Supporting Information

Rh-Catalyzed Cycloisomerization of 1,7-Ene-Dienes to Synthesize *trans*-Divinylpiperidines: A Formal Intramolecular Addition Reaction of Allylic C-H Bond into Dienes

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1. General information

Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Super-dried DCE and synthetic reagents were purchased from J&K, Energy, Acros, Aldrich, and Alfa Aesar, **especially $[Rh(coe)_2Cl]_2$ from Stream, $Rh(PPh_3)_3Cl$ catalyst from Alfa Aesar,** and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

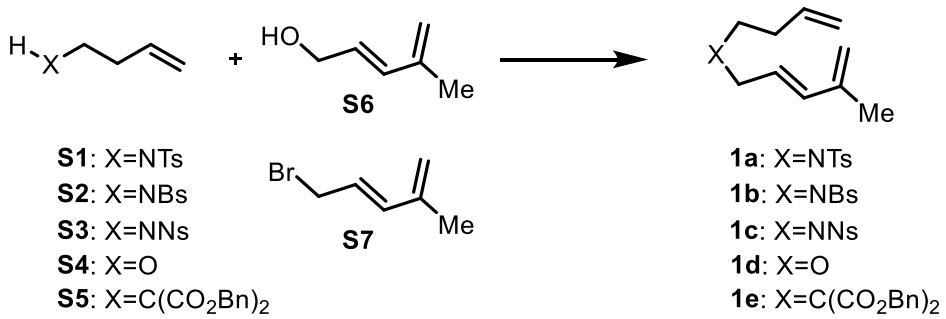
Known compounds as the synthetic intermediates were synthesized according to the reported literatures.: **S1**[1], **S2**[2], **S3**[3], **S5**[4], **S6**[5], **S7**[5], **S8**[6], **S9**[7], **S10**[8], **S11**[9], **S12**[10], **S13**[11], **S14**[6], **S15**[12], **S16**[13], **S17**[14], **S18**[15], **1o**[16], **1r**[17].

NMR spectra were measured on Bruker ARX 400 (^1H at 400 MHz, ^{13}C at 101 MHz), 500 (^1H at 500 MHz, ^{13}C at 126 MHz) and 600 (^1H at 600 MHz, ^{13}C at 151 MHz) nuclear magnetic resonance spectrometers. Data for ^1H-NMR spectra are reported as follows: chemical shift (ppm, referenced to residual solvent peak (CD_2Cl_2: 5.32 ppm, $CDCl_3$: 7.26 ppm); s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CD_2Cl_2: 54.00 ppm, $CDCl_3$: 77.16 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:
Bs = 4-brosyl
DCE = 1,2-dichloroethane
DMF = *N*, *N*-dimethylformamide
EA = ethyl acetate
MsCl = methanesulfonyl chloride
Ns = 4-nitrobenzenesulfonyl
PE = petroleum ether
THF = tetrahydrofuran
Ts = tosyl
DIAD = diisopropyl azodiformate

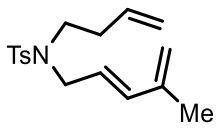
2. Substrates preparations

Preparation of substrates 1a-1e:



To a stirred solution of alcohol **S6** (1.0 g, 10.2 mmol) in THF at -78 °C (25 mL), *n*-BuLi (6.9 mL, 1.6 M in hexanes) was added carefully under inert atmosphere and stirred for 15 min. MsCl (0.85 mL, d = 1.48, 11 mmol, 1.1 eq) was added. After stirred for 15 min, LiBr powder (4.35 g, 50 mmol, 5.0 eq) was added to the above solution at -78 °C and then warmed to room temperature for 30 min. The bromide **S7** (ca. 0.3 M in THF) was synthesized *in situ* before use.

The protected amine **S1** (1.01 g, 4.5 mmol) in DMF (24 mL) was added into NaH (1.44 g, 60% in mineral oil, 36 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (20 mL, 0.3 M, 6.0 mmol, 1.3 eq) was added into above solution. The reaction was then warmed to room temperature and stirred for 16 h. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to yield **1a** (R_f: 0.65 (PE / EA = 5 / 1), 1.21 g, yield = 88 %) as a colorless oil.



1a:

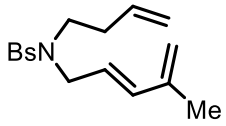
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.17 (d, *J* = 15.7 Hz, 1H), 5.70 (ddt, *J* = 17.1, 10.3, 7.0 Hz, 1H), 5.40 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.96 (s, 1H), 4.91 (s, 1H), 3.86 (d, *J* = 6.7 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.27 (dt, *J* = 7.5, 7.0 Hz, 2H), 1.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.2, 137.4, 136.6, 134.9, 129.7, 127.4, 124.3, 117.3, 117.1, 50.2, 47.0, 33.2, 21.6, 18.5.

HRMS (ESI) calcd for $C_{17}H_{23}NO_2SNa$ $(M+Na)^+$: 328.1342. Found: 328.1341.

The protected amine **S2** (0.58 g, 2.0 mmol) in DMF (12 mL) was added into NaH (0.64 g, 60% in mineral oil, 16 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (10 mL, 2.5 mmol, 1.3 eq) was added into above solution. The reaction was then warmed to room temperature and stirred for 16 h. Then, the

reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1b** (R_f: 0.66 (PE / EA = 5 / 1), 393.2 mg, yield = 53 %) as a colorless oil.



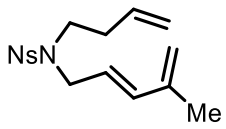
1b:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 6.19 (d, *J* = 15.4 Hz, 1H), 5.69 (ddt, *J* = 17.0, 10.1, 7.0 Hz, 1H), 5.39 (dt, *J* = 15.4, 6.7 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.1 Hz, 1H), 4.99 (s, 1H), 4.94 (s, 1H), 3.88 (d, *J* = 6.7 Hz, 2H), 3.26 (t, *J* = 7.3 Hz, 2H), 2.29 (dt, *J* = 7.3, 7.0 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.5, 137.0, 134.6, 132.4, 128.9, 127.5, 123.7, 117.7, 117.4, 50.2, 47.0, 33.1, 18.6.

HRMS (ESI) calcd for $C_{16}H_{21}BrNO_2S$ $(M+H)^+$: 370.0471. Found: 370.0463.

The protected amine **S3** (399.6 mg, 1.56 mmol) in DMF (10 mL) was added into NaH (0.5 g, 60% in mineral oil, 12.5 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (10 mL, 0.3 M, 3.0 mmol, 1.9 eq) was added into the above solution. The reaction was then stirred for 16 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 30 / 1) to yield **1c** (R_f: 0.38 (PE / EA = 10 / 1), 280 mg, yield = 53 %) as a yellow powder.



1c:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 15.6 Hz, 1H), 5.69 (ddt, *J* = 17.0, 10.4, 7.0 Hz, 1H), 5.39 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 5.01 (s, 1H), 4.95 (s, 1H), 3.94 (d, *J* = 6.8 Hz, 2H), 3.26 (t, *J* = 7.3 Hz, 2H), 2.31 (dt, *J* = 7.3, 7.0 Hz, 2H), 1.73 (s, 3H).

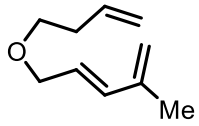
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 146.4, 140.8, 137.5, 134.3, 128.5, 124.4, 123.1, 118.1, 117.7, 50.2, 47.1, 33.1, 18.5.

HRMS (ESI) calcd for $C_{16}H_{21}N_2O_4S$ $(M+H)^+$: 337.1217. Found: 337.1214.

m.p.= 43 – 45 ℃

The alcohol **S4** (0.26 ml, d = 0.84, 3.0 mmol) in DMF (9 mL) was added into NaH (0.18 g, 60% in mineral oil, 4.5 mmol, 1.5 eq) at 0 °C. After 30 min, **S7** in THF (11 mL, 0.3 M, 3.3 mmol, 1.1 eq) was added into above solution. After stirring for 24 h and warmed to room temperature, another 9 mL DMF was added and heated to 50 °C. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl

and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE) to yield **1d** (R_f: 0.59 (PE / EA = 50 / 1), 113.4 mg, yield = 25 %) as a light yellow oil. The product **1d** is not stable for long time.



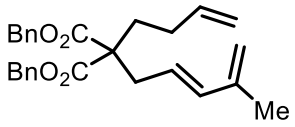
1d:

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, *J* = 15.7 Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.74 (dt, *J* = 15.7, 6.1 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.97 (s, 2H), 4.05 (d, *J* = 6.1 Hz, 2H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.36 (dt, *J* = 6.8, 6.8 Hz, 2H), 1.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 135.42, 135.39, 126.2, 116.8, 116.5, 71.6, 69.8, 34.4, 18.7

HRMS (ESI) calcd for $C_{10}H_{17}O$ $(M+H)^+$: 153.1274. Found: 153.1275.

S5 (1.02 g, 3.0 mmol) in DMF (16 mL) was added into NaH (0.96 g, 60% in mineral oil, 24 mmol 8.0 eq) at 0 °C. After 30 min, **S7** in THF (13 mmol, 13 mL, 1.3 eq) was added into above solution. After stirring for 24 h and warmed to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with sodium carbonate, brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1e** (R_f: 0.75 (PE / EA = 5 / 1), 807.2 mg, yield = 64 %) as a colorless oil.



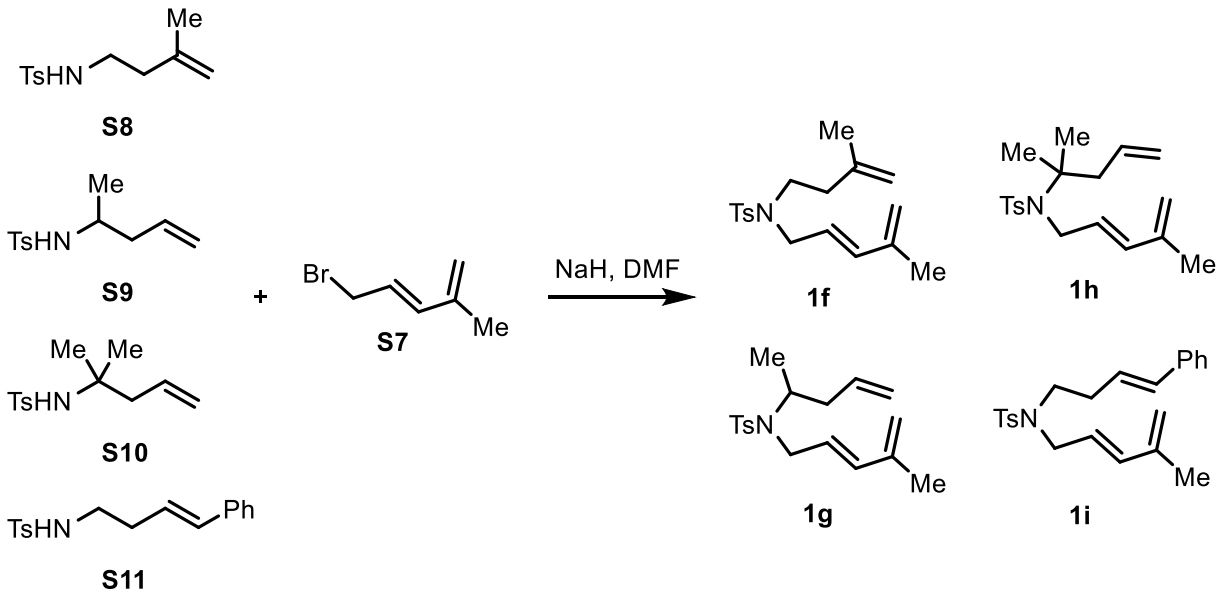
1e:

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37 – 7.26 (m, 10H), 6.14 (d, *J* = 15.4 Hz, 1H), 5.82 – 5.68 (m, 1H), 5.39 (dt, *J* = 15.4, 7.5 Hz, 1H), 5.11 (s, 4H), 4.96 (d, *J* = 15.3 Hz, 1H), 4.92 (d, *J* = 8.9 Hz, 1H), 4.91 (s, 1H), 4.86 (s, 1H), 2.73 (d, *J* = 7.5 Hz, 2H), 2.01 – 1.91 (m, 4H), 1.72 (s, 3H).

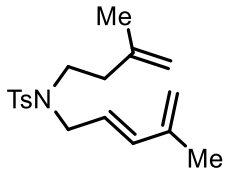
^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.2, 142.3, 138.1, 137.4, 136.2, 129.0, 128.8, 128.7, 124.1, 116.2, 115.4, 67.5, 58.2, 36.5, 32.3, 28.8, 18.8.

HRMS (ESI) calcd for $C_{27}H_{31}O_4$ $(M+H)^+$: 419.2217. Found: 419.2215.

Preparation of substrates 1f-1i:



The protected tosyl amine **S8** (482.0 mg, 2.0 mmol) in DMF (20 mL) was added into NaH (0.64 g, 60% in mineral oil, 16 mmol 8.0 eq) at 0 °C. After 30 min, **S7** in THF (8.3 mL, 0.3 M, 2.5 mmol, 1.25 eq) was added into above solution. The reaction was then stirred for 17 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1 - PE) to yield **1f** (R_f: 0.69 (PE / EA = 5 / 1), 576.6 mg, yield = 90 %) as a colorless oil.



1f

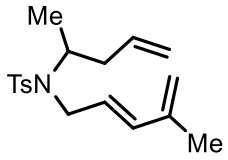
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 15.6 Hz, 1H), 5.40 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.96 (s, 1H), 4.91 (s, 1H), 4.75 (s, 1H), 4.66 (s, 1H), 3.86 (d, *J* = 6.8 Hz, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.41 (s, 3H), 2.22 (t, *J* = 8.1 Hz, 2H), 1.73 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 142.5, 141.1, 137.4, 136.7, 129.7, 127.3, 124.3, 117.2, 112.3, 50.1, 46.1, 36.8, 22.5, 21.6, 18.5.

HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1682.

The protected tosyl amine **S9** (477.6 mg, 2.0 mmol) in DMF (25 mL) was added into NaH (0.64 g, 60% in mineral oil, 16 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (8.3 mL, 0.3 M, 2.5 mmol, 1.25 eq) was added into above solution. The reaction was then stirred for 29 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and

concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1 - 20 / 1) to yield **1g** (R_f: 0.41 (PE / EA = 10 / 1), 343.5 mg, yield = 54 %) as a pale pink powder.



1g

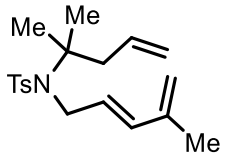
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.21 (d, *J* = 15.7 Hz, 1H), 5.70 – 5.53 (m, 2H), 5.02 – 4.97 (m, 2H), 4.96 (s, 1H), 4.93 (s, 1H), 4.08 – 3.98 (m, 1H), 3.89 (dd, *J* = 16.8, 6.6 Hz, 1H). 3.82 (dd, *J* = 16.8, 6.6 Hz, 1H), 2.41 (s, 3H), 2.30 – 2.19 (m, 1H), 2.16 – 2.06 (m, 1H), 1.77 (s, 3H), 1.04 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 141.4, 138.7, 135.2, 135.1, 129.6, 127.6, 127.3, 117.4, 116.8, 54.0, 45.5, 40.3, 21.6, 18.9, 18.7.

HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1677.

m.p.= 48 – 50 ℃.

The protected tosyl amine **S10** (303.6 mg, 1.2 mmol) in DMF (25 mL) was added into NaH (0.38 g, 60% in mineral oil, 9.6 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (5 mL, 0.3 M, 1.5 mmol, 1.25 eq) was added into above solution. The reaction was then stirred for 29 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to yield **1h** (R_f: 0.47 (PE / EA = 10 / 1), 284.3 mg, yield = 71 %) as a light yellow oil.



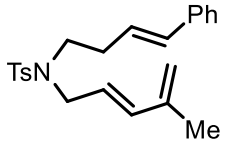
1h

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 6.21 (d, *J* = 15.7 Hz, 1H), 5.80 – 5.66 (m, 2H), 5.05 (d, *J* = 11.8 Hz, 1H), 5.04 (d, *J* = 15.7 Hz, 1H), 4.97 (s, 1H), 4.94 (s, 1H), 4.07 (d, *J* = 6.3 Hz, 2H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.84 (s, 3H), 1.31 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.5, 141.0, 134.7, 134.3, 129.5, 128.9, 127.2, 118.4, 116.6, 62.3, 48.5, 46.5, 27.8, 21.6, 18.8.

HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1827.

The protected tosyl amine **S11** (602.2 mg, 2.0 mmol) in DMF (25 mL) was added into NaH (0.64 g, 60% in mineral oil, 16 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (8.3 mL, 0.3 M, 2.5 mmol, 1.25 eq) was added into above solution. The reaction was then stirred for 29 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 50 / 1 - 20 / 1) to yield **1i** (R_f: 0.33 (PE / EA = 10 / 1), 406.8 mg, yield = 53 %) as a colorless oil.



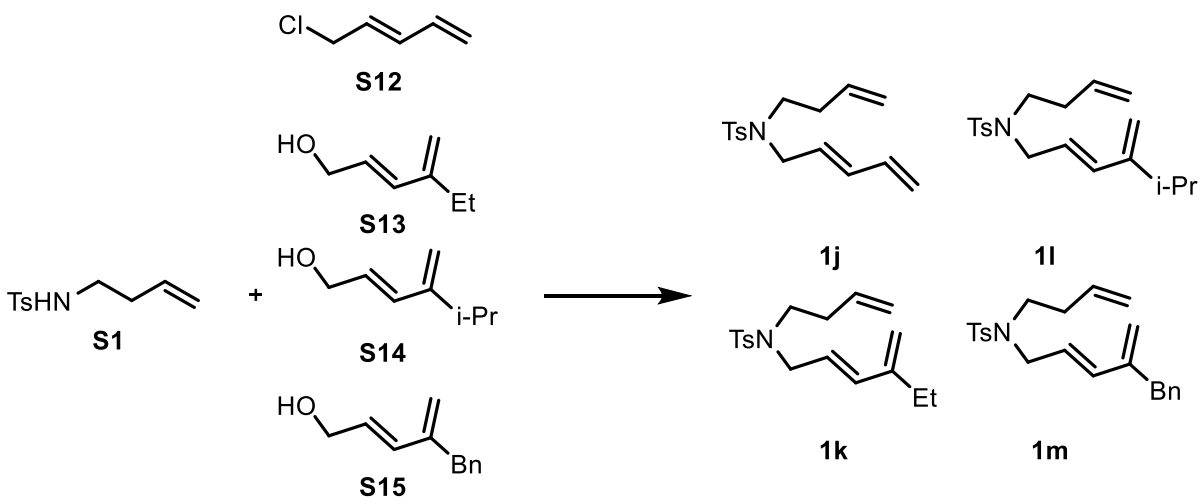
1i

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.18 (m, 7H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.23 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.43 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.98 (s, 1H), 4.94 (s, 1H), 3.88 (d, *J* = 6.7 Hz, 2H), 3.26 (d, *J* = 6.7 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.41 (s, 3H), 1.73 (s, 3H).

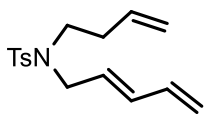
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.2, 137.38, 137.37, 136.7, 132.38, 132.36, 129.8, 128.6, 127.4, 126.6, 126.2, 124.4, 117.3, 50.3, 47.2, 32.6, 21.6, 18.6.

HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1827.

Preparation of substrates 1j-1m:



The protected amine **S1** (450.8 mg, 2.0 mmol) in DMF (25 mL) was added into NaH (0.64 g, 60% in mineral oil, 16 mmol, 8.0 eq) at 0 °C. After 30 min, **S12** (460.0 mg, 4.5 mmol) was added into the tosyl amide solution. The reaction was then stirred for 2 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1k** (R_f: 0.82 (PE / EA = 5 / 1), 362.4 mg, yield = 62 %) as a light yellow oil.



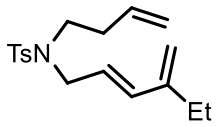
1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.24 (dt, *J* = 16.7, 10.3 Hz, 1H), 6.10 (dd, *J* = 15.2, 10.3 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.53 – 5.43 (m, 1H), 5.16 (d, *J* = 16.7 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 5.06 – 5.02 (m, 1H), 5.01 – 4.99 (m, 1H), 3.84 (d, *J* = 6.7 Hz,

2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.31 – 2.23 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.3, 135.9, 134.8, 134.6, 129.8, 128.3, 127.3, 118.1, 117.1, 49.8, 46.9, 33.1, 21.6.
HRMS (ESI) calcd for $C_{16}H_{22}NO_2S$ $(M+H)^+$: 292.1366. Found: 292.1371.

To a stirred solution of alcohol **S13** (335.7 mg, 3.0 mmol) in THF at -78 °C (15 mL), *n*-BuLi (2.3 mL, 1.6 M in hexanes) was added carefully under inert atmosphere and stirred for 15 min. MsCl (0.4 mL, d = 1.48, 5.1 mmol, 1.7 eq) was added. After stirred for 15 min, LiBr powder (1.3 g, 15 mmol, 5.0 eq) was added to the above solution at -78 °C and then warmed to room temperature for 30 min and used as a THF solution.

The protected amine **S1** (675 mg, 3.0 mmol) in DMF (15 mL) was added into NaH (0.96 g, 60% in mineral oil, 24 mmol, 8.0 eq) at 0 °C. After 30 min, The bromide which was synthesized before was added into the tosyl amide solution. The reaction was then stirred for 18 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1k** (R_f: 0.63 (PE / EA = 5 / 1), 576.7 mg, yield = 60 %) as a light pink oil.

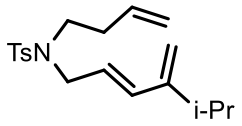


1k
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.12 (d, *J* = 15.8 Hz, 1H), 5.70 (ddt, *J* = 17.1, 10.0, 7.0 Hz, 1H), 5.43 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.96 (s, 1H), 4.92 (s, 1H), 3.86 (d, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.28 (dt, *J* =7.4, 7.0 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.3, 137.4, 136.2, 134.9, 129.8, 127.3, 123.3, 117.1, 115.2, 50.3, 46.9, 33.2, 24.8, 21.6, 12.6.
HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1671

To a stirred solution of alcohol **S14** (379.3 mg, 3.0 mmol) in THF at -78 °C (8 mL), *n*-BuLi (2.1 mL, 1.6 M in hexanes) was added carefully under inert atmosphere and stirred for 15 min. MsCl (0.26 mL, d = 1.48, 3.3 mmol, 1.1 eq) was added. After stirred for 15 min, LiBr powder (1.3 g, 15 mmol, 5.0 eq) was added to the above solution at -78 °C and then warmed to room temperature for 30 min and used as a THF solution.

The protected amine **S1** (540 mg, 2.4 mmol) in DMF (25 mL) was added into NaH (768 mg, 60% in mineral oil, 19.2 mmol, 8.0 eq) at 0 °C. After 30 min, The bromide which was synthesized before was added into the tosyl amide solution. The reaction was then stirred for 24 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 /

1 - PE) to yield **1l** (R_f: 0.63 (PE / EA = 5 / 1), 679.4 mg, yield = 85 %) as a light yellow oil.



1l

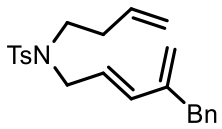
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.06 (d, *J* = 15.9 Hz, 1H), 5.70 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.45 (dt, *J* = 15.9, 6.8 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.93 (s, 1H), 4.91 (s, 1H), 3.86 (d, *J* = 6.8 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.41 – 2.34 (m, 1H), 2.28 (dt, *J* = 7.5, 6.8 Hz, 2H), 1.00 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 143.3, 137.4, 136.0, 134.9, 129.8, 127.3, 123.0, 117.1, 113.0, 50.4, 46.8, 33.1, 29.4, 22.2, 21.6.

HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1829.

To a stirred solution of alcohol **S15** (523.5 mg, 3.0 mmol) in THF at -78 °C (8 mL), *n*-BuLi (2.1 mL, 1.6 M in hexanes) was added carefully under inert atmosphere and stirred for 15 min. MsCl (0.26 mL, d = 1.48, 3.3 mmol, 1.1 eq) was added. After stirred for 15 min, LiBr powder (1.3 g, 15 mmol, 5.0 eq) was added to the above solution at -78 °C and then warmed to room temperature for 30 min and used as a THF solution.

The protected amine **S1** (540 mg, 2.4 mmol) in DMF (25 mL) was added into NaH (768 mg, 60% in mineral oil, 19.2 mmol, 8.0 eq) at 0 °C. After 30 min, The bromide which was synthesized before was added into the tosyl amide solution. The reaction was then stirred for 24 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = PE - 20 / 1) to yield **1m** (R_f: 0.56 (PE / EA = 5 / 1), 772.3 mg, yield = 84 %) as a light yellow oil.



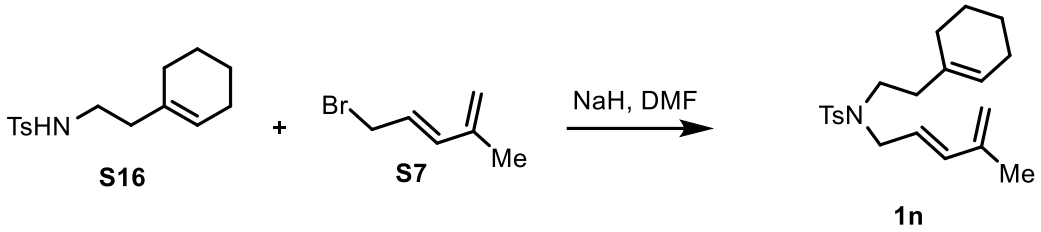
1m

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 6.17 (d, *J* = 15.8 Hz, 1H), 5.70 (ddt, *J* = 17.7, 9.6, 6.8 Hz, 1H), 5.40 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.12 (s, 1H), 5.02 – 5.00 (m, 1H), 4.99 – 4.96 (m, 1H), 4.94 (s, 1H), 3.81 (d, *J* = 6.8, 2H), 3.43 (s, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 2.13 (dt, *J* = 7.5, 6.8 Hz, 2H).

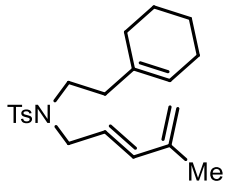
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.2, 139.2, 137.3, 135.4, 134.9, 129.8, 128.7, 128.4, 127.3, 126.3, 125.0, 118.7, 117.0, 50.2, 46.6, 38.9, 32.9, 21.6.

HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1826.

Preparation of substrates 1n:



The protected tosyl amine **S16** (835.7 mg, 3.0 mmol) in DMF (15 mL) was added into NaH (0.96 g, 60% in mineral oil, 24 mmol, 8.0 eq) at 0 °C. After 30 min, **S7** in THF (13.3 mL, 0.3 M, 4 mmol, 1.3 eq) was added into above solution. The reaction was then stirred for 16 h and warmed to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 30 / 1) to yield **1n** (R_f: 0.54 (PE / EA = 10 / 1), 531.4 mg, yield = 49 %) as a colorless oil.



1n

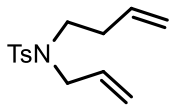
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.17 (d, *J* = 15.7 Hz, 1H), 5.40 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.40 – 5.36 (m, 1H)，4.96 (s, 1H), 4.91 (s, 1H), 3.86 (d, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.13 (t, *J* = 7.9 Hz, 2H), 1.98 – 1.92 (m, 2H), 1.89 – 1.83 (m, 2H), 1.73 (s, 3H), 1.63 – 1.47 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.2, 137.6, 136.6, 134.5, 129.7, 127.3, 124.4, 123.6, 117.2, 49.9, 46.2, 37.0, 28.3, 25.4, 23.0, 22.4, 21.6, 18.6.

HRMS (ESI) calcd for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992. Found: 360.1988.

Preparation of substrates 1o:

1o was prepared according to reported literature[16].

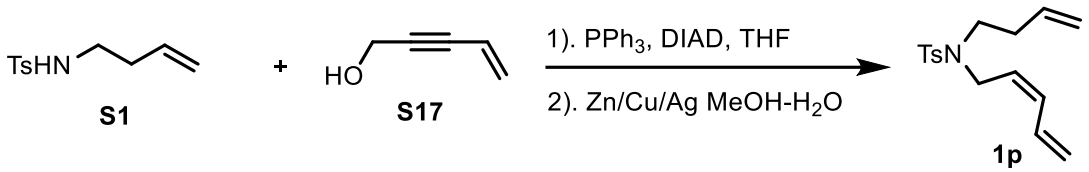


1o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.76 – 5.58 (m, 2H), 5.17 (d, *J* = 18.3 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 3.81 (d, *J* = 6.3 Hz, 2H), 3.19 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.27 (dt, *J* = 7.7, 7.1 Hz, 2H).

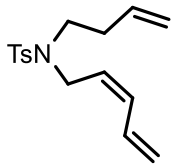
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 137.2, 134.8, 133.2, 129.7, 127.2, 118.8, 117.0, 50.7, 46.7, 32.9, 21.5.

Preparation of substrates 1p:



The protected amine **S1** (675 mg, 3.0 mmol) in THF (30 mL) was added into the mixture of **S17** (369 mg, 4.5 mmol) and PPh_3 (1.57 g, 6.0 mmol) at room temperature. Then DIAD (1.2 ml, 6.0 mmol) was added to the reaction mixture dropwise. The reaction was then stirred for 16 h and the solvent was removed under vacuum. The residue was purified by silica gel as a light yellow oil.

In a 100 mL round-bottomed flask, to the mixture of Zn powder (newly, activated by 3M hydrochloric acid, 3.9 g, 60 mmol), and 50 mL water, $Cu(OAc)_2 \cdot H_2O$ (0.60g, 3 mmol) was added and then the mixture was stirred for 15 min. After that, $AgNO_3$ (0.51g, 3 mmol) was added and stirred for another 10 min. The solvent was then removed and changed to the mixture of methanol and deionized water (60 mL, 1:1), then, the yellow oil in last step was added. The mixture was heated at 50 °C for 12 h. After filtered by a pad of Celite and extracted by EA, the organic layer was washed by water, brine and dried by Na_2SO_4. After filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1p** (R_f: 0.37 (PE / EA = 10 / 1), 399.0 mg, yield = 46 % for 2 steps) as a pale pink oil.



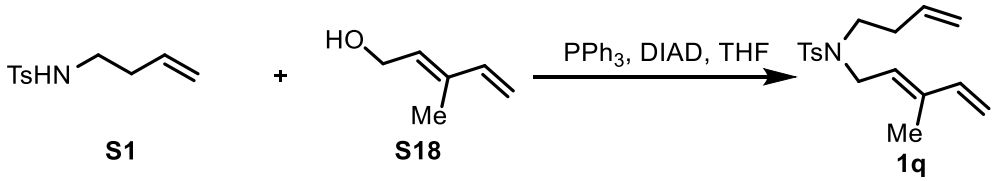
1p

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.60 – 6.49 (m, 1H), 6.09 (dd, *J* = 11.1, 11.1 Hz, 1H), 5.77 – 5.64 (m, 1H), 5.29 – 5.18 (m, 3H), 5.07 – 5.04 (m, 1H), 5.04 – 4.99 (m, 1H), 3.99 (d, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.28 (dt, *J* = 7.6, 7.1 Hz, 2H).

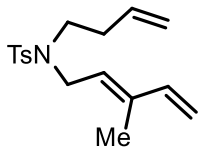
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.2, 134.8, 132.9, 130.8, 129.8, 127.3, 125.9, 120.2, 117.2, 46. 9, 44.8, 33.1, 21.6.

HRMS (ESI) calcd for $C_{16}H_{21}NO_2S$ $(M+H)^+$: 292.1366. Found: 292.1366.

Preparation of substrates 1q:



The protected amine **S1** (225 mg, 1.0 mmol) in THF (10 mL) was added into the mixture of **S18** (106.6 mg, 1.1 mmol) and PPh_3 (524 mg, 2.0 mmol) at room temperature. Then DIAD (0.40 ml, 2.0 mmol) was added to the reaction mixture dropwise. The reaction was then stirred for 40 h and the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to yield **1p** (R_f: 0.64 (PE / EA = 5 / 1), 147.4 mg, yield = 48 %) as a pale pink oil.



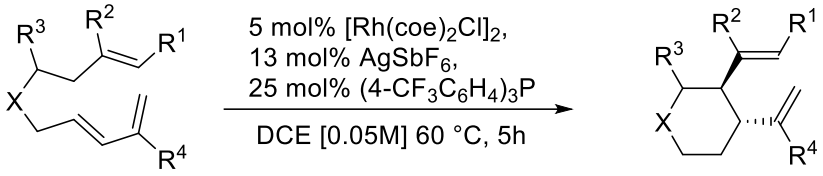
1q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.24 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.70 (ddt, *J* = 17.4, 10.3, 6.9 Hz, 1H), 5.28 (t, *J* = 6.9 Hz, 1H), 5.16 (d, *J* = 17.4 Hz, 1H), 5.05 – 4.99 (m, 3H), 3.95 (d, *J* = 6.9 Hz, 2H), 3.16 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.27 (dt, *J* = 7.5, 6.9 Hz, 1H), 1.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.4, 137.3, 137.2, 134.9, 129.7, 127.3, 126.5, 117.1, 113.2, 47.1, 45.7, 33.2, 21.6, 11.8.

HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1519.

3. General procedure for cycloisomerization reaction

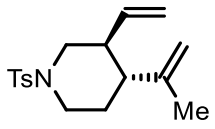


Synthesis of the catalyst ([Rh(coe)$_2$Cl]$_2$/AgSbF$_6$/(4-CF$_3$C$_6$H$_4$)$_3$P): In the glovebox, [Rh(coe)$_2$Cl]$_2$ (3.6 mg, 0.005 mmol, 10 mol % of Rh), $AgSbF_6$ (4.5 mg, 0.013 mmol) , (4-$CF_3C_6H_4$)$_3$P (11.7 mg, 0.025 mmol) were added to a 25 mL reaction tube. The mixture was stirred for 20 min at room temperature after adding 1 mL super-dried DCE as solvent. The reddish catalyst was used as a solution (For substrates **1a**-**1c**, **1f**-**1m**).

Synthesis of the catalyst (Rh(PPh$_3$)$_3$Cl/AgSbF$_6$): In the glovebox, Rh(PPh$_3$)$_3$Cl (9.3 mg, 0.01 mmol, 10 mol % of Rh), $AgSbF_6$ (4.5 mg, 0.013 mmol), were added to a 25 mL reaction tube. The mixture was stirred for 20 min at room temperature after adding 1 mL super-dried DCE as solvent. The reddish catalyst was used as a solution (For substrates **1l**-**1n**).

Rh(I) catalyzed cycloisomerization reaction: A solution of substrate **1** (0.1 mmol) in super-dried DCE (1 ml) was added to the above prepared catalyst (10 mol % Rh, 1 mL DCE) in the reaction tube. After stirred at room temperature for another 20 min, the mixture was heated by the oil bath (60 ºC). After 5 h, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was purified by flash column chromatography on silica gel to afford the cycloisomerization **2**. The yield data reported for cycloisomerization reaction is the average of two runs.

4. Products of cycloisomerization reaction

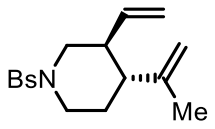


2a

Reaction time: 5 h, Eluted with PE / EA = 20 / 1
Catalyst: ($[Rh(coe)_2Cl]_2$/$AgSbF_6$/$(4\text{-}CF_3C_6H_4)_3P$)
Run 1: 30.4 mg **1a** was converted to 24.2 mg **2a**, yield 80 %. Run 2: 30.3 mg **1a** was converted to 24.1 mg **2a**, yield 80 %.
The average yield of two runs was 80 %.

1.0 mmol scale reaction:
A solution of substrate **1a** (305.4 mg 1.0 mmol) in super-dried DCE (10 ml) was added to the above prepared catalyst ($[Rh(coe)_2Cl]_2$ 36.2 mg, $AgSbF_6$ 45.4 mg, $(4\text{-}CF_3C_6H_4)_3P$, 116.7 mg, 10 mol% Rh, 10 mL DCE) in a round-bottomed flask. After stirred at room temperature for another 20 min, the mixture was heated by the oil bath (60 ºC). After 5 h, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was purified by flash column chromatography on silica gel to afford the cycloisomerization **2a** (233.0 mg Yield = 76%).

2a: colorless oil, TLC R_f : 0.43 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.44 (ddd, J = 17.5, 10.5, 8.1 Hz, 1H), 5.05 (d, J = 17.5 Hz, 1H), 5.02 (d, J = 10.5 Hz, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 3.87 – 3.75 (m, 2H), 2.43 (s, 3H), 2.39 – 2.27 (m, 1H), 2.27 – 2.16 (m, 1H), 1.99 (dd, J = 11.3, 11.3 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.67 – 1.61 (m, 1H), 1.59 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 143.6, 137.8, 133.2, 129.7, 127.8, 116.7, 112.3, 51.0, 49.2, 46.5, 43.0, 30.5, 21.6, 19.1.
HRMS (ESI) $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1520.



2b

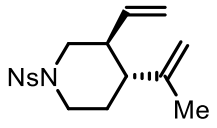
Reaction time: 5 h, Eluted with PE / EA = 20 / 1
Catalyst: ($[Rh(coe)_2Cl]_2$/$AgSbF_6$/$(4\text{-}CF_3C_6H_4)_3P$)
Run 1: 37.0 mg **1b** was converted to 24.2 mg **2b**, yield 65 %. Run 2: 37.0 mg **1b** was converted to 23.8 mg **2b**, yield 64 %.
The average yield of two runs was 65 %.

2b: yellow oil, TLC R_f : 0.53 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 5.44 (ddd, J = 17.2, 9.8, 7.2 Hz, 1H), 5.07 (d, J = 17.2 Hz, 1H), 5.04 (d, J = 9.8 Hz, 1H), 4.74 (s, 1H), 4.67 (s, 1H), 3.96 – 3.74

(m, 2H), 2.40 – 2.29 (m, 1H), 2.29 – 2.18 (m, 1H), 2.01 (dd, J = 11.3, 11.3 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.72 – 1.64 (m, 1H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 137.6, 135.4, 132.5, 129.3, 127.9, 117.0, 112.5, 51.0, 49.2, 46.5, 43.1, 30.5, 19.2.

HRMS (ESI) $C_{16}H_{21}BrNO_2S$ $(M+H)^+$: 370.0471. Found: 370.0465.



2c

Reaction time: 5 h, Eluted with PE / EA = 30 / 1

Catalyst: ($[Rh(coe)_2Cl]_2$/$AgSbF_6$/$(4\text{-}CF_3C_6H_4)_3P$)

Run 1: 33.6 mg **1c** was converted to 25.1 mg **2c**, yield 75 %. Run 2: 33.7 mg **1c** was converted to 23.6 mg **2c**, yield 70 %.

The average yield of two runs was 73 %.

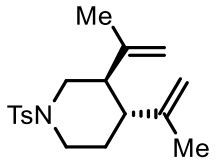
2c: yellow powder, TLC R_f : 0.53 (PE / EA = 10 / 1), m.p.= 81 – 83 ℃

Catalyst: ($[Rh(coe)_2Cl]_2$/$AgSbF_6$/$(4\text{-}CF_3C_6H_4)_3P$)

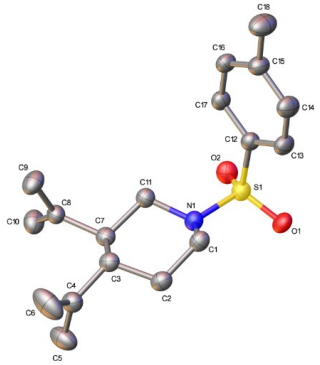
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 5.44 (ddd, J = 17.2, 10.2, 8.1 Hz, 1H), 5.09 (d, J = 17.2 Hz, 1H), 5.04 (d, J = 10.2 Hz, 1H), 4.75 (s, 1H), 4.67 (s, 1H), 3.95 – 3.80 (m, 2H), 2.41 – 2.26 (m, 2H), 2.07 (dd, J = 11.3 Hz, 11.3 Hz, 1H), 1.83 – 1.64 (m, 3H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 146.0, 142.5, 137.3, 128.9, 124.5, 117.2, 112.7, 50.9, 49.1, 46.5, 43.1, 30.5, 19.2.

HRMS (ESI) $C_{16}H_{21}N_2O_4S$ $(M+H)^+$: 337.1217. Found: 337.1211.



2f



CCDC: 1909585

Reaction time: 5 h, Eluted with PE / EA = 40 / 1 – 20 / 1

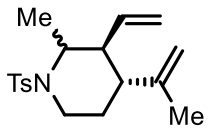
Catalyst: ($[Rh(coe)_2Cl]_2$/$AgSbF_6$/$(4\text{-}CF_3C_6H_4)_3P$)

Run 1: 31.9 mg **1f** was converted to 23.1 mg **2f**, yield 72 %. Run 2: 31.7 mg **1f** was converted to 22.0 mg **2f**, yield 69 %.

The average yield of two runs was 71 %.

2f: white powder, TLC R_f : 0.44 (PE / EA = 10 / 1), m.p.= 88 – 91 ℃

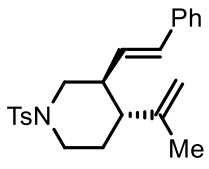
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.80 (s, 1H), 4.71 (s, 2H), 4.63 (s, 1H), 3.88 – 3.82 (m, 1H), 3.78– 3.72 (m, 1H), 2.43 (s, 3H), 2.37 (ddd, *J* = 11.3, 11,3, 4.0 Hz, 1H), 2.24 (ddd, *J* = 11.3, 11.3, 4.0 Hz, 1H), 2.09 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.97 (ddd, *J* = 11.3, 11.3, 5.0 Hz, 1H), 1.77 – 1.65 (m, 2H), 1.61 (s, 3H), 1.60 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 144.4, 143.6, 133.4, 129.8, 127.8, 113.5, 112.1, 50.9, 47.3, 46.9, 46.6, 30.9, 21.6, 20.3, 19.0.
HRMS (ESI) $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1682.



2g

Reaction time: 5 h, Eluted with PE / EA = 20 / 1
Catalyst: $([Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P)$
Run 1: 31.8 mg **1g** was converted to 12.2 mg **2g**, yield 38 %. Run 2: 31.7 mg **1g** was converted to 12.2 mg **2g**, yield 38 %.
The average yield of two runs was 38 %. (2:1 of d.r. mixture).

2g: colorless oil, TLC R_f : 0.34 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 4H, major) 7.72 (d, *J* = 8.2 Hz, 2H, minor), 7.30 (d, *J* = 8.2 Hz, 6H), 5.38 – 5.25 (m, 3H), 5.02 – 4.94 (m, 6H), 4.62 (s, 3H), 4.46 (s, 3H), 3.54 – 3.26 (m, 6H), 2.42 (s, 6H), 2.41 (s, 3H), 2.05 – 1.90 (m, 3H), 1.75 – 1.61 (m, 9H), 1.53 (s, 9H), 1.30 – 1.24 (m, 3H). 1.22 (d, *J* = 6.5 Hz, 6H), 1.06 – 0.87 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.2, 143.0, 139.2, 138.9, 138.3, 129.7, 129.6, 129.5, 128.0, 127.3, 127.2, 124.9, 116.9, 115.2, 112.3, 56.2, 54.1, 49.5, 47.4, 46.1, 41.8, 40.6, 35.0, 28.0, 25.5, 21.6, 20.4, 20.0, 18.7, 18.6, 16.4.
HRMS (ESI) $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1682.



2i

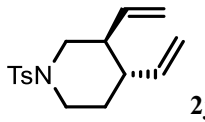
Reaction time: 5 h, Eluted with PE / EA = 20 / 1
Catalyst: $([Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P)$
Run 1: 38.1 mg **1i** was converted to 14.0 mg **2i** yield 37 %. Run 2: 38.0 mg **1i** was converted to 15.1 mg **2i**, yield 40 %.
The average yield of two runs was 39 %.

2i: yellow oil, TLC R_f : 0.49 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.17 (m, 5H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.84 (dd, *J* = 16.0, 8.4 Hz, 1H), 4.76 – 4.69 (m, 2H), 3.88 – 3.77 (m, 2H), 2.55

– 2.44 (m, 1H), 2.44 (s, 3H), 2.24 (ddd, *J* = 11.6, 11.6, 3.3 Hz, 1H), 2.07 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.86 (ddd, *J* = 11.1, 11.1, 4.1 Hz, 1H), 1.80 – 1.64 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.3, 144.3, 137.7, 133.7, 132.1, 130.22, 130.17, 129.1, 128.2, 127.9, 126.6, 112.5, 51.8, 49.9, 47.0, 43.1, 31.0, 21.8, 19.5.

HRMS (ESI) $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1836.



2j

Reaction time: 5 h, Eluted with PE / EA = 20 / 1

Catalyst: $([Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P)$

Run 1: 29.1 mg **1j** was converted to 19.8 mg **2j** yield 68 %. Run 2: 29.1 mg **1h** was converted to 18.2 mg **2j**, yield 63 %.

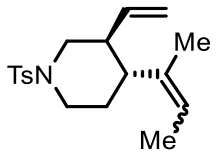
The average yield of two runs was 66 %.

2j: yellow oil, TLC R_f: 0.54 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.60 (ddd, *J* = 17.4, 10.4, 7.3 Hz, 1H), 5.48 (ddd, *J* = 17.8, 11.0, 7.3 Hz, 1H), 5.08 (d, *J* = 17.4 Hz, 1H), 5.05 (d, *J* = 10.4 Hz, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 17.8 Hz, 1H), 3.84 – 3.71 (m, 2H), 2.42 (s, 3H), 2.28 – 2.10 (m, 2H), 2.01 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.79 – 1.66 (m, 2H), 1.63 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 140.5, 138.1, 133.2, 129.8, 127.9, 117.3, 115.3, 50.7, 46.1, 45.1, 44.6, 30.9, 21.7.

HRMS (ESI) $C_{16}H_{22}NO_2S$ $(M+H)^+$: 292.1366. Found: 292.1363.



2k-iso

Reaction time: 5 h, Eluted with PE / EA = 30 / 1.

Catalyst: $([Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P)$

Run 1: 31.9 mg **1k** was converted to 23.0 mg **2k-iso** yield 72 %. Run 2: 31.8 mg **1k** was converted to 24.5 mg **2k-iso**, yield 78 %.

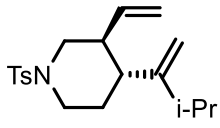
The average yield of two runs was 75 % (2:1 of Z/E mixture).

2k-iso: colorless oil, TLC R_f: 0.60 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 6H), 7.32 (d, *J* = 8.1 Hz, 6H), 5.48 – 5.35 (m, 3H), 5.28 – 5.20 (m, 1H), 5.20 – 5.13 (m, 2H), 5.05 – 4.95 (m, 6H), 3.89 – 3.76 (m, 6H), 2.43 (s, 9H), 2.40 – 2.27 (m, 3H), 2.25 – 2.13 (m, 3H), 1.99 (dd, 11.2, 11.2 Hz, 3H), 1.77 – 1.59 (m, 6H), 1.59 – 1.48 (m, 3H), 1.48 – 1.41 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.61, 143.56, 138.2, 137.8, 136.59, 136.47, 133.28, 133.27, 129.77, 129.73, 127.85, 127.84, 121.0, 120.8, 116.5, 116.3, 51.12, 51.09, 50.97, 46.62, 46.60, 42.7, 42.3, 41.4, 30.4, 28.9, 21.6, 19.0, 13.2, 12.9, 12.4.

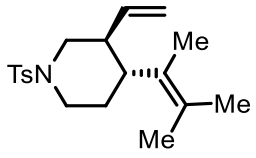
HRMS (ESI) $C_{19}H_{28}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1674.



2l

Reaction time: 5 h, Eluted with PE / EA = 20 / 1.
Catalyst: ($[Rh(PPh_3)_3Cl/AgSbF_6$)
Run 1: 33.3 mg **1l** was converted to 24.3 mg **2l** yield 73 %. Run 2: 33.2 mg **1l** was converted to 24.5 mg **2l**, yield 74 %.
The average yield of two runs was 74 %.

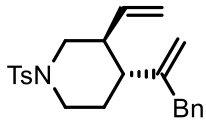
2l: yellow oil, TLC R_f : 0.46 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.43 (ddd, J = 17.8, 10.1, 7.9 Hz, 1H), 5.00 (d, J = 17.8 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.85 (s, 1H), 4.70 (s, 1H), 3.89 – 3.76 (m, 2H), 2.43 (s, 3H), 2.42 – 2.33 (m, 1H), 2.23 – 2.14 (m, 1H), 2.09 – 1.96 (m, 2H), 1.78 – 1.68 (m, 1H), 1.66 – 1.57 (m, 2H), 0.95 (d, J = 6.8, 3H), 0.93 (d, J = 6.8, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 143.6, 138.0, 133.3, 129.8, 127.9, 116.8, 108.0, 51.2, 46.9, 46.8, 44.8, 34.0, 32.9, 22.3, 22.1, 21.7.
HRMS (ESI) $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1830.



2l-iso

Reaction time: 5 h, Eluted with PE / EA = 20 / 1.
Catalyst: ($[Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P$)
Run 1: 33.3 mg **1l** was converted to 17.7 mg **2l-iso** yield 53 %. Run 2: 33.3 mg **1l** was converted to 19.4 mg **2l-iso**, yield 58 %.
The average yield of two runs was 56 %.

2l-iso: yellow oil, TLC R_f : 0.46 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.40 (ddd, J = 17.6, 10.5, 7.6 Hz, 1H), 5.00 (d, J = 17.6 Hz, 1H), 4.95 (d, J = 10.5 Hz, 1H), 3.87 – 3.77 (m, 2H), 2.44 (s, 3H), 2.42 – 2.33 (m, 1H), 2.29 – 2.17 (m, 2H), 2.00 (dd, J = 11.2, 11.2 Hz, 1H), 1.72 (ddd, J = 13.1, 12.5, 4.4 Hz, 1H), 1.60 (s, 3H), 1.56 (s, 3H), 1.47 (s, 3H), 1.45 – 1.40 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 144.5, 143.6, 133.4, 129.8, 127.8, 113.5, 112.1, 50.9, 47.3, 46.9, 46.7, 30.9, 29.8, 21.7, 20.3, 19.0.
HRMS (ESI) $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1832.



2m

Reaction time: 5 h, Eluted with PE / EA = 30 / 1.

Catalyst: ($[Rh(PPh_3)_3Cl/AgSbF_6$)

Run 1: 38.1 mg **1m** was converted to 29.5 mg **2m** yield 77 %. Run 2: 38.1 mg **1m** was converted to 28.0 mg **2m**, yield 73 %.

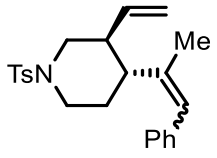
The average yield of two runs was 75 %.

2m: yellow oil, TLC R_f : 0.27 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 7.12 – 7.08 (m, 2H), 5.46 – 5.36 (m, 1H), 5.06 (d, *J* = 17.3 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H), 4.83 (s, 1H), 4.65 (s, 1H), 3.80 – 3.70 (m, 2H), 3.30 – 3.18 (m, 2H), 2.42 (s, 3H), 2.41 – 2.36 (m, 1H), 2.11 (ddd, *J* = 11.3, 11.3, 3.8 Hz, 1H), 1.96 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.72 – 1.63 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.9, 144.3, 139.8, 138.4, 133.6, 130.2, 129.9, 128.7, 128.2, 126.6, 117.1, 113.2, 51.6, 47.7, 47.2, 44.7, 42.0, 32.1, 21.8.

HRMS (ESI) $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1834.



2m-iso

Reaction time: 5 h, Eluted with PE / EA = 20 / 1.

Catalyst: ($[Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P$)

Run 1: 38.0 mg **1m** was converted to 29.9 mg **2m-iso** yield 79 %. Run 2: 38.0 mg **1m** was converted to 32.0 mg **2m-iso**, yield 84 %.

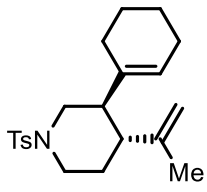
The average yield of two runs was 82 % (3:1 of Z/E mixture).

2m-iso: yellow oil, TLC R_f : 0.30 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 8.3 Hz, 6H, major), 7.59 (d, *J* = 8.3 Hz, 2H, minor), 7.40 – 7.33 (m, 6H), 7.35 – 7.22 (m, 12H), 7.18 (d, *J* = 8.3 Hz, 8H), 7.08 – 7.03 (m, 2H), 6.34 (s, 1H), 6.25 (s, 3H), 5.59 – 5.48 (m, 3H), 5.42 – 5.28 (m, 1H), 5.17 – 5.00 (m, 8H), 3.92 – 3.66 (m, 8H), 2.47 – 2.40 (m, 20H), 2.30 – 2.23 (m, 4H), 2.06 (dd, *J* = 11.3, 11.3 Hz, 4H), 1.91 – 1.81 (m, 8H), 1.76 (d, *J* = 1.3 Hz, 3H), 1.72 (d, *J* = 1.3 Hz, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.3, 140.2, 138.7, 138.6, 138.5, 138.2, 133.74, 133.65, 130.2, 129.4, 129.2, 129.1, 128.73, 128.68, 128.5, 128.23, 128.16, 128.0, 127.4, 127.3, 126.64, 126.60, 116.84, 116.82, 52.0, 51.5, 51.3, 47.0, 46.6, 43.6, 43.1, 42.6, 30.7, 30.1, 21.82, 21.79, 19.4, 14.9.

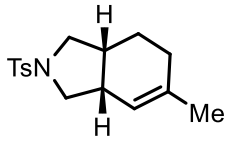
HRMS (ESI) $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1831.



2n

Reaction time: 5 h, Eluted with PE / EA = 30 / 1.
Catalyst: ($[Rh(PPh_3)_3Cl/AgSbF_6$)
Run 1: 35.9 mg **1n** was converted to 28.3 mg **2n** yield 79 %. Run 2: 35.9 mg **1n** was converted to 29.5 mg **2n**, yield 82 %.
The average yield of two runs was 81 %.

2n: white powder, TLC R_f: 0.43 (PE / EA = 10 / 1), m.p.= 102 – 104 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 4.68 (s, 1H), 4.60 (s, 1H), 3.82 (d, *J* = 11.1 Hz, 1H), 3.70 (d, *J* = 10.0 Hz, 1H), 2.44 (s, 3H), 2.25 – 2.17 (m, 2H), 2.08 (dd, *J* = 11.1, 11.1 Hz, 1H), 2.00 – 1.86 (m, 4H), 1.76 – 1.62 (m, 3H), 1.58 (s, 3H), 1.55 – 1.45 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 143.5, 136.5, 133.5, 129.7, 127.8, 124.7, 111.8, 51.1, 47.3, 47.0, 46.7, 31.0, 26.2, 25.3, 23.0, 22.6, 21.7, 19.1.
HRMS (ESI) $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992. Found: 360.1986.

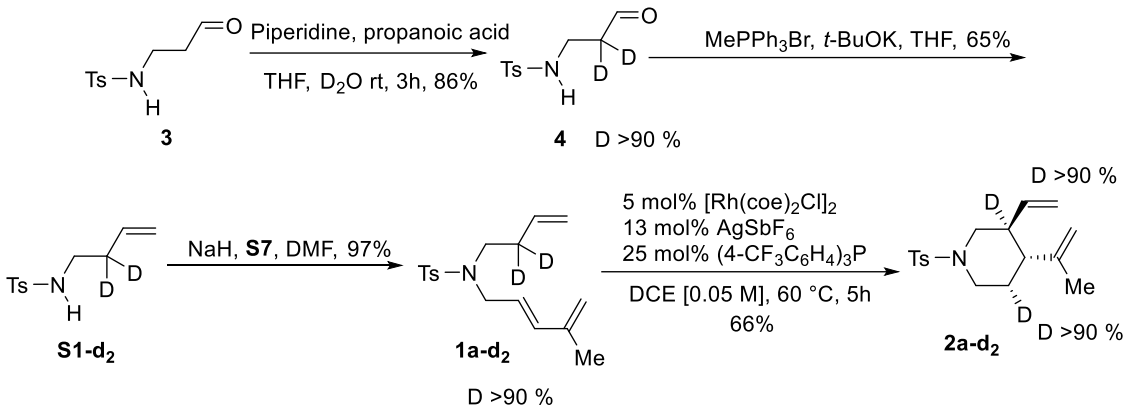


2r-DA

Reaction time: 5 h, Eluted with PE / EA = 30 / 1.
Catalyst: ($[Rh(coe)_2Cl]_2/AgSbF_6/(4\text{-}CF_3C_6H_4)_3P$)
58.2 mg **1r** was converted to 44.7 mg **2r-DA**, yield 77 %.

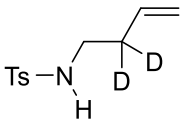
2r-DA: colorless oil, TLC R_f: 0.26 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.08 (s, 1H), 3.46 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.39 (dd, *J* = 9.8, 7.5 Hz, 1H), 3.02 (dd, *J* = 9.9, 4.9 Hz, 1H), 2.92 (dd, *J* = 9.7, 6.9 Hz, 1H), 2.59 – 2.45 (m, 1H), 2.41 (s, 3H), 2.26 – 2.12 (m, 1H), 1.89 – 1.70 (m, 2H), 1.57 – 1.48 (m, 4H), 1.33 – 1.25 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 135.9, 134.0, 129.5, 127.5, 120.1, 53.1, 51.8, 38.2, 35.6, 27.5, 23.6, 23.3, 21.5.
HRMS (ESI) $C_{16}H_{22}NO_2S$ $(M+H)^+$: 292.1366. Found: 292.1364.

5. Deuterium labeling study of the cycloisomerization reaction



Aldehyde **3** (913.0 mg, 4.0 mmol) was added in a round-bottomed flask, followed by adding THF (10 mL) and deuterium oxide (22 mL, 1.2 mol, 300 eq.). After that, propanoic acid (0.60 mL 8.0 mmol) and piperidine (0.37 mL, 4.0 mmol) was added into the mixture , the reaction was stirred at room temperature for 3 hours, after that, anhydrous ether (3×25 mL) was added to extract the product. After dried over anhydrous Na_2SO_4, the solution was filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 2 / 1) to yield **4** (R_f: 0.28 (PE / EA = 2 / 1), 796.0 mg, yield = 86 %) as a light yellow oil (Deuterium ratio > 90 % via crude ^{1}H-NMR).

In a round-bottomed flask, $MePPh_3Br$ salt was added and dried by vacuum under heating. After cooled by ice water bath, *t*-BuOK (672 mg, 6.0 mmol) and anhydrous THF (10 mL) were added to the flask under inert atmosphere. The mixture was stirred at 0 °C for 1 h, followed by adding aldehyde **4** (987.0 mg, 4.3 mmol) in anhydrous THF (10 mL). After warmed to room temperature for 1h, the reaction was quenched by H_2O, and extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA =10 / 1) to yield **S1-d$_2$** (R_f: 0.38 (PE / EA = 5 / 1), 639.3 mg, yield = 65 %) as a colorless oil.



S1-d$_2$

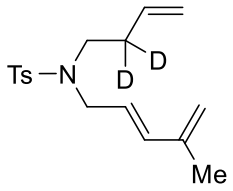
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.61 (dd, *J* = 16.7, 9.8 Hz, 1H), 5.05 (d, *J* = 9.8 Hz, 1H), 5.01 (d, *J* = 16.7 Hz, 1H), 4.75 – 4.65 (br, 1H), 2.98 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0, 134.2, 129.8, 127.2, 118.2, 42.1, 21.6.

HRMS (ESI) calcd for $C_{11}H_{14}D_2NO_2S$ $(M+H)^+$: 228.1022. Found: 228.1019.

The protected amine **S1-d$_2$** (601.4 mg, 2.65 mmol) in DMF (15 mL) was added into NaH (0.85 g, 60% in mineral oil, 21.2 mmol, 8.0 eq) at 0 °C, After 30 min, **S7** in THF (13.3 mL, 0.3 M, 4.0 mmol, 1.5 eq) was added into above solution. The reaction was then stirred for 16 h and warmed to room temperature.

Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 30 / 1) to yield **1a-d²** (R_f: 0.35 (PE / EA = 10 / 1), 735.2 mg, yield = 97 %) as a colorless oil (Deuterium ratio > 90 % via ^{1}H-NMR).



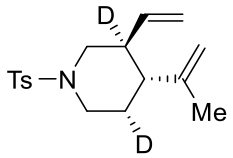
1a-d₂

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.17 (d, *J* = 15.7 Hz, 1H), 5.68 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.39 (dt, *J* = 14.4, 6.7 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.95 (s, 1H), 4.91 (s, 1H), 3.85 (d, *J* = 6.7 Hz, 2H), 3.15 (s, 2H), 2.40 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.1, 137.3, 136.6, 134.8, 129.7, 127.3, 124.3, 117.2, 117.1, 50.1, 46.8, 21.5, 18.5.

HRMS (ESI) calcd for $C_{17}H_{22}D_2NO_2S$ $(M+H)^+$: 308.1648. Found: 308.1639.

1a-d₂ was performed the same as the substrate **1a** for the cycloisomerization reaction.



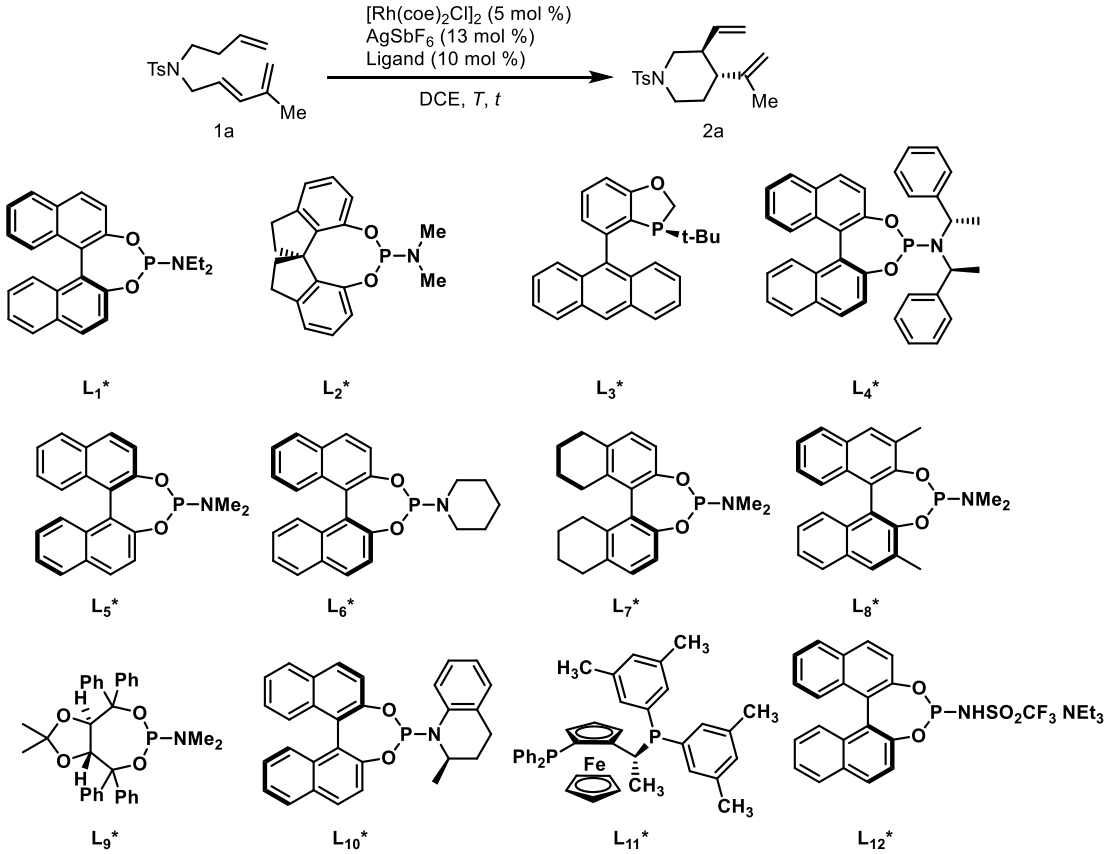
2a-d₂

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.43 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.05 (d, *J* = 17.3 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.71 (s, 1H), 4.64 (s, 1H), 3.83 (d, *J* = 11.5 Hz, 1H), 3.77 (d, *J* = 11.5, 1H), 2.42 (s, 3H), 2.19 (d, *J* = 11.6 Hz, 1H), 1.98 (d, *J* = 11.5 Hz, 1H), 1.73 (s, 1H), 1.61 (s, 1H), 1.58 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 143.6, 137.8, 133.1, 129.7, 127.8, 116.7, 112.3, 50.9, 49.0, 46.4, 21.6, 19.1.

HRMS (ESI) calcd for $C_{17}H_{22}D_2NO_2S$ $(M+H)^+$: 308.1648. Found: 308.1644.

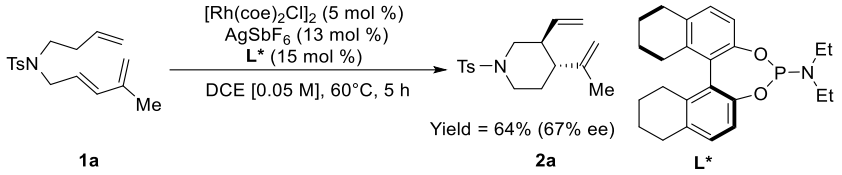
6. Enantioselective cycloisomerization reaction study



ligand	Time(h)	Temp.(°C)	Isolated Yield	ee
L_1*	3	60	74%	0
L_2*	12	60	53%	40%
L_3*	52	60-90	Complex mixture	
L_4*	52	60-90	Complex mixture	
L_5*	24	60	44%	-50%
L_6*	24	60	53%	58%
L_7*	24	60	39%	64%
L_8*	24	60	49%	3%
L_9*	31	60	NO reaction	
L_{10}*	6	60	Complex mixture	
L_{11}*	31	60-90	NO reaction	
L_{12}*	31	60-90	Complex mixture	

General procedure: In the glovebox, $[Rh(coe)_2Cl]_2$ (3.6 mg, 0.005 mmol, 10 mol % of Rh), $AgSbF_6$ (4.5 mg, 0.013 mmol), ligand (0.01 mmol) were added to a 25 mL reaction tube. The mixture was stirred for 20 min at room temperature after adding 1 mL super-dried DCE as solvent. The catalyst was used as a solution. A solution of substrate **1a** (0.1 mmol) in super-dried DCE (1 ml) was added to the above

prepared catalyst (10 mol % Rh, 1 mL DCE) in the reaction tube. After stirred at room temperature for another 20 min, the mixture was heated by the oil bath for 3−52 h. The crude mixture was purified by flash column chromatography on silica gel to afford the cycloisomerization **2a**. Similar procedure was used for ligand L* except 15 mol % ligand was used (see below). Absolute stereochemistry was not determined here (chiral OD-H, hexane/i-PrOH = 98/2, 1.0 mL/min, 25 °C).



1a **2a** **L***

Operator:user Timebase:U-3000 Sequence:cuiqi

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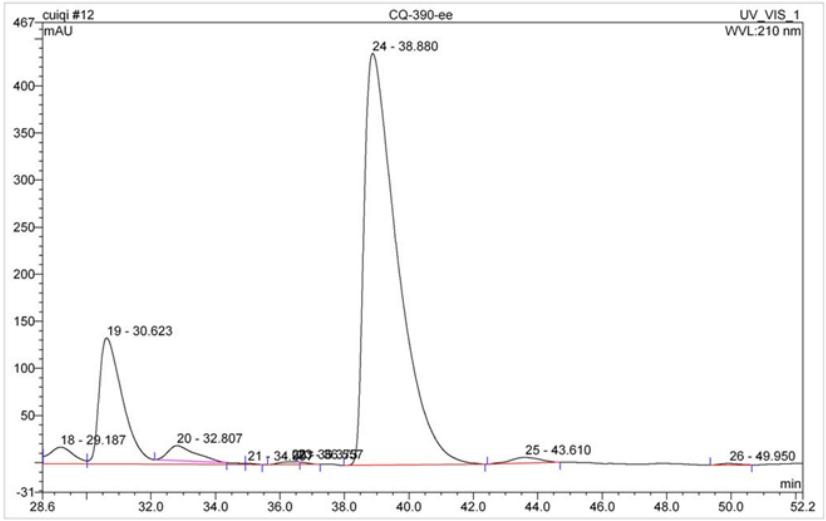
2019-6-8 3:44 下午

12 racemic OJ-H 1.2 ml/min 98:2

Sample Name:	**CQ-390-ee**	*Injection Volume:*	**2.0**
Vial Number:	**12**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**test**	*Bandwidth:*	**4**
Quantif. Method:	**Method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018-3-20 15:59**	*Sample Weight:*	**1.0000**
Run Time (min):	**60.00**	*Sample Amount:*	**1.0000**



	peak1	peak2	ee
area	102.19	525.78	67%

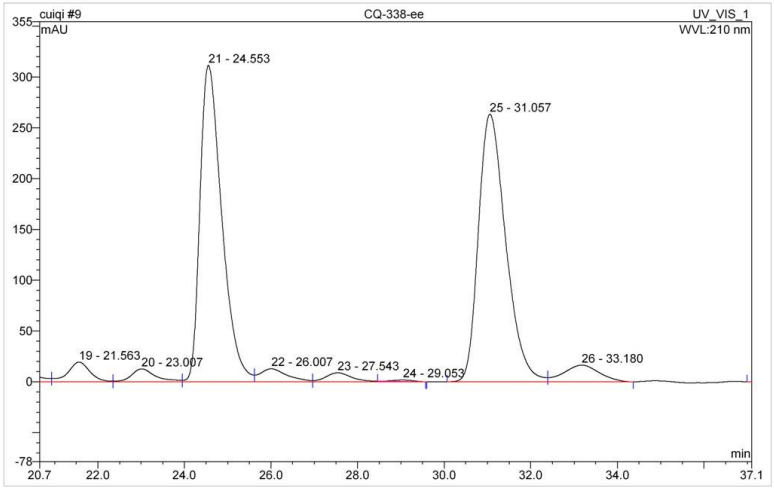
Racemic sample:

Operator:user Timebase:U-3000 Sequence:cuiqi

Page 1-1
2019-6-8 4:25 下午

9 racemic OJ-H 1.2 ml/min 98:2

Sample Name:	**CQ-338-ee**	*Injection Volume:*	**2.0**
Vial Number:	**9**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**test**	*Bandwidth:*	**4**
Quantif. Method:	**Method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2017-12-13 20:47**	*Sample Weight:*	**1.0000**
Run Time (min):	**60.00**	*Sample Amount:*	**1.0000**



	peak1	peak2	ee
area	181.96	181.59	0

7. References

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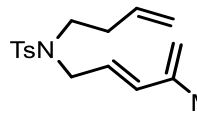
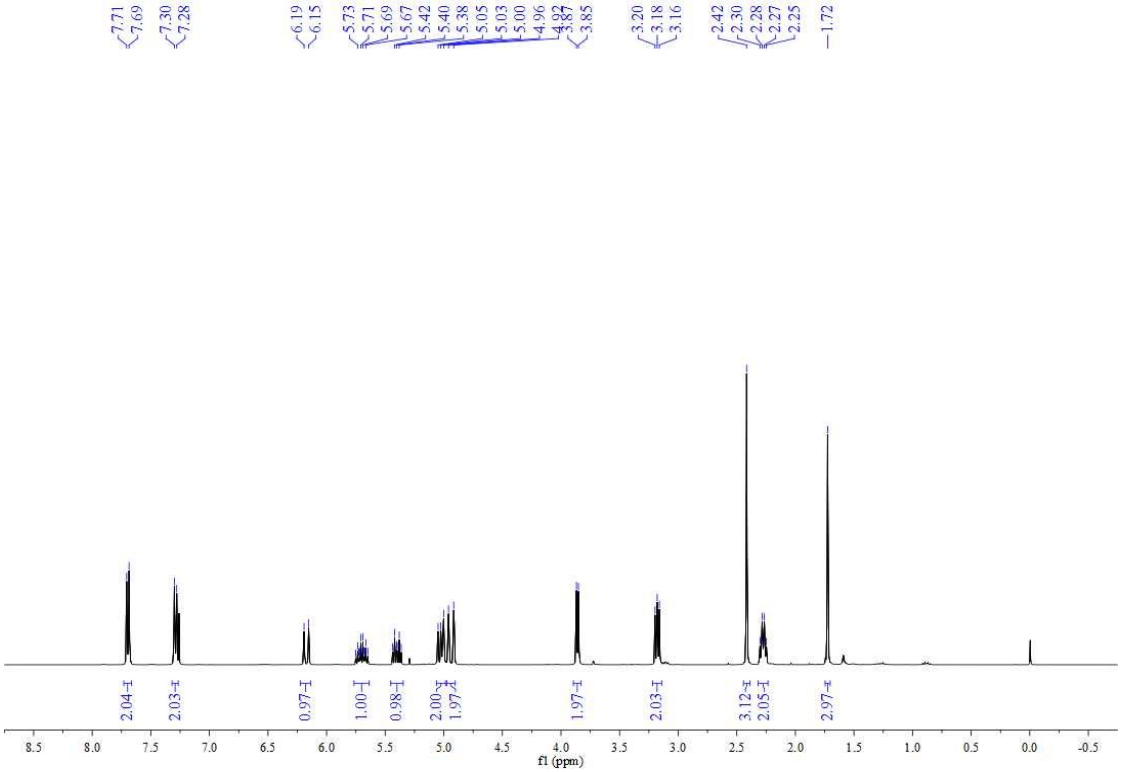
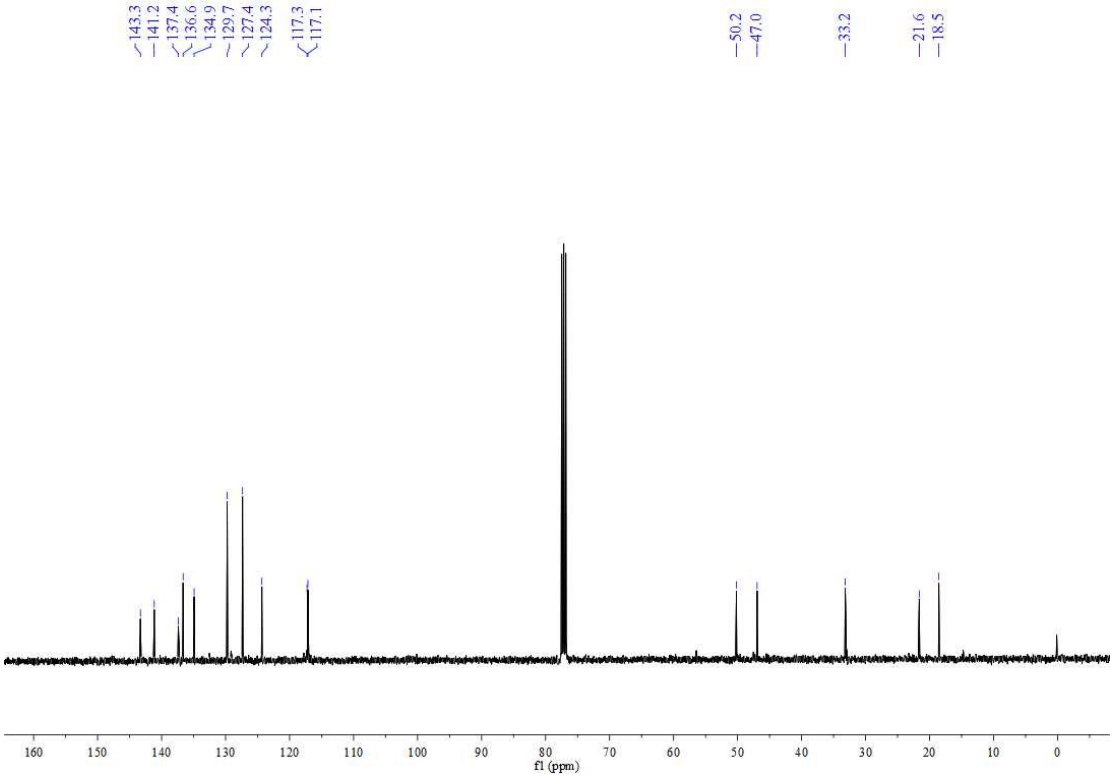
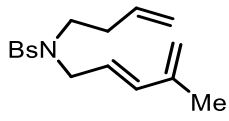
8. NMR spectra of new compounds



1a



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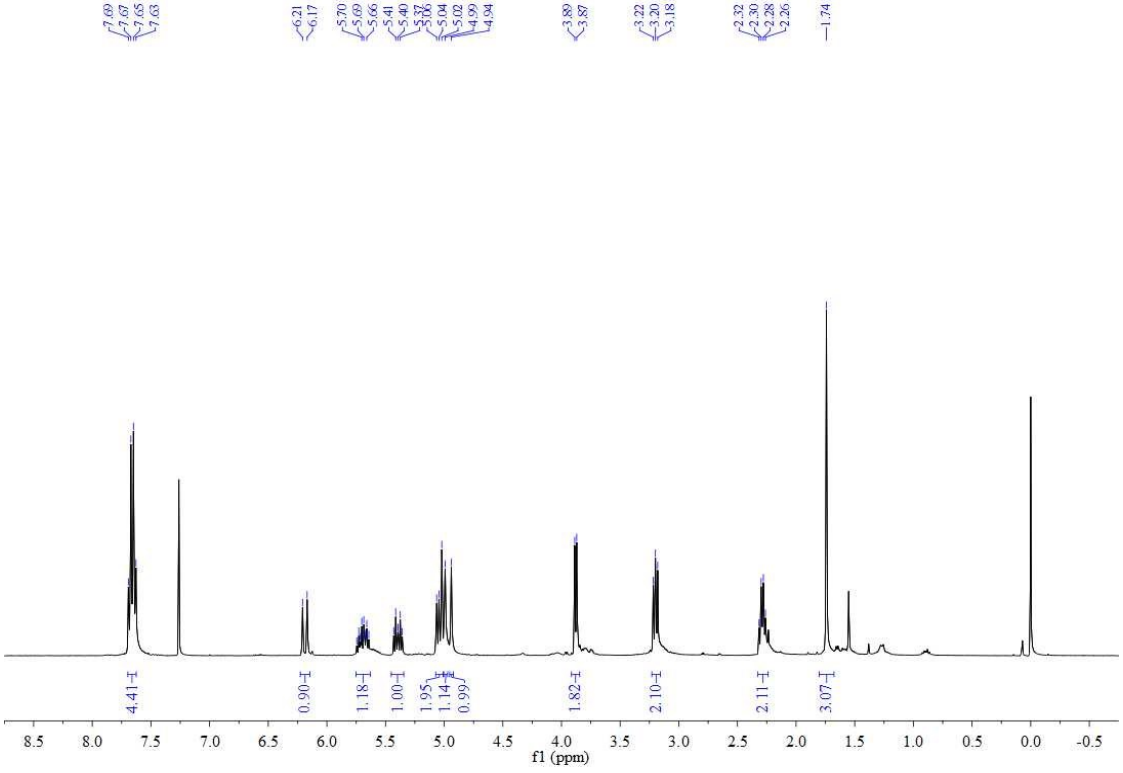
Me

1b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5.69
5.66
5.41
5.40
5.37
5.06
5.04
5.02
4.99
4.94
3.89
3.87
3.22
3.20
3.18
2.32
2.30
2.28
2.26
1.74
4.41
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1.00
1.95
1.14
0.99
1.82
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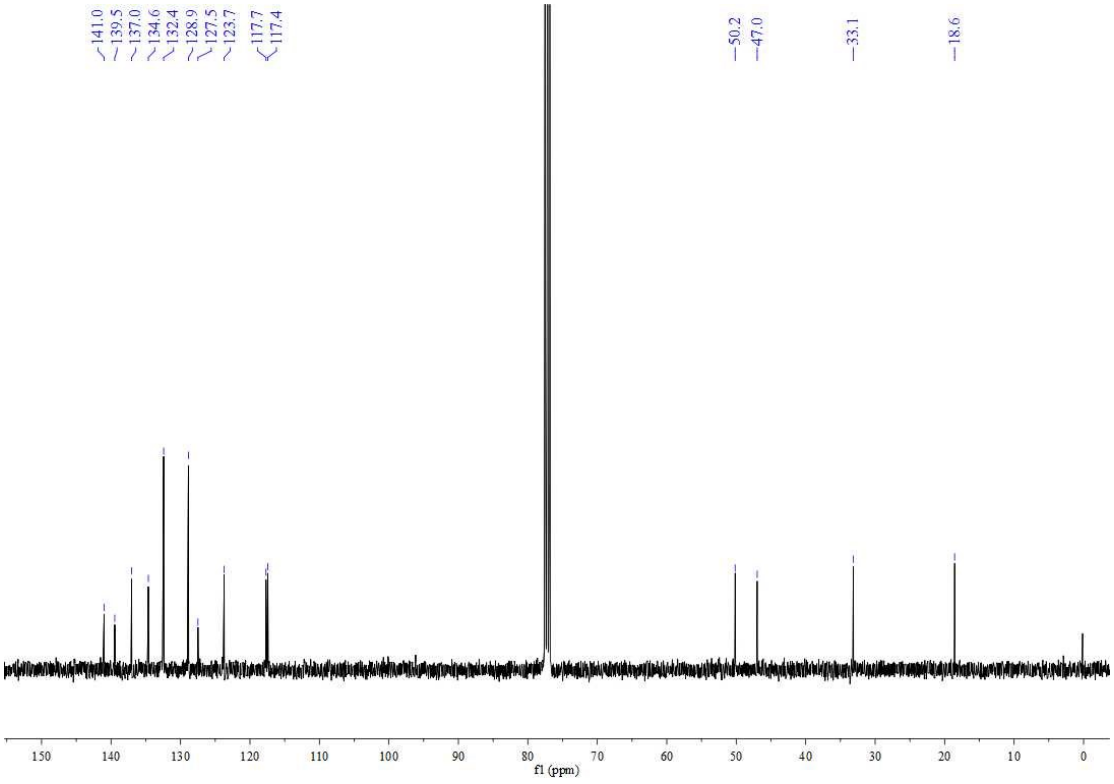
2.11
3.07
f1 (ppm)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127.5
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117.7
117.4
50.2
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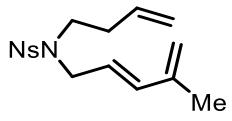
33.1
18.6
f1 (ppm)


NsN
Me

1c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8.33
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6.19
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5.68
5.65
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5.39
5.37
5.07
5.07
5.05
5.03
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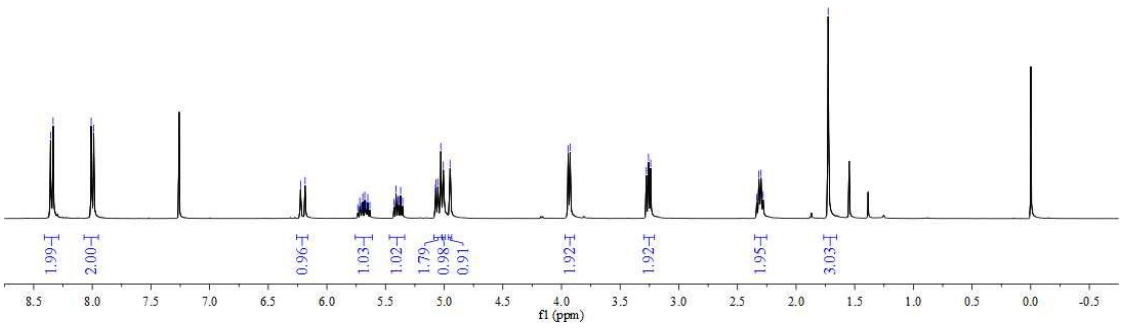
2.28
1.73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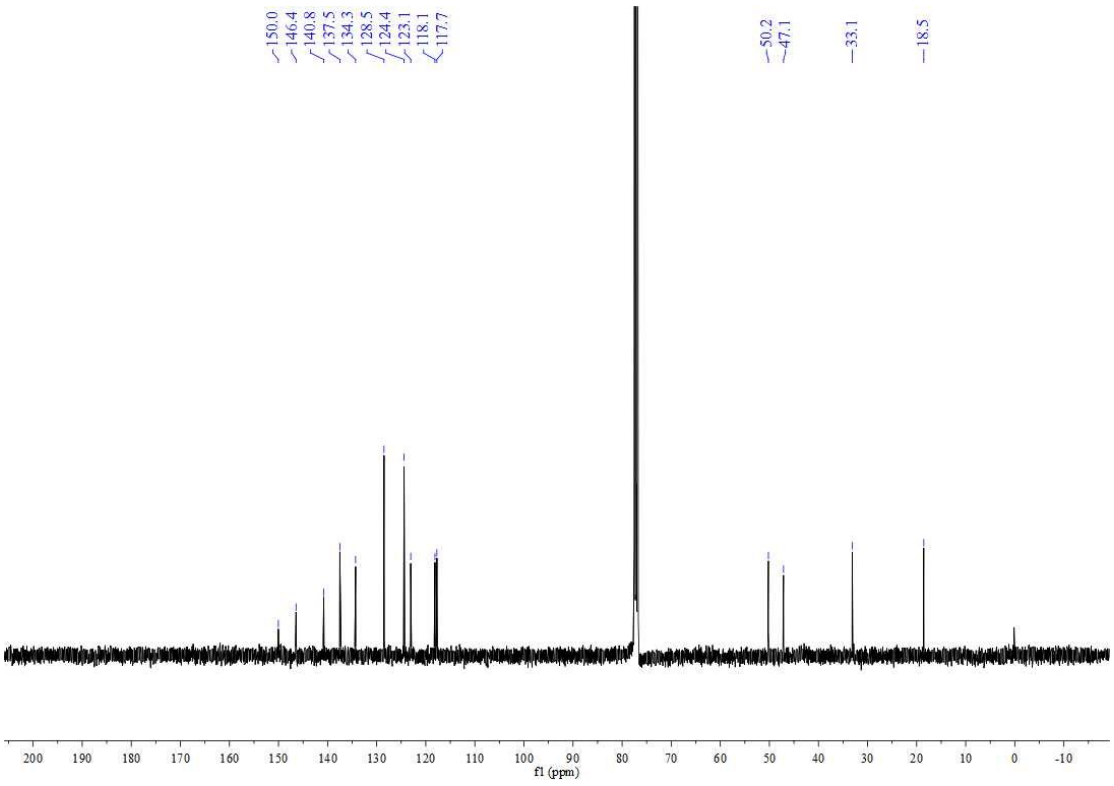
3.03
f1 (ppm)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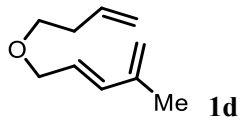
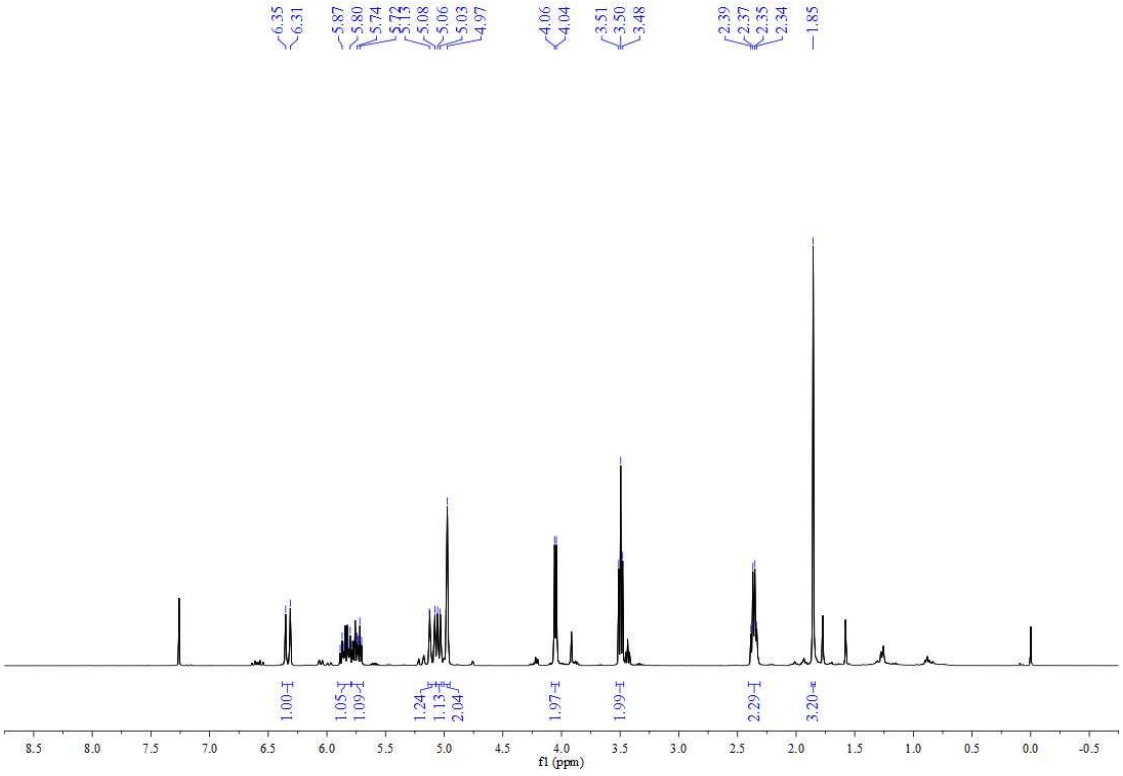
f1 (ppm)


O
Me

1d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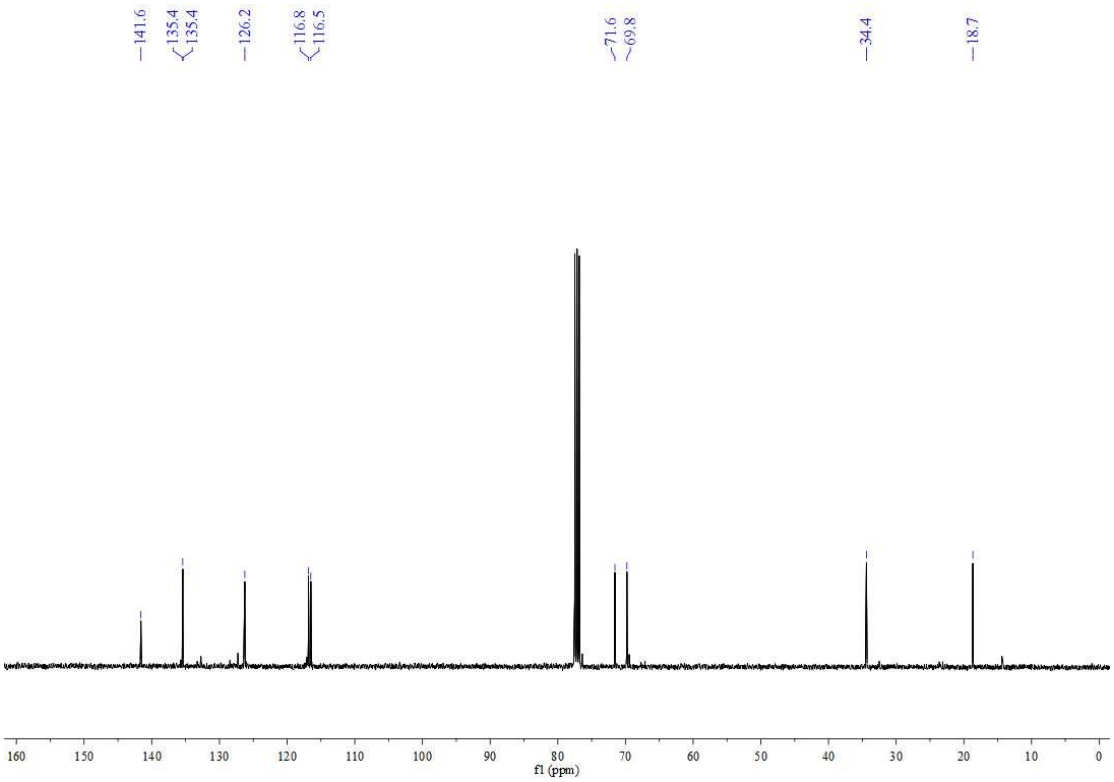
f1 (ppm)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18.7
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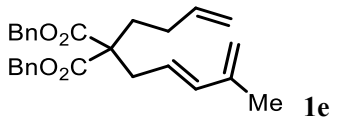
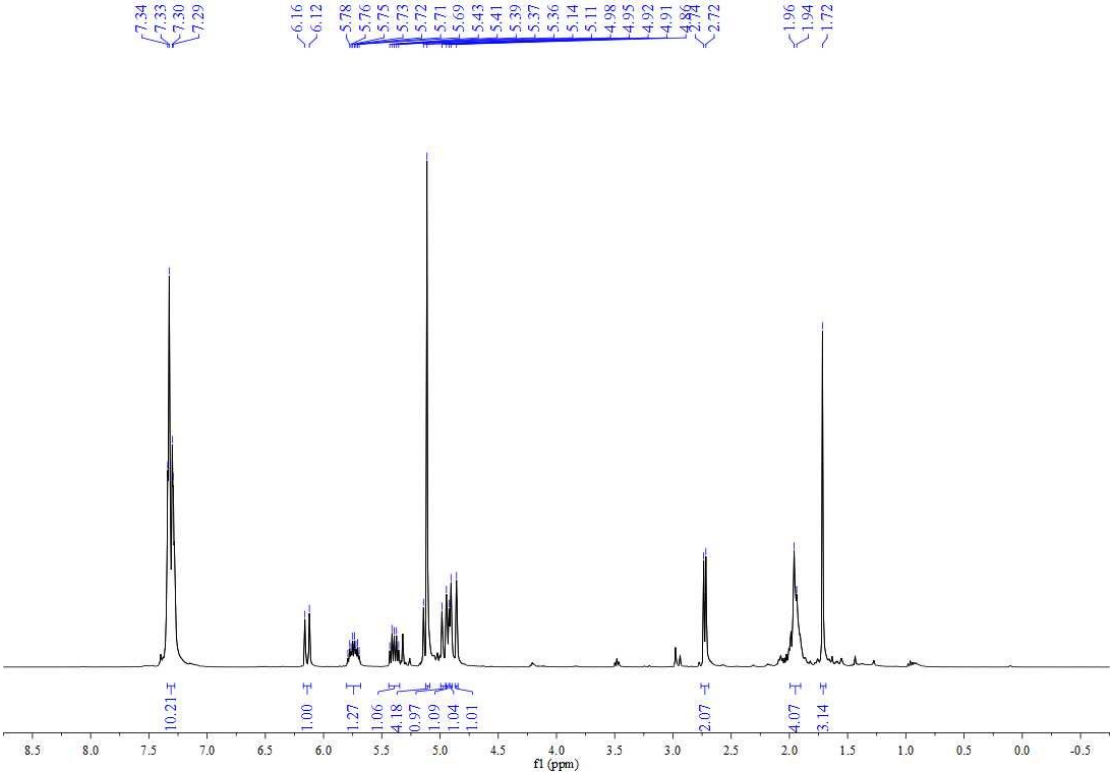

BnO2C
BnO2C
Me

1e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5.41
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5.36
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4.92
4.91
2.74
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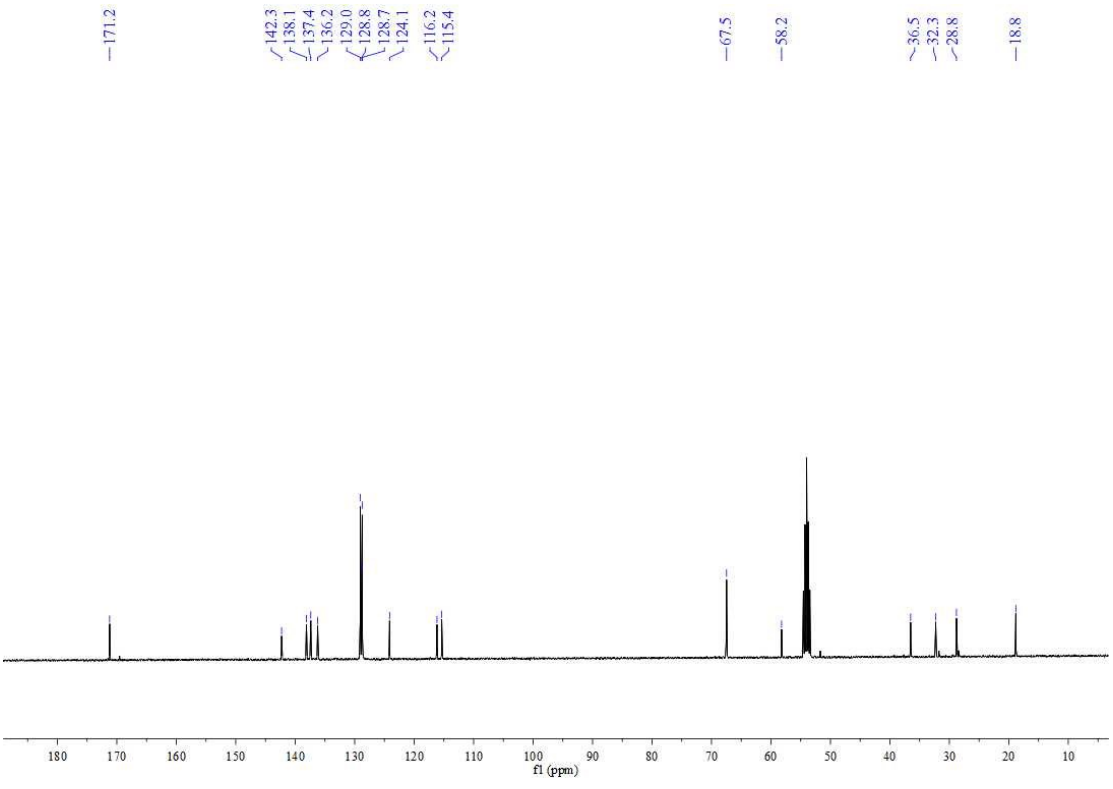
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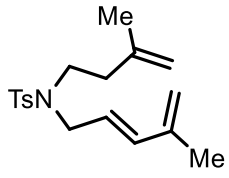
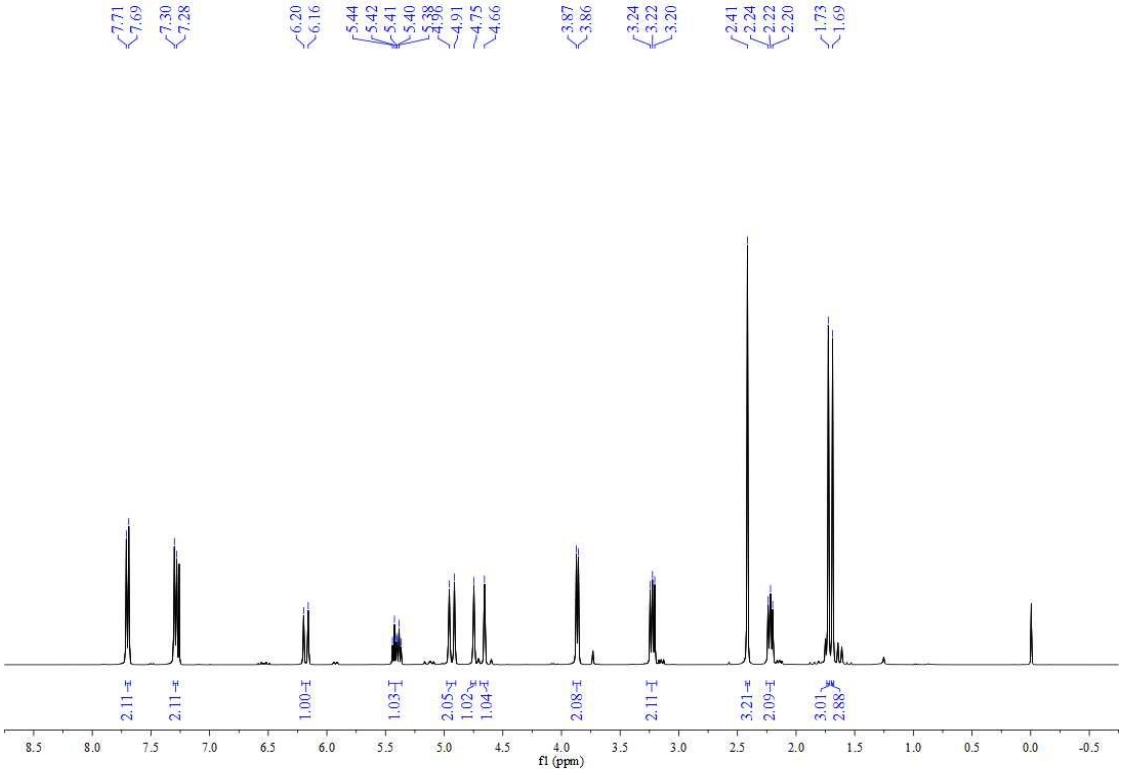
28.8
18.8
f1 (ppm)


Me
TsN
Me

1f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5.40
5.38
4.98
4.91
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4.66
3.87
3.86
3.24
3.22
3.20
2.41
2.24
2.22
2.20
1.73
1.69
2.11
2.11
1.00
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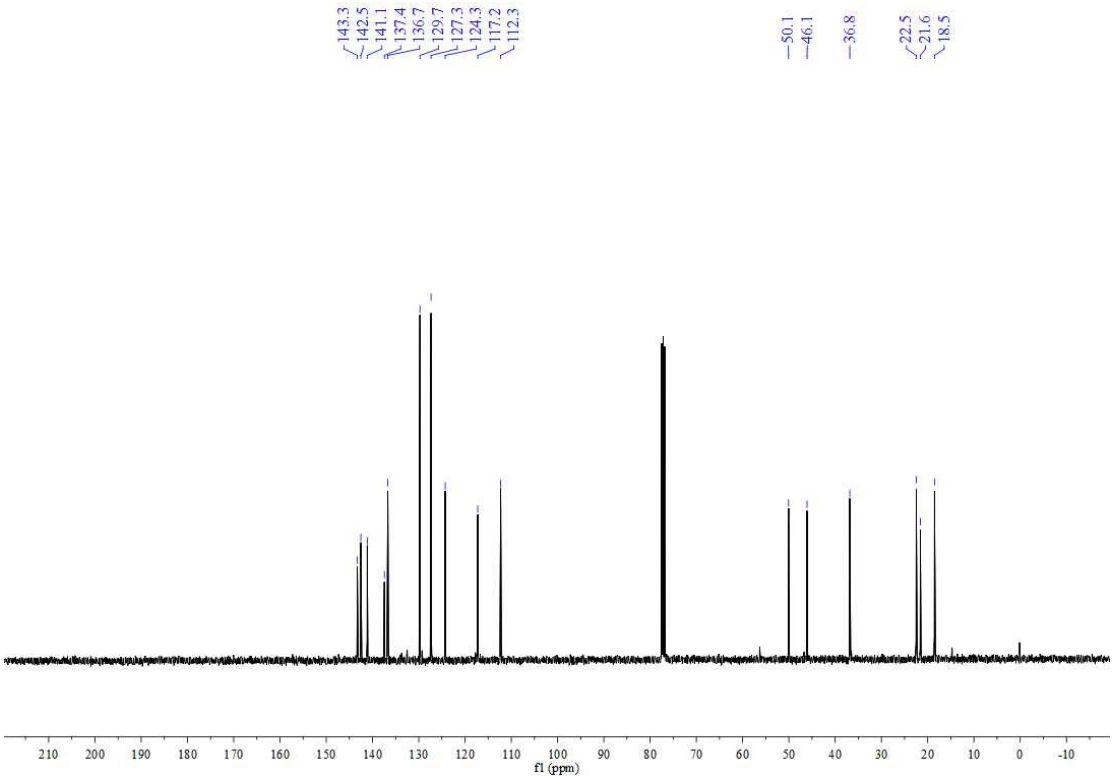
1.02
1.04
2.08
2.11
3.21
2.09
3.01
2.88
f1 (ppm)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124.3
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112.3
50.1
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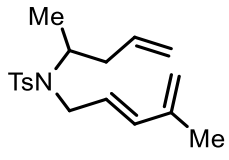
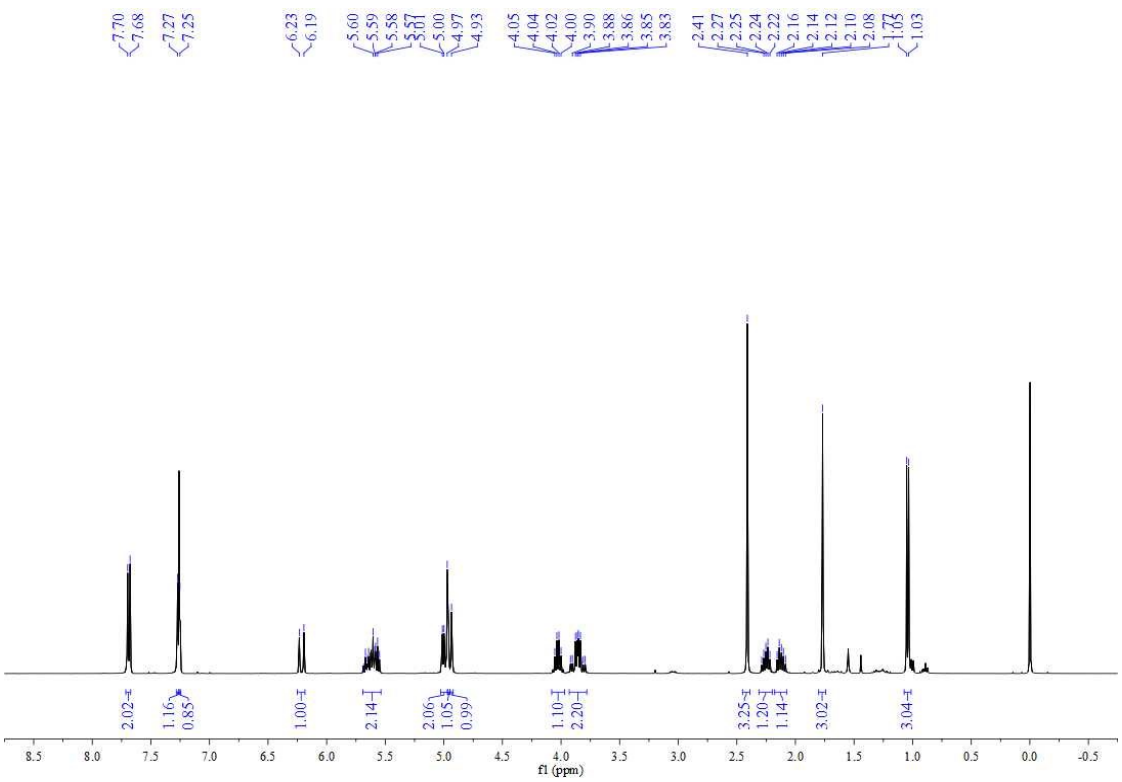
22.5
21.6
18.5
f1 (ppm)


Me
TsN
Me

1g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4.93
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3.85
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2.25
2.24
2.22
2.16
2.14
2.12
2.10
2.08
1.05
1.03
2.02
1.16
0.85
1.00
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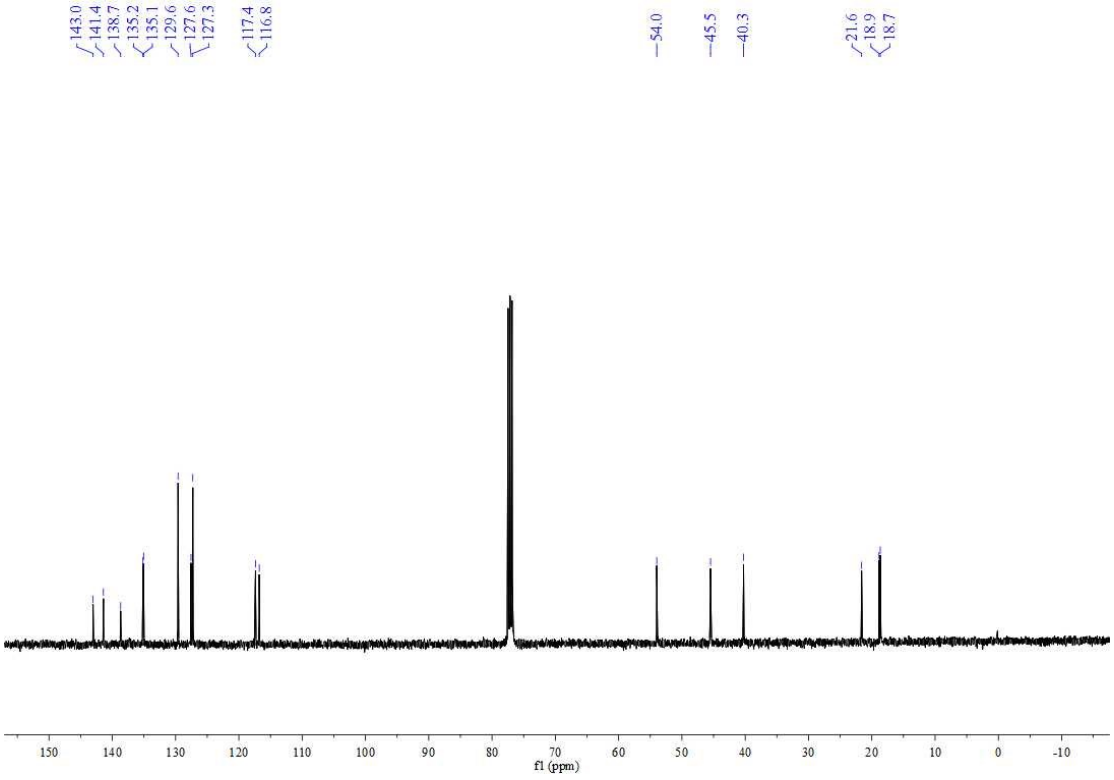
2.20
3.25
1.20
1.14
3.02
3.04
f1 (ppm)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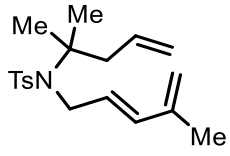
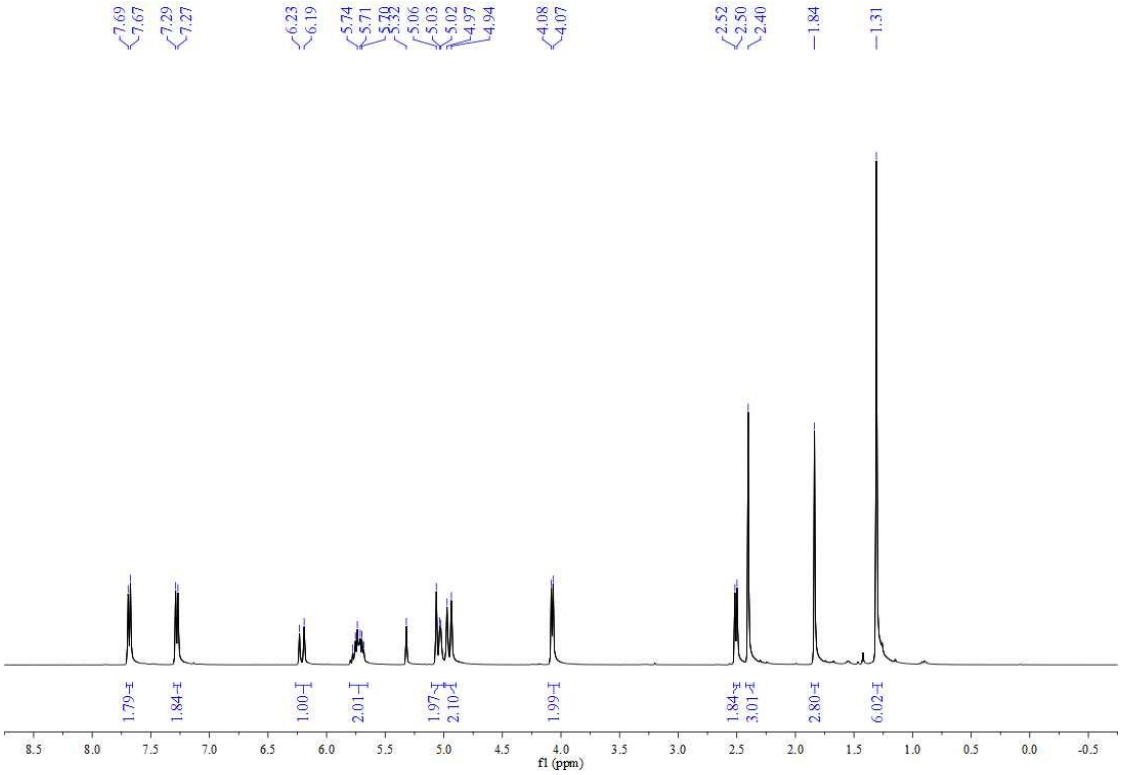
18.7
f1 (ppm)


Me
Me
TsN
Me

1h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5.02
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4.08
4.07
2.52
2.50
2.40
1.84
1.31
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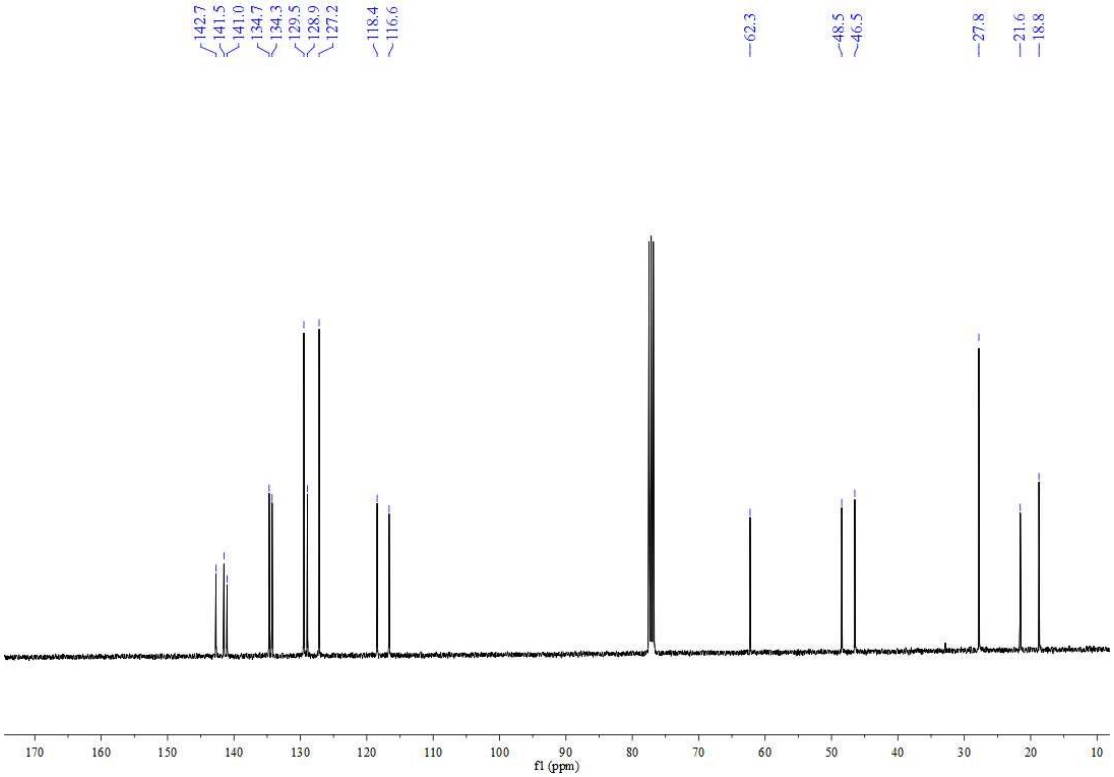
1.97
2.10
1.99
1.84
3.01
2.80
6.02
f1 (ppm)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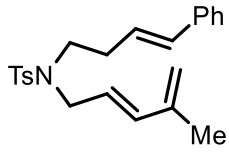
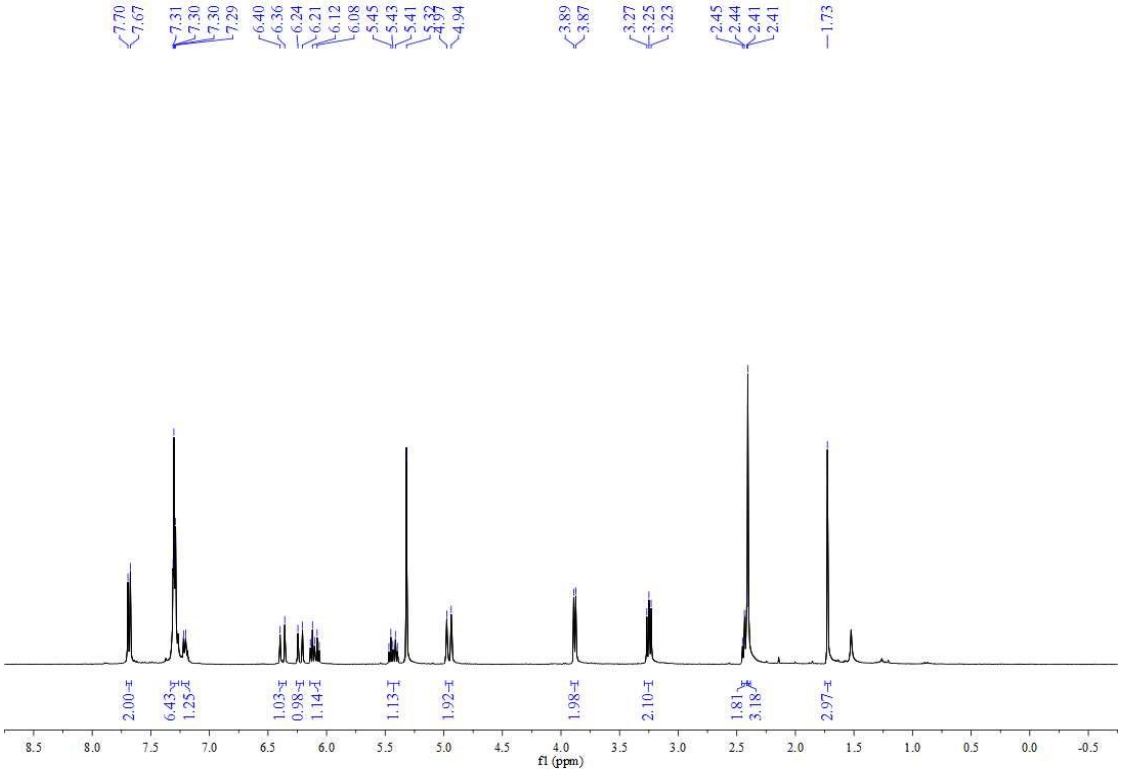
27.8
21.6
18.8
f1 (ppm)


Ph
TsN
Me

1i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7.29
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6.21
6.12
6.08
5.45
5.43
5.41
5.32
4.97
4.94
3.89
3.87
3.27
3.25
3.23
2.45
2.44
2.41
2.41
1.73
2.00
6.43
1.25
1.03
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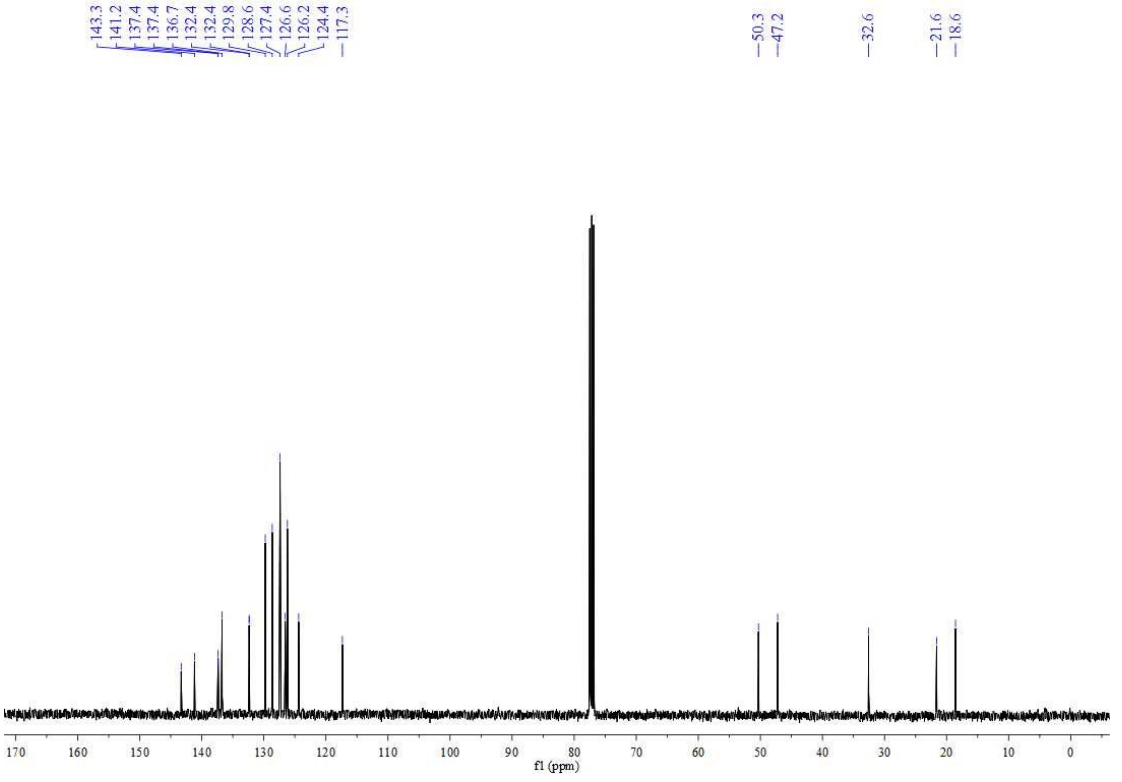
1.13
1.92
1.98
2.10
1.81
3.18
2.97
f1 (ppm)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137.4
137.4
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132.4
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127.4
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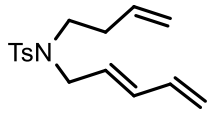
47.2
32.6
21.6
18.6
f1 (ppm)


TsN

1j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6.14
6.11
6.10
6.07
5.68
5.18
5.14
5.09
5.07
5.05
5.05
5.02
5.01
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3.17
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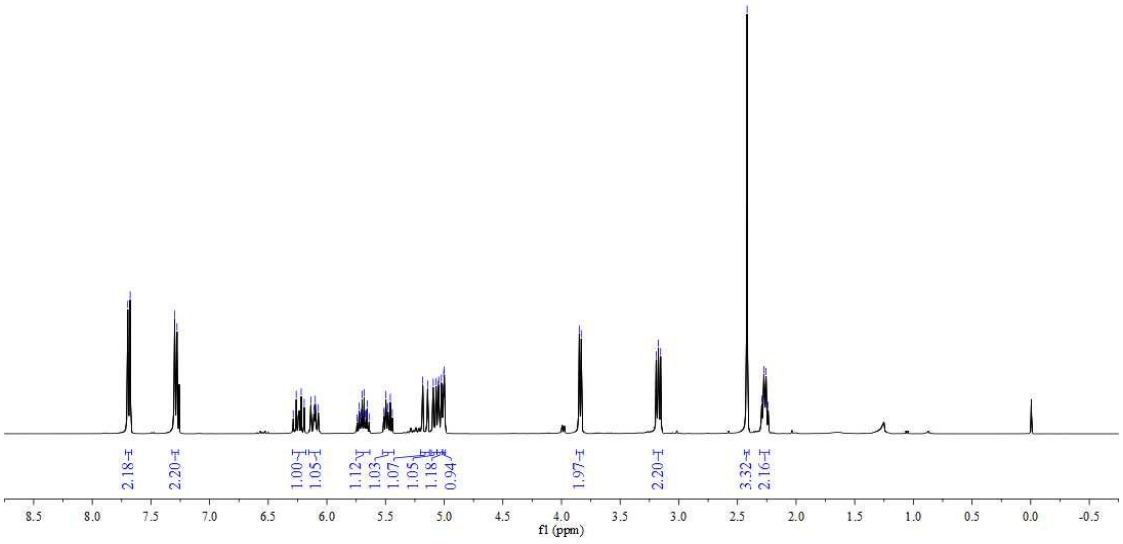
2.29
2.28
2.26
2.24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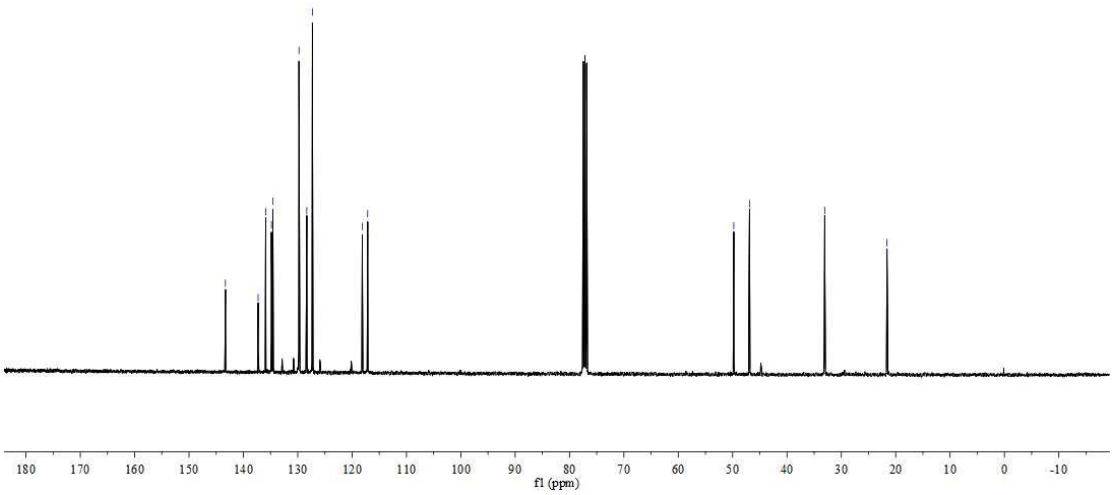
1.03
1.07
1.05
1.18
0.94
1.97
2.20
3.32
2.16
f1 (ppm)


143.3
137.3
135.9
134.8
134.6
129.8
128.3
127.3
118.1
117.1
49.8
46.9
33.1
21.6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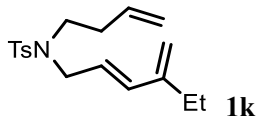
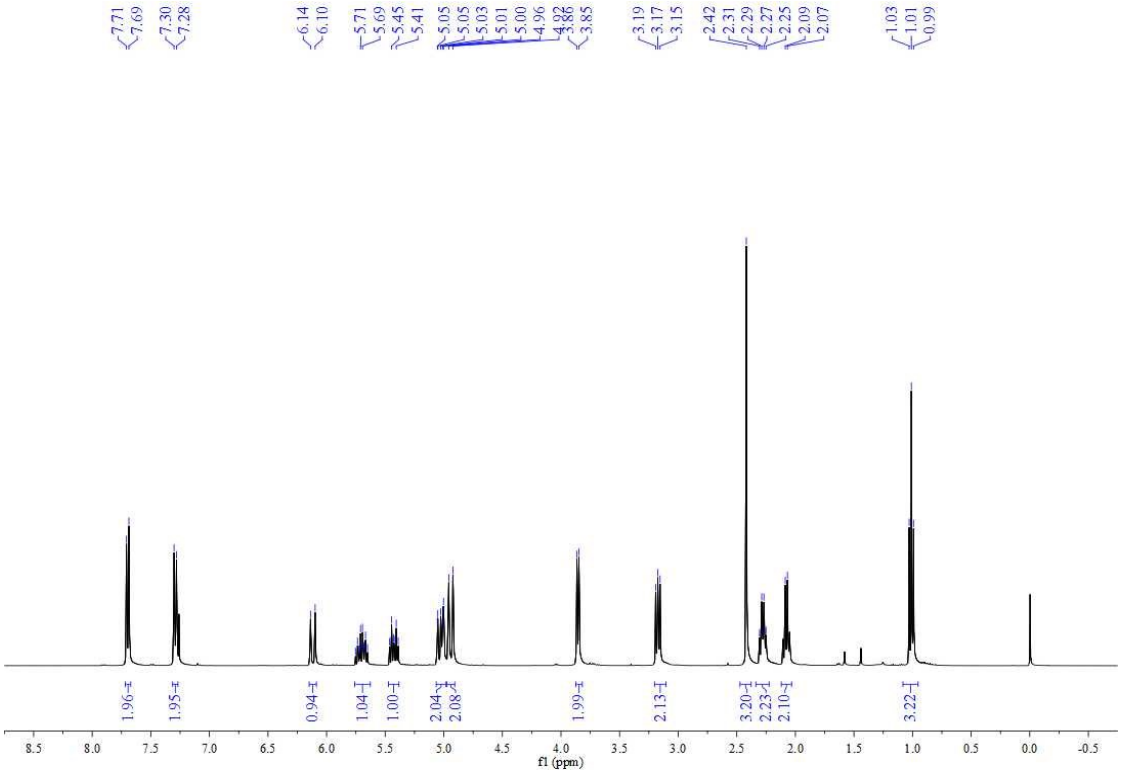

TsN
Et

1k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5.03
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5.00
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4.82
3.86
3.85
3.19
3.17
3.15
2.42
2.31
2.29
2.27
2.25
2.09
2.07
1.03
1.01
0.99
1.96
1.95
0.94
1.04
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2.04
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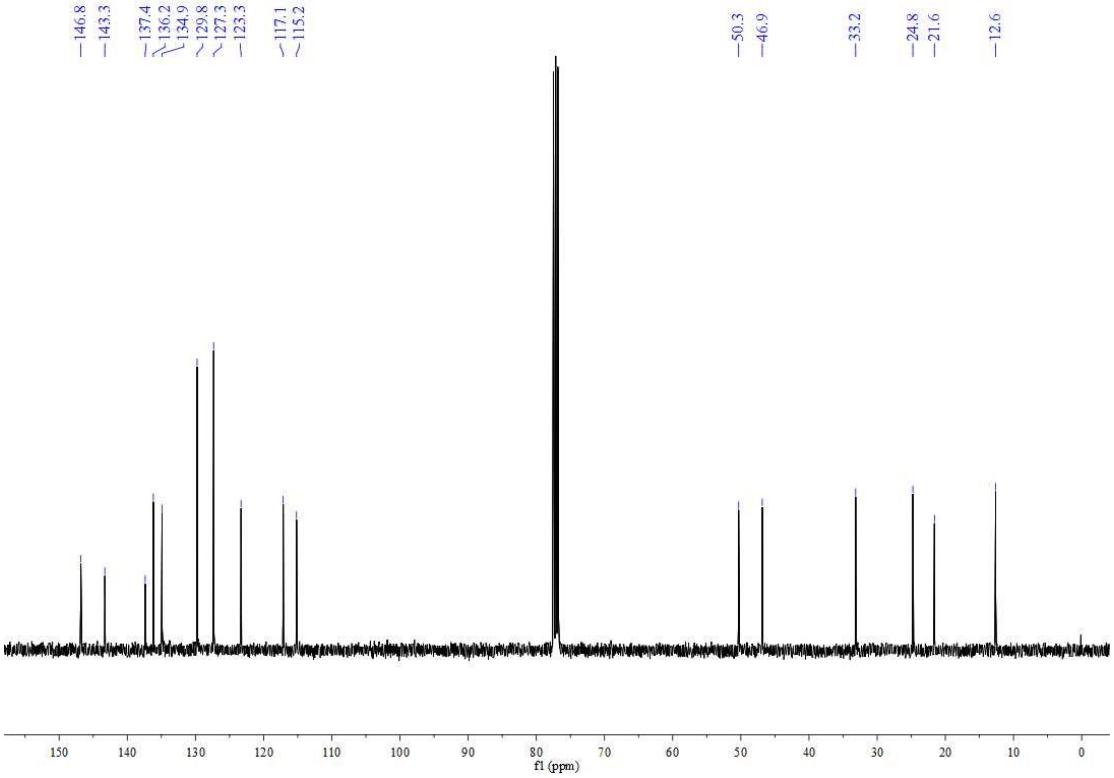
1.99
2.13
3.20
2.23
2.10
3.22
f1 (ppm)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46.9
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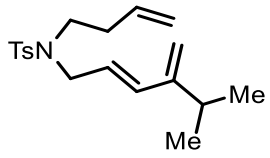
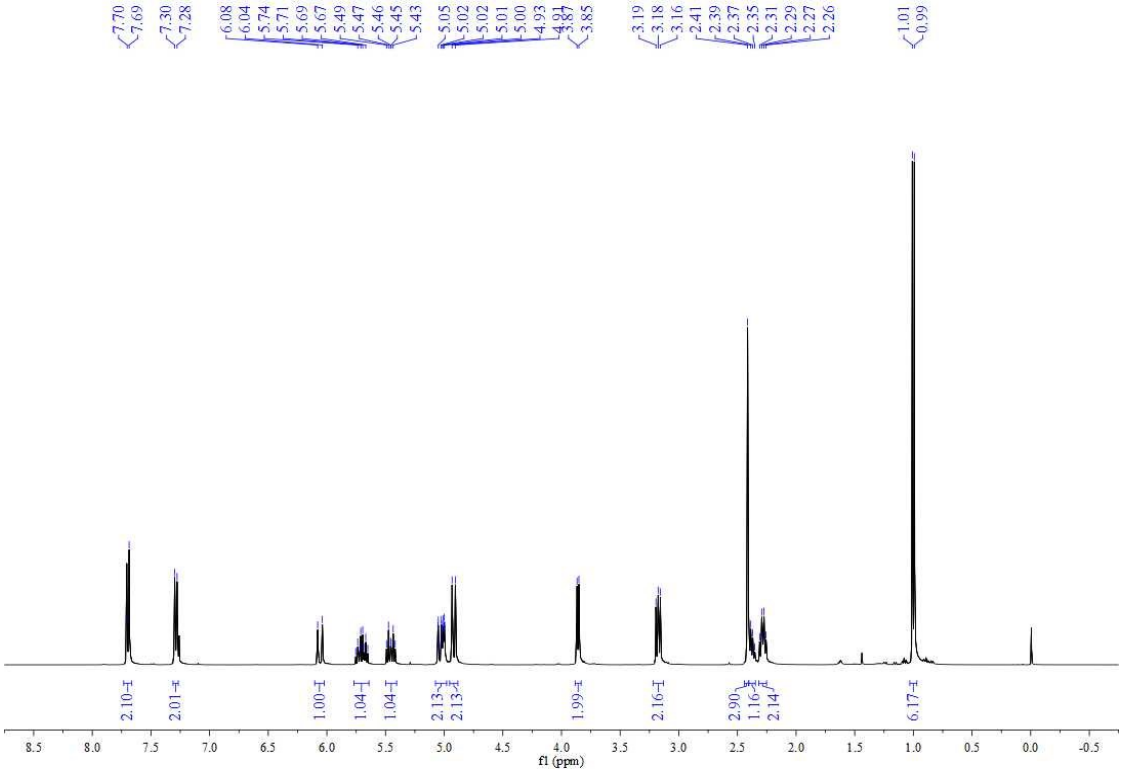
24.8
21.6
12.6
f1 (ppm)


TsN
Me
Me

1l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5.46
5.45
5.43
5.05
5.02
5.02
5.01
5.00
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3.87
3.85
3.19
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3.16
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2.37
2.35
2.31
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2.27
2.26
1.01
0.99
2.10
2.01
1.00
1.04
1.04
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2.13
1.99
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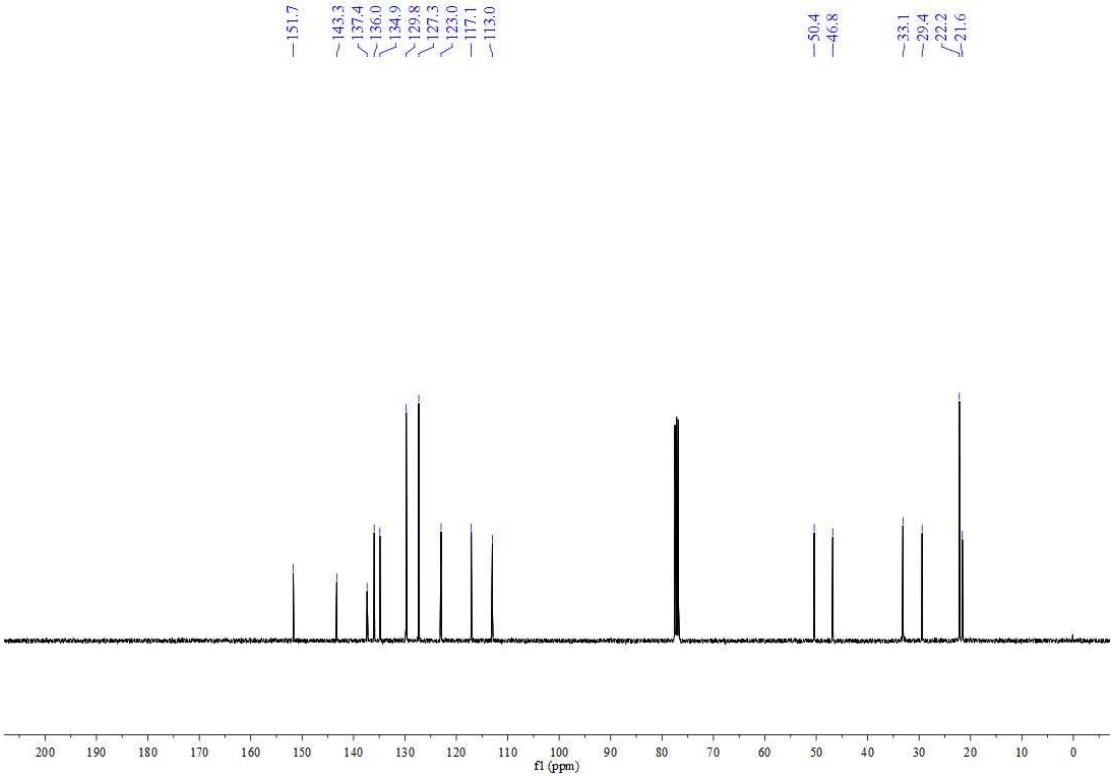
2.90
1.16
2.14
6.17
f1 (ppm)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113.0
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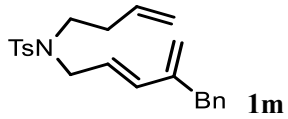
46.8
33.1
29.4
22.2
21.6
f1 (ppm)



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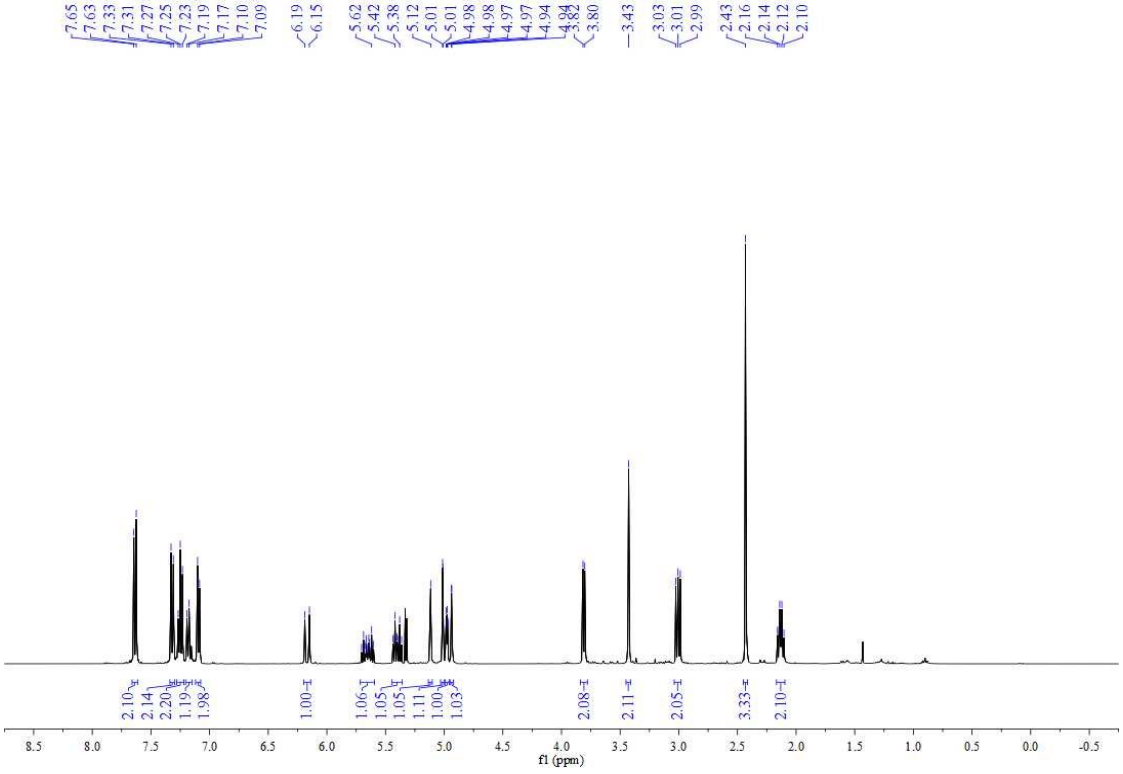
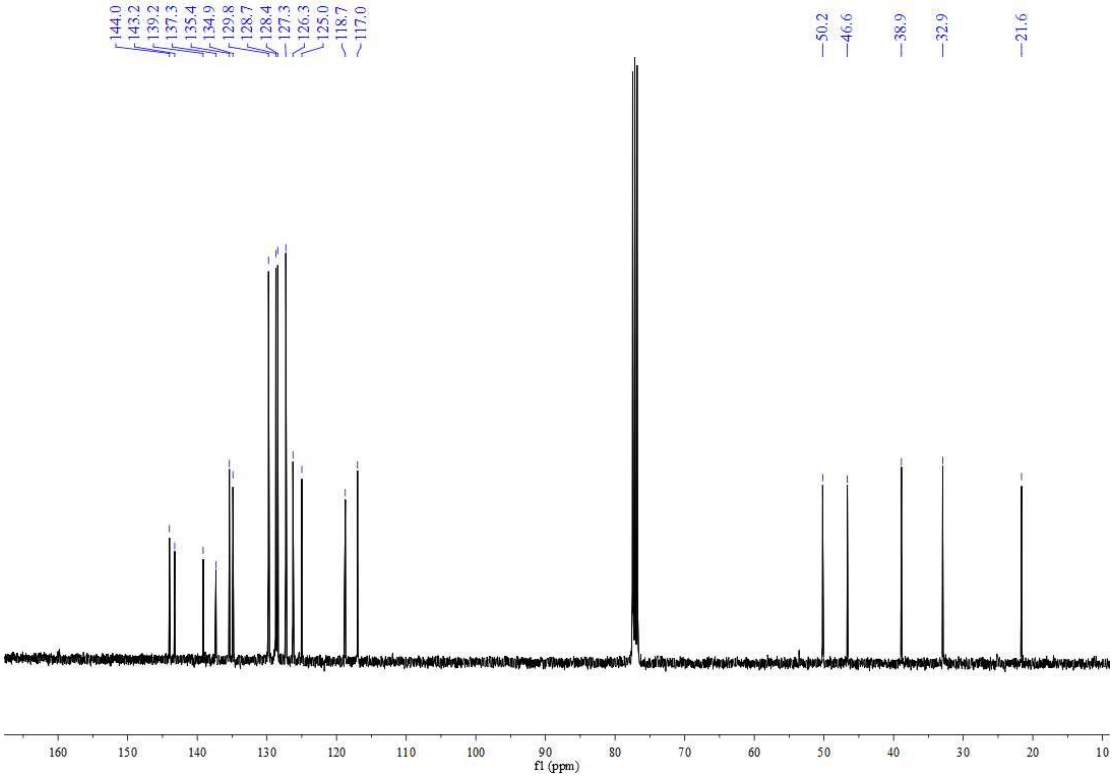
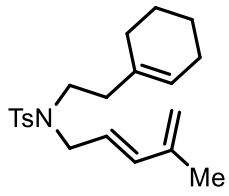
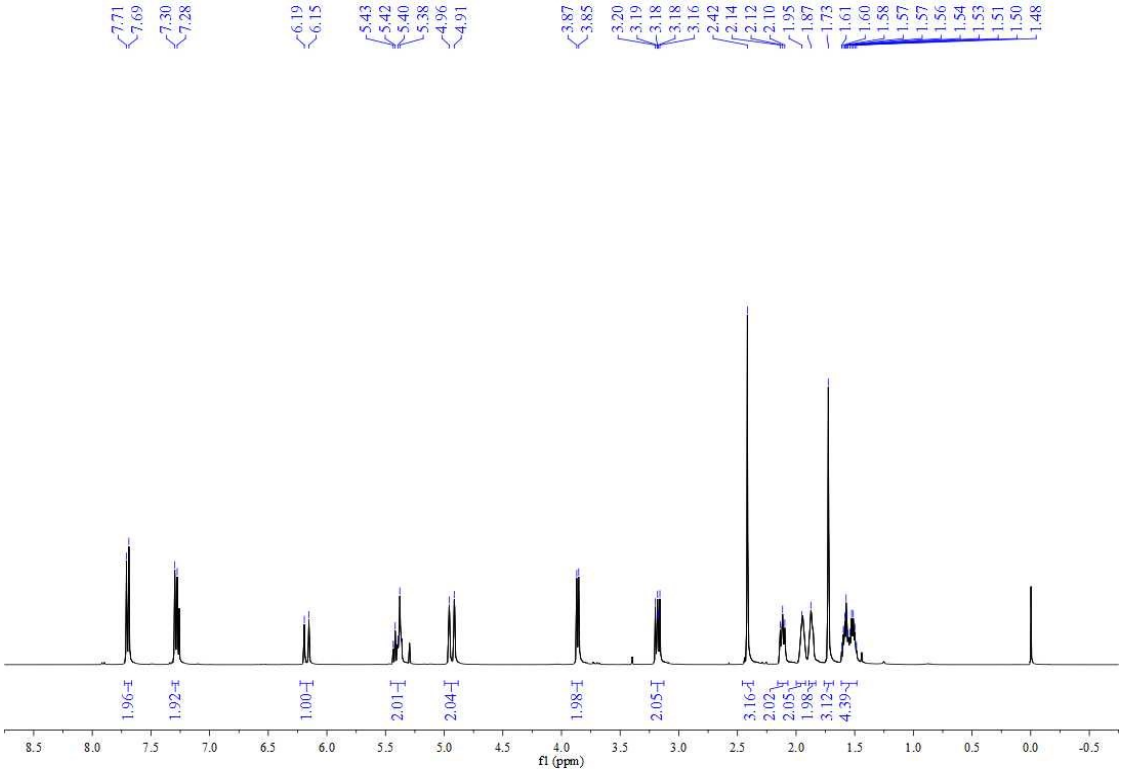





TsN
Me

1n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3.87
3.85
3.20
3.19
3.18
3.18
3.16
2.42
2.14
2.12
2.10
1.95
1.87
1.73
1.61
1.60
1.58
1.57
1.57
1.56
1.54
1.53
1.51
1.50
1.48
1.96
1.92
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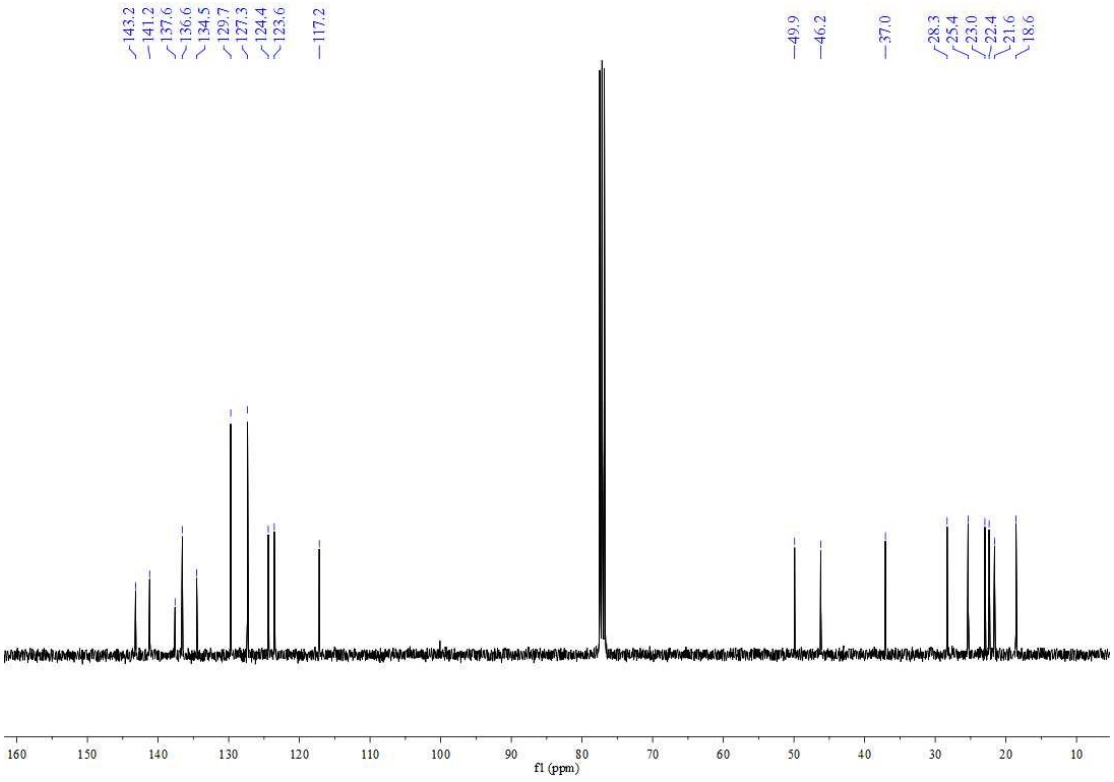
4.39
f1 (ppm)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134.5
129.7
127.3
124.4
123.6
117.2
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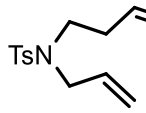
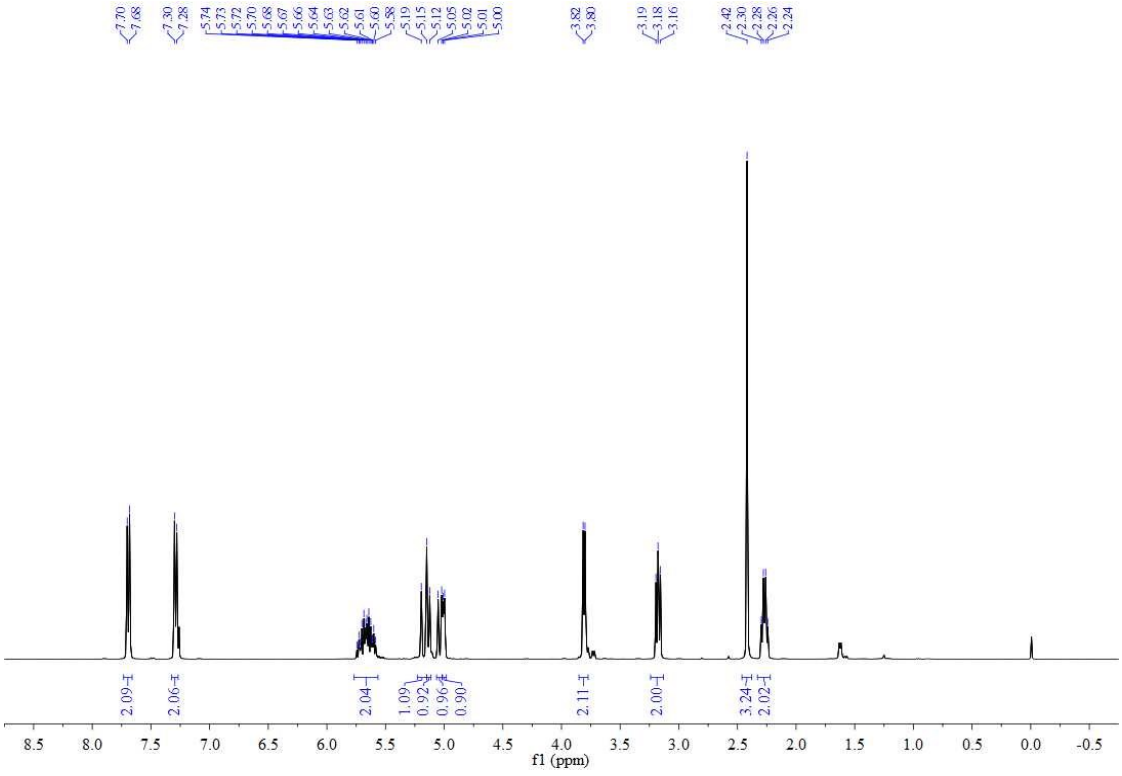
46.2
37.0
28.3
25.4
23.0
22.4
21.6
18.6
f1 (ppm)


TsN

1o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5.62
5.61
5.60
5.58
5.19
5.15
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3.19
3.18
3.16
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2.28
2.26
2.24
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1.09
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0.90
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2.00
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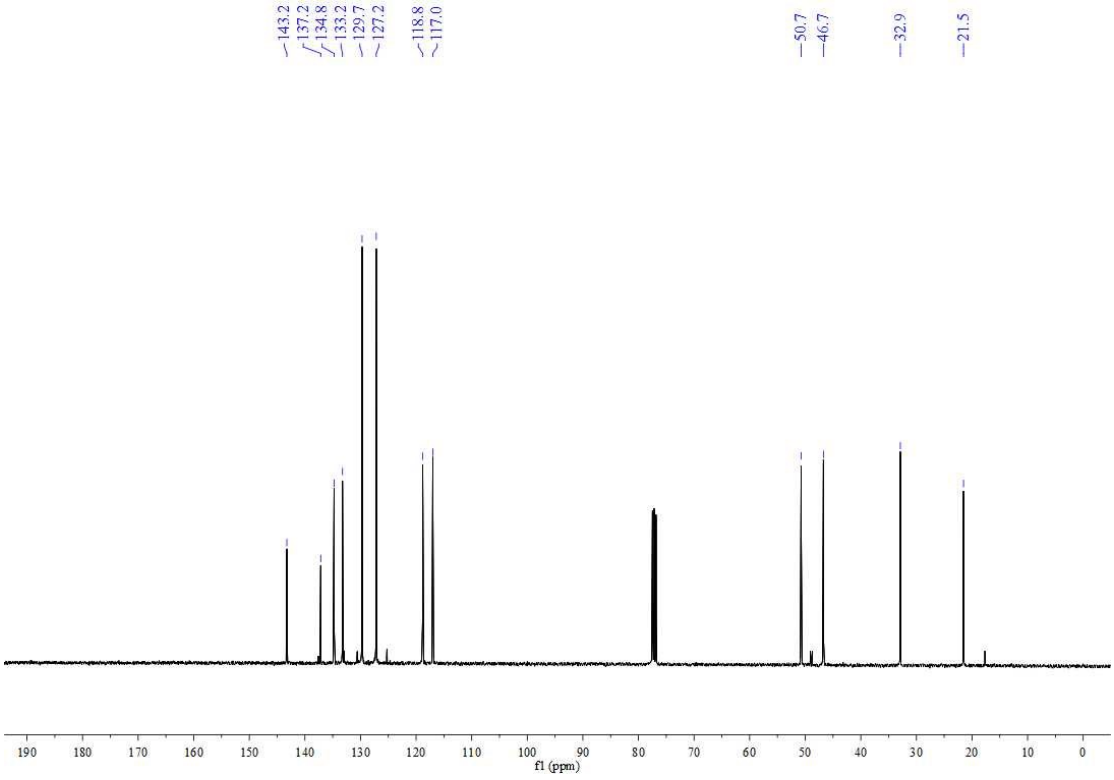
2.02
f1 (ppm)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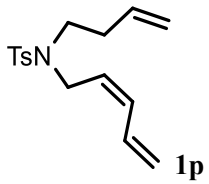
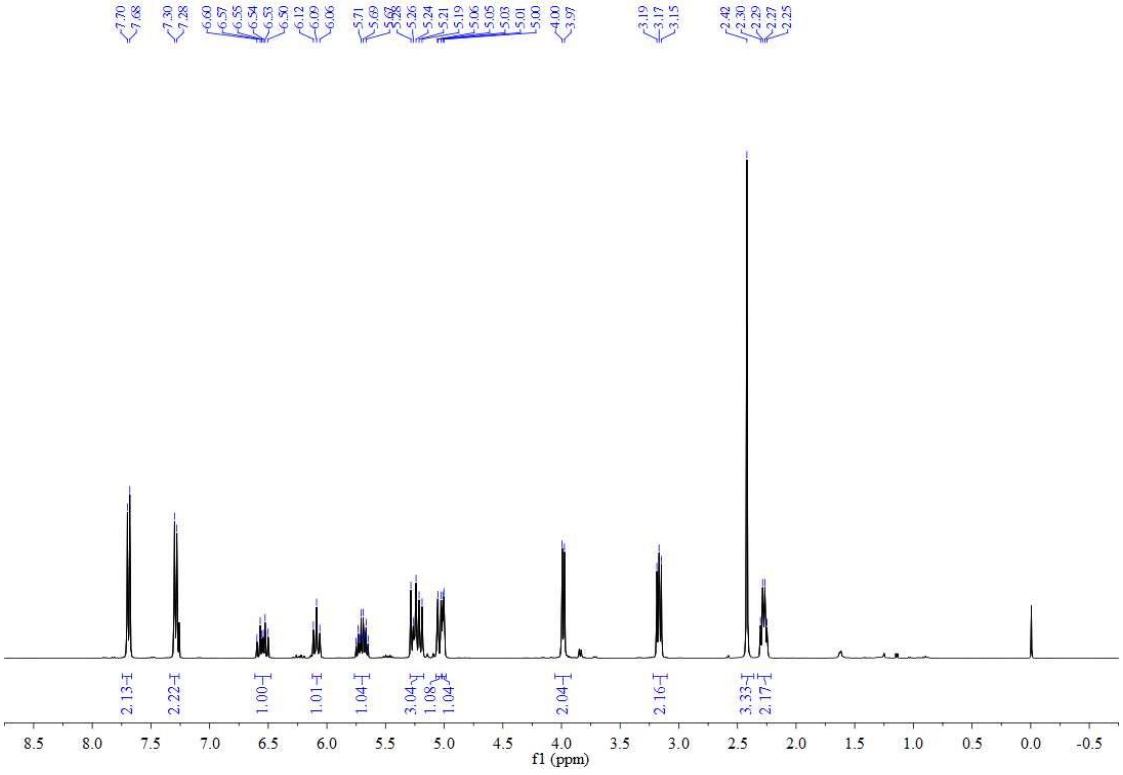
117.0
50.7
46.7
32.9
21.5
f1 (ppm)


TsN

1p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5.01
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2.25
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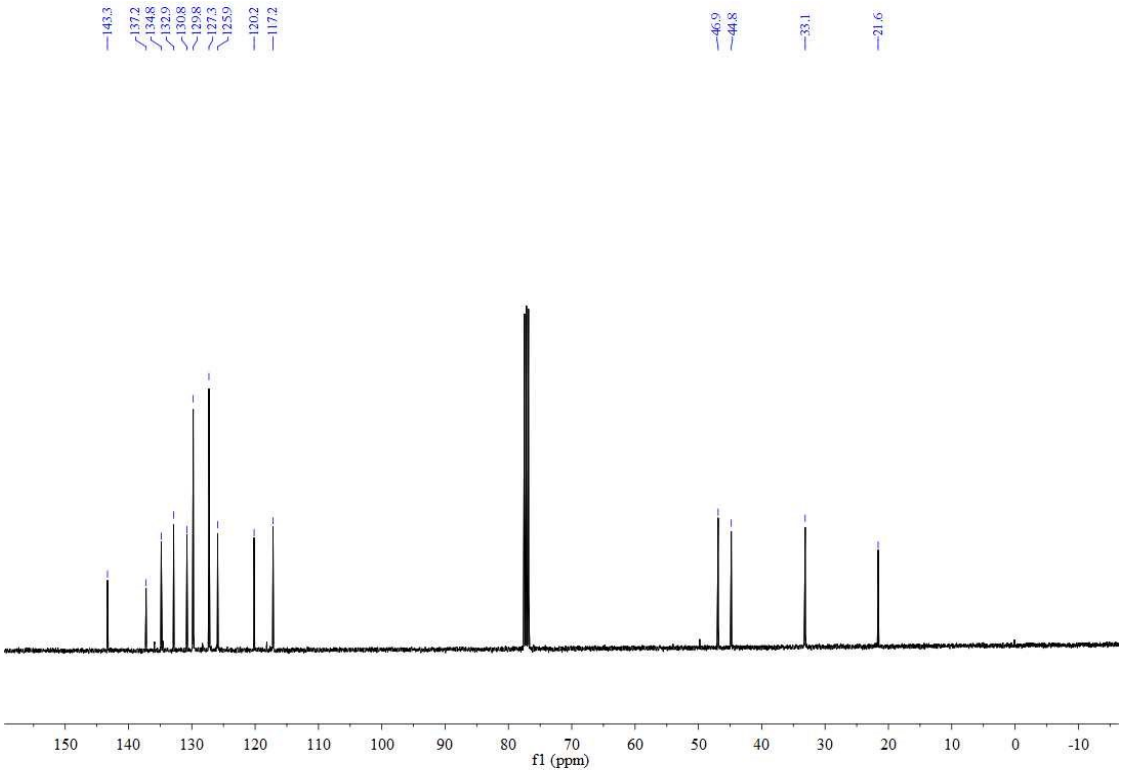
f1 (ppm)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134.8
132.9
130.8
129.8
127.3
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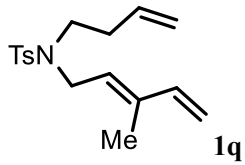
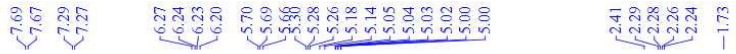
120.2
117.2
46.9
44.8
33.1
21.6
f1 (ppm)


TsN
Me

1q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5.28
5.26
5.18
5.14
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5.02
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5.00
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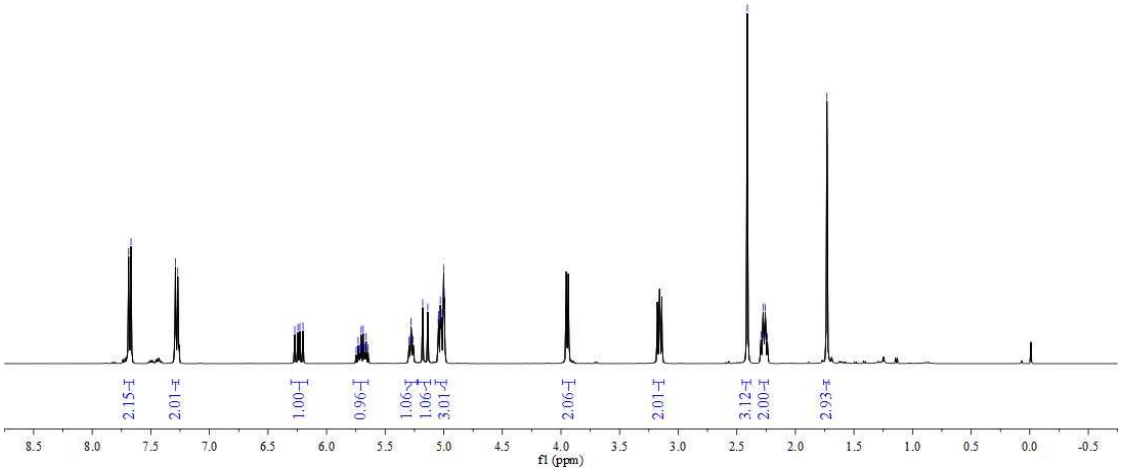
2.28
2.26
2.24
1.73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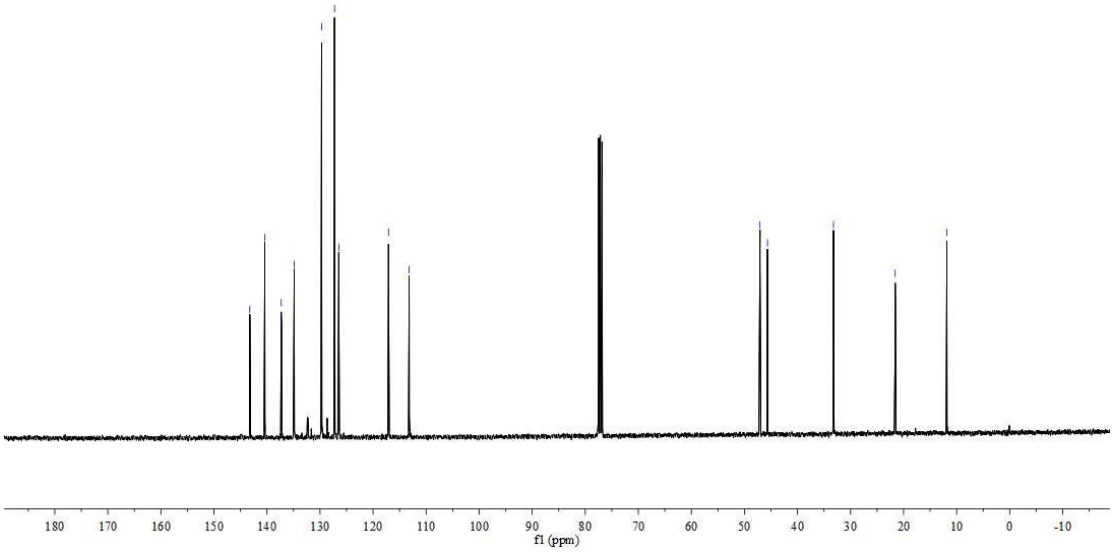
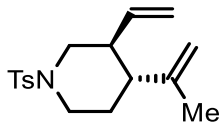
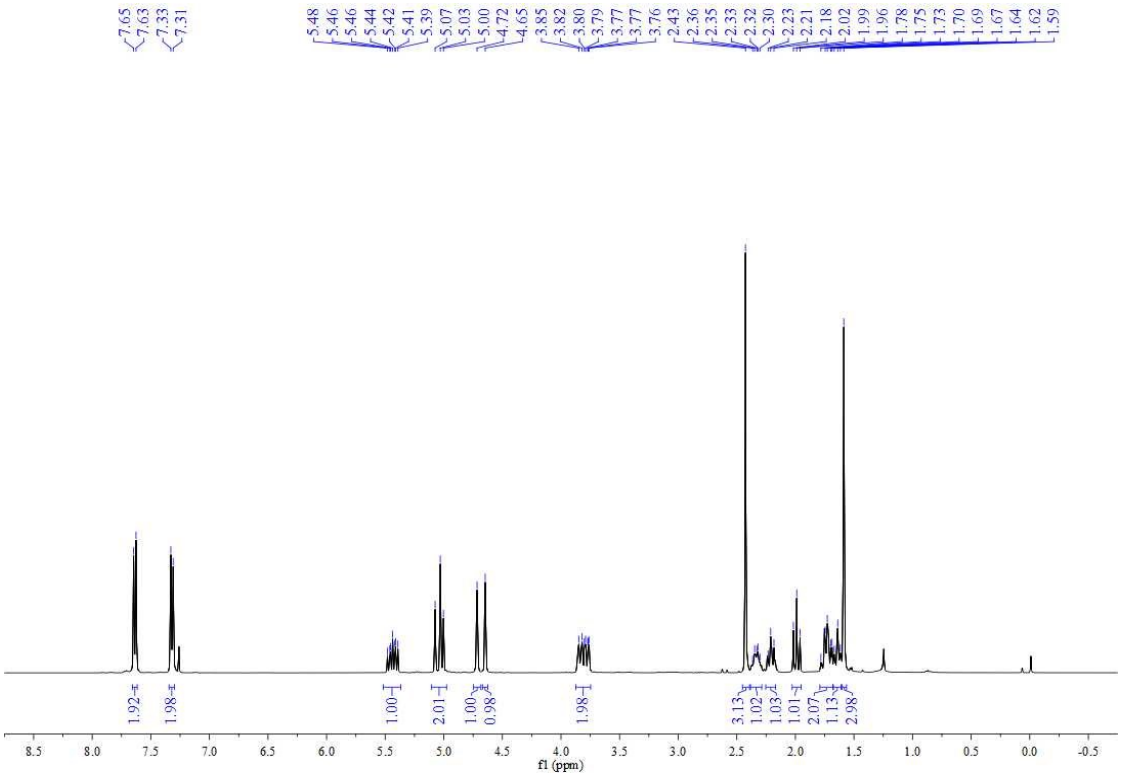
1.06
1.06
3.01
2.06
2.01
3.12
2.00
2.93
f1 (ppm)


143.2
140.4
137.3
137.2
134.9
129.7
127.3
126.5
117.1
113.2
47.1
45.7
33.2
21.6
11.8


f1 (ppm)


TsN
Me

2a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7.63
7.33
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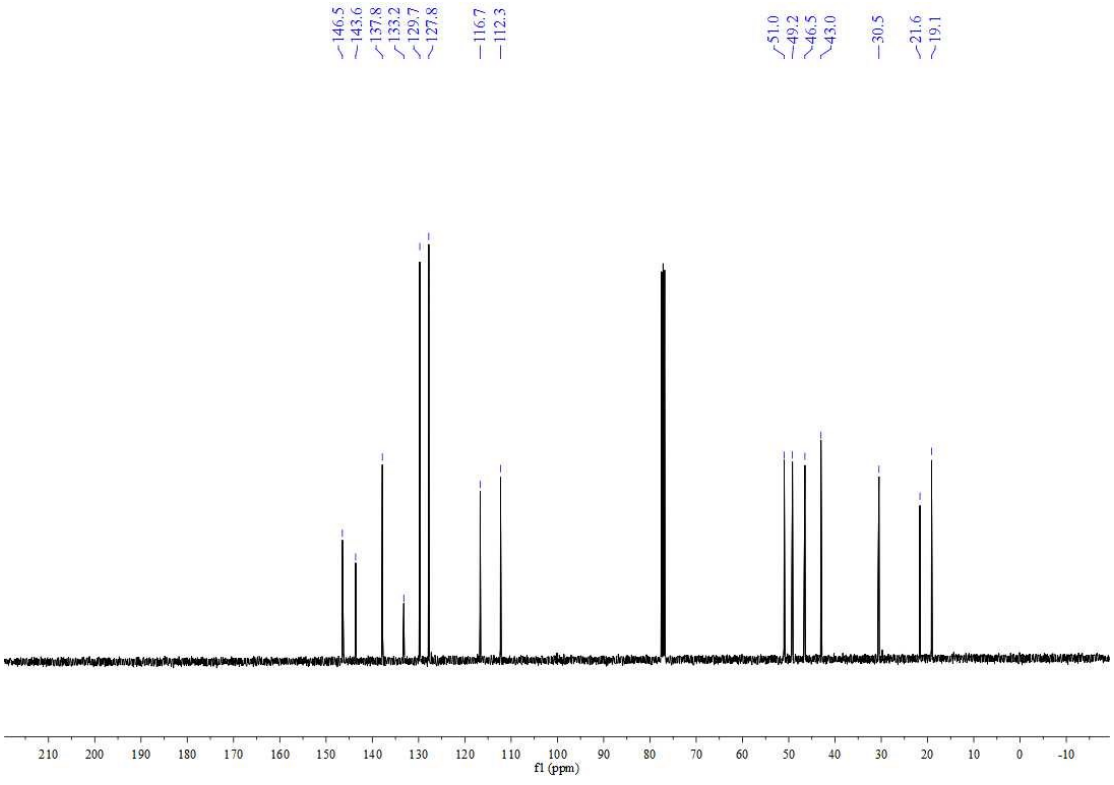
5.46
5.46
5.44
5.42
5.41
5.39
5.07
5.03
5.00
4.72
4.65
3.85
3.82
3.80
3.79
3.77
3.77
3.76
2.43
2.36
2.35
2.33
2.32
2.30
2.23
2.21
2.18
2.02
1.99
1.96
1.78
1.75
1.73
1.70
1.69
1.67
1.64
1.62
1.59
1.92
1.98
1.00
2.01
1.00
0.98
1.98
3.13
1.02
1.03
1.01
2.07
1.13
2.98
f1 (ppm)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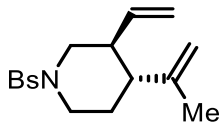
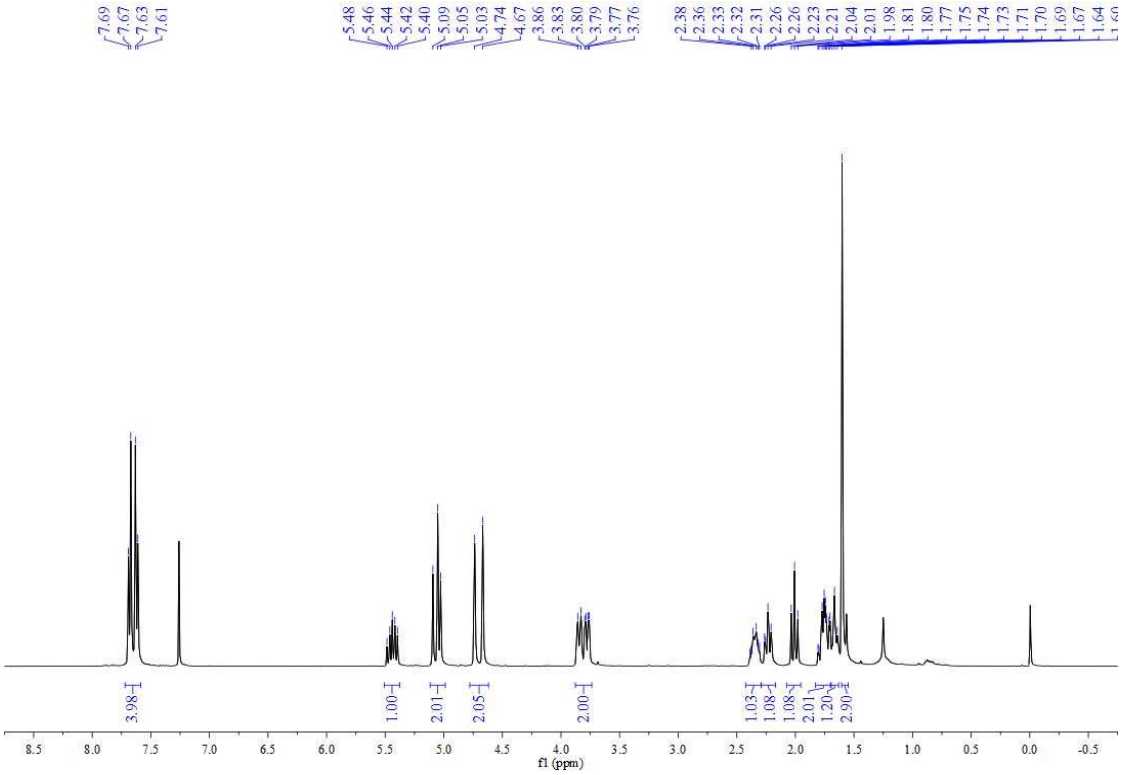
137.8
133.2
129.7
127.8
116.7
112.3
51.0
49.2
46.5
43.0
30.5
21.6
19.1
f1 (ppm)


BsN
Me

2b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7.67
7.63
7.61
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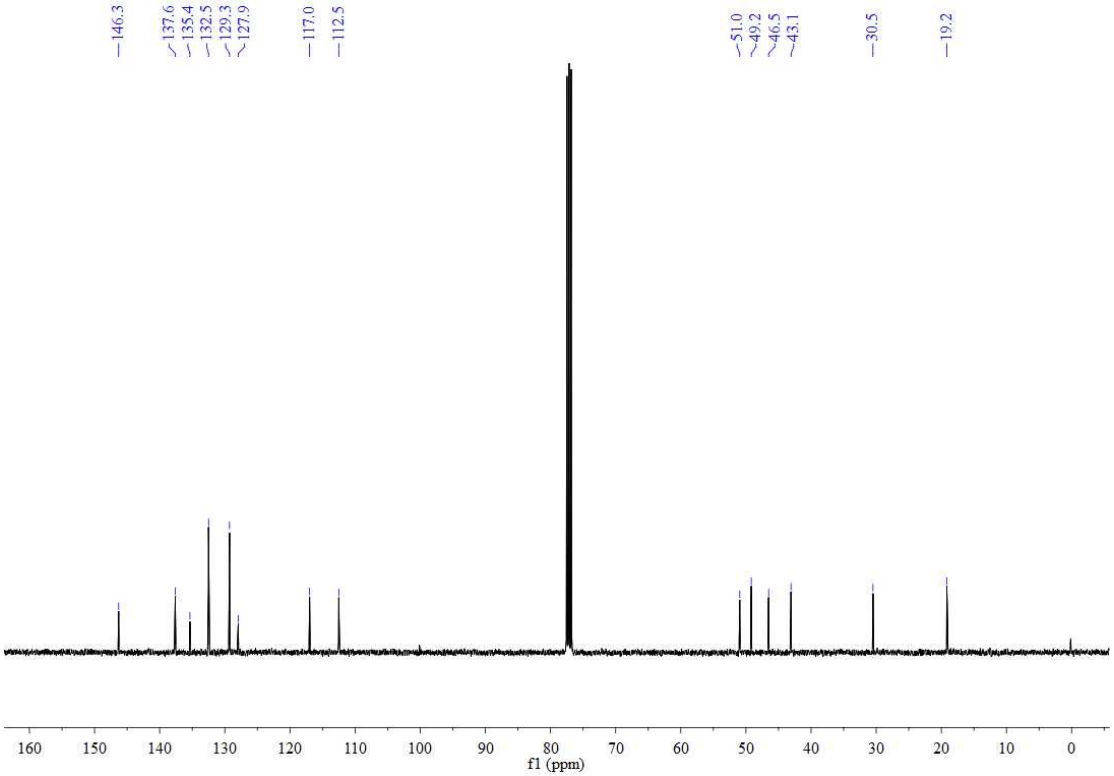
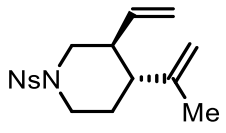
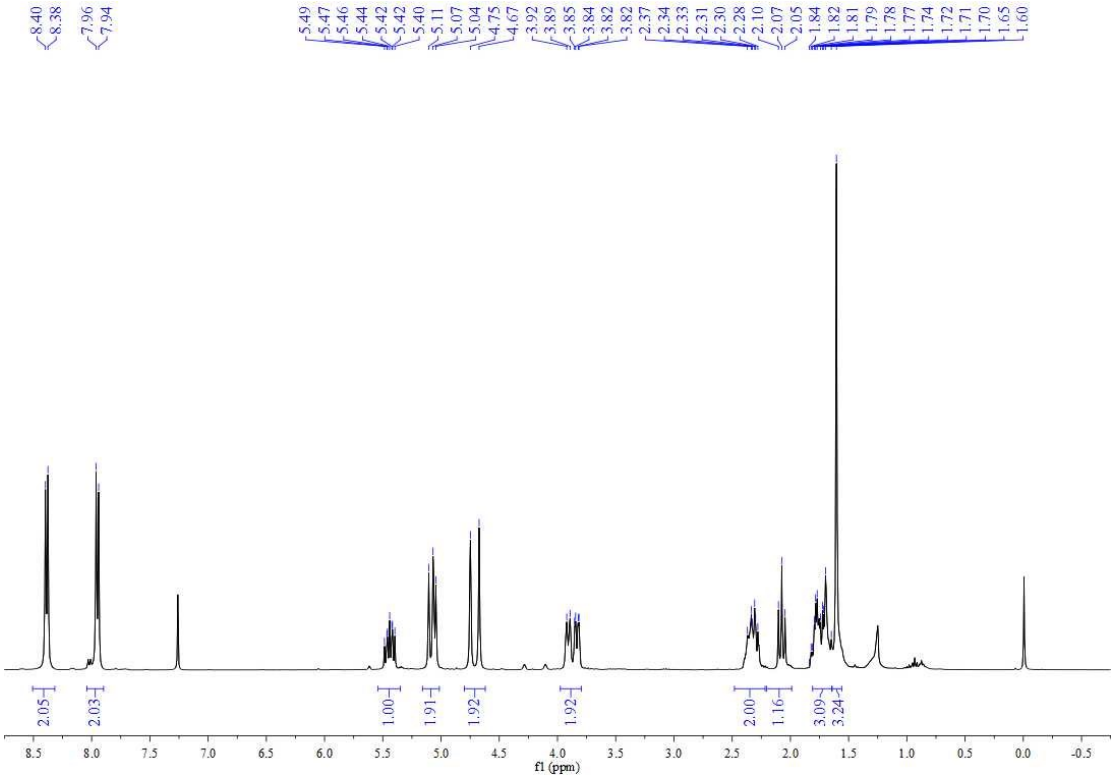
5.46
5.44
5.42
5.40
5.09
5.05
5.03
4.74
4.67
3.86
3.83
3.80
3.79
3.77
3.76
2.38
2.36
2.33
2.32
2.31
2.26
2.26
2.23
2.21
2.04
2.01
1.98
1.81
1.80
1.77
1.75
1.74
1.73
1.71
1.70
1.69
1.67
1.64
3.98
1.00
2.01
2.05
2.00
1.03
1.08
1.08
2.01
1.20
2.90
f1 (ppm)


146.3
137.6
135.4
132.5
129.3
127.9
117.0
112.5
51.0
49.2
46.5
43.1
30.5
19.2
f1 (ppm)


NsN
Me

2c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7.94
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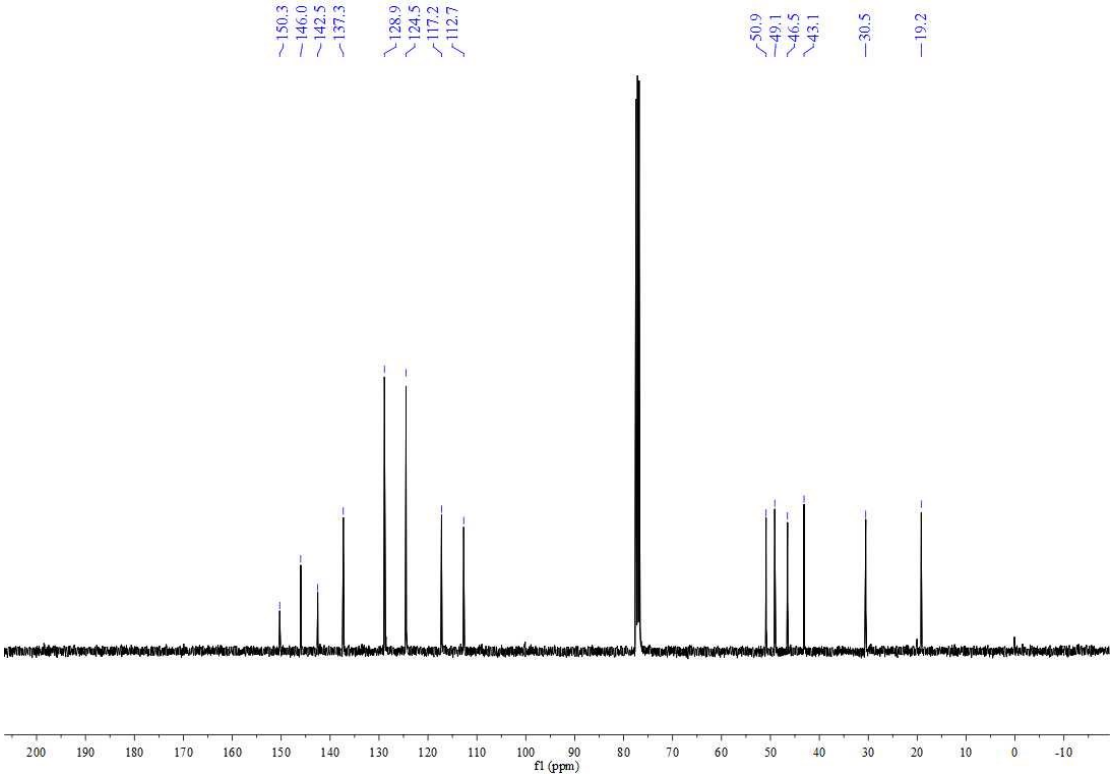
5.47
5.46
5.44
5.42
5.42
5.40
5.11
5.07
5.04
4.75
4.67
3.92
3.89
3.85
3.84
3.82
3.82
2.37
2.34
2.33
2.31
2.30
2.28
2.10
2.07
2.05
1.84
1.82
1.81
1.79
1.78
1.77
1.74
1.72
1.71
1.70
1.65
1.60
2.05
2.03
1.00
1.91
1.92
1.92
2.00
1.16
3.09
3.24
f1 (ppm)


150.3
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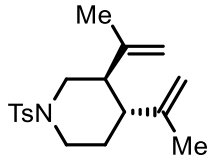
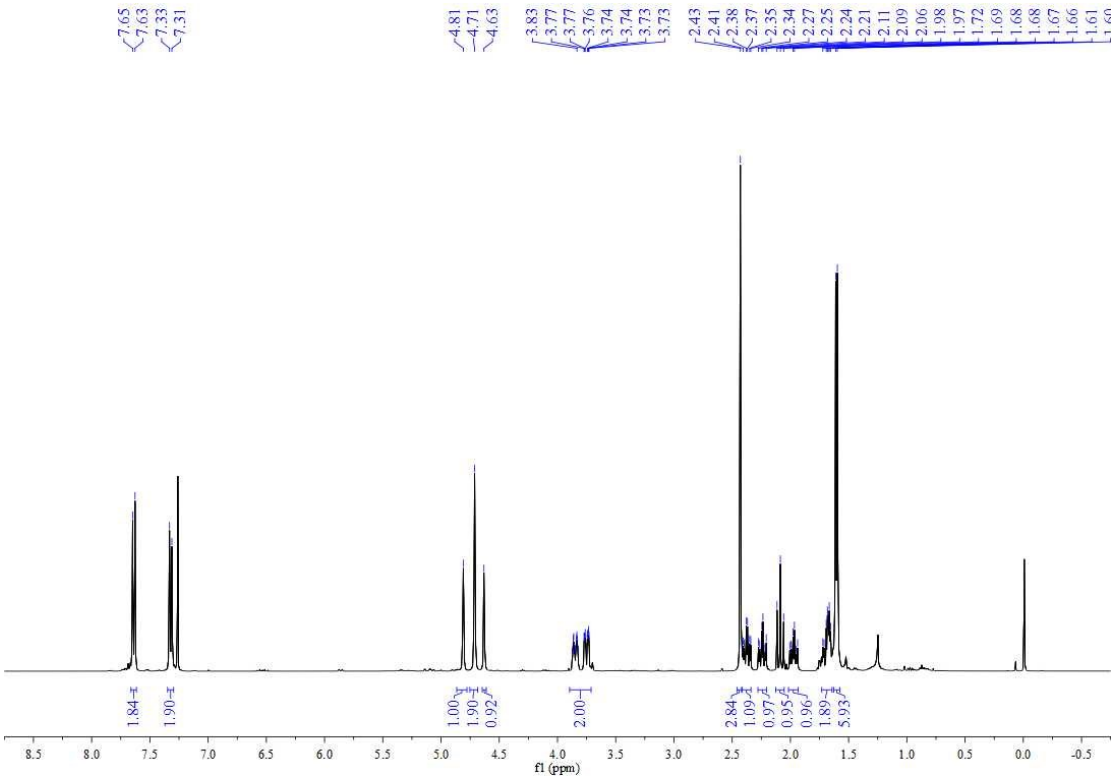
142.5
137.3
128.9
124.5
117.2
112.7
50.9
49.1
46.5
43.1
30.5
19.2
f1 (ppm)


Me
TsN
Me

2f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7.63
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7.31
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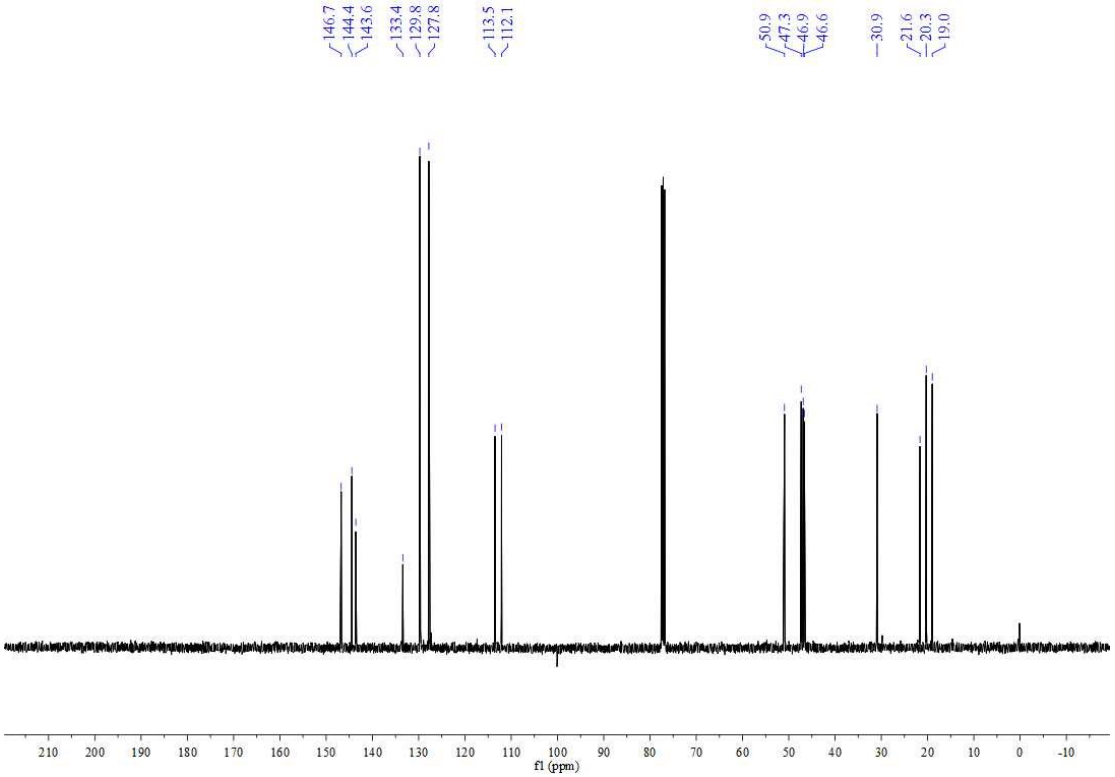
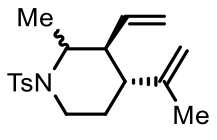
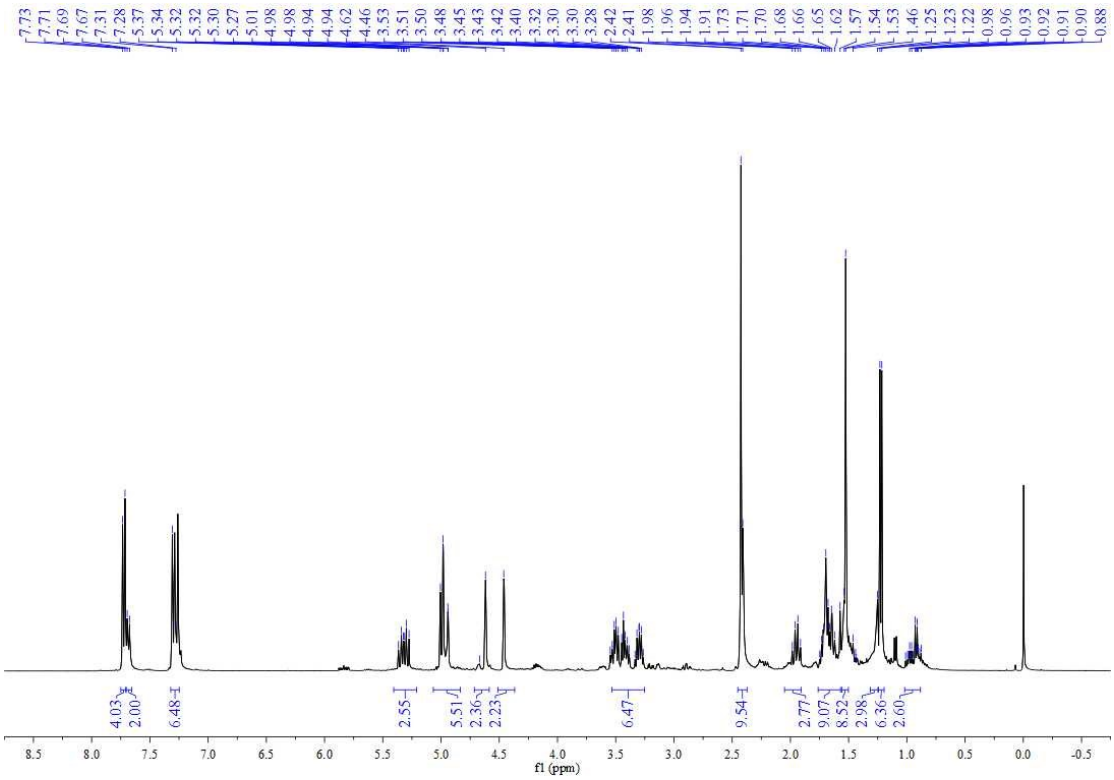
4.63
3.83
3.77
3.77
3.76
3.74
3.74
3.73
3.73
2.43
2.41
2.38
2.37
2.35
2.34
2.27
2.25
2.24
2.21
2.11
2.09
2.06
1.98
1.97
1.72
1.69
1.68
1.68
1.67
1.66
1.61
1.84
1.90
1.00
1.90
0.92
2.00
2.84
1.09
0.97
0.95
0.96
1.89
5.93
f1 (ppm)


146.7
144.4
143.6
133.4
129.8
127.8
113.5
112.1
50.9
47.3
46.9
46.6
30.9
21.6
20.3
19.0
f1 (ppm)


Me
TsN
Me

2g


7.73
7.71
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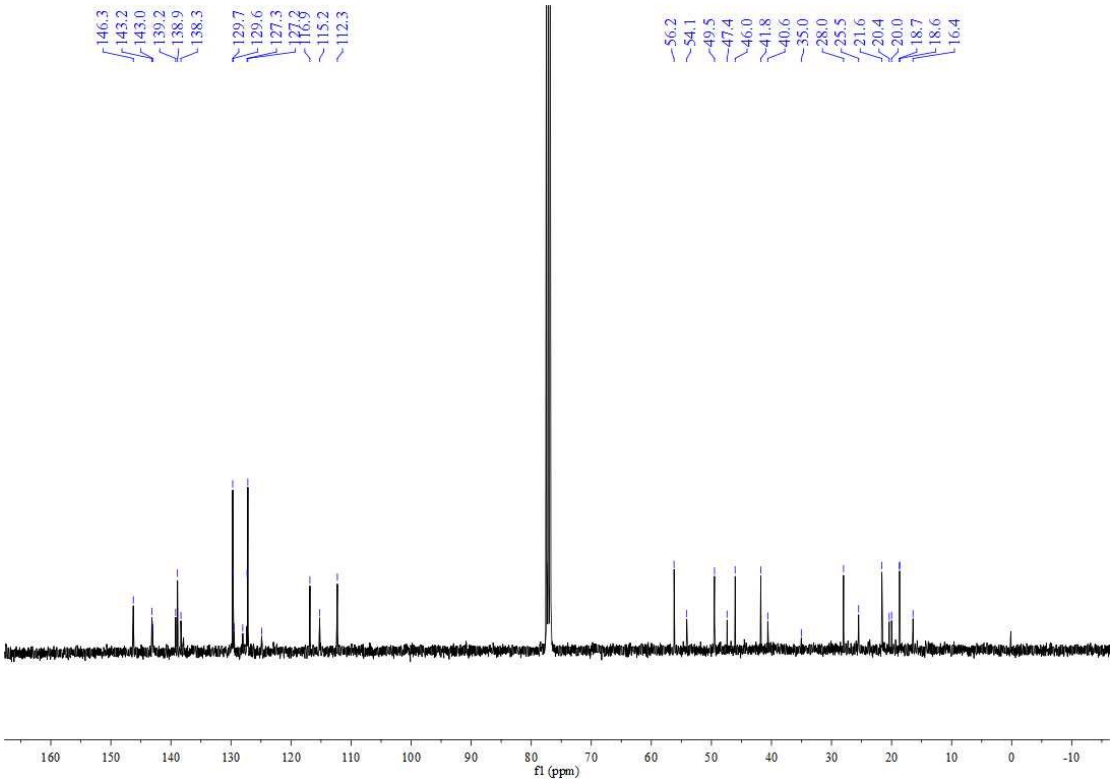
7.67
7.31
7.28
5.37
5.34
5.32
5.32
5.30
5.27
5.01
4.98
4.98
4.94
4.94
4.62
4.46
3.53
3.51
3.50
3.48
3.45
3.43
3.42
3.40
3.32
3.30
3.30
3.28
2.42
2.41
1.98
1.96
1.94
1.91
1.73
1.71
1.70
1.68
1.66
1.65
1.62
1.57
1.54
1.53
1.46
1.25
1.23
1.22
0.98
0.96
0.93
0.92
0.91
0.90
0.88
4.03
2.00
6.48
2.55
5.51
2.36
2.23
6.47
9.54
2.77
9.07
8.52
2.98
6.36
2.60
f1 (ppm)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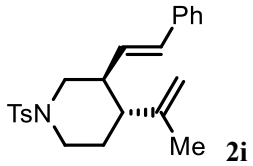
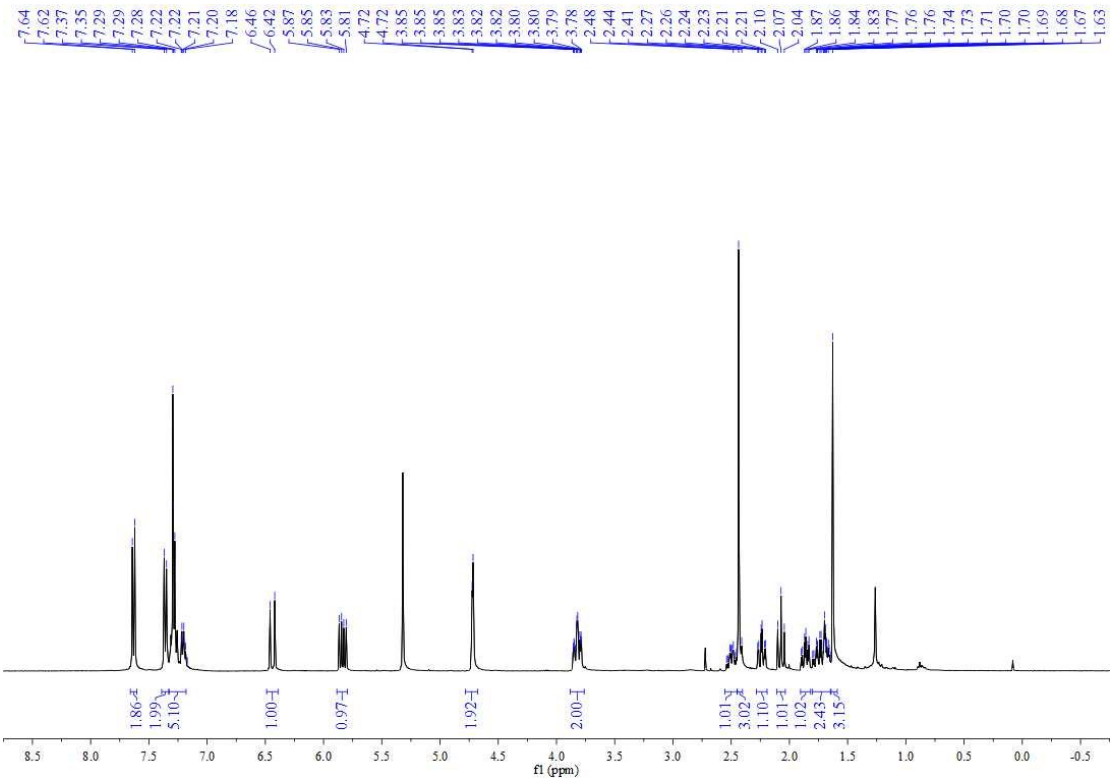
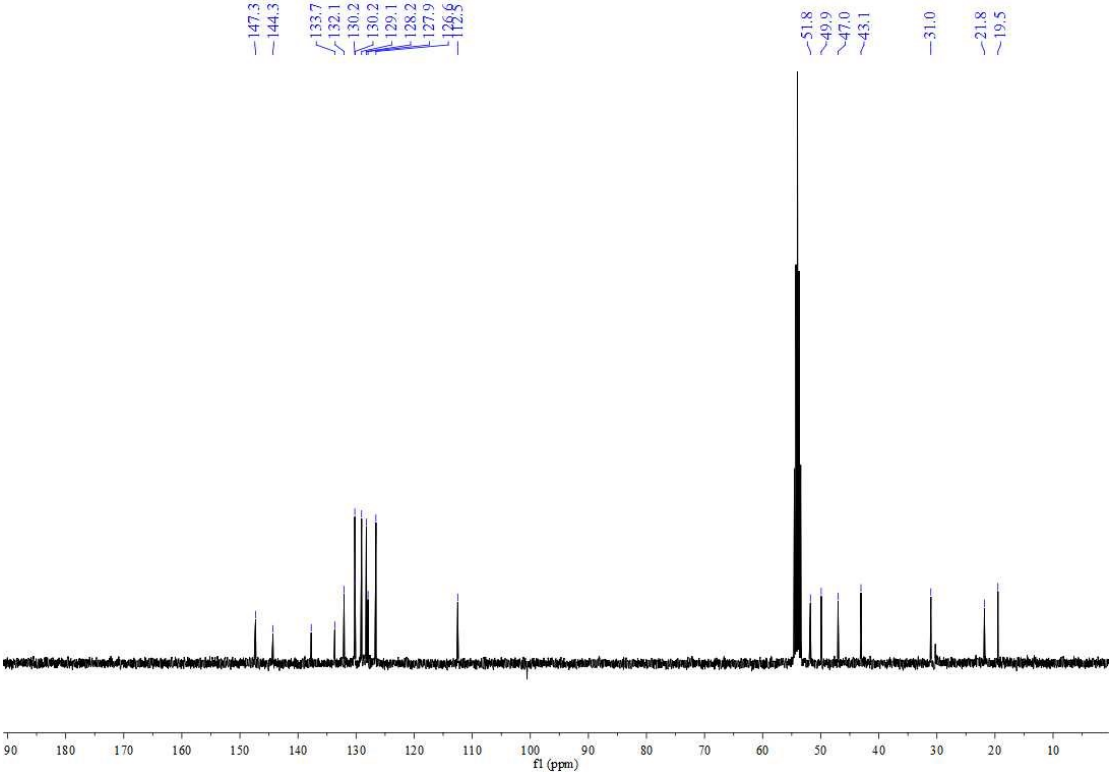
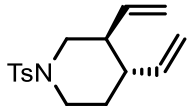
143.2
143.0
139.2
138.9
138.3
129.7
129.6
127.3
127.2
116.9
115.2
112.3
56.2
54.1
49.5
47.4
46.0
41.8
40.6
35.0
28.0
25.5
21.6
20.4
20.0
18.7
18.6
16.4
f1 (ppm)


Ph
TsN
Me

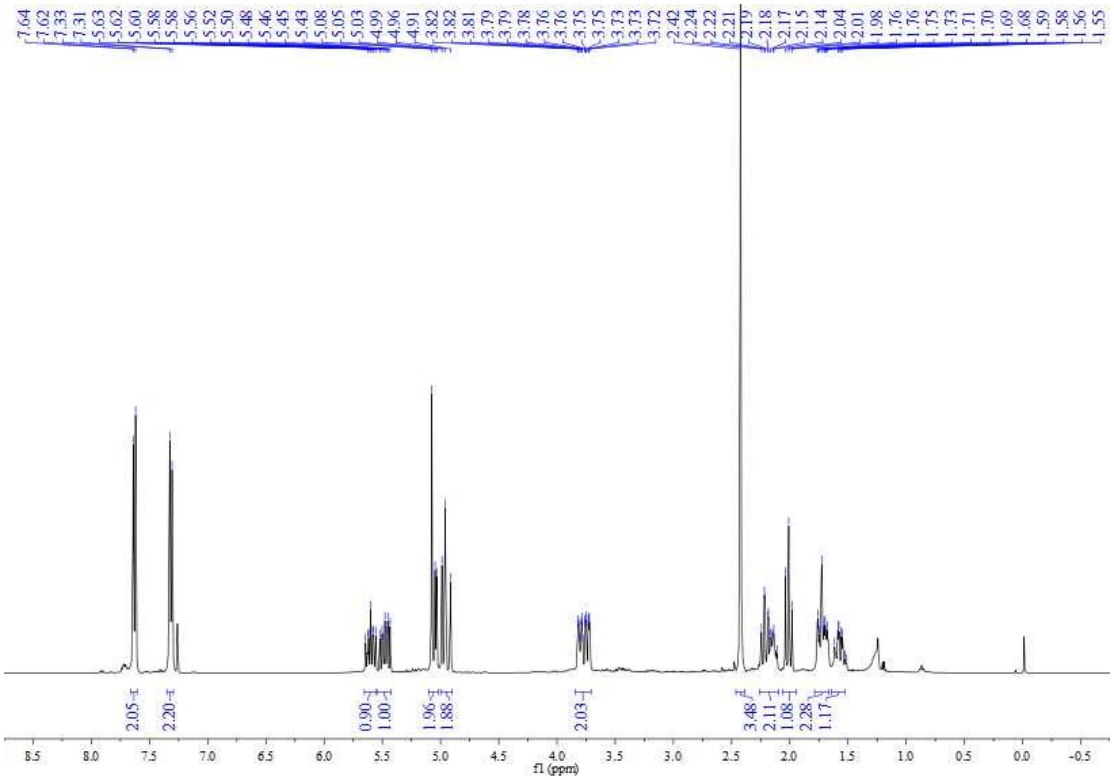
2i


7.64 7.62 7.37 7.35 7.29 7.29 7.28 7.22 7.22 7.21 7.20 7.18 6.46 6.42 5.87 5.85 5.83 5.81 4.72 4.72 3.85 3.85 3.85 3.83 3.82 3.82 3.80 3.80 3.79 3.78 2.48 2.44 2.41 2.27 2.26 2.24 2.23 2.21 2.21 2.10 2.07 2.04 1.87 1.86 1.84 1.83 1.77 1.76 1.76 1.74 1.73 1.71 1.70 1.70 1.69 1.68 1.67 1.63
1.86 1.99 5.10 1.00 0.97 1.92 2.00 1.01 3.02 1.10 1.01 1.02 2.43 3.15
f1 (ppm)


147.3 144.3 133.7 132.1 130.2 130.2 129.1 128.2 127.9 126.6 125.8 51.8 49.9 47.0 43.1 31.0 21.8 19.5
f1 (ppm)


TsN

2j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5.62
5.60
5.58
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5.56
5.52
5.50
5.48
5.46
5.45
5.43
5.08
5.05
5.03
4.99
4.96
4.91
3.82
3.82
3.81
3.79
3.79
3.78
3.76
3.76
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2.15
2.14
2.04
2.01
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1.76
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1.75
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1.71
1.70
1.69
1.68
1.59
1.58
1.56
1.55
2.05
2.20
0.90
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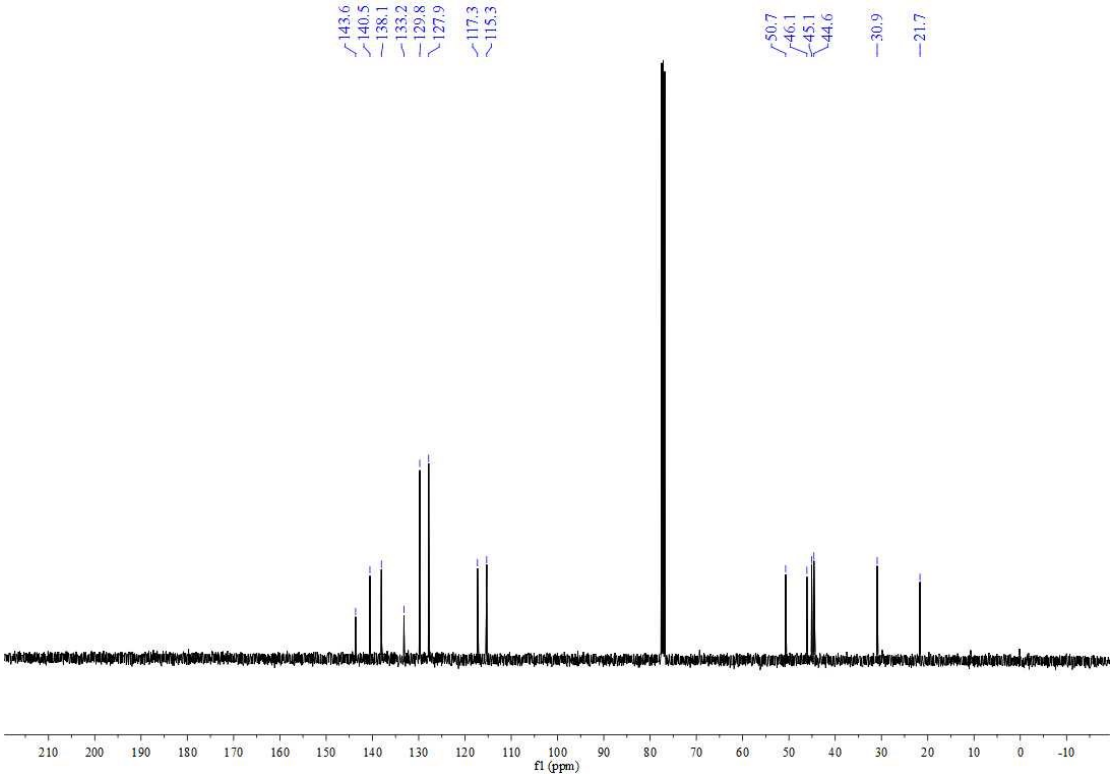
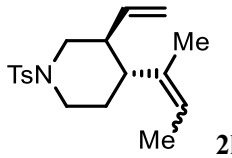
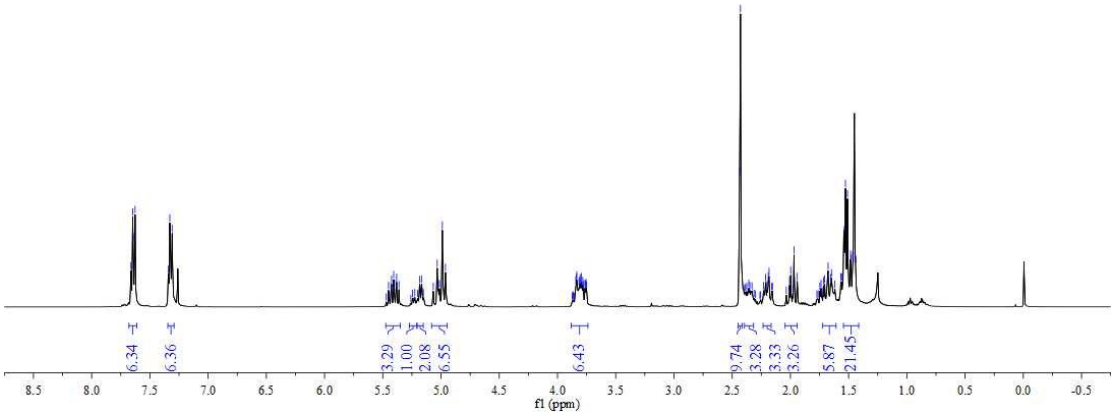
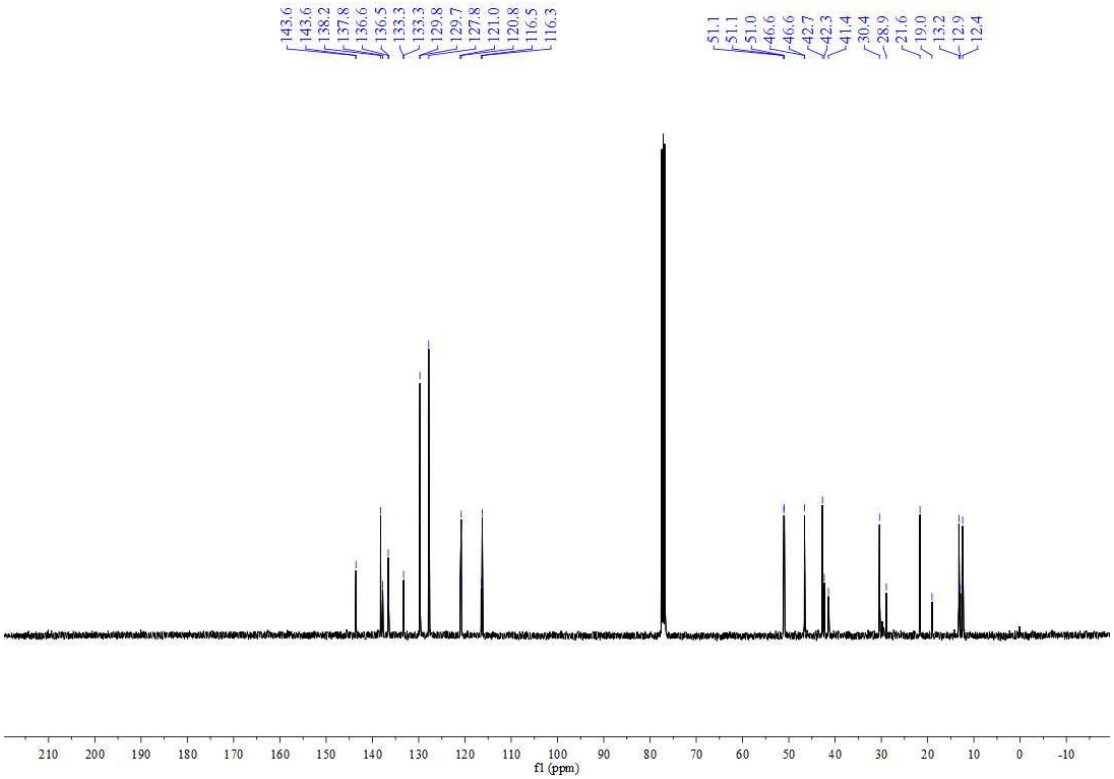
1.96
1.88
2.03
3.48
2.11
1.08
2.28
1.17
f1 (ppm)

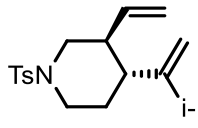

143.6
140.5
138.1
133.2
129.8
127.9
117.3
115.3
50.7
46.1
45.1
44.6
30.9
21.7
f1 (ppm)



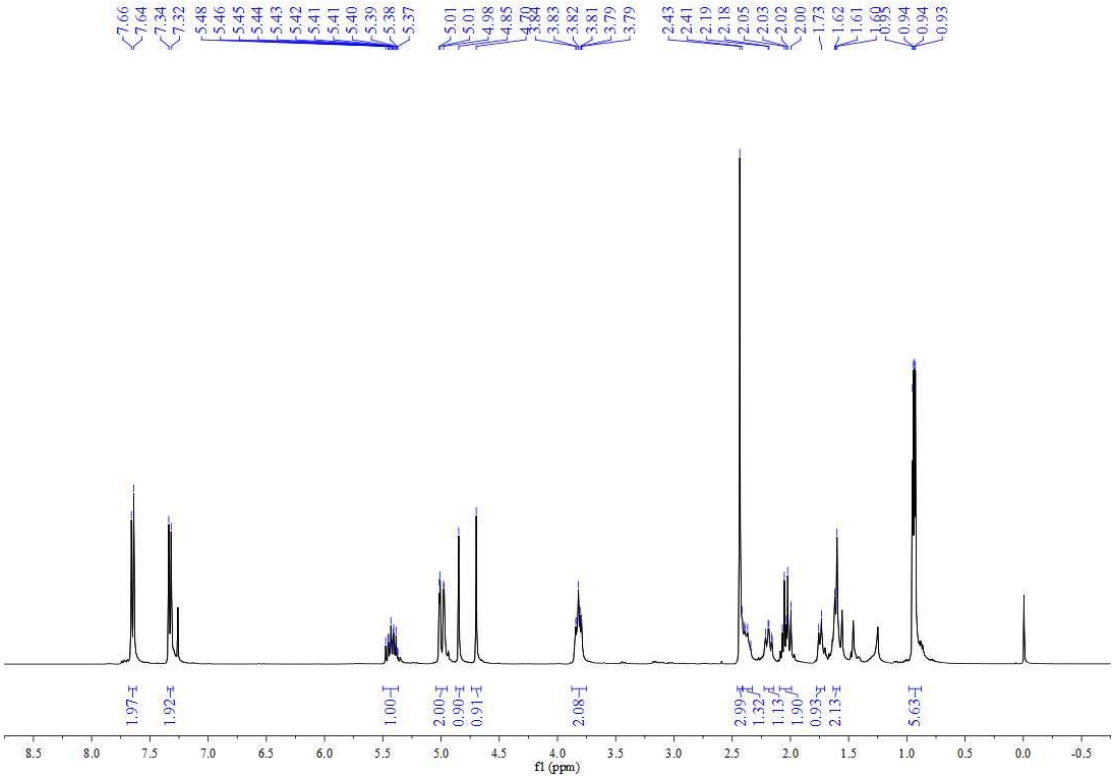
2k-iso






TsN
i-Pr

2l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7.32
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5.46
5.45
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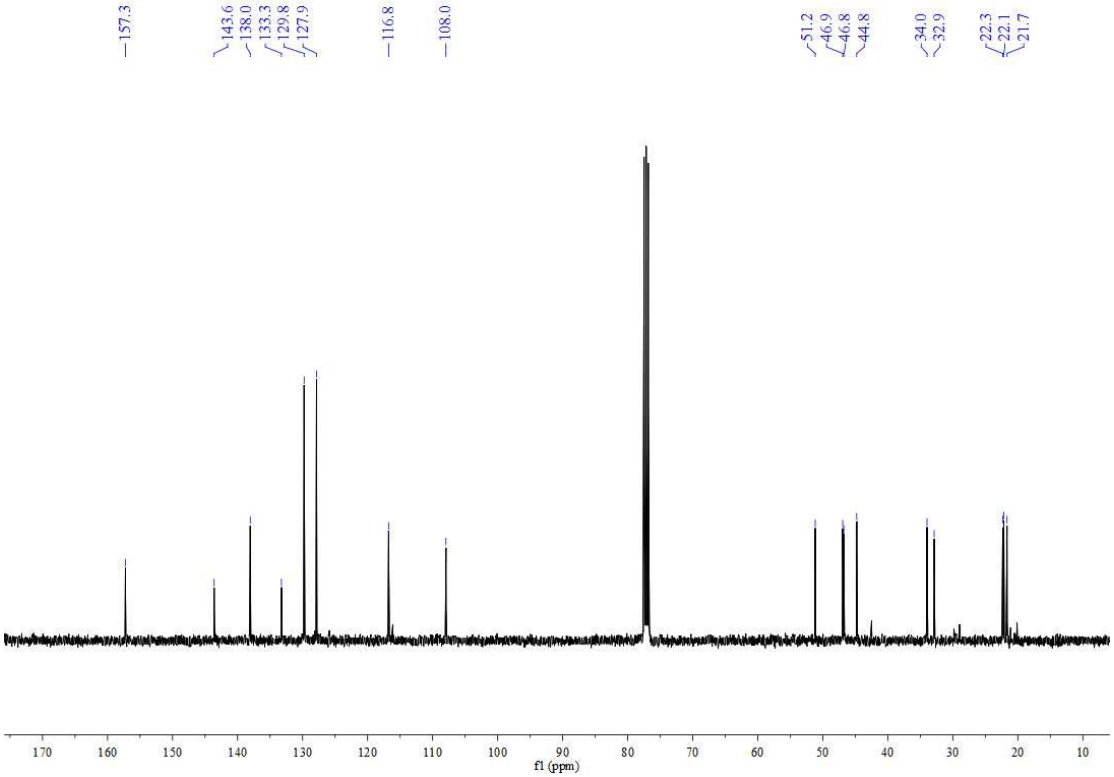
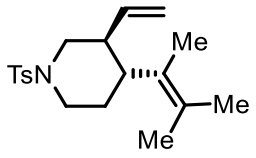
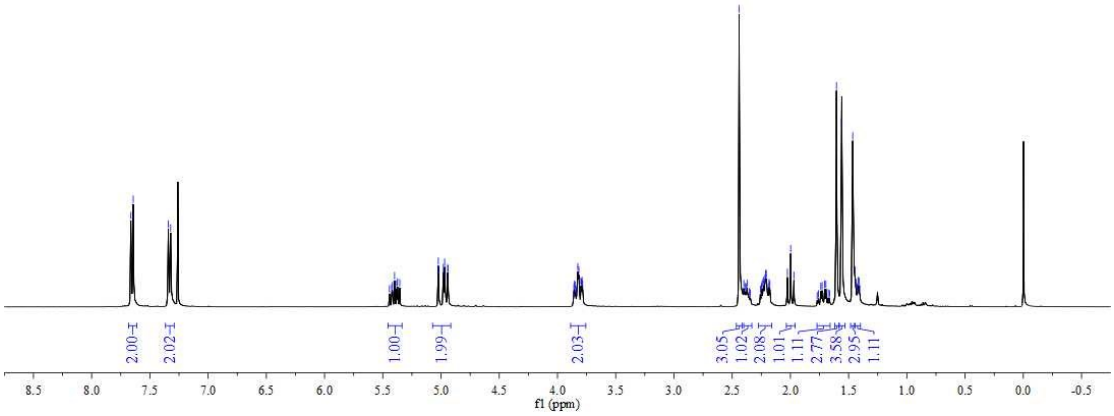
5.43
5.42
5.41
5.41
5.40
5.39
5.38
5.37
5.01
5.01
4.98
4.85
4.20
3.84
3.83
3.82
3.81
3.79
3.79
2.43
2.41
2.19
2.18
2.05
2.03
2.02
2.00
1.73
1.62
1.61
1.60
0.95
0.94
0.94
0.93
1.97
1.92
1.00
2.00
0.90
0.91
2.08
2.99
1.32
1.13
1.90
0.93
2.13
5.63
f1 (ppm)

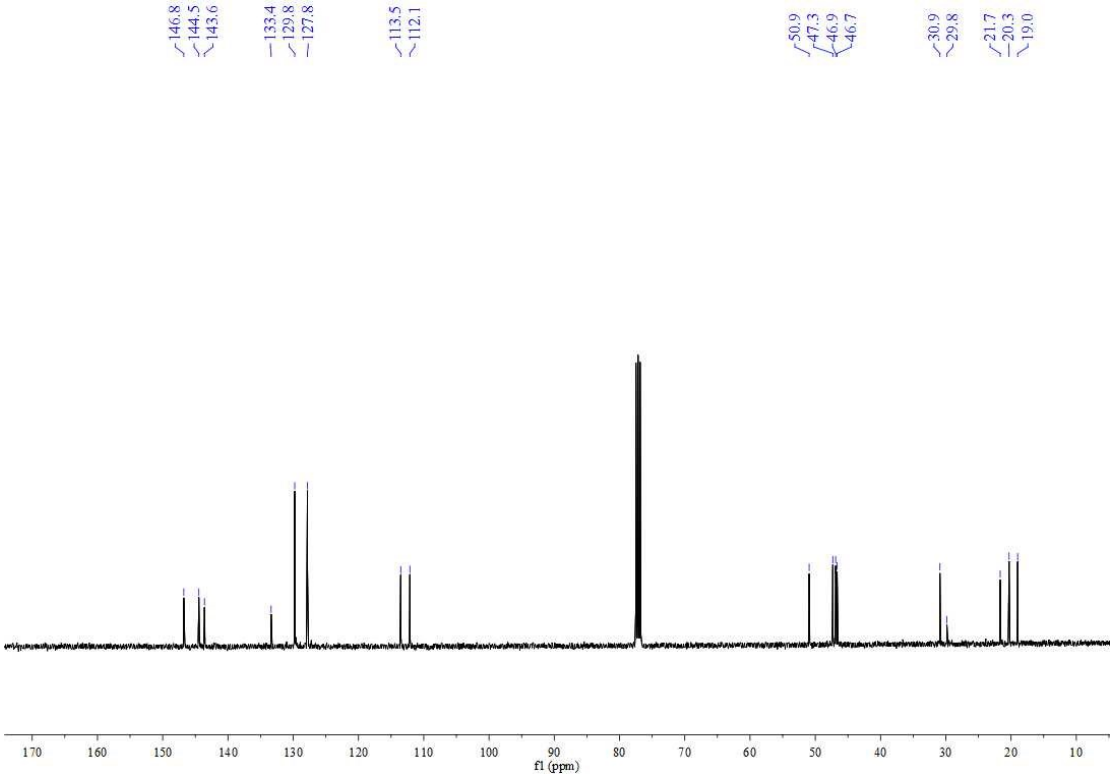

157.3
143.6
138.0
133.3
129.8
127.9
116.8
108.0
51.2
46.9
46.8
44.8
34.0
32.9
22.3
22.1
21.7
f1 (ppm)

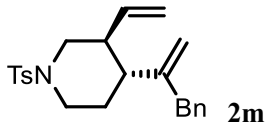

TsN
Me
Me
Me

2l-iso

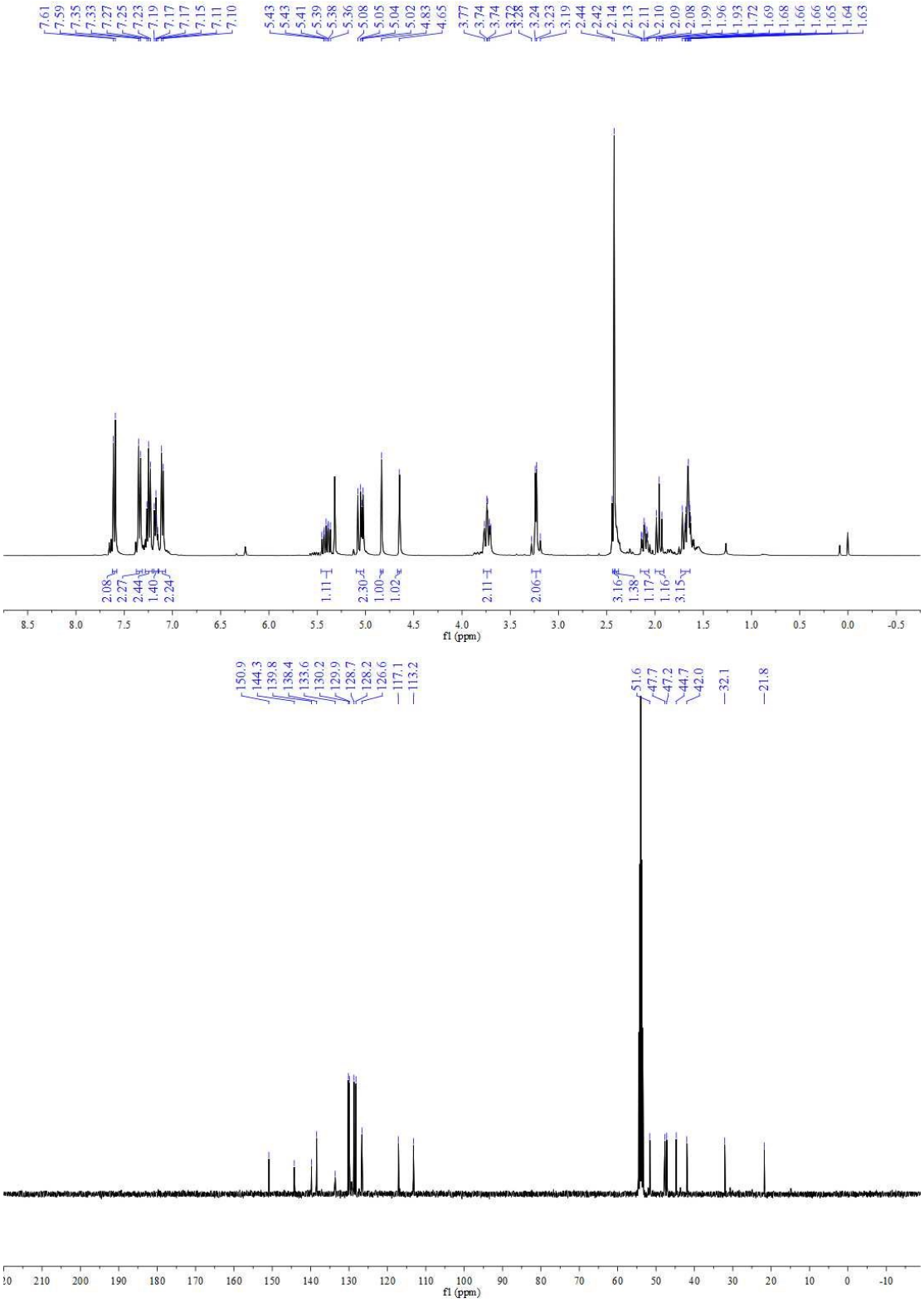

7.66 7.64 7.34 7.32 5.44 5.42 5.42 5.40 5.38 5.37 5.35 5.02 5.02 4.98 4.98 4.97 4.94 4.94 3.86 3.85 3.85 3.83 3.82 3.80 3.79 3.79 3.78 2.44 2.40 2.39 2.38 2.37 2.25 2.24 2.24 2.23 2.22 2.21 2.21 2.19 2.18 2.18 2.03 2.00 1.97 1.74 1.73 1.71 1.69 1.60 1.56 1.47 1.45 1.44 1.43 1.42 1.41 1.40

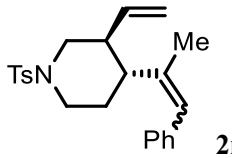

2.00 2.02 1.00 1.99 2.03 3.05 1.02 2.08 1.01 1.11 2.77 3.58 2.95 1.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.8 144.5 143.6 133.4 129.8 127.8 113.5 112.1 50.9 47.3 46.9 46.7 30.9 29.8 21.7 20.3 19.0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

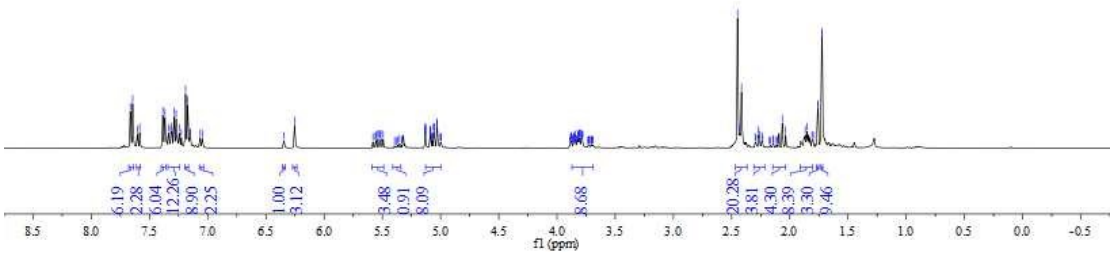


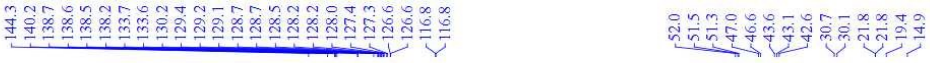
2m

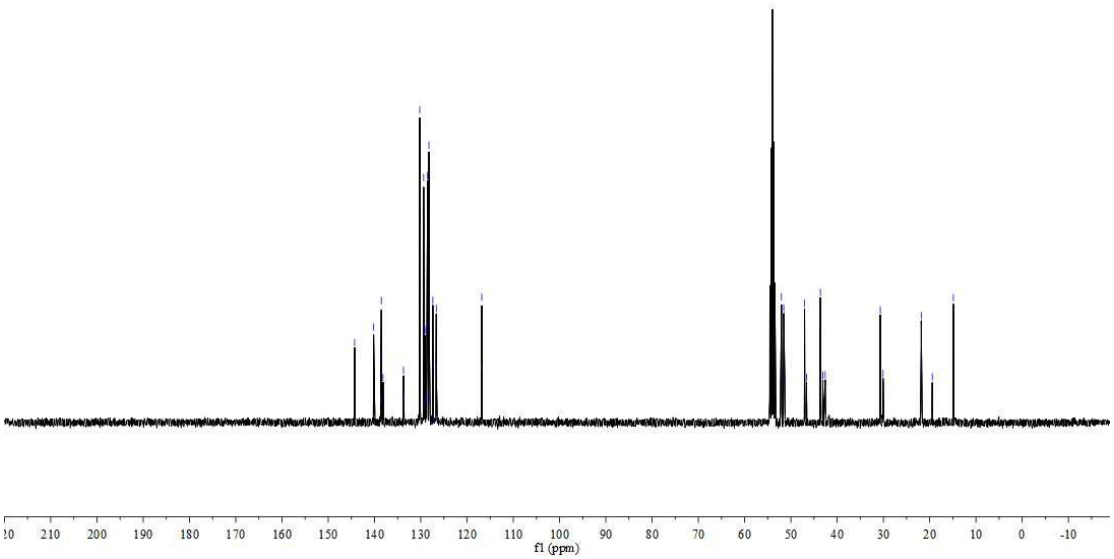


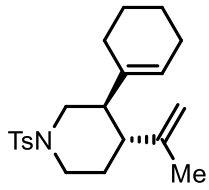


2m-iso



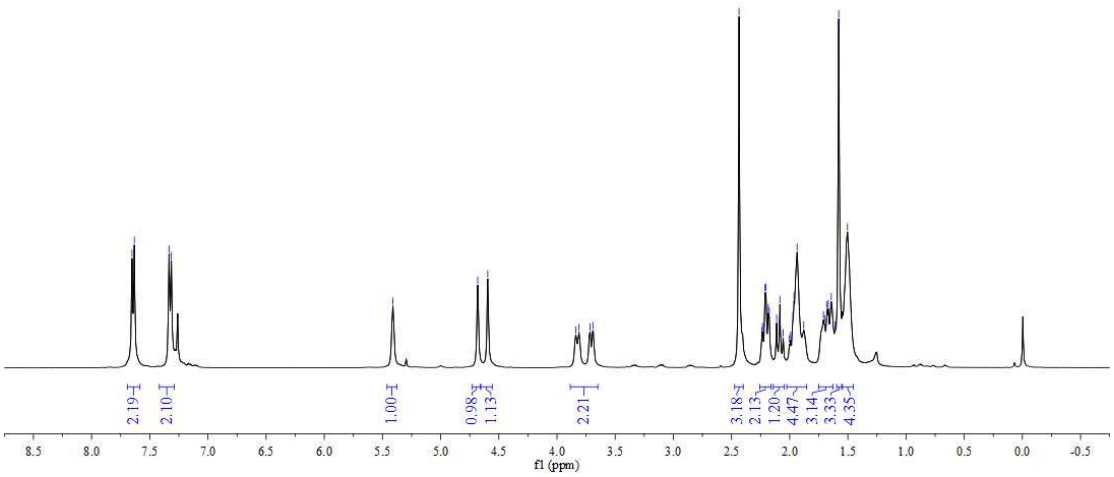


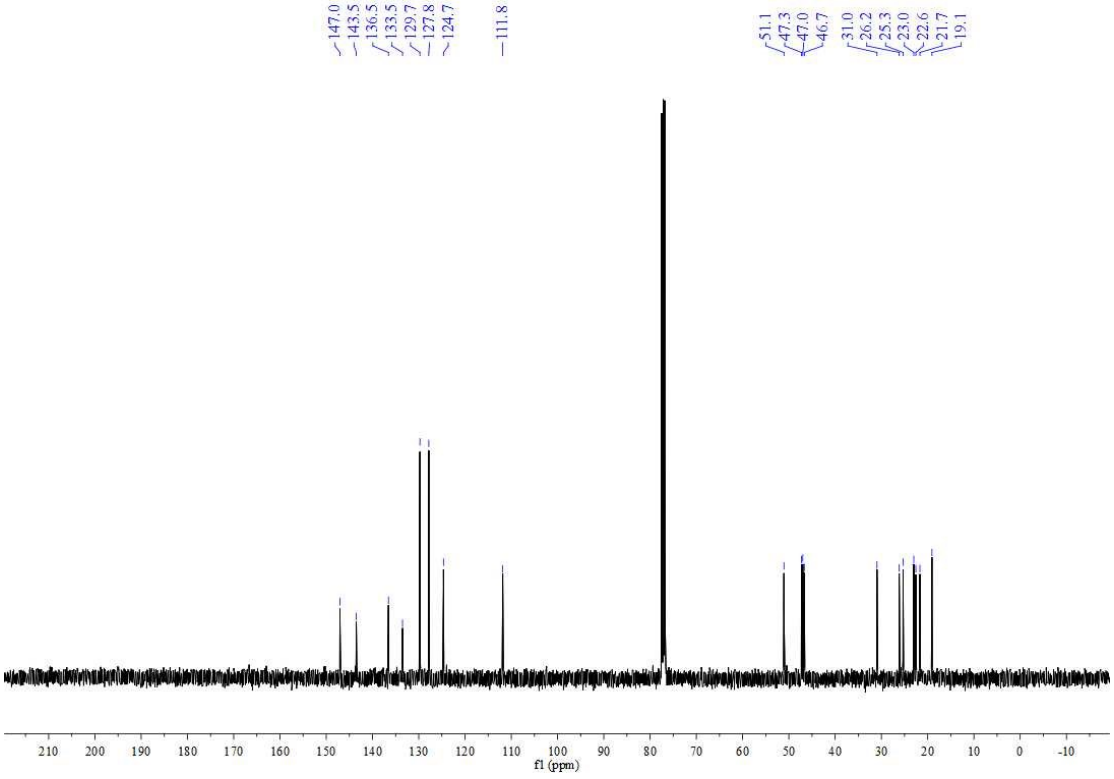


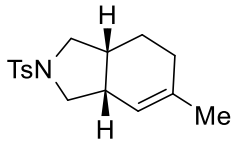

TsN
Me

2n

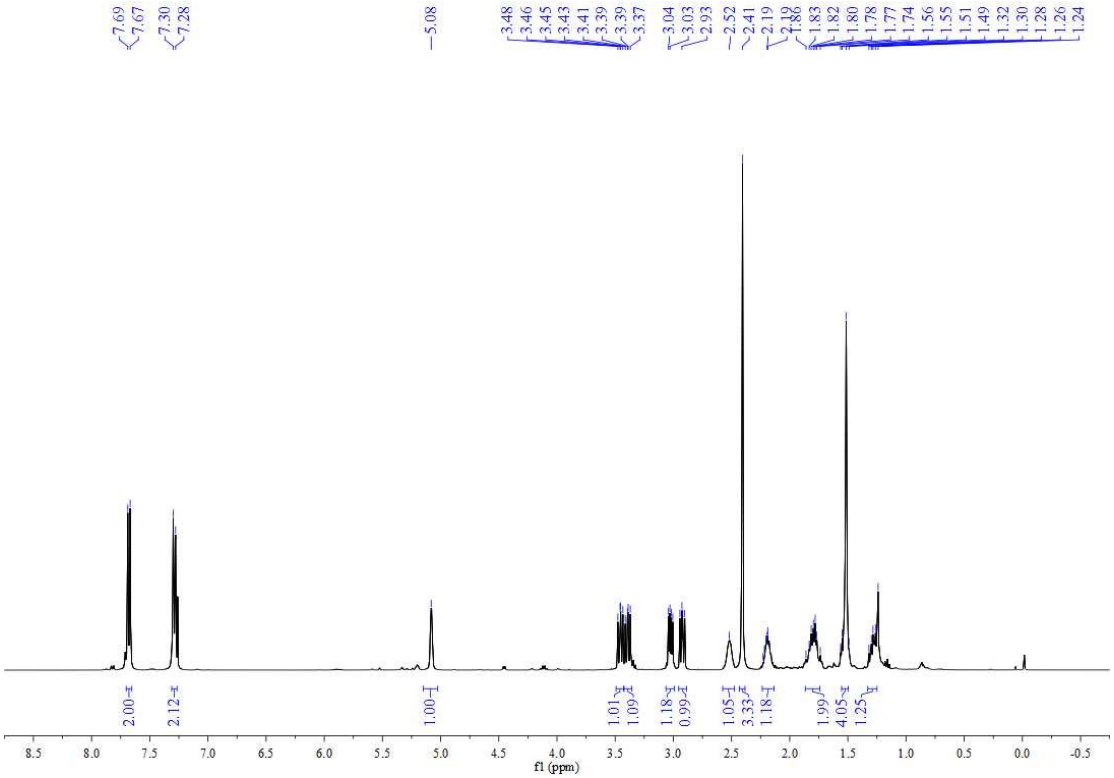

7.65
7.63
7.33
7.31
5.41
4.68
4.60
3.84
3.81
3.72
3.69
2.44
2.24
2.23
2.21
2.20
2.18
2.18
2.11
2.08
2.06
2.00
1.99
1.97
1.96
1.94
1.88
1.71
1.70
1.68
1.67
1.64
1.61
1.58
1.50

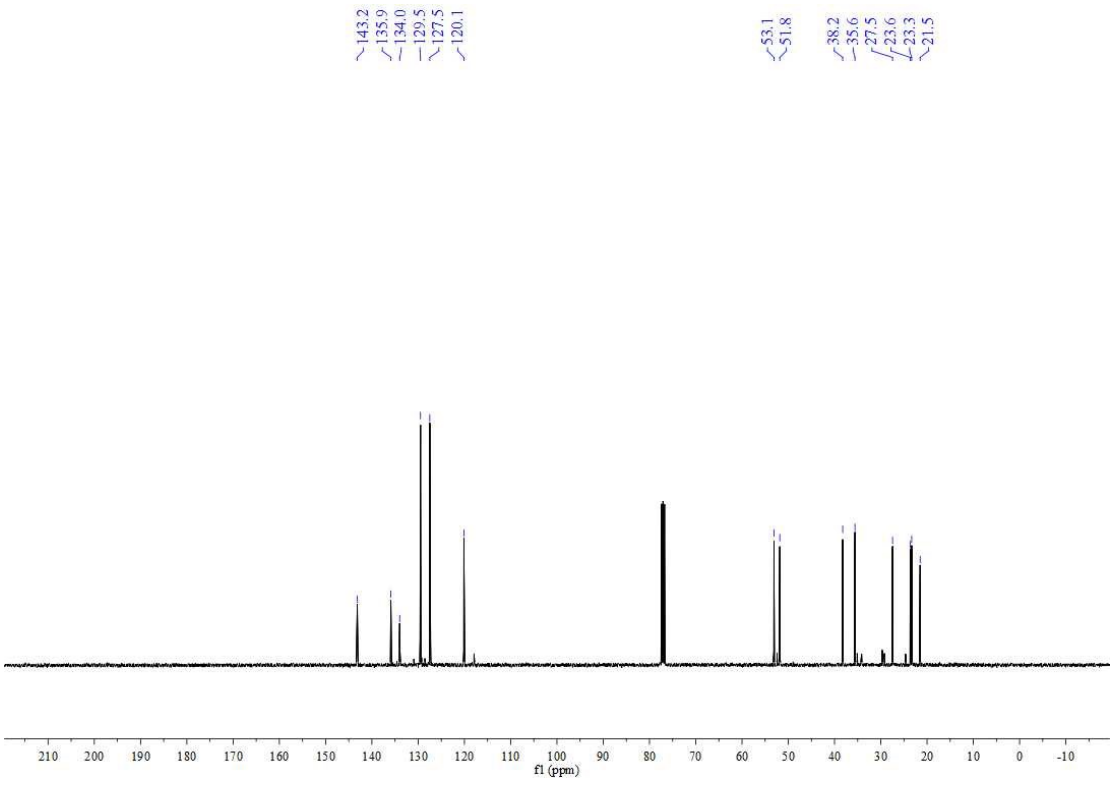

2.19
2.10
1.00
0.98
1.13
2.21
3.18
2.13
1.20
4.47
3.14
3.33
4.35
f1 (ppm)

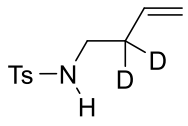

147.0
143.5
136.5
133.5
129.7
127.8
124.7
111.8
51.1
47.3
47.0
46.7
31.0
26.2
25.3
23.0
22.6
21.7
19.1
f1 (ppm)


H
TsN
Me
H

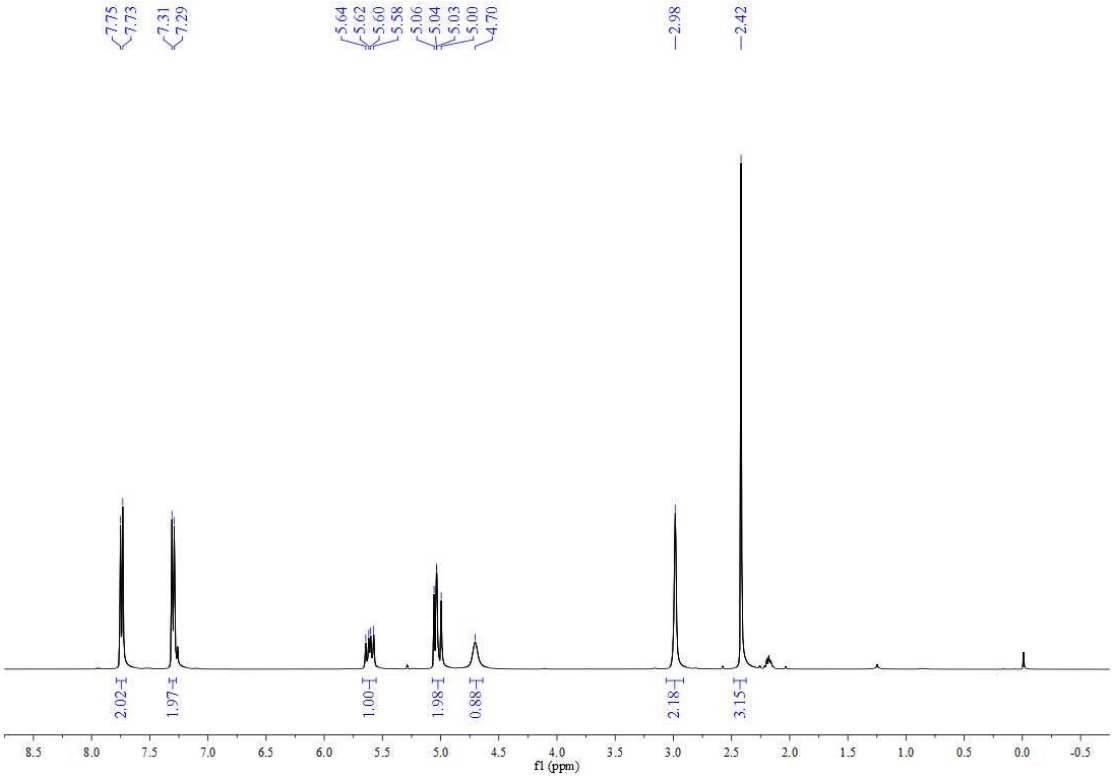
2r-DA

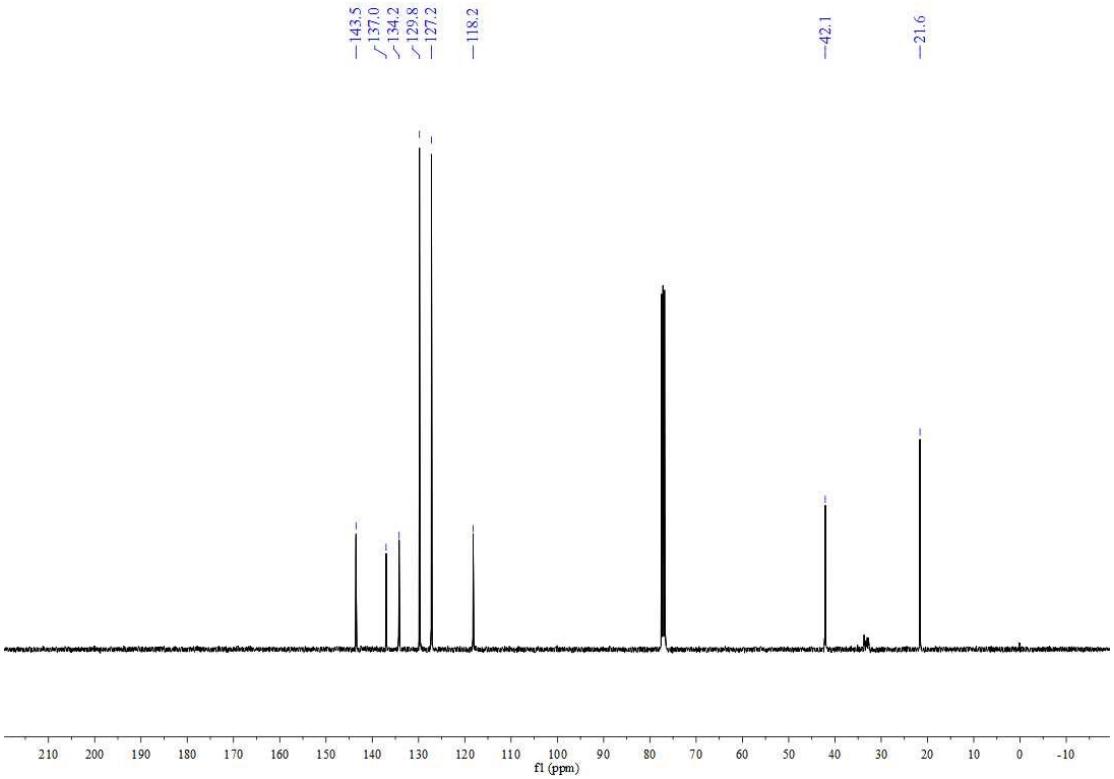

7.69
7.67
7.30
7.28
5.08
3.48
3.46
3.45
3.43
3.41
3.39
3.39
3.37
3.04
3.03
2.93
2.52
2.41
2.19
1.86
1.83
1.82
1.80
1.78
1.77
1.74
1.56
1.55
1.51
1.49
1.32
1.30
1.28
1.26
1.24
2.00
2.12
1.00
1.01
1.09
1.18
0.99
1.05
3.33
1.18
1.99
4.05
1.25
f1 (ppm)

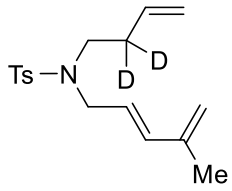

143.2
135.9
134.0
129.5
127.5
120.1
53.1
51.8
38.2
35.6
27.5
23.6
23.3
21.5
f1 (ppm)


Ts
N
H
D
D

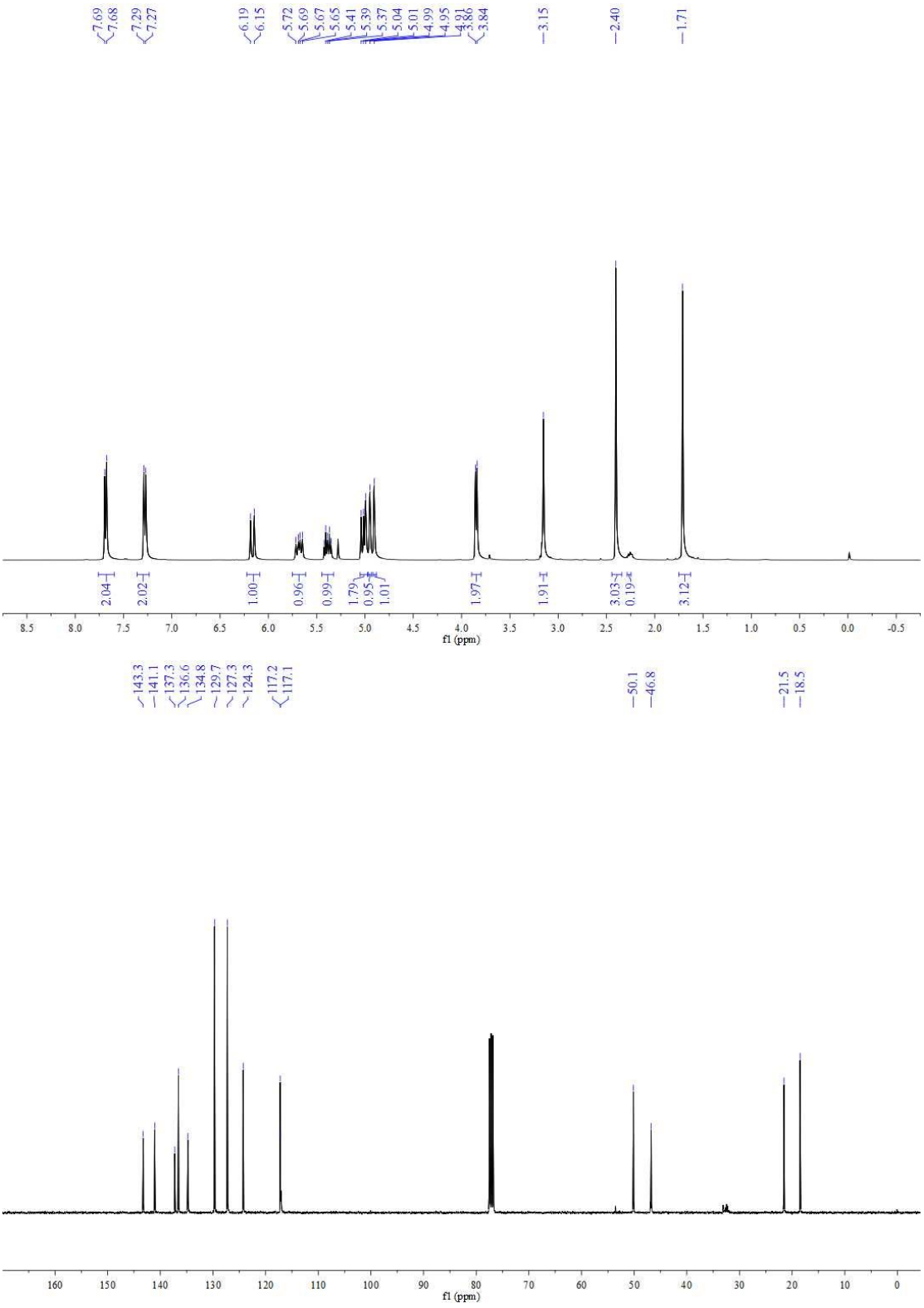
S1-d$_2$

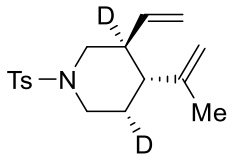

7.75
7.73
7.31
7.29
5.64
5.62
5.60
5.58
5.06
5.04
5.03
5.00
4.70
2.98
2.42
2.02
1.97
1.00
1.98
0.88
2.18
3.15
f1 (ppm)


143.5
137.0
134.2
129.8
127.2
118.2
42.1
21.6
f1 (ppm)

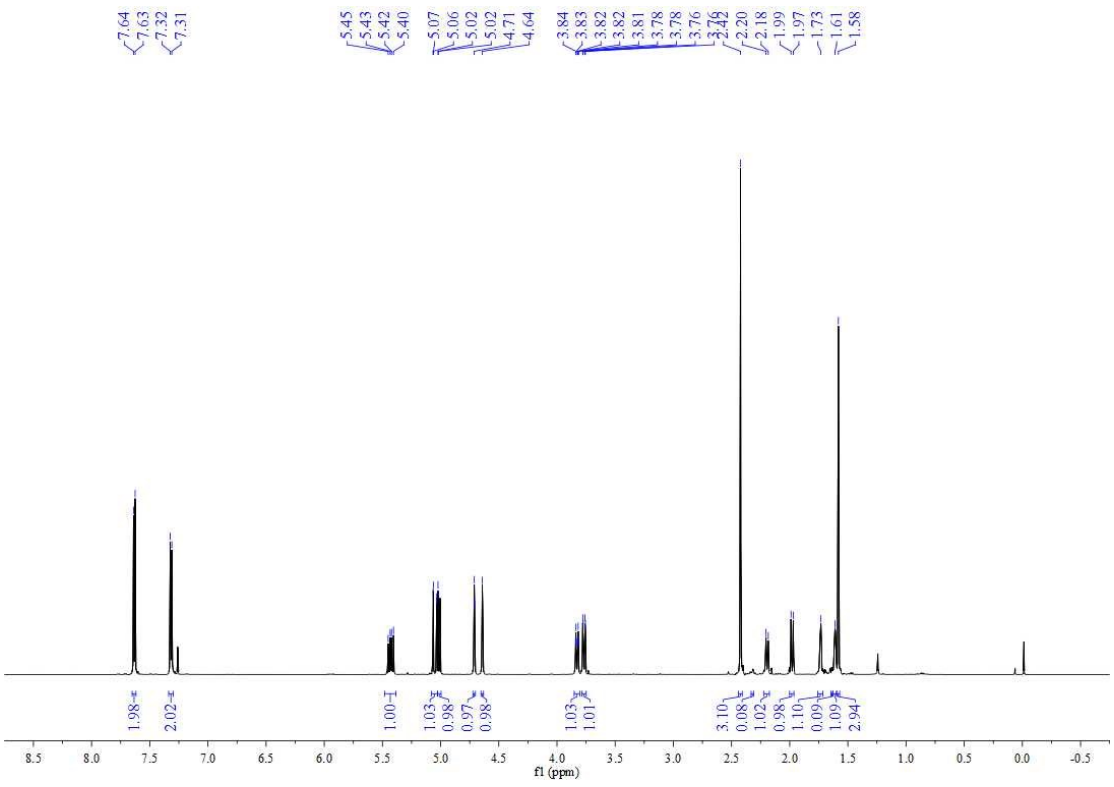

Ts
N
D
D
Me

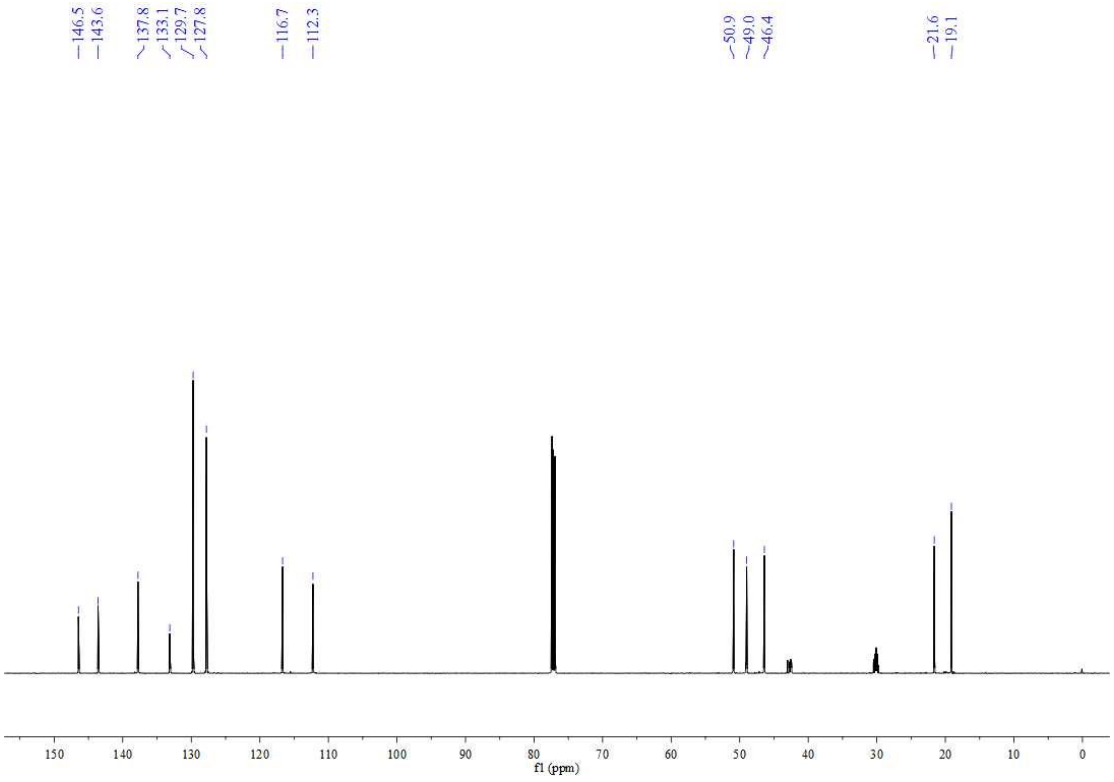
1a-d²


7.69
7.68
7.29
7.27
6.19
6.15
5.72
5.69
5.67
5.65
5.41
5.39
5.37
5.04
5.01
4.99
4.95
4.91
3.86
3.84
3.15
2.40
1.71
2.04
2.02
1.00
0.96
0.99
1.79
0.95
1.01
1.97
1.91
3.03
0.19
3.12
f1 (ppm)
143.3
141.1
137.3
136.6
134.8
129.7
127.3
124.3
117.2
117.1
50.1
46.8
21.5
18.5
f1 (ppm)

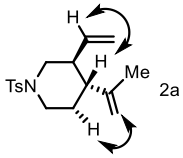

D
Ts
N
Me
D

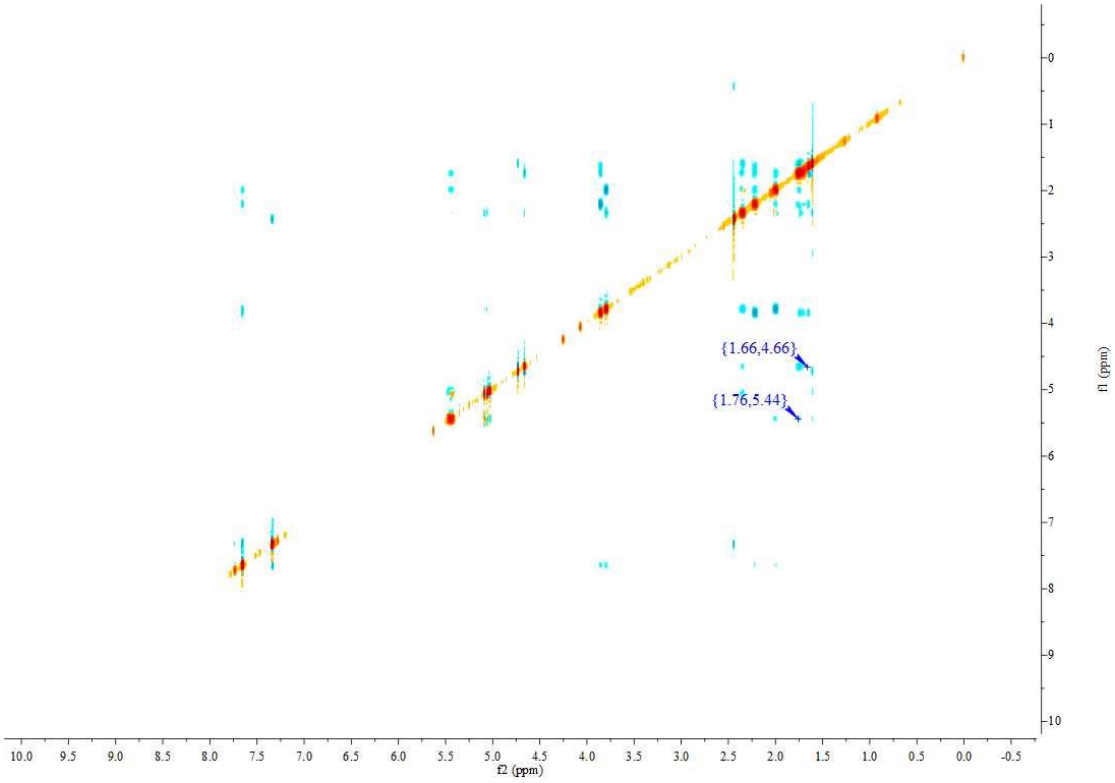
2a-d²

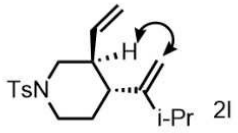

7.64
7.63
7.32
7.31
5.45
5.43
5.42
5.40
5.07
5.06
5.02
5.02
4.71
4.64
3.84
3.83
3.82
3.82
3.81
3.78
3.78
3.76
2.20
2.18
1.99
1.97
1.73
1.61
1.58
1.98
2.02
1.00
1.03
0.98
0.97
0.98
1.03
1.01
3.10
0.08
1.02
0.98
1.10
0.09
1.09
2.94
f1 (ppm)

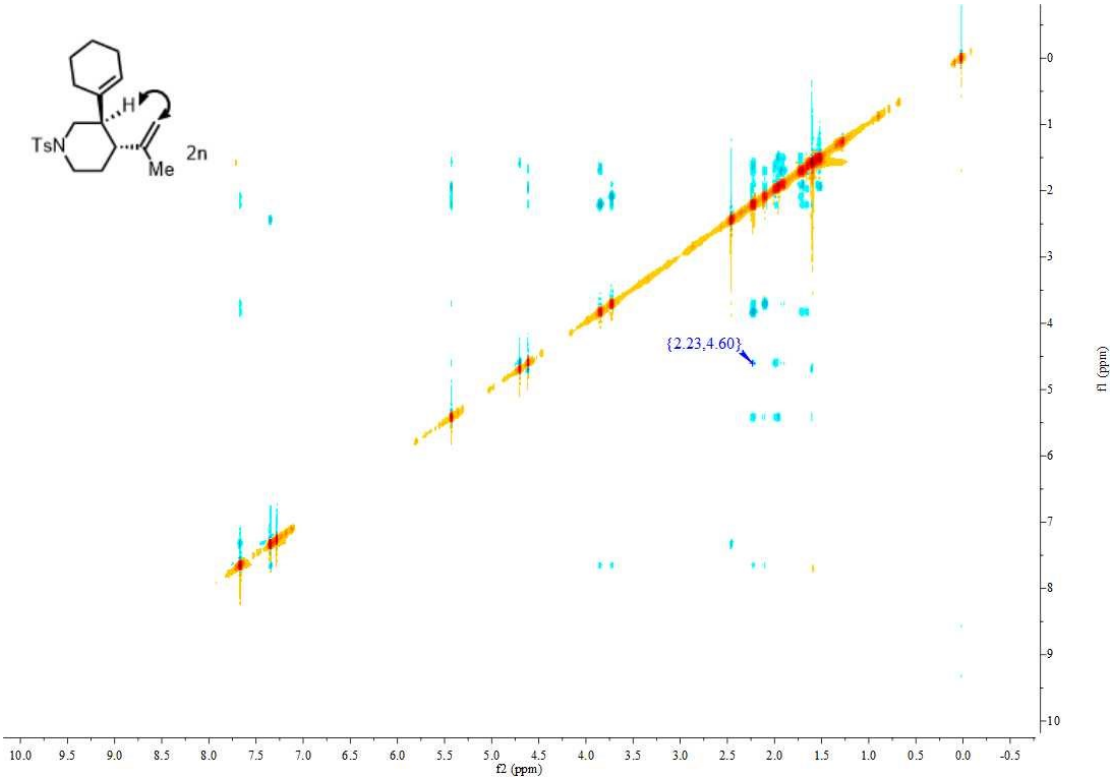

146.5
143.6
137.8
133.1
129.7
127.8
116.7
112.3
50.9
49.0
46.4
21.6
19.1
f1 (ppm)

NOESY of **2a**, **2l**, **2n**








TsN
H
Me
2n
{2.23,4.60}
f2 (ppm)
f1 (ppm)