Supporting Information for

Organoselenium-Catalyzed, Hydroxy-Controlled Regio- and Stereoselective Amination of Terminal Alkenes: Efficient Synthesis of 3-Amino Allylic Alcohols

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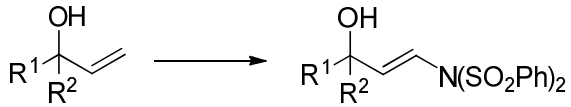
1. General considerations

Unless otherwise noted, commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, *J&K* or Adamas and used without further purification. THF was distilled from sodium prior to use. EtOAc was destilled from P_2O_5. Deuterated chloroform was basified over potassium carbonate. Flash column chromatography was carried out using 200-300 mesh silica gel (Qingdao, China). All catalytic reactions were carried out using pre-dried glassware.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Brucker ARX 400 MHz spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent signal. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for $^{13}C\{^1H\}$ NMR are reported as follows: chemical shift (δ ppm), multiplicity (d = doublet, t = triplet, q = quartet), coupling constant (Hz).

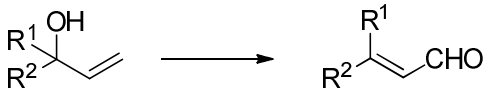
MS and HRMS were recorded on Thermo MAT95XP mass spectrometer at analytical center of Sun Yat-Sen University or Bruker Agilent 1290 mass spectrometer at analytical center of South China University of Technology.

2. General experimental procedures



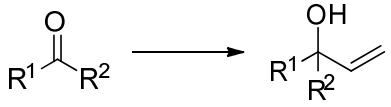
General procedure for organoselenium-catalyzed amination of allylic alcohols*:* A 5-mL glass vial was charged with a magnetic stir bar, allylic alcohol (0.20 mmol), NFSI (63.1 mg, 0.2 mmol), NaF (10.7 mg, 2.4 mmol), pyridine (17.8 mg, 0.20 mmol). A solution of PhSeSePh (3.2 mg, 0.01 mmol) in dry THF (1 mL) was subsequently added. Then the vial was capped. The mixture was stirred at ambient temperature for 4 hours. The solvent was removed on a rotary evaporator and the resultant residue

was directly purified by flash silica gel column chromatography to afford the corresponding desired product.

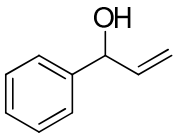


General procedure for organoselenium-catalyzed synthesis of α,β-unsaturated aldehydes: A 5-mL glass vial was charged with a magnetic stir bar, PhSeSePh (3.2 mg, 0.01 mmol.) and NFSI (63.1 mg, 0.20 mmol). The vial was flushed three times with nitrogen. Then allylic alcohol (0.20 mmol) and ethyl acetate (1 mL) were subsequently added under nitrogen atmosphere. The vial was capped. The solution was stirred at ambient temperature for 12 hours. The solvent was removed on a rotary evaporator and the resultant residue was directly purified by flash silica gel column chromatography to afford the corresponding α,*β*-unsaturated aldehyde.

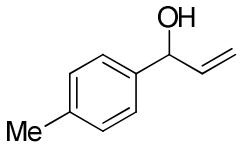
3. Synthesis of substrates



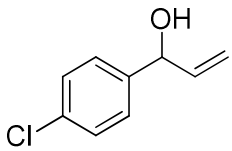
General procedure for synthesis of allylic alcohols: All allylic alcohols were synthesized according to the literature.[1] To a stirred solution of carbonyl compounds (2.00 mmol) in dry THF (10 mL) was added vinyl magnesium bromide (1.0 M in THF, 2 mL, 2.00 mmol) dropwise through a syringe at 0 °C. After stirring for 20 min the reaction mixture was allowed to warm to room temperature. The resulting mixture was stirred for additional 4 hours and then quenched by saturated NH_4Cl solution (20 mL). The organic phase was extracted with ethyl acetate (30 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum to afford the crude product. It was further purified by flash silica gel column chromatography.



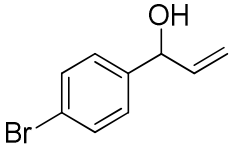
1-Phenylprop-2-en-1-ol (**1a**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1a** (238 mg, 1.78 mmol, 89%) as a colorless oil. This compound is known and its proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 7.33–7.27 (m, 1H), 6.13–5.99 (m, 1H), 5.36 (ddd, *J* = 16.5, 2.4, 1.3 Hz, 1H), 5.24 –5.16 (m, 2H), 2.16 (br, 1H).



1-(*p*-Tolyl)prop-2-en-1-ol (**1b**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1b** (240 mg, 1.62 mmol, 81%) as a colorless oil. This compound is known and the proton spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.28– 5.91 (m, 1H), 5.42–5.29 (m, 1H), 5.27–5.11 (m, 2H), 2.35 (s, 3H), 1.90 (br, 1H).

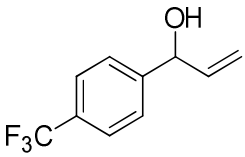


1-(4-Chlorophenyl)prop-2-en-1-ol (**1c**): Prepared by general procedure. Purified by silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to give **1c** as a colorless oil (672 mg, 4.00 mmol, 80 %). This compound is known and the proton spectrum is identical to that previously reported in the literature.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 4H), 6.08–5.95 (m, 1H), 5.35 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.21 (dt, *J* = 16.9, 3.9 Hz, 2H), 1.96 (br, 1H).

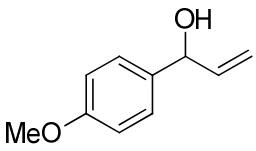


1-(4-Bromophenyl)prop-2-en-1-ol (**1d**): Prepared by general procedure. 4-Bromobenzaldehyde (920 mg, 5.00 mmol) and vinyl magnesium bromide (1.0 M in THF, 5.5 mL, 5.5 mmol) were used. The mixture was purified by silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to give **1d** as a colorless oil (848 mg, 4.00 mmol, 80 %). This compound is known and the ^{1}H NMR spectra is identical to

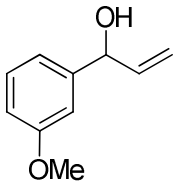
that previously reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.1, 4.5 Hz, 2H), 7.33–7.17 (m, 2H), 6.00 (ddd, *J* = 16.4, 10.4, 5.3 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.20 (dd, *J* = 13.9, 9.9 Hz, 2H), 1.98 (br, 1H).



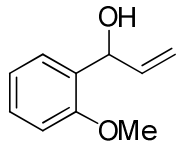
1-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (**1e**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1e** (335 mg, 1.66 mmol, 83%) as a colorless oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.14–5.93 (m, 1H), 5.38 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.33–5.16 (m, 2H), 2.04 (br, 1H).



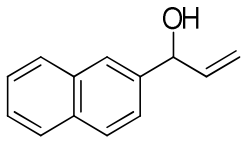
1-(4-Methoxyphenyl)prop-2-en-1-ol (**1f**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 10:1, v/v) to give **1f** (285 mg, 1.74 mmol, 87%) as a colorless oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 6.93–6.87 (m, 2H), 6.04 (ddd, *J* = 17.0, 10.3, 5.9 Hz, 1H), 5.33 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.23–5.13 (m, 2H), 3.80 (s, 3H), 2.03 (br, 1H).



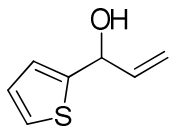
1-(3-Methoxyphenyl)prop-2-en-1-ol (**1g**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 10:1, v/v) to give **1g** (279 mg, 1.70 mmol, 85%) as a colorless oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 2H), 6.83 (ddd, *J* = 8.3, 2.5, 1.0 Hz, 1H), 6.04 (ddd, *J* = 17.1, 10.2, 6.1 Hz, 1H), 5.36 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.20 (ddd, *J* = 6.1, 3.7, 2.5 Hz, 2H), 3.81 (s, 3H), 1.96 (br, 1H).



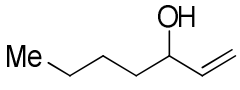
1-(2-Methoxyphenyl)prop-2-en-1-ol (**1h**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 10:1, v/v) to give **1h** (272 mg, 1.66 mmol, 83 %) as a colorless oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (ddd, *J* = 16.1, 7.8, 1.7 Hz, 2H), 7.00–6.87 (m, 2H), 6.14 (ddd, *J* = 17.2, 10.4, 5.5 Hz, 1H), 5.41 (t, *J* = 5.9, 1H), 5.31 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.17 (dt, *J* = 10.4, 1.5 Hz, 1H), 3.87 (s, 3H), 2.78 (br, 1H).



1-(Naphthalen-2-yl)prop-2-en-1-ol (**1i**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1i** (305 mg, 1.66 mmol, 83 %) as a yellow oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.2, 3.8 Hz, 4H), 7.56–7.42 (m, 3H), 6.13 (ddd, *J* = 17.0, 10.3, 6.0 Hz, 1H), 5.41 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.35 (d, *J* = 5.7, 1H), 5.25 (dt, *J* = 10.3, 1.3 Hz, 1H), 2.50 (br, 1H).

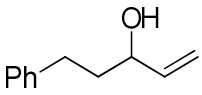


1-(Thiophen-2-yl)prop-2-en-1-ol (**1j**): Prepared by general procedure. Thiophene-2-carbaldehyde (448 mg, 4.00 mmol) and vinyl magnesium bromide (1.0 M in THF, 4.4 mL, 4.4 mmol) were used. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to give **1j** as an orange oil (168 mg, 1.20 mmol, 30%). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.02–6.96 (m, 2H), 6.21–6.06 (m, 1H), 5.50–5.36 (m, 2H), 5.26 (dt, *J* = 10.4, 1.1 Hz, 1H), 2.07 (br, 1H).

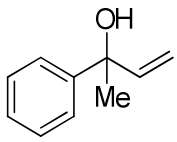


Hept-1-en-3-ol (**1k**): Prepared by general procedure. Pentanal (4 mmol) and vinyl magnesium bromide (1.0 M in THF, 6.0 mmol,

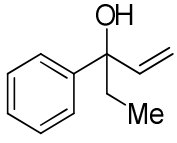
6.0 mL) were used. The residue was purified by flash column chromatography to give **1k** as pale yellow oil (302 mg, 2.65 mmol, 66%). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.10 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.10 (q, *J* = 6.3 Hz, 1H), 1.60–1.45 (m, 2H), 1.43–1.19 (m, 4H), 0.98–0.80 (m, 3H).



5-Phenylpent-1-en-3-ol (**1l**): Prepared by general procedure. Flash column chromatography (eluent: PE/EA = 30:1 to 5:1, v/v) to give **1l** as pale yellow liquid (169 mg, 1.04 mmol, 52%). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.25–7.17 (m, 3H), 5.99–5.85 (m, 1H), 5.26 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.20–5.12 (m, 1H), 4.24–3.97 (m, 1H), 2.86–2.61 (m, 2H), 1.97–1.79 (m, 2H), 1.74 (br, 1H).

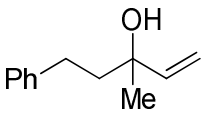


2-Phenylbut-3-en-2-ol (**1m**): Prepared by general procedure. Acetophenone (480 mg, 4.00 mmol) and vinyl magnesium bromide (1.0 M in THF, 4.8 mL, 4.8 mmol) were used. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1m** as a colorless liquid（473 mg, 3.20 mmol, 80 %). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.44 (m, 2H), 7.39–7.30 (m, 2H), 7.29–7.20 (m, 1H), 6.18 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.30 (dd, *J* = 17.3, 1.0 Hz, 1H), 5.15 (dd, *J* = 10.6, 1.0 Hz, 1H), 1.88 (br, 1H), 1.66 (s, 3H).

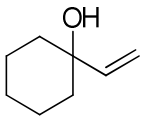


3-Phenylpent-1-en-3-ol (**1n**): Prepared by general procedure. Flash column chromatograph (eluent: PE/EtOAc = 15:1, v/v) to give the **1n**(211 mg, 1.30 mmol, 65 %) as a yellow oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the

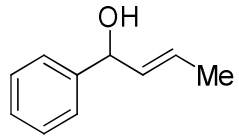
literature.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.39–7.31 (m, 2H), 7.29–7.21 (m, 1H), 6.20 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.30 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.17 (dd, *J* = 10.7, 1.1 Hz, 1H), 2.06–1.85 (m, 2H), 1.81 (br, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).



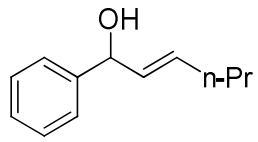
3-Methyl-5-phenylpent-1-en-3-ol (**1o**): Prepared by general procedure. Flash column chromatograph (eluent: PE/EtOAc =15:1, v/v) to give **1o** (229 mg, 1.30 mmol, 65 %) as a yellow oil. This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 7.23–7.14 (m, 3H), 5.98 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.27 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.12 (dd, *J* = 10.8, 1.1 Hz, 1H), 2.77–2.53 (m, 2H), 1.95–1.74 (m, 2H), 1.46 (br, 1H), 1.35 (s, 3H).



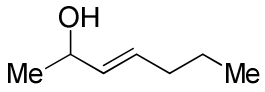
1-Vinylcyclohexanol (**1p**): Prepared by general procedure. Flash column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **1p** as a colorless liquid (206 mg, 1.64 mmol, 41 %). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.25 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.04 (dd, *J* = 10.8, 1.3, 1H), 1.78–1.43 (m, 10H).



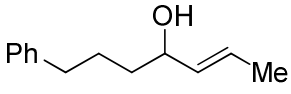
(E)-1-Phenylbut-2-en-1-ol (**4a**): Prepared by general procedure. (E)-But-2-enal (441 mg, 5.00 mmol) was used. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **4a** as a colorless liquid (518 mg, 3.50 mmol, 70 %). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (m, 4H), 7.31–7.23 (m, 1H), 5.84–5.64 (m, 2H), 5.17 (dd, *J* = 6.4, 3.2 Hz, 1H), 1.87 (br, 1H), 1.77–1.66 (m, 3H).



(E)-1-Phenylhex-2-en-1-ol (**4b**): Prepared by general procedure. (E)-Hex-2-enal (490 mg, 5 mmol) was used. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **4b** as a colorless liquid (660 mg, 3.75 mmol, 75 %). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (m, 4H), 7.31–7.21 (m, 1H), 5.83–5.59 (m, 2H), 5.17 (dd, *J* = 6.5, 3.6 Hz, 1H), 2.04 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.85 (br, 1H), 1.49–1.35 (m, 2H), 0.91 (q, *J* = 7.1 Hz, 3H).

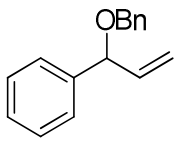


(E)-Hept-3-en-2-ol (**4c**): To a solution of (E)-hept-3-en-2-one (336 mg, 3 mmol) in methanol (4 mL) at 0 °C was added sodium borohydride (342 mg, 9 mmol) in methanol (4 mL). The reaction was stirred and slowly warmed to room temperature over 3 h, and then quenched with saturated aqueous NH_4Cl (10 mL). The resultant mixture was concentrated in vacuo and the residue was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (eluent: PE/EtOAc = 10:1, v/v) to afford **4d** as a colorless liquid (280 mg, 2.5 mmol, 82%). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.51 (dd, *J* = 15.4, 6.5 Hz, 1H), 4.26 (p, *J* = 6.3 Hz, 1H), 1.99 (q, *J* = 7.1 Hz, 2H), 1.44–1.34 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

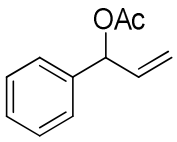


(E)-7-Phenylhept-2-en-4-ol (**4d**): Prepared by general procedure. (E)-Hex-2-enal (252 mg, 3.6 mmol) was used. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 15:1, v/v) to give **4c** as a colorless liquid (561 mg, 3.0 mmol, 82%). This compound is known and the proton NMR spectrum is identical to that previously reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.18 (dd, *J* = 5.0, 2.7

Hz, 3H), 5.73–5.57 (m, 1H), 5.47 (ddd, *J* = 15.3, 7.2, 1.5 Hz, 1H), 4.05 (d, *J* = 4.7 Hz, 1H), 2.63 (t, *J* = 7.4 Hz, 2H), 1.78–1.45 (m, 7H), 1.39 (br, 1H).

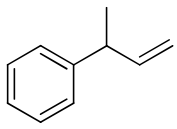


(1-(Benzyloxy)allyl)benzene (**7a**): To 1-phenylprop-2-en-1-ol (268 mg, 2.00 mmol) in anhydrous THF (5 mL) was added NaH (60% in mineral oil, 92 mg, 2.30 mmol) at room temperature. The mixture was stirred for 30 min and then cooled to 0 °C. Benzyl bromide (340 mg, 2.00 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. The reaction was quenched by water (5 mL) and the organic phase was extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: PE) to give the desire product **7a** as a colorless liquid (148 mg, 0.66 mmol, 33 %). This compound is known and the ^{1}H NMR spectra is identical to that previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.26 (m, 10H), 5.99 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.27 (ddt, *J* = 23.8, 10.3, 1.3 Hz, 2H), 4.84 (d, *J* = 6.6 Hz, 1H), 4.53 (s, 2H).



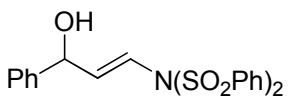
1-Phenylallyl acetate (**7b**): To a solution of 1-phenylprop-2-en-1-ol (268 mg, 2.00 mmol) in dry DCM (6 mL), Et_3N (404 mg, 4.00 mmol) and 4-dimethylaminopyridine (12 mg, 0.10 mmol) were subsequently added. The reaction was then cooled to 0 ºC and a solution of Ac_2O（306 mg, 1.50 mmol）in dry DCM (3 mL) was added dropwise through a syringe. After stirring for 20 min the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched by saturated NH_4Cl solution (20 mL). The organic phase was extracted with ethyl acetate (30 mL x 3). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to give the desire product **7b** as a colorless liquid (282 mg, 1.60 mmol, 80%). This compound is known and the ^{1}H NMR spectra is identical to

that previously reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.27 (m, 5H), 6.26 (dt, *J* = 5.9, 1.3 Hz, 1H), 6.01 (ddd, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.27 (ddt, *J* = 14.4, 10.4, 1.3 Hz, 2H), 2.12 (s, 3H).



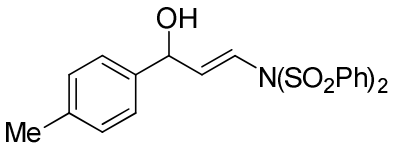
But-3-en-2-ylbenzene (**13**): To a stirred solution of Ph_3P (2.622 g, 10 mmol) in dry THF (20 mL) was added CH_3I (622.6 μL, 10 mmol) dropwise through a syringe at room temperature. The solution was stirred in a dark place under nitrogen at room temperature overnight and the solvent was removed in vacuo to form the $[Ph_3P^+CH_3]I^-$ as a white solid in quantitative yield. The salt $[Ph_3P^+CH_3]I^-$ was used without further purification. To a stirred solution of $[Ph_3P^+CH_3]I^-$ (2.021 g, 5 mmol) in dry THF (25 mL) was added NaHMDS (5 mL, 5 mmol, 1 M in THF) dropwise through a syringe at -20℃ under nitrogen and the solution was stirred for another 30 min at the same temperature. Then to the solution was added 2-phenylpropanal (656.1 μL, 4.9 mmol) in dry THF (4 mL) dropwise and the resulting solution was stirred at room temperature overnight. Water (20 mL) was added and the mixture was extracted with Et_2O (30 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (PE, 30~60 ℃) to give the desire product as a colorless liquid (432 mg, 67%). This compound is known and the ^{1}H NMR spectra is identical to that previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.25–7.18 (m, 3H), 6.02 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.11–5.02 (m, 2H), 3.48 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 3H).

4. Analytic data for aminated prodcuts

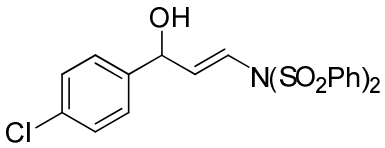


(E)-N-(3-hydroxy-3-phenylprop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide(2a): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford 2a (74.7 mg, 0.17 mmol, 87 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ

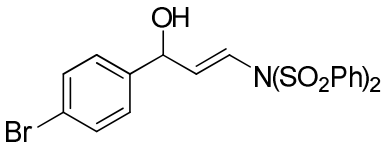
7.88 (d, *J* = 7.9 Hz, 4H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 4H), 7.35 (dt, *J* = 13.5, 7.3 Hz, 5H), 6.29 (d, *J* = 13.4 Hz, 1H), 5.98 (dd, *J* = 13.4, 6.0 Hz, 1H), 5.29 (d, *J* = 5.9 Hz, 1H), 2.64 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.65, 141.17, 139.21, 134.08, 129.16, 128.85, 128.34, 128.23, 126.54, 121.30, 72.51. HR-ESI-MS m/z calcd. $C_{21}H_{19}NO_5S_2$ [M+HCOO]$^-$: 474.0681, found: 474.0690.



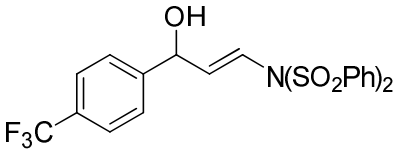
(E)-N-(3-Hydroxy-3-(*p*-tolyl)prop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2b**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2b** (71.8 mg, 0.16 mmol, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.83 (m, 4H), 7.69–7.56 (m, 2H), 7.47 (t, *J* = 7.9 Hz, 4H), 7.24–7.14 (m, 4H), 6.27 (dd, *J* = 13.4, 1.4 Hz, 1H), 5.99 (dd, *J* = 13.4, 5.8 Hz, 1H), 5.26 (d, *J* = 5.5 Hz, 1H), 2.52 (br, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.71, 139.32, 138.25, 138.12, 134.05, 129.51, 129.15, 128.25, 126.57, 121.19, 72.38, 21.29. HR-ESI-MS m/z calcd. $C_{22}H_{21}NO_5S_2$ [M+HCOO]$^-$: 488.0838, found: 488.0844.



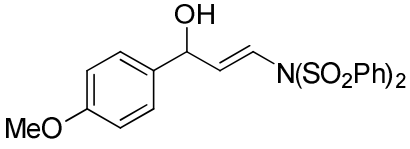
(E)-N-(3-(4-chlorophenyl)-3-hydroxyprop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2c**): Prepared by general procedure. Flash silica gel column chromatography(eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2c** (65.8mg, 0.14 mmol, 71%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J*=7.8 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 13.4 Hz, 1H), 5.93 (dd, *J* = 13.4, 6.2 Hz, 1H), 5.25 (d, *J* = 6.0 Hz, 1H), 2.95 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.96, 139.65, 139.12, 134.20, 134.01, 129.21, 128.95, 128.20, 127.90, 121.70, 71.75. HR-ESI-MS m/z calcd. $C_{21}H_{18}ClNO_5S_2$ [M+HCOO]$^-$: 508.0291, found: 508.0295.



(E)-N-(3-(4-Bromophenyl)-3-hydroxyprop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2d**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2d** (79.1 mg, 0.16 mmol, 78 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5, 6H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.28 (d, *J* = 13.4 Hz, 1H), 5.92 (dd, *J* = 13.4, 6.2 Hz, 1H), 5.24 (d, *J* = 6.2 Hz, 1H), 2.59 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.81, 140.18, 139.13, 134.21, 131.91, 129.22, 128.21, 122.19, 121.74, 71.82. HR-ESI-MS m/z calcd. $C_{21}H_{18}BrNO_5S_2$ $[M+HCOO]^-$: 551.9786, found: 551.9795.

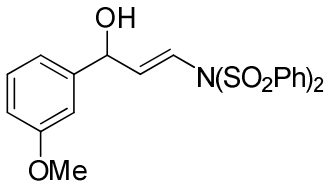


(E)-N-(3-Hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2e**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1,v/v) to afford **2e** (62.6 mg, 0.13 mmol, 63%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 4H), 7.62 (dd, *J* = 7.5, 4.7 Hz, 4H), 7.44 (dd, *J* = 16.4, 8.2 Hz, 6H), 6.33 (d, *J* = 13.4 Hz, 1H), 5.93 (dd, *J* = 13.4, 6.4 Hz, 1H), 5.35 (d, *J* = 6.2 Hz, 1H), 2.98 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.10, 140.13, 139.17, 134.30, 130.43 (q, *J* = 32.6 Hz) , 129.23, 128.25, 126.75, 125.78 (q, *J* = 3.7 Hz) ,124.12 (d, *J* = 272.1 Hz) , 122.23, 71.93. HR-ESI-MS m/z calcd. $C_{22}H_{18}F_3NO_5S_2$ $[M+HCOO]^-$: 542.0555, found: 542.0559.

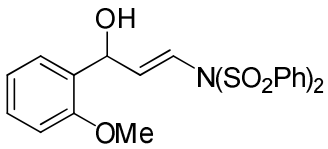


(E)-N-(3-Hydroxy-3-(4-methoxyphenyl)prop-1-en-1-yl)-N-(phenylsulfonyl)benzensulfonamide (**2f**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 3:1, v/v) to afford **2f** (66.1mg, 0.14 mmol, 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 4H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 4H), 7.37–7.21 (m, 2H), 6.92 (d, *J* =

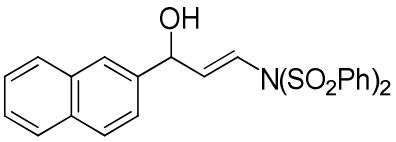
8.6 Hz, 2H), 6.30 (d, *J* = 13.4 Hz, 1H), 6.02 (dd, *J* = 13.3, 5.7 Hz, 1H), 5.28 (d, *J* = 5.5 Hz, 1H), 3.84 (s, 3H), 2.45 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66, 141.84, 139.36, 134.10, 133.41, 129.19, 128.28, 128.04, 121.15, 114.23, 72.16, 55.48. HR-ESI-MS m/z calcd. $C_{22}H_{21}NO_6S_2$ [M-H]$^-$: 458.0732, found: 458.0739.



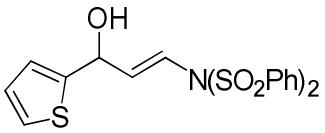
(E)-N-(3-Hydroxy-3-(3-methoxyphenyl)prop-1-en-1-yl) -N-(phenylsulfonyl)benzenesulfonamide (**2g**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 3:1, v/v) to afford **2g** (66.1 mg, 0.14 mmol, 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.77 (m, 4H), 7.72–7.54 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 4H), 7.36–7.19 (m, 2H), 7.06–6.71 (m, 3H), 6.29 (dd, *J* = 13.4, 1.3 Hz, 1H), 5.98 (dd, *J* = 13.4, 5.9 Hz, 1H), 5.42–5.21 (m, 1H), 3.80 (s, 1H), 2.61 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.04, 142.80, 141.48, 139.28, 134.08, 129.91, 129.17, 128.24, 121.42, 118.81, 114.22, 111.70, 72.44, 55.41. HR-ESI-MS m/z calcd. $C_{22}H_{21}NO_6S_2$ [M+HCOO]$^-$: 504.0787, found: 504.0793.



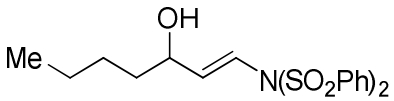
(E)-N-(3-Hydroxy-3-(2-methoxyphenyl)prop-1-en-1-yl) -N-(phenylsulfonyl)benzenesulfonamide (**2h**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 3:1, v/v) to afford **2h** (65.2 mg, 0.14 mmol, 71%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.30 (dd, *J* = 10.3, 5.2 Hz, 2H), 7.00–6.84 (m, 3H), 6.31 (d, *J* = 13.4 Hz, 1H), 6.00 (dd, *J* = 13.3, 6.0 Hz, 1H), 5.29 (d, *J* = 5.9 Hz, 1H), 3.82 (s, 3H), 2.87 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.00, 142.79, 141.65, 139.22, 134.09, 129.88, 129.16, 128.22, 121.35, 118.80, 114.17, 111.67, 72.37, 55.39. HR-ESI-MS m/z calcd. $C_{22}H_{21}NO_6S_2$ [M+HCOO]$^-$: 504.0787, found: 504.0782.



(E)-N-(3-Hydroxy-3-(naphthalen-2-yl)prop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2i**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2i** (70.9 mg, 0.15 mmol, 74 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.72 (m, 8H), 7.60–7.47 (m, 4H), 7.46–7.29 (m, 5H), 6.36 (dd, *J* = 13.4, 0.9 Hz, 1H), 6.07 (dd, *J* = 13.4, 6.0 Hz, 1H), 5.45 (d, *J* = 5.9 Hz, 1H), 2.93 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.50, 139.17, 138.59, 134.05, 133.35, 133.20, 129.11, 128.70, 128.19, 127.81, 126.49, 126.41, 125.37, 124.37, 121.44, 72.61. HR-ESI-MS m/z $C_{25}H_{21}NO_5S_2$ calcd. $[M+HCOO]^-$: 524.0838, found: 524.0844.

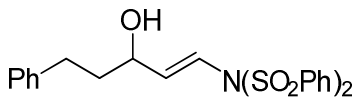


(E)-N-(3-Hydroxy-3-(thiophen-2-yl)prop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2j**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2j** (71.3 mg, 0.16 mmol, 82%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.87 (m, 4H), 7.63 (ddd, *J* = 7.0, 4.1, 1.2 Hz, 2H), 7.54–7.45 (m, 4H), 7.32–7.28 (m, 1H), 6.97 (d, *J* = 3.5 Hz, 2H), 6.33 (dd, *J* = 13.4, 1.3 Hz, 1H), 6.11 (dd, *J* = 13.4, 6.0 Hz, 1H), 5.53 (dd, *J* = 6.0, 1.1 Hz, 1H), 2.80 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.96, 140.16, 139.27, 134.15, 129.22, 128.24, 127.07, 125.95, 125.16, 122.11, 68.25. HR-ESI-MS m/z $C_{19}H_{17}NO_5S_3$ calcd. $[M+HCOO]^-$: 480.0251, found: 480.02548.

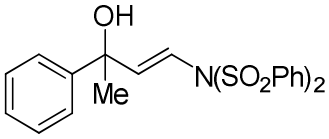


(E)-N-(3-Hydroxyhept-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2k**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2k** (64.6 mg, 0.16 mmol, 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 4H), 6.11 (d, *J* = 13.4 Hz, 1H), 5.86 (dd, *J* = 13.4, 6.3 Hz, 1H), 4.21 (q, *J* = 6.3 Hz, 1H), 2.22 (br, 1H), 1.64–1.41 (m, 2H), 1.39–1.11 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C

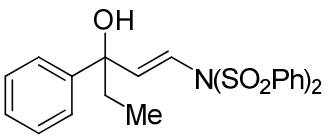
NMR (101 MHz, $CDCl_3$) δ 143.20, 139.44, 134.12, 129.20, 128.23, 121.13, 70.27, 36.54, 27.24, 22.60, 14.13. HR-ESI-MS m/z calcd. $C_{19}H_{23}NO_5S_2$ $[M+HCOO]^-$: 454.0994, found: 454.1000.



(E)-N-(3-Hydroxy-5-phenylpent-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2l**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2l** (86.8 mg, 0.19 mmol, 95%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7, 4H), 7.64 (t, *J* = 7.5, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 11.4, 7.5 Hz, 3H), 6.15 (d, *J* = 13.4 Hz, 1H), 5.92 (dd, *J* = 13.4, 6.3 Hz, 1H), 4.24 (q, *J* = 6.3 Hz, 1H), 2.78–2.60 (m, 2H), 2.44 (br, 1H), 1.98–1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.87, 141.34, 139.37, 134.16, 129.22, 128.58, 128.51, 128.20, 126.12, 121.51, 69.43, 38.22, 31.27. HR-ESI-MS m/z calcd. $C_{23}H_{23}NO_5S_2$ $[M - H]^-$: 456.0939, found: 456.0949.

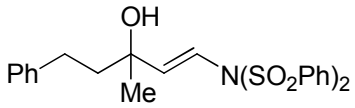


(E)-N-(3-Hydroxy-3-phenylbut-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2m**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2m** (63.8 mg, 0.14 mmol, 72%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 4H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32–7.27 (m, 1H), 6.24 (d, *J* = 13.3 Hz, 1H), 6.09 (d, *J* = 13.3 Hz, 1H), 2.47 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.92, 144.97, 139.31, 134.05, 129.15, 128.61, 128.25, 127.70, 125.25, 119.98, 73.89, 29.19. HR-ESI-MS m/z $C_{22}H_{21}NO_5S_2$ calcd. $[M+HCOO]^-$: 488.0838, found: 488.0842.

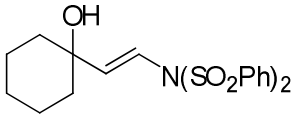


(E)-N-(3-Hydroxy-3-phenylpent-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2n**): Prepared by general procedure. Flash silica gel column chromatography

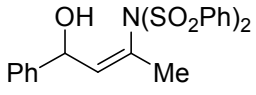
(eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2n** (61.2 mg, 0.13 mmol, 67%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 4H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 4H), 7.40 – 7.27 (m, 5H), 6.23 (d, *J* = 13.3 Hz, 1H), 6.12 (d, *J* = 13.3 Hz, 1H), 2.31 (br, 1H), 1.95 (q, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.47, 144.22, 139.32, 133.99, 129.14, 128.54, 128.19, 127.49, 125.49, 120.39, 76.65, 34.68, 7.93. HR-ESI-MS m/z calcd. $C_{23}H_{23}NO_5S_2$ $[M+HCOO]^-$: 502.0994, found: 502.0996.



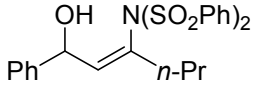
(E)-N-(3-Hydroxy-3-methyl-5-phenylpent-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2o**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2o** (73.5 mg, 0.16 mmol, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 4H), 7.69 – 7.59 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 7.29 (dd, *J* = 12.7, 5.4 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 3H), 6.20 (d, *J* = 13.3 Hz, 1H), 5.96 (d, *J* = 13.3 Hz, 1H), 2.66 (pd, *J* = 13.5, 6.4 Hz, 2H), 2.33 (br, 1H), 1.93–1.75 (m, 2H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.59, 141.92, 139.40, 134.08, 129.19, 128.56, 128.40, 128.17, 126.00, 120.05, 72.76, 44.14, 30.22, 28.32. HR-ESI-MS m/z calcd. $C_{24}H_{25}NO_5S_2$ $[M-H]^-$: 470.1096, found: 470.1104.



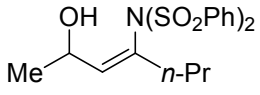
(E)-N-(2-(1-Hydroxycyclohexyl)vinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2p**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 10:1 to 5:1, v/v) to afford **2p** (70.7 mg, 0.17 mmol, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 6.14 (d, *J* = 13.3 Hz, 1H), 5.93 (d, *J* = 13.3 Hz, 1H), 1.96 (br, 1H), 1.70–1.38 (m, 8H), 1.35–1.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.19, 139.44, 134.05, 129.15, 128.26, 119.72, 71.43, 37.50, 25.26, 21.69. HR-ESI-MS m/z $C_{20}H_{23}NO_5S_2$ calcd. $[M + COO]^-$: 466.0994, found: 466.0993.



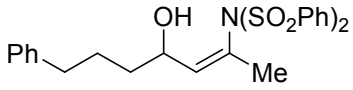
(Z)-N-(4-Hydroxy-4-phenylbut-2-en-2-yl)-N-(phenylsulfonyl)benzenesulfonamide (**5a**): Prepared by a modified general procedure. To a 5-mL glass vial was subsequently PhSeSePh (3.1 mg, 0.01 mmol, 5 mol%), NFSI (63.1 mg, 0.20 mmol), dry THF (1 mL) and **4a** (29.6 mg, 0.20 mmol,). The resulting solution was stirred at room temperature for 12 h. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 15:1 to 9:1, v/v) to give **5a** (71.8 mg, 0.16 mmol, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.58 (dd, J = 15.5, 7.8 Hz, 3H), 7.45–7.23 (m, 8H), 6.05 (d, J = 9.9 Hz, 1H), 5.09 (dd, J = 9.9, 2.2 Hz, 1H), 2.98 (br, J = 2.5 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.71, 139.25, 139.18, 134.58, 134.28, 131.66, 129.37, 129.12, 128.94, 128.86, 128.38, 127.77, 126.49, 68.46, 22.98. HR-ESI-MS m/z calcd. $C_{22}H_{21}NO_5S_2$ $[M+Cl]^-$: 478.0550, found: 478.0560.



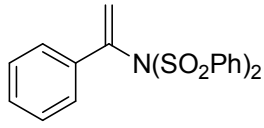
(Z)-N-(1-Hydroxy-1-phenylhex-2-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (**5b**): Prepared by a procedure similar to synthesis of **5a**. Silica gel column chromatography (eluent: PE/EtOAc = 15:1 to 12:1, v/v) to give **5b** (66.9 mg, 0.14 mmol, 71%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.03 (m, 2H), 7.97 (dd, J = 8.5, 1.1 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.64–7.48 (m, 3H), 7.41–7.21 (m, 8H), 6.03 (dt, J = 9.8, 1.4 Hz, 1H), 5.13 (dd, J = 9.8, 2.4 Hz, 1H), 2.98 (br, 1H), 2.54–1.98 (m, 1H), 1.84–1.69 (m, 1H), 1.65–1.38 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.88, 139.30, 139.19, 136.92, 136.18, 134.56, 134.24, 129.32, 129.06, 129.03, 128.94, 128.38, 127.74, 126.51, 68.26, 37.87, 20.67, 13.62. HR-ESI-MS m/z calcd. $C_{24}H_{25}NO_5S_2$ $[M+Cl]^-$: 506.0863, found: 506.0868.



(Z)-N-(2-Hydroxyhept-3-en-4-yl)-N-(phenylsulfonyl)benzenesulfonamide (**5c**): Prepared by a procedure similar to synthesis of **5a**. Silica gel column chromatography (eluent: PE/EtOAc = 15:1 to 12:1, v/v) to give **5c (**62.2 mg, 0.15 mmol, 76%) as white solid. A single crystal suitable for X-ray diffraction was achieved by slow evaporation of a solution of **5c** in mixed solvents of dichloromethane and hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–7.98 (m, 4H), 7.69 (td, *J* = 7.3, 1.6 Hz, 2H), 7.64–7.52 (m, 4H), 5.65 (d, *J* = 9.7 Hz, 1H), 3.86 (dqd, *J* = 12.1, 6.1, 2.0 Hz, 1H), 2.38 (br, 1H), 2.33–2.21 (m, 1H), 2.01–1.88 (m, 1H), 1.58–1.40 (m, 2H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.76, 139.21, 138.92, 134.45, 134.39, 134.36, 129.26, 129.22, 129.05, 128.84, 63.23, 38.04, 21.16, 20.73, 13.61. HR-ESI-MS m/z calcd. $C_{19}H_{23}NO_5S_2$ $[M+Na]^+$: 432.0915, found: 432.0914.

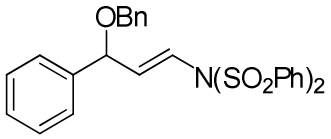


(Z)-N-(4-Hydroxy-7-phenylhept-2-en-2-yl)-N-(phenylsulfonyl)benzenesulfonamide (**5d**): Prepared by a procedure similar to synthesis of **5a**. Silica gel column chromatography (eluent: PE/EtOAc = 15:1 to 12:1, v/v) to give **5d** (89.4 mg, 0.18 mmol, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–7.94 (m, 4H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (dt, *J* = 15.3, 7.5 Hz, 3H), 7.45 (dd, *J* = 10.8, 5.0 Hz, 2H), 7.32 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.24–7.15 (m, 3H), 5.73 (dd, *J* = 9.8, 1.0 Hz, 1H), 3.67 (t, *J* = 9.3 Hz, 1H), 2.63–2.44 (m, 3H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.79–1.65 (m, 1H), 1.45–1.26 (m, 1H), 1.22–1.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.42, 140.35, 139.67, 138.89, 134.38, 134.29, 130.41, 129.27, 129.15, 128.80, 128.66, 128.57, 128.35, 125.84, 66.94, 35.95, 35.15, 27.24, 23.12. HR-ESI-MS m/z calcd. $C_{25}H_{27}NO_5S_2$ $[M+Na]^+$: 508.1228, found: 508.1223.

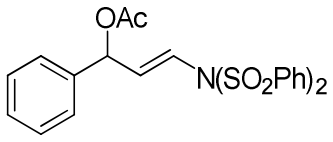


N-(1-Phenylvinyl)-N-(phenylsulfonyl)benzenesulfonamide (**6**): Prepared by a modified general procedure with $NaHCO_3$

(20.2 mg, 0.24 mmol) as the base. The residue was purified by silica gel column chromatography (eluent: PE/EA = 15:1, v/v) to give the desire product **6** as a pale solid (79.9 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.91 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.9, 4H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.31–7.26 (m, 1H), 7.21 (dd, *J* = 10.1, 4.6 Hz, 2H), 5.91 (d, *J* = 0.9 Hz, 1H), 5.06 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.05, 139.35, 135.33, 134.11, 129.18, 129.16, 128.90, 128.39, 127.15, 120.30. HR-ESI-MS m/z calcd. $C_{20}H_{17}NO_4S_2$ $[M+NH_4]^+$: 417.0943, found: 417.0916.



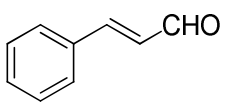
(E)-N-(3-(Benzyloxy)-3-phenylprop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**8a**): Prepared by general procedure. Purified by flash silica gel column chromatography (eluent: PE/EA = 10:1, v/v) to afford the corresponding product **8a** (60.2 mg, 0.12 mmol, 58%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 4H), 7.44–7.28 (m, 10H), 6.27 (d, *J* = 13.4 Hz, 1H), 5.96 (dd, *J* = 13.5, 6.7 Hz, 1H), 4.94 (d, *J* = 6.7 Hz, 1H), 4.60–4.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.17, 139.48, 139.32, 137.89, 134.06, 129.15, 128.80, 128.56, 128.32, 128.27, 127.86, 127.84, 127.09, 122.17, 78.47, 70.32. HR-ESI-MS m/z calcd. $C_{28}H_{25}NO_5S_2$ $[M+Na]^+$: 542.1072, found: 542.1064.



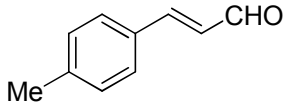
(E)-1-Phenyl-3-(N-(phenylsulfonyl)phenylsulfonamido) allyl acetate (**8b**): Prepared by general procedure. Purified by flash silica gel column chromatography (eluent: PE/EA = 10:1, v/v) to afford the corresponding product **8b** (36.6 mg, 0.08 mmol, 39%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.5, 1.2 Hz, 4H), 7.67–7.59 (m, 2H), 7.54–7.46 (m, 4H), 7.42–7.30 (m, 5H), 6.31 (d, *J* = 6.4 Hz, 1H), 6.26 (dd, *J* = 13.5, 1.2 Hz, 1H), 6.01 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.74, 139.26, 137.72, 136.75, 134.15, 129.18, 128.91,

128.81, 128.31, 127.30, 123.09, 73.41, 21.24. HR-ESI-MS m/z calcd. $C_{23}H_{21}NO_6S_2$ $[M+Na]^+$: 494.0708, found: 494.0703.

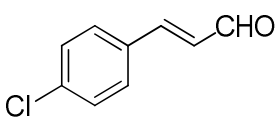
5. Analytic data for α,β-unsaturated aldehydes



(E)-Cinnamaldehyde (**3a**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to **3a** (24.3 mg, 0.18 mmol, 92%) as a yellow oil. This compound is known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously reported in the literature.[14] ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.61–7.54 (m, 2H), 7.52–7.40 (m, 4H), 6.73 (dd, *J* = 16.0, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.87, 152.95, 134.13, 131.42, 129.25, 128.74, 128.63.

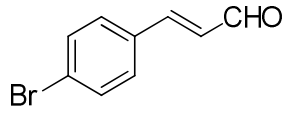


(E)-3-(p-Tolyl)acrylaldehyde (**3b**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3b** (28.3 mg, 0.19 mmol, 97%) as a white solid. This compound is known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously reported in the literature.[14] ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 7.7 Hz, 1H), 7.45 (dd, *J* = 12.1, 5.9 Hz, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.68 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.94, 153.10, 142.10, 131.43, 129.96, 128.65, 127.82, 21.69.



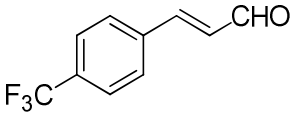
(E)-3-(4-Chlorophenyl)acrylaldehyde (**3c**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3c** (27.8 mg, 0.17 mmol, 84%) as a white soild. This compound is known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously reported in the literature.[15] ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 7.6 Hz, 1H), 7.54–7.47 (m, 2H), 7.46–7.38 (m, 3H),

6.68 (dd, J = 16.0, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.52, 151.19, 137.42, 132.62, 129.75, 129.58, 129.09.

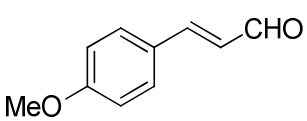


(E)-3-(4-Bromophenyl)acrylaldehyde (**3d**): Prepared by general procedure.

Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3d** (34.9 mg, 0.17 mmol, 83%) as a white soild. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, J = 7.6 Hz, 1H), 7.65–7.51 (m, 2H), 7.42 (dd, J = 12.2, 5.3 Hz, 3H), 6.70 (dd, J = 16.0, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.48, 151.22, 133.02, 132.53, 129.91, 129.15, 125.82.

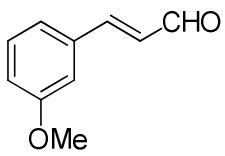


(E)-3-(4-(Trifluoromethyl)phenyl)acrylaldehyde (**3e**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3e** (32.8 mg, 0.16 mmol, 82%) as a white solid. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, J = 7.6 Hz, 1H), 7.76 – 7.59 (m, 4H), 7.51 (d, J = 16.0 Hz, 1H), 6.78 (dd, J = 16.0, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.35, 150.45, 137.43, 130.76 (q, J = 32.6 Hz), 130.65, 128.72, 126.22 (q, J = 3.7 Hz), 123.81 (d, J = 272.5 Hz).

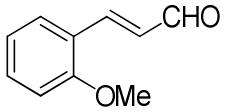


(E)-3-(4-Methoxyphenyl)acrylaldehyde (**3f**): Prepared by general procedure. Silica gel column chromatography (eluent: PE/EtOAc = 12:1, v/v) to afford **3f** (13.9 mg, 0.86 mmol, 43%) as a white solid. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.43 (d, J =

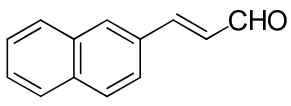
15.8 Hz, 1H), 6.93 (dd, *J* = 13.1, 10.4 Hz, 2H), 6.62 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.86, 162.34, 152.86, 130.50, 126.67, 114.71, 55.61.



(E)-3-(3-Methoxyphenyl)acrylaldehyde (**3g**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1 to 20:1, v/v) to afford **3g** (30.1 mg, 0.19 mmol, 93%) as a white solid. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 15.9 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.11–7.05 (m, 1H), 6.99 (ddd, *J* = 8.2, 2.5, 0.7 Hz, 1H), 6.70 (dd, *J* = 15.9, 7.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.80, 160.13, 152.80, 135.47, 130.24, 128.97, 121.34, 117.22, 113.41, 55.49.

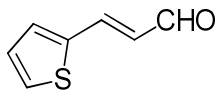


(E)-3-(2-Methoxyphenyl)acrylaldehyde (**3h**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1 to 20:1, v/v) to afford **3h** (31.0 mg, 0.19 mmol, 96%) as a white solid. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 16.1 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.46–7.37 (m, 1H), 7.07–6.92 (m, 2H), 6.79 (dd, *J* = 16.1, 7.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.71, 158.40, 148.35, 132.81, 129.19, 128.99, 123.08, 120.99, 111.40, 55.69.

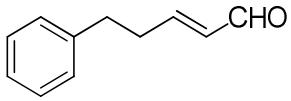


(E)-3-(Naphthalen-2-yl)acrylaldehyde (**3i**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3i** (33.9 mg, 0.18 mmol, 93%) as a white solid. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[14] ^{1}H NMR

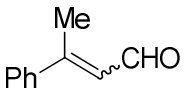
(400 MHz, $CDCl_3$) δ 9.76 (d, *J* = 7.7 Hz, 1H), 7.98 (s, 1H), 7.87 (dd, *J* = 15.2, 6.6 Hz, 3H), 7.59 (dddd, *J* = 14.7, 8.5, 7.9, 3.4 Hz, 4H), 6.83 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.81, 152.90, 134.75, 133.30, 131.66, 130.82, 129.09, 128.88, 128.81, 127.99, 127.94, 127.08, 123.64.



(E)-3-(Thiophen-2-yl)acrylaldehyde (**3j**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 20:1, v/v) to afford **3j** (19.3 mg, 0.14 mmol, 70%) as an orange oil. This compound is known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously reported in the literature.[14] ^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 15.6 Hz, 1H), 7.50 (d, *J* = 5.1 Hz, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.52 (dd, *J* = 15.6, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.03, 144.55, 139.42, 132.20, 130.53, 128.66, 127.52.

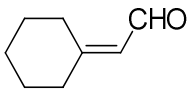


(E)-5-Phenylpent-2-enal (**3k**): Prepared by general procedure but the reaction was carried out at 60 °C. The residue was directly purified by flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3k** (22.8 mg, 0.14 mmol, 71%) as a colorless oil. This compound is known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously reported in the literature.[18] ^1H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.25–7.17 (m, 3H), 6.86 (dt, *J* = 15.6, 6.7 Hz, 1H), 6.14 (ddt, *J* = 15.6, 7.9, 1.4 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.74–2.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.10, 157.45, 140.39, 133.52, 128.72, 128.45, 126.51, 34.36, 34.20.



3-Phenylbut-2-enal (**3l**): Prepared by general procedure. Flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford the isomers **3l** (19.3 mg, 0.12 mmol, 66%, Z/E = 1: 5) as a white soild. They are known, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are identical to those previously

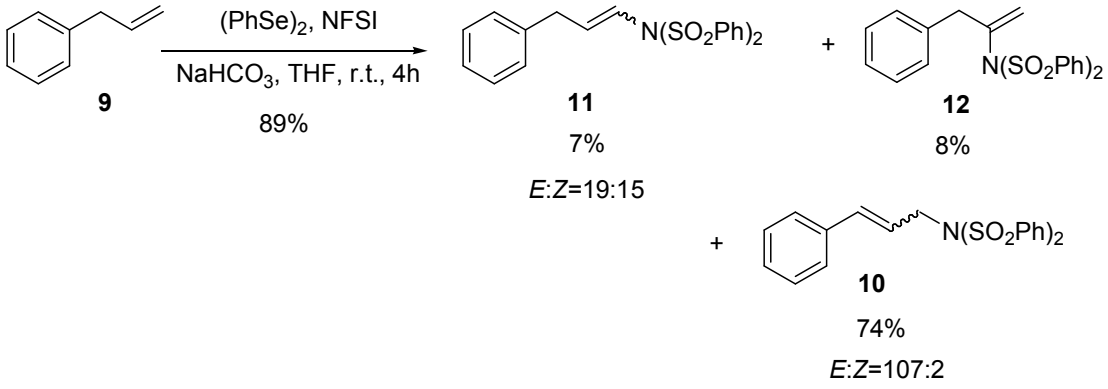
reported in the literature.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (d, *J* = 7.9 Hz, 1H), 9.47 (d, *J* = 8.2 Hz, 1H), 7.61–7.28 (m, 5H), 6.40 (ddd, *J* = 7.9, 2.4, 1.2 Hz, 1H), 6.14 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.58 (d, *J* = 1.2 Hz, 3H), 2.32 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.63, 191.43, 157.81, 140.69, 130.23, 129.30, 128.89, 128.57, 128.49, 127.41, 126.40, 26.59, 16.53.



2-Cyclohexylideneacetaldehyde (**3m**): Prepared by general procedure but the reaction was carried out at 60 °C. The residue was directly purified by flash silica gel column chromatography (eluent: PE/EtOAc = 30:1, v/v) to afford **3m** (15.1 mg, 0.12 mmol, 61%) as a colorless oil. This compound is known, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are identical to those previously reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 8.3 Hz, 1H), 5.82 (d, *J* = 8.3 Hz, 1H), 2.74–2.67 (m, 2H), 2.32–2.26 (m, 2H), 1.80–1.55 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.74, 168.28, 125.43, 38.22, 29.76, 28.56, 28.32, 26.31.

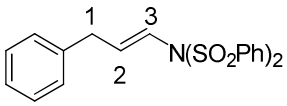
6. Experimental details for amination of the alkenes 9, 13 and 14

1) Amination of Allylbenzene 9



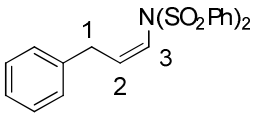
A 5-mL glass vial was charged with a magnetic stir bar, PhSeSePh (3.1 mg, 0.01 mmol), NFSI (63.1 mg, 0.20 mmol) and $NaHCO_3$ (20.2 mg, 0.24 mmol). Then allylbenzene **9** (23.6 mg, 0.20 mmol) was added. The vial was capped. The resulting mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo

and the residue was purified by silica gel column chromatography (eluent, PE/EA = 9:1, v/v) to give pale oil mixture of isomers **10**, **11**, **12**. It was difficult to separate the isomers **10**, **11** and **12** because of their similar polarity. Yields of the isomers were determined by proton NMR using benzyl benzoate (44.0 mg, 0.2073 mmol) as the internal standard. The total yield is 89%.



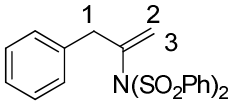
*i*1

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.22 (d, *J* = 6.8 Hz, ***H1***, 2H).



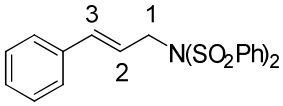
*i*2

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.43 (d, *J* = 5.7 Hz, ***H1***, 2H).



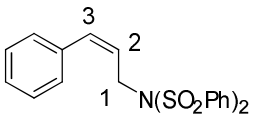
*i*3

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.98 (s, ***H2***, 1H), 4.80 (s, ***H3***, 1H), 3.59 (s, ***H1***, 2H).



*i*4

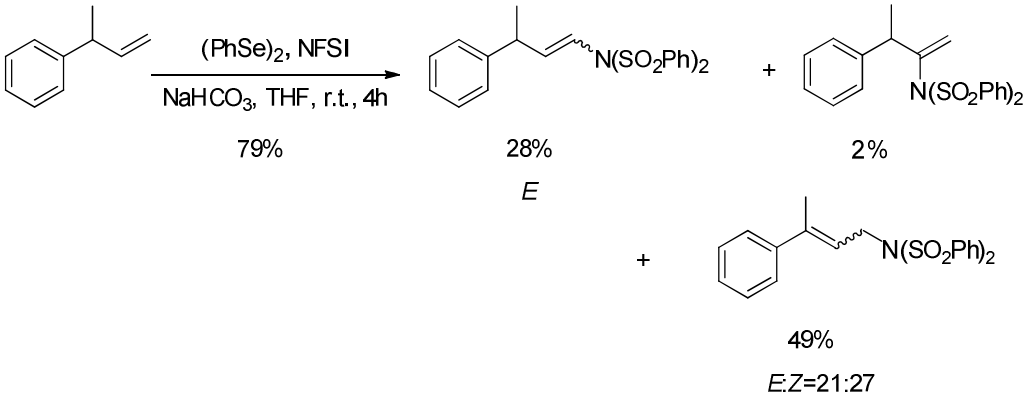
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 15.9 Hz, ***H3***, 1H), 6.07 (dt, *J* = 15.8, 6.7 Hz, ***H2***, 1H), 4.50 (d, *J* = 6.6 Hz, ***H1***, 2H). ^{1}H NMR signals were consistent with literature.[20]



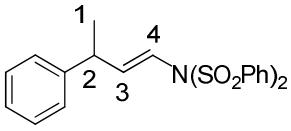
i5

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 6.2 Hz, ***H1***, 1H).

2) Amination of 3-Phenyl-1-butene 13

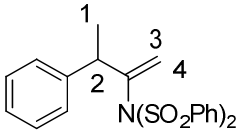


A 5-mL glass vial was charged with a magnetic stir bar, PhSeSePh (3.1 mg, 0.01 mmol), NFSI (63.1 mg, 0.20 mmol) and $NaHCO_3$ (20.2 mg, 0.24 mmol). Then 3-phenyl-1-butene **13** (26.4 mg, 0.20 mmol, 1.0 equiv) was added. The vial was capped. The resulting mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: PE/EA = 9:1, v/v) to give pale oil mixture of isomers. It was difficult to separate these isomers because of their similar polarity. Yields of the isomers were determined by proton NMR using benzyl benzoate (43.5 mg, 0.2050 mmol) as the internal standard. The total yield is 79%.



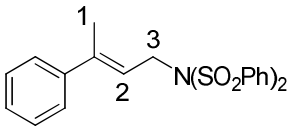
i1

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.98 – 5.87 (m, ***H3***, ***H4***, 2H), 3.62 – 3.52 (m, ***H2***, 1H), 1.38 (d, *J* = 7.0 Hz, ***H1***, 3H).



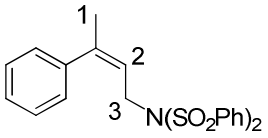
i2

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.46 (s, ***H3***, 1H), 4.86 (s, ***H4***, 1H).



i3

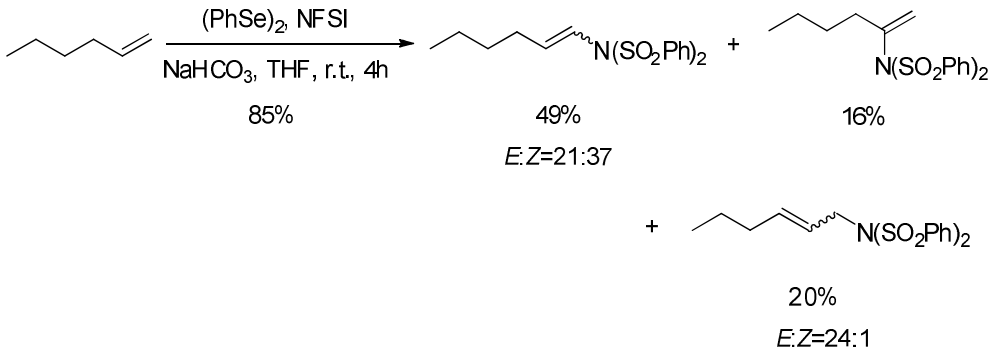
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.66 (td, *J* = 6.9, 1.1 Hz, ***H2***, 1H), 4.58 (d, *J* = 6.9 Hz, ***H3***, 2H), 2.12 (s, ***H1***, 3H).



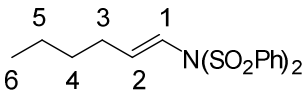
i4

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.41 (td, *J* = 6.2, 1.2 Hz, ***H2***, 1H), 4.33 (dd, *J* = 6.3, 0.9 Hz, ***H3***, 2H), 1.96 (d, *J* = 1.1 Hz, ***H1***, 3H).

3) Amination of Hex-1-ene 14

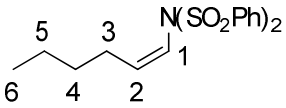


A 5-mL glass vial was charged with a magnetic stir bar, PhSeSePh (3.1 mg, 0.01 mmol), NFSI (63.1 mg, 0.20 mmol) and $NaHCO_3$ (20.2 mg, 0.24 mmol). Then hex-1-ene **14** (16.8 mg, 0.20 mmol) was added. The vial was capped. The resulting mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: PE/EA = 9:1, v/v) to give quite pure pale oil mixture of isomers (64.3 mg, 84.7%). It was difficult to separate these isomers because of their similar polarity. Yield of each isomer was determined by relative ratio of them in ^{1}H NMR.



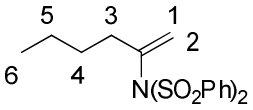
i1

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 1.82–1.74 (m, ***H3***, 2H). ***H1***, ***H2*** were overlapped with *i2* in δ 5.95–5.75 (m).



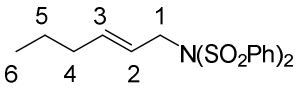
i2

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15–2.07 (m, ***H3***, 2H). ***H1***, ***H2*** were overlapped with *i1* in δ 5.95–5.75 (m).



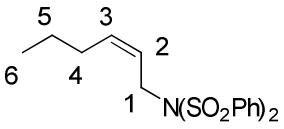
i3

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (d, *J* = 0.9 Hz, ***H1***, 1H), 4.78 (d, *J* = 1.0 Hz, ***H2***, 1H), 2.30–2.23 (m, ***H3***, 2H).



i4

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78–5.66 (m, ***H2***, 1H), 5.43 (dtt, *J* = 14.9, 6.6, 1.4 Hz, ***H3*** 1H), 4.30 (dd, *J* = 6.7, 0.8 Hz, ***H1***, 2H), 1.93 (q, *J* = 6.7 Hz, ***H4***, 2H), 1.52–1.41 (m, ***H5***, 2H), 0.77 (t, *J* = 7.0 Hz, ***H6***, 3H).



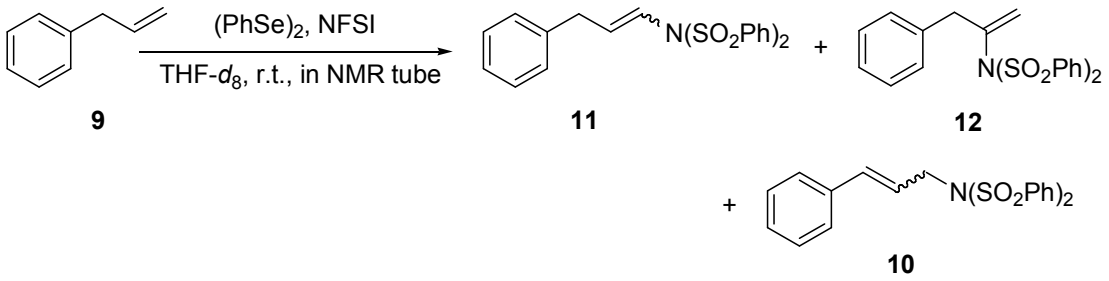
I5

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (d, *J* = 6.8 Hz, ***H1***, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.71, 143.47, 143.15, 140.16, 139.60, 139.50, 139.47, 137.08, 133.91, 133.88, 133.85, 133.73, 129.02, 128.96, 128.91, 128.72, 128.24, 128.14, 124.20, 120.53, 120.10, 119.14, 51.24, 35.80, 34.15, 30.51, 30.45, 29.66, 28.92, 27.30, 22.45, 22.09, 22.00, 21.91, 13.94, 13.79, 13.76.

HR-ESI-MS m/z calcd. $C_{18}H_{21}NO_4S_2$ $[M + NH_4]^+$: 397.1256, found: 397.1249.

7. NMR study of amination of allylbenzene 9

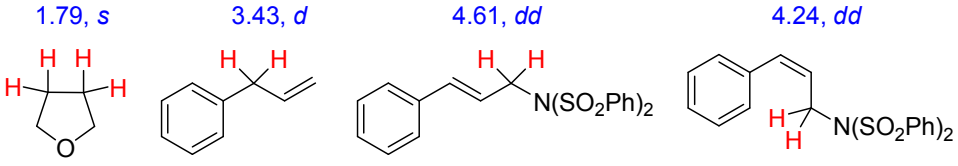


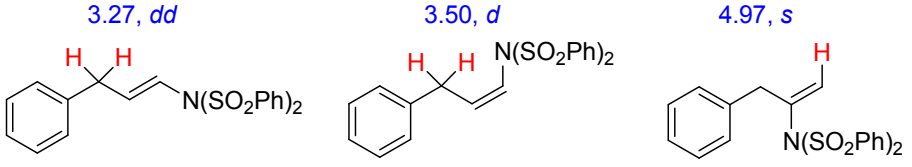
To a solution of allylbenzene (23.6 mg, 0.20 mmol) in THF-d_8 (0.5 mL) in a dry NMR tube was added a solution of PhSeSePh (3.1 mg, 0.01 mmol) and NFSI (63.1 mg, 0.20 mmol) in THF-d_8 (0.5 mL) at room temperature. The ^{1}H NMR spectra of reaction mixture was collected every 2 min or 4 min during the initial 4 h, every 1 h approximately during 4-12 h, and every 30 min approximately during 23-26 h.

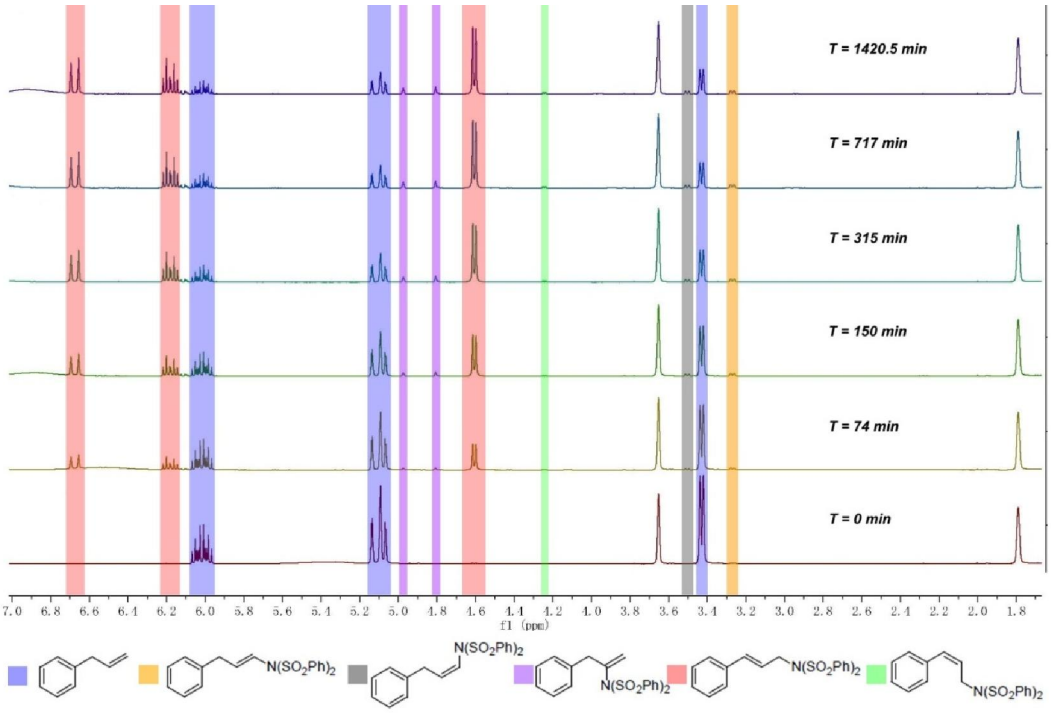
Table S1: Relative amount and NMR spectra data of allylbenzene and isomer products measured in THF-d_8[a]

Reaction Mixtures	Allylbenzene (**9**)	(*E*)-**10**	(*Z*)-**10**	(*E*)-**11**	(*Z*)-**11**	**12**
Relative Amount[b]	26 %	59 %	1 %	4 %	3 %	6 %

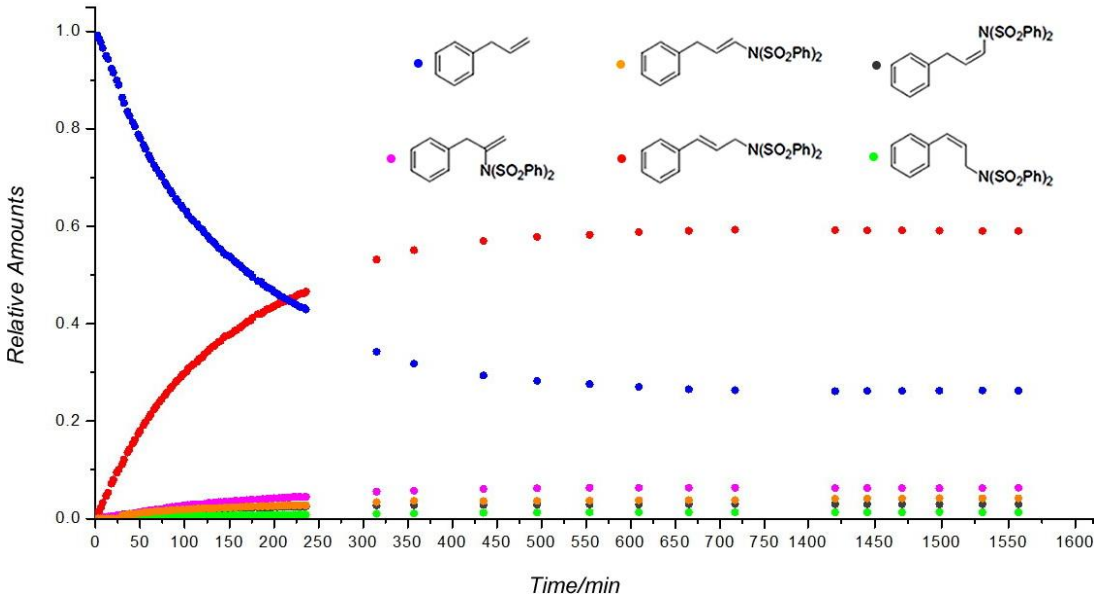
[a] Time = 717 min. [b] The relative amounts of allylbenzene and isomer products were determined by comparison of their ^{1}H NMR integral values to solvent signals. Characteristic hydrogen atoms and chemical shifts of solvent, allylbenzene and isomer products in THF-d_8 were showed as below:







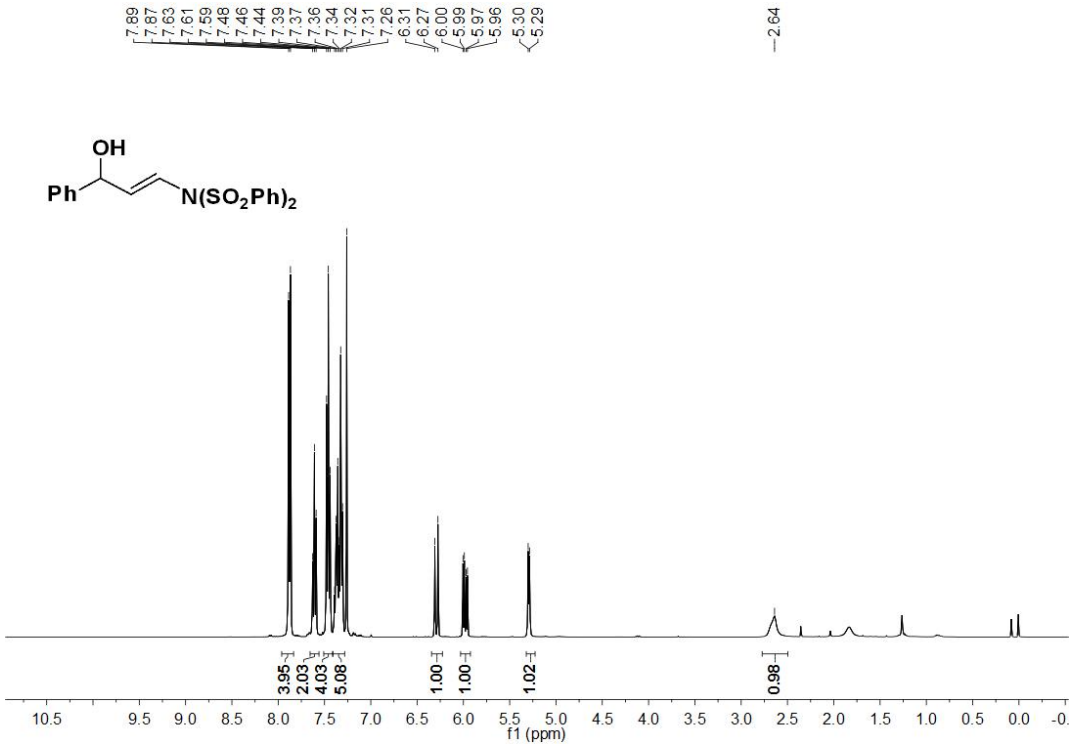
Scheme S1: Extract (1.70-7.00 ppm) of the ^{1}H NMR spectra of reaction mixture in THF-d_8.

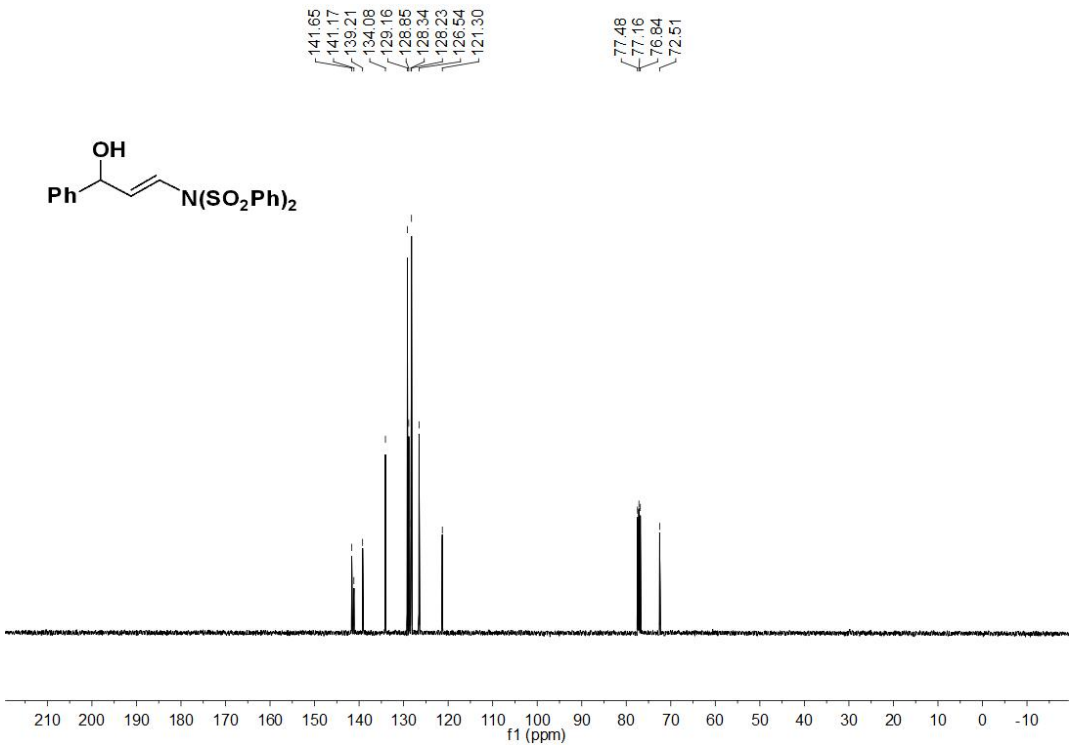


Scheme S2: Correlation between the relative amounts of allylbenzene and isomer products and the reaction time.

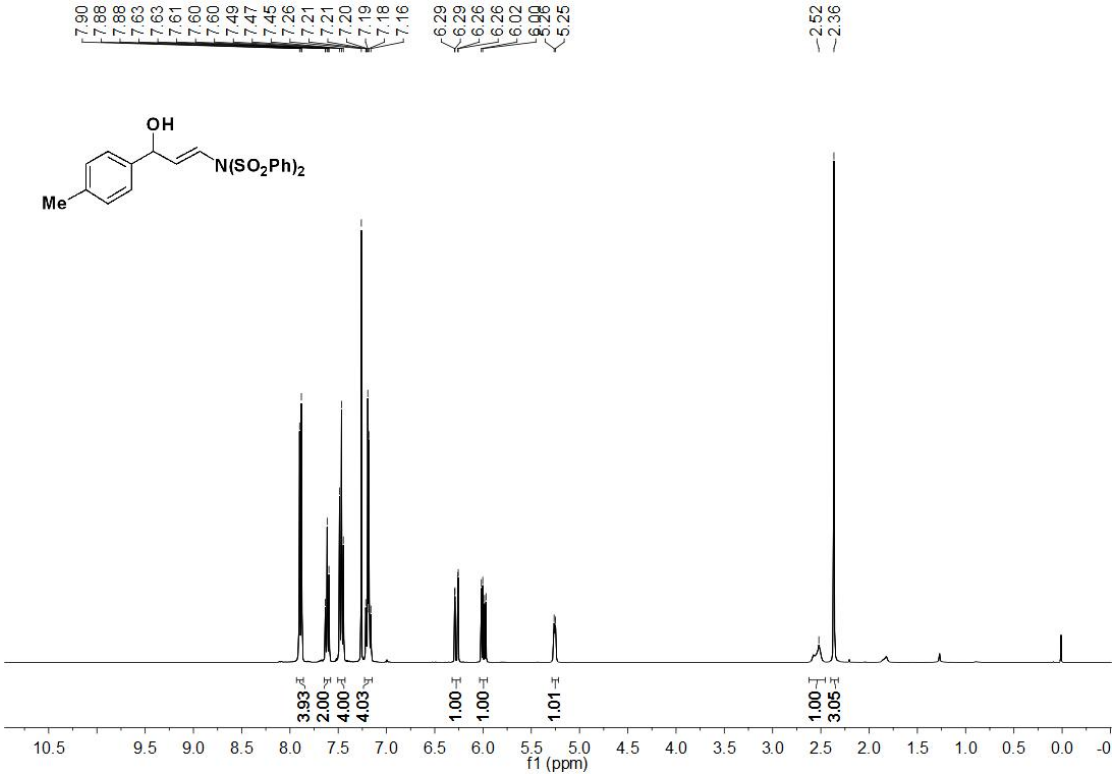
8. NMR spectra for new compounds

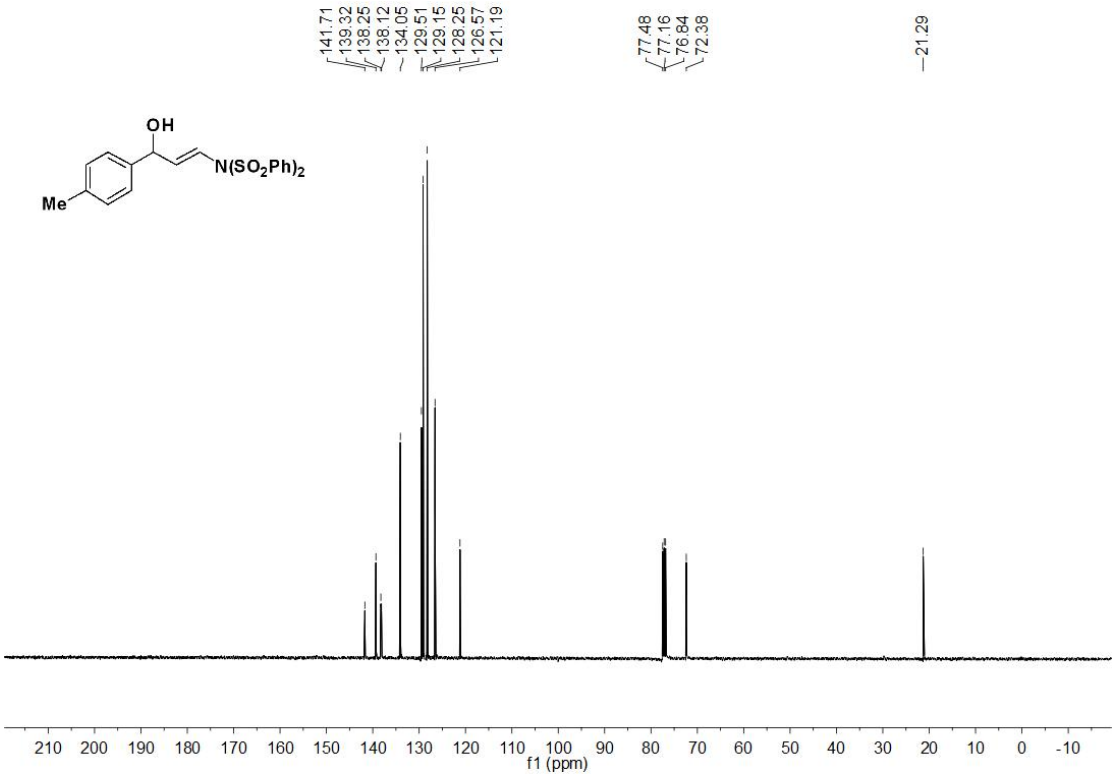
NMR Spectra of Product (2a)



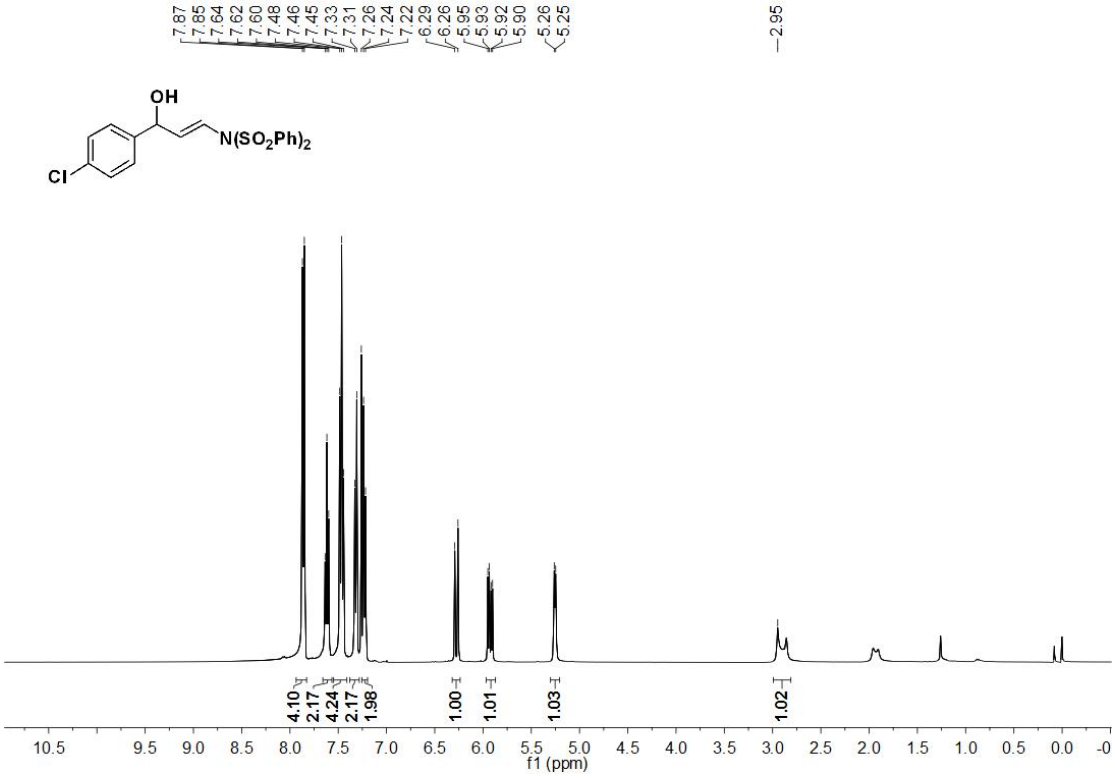


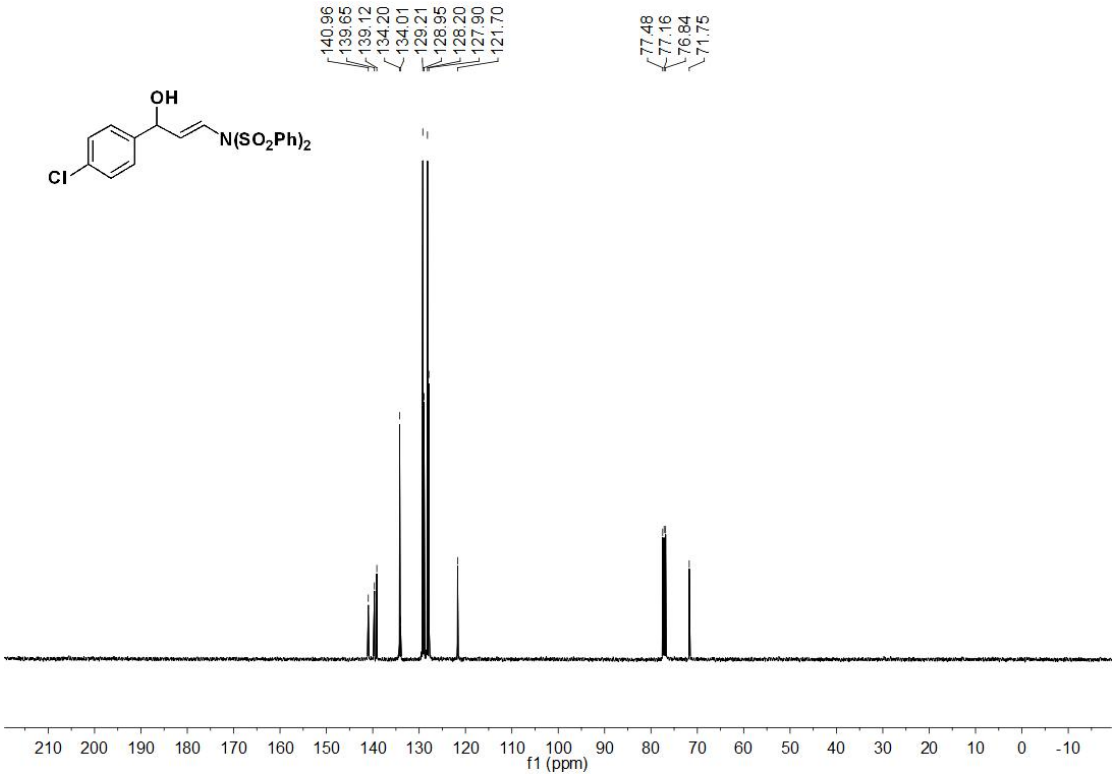
NMR Spectra of Product (2b)



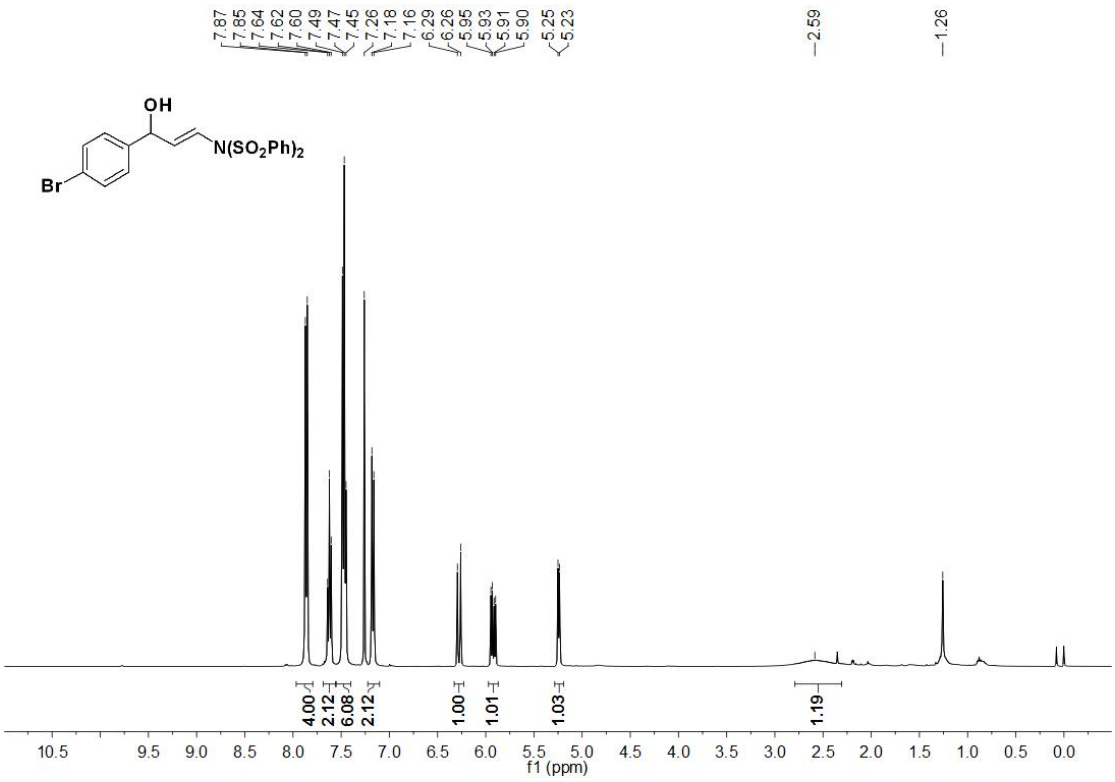


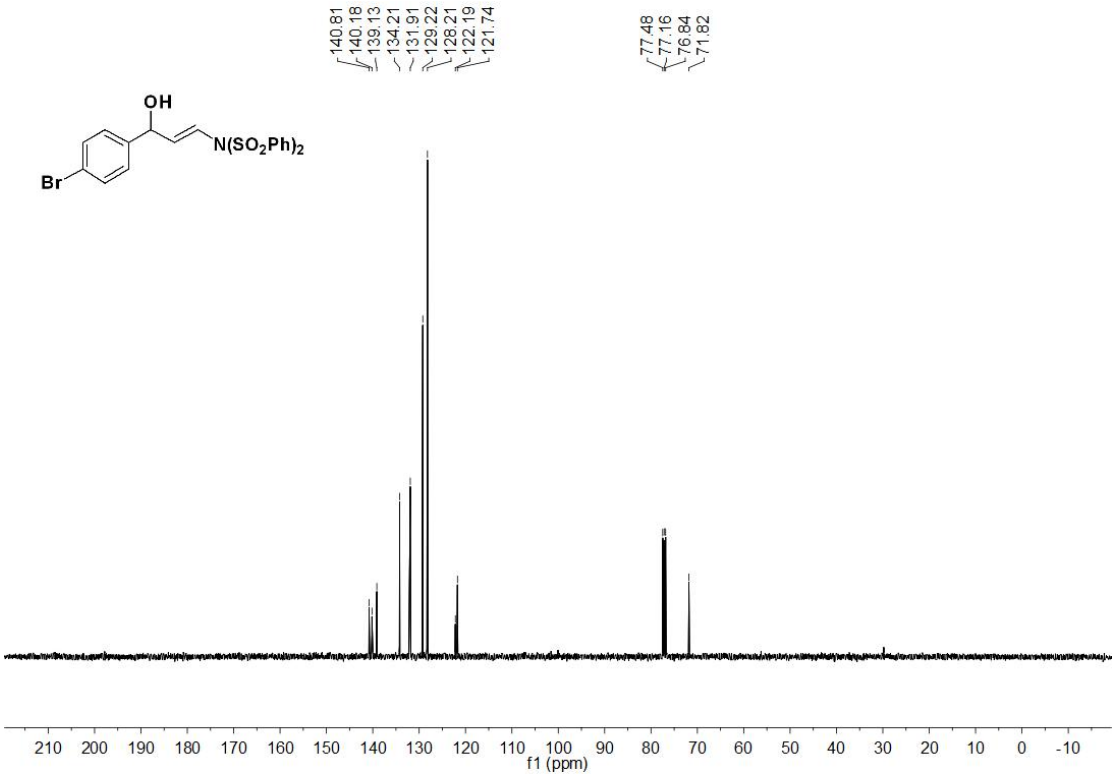
NMR Spectra of Product (2c)



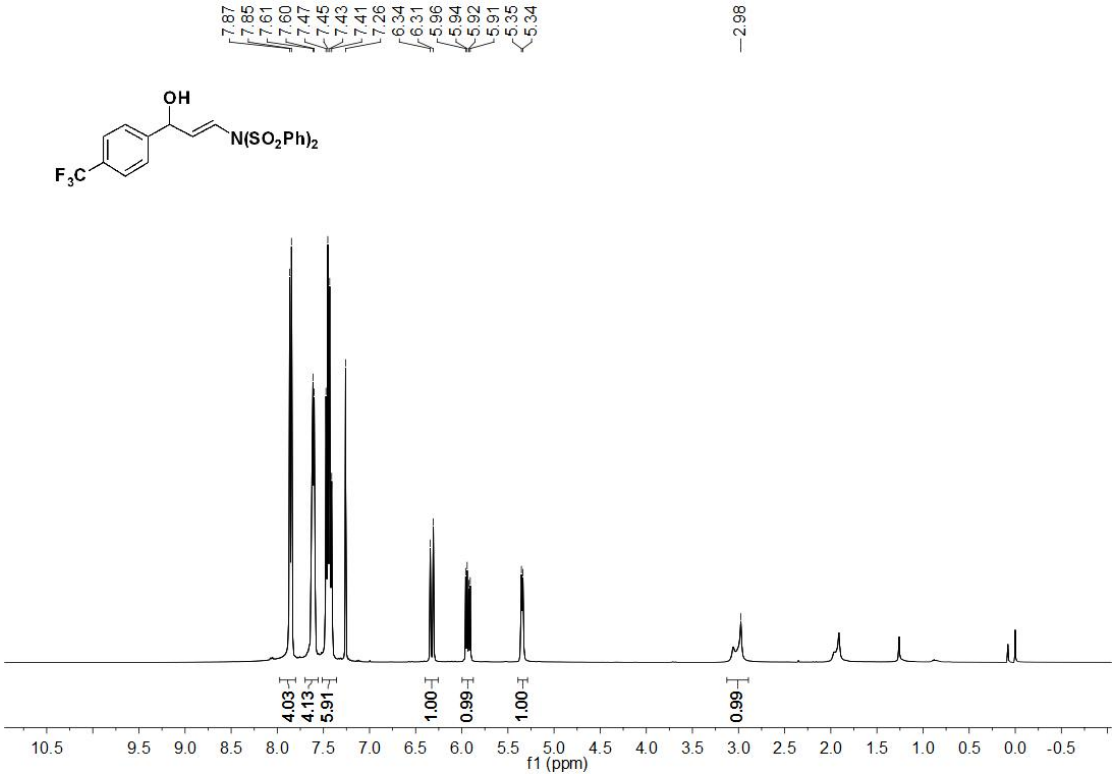


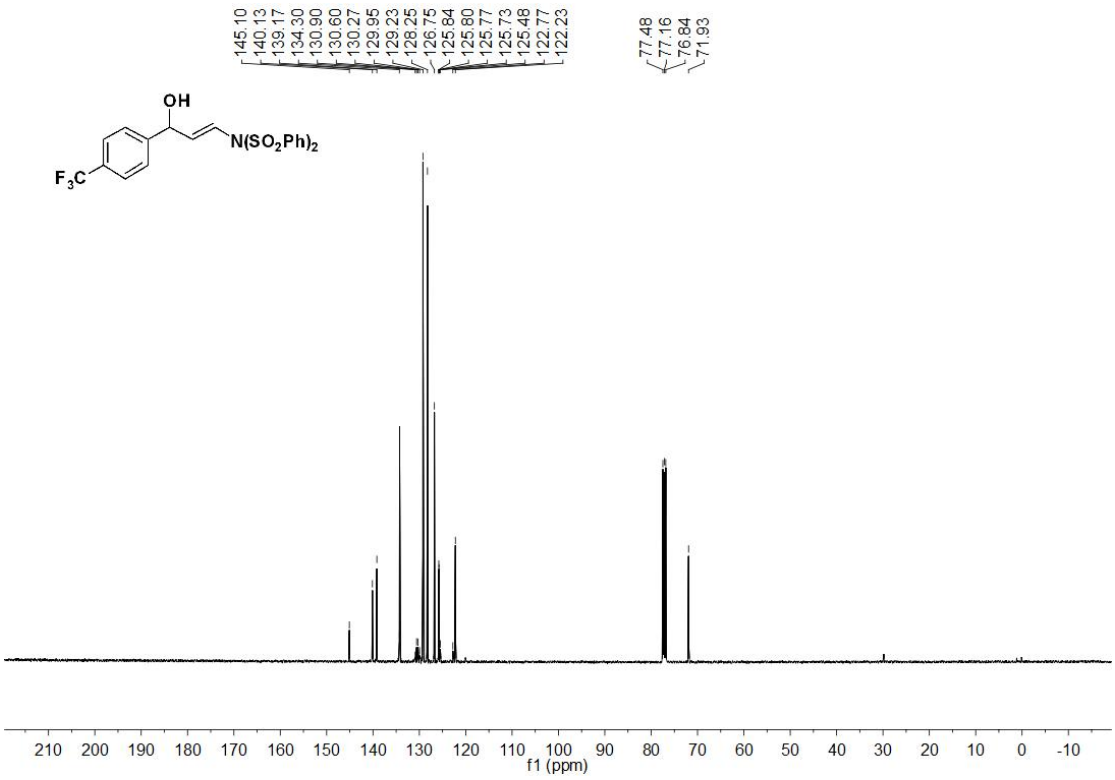
NMR Spectra of Product (2d)



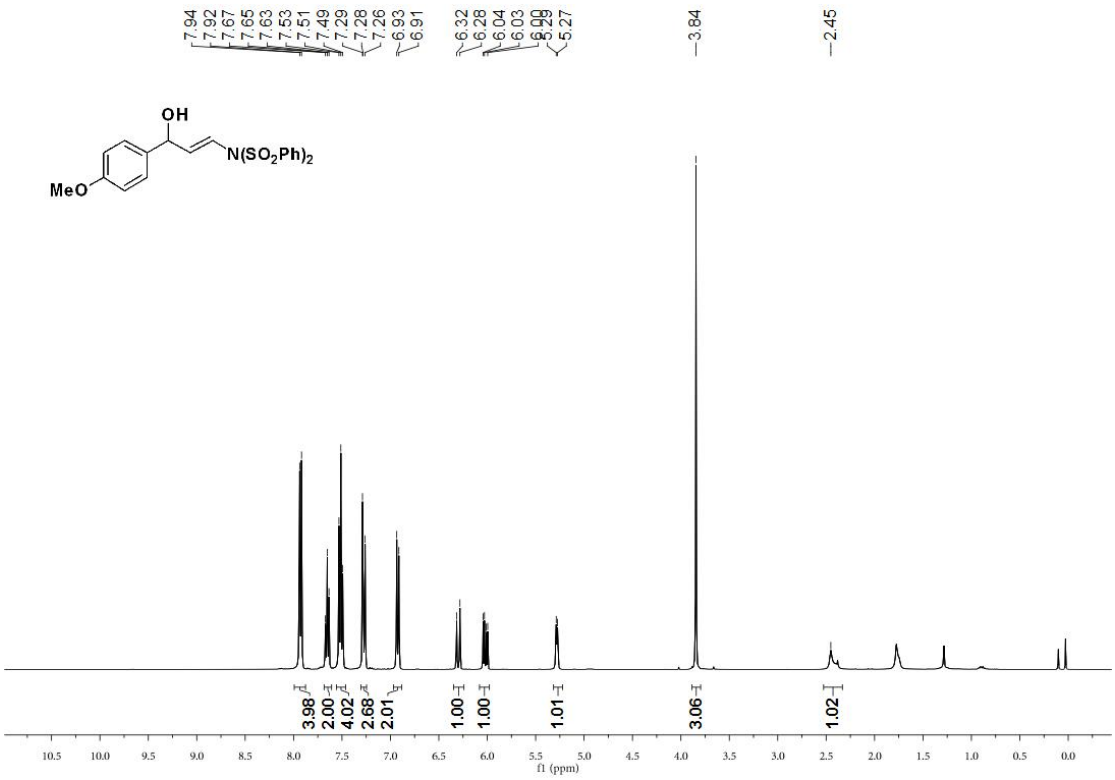


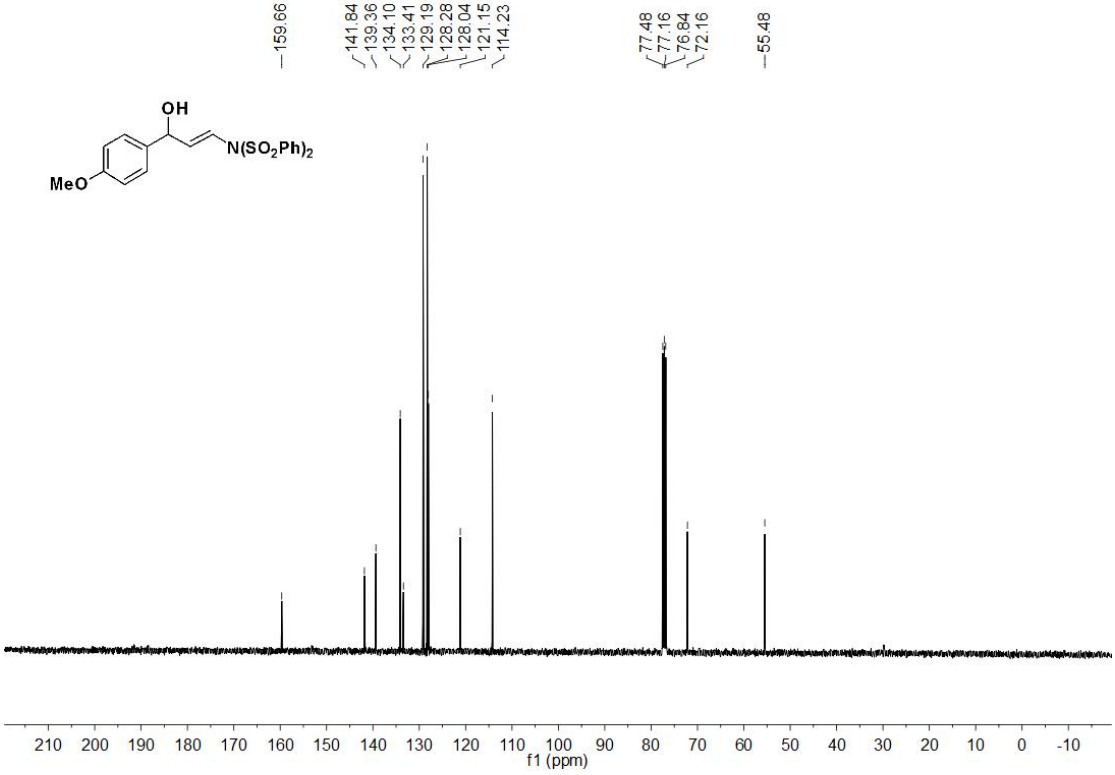
NMR Spectra of Product (2e)



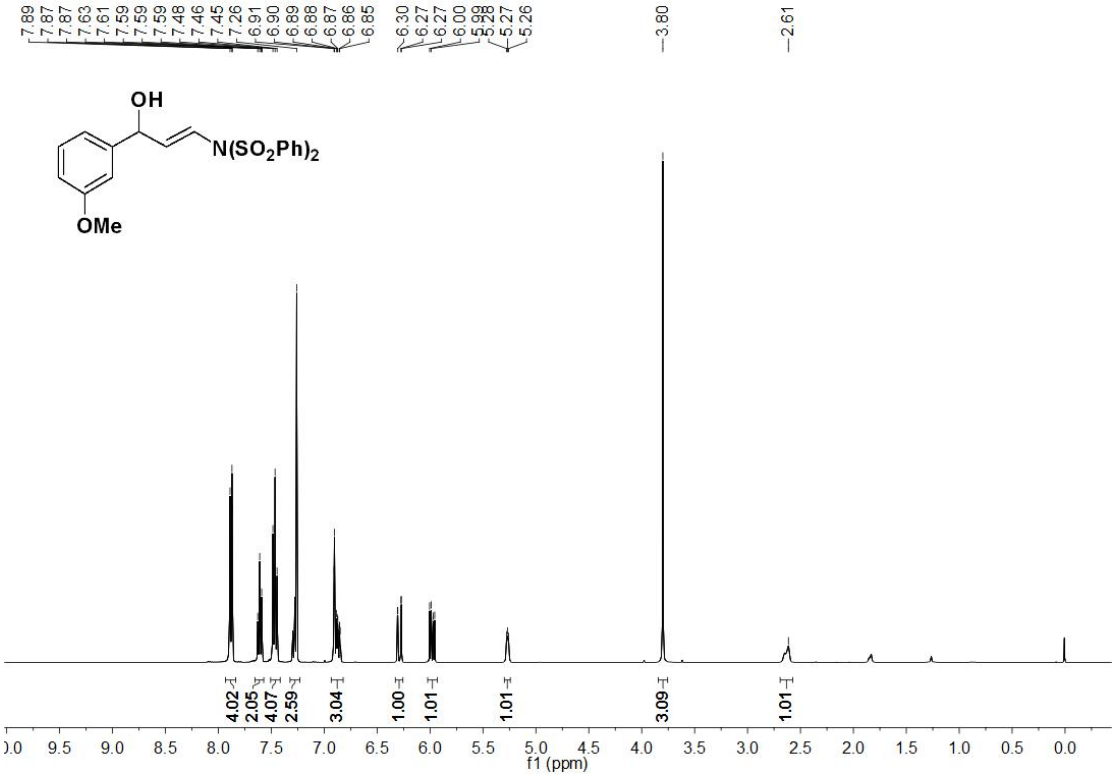


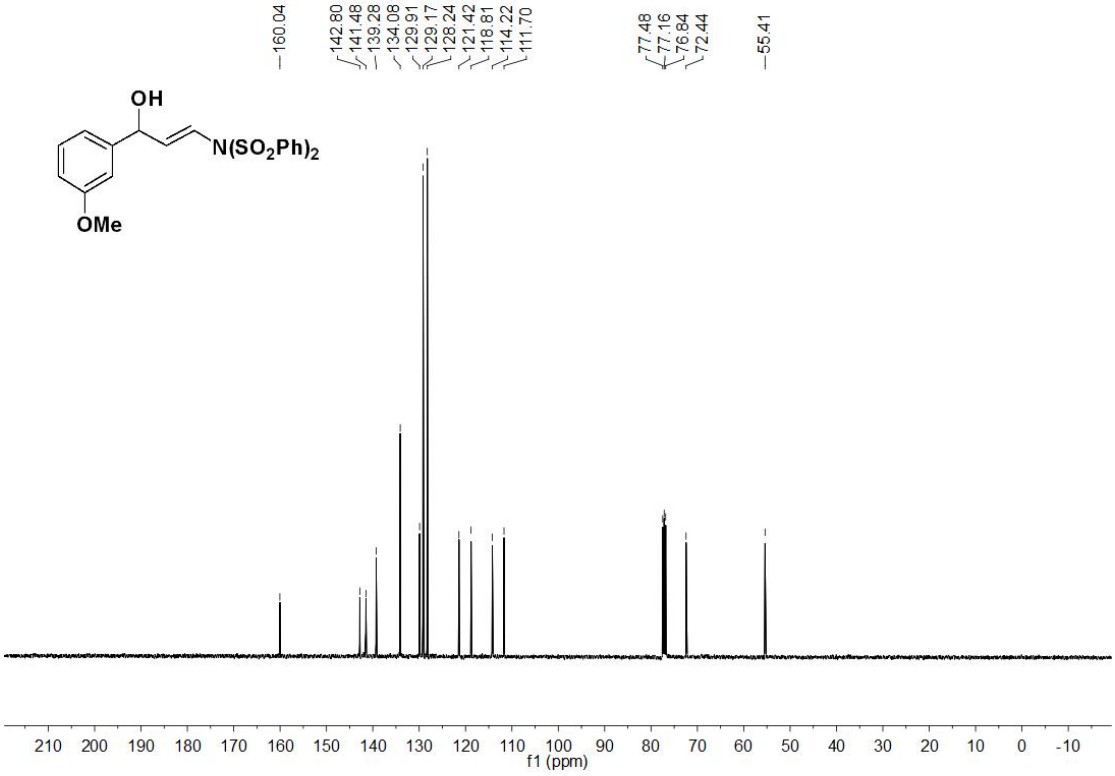
NMR Spectra of Product (2f)



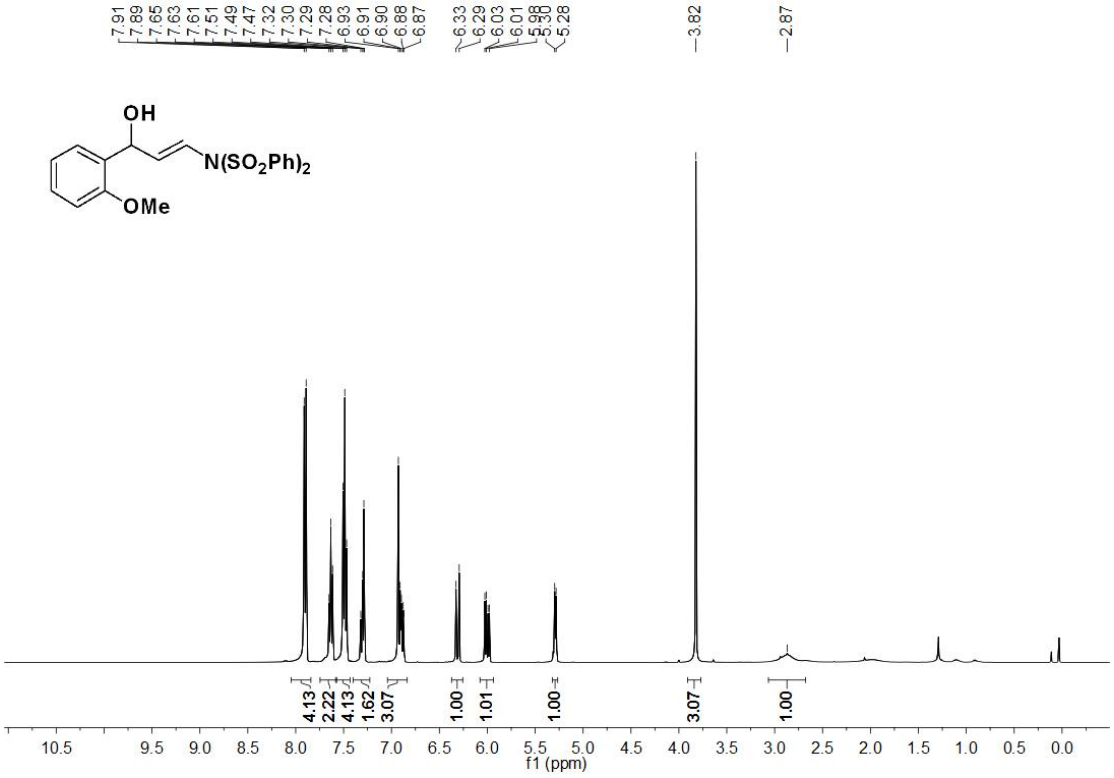


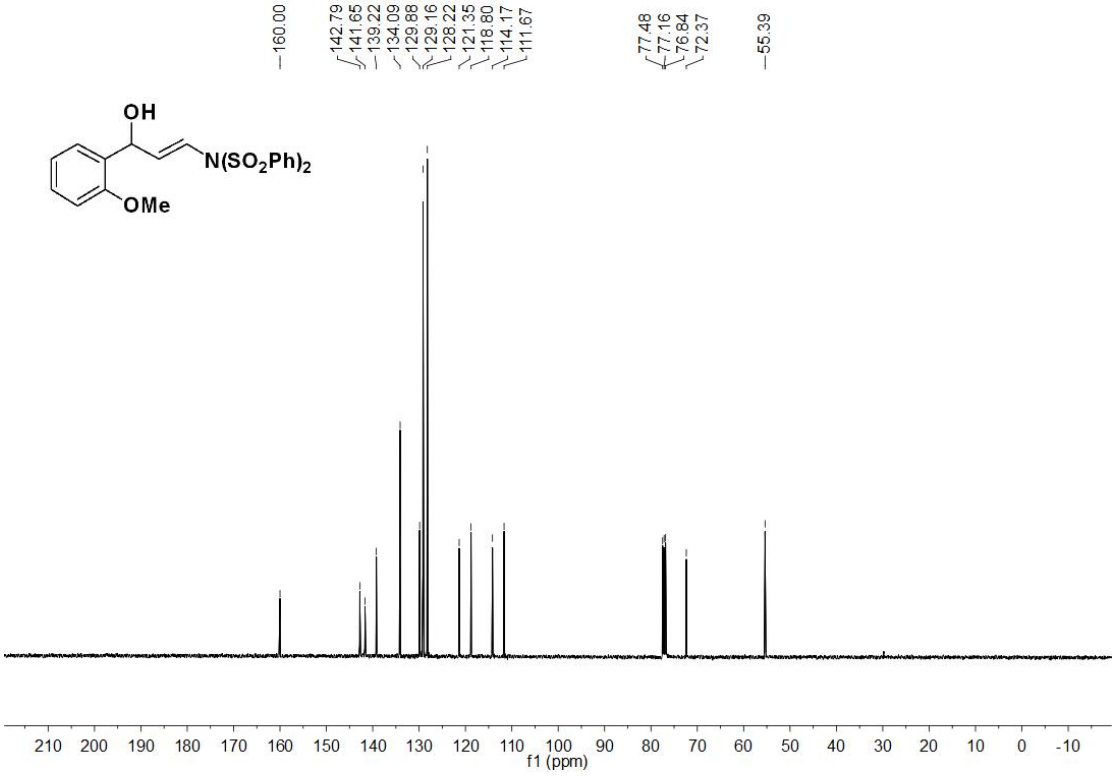
NMR Spectra of Product (2g)



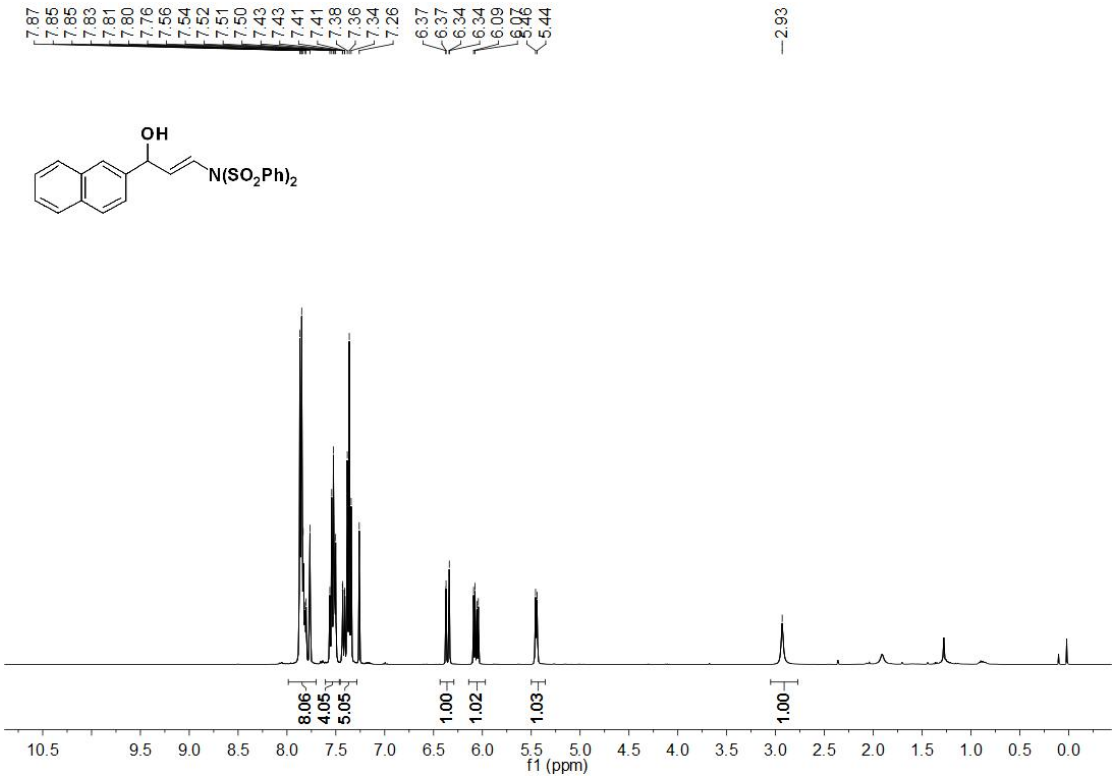


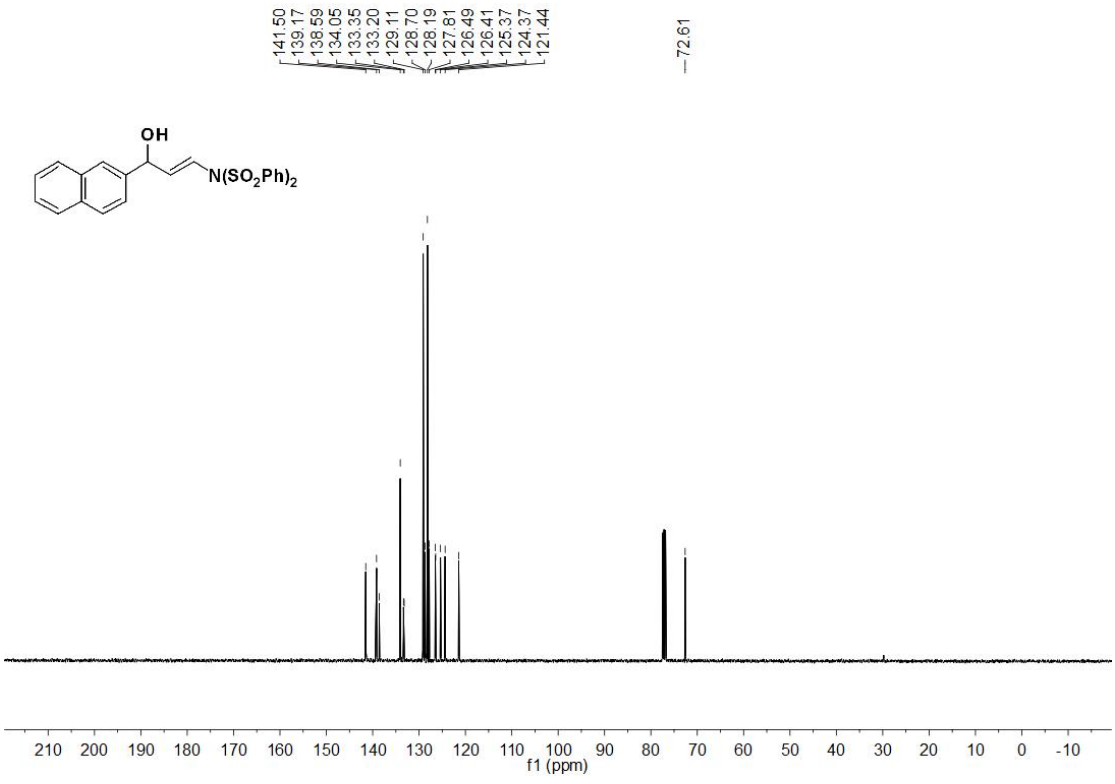
NMR Spectra of Product (2h)



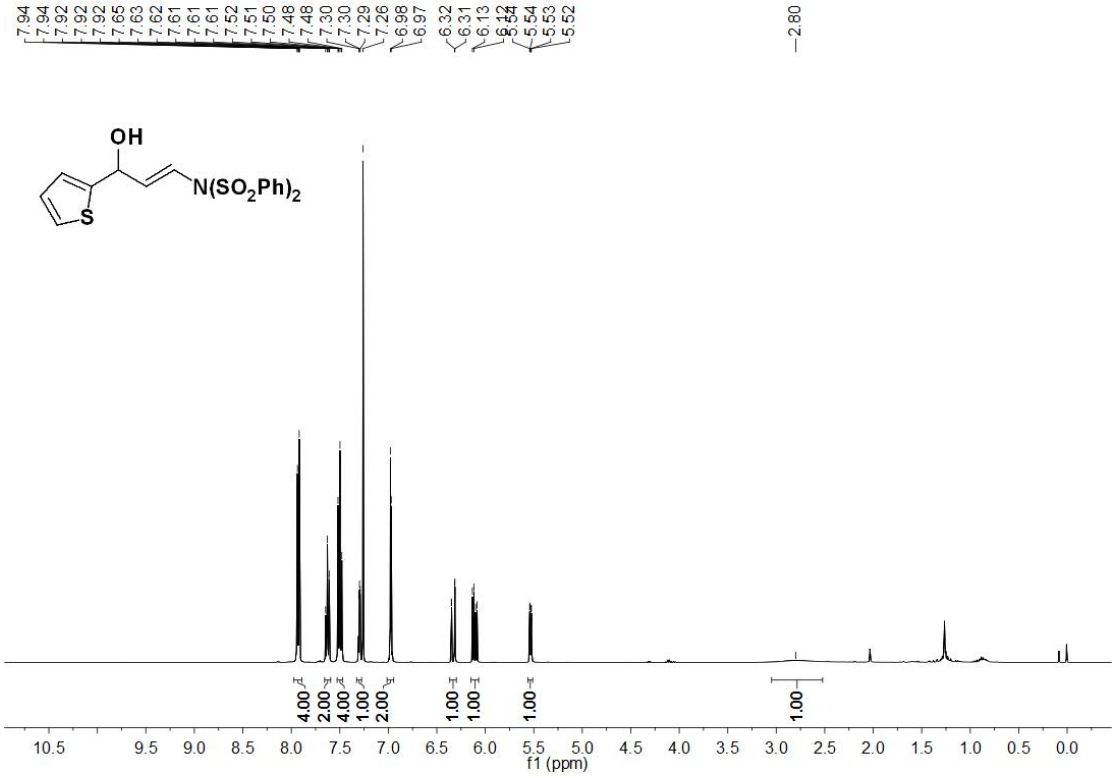


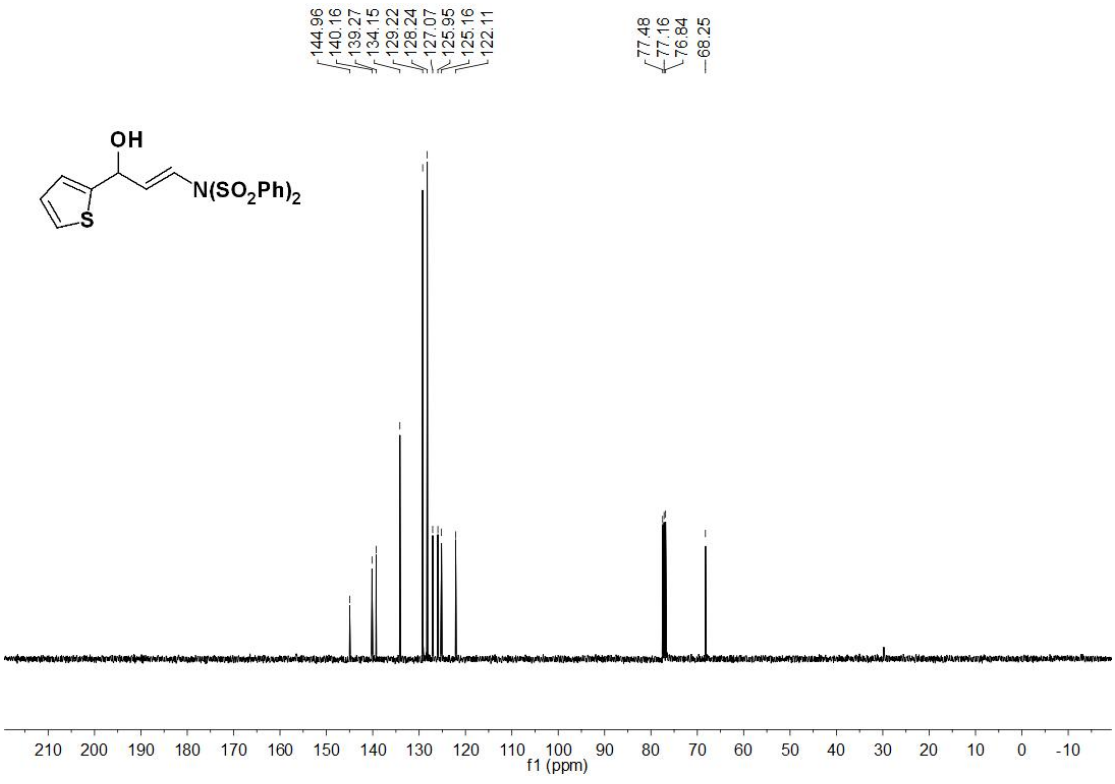
NMR Spectra of Product (2i)



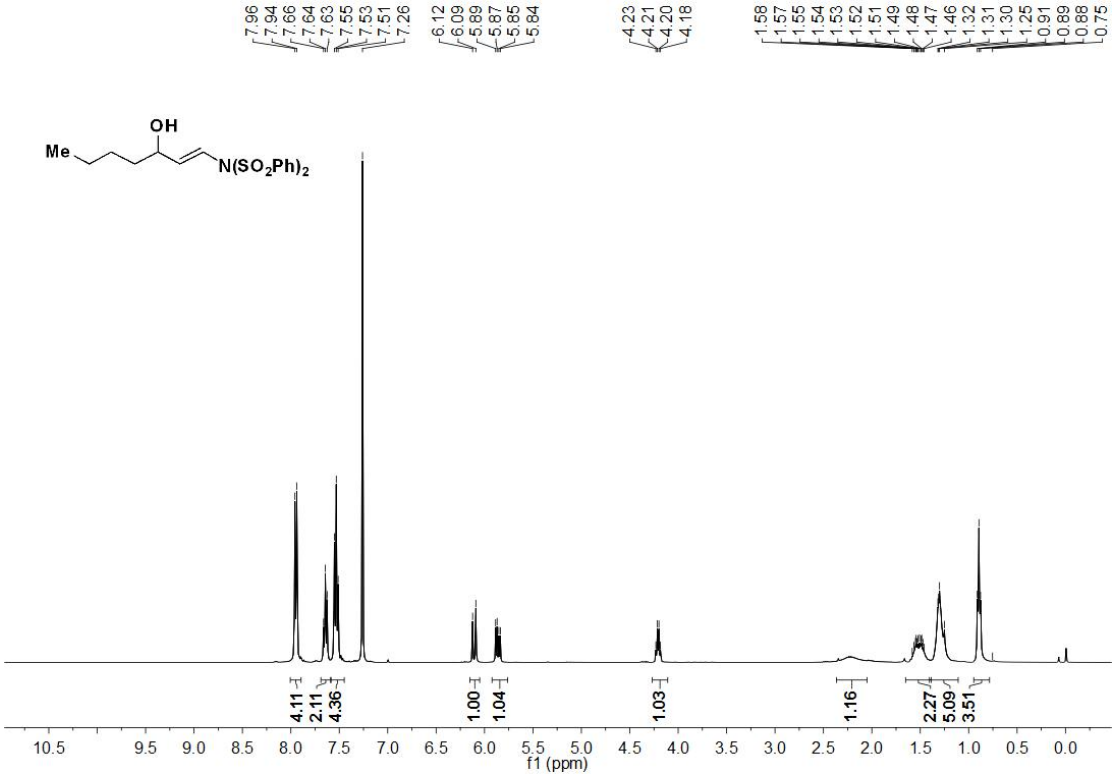


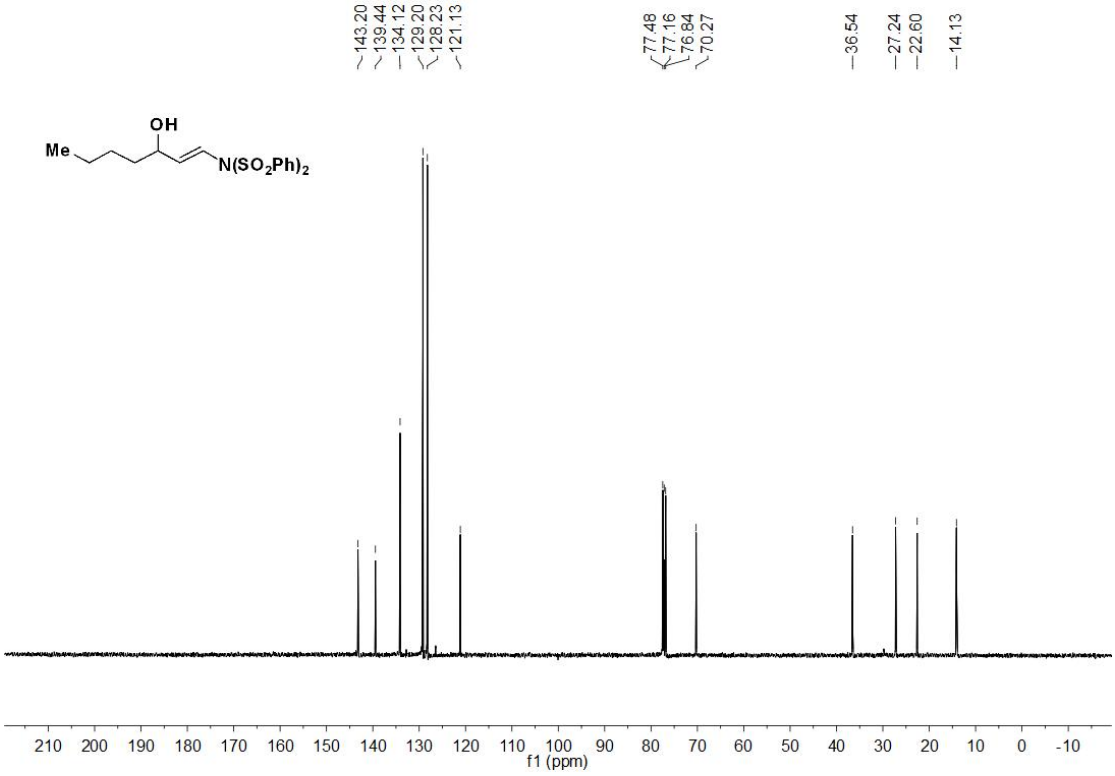
NMR Spectra of Product (2j)



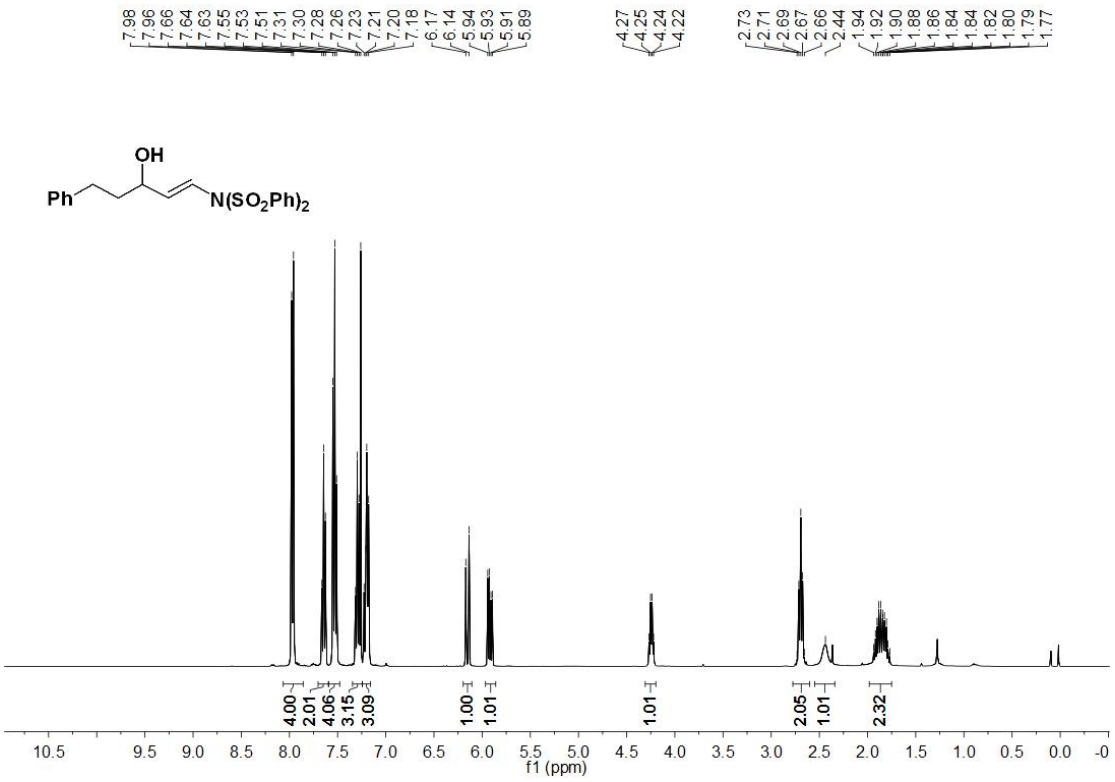


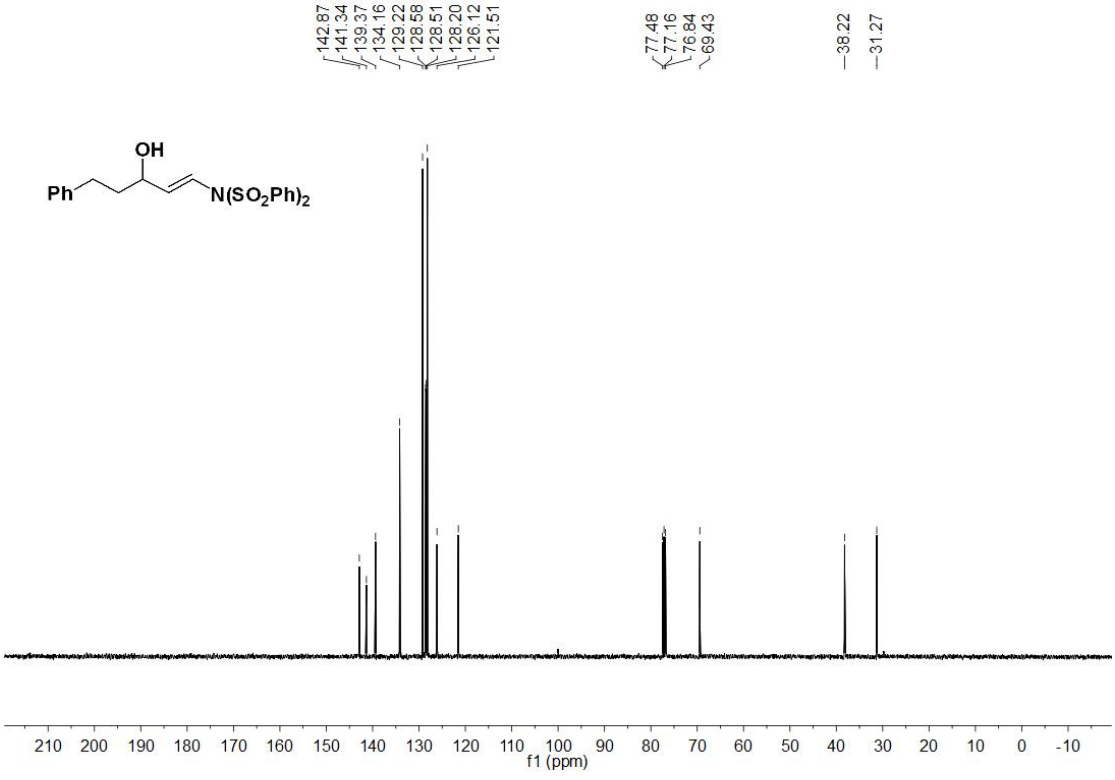
NMR Spectra of Product (2k)



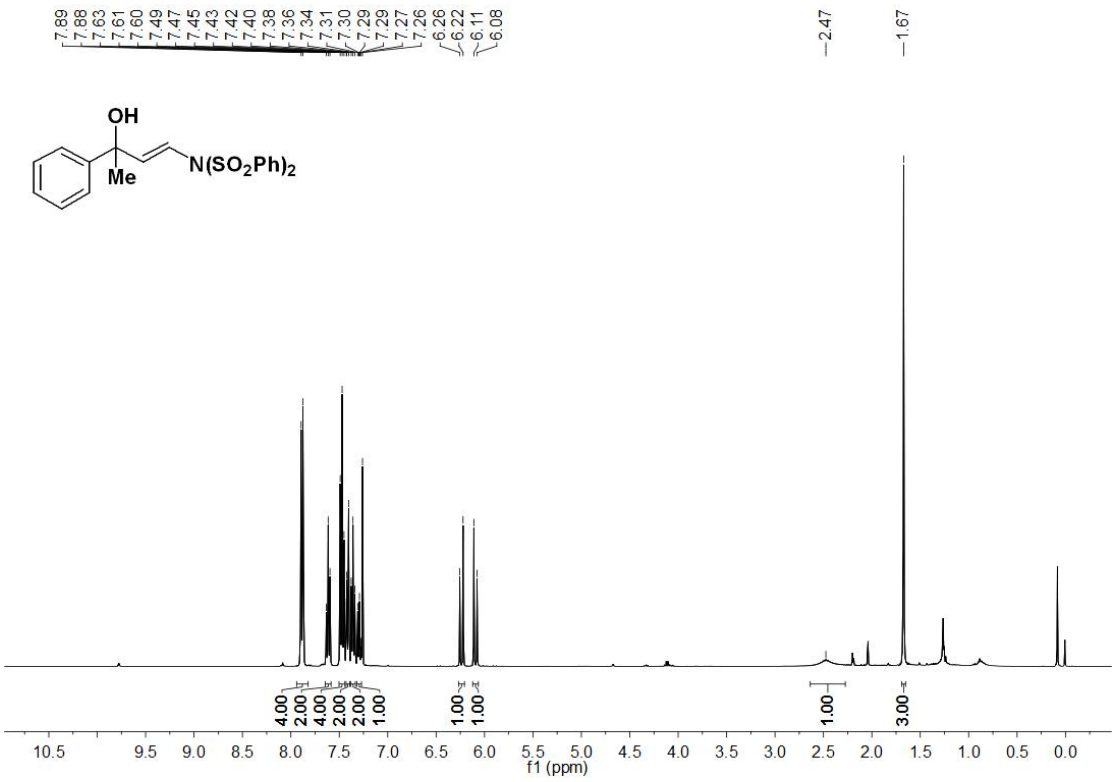


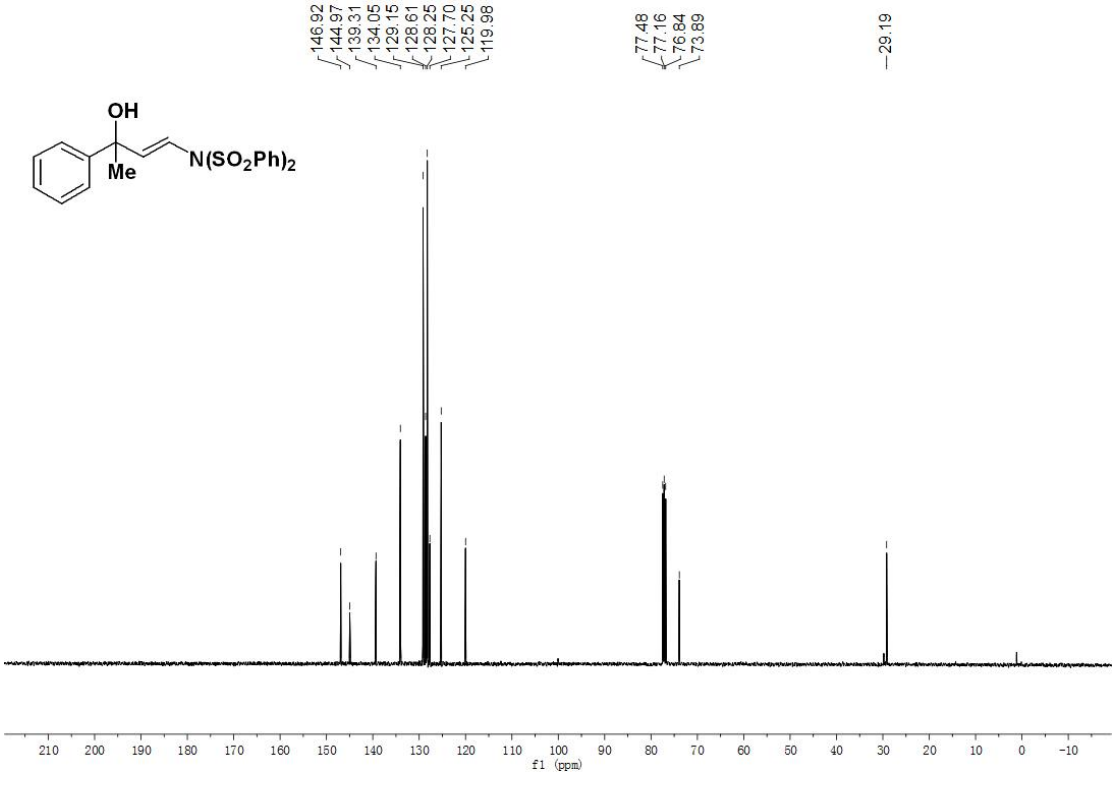
NMR Spectra of Product (2l)



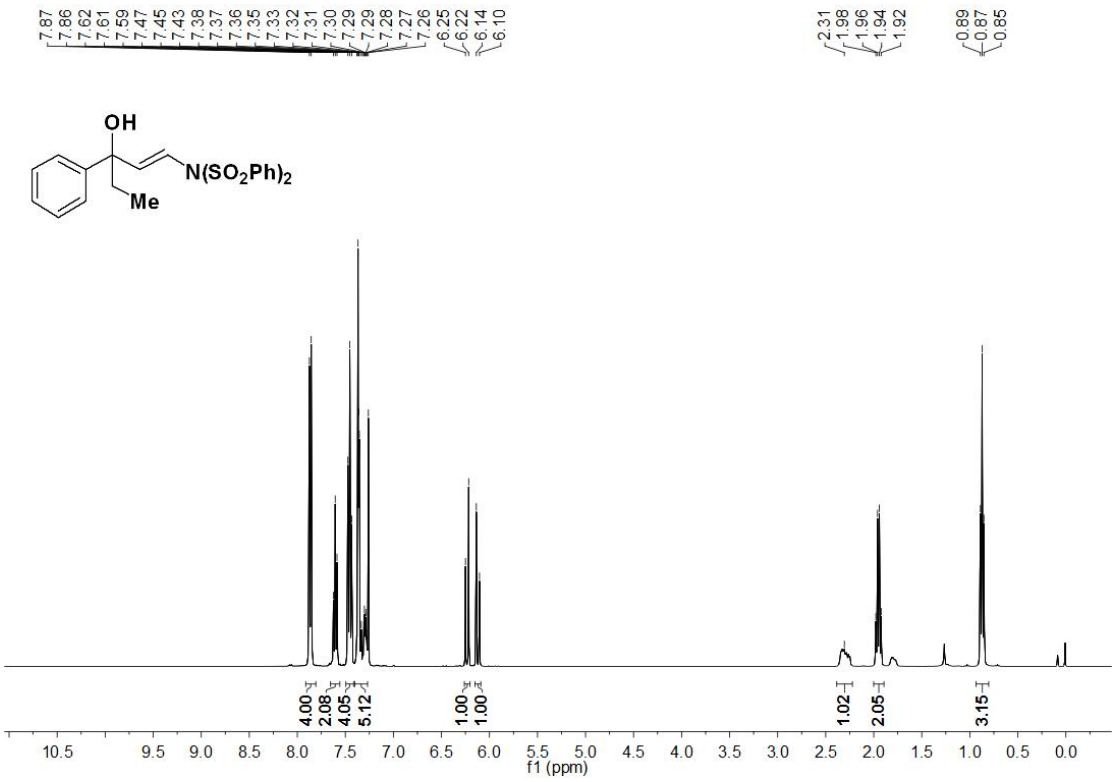


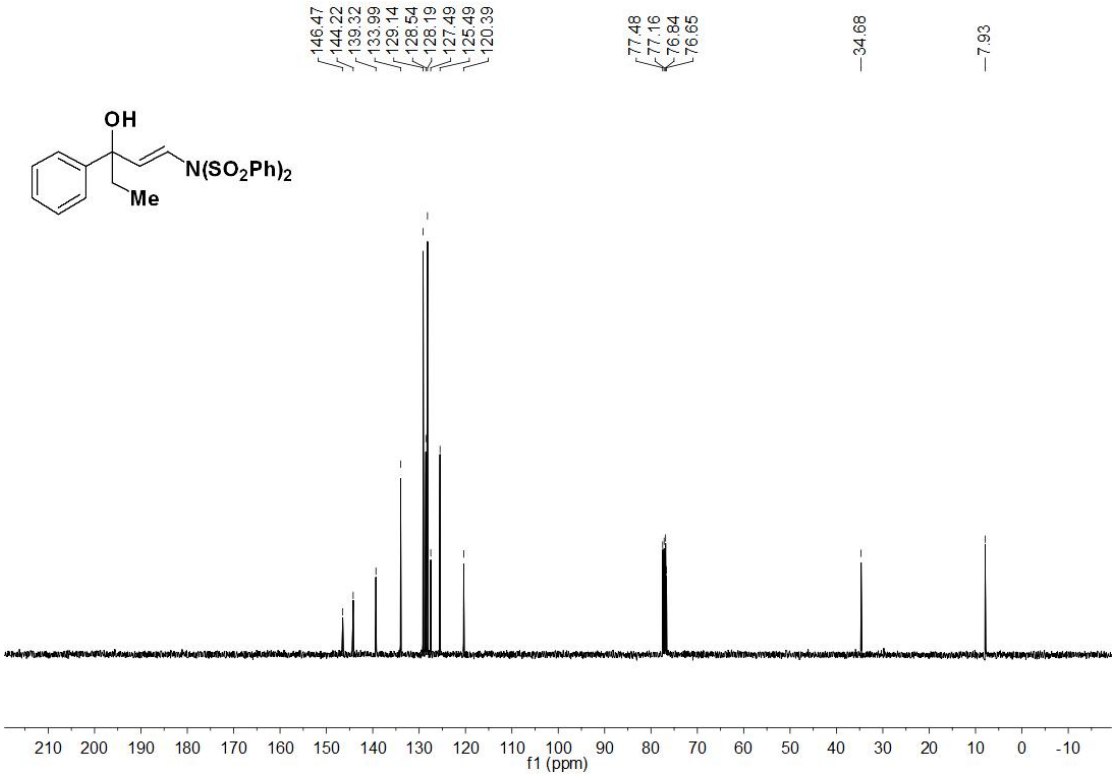
NMR spectra of Product (2m)



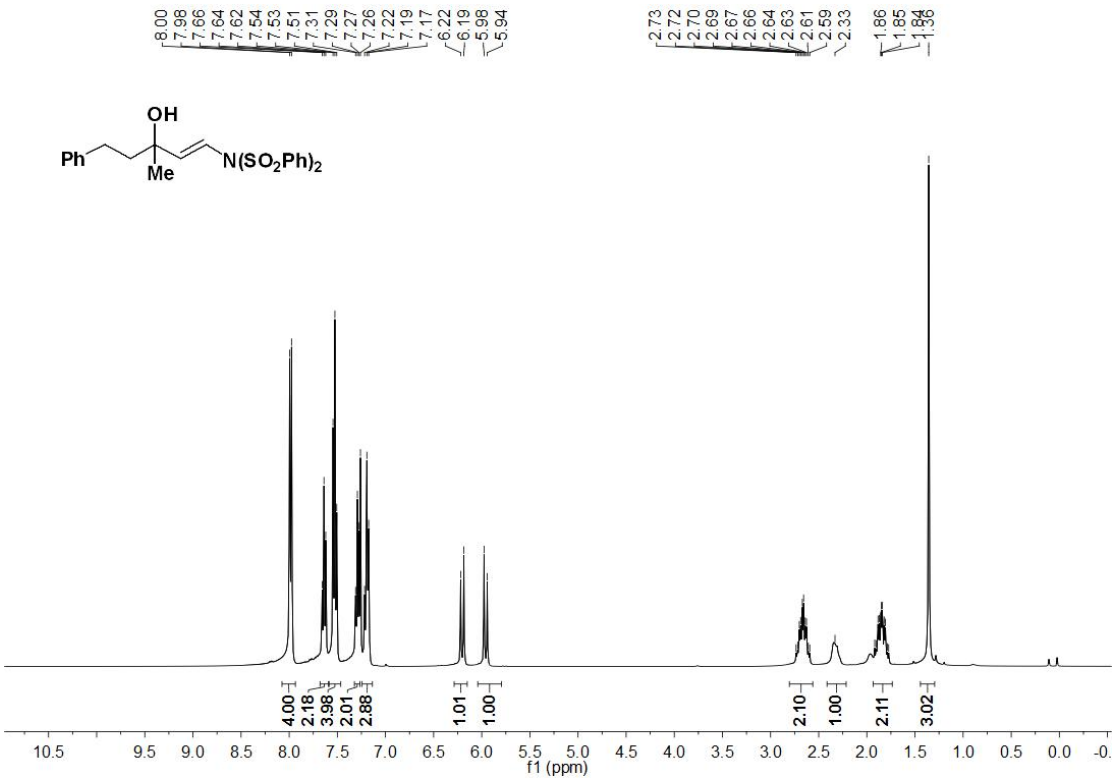


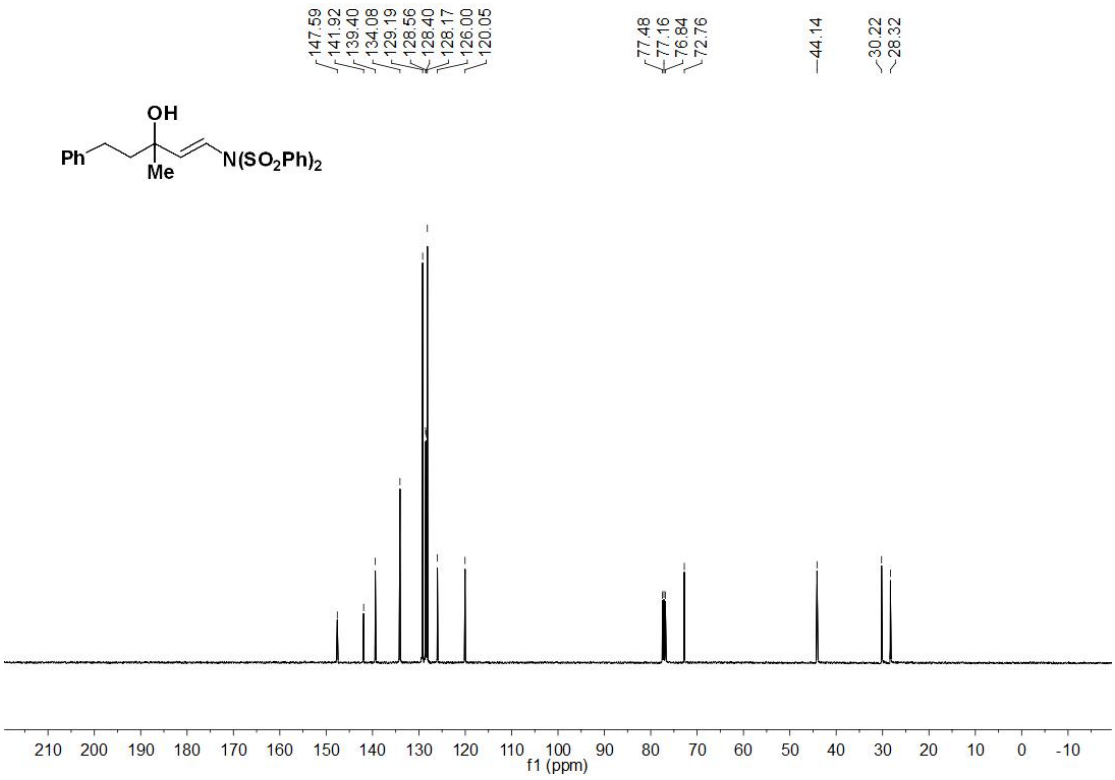
NMR Spectra of Product (2n)



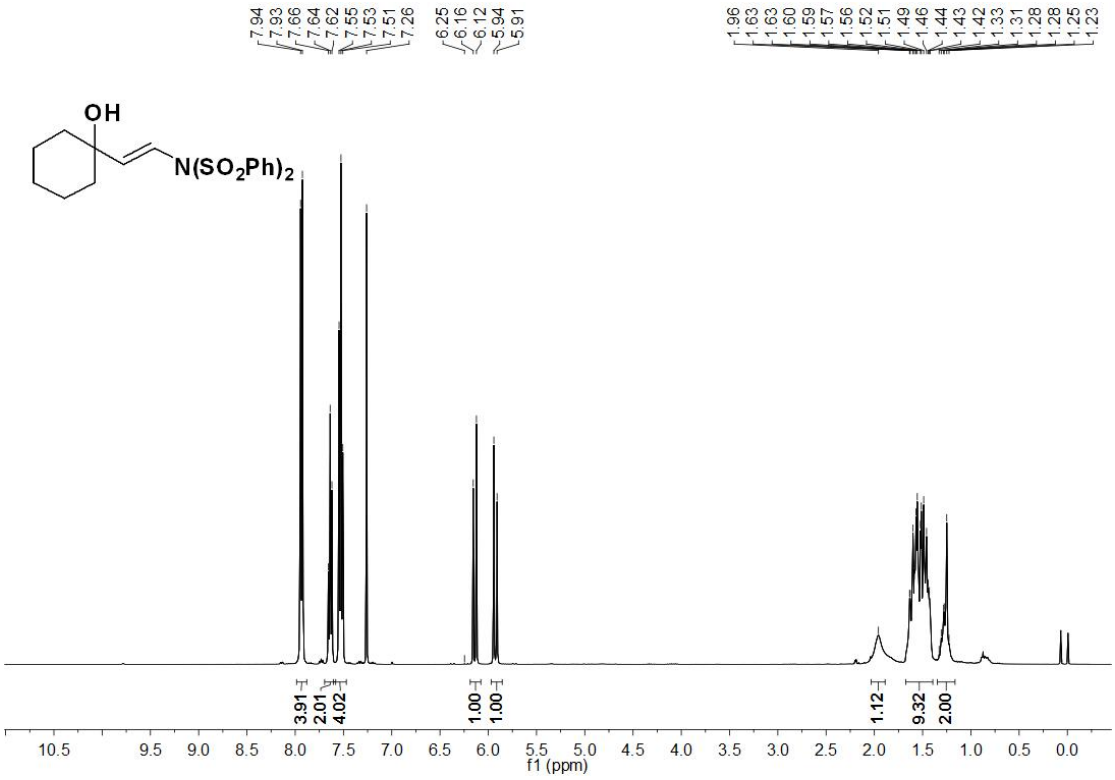


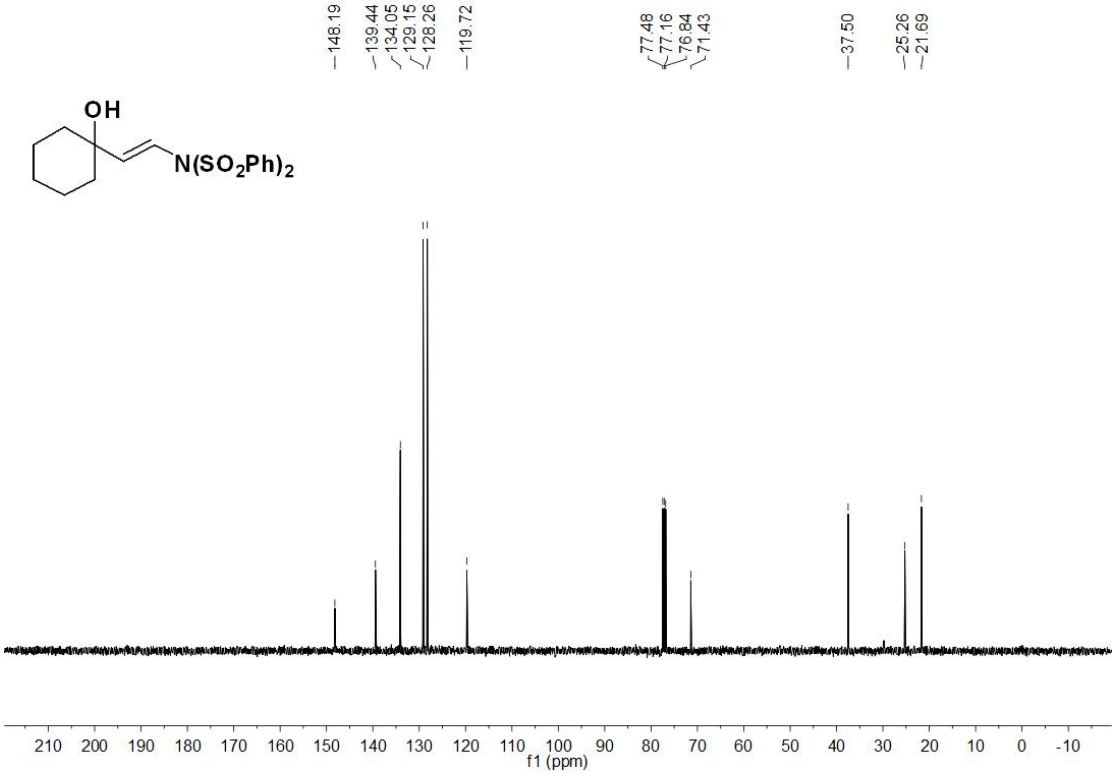
NMR Spectra of Product (2o)



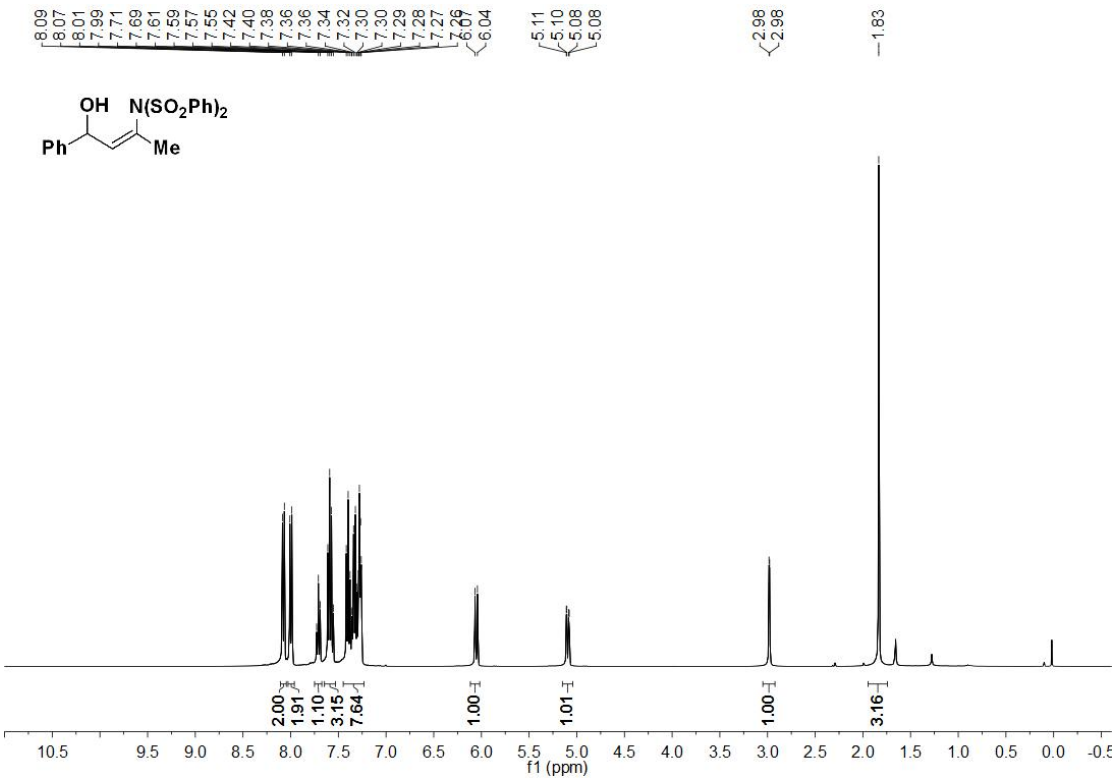


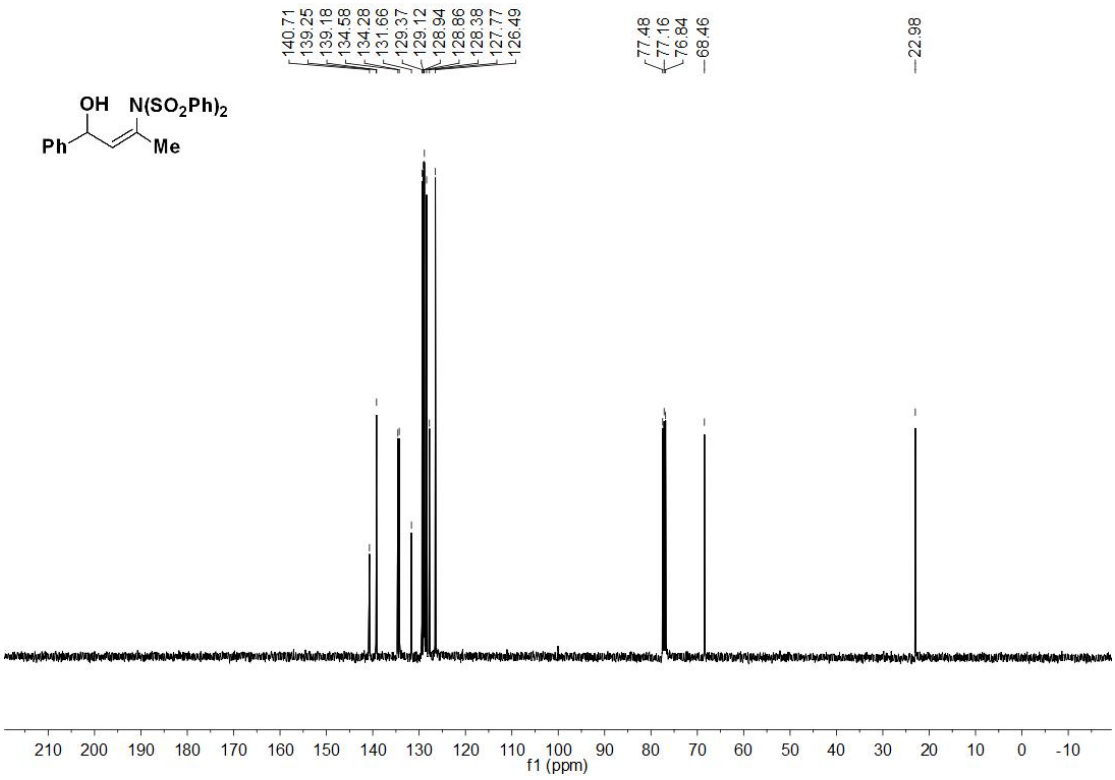
NMR Spectra of Product (2p)



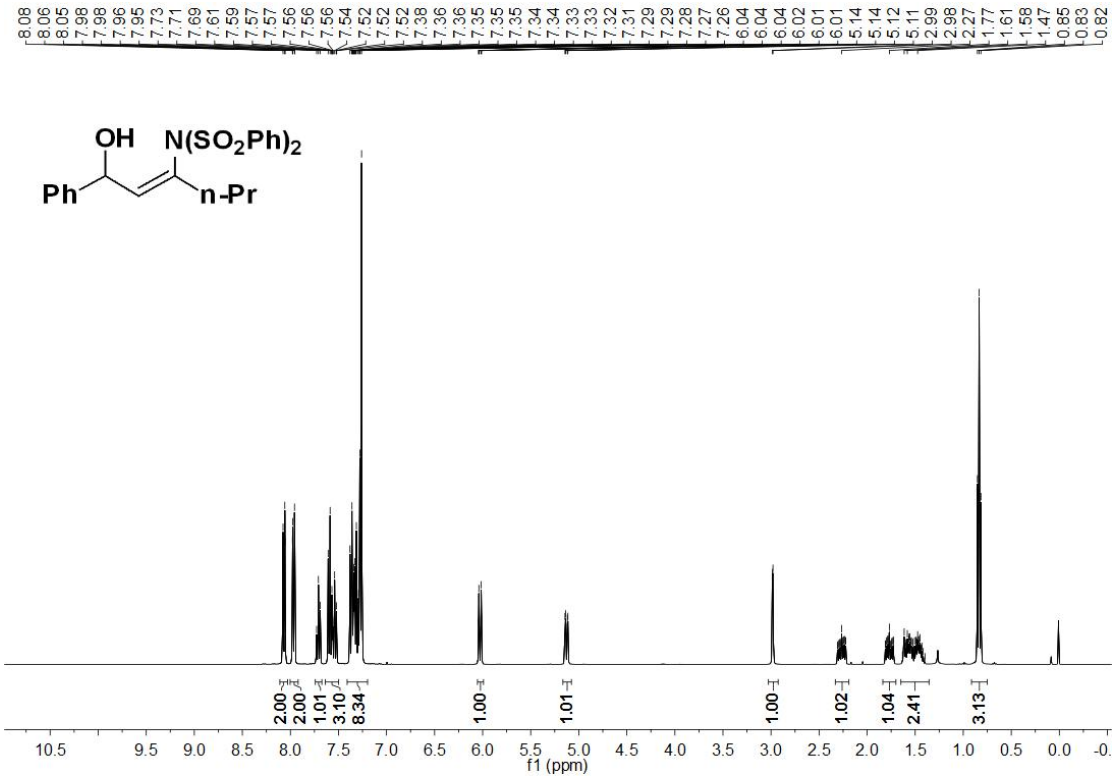


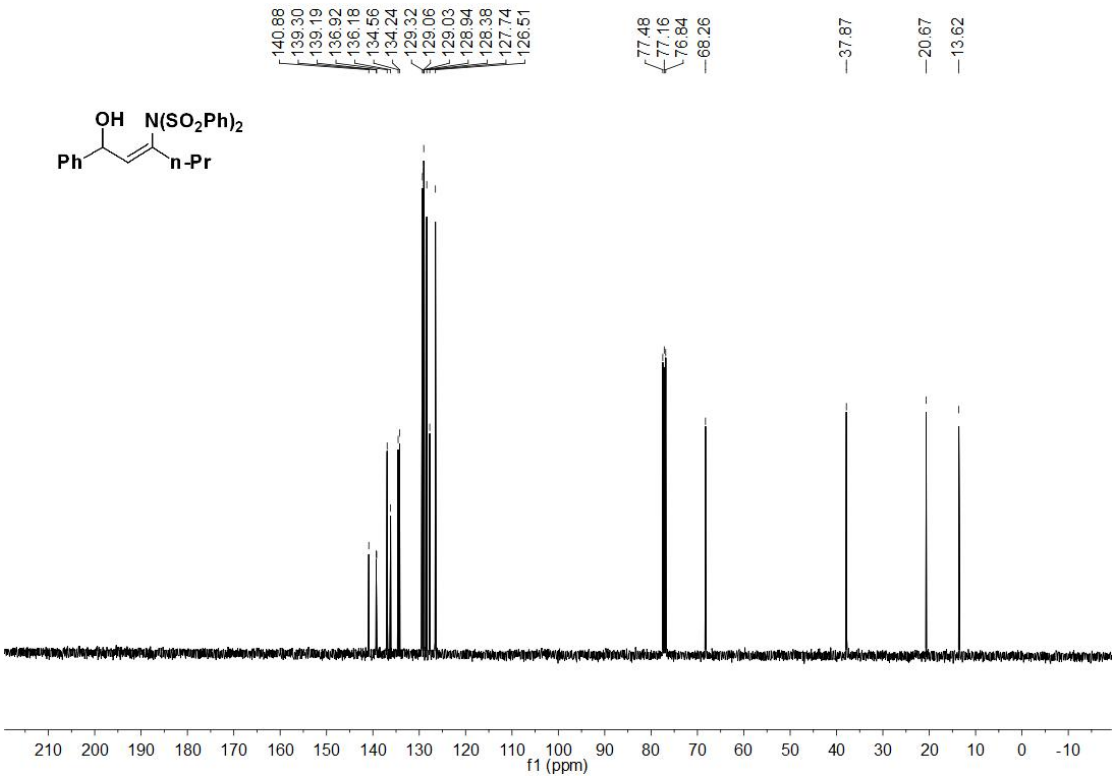
NMR Spectra of Product (5a)



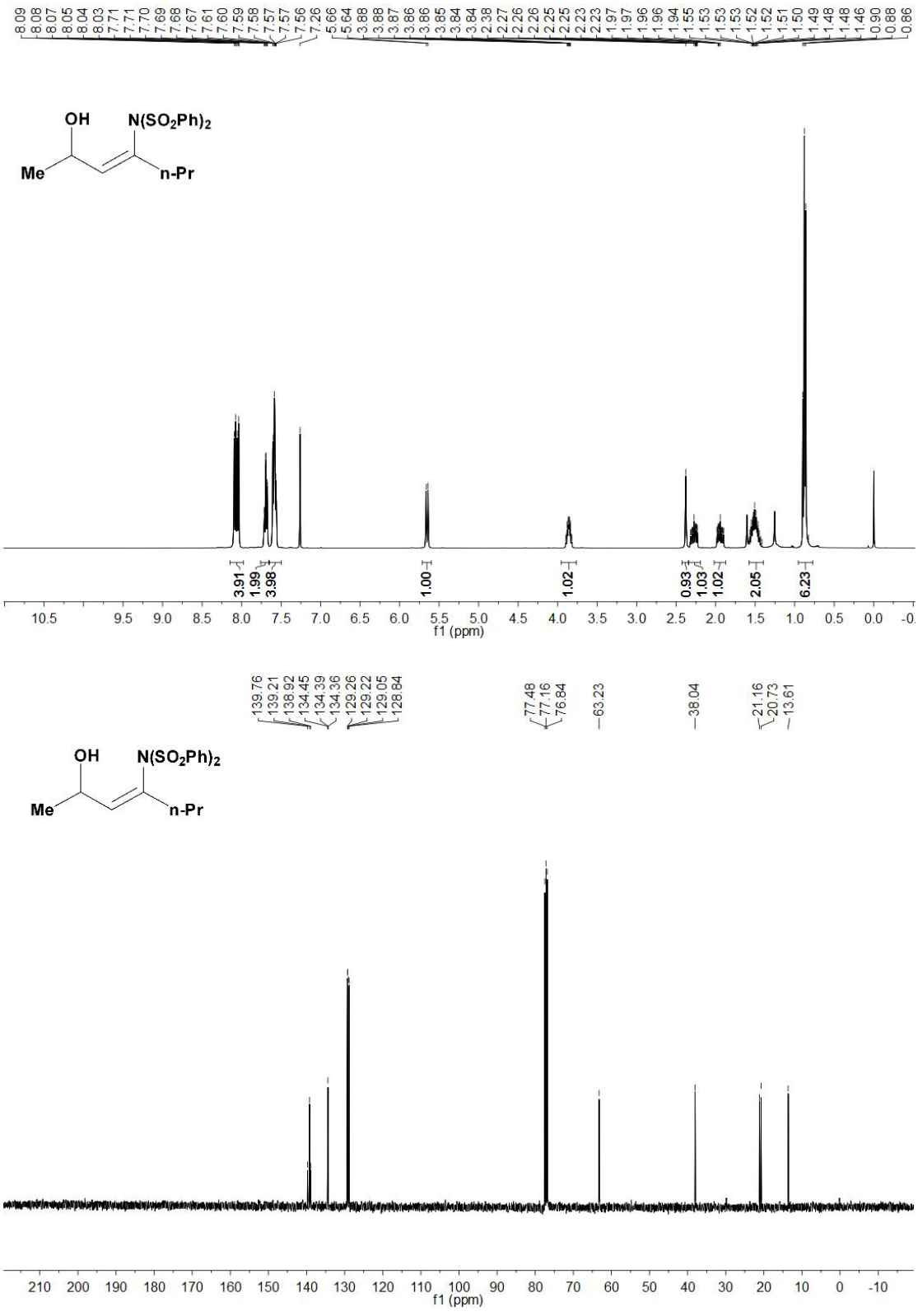


NMR Spectra of Product (5b)

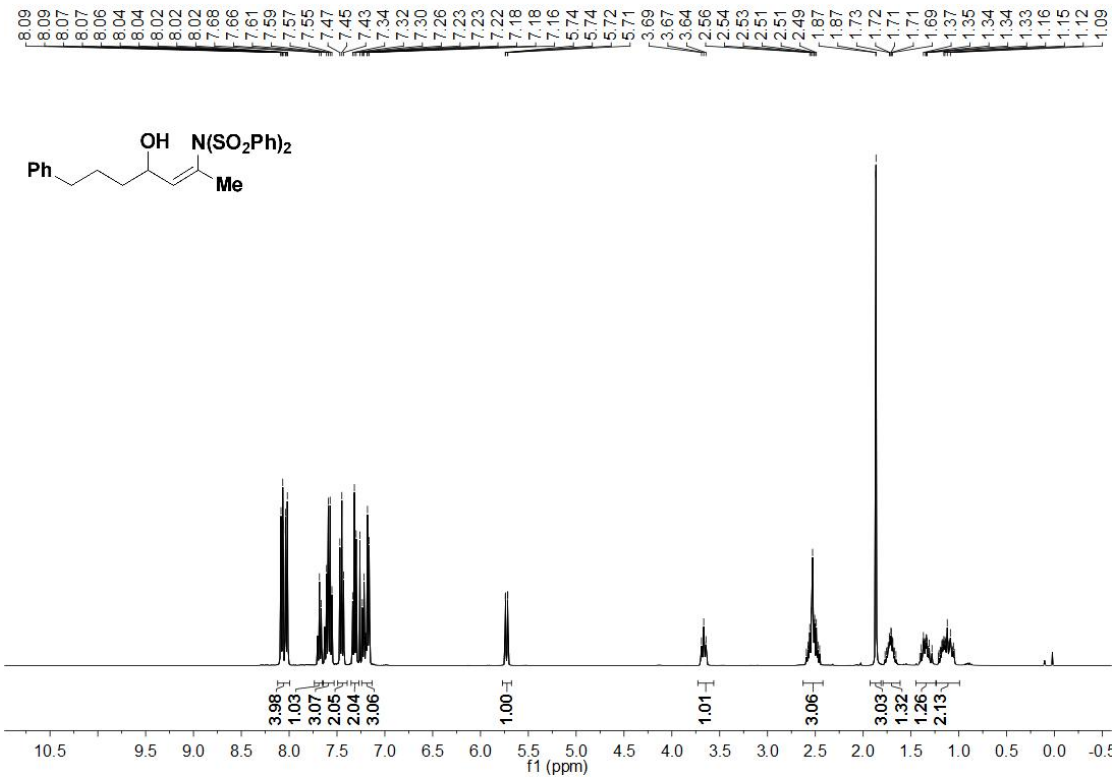


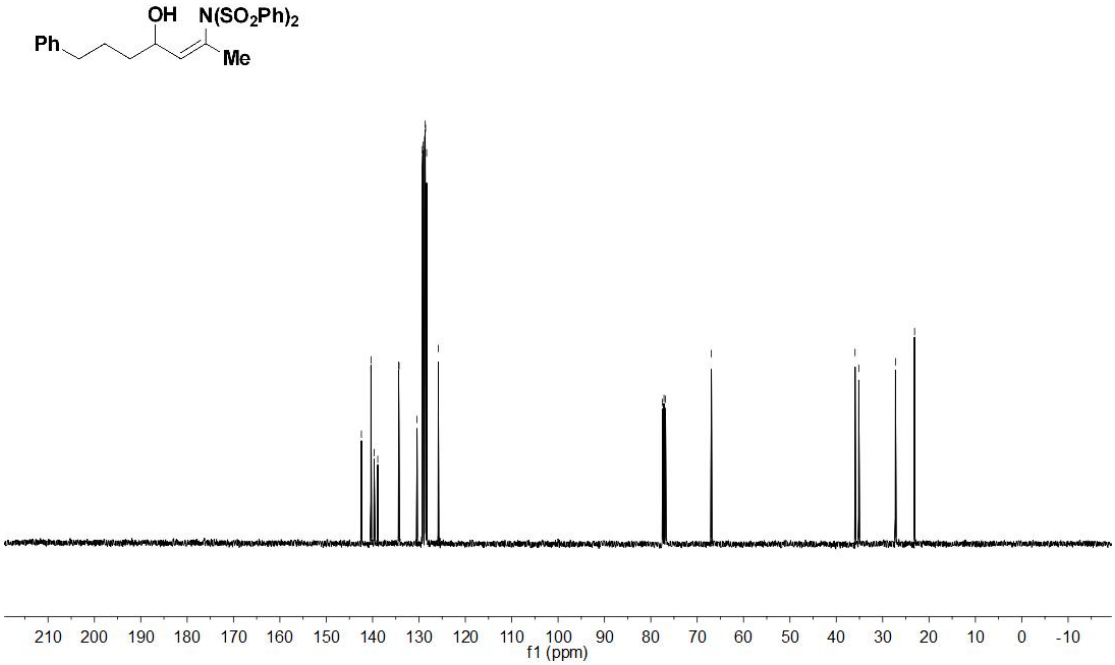


NMR Spectra of Product (5c)

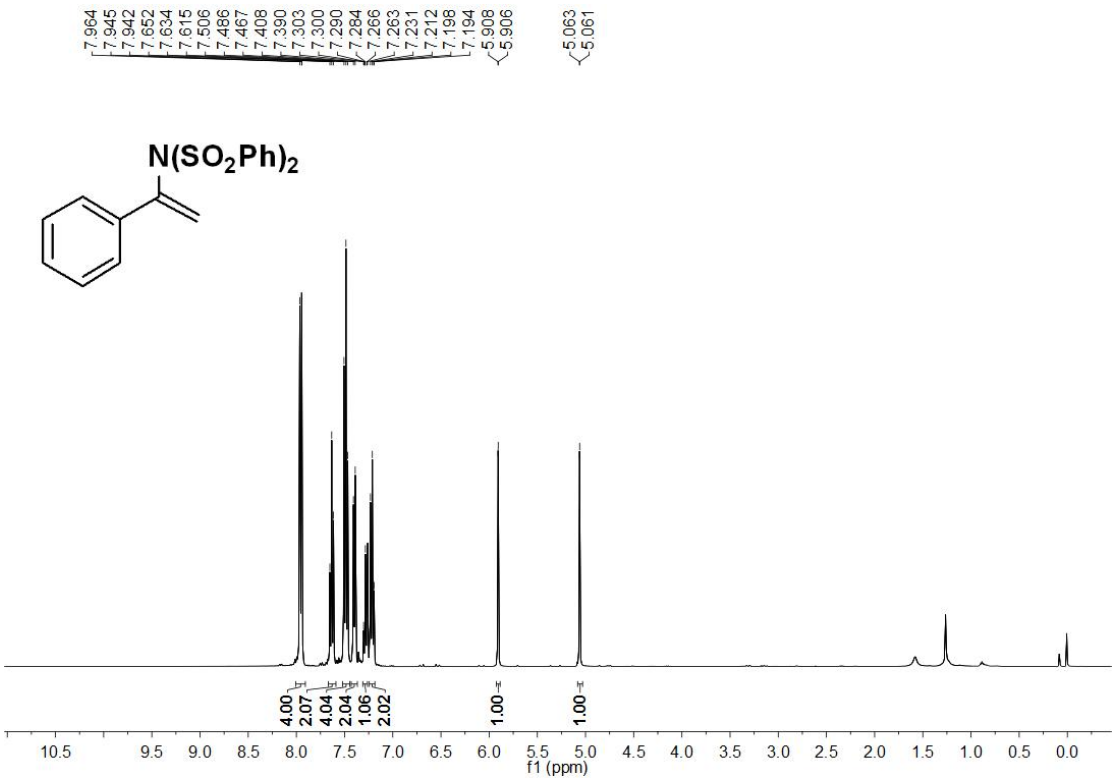


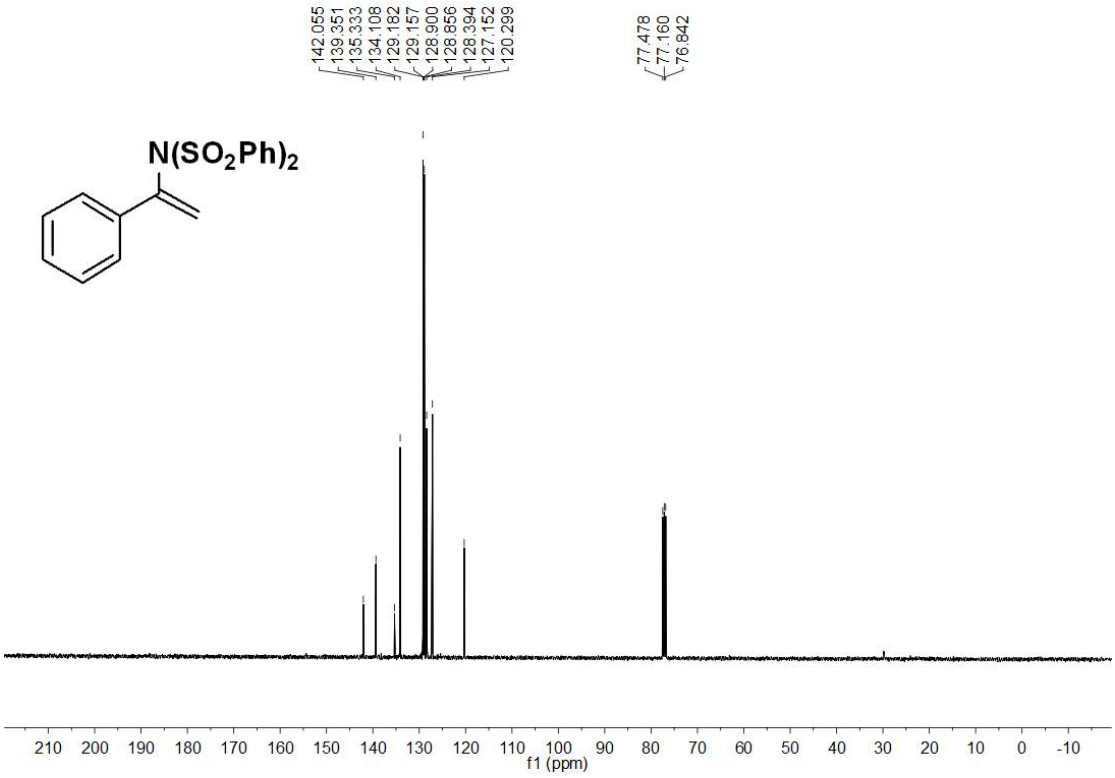
NMR Spectra of Product (5d)



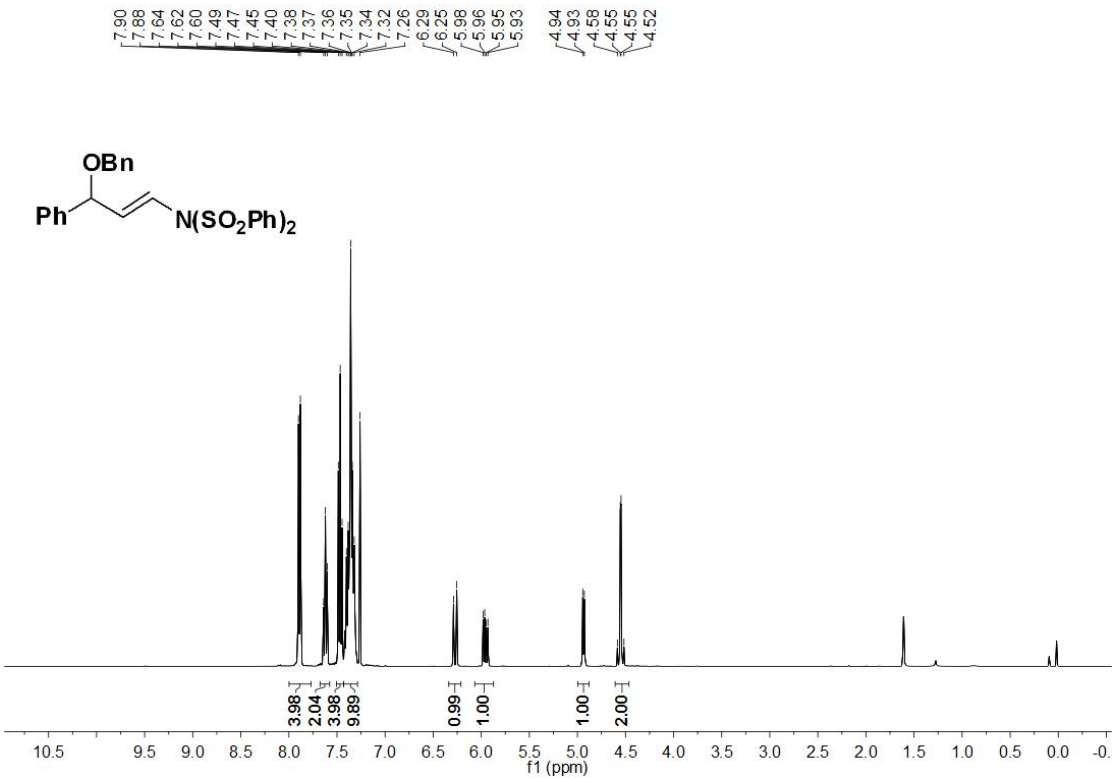


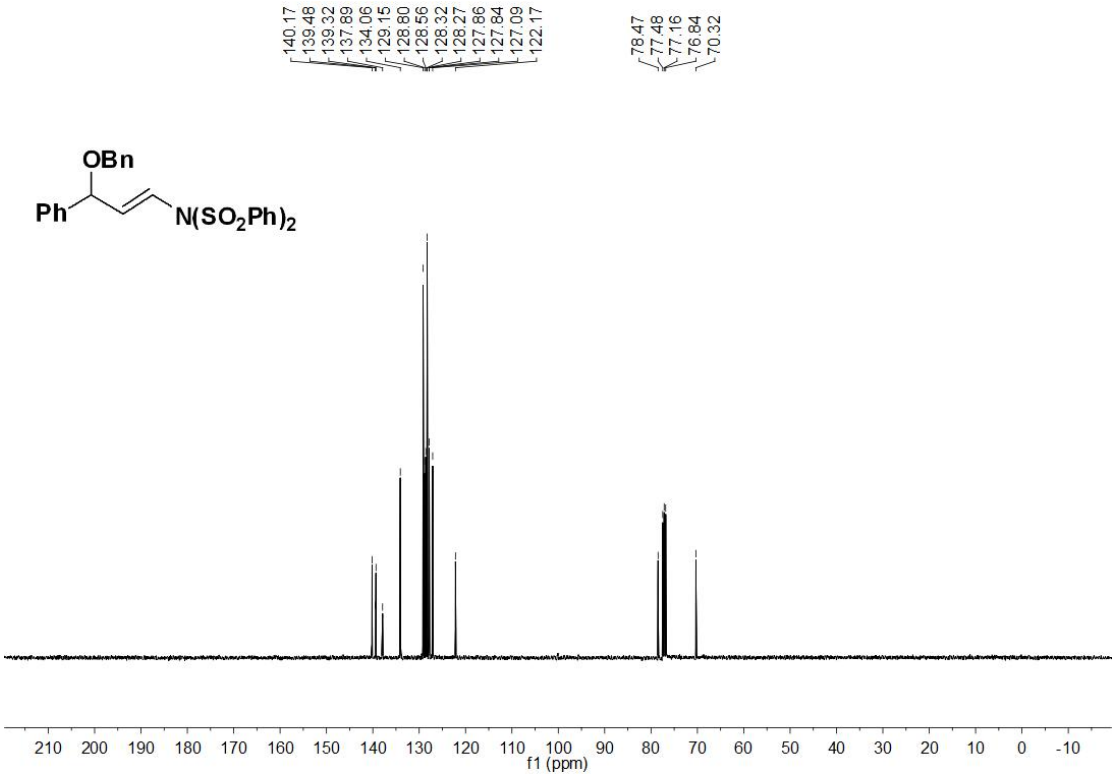
NMR Spectra of Product (6)



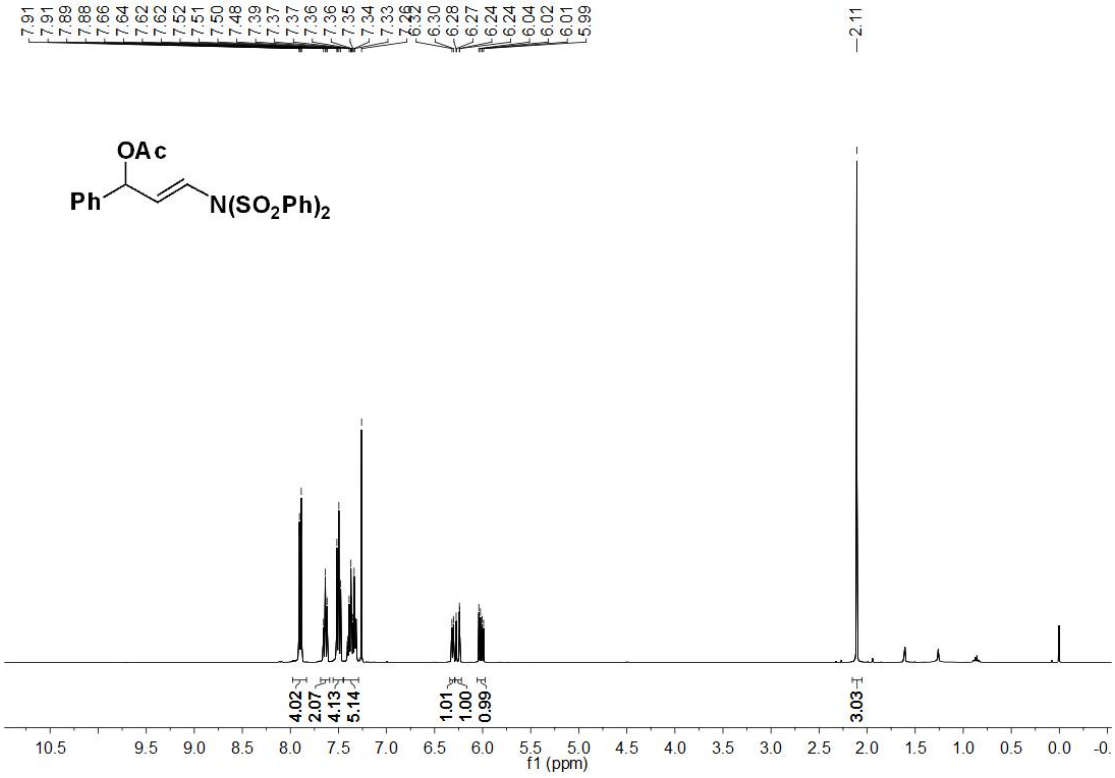


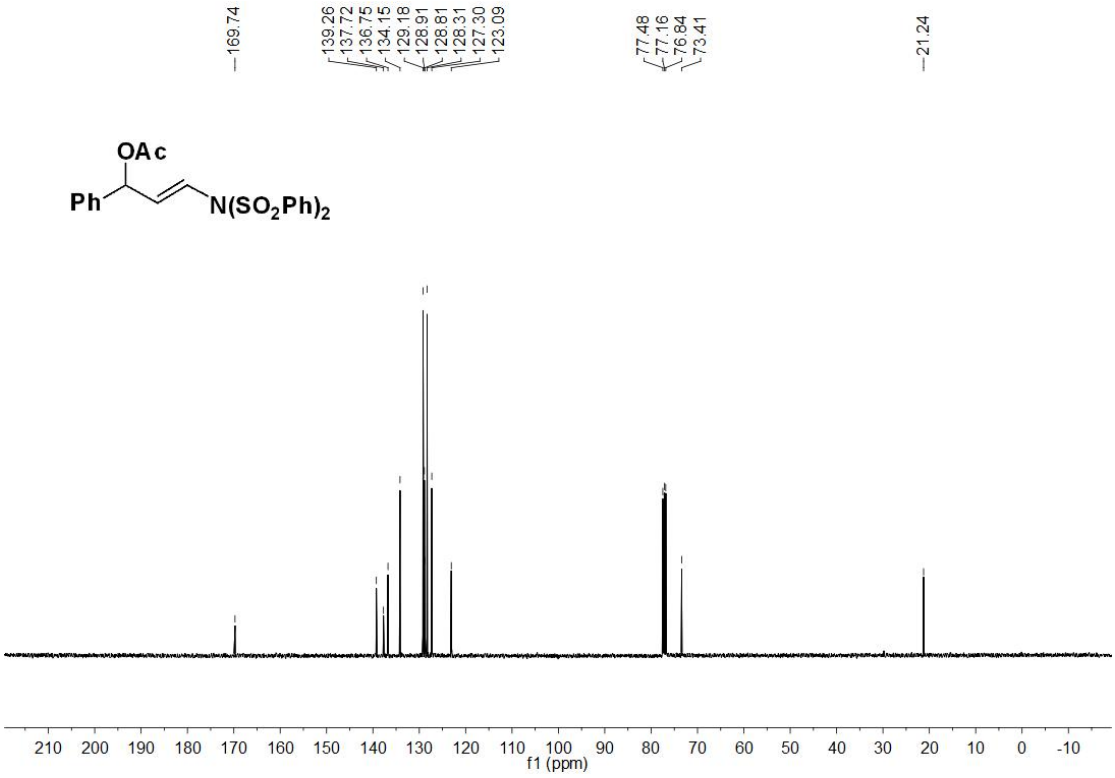
NMR Spectra of Product (8a)





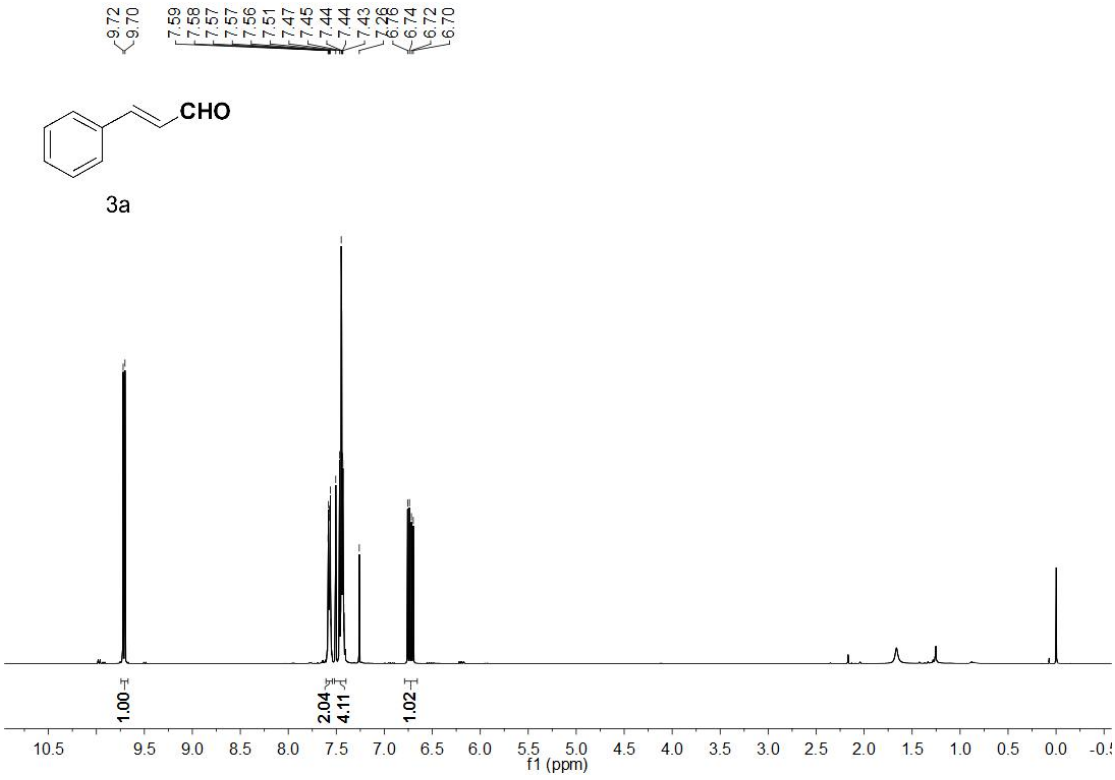
NMR Spectra of Product (8b)



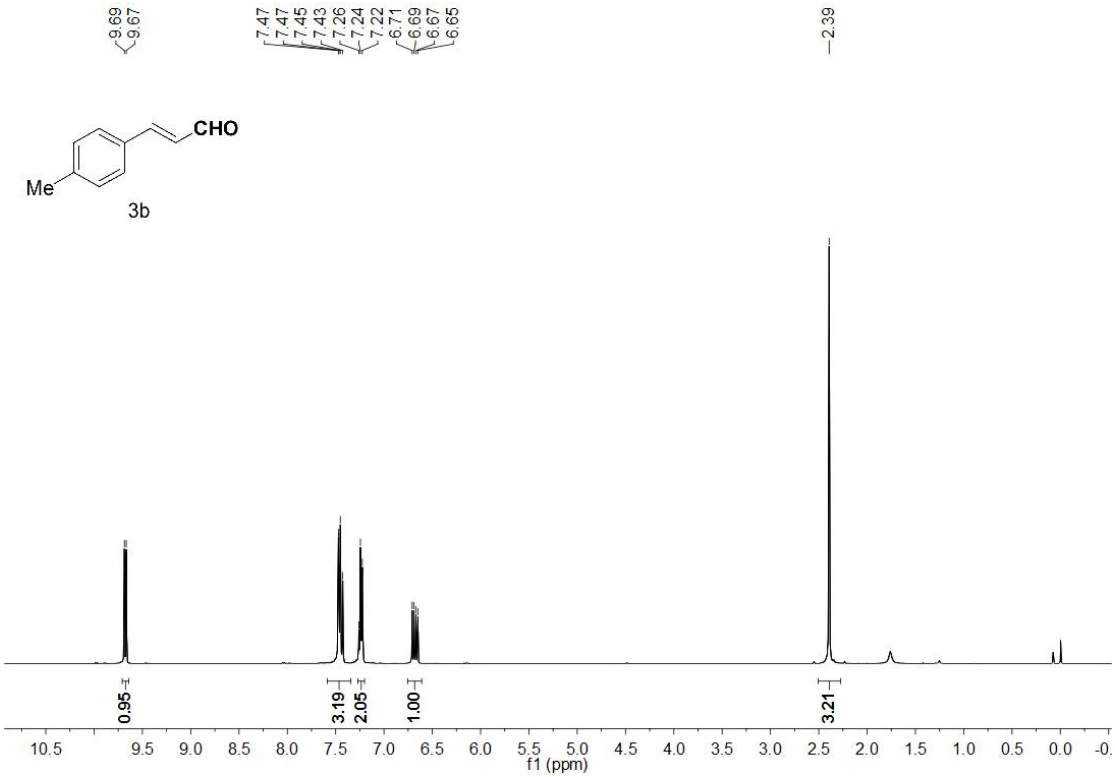


9. Proton NMR spectra for 3a-3m

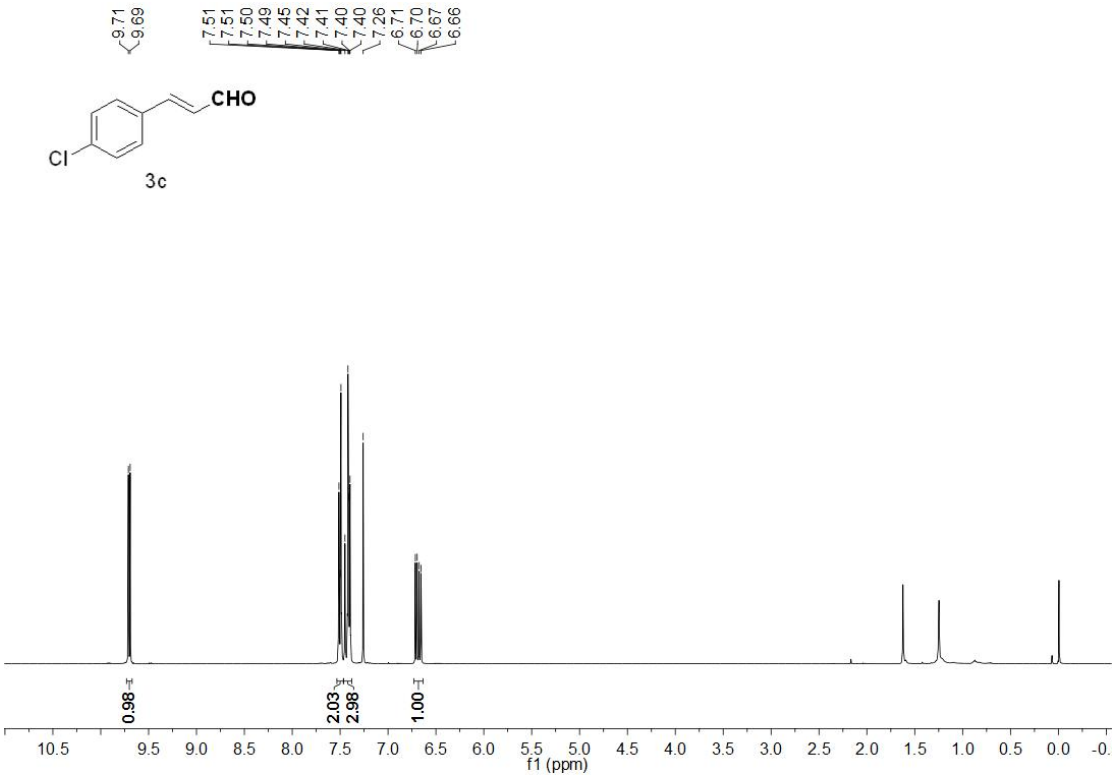
^{1}H NMR Spectrum of Product (3a)



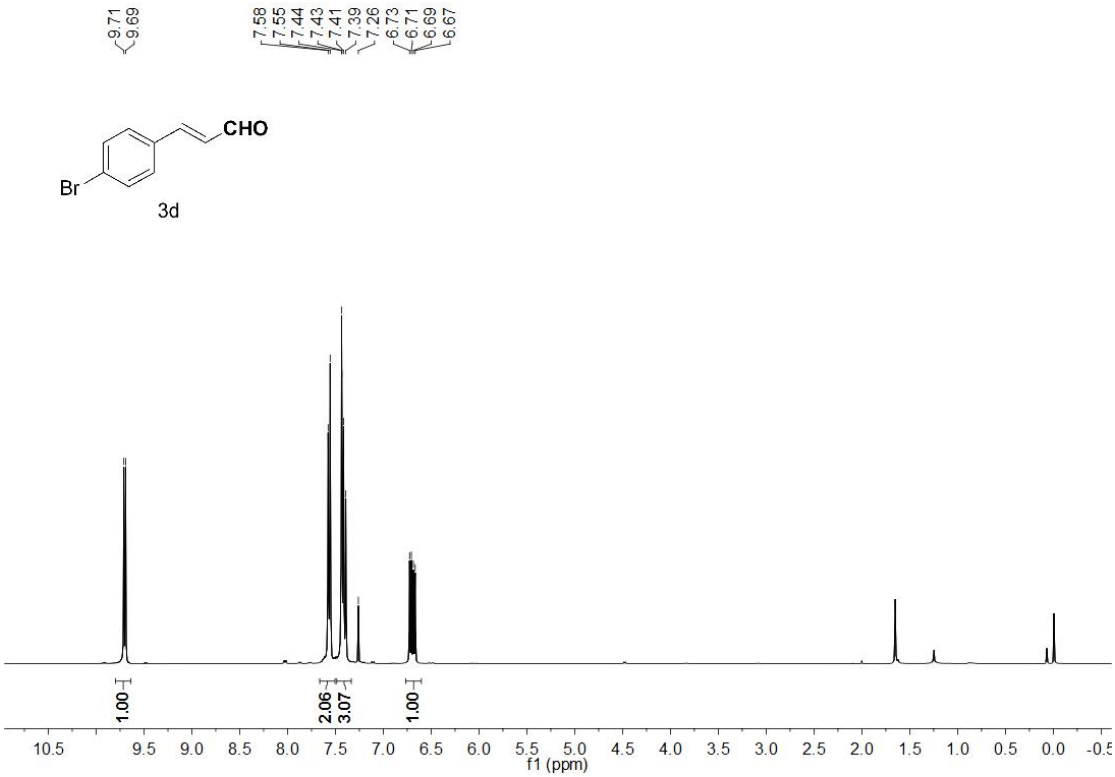
^{1}H NMR Spectrum of Product (3b)



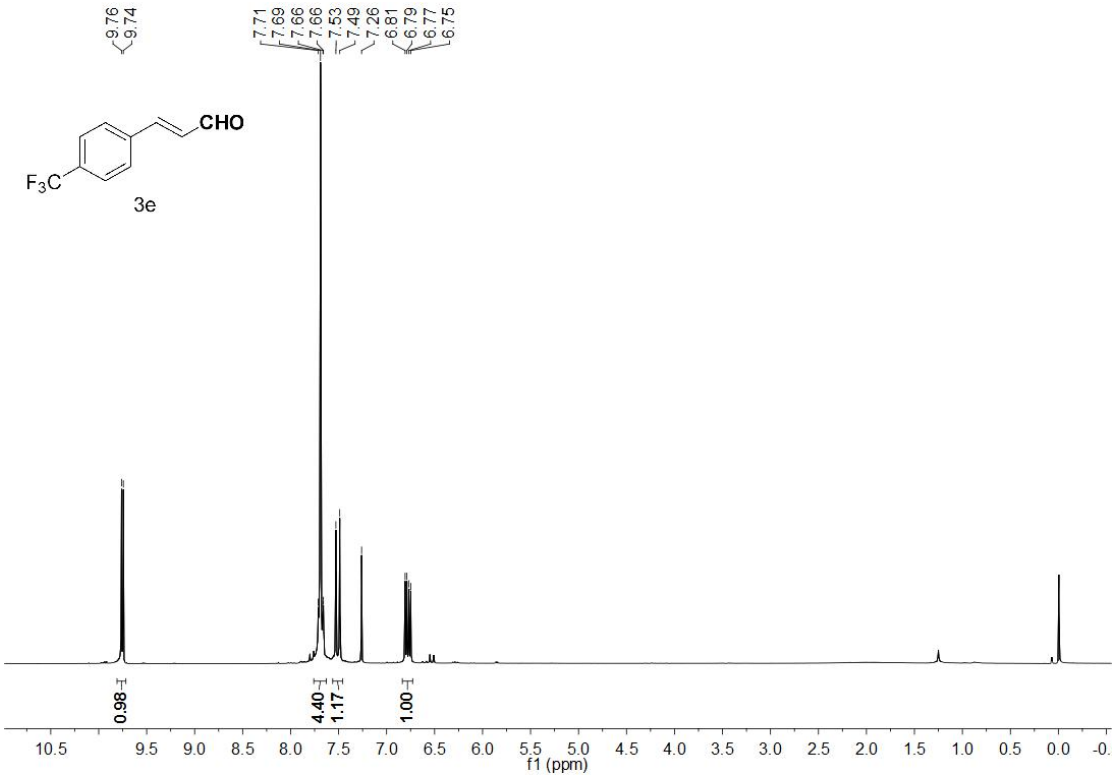
^{1}H NMR Spectrum of Product (3c)



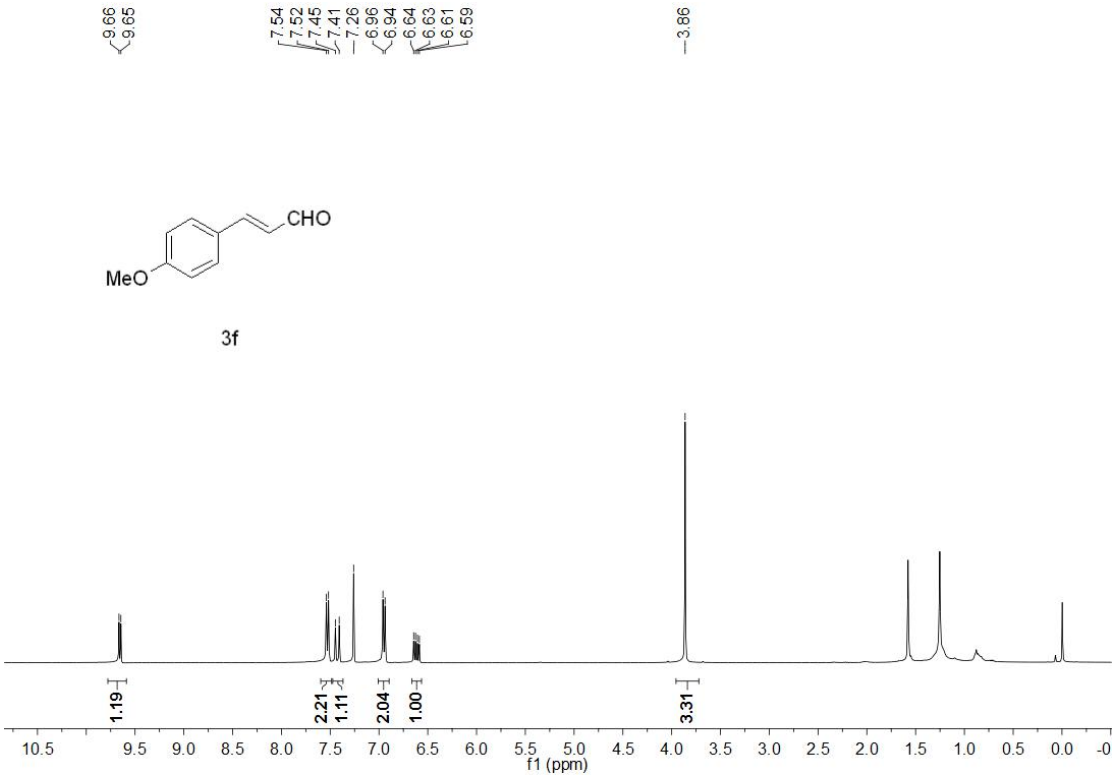
^{1}H NMR Spectrum of Product (3d)



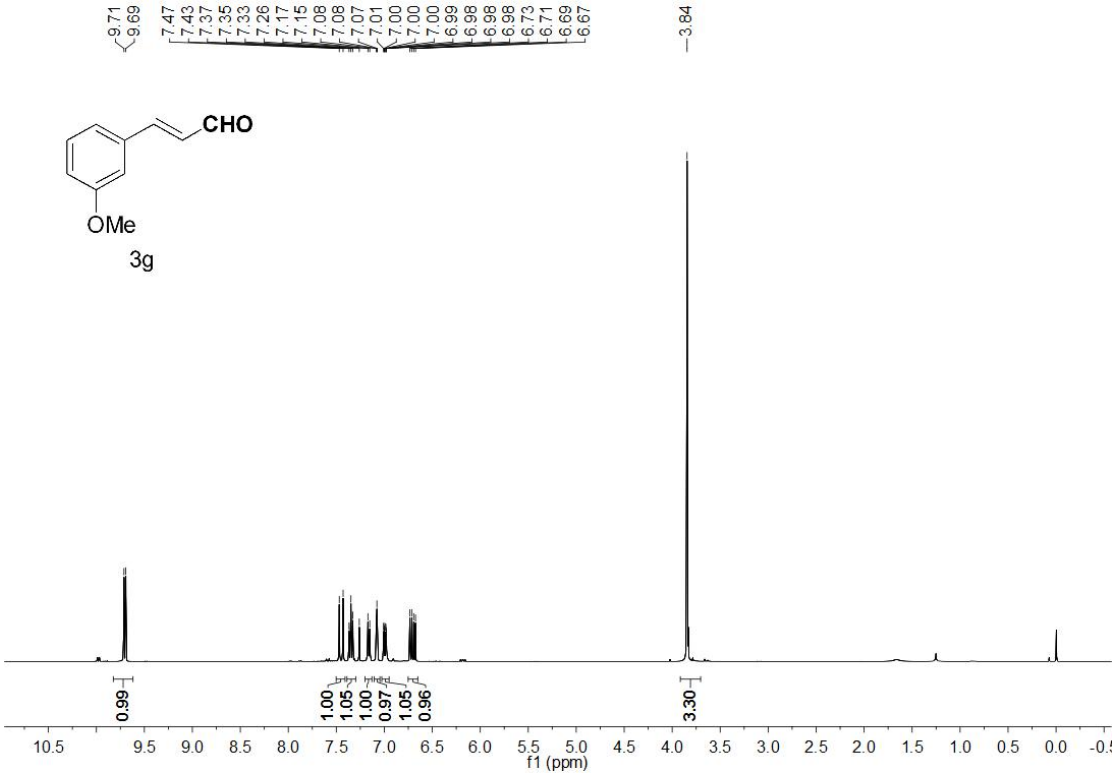
^{1}H NMR Spectrum of Product (3e)



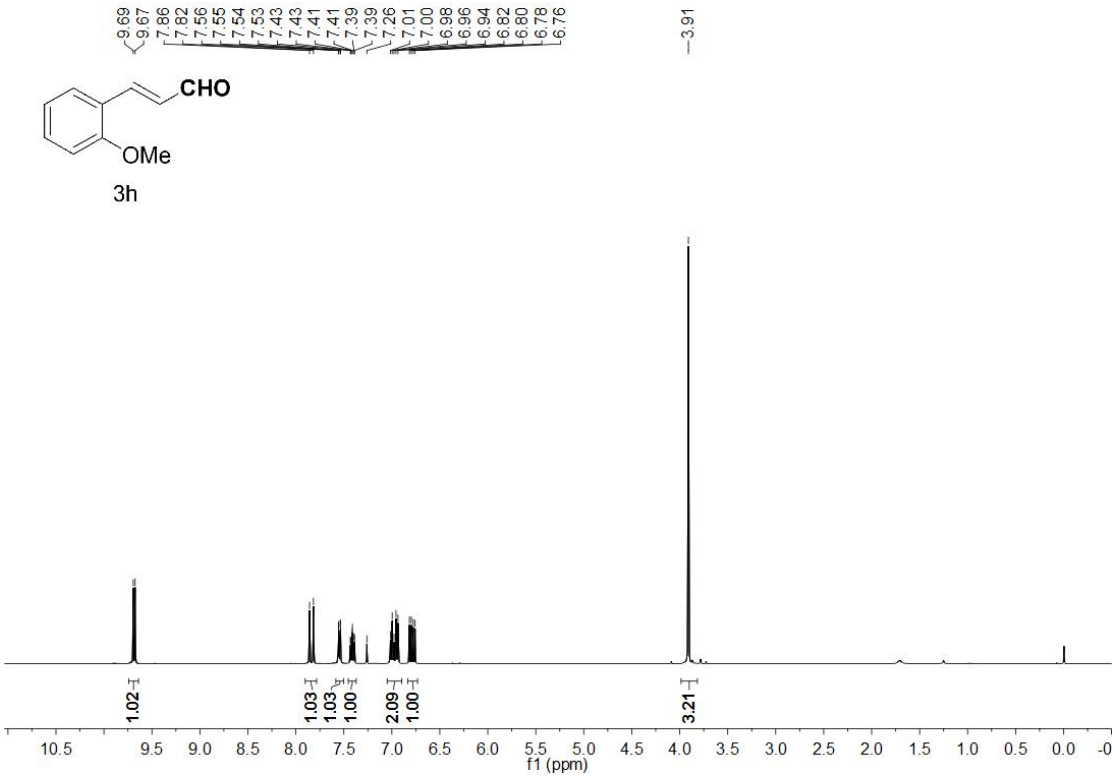
^{1}H NMR Spectrum of Product (3f)



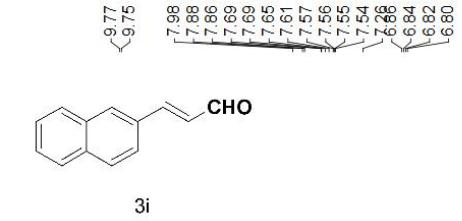
^{1}H NMR Spectrum of Product (3g)



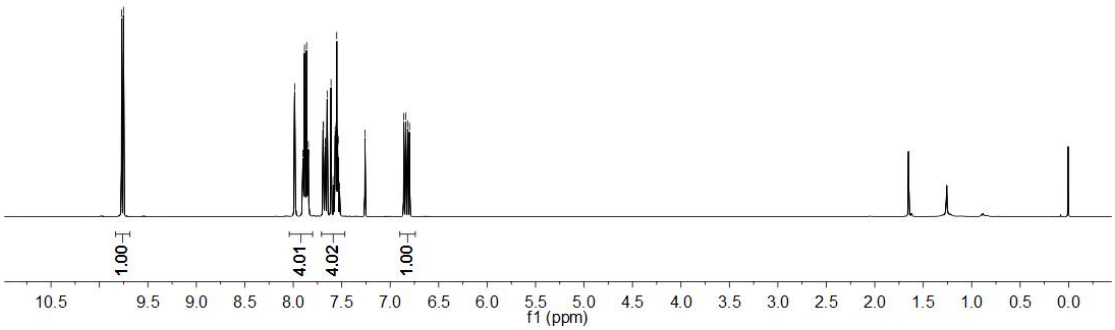
^{1}H NMR Spectrum of Product (3h)



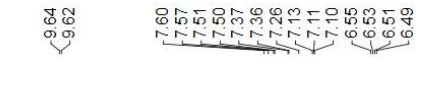
^{1}H NMR Spectrum of Product (3i)

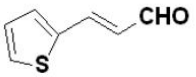


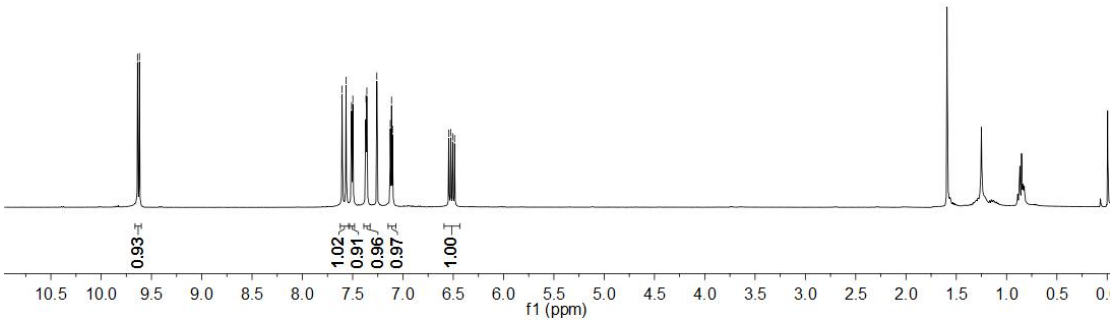
3i



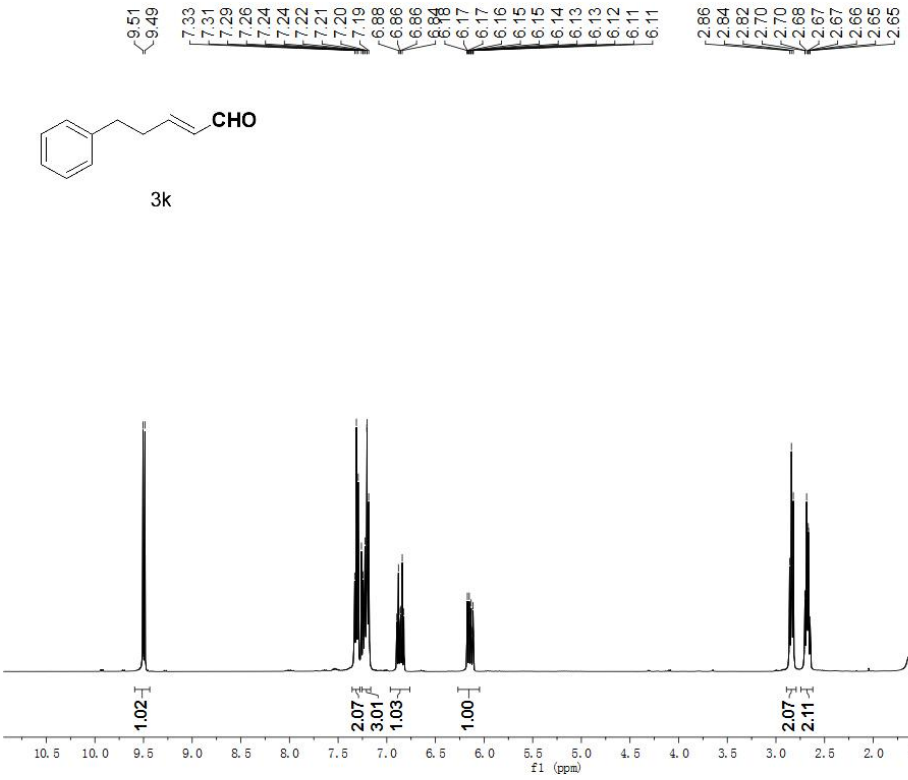
^{1}H NMR Spectrum of Product (3j)



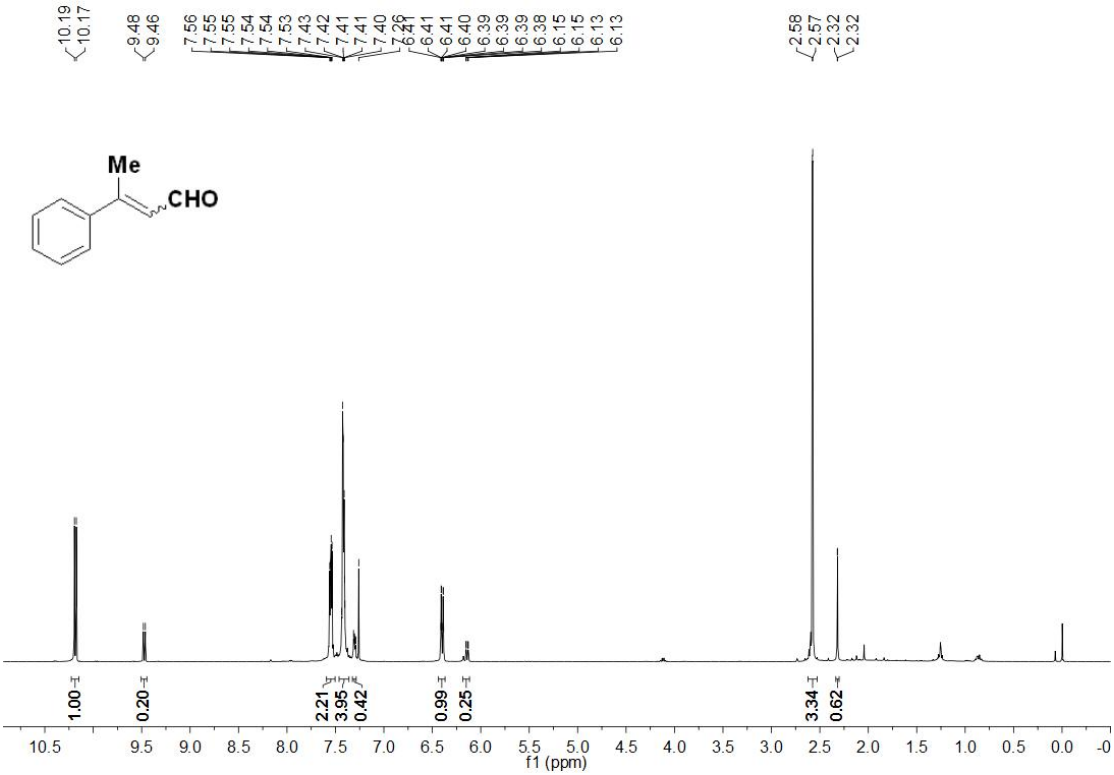




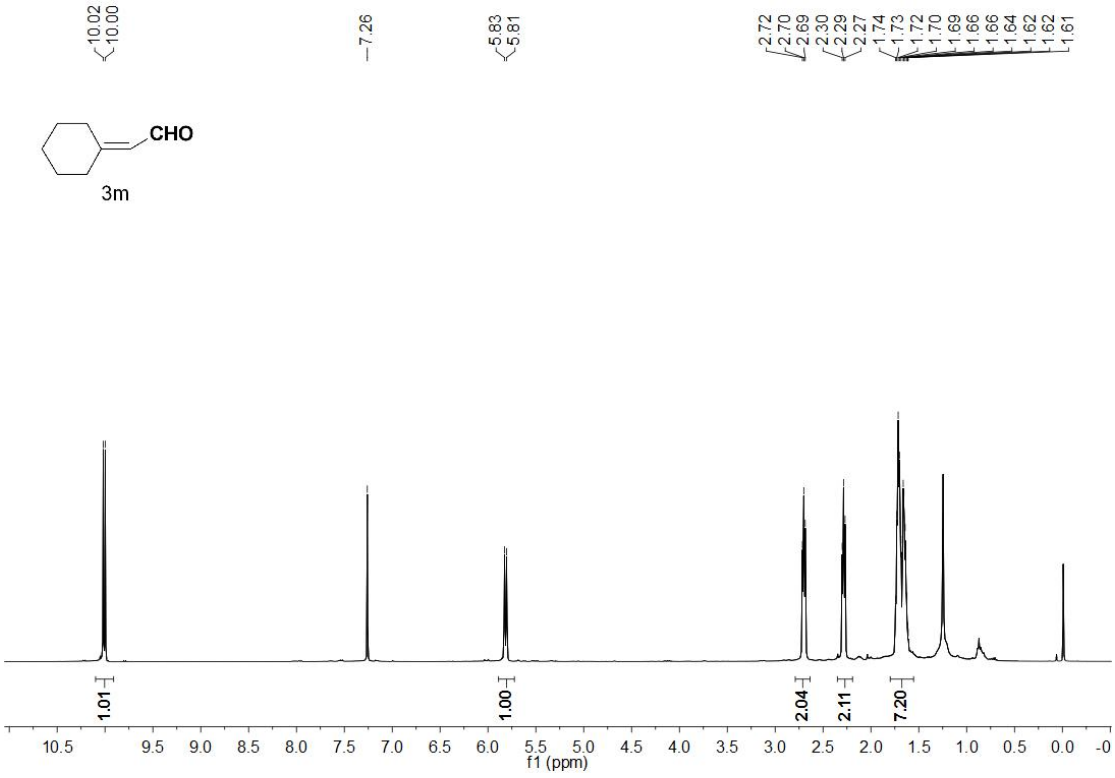
^{1}H NMR Spectrum of Product (3k)



^{1}H NMR Spectrum of Product (3l)



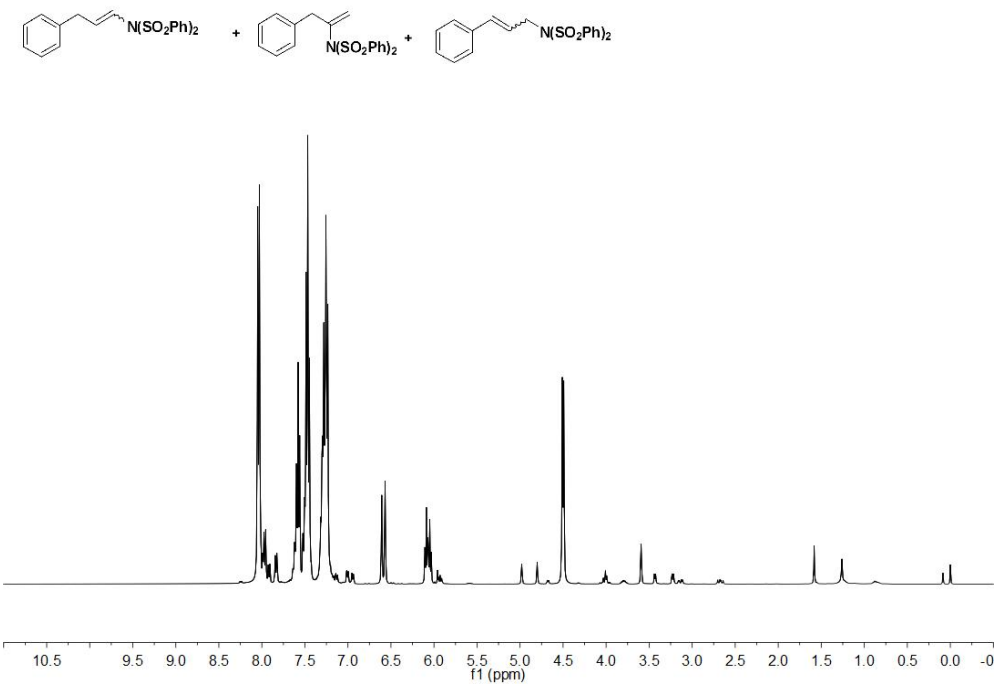
^{1}H NMR Spectrum of Product (3m)



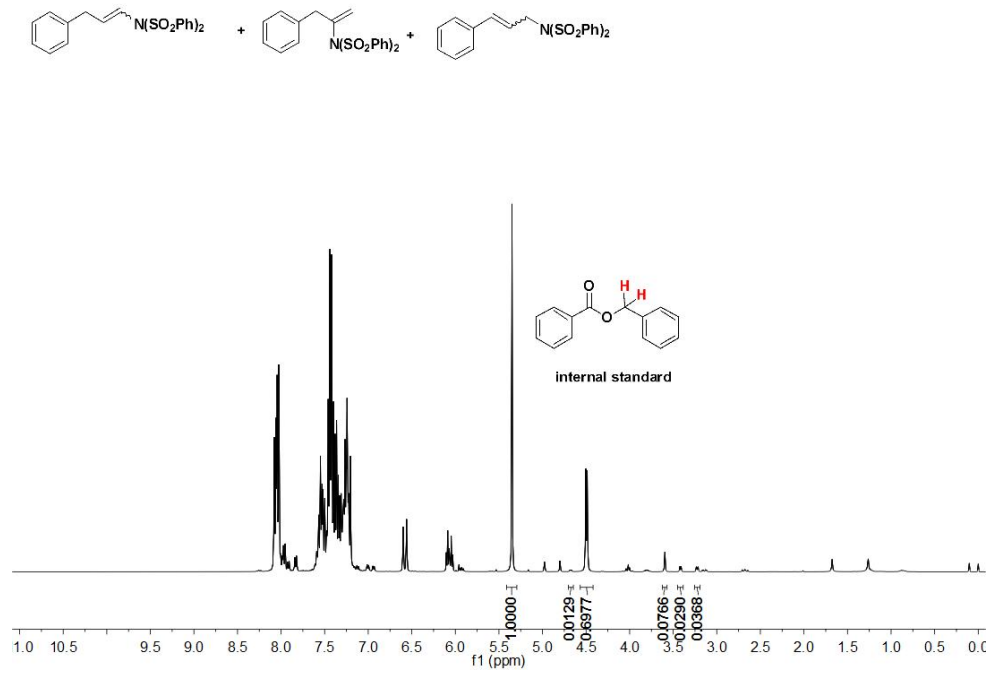
10. NMR spectra for amination of the alkenes 9, 13 and 14

1) The products of amination of allylbenzene 9

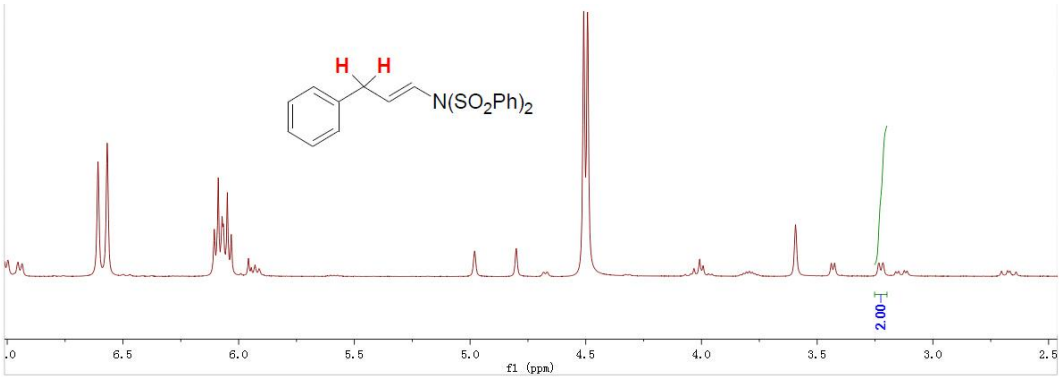
^{1}H NMR spectrum of the mixture products after flash column chromatography for amination of allylbenzene **9**:

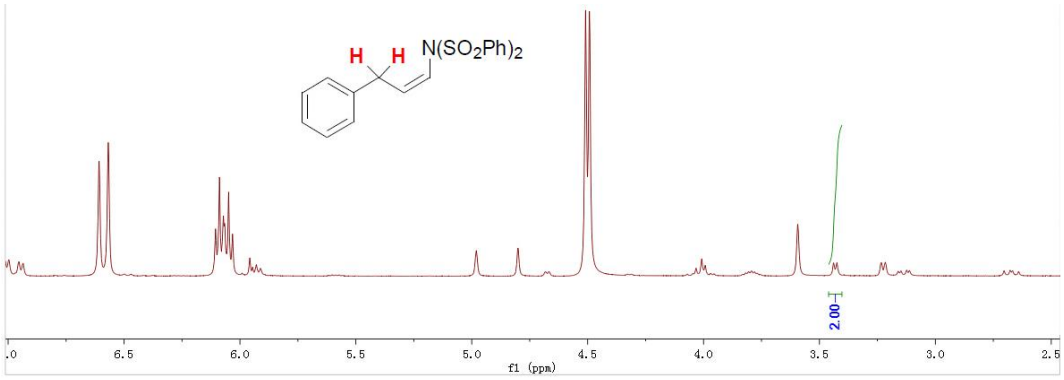


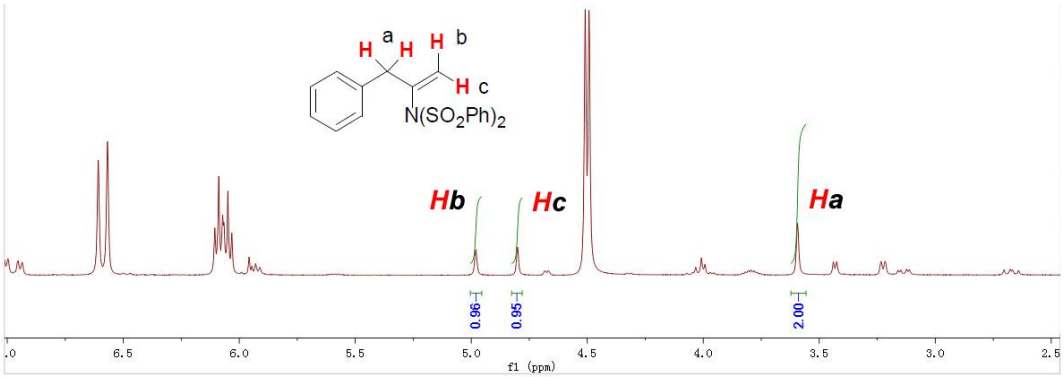
^{1}H NMR spectrum of the mixture products after flash column chromatography for amination of allylbenzene **9** using BzOBn as the internal standard:

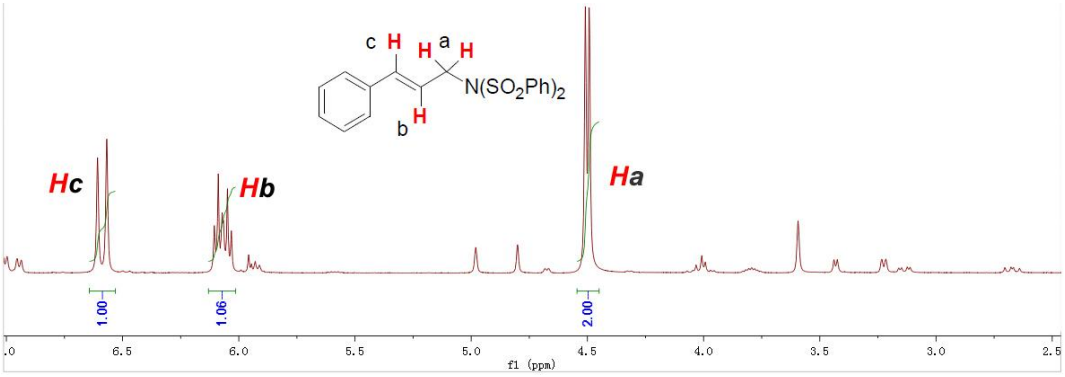


^{1}H NMR characteristic peaks of animation products:



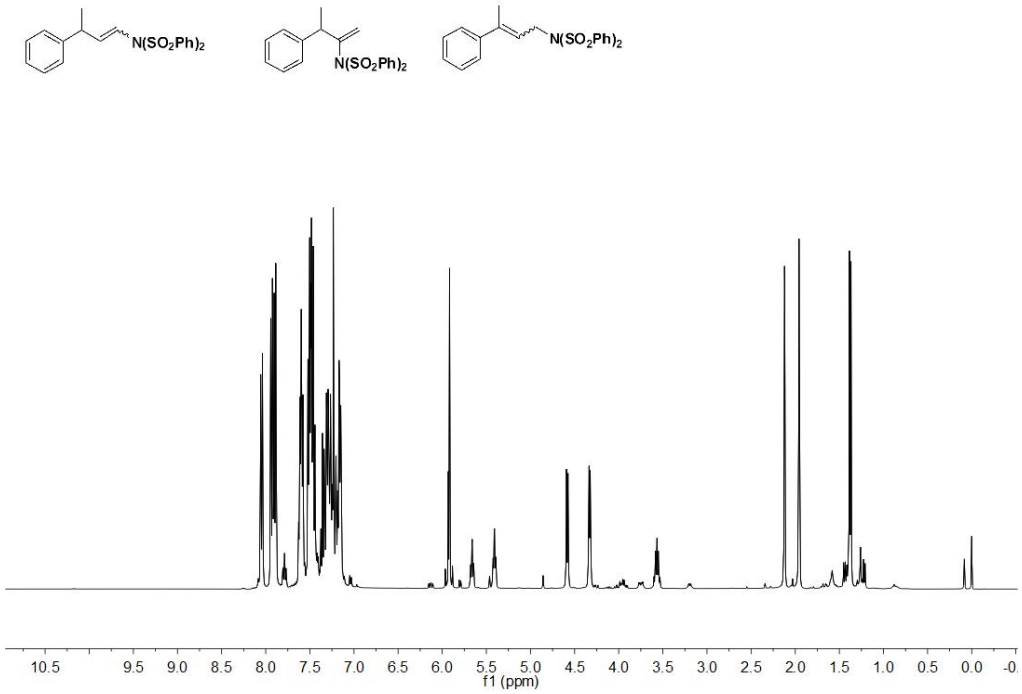




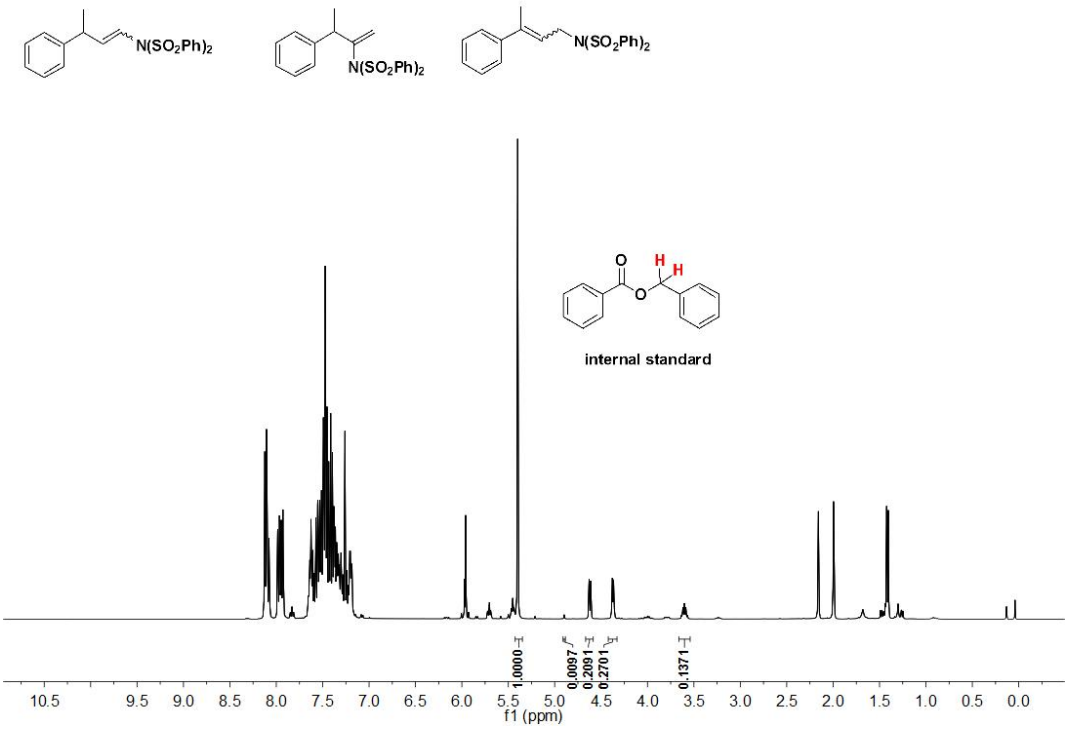


2) The products of amination of 3-phenyl-1-butene 13

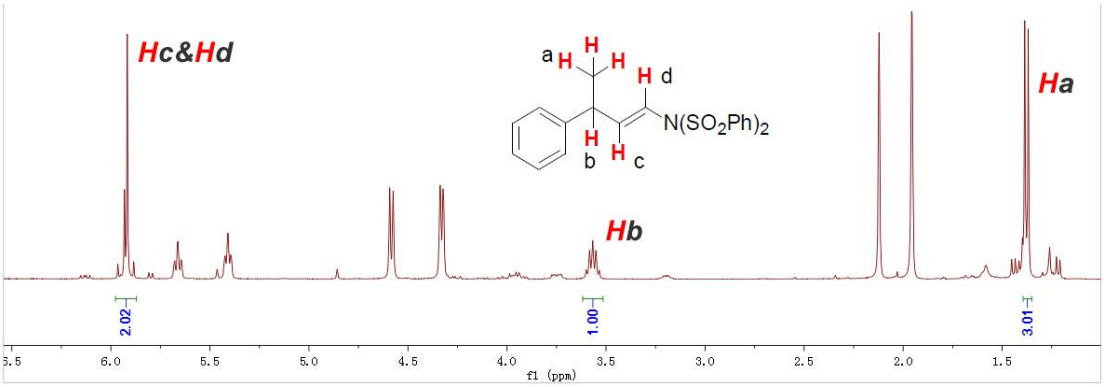
^{1}H NMR spectra for reaction mixture of 3-phenyl-1-butene **13** after flash column chromatography:

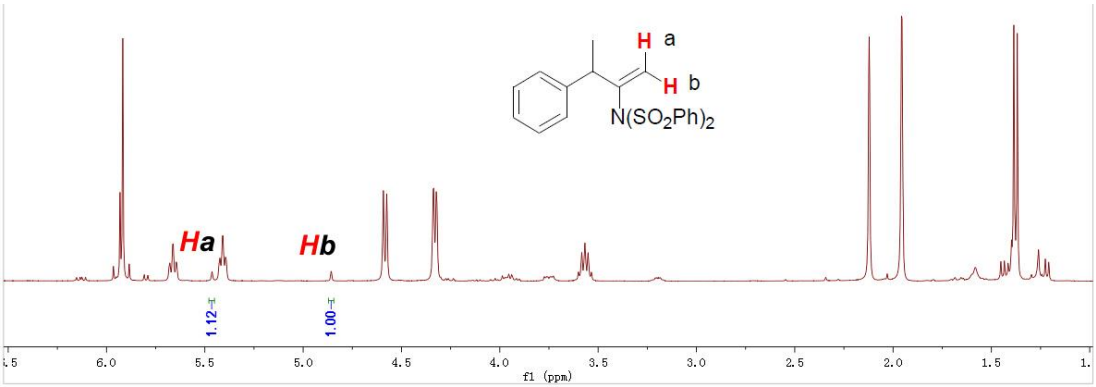


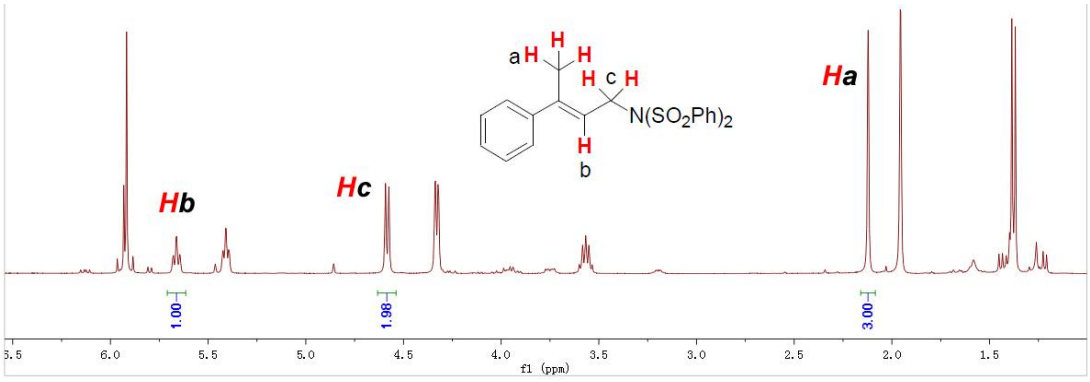
^{1}H NMR spectra for reaction mixture of 3-phenyl-1-butene **13** after flash column chromatography using BzOBn as the internal standard:

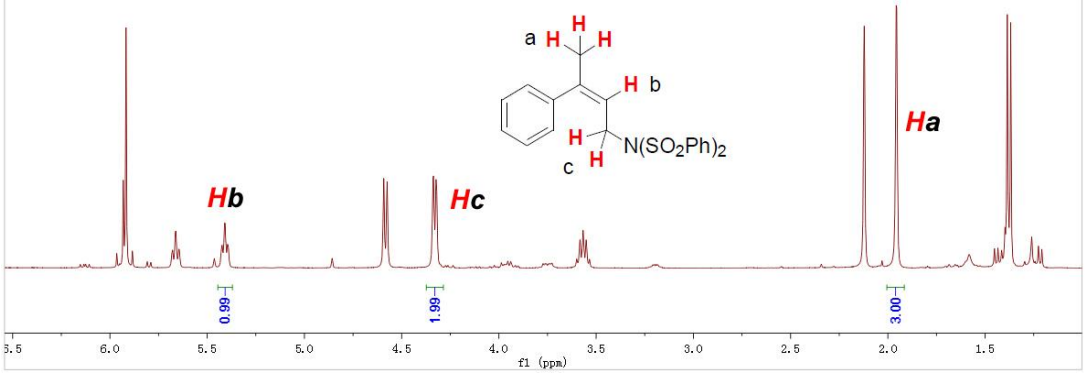


^{1}H NMR characteristic peaks of animation products of 3-phenyl-1-butene **13**:



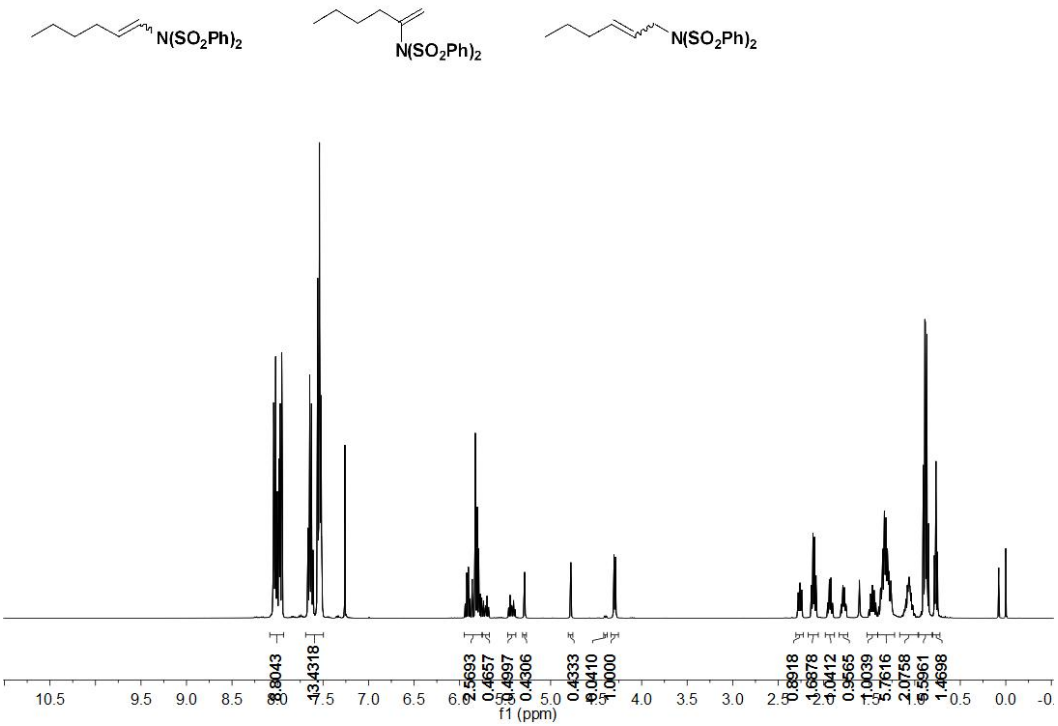




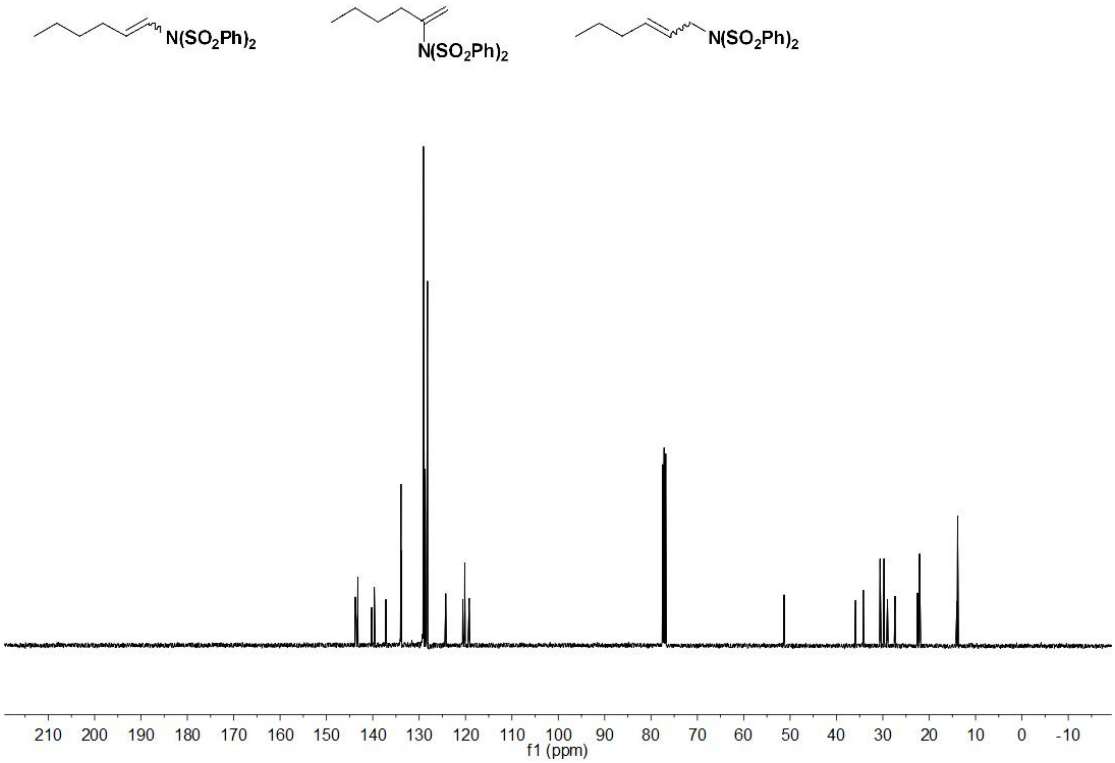


3) The products of amination of hex-1-ene 14

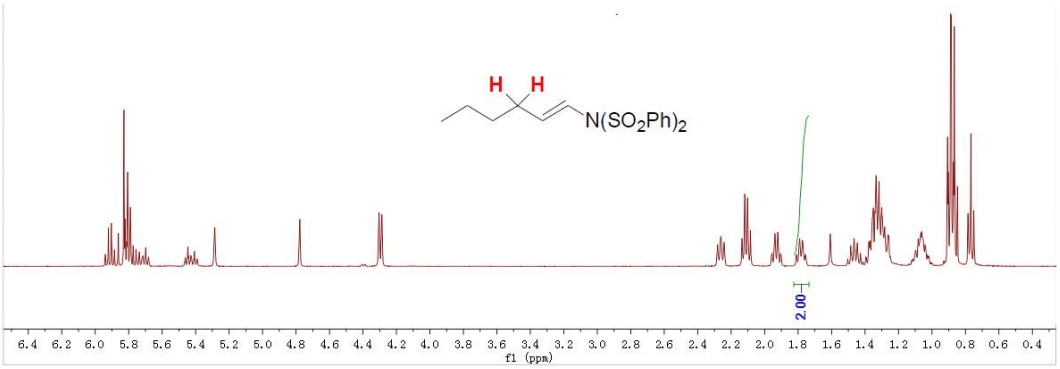
^{1}H NMR spectra for all amination products of hex-1-ene **14**:

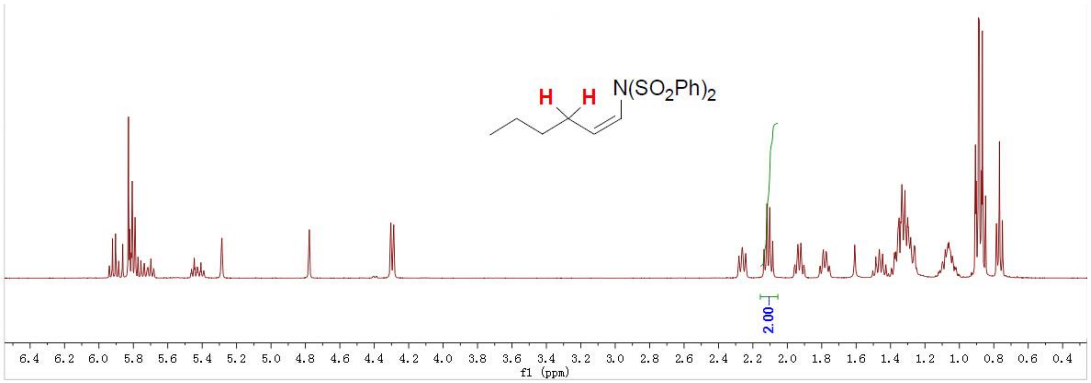


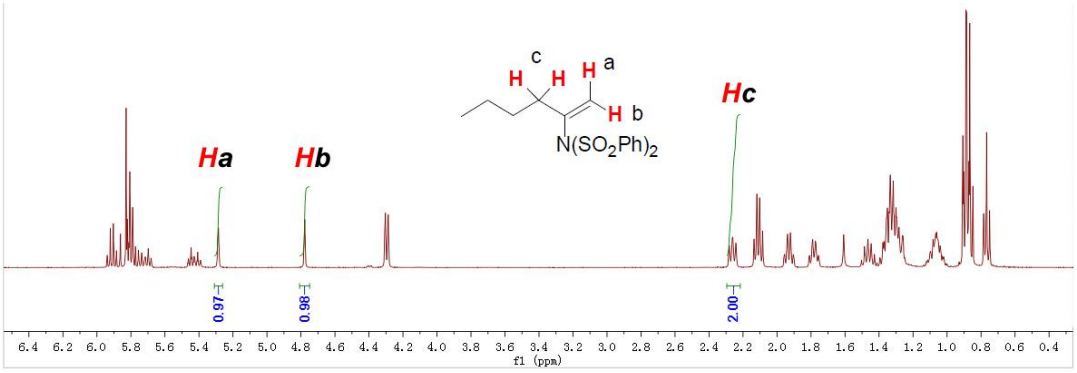
^{13}C NMR spectra for all amination products of hex-1-ene **14**:

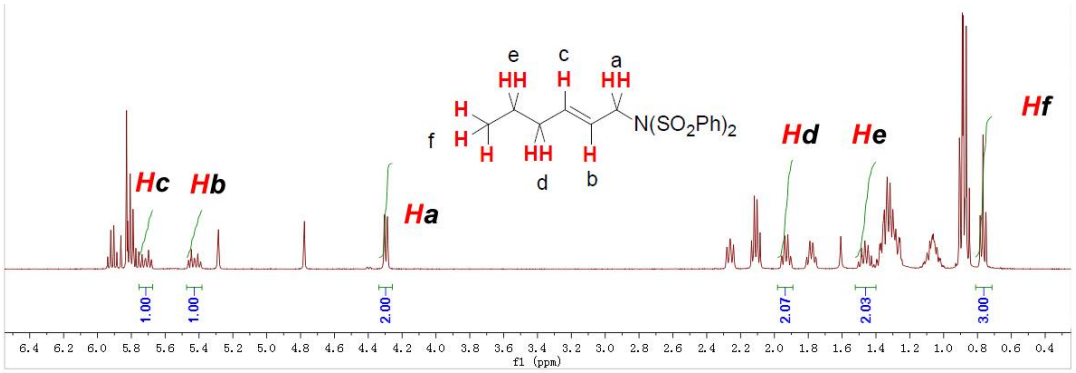


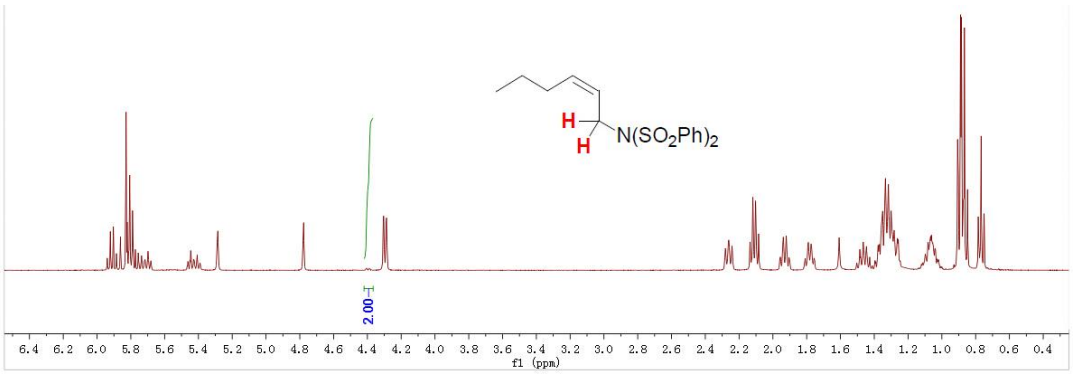
^{1}H NMR characteristic peaks of each animation product of hex-1-ene **14**:


H H
N(SO2Ph)2
2.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)

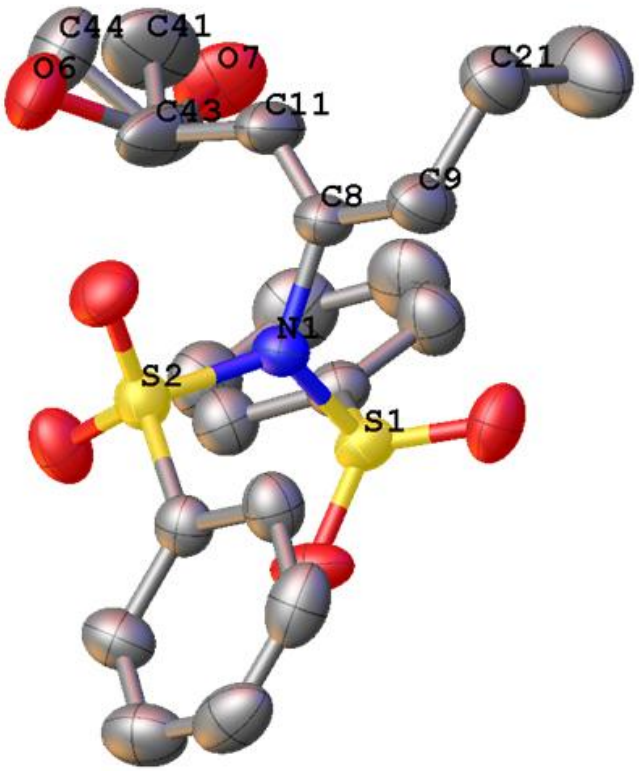

H H
N(SO2Ph)2
2.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)


c
H H
H a
H b
N(SO2Ph)2
Ha
Hb
Hc
0.97
0.98
2.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)


e c a
HH H HH
H
f H H HH H
N(SO2Ph)2
d b
Hc Hb
Ha
Hd He Hf
1.00
1.00
2.00
2.07
2.03
3.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)



11. Data for X-ray single crystal structure of 5c



Gray ball stands for carbon atom; yellow ball stands for sulfur atom; blue ball stands for nitrogen atom; red ball stands for oxygen atom. Because the racemic mixture was used, the methy group and the hydroryl group are in disorder and occupy in **C**44/**C**41 and **O**07/**O**06 with 50% possibility, respectively.

Table S2 Crystal data and structure refinement for **5c** (exp_19725).

Identification code	exp_19725
Empirical formula	$C_{19}H_{23}NO_5S_2$
Formula weight	404.49
Temperature/K	293.35(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.9459(4)
b/Å	8.3713(5)
c/Å	15.0845(6)
α/°	98.477(4)
β/°	91.135(4)
γ/°	97.754(5)
Volume/Å^3	982.54(9)
Z	2
ρ_{calc}^{g}/cm^3	1.3671
μ/mm^{-1}	0.300
F(000)	422.7
Crystal size/mm^3	0.1 × 0.08 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.76 to 52
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -19 ≤ l ≤ 9
Reflections collected	6194
Independent reflections	3842 [R_{int} = 0.0194, R_{sigma} = 0.0418]
Data/restraints/parameters	3842/0/262
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1359
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1442
Largest diff. peak/hole / e Å^{-3}	0.57/-0.37

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5c** (exp_19725). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	738.5(9)	7137.0(9)	8216.6(5)	40.3(2)
S2	1119.2(9)	6657.3(9)	6266.1(5)	41.1(2)
O1	-971(3)	6908(3)	7874.6(15)	55.1(6)
O2	1363(3)	8527(3)	8853.3(15)	57.5(6)
O3	159(3)	5085(3)	6185.6(15)	56.2(6)
O4	2555(3)	6912(3)	5729.0(14)	56.7(6)

N1	1943(3)	7200(3)	7327.2(15)	38.5(5)
C4	-250(4)	8094(4)	6116.7(18)	40.8(7)
C7	1116(4)	5395(4)	8671(2)	41.6(7)
C8	3789(4)	7625(4)	7480(2)	44.3(7)
C9	4415(4)	9431(4)	7630(3)	57.3(9)
C10	-2343(5)	10273(5)	5756(2)	64.8(10)
C11	4752(4)	6465(4)	7407(3)	61.2(9)
C12	366(4)	9734(4)	6260(2)	50.6(8)
C13	-1893(4)	7534(5)	5797(2)	53.8(8)
C14	333(4)	3871(4)	8265(2)	51.2(8)
C15	2127(5)	5570(5)	9440(2)	59.1(9)
C16	-703(5)	10836(4)	6076(2)	60.0(9)
C17	1603(6)	2662(5)	9390(3)	72.6(11)
C18	2356(6)	4170(5)	9806(3)	75.0(11)
C19	-2934(5)	8655(5)	5618(3)	66.7(10)
C20	596(5)	2513(5)	8627(3)	64.6(10)
C21	6194(4)	9974(5)	8028(3)	63.6(10)
O7	4836(9)	3837(8)	8035(5)	74.6(18)
C44	5158(13)	3898(11)	6488(7)	72(2)
C43	4252(5)	4665(5)	7134(4)	91.9(16)
C30	6315(7)	9798(7)	8981(3)	102.8(17)
O6	4724(7)	4479(8)	6006(4)	74.9(16)
C41	5193(15)	3698(13)	7411(10)	97(4)

Table S4 *A*nisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5c** (exp_19725). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{12}}$	$\mathbf{U_{13}}$	$\mathbf{U_{23}}$
S1	39.3(4)	41.3(4)	43.6(4)	15.0(3)	5.3(3)	8.1(3)
S2	43.2(4)	37.8(4)	41.4(4)	5.2(3)	-1.1(3)	3.5(3)
O1	34.9(11)	74.0(16)	64.8(14)	19.1(11)	8.8(10)	27.1(12)
O2	80.0(16)	40.5(13)	51.6(13)	15.7(1)	8.0(11)	-1.7(10)
O3	64.9(14)	36.2(12)	64.1(14)	0.4(10)	-17.2(11)	4.8(10)
O4	55.3(13)	67.1(16)	49.4(13)	14.4(12)	13.4(10)	7.8(11)
N1	30.9(12)	42.1(14)	41.7(13)	5.1(10)	0.3(10)	3.6(10)
C4	46.8(16)	40.8(16)	36.6(15)	8.2(13)	-0.4(12)	9.9(12)
C7	40.5(15)	40.7(16)	46.1(16)	10.0(13)	3.6(12)	11.0(13)
C8	32.7(14)	47.0(18)	50.9(17)	6.0(13)	-0.2(12)	-0.1(13)
C9	42.2(17)	46.6(19)	79(2)	3.6(15)	-2.0(16)	-0.0(17)

C10	73(3)	81(3)	53(2)	40(2)	8.3(18)	22.2(19)
C11	35.0(17)	55(2)	88(3)	8.2(15)	-0.2(16)	-7.0(18)
C12	59(2)	43.9(18)	48.5(18)	5.4(15)	-3.6(15)	7.3(14)
C13	44.3(17)	60(2)	57.5(19)	3.0(15)	-2.5(14)	16.4(16)
C14	55.8(19)	46.7(19)	51.6(18)	5.3(15)	0.3(15)	11.1(15)
C15	65(2)	56(2)	57(2)	12.0(17)	-11.3(16)	9.1(16)
C16	93(3)	46(2)	45.4(18)	17.8(19)	12.4(18)	11.9(15)
C17	89(3)	57(2)	80(3)	19(2)	4(2)	30(2)
C18	87(3)	79(3)	66(2)	23(2)	-15(2)	25(2)
C19	51(2)	86(3)	70(2)	17(2)	-1.6(17)	26(2)
C20	74(2)	45(2)	74(2)	5.6(18)	5(2)	13.6(18)
C21	54(2)	56(2)	76(2)	2.4(17)	-3.5(18)	0.5(18)
O7	83(4)	65(4)	91(5)	41(3)	8(4)	35(4)
C44	100(7)	57(5)	62(5)	20(5)	22(5)	7(4)
C43	53(2)	43(2)	172(5)	13.8(18)	14(3)	-19(3)
C30	95(4)	143(5)	68(3)	5(3)	-1(2)	21(3)
O6	71(4)	72(4)	72(4)	9(3)	18(3)	-23(3)
C41	90(8)	58(6)	150(12)	36(5)	-15(8)	17(8)

Table S5 Bond Lengths for **5c** (exp_19725).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	O1	1.422(2)	C9	C21	1.509(4)
S1	O2	1.421(2)	C10	C16	1.377(5)
S1	N1	1.667(2)	C10	C19	1.356(6)
S1	C7	1.758(3)	C11	C43	1.500(5)
S2	O3	1.417(2)	C12	C16	1.387(5)
S2	O4	1.423(2)	C13	C19	1.383(5)
S2	N1	1.692(2)	C14	C20	1.370(5)
S2	C4	1.762(3)	C15	C18	1.398(5)
N1	C8	1.467(3)	C17	C18	1.376(6)
C4	C12	1.377(4)	C17	C20	1.370(6)
C4	C13	1.379(4)	C21	C30	1.470(6)
C7	C14	1.390(4)	O7	C43	1.697(8)
C7	C15	1.376(4)	C44	C43	1.360(9)
C8	C9	1.509(4)	C43	O6	1.740(8)
C8	C11	1.308(4)	C43	C41	1.281(11)

Table S6 Bond Angles for **5c** (exp_19725)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O1	120.33(15)	C15	C7	C14	121.2(3)
N1	S1	O1	105.79(12)	C9	C8	N1	114.7(2)
N1	S1	O2	106.89(13)	C11	C8	N1	119.5(3)
C7	S1	O1	108.94(14)	C11	C8	C9	125.6(3)
C7	S1	O2	107.76(14)	C21	C9	C8	117.4(3)
C7	S1	N1	106.30(13)	C19	C10	C16	121.0(3)
O4	S2	O3	119.44(15)	C43	C11	C8	128.8(3)
N1	S2	O3	109.11(13)	C16	C12	C4	118.8(3)
N1	S2	O4	103.53(13)	C19	C13	C4	118.7(3)
C4	S2	O3	109.26(14)	C20	C14	C7	119.5(3)
C4	S2	O4	109.02(14)	C18	C15	C7	118.4(3)
C4	S2	N1	105.51(12)	C12	C16	C10	119.6(3)
S2	N1	S1	122.03(13)	C20	C17	C18	120.7(4)
C8	N1	S1	118.34(19)	C17	C18	C15	120.1(4)
C8	N1	S2	119.47(19)	C13	C19	C10	120.4(4)
C12	C4	S2	119.8(2)	C17	C20	C14	120.2(4)
C13	C4	S2	118.6(2)	C30	C21	C9	111.9(3)
C13	C4	C12	121.5(3)	C44	C43	O7	100.5(6)
C14	C7	S1	119.2(2)	C41	C43	O6	100.9(8)
C15	C7	S1	119.5(3)				

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5c** (exp_19725).

Atom	*x*	*y*	*z*	U(eq)
H9a	4345(4)	9822(4)	7059(3)	68.7(11)
H9b	3638(4)	9967(4)	8022(3)	68.7(11)
H10	-3057(5)	11013(5)	5634(2)	77.7(12)
H11	5904(4)	6804(4)	7542(3)	73.5(11)
H12	1477(4)	10096(4)	6475(2)	60.8(9)
H13	-2294(4)	6424(5)	5703(2)	64.5(10)
H14	-364(4)	3774(4)	7752(2)	61.5(9)
H15	2645(5)	6594(5)	9710(2)	70.9(11)
H16	-313(5)	11948(4)	6168(2)	72.0(11)
H17	1780(6)	1734(5)	9630(3)	87.2(13)
H18	3017(6)	4259(5)	10331(3)	89.9(14)
H19	-4045(5)	8298(5)	5401(3)	80.0(12)

H20	89(5)	1488(5)	8354(3)	77.5(11)
H21a	6971(4)	9330(5)	7698(3)	76.4(12)
H21b	6536(4)	11107(5)	7964(3)	76.4(12)
H30a	5930(50)	8689(12)	9050(4)	154(3)
H30b	7476(10)	10090(50)	9199(7)	154(3)
H30c	5620(40)	10510(40)	9317(5)	154(3)

Table S8 Atomic Occupancy for **5c** (exp_19725).

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
O7	0.500000	C44	0.500000	O6	0.500000
C41	0.500000				

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