Supporting Information

Conjugated Diene Assisted Allylic C-H Bond Activation: Cationic Rh(I) Catalyzed Syntheses of Polysubstituted Tetrahydropyrroles, Tetrahydrofurans, and Cyclopentanes from Ene-2-Dienes

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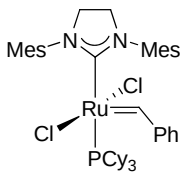
Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. 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 rotary evaporator with a desktop vacuum pump. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and 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 phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC. Some steps in the syntheses of the substrates had not been optimized in order to quickly obtain the designed substrates for tests.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) or Bruker AVANCE 600 (^{1}H at 600 MHz, ^{13}C at 150 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; 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 ($CDCl_3$: 77.0 ppm). 1D nOe experiments were conducted on a Bruker AVANCE 600 nuclear magnetic resonance spectrometer (^{1}H at 600 MHz). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:
DCE = 1,2-dichloroethane
DEAD = diethyl azodicarboxylate
DMF = *N*,*N*-dimethylformamide
DMP = Dess-Martin periodinane
EA = ethyl acetate
HMPA = hexamethylphosphoric acid triamide
PE = petroleum ether
TBAF = tetra-*n*-butylammonium fluoride
THF = tetrehydrofuran
TBS = *t*-butyldimethylsilyl

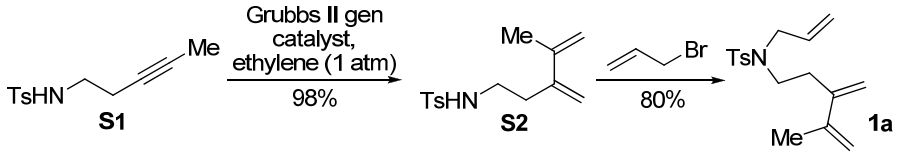


Grubbs II generation catalyst

2. Experimental Procedures and Characterization Data

2.1. Syntheses of Substrates

***N*-allyl-*N*-(4-methyl-3-methylenepent-4-enyl)-4-methylbenzenesulfonamide (1a)**



Sulfonamide **S1** [1] (223 mg, 0.94 mmol) and Grubbs II generation catalyst (12.0 mg, 0.014 mmol) were dissolved in dichloromethane (15 mL) under ethylene atmosphere. Ethylene was then bubbled to the solution for 5 min, and the reaction mixture was stirred under 1 atm ethylene at room temperature for 8 h. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluted with PE/EA = 10:1 to 3:1) to afford sulfonamide **S2** as a light brown oil (244.5 mg, 0.92 mmol, 98%).

Spectra data of **S2**:

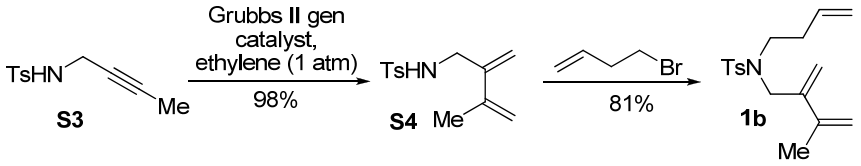
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.13 (s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 4.91 (s, 1H), 4.62-4.54 (br, 1H), 3.08 (q, J = 6.6 Hz, 2H), 2.44 (t, J = 6.6 Hz, 2H), 2.43 (s, 3H), 1.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.7, 143.3, 141.5, 137.0, 129.6, 127.1, 114.7, 113.4, 41.9, 33.6, 21.5, 20.9. IR (neat): υ 3289, 3103, 2957, 1445. HRMS (ESI) calcd for $C_{14}H_{20}NO_2S$ $(M+H)^+$: 266.1209. Found: 266.1207.

NaH (100 mg, 60%, 2.5 mmol) was suspended in DMF (5 mL) under argon and cooled to 0 °C. A DMF solution (10 mL) of **S2** (220 mg, 0.83 mmol) was added slowly to the above mixture. The reaction mixture was warmed to room temperature and stirred for 15 min. Then allyl bromide (250 mg, 2.07 mmol) was added dropwise to the above light yellow solution. The resulting mixture was stirred for 15 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford sulfonamide **1a** (200 mg, 0.65 mmol, 79%) as a pale oil.

Spectra data of **1a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 5.67 (ddt, J = 16.8 Hz, 10.1 Hz and 6.5 Hz, 1H), 5.18 (dq, J = 16.8 Hz and 1.5 Hz, 1H), 5.15 (dq, J = 10.1 Hz and 1.5 Hz, 1H), 5.11 (d, J = 0.7 Hz, 1 H), 5.10 (d, J = 0.7 Hz, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 3.83 (d, J = 6.4 Hz, 2H), 3.21 (t, J = 7.9 Hz, 2H), 2.54 (t, 7.9 Hz, 2H), 2.42 (s, 3H), 1.87 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.6, 143.1, 141.8, 137.2, 133.4, 129.6, 127.1, 118.8, 114.3, 113.3, 51.1, 47.4, 33.5, 21.5, 20.9. IR (neat): υ 3103, 2965, 2931, 2879, 1456. HRMS (ESI) calcd for $C_{17}H_{23}NNaO_2S$ $(M+Na)^+$: 328.1342. Found: 328.1340.

***N*-(but-3-enyl)-*N*-(3-methyl-2-methylenebut-3-enyl)-4-methylbenzenesulfonamide (1b)**



Sulfonamide **S4** was prepared by following the procedure for converting **S1** to **S2**. **S3** [2] (222 mg, 0.99 mmol) and Grubbs II generation catalyst (12.6 mg, 0.015 mmol) were used, and **S4** (244 mg, 0.97 mmol) was generated as a light brown oil in 98% yield.

Spectra data of **S4**:

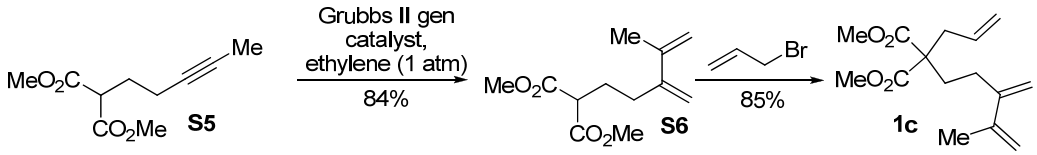
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.15 (s, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 4.94 (s, 1H), 4.61 (t, J = 5.9 Hz, 1H), 3.78 (d, J = 5.9 Hz, 2H), 2.43 (s, 3H), 1.83 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 142.3, 140.4, 136.8, 129.7, 127.2, 115.3, 113.7, 45.9, 21.5, 20.9. IR (neat): υ 3289, 2942, 2887, 1724, 1445. HRMS (ESI) calcd for $C_{13}H_{18}NO_2S$ $(M+H)^+$: 252.1053. Found: 252.1049.

Sulfonamide **1b** was synthesized by following the procedure for converting **S2** to **1a**. NaH (90 mg, 60%, 2.25 mmol), **S4** (198 mg, 0.79 mmol), and 4-bromo-1-butene (315 mg, 2.33 mmol) were used, and **1b** (195 mg, 0.64 mmol) was generated as a pale oil in 81% yield.

Spectra data of **1b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.52 (ddt, J = 17.5 Hz, 9.6 Hz and 6.4 Hz, 1H), 5.26 (s, 2H), 5.16 (s, 1H), 5.06 (s, 1H), 4.99-4.97 (m, 1H), 4.96-4.94 (m, 1H), 3.97 (s, 2H), 3.10 (t, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.20-2.14 (m, 2H), 1.92 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.2, 142.2, 140.4, 136.5, 134.9, 129.6, 127.3, 116.7, 115.8, 114.5, 51.5, 47.5, 33.0, 21.5, 21.3. IR (neat): υ 3091, 2983, 2961, 2928, 2879, 1646, 1460. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1522.

Dimethyl 2-allyl-2-(4-methyl-3-methylenepent-4-enyl)malonate (1c)



Dimethyl malonate **S6** was prepared by following the procedure for converting **S1** to **S2**. **S5** [3] (220 mg, 1.11 mmol) and Grubbs II generation catalyst (15 mg, 0.018 mmol) were used, and **S6** (210 mg, 0.93 mmol) was generated as a light brown oil in 84% yield.

Spectra data of **S6**:

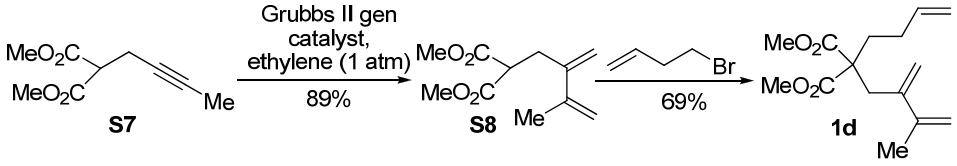
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1 H), 5.09 (s, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 3.74 (s, 6H), 3.40 (t, J = 7.5 Hz, 1H), 2.32 (m, 2H), 2.12-2.06 (m, 2H), 1.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.8, 146.3, 142.0, 113.2, 113.0, 52.4, 51.2, 31.3, 28.1, 21.0. IR (neat): υ 3103, 2961, 2268, 1758, 1739, 1441. HRMS (ESI) calcd for $C_{12}H_{18}NaO_4$ $(M+Na)^+$: 249.1097. Found: 249.1095.

Dimethyl malonate **S6** was dissolved in DMF (10 mL) under argon and the solution was cooled to 0 °C. Then NaH (110 mg, 60%, 2.75 mmol) was added to the above solution in one potion, and the resulting mixture was stirred at 0 °C for 15 min. After that, allyl bromide (320 mg, 2.64 mmol) was added dropwise. The reaction mixture was stirred for 20 min at 0°C and then saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 100:1 to 50:1) to afford **1c** (196 mg, 0.74 mmol, 85%) as a colorless oil.

Spectra data of **1c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.66 (ddt, J = 17.2 Hz, 10.2 Hz and 7.6 Hz, 1H), 5.13 (dt, J = 17.2 Hz and 1.5 Hz, 1H), 5.10 (dt, J = 10.2 Hz and 1.5 Hz, 1H), 5.09 (s, 1H), 5.05 (s, 1H), 4.98 (s, 1H), 4.97 (s, 1H), 3.73 (s, 6H), 2.70 (d, J = 7.6 Hz, 2H), 2.20-2.15 (m, 2H), 2.07-2.03 (m, 2H), 1.89 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.6, 147.1, 142.1, 132.4, 119.0, 112.79, 112.75, 105.5, 57.6, 52.3, 37.3, 32.4, 28.4, 21.1. IR (neat): υ 3103, 2957, 2868, 1739, 1441. HRMS (ESI) calcd for $C_{15}H_{22}NaO_4$ $(M+Na)^+$: 289.1410. Found: 289.1409.

Dimethyl 2-(but-3-enyl)-2-(3-methyl-2-methylenebut-3-enyl)malonate (1d)



Dimethyl malonate **S8** was prepared by following the procedure for converting **S1** to **S2**. **S7** [4] (400 mg, 2.17 mmol) and Grubbs II generation catalyst (30 mg, 0.035 mmol) were used, and **S8** (410 mg, 1.93 mmol) was generated as a light brown oil in 89% yield.

Spectra data of **S8**:

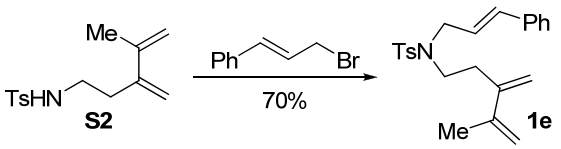
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 1H), 5.09 (s, 1H), 5.03 (s, 1H), 5.02 (s, 1H), 3.73 (s, 6H), 3.66 (t, J = 7.5 Hz, 1H), 2.92 (d, J = 7.5 Hz, 2H), 1.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.5, 143.8, 141.5, 114.6, 113.1, 52.4, 51.1, 32.8, 21.1. IR (neat): υ 3106, 2965, 2268, 1754, 1743, 1441. HRMS (ESI) calcd for $C_{11}H_{16}NaO_4$ $(M+Na)^+$: 235.0941. Found: 235.0938.

Dimethyl malonate **1d** was synthesized by following the procedure for converting **S6** to **1c**, but high temperature (25 °C) and longer reaction time (20 h) were needed. NaH (170 mg, 60%, 4.25 mmol), **S7** (280 mg, 1.79 mmol), and 4-bromo-1-butene (510 mg, 3.78 mmol) were used, and **1d** (330 mg, 1.24 mmol) was generated as a colorless oil in 69% yield.

Spectra data of **1d**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.80-5.70 (m, 1H), 5.20 (s, 1H), 5.01 (dd, J = 17.1 Hz and 1.5 Hz, 1H), 5.00 (s, 1H), 4.96 (dd, J = 10.3 Hz and 1.5 Hz, 1H), 4.93 (s, 1H), 4.92 (s, 1H), 3.67 (s, 6H), 2.95 (s, 2H), 1.99-1.92 (m, 4H), 1.87 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.7, 143.9, 143.6, 137.4, 116.1, 114.9, 112.8, 57.3, 52.2, 35.3, 31.3, 28.5, 21.5. IR (neat): υ 3103, 2961, 2849, 2268, 1739, 1650, 1453, 1441. HRMS (ESI) calcd for $C_{15}H_{22}NaO_4$ $(M+Na)^+$: 289.1410. Found: 289.1410.

_N_-cinnamyl-_N_-(4-methyl-3-methylenepent-4-enyl)-4-methylbenzenesulfonamide (1e)

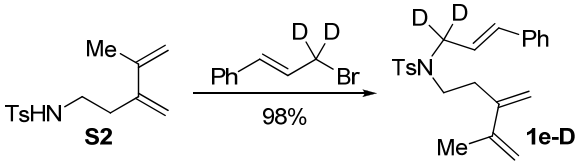


Sulfonamide **1e** was synthesized by following the procedure for converting **S2** to **1a**. **S2** (217 mg, 0.82 mmol), NaH (100 mg, 60%, 2.50 mmol), and (*E*)-(3-bromoprop-1-enyl)benzene (484 mg, 2.46 mmol) were used, and **1e** (190 mg, 0.50 mmol) was generated as a pale oil in 61% yield.

Spectra data of **1e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32-7.24 (m, 7H), 6.45 (d, J = 15.9 Hz, 1H), 5.99 (dt, J = 15.9 Hz and 6.9 Hz, 1H), 5.09 (s, 1H), 5.08 (s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 3.99 (dd, J = 6.9 Hz and 1.0 Hz, 2H), 3.25 (t, J = 8.0 Hz, 2H), 2.57 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H), 1.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5, 143.2, 141.7, 137.3, 136.2, 133.8, 129.6, 128.6, 127.9, 127.1, 126.4, 124.4, 114.4, 113.3, 50.6, 47.5, 33.8, 21.4, 20.9. IR (neat): υ 3103, 3036, 2957, 2931, 2872, 1456. HRMS (ESI) calcd for $C_{23}H_{27}KNO_2S$ $(M+K)^+$: 420.1394. Found: 420.1394.

Deuterated _N_-cinnamyl-_N_-(4-methyl-3-methylenepent-4-enyl)-4-methylbenzenesulfonamide (1e-D)

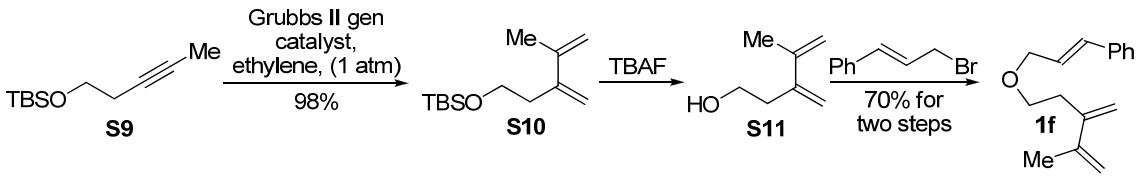


Sulfonamide **1e-D** was synthesized by following the procedure for converting **S2** to **1a**. **S2** (205 mg, 0.77 mmol), NaH (100 mg, 60%, 2.50 mmol), and deuterated (*E*)-(3-bromoprop-1-enyl)benzene [5] (200 mg, 1.00 mmol) were used, and **1e-D** (289 mg, 0.75 mmol) was generated as a pale oil in 98% yield.

Spectra data of **1e-D**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.32-7.24 (m, 7H), 6.46 (d, J = 15.9 Hz, 1H), 5.98 (d, J = 15.9 Hz, 1H), 5.09 (s, 1H), 5.08 (s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 3.25 (t, J = 8.1 Hz, 2H), 2.57 (t, J = 8.1 Hz, 2H), 2.42 (s, 3H), 1.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5, 143.2, 141.7, 137.3, 136.2, 133.9, 129.7, 128.6, 127.9, 127.2, 126.4, 124.3, 114.4, 113.3, 47.4, 33.8, 21.5, 20.9. HRMS (ESI) calcd for $C_{23}H_{25}D_2NNaO_2S$ $(M+Na)^+$: 406.1780. Found: 406.1777.

(*E*)-(3-(4-methyl-3-methylenepent-4-enyloxy)prop-1-enyl)benzene (1f)



Diene **S10** was prepared by following the procedure for converting **S1** to **S2**. **S9** [6] (560 mg, 2.82 mmol) and Grubbs II generation catalyst (21.8 mg, 0.026 mmol) were used, and **S10** (490 mg, 2.15

mmol) was generated as a colorless oil in 77% yield.

Spectra data of **S10**:

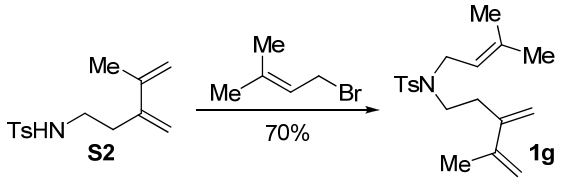
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 4.98 (s, 1H), 3.72 (t, J = 7.4 Hz, 2H), 2.53 (t, J = 7.4 Hz, 2H), 1.90 (s, 3H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5, 142.5, 113.9, 112.7, 63.0, 37.3, 26.0, 21.0, 18.4, -5.3. IR (neat): υ 2965, 2939, 2868, 1464. HRMS (ESI) calcd for $C_{13}H_{25}OSi$ $(M+H)^+$: 225.1669. Found: 225.1670.

Diene **S10** (460 mg, 2.03 mmol) was dissolved in THF (5 mL). TBAF (1M in THF, 6 mL) was then added dropwise to the above solution. The resulting mixture was stirred at room temperature for 2 h. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved in THF (10 mL), which was dropped to a suspension of NaH in THF at 0 °C. After addition, the reaction mixture was warmed to 25 °C and stirred for 1 h. Then a solution of (*E*)-(3-bromoprop-1-enyl)benzene (260 mg, 1.32 mmol) in THF (10 mL) was added dropwise to the reaction mixture. The mixture was stirred in a 45 °C oil bath for additional 2.5 h. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluted with PE/EA = 100:1) to afford **1f** (210 mg, 0.92 mmol, 70% for two steps) as a colorless oil.

Spectra data of **1f**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.21 (m, 5H), 6.60 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0 Hz and 5.9 Hz, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 4.16 (d, J = 5.9 Hz, 2H), 3.62 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 1.91 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.4, 142.5, 136.7, 132.2, 128.5, 127.6, 126.5, 126.2, 113.6, 112.8, 71.4, 69.7, 33.9, 21.0. IR (neat): υ 2965, 2935, 2879, 1449. HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1835. HRMS (ESI) calcd for $C_{16}H_{21}O$ $(M+H)^+$: 229.1587. Found: 229.1586.

***N*-(4-methyl-3-methylenepent-4-enyl)-*N*-(3-methylbut-2-enyl)-4-methylbenzenesulfonamide (1g)**



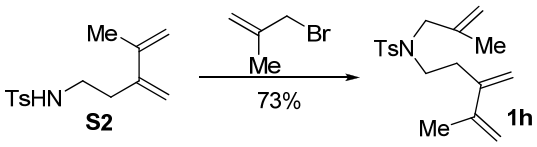
Sulfonamide **1g** was synthesized by following the procedure for converting **S2** to **1a**. **S2** (217 mg, 0.82 mmol), NaH (100 mg, 60%, 2.50 mmol), and 1-bromo-3-methylbut-2-ene (240 mg, 1.61 mmol) were used, and **1g** (191 mg, 0.57 mmol) was generated as a pale oil in 57% yield.

Spectra data of **1g**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.11 (s, 1H), 5.09 (s, 1H), 5.04 (tm, J = 7.1 Hz, 1H), 4.99 (s, 1H), 4.96 (s, 1H), 3.81 (d, J = 7.1 Hz, 2H), 3.16 (t, J = 8.2 Hz, 2H), 2.54 (t, J = 8.2 Hz, 2H), 2.42 (s, 3H), 1.87 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 142.9, 141.8, 137.3, 136.7, 129.5, 127.2, 119.4, 114.2, 113.2, 47.5, 45.9, 34.0, 25.8, 21.5, 20.9,

17.8. IR (neat): υ 3099, 2980, 2935, 2879, 1680, 1456. HRMS (ESI) calcd for $C_{13}H_{18}NO_2S$ $(M+H)^+$: 252.1053. Found: 252.1049. HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1835.

_N_-(4-methyl-3-methylenepent-4-enyl)-_N_-(2-methylallyl)-4-methylbenzenesulfonamide (1h)

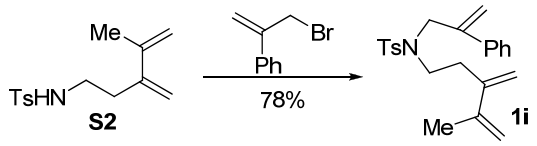


Sulfonamide **1h** was synthesized by following the procedure for converting **S2** to **1a**. **S2** (217 mg, 0.82 mmol), NaH (100 mg, 60%, 2.50 mmol), and 3-bromo-2-methylprop-1-ene (230 mg, 1.70 mmol) were used, and **1h** (190 mg, 0.59 mmol) was generated as a pale oil in 73% yield.

Spectra data of **1h**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.29 (J = 8.2 Hz, 2H), 5.083(s, 1H), 5.080 (s, 1H), 4.98 (s, 1H), 4.92 (s, 1H), 4.91 (s, 1H), 4.90 (s, 1H), 3.73 (s, 2H), 3.16 (t, J = 8.4 Hz, 2H), 2.49 (t, J = 8.4 Hz, 2H), 2.42 (s, 3H), 1.85 (s, 3H), 1.74 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 143.1, 141.8, 141.0, 137.1, 129.6, 127.1, 114.5, 114.2, 113.3, 54.9, 48.1, 33.2, 21.5, 20.9, 19.8. IR (neat): υ 3103, 2957, 2935, 2893, 2883, 1654, 1441. HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1678.

_N_-(4-methyl-3-methylenepent-4-enyl)-_N_-(2-phenylallyl)-4-methylbenzenesulfonamide (1i)

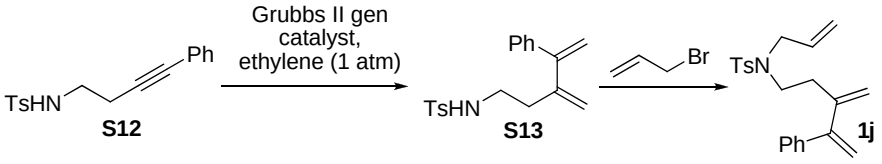


Sulfonamide **1i** was synthesized by following the procedure for converting **S2** to **1a**. **S2** (205 mg, 0.77 mmol), NaH (90 mg, 60%, 2.25 mmol), and (3-bromoprop-1-en-2-yl)benzene [7] (400 mg, 70%, 1.42 mmol) were used, and **1i** (236 mg, 0.62 mmol) was generated as a pale oil in 78% yield.

Spectra data of **1i**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.4 Hz, 2H), 7.47-7.44 (m, 2H), 7.35-7.25 (m, 5H), 5.50 (s, 1H), 5.25 (s, 1H), 5.04 (s, 2H), 4.95 (s, 1H), 4.84 (s, 1H), 4.25 (s, 2H), 3.11 (t, J = 8.5 Hz, 2H), 2.41 (s, 3H), 2.38 (t, J = 8.5 Hz, 2H), 1.82 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 143.18, 143.15, 141.7, 138.1, 136.4, 129.6, 128.4, 128.1, 127.3, 126.4, 116.4, 114.0, 113.2, 52.3, 47.8, 33.1, 21.4, 20.8. IR (neat): υ 3099, 3073, 3036, 2961, 2935, 2872, 1635, 1460. HRMS (ESI) calcd for $C_{23}H_{27}NNaO_2S$ $(M+Na)^+$: 404.1655. Found: 404.1651.

_N_-allyl-_N_-(3-methylene-4-phenylpent-4-enyl)-4-methylbenzenesulfonamide (1j)



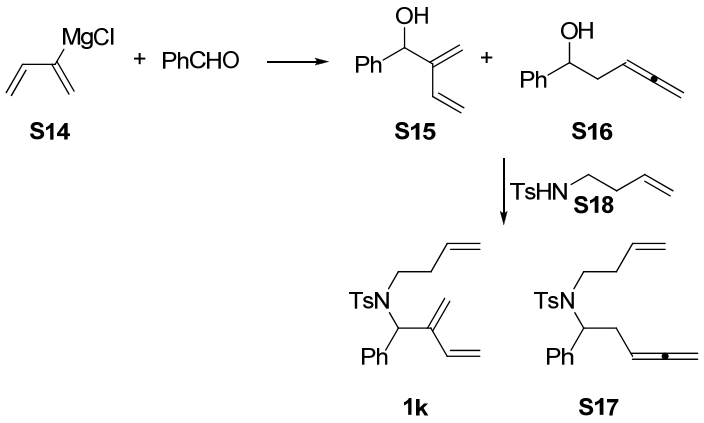
Sulfonamide **S13** (450 mg, 1.50 mmol) was synthesized from **S12** [8] by following the procedures for converting **S1** to **S2**. But higher temperature (80 °C) and longer reaction time (12 h) were needed. The reaction gave the desired product **S13** along with an inseparable byproduct.

Sulfonamide **S13** together with the inseparable byproduct was dissolved in DMF (15 mL) under argon, and the solution was cooled to 0 °C. Then NaH was added to the above cooled solution in one potion. The resulting mixture was stirred at room temperature for 15 min, and then allyl bromide (450 mg, 3.72 mmol) was added dropwise. The resulting mixture was stirred for an additional 15 min. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford **1j** (270 mg, together with an inseparable byproduct) as a colorless oil.

Spectra data of **1j**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.2 Hz, 2H), 7.33-7.23 (m, 7H), 5.65-5.56 (m, 1H), 5.29 (s, 1H), 5.17 (s, 1H), 5.10-5.06 (m, 3H), 5.00 (s, 1H), 3.77 (d, J = 5.8 Hz, 2H), 3.24-3.19 (m, 2H), 2.76 (t, J = 8.2 Hz, 1H), 2.49 (t, J = 8.2 Hz, 1H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.7, 145.4, 143.1, 140.7, 140.1, 137.2, 137.0, 136.5, 133.41, 133.36, 133.1, 129.7, 129.6, 128.6, 128.4, 128.1, 127.5, 127.11, 127.09, 118.8, 117.6, 114.3, 51.1, 50.1, 46.6, 46.0, 33.6, 29.7, 26.8, 21.5. The redundant peaks are for the inseparable byproduct. IR (neat): υ 3088, 3036, 2935, 2879, 2265, 1456. $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1678.

***N*-(but-3-enyl)-*N*-(2-methylene-1-phenylbut-3-enyl)-4-methylbenzenesulfonamide (1k)**



Benzaldehyde (1.43 g, 12.69 mmol) was dissolved in THF (10 mL) and the solution was cooled to 0 °C. Magnesium chloride **S14** [9] (0.27 M in 50 mL THF, 13.5 mmol) was added dropwise to the above cooled solution. After addition, the reaction mixture was stirred at 0 °C for 10 min, and then saturated aqueous NH_4Cl was added to quench the reaction. The reaction mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with pentane/ether =10:1 to 5:1) to afford an inseparable mixture of **S15** and **S16** as a colorless oil, which was used directly in the next step. The ratio of **S15** to **S16** was 2:3 as determined by NMR spectra.

The inseparable **S15** and **S16** together with tosylamide **S18** (2.86 g, 12.69 mmol) and triphenylphosphine (6.66 g, 25.39 mmol) were dissolved in THF (60 mL) under argon. DEAD (4.64 g,

26.66 mmol) was added dropwise to the above solution, and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluted with PE/EA = 100:1 to 50:1) to afford **1k** (307 mg, 0.84 mmol, 7% for 2 steps) as a white soild (melting point: 64-65 °C) and **S17** (1.00 g, 2.72 mmol, 22% for two steps) as a pale oil.

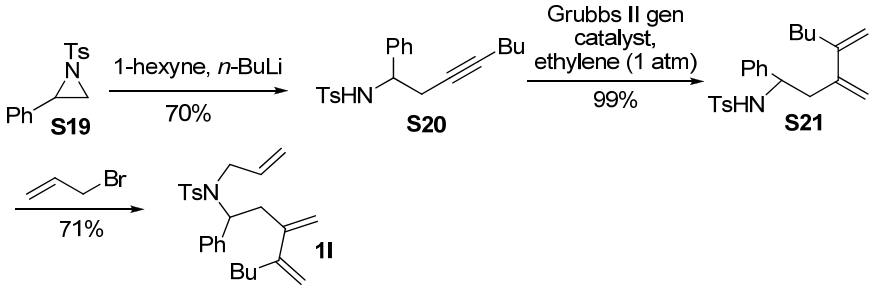
Spectra data of **1k**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, J = 8.1 Hz and 1.9 Hz, 2H), 7.24-7.19 (m, 5H), 7.10-7.08 (m, 2H), 6.27 (dd, J = 17.8 Hz and 11.2 Hz, 1H), 6.02 (s, 1H), 5.43 (ddt, J = 17.1 Hz, 11.2 Hz and 7.0 Hz, 1H), 5.27 (s, 1H), 5.17 (d, J = 17.8 Hz, 1H), 5.05 (d, J = 11.2 Hz, 1H), 4.85 (dt, J = 10.3 Hz and 1.1 Hz, 1H), 4.79 (s, 1H), 4.75 (dq, J = 17.1 Hz and 1.6 Hz, 1H), 3.31 (ddd, J = 14.8 Hz, 11.5 Hz and 5.2 Hz, 1H), 3.10 (ddd, J = 14.8, 11.6 Hz and 4.8 Hz, 1H), 2.40 (s, 3H), 2.24-2.15 (m, 1H), 1.58-1.48 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 142.9, 137.7, 137.5, 136.7, 134.9, 129.2, 128.9, 128.4, 127.7, 127.4, 119.2, 116.4, 116.0, 62.2, 46.0, 35.1, 21.5. IR (neat): υ 3095, 3080, 2939, 2872, 1643, 1456. HRMS (ESI) calcd for $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1679.

Spectra data of **S17**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.29-7.22 (m,7H), 5.51 (ddt, J = 17,1 Hz, 10.0 Hz and 7.1 Hz, 1H), 5.07 (dd, J = 9.8 Hz and 6.0 Hz, 1H), 4.95-4.88 (m, 2H), 4.85 (dd, J = 17.1 Hz and 2.0 Hz, 1H), 4.64-4.53 (m, 2H), 3.12-2.99 (m, 2H), 2.78-2.69 (m, 1H), 2.43 (s, 3H), 2.45-2.36 (m, 1H), 2.22-2.13 (m, 1H), 1.87-1.77 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 209.4, 143.1, 138.2, 137.9, 134.9, 129.6, 128.4, 127.9, 127.3, 116.6, 86.5, 75.3, 60.2, 44.0, 35.1, 30.4, 21.5. IR (neat): υ 3077, 3039, 1963, 1743, 1453. HRMS (ESI) calcd for $C_{22}H_{25}NNaO_2S$ $(M+Na)^+$: 390.1498. Found: 390.1497.

***N*-allyl-*N*-(3,4-dimethylene-1-phenyloctyl)-4-methylbenzenesulfonamide (1l)**



To a cold solution (-78 °C) of 1-hexyne (1.0 mL, 8.70 mmol) in THF (5 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 4.0 mL, 6.4 mmol) over a period of 10 min, and the mixture was stirred at -78 °C for 15 min and at 0 °C for 15 min. After cooling to -78 °C and then addition of HMPA (0.8 mL, 4.60 mmol), a THF (10 mL) solution of **S19** [10] (1.10g, 4.02 mmol) was added dropwise over 10 min. The mixture was allowed to warm to room temperature and stirred for an additional 12 h. After that, saturated aqueous NH_4Cl and water were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate, and the combined extract was washed with water and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (eluted with PE/EA = 20:1 to 10:1) to afford **S20** (0.99 g, 2.78 mmol, 70%) as a light yellow oil.

Spectra data of **S20**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.9 Hz, 2H), 7.20-7.14 (m, 7H), 5.22 (d, J = 5.9 Hz, 1H), 4.42 (q, J = 6.2 Hz, 1H), 2.55-2.53 (m, 2H), 2.38 (s, 3H), 2.09-2.05 (m, 2H), 1.42-1.25 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.2, 139.8, 137.4, 129.4, 128.3, 127.6, 127.2, 126.6, 84.6, 74.4, 56.1, 30.8, 27.7, 21.8, 21.5, 18.3, 13.5. IR (neat): υ 3289, 2965, 2939, 2875, 1460, 1427. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_2S$ $(M+Na)^+$: 378.1498. Found: 378.1495.

Sulfonamide **S20** (360 mg, 1.01 mmol) and Grubbs II generation catalyst (20 mg, 0.024 mmol) were dissolved in toluene (20 mL) under ethylene atmosphere. Then ethylene was bubbled to the solution for 5 min, and the reaction mixture was stirred under 1 atm ethylene at 70 °C for 5 h. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluted with PE/EA = 20:1 to 10:1 to 5:1) to afford sulfonamide **S21** (389 mg, quantitative) as a colorless oil.

Spectra data of **S21**:

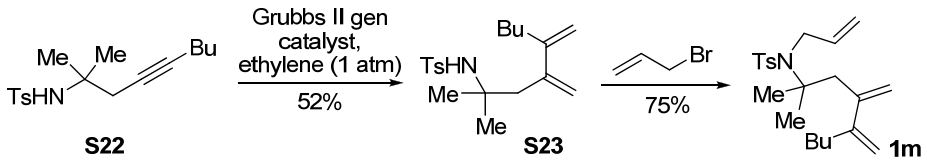
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.8 Hz, 2H), 7.17-7.06 (m, 7H), 5.06 (s, 1H), 5.00 (s, 1H), 5.00-4.91 (br, 1H), 4.92 (s, 1H), 4.80 (s, 1H), 4.37 (q, J = 6.6 Hz, 1H), 2.66-2.56 (m, 2H), 2.36 (s, 3H), 2.13-2.02 (m, 2H), 1.36-1.24 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.5, 142.95, 142.88, 140.9, 137.3, 129.1, 128.2, 127.3, 127.2, 126.7, 115.8, 112.6, 56.7, 43.1, 33.6, 30.6, 22.6, 21.4, 13.9. IR (neat): υ 3274, 2965, 2942, 2879, 1460, 1441, 1415. HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1835. HRMS (ESI) calcd for $C_{23}H_{29}NNaO_2S$ $(M+Na)^+$: 406.1811. Found: 406.1808.

Sulfonamide **1l** was synthesized by following the procedure for converting **S2** to **1a**. **S21** (370 mg, 0.96 mmol), NaH (120 mg, 60%, 3.00 mmol), and allyl bromide (350 mg, 2.89 mmol) were used, and **1l** (296 mg, 0.70 mmol) was generated as a pale oil in 73% yield.

Spectra data of **1l**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.1 Hz, 2H), 7.25-7.20 (m, 5H), 7.10-7.08 (m, 2H), 5.65-5.55 (m, 1H), 5.19 (dd, J = 10.0 Hz and 5.0 Hz, 1H), 5.06 (dd, J = 17.5 Hz and 1.2 Hz, 1H), 5.011 (s, 1H), 5.010 (dd, J = 10.0 Hz and 1.2 Hz, 1H), 5.00 (s, 1H), 4.93 (s, 1H), 4.82 (s, 1H), 3.89 (dd, J = 16.2 Hz and 4.9 Hz, 1H), 3.60 (dd, J = 16.2 Hz and 7.9 Hz, 1H), 3.03 (dd, J = 14.9 Hz and 10.3 Hz, 1H), 2.86 (dd, J = 14.9 Hz and 5.0 Hz), 2.41 (s, 3H), 2.20-2.07 (m, 2H), 1.28-1.17 (m, 4H), 0.83 (t, J = 7.1 Hz, 3H .) ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.5, 143.6, 142.9, 138.4, 137.5, 136.0, 129.4, 129.0, 128.1, 127.7, 127.3, 117.0, 114.8, 112.0, 59.5, 47.4, 37.1, 33.9, 30.5, 22.5, 21.5, 13.9. IR (neat): υ 3095, 3039, 2965, 2935, 2872, 1460. HRMS (ESI) calcd for $C_{26}H_{34}NO_2S$ $(M+H)^+$: 424.2305. Found: 424.2302.

_N_-allyl-_N_-(2-methyl-4,5-dimethylenenonan-2-yl)-4-methylbenzenesulfonamide (1m)



Sulfonamide **S22** [11] (250 mg, 0.81 mmol) and Grubbs II generation catalyst (45 mg, 0.053 mmol) were dissolved in toluene (15 mL) under ethylene atmosphere. Ethylene was then bubbled to the solution for 5 min, and the reaction mixture was stirred under 1 atm ethylene at 80 °C for 16 h. The reaction mixture was

concentrated under reduced pressure, and the crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 20:1 to 10:1) to afford sulfonamide **S23** as a light yellow oil (142 mg, 0.42 mmol, 52%).

Spectra data of **S23**:

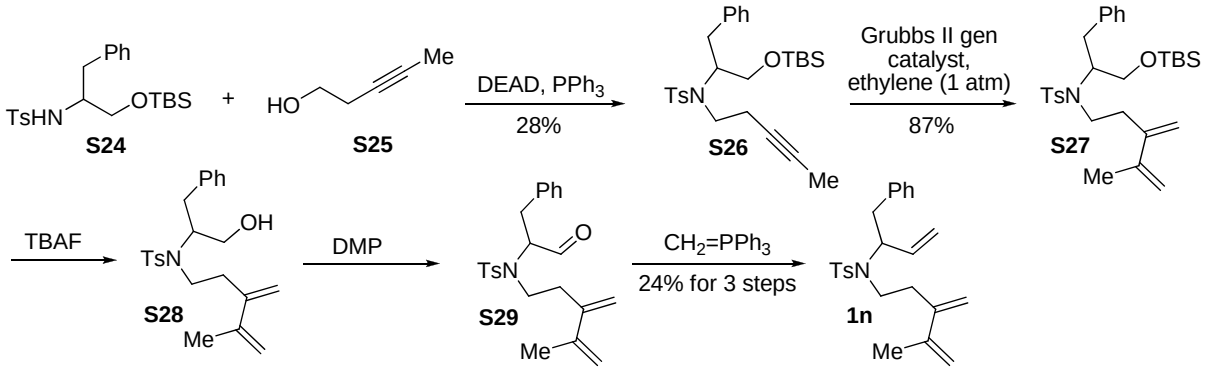
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.29 (s, 1H), 5.08 (s, 1H), 4.99 (s, 1H), 4.96 (s, 1H), 4.71 (s, 1H), 2.47 (s, 2H), 2.41 (s, 3H), 2.25 (t, J = 7.2 Hz, 2H), 1.42-1.30 (m, 4H), 1.17 (s, 6H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.9, 144.2, 142.7, 140.7, 129.4, 126.9, 117.7, 112.8, 56.9, 46.3, 34.1, 30.5, 27.8, 22.5, 21.5, 14.0. IR (neat): υ 3285, 2965, 2939, 2875, 1471, 1430. HRMS (ESI) calcd for $C_{19}H_{30}NO_2S$ $(M+H)^+$: 336.1992. Found: 336.1990.

Sulfonamide **1m** was synthesized by following the procedure for converting **S2** to **1a. S23** (130 mg, 0.39 mmol), NaH (80 mg, 60%, 2.00 mmol), and allyl bromide (150 mg, 1.24 mmol) were used, and **1m** (110 mg, 0.29 mmol) was generated as a pale oil in 75% yield.

Spectra data of **1m**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 5.99 (ddt, J = 16.6 Hz, 10.3 HZ and 6.4 Hz, 1H), 5.21 (d, J = 9.9 Hz, 1H), 5.18 (d, J = 11.3 Hz, 1H), 5.16 (d, J = 16.6 Hz, 1H), 5.10 (s, 1H), 4.93 (s, 1H), 4.89 (s, 1H), 4.07 (d, J = 6.4 Hz, 2H), 2.82 (s, 2H), 2.40 (s, 3H), 2.21 (t, J = 7.5 Hz, 2H), 1.39-1.25 (m, 4H), 1.29 (s, 6H), 0.89 (t, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.5, 144.9, 142.5, 141.3, 137.7, 129.4, 126.9, 117.0, 116.8, 112.5, 63.3, 49.0, 44.0, 34.1, 30.6, 27.7, 22.6, 21.5, 14.0. IR (neat): υ 2965, 2942, 2879, 1475. HRMS (ESI) calcd for $C_{22}H_{33}KNO_2S$ $(M+K)^+$: 414.1864. Found: 414.1864.

***N*-(4-methyl-3-methylenepent-4-enyl)-*N*-(1-phenylbut-3-en-2-yl)-4-methylbenzenesulfonamide (1n)**



To a flask charged with **S24** [12] (1.60 g, 3.81 mmol), **S25** (0.49 g, 5.83 mmol) and triphenylphosphine (3.11 g, 11.86 mmol) in THF (40 mL) under argon was added DEAD (2.30 g, 13.20 mmol) dropwise. The resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford **S26** (0.51 g, 1.05 mmol, 28%) as a colorless oil.

Spectra data of **S26**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.2 Hz, 2H), 7.22-7.18 (m, 5H), 7.10 (d, J = 6.6 Hz, 2H), 4.02-3.96 (m, 1H), 3.55 (d, J = 4.5 Hz, 2H), 3.51-3.43 (m, 1H), 3.40-3.32 (m, 1H), 2.98 (dd, J = 13.4 Hz and 8.8 Hz, 1H), 2.66 (dd, J = 13.4 Hz and 6.1 Hz, 1H), 2.54-2.48 (m, 2H), 2.39 (s, 3H), 1.76 (t, J = 2.4 Hz,

3H), 0.87 (s, 9H), -0.04 (s, 3H), -0.05 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.0, 138.3, 137.9, 129.5, 129.1, 128.4, 127.2, 126.4, 77.2, 76.2, 63.5, 61.2, 44.5, 36.0, 25.9, 21.6, 21.4, 18.1, 3.4, -5.69, -5.73. IR (neat): υ 3039, 2961, 2935, 2861, 1471. HRMS (ESI) calcd for $C_{27}H_{40}NO_3SSi$ $(M+H)^+$: 486.2493. Found: 486.2486.

Sulfonamide **S27** was prepared by following the procedure for converting **S1** to **S2**. **S26** (500 mg, 1.03 mmol) and Grubbs II generation catalyst (14.7 mg, 0.017 mmol) were used, and **S27** (460 mg, 0.90 mmol) was generated as a colorless oil in 87% yield.

Spectra data of **S27**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.2 Hz, 2H), 7.24-7.17 (m, 5H), 7.13 (d, J = 6.6 Hz, 2H), 5.22 (s, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.98 (s, 1H), 4.06-4.00 (m, 1H), 3.62-3.54 (m, 2H), 3.49-3.42 (m, 1H), 3.36-3.28 (m, 1H), 3.00 (dd, J = 13.7 Hz and 8.9 Hz, 1H), 2.80 (dd, J = 13.7 Hz and 6.0 Hz, 1H), 2.72-2.58 (m, 2H), 2.38 (s, 3H), 1.89 (s, 3H), 0.82 (s, 9H), -0.06 (s, 3H), -0.08 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.4, 142.8, 142.0, 138.4, 138.2, 129.5, 129.1, 128.4, 127.1, 126.4, 113.7, 113.4, 63.6, 61.5, 45.5, 36.6, 35.9, 25.8, 21.4, 20.9, 18.1, -5.6, -5.7. IR (neat): υ 3099, 3073, 3036, 2961, 2935, 2861, 1468. HRMS (ESI) calcd for $C_{29}H_{44}NO_3SSi$ $(M+H)^+$: 514.2806. Found: 514.2800.

To a flask charged with **S27** (440 mg, 0.86 mmol) in THF (15 mL) was added TBAF (700 mg, 2.68 mmol) in one potion. The reaction mixture was stirred at room temperature for 2 h. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$ and concentrated. The crude **S28** was directly used in the next step without further purification.

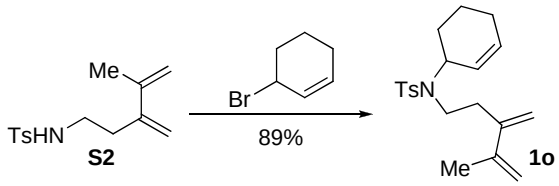
Sulfonamide **S28** was dissolved in dichloromethane (9 mL) under argon. The mixture was cooled to 0 °C, then DMP and $NaHCO_3$ were added in one potion. The reaction was stirred at room temperature for 2 h, and the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography (eluted with PE/EA = 10:1) to afford aldehyde **S29** as a colorless oil.

To a suspension of methyltriphenylphosphonium bromide (1.02 g, 2.86 mmol) in THF (5 mL) at 0 °C was added *n*-BuLi (2.5 M solution in hexane, 0.9 mL, 2.25 mmol), and the resulting solution was stirred for 30 min at 0 °C. A solution of aldehyde **S29** in THF (5 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 10 min at room temperature. Saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford **1n** (80 mg, 0.20 mmol, 24% for three steps) as a colorless oil.

Spectra data of **1n**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.27-7.20 (m, 5H), 7.15 (d, J = 7.4 Hz, 2H), 5.70 (ddd, J = 17.1 Hz, 10.5 Hz and 6.4 Hz, 1H), 5.21 (s, 1H), 5.14 (s, 1H), 5.07 (d, J = 10.5 Hz, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 4.99 (d, J = 17.1 Hz, 1H), 4.67-4.61 (m, 1H), 3.31-3.16 (m, 2H), 2.94 (tt, J = 13.6 Hz and 7.6 Hz, 2H), 2.73-2,57 (m, 2H), 2.39 (s, 3H), 1.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.2, 142.9, 141.9, 137.9, 137.8, 135.4, 129.4, 129.2, 128.4, 127.3, 126.4, 118.4, 114.1, 113.4, 61.4, 45.2, 39.5, 35.8, 21.4, 20.9. IR (neat): υ 2969, 2924, 2857, 1460. HRMS (ESI) calcd for $C_{24}H_{30}NO_2S$ $(M+H)^+$: 396.1992. Found: 396.1989.

***N*-(cyclohex-2-enyl)-*N*-(4-methyl-3-methylenepent-4-enyl)-4-methylbenzenesulfonamide (1o)**

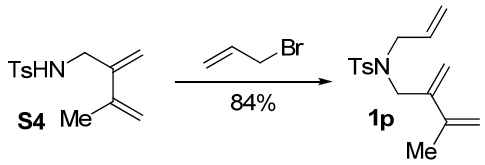


Sulfonamide **1o** was synthesized by following the procedures for converting **S2** to **1a**. **S2** (180 mg, 0.68 mmol), NaH (100 mg, 60%, 2.50 mmol), and 3-bromocyclohex-1-ene (300 mg, 2.17 mmol) were used, and **1o** (208 mg, 0.60 mmol) was generated as a pale oil in 89% yield.

Spectra data of **1o**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.80-5.76 (m, 1H), 5.26 (s, 1H), 5.12 (s, 1H), 5.07 (d, J = 9.9 Hz, 1H), 5.03 (s, 1H), 5.00 (s, 1H), 4.52-4.47 (m, 1H), 3.21 (ddd, J = 15.0 Hz, 12.0 Hz and 5.0 Hz, 1H), 3.03 (ddd, 15.0 Hz, 11.8 Hz and 5.5 Hz, 1H), 2.82 (td, J = 13.1 Hz and 5.0 Hz, 1H), 2.60 (td, J = 13.1 Hz and 5.5 Hz, 1H), 2.42 (s, 3H), 1.95-1.91 (m, 2H), 1.89 (s, 3H), 1.91-1.86 (m, 1H), 1.80-1.75 (m, 1H), 1.65-1.45 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.3, 142.9, 141.9, 138.1, 132.2, 129.6, 127.7, 127.1, 114.0, 113.5, 55.4, 44.7, 36.9, 28.9, 24.4, 21.8, 21.5, 20.9. IR (neat): υ 2954, 2879, 2853, 1758, 1743, 1456. HRMS (ESI) calcd for $C_{20}H_{27}NNaO_2S$ $(M+Na)^+$: 368.1655. Found: 368.1652.

***N*-allyl-*N*-(3-methyl-2-methylenebut-3-enyl)-4-methylbenzenesulfonamide (1p)**

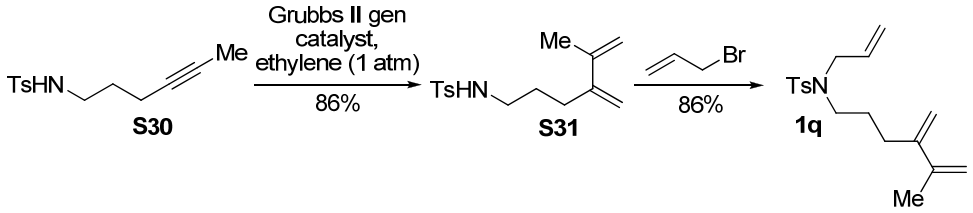


Sulfonamide **1p** was synthesized by following the procedure for converting **S2** to **1a**. **S4** (200 mg, 0.80 mmol), NaH (100 mg, 60%, 2.50 mmol), and allyl bromide (300 mg, 2.48 mmol) were used, and **1p** (196 mg, 0.66 mmol) was generated as a pale oil in 83% yield.

Spectra data of **1p**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.52 (ddt, J = 17.3 Hz, 9.7 Hz and 6.3 Hz, 1H), 5.26 (s, 1H), 5.19 (s, 1H), 5.14 (s, 1H), 5.08-5.07 (m, 1H), 5.04-5.03 (m, 1H), 5.02 (s, 1H), 3.99 (s, 2H), 3.76 (d, J = 6.5 Hz, 2H), 2.43 (s, 3H), 1.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.2, 141.7, 140.8, 137.0, 132.5, 129.6, 127.3, 118.9, 115.4, 113.9, 49.8, 49.5, 21.5, 21.3. IR (neat): υ 3266, 3062, 2987, 1427, 1270. HRMS (ESI) calcd for $C_{16}H_{22}NO_2S$ $(M+H)^+$: 292.1366. Found: 292.1362.

***N*-allyl-4-methyl-*N*-(5-methyl-4-methylenehex-5-enyl)benzenesulfonamide (1q)**



Sulfonamide **S31** [13] was prepared by following the procedures for converting **S1** to **S2**. **S30** (195 mg, 0.78 mmol) and Grubbs II generation catalyst (11.8 mg, 0.014 mmol) were used, and **S31** (187 mg, 0.67 mmol) was generated as a light brown oil in 86% yield.

Spectra data of **S31**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 5.05 (s, 1H), 4.97 (s, 1H), 4.94 (s, 1H), 4.88 (s, 1H), 4.67-4.58 (br, 1H), 2.95 (q, J = 6.7 Hz, 2H), 2.43 (s, 3H), 2.25 (t, J = 7.5 Hz, 2H), 1.86 (s, 3H), 1.63 (quintet, J = 7.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.5, 143.3, 142.2, 137.0, 129.7, 127.1, 112.82, 112.80, 43.0, 30.6, 28.5, 21.5, 21.1. IR (neat): υ 3296, 3099, 2954, 2894, 1460, 1419. HRMS (ESI) calcd for $C_{15}H_{22}NO_2S$ $(M+H)^+$: 280.1366. Found: 280.1365.

Sulfonamide **1q** was synthesized by following the procedure for converting **S2** to **1a**. **S31** (170 mg, 0.61 mmol), NaH (80 mg, 60%, 2.00 mmol), and allyl bromide (160 mg, 1.32 mmol) were used, and **1q** (167 mg, 0.52 mmol) was generated as a colorless oil in 86% yield.

Spectra data of **1q**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.63 (ddt, J = 17.2 Hz, 10.5 Hz and 6.3 Hz, 1H), 5.16 (d, J = 17.2 Hz, 1H), 5.12 (d, J = 10.5 Hz, 1H), 5.08 (s, 1H), 5.00 (s, 1H), 4.96 (s, 1H), 4.93 (s, 1H), 3.79 (d, J = 6.4 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 2.23 (t, J = 7.6 Hz, 2H), 1.89 (s, 3H), 1.67 (quintet, J = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 143.1, 142.4, 137.2, 133.3, 129.6, 127.2, 118.7, 112.7, 112.4, 50.6, 47.1, 30.7, 27.1, 21.5, 21.1. IR (neat): υ 3088, 2961, 2931, 2879, 1456. HRMS (ESI) calcd for $C_{18}H_{25}NNaO_2S$ $(M+Na)^+$: 342.1498. Found: 342.1496.

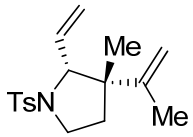
2.2 General Procedures for Rh(I)-Catalyzed C-H Activation/addition Reactions

General Procedures

General Procedures for the C-H Activation/addition Reactions: Anhydrous DCE (1.0 mL) was added to a mixture of $RhCl(PPh_3)_3$ (9.0 mg, 9.7 μmol) and $AgSbF_6$ (4.3 mg,12.6 μmol, 1.3 equiv. to Rh) under argon. The mixture was stirred at room temperature for 10 min. To the resulting brown suspension was added dropwise a DCE (1.2 mL) solution of the substrate (97 μmol). The reaction tube was immersed into an oil bath (The temperature was indicated in each case). When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and filtered through a thin pad of silica gel. The filter cake was washed with PE and EA (PE/EA = 5:1), and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product.

Experimental data for cycloadducts

3-methyl-3-(prop-1-en-2-yl)-1-tosyl-2-vinylpyrrolidine (2a)



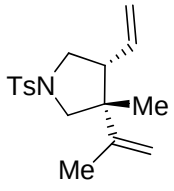
2a

Following the general procedure, sulfonamide **1a** (29.6 mg, 97 μmol) was converted to product **2a** (26.7 mg, 87 μmol, 90%) as a colorless oil. Reaction temperature: 65 ºC, reaction time: 2 h. A single diastereomer was observed by ^{1}H-NMR spectrum. The structure of **2a** was determined by analogy.

Spectra data of **2a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.55 (ddd, J = 16.8 Hz, 10.0 Hz and 6.8 Hz, 1H), 5.28 (dt, J = 16.8 Hz and 1.4 Hz, 1H), 5.11 (dt, J = 10.0 Hz and 1.4 Hz, 1H), 4.76 (t, J = 1.4 Hz, 1H), 4.65 (s, 1H), 3.99 (d, J = 6.8 Hz, 1H), 3.48 (t, J = 9.3 Hz, 1H), 3.29 (ddd, J = 10.9 Hz, 9.3 Hz and 6.8 Hz, 1H), 2.42 (s, 3H), 2.16 (q, J = 10.8 Hz, 1H), 1.70 (s, 3H), 1.55 (dd, J = 12.3 Hz and 6.8 Hz, 1H), 0.72 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.6, 143.1, 135.9, 135.5, 129.4, 127.4, 117.0, 111.5, 69.4, 50.6, 45.4, 32.8, 23.4, 21.5, 20.3. IR (neat): υ 3095, 2980, 2890, 1650, 1598, 1497, 1456, 1408. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1520.

3-methyl-3-(prop-1-en-2-yl)-1-tosyl-4-vinylpyrrolidine (2b)



2b

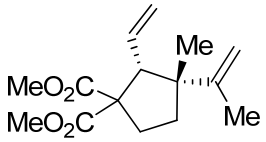
Following the general procedure, sulfonamide **1b** (29.6 mg, 97 μmol) was converted to product **2b** (22.5 mg, 74 μmol, 76%) as a colorless oil. Reaction temperature: 70 ºC, reaction time: 2 h. A single

diastereomer was observed by ^{1}H-NMR spectrum. Structure of **2b** was determined by 1D nOe experiment.

Spectra data of **2b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.26 (ddd, J = 17.0 Hz, 10.0 Hz and 8.9 Hz, 1H), 4.90 (d, J = 17.0 Hz, 1H), 4.88 (d, J = 8.9 Hz, 1H), 4.75 (s, 1H), 4.56 (s, 1H), 3.58 (dd, J = 10.0 Hz and 6.7 Hz, 1H), 3.46 (d, J = 9.3 Hz, 1H), 3.25 (dd, J = 10.3 Hz and 3.4 Hz, 1H), 3.19 (d, J = 9.3 Hz, 1H), 2.44 (s, 3H), 2.42-2.38 (m, 1H), 1.64 (s, 3H), 1.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.6, 143.3, 136.3, 134.3, 129.6, 127.3, 116.1, 111.3, 56.3, 51.8, 51.1, 50.1, 24.5, 21.5, 20.4. IR (neat): υ 3088, 2980, 2931, 2909, 2879, 1471, 1643, 1456. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1522.

Dimethyl 3-methyl-3-(prop-1-en-2-yl)-2-vinylcyclopentane-1,1-dicarboxylate (2c)



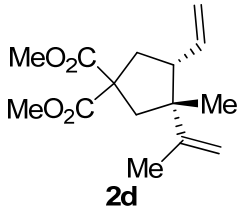
2c

Following the general procedure, sulfonamide **1c** (25.8 mg, 97 μmol) was converted to product **2c** (19.4 mg, 73 μmol, 75%) as a colorless oil. Reaction temperature: 80 ºC, reaction time: 2 h. A single diastereomer was observed by ^{1}H-NMR spectrum. Structure of **2c** was determined by 1D nOe experiment.

Spectra data of **2c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.42 (dt, J = 16.8 Hz and 10.4 Hz, 1H), 5.01 (dd, J = 16.8 Hz and 2.0 Hz, 1H), 4.92 (dd, J = 10.4 Hz and 2.0 Hz, 1H), 4.70 (s, 2H), 3.75 (s, 3H), 3.58 (s, 3H), 3.36 (d, J = 10.4 Hz, 1H), 2.80-2.72 (m, 1H), 2.23-2.11 (m, 2H), 1.68 (s, 3H), 1.58-1.51 (m, 1H), 1.02 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.1, 171.0, 149.5, 136.2, 116.8, 110.1, 65.3, 56.9, 52.7, 52.4, 35.1, 31.1, 25.1, 20.1. IR (neat): υ 3091, 2961, 2894, 2853, 1739, 1646, 1441. HRMS (ESI) calcd for $C_{15}H_{22}NaO_4$ $(M+Na)^+$: 289.1410. Found: 289.1409.

Dimethyl 3-methyl-3-(prop-1-en-2-yl)-4-vinylcyclopentane-1,1-dicarboxylate (2d)



2d

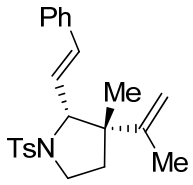
Following the general procedure, sulfonamide **1d** (25.8 mg, 97 μmol) was converted to product **2d** (21.2 mg, 80 μmol, 82%) as a colorless oil. Reaction temperature: 70 ºC, reaction time: 2 h. A single diastereomer was observed by ^{1}H-NMR spectrum. Structure of **2d** was determined by 1D nOe experiment.

Spectra data of **2d**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.66 (ddd, J = 17.1 Hz, 10.4 Hz and 8.5 Hz, 1H), 4.98 (d, J = 17.1 Hz, 1H),

4.93 (d, J = 10.4 Hz, 1H), 4.77 (s, 1H), 4.72 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.79 (d, J = 14.5 Hz, 1H), 2.72 (dd, J = 14.5 Hz and 7.0 Hz, 1H), 2.47 (dd, J = 15.1 Hz and 6.6 Hz, 1H), 2.27 (t, J = 2.6 Hz, 1H), 2.23 (t, J = 2.6 Hz, 1H), 1.69 (s, 3H), 1.12 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.5, 173.0, 149.6, 139.0, 114.7, 110.9, 58.4, 53.3, 52.89, 52.86, 51.3, 44.0, 38.9, 26.1, 20.9. IR (neat): υ 3091, 2961, 2268, 1732, 1639, 1441. HRMS (ESI) calcd for $C_{15}H_{22}NaO_4$ $(M+Na)^+$: 289.1410. Found: 289.1411.

3-methyl-3-(prop-1-en-2-yl)-2-styryl-1-tosylpyrrolidine (2e)



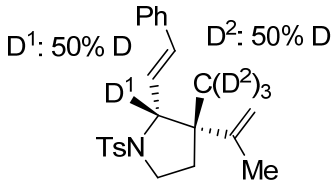
2e

Following the general procedure, sulfonamide **1e** (37.0 mg, 97 μmol) was converted to product **2e** (25.3 mg, 66 μmol, 69%) as a colorless oil. Reaction temperature: 80 ºC, reaction time: 24 h. A single diastereomer was observed by ^{1}H-NMR spectrum. The structure of **2e** was determined by analogy.

Spectra data of **2e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.6 Hz, 2H), 7.29-7.18 (m, 7H), 6.51 (d, J = 15.6 Hz, 1H), 5.73 (dd, J = 15.6 Hz and 7.9 Hz, 1H), 4.74 (t, J = 1.4 Hz, 1H), 4.67 (s, 1H), 4,19 (d, J = 7.9 Hz, 1H), 3.51 (t, J = 9.3 Hz, 1H), 3.42 (ddd, J = 10.8 Hz, 9.3 Hz and 6.7 Hz, 1H), 2.36 (s, 3H), 2.29-2.19 (m, 1H), 1.71 (s, 3H), 1.64 (dd, J = 12.2 Hz and 6.7 Hz, 1H), 0.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.7, 143.0, 136.8, 136.4, 132.2, 129.4, 128.3, 127.51, 127.47, 126.9, 126.6, 111.6, 69.2, 51.0, 45.4, 33.2, 23.7, 21.4, 20.2. IR (neat): υ 3069, 3039, 2976, 2935, 2890, 2861, 1650, 1456, 1373. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1832.

Deuterated 3-methyl-3-(prop-1-en-2-yl)-2-styryl-1-tosylpyrrolidine (2e-D)



2e-D

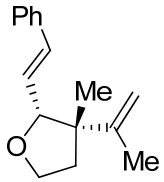
Following the general procedure, sulfonamide **1e-D** (37.2 mg, 97 μmol) was converted to product **2e-D** (26.0 mg, 68 μmol, 70%) as a colorless oil. Reaction temperature: 80 ºC, reaction time: 24 h. A single diastereomer was observed by ^{1}H-NMR spectrum.

Spectra data of **2e-D**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.29-7.17 (m, 7H), 6.51 (d, J = 16.4 Hz, 1H), 5.77-5.71 (m, 1H), 4.74 (s, 1H), 4.67 (s, 1H), 4.19 (d, J = 8.6 Hz, 0.51H), 3.50 (t, J = 9.4 Hz, 1H), 3.45-3.39 (m, 1H), 2.36 (s, 3H), 2.25 (q, J = 10.8 Hz, 1H), 1.71 (s, 3H), 1.64 (dd, J = 12.3 Hz and 6.7 Hz, 1H), 0.90-0.86 (m, 1.55H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.7, 143.0, 136.8, 136.4, 132.2, 129.4, 128.4, 127.50, 127.47, 126.9, 126.8, 126.6, 111.6, 69.1, 50.9, 45.4, 33.14, 33.12, 21.4, 20.2. The redundant peaks

are for the other deuterium substituted products. HRMS (ESI) calcd for $C_{23}H_{26}D_2NO_2S$ $(M+H)^+$: 384.1961. Found: 384.1958.

3-methyl-3-(prop-1-en-2-yl)-2-styryltetrahydrofuran (2f)



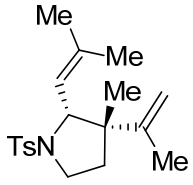
2f

Following the general procedure, sulfonamide **1f** (22.1 mg, 97 μmol) was converted to product **2f** (13.7 mg, 60 μmol, 62%) as a colorless oil. Reaction temperature: 60 ºC, reaction time: 3 h. An inseparable mixture of two diastereomers was observed by ^{1}H-NMR spectrum with dr = 5:1 (based on the ^{1}H-NMR peaks in 1.27 ppm of the major isomer and 1.12 ppm of the minor isomer). Structure of the major isomer was determined by 1D nOe experiment.

Spectra data of **2f**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.19 (m, 5H), 6.56 (d, J = 15.8 Hz, 1H), 6.04 (dd, J = 15.8 Hz and 6.8 Hz, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 4.21 (d, J = 6.8 Hz, 1H), 4.12 (td, J = 9.0 Hz and 3.0 Hz, 1H), 4.06-3.92 (m, 1H), 2.29 (dt, J = 12.0 Hz and 9.5 Hz, 1H), 1.78 (s, 3H), 1.76-1.70 (m, 1H), 1.27 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 137.1, 132.1, 131.3, 128.5, 128.4, 127.9, 127.44, 127.40, 126.70, 126.52, 126.46, 111.2, 87.1, 66.6, 63.0, 51.2, 36.0, 24.6, 21.0. The redundant peaks are for the other diastereomer. IR (neat): υ 3091, 3039, 2976, 2950, 2890, 2253, 1646, 1456. HRMS (ESI) calcd for $C_{16}H_{20}NaO$ $(M+Na)^+$: 251.1406. Found: 251.1405.

3-methyl-2-(2-methylprop-1-enyl)-3-(prop-1-en-2-yl)-1-tosylpyrrolidine (2g)



2g

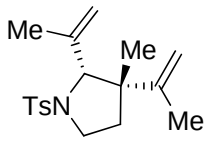
Following the general procedure, sulfonamide **1g** (32.3 mg, 97 μmol) was converted to product **2g** (14.6 mg, 44 μmol, 45%) as a colorless oil. Reaction temperature: 80 ºC, reaction time: 30 h. An inseparable mixture of two diastereomers was observed by ^{1}H-NMR spectrum with dr = 11:1 (based on the ^{1}H-NMR peaks in 0.91 ppm of the major isomer and 0.97 ppm of the minor isomer). Structure of the major isomer was determined by 1D nOe experiment.

Spectra data of **2g**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 4.72-4.66 (m, 2H), 4.60 (s, 1H), 4.24 (d, J = 11.4 Hz, 1H), 3.42-3.37 (m, 2H), 2.41 (s, 3H), 2.20 (q, J = 10.9 Hz, 1H), 1.78 (d, J = 0.9 Hz, 3H), 1.69-1.62 (m, 1H), 1.58 (s, 3H), 1.57 (s, 3H), 0.91 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$):

δ 147.8, 142.7, 136.8, 134.1, 129.1, 127.3, 122.5, 110.5, 64.8, 50.8, 45.2, 33.5, 25.8, 24.2, 21.5, 19.8, 18.0. IR (neat): υ 2976, 2935, 2894, 2868, 1646, 1453. HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ $(M+H)^+$: 334.1835. Found: 334.1833.

3-methyl-2,3-di(prop-1-en-2-yl)-1-tosylpyrrolidine (2h)



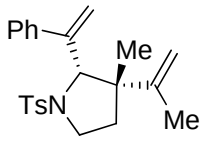
2h

Following the general procedure, sulfonamide **1h** (31.0 mg, 97 μmol) was converted to product **2h** (25.2 mg, 79 μmol, 81%) as a white solid (crystallization from a mixture of dichloromethane and petrol ether to afford a colorless crystal, melting point: 140-142 ºC). Reaction temperature: 80 ºC, reaction time: 12 h. A single diastereomer was observed by ^{1}H-NMR spectrum.

Spectra data of **2h**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.92 (s, 1H), 4.86 (t, J = 1.4 Hz, 1H), 4.79 (t, J = 1.4 Hz, 1H), 4.71 (s, 1H), 4.03 (s, 1H), 3.56 (td, J = 9.2 Hz and 0.8 Hz, 1H), 3.40 (ddd, J = 11.2 Hz, 9.2 Hz and 7.1 Hz, 1H), 2.42 (s, 3H), 2.37 (q, J = 11.2 Hz, 1H), 1.74 (s, 3H), 1.57 (dd, J = 12.3 Hz and 7.1 Hz,1H), 1.51 (s, 3H), 0.81 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 144.1, 143.0, 135.8, 129.3, 127.3, 116.5, 111.4, 73.9, 51.3, 46.2, 33.9, 25.5, 21.5, 20.5, 18.7. IR (neat): υ 2972, 2931, 2868, 1646, 1456. HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1677.

3-methyl-2-(1-phenylvinyl)-3-(prop-1-en-2-yl)-1-tosylpyrrolidine (2i)



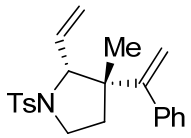
2i

Following the general procedure, sulfonamide **1i** (37.0 mg, 97 μmol) was converted to product **2i** (30.0 mg, 79 μmol, 81%) as a pale yellow oil. Reaction temperature: 80 ºC, reaction time: 20 h. A single diastereomer was observed by ^{1}H-NMR spectrum. Structure of **2i** was determined by 1D nOe experiment.

Spectra data of **2i**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.0 Hz, 2H), 7.34-7.23 (m, 7H), 5.09 (s, 1H), 5.01 (s, 1H), 4.64 (s, 1H), 4.56 (s, 1H), 4.54 (s, 1H), 3.52 (t, J = 9.0 Hz, 1H), 3.35 (ddd, J = 10.8 Hz, 9.0 Hz and 6.5 Hz, 1H), 2.42 (s, 3H), 2.25 (q, J = 10.6 Hz, 1H), 1.42 (dd, J = 12.0 Hz and 6.6 Hz, 1H), 1.16 (s, 3H), 0.72 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.8, 145.5, 143.1, 141.9, 135.8, 129.4, 128.0, 127.8, 127.3, 127.1, 116.7, 112.4, 71.4, 51.4, 45.6, 32.2, 24.2, 21.5, 20.8. IR (neat): υ 3095, 3069, 3035, 2983, 2942, 2890, 1646, 1453. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1833.

3-methyl-3-(1-phenylvinyl)-1-tosyl-2-vinylpyrrolidine (2j)



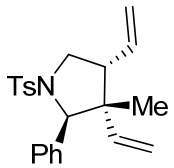
2j

Following the general procedure, sulfonamide **1j** (35.6 mg, 97 μmol) was converted to product **2j** (22.8 mg, 62 μmol, 64% based on the unpure substrate) as a pale yellow oil. Reaction temperature: 65 ºC, reaction time: 2 h. An inseparable mixture of two diastereomers was observed by ^{1}H-NMR spectrum with dr = 11:1 (based on the ^{1}H-NMR peaks in 7.73 ppm of the major isomer and 7.68 ppm of the minor isomer). Structure of the main isomer was determined by 1D nOe experiment.

Spectra data of **2j**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.9 Hz, 2H), 7.29-7.26 (m, 5H), 7.21-7.19 (m, 2H), 5.75 (ddd, J = 16.8 Hz, 10.2 Hz and 6.0 Hz, 1H), 5.28 (dt, J = 16.8 Hz and 1.5 Hz, 1H), 5.160 (dt, J = 10.2 Hz and 1.5 Hz, 1H), 5.158 (s, 1H), 5.11 (s, 1H), 4.30 (d, J = 6.0 Hz, 1H), 3.46 (t, J = 9.0 Hz, 1H), 3.26 (ddd, J = 10.6 Hz, 9.0 Hz and 6.9 Hz, 1H), 2.40 (s, 3H), 2.23 (q, J = 10.9 Hz, 1H), 1.59 (dd, J = 12.5 Hz and 6.9 Hz, 1H), 0.79 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.8, 143.1, 142.9, 135.9, 129.4, 128.0, 127.8, 127.3, 127.1, 117.5, 117.3, 116.6, 69.7, 50.3, 44.7, 34.1, 25.3, 21.5. IR (neat): υ 3091, 3069, 2987, 2939, 2894, 2261, 1624, 1456, 1400. HRMS (ESI) calcd for $C_{22}H_{25}NNaO_2S$ $(M+Na)^+$: 390.1498. Found: 390.1494.

3-methyl-2-phenyl-1-tosyl-3,4-divinylpyrrolidine (2k)



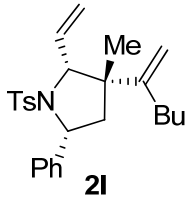
2k

Following the general procedure, sulfonamide **1k** (35.6 mg, 97 μmol) was converted to product **2k** (24.9 mg, 68 μmol, 70%) as a pale yellow oil. Reaction temperature: 65 ºC, reaction time: 2 h. A single diastereomer was observed by ^{1}H-NMR spectrum.

Spectra data of **2k**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 8.4 Hz, 2H), 7.27-7.22 (m, 5H), 7.09 (d, J = 7.2 Hz, 2H), 5.49-5.42 (m, 2H), 5.06 (d, J = 10.4 Hz, 1H), 5.01 (d, J = 17.2 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 4.95 (d, J = 17.4 Hz, 1H), 4.70 (s, 1H), 3.75 (t, J = 8.7 Hz, 1H), 3.33 (t, J = 10.1 Hz, 1H), 2.72 (dt, J = 10.6 and 8.5 Hz, 1H), 2.41 (s, 3H), 0.57 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.1, 140.10, 140.08, 135.6, 133.5, 129.3, 128.0, 127.4, 127.3, 118.7, 114.2, 71.9, 51.0, 50.9, 50.2, 21.5, 19.2. IR (neat): υ 3084, 3039, 2980, 2935, 2879, 1739, 1639, 1460, 1415. HRMS (ESI) calcd for $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1677.

3-(hex-1-en-2-yl)-3-methyl-5-phenyl-1-tosyl-2-vinylpyrrolidine (2l)



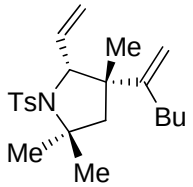
2l

Following the general procedure, sulfonamide **1l** (41.0 mg, 97 μmol) was converted to product **2l** (24.2 mg, 57 μmol, 59%) as a colorless oil. Reaction temperature: 60 ºC, reaction time: 2 h. An inseparable mixture of two diastereomers was observed by ^{1}H-NMR spectrum with dr = 15:1 (based on the ^{1}H-NMR peaks in 1.07 ppm of the major isomer and 1.02 ppm of the minor isomer). Structure of the major isomer was determined by 1D nOe experiment.

Spectra data of **2l**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 8.4 Hz, 2H), 7.19 (s, 5H), 7.06 (d, J = 8.4 Hz, 2H), 5.70 (ddd, J = 17.0 Hz, 9.8 Hz and 8.8 Hz, 1H), 5.32 (d, J = 17.0 Hz, 1H), 5.15 (d, J = 9.8 Hz, 1H), 4.83 (dd, J = 11.0 Hz and 6.4 Hz, 1H), 4.80 (s, 1H), 4.72 (s, 1H), 4.40 (d, J = 8.7 Hz, 1H), 2.34 (s, 3H), 2.19 (t, J = 12.0 Hz, 1H), 2.05 (dd, J = 12.6 Hz and 6.7 Hz, 1H), 2.02-1.97 (m, 1H), 1.90-1.85 (m, 1H), 1.50-1.44 (m, 1H), 1.39-1.26 (m, 3H), 1.07 (s, 3H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 151.3, 142.7, 141.6, 137.2, 136.4, 128.9, 128.2, 127.4, 127.21, 127.15, 117.7, 109.4, 70.9, 63.1, 50.4, 46.0, 31.8, 30.6, 24.3, 22.8, 21.4, 14.1. IR (neat): υ 2972, 2950, 2879, 2261, 1646, 1460. HRMS (ESI) calcd for $C_{26}H_{34}NO_2S$ $(M+H)^+$: 424.2305. Found: 424.2302.

4-(hex-1-en-2-yl)-2,2,4-trimethyl-1-tosyl-5-vinylpyrrolidine (2m)



2m

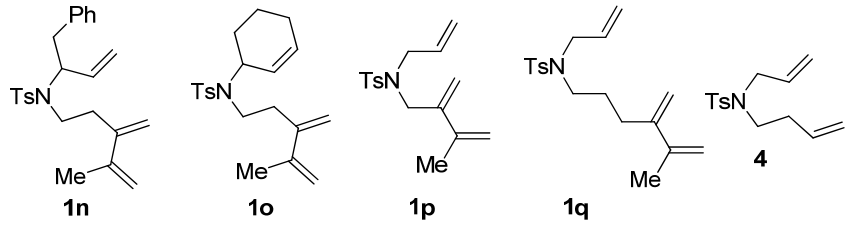
Following the general procedure, sulfonamide **1m** (36.4 mg, 97 μmol) was converted to product **2m** (27.7 mg, 74 μmol, 76%) as a colorless oil. Reaction temperature: 60 ºC, reaction time: 2 h. An inseparable mixture of two diastereomers was observed by ^{1}H-NMR spectrum with dr = 8:1 (based on the ^{1}H-NMR peaks in 4.05 ppm of the major isomer and 4.00 ppm of the minor isomer). Structure of the major isomer was determined by 1D nOe experiment.

Spectra data of **2m**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 5.60 (ddd, J = 16.9 Hz, 10.5 Hz and 8.7 Hz, 1H), 5.23 (d, J = 16.9 HZ, 1H), 5.07 (d, J = 10.5 Hz, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 4.05 (d, J = 8.7 Hz, 1H), 2.41 (s, 3H), 2.37 (d, J = 13.2 Hz, 1H), 1.96-1.77 (m, 2H), 1.69 (d, J = 13.2 Hz, 1H), 1.57 (s, 3H), 1.55 (s, 3H), 1.47-1.40 (m, 1H), 1.37-1.25 (m, 3H), 0.98 (s, 3H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 152.1, 142.5, 139.6, 135.6, 129.1, 127.6, 117.9, 109.5, 72.4, 64.5, 50.8, 49.8, 34.3, 31.5, 30.8, 28.9, 25.7, 22.8, 21.4, 14.1. IR (neat): υ 2965, 2935, 1646, 1497, 1464. HRMS (ESI)

calcd for $C_{22}H_{34}NO_2S$ $(M+H)^+$: 376.2305. Found: 376.2302.

Reaction of substrates 1n, 1o 1p, 1q and ene-ene 4 [14]



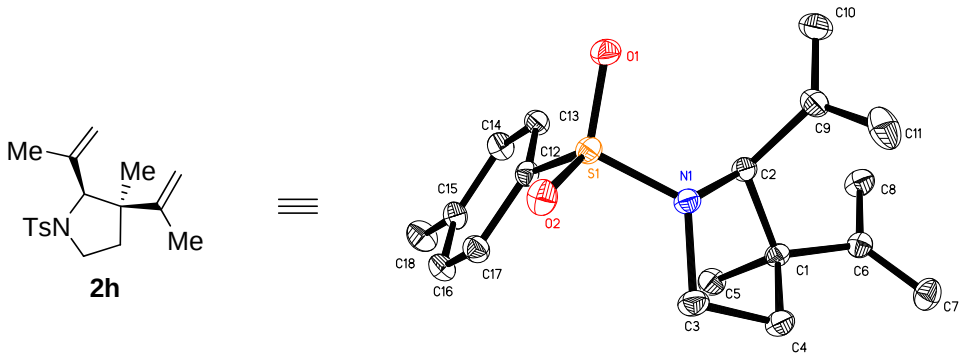
1n **1o** **1p** **1q** **4**

Substrates **1n**, **1o**, **1p**, **1q** and **4** were subjected to the standard reaction condition, but complex mixtures were generated and no desired products were detected in these mixtures

2.3 Stereochemical Determination

The relative configuration of compound **2h** was determined by X-ray crystallography. The relative configurations of compounds **2b**, **2c**, **2d**, **2f**, **2g**, **2i**, **2j**, **2k**, **2l** and **2m** were determined by 1D nOe experiments. The relative configuration of compound **2a** and **2e** were deduced by analogy.

Determination of the stereostructure of compound 2h by X-ray crystallography. See figures below for details.



Determination of the stereostructures of compounds 2b, 2c, 2d, 2f, 2g, 2i, 2j, 2k, 2l and 2m by 1D nOe experiments.

The nOe correlation between the quaternary methyl group and the indicated allylic proton (2.42-2.38 ppm) in cycloadduct **2b** indicates a *cis* relationship of the two vinyl groups (Figure S1).

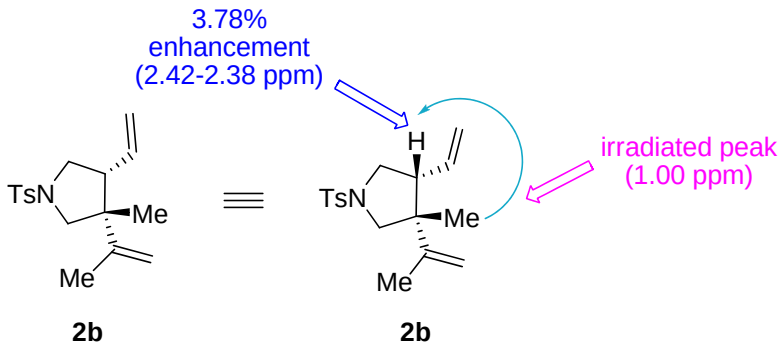


Figure S1. NMR analysis of cycloadduct **2b** (The 1D nOe spectrum is shown in page S74).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (3.36 ppm) in cycloadduct **2c** indicates a *cis* relationship of the two vinyl groups (Figure S2).

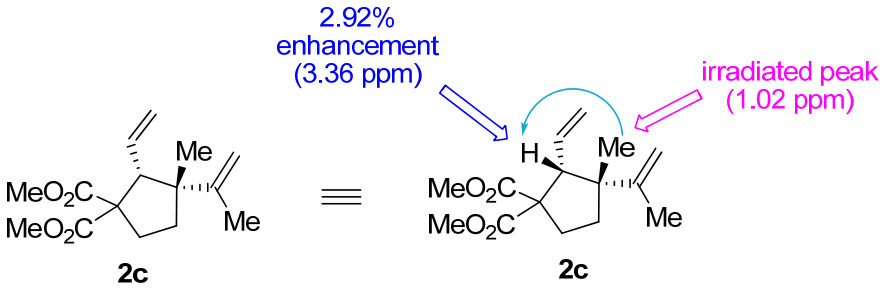


Figure S2. NMR analysis of cycloadduct **2c** (The 1D nOe spectrum is shown in page S75).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (2.47 ppm) in cycloadduct **2d** indicates a *cis* relationship of the two vinyl groups (Figure S3).

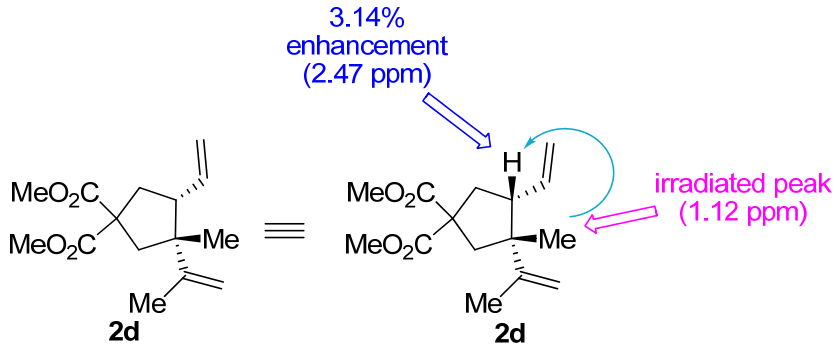


Figure S3. NMR analysis of cycloadduct **2d** (The 1D nOe spectrum is shown in page S76).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.21 ppm) in cycloadduct **2f** indicates a *cis* relationship of the two vinyl groups (Figure S4).

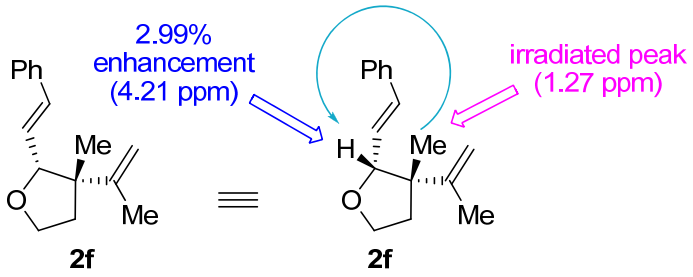


Figure S4. NMR analysis of cycloadduct **2f** (The 1D nOe spectrum is shown in page S77).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.24 ppm) in cycloadduct **2g** indicates a *cis* relationship of the two vinyl groups (Figure S5).

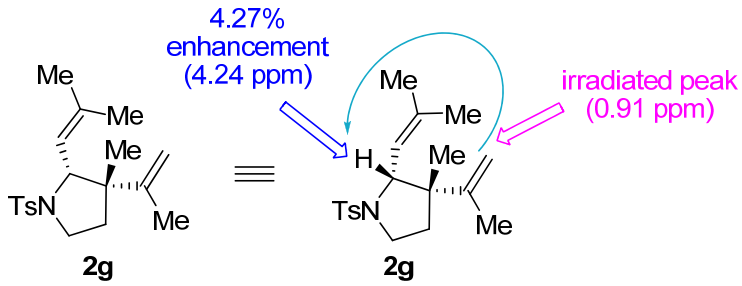


Figure S5. NMR analysis of cycloadduct **2g** (The 1D nOe spectrum is shown in page S78).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.536 ppm) in cycloadduct **2i** indicates a *cis* relationship of the two vinyl groups (Figure S6).

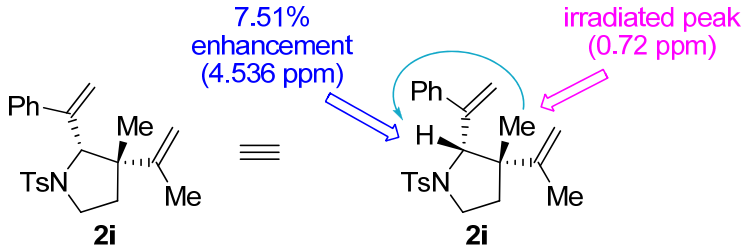


Figure S6. NMR analysis of cycloadduct **2i** (The 1D nOe spectrum is shown in page S79).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.30 ppm) in cycloadduct **2j** indicates a *cis* relationship of the two vinyl groups (Figure S7).

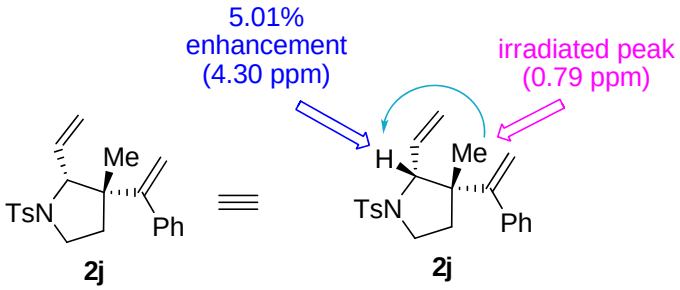


Figure S7. NMR analysis of cycloadduct **2j** (The 1D nOe spectrum is shown in page S80).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (2.74-2.69 ppm) in cycloadduct **2k** indicates a *cis* relationship of the two vinyl groups. And the nOe correlation between the benzylic proton and the indicated vinyl group (5.44 ppm and 4.95 ppm) indicates a *cis* relationship of the phenyl and the quaternary methyl group (Figure S8).

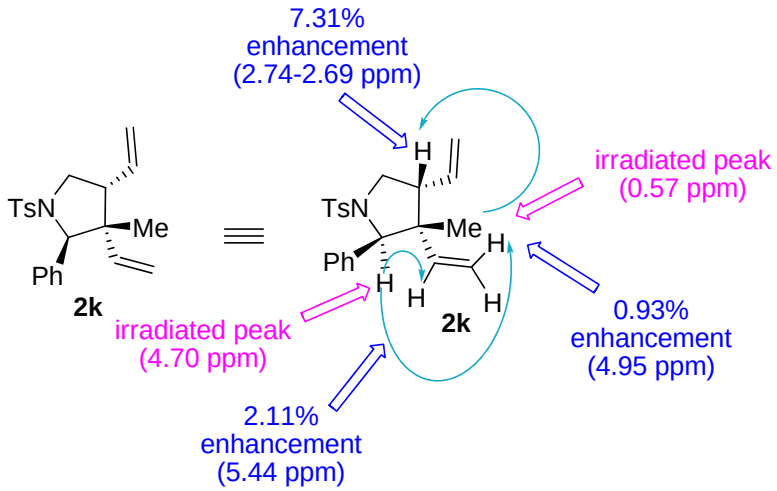


Figure S8. NMR analysis of cycloadduct **2k** (The 1D nOe spectra are in pages S81-S82).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.40 ppm) in cycloadduct **2l** indicates a *cis* relationship of the two vinyl groups. And the nOe correlation between the indicated vinyl proton (5.70 ppm) and the phenyl group indicates a *cis* relationship of this vinyl group and the phenyl group. Besides, the nOe correlation between the quaternary methyl group and the benzylic proton further verifies this relative configuration (Figure S9).

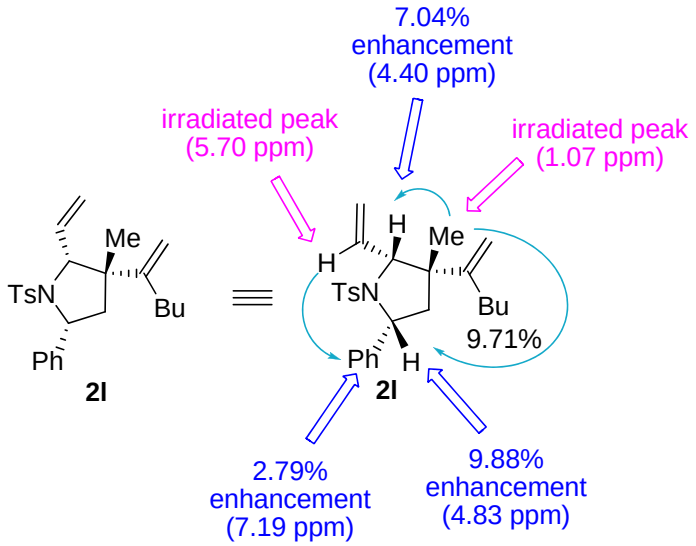


Figure S9. NMR analysis of cycloadduct **2l** (The 1D nOe spectra are shown in pages S83-S84).

The nOe correlation between the quaternary methyl group and the indicated allylic proton (4.05 ppm) in cycloadduct **2m** indicates a *cis* relationship of the two vinyl groups (Figure S10).

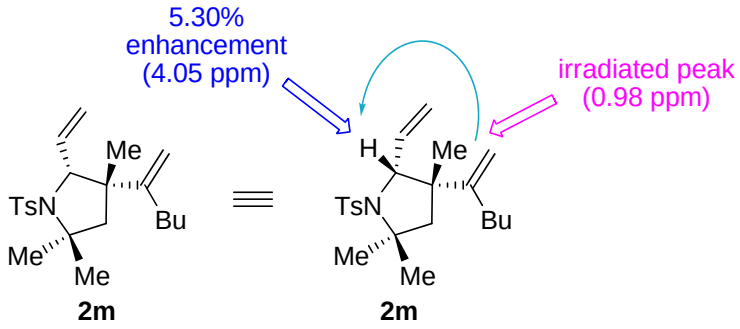


Figure S10. NMR analysis of cycloadduct **2m** (The 1D nOe spectrum is shown in page S85).

2.4 References

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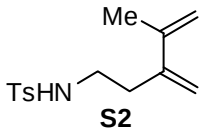
3. ^{1}H and ^{13}C-NMR Spectra for New Compounds



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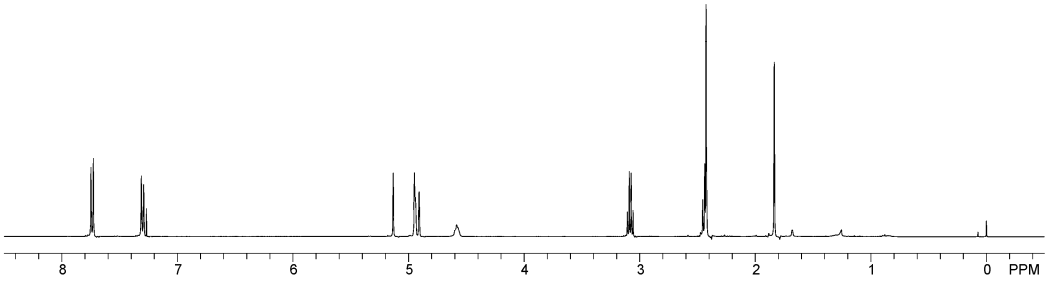

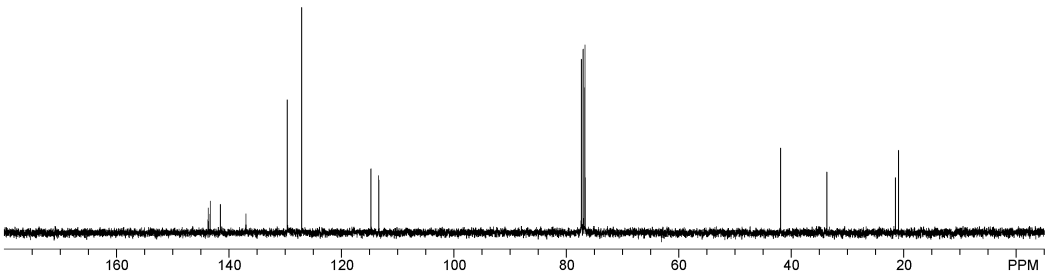

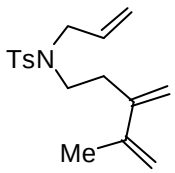

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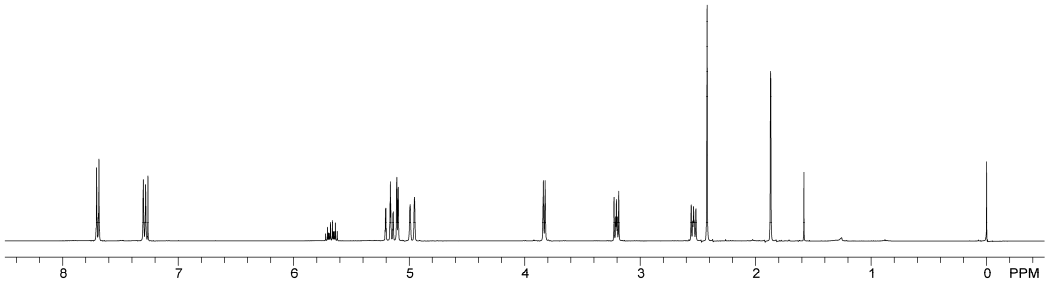

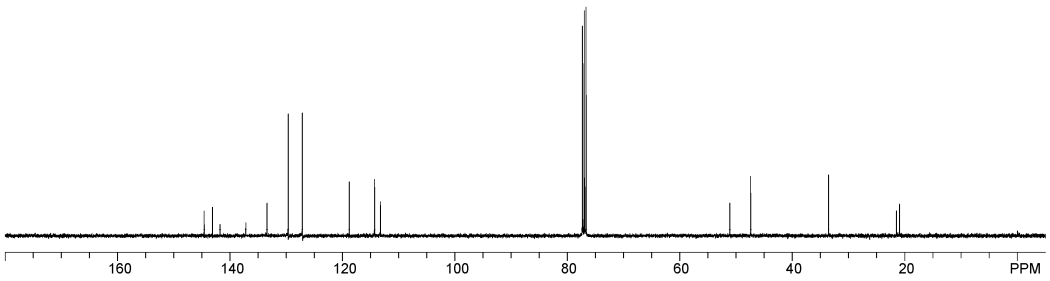

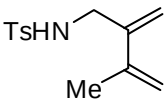

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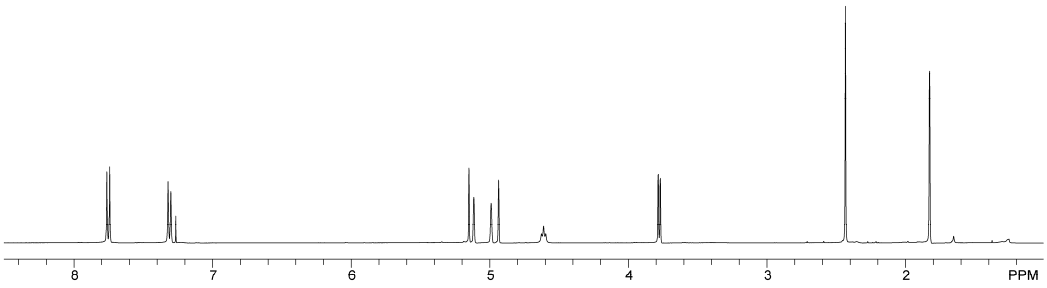

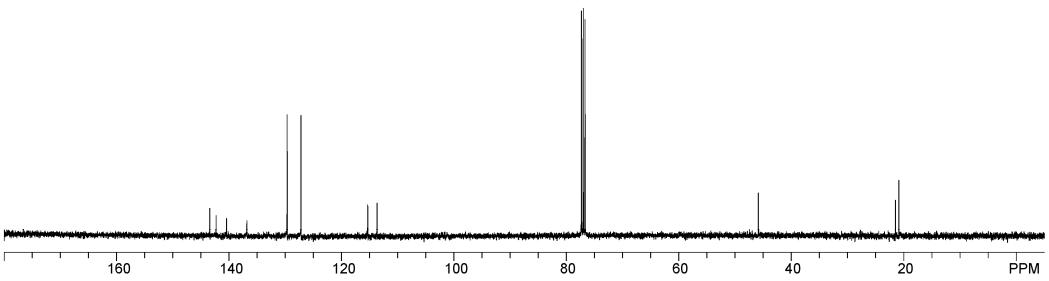

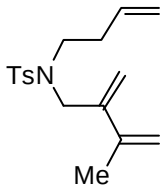

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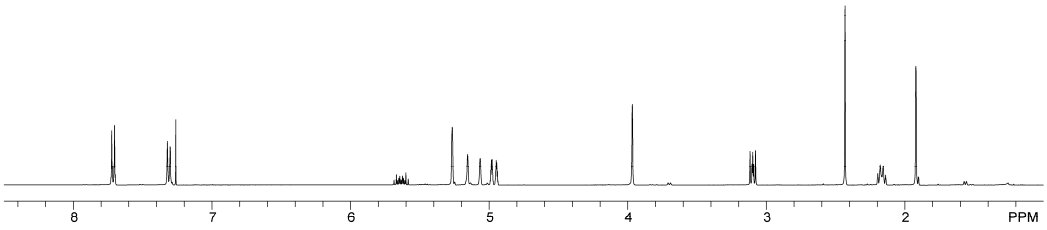

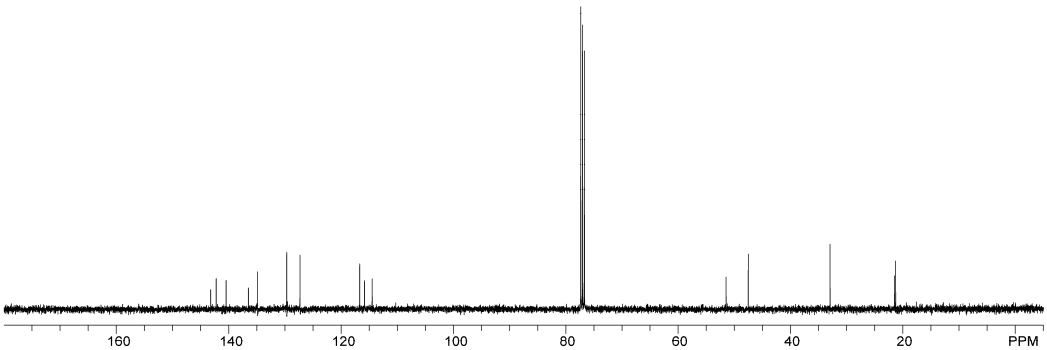

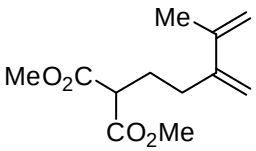

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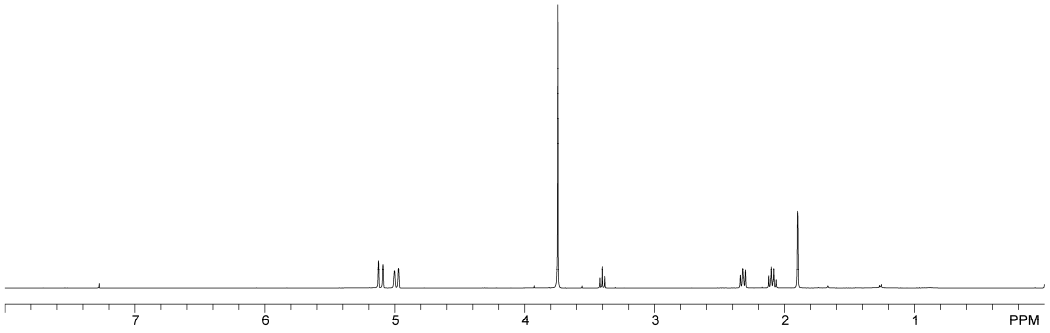

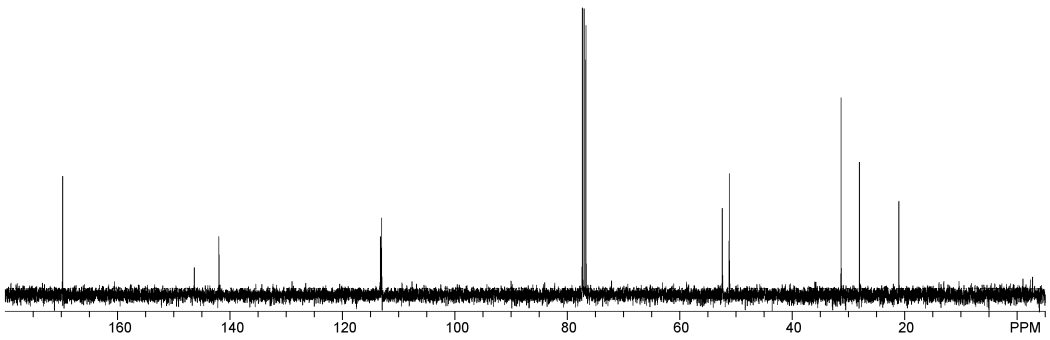

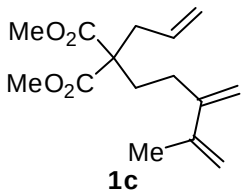

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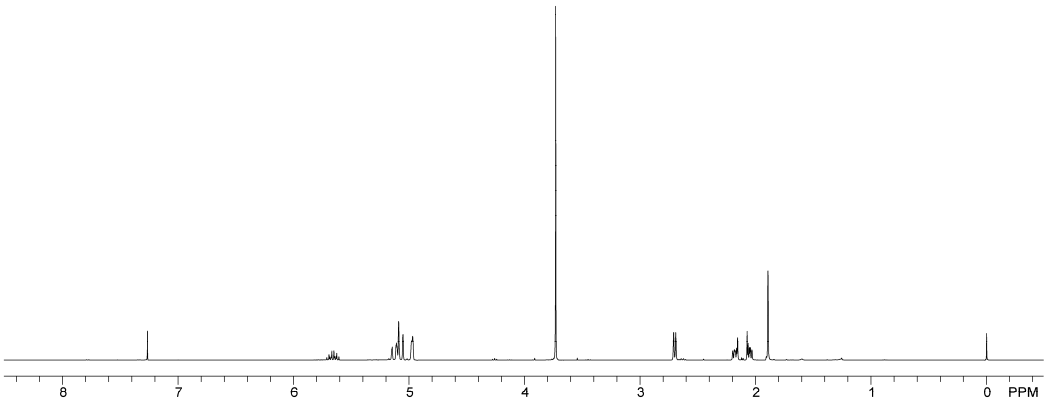

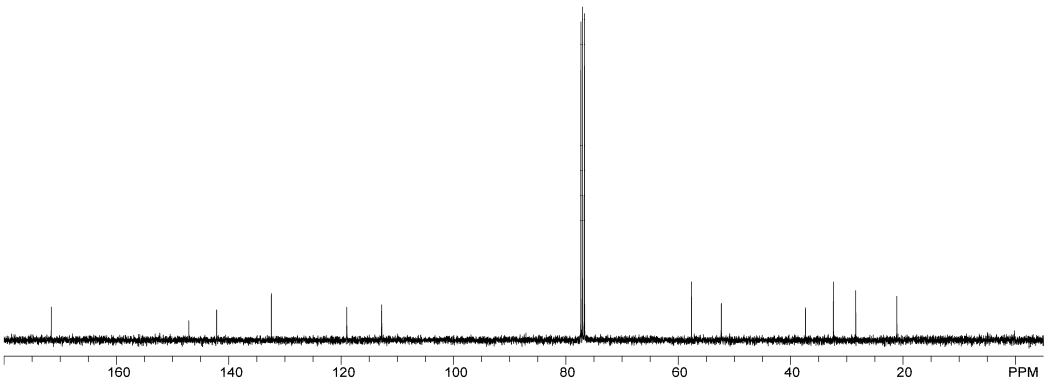

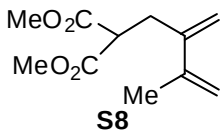

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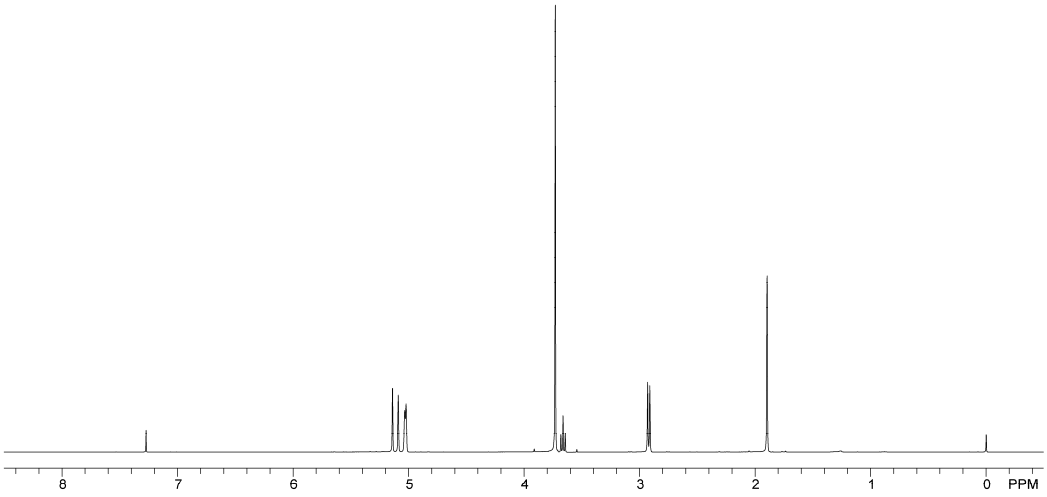

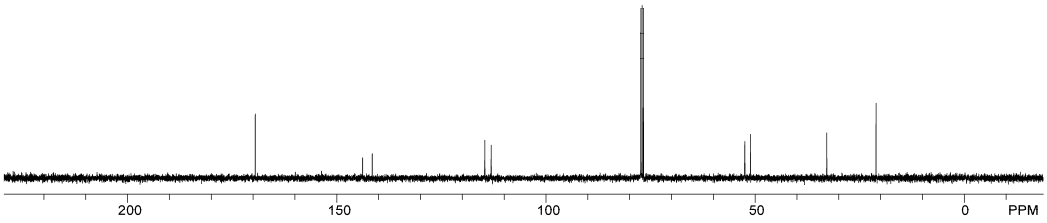

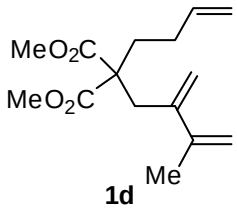

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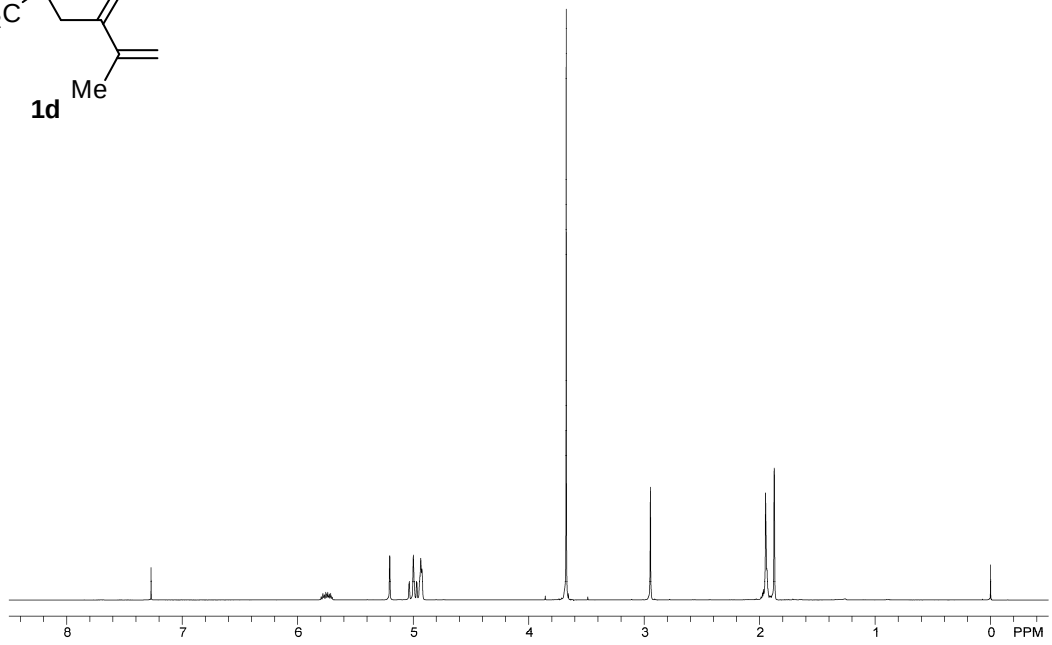

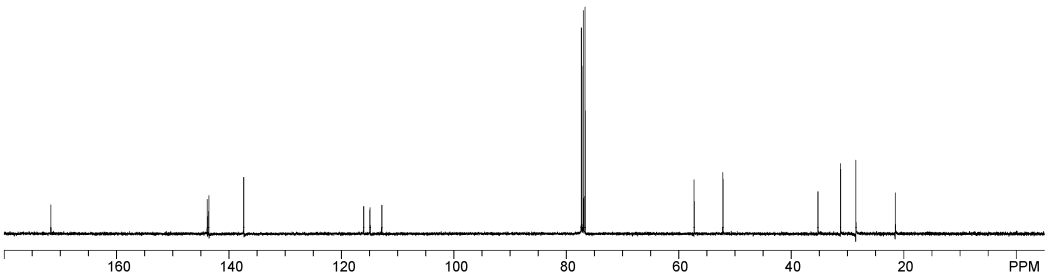

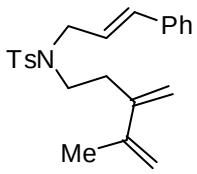

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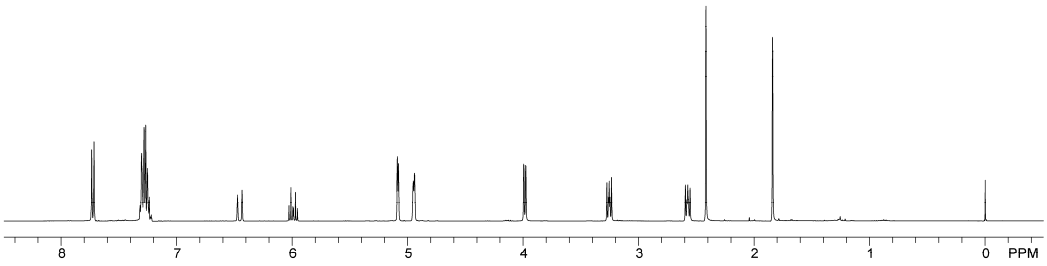

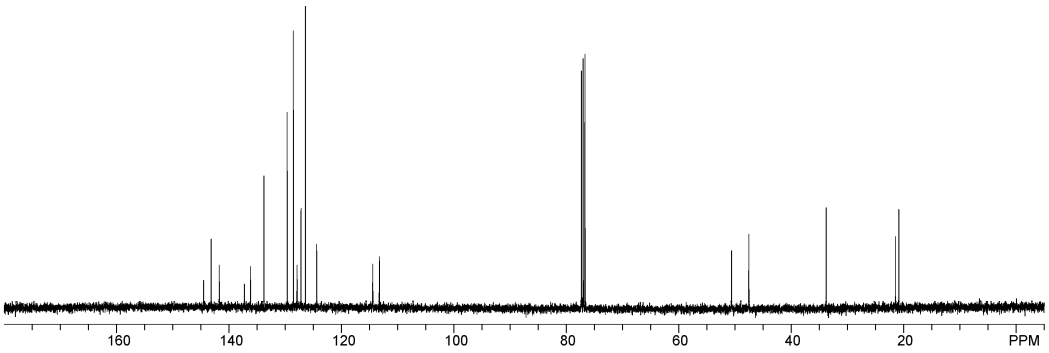

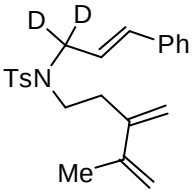

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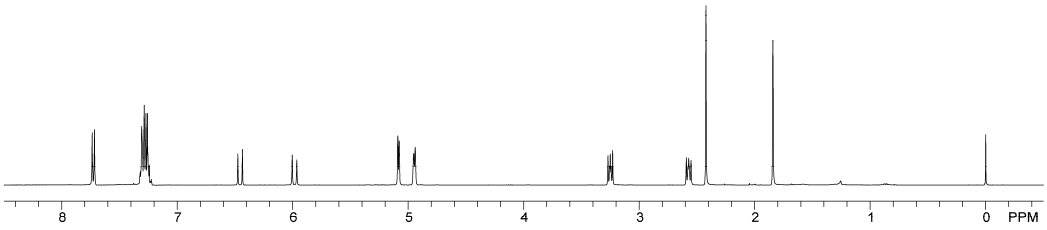

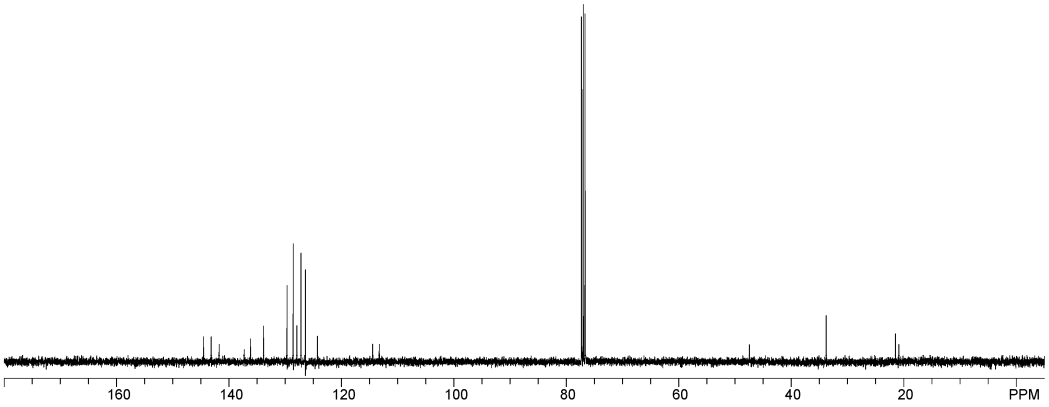

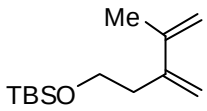

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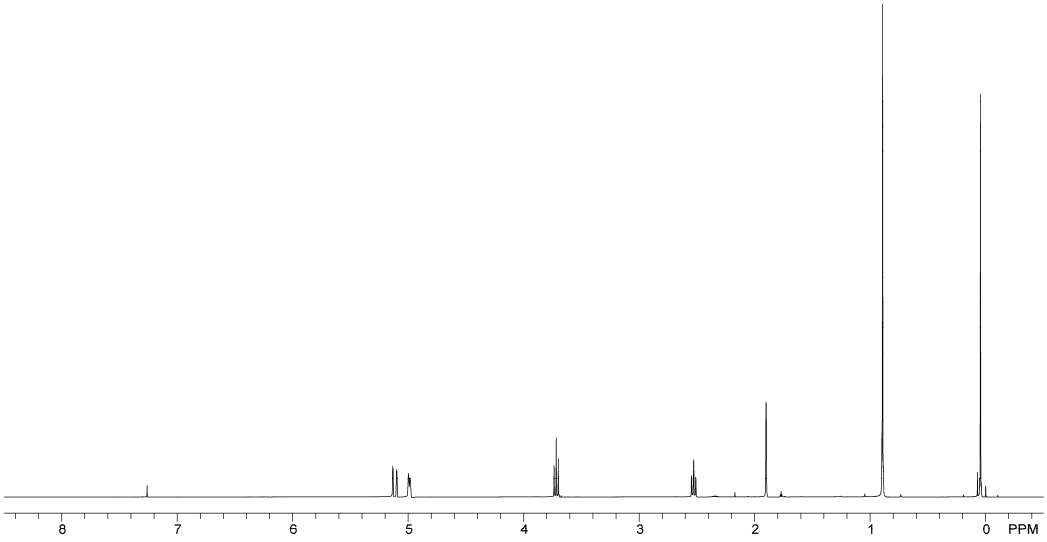

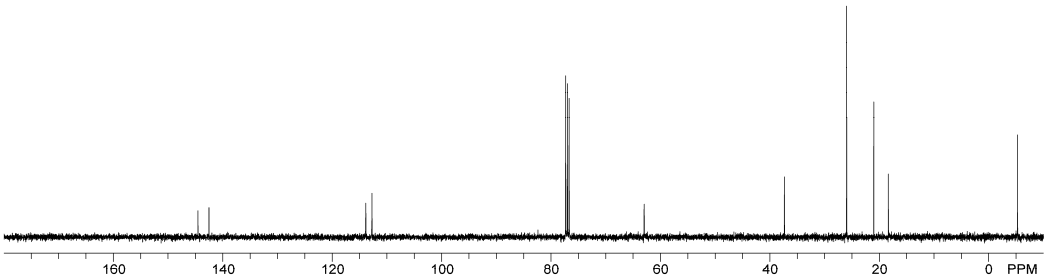

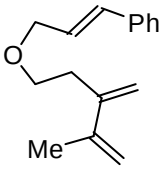

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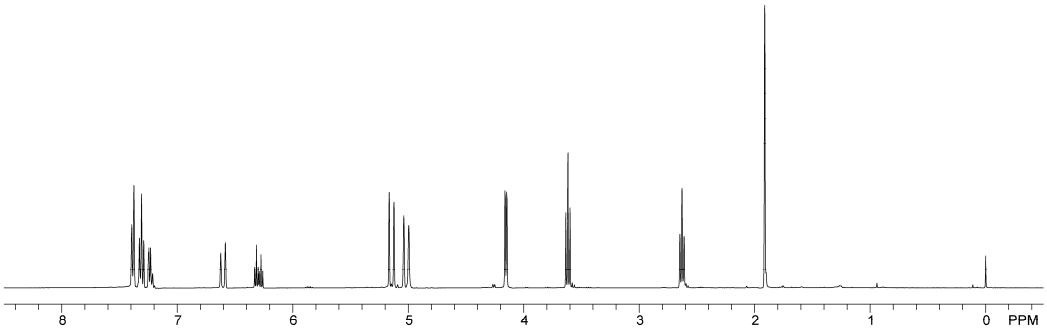

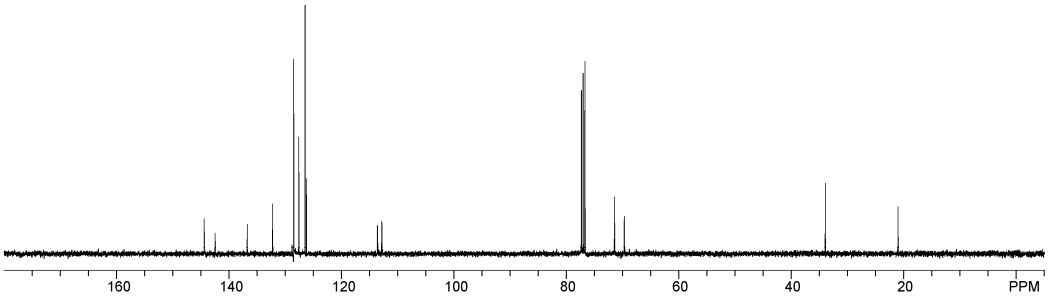

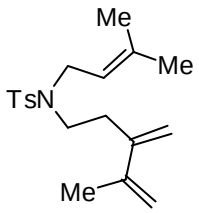

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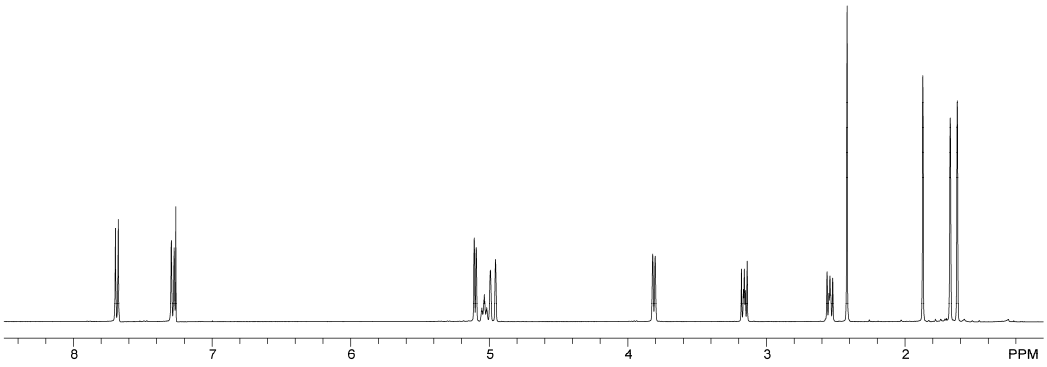

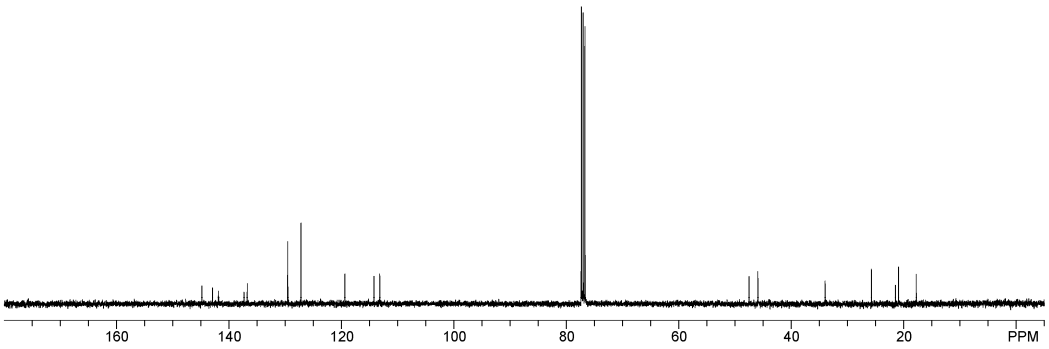

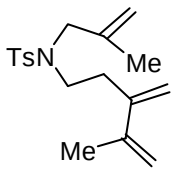

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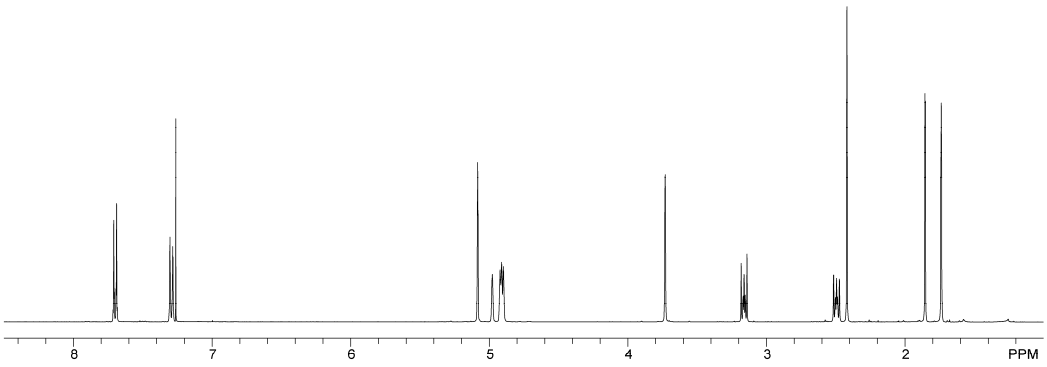

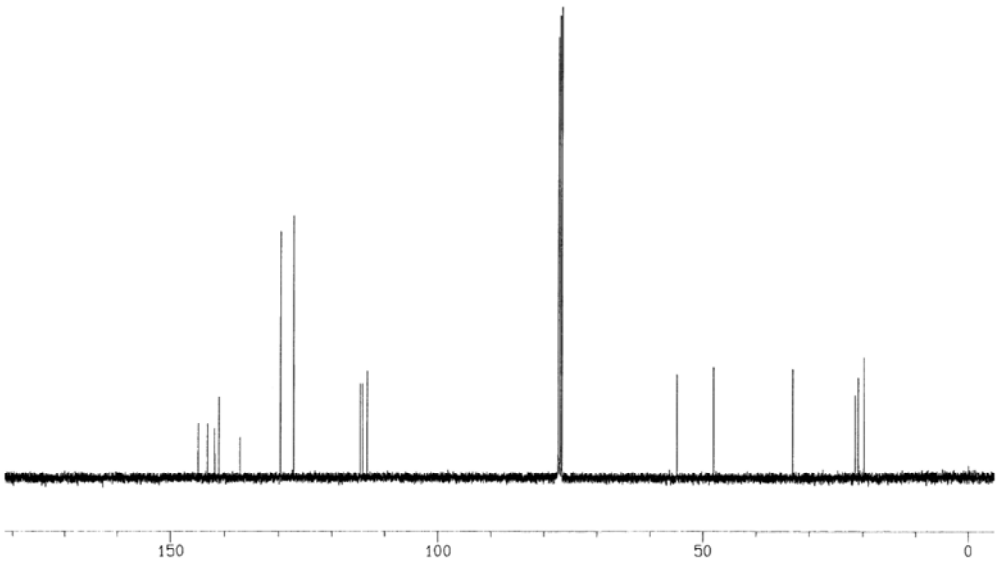

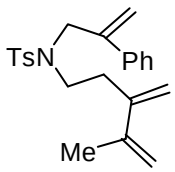

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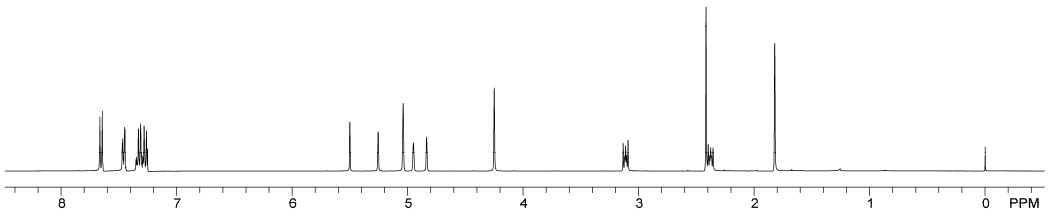

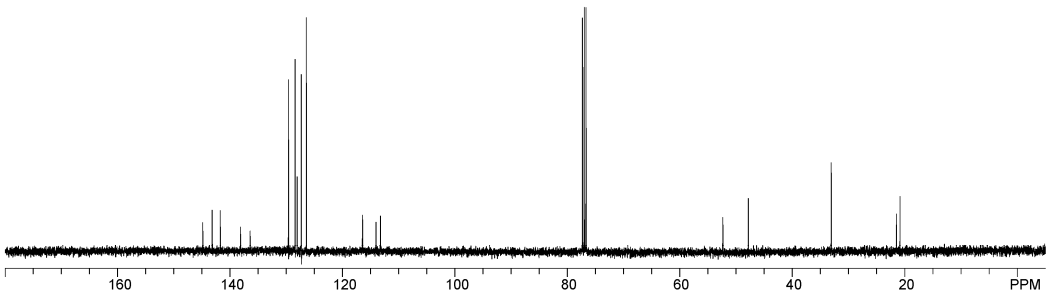

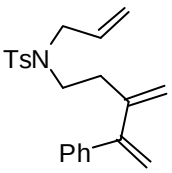

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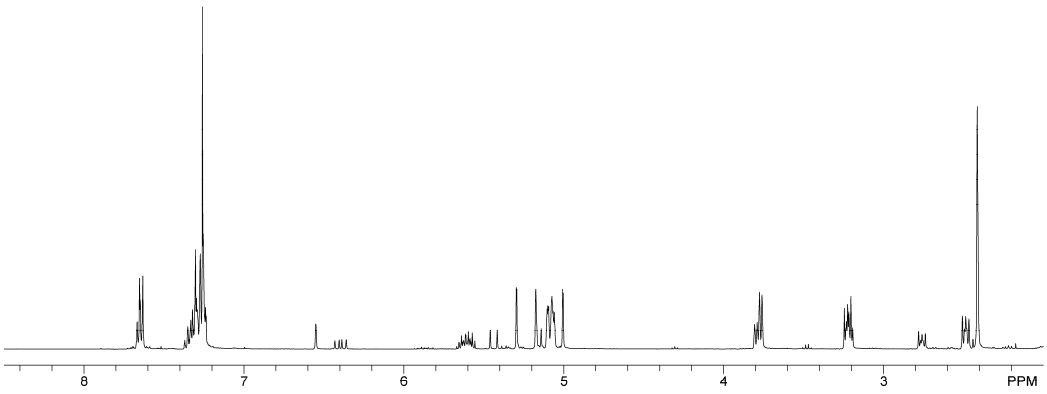

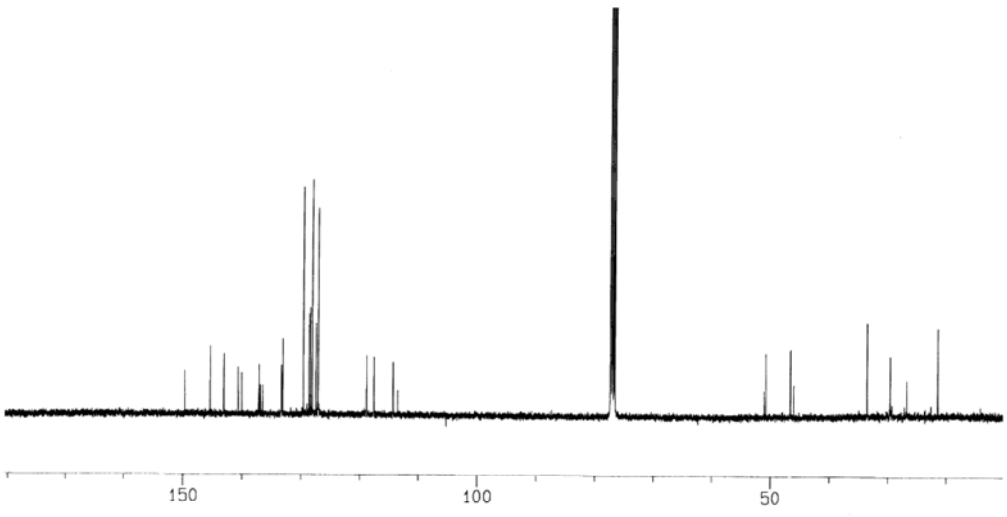

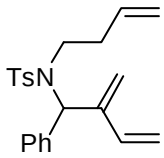

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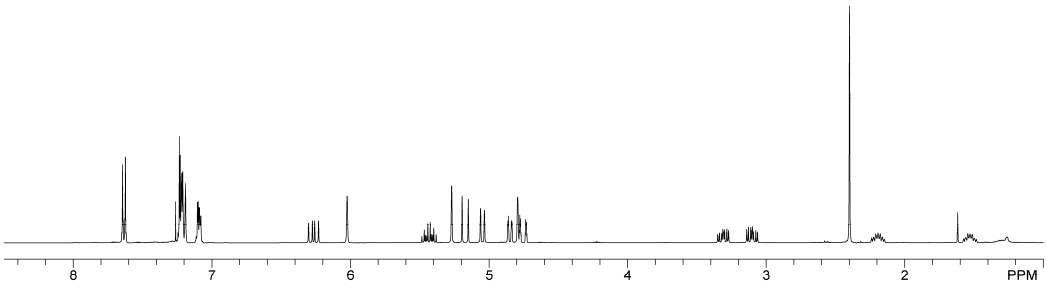

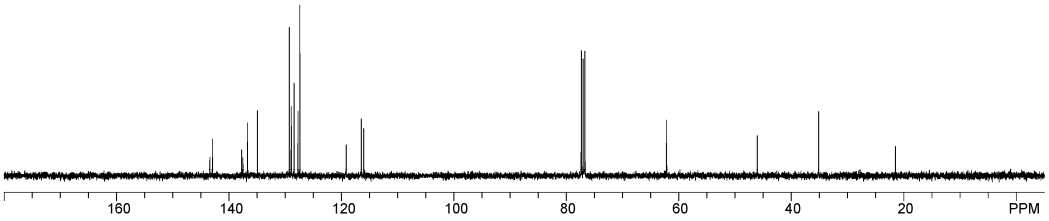

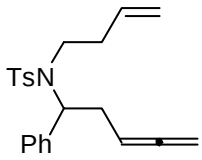

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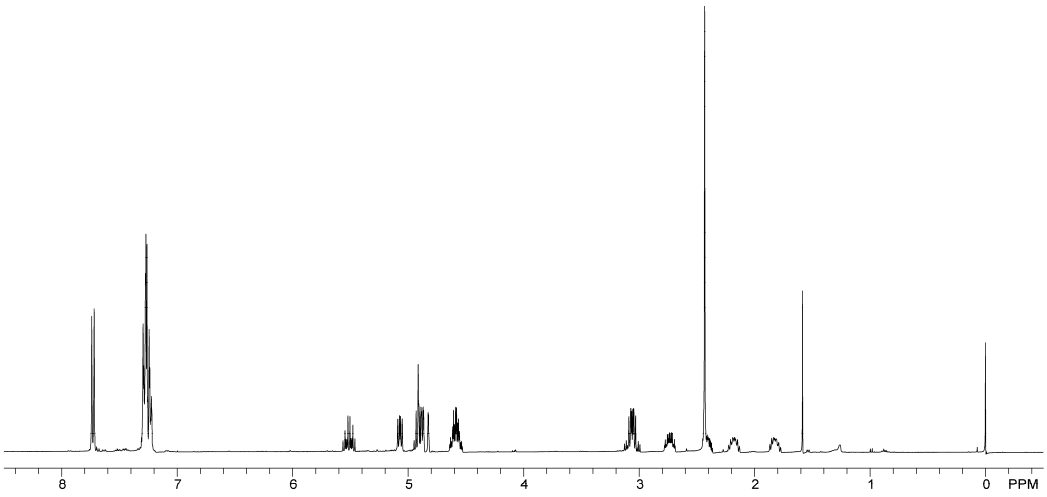

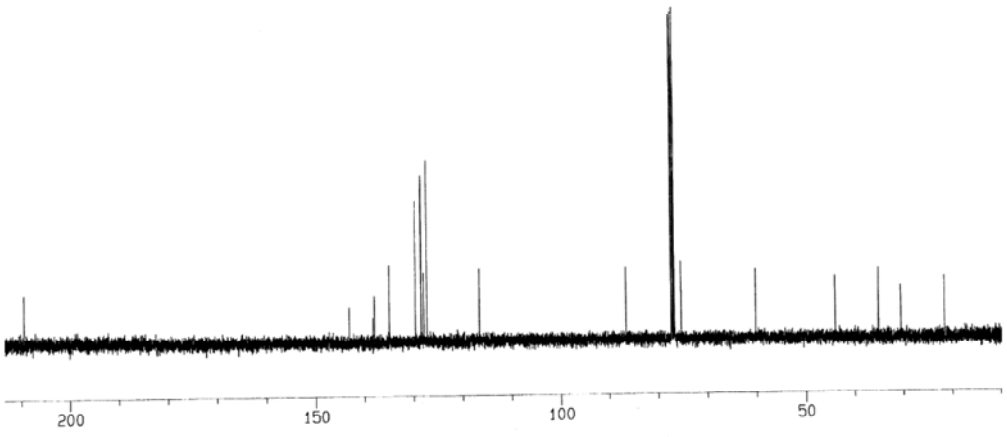

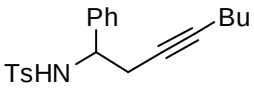

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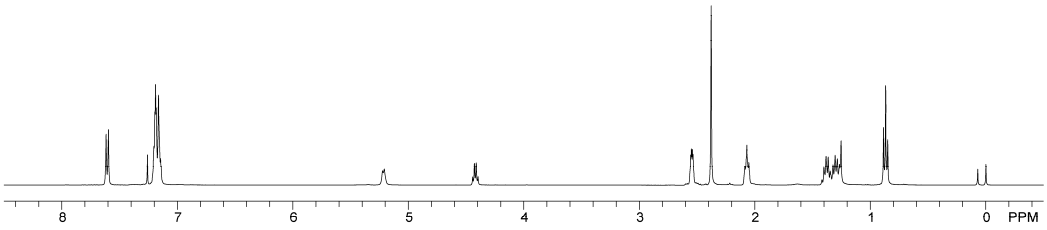

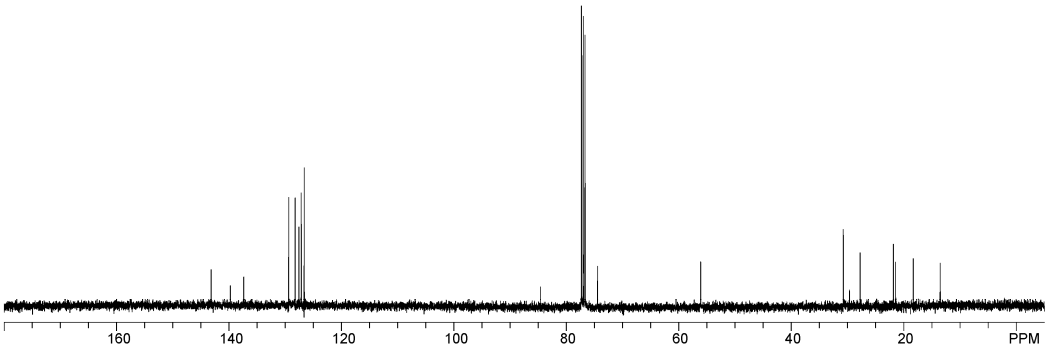

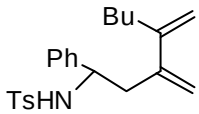

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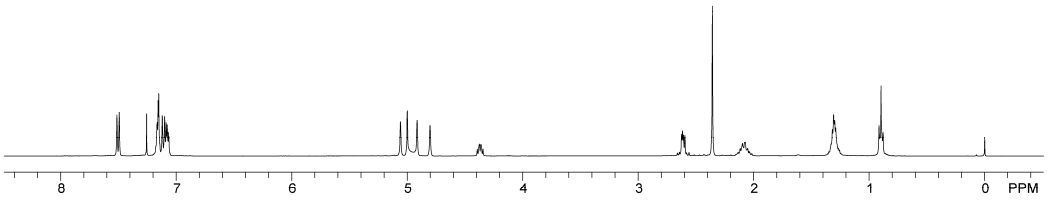

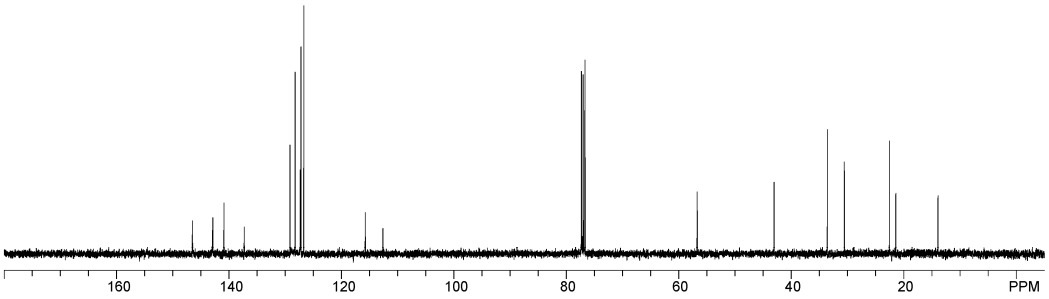

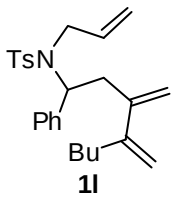

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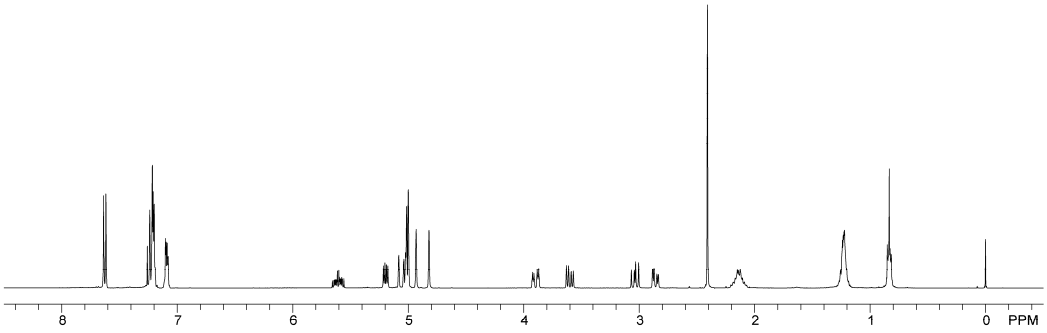

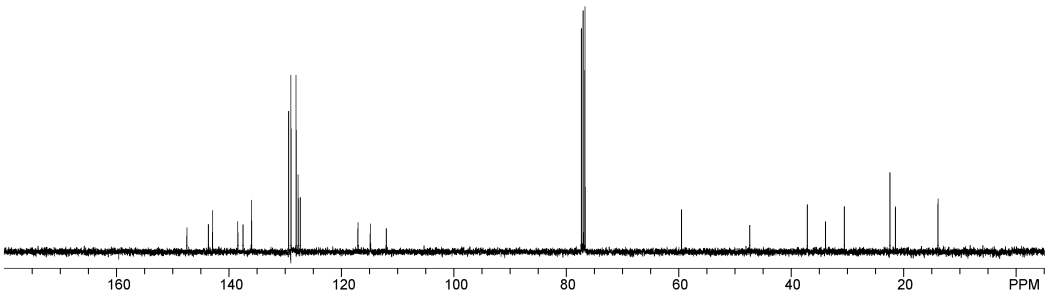

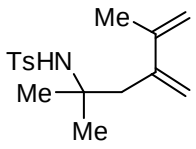

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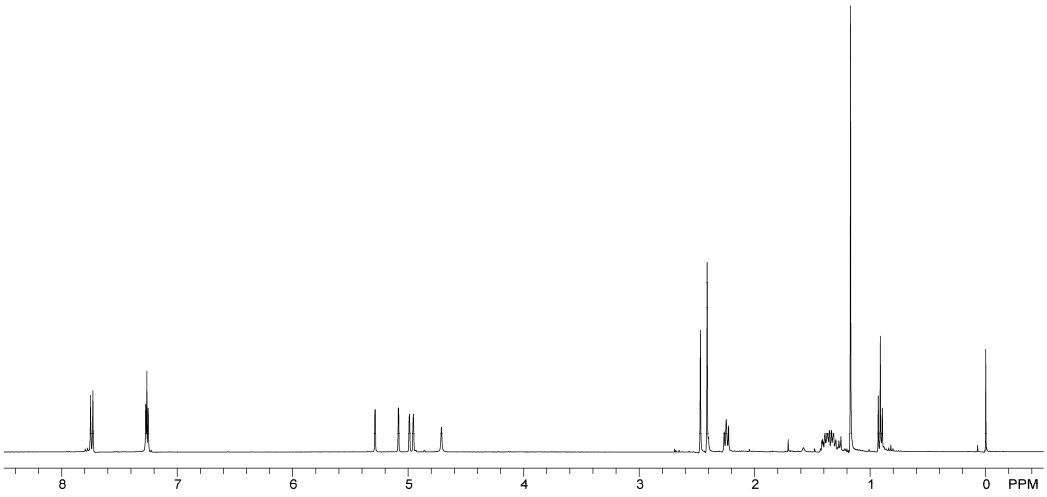

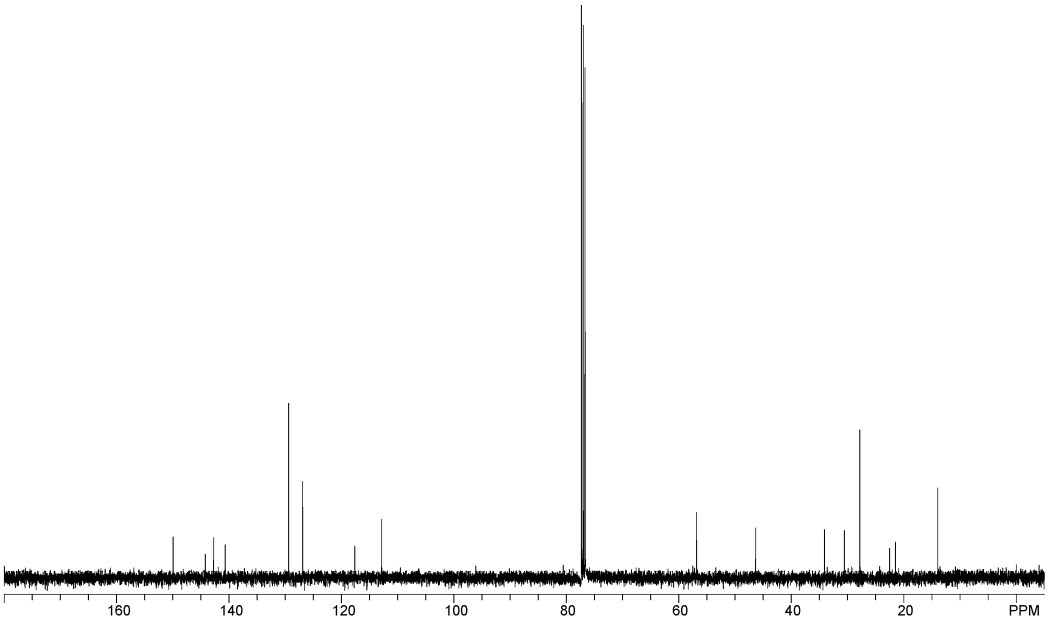

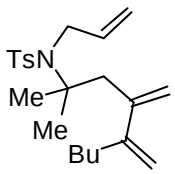

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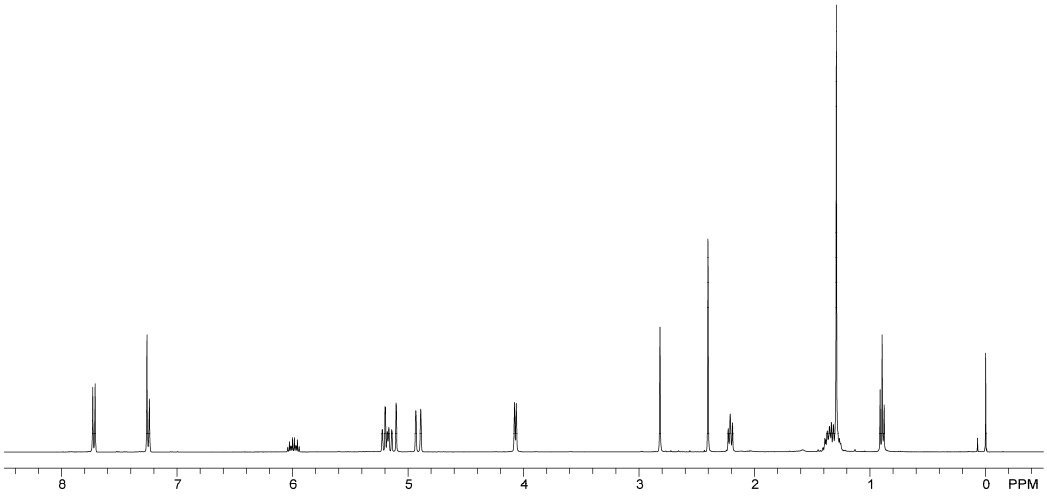

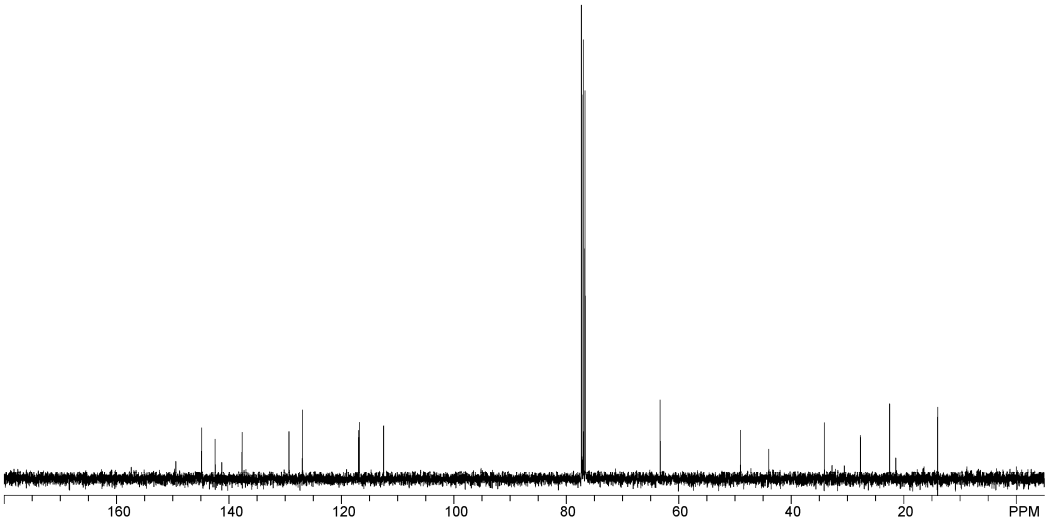

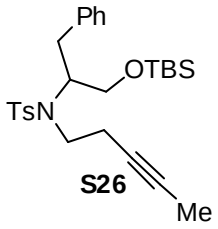

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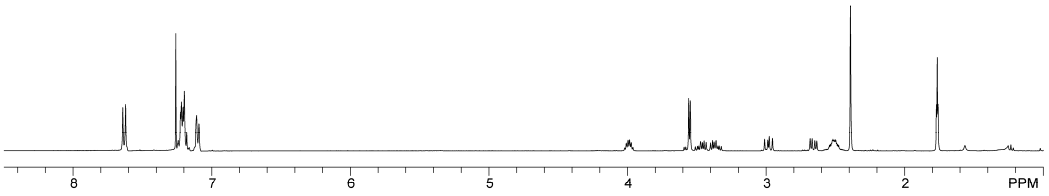

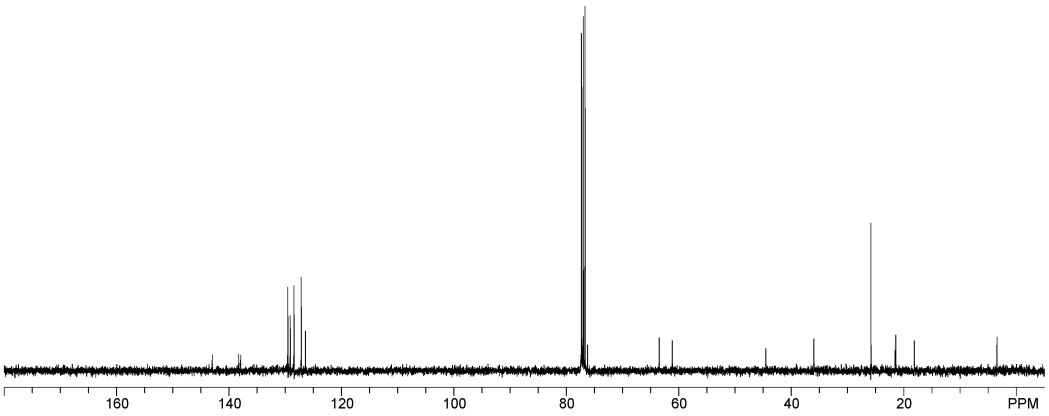

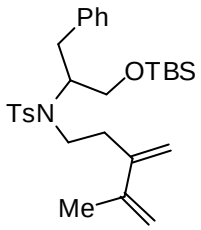

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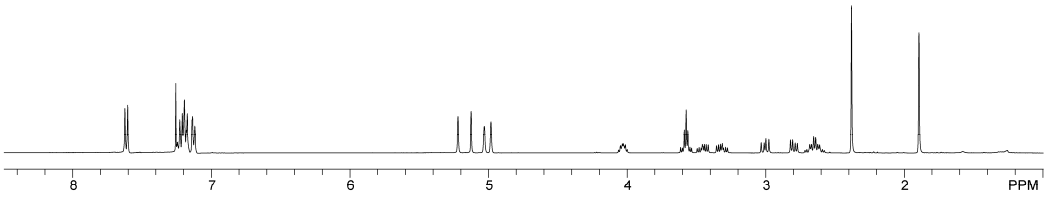

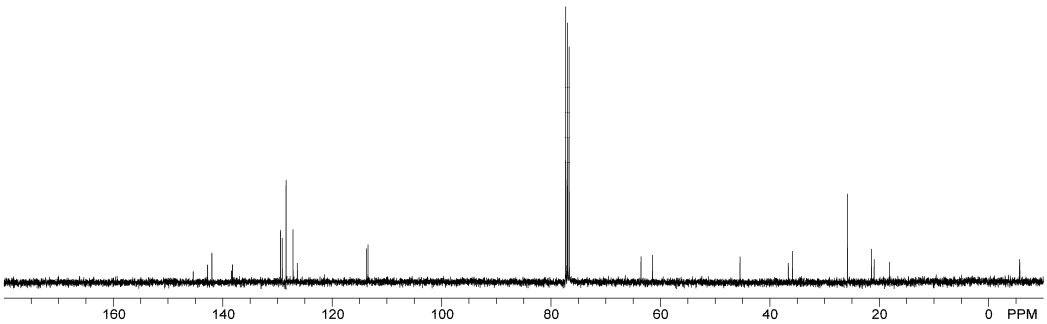

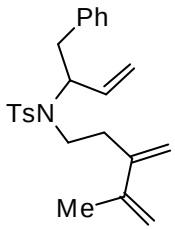

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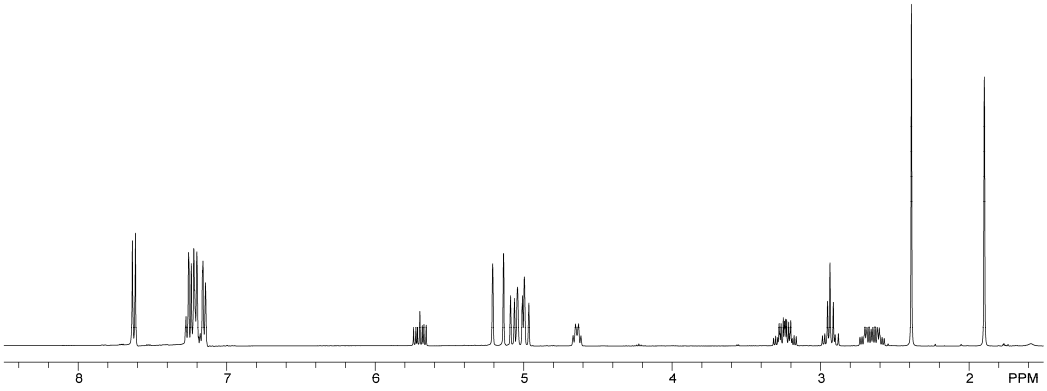

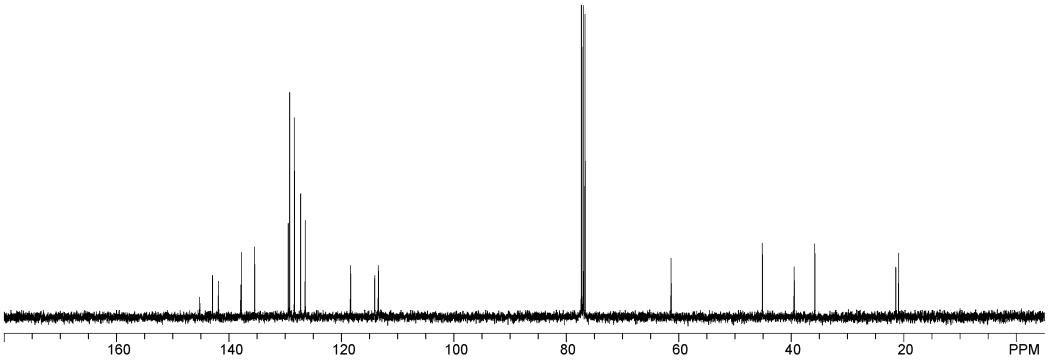

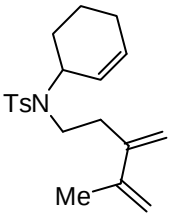

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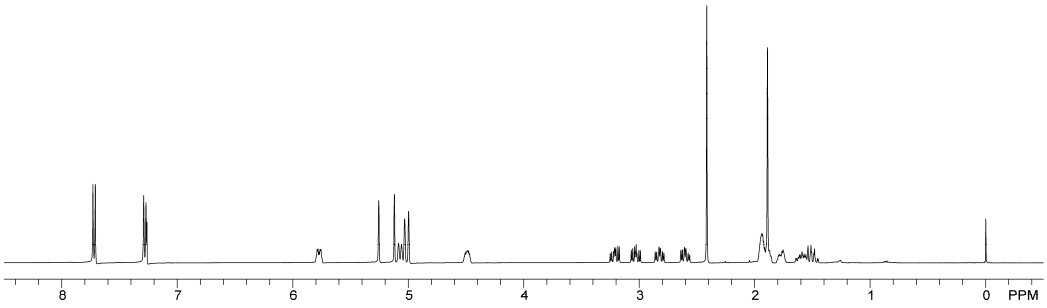

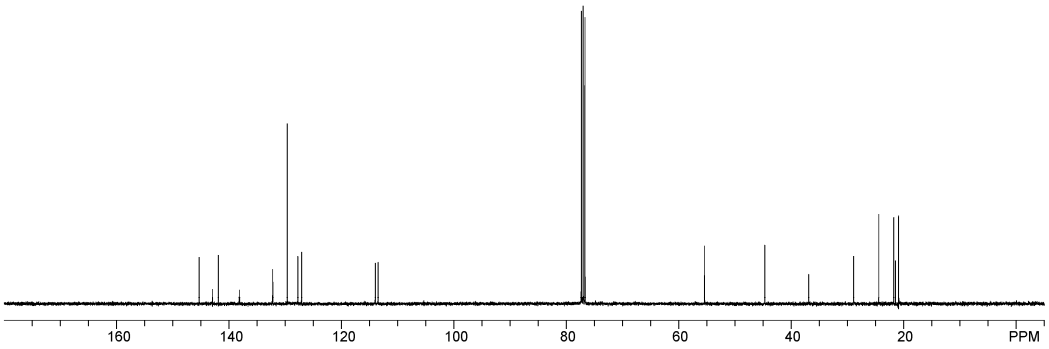

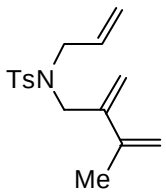

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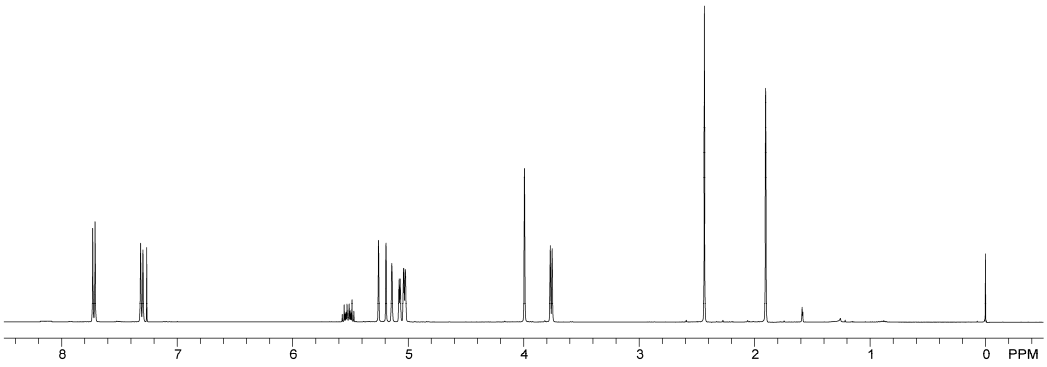

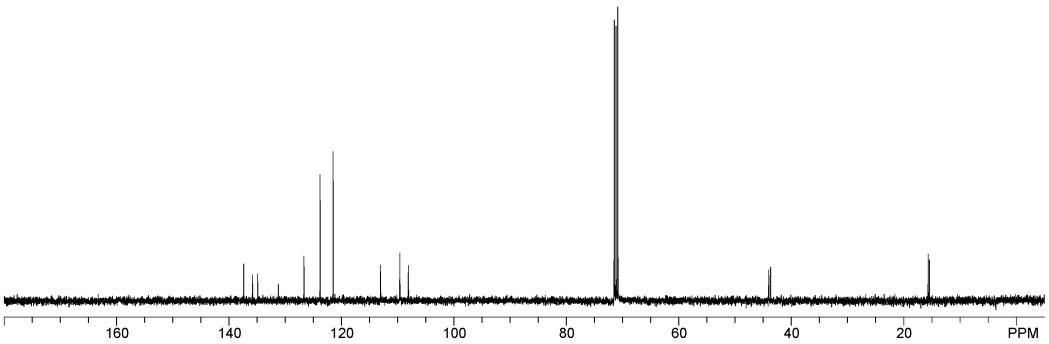

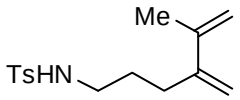

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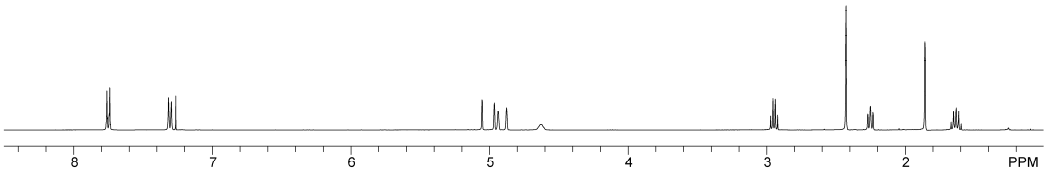

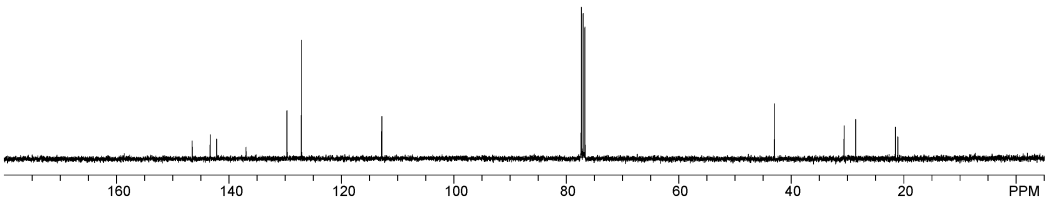

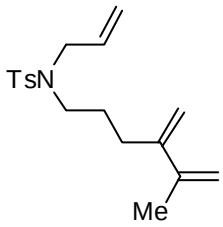

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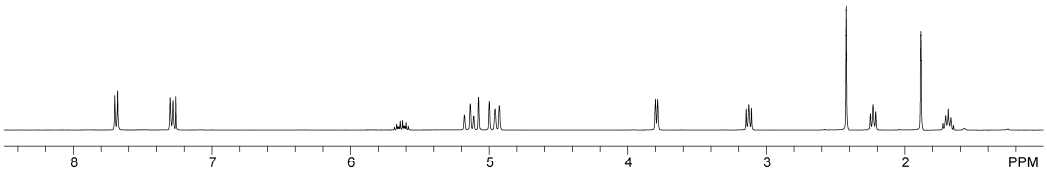

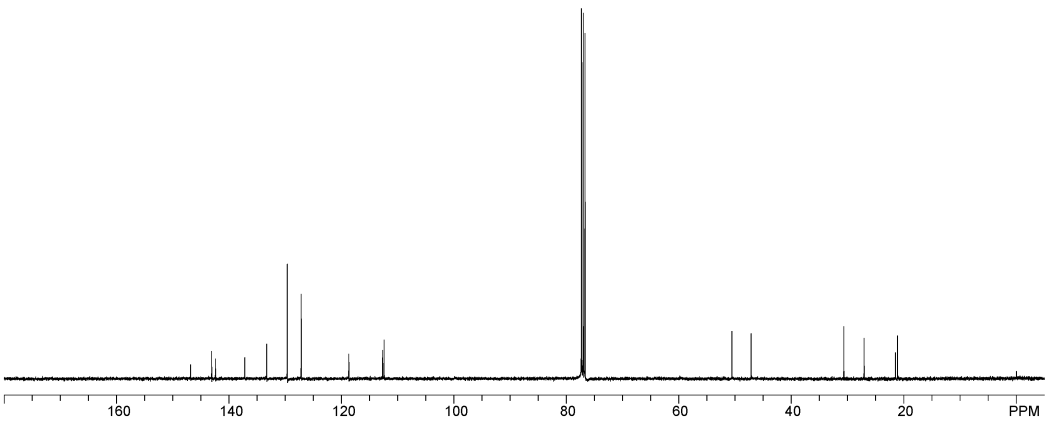

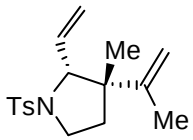

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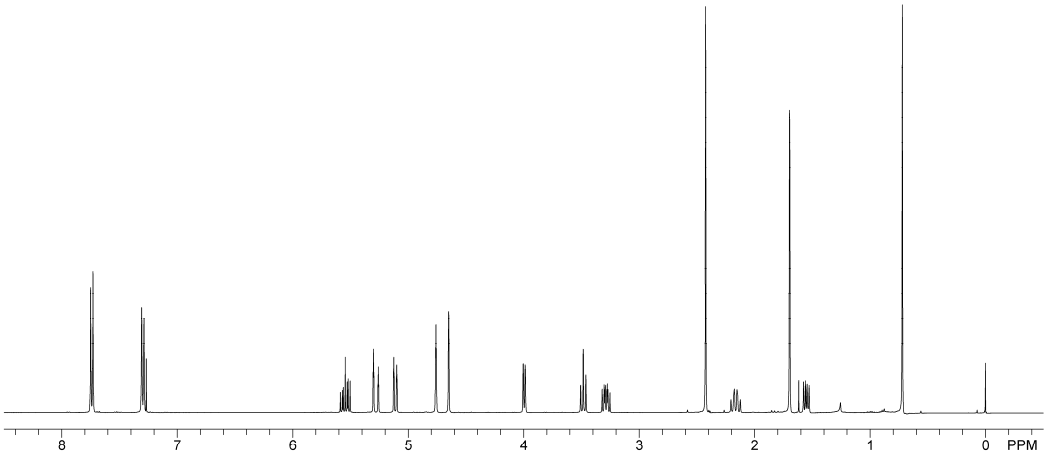

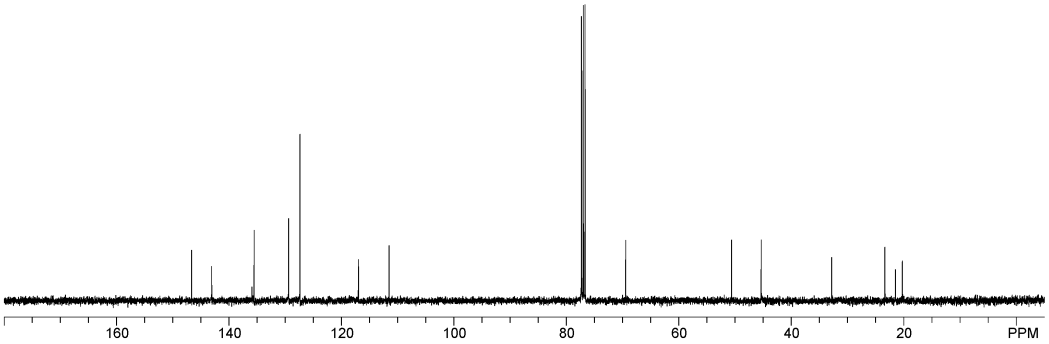

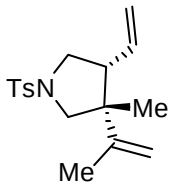

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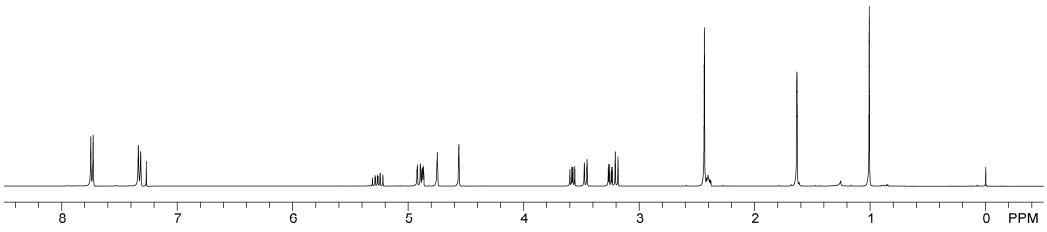

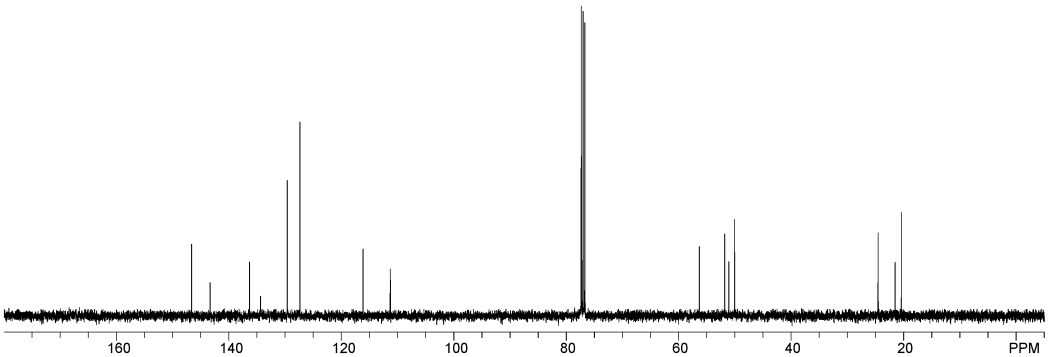

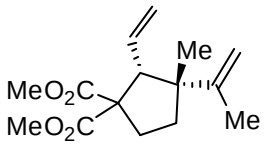

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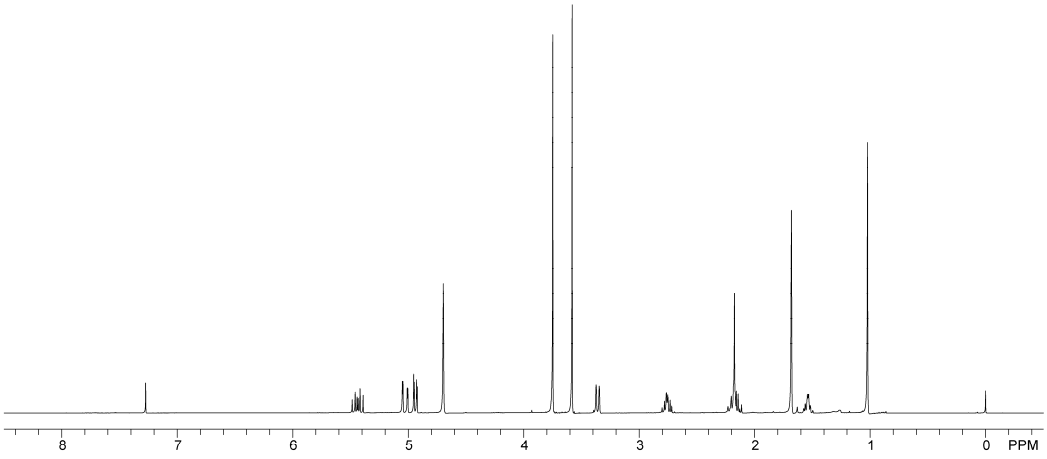

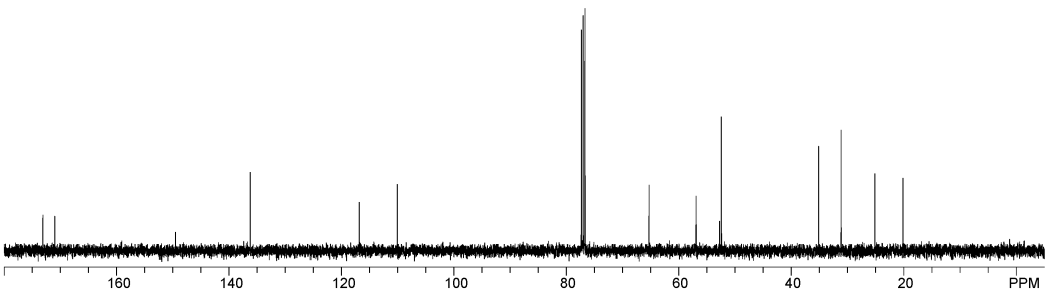

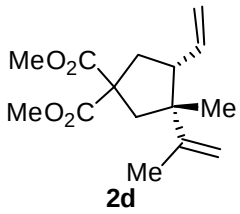

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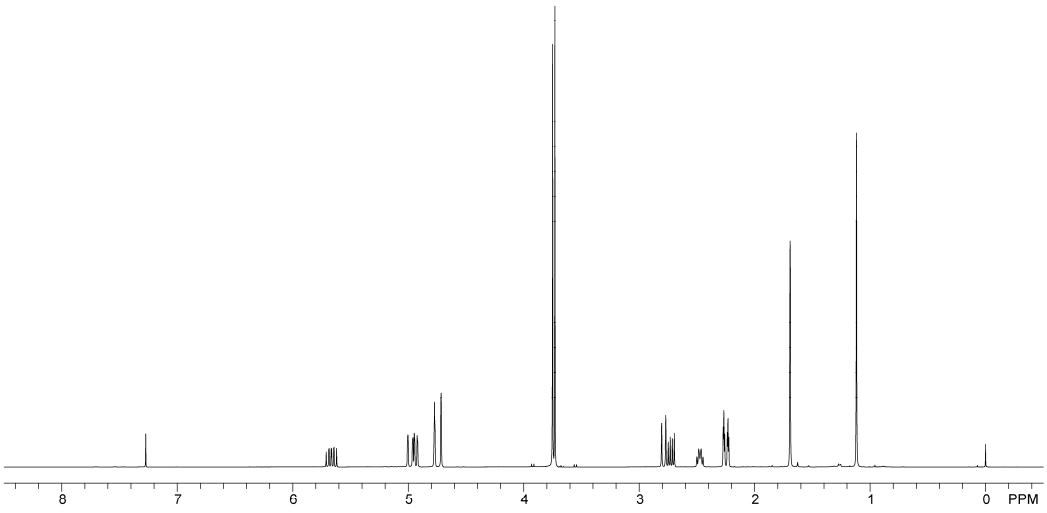

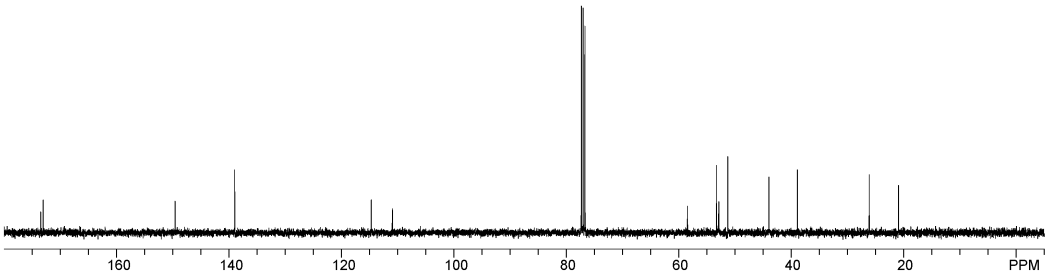

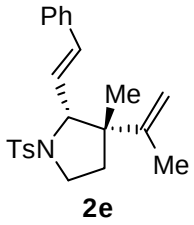

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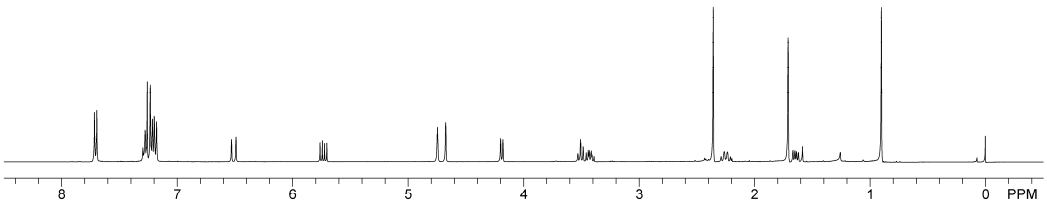

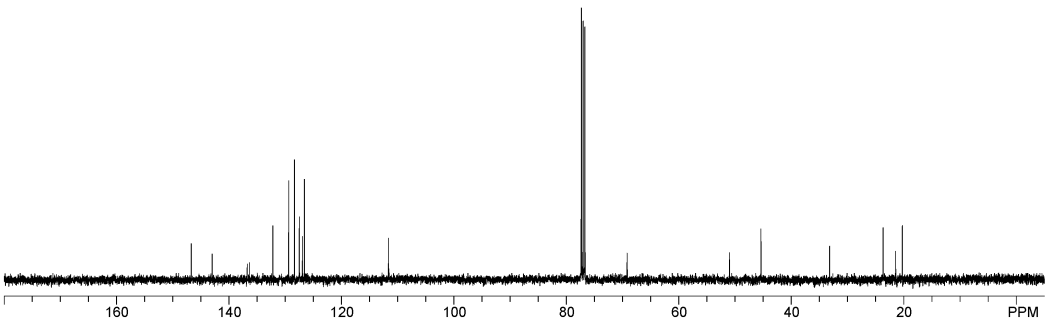

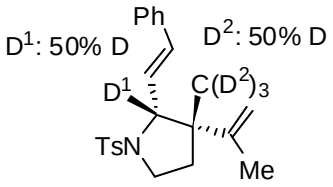
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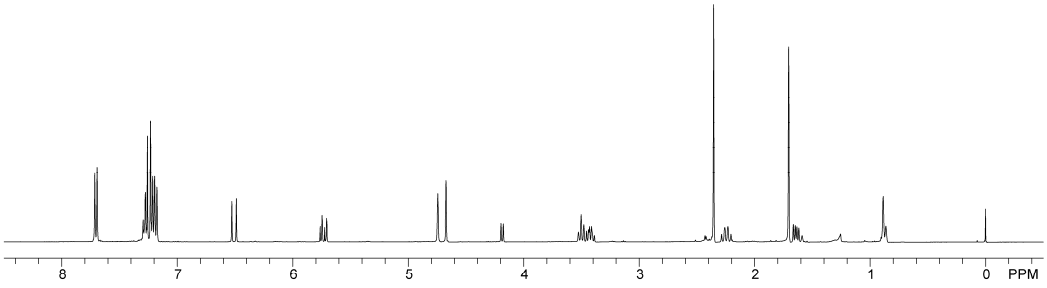
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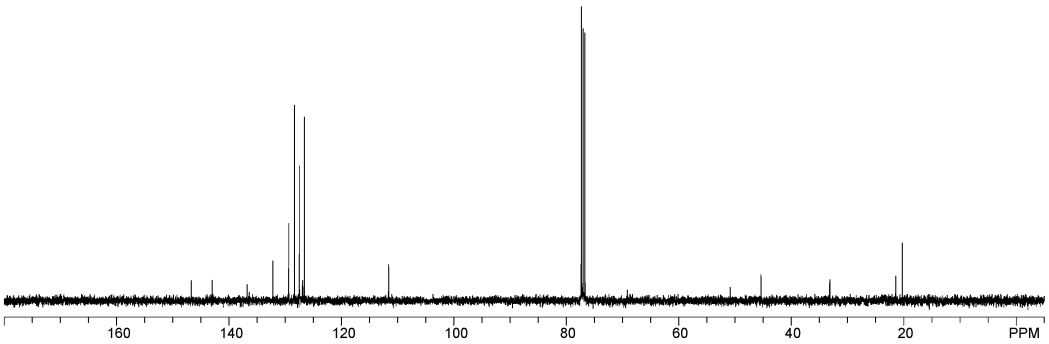
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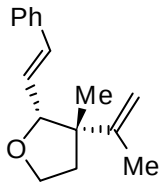

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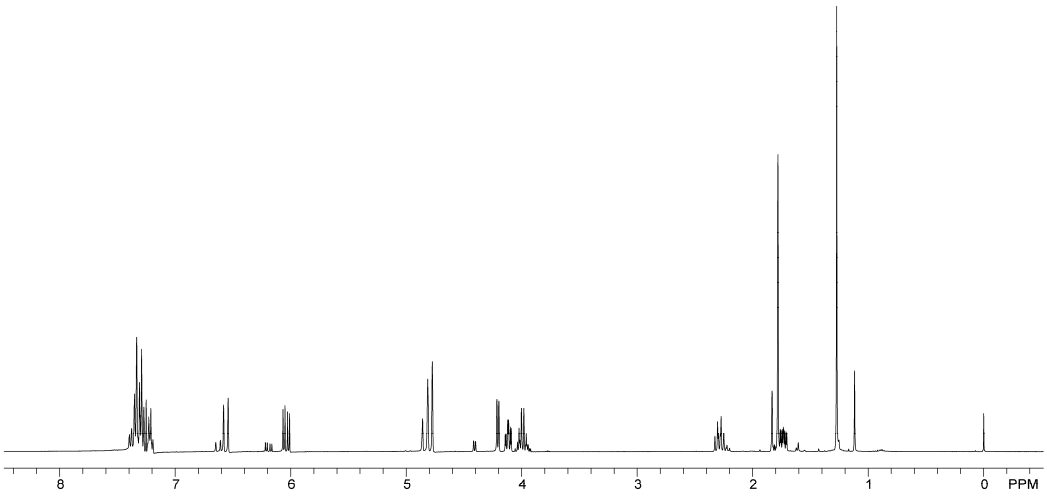

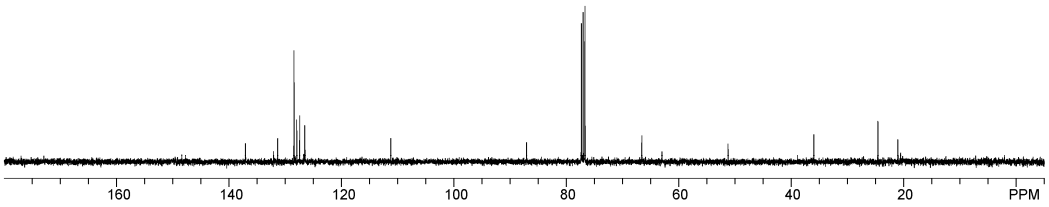

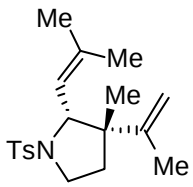

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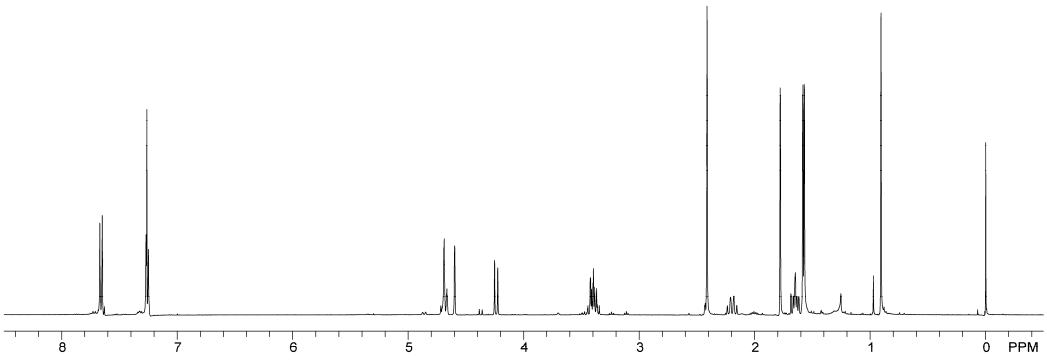

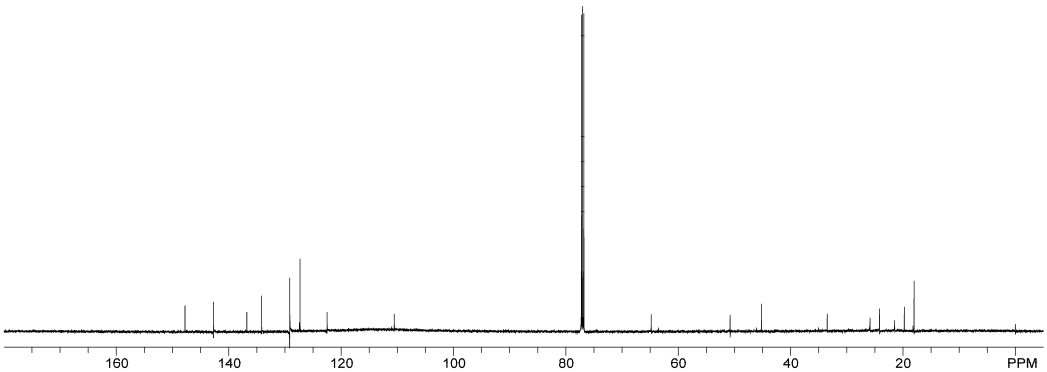

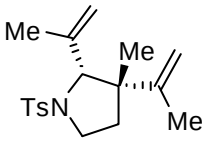

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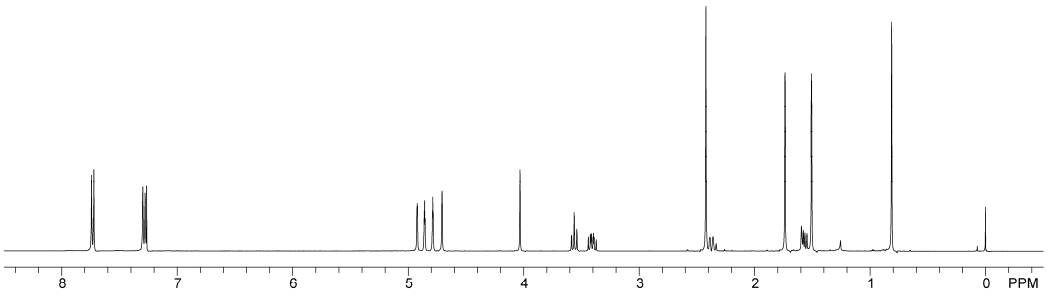
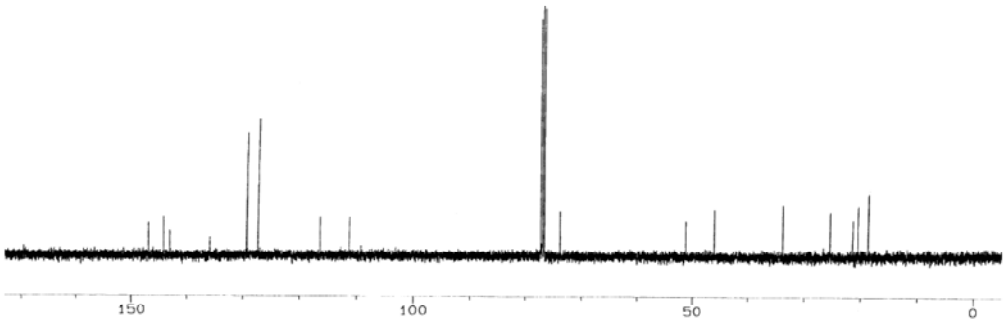
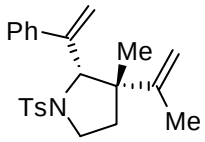
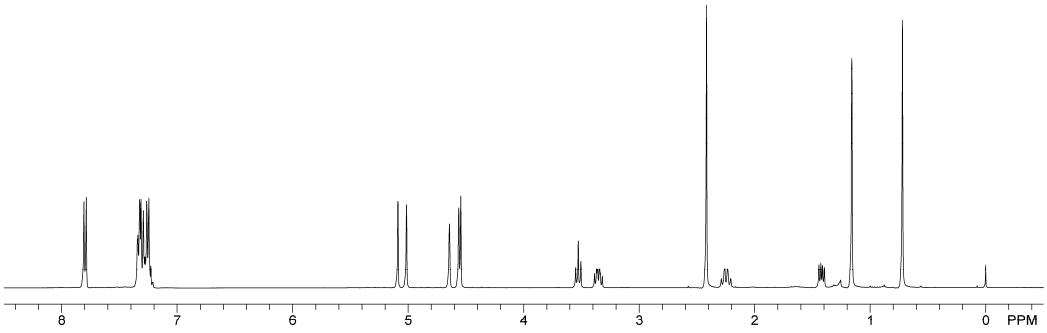
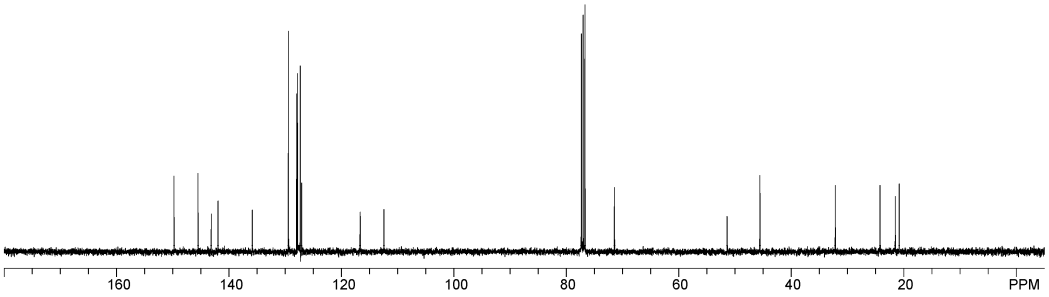


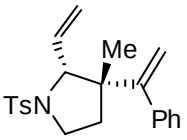




2i







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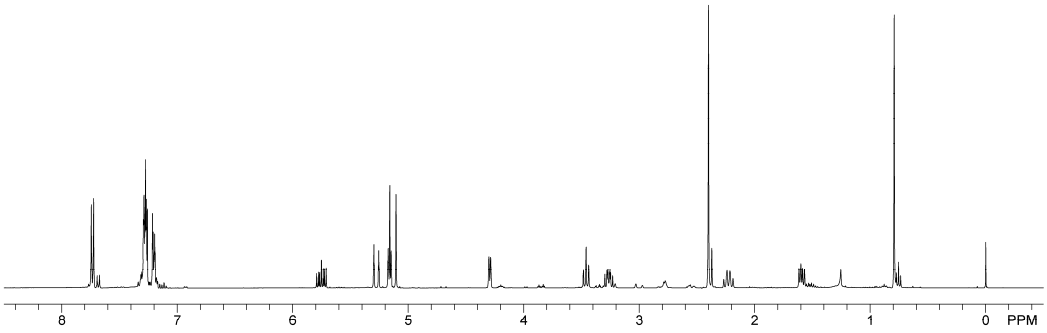
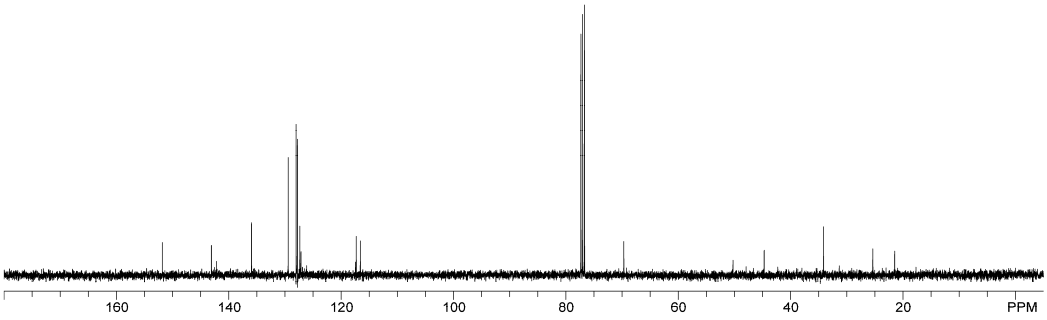
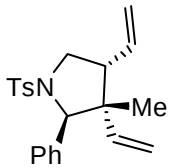
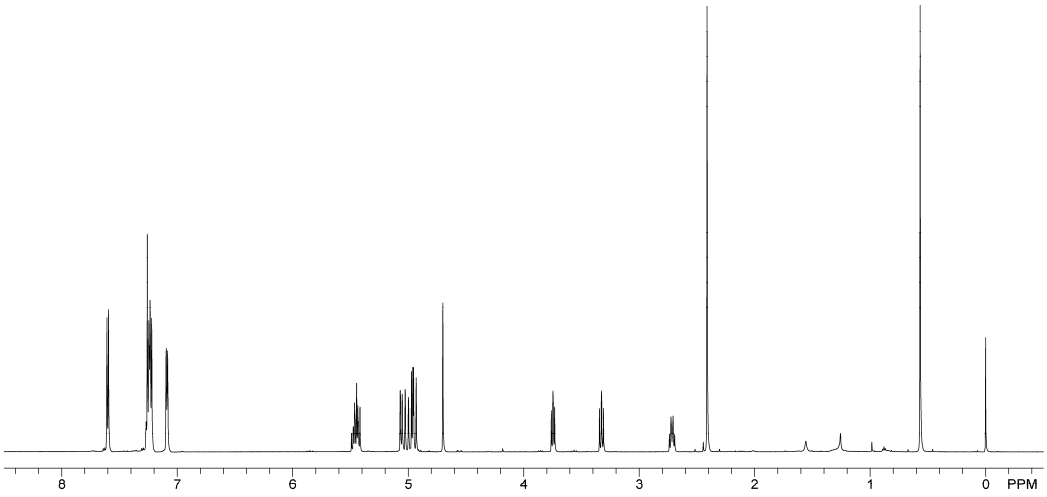
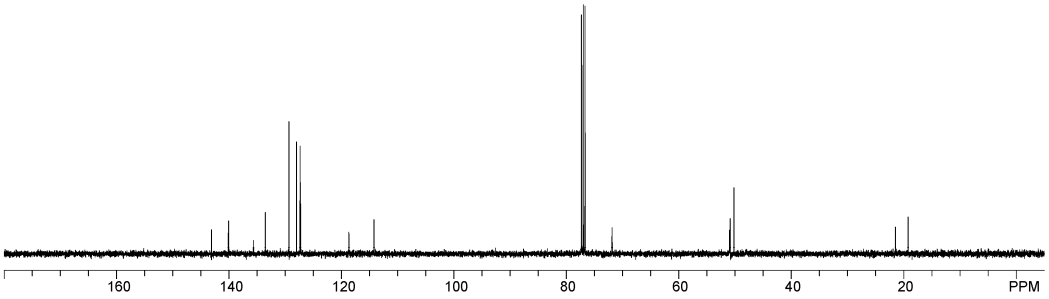


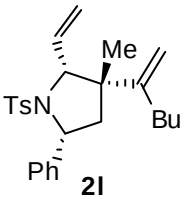




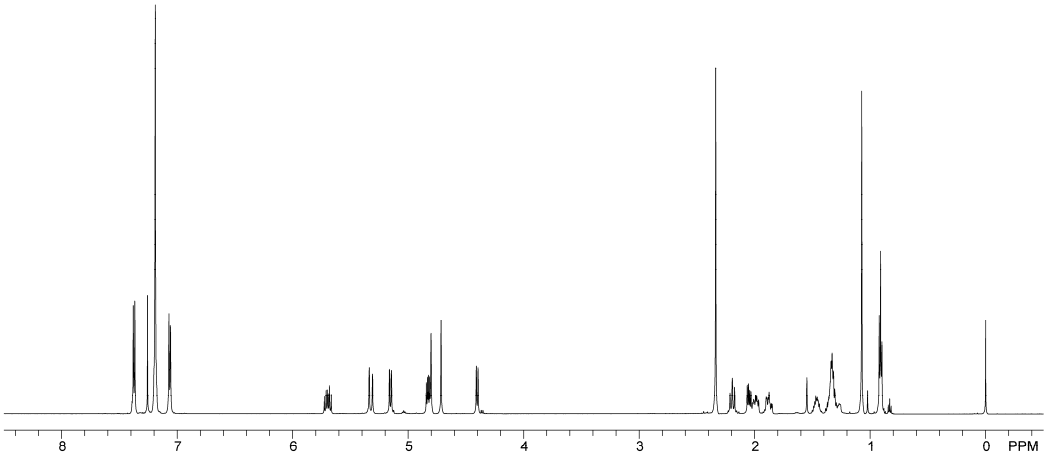
2k

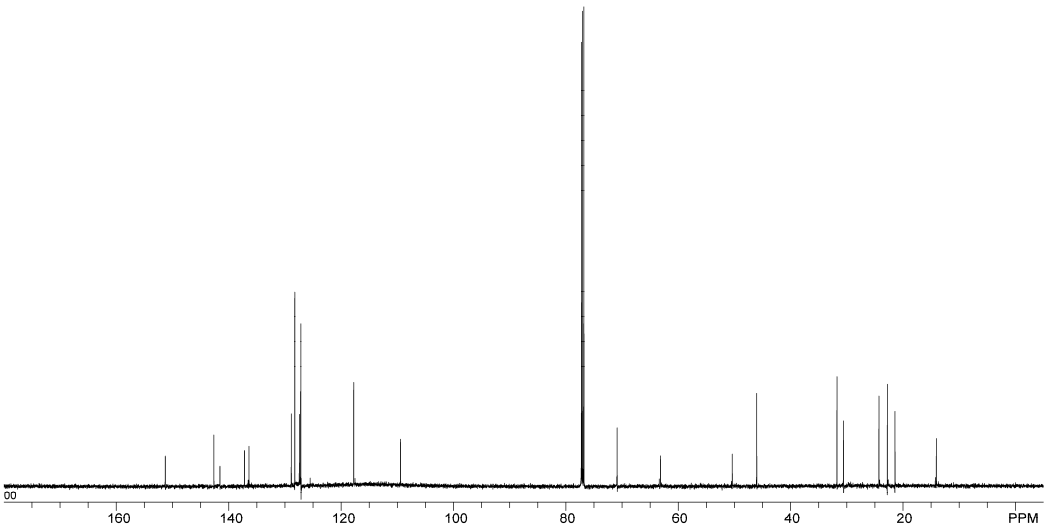


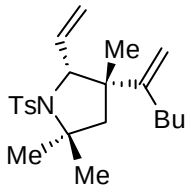




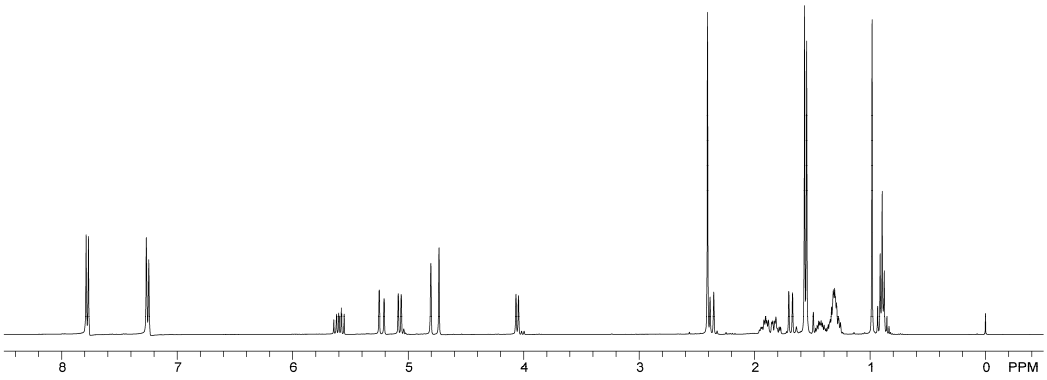
2l

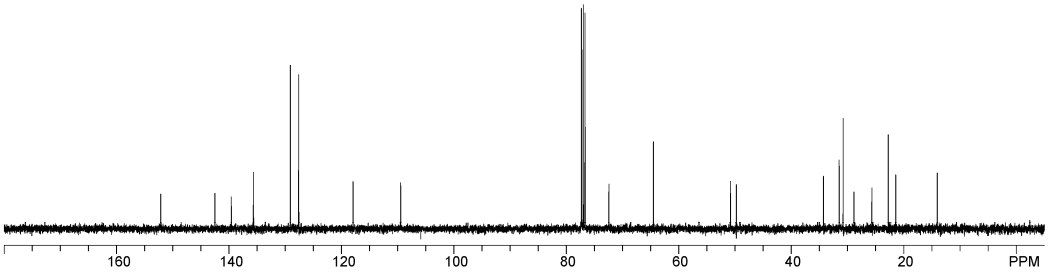






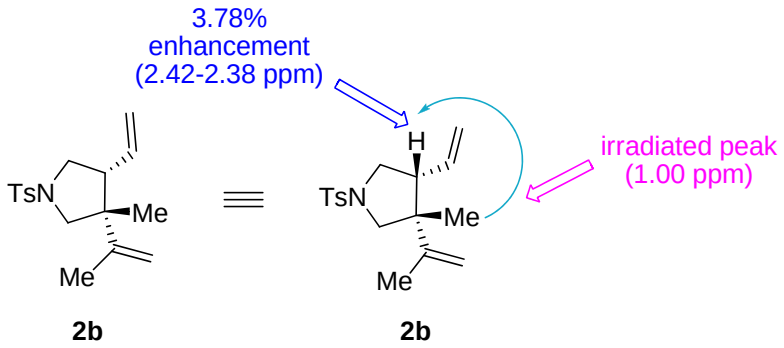
2m

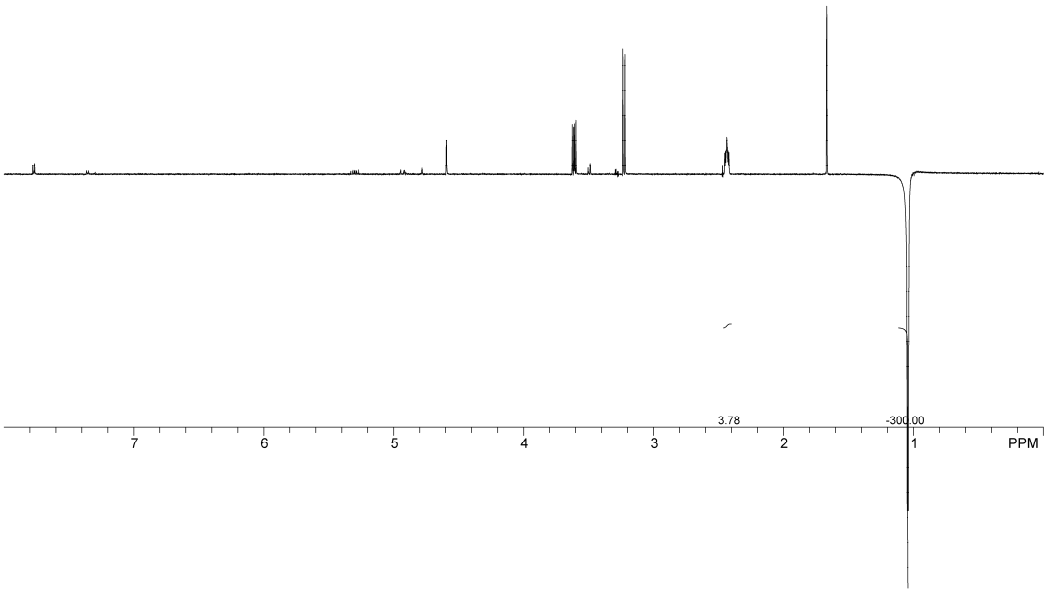




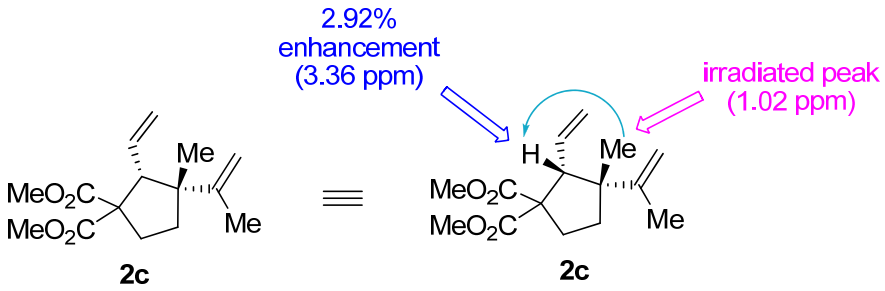
4. NMR Spectra for Stereochemical Determination

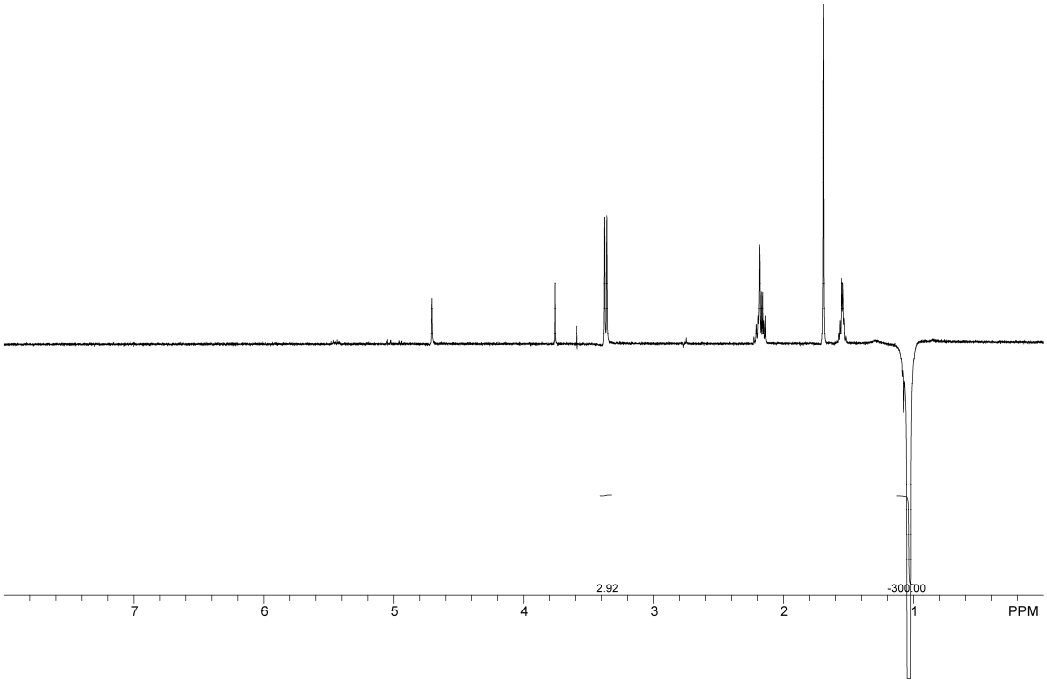
1D nOe spectrum of **2b**



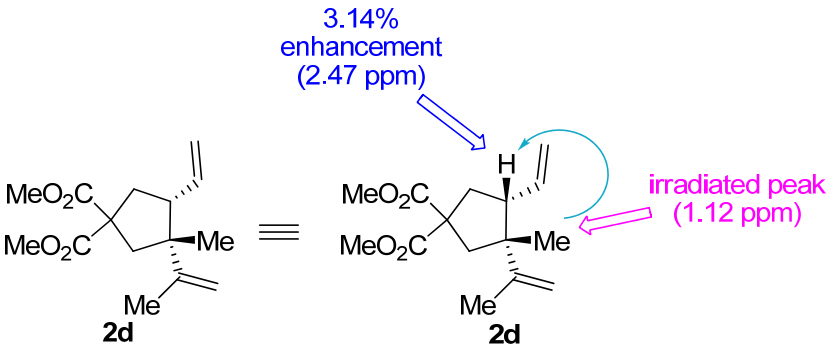


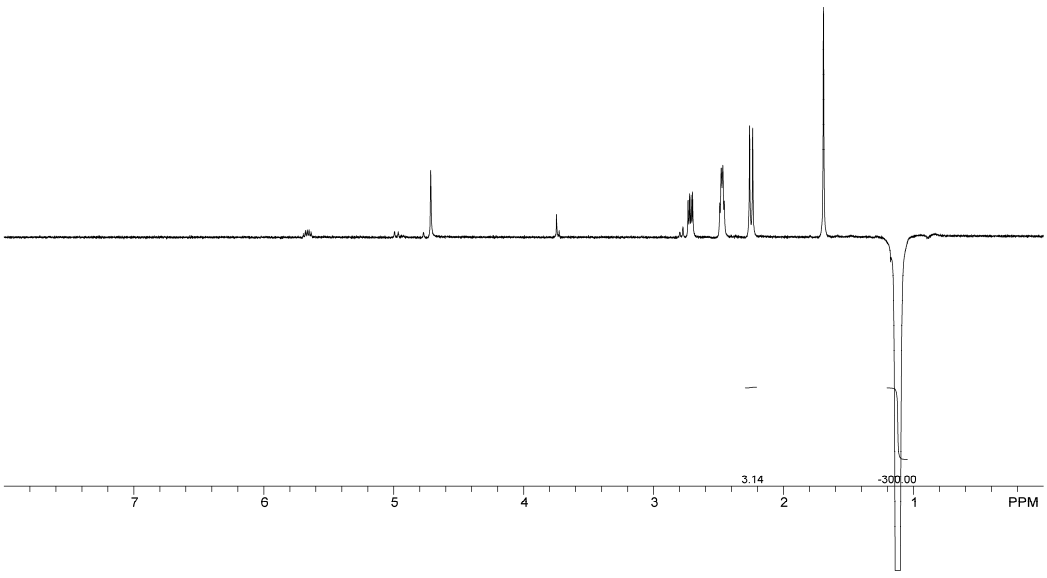
1D nOe spectrum of **2c**



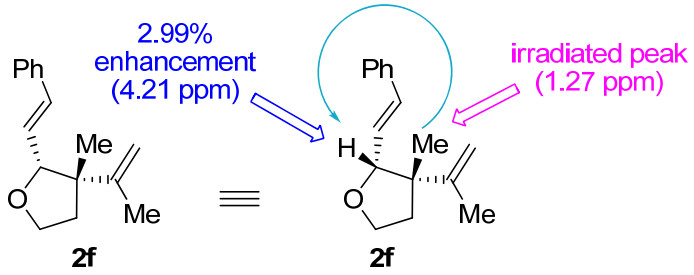


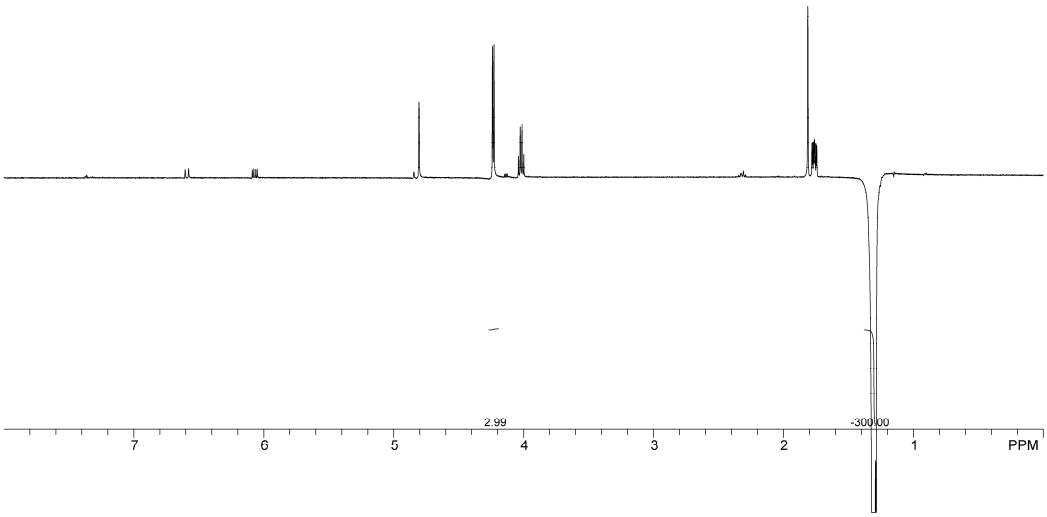
1D nOe spectrum of **2d**



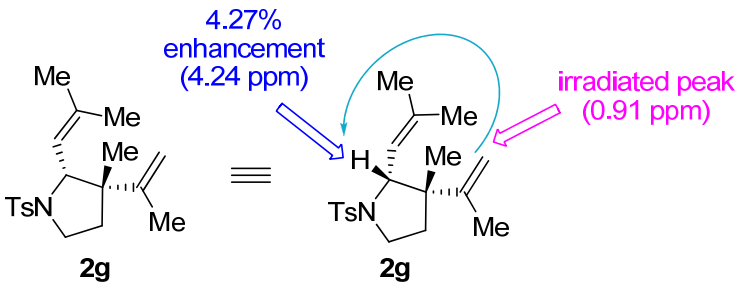


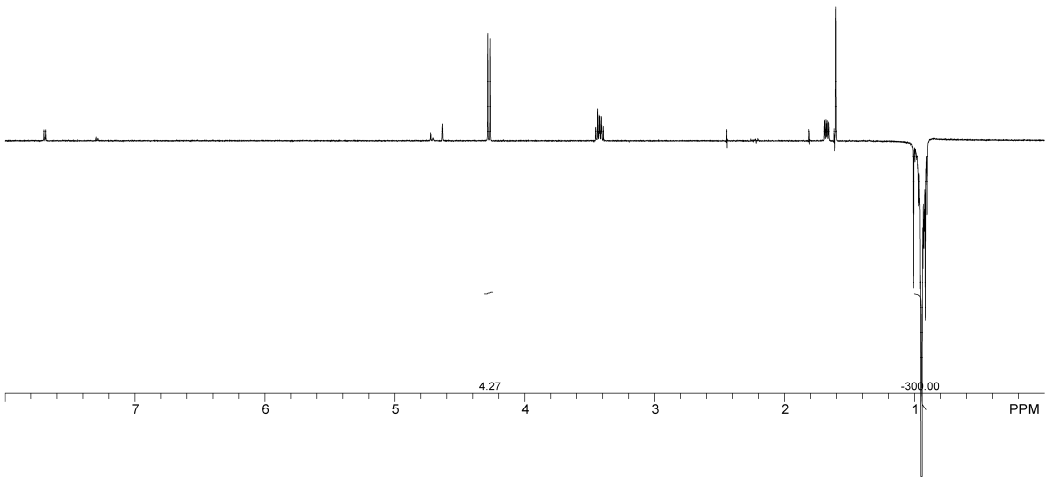
1D nOe spectrum of **2f**



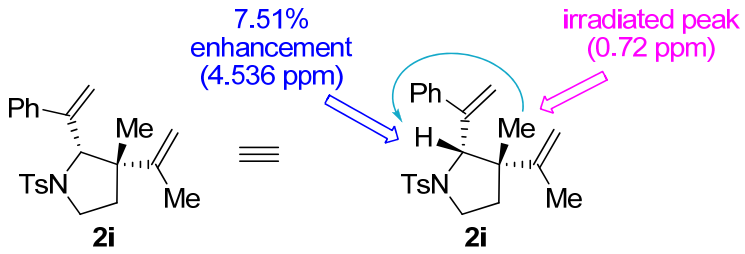


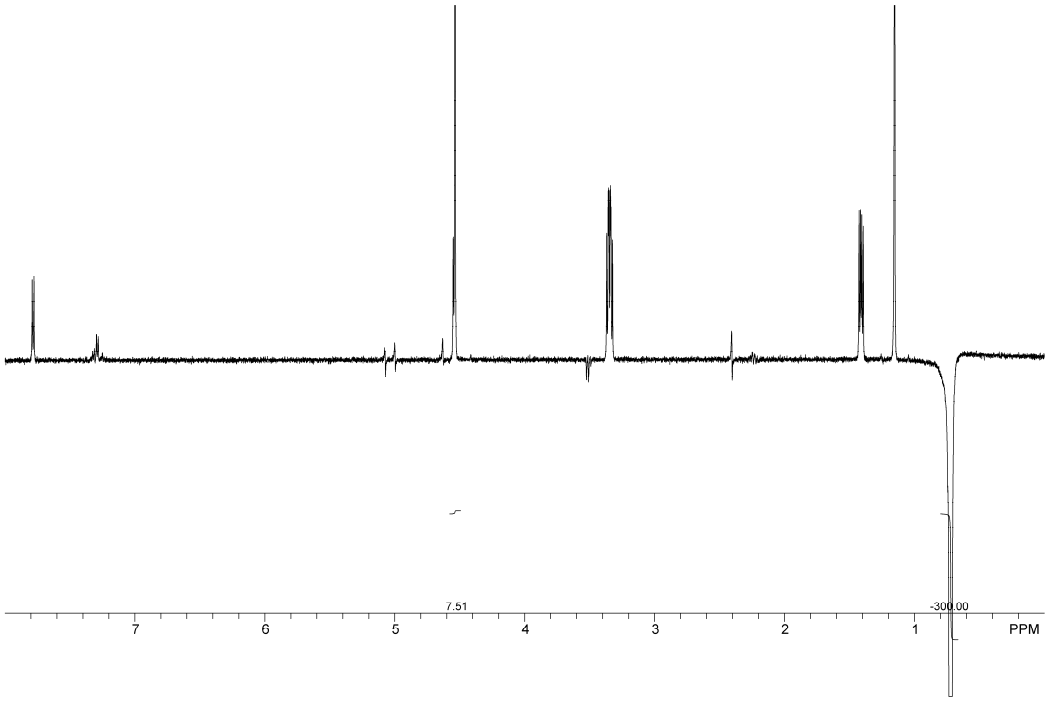
1D nOe spectrum of **2g**



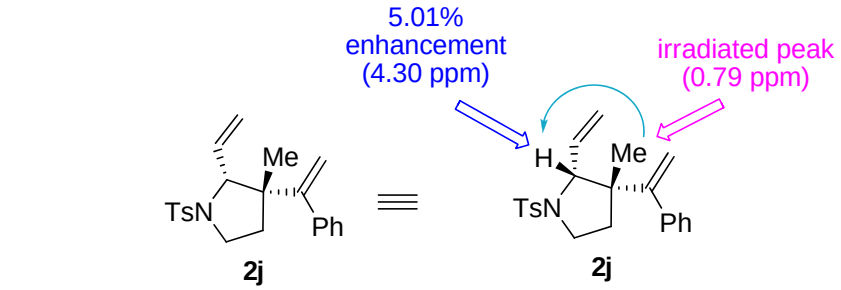


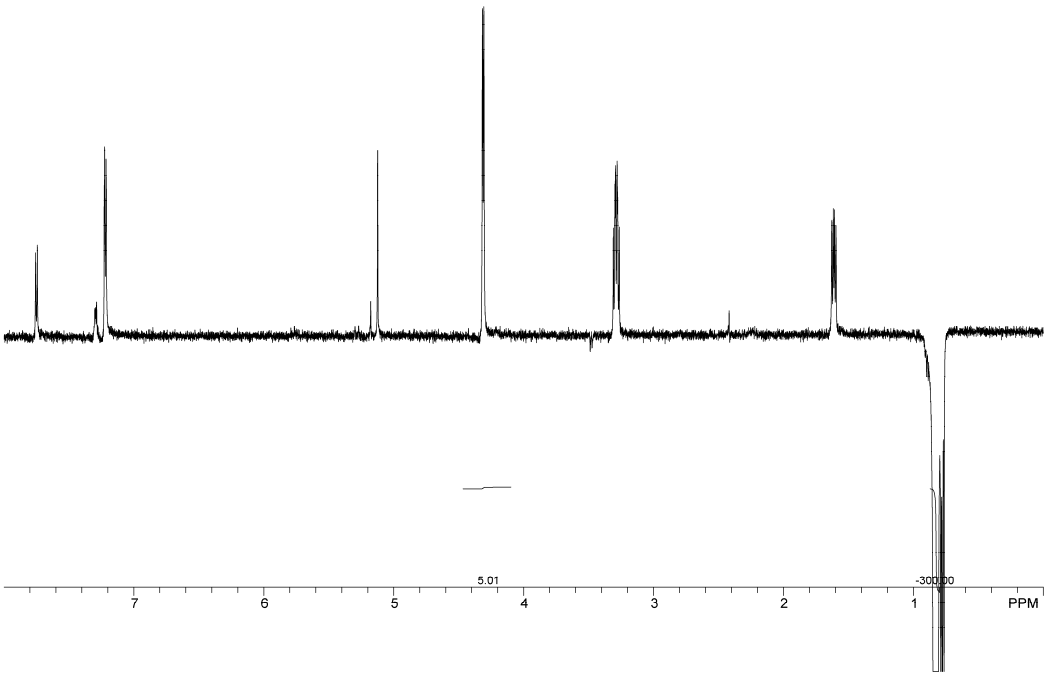
1D nOe spectrum of **2i**



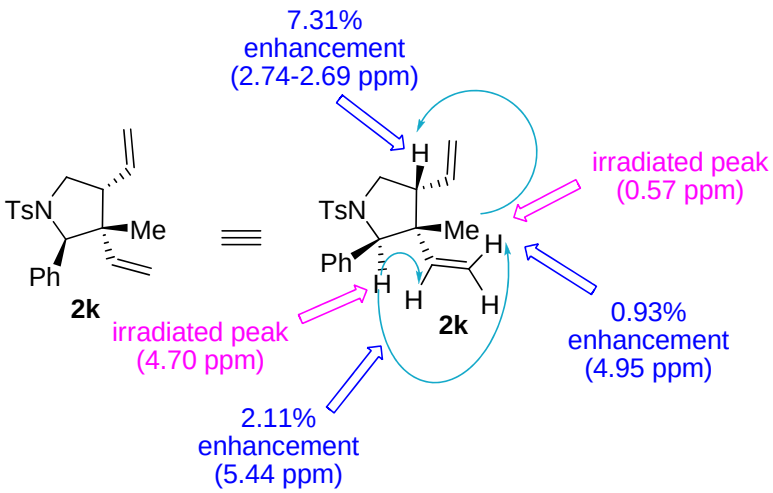


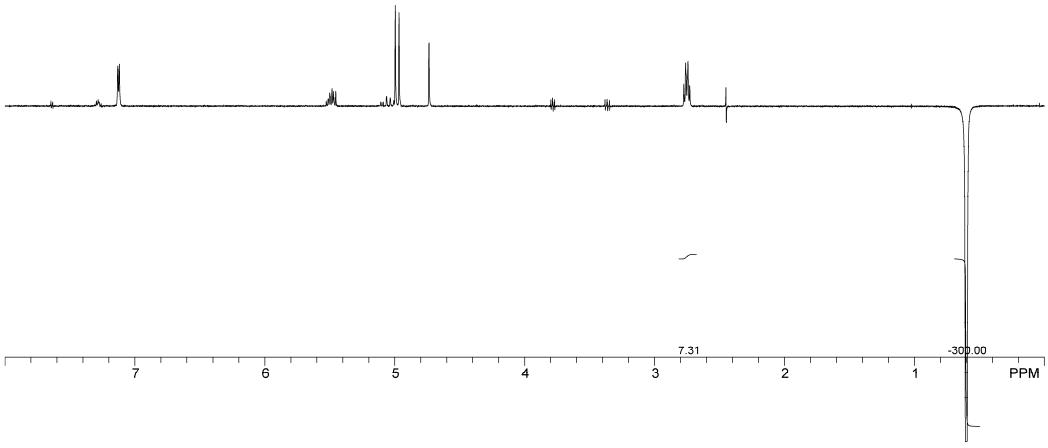
1D nOe spectrum of **2j**



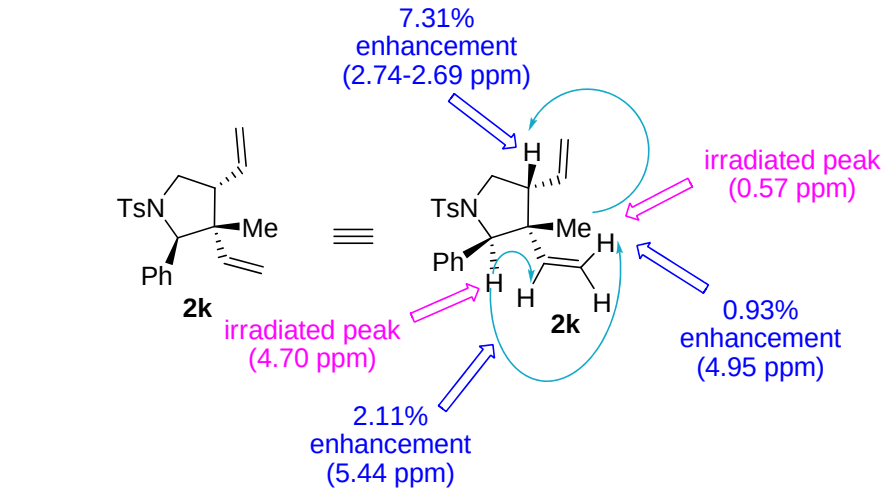


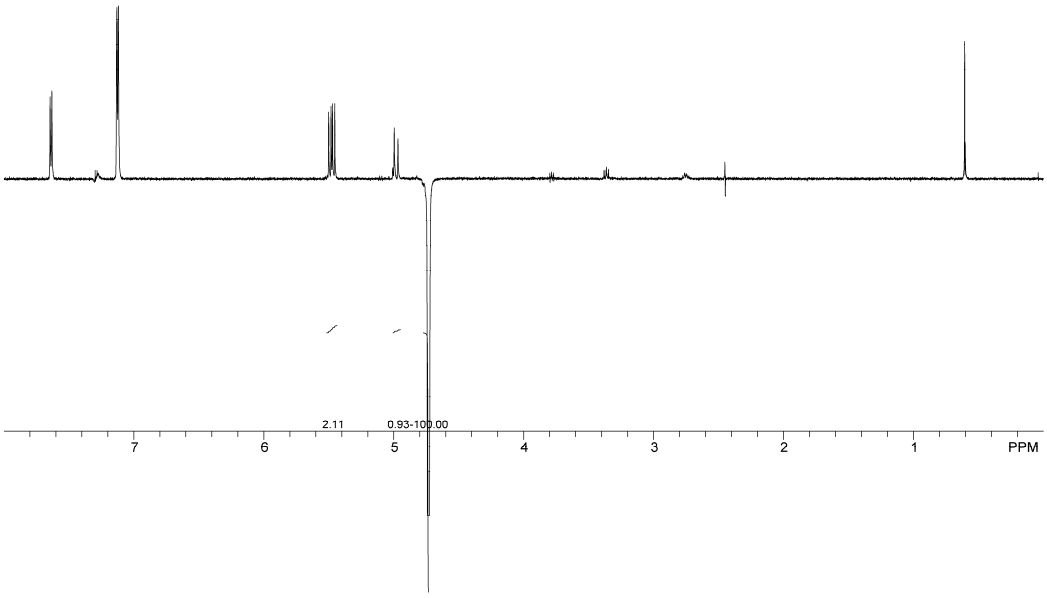
1D nOe spectrum of **2k**



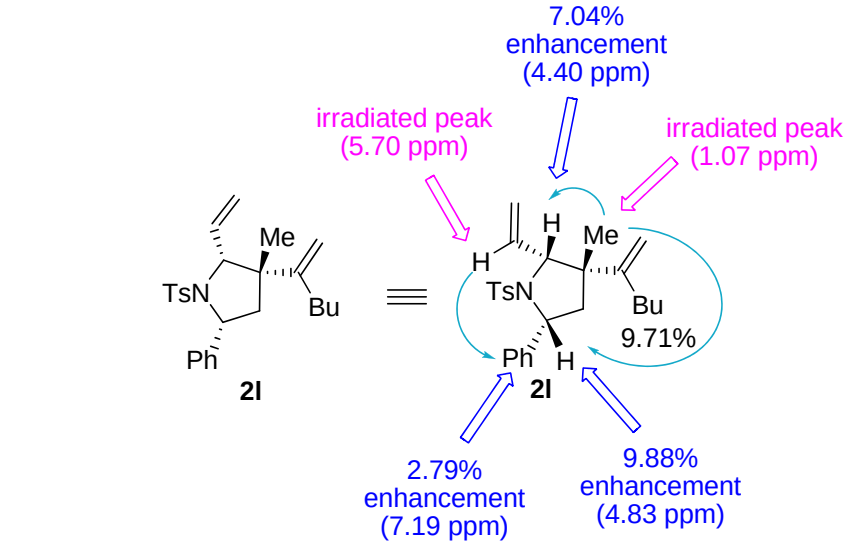


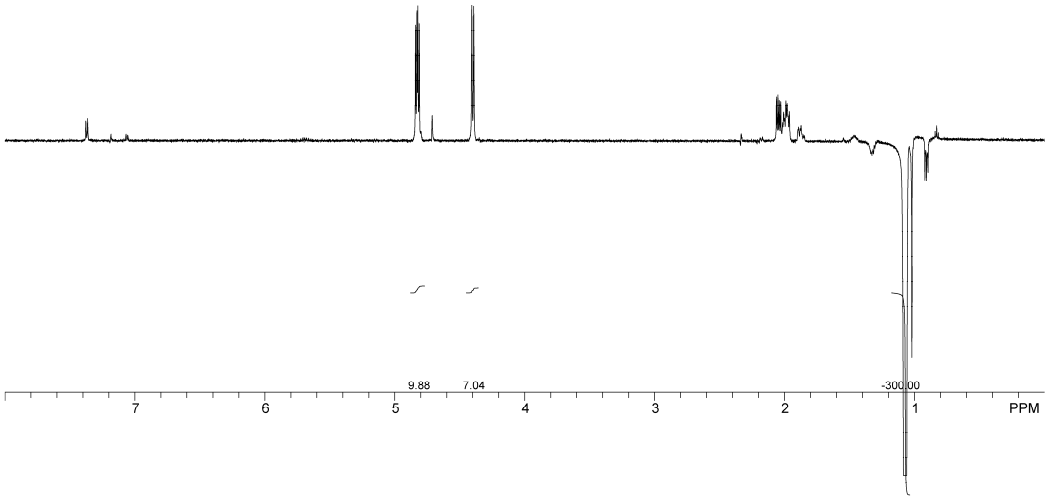
1D nOe spectrum of **2k**



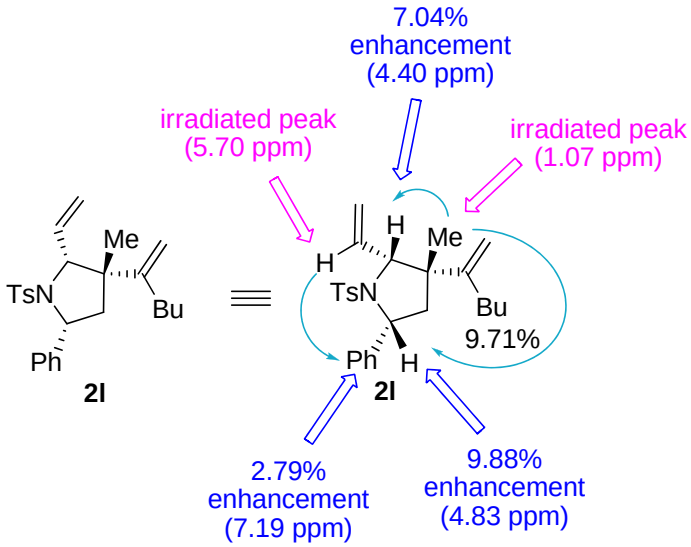


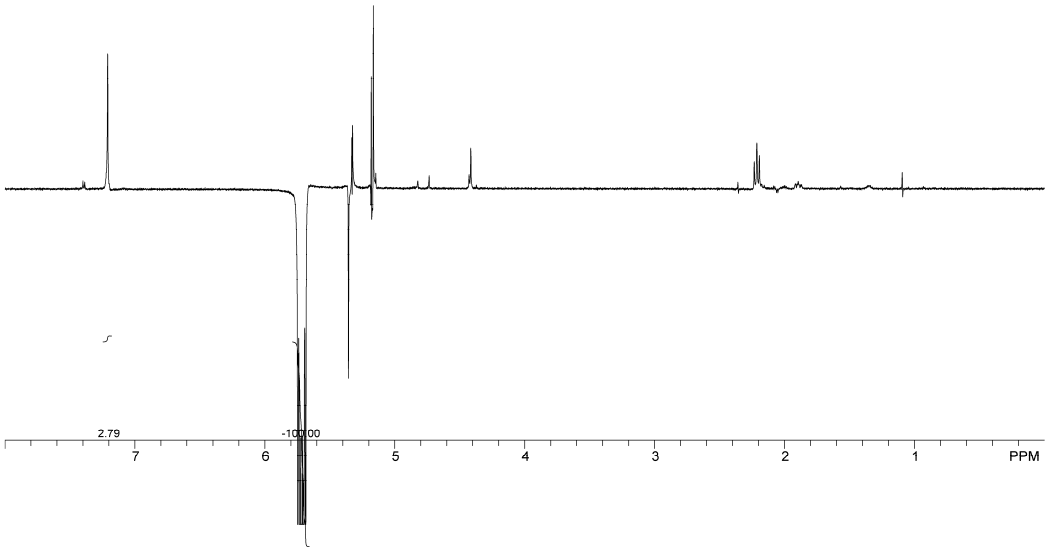
1D nOe spectrum of **2l**



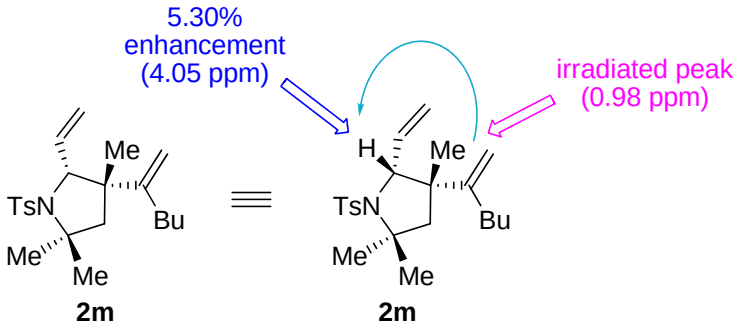


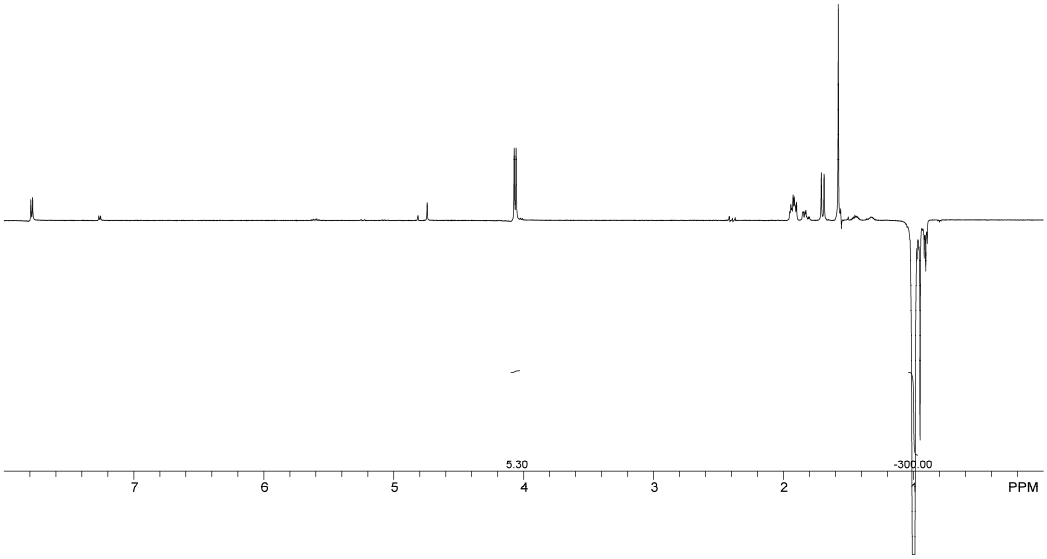
1D nOe spectrum of **2l**



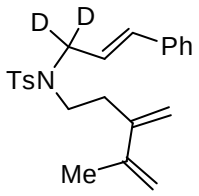


1D nOe spectrum of **2m**





5. HRMS for Deuterium-labeled Substrate 1e-D and Cycloadduct 2e-D

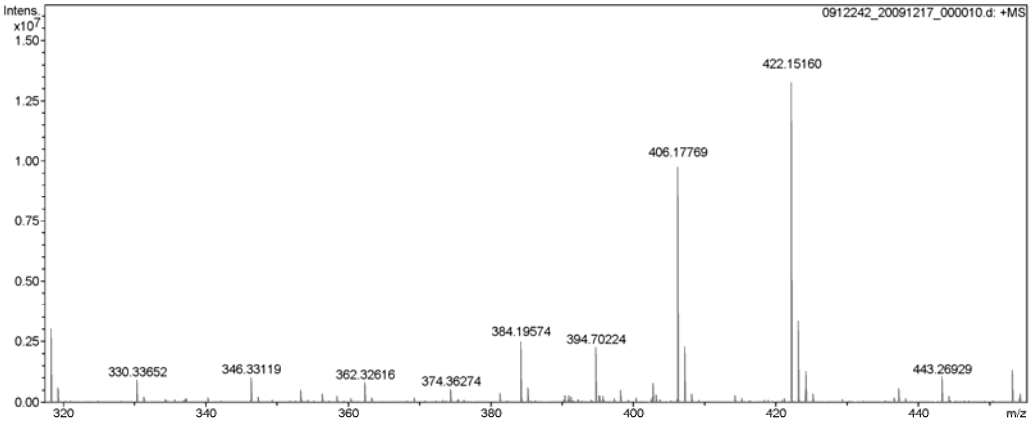


1e-D

Peking University Mass Spectrometry Sample Analysis Report

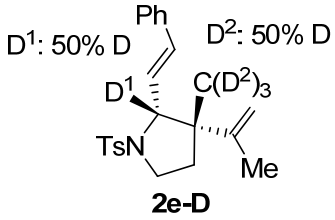
Analysis Info

Analysis Name	0912242_20091217_000010.d	Acquisition Date	12/17/2009 9:40:36 AM
Sample	LQ2-038	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
406.17769	1	C 23 H 25 D 2 N Na O 2 S	100.00	406.17802	0.3	0.8	24.5	10.5	even	ok
422.15160	1	C 23 H 25 D 2 K N O 2 S	100.00	422.15196	0.4	0.9	28.0	10.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/17/2009 9:42:00 AM Page 1 of 1

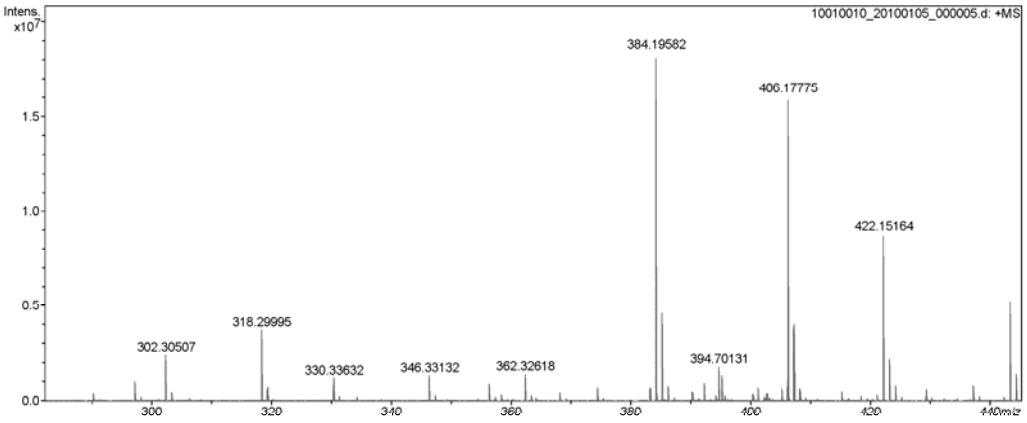


2e-D

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	10010010_20100105_000005.d	Acquisition Date	1/5/2010 3:05:58 PM
Sample	LQ2-046	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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406.17775	1	C 23 H 25 D 2 N Na O 2 S	100.00	406.17802	0.3	0.7	20.9	10.5	even	ok

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