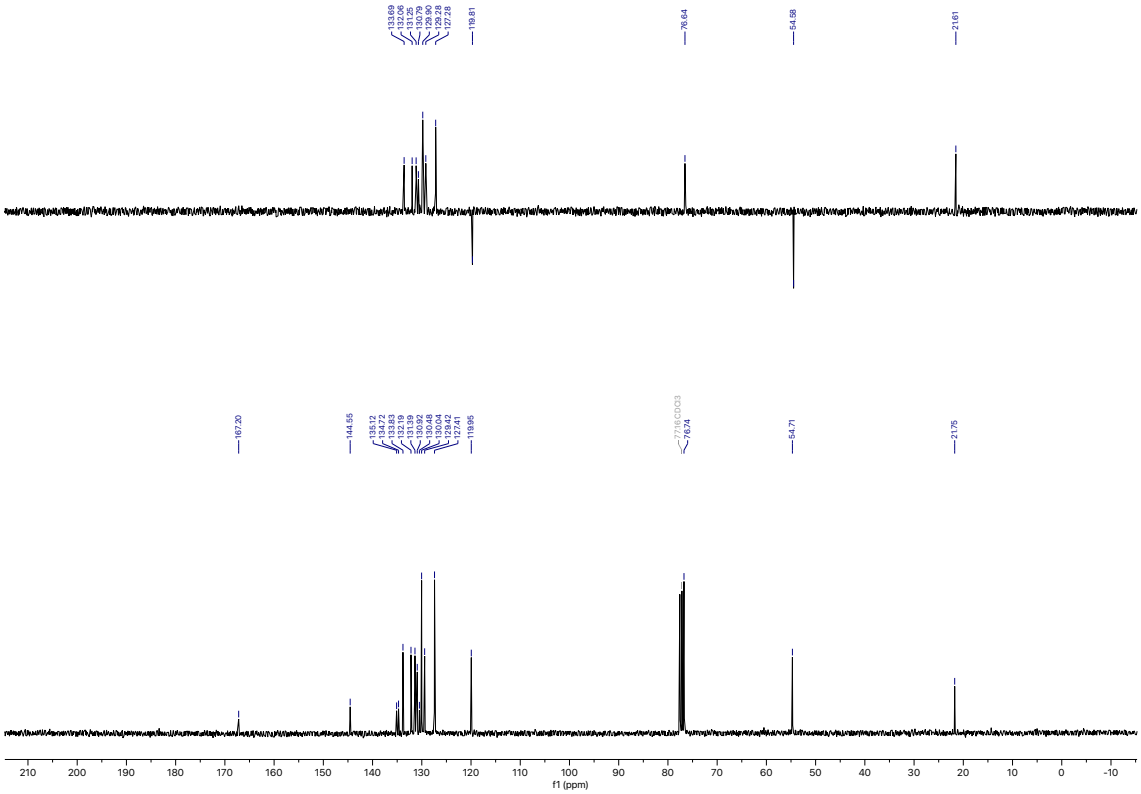
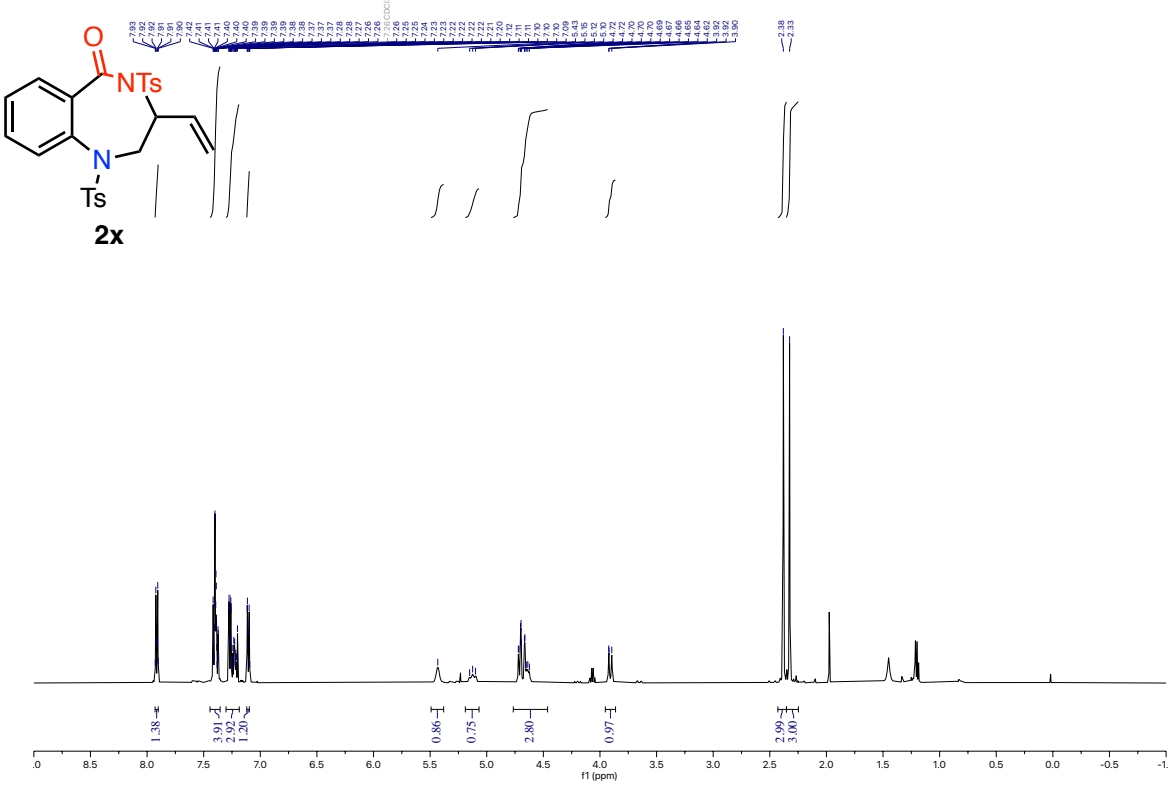


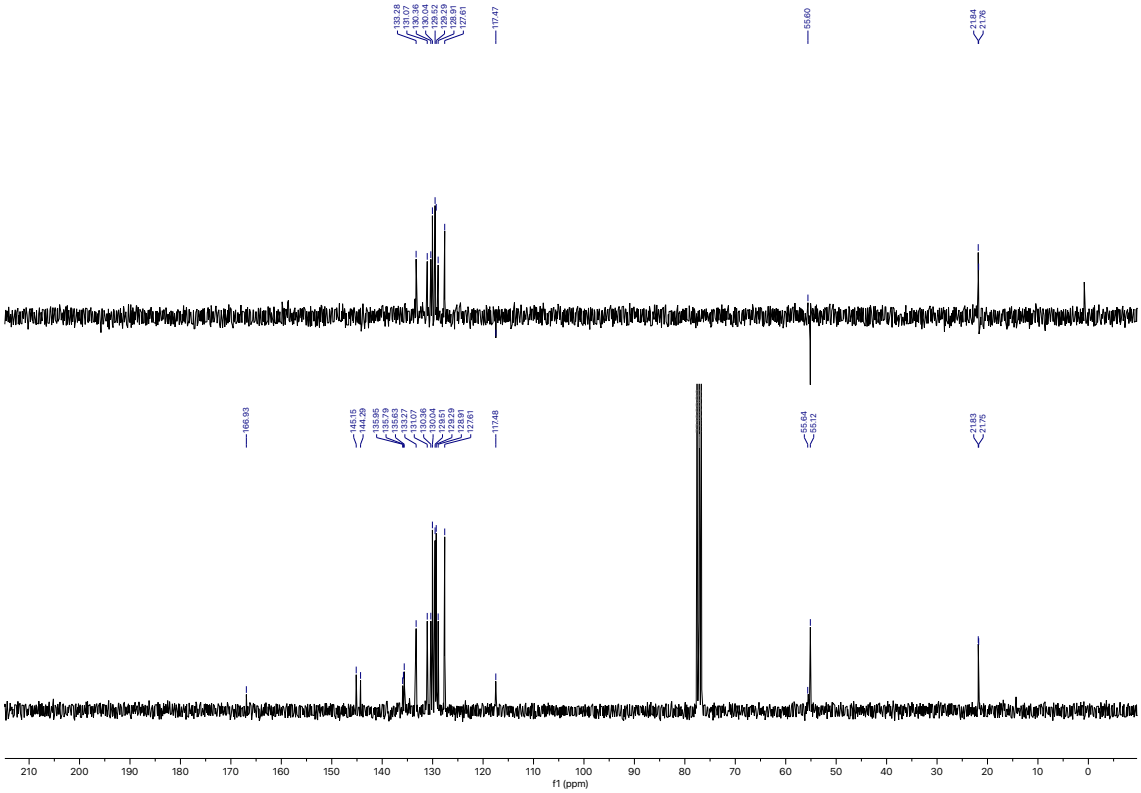
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



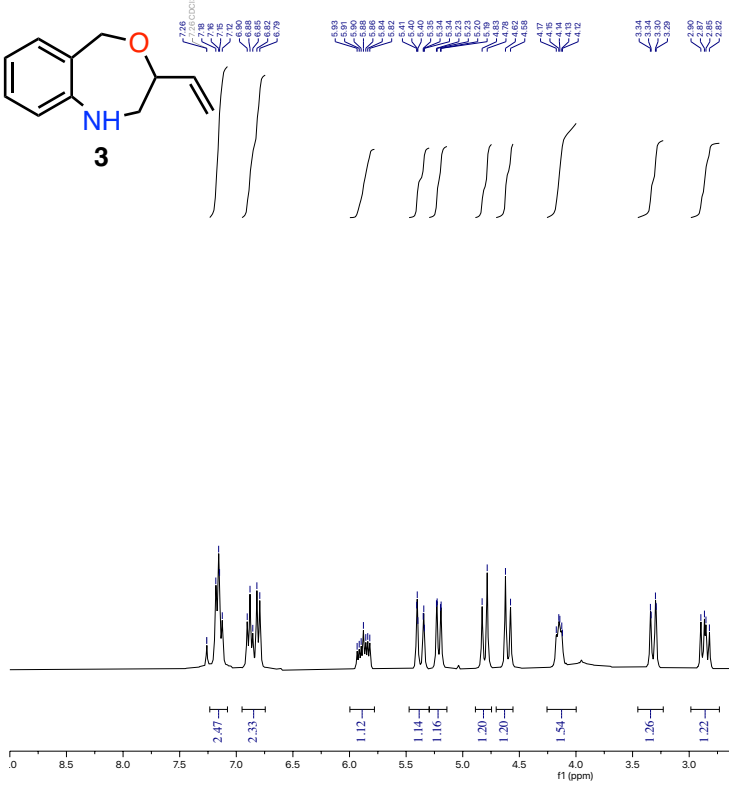
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



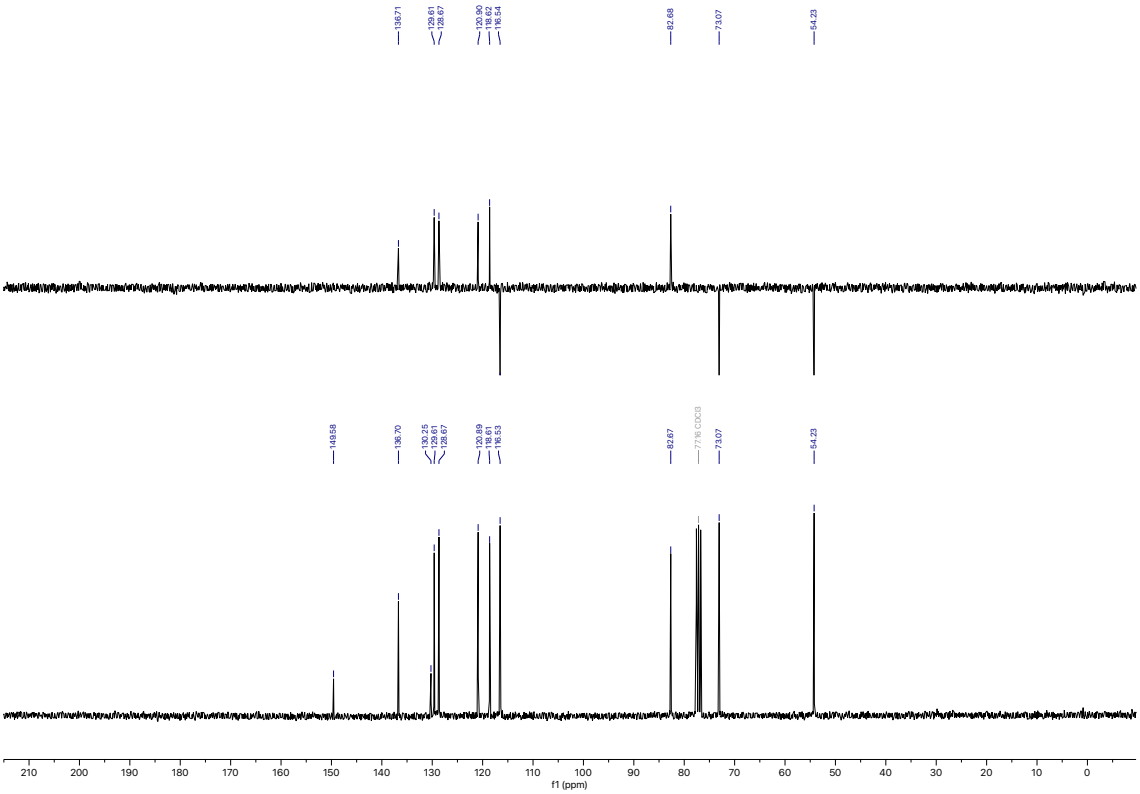
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



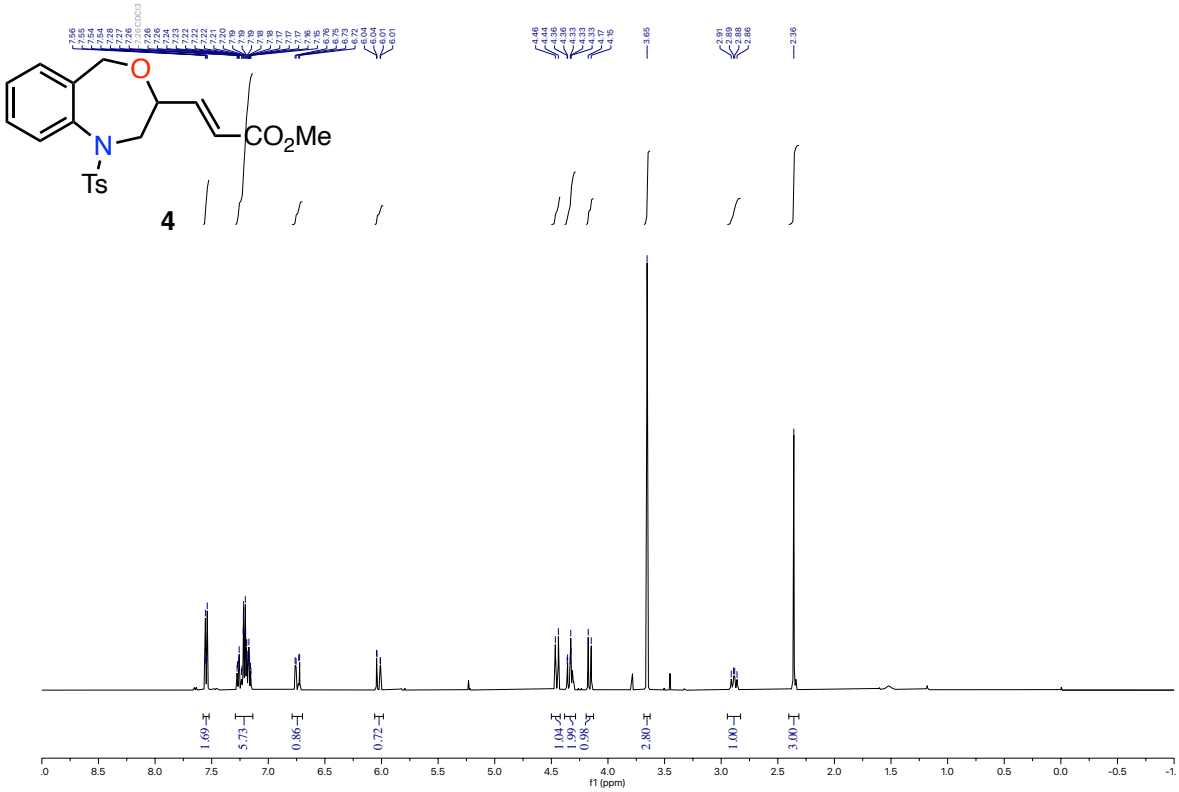
^{1}H-NMR (300 MHz). Solvent $CDCl_3$



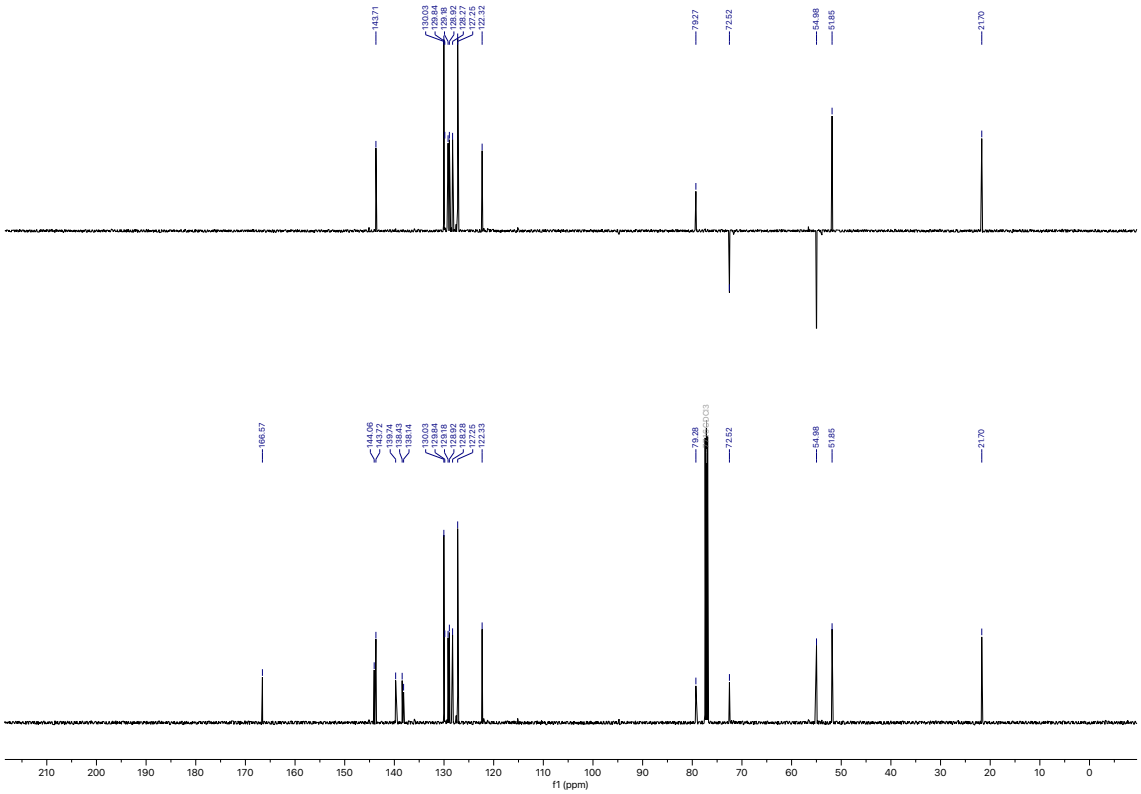
^{13}C-NMR (75 MHz). Solvent $CDCl_3$



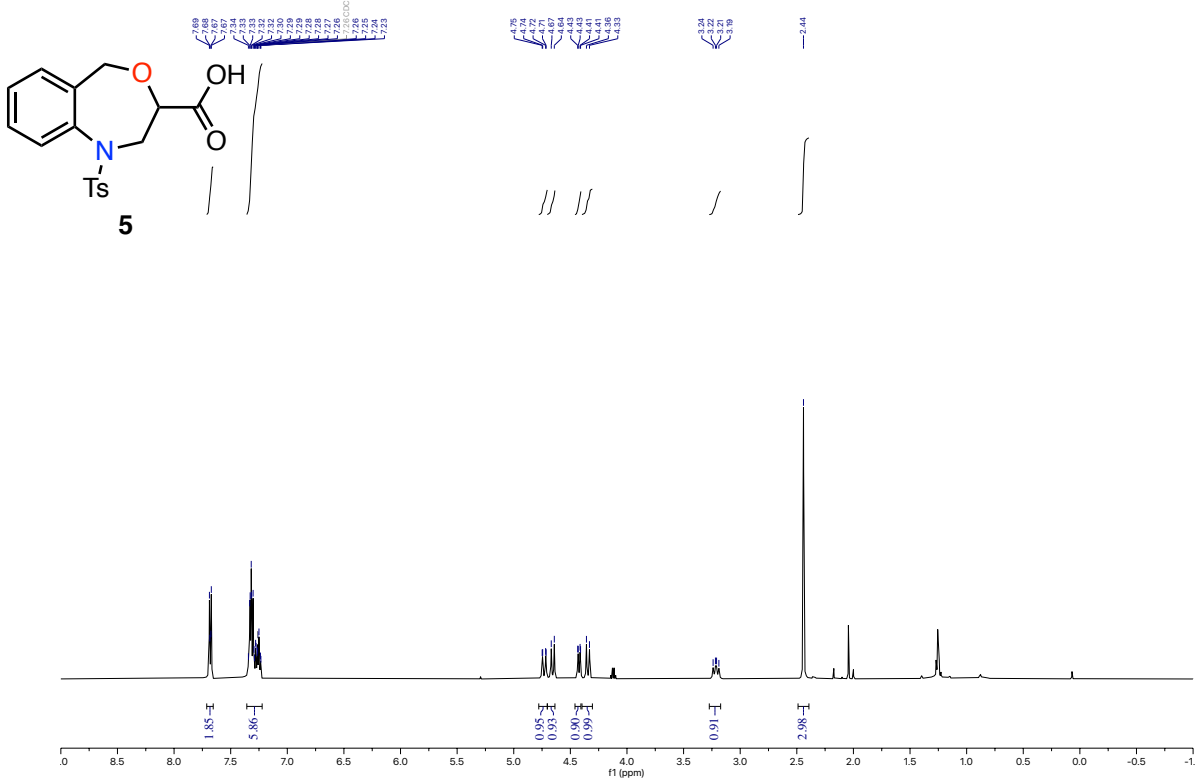
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



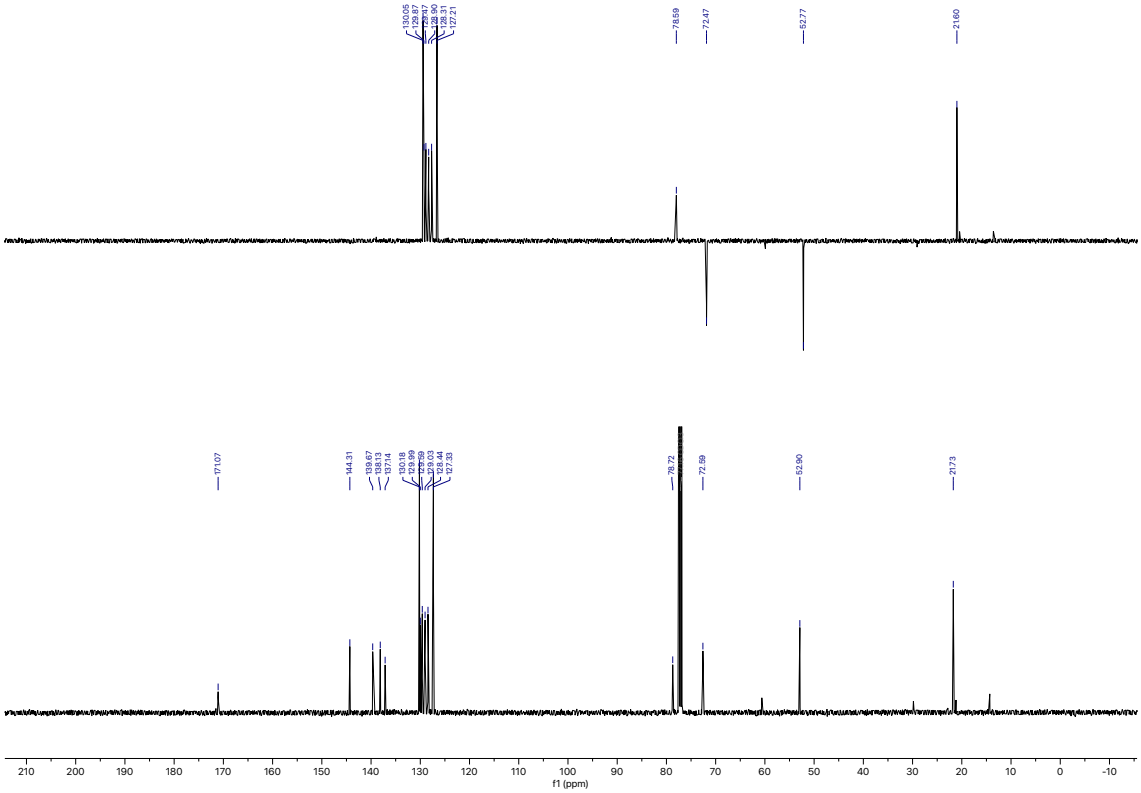
^{13}C-NMR (126 MHz). Solvent $CDCl_3$



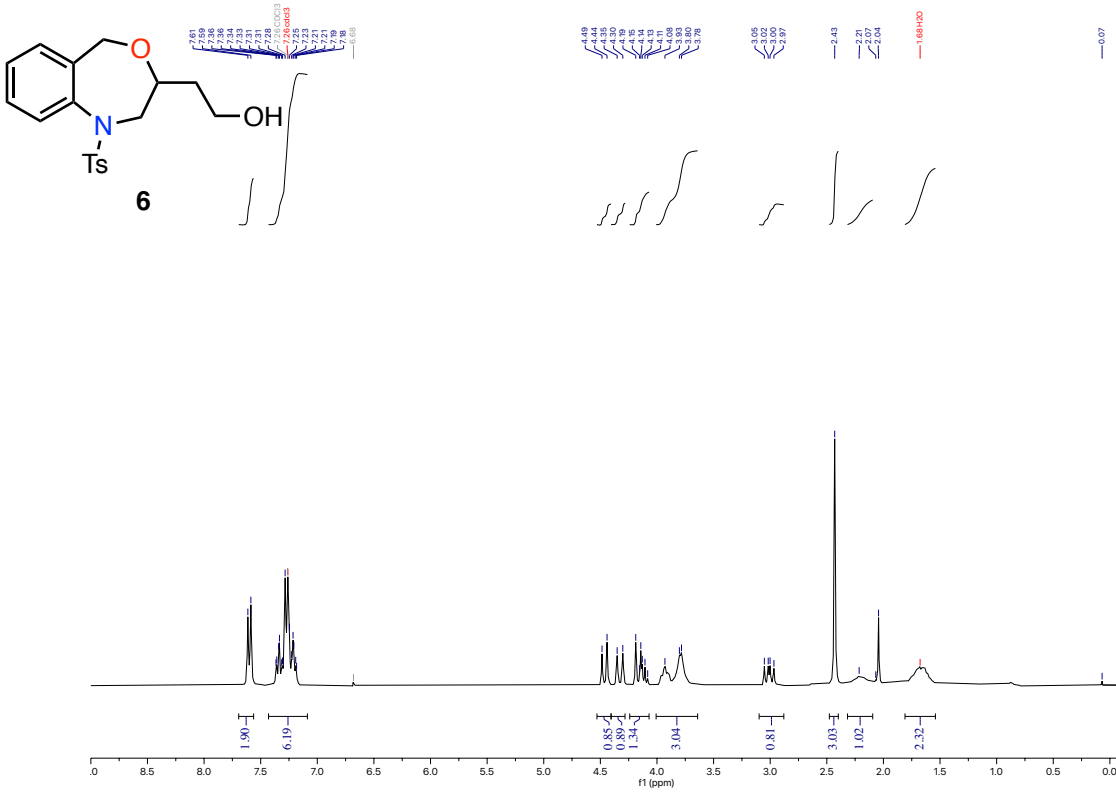
^{1}H-NMR (500 MHz). Solvent $CDCl_3$



^{13}C-NMR (126 MHz). Solvent $CDCl_3$



^{1}H-NMR (300 MHz). Solvent $CDCl_3$



^{13}C-NMR (75 MHz). Solvent $CDCl_3$