Supporting Information

Reaction of α-ene-Vinylcyclopropanes: Type II Intramolecular [5+2] Cycloaddition or [3+2] Cycloaddition?

Qian Li, Guo-Jie Jiang, Lei Jiao, and Zhi-Xiang Yu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, P. R. China

E-mail: yuzx@pku.edu.cn

Contents

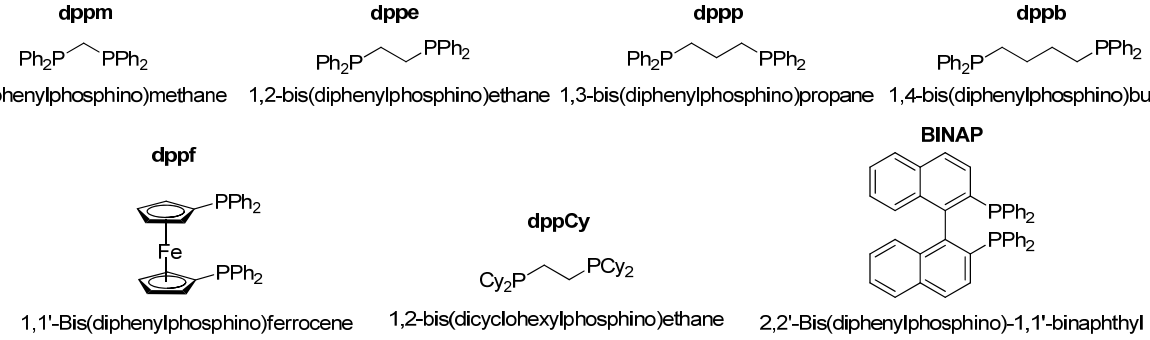
1. General

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, diethyl ether, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 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 show 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 Varian Mercury 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz), 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). 2D NMR 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:

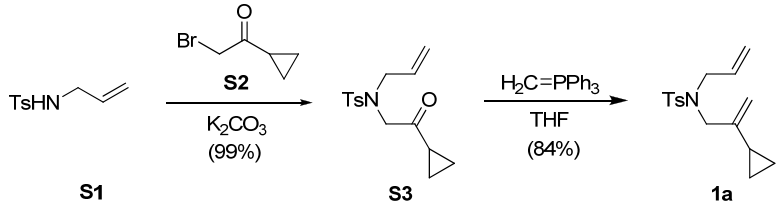
DCE = 1,2-dichloroethane
DEAD = diethyl azodicarboxylate
DMP = Dess-Martin periodinane
EA = ethyl acetate
PCC = pyridinium chlorochromate
PE = petroleum ether
TBAF = tetra-*n*-butylammonium fluoride
THF = tetrehydrofuran
TMEDA = *N, N, N', N'*-tetramethylethylenediamine
TMSCl = trimethylsilyl chloride
TBS = *t*-butyldimethylsilyl



2. Experimental Procedures and Characterization Data

2.1 Synthesis of α-ene-VCP Substrates

α-(*N*-Allyl-*N*-tosyl aminomethyl)vinylcyclopropane (1a)



To a flask charged with tosylamide **S1** (3.00 g, 14.20 mmol) and acetone (60 ml) was added K_2CO_3 (2.74 g, 19.86 mmol), followed by α-bromoketone **S2**[1] (2.57 g, 15.77 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was filtered and the filtrate was concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 30:1 to 10:1) to afford ketone **S3** as a pale yellow oil (4.12g, 99%).

Spectra data of **S3**:

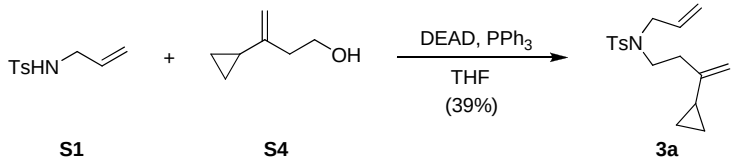
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.66 (ddt, J = 16.8 Hz, 10.1 Hz and 6.5 Hz, 1H), 5.18-5.10 (m, 2H), 4.11 (s, 2H), 3.8 (d, J = 6.5 Hz, 2H), 2.42 (s, 3H), 2.15-2.09 (m, 1H), 1.04-1.00 (m, 2H), 0.98-0.92 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.8, 143.5, 136.3, 132.0, 129.6, 127.3, 120.0, 55.5, 51.3, 21.5, 17.8, 11.7. IR (neat): υ 2935, 1721, 1650, 1605, 1492, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}NO_3S$ $(M+H)^+$: 291.1158. Found: 291.1155.

To a suspension of methyltriphenylphosphonium bromide (10.14 g, 28.39 mmol) in THF (150 mL) at 0 °C was added *n*-BuLi (2.5 M solution in hexane, 10.00 mL, 25.00 mmol), and the resulting solution was stirred for 30 min at 0 °C. A solution of ketone **S3** (4.17 g, 14.21 mmol) in THF (50 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 30 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 30:1 to 20:1) to afford α-ene-VCP **1a** as a pale yellow oil (3.48 g, 84%).

Spectra data of **1a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 5.57-5.4 (m, 1H), 5.09 (d, J = 10.8 Hz, 1 H), 5.08 (d, J = 17.1 Hz, 1H), 4.76 (s, 1H), 4.72 (s, 1H), 3.811 (s, 2H), 3.806 (d, J = 4.4 Hz, 2H), 2.43 (s, 3H), 1.32-1.25 (m, 1H), 0.65 (ddd, J = 8.2 Hz, 6.3 Hz and 4.2 Hz, 2H), 0.44 (ddd, J = 9.3 Hz, 6.1 Hz and 4.1 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.4, 143.1, 137.5, 132.3, 129.6, 127.2, 119.1, 109.7, 51.9, 49.3, 21.5, 13.5, 6.7. IR (neat): υ 2963, 2931, 1654, 1605, 1501, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}NO_2S$ $(M+H)^+$: 292.1366. Found: 291.1365.

α- (*N*-Allyl-*N*-tosyl 2-aminoethyl)vinylcyclopropane (3a)

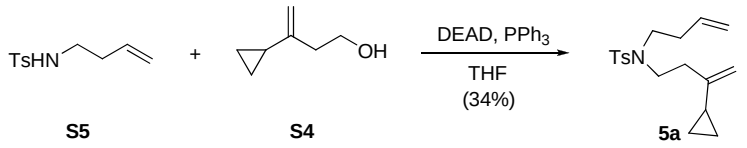


To a stirred solution of tosylamide **S1** (1.89 g, 8.94 mmol), alcohol **S4**[2] (900 mg, 8.02 mmol), and PPh_3 (4.64 g, 17.71 mmol) in THF (100 mL) was added DEAD (3.22 g, 18.51 mmol) dropwise at 0 °C and the mixture was stirred overnight at room temperature. The resulting solution was evaporated and the residue was purified by a short silica gel column (eluted with PE/EA 10:1) to afford a colorless oil, which was subjected to further purification by flash column chromatography (eluted with PE/EA 100:1 to 50:1 to 30:1) to afford α-ene-VCP **3a** as a colorless oil (942 mg, 39%).

Spectra data of **3a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 5.66 (ddt, J = 16.9 Hz, 10.1 Hz and 6.4 Hz, 1H), 5.22-5.14 (m, 2H), 4.66 (s, 1H), 4.61 (s, 1H), 3.83 (d, J = 6.4 Hz, 2H), 3.27 (t, J = 8.2 Hz, 2H), 2.42 (s, 3H), 2.23 (t, J = 8.2 Hz, 2H), 1.29-1.22 (m, 1H), 0.63 (ddd, J = 8.0 Hz, 6.2Hz and 4.4 Hz, 2H), 0.41 (ddd, J = 9.7 Hz, 6.2 Hz and 4.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.6, 143.1, 137.1, 133.2, 129.6, 127.1, 118.7, 108.3, 50.7, 46.6, 34.7, 21.4, 15.9, 6.1. IR (neat): υ 2939, 2887, 1646, 1605, 1497, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1517.

α-(*N*-(But-3-enyl)-*N*-tosyl aminoethyl)vinylcyclopropane (5a)

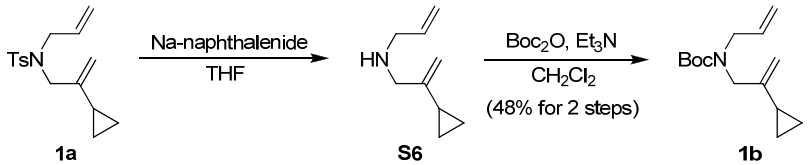


The tosylamide **S5** (771 mg, 3.42 mmol) and alcohol **S4** (319 mg, 2.85 mmol) were converted to α-ene-VCP **5a** as a colorless oil (313 mg, 34%) following the procedure for converting **S1** to **3a**.

Spectra data of **5a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.73 (ddt, J = 17.0 Hz, 10.1 Hz and 7.0 Hz, 1H), 5.09-5.02 (m, 2H), 4.67 (s, 1H), 4.62-4.61 (m, 1H), 3.28 (t, J = 8.2 Hz, 2H), 3.22 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.34-2.23 (m, 4H), 1.28-1.24 (m, 1H), 0.64 (ddd, J = 8.4 Hz, 6.2 Hz and 4.0 Hz, 2H), 0.42 (ddd, J = 6.2 Hz, 5.5 Hz and 4.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.6, 143.1, 137.1, 134.7, 129.6, 127.1, 117.0, 108.2, 47.7, 47.6, 35.2, 33.2, 21.5, 15.9, 6.1. IR (neat): υ 2961, 2928, 1650, 1602, 1497, 1464 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1679. Found: 320.1679.

α-(*N*-Allyl-*N*-*t*-butoxycarbonyl aminomethyl)vinylcyclopropane (1b)



To a solution of sodium naphthalenide (0.16 M in THF, 50 mL, 8.00 mmol) was added a solution of α-ene-VCP **1a** (561 mg, 1.93 mmol) in THF (6 mL) at -78 °C, and the mixture was stirred at -78 °C for 1 h. After the reaction mixture was quenched by water, the aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residual crude **S6** was used in the next step without further purification.

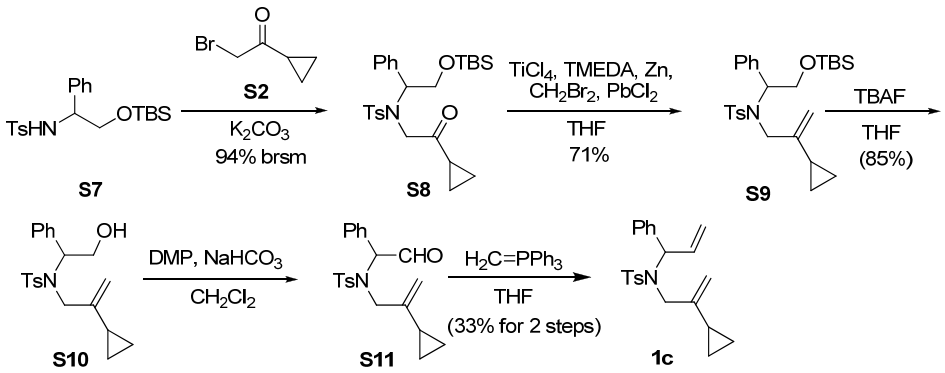
To the crude amine **S6** in CH_2Cl_2 (20 mL) was added Et_3N (600 mg, 5.90 mmol) and Boc_2O (850 mg, 3.90 mmol), and the reaction mixture was stirred at room temperature for 4 h. The reaction was quenched by water,

the aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was filtered through a pad of silica gel (eluted with PE/EA 5:1) to afford the crude product **1b.** To remove residual Boc_2O, water (1 mL) and NaOH solution (6 M, 1 mL) were added to the crude α-ene-VCP **1b** in ethanol (4 mL). After 30 mins stirring, water was added, the mixture was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ before concentration. The residue was purified by flash column chromatography (eluted with PE/EA 30:1) to afford α-ene-VCP **1b** as a colorless oil (222 mg, 48% for 2 steps).

Spectra data of **1b**:

^{1}H-NMR (400 MHz, $CDCl_3$):δ 5.85-5.70 (br, 1H), 5.18-5.05 (br, 2H), 4.71 (s, 1H), 4.68 (s, 1H), 3.87-3.75 (m, 4H), 1.45 (s, 9H), 1.31-1.19 (br, 1H), 0.64 (ddd, J = 8.4 Hz, 6.2 Hz and 4.4 Hz, 2H), 0.45 (d, J = 4.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.6, 146.6, 133.8, 116.5, 116.0, 107.3, 105.3, 79.4, 62.9, 50.7, 50.5, 48.6, 48.3, 28.5, 28.3, 27.7, 13.8, 5.9, 5.8. The redundant peaks are due to the rotation of the C-N bond in the molecule. IR (neat): υ 2987, 2939, 1702, 1650, 1460, 1412 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{23}NNaO_2$ $(M+Na)^+$: 260.1621. Found: 260.1616.

α-(*N*-(1-Phenylallyl)-*N*-tosyl aminomethyl)vinylcyclopropane (1c)



The protected amino alcohol **S7**[3] (3.00 g, 7.40 mmol) was converted to ketone **S8** as a colorless oil (1.78 g, 94% brsm) following the procedure for converting **S1** to **S3**.

The synthesis of **S9** from ketone **S8** follows the procedure of Takai *et al.*[4] In a flame-dried flask a solution of $TiCl_4$ (1 M in CH_2Cl_2, 18.25 mL, 18.25 mmol) was added dropwise to freshly distilled THF (40 mL) at 0 ºC under argon. The flask was warmed to 25 ºC and TMEDA (5.53 mL, 36.50 mmol) was added. After stirring for 10 min, activated Zn dust (2.37 g, 36.50 mmol) and $PbCl_2$ (40.0 mg, 0.14 mmol) was added and the reaction mixture turned dark-blue immediately. After stirred for 30 min, a solution of CH_2Br_2 (2.54 g, 14.6 mmol) and ketone **S8** (1.78 g, 3.65 mmol) in THF (25 mL) was added dropwise. The reaction mixture gradually became brown and the reaction completed within 2 h. Triethylamine (8 mL) and saturated aqueous K_2CO_3 (11 mL) was added to quench the reaction. The mixture was filtered through a thin pad of silica gel to remove the Ti/Zn complex and the combined filtrate was evaporated. The residue was purified by flash column chromatography (eluted with PE/EA 50:1) to afford **S9** as a pale yellow oil (1.25 g, 71%).

To compound **S9** (1.25 g, 2.57 mmol) in THF (30 mL) was added TBAF (2.02 g, 7.71 mmol) and the resulting solution was stirred at room temperature for 3 h. Saturated aqueous NH_4Cl was added to quench the reaction, and the reaction mixture was extracted by ether. The combined organic layer was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (eluted with PE/EA 20:1 to 5:1) to afford alcohol **S10** as a pale yellow oil (810 mg, 85%).

Spectra data of **S9**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.6 Hz, 2H), 7.26-7.20 (m, 5H), 7.10-7.07 (m, 2H), 4.96 (dd, J = 8.0 Hz and 6.2 Hz, 1H), 4.69 (s, 1H), 4.59 (s, 1H), 4.14 (ddd, J = 17.2 Hz, 10.6 Hz and 6.6 Hz, 2H), 3.98 (d, J = 15.9 Hz, 1H), 3.52 (d, J = 15.9 Hz, 1H), 2.42 (s, 3H), 1.28-1.21 (m, 1H), 0.78 (s, 9H), 0.66-0.52 (m, 2H), 0.40-0.30 (m, 2H), 0.000 (s, 3H), -0.005 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.9, 142.9, 138.2, 136.4, 129.4, 129.1, 128.0, 127.6, 127.5, 108.6, 63.3, 62.6, 51.0, 25.7, 21.5, 18.1, 13.2, 7.5, 7.2, -5.4, -5.5.

Spectra data of **S10**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.24-7.17 (m, 3H), 6.86 (d, J = 7.9 Hz, 2H), 4.98 (dd, J = 8.5 Hz and 6.0 Hz, 1H), 4.77 (s, 1H), 4.66 (s, 1H), 4.20 (ddd, J = 11.5 Hz, 8.5 Hz and 5.5 Hz, 1H), 4.06 (d, J = 16.3 Hz, 1H), 4.06-4.00 (m, 1H), 3.42 (d, J = 16.3 Hz, 1H), 2.45 (s, 3H), 2.37 (t, J = 6.3 Hz, 1H), 1.33-1.26 (m, 1H), 0.73-0.60 (m, 2H), 0.47-0.36 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.0, 143.5, 137.8, 135.1, 129.6, 128.6, 128.5, 128.3, 127.4, 108.6, 62.9, 62.8, 50.7, 21.5, 13.1, 7.40, 7.36. IR (neat): υ 3635-3155(br), 2965, 2935, 1650, 1602, 1497, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_3S$ $(M+Na)^+$: 394.1447. Found: 394.1440.

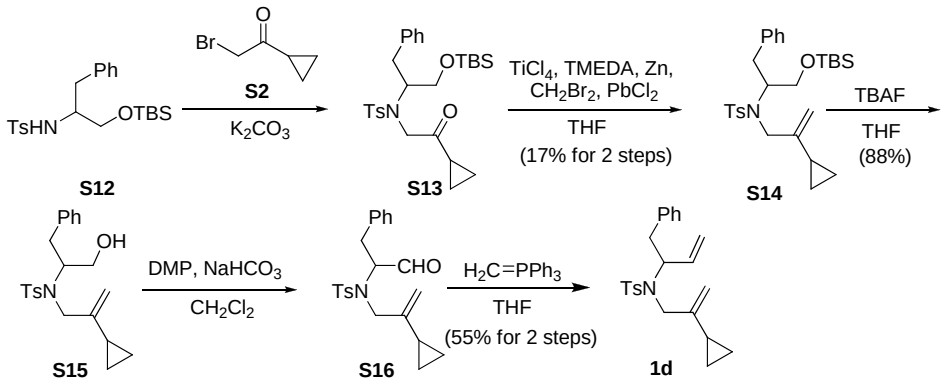
To a stirred suspension of DMP (1.92 g, 4.53 mmol) and $NaHCO_3$ (400 mg, 4.76 mmol) in CH_2Cl_2 (20 mL) was added a solution of alcohol **S10** (810 mg, 2.18 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting solution was diluted with ether (40 mL), saturated aqueous $NaHCO_3$ (20 mL) and saturated aqueous NaS_2O_3 (20 mL). Stirring was continued until the organic phase became clear. The mixture was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and saturated aqueous NaS_2O_3 (2 × 20 mL), dried over $MgSO_4$, and concentrated to afford crude aldehyde **S11,** which was used in the next step without further purification.

Following the procedure for converting **S3** to **1a,** the aldehyde **S11** was converted to α-ene-VCP **1c** as a pale yellow oil (264 mg, 33% for 2 steps).

Spectra data of **1c**:

^{1}H-NMR (400 MHz, $CDCl_3$):δ 7.65 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.24-7.21 (m, 5H), 6.17 (ddd, J = 17.3 Hz, 10.7 Hz and 7.8 Hz, 1H), 5.57 (d, J = 7.8 Hz, 1H), 5.24 (dt, J = 10.7 Hz and 1.4 Hz, 1H), 5.10 (dt, J = 17.3 Hz and 1.4 Hz, 1H), 4.62 (d, J = 0.9 Hz, 1H), 4.54 (t, J = 1.0 Hz, 1H), 3.92 (d, J = 16.4 Hz, 1H), 3.76 (d, J = 16.4 Hz, 1H), 2.41 (s, 3H), 1.13-1.06 (m, 1H), 0.60-0.43 (m, 2H), 0.35-0.21 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 142.9, 138.4, 138.0, 134.9, 129.2, 128.5, 128.1, 127.55, 127.48, 119.0, 109.2, 64.1, 51.0, 21.4, 13.4, 6.9, 6.8. IR (neat): υ 2965, 2928, 1650, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1678.

α-(*N*-(1-Benzylallyl)-*N*-tosyl aminomethyl)vinylcyclopropane (1d)



The protected amino alcohol **S12**[3] (5.00 g, 11.91 mmol) was converted to α-ene-VCP **1d** as a colorless oil (369 mg, 8% for 5 steps) following the procedure for converting **S7** to **1c**.

Spectra data of **S14** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.3 Hz, 2H), 7.23-7.11 (m, 7H), 4.89 (s, 1H), 4.70 (s, 1H), 4.01-3.97 (m, 3H), 3.69 (dd, J = 10.7 Hz and 6.8 Hz, 1H), 3.53 (dd, J = 10.7 Hz and 6.8 Hz, 1H), 2.96 (s, 1H), 2.94 (s, 1H), 2.38 (s, 3H), 1.42-1.35 (m, 1H), 0.78 (s, 9H), 0.71-0.65 (m, 2H), 0.50-0.42 (m, 2H), -0.10 (s, 3H), -0.13 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.3, 142.7, 138.8, 138.2, 129.4, 129.0, 128.3, 127.2, 126.2, 108.3, 62.8, 62.1, 51.2, 36.1, 25.7, 21.4, 18.1, 13.3, 7.5, 7.4, -5.68, -5.74. IR (neat): υ 2965, 2939, 1650, 1605, 1501, 1471 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{42}NO_3SSi$ $(M+H)^+$: 500.2649. Found: 500.2652.

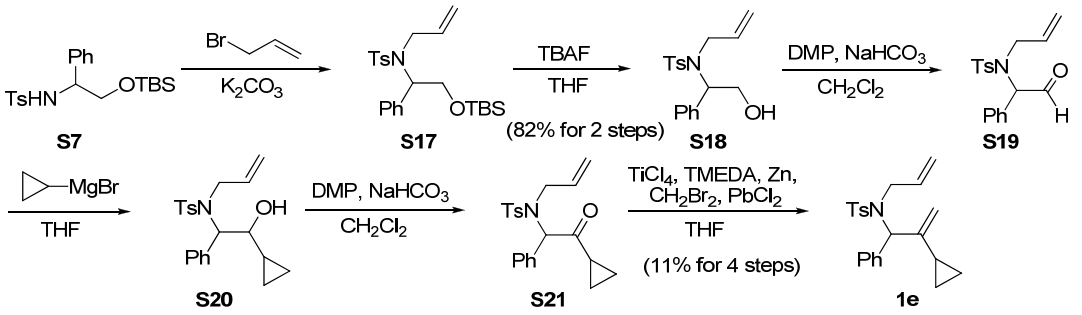
Spectra data of **S15** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 7.24-7.26 (m, 3H), 7.00 (dt, J = 6.2 Hz and 1.8 Hz, 2H), 4.97 (s, 1H), 4.76 (s, 1H), 4.11 (d, J = 16.0 Hz, 1H), 3.99-3.92 (m, 1H), 3.91 (d, J = 16.0 Hz, 1H), 3.68 (ddd, J = 12.0 Hz, 8.0 Hz and 6.3 Hz, 1H), 3.58 (ddd, J = 12.0 Hz, 6.6 Hz and 3.6 Hz, 1H), 2.79 (dd, J = 13.3 Hz and 10.2 Hz, 1H), 2.62 (dd, J = 13.3 Hz and 4.9 Hz, 1H), 2.43 (s, 3H), 2.04 (t, J = 6.5 Hz, 1H), 1.43-1.38 (m, 1H), 0.77-0.72 (m, 2H), 0.53-0.49 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.5, 143.5, 137.9, 137.6, 129.7, 129.0, 128.6, 127.3, 126.6, 108.7, 62.3, 62.2, 51.0, 35.8, 21.5, 13.3, 7.7, 7.6. IR (neat): υ 3632-3226 (br), 2965, 2931, 1650, 1609, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{28}NO_3S$ $(M+H)^+$: 386.1784. Found: 386.1786.

Spectra data of **1d**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.26-7.15 (m, 5H), 7.12 (dd, J = 8.4 Hz and 1.8 Hz, 2H), 5.75 (ddd, J = 17.2 Hz, 10.2 Hz and 7.6 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.84 (d, J = 1.2 Hz, 1H), 4.78 (dt, J = 17.2 Hz and 1.1 Hz, 1H), 4.71 (s, 1H), 4.44-4.38 (m, 1H), 3.95 (d, J = 16.0 Hz, 1H), 3.79 (d, J = 16.0 Hz, 1H), 3.10 (dd, J = 13.2 Hz and 4.9 Hz, 1H), 2.98 (dd, J = 13.2 Hz and 9.8 Hz, 1H), 2.40 (s, 3H), 1.35-1.29 (m, 1H), 0.69-0.64 (m, 2H), 0.47-0.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.7, 143.0, 138.3, 138.0, 134.8, 129.4, 129.3, 128.2, 127.4, 126.3, 119.2, 109.1, 62.8, 51.1, 40.2, 21.5, 13.4, 7.5, 7.3. IR (neat): υ 2965, 2931, 2872, 1646, 1605, 1497, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1838.

α-(*N*-Allyl-*N*-tosyl aminobenzyl)vinylcyclopropane (1e)



To a flask charged with protected amino alcohol **S7** (3.00 g, 7.40 mmol) and acetone (50 ml) was added K_2CO_3 (2.04 g, 14.80 mmol), followed by allyl bromide (4.48 g, 37.00 mmol). The reaction mixture refluxed for 48 h. The resulting solution was filtered; the filtrate was concentrated and dealt with a thin pad of silica gel (eluted with PE/EA 30:1) to afford crude compoud **S17,** which was used in the next step without further purification.

The protected alcohol **S17** was deprotected and oxidized to obtain crude aldehyde **S19** following the procedure for converting **S9** to **S11**. To aldehyde **S19** in THF (70 mL) was added a 1.0 M solution of cyclopropylmagnesium bromide in THF (7.84 mL, 7.84 mmol) at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h. Saturated aqueous NH_4Cl was added to quench the reaction, and the reaction mixture was extracted by ether. The combined organic layer was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, and concentrated. The residue was filtered through a thin pad of silica gel (eluted with PE/EA 30:1) to afford crude alcohol **S20,** which was used in the next step without further purification.

The alcohol **S20** was oxidized to obtain crude ketone **S21** following the procedure for converting **S10** to **S11**. Crude ketone **S21** was converted to α-ene-VCP **1e** as a colorless oil (239 mg, 9% for 6 steps) following the procedure for converting **S8** to **S9**.

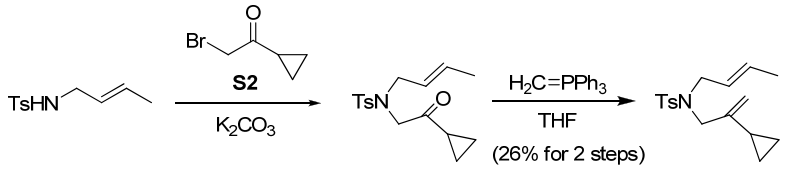
Spectra data of **S18** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.26-7.24 (m, 3H), 7.01-6.98 (m, 2H), 5.73-5.63 (m, 1H), 5.11-5.04 (m, 3H), 4.12 (ddd, J = 11.5 Hz, 8.4 Hz and 5.4 Hz, 1H), 4.05 (ddd, J = 11.5 Hz, 6.5 Hz, 5.7 Hz, 1H), 3.91 (ddt, J = 16.4 Hz, 4.9 Hz and 1.8 Hz, 1H), 3.53 (dd, J = 16.4 Hz and 7.4 Hz, 1H), 2.44 (s, 3H), 2.15 (dd, J = 6.8 Hz and 5.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.5, 138.0, 135.7, 135.4, 129.6, 128.6, 128.2, 128.1, 127.4, 127.8, 77.2, 62.3, 47.4, 21.5. IR (neat): υ 3643-3252 (br), 2965, 2931, 1646, 1605, 1501, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{21}NNaO_3S$ $(M+Na)^+$: 354.1134. Found: 354.1124.

Spectra data of **1e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.3 Hz, 2H), 7.26-7.20 (m, 5H), 7.16-7.14 (m, 2H), 5.75 (s, 1H), 5.33 (ddt, J = 16.8 Hz, 10.5 Hz and 6.6 Hz, 1H), 4.87-4.78 (m, 3H), 4.65 (d, J = 1.8 Hz, 1H), 3.92 (dd, J = 16.3 Hz and 6.6 Hz, 1H), 3.78 (ddt, J = 16.3 Hz, 6.6 Hz and 1.4 Hz, 1H), 2.40 (s, 3H), 1.10-1.03 (m, 1H), 0.65-0.60 (m, 2H), 0.56-0.40 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.4, 142.9, 137.9, 137.5, 135.0, 129.4, 129.1, 128.2, 127.7, 127.5, 116.7, 109.7, 66.4, 48.4, 21.4, 14.7, 8.1, 7.7. IR (neat): υ 2965, 2935, 1654, 1602, 1501, 1460, 1438 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{25}NNaO_2S$ $(M+Na)^+$: 390.1498. Found: 390.1490.

α-((*E*)-*N*-(But-2-enyl)-*N*-tosyl aminomethyl)vinylcyclopropane (1f)



S22 **S23** **1f**

The tosylamide **S22** (2.00 g, 8.88 mmol) was converted to α-ene-VCP **1f** as a colorless oil (231 mg, 26% for 2 steps) following the procedure for converting **S1** to **1a**.

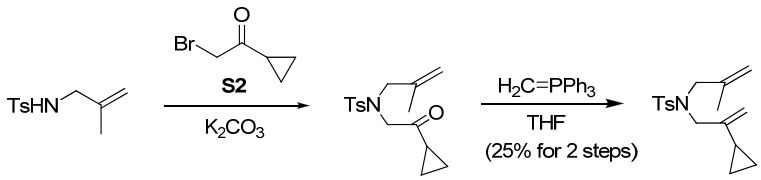
Spectra data of **S23** (a pale yellow oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.56-5.51 (m, 1H), 5.33-5.26 (m, 1H), 4.03 (s, 2H), 3.74 (d, J = 6.4 Hz, 2H), 2.42 (s, 3H), 2.18 (m, 1H), 1.62 (dd, J = 6.8 Hz and 1.2 Hz, 3H), 1.03-0.99 (m, 2H), 0.96-0.91(m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.1, 143.4, 136.3, 131.8, 129.5, 127.2, 124.7, 55.6, 50.8, 21.4, 17.7, 17.5, 11.5. IR (neat): υ 2969, 2928, 1717, 1605, 1497, 1453 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}NO_3S$ $(M+H)^+$: 308.1315. Found: 308.1311.

Spectra data of **1f**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.50 (dtq, J = 15.5 Hz, 6.7 Hz and 1.2 Hz, 1H), 5.16 (dtq, J = 15.5Hz, 7.1 Hz and 1.6 Hz, 1H), 4.75-4.74 (m, 1H), 4.72-4.71 (m, 1H), 3.79 (s, 2H), 3.74 (d, J = 6.9 Hz, 2H), 2.42 (s, 3H), 1.59 (dq, J = 6.7 Hz and 1.3 Hz, 3H), 1.31-1.24 (m, 1H), 0.65 (ddd, J = 10.6 Hz, 6.6 Hz and 4.4 Hz, 2H), 0.43 (ddd, J = 9.34 Hz, 6.2 Hz and 4.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.7, 143.9, 137.7, 130.6, 129.5, 127.2, 124.9, 109.4, 51.7, 48.7, 21.5, 17.6, 13.5, 6.7. IR (neat): υ 2965, 2931, 1654, 1605, 1501, 1464 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1519.

α-(*N*-(2-Methylallyl)-*N*-tosyl aminomethyl)vinylcyclopropane (1g)



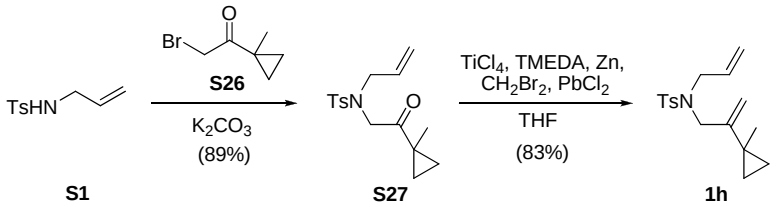
S24 **S25** **1g**

Tosylamide **S24** (590 mg, 2.62 mmol) was converted to α-ene-VCP **1g** as a colorless oil (197 mg, 25% for 2 steps) following the procedure for converting **S1** to **1a**.

Spectra data of **1g**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.86 (t, J = 1.0 Hz, 1H), 4.78 (t, J = 1.0 Hz, 1H), 4.68 (q, J = 1.3 Hz, 1H), 4.67 (m, 1H), 3.82 (s, 2H), 3.75 (s, 2H), 2.41 (s, 3H), 1.61 (s, 3H), 1.20-1.13 (m, 1H), 0.58 (ddd, J = 8.4 Hz, 6.1 Hz and 3.9 Hz, 2H), 0.38 (ddd, J = 9.3 Hz, 6.0 Hz and 3.9 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.4, 143.0, 140.1, 137.7, 129.4, 127.3, 114.5, 109.6, 53.1, 52.3, 21.5, 20.0, 13.6, 6.8. IR (neat): υ 2931, 1654, 1602, 1497, 1453 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1520.

α-(*N*-Allyl-*N*-tosyl aminomethyl)vinyl(1-methyl)cyclopropane (1h)



Tosylamide **S1** (1.46 g, 6.91 mmol) was converted to ketone **S27** (1.90 g, 89%) by alkylation with α-bromoketone **S26**[5] (1.60 g, 9.04 mmol) following the procedure for converting **S1** to **S3**. The ketone **S27** (960 mg, 3.10 mmol) was converted to α-ene-VCP **1h** as a colorless oil (787 mg, 83%) following the procedure for converting **S8** to **S9**.

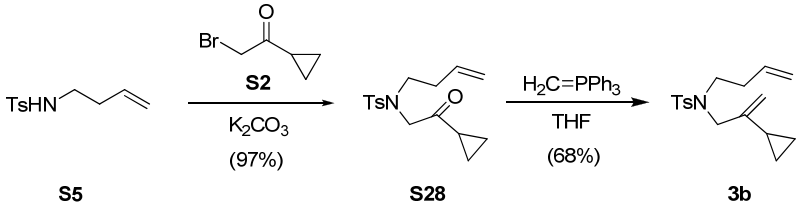
Spectra data of **S27** (a pale yellow oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 5.68 (ddt, J = 16.8 Hz, 10.2 Hz and 6.7 Hz, 1H), 5.18-5.10 (m, 2H), 4.24 (s, 2H), 3.83 (d, J = 6.7 Hz, 2H), 2.42 (s, 3H), 1.34 (s, 3H), 1.20 (dd, J =6.8 Hz and 4.0 Hz, 2H), 0.71 (dd, J =6.8 Hz and 4.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.2, 143.3, 137.2, 132.7, 129.4, 127.4, 119.5, 51.1, 50.3, 25.5, 21.5, 19.0, 18.7. IR (neat): υ 2969, 2935, 1717, 1646, 1602, 1497, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}NO_3S$ (M+H)$^+$: 308.1315. Found: 308.1310.

Spectra data of **1h**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.52 (ddt, J = 17.1 Hz, 10.4 Hz and 6.6 Hz, 1H), 5.09-5.04 (m, 2H), 5.00 (d, J = 1.3 Hz, 1H), 4.93 (d, J = 1.3 Hz, 1H), 3.79 (s, 2H), 3.78 (d, J = 5.9 Hz, 2H), 2.43 (s, 3H), 1.14 (s, 3H), 0.60 (dd, J = 4.4 Hz and 6.2 Hz, 2H), 0.39 (dd, J = 4.4 Hz and 6.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 143.1, 137.5, 132.5, 129.6, 127.2, 119.2, 112.0, 49.7, 49.0, 23.8, 21.5, 19.8, 12.9. IR (neat): υ 2961, 2931, 1654, 1605, 1497, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ (M+H)$^+$: 306.1522. Found: 306.1519.

α-(*N*-(But-3-enyl)-*N*-tosyl aminomethyl)vinylcyclopropane (3b)



Tosylamide **S5** (2.80 g, 12.43 mmol) was converted to α-ene-VCP **3b** as a colorless oil (2.41 g, 63% for 2 steps) following the procedure for converting **S1** to **1a**.

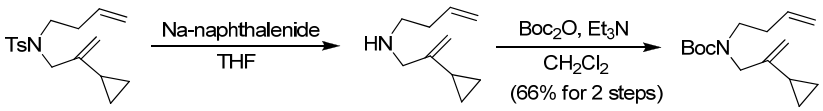
Spectra data of **S28** (a pale yellow oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 5.69 (ddt, J = 17.3 Hz, 10.3 Hz and 6.5 Hz, 1H), 5.07-5.00 (m, 2H), 4.13 (s, 2H), 3.24 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H), 2.26 (qt, J = 7.1 Hz and 1.4 Hz, 2H), 2.19 (tt, J = 7.5 Hz and 4.5 Hz, 1H), 1.06-1.02 (m, 2H), 1.00-0.94 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.2, 143.5, 136.3, 134.4, 129.6, 127.3, 117.2, 57.1, 48.5, 32.5, 21.5, 17.8, 11.9. IR (neat): υ 2965, 2935, 1721, 1650, 1602, 1497, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}NO_3S$ (M+H)$^+$: 308.1315. Found: 308.1313.

Spectra data of **3b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 5.66 (m, 1H), 5.00 (dq, J = 8.2 Hz and 1.2 Hz, 1H), 4.97 (t, J = 1.2 Hz, 1H), 4.78 (q, J = 1.2 Hz, 1H), 4.70 (s, 1H), 3.81 (s, 2H), 3.17 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.28-2.21 (m, 2H), 1.36-1.29 (m, 1H), 0.68 (ddd, J = 8.7 Hz, 6.3 Hz and 4.3 Hz, 2H), 0.47 (ddd, J = 9.2 Hz, 6.3 Hz and 4.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.2, 143.1, 134.8, 129.6, 127.2, 116.7, 109.5, 105.3, 53.9, 47.1, 32.7, 21.5, 13.4, 7.2. IR (neat): υ 2961, 2935, 1650, 1602, 1497, 1450 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1525.

α-(*N*-(But-3-enyl)-*N*-*t*-butoxycarbonyl aminomethyl)vinylcyclopropane (3c)



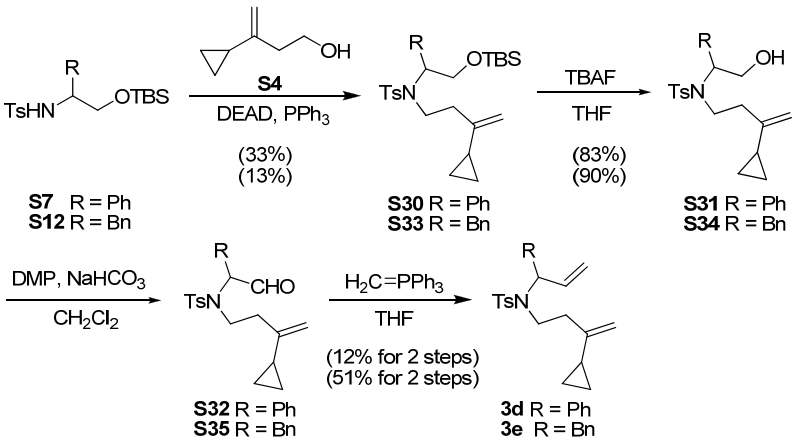
3b **S29** **3c**

The tosyl substituted α-ene-VCP **3b** (309.9 mg, 1.01 mmol) was converted to Boc-substituted α-ene-VCP **3c** as a colorless oil (167.4 mg, 66% for 2 steps) following the procedure for converting **1a** to **1b**.

Spectra data of **3c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.84-5.70 (m, 1H), 5.06 (d, J = 17.3 Hz, 1H), 5.01 (d, J = 10.2 Hz, 1H), 4.70-4.69 (m, 1H), 4.68-4.67 (m, 1H), 3.90-3.80 (m, 2H), 3.27-3.17 (m, 2H), 2.28 (s, 2H), 1.47-1.44 (m, 9H), 1.30-1.18 (m, 1H), 0.65 (ddd, J = 8.3 Hz, 6.5 Hz and 4.3 Hz, 2H), 0.48-0.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.9, 135.6, 116.4, 107.3, 107.2, 105.3, 79.3, 52.0, 51.4, 46.0, 32.9, 32.4, 28.4, 13.8, 6.1, 5.9. The redundant peaks are due to the rotation of C-N bond in the molecule. IR (neat): υ 2983, 2935, 1702, 1650, 1468, 1415 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{25}NNaO_2$ $(M+Na)^+$: 274.1778. Found: 274.1777.

α-(*N*-(1-Phenylallyl)-*N*-tosyl 2-aminoethyl)vinylcyclopropane (3d)
α-(*N*-(1-Benzylallyl)-*N*-tosyl 2-aminoethyl)vinylcyclopropane (3e)



The protected amino alcohols **S7** (1.83 g, 4.51 mmol) and **S12** (2.43 g, 5.79 mmol) were converted to **S30** (750 mg, 33%) and **S33** (382 mg, 13%), respectively, following the procedure for converting **S1** to **3a**. Then **S30** (750 mg, 1.50 mmol) and **S33** (382 mg, 0.74 mmol) were converted to α-ene-VCPs **3d** (55 mg, 10% for 3 steps) and **3e** (134 mg, 46% for 3 steps) as colorless oils, respectively, following the procedure for converting **S9** to **1c**.

Spectra data of **S30** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$):δ 7.74 (d, J = 8.4 Hz, 2H), 7.28-7.23 (m, 7H), 5.02 (dd, J = 7.0 Hz and 5.9 Hz, 1H), 4.56 (d, J = 1.4 Hz, 1H), 4.43 (d, J = 1.4 Hz, 1H), 4.10 (dd, J = 10.6 Hz and 7.0 Hz, 1H), 3.96 (dd, J = 10.6 Hz and 5.9 Hz, 1H), 3.31 (ddd, J = 15.0 Hz, 11.8 Hz and 4.8 Hz, 1H), 3.20 (ddd, J = 15.0 Hz, 12.0 Hz and 5.3 Hz, 1H), 2.42 (s, 3H), 2.20 (td, J = 12.4 Hz and 5.2 Hz, 1H), 1.86 (td, J = 12.4 Hz and 5.0 Hz, 1H), 1.12-1.05 (m, 1H), 0.81 (s, 9H), 0.59-0.49 (m, 2H), 0.34-0.24 (m, 2H), 0.01 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.1, 143.0, 138.4, 137.4, 129.5, 128.5, 128.2, 127.7, 127.3, 107.8, 63.2, 61.6, 45.2, 37.0, 25.7, 21.5, 18.1, 15.9, 6.04, 6.01, -5.5. IR (neat): υ 2961, 2935, 1646, 1605, 1497, 1464 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{41}NNaO_3SSi$ $(M+Na)^+$: 522.2469. Found: 522.2457.

Spectra data of **S31** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.26-7.22 (m, 3H), 7.03-7.00 (m, 2H), 5.04 (t, J = 6.6 Hz, 1H), 4.58 (d, J = 1.3 Hz, 1H), 4.44 (d, J = 1.3 Hz, 1H), 4.15-4.07 (m, 2H), 3.28 (ddd, J = 15.0 Hz, 11.7 Hz and 5.1 Hz, 1H), 3.17 (ddd, J = 15.0 Hz, 11.5 Hz and 5.3 Hz, 1H), 2.45 (s, 3H), 2.23-2.19 (m, 2H), 1.94 (td, J = 12.0 Hz and 4.9 Hz, 1H), 1.15-1.08 (m, 1H), 0.60-0.52 (m, 2H), 0.36-0.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.9, 143.5, 137.9, 136.0, 129.7, 128.7, 128.3, 128.1, 127.4, 108.2, 62.3, 62.1, 44.7, 37.1, 21.5, 15.8, 6.2, 6.1. IR (neat): υ 3643-3229(br), 2965, 2931, 1646, 1602, 1497, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{27}NNaO_3S$ $(M+Na)^+$: 408.1604. Found: 408.1605.

Spectra data of **3d**:

^{1}H-NMR (400 MHz, $CDCl_3$):δ 7.72 (d, J = 8.5 Hz, 2H), 7.31-7.26 (m, 7H), 5.96 (ddd, J = 17.2 Hz, 10.1 Hz and 6.2 Hz, 1H), 5.69 (d, J = 6.1 Hz, 1H), 5.25 (dt, J = 10.1 Hz and 1.3 Hz, 1H), 5.05 (dt, J = 17.2 Hz and 1.3 Hz, 1H), 4.54 (t, J = 1.3 Hz, 1H), 4.38 (d, J = 1.3 Hz, 1H), 3.28 (ddd, J = 14.7 Hz, 12.0 Hz and 5.4 Hz, 1H), 3.15 (ddd, J = 14.7 Hz, 12.1 Hz and 4.8 Hz, 1H), 2.42 (s, 3H), 2.18 (td, J = 12.4 Hz and 4.9 Hz, 1H), 1.59 (td, J = 12.4 Hz and 4.9 Hz, 1H), 1.07-1.02 (m, 1H), 0.57-0.47 (m, 2H), 0.31-0.20 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.1, 143.1, 138.7, 137.8, 134.1, 129.4, 128.5, 128.4, 127.9, 127.5, 119.0, 107.9, 63.1, 45.2, 36.6, 21.5, 15.8, 6.0, 5.9. IR (neat): υ 2965, 2931, 1646, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$: 382.1835. Found: 382.1829; calcd for $C_{23}H_{27}NNaO_2S$ $(M+Na)^+$: 404.1655. Found: 404.1647.

Spectra data of **S33** (a colorless oil):

^{1}H-NMR (400 MHz, $CDCl_3$):δ 7.62 (d, J = 8.6 Hz, 2H), 7.25-7.19 (m, 7H), 4.67 (s, 1H), 4.62 (d, J = 1.3 Hz, 1H), 4.05-4.00 (m, 1H), 3.63-3.55 (m, 2H), 3.47 (ddd, J = 14.7 Hz, 11.0 Hz and 5.3 Hz, 1H), 3.37 (ddd, J = 14.7 Hz, 11.0 Hz and 6.0 Hz, 1H), 3.00 (dd, J = 13.6 Hz and 8.4 Hz, 1H), 2.79 (dd, J = 13.6 Hz and 6.2Hz, 1H), 2.39 (s, 3H), 2.41-2.28 (m, 2H), 1.33-1.25 (m, 1H), 0.83 (s, 9H), 0.67-0.63 (m, 2H), 0.46-0.43 (m, 2H), -0.05 (s, 3H), -0.06 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.4, 142.8, 138.4, 138.2, 129.5, 129.1, 128.4, 127.2, 126.4, 107.6, 63.6, 61.4, 44.8, 37.4, 36.6, 25.8, 21.4, 18.2, 16.2, 6.2, 6.1, -5.61, -5.64. IR (neat): υ 2961, 2935, 1646, 1609, 1497, 1464 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{43}NNaO_3SSi$ $(M+Na)^+$: 536.2625. Found: 536.2623.

Spectra data of **S34** (a colorless oil):

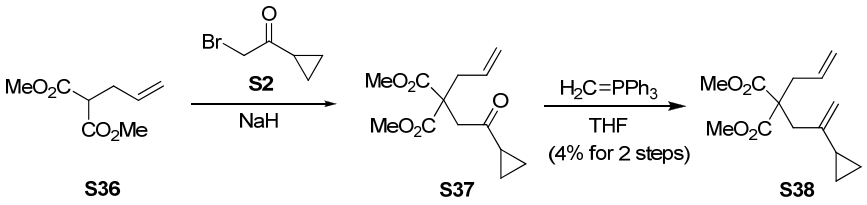
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.7 Hz, 2H), 7.27-7.19 (m, 5H), 7.02 (dd, J = 7.7 Hz and 2.0 Hz, 2H), 4.71 (s, 1H), 4.67 (s ,1H), 4.03-3.98 (m, 1H), 3.63-3.58 (m, 2H), 3.45 (ddd, J = 14.6 Hz, 10.2 Hz and 6.0 Hz, 1H), 3.34 (ddd, J = 14.6 Hz, 9.8 Hz and 6.6 Hz, 1H), 2.74-2.61 (m, 2H), 2.41 (s, 3H), 2.40 (m, 2H), 2.00 (t, J = 5.7 Hz, 1H), 1.35-1.25 (m, 1H), 0.68 (ddd, J = 8.0 Hz, 6.4 Hz and 4.0 Hz, 2H), 0.47 (ddd, J = 9.7 Hz, 6.2 Hz and 4.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.1, 143.4, 138.4, 137.6, 129.7, 128.9, 128.6, 127.2,

126.7, 108.2, 62.5, 62.1, 44.4, 37.5, 36.4, 21.5, 16.0, 6.4, 6.3. IR (neat): υ 3602-3226 (br), 2965, 2931, 1669, 1646, 1605, 1497, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{29}NNaO_3S$ $(M+Na)^+$: 422.1760. Found: 422.1761.

Spectra data of **3e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 2H), 7.28-7.14 (m, 7H), 5.70 (ddd, J = 17.3 Hz, 10.6 Hz and 6.3 Hz, 1H), 5.08 (dt, J = 10.6 Hz and 1.3 Hz, 1H), 4.99 (dt, J = 17.3 Hz and 1.3 Hz, 1H), 4.68 (s, 1H), 4.66-4.60 (m, 2H), 3.35-3.20 (m, 2H), 2.99-2.89 (m, 2H), 2.39 (s, 3H), 2.39-2.26 (m, 2H), 1.32-1.25 (m, 1H), 0.68-0.63 (m, 2H), 0.45-0.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.2, 143.0, 137.9, 137.8, 135.4, 129.5, 129.2, 128.4, 127.3, 126.5, 118.4, 108.0, 61.4, 44.4, 39.6, 37.3, 21.4, 16.1, 6.2, 6.1. IR (neat): υ 2965, 2931, 1646, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{29}NNaO_2S$ $(M+Na)^+$: 418.1811. Found: 418.1811.

Dimethyl 2-allyl-2-(2-cyclopropylallyl)malonate (S38)



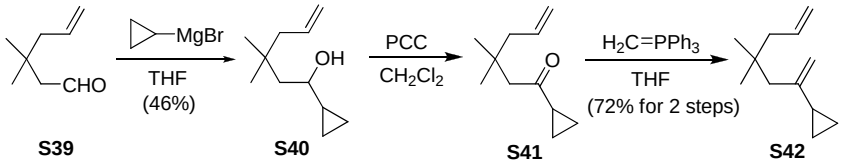
To a flask charged with NaH (242 mg, 10.1 mmol) and THF (20 mL) was added dimethyl ester **S36** (1.75 g, 10.2 mmol) dropwise, followed by bromide ketone **S2** (1.66 g, 10.20 mmol) 10 min later at 0 °C. After stirred at room temperature for 2 h, the reaction mixture was quenched with brine, extracted with Et_2O, dried over $MgSO_4$ and concentrated. The residue was filtered through a thin pad of silica gel (eluted with PE/EA 30:1) to afford crude ketone **S37,** which was used in the next step without further purification.

The ketone **S37** was converted to α-ene-VCP **S38** as a colorless oil (112 mg, 4% for 2 steps) following the procedure for converting **S3** to **1a**.

Spectra data of **S38**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.76-5.66 (m, 1H), 5.12-5.07 (m, 2H), 4.70-4.68 (m, 2H), 3.71 (s, 6H), 2.83 (s, 2H), 2.72 (d, J = 7.2 Hz, 2H), 1.14-1.07 (m, 1H), 0.63 (ddd, J = 8.4 Hz, 6.2 Hz and 4.0 Hz, 2H), 0.43 (ddd, J = 9.6 Hz, 6.3 Hz and 4.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.5, 146.0, 132.8, 118.9, 110.9, 57.6, 52.3, 40.2, 36.9, 16.1, 7.6.

α-(2,2-Dimethylpent-4-enyl)vinylcyclopropane (S42)



The aldehyde **S39**[6] (1.00 g, 7.92 mmol) was converted to alcohol **S40** as a colorless oil (615 mg, 46%) following the procedure for converting **S19** to **S20**.

To alcohol **S40** (600 mg, 3.56 mmol) in CH_2Cl_2 (35 mL) was added PCC (1.18 g, 5.47 mmol) and the reaction mixture was stirred at room temperature overnight. The resulting solution was diluted with *n*-pentane and filtered through a short silica gel column (eluted with *n*-pentane/ether 10:1). After removal of the solvent, the crude ketone **S41** was used in the next step without further purification.

The ketone **S41** was converted to α-ene-VCP **S42** as a colorless oil (420 mg, 72% for 2 steps) following the procedure for converting **S3** to **1a**.

Spectra data of **S40**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.85 (ddt, J = 16.8 Hz, 10.2 Hz and 7.5 Hz, 1H), 5.05-4.98 (m, 2H), 2.99 (td, J = 7.9 Hz and 3.6 Hz, 1H), 2.05-2.02 (m, 2H), 1.57 (d, J = 3.6 Hz, 1H), 1.56 (d, J = 7.9 Hz, 1H), 1.41 (br s, 1H), 0.98-0.90 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H), 0.55-0.46 (m, 2H), 0.32-0.26 (m, 1H), 0.22-0.15 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.8, 116.8, 74.3, 48.7, 47.2, 32.8, 27.6, 20.0, 3.3, 3.0. IR (neat): υ 3531-3158 (br), 2928 cm^{-1}.

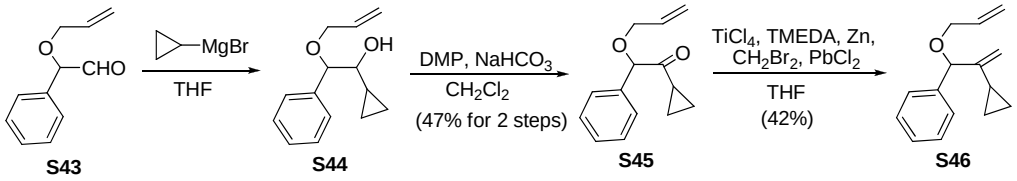
Spectra data of **S41** (a colorless oil):

^{1}H-NMR (200 MHz, $CDCl_3$): δ 5.94-5.72 (m, 1H), 5.08-4.97 (m, 2H), 2.45 (s, 2H), 2.09 (d, J = 7.5 Hz, 2H), 1.97-1.84 (m, 1H), 1.06-0.95 (m, 2H), 1.02 (s, 6H), 0.91-0.79 (m, 2H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 210.6, 135.0, 117.5, 54.3, 46.8, 33.8, 27.3, 22.2, 11.0. IR (neat): υ 2965, 2928, 1732 cm^{-1}.

Spectra data of **S42**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.87 (ddt, J = 16.5 Hz, 10.0 Hz and 7.5 Hz, 1H), 5.05-4.98 (m, 2H), 4.59-4.58 (m, 1H), 4.56-4.55 (m, 1H), 2.08 (s, 2H), 2.03 (dt, J = 7.5 Hz and 1.2 Hz, 2H), 1.25-1.18 (m, 1H), 0.92 (s, 6H), 0.69 (ddd, J = 8.2 Hz, 6.1 H and 4.2 Hz, 2H), 0.45 (ddd, J = 9.4 Hz, 6.1 H and 4.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.4, 135.9, 116.8, 108.2, 50.0, 47.3, 34.0, 27.3, 17.4, 8.7. IR (neat): υ 2961, 2935 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{20}Na$ $(M+Na)^+$: 187.1457. Found: 187.1465.

α-(Allyloxybenzyl)vinylcyclopropane (S46)



S43 S44 S45 S46

The aldehyde **S43**[7] (2.21 g, 12.54 mmol) was converted to α-ene-VCP **S46** as a colorless oil (521 mg, 19% for 3 steps) following the procedure for converting **S19** to **1e**.

Spectra data of **S45** (a colorless oil):

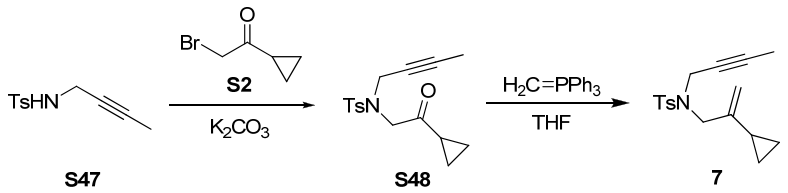
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.39-7.30 (m, 3H), 5.96 (ddt, J = 17.3 Hz, 10.2 Hz and 5.8 Hz, 1H), 5.32 (dq, J = 17.3 Hz and 1.8 Hz, 1H), 5.23 (dq, J = 10.2 Hz and 1.8 Hz, 1H), 4.90 (s, 1H), 4.07 (dm, J = 5.8 Hz, 2H), 2.30 (tt, J = 7.8 Hz and 4.9 Hz, 1H), 1.06-0.95 (m, 2H), 0.91-0.81 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.9, 136.4, 134.0, 128.6, 128.4, 127.1, 117.6, 86.7, 70.3, 16.5, 11.9, 11.5. IR (neat): υ 2965, 2931, 1706, 1609, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ $(M+Na)^+$: 239.1043. Found: 239.1036.

Spectra data of **S46**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.28-7.23 (m, 1H), 5.96 (ddt, J = 17.3 Hz, 10.6 Hz and 5.3 Hz, 1H), 5.30 (dq, J = 17.3 Hz and 1.8 Hz, 1H), 5.17 (dq, J = 10.2 Hz and 1.8 Hz, 1H), 5.05 (s, 1H), 4.87 (s, 1H), 4.76 (s, 1H), 4.04 (ddt, J = 12.9 Hz, 5.3 Hz and 1.6 Hz, 1H), 3.96 (ddt, J = 12.9 Hz, 5.6 Hz and 1.6 Hz, 1H), 1.21-1.14 (m, 1H), 0.62-0.49 (m, 2H), 0.42-0.29 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.9, 140.9, 135.0, 128.0, 127.3, 127.0, 116.5, 107.6, 84.3, 69.3, 12.2, 7.0, 6.9. IR (neat): υ 2920, 1646,

1609, 1494, 1453 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{18}NaO$ $(M+Na)^+$: 237.1250. Found: 237.1246.

***N*-(But-2-ynyl)-*N*-(2-cyclopropylallyl)-4-methylbenzenesulfonamide (7)**



The tosylamide **S47** (1.56 g, 7.00 mmol) was converted to α-yne-VCP **7** as a colorless oil (1.07 g, 50% for 2 steps) following the procedure for converting **S1** to **1a**.

Spectra data of **S48** (a pale yellow oil):

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 4.15 (s, 2H), 4.11 (q, J = 2.3 Hz, 2H), 2.43 (s, 3H), 2.24-2.17 (m, 1H), 1.59 (t, J = 2.3 Hz, 3H), 1.07 (ddd, J = 7.5 Hz, 4.5 Hz and 2.9 Hz, 2H), 0.97 (ddd, J = 7.7 Hz 6.4 Hz and 2.9 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.5, 143.6, 135.6, 129.4, 127.6, 82.3, 71.3, 55.3, 38.3, 21.4, 17.7, 11.6, 3.2. IR (neat): υ 2864, 1717, 1453 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{20}NO_3S$: 306.1158. Found: 306.1156.

Spectra data of **7**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 4.86 (s, 1H), 4.77 (s, 1H), 4.02 (dd, J = 5.2 Hz and 2.2 Hz, 2H), 3.79 (s, 2H), 2.45 (s, 3H), 1.50 (t, J = 2.3 Hz, 3H), 1.42-1.36 (m, 1H), 0.71 (ddd, J = 8.1 Hz , 6.2 Hz and 4.4 Hz, 2H), 0.50 (ddd, J = 9.5 Hz, 5.9 Hz and 4.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.9, 143.1, 136.2, 129.1, 127.9 110.4, 81.5, 71.499, 51.6, 36.0, 21.5, 13.5, 6.9, 3.2. IR (neat): υ 2969, 2928, 1654, 1598, 1497, 1449 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{22}NO_2S$: 304.1366. Found: 304.1369.

2.2 General Procedures for Rh(I)-Catalyzed [3+2] Cycloadditions

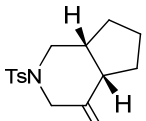
General Procedures

Preparation of the cationic Rh(I) catalyst solution: Anhydrous DCE (6.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (9.9 mg, 25.4 μmol) and $AgSbF_6$ (21.0 mg, 61.1 μmol, 1.2 equiv. to Rh) under argon. The mixture was stirred at room temperature for 10 min. The resulting yellow suspension was left to stand until the formed AgCl precipitated. The supernatant was used in the [3+2] cycloaddition reactions as the catalyst precursor ($[Rh(I)^+]$ = 8.5 μmol/mL).

General Procedure for the intramolecular [3+2] cycloaddition reaction: Under argon, the above $Rh(I)^+$ solution (1.0 mL, 8.5 μmol) was added to a flame-dried reaction tube containing 1,3-bis(diphenylphosphino)methane [dppm, 3.9 mg, 10.2 μmol, 1.2 equiv. to $Rh(I)^+$] and newly activated 4 Å molecular sieve (100 mg). The resulting orange suspension was stirred at room temperature for 10 min, and then a solution of the α-ene-VCP substrate (0.086 mmol) in DCE (1.2 mL) was added. The reaction tube was immersed into an oil bath (85 ºC or 95 ºC as indicated). 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/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 [3+2] cycloadduct.

Experimental data for cycloadducts

***Cis*-5-Methylene-*N*-tosyl 3-azabicyclo[4.3.0]nonane (2a)**



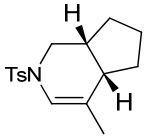
2a

Following the general procedure, α-ene-VCP **1a** (25.0 mg, 0.086 mmol) was converted to cycloadduct **2a** as a white solid (23.5 mg, 94%). Substrate concentration: 0.04 M, temperature: 85 ºC, reaction time: 6 h.

Spectra data of **2a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.93-4.92 (m, 1H), 4.88-4.87 (m, 1H), 3.72 (d, J = 12.5 Hz, 1H), 3.40 (d, J = 12.5 Hz, 1H), 3.28 (ddd, J = 12.0 Hz, 5.2 Hz and 1.5 Hz, 1H), 2.57-2.50 (m, 2H), 2.44 (s, 3H), 2.28-2.19 (m, 1H), 1.79-1.53 (m, 5H), 1.45-1.37 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 142.3, 129.6, 127.7, 127.6, 112.1, 49.6, 47.0, 44.6, 39.5, 28.8, 28.3, 22.9, 21.5. IR (neat): υ 2965, 2931, 1657, 1605, 1497, 1464 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}NO_2S$ (M+H): 292.1366. Found: 292.1362.

***Cis*-5-Methyl-*N*-tosyl 3-azabicyclo[4.3.0]non-4-ene (2a')**



2a'

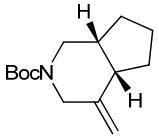
2a' (a colorless oil) is a byproduct of the [3+2] reaction of α-ene-VCP **1a**, when 4Å molecular sieves were not

used in the reaction system.

Spectra data of **2a'**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.40 (s, 1H), 3.45 (dd, J = 12.0 Hz and 4.8 Hz, 1H), 2.61 (dd, J = 12.0 Hz and 10.2 Hz, 1H), 2.42 (s, 3H), 2.08-1.79 (m, 4H), 1.67 (t, J = 1.1 Hz, 3H), 1.63-1.54 (m, 1H), 1.48-1.40 (m, 1H), 1.31-1.22 (m, 1H), 1.12 (ddt, J = 12.4 Hz, 8.9 Hz and 8.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 135.6, 129.6, 127.0, 121.0, 119.0, 45.6, 41.5, 35.3, 31.3, 28.7, 23.4, 21.5, 19.7. IR (neat): υ 2965, 2928, 1676, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}NNaO_2S$ (M+Na): 314.1185. Found: 314.1181.

***Cis*-*N*-*t*-Butoxycarbonyl-5-methylene 3-aza-bicyclo[4.3.0]nonane (2b)**



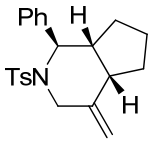
2b

Following the general procedure, α-ene-VCP **1b** (20.4 mg, 0.086 mmol) was converted to cycloadduct **2b** as a colorless oil (14.1 mg, 69%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 24 h.

Spectra data of **2b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.91 (s, 1H), 4.84 (s, 1H), 3.93 (d, J = 14.2 Hz, 1H) 3.87 (d, J = 14.2 Hz, 1H), 3.53 (m, 1H), 2.98 (m, 1H), 2.66 (q, J = 8.0 Hz, 1 H), 2.29-2.17 (m, 1H), 1.80-1.50 (m, 4H), 1.46 (s, 9H) , 1.35-1.25 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 155.0, 144.8, 144.5, 144.2, 110.83, 110.76, 110.5, 110.3, 79.2, 48.8, 47.9, 45.1, 45.0, 44.6, 44.5, 44.1, 40.0, 29.7, 29.0, 28.6, 28.5, 28.3, 24.3. The redundant peaks are due to the rotation of C-N bond in the molecule. IR (neat): υ 2965, 2931, 1702 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{23}NNaO_2$ $(M+Na)^+$: 260.1621. Found: 260.1618.

(±)-(*1R,2R,6S*)-5-Methylene-2-phenyl-*N*-tosyl 3-aza-bicyclo[4.3.0]nonane (2c)



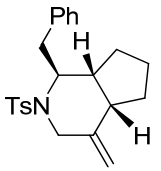
2c

Following the general procedure, α-ene-VCP **1c** (31.6 mg, 0.086 mmol) was converted to cycloadduct **2c** as a colorless oil (27.8 mg, 88%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 36 h.

Spectra data of **2c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.5 Hz, 2H), 7.28-7.16 (m, 7H), 5.03 (d, J = 2.0 Hz, 1H), 4.87 (t, J = 1.1 Hz, 1H), 4.78 (s, 1H), 4.14 (d, J = 13.5 Hz, 1H), 3.78 (d, J = 13.5 Hz, 1H), 2.68 (dd, J = 12.9 Hz and 7.6 Hz, 1H), 2.56 (ddt, J = 10.2 Hz, 2.6 Hz and 7.6 Hz, 1H), 2.39 (s, 3H), 1.77-1.60 (m, 4H), 1.49-1.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.9, 142.6, 141.3, 137.3, 129.3, 128.1, 127.3, 127.2, 126.8, 111.4, 58.9, 47.2, 44.9, 40.5, 30.6, 30.0, 23.1, 21.5. IR (neat): υ 2961, 2935, 1657, 1605, 1501, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1681.

(±)-(*1R,2S,6S*)-2-Benzyl -5-methylene-*N*-tosyl 3-aza-bicyclo[4.3.0]nonane (2d)



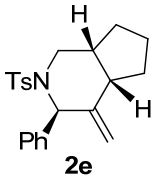
2d

Following the general procedure, α-ene-VCP **1d** (32.8 mg, 0.086 mmol) was converted to cycloadduct **2d** as a colorless oil (23.6 mg, 72%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 36 h.

Spectra data of **2d**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.64 (d, J = 8.2 Hz, 2H), 7.29-7.20 (m, 5H), 7.14 (d, J = 7.0 Hz, 2H), 4.97 (s, 1H), 4.94 (s, 1H), 4.16 (d, J = 14.1 Hz, 1H), 4.09 (dd, J = 10.4 Hz and 5.0 Hz, 1H), 3.72 (d, J = 13.7 Hz, 1H), 2.82 (dd, J =13.4 Hz and 10.7 Hz, 1H), 2.79-2.74 (m, 2H), 2.39 (s, 3H), 2.00 (q, J = 8.6 Hz, 1H), 1.70-1.60 (m, 3H), 1.51-1.47 (m, 1H), 1.34-1.26 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 143.0, 142.9, 138.8, 137.4, 129.6, 129.3, 128.6, 127.1, 126.4, 111.1, 57.9, 46.2, 41.1, 40.7, 39.4, 30.1, 29.7, 23.9, 21.5. IR (neat): υ 2961, 2935, 1657, 1602, 1491, 1456cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1824.

(±)-(*1R,4S,6S*)-5-Methylene-4-phenyl-*N*-tosyl 3-aza-bicyclo[4.3.0]nonane (2e)



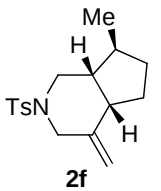
2e

Following the general procedure, α-ene-VCP **1e** (31.6 mg, 0.086 mmol) was converted to cycloadduct **2e** as a colorless oil (9.5 mg, 30%). Recovered starting material: 14.3 mg (yield: 55% brsm). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 40 h.

Spectra data of **2e**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.67 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.32-7.22 (m, 5H), 5.32 (s, 1H), 4.89 (s, 1H), 4.83 (s, 1H), 3.63 (dd, J = 11.5 Hz and 4.4 Hz, 1H), 2.55 (t, J = 10.6 Hz, 1H), 2.43 (s, 3H), 2.37-2.26 (m, 2H), 1.78-1.70 (m, 2H), 1.63-1.57 (m, 1H), 1.43-1.37 (m, 1H), 1.35-1.27 (m, 1H), 1.09-1.02 (m, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 146.6, 143.1, 140.5, 135.4, 129.5, 128.2, 127.4, 127.0, 126.5, 113.3, 64.4, 46.9, 40.0, 37.0, 29.6, 29.0, 24.6, 21.5. IR (neat): υ 2961, 2935, 1654, 1602, 1494, 1453 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1670.

(±)-(*1R,6S,9S*)-9-Methyl-5-methylene-*N*-tosyl 3-aza-bicyclo[4.3.0]nonane (2f)



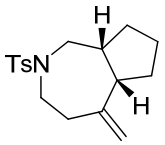
2f

Following the general procedure, α-ene-VCP **1f** (26.3 mg, 0.086 mmol) was converted to cycloadduct **2f** as a colorless oil (6.6 mg, 25%). Recovered starting material: 13.6 mg (yield: 52% brsm). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 48 h.

Spectra data of **2f**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 4.91 (t, J = 1.2 Hz, 1H), 4.87 (s, 1H), 3.67 (d, J = 12.8 Hz, 1H), 3.50 (d, J = 12.8 Hz, 1H), 3.10 (dd, J = 11.8 Hz and 4.8 Hz, 1H), 2.85 (dd, J = 11.8 Hz and 6.6 Hz, 1H), 2.63 (q, J = 7.5 Hz, 1H), 2.44 (s, 3H), 1.93-1.61 (m, 4H), 1.28-1.13 (m, 2H), 0.99 (d, J = 6.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 142.5, 133.8, 129.6, 127.7, 111.8, 50.4, 47.2, 46.2, 43.5, 32.6, 29.7, 28.6, 21.5, 20.0. IR (neat): υ 2961, 2931, 1657, 1605, 1497, 1468 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{23}NNaO_2S$ $(M+Na)^+$: 328.1342. Found: 328.1334.

***Cis*-6-Methylene-*N*-tosyl 3-azabicyclo[5.3.0]decane (4a)**

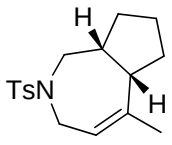


4a

Following the general procedure, α-ene-VCP **3a** (26.2 mg, 0.086 mmol) was converted to cycloadduct **4a** as a colorless oil (23.8 mg, 91%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 10 h.

Spectra data of **4a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.80-4.79 (m, 1H), 4.76-4.75 (m, 1H), 3.47-3.41 (m, 1H), 3.30 (ddd, J = 14.1 Hz, 3.1 Hz and 0.9 Hz, 1H), 2.90 (ddd, J = 11.9 Hz, 8.9 Hz and 3.3 Hz, 1H), 2.77-2.69 (m, 2H), 2.47 (ddd, J = 13.3 Hz, 6.7 Hz and 3.2 Hz, 1H), 2.41 (s, 3H), 2.39-2.36 (m, 1H), 2.26 (ddd, J = 13.3 Hz, 8.9 Hz and 3.6 Hz, 1H), 1.93-1.85 (m, 1H), 1.82-1.71 (m, 2H), 1.56-1.39 (m, 2H), 1.33-1.25 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.4, 143.0, 136.0, 129.6, 121.0, 112.5, 51.7, 51.4, 48.4, 41.6, 37.4, 31.1, 30.8, 25.9, 21.4. IR (neat): υ 2957, 1739, 1646, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1518.



4a'

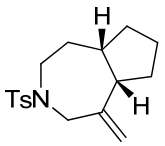
4a' (a colorless oil) is a byproduct of the [3+2] reaction of α-ene-VCP **3a**, when 4Å molecular sieves were not used in the reaction system.

Spectra data of **4a'**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.48 (t, J = 6.0 Hz, 1H), 3.58 (dd, J = 9.7 Hz and 7.5, 1H), 3.42 (dd, J = 9.7 Hz and 6.3 Hz, 1H), 3.00 (m, 1H), 2.68-2.62 (m, 1H), 2.41 (s, 3H), 2.22-2.09 (m, 2H), 1.86-1.80 (m, 1H), 1.65 (d, J = 1.2 Hz, 3H), 1.62-1.55 (m, 1H), 1.50-1.45 (m, 1H), 1.36-1.18 (m, 2H), 0.92-0.80 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 134.0, 132.8, 129.6, 127.5, 126.1, 55.7, 50.0, 47.3, 39.8, 30.5, 27.5, 25.8, 25.0, 21.5. IR (neat): υ 2931, 1602, 1482, 1456 cm^{-1}. HRMS (ESI)

calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1517.

***Cis*-2-Methylene-*N*-tosyl 4-aza-bicyclo[5.3.0]decane (4b)**



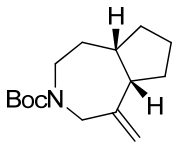
4b

Following the general procedure, α-ene-VCP **3b** (26.3 mg, 0.086 mmol) was converted to cycloadduct **4b** as a colorless oil (18.6 mg, 71%). Recovered starting material: 2.8 mg (yield: 79% brsm). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 36 h.

Spectra data of **4b**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.69 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 5.00 (s, 1H), 4.91 (s, 1H), 3.99 (d, J = 14.0 Hz, 1H), 3.70 (d, J = 14.0 Hz, 1H), 3.33-3.28 (m, 1H), 3.11 (dt, J = 12.4 Hz and 4.7 Hz, 1H), 2.91 (dd, J = 17.3 Hz and 9.2 Hz, 1H), 2.46 (s, 3H), 2.33-2.27 (m, 1H), 1.88-1.78 (m, 2H), 1.76-1.71 (m, 1H), 1.70-1.64 (m, 2H), 1.63-1.53 (m, 1H), 1.51-1.44 (m, 1H), 1.18-1.11 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.1, 143.0, 135.4, 129.6, 127.2, 111.6, 53.3, 47.0, 46.1, 40.2, 33.4, 30.9, 29.3, 25.1, 21.5. IR (neat): υ 2954, 1646, 1605, 1497, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1518.

***Cis*-*N*-*t*-Butoxycarbonyl-2-methylene 4-aza-bicyclo[5.3.0]decane (4c)**



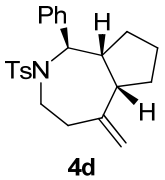
4c

Following the general procedure, α-ene-VCP **3c** (21.6 mg, 0.086 mmol) was converted to cycloadduct **4c** as a colorless oil (17.7 mg, 82%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 36 h.

Spectra data of **4c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.99 (m, 1H), 4.87 (s, 1H), 4.14-3.92 (m, 2H), 3.50-3.28 (m, 2H), 2.70 (q, J = 8.0 Hz, 1H), 2.20-2.07 (br, 1H), 1.87-1.48 (m, 7H), 1.47 (s, 9H), 1.31-1.21 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.4, 148.3, 148.0, 145.6, 112.0, 111.9, 79.3, 51.6, 51.0, 47.5, 47.4, 44.6, 44.5, 41.0, 40.8, 33.2, 32.8, 31.8, 31.6, 29.7, 29.3, 29.1, 28.8, 28.5, 28.3, 24.0, 23.9. The redundant peaks are due to the rotation of C-N bond in the molecule. IR (neat): υ 2961, 2946, 1702, 1646, 1497, 1460, 1415 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{25}NNaO_2$ $(M+Na)^+$: 274.1778. Found: 274.1779.

(±)-(*1R,2R,7S*)-6-Methylene-2-phenyl-*N*-tosyl 3-aza-bicyclo[5.3.0]decane (4d)



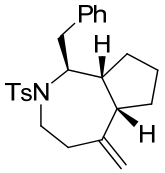
4d

Following the general procedure, α-ene-VCP **3d** (32.8 mg, 0.086 mmol) was converted to cycloadduct **4d** as a colorless oil (18.4 mg, 56%). Recovered starting material: 12.4 mg (yield: 90%, brsm). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 60 h.

Spectra data of **4d**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.15-7.06 (m, 7H), 6.96 (d, J = 8.2 Hz, 2H), 4.94 (s, 1H), 4.92 (s, 1H), 4.63 (d, J = 9.3 Hz, 1H), 3.68-3.59 (m, 2H), 2.89-2.82 (m, 2H), 2.74-2.69 (m, 1H), 2.40-2.36 (m, 1H), 2.30 (s, 3H), 1.94-1.89 (m, 1H), 1.81-1.72 (m, 2H), 1.48-1.40 (m, 2H), 1.24-1.19 (m, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 147.1, 141.9, 140.6, 139.0, 128.8, 128.4, 127.9, 127.0, 126.5, 112.7, 64.8, 47.4, 45.7, 44.8, 39.4, 31.8, 30.8, 25.0, 21.3. IR (neat): υ 2961, 2935, 1654, 1605, 1501, 1460 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1838.

(±)-(*1R,2S,7S*)-2-Benzyl -6-methylene-*N*-tosyl 3-aza-bicyclo[5.3.0]decane (4e)



4e

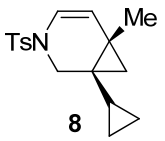
Following the general procedure, α-ene-VCP **3e** (34.2 mg, 0.086 mmol) was converted to cycloadduct **4e** as a white solid (30.8 mg, 90%). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 20 h.

Spectra data of **4d**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.26-7.19 (m, 5H), 7.05 (d, J = 7.1 Hz, 2H), 4.89 (d, J = 2.2 Hz, 1H), 4.75 (d, J = 1.6 Hz, 1H), 4.42 (m, 1H), 3.93 (m, 1H), 3.01-2.87 (m, 3H), 2.49 (td, J = 13.2 Hz and 3.3 Hz, 1H), 2.38 (s, 3H), 2.36-2.28 (m, 2H), 1.98 (m, 1H), 1.91 (dt, J = 13.2 Hz and 7.6 Hz, 1H), 1.86-1.81 (m, 1H), 1.77 (dt, J = 11.6 Hz and 6.6 Hz, 1H), 1.61-1.57 (m, 1H), 1.51-1.44 (m, 1H), 1.35-1.27 (m, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 152.4, 142.9, 139.1, 137.9, 129.7, 129.0, 128.6, 126.9, 126.4, 113.3, 60.7, 46.5, 45.0, 43.0, 35.8, 35.5, 34.5, 31.9, 25.9, 21.5. IR (neat): υ 2957, 1643, 1605, 1501, 1456 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{30}NO_2S$ $(M+H)^+$: 396.1992. Found: 396.1993.

When the carbon and oxygen tethered substrates **S38**, **S42** and **S46** were subjected to the standard reaction conditions, complex mixtures were obtained.

(±)-(1*R*,6*S*)-1-Cyclopropyl-6-methyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (8)



8

Following the general procedure, α-yne-VCP **7** (26.1 mg, 0.086 mmol) was converted to cycloadduct **8** as a white solid (8.6 mg, 33%). Recovered starting material: 8.9 mg (yield: 50% brsm). Substrate concentration: 0.04 M, temperature: 95 ºC, reaction time: 36 h.

Synthesis of product **8** using $[Rh(CO)_2Cl]_2$ as the catalyst:

Under argon, $[Rh(CO)_2Cl]_2$ (1.7 mg, 4.3 μmol) was added to a flame-dried reaction tube. A solution of the

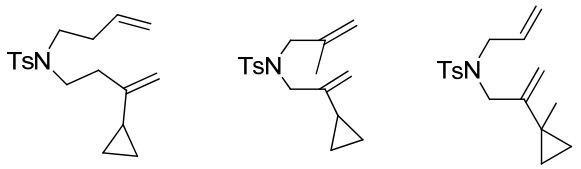
α-yne-VCP **7** (26.1 mg, 0.086 mmol) in DCE (2.2 mL) was added. Then mixed gas of CO/N_2 (1/4) was bubbled to the above solution for 1 min. After that the reaction tube was immersed into an oil bath (80 ºC) and kept under the balloon pressured mixed gas of CO/N_2 (CO/N_2=1/4, we specify this condition as 0.2 atm CO) for 20 h. 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/EA 5:1, and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel to afford product **8** as a white solid (17.0 mg, 65%).

Spectra data of **8**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.26 (d, J = 8.1 Hz, 1H), 5.21 (d, J = 8.1 Hz, 1H), 3.79 (d, J = 10.9 Hz, 1H), 2.84 (d, J = 11.7 Hz, 1H), 2.42 (s, 3H), 1.16 (s, 3H), 0.90-0.86 (m, 1H), 0.57-0.52 (m, 1H), 0.47 (d, J = 4.4 Hz, 1H), 0.46-0.42 (m, 1H), 0.22 (d, J = 4.4 Hz, 1H), 0.18-0.14 (m, 1H), 0.11-0.07 (m,1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 143.6, 135.0, 129.7, 127.0, 119.9, 118.4, 46.0, 34.9, 29.7, 21.5, 21.1, 18.6, 18.4, 11.1, 4.5, 2.7. IR (neat): 2965, 2931, 1654, 1605, 1497, 1464, 1356, 1166 υ cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{22}NO_2S$: 304.1366. Found: 304.1360.

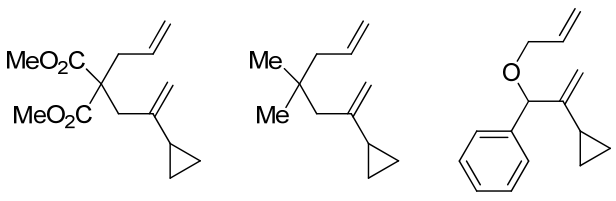
Reaction of other substrates

Substrates give no products:



5a **1g** **1h**

Substrates give mixtures:



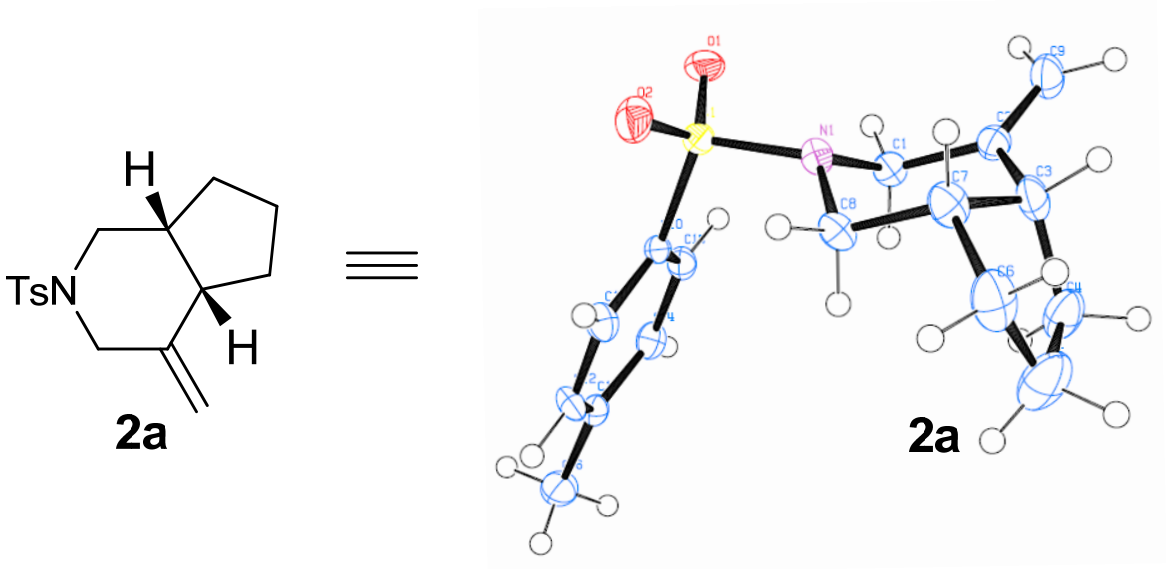
S38 **S42** **S46**

2.3 Stereochemical Determination

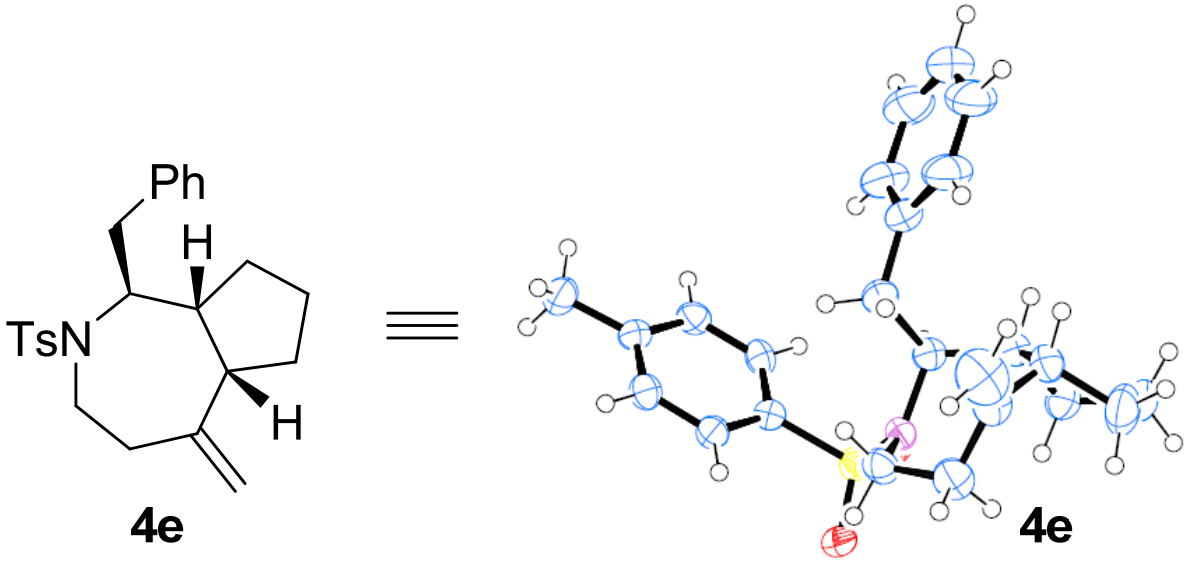
The relative configuration of compounds **2a**, **4e** and **8** was determined by X- ray crystallography. The relative configuration of compounds **2c**, **2e**, **4a** and **4b** was determined by NOESY experiments and the relative configuration of compound **2d** and **4d** were deduced by analogy to **2c**/**2e** and **4a**/**4b**, respectively.

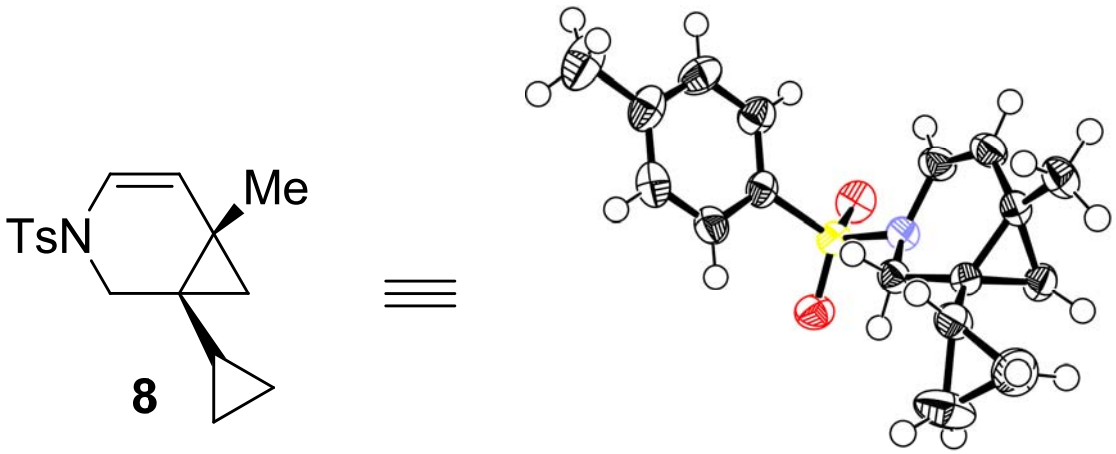
Determination of the stereostructures of compounds 2a, 4e and 8 by X- ray crystallography. See figures below for details.

CCDC Number for **2a**: 749396



CCDC Number for **4e**: 749397





Determination of the stereostructures of compounds 2c, 2e, 4a and 4b by 2D NOESY experiments. See figures below for details.

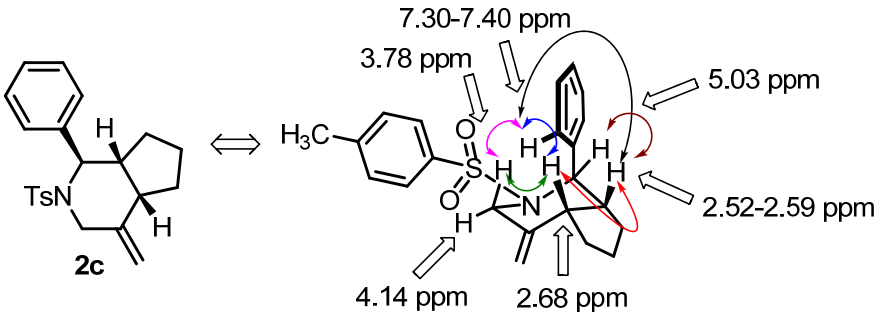


Figure S1. NMR analysis of cycloadduct **2c** (the DEPT and 2D NMR spectra are in page 75-76).

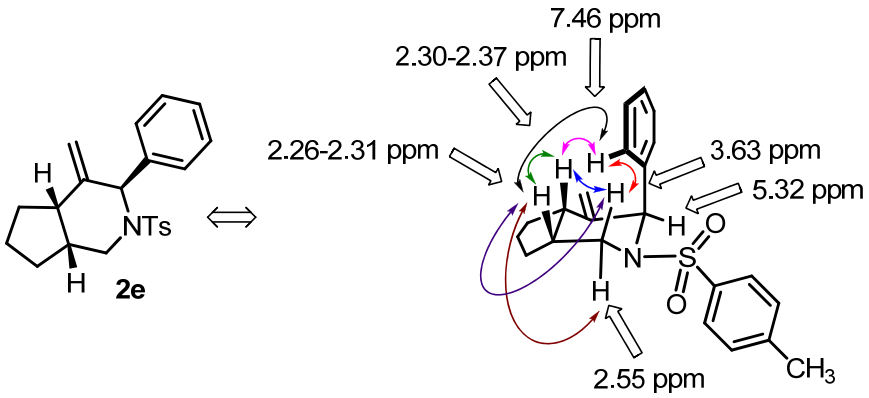


Figure S2. NMR analysis of cycloadduct **2e** (the DEPT and 2D NMR spectra are in page 77-78).

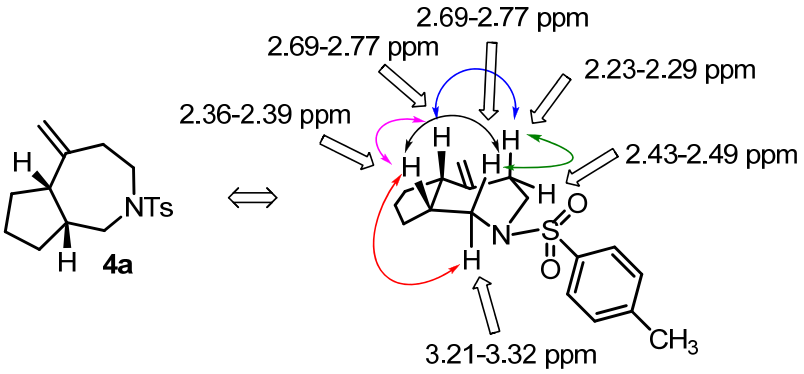


Figure S3. NMR analysis of cycloadduct **4a** (the DEPT and 2D NMR spectra are in page 79-80).

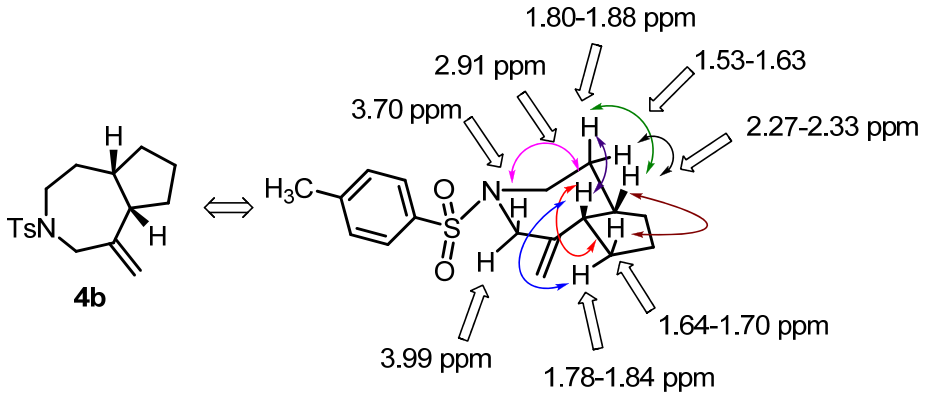


Figure S4. NMR analysis of cycloadduct **4b** (the DEPT and 2D NMR spectra are in page 81-82).

2.4 References

(1) M. Laurent, M. Cérésiat, J. Marchand-Brynaert, *Eur. J. Org. Chem.* **2006**, 3755.

(2) J. R. Walker, S. C. Rothman, C. D. Poulter, *J. Org. Chem.* **2008**, *73*, 726.

(3) L. A. Gandon, A. G. Russell, T. Guveli, A. E. Brodwolf, B. M. Kariuki, N. Spencer, J. S. Snaith, *J. Org. Chem.* **2006**, *71*, 5198.

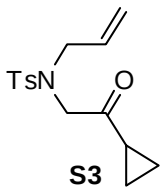
(4) K. Takai, Y. Kataoka, J. Miyai, T. Okazoe, K. Oshima, K. Utimoto, *Org. Synth.* **1998**, *Coll. Vol. 9*, 404.

(5) B. L. Palucki, M. K. Park, R. P. Nargund, R. Tang, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1993.

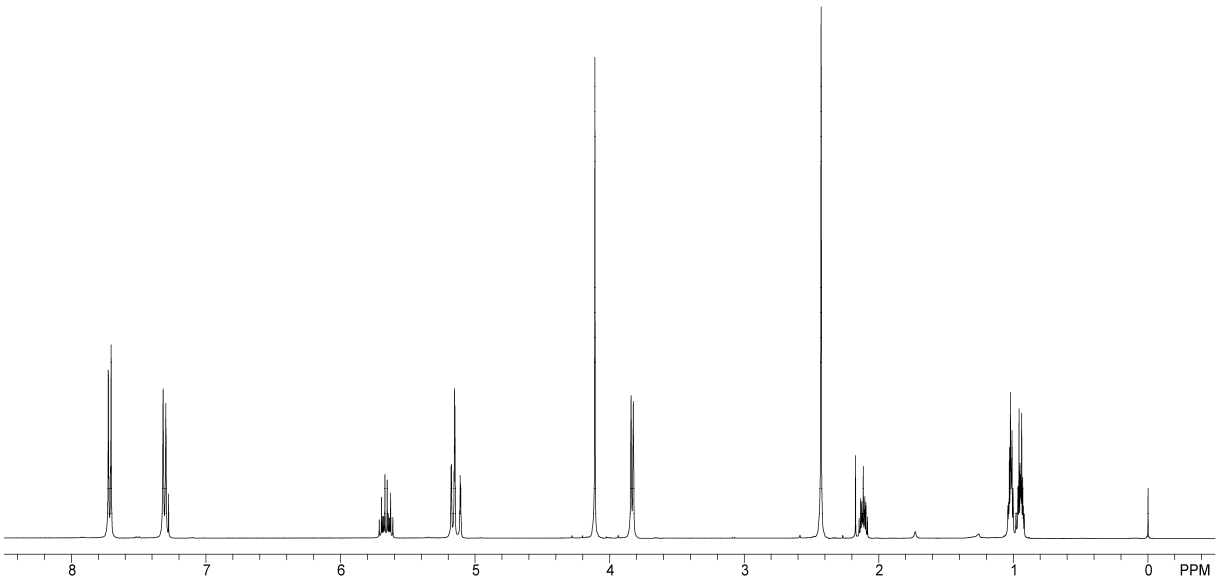
(6) B. M. Trost, D. Romero, F. Rise, *J. Am. Chem. Soc.* **1994**, *116*, 4268.

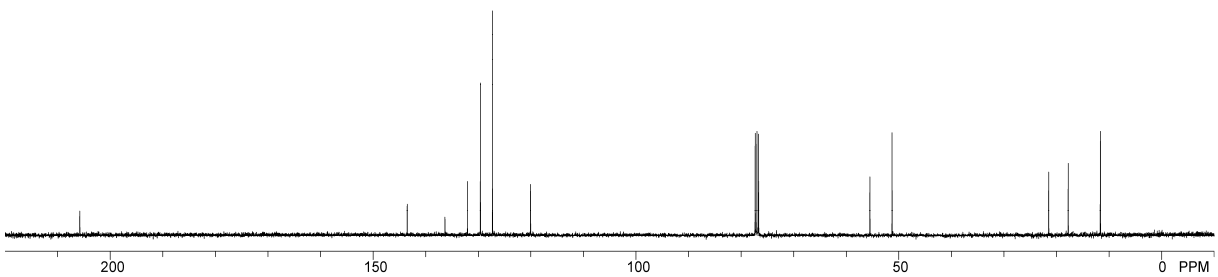
(7) B. Schmidt, *J. Org. Chem.* **2004**, *69*, 7672.

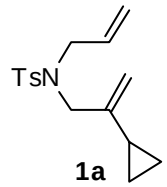
3. ^{1}H and ^{13}C-NMR Spectra for New Compounds



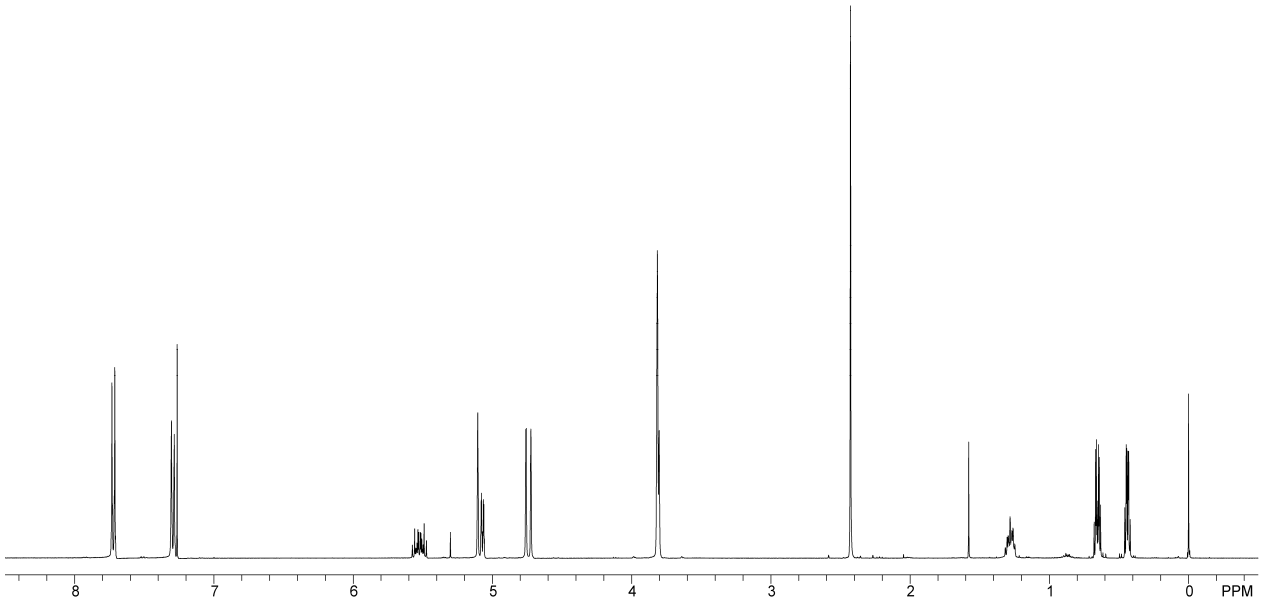
S3

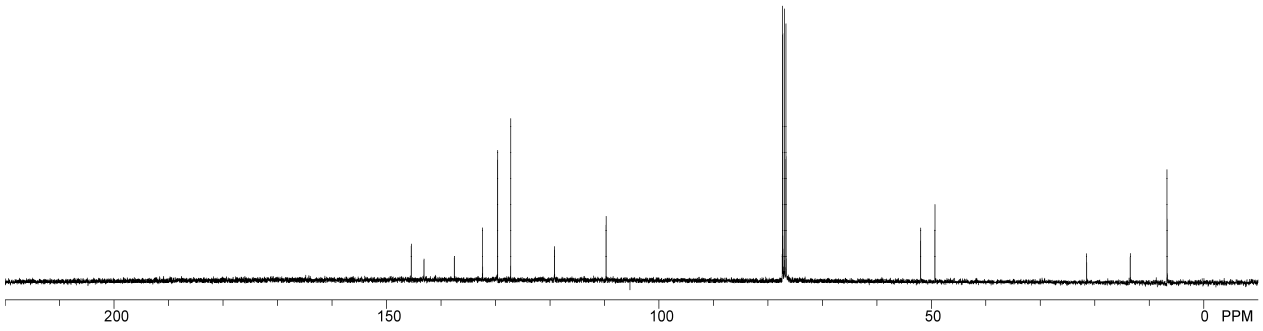


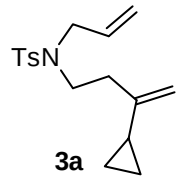




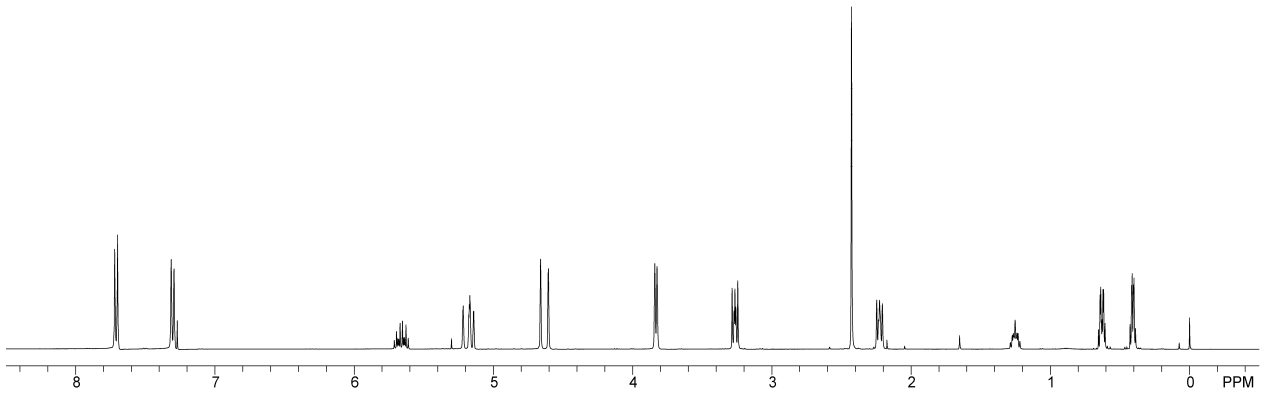
1a

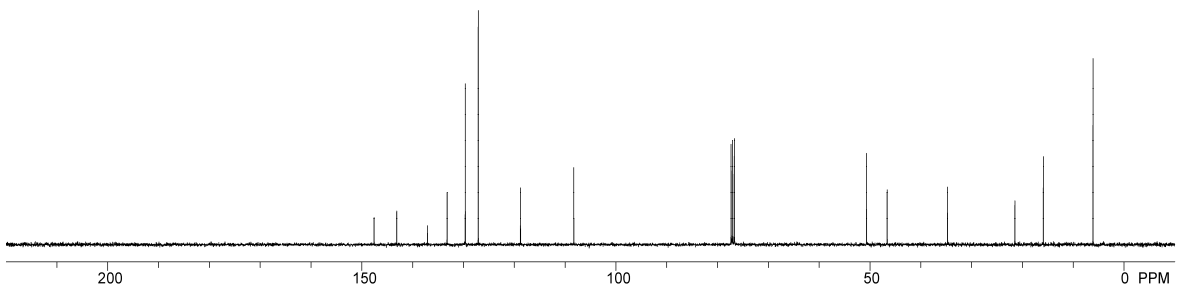


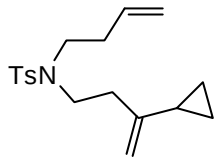




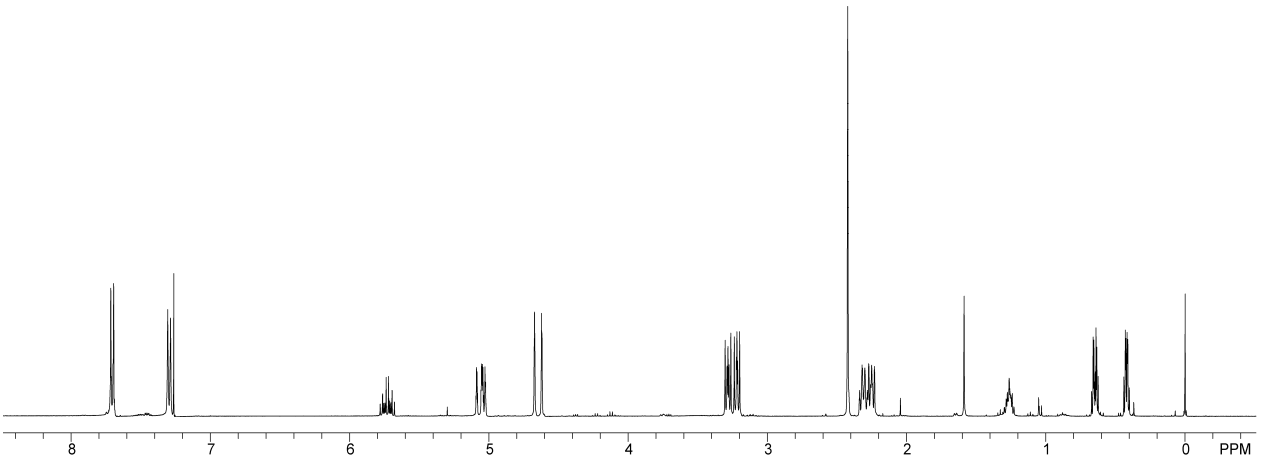
3a

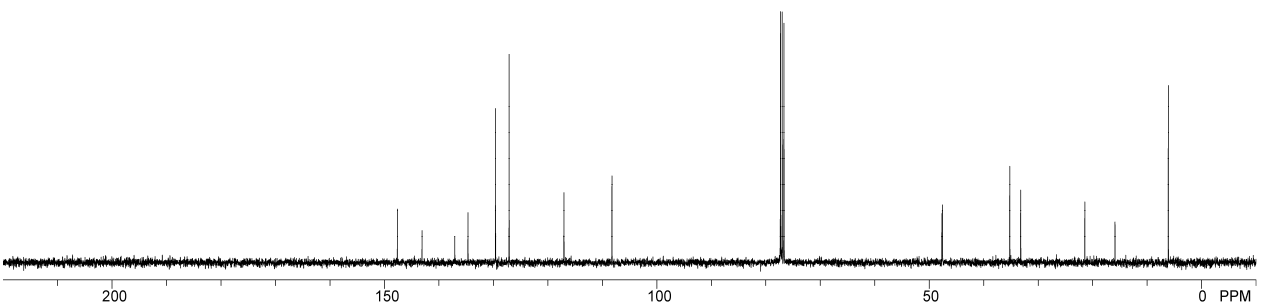


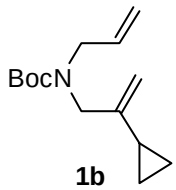




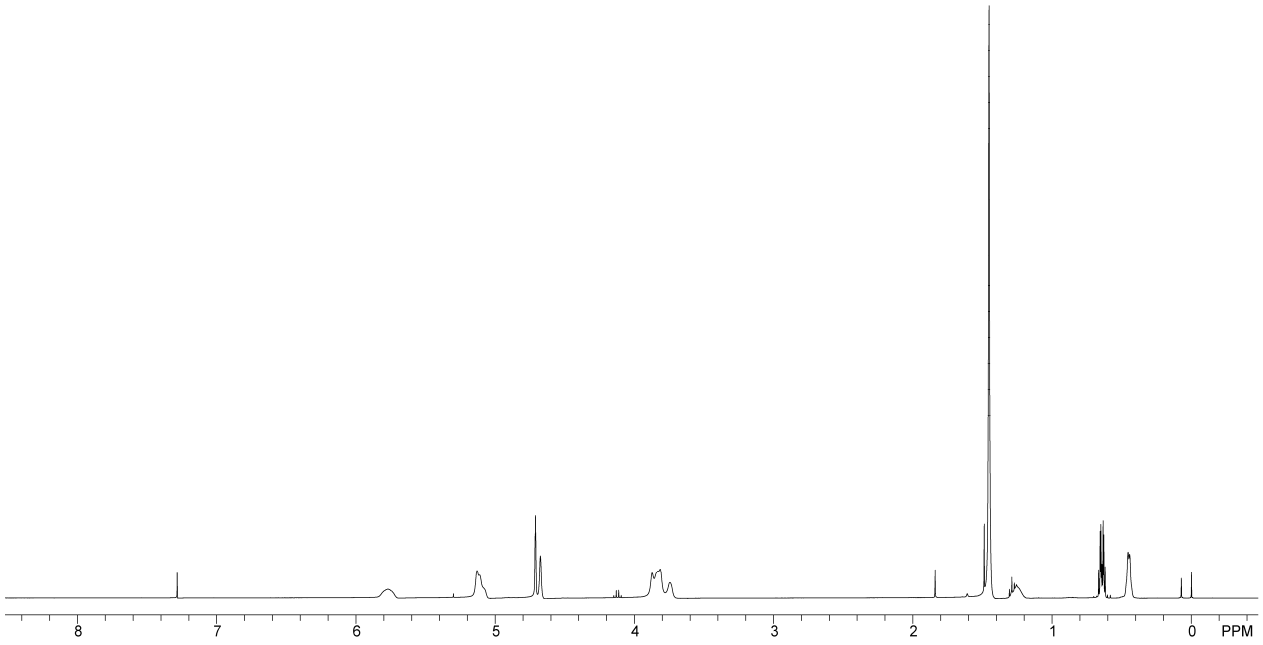
5a

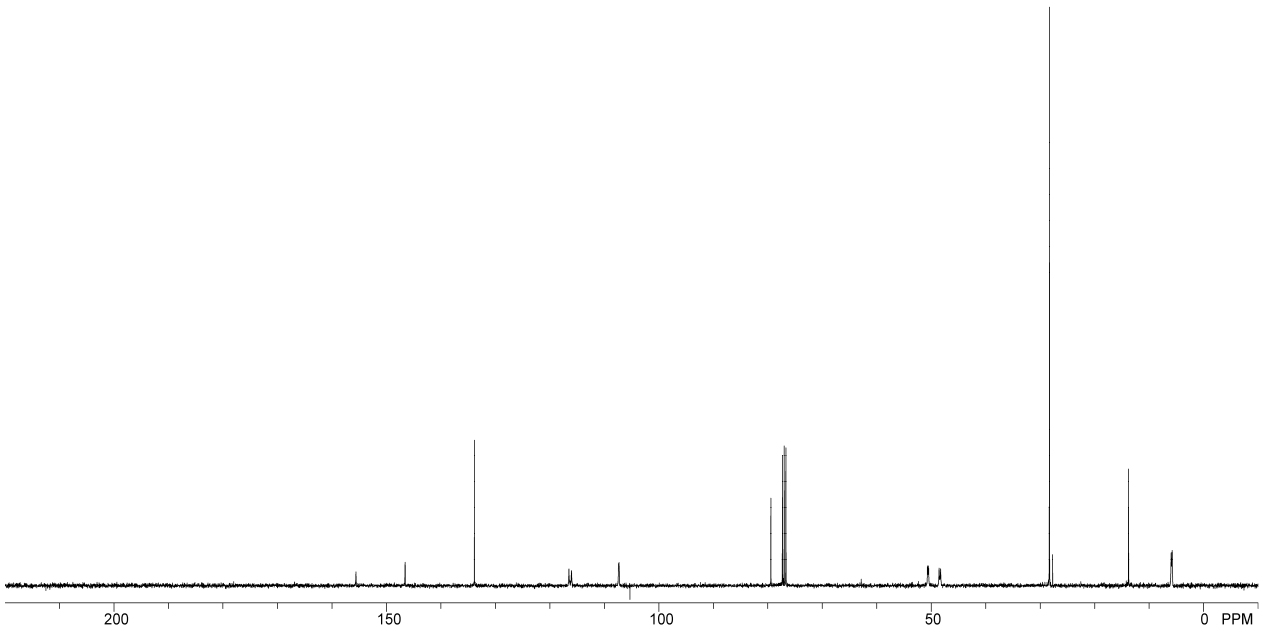


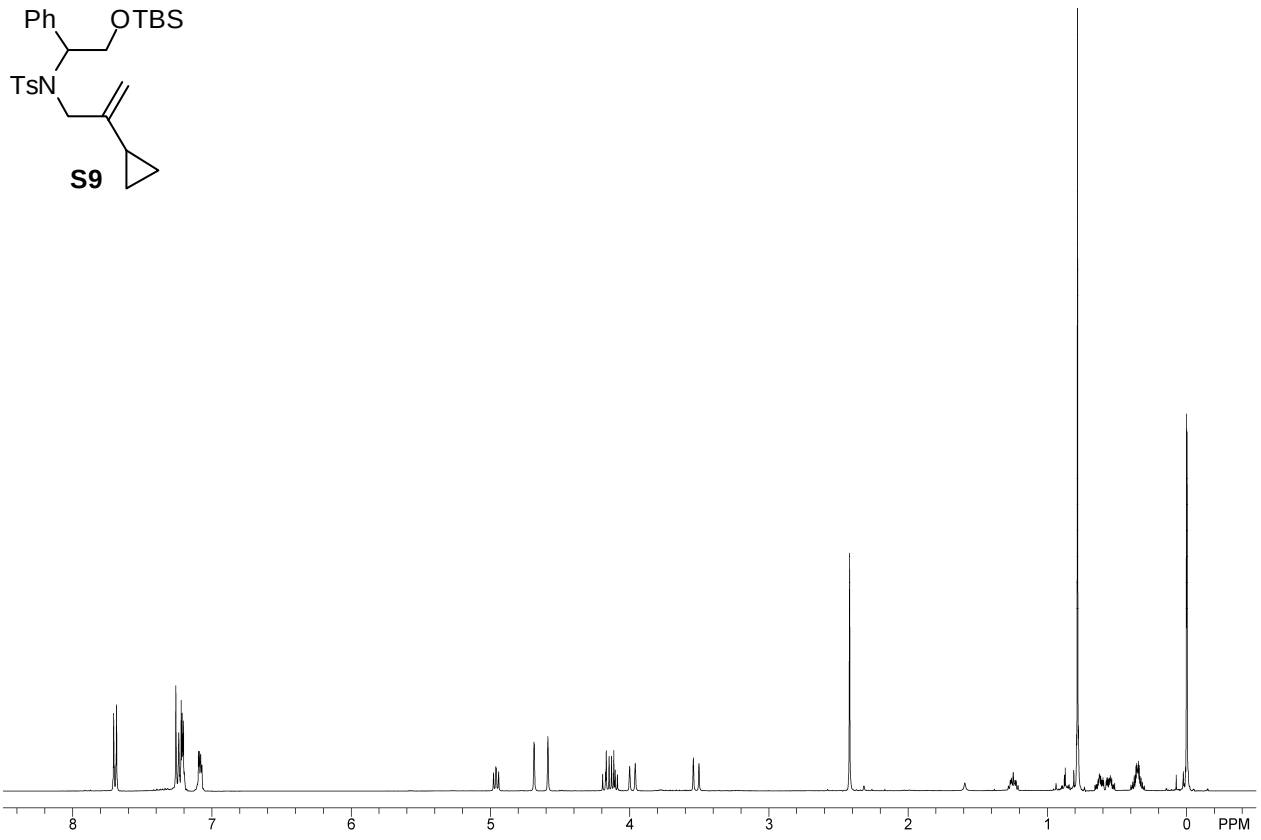


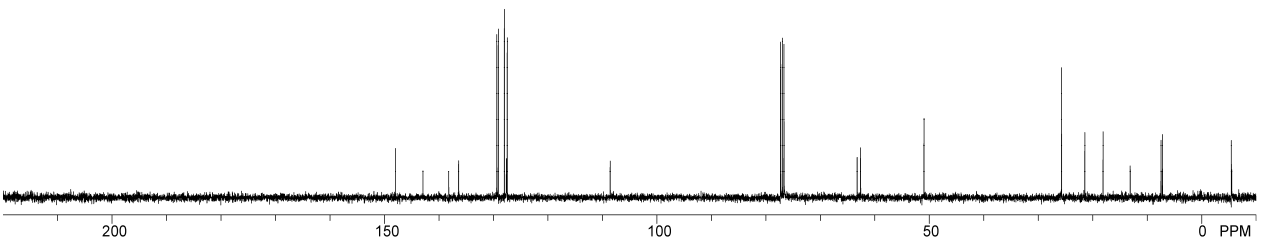


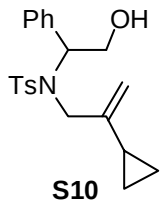
1b



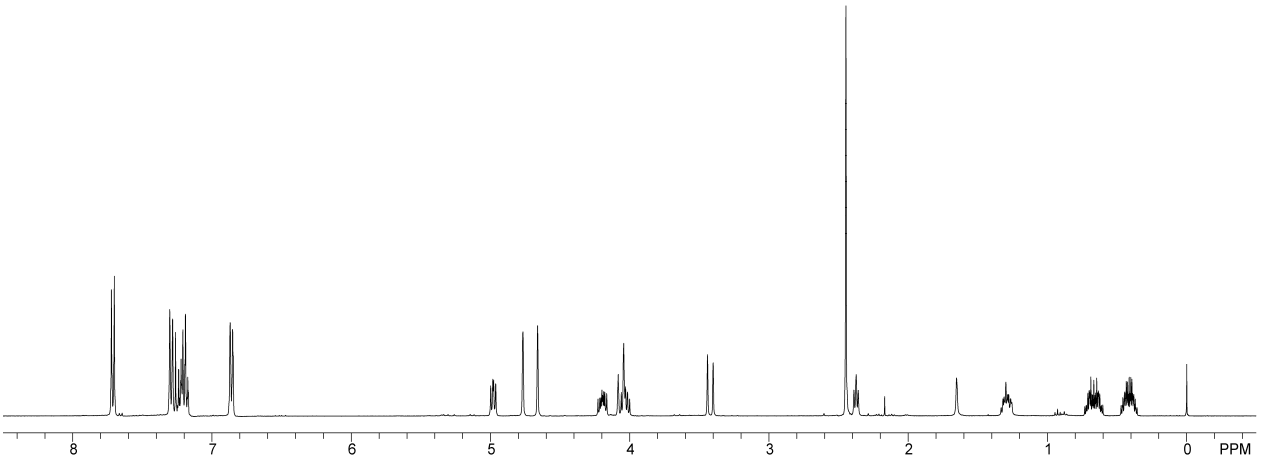


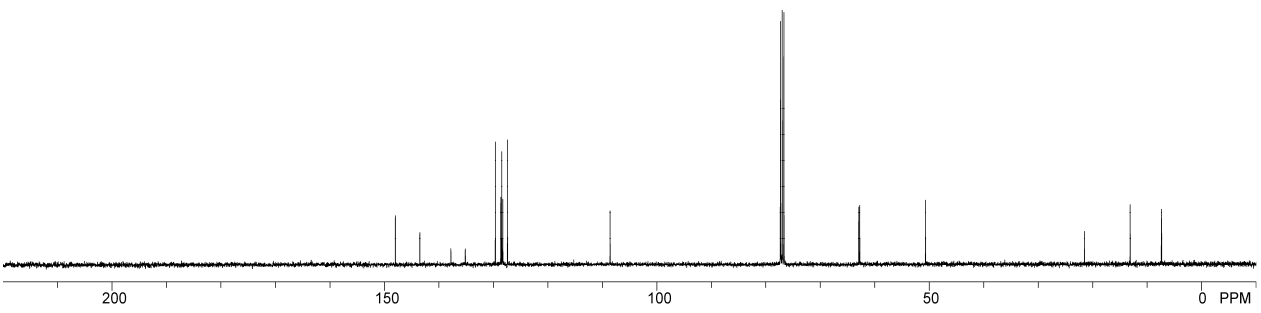

Ph
OTBS
TsN
S9
8
7
6
5
4
3
2
1
0
PPM

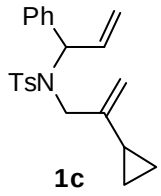

200
150
100
50
0
PPM



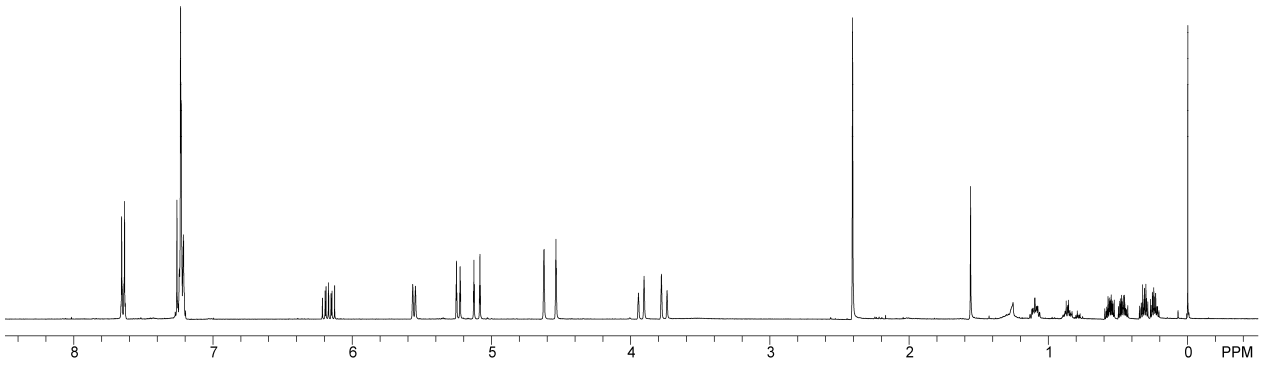
S10

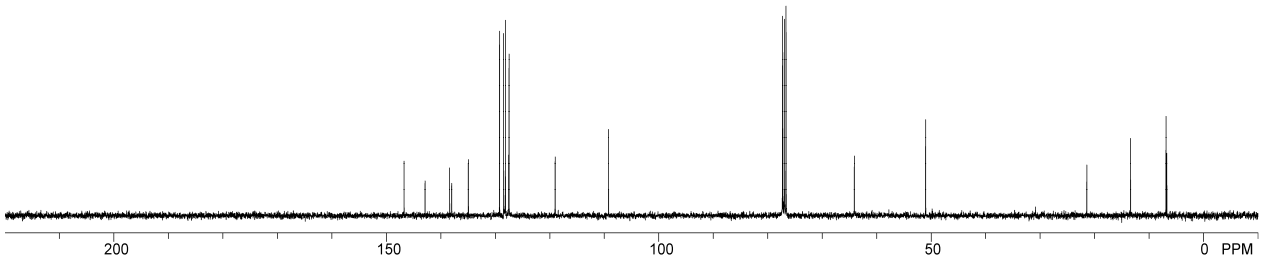


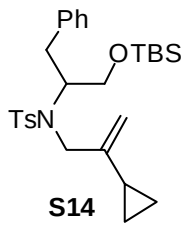




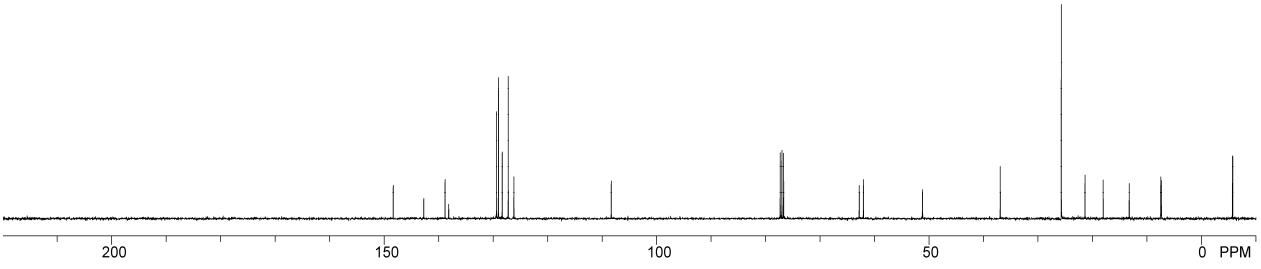
1c

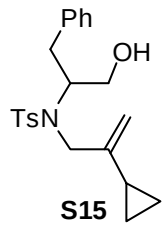




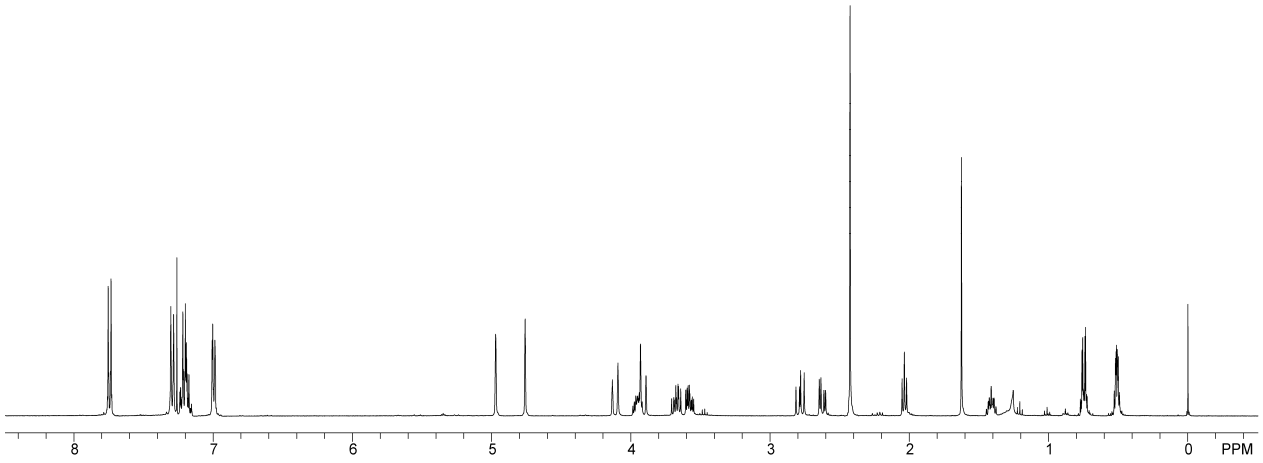


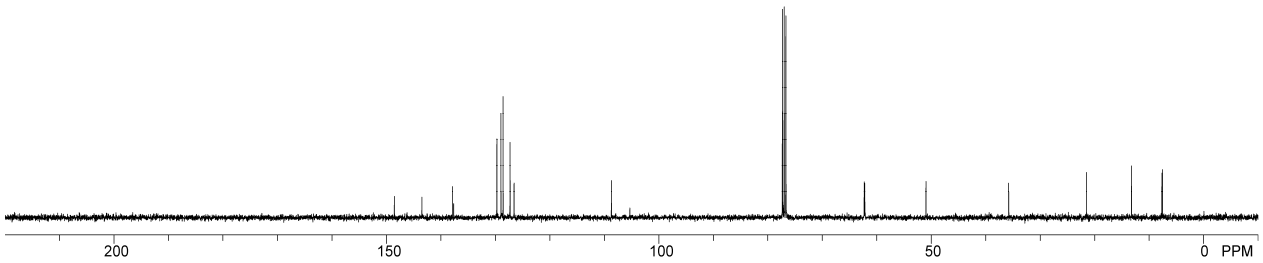
S14

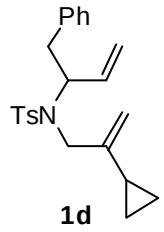




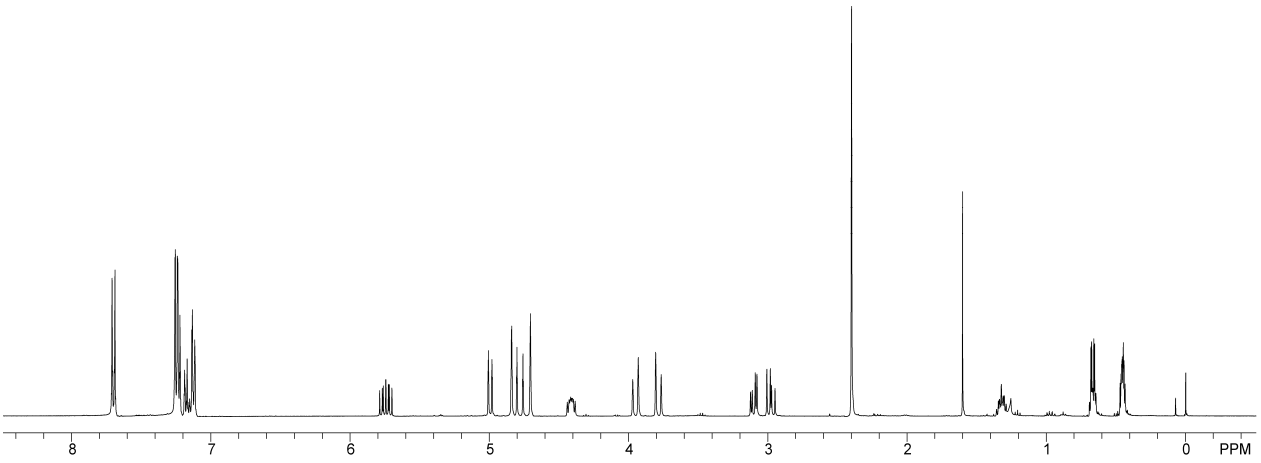
S15

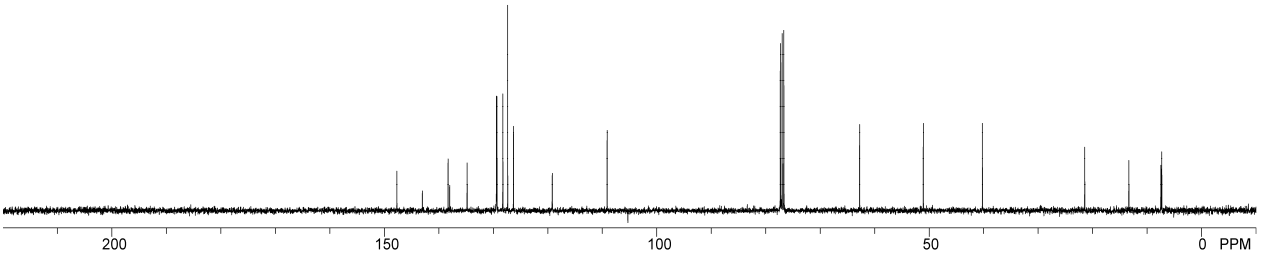


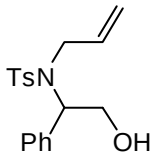




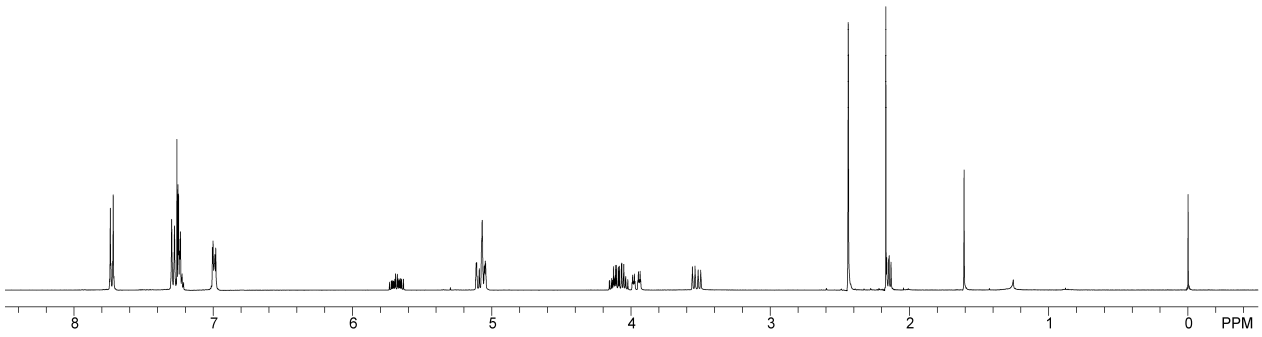
1d

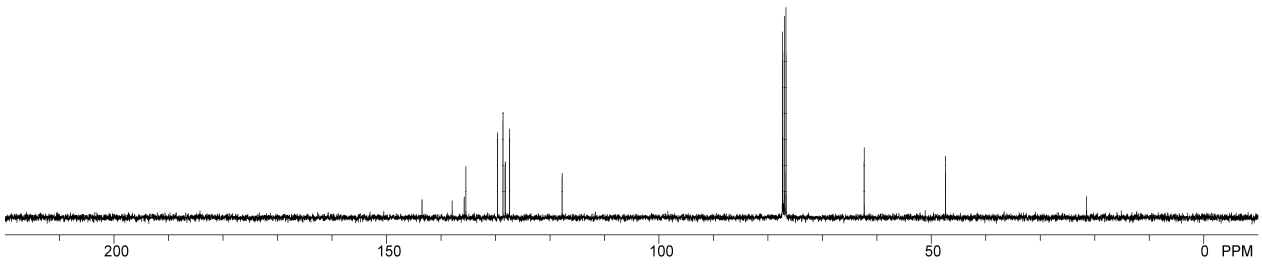


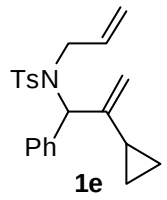




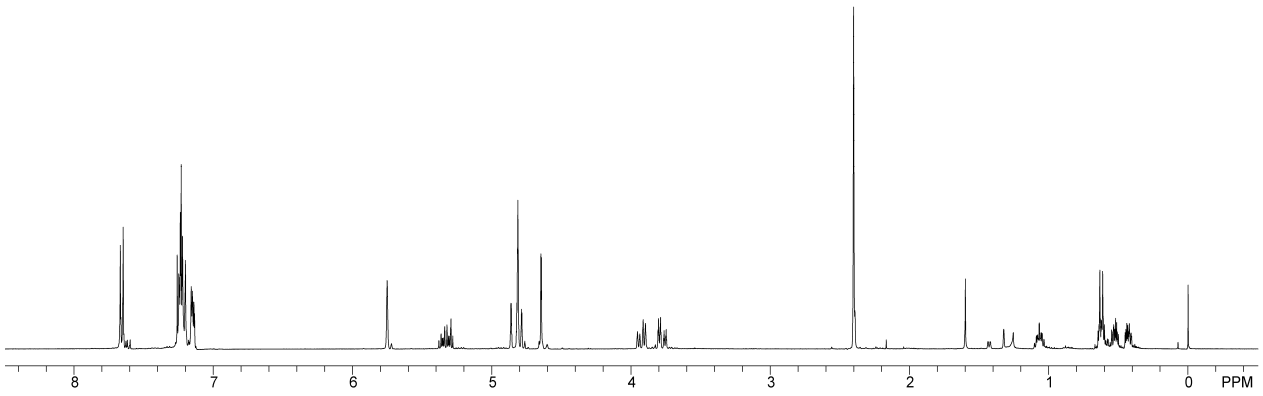
S18

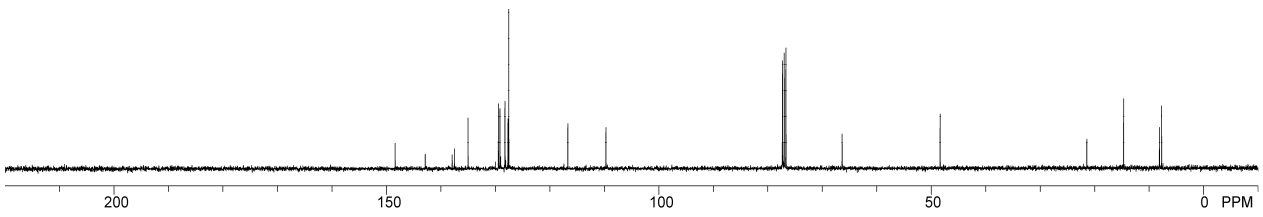


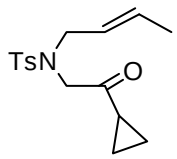




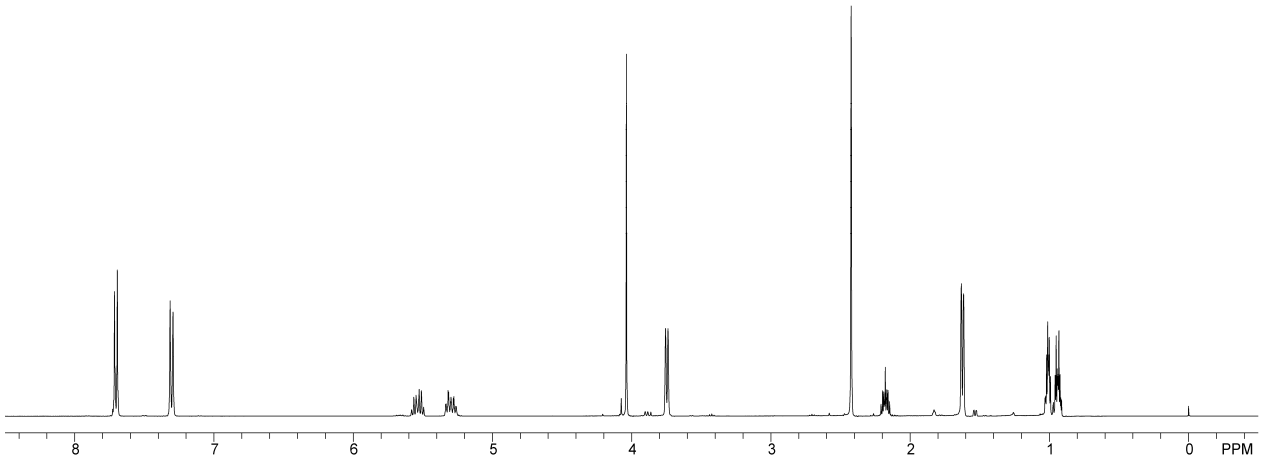
1e

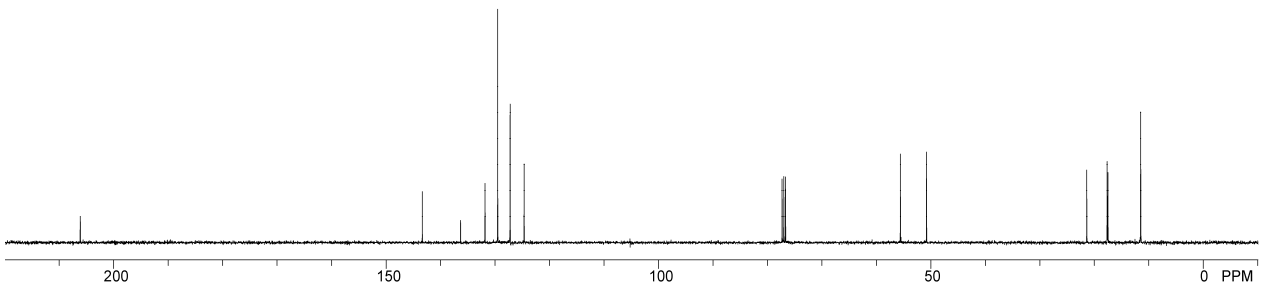


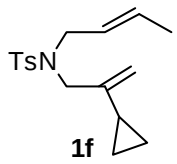




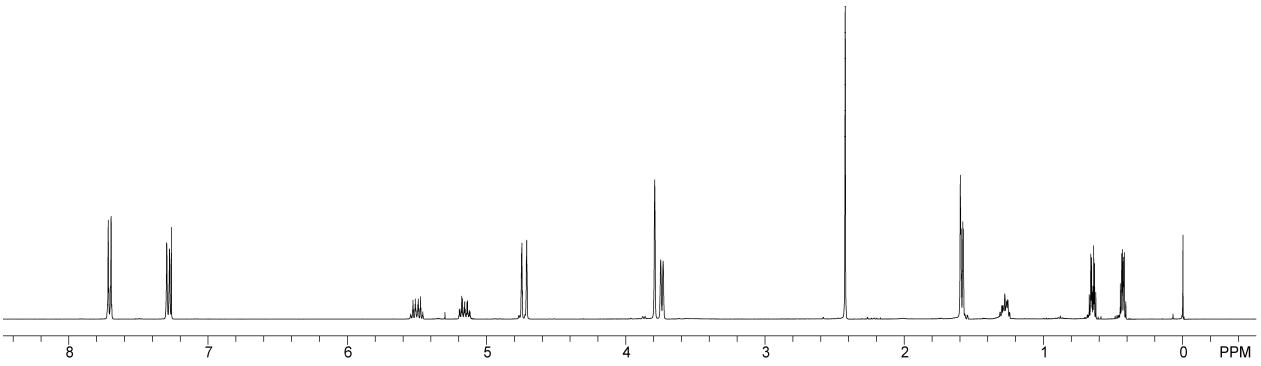
S23

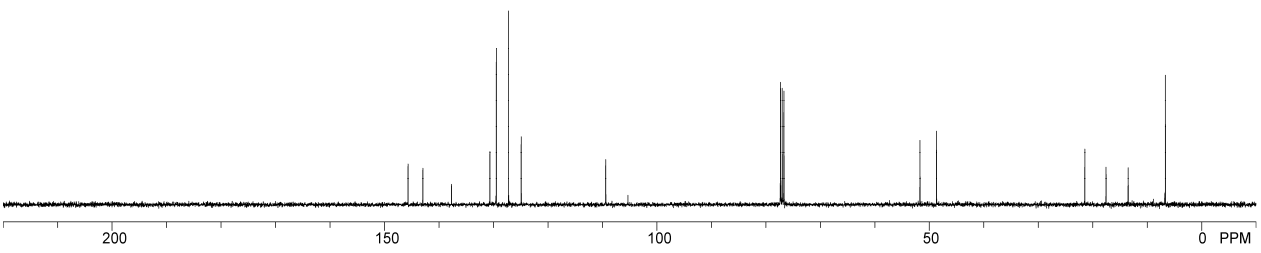


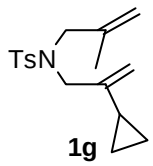




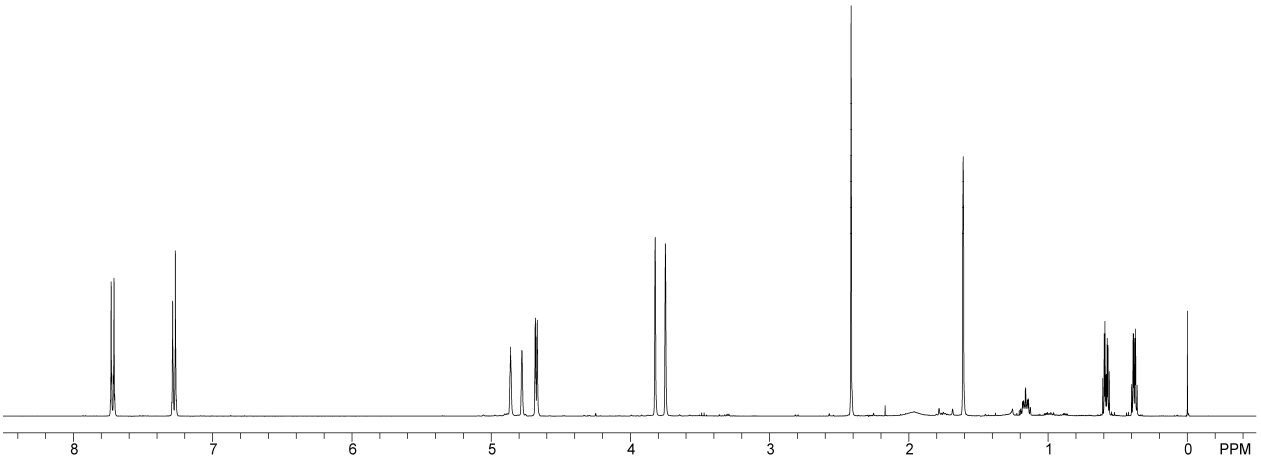
1f

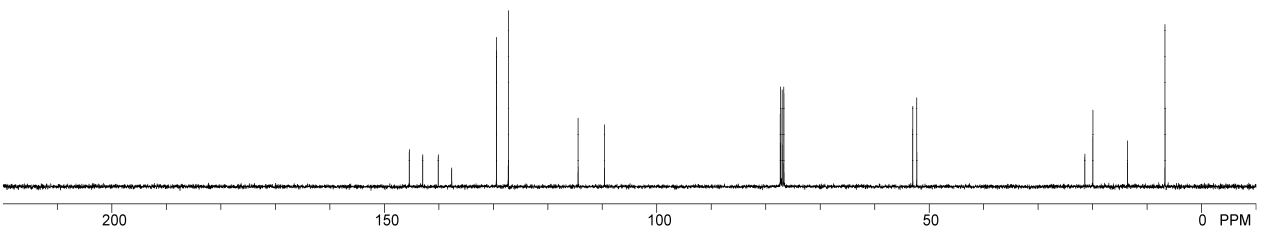


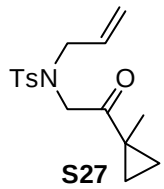




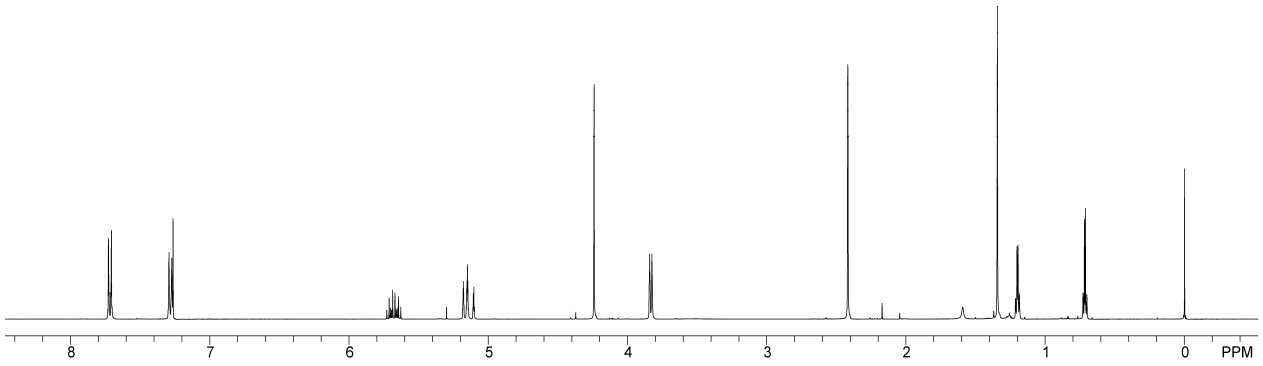
1g

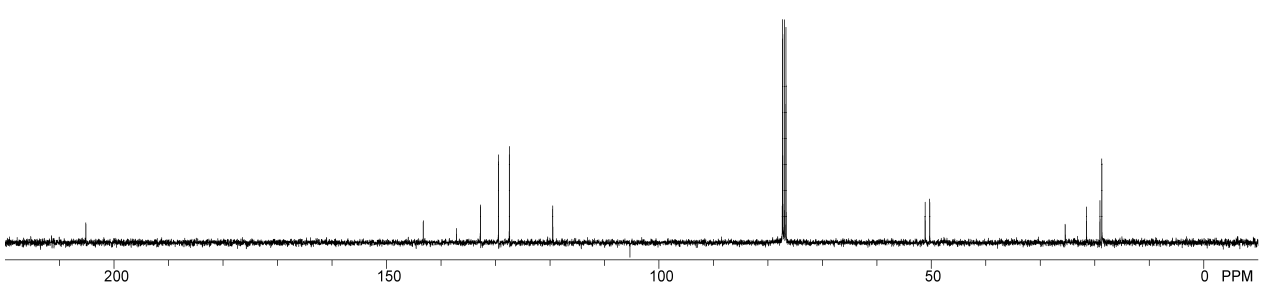


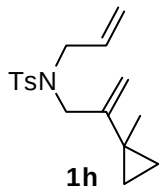




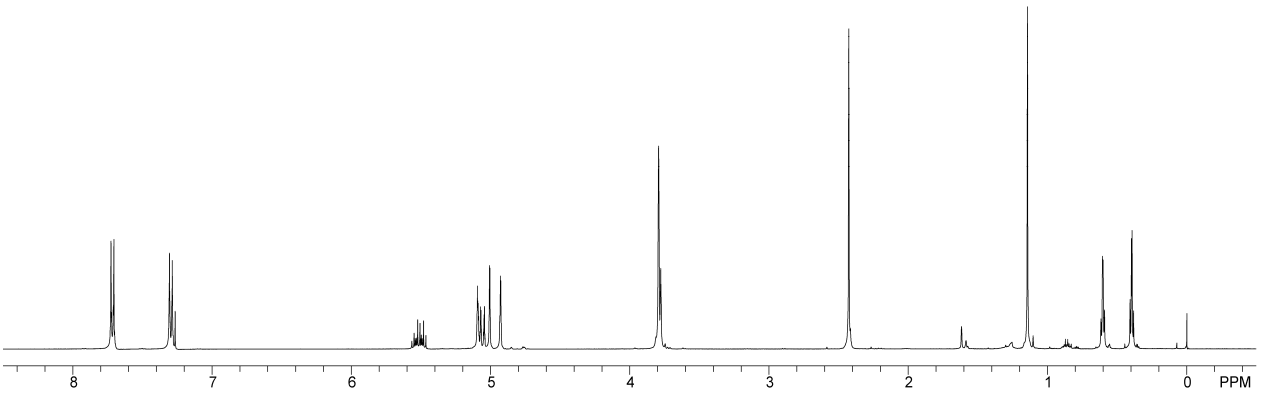
S27

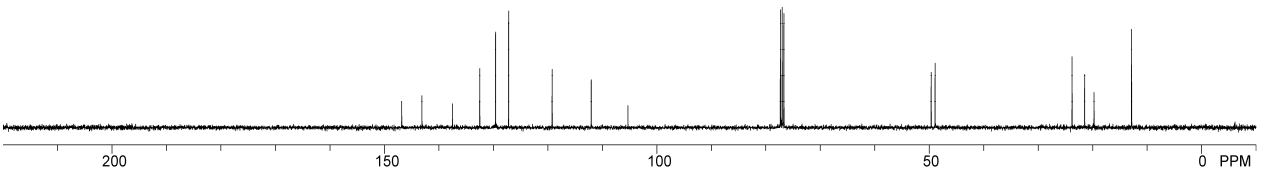


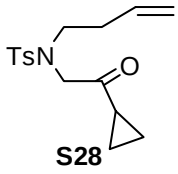




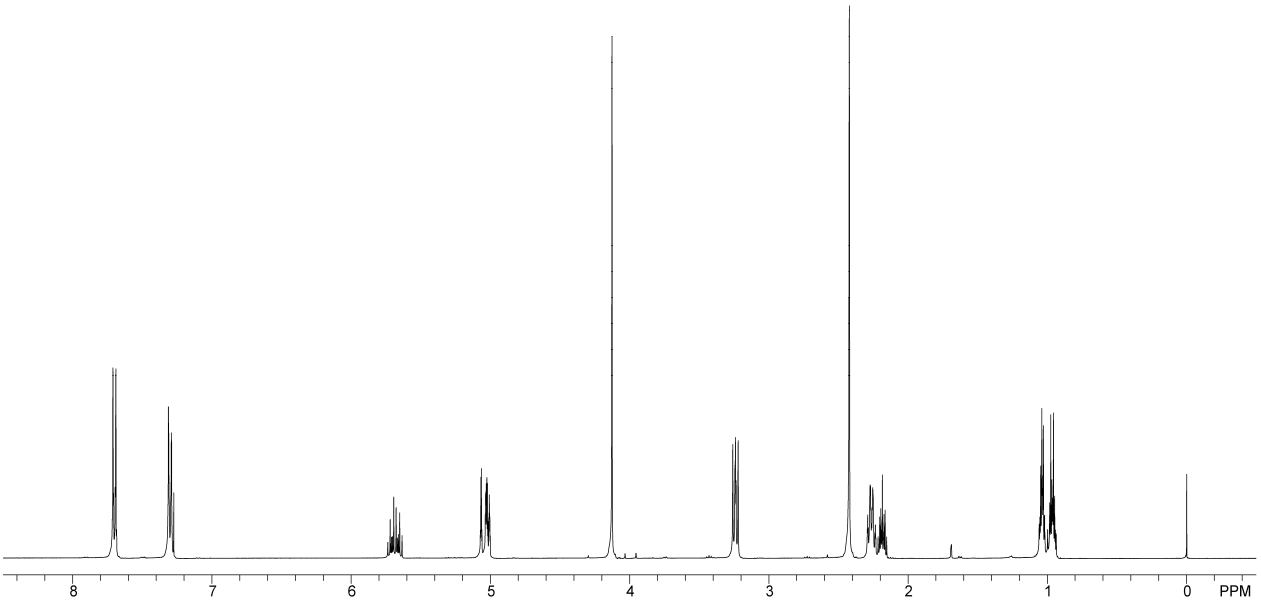
1h

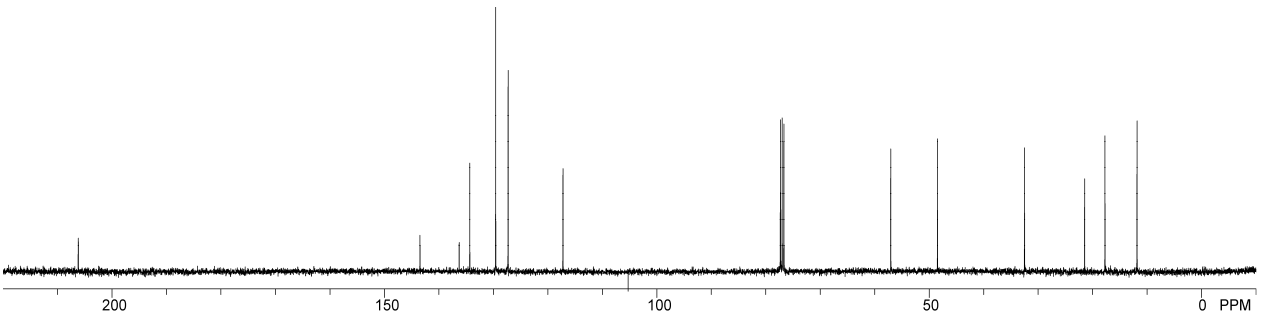


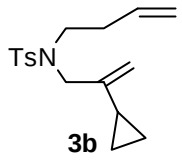




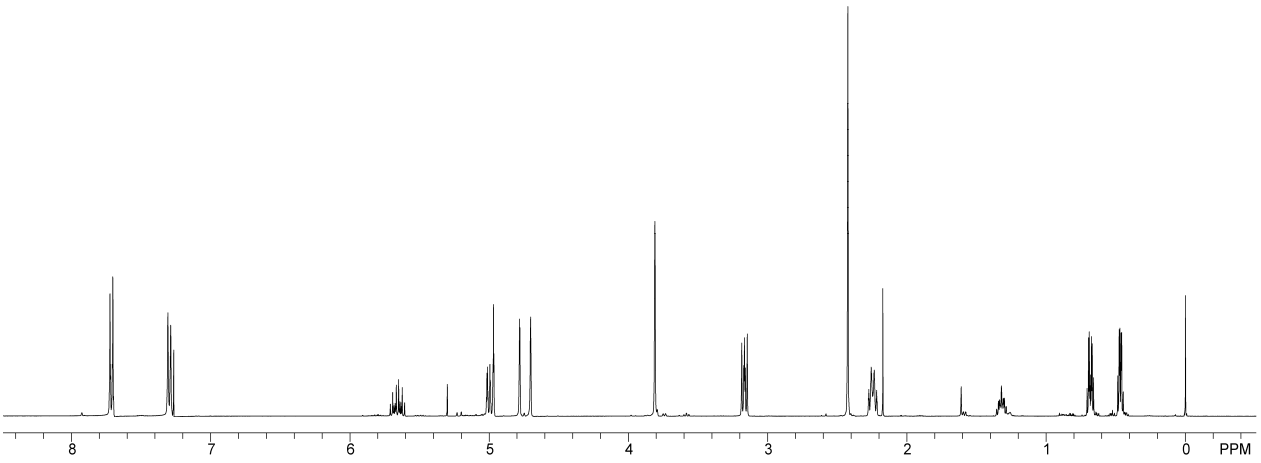
S28

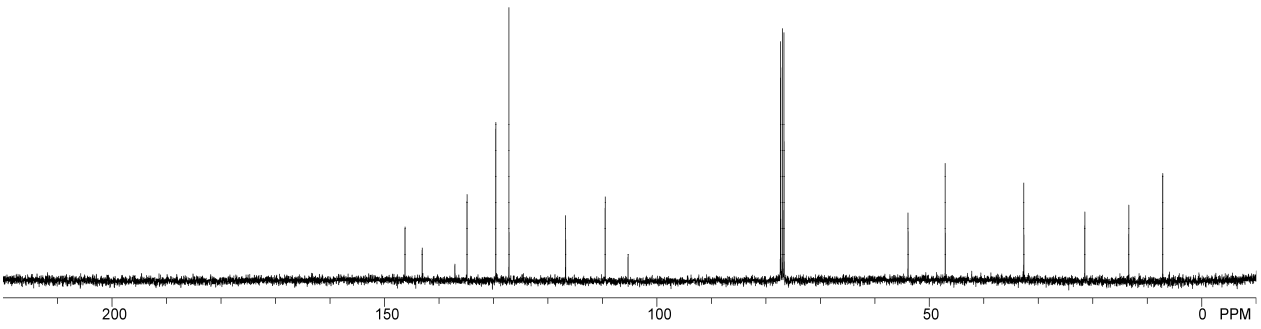


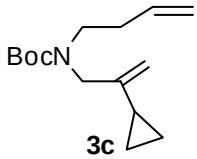




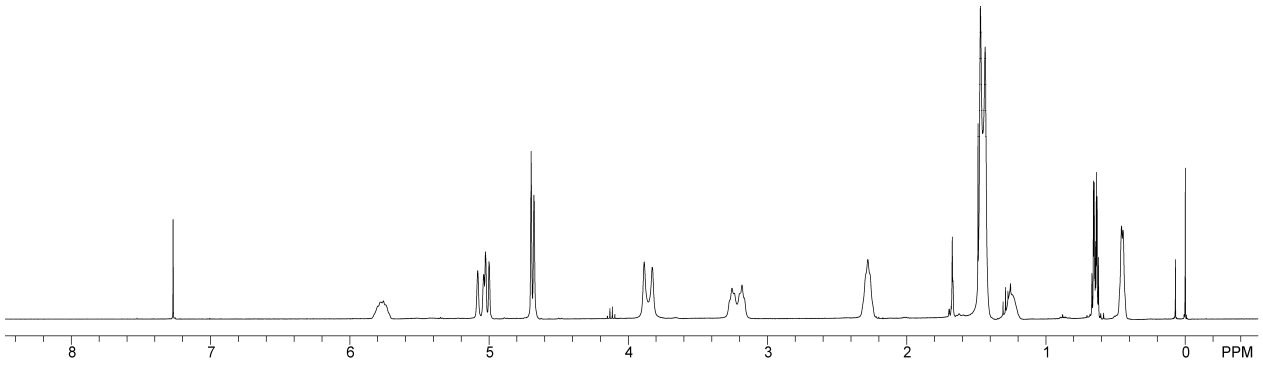
3b

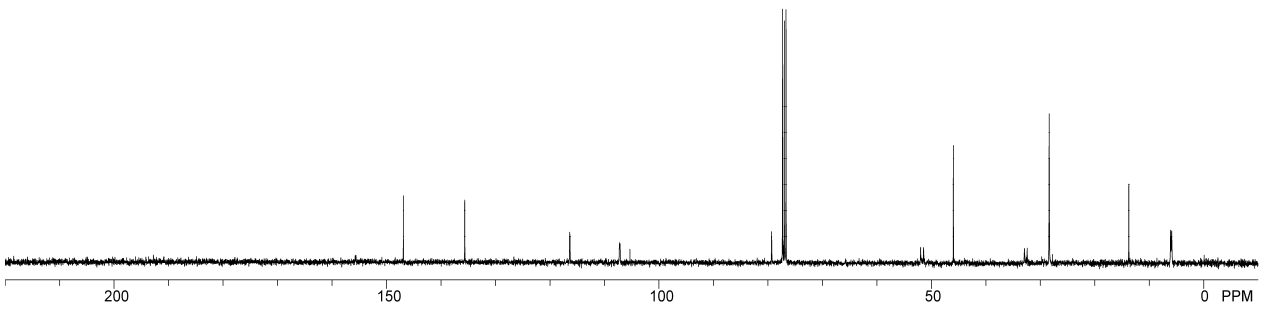


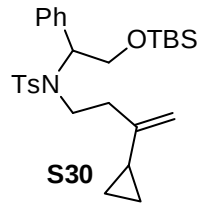




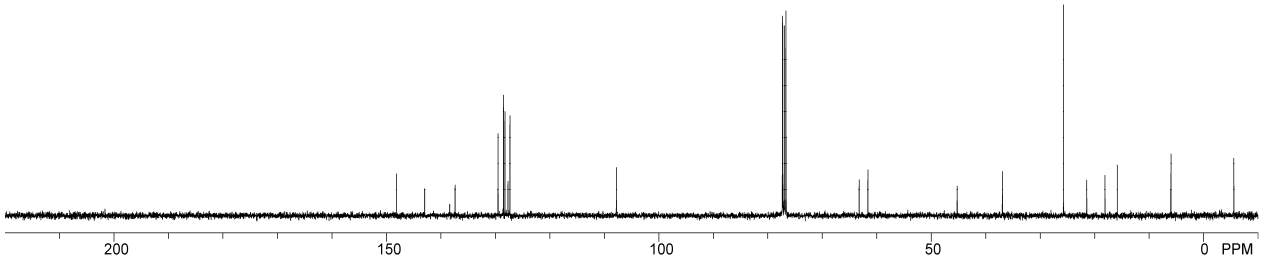
3c

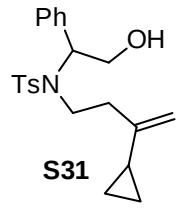




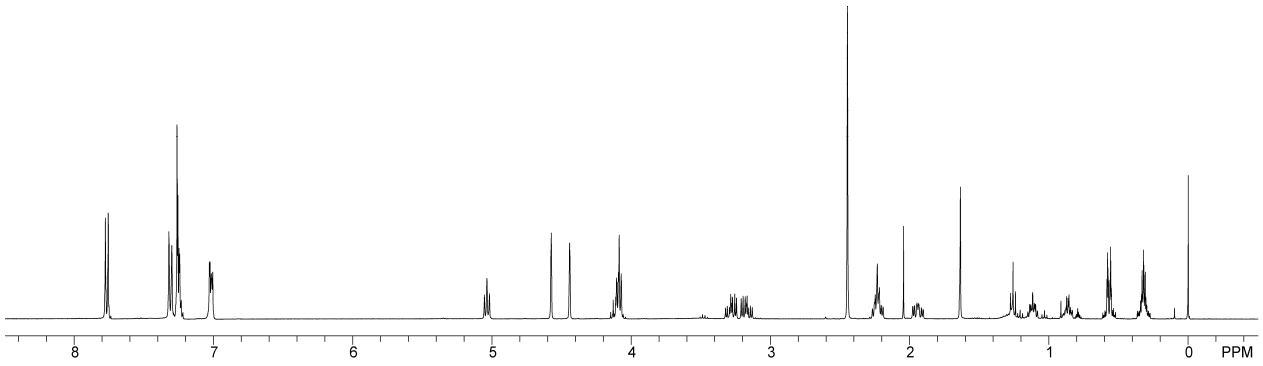


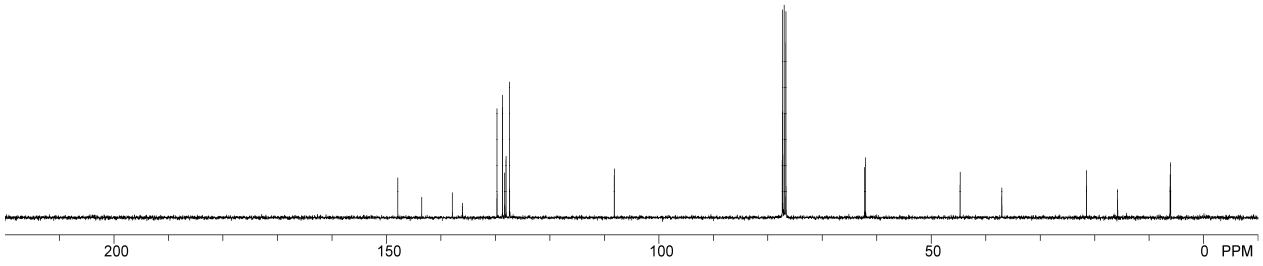
S30

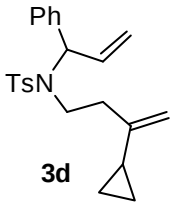




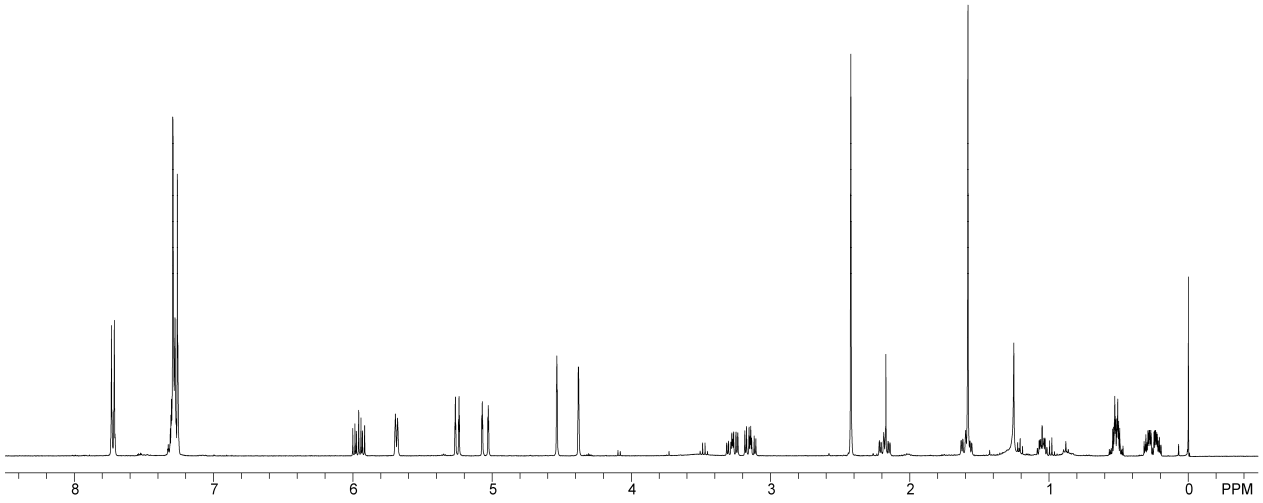
S31

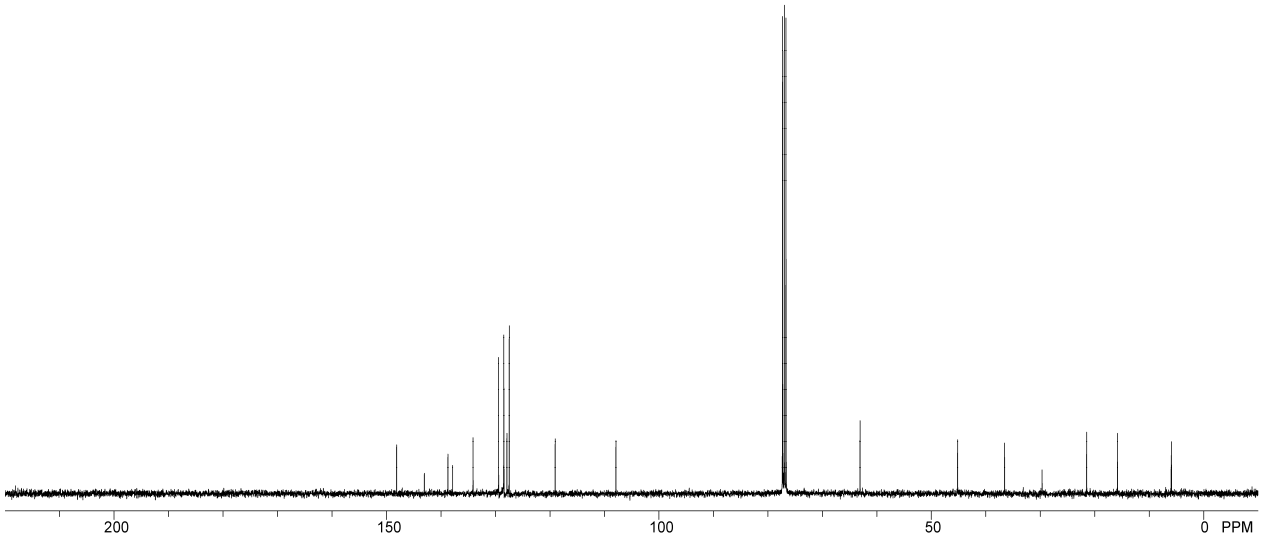


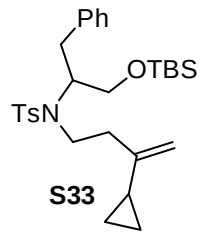




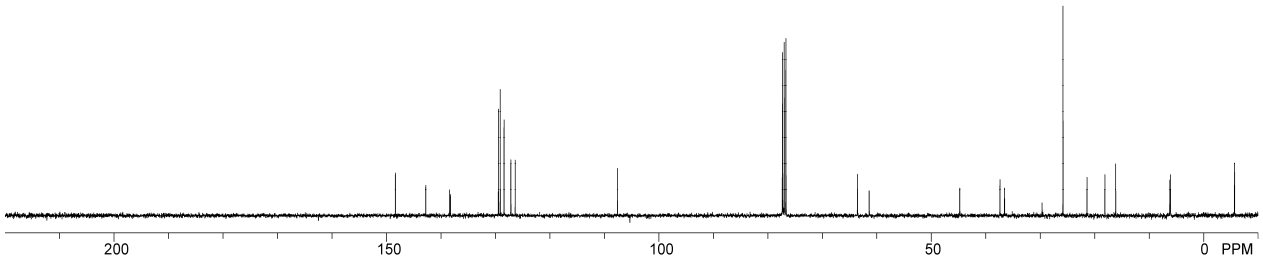
3d

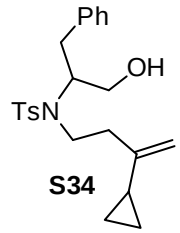




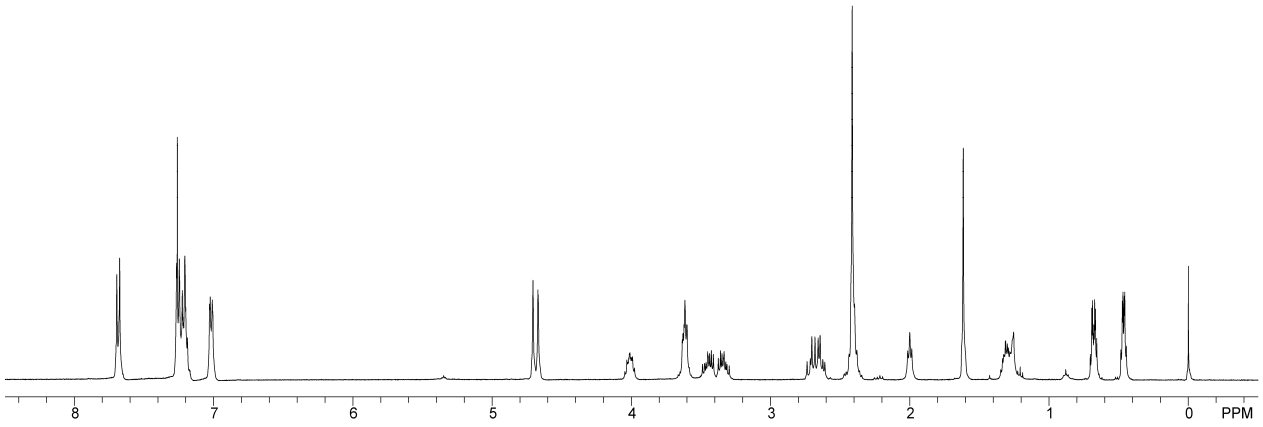


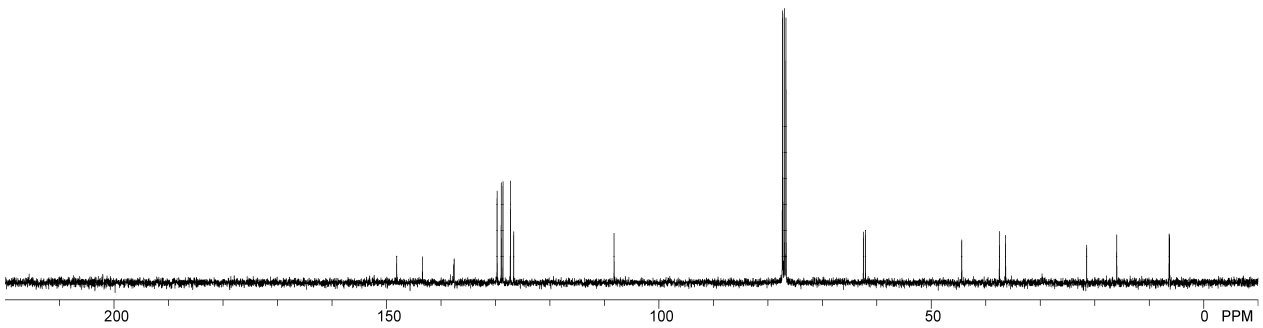
S33

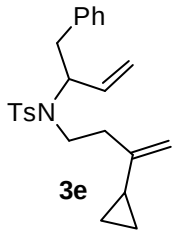




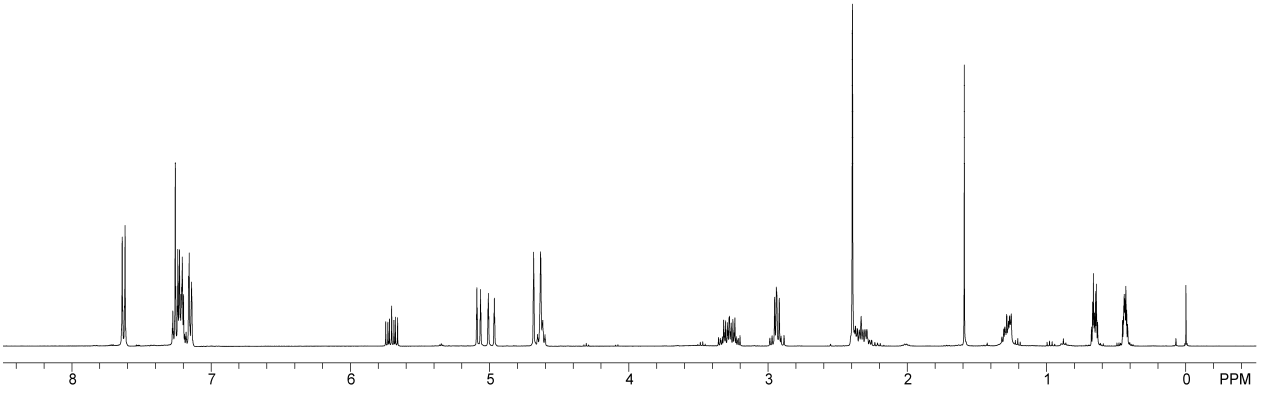
S34

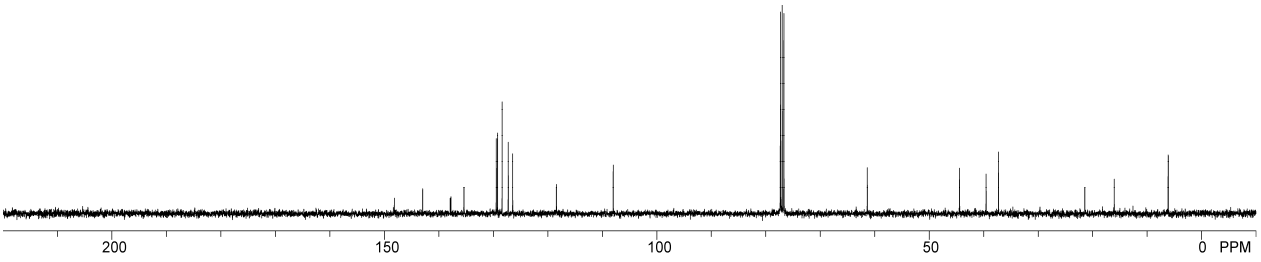


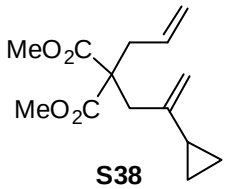




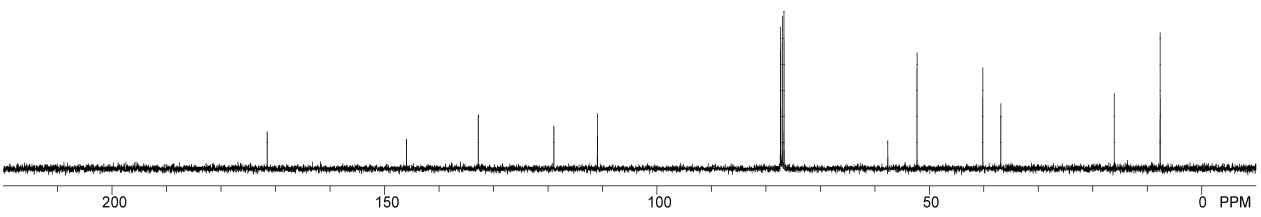
3e

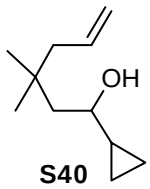




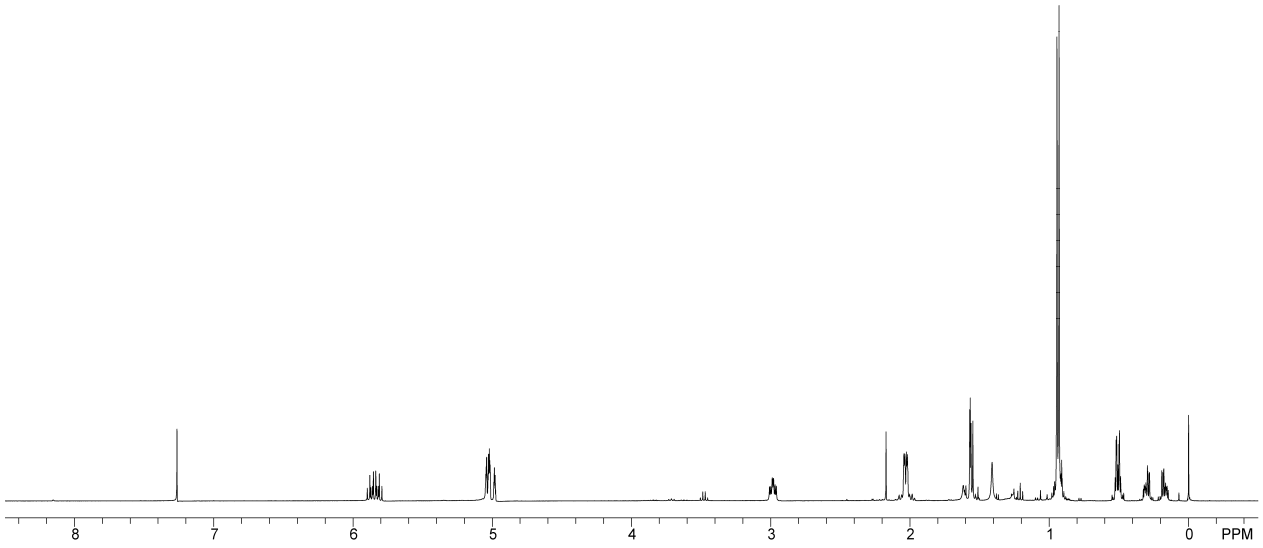


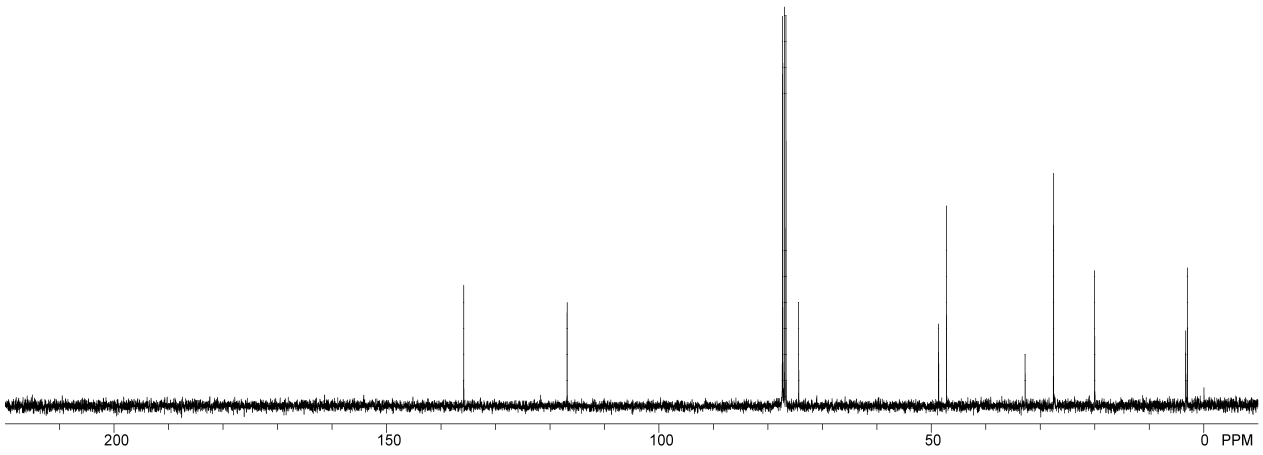
S38

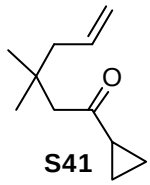




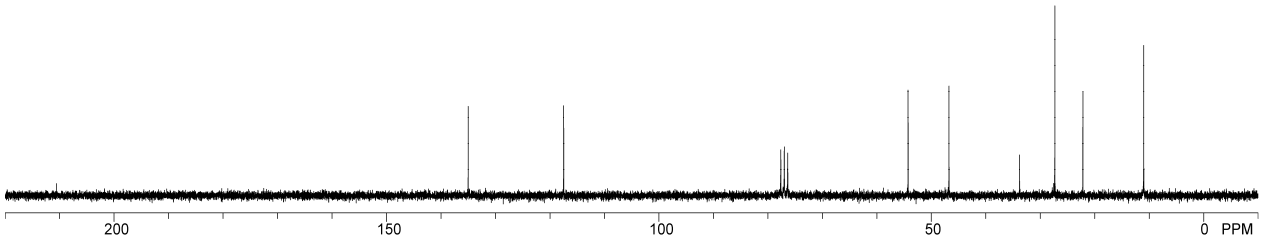
S40

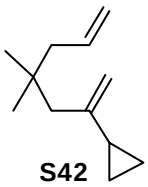




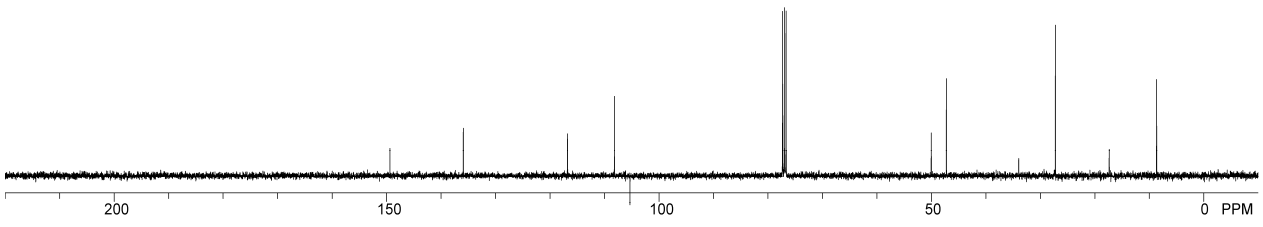


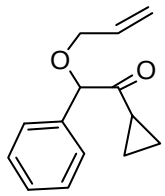
S41



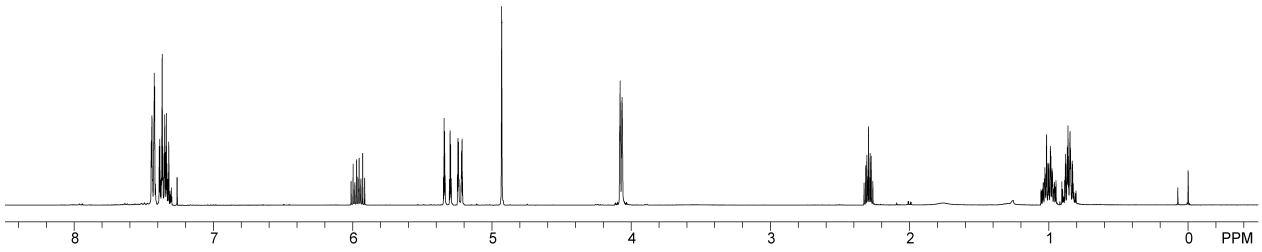


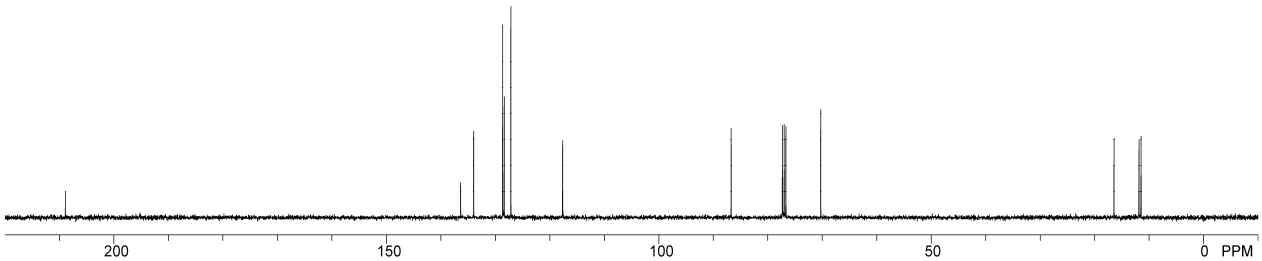
S42

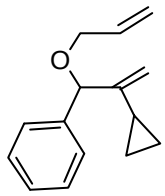




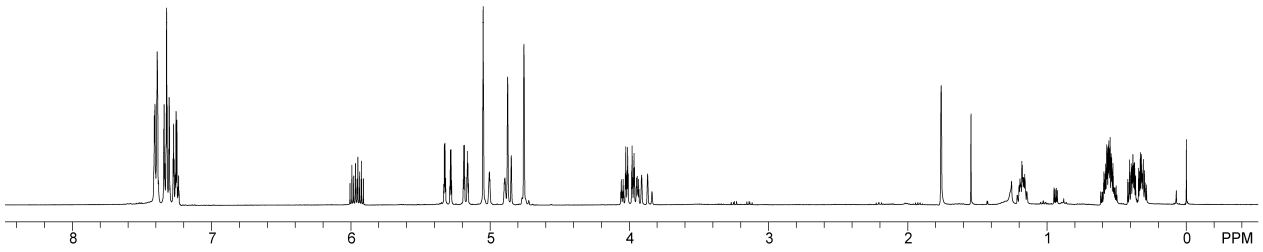
S45

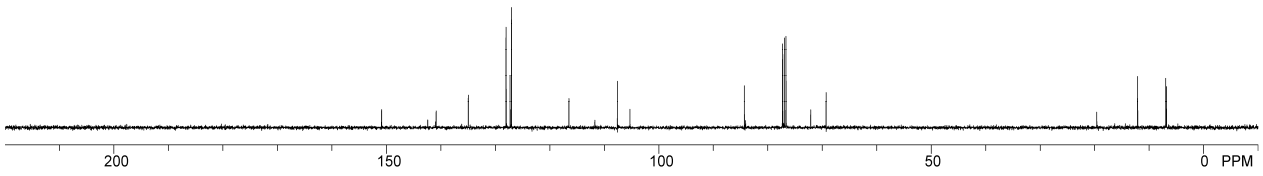


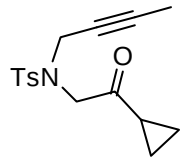




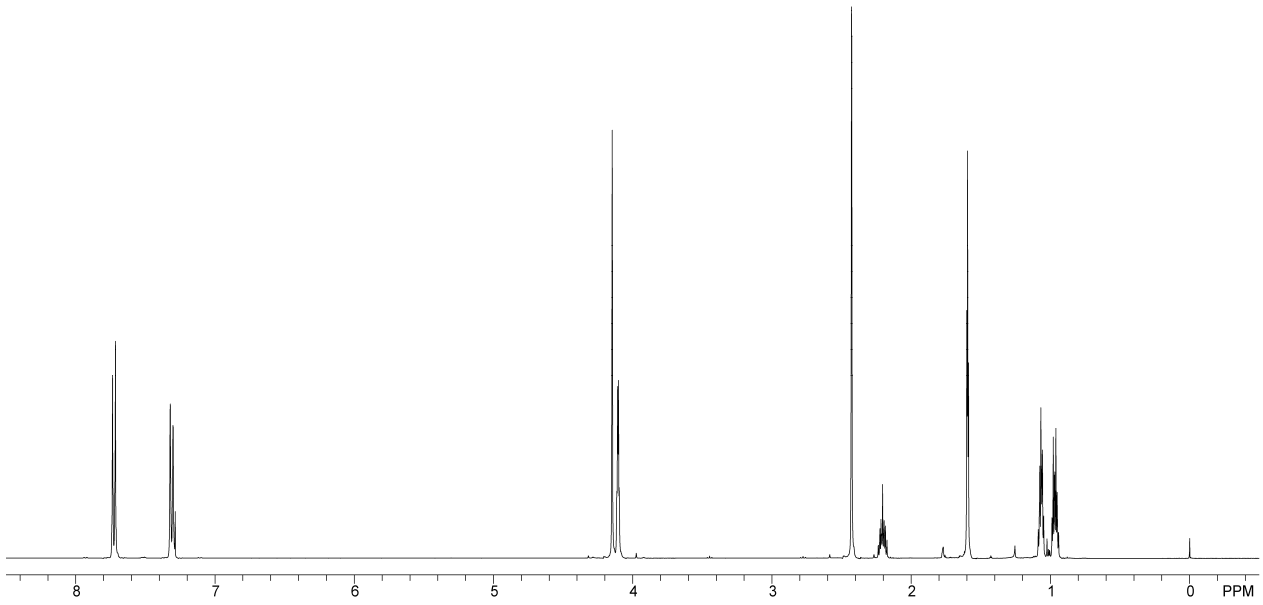
S46

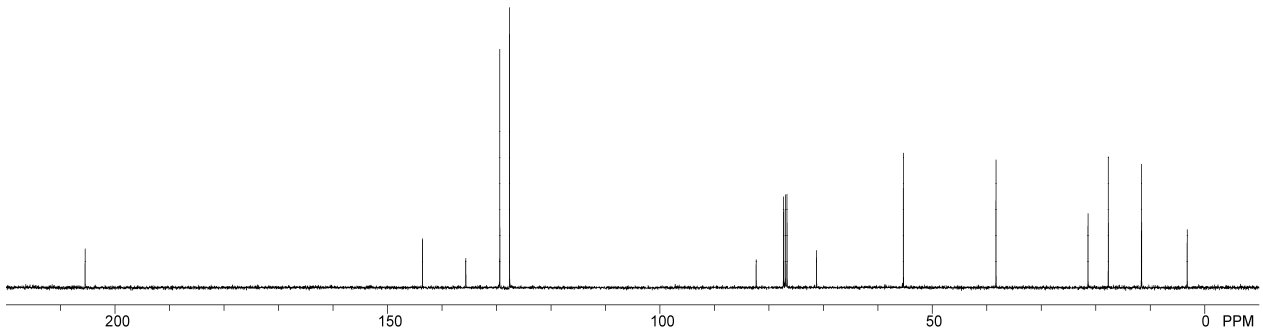


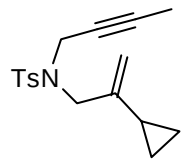




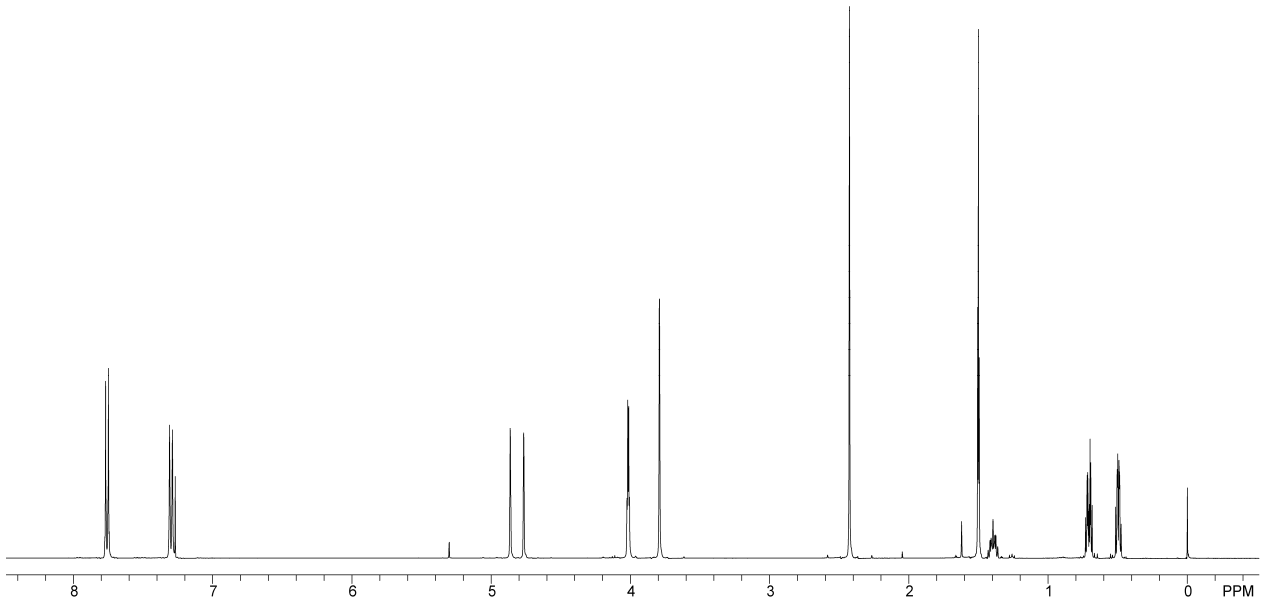
S48

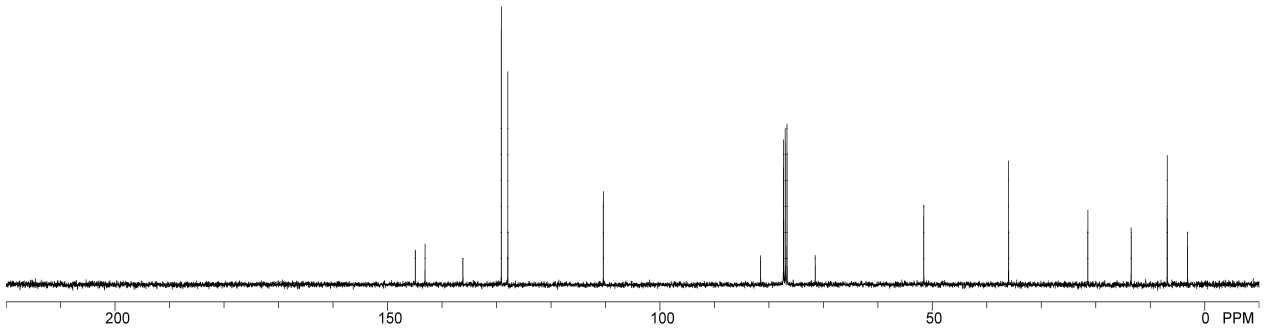


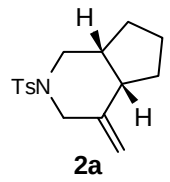




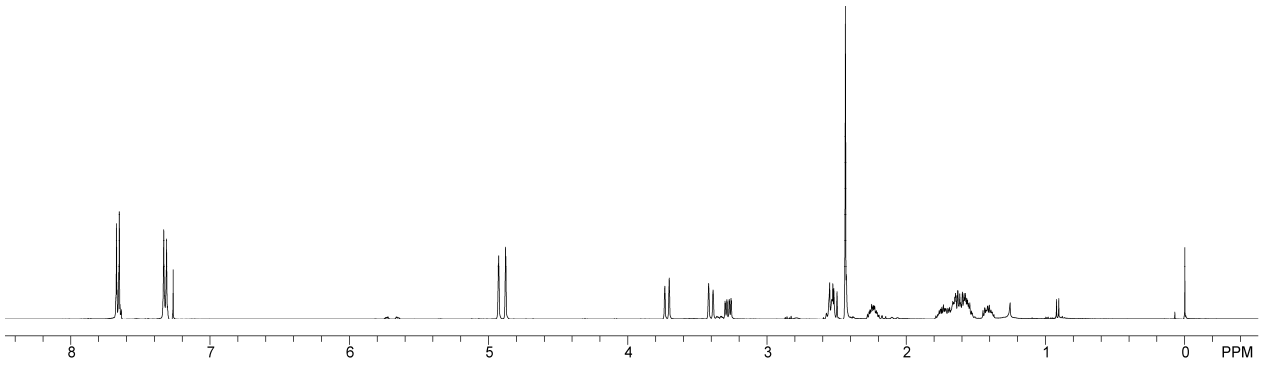
7

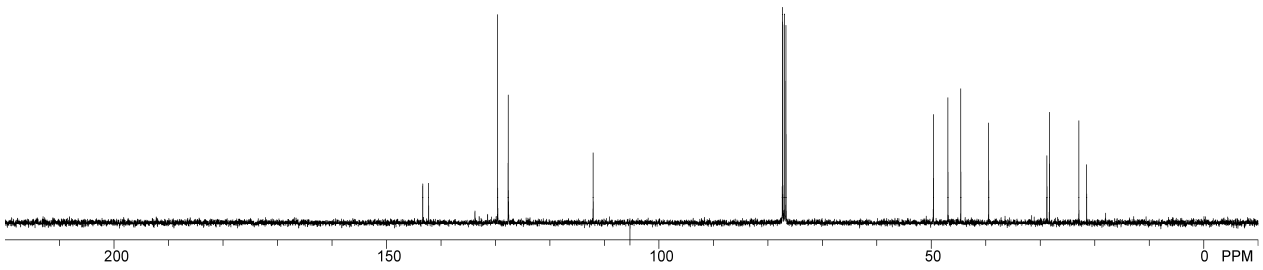


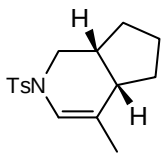




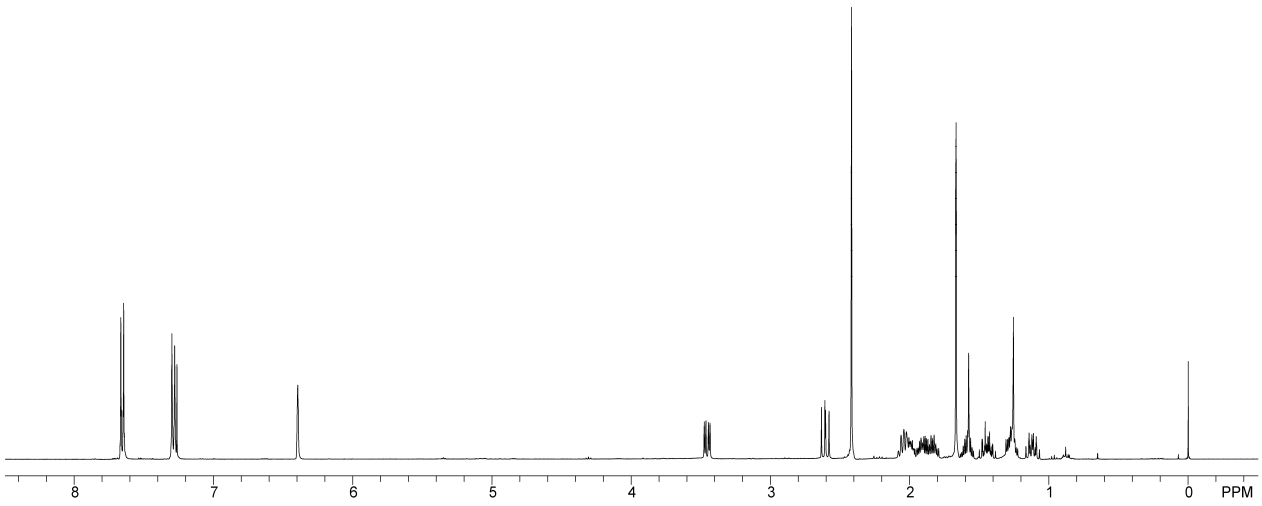
2a

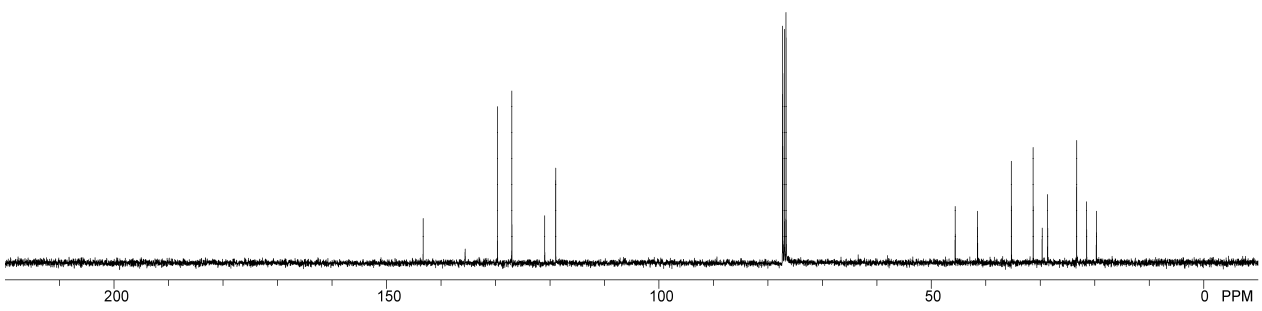


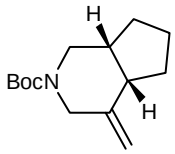




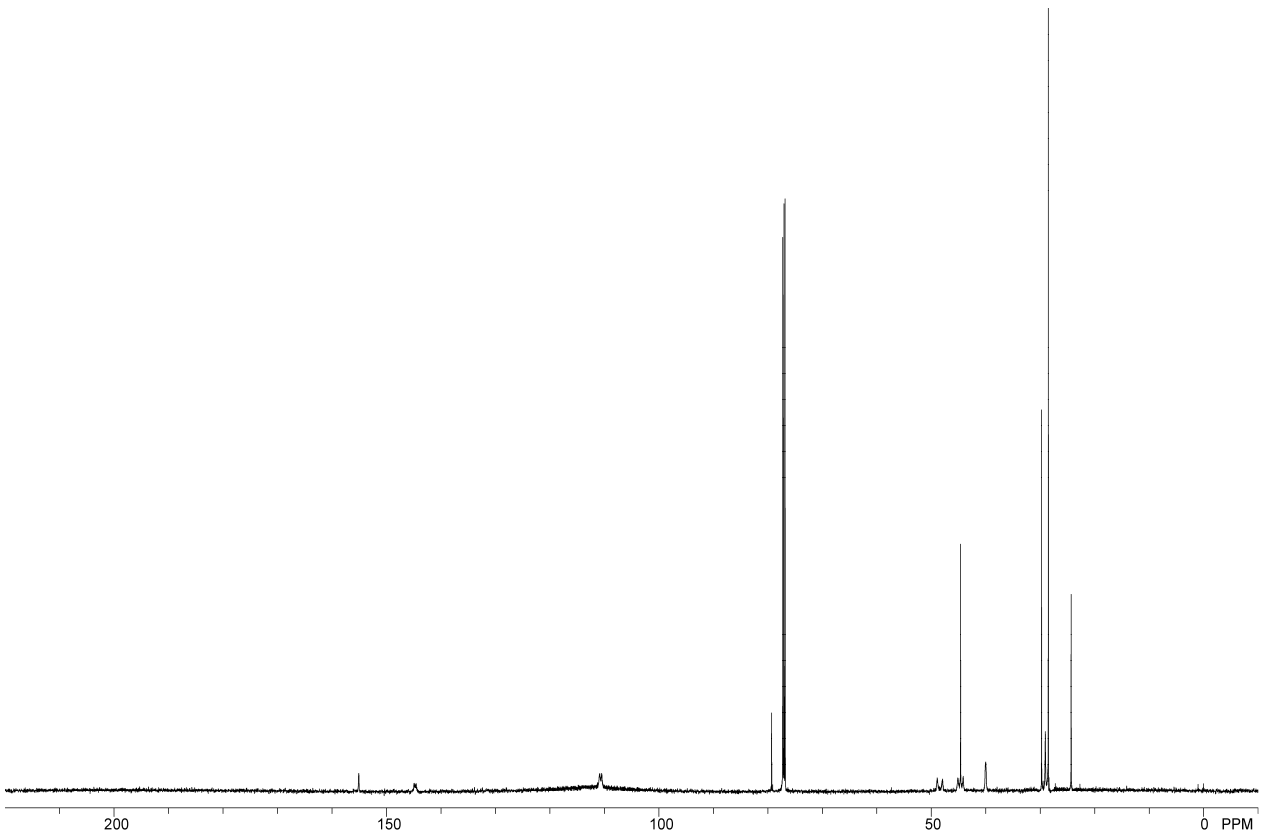
2a'

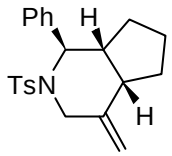




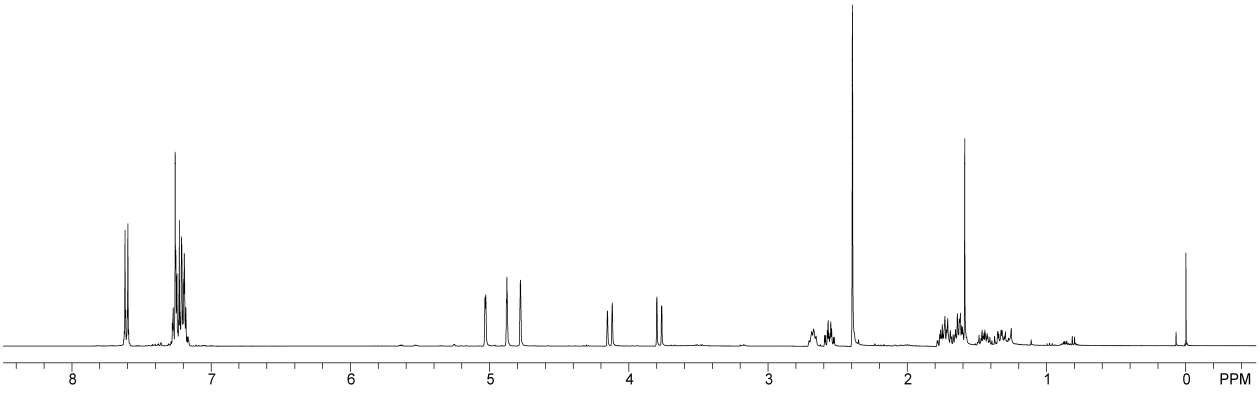


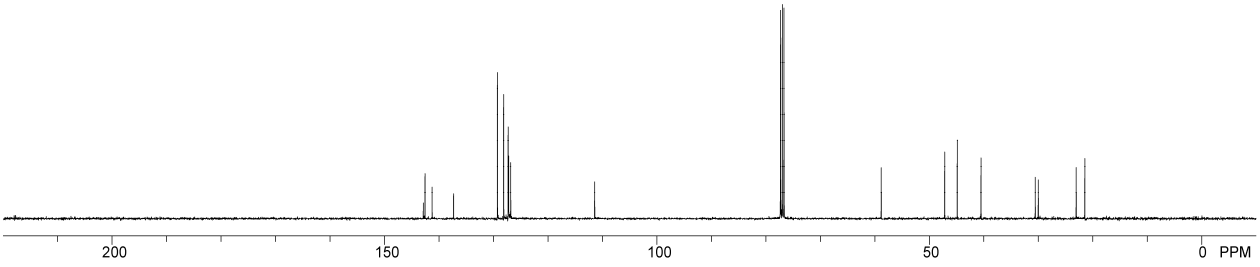
2b

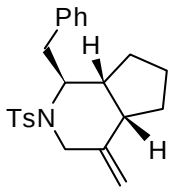




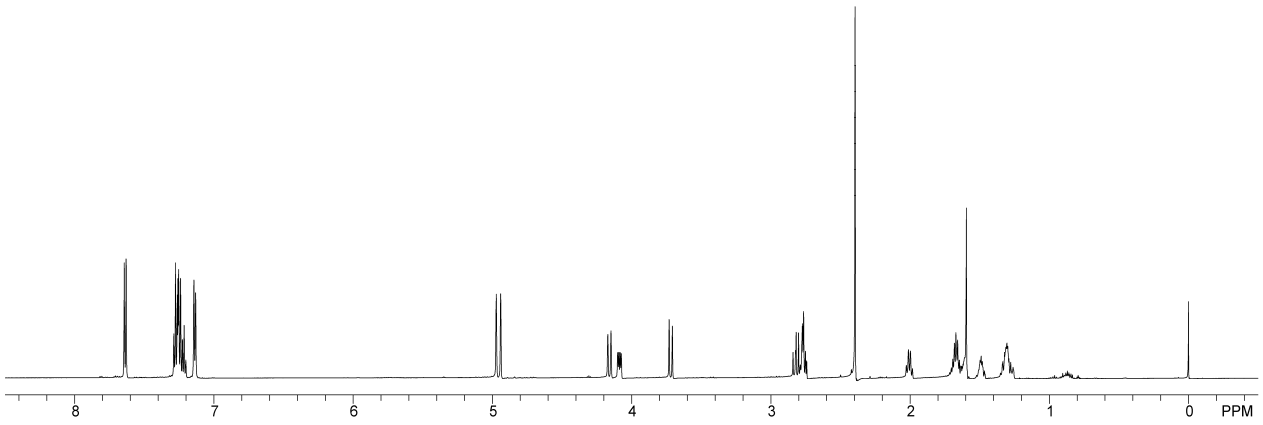
2c

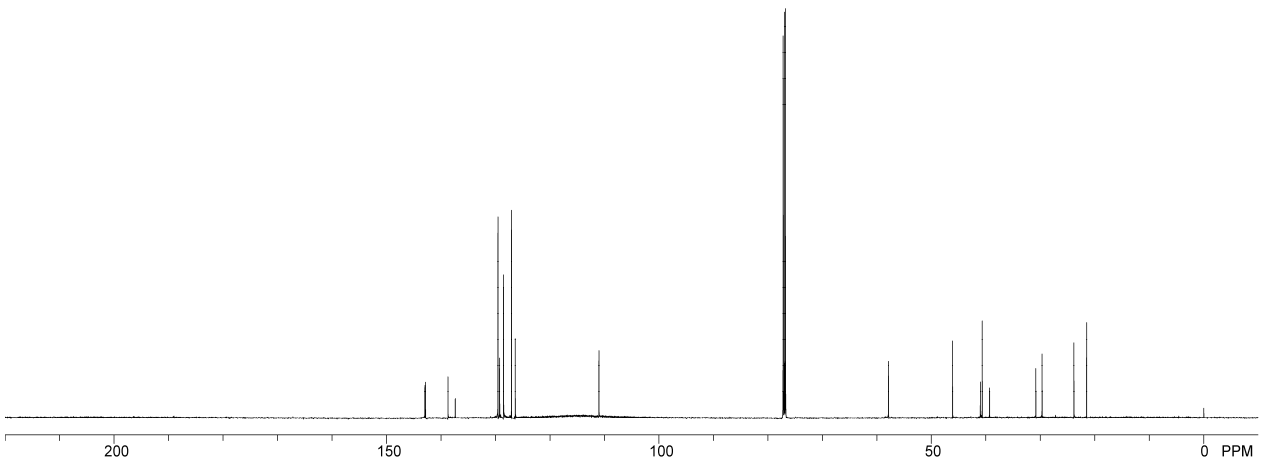


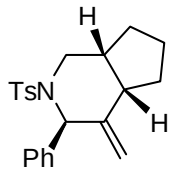




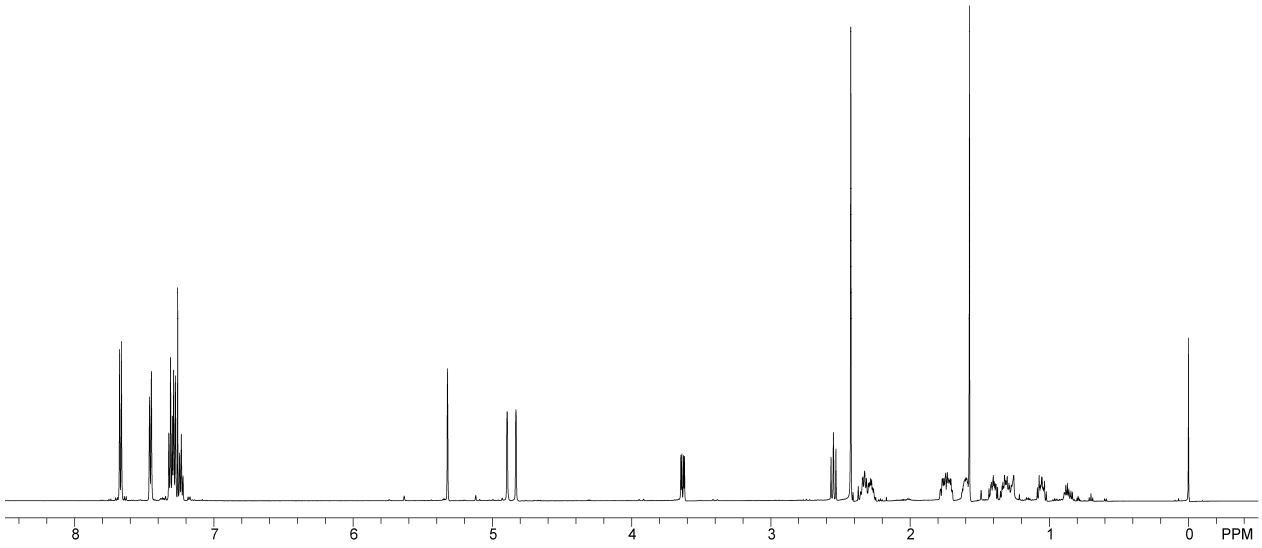
2d

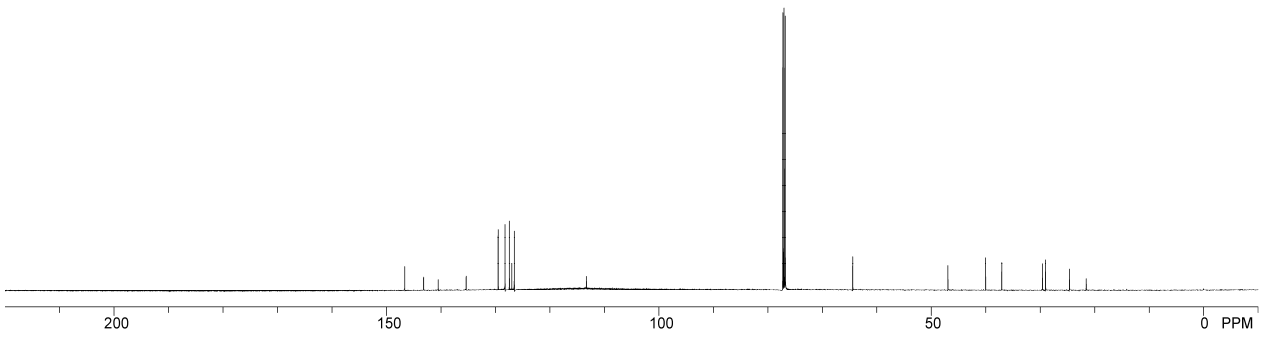


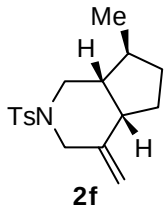




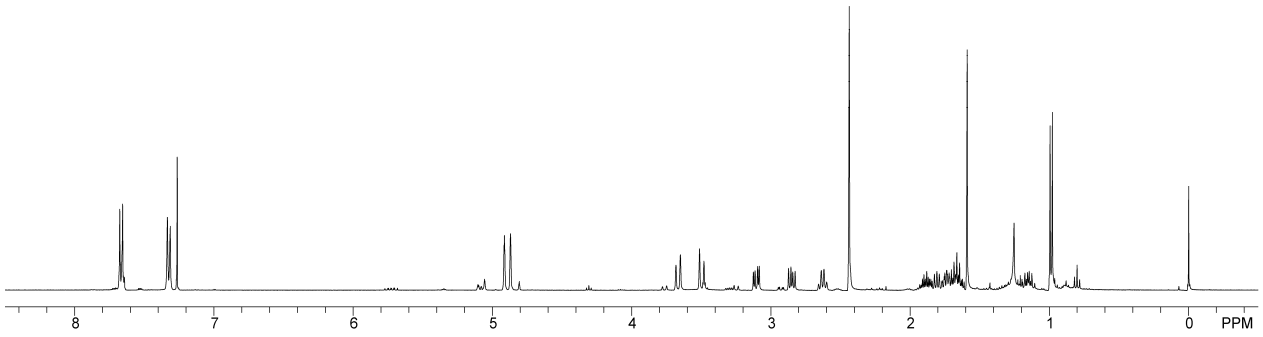
2e

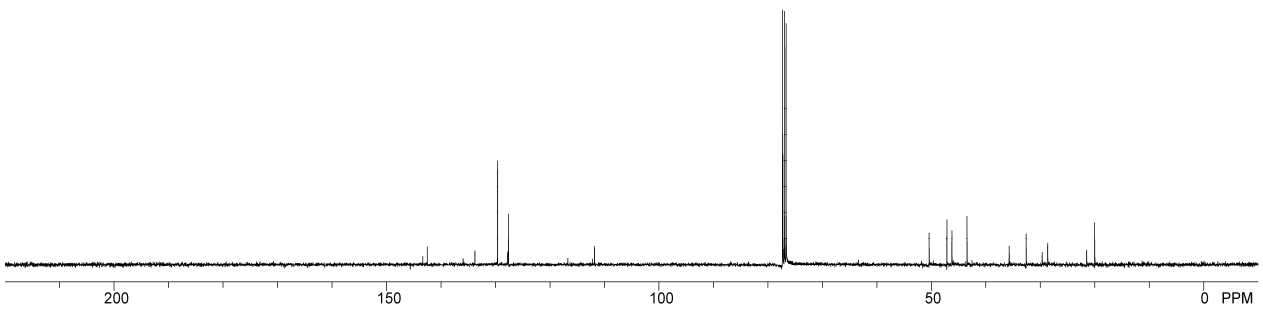


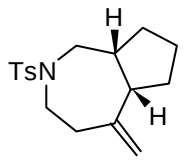




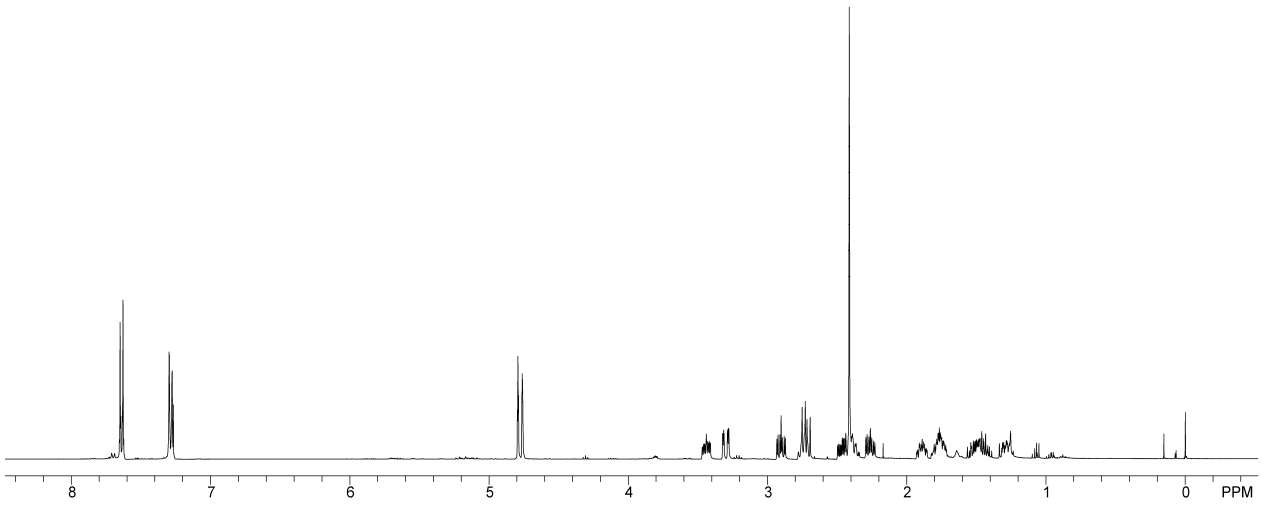
2f

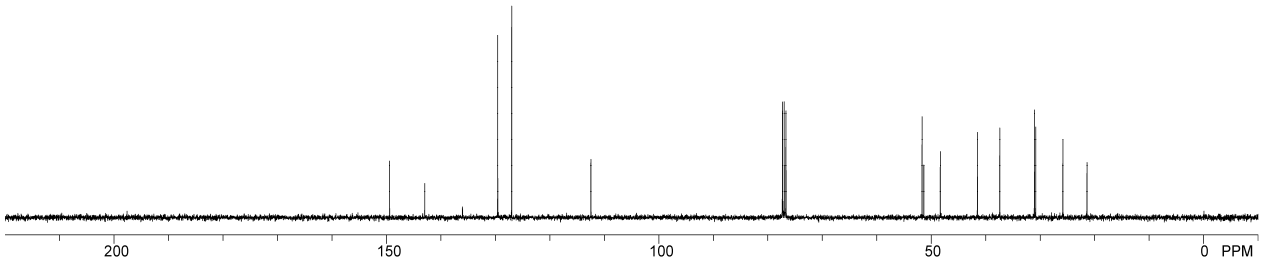


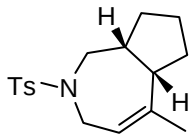




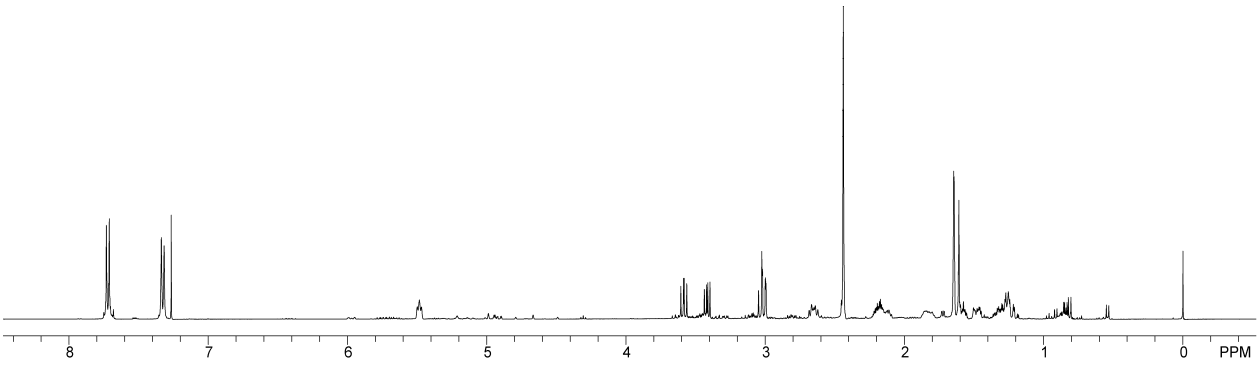
4a

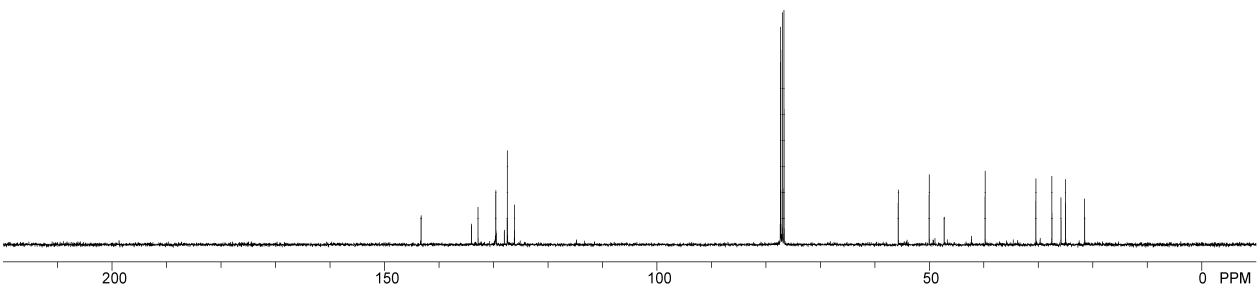


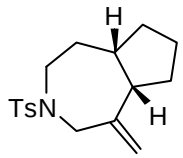




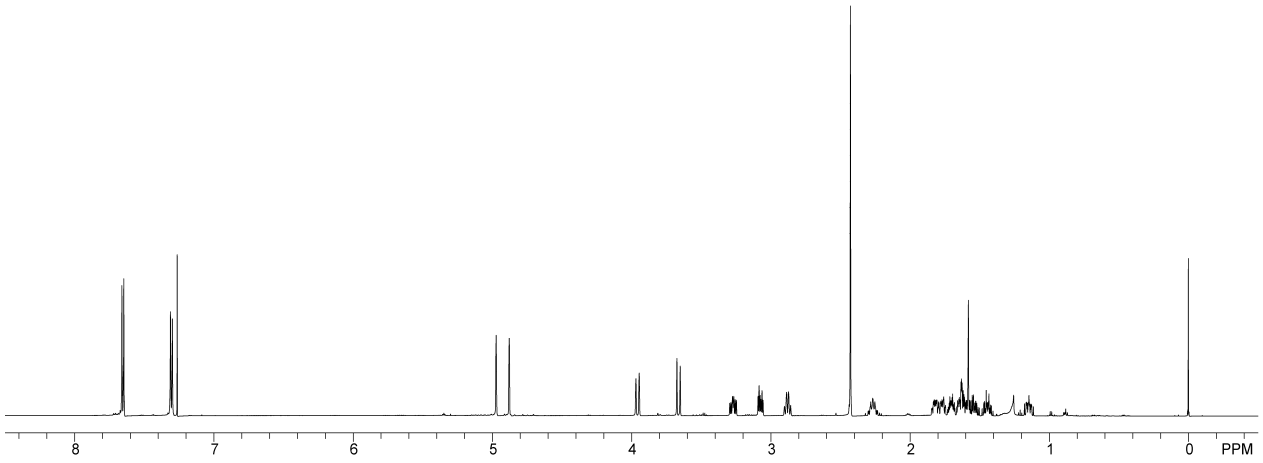
4a'

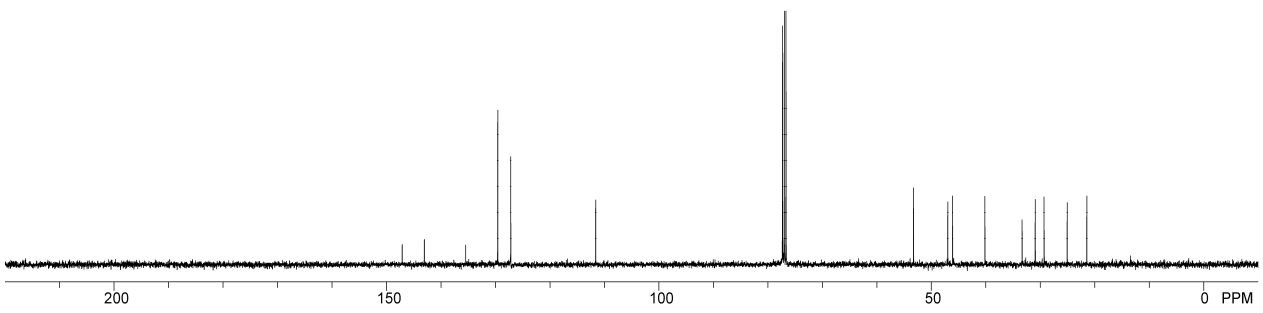


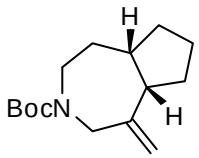




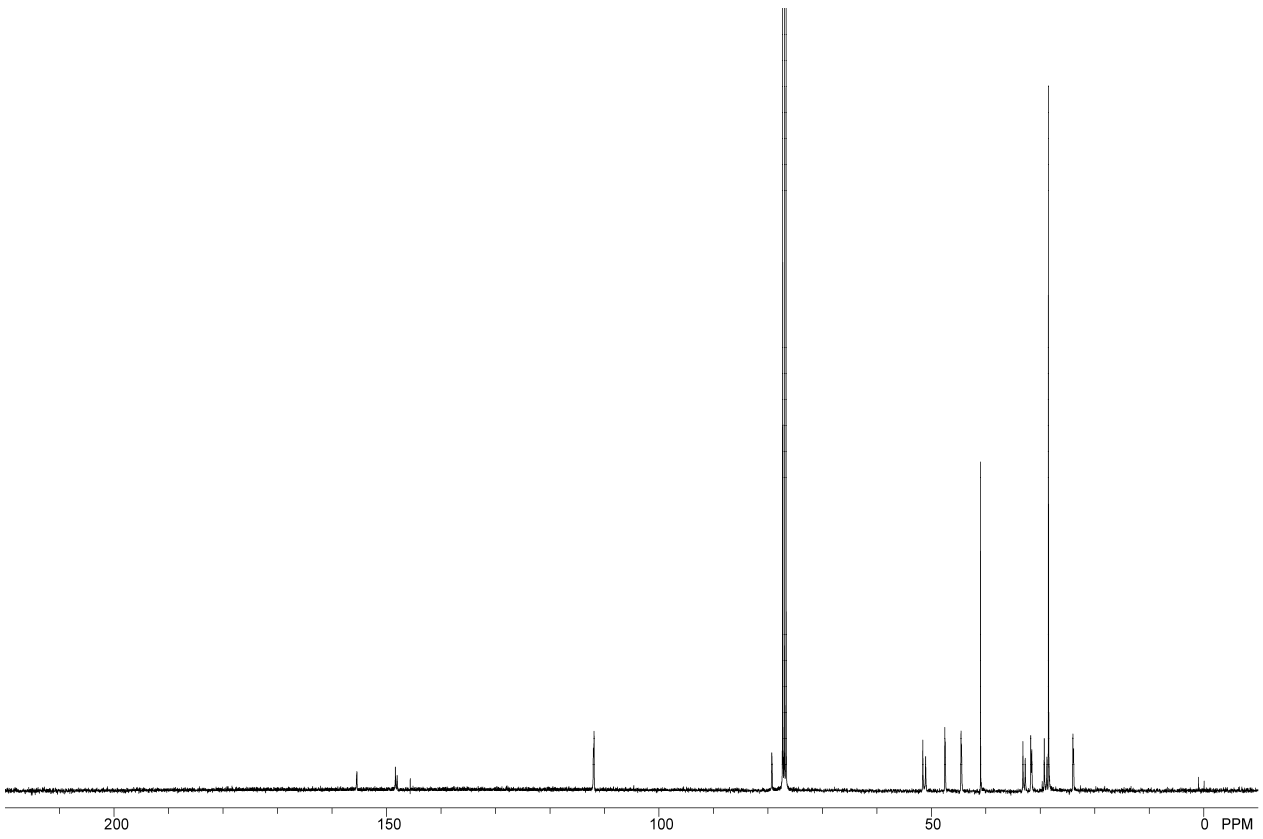
4b

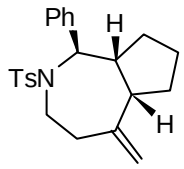




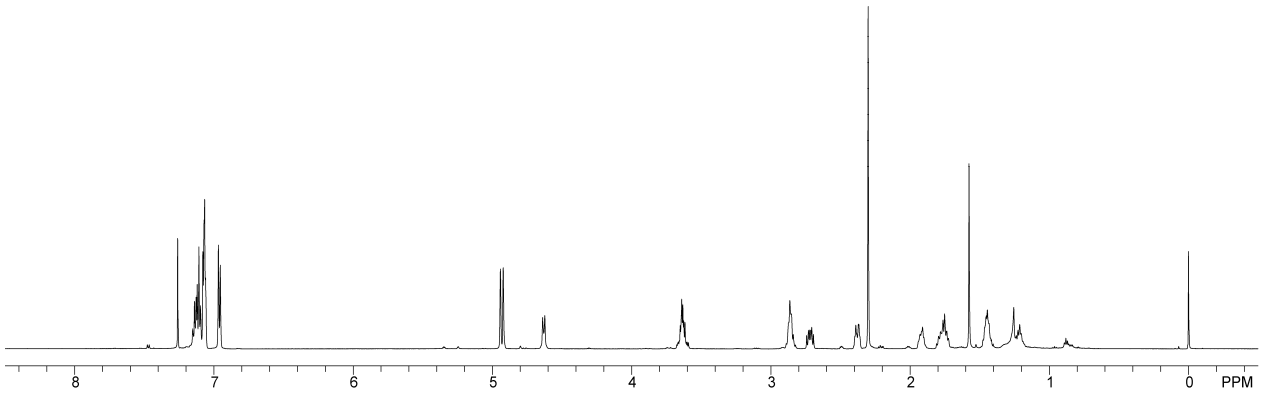


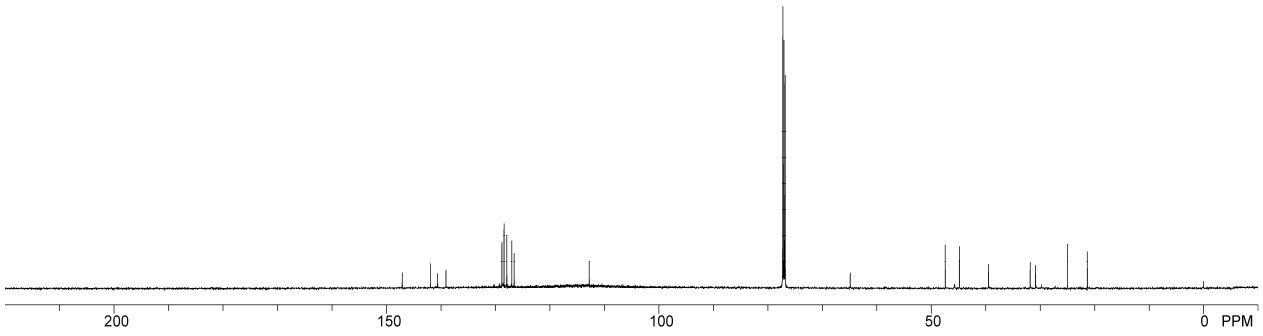
4c

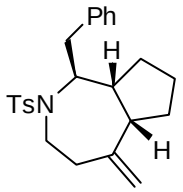




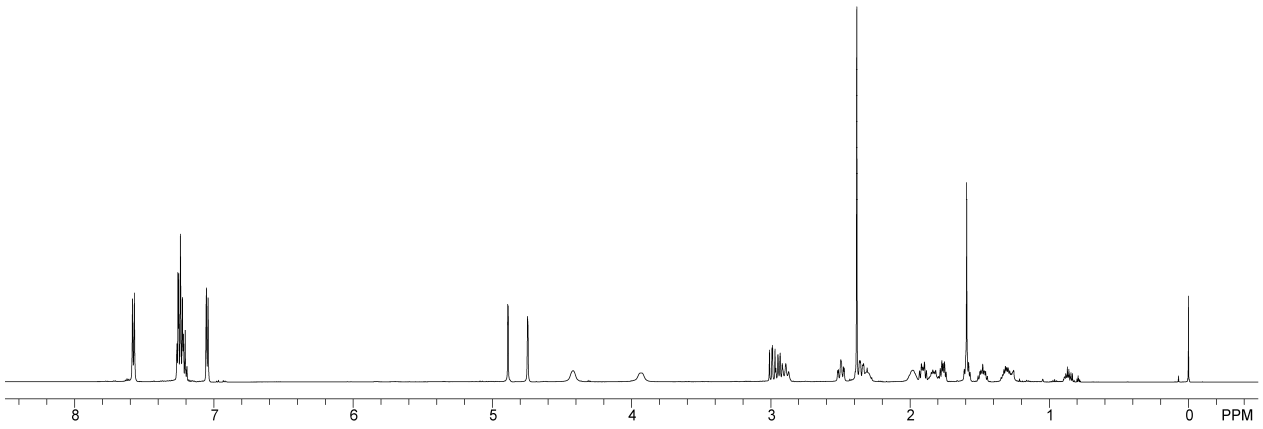
4d

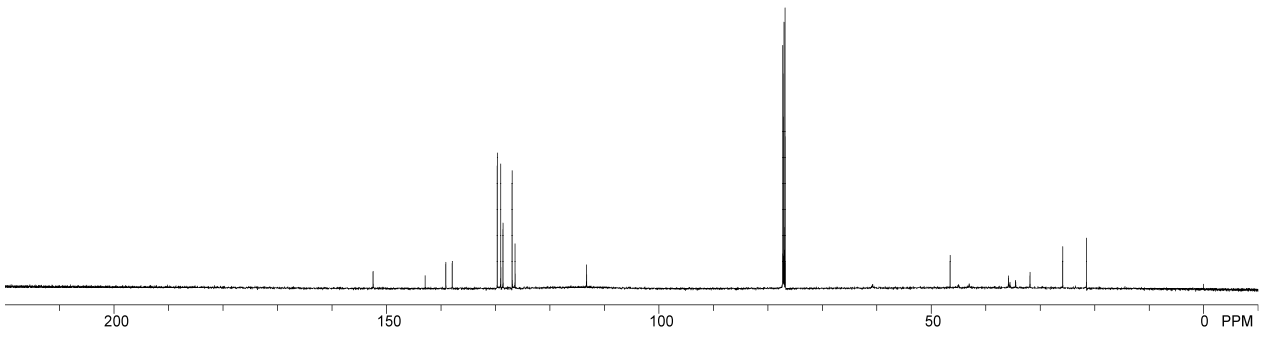


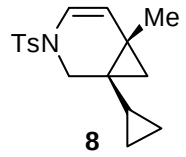




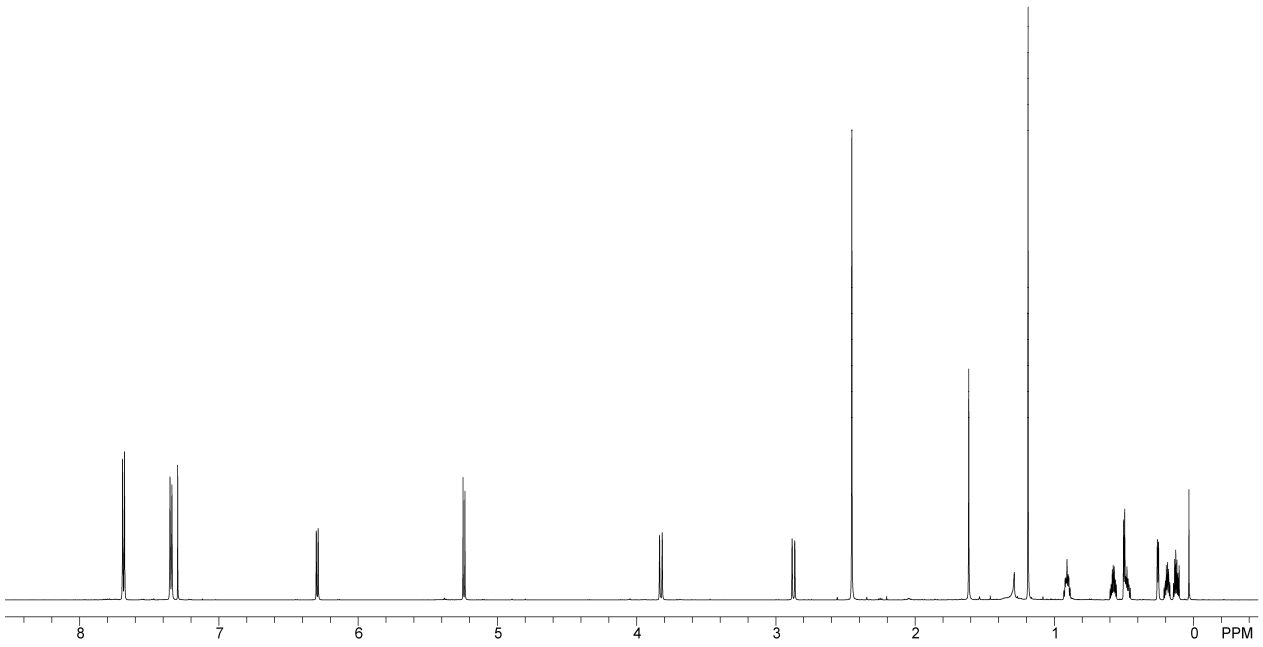
4e

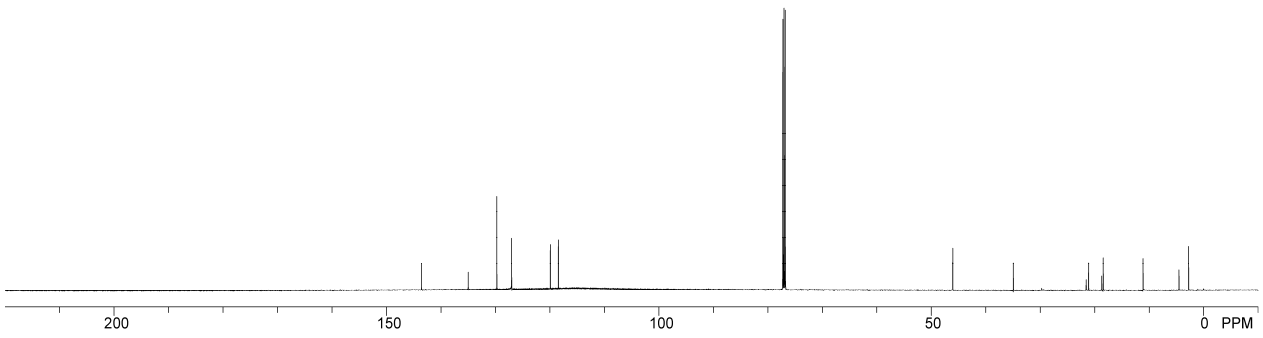




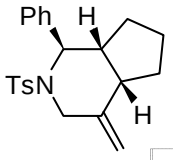


8

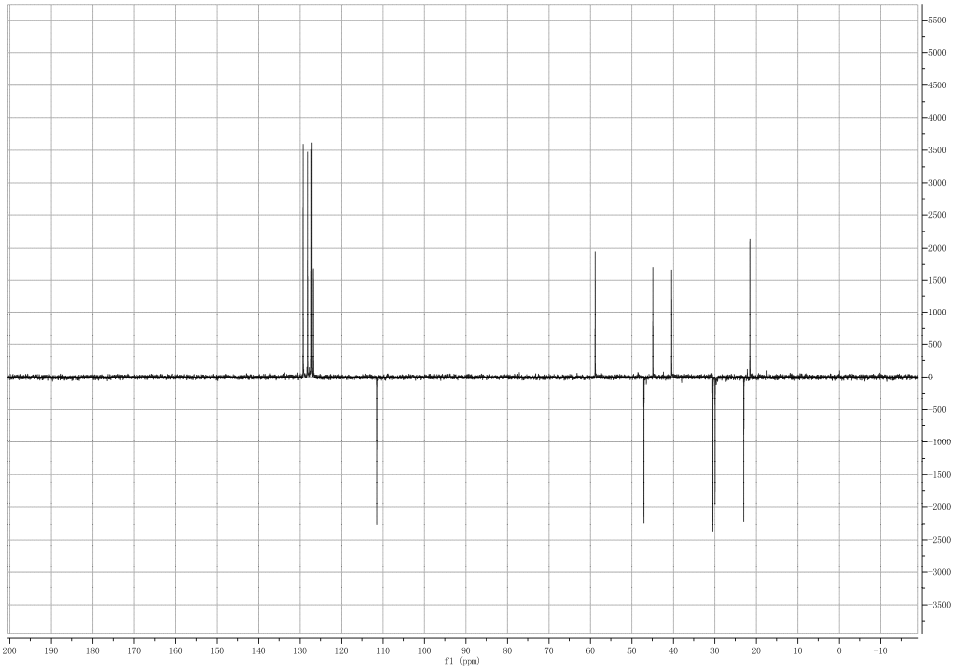


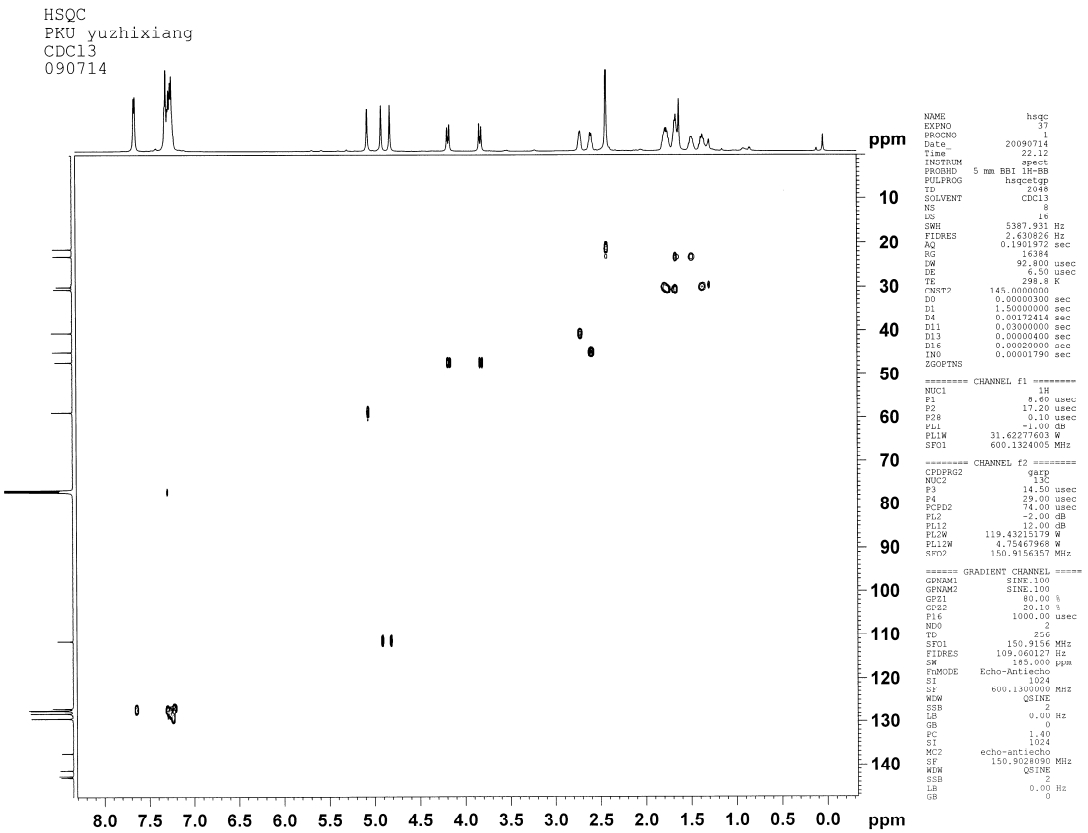


4. NMR Spectra for Stereochemical Determination

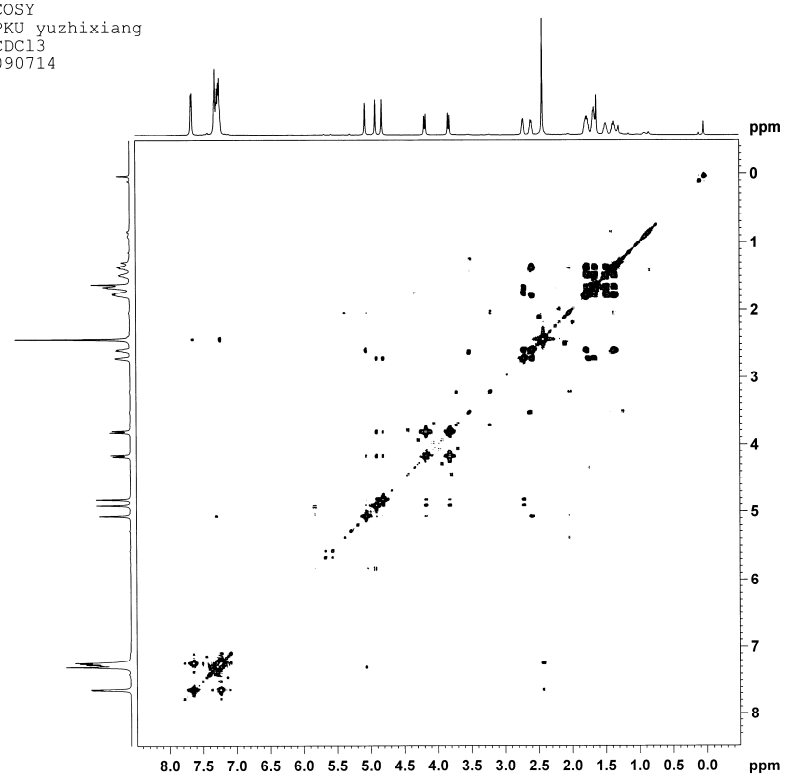


2c



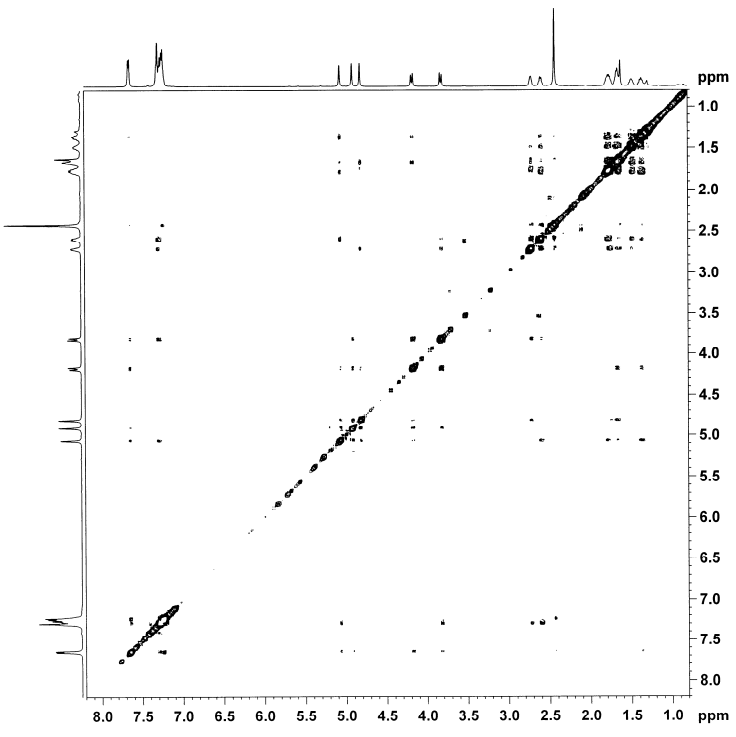


COSY
PKU yuzhixiang
CDCl3
090714

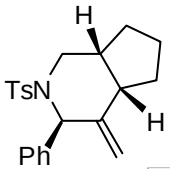


NAME	cosy
EXPNO	55
PROCNO	1
Date_	20090714
Time	21.12
INSTRUM	spect
PROBHD	5 mm BBI 1H-BB
PULPROG	cosygpqf
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901972 sec
RG	512
DW	92.800 usec
DE	6.50 usec
TE	298.3 K
D0	0.00000300 sec
D1	1.50000000 sec
D13	0.00000400 sec
D16	0.00000000 sec
IN0	0.00018560 sec
======== CHANNEL f1 ========	
NUC1	1H
P0	4.30 usec
P1	8.60 usec
PL1	-1.00 dB
PL1W	31.62277603 W
SFO1	600.1324005 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
ND0	1
TD	256
SFO1	600.1324 MHz
FIDRES	21.046635 Hz
SW	8.978 ppm
FnMODE	QF
SI	1024
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	QF
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

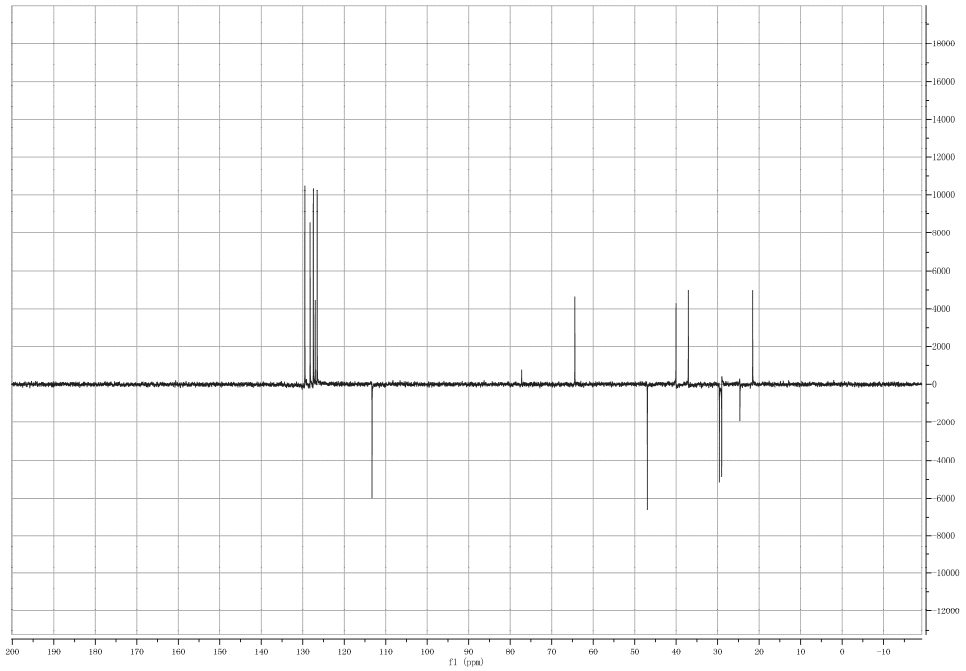
NOESY
PKU yuzhixiang
CDCl3
090714

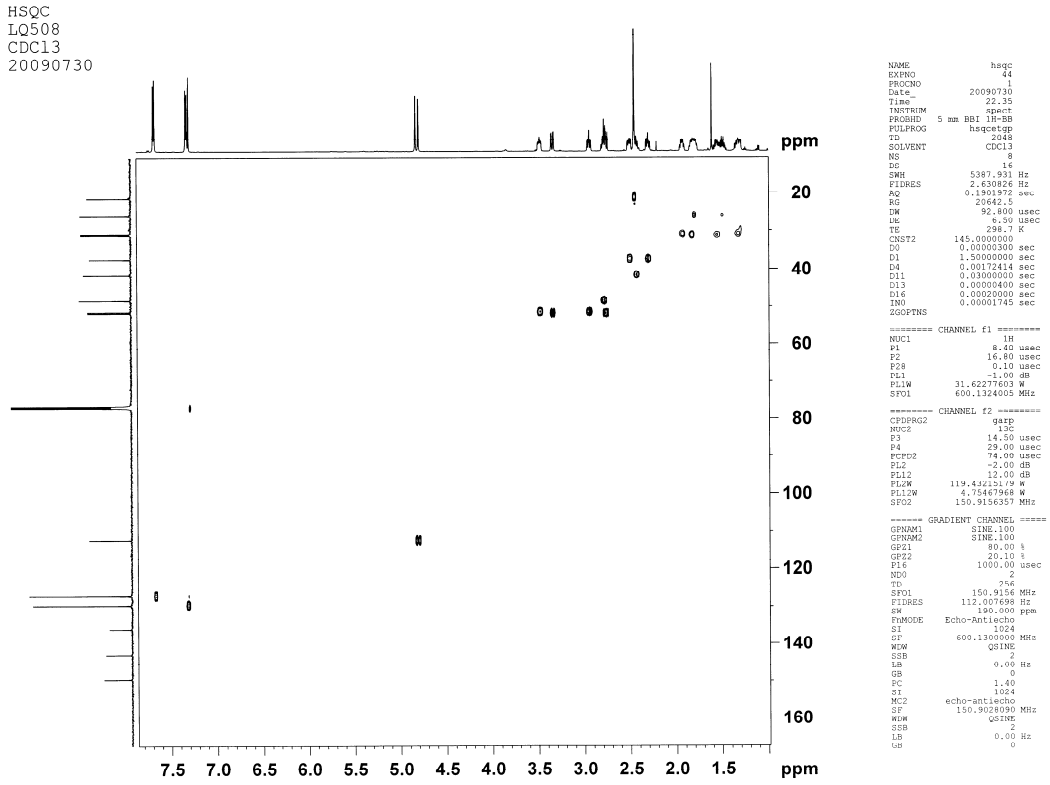


NAME	noesy
EXPNO	59
PROCNO	1
Date_	20090714
Time	23.11
INSTRUM	spect
PROBHD	5 mm BBI 1H-BB
PULPROG	noesygpph
TD	2048
SOLVENT	CDCl3
NS	0
DS	16
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901972 sec
RG	90.5
DW	92.800 usec
DE	6.50 usec
TE	298.3 K
D0	0.00000105 sec
D1	1.50000000 sec
D8	0.80000001 sec
D16	0.00020000 sec
IN0	0.00018560 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	8.60 usec
P2	17.20 usec
PL1	-1.00 dB
PL1W	31.62277603 W
SFO1	600.1324005 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	40.00 %
GPZ2	-40.00 %
P16	1000.00 usec
ND0	1
TD	256
SFO1	600.1324 MHz
FIDRES	21.046659 Hz
SW	8.978 ppm
FnMODE	States-TPPI
SI	1024
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	States-TPPI
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0



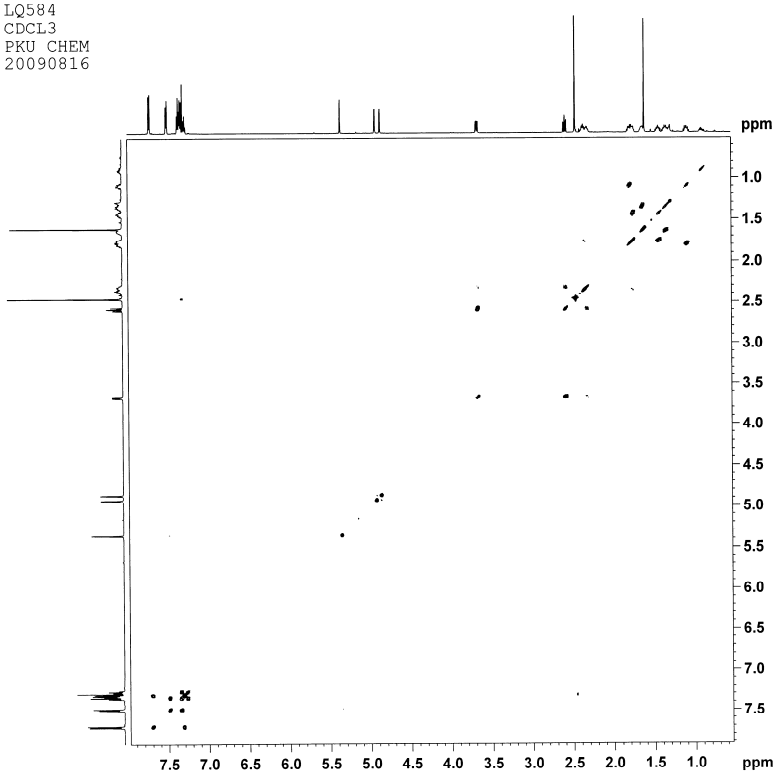
2e





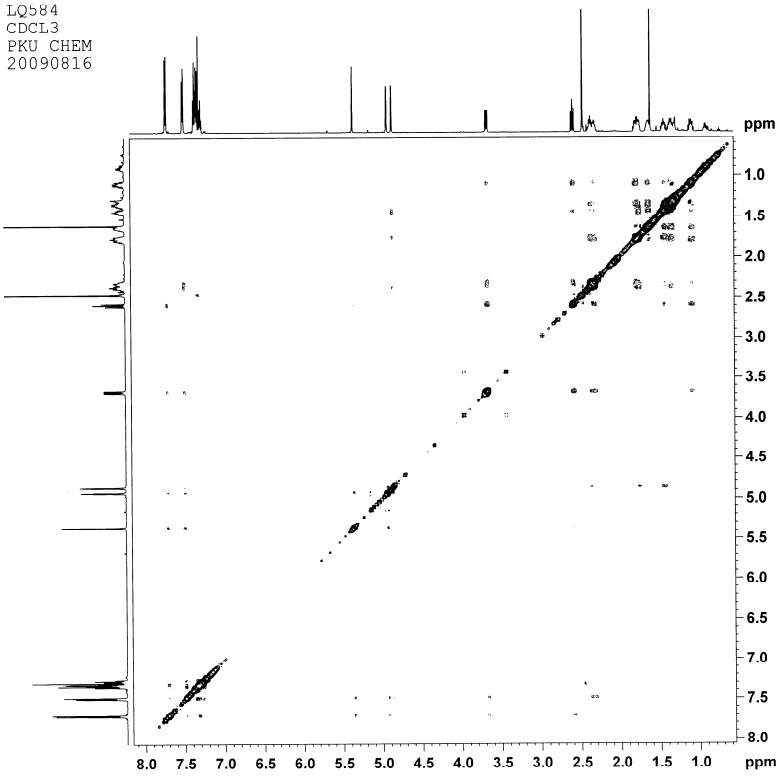

```
NAME                hsqc
EXPNO                 44
PROCNO                 1
Date_           20090730
Time                22.35
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG         hsqcetgp
TD                  2048
SOLVENT             CDCl3
NS                     8
DS                    16
SWH              5387.931 Hz
FIDRES           2.630826 Hz
AQ               0.1901972 sec
RG                 20642.5
DW                92.800 usec
DE                 6.50 usec
TE                298.7 K
CNST2          145.0000000
D0              0.00000300 sec
D1              1.50000000 sec
D4              0.00172414 sec
D11             0.03000000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00001745 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.40 usec
P2                  16.80 usec
P28                  0.10 usec
PL1                 -1.00 dB
PL1W          31.62277603 W
SFO1         600.1324005 MHz

======== CHANNEL f2 ========
CPDPRG2             garp
NUC2                  13C
P3                  14.50 usec
P4                  29.00 usec
PCPD2               74.00 usec
PL2                 -2.00 dB
PL12                12.00 dB
PLW          119.4321519 W
PL12W          4.75467968 W
SFO2         150.9156357 MHz

======= GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec
ND0                   2
TD                  256
SFO1         150.9156 MHz
FIDRES       112.007698 Hz
SW              190.000 ppm
FnMODE     Echo-Antiecho
SI                 1024
SF           600.1300000 MHz
WDW                QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
PC                 1.40
SI                 1024
MC2        echo-antiecho
SF          150.9028090 MHz
WDW                QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
```

COSY
LQ584
CDCL3
PKU CHEM
20090816

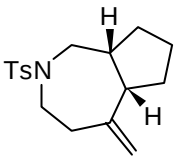



```
NAME                cosy
EXPNO                 65
PROCNO                 1
Date_           20090816
Time                22.17
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG         cosygpqf
TD                  2048
SOLVENT             CDCl3
NS                     4
DS                    16
SWH             5387.931 Hz
FIDRES          2.630826 Hz
AQ              0.1901972 sec
RG                   256
DW                92.800 usec
DE                 6.50 usec
TE                297.8 K
D0              0.00000300 sec
D1              1.50000000 sec
D13             0.00000400 sec
D16             0.00000000 sec
TN0             0.00018560 sec

======== CHANNEL f1 ========
NUC1                  1H
P0                  4.30 usec
P1                  8.60 usec
PL1                -1.00 dB
PL1W          31.62277603 W
SFO1          600.1324005 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPZ1               10.00 %
P16              1000.00 usec
ND0                    1
TD                   256
SFO1            600.1324 MHz
FIDRES         21.046597 Hz
SW                 8.978 ppm
FnMODE                QF
SI                  1024
SF          600.1300000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
SI                  1024
MC2                   QF
SF          600.1300000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
```

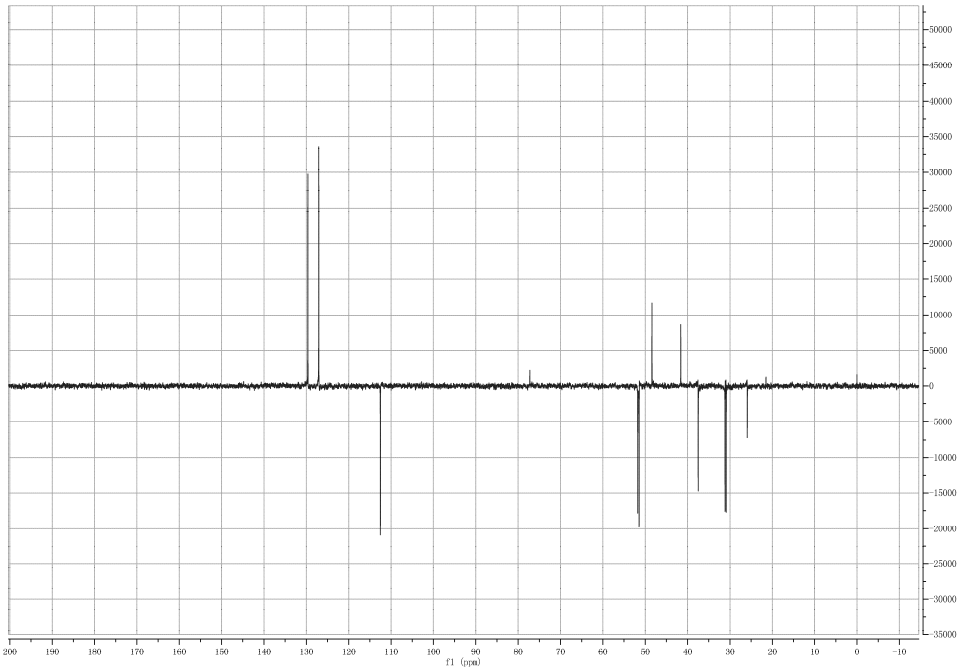
NOESY
LQ584
CDCL3
PKU CHEM
20090816



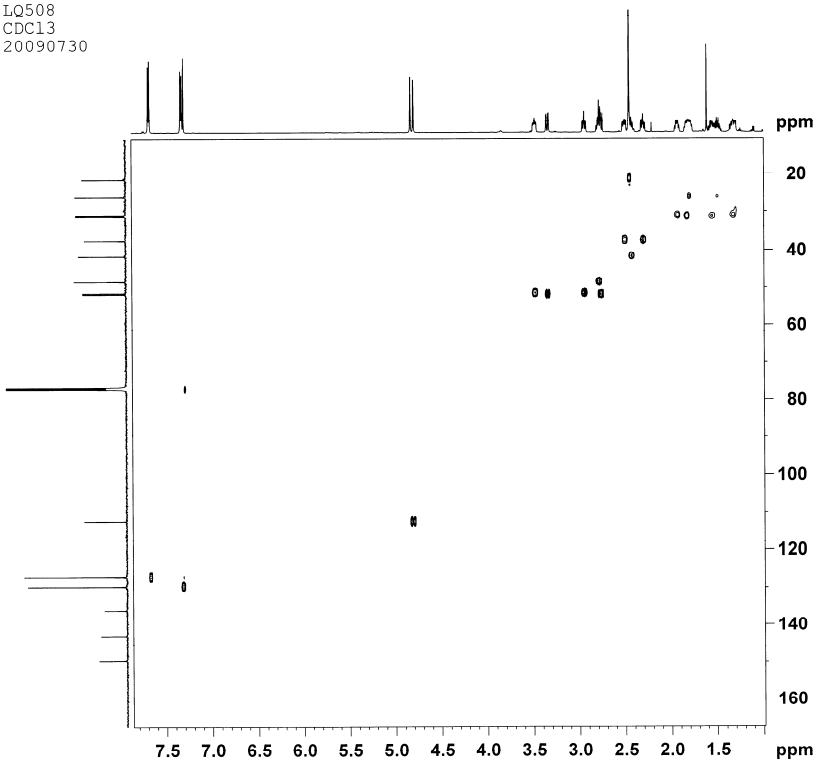

```
NAME                noesy
EXPNO                 77
PROCNO                 1
Date_           20090816
Time                22.47
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG         noesygpph
TD                  2048
SOLVENT             CDCl3
NS                     4
DS                    16
SWH             5387.931 Hz
FIDRES          2.630826 Hz
AQ              0.1901972 sec
RG                   256
DW                92.800 usec
DE                 6.50 usec
TE                297.7 K
D0              0.00008210 sec
D1              2.00000000 sec
D8              0.80000001 sec
D16             0.00020000 sec
IN0             0.00018560 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.40 usec
P2                 16.80 usec
PL1                -1.00 dB
PL1W          31.62277603 W
SFO1          600.1324005 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPZ1               40.00 %
GPZ2              -40.00 %
P16              1000.00 usec
ND0                    1
TD                   256
SFO1            600.1324 MHz
FIDRES         21.046597 Hz
SW                 8.978 ppm
FnMODE       States-TPPI
SI                  1024
SF          600.1300000 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.40
SI                  1024
MC2          States-TPPI
SF          600.1300000 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```



4a

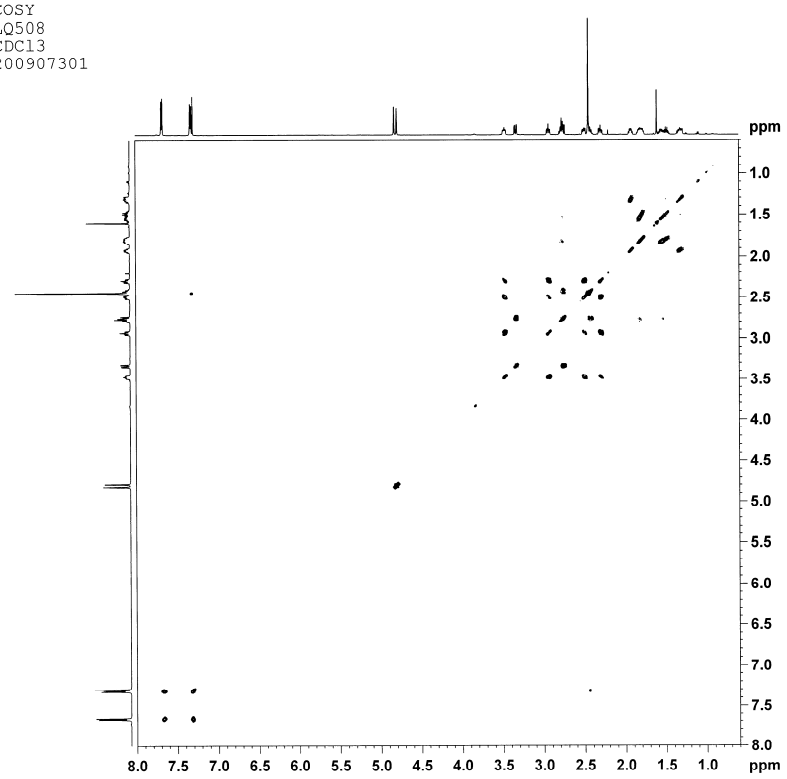


HSQC
LQ508
CDCl3
20090730



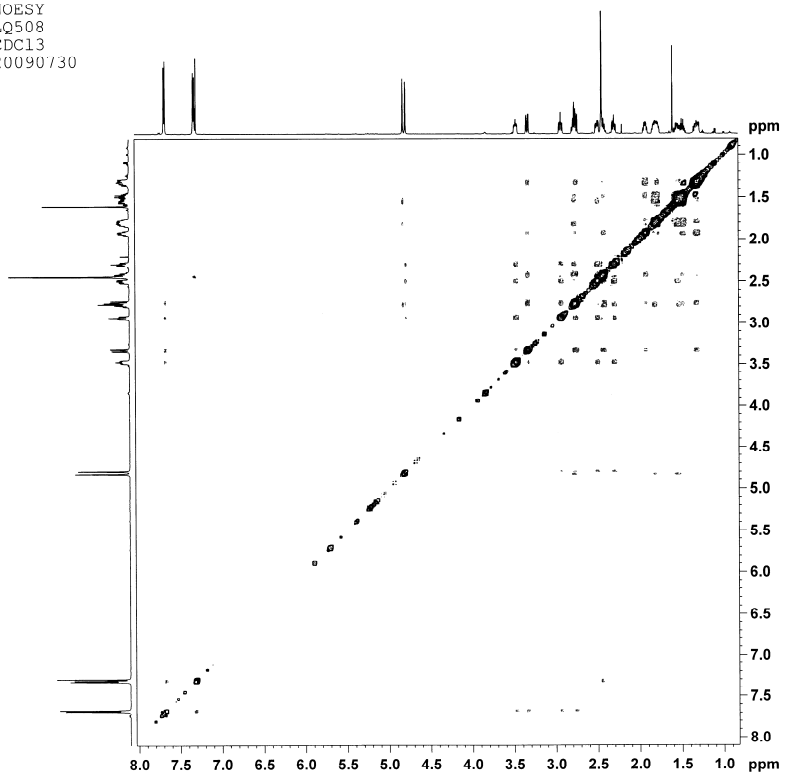

```
NAME                 hsqc
EXPNO                  44
PROCNO                  1
Date_             20090730
Time                 22.35
INSTRUM              spect
PROBHD    5 mm BBI 1H-BB
PULPROG          hsqcetgp
TD                   2048
SOLVENT              CDCl3
NS                      8
DS                     16
SWH               5387.931 Hz
FIDRES            2.630826 Hz
AQ                0.1901972 sec
RG                  20642.5
DW                  92.800 usec
DE                   6.50 usec
TE                  298.7 K
CNST2           145.0000000
D0                0.00000300 sec
D1                1.50000000 sec
D4                0.00172414 sec
D11               0.03000000 sec
D13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00001745 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.40 usec
P2                  16.80 usec
P28                  0.10 usec
PL1                 -1.00 dB
PL1W           31.62277603 W
SFO1          600.1324005 MHz

======== CHANNEL f2 ========
CPDPRG2              garp
NUC2                   13C
P3                  14.50 usec
P4                  29.00 usec
PCPD2               74.00 usec
PL2                 -2.00 dB
PL12                12.00 dB
PLW           119.43215179 W
PL12W          4.75467968 W
SFO2          150.9156357 MHz

======= GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec
ND0                     2
TD                    256
SFO1          150.9156 MHz
FIDRES        112.007698 Hz
SW                190.000 ppm
FnMODE      Echo-Antiecho
SI                   1024
SF            600.1300000 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2         echo-antiecho
SF            150.9028090 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

COSY
LQ508
CDCl3
200907301

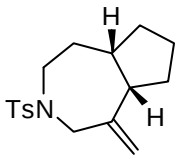


NAME	cosy
EXPNO	62
PROCNO	1
Date_	20090731
Time	0.36
INSTRUM	spect
PROBHD	5 mm BBI 1H-BB
PULPROG	cosygpqf
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901972 sec
RG	812.7
DW	92.800 usec
DE	6.50 usec
TE	298.4 K
D0	0.00000300 sec
D1	1.50000000 sec
D13	0.00000400 sec
D16	0.00000000 sec
IN0	0.00018560 sec
======== CHANNEL f1 ========	
NUC1	1H
P0	4.30 usec
P1	8.60 usec
PL1	-1.00 dB
PL1W	31.62277603 W
SFO1	600.1324005 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
ND0	1
TD	256
SFO1	600.1324 MHz
FIDRES	21.046597 Hz
SW	8.978 ppm
FnMODE	QF
SI	1024
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	QF
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

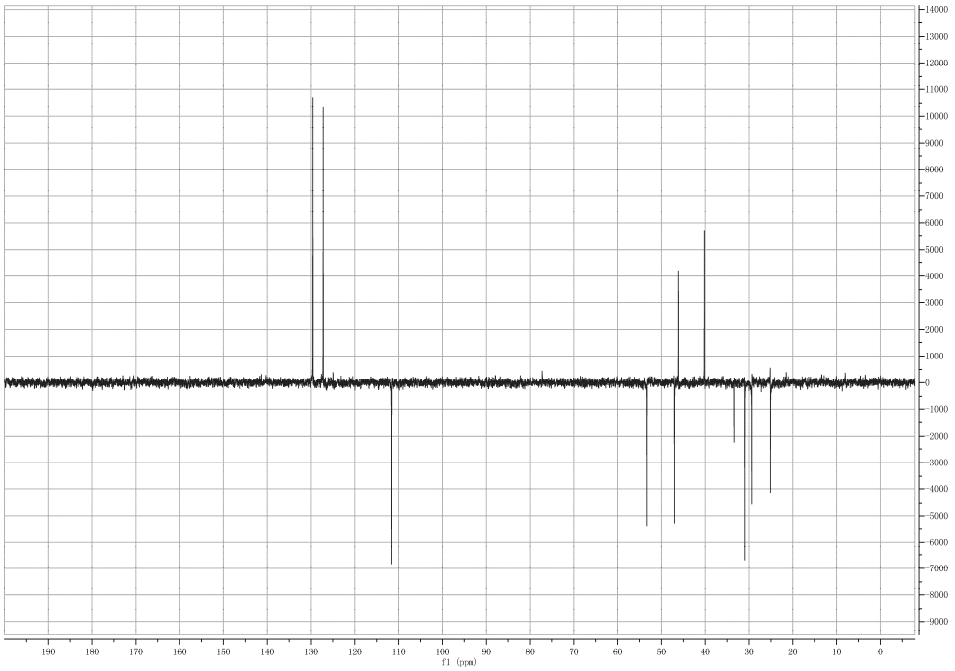
NOESY
LQ508
CDCl3
20090730

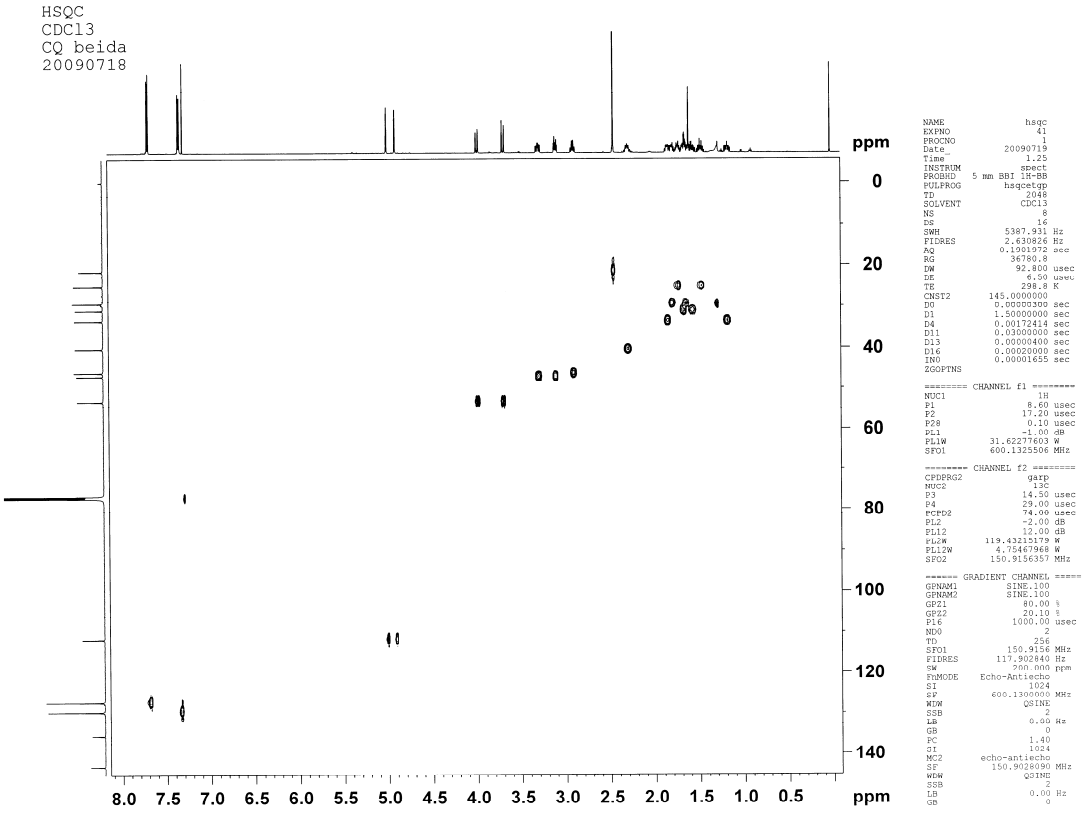


NAME	noesy
EXPNO	70
PROCNO	1
Date_	20090730
Time	21.09
INSTRUM	spect
PROBHD	5 mm BBI 1H-BB
PULPROG	noesygpph
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901972 sec
RG	128
DW	92.800 usec
DE	6.50 usec
TE	298.2 K
D0	0.00009210 sec
D1	1.50000000 sec
D8	0.80000001 sec
D16	0.00020000 sec
IN0	0.00018560 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	8.40 usec
P2	16.80 usec
PL1	-1.00 dB
PL1W	31.62277603 W
SFO1	600.1324005 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	40.00 %
GPZ2	-40.00 %
P16	1000.00 usec
ND0	1
TD	256
SFO1	600.1324 MHz
FIDRES	21.046597 Hz
SW	8.978 ppm
FnMODE	States-TPPI
SI	1024
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	States-TPPI
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

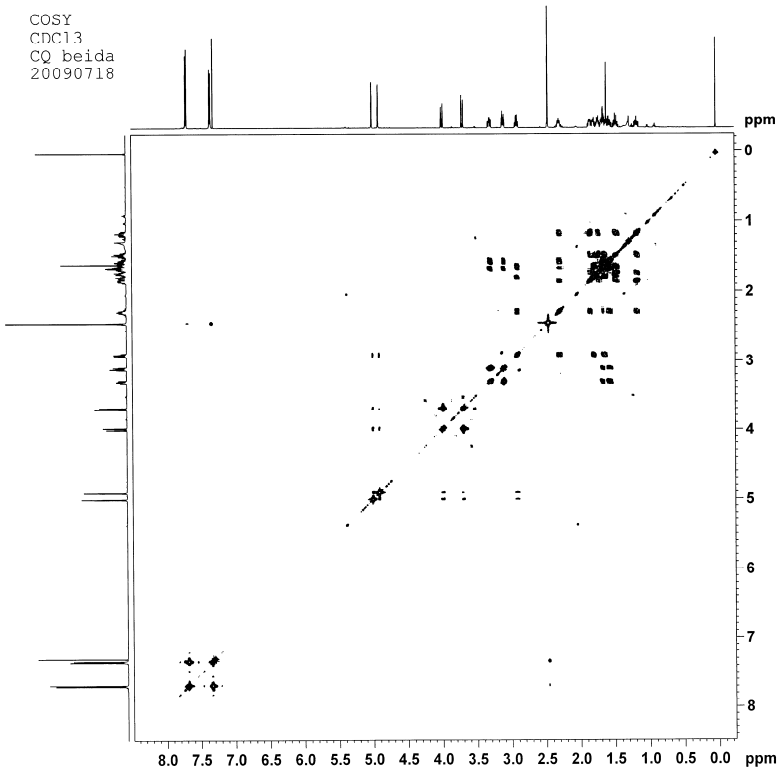


4b

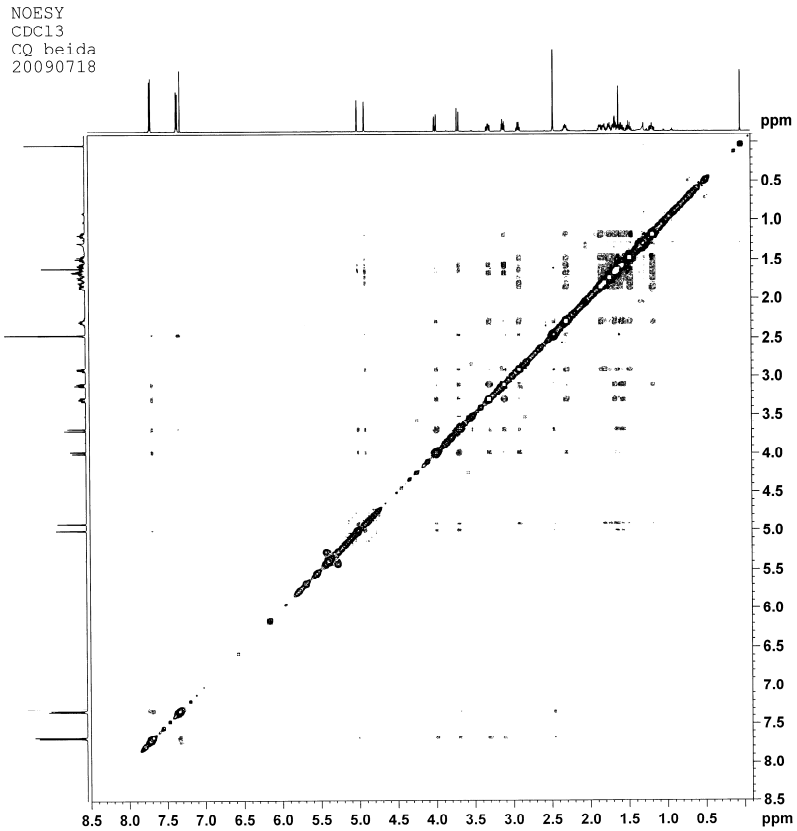




NAME	hsqc
EXPNO	41
PROCNO	1
Date_	20090719
Time	1.25
INSTRUM	spect
PROBHD	5 mm BBI 1H-BB
PULPROG	hsqcetgp
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901972 sec
RG	36780.8
DW	92.800 usec
DE	6.50 usec
TE	298.8 K
CNST2	145.0000000
D0	0.00000300 sec
D1	1.50000000 sec
D4	0.00172414 sec
D11	0.03000000 sec
D13	0.00000400 sec
D16	0.00020000 sec
IN0	0.00001655 sec
ZGOPTNS	
======== CHANNEL f1 ========	
NUC1	1H
P1	8.60 usec
P2	17.20 usec
P28	0.10 usec
PL1	-1.00 dB
PL1W	31.62277603 W
SFO1	600.1325506 MHz
======== CHANNEL f2 ========	
CPDPRG2	garp
NUC2	13C
P3	14.50 usec
P4	29.00 usec
PCPD2	74.00 usec
PL2	-2.00 dB
PL12	12.00 dB
PL2W	119.43215179 W
PL12W	4.75467968 W
SFO2	150.9156357 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	80.00 %
GPZ2	20.10 %
P16	1000.00 usec
ND0	2
TD	256
SFO1	150.9156 MHz
FIDRES	117.902840 Hz
SW	200.000 ppm
FnMODE	Echo-Antiecho
SI	1024
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	echo-antiecho
SF	150.9026090 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0




```
NAME                cosy
EXPNO                 59
PROCNO                 1
Date_           20090718
Time                18.11
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG         cosygpqf
TD                  2048
SOLVENT             CDCl3
NS                     4
DS                    16
SWH              5387.931 Hz
FIDRES           2.630826 Hz
AQ               0.1901972 sec
RG                 812.7
DW                92.800 usec
DE                 6.50 usec
TE                298.4 K
D0           0.00000300 sec
D1           1.50000000 sec
D13          0.00000400 sec
D16          0.00000000 sec
IN0          0.00018560 sec

======== CHANNEL f1 ========
NUC1                1H
P0                4.30 usec
P1                8.60 usec
PL1              -1.00 dB
PL1W       31.62277603 W
SFO1       600.1325506 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPZ1              10.00 %
P16             1000.00 usec
ND0                    1
TD                   256
SFO1           600.1326 MHz
FIDRES        21.046602 Hz
SW                8.978 ppm
FnMODE               QF
SI                 1024
SF          600.1300000 MHz
WDW              SINE
SSB                 0
LB                0.00 Hz
GB                  0
PC                1.40
SI                1024
MC2                 QF
SF          600.1300000 MHz
WDW              SINE
SSB                 0
LB                0.00 Hz
GD                  0
```




```
NAME              noesy
EXPNO                64
PROCNO                1
Date            20090718
Time               23.59
INSTRUM            spect
PROBHD   5 mm BBI 1H-BB
PULPROG        noesygpph
TD                 2048
SOLVENT            CDCl3
NS                     8
DS                    16
SWH             5387.931 Hz
FIDRES          2.630826 Hz
AQ              0.1901972 sec
RG                 456.1
DW                92.800 usec
DE                 6.50 usec
TE                298.3 K
D0           0.00008185 sec
D1           1.50000000 sec
D8           0.80000001 sec
D16          0.00020000 sec
IN0          0.00018560 sec

======== CHANNEL f1 ========
NUC1                1H
P1                8.60 usec
P2               17.20 usec
PL1              -1.00 dB
PL1W       31.62277603 W
SFO1       600.1325506 MHz

------ GRADIENT CHANNEL -----
GPNAM1          SINE.100
GPNAM2          SINE.100
GPZ1              40.00 %
GPZ2             -40.00 %
P16             1000.00 usec
ND0                    1
TD                   256
SFO1           600.1326 MHz
FIDRES        21.046602 Hz
SW                8.978 ppm
FnMODE       States-TPPI
SI                 1024
SF          600.1300000 MHz
WDW              QSINE
SSB                 2
LB                0.00 Hz
GB                  0
PC                1.40
SI                1024
MC2          States-TPPI
SF          600.1300000 MHz
WDW              QSINE
SSB                 2
LB                0.00 Hz
GD                  0
```