# Supplementary Methods

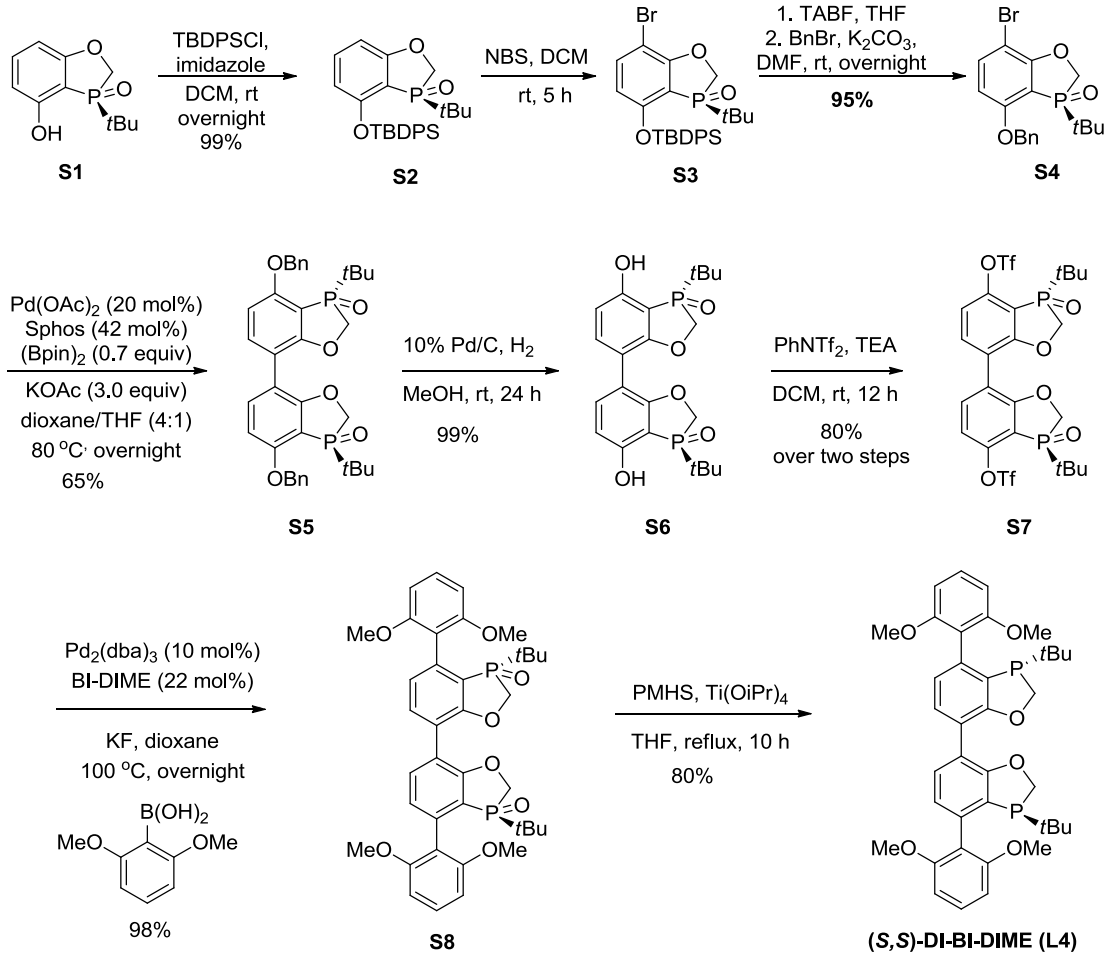
## General Information and Materials

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. All anhydrous solvents were purchased from J & K Chemicals or Alfa Chemicals Inc, or used after standard purification procedures. $Ni(cod)_2$ was purchased from Strem chemicals. Commercialized reagents were used without further purifications. All air sensitive ligands were stored in a nitrogen-filled glove box before use. Chiral ligand intermediates were prepared according to our reported procedures. Tf = trifluoromethylsulfonate, cod = 1,5-cyclooctadiene, PMHS = polymethylhydrosiloxane.

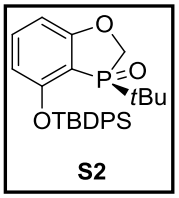
$^{1}H$, $^{31}P$, $^{19}F$ and $^{13}C$ NMR data were recorded on a BrukerDRX500, DRX400, NMR Spectrometer with $CDCl_3$, or $CD_3OD$ as the solvent. $^{1}H$ chemical shifts were referenced to $CDCl_3$ at 7.26 ppm. $^{13}C$ chemical shifts were referenced to $CDCl_3$ at 77.16 ppm and obtained with $^{1}H$ decoupling. $^{31}P$ shifts were referenced to 85% $H_3PO_4$ in $D_2O$ at 0.0 ppm as external standard and obtained with $^{1}H$ decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). MS was measured on Agilent 5973N (EI), Agilent 1100 Series LC/MSD (ESI) mass spectrometers. Column chromatography was performed with silica gel (200-300 mesh). X-Ray crystallographic analysis data were collected using a Bruker Smart-APEX instrument (CCD detector) or a Bruker Kappa APEX-II instrument (CCD detector). HPLC analyses and purifications were performed on a Agilent LC system with UV/VIS detector using chiralcel columns.

## Ligand Synthesis

Chiral ligands **(*S*)-Me-BIDIME** (**L2**) and **(*S*)-BIDIME** (**L3**) were prepared according to a procedure reported previously in our laboratory[1]. All commercial available ligands were purchased from Sigma-Aldrich, Alfa Chemicals, Strem chemicals or J & K Chemicals Inc.

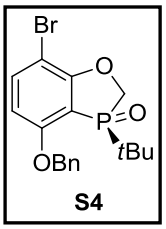



**Supplementary Figure 1.** Synthesis of Ligand **(*S*,*S*)-DI-BI-DIME (L4)**.




**(*R*)-3-(*tert*-butyl)-4-((*tert*-butyldiphenylsilyl)oxy)-2H-benzo[d][1,3]oxaphosphole 3-oxide (S2)**: To a solution of **S1** (2.00 g, 8.84 mmol, 1.0 equiv) and imidazole (1.20 g, 17.68 mmol, 2.0 equiv) in DCM (25 mL) at rt was added TBDPSCl (3.20 g, 11.49 mmol, 1.3 equiv) dropwisely under $N_2$. After stirring at rt overnight, the reaction was quenched with water, extracted with DCM, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: DCM/MeOH 100/1) to afford **S2** as white solid (4.11

g, 99%). **S2**: $[\alpha]_D^{25}$ = – 8.2 (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.81 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.39 – 7.35 (m, 1H), 7.34 – 7.29 (m, 2H), 6.90 (t, *J* = 8.2 Hz, 1H), 6.39 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.02 (dd, *J* = 8.1, 3.5 Hz, 1H), 4.56 (d, *J* = 13.7 Hz, 1H), 4.38 (dd, *J* = 13.2, 10.8 Hz, 1H), 1.32 (d, *J* = 16.0 Hz, 9H), 1.12 (s, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.29 (d, *J* = 17.6 Hz), 157.97 (d, *J* = 1.5 Hz), 135.51 (d, *J* = 40.3 Hz), 135.44 (d, *J* = 0.8 Hz), 132.14 (d, *J* = 183.7 Hz), 130.14 (d, *J* = 1.9 Hz), 128.01 (d, *J* = 19.6 Hz), 113.03 (d, *J* = 5.8 Hz), 106.43 (d, *J* = 5.4 Hz), 104.70 (d, *J* = 92.8 Hz), 65.79 (d, *J* = 60.0 Hz), 34.22 (d, *J* = 73.2 Hz), 26.56, 24.69 (d, *J* = 0.8 Hz), 19.62; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 63.13; HRMS (ESI) calculated for [M+Na, $C_{27}H_{33}NaO_3PSi]^+$: 487.1829; found: 487.1832.



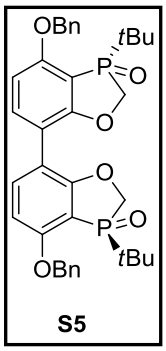
**S4**

**(*R*)-4-(benzyloxy)-7-bromo-3-(*tert*-butyl)-2H- benzo[d][1,3]-oxaphosphole 3-oxide (S4)**: To a solution of **S2** (4.10 g, 8.82 mmol, 1.0 equiv) in DCM (90 mL) at rt was added NBS (1.65 g, 9.27 mmol, 1.05 equiv) under $N_2$. After stirring at rt for 4 h, the reaction was quenched with water, extracted with DCM, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue (**S3**) was used without further purification.

To a solution of the above residue (**S3**) in THF (20 mL) at 0 $^o$C was added TBAF (13.3 mL, 13.24 mmol, 1.5 equiv, 1.0 M in THF) and stirred at 0 $^o$C for 5 min. Quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was used without further purification.

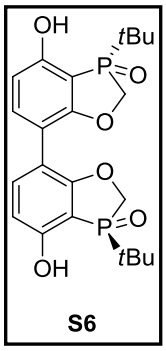
To a solution of the above residue and $K_2CO_3$ (3.66 g, 26.47 mmol, 3.0 equiv) in DMF (50 mL) at 0 $^o$C was added BnBr (1.26 mL, 10.59 mmol, 1.2 equiv) dropwisely under $N_2$ and stirred at rt overnight. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: DCM/MeOH 50/1) to afford **S4** as light yellow solid (3.3 g, 95%). **S4**: $[\alpha]_D^{25}$ = – 41.9 (c = 1.0, MeOH). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 6.44 (dd, *J* = 8.7, 4.5 Hz, 1H), 5.13 (q, *J* = 12.0 Hz, 2H), 4.60 (dd, *J* = 14.0, 3.1 Hz, 1H), 4.48 (dd, *J* = 14.0, 10.6 Hz, 1H), 1.21 (d, *J* = 16.6 Hz, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.23 (d, *J* = 16.7 Hz), 159.61 (d, *J* = 2.1 Hz), 138.97 (d, *J* = 1.3 Hz), 135.48, 128.65, 128.25, 127.41, 106.54 (d, *J* = 6.2 Hz), 105.07 (d, *J* = 88.2 Hz), 98.19 (d, *J* = 6.9 Hz), 70.99, 66.87 (d, *J* = 58.4 Hz), 34.00 (d, *J* =

73.6 Hz), 24.65 (d, $J$ = 0.8 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) δ 65.18; HRMS (ESI) calculated for [M+H, $C_{18}H_{21}BrO_3P]^+$: 395.0407; found: 395.0406.



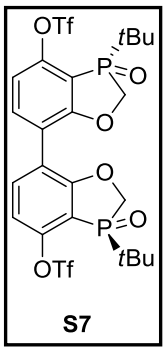
**S5**

**(3*R*,3'*R*)-4,4'-bis(benzyloxy)-3,3'-di-*tert*-butyl-2H,2'H-[7,7'-bibenzo[d][1,3]oxaphosphole] 3,3'-dioxide** (**S5**): **S4** (1.30 g, 3.29 mmol, 1.0 equiv), $Pd(OAc)_2$ (148 mg, 0.66 mmol, 0.2 equiv), Sphos (567 mg, 1.38 mmol, 0.42 equiv), $(BPin)_2$ (585 mg, 2.30 mmol, 0.7 equiv) and KOAc (968 mg, 9.87 mmol, 3.0 equiv) were dissolved in dioxane/$H_2O$ (15 mL, 4/1) at rt under $N_2$ and stirred at 80 $^o$C for 24 h. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: DCM/MeOH 20/1) to afford **S5** as light yellow solid (670 mg, 65%). **S5**: $[\alpha]_D^{25}$ = – 32.7 (c = 1.0, MeOH). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.40 – 7.33 (m, 6H), 7.33 – 7.27 (m, 2H), 6.59 – 6.53 (m, 2H), 5.24 – 5.14 (m, 4H), 4.51 – 4.33 (m, 4H), 1.24 (d, $J$ = 16.4 Hz, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.71 (d, $J$ = 16.5 Hz), 159.85 (d, $J$ = 2.0 Hz), 137.77, 135.99, 128.66, 128.15, 127.45, 115.06 (d, $J$ = 5.7 Hz), 104.77 (d, $J$ = 6.2 Hz), 103.35 (d, $J$ = 91.2 Hz), 70.78, 66.31 (d, $J$ = 59.3 Hz), 33.78 (d, $J$ = 73.7 Hz), 24.79; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 64.88; HRMS (ESI) calculated for [M+H, $C_{36}H_{41}O_6P_2]^+$: 631.2373; found: 631.2377.



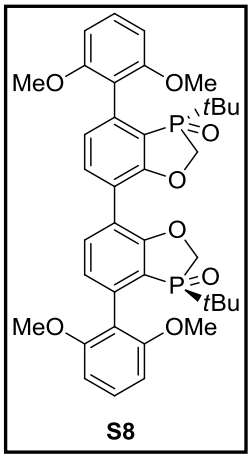
**S6**

**(3*R*,3'*R*)-3,3'-di-*tert*-butyl-4,4'-dihydroxy-2H,2'H-[7,7'-bibenzo[d][1,3]oxaphosphole] 3,3'-dioxide** (**S6**): **S5** (825 mg, 1.31 mmol, 1.00 equiv), Pd/C (800 mg, 10%), and MeOH (15 mL) were combined, and the reaction vessel was evacuated and back-filled with hydrogen (1 atm). The reaction mixture was stirred under hydrogen overnight, then filtered over a plug of silica gel topped with Celite (EtOAc eluent) to afford **S6** as white solid (560 mg, 95%). **S6**: $[\alpha]_D^{25}$ = +12.1 (c = 1.0, MeOH). $^1$H NMR (500 MHz, $CD_3OD$) δ 7.34 (d, $J$ = 8.3 Hz, 2H), 6.51 (dd, $J$ = 8.2, 4.6 Hz, 2H), 4.69 (dd, $J$ = 14.3, 3.2 Hz, 2H), 4.28 (dd, $J$ = 14.2, 10.7 Hz, 2H), 1.30 (d, $J$ = 16.6 Hz, 18H); $^{13}$C NMR (126 MHz, $CD_3OD$) δ 165.00 (d, $J$ = 17.0 Hz), 160.58 (d, $J$ = 2.3 Hz), 139.49, 114.58 (d, $J$ = 5.9 Hz), 108.90 (d, $J$ = 6.8 Hz), 101.68 (d, $J$ = 94.2 Hz), 66.76 (d, $J$ = 60.7 Hz), 34.41 (d, $J$ = 74.0 Hz), 24.82; $^{31}$P NMR (162 MHz, $CD_3OD$) δ 69.13; HRMS (ESI) calculated for [M+H, $C_{22}H_{29}O_6P_2]^+$: 451.1434; found: 451.1432.



S7

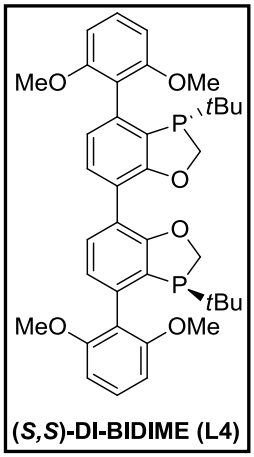
**(3*R*,3'*R*)-3,3'-di-*tert*-butyl-3,3'-dioxido-2H,2'H-[7,7'-bibenzo[d][1,3]oxaphosphole]-4,4'-diyl bis(trifluoromethanesulfonate)** (**S7**): To a solution of **S6** (560 mg, 1.31 mmol, 1.0 equiv) in DCM at rt was added $Et_3N$ (2.2 mL, 15.70 mmol, 12.0 equiv) and $PhNTf_2$ (3.74 g, 10.47 mmol, 8.0 equiv) under $N_2$ and then stirred at rt overnight. Then the reaction was quenched with water, extracted with DCM, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: DCM/MeOH 50/1) to afford **S7** as white solid (735 mg, 78%). **S7**: $[\alpha]_D^{25}$ = + 15.6 (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.13 (dd, *J* = 8.4, 3.6 Hz, 2H), 4.58 (dd, *J* = 14.1, 1.7 Hz, 2H), 4.48 (dd, *J* = 13.9, 10.9 Hz, 2H), 1.26 (d, *J* = 16.9 Hz, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.39 (d, *J* = 16.5 Hz), 149.76, 137.48, 121.04 (d, *J* = 5.1 Hz), 118.58 (q, *J* = 320.8 Hz), 113.75 (d, *J* = 4.7 Hz), 108.45 (d, *J* = 84.8 Hz), 66.54 (d, *J* = 59.1 Hz), 34.47 (d, *J* = 72.1 Hz), 24.08; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 63.67; HRMS (ESI) calculated for [M+Na, $C_{24}H_{26}F_6NaO_{10}P_2S_2]^+$: 737.0239; found: 737.0240.



S8

**(3*R*,3'*R*)-3,3'-di-*tert*-butyl-4,4'-bis(2,6-dimethoxyphenyl)-2H,2'H-[7,7'-bibenzo[d][1,3]ox -a phosphole] 3,3'-dioxide** (**S8**): To a solution of **S7** (735 mg, 1.03 mmol, 1.0 equiv), (2,6-dimethoxyphenyl)boronic acid (1.85 g, 8.23 mmol, 8.0 equiv) and KF (657 mg, 11.3 mmol, 11.0 equiv) in 10 mL superdry dioxane at rt was added $Pd_2(dba)_3$ (94 mg, 0.10 mmol, 0.1 equiv) and BI-DIME (75 mg, 0.23 mmol, 0.22 equiv) in the glovebox and stirred at 100 $^o$C overnight. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: DCM/MeOH 20/1) to afford **S8** as gray solid (700 mg, 98%). **S8**: $[\alpha]_D^{25}$ = +48.1 (c = 1.0, MeOH). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.4 Hz, 2H), 6.98 (dd, *J* = 7.6, 3.6 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 2H), 4.46 (dd, *J* = 13.8, 0.9 Hz, 2H), 4.36 (dd, *J* = 13.6, 10.4 Hz, 2H), 3.82 (s, 6H), 3.76 (s, 6H), 0.93 (d, *J* = 15.9 Hz, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.43 (d, *J* = 19.3 Hz), 158.81, 157.61, 137.91 (d, *J* = 5.8 Hz), 135.58, 130.13, 125.08 (d, *J* = 9.2 Hz), 121.37 (d, *J* = 6.4 Hz), 117.30 (d, *J* = 1.9 Hz), 114.63 (d, *J* = 91.6 Hz), 104.52, 103.19, 65.22 (d, *J* = 60.9 Hz), 56.08,

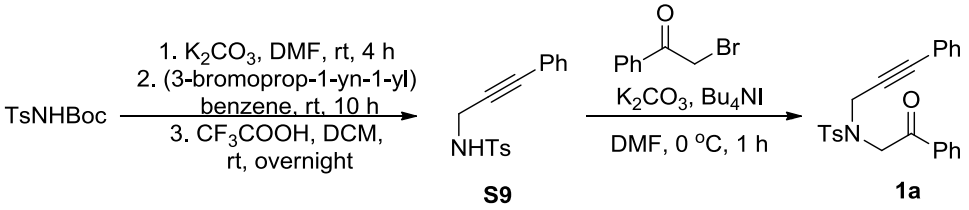
55.52, 33.80 (d, $J$ = 71.6 Hz), 23.81; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 62.75; HRMS (ESI) calculated for [M+H, $C_{38}H_{45}O_8P_2]^+$: 691.2584; found: 691.2583.



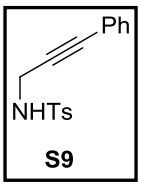
**(*S,S*)-DI-BIDIME (L4)**

**(3*S*,3'*S*)-3,3'-di-*tert*-butyl-4,4'-bis(2,6-dimethoxyphenyl)-2,2',3,3'-tetra hydro-7,7'-bibenz -o[d]- [1,3]oxaphosphole** [**(*S,S*)-DI-BI-DIME (L4)**]: To a solution of **S8** (680 mg, 0.98 mmol, 1.0 equiv) in THF (20 mL) at room temperature was added polymethylhydrosiloxane (PMHS, 5.4 g) and titanium isopropoxide (2.3 mL, 7.88 mmol, 8.0 equiv). The mixture was stirred at reflux under nitrogen for 12 h and then distilled under vacuum to remove most of THF. To the residue was charged carefully with 30% degassed NaOH solution (30 mL). Gas was released during the addition. Extracted with degassed $Et_2O$, dried with anhydrous $Na_2SO_4$, filtered, concentrated under vacuum, and passed through a neutral alumina plug ($Et_2O$) to provide the desired product **(*S,S*)-DI-BI-DIME (L4)** as white solid (610 mg, 90%). **L4**: $[\alpha]_D^{25}$ = +47.1 (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 7.7 Hz, 2H), 7.31 (t, $J$ = 8.3 Hz, 2H), 6.96 – 6.90 (m, 2H), 6.68 (d, $J$ = 8.4 Hz, 2H), 6.61 (d, $J$ = 8.4 Hz, 2H), 4.82 (dd, $J$ = 12.6, 1.4 Hz, 2H), 4.51 (dd, $J$ = 24.7, 12.5 Hz, 2H), 3.79 (s, 6H), 3.73 (s, 6H), 0.81 (d, $J$ = 12.0 Hz, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.63, 158.04, 157.37, 137.40 (d, $J$ = 18.4 Hz), 132.05, 129.03, 125.27 (d, $J$ = 12.8 Hz), 123.66 (d, $J$ = 4.5 Hz), 120.51, 120.01, 104.56, 103.70, 70.19 (d, $J$ = 26.1 Hz), 55.96 (d, $J$ = 1.7 Hz), 55.47, 31.10 (d, $J$ = 18.6 Hz), 26.74 (d, $J$ = 14.5 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) δ – 6.93; HRMS (ESI) calculated for [M+H, $C_{38}H_{45}O_6P_2]^+$: 659.2686; found: 659.2687.

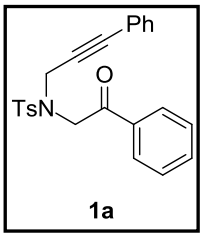
## Substrate Synthesis




**Supplementary Figure 2.** General procedure for substrate **1a**



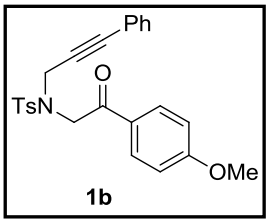

**4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (S9).** *Tert*-butyl tosylcarbamate (17.7 g, 65.3 mmol, 1.0 equiv) and $K_2CO_3$ (13.5 g, 97.9 mmol, 1.5 equiv) were dissolved in 65 mL DMF and stirred at rt for 4 h. Then (3-bromoprop-1-yn-1-yl)benzene[2] (14.0 g, 71.8 mmol, 1.1 equiv) was added to the above solution and stirred at rt for 10 h. The reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was dissolved in 60 mL DCM and 20 mL $CF_3COOH$ and stirred at rt overnight. The reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was recrystallized with hexane/EtOAc to afford **S9** as white solid (17.5 g, 94%). **S9**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.32 – 7.27 (m, 3H), 7.26 – 7.20 (m, 2H), 7.17 – 7.09 (m, 2H), 4.63 (t, *J* = 5.8 Hz, 1H), 4.08 (d, *J* = 6.1 Hz, 2H), 2.36 (s, 3H); ESI-MS: m/z 286.2 $[M+H]^+$. The $^1$H NMR spectra and ESI-MS are in agreement with those reported in the literature. [3]



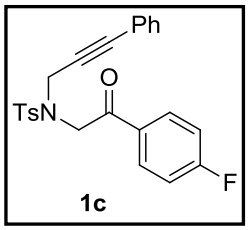

**4-Methyl-*N*-(2-oxo-2-phenylethyl)-*N*-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (1a).** To a solution of **S2** (5.0 g, 17.5 mmol, 1.0 equiv), 2-bromo-1-phenylethan-1-one (3.7 g, 18.4 mmol, 1.05 equiv), $Bu_4NI$ (647.2 mg, 1.75 mmol, 0.1 equiv) in 35 mL DMF at 0 °C was added $K_2CO_3$ (3.6 g, 26.3 mmol, 1.5 equiv) and stirred at 0 °C for 1 h. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was recrystallized with hexane/EtOAc to afford **1a** as white solid (6.0 g, 85%). **1a**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.84 – 7.79 (m, 2H), 7.63 – 7.57 (m, 1H), 7.51 – 7.45 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 7.12 – 7.07 (m, 2H), 4.81 (s, 2H), 4.49 (s, 2H), 2.39 (s, 3H); $^{13}$C NMR (126

MHz, $CDCl_3$) δ 193.46, 143.90, 136.12, 135.00, 133.92, 131.69, 129.79, 128.92, 128.64, 128.24, 128.22, 127.80, 122.07, 86.33, 81.67, 51.99, 38.41, 21.60; ESI-MS: m/z 404.3 $[M+H]^+$. The $^1H$, $^{13}C$ NMR spectra and ESI-MS are in agreement with those reported in the literature.[4]

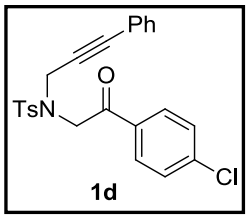
Preparations of **1b-i** were carried out according to a procedure similar to that for the synthesis of **1a** from corresponding α-bromoketones.



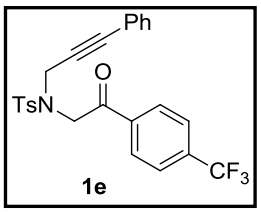

**1b**: white solid, 92% yield. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.84 – 7.78 (m, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.13 – 7.07 (m, 2H), 6.97 – 6.91 (m, 2H), 4.75 (s, 2H), 4.47 (s, 2H), 3.87 (s, 3H), 2.38 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 191.95, 164.15, 143.87, 136.20, 131.74, 130.67, 129.79, 128.62, 128.25, 128.07, 127.87, 122.20, 114.12, 86.28, 81.79, 55.67, 51.75, 38.42, 21.63; HRMS (ESI) calculated for [M+Na, $C_{25}H_{23}NNaO_4S]^+$: 456.1240; found: 456.1244.



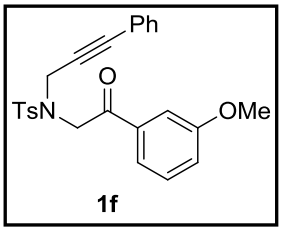

**1c**: white powder, 80% yield. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.85 – 7.77 (m, 2H), 7.33 – 7.21 (m, 5H), 7.19 – 7.06 (m, 4H), 4.76 (s, 2H), 4.47 (s, 2H), 2.39 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 192.08, 166.19 (d, $J$ = 256.1 Hz), 144.03, 135.93, 131.69, 131.45 (d, $J$ = 3.0 Hz), 131.08 (d, $J$ = 9.4 Hz), 129.83, 128.71, 128.27, 127.84, 122.03, 116.11 (d, $J$ = 22.0 Hz), 86.46, 81.52, 52.09, 38.50, 21.61; HRMS (ESI) calculated for [M+Na, $C_{24}H_{20}FNNaO_3S]^+$: 444.1040; found: 444.1042.



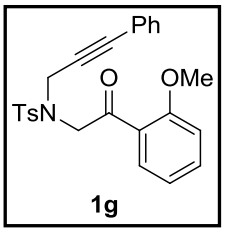

**1d**: white powder, 73% yield. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.82 – 7.78 (m, 2H), 7.47 – 7.42 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.13 – 7.06 (m, 2H), 4.74 (s, 2H), 4.45 (s, 2H), 2.38 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 192.57, 144.07, 140.45, 135.88, 133.33, 131.71, 129.86, 129.77, 129.28, 128.74, 128.29, 127.85, 122.01, 86.52, 81.48, 52.19, 38.53, 21.64; HRMS (ESI) calculated for [M+Na, $C_{24}H_{20}ClNNaO_3S]^+$: 460.0745; found: 460.0745.



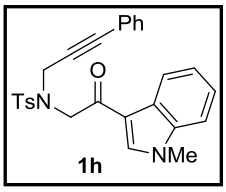

**1e**: white powder, 64% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.84 – 7.79 (m, 2H), 7.76 – 7.71 (m, 2H), 7.35 – 7.21 (m, 5H), 7.12 – 7.06 (m, 2H), 4.79 (s, 2H), 4.46 (s, 2H), 2.40 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 193.03, 144.18, 137.70, 135.71, 135.04 (q, *J* = 32.6 Hz), 131.68, 129.90, 128.80, 128.75, 128.30, 127.85, 125.96 (q, *J* = 3.6 Hz), 123.56 (d, *J* = 272.8 Hz), 121.91, 86.66, 81.35, 52.58, 38.63, 21.61; HRMS (ESI) calculated for [M+Na, $C_{25}H_{20}F_3NNaO_3S]^+$: 494.1008; found: 494.1009.



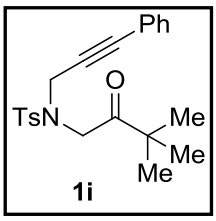

**1f**: light yellow solid, 92% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.59 – 7.54 (m, 1H), 7.54 – 7.48 (m, 1H), 7.41 – 7.36 (m, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 7.17 – 7.07 (m, 3H), 4.79 (s, 2H), 4.48 (s, 2H), 3.85 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 193.39, 160.01, 143.92, 136.29, 136.10, 131.71, 129.93, 129.81, 128.66, 128.25, 127.81, 122.08, 120.74, 120.53, 112.49, 86.36, 81.65, 55.62, 52.16, 38.42, 21.62; HRMS (ESI) calculated for [M+Na, $C_{25}H_{23}NNaO_4S]^+$: 456.1240; found: 456.1242.



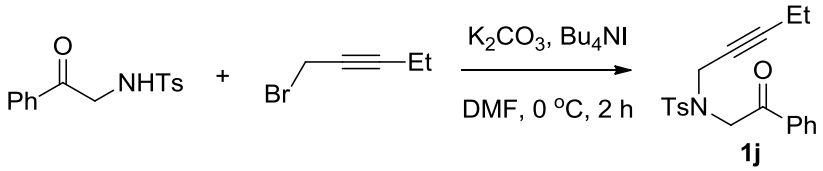

**1g**: light yellow solid, 86% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 3H), 7.54 – 7.47 (m, 1H), 7.31 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.15 – 7.10 (m, 2H), 7.04 – 6.95 (m, 2H), 4.83 (s, 2H), 4.51 (s, 2H), 3.91 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 194.97, 159.14, 143.54, 136.72, 134.67, 131.65, 130.99, 129.60, 128.51, 128.23, 127.76, 125.52, 122.36, 121.05, 111.67, 85.83, 82.38, 56.11, 55.73, 38.43, 21.60; HRMS (ESI) calculated for [M+Na, $C_{25}H_{23}NNaO_4S]^+$: 456.1240; found: 456.1243.



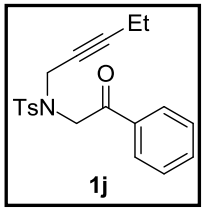

**1h**: light yellow solid, 79% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 8.06 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.14 (m, 3H), 7.13 – 7.07 (m, 2H), 6.99 – 6.93 (m, 2H), 4.42 (s, 2H), 4.35 (s, 2H), 3.74 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.54, 143.99, 137.30, 136.83, 135.72, 131.72, 129.78, 128.52, 128.17, 127.96, 126.72, 123.74, 123.06, 122.63, 122.26, 113.99, 109.86, 86.41, 81.51, 53.34, 38.55, 33.83, 21.59; HRMS (ESI) calculated for [M+H, $C_{27}H_{25}N_2O_3S]^+$: 457.1580; found: 457.1582.



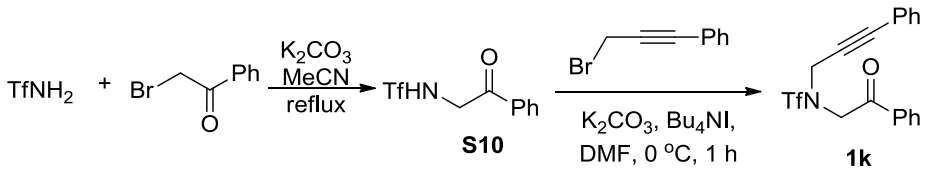

**1i**: white solid, 79% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.32 – 7.24 (m, 5H), 7.17 – 7.12 (m, 2H), 4.45 (s, 2H), 4.40 (s, 2H), 2.39 (s, 3H), 1.18 (s, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 208.92, 143.74, 136.42, 131.68, 129.73, 128.70, 128.34, 127.68, 122.16, 86.11, 81.88, 49.72, 43.64, 37.85, 26.48, 21.60; HRMS (ESI) calculated for [M+Na, $C_{20}H_{25}NNaO_3S]^+$: 406.1447; found: 406.1447.



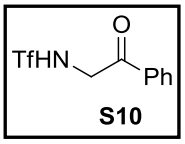

**Supplementary Figure 3.** Synthetic procedure of substrate **1j**



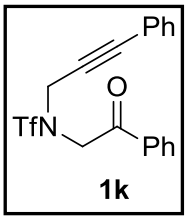

**4-Methyl-*N*-(2-oxo-2-phenylethyl)-*N*-(pent-2-yn-1-yl)benzenesulfonamide (1j).** To a solution of 4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide[5] (1.0 g, 3.46 mmol, 1.0 equiv), 1-bromopent-2-yne (0.48 mL, 4,50 mmol, 1.3 equiv), $Bu_4NI$ (129 mg, 0.35 mmol, 0.1 equiv) in 10 mL DMF at 0 °C was added $K_2CO_3$ (1.1 g, 7.85 mmol, 2.5 equiv) under $N_2$, and stirred at 0 °C for 2 h. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 10/1) to afford **1j** as white solid (1.0 g, 82% yield). **1j**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 4.21 (s, 2H), 2.42 (s, 3H), 1.94 (tq, *J* = 7.5, 2.0 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 193.62, 143.67, 136.29, 135.10, 133.82, 129.61, 128.88, 128.18, 127.81, 88.45, 71.81, 51.80, 38.04, 21.64, 13.56, 12.27; HRMS (ESI) calculated for [M+Na, $C_{20}H_{21}NNaO_3S]^+$: 378.1134; found: 378.1138.



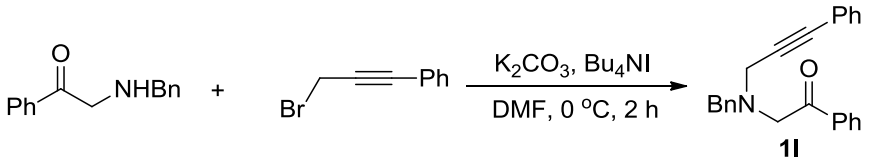

**Supplementary Figure 4.** Synthetic procedure of substrate **1k**



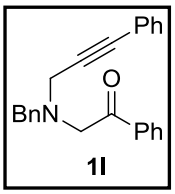

**1,1,1-Trifluoro-*N*-(2-oxo-2-phenylethyl)methanesulfonamide (S10):** 2-Bromo-1-phenylethan-1-one (2.7 g, 13.4 mol, 1.0 equiv), Trifluoromethanesulfonamide (4.0 g, 26.8 mmol, 2.0 equiv), and $K_2CO_3$ (3.7 g, 26.8 mmol, 2.0 equiv) were dissolved in 100 mL MeCN, and heated to reflux for 1 h. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified through column chromatography (hexane/EtOAc 30/1) to afford **S10** as white solid (3.8 g, 75%). **S10**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.71 – 7.64 (m, 1H), 7.58 – 7.49 (m, 2H), 6.24 (s, 1H), 4.78 (s, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 191.54, 135.10, 133.30, 129.32, 128.19, 119.81 (q, $J$ = 320.9 Hz), 49.64; MALDI-TOF-HR-MS calculated for [M+H, $C_9H_9F_3NO_3S]^+$: m/z 268.0250; found: 268.0247.



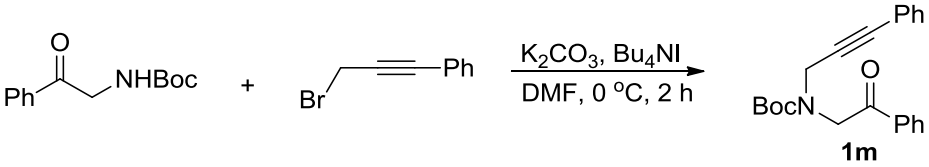

**1k:** To a solution of **S2** (300 mg, 1.12 mmol, 1.00 equiv), (3-bromoprop-1-yn-1-yl)benzene (241 mg, 1.23 mmol, 1.10 equiv), $Bu_4NI$ (42 mg, 0.11 mmol, 0.10 equiv) in 2.5 mL DMF at 0 °C was added $K_2CO_3$ (171 mg, 1.23 mmol, 1.10 equiv) and stirred at 0 °C for 1 h. Then the reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified through column chromatography (hexane/EtOAc 50/1) to afford **1k** as white solid (370 mg, 86%). **1k**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.69 – 7.62 (m, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.27 (m, 5H), 5.05 (s, 2H), 4.67 (s, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 191.55, 134.50, 134.20, 131.96, 129.22, 129.18, 128.53, 128.09, 121.64, 119.91 (q, $J$ = 322.3 Hz), 87.12, 80.73, 52.32, 39.89; HRMS (ESI) calculated for [M+Na, $C_{18}H_{14}F_3NNaO_3S]^+$: 404.0539; found: 404.0541.



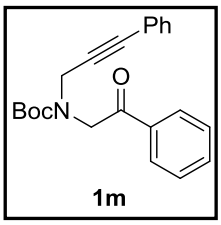

**Supplementary Figure 5.** Synthetic procedure of substrate **1l**



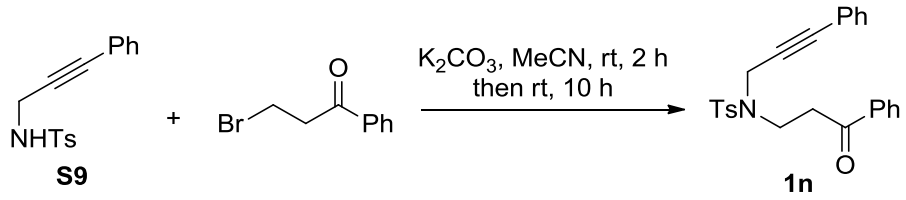

**1l**: (*N*-benzyl-3-phenylprop-2-yn-1-amine[6] was used), white solid, 77% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.53 – 7.47 (m, 1H), 7.42 – 7.31 (m, 6H), 7.29 – 7.17 (m, 6H), 4.01 (s, 2H), 3.78 (s, 2H), 3.66 (s, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.52, 138.03, 136.23, 133.35, 131.92, 129.50, 128.65, 128.55, 128.45, 128.43, 128.32, 127.59, 123.21, 86.29, 84.21, 59.58, 58.38, 43.46; HRMS (ESI) calculated for [M+H, $C_{24}H_{22}NO$]$^{+}$: 340.1696; found: 340.1699.



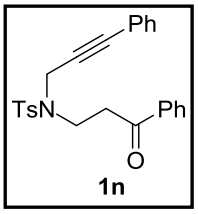

**Supplementary Figure 6.** Synthetic procedure of substrate **1m**



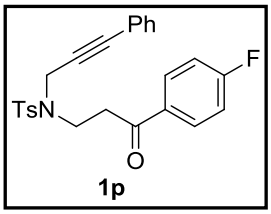

**1m:** (*tert*-butyl (2-oxo-2-phenylethyl) carbamate[7] was used), white solid, 75% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.22 (m, 5H), 5.78 (d, *J* = 8.3 Hz, 1H), 5.56 – 5.48 (m, 1H), 3.04 (dd, *J* = 17.1, 5.8 Hz, 1H), 2.89 (dd, *J* = 17.0, 5.1 Hz, 1H), 1.47 (s, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.35, 155.27, 134.88, 133.84, 131.71, 128.93, 128.75, 128.22, 128.07, 123.16, 84.17, 84.12, 80.16, 53.93, 28.45, 24.75; HRMS (ESI) calculated for [M+Na, $C_{22}H_{23}NNaO_3$]$^{+}$: 372.1570; found: 372.1573.



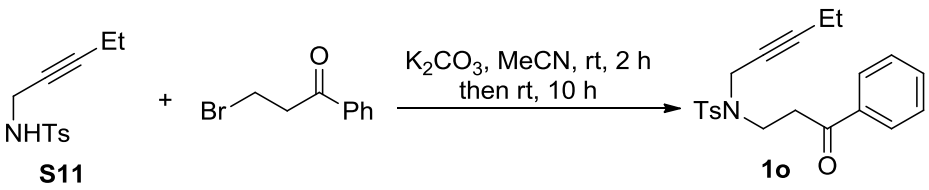

**Supplementary Figure 7.** Synthetic procedure of substrate **1n**




**1n:** To a solution of **S9** (2.0 g, 7.01 mmol, 1.0 equiv) in 15 mL MeCN at 0 $^{o}$C was added $K_2CO_3$ (1.07 g, 7.71 mmol, 1.1 equiv) and stirred for 2 h， followed by the addition of 3-bromo-1-phenylpropan-1-one[7] (1.5 g, 7.01 mmol, 1.0 equiv) in one portion, and stirred for 10 h. The reaction was quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was recrystallized with hexane/EtOAc to afford **1n** as white solid (2.6 g, 90%). **1n**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.85 – 7.77 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 7.31 – 7.18 (m, 5H), 7.11 – 7.05 (m, 2H), 4.44 (s, 2H), 3.71 (t, *J* = 7.1 Hz, 2H), 3.45 (t, *J* = 7.1 Hz, 2H), 2.33 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.10, 143.65, 136.47, 135.61, 133.42, 131.53, 129.61, 128.68, 128.45, 128.13, 128.07, 127.83, 122.11, 85.58, 82.31, 42.82, 39.01, 38.57, 21.44; HRMS (ESI) calculated for [M+H, $C_{25}H_{24}NO_3S]^+$: 418.1471; found: 418.1465.



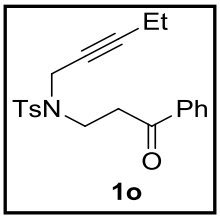

**1p:** Preparation of **1p** was carried out according to a procedure similar to that for the synthesis of **1n** from corresponding β-bromoketone. White solid, 93% yield. **1p**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.20 (m, 5H), 7.20 – 7.04 (m, 4H), 4.42 (s, 2H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 196.66, 167.02, 164.99, 143.80, 135.62, 133.05 (d, *J* = 3.0 Hz), 131.61, 130.86 (d, *J* = 9.4 Hz), 129.71, 128.57, 128.22, 127.93, 122.16, 85.67, 82.35, 42.92, 39.21, 38.71, 21.53; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –104.62 (m).HRMS (ESI) calculated for [M+Na, $C_{25}H_{22}FNNaO_3S]^+$: 458.1197; found: 458.1204.



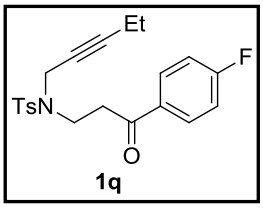

**Supplementary Figure 8.** Synthetic procedure of substrate **1o**

**4-Methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide (S11):** Preparations of **S11** were carried out according to procedures similar to that for the synthesis of **S9.** All the physical and spectroscopic data of this compound are in agreement with those reported in the literature.[8]

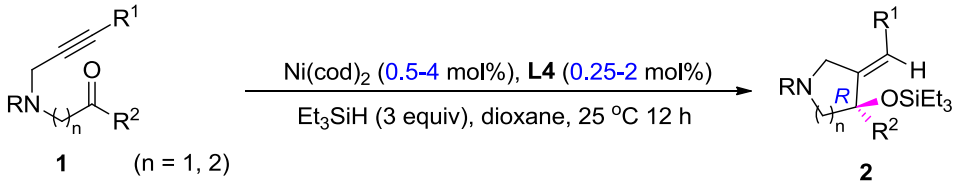
`




**1o:** Preparation of **1o** was carried out according to a procedure similar to that for the synthesis of **1n** from substrate **S11.** .**1o:** white solid, 80% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.15 (t, *J* = 2.2 Hz, 2H), 3.60 (t, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.92 (qt, *J* = 7.5, 2.2 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.29, 143.52, 136.61, 135.87, 133.49, 129.51, 128.77, 128.15, 127.93, 87.62, 72.39, 42.64, 38.62, 38.57, 21.60, 13.54, 12.24; HRMS (ESI) calculated for [M+H, $C_{21}H_{23}NO_3S]^+$: 370.1471; found: 370.1472.

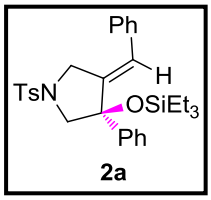



**1q:** Preparation of **1q** was carried out according to a procedure similar to that for the synthesis of **1n** from substrate **S11** and corresponding β-bromoketone**. 1q**: white solid, 85% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 4.14 (s, 2H), 3.59 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.93 (dd, *J* = 15.1, 7.6 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 196.79, 167.07, 165.04, 143.61, 135.84, 133.14 (d, *J* = 2.9 Hz), 130.87 (d, *J* = 9.3 Hz), 129.57, 128.65 (d, *J* = 267.4 Hz), 127.97, 116.03, 115.86, 87.68, 72.42, 42.69, 38.76, 38.76, 21.64, 13.58, 12.28; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –104.69 (m); HRMS (ESI) calculated for [M+Na, $C_{21}H_{22}FNNaO_3S]^+$: 410.1197; found: 410.1201.



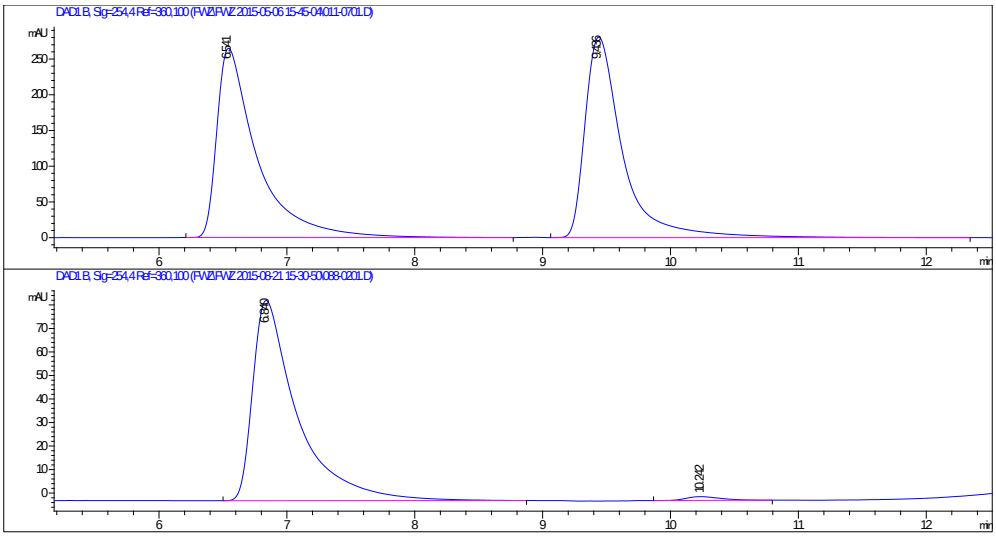

**Supplementary Figure 9**. Asymmetric nickel-catalyzed reductive cyclization of *N*-alkynones

**General Procedure**: $Ni(cod)_2$ (2 μ mol, 1 mol %), **(*S*,*S*)-DI-BIDIME** (**L4**, 1 μ mol, 0.5 mol %), and dioxane (0.5 mL) were added to a 5 mL screw-cap vial equipped with a magnetic stirring bar in the glove box. Substrate **1** (0.2 mmol, 1.0 equiv.) was added to the solution in one portion, stirred for 5 mins, followed by the addition of triethylsilane ($Et_3SiH$, 0.6 mmol, 3.0 equiv.). The vial was closed with a screw-cap, and the resulting mixture was stirred at 25 °C for 12 h. Quenched with saturated sodium bicarbonate ($NaHCO_3$), extracted with ethyl acetate (EtOAc), washed with saturated NaCl, dried over anhydrous sodium sulfate ($Na_2SO_4$), filtered, and concentrated under vacuum. The residue was purified by column chromatography (10% petroleum ether/EtOAc) to afford compound **2**.



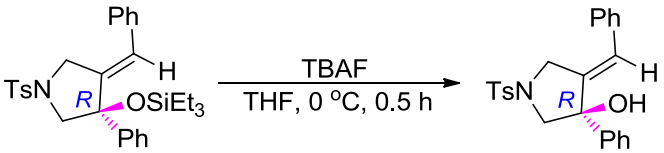
**2a**

**2a**: colorless oil, 98% yield, 99:1 er with **L4** (0.1 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 98/2, 254 nm, 6.8 min (*R*), 10.2 min (*S*). The absolute configuration was assigned by the X-ray structure of **3a** (desilylation product of **2a**). **2a**: $[\alpha]_D^{25}$ = +23.6 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.25 (m, 8H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.45 (s, 1H), 4.38 (d, *J* = 14.9 Hz, 1H), 4.21 (dd, *J* = 14.9, 1.8 Hz, 1H), 3.68 (d, *J* = 9.6 Hz, 1H), 3.44 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.7 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.01, 143.98, 142.39, 135.92, 132.59, 129.89, 128.78, 128.59, 128.19, 127.95, 127.75, 127.55, 126.10, 126.10, 83.10, 60.68, 50.56, 21.65, 7.14, 6.25; HRMS (ESI) calculated for [M+Na, $C_{30}H_{37}NNaO_3SSi]^+$: 542.2156; found: 542.2159.

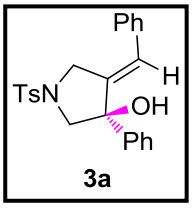



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 6.840 | BB | 0.3442 | 2059.34668 | 85.13765 | 98.5504 |
| 2 | 10.242 | BB | 0.2700 | 30.29120 | 1.60639 | 1.4496 |

**Supplementary Figure 10.** HPLC chromatogram of chiral product **2a**



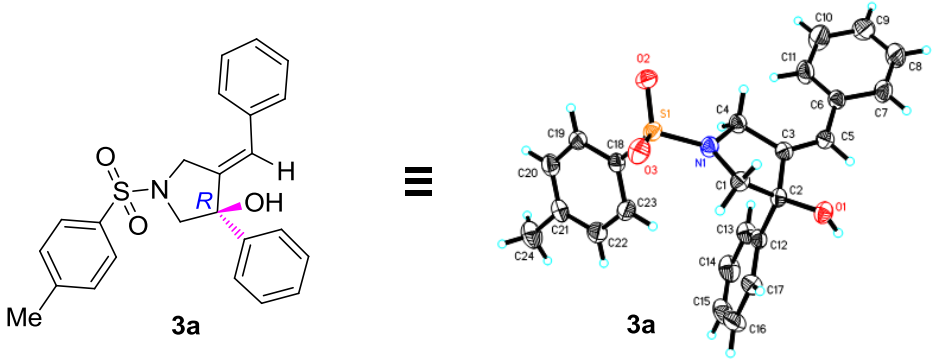

**2a** **3a**



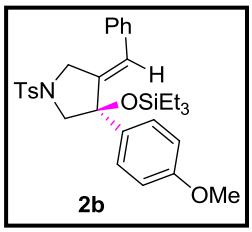

**3a**

To a solution of **2a** (520 mg, 1.0 mmol, 1.0 equiv.) in THF (10 mL) at 0 °C was added TBAF (1.0 M solution in THF, 1.5 ml, 1.5 equiv.), stirred at 0 °C for 0.5 h. Quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (20% petroleum ether/EtOAc) to give compound **3a** as white solid (390 mg, 96%). **3a**: $[\alpha]_D^{25}$ = +24.5 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.13 (m, 8H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.19 (t, *J* = 2.3 Hz, 1H), 4.40 (dd, *J* = 15.0, 2.4 Hz, 1H), 4.16 (dd, *J* = 15.0, 2.5 Hz, 1H), 3.47 (q, *J* = 10.4 Hz, 2H), 2.42 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.03, 142.58, 141.59, 135.64, 132.98, 129.93, 128.76, 128.65, 128.44, 128.01, 127.97, 127.94, 126.61, 126.31, 82.05, 61.50, 50.72, 21.68; HRMS (ESI) calculated for [M+Na, $C_{24}H_{23}NNaO_3S]^+$: 428.1291; found: 428.1292.

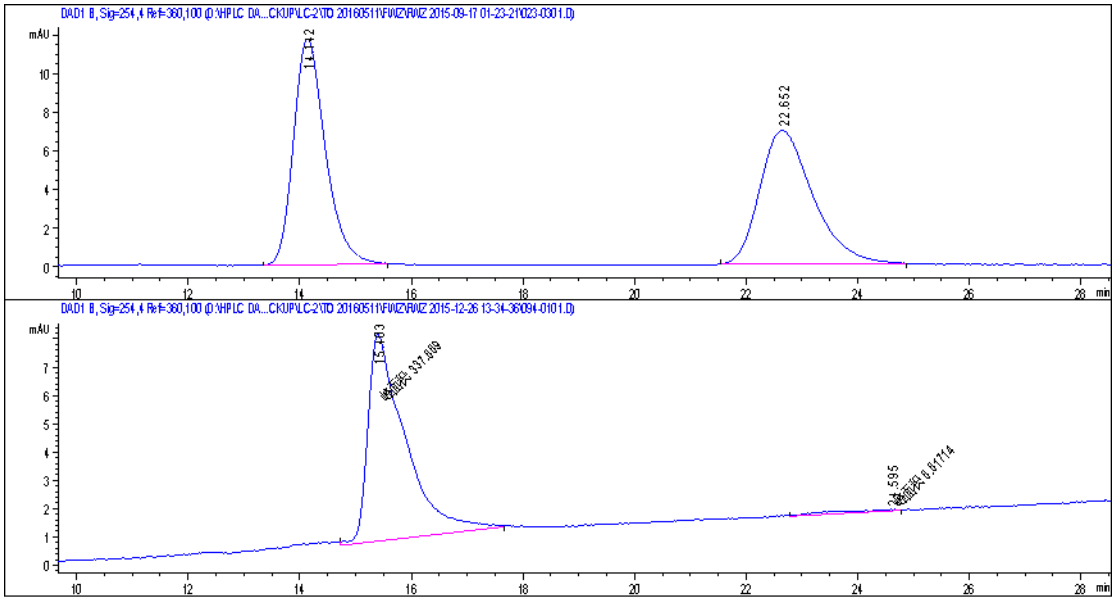
Crystalization from hexanes/EtOAc (9:1) gave crystals suitable for X-ray crystallographic analysis, which revealed its absolute configuration for the chiral tertiary alcohol **3a** as shown in **Figure 1**.




**Supplementary Figure 11.** X-ray derived ORTEP representation of **3a** (CCDC1532676 contains the supplementary crystallographic data of **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)

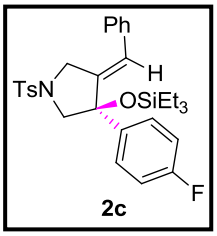



**2b**: colorless oil, 87% yield, 98:2 er with **L4** (0.5 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 98/2, 254 nm, 15.4 min (*R*), 24.6 min (*S*). **2b**: $[\alpha]_D^{25}$ = +19.1 (c = 1.0, $CHCl_3$); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.26 (m, 7H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.47 (s, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.18 (d, *J* = 14.8 Hz, 1H), 3.82 (s, 3H), 3.68 (d, *J* = 9.5 Hz, 1H), 3.39 (d, *J* = 9.5 Hz, 1H), 2.43 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.53 (dd, *J* = 15.6, 7.7 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 159.01, 143.91, 142.39, 135.96, 135.70, 132.73, 129.87, 128.76, 128.60, 127.89, 127.68, 127.47, 125.53, 113.49, 82.70, 60.30, 55.35, 50.33, 21.64, 7.14, 6.24; HRMS (ESI) calculated for [M+H, $C_{31}H_{40}NO_4SSi]^+$: 550.2447; found: 550.2431.



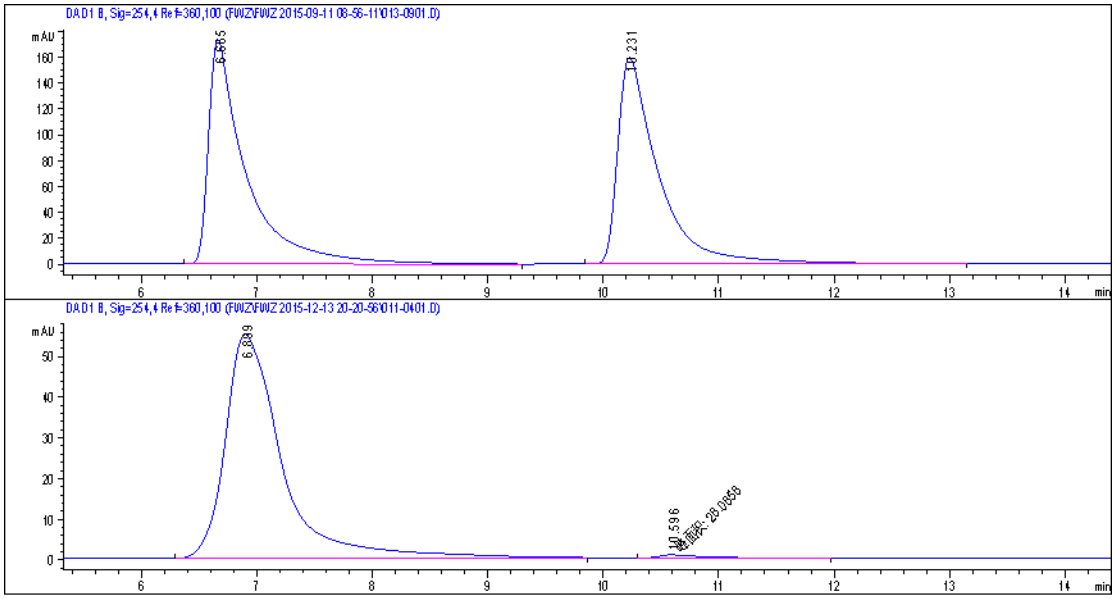

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 15.403 | MM | 0.7707 | 337.66885 | 7.30240 | 98.0780 |
| 2 | 24.595 | MM | 2.0871 | 6.61714 | 5.28408e-2 | 1.9220 |

**Supplementary Figure 12.** HPLC chromatogram of chiral product **2b**



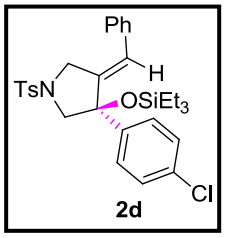

**2c**: colorless oil, 90% yield, 99:1 er with **L4** (0.5 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 98/2, 254 nm, 6.9 min (*R*), 10.6 min (*S*). **2c**: $[\alpha]_D^{25}$ = +11.9 (c = 1.0, $CHCl_3$); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* =

8.2 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.31 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.44 (t, *J* = 2.3 Hz, 1H), 4.34 (dd, *J* = 14.9, 2.3 Hz, 1H), 4.21 (dd, *J* = 14.9, 2.6 Hz, 1H), 3.66 (d, *J* = 9.6 Hz, 1H), 3.40 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.58 – 0.49 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.16 (d, *J* = 246.4 Hz), 144.08, 142.13, 139.95 (d, *J* = 3.1 Hz), 135.74, 132.47, 129.91, 128.81, 128.57, 127.91, 127.86 (d, *J* = 2.0 Hz), 127.80, 126.08, 114.98 (d, *J* = 21.4 Hz), 82.63, 60.46, 50.43, 21.62, 7.09, 6.23; HRMS (ESI) calculated for [M+H, $C_{30}H_{37}O_3NFSSi$]$^+$: 538.2247; found: 538.2234.



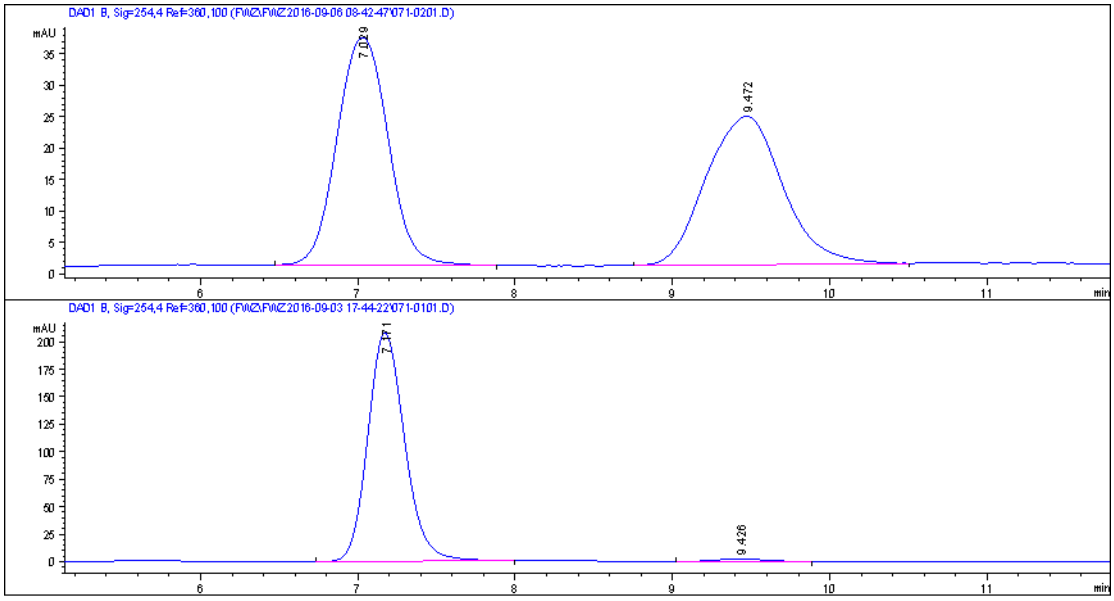

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 6.899 | BB | 0.5163 | 1866.99622 | 54.96024 | 98.6231 |
| 2 | 10.596 | MM | 0.5501 | 26.06558 | 7.89789e-1 | 1.3769 |

**Supplementary Figure 13.** HPLC chromatogram of chiral product **2c**



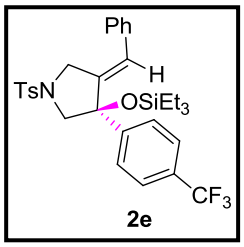

**2d**: colorless oil, 74% yield, 99:1 er with **L4** (0.5 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 7.2 min (*R*), 9.4 min (*S*). **2d**: $[\alpha]_D^{25}$ = +11.6 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.32 (m, 6H), 7.31 – 7.25 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 1H), 4.35 (dd, *J* = 15.0, 2.3 Hz, 1H), 4.20 (dd, *J* = 15.0, 2.6 Hz, 1H), 3.63 (d, *J* = 9.7 Hz, 1H), 3.40 (d, *J* = 9.7 Hz, 1H), 2.44 (s, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.58 – 0.48 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.14, 142.91, 141.98, 135.70, 133.42, 132.43, 129.94,

128.84, 128.59, 128.36, 127.93, 127.51, 126.34, 110.10, 82.69, 60.50, 50.50, 21.67, 7.11, 6.25; HRMS (ESI) calculated for [M+H, $C_{30}H_{37}O_3NClSSi]^+$: 554.1952; found: 554.1935.

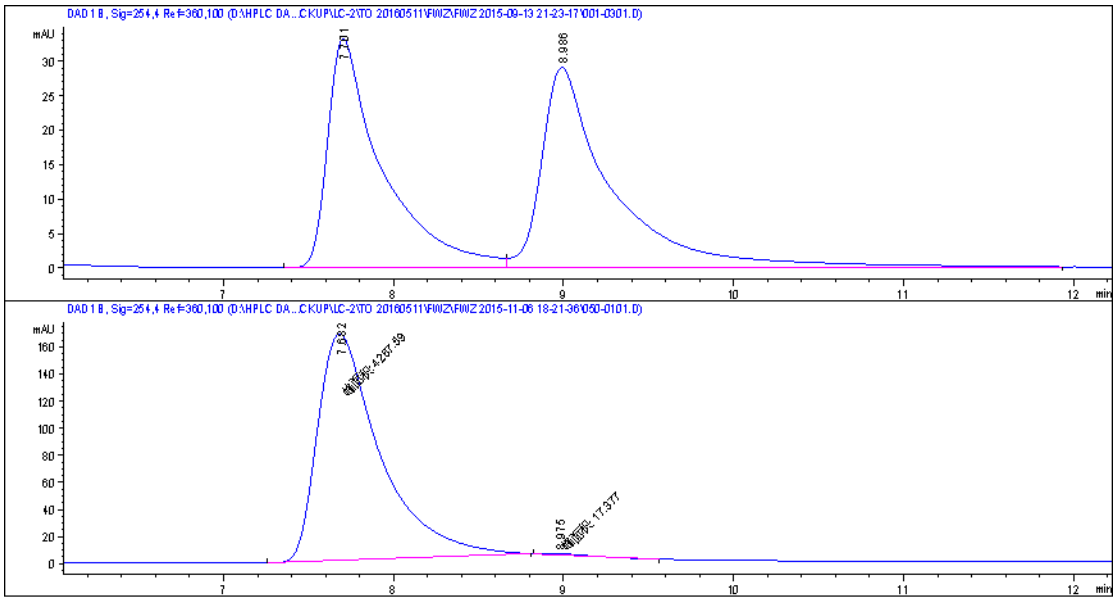



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.171 | BB | 0.2519 | 3382.08496 | 207.80231 | 98.6806 |
| 2 | 9.426 | BB | 0.2448 | 45.21954 | 2.28586 | 1.3194 |

**Supplementary Figure 14.** HPLC chromatogram of chiral product **2d**

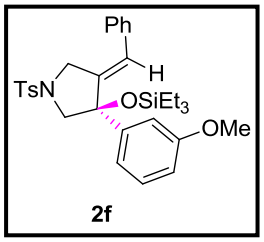



**2e**: colorless oil, 98% yield, > 99:1 er with **L4** (0.25 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 7.7 min (*R*), 9.0 min (*S*). **2e**: $[\alpha]_D^{25}$ = +13.4 (c = 1.0, $CHCl_3$); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.59 (dd, *J* = 19.6, 8.4 Hz, 4H), 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.41 (s, 1H), 4.38 (dd, *J* = 15.0, 2.0 Hz, 1H), 4.26 (dd, *J* = 15.0, 2.3 Hz, 1H), 3.65 (d, *J* = 9.8 Hz, 1H), 3.44 (d, *J* = 9.8 Hz, 1H), 2.45 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.61 – 0.51 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 148.77, 144.26, 141.87, 135.57, 132.20, 129.96, 129.70 (q, *J* = 32.4 Hz), 128.86, 128.57, 128.04, 127.98, 126.91, 126.27, 125.21 (q, *J* = 3.7 Hz), 124.21 (q, *J* = 272.2 Hz), 82.87, 60.73, 50.69, 21.61, 7.07, 6.24; HRMS (ESI) calculated for [M+H, $C_{31}H_{37}O_3NF_3SSi]^+$: 588.2210; found: 588.2216.

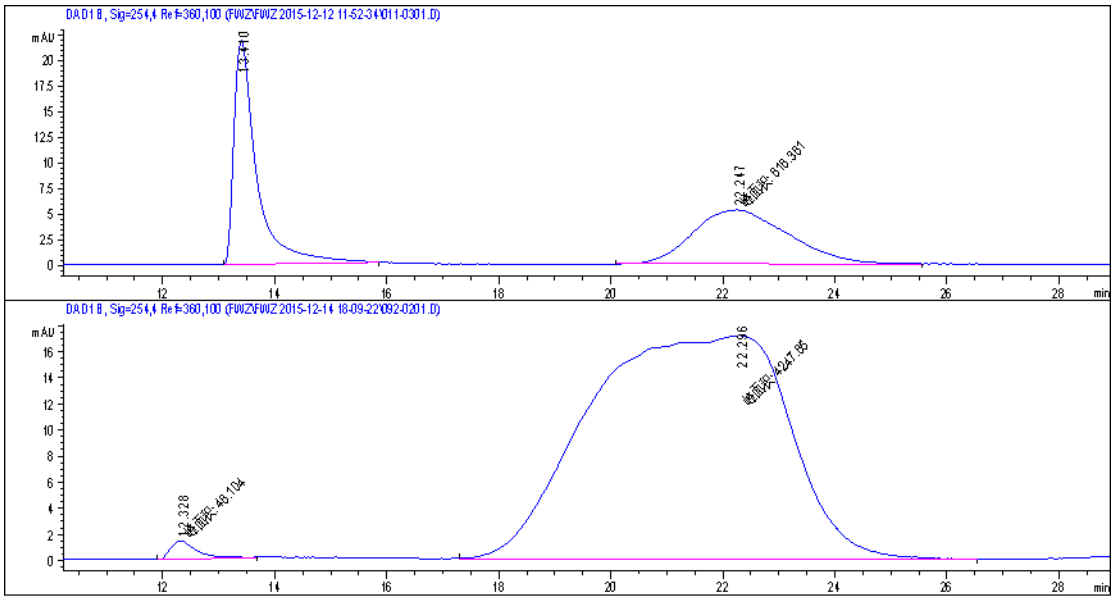



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.682 | MM | 0.4258 | 4267.58789 | 167.03578 | 99.5945 |
| 2 | 8.975 | MM | 0.2637 | 17.37698 | 1.09829 | 0.4055 |

**Supplementary Figure 15.** HPLC chromatogram of chiral product **2e**

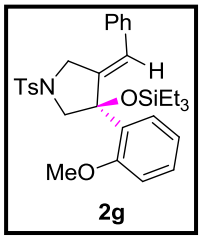



**2f**: colorless oil, 98% yield, 99:1 er with **L4** (0.25 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 12.3 min (*S*), 22.3 min (*R*). **2f**: $[\alpha]_D^{25}$ = +34.3 (c = 1.0, $CHCl_3$); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.13 – 7.09 (m, 1H), 7.02 – 6.97 (m, 1H), 6.84 – 6.80 (m, 1H), 6.44 (t, *J* = 2.3 Hz, 1H), 4.40 (dd, *J* = 14.9, 2.3 Hz, 1H), 4.21 (dd, *J* = 14.9, 2.6 Hz, 1H), 3.81 (s, 3H), 3.64 (d, *J* = 9.7 Hz, 1H), 3.46 (d, *J* = 9.7 Hz, 1H), 2.44 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.6 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 159.46, 145.83, 143.98, 142.23, 135.91, 132.57, 129.88, 129.19, 128.77, 128.58, 127.93, 127.76, 126.33, 118.47, 112.71, 112.19, 83.14, 60.96, 55.29, 50.63, 21.63, 7.15, 6.26; HRMS (ESI) calculated for [M+H, $C_{31}H_{40}NO_4SSi]^+$: 550.2447; found: 550.2432.

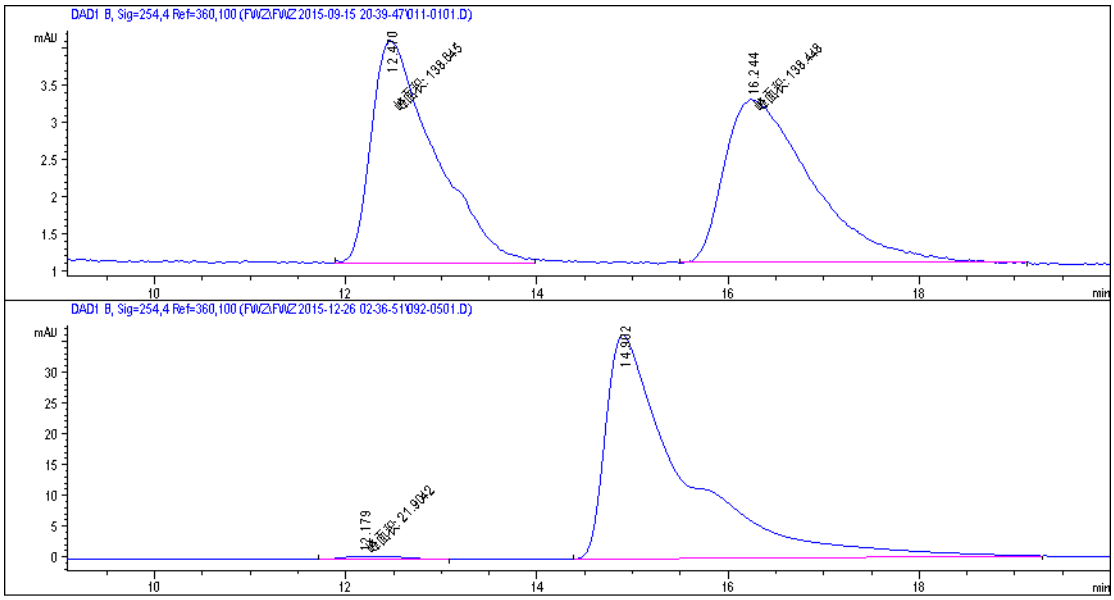



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.328 | MM | 0.5451 | 46.10400 | 1.40972 | 1.0737 |
| 2 | 22.296 | MM | 4.1266 | 4247.65088 | 17.15571 | 98.9263 |

**Supplementary Figure 16.** HPLC chromatogram of chiral product **2f**

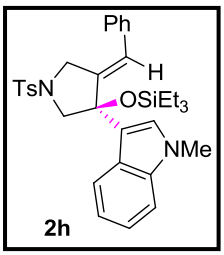



**2g**: colorless oil, 98% yield, 99:1 er with **L4** (0.5 mol%) at 60 °C. Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 12.2 min (*S*), 14.9 min (*R*). **2g**: $[\alpha]_D^{25}$ = +27.0 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 7.00 (td, *J* = 7.6, 0.8 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.04 (t, *J* = 2.1 Hz, 1H), 4.63 (dd, *J* = 14.1, 2.0 Hz, 1H), 4.03 (dd, *J* = 14.1, 2.9 Hz, 1H), 3.55 (s, 2H), 3.10 (s, 3H), 2.45 (s, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.79 – 0.63 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.26, 144.43, 143.70, 136.67, 132.92, 132.06, 129.62, 128.86, 128.71, 128.49, 128.31, 127.45, 127.33, 124.48, 120.36, 111.05, 82.94, 60.39, 54.33, 51.97, 21.65, 7.30, 6.16; HRMS (ESI) calculated for [M+H, $C_{31}H_{40}NO_4SSi]^+$: 550.2447; found: 550.2433.

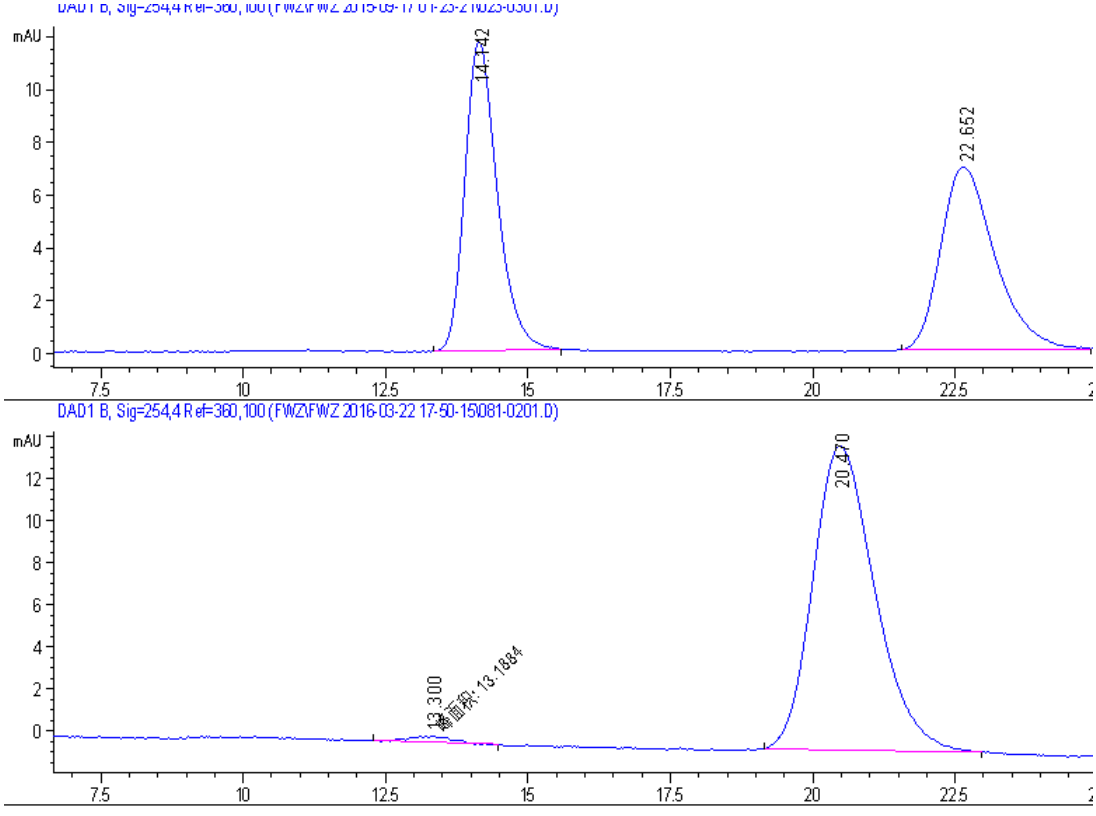



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.179 | MM | 0.6461 | 21.90422 | 5.65021e-1 | 1.0578 |
| 2 | 14.902 | BB | 0.7538 | 2048.74268 | 36.33746 | 98.9422 |

**Supplementary Figure 17.** HPLC chromatogram of chiral product **2g**

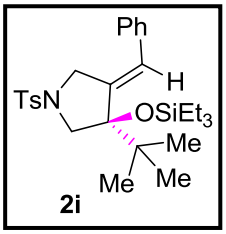



**2h**: colorless oil, 80% yield, 99:1 er with **L4** (1 mol%) at 80 °C. Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 98/2, 254 nm, 13.3 min (*S*), 20.5 min (*R*). **2h**: $[\alpha]_D^{25}$ = +25.9 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.27 (m, 7H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.09 (s, 1H), 6.44 (t, *J* = 3.0 Hz, 1H), 4.71 (d, *J* = 3.0 Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.62 (q, *J* = 8.0 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.33, 138.65, 137.12, 137.10, 133.16, 131.54, 130.08, 128.72, 128.02, 127.82, 127.60, 127.00, 126.49, 123.28, 122.38, 120.18, 119.91, 117.53, 109.66, 105.90, 53.17, 33.05, 21.68, 6.71, 5.92; HRMS (ESI) calculated for [M-OTES, $C_{27}H_{25}N_2O_2S]^+$: 441.1637; found: 441.1619.

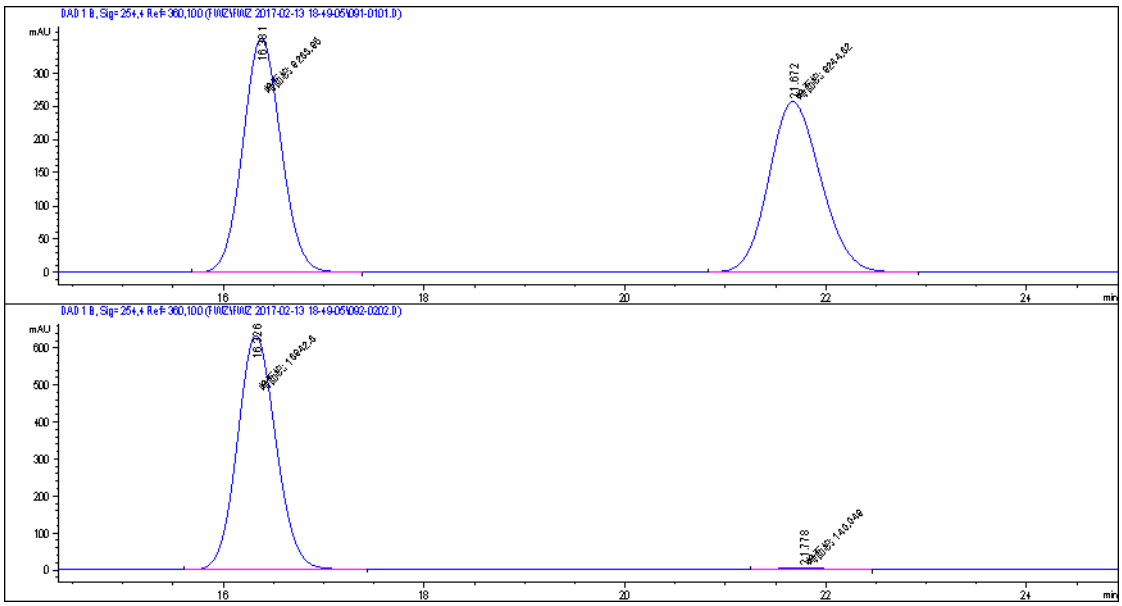



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.300 | MM | 0.7955 | 13.18840 | 2.76326e-1 | 1.1925 |
| 2 | 20.470 | BB | 0.8972 | 1092.72534 | 14.43462 | 98.8075 |

**Supplementary Figure 18.** HPLC chromatogram of chiral product **2h**

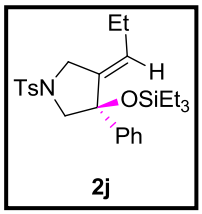



**2i**: colorless oil, 94% yield, > 99:1 er with **L4** (1 mol%) at 80 °C. Enantiomeric ratio was determined by chiral HPLC with **3i**, the desilylation product of **2i**. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 16.3 min (*R*), 21.8 min (*S*). **2i**: $[\alpha]_D^{25}$ = –40.7 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 7.18 – 7.14 (m, 2H), 6.45 (t, *J* = 2.4 Hz, 1H), 4.26 (dd, *J* = 14.9, 2.8 Hz, 1H), 4.05 (dd, *J* = 14.9, 2.2 Hz, 1H), 3.82 (d, *J* = 10.0 Hz, 1H), 2.89 (d, *J* = 10.0 Hz, 1H), 2.40 (s, 3H), 0.96 (s, 9H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.46 – 0.28 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.93, 140.19, 136.05, 132.24, 129.84, 128.81, 128.65, 127.89, 127.51, 126.77, 86.32, 54.49, 51.48, 39.95, 25.13, 21.62, 7.23, 6.46; HRMS (ESI) calculated for [M+Na, $C_{28}H_{41}NNaO_3SSi]^+$: 522.2469; found: 522.2465.

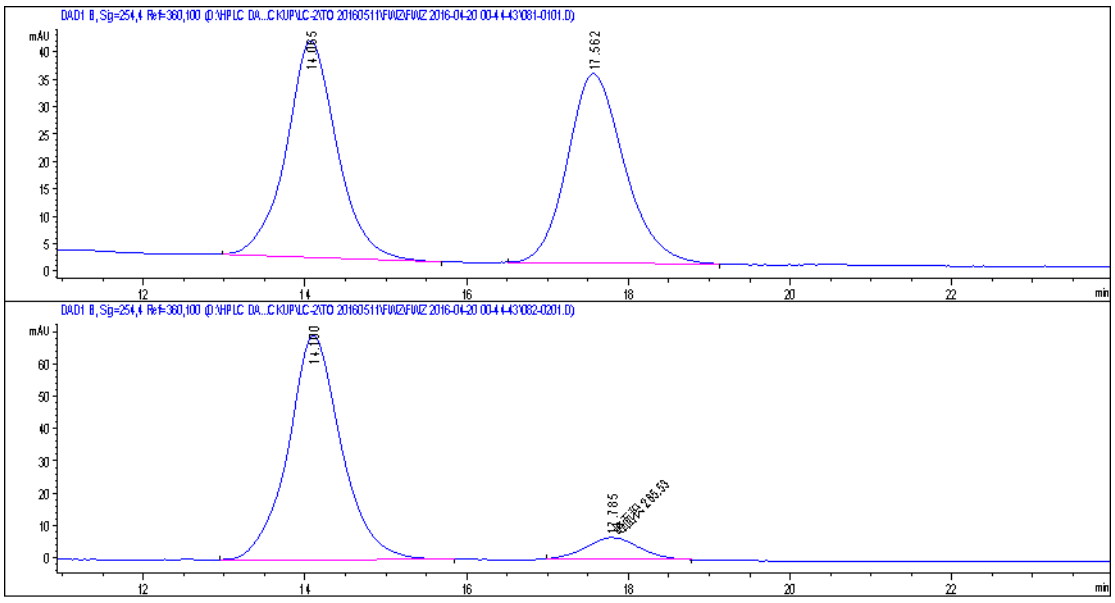



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 16.326 | MM | 0.4457 | 1.69428e4 | 633.54675 | 99.1802 |
| 2 | 21.778 | MM | 0.5584 | 140.04918 | 4.17986 | 0.8198 |

**Supplementary Figure 19.** HPLC chromatogram of chiral **3i**, the desilylation product of **2i**

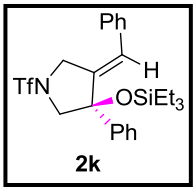



**2j**: colorless oil, 83% yield, 92:8 er with 1 mol% **L4** at 80 °C. Enantiomeric ratio was determined by chiral HPLC with the desilylation product of **2j**. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 85/15, 230 nm, 14.1 min (*R*), 17.8 min (*S*). **2j**: $[\alpha]_D^{25}$ = +17.1 (c = 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.30 – 7.22 (m, 3H), 5.35 (tt, *J* = 7.3, 2.5 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.85 – 3.79 (m, 1H), 3.48 – 3.41 (m, 2H), 2.46 (s, 3H), 1.99 – 1.91 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.7 Hz, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 144.24, 143.87, 140.76, 132.58, 129.80, 129.08, 128.05, 127.95, 127.24, 126.15, 82.18, 62.86, 49.59, 22.77, 21.68, 13.23, 7.15, 6.26; HRMS (ESI) calculated for [M+H, $C_{26}H_{38}NO_3SSi]^+$: 472.2336; found: 472.2338.



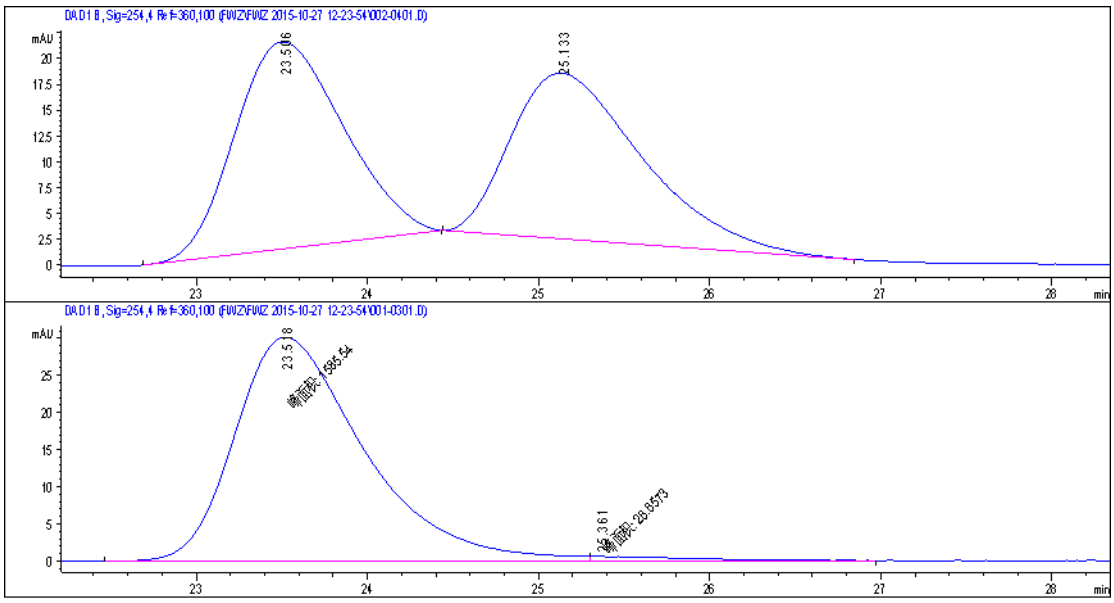

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.100 | BB | 0.6801 | 3164.41577 | 69.38689 | 91.7236 |
| 2 | 17.785 | MM | 0.7336 | 285.52991 | 6.48690 | 8.2764 |

**Supplementary Figure 20.** HPLC chromatogram of chiral product **2j**



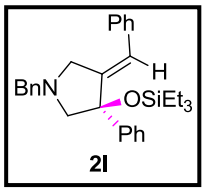

**2k**: light yellow oil, 19% yield, 98:2 er with **L4** (0.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99.8/0.2, 254 nm, 23.5 min (*R*), 25.4 min (*S*). **2k**: $[\alpha]_D^{25}$ = +16.3 (c = 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.46 – 7.29 (m, 6H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.68 (s, 1H), 4.69 (d, *J* = 14.4 Hz, 1H),

4.46 (d, *J* = 14.6 Hz, 1H), 4.00 (d, *J* = 8.3 Hz, 1H), 3.77 (d, *J* = 9.9 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H); $^{13}$C NMR (126 MHz, cdcl$_3$) δ 141.21, 139.96, 135.30, 128.97, 128.81, 128.55, 128.32, 128.29, 126.60, 120.28 (q, *J* = 323.4 Hz), 82.99, 60.71, 50.74, 7.13, 6.29; HRMS (EI) calculated for [M, $C_{24}H_{30}NO_3F_3SSi]^+$: 497.1668; found: 497.1670.

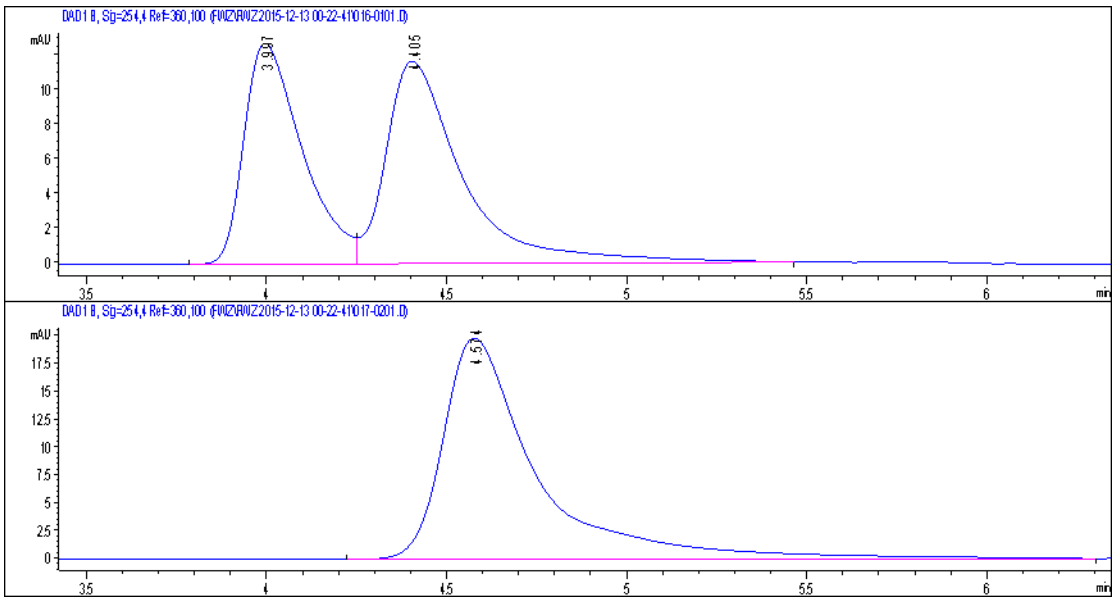



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 23.518 | MF | 0.8760 | 1585.53564 | 30.16458 | 98.3465 |
| 2 | 25.361 | FM | 0.7077 | 26.65726 | 6.27803e-1 | 1.6535 |

**Supplementary Figure 20.** HPLC chromatogram of chiral product **2k**

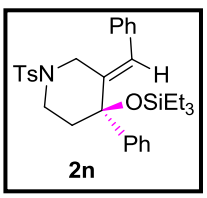



**2l**: colorless oil, 10% yield, > 99:1 er with **L4** (0.5 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 3.99 min (*S*), 4.57 min (*R*). **2l**: $[\alpha]_D^{25}$ = +36.5 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.27 (m, 10H), 7.25 – 7.17 (m, 3H), 6.31 (s, 1H), 3.91 (d, *J* = 14.6 Hz, 1H), 3.79 (dd, *J* = 34.0, 12.9 Hz, 2H), 3.64 (d, *J* = 14.6 Hz, 1H), 3.10 (d, *J* = 9.5 Hz, 1H), 2.95 (d, *J* = 9.6 Hz, 1H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.69 (q, *J* = 7.2 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 148.42, 147.35, 138.58, 137.48, 128.90, 128.52, 128.41, 128.40, 127.69, 127.22, 126.92, 126.65, 126.36, 125.79, 84.06, 69.54, 60.49, 58.25, 7.36, 6.37; HRMS (ESI) calculated for [M+H, $C_{30}H_{38}NOSi]^+$: 456.2717; found: 456.2712.



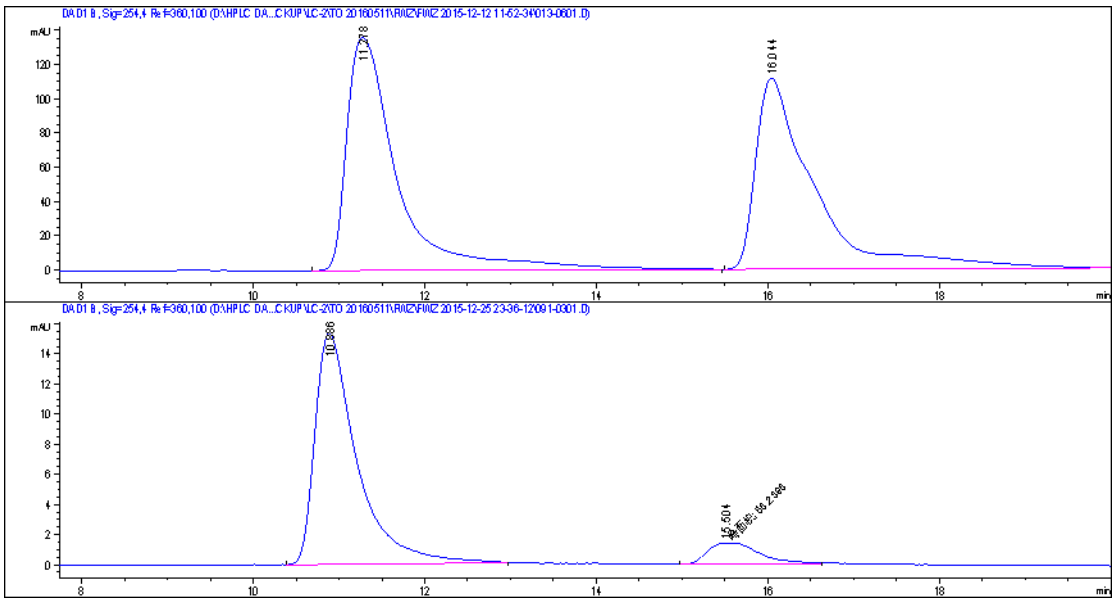

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 4.574 | BB | 0.2609 | 358.97141 | 19.85916 | 100.0000 |

**Supplementary Figure 21.** HPLC chromatogram of chiral product **2l**



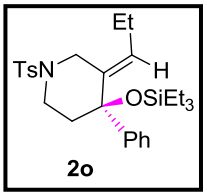

**2n**: colorless oil, 95% yield, 90:10 er with **L4** (2 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 10.9 min (*R*), 15.5 min (*S*). **2n**: $[\alpha]_D^{25}$ = –14.9 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.32 – 7.22 (m, 6H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.85 (s, 1H), 4.35 (d, *J* = 12.8 Hz, 1H), 3.67 – 3.58 (m, 1H), 3.18 (d, *J* = 12.8 Hz, 1H), 3.03 (t, *J* = 10.1 Hz, 1H),

2.67 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 2.17 – 2.07 (m, 1H), 0.74 (t, *J* = 7.9 Hz, 9H), 0.39 – 0.18 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.51, 141.58, 138.51, 136.65, 133.85, 129.63, 129.10, 128.55, 128.52, 128.05, 127.82, 127.40, 127.31, 127.17, 77.32, 45.02, 43.96, 37.82, 21.60, 7.04, 6.38; HRMS (ESI) calculated for [M+H, $C_{31}H_{40}NO_3SSi]^+$: 534.2493; found: 534.2495.



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 10.886 | BB | 0.5043 | 521.52954 | 15.35403 | 89.9547 |
| 2 | 15.504 | MM | 0.6856 | 58.23959 | 1.41584 | 10.0453 |

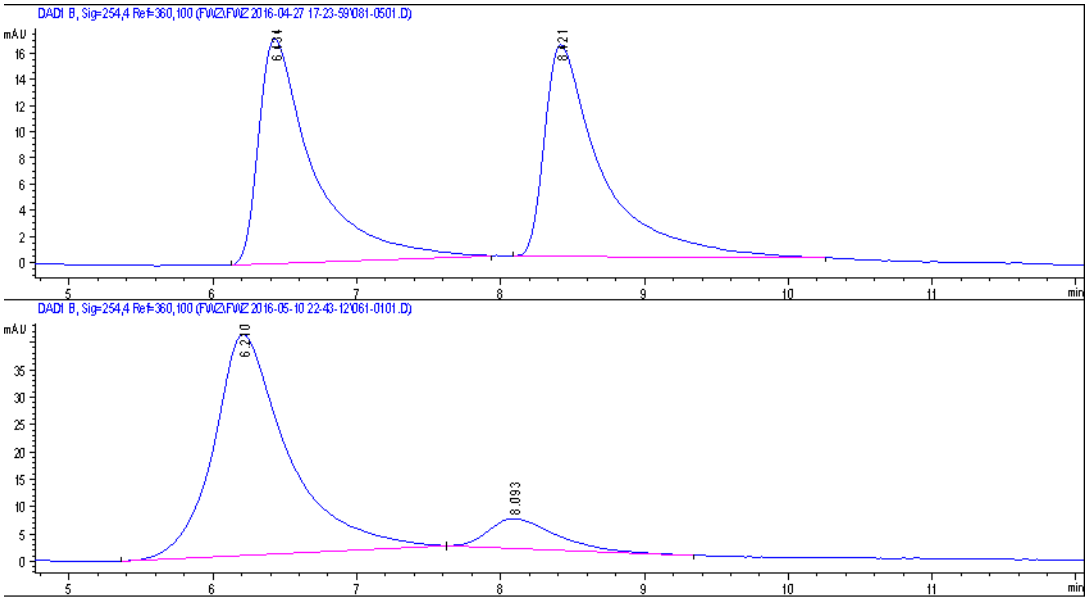
**Supplementary Figure 22.** HPLC chromatogram of chiral product **2n**



**2o**

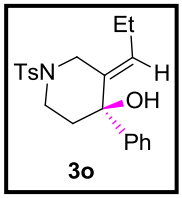
**2o**: colorless oil, 98% yield, 89:11 er with **L4** (2 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 6.2 min (*R*), 8.1 min (*S*). The absolute configuration was assigned by the X-ray structure of **3o** (desilylation of **2o**). **2o**: $[\alpha]_D^{25}$ = –18.9 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.18 (m, 7H), 5.58 (t, *J* = 7.4 Hz, 1H), 3.99 (d, *J* = 12.7 Hz, 1H), 3.43 – 3.37 (m, 1H), 3.21 (d, *J* = 12.8 Hz, 1H), 3.03 (ddd, *J* = 12.1, 9.3, 3.1 Hz, 1H), 2.45 (ddd, *J* = 13.3, 6.4, 3.2 Hz, 1H), 2.35 (s, 3H), 2.11 (dtd, *J* = 14.8, 7.4, 3.5 Hz, 2H), 1.92 (ddd, *J* = 13.2, 9.1, 3.9 Hz, 1H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.67 (t, *J* = 7.9 Hz, 9H), 0.29 – 0.13 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.48, 142.37, 135.41, 134.08, 129.67, 129.60, 128.23, 127.76, 127.71, 127.36, 77.19, 44.12,

43.71, 38.17, 21.60, 20.83, 14.34, 7.03, 6.41; HRMS (ESI) calculated for [M+Na, $C_{27}H_{39}NNaO_3SSi]^+$: 508.2312; found: 508.2320.



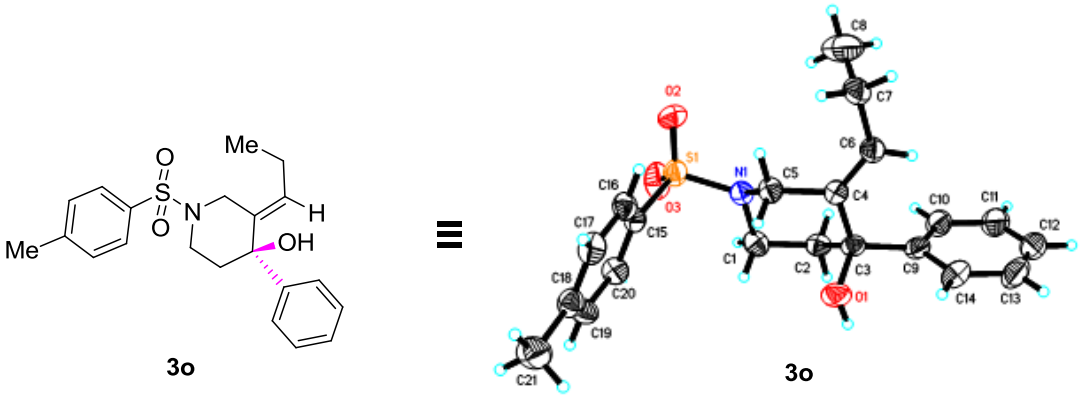

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 6.210 | BB | 0.5070 | 1458.21436 | 40.40800 | 88.9806 |
| 2 | 8.093 | BB | 0.4331 | 180.58548 | 5.47130 | 11.0194 |

**Supplementary Figure 22.** HPLC chromatogram of chiral product **2o**

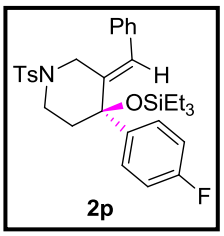



**3o** (desilylation of **2o**): Preparations of **3o** were carried out according to procedures same as **3a. 3o**: white solid; $[\alpha]_D^{25}$ = –24.8 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CHCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.28 (m, 6H), 7.28 – 7.24 (m, 1H), 5.14 (t, *J* = 7.3 Hz, 1H), 4.16 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.17 (td, *J* = 11.7, 2.8 Hz, 1H), 2.44 (s, 3H), 2.39 – 2.31 (m, 1H), 2.17 – 1.99 (m, 2H), 1.84 – 1.79 (m, 1H), 1.78 (s, 1H), 0.90 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CHCl_3$) δ 143.74, 143.62, 135.52, 134.02, 131.74, 129.78, 128.22, 127.78, 127.47, 126.35, 77.41, 77.16, 76.91, 75.34, 43.84, 42.90, 38.79, 21.63, 20.78, 13.96; HRMS (ESI) calculated for [M+H, $C_{21}H_{26}NO_3S]^+$: 372.1628; found: 372.1629.

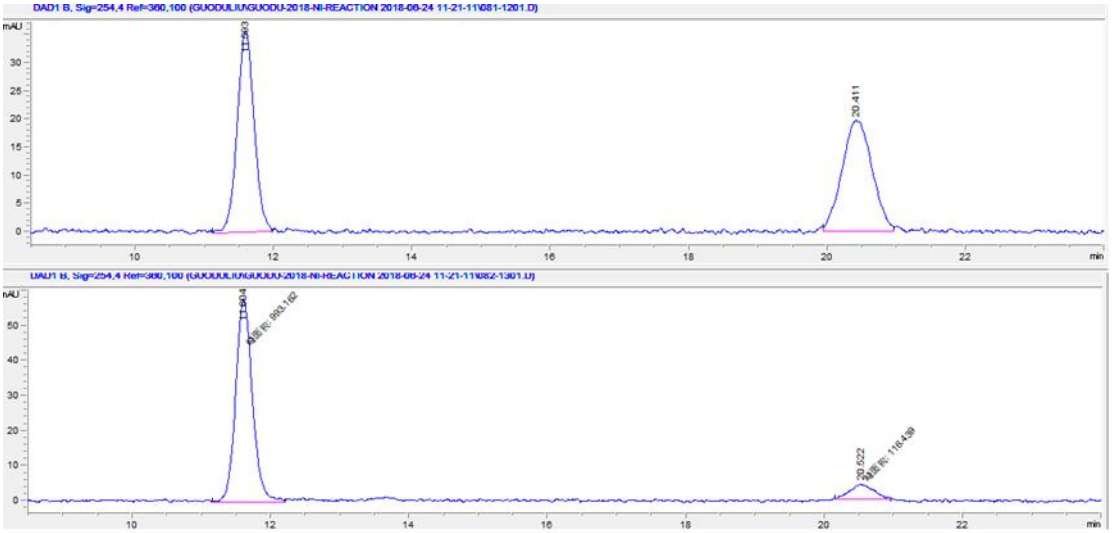
Crystalization from hexanes/DCM (9:1) gave crystals suitable for X-ray crystallographic analysis, which revealed its absolute configuration for the chiral tertiary alcohol **3o** as shown in **Figure 2**.




**Supplementary Figure 23.** X-ray derived ORTEP representation of **3o.** (CCDC1532677 contains the supplementary crystallographic data of **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)

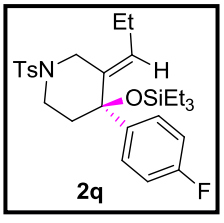



**2p**: colorless oil, 96% yield, 90:10 er with **L4** (2 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 11.6 min (*R*), 20.5 min (*S*). **2p**: $[\alpha]_D^{25}$ = –28.5 (c = 1.0, $CHCl_3$); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.16 (m, 9H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.83 (s, 1H), 4.33 (d, *J* = 12.8 Hz, 1H), 3.60 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.99 (t, *J* = 10.2 Hz, 1H), 2.62 (ddd, *J* = 13.4, 5.2, 3.1 Hz, 1H), 2.37 (s, 3H), 2.18 – 2.08 (m, 1H), 0.75 (t, *J* = 7.9 Hz, 9H), 0.39 – 0.20 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.35, 161.38, 143.62, 138.37, 137.62 (d, *J* = 3.2 Hz), 136.45, 133.62, 129.66, 129.21 (d, *J* = 8.0 Hz), 128.59, 127.82, 127.34 (d, *J* = 12.3 Hz), 115.45, 115.28, 44.98, 43.92, 37.90, 21.61, 7.02, 6.41; $^{19}$F NMR (376 MHz, cdcl$_3$) δ –114.20 (m); HRMS (ESI) calculated for [M+Na, $C_{31}H_{38}FNNaO_3SSi]^+$: 574.2218; found: 574.2224.



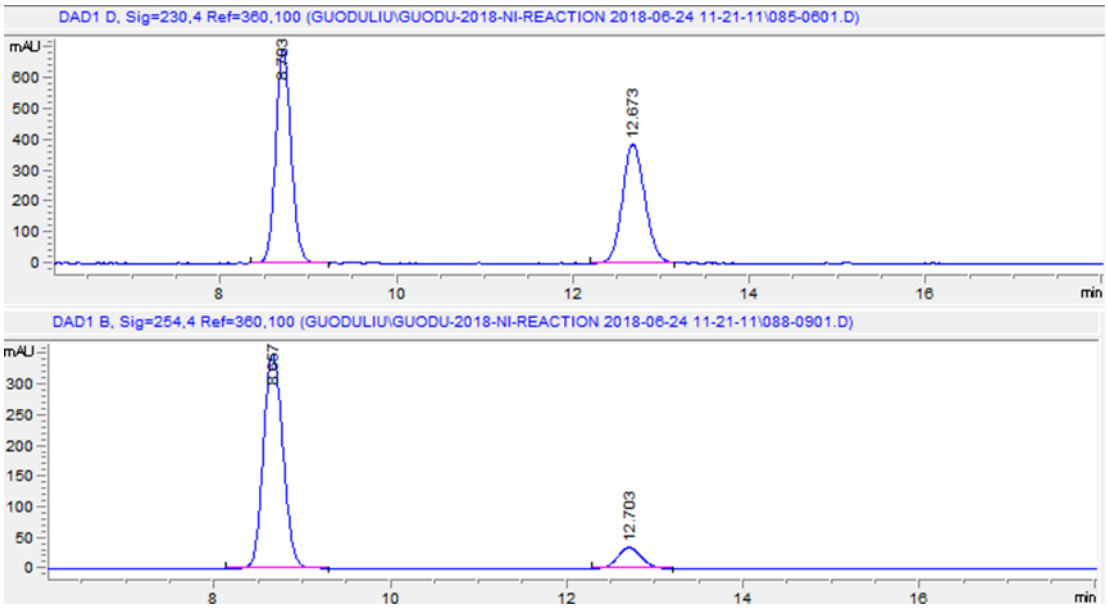
| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.604 | 993.2 | 58.2 | 0.2847 | 0.819 | 89.506 |
| 2 | 20.522 | 116.4 | 4.5 | 0.4267 | 0.805 | 10.494 |

**Supplementary Figure 24.** HPLC chromatogram of chiral product **2p**




**2q**: colorless oil, 98% yield, 89:11 er with **L4** (2 mol%). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 $^{o}$C, flow rate: 1 mL/min, hexanes/isopropanol: 99/1, 254 nm, 8.7 min (*R*), 12.7 min (*S*). **2q**: $[\alpha]_D^{25}$ = – 26.9 (c = 1.0, $CHCl_3$); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.17 (m, 4H), 6.92 (t, *J* = 8.6 Hz, 2H), 5.58 (t, *J* = 7.4 Hz,

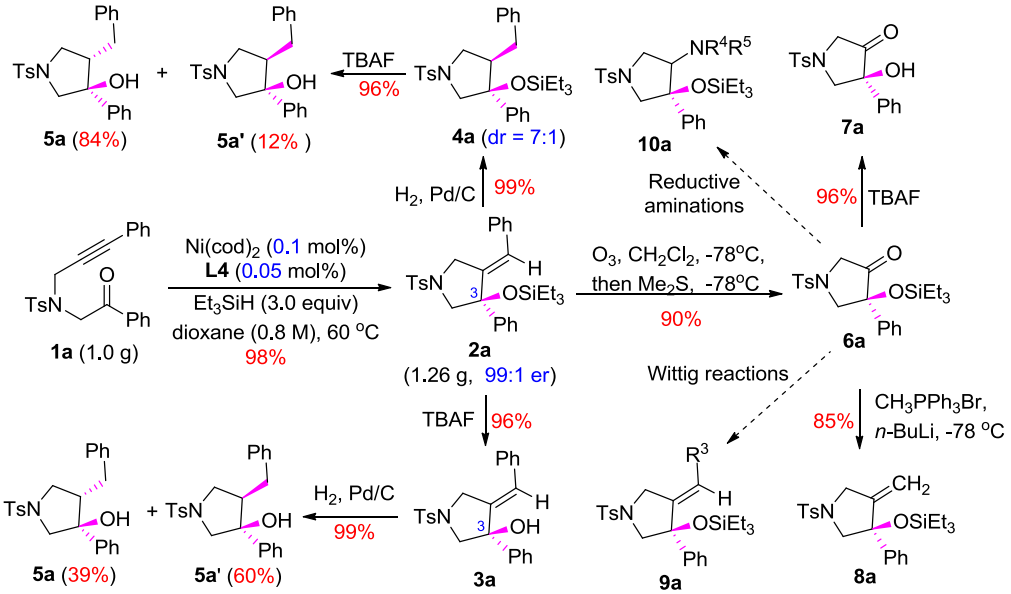
1H), 3.99 (d, *J* = 12.7 Hz, 1H), 3.47 – 3.36 (m, 1H), 3.20 (d, *J* = 12.7 Hz, 1H), 3.02 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.48 – 2.32 (m, 4H), 2.18 – 2.07 (m, 2H), 1.96 (ddd, *J* = 13.0, 10.4, 5.9 Hz, 1H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.69 (t, *J* = 7.9 Hz, 9H), 0.39 – 0.10 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.14, 161.18, 143.55, 138.30 (d, *J* = 3.2 Hz), 135.36, 133.81, 129.66, 129.10 (d, *J* = 8.0 Hz), 127.72, 115.01 (d, *J* = 21.1 Hz), 76.72, 44.04, 43.63, 38.18, 21.55, 20.78, 14.27, 6.96, 6.38; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –114.82 (m); HRMS (ESI) calculated for [M+Na, $C_{27}H_{38}FNNaO_3SSi]^+$: 526.2218; found: 526.2220.



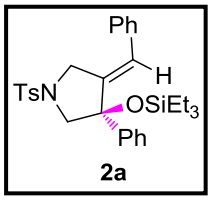

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 8.657 | 5423.5 | 350.4 | 0.2446 | 0.856 | 89.174 |
| 2 | 12.703 | 658.4 | 34.4 | 0.2713 | 0.928 | 10.826 |

**Supplementary Figure 25.** HPLC chromatogram of chiral product **2q**

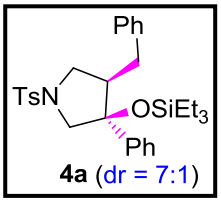
## Synthetic Applications



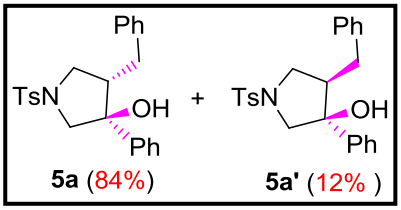

**Supplementary Figure 26.** Gram-scale reaction and further transformation of cyclization product **2a**



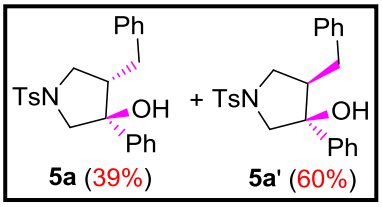

**2a** (gram scale): To a stirred yellow solution of $Ni(cod)_2$ (0.682 mg, 2.48 μ mol, 0.1 mol%), **L4** (0.816 mg, 1.24 μ mol, 0.05 mol%) in dioxane (3 mL) in a 10 mL screw-cap vial, were added alkynone **1a** (1.0 g, 2.48 mmol, 1.0 equiv.) in the glove box. The resulting brown solution was stirred for 15 mins, followed by the addition of triethylsilane ($Et_3SiH$, 1.19 mL, 7.44 mmol, 3.0 equiv.). The vial was closely sealed, and the resulting mixture was stirred at 60 °C for 12 h. Quenched with saturated sodium bicarbonate ($NaHCO_3$), extracted with ethyl acetate (EtOAc), washed with saturated NaCl, dried over anhydrous sodium sulfate ($Na_2SO_4$), filtered, and concentrated under vacuum. The residue was purified by column chromatography (10% petroleum ether/EtOAc) to afford compound **2a** as colorless oil (1.26 g, 98% yield, 99:1 er). All physical and spectroscopic data of this compound matched those mentioned above.



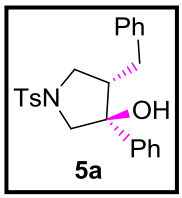

**4a** (dr = 7:1): To a solution of **2a** (104 mg, 0.2 mmol, 1.0 equiv.) in MeOH/EA (1:1, 4 mL) was added 10% Pd/C (22 mg, 0.02 mmol, 0.1 equiv.) in one portion. The reaction flask was degassed and purged with hydrogen three times. The reaction mixture was stirred under hydrogen (1 atm) for 24 h, then filtered over a plug of silica gel topped with Celite (MeOH eluent), concentrated to afford white solid as analytically pure which was used without further purification (99% yield, dr = 7:1). **4a**: Rf = 0.6 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –20.7 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H, minor), 7.64 (d, *J* = 8.2 Hz, 2H, major), 7.31 – 7.04 (m, 10H, major + minor), 6.82 (d, *J* = 6.9 Hz, 2H, major), 6.77 (d, *J* = 7.0 Hz, 2H, minor), 3.74 (dd, *J* = 137.7, 10.4 Hz, 2H, minor), 3.68 (dd, *J* = 85.9, 10.9 Hz, 2H, major), 3.45 (dd, *J* = 9.9, 6.4 Hz, 1H, minor), 3.28 (dd, *J* = 10.1, 7.5 Hz, 1H, major), 3.15 (t, *J* = 9.8 Hz, 1H, major), 3.05 (dd, *J* = 9.9, 5.2 Hz, 1H, minor), 2.58 (dd, *J* = 13.9, 3.5 Hz, 1H, major + minor), 2.39 (s, 3H, major), 2.33 (s, 3H, minor), 2.38 (dd, *J* = 13.8, 3.4 Hz, major + minor), 2.07 (qd, *J* = 11.0, 3.6 Hz, 1H, major + minor), 0.85 (t, *J* = 7.9 Hz, 9H, major), 0.71 (t, *J* = 7.9 Hz, 9H, minor), 0.58 – 0.45 (m, 3H, major), 0.34 – 0.21 (m, 1H, minor); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.67 (major + minor), 142.71 (major + minor), 139.98 (major), 139.71 (minor), 134.93(minor), 134.51(major), 129.87 (major + minor), 128.70 (minor), 128.62 (major), 128.53 (major), 128.43 (minor), 128.35 (major), 128.12 (minor), 127.60, 127.56, 127.50, 126.70, 126.28 (minor), 126.22 (major), 125.52 (major + minor), 83.87 (minor), 83.77 (major), 59.87 (major), 56.85 (minor), 54.47 (major), 53.03 (minor), 51.76 (major), 50.30 (minor), 35.03 (minor), 32.33 (major), 21.69 (major + minor), 7.26 (major), 6.99 (minor), 6.47 (major), 6.17 (minor); HRMS (ESI) calculated for [M+Na, $C_{30}H_{39}NNaO_3SSi]^+$: 544.2312; found: 544.2318.



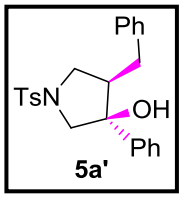

**Deprotection of 4a**: To a solution of **4a** (dr = 7:1, 52 mg, 0.1 mmol, 1.0 equiv.) in THF (2 mL) at 0 °C was added TBAF (1.0 M solution in THF, 0.15 ml, 1.5 equiv.), stirred at 0 °C for 0.5 h. Quenched with water, extracted with EtOAc, washed with saturated brine, dried with anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography (20% petroleum ether/EtOAc) to give compound **5a** (34.2 mg, 0.084 mmol, 84% yield) and its diastereoisomer **5a'** (4.9 mg, 0.084 mmol, 12% yield) as white solids.



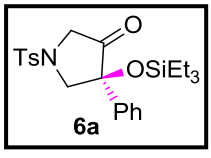

**Hydrogenation of 3a**: To a solution of **3a** (81 mg, 0.2 mmol, 1.0 equiv.) in MeOH/EA (1:1, 4 mL) was added 10% Pd/C (22 mg, 0.02 mmol, 0.1 equiv.) in one portion. The reaction flask was degassed and purged with hydrogen three times. The reaction mixture was stirred under hydrogen (1 atm) for 24 h, then filtered over a plug of silica gel topped with Celite (MeOH eluent), concentrated under vacuum. The residue was purified by column chromatography (20% petroleum ether/EtOAc) to give compound **5a** (31.8 mg, 0.78 mmol, 39% yield) and its diastereoisomer **5a'** (48.9 mg, 1.2 mmol, 60% yield) as white solids.




**5a**: $R_f$ = 0.3 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –19.3 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.10 (m, 10H), 6.97 (d, *J* = 7.6 Hz, 2H), 3.59 (dd, *J* = 41.3, 11.5 Hz, 2H), 3.50 (t, *J* = 8.5 Hz, 1H), 3.29 (t, *J* = 10.1 Hz, 1H), 2.65 – 2.48 (m, 2H), 2.44 (s, 3H), 2.08 – 1.90 (m, 1H), 1.65 (t, *J* = 6.5 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.75, 140.43, 139.54, 134.26, 129.89, 128.74, 128.68, 128.49, 127.91, 127.62, 126.45, 125.20, 110.11, 81.36, 62.99, 51.83, 51.46, 31.93, 21.72; HRMS (ESI) calculated for $[M+Na, C_{24}H_{25}NNaO_3S]^+$: 1447; found: 430.1450.

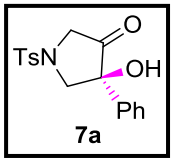



**5a'**: $R_f$ = 0.2 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –24.9 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 17.6, 5.2 Hz, 7H), 7.19 (dt, *J* = 19.1, 7.7 Hz, 3H), 6.89 (d, *J* = 7.4 Hz, 2H), 4.07 (d, *J* = 10.6 Hz, 1H), 3.57 (d, *J* = 10.6 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.22 (dd, *J* = 9.8, 3.8 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.47 – 2.30 (m, 4H), 2.03 (dd, *J* = 6.0, 3.4 Hz, 1H), 1.76 (t, *J* = 12.9 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.70, 140.53, 139.24, 134.30, 129.87, 128.89, 128.79, 128.63, 128.46, 127.64, 126.45, 126.09, 82.31, 57.73, 51.25, 50.71, 35.66, 21.69; HRMS (ESI) calculated for $[M+Na, C_{24}H_{25}NNaO_3S]^+$: 430.1447; found: 430.1447.



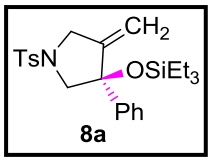

**6a**: A solution of **2a** (260 mg, 0.5 mmol) in $CH_2Cl_2$ (10 mL) was treated with a stream of ozone ($O_3$) at –78 °C for 15 mins until the starting material was disappeared on TLC. The excess ozone was purged from the solution with a stream of oxygen ($O_2$) and $Me_2S$ (1 mL) was added. The reaction was allowed to warm slowly to room temperature, at which point it was diluted with water (10 mL). The subsequent mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers

were washed with brine, dried ($Na_2SO4$), filtered, evaporated and purified by flash chromatography on silica gel eluting with petroleum hexanes/ethyl acetate (15:1) to provided compound **6a** as colorless oil (200 mg, 0.45 mmol, 90% yield). **6a**: $R_f$ = 0.8 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –18.9 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.41 – 7.31 (m, 5H), 4.22 (d, *J* = 10.1 Hz, 1H), 3.80 (dd, *J* = 17.9, 0.6 Hz, 1H), 3.47 (d, *J* = 17.8 Hz, 1H), 3.31 (d, *J* = 10.1 Hz, 1H), 2.46 (s, 2H), 0.79 (t, *J* = 7.9 Hz, 9H), 0.39 (qd, *J* = 7.9, 2.8 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 206.25, 144.61, 137.72, 131.24, 130.00, 128.88, 128.69, 127.93, 126.26, 80.89, 57.18, 51.91, 21.59, 6.67, 5.83; HRMS (ESI) calculated for [M+Na, $C_{23}H_{31}NNaO_4SSi]^+$: 468.1635; found: 468.1637.



**7a**

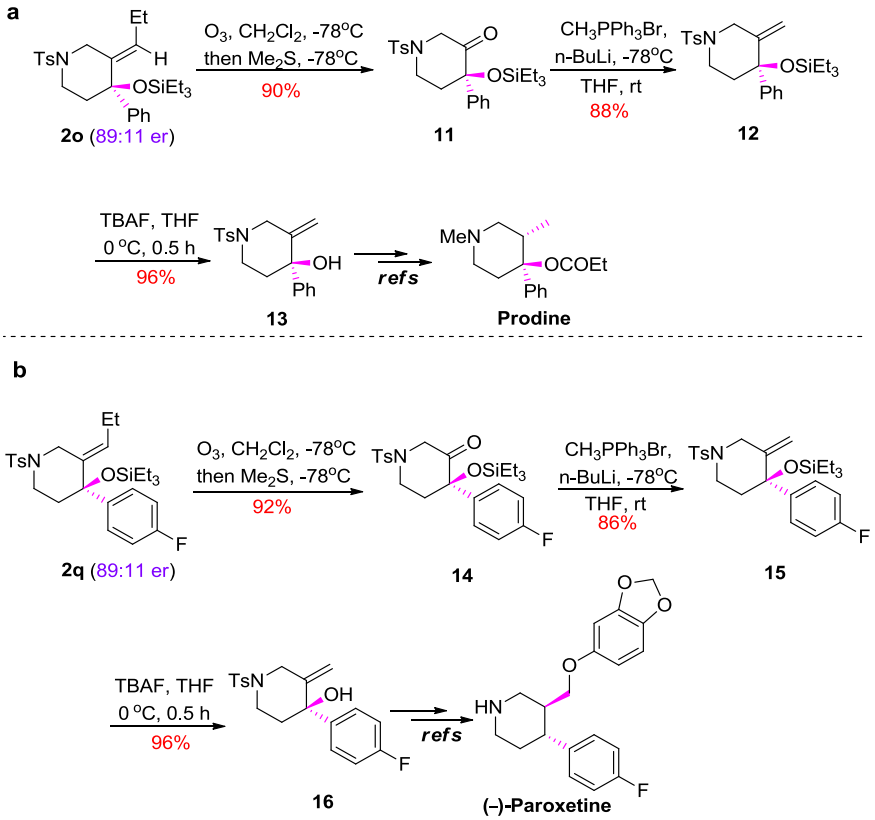
**7a**: (desilylation of **6a**): Preparation of **7a** was carried out according to procedure same as **3a. 7a**: white solid; **6a**: $R_f$ = 0.2 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –24.6 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.38 (d, *J* = 6.4 Hz, 5H), 4.22 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 18.1 Hz, 1H), 3.56 (d, *J* = 18.1 Hz, 1H), 3.37 (d, *J* = 10.4 Hz, 1H), 3.25 (bs, 1H), 2.45 (d, *J* = 12.6 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 207.79, 144.70, 137.35, 131.43, 130.09, 129.10, 129.04, 127.91, 125.44, 79.45, 57.04, 52.12, 21.60; HRMS (ESI) calculated for [M+Na, $C_{17}H_{17}NNaO_4S]^+$: 354.0770; found: 354.0773.



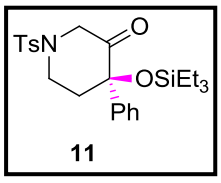
**8a**

**8a**: To a stirred slurry of $CH_3PPh_3Br$ (475 mg, 1.32 mmol, 3.3 equiv.) in THF (10 mL) were added n-BuLi (2.5 M solution in THF, 0.48 mL, 1.2 mmol, 3.0 equiv.) at –78 $^o$C. The resulting mixture was stirred at –78 $^o$C for 1h, followed by dropwise addition of a solution of **6a** (178 mg, 0.4 mmol, 1.0 equiv.) in THF (2 mL) at this temperature. The mixture was stirred for another 1h at –78 $^o$C, then slowly warmed to 25 $^o$C and kept for 5 h before quenched with Sat.aq NH4Cl (10 mL). The layer was separated and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$), concentrated and purified by flash chromatography eluting with hexanes /ethyl acetate (19:1) to yield compound **8a** as colorless oil (151 mg, 0.34 mmol, 85% yield). **8a**: $R_f$ = 0.4 (silica gel, EtOAc/hexanes 1:19); $[\alpha]_D^{25}$ = –21.8 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.22 (m, 3H), 5.09 (d, *J* = 27.2 Hz, 2H), 4.00 (d, *J* = 14.1 Hz, 1H), 3.87 (d, *J* = 14.0 Hz, 1H), 3.67 (d, *J* = 9.6 Hz, 1H), 3.35 (d, *J* = 9.6 Hz, 1H), 2.43 (s, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.57 – 0.34 (m, 6H); $^{13}$C NMR (101

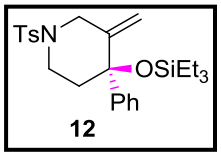
MHz, $CDCl_3$) δ 150.29, 143.84, 143.23, 132.52, 129.74, 128.05, 127.86, 127.48, 125.85, 110.14, 81.44, 60.98, 51.20, 21.58, 6.96, 6.10; HRMS (ESI) calculated for [M+Na, $C_{24}H_{33}NNaO_3SSi]^+$: 466.1843; found: 466.1846.



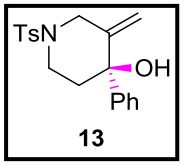

**Supplementary Figure 27.** Synthetic applications to intermediates of prodine and (–)-paroxetine



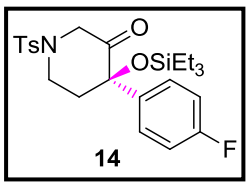

**11**: Preparation of **11** was carried out according to procedure same as **6a**. **11**: colorless oil, 90% yield, $R_f$ = 0.8 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = – 18.4 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 6.7 Hz, 5H), 7.21 (dd, *J* = 6.1, 1.7 Hz, 2H), 3.94 (d, *J* = 14.9 Hz, 1H), 3.68 (d, *J* = 14.9 Hz, 1H), 3.52 (dt, *J* = 10.6, 5.3 Hz, 1H), 3.19 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.67 – 2.52 (m, 1H), 2.44 (d, *J* = 13.5 Hz, 3H), 2.24 (ddd, *J* = 9.3, 6.7, 3.0 Hz, 1H), 0.73 (td, *J* = 7.8, 0.9 Hz, 9H), 0.43 – 0.24 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 201.73, 144.25, 139.07, 133.10, 130.01, 128.72, 128.68, 127.79, 126.98, 80.34, 54.21, 42.71, 38.03, 21.65, 6.92, 6.23; HRMS (ESI) calculated for [M+Na, $C_{24}H_{33}NNaO_4SSi]^+$: 482.1792; found: 482.1790.



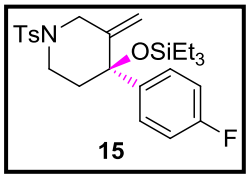

**12**: Preparation of **12** was carried out according to procedure same as **8a**. **12**: colorless oil, 88% yield, $R_f$ = 0.6 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –31.3 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.34 – 7.21 (m, 7H), 5.19 (s, 2H), 3.96 (d, *J* = 12.4 Hz, 1H), 3.59 – 3.43 (m, 1H), 3.24 (d, *J* = 12.3 Hz, 1H), 3.05 (t, *J* = 10.7 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.39 (s, 3H), 2.07 – 1.92 (m, 1H), 0.71 (td, *J* = 7.9, 1.6 Hz, 9H), 0.33 – 0.18 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.67, 143.47, 141.08, 133.74, 129.57, 128.25, 127.90, 127.69, 127.13, 113.61, 50.62, 43.82, 37.31, 21.47, 6.84, 6.21; HRMS (ESI) calculated for [M+Na, $C_{25}H_{35}NNaO_3SSi]^+$: 480.1999; found: 480.2003.



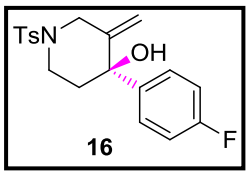

**13**: Preparation of **13** was carried out according to similar procedure as **3a. 13**: white solid; 96% yield, $R_f$ = 0.2 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –36.1 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.26 (m, 7H), 5.11 (s, 1H), 4.71 (s, 1H), 3.89 (d, *J* = 12.6 Hz, 1H), 3.69 (d, *J* = 12.7 Hz, 1H), 3.44 (dt, *J* = 9.4, 4.1 Hz, 1H), 3.25 – 3.11 (m, 1H), 2.51 – 2.33 (m, 4H), 1.93 (s, 1H), 1.83 (ddd, *J* = 13.9, 4.9, 3.1 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.16, 143.64, 142.75, 133.60, 129.72, 128.26, 127.77, 127.65, 126.08, 115.20, 74.60, 50.17, 43.00, 38.32, 21.55; HRMS (ESI) calculated for [M+Na, $C_{19}H_{21}NNaO_3S]^+$: 366.1134; found: 366.1141.



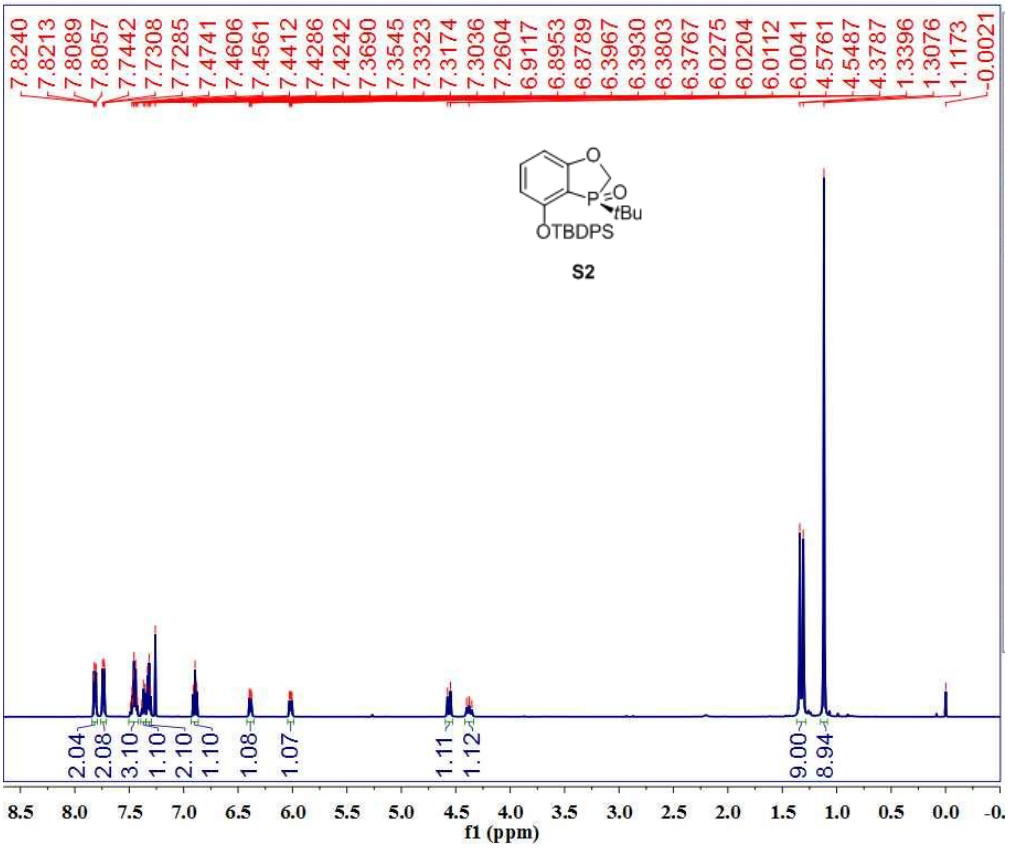

**14**: Preparation of **14** was carried out according to procedure same as **6a**. **14**: colorless oil, 92% yield, $R_f$ = 0.8 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –24.1 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.19 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.00 (t, *J* = 8.5 Hz, 2H), 3.80 (dd, *J* = 78.6, 14.9 Hz, 2H), 3.48 – 3.38 (m, 1H), 3.26 (ddd, *J* = 12.1, 8.3, 3.9 Hz, 1H), 2.54 (ddd, *J* = 14.2, 6.7, 4.0 Hz, 1H), 2.43 (d, *J* = 8.3 Hz, 3H), 2.34 – 2.20 (m, 1H), 0.79 – 0.63 (m, 9H), 0.33 (qd, *J* = 15.1, 7.5 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 201.31, 163.70, 161.72, 144.36, 135.08 (d, *J* = 3.4 Hz), 132.89, 130.03, 128.92 (d, *J* = 8.2 Hz), 127.81, 115.57 (d, *J* = 21.5 Hz), 79.59, 53.95, 42.48, 37.97, 21.66, 6.90, 6.24; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –112.91 (m); HRMS (ESI) calculated for [M+Na, $C_{24}H_{32}FNNaO_4SSi]^+$: 500.1698; found: 500.1709.

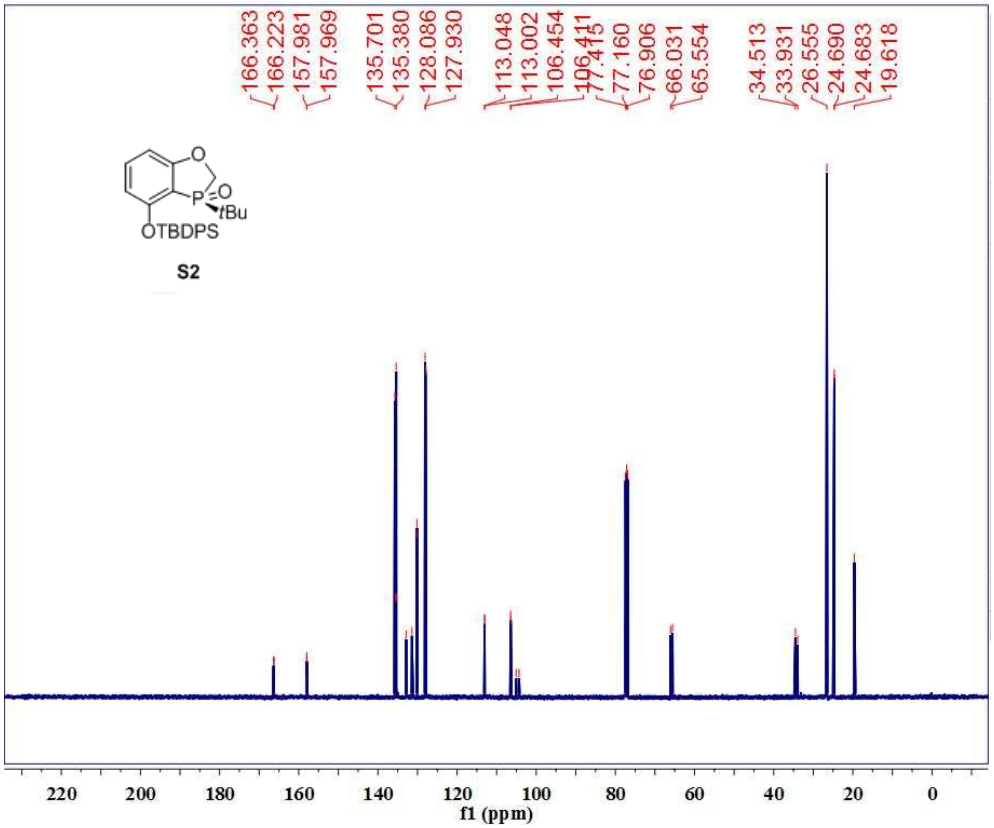


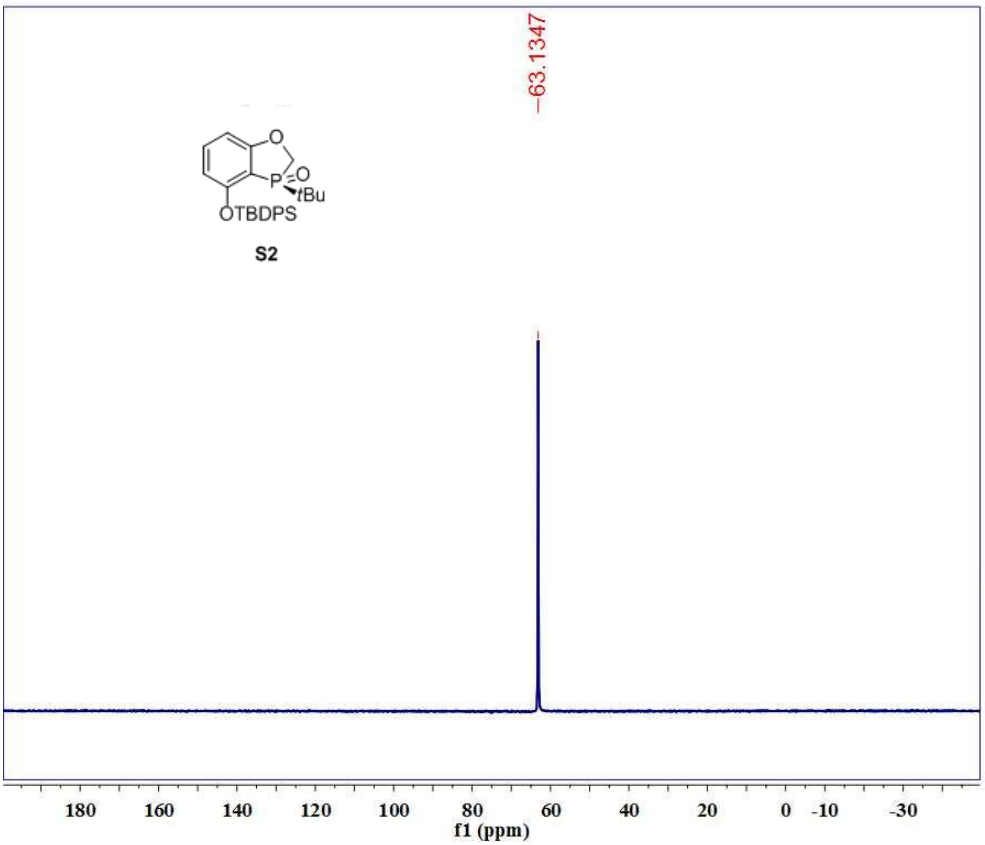

**15**: Preparation of **15** was carried out according to procedure same as **8a**. **15**: colorless oil, 86% yield, $R_f$ = 0.6 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –53.3 (c = 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 6.2 Hz, 4H), 6.97 (t, *J* = 8.2 Hz, 2H), 5.18 (d, *J* = 9.8 Hz, 2H), 3.95 (d, *J* = 12.4 Hz, 1H), 3.57 – 3.41 (m, 1H), 3.21 (d, *J* = 12.4 Hz, 1H), 3.01 (dd, *J* = 15.5, 5.9 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.41 (s, 3H), 2.01 (ddd, *J* = 13.4, 9.8, 3.6 Hz, 1H), 0.72 (t, *J* = 7.9 Hz, 9H), 0.34 – 0.18 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.37, 161.40, 145.70, 143.69, 137.29 (d, *J* = 3.3 Hz), 133.73, 129.74, 129.10 (d, *J* = 8.1 Hz), 127.85, 115.23 (d, *J* = 21.2 Hz), 113.88, 76.39, 50.67, 43.89, 37.56, 21.63, 6.96, 6.38; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –114.35 (m); HRMS (ESI) calculated for [M+Na, $C_{25}H_{34}FNNaO_3SSi]^+$: 498.1905; found: 498.1908.



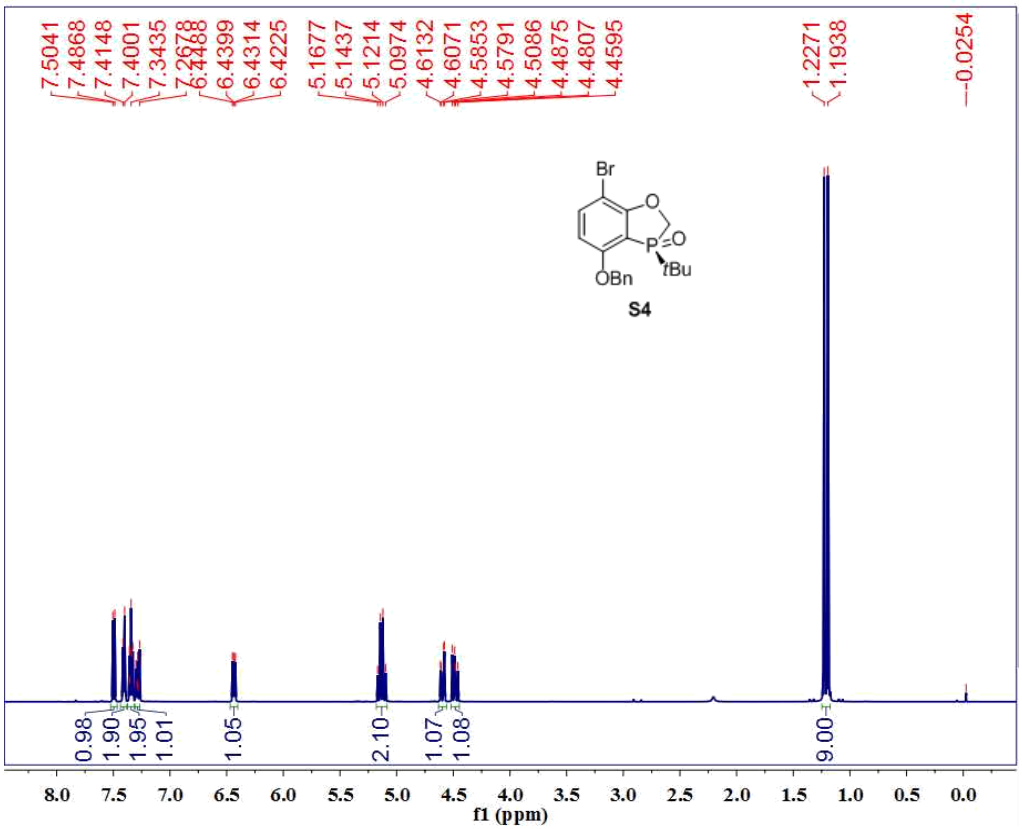

**16**: Preparation of **16** was carried out according to similar procedure as **3a.** **16**: white solid; 96% yield, $R_f$ = 0.2 (silica gel, EtOAc/Hexanes 1:9); $[\alpha]_D^{25}$ = –46.9 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.23 (m, 4H), 6.99 (t, *J* = 8.7 Hz, 2H), 5.11 (s, 1H), 4.69 (s, 1H), 3.87 (d, *J* = 12.7 Hz, 1H), 3.66 (d, *J* = 12.7 Hz, 1H), 3.52 – 3.35 (m, 1H), 3.23 – 3.08 (m, 1H), 2.43 (s, 3H), 2.32 (ddd, *J* = 14.2, 10.3, 4.2 Hz, 1H), 1.97 (s, 1H), 1.82 (ddd, *J* = 13.9, 4.7, 3.1 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.35, 160.90, 145.12, 143.77, 138.63 (d, *J* = 3.2 Hz), 133.44, 129.77, 127.97 (d, *J* = 8.0 Hz), 127.78, 115.25 (d, *J* = 14.4 Hz), 114.96, 74.32, 50.11, 42.98, 38.52, 21.57; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –114.98 (m); HRMS (ESI) calculated for [M+Na, $C_{19}H_{20}FNNaO_3S]^+$: 384.1040; found: 384.1046.

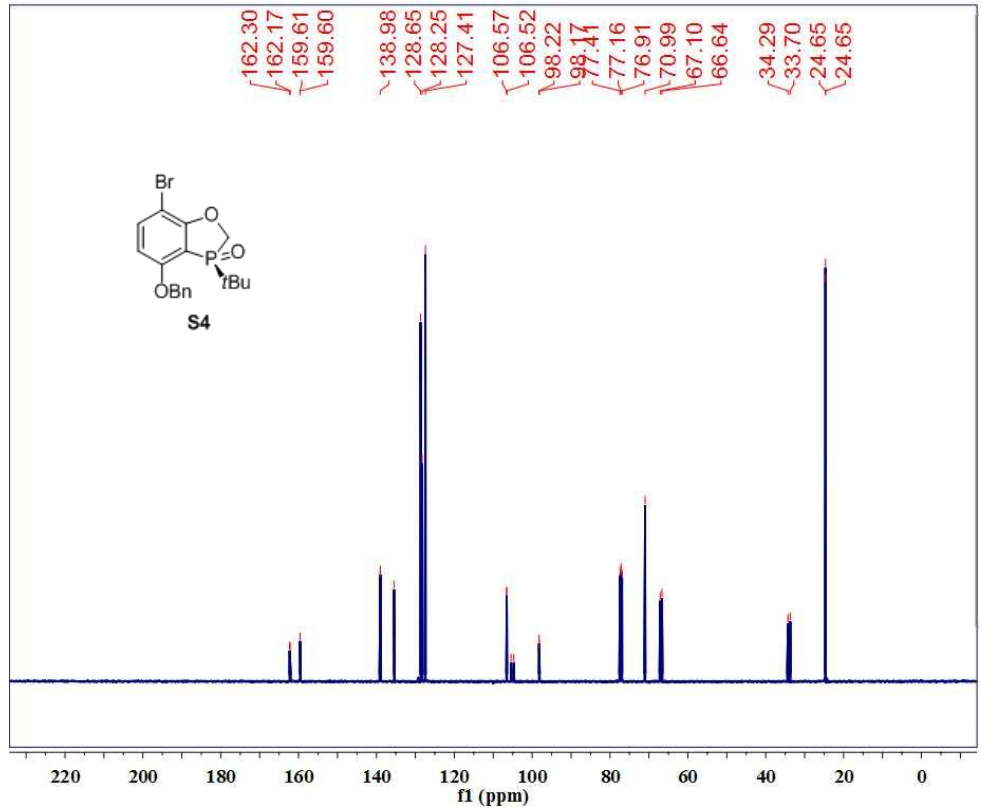

7.8240
7.8213
7.8089
7.8057
7.7442
7.7308
7.7285
7.4741
7.4606
7.4561
7.4412
7.4286
7.4242
7.3690
7.3545
7.3323
7.3174
7.3036
7.2604
6.9117
6.8953
6.8789
6.3967
6.3930
6.3803
6.3767
6.0275
6.0204
6.0112
6.0041
4.5761
4.5487
4.3787
1.3396
1.3076
1.1173
-0.0021
O
P
O
tBu
OTBDPS
S2
2.04
2.08
3.10
1.10
2.10
1.10
1.08
1.07
1.11
1.12
9.00
8.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

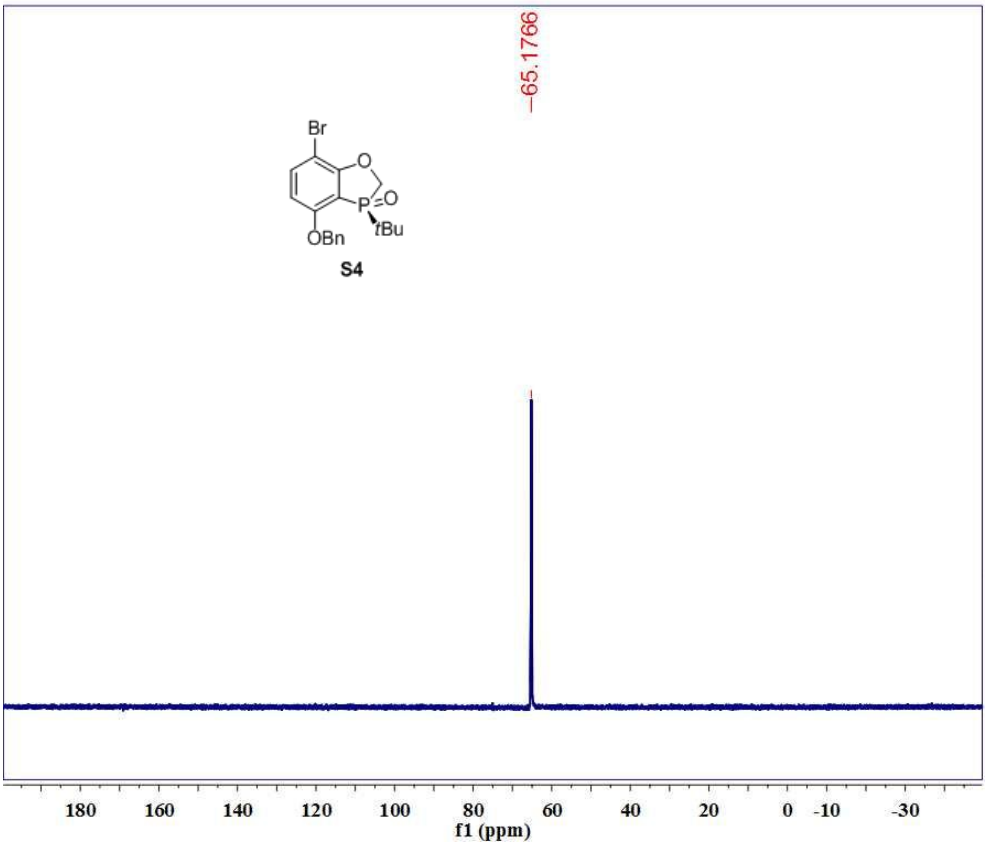

166.363
166.223
157.981
157.969
135.701
135.380
128.086
127.930
113.048
113.002
106.454
106.411
77.415
77.160
76.906
66.031
65.554
34.513
33.931
26.555
24.690
24.683
19.618
O
P
O
tBu
OTBDPS
S2
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)



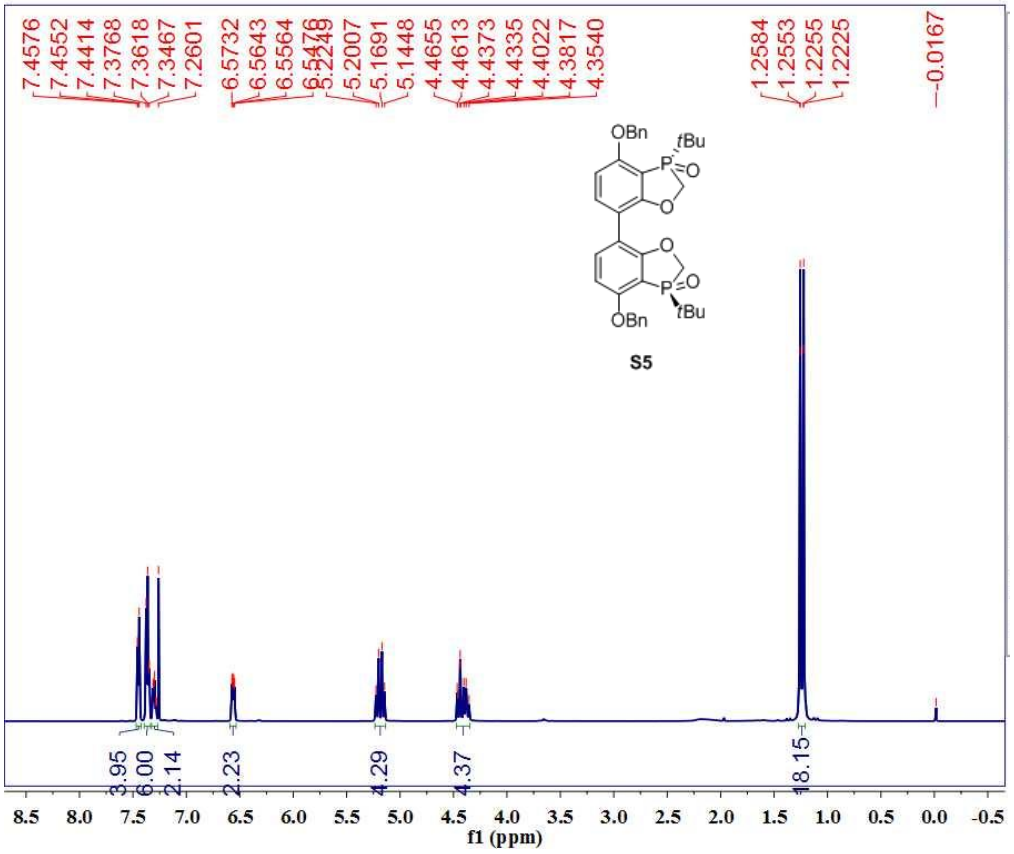

**Supplementary Figure 28.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S2**

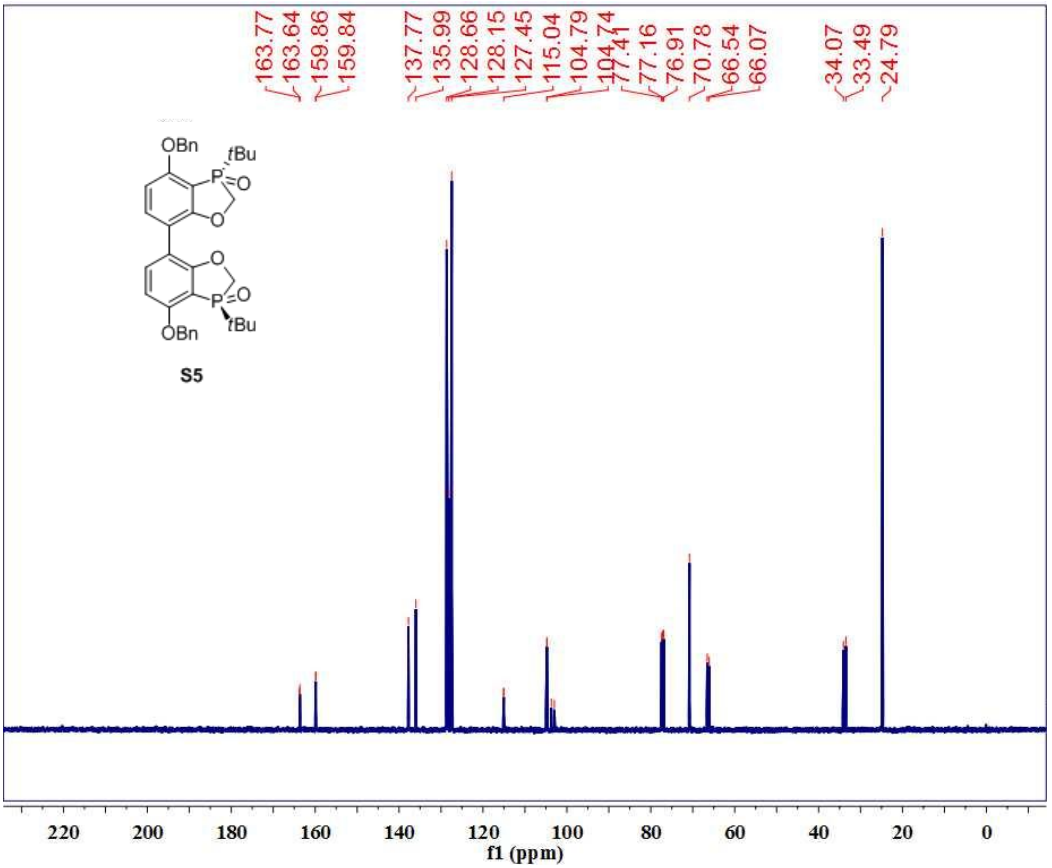


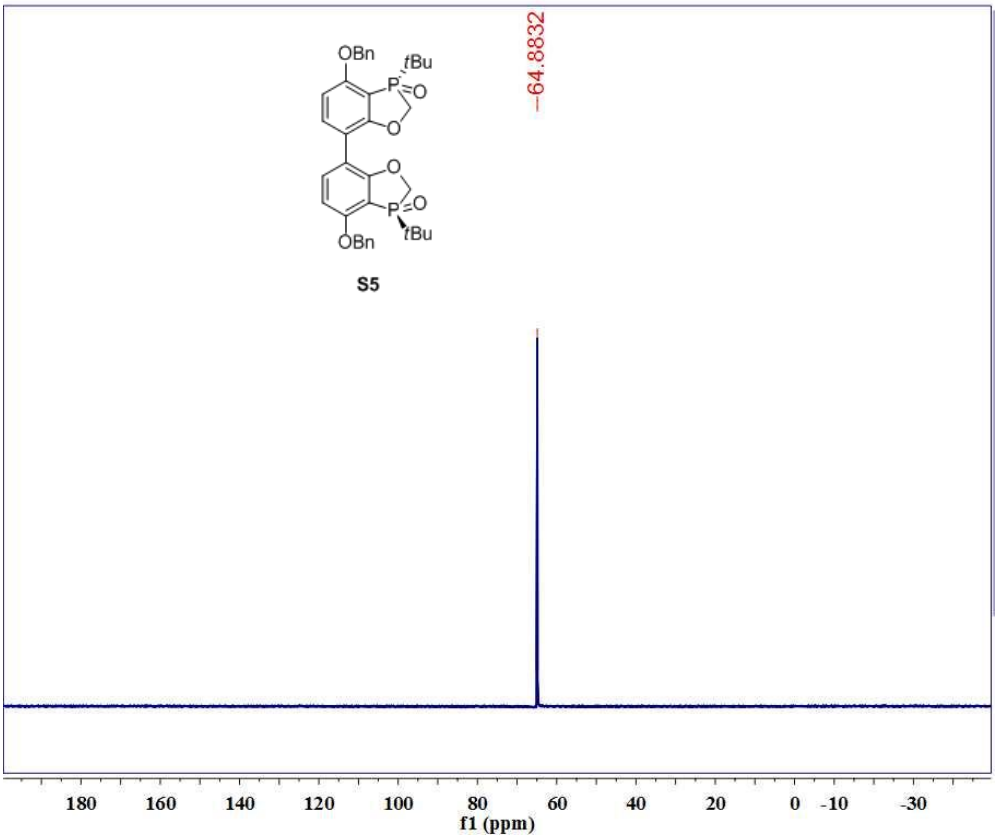


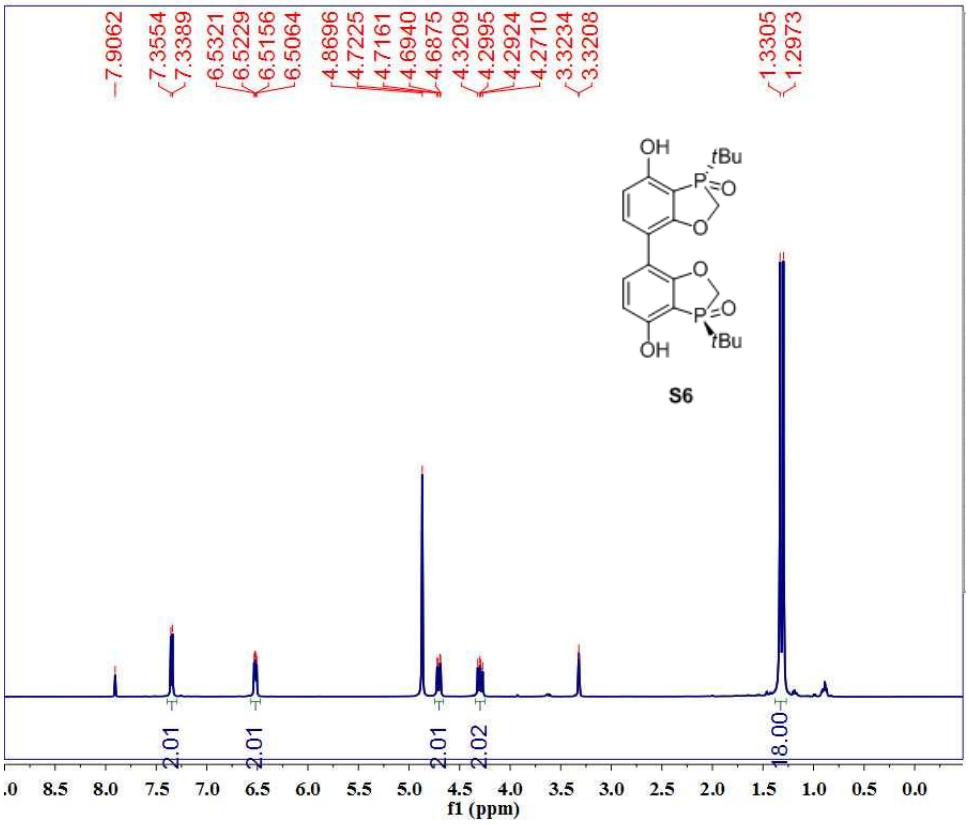

**Supplementary Figure 29.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S4**

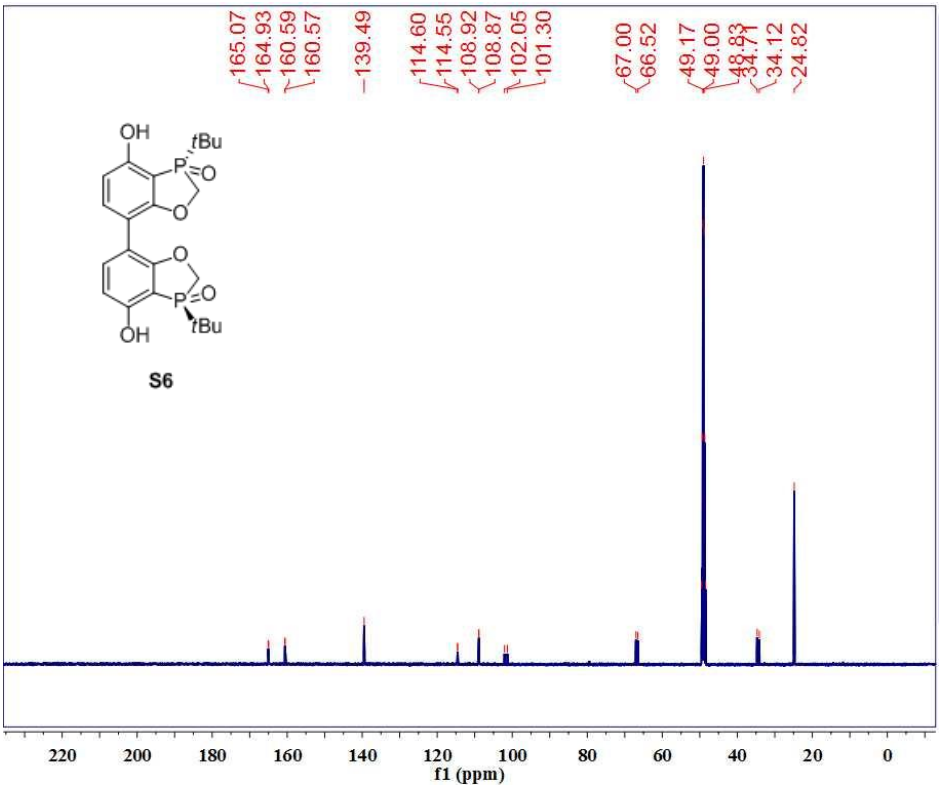

7.4576
7.4552
7.4414
7.3768
7.3618
7.3467
7.2601
6.5732
6.5643
6.5564
5.2007
5.1691
5.1448
4.4655
4.4613
4.4373
4.4335
4.4022
4.3817
4.3540
1.2584
1.2553
1.2255
1.2225
-0.0167
OBn
tBu
P
O
O
O
P
O
tBu
OBn
S5
3.95
6.00
2.14
2.23
4.29
4.37
18.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

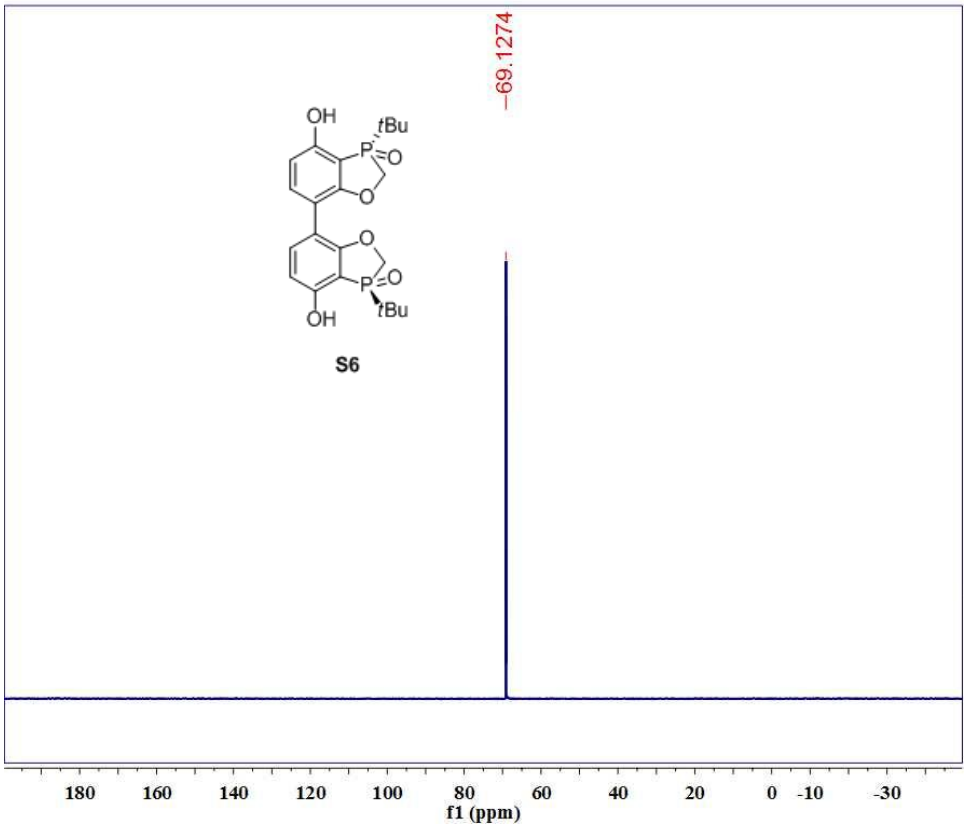

163.77
163.64
159.86
159.84
137.77
135.99
128.66
128.15
127.45
115.04
104.79
104.74
77.41
77.16
76.91
70.78
66.54
66.07
34.07
33.49
24.79
OBn
tBu
P
O
O
O
P
O
tBu
OBn
S5
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)



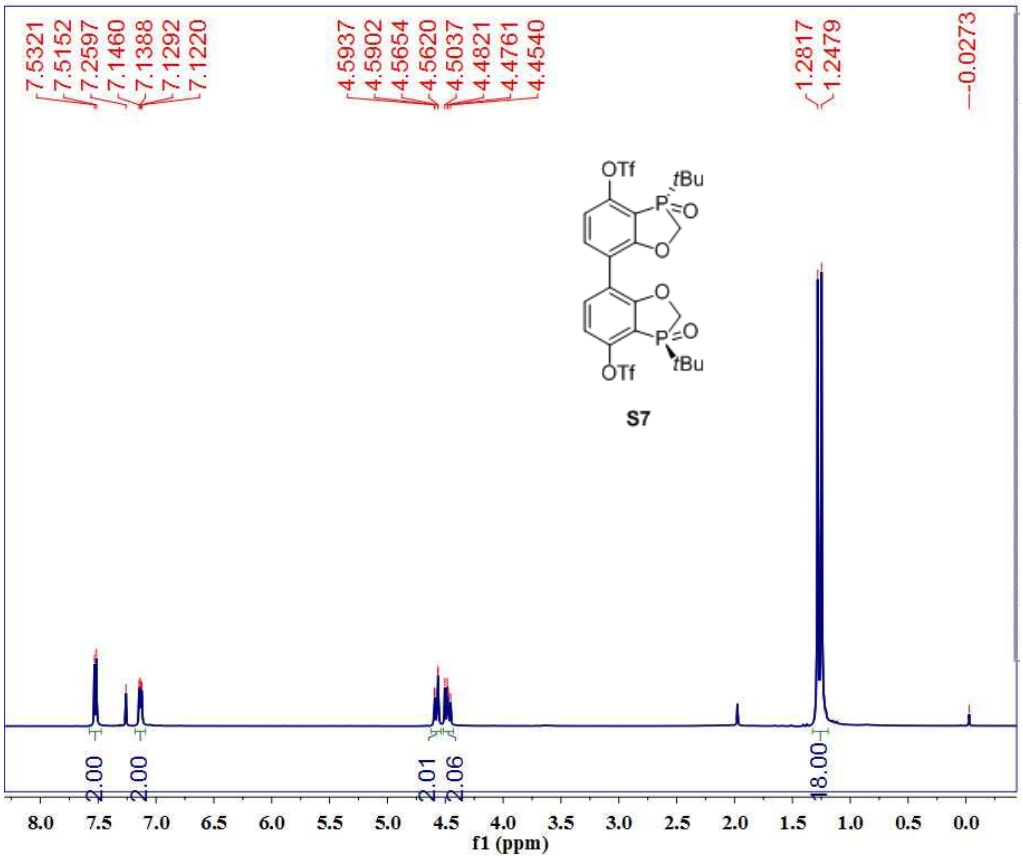

**Supplementary Figure 30.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S5**

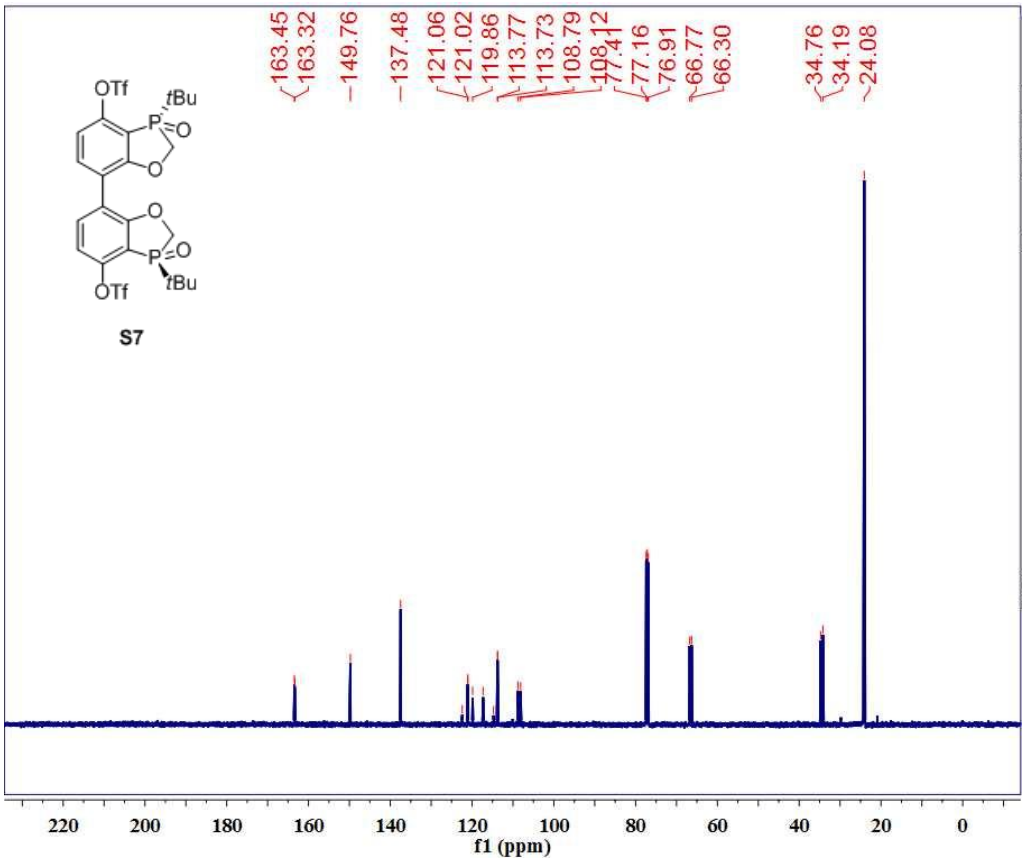


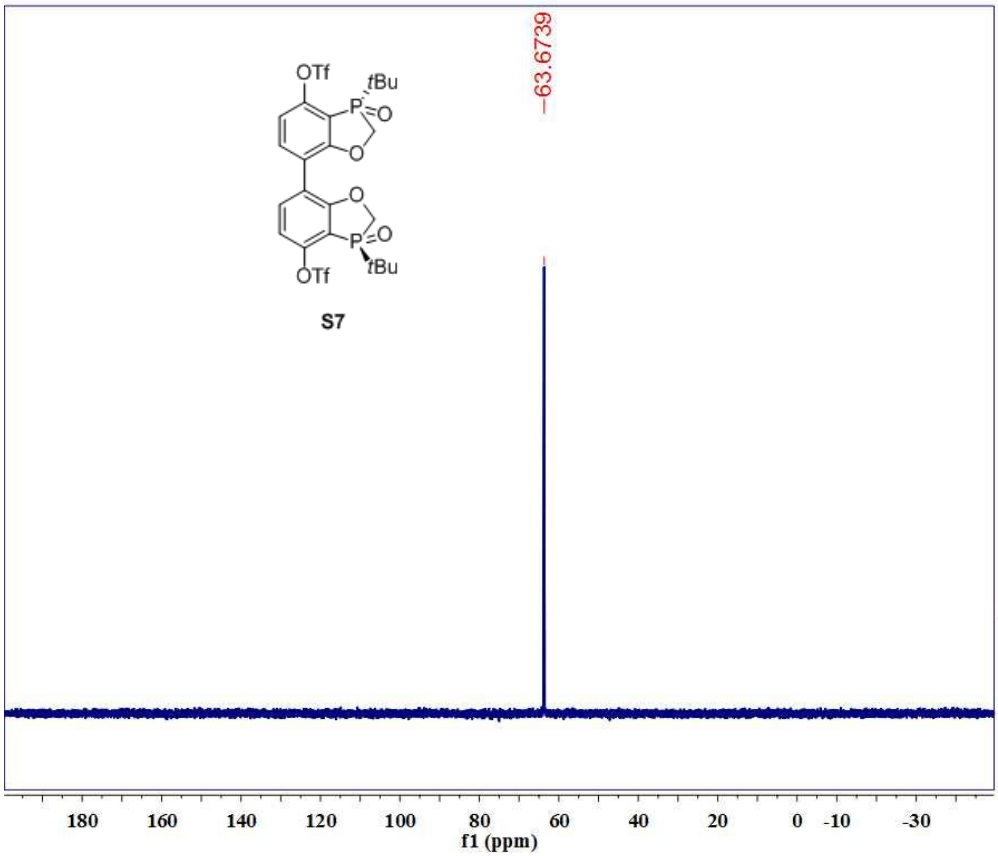


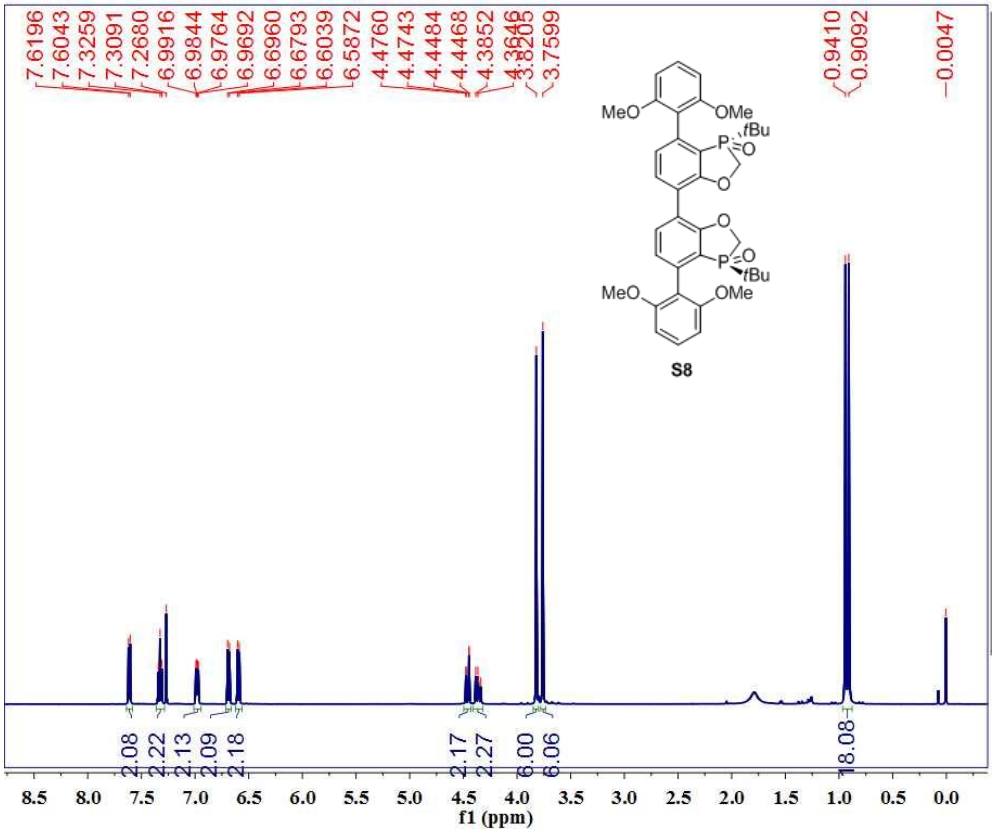

**Supplementary Figure 31.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S6**

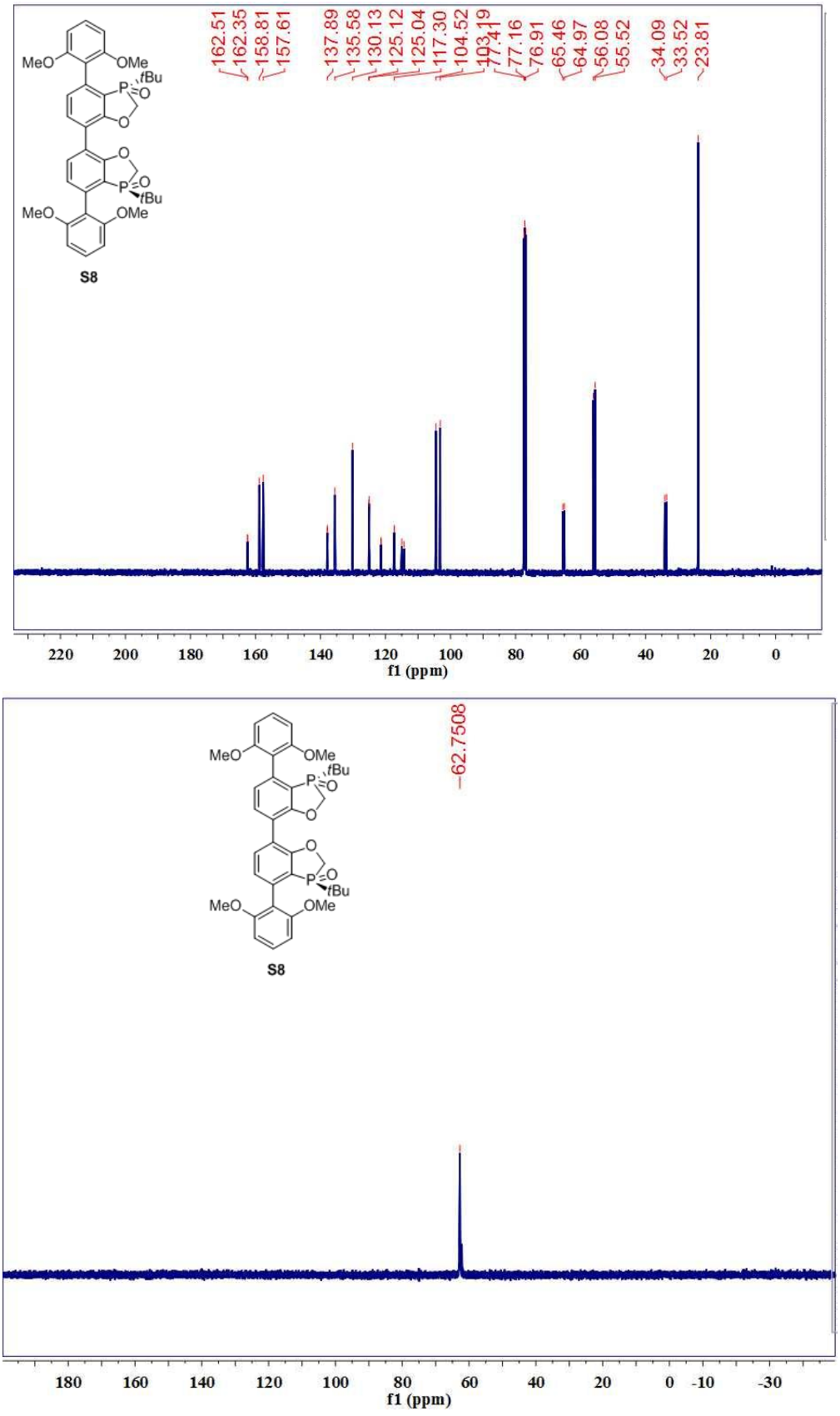

7.5321
7.5152
7.2597
7.1460
7.1388
7.1292
7.1220
4.5937
4.5902
4.5654
4.5620
4.5037
4.4821
4.4761
4.4540
1.2817
1.2479
-0.0273
OTf
tBu
P
O
O
O
P
O
tBu
OTf
S7
2.00
2.00
2.01
2.06
18.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.45
163.32
149.76
137.48
121.06
121.02
119.86
113.77
113.73
108.79
108.12
77.41
77.16
76.91
66.77
66.30
34.76
34.19
24.08
OTf
tBu
P
O
O
O
P
O
tBu
OTf
S7
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

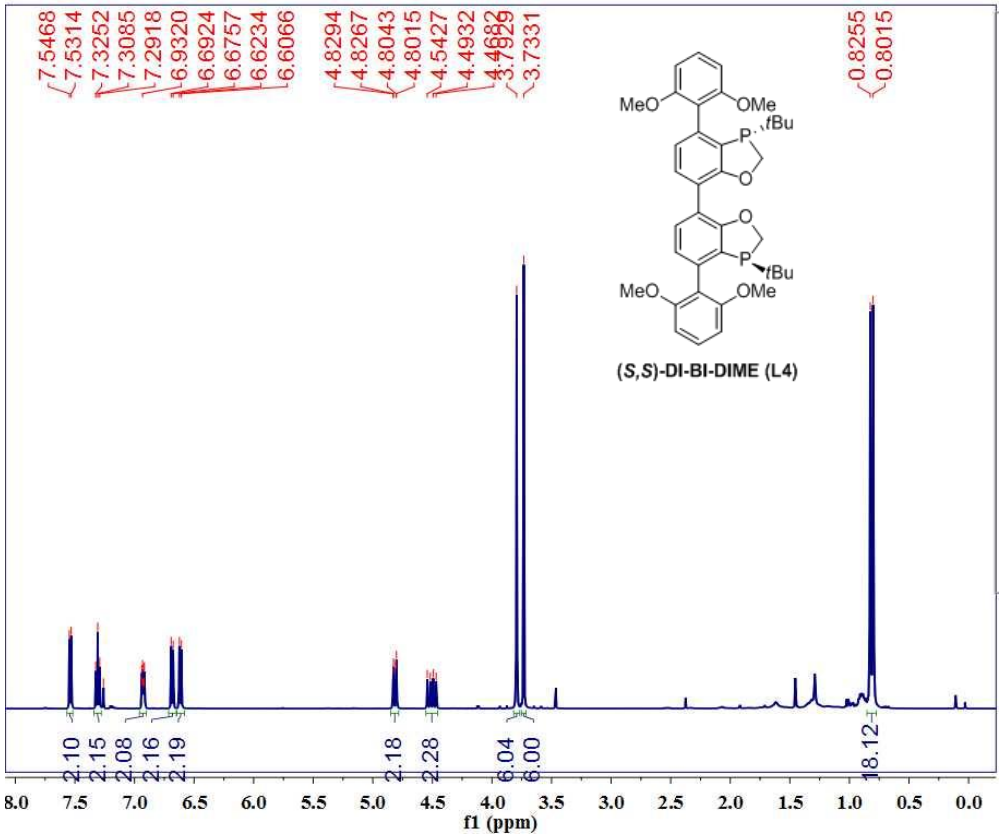


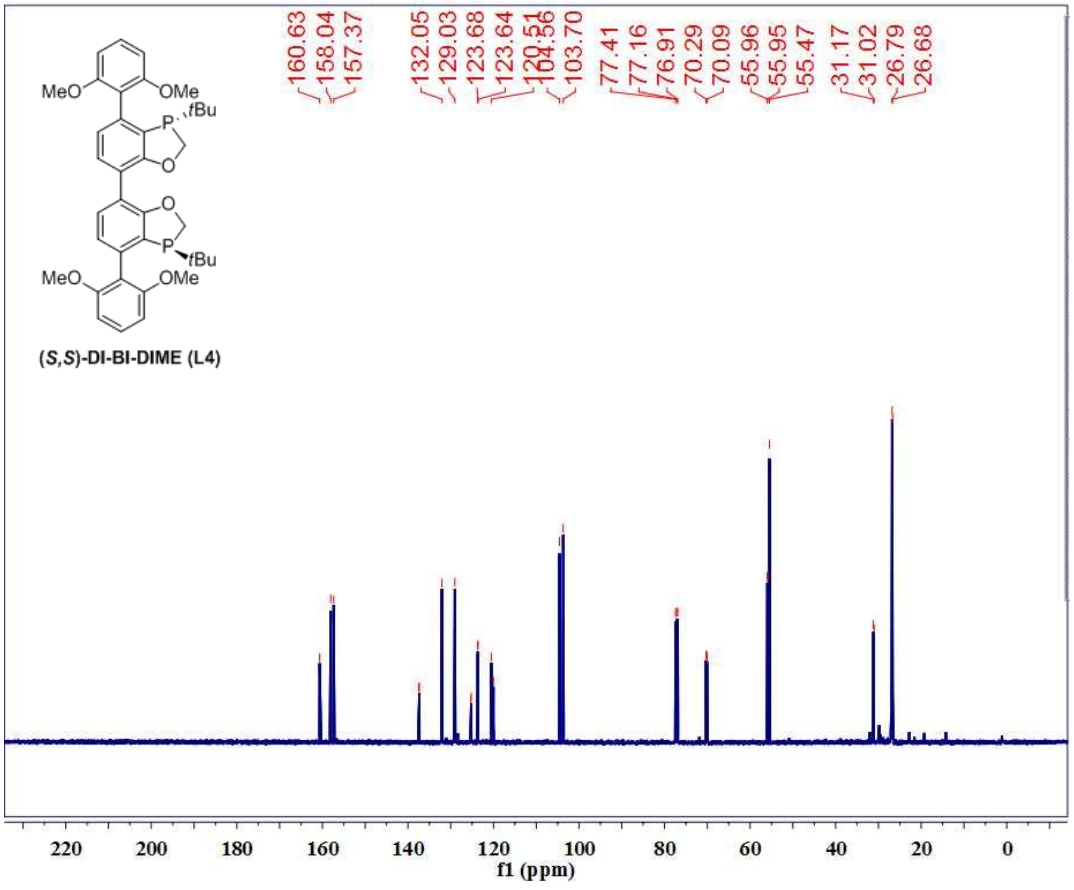

**Supplementary Figure 32.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S7**

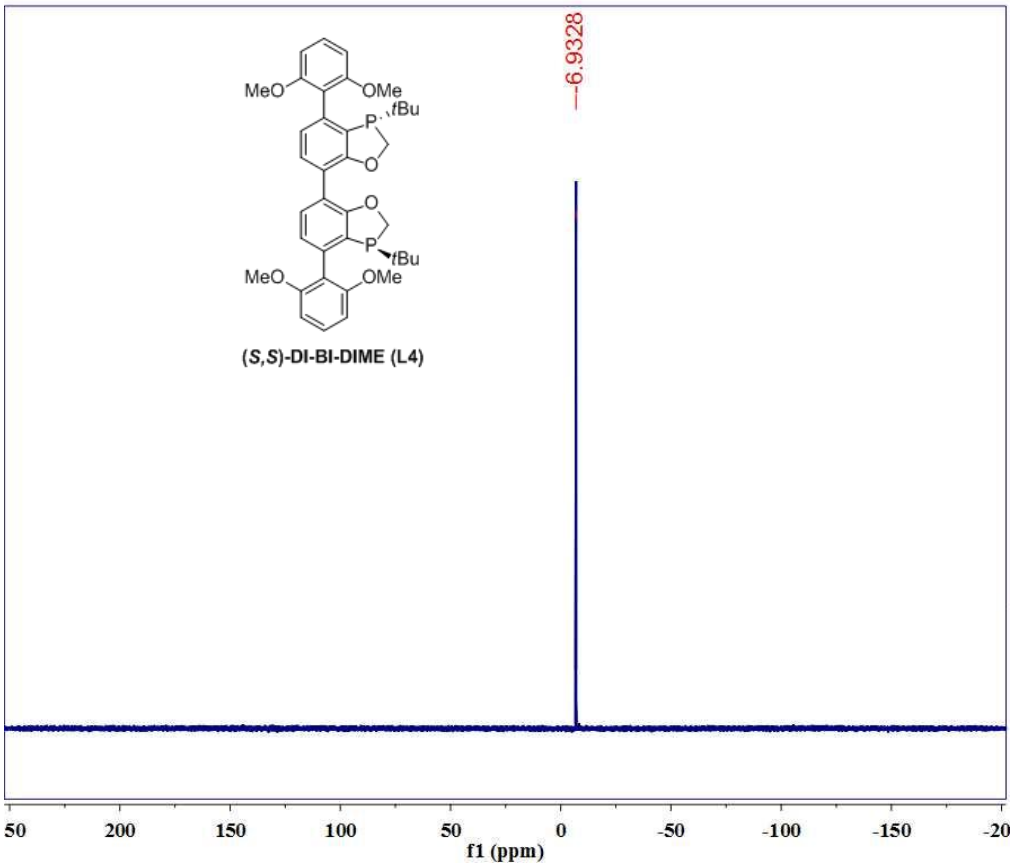




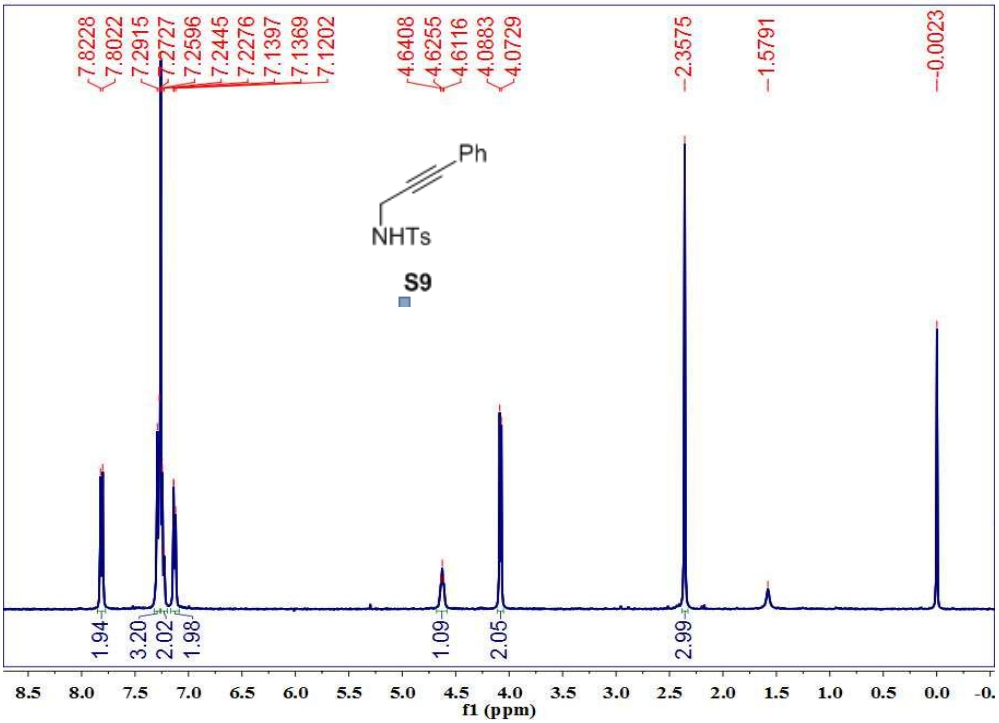

**Supplementary Figure 33.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **S8**


7.5468
7.5314
7.3252
7.3085
7.2918
6.9320
6.6924
6.6757
6.6234
6.6066
4.8294
4.8267
4.8043
4.8015
4.5427
4.4932
3.7929
3.7331
0.8255
0.8015
MeO
OMe
tBu
P
O
O
P
tBu
MeO
OMe
(S,S)-DI-BI-DIME (L4)
2.10
2.15
2.08
2.16
2.19
2.18
2.28
6.04
6.00
18.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

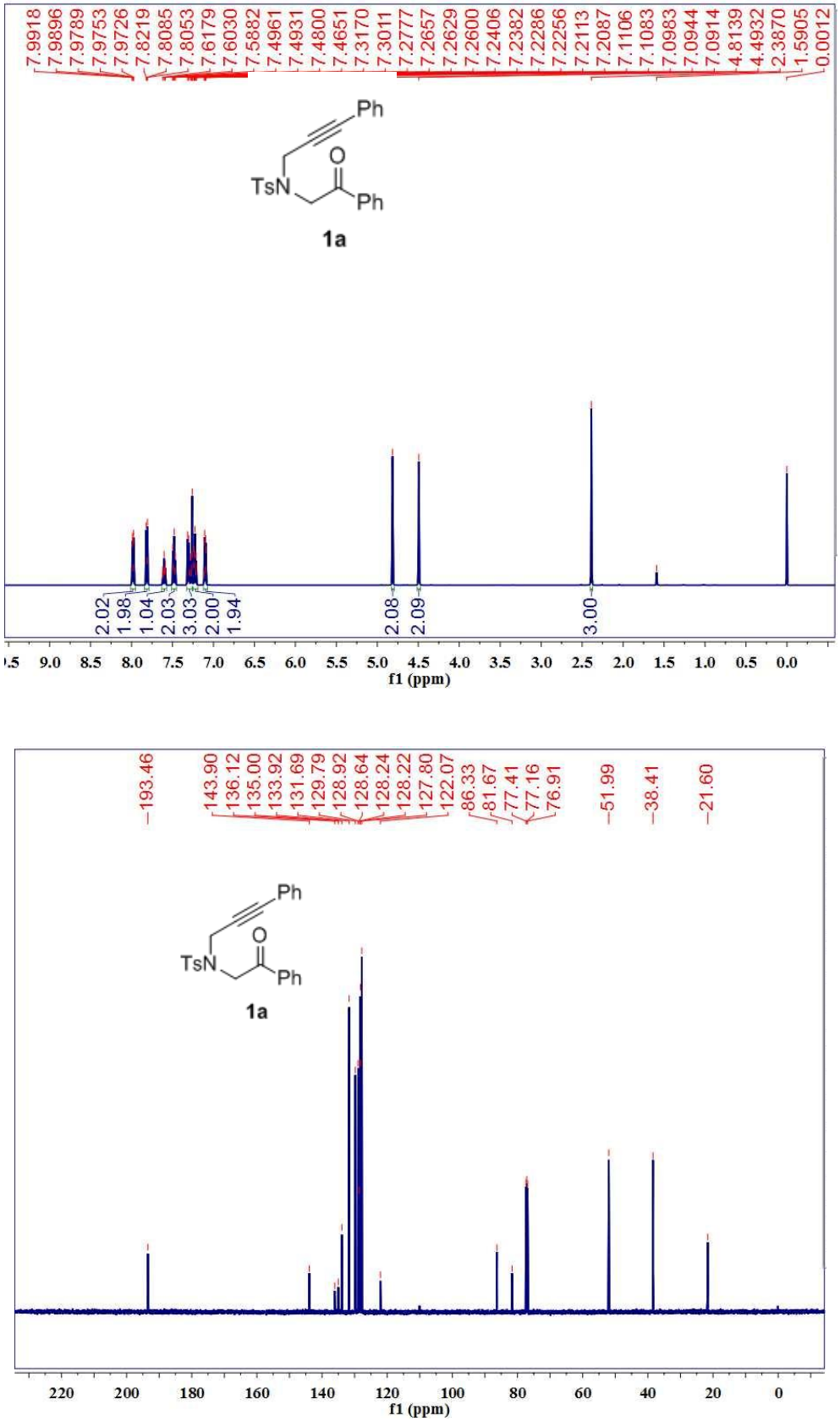

160.63
158.04
157.37
132.05
129.03
123.68
123.64
120.51
104.56
103.70
77.41
77.16
76.91
70.29
70.09
55.96
55.95
55.47
31.17
31.02
26.79
26.68
MeO
OMe
tBu
P
O
O
P
tBu
MeO
OMe
(S,S)-DI-BI-DIME (L4)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



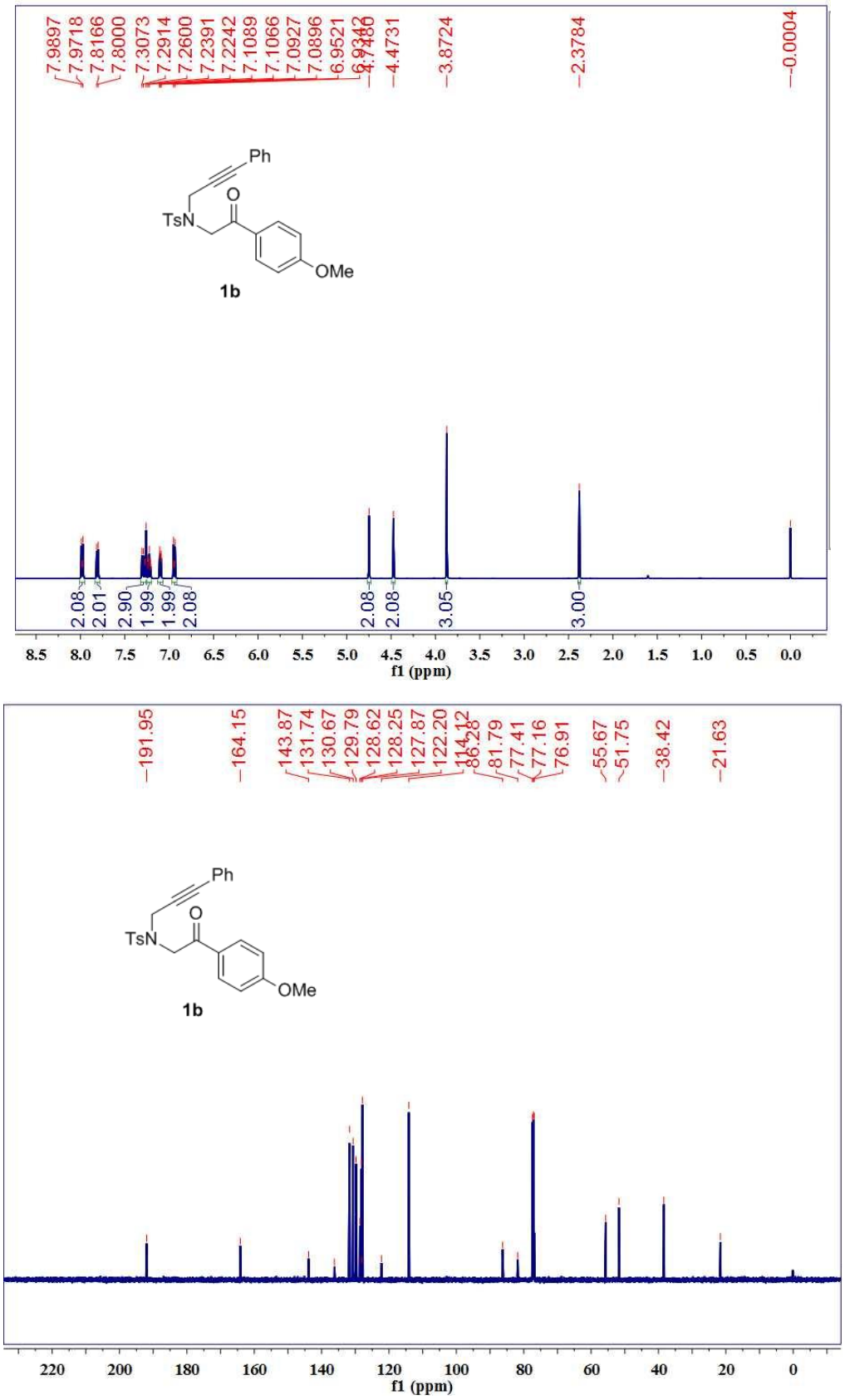

**Supplementary Figure 34.** $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra for compound **(*S*,*S*)-DI-BIDIME (L4)**



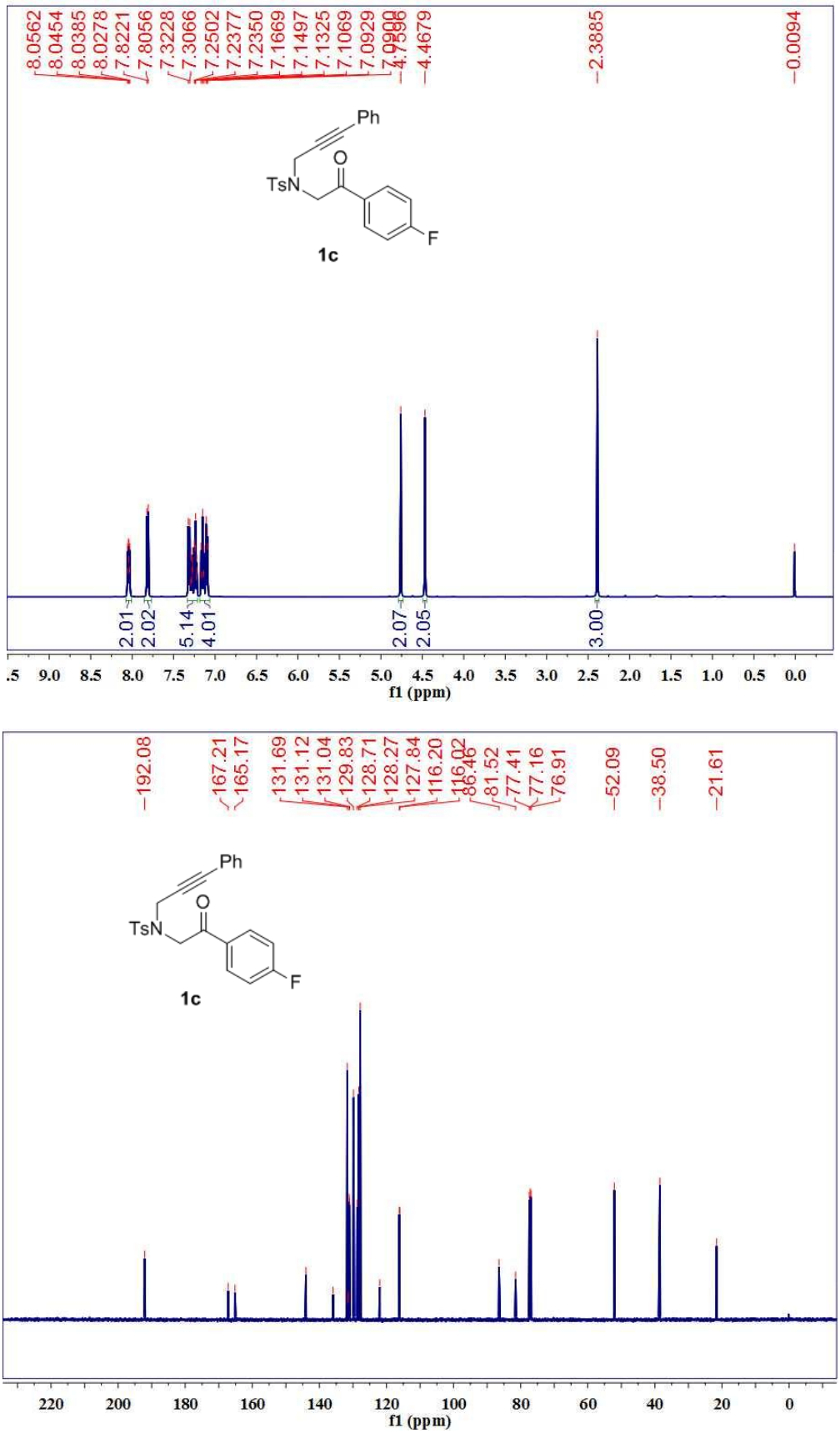

**Supplementary Figure 35.** $^{1}H$ NMR spectra for compound **S9**



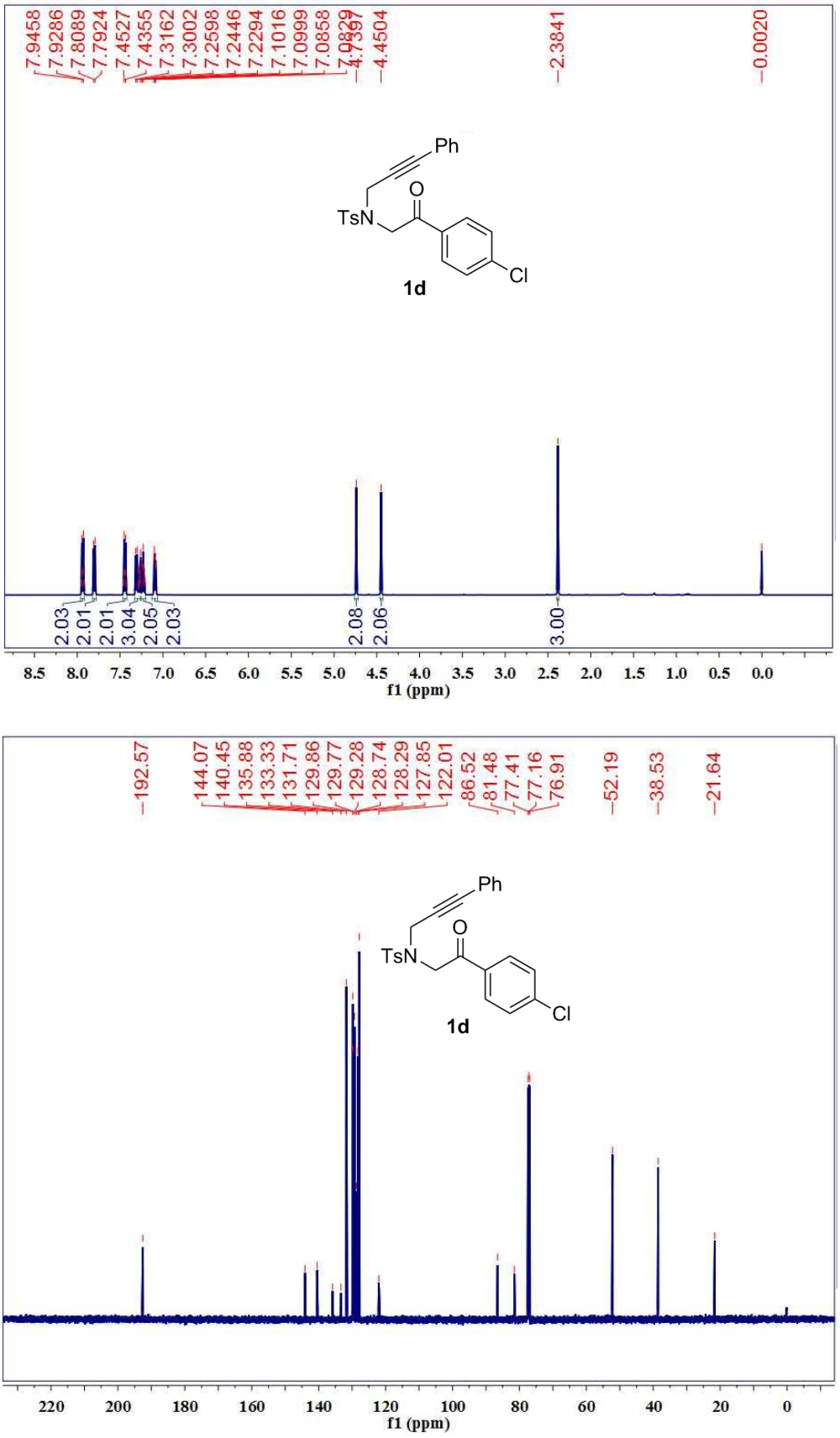

**Supplementary Figure 36.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1a**



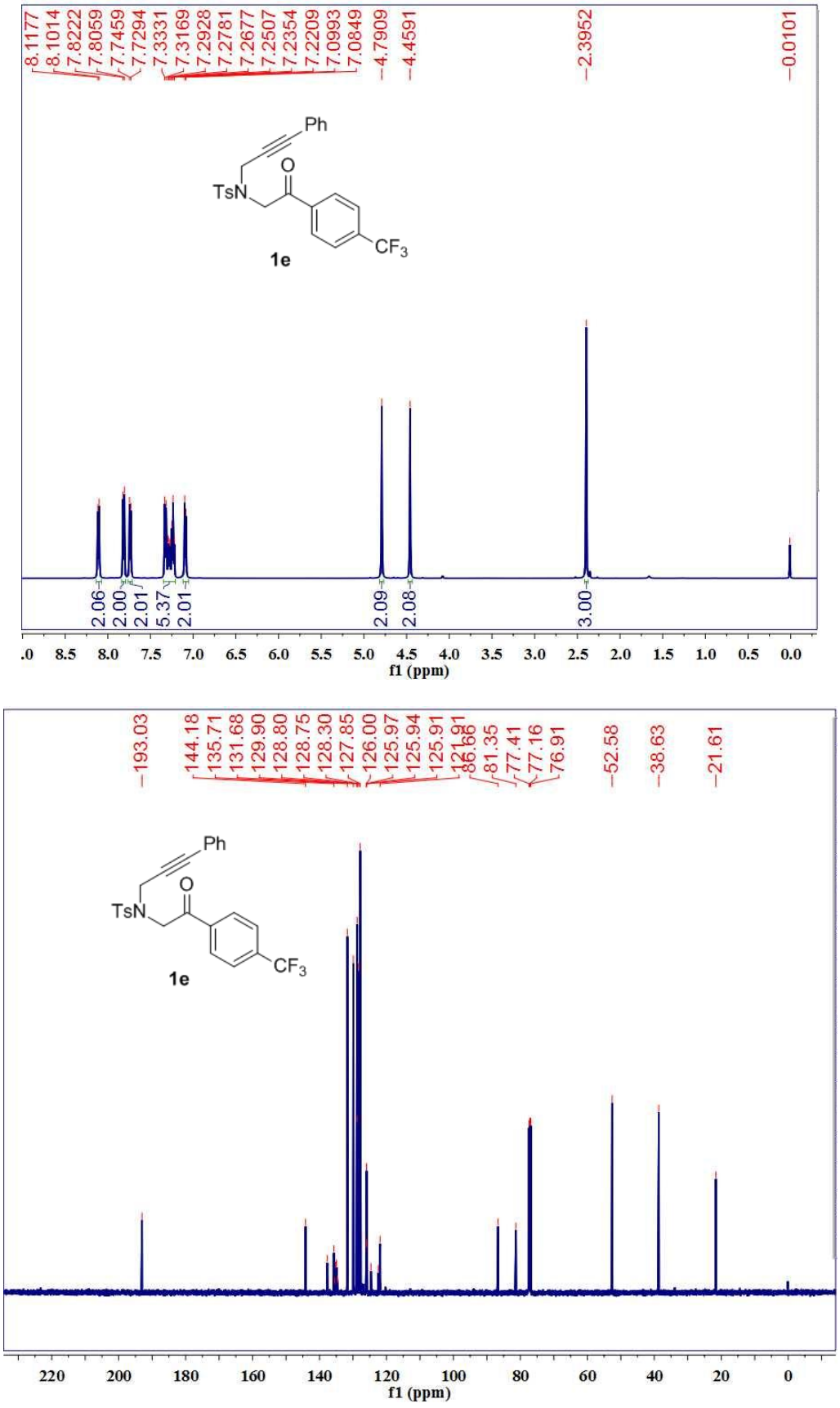

**Supplementary Figure 37.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1b**



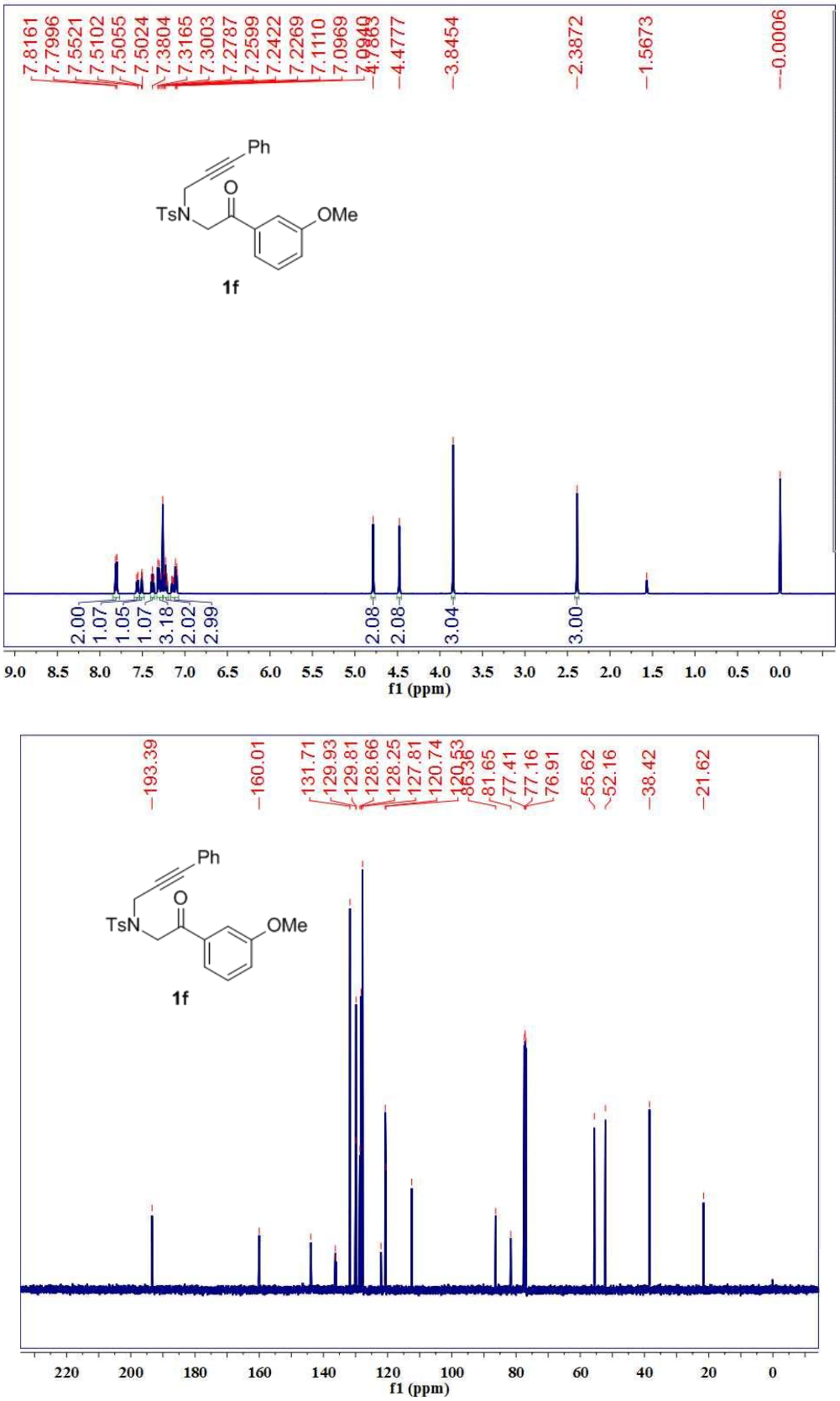

**Supplementary Figure 38.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1c**



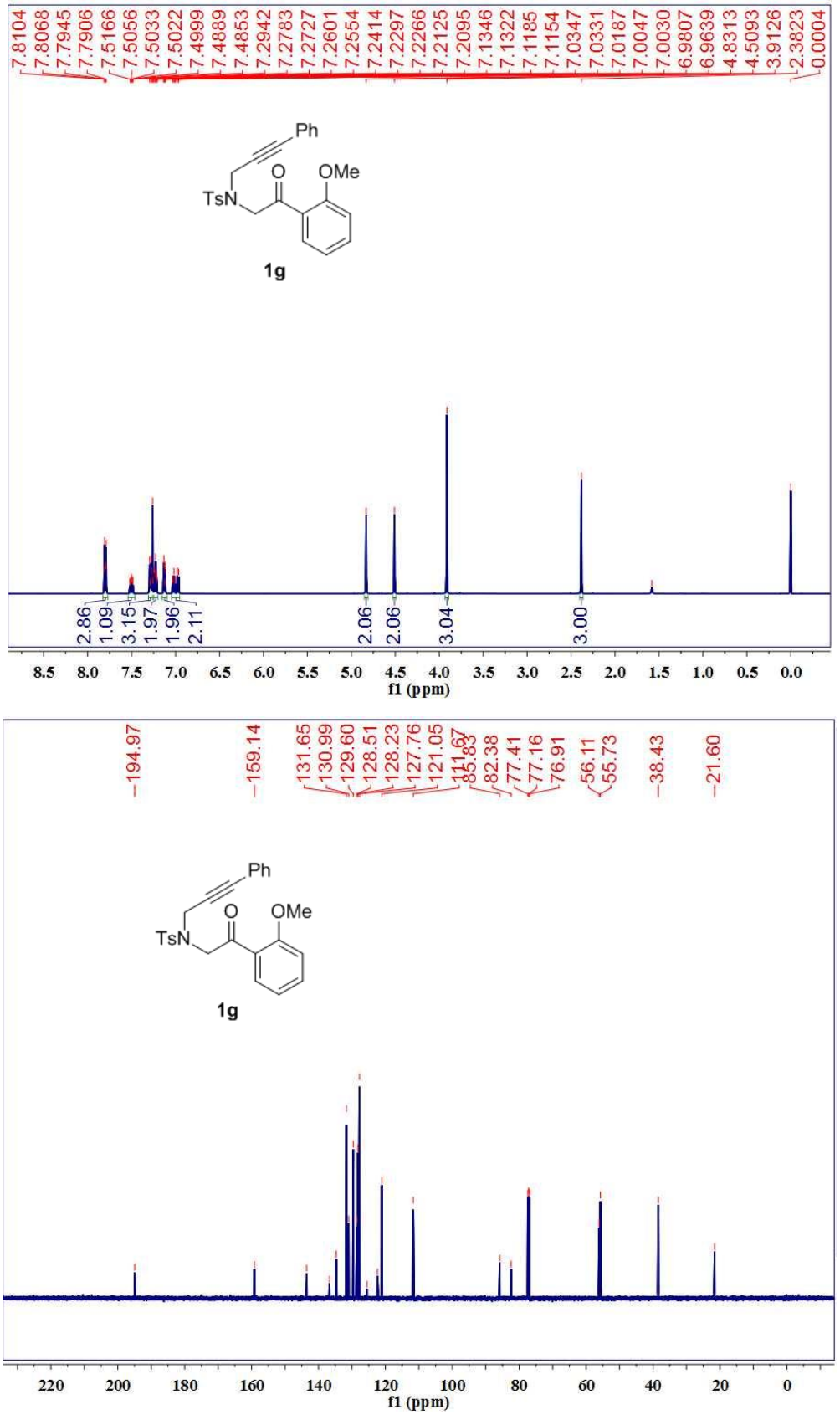

**Supplementary Figure 39.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1d**



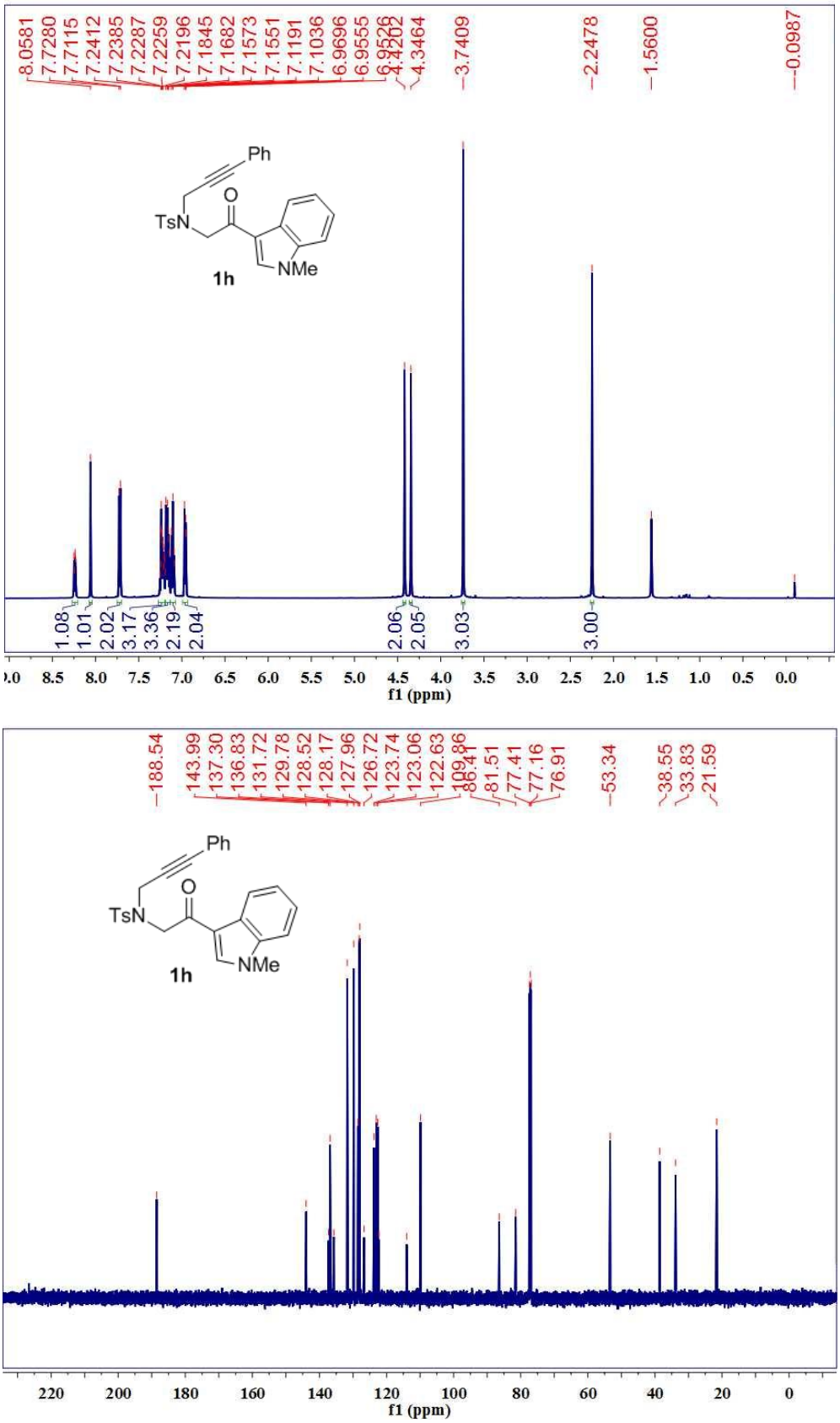

**Supplementary Figure 40.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1e**



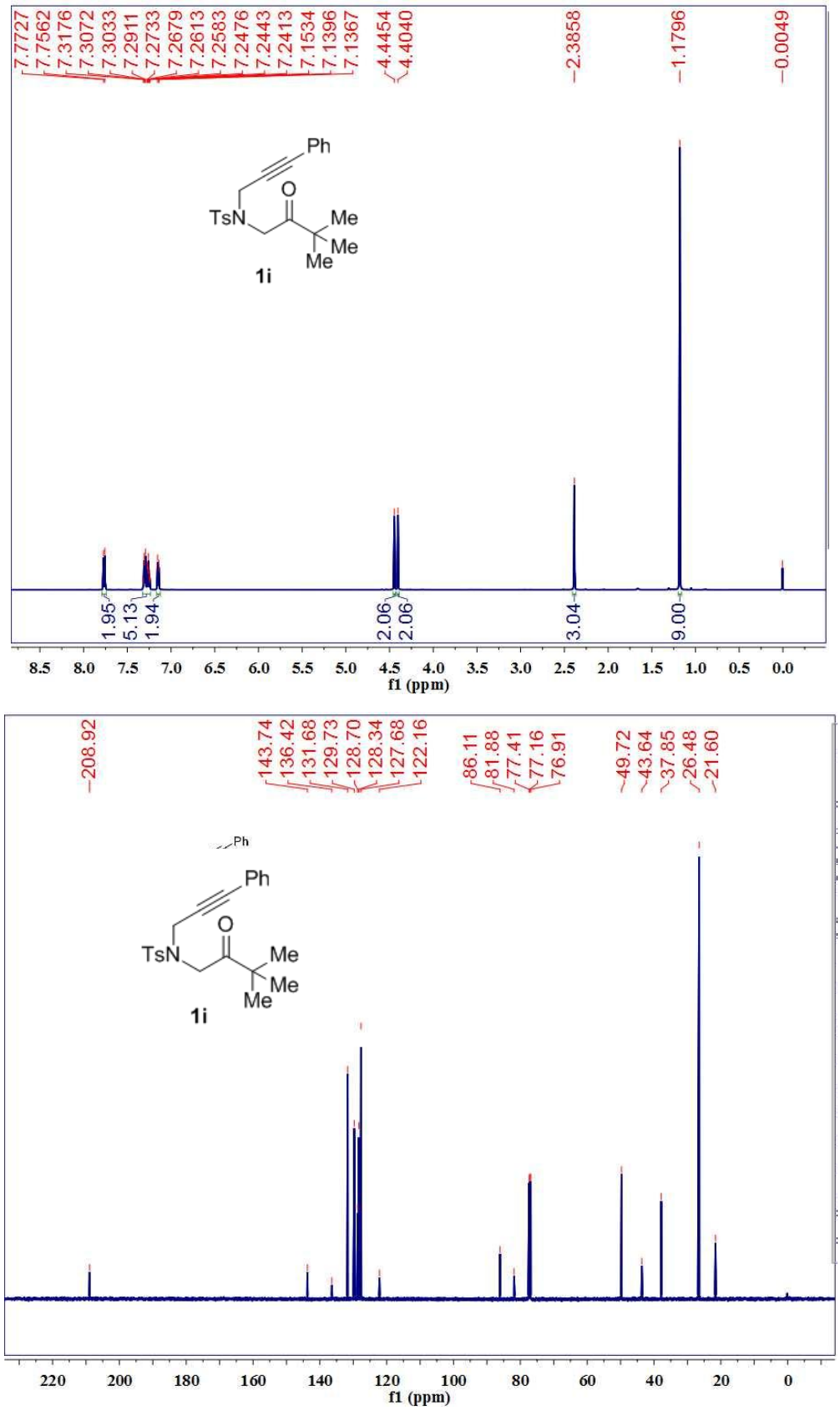

**Supplementary Figure 41.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1f**



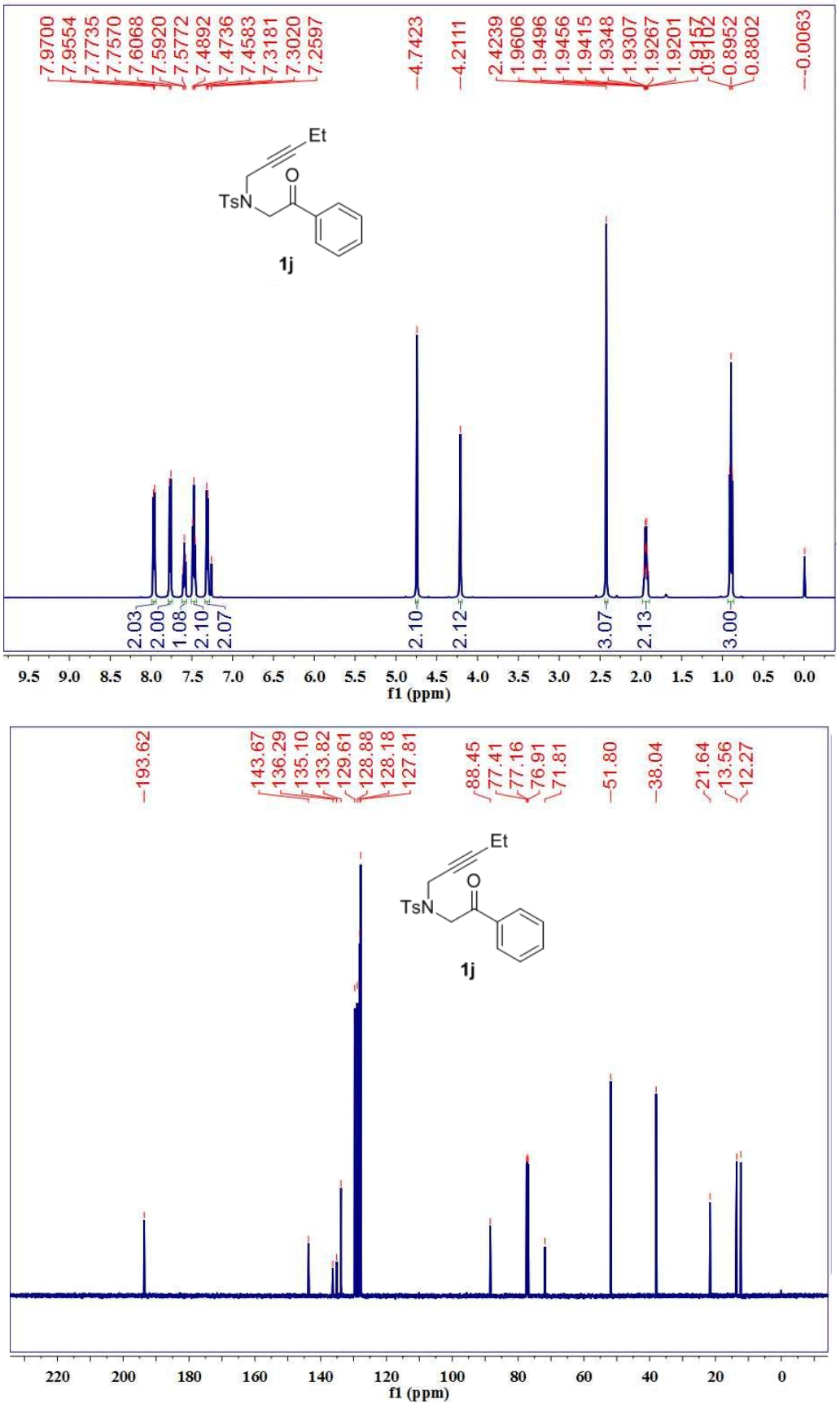

**Supplementary Figure 42.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1g**



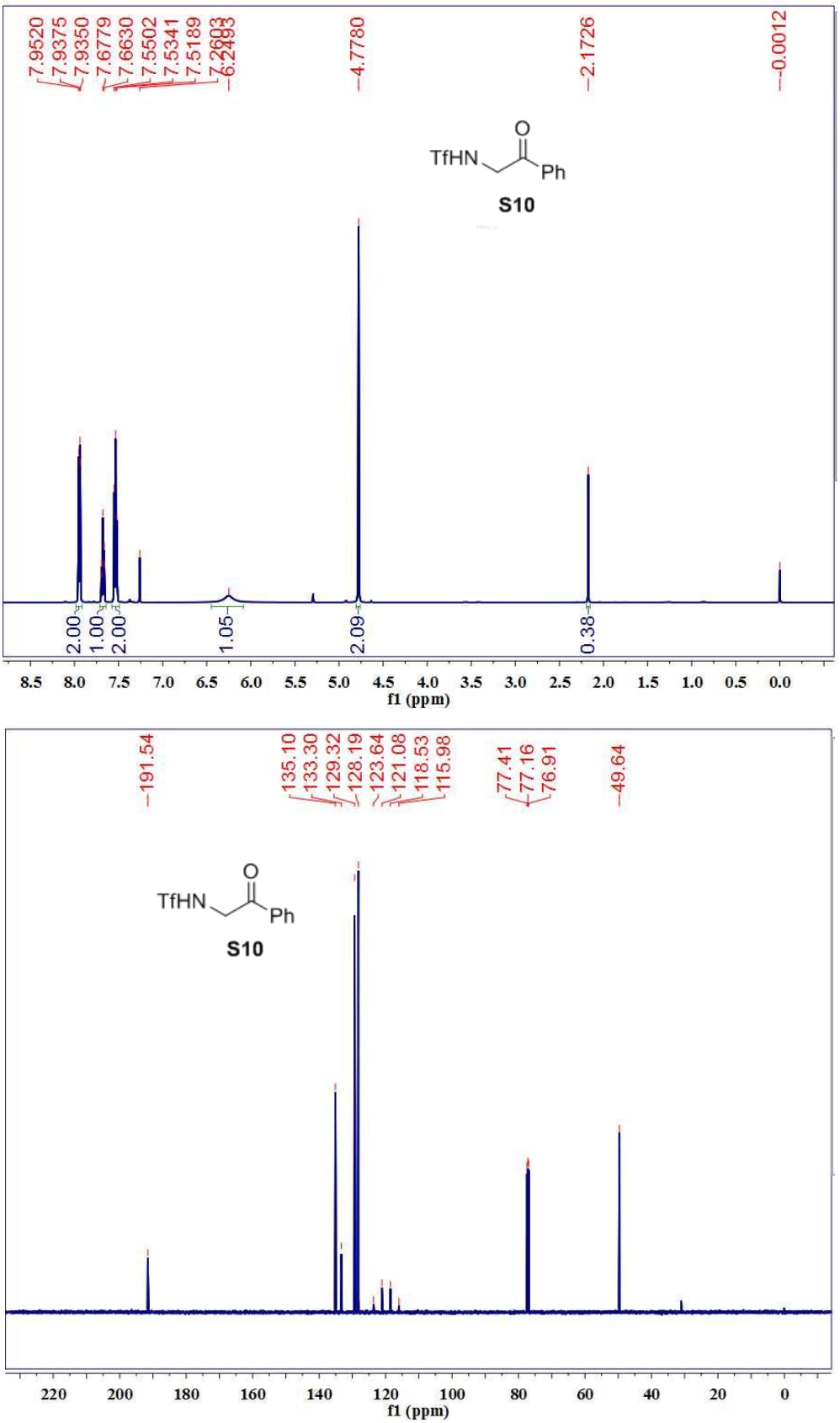

**Supplementary Figure 43.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1h**



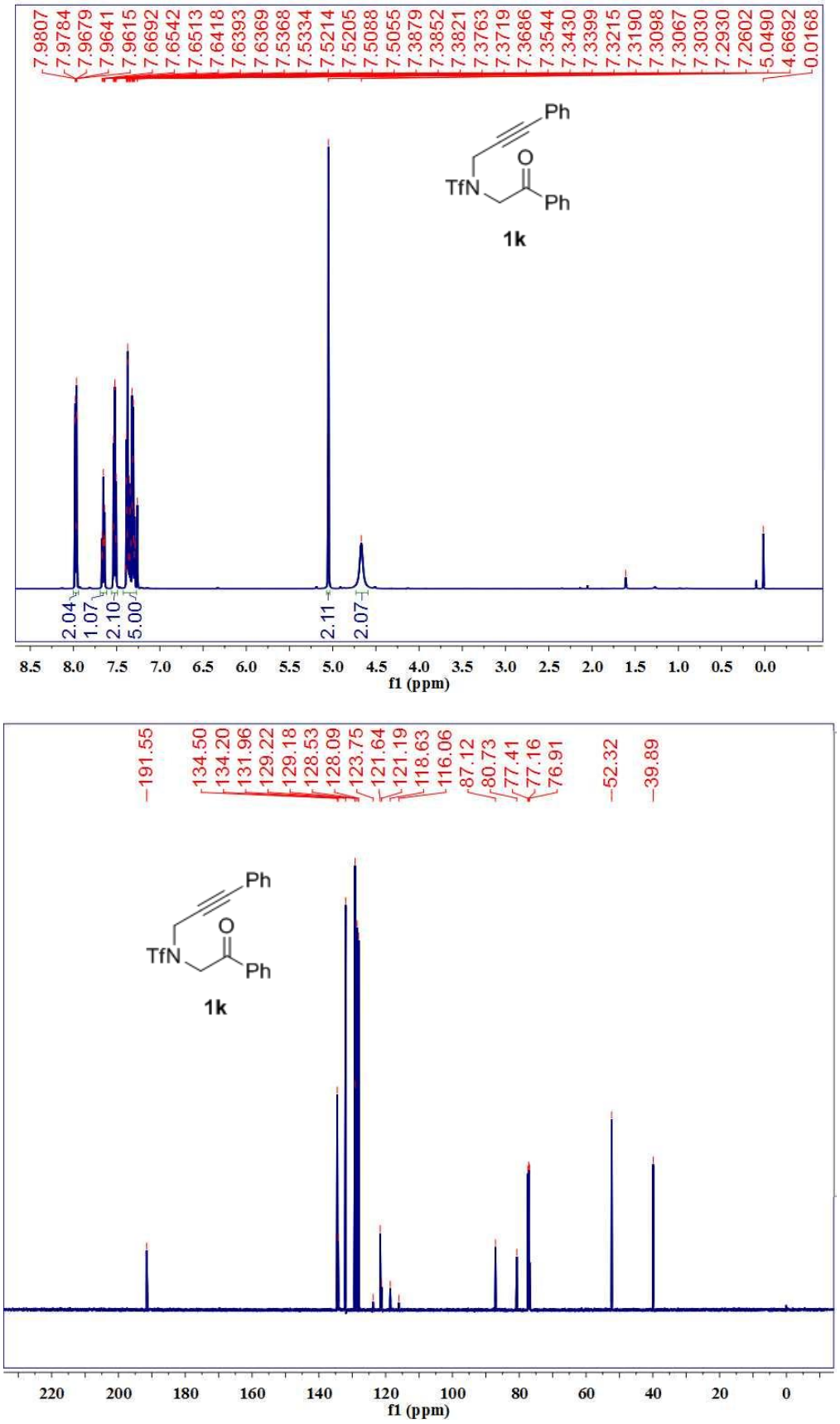

**Supplementary Figure 44.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1i**



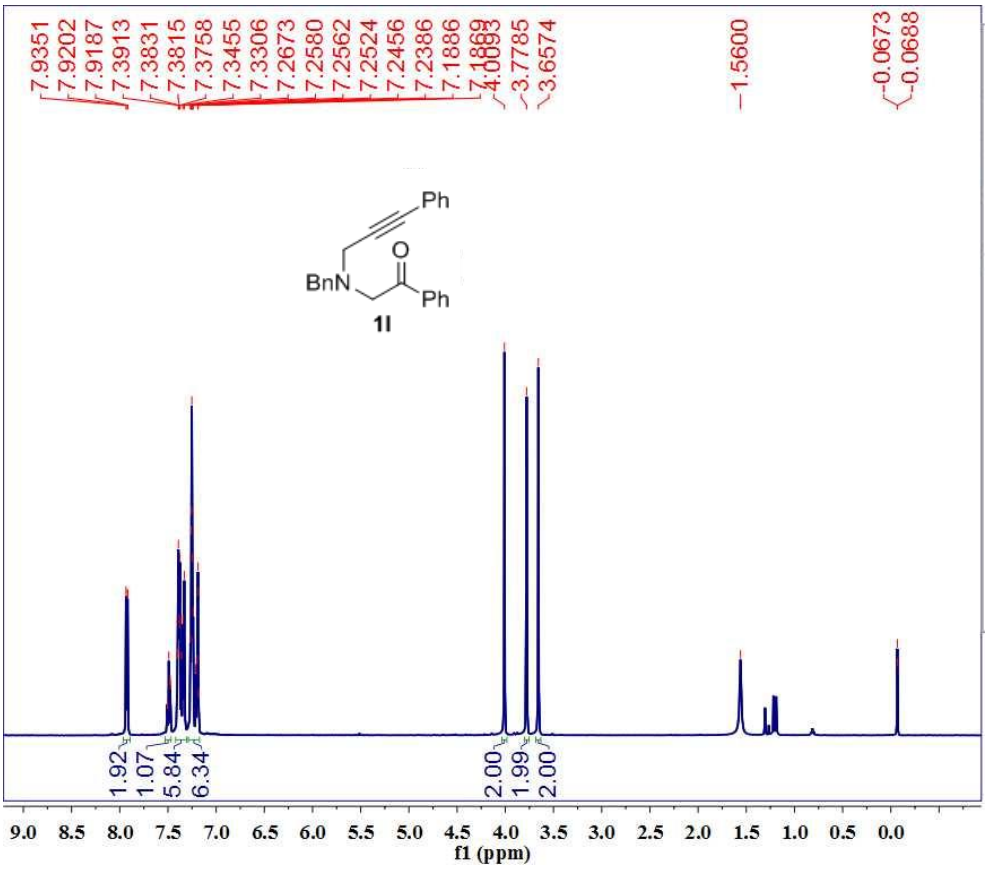

**Supplementary Figure 45.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1j**

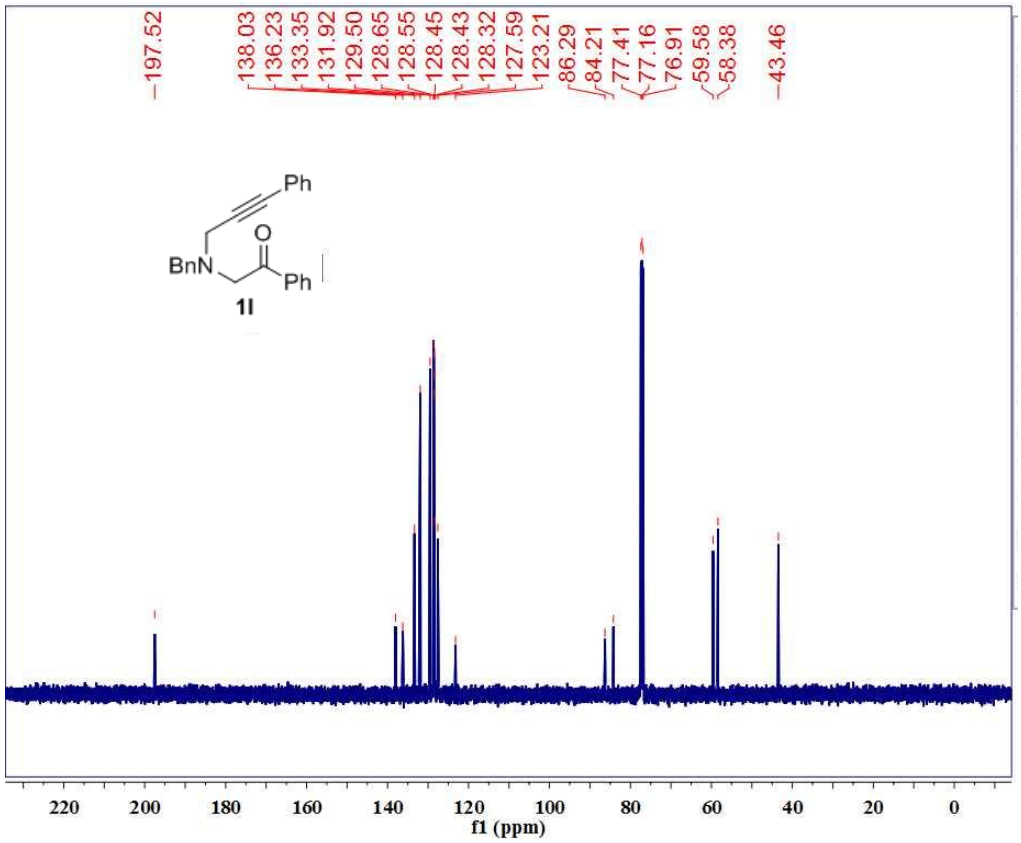



**Supplementary Figure 46.** $^{1}H$ and $^{13}C$ NMR spectra for compound **S10**

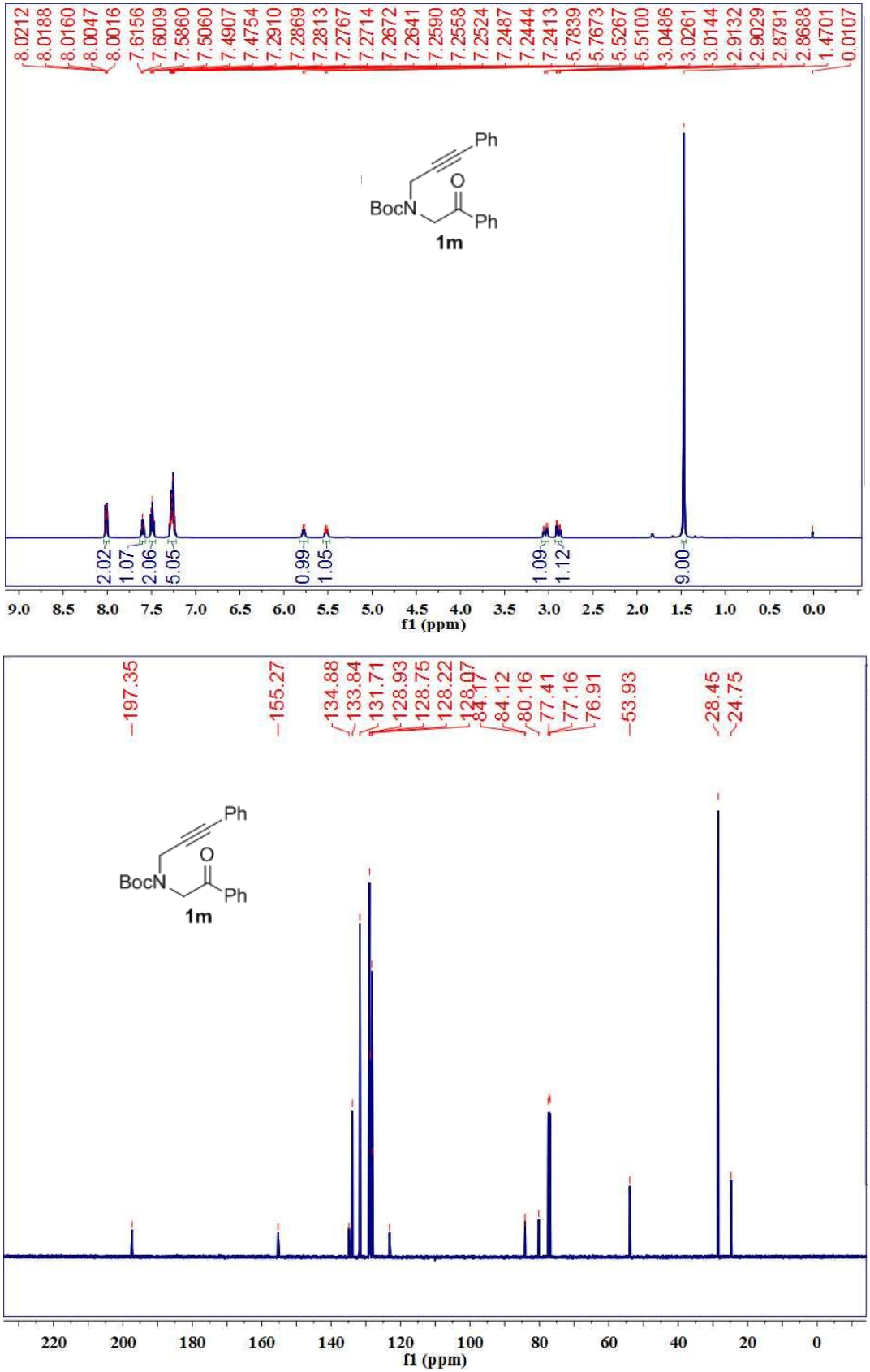



**Supplementary Figure 47.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1k**

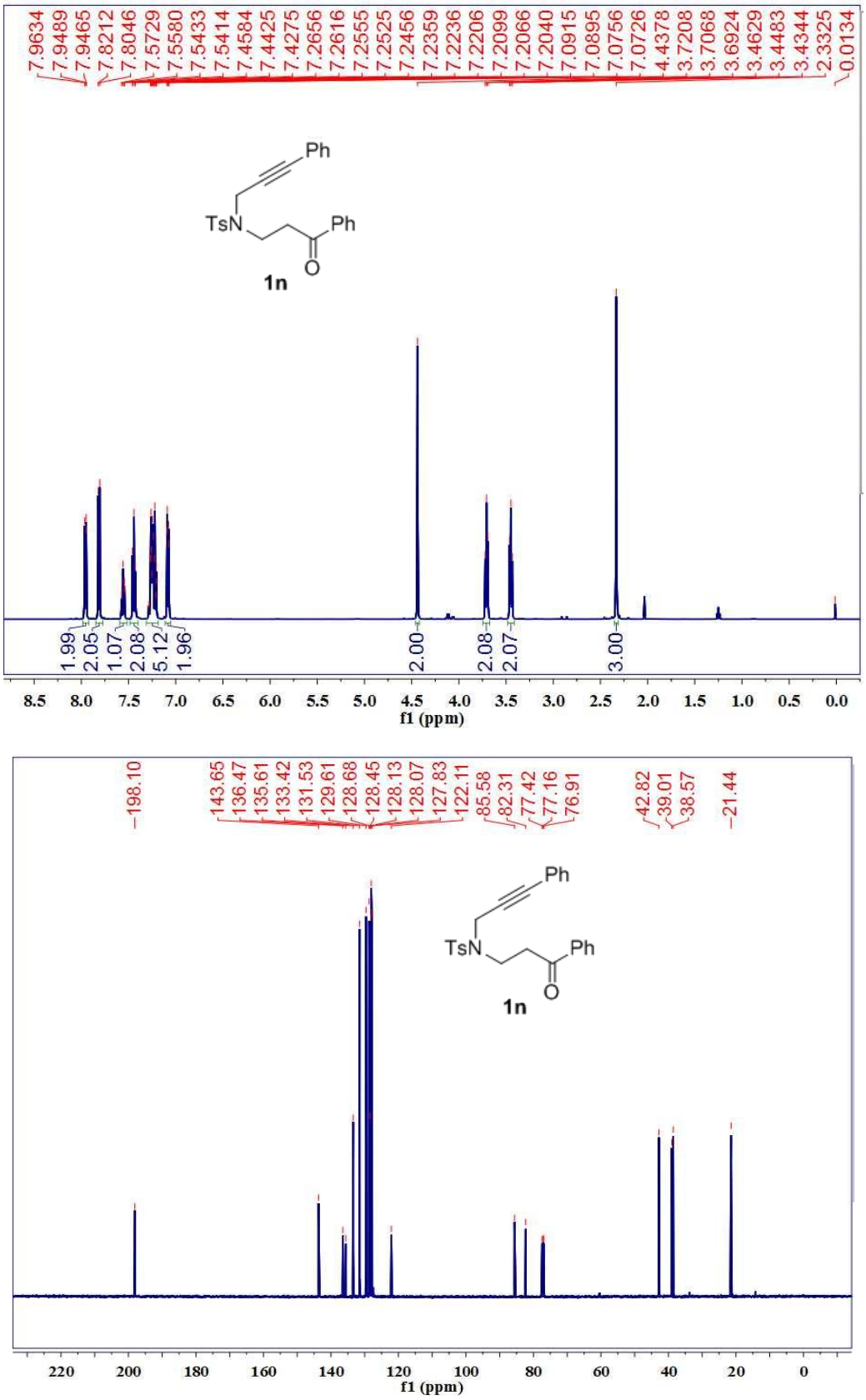


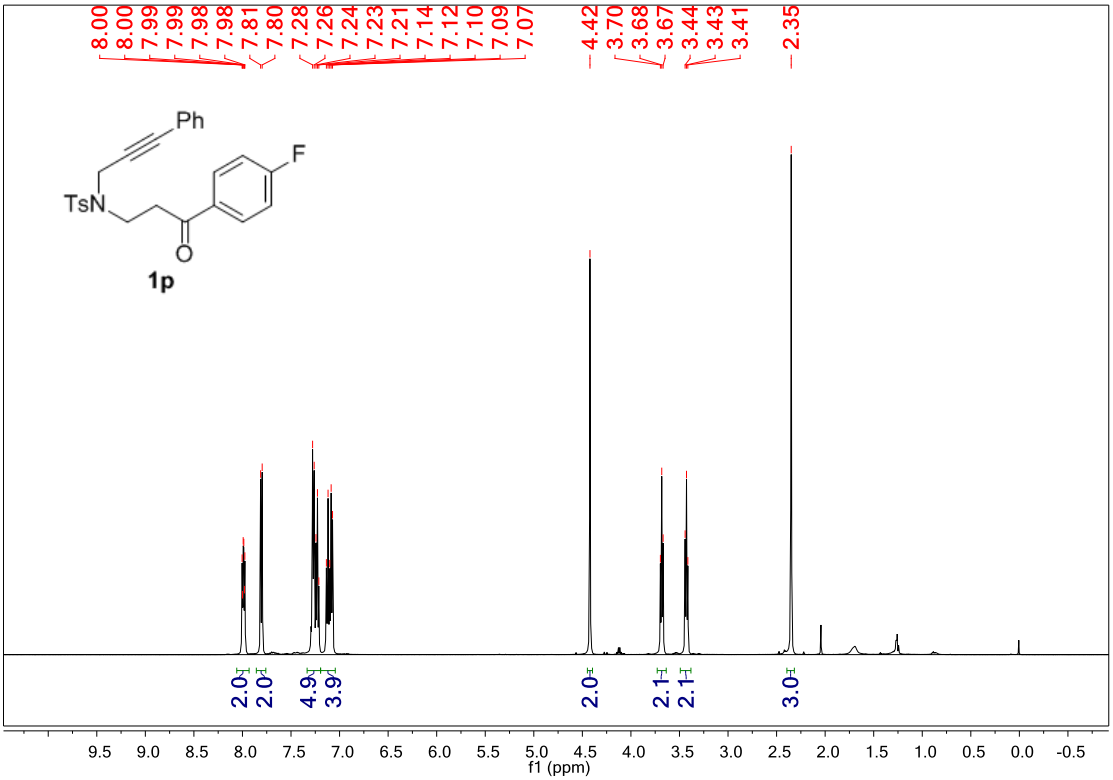

**Supplementary Figure 48.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1l**

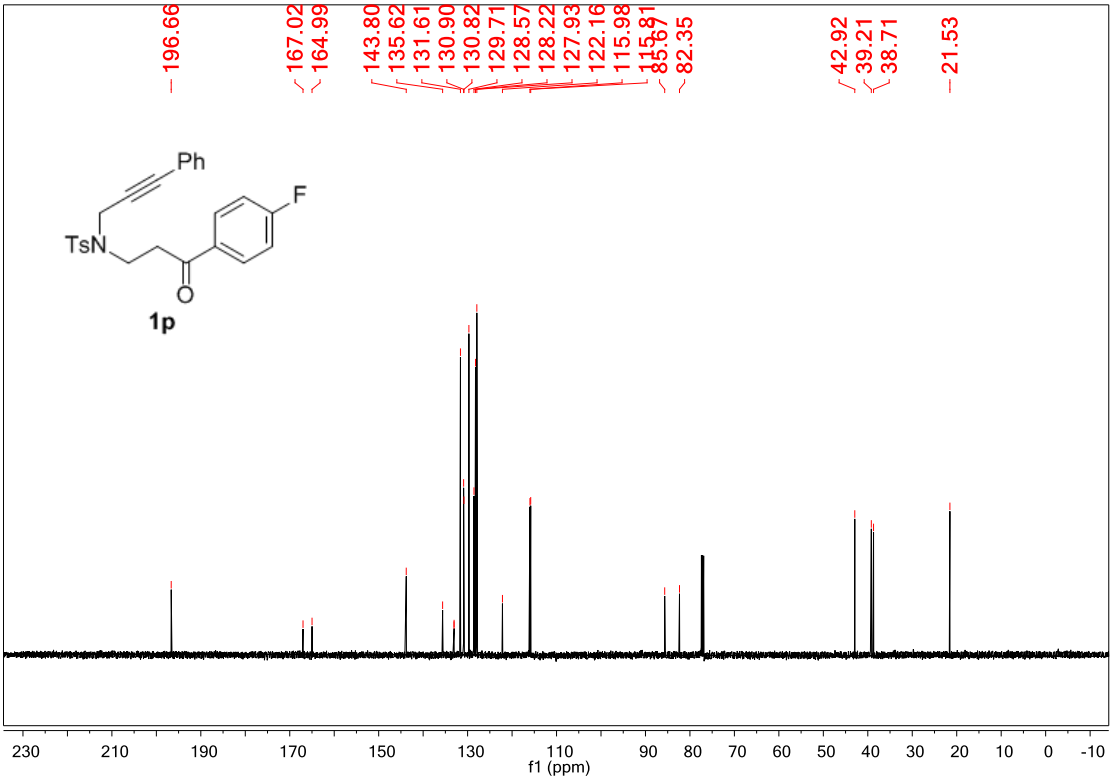


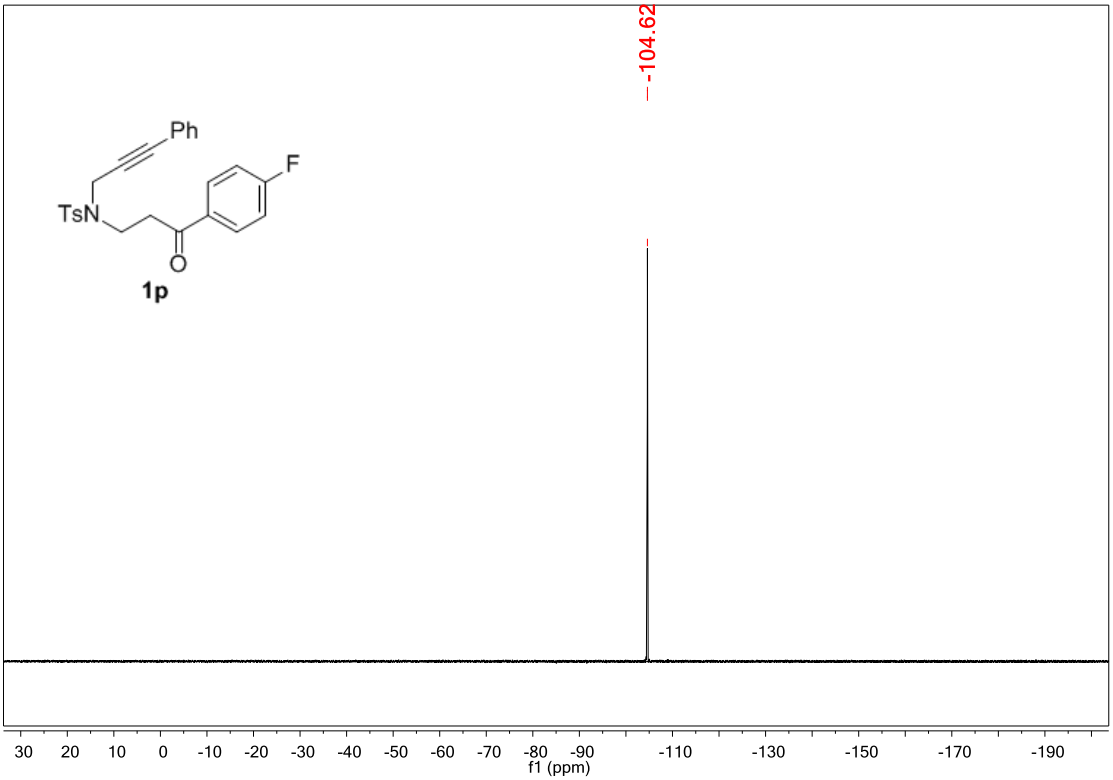

**Supplementary Figure 49.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1m**



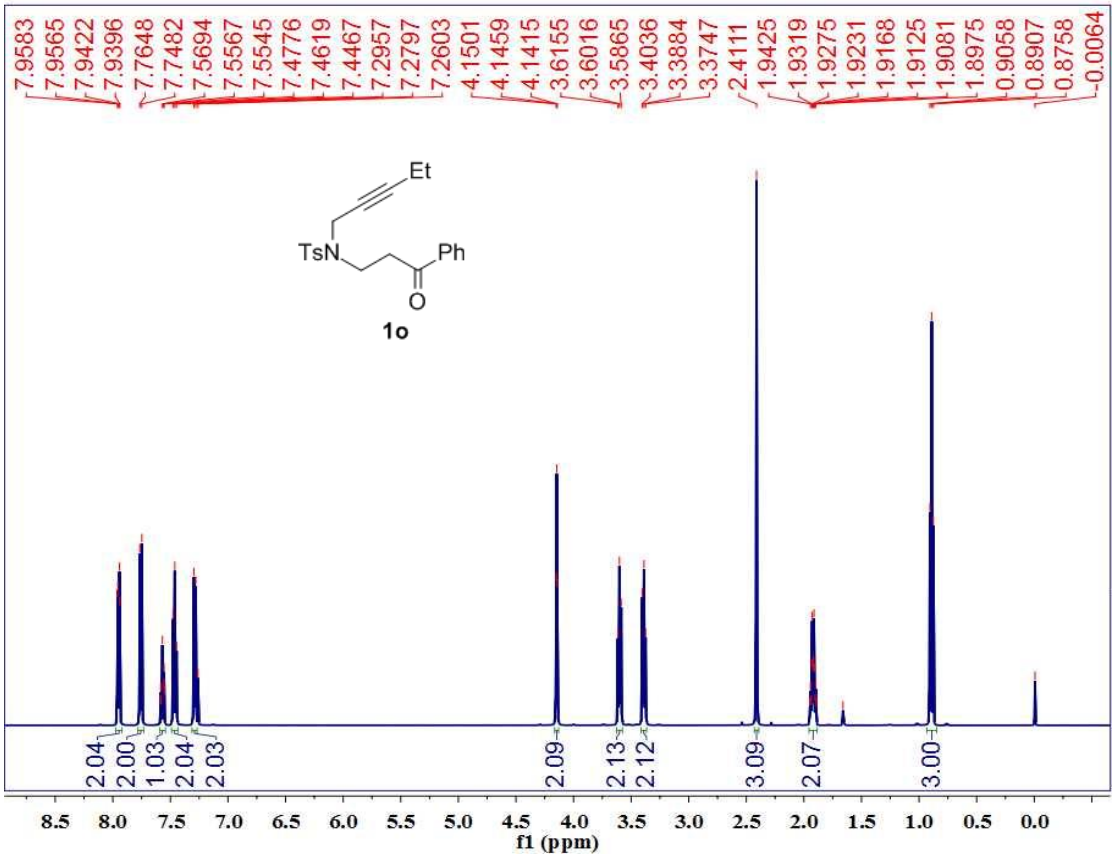

**Supplementary Figure 50.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1n**

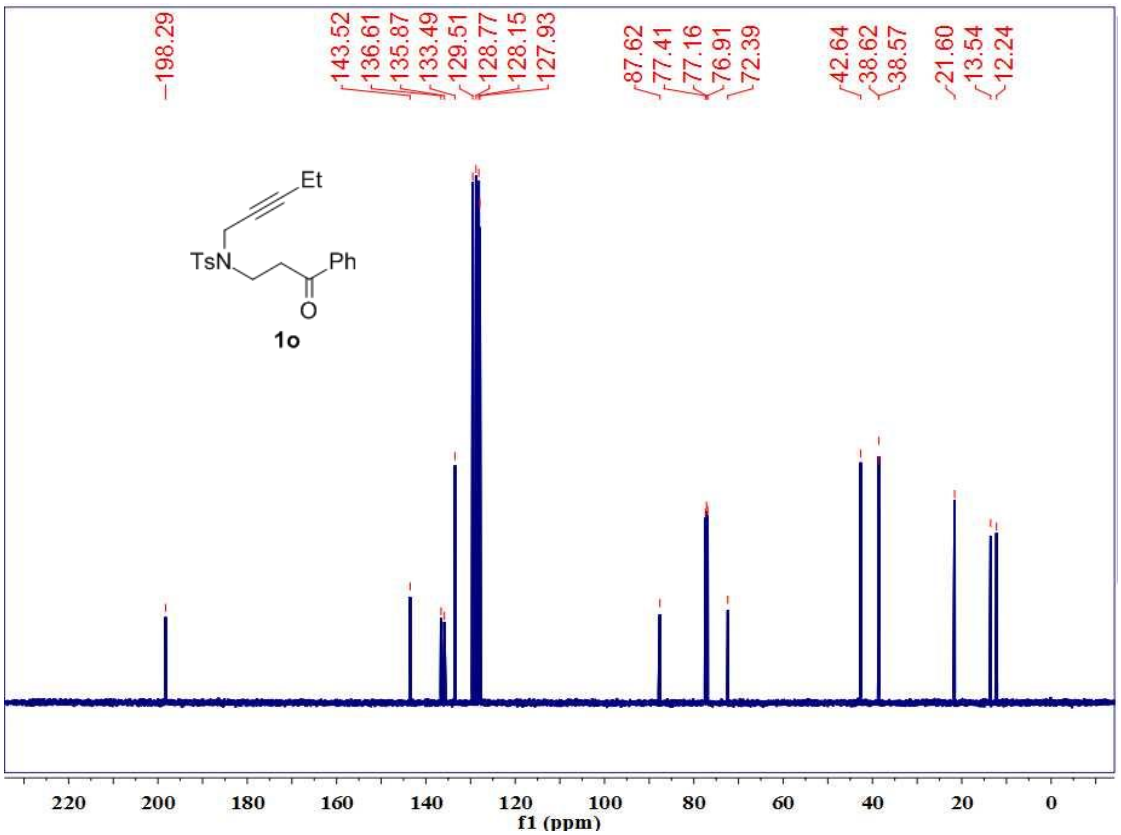

8.00
8.00
7.99
7.99
7.98
7.98
7.81
7.80
7.28
7.26
7.24
7.23
7.21
7.14
7.12
7.10
7.09
7.07
4.42
3.70
3.68
3.67
3.44
3.43
3.41
2.35
Ph
F
TsN
O
1p
2.0
2.0
4.9
3.9
2.0
2.1
2.1
3.0
f1 (ppm)


196.66
167.02
164.99
143.80
135.62
131.61
130.90
130.82
129.71
128.57
128.22
127.93
122.16
115.98
115.81
85.67
82.35
42.92
39.21
38.71
21.53
Ph
F
TsN
O
1p
f1 (ppm)

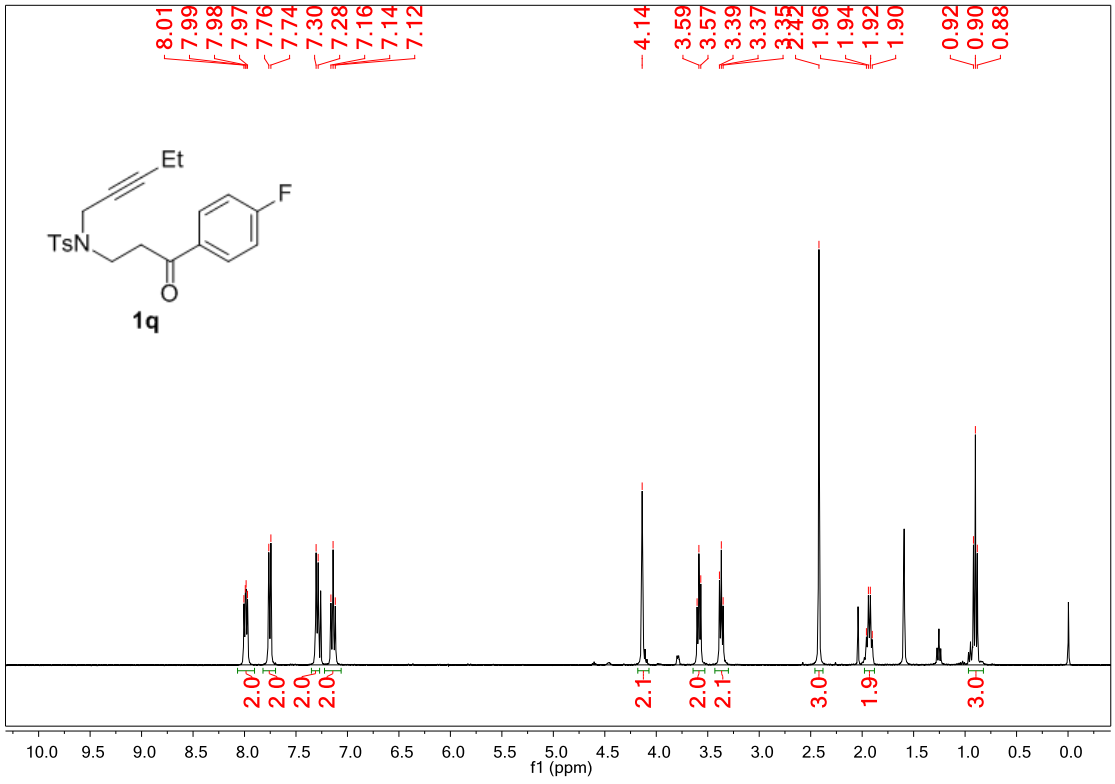


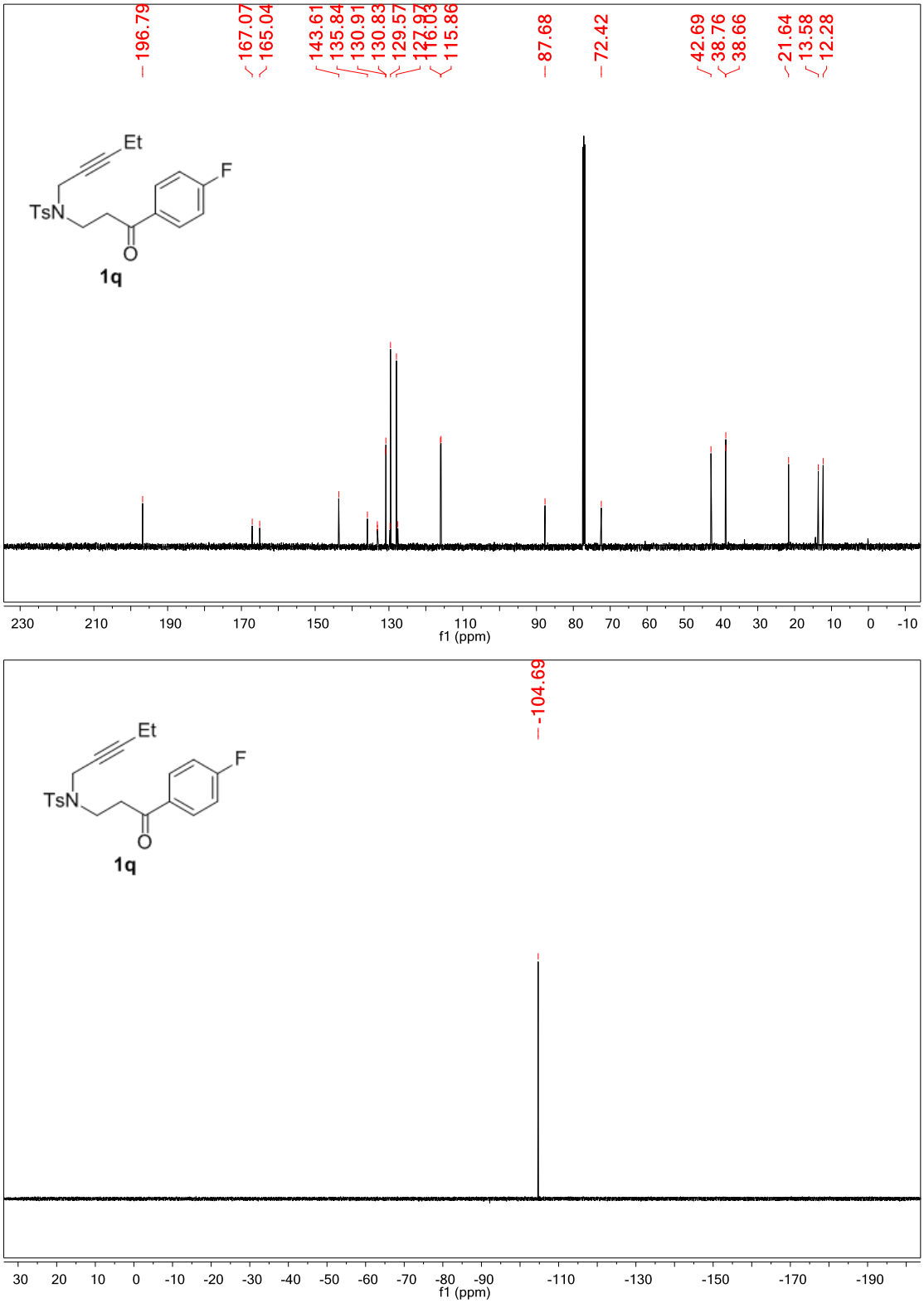

**Supplementary Figure 51.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **1p**



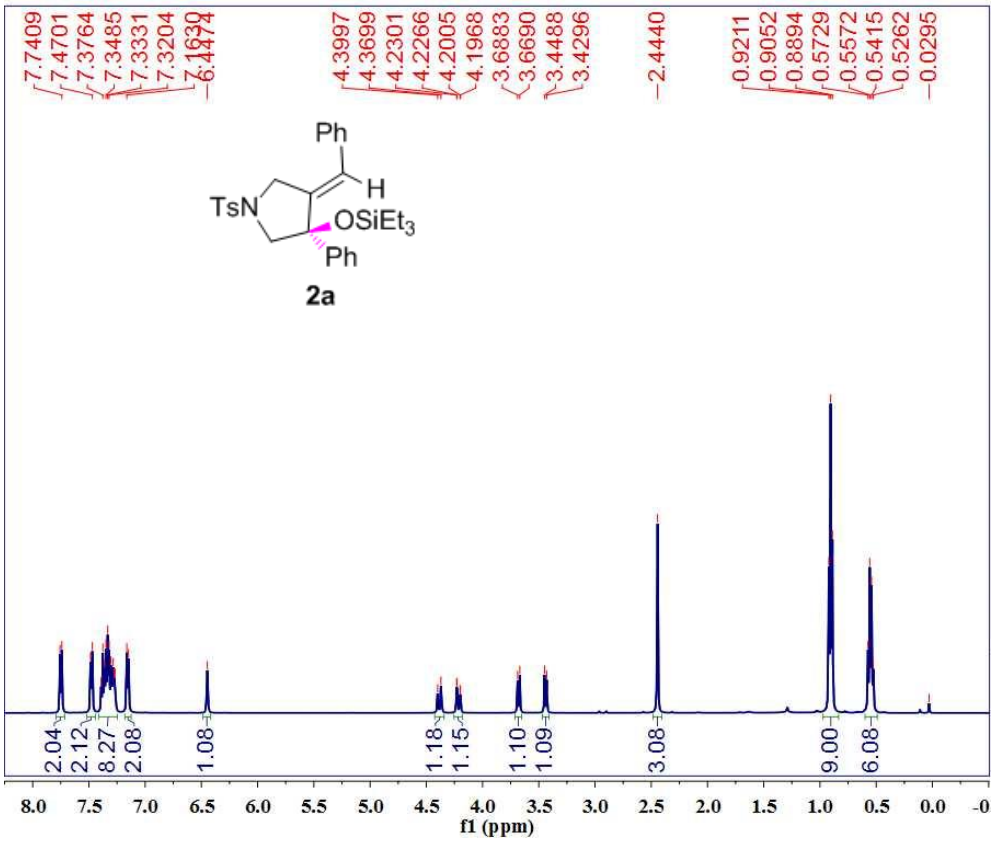


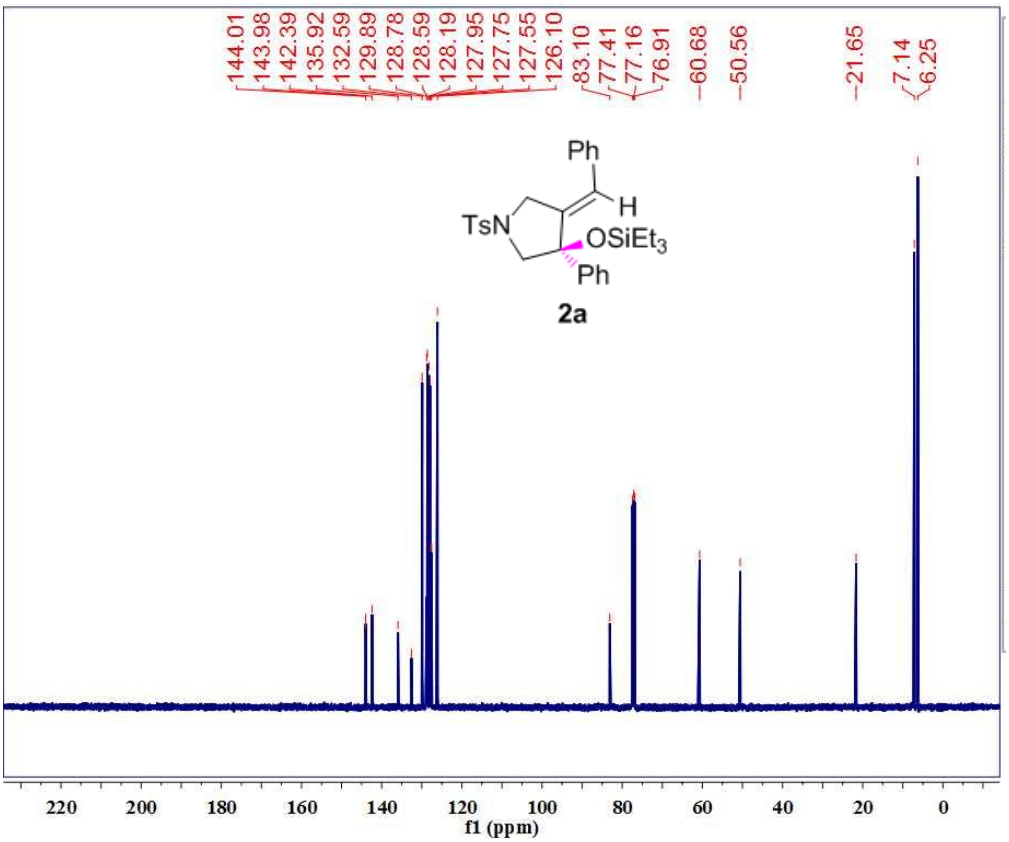

**Supplementary Figure 52.** $^{1}H$ and $^{13}C$ NMR spectra for compound **1o**



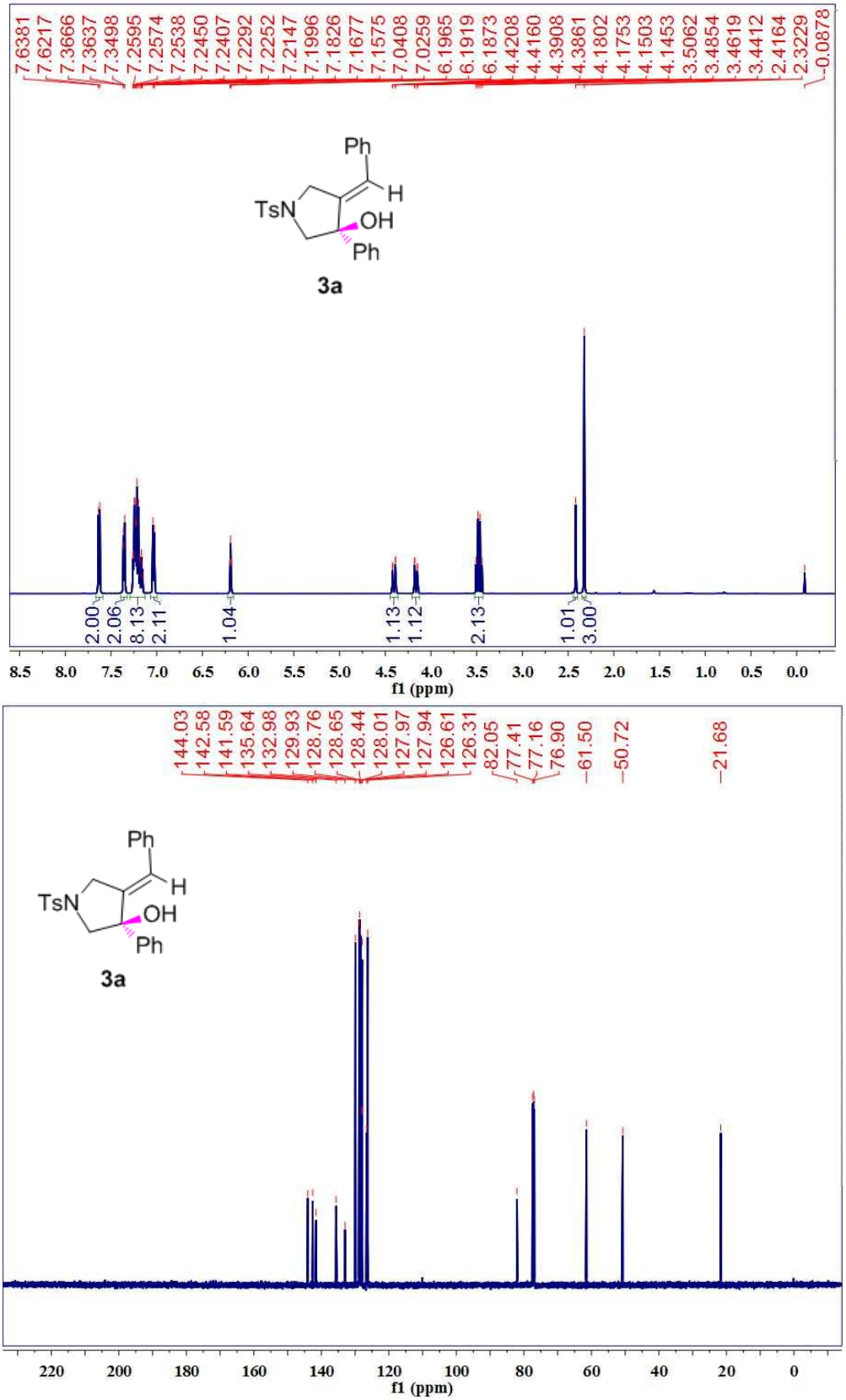



**Supplementary Figure 53.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **1q**

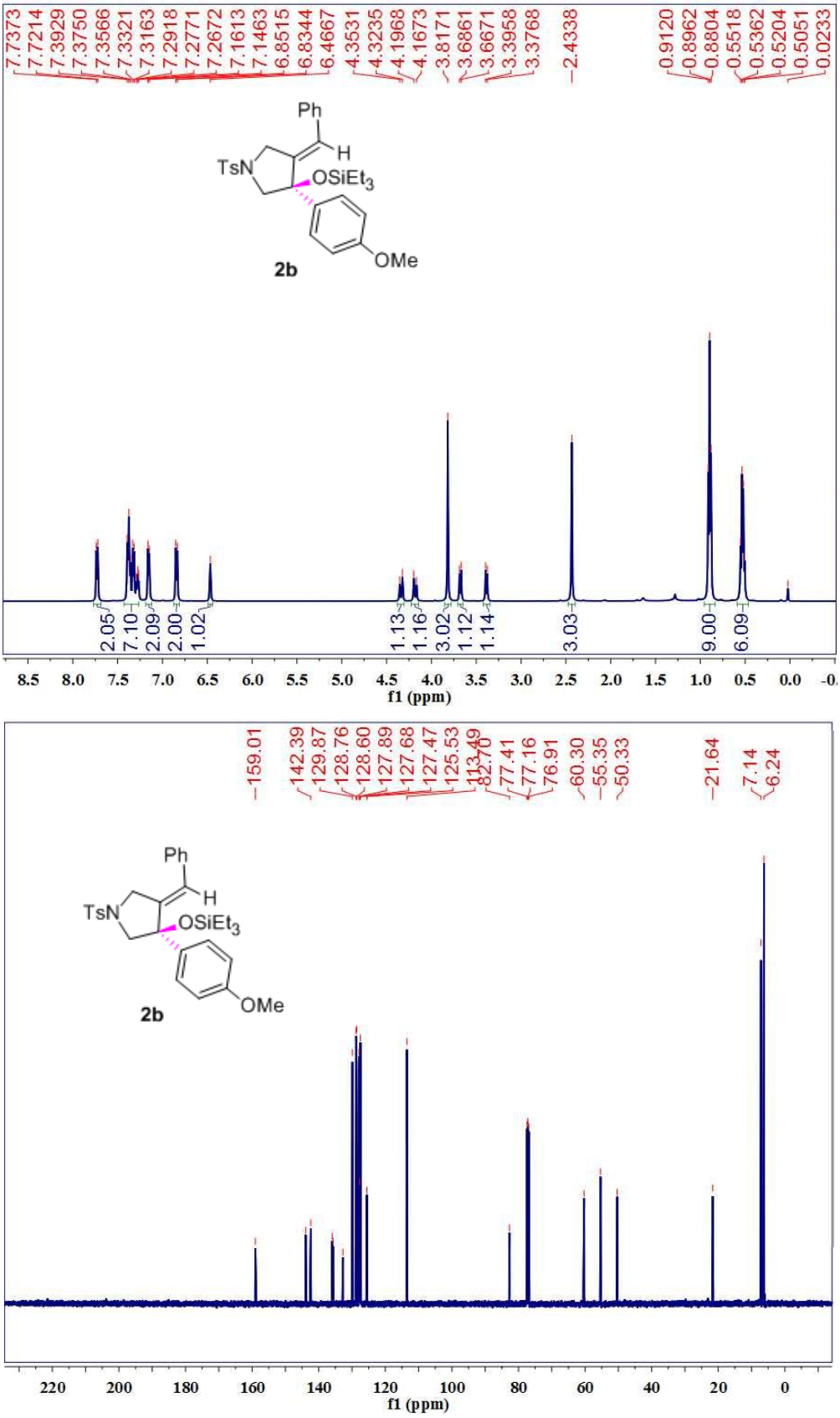


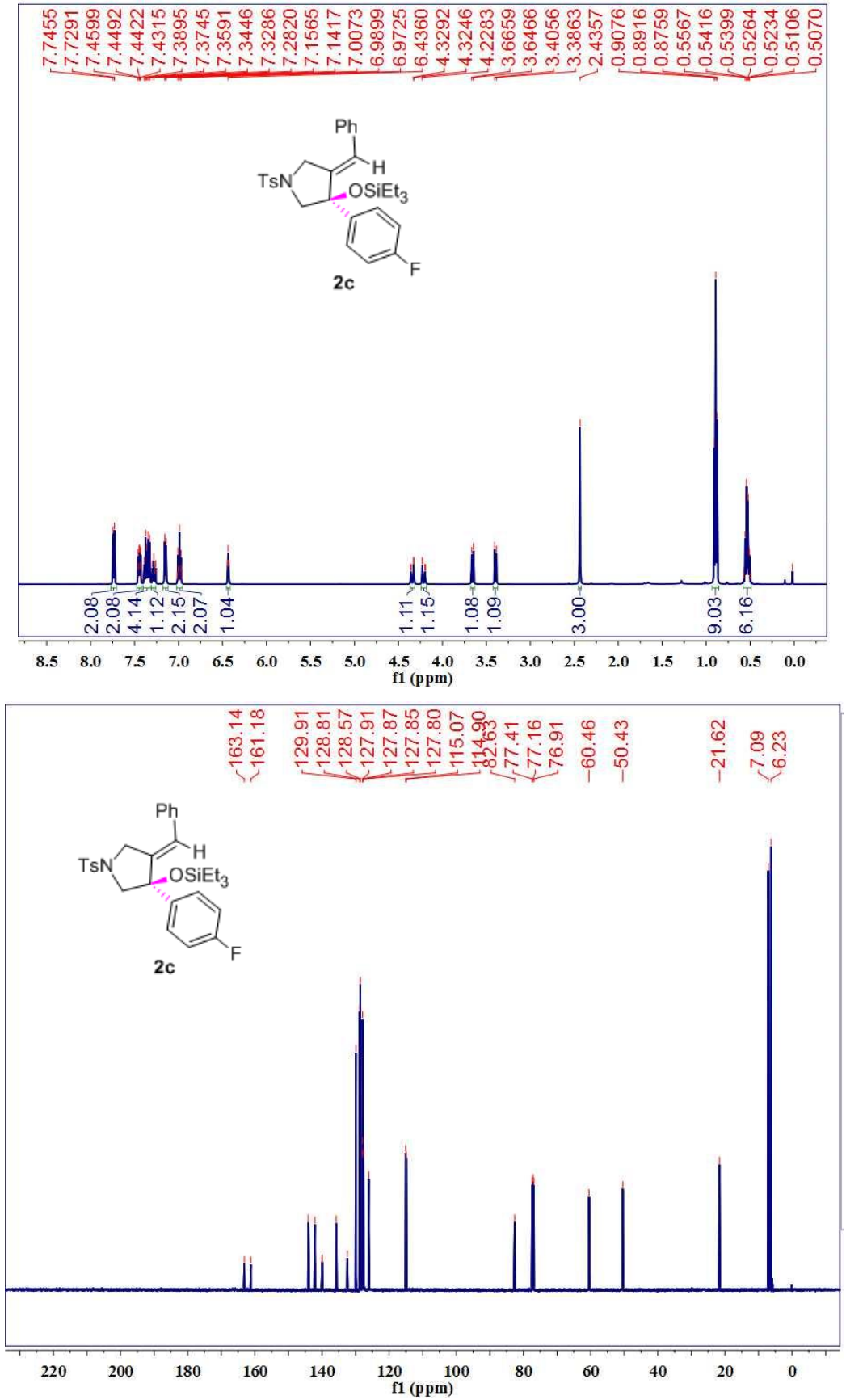

**Supplementary Figure 54.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2a**



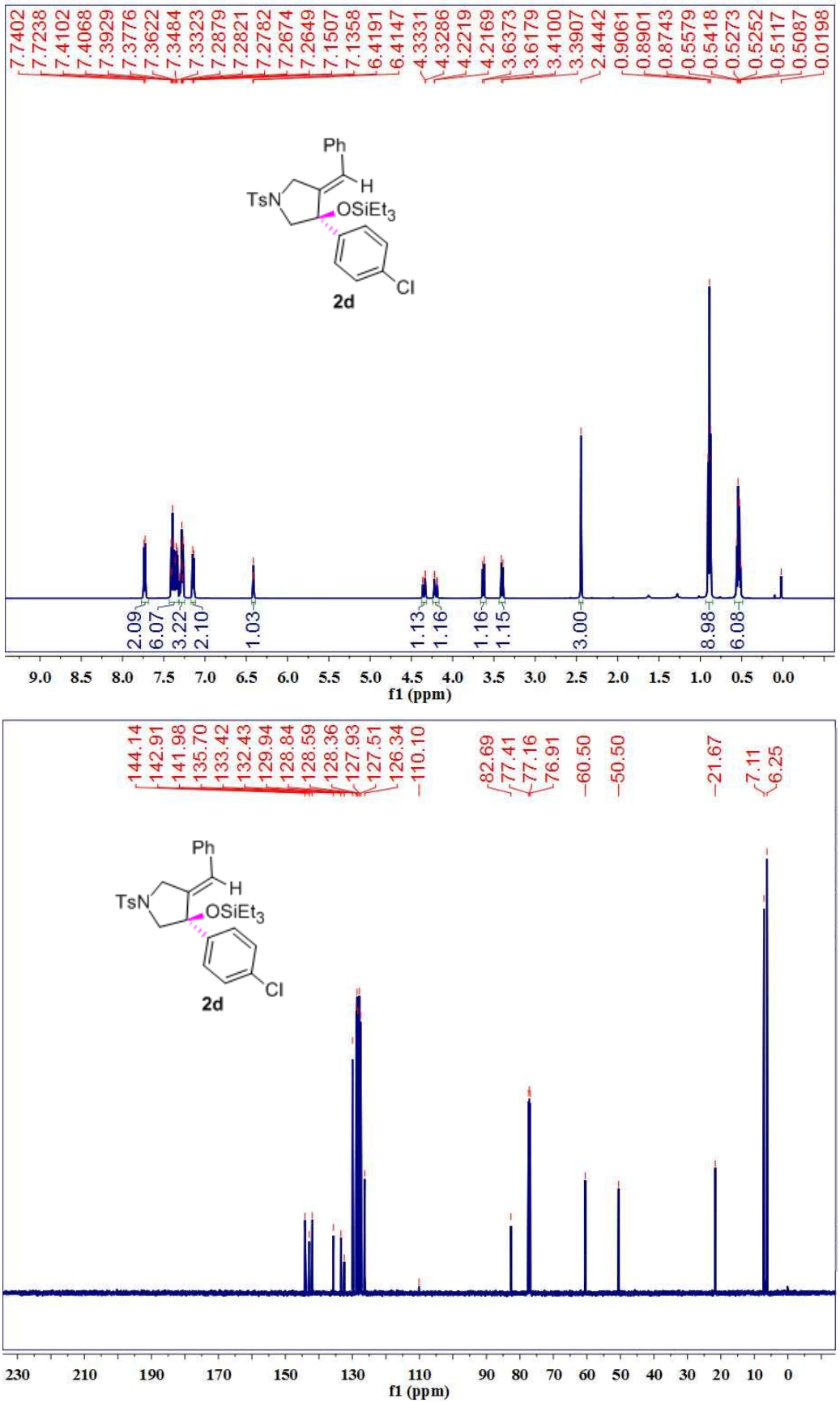

**Supplementary Figure 55.** $^{1}H$ and $^{13}C$ NMR spectra for compound **3a**



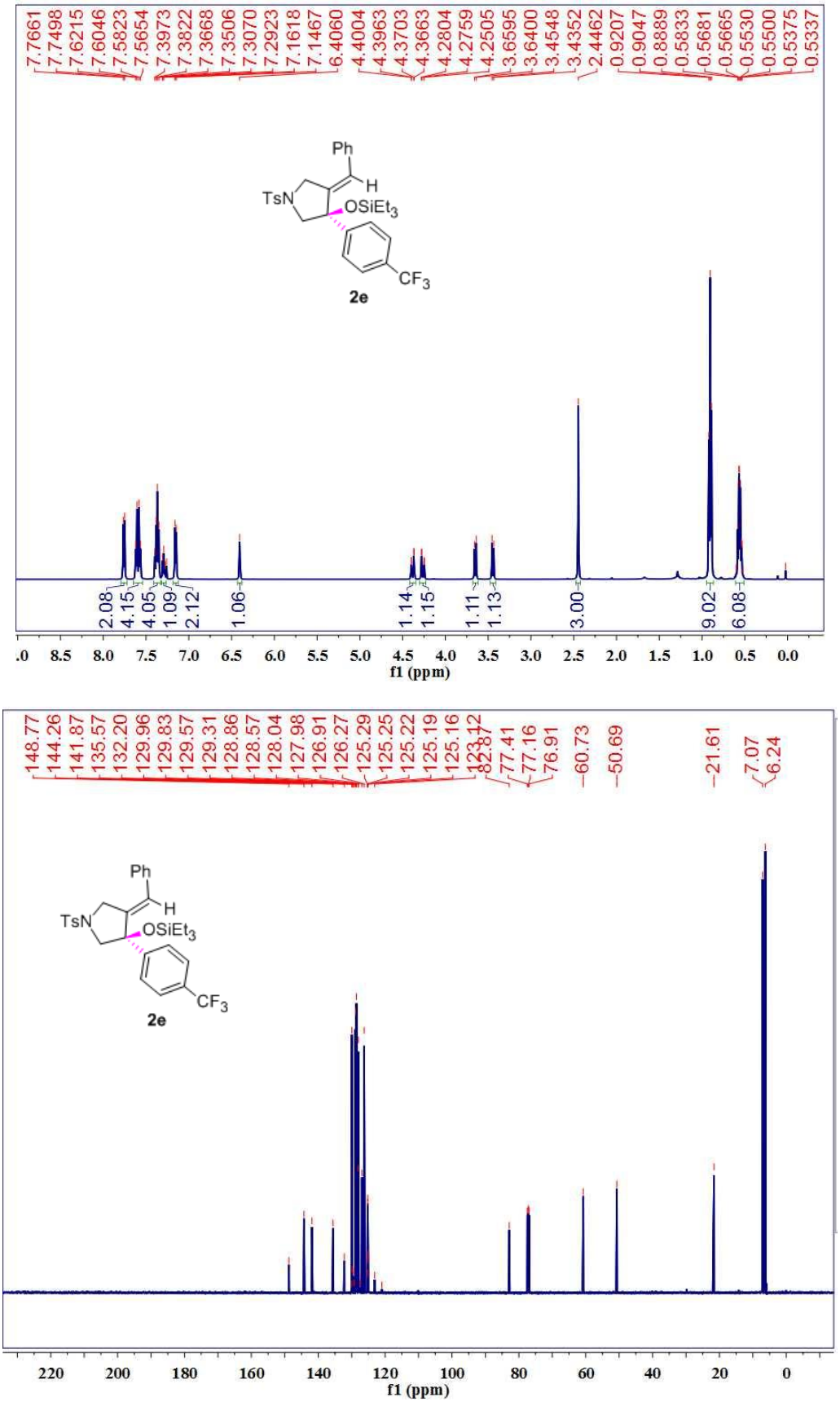

**Supplementary Figure 56.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2b**



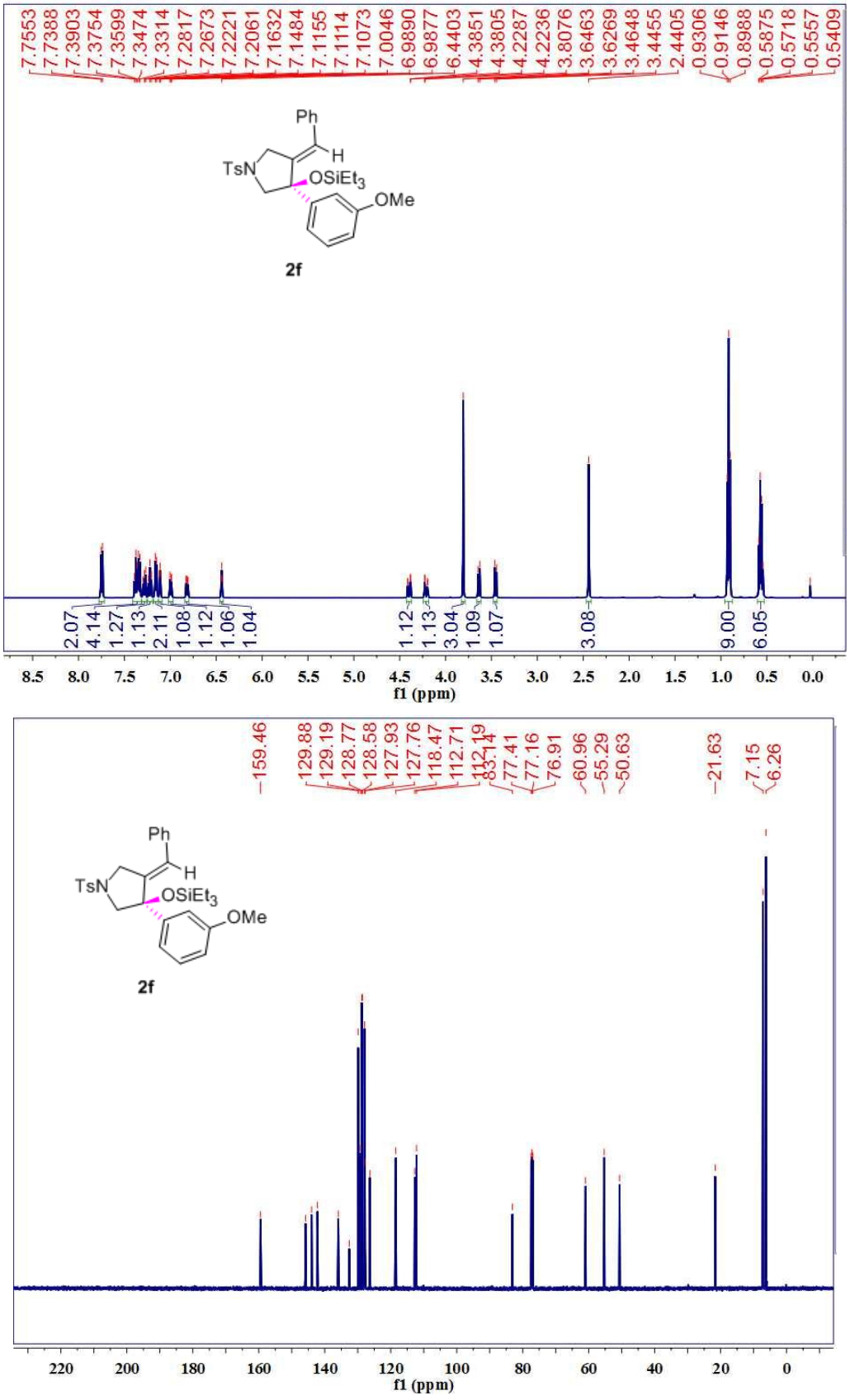

**Supplementary Figure 57.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2c**



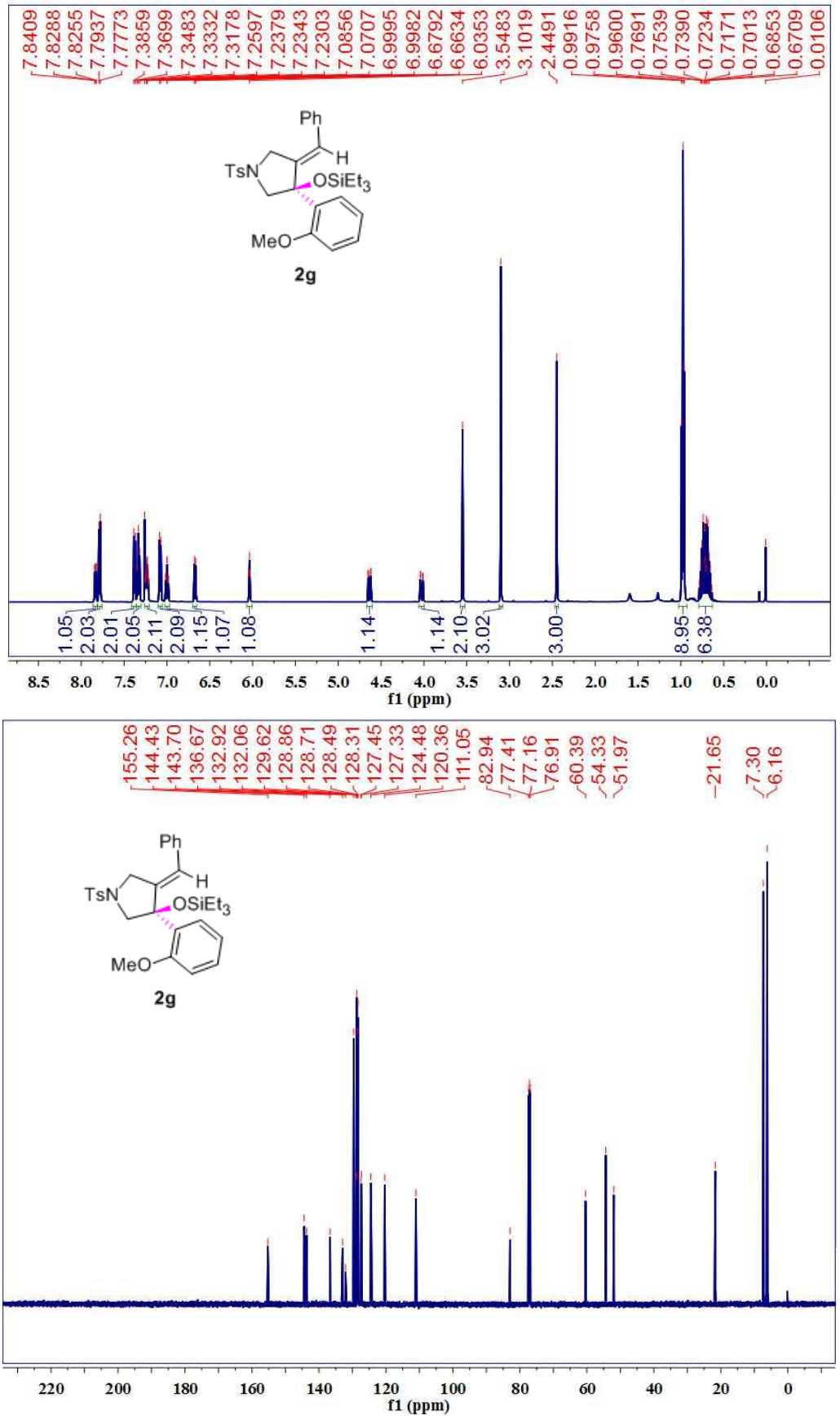

**Supplementary Figure 58.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2d**



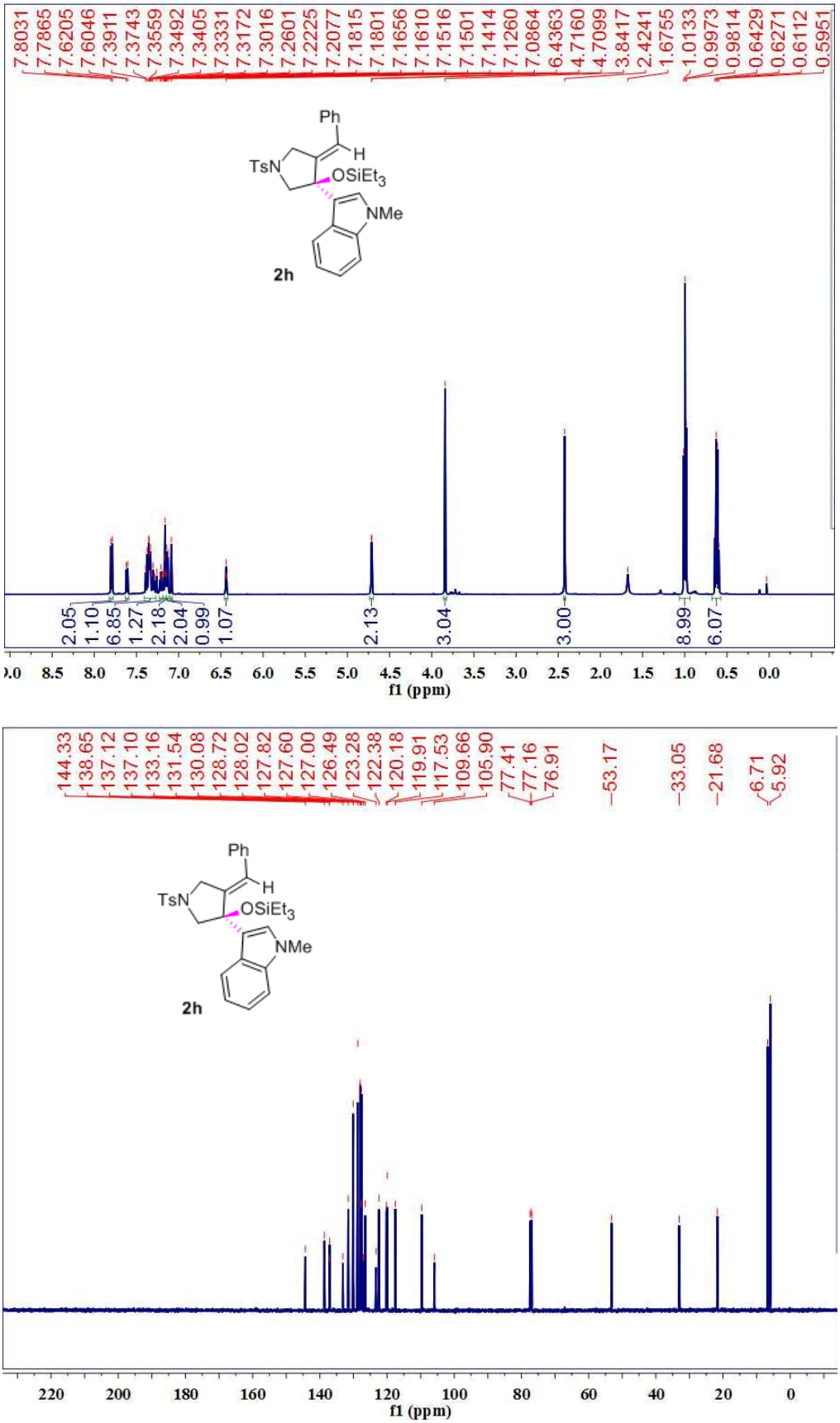

**Supplementary Figure 59.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2e**



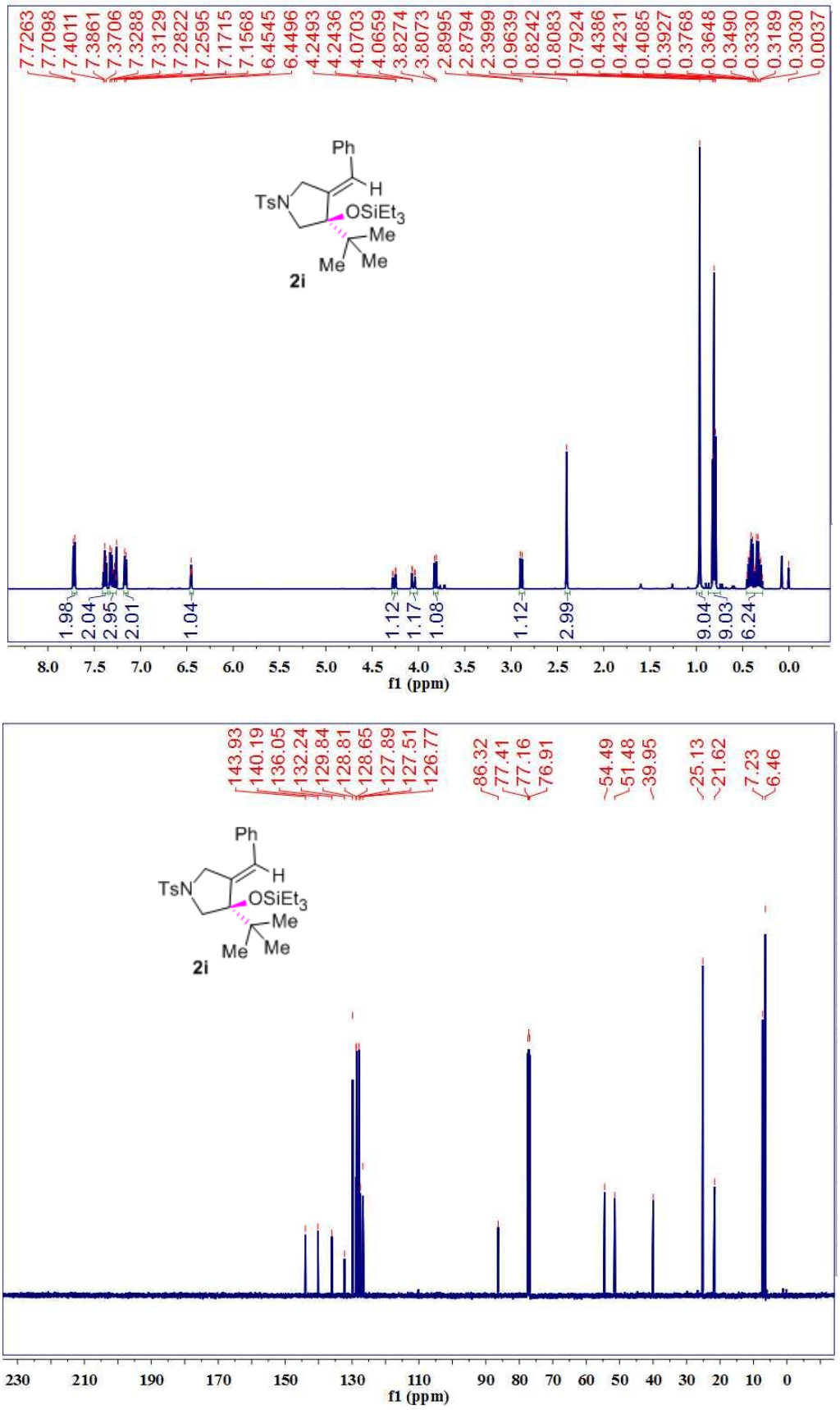

**Supplementary Figure 60.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2f**



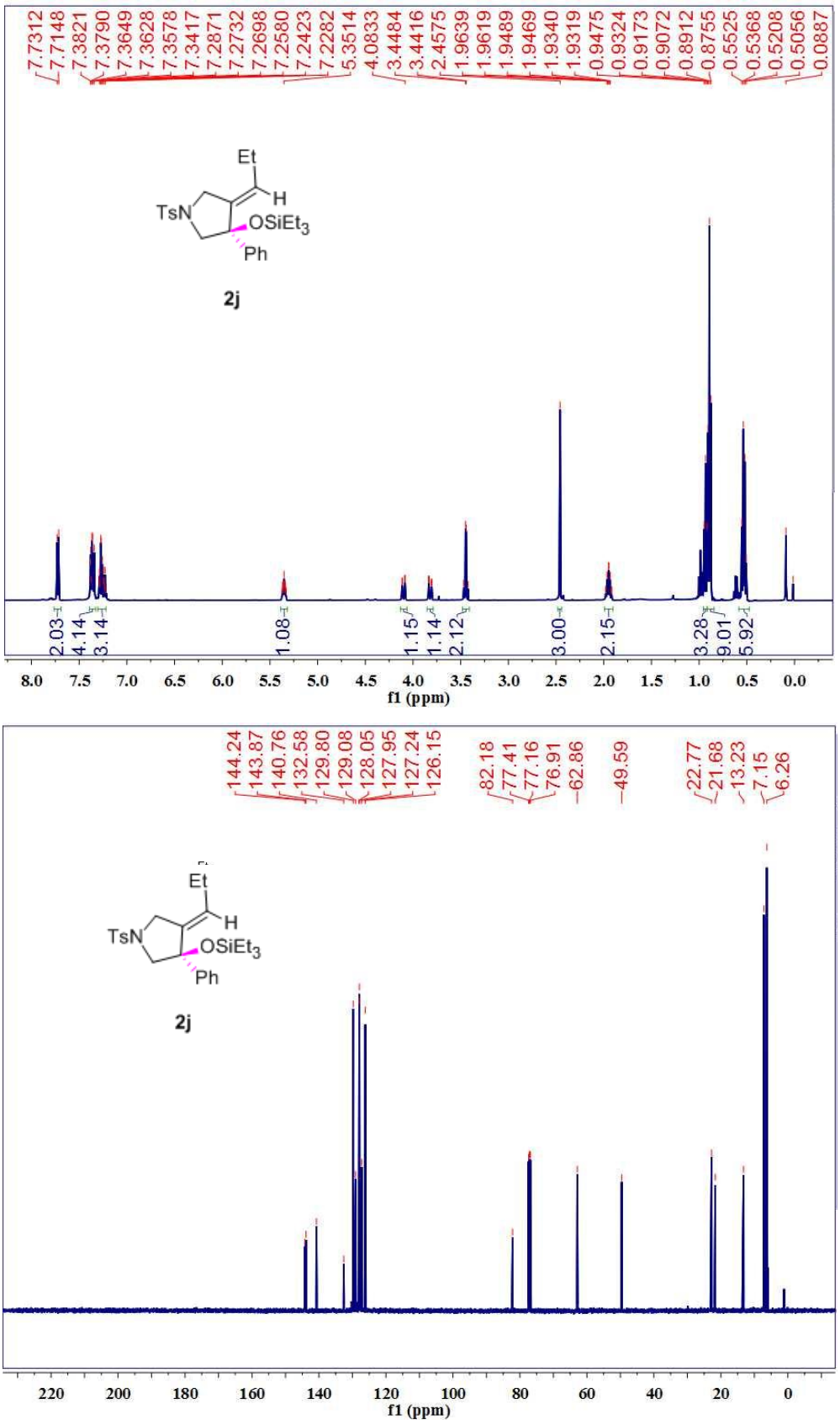

**Supplementary Figure 61.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2g**



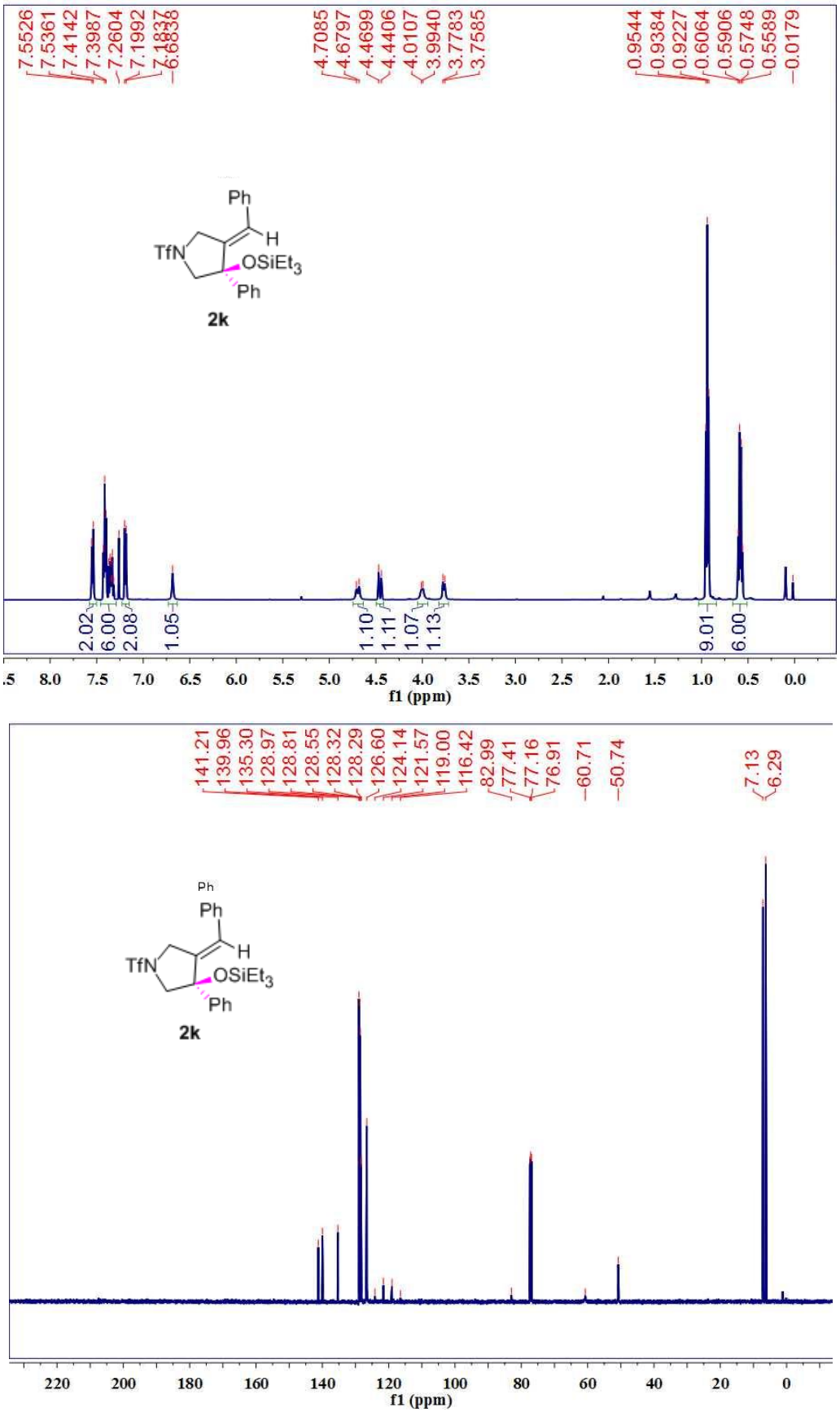

**Supplementary Figure 62.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2h**



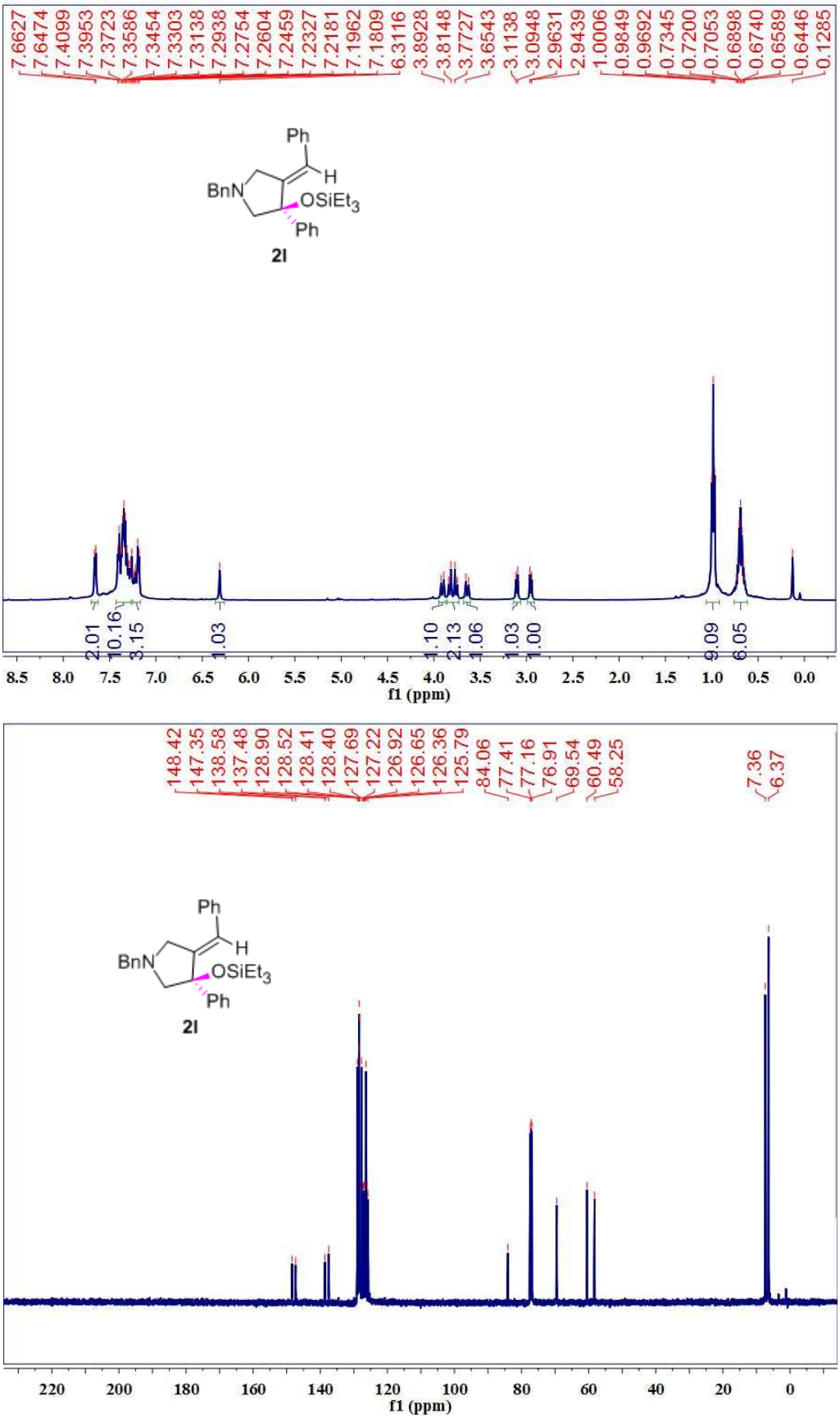

**Supplementary Figure 63.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2i**



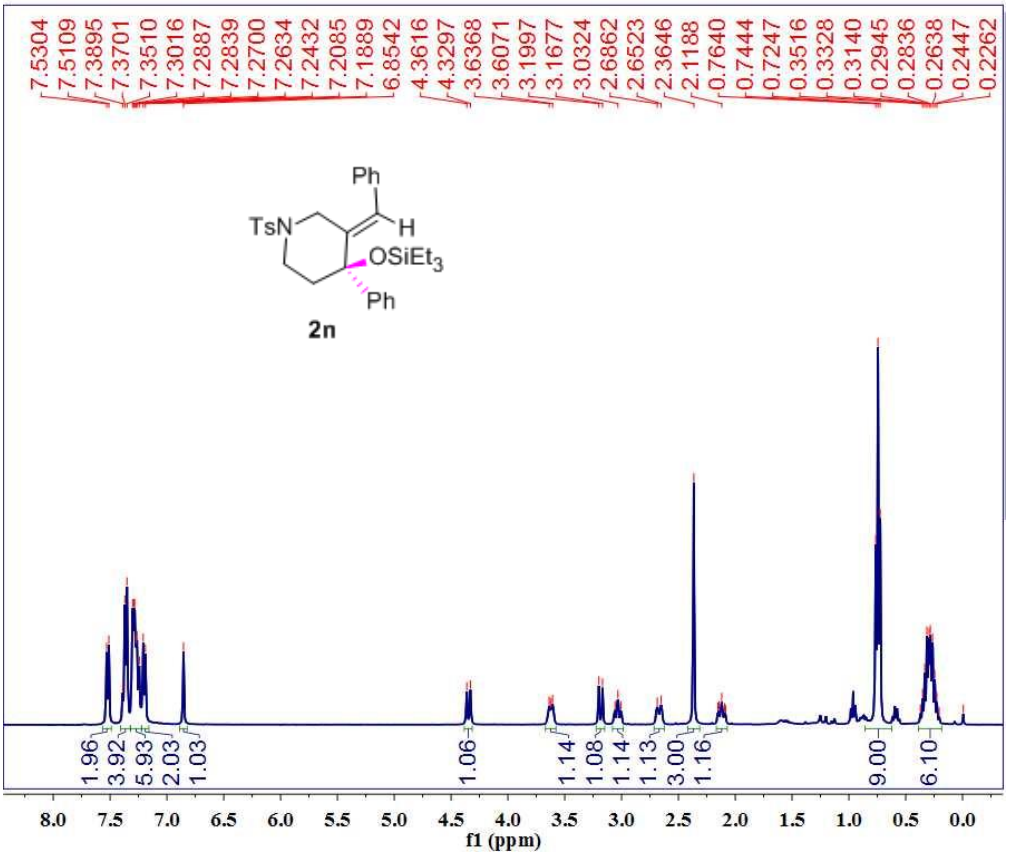

**Supplementary Figure 64.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2j**

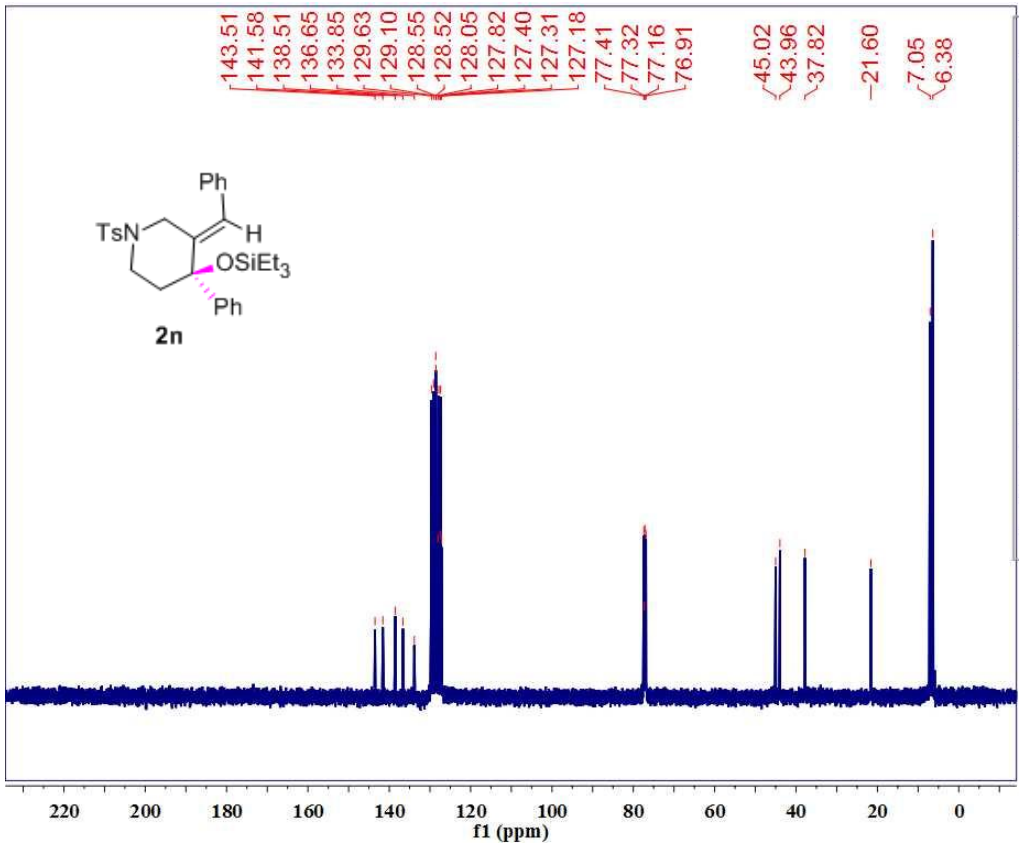



**Supplementary Figure 65.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2k**

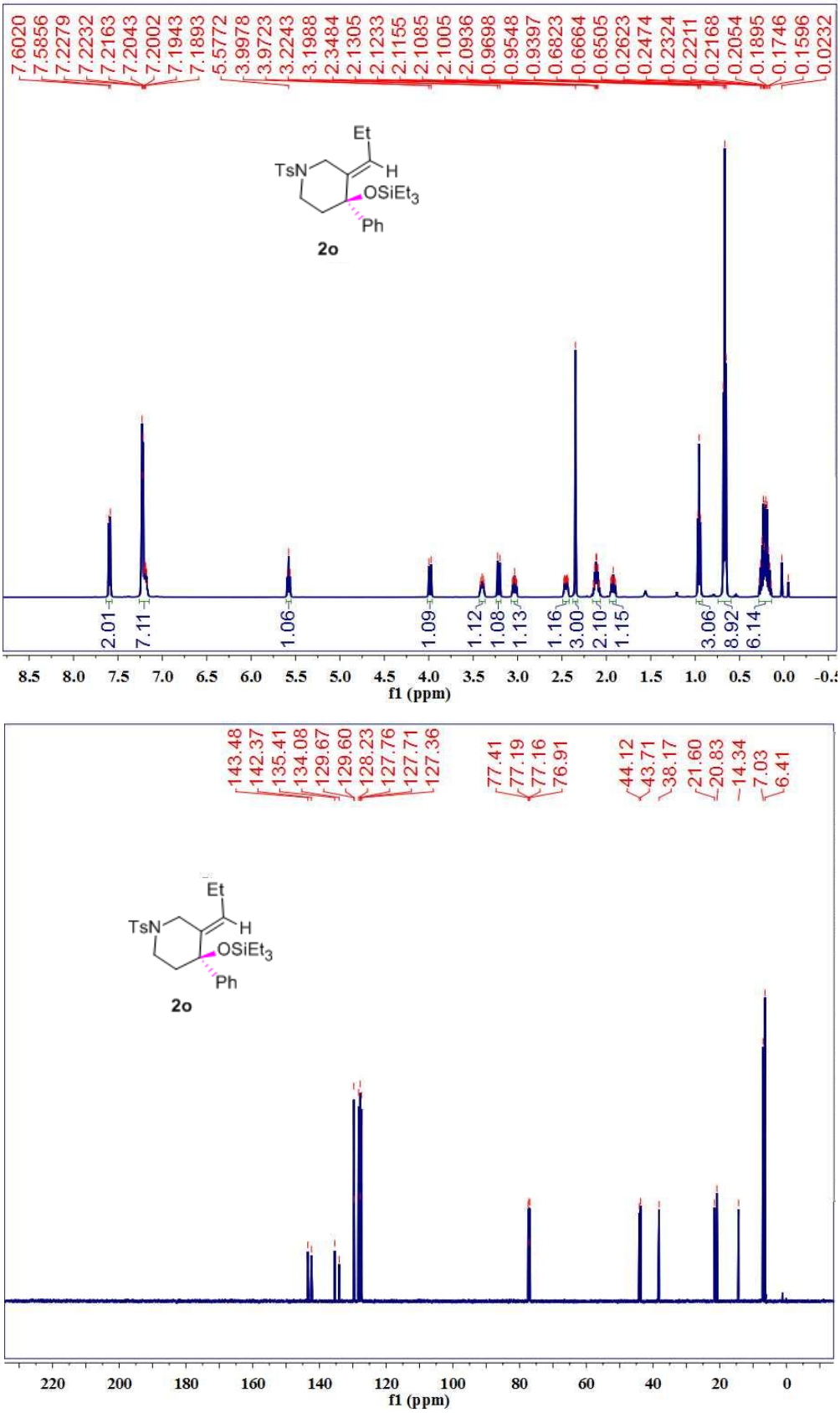



**Supplementary Figure 66.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2l**

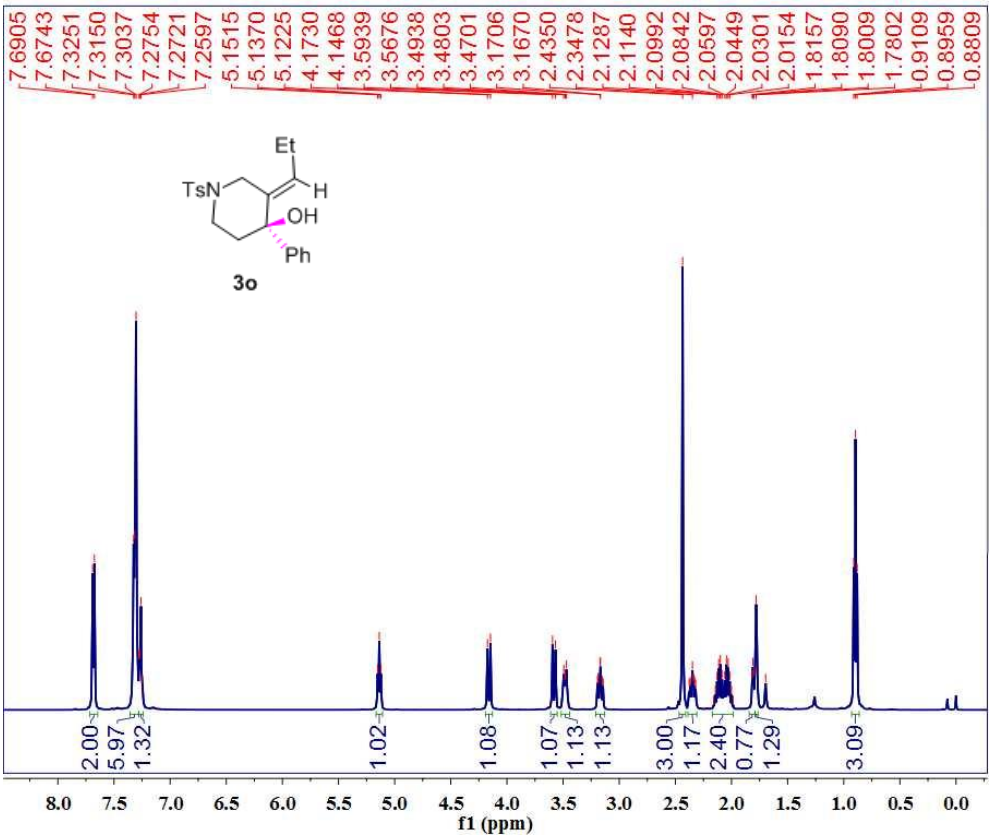


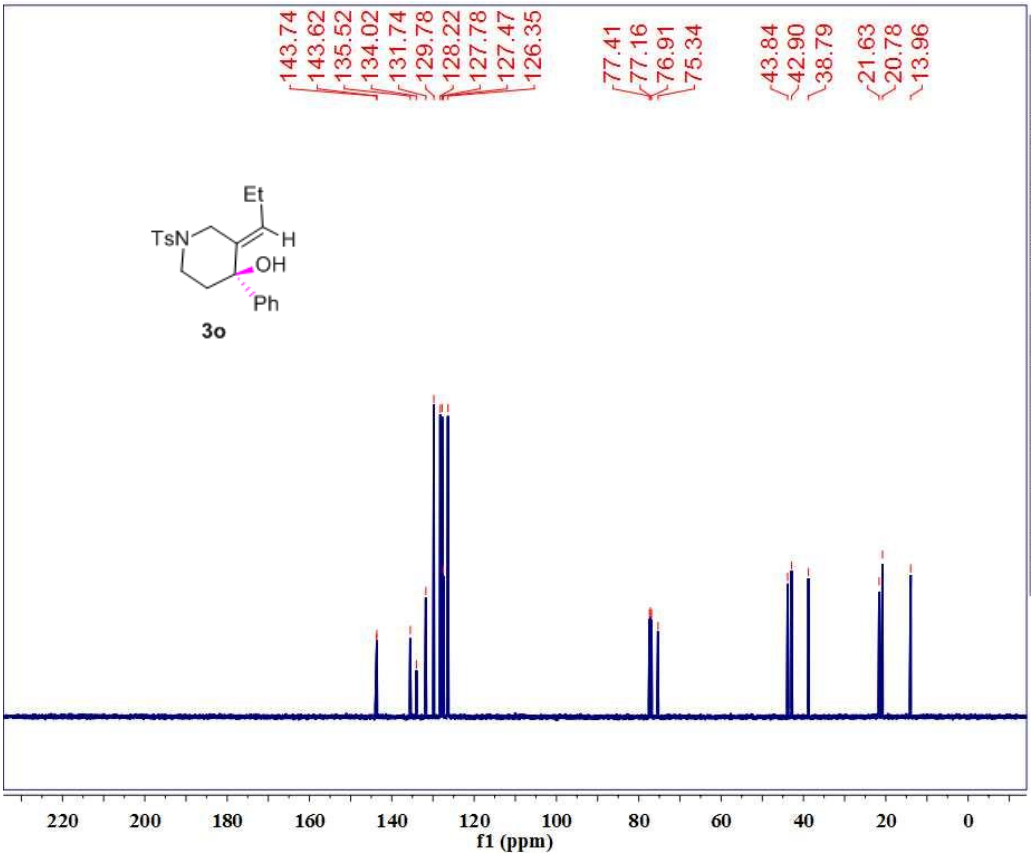




**Supplementary Figure 67.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2n**

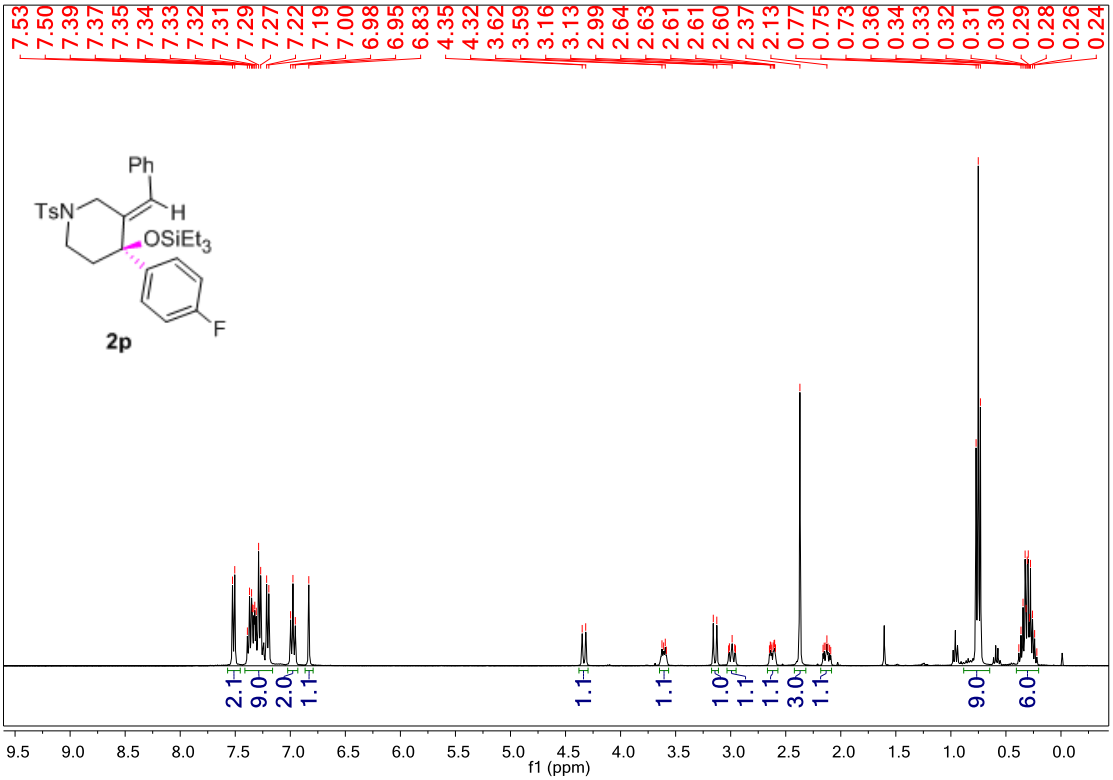


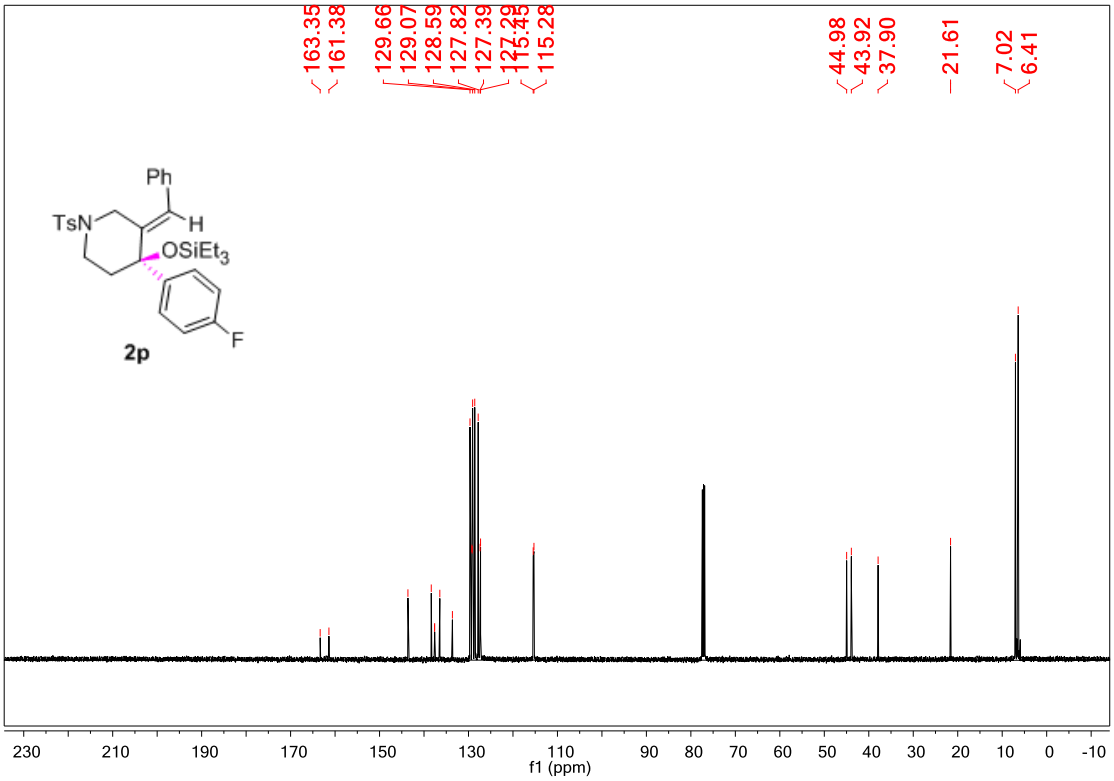

**Supplementary Figure 68.** $^{1}H$ and $^{13}C$ NMR spectra for compound **2o**

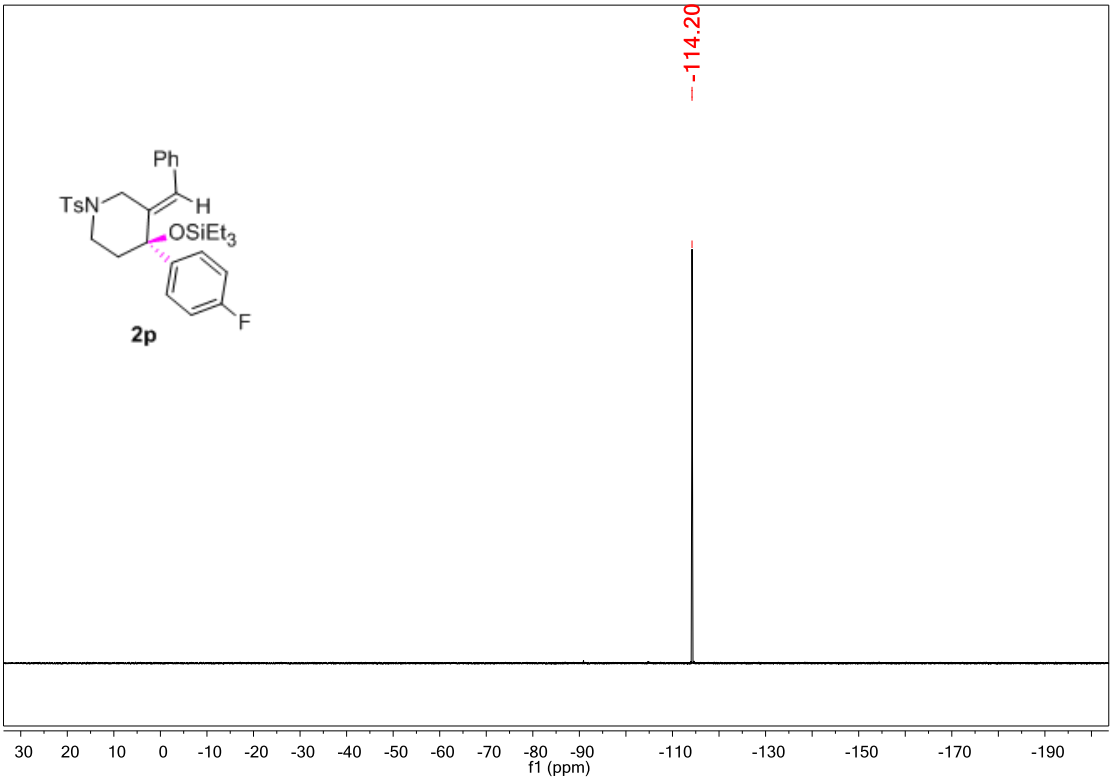


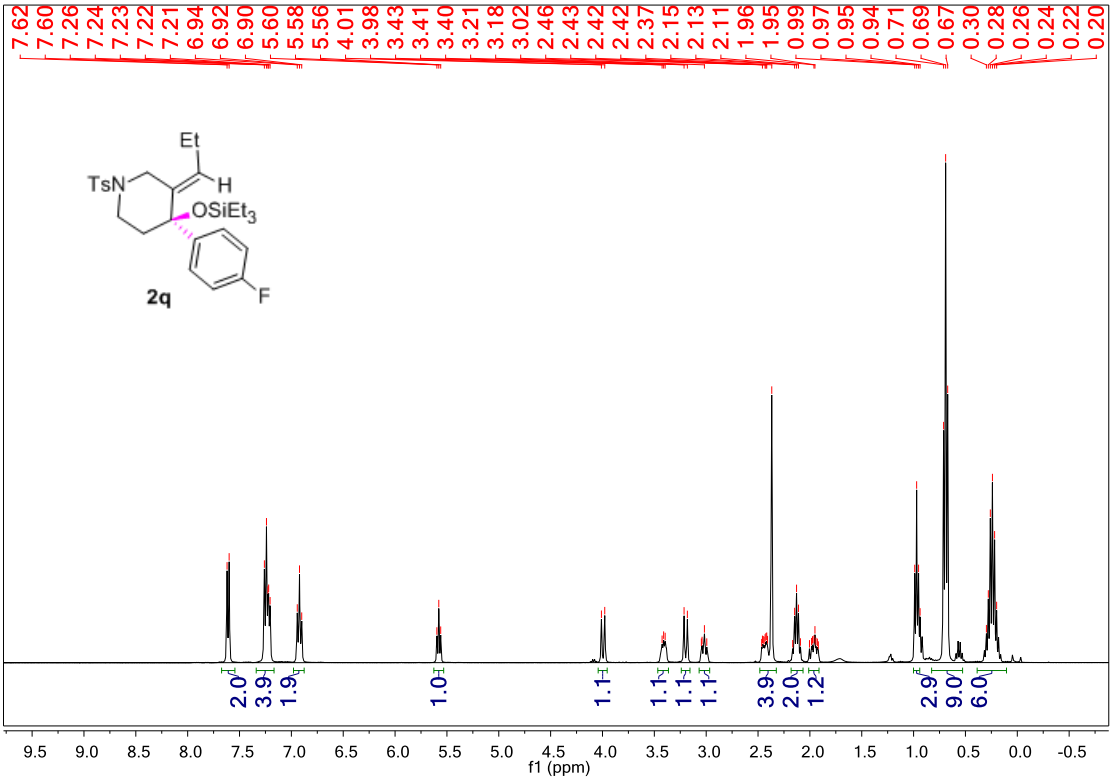

**Supplementary Figure 69.** $^{1}H$ and $^{13}C$ NMR spectra for compound **3o**

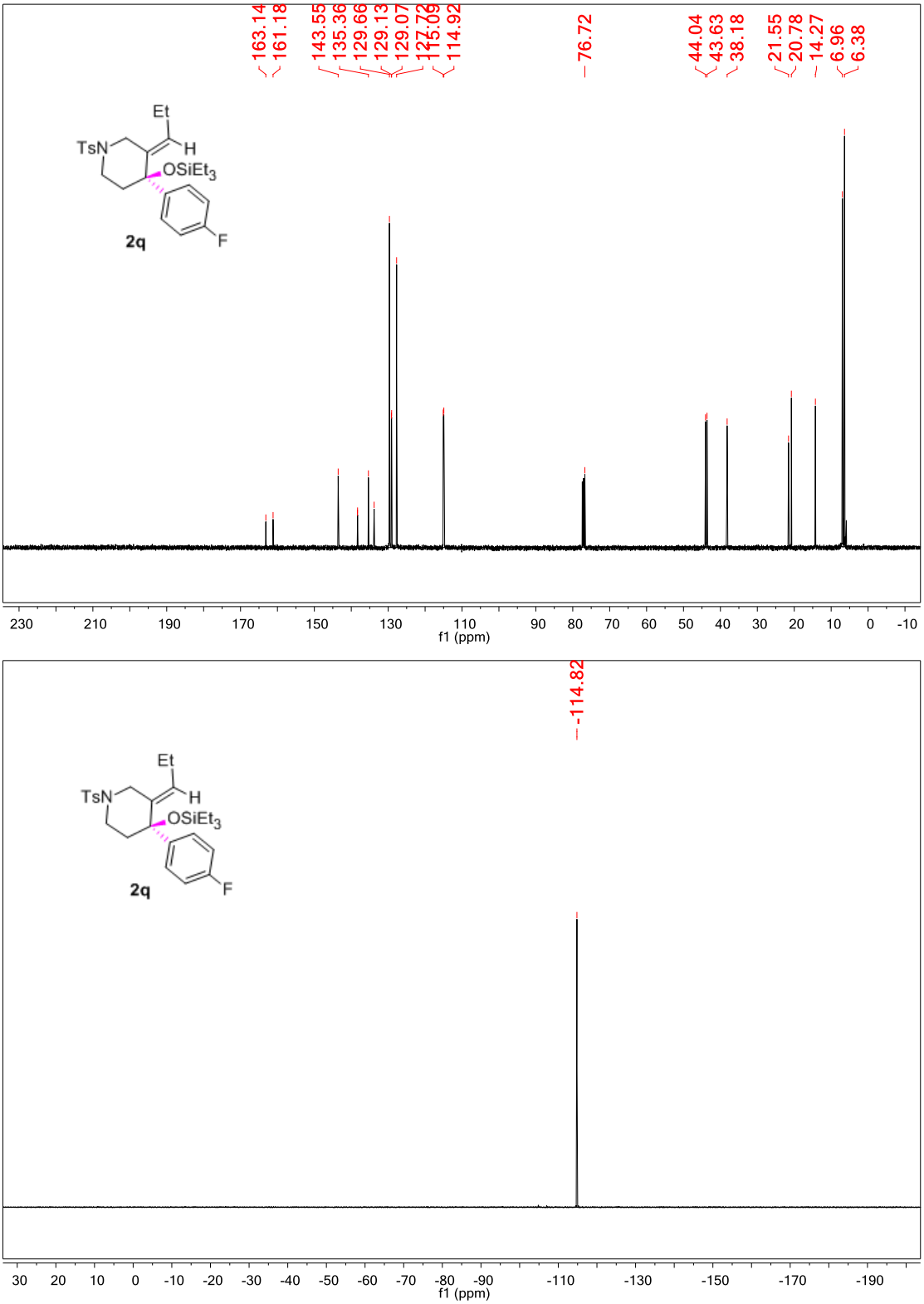

7.53 7.50 7.39 7.37 7.35 7.34 7.33 7.32 7.31 7.29 7.27 7.22 7.19 7.00 6.98 6.95 6.83 4.35 4.32 3.62 3.59 3.16 3.13 2.99 2.64 2.63 2.61 2.61 2.60 2.37 2.13 0.77 0.75 0.73 0.36 0.34 0.33 0.32 0.31 0.30 0.29 0.28 0.26 0.24
Ph
TsN
H
OSiEt3
F
2p
2.1 9.0 2.0 1.1 1.1 1.1 1.0 1.1 1.1 3.0 1.1 9.0 6.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.35 161.38 129.66 129.07 128.59 127.82 127.39 115.45 115.28 44.98 43.92 37.90 21.61 7.02 6.41
Ph
TsN
H
OSiEt3
F
2p
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

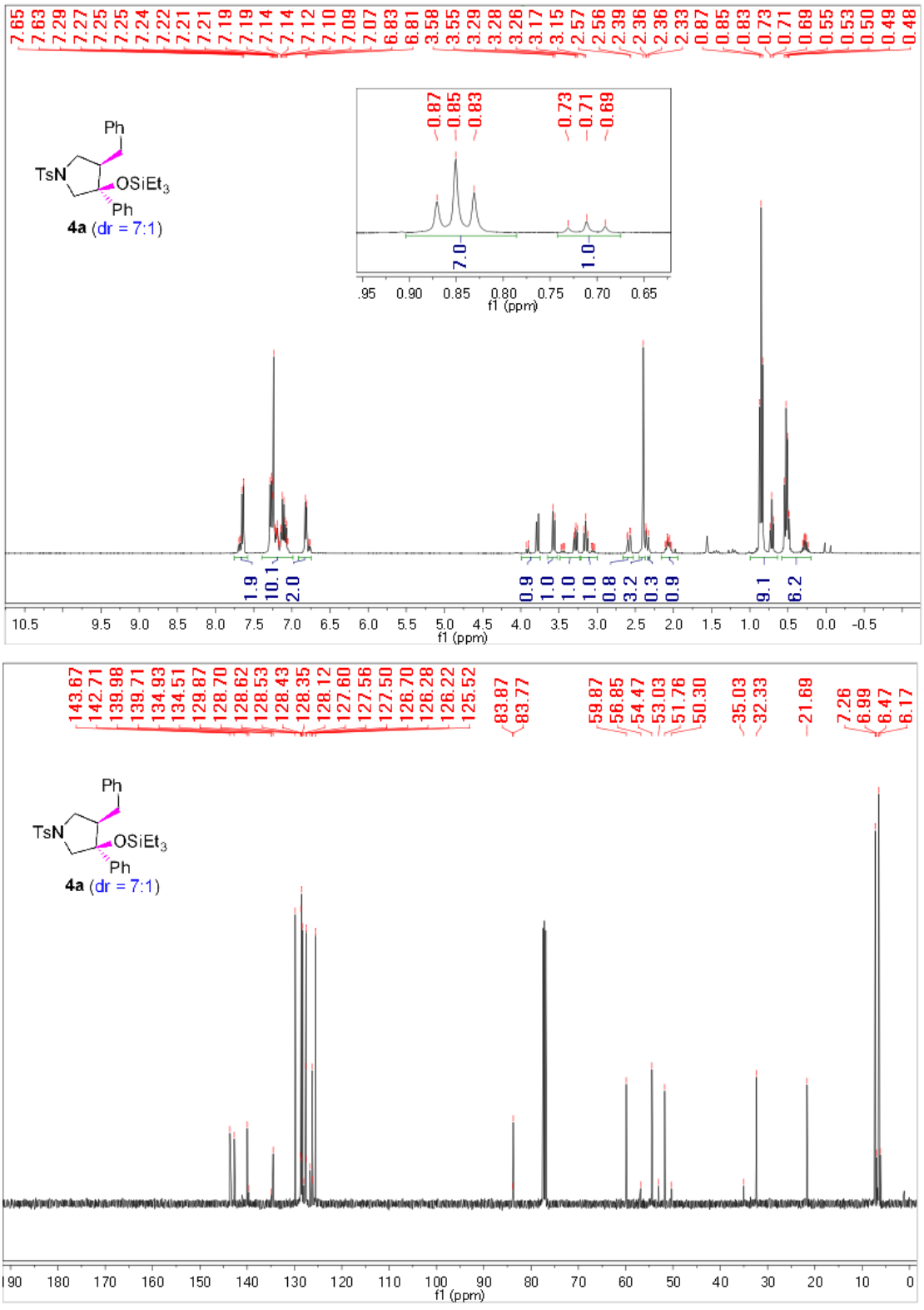



**Supplementary Figure 70.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **2p**

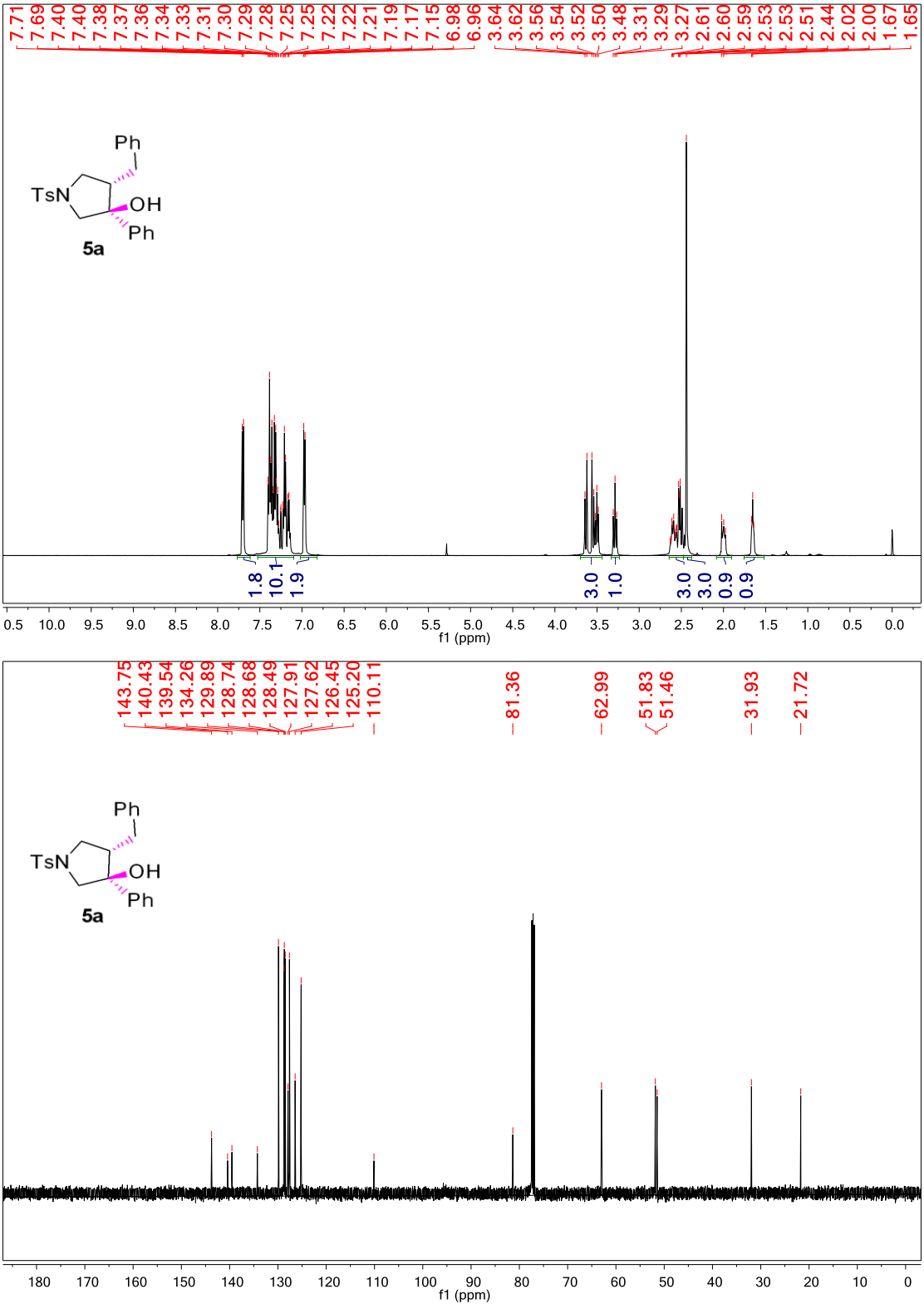




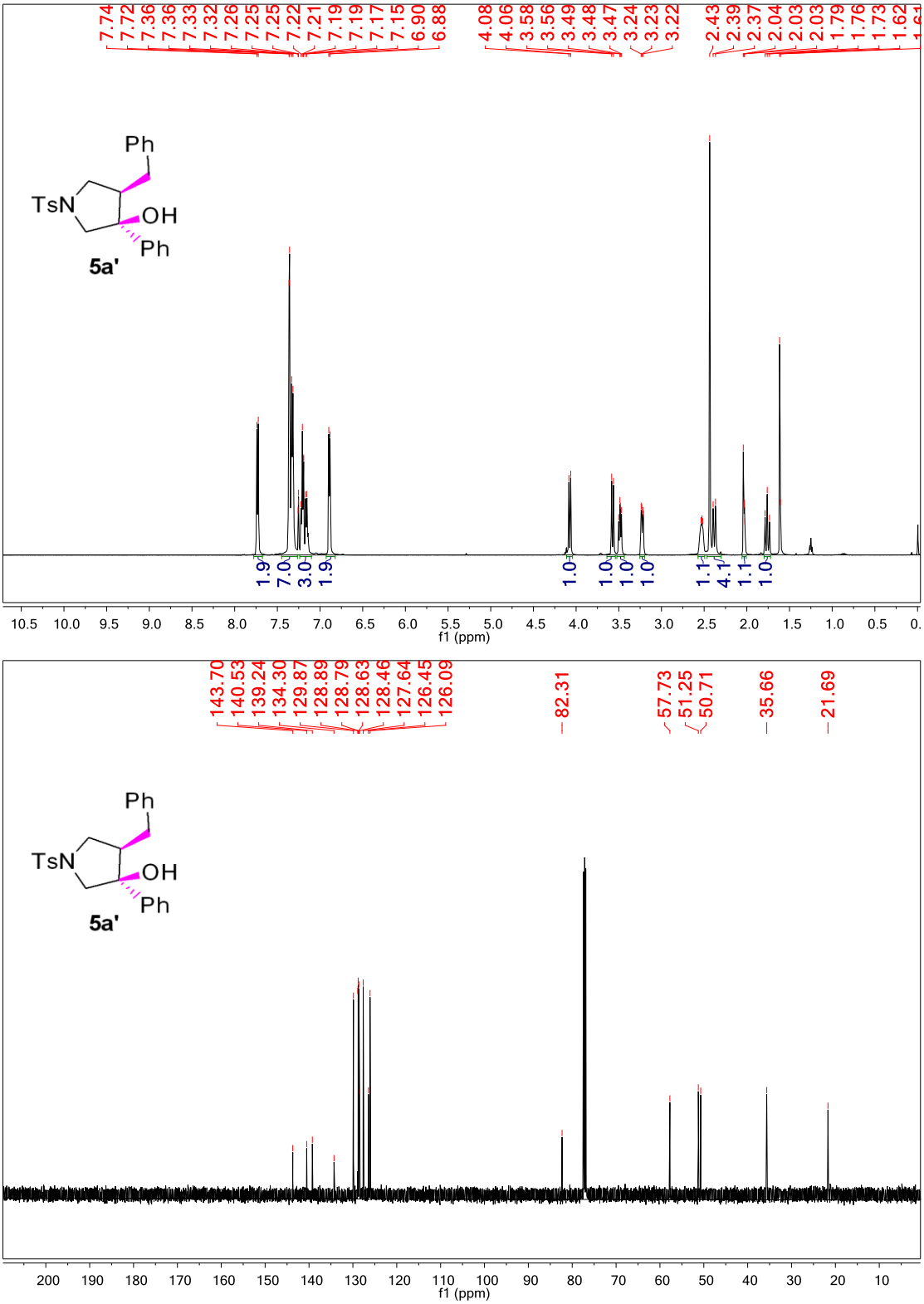

**Supplementary Figure 71.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **2q**



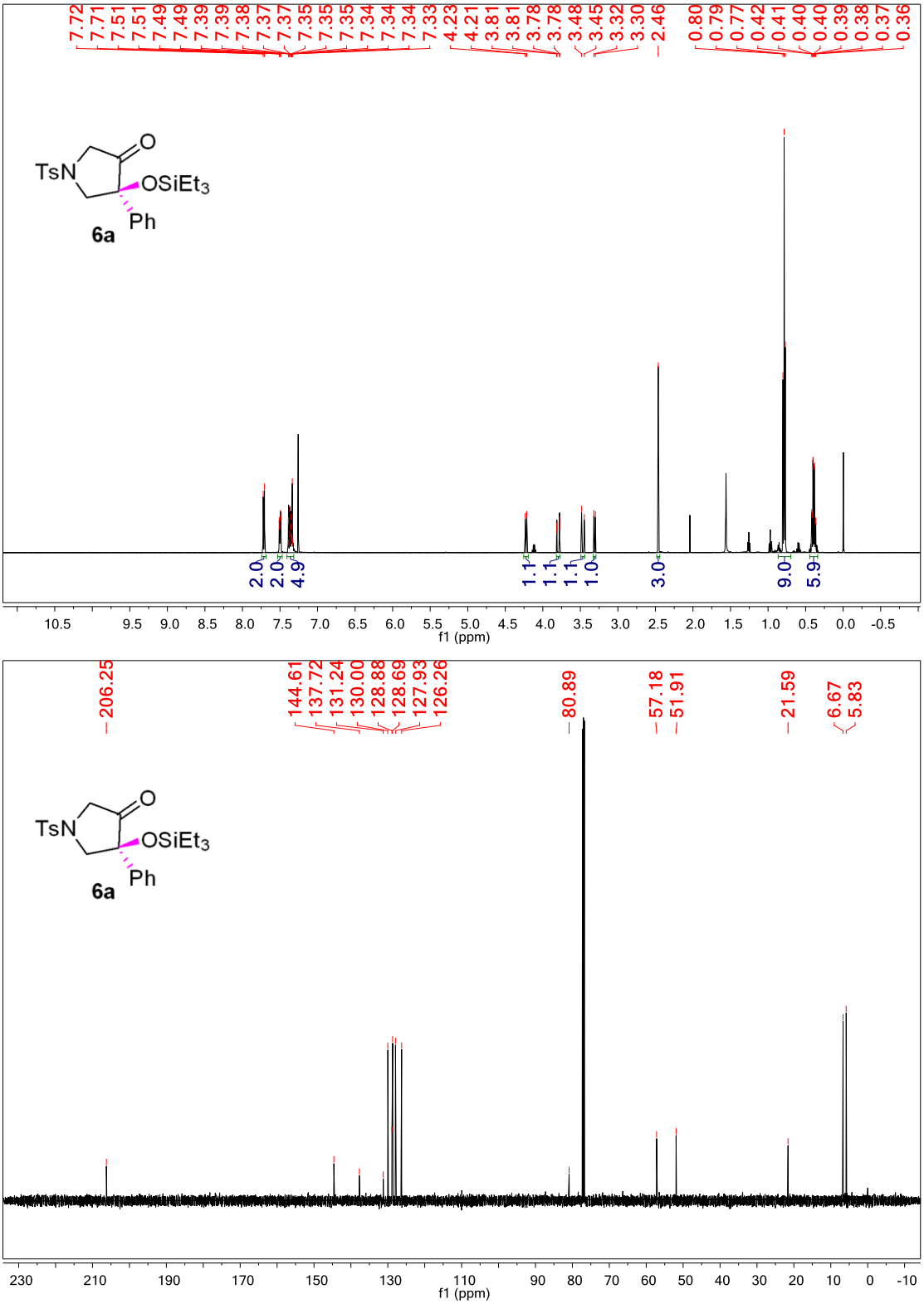

**Supplementary Figure 72.** $^{1}H$ and $^{13}C$ NMR spectra for compound **4a**



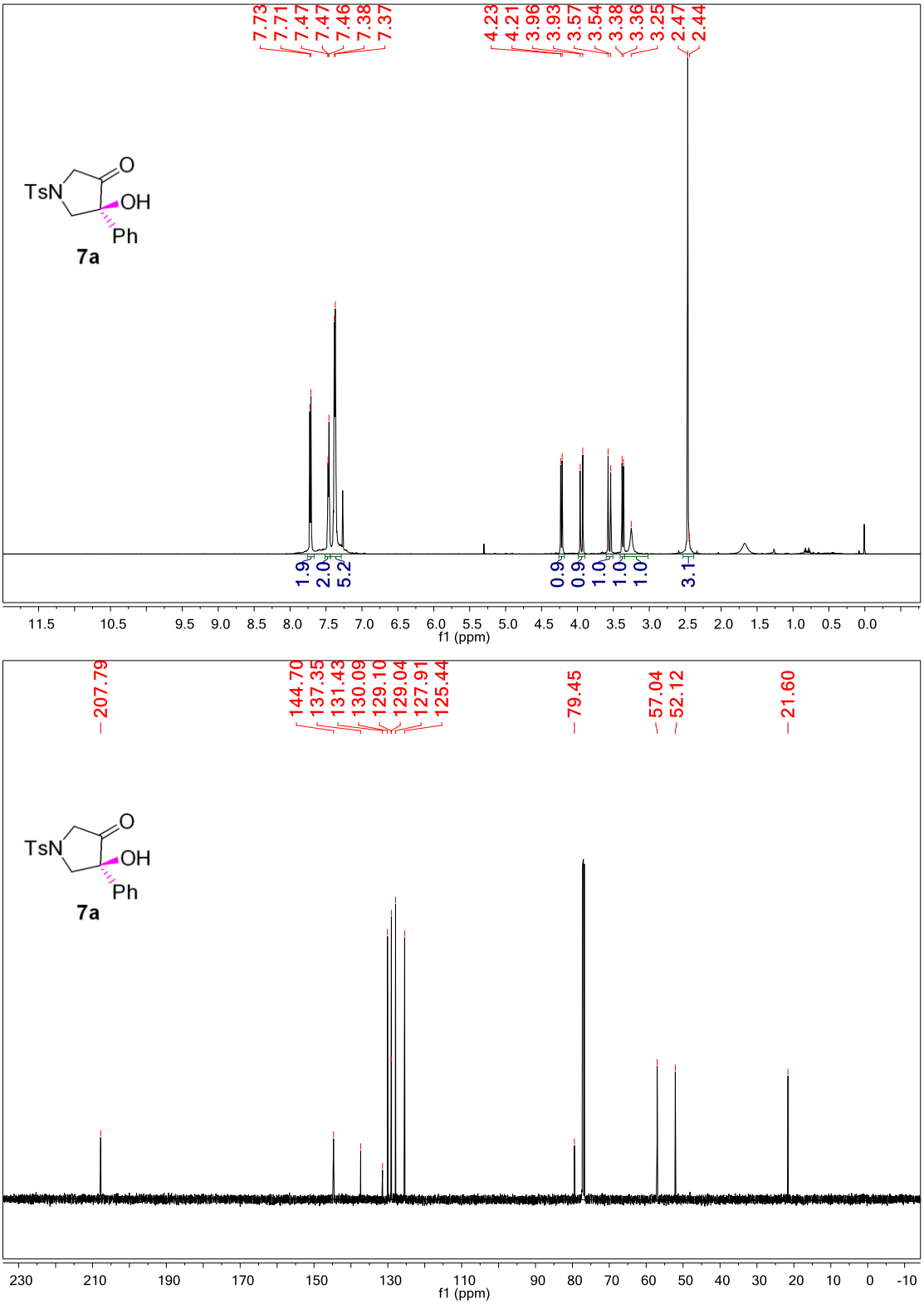

**Supplementary Figure 73.** $^{1}H$ and $^{13}C$ NMR spectra for compound **5a**



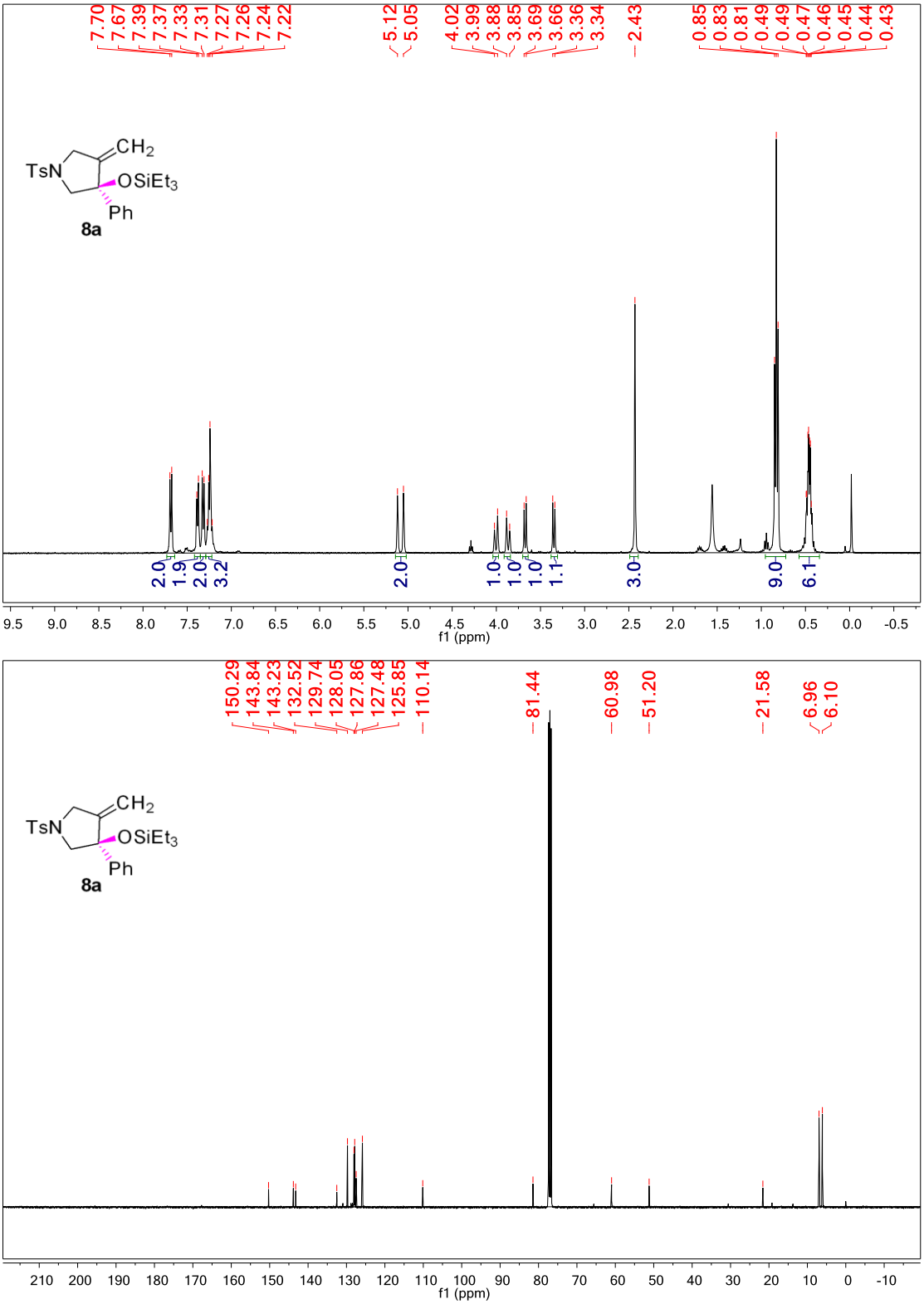

**Supplementary Figure 74.** $^{1}H$ and $^{13}C$ NMR spectra for compound **5a'**



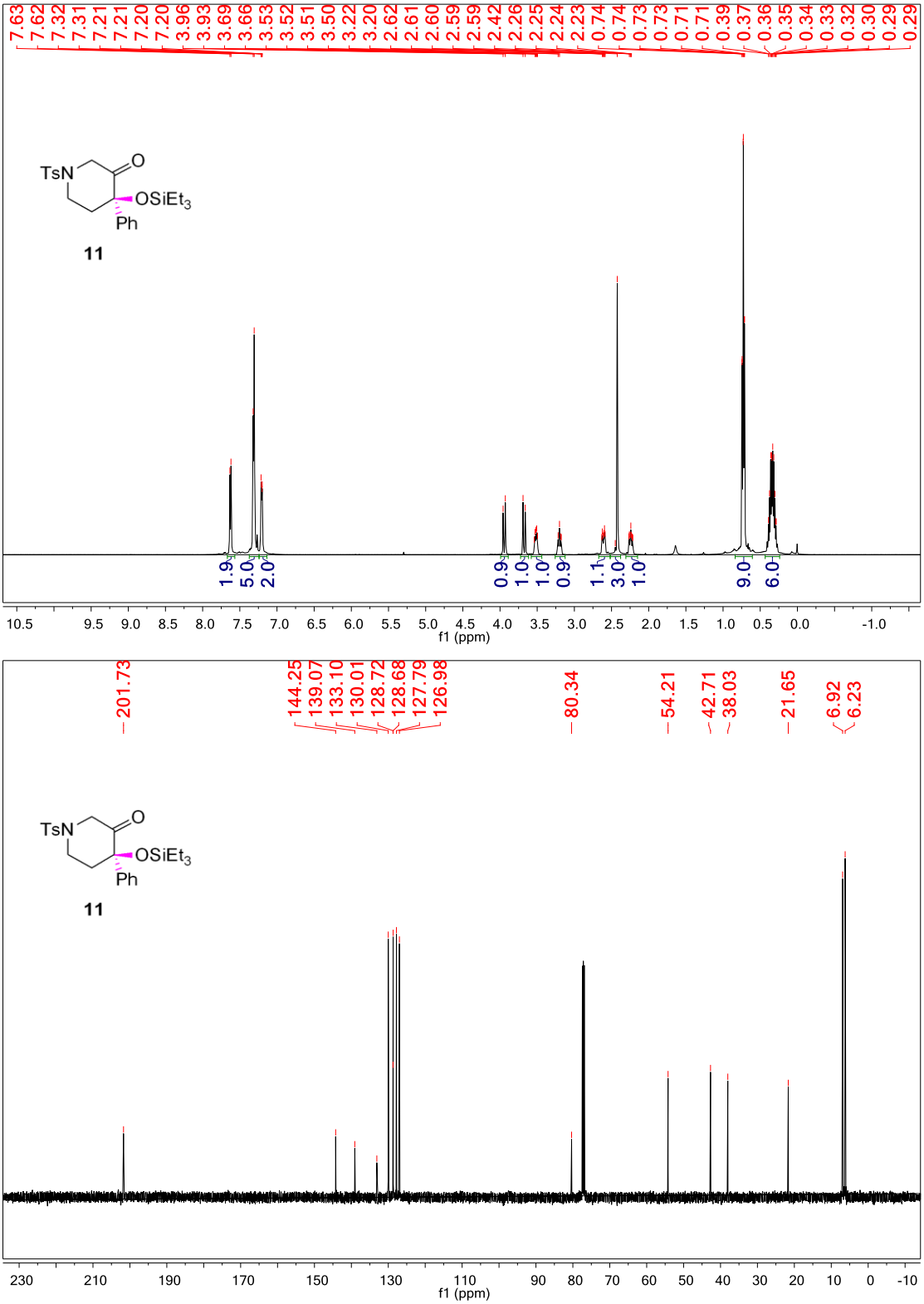

**Supplementary Figure 75.** $^{1}H$ and $^{13}C$ NMR spectra for compound **6a**



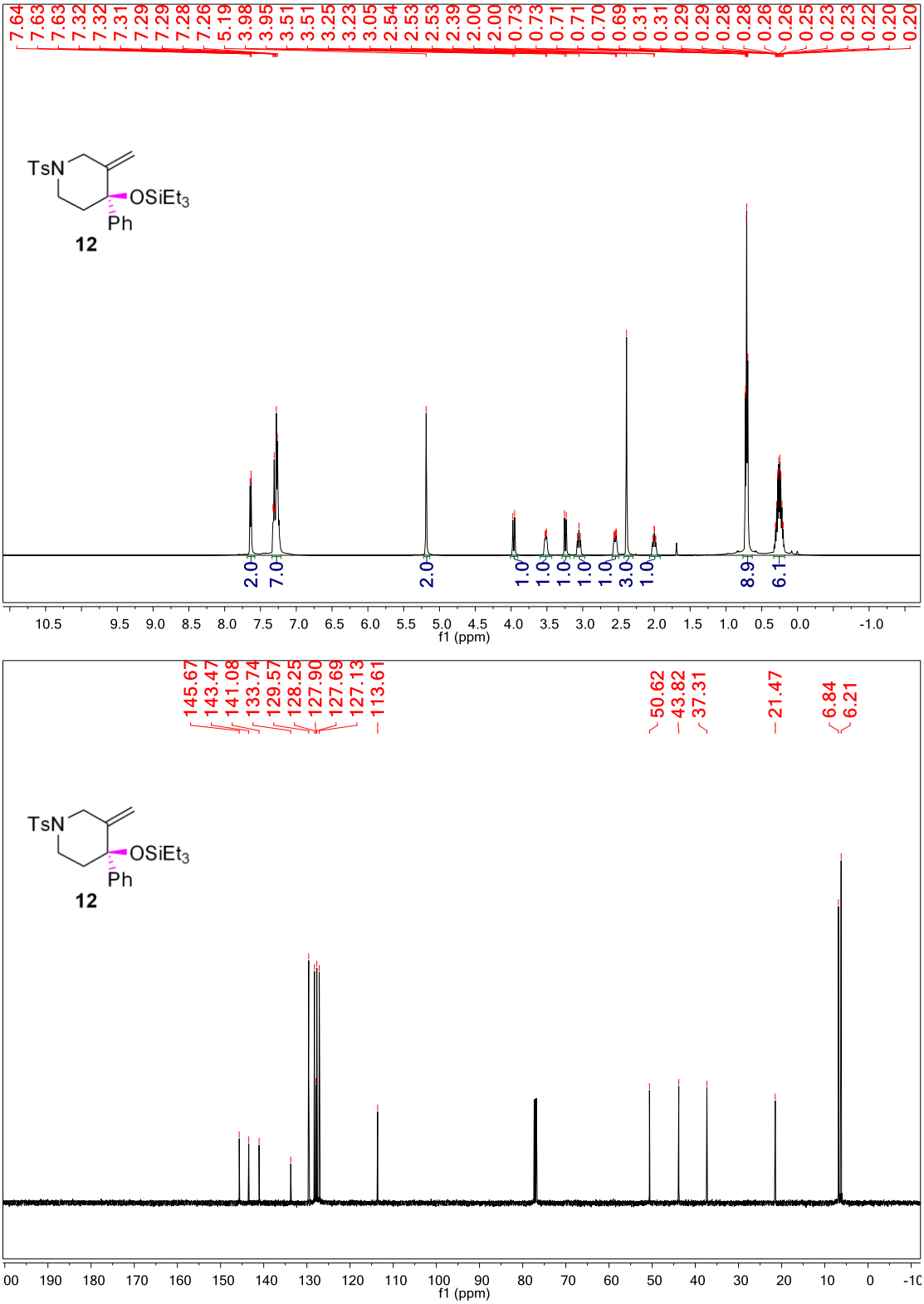

**Supplementary Figure 76.** $^{1}H$ and $^{13}C$ NMR spectra for compound **7a**



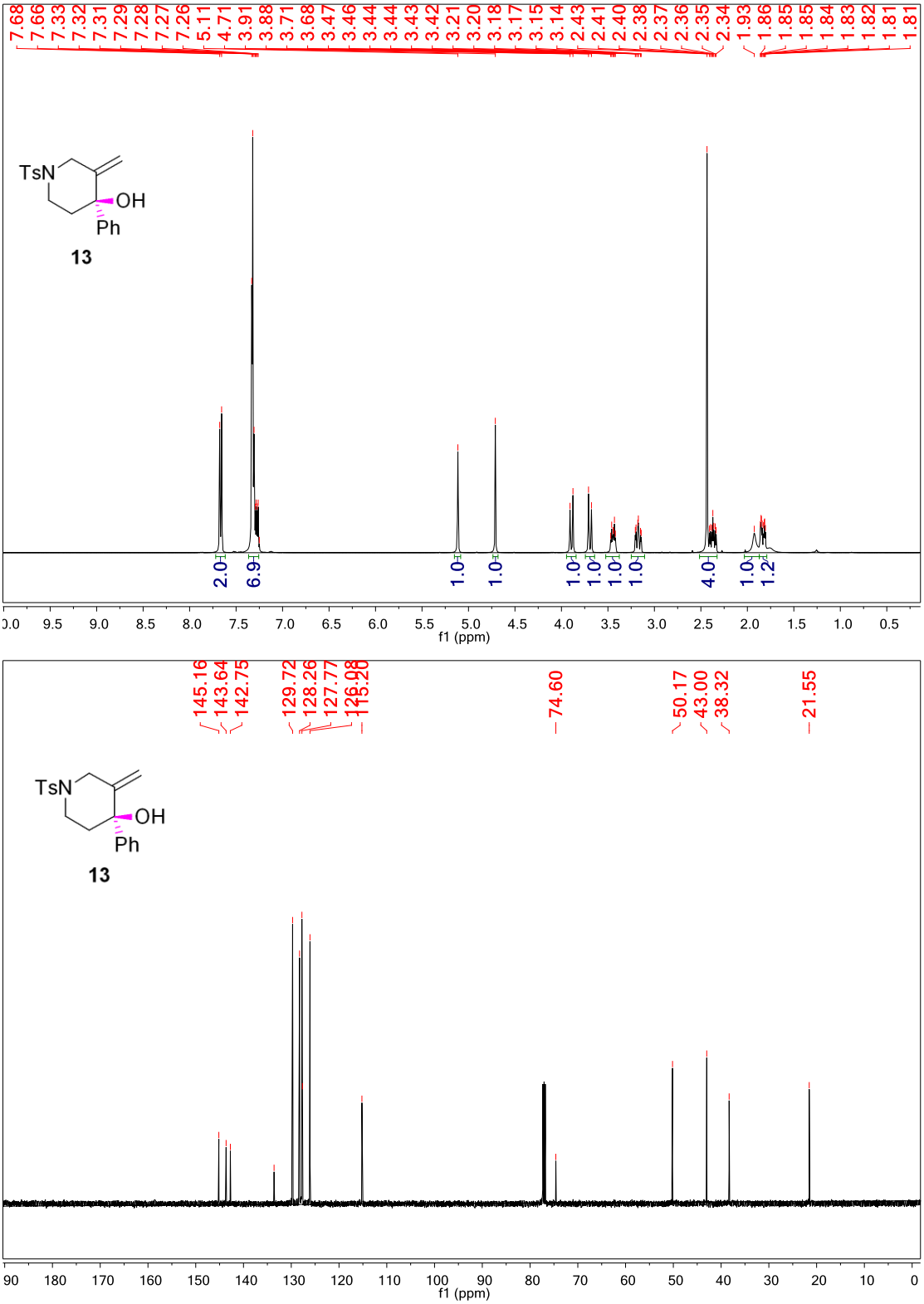

**Supplementary Figure 77.** $^{1}H$ and $^{13}C$ NMR spectra for compound **8a**



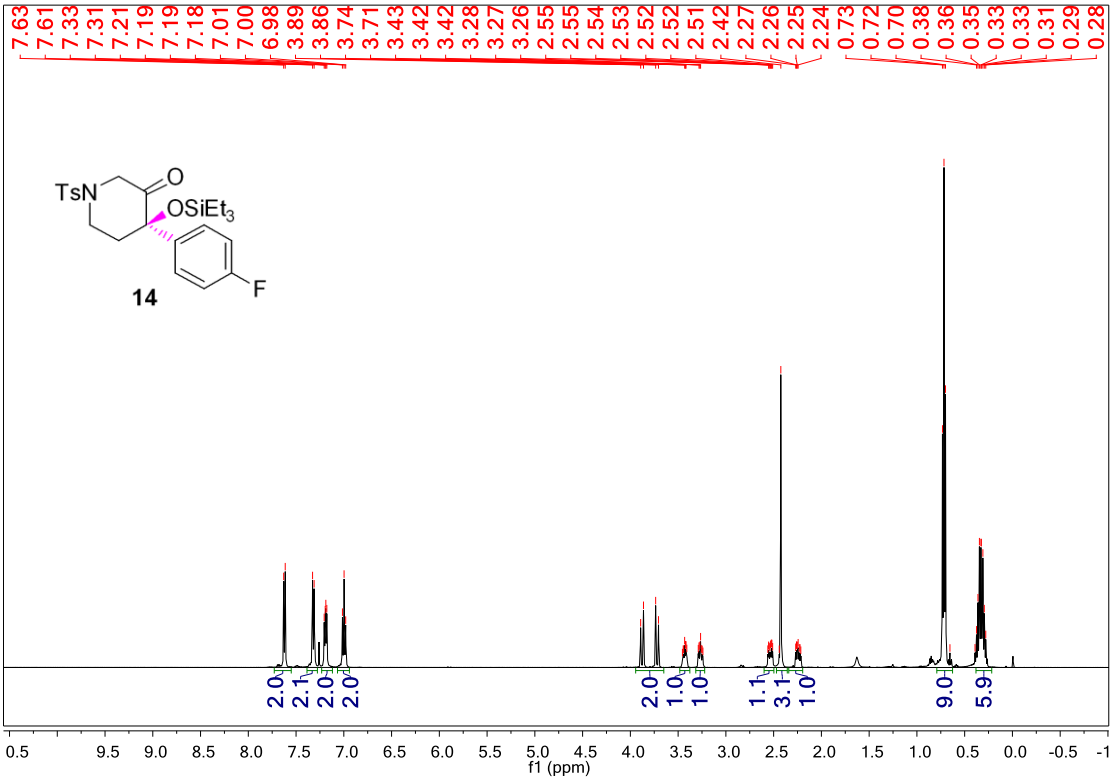

**Supplementary Figure 78.** $^{1}H$ and $^{13}C$ NMR spectra for compound **11**

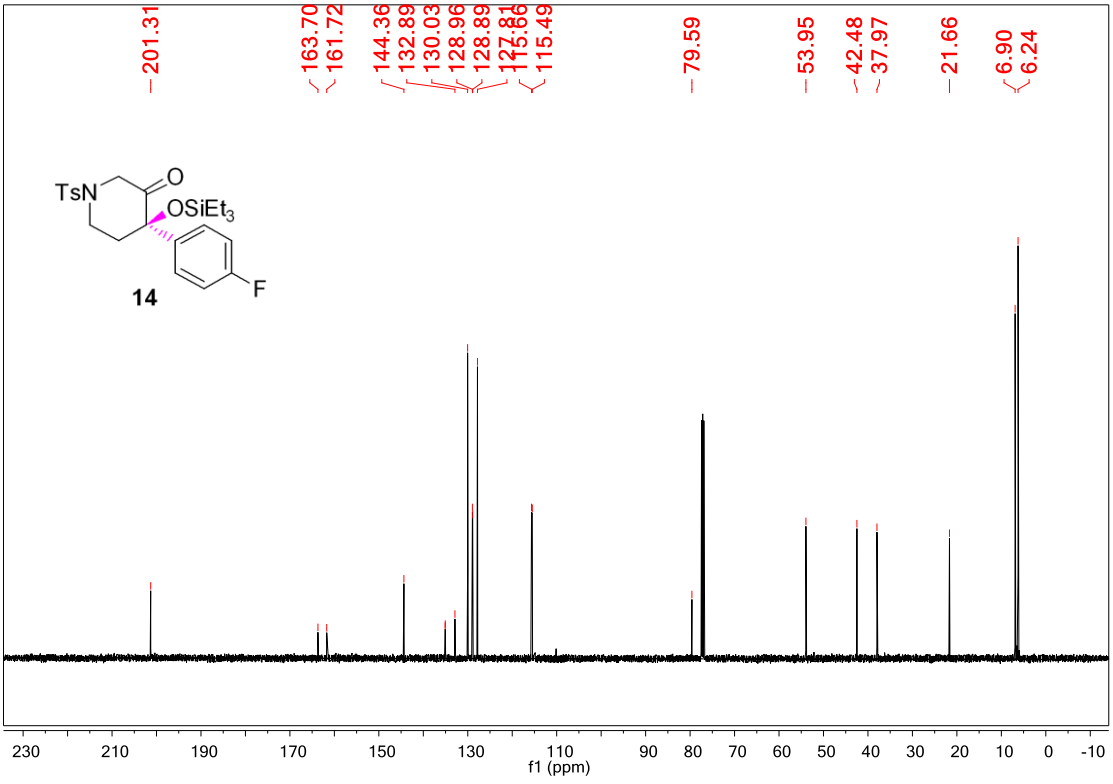


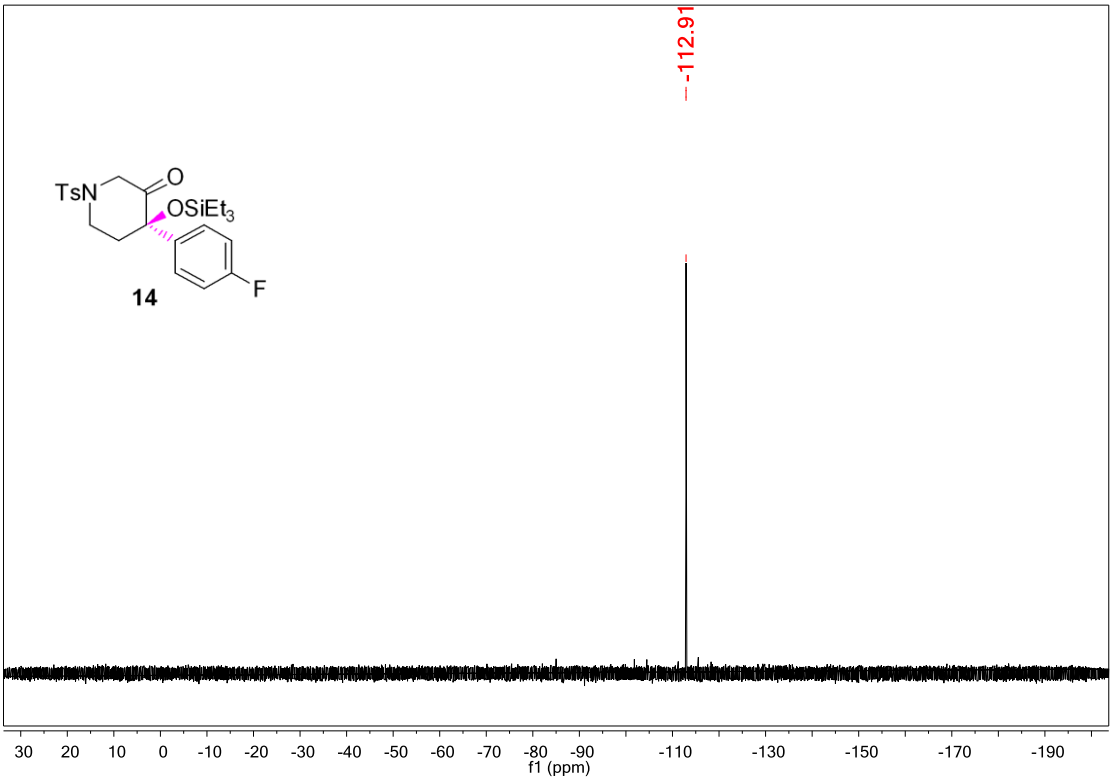

**Supplementary Figure 79.** $^{1}H$ and $^{13}C$ NMR spectra for compound **12**



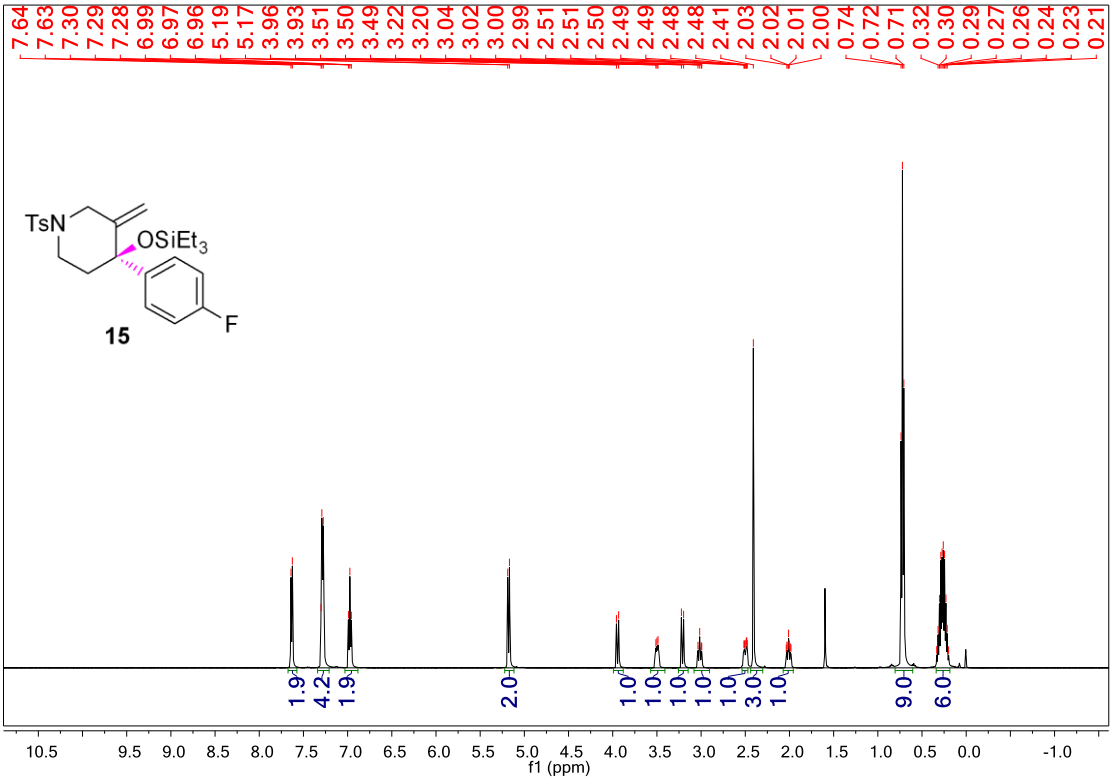

**Supplementary Figure 80.** $^{1}H$ and $^{13}C$ NMR spectra for compound **13**

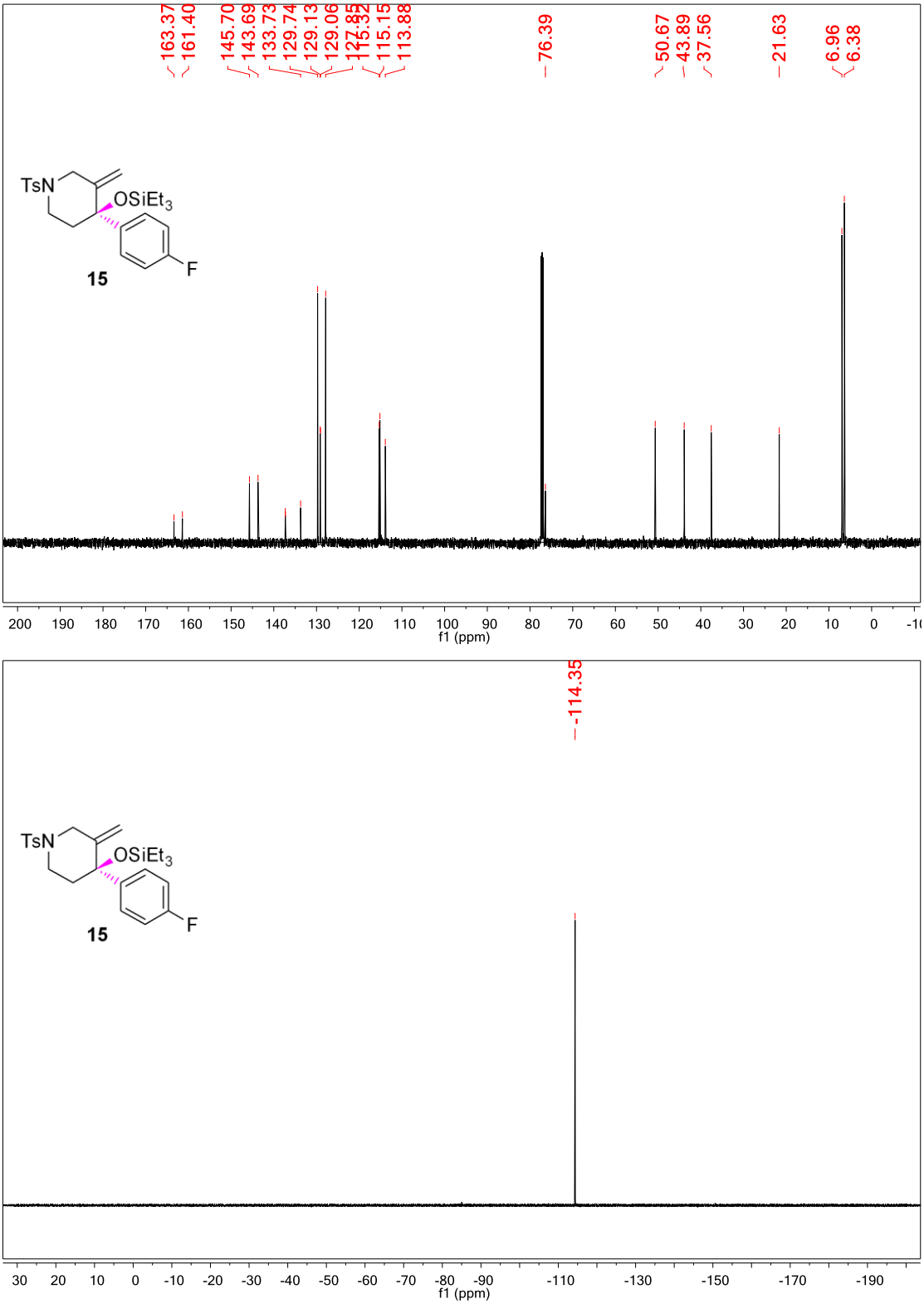

7.63 7.61 7.33 7.31 7.21 7.19 7.19 7.18 7.01 7.00 6.98 3.89 3.86 3.74 3.71 3.43 3.42 3.42 3.28 3.27 3.26 2.55 2.55 2.54 2.53 2.52 2.52 2.51 2.42 2.27 2.26 2.25 2.24 0.73 0.72 0.70 0.38 0.36 0.35 0.33 0.33 0.31 0.29 0.28
TsN
O
OSiEt3
F
14
2.0 2.1 2.0 2.0 2.0 1.0 1.0 1.1 3.1 1.0 9.0 5.9
f1 (ppm)


201.31 163.70 161.72 144.36 132.89 130.03 128.96 128.89 127.81 115.86 115.49 79.59 53.95 42.48 37.97 21.66 6.90 6.24
TsN
O
OSiEt3
F
14
f1 (ppm)

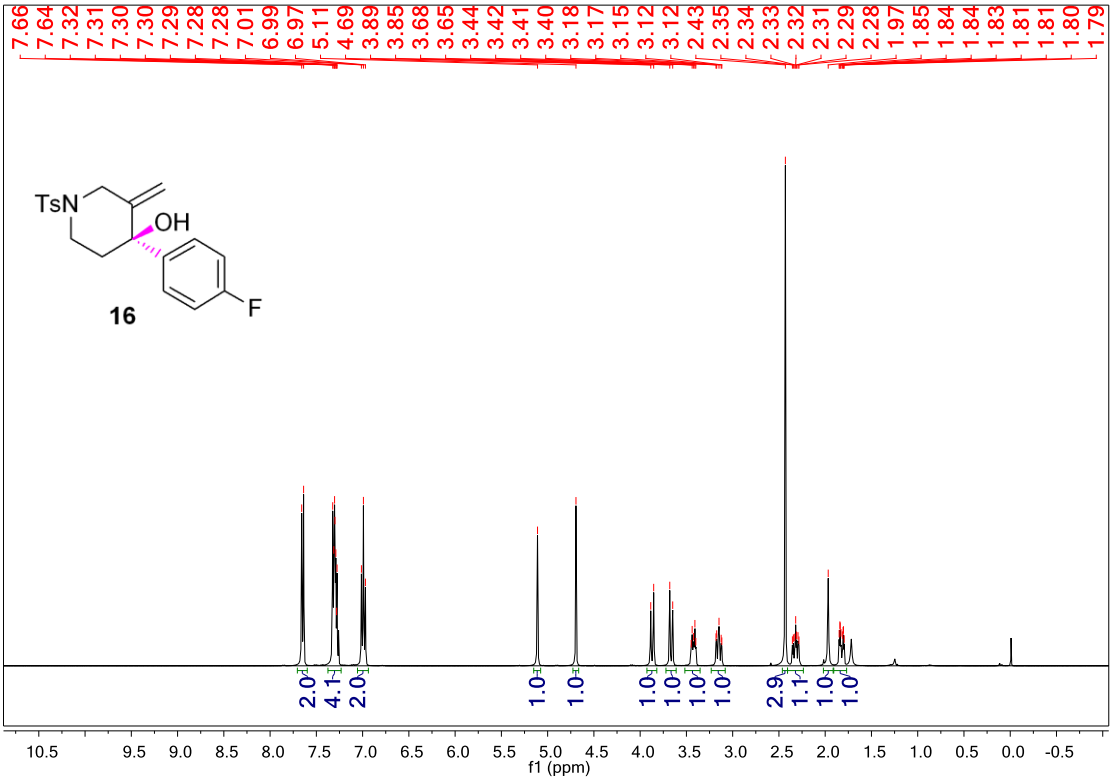


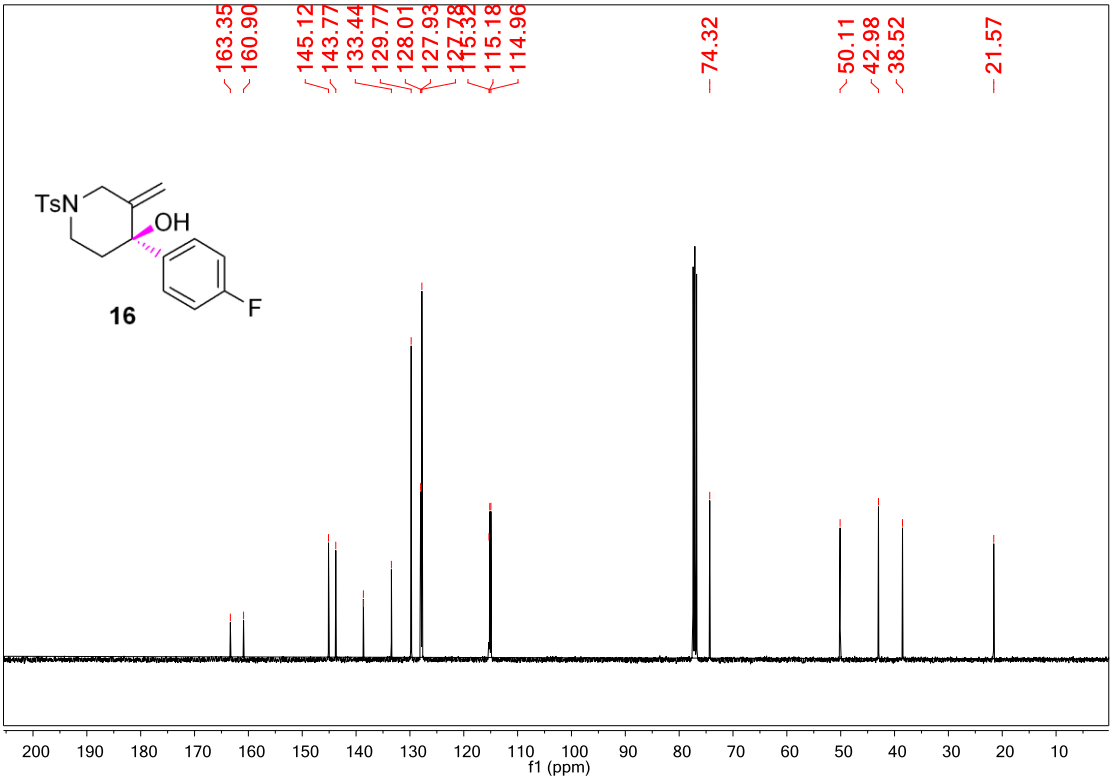

**Supplementary Figure 81.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **14**






**Supplementary Figure 82.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **15**


7.66
7.64
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.01
6.99
6.97
5.11
4.69
3.89
3.85
3.68
3.65
3.44
3.42
3.41
3.40
3.18
3.17
3.15
3.12
3.12
2.43
2.35
2.34
2.33
2.32
2.31
2.29
2.28
1.97
1.85
1.84
1.84
1.83
1.81
1.81
1.80
1.79
TsN
OH
F
16
2.0
4.1
2.0
1.0
1.0
1.0
1.0
1.0
1.0
2.9
1.1
1.0
1.0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.35
160.90
145.12
143.77
133.44
129.77
128.01
127.93
127.78
127.32
115.18
114.96
74.32
50.11
42.98
38.52
21.57
TsN
OH
F
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


**Supplementary Figure 83.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra for compound **16**

## Supplementary References


1 Tang, W., Capacci, A. G., Wei, X. D., Li, W. J., White, A., Patel, N. D., Savoie, J., Gao, J. J., Rodriguez, S., Qu, B., Haddad, N., Lu, B. Z., Krishnamurthy, D., Yee, N. K. & Senanayake, C. H. A general and special catalyst for Suzuki–Miyaura coupling processes. *Angew. Chem. Int. Ed.* **49**, 5879 –5883 (2010).

2 Bera, K., Sarkar, S., Biswas, S., Maiti, S. & Jana, U. Iron-catalyzed synthesis of functionalized 2*H*-chromenes *via* intramolecular alkyne−carbonyl metathesis. *J. Org. Chem.* **76**, 3539–3544 (2011).

3 Nieto-Oberhuber, C., Pérez-Galán, P., Herrero-Gómez, E., Lauterbach, T., Rodríguez, C., López, S., Bour, C., Rosellón, A., Cárdenas, D. J. & Echavarren, A. M. Gold(I)-catalyzed intramolecular [4+2] cycloadditions of arylalkynes or 1,3-enynes with alkenes: scope and mechanism. *J. Am. Chem. Soc.* **130**, 269–279 (2008).

4 Shen, K., Han, X. & Lu, X. Cationic Pd(II)-catalyzed reductive cyclization of alkyne-tethered ketones or aldehydes using ethanol as hydrogen source. *Org. Lett.* **15**, 1732–1735 (2013).

5 Li, X., Chen, M., Xie, X., Sun, N., Li, S. & Liu, Y. Synthesis of multiple-substituted pyrroles *via* Gold(I)-catalyzed hydroamination/cyclization cascade. *Org. Lett.* **17**, 2984–2987 (2015).

6 Egorov, M., Delpech, B., Aubert, G., Cresteil, T., Garcia-Alvarez, M. C., Collin, P. & Marazano, C. A concise formation of *N*-substituted 3,4-diarylpyrroles – synthesis and cytotoxic activity. *Org. Biomol. Chem.* **12**, 1518-1524 (2014).

7 Myers, M. C., Iera, J. A., Bang, J.-k., Hara, T., Saito, S., Zambetti, G. P. & Appella, D. H. A new family of small molecules to probe the reactivation of mutant p53. *J. Am. Chem. Soc.* **127**, 6152–6153 (2005).

8 Cassffl, D., Parella, T., Sol, M. Pla-Quintana, A. & Roglans, A. Rhodium-catalyzed [2+2+2] cycloaddition reactions of linear allene-ene-ynes to afford fused tricyclic scaffolds: insights into the mechanism. *Chem. Eur. J.* **23**, 14889–14899 (2017).