Supporting Information

Rh-Catalyzed Asymmetric Allylation of tert-Butanesulfinamide

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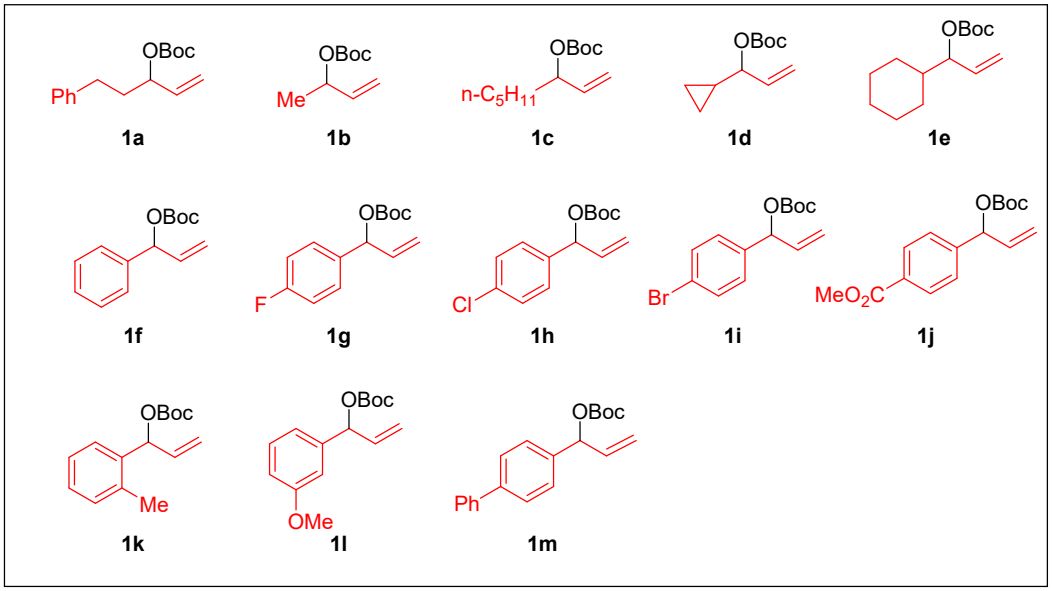
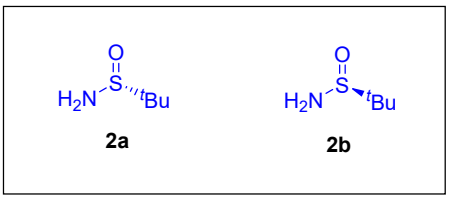
1. General information.

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under dry argon atmosphere. All reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted by solvent purification system (Vigor YJC-7). Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 101 MHz, ^{13}C); Bruker-400 instrument (400 MHz, ^{1}H; 101 MHz, ^{13}C); Bruker-500 instrument (500 MHz, ^{1}H; 126 MHz, ^{13}C), spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. ^{19}F NMR spectra were recorded on a Bruker-400 (376 MHz, respectively) and referenced relative to $PhCF_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). XRD and High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. The *ee* values were determined by HPLC using a Daicel chiral column. Melting points were measured with Hanon MP100 melting point apparatus. Optical rotations were measured on an Anton Paar MCP100 automatic polarimeter using a 100 mm path-length cell at 589 nm.

2. Substrate list.



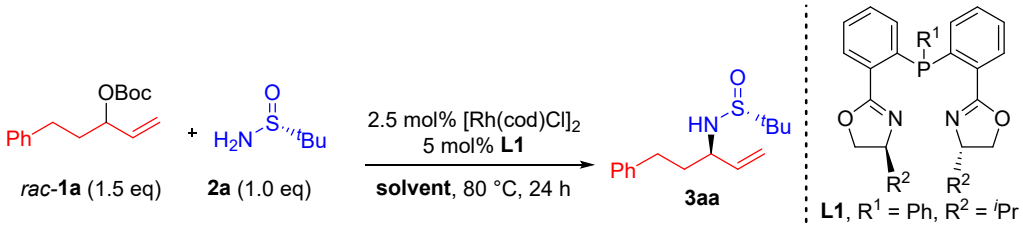
1a-1f[1], **1g-1k, 1m**[2] **, 1l**[3]were prepared according to the literature.



The subatrates **2a** and **2b** were purchased from Shanghai Bidepharmatech Co., Ltd.

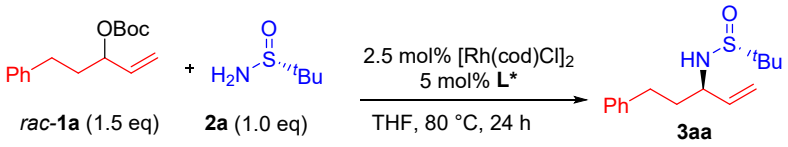
3. Optimization of reaction conditions.

Table S1. Solvent screening

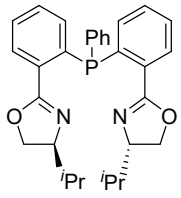


entry	solvent	yield of **3aa** (%)	*dr* of **3aa**	**b/l**
1	toluene	49	>20/1	2.5/1
2	THF	47	>20/1	4.2/1
3	1,4-Dioxane	45	>20/1	3.5/1
4	CH_3CN	<5	-	-
5	DMF	NR	-	-
6	DCE	<5	-	-

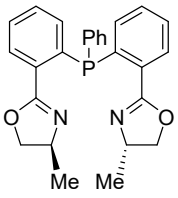
Table S2. Ligands screening of synthesis of 3aa



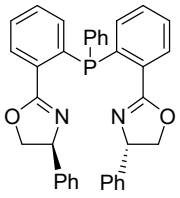
rac-**1a** (1.5 eq) **2a** (1.0 eq) **3aa**



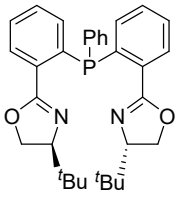
L1, 47%
dr > 20/1, b/l = 4.2/1



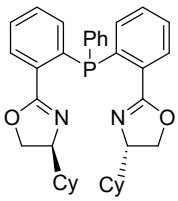
L2, < 5%



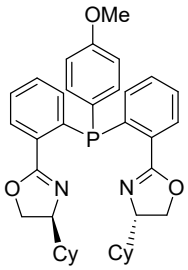
L3, 77%
dr > 20/1, b/l = 6/1



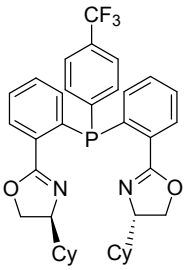
L4, < 5%



L5, 88%
dr > 20/1, b/l = 10/1

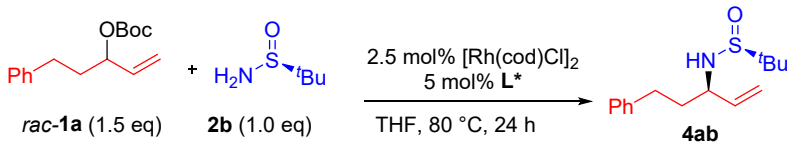


L6, 73%
dr > 20/1, b/l = 10/1

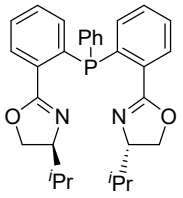


L7, 80%
dr > 20/1, b/l = 10/1

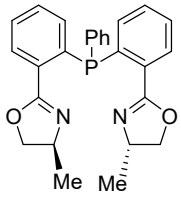
Table S3. Ligands screening of synthesis of 4ab



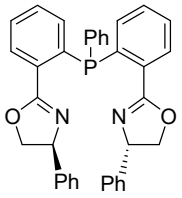
rac-**1a** (1.5 eq) **2b** (1.0 eq) **4ab**



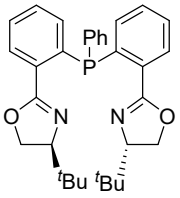
L1, 65%
dr > 20/1, b/l = 10/1
rac-L1, 66%
dr = 1.7/1, b/l = 10/1



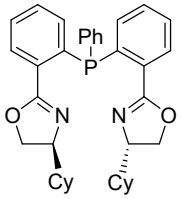
L2, < 5%



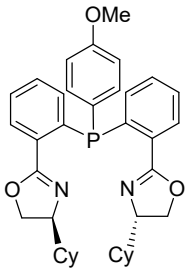
L3, 72%
dr > 20/1, b/l = 17/1



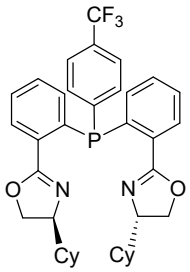
L4, 17%
dr > 20/1, b/l = 5/1



L5, 92%
dr > 20/1, b/l > 20/1

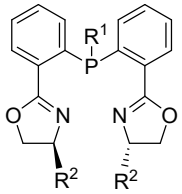


L6, 92%
dr > 20/1, b/l = 17/1



L7, 85%
dr > 20/1, b/l = 17/1

4. Procedure for ligand synthesis.



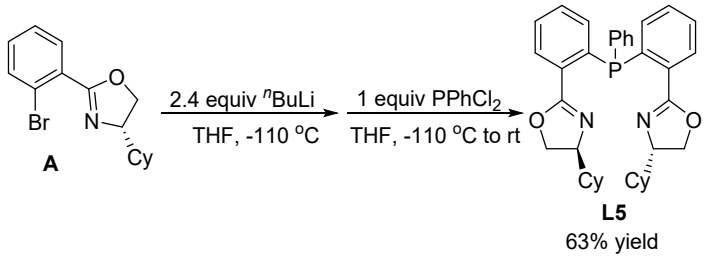
L1: R^1 = Ph, R^2 = ^{i}Pr
L2: R^1 = Ph, R^2 = Me
L3: R^1 = Ph, R^2 = Ph
L4: R^1 = Ph, R^2 = ^{t}Bu
L5: R^1 = Ph, R^2 = Cy
L6: R^1 = 4-OMeC_6H_4, R^2 = Cy
L7: R^1 = 4-$CF_3C_6H_4$, R^2 = Cy

L1-L4 were synthesized according to the reported literature[4].

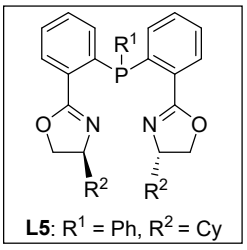
L5 and (*ent*)-**L5** were synthesized according to the **Method 1**.

L6 and **L7** were synthesized according to the **Method 2**.

Method 1:



In a flame dried Shlenk tube, compound **A** (4.4 mmol, 2.2 eq) was dissolved in THF (18 mL) under an argon atmosphere and cooled down to -110 °C. ^{n}BuLi (2.4 eq, 2.5 M in THF) was added dropwise and the mixture was stirred for 1 h at this temperature. Then phenylphosphine dichloride (2.0 mmol, 1.0 eq) in 1 mL of THF was added slowly. The reaction mixture was stirred at -110 °C for one hour and warmed to room temperature. After 12 hours, the reaction mixture was quenched with water and extracted with ethyl acetate. Organic phase was washed with brine and dried over Na_2SO_4. Solvent was removed under reduced pressure and crude product was purified by flash column chromatography on silica gel using petrolium ether/ethyl acetate as eluent to obtain the pure product **L5**.



710 mg, 63%, yellow oil, R_f = 0.5 (PE/EA = 5/1), $[\alpha]_D^{25}$ = -31.2 (*c* = 0.5, $CHCl_3$).

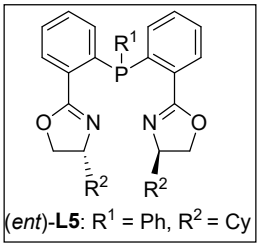
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.35 – 7.26 (m, 7H), 7.26 – 7.20 (m, 2H), 6.95 – 6.93 (m, 1H), 6.89 – 6.87 (m, 1H), 4.19 – 4.06 (m, 2H), 3.95 – 3.73 (m, 4H), 1.63 – 1.53 (m, 8H), 1.34 – 1.28 (m, 2H), 1.14 – 1.02 (m, 8H), 0.87 – 0.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 2.0 Hz), 162.6 (d, *J* = 2.3 Hz), 140.5 (d, *J* = 28.4 Hz), 139.9 (d, *J* = 22.5 Hz), 139.1 (d, *J* = 13.6 Hz), 134.5, 134.4 (d, *J* = 12.6 Hz), 133.8, 132.1 (d, *J* = 20.1 Hz),

131.9 (d, J = 20.5 Hz), 130.1 (d, J = 17.1 Hz), 129.6 (d, J = 3.7 Hz), 129.5, 128.2 (d, J = 7.1 Hz), 127.6 (d, J = 8.8 Hz), 72.1, 71.9, 70.0, 70.0, 42.7, 42.6, 29.1, 29.0, 28.9, 28.8, 26.4, 26.4, 26.1, 26.0, 25.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.6.

HRMS (ESI): *m/z* calculated for $C_{36}H_{42}N_2O_2P$ $[M + H]^+$ = 565.2978; found 565.2967.



(*ent*)-**L5**: R^1 = Ph, R^2 = Cy

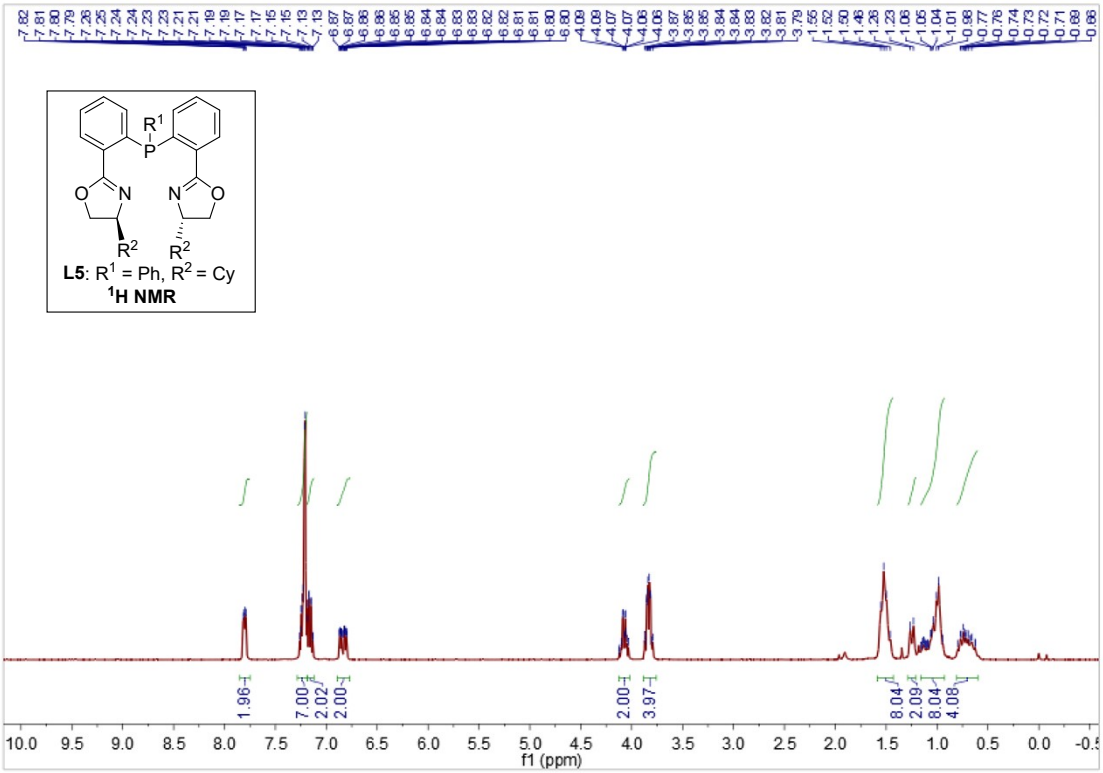
620 mg, 55%, yellow solid, R_f = 0.5 (PE/EA = 5/1), $[\alpha]_D^{25}$ = +33.6 (c = 0.25, $CHCl_3$). m.p. = 70.0-71.8 °C.

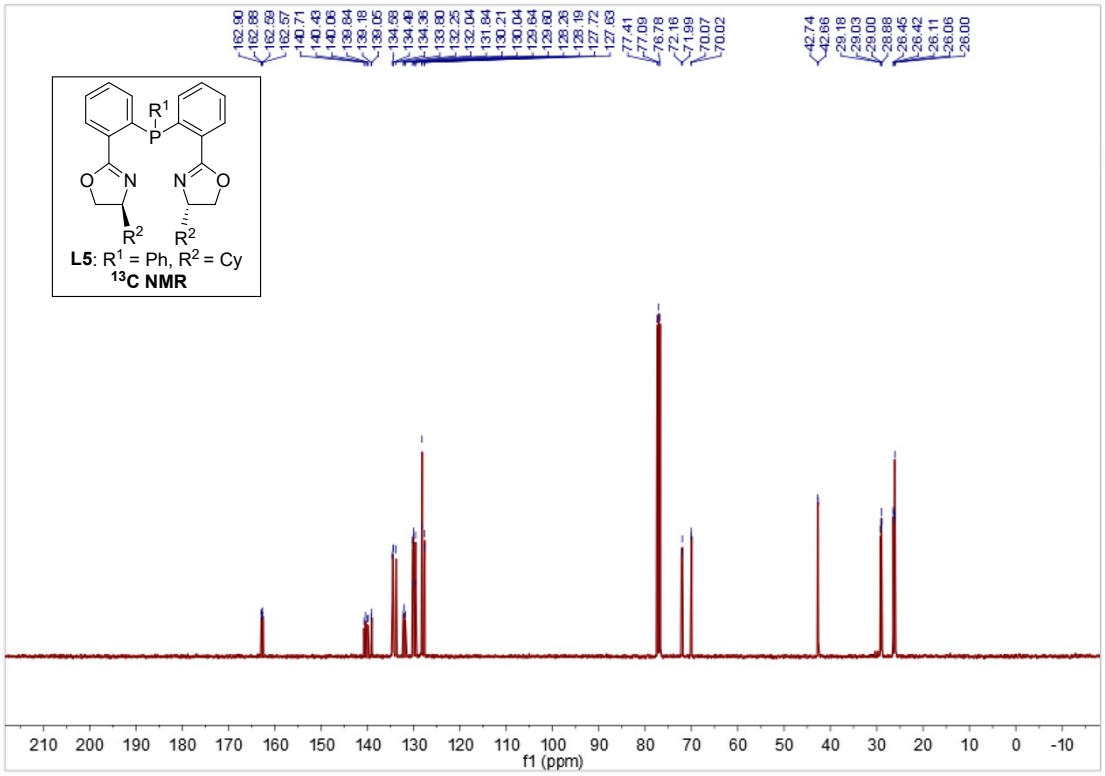
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 2H), 7.35 – 7.20 (m, 9H), 6.95 – 6.92 (m, 1H), 6.89 – 6.87 (m, 1H), 4.22 – 4.10 (m, 2H), 3.99 – 3.79 (m, 4H), 1.63 – 1.54 (m, 8H), 1.34 – 1.31 (m, 2H), 1.19 – 0.98 (m, 8H), 0.78 – 0.70 (m, 4H).

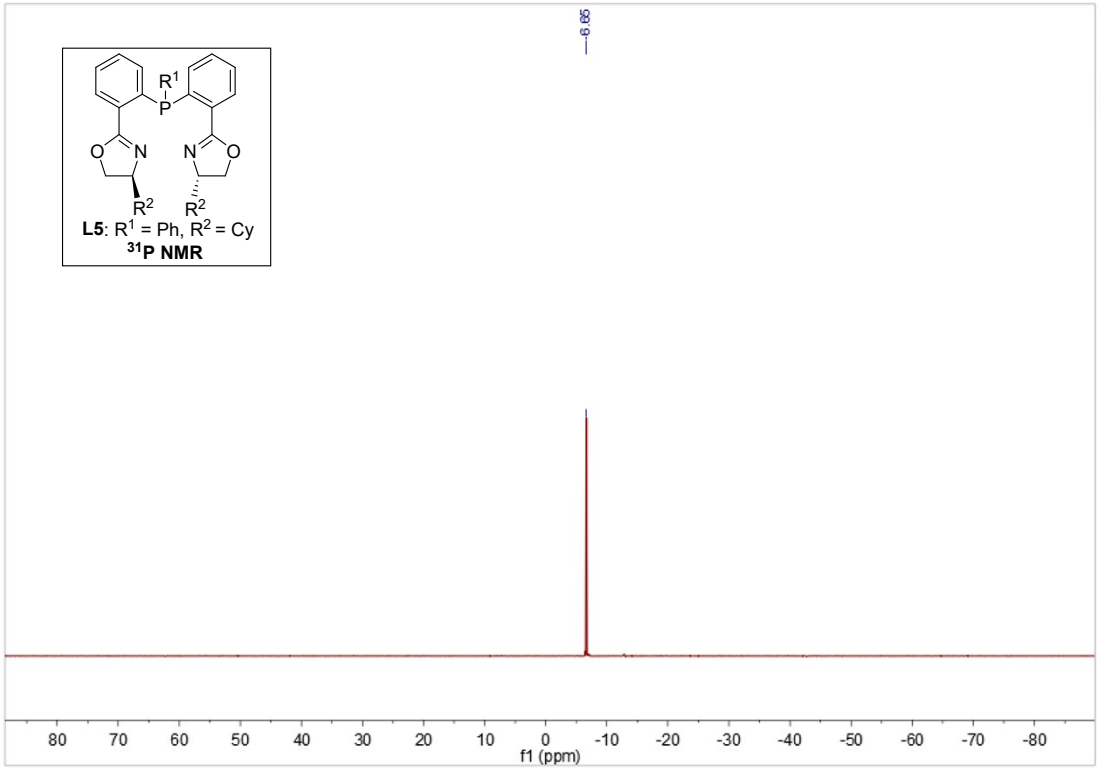
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J = 2.1 Hz), 162.6 (d, J = 2.2 Hz), 140.5 (d, J = 28.6 Hz), 139.9 (d, J = 22.5 Hz), 139.1 (d, J = 13.7 Hz), 134.5, 134.4 (d, J = 12.7 Hz), 133.8, 132.1 (d, J = 20.2 Hz), 131.9 (d, J = 20.3 Hz), 130.1 (d, J = 17.1 Hz), 129.6 (d, J = 3.7 Hz), 129.5, 128.2 (d, J = 7.0 Hz), 127.6 (d, J = 8.9 Hz), 72.1, 71.9, 70.0, 70.0, 42.7, 42.6, 29.1, 29.0, 28.9, 28.8, 26.4, 26.4, 26.1, 26.0, 25.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.6.

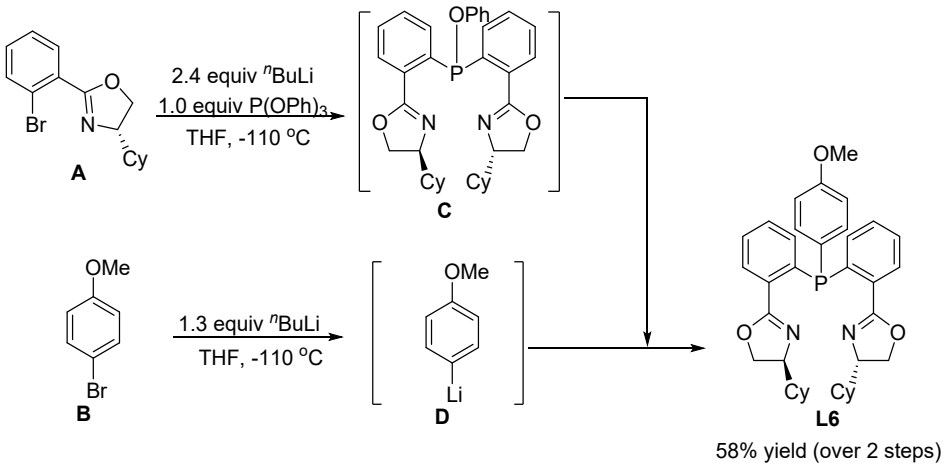
HRMS (ESI): *m/z* calculated for $C_{36}H_{42}N_2O_2P$ $[M + H]^+$ = 565.2978; found 565.2969.




L5: R1 = Ph, R2 = Cy
13C NMR
f1 (ppm)

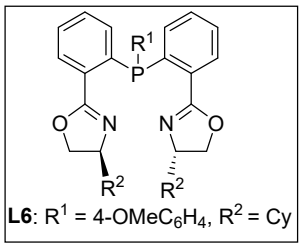

L5: R1 = Ph, R2 = Cy
31P NMR
f1 (ppm)

Method 2:



In a flame dried Shlenk tube, compound **A** (4.4 mmol, 2.2 eq) was dissolved in THF solvent (16 mL) under an argon atmosphere and cooled down to -110 °C. ^{n}BuLi (2.4 eq, 2.5 M in THF) was added dropwise and the mixture was stirred for 1 h at this temperature. The reaction mixture was added triphenylphosphite (2.0 mmol, 1.0 eq) in 2.0 mL of THF in one portion under vigorous stirring. The reaction was slowly warmed up to room temperature and stirred for 5 hours. Phosphinite reaction mixture **C** was used in situ for further substitution to get the desired ligand.

In another flame dried Shlenk tube, lithiation of the substituted benzene was carried out from their corresponding 1-bromo-4-methoxybenzene **B** (2.0 mmol, 1.0 eq) using ^{n}BuLi (1.3 eq) at -110 °C. Then the reaction mixture was added to the phosphinite solution **C** via syringe over 10 minutes. Combined reaction mixture was allowed to warm to room temperature slowly and stirred overnight. The reaction mixture was quenched with water and extracted with ethyl acetate. The solvent was removed and the residue was purified by flash column chromatography on silica gel using petrolium ether/ethyl acetate as eluent to obtain the pure product.



L6: R^1 = 4-OMeC_6H_4, R^2 = Cy

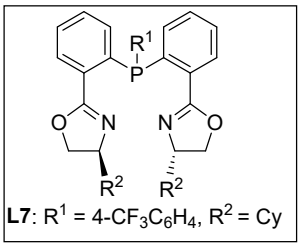
689 mg, 58%, yellow oil, R_f = 0.5 (PE/EA = 5/1), $[\alpha]_D^{25}$ = -22.8 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 2H), 7.34 – 7.20 (m, 6H), 6.97 – 6.90 (m, 2H), 6.86 – 6.84 (m, 2H), 4.20 – 4.09 (m, 2H), 3.94 – 3.83 (m, 4H), 3.79 (s, 3H), 1.69 – 1.54 (m, 8H), 1.35 – 1.32 (m, 2H), 1.17 – 1.00 (m, 8H), 0.91 – 0.68 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 2.2 Hz), 162.7 (d, *J* = 2.5 Hz), 159.9, 140.9 (d, *J* = 27.8 Hz), 140.4 (d, *J* = 22.2 Hz), 136.2, 136.0, 134.2, 133.5, 132.0 (d, *J* = 18.8 Hz), 131.8 (d, *J* = 19.4 Hz), 130.0 (d, *J* = 15.0 Hz), 129.6 (d, *J* = 4.2 Hz), 129.6 (d, *J* = 2.8 Hz), 129.5, 127.5 (d, *J* = 7.3 Hz), 113.9 (d, *J* = 8.5 Hz), 72.1, 71.9, 70.0, 70.0, 55.0, 42.7, 42.6, 29.2, 29.0, 28.9, 28.8, 26.4, 26.4, 26.1, 26.0, 26.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.0.

HRMS (ESI): *m/z* calculated for $C_{37}H_{44}N_2O_3P$ $[M + H]^+$ = 595.3084; found 595.3075.



L7: R^1 = 4-$CF_3C_6H_4$, R^2 = Cy

750 mg, 60%, yellow solid, R_f = 0.5 (PE/EA = 5/1), $[\alpha]_D^{25}$ = -10.4 (*c* = 0.25, $CHCl_3$). m.p. = 61.6-63.2 ℃.

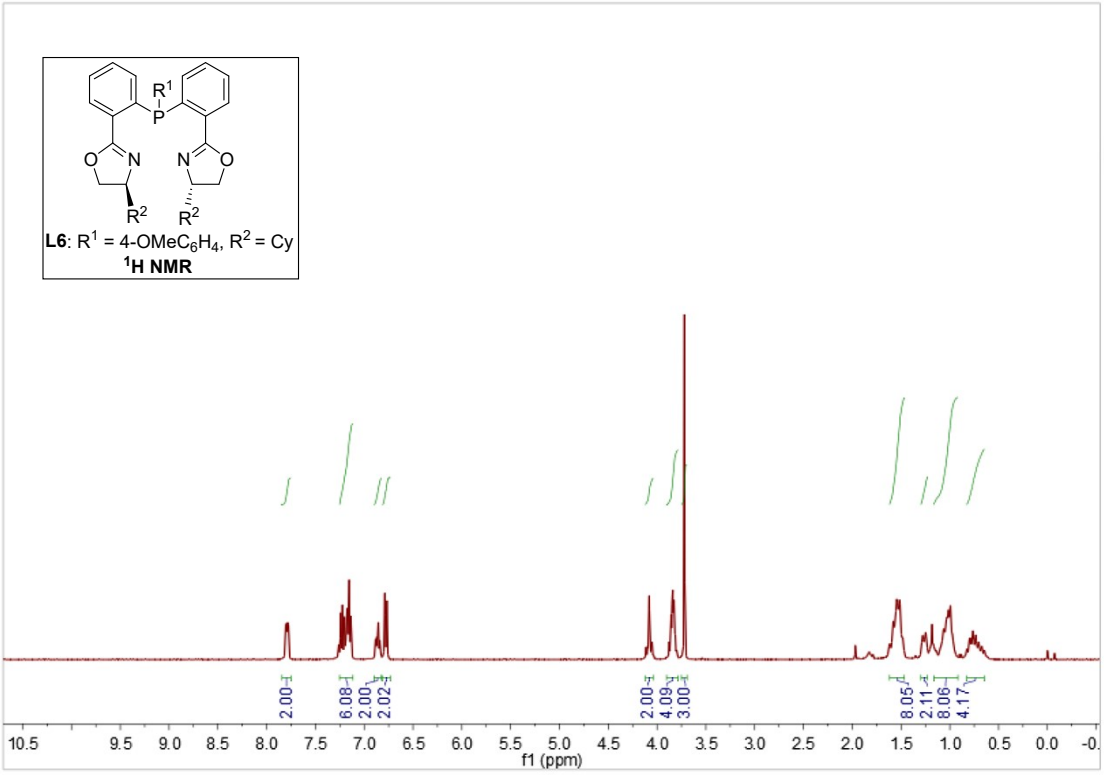
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.53 – 7.51 (m, 2H), 7.40 – 7.32 (m, 4H), 7.27 – 7.23 (m, 2H), 6.93 – 6.90 (m, 1H), 6.86 – 6.79 (m, 1H), 4.23 – 4.14 (m, 2H), 4.00 – 3.83 (m, 4H), 1.58 – 1.56 (m, 6H), 1.48 – 1.45 (m, 2H), 1.33 – 1.20 (m, 2H), 1.15 – 0.98 (m, 8H), 0.83 – 0.73 (m, 2H), 0.70 – 0.57 (m, 2H).

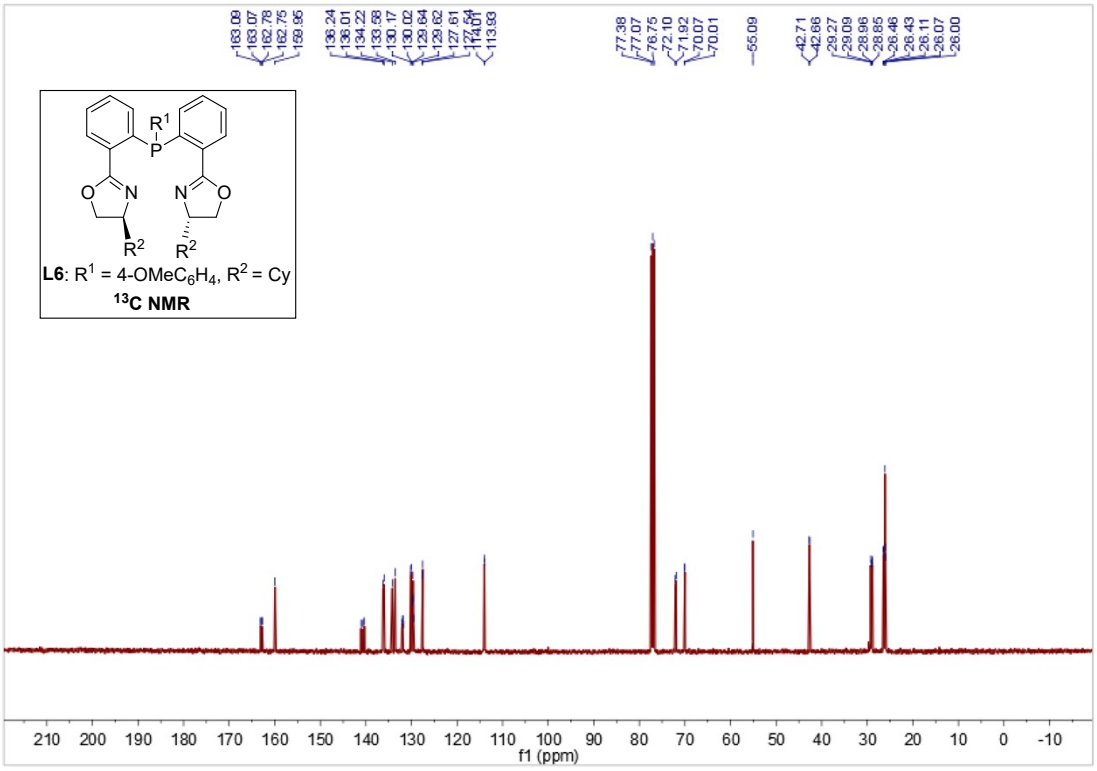
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 2.5 Hz), 162.0 (d, *J* = 3.2 Hz), 145.3 (d, *J* = 17.5 Hz), 139.9 (d, *J* = 29.2 Hz), 139.2 (d, *J* = 21.2 Hz), 134.6, 134.4, 134.2, 133.8, 132.0 (d, *J* = 21.0 Hz), 131.8 (d, *J* = 21.9 Hz), 130.2 (d, *J* = 18.3 Hz), 129.8 (d, *J* = 32.2 Hz), 129.6 (d, *J* = 2.5 Hz), 129.5 (d, *J* = 4.0 Hz), 128.0 (d, *J* = 8.9 Hz), 124.7 (q, *J* = 3.6 Hz), 124.3 (d, *J* = 272.3 Hz), 72.2, 72.1, 70.0, 70.0, 42.8, 42.6, 29.0, 28.9, 28.9, 28.8, 26.3, 26.3, 26.0, 26.0, 25.9.

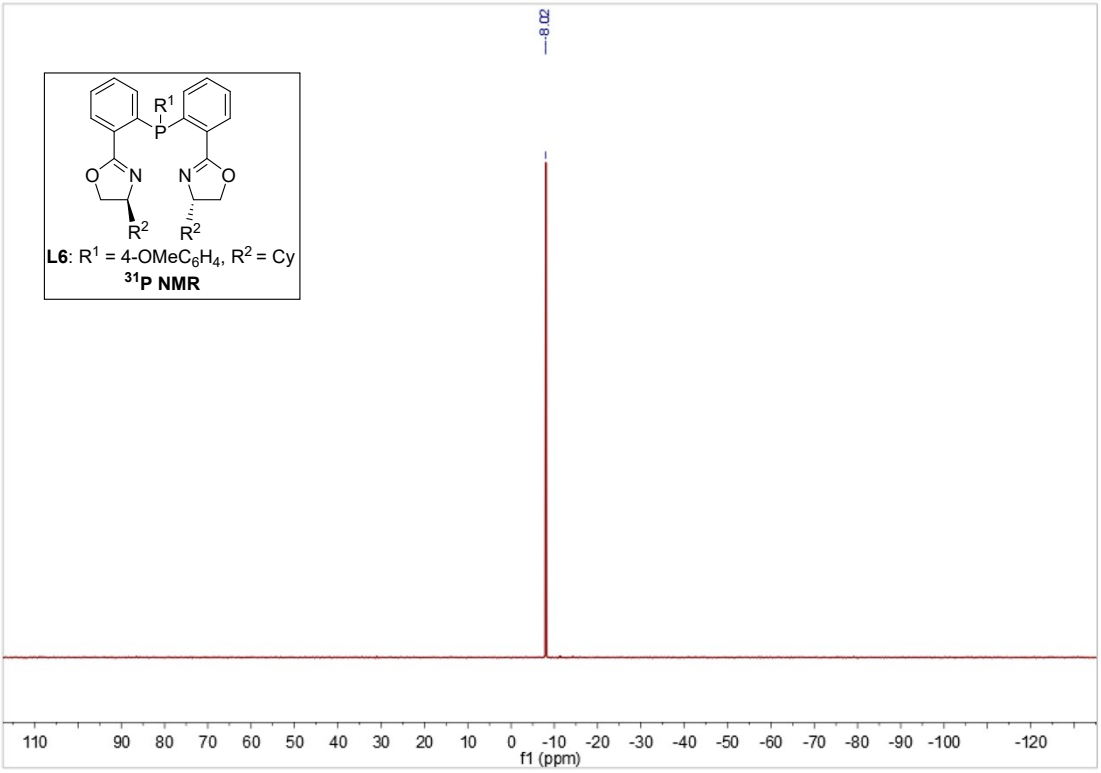
^{31}P NMR (162 MHz, $CDCl_3$) δ -7.6.

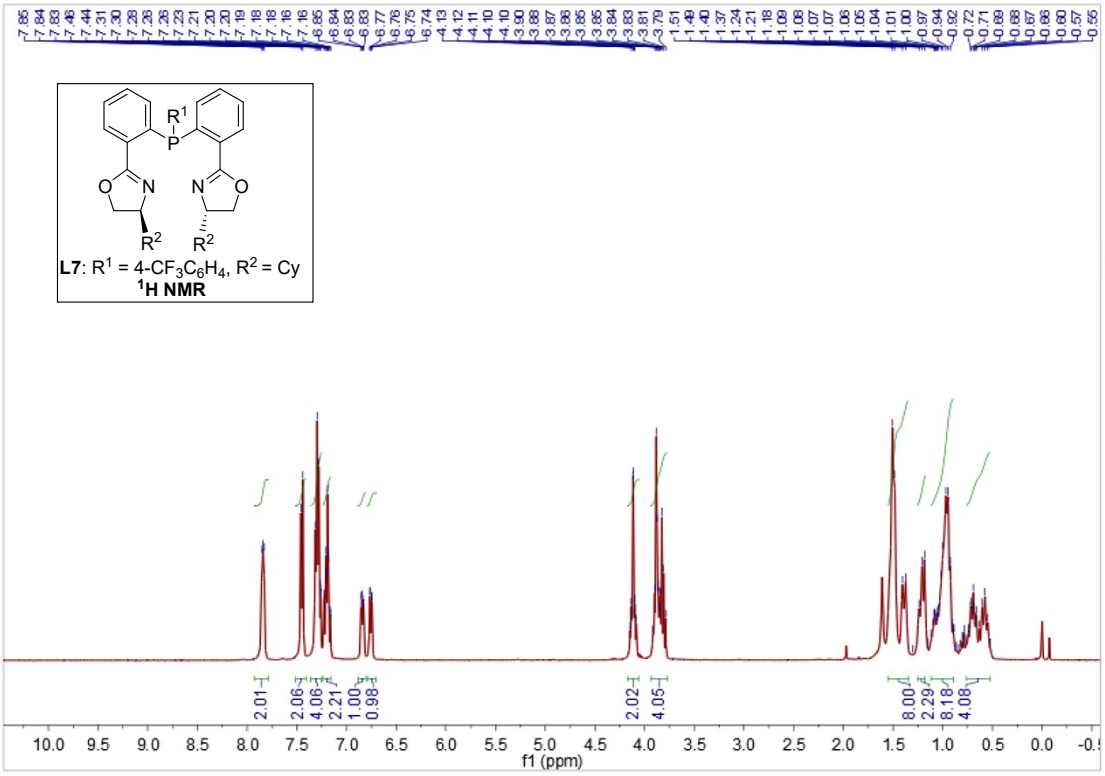
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.5.

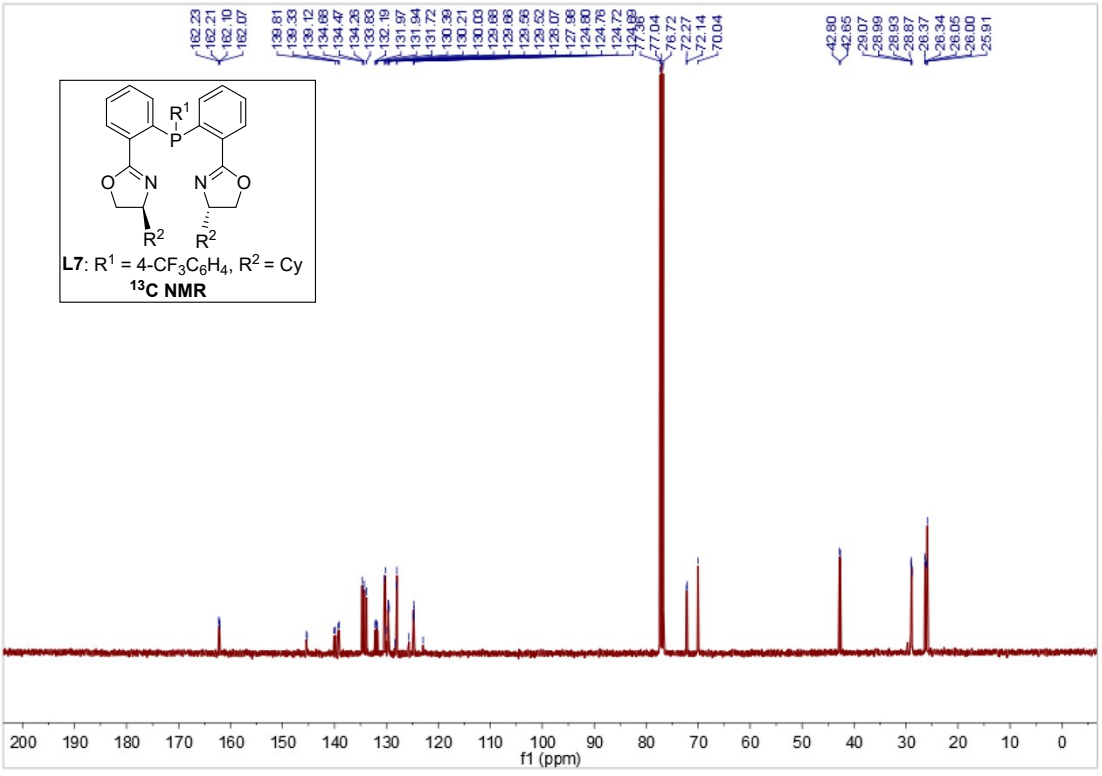
HRMS (ESI): *m/z* calculated for $C_{37}H_{41}F_3N_2O_2P$ $[M + H]^+$ = 633.2852; found 633.2844.

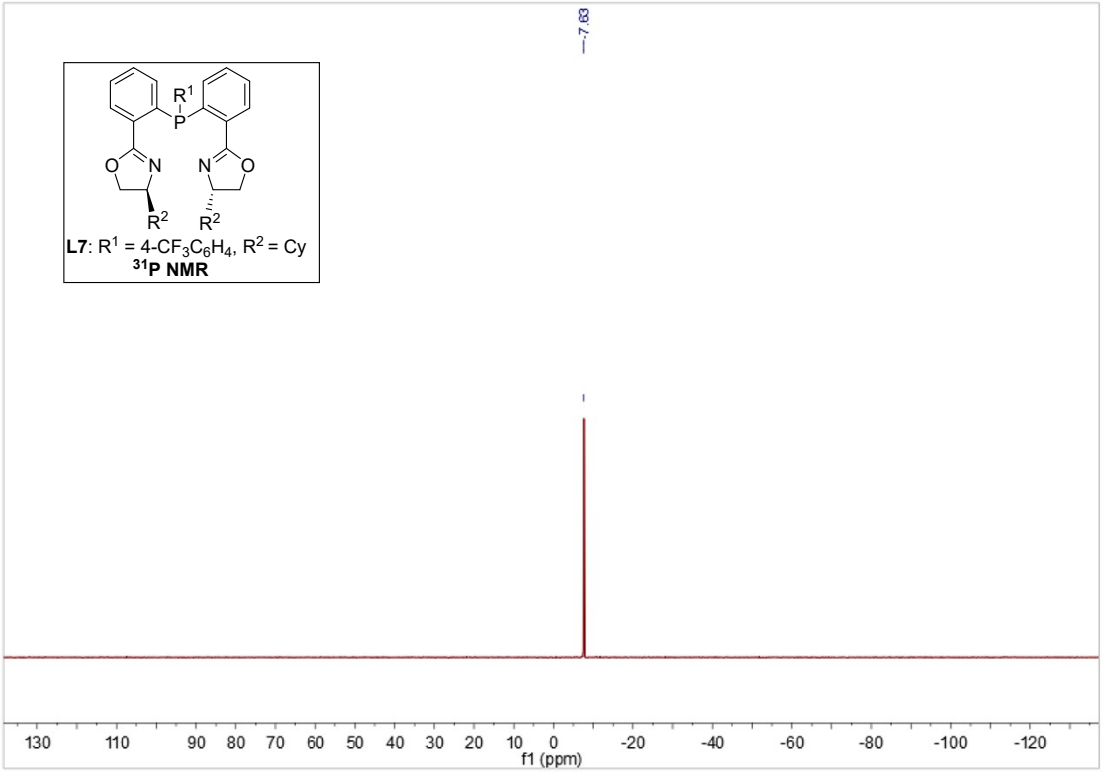



163.09
163.07
162.78
162.75
159.95
136.24
136.01
134.22
133.88
130.17
130.02
129.64
129.62
127.61
127.54
114.01
113.93
77.38
77.07
76.75
72.10
71.92
70.07
70.01
55.09
42.71
42.66
29.27
29.06
28.96
28.85
26.46
26.43
26.11
26.07
26.00
L6: R1 = 4-OMeC6H4, R2 = Cy
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

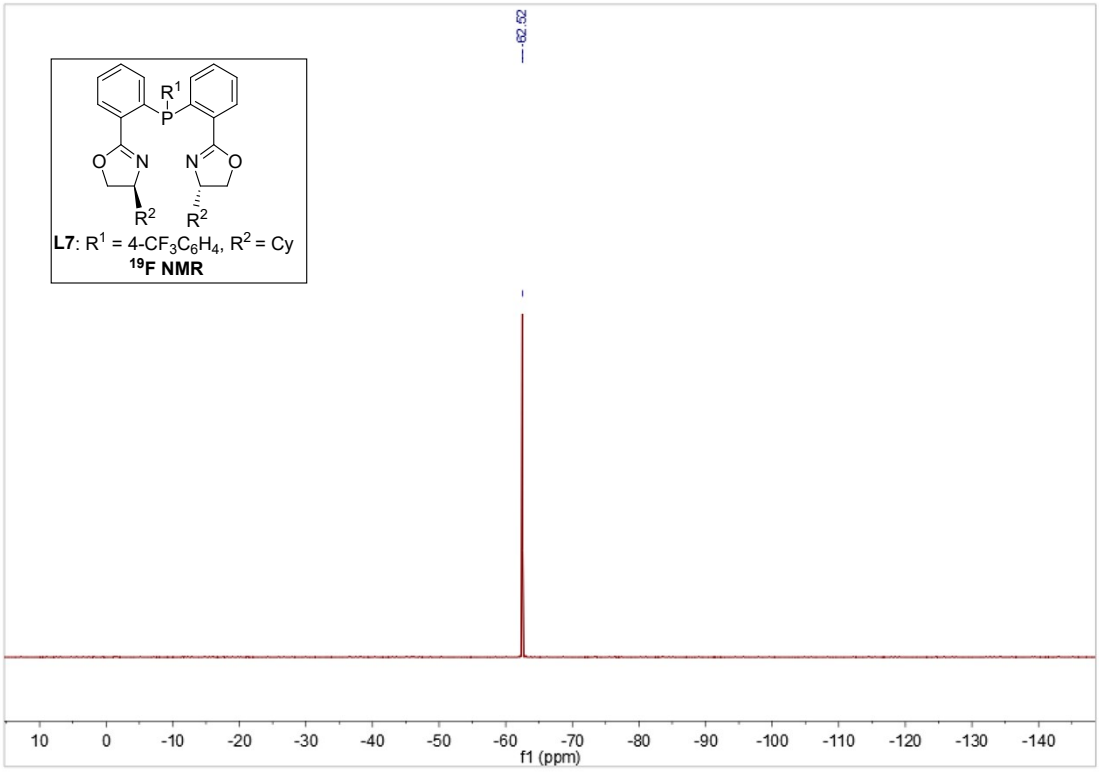

8.02
L6: R1 = 4-OMeC6H4, R2 = Cy
31P NMR
110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120
f1 (ppm)


L7: R1 = 4-CF3C6H4, R2 = Cy
1H NMR
f1 (ppm)


L7: R1 = 4-CF3C6H4, R2 = Cy
13C NMR
f1 (ppm)

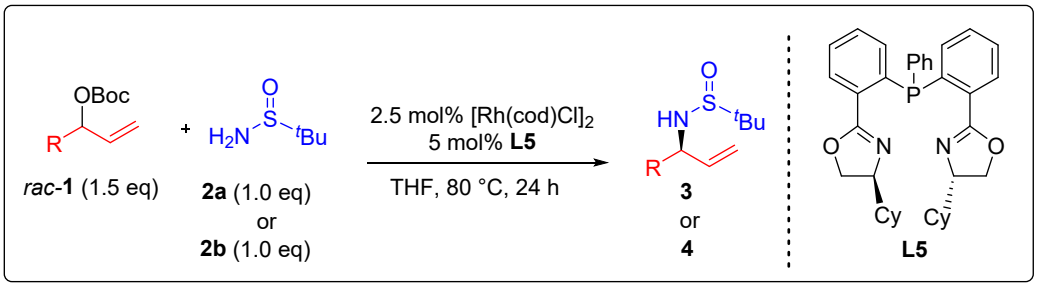


L7: R^1 = 4-$CF_3C_6H_4$, R^2 = Cy
^{31}P NMR



L7: R^1 = 4-$CF_3C_6H_4$, R^2 = Cy
^{19}F NMR

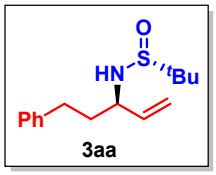
5. General procedure for Rh(I)-catalyzed asymmetric allylation.



In a N_2-filled glovebox, a pressure tube equipped with a magnetic stir bar was charged with $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%), **L5** (5.6 mg, 5.0 mol%), THF (1.0 mL). The reaction mixture was stirred at room temperature for 15 minutes. *rac*-**1** (0.3 mmol, 1.5 eq) and **2a** or **2b** (24.2 mg, 0.2 mmol, 1.0 eq) were added to the above solution. The tube was tightly capped, transferred out of the glovebox and heated at 80 ℃ for 24 hours. After cooling down, the crude mixture was concentrated and the residue was purified by column chromatography to get the corresponding product **3** or **4**.

6. Analytic data for new products.

(*R*)-2-Methyl-N-((*R*)-5-phenylpent-1-en-3-yl)propane-2-sulfinamide (3aa)



3aa

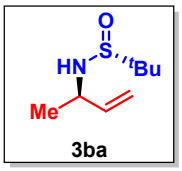
46.5 mg, 88%, colorless oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l = 10:1, $[\alpha]_D^{25}$ = -43.2 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 5.93 – 5.84 (m, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 3.84 – 3.75 (m, 1H), 3.16 (d, *J* = 6.1 Hz, 1H), 2.73 – 2.61 (m, 2H), 2.05 – 1.94 (m, 1H), 1.88 – 1.80 (m, 1H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 139.5, 128.5, 128.4, 126.0, 117.0, 58.2, 55.8, 37.0, 31.8, 22.6.

HRMS (ESI): *m/z* calculated for $C_{15}H_{23}NOS$ $[M + Na]^+$ = 288.1393; found 288.1390.

(*R*)-N-((*R*)-but-3-en-2-yl)-2-methylpropane-2-sulfinamide (3ba)



3ba

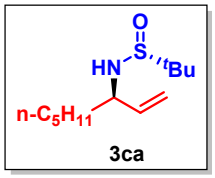
29.1 mg, 83%, colorless oil, R_f = 0.3 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -31.4 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.84 (m, 1H), 5.26 – 5.21 (d, *J* = 16.0 Hz, 1H), 5.11 (d, *J* = 10.3, 1H), 4.01 – 3.85 (m, 1H), 3.18 (d, *J* = 3.6 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 115.3, 55.4, 53.3, 22.5, 21.1.

HRMS (ESI): *m/z* calculated for $C_8H_{17}NOS$ $[M + Na]^+$ = 198.0923; found 198.0919.

(*R*)-2-Methyl-N-((*R*)-oct-1-en-3-yl)propane-2-sulfinamide (3ca)



3ca

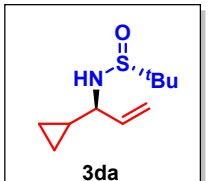
41.3 mg, 90%, colorless oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l = 10:1, $[\alpha]_D^{25}$ = -51.6 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.78 (m, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.3 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.09 (d, *J* = 5.6 Hz, 1H), 1.69 – 1.62 (m, 1H), 1.54 – 1.46 (m, 1H), 1.39 – 1.25 (m, 6H), 1.22 (s, 9H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 116.3, 58.7, 55.7, 35.2, 31.4, 25.1, 22.6, 22.5, 14.0.

HRMS (ESI): *m/z* calculated for $C_{12}H_{25}NOS$ $[M + Na]^+$ = 254.1549; found 254.1544.

(*R*)-N-((*S*)-1-cyclopropylallyl)-2-methylpropane-2-sulfinamide (3da)



3da

36.0 mg, 90%, yellow oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -65.6 (*c* = 0.25, $CHCl_3$).

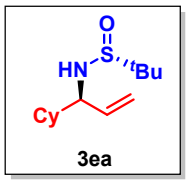
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.85 (m, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.13

(d, J = 10.3 Hz, 1H), 3.30 (d, J = 4.4 Hz, 1H), 3.20 – 3.06 (m, 1H), 1.21 (s, 9H), 0.95 – 0.84 (m, 1H), 0.66 – 0.59 (m, 1H), 0.55 – 0.48 (m, 1H), 0.45 – 0.40 (m, 1H), 0.24 – 0.18 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 116.1, 62.5, 55.5, 22.5, 15.6, 4.7, 2.4.

HRMS (ESI): *m/z* calculated for $C_{10}H_{19}NOS$ $[M + Na]^+$ = 224.1080; found 224.1076.

(*R*)-N-((*S*)-1-cyclohexylallyl)-2-methylpropane-2-sulfinamide (3ea)



3ea

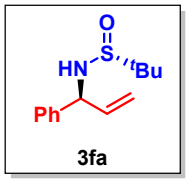
36.9 mg, 76%, yellow oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l = 4:1, $[\alpha]_D^{25}$ = -28.3 (c = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.80 (m, 1H), 5.25 (d, J = 1.1 Hz, 1H), 5.20 (d, J = 1.0 Hz, 1H), 3.57 – 3.52 (m, 1H), 3.08 (d, J = 7.4 Hz, 1H), 1.79 – 1.62 (m, 6H), 1.52 – 1.49 (m, 1H), 1.23 (s, 9H), 1.22 – 1.19 (m, 2H), 1.14 – 1.07 (m, 1H), 1.03 – 0.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 117.1, 64.2, 56.0, 42.3, 29.1, 28.7, 26.5, 26.1, 26.1, 22.7.

HRMS (ESI): *m/z* calculated for $C_{13}H_{25}NOS$ $[M + Na]^+$ = 266.1549; found 266.1543.

(*R*)-2-Methyl-N-((*S*)-1-phenylallyl)propane-2-sulfinamide (3fa)



3fa

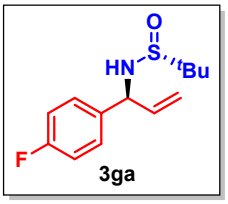
34.0 mg, 72%, yellow oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -33.6 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 6.07 – 6.02 (m, 1H), 5.30 (d, J = 17.0 Hz, 1H), 5.20 (d, J = 10.2 Hz, 1H), 4.99 – 4.96 (m, 1H), 3.49 (d, J = 1.6 Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 139.3, 128.6, 127.8, 127.8, 116.6, 61.6, 55.7, 22.6.

HRMS (ESI): *m/z* calculated for $C_{13}H_{19}NOS$ $[M + Na]^+$ = 260.1080; found 260.1075.

(*R*)-N-((*S*)-1-(4-fluorophenyl)allyl)-2-methylpropane-2-sulfinamide (3ga)



3ga

40.3 mg, 80%, colorless oil, R_f = 0.3 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -41.0 (c = 0.5, $CHCl_3$).

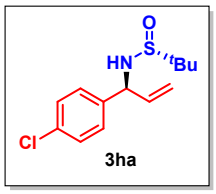
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.06 – 7.01 (m, 2H), 6.06 – 5.07 (m, 1H), 5.28 (d, J = 17.0 Hz, 1H), 5.21 (d, J = 10.2 Hz, 1H), 4.97 (dd, J = 6.6, 3.0 Hz, 1H), 3.49 (d, J = 2.4 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 246.3 Hz), 139.1, 136.0 (d, J = 3.0 Hz), 129.4 (d, J = 8.1 Hz), 116.8, 115.5 (d, J = 21.3 Hz), 60.7, 55.7, 22.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.4.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}FNOS$ $[M + Na]^+$ = 278.0985; found 278.0987.

(*R*)-N-((*S*)-1-(4-chlorophenyl)allyl)-2-methylpropane-2-sulfinamide (3ha)



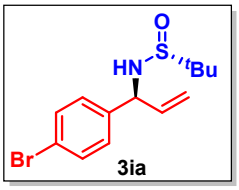
36.8 mg, 68%, colorless solid, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -35.4 (*c* = 0.5, $CHCl_3$). m.p. = 82.4-83.0 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 6.04 – 5.96 (m, 1H), 5.28 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.96 (dd, *J* = 6.6, 2.9 Hz, 1H), 3.48 (d, *J* = 2.1 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.8, 133.6, 129.2, 128.8, 117.0, 60.8, 55.8, 22.5.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}ClNOS$ $[M + Na]^+$ = 294.0690; found 294.0685.

(*R*)-N-((*S*)-1-(4-bromophenyl)allyl)-2-methylpropane-2-sulfinamide (3ia)



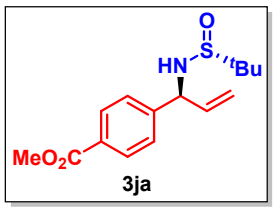
39.6 mg, 63%, yellow solid, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -38.0 (*c* = 0.5, $CHCl_3$). m.p. = 104.2-104.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.04 – 5.95 (m, 1H), 5.28 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.94 (dd, *J* = 6.4, 2.7 Hz, 1H), 3.47 (d, *J* = 1.4 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.7, 131.7, 129.5, 121.8, 117.1, 60.8, 55.8, 22.5.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}BrNOS$ $[M + Na]^+$ = 338.0185; found 338.0187.

Methyl 4-((*S*)-1-(((*R*)-tert-butylsulfinyl)amino)allyl)benzoate (3ja)



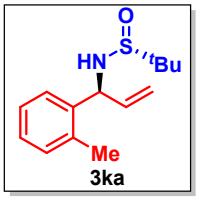
46.8 mg, 80%, yellow solid, R_f = 0.3 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -29.2 (*c* = 0.25, $CHCl_3$). m.p. = 97.7-98.0 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.07 – 6.00 (m, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.05 – 5.03 (m, 1H), 3.91 (s, 3H), 3.54 (d, *J* = 2.2 Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.5, 138.5, 129.9, 129.7, 127.8, 117.4, 61.2, 55.9, 52.1, 22.6.

HRMS (ESI): *m/z* calculated for $C_{15}H_{21}NOS$ $[M + Na]^+$ = 318.1134; found 318.1133.

(*R*)-2-Methyl-N-((*S*)-1-(o-tolyl)allyl)propane-2-sulfinamide (3ka)



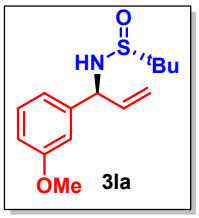
41.1 mg, 82%, colorless oil, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -29.2 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 1H), 7.24 – 7.11 (m, 3H), 6.08 – 6.00 (m, 1H), 5.25 – 5.18 (m, 3H), 3.48 (d, *J* = 2.3 Hz, 1H), 2.39 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.2, 136.2, 130.6, 127.5, 127.3, 126.2, 116.7, 57.5, 55.7, 22.6, 19.4.

HRMS (ESI): *m/z* calculated for $C_{15}H_{21}NOS$ $[M + Na]^+$ = 318.1134; found 318.1133.

(*R*)-N-((*S*)-1-(3-methoxyphenyl)allyl)-2-methylpropane-2-sulfinamide (3la)



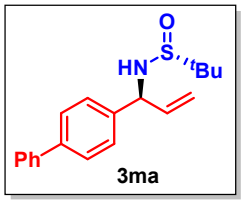
42.2 mg, 79%, yellow oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -51.3 (*c* = 0.6, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.97 – 6.86 (m, 2H), 6.85 – 6.80 (m, 1H), 6.07 – 5.99 (m, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 4.96 – 4.93 (m, 1H), 3.80 (s, 3H), 3.48 (d, *J* = 3.3 Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 143.1, 138.1, 129.9, 119.4, 117.5, 113.2, 112.9, 61.4, 55.7, 55.2, 22.7.

HRMS (ESI): *m/z* calculated for $C_{14}H_{21}NO_2S$ $[M + Na]^+$ = 290.1185; found 290.1181.

(*R*)-N-((*S*)-1-([1,1'-biphenyl]-4-yl)allyl)-2-methylpropane-2-sulfinamide (3ma)



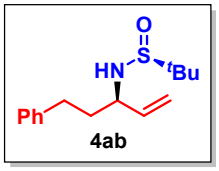
55.5 mg, 89%, yellow solid, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = -44.0 (*c* = 0.25, $CHCl_3$). m.p. = 157.7-157.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 4H), 7.45 – 7.40 (m, 4H), 7.36 – 7.32 (m, 1H), 6.12 – 6.04 (m, 1H), 5.33 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.02 (dd, *J* = 6.3, 3.3 Hz, 1H), 3.52 (d, *J* = 2.7 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.6, 139.4, 139.2, 128.7, 128.2, 127.3, 127.1, 116.7, 61.3, 55.8, 22.6.

HRMS (ESI): *m/z* calculated for $C_{19}H_{23}NOS$ $[M + Na]^+$ = 336.1393; found 336.1386.

(*S*)-2-Methyl-N-((*R*)-5-phenylpent-1-en-3-yl)propane-2-sulfinamide (4ab)



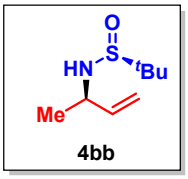
48.7 mg, 92%, colorless oil, R_f = 0.5 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +44.4 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.80 – 5.62 (m, 1H), 5.38 – 5.17 (m, 2H), 3.89 – 3.77 (m, 1H), 3.16 (d, *J* = 2.6 Hz, 1H), 2.79 – 2.57 (m, 2H), 1.96 – 1.86 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 138.8, 128.5, 128.4, 126.0, 117.5, 58.0, 55.4, 37.9, 31.8, 22.5.

HRMS (ESI): *m/z* calculated for $C_{15}H_{23}NOS$ $[M + Na]^+$ = 288.1393; found 288.1390.

(*S*)-N-((*R*)-but-3-en-2-yl)-2-methylpropane-2-sulfinamide (4bb)



4bb

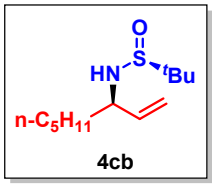
29.1 mg, 83%, colorless oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +33.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.70 (m, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 4.11 – 3.87 (m, 1H), 3.06 (d, *J* = 4.0 Hz, 1H), 1.35 (t, *J* = 10.0 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 115.5, 55.4, 53.6, 22.8, 22.5.

HRMS (ESI): *m/z* calculated for $C_8H_{17}NOS$ $[M + Na]^+$ = 198.0923; found 198.0919.

(*S*)-2-Methyl-N-((*R*)-oct-1-en-3-yl)propane-2-sulfinamide (4cb)



4cb

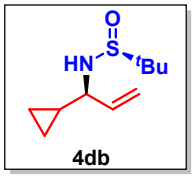
42.2 mg, 91%, colorless oil, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +50.4 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 – 5.59 (m, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 3.83 – 3.73 (m, 1H), 3.10 (s, 1H), 1.63 – 1.50 (m, 2H), 1.35 – 1.29 (m, 6H), 1.21 (s, 9H), 0.88 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 117.0, 58.2, 55.3, 36.4, 31.5, 25.2, 22.6, 22.5, 14.0.

HRMS (ESI): *m/z* calculated for $C_{12}H_{25}NOS$ $[M + Na]^+$ = 254.1549; found 254.1545.

(*S*)-N-((*S*)-1-cyclopropylallyl)-2-methylpropane-2-sulfinamide (4db)



4db

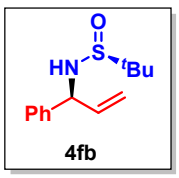
37.9 mg, 94%, colorless oil, R_f = 0.5 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +74.0 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.75 (m, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.3 Hz, 1H), 3.31 (s, 1H), 3.10 – 2.97 (m, 1H), 1.23 (s, 9H), 1.01 – 0.95 (m, 1H), 0.64 – 0.56 (m, 2H), 0.44 – 0.38 (m, 1H), 0.35 – 0.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 116.6, 62.9, 55.3, 22.6, 17.2, 4.3, 3.5.

HRMS (ESI): *m/z* calculated for $C_{10}H_{19}NOS$ $[M + Na]^+$ = 224.1080; found 224.1078.

(*S*)-2-Methyl-N-((*S*)-1-phenylallyl)propane-2-sulfinamide (4fb)



4fb

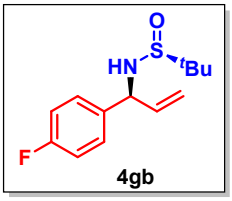
46.5 mg, 95%, yellow oil, R_f = 0.5 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +66.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 4H), 7.32 – 7.24 (m, 1H), 5.99 – 5.83 (m, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 4.98 – 4.96 (m, 1H), 3.47 (s, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 138.3, 128.9, 128.0, 127.1, 117.5, 61.5, 55.6, 22.7.

HRMS (ESI): *m/z* calculated for $C_{13}H_{19}NOS$ [M + Na]$^+$ = 260.1080; found 260.1074.

(*S*)-N-((*S*)-1-(4-fluorophenyl)allyl)-2-methylpropane-2-sulfinamide (4gb)



25.9 mg, 51%, yellow oil, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +48.4 (*c* = 0.5, $CHCl_3$).

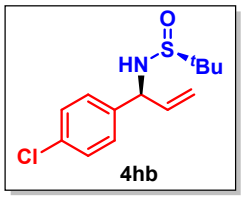
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.06 – 7.02 (m, 2H), 5.99 – 5.81 (m, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.96 (dd, *J* = 7.2, 2.3 Hz, 1H), 3.42 (d, *J* = 4.0 Hz,1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.8 Hz), 138.1, 137.3 (d, *J* = 3.1 Hz), 128.9 (d, *J* = 8.2 Hz), 117.6, 115.7 (d, *J* = 21.4 Hz), 60.8, 55.7, 22.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.0.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}FNOS$ [M + Na]$^+$ = 278.0985; found 278.0982.

(*S*)-N-((*S*)-1-(4-chlorophenyl)allyl)-2-methylpropane-2-sulfinamide (4hb)



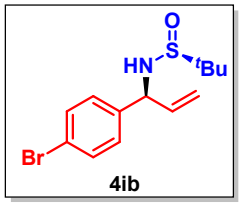
45.7 mg, 84%, yellow solid, R_f = 0.7 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +80.0 (*c* = 0.5, $CHCl_3$). m.p. = 60.7-61.0 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 5.94 – 5.85 (m, 1H), 5.37 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.95 (dd, *J* = 7.1, 2.2 Hz, 1H), 3.43 (d, *J* = 2.0 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 137.8, 133.8, 129.0, 128.6, 117.8, 60.9, 55.7, 22.6.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}ClNOS$ [M + Na]$^+$ = 294.0690; found 294.0690.

(*S*)-N-((*S*)-1-(4-bromophenyl)allyl)-2-methylpropane-2-sulfinamide (4ib)



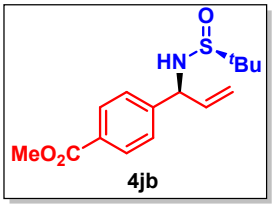
44.0 mg, 88%, yellow solid, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +70.6 (*c* = 0.5, $CHCl_3$). m.p. = 100.1-100.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.93 – 5.85 (m, 1H), 5.37 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.94 – 4.93 (m, 1H), 3.43 (d, *J* = 4.0 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 137.7, 132.0, 128.9, 121.9, 117.9, 60.9, 55.7, 22.6.

HRMS (ESI): *m/z* calculated for $C_{13}H_{18}BrNOS$ [M + Na]$^+$ = 338.0185; found 338.0184.

Methyl 4-((*S*)-1-(((*S*)-tert-butylsulfinyl)amino)allyl)benzoate (4jb)



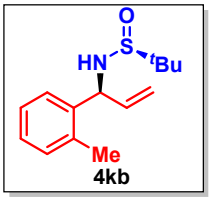
55.0 mg, 93%, colorless oil, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +51.2 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.96 – 5.87 (m, 1H), 5.39 (d, *J* = 17.0 Hz, 2H), 5.28 (d, *J* = 10.1 Hz, 2H), 5.03 (dd, *J* = 7.3, 2.5 Hz, 1H), 3.91 (s, 1H), 3.53 (d, *J* = 4.0 Hz, 1H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 146.3, 137.6, 130.2, 129.8, 127.2, 118.2, 61.3, 55.8, 52.1, 22.6.

HRMS (ESI): *m/z* calculated for $C_{15}H_{21}NOS$ $[M + Na]^+$ = 318.1134; found 318.1132.

(*S*)-2-Methyl-N-((*S*)-1-(o-tolyl)allyl)propane-2-sulfinamide (4kb)



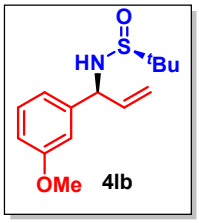
44.0 mg, 88%, colorless oil, R_f = 0.6 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +43.2 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 1H), 7.25 – 7.12 (m, 3H), 5.91 – 5.82 (m, 1H), 5.37 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 5.20 – 5.18 (m, 1H), 3.41 (d, *J* = 4.0 Hz, 1H), 2.40 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.6, 135.7, 130.9, 127.7, 126.5, 117.5, 57.1, 55.6, 22.7, 19.3.

HRMS (ESI): *m/z* calculated for $C_{14}H_{21}NOS$ $[M + Na]^+$ = 274.1232; found 274.1236.

(*S*)-N-((*S*)-1-(3-methoxyphenyl)allyl)-2-methylpropane-2-sulfinamide (4lb)



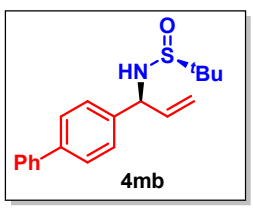
43.8 mg, 82%, colorless oil, R_f = 0.4 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +57.1 (*c* = 0.7, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.97 – 6.91 (m, 2H), 6.85 – 6.82 (m, 1H), 5.96 – 5.87 (m, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 4.95 – 4.93 (m, 1H), 3.81 (s, 3H), 3.48 (s, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 142.0, 139.2, 129.6, 120.1, 116.7, 113.3, 113.2, 61.6, 55.8, 55.2, 22.6.

HRMS (ESI): *m/z* calculated for $C_{14}H_{21}NO_2S$ $[M + Na]^+$ = 290.1185; found 290.1190.

(*S*)-N-((*S*)-1-([1,1'-biphenyl]-4-yl)allyl)-2-methylpropane-2-sulfinamide (4mb)



49.0 mg, 78%, yellow oil, R_f = 0.5 (PE/EA = 1/1), dr > 20:1, b/l > 20:1, $[\alpha]_D^{25}$ = +42.0 (*c* = 0.25, $CHCl_3$).

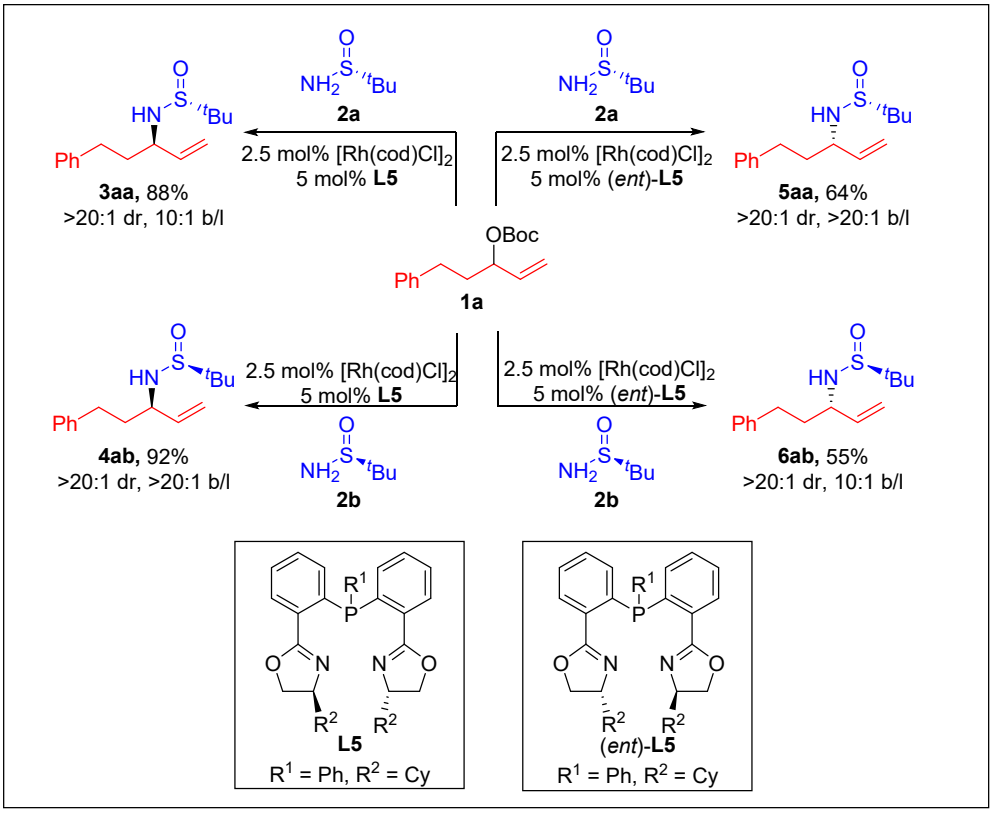
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 4H), 7.46 – 7.40 (m, 4H), 7.36 – 7.34 (m, 1H), 6.01 – 5.92 (m, 1H), 5.42 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* =

10.1 Hz, 1H), 5.02 (d, J = 6.0 Hz, 1H), 3.51 (d, J = 4.0 Hz, 1H),1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.6, 140.5, 138.2, 128.8, 127.6, 127.6, 127.4, 127.1, 117.6, 60.8, 55.7, 22.7.

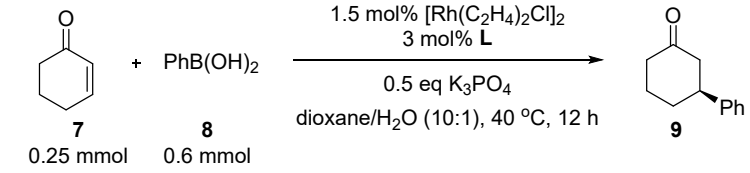
HRMS (ESI): *m/z* calculated for $C_{19}H_{23}NOS$ $[M + Na]^+$ = 336.1393; found 336.1392.

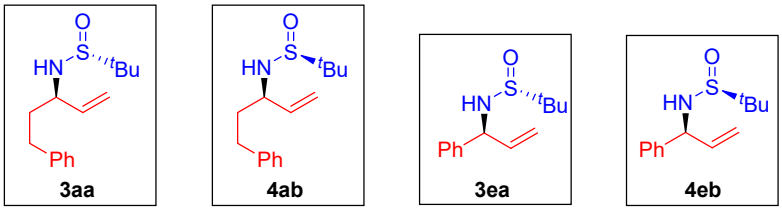
7. Stereodivergent synthesis of all four stereoisomers.



In a N_2-filled glovebox, a pressure tube equipped with a magnetic stir bar was charged with $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%), **L5** or (*ent*)-**L5** (5.6 mg, 5.0 mol%) and THF (1.0 mL). The reaction mixture was stirred at room temperature for 15 minutes. **1a** (78.6 mg, 0.3 mmol, 1.5 eq) and **2a** or **2b** (24.2 mg, 0.2 mmol, 1.0 eq) were added to the above solution. The tube was tightly capped, transferred out of the glovebox and heated at 80 °C for 24 hours. After cooling down, the crude mixture was concentrated and the residue was purified by column chromatography to get the corresponding product.

8. Synthetic applications.





entry	Ligand	Yield	*ee*
1	**3aa**	96%	53%
2	**4ab**	93%	-87%
3	**3ea**	97%	-80%
4	**4eb**	95%	80%

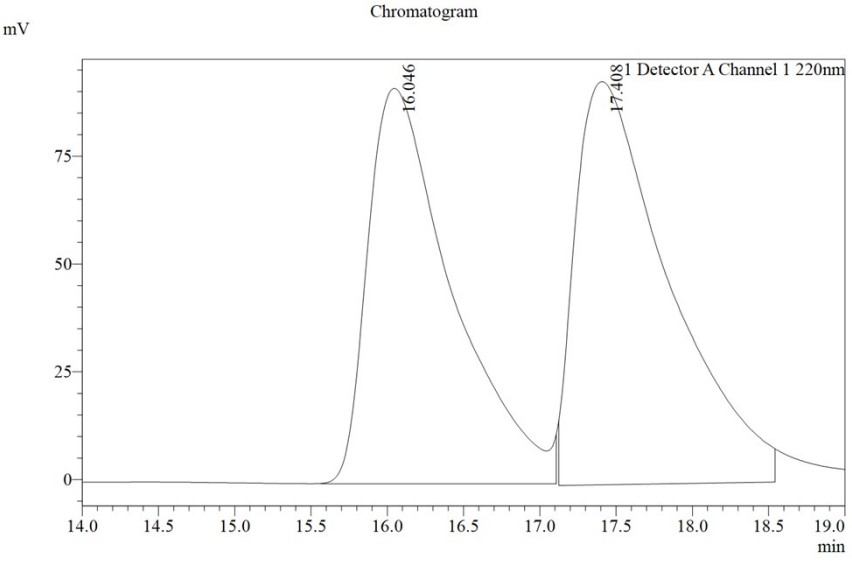
General procedure: A pressure tube equipped with a magnetic stir bar was charged with $[Rh(C_2H_4)_2Cl]_2$ (1.5 mg, 1.5 mol%), **L** (3.0 mol%). The tube was purged with argon for 3 minutes. Dioxane (0.5 mL) and H_2O (0.05 mL) were added, followed by the 2-cyclohexen-1-one (24.0 mg, 0.25 mmol，1.0 equiv.), phenylboronic acid (73.2 mg, 0.6 mmol，2.4 equiv.) and K_3PO_4 (26.5 mg, 0.5 equiv.). The tube was sealed with a PTFE lined cap and was stirred in an oil bath at 40 ℃ for 12 hours. After cooled down, the crude reaction mixture was directly subjected to flash column chromatography.

(*S*)-3-phenylcyclohexan-1-one (9) 40.5 mg, 93%, colorless oil, R_f = 0.4 (PE/EA = 20/1).

The NMR data was reported according to the literature[5].

HPLC (Shimadzu LC-2030) (Daicel Chiralcel® OD-H Column, ^{i}PrOH : Hexane = 1.0 : 99.0, 1.0 ml/min), 40 ˚C, 220 nm, R*t* = 15.801 min (major) and 17.319 min (minor), 93.3 : 6.7 *er*.

Chromatogram

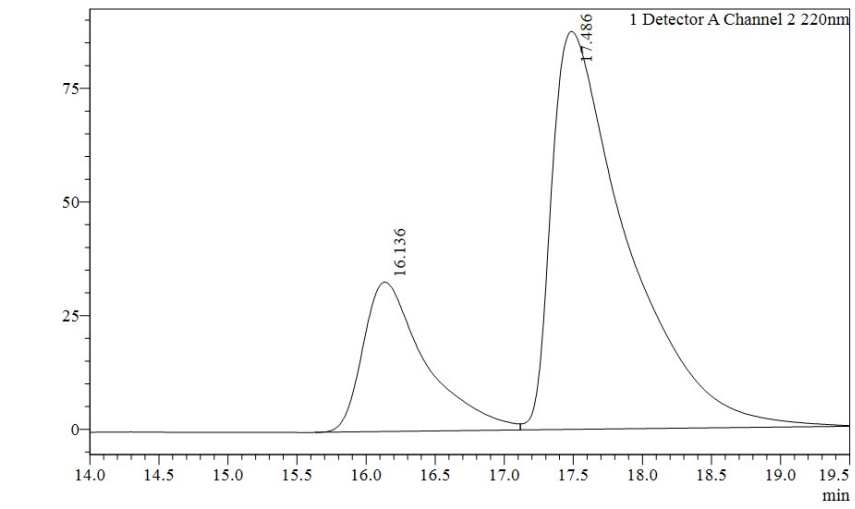


Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	16.046	3531054	91640	47.052
2	17.408	3973454	93441	52.948
Total		7504508	185081	100.000

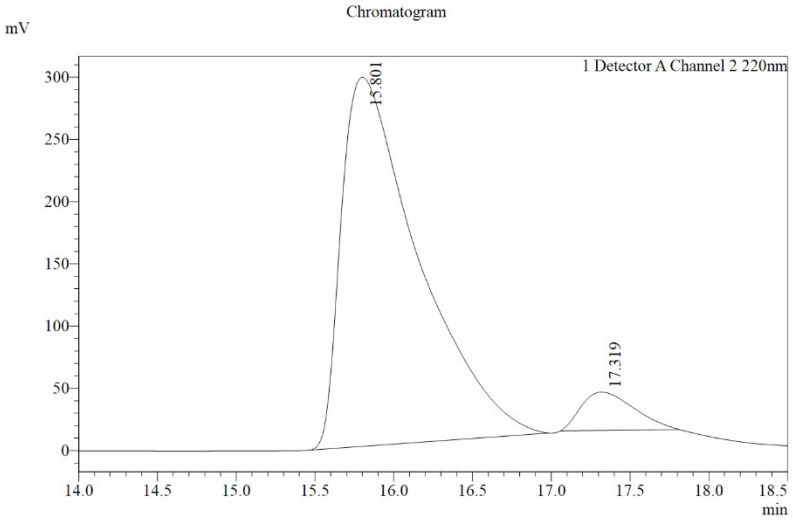
Chromatogram



Peak Table

Detector A Channel 2 220nm

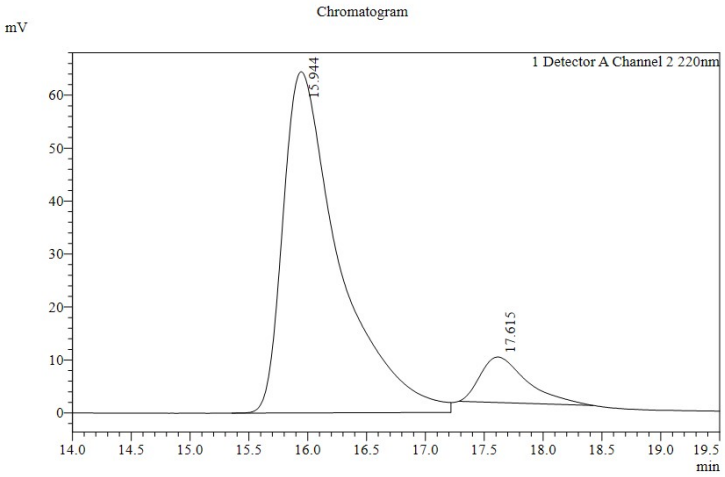
Peak#	Ret. Time	Area	Height	Area%
1	16.136	1037177	32889	23.702
2	17.486	3338725	87559	76.298
Total		4375902	120448	100.000



Peak Table

Detector A Channel 2 220nm

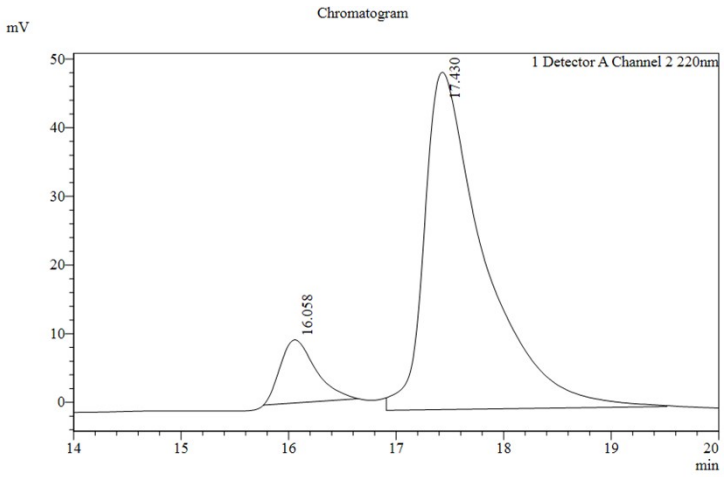
Peak#	Ret. Time	Area	Height	Area%
1	15.801	10118693	296630	93.325
2	17.319	723716	30852	6.675
Total		10842409	327483	100.000



Peak Table

Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%
1	15.944	2143391	64425	90.021
2	17.615	237601	8573	9.979
Total		2380992	72998	100.000

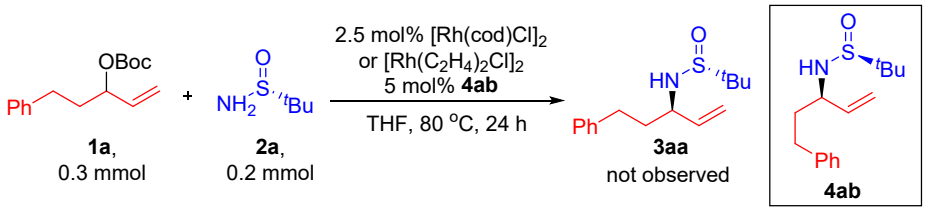


Peak Table

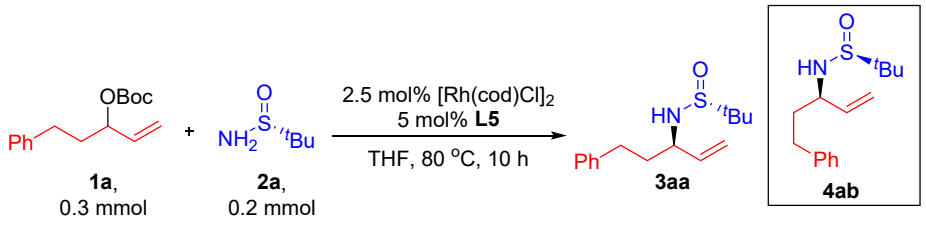
Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%
1	16.058	210628	9185	9.944
2	17.430	1907497	49110	90.056
Total		2118125	58294	100.000

9. The inhibition effect of allylic tert-butanesulfinamide.



In a N_2-filled glovebox, a pressure tube equipped with a magnetic stir bar was charged with $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%) or $[Rh(C_2H_4)_2Cl]_2$ (1.9 mg, 2.5 mol%), **4ab** (2.7 mg, 5.0 mol%), THF (1.0 mL). The reaction mixture was stirred at room temperature for 15 minutes. **1a** (78.6 mg, 0.3 mmol, 1.5 eq) and **2a** (24.2 mg, 0.2 mmol, 1.0 eq) were added to the above solution. The tube was tightly capped, transferred out of the glovebox and heated at 80 ℃ for 24 hours. **3aa** was not observed.

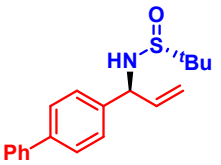


without additive	57%, >20:1 dr, 10:1 b/l	(eq 1)
with 20 mol% **4ab**	39%, >20:1 dr, 10:1 b/l	(eq 2)

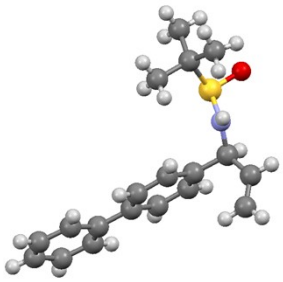
In a N_2-filled glovebox, a pressure tube equipped with a magnetic stir bar was charged with $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%), **L5** (5.6 mg, 5.0 mol%), THF (1.0 mL). The reaction mixture was stirred at room temperature for 15 minutes. **1a** (78.6 mg, 0.3 mmol, 1.5 eq) and **2a** (24.2 mg, 0.2 mmol, 1.0 eq) were added to the above solution. The tube was tightly capped, transferred out of the glovebox and heated at 80 ℃ for 10 hours. After cooling down, the crude mixture was concentrated and the residue was purified by column chromatography to get **3aa** (57% yield, 30.2 mg, > 20:1 dr, 10:1 b/l).

In a N_2-filled glovebox, a pressure tube equipped with a magnetic stir bar was charged with $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%), **L5** (5.6 mg, 5.0 mol%), **4ab** (10.6 mg, 20.0 mol%), THF (1.0 mL). The reaction mixture was stirred at room temperature for 15 minutes. **1a** (78.6 mg, 0.3 mmol, 1.5 eq) and **2a** (24.2 mg, 0.2 mmol, 1.0 eq) were added to the above solution. The tube was tightly capped, transferred out of the glovebox and heated at 80 ℃ for 10 hours. After cooling down, the crude mixture was concentrated and the residue was purified by column chromatography to get **3aa** (39% yield, 20.7 mg, > 20:1 dr, 10:1 b/l).

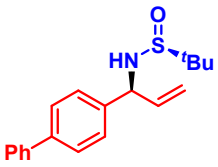
10. Single crystal X-ray diffraction data.



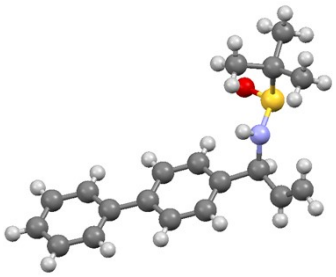
CCDC 2341377



Empirical formula	$C_{19}H_{23}NOS$
Formula weight	313.44
CCDC Number	2341377
Crystal habit, colour	colourless
Crystal size, mm^3	0.220 x 0.200 x 0.180
Temperature, K	173(2)
Wavelength, λ (Å)	1.54178
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	*a* = 5.7083(3) Å alpha = 90 deg
	b = 17.0851(9) Å beta = 90 deg
	c = 17.0851(9) Å gamma = 90 deg
Volume, *V* ($Å^3$)	1666.26(15)
Z	4
Calculated density, $mg \cdot m^{-3}$	1.249
Absorption coefficient, μ (mm^{-1})	1.721
F(000)	672
θ range for data collection	3.659 to 68.286 deg.
Limiting indices	-6≤h≤6, -20≤k≤20, -17≤l≤20
Reflection collected/unique	24611 / 3036 [R(int) = 0.0354]
Completeness to θ	67.679 99.8 %
Absolute structure parameter	0.034(4)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3036 / 0 / 202
Goodness–of–fit on F^2	1.009
Final *R* indices [*I*>2sigma(*I*)]	*R1 = 0.0312, wR2 = 0.0883*
R indices (all data)	*R1 = 0.0318, wR2 = 0.0888*
Largest diff. peak and hole	0.354 and -0.285 $e \cdot Å^{-3}$

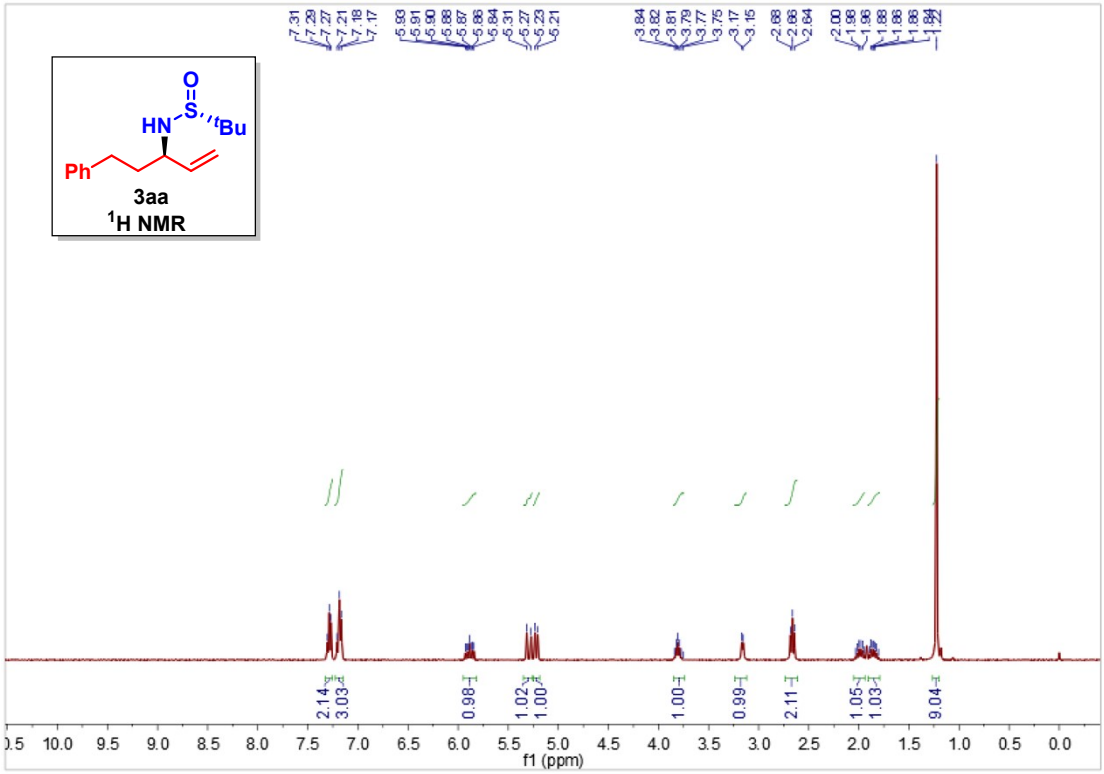


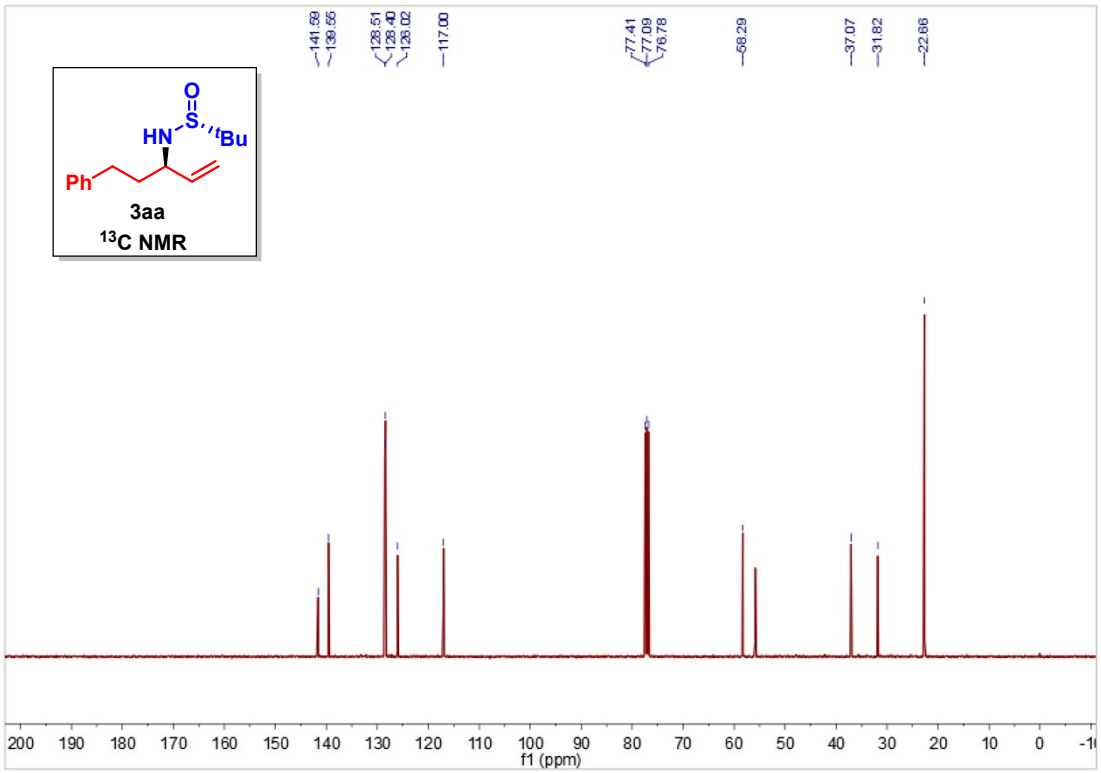
CCDC 2341379

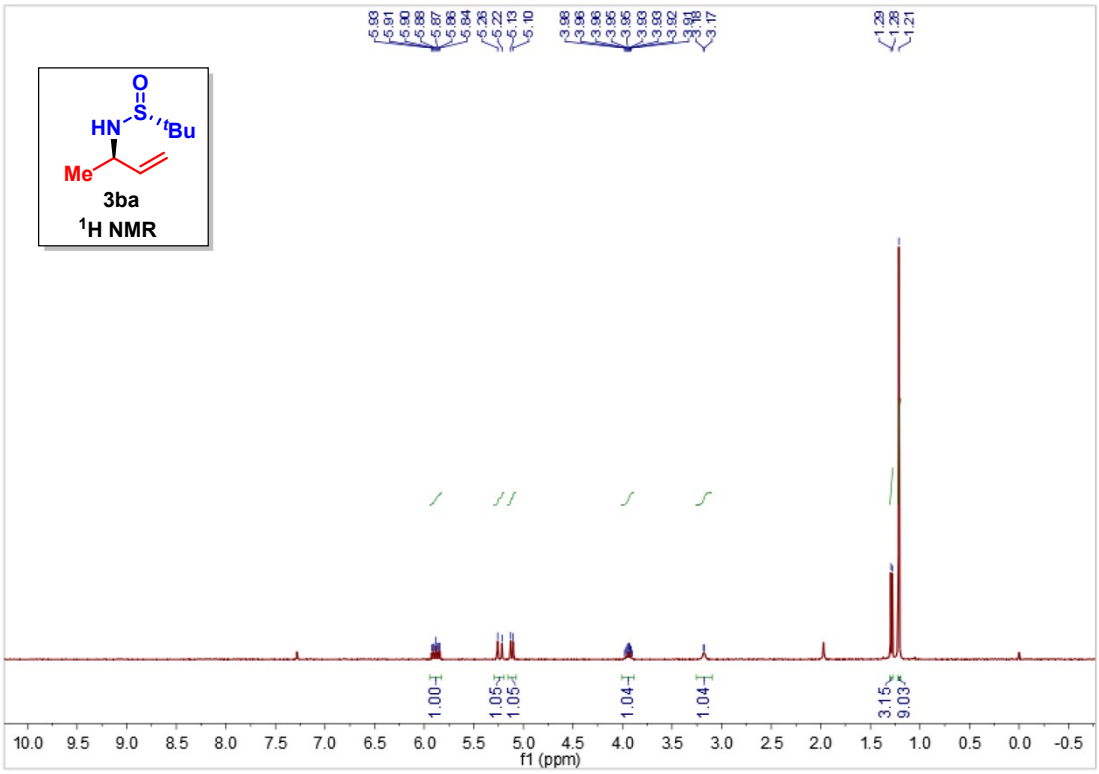


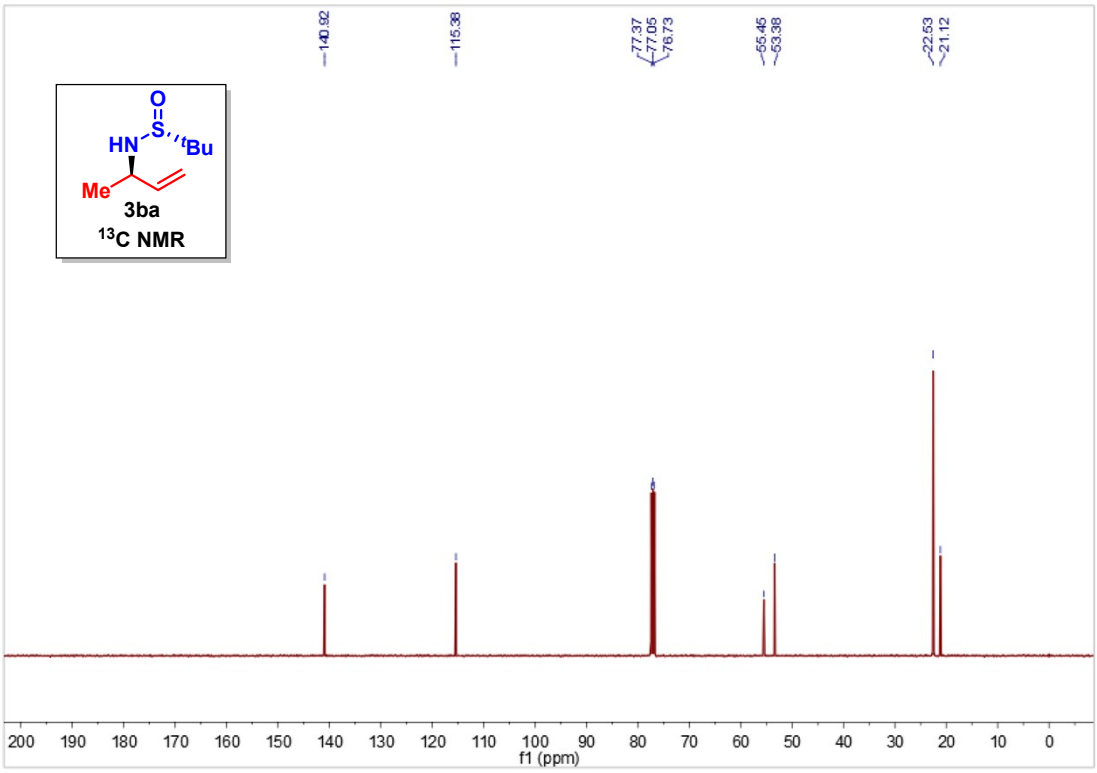
Empirical formula	$C_{19}H_{23}NOS$
Formula weight	313.44
CCDC Number	2341379
Crystal habit, colour	colourless
Crystal size, mm^3	0.180 x 0.160 x 0.140
Temperature, K	100(2)
Wavelength, λ (Å)	1.54184
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	*a* = 5.52328(9) Å alpha = 90 deg
	b = 10.30853(16) Å beta = 90 deg
	c = 28.9172(5) Å gamma = 90 deg
Volume, *V* ($Å^3$)	1646.46(5)
Z	4
Calculated density, $mg \cdot m^{-3}$	1.264
Absorption coefficient, μ (mm^{-1})	1.742
F(000)	672
θ range for data collection	3.056 to 75.259 deg.
Limiting indices	-6≤h≤6, -9≤k≤12, -35≤l≤35
Reflection collected/unique	8412 / 3084 [R(int) = 0.0288]
Completeness to θ	67.684 100.0 %
Absolute structure parameter	0.011(12)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3084 / 0 / 205
Goodness–of–fit on F^2	1.034
Final *R* indices [*I*>2sigma(*I*)]	*R1 = 0.0318, wR2 = 0.0864*
R indices (all data)	*R1 = 0.0331, wR2 = 0.0874*
Largest diff. peak and hole	0.205 and -0.273 $e \cdot Å^{-3}$

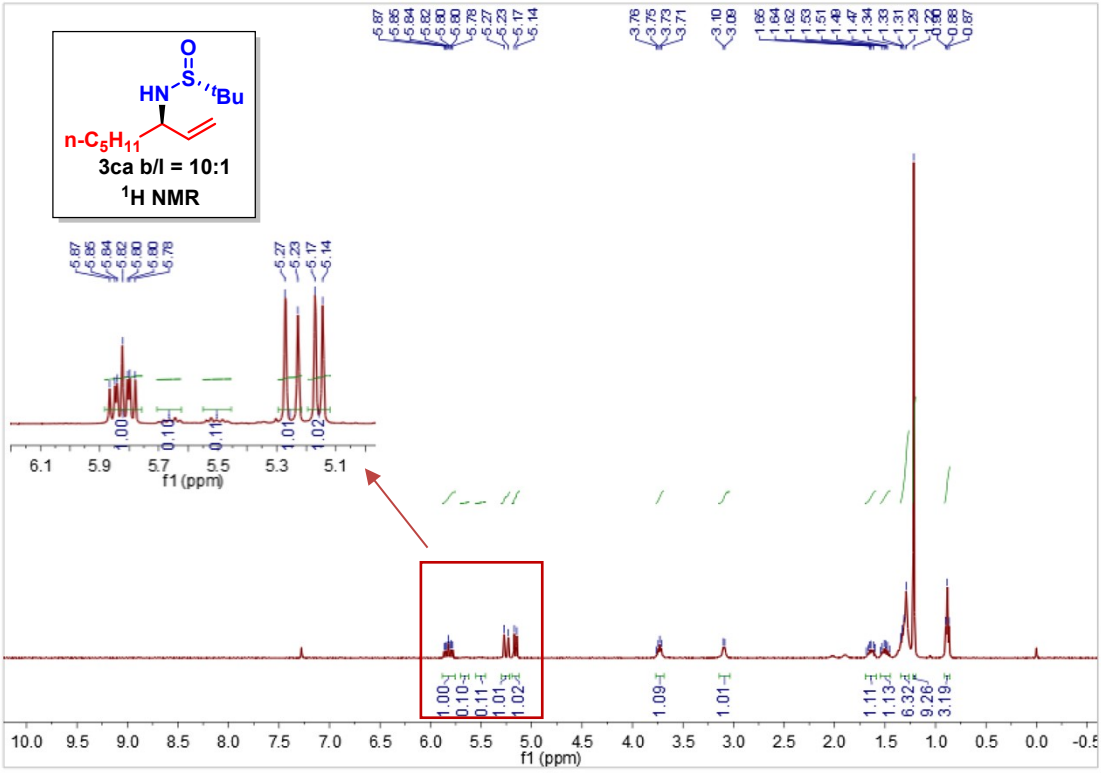
11. NMR spectra of new compounds.

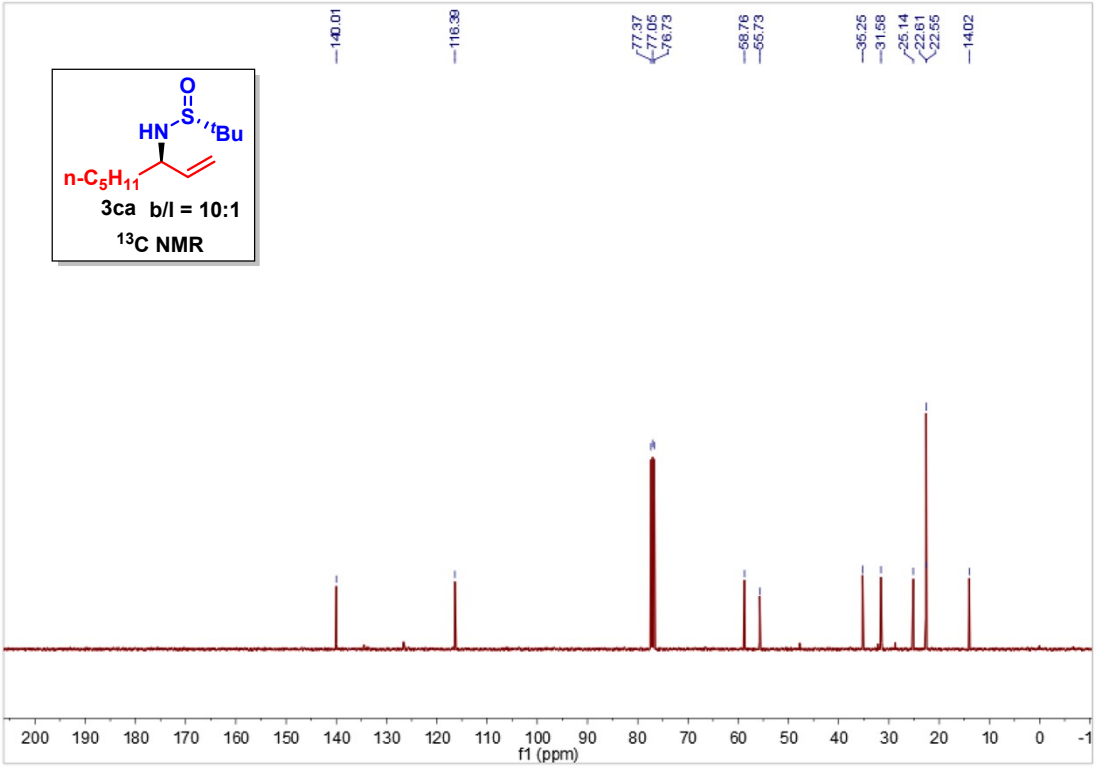


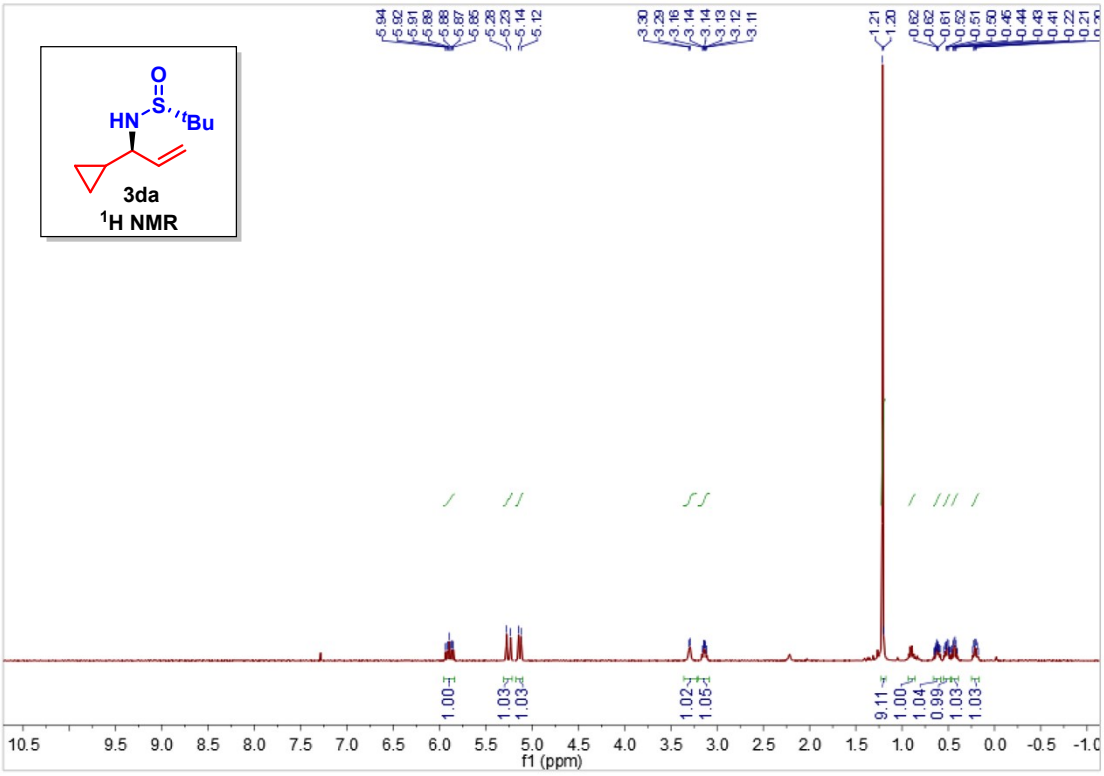


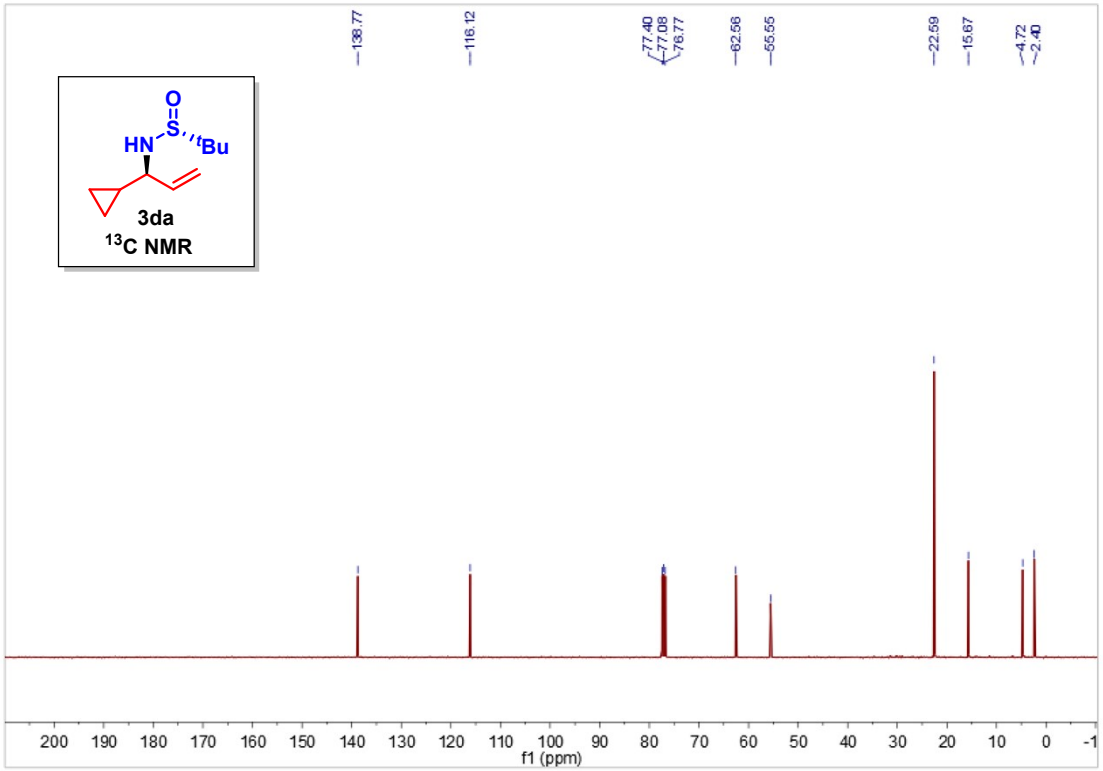

3ba
1H NMR
f1 (ppm)

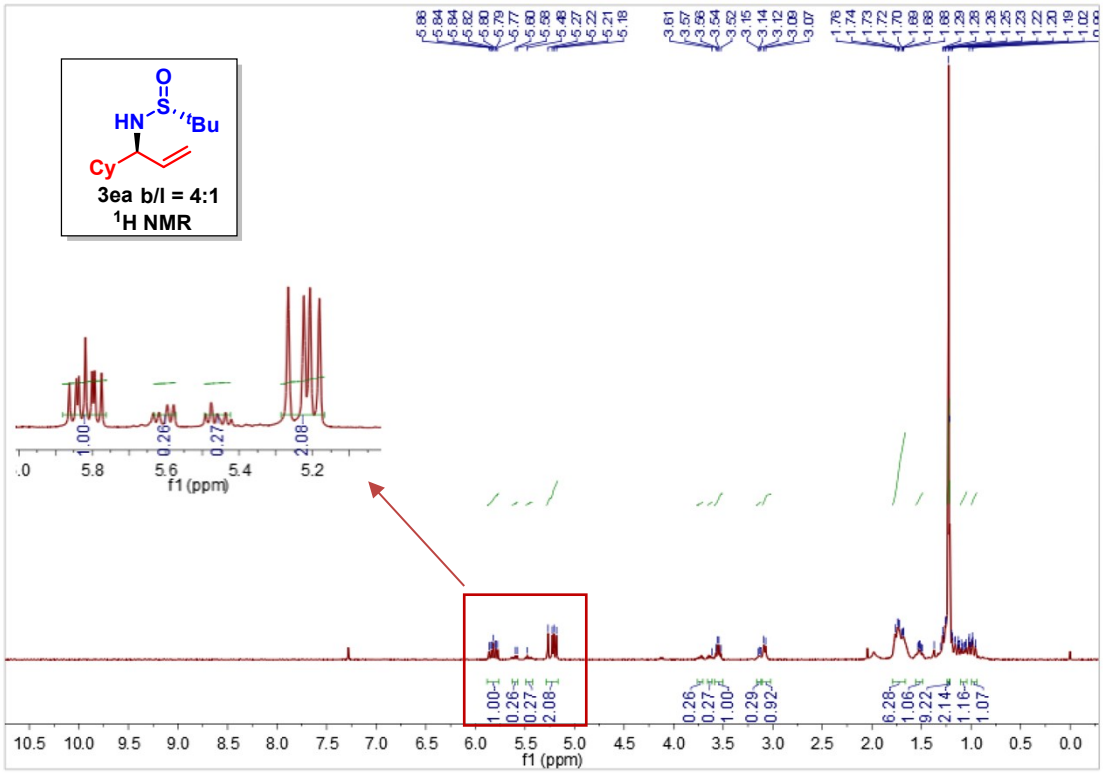

3ba
13C NMR
f1 (ppm)


3ca b/l = 10:1
1H NMR
f1 (ppm)

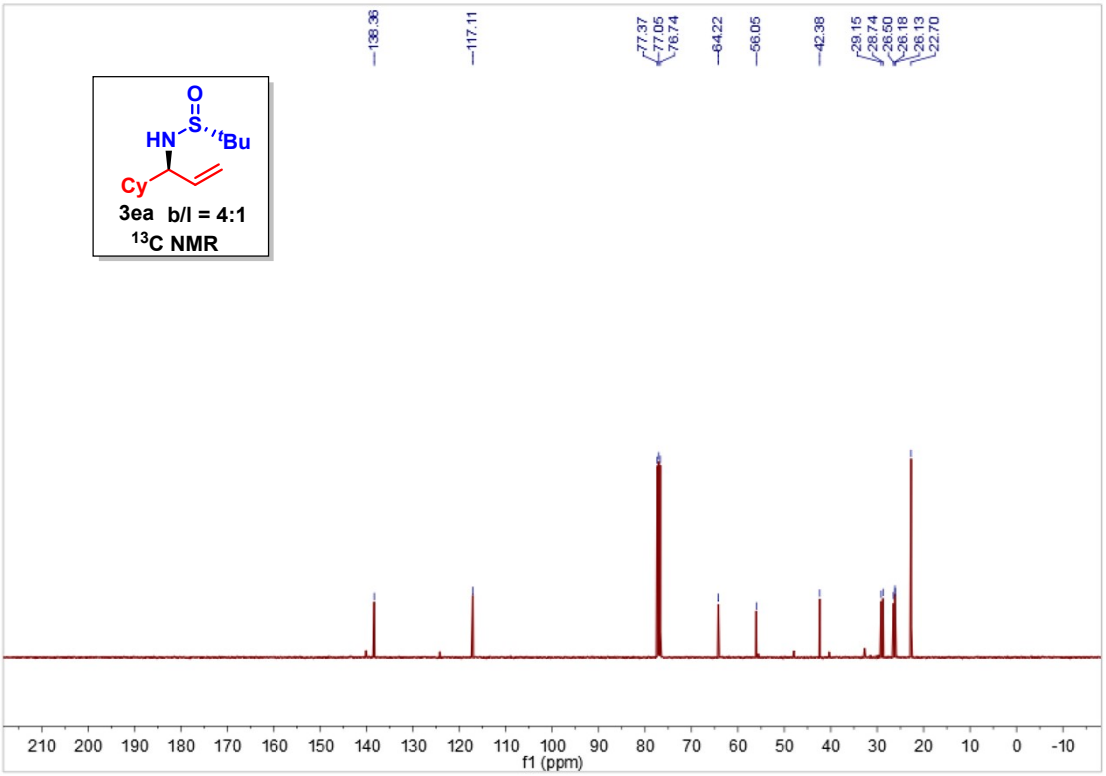

3ca b/l = 10:1
13C NMR
f1 (ppm)

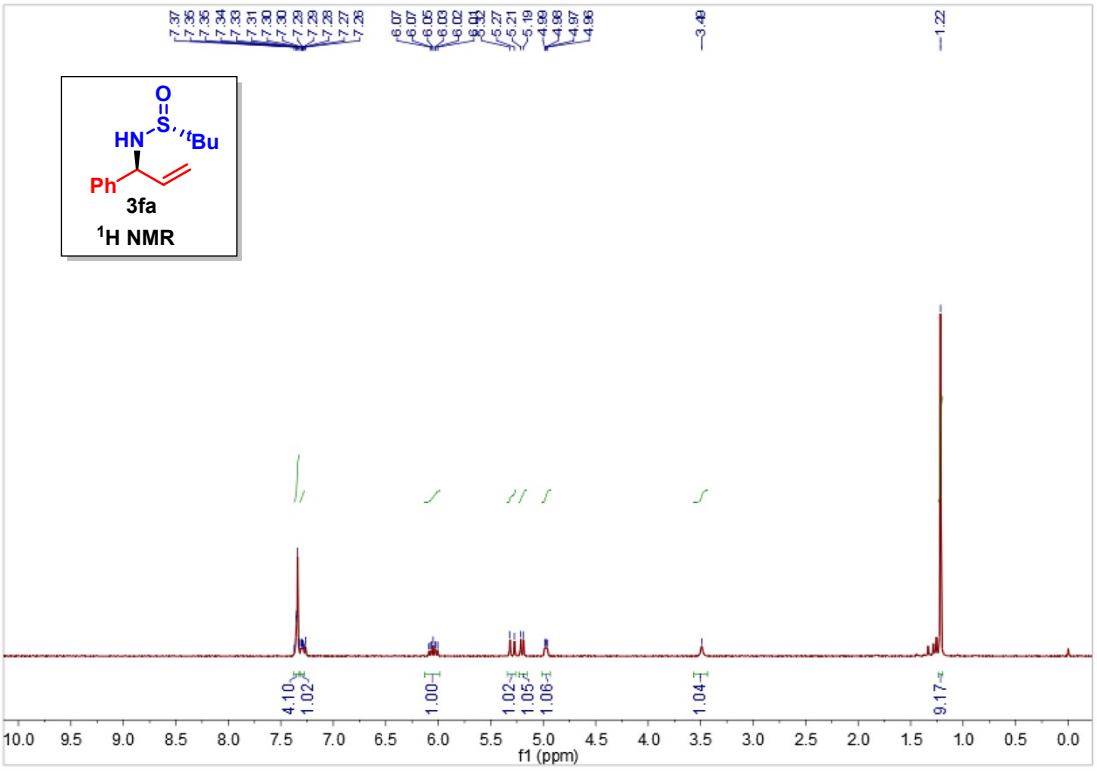

3da
^{1}H NMR
f1 (ppm)

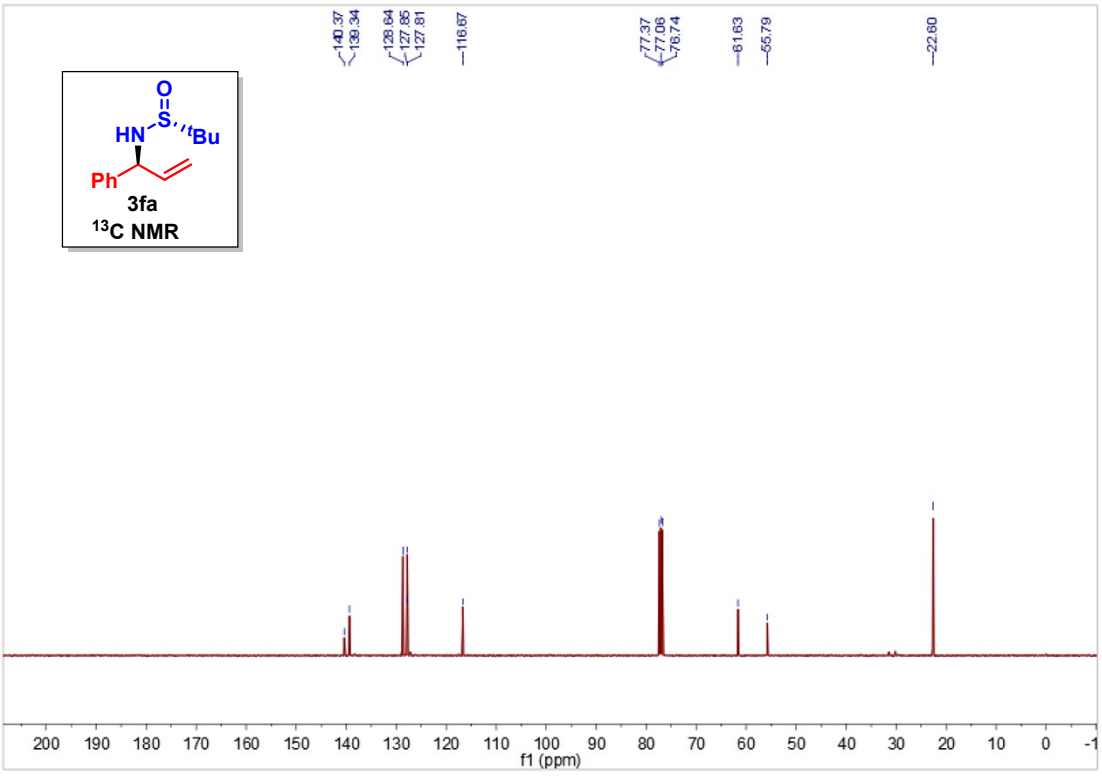

3da
^{13}C NMR
f1 (ppm)

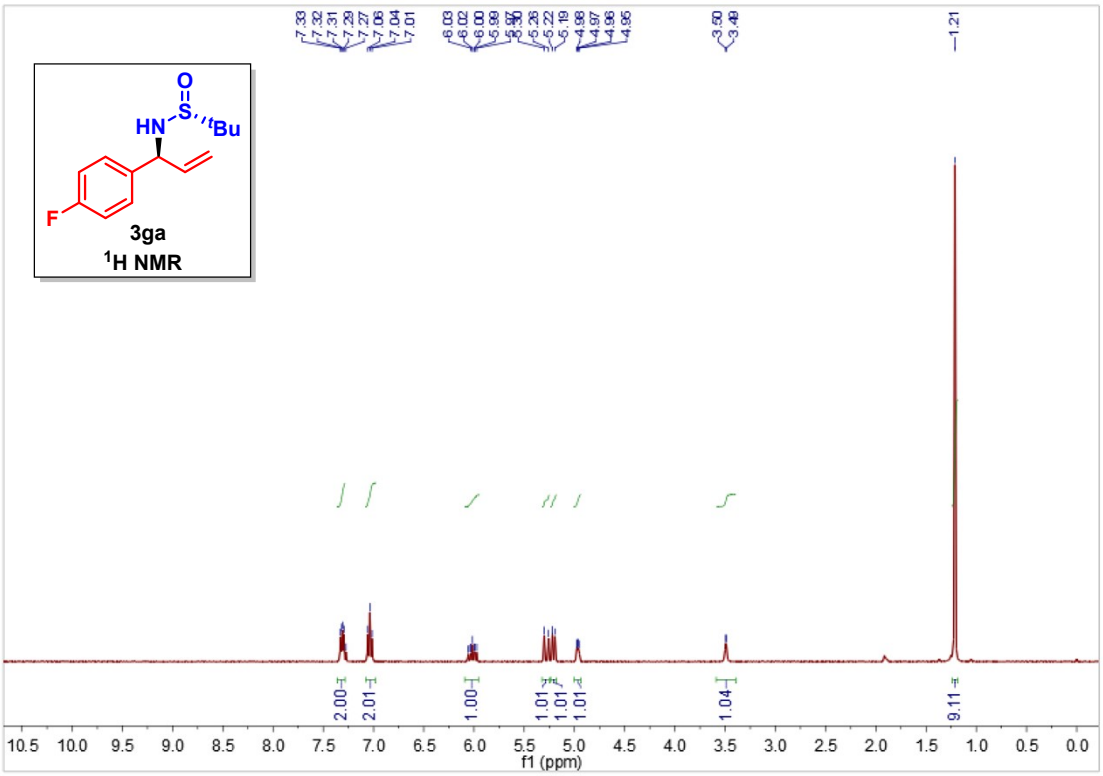

3ea b/l = 4:1
1H NMR
f1 (ppm)

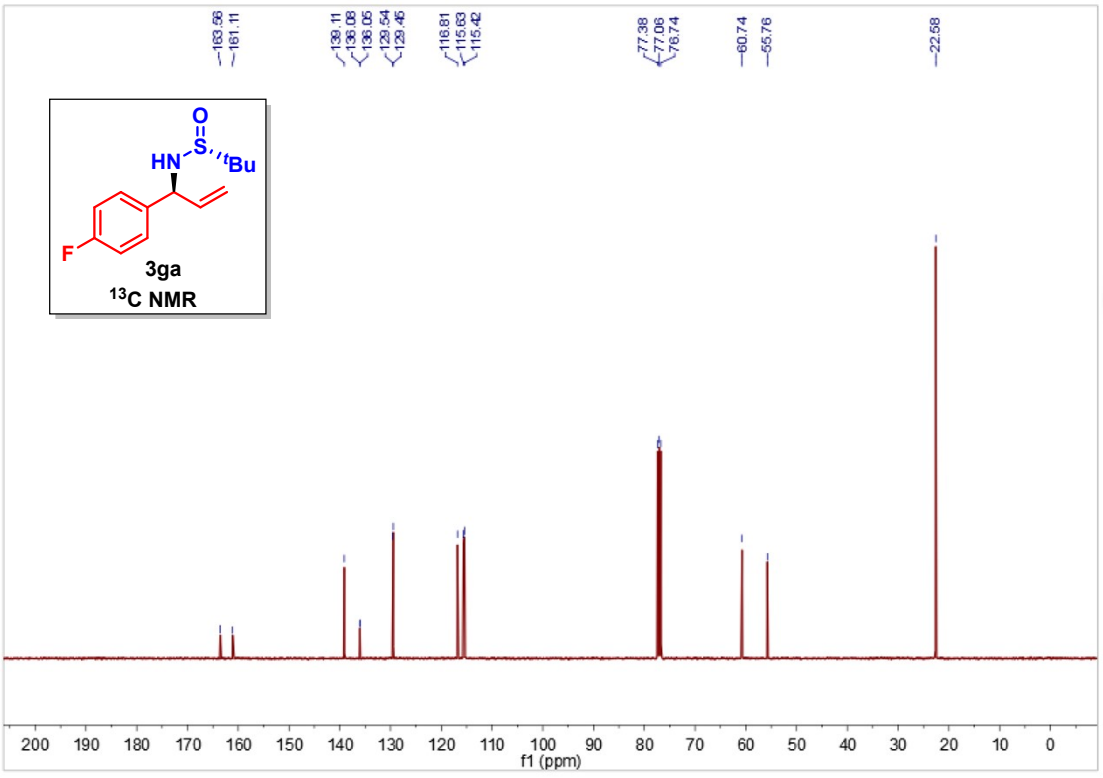
,

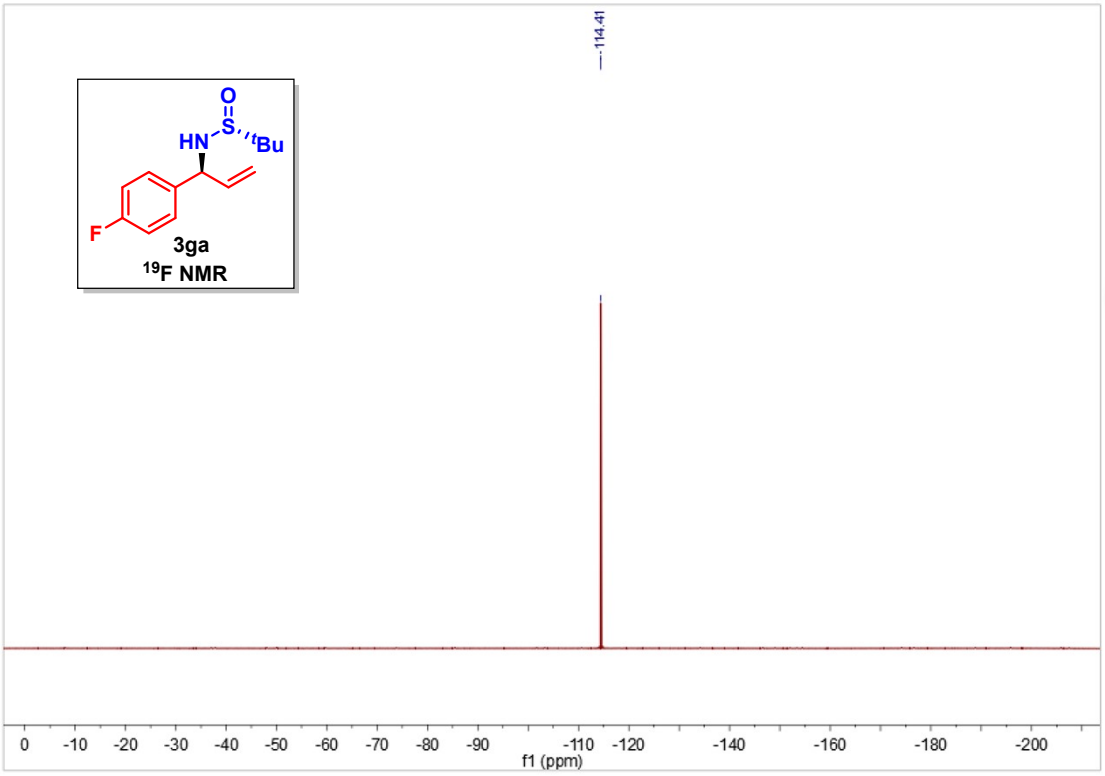

3ea b/l = 4:1
13C NMR
f1 (ppm)

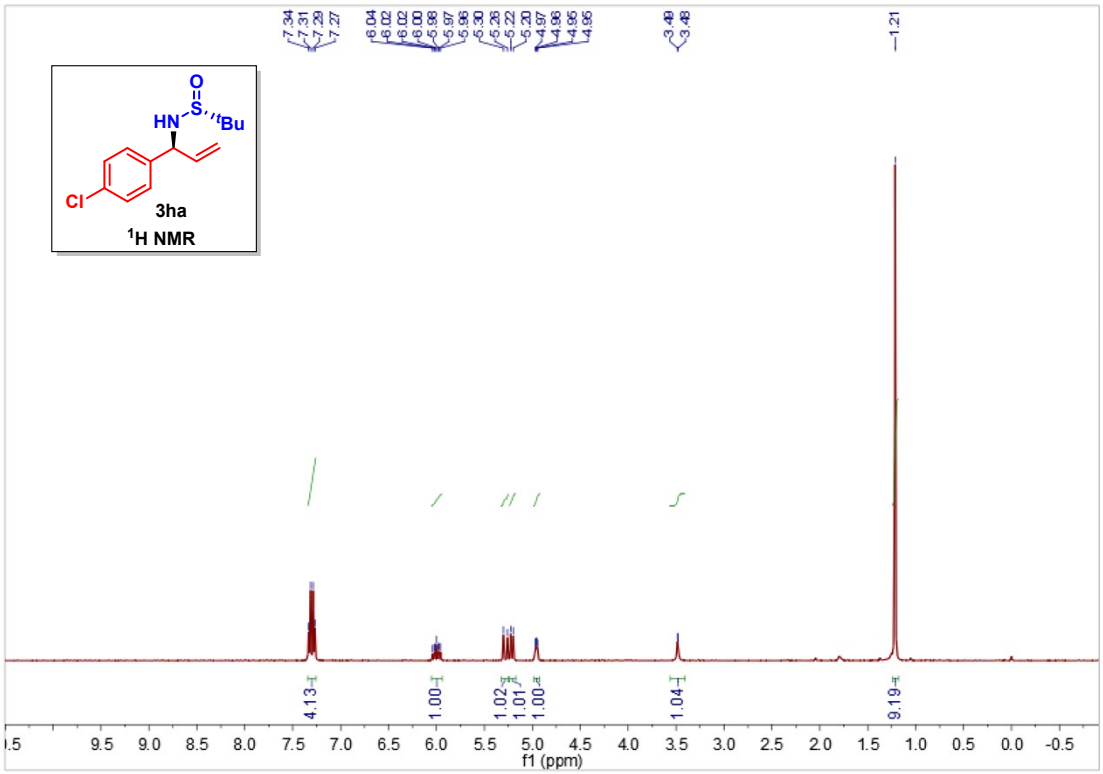

3fa
1H NMR
f1 (ppm)

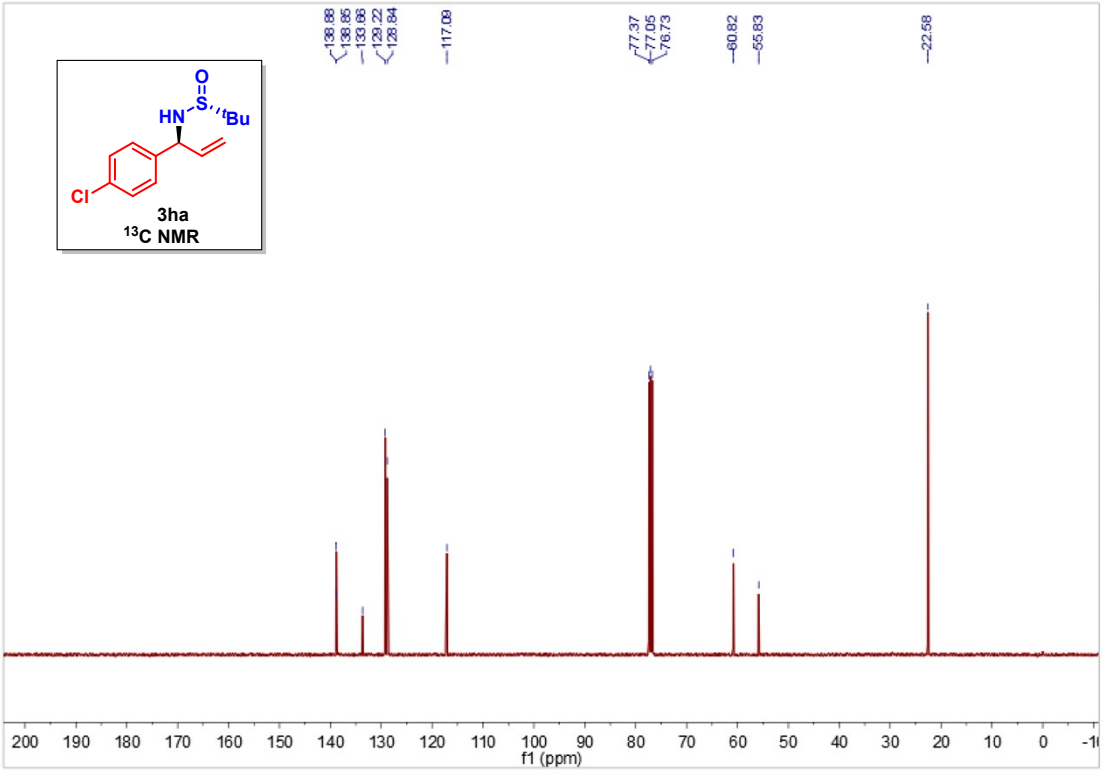

3fa
13C NMR
f1 (ppm)

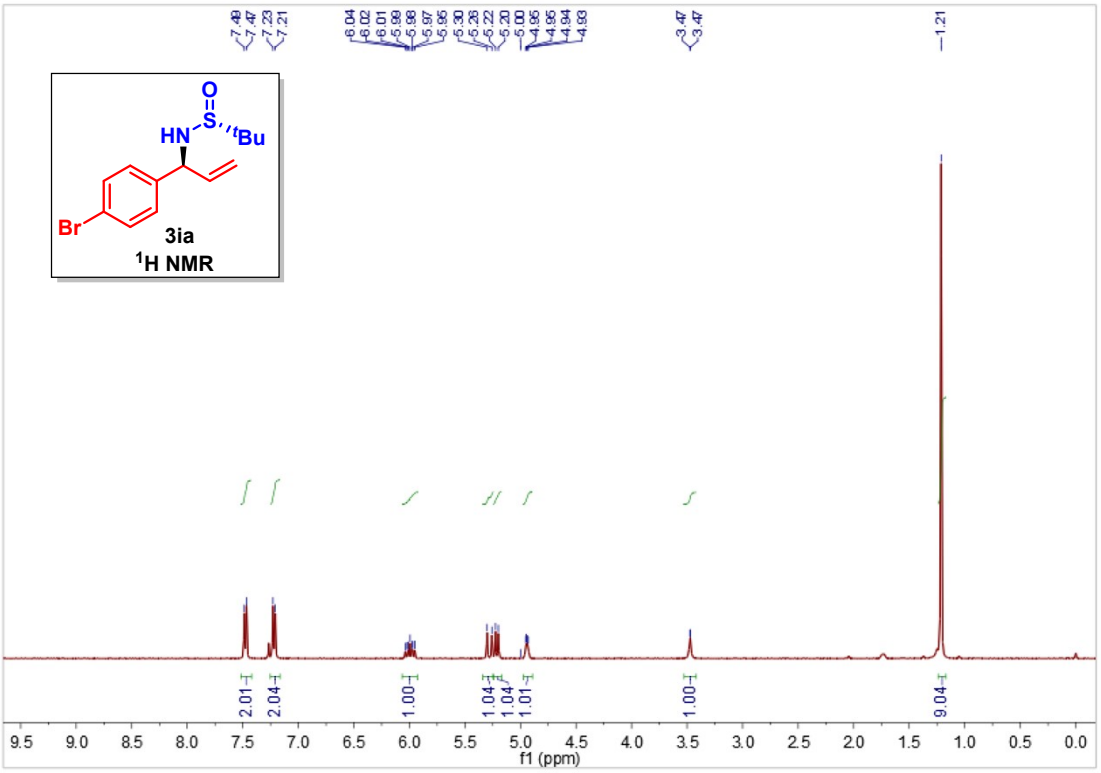

3ga
1H NMR
f1 (ppm)

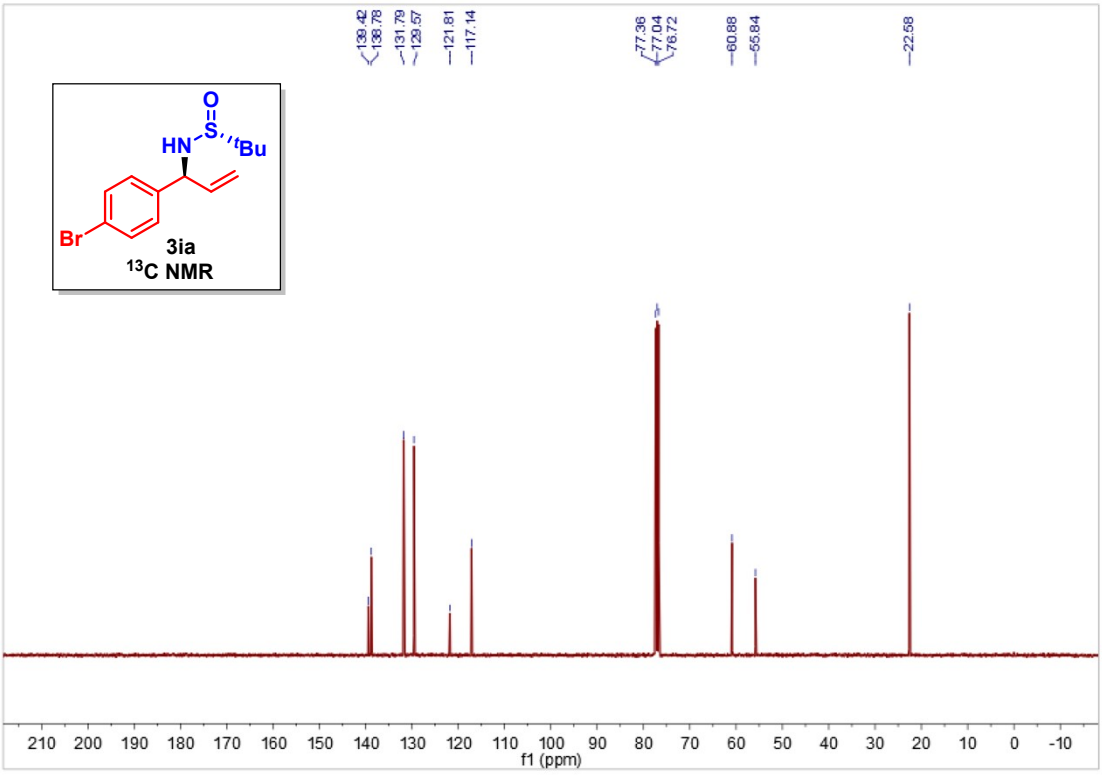

3ga
13C NMR
f1 (ppm)

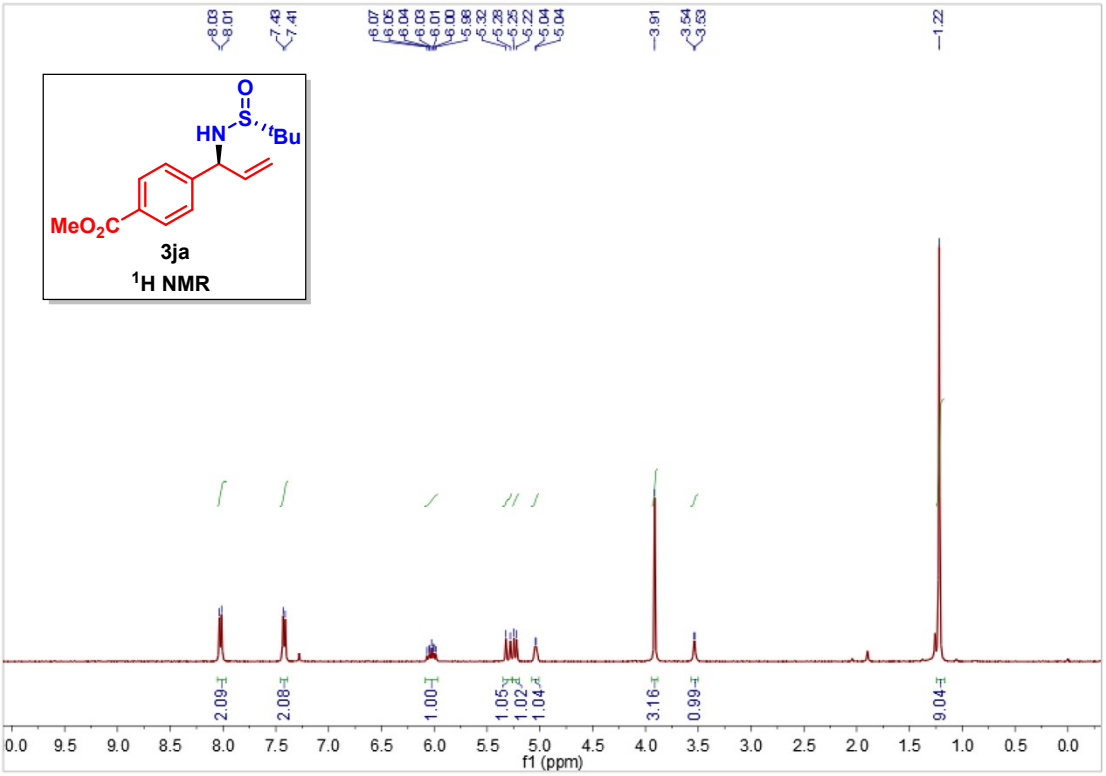

-114.41
O
S
HN
tBu
F
3ga
19F NMR
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
-180
-200
f1 (ppm)

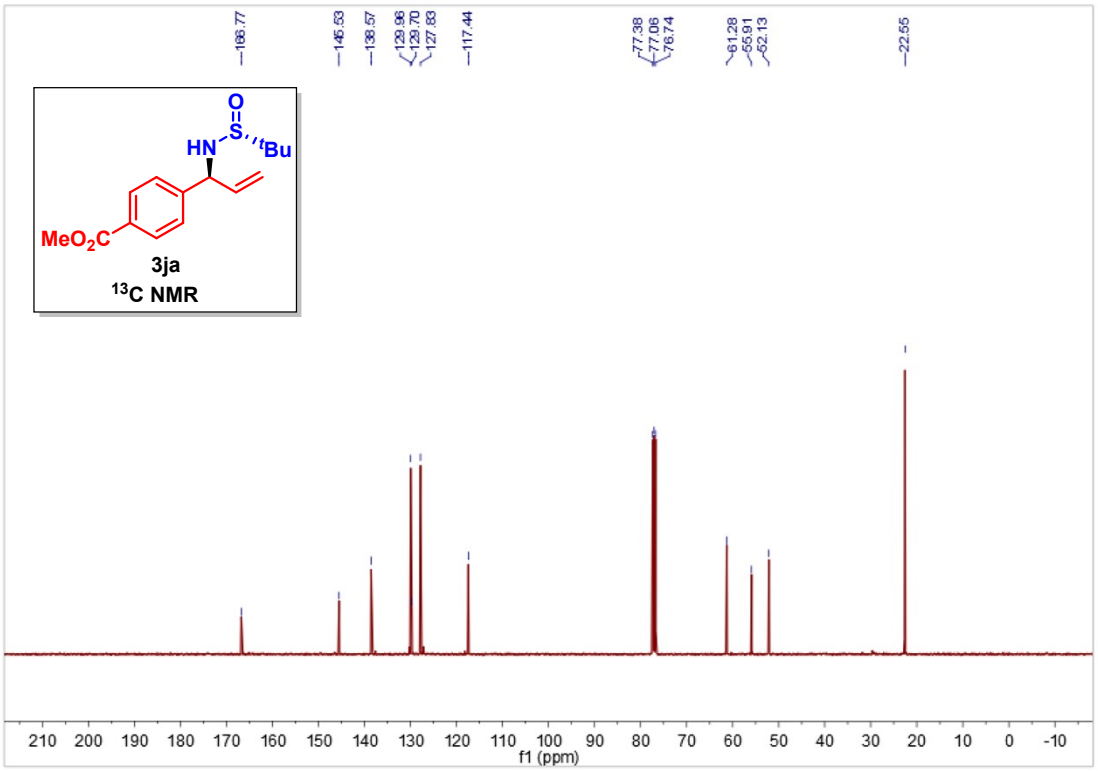

3ha
1H NMR
f1 (ppm)


3ha
13C NMR
f1 (ppm)


3ia
1H NMR
f1 (ppm)


3ia
13C NMR
f1 (ppm)


3ja
1H NMR
f1 (ppm)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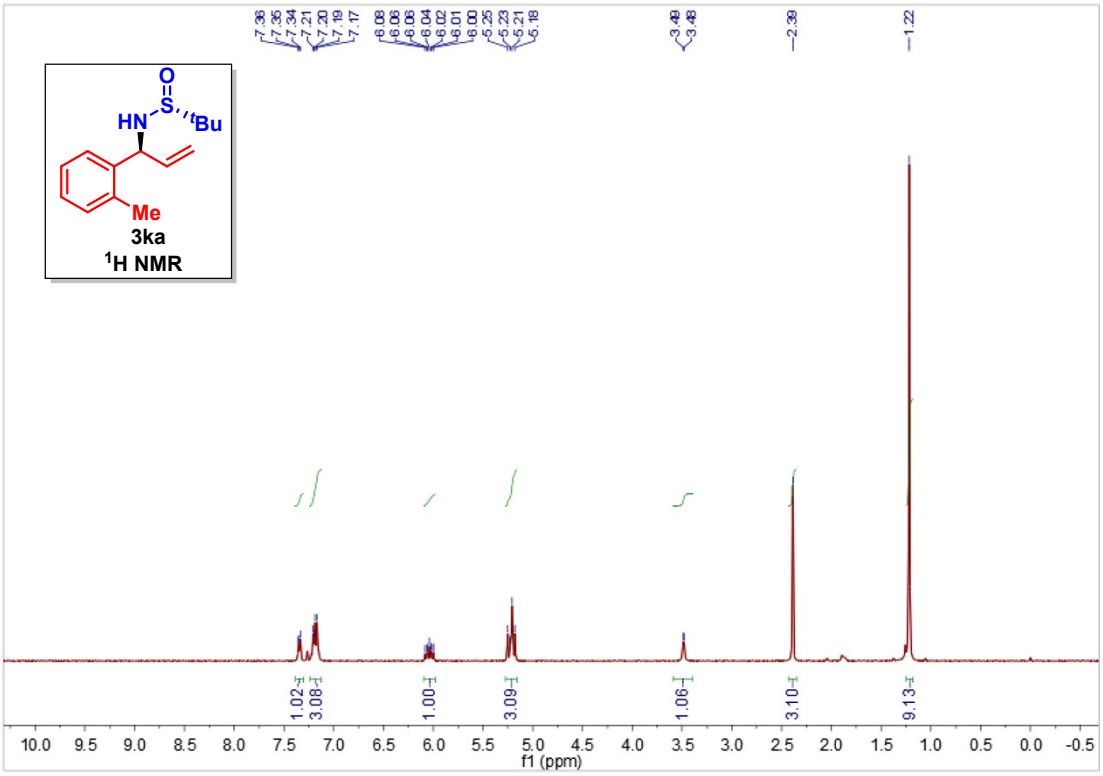
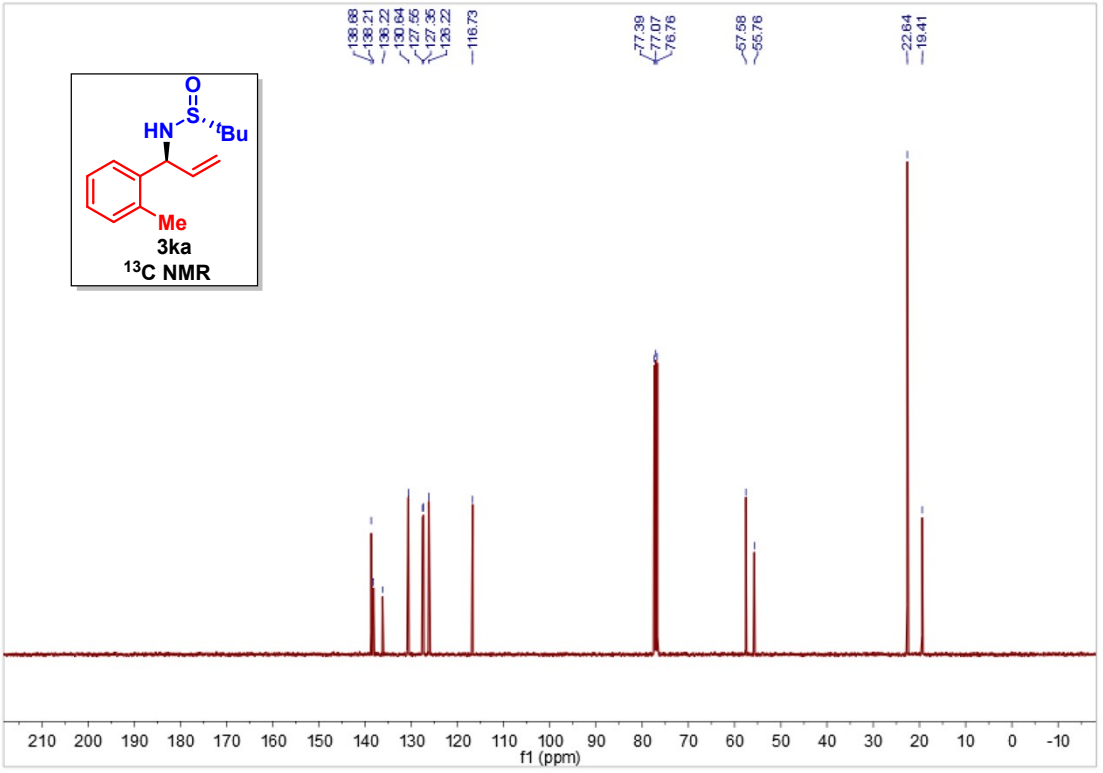
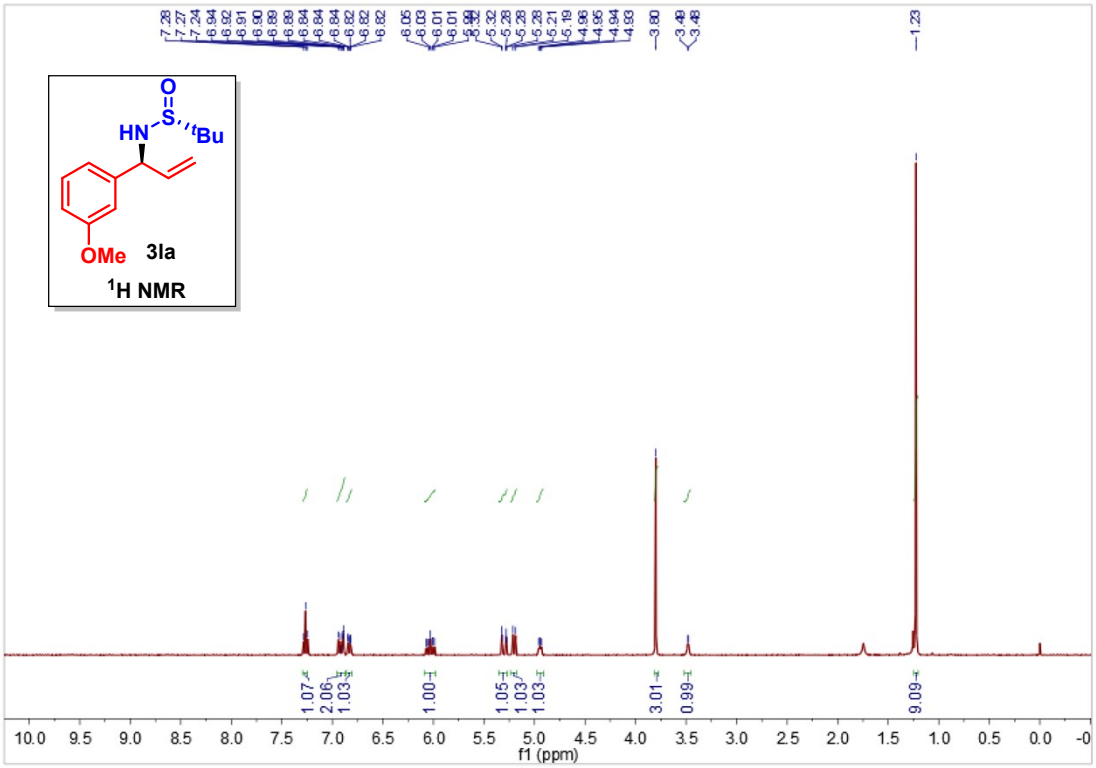
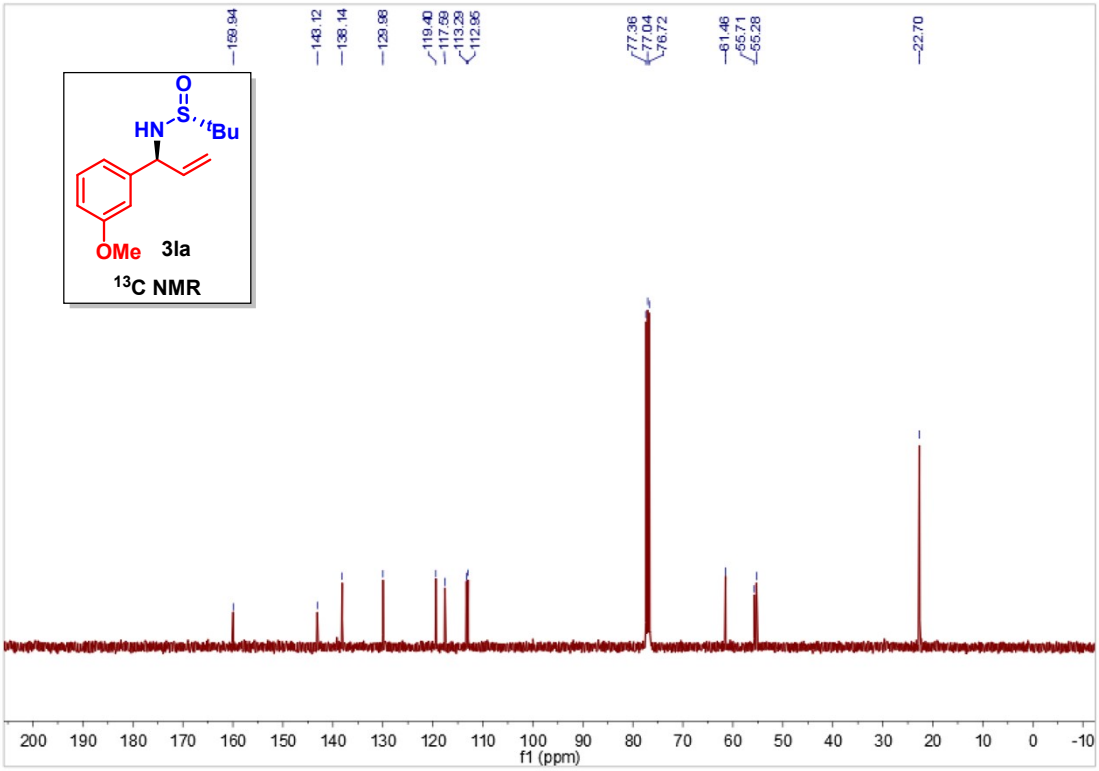
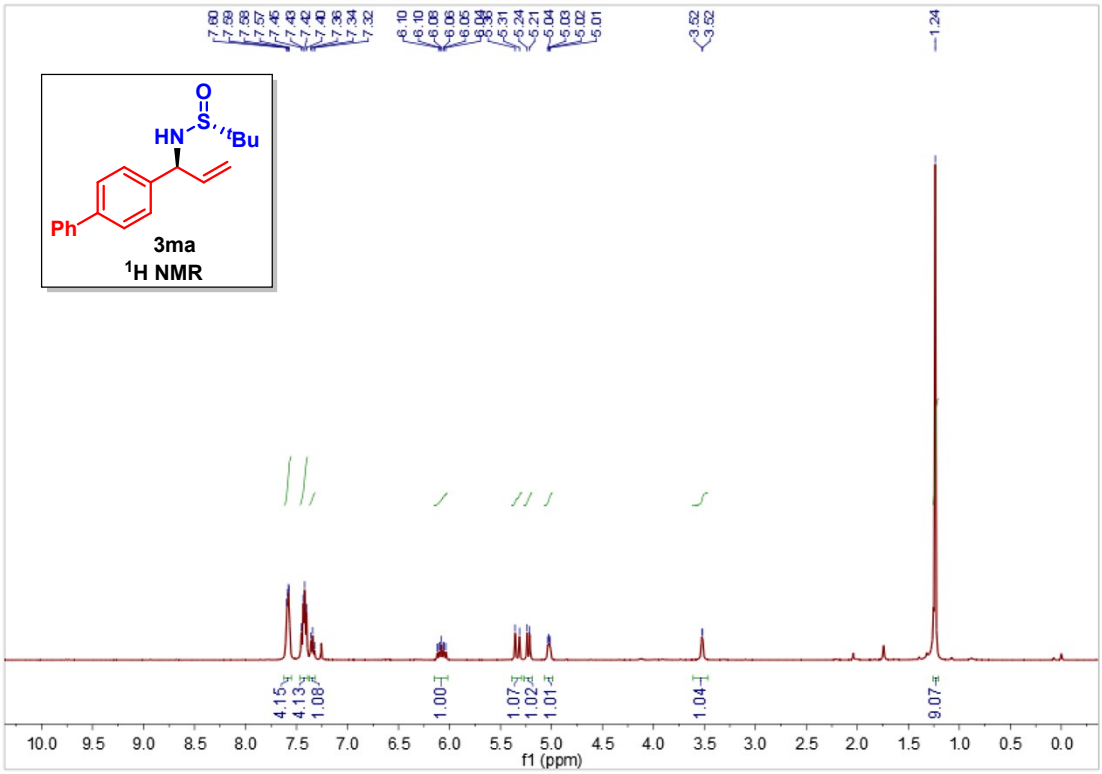
13C NMR
f1 (ppm)

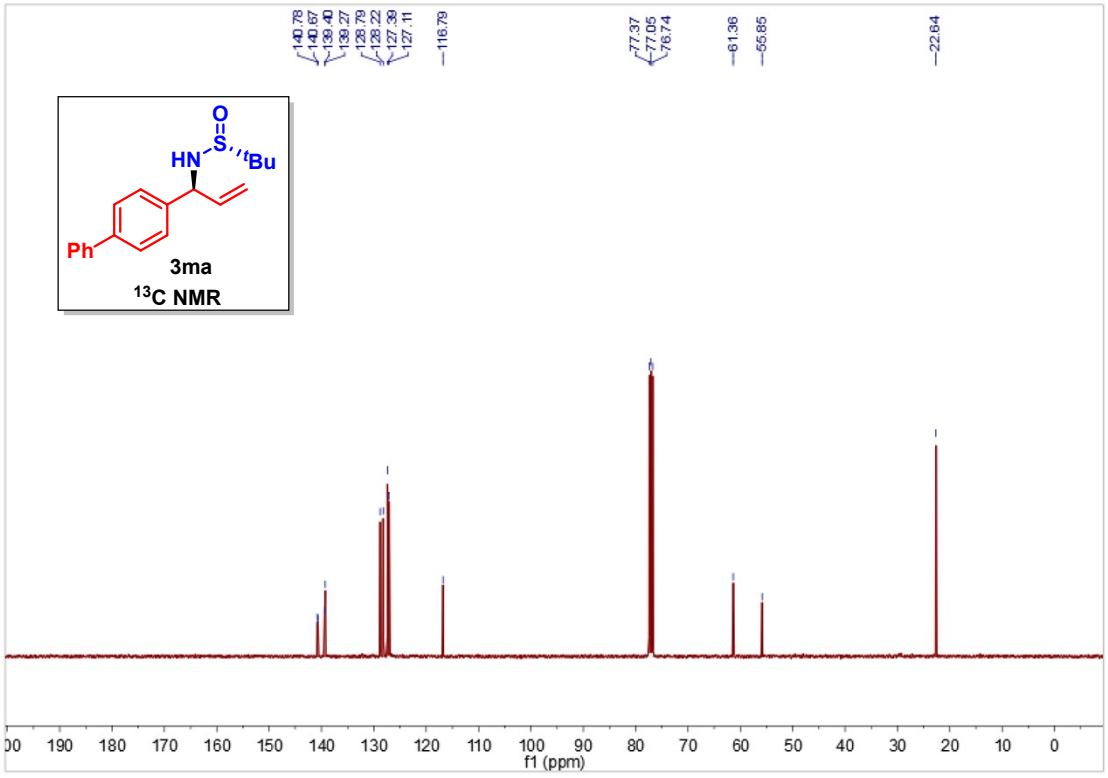

HN
S
O
tBu
Me
3ka
1H NMR
f1 (ppm)

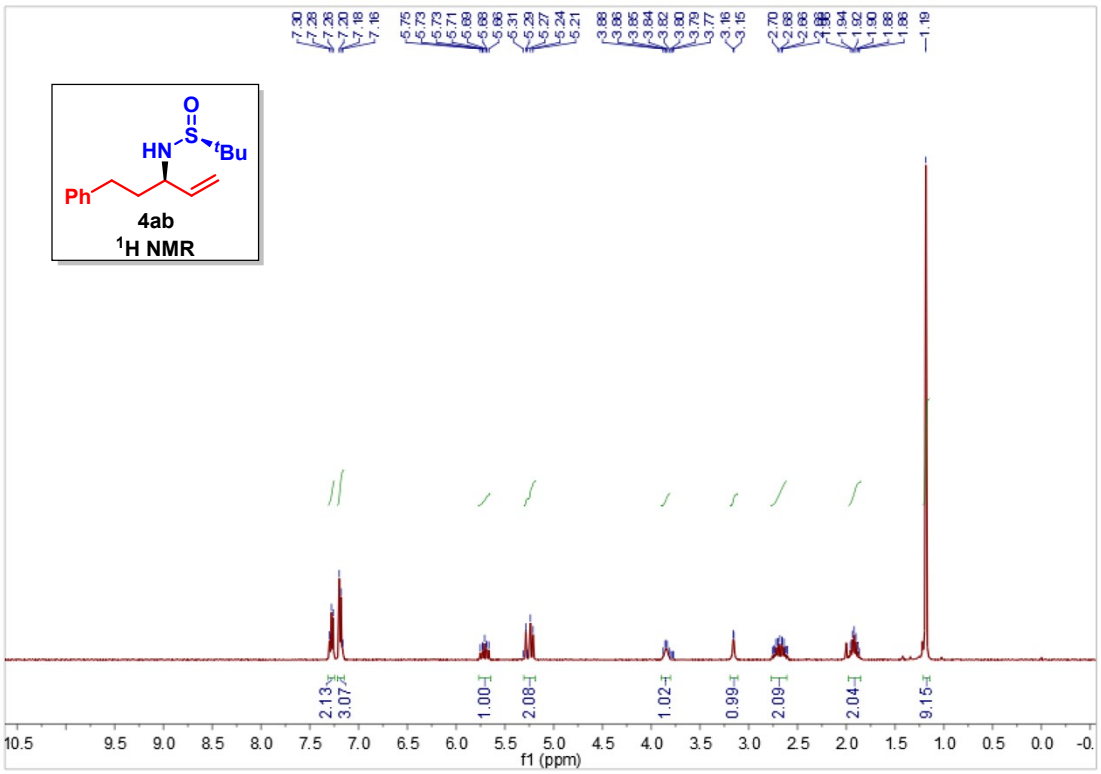

HN
S
O
tBu
Me
3ka
13C NMR
f1 (ppm)

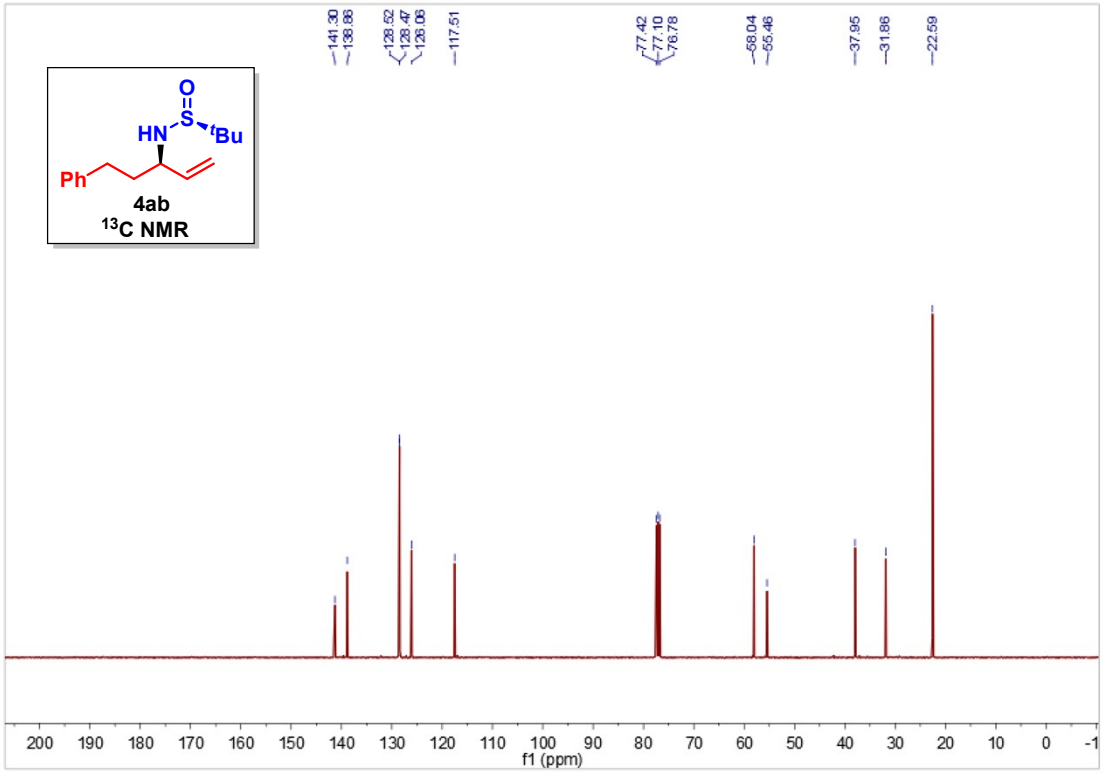

3la
^{1}H NMR
f1 (ppm)

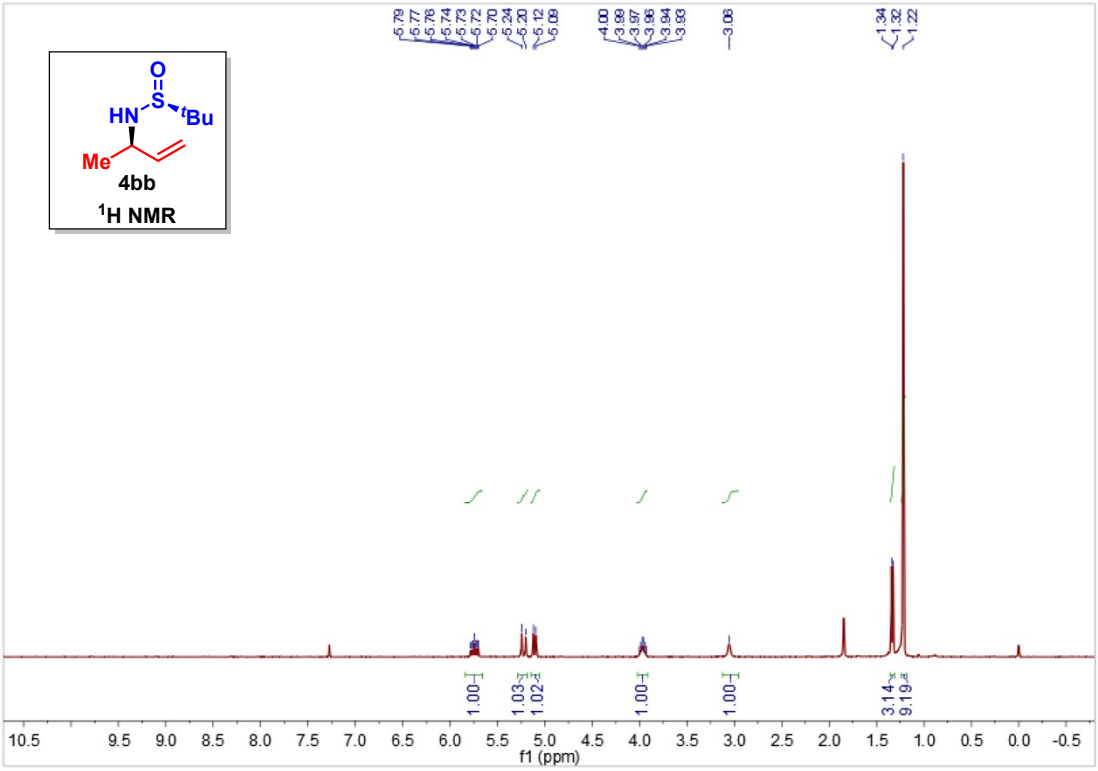

3la
^{13}C NMR
f1 (ppm)

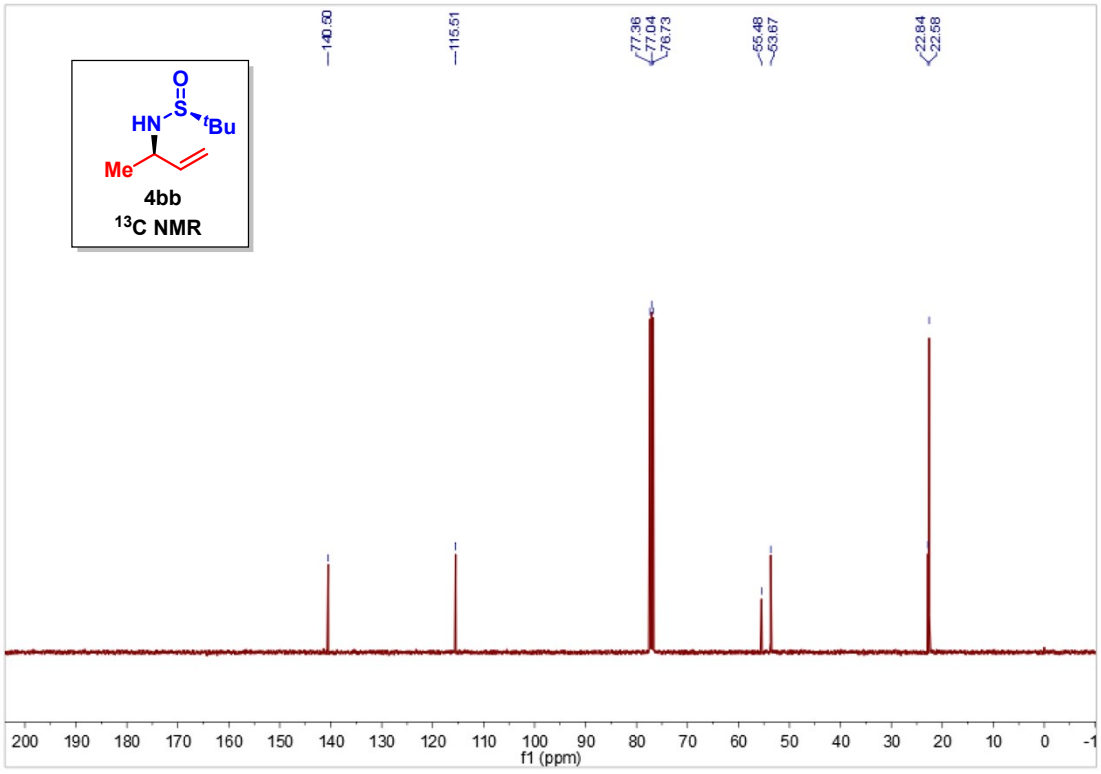

3ma
1H NMR
f1 (ppm)

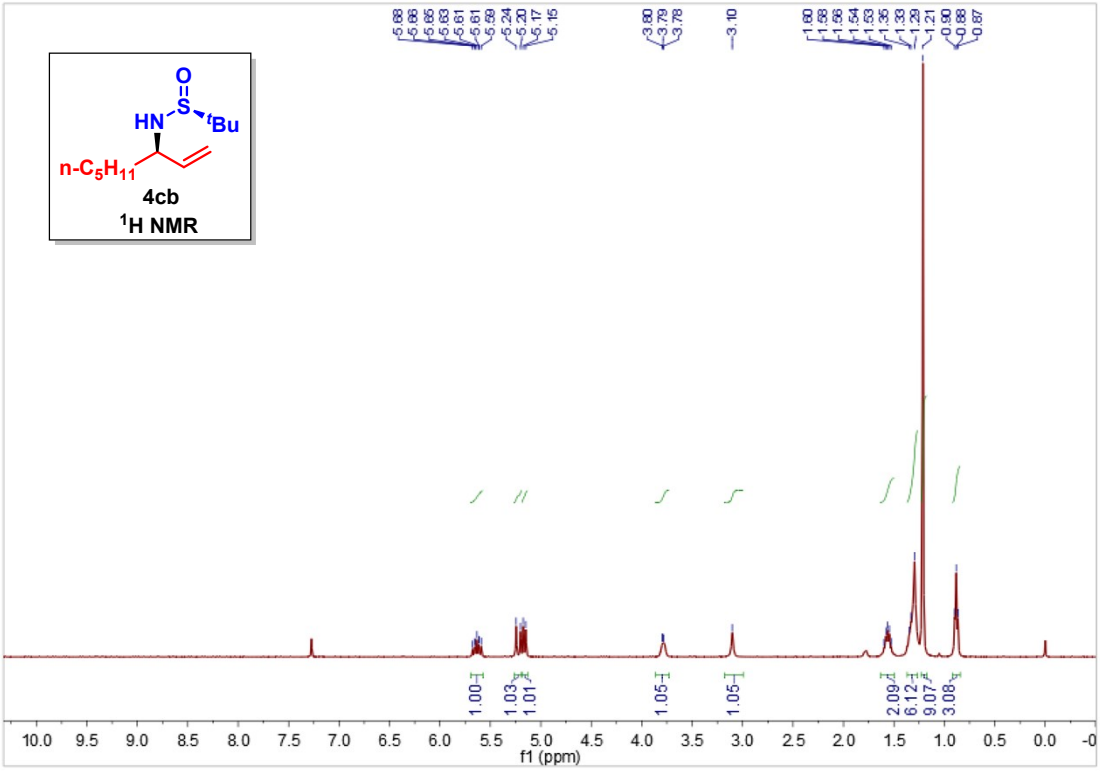

3ma
13C NMR
f1 (ppm)

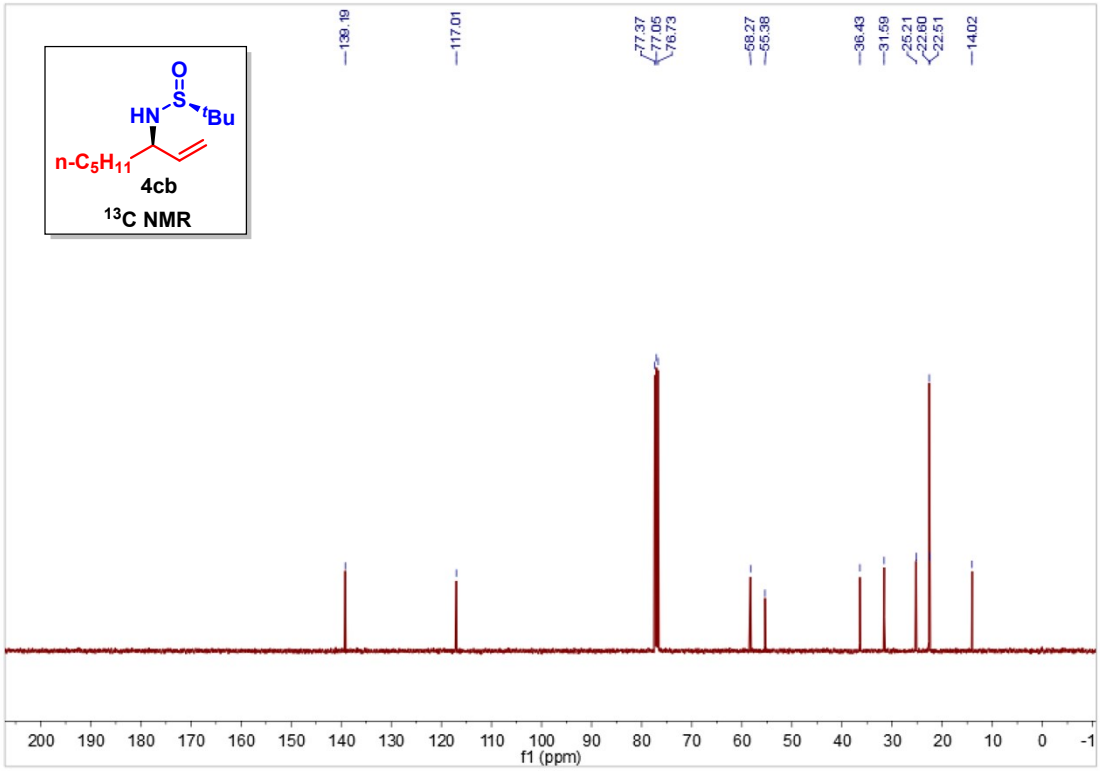

4ab
1H NMR
f1 (ppm)

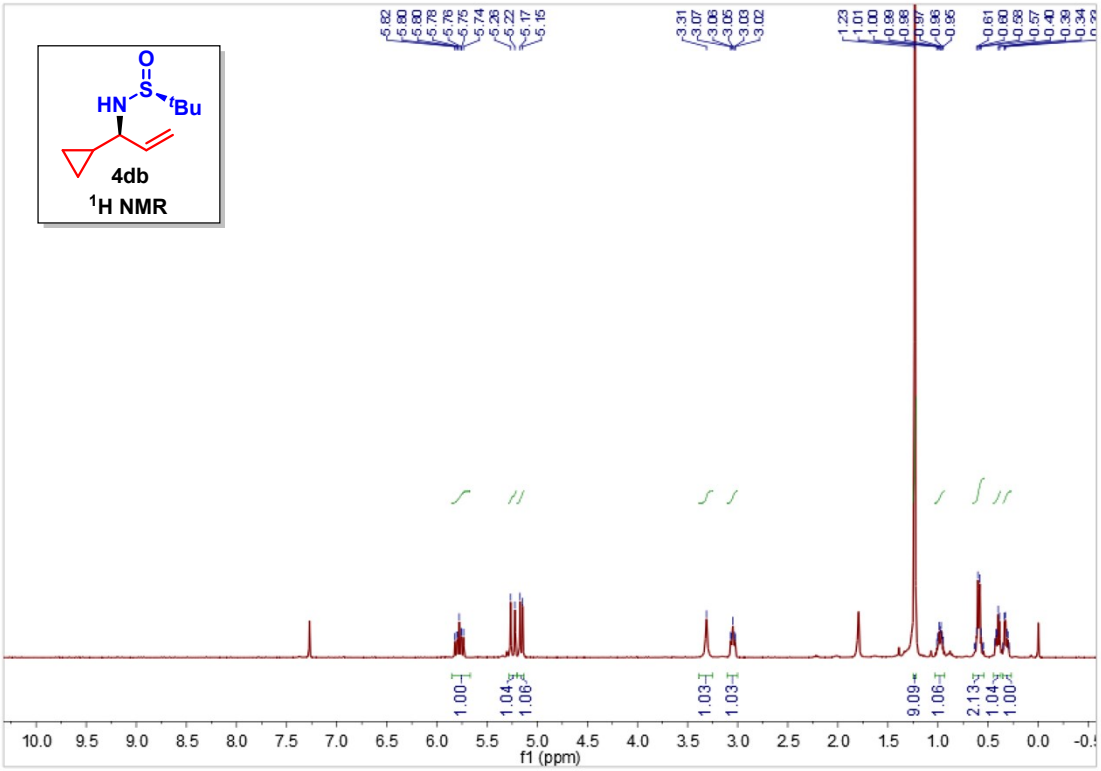

4ab
13C NMR
f1 (ppm)

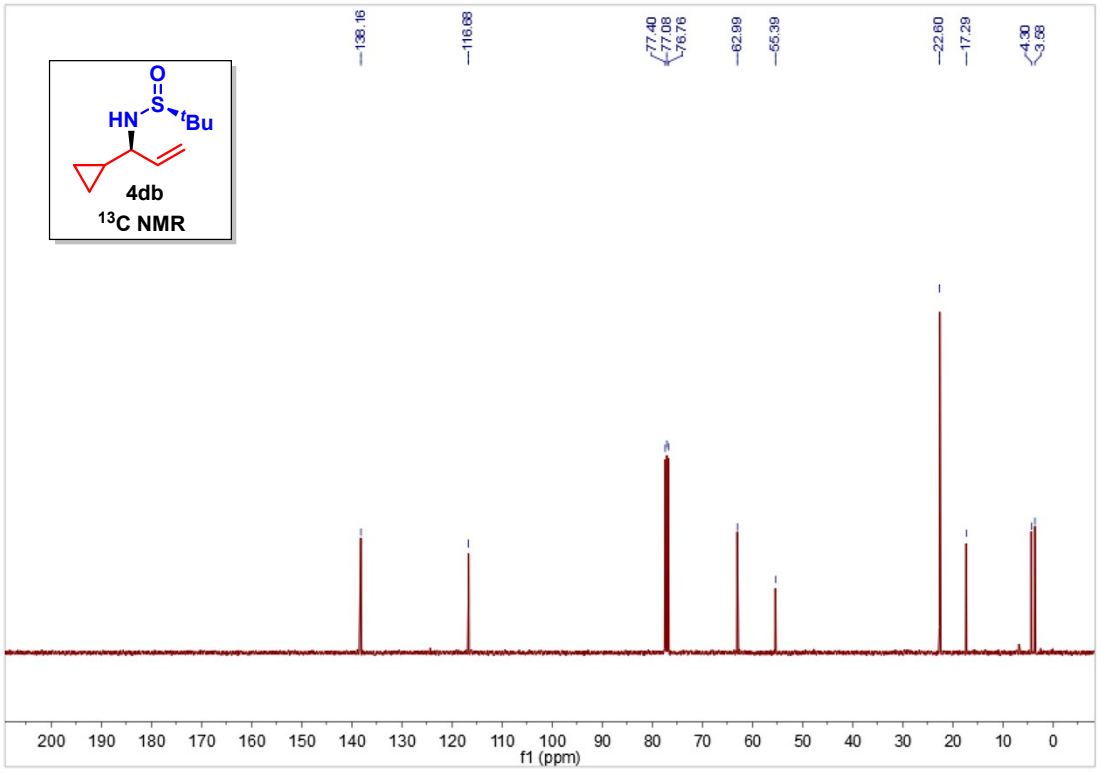

4bb
1H NMR
f1 (ppm)

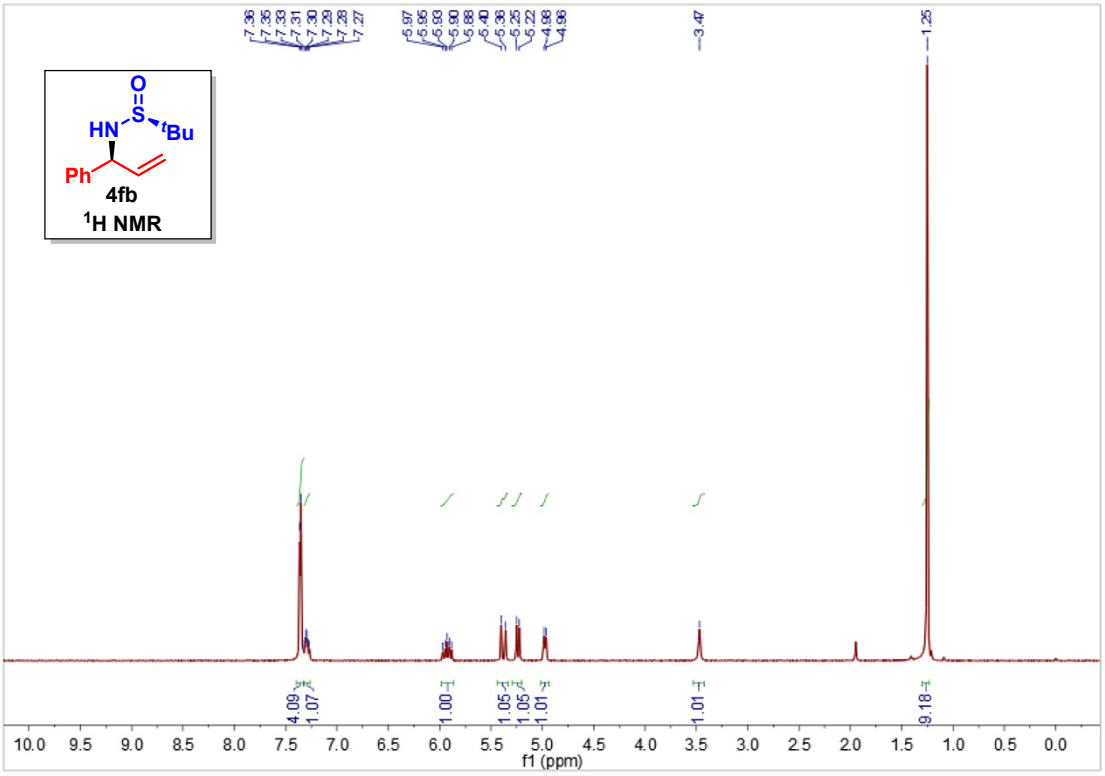

4bb
13C NMR
f1 (ppm)

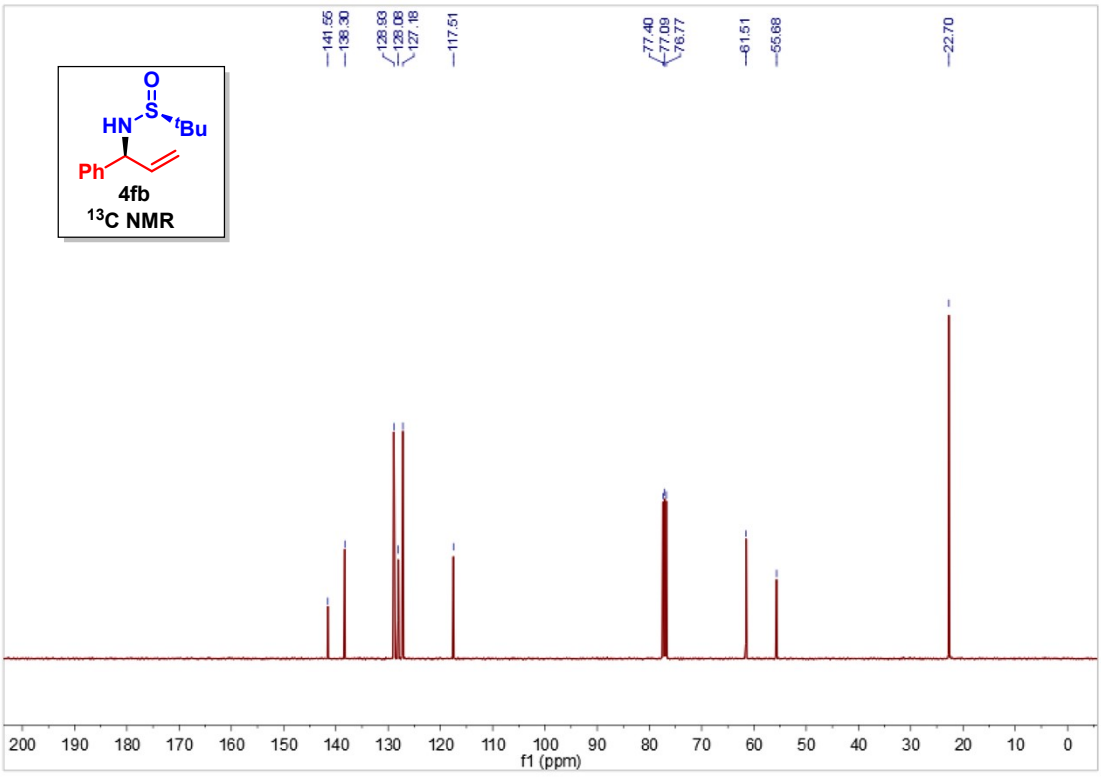

4cb
1H NMR
f1 (ppm)


4cb
13C NMR
f1 (ppm)


4db
^{1}H NMR
f1 (ppm)


4db
^{13}C NMR
f1 (ppm)


4fb
1H NMR
f1 (ppm)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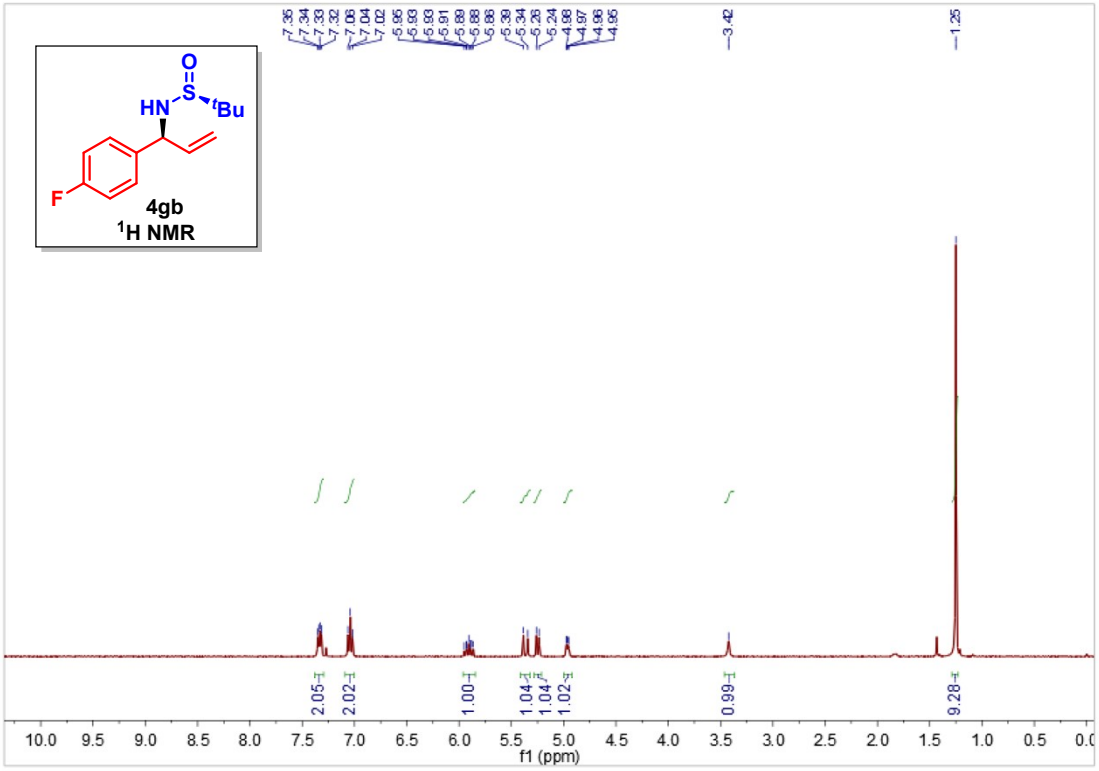
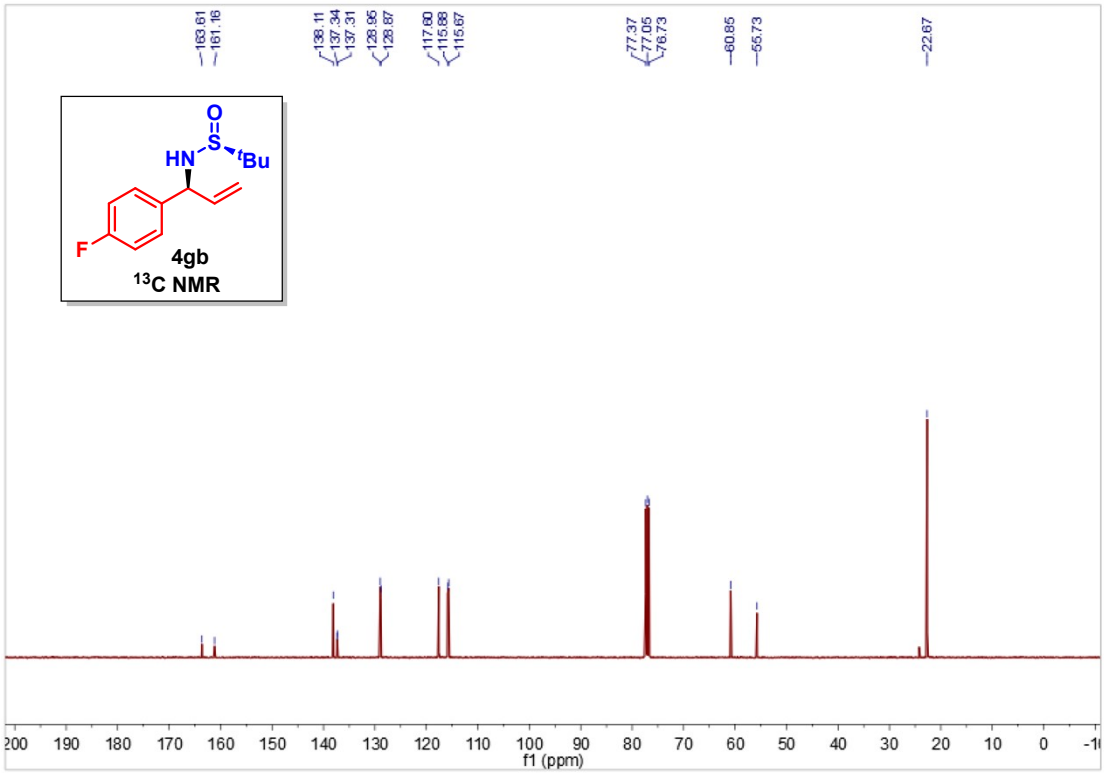
13C NMR
f1 (ppm)


4gb
^{1}H NMR
f1 (ppm)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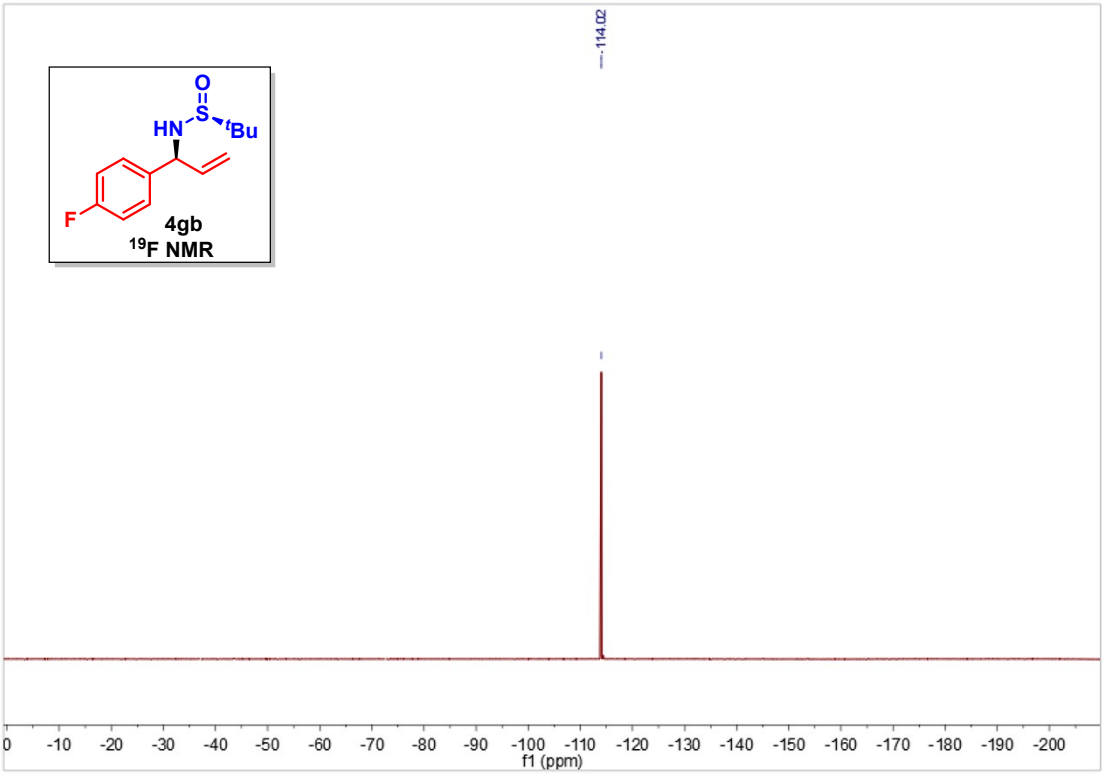
^{13}C NMR
f1 (ppm)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O
S
HN
tBu
F
4gb
19F NMR
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-30
-40
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-170
-180
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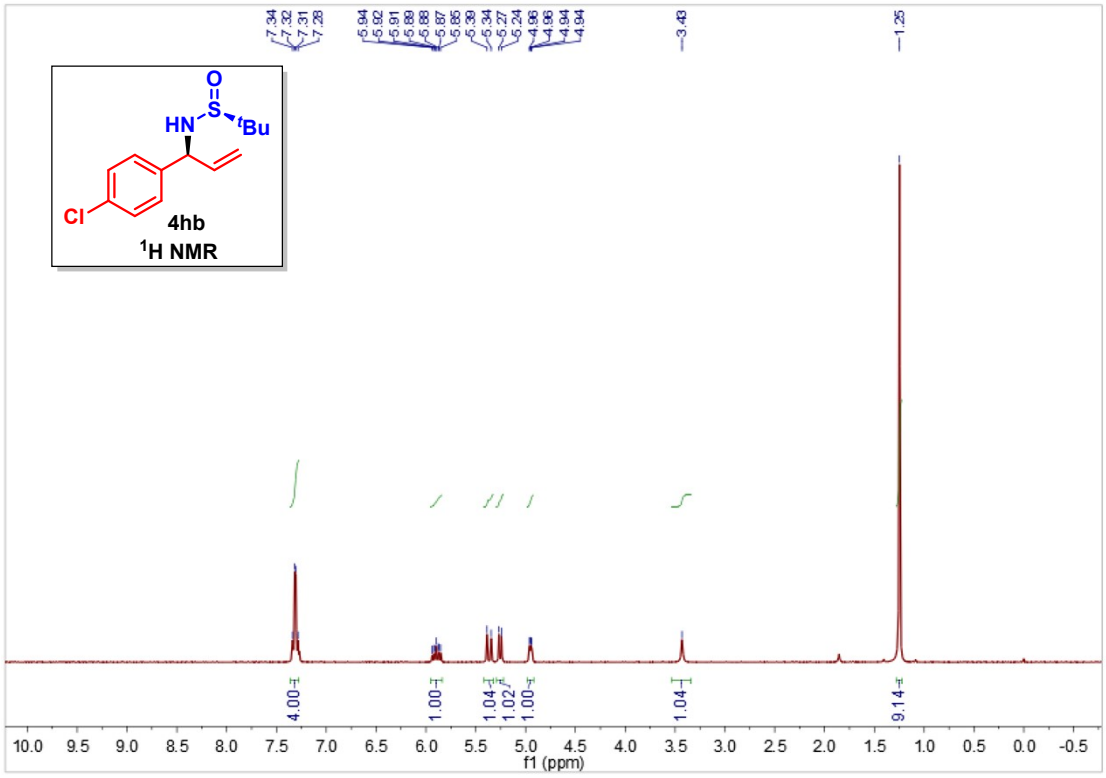
-200
f1 (ppm)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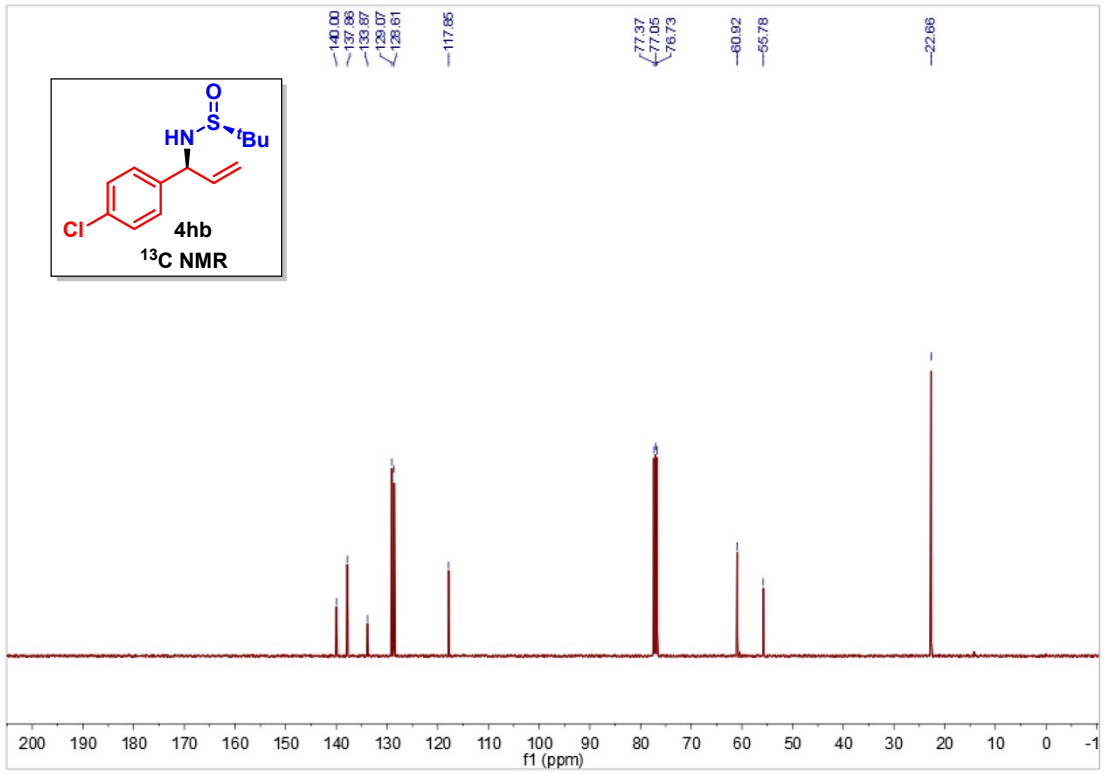
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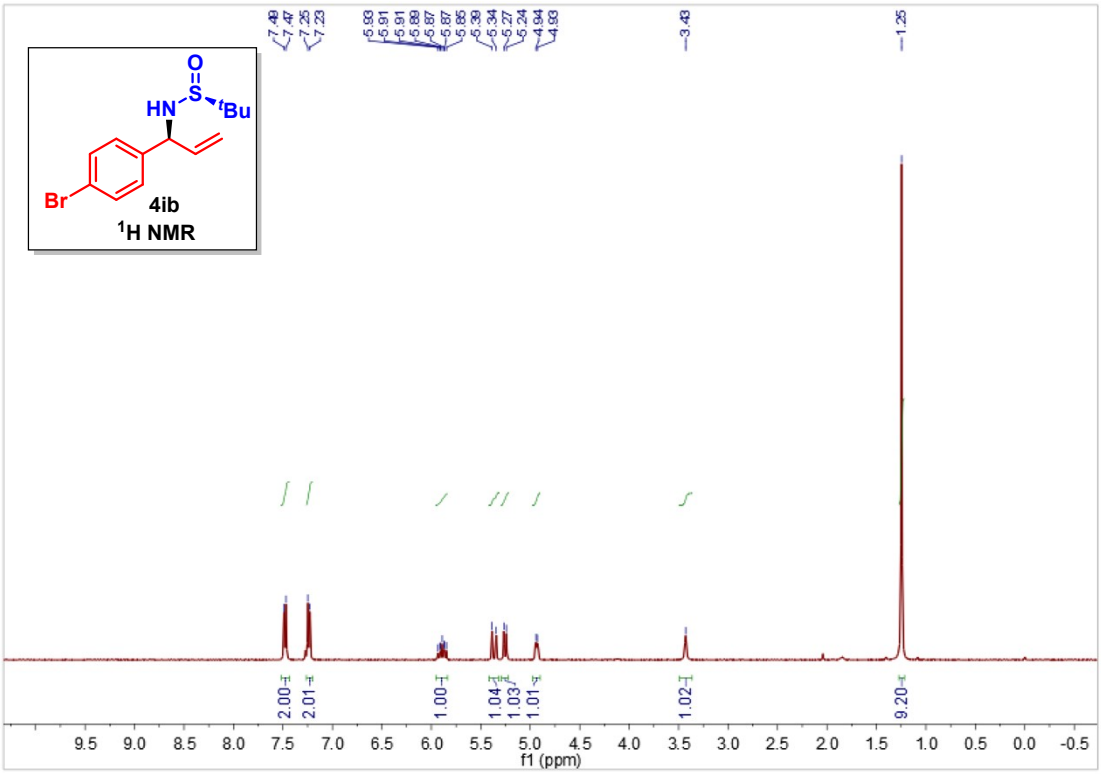
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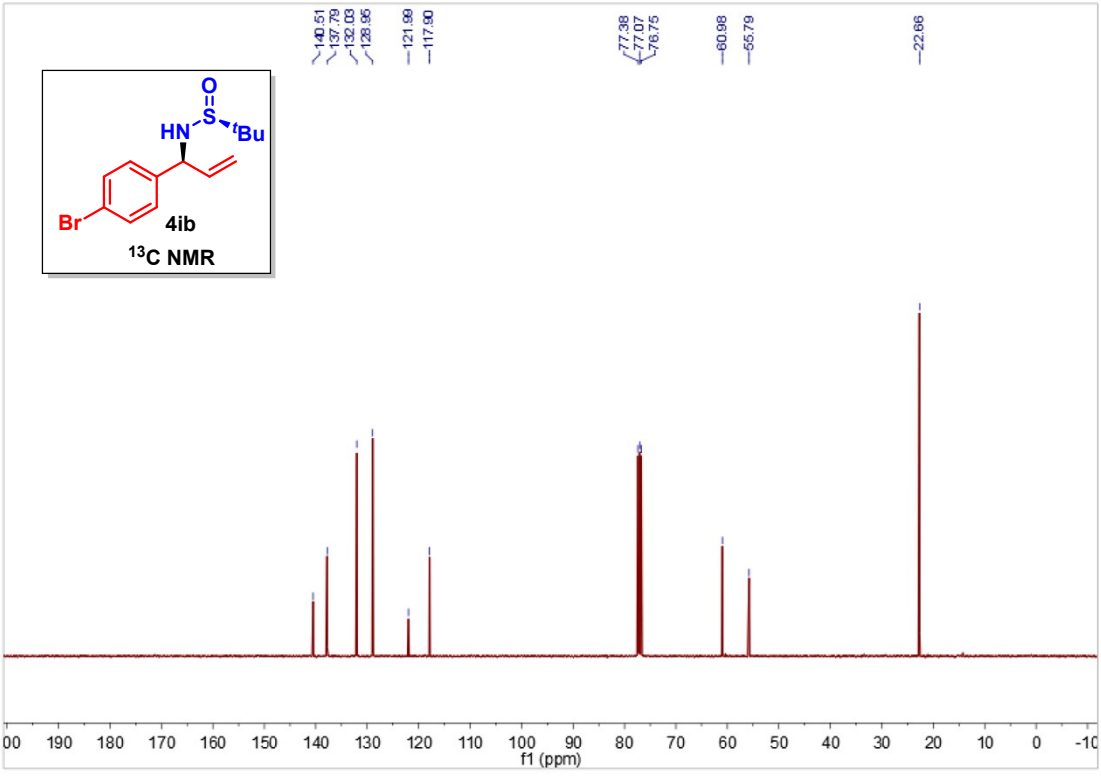
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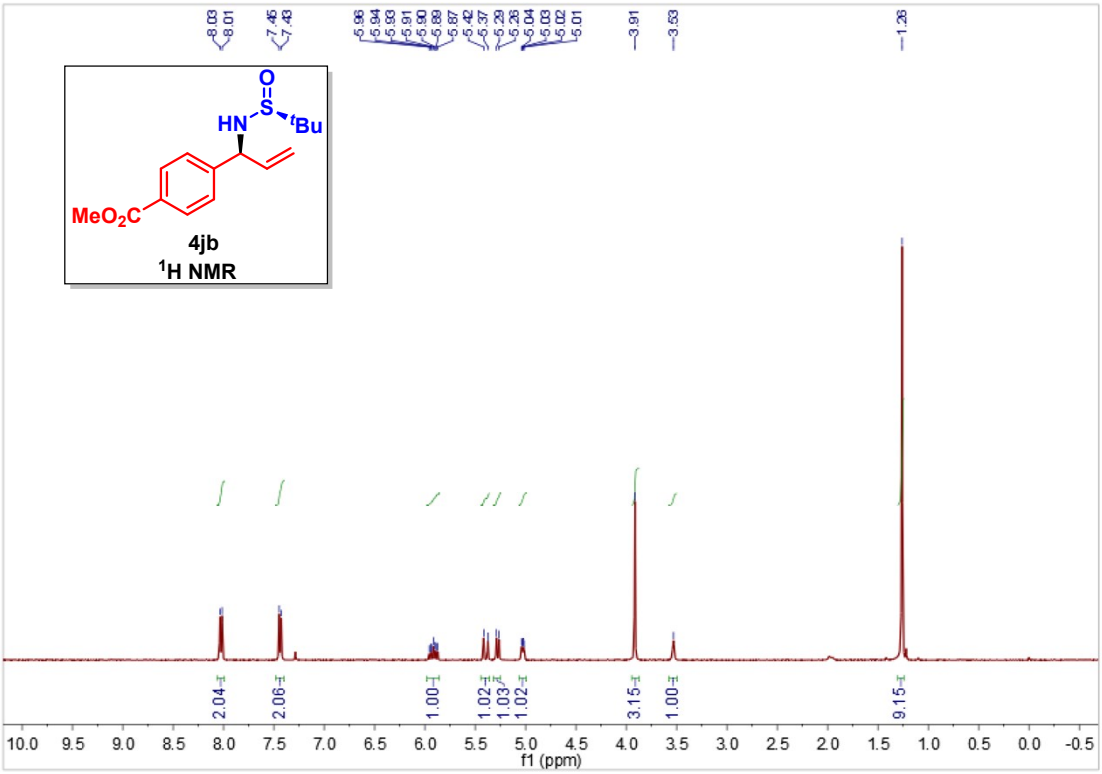
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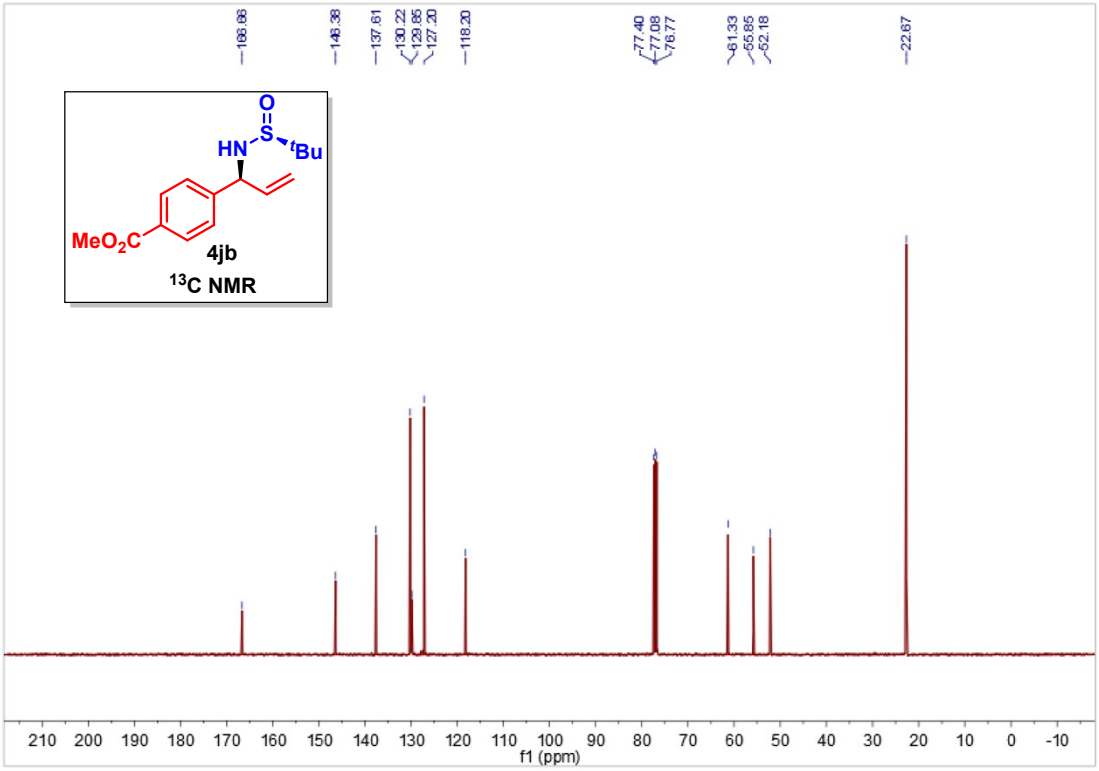
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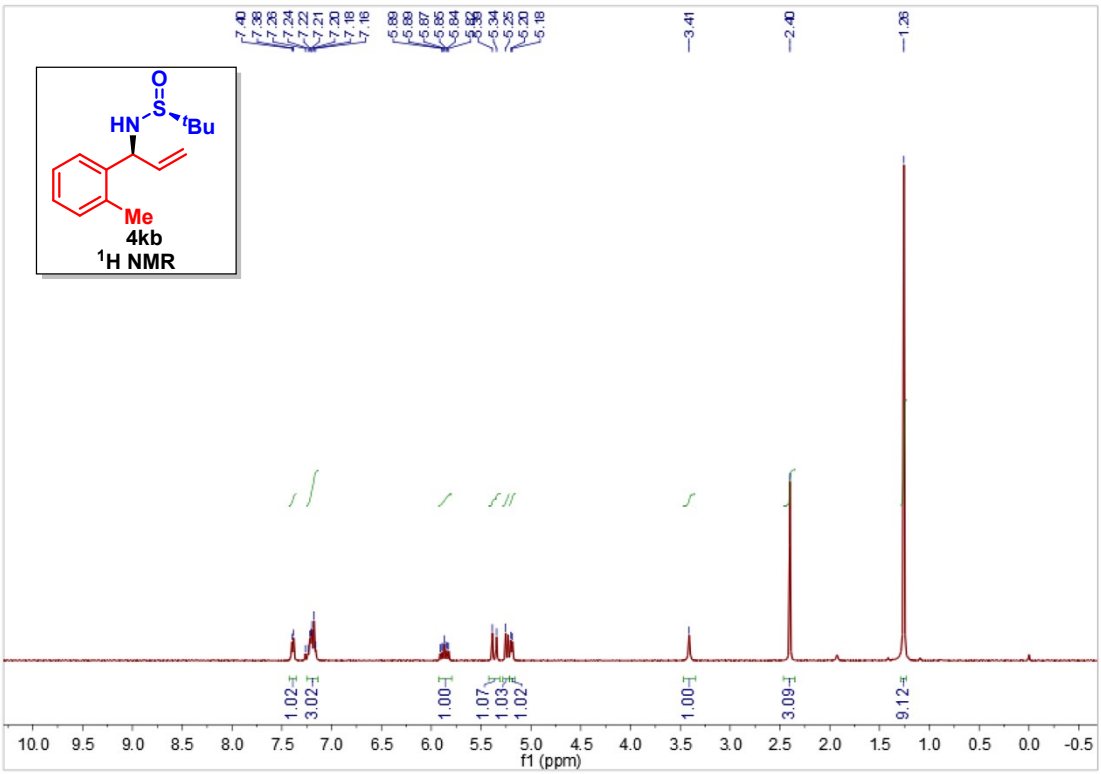
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Me
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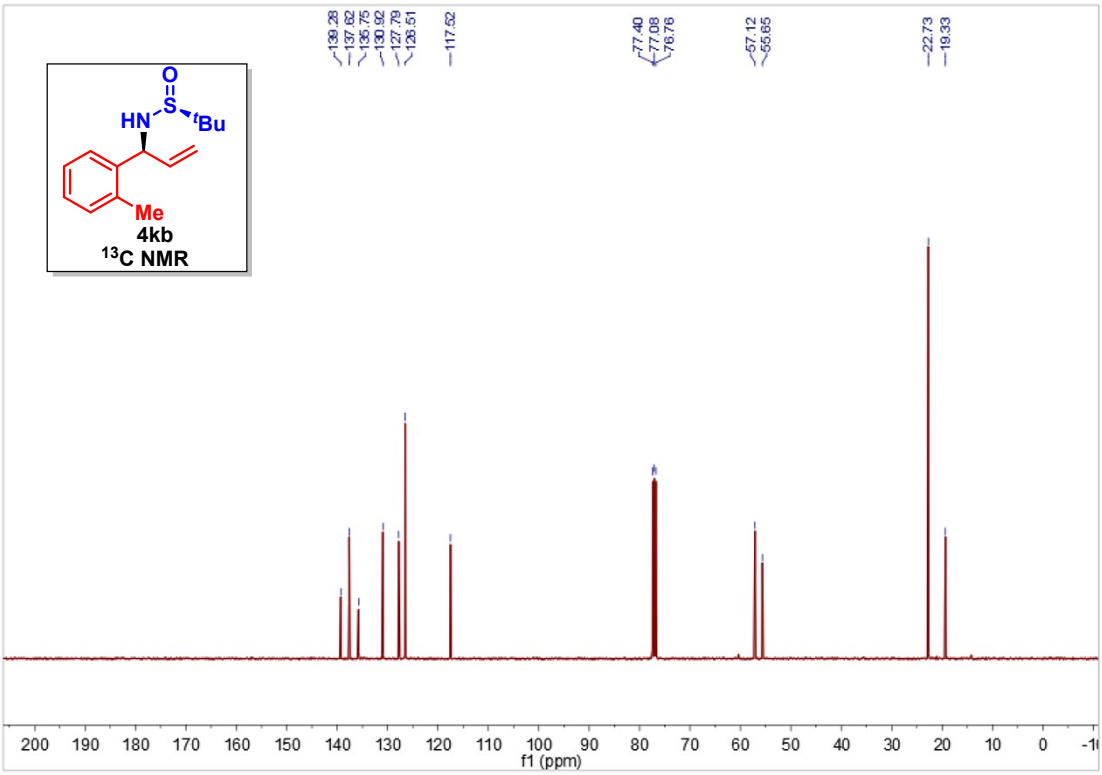
1H NMR
f1 (ppm)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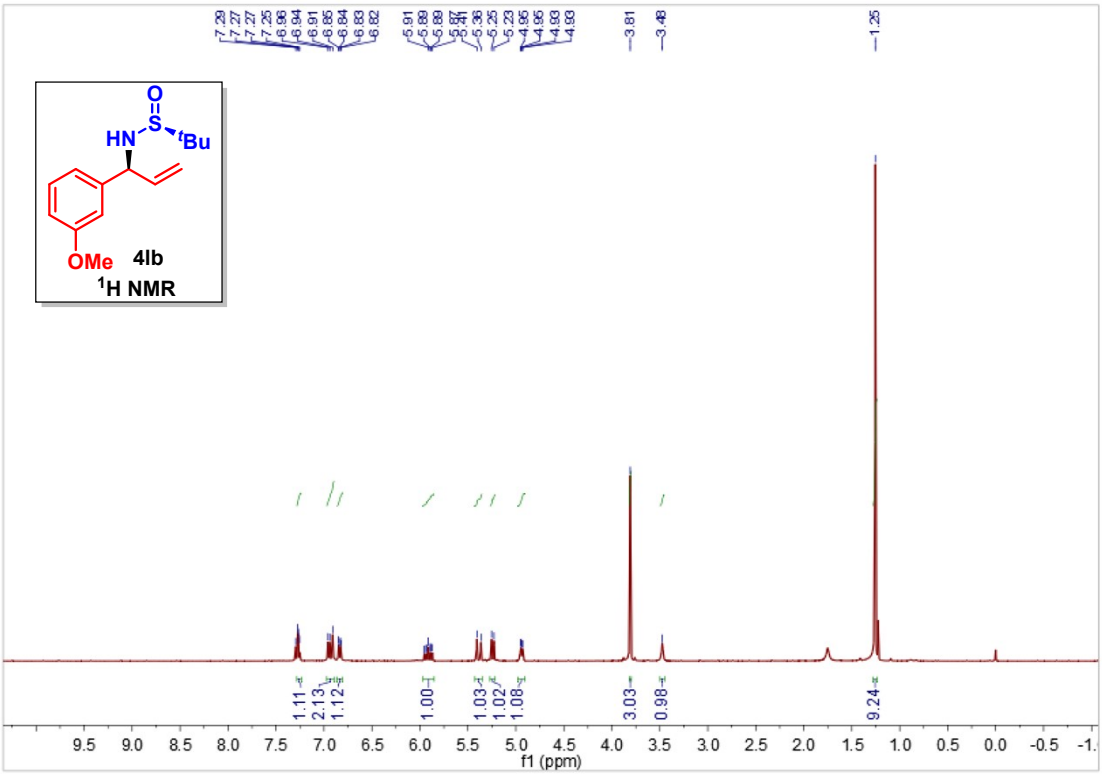
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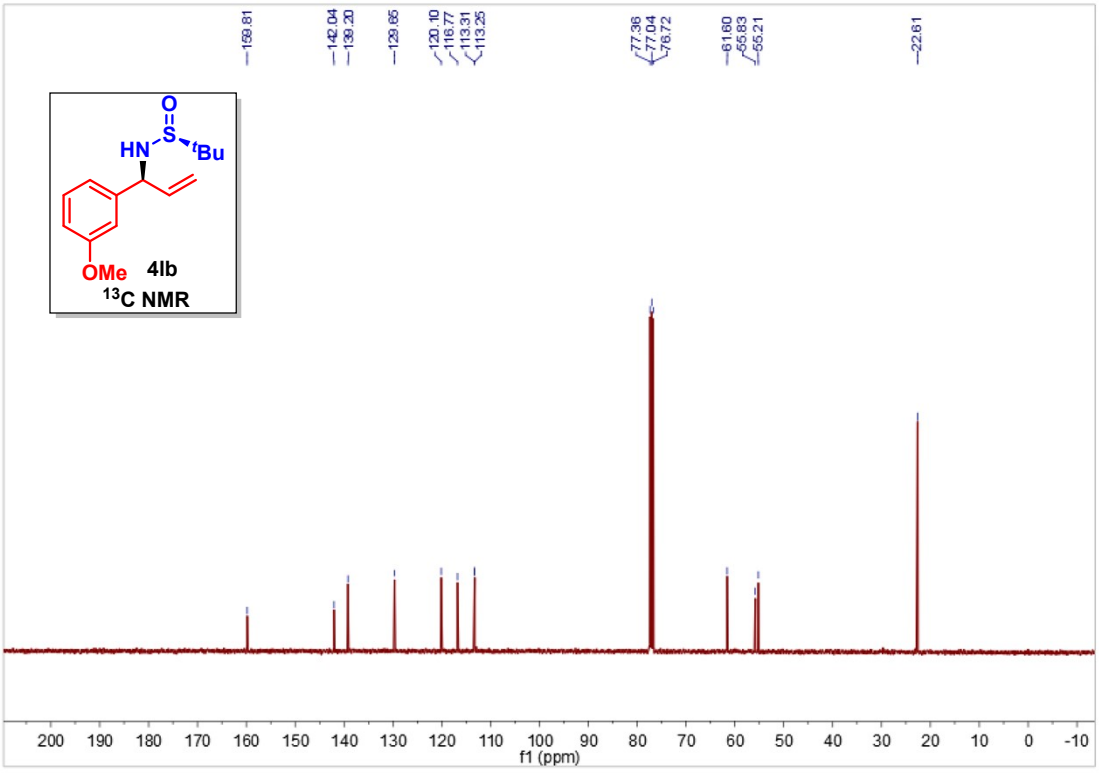
^{1}H NMR
f1 (ppm)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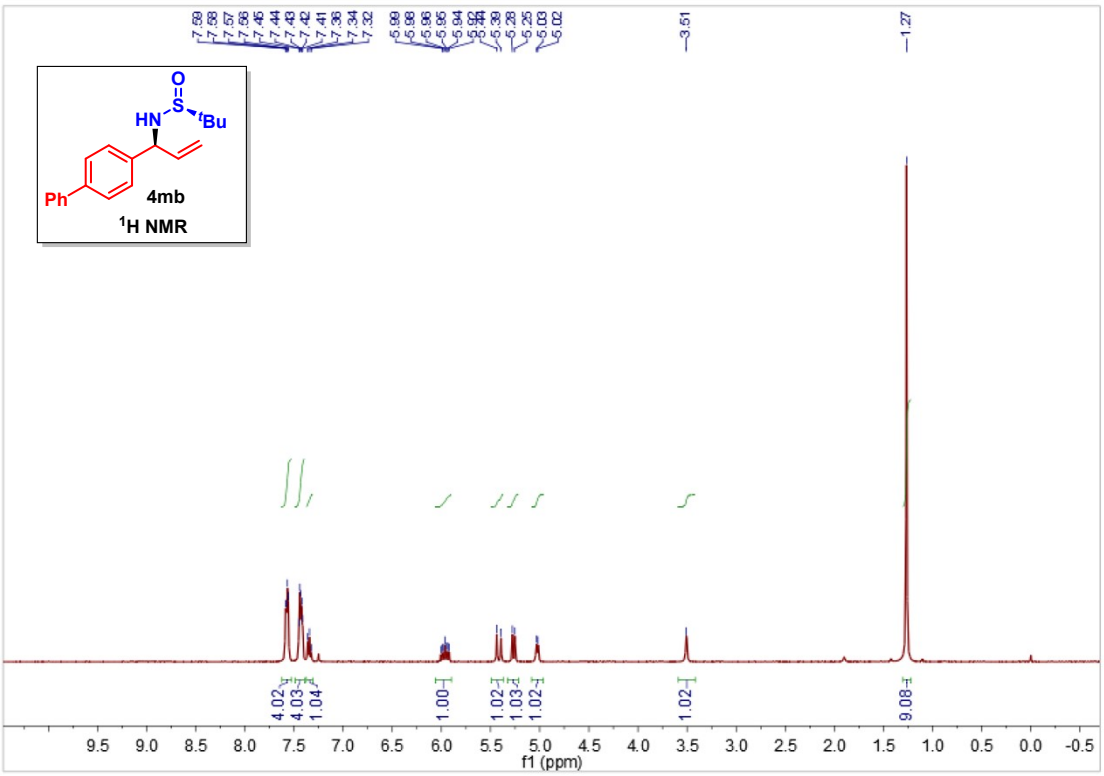
f1 (ppm)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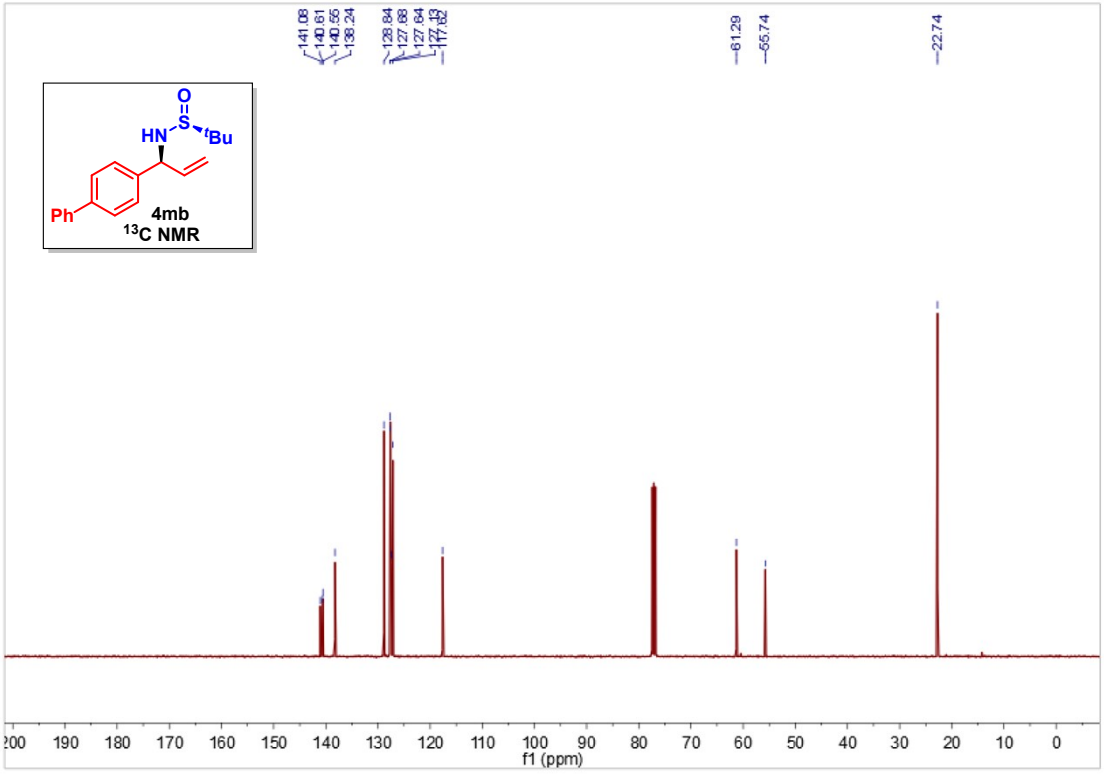
4mb
13C NMR
f1 (ppm)

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