Supporting Information

Chiral Spirosiladiphosphines: Ligand Development and Applications in Rh-Catalyzed Asymmetric Hydrosilylation/ Cyclization of 1,6-Enynes with Enhanced Reactivity

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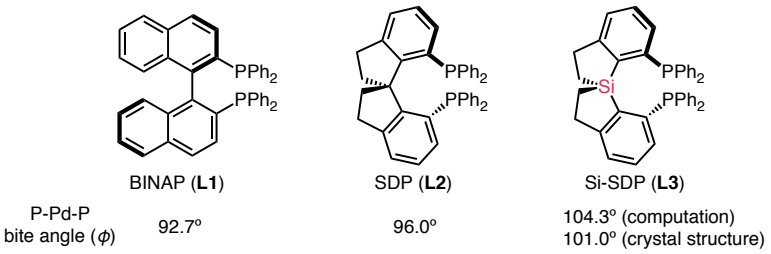
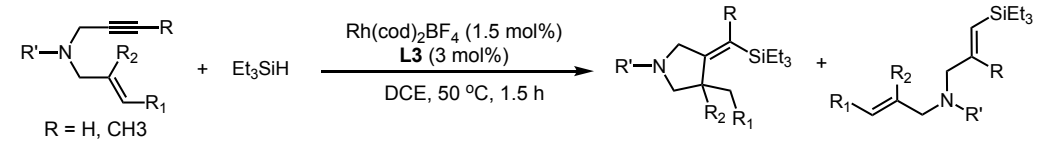
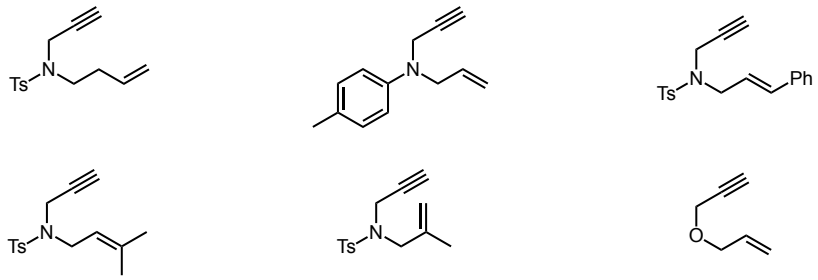
1. Supporting Figures and Tables.

Figure S1. Comparision of calculated structure of L3 with BINAP (L1) and SDP (L2).



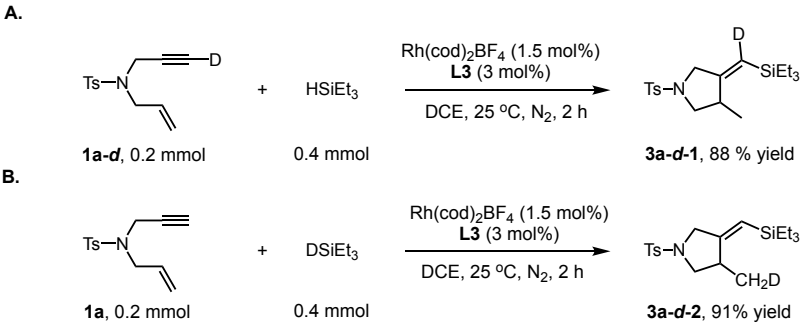
Scheme S1. Unsuccessful substrates.



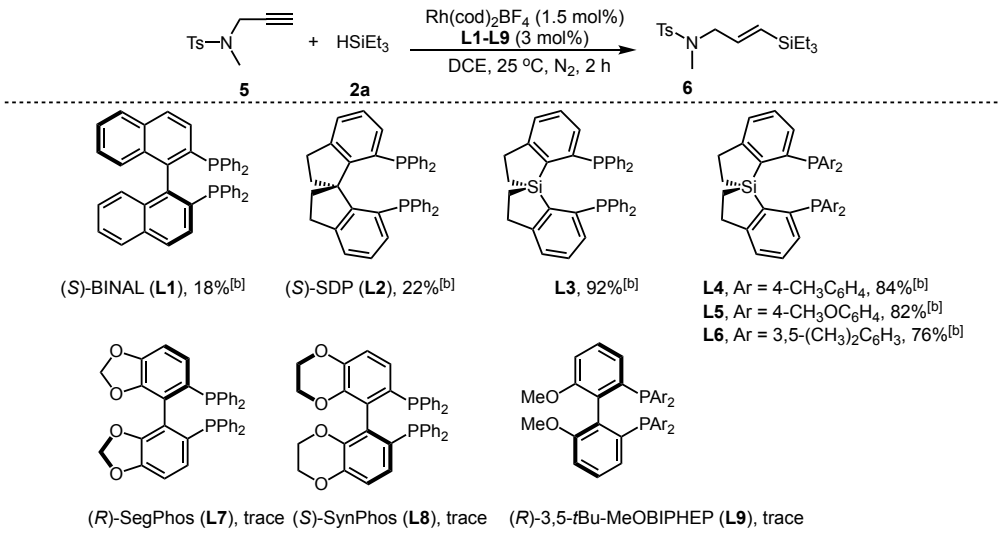


Reaction conditions: Reactions were performed with 1,6-enynes (0.2 mmol), Et_3SiH (0.4 mmol), $Rh(cod)_2BF_4$ (1.5 mol%), **L3** (3 mol%) in DCE (2.0 mL).

Scheme S2. Deuterium labeling experiments.

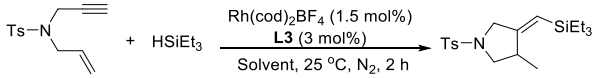


Scheme S3 Effect of ligands for hydrosilylation.[a]



[a] Reactions were performed with **5** (0.2 mmol), **2a** (0.4 mmol), $Rh(cod)_2BF_4$ (1.5 mol%), **L1-L9** (3 mol%) in solvent (2.0 mL). [b] Isolated yield.

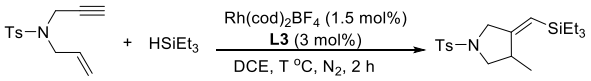
Table S1. Effect of solvents.[a]



Entry	Solvent	Yield (%)[b]	ee% (**3a**)
1	**DCE**	**93**	**91**
2	THF	69.5	90
3	1,4-Dioxane	55	90
4	DCM	88	89
5	Toluene	30	75
6	EtOH	21	73
7	DMSO	9	74
8	CH_3CN	NR	--
9	Et_2O	NR	--

[a] Reactions were performed with **1a** (0.2 mmol), **2a** (0.4 mmol), $Rh(cod)_2BF_4$ (1.5 mol%), **L3** (3 mol%) in solvent (2.0 mL). [b] Isolated yield. [c] ee values were determined by chiral HPLC of the desilylated compounds.

Table S2. Effect of temperature. [a]

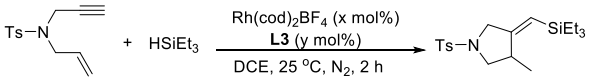


1a 2a 3a

Entry	*T*/°C	Time/h	Yield/%[b]	ee/%[c]
1	90	1	68.5	90
2	50	1.5	87	90
3	**rt**	**2**	**91**	**91**
4	0	12	80	91

[a] Reactions were performed with **1a** (0.2 mmol), **2a** (0.4 mmol), $Rh(cod)_2BF_4$ (1.5 mol%), **L3** (3 mol%) in DCE (2.0 mL). [b] Isolated yield. [c] ee values were determined by chiral HPLC of the desilylated compounds.

Table S3 Effect of Rh/L3 ratio. [a]



1a 2a 3a

Entry	x,y/mol%	Yield/%[b]	ee/%[c]
1	5, 6	92	91
2	2.5, 3	93	91
3	1, 2	82	90
4	1, 3	82	90
5	1.5, 2	88	91
6	**1.5, 3**	**91**	**91**

[a] Reactions were performed with **1a** (0.2 mmol), **2a** (0.4 mmol) in DCE (2.0 mL). [b] Isolated yield. [c] ee values were determined by chiral HPLC of the desilylated compounds.

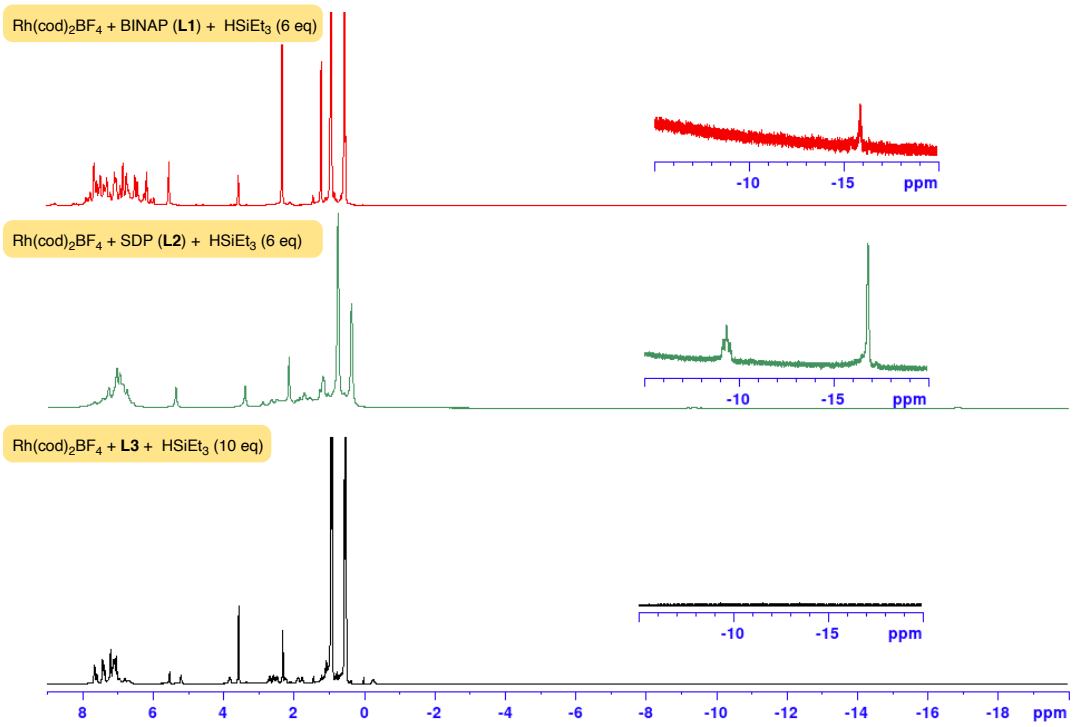


Figure S2. ^{1}H NMR spectra of mixtures of Rh(cod)$_2$BF$_4$, ligands, and HSiEt$_3$.

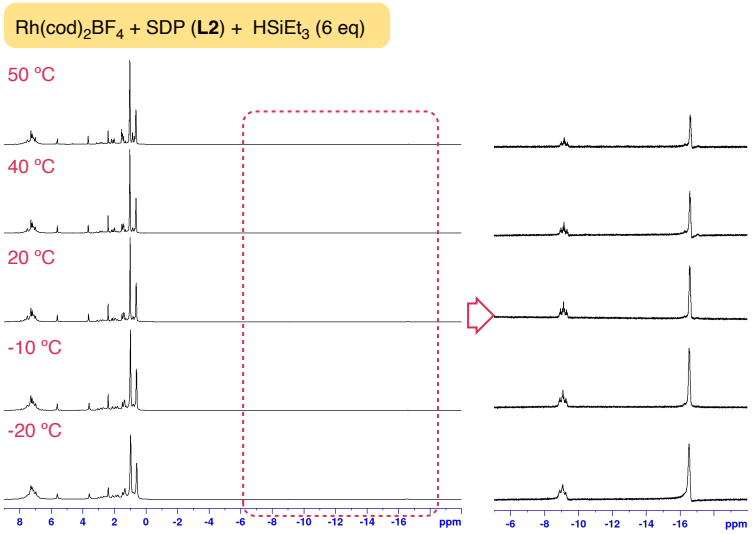


Figure S3. Variable temperature ^{1}H NMR spectra of Rh(cod)$_2$BF$_4$, SDP (L2), and HSiEt$_3$.

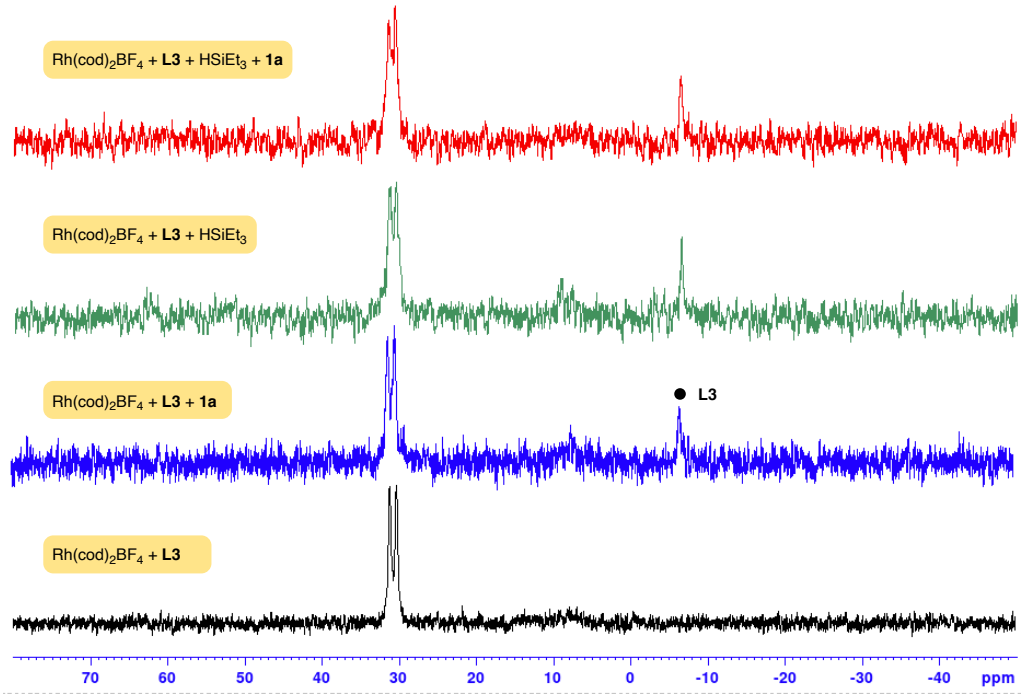


Figure S4. 31P NMR spectra of reaction mixtures.

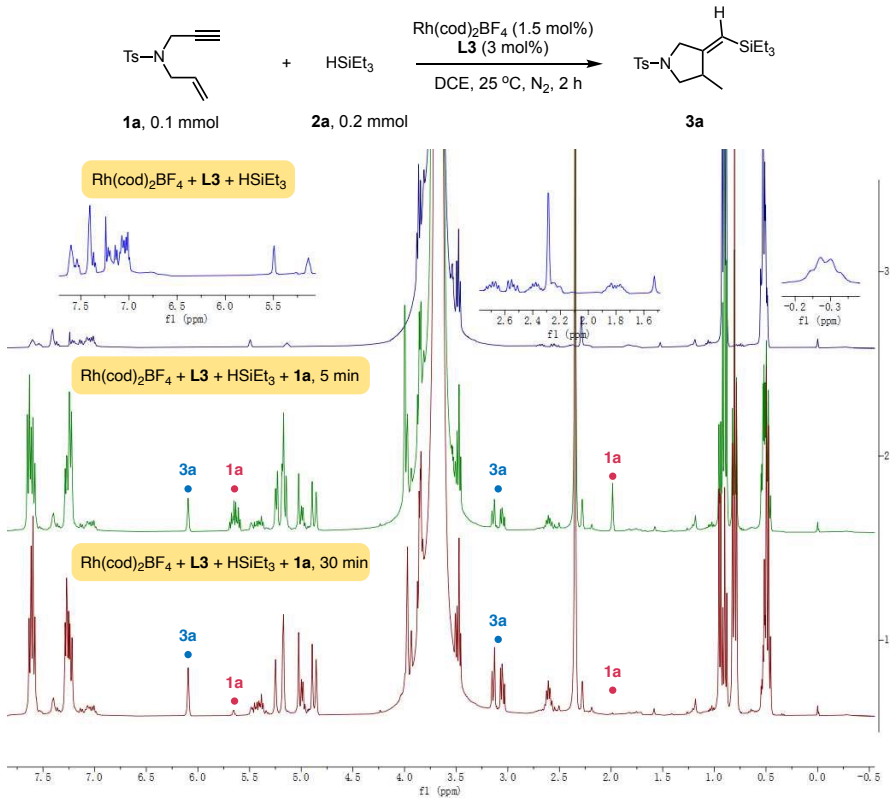


Figure S5. Reaction of 1a and 2a catalyzed by Rh/L3 monitored by *in situ* ^{1}H NMR.

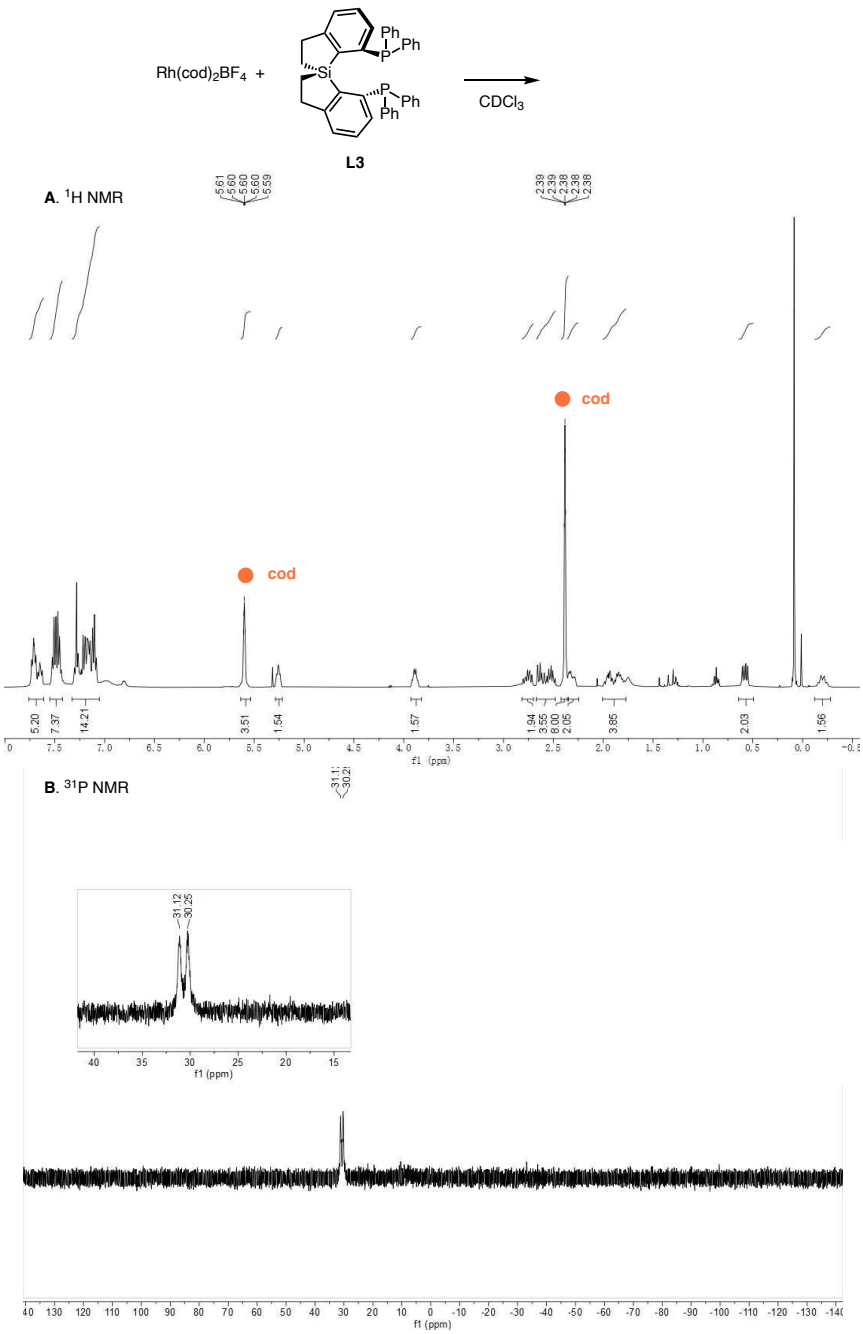


Figure S6. NMR spectra of L3 coordinated with $Rh(cod)_2BF_4$.

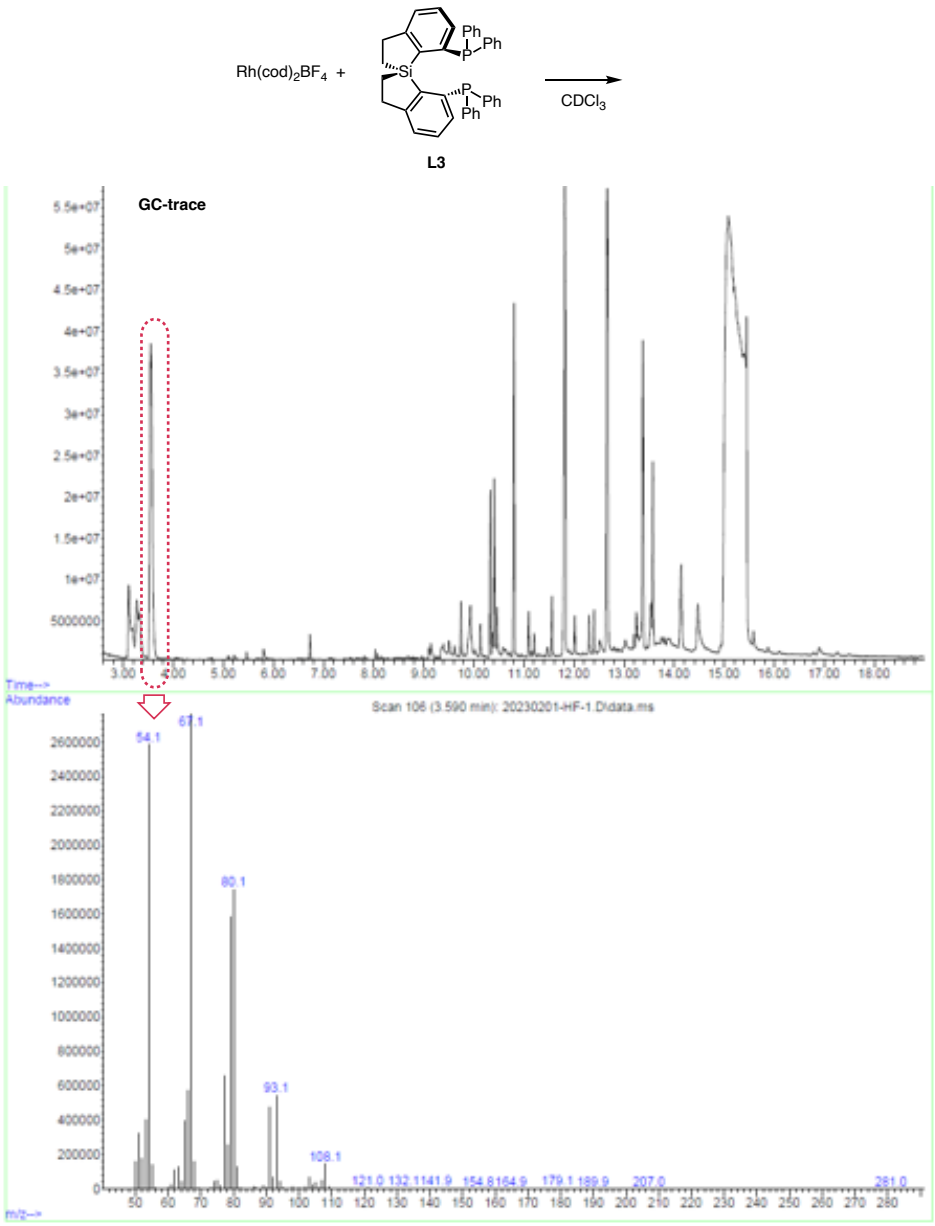


Figure S7. GC-MS analysis of the mixture of $Rh(cod)_2BF_4$ and L3.

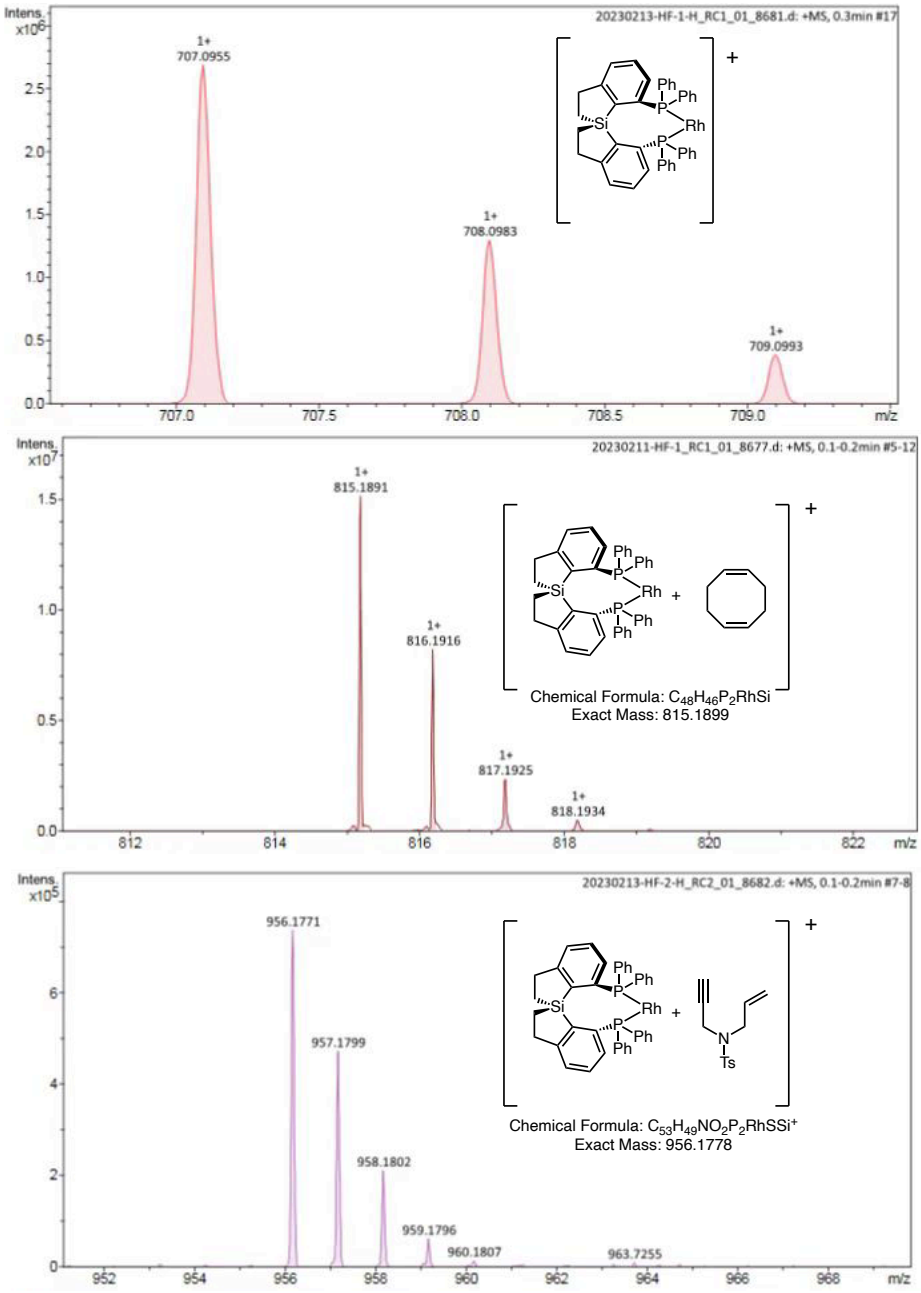


Figure S8. HRMS analysis of Rh/L3.

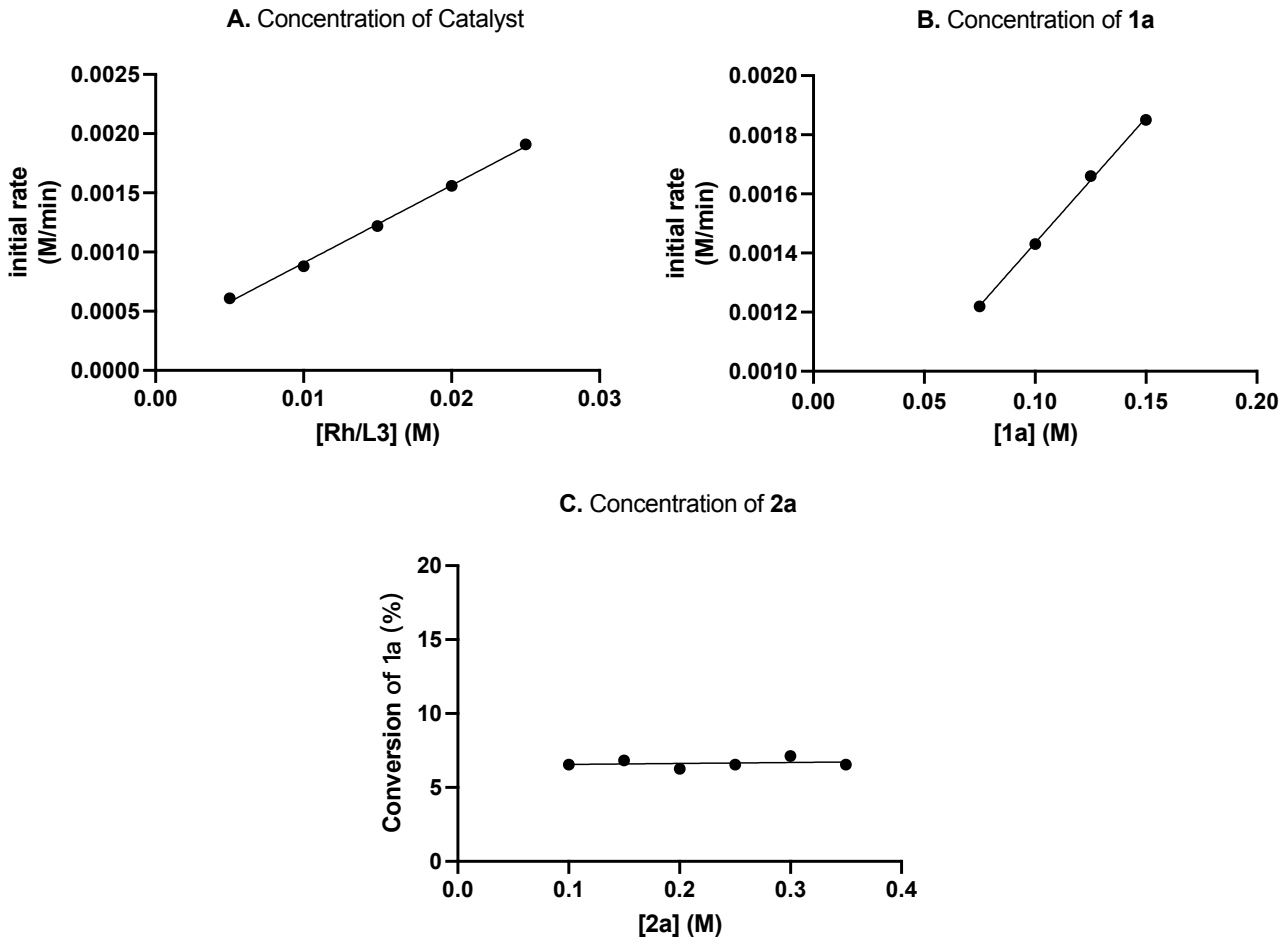


Figure S9. Initial rate studies.

Conditions for **A** and **B**: Reactions were performed with $Rh(cod)_2BF_4$, **L3**, **1a**, and **2a** (2.0 mmol) in DCE (10 mL). Aliquots were removed every 3 min, quenched with saturated NH_4Cl solution, and analyzed by ^1H NMR using dibromoethane as an internal standard.

Conditions for **C**: Reactions were performed with $Rh(cod)_2BF_4$ (0.01 mmol), **L3** (0.02 mmol), **1a** (1.0 mmol) and **2a** (1.0 mmol to 3.5 mmol) in DCE (10 mL). The reactions were quenched after 10 min using saturated NH_4Cl solution and analyzed by GC-MS.

2. General Procedures.

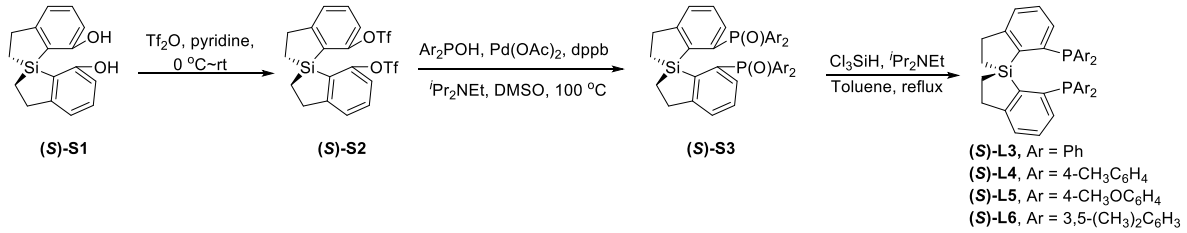
All commercial solvents and chemicals were purchased from Bidepharm, Leyan, Energy Chemical, and TCI and used as received. Dichloroethane (DCE) was purified by passing through activated alumina and stored over 4Å MS. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen.

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to UV light (254 nm). Flash column chromatography was performed using granular silica gel (60-Å pore size, 40–63 μm, 4–6% H_2O content, Syhtnwre).

^1H NMR spectra were recorded with a Bruker AM400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) units on the delta (δ) scale, and are referenced from the residual protium in the $CDCl_3$ (7.26 ppm). Data are reported as follows: chemical shift, [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz (Hz). ^{13}C NMR spectra were recorded with a Bruker AM 400 (100 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) units on the delta (δ) scale, and are referenced from the carbon resonances of $CDCl_3$ (77.23 ppm). ^{31}P NMR spectra were recorded with a Bruker AM400 (161 MHz) spectrometer. ^{19}F NMR spectra were recorded with a Bruker AM400 (376 MHz) spectrometer.

Optical rotations were measured on a Autopol I polarimeter. Enatiomeric excess of **3a-3ac** was determined from the corresponding desilylated products using chiral HPLC chromatography. All HPLC analyses were performed on an Agilent 1220 Series HPLC system with *n*-hexane, isopropanol. High resolution mass spectra (HRMS) were recorded on a a Bruker microTOF Q III spectrometer with electronspray ionization (ESI). Melting points (mp) were recorded on an SRS–optic melting point apparatus.

3. Preparation of Si-SDP ligand L3-L6.

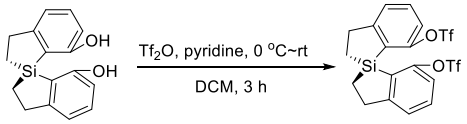


(*S*)-S1 (*S*)-S2 (*S*)-S3

(*S*)-L3, Ar = Ph
(*S*)-L4, Ar = 4-$CH_3C_6H_4$
(*S*)-L5, Ar = 4-$CH_3OC_6H_4$
(*S*)-L6, Ar = 3,5-$(CH_3)_2C_6H_3$

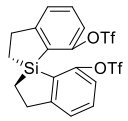
Compound **(*S*)-S1** was synthesized according to literature reports. [1-2]

3.1. Synthesis of Compound (*S*)-S2.



(*S*)-S1 (*S*)-S2

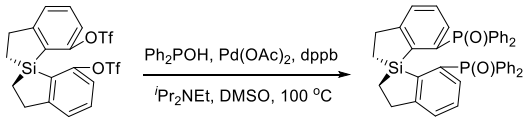
To a solution of (*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silole]-7,7'-diol (**(*S*)-S1**) (2.68 g, 10 mmol) in 30 mL of CH_2Cl_2 was added pyridine (2.5 mL, 30 mmol), and followed by dropwise addition of triflic anhydride (4.25 mL, 25 mmol) at 0 ℃. The mixture was stirred at room temperature for 3 h. After removal of the solvent, the residue was diluted with EtOAc (30 mL) and then washed with 5% aqueous HCl, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by silica gel column chromatography with pretrolum ether/EtOAc (10:1) as eluent to give (*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silole]-7,7'-diylbis(trifluoro methanesulfonate) (**(*S*)-S2**) (5.2 g, 98% yield) as a white solid.



(*S*)-S2

(*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl bis(trifluoromethanesulfonate)((*S*)-S2). White solid (5.2 g, 65% yield), mp: 76.2-77.0 ºC. $[\alpha]_D^{25}$ = -75.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.45 (ddd, *J* = 16.0, 9.5, 6.1 Hz, 2H), 3.29 (ddd, *J* = 17.4, 9.9, 4.1 Hz, 2H), 1.64 (ddd, *J* = 15.7, 9.6, 4.2 Hz, 2H), 1.34 (dt, *J* = 15.6, 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.0, 132.9, 128.1, 125.9, 118.4 (q, *J* = 320.2 Hz), 117.0, 31.4, 9.0. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -74.11. HRMS (ESI) *m/z* calcd for $C_{18}H_{14}F_6NaO_6S_2Si$, $[M + Na]^+$ = 554.9797, found: 554.9799.

3.2. Synthesis of Compound (*S*)-S3-1.

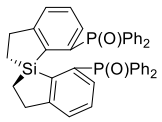


(*S*)-S2 (*S*)-S3-1

To a mixture of (*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silole]-7,7'-diyl bis(trifluoromethanesulfonate) (**(S)-S2**) (2.128 g, 4.0 mmol), diphenylphosphine oxide (3.232 g, 16 mmol), palladium acetate (45 mg, 0.2 mmol) and 1,4-bis(diphenylphospino)butane (dppb, 85 mg, 0.2 mmol) was added 25 mL of degassed DMSO and diisopropylethylamine (2.16 g, 16.8 mmol). The mixture was heated with stirring at 100 ℃ for 8 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc, washed with 5% aqueous HCl and saturated aqueous $NaHCO_3$ solution. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with pretrolum ether/EtOAc (3:1) as eluent to give (*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silol]-7-yl)diphenylphosphine oxide (**(*S*)-S3-1**) (1.35 g,

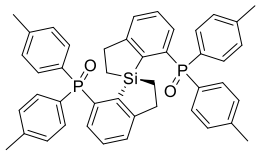
75% yield) as a white solid.

((*S*)-S3-2), **((*S*)-S3-3**, **((*S*)-S3-4)** were synthesized from **(*S*)-S2** by the same procedure as that for **(*S*)-S3-1**.



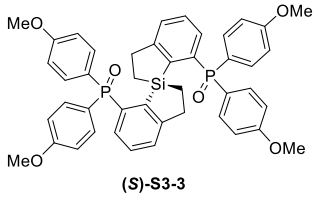
(*S*)-S3-1

(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(diphenylphosphine oxide) ((*S*)-S3-1). White solid (1.35 g, 75% yield), mp: 102.5-103.5 ºC. [α] $_D^{25}$ = -82.4 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 11.2, 8.0 Hz, 4H), 7.46-7.33 (m, 8H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.22 (dd, *J* = 10.9, 7.4 Hz, 6H), 7.13 (t, *J* = 6.2 Hz, 4H), 6.98 (dd, *J* = 12.4, 7.4 Hz, 2H), 3.67-3.53 (m, 2H), 3.19-3.05 (m, 2H), 1.30-1.23 (m, 2H), 0.94-0.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (d, *J* = 13.3 Hz), 143.8 (d, *J* = 14.3 Hz), 134.9 (d, *J* = 108 Hz), 134.5 (d, *J* = 99 Hz), 134.1, 133.6 (d, *J* = 100.5 Hz), 133.1 (d, *J* = 2.4 Hz), 130.8 (d, *J* = 2.5 Hz), 129.4, 129.3, 129.2 (d, *J* = 3.2 Hz), 128.1, 128.0 (d, *J* = 1.5 Hz), 127.6 (d, *J* = 11.9 Hz), 32.4, 11.5. ^{31}P NMR (161 MHz, $CDCl_3$) *δ* 30.0. HRMS (ESI) *m/z* calcd for $C_{40}H_{34}NaO_2P_2Si$, $[M + Na]^+$ = 659.1696, found: 659.1698.



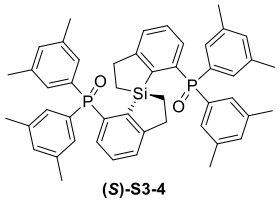
(*S*)-S3-2

(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(4-methylphenyl)phosphine oxide) ((*S*)-S3-2). White solid (40%), mp: 180.3-182.1 ºC. [α] $_D^{25}$ = -108.3 (*c* = 0.5 , CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 4H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.26-7.13 (m, 10H), 6.99 (dd, *J* = 12.4, 7.6 Hz, 2H), 6.93 (dd, *J* = 8.0, 2.4 Hz, 4H), 3.65-3.56 (m, 2H), 3.16-3.08 (m, 2H), 2.39 (s, 6H), 2.27 (s, 6H), 1.38-1.30 (m, 2H), 0.97-0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.69 (d, *J* = 13.3 Hz), 143.88 (d, *J* = 14.5 Hz), 141.51 (d, *J* = 2.7 Hz), 141.03 (d, *J* = 2.8 Hz), 135.75 (d, *J* = 108.6 Hz), 132.47 (d, *J* = 10.4 Hz), 132.00 (d, *J* = 9.7 Hz), 131.41 (d, *J* = 58.6 Hz), 130.39 (d, *J* = 60.0 Hz), 129.51 (d, *J* = 15.6 Hz), 129.29 (d, *J* = 3.1 Hz), 128.94 (d, *J* = 12.0 Hz), 128.52 (d, *J* = 12.4 Hz), 128.07 (d, *J* = 13.6 Hz), 32.60, 21.59, 11.78.^{31}P NMR (161 MHz, $CDCl_3$) *δ* 30.11. HRMS (ESI) *m/z* calcd for $C_{44}H_{42}NaO_2P_2Si$, $[M + Na]^+$ = 715.2322, found: 715.2315.



(*S*)-S3-3

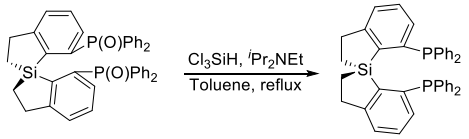
(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(4-methoxyphenyl)phosphine oxide) ((*S*)-S3-3). White solid (62%), mp: 160.5-162.0 ºC. [α] $_D^{25}$ = -113.3 (*c* = 0.5 , CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.25-7.21 (m, 2H), 7.20-7.12 (m, 4H), 7.02-6.96 (m, 2H), 6.95-6.88 (m, 4H), 6.66-6.58 (m, 4H), 3.84 (s, 6H), 3.71 (s, 6H), 3.63-3.53 (m, 2H), 3.17-3.09 (m, 2H), 1.40-1.31 (m, 2H), 0.96-0.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 2.8 Hz), 161.5 (d, *J* = 2.8 Hz), 156.5 (d, *J* = 13.3 Hz), 144.0 (d, *J* = 14.1 Hz), 136.0 (d, *J* = 109.5 Hz), 134.2 (d, *J* = 11.6 Hz), 133.7 (d, *J* = 10.6 Hz), 129.4 (d, *J* = 15.6 Hz), 125.8 (d, *J* = 106 Hz), 125.3 (d, *J* = 107 Hz), 128.0 (d, *J* = 13.4 Hz), 113.7 (d, *J* = 12.6 Hz), 113.2 (d, *J* = 13.1 Hz), 55.2, 54.9, 32.5, 11.7. ^{31}P NMR (161 MHz, $CDCl_3$) *δ* 29.54. HRMS (ESI) *m/z* calcd for $C_{44}H_{42}NaO_6P_2Si$, $[M + Na]^+$ = 779.2116, found: 779.2113.



(*S*)-S3-4

(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(3,5-dimethylphenyl)phosphine oxide) ((*S*)-S3-4). White solid (51%), mp: 153.0-155.2 ºC. $[\alpha]_D^{25}$ = -120.1 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.31-7.26 (m, 8H), 7.15-7.08 (m, 4H), 6.95 (s, 2H), 6.88 (d, *J* = 12.4 Hz, 2H), 3.63-3.55 (m, 2H), 3.19-3.08 (m, 2H), 2.32 (s, 12H), 2.04 (s, 12H), 1.27-1.20 (m, 2H), 0.95-0.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9 (d, *J* = 13.4 Hz), 144.5 (d, *J* = 13.8 Hz), 137.6 (d, *J* = 12.1 Hz), 137.1 (d, *J* = 12.6 Hz), 135.7 (d, *J* = 107.9 Hz), 134.5 (d, *J* = 10.9 Hz), 133.5 (d, *J* = 12.9 Hz), 132.9 (d, *J* = 2.9 Hz), 132.8 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 10.3 Hz), 129.6 (d, *J* = 9.1 Hz), 129.4 (d, *J* = 15.6 Hz), 129.1, 128.1 (d, *J* = 13.5 Hz), 32.4, 21.4, 21.1, 11.76. ^{31}P NMR (161 MHz, $CDCl_3$) *δ* 29.87. HRMS (ESI) *m/z* calcd for $C_{48}H_{51}O_2P_2Si$, $[M + H]^+$ = 749.3128, found: 749.3118.

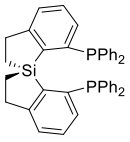
3.3. Synthesis of Ligands L3-L6.



(*S*)-9-1 L3

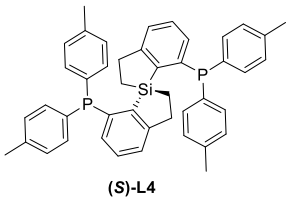
To a mixture of (*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silol]-7-yl)diphenylphosphine oxide (**(*S*)-S3-1**) (0.636 g, 1 mmol) and diisopropylethylamine (5.47 g, 82 mmol) in toluene (20 mL) was added Cl_3SiH (3.0 mL, 30 mmol) at 0 ℃. The reaction mixture was stirred at 110 ℃ for 3 days. After cooling to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with pretrolum ether/EtOAc (50:1) as eluent to give (S)-7,7'-bis(diphenylphosphanyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[b]silole] (**(*S*)-L3**) as a white solid (483 mg, 80% yield). The product was dissolved in pretrolum ether and CH_2Cl_2, layered with hexane, and allowed to stand at room temperature to give white crystals of the title compound, suitable for X-ray study.

(*S*)-L4, **(*S*)-L5**, **(*S*)-L6** were synthesized from **(*S*)-S2** by the same procedure as that for **(*S*)-L3**.



(*S*)-L3

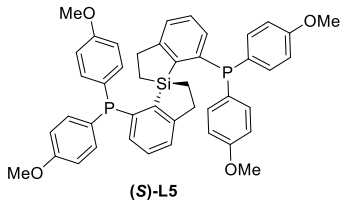
(*S*)-7,7'-bis(diphenylphosphaneyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] ((*S*)-L3). White solid (483 mg, 80% yield), mp: 162.2-163.2 ℃. $[\alpha]_D^{25}$ = -190.2 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.29-6.94 (m, 20H), 6.87 (s, 2H), 6.71 (s, 4H), 3.65-3.46 (m, 2H), 3.27-3.07 (m, 2H), 1.20-1.08 (m, 2H), 1.07-0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1 (d, *J* = 15.4 Hz), 146.2, 145.7, 142.4 (d, *J* = 7.7 Hz), 138.7 (d, *J* = 12.6 Hz), 137.4 (d, *J* = 12.4 Hz), 133.4 (d, *J* = 19.6 Hz), 132.9 (d, *J* = 18.1 Hz), 130.8, 129.9, 128.2 (d, *J* = 5.9 Hz), 127.9, 127.8, 126.5, 31.9 (d, *J* = 8.7 Hz), 9.9 (d, *J* = 5.1 Hz). ^{31}P NMR (161 MHz, $CDCl_3$) *δ* -6.58. HRMS (ESI) *m/z* calcd for $C_{40}H_{35}P_2Si$, $[M + H]^+$ = 605.1978, found: 605.1975.



(*S*)-L4

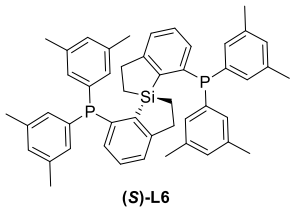
(*S*)-7,7'-bis(4-CH_3-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] ((*S*)-L4). White solid

(75 mg, 60% yield), mp: 145.6-147.1 ℃. $[\alpha]_D^{25}$ = -194.2 (*c* = 1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 4H), 7.14-7.09 (m, 4H), 7.08-7.04 (m, 4H), 6.93-6.90 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 4H), 6.66 (t, *J* = 8.0 Hz, 4H), 3.64-3.56 (m, 2H), 3.25-3.19 (m, 2H), 2.36 (s, 6H), 2.28 (s, 6H), 1.21-1.14 (m, 2H), 1.07-0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2 (d, *J* = 15.4 Hz), 146.0, 145.5, 143.1 (d, *J* = 8.1 Hz), 137.66 (d, *J* = 5. Hz), 135.5 (d, *J* = 11.1 Hz), 134.1 (d, *J* = 11.1 Hz), 133.6 (d, *J* = 19.9 Hz), 133.0 (d, *J* = 18.1 Hz), 130.6, 129.8, 129.0 (d, *J* = 6.2 Hz), 128.7 (d, *J* = 7.2 Hz), 126.4, 31.9 (d, *J* = 8.6 Hz), 21.3, 21.3, 10.0 (d, *J* = 5.2 Hz). ^{31}P NMR (161 MHz, $CDCl_3$) δ -8.27. HRMS (ESI) *m/z* calcd for $C_{44}H_{42}NaP_2Si$, $[M + H]^+$ = 661.2604, found: 661.2580.



(*S*)-L5

(*S*)-7,7'-bis(4-OCH$_3$-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] ((*S*)-L5). White solid (46.8 mg, 75% yield), mp: 185.5-187.1 ℃. $[\alpha]_D^{25}$ = -201.1 (*c* = 1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.9 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 4H), 6.87 (t, *J* = 10.0 Hz, 6H), 6.64 (m, 8H), 3.82 (s, 6H), 3.73 (s, 6H), 3.60 (m, 2H), 3.23 (m, 2H), 1.19 (m, 2H), 1.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 155.2 (d, *J* = 14.7 Hz), 143.8, 135.0 (d, *J* = 21.2 Hz), 134.3 (d, *J* = 19.3 Hz), 130.3, 130.0, 130.1, 129.8, 128.7, 128.6, 126.3, 113.9 (d, *J* = 6.7 Hz), 113.5 (d, *J* = 7.9 Hz), 55.1, 54.97, 32.0 (d, *J* = 8.3 Hz), 10.0 (d, *J* = 6.3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$) δ -9.92. HRMS (ESI) *m/z* calcd for $C_{44}H_{43}O_4P_2Si$, $[M + H]^+$ = 725.2394, found: 725.2393.

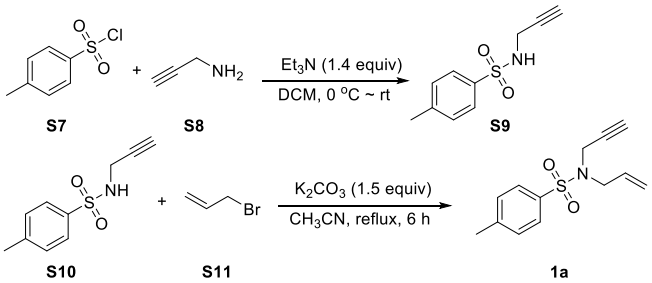


(*S*)-L6

(*S*)-7,7'-bis(3,5-(CH$_3$)$_2$-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] ((*S*)-L6). White solid (36 mg, 50% yield), mp: 163.7-165.2 ℃. $[\alpha]_D^{25}$ = -155.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 7.09 (s, 2H), 6.88 (s, 2H), 6.77-6.73 (m, 6H), 6.38-6.22 (m, 4H), 3.59-3.50 (m, 2H), 3.28-3.10 (m, 2H), 1.99 (s, 12H), 2.22 (s, 12H), 1.14-0.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1 (d, *J* = 16.0 Hz), 146.9, 146.3, 143.3 (d, *J* = 8.6 Hz), 139.1 (d, *J* = 11.9 Hz), 137.5, 137.3 (d, *J* = 6.6 Hz), 137.0 (d, *J* = 7.8 Hz), 131.5 (d, *J* = 20.5 Hz), 130.8, 130.5 (d, *J* = 17.7 Hz), 129.9, 129.8 (d, *J* = 62.8 Hz), 126.4, 31.9 (d, *J* = 9.2 Hz), 21.4, 21.1, 10.0 (d, *J* = 5.5 Hz). ^{31}P NMR (161 MHz, $CDCl_3$) δ -5.80. HRMS (ESI) *m/z* calcd for $C_{48}H_{51}P_2Si$, $[M + H]^+$ = 717.3230, found: 717.3222.

4. Preparation of 1,6-enynes substrates (1a-1s).

4.1. Preparation of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a).

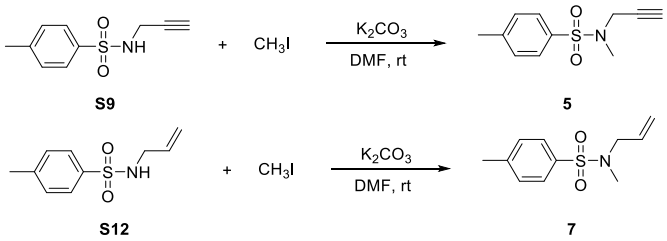


To a solution of propargylamine (3.35 g, 3.84 mL, 60 mmol) and triethylamine (8.48 g, 11.65 mL, 84 mmol) was added tosyl chloride (9.53 g, 50 mmol) portionwise at 0°C. The mixture was stirred at 25 ºC for 3 h. Water (50 mL) was added to the mixture. The mixture was extracted by dichloromethane (2 × 50 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used directly in the next step without further purification.

To a suspension of *N*-(prop-2-yn-1-yl)-4-methylbenzenesulfonamide (3.2 g, 15.3 mmol) and K_2CO_3 (3.16 g, 23 mmol) in acetonitrile was added allyl bromide (2.98 g, 2.13 mL, 23 mmol) dropwise. The mixture was stirred at 80 ºC for 3 h and concentrated under reduced pressure. The mixture was diluted with EtOAc and filtered through Celite. The solid was washed with EtOAc. The combined filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (15:1) to give the product **1a.**

1,6-enynes **1a-1s** were prepared following the general procedures. **1a**[3], **1b**[3], **1e**[5], **1g**[4], **1i**[5], **1n**[6], **1p**[7], **1r**[3] were reported compounds.

4.2. Preparation of *N*-Methyl-*N*-prop-2-ynyl-p-toluenesulfonamide (5) and *N*-allyl-*N*,4-dimethylbenzenesulfonamide (7) .[8]



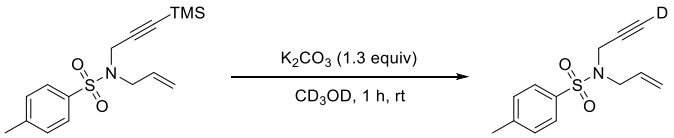
4-Methyl-*N*-(prop-2-yn-1-yl)benzene-1-sulfonamide (2.88 g, 13.8 mmol) was dissolved in DMF and the solution was stirred at room temperature. To this solution was added K_2CO_3 (2.85 g, 20.7 mmol), followed by MeI (2.93 g, 1.28 mL, 20.7 mmol). The mixture was stirred overnight at room temperature. The reaction mixture was dissolved in EtOAc and washed with water and satured NH_4Cl. The resulting suspension was filtered through Celite and the solid was washed with EtOAc. The combined filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with pretrolum ether/EtOAc (15:1) as eluent to give *N*-methyl-*N*-prop-2-ynyl-*p*-toluenesulfonamide (**5**, 2.88 g, 94%).

Compound **5**. White solide, mp: 71.2-72.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 4.03 (d, *J* = 2.8 Hz, 2H), 2.83 (s, 3H), 2.44 (s, 3H), 2.10 (t, *J* = 2.4 Hz, 1H).

N-allyl-4-methylbenzenesulfonamide (2.11 g, 10 mmol) was dissolved in DMF and the solution was stirred at room temperature. K_2CO_3 (2.07 g, 15 mmol) was added to this solution, followed by MeI (2.13 g, 0.93 mL, 15 mmol). The mixture was stirred overnight at room temperature. The reaction mixture was dissolved in AcOEt and washed with water and satured NH_4Cl. The resulting suspension was filtered through Celite and the solid was washed with EtOAc. The combined filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with pretrolum ether/EtOAc (15:1) as eluent to give *N*-allyl-*N*,4-dimethylbenzenesulfonamide (**7**, 2.0 g, 90%).

Compound **7**. White solide, mp: 75.8-76.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.74-5.62 (m, 1H), 5.17 (dd, *J* = 16.4, 5.9 Hz, 2H), 3.61 (d, *J* = 6.0 Hz, 2H), 2.65 (s, 3H), 2.42 (s, 3H).

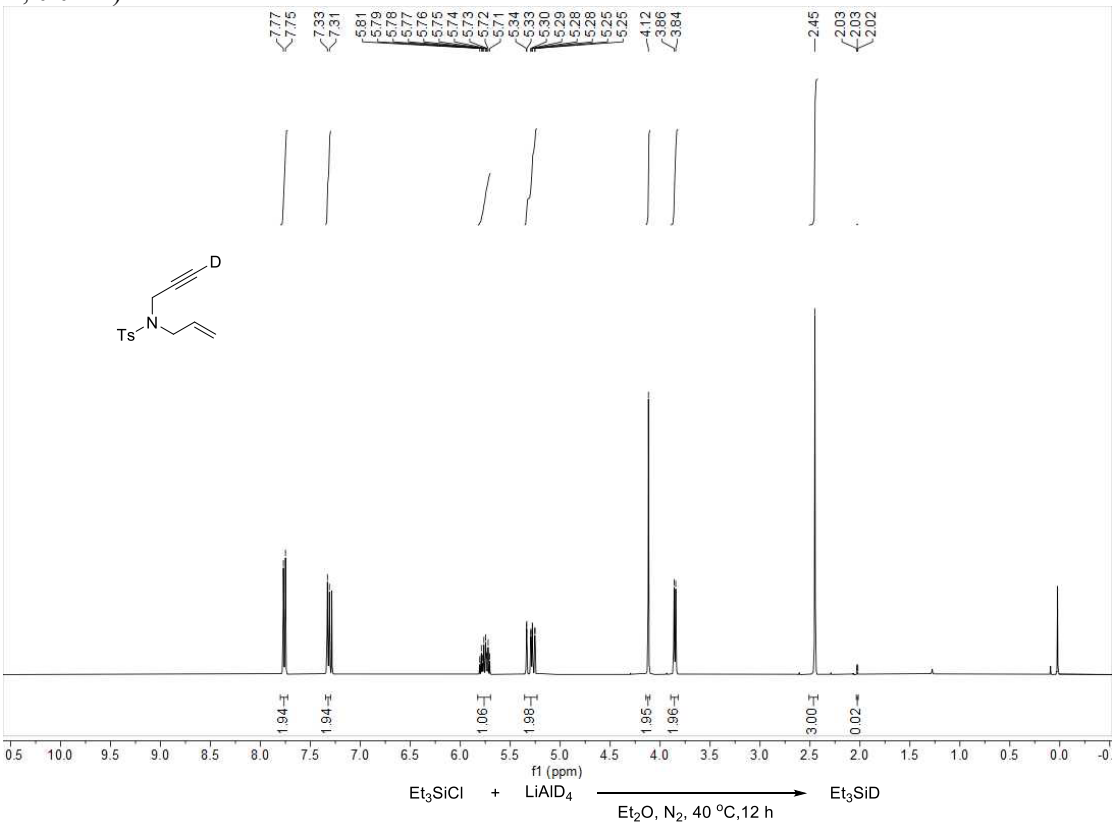
4.3. Preparation of 1a-*d* and Et_3SiD.



S13 **1a-*d***

S13 (96 mg, 0.3 mmol)[9] was added to a suspension of K_2CO_3 (54 mg, 0.39 mmol) in CD_3OD (2 mL), and then stirred at 25 ℃ for 1 hour under N_2. The mixture was extracted with D_2O and $CDCl_3$. The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to gave **1a-*d*** (65 mg, 86% yield, 99.8 D). [10a]

Compound **1a-*d***. White solide, mp: 60.3-60.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 5.80-5.70 (m, 1H), 5.51-5.14 (m, 1H), 4.12 (s, 1H), 3.85 (d, J = 6.4 Hz, 1H), 2.45 (s, 2H). 2.02 (t, J = 2.4 Hz, 0.02 H).

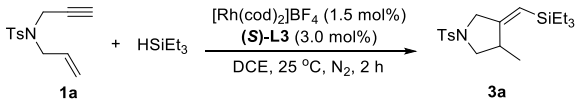


Et_3SiCl + $LiAlD_4$ → Et_3SiD (Et_2O, N_2, 40 °C, 12 h)

Et_3SiCl (15 mmol, 3.0 equiv) was added dropwise to a stirred solution of $LiAlD_4$ (5 mmol, 1.0 equiv) in anhydrous diethyl ether (15 mL) under N_2 atmosphere. The reaction mixture was refluxed at 40 ºC for 12 h and cooled to room temperature. The reaction was quenched by adding aqueous solution of sodium hydroxide (15 ml, 10 wt%). The mixture was extracted by diethyl ether (10 mL x 3). The combined organic layers were dried over Na_2SO_4, evaporated under reduced pressure, and purified by column chromatography on silica gel (pretrolum ether/EtOAc (50:1)) to give Et_3SiD (0.9 g, 51% yield, >99% D). [10b] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H).

5. Silylcyclization of 1,6-enynes and derivatization of the silylcyclization products.

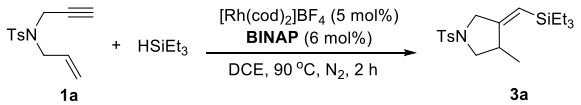
5.1. General procedure for asymmetric silylcyclization of 1,6-enynes.



1a **3a**

A mixture of $[Rh(cod)_2]BF_4$ (0.12 mg, 0.003 mmol) and **(*S*)-L3** (3.6 mg, 0.006 mmol) in dichloroethane (DCE, 1 mL) was stirred under nitrogen at 25 ℃ for 30 min. Triethylsilane (46 .4 mg, 0.4 mmol) was added at 25 ℃. After stirring for another 20 min, 1,6-enyne (**1a**, 50.0 mg, 0.2 mmol) in 1.0 mL of DCE was added and stir at room temperature for 2.0 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with pretrolum ether/EtOAc (20:1) as eluent to give **3a** (Colorless oil, 67 mg, 92% yield).

5.2. General procedure for the synthesis of racemic products.

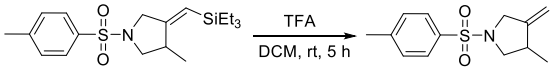


1a **3a racemic**

The mixture of $[Rh(cod)_2]BF_4$ (4 mg, 0.01 mmol) and **(±)-BINAP** (7.5 mg, 0.012 mmol) in dichloroethane (DCE, 1 mL) was stirred under nitrogen at 25 ℃ for 30 min. Triethylsilane (46 .4 mg, 0.4 mmol) was added at 25 ℃. After stirring for another 20 min, 1,6-enyne (**1a**, 50.0 mg, 0.2 mmol) in 1.0 mL of DCE was added and stir at 90 ℃ for 2.0 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with pretrolum ether/EtOAc (20:1) as eluent to give **(±)-3a** (Colorless oil, 44.6 mg, 62% yield).

5.3. General procedure for desilylation.

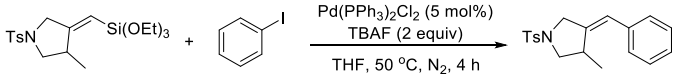
The enantiomeric excesses of silylcyclization products were determined by chiral HPLC of their desilylated compounds **3a'**.



3a **3a'**

A solution of **3a** (36.5 mg, 0.1 mmol) in 0.5 mL of trifluoroacetic acid and 2 mL of CH_2Cl_2 was stirred at room temperature for 5 h, and then quenched with saturated aqueous sodium carbonate. After extraction with CH_2Cl_2, the organic layer was washed with water and brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (6:1) to give the desilylated compound **3a'** (33.2 mg, 91% yield).

5.4. Coupling of 3aa with iodobenzene. [4,11]

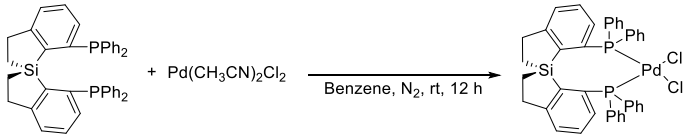


3aa **S14**

Under a nitrogen atmosphere, the solution of **3aa** (60 mg, 0.15 mmol), tetrabutylammonium fluoride hydrate (95 mg, 0. mmol) and iodobenzene (41.0 mg, 0.2 mmol) in 0.5 mL THF was stirred at room temperature for 15 min. $Pd(PPh_3)_2Cl_2$ (5.3 mg, 5 mol%) was added, and the resulting mixture was heated at 40 ℃ for 4. The filtrate was concentrated under reduce pressure and the residue was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (10:1) to give the compound **S14** (44 mg, 90% yield, 93% ee).

Compound **S14.** Colorless oil. $[\alpha]_D^{25} = 45.57$ (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24-7.21 (m, 3H), 6.27 (q, *J* = 2.0 Hz, 1H), 4.18 (dt, *J* = 14.0, 1.6 Hz, 1H), 3.81 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.36-3.12 (m, 3H), 2.46 (s, 3H), 1.15 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.9, 136.4, 132.6, 129.7, 128.5, 128.0, 127.8, 127.0, 122.4, 55.7, 53.0, 35.1, 21.5, 18.5. The ee value of product **S14** was determined by HPLC using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; *t*R = 11.53 min (minor) and 13.97 min (major).

6. Preparation {$PdCl_2$[(S)-L3]} (S15).



(S)-L3 S15

A solution of **(*S*)-Si-SDP (L3)** (60.4 mg, 0.1 mmol) in 1.0 mL of benzene was added to a mixture of $Pd(CH_3CN)_2Cl_2$ (25.7 mg, 0.1 mmol) in 2.0 mL of benzene at room temperature, and the mixture was stirred overnight. The pale-yellow precipitate formed was collected by filtration, washed with benzene, dried under vacuum to provide **S15** as a yellow solid (70.2 mg, 90% yield).

Yellow solid. mp: 270 ℃ dec. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.92 (m, 3H), 7.55-7.50 (m, 3H), 7.46-7.35 (m, 10H), 7.28-7.18 (m, 4H), 7.11-7.04 (dt, *J* = 15.5, 8.0 Hz, 6H), 2.85-2.59 (m, 4H), 0.58 (q, *J* = 7.2 Hz, 2H), -0.06--0.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (d, *J* = 13.3 Hz), 139.4 (d, *J* = 21.1 Hz), 135.60, 133.6 (d, *J* = 61.6 Hz), 133.5 (d, *J* = 11.0 Hz), 132.8 (d, *J* = 9.9 Hz), 131.0 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 10.2 Hz), 130.1 (d, *J* = 2.8 Hz), 128.9 (d, *J* = 2.1 Hz), 128.8 (d, *J* = 3.2 Hz), 128.6 (d, *J* = 10.8 Hz), 128.3 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 11.7 Hz), 30.78, 9.53. ^{31}P NMR (CDCl3): δ 37.24. HRMS (ESI) *m/z* calcd for $C_{40}H_{32}ClP_2PdSi$, $[M]^+$ = 735.0234, found: 735.0232.

7. Characterization of Rh-L3.

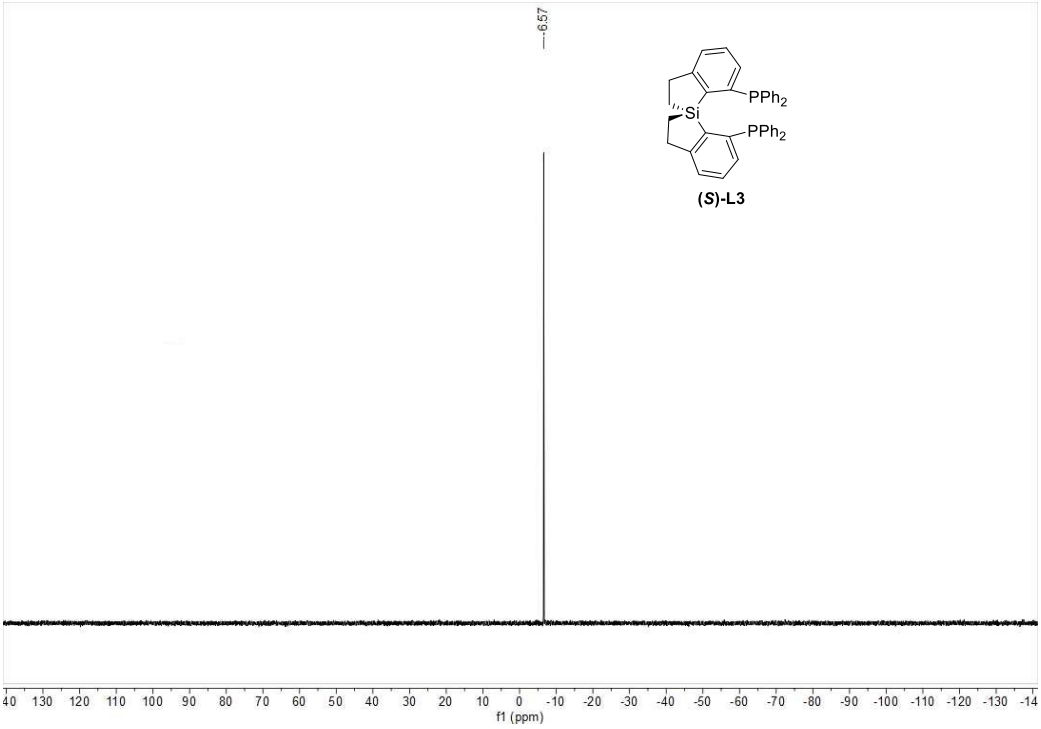
Inside an argon-filled glovebox, an oven-dried 5 mL vial was charged with $[Rh(cod)BF_4]_2$ (8 mg, 0.025 mmol), (*S*)-**(L3)** (18 mg, 0.03 mmol) and 1 mL DCE. The mixture was stirred at room temperature for 30 min and analyzed with NMR.

^{31}P NMR

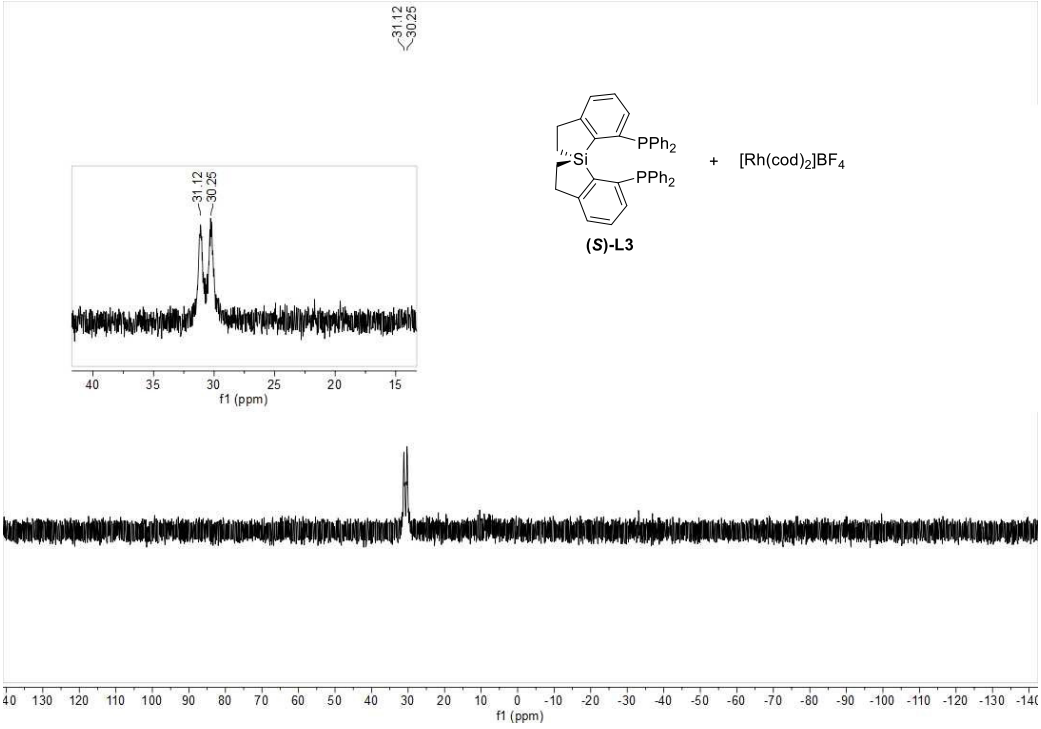
1) (*S*)-Si-SDP (**L3)** (12 mg, 0.02 mmol) in 1 mL $CDCl_3$. ^{31}P NMR (161 MHz, $CDCl_3$): δ -6.57

2) $[Rh(cod)BF_4]_2$ (8 mg, 0.025 mmol), (*S*)-Si-SDP **(L3)** (18 mg, 0.03 mmol) and 1 mL $CDCl_3$. The mixture was stirred at room temperature for 30 min. ^{31}P NMR (161 MHz, $CDCl_3$): δ 30.68 (d, J = 140.07 Hz).

1)

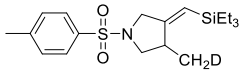


2)

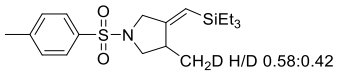


8. Characterization data.

8.1. Characterization Data of Deuterated compounds.

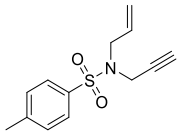


(*E*)-1-tosyl-3-((triethylsilyl)methylene)pyrrolidine-4-*d* (3a-*d*-2). Colorless oil, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.25 (q, J = 2.4 Hz), 4.09-4.05 (m, 1H), 3.59 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.26 (dd, *J* = 9.6, 1.2 Hz, 1H), 3.15 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.72-2.67 (m, 1H), 2.43 (s, 3H), 1.04 (dt, *J* = 6.8, 2.0 Hz, 2H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 143.5, 133.0, 129.65, 127.7, 117.8, 55.5, 53.7, 37.7, 21.5, 20.6(t, *J* = 19.5 Hz), 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{31}DNO_2SSi$, $[M + H]^+$ = 367.1980, found: 367.1990.

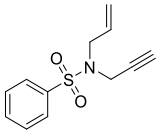


(*E*)-1-tosyl-3-((triethylsilyl)methylene)pyrrolidine-4-*d* (3a-*d*-3). Colorless oil, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.26 (q, *J* = 2.0 Hz, 1H), 4.07 (dt, *J* = 14.0, 1.6 Hz, 1H), 3.60 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.27 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.15 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.76-2.65 (m, 1H), 2.44 (s, 3H), 1.05 (m, 2.58 H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 143.5, 133.0, 129.6, 127.7, 117.8, 55.5, 53.7, 37.8, 21.5, 20.9, 20.6 (t, *J* = 19.0 Hz), 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{31}DNO_2SSi$, $[M + H]^+$ = 367.1980, found: 367.1985.

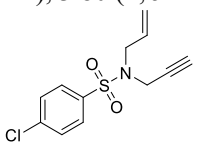
8.2. Characterization Data of 1,6-enynes.



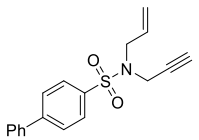
***N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a).**[3] White solid. 88% yield. m.p: 59.1-60.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.69-5.80 (m, 1H), 5.36-5.23 (m, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 3.84 (dt, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.02 (t, *J* = 2.4 Hz, 1H).



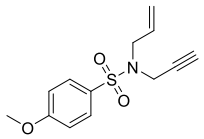
***N*-allyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b).**[3] Colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 2H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 2H), 5.71-5.61 (m, 1H), 5.29-5.15 (m, 2H), 4.04 (d, *J* = 2.4 Hz, 2H), 3.80 (d, *J* = 6.4, 2H), 2.00 (t, *J* = 2.4 Hz, 1H).



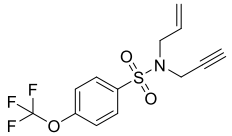
***N*-allyl-4-chloro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c).** White solid. 90% yield. m.p: 71.1-72.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 5.80-5.70 (m, 1H), 5.36-5.25 (m, 2H), 4.12 (d, *J* = 2.4 Hz, 2H), 3.84 (d, *J* = 4.0 Hz, 2H), 2.05 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.5, 131.5, 129.2, 129.1, 120.3, 76.1, 74.0, 49.0, 35.7. HRMS (ESI) *m/z* calcd for $C_{12}H_{13}ClNO_2S$, $[M + H]^+$ = 270.0350, found: 270.0355.



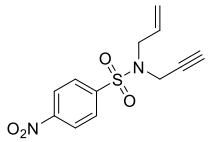
***N*-allyl-*N*-(prop-2-yn-1-yl)-[1,1'-biphenyl]-4-sulfonamide (1d).** White solid. 83% yield. m.p: 77.0-78.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.54-7.48 (m, 2H), 7.47-7.42 (m, 1H), 5.79 (m, 1H), 5.38-5.27 (m, 2H), 4.16 (d, *J* = 2.5 Hz, 2H), 3.91 (d, *J* = 6.5 Hz, 2H), 2.03 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.2, 137.4, 131.8, 129.1, 128.5, 128.3, 127.5, 127.3, 120.2, 76.4, 73.9, 49.1, 35.8. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2S$, $[M + H]^+$ = 312.1053, found: 312.1049.



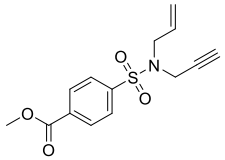
***N*-allyl-4-methoxy-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1e).**[5] White solid. 78% yield. m.p: 100.2-101.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.80-5.70 (m, 1H), 5.36-5.20 (m, 2H), 4.10 (d, *J* = 2.8 Hz, 1H), 3.88 (s, 3H), 3.83 (d, *J* = 6.4 Hz, 2H), 2.03 (t, *J* = 2.4 Hz, 1H).



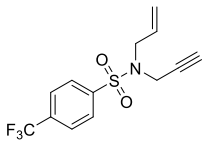
***N*-allyl-*N*-(prop-2-yn-1-yl)-4-(trifluoromethoxy)benzenesulfonamide (1f).** Light yellow liquid, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.82-5.70 (m, 1H), 5.35-5.26 (m, 2H), 4.12 (d, *J* = 2.4 Hz, 2H), 3.86 (d, *J* = 6.4 Hz, 2H), 1.99 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 137.3, 131.4, 129.9, 120.8, 120.4, 120.2 (q, *J* = 258.2 Hz), 75.9, 74.0, 49.0, 35.7. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -57.57. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}F_3NO_3S$, $[M + H]^+$ = 320.0563, found: 320.0570.



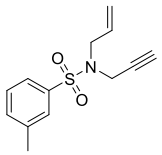
***N*-allyl-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1g)**[4]. White solid. 83% yield. m.p: 100.2-101.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 5.82-5.72 (m, 1H), 5.38-5.30 (m, 2H), 4.18 (d, *J* = 2.4 Hz, 2H), 3.87 (d, *J* = 6.0, 2H), 2.04 (d, *J* = 2.5, 1H).



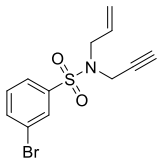
Methyl 4-(*N*-allyl-*N*-(prop-2-yn-1-yl)sulfamoyl)benzoate (1h). White solid. 88% yield. m.p: 87.3-88.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 5.78-5.68 (m, 1H), 5.35-5.24 (m, 2H), 4.13 (d, *J* = 2.4 Hz, 2H), 3.97 (s, 3H), 3.86 (d, *J* = 6.4 Hz, 2H), 1.98 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.9, 133.9, 131.4, 130.1, 127.7, 120.4, 75.9, 74.1, 52.6, 49.0, 35.8. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO_4S$, $[M + H]^+$ = 294.0795, found: 294.0788.



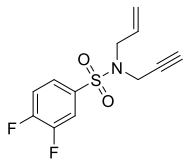
***N*-allyl-*N*-(prop-2-yn-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1i).**[5] Colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 5.79-5.69 (m, 1H), 5.39-5.21 (m, 1H), 4.14 (d, *J* = 2.8 Hz, 1H), 3.87 (d, *J* = 6.4 Hz, 1H), 2.01 (t, *J* = 2.4 Hz, 1H).



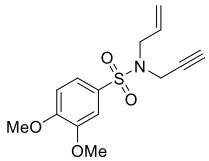
***N*-allyl-3-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1j).** Light yellow liquid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.61 (m, 2H), 7.38 (d, *J* = 4.8 Hz, 2H), 5.72 (m, 1H), 5.33-5.21 (m, 2H), 4.10 (d, *J* = 2.4 Hz, 2H), 3.83 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 2.02 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.6, 133.6, 131.8, 128.7, 128.0, 124.8, 120.0, 76.3, 73.7, 49.0, 35.8, 21.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}NO_2S$, $[M + H]^+$ = 250.0896, found: 250.0892.



***N*-allyl-3-bromo-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1k).** Light yellow liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (q, *J* = 1.6 Hz, 1H), 7.80-7.77 (m, 1H), 7.72-7.69 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 5.79-5.58 (m, 1H), 5.34-5.26 (m, 2H), 4.12 (d, *J* = 2.0 Hz, 2H), 3.83 (dd, *J* = 6.8, 1.6 Hz, 2H), 2.07 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 135.8, 131.43, 130.6, 130.4, 126.2, 122.8, 120.4, 76.0, 74.2, 49.1, 35.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}BrNaNO_2S$, $[M + H]^+$ = 335.9664, found: 335.9669.

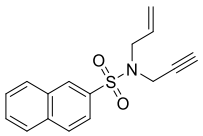


***N*-allyl-3,4-difluoro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1l).** White solid. 88% yield. m.p: 73.6-74.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.45 (m, 1H), 7.67-7.63 (m, 1H), 7.35-7.28 (m, 1H), 5.80-5.69 (m, 1H), 5.35-5.27 (m, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 3.83 (dd, *J* = 6.4, 2.0 Hz, 2H), 2.07 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (dd, *J* = 255.4, 12.6 Hz), 149.9 (dd, *J* = 252.4, 13.4 Hz), 135.7 (t, 4.5 Hz), 131.3, 124.9 (q, *J* = 4.0 Hz), 120.5, 117.9 (d, *J* = 18.3 Hz), 117.6 (dd, *J* = 19.8, 1.9 Hz), 75.9, 74.2, 49.1, 35.8. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -129.52 (d, *J* = 18.8 Hz), -134.14 (d, *J* = 22.56 Hz). HRMS (ESI) *m/z* calcd for $C_{12}H_{12}F_2NO_2S$, $[M + H]^+$ = 272.0551, found: 272.0555.

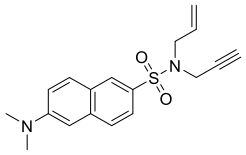


***N*-allyl-3,4-dimethoxy-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1m).** Light yellow liquid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.78-5.68 (m, 1H), 5.33-5.22 (m, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 3.81 (d, *J* = 6.4 Hz, 2H), 2.05 (t, *J* = 2.4 Hz,

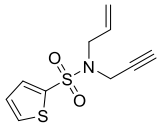
1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.8, 131.8, 130.5, 121.7, 120.0, 110.3, 110.2, 77.2, 73.7, 56.2, 56.1, 48.9, 35.7. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NO_4S$, $[M + H]^+$ = 296.0951, found: 296.0954.



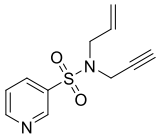
***N*-allyl-*N*-(prop-2-yn-1-yl)naphthalene-2-sulfonamide (1n)**.[6] White solid. 85% yield. m.p: 89.6-91.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.9 Hz, 1H), 8.02-7.95 (m, 2H), 7.94-7.91 (m, 1H), 7.86 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.68-7.60 (m, 2H), 5.82-5.72 (m, 1H), 5.35-5.24 (m, 2H), 4.18 (d, *J* = 2.4 Hz, 2H), 3.92 (d, *J* = 6.4, Hz, 2H), 1.93 (t, *J* = 2.4 Hz, 1H).



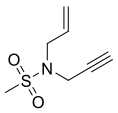
***N*-allyl-6-(dimethylamino)-*N*-(prop-2-yn-1-yl)naphthalene-2-sulfonamide (1o).** Fluorescent green oil, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dt, *J* = 8.4, 1.2 Hz, 1H), 8.32 (dt, *J* = 8.8, 1.2 Hz, 1H), 8.27 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59-7.51 (m, 2H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.74-5.64 (m, 1H), 5.32-5.20 (m, 2H), 4.15 (d, *J* = 2.4 Hz, 2H), 4.00 (d, *J* = 6.4 Hz, 2H), 2.89 (s, 6H), 2.09 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 134.4, 131.9, 130.6, 130.1, 130.0, 128.1, 123.1, 120.1, 119.5, 115.2, 77.1, 73.3, 48.8, 45.4, 35.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_2O_2S$, $[M + H]^+$ = 329.1318, found:329.1320.



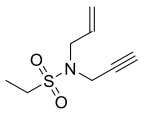
***N*-allyl-*N*-(prop-2-yn-1-yl)thiophene-2-sulfonamide (1p)**.[7] Light yellow liquid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.4, 3.6 Hz, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 5.92-5.73 (m, 1H), 5.40-5.25 (m, 3H), 4.13 (d, *J* = 2.4 Hz, 2H), 3.92 (d, *J* = 6.4 Hz, 2H), 2.06 (t, *J* = 2.4 Hz, 1H).



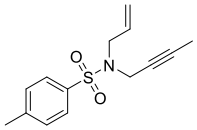
***N*-allyl-*N*-(prop-2-yn-1-yl)pyridine-3-sulfonamide (1q).** Hydrazone black solid, 70% yield, m.p: 54.3-55.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 2.4 Hz, 1H), 8.82 (dd, *J* = 4.8, 2.4 Hz, 1H), 8.16 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.50-7.47 (m, 1H), 5.81-5.71 (m, 1H), 5.37-5.27 (m, 2H), 4.15 (d, *J* = 2.4 Hz, 2H), 3.87 (d, *J* = 6.4 Hz, 2H), 2.05 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 148.4, 135.5, 135.4, 131.2, 123.5, 120.5, 75.9, 74.4, 49.0, 35.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{13}N_2O_2S$, $[M + H]^+$ = 237.0692, found:237.0696.



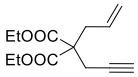
***N*-allyl-*N*-(prop-2-yn-1-yl)methanesulfonamide (1r).**[3] Light yellow liquid, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.41-5.27 (m, 2H), 4.06 (d, *J* = 2.4 Hz, 2H), 3.89 (d, *J* = 6.4 Hz, 2H), 2.95 (s, 3H), 2.39 (t, *J* = 2.4 Hz, 1H).



***N*-allyl-*N*-(prop-2-yn-1-yl)ethanesulfonamide (1s)**. Colorless oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.70 (m, 1H), 5.35-5.24 (m, 2H), 4.02 (d, *J* = 3.6 Hz, 2H), 3.92 (dd, *J* = 8.8, 3.2 Hz, 4H), 3.08 (q, *J* = 3.2 Hz, 2H), 2.36 (t, *J* = 2.4 Hz, 1H), 1.36 (t, 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 119.8, 77.6, 73.8, 49.3, 46.5, 35.4, 7.7. HRMS (ESI) *m/z* calcd for $C_8H_{14}NO_2S$, $[M + H]^+$ = 188.0740, found:188.0744.

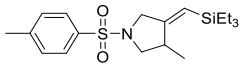


***N*-allyl-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (1t).** [3] Colorless oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.75-5.65 (m, 1H), 5.29-5.13 (m, 2H), 4.05-3.94 (m, 2H), 3.77 (q, *J* = 6.0 Hz, 2H), 2.39 (s, 3H), 1.50 (s, 3H).

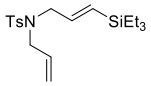


diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (1u). Colorless oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64-5.53 (m, 1H), 5.17-5.05 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 2.80-2.70 (m, 4H), 1.98 (t, *J* = 2.8 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 131.7, 119.7, 71.3, 61.5, 56.5, 36.2, 22.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}O_4$, $[M + H]^+$ = 239.1278, found:239.1277.

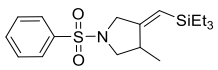
8.3. Characterization data of the silylcyclization products (3) and hydrosilylation product (4).



(*E*)-3-methyl-1-tosyl-4-((triethylsilyl)methylene)pyrrolidine (3a). Colorless oil, 92% yield. $[\alpha]_D^{25}$ = 20.8 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.25 (q, *J* = 1.6 Hz, 1H), 4.07 (dt, *J* = 14.0, 1.6 Hz, 1H), 3.59 (dd, *J* = 14.0, 2 Hz, 1H), 3.26 (d, *J* = 9.2 Hz, 1H), 3.15 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.43 (s, 3H), 2.73-2.66 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 143.4, 133.1, 129.6, 127.7, 117.8, 55.5, 53.7, 37.8, 21.5, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NO_2SSi$, $[M + H]^+$ = 366.1918, found:366.1911.

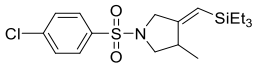


(*E*)-*N*-allyl-4-methyl-*N*-(3-(triethylsilyl)allyl)benzenesulfonamide (4a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.78-5.57 (m, 3H), 5.18-5.10 (m, 2H), 3.87 (d, *J* = 4.4 Hz, 2H), 3.81 (dd, *J* = 6.4, 1.6 Hz, 2H), 2.45 (s, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.51 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.9, 137.6, 132.7, 131.5, 129.6, 127.1, 118.8, 51.8, 49.4, 21.4, 7.2, 3.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NO_2SSi$, $[M + H]^+$ = 366.1918, found: 366.1926.

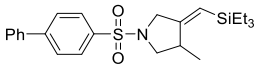


(*E*)-3-methyl-1-(phenylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3b). Colorless oil, 85% yield. $[\alpha]_D^{25}$ = 19.4 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.64-7.59 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 5.26 (s, 1H), 4.09 (d, *J* = 14.0 Hz, 1H), 3.62 (d, *J* = 14.4 Hz, 1H), 3.29 (d, *J* = 9.2 Hz, 1H), 3.18 (dd, *J* = 8, 5.2

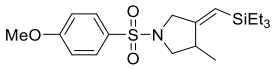
Hz, 1H), 2.74-2.67 (m, 1H), 1.04 (d, J = 7.2 Hz, 3H), 0.89 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 136.1, 132.7, 129.0, 127.6, 118.0, 55.5, 53.6, 37.8, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{30}NO_2SSi$, $[M + H]^+$ = 352.1761, found:352.1766.



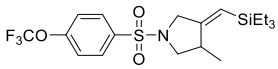
(*E*)-1-((4-chlorophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3c). Colorless oil, 85% yield. $[\alpha]_D^{25}$ = 22.6 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 6.8 Hz, 2H), 7.52 (d, J = 6.4 Hz, 2H), 5.27 (s, 1H), 4.09 (d, J = 14.0 Hz, 1H), 3.59 (d, J = 14.4 Hz, 1H), 3.28 (d, J = 9.6 Hz, 1H), 3.16 (dd, J = 8.0, 5.2 Hz, 1H), 2.75-2.69 (m, 1H), 1.06 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.58 (d, J = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 139.2, 134.7, 129.3, 129.0, 118.3, 55.6, 53.5, 37.8, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{28}ClNaNO_2SSi$, $[M + Na]^+$ = 408.1196, found:408.1202.



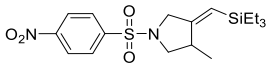
(*E*)-1-([1,1'-biphenyl]-4-ylsulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3d). Colorless oil, 95% yield. $[\alpha]_D^{25}$ = 25.1 (c = 1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.66-7.61 (m, 2H), 7.53-7.47 (m, 2H), 7.46-7.41 (m, 1H), 5.30 (s, 1H), 4.14 (d, J = 14.0, 1H), 3.68 (dd, J = 14.0, 2.0 Hz, 1H), 3.34 (dd, J = 9.6, 1.6 Hz, 1H), 3.23 (dd, J = 9.2, 5.6 Hz, 1H), 2.78-2.71 (m, 1H), 1.09 (d, J = 7.2 Hz, 3H), 0.91 (t, J = 8.0 Hz, 9H), 0.59 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 145.5, 139.2, 134.7, 129.0, 128.51, 128.2, 127.6, 127.3, 118.0, 55.6, 53.7, 37.9, 20.9, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{34}NO_2SSi$, $[M + H]^+$ = 428.2074, found:428.2075.



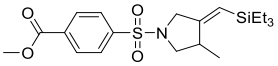
(*E*)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3e). Colorless oil, 85% yield. $[\alpha]_D^{25}$ = 18.6 (c = 0.5, CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.26 (s, 1H), 4.06 (dt, J = 14.0, 2.0 Hz, 1H), 3.88 (s, 3H), 3.59 (dd, J = 14.0, 1.6 Hz, 1H), 3.25 (dd, J = 9.2, 1.6 Hz, 1H), 3.15 (dd, J = 9.2, 6.0 Hz, 1H), 2.74-2.67 (m, 1H), 1.06 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.3, 129.8, 127.7, 117.8, 114.1, 55.6, 55.5, 53.7, 37.8, 20.9, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NO_3SSi$, $[M + H]^+$ = 382.1867, found:382.1862.



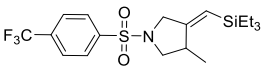
(*E*)-3-methyl-4-((triethylsilyl)methylene)-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (3f). Colorless oil, 83% yield. $[\alpha]_D^{25}$ = 24.2 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 5.28 (s, 1H), 4.11 (d, J = 17.6 Hz, 1H), 3.63 (dd, J = 14.0, 2.0 Hz, 1H), 3.30 (dd, J = 9.2, 1.2 Hz, 1H), 3.19 (dd, J = 9.2, 6 Hz, 1H), 2.77-2.70 (m, 1H), 1.06 (d, J = 7.2 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 152.2, 134.7, 129.7, 120.8, 120.2 (q, J = 259.6 Hz), 118.4, 55.6, 53.5, 37.8, 20.7, 7.4, 4.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.74. HRMS (ESI) *m/z* calcd for $C_{19}H_{29}F_3NO_3SSi$, $[M + H]^+$ = 436.1584, found: 436.1580.



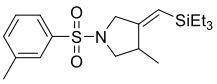
(*E*)-3-methyl-1-((4-nitrophenyl)sulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3g). White solid. 88% yield. mp: 88.5-89.5 °C. $[\alpha]_D^{25}$ = 21.3 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 10.0 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H), 5.30 (s, 1H), 4.15 (d, J = 14.0 Hz, 1H), 3.64 (d, J = 14.0 Hz, 1H), 3.35 (d, J = 9.2 Hz, 1H), 3.21 (dd, J = 8.4, 5.6 Hz, 1H), 2.79-2.72 (m, 1H), 1.06 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 150.1, 142.3, 128.6, 124.3, 118.9, 55.7, 53.4, 37.9, 20.7, 7.4, 4.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{29}N_2O_4SSi$, $[M + H]^+$ = 397.1612, found: 397.1618.



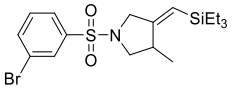
methyl-(*E*)-4-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)benzoate (3h). White solid. 95% yield. mp: 86.7-87.3 °C. $[\alpha]_D^{25}$ = 23.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 5.25 (s, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 3.95 (s, 3H), 3.61 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.29 (dd, *J* = 9.6, 1.2 Hz, 1H), 3.17 (dd, *J* = 9.2, 4.8 Hz, 1H), 2.74-2.67 (m, 1H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 157.5, 140.1, 133.8, 130.2, 127.5, 118.4, 77.2, 55.6, 53.4, 52.6, 37.8, 20.7, 7.4, 4.1. HRMS (ESI) *m/z* calcd for $C_{20}H_{32}NO_4SSi$, $[M + H]^+$ = 410.1816, found: 410.1812.



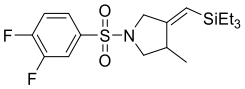
(*E*)-3-methyl-4-((triethylsilyl)methylene)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3i). Colorless oil, 80% yield. $[\alpha]_D^{25}$ = 17.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.63 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.33 (dd, *J* = 9.6, 2.0 Hz, 1H), 3.20 (dd, *J* = 9.2, 6.4 Hz, 1H), 2.77-2.70 (m, 1H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 140.0, 134.3 (q, *J* = 32.8 Hz), 128.0, 126.2 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 271.3 Hz), 118.6, 55.6, 53.5, 37.8, 20.8, 7.4, 4.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{29}F_3NO_2SSi$, $[M + H]^+$ = 420.1635, found: 420.1633.



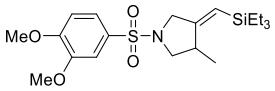
(*E*)-3-methyl-1-(m-tolylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3j). Colorless oil, 71% yield. $[\alpha]_D^{25}$ = 18.9 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.45-7.39 (m, 2H), 5.27 (s, 1H), 4.10-4.05 (m, 1H), 3.61 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.28 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.17 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.76-2.66 (m, 1H), 2.44 (s, 3H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 139.2, 135.9, 133.5, 128.8, 128.0, 124.8, 117.9, 55.5, 53.6, 37.8, 21.4, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NO_2SSi$, $[M + H]^+$ = 366.1918, found: 366.1920.



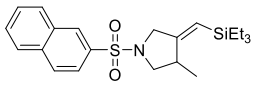
(*E*)-1-((3-bromophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3k). Colorless oil, 85% yield. $[\alpha]_D^{25}$ = 14.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 1H), 7.77-7.11 (m, 2H), 7.45-7.40 (m, 1H), 5.29 (s, 1H), 4.10 (d, *J* = 14.4 Hz, 1H), 3.61 (d, *J* = 14.0 Hz, 1H), 3.30 (d, *J* = 9.2 Hz, 1H), 3.19 (dd, *J* = 9.2, 6.0 Hz 1H), 2.80-2.70 (m, 1H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 138.2, 135.7, 130.6, 130.4, 126.1, 123.1, 118.4, 55.6, 53.5, 37.8, 20.8, 7.48, 4.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{28}BrNaNO_2SSi$, $[M + Na]^+$ = 452.0691, found: 452.0682.



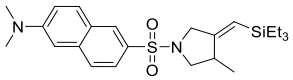
(*E*)-1-((3,4-difluorophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)-3l3-pyrrolidine (3l). Colorless oil, 88% yield. $[\alpha]_D^{25}$ = 16.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 1H), 7.65-7.61 (m, 1H), 7.36 (q, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 4.15-4.08 (m, 1H), 3.61 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.30 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.18 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.78-2.72 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 153.1 (dd, *J* = 255.2, 12.5 Hz), 150.1 (dd, *J* = 253.1, 13.4 Hz), 133.3, 124.6 (dd, *J* = 7.3, 4.0 Hz), 118.5, 118.2 (d, *J* = 18.2 Hz), 117.4 (d, *J* = 19.3 Hz), 55.6, 55.5, 37.8, 20.8, 7.4, 4.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.55 (d, *J* = 5.5 Hz, 1F), -133.66 (d, *J* = 5.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{18}H_{28}F_2NO_2SSi$, $[M + H]^+$ = 388.1573, found: 388.1575.



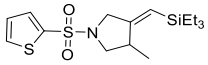
(*E*)-1-((3,4-dimethoxyphenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3m). Colorless oil, 90% yield. $[\alpha]_D^{25}$ = 19.6 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.26 (s, 1H), 4.06 (d, *J* = 14.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.59 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.26 (dd, *J* = 9.2, 2.0 Hz, 1H), 3.15 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.79-2.66 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.5, 148.9, 127.8, 121.6, 117.9, 110.5, 110.2, 56.2, 56.16, 55.6, 53.7, 37.8, 20.9, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{20}H_{34}NO_4SSi$, $[M + H]^+$ = 412.1972, found: 412.1975.



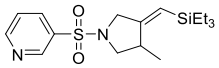
(*E*)-3-methyl-1-(naphthalen-2-ylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3n). Colorless oil, 85% yield. $[\alpha]_D^{25}$ = 10.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.6 Hz, 1H), 8.04-7.97 (m, 2H), 7.96-7.91 (m, 1H), 7.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69-7.60 (m, 2H), 5.26 (s, 1H), 4.20-4.13 (m, 1H), 3.68 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.38 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.24 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.76-2.67 (m, 1H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 134.8, 133.2, 132.2, 129.28, 129.25, 128.9, 128.7, 127.9, 127.5, 123.1, 118.0, 55.6, 53.7, 37.9, 20.9, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{32}NO_2SSi$, $[M + H]^+$ = 402.1918, found: 402.1914.



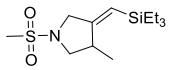
(*E*)-N,N-dimethyl-6-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)naphthalen-2-amine (3o). Yellow oil, 75% yield, $[\alpha]_D^{25}$ = 11.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 8.26 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56 (q, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 5.26 (s, 1H), 4.15-4.08 (m, 1H), 3.79 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.46-3.37 (m, 2H), 2.90 (s, 6H), 2.80-2.72 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 151.4, 133.6, 130.6, 130.5, 130.1, 130.0, 127.9, 123.2, 119.8, 117.7, 115.1, 55.0, 53.1, 45.4, 38.2, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{37}N_2O_2SSi$, $[M + H]^+$ = 445.2340, found: 445.2332.



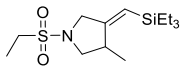
(*E*)-3-methyl-1-(thiophen-2-ylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3p). White solid. 86% yield. m.p: 83.3-84.1 ℃. $[\alpha]_D^{25}$ = 19.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.16 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.29 (s, 1H), 4.15-4.11 (m, 1H), 3.69 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.30 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.24 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.78-2.71 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 8.0Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 136.1, 132.2, 131.8, 127.5, 118.2, 55.7, 53.7, 37.9, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{28}NO_2S_2Si$, $[M + H]^+$ = 358.1325, found: 358.1327.



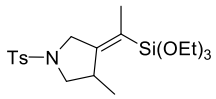
(*E*)-3-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)pyridine (3q). Colorless oil, 72% yield. $[\alpha]_D^{25}$ = 16.9 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (dd, *J* = 2.4, 1.2 Hz, 1H), 8.82 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.11 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.51-7.48 (m, 1H), 5.28 (s, 1H), 4.12 (d, *J* = 11.6 Hz, 1H), 3.63 (dd, *J* = 14.4, 1.2 Hz, 1H), 3.32 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.19 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.76-2.69 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 153.3, 148.3, 135.2, 133.1, 123.78, 118.7, 55.5, 53.4, 37.8, 20.7, 7.4, 4.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{29}N_2O_2SSi$, $[M + H]^+$ = 353.1714, found: 353.1719.



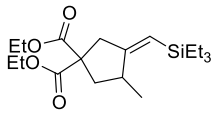
(*E*)-3-methyl-1-(methylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3r). Colorless oil, 82% yield. $[\alpha]_D^{25}$ = 18.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 4.20-4.45 (m, 1H), 3.78 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.37-3.29 (m, 2H), 2.85 (s, 3H), 2.80-2.88 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.63 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 118.3, 55.4, 53.4, 38.2, 34.6, 20.8, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{28}NO_2SSi$, $[M + H]^+$ = 290.1605, found: 290.1609.



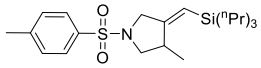
(*E*)-1-(ethylsulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3s). Colorless oil, 67% yield. $[\alpha]_D^{25}$ = 16.1 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 1H), 4.20-4.15 (m, 1H), 3.83 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.41 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.31 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.02 (q, *J* = 7.2 Hz, 2H), 2.85-2.78 (m, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.62 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 117.9, 55.3, 53.2, 44.4, 38.2, 20.7, 7.9, 7.4, 4.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{30}NO_2SSi$, $[M + H]^+$ = 304.1761, found: 304.1768.



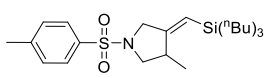
1-(4-Toluenesulfonyl)-3-(*E*)-(1-(triethoxysilyl)ethylidene)-4-methylpyrrolidine (3t). Colorless liquid, 60 % yield, [a] $_D^{25}$ = 35.6 (c =1.5, DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.96 (dt, *J* = 15.2, 1.2 Hz, 1H), 3.70 (q, *J* = 6.8 Hz, 6H), 3.47 (dd, *J* = 15.2, 1.2 Hz, 1H), 3.22 (d, *J* = 9.2 Hz, 1H), 3.11-3.04 (m, 1H), 2.90 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.37 (s, 3H), 1.52 (q, *J* = 0.8 Hz, 3H), 1.12 (t, *J* = 6.8 Hz, 9H), 1.04 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 143.5, 132.6, 129.6, 127.8, 119.7, 58.4, 55.2, 50.5, 37.8, 21.5, 21.3, 18.1, 17.5. HRMS (ESI) *m/z* Calcd for $C_{20}H_{34}NO_3SSi$, $[M + H]^+$ = 395.1945. Found: 395.1940.



4,4-Bis(methoxycarbonyl)-1-(*E*)-(triethylsilyl)methylidene-2-methylcyclopentane (3u): Colorless liquid, 75 % yield, $[a]_D^{25}$ = -2.3 (c = 0.5, DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.20 (m, 1H), 4.17-4.04 (m, 4H), 3.20 (td, *J* = 16.0, 2.4 Hz, 1H), 2.69 (d, *J* = 2.4 Hz, 1H), 2.65-2.55 (m, 2H), 1.84-1.78 (m, 1H), 1.19-1.13 (m, 6H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 8.0 Hz, 9H), 0.51 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 163.7, 117.3, 61.42, 61.3, 58.5, 44.5, 41.9, 36.9, 22.5, 14.0, 7.5, 4.3. HRMS (ESI) *m/z* Calcd for $C_{19}H_{35}O_4Si$, $[M + H]^+$ =355.2299. Found: 355.2294.

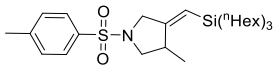


(*E*)-3-methyl-1-tosyl-4-((tripropylsilyl)methylene)pyrrolidine (3v). Colorless oil, 90% yield. $[\alpha]_D^{25}$ = 15.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.25 (s, 1H), 4.03-4.07 (m, 1H), 3.58 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.26 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.15 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.72-2.65 (m, 1H), 2.44 (s, 3H), 1.31-1.21 (m, 6H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 9H), 0.55 (q, *J* = 4.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 143.4, 133.1, 129.6, 127.7, 118.7, 55.5, 53.7, 37.7, 21.5, 20.8, 18.5, 17.4, 16.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{38}NO_2SSi$, $[M + H]^+$ = 408.2387, found: 408.2381.

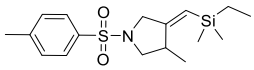


(*E*)-3-methyl-1-tosyl-4-((tributylsilyl)methylene)pyrrolidine (3w). Colorless oil, 90% yield. $[\alpha]_D^{25}$ = 13.1 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 1H), 4.06 (dt, *J* =

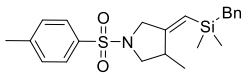
14.0, 1.6 Hz, 1H), 3.58 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.26 (d, *J* = 9.2 Hz, 1H), 3.14 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.72-2.66 (m, 1H), 2.43 (s, 3H), 1.36-1.16 (m, 12H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.86 (q, *J* = 7.2 Hz, 9H), 0.55 (t, *J* = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 143.4, 133.0, 129.6, 127.7, 118.7, 55.5, 53.6, 37.8, 26.7, 26.1, 21.5, 20.7, 13.7, 13.0. HRMS (ESI) *m/z* calcd for $C_{25}H_{44}NO_2SSi$, $[M + H]^+$ = 450.2857, found: 450.2852.



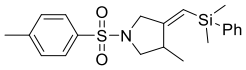
(*E*)-3-methyl-1-tosyl-4-((triHexsilyl)methylene)pyrrolidine (3x). Colorless oil, 90% yield. $[\alpha]_D^{25}$ = 11.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 1H), 4.06 (dt, *J* = 14.0, 1.6 Hz, 1H), 3.58 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.27 (dd, *J* = 9.6, 1.2 Hz, 1H), 3.13 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.15-3.11 (m, 1H), 2.43 (s, 3H), 1.38-1.16 (m, 24H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.90-0.84 (m, 9H), 0.57-0.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 143.4, 133.1, 129.6, 127.7, 118.7, 55.5, 53.6, 37.8, 33.4, 31.4, 23.8, 22.5, 21.5, 20.7, 14.1, 13.3. HRMS (ESI) *m/z* calcd for $C_{31}H_{56}NO_2SSi$, $[M + H]^+$ = 534.3796, found: 534.3790.



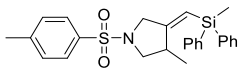
(*E*)-3-((ethyldimethylsilyl)methylene)-4-methyl-1-tosyl-4l3-pyrrolidine (3y). Colorless oil, 85% yield. $[\alpha]_D^{25}$ =33.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 5.29-5.27 (m, 1H), 4.06-4.02 (m, 1H), 3.56 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.25 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.14 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.78-2.72 (m, 1H), 2.43 (s, 3H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 3H), 0.51 (q, *J* = 8.0 Hz, 2H). 0.04 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 143.5, 132.8, 129.6, 127.8, 119.9, 55.5, 53.7, 37.4, 21.5, 21.0, 8.0, 7.3, -2.3, -2.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{28}NO_2SSi$, $[M + H]^+$ = 338.1605, found: 338.1610.



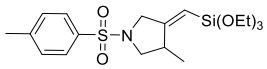
(*E*)-3-((benzyldimethylsilyl)methylene)-4-methyl-1-tosylpyrrolidine (3z). Colorless oil, 96% yield. $[\alpha]_D^{25}$ = 27.9 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 6.8 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 6.4 Hz, 2H), 5.27-5.26 (m, 1H), 4.09-4.04 (m, 1H), 3.56 (dd, *J* = 17.6, 2.0 Hz, 1H), 3.22 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.03 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.58-2.50 (m, 1H), 2.46 (s, 3H), 2.11 (s, 2H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 143.6, 139.5, 132.7, 129.6, 128.1, 128.1, 127.8, 124.1, 118.8, 55.4, 53.7, 37.5, 26.5, 21.6, 20.9, -1.9, -2.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{30}NO_2SSi$, $[M + H]^+$ = 400.1761, found: 400.1758.



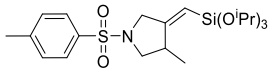
(*E*)-3-((benzyldimethylsilyl)methylene)-4-methyl-1-tosylpyrrolidine (3aa). Colorless oil, 78% yield. $[\alpha]_D^{25}$ = 25.1 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.38-7.32 (m, 5H), 5.48 (q, *J* = 2.0 Hz, 1H), 4.12-4.06 (m, 1H), 3.63 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.21 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.11 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.70-2.61 (m, 1H), 2.46 (s, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.38 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 143.5, 138.5, 133.6, 132.8, 129.6, 129.1, 127.9, 127.8, 119.0, 55.4, 53.8, 37.3, 21.5, 20.6, -1.1, -1.3. HRMS (ESI) *m/z* calcd for $C_{21}H_{28}NO_2SSi$, $[M + H]^+$ = 386.1605, found: 386.1601.



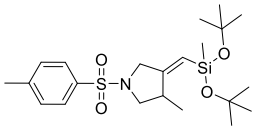
(*E*)-3-(2,2-diphenylpropylidene)-4-methyl-1-tosylpyrrolidine (3ab). Colorless oil, 40% yield. $[\alpha]_D^{25}$ =17.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.50 (td, *J* = 7.6, 1.6 Hz, 4H), 7.44-7.35 (m, 8H), 5.70 (s, 1H), 4.20-4.12 (m, 1H), 3.72 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.17 (dd, *J* = 9.2, 2.0 Hz, 1H), 3.10 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.58-2.50 (m, 1H), 2.47 (s, 3H), 0.82 (d, *J* = 7.2 Hz, 3H), 0.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 143.6, 136.7, 136.42, 134.6, 134.6, 134.0, 132.9, 129.6, 129.5, 129.4, 127.9, 127.9, 127.8, 117.1, 55.4, 54.0, 37.3, 21.60, 20.3, -2.2. HRMS (ESI) *m/z* calcd for $C_{26}H_{30}NO_2SSi$, $[M + H]^+$ = 448.1761, found: 448.1767.



(*E*)-3-methyl-1-tosyl-4-((triethoxysilyl)methylene)-3l3-pyrrolidine (3ac). Colorless oil, 50% yield. $[\alpha]_D^{25}$ = 22.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 1H), 4.07 (dt, *J* = 14.8, 2.0 Hz, 1H), 3.78 (q, *J* = 6.8 Hz, 6H), 3.59 (dd, *J* = 15.2, 2.0 Hz, 1H), 3.24 (dd, *J* = 8.8, 1.6 Hz, 1H), 3.13 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.09 -3.01 (m, 1H), 2.44 (s, 3H), 1.20 (t, *J* = 6.8 Hz, 9H), 1.13 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 143.6, 132.5, 129.6, 127.8, 110.8, 58.4, 55.4, 53.7, 38.0, 21.5, 20.5, 18.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}NO_5SSi$, $[M + H]^+$ = 414.1765, found: 414.1761.

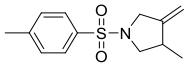


(*E*)-3-methyl-1-tosyl-4-((triisopropoxysilyl)methylene)pyrrolidine (3ad). Colorless oil, 56% yield. $[\alpha]_D^{25}$ = 22.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 4.23-4.15 (m, 3H), 4.10-4.05 (m, 1H), 3.57 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.25 (d, *J* = 8.4 Hz, 1H), 3.18-3.08 (m, 2H), 2.44 (s, 3H), 1.17 (d, *J* = 2.8 Hz, 9H), 1.16 (d, *J* = 2.4 Hz, 9H), 1.13 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 143.5, 132.5, 129.6, 127.8, 112.6, 65.2, 55.4, 53.7, 37.7, 25.5, 25.4, 21.5, 20.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{38}NO_5SSi$, $[M + H]^+$ = 456.2234, found: 456.2238.

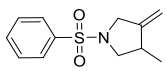


(*E*)-3-((di-tert-butoxy(methyl)silyl)methylene)-4-methyl-1-tosylpyrrolidine (3ae). Colorless oil, 70% yield. $[\alpha]_D^{25}$ = 21.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.15 (q, *J* = 2.0 Hz, 1H), 4.06-4.01 (m, 1H), 3.55 (dd, *J* = 9.2, 1.6 Hz, 1H), 3.24 (dd, *J* = 9.2, 2.0 Hz, 1H), 3.13 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.02-2.92 (m, 1H), 2.44 (s, 3H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.13 (s, 3H), 0.08 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.5, 132.5, 129.6, 127.8, 118.7, 55.4, 53.6, 37.3, 21.5, 20.9, 1.8. HRMS (ESI) *m/z* calcd for $C_{22}H_{38}NO_4SSi$, $[M + H]^+$ = 440.2285, found: 440.2293.

8.4. Characterization data for the desilylated compounds.

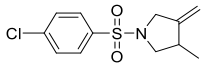


1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). White solid, 91% yield. mp: 62.3-63.3 ℃, 91% ee. $[\alpha]_D^{25}$ = 26.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 4.92 (d, *J* = 2.0 Hz, 1H), 4.87 (d, *J* = 2.4 Hz, 1H), 3.99-3.94 (m, 1H), 3.77-3.72 (m, 1H), 3.61-3.56 (m, 1H), 2.74-2.65 (m, 2H), 2.45 (s, 3H), 1.06 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 143.6, 132.8, 129.6, 127.8, 106.0, 55.0, 52.1, 37.4, 21.5, 16.0. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NO_2S$, $[M + H]^+$ = 252.1053, found: 252.1059. The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.48 min (major) and 15.62 min (minor).

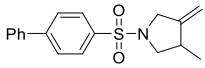


3-methyl-4-methylene-1-(phenylsulfonyl)pyrrolidine (3b'). Colorless oil, 83% yield. 91% ee. $[\alpha]_D^{25}$ = 23.9 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.65-7.60 (m, 1H), 7.59-7.52 (m, 2H), 4.93-4.91 (m, 1H), 4.87-4.86 (m, 1H), 3.98 (d, *J* = 15.2 Hz, 1H), 3.79-3.74 (m, 1H), 3.67-3.56 (m, 1H), 2.78-2.61 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 135.8, 132.8, 129.0, 127.7, 106.1, 55.0, 52.1, 37.4, 16.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{16}NO_2S$, $[M + H]^+$ = 238.0896, found: 238.0891. The ee of **3b'** was determined by HPLC

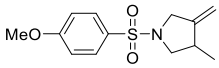
analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 12.81 min (major) and 14.57 min (minor).



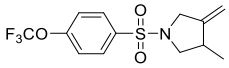
1-((4-chlorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3c'). White solid, 90% yield. mp: 94.5-95.5 ℃, 92% ee. $[\alpha]_D^{25}$ = 20.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 4.95-4.93 (m, 1H), 4.90-4.89 (m, 1H), 3.98 (dt, *J* = 14.0, 2.4 Hz, 1H), 3.78-3.73 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.37 (m, 2H), 1.07 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.3, 134.5, 129.4, 129.1, 106.4, 55.0, 52.1, 37.4, 15.9. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}ClNO_2S$, $[M + H]^+$ = 272.0507, found: 272.0504. The ee of **3c'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.28 min (major) and 16.56 min (minor).



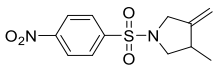
1-([1,1'-biphenyl]-4-ylsulfonyl)-3-methyl-4-methylenepyrrolidine (3d'). White solid, 79% yield. mp: 99.5-101.2 ℃, 91% ee. $[\alpha]_D^{25}$ = 17.1 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.66-7.61 (m, 2H), 7.53-7.47 (m, 2H), 7.46-7.41 (m, 1H), 4.95-4.93 (m, 1H), 4.90-4.89 (m, 1H), 4.04-3.99 (m, 1H), 3.84-3.79 (m, 1H), 3.67-3.61 (m 1H), 2.80-2.65 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 145.6, 139.2, 134.4, 130.3, 129.0, 128.5, 128.2, 127.6, 127.3, 106.2, 55.1, 52.2, 37.5, 16.0. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO_2S$, $[M + H]^+$ = 314.1209, found: 314.1202. The ee of **3d'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.13 min (major) and 14.66 min (minor).



1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3e'). White solid, 75% yield. mp: 57.6-58.4 ℃, 91% ee. $[\alpha]_D^{25}$ = 9.9 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.2 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.92-4.90 (m, 1H), 4.87-4.85 (m, 1H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.89 (s, 3H), 3.84-3.67 (m, 1H), 3.65-3.40 (m, 1H), 2.82-2.32 (m, 2H), 1.06 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 149.3, 129.8, 127.4, 114.2, 106.0, 55.6, 55.1, 52.2, 37.4, 16.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NO_3S$, $[M + H]^+$ = 268.1002, found: 268.1005. The ee of **3e'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 93:7, 0.8 mL/min, 25 ℃, 254 nm; *t*R = 27.18 min (major) and 30.87 min (minor).

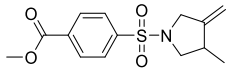


3-methyl-4-methylene-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (3f'). White solid, 80% yield. mp: 71.2-72.1 ℃, 91% ee. $[\alpha]_D^{25}$ =13.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.96-4.94 (m, 1H), 4.91-4.90 (m, 1H), 3.97-3.40 (m, 1H), 3.81-3.76 (m, 1H), 3.64-3.59 (m, 1H), 2.85-2.63 (m, 2H), 1.08 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 148.7, 134.5, 129.7, 120.9, 120.2 (q, *J* = 258.0 Hz), 106.4, 55.0, 52.1, 37.5, 16.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.68. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}F_3NO_3S$, $[M + H]^+$ = 322.0719, found: 322.0714. The ee of **3f'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, 25 ℃, 254 nm; *t*R = 9.04 min (major) and 9.95 min (minor).

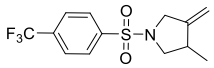


3-methyl-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidine (3g'). White solid, 82% yield. mp: 150.8-151.7 ℃, 88% ee. $[\alpha]_D^{25}$ =21.6 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 4.95-4.93 (m, 1H), 4.90-4.89 (m, 1H), 3.98 (dt, *J* = 14.0, 2.4 Hz, 1H), 3.78-3.73 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.37 (m, 2H), 1.07 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 148.1, 142.1, 128.7, 124.4, 106.8, 55.0, 52.1, 37.5, 15.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}N_2O_4S$, $[M + H]^+$ = 283.0747, found: 283.0741. The ee of **3g'**

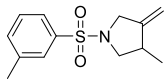
was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90:10, 1 mL/min, 25 ℃, 254 nm; *t*R = 17.58 min (major) and 22.29 min (minor).



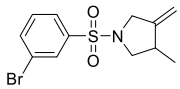
methyl 4-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)benzoate (3h'). White solid, 68% yield. mp: 109.4-111.3 ℃, 88% ee. $[\alpha]_D^{25}$ =25.1 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 4.92-4.91 (m, 1H), 4.87-4.86 (m, 1H), 4.00-3.96 (m, 1H), 3.96 (s, 3H), 3.74-3.79 (m, 1H), 359-3.63 (m, 1H), 2.65-2.73 (m, 2H),1.04 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.6, 139.9, 133.9, 130.2, 127.6, 106.4, 55.0, 52.6, 52.1, 37.4, 15.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NO_4S$, $[M + H]^+$ = 296.0951, found: 296.0948. The ee of **3h'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, 25 ℃, 254 nm; *t*R = 14.59 min (major) and 16.82 min (minor).



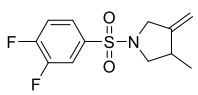
3-methyl-4-methylene-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3i'). White solid, 63% yield. mp: 124.7-126.3 ℃, 91% ee. $[\alpha]_D^{25}$ =20.5 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 4.97-4.95 (m, 1H), 4.91-4.89 (m, 1H), 4.03-3.98 (m, 1H), 3.82-3.77 (m, 1H), 3.68-3.60 (m, 1H), 2.78-2.67 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 134.5 (q, *J* = 32.9 Hz), 128.1, 126.2 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 271.4), 106.5, 55.0, 52.1, 37.5, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.79. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}F_3NO_2S$, $[M + H]^+$ = 306.0770, found: 306.0774. The ee of **3i'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1 mL/min, 25 ℃, 254 nm; *t*R = 9.15 min (major) and 10.26 min (minor).



3-methyl-4-methylene-1-(m-tolylsulfonyl)pyrrolidine (3j'). White solid, 84% yield. mp: 63.1-64.3 ℃, 90% ee. $[\alpha]_D^{25}$ =25.5 (*c* = 0.25, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 5.6 Hz, 2H), 4.93-4.91 (m, 1H), 4.89-4.87 (m, 1H), 3.99-3.95 (m, 1H), 3.79-3.74 (m, 1H), 3.64-3.56 (m, 1H), 2.75-2.64 (m, 2H), 2.45 (s, 3H), 1.06 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 139.2, 135.6, 133.6, 128.9, 128.0, 124.9, 106.0, 55.0, 52.1, 37.4, 21.4, 16.0. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NO_2S$, $[M + H]^+$ = 252.1053, found: 252.1055. The ee of **3j'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98:2, 0.5 mL/min, 25 ℃, 254 nm; *t*R = 26.57 min (major) and 28.51 min (minor).

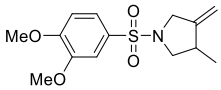


1-((3-bromophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3k'). White solid, 76% yield. mp: 53.5-54.1 ℃, 92% ee. $[\alpha]_D^{25}$ =14.5 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 2.0 Hz, 1H), 7.79-7.73 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 4.96-4.95 (m, 1H), 4.91-4.90 (m, 1H), 4.01-3.96 (m, 1H), 3.81-3.76 (m, 1H), 3.65-3.58 (m, 1H), 2.77-2.67 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.9, 135.8, 130.6, 130.4, 126.1, 123.2, 106.4, 55.0, 52.1, 37.5, 16.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}BrNO_2S$, $[M + H]^+$ = 316.0001 found: 316.0008. The ee of **3k'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 99:1, 0.5 mL/min, 25 ℃, 254 nm; *t*R = 45.63 min (major) and 50.01 min (minor).

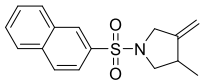


1-((3,4-difluorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3l'). White solid, 79% yield. mp: 92.3-93.5 ℃, 90% ee. $[\alpha]_D^{25}$ =14.9 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 1H), 7.65-7.60 (m, 1H), 7.39-

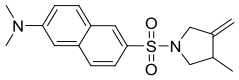
7.33 (m, 1H), 4.96-4.94 (m, 1H), 4.92-4.90 (m, 1H), 4.01-3.96 (m, 1H), 3.80-3.75 (m, 1H), 3.66-3.57 (m, 1H), 2.77-2.68 (m, 2H), 1.09 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (dd, J = 255.7, 12.6 Hz), 150.2 (dd, J = 253.2, 13.1 Hz), 148.5, 133.0, 124.7 (dd, J = 7.4, 4.0 Hz), 118.2 (d, J = 18.1 Hz), 117.5 (dd, J = 19.3, 1.7 Hz), 55.0, 52.1, 37.5, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.37 (d, J = 20.4 Hz), -133.55 (d, J = 20.9 Hz). HRMS (ESI) *m/z* calcd for $C_{12}H_{14}F_2NO_2S$, $[M + H]^+$ = 274.0708, found: 274.0712. The ee of **3l'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 97:3, 0.8 mL/min, 25 ℃, 254 nm; *t*R = 14.71 min (major) and 18.39 min (minor).



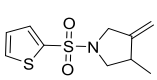
1-((3,4-dimethoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3m'). White solid, 86% yield. mp: 84.3-85.6 ℃, 90% ee. $[\alpha]_D^{25}$ =10.5 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.4, 2.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 4.92-4.90 (m, 1H), 4.87-4.85 (m, 1H), 4.01-3.96 (m, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.76-3.71 (m, 1H), 3.60-3.53 (m, 1H), 2.73-2.62 (m, 2H). 1.05 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 149.2, 149.0, 127.5, 121.6, 110.6, 110.2, 106.0, 56.2, 56.1, 55.1, 52.2, 37.4, 16.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{20}NO_4S$, $[M + H]^+$ = 298.1108, found: 298.1105. The ee of **3m'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 93:7, 0.8 mL/min, 25 ℃, 254 nm; *t*R = 27.18 min (major) and 30.87 min (minor).



3-methyl-4-methylene-1-(naphthalen-2-ylsulfonyl)pyrrolidine (3n'). White solid, 70% yield. mp: 63.2-64.3 ℃, 86% ee. $[\alpha]_D^{25}$ =27.1 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 1.6 Hz, 1H), 8.06-7.98 (m, 2H), 7.94 (dd, J = 7.2, 1.6 Hz, 1H), 7.84 (dd, J = 8.4, 1.6 Hz, 1H), 7.71-7.61 (m, 2H), 4.92-4.90 (m, 1H), 4.86-4.84 (m, 1H), 4.07-4.02 (m, 1H), 3.86-3.81 (m, 1H), 3.70-3.66 (m, 1H), 2.78 (t, J = 8.8 Hz, 1H), 2.74-2.63 (m, 1H), 1.04 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 134.9, 133.0, 132.2, 129.3, 129.2, 129.0, 128.8, 127.9, 127.5, 123.1, 106.1, 55.1, 52.2, 37.5, 16.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}NO_2S$, $[M + H]^+$ = 288.1053, found: 288.1058. The ee of **3n'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 10.44 min (major) and 11.28 min (minor).

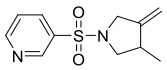


***N,N*-dimethyl-6-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)naphthalen-2-amine (3o').** Yellow oil, 77% yield. 88% ee. $[\alpha]_D^{25}$ =23.5 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, J = 8.8, 1.2 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.24 (dd, J = 7.2, 1.2 Hz, 1H), 7.58-7.53 (m, 2H), 7.20 (dd, J = 7.6, 1.2 Hz, 1H), 4.92-4.90 (m, 1H), 4.89-4.87 (m, 1H), 4.07-4.02 (m, 1H), 3.94-3.89 (m, 1H), 3.72-3.67 (m, 1H), 2.92 (t, J = 8.8 Hz, 1H), 2.90 (s, 6H), 2.82-2.70 (m, 1H), 1.07 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 149.4, 133.3, 130.6, 130.5, 130.1, 130.0, 128.0, 123.2, 119.7, 115.2, 105.9, 54.6, 51.7, 45.4, 37.8, 16.0. HRMS (ESI) *m/z* calcd for $C_{18}H_{23}N_2O_2S$, $[M + H]^+$ = 331.1475, found: 335.1471. The ee of **3o'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98:2, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 37.15 min (major) and 39.73 min (minor).

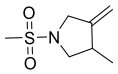


3-methyl-4-methylene-1-(thiophen-2-ylsulfonyl)pyrrolidine (3p'). White solid, 82% yield. mp: 58.6-59.4 ℃, 89% ee. $[\alpha]_D^{25}$ =13.3 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 2H), 7.17 (dd, J = 5.2, 3.6 Hz, 1H), 4.97-4.95 (m, 1H), 4.91-4.89 (m, 1H), 4.09-3.99 (m, 1H), 3.87-3.82 (m, 1H), 3.66-3.62 (m, 1H), 2.79 (t, J = 9.2 Hz, 1H), 2.75-2.64 (m, 1H), 1.08 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 135.9, 132.4, 132.0, 127.6, 106.3, 55.2, 52.3, 37.4, 16.0. HRMS (ESI) *m/z* calcd for $C_{10}H_{14}NO_2S_2$, $[M + H]^+$ = 244.0460, found: 244.0463. The ee of **3p'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-

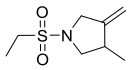
hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 7.50 min (major) and 8.30 min (minor).



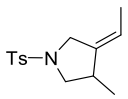
3-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)pyridine (3q'). White solid, 66% yield. mp: 53.3-54.5 ℃, 86% ee. $[\alpha]_D^{25}$ =26.3 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.85 (d, *J* = 4.4 Hz, 1H), 8.1-8.11 (m, 1H), 7.52 (dd, *J* = 8.0, 4.4 Hz, 1H), 4.96-4.94 (m, 1H), 4.91-4.89 (m, 1H), 4.03-3.98 (m, 1H), 3.83-3.78 (m, 1H), 3.67-3.63 (m, 1H), 2.76 (t, *J* = 8.4 Hz, 1H), 2.74-2.65 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 148.4, 135.3, 132.9, 123.8, 106.6, 55.0, 52.0, 37.4, 15.9. HRMS (ESI) *m/z* calcd for $C_{11}H_{15}N_2O_2S$, $[M + H]^+$ = 239.0849, found: 239.0844. The ee of **3q'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 29.51 min (major) and 72.97 min (minor).



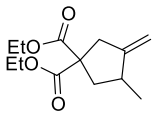
3-methyl-4-methylene-1-(methylsulfonyl)pyrrolidine (3r'). White solid, 52% yield. mp: 83.2-85.6 ℃, 81% ee, $[\alpha]_D^{25}$ = 42.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03-5.01 (m, 1H), 4.99-4.97 (m, 1H), 4.08-4.03 (m, 1H), 3.95-3.90 (m, 1H), 3.69-3.65 (m, 1H), 2.88 (d, *J* = 8.8 Hz, 1H), 2.83 (s, 3 H), 2.9-2.83 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 106.4, 54.9, 52.1, 37.8, 34.4, 15.9. HRMS (EI) Calcd for $C_7H_{14}NO_2S$: 176.0740 Found: 176.0748. The ee of **3r'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 94:6, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 12.99 min (major) and 14.15 min (minor).



1-(ethylsulfonyl)-3-methyl-4-methylenepyrrolidine (3s'). Colorless oil, 55% yield. 87% ee, $[\alpha]_D^{25}$ = 45.7 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (d, *J* = 2.8 Hz, 1H), 4.98-4.96 (m, 1H), 4.10-4.08 (m, 1H), 3.98 (d, *J* = 14.0 Hz, 1H), 3.70 (t, *J* = 8.4 Hz, 1H), 3.03 (q, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 1H), 2.85-2.77 (m, 1H), 1.38 (t, *J* = 7.6 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 106.1, 54.8, 52.0, 44.2, 37.9, 15.8, 7.9. HRMS (EI) Calcd for $C_8H_{16}NO_2S$: 190.0896. Found: 190.0892. The ee of **3s'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 93:7, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 10.81 min (major) and 11.98 min (minor).

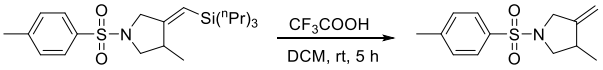


1-(4-Toluenesulfonyl)-3-(*Z*)-ethylidene-4-methylpyrrolidine (3t'): Colorless liquid, 85 % yield, 92% ee, [a] $_D^{25}$ = 26.8 (c = 1.0, DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.18-5.09 (m, 2.4 Hz, 1H), 3.81-3.76 (m, 1H), 3.65-3.60 (m, 1H), 3.48-3.37 (m, 1H), 2.60-2.50 (m, 2H), 2.35 (s, 3H), 1.45 (dd, *J* = 6.8, 1.6 Hz, 3H), 0.92 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCL_3$) δ 143.5, 140.4, 132.7, 129.6, 127.8, 116.0, 55.1, 49.7, 37.2, 21.5, 16.6, 14.4. HRMS (ESI) *m/z* Calcd for $C_{14}H_{20}NO_2S$, $[M + H]^+$ = 266.1209. Found: 266.1205. The ee of **3t'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID) conditions: *n*-hexane/*i*PrOH = 99/1, 0.5 mL/min, 25 ℃, 254 nm; *t*R = 31.526 min (major) and 33.416 min (minor).



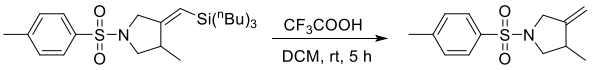
4,4-Bis(ethoxycarbonyl)-1-methylidene-2-methyl-cyclopentane (3u'). Colorless liquid, 55 % yield, 80% ee, [a] $_D^{25}$ = 1.2 (c = -0.5, DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (q, *J* = 2.4 Hz, 1H), 4.73 (q, *J* = 2.4 Hz, 1H), 4.14-4.08 (m, 4H), 2.98 (d, *J* = 16.8 Hz, 1H), 2.92-2.80 (m, 1H), 2.57-2.42 (m, 2H), 1.73-1.64 (m, 1H), 1.17 (td, *J* = 7.2, 1.8 Hz,

6H), 1.04 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.9, 153.4, 105.4, 61.4, 58.2, 42.1, 40.5, 37.2, 17.9, 14.0. HRMS (ESI) *m/z* Calcd for $C_{13}H_{21}O_4$, $[M + H]^+$ = 241.1434. Found: 241.1436. The ee of **3u'** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID) + Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*PrOH = 99/1, 0.3 mL/min, 25 ℃, 230 nm; *t*R = 49.71 min (minor) and 53.11 min (major).



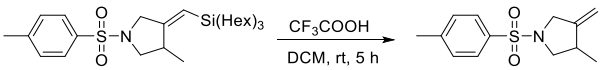
3t 3a'

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 75% yield. 83% ee. $[\alpha]_D^{25}$ = 18.3 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.31 min (major) and 15.34 min (minor).



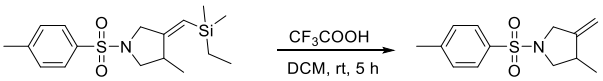
3u 3a'

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 70% yield. 75% ee. $[\alpha]_D^{25}$ = 16.5 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.81 min (major) and 15.91 min (minor).



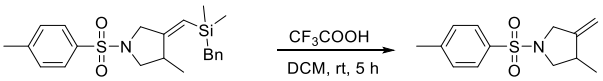
3v 3a'

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 80% yield. 72% ee. $[\alpha]_D^{25}$ = 13.3 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.62 min (major) and 15.66 min (minor).



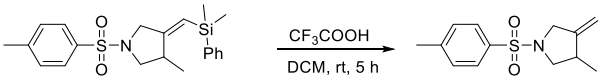
3w 3a'

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 80% yield. 84% ee. $[\alpha]_D^{25}$ = 16.6 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.94 min (major) and 16.15 min (minor).



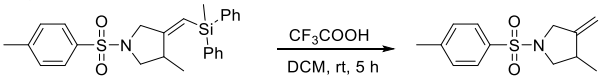
3x 3a'

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 83% yield. 90% ee. $[\alpha]_D^{25}$ = 24.5 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.36 min (major) and 15.49 min (minor).



3y 3a'

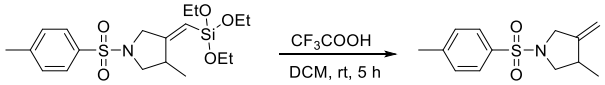
1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 63% yield. 90% ee. $[\alpha]_D^{25}$ = 24.6 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.44 min (major) and 15.49 min (minor).



3z 3a'

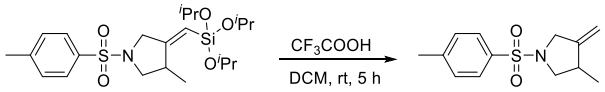
1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 60% yield. 91% ee. $[\alpha]_D^{25}$ = 25.9 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm

ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 14.05 min (major) and 16.36 min (minor).



3aa **3a'**

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 75% yield. 90% ee. [α] $_D^{25}$ = 25.1 (*c* = 0.5, CH_2Cl_2). The ee of **3aa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 90:10, 1.0 mL/min, 25 ℃, 254 nm; tR = 9.33 min (major) and 10.54 min (minor).



3ab **3a'**

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 85% yield. 92% ee. [α] $_D^{25}$ = 27.6 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.49 min (major) and 15.54 min (minor).

3ac **3a'**

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a'). 82% yield. 92% ee. [α] $_D^{25}$ = 28.1 (*c* = 0.5, CH_2Cl_2). The ee of **3a'** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 25 ℃, 254 nm; *t*R = 13.41 min (major) and 15.51 min (minor).

9. X-ray Diffraction Analysis.

9.1. Crystal structure of L3.

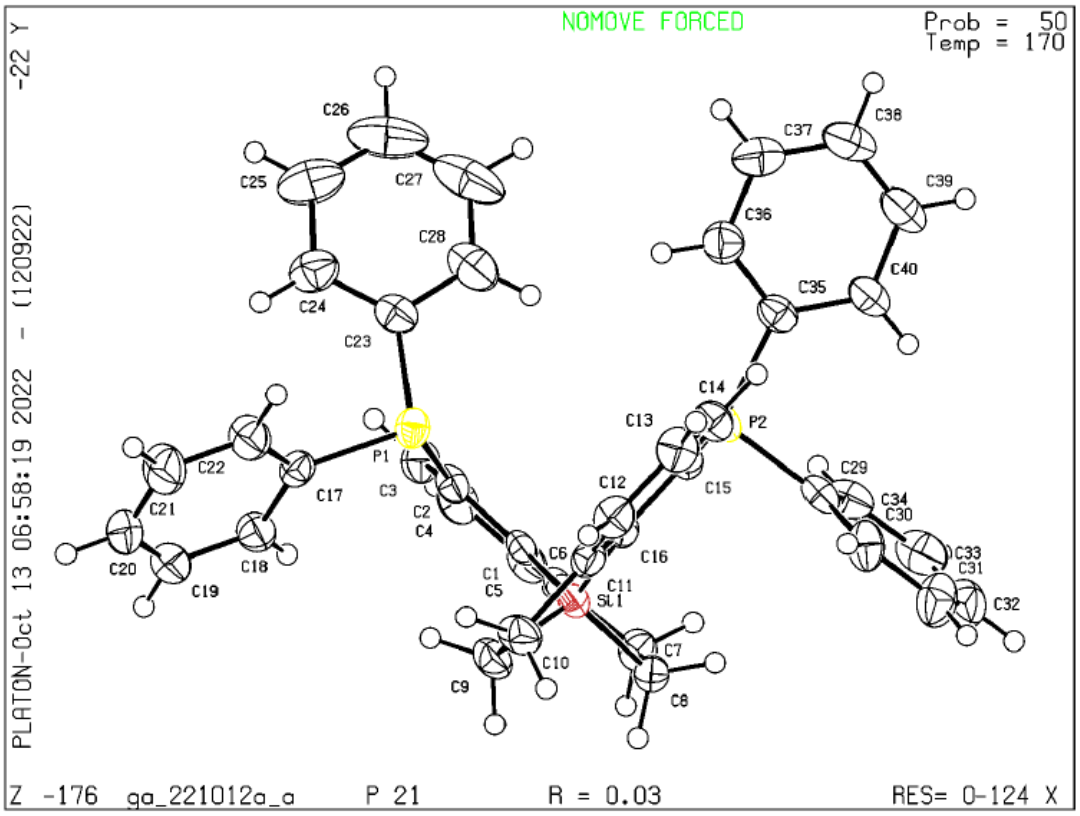


Table S4. Crystal data and structure refinement for ga_221012a_a.

Identification code	ga_221012a_a	
Empirical formula	C40 H34 P2 Si	
Formula weight	604.70	
Temperature	170(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.6462(5) Å	α= 90°.
	b = 8.7260(4) Å	β= 108.620(2)°.
	c = 16.7421(8) Å	γ = 90°.
Volume	1612.35(13) $Å^3$	
Z	2	
Density (calculated)	1.246 Mg/m^3	
Absorption coefficient	1.163 mm^{-1}	
F(000)	636	

Crystal size	0.100 x 0.060 x 0.050 mm^3
Theta range for data collection	4.841 to 53.898°.
Index ranges	-13<=h<=14, -10<=k<=10, -20<=l<=20
Reflections collected	17268
Independent reflections	5819 [R(int) = 0.0394]
Completeness to theta = 53.594°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.752 and 0.527
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5819 / 1 / 388
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0751
R indices (all data)	R1 = 0.0355, wR2 = 0.0778
Absolute structure parameter	0.071(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.210 and -0.155 $e.Å^{-3}$

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ga_221012a_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	7079(1)	6679(1)	2173(1)	31(1)
P(2)	3866(1)	5185(1)	3055(1)	32(1)
Si(1)	4553(1)	4355(1)	1225(1)	29(1)
C(1)	6045(2)	3765(3)	1995(2)	28(1)
C(2)	7123(2)	4594(3)	2346(2)	30(1)
C(3)	8149(3)	3837(4)	2856(2)	37(1)
C(4)	8109(3)	2276(4)	3020(2)	40(1)
C(5)	7043(3)	1471(3)	2689(2)	37(1)
C(6)	6006(3)	2194(3)	2176(2)	31(1)
C(7)	4806(3)	1376(3)	1820(2)	41(1)
C(8)	3862(3)	2386(3)	1190(2)	36(1)
C(9)	4627(3)	5170(4)	199(2)	40(1)
C(10)	3770(3)	6542(4)	-18(2)	41(1)
C(11)	3361(2)	7003(3)	721(2)	31(1)
C(12)	2720(3)	8336(3)	723(2)	35(1)
C(13)	2350(3)	8706(4)	1402(2)	40(1)
C(14)	2650(3)	7752(3)	2104(2)	36(1)
C(15)	3318(2)	6423(3)	2127(2)	29(1)
C(16)	3682(2)	6034(3)	1431(2)	27(1)
C(17)	8042(2)	6980(3)	1507(2)	30(1)
C(18)	8581(3)	5828(4)	1188(2)	37(1)
C(19)	9228(3)	6147(4)	646(2)	42(1)
C(20)	9346(3)	7638(4)	407(2)	47(1)
C(21)	8812(3)	8811(4)	717(2)	53(1)
C(22)	8167(3)	8490(4)	1259(2)	44(1)
C(23)	8054(3)	7314(3)	3214(2)	36(1)
C(24)	9180(3)	7988(4)	3380(2)	49(1)
C(25)	9805(4)	8497(5)	4193(3)	72(1)
C(26)	9323(5)	8313(6)	4828(2)	83(2)
C(27)	8226(6)	7624(6)	4676(3)	82(2)
C(28)	7586(4)	7142(4)	3873(2)	58(1)
C(29)	2693(3)	3702(3)	2866(2)	34(1)

C(30)	1547(3)	3828(4)	2275(2)	43(1)
C(31)	723(3)	2640(4)	2161(3)	53(1)
C(32)	1019(3)	1312(4)	2635(2)	52(1)
C(33)	2147(4)	1180(4)	3223(2)	52(1)
C(34)	2989(3)	2352(4)	3331(2)	44(1)
C(35)	3582(3)	6346(3)	3890(2)	33(1)
C(36)	4276(3)	7655(4)	4161(2)	43(1)
C(37)	4189(3)	8497(4)	4843(2)	50(1)
C(38)	3420(4)	8026(5)	5266(2)	55(1)
C(39)	2728(4)	6750(5)	5009(2)	58(1)
C(40)	2791(3)	5910(4)	4319(2)	46(1)

9.2. Crystal structure of L3-$PdCl_2$

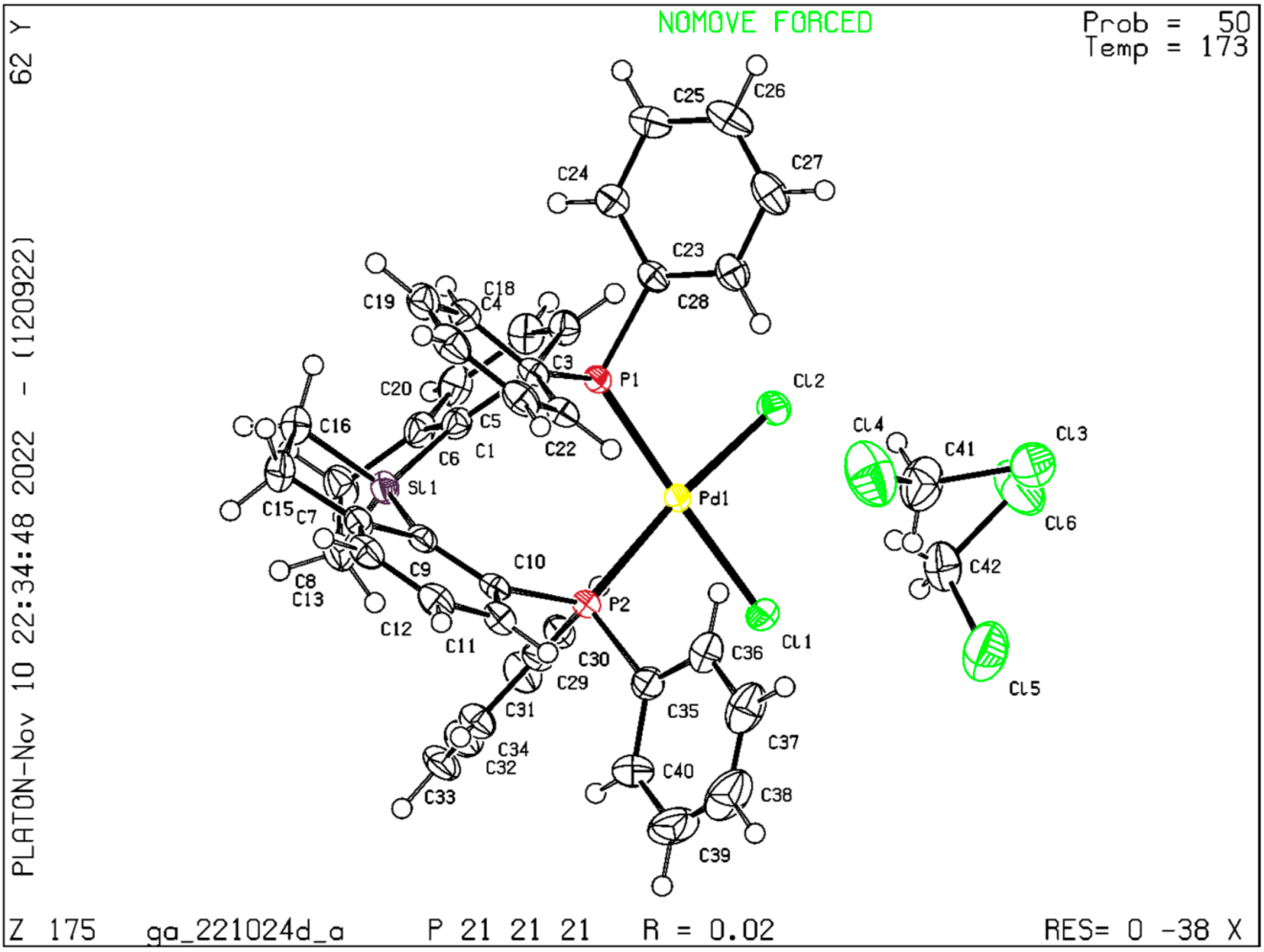


Table S5. Crystal data and structure refinement for ga_221024d_a.

Identification code	ga_221024d_a	
Empirical formula	C42 H38 Cl6 P2 Pd Si	
Formula weight	951.85	
Temperature	173(2) K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.9943(14) Å	a= 90°.
	b = 20.420(3) Å	b= 90°.
	c = 20.447(3) Å	g = 90°.
Volume	4172.9(10) $Å^3$	
Z	4	
Density (calculated)	1.515 Mg/m^3	
Absorption coefficient	5.600 mm^{-1}	

F(000)	1928
Crystal size	0.270 x 0.140 x 0.040 mm^3
Theta range for data collection	4.207 to 57.489°.
Index ranges	-12<=h<=12, -25<=k<=25, -25<=l<=25
Reflections collected	29824
Independent reflections	8649 [R(int) = 0.0259]
Completeness to theta = 53.594°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.805 and 0.502
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8649 / 0 / 469
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0522
R indices (all data)	R1 = 0.0251, wR2 = 0.0528
Absolute structure parameter	0.092(3)
Extinction coefficient	n/a

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ga_221024d_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	4982(1)	5479(1)	6490(1)	19(1)
Cl(1)	3838(1)	6433(1)	6183(1)	30(1)
Cl(2)	3224(1)	5258(1)	7217(1)	29(1)
P(1)	5856(1)	4499(1)	6787(1)	19(1)
P(2)	6371(1)	5759(1)	5637(1)	20(1)
Si(1)	7028(1)	4044(1)	5103(1)	25(1)
C(1)	5465(3)	3855(2)	5579(2)	24(1)
C(2)	5036(4)	3935(1)	6229(1)	22(1)
C(3)	3795(3)	3686(2)	6427(2)	27(1)
C(4)	2978(4)	3361(2)	5984(2)	32(1)
C(5)	3367(4)	3297(2)	5338(2)	32(1)
C(6)	4605(3)	3534(2)	5135(2)	28(1)
C(7)	5085(5)	3464(2)	4434(2)	37(1)
C(8)	6161(4)	3990(2)	4296(2)	34(1)
C(9)	8195(3)	4735(2)	5311(2)	23(1)
C(10)	8039(3)	5402(2)	5489(1)	22(1)
C(11)	9165(3)	5787(2)	5584(2)	26(1)
C(12)	10453(3)	5529(2)	5536(2)	30(1)
C(13)	10617(4)	4878(2)	5383(2)	29(1)
C(14)	9502(3)	4483(2)	5262(2)	26(1)
C(15)	9674(4)	3772(2)	5063(2)	35(1)
C(16)	8359(4)	3399(2)	5138(2)	34(1)
C(17)	7654(3)	4379(2)	6788(2)	22(1)
C(18)	8184(4)	3747(2)	6756(2)	28(1)
C(19)	9553(4)	3653(2)	6845(2)	34(1)
C(20)	10364(4)	4184(2)	6967(2)	36(1)
C(21)	9843(4)	4807(2)	7015(2)	30(1)
C(22)	8478(3)	4903(2)	6928(2)	25(1)
C(23)	5520(3)	4204(2)	7616(2)	24(1)
C(24)	5460(4)	3535(2)	7741(2)	31(1)
C(25)	5356(4)	3306(2)	8376(2)	37(1)
C(26)	5305(4)	3744(2)	8887(2)	39(1)

C(27)	5392(4)	4405(2)	8771(2)	38(1)
C(28)	5507(3)	4640(2)	8137(2)	30(1)
C(29)	5484(3)	5620(2)	4872(2)	25(1)
C(30)	4171(4)	5394(2)	4869(2)	28(1)
C(31)	3501(4)	5297(2)	4285(2)	34(1)
C(32)	4133(4)	5419(2)	3692(2)	34(1)
C(33)	5448(4)	5640(2)	3691(2)	35(1)
C(34)	6121(4)	5728(2)	4275(2)	31(1)
C(35)	6784(4)	6624(2)	5696(2)	28(1)
C(36)	7173(4)	6856(2)	6307(2)	35(1)
C(37)	7699(4)	7482(2)	6374(3)	49(1)
C(38)	7815(5)	7877(2)	5830(3)	62(1)
C(39)	7404(5)	7661(2)	5231(3)	61(1)
C(40)	6873(5)	7035(2)	5157(2)	42(1)
C(41)	4291(6)	6716(3)	7977(3)	60(1)
Cl(3)	3602(2)	7147(1)	8642(1)	69(1)
Cl(4)	6012(2)	6642(1)	8055(1)	83(1)
C(42)	827(5)	6729(2)	6967(2)	48(1)
Cl(5)	1384(2)	7539(1)	6905(1)	74(1)
Cl(6)	-86(2)	6593(1)	7684(1)	82(1)

10. Computational Details

10.1 Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 16[12] and ORCA 5.0.3.[13] Geometries of intermediates and transition states were optimized using the dispersion-corrected B3LYP-D3(BJ) [14, 15] functional and the def2-svp basis set.[16] Vibrational frequency calculations and IRC calculations[17] at the same level of theory of the optimization were performed to confirm if each structure is a local minimum or a transition state. Single-point energy calculations were carried out using the M06-D3 functional[18] with the def2-tzvpp basis set. Solvation energy corrections were calculated in the single-point energy calculations using the CPCM solvation mode and dichloroethane as solvent. A conformation search was performed by manually exchanging the coordinating groups on the metal center of the intermediates and transition states, and the structures were fully optimized using DFT. Only the lowest-energy conformer of each species is reported in the text. The structures were visualized using CYLview[19]. The structure of Pd-**L3** (**Figure S1**) complex was optimized using D3(BJ)-B3LYP/def2-svp. The reliability of the method was confirmed by comparing the calculated structures of Pd-**L1** and Pd-**L2** with the corresponding crystal structures.

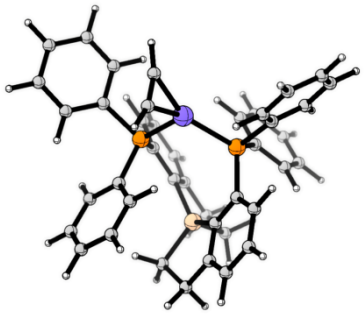
10.2 Energy Profiles Computed for Hydrosilylation

Si-SDP	D3(BJ)-B3LYP/ def2-svp	zpe	D3-M06/ def2tzvpp-CPCM(DCE)
S_{Si}	-2995.473268	0.687529	-2996.057063
TS_{Si}-1	-2995.471066	0.687915	-2996.049941
I_{Si}	-2995.476078	0.688733	-2996.055257
TS_{Si}-2	-2995.463165	0.687965	-2996.046464
II_{Si}	-2995.497366	0.690766	-2996.066617
TS_{Si}-3	-2995.484792	0.689635	-2996.058637
P_{Si}	-2995.497366	0.690766	-2996.122153

SDP	D3(BJ)-B3LYP/ def2-svp	zpe	D3-M06/ def2tzvpp-CPCM(DCE)
S_C	-2744.096616	0.695511	-2744.627494
TS_C-1	-2744.094298	0.695489	-2744.621005
I_C	-2744.102384	0.697004	-2744.6271
TS_C-2	-2744.087218	0.696457	-2744.613491
II_C	-2744.117775	0.698223	-2744.634664
TS_C-3	-2744.110915	0.697521	-2744.6292
P_C	-2744.163533	0.702274	-2744.69438

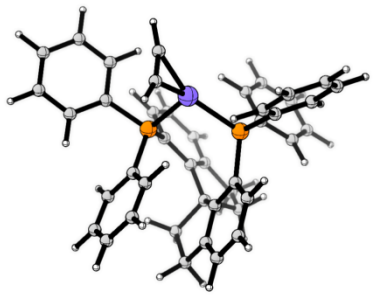
10.3 Cartesian Coordinates

Rh-**L3** (Si-SDP)



P	-1.69225300	-0.58317200	0.19811200
P	1.69214400	-0.58320300	-0.19868200
C	1.01716700	3.73482600	1.16788400
H	1.94431000	3.22514600	1.45923400
H	1.29555600	4.70367900	0.72825100
C	0.09005700	3.88898000	2.39181200
H	0.65083600	4.09671100	3.31717800
H	-0.58760300	4.75009900	2.24849500
C	-0.75400700	2.63721100	2.56013500
C	-1.36542800	2.30845600	3.77685100
H	-1.23037300	2.96060500	4.64372400
C	-2.13946800	1.15446100	3.88546300
H	-2.62278000	0.90417300	4.83253600
C	-2.29188300	0.30574700	2.78521900
H	-2.88818000	-0.60148700	2.88518700
C	-1.67860100	0.62279800	1.56483600
C	-0.91219500	1.80141700	1.43011400
C	-1.01674500	3.73523300	-1.16644400
H	-1.94341400	3.22537000	-1.45894500
H	-1.29591600	4.70362600	-0.72629100
C	-0.08871400	3.89076800	-2.38949800
H	-0.64878600	4.09949700	-3.31506600
H	0.58880800	4.75175200	-2.24470900
C	0.75550200	2.63919200	-2.55848300
C	1.36765700	2.31152100	-3.77512100
H	1.23313000	2.96443500	-4.64150000
C	2.14176100	1.15761500	-3.88428200
H	2.62565100	0.90816900	-4.83128100
C	2.29345700	0.30788900	-2.78472300
H	2.88975600	-0.59929400	-2.88515300
C	1.67943900	0.62386400	-1.56442700
C	0.91304600	1.80241700	-1.42909900
C	-2.91444600	-1.90050700	0.54975300
C	-4.07481400	-2.09133600	-0.21921000
H	-4.33660700	-1.37908100	-1.00240200
C	-4.89478200	-3.19550200	0.01849000
H	-5.80046500	-3.33249900	-0.57630900
C	-4.56097700	-4.12669900	1.00791100
H	-5.20638400	-4.98980800	1.18469900
C	-3.39990800	-3.95566600	1.76644300
H	-3.13432600	-4.68163400	2.53779200
C	-2.57635900	-2.85035800	1.53997900
H	-1.67473100	-2.71088100	2.14504600
C	-2.31024500	0.32093900	-1.25277700
C	-3.44755700	1.13745700	-1.12794400
H	-3.91848600	1.27608600	-0.15201300
C	-3.96896500	1.77725100	-2.25250900
H	-4.85560500	2.40768600	-2.15757900
C	-3.34621500	1.62288900	-3.49733900
H	-3.75035100	2.13414000	-4.37392500
C	-2.20850900	0.82072600	-3.61976300
H	-1.71650300	0.70807000	-4.58778900
C	-1.69480100	0.16099600	-2.50110000
H	-0.80737900	-0.46890800	-2.58535600
C	2.91397800	-1.90072800	-0.55082300
C	4.07370200	-2.09285300	0.21879200
H	4.33535600	-1.38137000	1.00273300
C	4.89319400	-3.19729600	-0.01924200
H	5.79839900	-3.33529300	0.57605600
C	4.55952100	-4.12751400	-1.00963400
H	5.20454800	-4.99085600	-1.18666800
C	3.39907900	-3.95520000	-1.76883000
H	3.13361300	-4.68038900	-2.54095100
C	2.57602200	-2.84958100	-1.54206000
H	1.67493500	-2.70906100	-2.14770000
C	2.30980300	0.31948800	1.25321400
C	1.69410700	0.15831100	2.50125500
H	0.80672100	-0.47173700	2.58474900
C	2.20750300	0.81704000	3.62064300
H	1.71527000	0.70345800	4.58844300
C	3.34517400	1.61940800	3.49922000
H	3.74906300	2.12989000	4.37636900
C	3.96824300	1.77490800	2.25469500
H	4.85489300	2.40544900	2.16056300
C	3.44713800	1.13612300	1.12941300
H	3.91829300	1.27567400	0.15372200
Rh	-0.00015700	-1.94889300	-0.00143100
Si	0.00013400	2.65187600	0.00063600

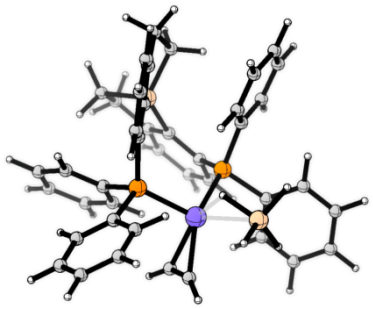
Rh-**L2** (SDP)



P	-1.61331700	-0.50608900	0.26943900
P	1.61305000	-0.50662700	-0.26904200
C	1.15861800	3.53588600	0.50465300
H	2.10570800	2.99121600	0.44882300
H	1.25871200	4.42872000	-0.12762000
C	0.82196100	3.85298400	1.96701100
H	1.71945900	3.93825300	2.59862500

H	0.27125300	4.80402200	2.06680200
C	-0.05428400	2.69944000	2.38507500
C	-0.46664200	2.41046200	3.68403400
H	-0.13120200	3.03241200	4.51725400
C	-1.31738600	1.32684400	3.90372200
H	-1.66867200	1.09324900	4.91099500
C	-1.71731200	0.52956000	2.83217100
H	-2.36892000	-0.32128000	3.02658700
C	-1.29319900	0.79848600	1.51457300
C	-0.45757500	1.91697600	1.28461200
C	-1.15766700	3.53615900	-0.50623800
H	-2.10500800	2.99196700	-0.45000400
H	-1.25728200	4.42937700	0.12556600
C	-0.82101400	3.85232400	-1.96879300
H	-1.71852600	3.93769400	-2.60037000
H	-0.26985800	4.80304500	-2.06912700
C	0.05465800	2.69816100	-2.38633400
C	0.46669700	2.40828500	-3.68519500
H	0.13135600	3.02989000	-4.51871300
C	1.31699400	1.32422400	-3.90440100
H	1.66801600	1.08991100	-4.91159900
C	1.71682300	0.52742500	-2.83245200
H	2.36810500	-0.32375300	-3.02648200
C	1.29303700	0.79726900	-1.51494100
C	0.45780700	1.91616100	-1.28548800
C	-2.88405400	-1.66329400	0.91179600
C	-4.18151800	-1.74993500	0.38160600
H	-4.50883300	-1.05282100	-0.38957200
C	-5.05802100	-2.73777900	0.83552000
H	-6.06755400	-2.79261400	0.42246900
C	-4.64902500	-3.65662600	1.80671900
H	-5.33916300	-4.42885700	2.15331800
C	-3.35377600	-3.59081500	2.32821300
H	-3.02702200	-4.30930600	3.08290900
C	-2.47355700	-2.60310700	1.88312500
H	-1.46237500	-2.54785500	2.29899700
C	-2.34081100	0.24197700	-1.22001500
C	-3.40937700	1.14741500	-1.11525400
H	-3.78488700	1.44142100	-0.13214000
C	-3.99214300	1.67280400	-2.26968600
H	-4.82355000	2.37622900	-2.18720000
C	-3.50749000	1.30183800	-3.52905500
H	-3.96074600	1.71987200	-4.43070600
C	-2.44882800	0.39549800	-3.63470800
H	-2.06787500	0.10808400	-4.61650800
C	-1.87076000	-0.14013400	-2.48315600
H	-1.03617800	-0.84066000	-2.55216200
C	2.88335300	-1.66456400	-0.91098600
C	4.18103200	-1.75095800	-0.38128400
H	4.50874400	-1.05334200	0.38927000
C	5.05726000	-2.73920000	-0.83486800
H	6.06695700	-2.79383700	-0.42219200
C	4.64778800	-3.65868100	-1.80526500
H	5.33771500	-4.43120900	-2.15161900
C	3.35232700	-3.59311200	-2.32626200
H	3.02519400	-4.31209000	-3.08033100
C	2.47238100	-2.60501900	-1.88148700
H	1.46104200	-2.54994000	-2.29701000
C	2.34121700	0.24225000	1.21969700
C	1.87123400	-0.13860500	2.48323600
H	1.03623100	-0.83855600	2.55297300
C	2.44990700	0.39754900	3.63424900
H	2.06900900	0.11112000	4.61635900
C	3.50910300	1.30315300	3.52765300
H	3.96284400	1.72158200	4.42887700
C	3.99366900	1.67288100	2.26788300
H	4.82547000	2.37575400	2.18466500
C	3.41029100	1.14698900	1.11399100
H	3.78568900	1.44010100	0.13056400
Rh	-0.00026500	-1.95435100	0.00097600
C	0.00029100	2.61694600	-0.00059800

S_{si} (Si-SDP)



P	-1.652680	0.270741	-0.371259
P	1.715606	0.393889	0.161457
C	0.982451	-4.168100	-0.585023
H	1.941102	-3.743706	-0.904772
H	1.200417	-5.062953	0.015997
C	0.107111	-4.489512	-1.816812
H	0.706198	-4.844647	-2.670705
H	-0.595911	-5.308237	-1.579112
C	-0.700030	-3.265517	-2.215409
C	-1.255263	-3.113804	-3.492171
H	-1.103096	-3.890485	-4.246271
C	-1.998791	-1.975801	-3.801405
H	-2.442592	-1.863409	-4.793234
C	-2.176949	-0.968474	-2.847578
H	-2.758826	-0.084384	-3.105963
C	-1.614102	-1.105062	-1.570909
C	-0.882534	-2.263574	-1.235886
C	-1.153107	-3.779340	1.595736
H	-2.092046	-3.234160	1.753810
H	-1.410953	-4.803964	1.290660
C	-0.296049	-3.744328	2.876250
H	-0.904306	-3.826816	3.791063
H	0.396868	-4.605246	2.893961
C	0.523770	-2.466088	2.907020
C	1.018712	-1.941629	4.106838
H	0.812768	-2.457300	5.048399

C	1.763683	-0.765679	4.100516
H	2.158904	-0.357237	5.033295
C	2.005741	-0.098549	2.897238
H	2.593605	0.816976	2.912772
C	1.510130	-0.607697	1.686493
C	0.768445	-1.812279	1.674275
C	-2.868972	1.523592	-0.935110
C	-3.958605	1.902712	-0.131853
H	-4.184433	1.353587	0.782130
C	-4.752820	2.992340	-0.493664
H	-5.597591	3.276307	0.137630
C	-4.469381	3.719655	-1.653369
H	-5.091459	4.573736	-1.929607
C	-3.387464	3.351444	-2.458154
H	-3.159566	3.915310	-3.365153
C	-2.587724	2.265087	-2.101336
H	-1.731537	2.002935	-2.724606
C	-2.404704	-0.443682	1.128549
C	-3.567805	-1.224365	1.003308
H	-3.971052	-1.447428	0.013028
C	-4.205596	-1.714878	2.141854
H	-5.110977	-2.317169	2.041256
C	-3.678517	-1.443936	3.411011
H	-4.174983	-1.835549	4.301618
C	-2.516953	-0.678968	3.537721
H	-2.095814	-0.476300	4.524283
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H	4.484633	0.599356	-0.982687
C	5.361400	2.347889	-0.089836
H	6.289526	2.245669	-0.656344
C	5.197072	3.409345	0.800473
H	5.997066	4.139918	0.938196
C	3.997224	3.539239	1.508577
H	3.854678	4.372383	2.200295
C	2.973711	2.611808	1.325100
H	2.031958	2.748441	1.856787
C	2.294605	-0.788442	-1.098957
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H	0.855318	-0.209121	-2.597172
C	2.244096	-1.687050	-3.348845
H	1.781022	-1.727101	-4.336550
C	3.349325	-2.489065	-3.055914
H	3.763156	-3.150495	-3.820238
C	3.921558	-2.455013	-1.778253
H	4.777580	-3.091077	-1.543378
C	3.388797	-1.619452	-0.797118
H	3.824299	-1.610027	0.204328
Rh	0.063960	1.796001	-0.373436
H	-0.418823	2.262623	1.330361
Si	-1.069334	3.657562	1.519163
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H	-1.802741	4.179241	0.342442
H	-2.018969	3.394301	2.633536
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C	1.064260	2.507362	-2.042635
H	1.107626	4.538210	-1.010132
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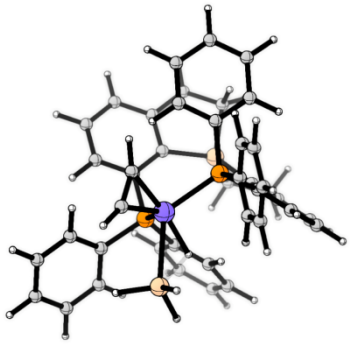
TS_{Si}-1 (Si-SDP)



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C	-0.480535	2.949824	-2.493492
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C	1.254325	2.055968	-3.925336
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C	0.012007	2.206639	-1.392530
C	-0.518583	4.071794	1.226417
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H	-0.663166	5.070569	0.789393
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H	-0.898143	4.247075	3.396387
H	-2.336753	4.404110	2.393139
C	-1.696853	2.377724	2.658046
C	-2.099317	1.834227	3.884317
H	-2.182053	2.478865	4.763279
C	-2.393866	0.475808	3.982942
H	-2.721362	0.052897	4.935433
C	-2.269879	-0.356442	2.865509
H	-2.508508	-1.414686	2.961467
C	-1.852431	0.173229	1.636471
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C	5.761386	-0.484771	0.026207

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C	1.849990	1.259237	1.211691
C	2.571513	2.462601	1.099139
H	2.937317	2.792675	0.124516
C	2.829992	3.231125	2.232969
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C	2.349612	2.819822	3.482252
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H	-2.436571	0.607882	-4.434855
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C	-4.723285	0.500859	-1.900975
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H	-4.302739	-0.094997	0.130302
Rh	0.634322	-1.738540	-0.227624
H	1.057881	-1.713721	1.387509
Si	2.290103	-2.884406	1.371509
H	1.654294	-4.192557	1.681194
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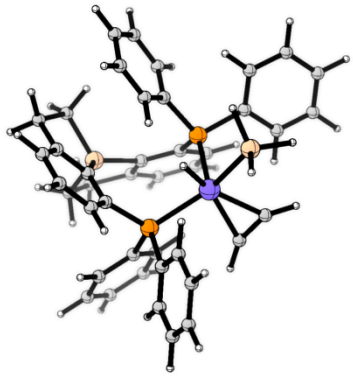
$\mathbf{I}_{si}$ (Si-SDP)



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H	2.105922	-4.564526	-0.709853
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H	1.502957	-3.943485	-3.313419
H	0.332232	-4.818210	-2.329857
C	-0.132644	-2.744535	-2.570141
C	-0.722277	-2.481618	-3.812610
H	-0.435095	-3.076982	-4.683230
C	-1.669417	-1.470675	-3.936693
H	-2.142108	-1.269101	-4.900423
C	-2.023379	-0.708347	-2.821799
H	-2.779619	0.062953	-2.939019
C	-1.431869	-0.948218	-1.570747
C	-0.475369	-1.983892	-1.424444
C	-0.325991	-3.986915	1.147208
H	-1.339889	-3.663316	1.405743
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H	0.006385	-4.242443	3.314967
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C	1.258638	-2.643975	2.569880
C	1.851066	-2.250907	3.777215
H	1.800370	-2.910500	4.647580
C	2.508007	-1.025562	3.865614
H	2.981578	-0.723362	4.802513
C	2.564016	-0.171572	2.758172
H	3.079471	0.784370	2.846529
C	1.956966	-0.545265	1.552109
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C	-4.599079	0.801654	0.241158
H	-4.565586	0.140254	1.105174
C	-5.778566	1.500722	-0.033961
H	-6.645858	1.363683	0.615238
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H	-2.657934	2.066403	-2.264049
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C	-3.037955	-2.629640	3.315542
H	-3.351309	-3.280686	4.134512
C	-2.059217	-1.657748	3.529963
H	-1.595338	-1.548901	4.512002
C	-1.666482	-0.815431	2.486508
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C	4.776089	3.547461	0.154927
H	5.675574	3.786085	-0.416896
C	4.349835	4.398086	1.176706
H	4.914316	5.304072	1.407362
C	3.193215	4.088801	1.900271
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C	2.468930	2.935599	1.600828
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H	1.048590	0.249489	-2.641827
C	2.676649	-0.806383	-3.593959
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C	3.929829	-1.398535	-3.421609
H	4.430607	-1.874008	-4.267875
C	4.542913	-1.391518	-2.162209
H	5.518432	-1.862903	-2.025154
C	3.902111	-0.793035	-1.077883
H	4.371059	-0.805363	-0.091487
Rh	-0.292423	1.753423	-0.010542
H	-0.328610	1.262758	1.466650
Si	-1.861913	3.022360	1.307554
H	-0.977008	3.949447	2.079353
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H	-2.635143	2.197581	2.279375
C	-0.589742	3.386315	-1.313475
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H	-1.364907	4.133495	-1.441346
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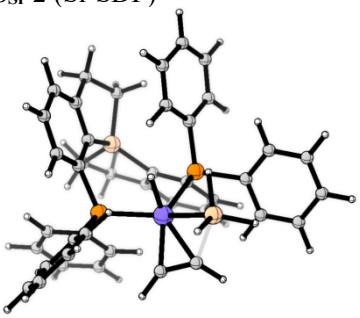
Si	0.520924	-2.736627	0.013279

TS_{Si}-2 (Si-SDP)



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H	2.314122	-3.145181	-1.454583
H	1.812225	-4.671280	-0.714642
C	0.521568	-3.980963	-2.367208
H	1.088082	-4.077466	-3.307637
H	-0.024647	-4.933537	-2.244874
C	-0.501769	-2.865076	-2.489551
C	-1.234565	-2.680193	-3.669297
H	-1.040619	-3.322217	-4.532612
C	-2.215203	-1.696070	-3.734315
H	-2.806141	-1.563946	-4.643432
C	-2.451035	-0.869451	-2.632012
H	-3.233316	-0.117124	-2.700720
C	-1.702859	-1.018432	-1.454826
C	-0.724216	-2.037901	-1.362684
C	-0.519432	-3.916724	1.236183
H	-1.494539	-3.512592	1.532503
H	-0.696091	-4.915759	0.811451
C	0.435910	-3.954781	2.445802
H	-0.096025	-4.155810	3.389756
H	1.164872	-4.776817	2.328908
C	1.207822	-2.650321	2.549699
C	1.872758	-2.280562	3.726294
H	1.816411	-2.927168	4.606017
C	2.605069	-1.097685	3.773239
H	3.133050	-0.812625	4.686043
C	2.665171	-0.263772	2.651779
H	3.237636	0.661459	2.707086
C	1.990414	-0.614097	1.474255
C	1.258955	-1.820638	1.404841
C	-3.439214	1.146038	-0.413132
C	-4.491487	1.201258	0.512717
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C	-5.593107	2.031534	0.281262
H	-6.401467	2.067689	1.014712
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H	-6.526697	3.449990	-1.056061
C	-4.611772	2.768273	-1.799781
H	-4.652140	3.381127	-2.702957
C	-3.503337	1.957312	-1.563803
H	-2.674203	1.968526	-2.272800
C	-2.313213	-0.826772	1.381445
C	-3.368377	-1.753088	1.286563
H	-3.899964	-1.880443	0.340993
C	-3.734874	-2.511964	2.396653
H	-4.555680	-3.227929	2.318383
C	-3.042477	-2.365106	3.605611
H	-3.326612	-2.965567	4.472576
C	-1.985104	-1.458516	3.699529
H	-1.432222	-1.350459	4.634589
C	-1.624437	-0.686920	2.591315
H	-0.792740	0.015089	2.670228
C	3.165031	1.872524	0.472343
C	4.401917	1.954235	-0.180014
H	4.672990	1.229938	-0.947538

C	5.296943	2.983190	0.135615
H	6.254907	3.040642	-0.385807
C	4.969194	3.930833	1.105539
H	5.670728	4.731342	1.349976
C	3.731951	3.858598	1.756622
H	3.463455	4.602252	2.510087
C	2.832388	2.844196	1.434863
H	1.858154	2.811213	1.928322
C	2.520310	-0.304131	-1.377692
C	1.810474	-0.246468	-2.584562
H	0.869025	0.303321	-2.635179
C	2.294385	-0.913019	-3.713116
H	1.728921	-0.876485	-4.646288
C	3.492651	-1.627417	-3.643456
H	3.872776	-2.144321	-4.527364
C	4.202698	-1.692431	-2.438212
H	5.131632	-2.263560	-2.379513
C	3.714013	-1.043651	-1.304421
H	4.251203	-1.123633	-0.356933
Rh	-0.131178	1.669731	-0.155657
H	-0.141133	1.174798	1.298963
Si	-1.538271	3.613638	0.790348
H	-0.677045	4.693384	1.338105
H	-2.794298	4.170844	0.234851
H	-1.904706	2.714493	1.922772
C	-0.535259	3.533066	-1.118937
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H	-1.184733	4.209788	-1.685508
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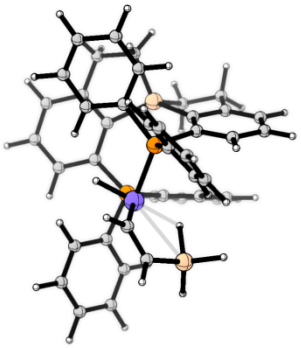
Si	0.349360	-2.751856	0.030231

II_{Si} (Si-SDP)



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H	-1.245301	-4.873735	-2.367526
H	-2.623385	-4.809193	-1.273511
C	-2.044187	-2.892333	-2.026744
C	-2.593722	-2.641213	-3.291889
H	-2.757287	-3.468892	-3.987216
C	-2.934072	-1.340882	-3.664322
H	-3.372559	-1.151220	-4.646755
C	-2.713260	-0.270999	-2.788101
H	-2.979507	0.742115	-3.092194
C	-2.148540	-0.512563	-1.530450
C	-1.817669	-1.824179	-1.134124
C	-2.538558	-2.829717	1.791779
H	-3.194057	-1.951228	1.856213
H	-3.175165	-3.700990	1.579636
C	-1.731040	-2.992124	3.090989
H	-2.310558	-2.711912	3.985105
H	-1.446812	-4.050582	3.233701
C	-0.459927	-2.164209	3.015890
C	0.229540	-1.801620	4.180252
H	-0.161804	-2.105096	5.154759
C	1.404935	-1.063808	4.096415
H	1.954202	-0.791035	5.000176
C	1.887454	-0.665912	2.847418
H	2.814799	-0.100330	2.802773
C	1.200920	-1.004365	1.671194
C	0.013413	-1.779165	1.736186
C	-2.028136	2.454001	-1.105933
C	-2.701753	3.423277	-0.338662
H	-3.142546	3.148008	0.620476
C	-2.803895	4.736006	-0.798502
H	-3.334247	5.478128	-0.197755
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H	-0.930797	2.099497	-2.954002
C	-2.634569	0.646926	1.094134
C	-4.018946	0.428705	0.991856
H	-4.487000	0.346079	0.008282
C	-4.791128	0.304157	2.146441
H	-5.866774	0.133176	2.066240
C	-4.185836	0.389663	3.406755
H	-4.791964	0.284173	4.309292
C	-2.809378	0.604745	3.511160
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H	6.654149	-0.509522	-1.084797
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C	3.951241	1.161841	1.140388
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H	0.834360	-2.821526	-4.142636
C	2.051515	-3.954648	-2.759250
H	2.152192	-4.814857	-3.424624
C	2.646631	-3.977524	-1.491602
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Rh	0.646575	1.498726	-0.492536
H	0.811147	0.860038	-1.879602
Si	1.060683	3.710802	1.255048
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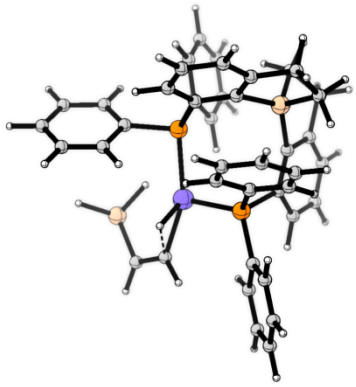
TS_{Si}-3



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C	-1.315858	-3.507739	1.896802
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C	1.344417	-1.884280	4.089819
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H	2.185261	-2.973369	-4.642152
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Si	-1.089548	4.319234	0.900370
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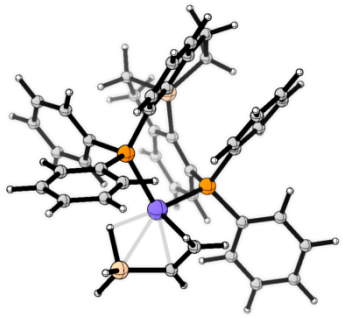

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C	-1.188315	-2.927405	-2.338517
C	-1.706475	-2.578127	-3.593221
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H	-2.681638	-1.048945	-4.763396
C	-2.274158	-0.379666	-2.753169
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H	2.024216	-2.680798	-4.887091
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Rh	0.311686	1.732174	0.391258
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Si	-0.166197	4.179250	1.192974
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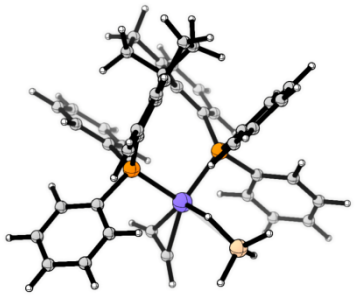

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C	0.598165	3.818405	0.965543
H	1.605771	3.417665	0.819719
H	0.556709	4.792394	0.459080
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H	-1.587508	0.387297	5.053895
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H	6.163674	-1.819879	-0.832049
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C	-4.490902	-3.933192	1.586793
H	-5.152157	-4.746723	1.892791
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H	-1.318672	-2.796345	2.069217
C	-2.440265	0.331042	-1.109605
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H	-2.269737	0.854167	-4.475822
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C	-4.303690	1.690161	-1.866722
H	-5.215881	2.248870	-1.646258
C	-3.612338	1.055419	-0.833769
H	-3.986006	1.122107	0.190474
Rh	0.226112	-1.768394	-0.286335
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H	1.562128	-4.566867	1.779111
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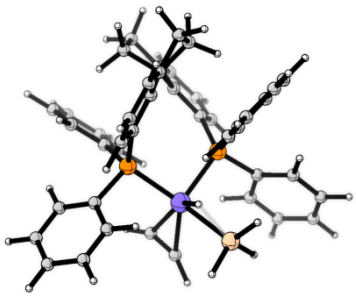

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C	0.860604	1.968316	-3.845114
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C	1.395575	1.162595	-2.841508
H	2.156623	0.436333	-3.114984
C	0.985138	1.278669	-1.496368
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C	0.556464	3.859935	0.707089
H	1.567755	3.453761	0.616185
H	0.524031	4.790034	0.123282
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H	-1.790683	0.785635	4.991303
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C	-1.440690	0.739355	1.577795
C	-0.795934	1.986364	1.410236
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C	5.337240	-1.631499	-1.027707
H	6.317996	-1.621053	-0.547644
C	5.112370	-2.434119	-2.146449
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C	-2.776329	-1.804948	0.872801
C	-4.053222	-1.993861	0.324004
H	-4.425442	-1.330497	-0.455262
C	-4.860538	-3.049213	0.760606
H	-5.852049	-3.182777	0.322509
C	-4.404961	-3.927435	1.744557
H	-5.038400	-4.750434	2.082365
C	-3.128353	-3.753761	2.289719
H	-2.758343	-4.441212	3.053408
C	-2.317390	-2.708539	1.851915
H	-1.314647	-2.601485	2.267553
C	-2.490583	0.248189	-1.155573
C	-2.022649	0.073943	-2.463770
H	-1.092974	-0.467883	-2.635646
C	-2.723097	0.622957	-3.539161
H	-2.341739	0.495765	-4.554076
C	-3.900276	1.341234	-3.315144
H	-4.449079	1.769123	-4.157060
C	-4.377260	1.513559	-2.010913
H	-5.297475	2.074116	-1.832533
C	-3.674172	0.972759	-0.933667
H	-4.046924	1.112050	0.083724
Rh	0.271383	-1.816202	-0.110339
H	0.894898	-1.846991	1.402329
Si	2.035242	-3.143028	1.207959
H	1.357266	-4.270408	1.903680
H	2.880518	-3.660782	0.101144
H	2.946678	-2.456628	2.167925
C	0.072317	-3.713622	-0.993931
C	-0.807531	-2.949712	-1.504176
H	0.512468	-4.700434	-0.892997
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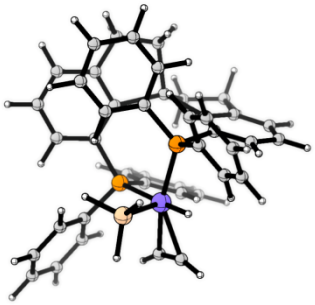
I$_{C}$ (SDP)



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H	-0.943807	4.017561	-3.385390
H	0.154594	4.871070	-2.306432
C	0.623737	2.796363	-2.533505
C	1.350356	2.571167	-3.709193
H	1.163611	3.193067	-4.588664
C	2.313004	1.566404	-3.753605
H	2.895140	1.399242	-4.662517
C	2.531620	0.759079	-2.635405
H	3.284247	-0.025034	-2.691548
C	1.797020	0.956188	-1.454190
C	0.840621	1.999052	-1.382406
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H	1.674248	3.870886	1.219668
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C	-0.849595	2.670269	2.573346
C	-1.364296	2.268993	3.813812
H	-1.252532	2.922387	4.682973
C	-2.014121	1.045917	3.937092
H	-2.425626	0.735026	4.900062
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H	6.573095	-1.242263	1.435609
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C	3.949099	-1.931730	-1.332036
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C	1.959822	0.489858	1.468840
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H	3.239339	2.096971	0.782697
C	2.893661	2.199245	2.912614
H	3.503884	3.095667	3.042618
C	2.264835	1.612459	4.013995
H	2.382630	2.051653	5.007033
C	1.486525	0.463875	3.845010
H	0.988432	0.006365	4.701174
C	1.338307	-0.098920	2.578207
H	0.731201	-0.992719	2.452383
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C	-4.771699	-3.898729	1.317251
H	-5.462671	-4.702415	1.580253
C	-3.515419	-3.823169	1.926551
H	-3.218349	-4.567540	2.668520
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H	-1.651011	-2.768008	2.059338
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C	-2.113544	0.459994	-2.445067
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C	-2.810913	1.168843	-3.427616
H	-2.434453	1.185453	-4.452400
C	-3.982286	1.853308	-3.096353
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H	-5.349031	2.402217	-1.509260
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H	-4.095513	1.170139	0.243344
Rh	0.206578	-1.739371	-0.824543
H	1.465371	-2.449568	-1.418028
Si	0.881937	-3.347133	0.713386
H	2.359708	-3.485615	0.819127
H	0.373300	-3.026590	2.078870
H	0.287070	-4.647093	0.291162
C	-0.323873	-3.171180	-2.353882
C	-1.404682	-2.724426	-1.915265
H	0.335877	-3.804641	-2.926942
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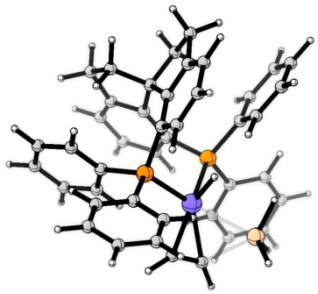
TS_C-2 (SDP)



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H	2.004119	3.976852	2.671462
H	0.631932	4.935786	2.100737
C	0.164122	2.856871	2.374138
C	-0.327396	2.610988	3.654111
H	0.029552	3.200548	4.501713
C	-1.295474	1.625621	3.827104

H	-1.722449	1.431032	4.813228
C	-1.732434	0.883121	2.730645
H	-2.503005	0.135500	2.896749
C	-1.219050	1.087654	1.433415
C	-0.255026	2.112397	1.252254
C	-0.755463	3.753380	-0.588820
H	-1.733564	3.266004	-0.593275
H	-0.844904	4.655764	0.031826
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C	0.541000	2.841649	-2.377313
C	1.039365	2.534759	-3.641252
H	0.792257	3.166070	-4.498110
C	1.868804	1.424053	-3.789703
H	2.290432	1.172066	-4.765077
C	2.165487	0.624707	-2.685729
H	2.807573	-0.241728	-2.832067
C	1.647620	0.905266	-1.404151
C	0.827134	2.046230	-1.248574
C	-3.158332	-1.066316	0.810299
C	-4.409209	-1.087380	0.176959
H	-4.598770	-0.461265	-0.693480
C	-5.424234	-1.931694	0.640658
H	-6.389969	-1.938579	0.130780
C	-5.206633	-2.761302	1.740095
H	-6.002291	-3.416536	2.100860
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C	-2.940520	-1.929545	1.904279
H	-1.961879	-1.969295	2.385456
C	-2.428877	0.826989	-1.259463
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H	-3.853415	1.875554	-0.001811
C	-4.040231	2.452663	-2.070987
H	-4.855460	3.152897	-1.876864
C	-3.550769	2.285637	-3.372504
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C	-2.502040	1.396757	-3.615243
H	-2.108661	1.271654	-4.625869
C	-1.943884	0.667797	-2.561890
H	-1.113624	-0.012825	-2.757133
C	3.245319	-1.470113	-0.738172
C	4.540394	-1.328141	-0.221085
H	4.749085	-0.602730	0.563609
C	5.580846	-2.136827	-0.690495
H	6.582517	-2.020181	-0.271194
C	5.342078	-3.089467	-1.681667
H	6.156657	-3.719339	-2.045655
C	4.050834	-3.242792	-2.198276
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H	2.000654	-2.590036	-2.114783
C	2.336579	0.213387	1.455994
C	1.714971	-0.269883	2.616237
H	0.903485	-0.994461	2.533928
C	2.112625	0.192485	3.870896
H	1.612779	-0.177649	4.767921
C	3.139737	1.133764	3.976555
H	3.449346	1.497340	4.958839
C	3.773444	1.610143	2.824441
H	4.580626	2.341568	2.904429
C	3.375145	1.151823	1.567815
H	3.873512	1.525786	0.671551
Rh	-0.082288	-1.747459	-0.131340
H	-0.129741	-1.151513	-1.534000
Si	-1.839381	-3.429175	-1.096477
H	-1.300282	-4.557798	-1.902911
H	-3.022876	-3.865864	-0.321490
H	-2.251026	-2.376074	-2.067854
C	-0.385117	-3.807509	0.443659
C	0.854172	-3.394490	0.542332
H	-0.929674	-4.672235	0.842485
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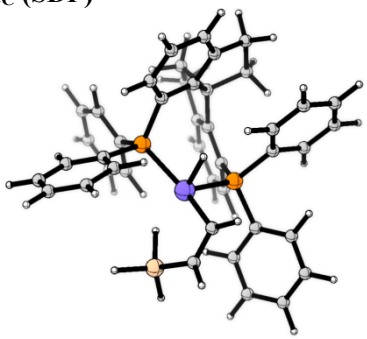
II_C (SDP)



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H	0.968186	-4.665014	0.313179
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H	1.361201	-4.371103	-2.452156
H	-0.073010	-5.191989	-1.823363
C	-0.416172	-3.119873	-2.281072
C	-0.919773	-2.939647	-3.570801
H	-0.620882	-3.613360	-4.377562
C	-1.829950	-1.909041	-3.809053
H	-2.255153	-1.768531	-4.805175
C	-2.199355	-1.046226	-2.773540
H	-2.895119	-0.233307	-2.982046
C	-1.669117	-1.196220	-1.479979
C	-0.776286	-2.260264	-1.229438
C	-1.467755	-3.716312	0.645394
H	-2.399081	-3.148867	0.541822
H	-1.585817	-4.643547	0.068492
C	-1.162136	-3.941780	2.124791
H	-2.069359	-3.983868	2.746757

H	-0.613160	-4.883854	2.296108
C	-0.287494	-2.768774	2.478631
C	0.076015	-2.412328	3.775516
H	-0.316479	-2.974008	4.626328
C	0.955578	-1.351564	3.965236
H	1.279549	-1.065311	4.967992
C	1.435496	-0.650688	2.859983
H	2.139410	0.157611	3.036077
C	1.052816	-0.973325	1.541135
C	0.174398	-2.073999	1.339400
C	-2.903911	1.473056	-1.010209
C	-4.091515	1.889285	-0.391135
H	-4.489138	1.333921	0.459172
C	-4.762544	3.024877	-0.853352
H	-5.691018	3.335715	-0.369228
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C	-3.062751	3.365864	-2.541101
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C	-2.394389	2.224765	-2.093231
H	-1.484492	1.901145	-2.610595
C	-2.626373	-0.350200	1.233475
C	-3.748839	-1.193399	1.207624
H	-4.142334	-1.549606	0.252491
C	-4.359277	-1.576825	2.402860
H	-5.230329	-2.235461	2.382168
C	-3.856053	-1.116410	3.625196
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C	-2.747569	-0.265494	3.652290
H	-2.352759	0.091628	4.605437
C	-2.134038	0.118438	2.458979
H	-1.253097	0.762349	2.476855
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C	4.221916	1.379283	0.394467
H	4.539251	0.703373	-0.398505
C	5.102268	2.371233	0.837181
H	6.097035	2.442826	0.392263
C	4.713863	3.266977	1.833521
H	5.403613	4.041454	2.175530
C	3.432094	3.173716	2.387002
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C	2.549990	2.191678	1.944372
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C	2.630413	-0.929958	-0.910382
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H	1.565080	-0.451245	-2.730166
C	3.117700	-1.909565	-3.072098
H	2.897247	-1.992638	-4.138204
C	4.139887	-2.671409	-2.503560
H	4.726530	-3.351234	-3.125348
C	4.411956	-2.565312	-1.134099
H	5.208033	-3.162087	-0.684093
C	3.658193	-1.704691	-0.338659
H	3.860859	-1.642374	0.732783
Rh	0.146211	1.495018	-0.619954
H	0.396013	0.618996	-1.844180
Si	0.014751	4.163097	0.505203
H	-0.380568	2.692668	0.799222
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H	-1.271940	4.856844	0.228844
C	1.245548	4.097501	-0.894267
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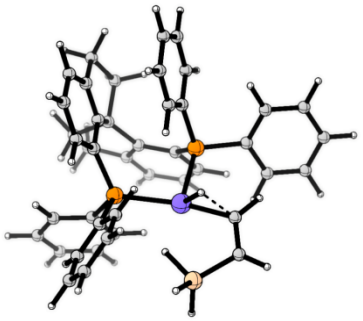

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H	1.211758	-4.643008	0.937825
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C	-0.130607	-3.405132	-1.831212
C	-0.619078	-3.383311	-3.136323
H	-0.331896	-4.163891	-3.844731
C	-1.493612	-2.365873	-3.514747
H	-1.910687	-2.341354	-4.523792
C	-1.839613	-1.366759	-2.604011
H	-2.520966	-0.582725	-2.927644
C	-1.330118	-1.355775	-1.290763
C	-0.475131	-2.409553	-0.898257
C	-1.150133	-3.594634	1.195335
H	-2.082935	-3.041475	1.054691
H	-1.295782	-4.593897	0.762634
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H	-1.649472	-3.542707	3.341191
H	-0.236858	-4.537440	2.959031
C	0.140321	-2.424865	2.823078
C	0.589219	-1.897388	4.031129
H	0.253184	-2.328640	4.977036
C	1.481144	-0.828239	4.009775
H	1.871452	-0.407807	4.938913
C	1.882302	-0.287968	2.789374
H	2.585459	0.538668	2.808330
C	1.416521	-0.786110	1.552595
C	0.534212	-1.897156	1.574345
C	-2.855723	1.148955	-1.170578
C	-4.135885	1.436004	-0.677997

H	-4.492041	0.969063	0.239804
C	-4.966160	2.339118	-1.351772
H	-5.960932	2.552782	-0.954551
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C	-3.250677	2.688320	-3.016257
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C	-2.416806	1.798445	-2.341179
H	-1.411473	1.612312	-2.722981
C	-2.552609	-0.432504	1.243572
C	-3.682446	-1.262530	1.145657
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C	-2.802234	-0.392856	3.656364
H	-2.450817	-0.060732	4.635273
C	-2.117195	-0.001405	2.503187
H	-1.223362	0.622422	2.586271
C	3.396466	1.136395	0.431574
C	4.546129	0.875466	-0.330807
H	4.522388	0.148089	-1.139769
C	5.739753	1.557208	-0.074212
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C	5.804626	2.511691	0.940996
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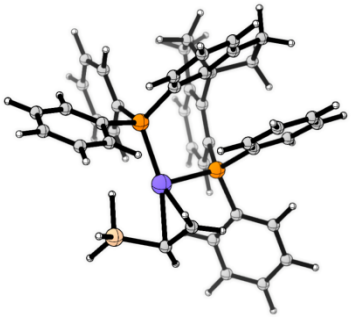
H	4.689605	3.564021	2.469704
C	3.465389	2.130850	1.427860
H	2.571345	2.409215	1.986246
C	2.113566	-0.695944	-1.394609
C	1.496225	-0.353656	-2.605098
H	0.773055	0.461401	-2.627272
C	1.792032	-1.065093	-3.767924
H	1.294683	-0.803698	-4.703582
C	2.715329	-2.112836	-3.732135
H	2.945384	-2.669430	-4.643243
C	3.349850	-2.446471	-2.531428
H	4.081980	-3.256399	-2.503297
C	3.051872	-1.740308	-1.365828
H	3.563025	-1.989972	-0.434365
Rh	0.073125	1.761209	0.062418
H	0.625590	2.469949	-1.200392
Si	-1.308439	4.312998	0.411214
H	-1.427426	2.774402	0.415638
H	-1.873024	4.709025	1.728729
H	-2.198019	4.741589	-0.697552
C	0.508480	4.636260	0.172898
C	1.203719	3.506997	-0.091050
H	0.999681	5.614873	0.248559
H	2.280591	3.541808	-0.286639

P_c (SDP)



P	-1.671022	0.288505	-0.127538
P	1.681566	0.186973	0.156357
C	-0.141412	-2.889760	0.011631
C	0.945151	-3.867741	-0.538033
H	1.923114	-3.378822	-0.514780
H	1.018967	-4.767697	0.087753
C	0.531355	-4.159779	-1.986279
H	1.395279	-4.280885	-2.657485
H	-0.063965	-5.085524	-2.065122
C	-0.311974	-2.967071	-2.361927
C	-0.784177	-2.661495	-3.635419
H	-0.522027	-3.293433	-4.487143
C	-1.606161	-1.547468	-3.799902
H	-2.010924	-1.297216	-4.782895
C	-1.915441	-0.739889	-2.705835
H	-2.556590	0.122658	-2.869900
C	-1.425431	-1.016971	-1.412091
C	-0.623674	-2.168942	-1.243185
C	-1.315599	-3.753680	0.572345
H	-2.242825	-3.174986	0.539235
H	-1.471932	-4.651705	-0.040818
C	-0.936218	-4.059057	2.025239
H	-1.810333	-4.091930	2.693471
H	-0.424434	-5.031856	2.122558
C	0.006390	-2.939376	2.386612
C	0.484931	-2.660613	3.663346
H	0.154006	-3.255438	4.517816
C	1.402051	-1.624412	3.825772
H	1.817194	-1.397815	4.810113
C	1.795700	-0.865589	2.724891
H	2.515087	-0.069146	2.890005
C	1.299095	-1.108589	1.426202
C	0.399127	-2.189334	1.258069
C	-3.026067	1.357624	-0.780729
C	-4.313597	1.381969	-0.229181
H	-4.576701	0.716570	0.592014
C	-5.272431	2.278458	-0.714383
H	-6.270964	2.287481	-0.271965
C	-4.958556	3.156832	-1.752042
H	-5.710312	3.854155	-2.127926
C	-3.672250	3.146042	-2.303366
H	-3.414432	3.835408	-3.110415
C	-2.713284	2.260343	-1.816022
H	-1.704811	2.272265	-2.236140
C	-2.349009	-0.446383	1.393343

C	-3.431837	-1.340420	1.368030
H	-3.868999	-1.643042	0.413843
C	-3.951620	-1.842199	2.561928
H	-4.792888	-2.538362	2.538458
C	-3.394028	-1.455226	3.786028
H	-3.799832	-1.853166	4.718826
C	-2.321474	-0.560400	3.815595
H	-1.881181	-0.261702	4.768793
C	-1.802390	-0.053967	2.623052
H	-0.950792	0.629983	2.638401
C	3.226594	1.017054	0.734917
C	4.452649	0.896487	0.064537
H	4.541607	0.264172	-0.817409
C	5.576559	1.600900	0.509396
H	6.522028	1.495806	-0.027090
C	5.493637	2.432428	1.626526
H	6.374058	2.977874	1.972849
C	4.272390	2.572173	2.294429
H	4.193479	3.228771	3.163763
C	3.148049	1.880783	1.845372
H	2.193475	2.019054	2.357090
C	2.150830	-0.592912	-1.421436
C	1.581439	-0.118774	-2.610999
H	0.815965	0.656251	-2.565882
C	1.965094	-0.660588	-3.838077
H	1.503958	-0.297435	-4.758330
C	2.927539	-1.672154	-3.885795
H	3.227976	-2.096383	-4.846415
C	3.508319	-2.142552	-2.703111
H	4.264212	-2.930138	-2.738430
C	3.122279	-1.605817	-1.474152
H	3.582756	-1.970301	-0.553471
Rh	0.077558	1.789508	0.114015
H	0.797544	3.192237	-2.012876
Si	-0.533819	4.299279	0.461479
H	-1.252867	2.887956	0.648816
H	-0.683987	4.949506	1.784264
H	-1.291648	4.972352	-0.620231
C	1.183891	3.759588	0.053303
C	1.437210	3.076625	-1.131068
H	1.987588	3.835246	0.790549
H	2.437438	2.682423	-1.3327

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Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

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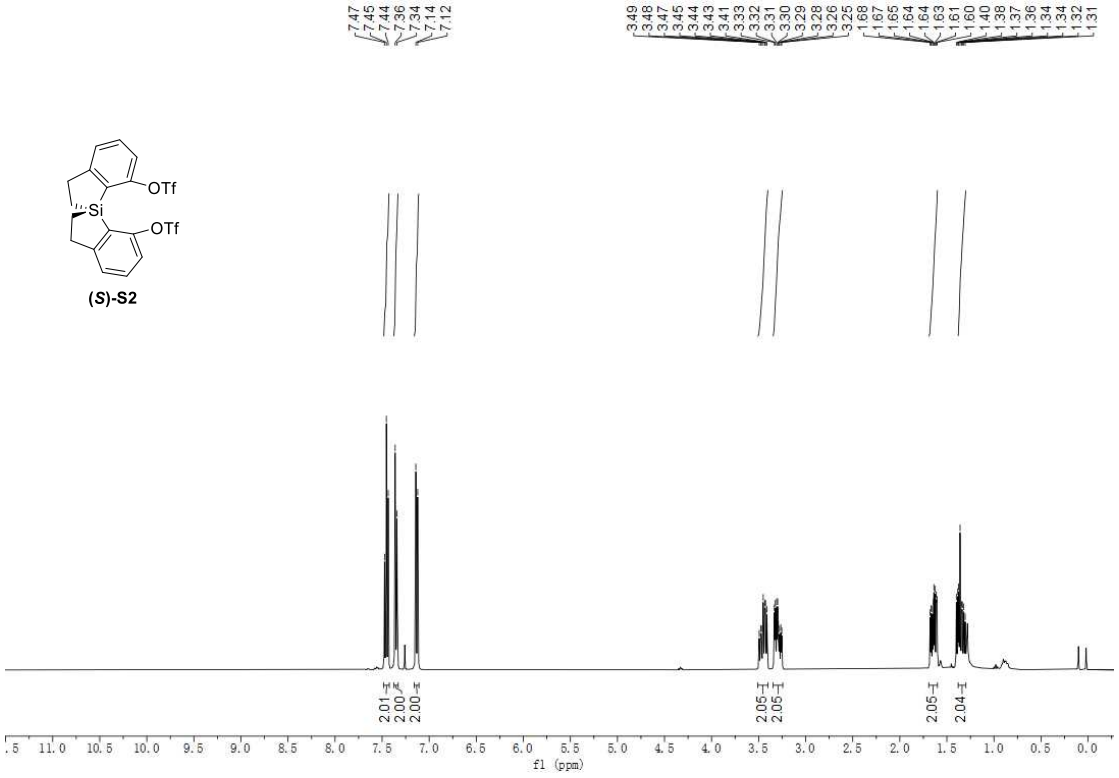
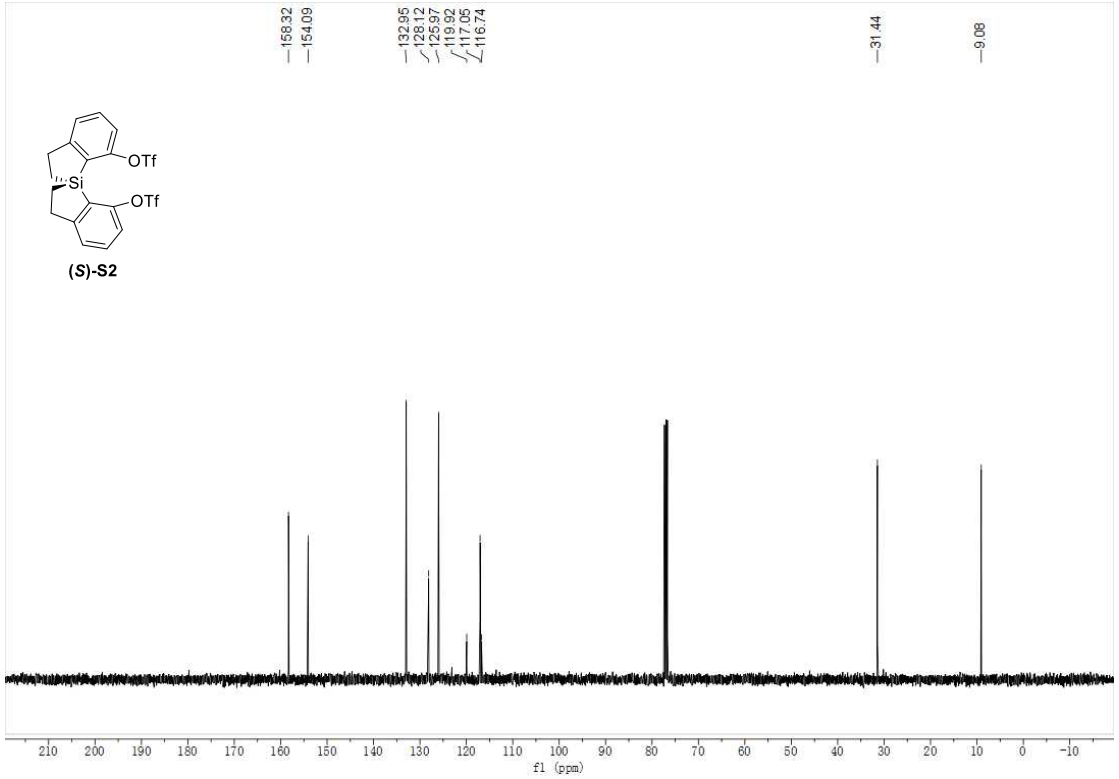
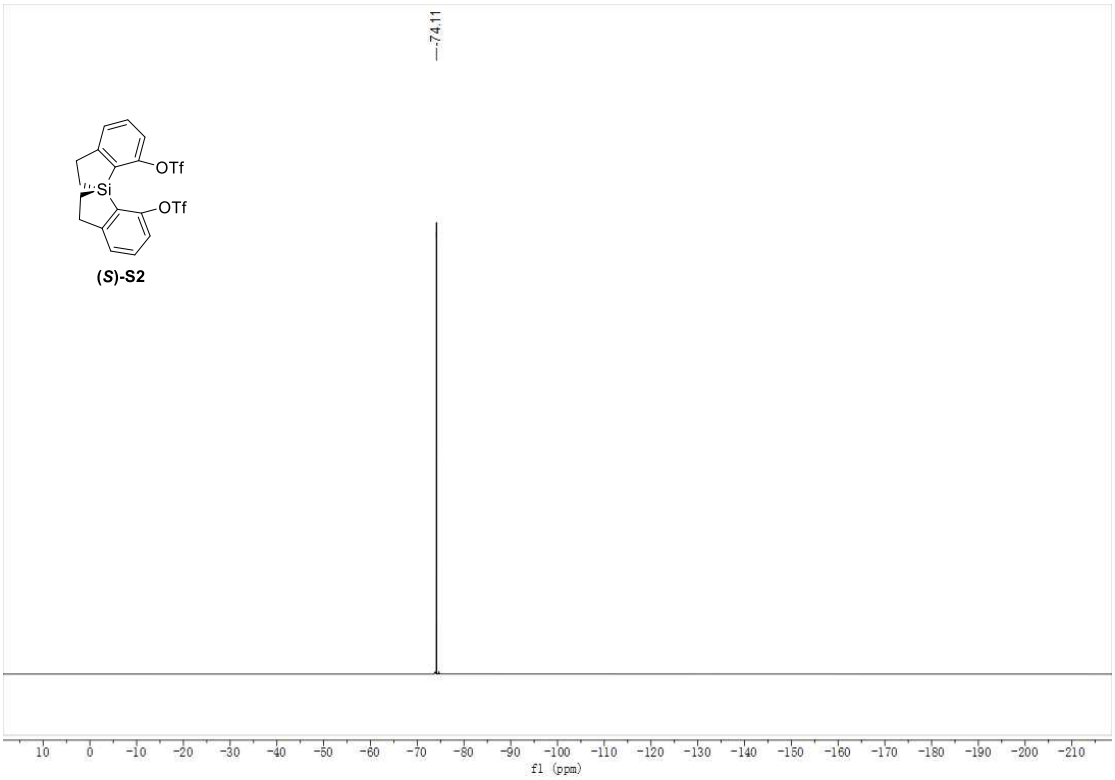
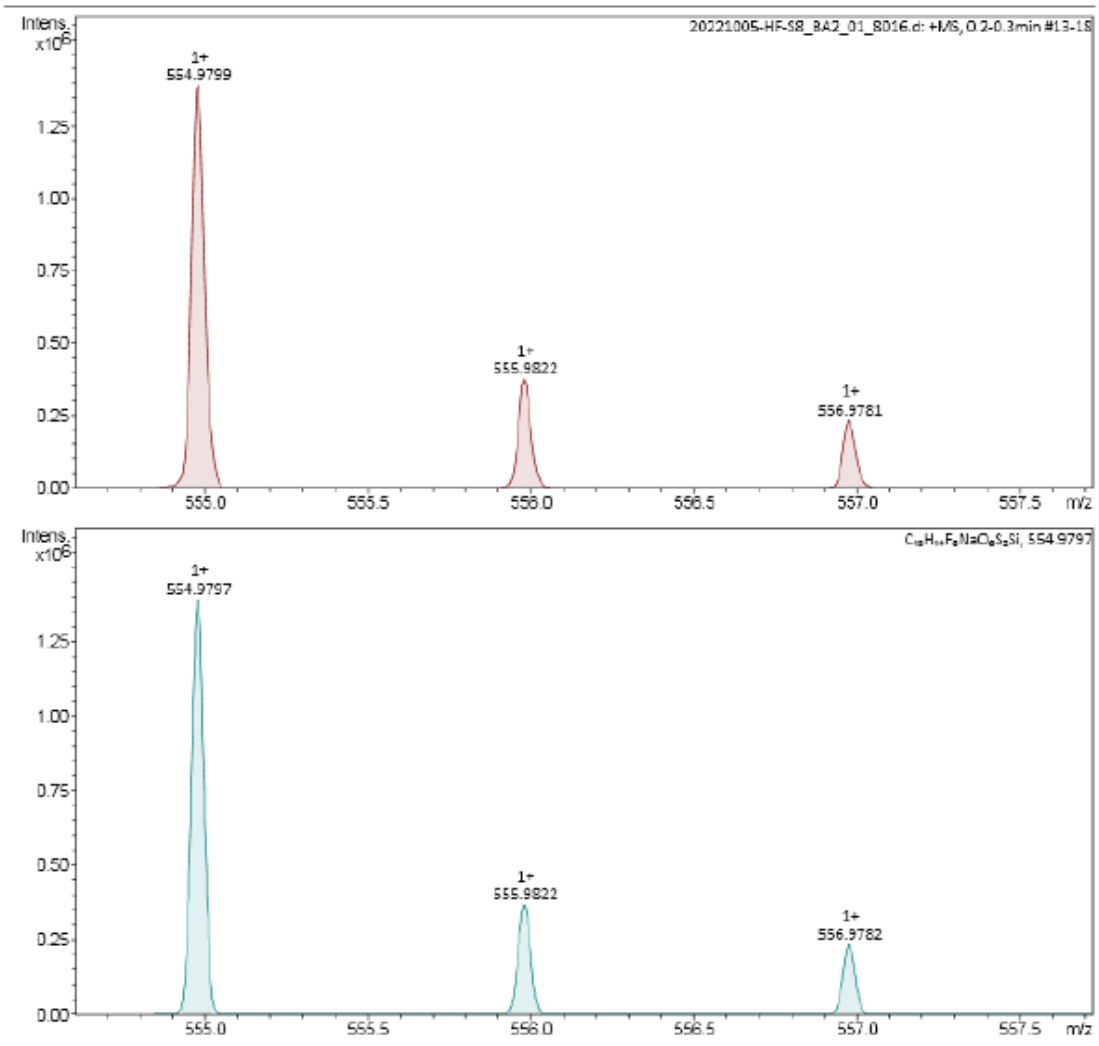
12. NMR Spectra.

(*S*)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl bis(trifluoromethanesulfonate) ((*S*)-S2)

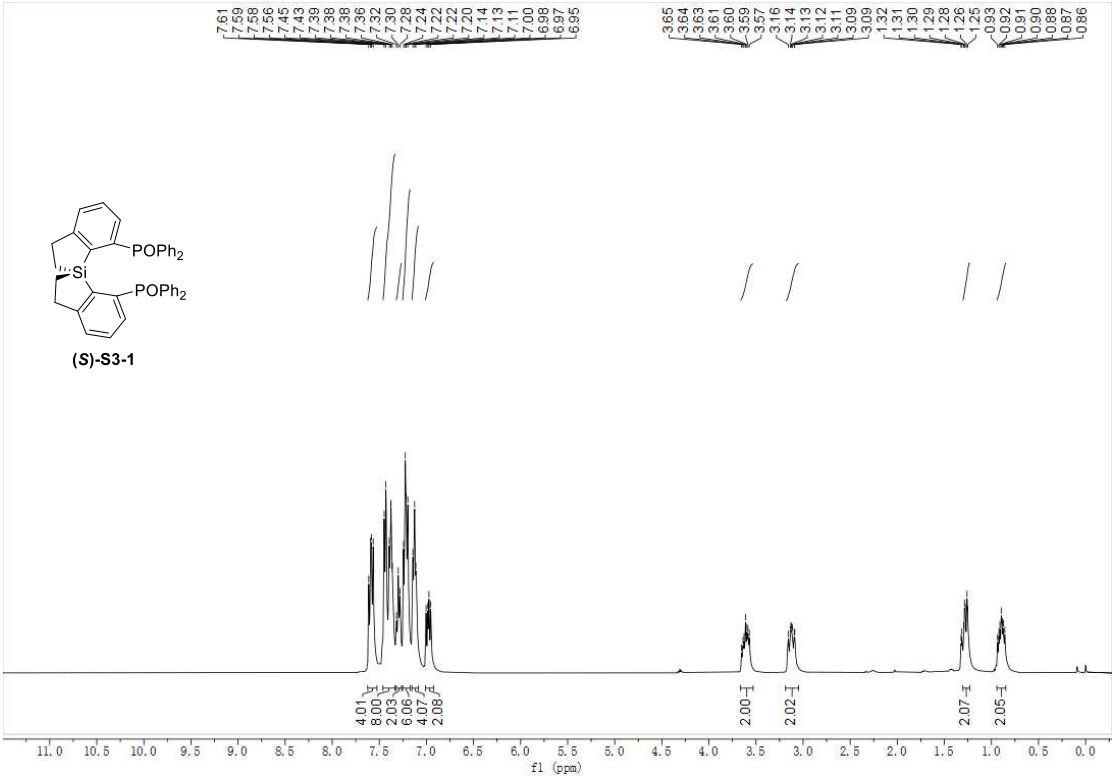


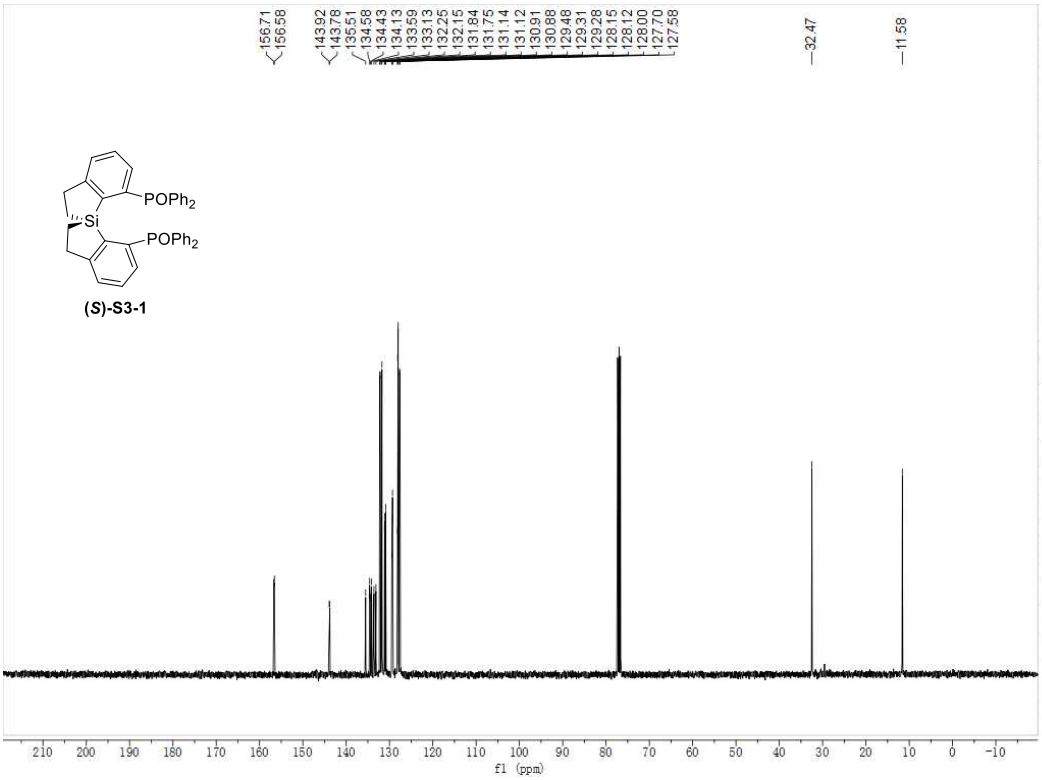


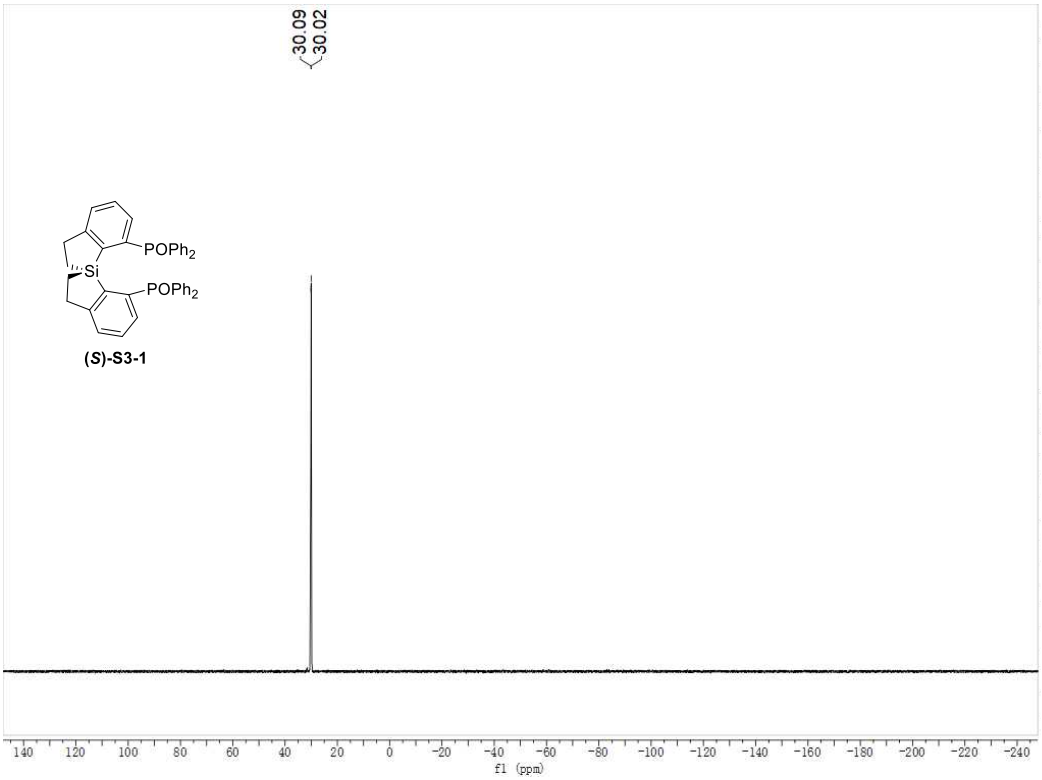

-74.11
OTf
OTf
Si
(S)-S2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

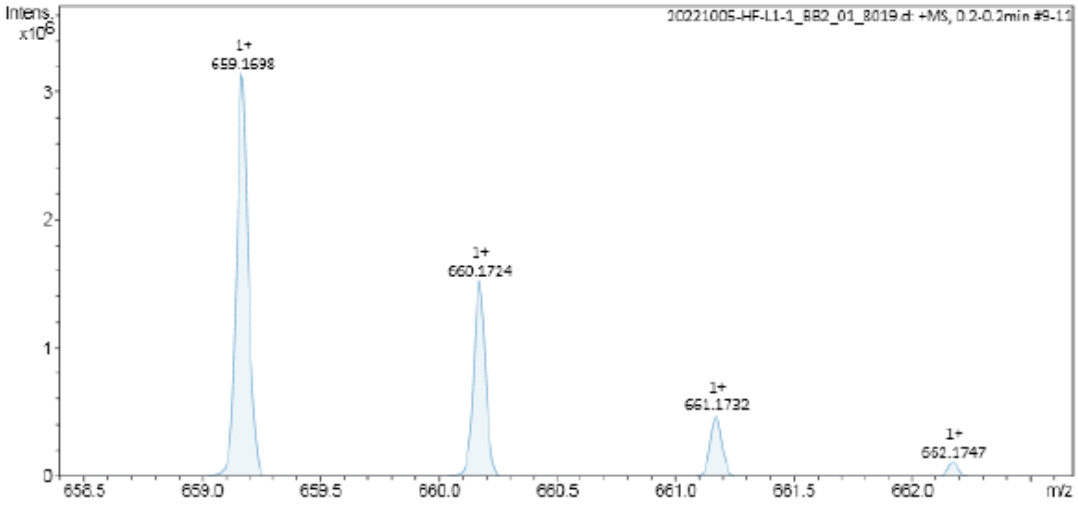

Intens.
x10^6
20221005-HF-S8_BA2_01_8016.d: +MS, 0.2-0.3min #13-18
1+
554.9799
1+
555.9822
1+
556.9781
0.00
0.25
0.50
0.75
1.00
1.25
555.0
555.5
556.0
556.5
557.0
557.5
m/z
Intens.
x10^6
C18H14F6NaO6S2Si, 554.9797
1+
554.9797
1+
555.9822
1+
556.9782
0.00
0.25
0.50
0.75
1.00
1.25
555.0
555.5
556.0
556.5
557.0
557.5
m/z

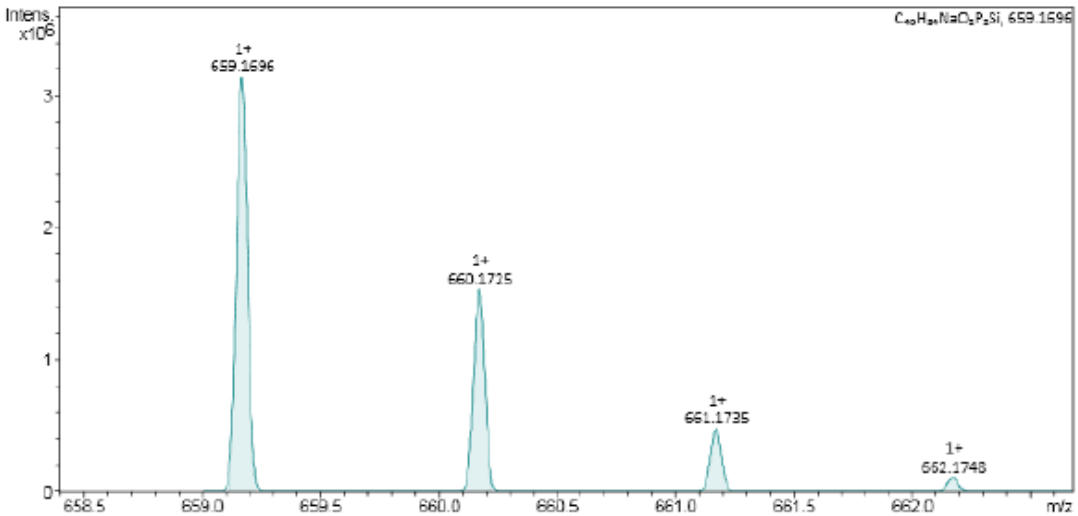
(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(diphenylphosphine oxide) ((*S*)-S3-1)



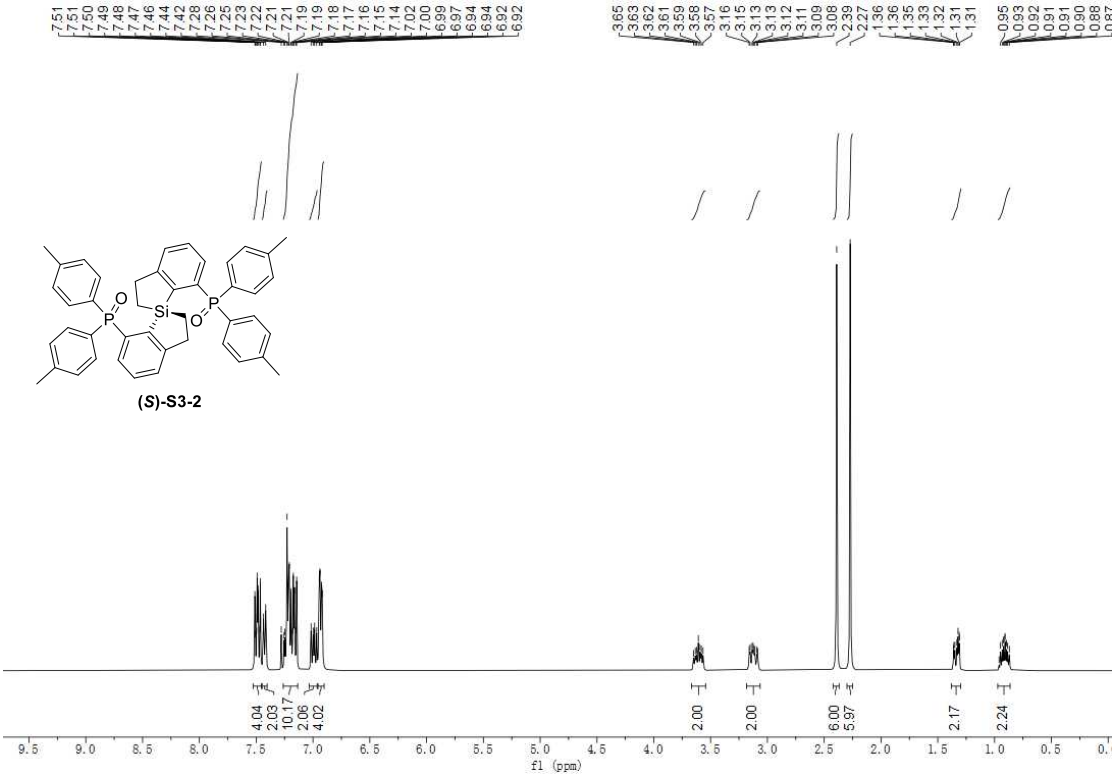


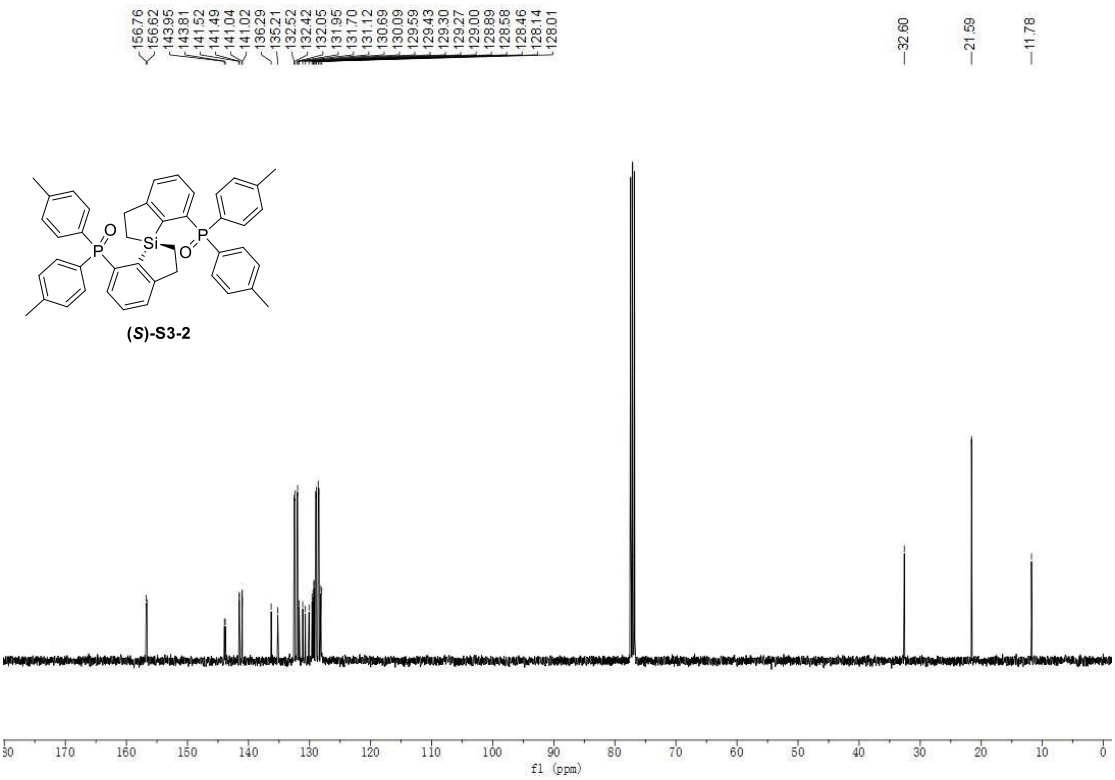

30.09
30.02
POPh2
Si
POPh2
(S)-S3-1
f1 (ppm)

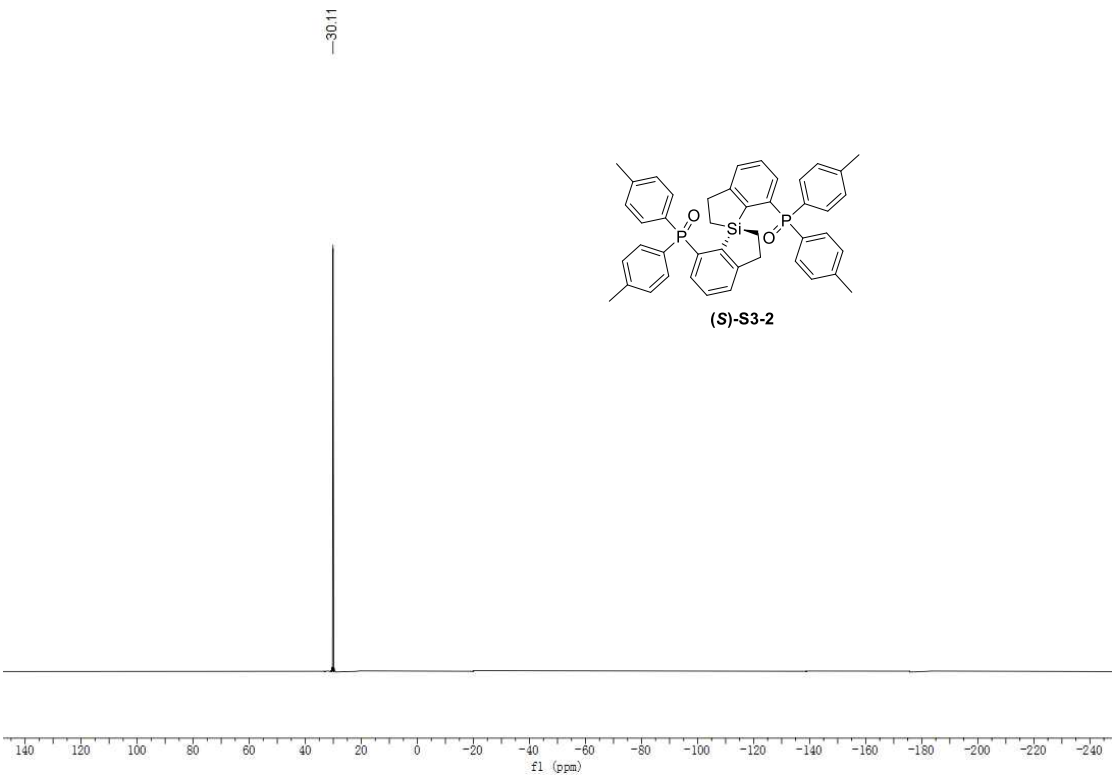

20221005-HF-L1-1_BB2_01_8019.d: +MS, 0.2-0.2min #9-11
Intens.
x10^6
1+
659.1698
1+
660.1724
1+
661.1732
1+
662.1747
m/z


C40H34NaO2P2Si, 659.1696
Intens.
x10^6
1+
659.1696
1+
660.1725
1+
661.1735
1+
662.1748
m/z

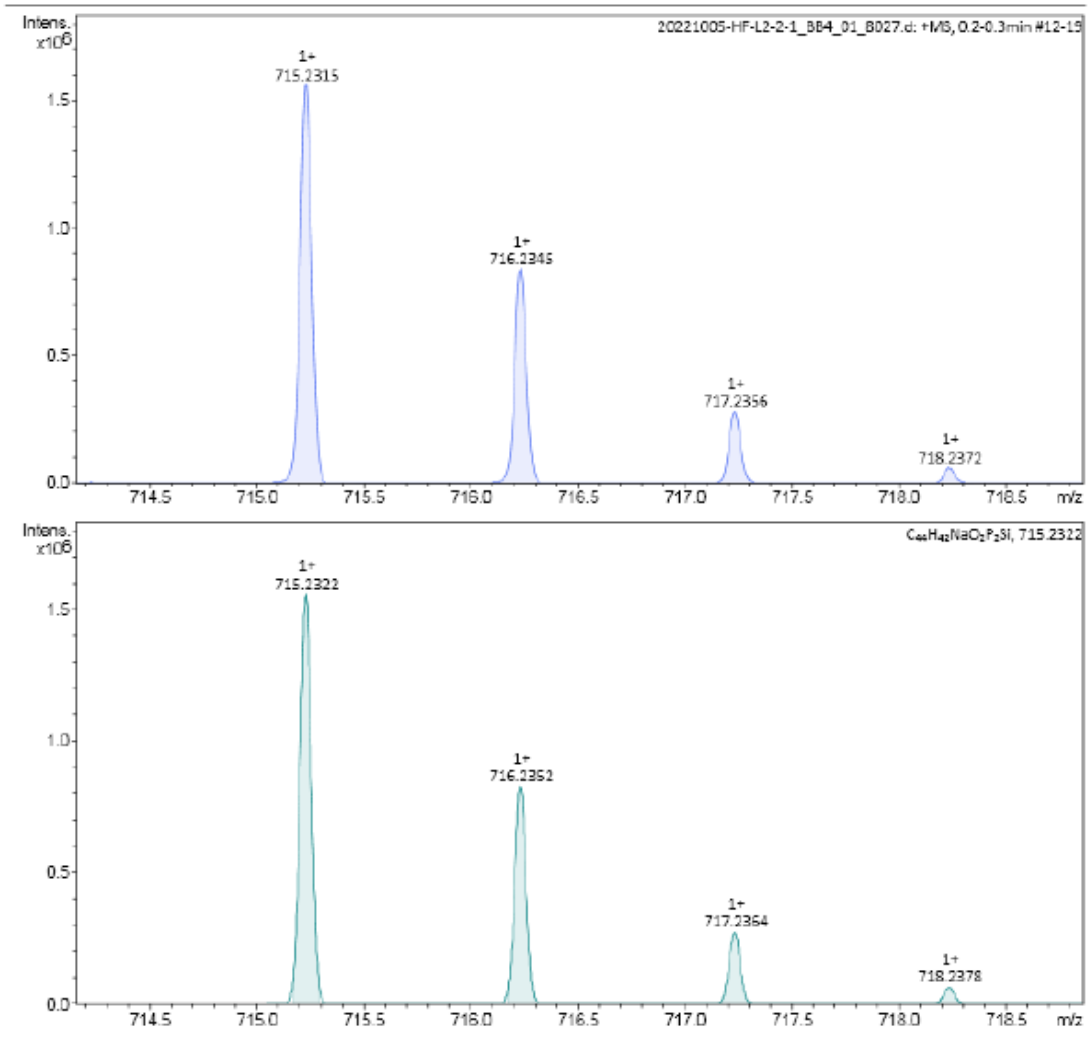
(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(4-methylphenyl)phosphine oxide) ((*S*)-S3-2)



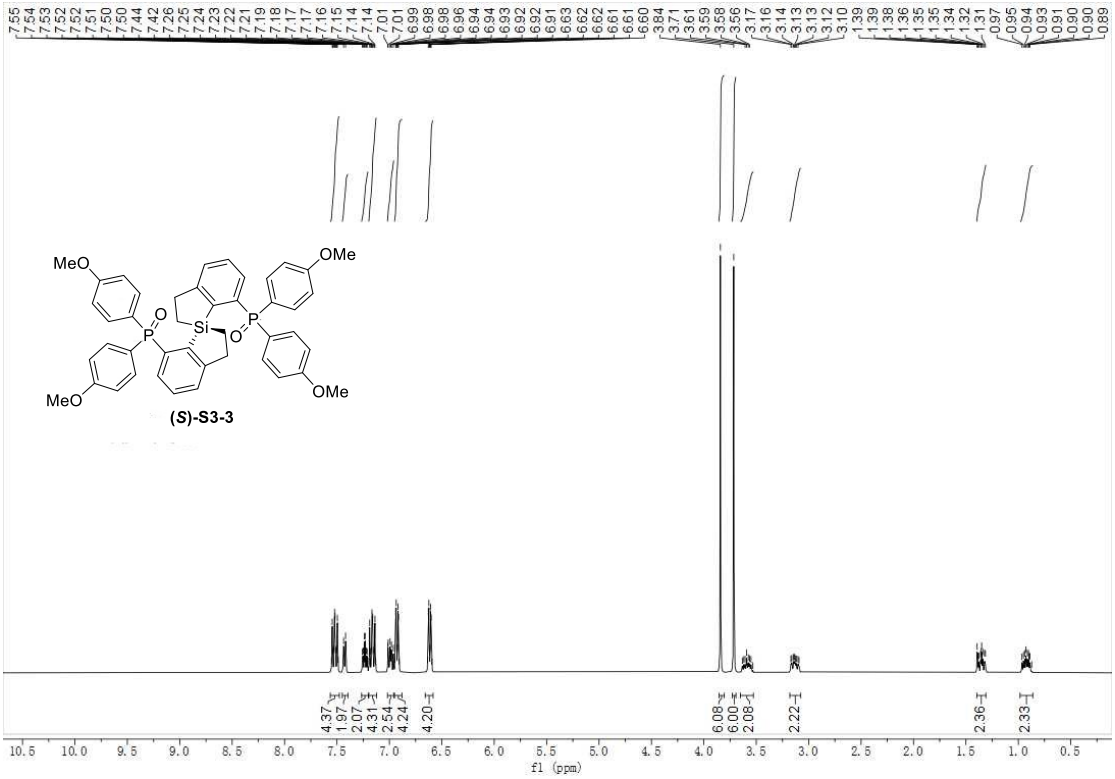


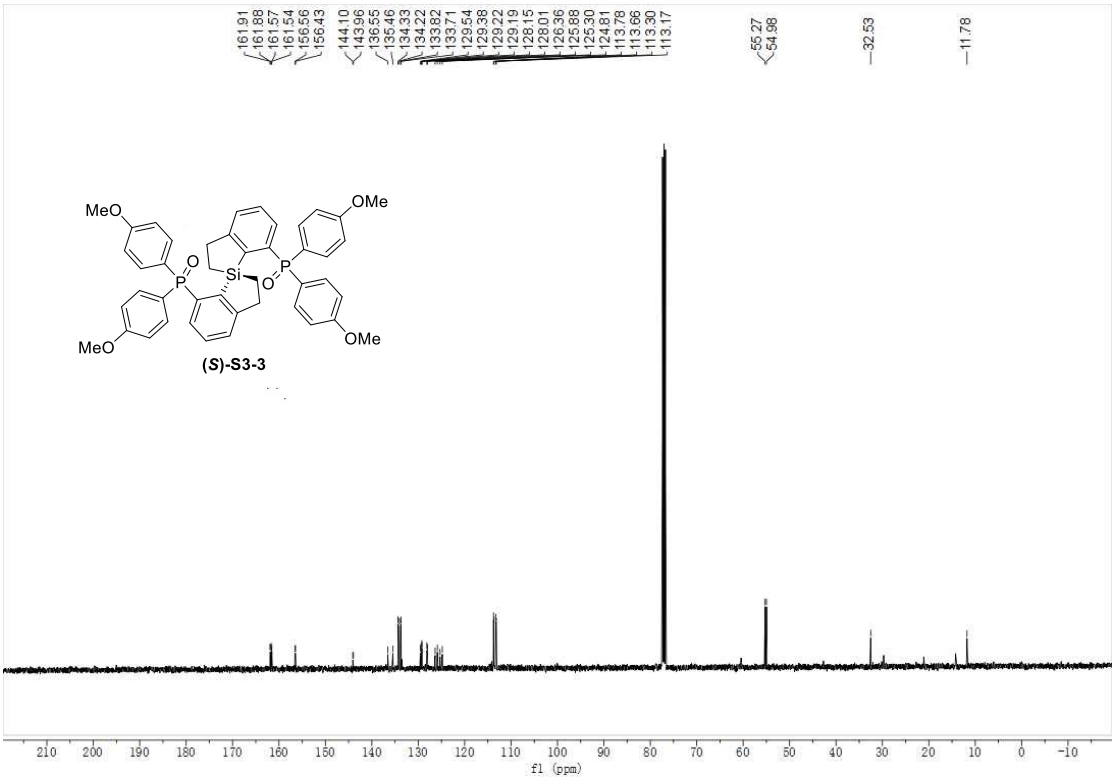

30.11
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

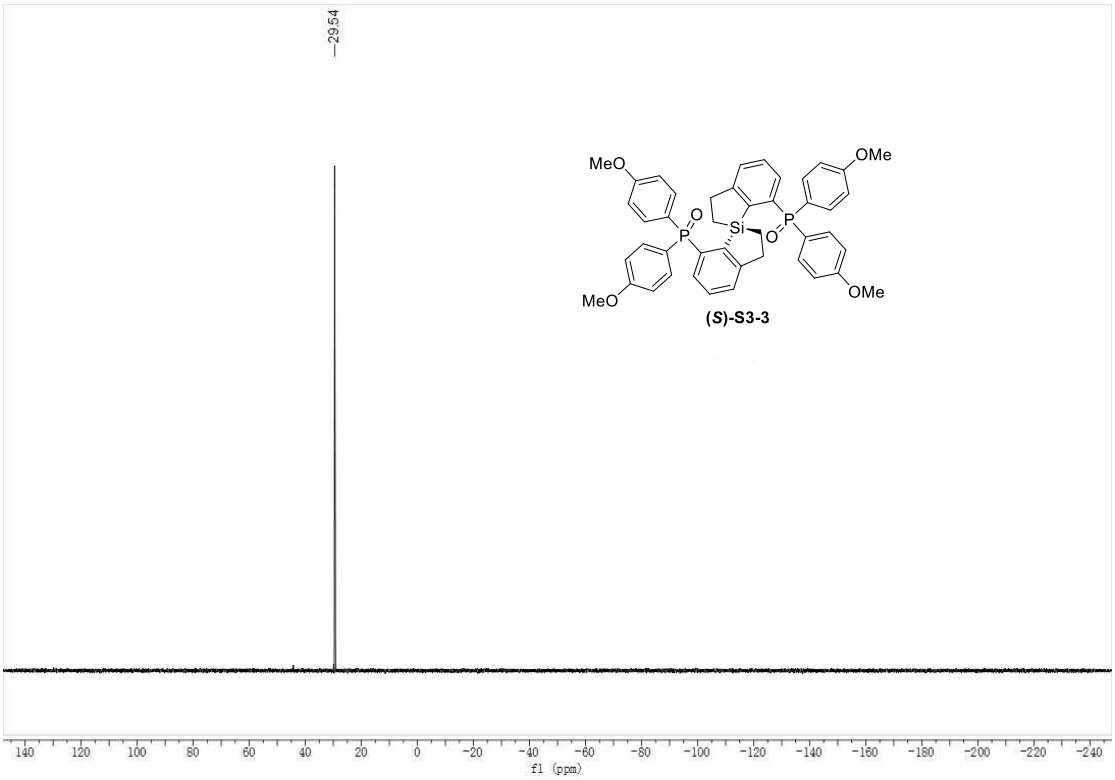
(*S*)-S3-2

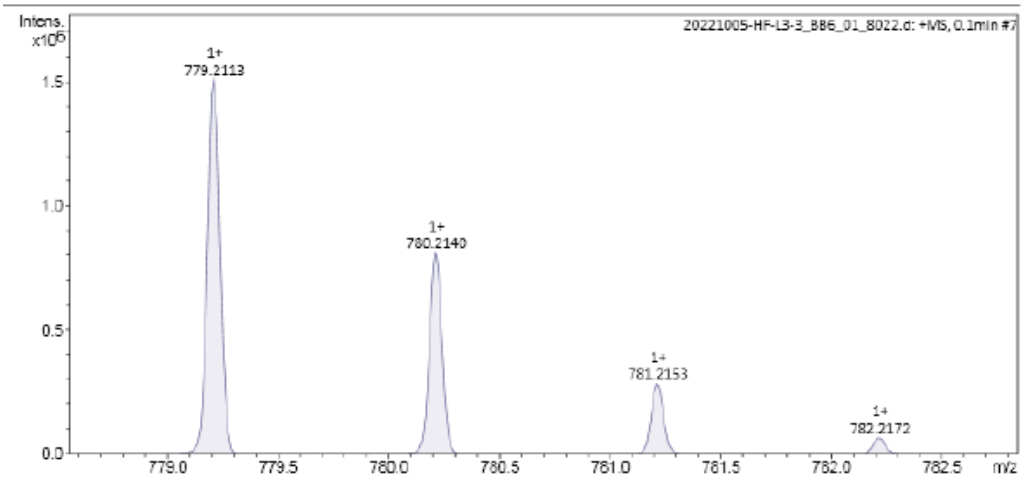

Intens.
x10⁶
20221005-HF-L2-2-1_BB4_01_8027.d: +MS, 0.2-0.3min #12-19
1+
715.2315
1+
716.2345
1+
717.2356
1+
718.2372
714.5 715.0 715.5 716.0 716.5 717.0 717.5 718.0 718.5 m/z
Intens.
x10⁶
C44H42NaO2P2Si, 715.2322
1+
715.2322
1+
716.2352
1+
717.2364
1+
718.2378
714.5 715.0 715.5 716.0 716.5 717.0 717.5 718.0 718.5 m/z

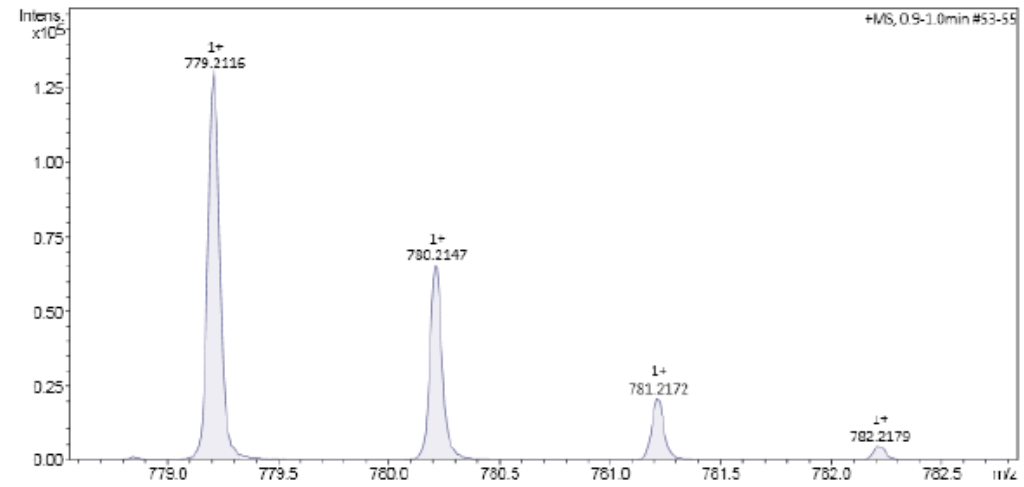
(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(4-methoxyphenyl)phosphine oxide) ((*S*)-S3-3)



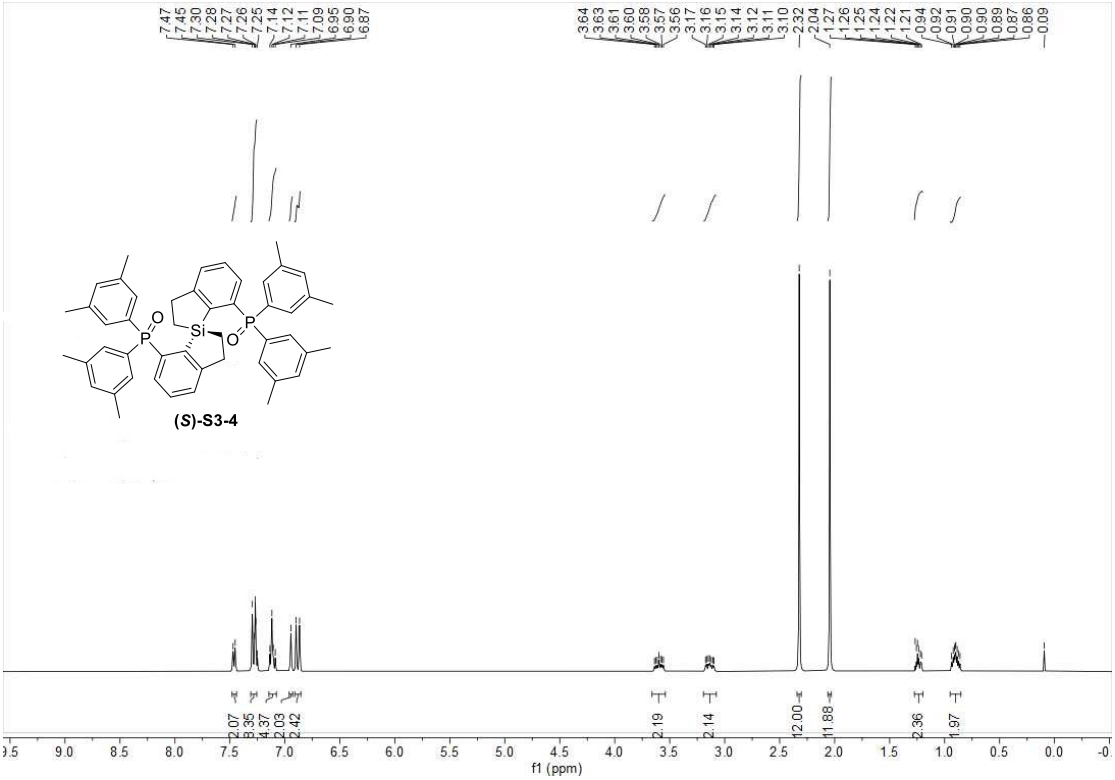


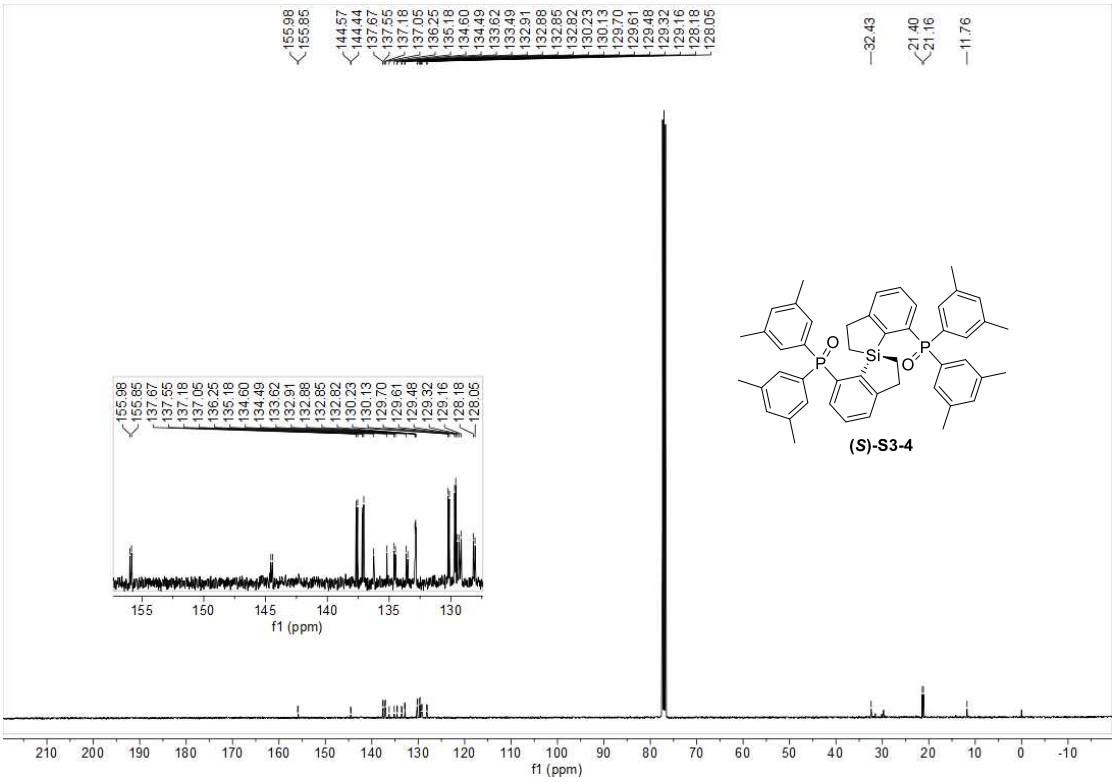

29.54
MeO
OMe
Si
O
P
O
P
MeO
OMe
(S)-S3-3
f1 (ppm)

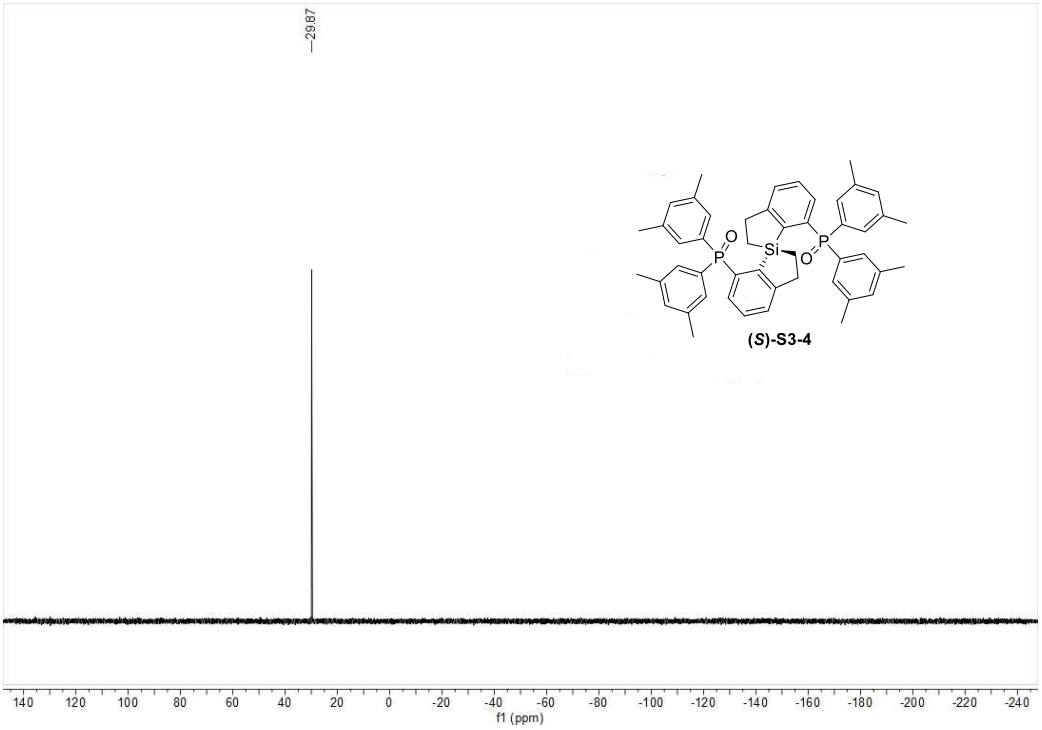

Intens.
x10^5
20221005-HF-L3-3_886_01_8022.d: +MS, 0.1min #7
1+
779.2113
1+
780.2140
1+
781.2153
1+
782.2172
m/z

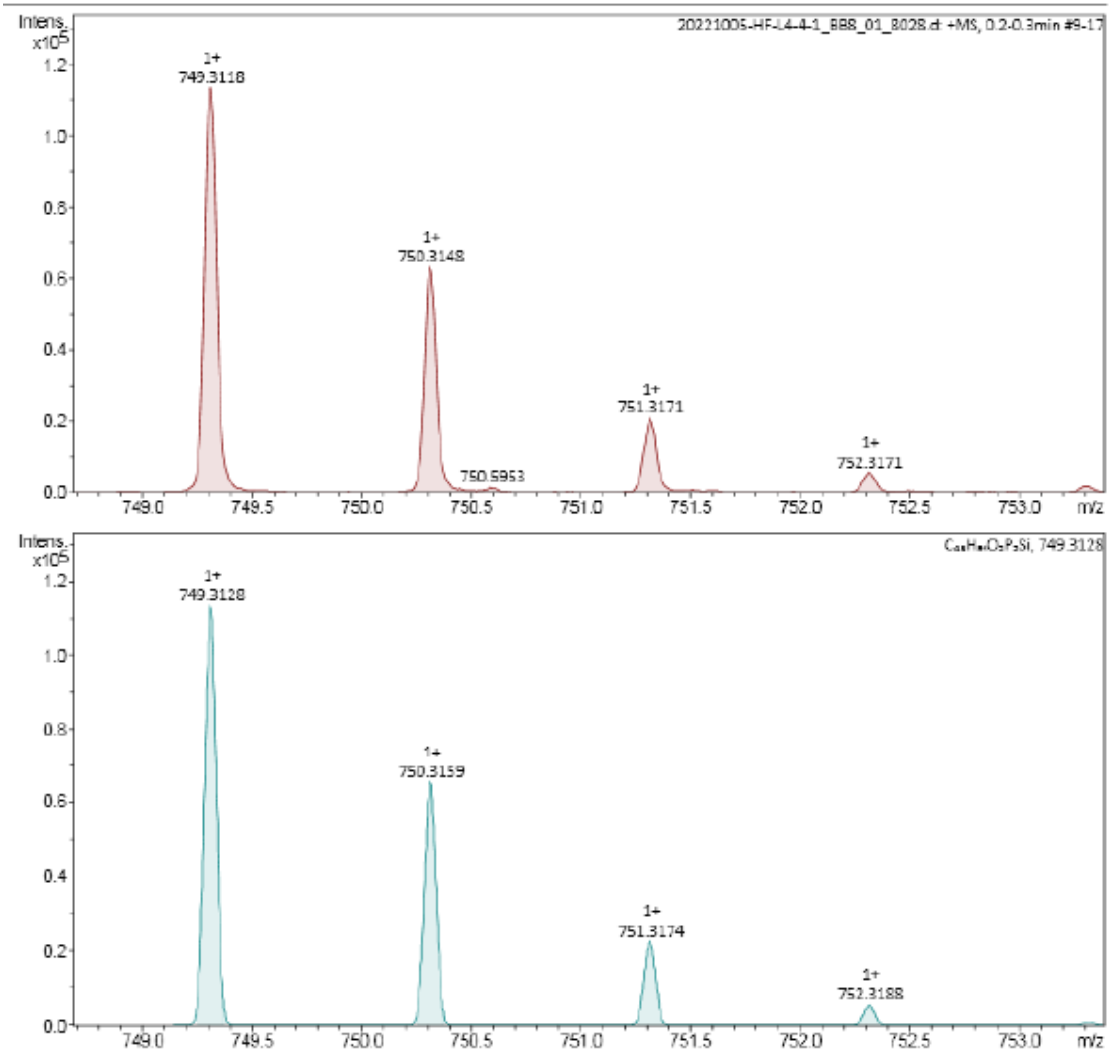

Intens.
x10^5
+MS, 0.9-1.0min #53-55
1+
779.2116
1+
780.2147
1+
781.2172
1+
782.2179
m/z

(*S*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole]-7,7'-diyl)bis(dbis(3,5-dimethylphenyl)phosphine oxide) ((*S*)-S3-4)

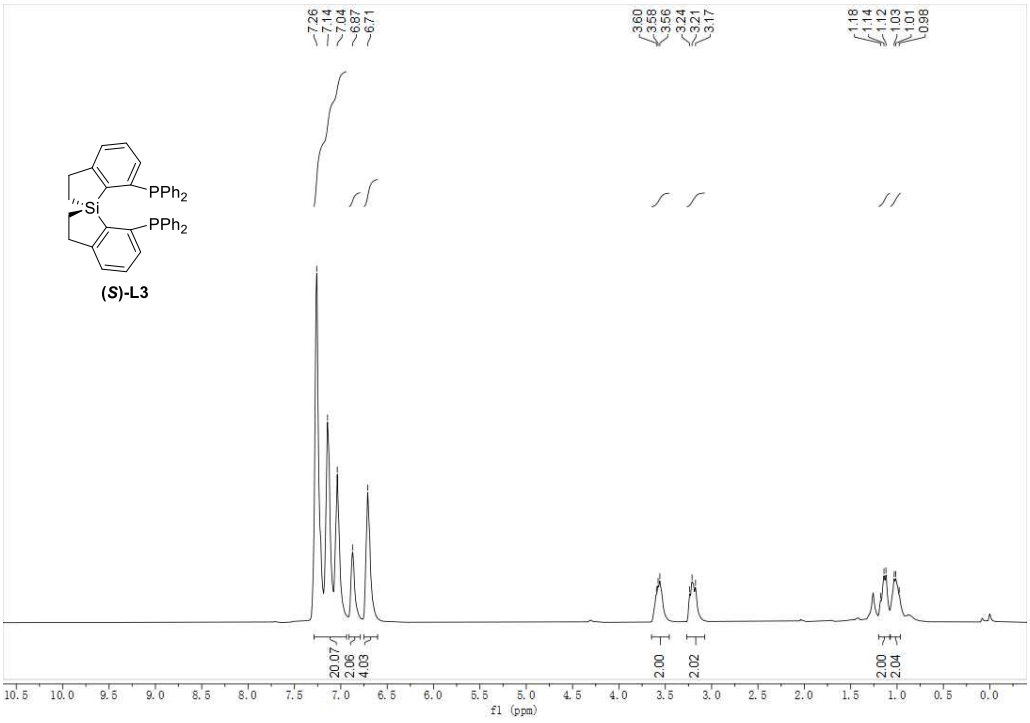


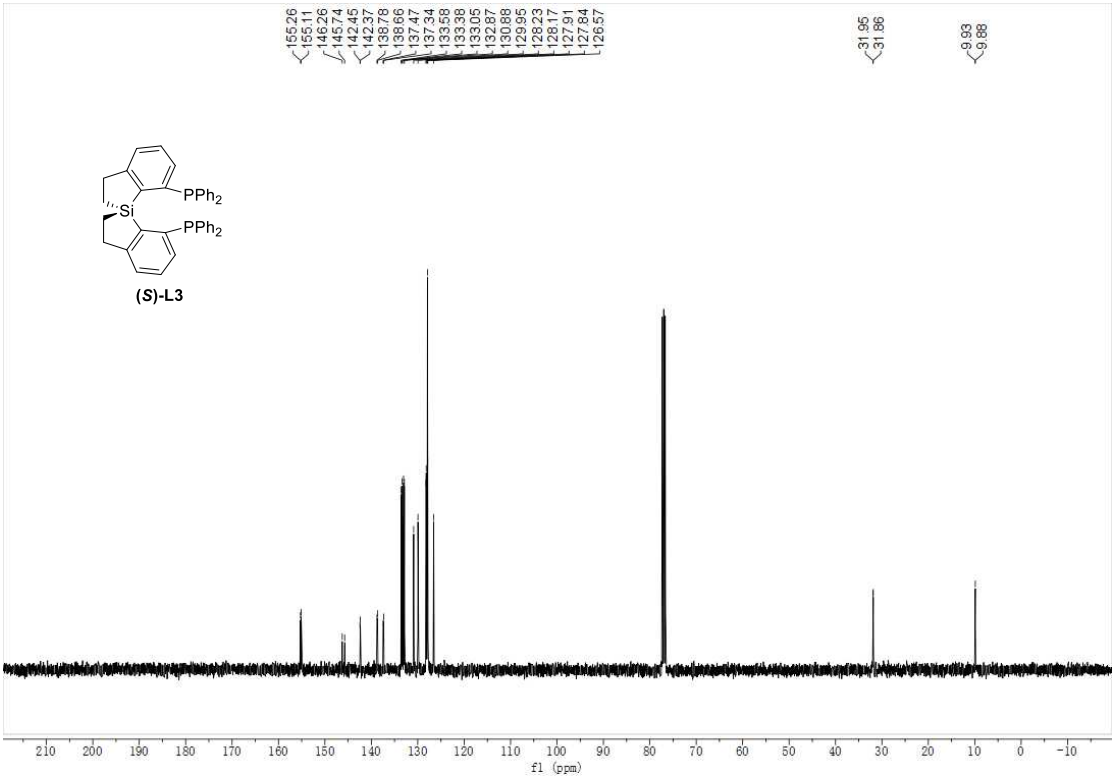


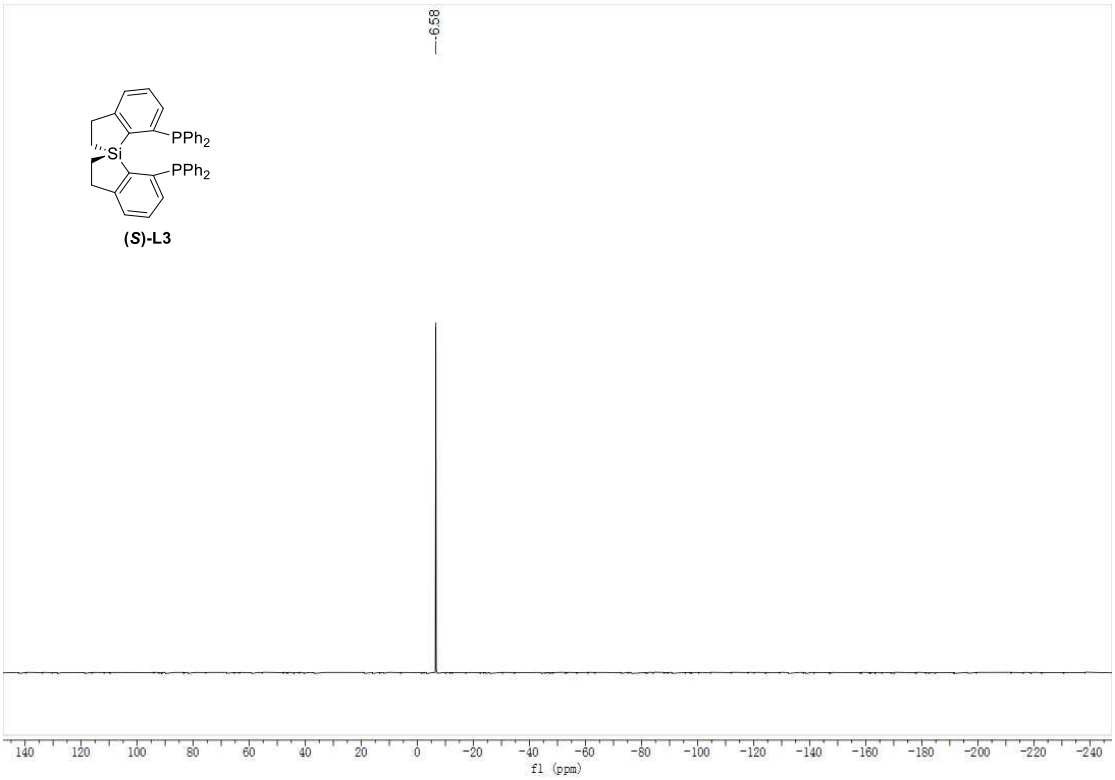

29.87
(S)-S3-4
f1 (ppm)

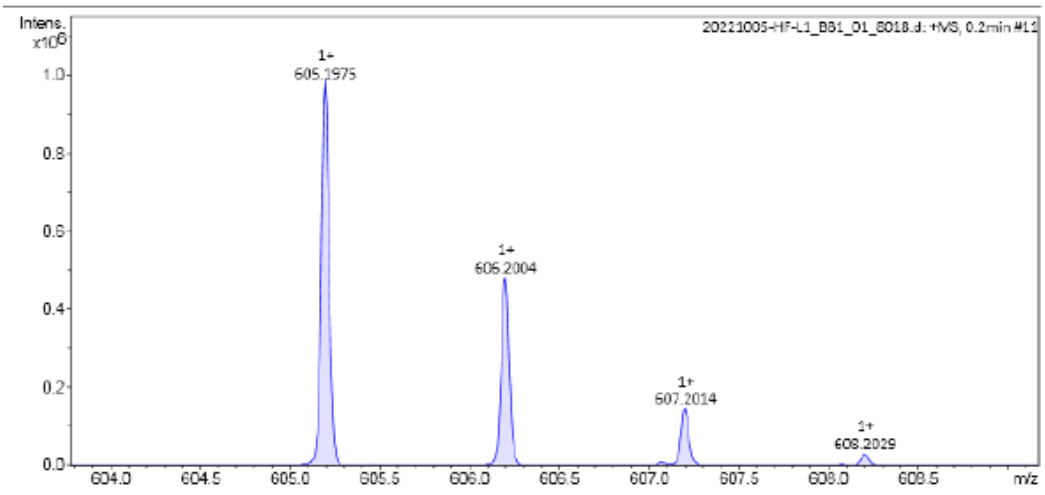

Intens.
x10^5
20221006-HF-J-4-4-1_888_01_8028.d: +MS, 0.2-0.3min #9-17
1+
749.3118
1+
750.3148
750.5953
1+
751.3171
1+
752.3171
m/z
Intens.
x10^5
C48H54O2P2Si, 749.3128
1+
749.3128
1+
750.3159
1+
751.3174
1+
752.3188
m/z

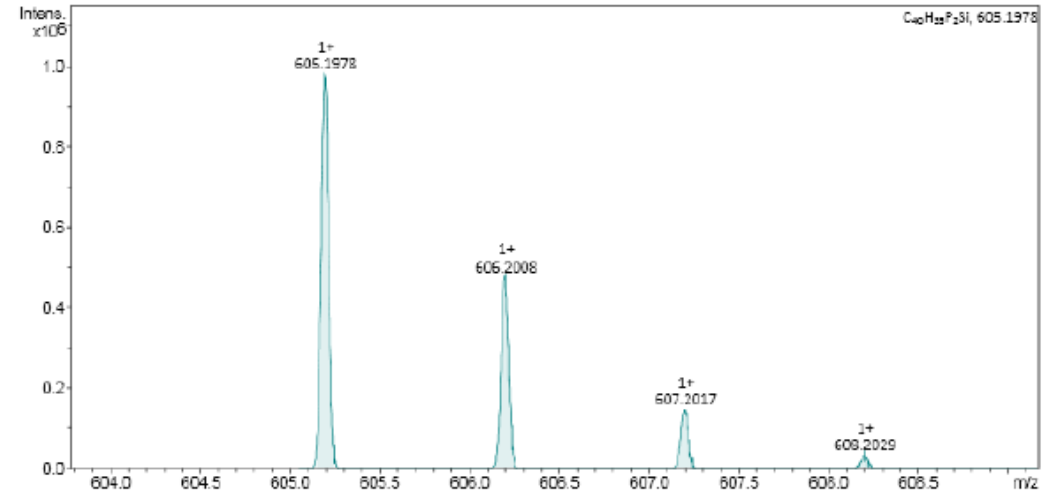
(*S*)-7,7'-bis(diphenylphosphaneyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] (L-3)



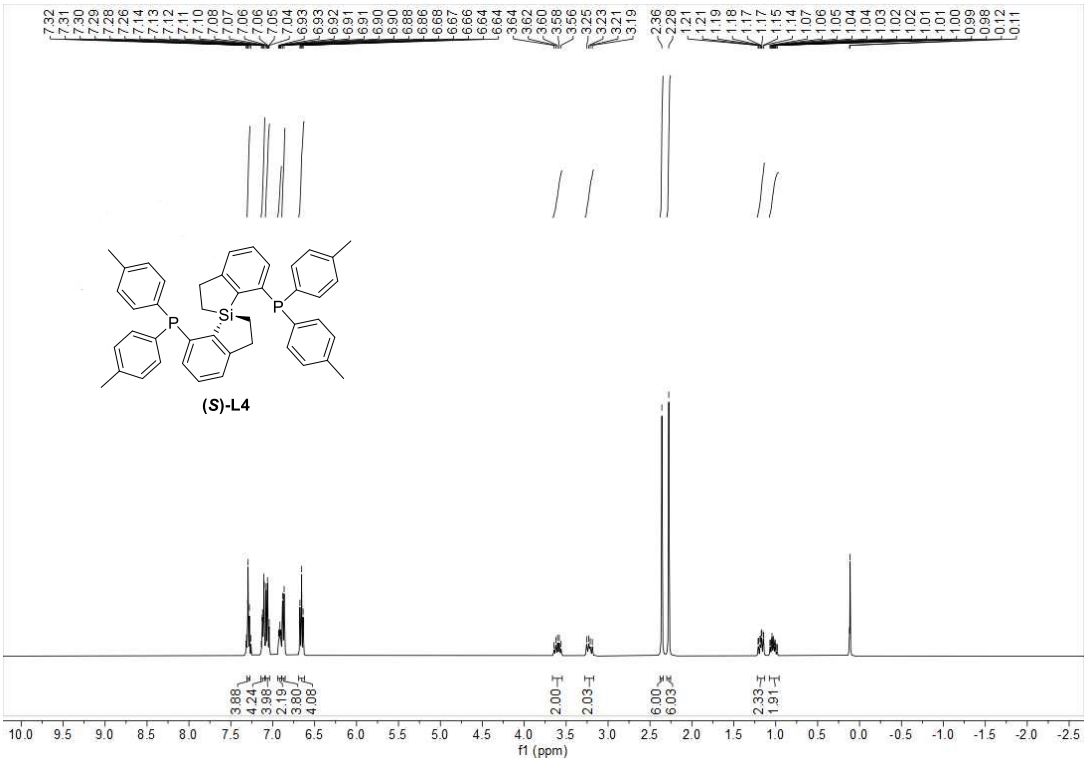


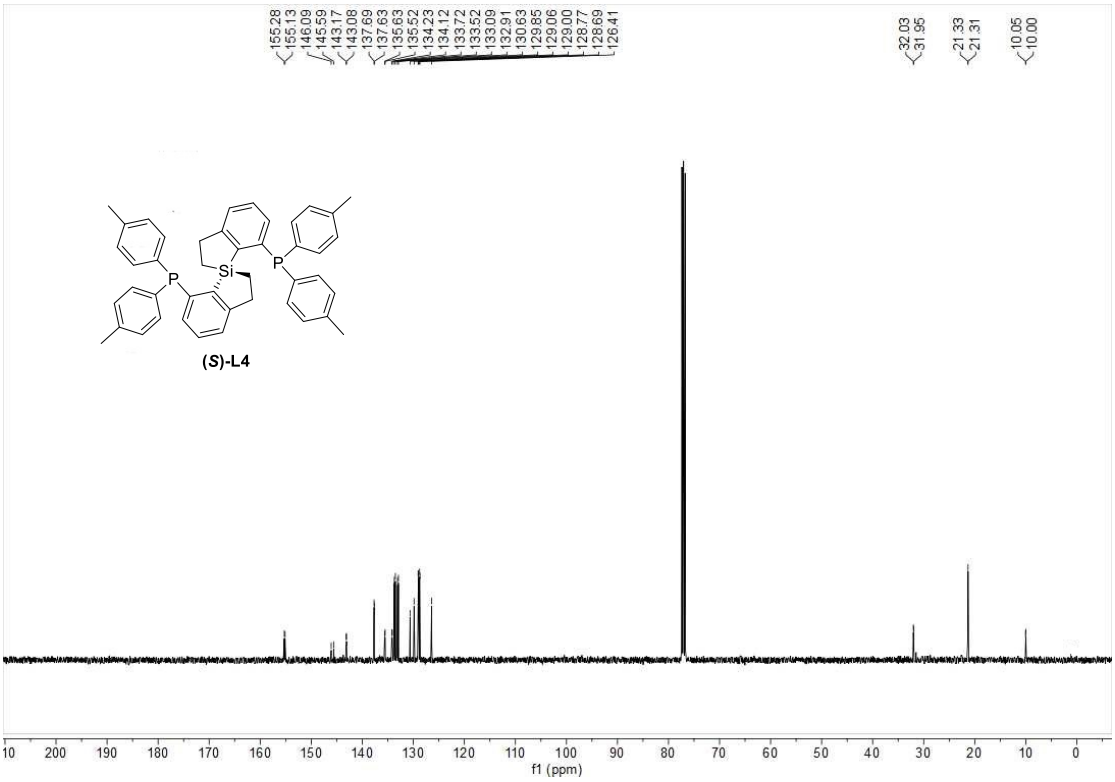

-6.58
PPh2
Si
PPh2
(S)-L3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

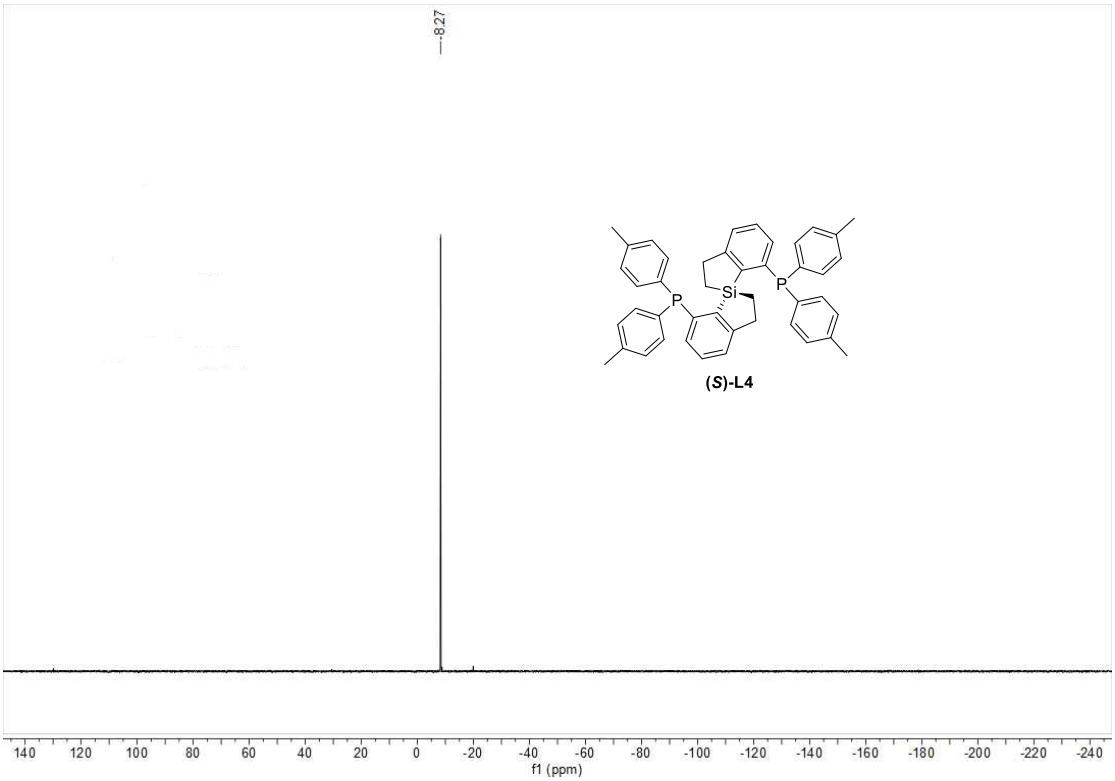

Intens.
x10^6
20221005-HF-L1_BS1_01_8018.d: +MS, 0.2min #11
1+
605.1975
1+
606.2004
1+
607.2014
1+
608.2029
604.0 604.5 605.0 605.5 606.0 606.5 607.0 607.5 608.0 608.5
m/z

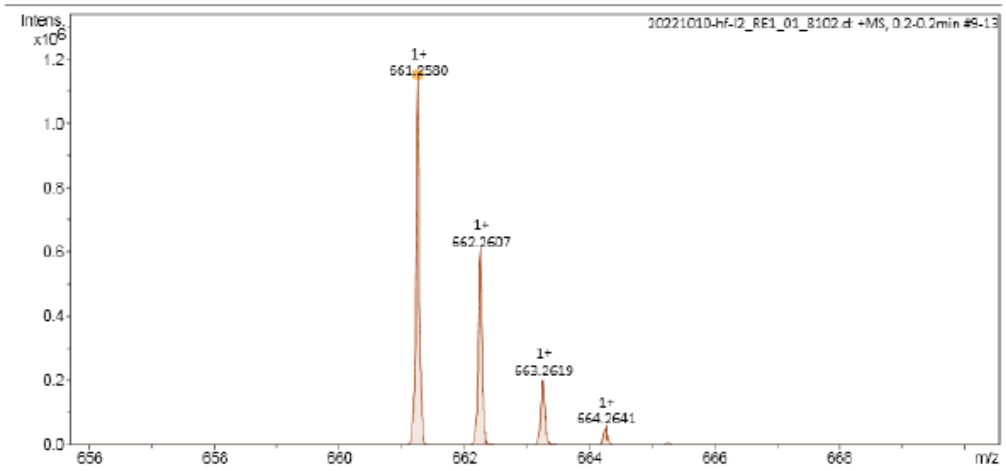

Intens.
x10^6
C40H33P2Si, 605.1978
1+
605.1978
1+
606.2008
1+
607.2017
1+
608.2029
604.0 604.5 605.0 605.5 606.0 606.5 607.0 607.5 608.0 608.5
m/z

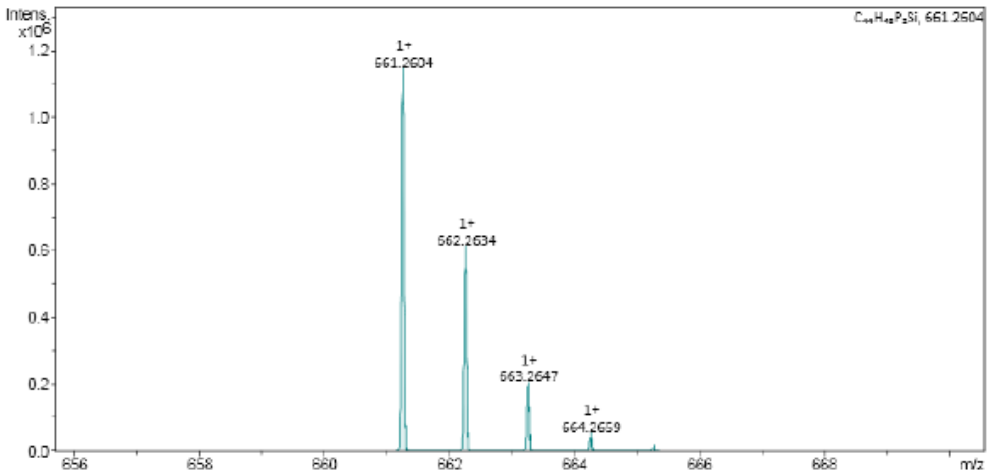
(*S*)-7,7'-bis(4-CH_3-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] (L-4)



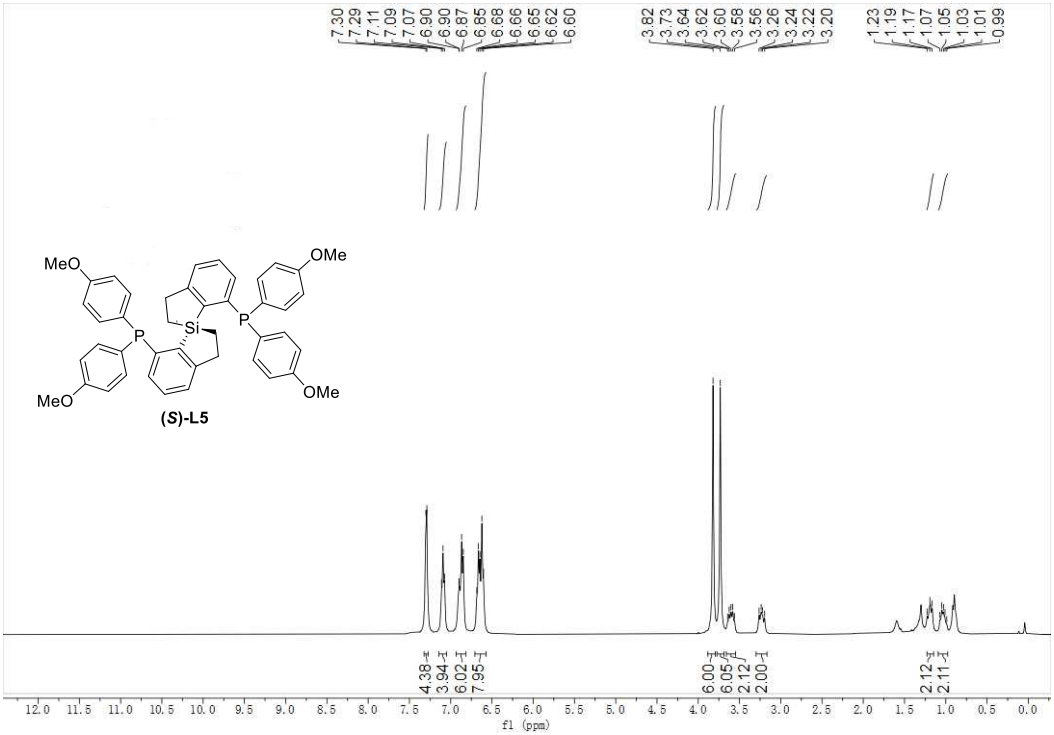


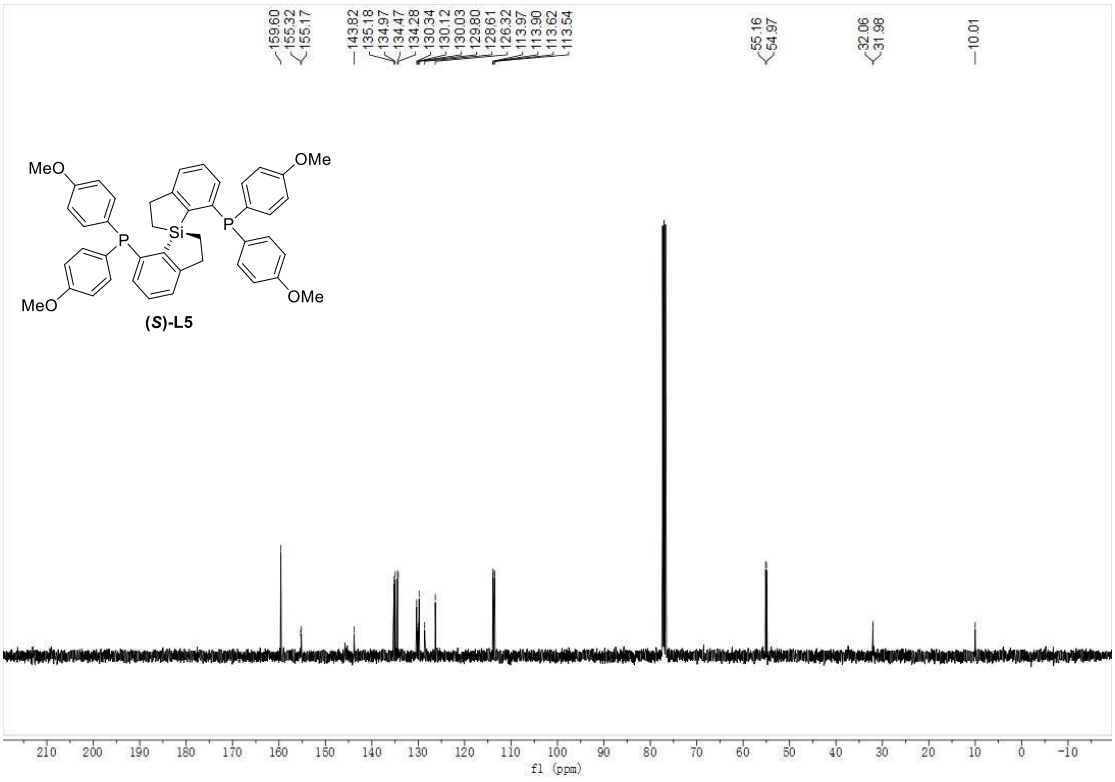

-8.27
Si
P
P
(S)-L4
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

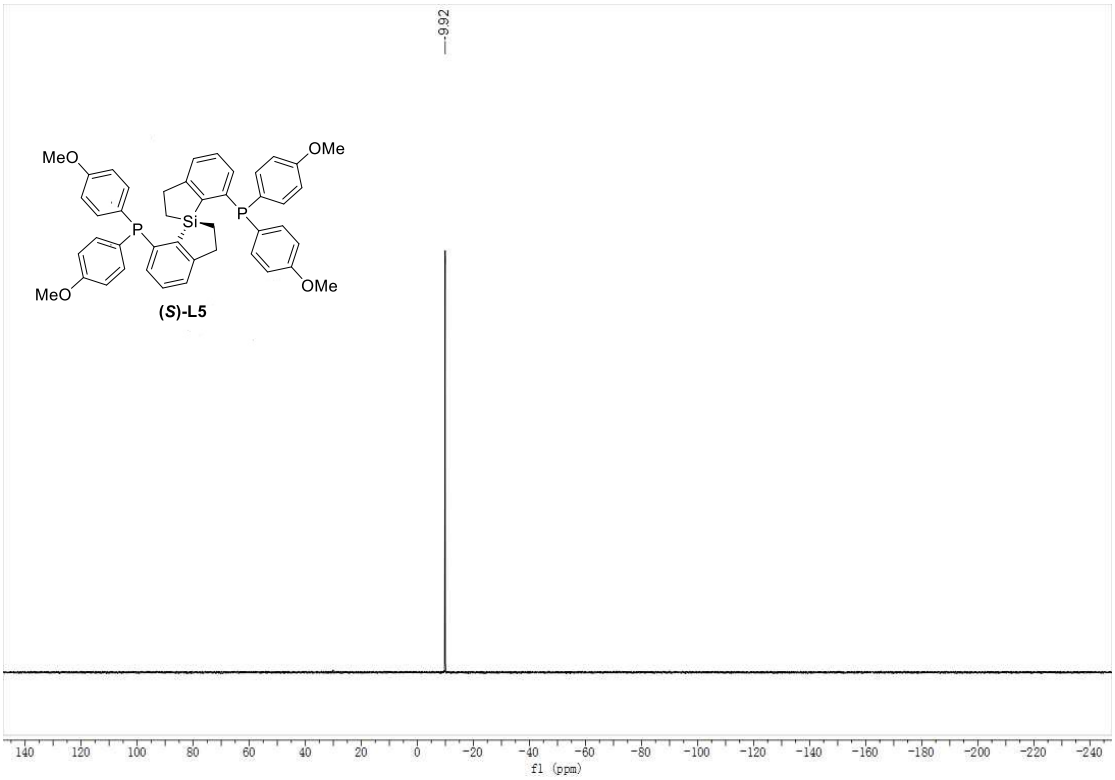

Intens.
x10^6
20221010-hf-l2_RE1_01_8102.d: +MS, 0.2-0.2min #9-13
1+
661.2580
1+
662.2607
1+
663.2619
1+
664.2641
656 658 660 662 664 666 668
m/z

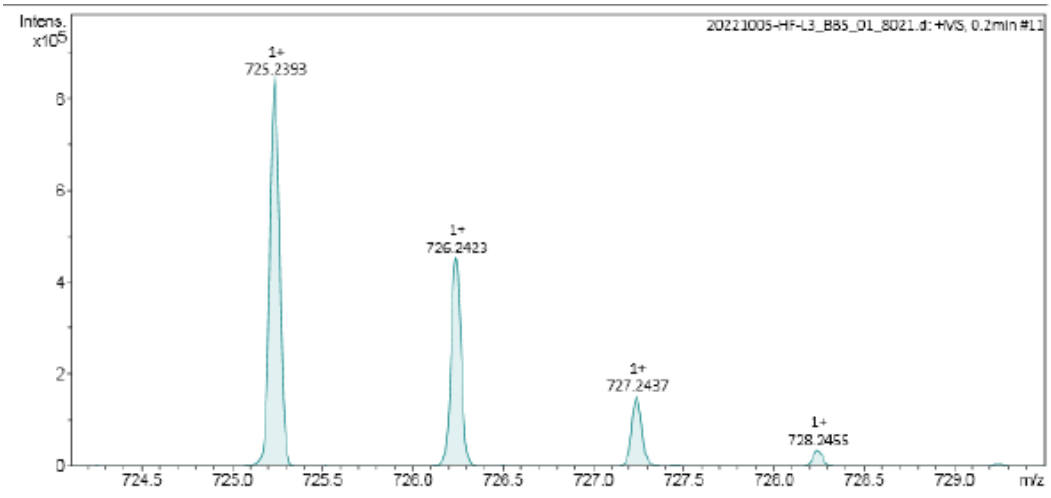

Intens.
x10^6
C44H48P2Si, 661.2504
1+
661.2604
1+
662.2634
1+
663.2647
1+
664.2659
656 658 660 662 664 666 668
m/z

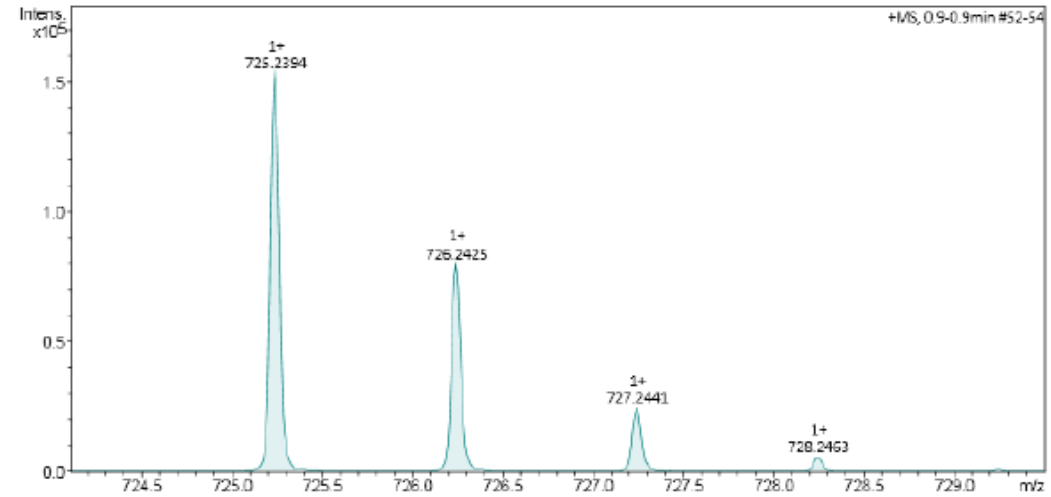
(*S*)-7,7'-bis(4-OCH$_3$-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] (L-5)



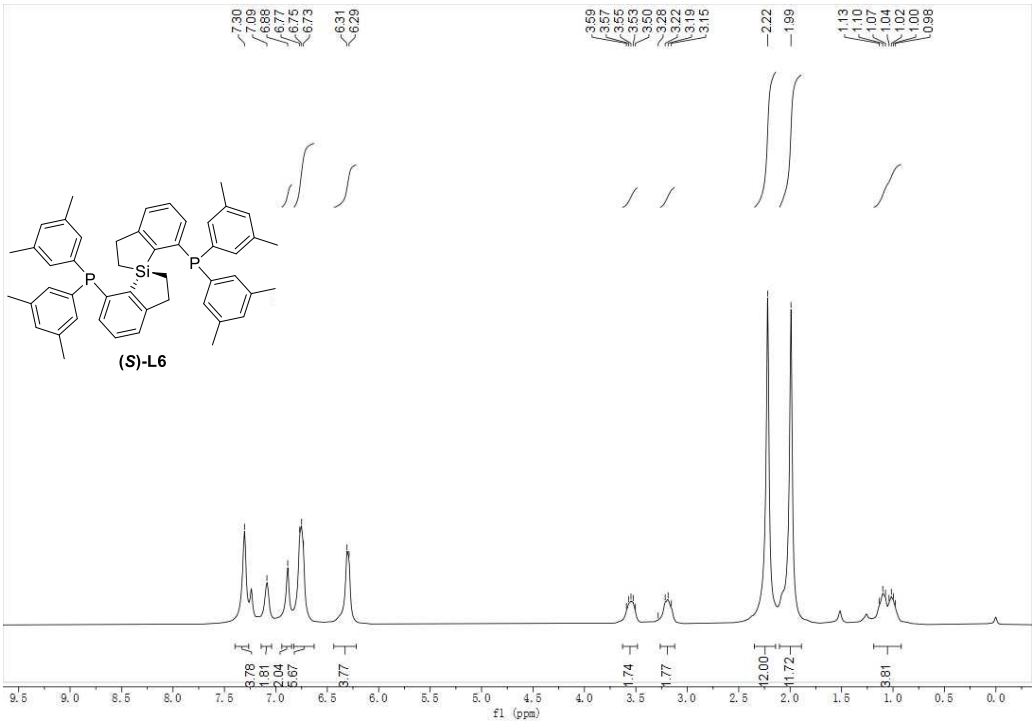


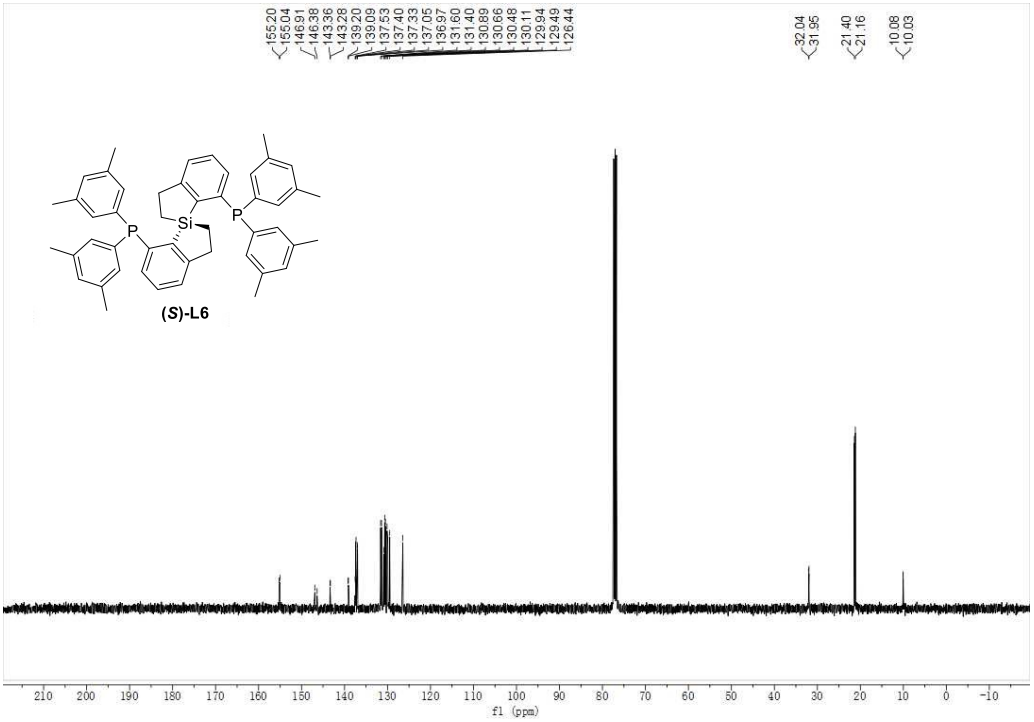

-9.92
MeO
OMe
Si
P
P
MeO
OMe
(S)-L5
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

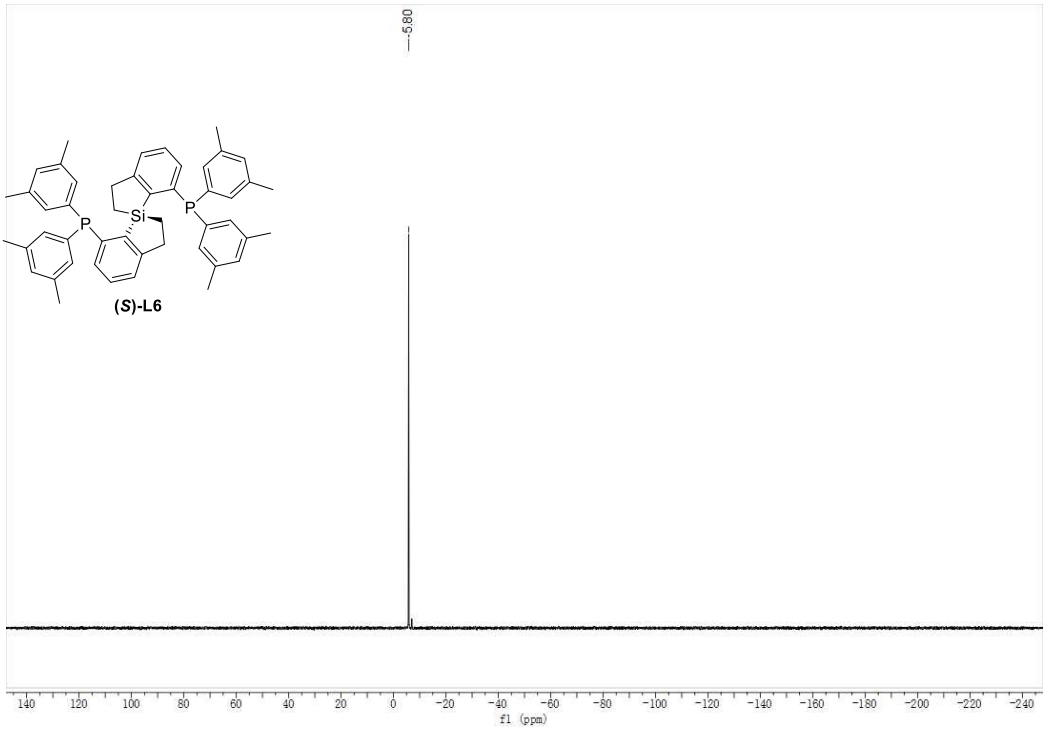

Intens.
x10^5
20221005-HF-L3_B85_01_8021.d: +MS, 0.2min #11
1+
725.2393
1+
726.2423
1+
727.2437
1+
728.2455
724.5 725.0 725.5 726.0 726.5 727.0 727.5 728.0 728.5 729.0 m/z

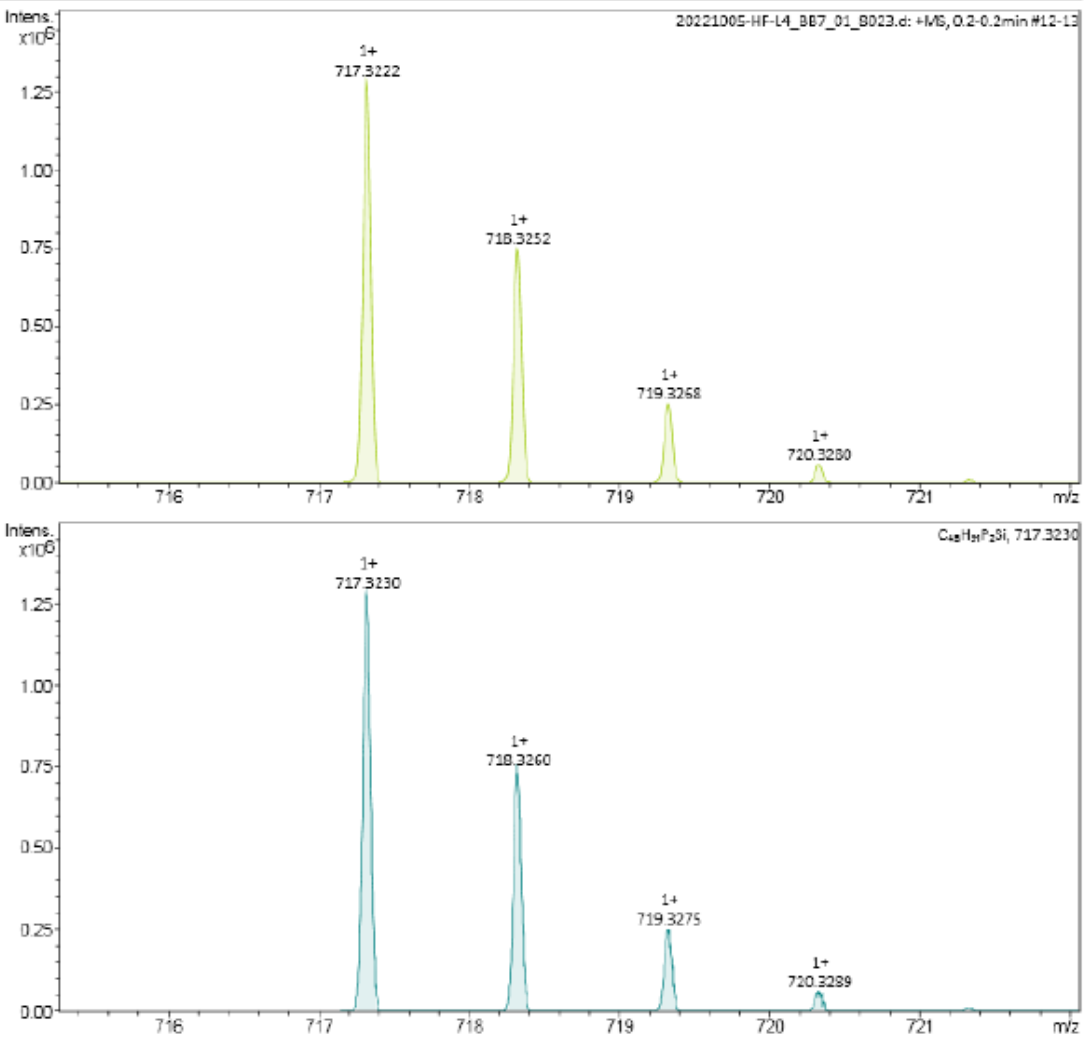

Intens.
x10^5
+MS, 0.9-0.9min #52-54
1+
725.2394
1+
726.2425
1+
727.2441
1+
728.2463
724.5 725.0 725.5 726.0 726.5 727.0 727.5 728.0 728.5 729.0 m/z

(*S*)-7,7'-bis(3,5-(CH_3)$_2$-(diphenylphosphaneyl))-2,2',3,3'-tetrahydro-1,1'-spirobi[benzo[*b*]silole] (L-6)

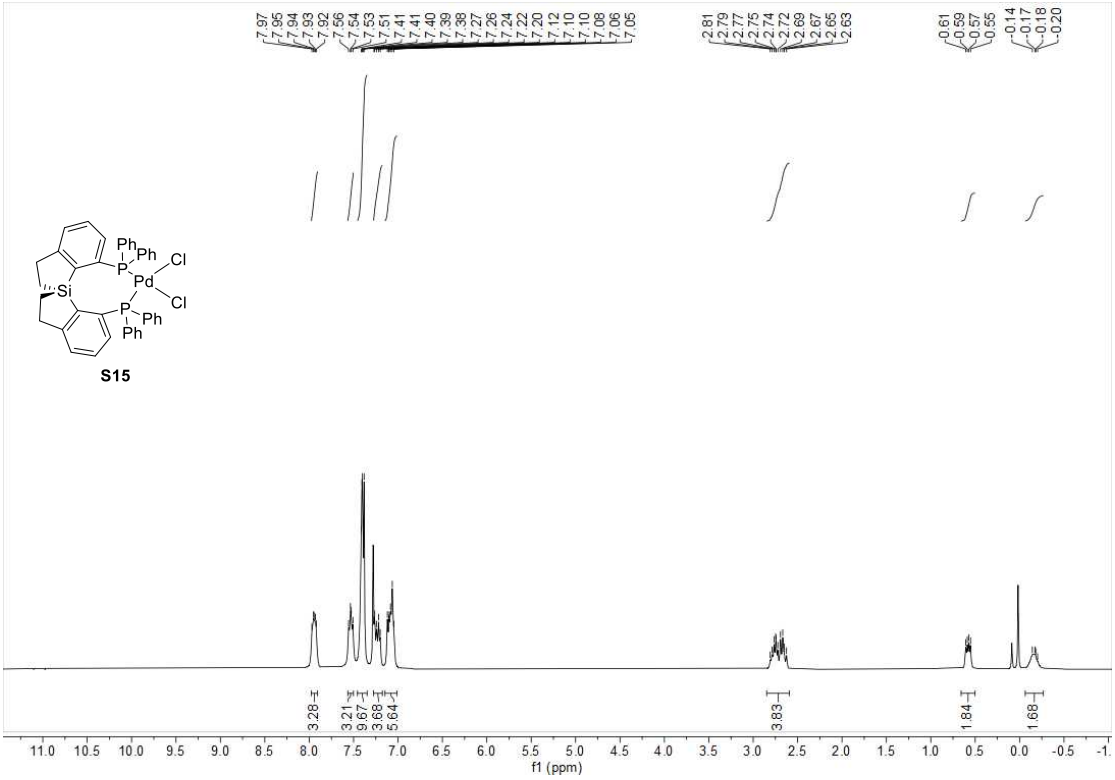


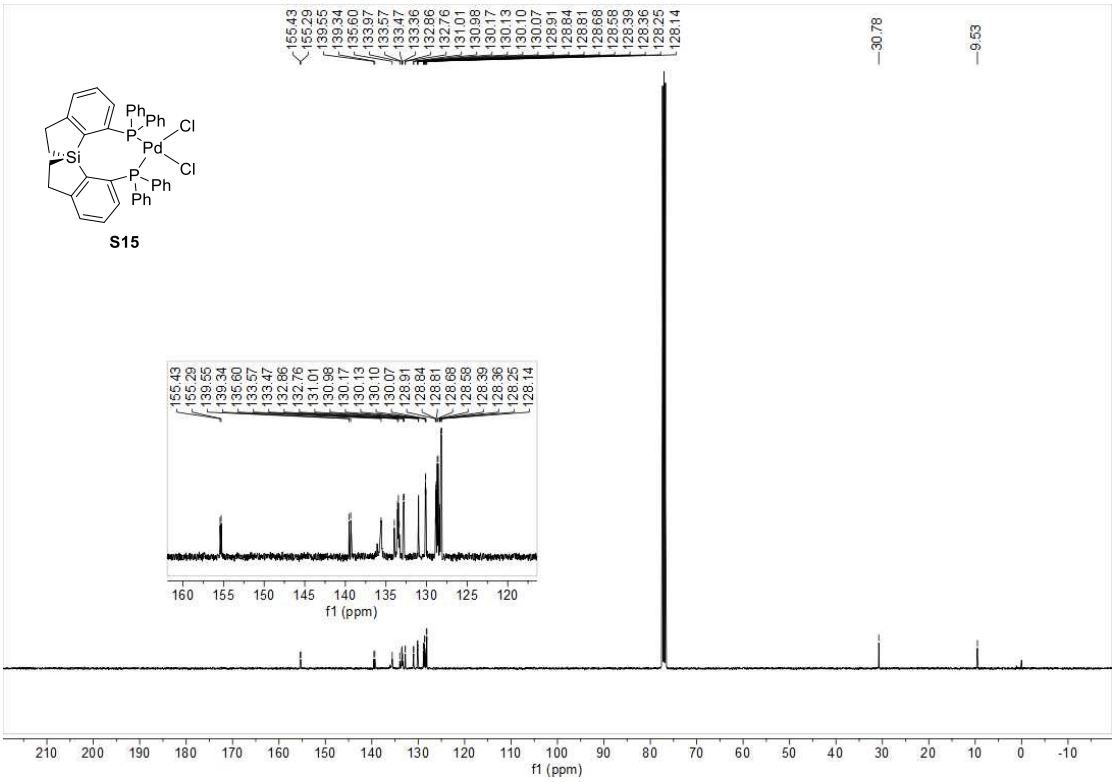


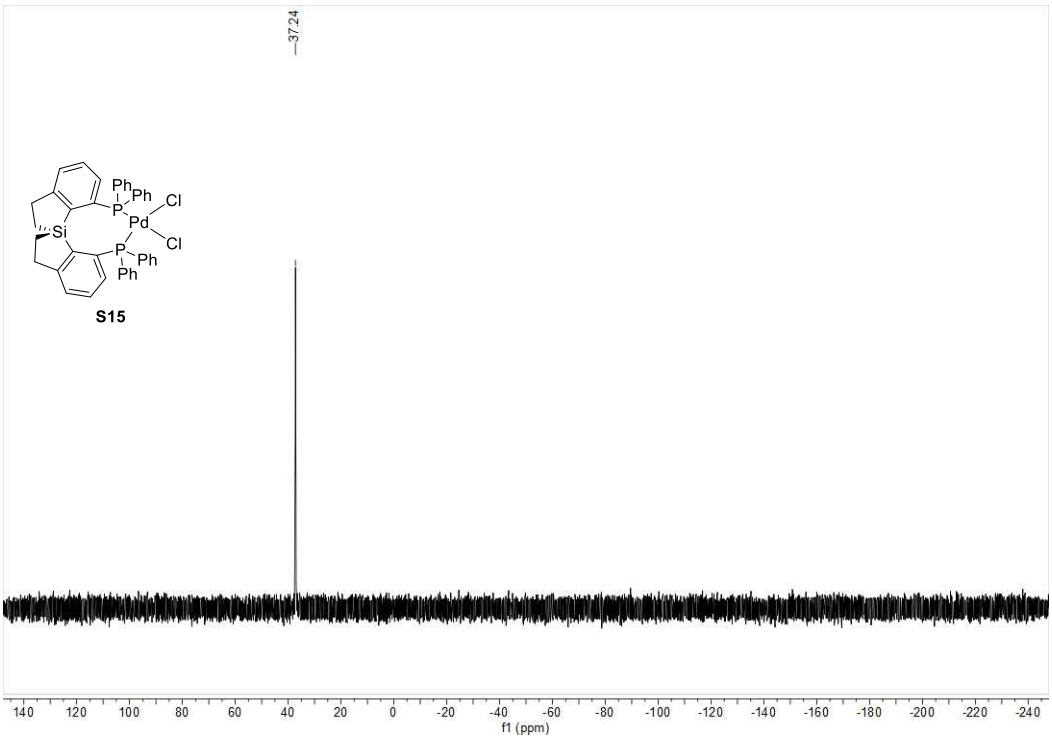

-5.80
Si
P
P
(S)-L6
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

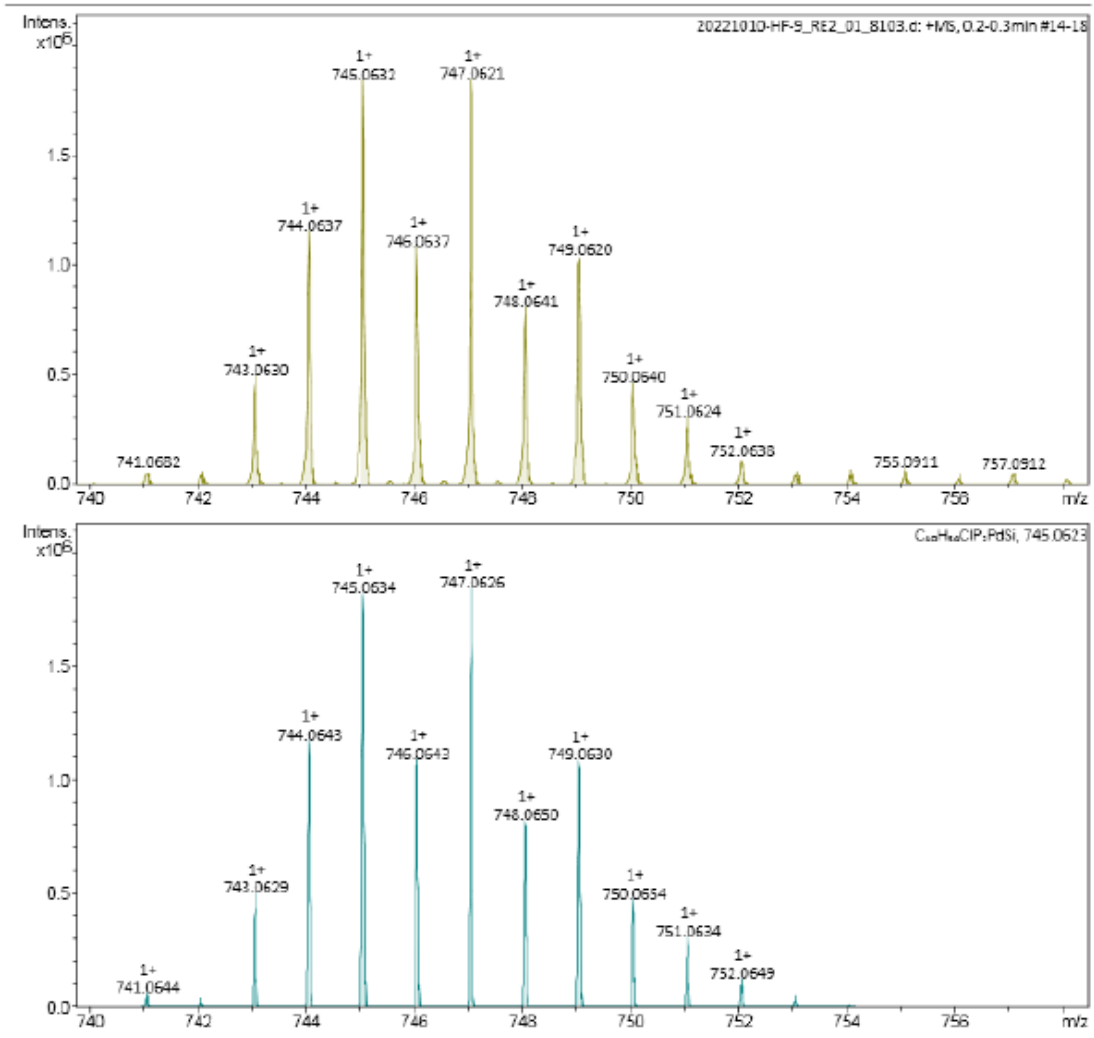

Intens.
x10^6
20221005-HF-L4_BB7_01_8023.d: +MS, 0.2-0.2min #12-13
1+
717.3222
1+
718.3252
1+
719.3268
1+
720.3280
1.25
1.00
0.75
0.50
0.25
0.00
716 717 718 719 720 721 m/z
Intens.
x10^6
C48H51P2Si, 717.3230
1+
717.3230
1+
718.3260
1+
719.3275
1+
720.3289
1.25
1.00
0.75
0.50
0.25
0.00
716 717 718 719 720 721 m/z

{$PdCl_2$[(S)-L3]}(S15)

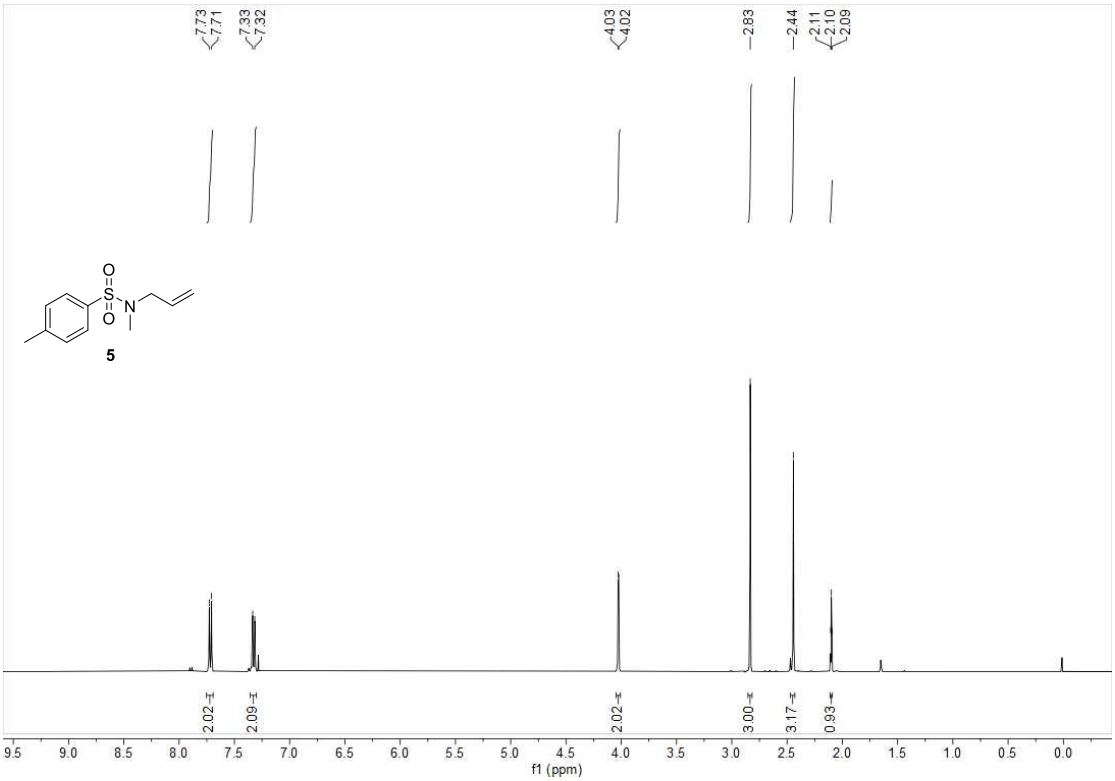




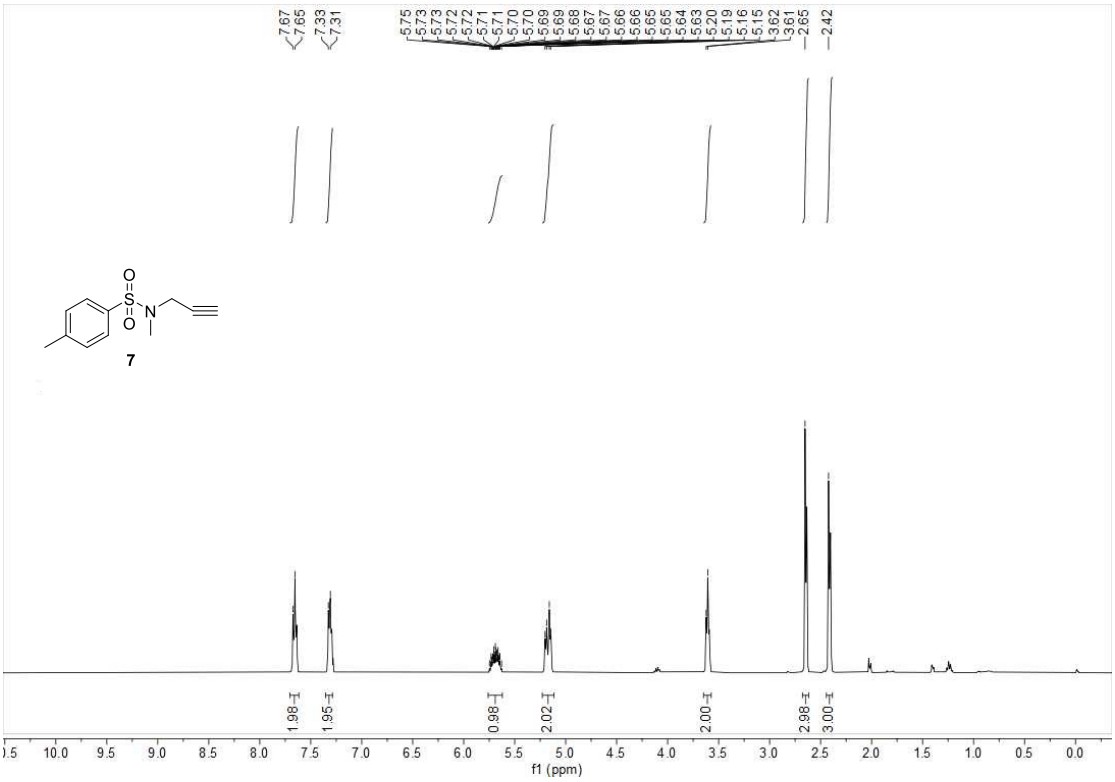

37.24
Ph
Ph
P
Pd
Cl
Cl
Si
P
Ph
Ph
S15
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


Intens.
x10^6
20221010-HF-S_RE2_01_8103.d: +MS, 0.2-0.3min #14-18
1+ 745.0631
1+ 747.0621
1+ 744.0637
1+ 746.0637
1+ 749.0620
1+ 748.0641
1+ 743.0630
1+ 750.0640
1+ 751.0624
1+ 752.0638
741.0682
755.0911
757.0912
0.0
0.5
1.0
1.5
740 742 744 746 748 750 752 754 756 m/z
Intens.
x10^6
C50H44ClP2PdSi, 745.0623
1+ 745.0634
1+ 747.0626
1+ 744.0643
1+ 746.0643
1+ 749.0630
1+ 748.0650
1+ 743.0629
1+ 750.0654
1+ 751.0634
1+ 741.0644
1+ 752.0649
0.0
0.5
1.0
1.5
740 742 744 746 748 750 752 754 756 m/z

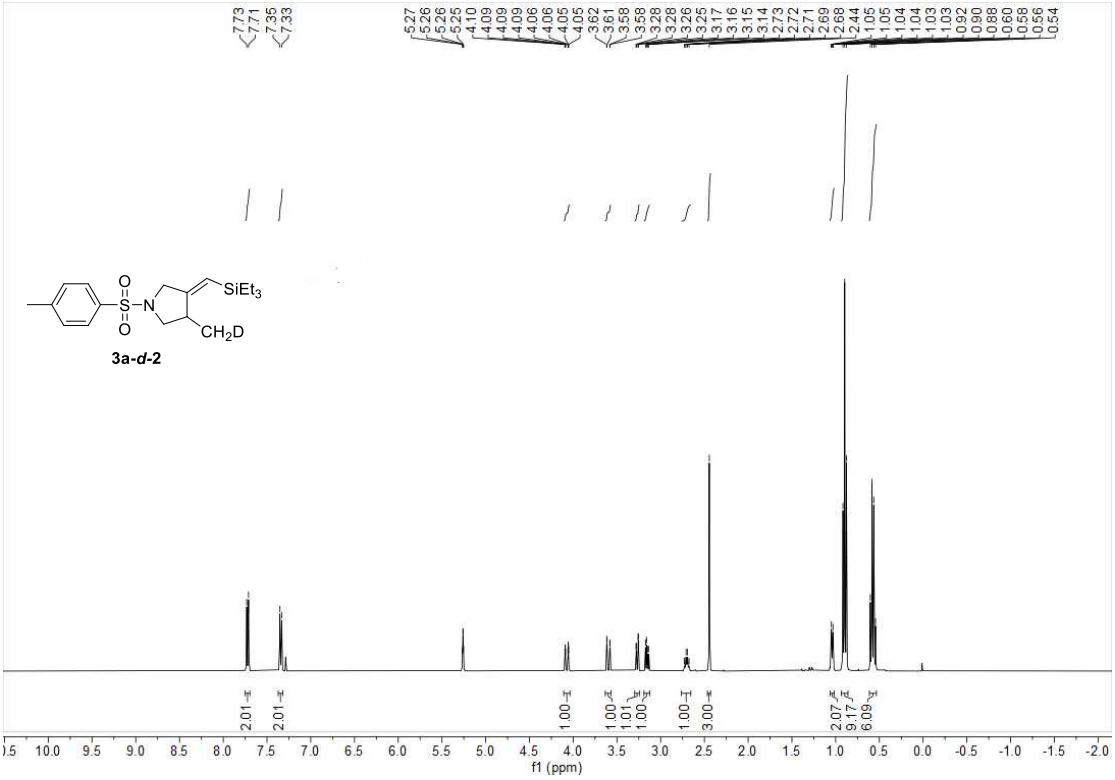
***N*,4-dimethyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5)**

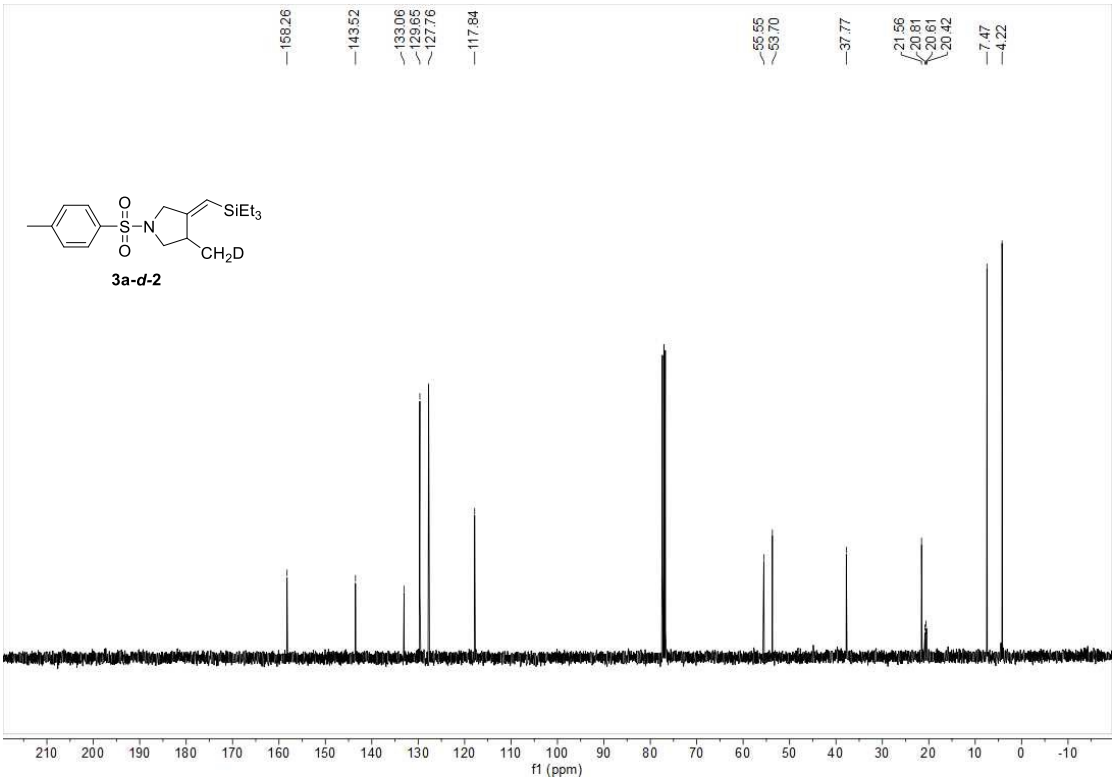


***N*-allyl-*N*,4-dimethylbenzenesulfonamide (7)**

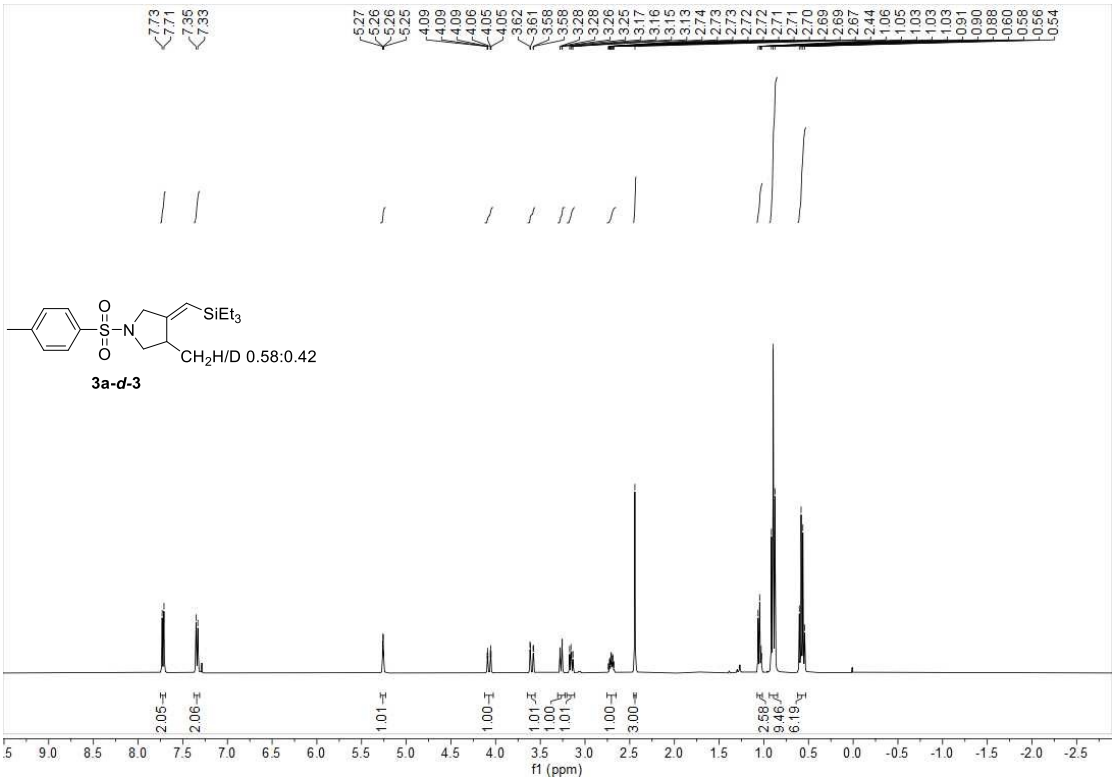


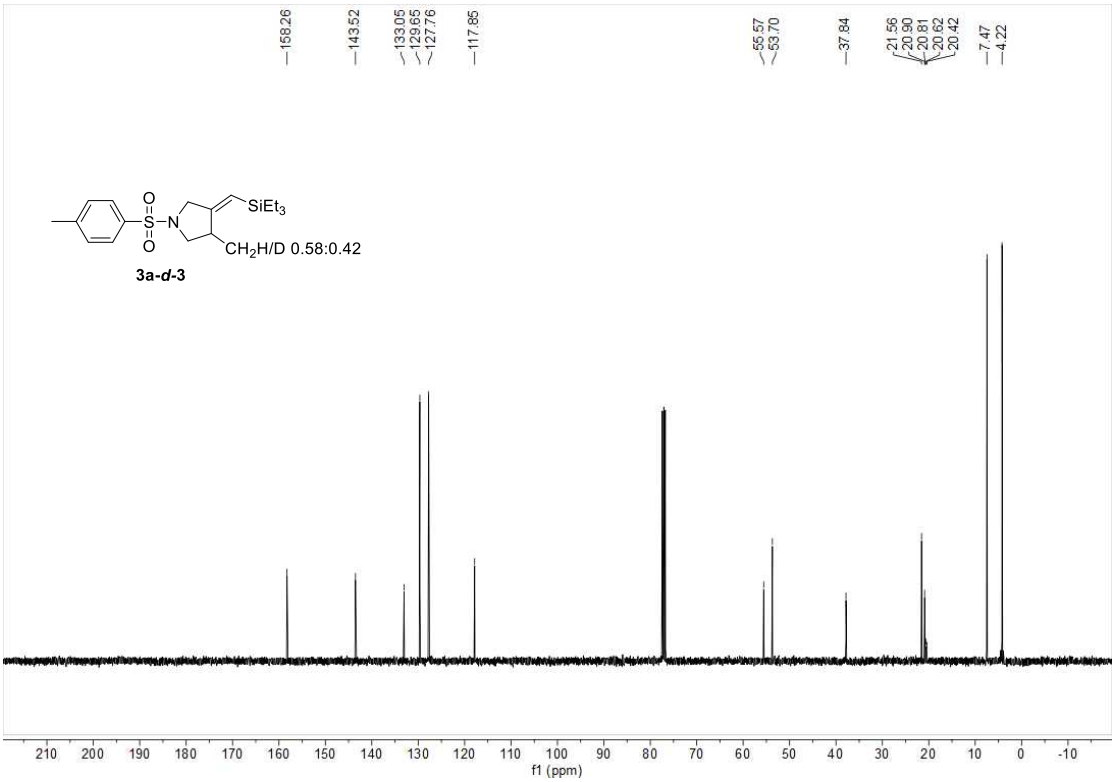
(*E*)-1-tosyl-3-((triethylsilyl)methylene)pyrrolidine-4-*d* (3a-*d*-2)



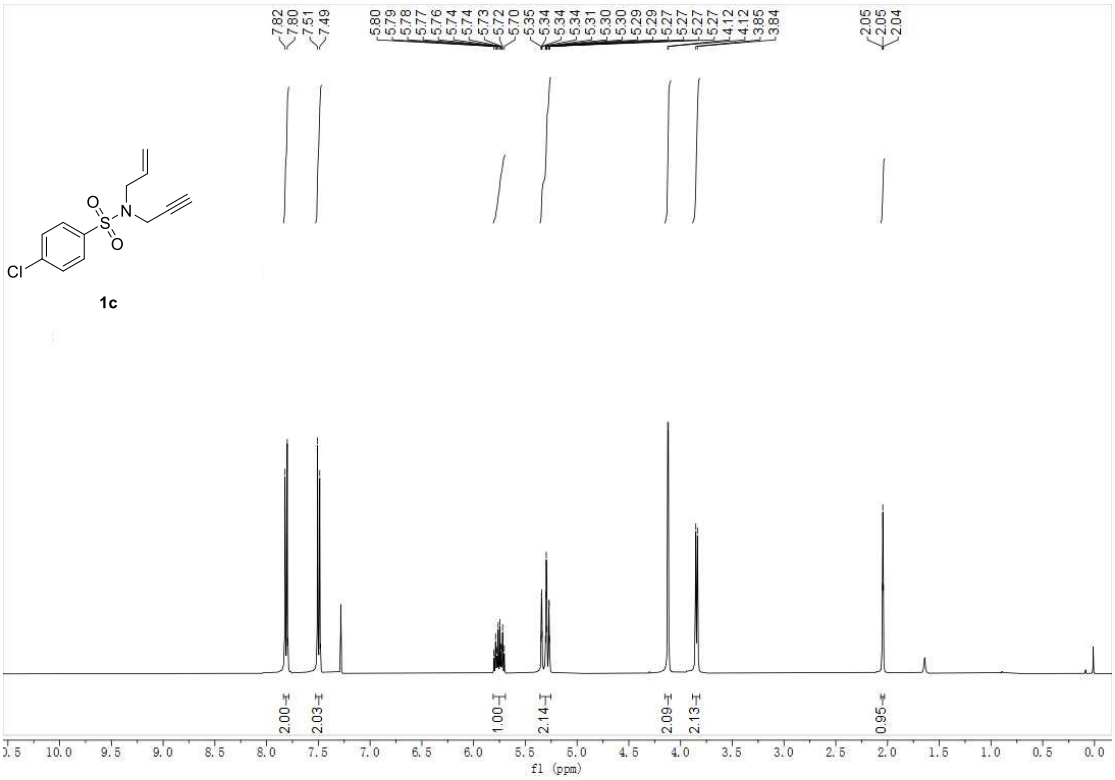


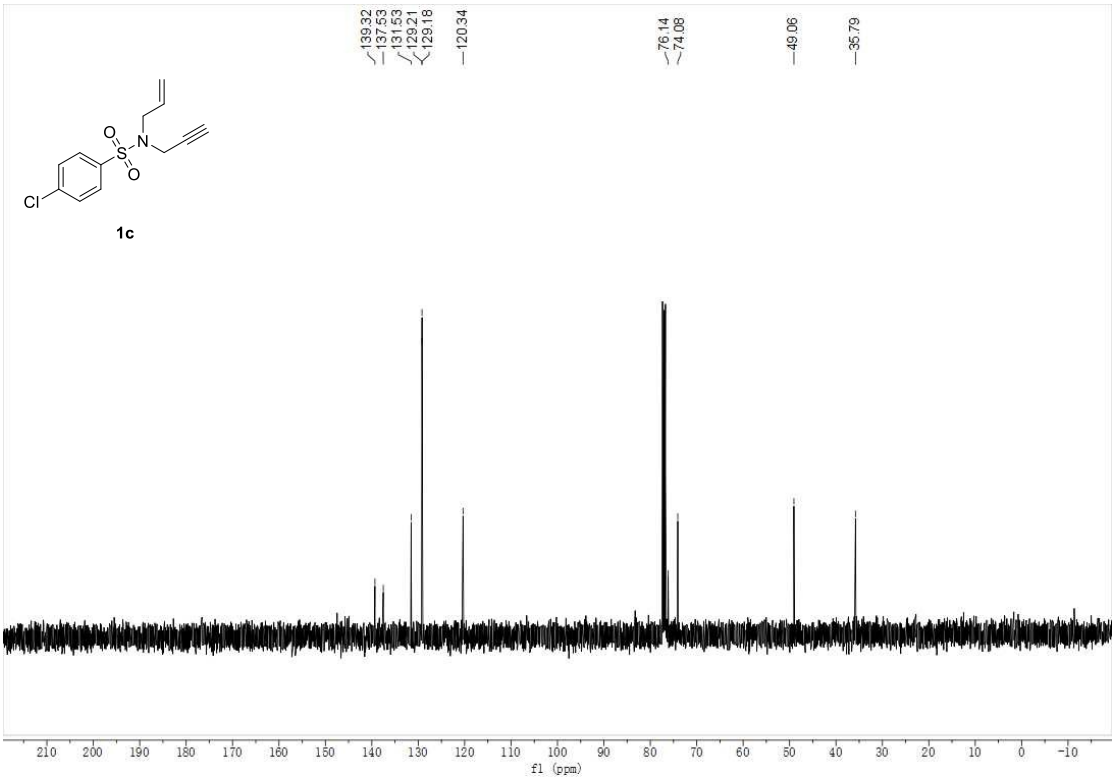
(*E*)-1-tosyl-3-((triethylsilyl)methylene)pyrrolidine-4-*d* (3a-*d*-3)



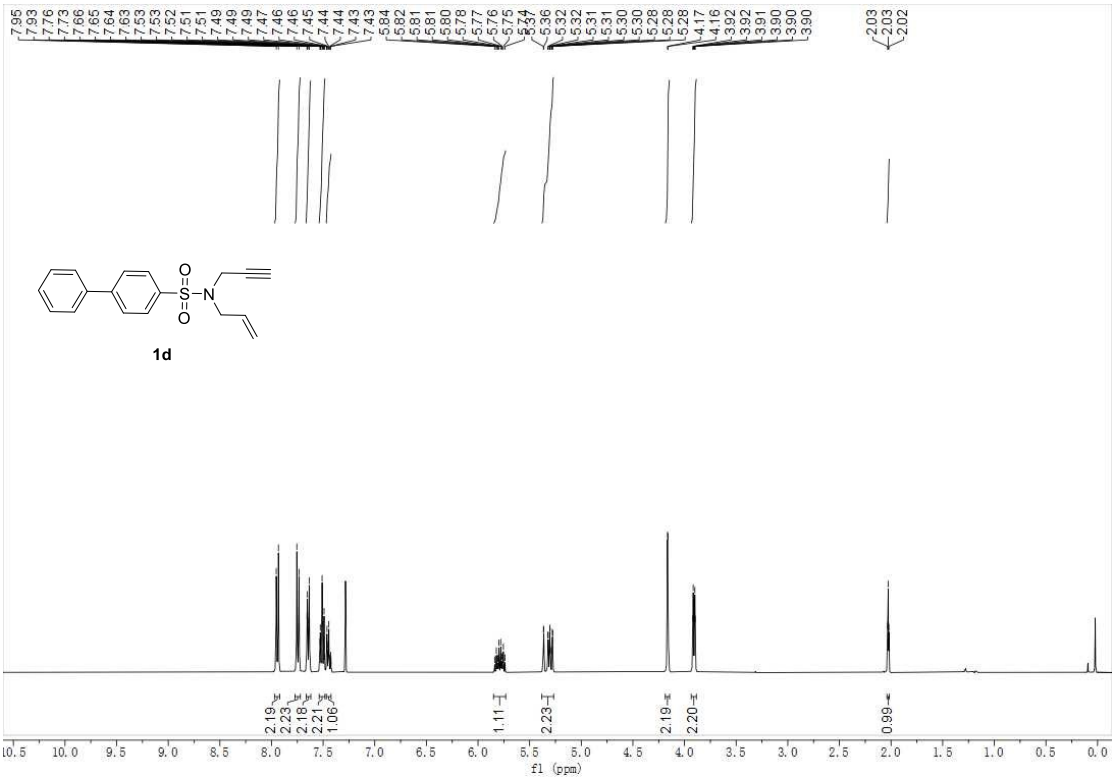


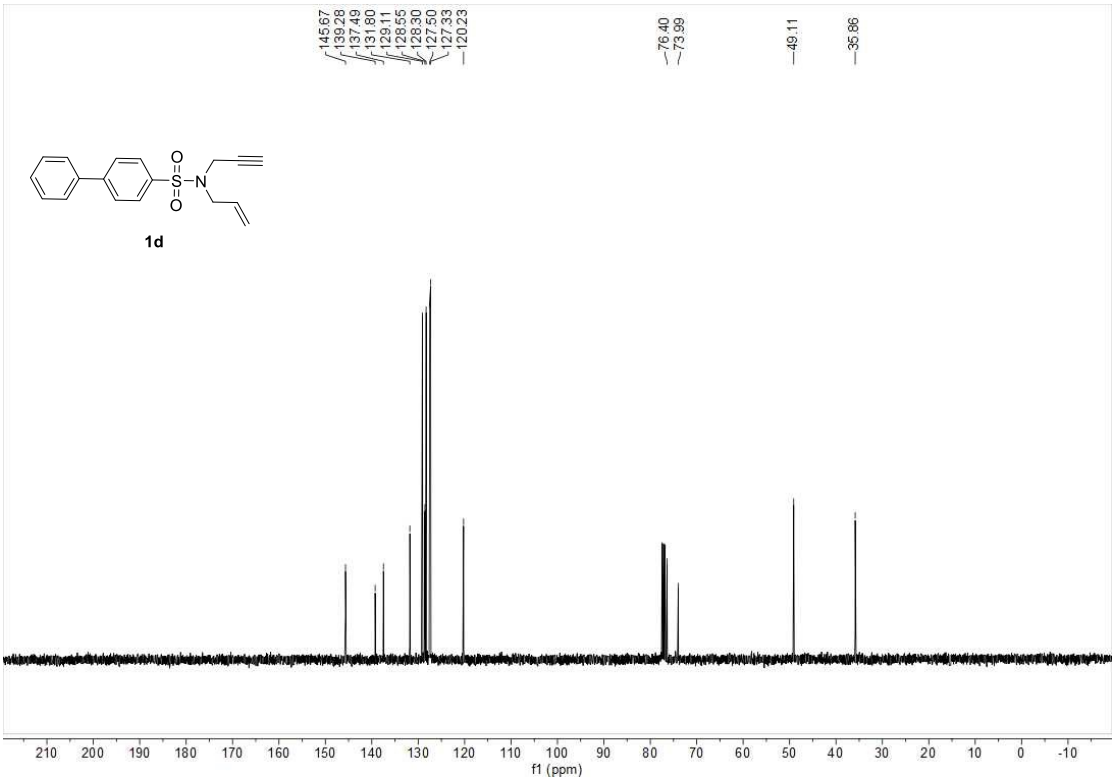
***N*-allyl-4-chloro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c)**



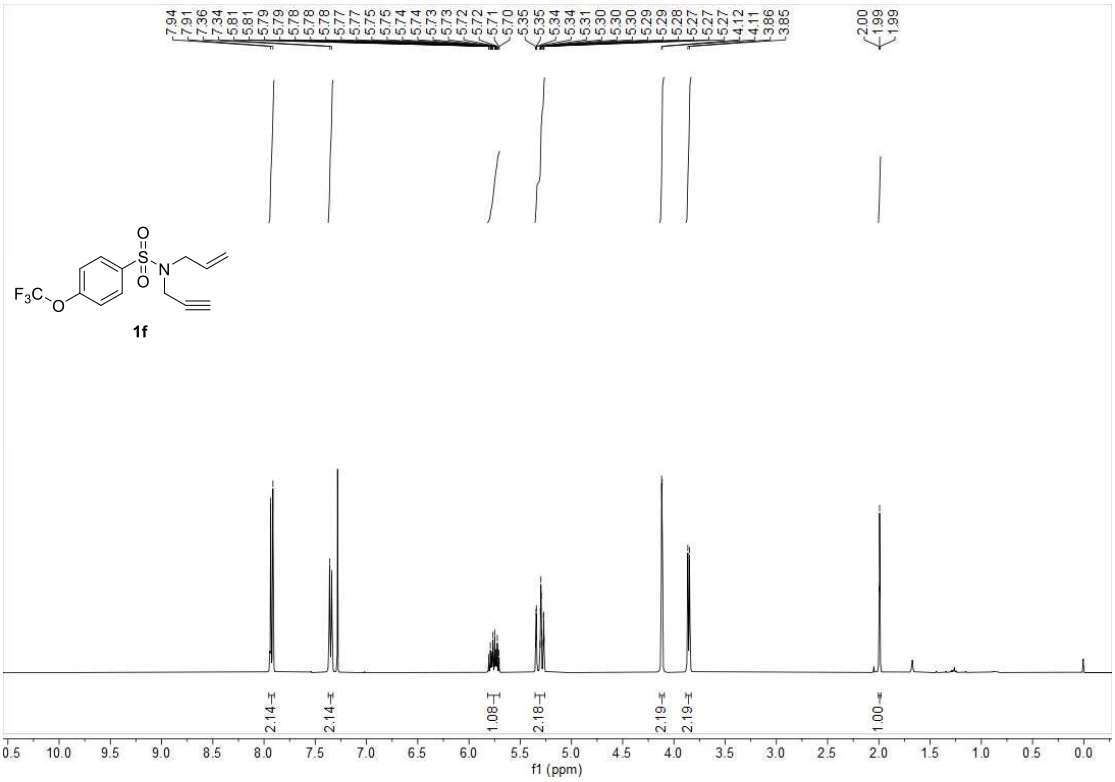


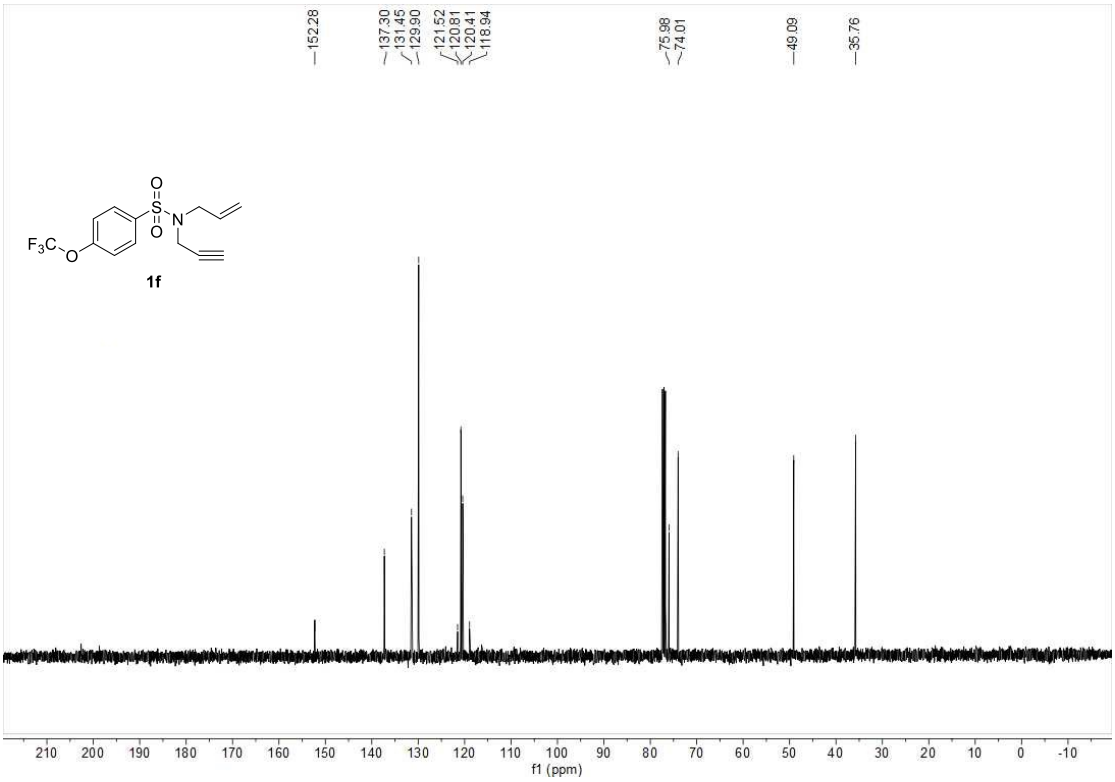
***N*-allyl-N-(prop-2-yn-1-yl)-[1,1'-biphenyl]-4-sulfonamide (1d)**

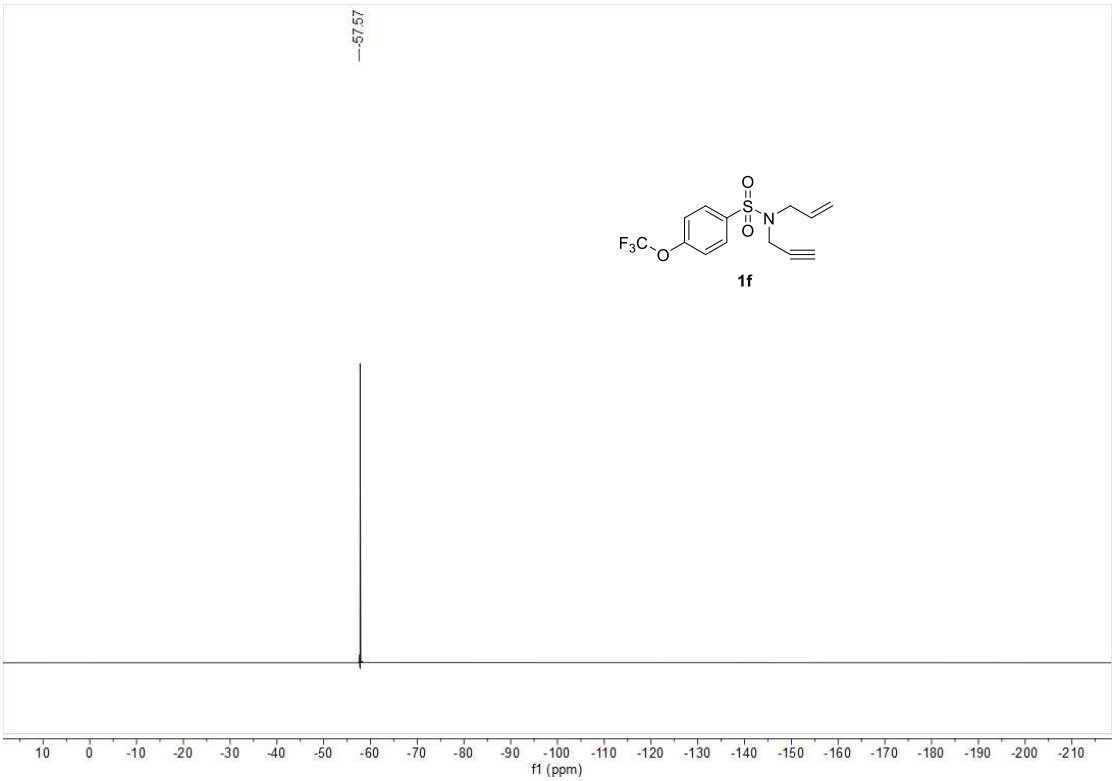




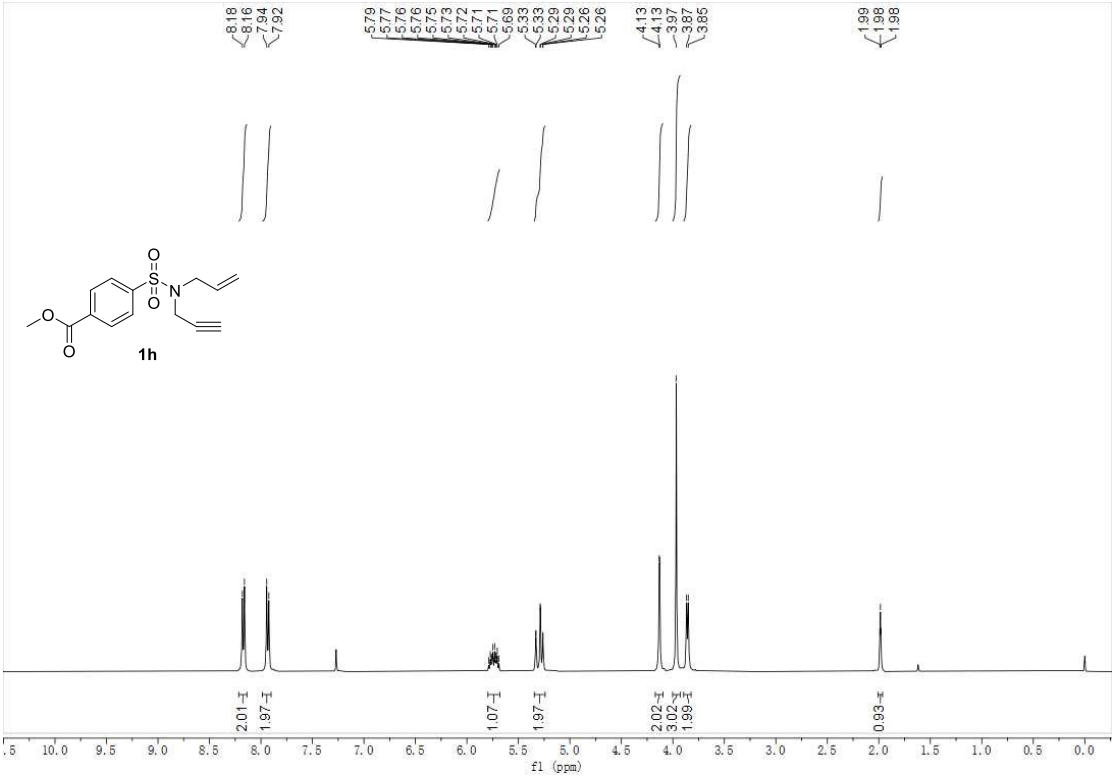
***N*-allyl-N-(prop-2-yn-1-yl)-4-(trifluoromethoxy)benzenesulfonamide (1f)**

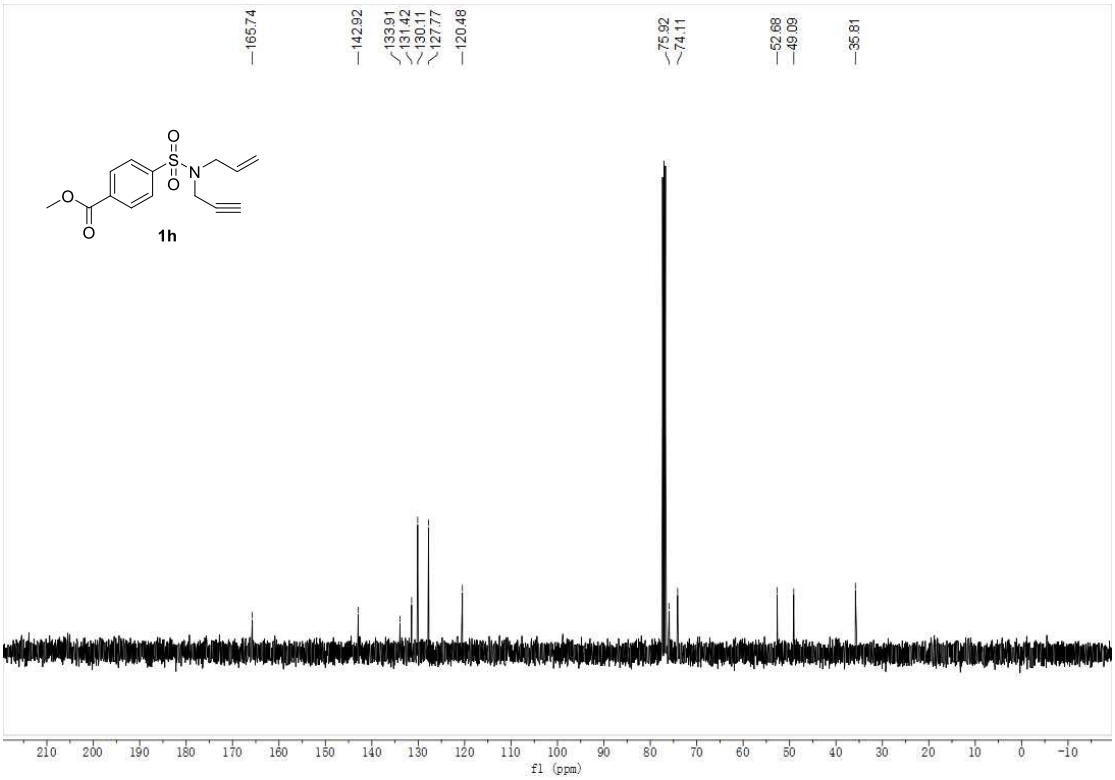




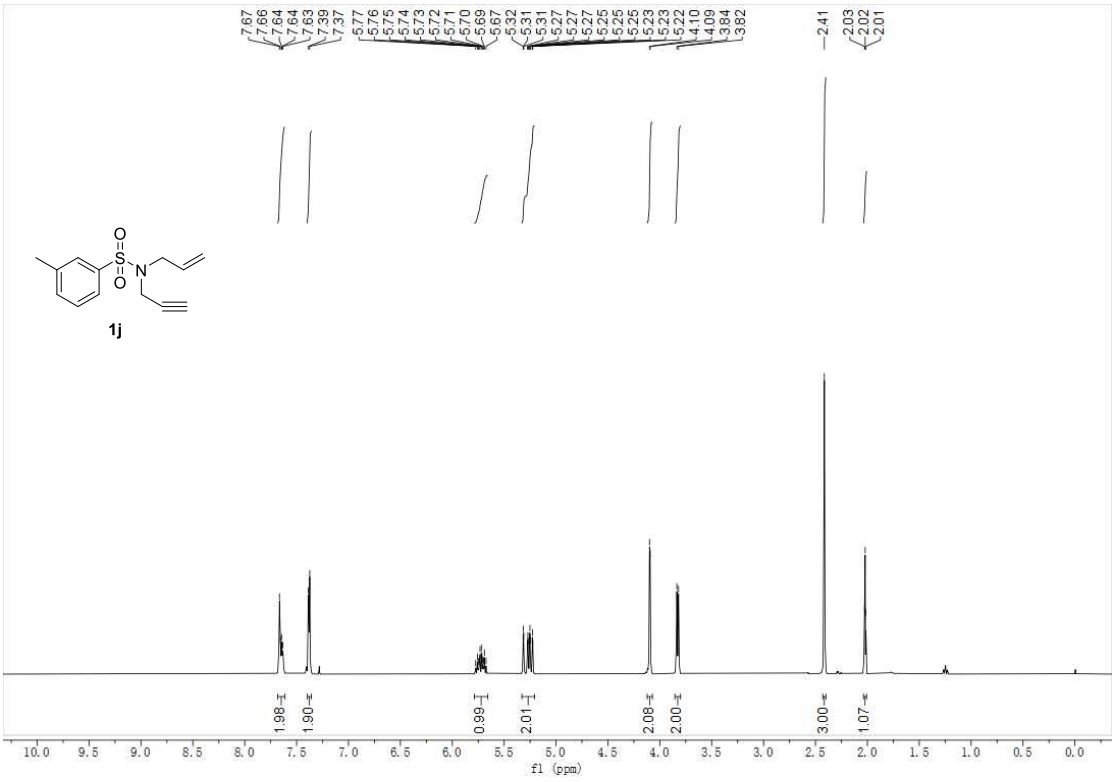


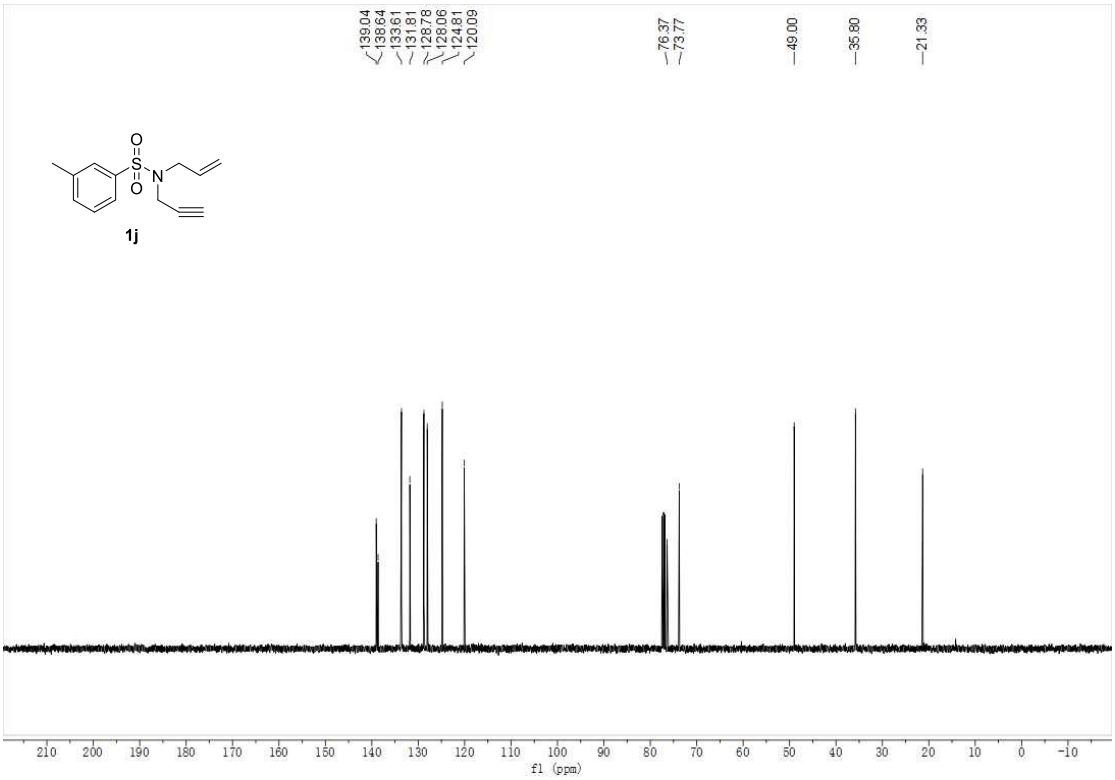
Methyl 4-(*N*-allyl-*N*-(prop-2-yn-1-yl)sulfamoyl)benzoate (1h)



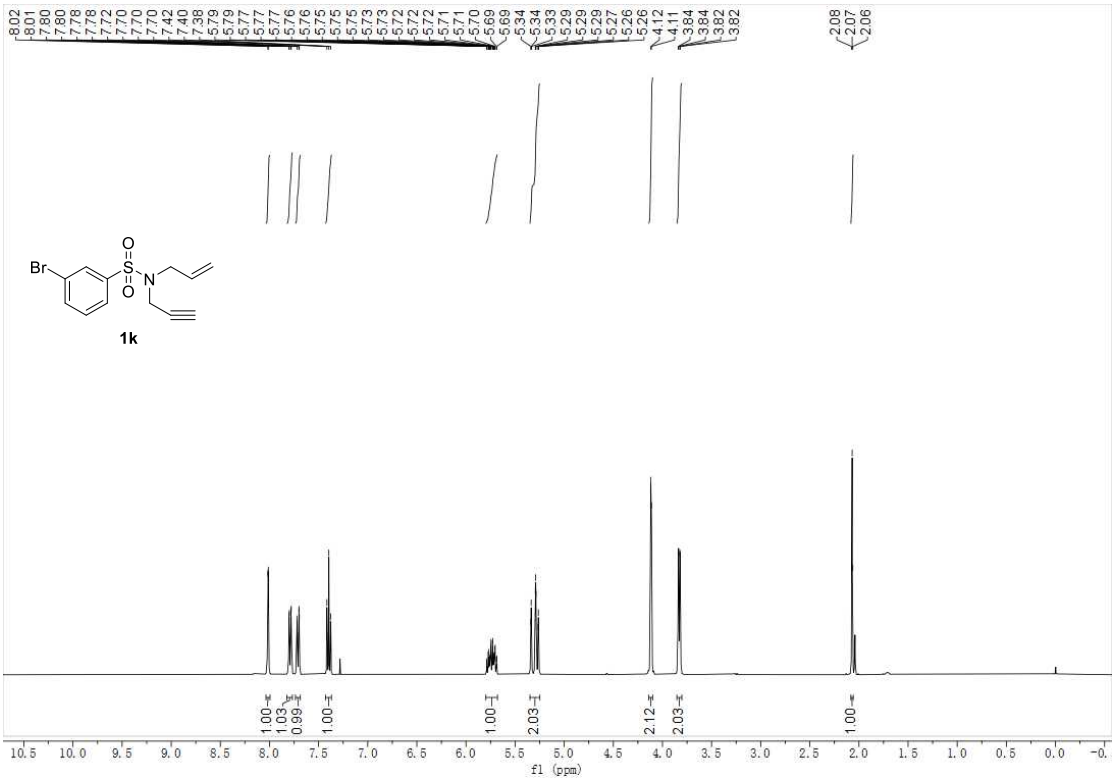


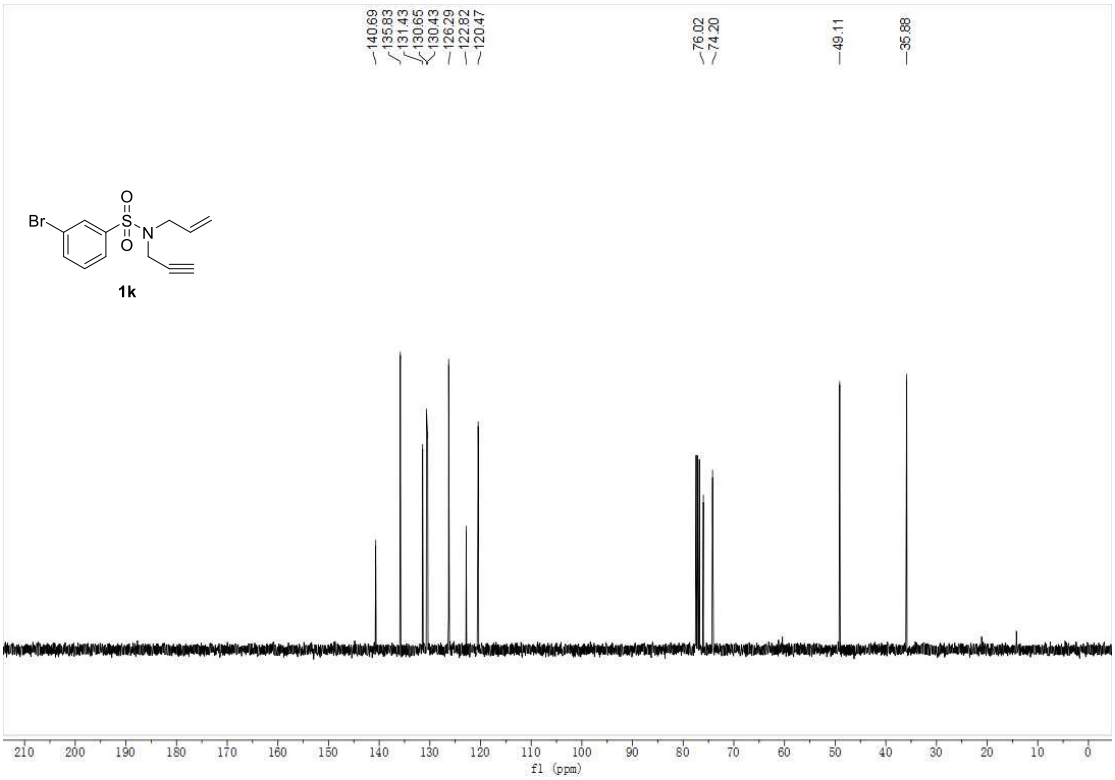
***N*-allyl-3-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1j)**



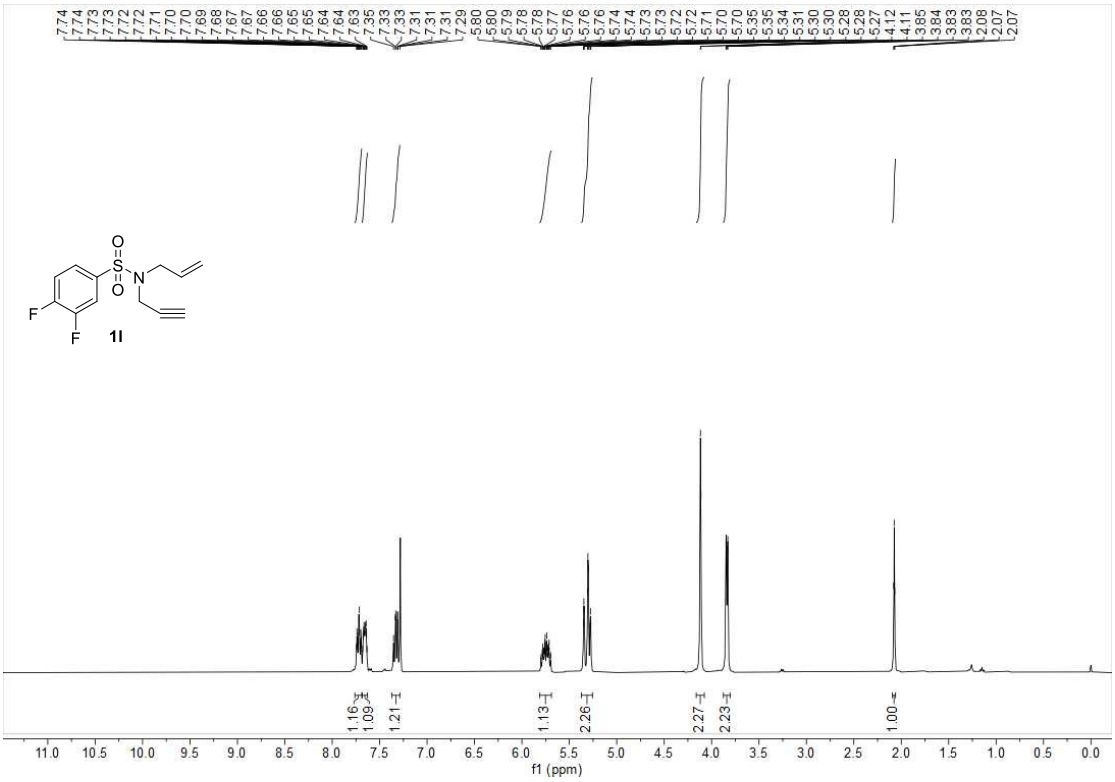


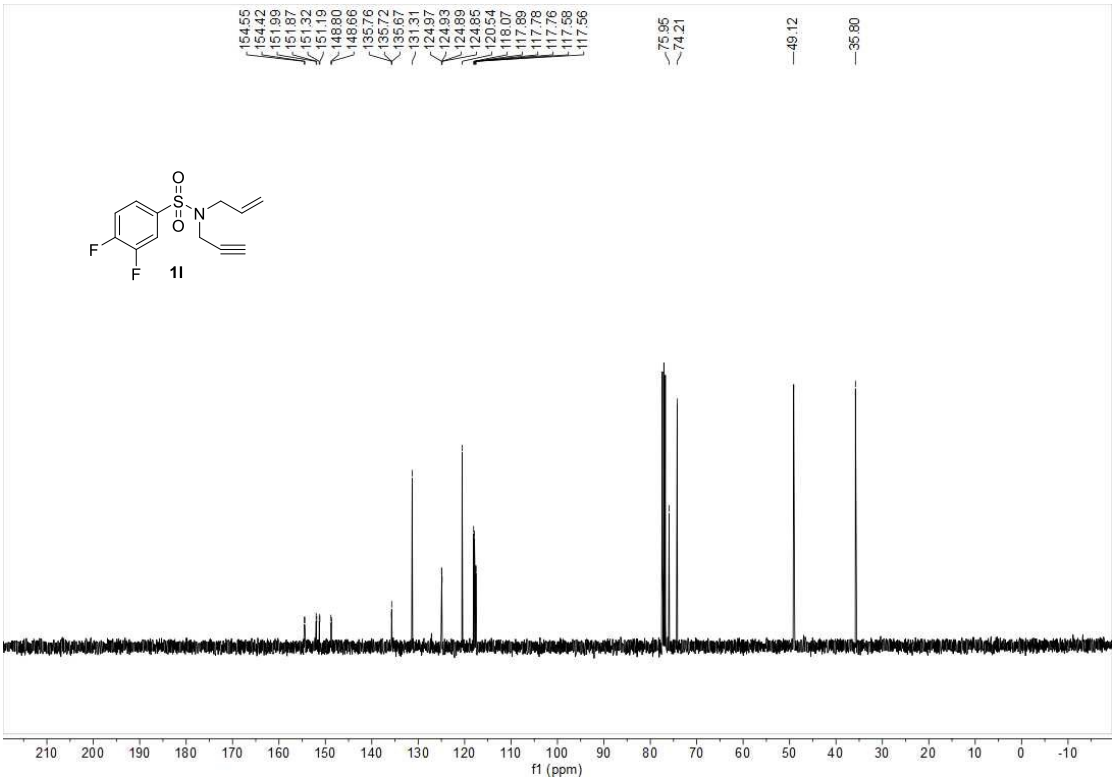
***N*-allyl-3-bromo-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1k)**

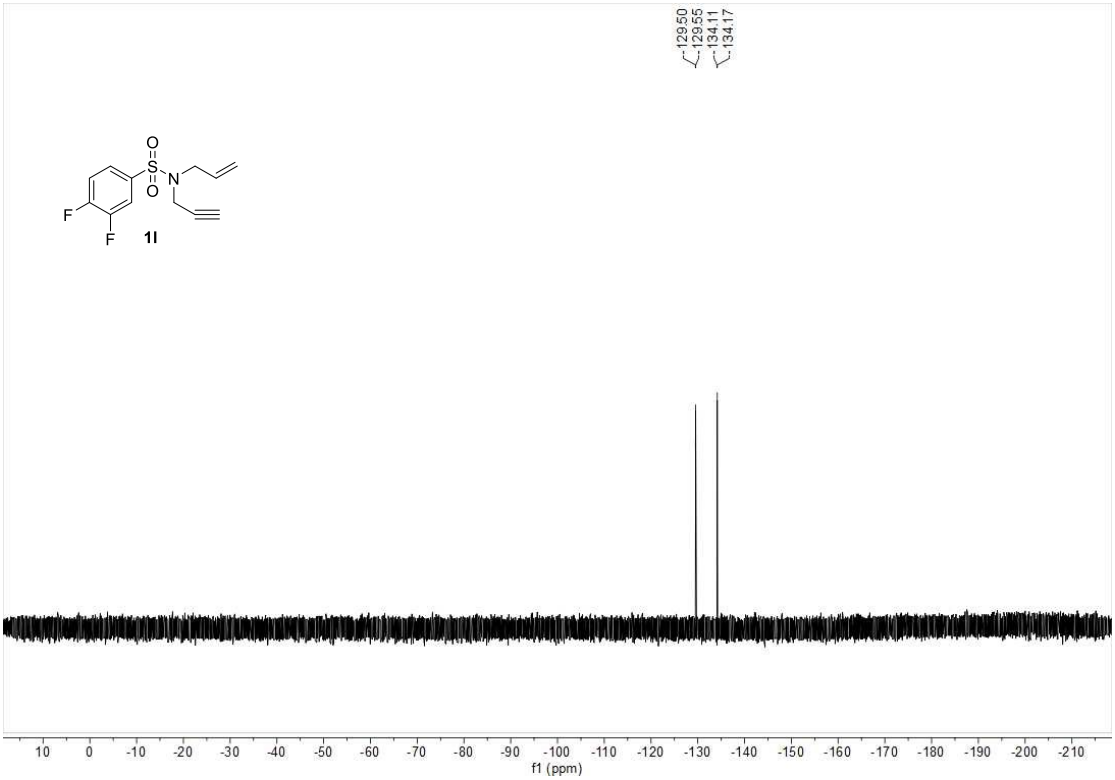




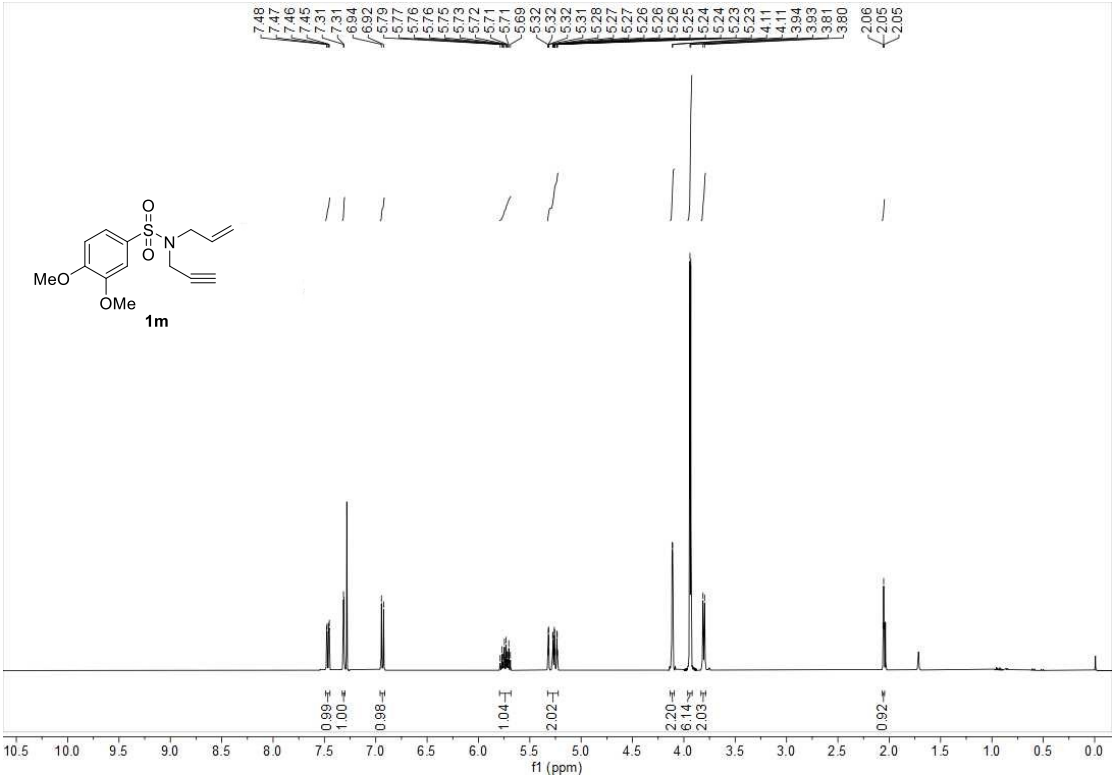
***N*-allyl-3,4-difluoro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1l)**

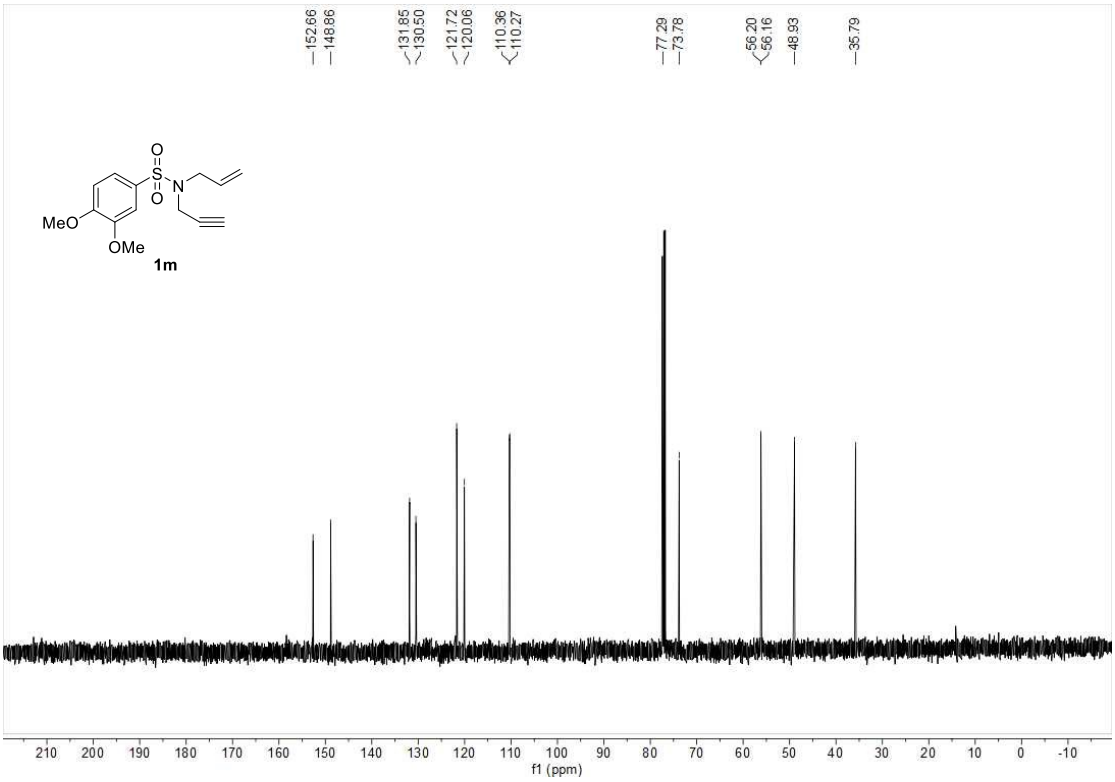



154.55
154.42
151.99
151.87
151.32
151.19
148.80
148.66
135.76
135.72
135.67
131.31
124.97
124.93
124.89
124.85
120.54
118.07
117.89
117.78
117.76
117.58
117.56
75.95
74.21
49.12
35.80
1l
f1 (ppm)

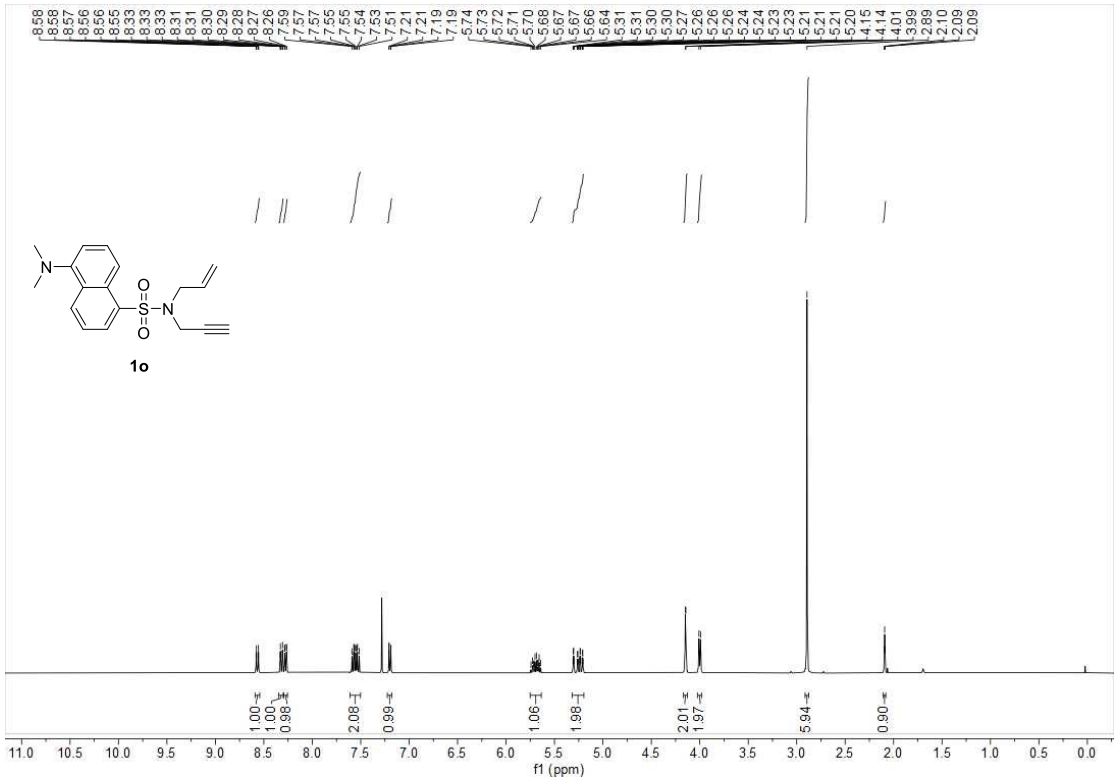

129.50
129.55
134.11
134.17
1l
f1 (ppm)

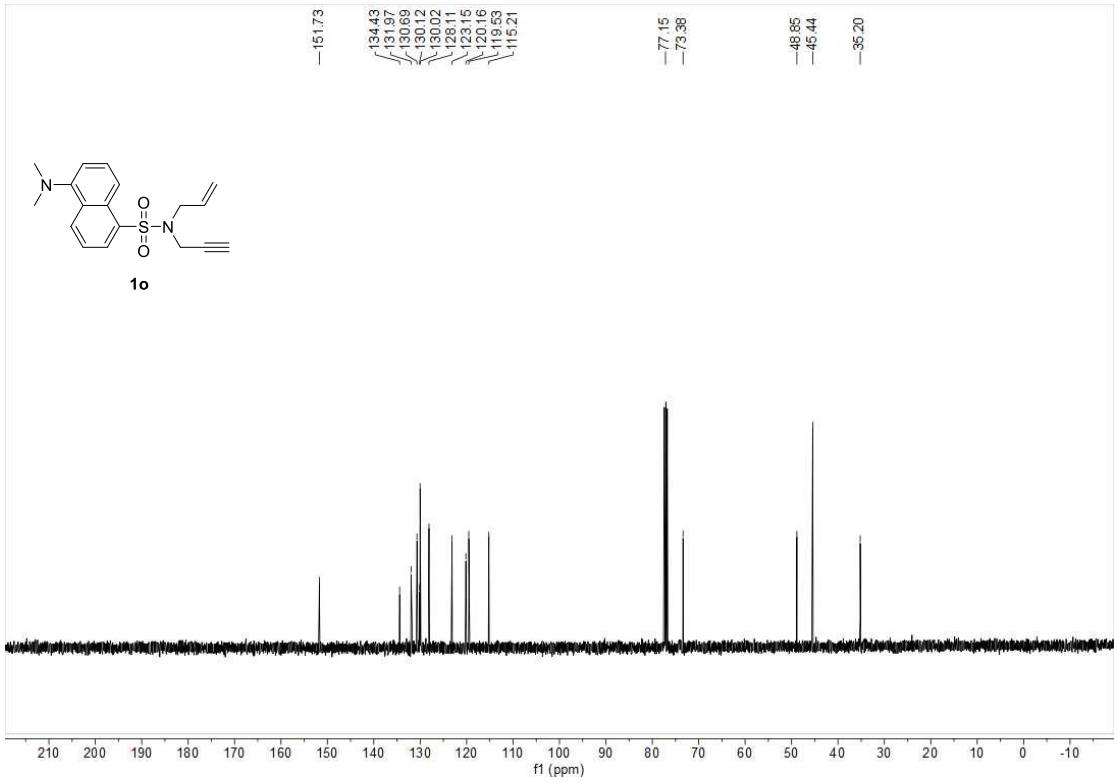
***N*-allyl-3,4-dimethoxy-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1m)**



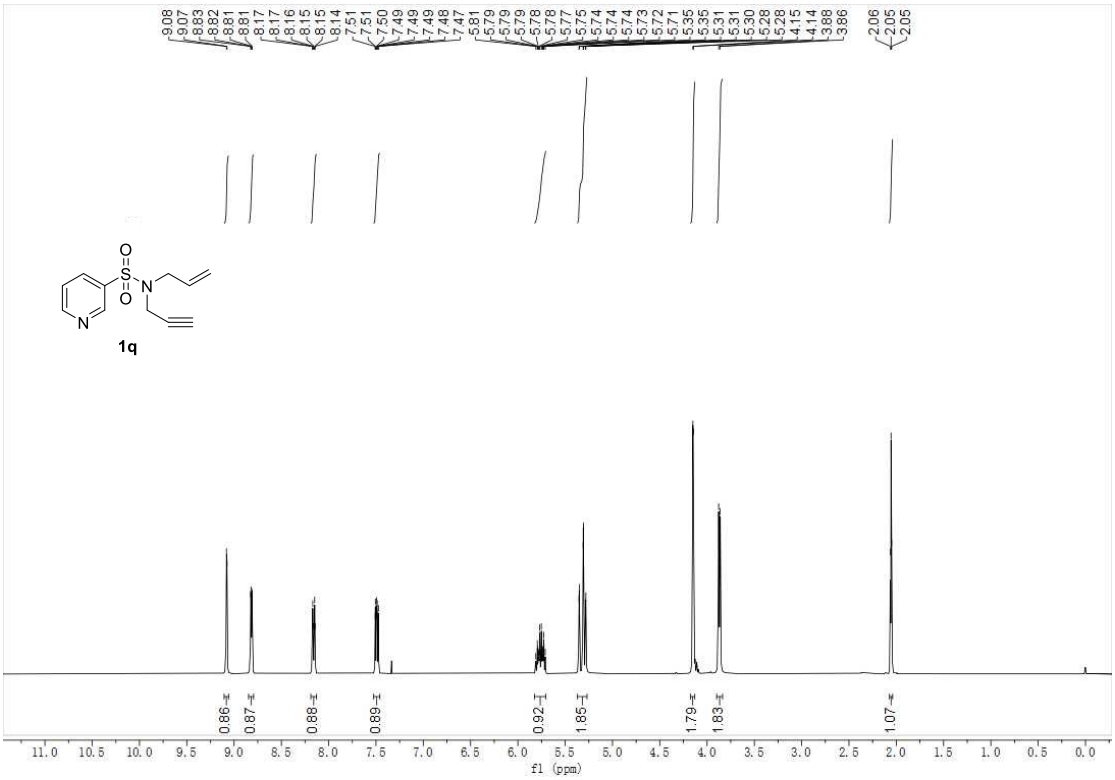


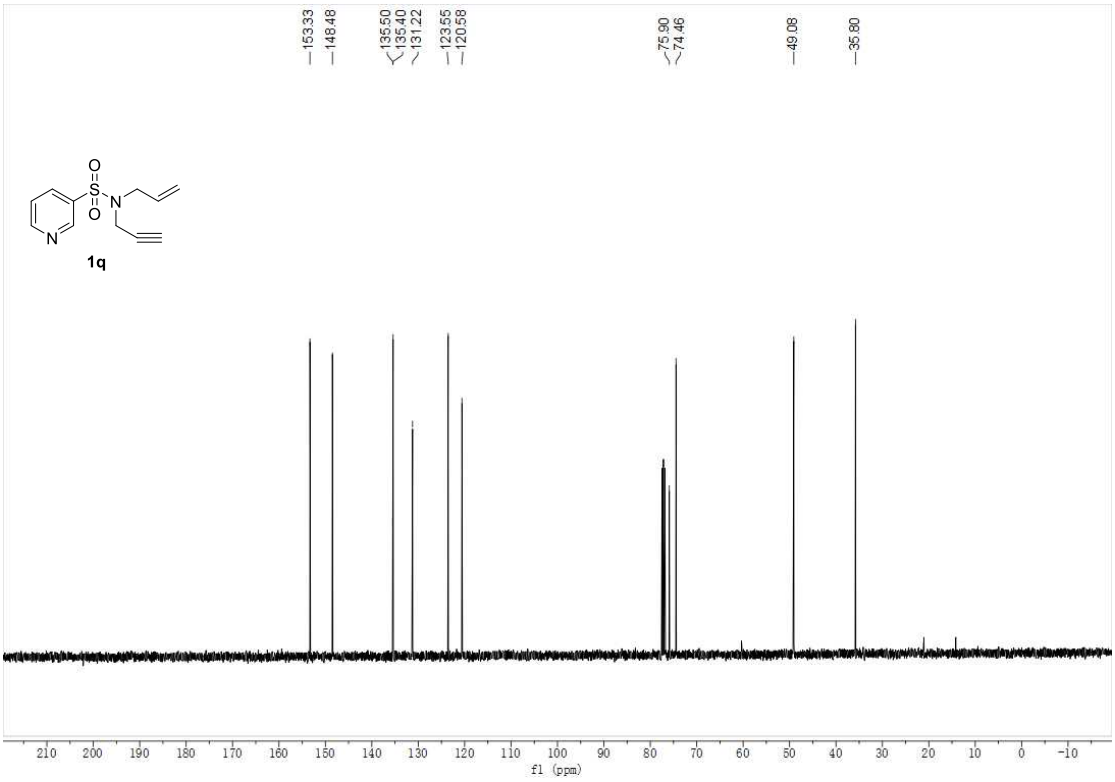
***N*-allyl-6-(dimethylamino)-*N*-(prop-2-yn-1-yl)naphthalene-2-sulfonamide (1o)**



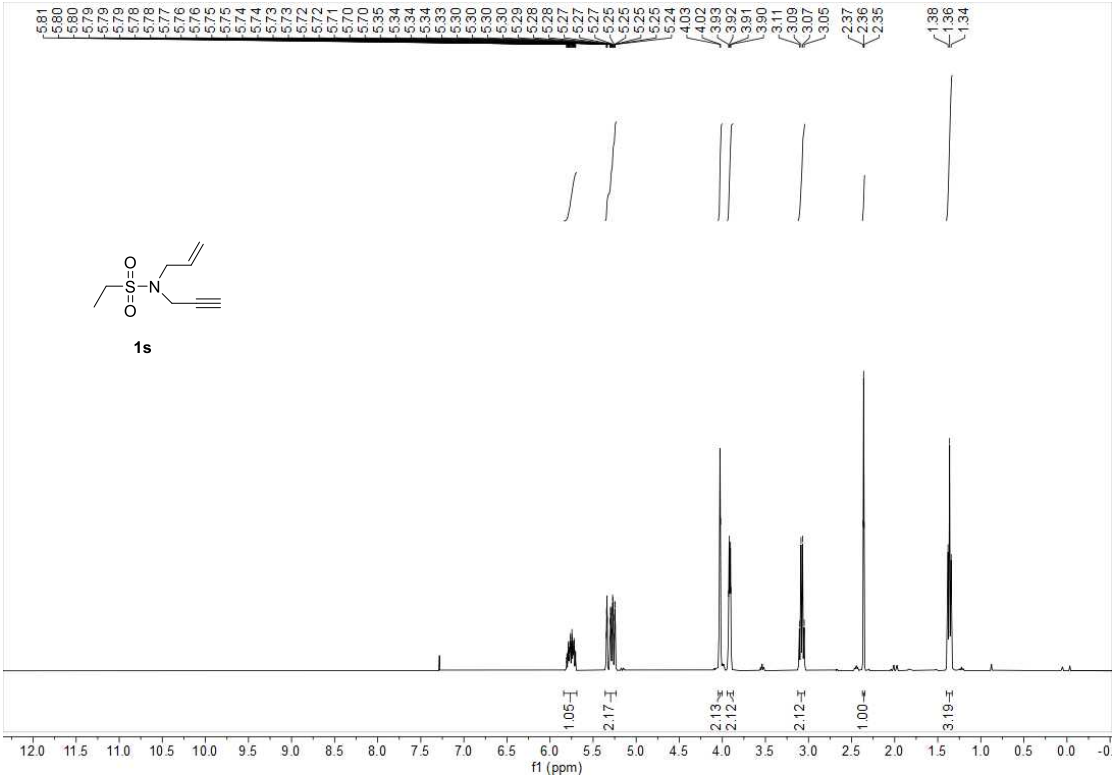


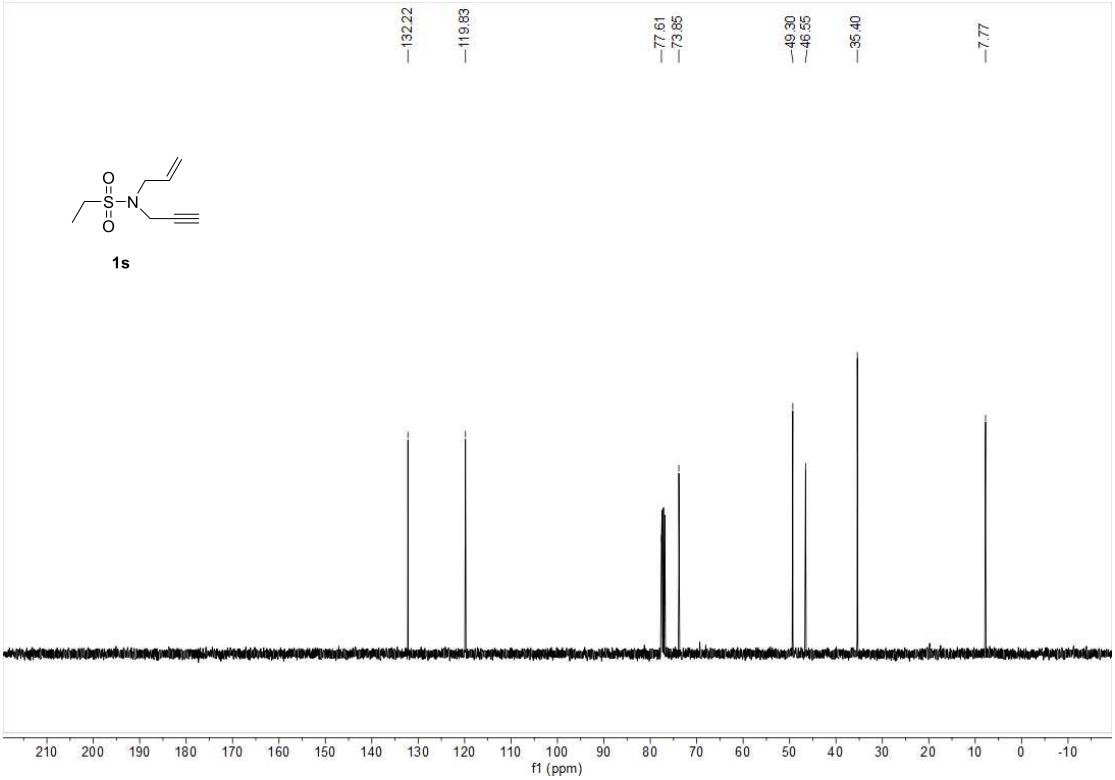
***N*-allyl-*N*-(prop-2-yn-1-yl)pyridine-3-sulfonamide (1q)**



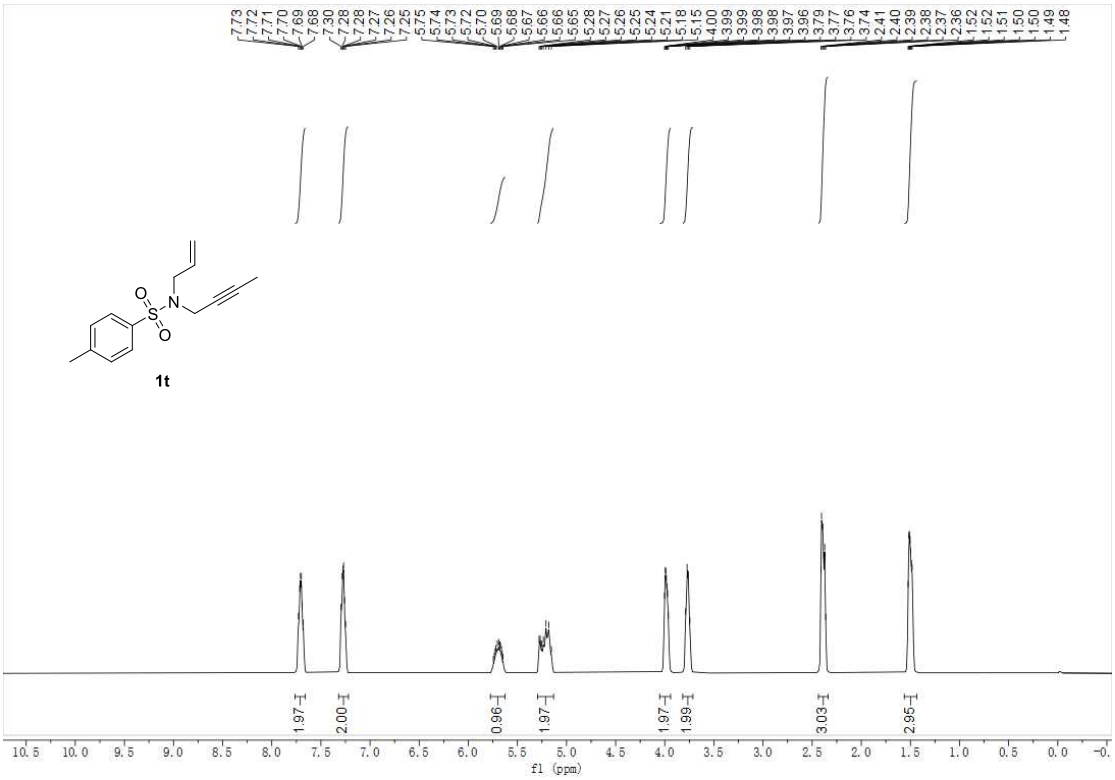


***N*-allyl-*N*-(prop-2-yn-1-yl)ethanesulfonamide (1s)**

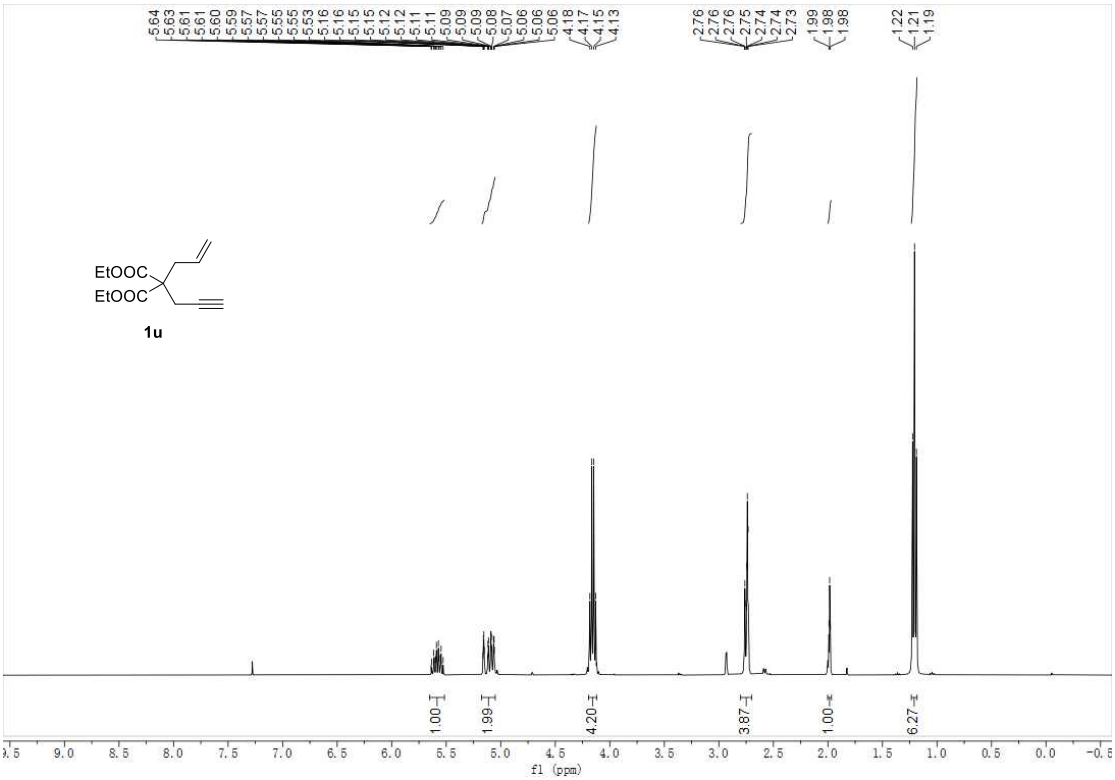


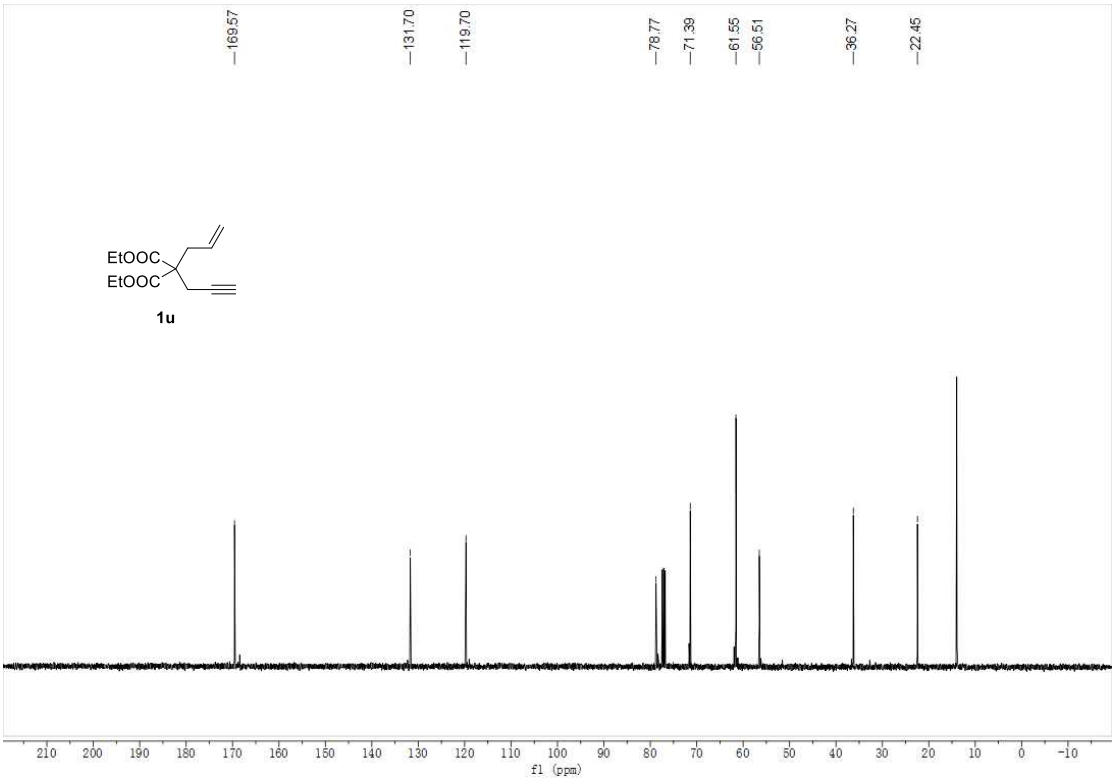


***N*-allyl-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (1t)**

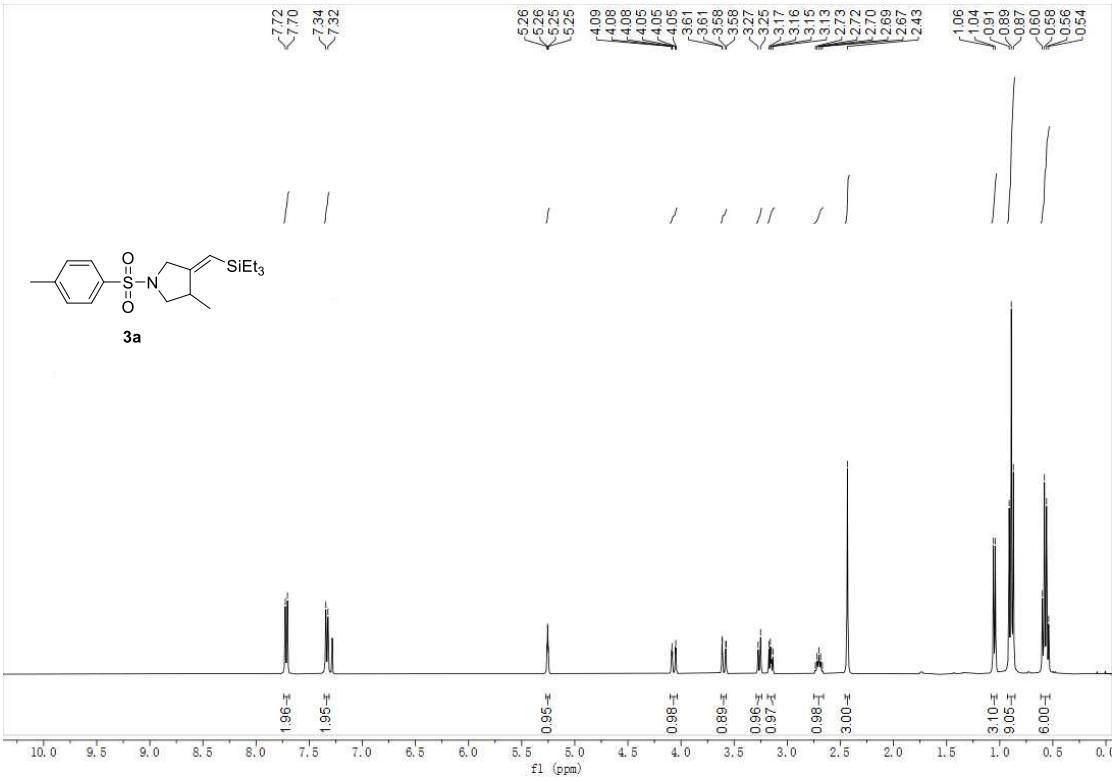


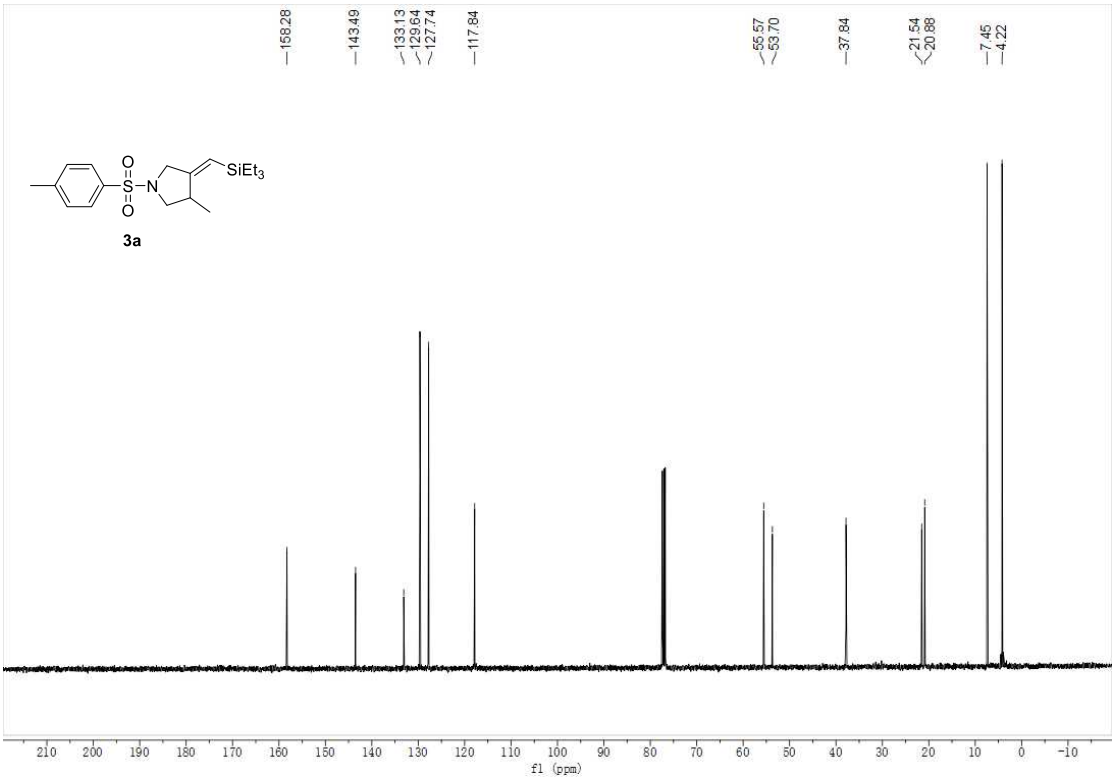
diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (1u)



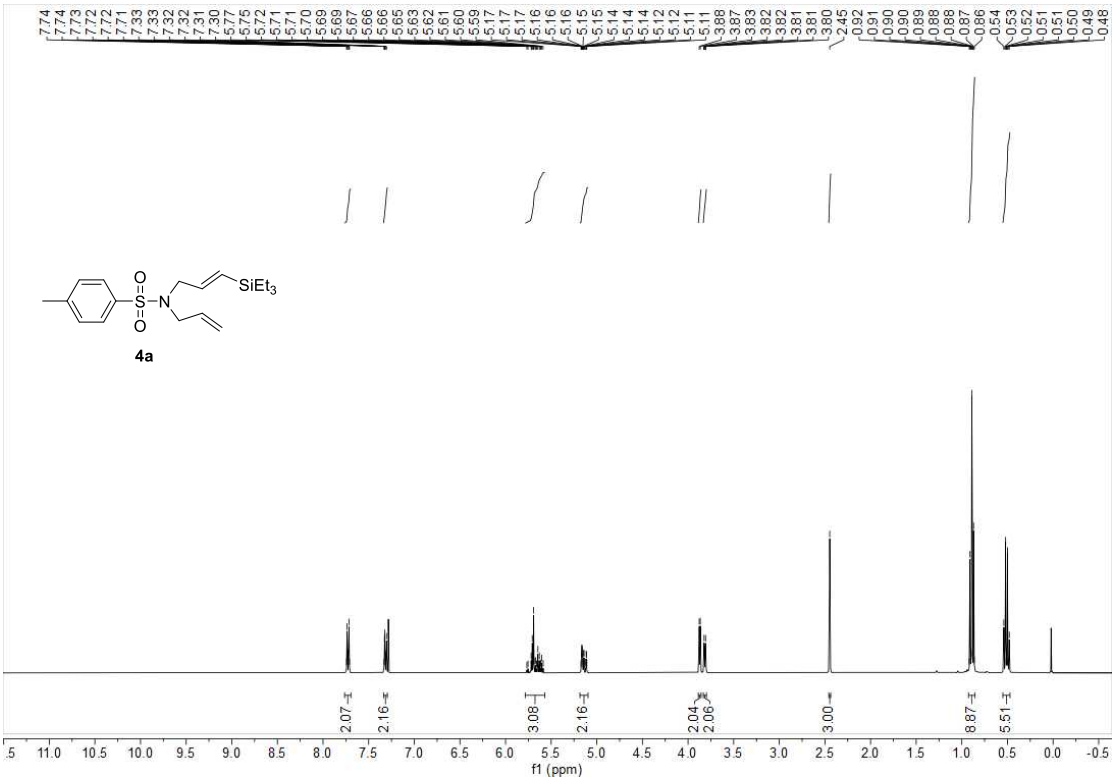


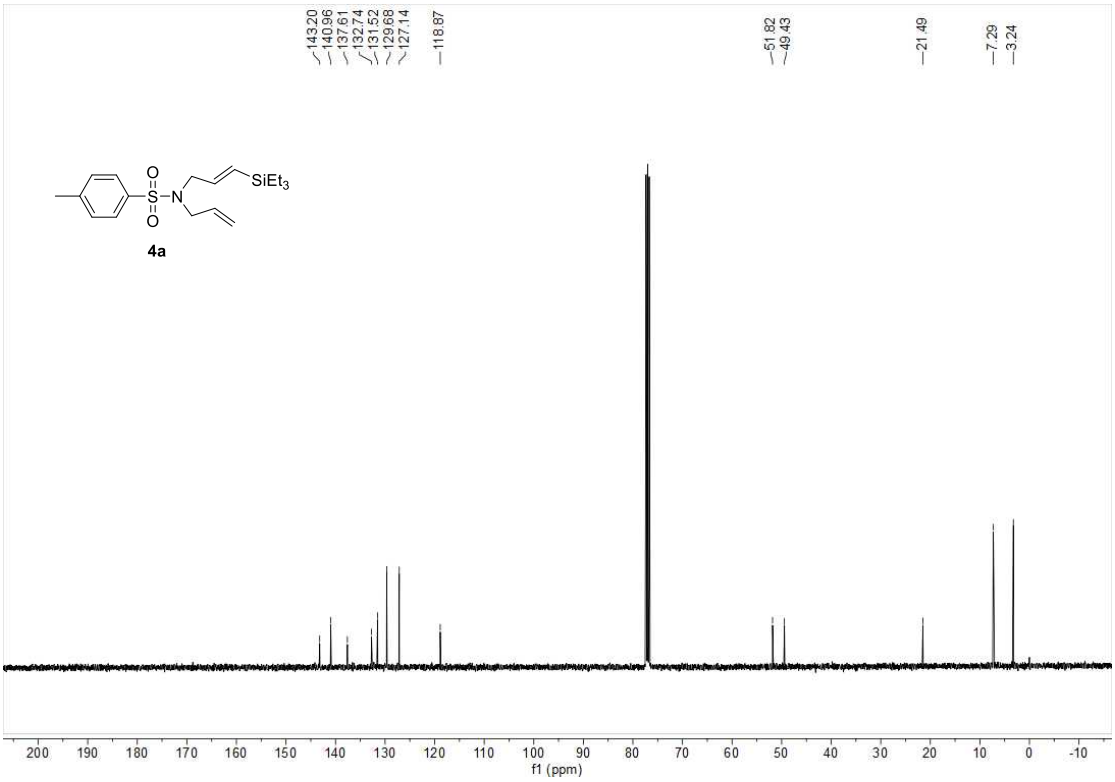
(*E*)-3-methyl-1-tosyl-4-((triethylsilyl)methylene)pyrrolidine (3a)



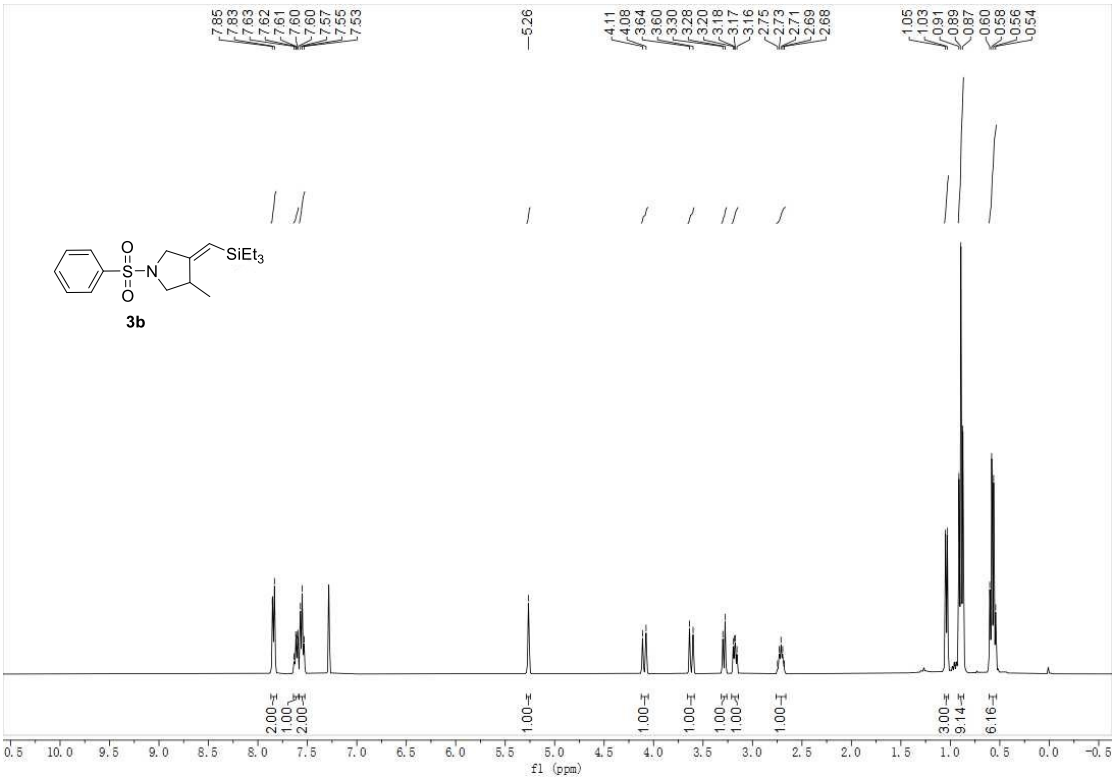


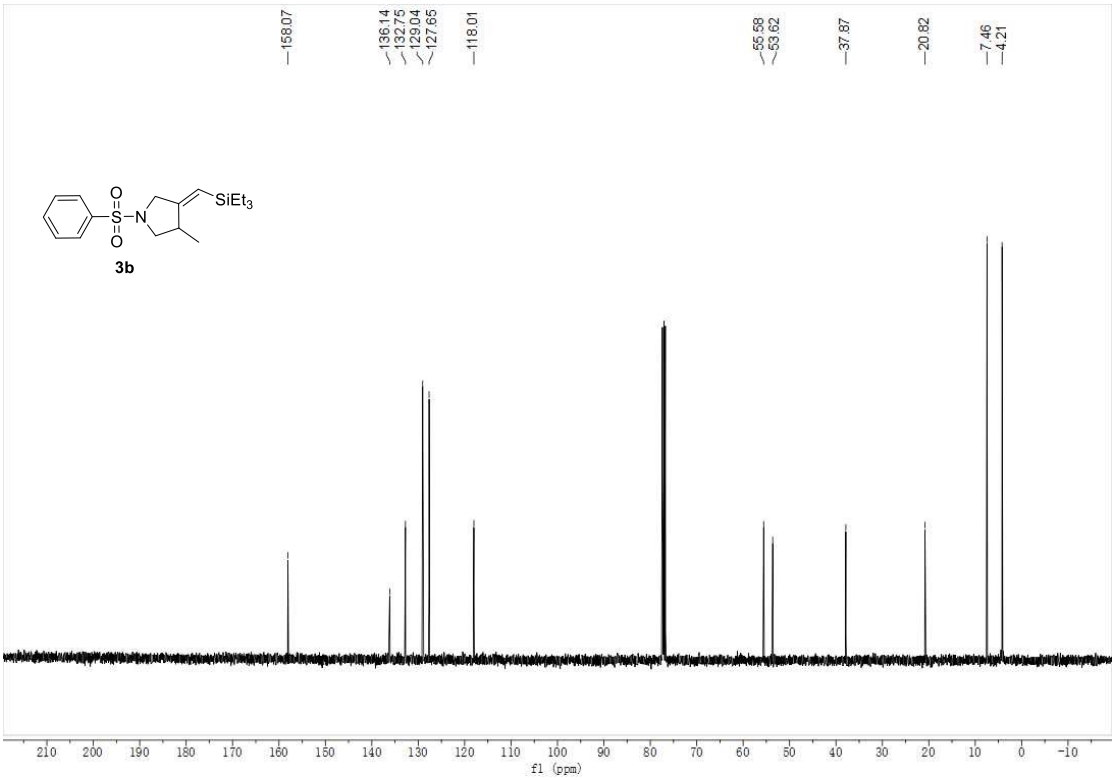
(*E*)-*N*-allyl-4-methyl-*N*-(3-(triethylsilyl)allyl)benzenesulfonamide (4a)



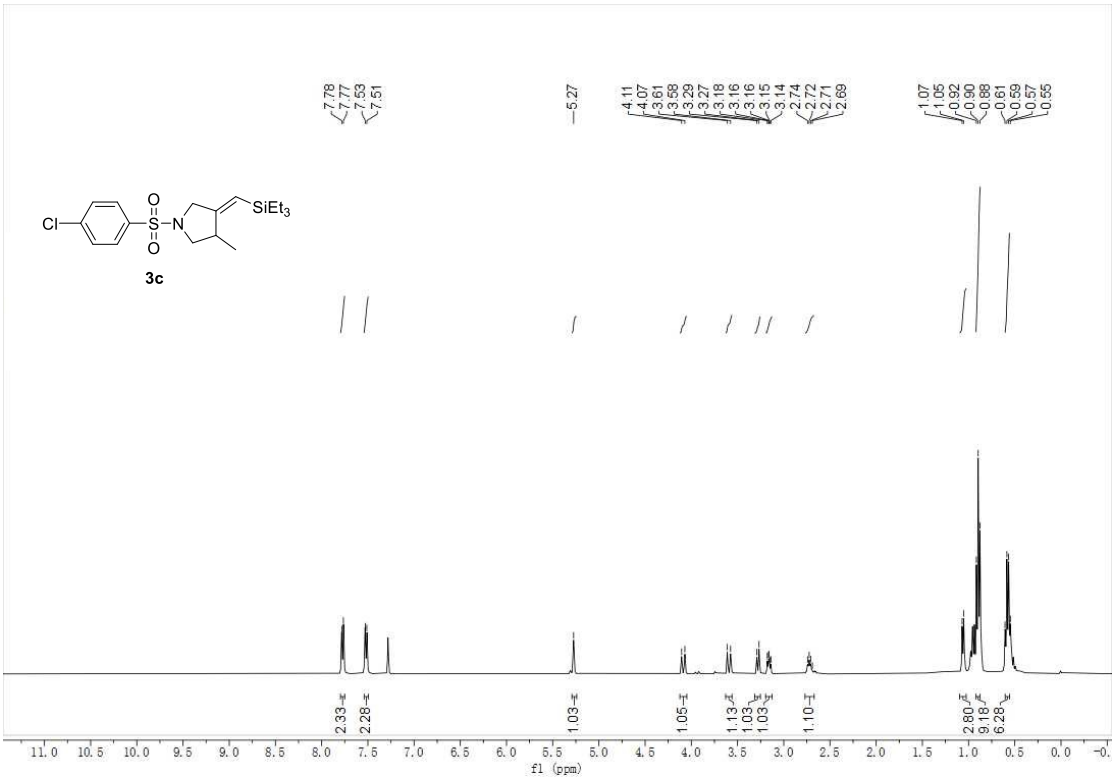


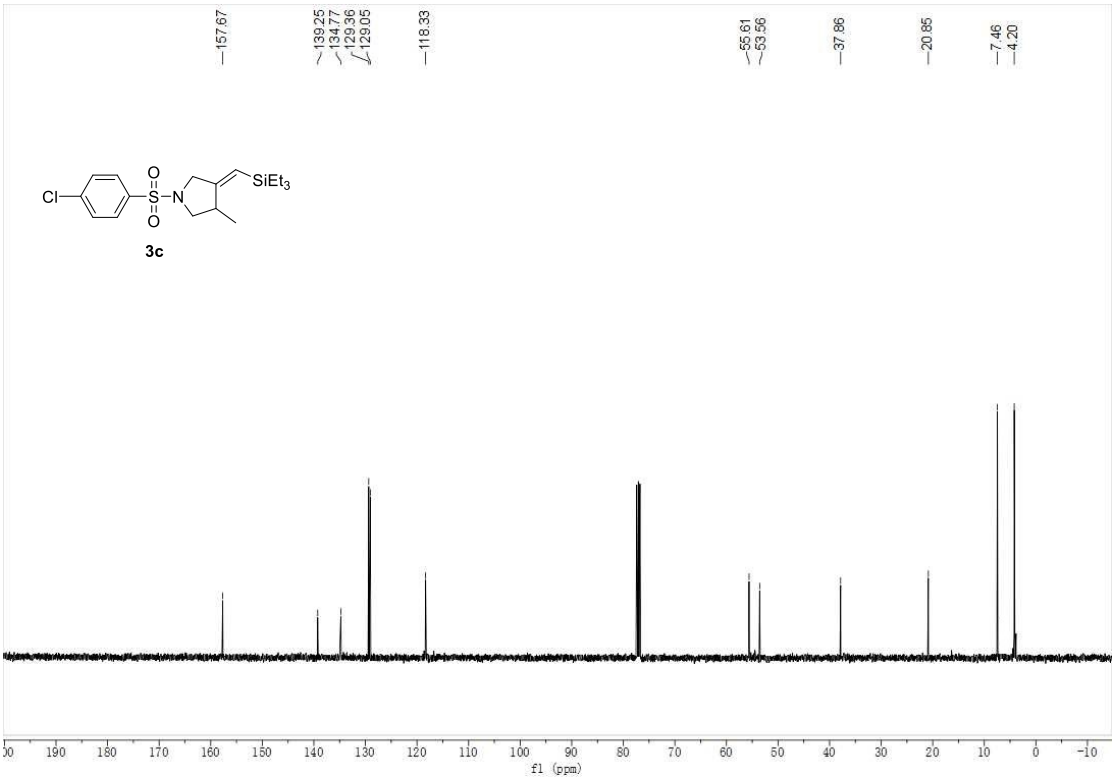
(*E*)-3-methyl-1-(phenylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3b)



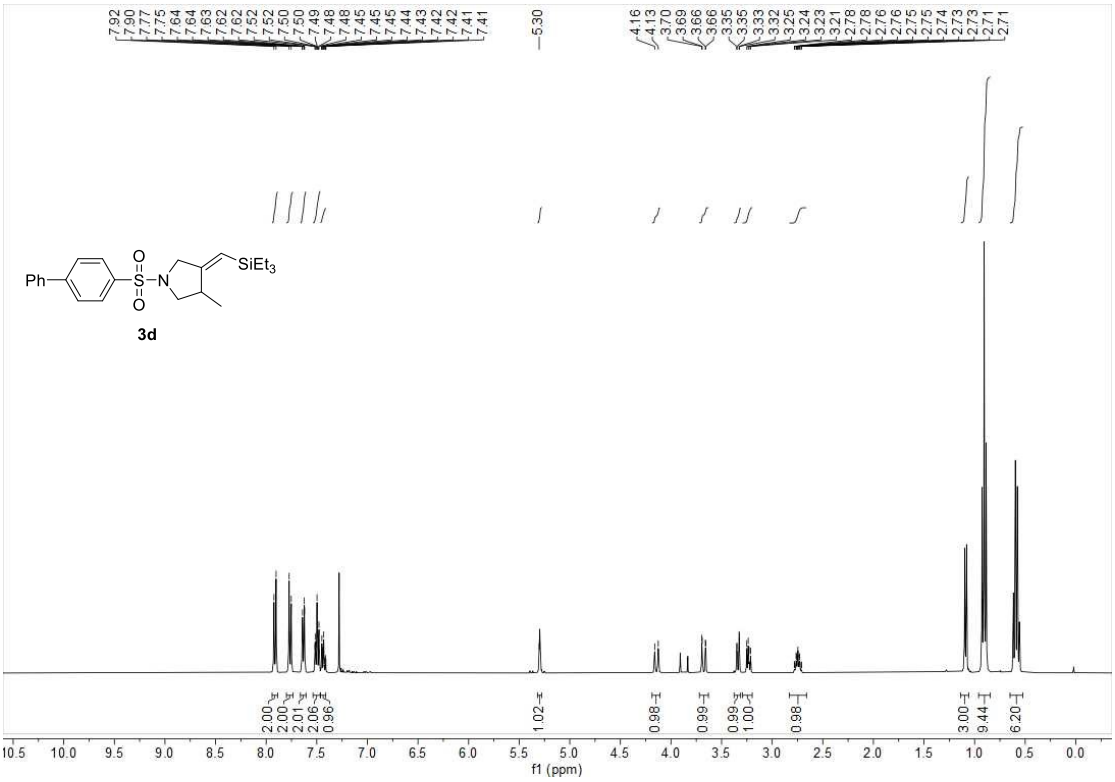


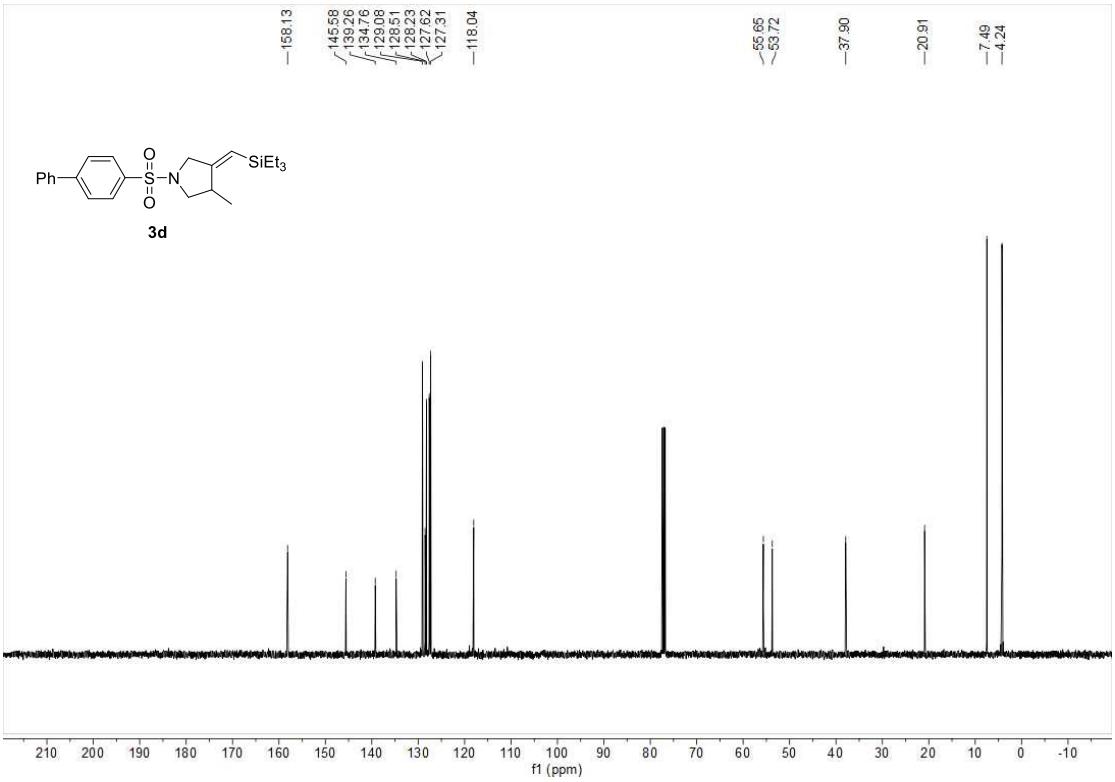
(*E*)-1-((4-chlorophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3c)



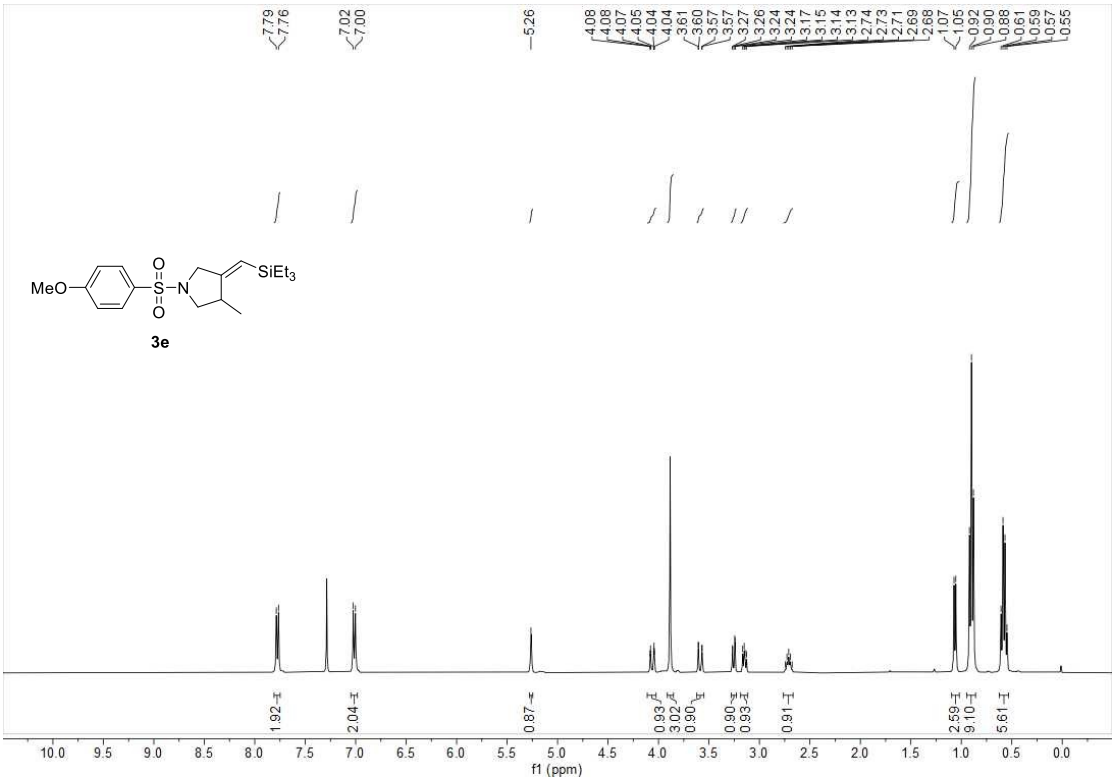


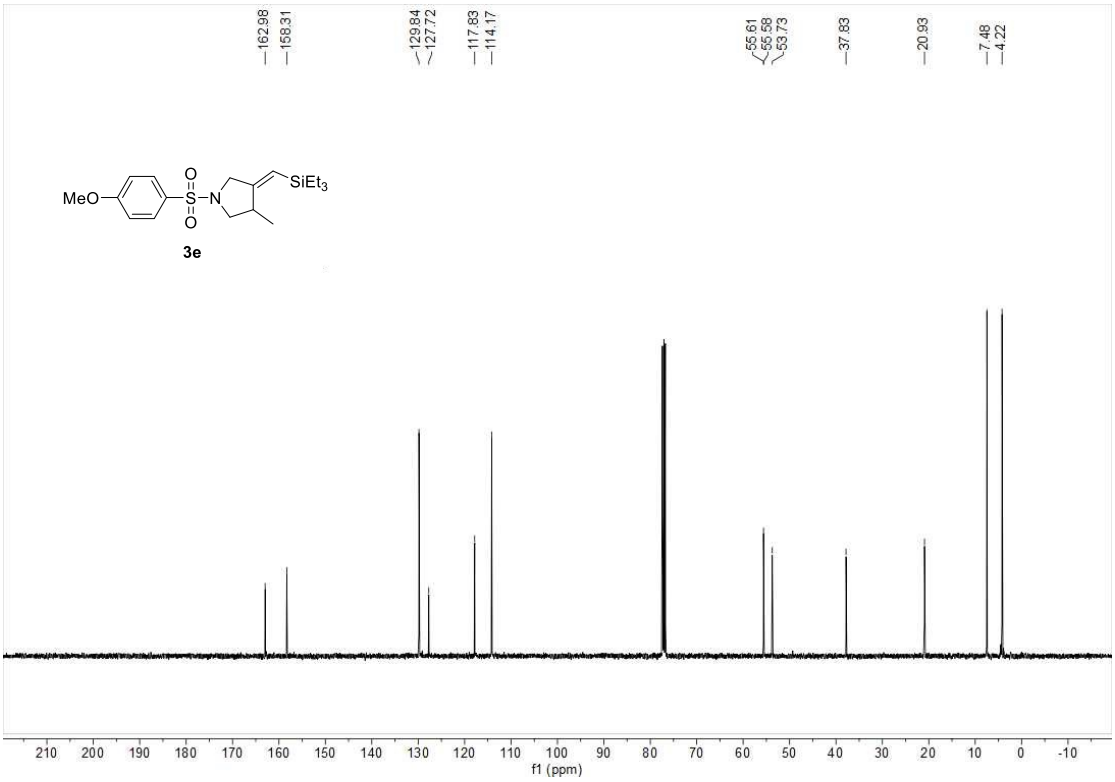
(*E*)-1-([1,1'-biphenyl]-4-ylsulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3d)



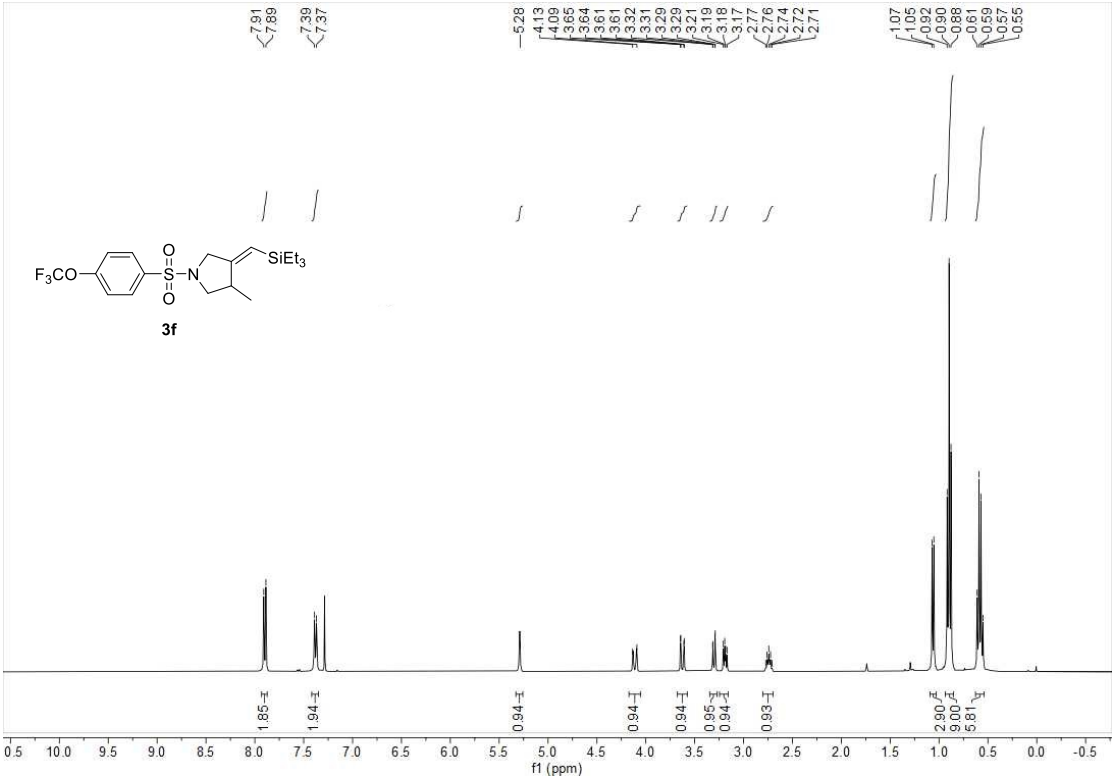


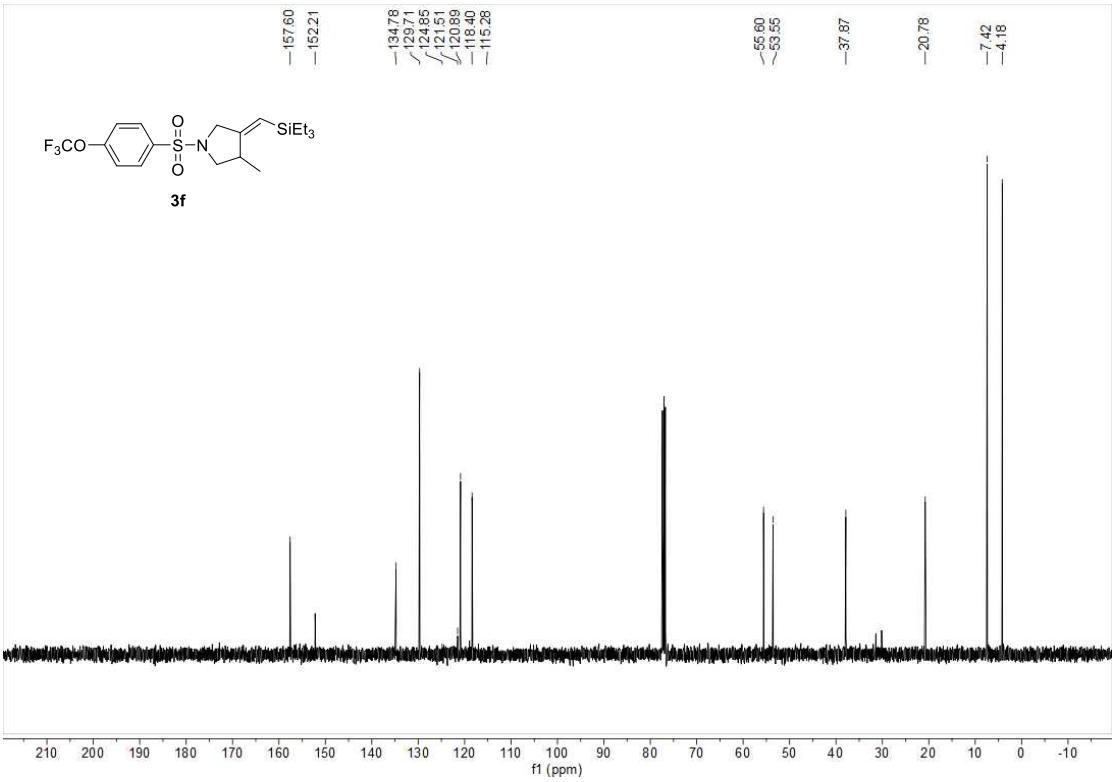
(*E*)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3e)

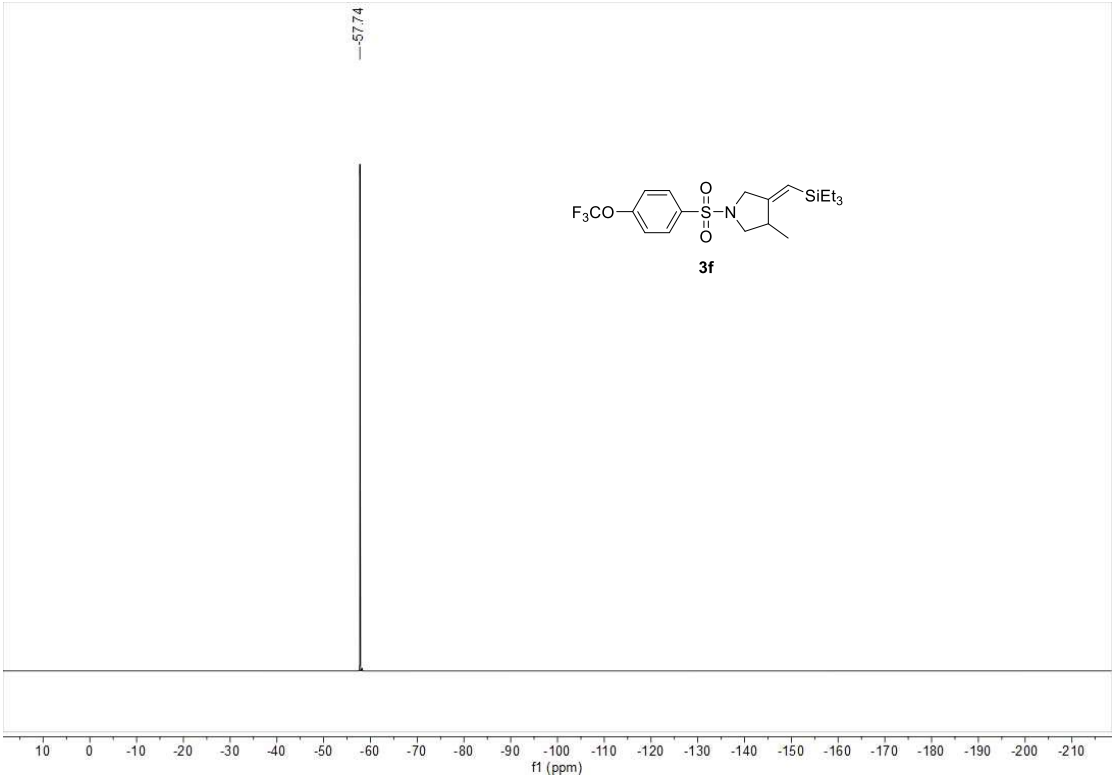




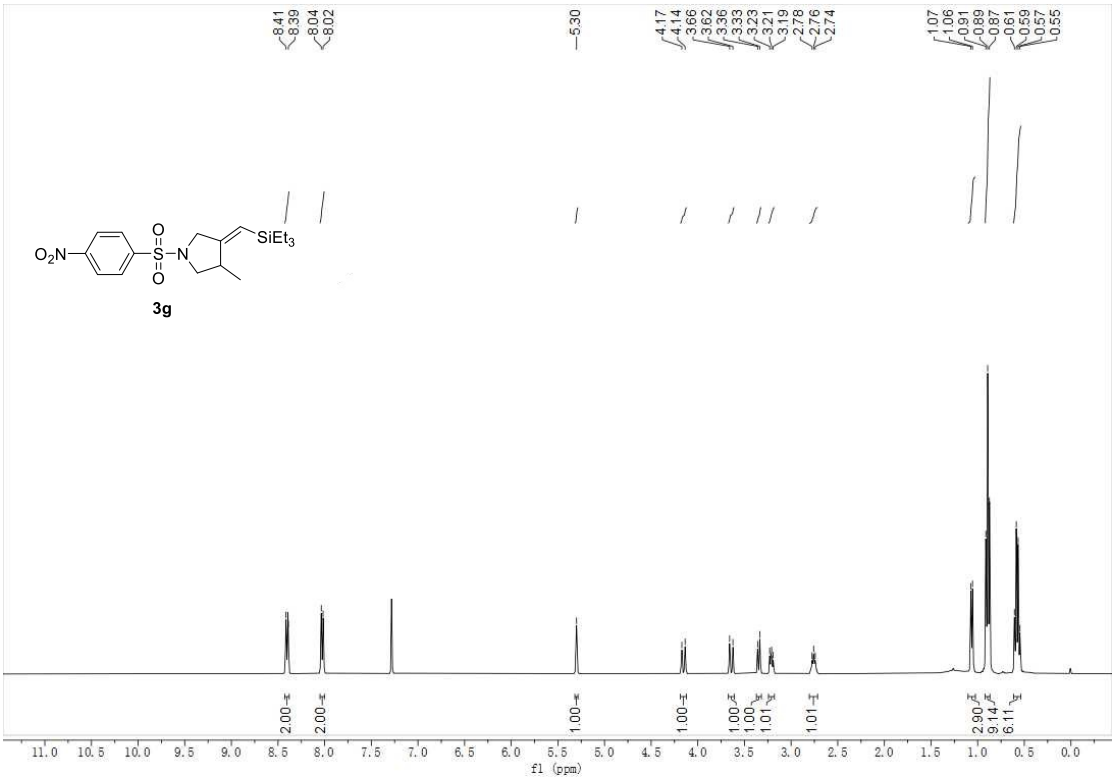
(*E*)-3-methyl-4-((triethylsilyl)methylene)-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (3f)

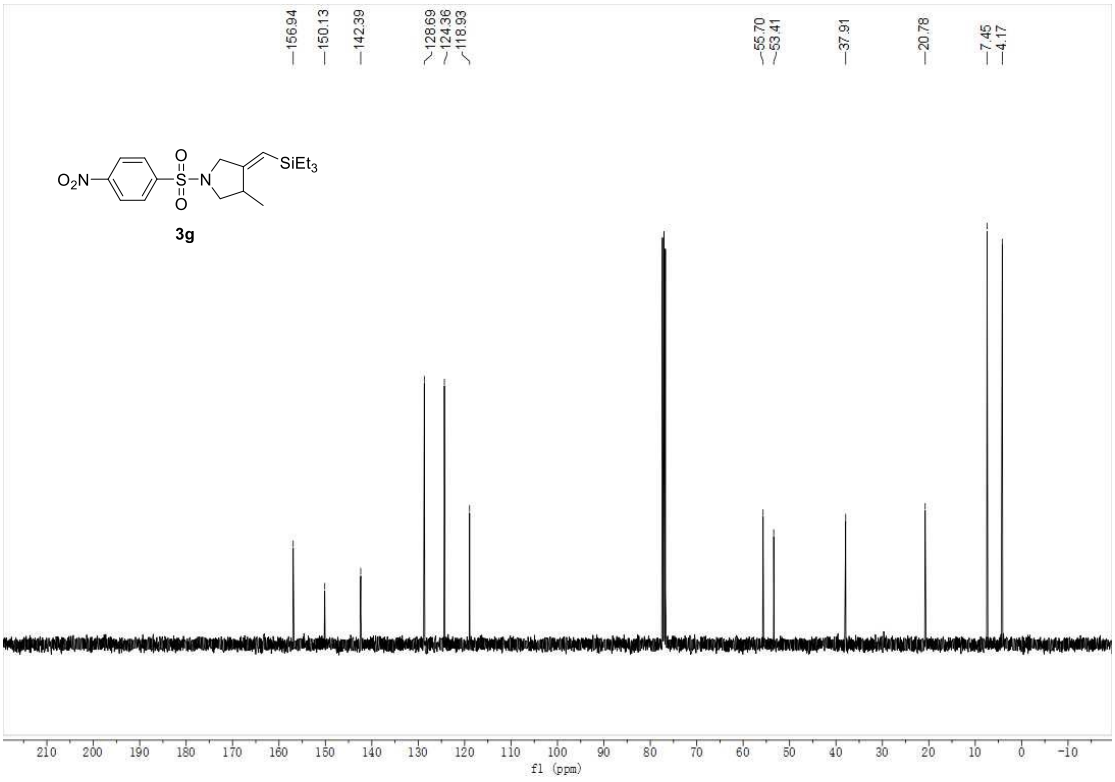



157.60
152.21
134.78
129.71
124.85
121.51
120.89
118.40
115.28
55.60
53.55
37.87
20.78
7.42
4.18
F3CO
SiEt3
3f
f1 (ppm)

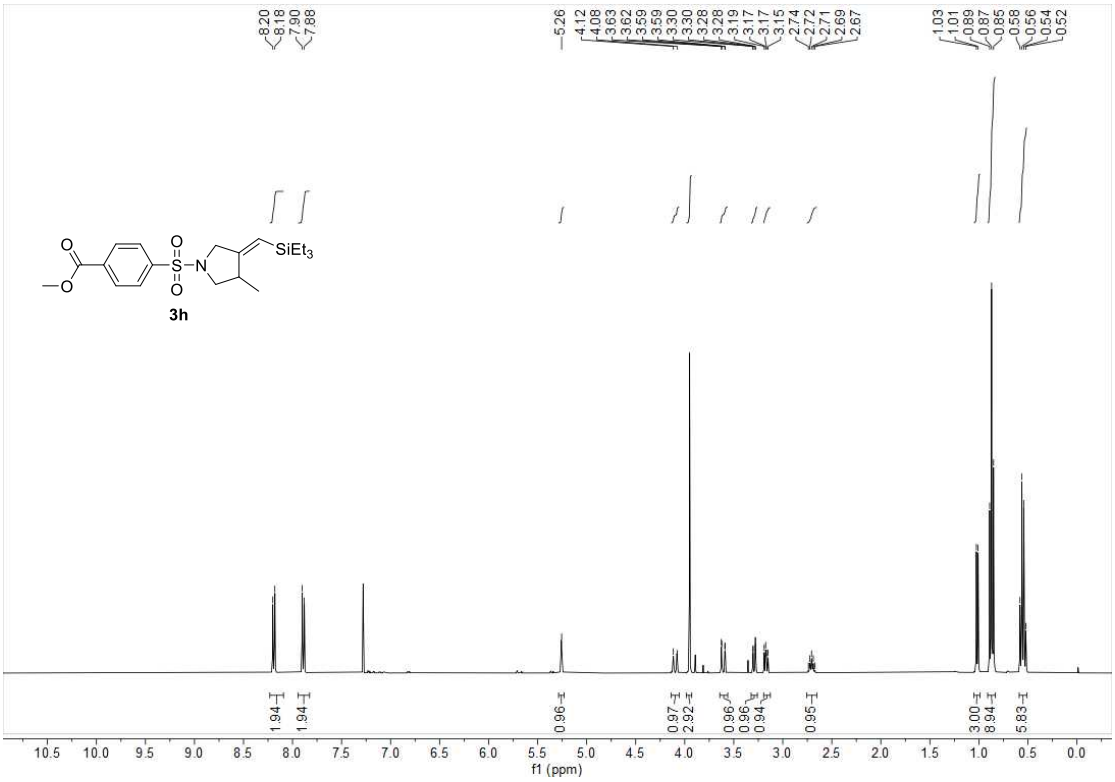

-57.74
F3CO
SiEt3
3f
f1 (ppm)

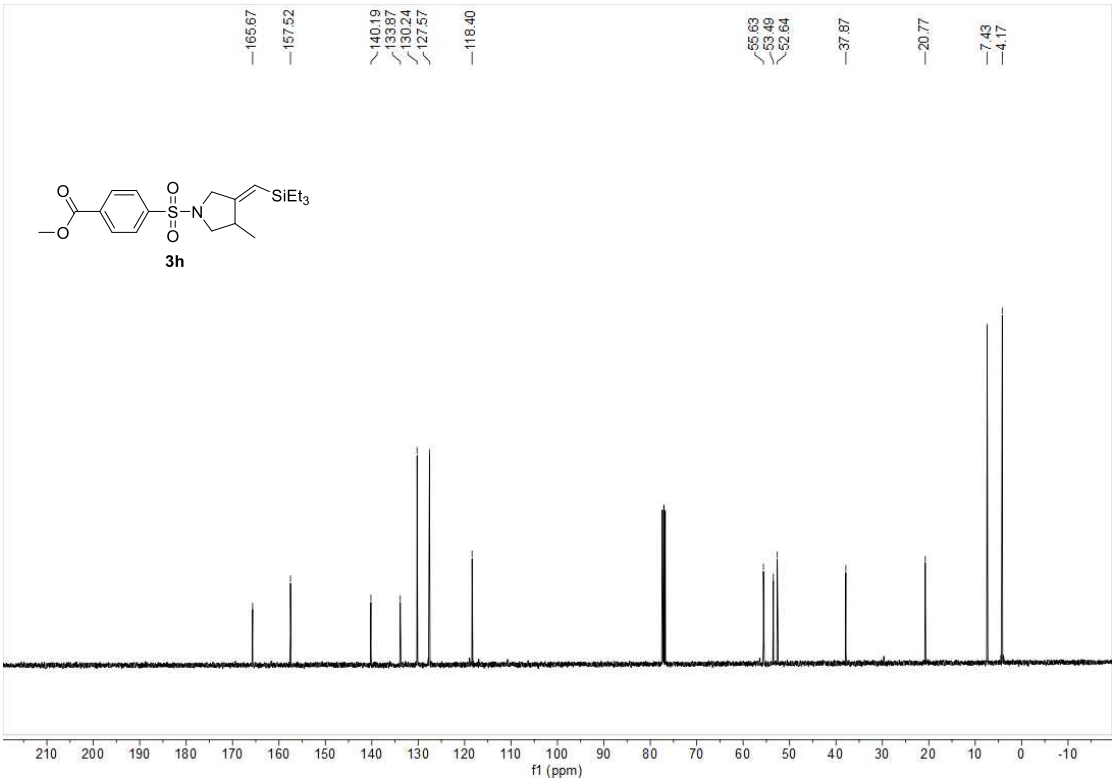
(*E*)-3-methyl-1-((4-nitrophenyl)sulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3g)



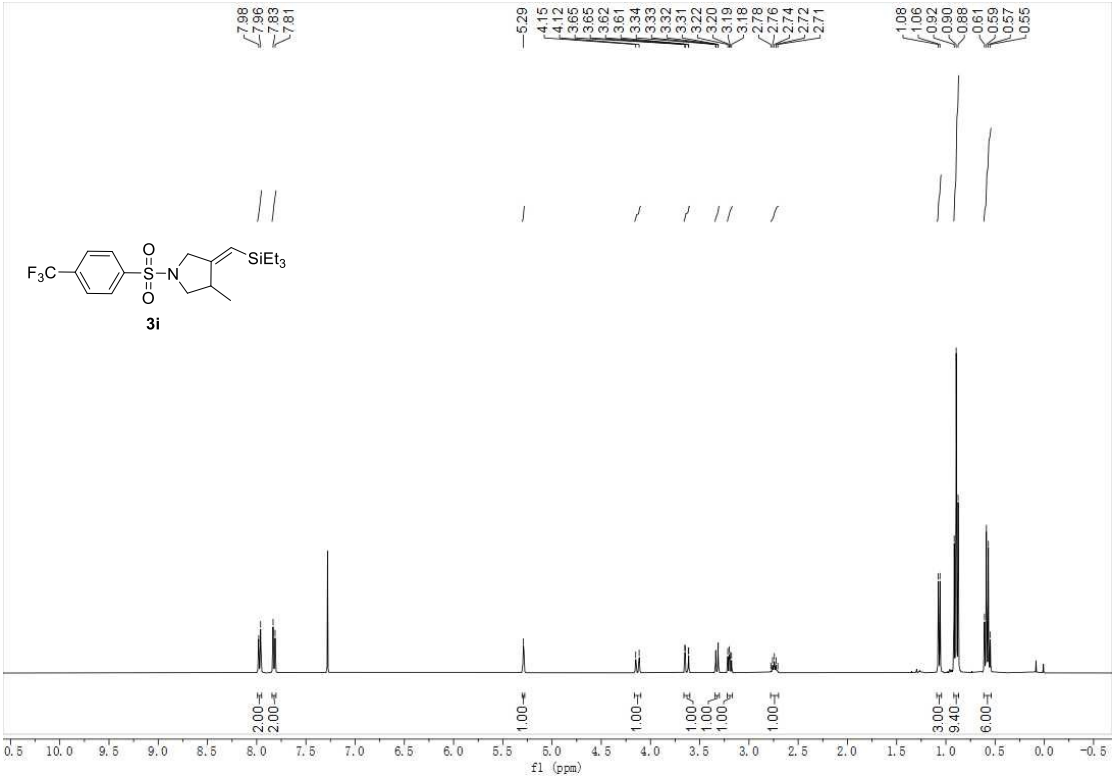


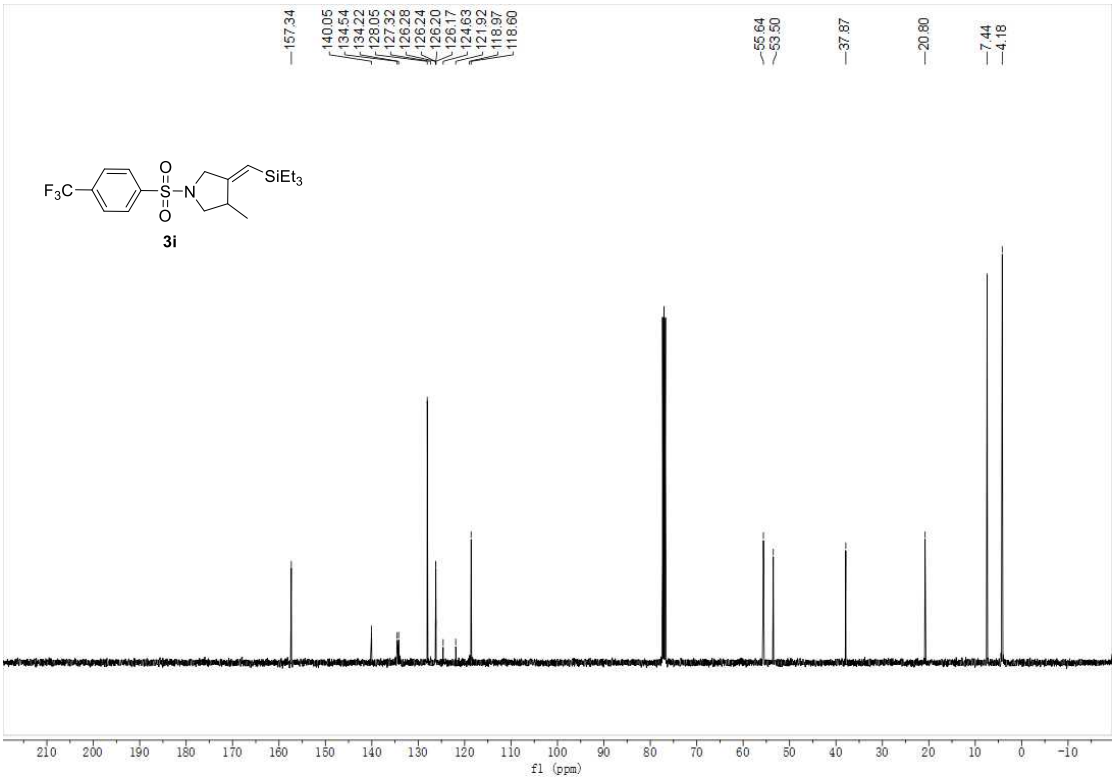
methyl(*E*)-4-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)benzoate (3h)

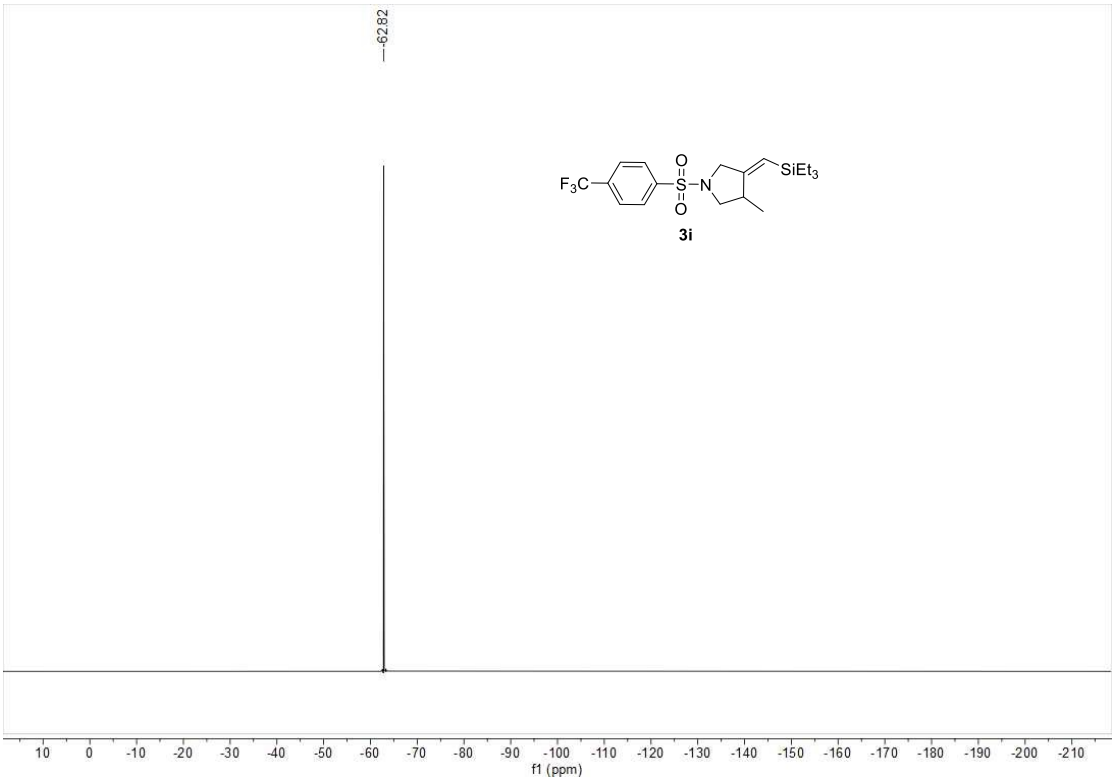




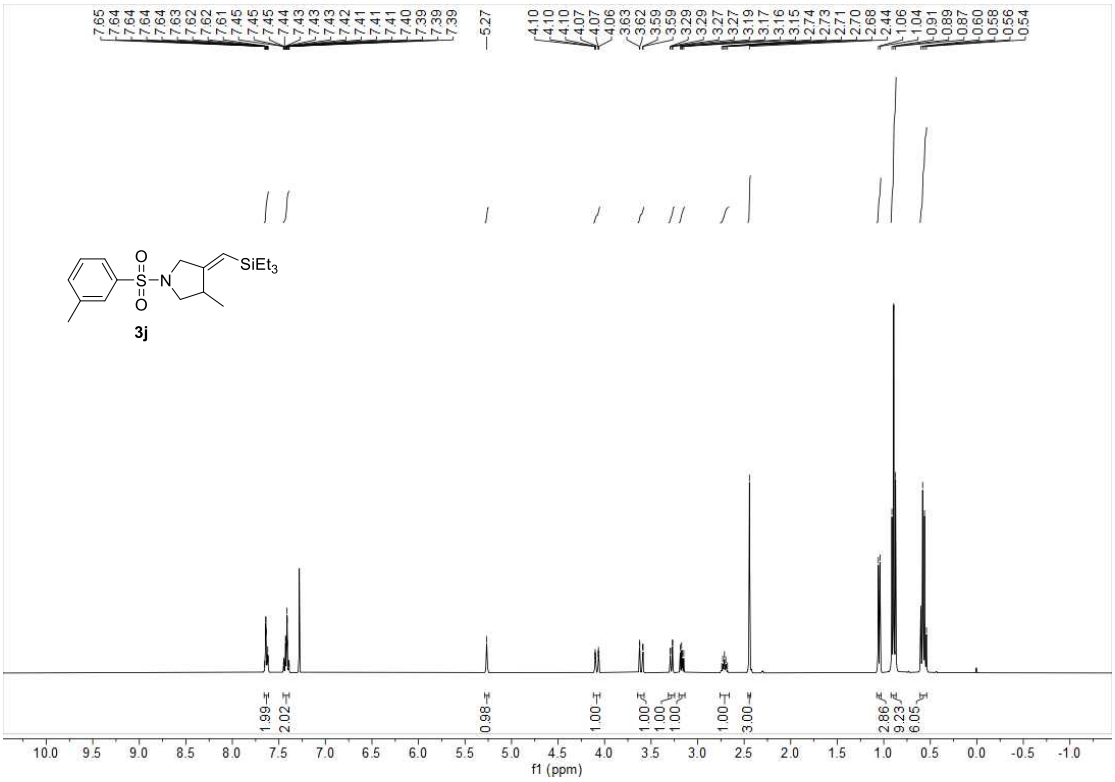
(*E*)-3-methyl-4-((triethylsilyl)methylene)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3i)

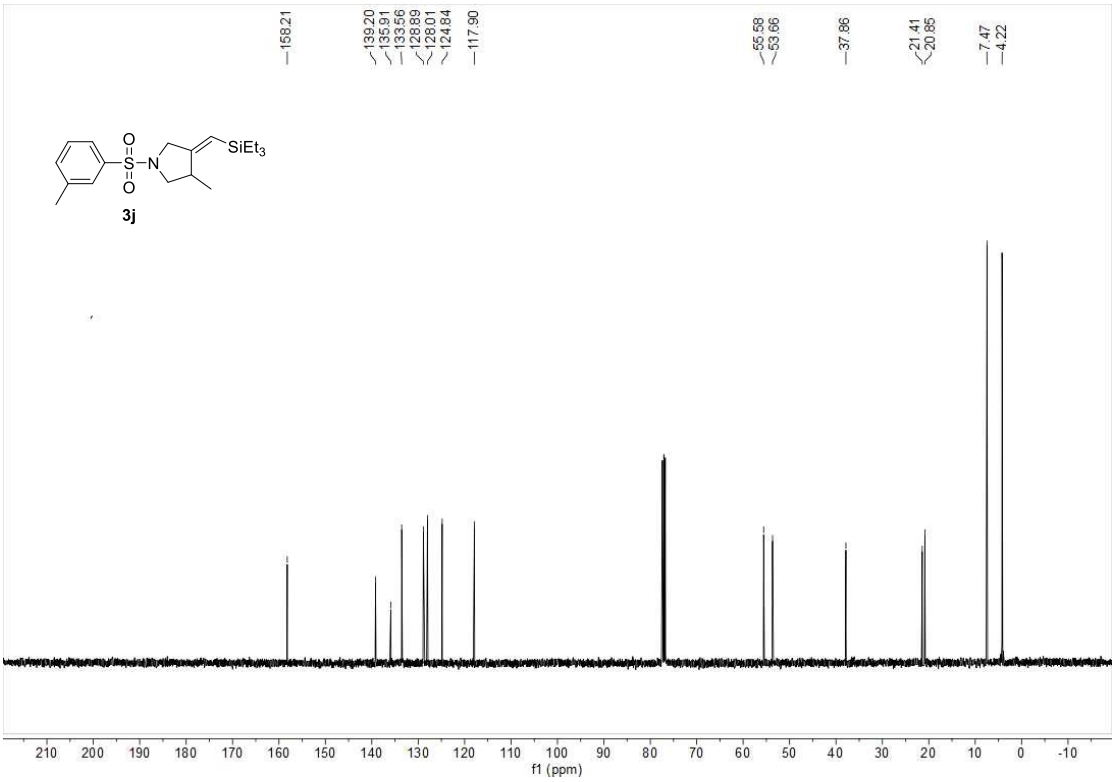




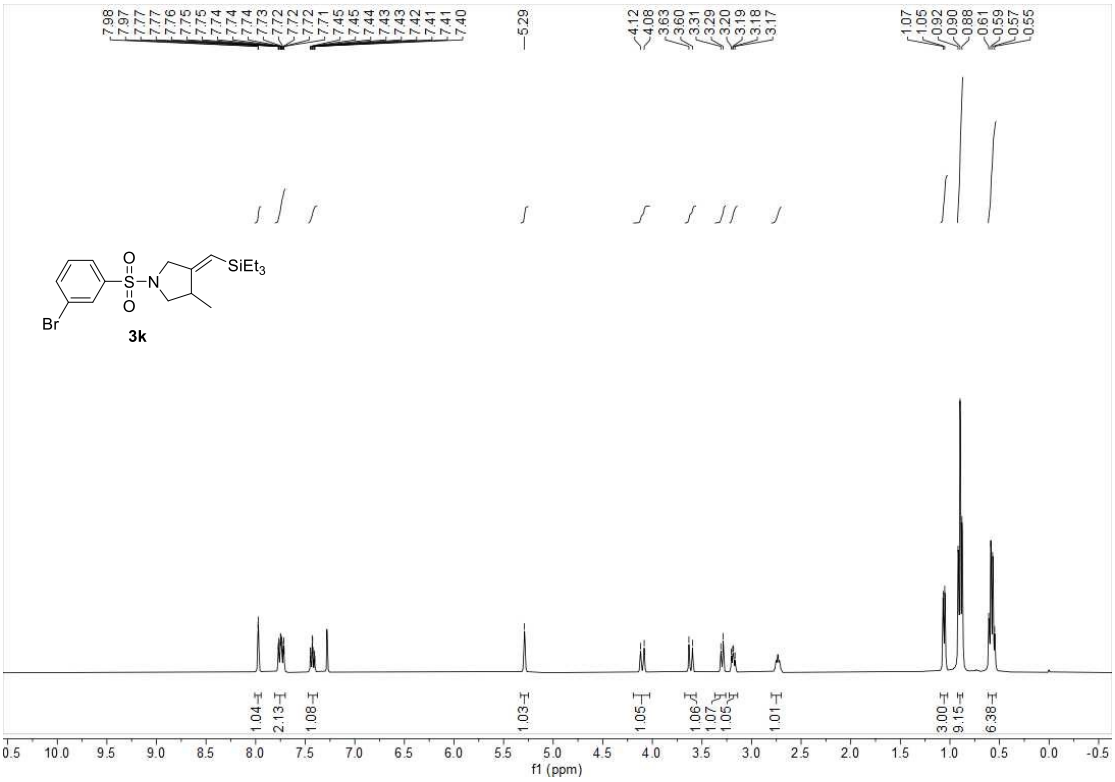


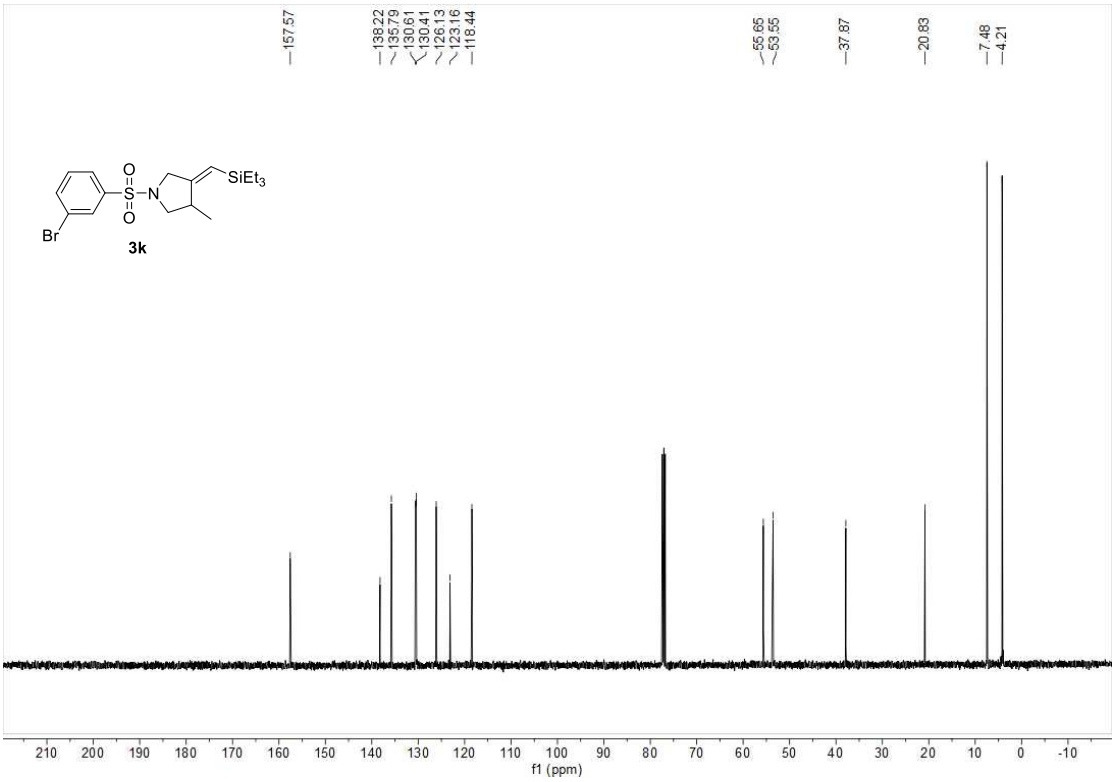
(*E*)-3-methyl-1-(m-tolylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3j)



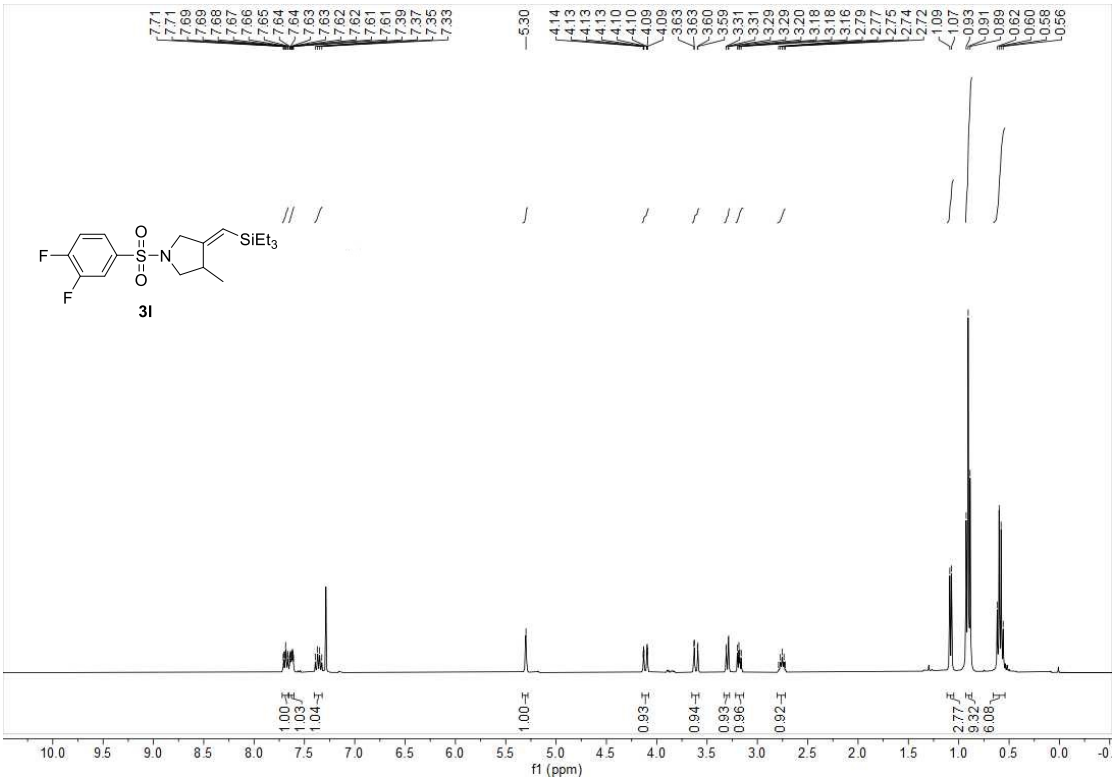


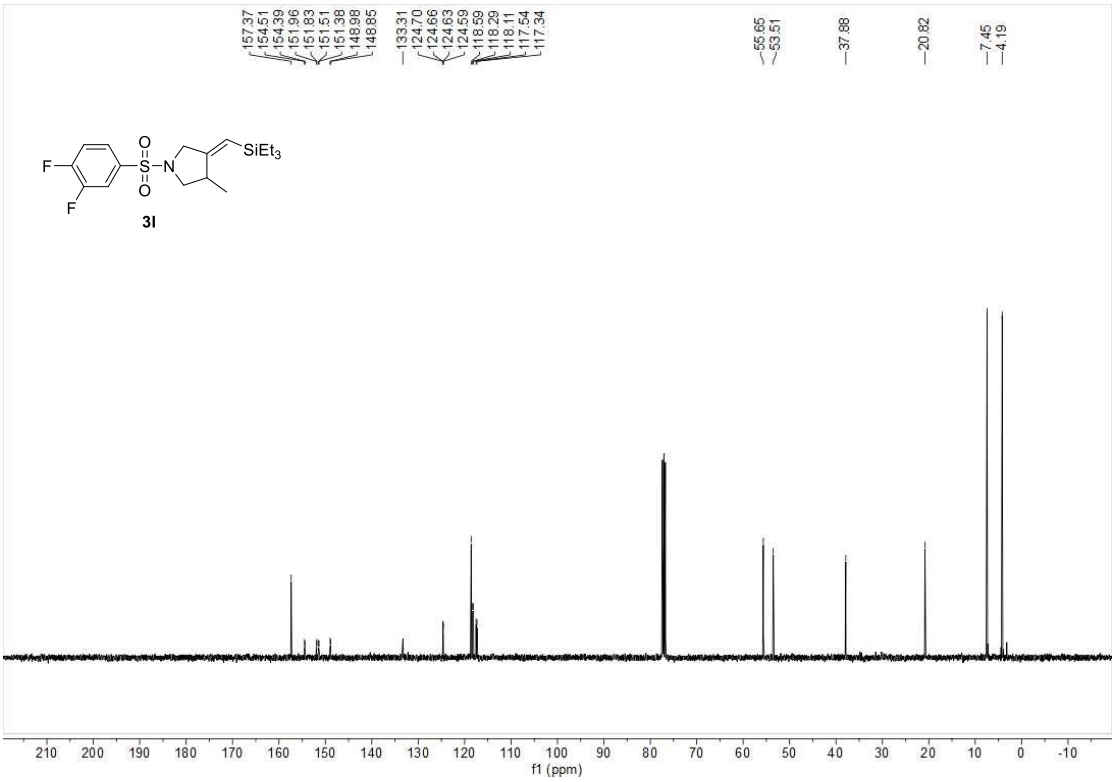
(*E*)-1-((3-bromophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3k)

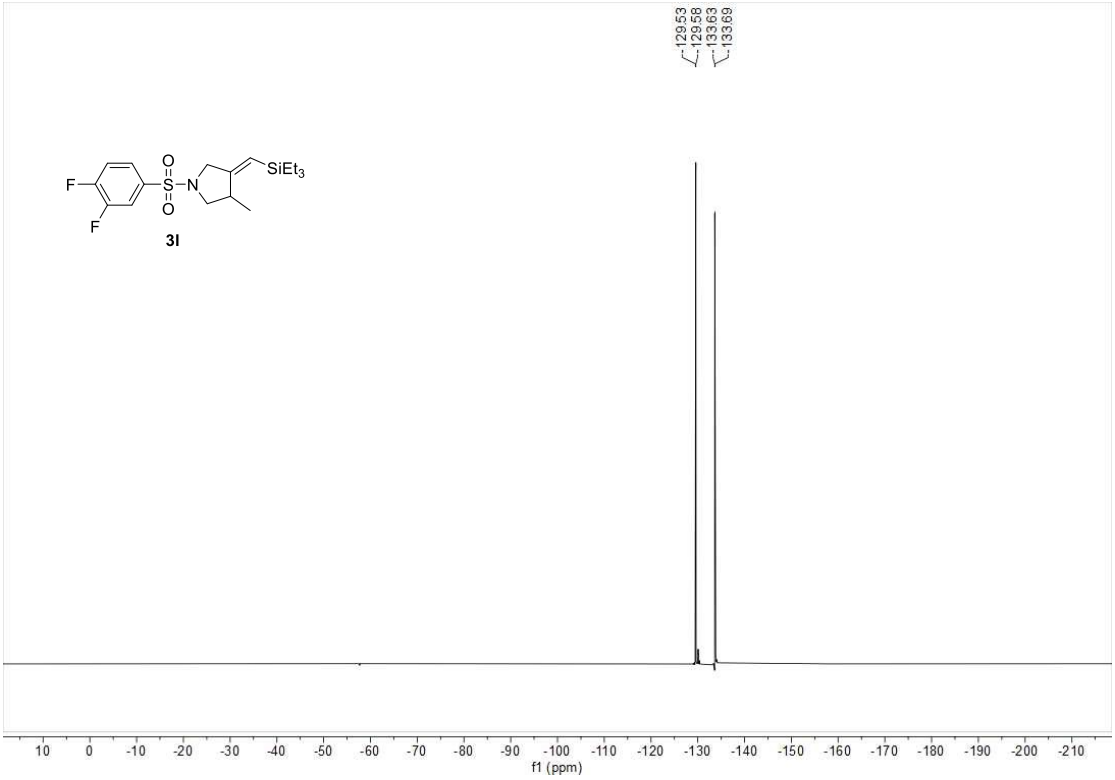




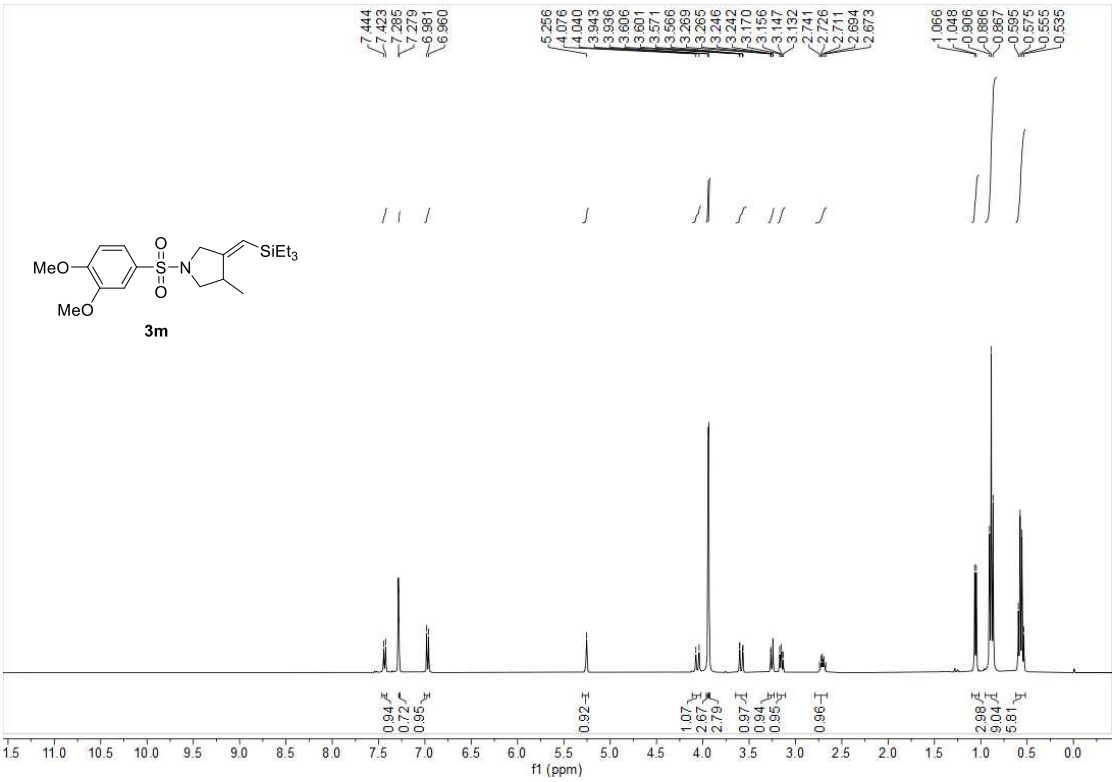
(*E*)-1-((3,4-difluorophenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)-3l3-pyrrolidine (3l)

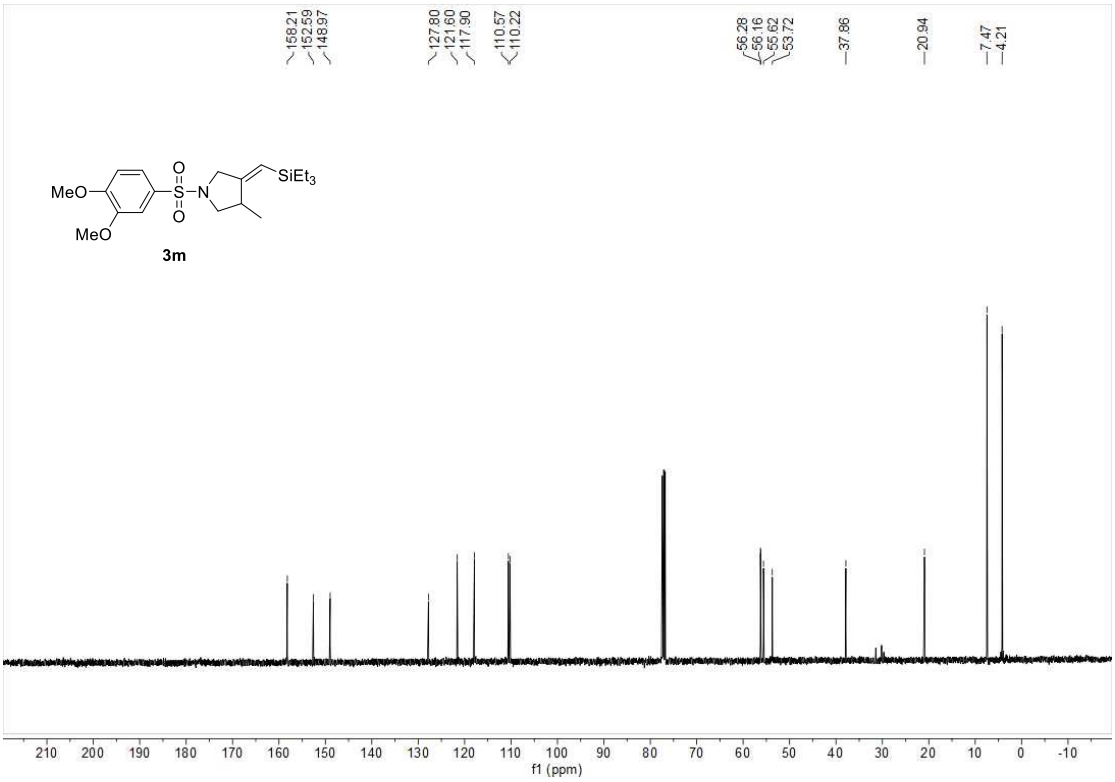



157.37
154.51
154.39
151.96
151.83
151.51
151.38
148.98
148.85
133.31
124.70
124.66
124.63
124.59
118.59
118.29
118.11
117.54
117.34
55.65
53.51
37.88
20.82
7.45
4.19
SiEt3
F
F
O
S
N
O
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

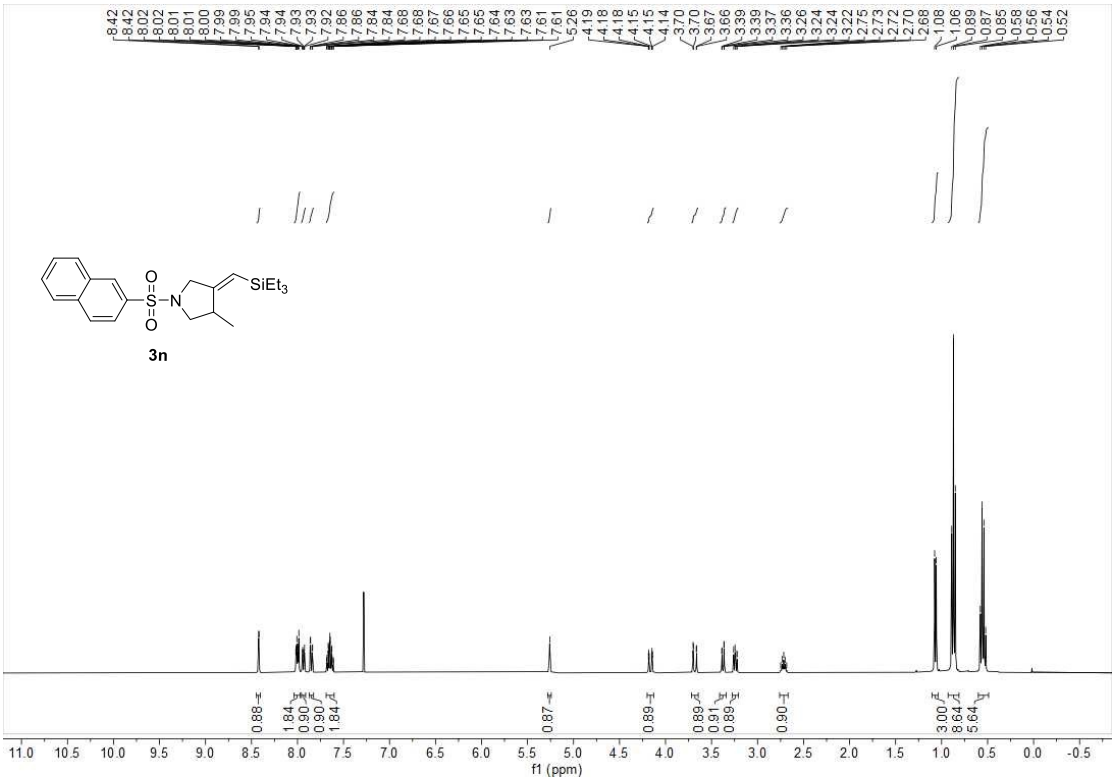

129.53
129.58
133.63
133.69
SiEt3
F
F
O
S
N
O
3l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

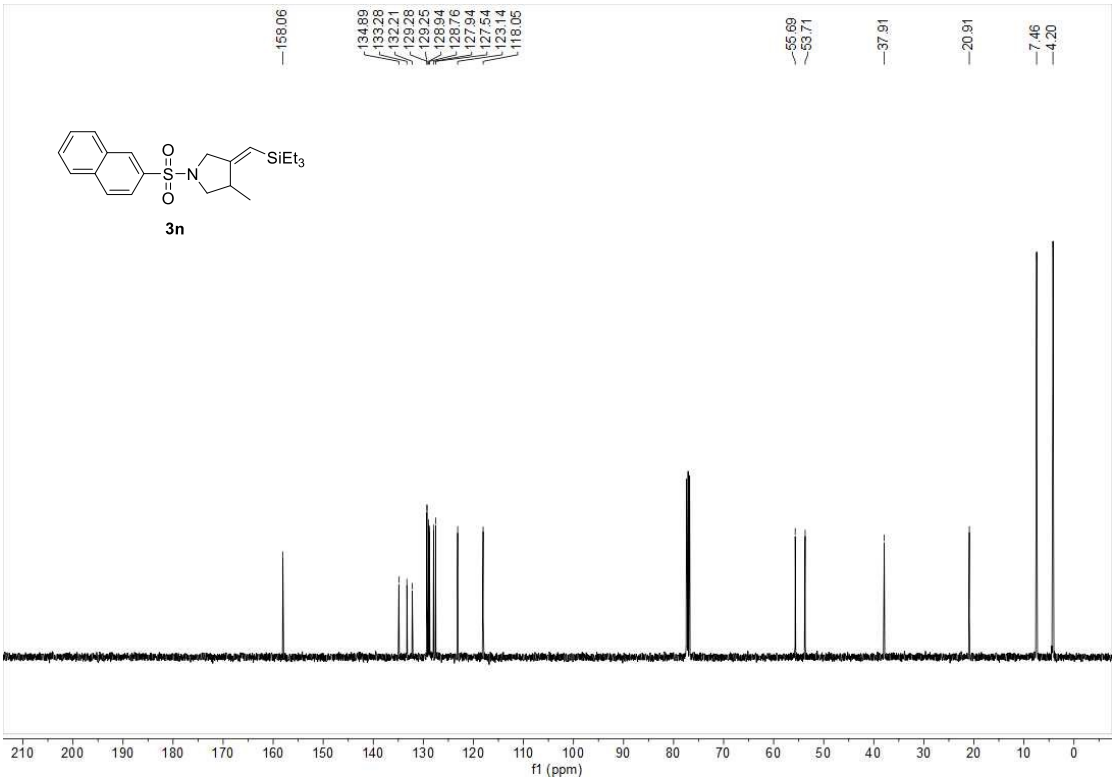
(*E*)-1-((3,4-dimethoxyphenyl)sulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3m)



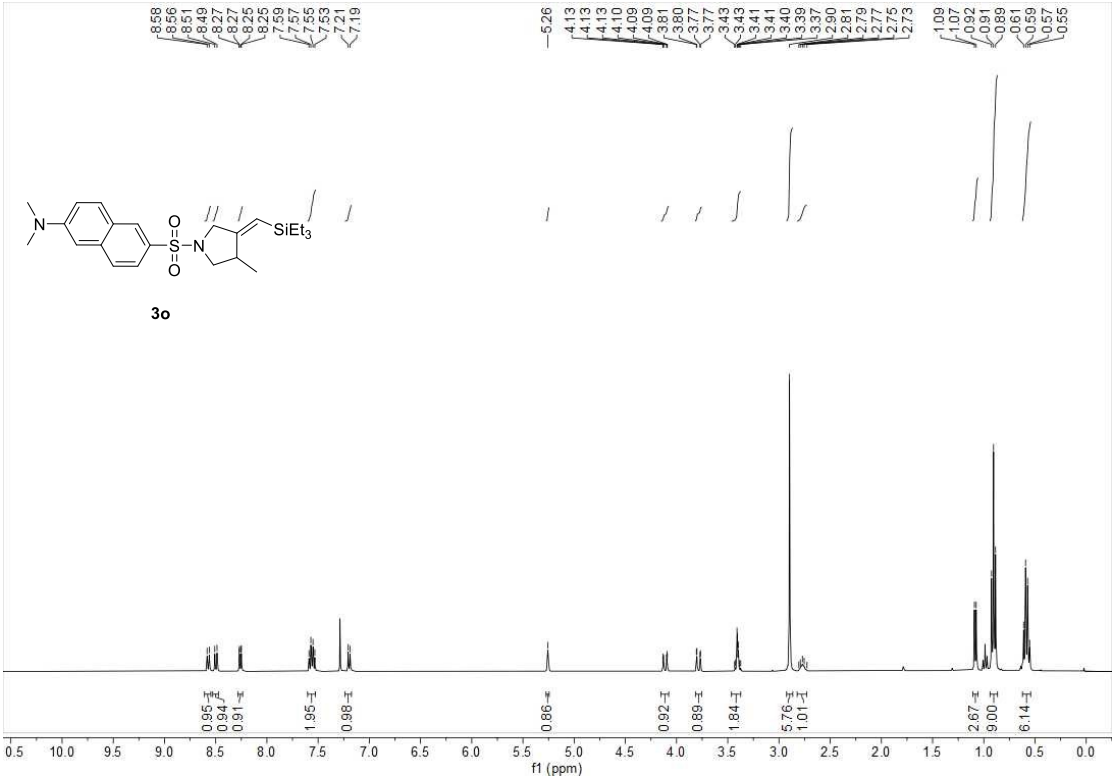


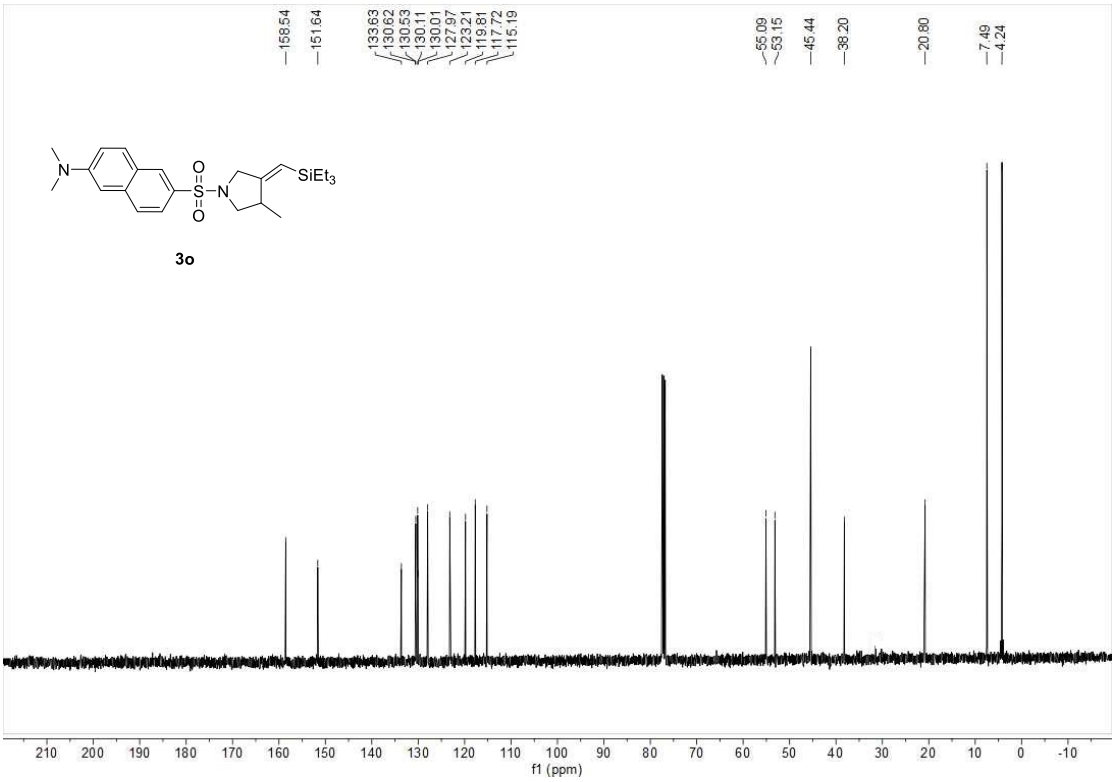
(*E*)-3-methyl-1-(naphthalen-2-ylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3n)



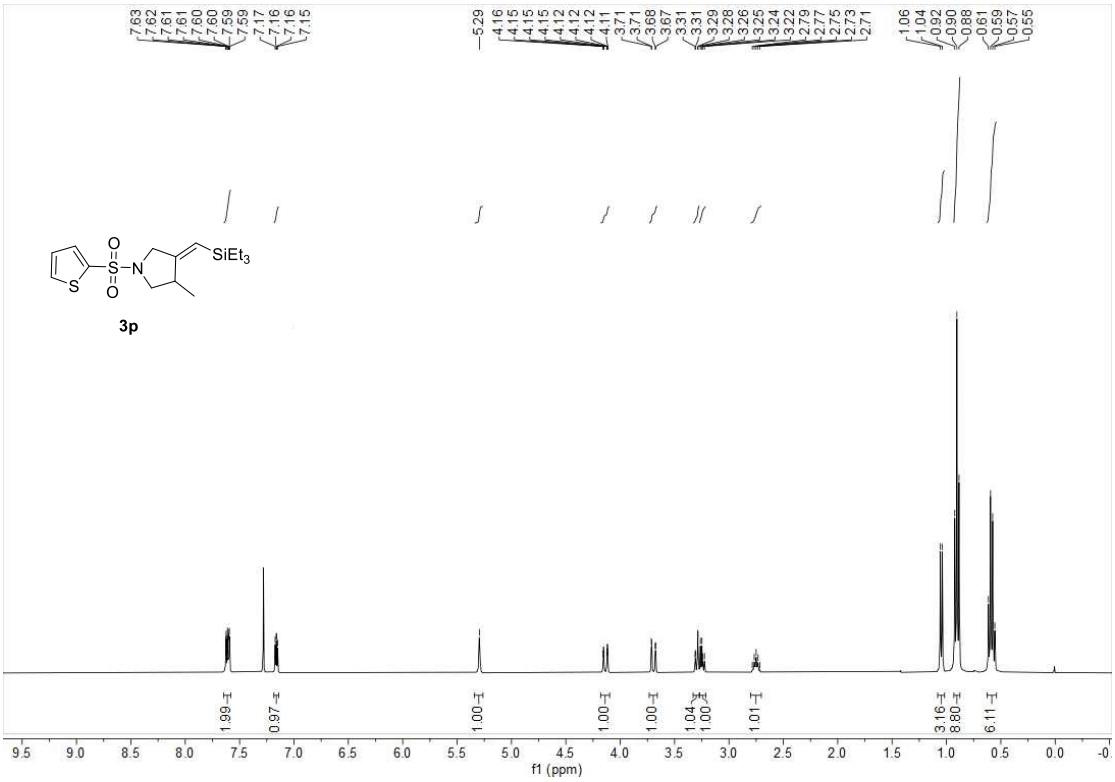


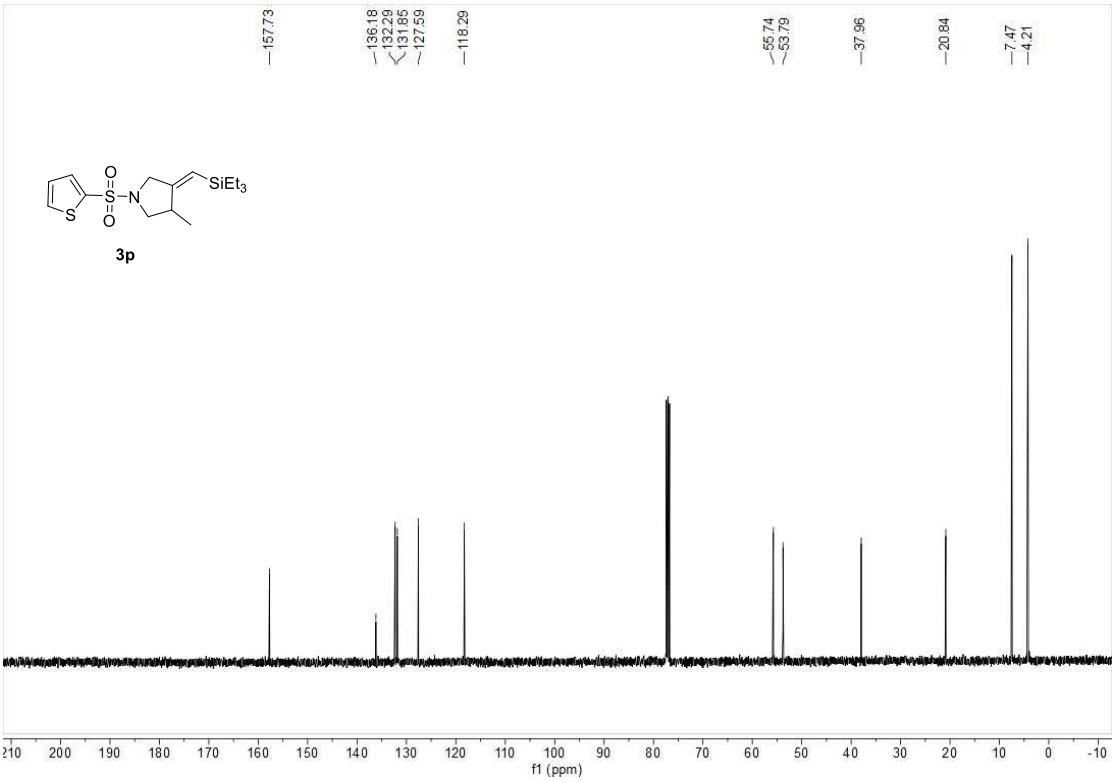
(*E*)-*N*,*N*-dimethyl-6-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)naphthalen-2-amine (3o)



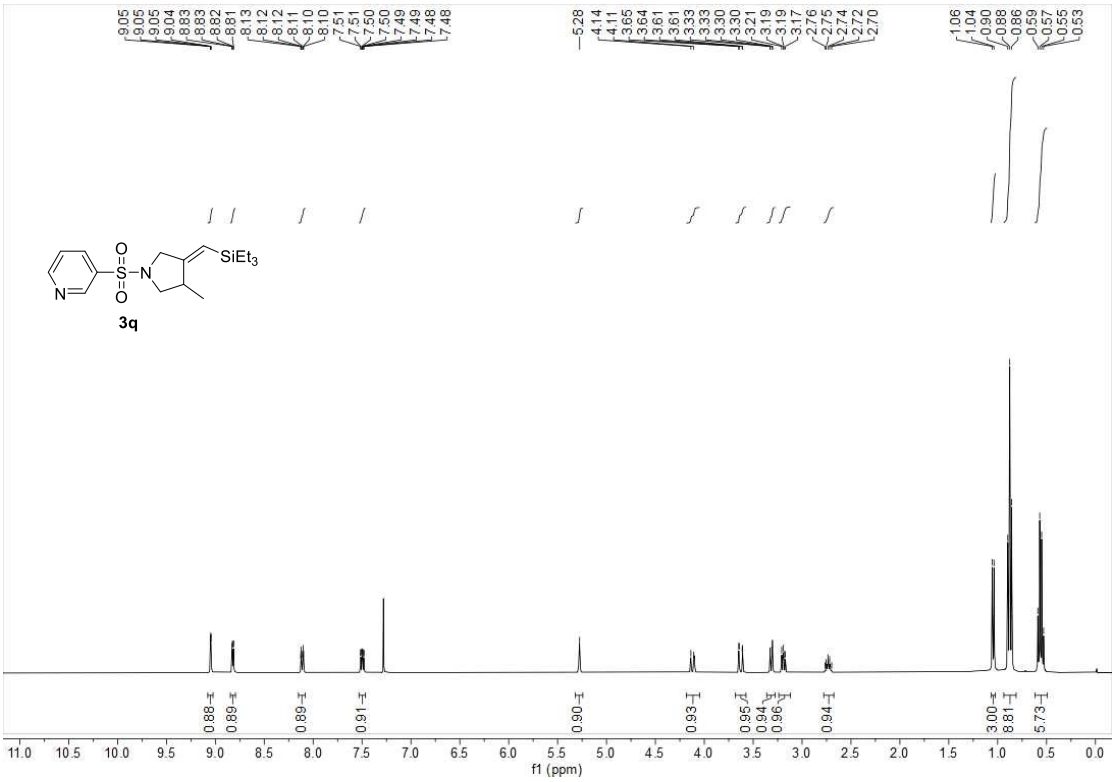


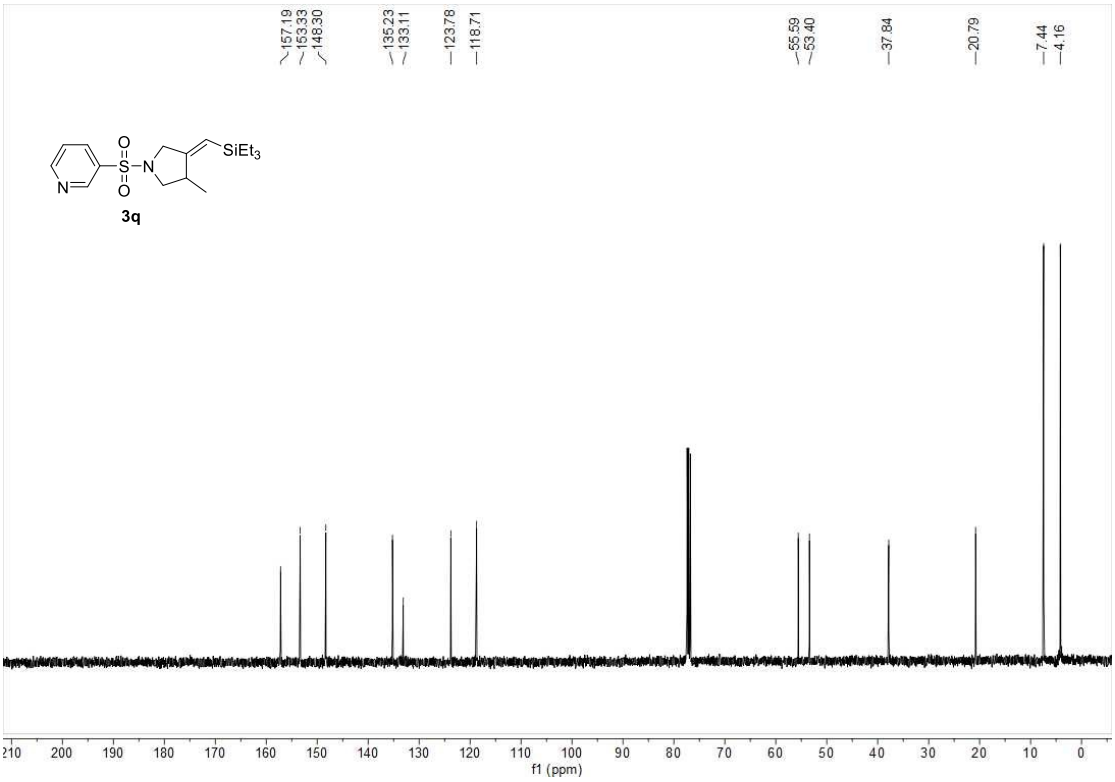
(*E*)-3-methyl-1-(thiophen-2-ylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3p)



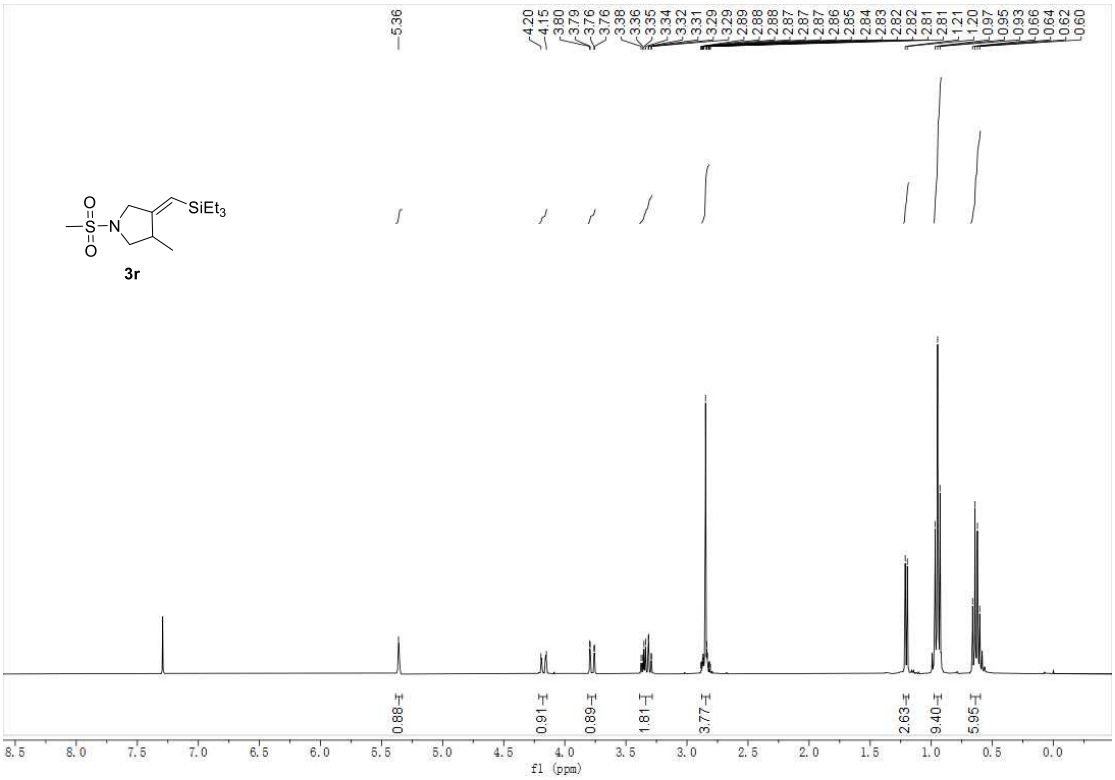


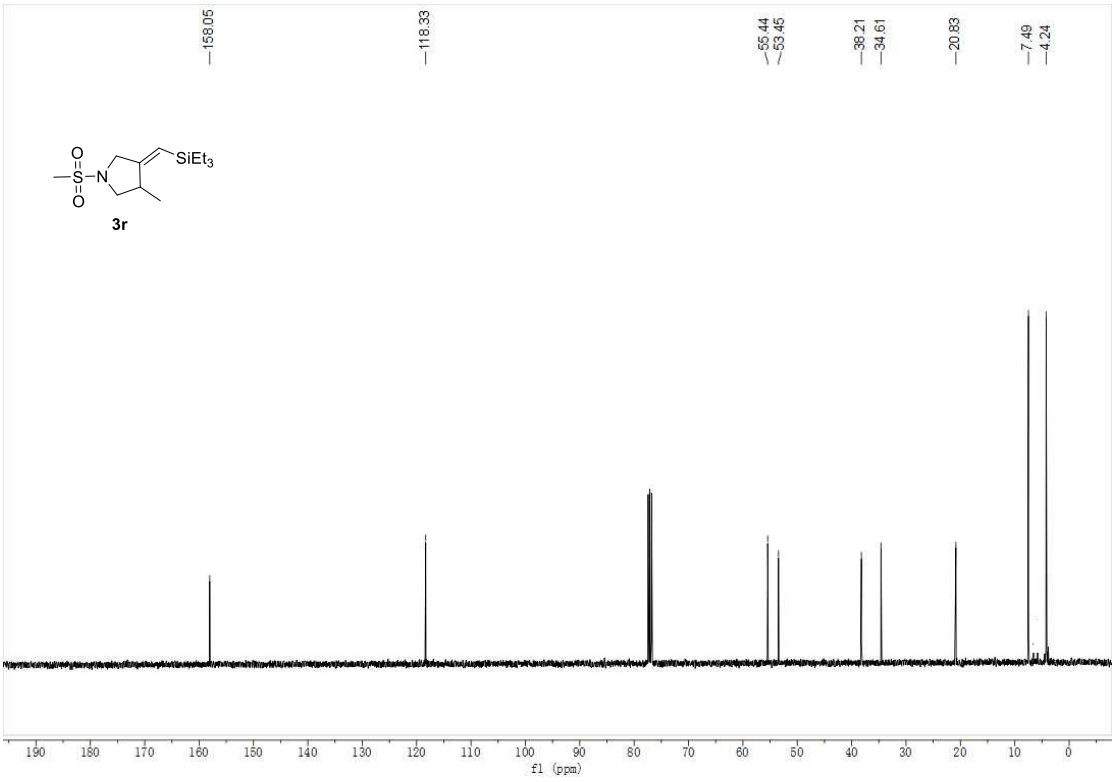
(*E*)-3-((3-methyl-4-((triethylsilyl)methylene)pyrrolidin-1-yl)sulfonyl)pyridine (3q)



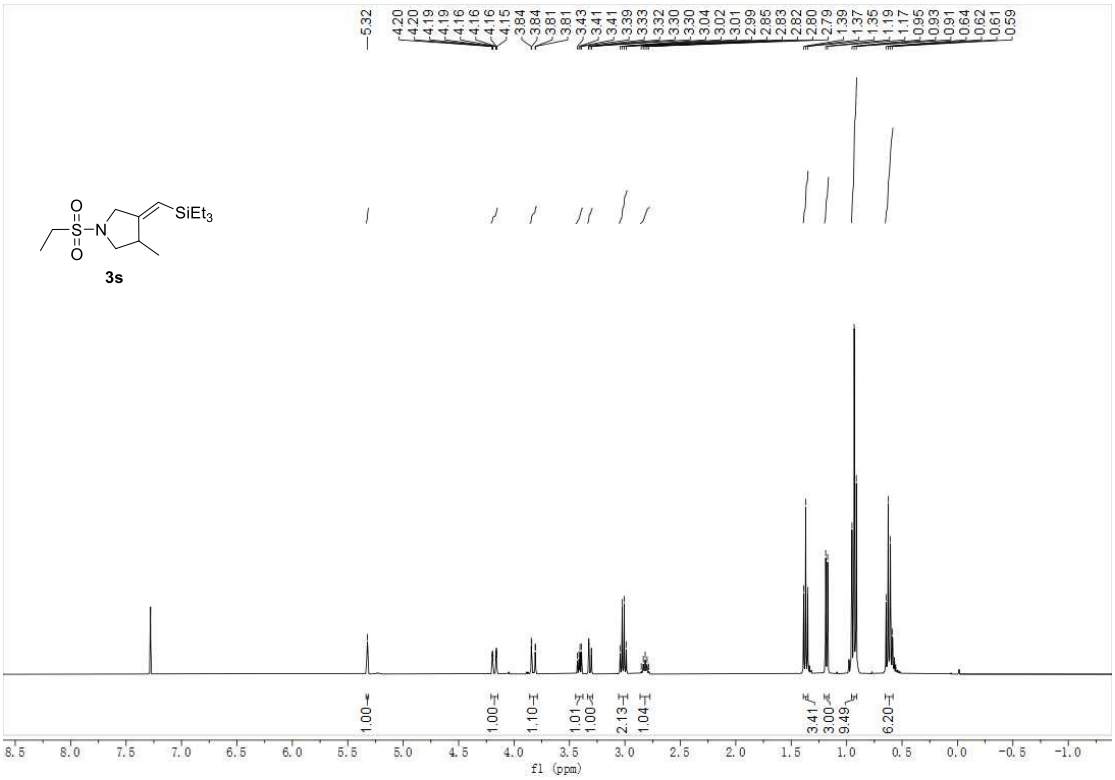


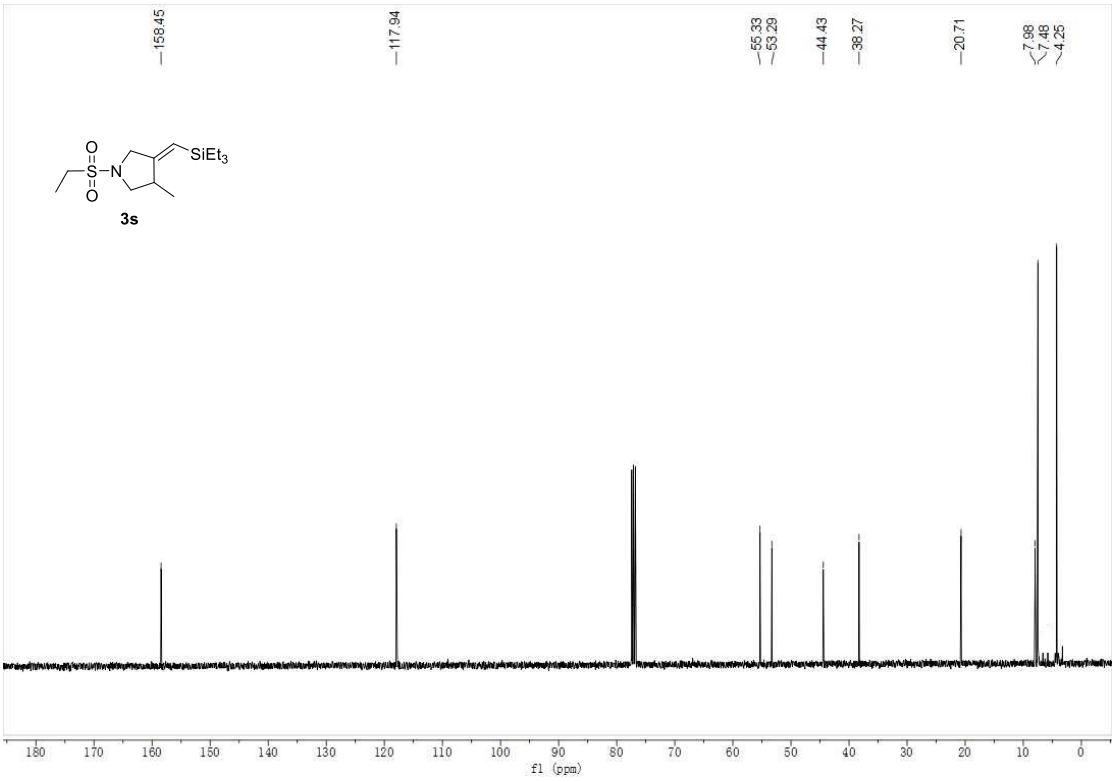
(*E*)-3-methyl-1-(methylsulfonyl)-4-((triethylsilyl)methylene)pyrrolidine (3r)



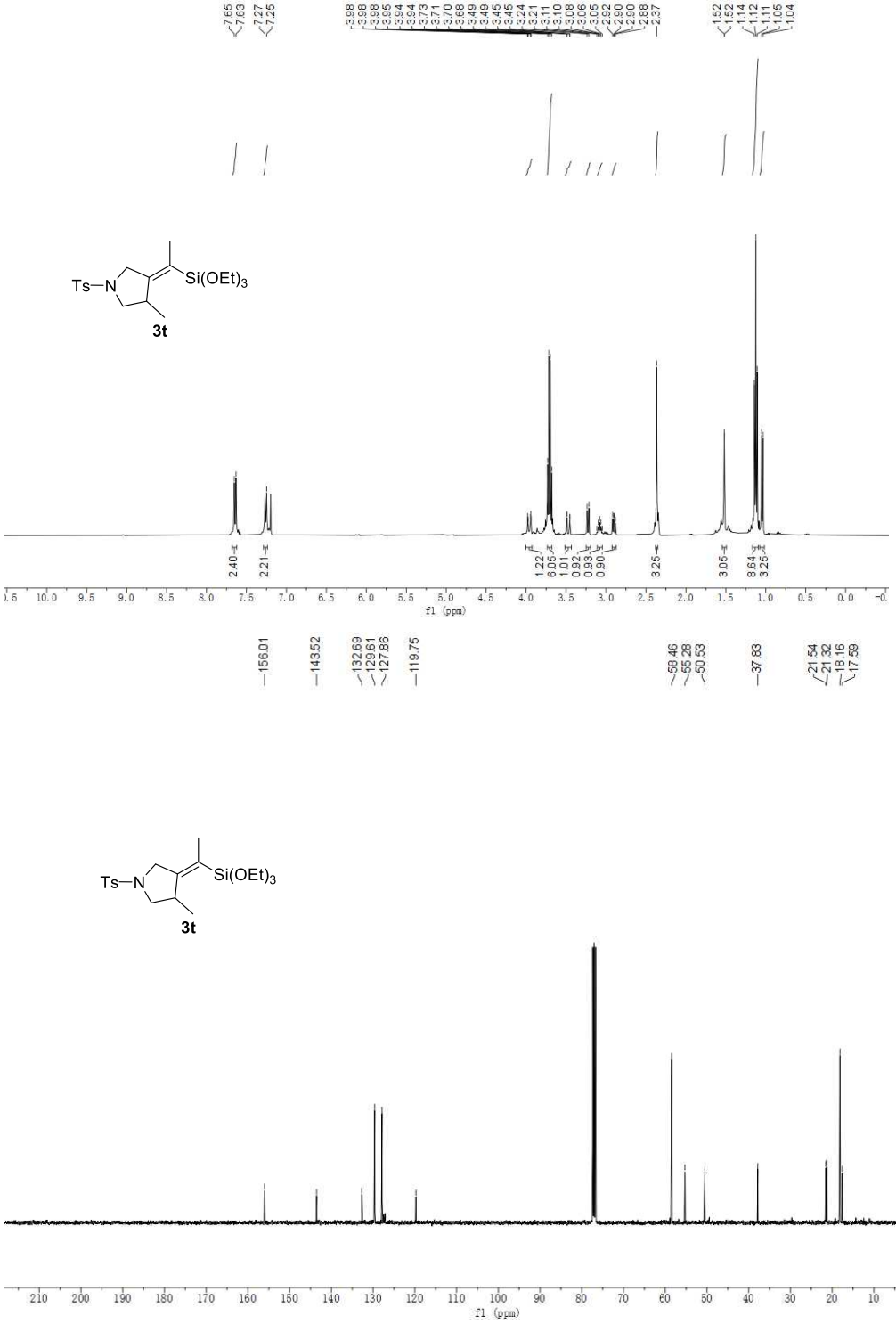


(*E*)-1-(ethylsulfonyl)-3-methyl-4-((triethylsilyl)methylene)pyrrolidine (3s)

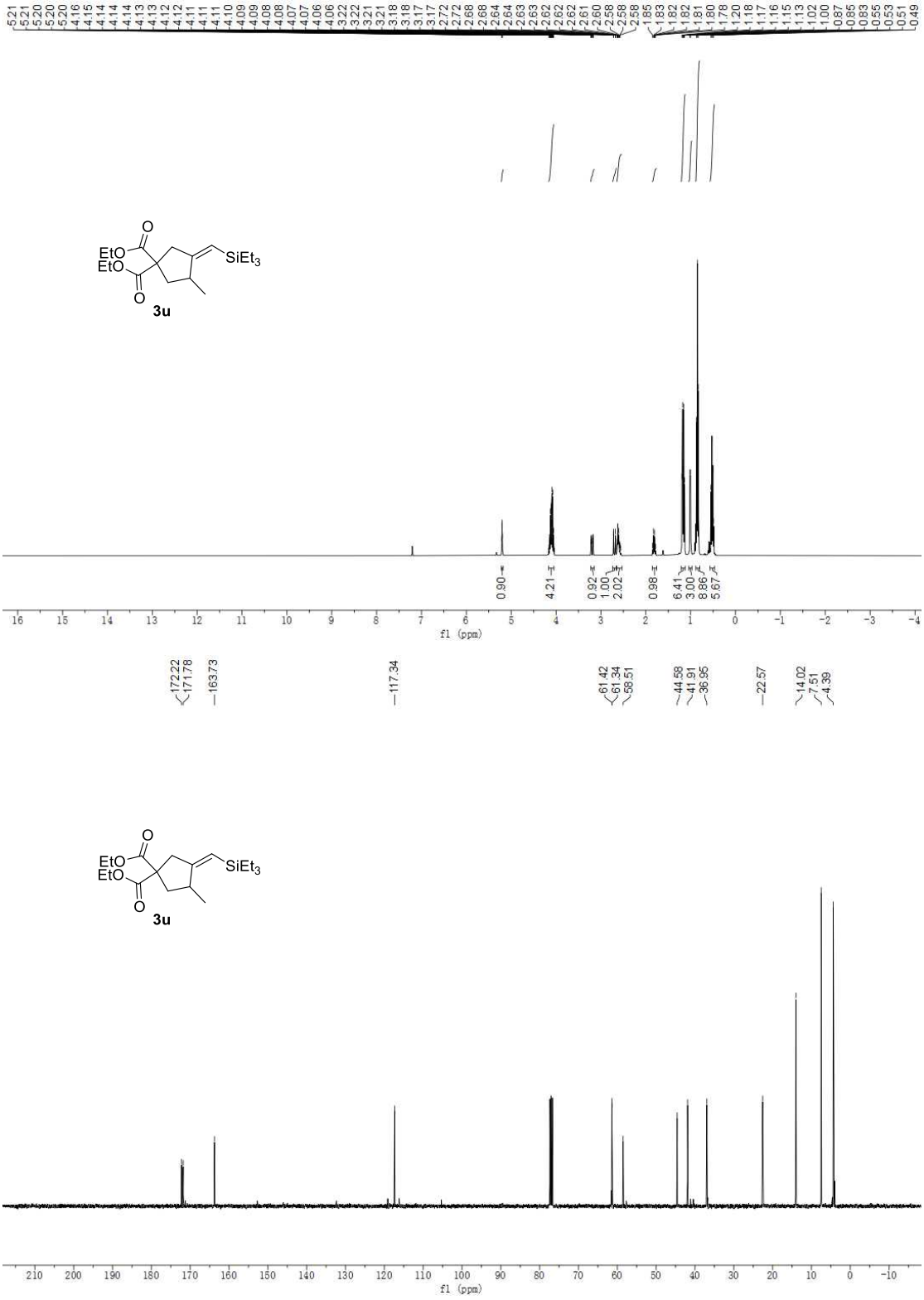




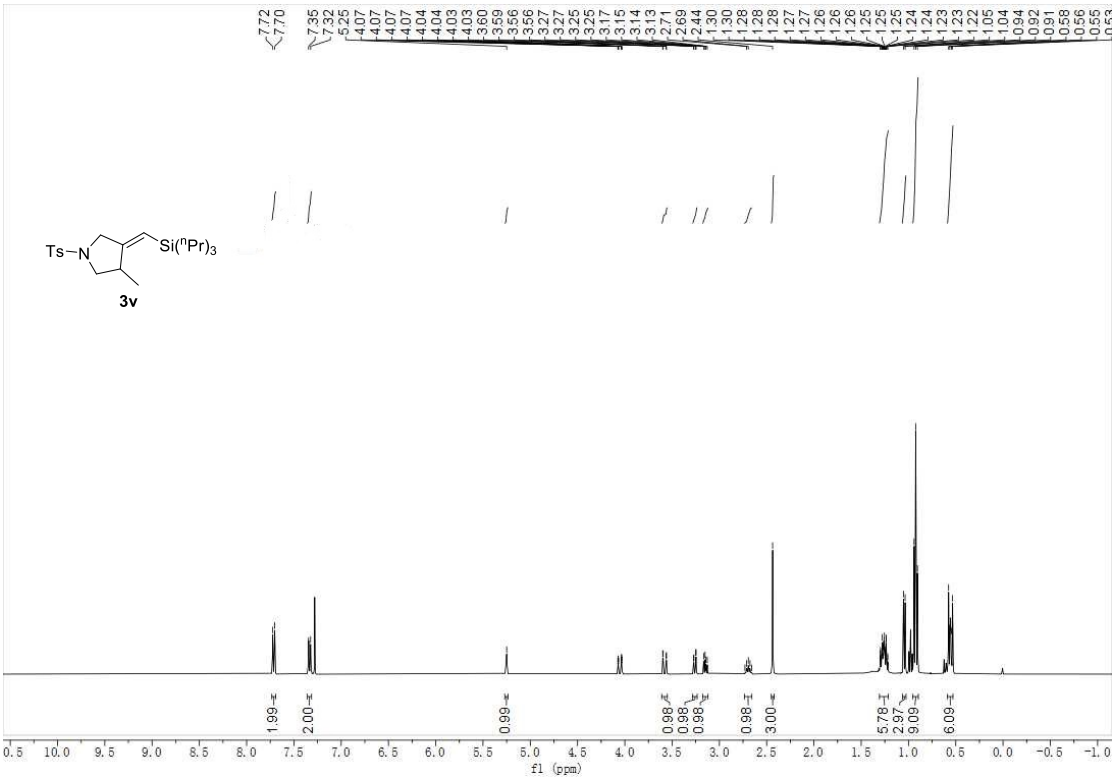
1-(4-Toluenesulfonyl)-3-(*E*)-(1-(triethoxysilyl)ethylidene)-4-methylpyrrolidine (3t)

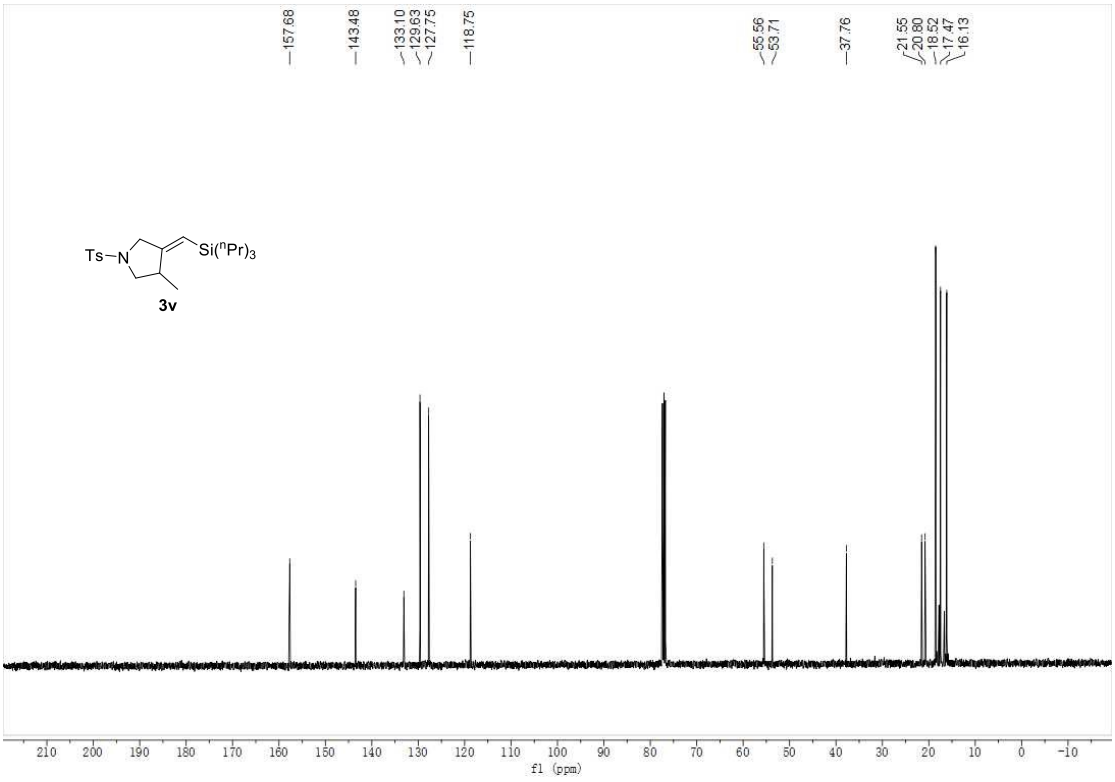


4,4-Bis(methoxycarbonyl)-1-(*Z*)-(triethylsilyl)methylidene-2-methylcyclopentane (3u)

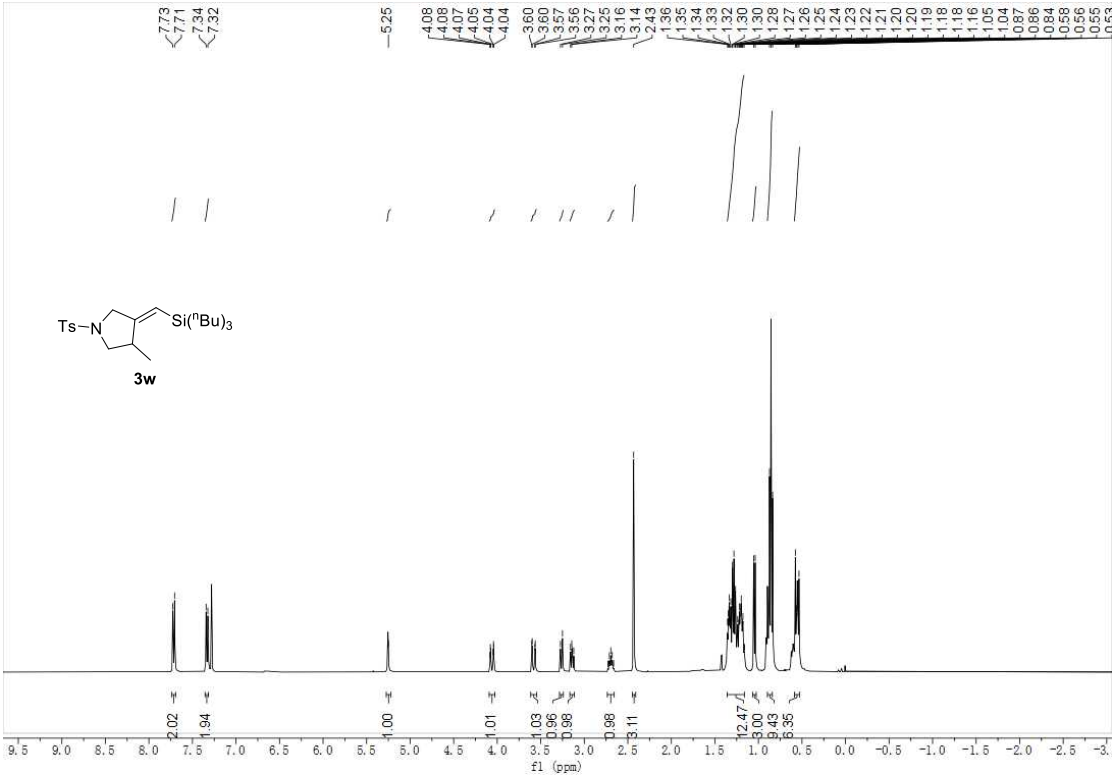


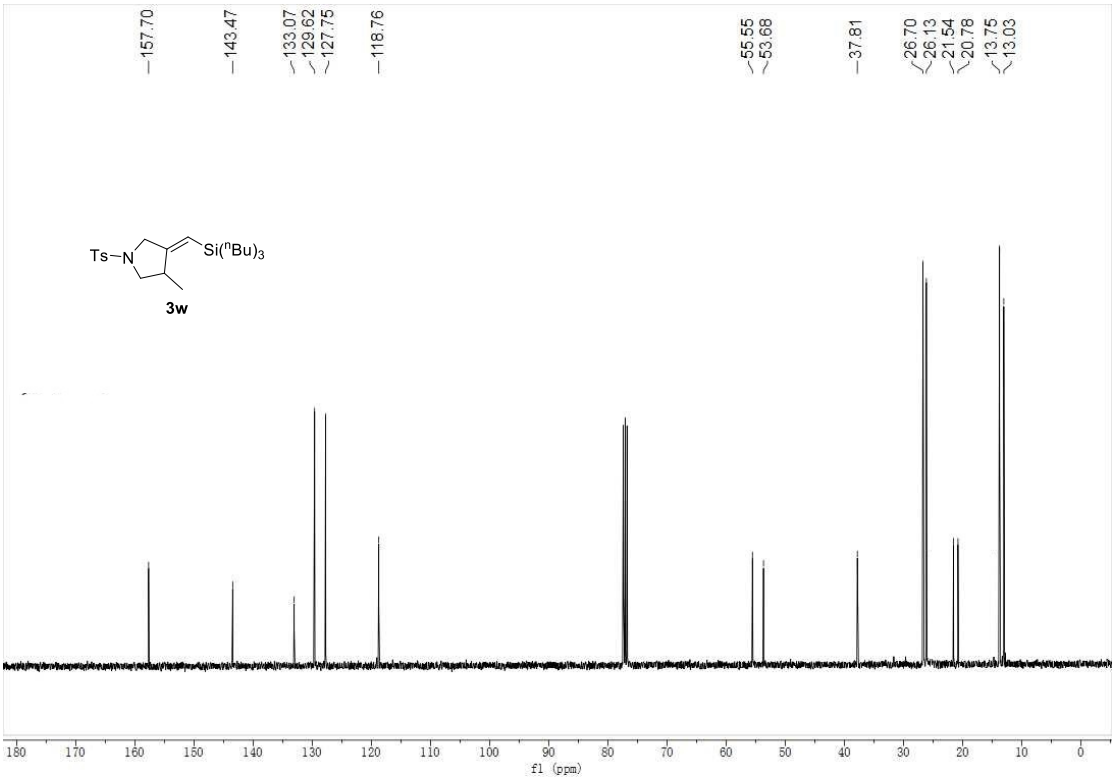
(*E*)-3-methyl-1-tosyl-4-((tripropylsilyl)methylene)pyrrolidine (3v)



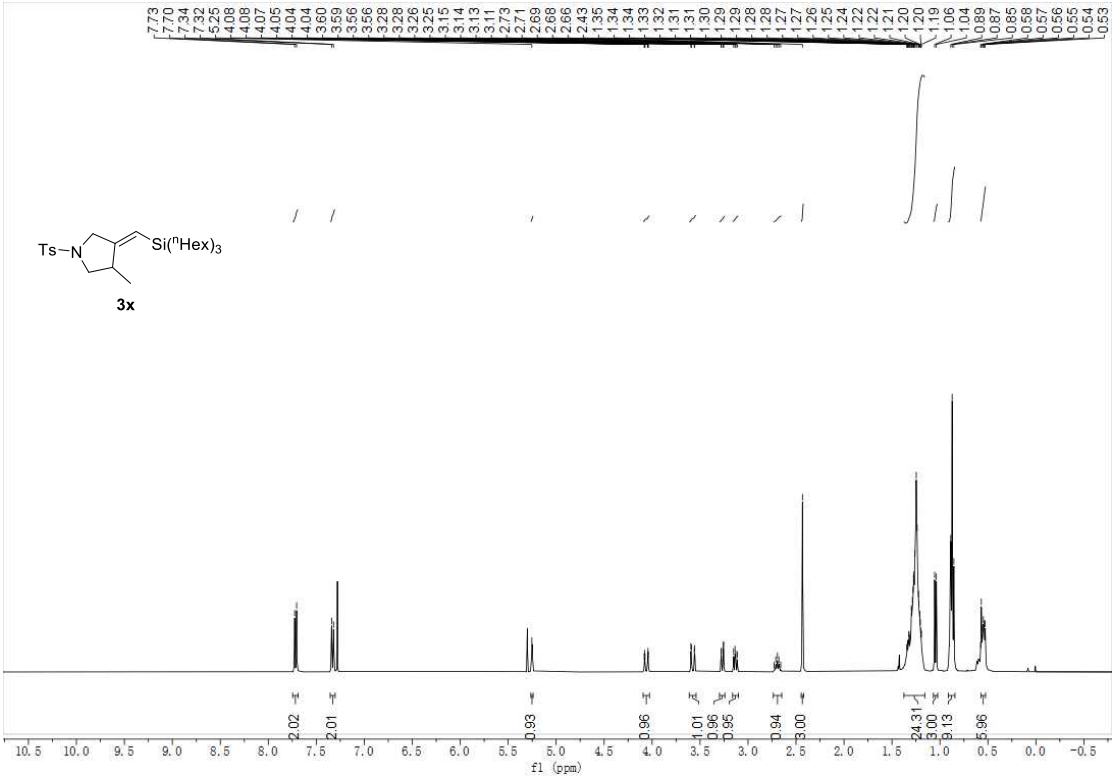


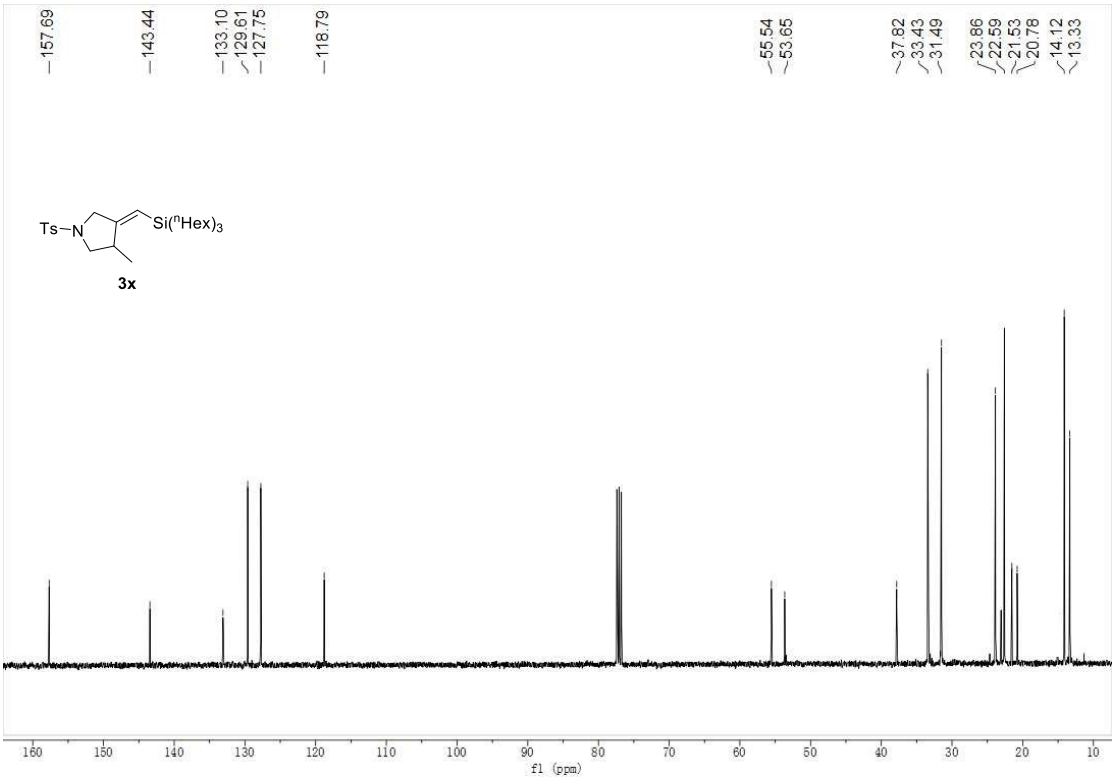
(*E*)-3-methyl-1-tosyl-4-((tributylsilyl)methylene)pyrrolidine (3w)



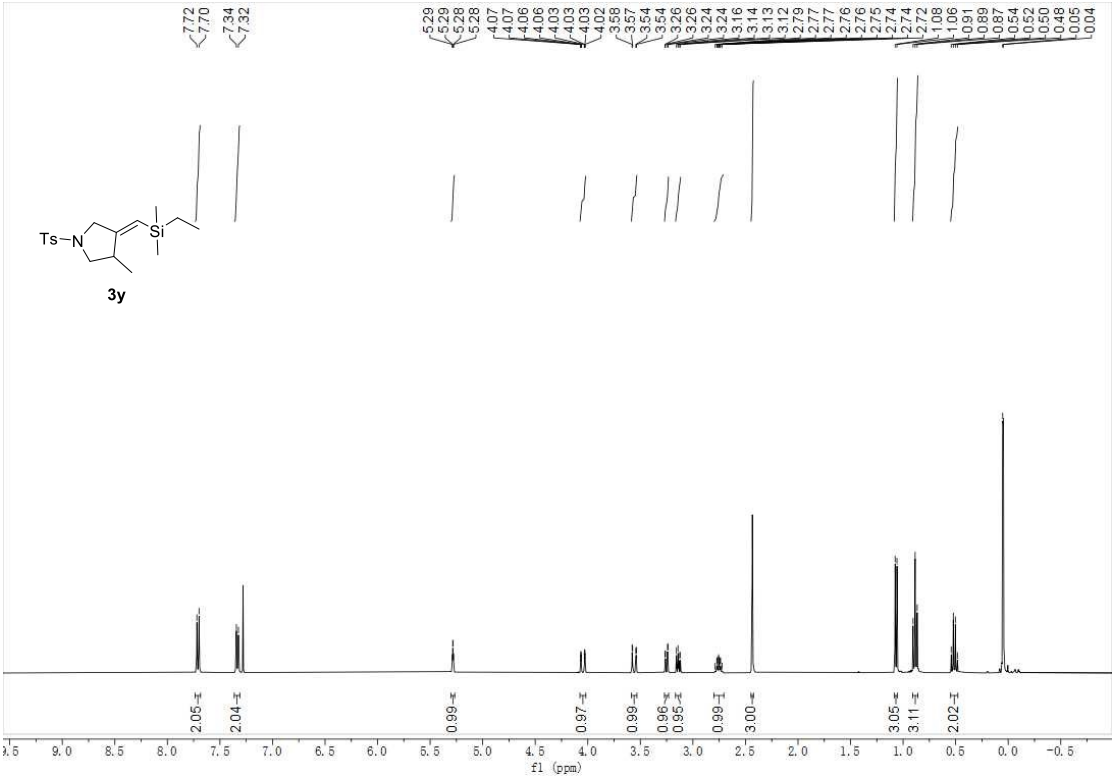


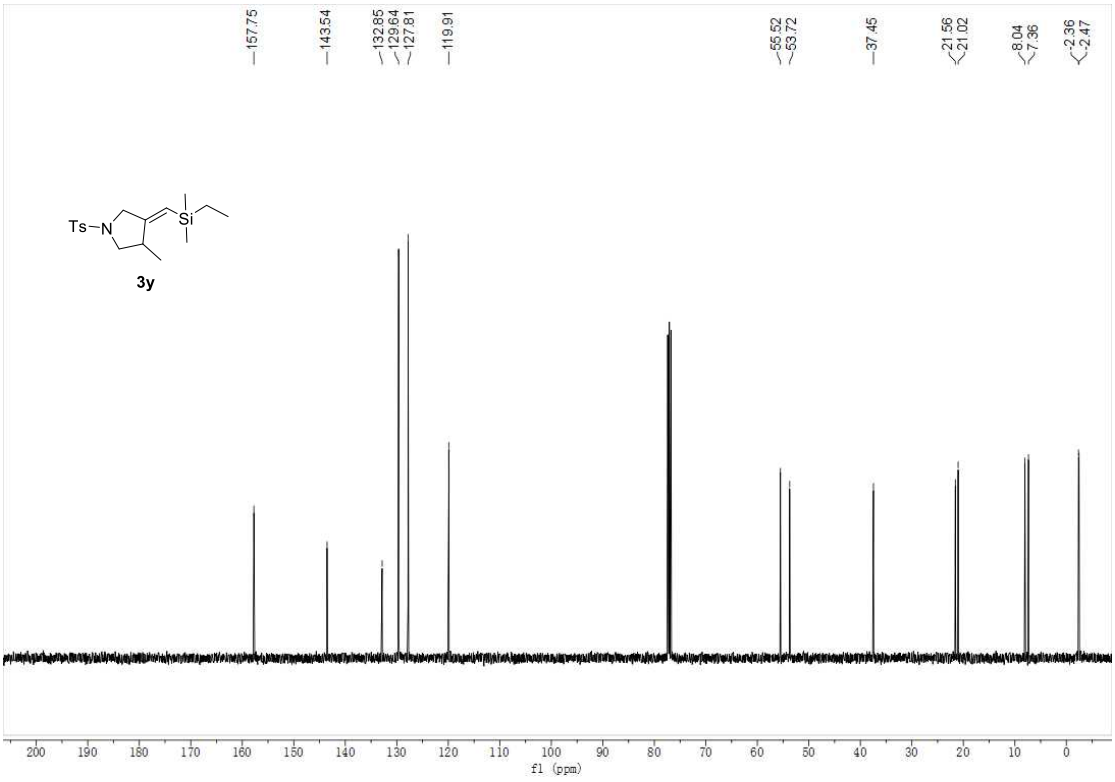
(*E*)-3-methyl-1-tosyl-4-((triHexsilyl)methylene)pyrrolidine (3x)



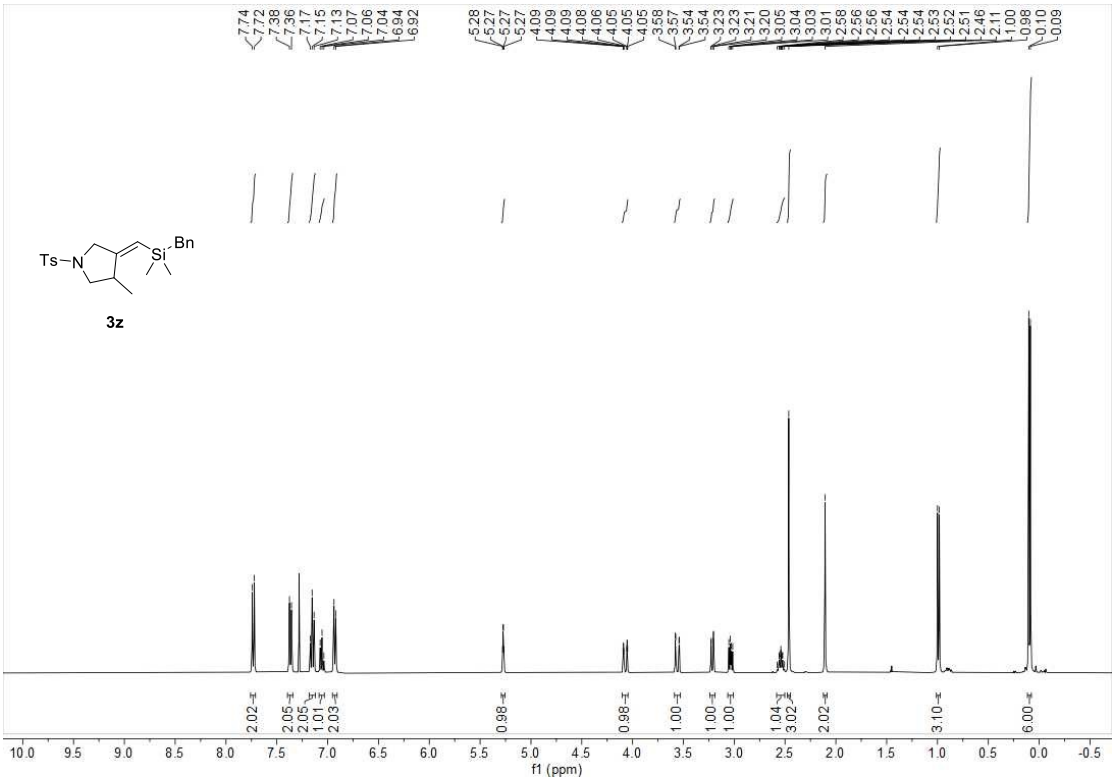


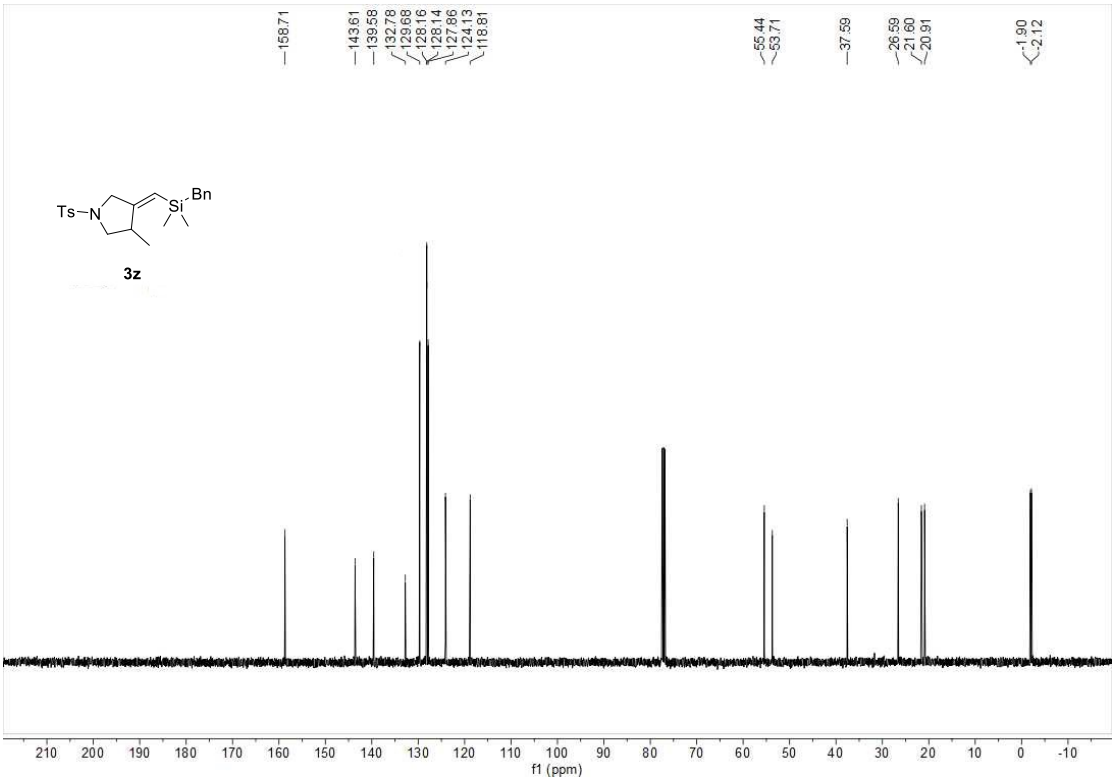
(*E*)-3-((ethyldimethylsilyl)methylene)-4-methyl-1-tosyl-4l3-pyrrolidine (3y)



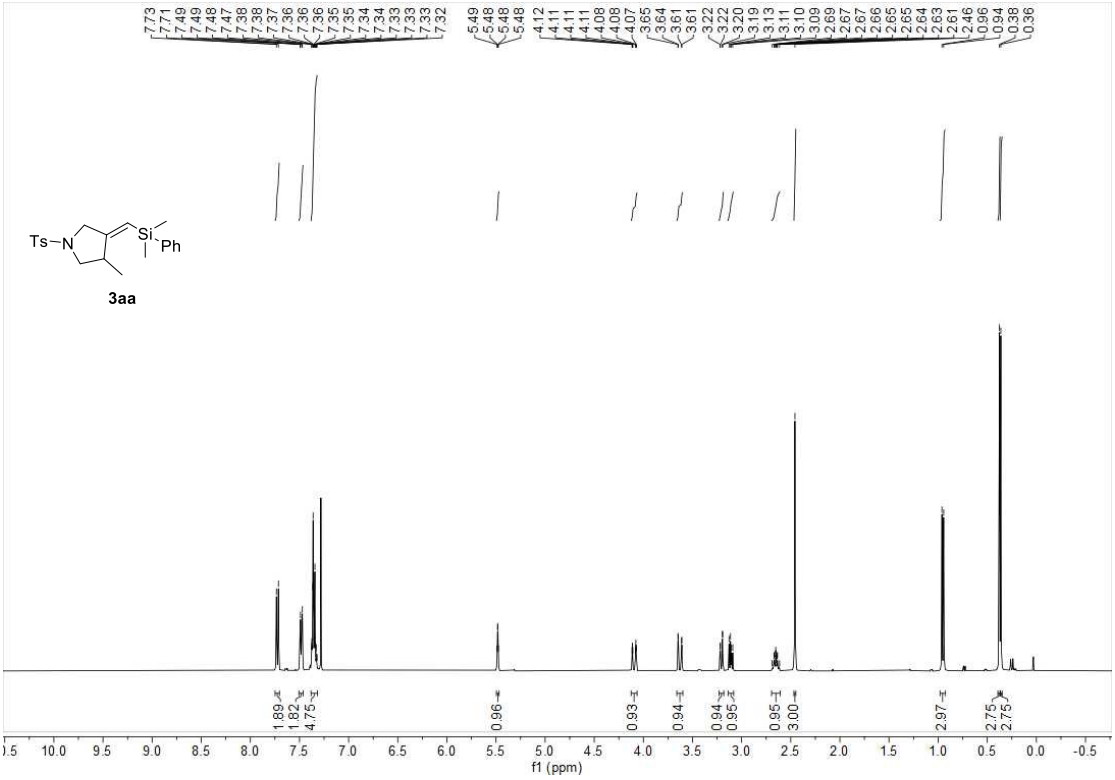


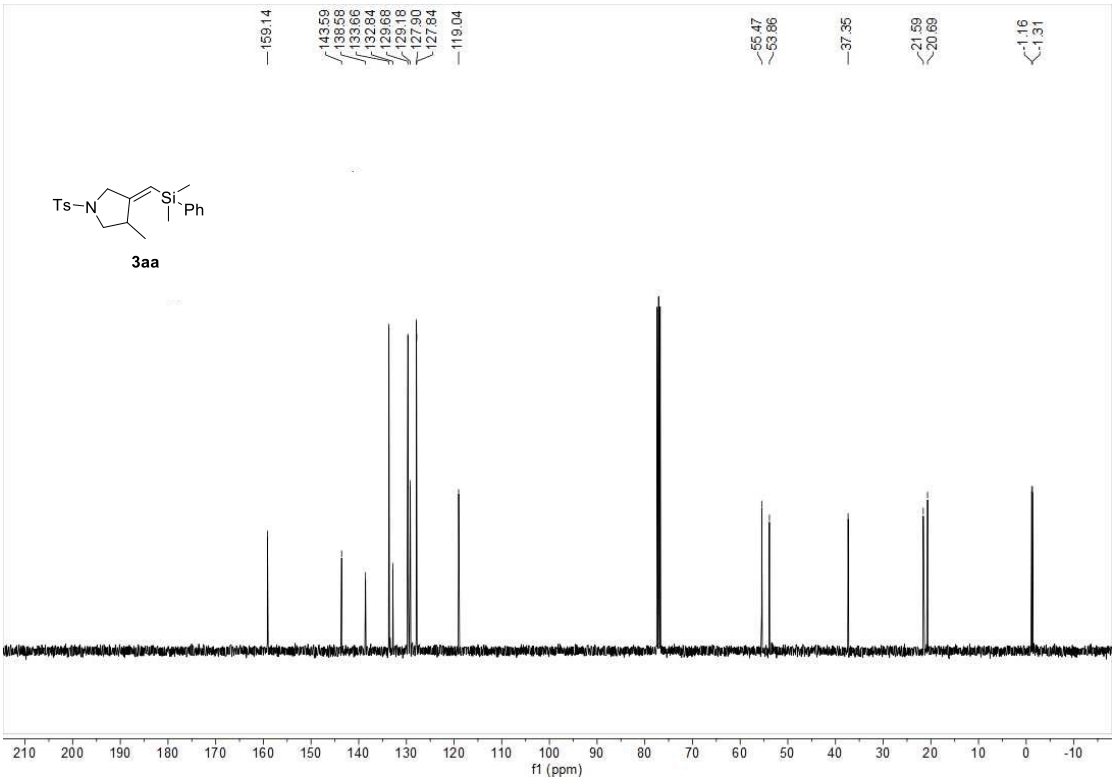
(*E*)-3-((benzyldimethylsilyl)methylene)-4-methyl-1-tosylpyrrolidine (3z)



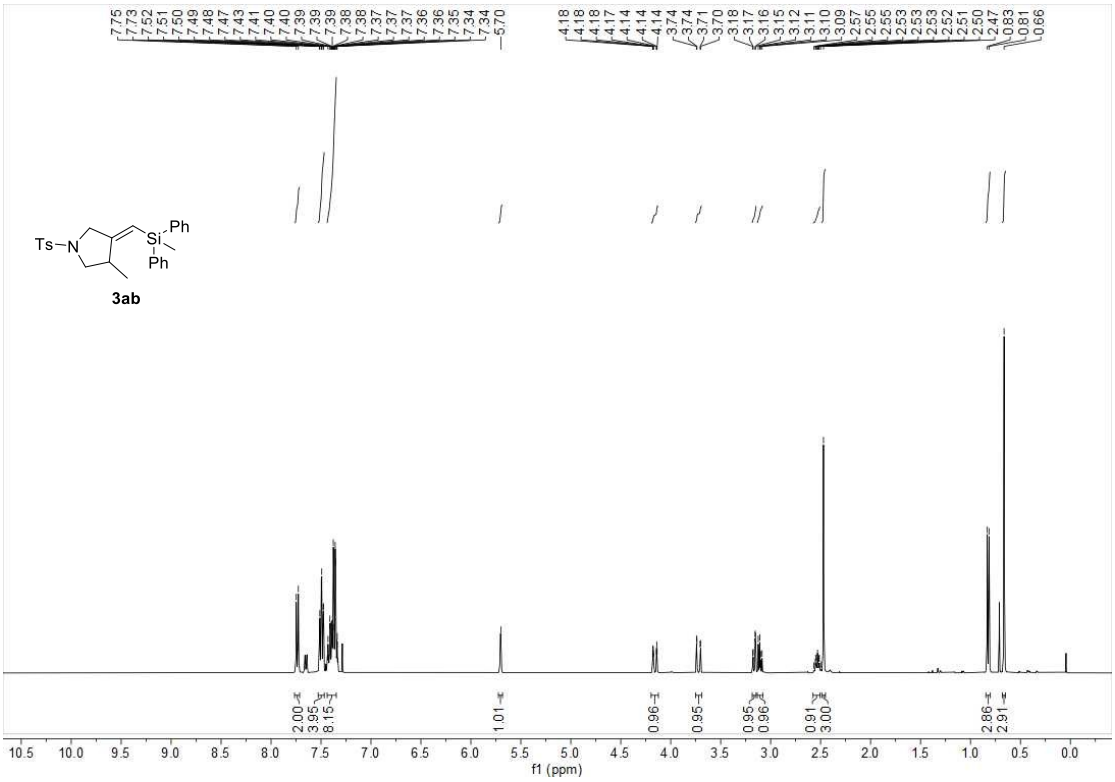


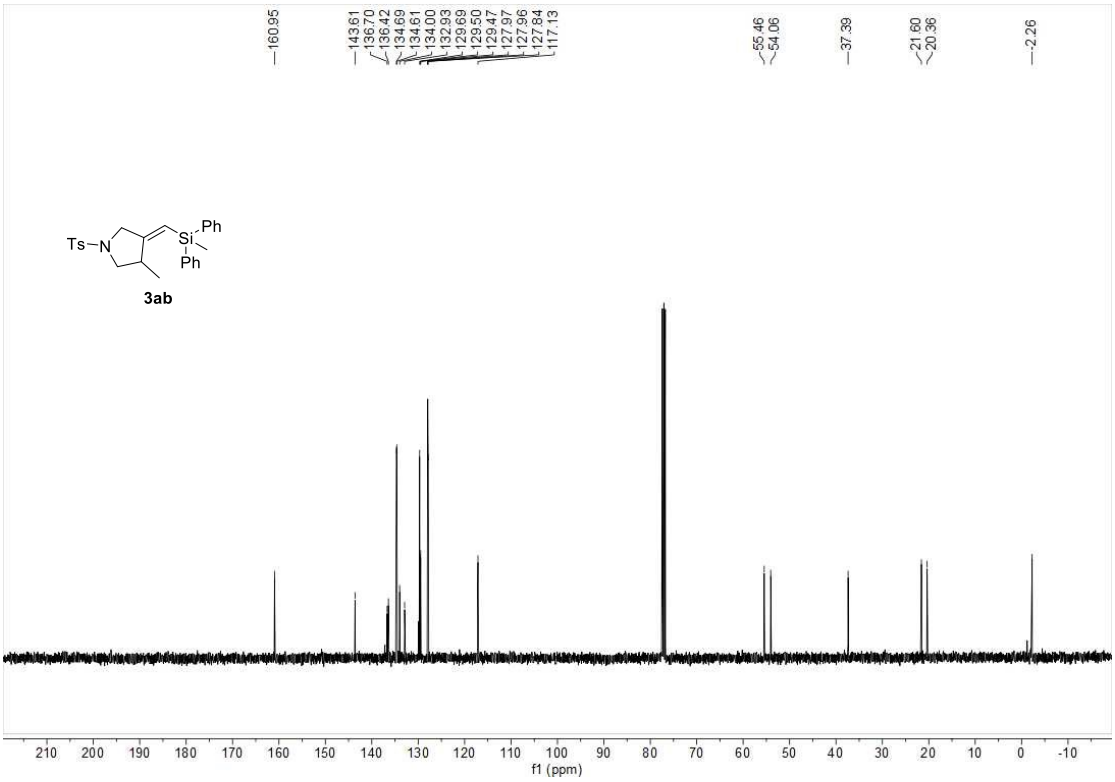
(*E*)-3-((benzyldimethylsilyl)methylene)-4-methyl-1-tosylpyrrolidine (3aa)



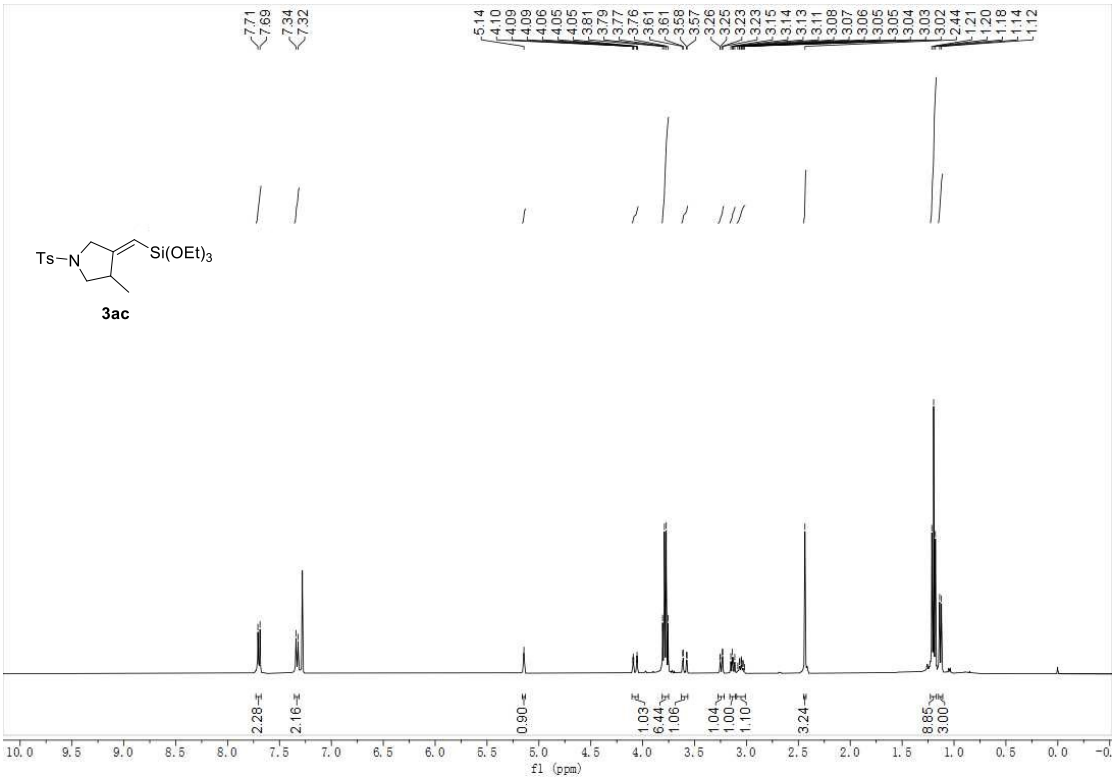


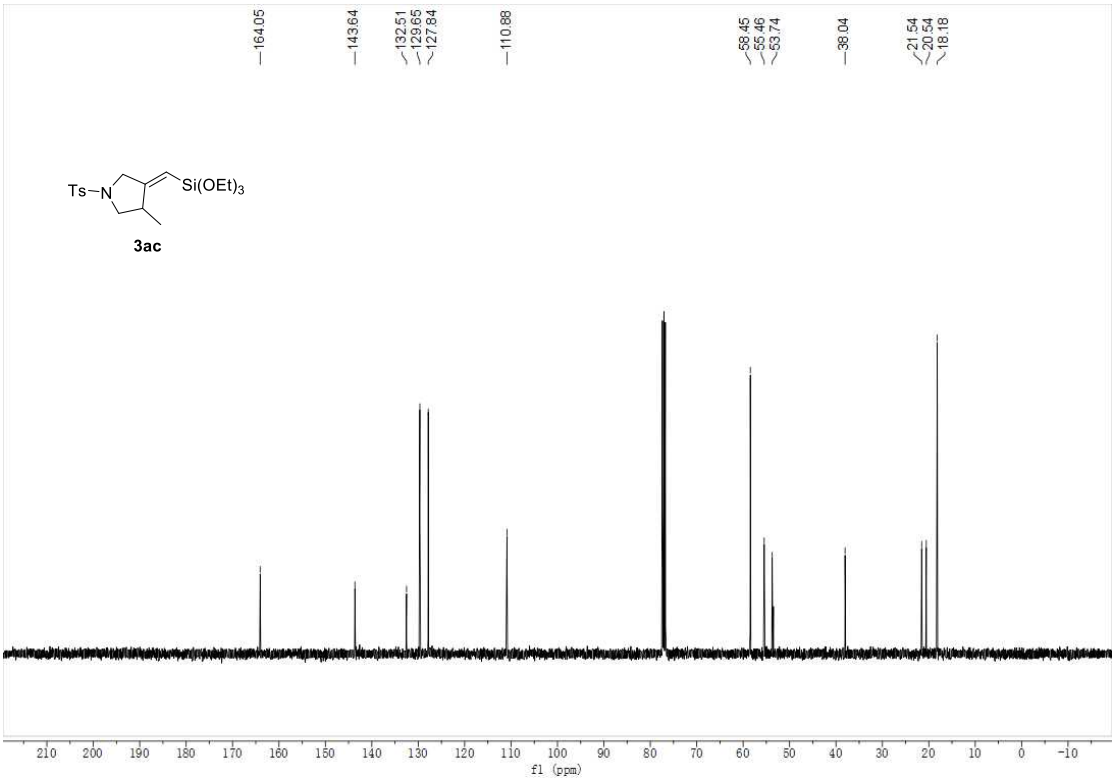
(*E*)-3-(2,2-diphenylpropylidene)-4-methyl-1-tosylpyrrolidine (3ab)



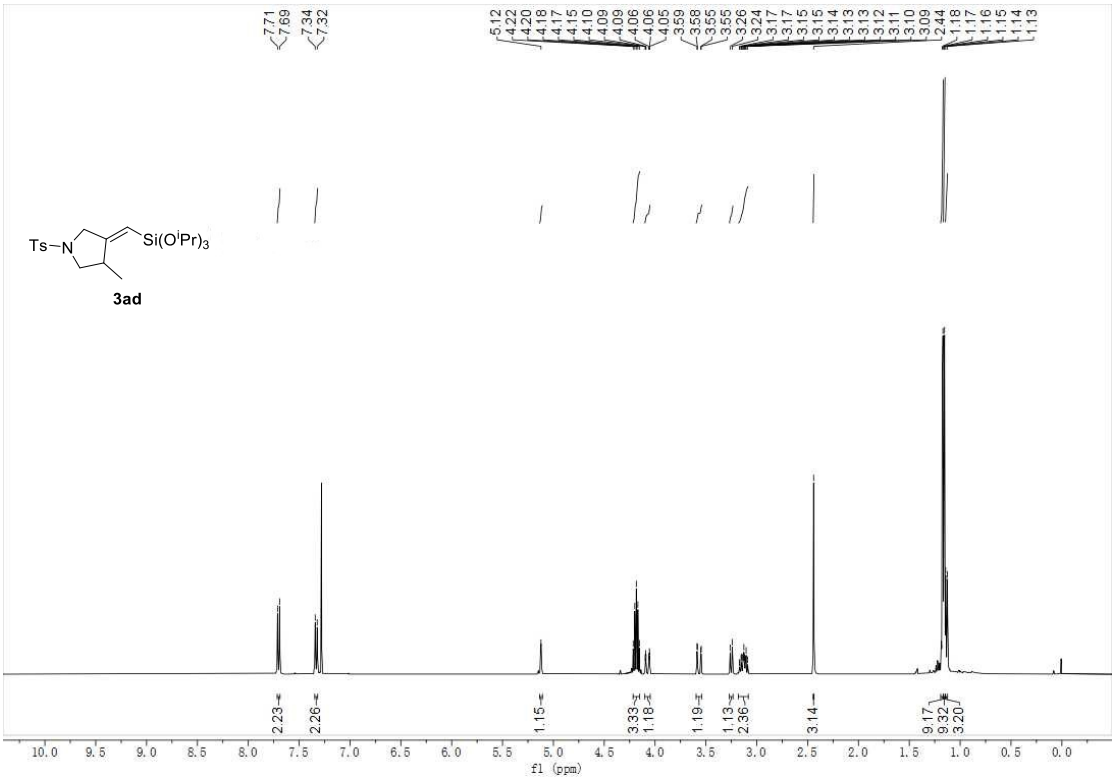


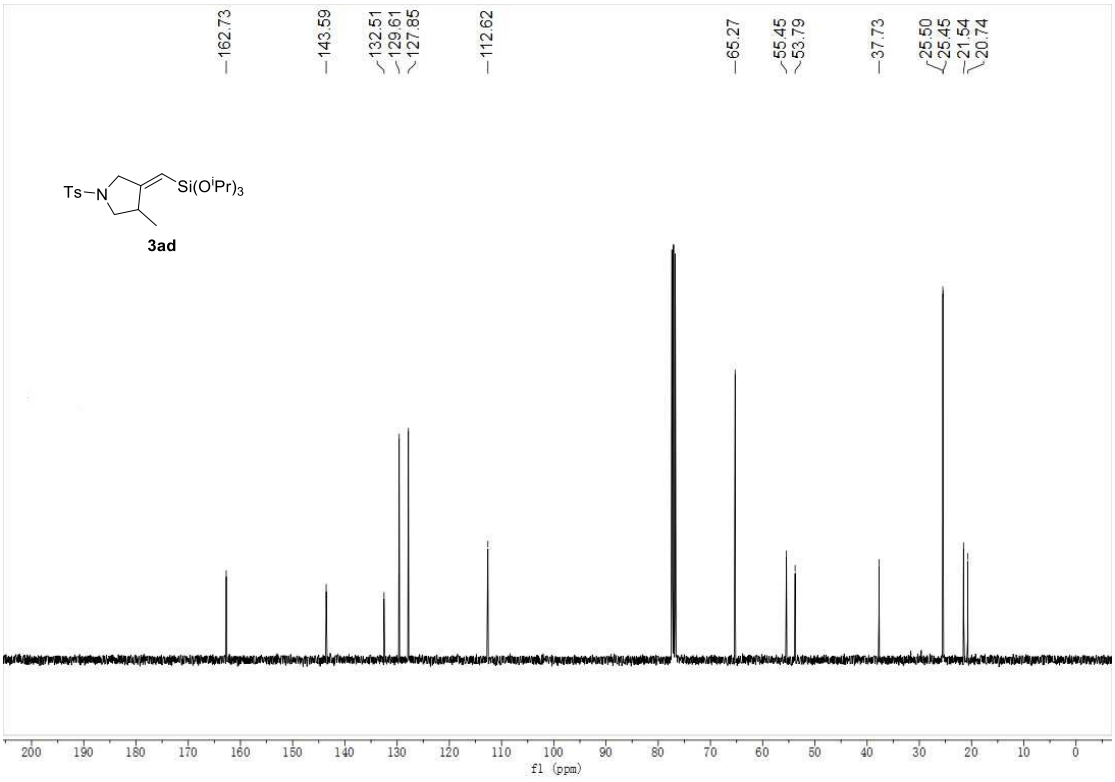
(*E*)-3-methyl-1-tosyl-4-((triethoxysilyl)methylene)-3l3-pyrrolidine (3ac)



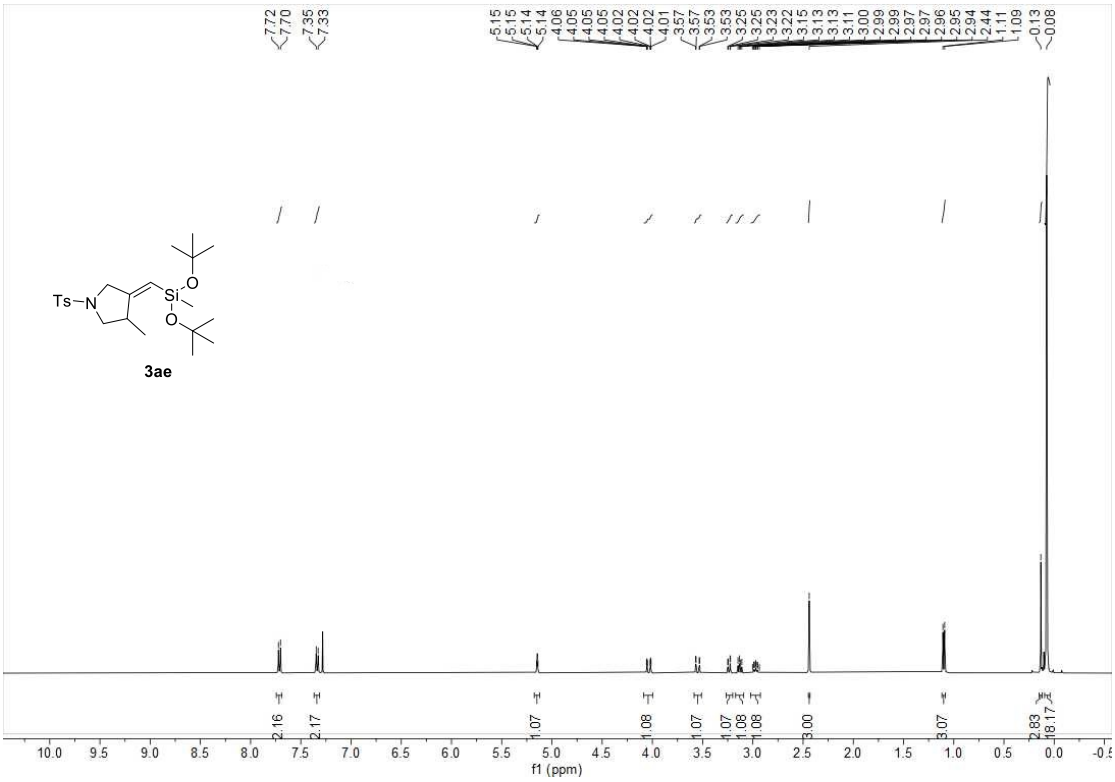


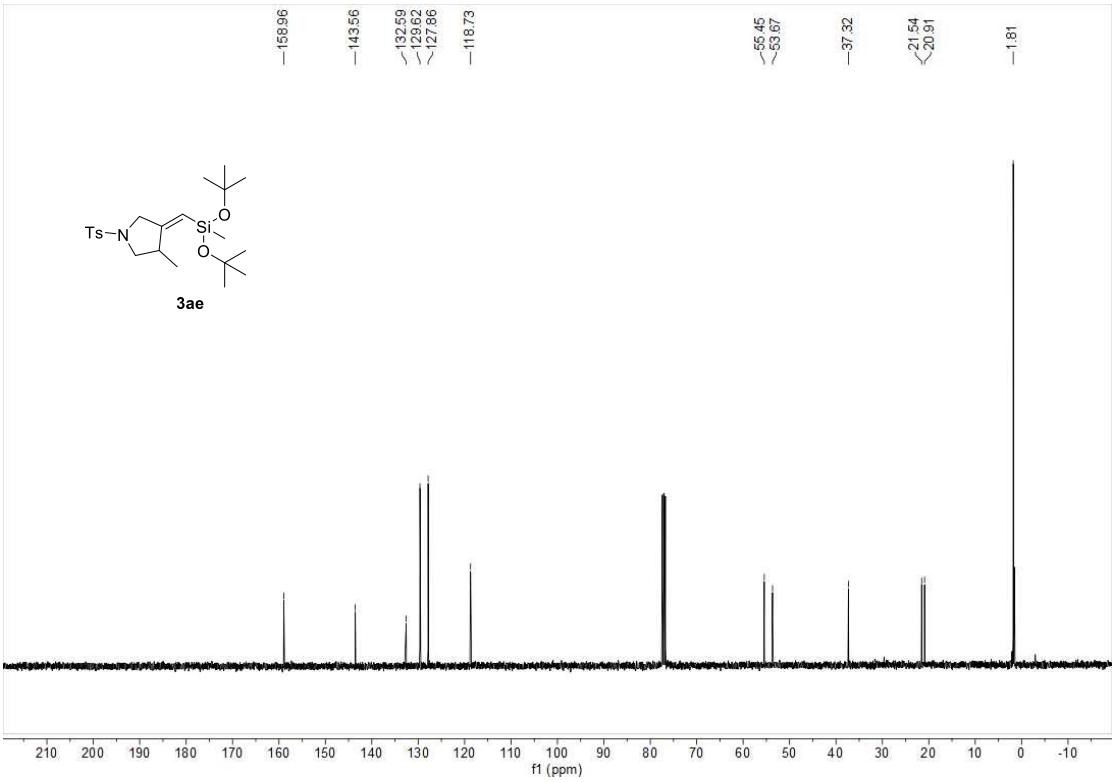
(*E*)-3-methyl-1-tosyl-4-((triisopropoxysilyl)methylene)pyrrolidine (3ad)



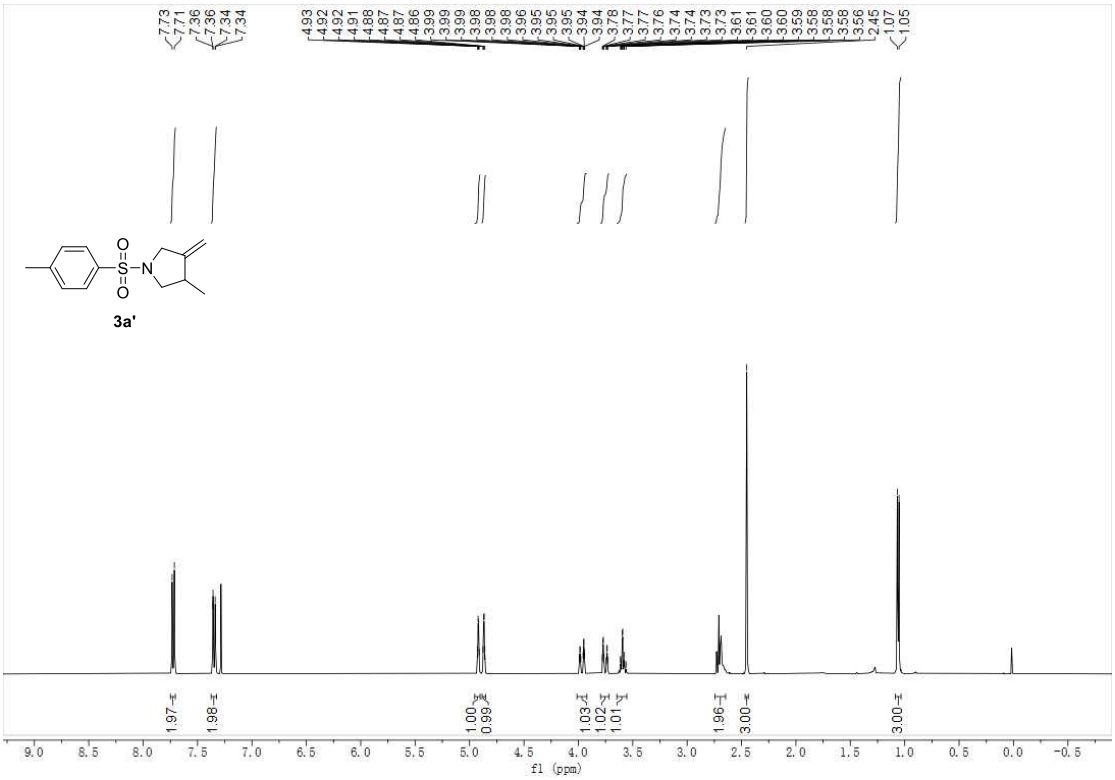


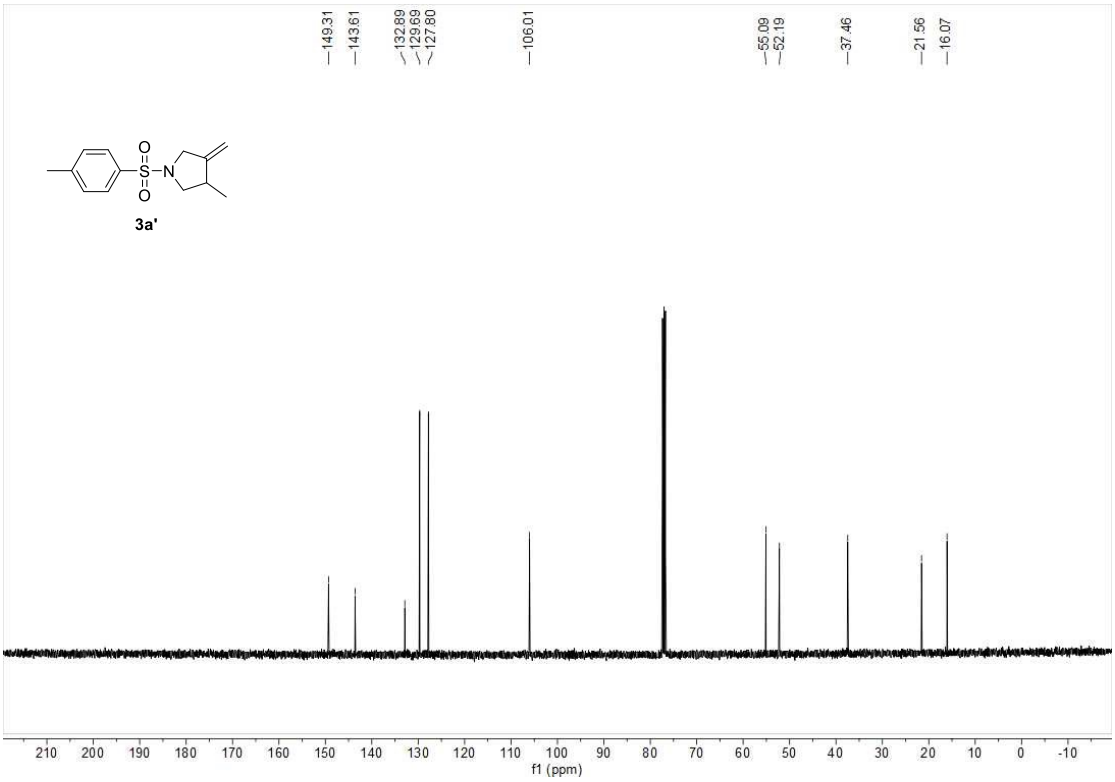
(*E*)-3-((di-tert-butoxy(methyl)silyl)methylene)-4-methyl-1-tosylpyrrolidine (3ae)



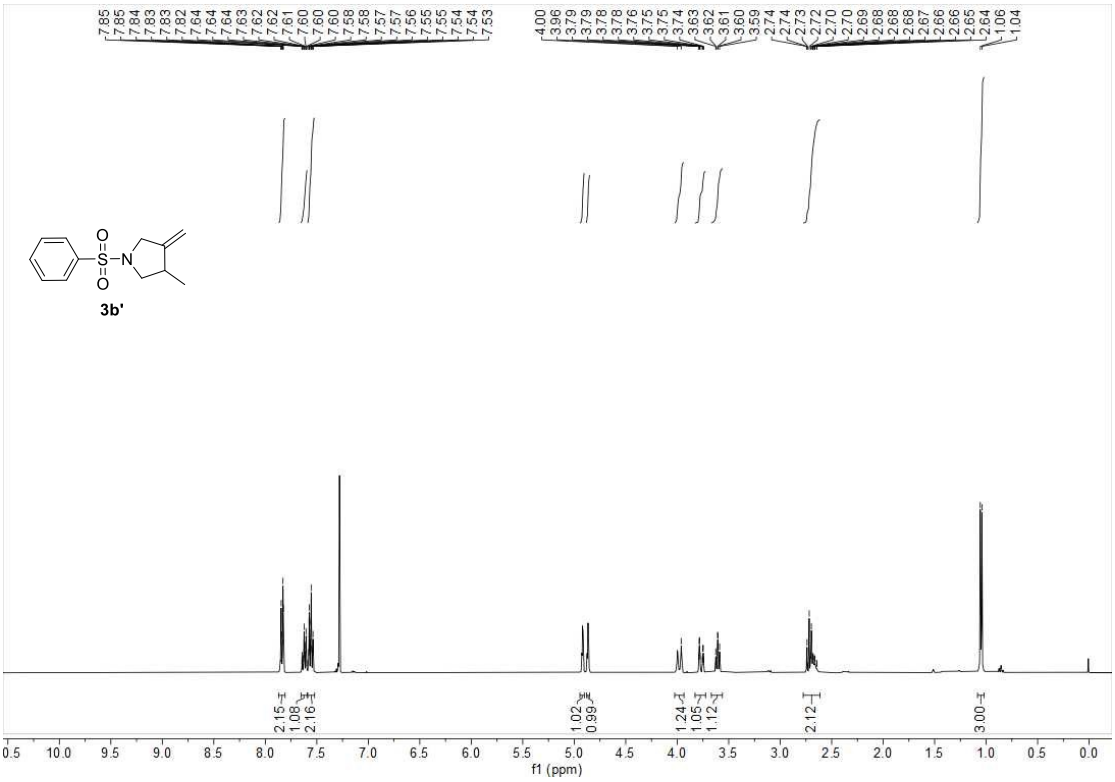


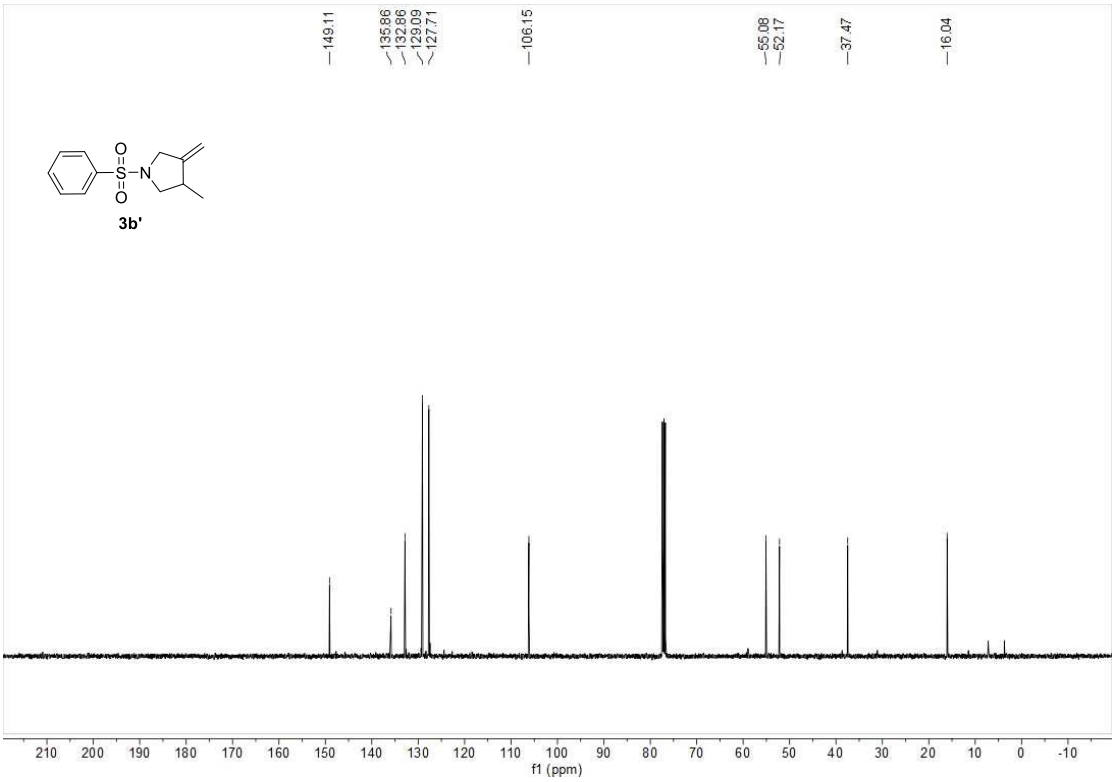
1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3a')



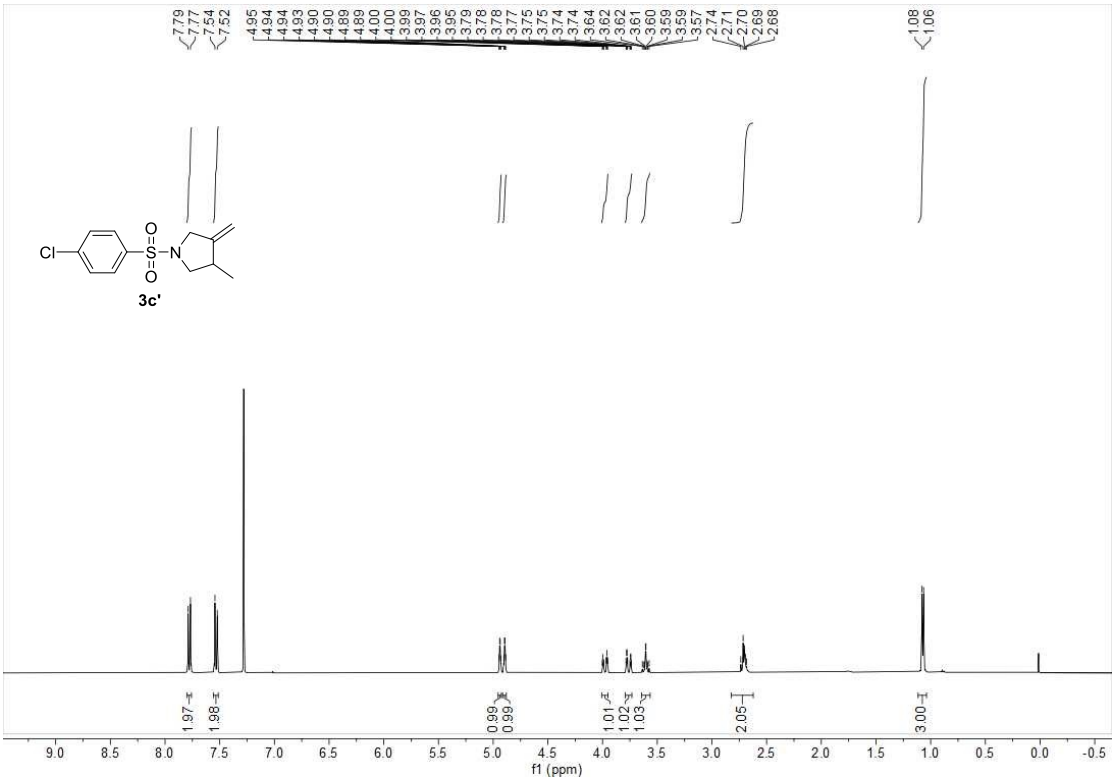


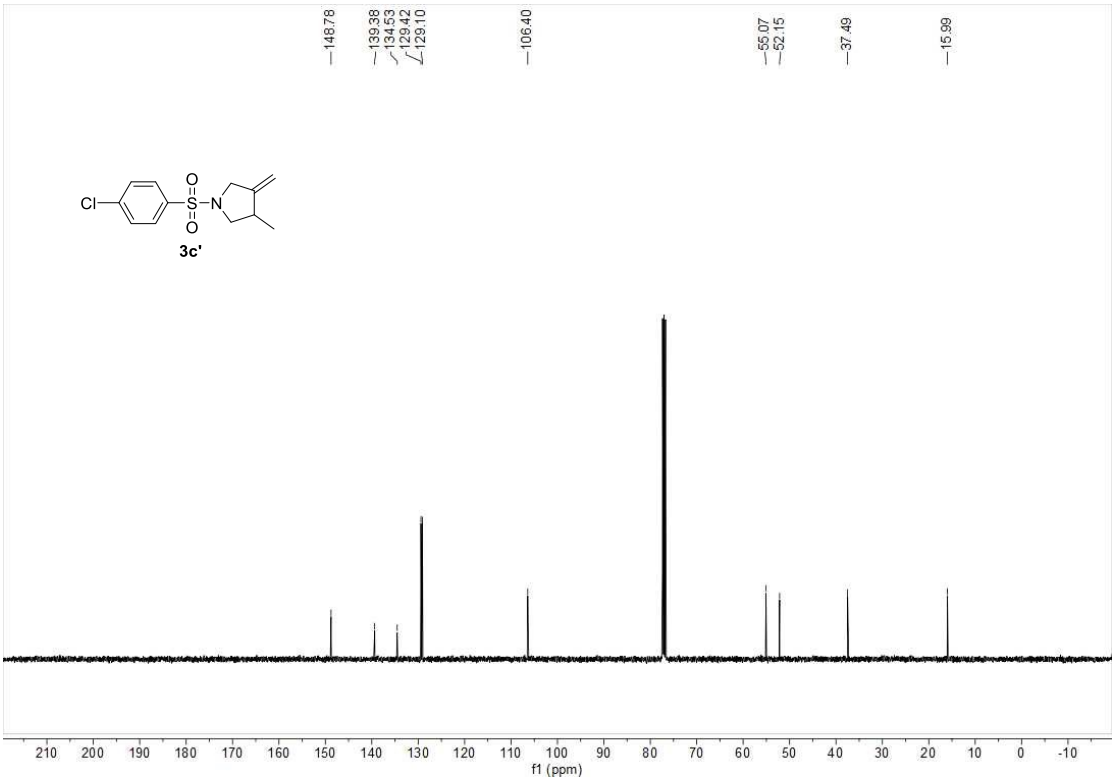
3-methyl-4-methylene-1-(phenylsulfonyl)pyrrolidine (3b')



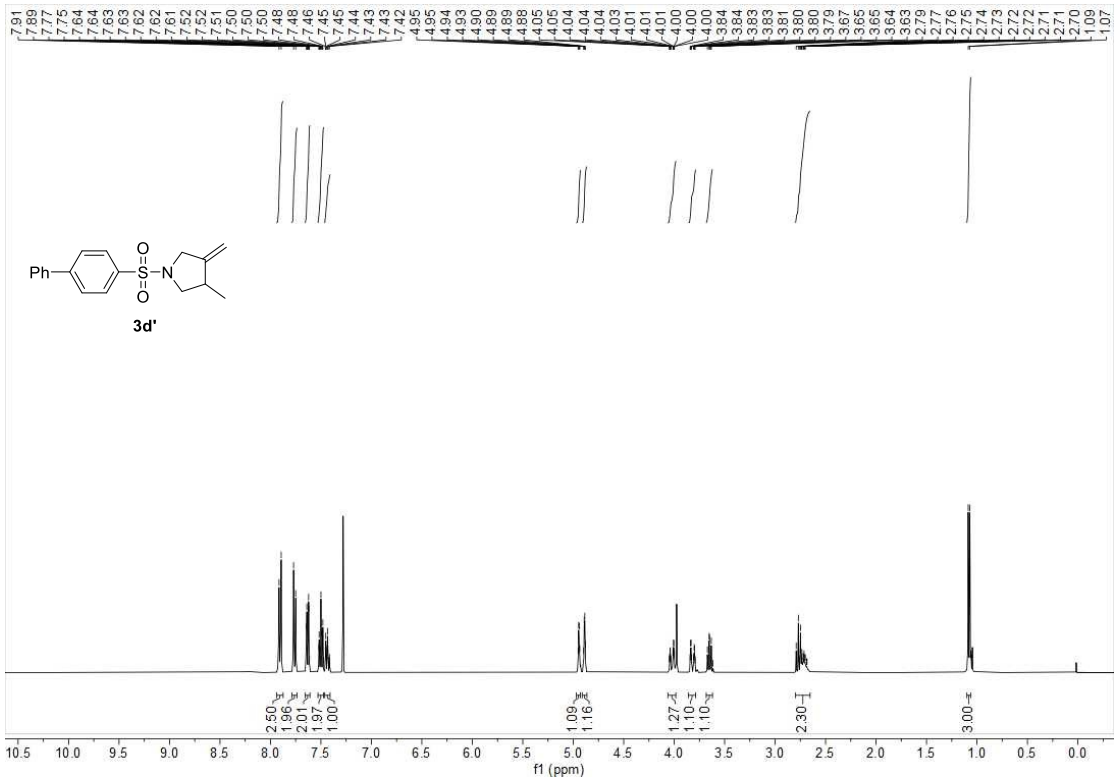


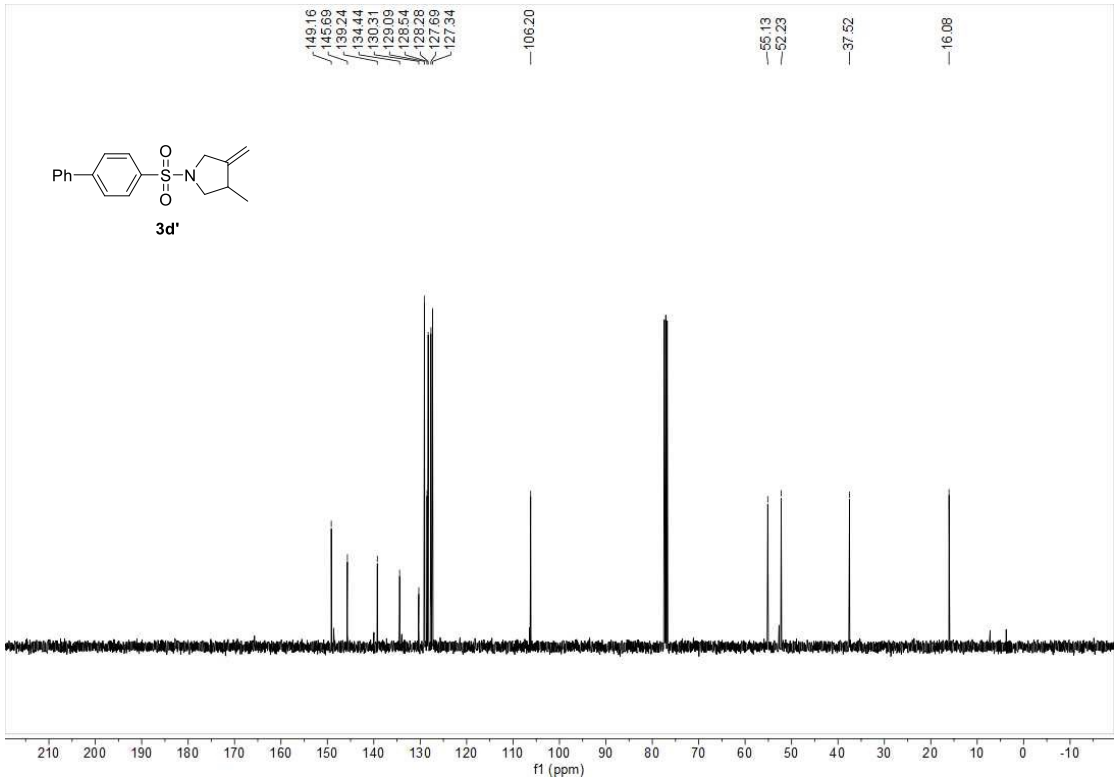
1-((4-chlorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3c')



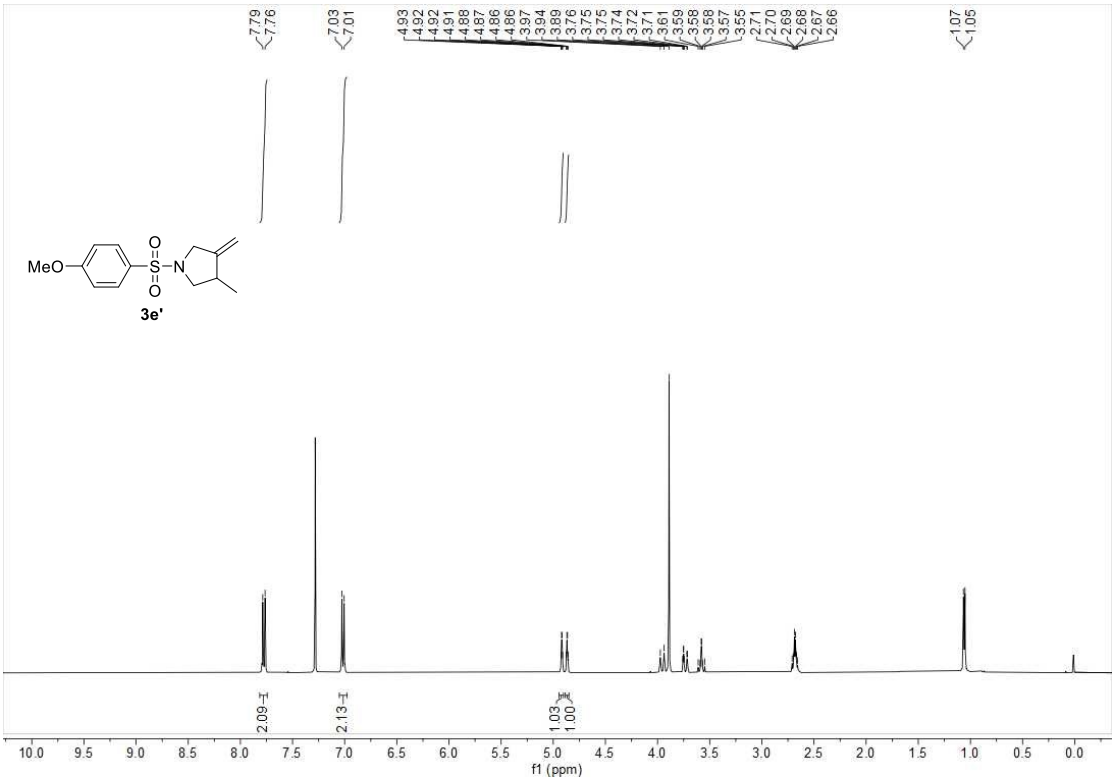


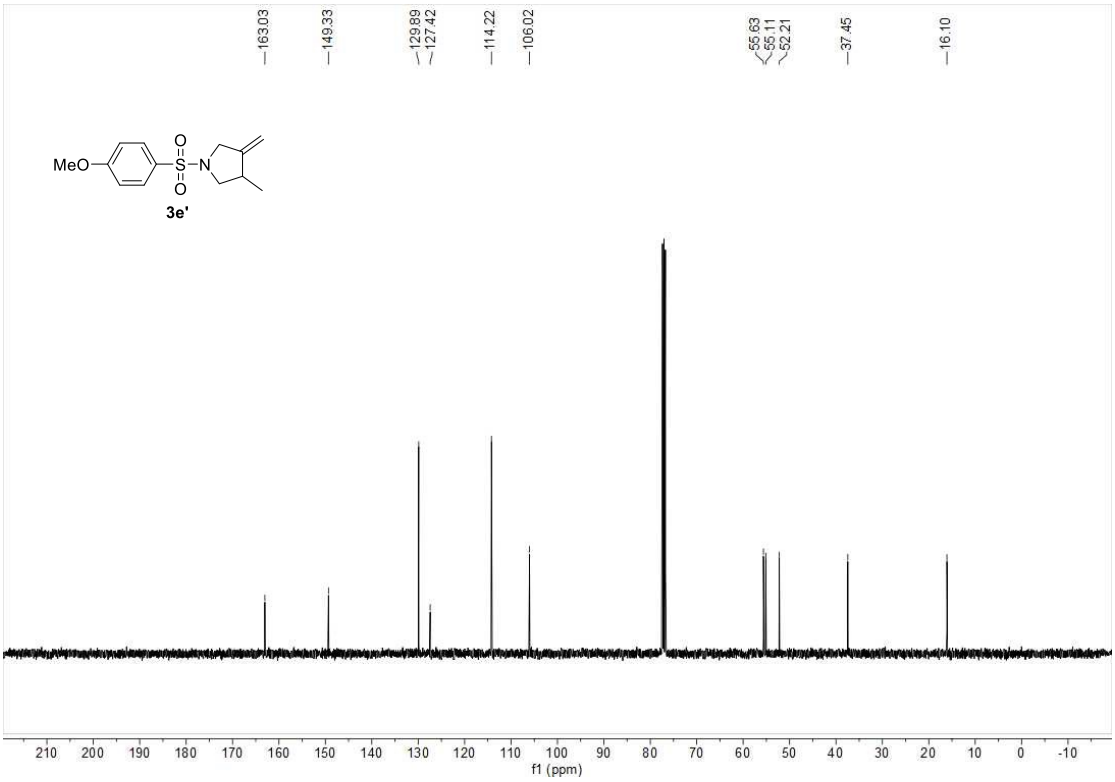
1-([1,1'-biphenyl]-4-ylsulfonyl)-3-methyl-4-methylenepyrrolidine (3d')



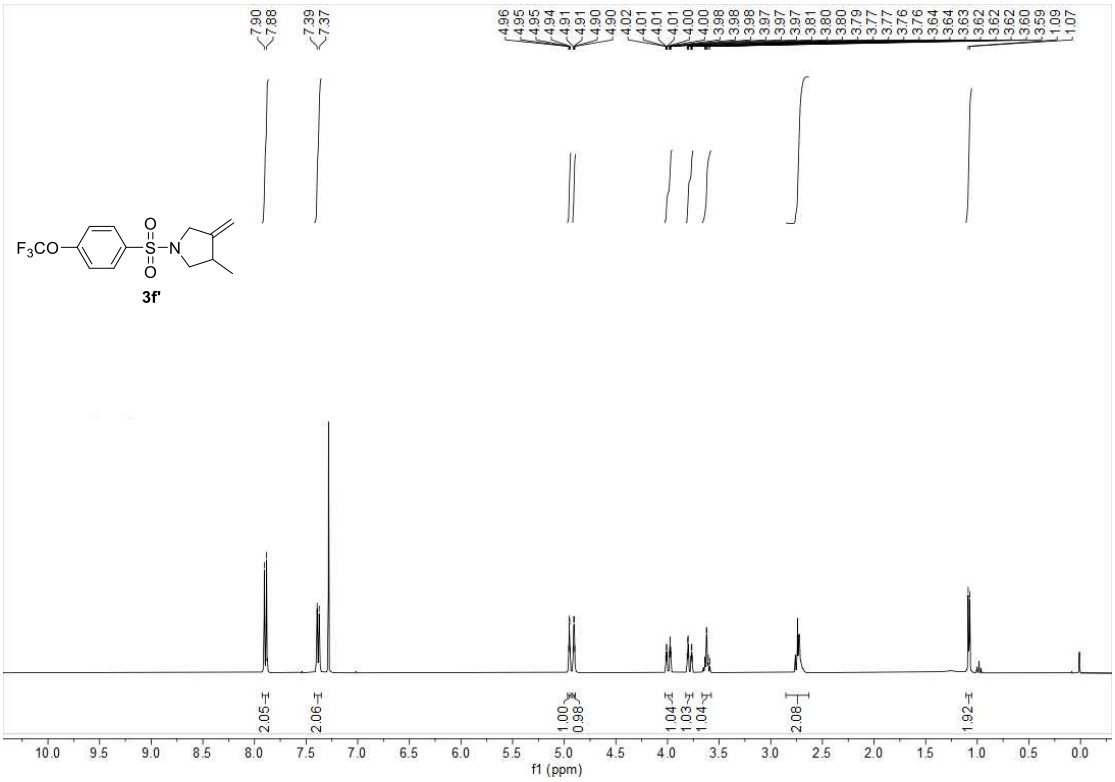


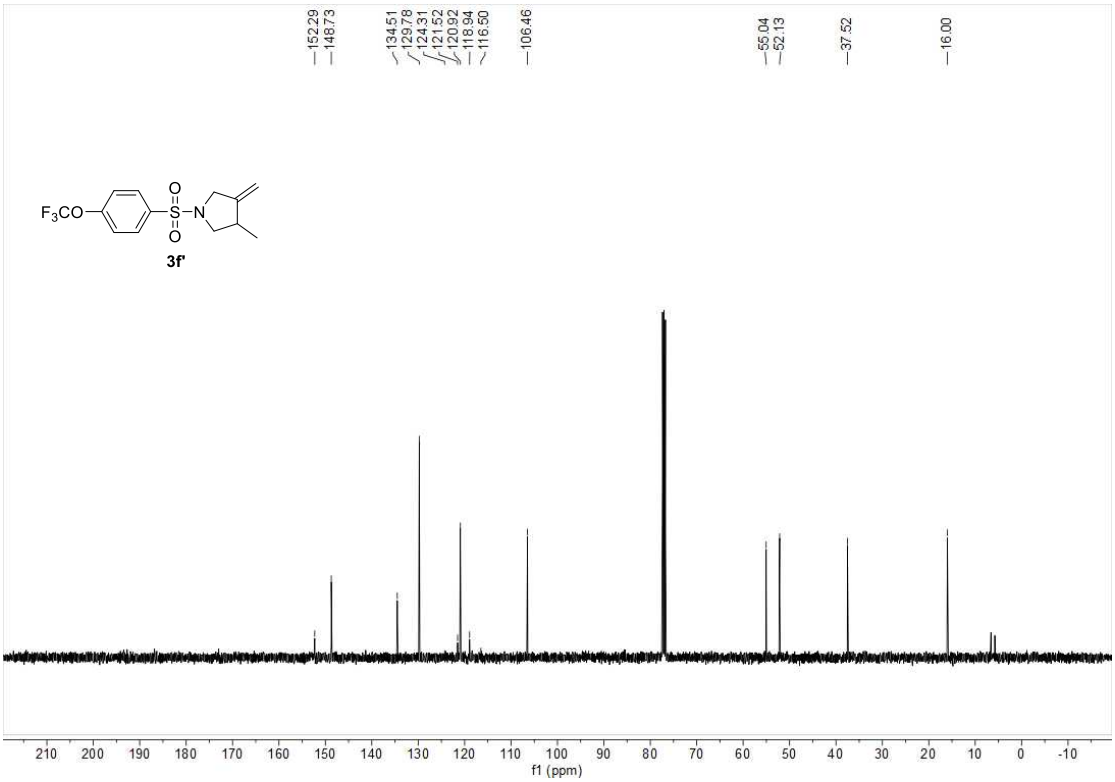
1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3e')

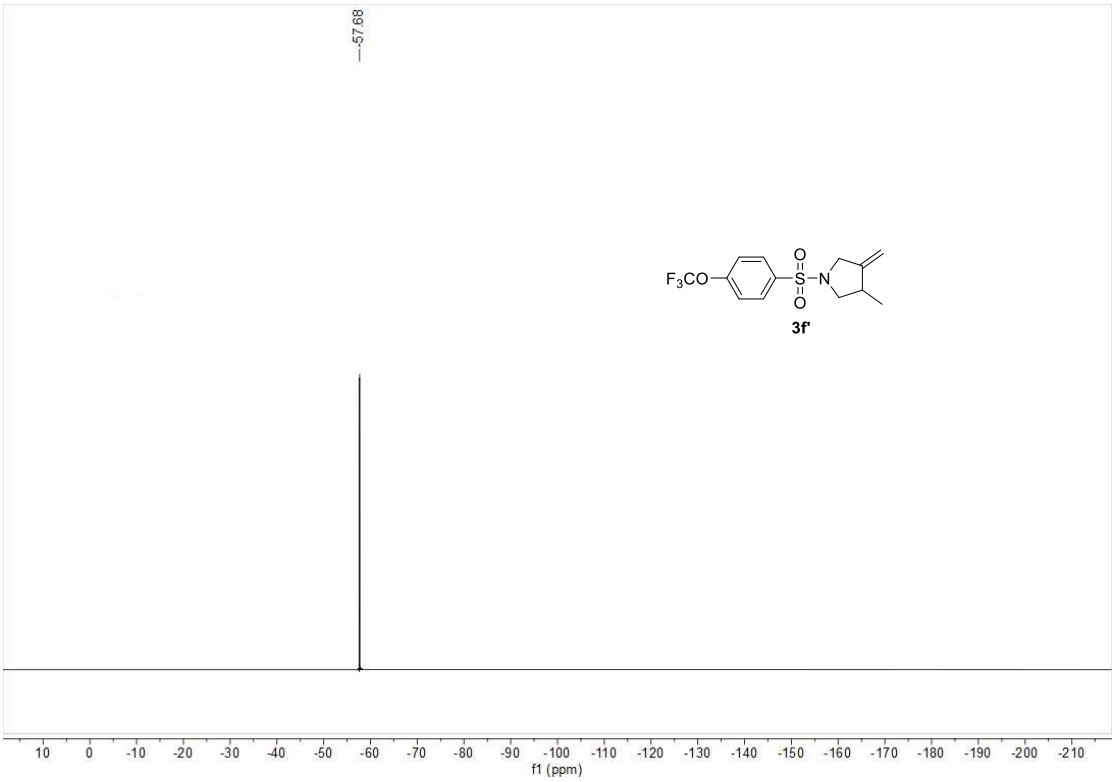




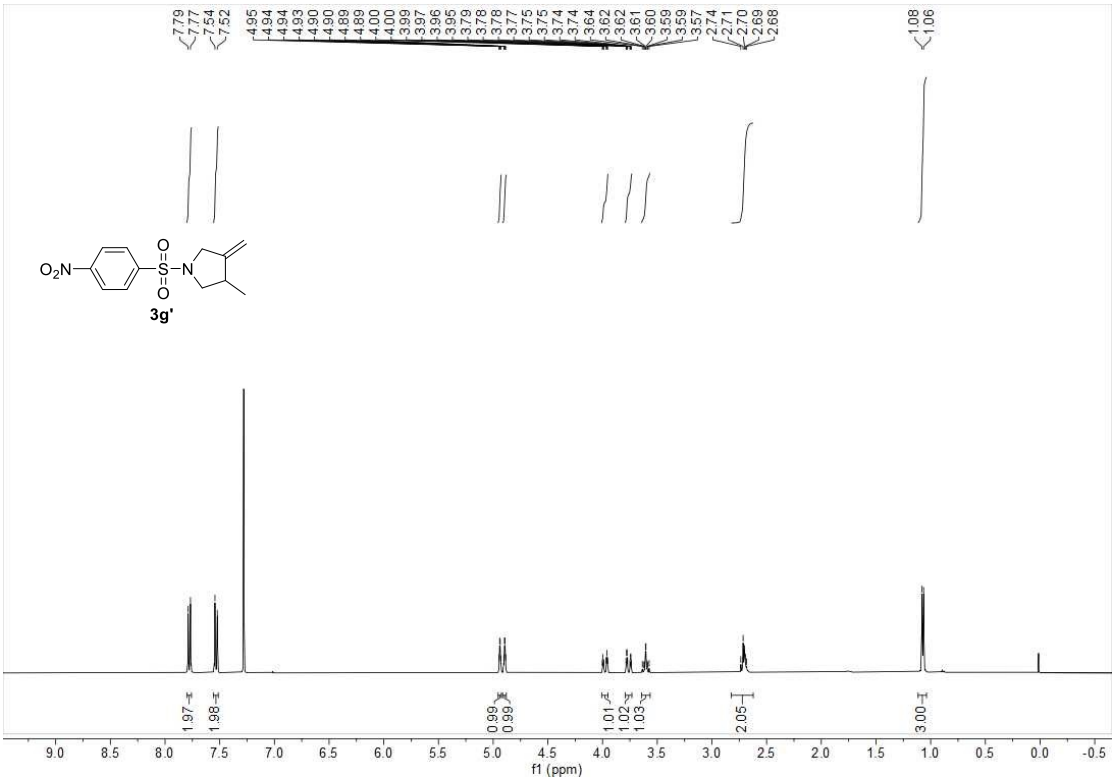
3-methyl-4-methylene-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (3f')

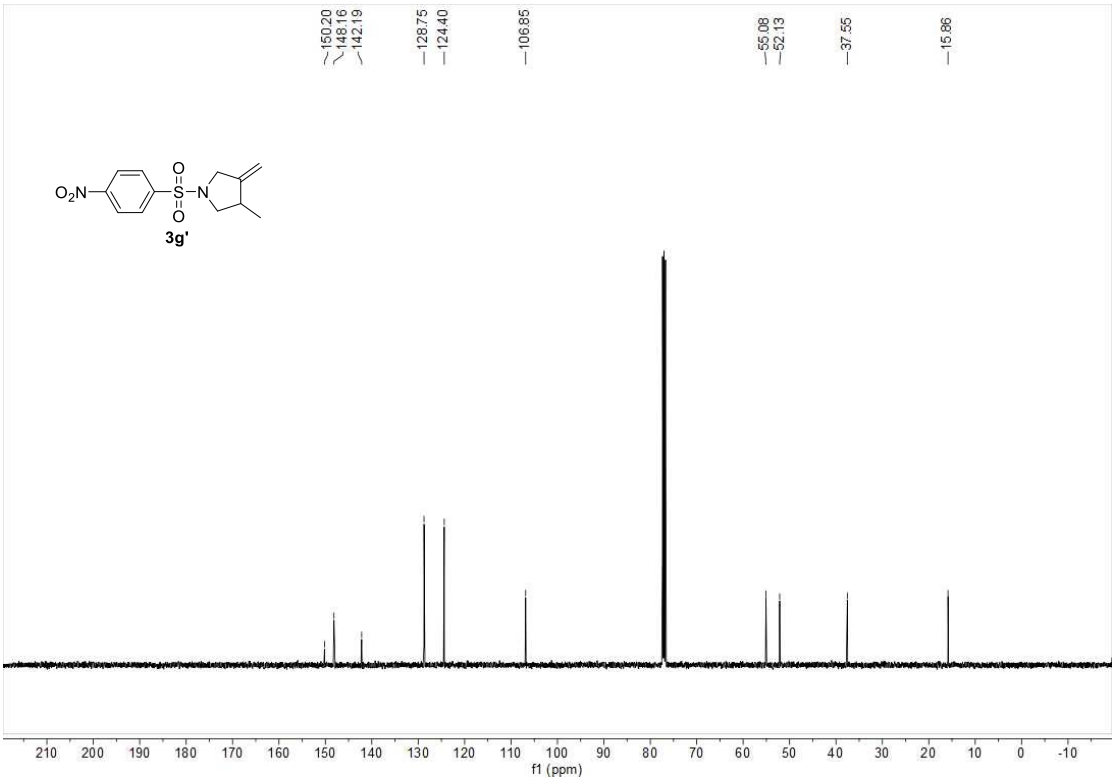




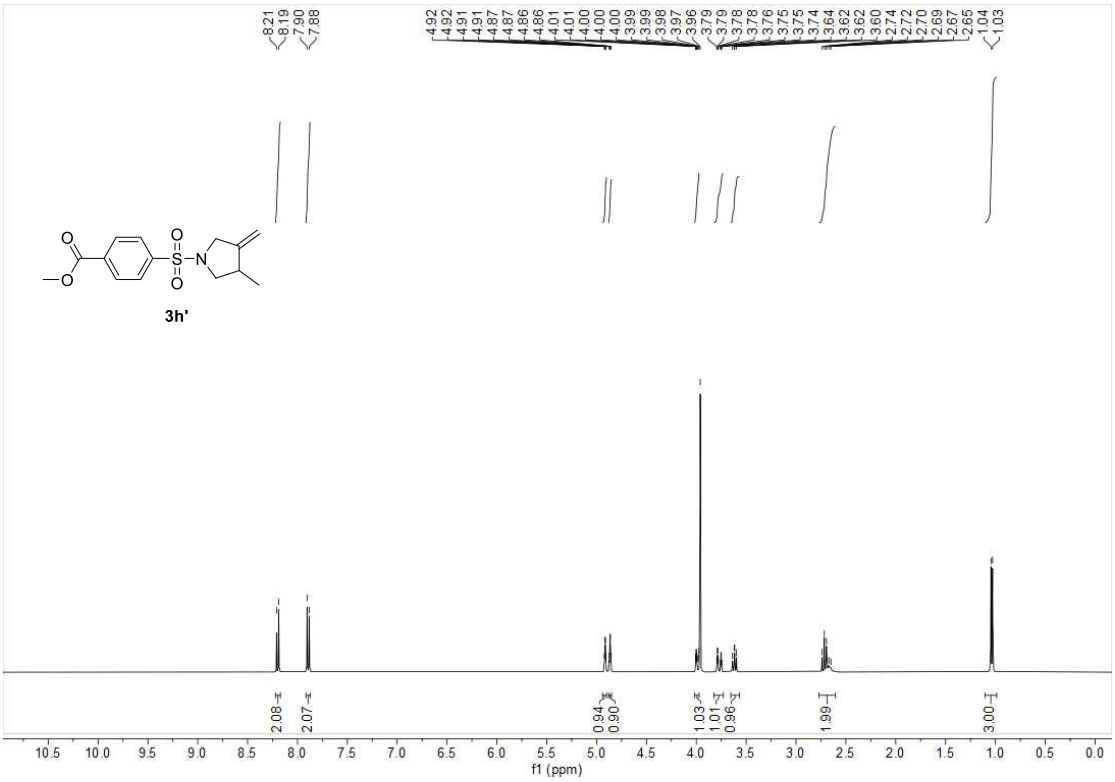


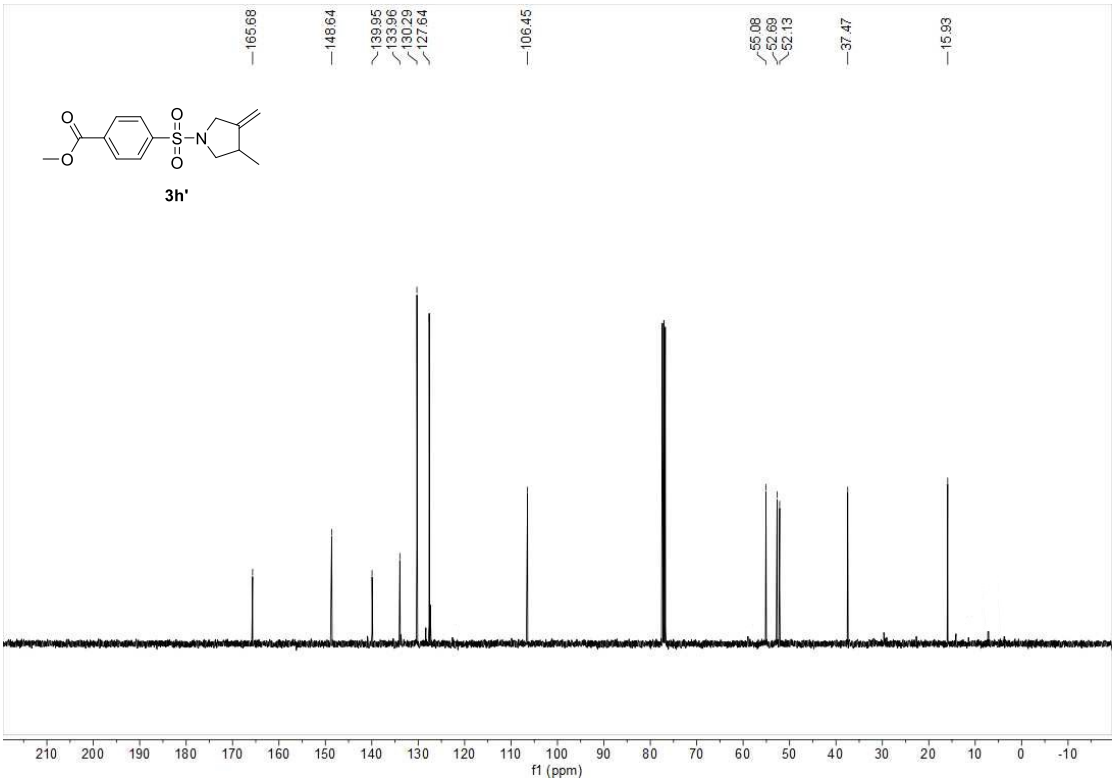
3-methyl-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidine (3g')



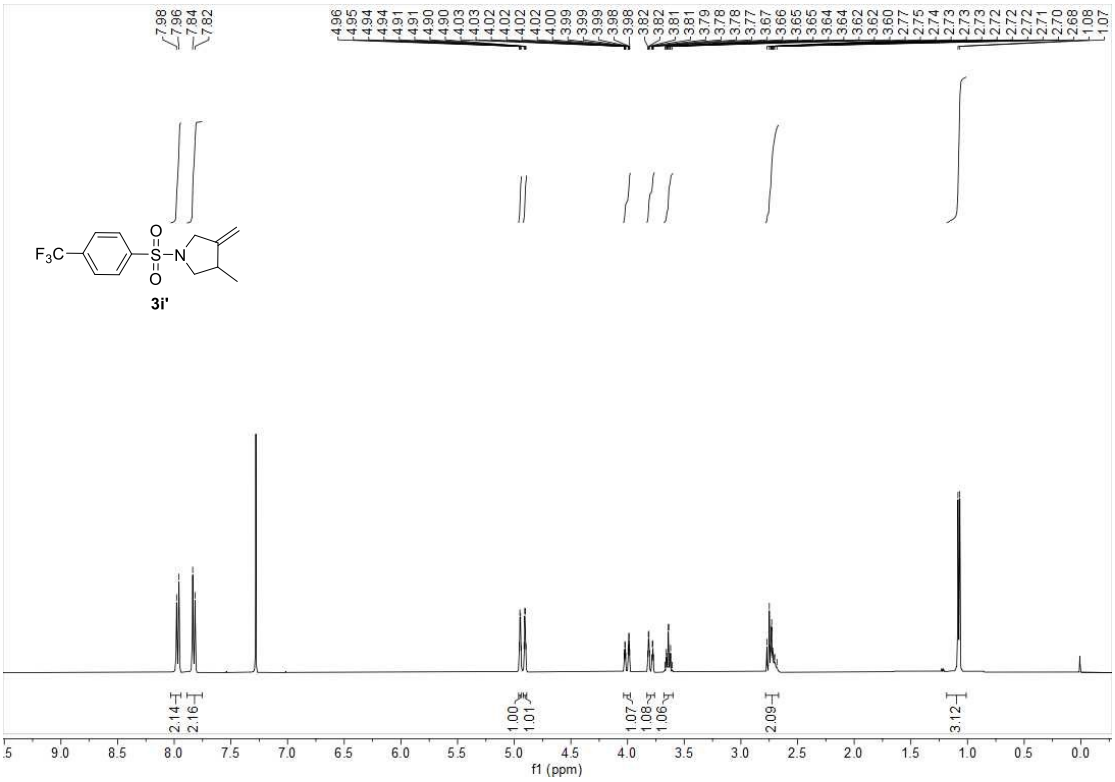


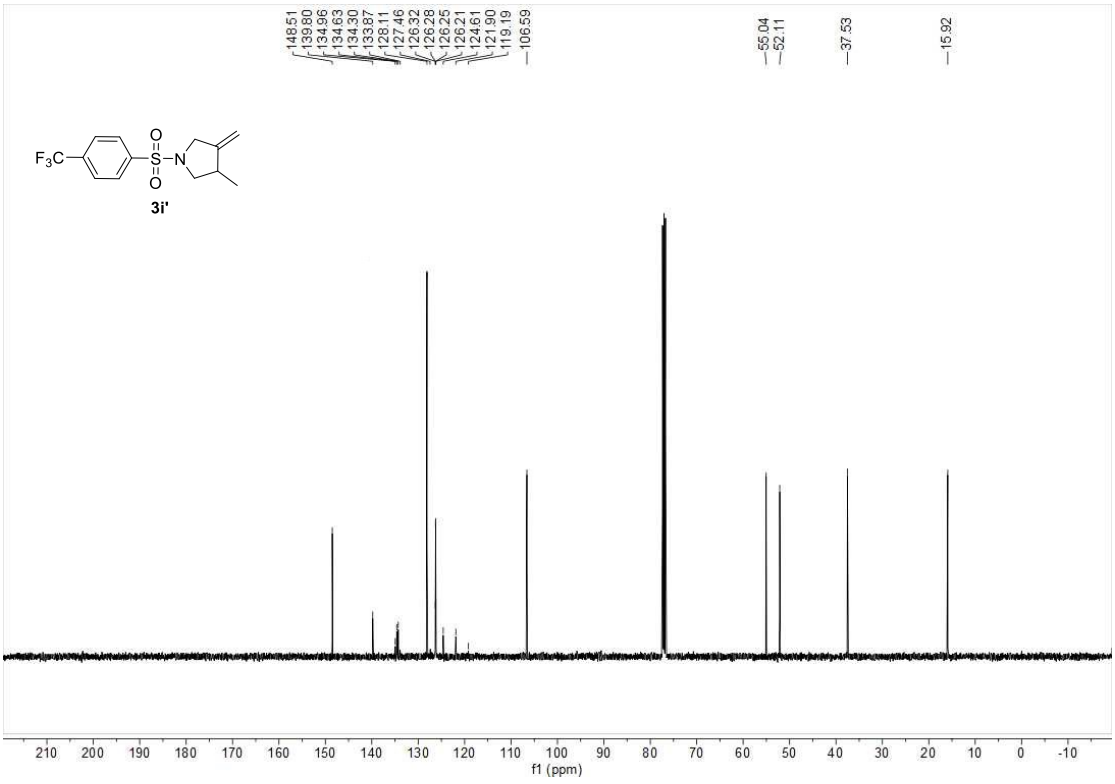
methyl 4-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)benzoate (3h')





3-methyl-4-methylene-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3i')

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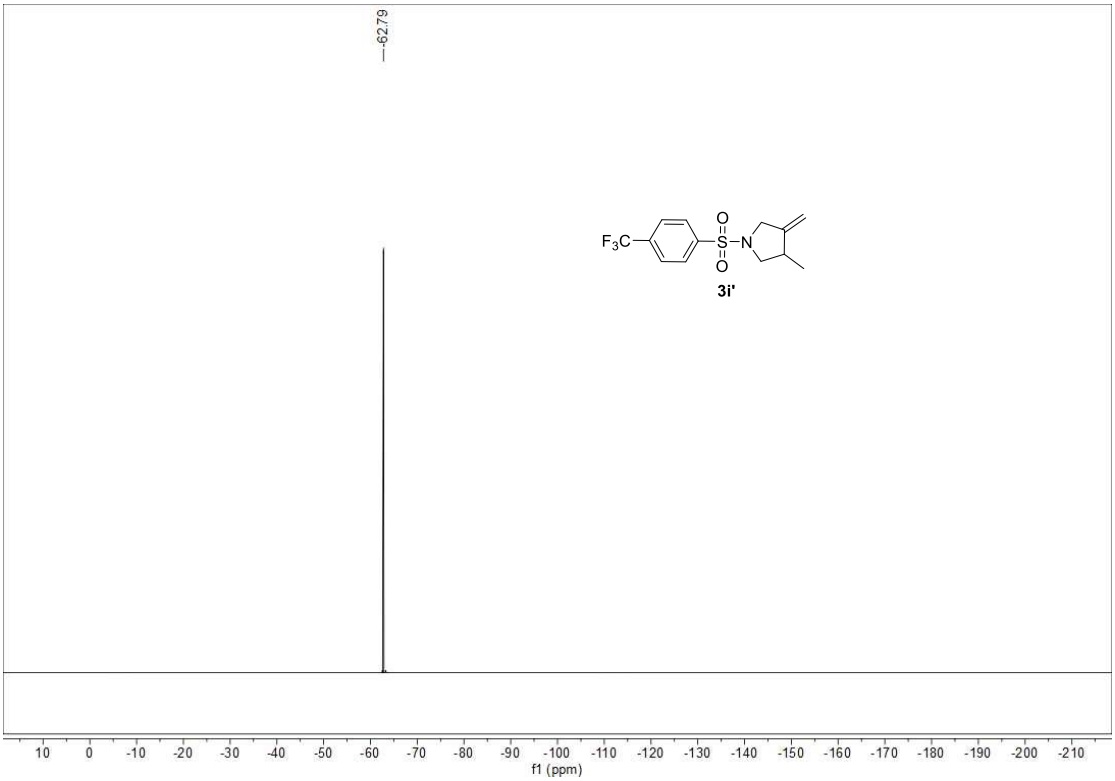
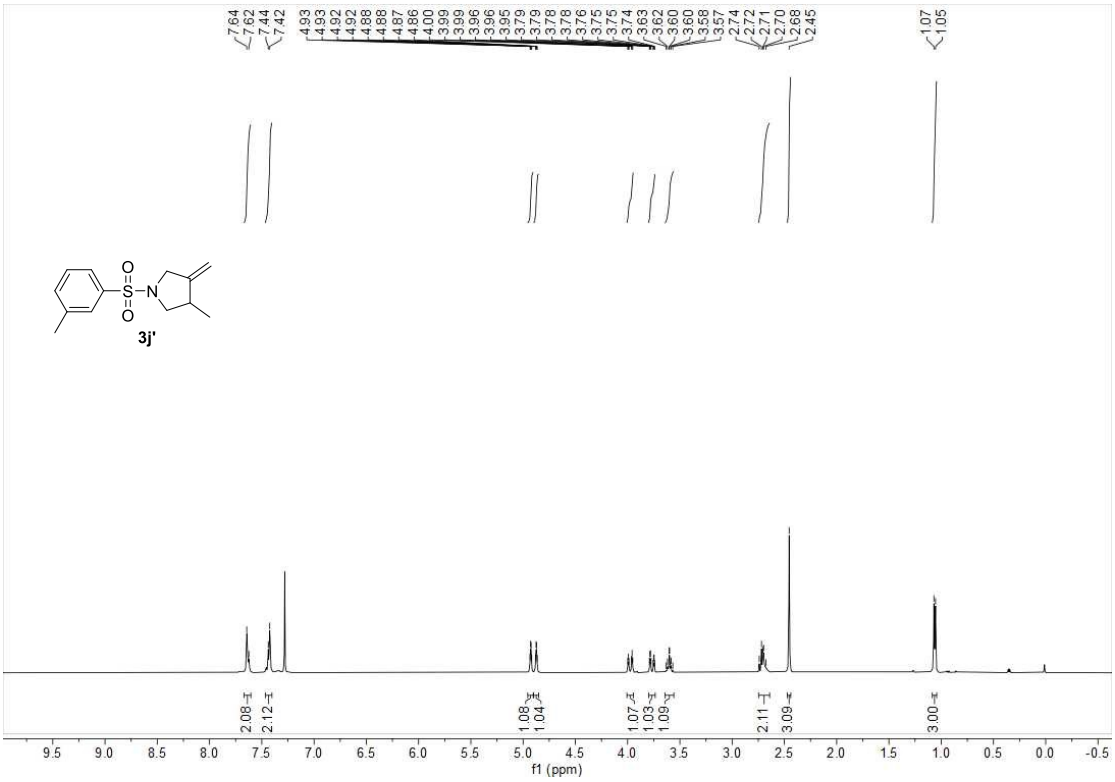
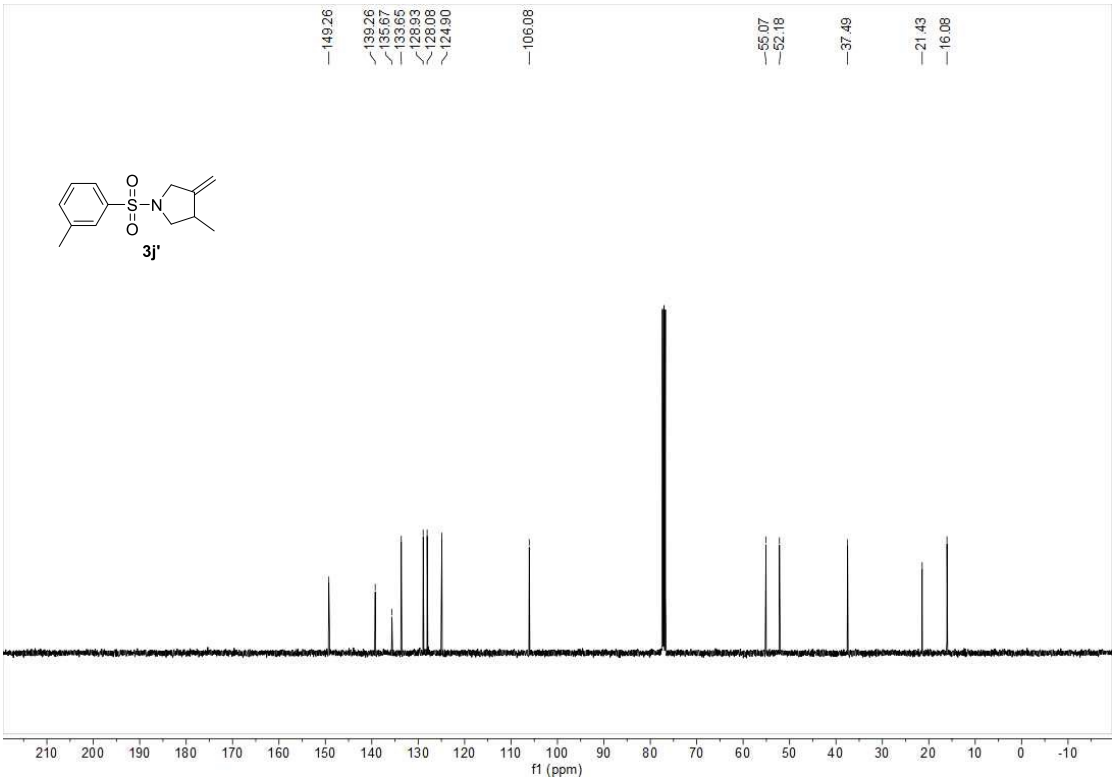
F3C
O
S
N
O
3i'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

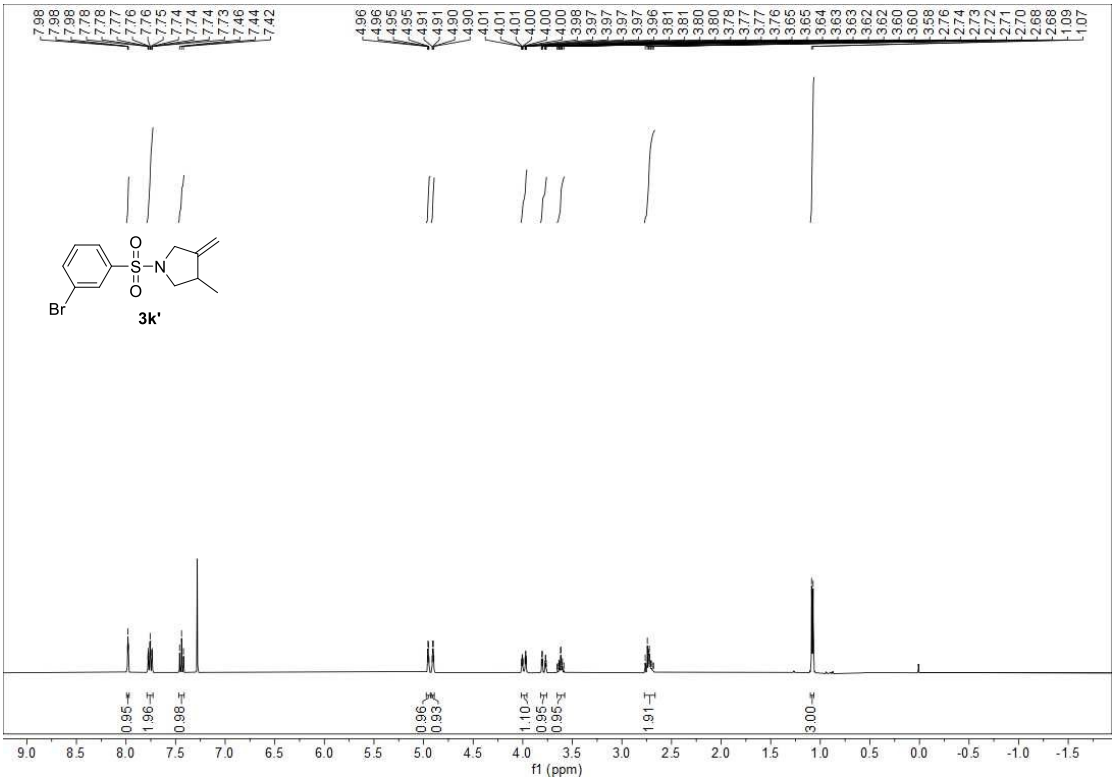

-62.79
F3C
O
S
N
O
3i'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

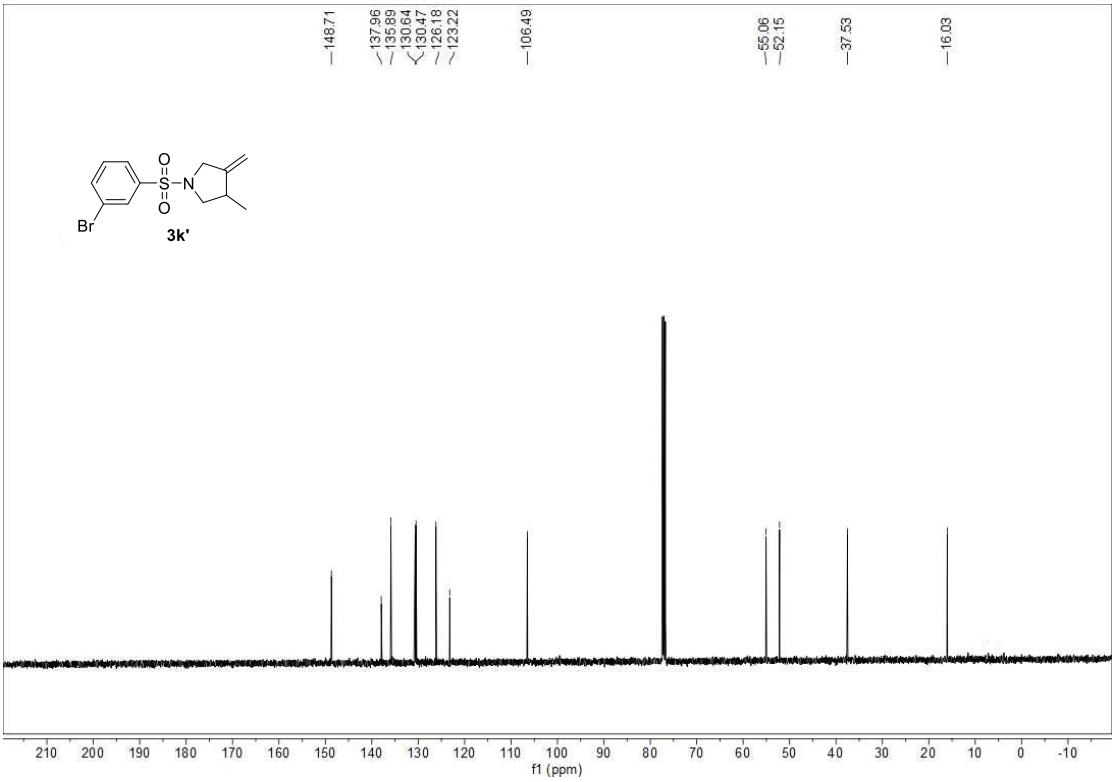
3-methyl-4-methylene-1-(m-tolylsulfonyl)pyrrolidine (3j')



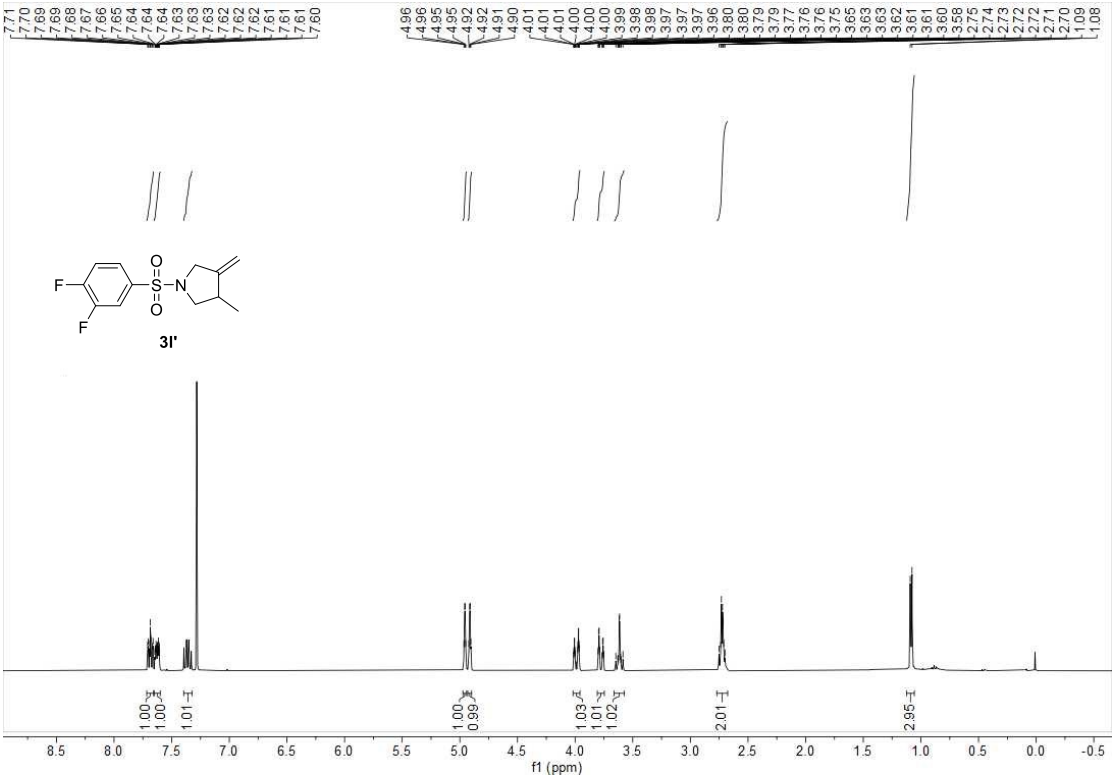


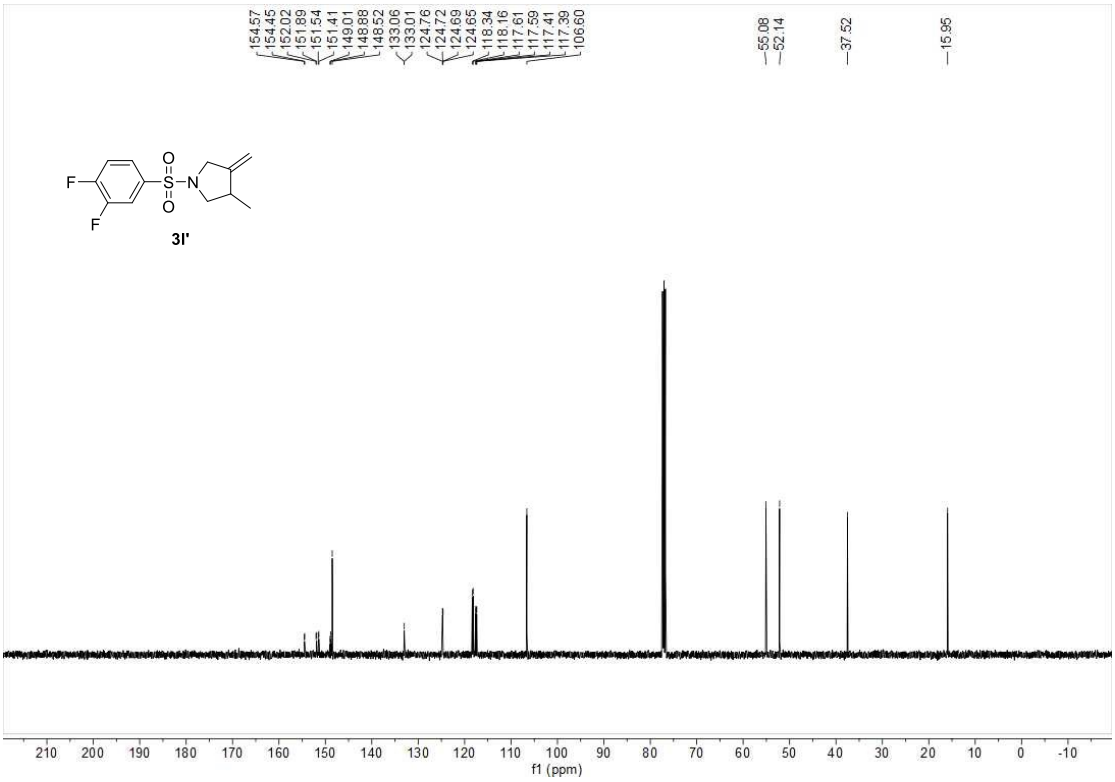
1-((3-bromophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3k')

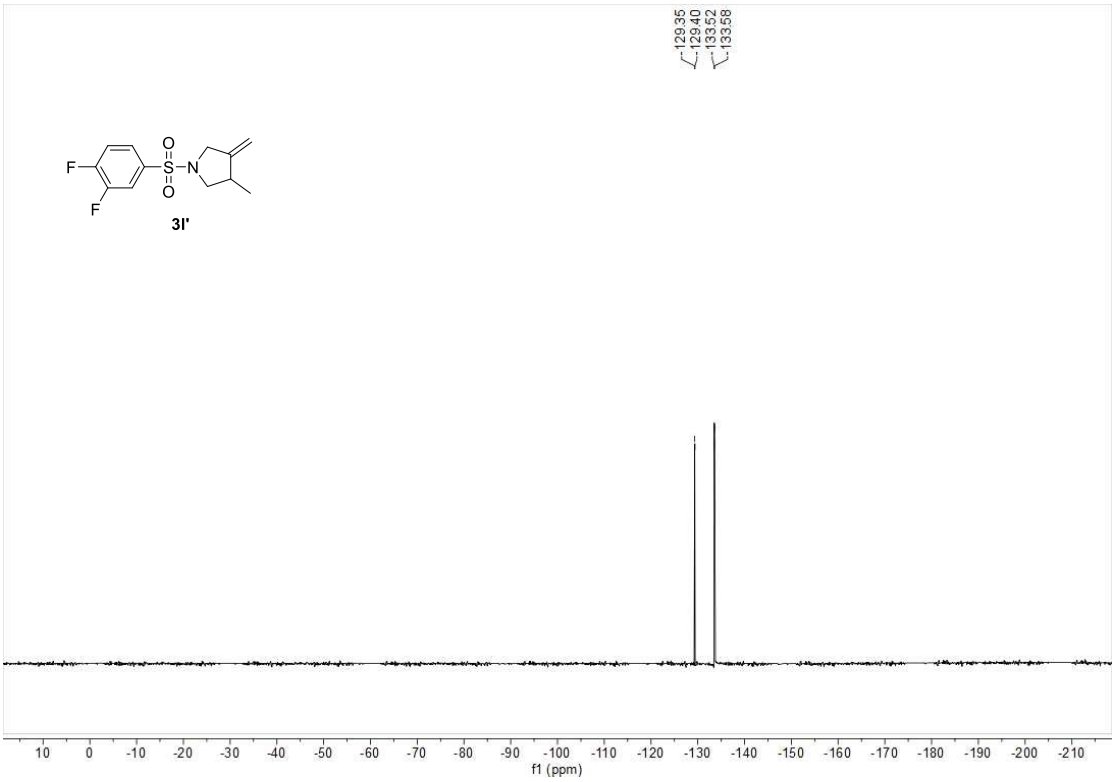




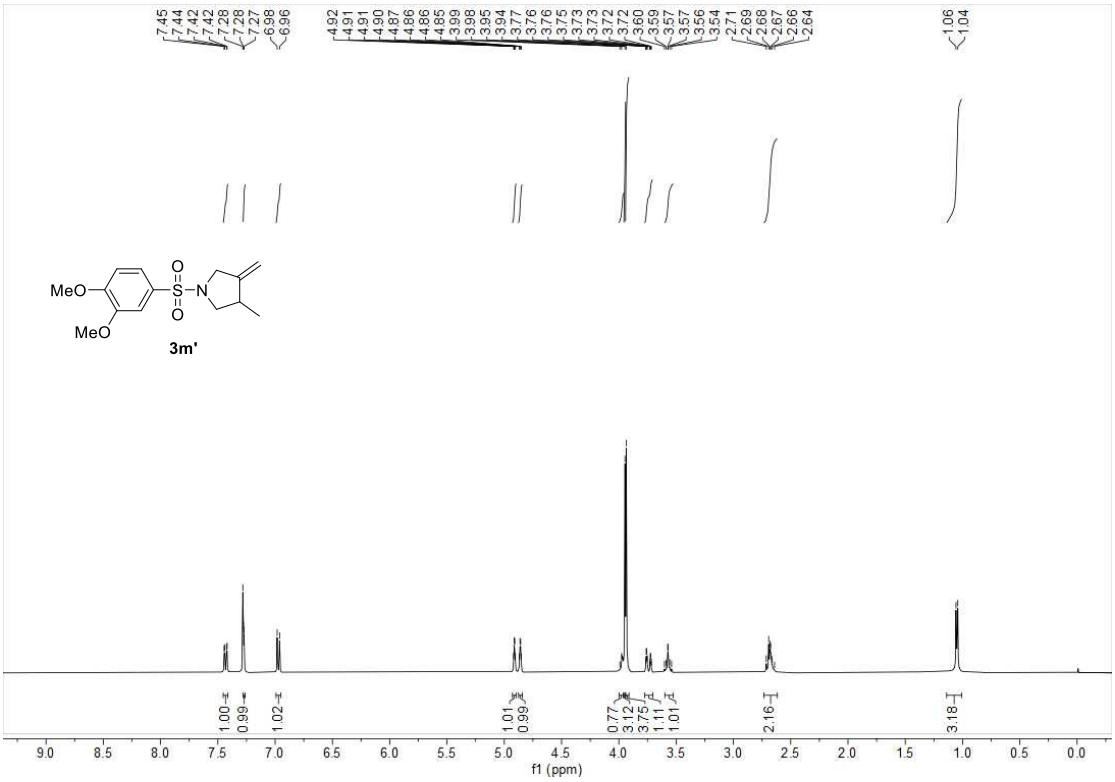
1-((3,4-difluorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3l')

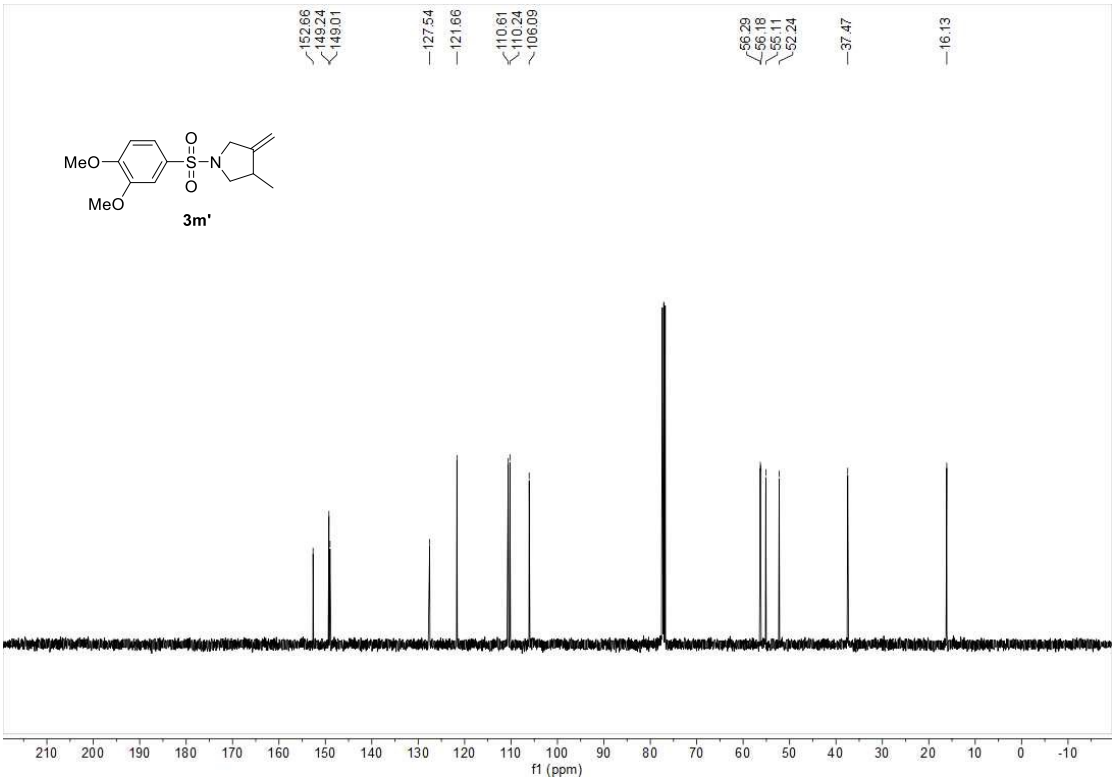




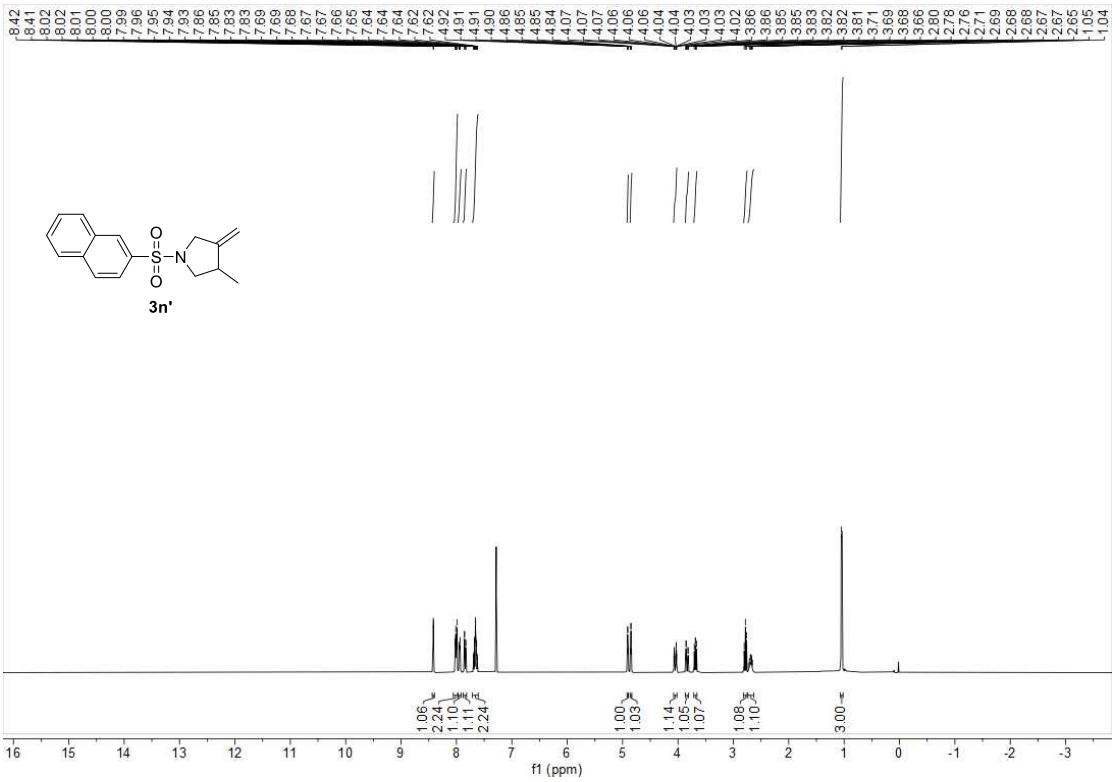


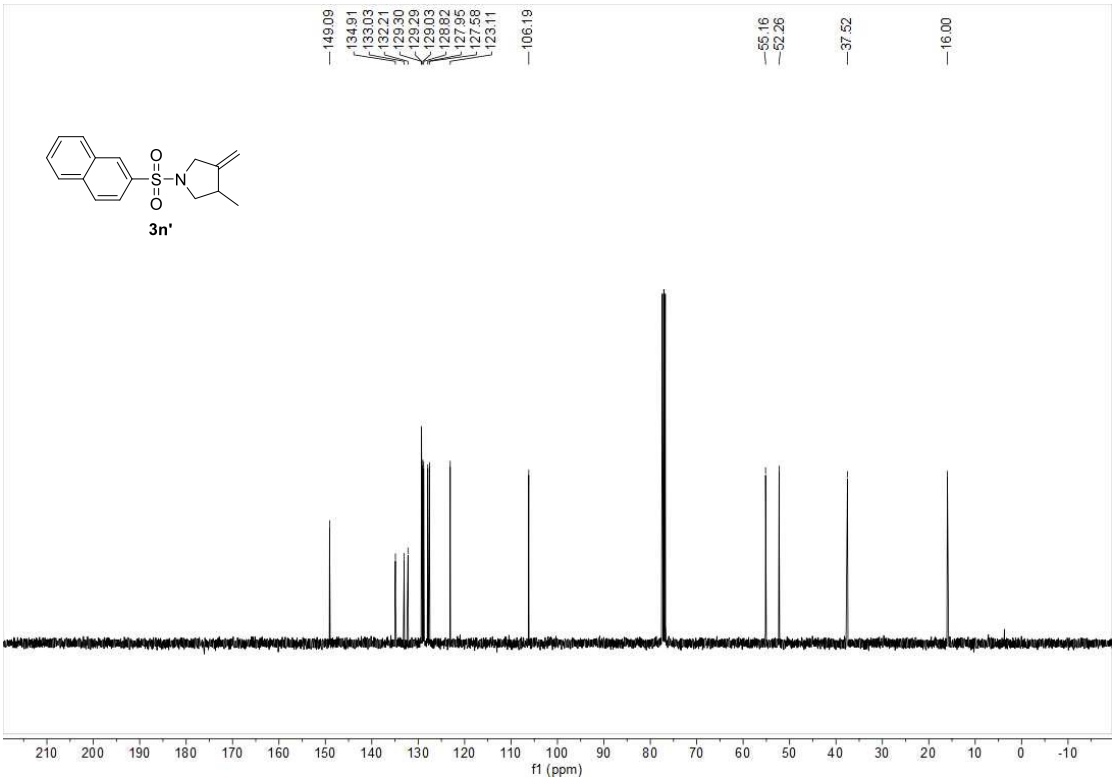
1-((3,4-dimethoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3m')



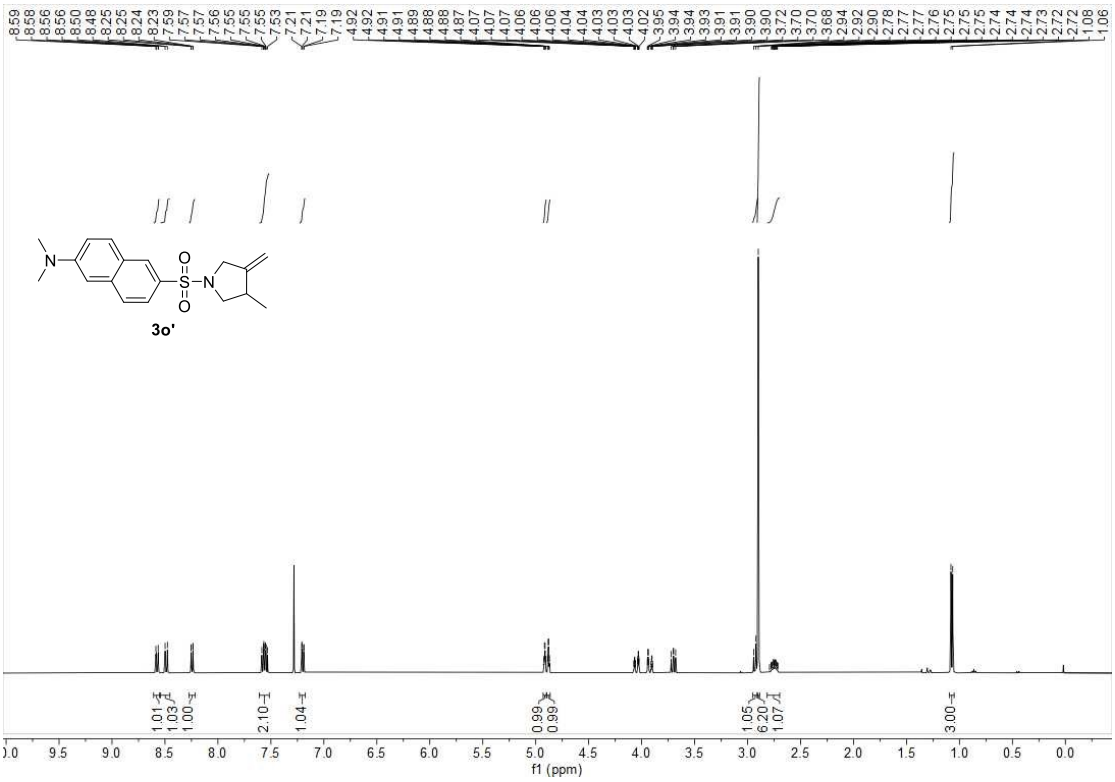


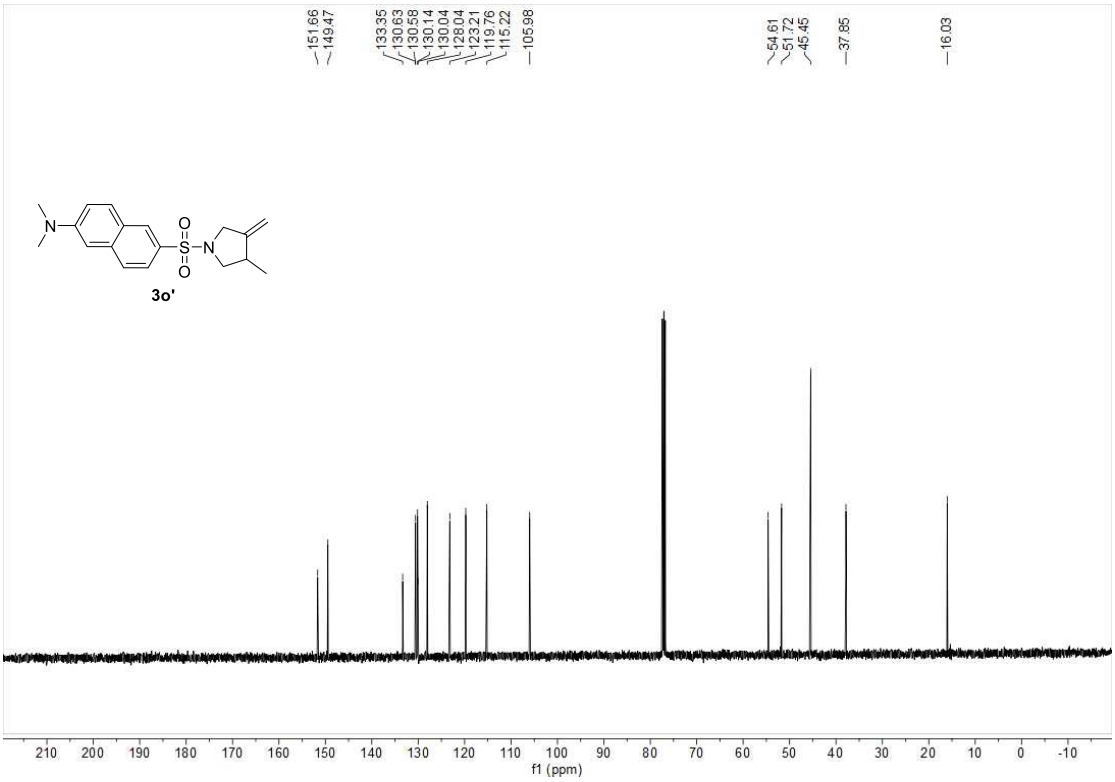
3-methyl-4-methylene-1-(naphthalen-2-ylsulfonyl)pyrrolidine (3n')



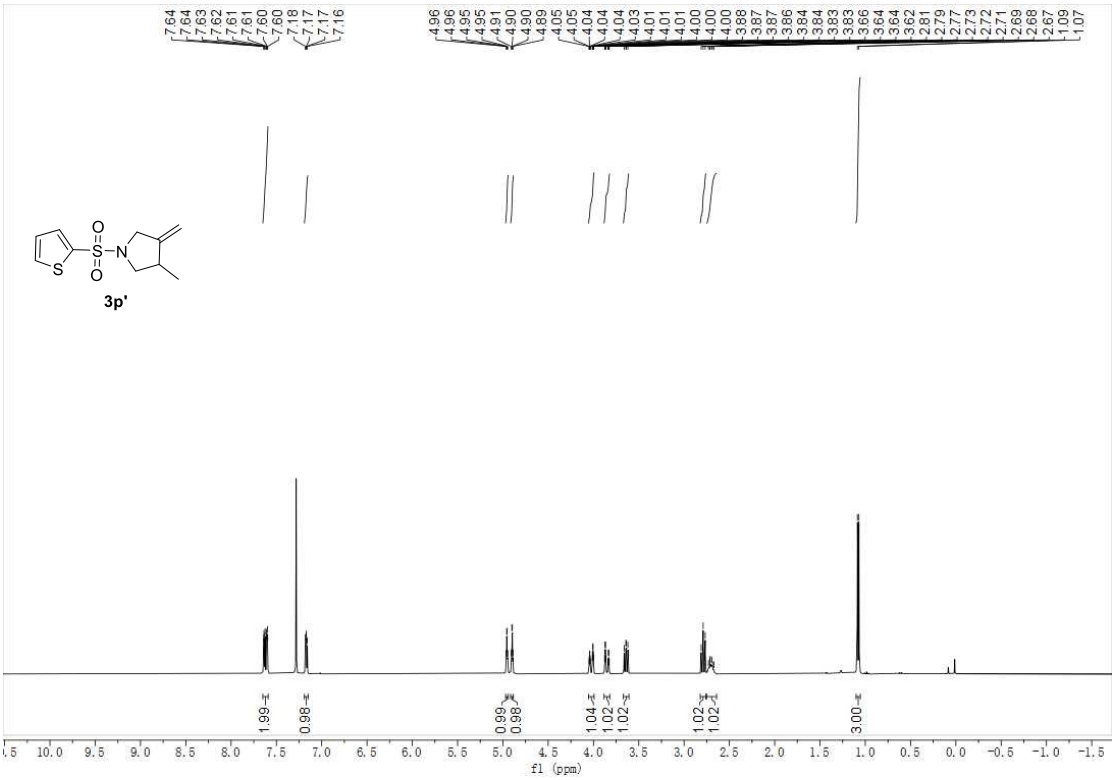


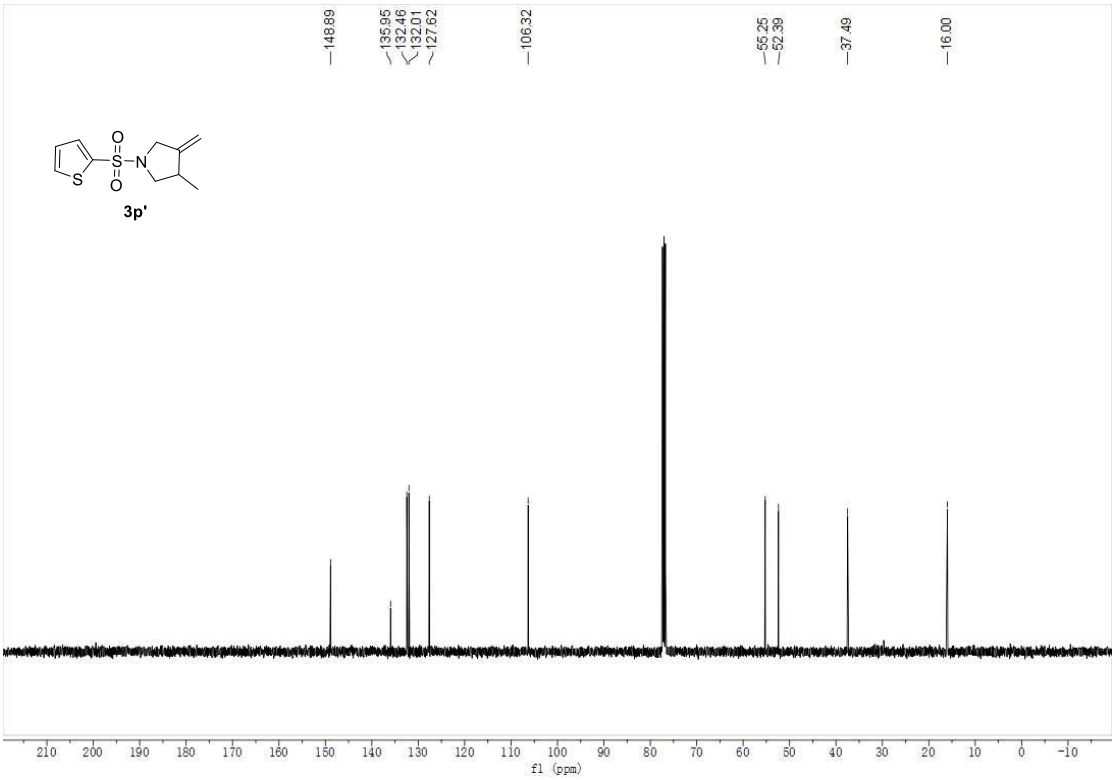
***N,N*-dimethyl-6-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)naphthalen-2-amine (3o')**



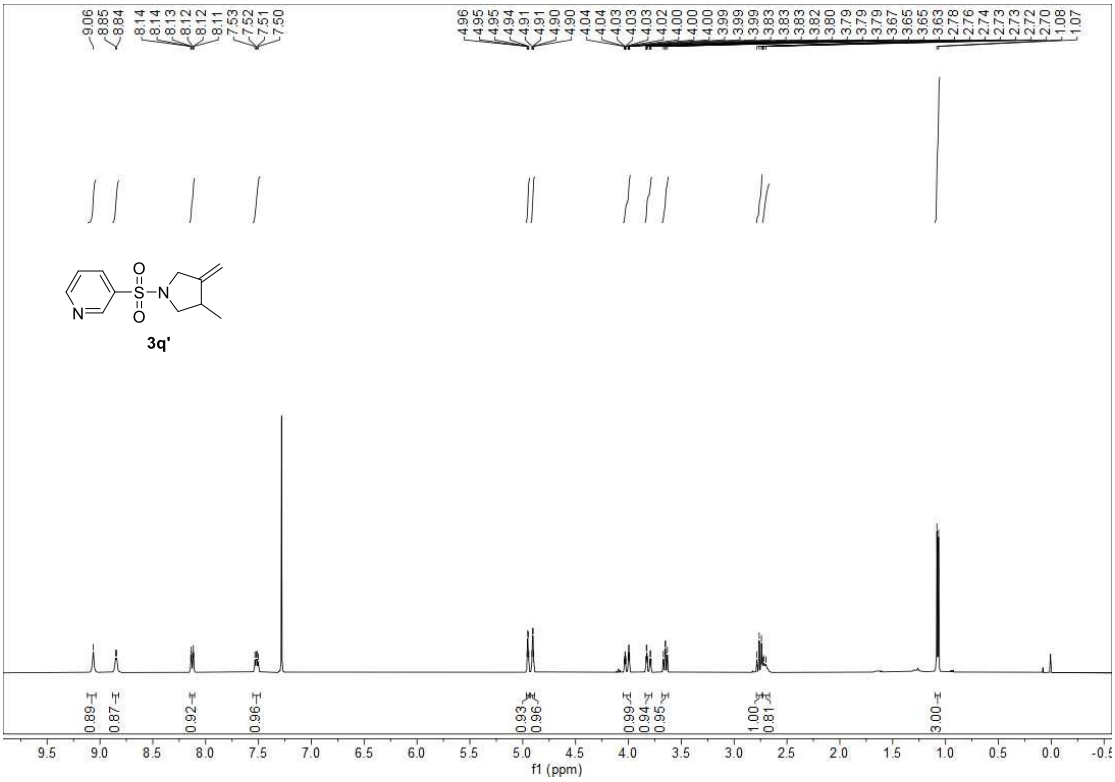


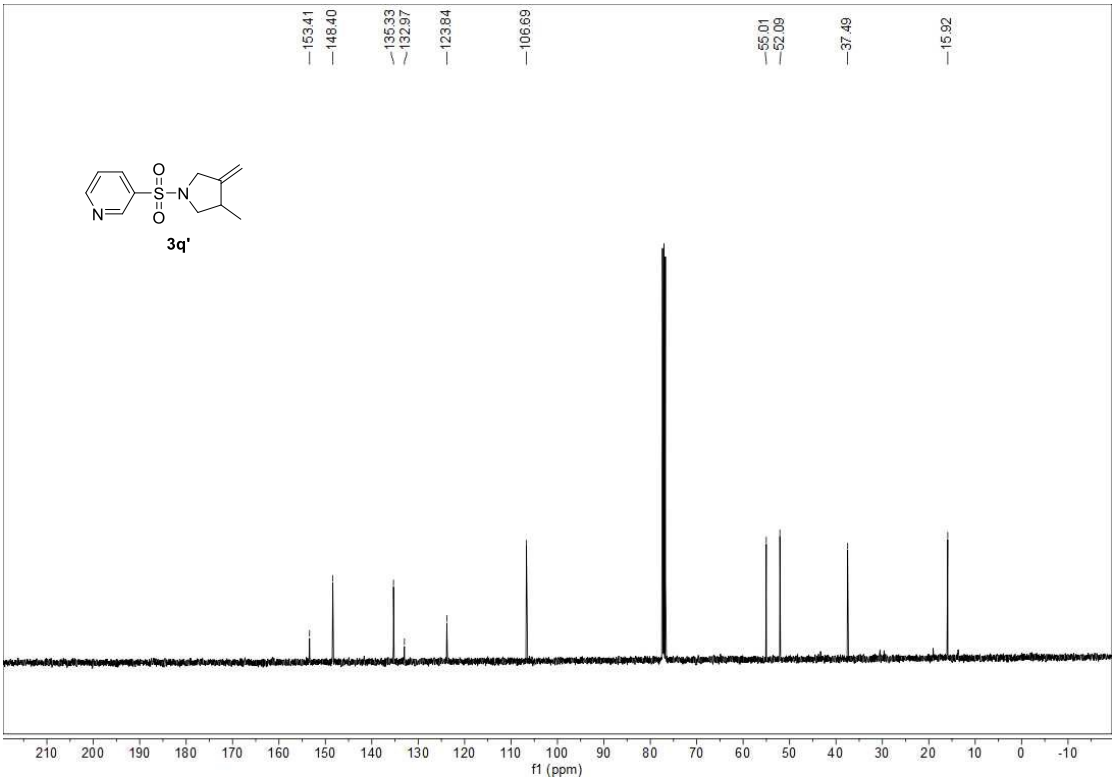
3-methyl-4-methylene-1-(thiophen-2-ylsulfonyl)pyrrolidine (3p')



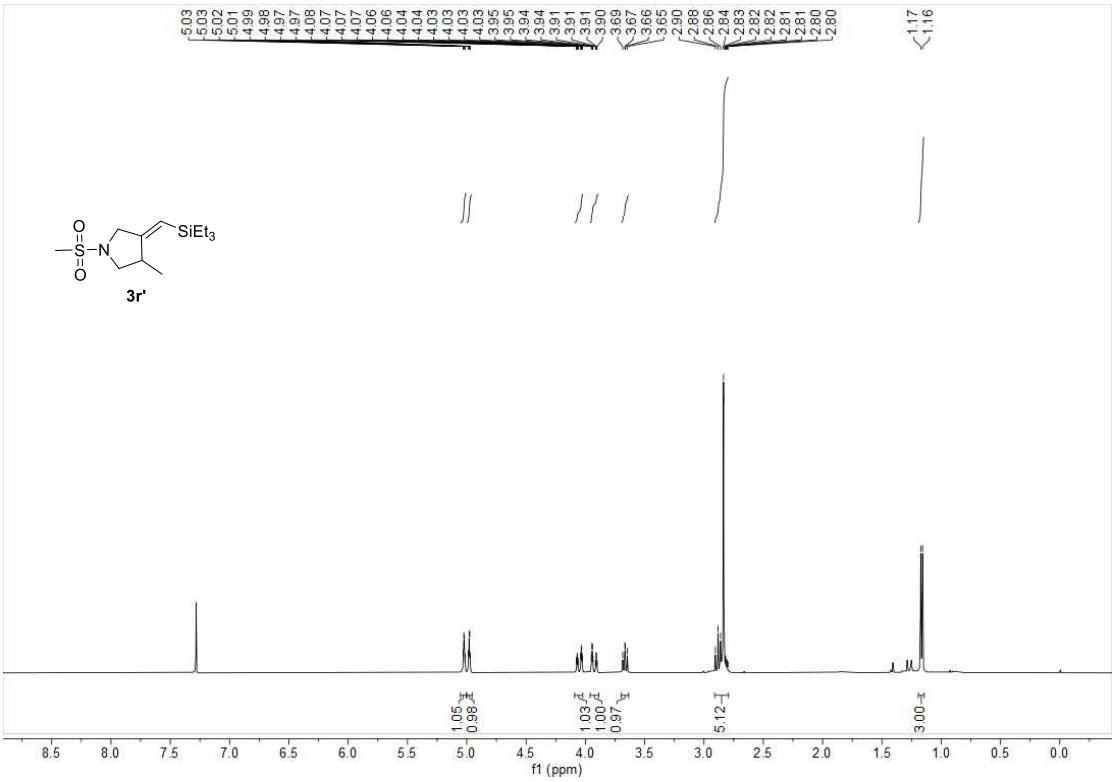


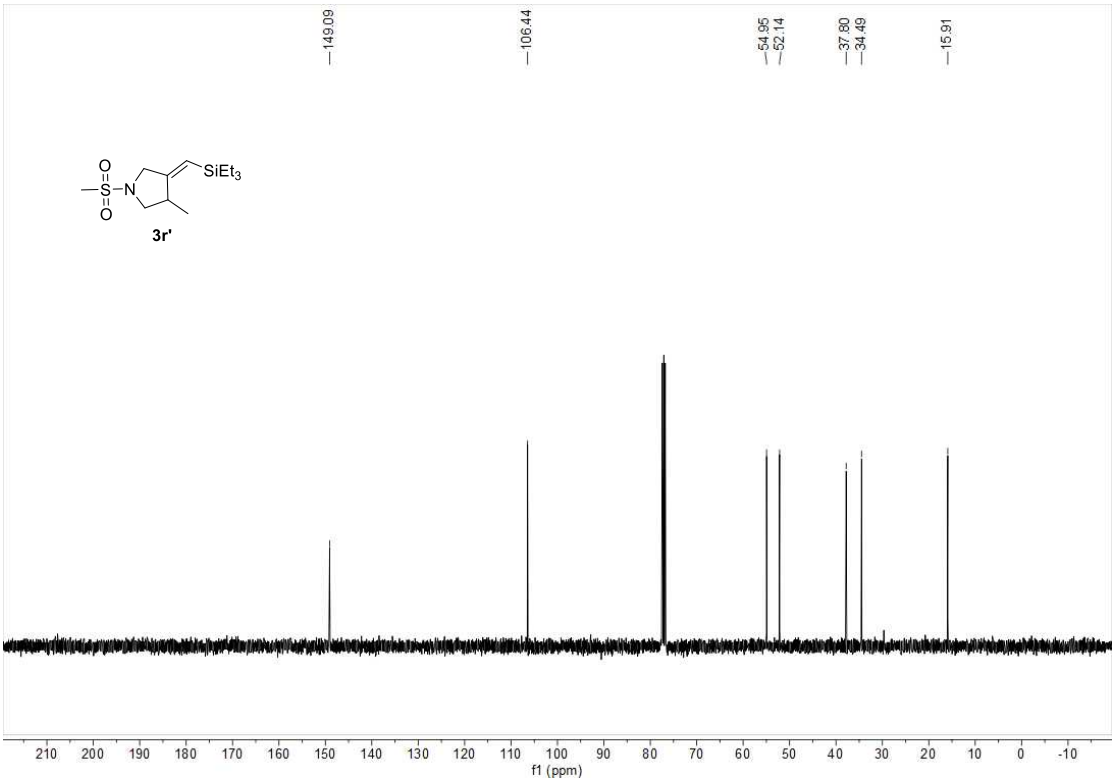
3-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)pyridine (3q')



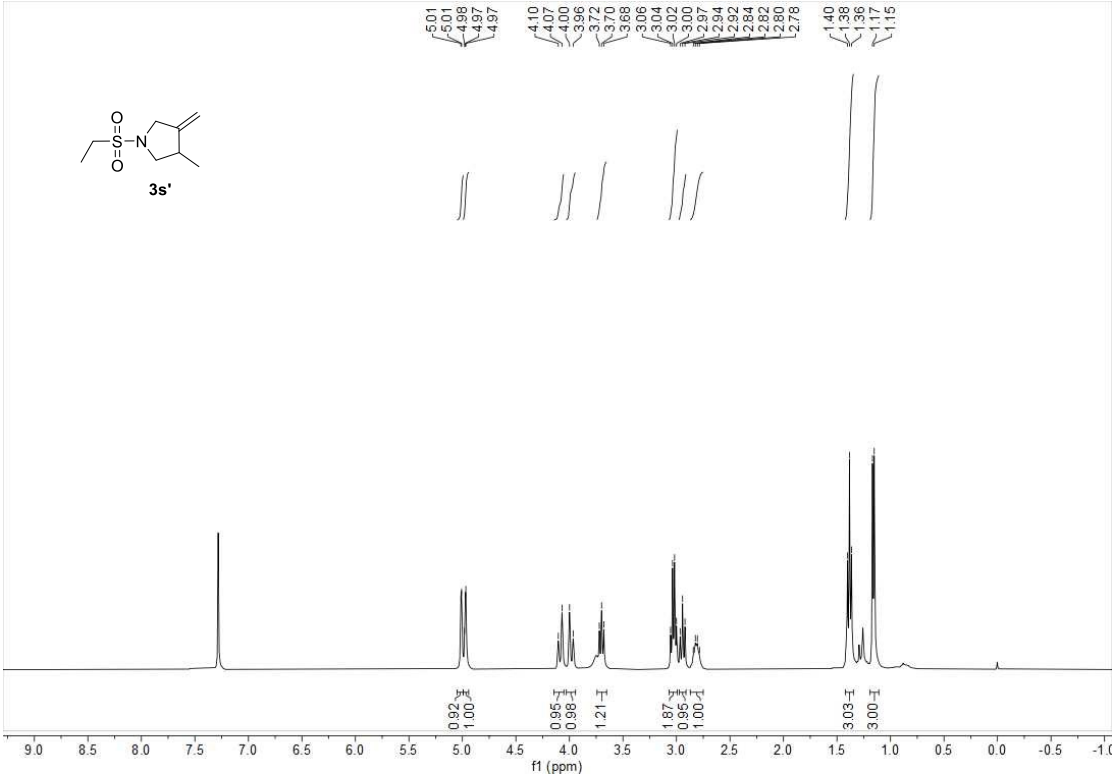


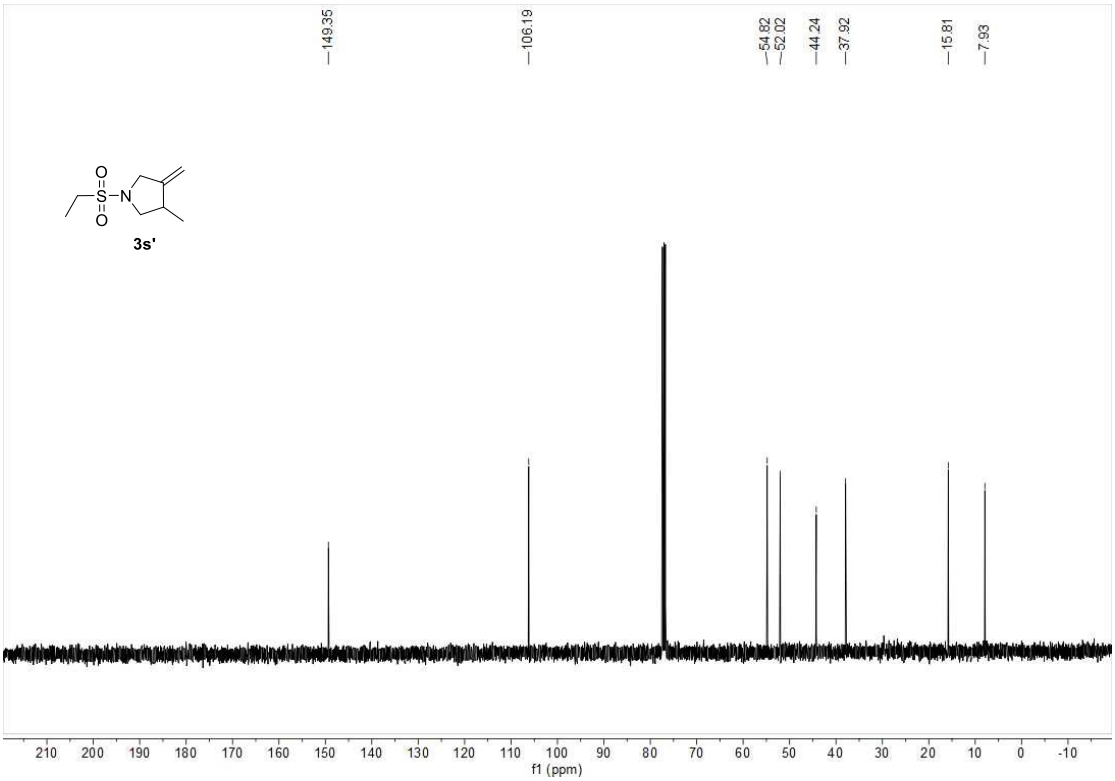
3-methyl-4-methylene-1-(methylsulfonyl)pyrrolidine (3r')



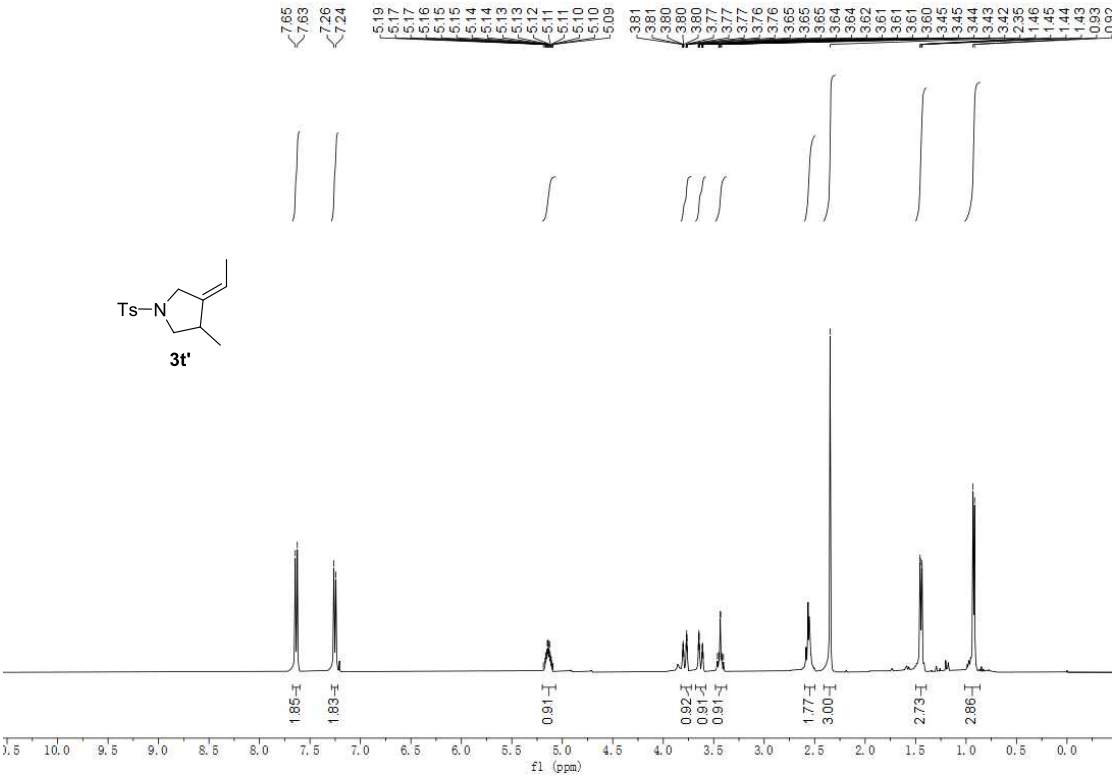


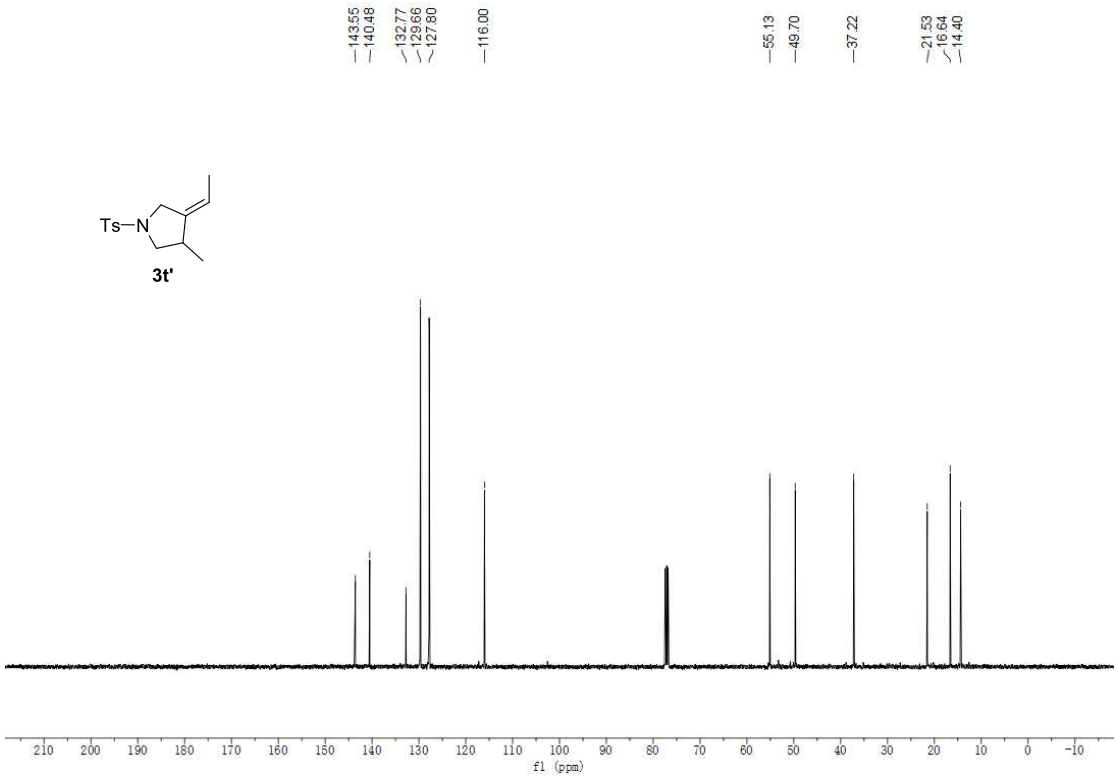
1-(ethylsulfonyl)-3-methyl-4-methylenepyrrolidine (3s')



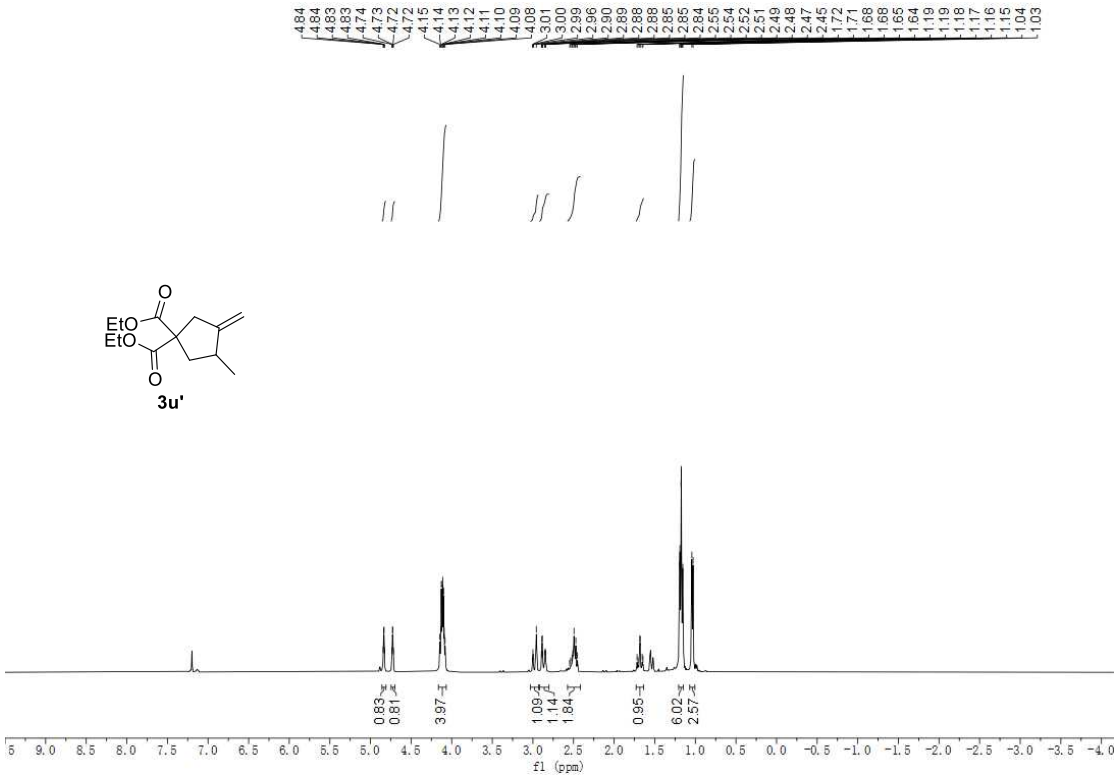


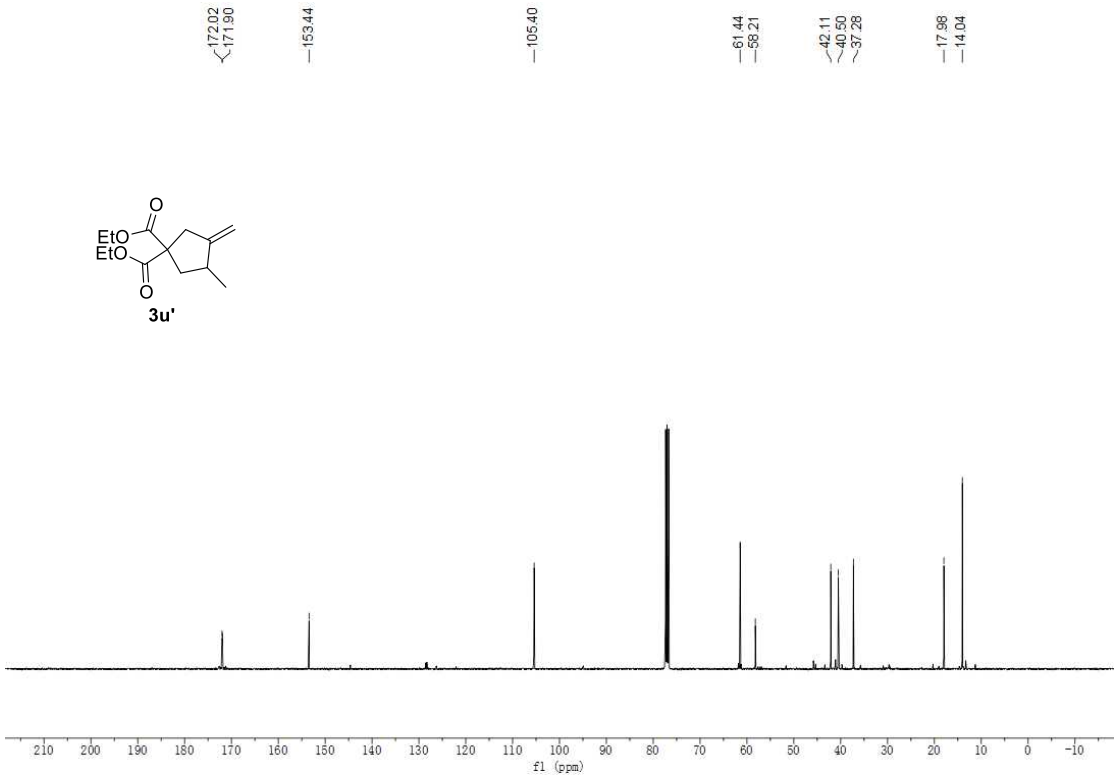
1-(4-Toluenesulfonyl)-3-(*Z*)-ethylidene-4-methylpyrrolidine (3t')



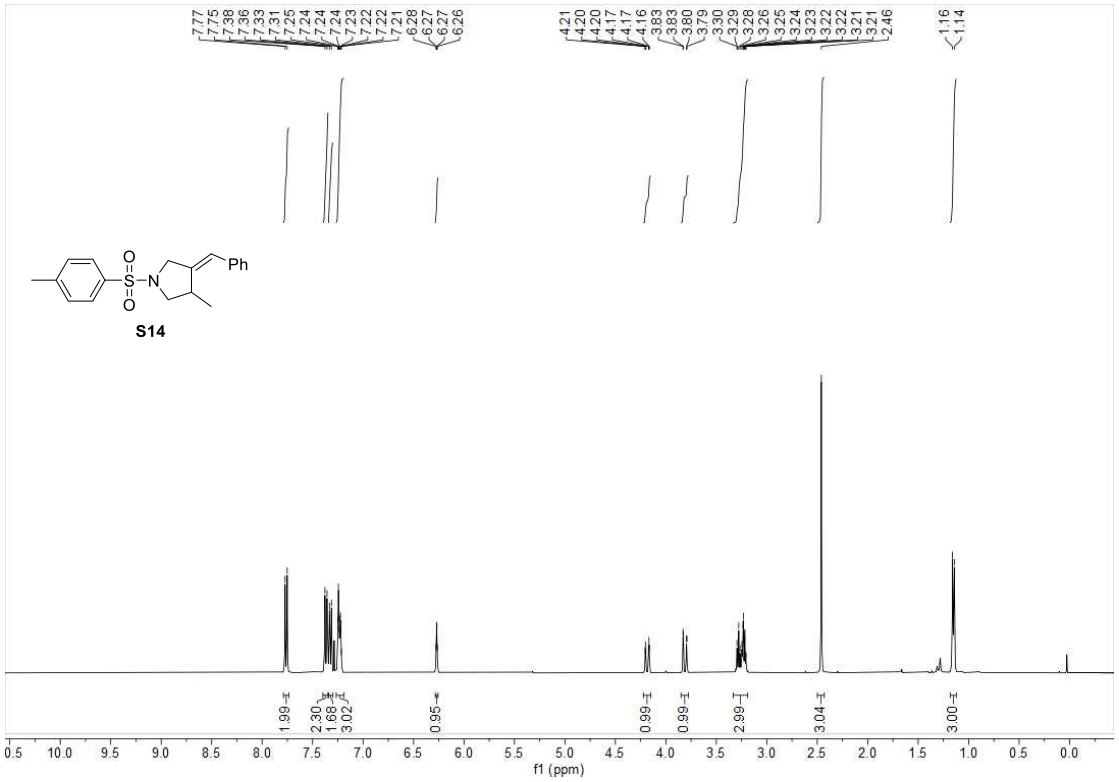


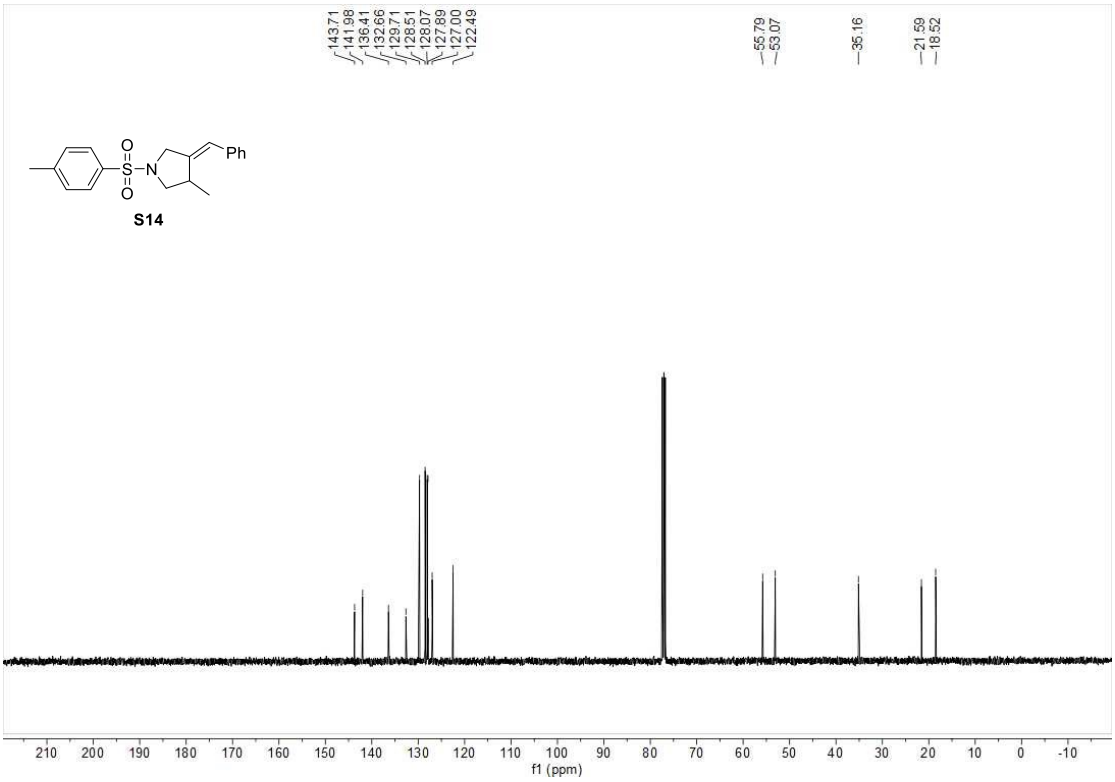
4,4-Bis(ethoxycarbonyl)-1-methylidene-2-methyl-cyclopentane (3u')





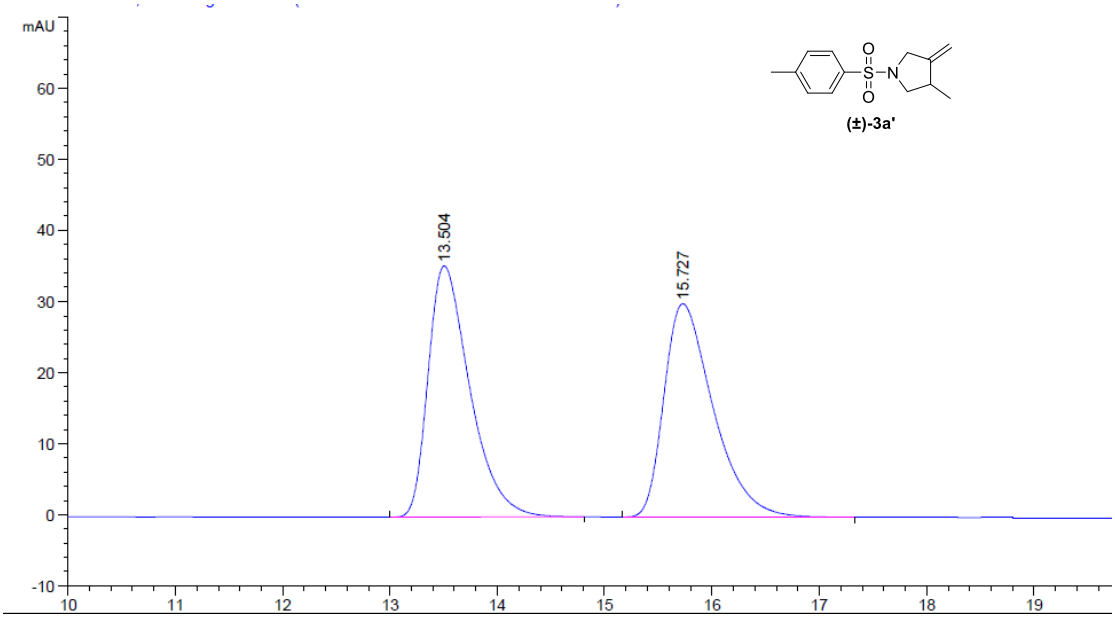
(*E*)-3-benzylidene-4-methyl-1-tosylpyrrolidine (S14)



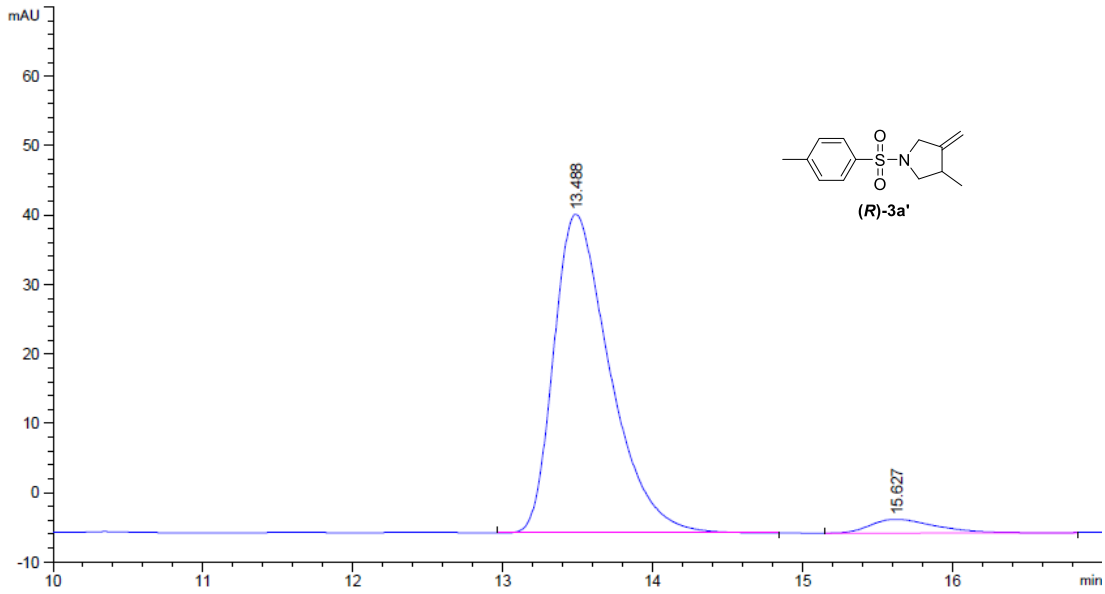

143.71
141.98
136.41
132.66
129.71
128.51
128.07
127.89
127.00
122.49
55.79
53.07
35.16
21.59
18.52
Ph
S14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

13. HPLC charts for the desilylated compounds.

3-methyl-4-methylene-1-tosylpyrrolidine (3a')

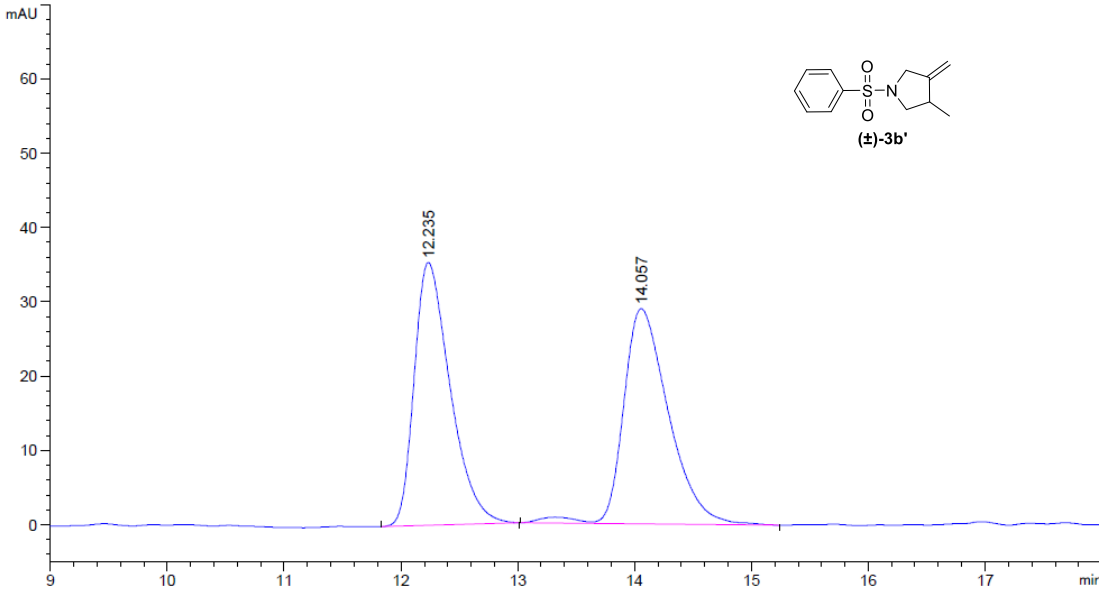


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.504	BB	0.4120	953.52020	35.31762	49.9459
2	15.727	BB	0.4844	955.58545	30.02065	50.0541

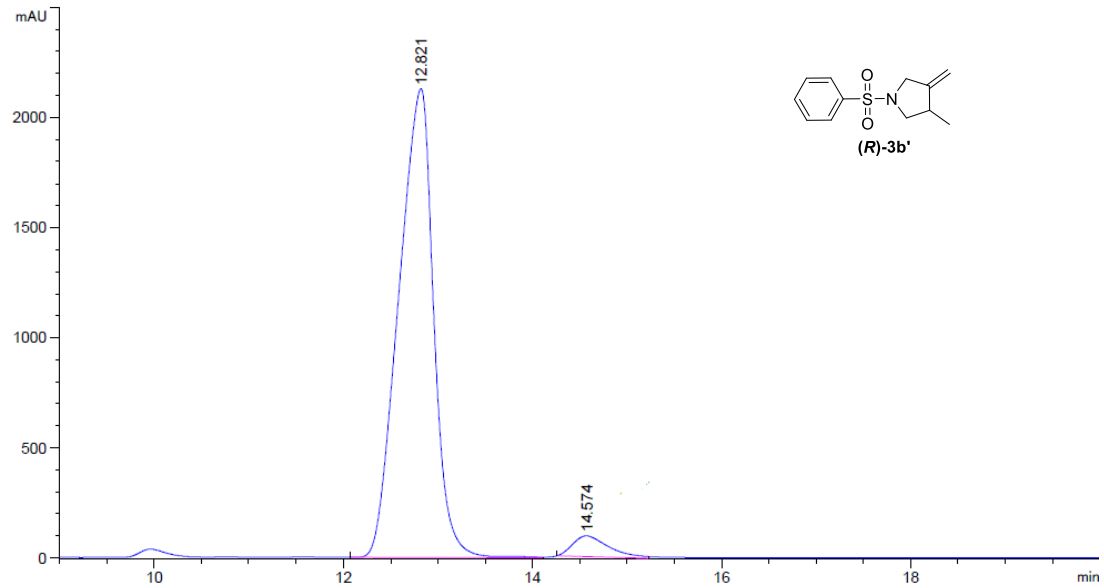


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.488	BB	0.3959	1195.50586	45.90158	95.2031
2	15.627	BB	0.4453	60.23728	1.99462	4.7969

3-methyl-4-methylene-1-(phenylsulfonyl)pyrrolidine (3b')

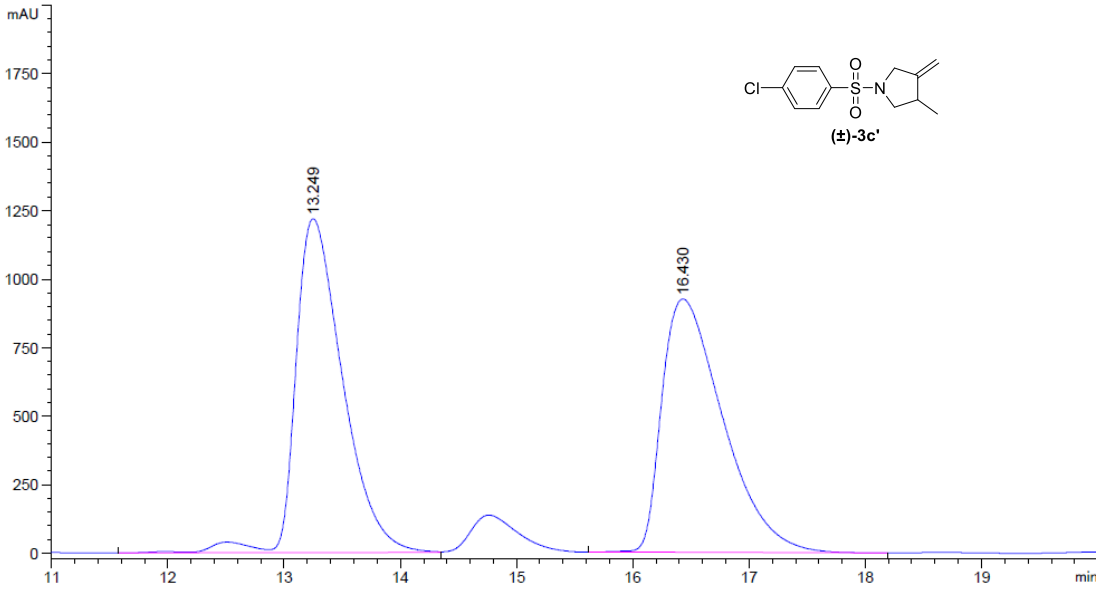


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.235	BB	0.3269	758.20026	35.39188	49.2659
2	14.057	VB R	0.4104	780.79572	28.97334	50.7341

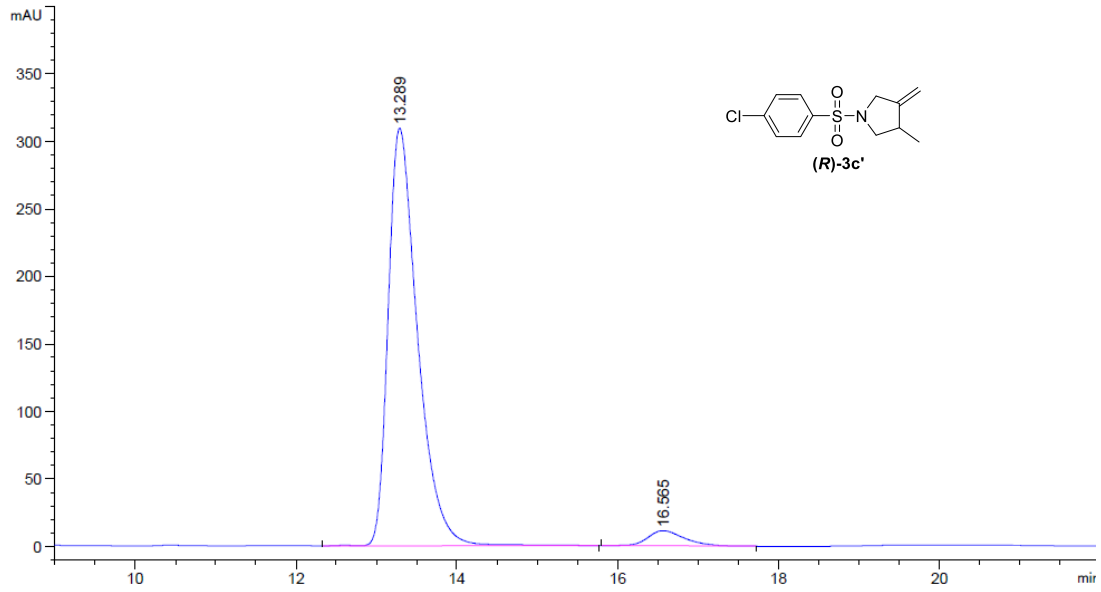


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.821	BV R	0.4053	5.43749e4	2129.37427	95.6221
2	14.574	MM	0.4421	2489.45972	93.84461	4.3779

1-((4-chlorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3c')

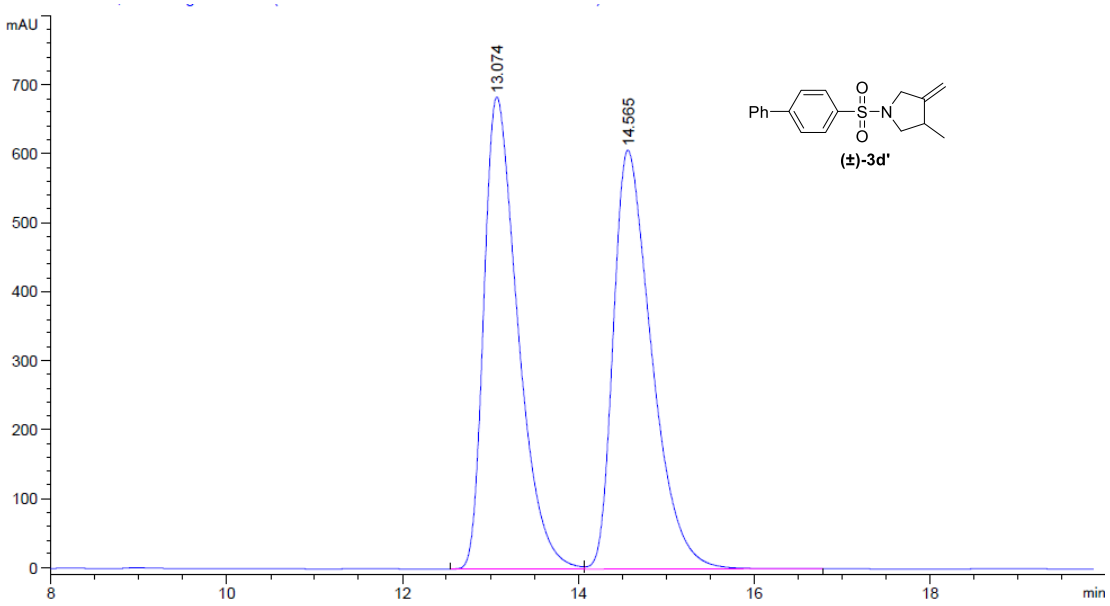


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.249	VV R	0.4208	3.43861e4	1218.28674	50.3688
2	16.430	BB	0.5637	3.38826e4	924.23279	49.6312

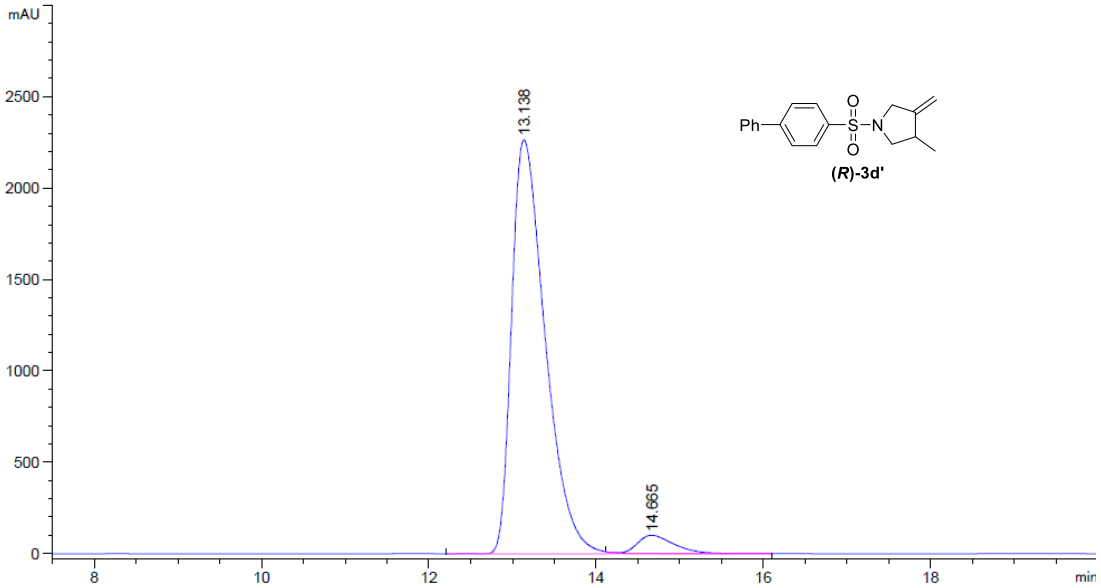


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.289	VB R	0.3834	7855.53369	309.20459	95.7176
2	16.565	BB	0.4711	351.45804	11.20060	4.2824

1-([1,1'-biphenyl]-4-ylsulfonyl)-3-methyl-4-methylenepyrrolidine (3d')

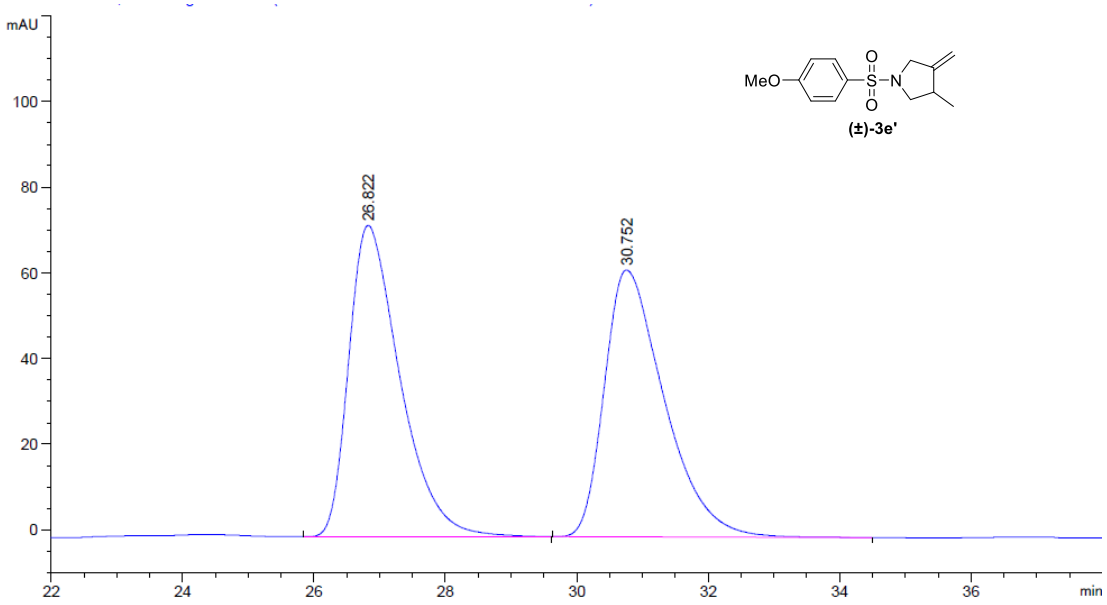


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.074	BV	0.4097	1.83290e4	683.88898	49.9142
2	14.565	VB	0.4667	1.83920e4	606.72156	50.0858

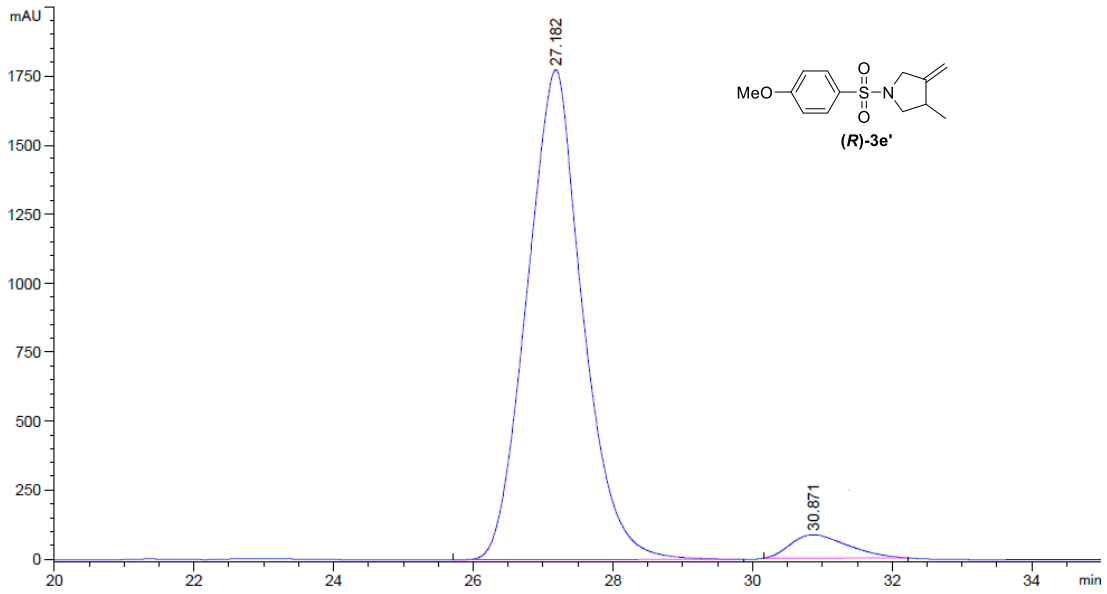


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.138	VV R	0.4274	6.31682e4	2264.83057	95.3583
2	14.665	VB E	0.4605	3074.81201	100.90148	4.6417

1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3e')

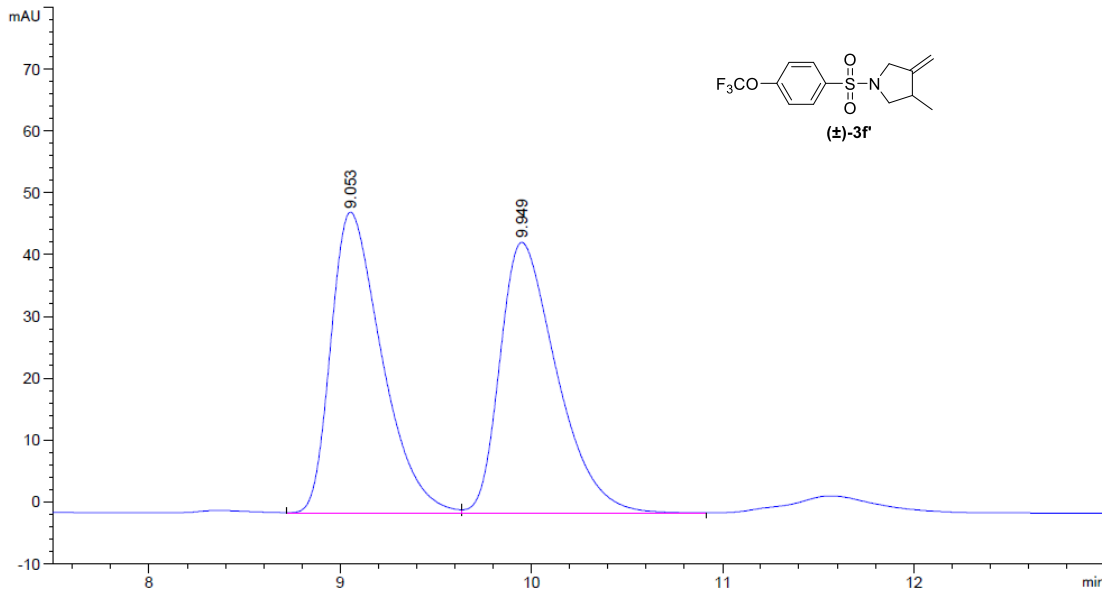


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.822	BB	0.8241	3936.45728	72.66045	49.9422
2	30.752	BB	0.9303	3945.56958	62.26105	50.0578

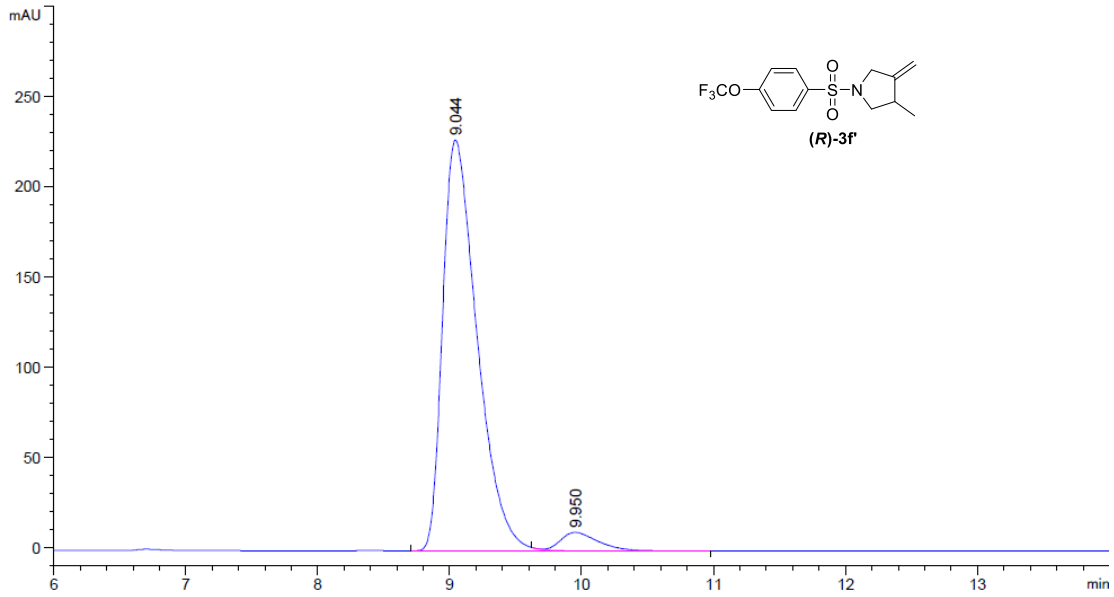


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.182	BB	0.8178	9.78740e4	1773.73535	95.3008
2	30.871	MM	0.9494	4826.10449	84.72484	4.6992

3-methyl-4-methylene-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (3f')

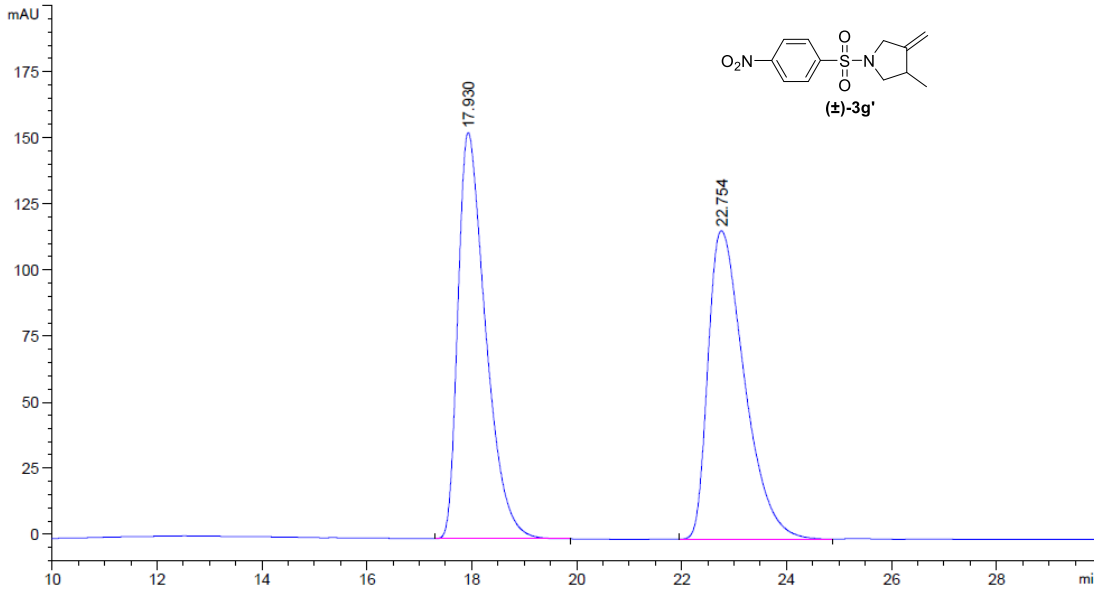


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.053	BV	0.2816	897.57318	48.57972	49.8961
2	9.949	VB	0.3155	901.31171	43.72869	50.1039

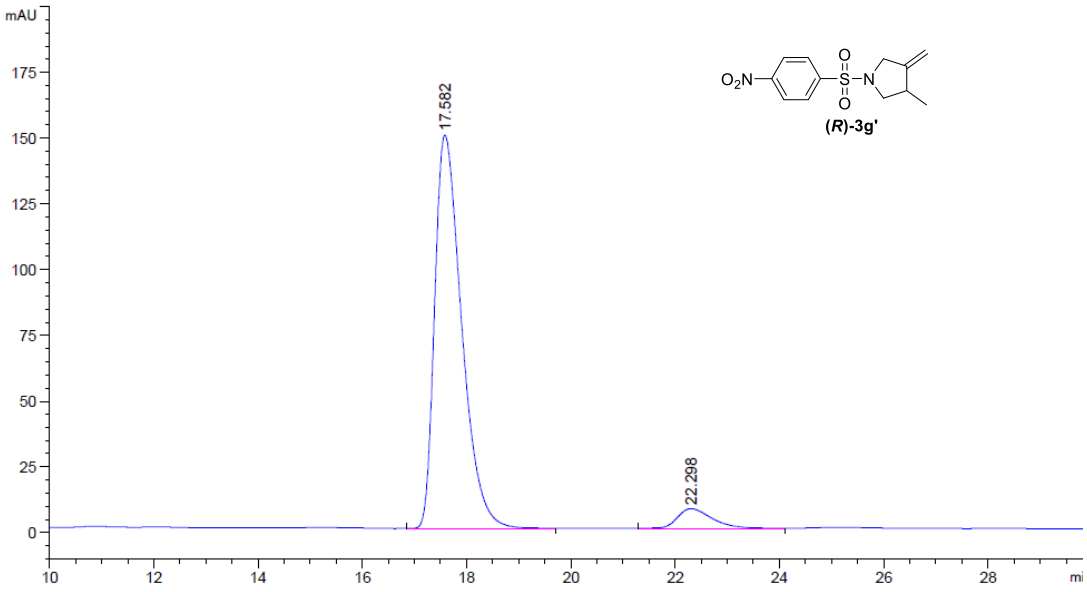


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.044	BV R	0.2776	4128.34082	227.59370	95.2994
2	9.950	VB E	0.2996	203.62993	10.25701	4.7006

3-methyl-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidine (3g')

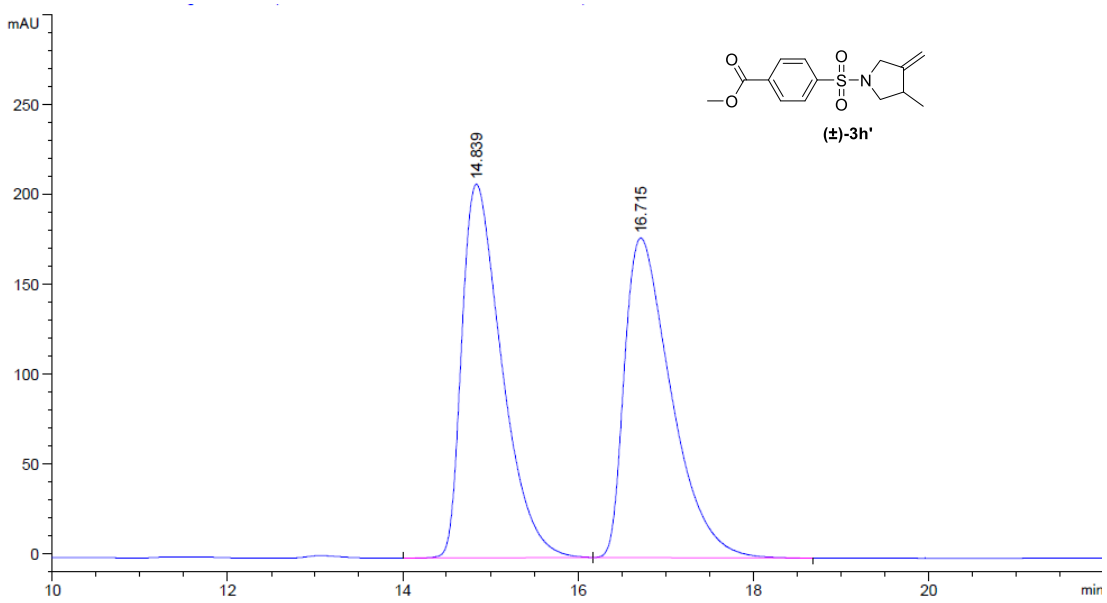


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.930	BB	0.5589	5619.29883	153.57312	50.0271
2	22.754	BB	0.7409	5613.21045	116.54325	49.9729

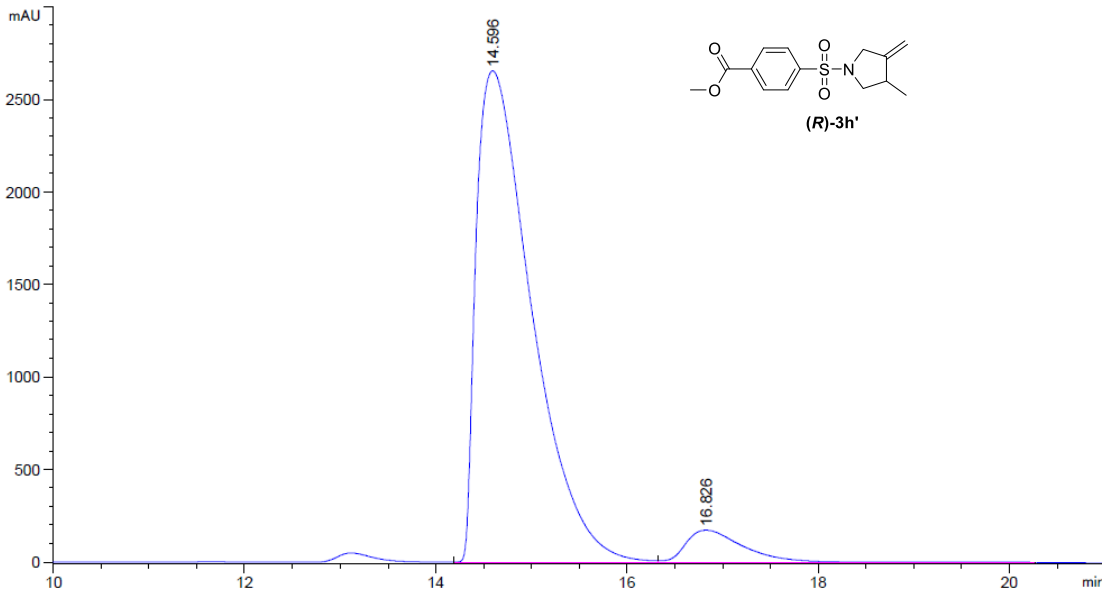


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.582	BB	0.5504	5362.68262	149.52744	94.0172
2	22.298	BB	0.6781	341.25388	7.49697	5.9828

methyl 4-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)benzoate (3h')

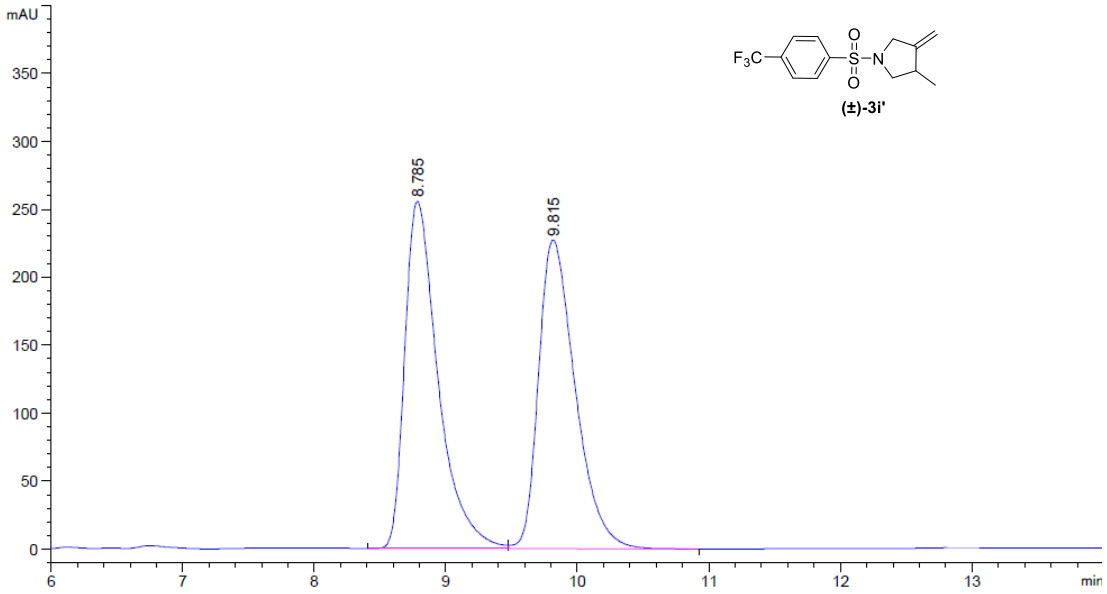


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.839	BB	0.4814	6582.38623	207.87241	50.0203
2	16.715	BB	0.5585	6577.04004	177.82298	49.9797

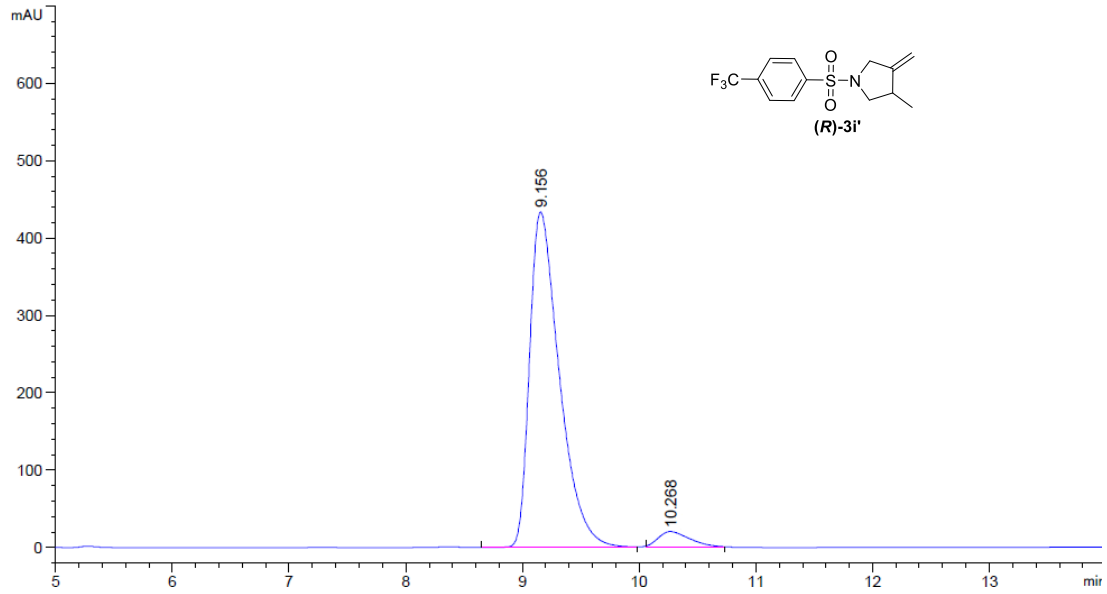


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.596	BV	0.6164	1.06793e5	2654.16748	93.7077
2	16.826	VB	0.6244	7170.99219	173.05762	6.2923

3-methyl-4-methylene-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3i')

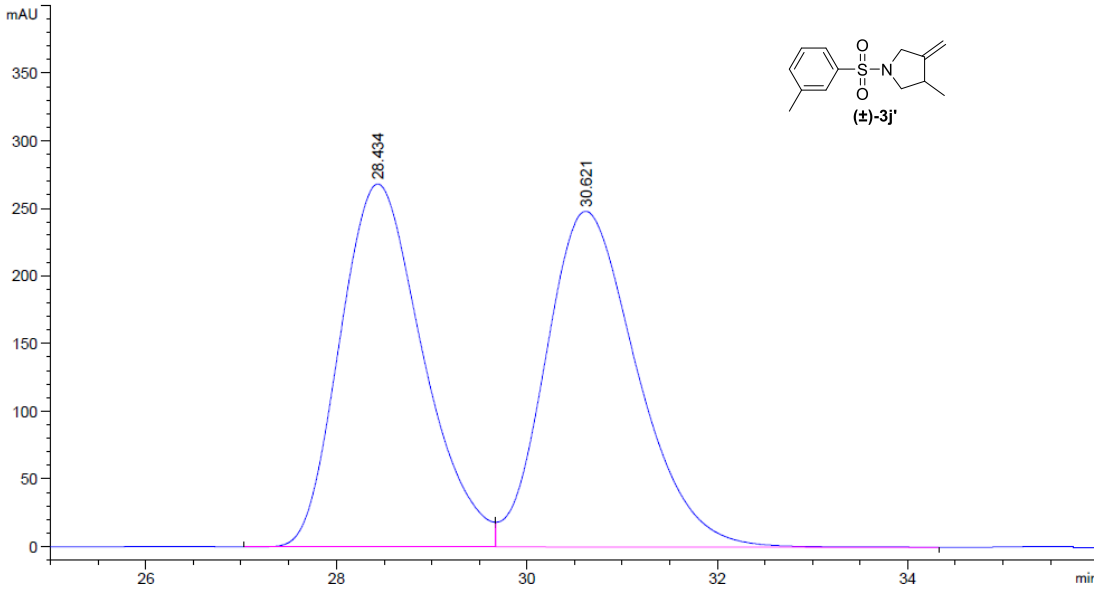


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.785	BV	0.2664	4498.18945	255.54601	50.5495
2	9.815	VB	0.2970	4400.40234	227.16895	49.4505

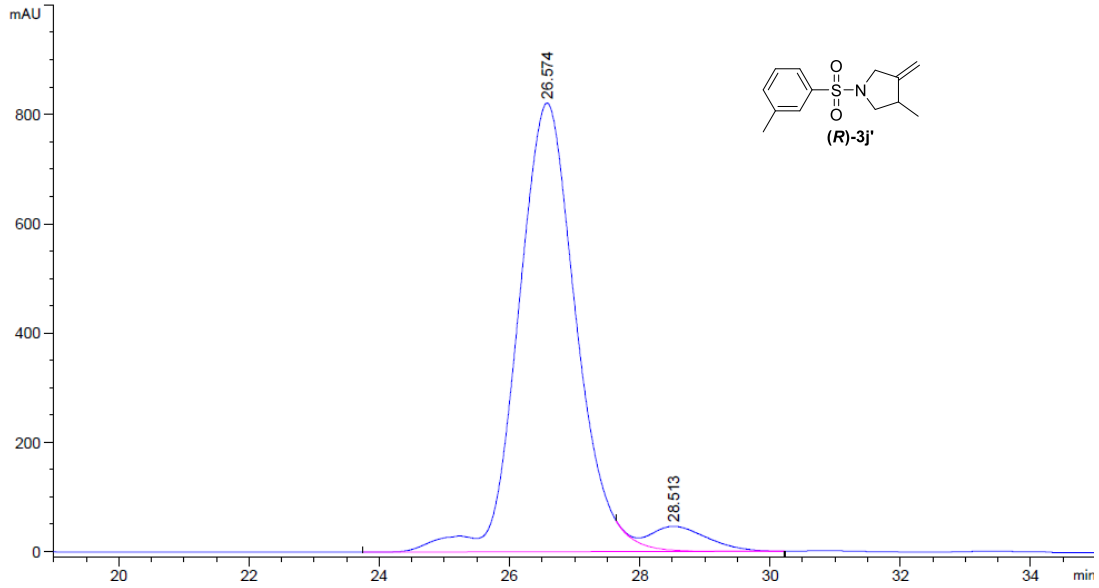


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.156	BV	0.2687	7719.47021	433.70844	95.5498
2	10.268	MM	0.3069	359.53082	19.52627	4.4502

3-methyl-4-methylene-1-(m-tolylsulfonyl)pyrrolidine (3j')

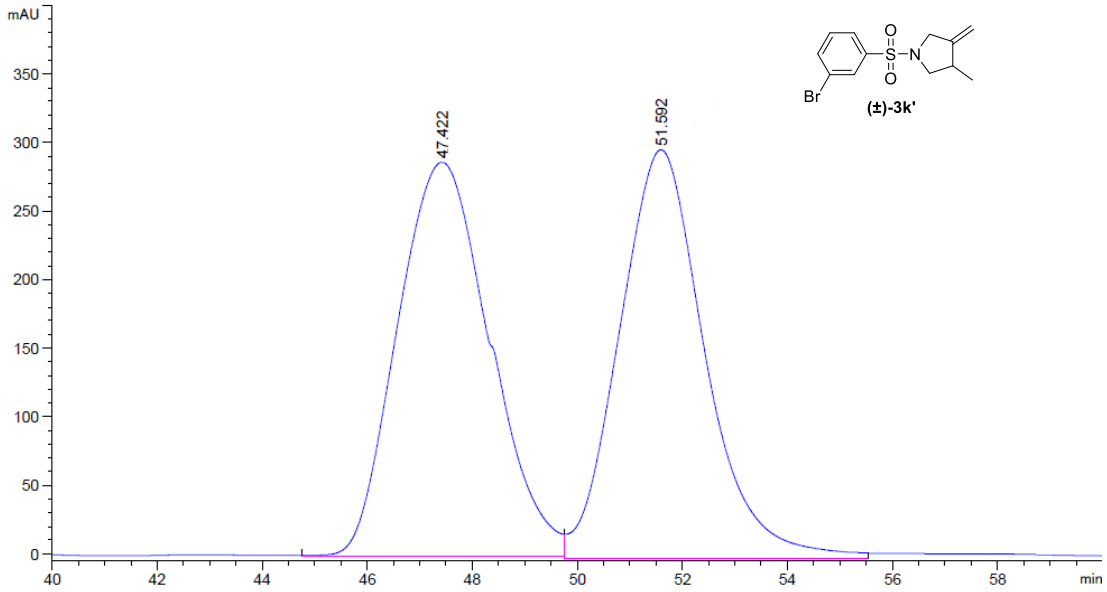


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.434	BV	0.9006	1.62039e4	268.28812	49.4709
2	30.621	VB	1.0041	1.65505e4	248.15471	50.5291

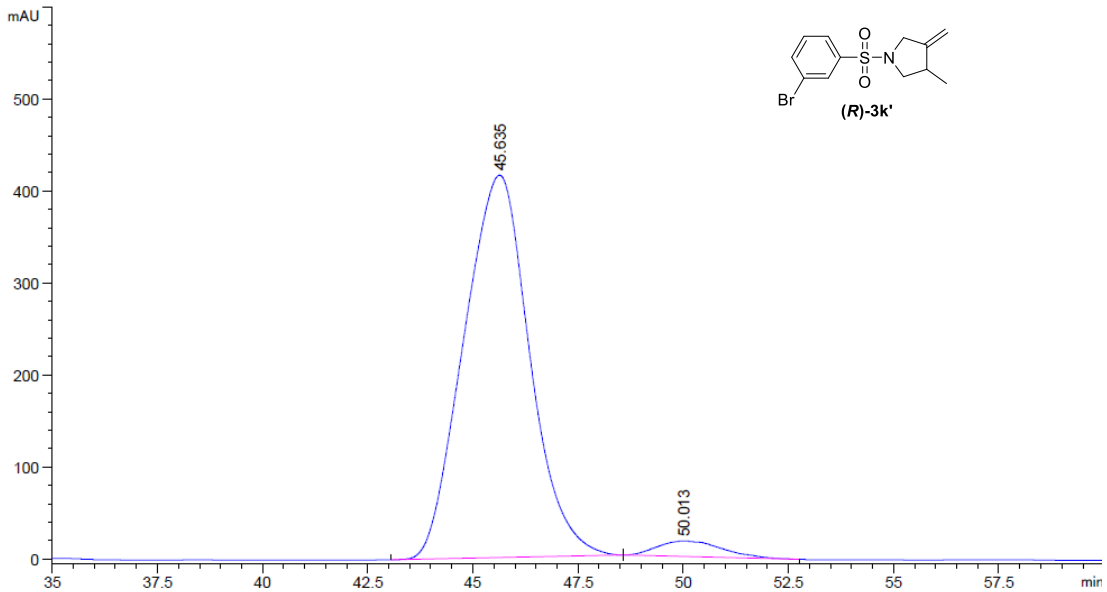


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.574	VV R	0.9247	5.07752e4	820.88275	95.1154
2	28.513	VB E	0.9042	2607.52612	43.63053	4.8846

1-((3-bromophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3k')

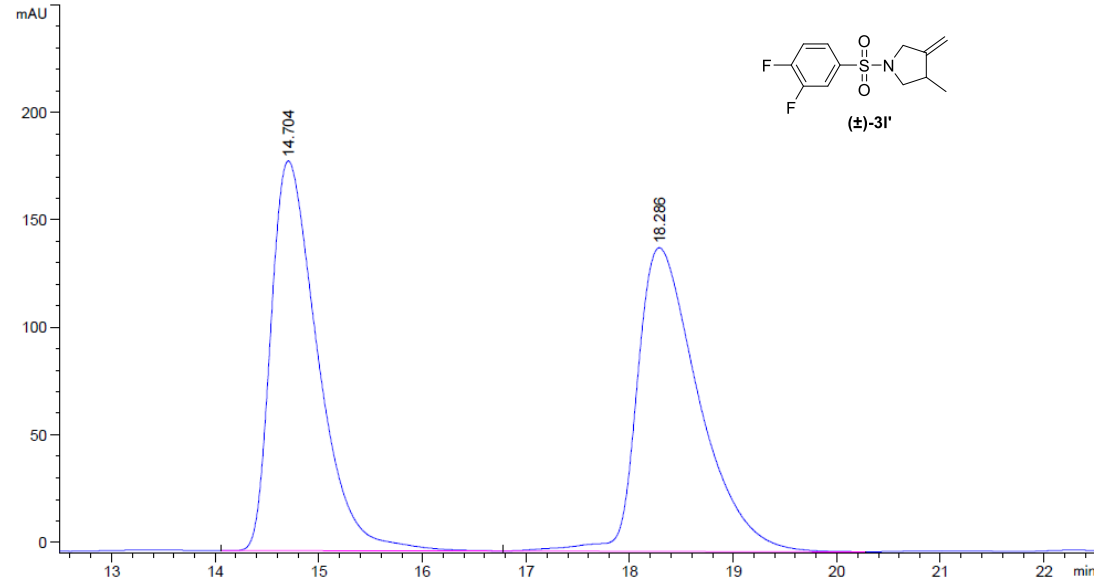


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.422	MM	2.0355	3.51503e4	287.80951	50.9808
2	51.592	MM	1.8882	3.37977e4	298.32104	49.0192

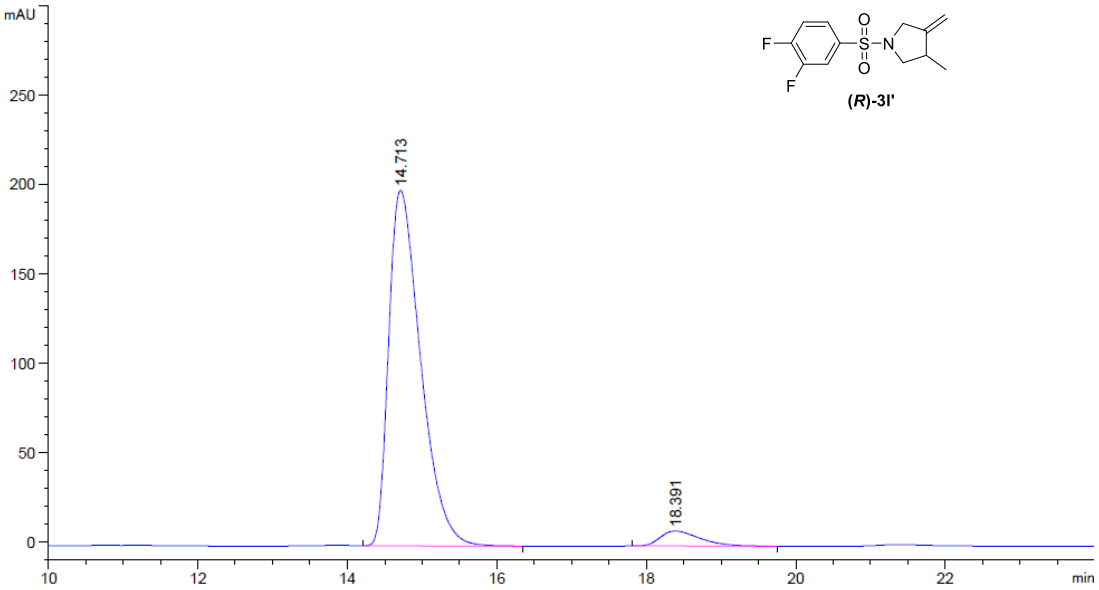


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.635	BB	1.5772	4.52316e4	415.44534	96.1362
2	50.013	BB	1.4459	1817.90588	16.78103	3.8638

1-((3,4-difluorophenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3l')

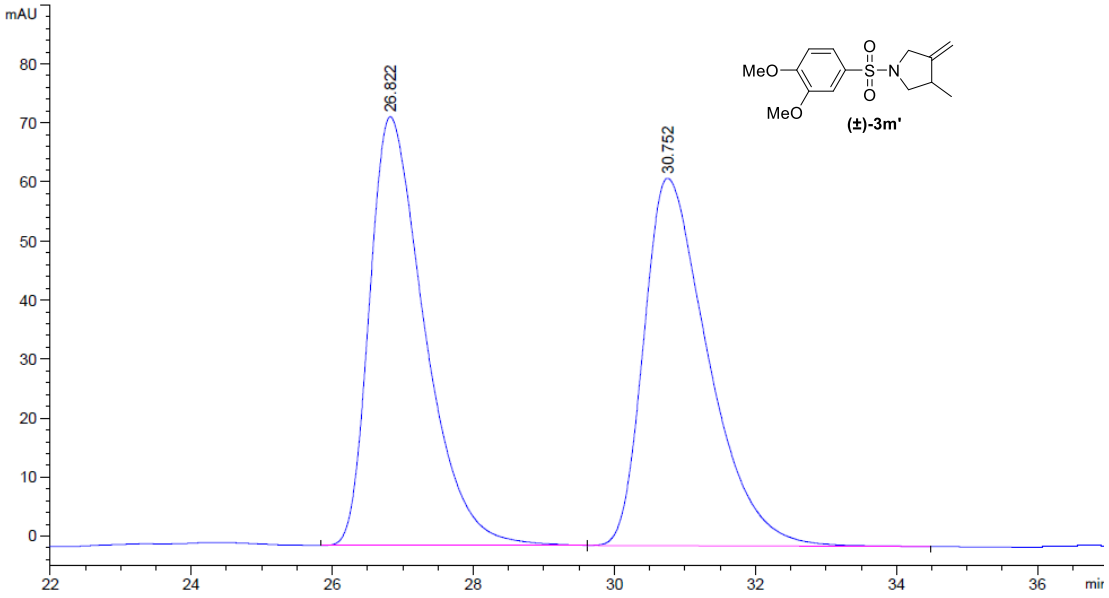


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.704	BB	0.4804	5676.40820	181.25691	49.4482
2	18.286	BB	0.6277	5803.10449	141.14828	50.5518

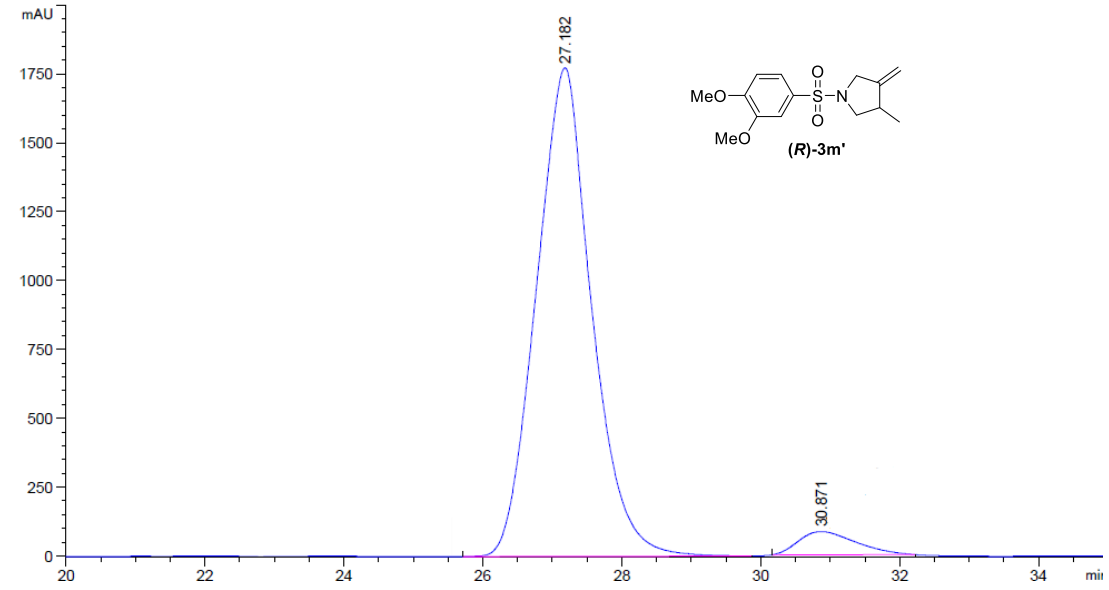


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.713	BB	0.4567	5894.42285	198.93617	95.0595
2	18.391	BB	0.5530	306.34933	8.40885	4.9405

1-((3,4-dimethoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3m')

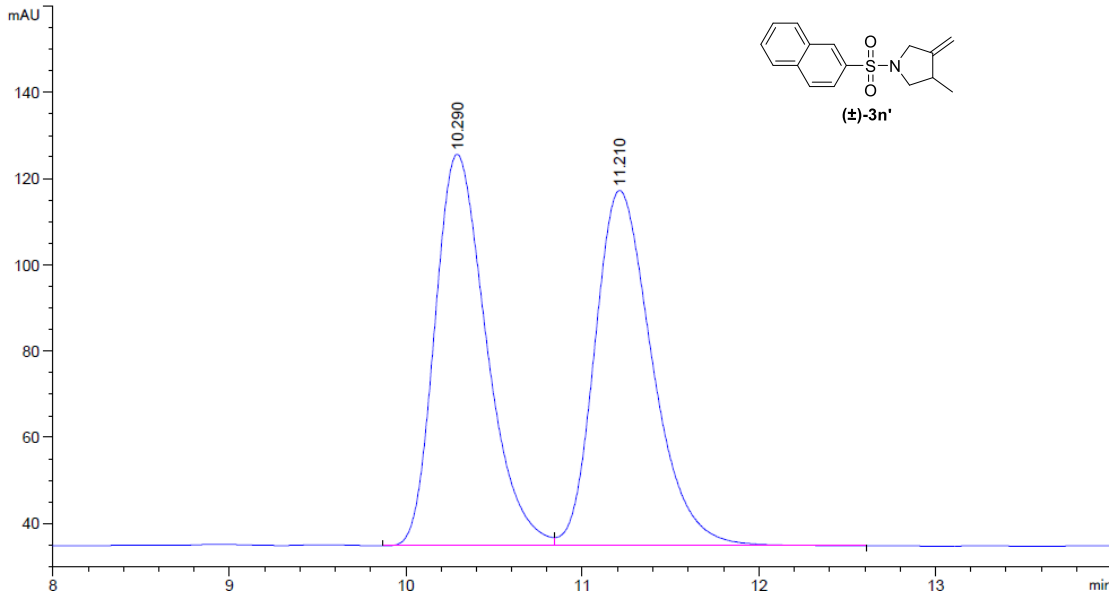


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.822	BB	0.8241	3936.45728	72.66045	49.9422
2	30.752	BB	0.9303	3945.56958	62.26105	50.0578

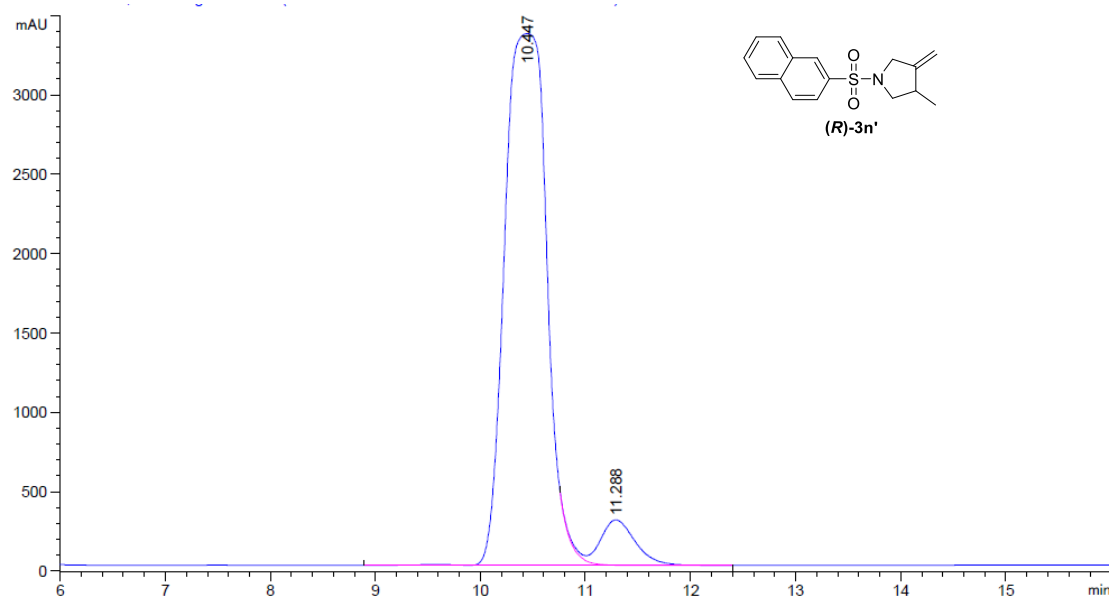


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.182	BB	0.8178	9.78740e4	1773.73535	95.3008
2	30.871	MM	0.9494	4826.10449	84.72484	4.6992

3-methyl-4-methylene-1-(naphthalen-2-ylsulfonyl)pyrrolidine (3n')

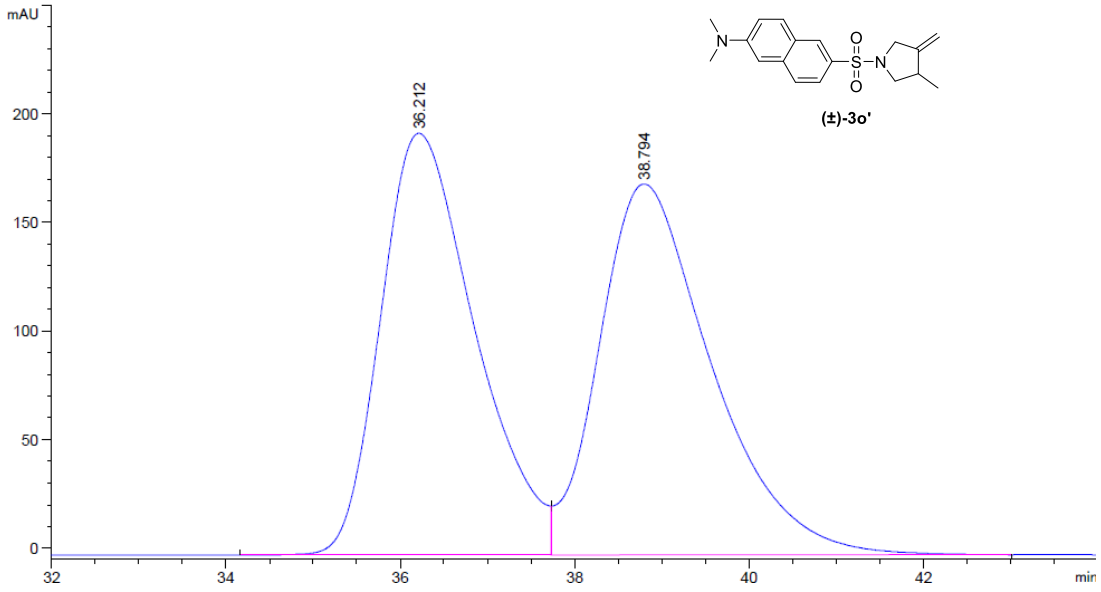


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.290	BV	0.3135	1840.23926	90.76534	49.6050
2	11.210	VB	0.3496	1869.55017	82.41641	50.3950

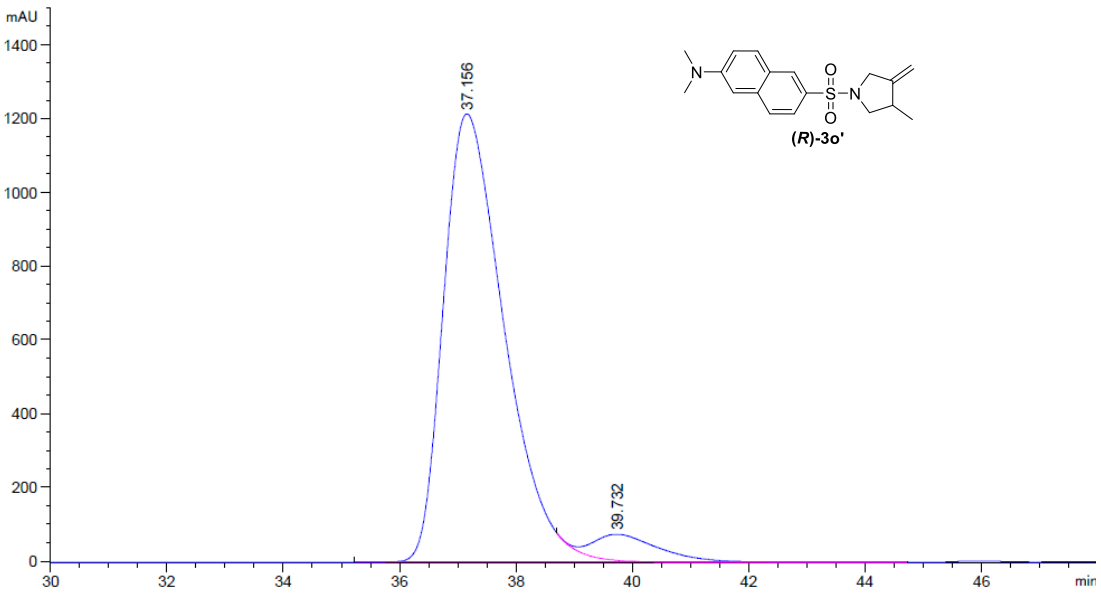


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.447	VV R	0.4397	9.31753e4	3351.21875	93.2691
2	11.288	VB E	0.3589	6724.10840	285.32446	6.7309

***N,N*-dimethyl-6-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)naphthalen-2-*a*mine (3o')**

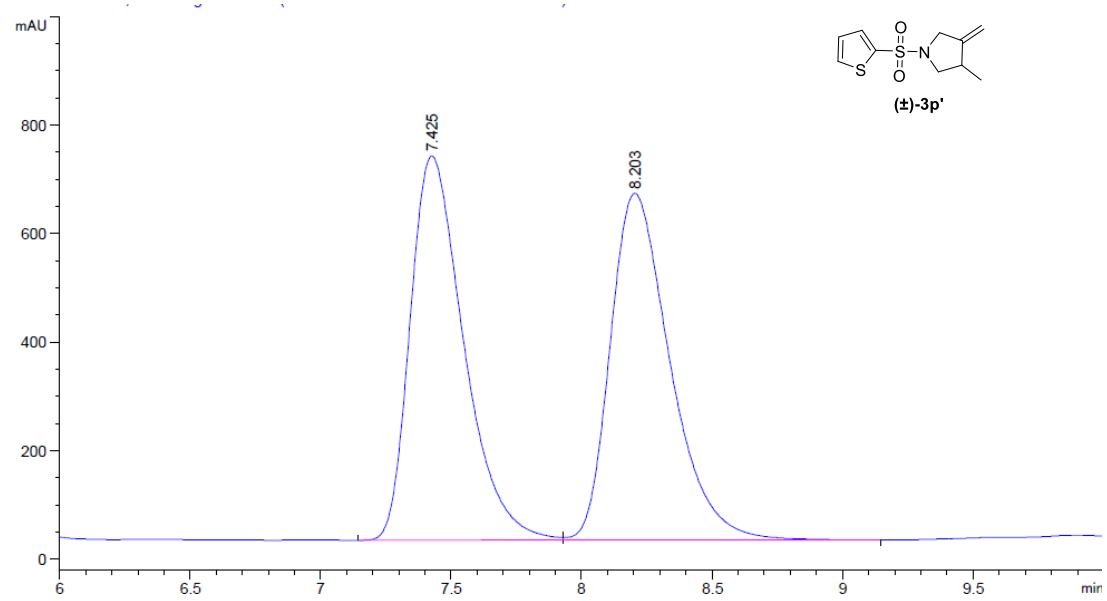


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.212	BV	1.1193	1.46377e4	194.22481	48.8216
2	38.794	VB	1.3171	1.53443e4	170.79376	51.1784

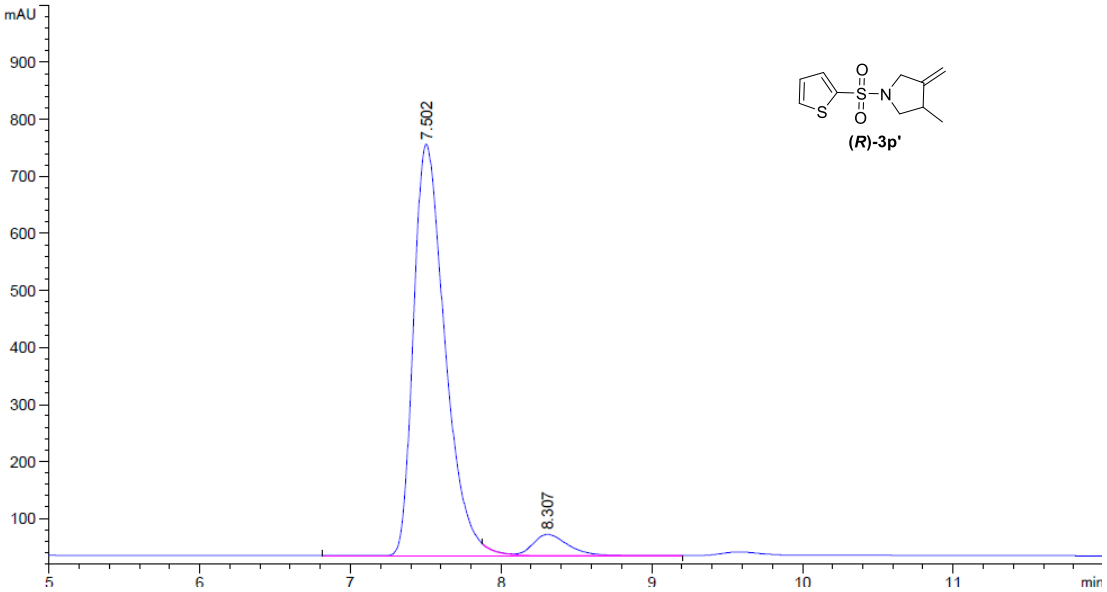


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.156	BV R	1.0911	8.85723e4	1215.49426	94.0427
2	39.732	VB E	1.1468	5610.71973	70.70194	5.9573

3-methyl-4-methylene-1-(thiophen-2-ylsulfonyl)pyrrolidine (3p')

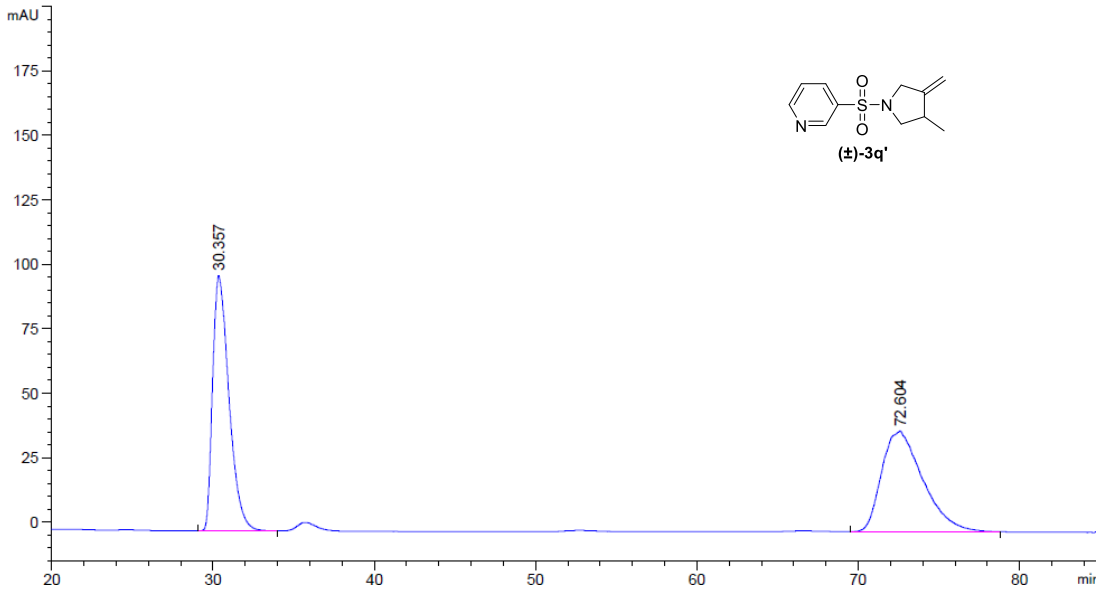


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.425	BV	0.2173	1.00901e4	707.96863	49.8178
2	8.203	VB	0.2436	1.01639e4	639.05658	50.1822

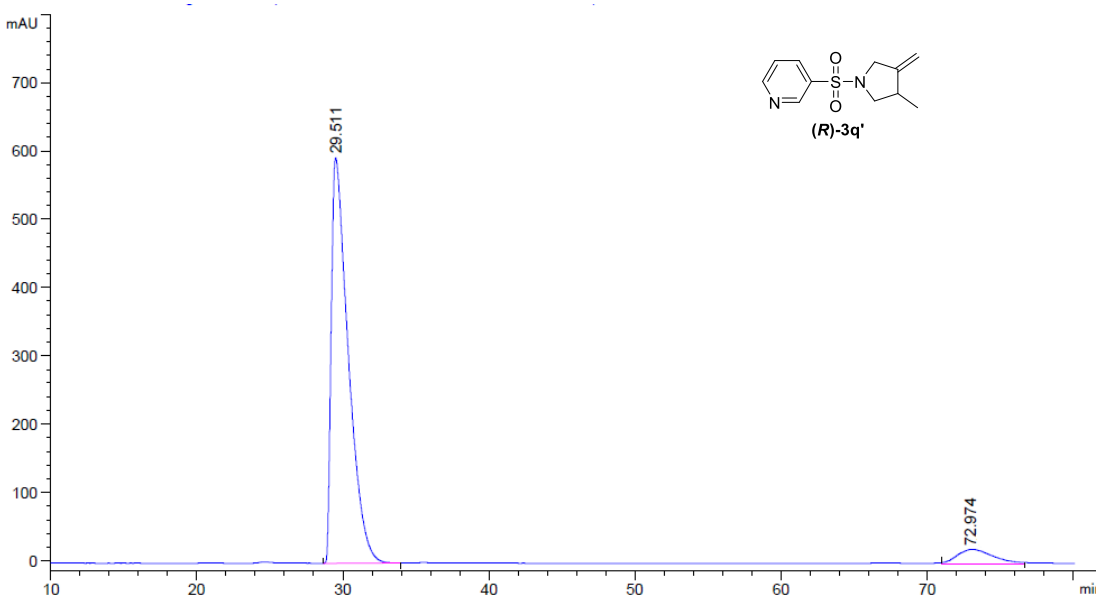


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.502	VV R	0.2234	1.04849e4	721.94165	94.5471
2	8.307	VB E	0.2479	604.70184	37.14797	5.4529

3-((3-methyl-4-methylenepyrrolidin-1-yl)sulfonyl)pyridine (3q')

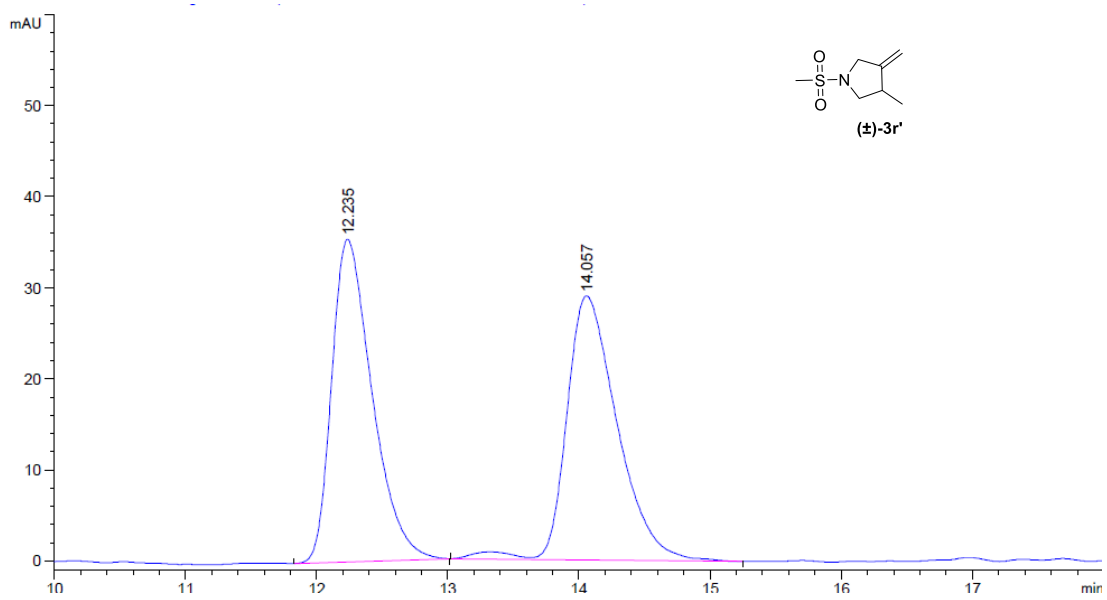


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.357	BB	1.0969	6962.95068	98.95885	50.2152
2	72.604	BB	2.1127	6903.27686	39.06319	49.7848

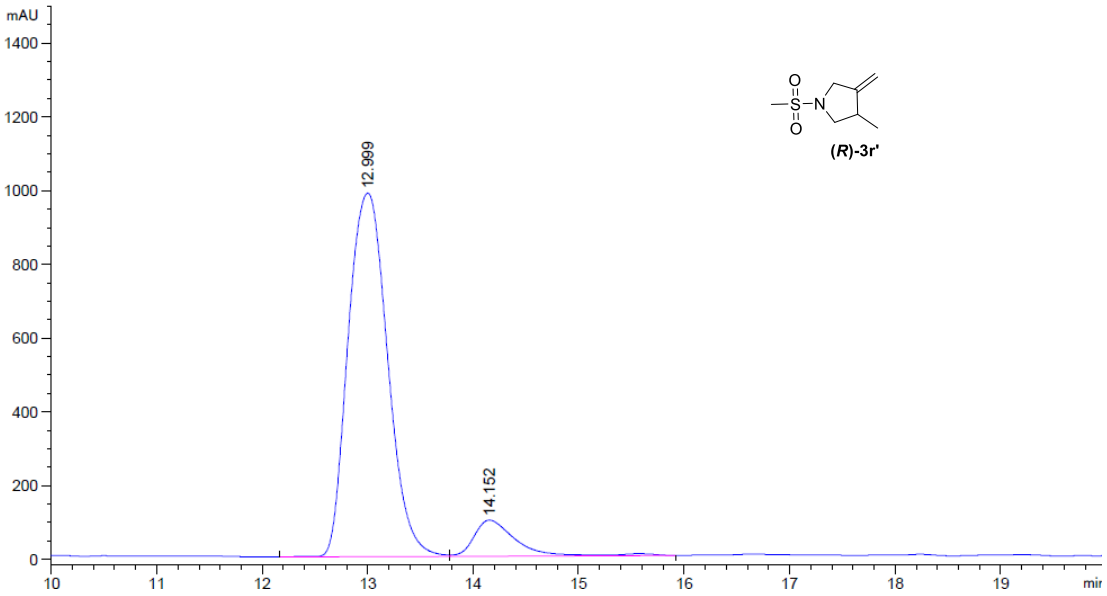


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.511	BB	1.1704	4.80333e4	593.98621	92.9775
2	72.974	MM	2.8530	3627.88818	21.19357	7.0225

3-methyl-4-methylene-1-(methylsulfonyl)pyrrolidine (3r')

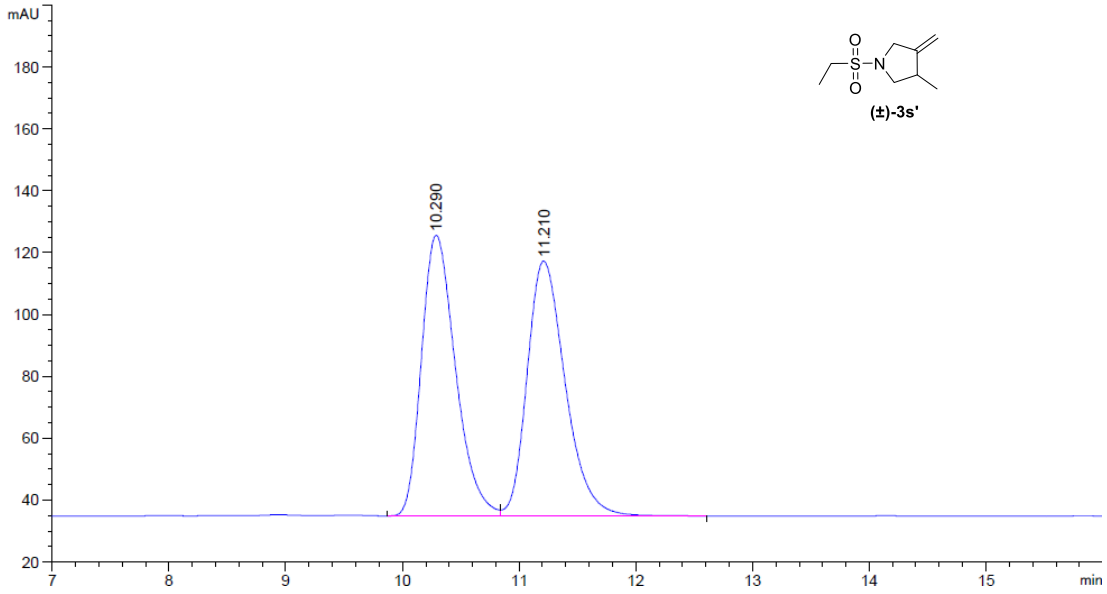


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.235	BB	0.3269	758.20026	35.39188	49.2659
2	14.057	VB R	0.4104	780.79572	28.97334	50.7341

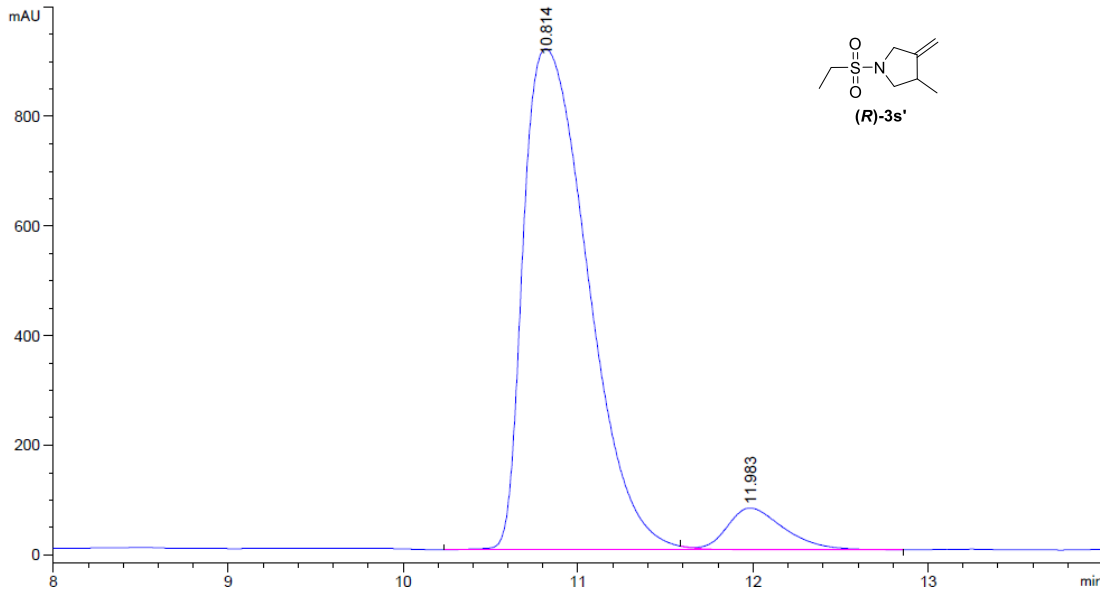


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.999	VV R	0.4180	2.56081e4	985.85498	90.3747
2	14.152	VV R	0.4046	2727.36646	97.86531	9.6253

1-(ethylsulfonyl)-3-methyl-4-methylenepyrrolidine (3s')

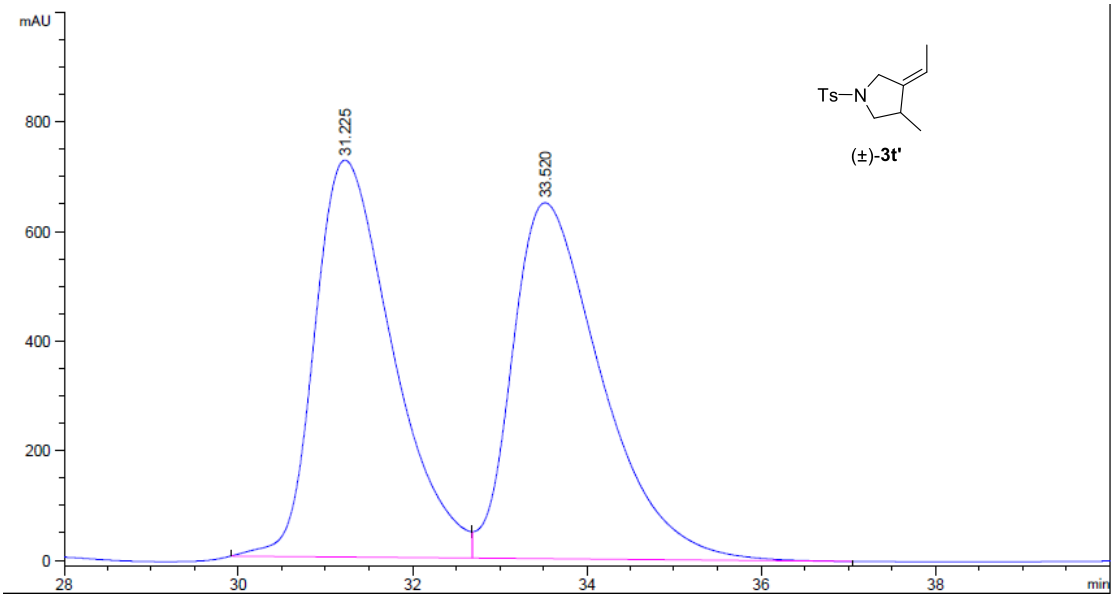


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.290	BV	0.3135	1840.23926	90.76534	49.6050
2	11.210	VB	0.3496	1869.55017	82.41641	50.3950

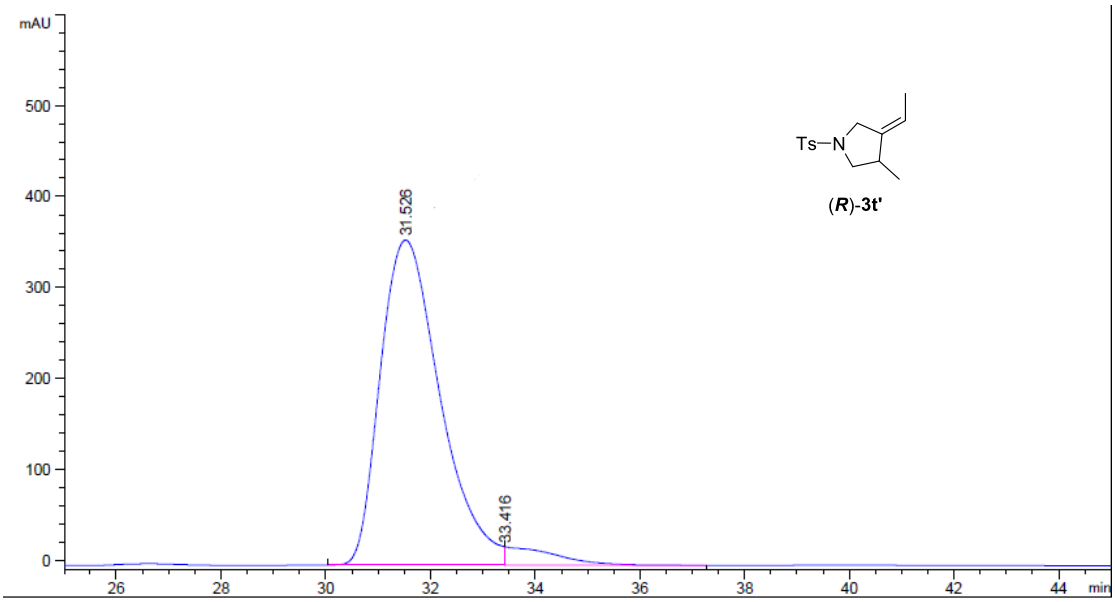


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.814	BV R	0.4084	2.34011e4	914.76959	93.2202
2	11.983	VB E	0.3391	1701.92712	76.05640	6.7798

1-(4-Toluenesulfonyl)-3-(*Z*)-ethylidene-4-methylpyrrolidine (3ad')

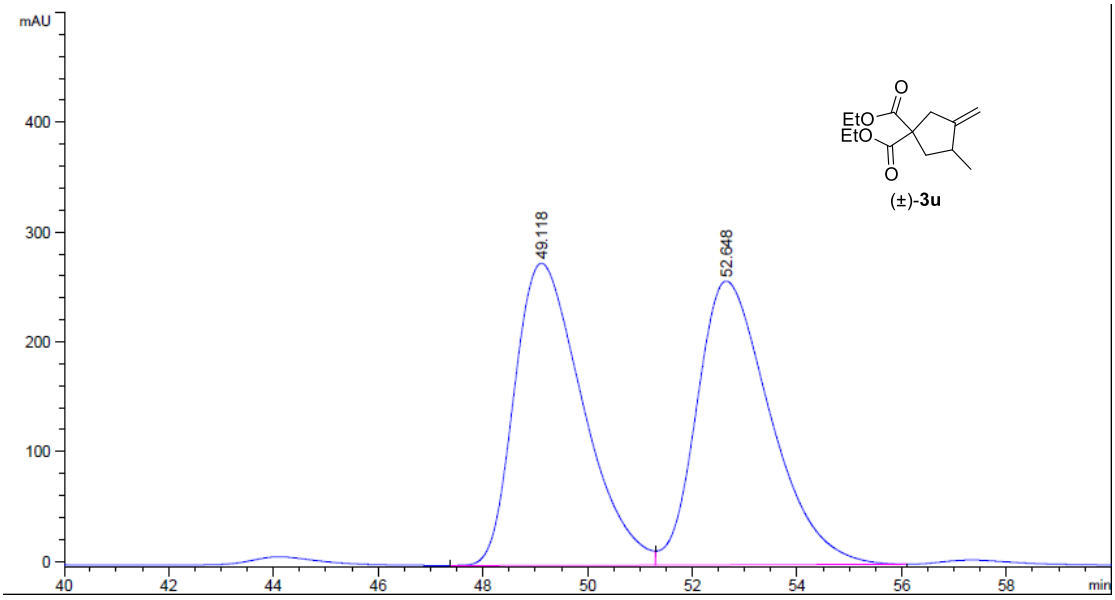


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.225	BV	0.9094	4.50769e4	723.98248	49.3932
2	33.520	VB	1.0809	4.61845e4	649.28455	50.6068

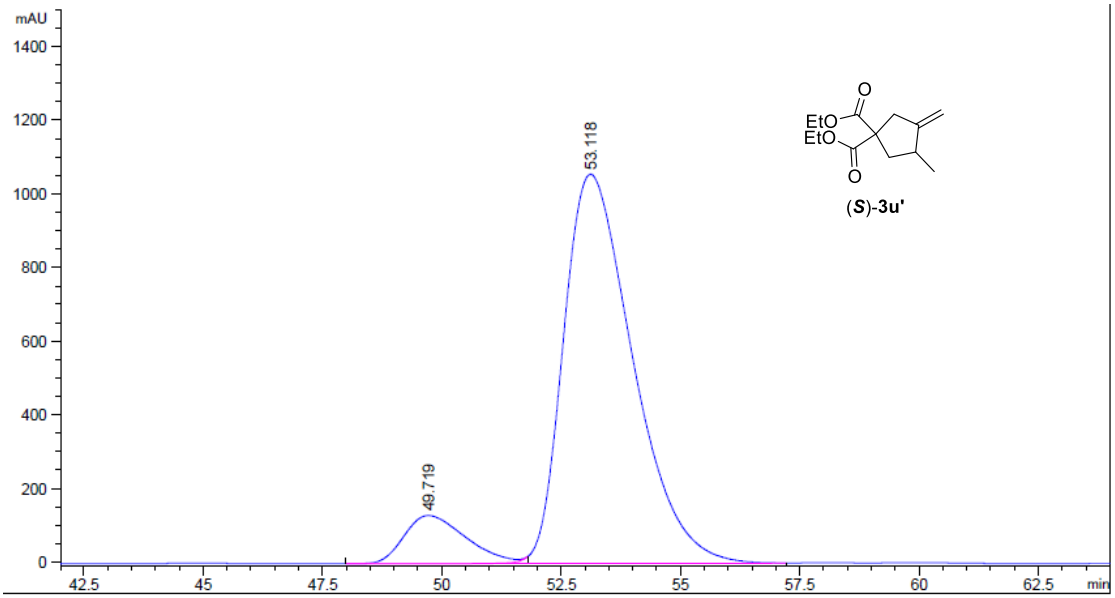


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.526	MF	1.3226	2.83259e4	356.94998	95.5217
2	33.416	FM	1.1032	1327.99658	20.06285	4.4783

4,4-Bis(ethoxycarbonyl)-1-methylidene-2-methyl-cyclopentane (3u')

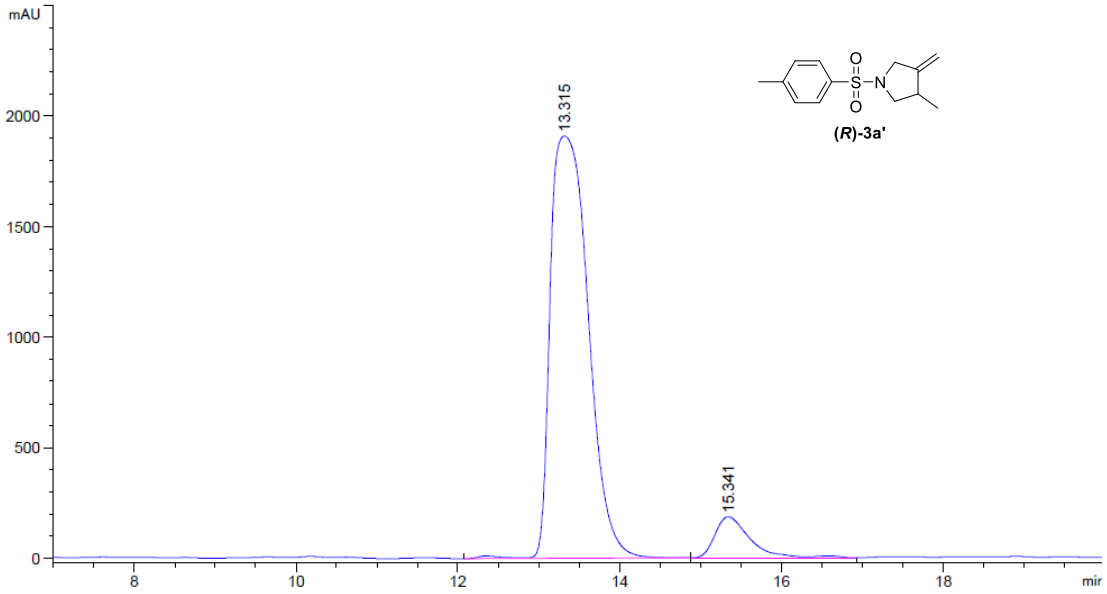


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.118	BV	1.3895	2.49200e4	274.91559	49.7436
2	52.648	VB	1.4867	2.51769e4	258.40640	50.2564



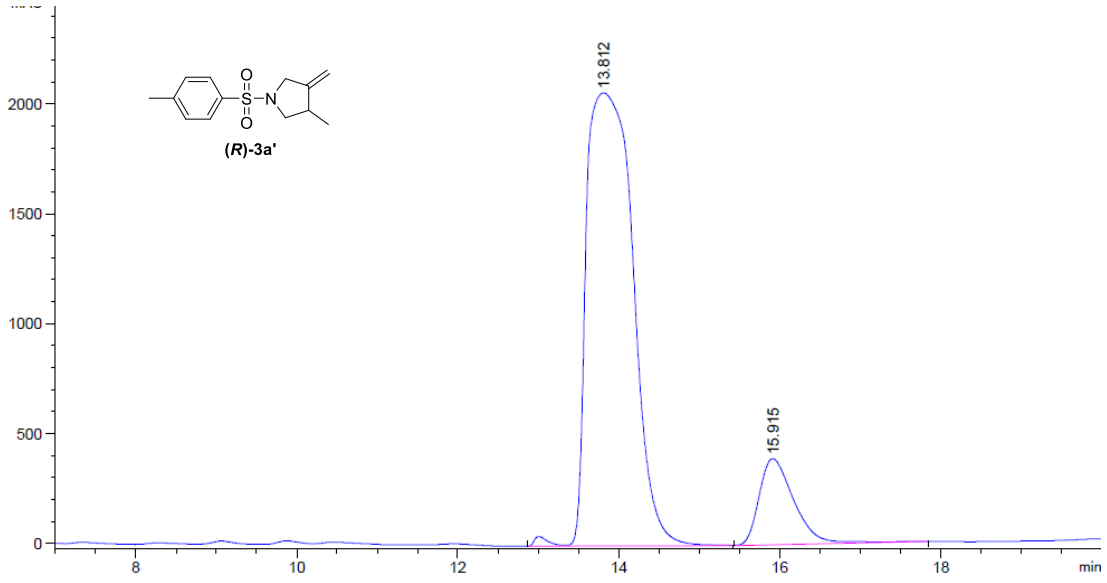
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.719	BV E	1.3449	1.17228e4	130.76067	9.9119
2	53.118	VB R	1.5345	1.06547e5	1056.58984	90.0881

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3v')



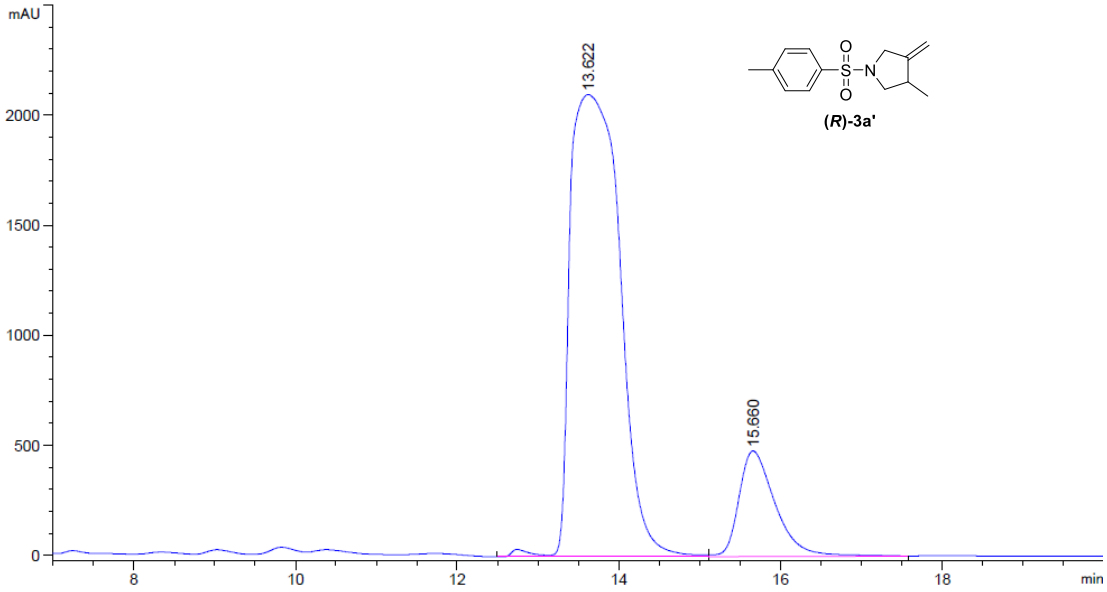
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.315	VV R	0.5207	6.22680e4	1908.94250	91.6957
2	15.341	BV R	0.4435	5639.23438	185.66132	8.3043

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3w')



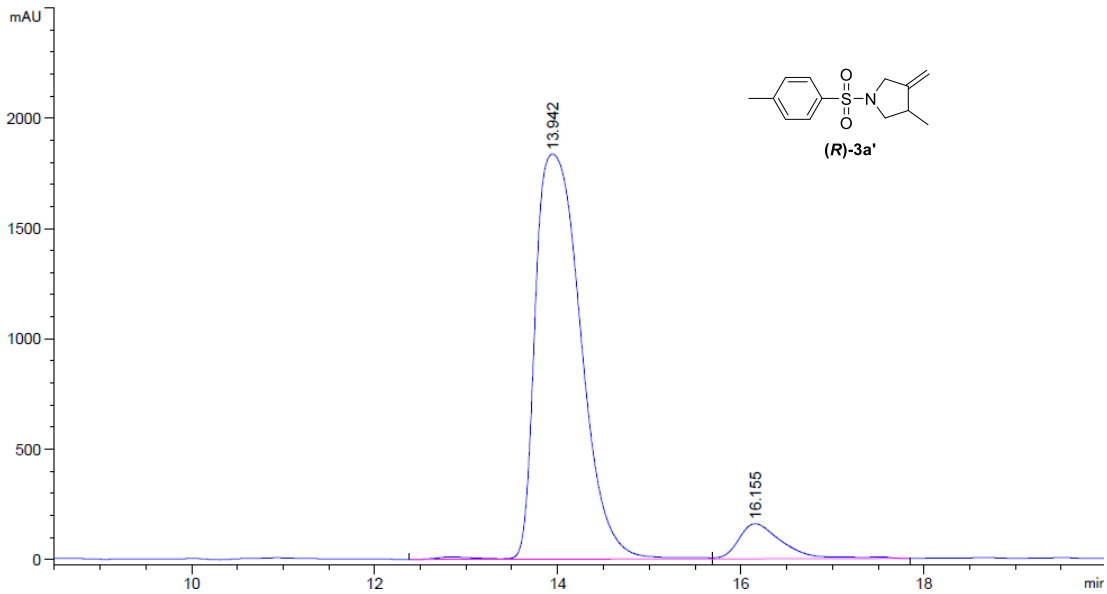
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.812	VB R	0.6477	8.26497e4	2061.63867	87.5968
2	15.915	BV R	0.4539	1.17027e4	391.23346	12.4032

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3x')



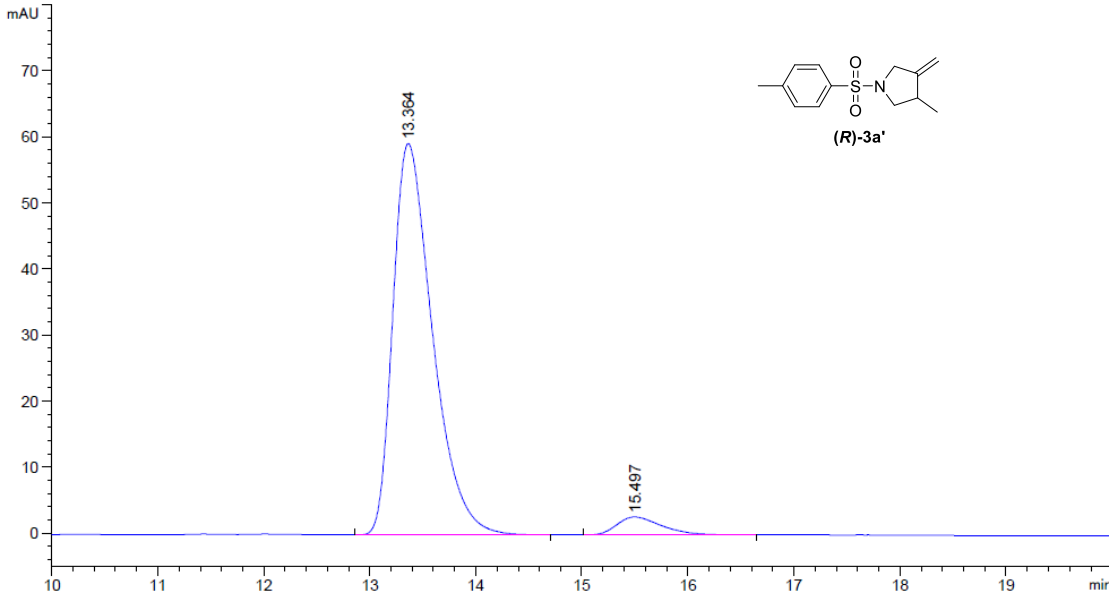
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.622	VV R	0.6930	8.98161e4	2099.27246	85.7615
2	15.660	VB	0.4735	1.49117e4	478.53925	14.2385

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3y')



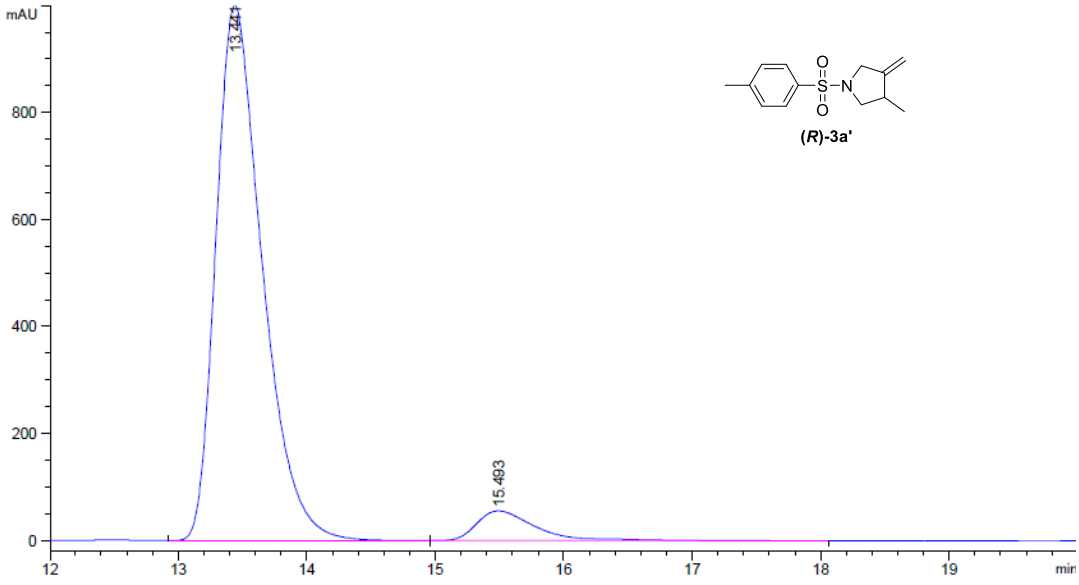
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.942	VV R	0.5474	6.33794e4	1835.45374	92.1752
2	16.155	VV R	0.4962	5380.28320	159.54355	7.8248

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3z')



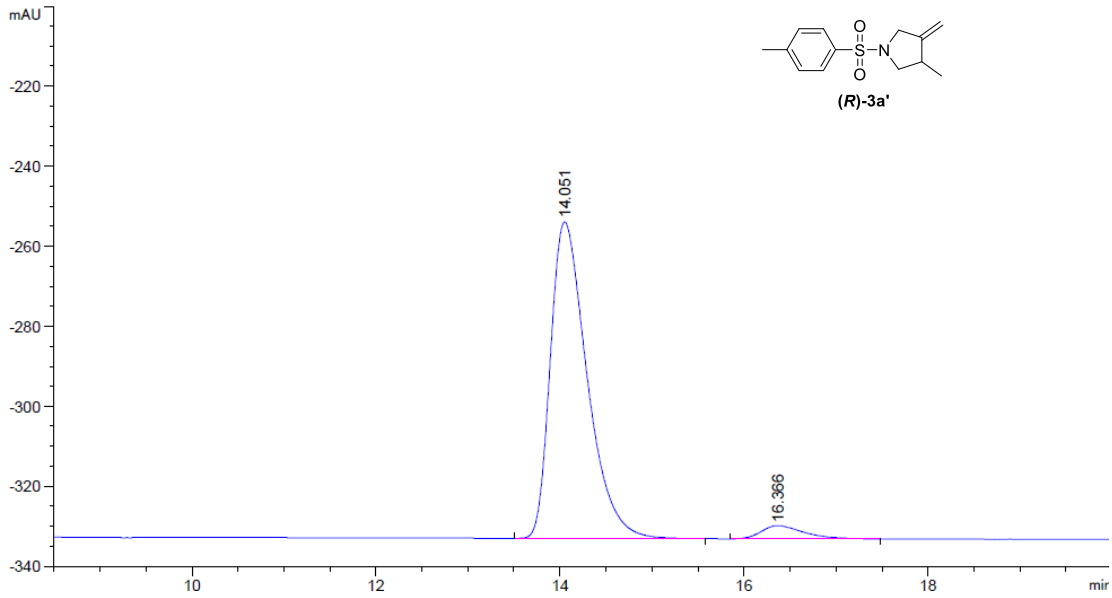
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.364	BB	0.3983	1538.78296	59.19247	95.0660
2	15.497	BB	0.4357	79.86419	2.71861	4.9340

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3aa')



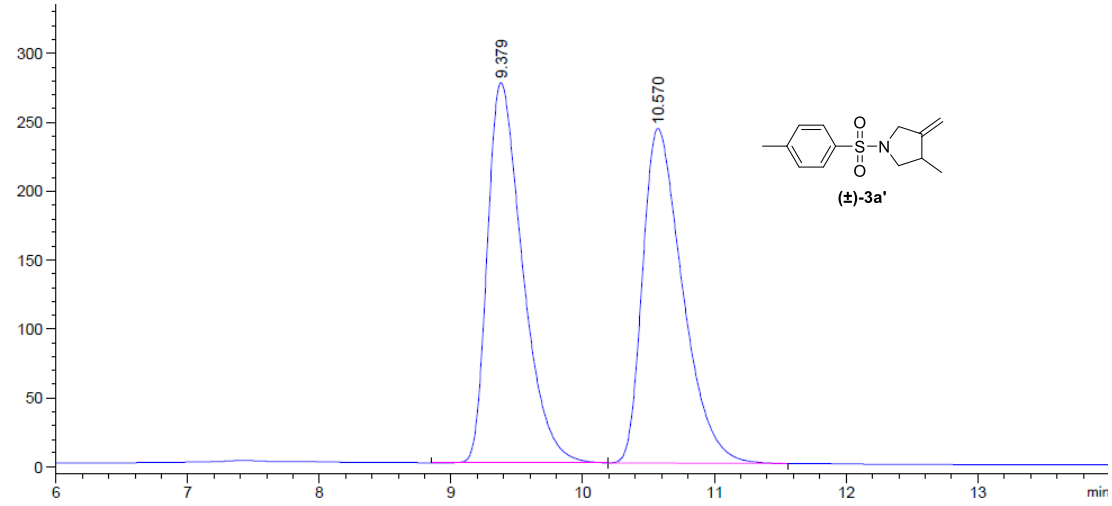
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.440	BB	0.3791	2.50682e4	1001.39874	94.8003
2	15.492	MM	0.4483	1374.95581	51.11588	5.1997

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3ab')

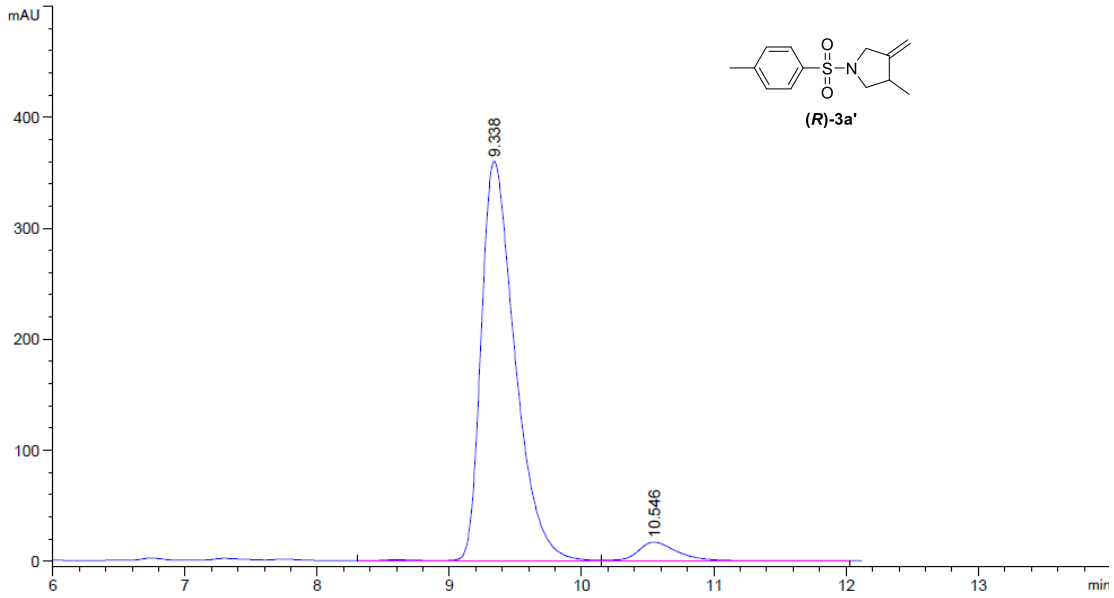


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.051	BB	0.4223	2185.33789	79.10061	95.4803
2	16.366	BB	0.4743	103.44588	3.25914	4.5197

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3ac')

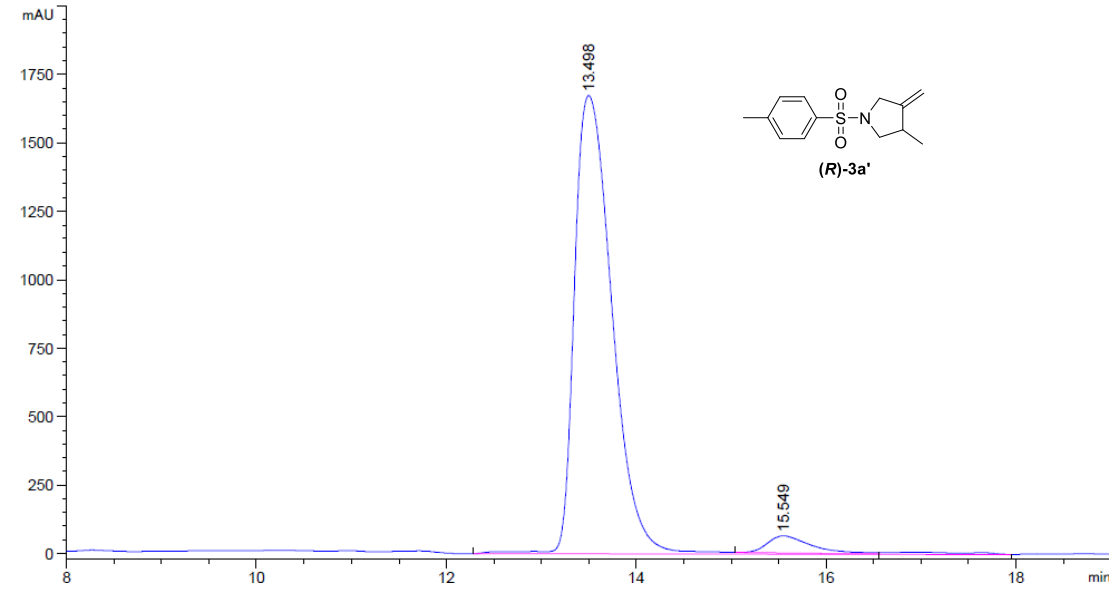


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.379	BB	0.2835	5121.37012	275.93030	49.9936
2	10.570	BB	0.3221	5122.68164	242.81082	50.0064



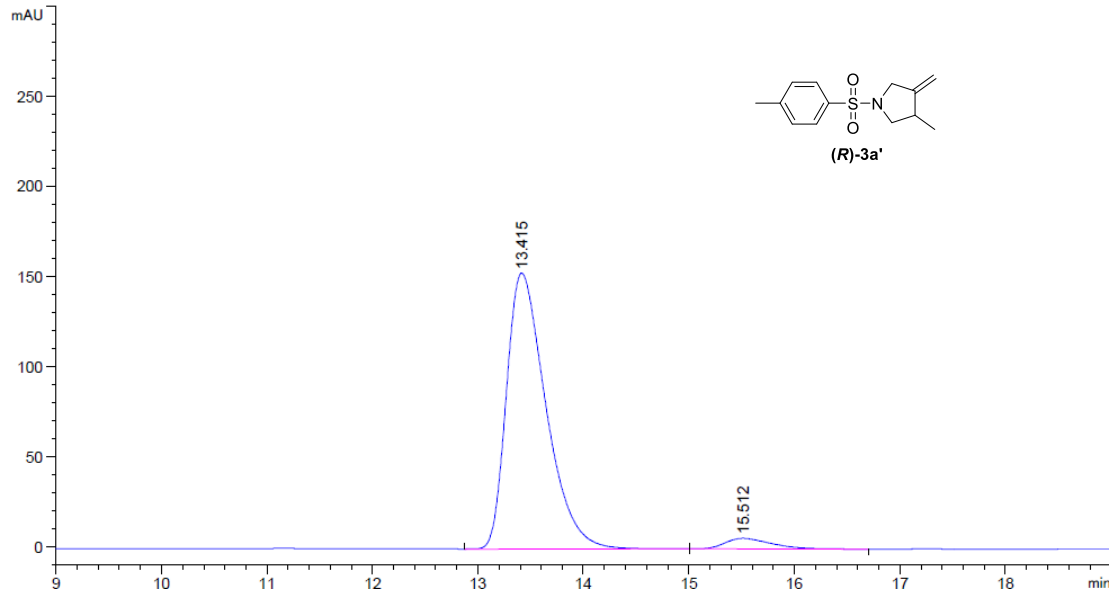
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.338	VV R	0.2678	6383.76709	360.12320	94.7966
2	10.546	VB	0.3083	350.40326	16.87083	5.2034

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3ad')



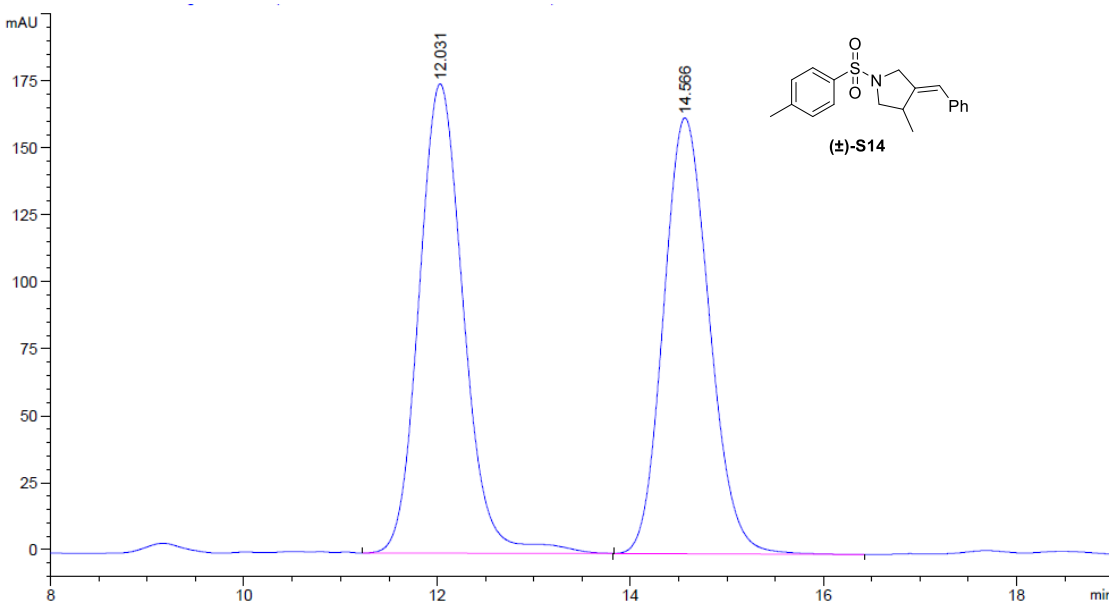
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.498	VV R	0.4346	4.69955e4	1673.39502	95.9192
2	15.549	VV E	0.4733	1999.40540	62.48328	4.0808

1-(4-Toluenesulfonyl)-3-methylidene-4-methylpyrrolidine (3ae')

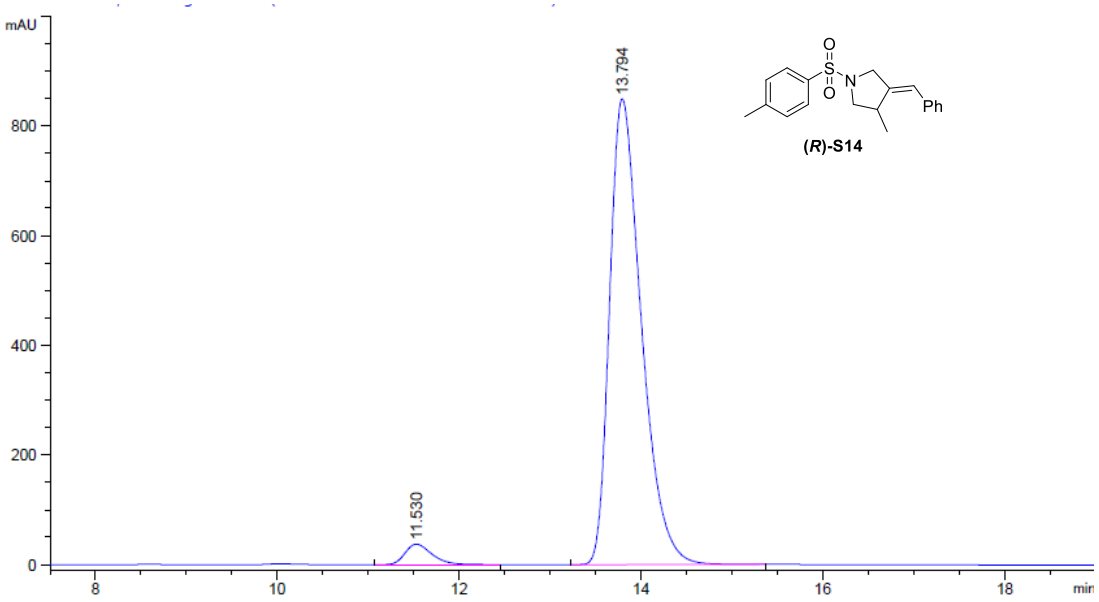


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.415	BB	0.3980	3975.87012	153.07588	95.7132
2	15.512	BB	0.4578	178.07050	5.87211	4.2868

(*E*)-3-benzylidene-4-methyl-1-tosylpyrrolidine (S14)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.031	BB	0.4952	5600.27637	175.08325	51.0776
2	14.566	BB	0.5168	5363.96631	162.61739	48.9224



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.530	BB	0.3164	774.02161	37.41423	3.6197
2	13.794	BB	0.3691	2.06095e4	849.34552	96.3803