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Stereoselective Formal Alkenylation of β, β-Disubstituted Enesulfinamides for Constructing 1,5- and 1,4-Dicarbonyl Derivatives Bearing Less-Accessible α-Acyclic Quaternary Stereocenters

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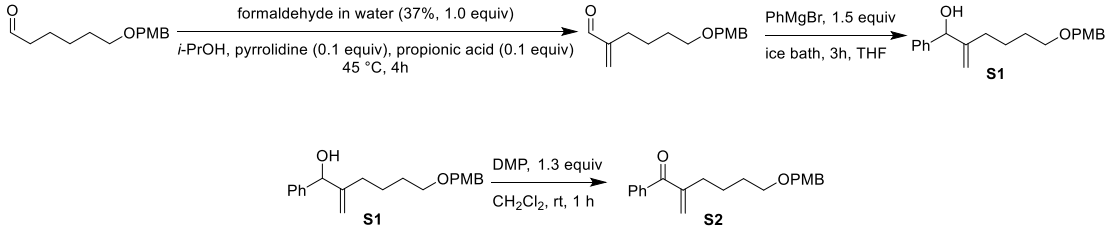
General Experimental Information

All reactions were performed under a positive pressure of argon atmosphere in flame-dried glassware with magnetic stirring using standard Schlenk techniques. All solvents were dried and distilled before use. Column chromatography was performed using 100−200 mesh silica gel. Visualization on TLC (thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with aqueous ceric ammonium molybdate staining followed by heating. The melting point (m.p.) values were measured using a Buchi melting point apparatus M-560 and are uncorrected. High-resolution mass spectra (HRMS) were measured using electron spray ionization with a LTQ-Orbitrap mass analyzer (ESI-Orbitrap) or with a Q-TOF mass analyzer (ESI-TOF). SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα. Optical rotations were measured on an Autopol IV (Rudolph Research Analytical).

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C{^{1}H} NMR) were recorded on a 400 MHz (^{1}H NMR at 400 MHz and ^{13}C{^{1}H} NMR at 100 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm; ^{13}C{^{1}H} NMR, $CDCl_3$ at 77.16 ppm, C_6D_6 at 128.06 ppm). ^{1}H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, dd = doublet doublet, m = multiplet), coupling constant(s) in Hz, and integration. Diasteromeric ratio (dr) was determined by ^{1}H NMR analysis or HPLC analysis [a UV-visible detector using chiral stationary columns (0.46 cm × 25 cm) from Daicel] of crude reaction mixture.

Materials: Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from CaH_2. All commercially available reagents were used without further purification unless otherwise noted. The chemicals of *t*BuOK (1.0 M in THF) used in this study was manufactured by Adamas. The α-substituted α,β-unsaturated *N*-sulfinyl ketimines **S5** and **S6** in this study were new compounds and prepared according to our previously reported procedures.[S1,S2] All of the *N*-*tert*-butanesulfinyl enesulfinamides used in this study were known compounds [except (*Ss, E*)-**1a**, (*Rs, E*)-**1n**, **1x** and **1y**] and prepared according to our previously reported procedures.[S2] β-Nitroenones **2a**–**2g** were known compounds, but the yields for the step of elimination (MsCl, Et_3N) are relatively low (≤44%).[S3] We have modified the reported elimination procedure and the new method (Tf_2O, Et_3N) gave much higher yield of the desired products. β-Nitroenones **2h**–**2i** were prepared according reported procedures.[S3] (*E*)-*β*-tosyl acrylonitrile **4a** were known compounds and prepared according the reported procedures.[S4] (*E*)-3-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)acrylonitrile **4b** were prepared according the reported procedures.[S4]

Procedure for the preparation of ketones S1–S4

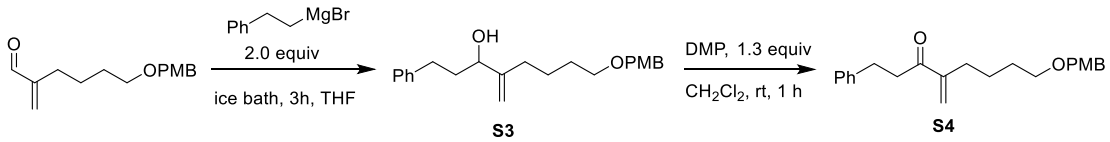


To a mixture of aqueous formaldehyde solution (37% formaldehyde in water, 0.30 mL, 4.07 mmol, 1.0 equiv) and aldehyde[S5] (962.0 mg, 4.07 mmol, 1.0 equiv) in *i*-PrOH (0.4 mL) were added propionic acid (31 μL, 0.41 mmol, 0.1 equiv) and pyrrolidine (31 μL, 0.41 mmol, 0.1 equiv). After stirring at 45 ℃ for 4 h, the reaction mixutre was quenched with $NaHCO_3$ (10 mL, sat. aq.) and extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (3-5% ethyl acetate/petroleum ether) to afford the α-methylene aldehyde.

To a solution of 6-((4-methoxybenzyl)oxy)-2-methylenehexanal (0.55 g, 2.263 mmol, 1.0 equiv) in freshly distilled THF (10 mL) at 0 ℃ was added phenylmagnesium bromide (1 M, 3.40 mL, 3.395 mmol, 1.5 equiv) dropwise under argon atmosphere. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (20 mL) was added carefully and the mixture was extracted with ethyl acetate (30 mL×3). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (30% ethyl acetate/petroleum ether) to give **S1** as a colorless oil (0.636 g, 88% yield). Analytical data for **S1**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.12 (m, 7H), 6.81–6.76 (m, 2H), 5.19–5.16 (m, 1H), 5.05 (s, 1H), 4.91–4.86 (m, 1H), 4.31 (s, 2H), 3.71 (s, 3H), 3.29 (t, J = 6.2 Hz, 2H), 2.02–1.67 (m, 3H), 1.52–1.31 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 150.9, 142.3, 130.8, 129.4, 128.5, 127.8, 126.8, 113.9, 110.1, 77.4, 72.6, 70.0, 55.4, 31.6, 29.5, 24.5; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{27}O_3$ 327.1955; Found 327.1954.

The alcohol **S1** (0.570 g, 1.745 mmol, 1.0 equiv) obtained above was dissolved in CH_2Cl_2 (10 mL) and DMP (0.962 g, 2.268 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h, the mixture was diluted with CH_2Cl_2 (10 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous

$NaHCO_3$ solution (15 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate/petroleum ether) to give **S2** as a colorless oil (0.510 g, 90% yield). Analytical data for **S2**: R_f = 0.40 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 2H), 7.50–7.43 (m, 1H), 7.40–7.32 (m, 2H), 7.20 (s, 1H), 7.18–7.16 (m, 1H), 6.84–6.74 (m, 2H), 5.80–5.71 (m, 1H), 5.55–5.47 (m, 1H), 4.36 (s, 2H), 3.73 (s, 3H), 3.40 (t, J = 6.4 Hz, 2H), 2.46–2.37 (m, 2H), 1.65–1.57 (m, 2H), 1.56–1.49 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.5, 159.3, 148.2, 138.0, 132.3, 130.8, 129.7, 129.4, 128.3, 125.7, 113.9, 72.7, 69.9, 55.4, 32.2, 29.6, 24.9; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{25}O_3$ 325.1798; Found 325.1804.



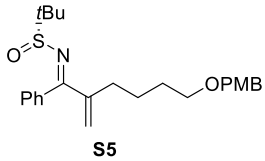
To a solution of 6-((4-methoxybenzyl)oxy)-2-methylenehexanal (2.830 g, 11.4 mmol, 1.0 equiv) in freshly distilled THF (110 mL) at 0 ℃ was added phenethylmagnesium bromide (1 M, 23.0 mL, 22.8 mmol, 2.0 equiv) dropwise under argon atmosphere. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (20 mL) was added carefully and the mixture was extracted with ethyl acetate (30 mL×3). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (30% ethyl acetate/petroleum ether) to give **S3** as a colorless oil (2.201 g, 62% yield). Analytical data for **S3**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 1H), 7.26–7.21 (m, 3H), 7.20–7.14 (m, 3H), 6.90–6.81 (m, 2H), 5.03 (s, 1H), 4.88–4.84 (m, 1H), 4.41 (s, 2H), 4.09–4.03 (m, 1H), 3.77 (s, 3H), 3.43 (t, J = 6.4 Hz, 2H), 2.78–2.55 (m, 2H), 2.14–1.92 (m, 2H), 1.92–1.76 (m, 2H), 1.66–1.57 (m, 2H), 1.56–1.46 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.1, 151.6, 142.1, 130.7, 129.3, 128.5, 128.4, 125.8, 113.8, 109.8, 74.7, 72.6, 69.9, 55.3, 37.1, 32.0, 31.1, 29.6, 24.7; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}O_3$ 355.2268; Found 355.2260.

The alcohol **S3** obtained above was dissolved in CH_2Cl_2 (100 mL) and DMP (3.451 g, 8.138 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h, the mixture was diluted with CH_2Cl_2 (100 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (50 mL, v/v =

1/1). The aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate/petroleum ether) to give **S4** as a colorless oil (1.66 g, 80% yield). Analytical data for **S4**: R_f = 0.40 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 3H), 7.26–7.24 (m, 1H), 7.23–7.17 (m, 3H), 6.91–6.85 (m, 2H), 5.97 (s, 1H), 5.71 (s, 1H), 4.43 (s, 2H), 3.80 (s, 3H), 3.45 (t, J = 6.4 Hz, 2H), 3.07–2.89 (m, 4H), 2.35–2.25 (m, 2H), 1.66–1.55 (m, 2H), 1.53–1.44 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.0, 159.2, 148.7, 141.4, 130.8, 129.3, 128.6, 128.5, 126.2, 124.0, 113.9, 72.7, 69.9, 55.4, 39.7, 30.7, 30.5, 29.5, 25.1; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{28}NaO_3$ 375.1931; Found 375.1922.

Procedure for the pereperation of α-substituted α, β-unsaturated *N*-sulfinyl ketimines

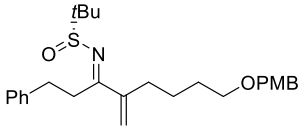
To a stirring solution of α-substituted α, β-unsaturated ketone (1.0 equiv) in dry THF (~1 M) in flame-dried round-bottom flask equipped with a magnetic stirring bar was added *N-tert*-butanesulfinamide (1.5 equiv) and $Ti(OEt)_4$ (tech. grade, ~20% Ti; 2.0 equiv). Then the flask was heated in a heating mantle at 76 ℃. The reaction progress was monitored by TLC and the reaction mixture was cooled to room temperature after 20–30 h. The mixture was diluted with ethyl acetate (EtOAc) and an equal volume of brine was added with rapid stirring. The resulting suspension was filtered through a plug of celite and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted once with a small volume of EtOAc, and the combined organic portions were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography.



S5

(*R,Z*)-*N*-(6-((4-Methoxybenzyl)oxy)-2-methylene-1-phenylhexylidene)-2-methylpropane-2-sulfinamide (**S5**): The title compound was prepared according to the above procedure using 6-((4-methoxybenzyl)oxy)-2-methylene-1-phenylhexan-1-one (**S2**) (1.46 g, 4.500 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (0.86 g, 6.75 mmol, 1.5 equiv), and titanium ethoxide (2.0 mL, 9.01 mmol, 2.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether) afforded **S5** (1.576 g, 82%) as a yellow oil. Analytical data for **S5** (mixture of imino *Z*/*E* isomers): R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{20}_D$ = – 93.0 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.87 (s,

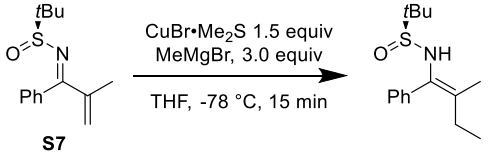
1H), 7.29–7.15 (m, 3H), 7.10 (s, 3H), 6.85–6.76 (m, 2H), 5.49–5.20 (m, 1H), 5.08 (s, 1H), 4.30 (s, 2H), 3.34 (s, 5H), 2.69–2.12 (m, 2H), 1.72–1.44 (m, 4H), 1.22 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 180.1, 159.6, 150.3, 146.6, 137.1, 132.1, 131.4, 129.4, 128.9, 115.8, 114.1, 72.7, 69.9, 56.3, 54.9, 35.8, 32.3, 30.0, 26.0, 24.0, 22.5; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{34}NO_3S$ 428.2254 ; Found 428.2253.



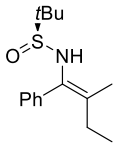
S6

(*R*,*E*)-*N*-(8-((4-Methoxybenzyl)oxy)-4-methylene-1-phenyloctan-3-ylidene)-2-methylpropane-2-sulfinamide (**S6**): Synthetic procedure same with **S5** was followed using 8-((4-methoxybenzyl)oxy)-4-methylene-1-phenyloctan-3-one (**S4**) (1.660 g, 3.51 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (0.642 g, 5.26 mmol, 1.5 equiv), and titanium ethoxide (1.8 mL, 7.02 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded **S6** (1.95 g, 90%) as a pale yellow oil. Analytical data for **S6**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = – 113.7 (*c* 0.11, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.37–7.28 (m, 2H), 7.28–7.22 (m, 2H), 7.13 (s, 2H), 7.09–7.03 (m, 1H), 6.85–6.79 (m, 2H), 5.42 (s, 1H), 5.18 (s, 1H), 4.35 (s, 2H), 3.40–3.33 (m, 2H), 3.34–3.28 (m, 4H), 3.28–3.16 (m, 1H), 3.10–2.98 (m, 1H), 2.93–2.82 (m, 1H), 2.37–2.25 (m, 2H), 1.66–1.50 (m, 4H), 1.21 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 178.4, 159.7, 148.6, 141.4, 131.4, 129.4, 129.0, 128.8, 126.6, 120.4, 114.1, 72.8, 70.0, 57.5, 54.8, 35.9, 33.9, 33.0, 30.2, 26.1, 22.9; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{38}NO_3S$ 456.2567; Found 456.2559.

Procedures for the preparation of unknown enesulfinamides



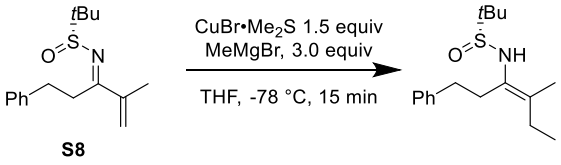
S7



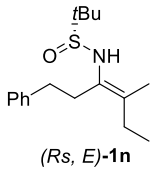
(S, E)-**1a**

(*S*,*E*)-2-methyl-*N*-(2-methyl-1-phenylbut-1-en-1-yl)propane-2-sulfinamide ((*Ss, E*)-**1a**): To a 10 mL Schlenk flask containing anhydrous CuBr·Me_2S (flame dried and backfilled with argon) (92.73 mg, 0.451 mmol, 1.5 equiv) was added freshly distilled THF (0.15 M). This suspension was cooled to –78 ℃ and methylmagnesium bromide in diethoxymethane (3.0 M, 0.3 mL, 0.9 mmol, 3.0 equiv) was added, after which a clear colorless solution formed. A solution of **S7** (74.98 mg, 0.300 mmol, 1.0 equiv) in THF (0.1 M) was then added via syringe. The flask containing the imine solution was rinsed once with 0.5 mL of THF and

the resulting solution was added by syringe to the reaction flask. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (5 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ℃ water bath). The reaction using **S7** (1.0 equiv)/CuBr·Me_2S (1.5 equiv)/MeMgBr (3.0 equiv) afforded enesulfinamides with ~1:1 *Z/E* (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture). The residue was purified by column chromatography (5% ethyl acetate/petroleum ether) to afford (*S,E*)-2-methyl-*N*-(2-methyl-1-phenylbut-1-en-1-yl) propane-2-sulfinamide ((*Ss, E*)-**1a**) (solvent was removed under reduced pressure in ≤ 37 ℃ water bath) (28.6 mg, 36% yield). Analytical data for (*Ss, E*)-**1a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 96–97 ℃; $[\alpha]^{20}_D$ = –55.9 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.51–7.45 (m, 2H), 7.15–7.12 (m, 2H), 7.09–7.01 (m, 1H), 4.94 (s, 1H), 1.95 (q, *J* = 7.6 Hz, 2H), 1.71 (s, 3H), 0.93 (s, 9H), 0.84 (t, *J* = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 131.7, 126.8, 123.6, 121.5, 121.0, 117.1, 48.5, 21.0, 15.5, 9.4, 6.4; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{24}NOS$ 266.1573; Found 266.1568. (Note: Very recently, we were succeeded in stereoselective synthesis of this enesulfinamide via 1,4-reduction using suitable α,β-unsaturated ketimine. The more effective 1,4-reduction protocol will be published in near future.)



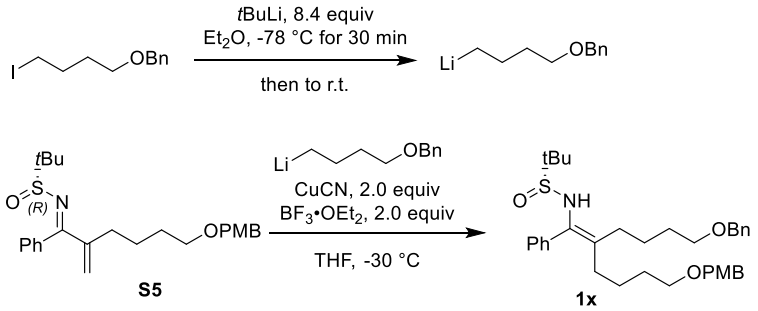
S8

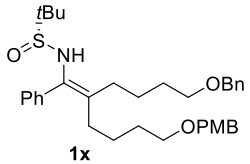


(Rs, E)-**1n**

(*R*,*E*)-2-Methyl-*N*-(4-methyl-1-phenylhex-3-en-3-yl)propane-2-sulfinamide ((*Rs, E*)-**1n**): To a 10 mL Schlenk flask containing anhydrous CuBr·Me_2S (flame dried and backfilled with argon) (92.73 mg, 0.451 mmol, 1.5 equiv) was added freshly distilled THF (0.15 M). This suspension was cooled to –78 ℃ and methylmagnesium bromide in diethoxymethane (3.0 M, 0.3 mL, 0.9 mmol, 3.0 equiv) was added, after which a clear colorless solution formed. A solution of **S8** (83.15 mg, 0.300 mmol, 1.0 equiv) in THF (0.1 M) was then added via syringe. The flask containing the imine solution was rinsed once with 0.5 mL of THF and the resulting solution was added by syringe to the reaction flask. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was quenched

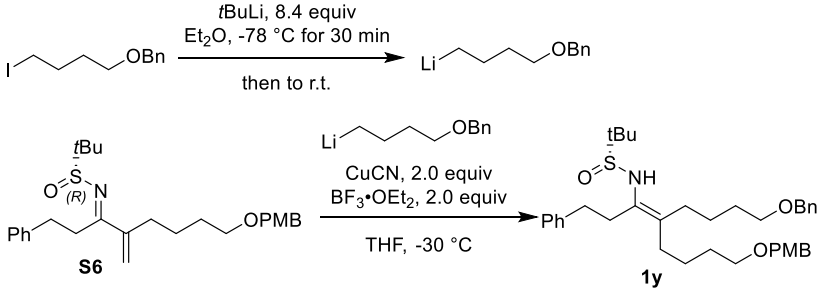
with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (5 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ℃ water bath). The reaction using unsaturated **S8** (1.0 equiv)/ $CuBr{\cdot}Me_2S$ (1.5 equiv)/MeMgBr (3.0 equiv) afforded enesulfinamides with ~1.5:1 *Z/E* (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture). The residue was purified by column chromatography (5% ethyl acetate/petroleum ether) to afford (*R,E*)-2-methyl-*N*-(4-methyl-1-phenylhex-3-en-3-yl)propane-2-sulfinamide (*Rs, E*)-**1n** (solvent was removed under reduced pressure in ≤ 37 ℃ water bath) (29.5 mg, 34% yield) as a colorless oil. Analytical data for (*Rs, E*)-**1n**: R_f = 0.3 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = – 25.8 (*c* 0.10, CH_2Cl_2); ^1H NMR (400 MHz, C_6D_6) δ 7.20–7.16 (m, 3H), 7.16–7.13 (m, 1H), 7.09–7.04 (m, 1H), 4.57 (s, 1H), 2.92–2.83 (m, 1H), 2.83–2.74 (m, 1H), 2.71–2.62 (m, 1H), 2.56–2.46 (m, 1H), 1.86–1.78 (m, 2H), 1.58 (s, 3H), 1.04 (s, 9H), 0.77 (t, *J* = 7.6 Hz, 3H); ^{13}C {^1H} NMR (100 MHz, C_6D_6) δ 142.2, 131.5, 128.9, 128.7, 126.3, 123.9, 55.5, 34.8, 33.6, 27.1, 22.5, 16.3, 13.1; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{28}NOS$ 294.1886; Found 294.1878. (Note: Very recently, we were succeeded in stereoselective synthesis of this enesulfinamide via 1,4-reduction using suitable α,β-unsaturated ketimine. The more effective 1,4-reduction protocol will be published in near future.)

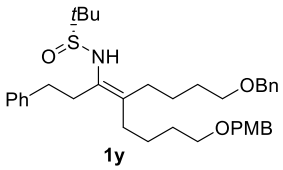




(*R,E*)-*N*-(6-(benzyloxy)-2-(4-((4-methoxybenzyl)oxy)butyl)-1-phenylhex-1-en-1-yl)-2-methylpropane-2-sulfinamide (**1x**): To a solution of 3-benzyloxypropyl iodide (132.8 mg, 0.481 mmol, 4.0 equiv) in 10 mL Schlenk flask in dry diethyl ether (2.5 mL) at −78 ℃ under argon atmosphere was added *t*BuLi (1.3 M in hexane, 0.777 mL, 1.011 mmol, 8.4 equiv) dropwise via syringe. The mixture was stirred at −78 ℃ for 30 min and then warmed to rt and stirred for further 30 min to form clear colorless solution. To a separate 10 mL Schlenk flask containing anhydrous CuCN (flame dried and backfilled with argon) (21.6 mg, 0.241 mmol, 2.0 equiv) was added freshly

distilled THF (1.6 mL). This suspension was cooled to −30 ℃ and (3-(benzyloxy)propyl)lithium prepared above was transferred via syringe to this flask. Then it was warmed to 0 ℃ and stirred for 10 min to form a clear solution. The solution was cooled back to −30 ℃. A solution of **S5** (51.2 mg, 0.120 mmol, 1.0 equiv) in THF (1.0) was added via syringe. The flask containing the imine solution was rinsed once with 0.5 mL of THF and the resulting solution was added by syringe to the reaction flask. The reaction progress was monitored by TLC. After 10 min, it was quenched by addition of saturated aqueous ammonium chloride (2.0 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure (in ≤ 25 ℃ water bath). The residue was purified by column chromatography (25% ethyl acetate/petroleum ether) to afford **1x** (solvent was removed under reduced pressure in ≤ 37 ℃ water bath) (58.7 mg, 84%) as a colorless oil. Analytical data for **1x**: R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{20}_D$ = + 29.6 (*c* 0.11, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.53–7.48 (m, 2H), 7.37–7.32 (m, 2H), 7.24–7.17 (m, 5H), 7.13–7.05 (m, 2H), 6.87–6.78 (m, 2H), 5.22 (s, 1H), 4.37 (s, 2H), 4.28 (s, 2H), 3.43–3.36 (m, 2H), 3.31 (s, 3H), 3.23–3.18 (m, 2H), 2.36–2.26 (m, 2H), 2.16–1.99 (m, 2H), 1.75–1.64 (m, 4H), 1.57–1.41 (m, 4H), 0.97 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 159.6, 139.5, 138.7, 135.0, 131.5, 130.8, 129.3, 128.6, 128.5, 128.0, 127.6, 126.0, 114.1, 73.0, 72.7, 70.3, 69.9, 55.5, 54.8, 32.2, 30.3, 29.94, 29.92, 25.8, 25.3, 22.5 ; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{35}H_{48}NO_4S$ 578.3299; Found 578.3295.

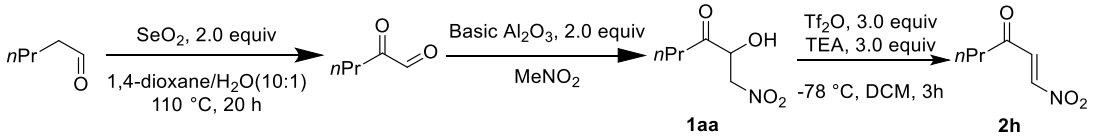




(*R*,*E*)-*N*-(8-(Benzyloxy)-4-(4-((4-methoxybenzyl)oxy)butyl)-1-phenyloct-3-en-3-yl)-2-methylpropane-2-sulfinamide (**1y**): Synthetic procedure same with **1x** was followed using 3-benzyloxypropyl iodide (132.8 mg, 0.481 mmol, 4.0 equiv), *t*BuLi (1.3 M in hexane, 0.777 mL, 1.011 mmol, 8.4 equiv), CuCN (flame dried and backfilled with argon) (21.6 mg, 0.241 mmol, 2.0 equiv), **S6** (54.6 mg, 0.120 mmol, 1.0 equiv). Purification by column chromatography (30% ethyl

acetate/petroleum ether) afforded **1y** (44.1 mg, 61%) as a colorless oil. Analytical data for **1y**: R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{20}_D$ = –25.7 (*c* 0.11, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.38–7.29 (m, 2H), 7.29–7.18 (m, 7H), 7.13–7.03 (m, 2H), 6.85–6.78 (m, 2H), 4.82 (s, 1H), 4.35 (d, *J* = 3.6 Hz, 4H), 3.36–3.28 (m, 7H), 2.94–2.77 (m, 2H), 2.77–2.58 (m, 2H), 2.26–2.15 (m, 1H), 2.07–1.97 (m, 1H), 1.95–1.81 (m, 2H), 1.62–1.51 (m, 6H), 1.45–1.34 (m, 2H), 1.07 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 159.7, 142.1, 139.5, 132.5, 131.5, 129.4, 129.0, 128.7, 128.6, 127.6, 126.6, 126.3, 114.1, 73.0, 72.8, 70.3, 55.5, 54.8, 34.8, 33.3, 31.7, 30.4, 30.36, 30.31, 26.0, 25.5, 22.6; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{37}H_{52}NO_4S$ 606.3612; Found 606.3599.

Procedure for the preparation of β-nitroenones with modified elimination conditions



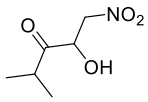
In an oven-dried 100 mL round-bottom flask equipped with a reflux condenser and an argon inlet, selenium dioxide (2.22 g, 20.0 mmol, 2.0 equiv) was taken in 11 mL 1,4-dioxane/H_2O (10:1) and refluxed at 110 ℃ for 20 min. Then the resulting solution was cooled to 50 ℃ and pentanal (0.86 g, 10.0 mmol, 1.0 equiv) was added. After refluxing at 110 ℃ for 20 h, the reaction mixture was cooled to 25 ℃, filtered, extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford the 2-oxopentanal as a pale yellow oil (0.31 g, 31% yield) which was used for the next step.

In an oven-dried 25 mL round-bottom flask, 2-oxopentanal (320 mg, 3.2 mmol, 1.0 equiv) was taken in 4 mL nitromethane along with basic alumina (652.4 mg, 6.4 mmol, 2.0 equiv). The resulting mixture was stirred vigorously at 25 ℃ for 3 h. The reaction mixture was then filtered through a pad of celite and washed with EtOAc. The combined organic layer was concentrated in vacuo. The crude residue was purified by flash chromatography (20% ethyl acetate/petroleum ether) to obtain 2-hydroxy-1-nitrohexan-3-one **1aa** as a brown oil (232 mg, 46% yield) which was used for the next step. Analytical data for compound **1aa:** R_f = 0.3 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (dd, *J* = 13.6, 3.6 Hz, 1H), 4.73 (dd, *J* = 14.0, 5.2 Hz, 1H), 4.57–4.51 (m,

1H), 4.04 (s, 1H), 2.68–2.50 (m, 2H), 1.76–1.60 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.4, 77.1, 73.7, 39.9, 16.9, 13.6; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_6H_{12}NO_4$ 162.0761; Found 162.0757.

In an oven-dried 25 mL two-neck round-bottom flask equipped with an argon inlet, 2-hydroxy-1-nitrohexan-3-one **1aa** (56.9 mg, 0.35 mmol, 1.0 equiv) was taken in 4 mL CH_2Cl_2 and cooled to –78 °C. Tf_2O (296.2 mg, 1.05 mmol, 3.0 equiv) was added and stirred at –78 °C for 15 min. Then triethyl amine (106.3 mg, 1.05 mmol, 3.0 equiv) was added and the resulting solution was stirred at –78 °C for 2 h. The reaction mixture was quenched by the addition of water, extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuo to obtain a brown oil which was purified by silica gel (200-300 mesh) column chromatography using (5% ethyl acetate/petroleum ether) to obtain **2h** as a pale brown oil (18.1 mg, 36% yield). Analytical data for compound **2h:** R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 13.6 Hz, 1H), 7.30–7.24 (m, 1H), 2.67 (t, J = 7.2 Hz, 2H), 1.76–1.64 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.3, 146.9, 131.7, 45.1, 17.0, 13.6; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_6H_{10}NO_3$ 144.0655; Found 144.0651.

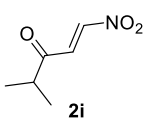
The same procedure as above was followed for the synthesis of **1ab** and **2i**.



1ab

2-Hydroxy-4-methyl-1-nitropentan-3-one (**1ab**)**:** According the above procedure, the reaction using selenium dioxide (2.22 g, 20.0 mmol, 2.0 equiv), 11 mL 1,4-dioxane/H_2O (10:1), 3-methylbutanal (0.86 g, 10.0 mmol, 1.0 equiv) afforded 3-methyl-2-oxobutanal as a light brown oil (0.32 g, 32% yield) which was used for the next step.

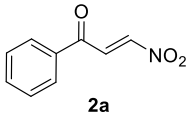
The reaction using 3-methyl-2-oxobutanal (321.0 mg, 3.2 mmol, 1.0 equiv), nitromethane (4 mL), and basic alumina (652.4 mg, 6.4 mmol, 2.0 equiv), afforded 2-hydroxy-4-methyl-1-nitropentan-3-one (**1ab**) as a pale brown oil (252.6 mg, 49% yield). Analytical data for compound **1ab:** R_f = 0.2 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86–4.68 (m, 3H), 3.78 (s, 1H), 3.07–2.95 (m, 1H), 1.20 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 211.3, 72.2, 67.1, 36.3, 19.1, 17.8; HRMS (ESI-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_6H_{12}NO_4$ 162.0761; Found 162.0757.



2i

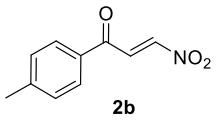
(*E*)-4-Methyl-1-nitropent-1-en-3-one (**2i**): According the above procedure, the reaction using 2-hydroxy-4-methyl-1-nitropentan-3-one (**1ab**) (162.0 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8

mg, 3.01 mmol, 3.0 equiv) afforded pure **2i** as a pale brown oil (100.1 mg, 70% yield). Analytical data for compound **2i:** R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 13.6 Hz, 1H), 7.38 (d, J = 13.2 Hz, 1H), 2.92–2.74 (m, 1H), 1.16 (d, J = 6.8 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.7, 147.1, 130.6, 41.5, 17.5; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_6H_{10}NO_3$ 144.0655; Found 144.0650.



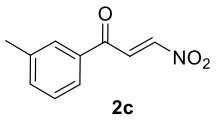
2a

(*E*)-3-Nitro-1-phenylprop-2-en-1-one (**2a**): According the above procedure, the reaction of 2-hydroxy-3-nitro-1-phenylpropan-1-one (195.2 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2a** as a yellow solid (150.6 mg, 85% yield). The NMR data for **2a** were identical to the reported.[S3]



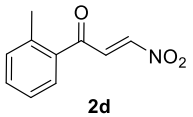
2b

(*E*)-3-Nitro-1-(*p*-tolyl)prop-2-en-1-one (**2b**): According the above the procedure reaction of 2-hydroxy-3-nitro-1-(p-tolyl) propan-1-one (209.2 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2b** as a yellow solid (145.3 mg, 76% yield). The NMR data for **2b** were identical to the reported.[S3]



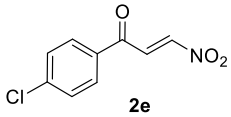
2c

(*E*)-3-Nitro-1-(*m*-tolyl)prop-2-en-1-one (**2c**): According the above procedure, the reaction of 2-hydroxy-3-nitro-1-(m-tolyl) propan-1-one (209.2 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2c** as a yellow solid (137.6 mg, 72% yield). The NMR data for **2c** were identical to the reported.[S3]



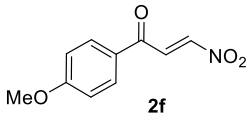
2d

(*E*)-3-Nitro-1-(*o*-tolyl)prop-2-en-1-one (**2d**): According the above procedure, the reaction of 2-hydroxy-3-nitro-1-(o-tolyl) propan-1-one (209.6 mg, 1.01 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2d** as a yellow solid (143.2 mg, 75% yield). The NMR data for **2d** were identical to the reported.[S3]



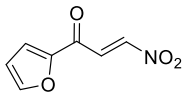
2e

(*E*)-1-(4-Chlorophenyl)-3-nitroprop-2-en-1-one (**2e**): According the above procedure, the reaction of 1-(4-chlorophenyl)-2-hydroxy-3-nitropropan-1-one (229.6 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2e** as a yellow solid (114.3 mg, 54% yield). The NMR data for **2e** were identical to the reported.[S3]



2f

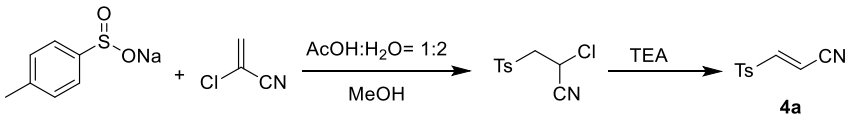
(*E*)-1-(4-Methoxyphenyl)-3-nitroprop-2-en-1-one (**2f**): According the above procedure, the reaction of 2-hydroxy-1-(4-methoxyphenyl)-3-nitropropan-1-one (225.2 mg, 1.00 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv) triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2f** as a yellow solid (134.7 mg, 65% yield). The NMR data for **2f** were identical to the reported.[S3]



2g

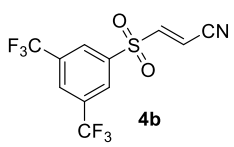
(*E*)-1-(Furan-2-yl)-3-nitroprop-2-en-1-one (**2g**): According the above procedure, the reaction of 1-(furan-2-yl)-2-hydroxy-3-nitropropan-1-one (183.9 mg, 1.01 mmol, 1.0 equiv), Tf_2O (846.4 mg, 3.01 mmol, 3.0 equiv), and triethyl amine (303.8 mg, 3.01 mmol, 3.0 equiv) afforded **2g** as a yellow solid (120.0 mg, 73% yield). The NMR data for **2g** were identical to the reported.[S3]

Procedure for the preparation of β-sulfonyl acrylonitriles 4a and 4b



4a

Sodium 4-methylbenzenesulfinate (8.9 g, 50 mmol, 1.0 equiv) was dissolved in water/acetic acid (2:1, 26.5 mL), and 2-chloroprop-2-enenitrile (4.41 g, 50 mmol, 1.0 equiv) was added. After 20 min, methanol (14.7 mL) was added, and 2-chloro-3-tosylpropanenitrile precipitated. The product was collected by filtration and dissolved without further purification in CH_2Cl_2 (65 mL). The solution was cooled to 0 ℃, and triethylamine (4.7 g, 47 mmol, 0.95 equiv) was added dropwise. After 1 h, the reaction mixture was extracted with aqueous HCl (1 N, 3 × 50 mL). The aqueous phase was adjusted to pH 8 with sodium bicarbonate and again extracted with CH_2Cl_2 (3 × 17 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was recrystallized from EtOAc/hexane (7:3), and the (*E*)-3-tosylacrylonitrile (9.1 g, 88%) was obtained as colorless needles. The NMR data for **4a** were identical to the reported.[S6]



4b

(*E*)-3-((3,5-Bis(trifluoromethyl)phenyl)sulfonyl)acrylonitrile (**4b**): The same procedure for the preparation of **4a** was followed using sodium 3,5-bis(trifluoromethyl) benzenesulfinate (14.95 g, 50 mmol, 1.0 equiv), water/acetic acid (2:1, 26.5 mL), 2-chloroprop-2-enenitrile (4.41 g, 50 mmol, 1.0 equiv), and

methanol (14.7 mL). The crude product was recrystallized from EtOAc/hexane (7:3), and the (*E*)-3-((3,5-bis(trifluoromethyl) phenyl) sulfonyl) acrylonitrile (13.65 g, 83%) was obtained as colorless needles. Analytical data for compound **4b:** R_f = 0.2 (petroleum ether/ethyl acetate = 6/1); mp 166–167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.29 (m, 2H), 8.23 (s, 1H), 7.25 (d, J = 15.6 Hz, 1H), 6.72 (d, J = 15.6 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 140.6, 134.2 (q, J_{C-F} = 34.8 Hz), 128.9 (d, J_{C-F} = 3.0 Hz), 128.8-128.7 (m), 122.2 (q, J_{C-F} = 272.0 Hz), 113.7, 112.8; HRMS (ESI-TOF) *m/z*: $[M - H]^-$ Calcd for $C_{11}H_4F_6NO_2S$ 327.9872; Found 327.9871.

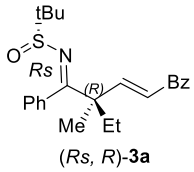
General procedure A for synthesis of 1,5-dicarbonyl analogs using β-nitroenone 2

Enesulfinamide **1** (1.0 equiv) or *N*-sulfinyl ketimine **6** in freshly distilled THF (0.1 M) was added to a flame dried Schlenk tube equipped with magnetic stirring bar under argon. The resulting clear solution was then cooled to −78 ℃ and a solution of potassium *tert*-butoxide in THF (1.0 M, 1.2 equiv) was added dropwise to the mixture via syringe. After 30 min, β-nitroenone **2** (1.5 equiv) in dry THF (0.1 M) was added dropwise by syringe at −78 ℃. The reaction progress was monitored by TLC analysis. Upon completion (usually 1−2 h), the reaction mixture was quenched with saturated aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (3 times) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

General procedure B for synthesis of 1,5-dicarbonyl analogs using β-nitroenone 2

Enesulfinamide **1** (1.0 equiv) in freshly distilled Et_2O (0.1 M) was added to a flame dried Schlenk tube equipped with magnetic stirring bar under argon. The resulting clear solution was then cooled to −78 ℃ and a solution of potassium *tert*-butoxide in THF (1.0 M, 1.2 equiv) was added dropwise to the mixture via syringe. After 30 min, β-nitroenones **2** (1.5 equiv) in dry Et_2O (0.1 M) was added dropwise by syringe at −78 ℃. The reaction progress was monitored by TLC analysis. Upon completion (usually 2−3 h), DBU (4.0 equiv) was added at −78 ℃ and the reaction mixture was allowed to warm to room temperature in 5 h. After stirring at room temperature for 12 hours, the reaction mixture was quenched with saturated aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (3 times) and the combined organic extracts were dried over

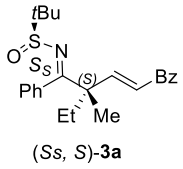
anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.


(*Rs, R*)-**3a**

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*R*$_S$, *R*)-**3a**): According to the general procedure A, reaction was performed using enesulfinamide **1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), and **2a** (26.6 mg, 0.15 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *R*)-**3a** as a light yellow solid (38.4 mg, 97%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*R*$_S$, *R*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 79–80 °C; $[\alpha]^{25}_D$ = –83.6 (*c* 0.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 2H), 7.60–7.52 (m, 1H), 7.49–7.41 (m, 2H), 7.40–7.35 (m, 3H), 7.14–7.05 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H), 1.94–1.75 (m, 2H), 1.39 (s, 3H), 1.20 (s, 9H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 188.1, 152.3, 137.7, 136.6, 133.0, 129.0, 128.68, 128.66, 128.0, 126.6, 125.4, 56.4, 52.6, 31.2, 22.3, 21.0, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1988.

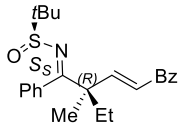
Gram scale preparation of (*Rs*, *R*)-3a

According to the general procedure A, reaction was performed using enesulfinamide **1a** (1.07 g, 4.03 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 4.85 mL, 4.845 mmol, 1.2 equiv), and **2a** (1.062 g, 6.0 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *R*)-**3a** as a light yellow solid (1.640 g, 97%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1).


(*Ss, S*)-**3a**

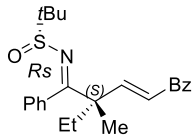
(*S*)-*N*-((*S*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*$_S$, *S*)-**3a**): According to the general procedure A, reaction was performed using enesulfinamide (*S*$_S$, *Z*)-**1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*S*$_S$, *S*)-**3a** as a light yellow oil (37.9 mg, 96%). Diastereomeric ratio was determined by ^{1}H

NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*S*$_S$, *S*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +86.4 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 2H), 7.59–7.51 (m, 1H), 7.49–7.42 (m, 2H), 7.40–7.34 (m, 3H), 7.14–7.05 (m, 3H), 6.85 (d, *J* = 16.0 Hz, 1H), 1.94–1.77 (m, 2H), 1.40 (s, 3H), 1.21 (s, 9H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.7, 188.1, 152.3, 137.8, 136.6, 133.0, 129.0, 128.70, 128.68, 128.1, 126.6, 125.5, 56.4, 52.6, 31.3, 22.3, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1986.



(*Ss, R*)-**3a**

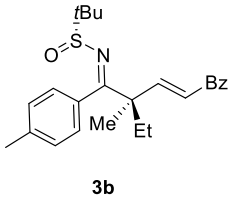
(*S*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*$_S$, *R*)-**3a**): According to the general procedure A, reaction was performed using enesulfinamide (*S*$_S$, *E*)-**1a** (26.7 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*S*$_S$, *R*)-**3a** as a light brown solid (36.4 mg, 92%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*S*$_S$, *R*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 92–93 °C; $[\alpha]^{25}_D$ = +94.2 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.61–7.52 (m, 1H), 7.49–7.42 (m, 2H), 7.41–7.33 (m, 3H), 7.14–7.04 (m, 3H), 6.83 (d, *J* = 16.0 Hz, 1H), 1.98–1.83 (m, 2H), 1.37 (s, 3H), 1.21 (s, 9H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 188.2, 152.3, 137.7, 136.6, 133.0, 129.0, 128.71, 128.68, 128.1, 126.6, 125.5, 56.4, 52.7, 31.3, 22.3, 21.0, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1985.



(*Rs, S*)-**3a**

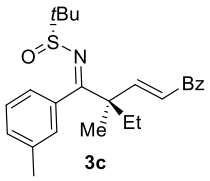
(*R*)-*N*-((*S*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide((*R*$_S$, *S*)-**3a**): According to the general procedure A, reaction was performed using enesulfinamide (*R*$_S$, *E*)-**1a** (26.8 mg, 0.102 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **2a** (26.7 mg, 0.151 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *S*)-**3a** as a light brown solid (36.5 mg, 92%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*R*$_S$, *S*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 104–105 °C; $[\alpha]^{25}_D$ = –92.0 (*c* 0.26, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.59–7.51 (m, 1H), 7.49–7.41 (m, 2H), 7.39–7.33 (m, 3H), 7.14–7.04 (m, 3H), 6.82 (d, *J* = 15.6 Hz, 1H), 1.96–1.84 (m, 2H), 1.37 (s, 3H),

1.21 (s, 9H), 0.95 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.6, 188.2, 152.2, 137.7, 136.6, 133.0, 129.0, 128.7, 128.6, 128.0, 126.6, 125.5, 56.4, 52.6, 31.3, 22.3, 21.0, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1989.



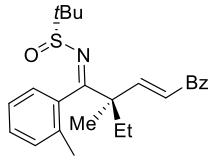
3b

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-5-phenyl-1-(p-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3b**): According to the general procedure A, reaction was performed using enesulfinamide **1b** (28.1 mg, 0.102 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 125 μL, 0.122 mmol, 1.2 equiv), **2a** (27.0 mg, 0.153 mmol, 1.5 equiv), DBU (60.9 mg, 0.408 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3b** as a light yellow oil (37.9 mg, 92%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3b**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –106.6 (*c* 0.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 2H), 7.59–7.52 (m, 1H), 7.49–7.42 (m, 2H), 7.20–7.14 (m, 2H), 7.09 (d, J = 16.0 Hz, 1H), 7.02–6.96 (m, 2H), 6.84 (d, J = 15.6 Hz, 1H), 2.35 (s, 3H), 1.95–1.74 (m, 2H), 1.39 (s, 3H), 1.20 (s, 9H), 0.94 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.7, 188.5, 152.5, 139.0, 137.8, 133.7, 132.9, 128.73, 128.69, 128.68, 126.6, 125.4, 56.4, 52.7, 31.3, 22.3, 21.5, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2144.



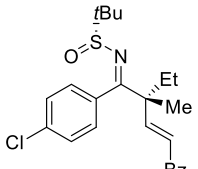
3c

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-5-phenyl-1-(m-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3c**): According to the general procedure A, reaction was performed using enesulfinamide **1c** (27.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded as a brown oil (40.1 mg, 98%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr = 20:1). Analytical data for **3c**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –75.2 (*c* 0.25, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.57–7.50 (m, 1H), 7.47–7.39 (m, 2H), 7.26–7.20 (m, 1H), 7.19–7.14 (m, 1H), 7.07 (d, J = 15.6 Hz, 1H), 6.91–6.77 (m, 3H), 2.32 (s, 3H), 1.94–1.73 (m, 2H), 1.38 (s, 3H), 1.19 (s, 9H), 0.92 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.8, 188.6, 152.4, 137.8, 137.7, 136.6, 132.9, 129.8, 128.65, 128.64, 127.9, 127.0, 125.5, 123.8, 56.3, 52.5, 31.3, 22.2, 21.7, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2144.



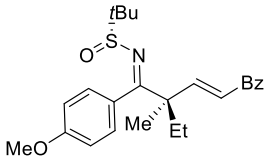
3d

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-5-phenyl-1-(o-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3d**): According to the general procedure A, reaction was performed using enesulfinamide **1d** (27.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3d** as a light yellow oil (38.1 mg, 93%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 90:10), HPLC (IA-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.8 min (major), 8.7 min (minor). Analytical data for **3d** (mixture of imino *Z*/*E* isomers): R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –224.9 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.73 (m, 2H), 7.61–7.51 (m, 1H), 7.48–7.39 (m, 2H), 7.30–7.26 (m, 1H), 7.23–7.01 (m, 3H), 6.93–6.74 (m, 2H), 2.21 (d, *J* = 36.0 Hz, 3H), 2.00–1.86 (m, 2H), 1.38 (s, 3H), 1.22 (d, *J* = 20.8 Hz, 9H), 0.97–0.90 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.1, 190.6, 189.9, 188.2, 152.6, 137.8, 137.7, 137.4, 136.3, 134.7, 132.92, 132.86, 132.7, 130.6, 130.2, 129.0, 128.9, 128.69, 128.67, 128.65, 128.6, 127.0, 125.7, 125.66, 125.64, 125.34, 125.25, 125.1, 56.6, 56.4, 53.1, 52.6, 32.1, 31.8, 22.4, 22.2, 21.31, 21.28, 20.4, 19.5, 9.1, 8.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2146.



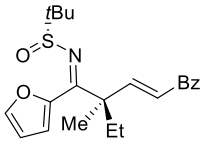
3e

(*R*)-*N*-((*R*,1*Z*,3*E*)-1-(4-chlorophenyl)-2-ethyl-2-methyl-5-oxo-5-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3e**): According to the general procedure A, reaction was performed using enesulfinamide **1e** (30.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3e** as a light yellow oil (40.8 mg, 95%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3e**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –102.1 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89–7.84 (m, 2H), 7.60–7.54 (m, 1H), 7.50–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.09–7.02 (m, 3H), 6.85 (d, *J* = 16.0 Hz, 1H), 1.92–1.75 (m, 2H), 1.38 (s, 3H), 1.22 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.4, 186.3, 151.8, 137.7, 135.2, 134.8, 133.1, 128.8, 128.7, 128.3, 128.1, 125.5, 56.9, 52.7, 31.2, 22.4, 21.0, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{29}ClNO_2S$ 430.1602; Found 430.1595.



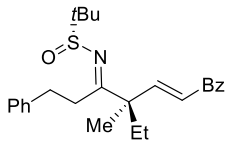
3f

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-1-(4-methoxyphenyl)-2-methyl-5-oxo-5-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3f**): According to the general procedure A, reaction was performed using enesulfinamide **1f** (29.6 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **3f** as a light yellow oil (37.9 mg, 89%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3f**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –104.8 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.84 (m, 2H), 7.60–7.52 (m, 1H), 7.50–7.42 (m, 2H), 7.14–7.02 (m, 3H), 6.91–6.82 (m, 3H), 3.81 (s, 3H), 1.93–1.76 (m, 2H), 1.40 (s, 3H), 1.21 (s, 9H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.7, 188.5, 159.9, 152.7, 137.8, 133.0, 128.9, 128.73, 128.72, 128.3, 125.3, 113.5, 56.3, 55.3, 52.8, 31.3, 22.3, 21.3, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}NO_3S$ 426.2097; Found 426.2093.



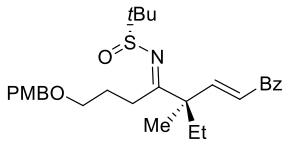
3g

(*R*)-*N*-((*R*,1*Z*,3*E*)-2-ethyl-1-(furan-2-yl)-2-methyl-5-oxo-5-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3g**): According to the general procedure A, reaction was performed using enesulfinamide **1g** (25.6 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3g** as a light yellow oil (36.2 mg, 94%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (AD-3, *n*-hexane/*i*PrOH = 97/03, flow rate = 1.0 mL/min, l = 254 nm) t_R = 33.8 min (major), 37.5 min (minor). Analytical data for **3g**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –156.2 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 2H), 7.56–7.48 (m, 2H), 7.46–7.39 (m, 2H), 7.25–7.20 (m, 2H), 6.80 (d, *J* = 15.6 Hz, 1H), 6.51–6.46 (m, 1H), 2.05–1.86 (m, 2H), 1.46 (s, 3H), 1.26 (s, 9H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.0, 174.2, 153.2, 147.0, 144.5, 137.9, 132.9, 128.68, 128.67, 124.6, 119.5, 111.9, 57.2, 52.4, 31.6, 22.8, 22.4, 9.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{28}NO_3S$ 386.1784; Found 386.1780.



3h

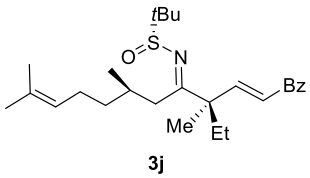
(*R*)-*N*-((*R*,3*E*,5*E*)-4-ethyl-4-methyl-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3h**): According to the general procedure B, reaction was performed using enesulfinamide **1h** (29.4 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv), DBU (61.0 mg, 0.404 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3h** as a light yellow oil (31.8 mg, 75%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 96:4), HPLC (OD-3, *n*-hexane/*i*PrOH = 97/03, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.0 min (major), 7.5 min (minor). Analytical data for **3h**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –95.1 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 2H), 7.63–7.54 (m, 1H), 7.54–7.41 (m, 2H), 7.25–7.20 (m, 4H), 7.20–7.11 (m, 2H), 6.95 (d, *J* = 16.0 Hz, 1H), 3.31–3.19 (m, 1H), 3.13–2.99 (m, 1H), 2.82–2.65 (m, 2H), 1.97–1.84 (m, 1H), 1.84–1.73 (m, 1H), 1.38 (s, 3H), 1.31 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.3, 186.4, 152.3, 140.7, 137.8, 133.1, 128.8, 128.65, 128.56, 126.4, 125.1, 57.8, 53.5, 34.9, 33.7, 31.0, 22.9, 20.8, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{26}H_{34}NO_2S$ 424.2305; Found 424.2300.



3i

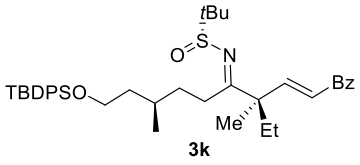
(*R*)-*N*-((*R*,4*E*,6*E*)-5-ethyl-1-((4-methoxybenzyl)oxy)-5-methyl-8-oxo-8-phenyloct-6-en-4-ylidene)-2-methylpropane-2-sulfinamide (**3i**): According to the general procedure B, reaction was performed using enesulfinamide **1i** (36.8 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv), DBU (61.0 mg, 0.404 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3i** as a light yellow oil (33.8 mg, 68%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 93:7), HPLC (ID-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 34.5 min (major), 38.8 min (minor). Analytical data for **3i**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –131.8 (*c* 0.08, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H), 7.61–7.52 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.22–7.16 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.85–6.78 (m, 2H), 4.38 (s, 2H), 3.77 (s, 3H), 3.51–3.40 (m, 2H), 2.98–2.88 (m, 1H), 2.64–2.52 (m, 1H), 2.07–1.76 (m, 4H), 1.34 (s, 3H), 1.25 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.4, 187.9, 159.2, 152.7, 137.9, 133.0,

130.6, 129.3, 128.7, 128.6, 124.9, 113.8, 72.5, 69.7, 57.4, 55.3, 53.4, 30.9, 29.6, 28.3, 22.7, 20.9, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{29}H_{40}NO_4S$ 498.2673; Found 498.2663.



3j

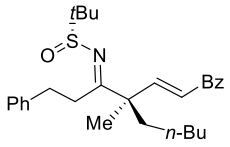
(*R*)-*N*-((2*E*,4*R*,5*E*,7*R*)-4-ethyl-4,7,11-trimethyl-1-oxo-1-phenyldodeca-2,10-dien-5-ylidene)-2-methylpropane-2-sulfinamide (**3j**): According to the general procedure B, reaction was performed using enesulfinamide **1j** (31.3 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv), DBU (62.0 mg, 0.411 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3j** as a light yellow oil (40.8 mg, 92%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 97:3), HPLC (ID-3, *n*-hexane/*i*PrOH = 95/05, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.0 min (minor), 14.4 min (major). Analytical data for **3j**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –144.7 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.86 (m, 2H), 7.59–7.52 (m, 1H), 7.51–7.42 (m, 2H), 7.14 (d, *J* = 16.0 Hz, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 5.08–4.91 (m, 1H), 3.17–3.07 (m, 1H), 2.50–2.36 (m, 1H), 2.13–1.69 (m, 6H), 1.58 (s, 3H), 1.52 (s, 3H), 1.36 (s, 3H), 1.25 (s, 9H), 1.22–1.14 (m, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 188.5, 153.2, 137.9, 133.0, 131.6, 128.7, 128.6, 124.6, 124.3, 57.4, 53.2, 39.2, 37.6, 32.1, 31.8, 25.73, 25.72, 22.7, 21.3, 19.7, 17.8, 9.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{27}H_{42}NO_2S$ 444.2931; Found 444.2921.



3k

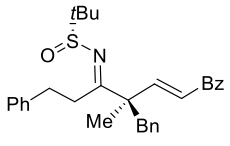
(*R*)-*N*-((2*E*,4*R*,5*E*,8*R*)-10-((tert-butyldiphenylsilyl)oxy)-4-ethyl-4,8-dimethyl-1-oxo-1-phenyldec-2-en-5-ylidene)-2-methylpropane-2-sulfinamide (**3k**): According to the general procedure B, reaction was performed using enesulfinamide **1k** (26.5 mg, 0.051 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 60 μL, 0.060 mmol, 1.2 equiv), **2a** (13.4 mg, 0.0751 mmol, 1.5 equiv), DBU (31.0 mg, 0.205 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3k** as a light yellow oil (22.7 mg, 69%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 95:5), HPLC (ID-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.1 min (major), 7.7 min (minor). Analytical data for **3k**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –83.1 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.87 (m, 2H), 7.70–7.60 (m, 4H), 7.59–7.53 (m, 1H), 7.51–7.43 (m, 2H), 7.43–7.33 (m, 6H), 7.10 (d, *J* = 15.6 Hz, 1H) (7.16), 6.90 (d, *J* = 16.0 Hz, 1H), 3.75–3.59 (m, 2H), 3.07–2.88

(m, 1H), 2.44–2.33 (m, 1H), 1.94–1.67 (m, 3H), 1.67–1.54 (m, 3H), 1.49–1.38 (m, 1H), 1.34 (s, 3H), 1.25 (s, 9H), 1.02 (s, 9H), 0.92–0.81 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.3, 188.7, 152.8, 137.9, 135.7, 134.2, 133.0, 129.6, 128.8, 128.6, 127.7, 124.9, 62.2, 57.3, 53.4, 39.1, 34.4, 31.1, 30.4, 30.2, 27.0, 22.7, 20.8, 19.3, 19.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{40}H_{56}NO_3SSi$ 658.3745; Found 658.3743.



3l

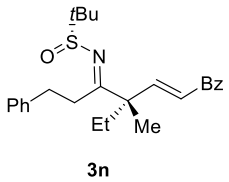
(*R*)-2-methyl-*N*-((*R*,*E*)-4-methyl-4-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)-1-phenylnonan-3-ylidene)propane-2-sulfinamide (**3l**): According to the general procedure B, reaction was performed using enesulfinamide **1l** (25.5 mg, 0.076 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 90 μL, 0.091 mmol, 1.2 equiv), **2a** (20.0 mg, 0.113 mmol, 1.5 equiv), DBU (46.3 mg, 0.304 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3l** as a light yellow oil (30.5 mg, 86%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3l**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_{D}$ = –80.6 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.91 (m, 2H), 7.62–7.55 (m, 1H), 7.53–7.45 (m, 2H), 7.27–7.13 (m, 6H), 6.95 (d, *J* = 15.6 Hz, 1H), 3.32–3.15 (m, 1H), 3.10–2.99 (m, 1H), 2.80–2.65 (m, 2H), 1.92–1.78 (m, 1H), 1.76–1.64 (m, 1H), 1.39 (s, 3H), 1.37–1.15 (m, 15H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.3, 186.4, 152.6, 140.7, 137.8, 133.1, 128.8, 128.64, 128.62, 128.56, 126.4, 124.8, 57.8, 53.2, 38.4, 34.9, 33.7, 32.5, 24.3, 22.8, 22.6, 21.4, 14.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{29}H_{40}NO_2S$ 466.2774; Found 466.2766.



3m

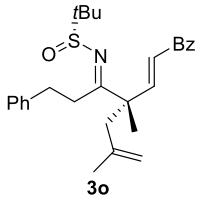
(*R*)-*N*-((*R*,3*E*,5*E*)-4-benzyl-4-methyl-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3m**): According to the general procedure B, reaction was performed using enesulfinamide **1m** (35.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.7 mg, 0.150 mmol, 1.5 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3m** as a light yellow oil (43.7 mg, 90%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3m**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_{D}$ = –150.1 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 2H), 7.62–7.56 (m, 1H), 7.51–7.45 (m, 2H), 7.34–7.26 (m, 3H), 7.25–7.13 (m, 6H), 7.12–7.07 (m, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 3.43–3.32 (m, 1H), 3.21 (d, *J* = 13.6 Hz, 1H), 3.16–3.06 (m, 1H), 3.03 (d, *J* = 13.6 Hz, 1H),

2.89–2.66 (m, 2H), 1.35 (s, 3H), 1.22 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.0, 185.4, 151.5, 140.6, 137.7, 136.4, 133.1, 130.7, 128.8, 128.7, 128.6, 128.3, 126.9, 126.4, 125.6, 58.0, 54.1, 44.7, 35.3, 33.6, 22.8, 20.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{31}H_{36}NO_2S$ 486.2461; Found 486.2453.



3n

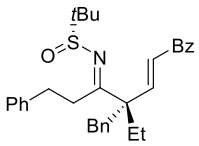
(*R*)-*N*-((*S*,3*E*,5*E*)-4-ethyl-4-methyl-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3n**): According to the general procedure B, reaction was performed using enesulfinamide **1n** (29.5 mg, 0.102 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3n** as a light yellow oil (36.4 mg, 86%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 94.5:5.5), HPLC (OD-3, *n*-hexane/*i*PrOH = 97/03, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.0 min (minor), 7.5 min (major). Analytical data for **3n**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –143.9 (*c* 0.205, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.62–7.54 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.26–7.11 (m, 6H), 6.95 (d, *J* = 16.0 Hz, 1H), 3.23–3.12 (m, 1H), 3.07–2.97 (m, 1H), 2.86–2.67 (m, 2H), 1.86 (q, *J* = 7.6 Hz, 2H), 1.39 (s, 3H), 1.31 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.3, 186.8, 152.3, 140.7, 137.8, 133.1, 128.8, 128.64, 128.62, 128.5, 126.4, 125.1, 57.7, 53.5, 35.2, 34.0, 31.1, 22.8, 21.2, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{26}H_{34}NO_2S$ 424.2305; Found 424.2298.



3o

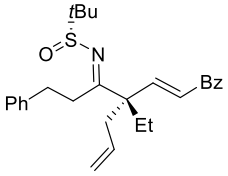
(R)-2-methyl-*N*-((*S*,3*E*,5*E*)-4-methyl-4-(2-methylallyl)-7-oxo-1,7-diphenylhept-5-en-3-ylidene)propane-2-sulfinamide (**3o**): According to the general procedure B, reaction was performed using enesulfinamide **1o** (32.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3o** as a light yellow solid (32.3 mg, 72%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 99:1), HPLC (AD-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 6.8 min (major), 7.5 min (minor). Analytical data for **3o**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); mp 87–88 °C; $[\alpha]^{25}_D$ = –75.9 (*c* 0.17, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.91 (m, 2H), 7.62–7.56 (m, 1H), 7.53–7.46 (m, 2H), 7.32 (d, *J* = 15.6 Hz, 1H), 7.25–7.21 (m, 4H), 7.20–

7.13 (m, 1H), 6.97 (d, J = 16.0 Hz, 1H), 4.94–4.87 (m, 1H), 4.73 (s, 1H), 3.25–3.11 (m, 1H), 3.06–2.92 (m, 1H), 2.89–2.74 (m, 2H), 2.67–2.48 (m, 2H), 1.70 (s, 3H), 1.45 (s, 3H), 1.31 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.1, 186.5, 152.4, 141.3, 140.7, 137.8, 133.1, 128.79, 128.67, 128.62, 128.56, 126.4, 124.8, 116.2, 57.8, 53.0, 47.0, 35.7, 34.4, 24.8, 22.9, 21.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{28}H_{36}NO_2S$ 450.2461; Found 450.2452.



3p

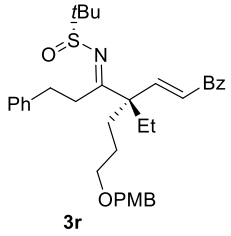
(*R*)-*N*-((*S*,3*E*,5*E*)-4-benzyl-4-ethyl-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3p**): According to the general procedure B, reaction was performed using enesulfinamide **1p** (36.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3p** as a light yellow solid (35.0 mg, 70%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3p**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); mp 132–133 °C; $[\alpha]^{25}_D$ = –73.6 (*c* 0.19, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 2H), 7.62–7.55 (m, 1H), 7.50–7.44 (m, 2H), 7.25–7.19 (m, 7H), 7.19–7.10 (m, 2H), 7.10–7.04 (m, 2H), 6.85 (d, J = 16.0 Hz, 1H), 3.31 – 3.03 (m, 4H), 2.77–2.62 (m, 2H), 1.99–1.87 (m, 1H), 1.83–1.71 (m, 1H), 1.31 (s, 9H), 1.01 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 190.0, 185.3, 150.4, 140.7, 137.7, 136.9, 133.1, 130.5, 128.8, 128.62, 128.61, 128.59, 128.2, 126.8, 126.6, 126.4, 58.1, 57.8, 41.0, 35.8, 33.4, 26.0, 22.9, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{32}H_{38}NO_2S$ 500.2618; Found 500.2610.



3q

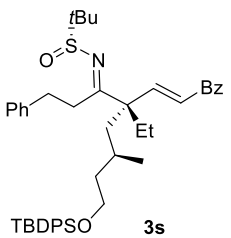
(*R*)-*N*-((*S*,3*E*,5*E*)-4-allyl-4-ethyl-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3q**): According to the general procedure B, reaction was performed using enesulfinamide **1q** (32.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3q** as a light yellow oil (39.6 mg, 88%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 99:1), HPLC (ID-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 11.4 min (major), 12.3 min (minor). Analytical data for **3q**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –103.4 (*c* 0.23, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.63–7.54 (m, 1H), 7.53–

7.44 (m, 2H), 7.24–7.18 (m, 4H), 7.17–7.07 (m, 2H), 6.99 (d, J = 16.0 Hz, 1H), 5.75–5.59 (m, 1H), 5.18–5.07 (m, 2H), 3.26–3.15 (m, 1H), 3.13–3.03 (m, 1H), 2.77–2.53 (m, 4H), 2.03–1.92 (m, 1H), 1.88–1.78 (m, 1H), 1.33 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.1, 185.2, 150.7, 140.6, 137.7, 133.4, 133.1, 128.8, 128.65, 128.62, 128.5, 126.4, 126.3, 118.8, 57.8, 56.7, 38.4, 35.2, 33.4, 27.0, 22.9, 8.6; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{28}H_{36}NO_2S$ 450.2461; Found 450.2452.



3r

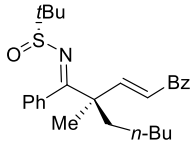
(*R*)-*N*-((*S*,3*E*,5*E*)-4-ethyl-4-(3-((4-methoxybenzyl)oxy)propyl)-7-oxo-1,7-diphenylhept-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**3r**): According to the general procedure B, reaction was performed using enesulfinamide **1r** (34.2 mg, 0.075 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 90 μL, 0.90 mmol, 1.2 equiv), **2a** (19.8 mg, 0.112 mmol, 1.5 equiv), DBU (45.7 mg, 0.300 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3r** as a light yellow oil (35.3 mg, 80%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (IC-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 20.7 min (minor), 22.8 min (major). Analytical data for **3r**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –91.9 (*c* 0.14, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.62–7.54 (m, 1H), 7.51–7.43 (m, 2H), 7.26–7.19 (m, 6H), 7.19–7.10 (m, 2H), 7.00 (d, J = 16.0 Hz, 1H), 6.89–6.82 (m, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.52–3.38 (m, 2H), 3.26–3.01 (m, 2H), 2.83–2.61 (m, 2H), 2.04–1.89 (m, 2H), 1.89–1.77 (m, 2H), 1.57–1.45 (m, 2H), 1.32 (s, 9H), 0.87 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.1, 185.7, 159.3, 151.3, 140.7, 133.1, 130.6, 129.3, 128.8, 128.7, 128.66, 128.61, 126.4, 125.9, 113.9, 72.8, 70.1, 57.8, 56.7, 55.4, 35.2, 33.6, 30.5, 27.6, 24.8, 22.9, 8.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{36}H_{46}NO_4S$ 588.3142; Found 588.3137.



3s

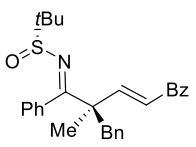
(*R*)-*N*-((4*S*,6*R*,*E*)-8-((tert-butyldiphenylsilyl)oxy)-4-ethyl-6-methyl-4-((E)-3-oxo-3-phenylprop-1-en-1-yl)-1-phenyloctan-3-ylidene)-2-methylpropane-2-sulfinamide (**3s**): According to the general procedure B, reaction was performed using enesulfinamide **1s** (30.2 mg, 0.051 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 60 μL, 0.062 mmol, 1.2 equiv), **2a** (13.3 mg, 0.075 mmol, 1.5 equiv), DBU (31.1 mg, 0.204 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3s** as a light yellow oil (27.5 mg, 75%).

Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (ID-3, *n*-hexane/*i*PrOH = 95/05, flow rate = 1.0 mL/min, l = 254 nm) t_R =10.2 min (minor), 11.6 min (major). Analytical data for **3s**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –50.5 (*c* 0.1, CH_2Cl_2);; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.69–7.60 (m, 4H), 7.60–7.54 (m, 1H), 7.54–7.43 (m, 2H), 7.42–7.30 (m, 6H), 7.28–7.24 (m, 1H), 7.23–7.16 (m, 4H), 7.16–7.10 (m, 1H), 6.98 (d, *J* = 16.0 Hz, 1H), 3.78–3.57 (m, 2H), 3.28–3.02 (m, 2H), 2.80–2.56 (m, 2H), 2.10–1.98 (m, 1H), 1.96–1.83 (m, 2H), 1.77–1.57 (m, 3H), 1.40–1.35 (m, 1H), 1.31 (s, 9H), 1.02 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.0, 185.8, 152.2, 140.8, 137.9, 135.6, 134.0, 133.9, 133.1, 129.7, 128.8, 128.61, 128.59, 127.7, 126.3, 125.4, 61.8, 57.8, 57.2, 42.4, 41.7, 35.4, 33.6, 27.2, 27.0, 25.7, 23.0, 21.4, 19.3, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{46}H_{60}NO_3SSi$ 734.4058; Found 734.4044.



3t

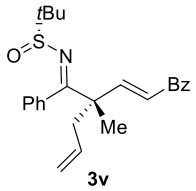
(*R*)-2-methyl-*N*-((*R*,*Z*)-2-methyl-2-((E)-3-oxo-3-phenylprop-1-en-1-yl)-1-phenylheptylidene)propane-2-sulfinamide (**3t**): According to the general procedure A, reaction was performed using enesulfinamide **1t** (30.7 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3t** as a light yellow oil (37.6 mg, 86%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 20:1). Analytical data for **3t**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –127.3 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.84 (m, 2H), 7.59–7.52 (m, 1H), 7.50–7.41 (m, 2H), 7.40–7.33 (m, 3H), 7.15–7.05 (m, 3H), 6.85 (d, *J* = 16.0 Hz, 1H), 1.87–1.66 (m, 2H), 1.41 (s, 3H), 1.38–1.24 (m, 6H), 1.20 (s, 9H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 188.2, 152.6, 137.7, 136.6, 133.0, 129.0, 128.69, 128.68, 128.0, 126.6, 125.1, 56.4, 52.4, 38.5, 32.4, 24.4, 22.6, 22.3, 21.7, 14.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{27}H_{36}NO_2S$ 438.2461; Found 438.2454.



3u

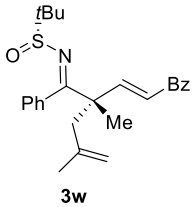
(*R*)-*N*-((*R*,1*Z*,3*E*)-2-benzyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3u**): According to the general procedure A, reaction was performed using enesulfinamide **1u** (32.7 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Column chromatography (25% ethyl acetate/petroleum ether as

eluent) afforded **3u** as a light brown solid (41.2 mg, 90%). Analytical data for **3u**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); mp 135–136 °C; $[\alpha]^{25}_D$ = –180.5 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.73 (m, 2H), 7.59–7.51 (m, 1H), 7.47–7.40 (m, 2H), 7.40–7.35 (m, 3H), 7.25–7.18 (m, 4H), 7.13–7.02 (m, 4H), 6.63 (d, *J* = 16.0 Hz, 1H), 3.28 (d, *J* = 13.2 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 1.31 (s, 3H), 1.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.3, 187.6, 151.5, 137.6, 136.64, 136.56, 133.0, 130.9, 129.0, 128.7, 128.6, 128.1, 126.8, 126.6, 126.0, 56.8, 53.2, 45.3, 22.4, 21.2; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{29}H_{32}NO_2S$ 458.2148; Found 458.2137.



3v

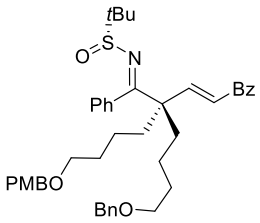
(*R*)-*N*-((*S*,1*Z*,3*E*)-2-allyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3v**): According to the general procedure A, reaction was performed using enesulfinamide **1v** (27.8 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3v** as a light yellow oil (38.3 mg, 94%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr >20:1). Analytical data for **3v**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –51.1 (*c* 0.08, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.61–7.53 (m, 1H), 7.49–7.42 (m, 2H), 7.41–7.33 (m, 3H), 7.14–7.04 (m, 3H), 6.82 (d, *J* = 15.6 Hz, 1H), 5.85–5.69 (m, 1H), 5.21–5.06 (m, 2H), 2.66 (d, *J* = 7.2 Hz, 2H), 1.36 (s, 3H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.4, 187.6, 151.5, 137.7, 136.4, 133.3, 133.1, 129.1, 128.73, 128.68, 128.1, 126.7, 125.8, 119.3, 56.5, 52.0, 42.9, 22.3, 21.7; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{30}NO_2S$ 408.1992; Found 408.1985.



3w

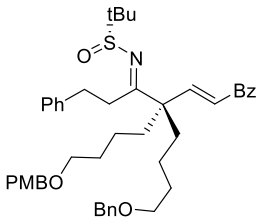
(*R*)-2-methyl-*N*-((*S*,1*Z*,3*E*)-2-methyl-2-(2-methylallyl)-5-oxo-1,5-diphenylpent-3-en-1-ylidene)propane-2-sulfinamide (**3w**): According to the general procedure A, reaction was performed using enesulfinamide **1w** (29.2 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.8 mg, 0.151 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3w** as a light yellow oil (38.8 mg, 92%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3w**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = – 174.2 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 2H), 7.60–7.53 (m, 1H), 7.51–7.42 (m, 2H), 7.42–7.33 (m, 3H), 7.19 (d, *J* = 15.6

Hz, 1H), 7.14–7.05 (m, 2H), 6.82 (d, J = 15.6 Hz, 1H), 4.93–4.89 (m, 1H), 4.79–4.74 (m, 1H), 2.69 (s, 2H), 1.71 (s, 3H), 1.38 (s, 3H), 1.22 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.3, 188.2, 152.5, 141.5, 137.7, 136.5, 133.1, 129.1, 128.8, 128.7, 128.1, 126.8, 125.4, 116.1, 56.5, 52.2, 46.8, 25.0, 22.3, 21.6; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{26}H_{32}NO_2S$ 422.2148; Found 422.2141.



3x

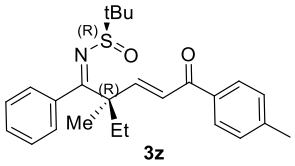
(*R*)-*N*-((*Z*)-6-(benzyloxy)-2-(4-((4-methoxybenzyl)oxy)butyl)-2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)-1-phenylhexylidene)-2-methylpropane-2-sulfinamide (**3x**): According to the general procedure B, reaction was performed using enesulfinamide **1x** (43.3 mg, 0.075 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 90 μL, 0.090 mmol, 1.2 equiv), **2a** (20.0 mg, 0.113 mmol, 1.5 equiv) with THF as solvent, DBU (45.8 mg, 0.301 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **3x** as a light yellow oil (43.0 mg, 81%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (IG-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 48.5 min (major), 53.7 min (minor). Analytical data for **3x**: R_f = 0.30 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{25}_D$ = – 296.2 (*c* 0.16, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.59–7.52 (m, 1H), 7.48–7.42 (m, 2H), 7.39–7.29 (m, 7H), 7.29–7.26 (m, 1H), 7.24–7.20 (m, 2H), 7.11–7.01 (m, 3H), 6.88–6.77 (m, 3H), 4.47 (s, 2H), 4.40 (s, 2H), 3.77 (s, 3H), 3.49–3.37 (m, 4H), 1.95–1.76 (m, 4H), 1.65–1.55 (m, 4H), 1.49–1.33 (m, 4H), 1.20 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.4, 187.2, 159.2, 151.3, 138.6, 137.7, 136.5, 133.0, 130.7, 129.3, 129.1, 128.73, 128.68, 128.5, 128.0, 127.7, 127.63, 126.5, 126.3, 113.9, 73.0, 72.7, 70.0, 69.6, 56.5, 55.9, 55.4, 34.3, 34.2, 30.2, 22.3, 21.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{44}H_{54}NO_5S$ 708.3717; Found 708.3696.



3y

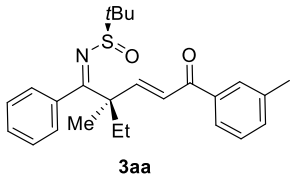
(*R*)-*N*-((*E*)-8-(benzyloxy)-4-(4-((4-methoxybenzyl)oxy)butyl)-4-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)-1-phenyloctan-3-ylidene)-2-methylpropane-2-sulfinamide (**3y**): According to the general procedure B, reaction was performed using enesulfinamide **1y** (48.4 mg, 0.080 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 100 μL, 0.096 mmol, 1.2 equiv), **2a** (21.3 mg, 0.120 mmol, 1.5 equiv), DBU (48.9 mg, 0.321 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **3y** as a light yellow oil (36.5 mg, 62%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 96.5:3.5),

HPLC (IG-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 46.0 min (minor), 50.2 min (major). Analytical data for **3y**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –258.8 (*c* 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.88 (m, 2H), 7.58–7.51 (m, 1H), 7.48–7.41 (m, 2H), 7.30–7.26 (m, 3H), 7.25–7.21 (m, 2H), 7.21–7.17 (m, 6H), 7.15–7.09 (m, 2H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.86–6.76 (m, 2H), 4.44 (s, 2H), 4.37 (s, 2H), 3.73 (s, 3H), 3.46–3.35 (m, 4H), 3.18–2.97 (m, 2H), 2.74–2.58 (m, 2H), 1.92–1.81 (m, 2H), 1.81–1.73 (m, 2H), 1.64–1.55 (m, 4H), 1.27 (s, 12H), 1.23 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2, 185.7, 159.2, 151.6, 140.7, 138.5, 137.8, 133.1, 130.6, 129.3, 128.8, 128.64, 128.56, 128.5, 127.7, 127.6, 126.4, 125.7, 113.9, 73.0, 72.7, 70.0, 69.7, 57.8, 56.7, 55.3, 34.8, 34.6, 33.7, 30.4, 22.9, 21.11, 21.07; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{46}H_{58}NO_5S$ 736.4030; Found 736.4027.



3z

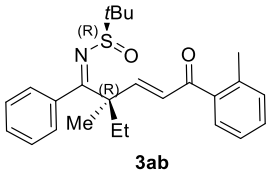
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-2-methyl-5-oxo-1-phenyl-5-(p-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3z**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2b** (28.7 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded to afford **3z** as a pale yellow solid (36.9 mg, 90%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3z**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 103–104 °C; $[\alpha]^{25}_D$ = –299.2 (*c* 0.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.42–7.33 (m, 3H), 7.24 (s, 2H), 7.13–7.04 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H), 1.93–1.76 (m, 2H), 1.39 (s, 3H), 1.21 (s, 9H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 188.1, 151.7, 143.9, 136.6, 135.2, 129.4, 129.0, 128.8, 128.0, 126.6, 125.4, 56.4, 52.6, 31.2, 22.3, 21.8, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2143.



3aa

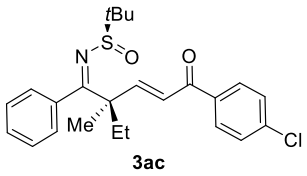
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-2-methyl-5-oxo-1-phenyl-5-(m-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3aa**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2c** (28.7 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent)

afforded **3aa** as a light yellow solid (38.9 mg, 95%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr> 20:1). Analytical data for **3aa**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 80–81 °C; $[\alpha]^{25}_D$ = –236.4 (*c* 0.26, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.42–7.33 (m, 3H), 7.24 (s, 2H), 7.13–7.04 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H), 1.93–1.76 (m, 2H), 1.39 (s, 3H), 1.21 (s, 9H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.7, 188.0, 152.1, 138.6, 137.8, 136.6, 133.8, 129.1, 129.0, 128.5, 128.0, 126.6, 125.9, 125.6, 56.4, 52.6, 31.2, 22.3, 21.5, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2139.



3ab

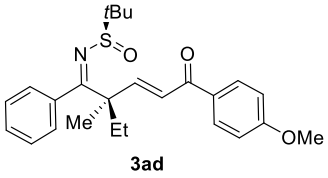
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-2-methyl-5-oxo-1-phenyl-5-(o-tolyl)pent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3ab**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2d** (28.7 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ab** as a light yellow oil (37.3 mg, 91%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ab**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –285.3 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 4H), 7.26–7.15 (m, 3H), 7.09–7.01 (m, 2H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H), 1.91–1.70 (m, 2H), 1.35 (s, 3H), 1.16 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 188.0, 153.9, 138.6, 136.8, 136.5, 131.3, 130.5, 129.9, 129.0, 128.02, 127.96, 126.5, 125.4, 56.4, 52.5, 31.2, 22.2, 21.1, 20.2, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{32}NO_2S$ 410.2148; Found 410.2140.



3ac

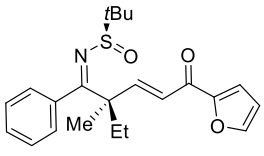
(*R*)-*N*-((*R*,1*E*,3*E*)-5-(4-chlorophenyl)-2-ethyl-2-methyl-5-oxo-1-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3ac**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2e** (31.7 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ac** as a light yellow solid (37.8 mg, 88%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ac**:

R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 91–92 °C; $[\alpha]^{25}_D$ = –236.1 (*c* 0.23, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83–7.76 (m, 2H), 7.45–7.39 (m, 2H), 7.40–7.35 (m, 3H), 7.13–7.06 (m, 3H), 6.80 (d, *J* = 15.8 Hz, 1H), 1.86 (m, 2H), 1.38 (s, 3H), 1.20 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.4, 188.1, 152.9, 139.4, 136.5, 136.0, 130.1, 129.04, 129.01, 128.1, 126.6, 125.0, 56.4, 52.6, 31.3, 22.3, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{29}ClNO_2S$ 430.1602; Found 430.1595.



3ad

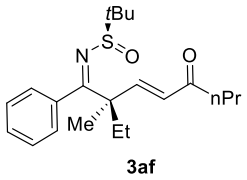
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-5-(4-methoxyphenyl)-2-methyl-5-oxo-1-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3ad**):According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2f** (31.1 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ad** as a light yellow solid (39.1 mg, 92%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ad**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 88–89 °C; $[\alpha]^{25}_D$ = –348.7 (*c* 0.15, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.86 (m, 2H), 7.41–7.33 (m, 2H), 7.13–7.02 (m, 3H), 6.97–6.90 (m, 2H), 6.86 (d, *J* = 15.6 Hz, 1H), 3.87 (s, 3H), 1.92–1.75 (m, 3H), 1.39 (s, 3H), 1.21 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.8, 188.2, 163.6, 151.2, 136.7, 131.1, 130.7, 129.0, 128.1, 126.7, 125.2, 114.0, 56.4, 55.6, 52.5, 31.2, 22.3, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}NO_3S$ 426.2097; Found 426.2089.



3ae

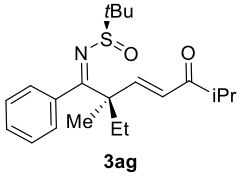
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-5-(furan-2-yl)-2-methyl-5-oxo-1-phenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3ae**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2g** (25.1 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ae** as a light brown solid (31.6 mg, 82%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ae**: R_f = 0.30 (petroleum ether/ethyl acetate = 31); mp 106–107 °C; $[\alpha]^{25}_D$ = –254.0 (*c* 0.25, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.59 (m, 1H), 7.39–7.32 (m, 3H), 7.26–7.16 (m, 2H), 7.11–7.03 (m, 2H), 6.80 (d, *J*

= 16.0 Hz, 1H), 6.57–6.54 (m, 1H), 1.92–1.75 (m, 2H), 1.37 (s, 3H), 1.20 (s, 9H), 0.92 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 188.0, 177.7, 153.3, 151.7, 146.8, 136.5, 129.0, 128.0, 126.6, 124.3, 118.1, 112.6, 56.4, 52.5, 31.2, 22.3, 20.9, 9.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{28}NO_3S$ 386.1784; Found 386.1779.



3af

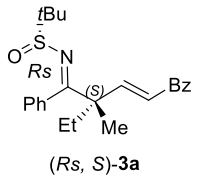
(*R*)-*N*-((*R*,1*E*,3*E*)-2-ethyl-2-methyl-5-oxo-1-phenylnon-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3af**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2h** (21.5 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3af** as a light yellow oil (31.2 mg, 83%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3af**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –204.4 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 3H), 7.10–7.00 (m, 2H), 6.88 (d, *J* = 16.4 Hz, 1H), 6.06 (d, *J* = 16.4 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.83–1.75 (m, 2H), 1.66–1.56 (m, 2H), 1.30 (s, 3H), 1.20 (s, 9H), 0.94–0.87 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 200.5, 188.2, 149.9, 136.5, 129.5, 129.0, 128.1, 126.6, 56.4, 52.2, 42.3, 31.2, 22.3, 20.9, 17.8, 13.9, 9.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{21}H_{32}NO_2S$ 362.2148; Found 362.2141.



3ag

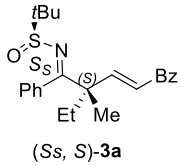
(*R*)-*N*-((*R*,1*E*,3E)-2-ethyl-2,6-dimethyl-5-oxo-1-phenylhept-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**3ag**): According to the general procedure B, reaction was performed using enesulfinamide **1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2i** (21.5 mg, 0.150 mmol, 1.5 equiv) with THF as solvent, DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether as eluent) afforded **3ag** as a light yellow oil (35.0 mg, 97%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 30:1). Analytical data for **3ag**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = –231.2 (*c* 0.19, CH_2Cl_2); dr > 20:1 (diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.29 (m, 3H), 7.08–6.99 (m, 2H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.12 (d, *J* = 16.0 Hz, 1H), 2.90–2.71 (m, 1H), 1.90–1.66 (m, 2H), 1.30 (s, 3H), 1.19 (s, 9H), 1.07 (dd, *J* = 6.8, 5.2 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 203.7, 188.1, 149.8, 136.5, 129.0, 128.0, 127.7, 126.6, 56.4, 52.2, 38.7,

31.1, 22.2, 20.9, 18.5, 18.4, 9.0; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{32}NO_2S$ 362.2148; Found 362.2148.



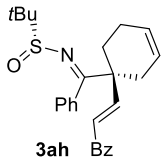
(*Rs, S*)-**3a**

(*R*)-*N*-((*S*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*R*$_S$, *S*)-**3a**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (*R*$_S$, *S*)-**1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *S*)-**3a** as a pale brown solid (36.4 mg, 92%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*R*$_S$, *S*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 104–105 °C; $[\alpha]^{25}_D$ = –94.2 (*c* 0.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.43 (m, 2H), 7.39–7.34 (m, 3H), 7.15–7.05 (m, 3H), 6.83 (d, *J* = 16.0 Hz, 1H), 1.97–1.84 (m, 2H), 1.37 (s, 3H), 1.21 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 188.2, 152.3, 137.8, 136.7, 133.0, 129.0, 128.72, 128.69, 128.1, 126.6, 125.6, 56.4, 52.7, 31.3, 22.3, 21.1, 9.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1989.

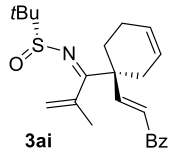


(*Ss, S*)-**3a**

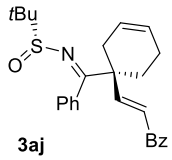
(*S*)-*N*-((*S*,1*Z*,3*E*)-2-ethyl-2-methyl-5-oxo-1,5-diphenylpent-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*$_S$, *S*)-**3a**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (*S*$_S$, *S*)-**1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *S*)-**3a** as a pale yellow oil (38.8 mg, 98%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*S*$_S$, *S*)-**3a**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +86.1 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.59–7.51 (m, 1H), 7.48–7.41 (m, 2H), 7.39–7.34 (m, 3H), 7.12–7.06 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H), 1.94–1.76 (m, 2H), 1.39 (s, 3H), 1.20 (s, 9H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 188.0, 152.2, 137.7, 136.6, 132.9, 129.0, 128.7, 128.6, 128.0, 126.6, 125.4, 56.4, 52.6, 31.2, 22.3, 21.1, 9.0; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{30}NO_2S$ 396.1992; Found 396.1989.



(*R*)-2-methyl-*N*-((*Z*)-((*R*)-1-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)cyclohex-3-en-1-yl)(phenyl)methylene)propane-2-sulfinamide (**3ah**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (R_S, *R*)-**1ah** (28.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ah** as a pale brown solid (40.7 mg, 97%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 30:1). Analytical data for **3ah**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); mp 139–140 °C; $[\alpha]^{25}_D$ = –169.1 (*c* 0.27, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.83 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.42 (m, 2H), 7.40–7.31 (m, 3H), 7.13–7.08 (m, 2H), 7.00 (d, *J* = 15.6 Hz, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 5.75–5.62 (m, 2H), 2.54–2.45 (m, 1H), 2.32–2.14 (m, 3H), 2.11–1.97 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2, 187.4, 150.1, 137.7, 136.3, 133.1, 129.1, 128.7, 128.6, 127.9, 127.4, 126.8, 126.4, 124.0, 56.4, 51.2, 32.5, 30.1, 22.9, 22.2; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{26}H_{30}NO_2S$ 420.1992; Found 420.1985.

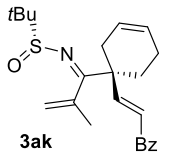


(*R*)-2-methyl-*N*-((*E*)-2-methyl-1-((*R*)-1-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)cyclohex-3-en-1-yl)allylidene)propane-2-sulfinamide (**3ai**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (R_S, *R*)-**1ai** (25.3 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ai** as a colorless oil (37.9 mg, 99%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ai**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –118.1 (*c* 0.34, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.85 (m, 2H), 7.59–7.51 (m, 1H), 7.49–7.42 (m, 2H), 7.00–6.88 (m, 2H), 5.77–5.63 (m, 2H), 5.15 (s, 1H), 4.80 (s, 1H), 2.62 (d, *J* = 17.6 Hz, 1H), 2.39 (d, *J* = 17.6 Hz, 1H), 2.23–1.95 (m, 4H), 1.93 (s, 3H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 189.2, 150.1, 142.0, 137.7, 133.1, 128.7, 128.6, 127.1, 125.9, 124.2, 116.4, 56.4, 50.2, 32.1, 30.0, 24.5, 22.8, 22.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{30}NO_2S$ 384.1992; Found 384.1992.



3aj

(*R*)-2-methyl-*N*-((*Z*)-((*S*)-1-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)cyclohex-3-en-1-yl)(phenyl)methylene)propane-2-sulfinamide (**3aj**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (*R*$_S$, *S*)-**1aj** (28.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3aj** as a pale brown solid (39.8 mg, 95%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3aj**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –256.6 (*c* 0.28, CH_2Cl_2); mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.83 (m, 2H), 7.60–7.51 (m, 1H), 7.49–7.41 (m, 2H), 7.39–7.30 (m, 3H), 7.13–7.07 (m, 2H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), 5.78–5.57 (m, 2H), 2.54–2.41 (m, 1H), 2.33–2.12 (m, 3H), 2.11–1.97 (m, 2H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2, 186.5, 150.1, 137.7, 136.4, 133.0, 129.0, 128.71, 128.66, 127.9, 127.4, 126.7, 126.5, 124.2, 56.6, 51.1, 32.7, 30.0, 23.0, 22.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{26}H_{30}NO_2S$ 420.1992; Found 420.1987.



3ak

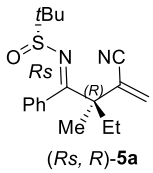
(*R*)-2-methyl-*N*-((*E*)-2-methyl-1-((*S*)-1-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)cyclohex-3-en-1-yl)allylidene)propane-2-sulfinamide (**3ak**): According to the general procedure A, reaction was performed using *N*-*tert*-butanesulfinyl ketimine (*R*$_S$, *S*)-**1ak** (25.3 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **2a** (26.6 mg, 0.150 mmol, 1.5 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **3ak** as a colorless oil (36.8 mg, 96%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **3ak**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –240.3 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.85 (m, 2H), 7.59–7.51 (m, 1H), 7.48–7.41 (m, 2H), 6.97 (s, 2H), 5.81–5.60 (m, 2H), 5.14 (s, 1H), 4.82 (s, 1H), 2.60–2.51 (m, 1H), 2.44–2.35 (m, 1H), 2.22–2.06 (m, 2H), 2.06–1.96 (m, 2H), 1.93 (s, 3H), 1.24 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2, 188.6, 150.4, 142.2, 137.7, 133.0, 128.7, 128.6, 127.3, 125.9, 124.2, 116.1, 56.5, 50.1, 32.3, 30.1, 24.2, 22.9, 22.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{30}NO_2S$ 384.1992; Found 384.1989.

General procedure C for synthesis of 1,4-dicarbonyl analogs using β-sulfonyl acrylonitrile 4a

Enesulfinamide **1** (1.0 equiv) or *N*-sulfinyl ketimine **6** in freshly distilled THF (0.1 M) was added to a flame dried Schlenk tube equipped with magnetic stirring bar under argon. The resulting solution was then cooled to −78 ℃ and a solution of potassium *tert*-butoxide in THF (1.0 M, 1.2 equiv) was added dropwise to the mixture via syringe. After 30 min, (*E*)-3-tosylacrylonitrile **4a** (2.0 equiv) in dry THF (0.1 M) was added dropwise by syringe at −78 ℃. The reaction progress was monitored by TLC analysis. Upon completion (usually 2−3 h), DBU (4.0 equiv) was added at −78 ℃ and the reaction mixture was allowed to warm to room temperature in 5 h. After stirring at room temperature for 12 hours, the reaction mixture was quenched with saturated aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (3 times) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

General procedure D for synthesis of 1,4-dicarbonyl analogs using β-sulfonyl acrylonitrile 4b

Enesulfinamide **1** (1.0 equiv) in freshly distilled Et_2O (0.1 M) was added to a flame dried Schlenk tube equipped with magnetic stirring bar under argon. The resulting clear solution was then cooled to −78 ℃ and a solution of lithium bis(trimethylsilyl)amide in THF (1.0 M, 1.2 equiv) was added dropwise to the mixture via syringe. After 30 min, (*E*)-3-((3,5-bis(trifluoromethyl)phenyl)sulfonyl) acrylonitrile **4b** (2.0 equiv) in dry Et_2O (0.1 M) was added dropwise by syringe at −78 ℃. The reaction progress was monitored by TLC analysis. Upon completion (usually 2−4 h), DBU (4.0 equiv) was added at −78 ℃ and the reaction mixture was allowed to warm to room temperature in 5 h. After stirring at room temperature for 12 hours, the reaction mixture was quenched with saturated aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (3 times) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.



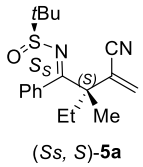
(*Rs, R*)-**5a**

(*R*)-*N*-((*R*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methyl propane-2-sulfinamide ((*R*$_S$, *R*)-**5a**): According to the general procedure C, reaction was performed using enesulfinamide **1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum

ether as eluent) afforded (R_S, R)-**5a** as a yellow oil (28.4 mg, 90%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (R_S, R)-**5a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –132.5 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.36 (m, 3H), 7.15–7.09 (m, 2H), 6.11 (s, 1H), 5.79 (s, 1H), 1.99–1.88 (m, 1H), 1.79–1.69 (m, 1H), 1.38 (s, 3H), 1.24 (s, 9H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.5, 135.7, 131.5, 129.1, 128.1, 127.6, 126.8, 118.3, 56.7, 53.7, 29.4, 22.3, 20.2, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1679.

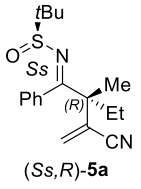
Gram scale preparation of (*Rs, R*)-5a

According to the general procedure C, reaction was performed using enesulfinamide **1a** (1.07 g, 4.03 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 4.85 mL, 4.845 mmol, 1.2 equiv), and **4a** (1.67 g, 8.06 mmol, 2.0 equiv), DBU (2.45 g, 16.15 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded (R_S, R)-**5a** as a light yellow solid (1.081 g, 85%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1).



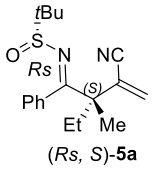
(*Ss, S*)-**5a**

(*S*)-*N*-((*S*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide((*S*$_S$, *S*)-**5a**): According to the general procedure C, reaction was performed using enesulfinamide (*S*$_S$, *Z*)-**1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded (*S*$_S$, *S*)-**5a** as a white solid (26.9 mg, 85%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*S*$_S$, *S*)-**5a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 56–58 °C; $[\alpha]^{25}_D$ = +138.4 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.32 (m, 3H), 7.16–7.05 (m, 2H), 6.11 (s, 1H), 5.79 (s, 1H), 1.99–1.86 (m, 1H), 1.79–1.64 (m, 1H), 1.37 (s, 3H), 1.23 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.5, 135.7, 131.6, 129.1, 128.1, 127.5, 126.7, 118.3, 56.7, 53.7, 29.4, 22.2, 20.2, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1678.



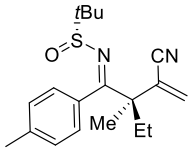
(*Ss,R*)-**5a**

(*S*)-*N*-((*R*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*$_S$, *R*)-**5a**): According to the general procedure C, reaction was performed using enesulfinamide (*S*$_S$, *E*)-**1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded (*S*$_S$, *R*)-**5a** as a white solid (27.2 mg, 86%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 25:1). Analytical data for (*S*$_S$, *R*)-**5a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 55–57 °C; $[\alpha]^{25}_D$ = +112.4 (*c* 0.24, CH_2Cl_2); dr= 25:1 (diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.31 (m, 3H), 7.15–7.08 (m, 2H), 6.10 (s, 1H), 5.74 (s, 1H), 2.13–2.02 (m, 1H), 2.02–1.91 (m, 1H), 1.29 (s, 3H), 1.24 (s, 9H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.9, 135.7, 132.0, 129.1, 128.0, 127.5, 126.8, 118.1, 56.8, 53.7, 29.3, 22.3, 20.5, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1677.



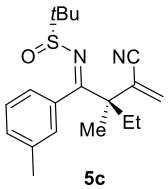
(*Rs, S*)-**5a**

(*R*)-*N*-((*S*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*R*$_S$, *S*)-**5a**): According to the general procedure C, reaction was performed using enesulfinamide (*R*$_S$, *E*)-**1a** (26.6 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *S*)-**5a** as a white solid (27.5 mg, 87%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*R*$_S$, *S*)-**5a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 61–62 °C; $[\alpha]^{25}_D$ = –107.3 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.31 (m, 3H), 7.17–7.06 (m, 2H), 6.09 (s, 1H), 5.74 (s, 1H), 2.10–1.90 (m, 2H), 1.28 (s, 3H), 1.23 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.8, 135.7, 131.9, 129.1, 127.9, 127.4, 126.8, 118.0, 56.7, 53.6, 29.3, 22.3, 20.5, 8.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1680.



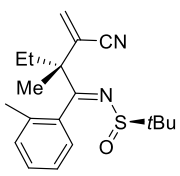
5b

(*R*)-*N*-((*R*,*E*)-3-cyano-2-ethyl-2-methyl-1-(p-tolyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5b**): According to the general procedure C, reaction was performed using enesulfinamide **1b** (28.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.121 mmol, 1.2 equiv), **4a** (41.8 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5b** as a pale yellow solid (29.1 mg, 88%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5b**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 91–92 °C; $[\alpha]^{25}_D$ = –256.9 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.15 (m, 2H), 7.03–6.99 (m, 2H), 6.10 (s, 1H), 5.79 (s, 1H), 2.36 (s, 3H), 1.97–1.86 (m, 1H), 1.79–1.69 (m, 1H), 1.37 (s, 3H), 1.23 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.0, 139.1, 132.8, 131.5, 128.7, 127.7, 126.7, 118.4, 56.6, 53.8, 29.4, 22.2, 21.5, 20.2, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_2OS$ 331.1839; Found 331.1837.



5c

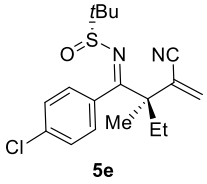
(*R*)-*N*-((*R*,*E*)-3-cyano-2-ethyl-2-methyl-1-(m-tolyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5c**): According to the general procedure C, reaction was performed using enesulfinamide **1c** (28.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.121 mmol, 1.2 equiv), **4a** (41.8 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5c** as a pale yellow oil (25.1 mg, 76%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5c**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –87.2 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 1H), 7.24–7.15 (m, 1H), 6.92 (s, 2H), 6.12 (s, 1H), 5.81 (s, 1H), 2.38 (s, 3H), 2.02–1.84 (m, 1H), 1.80–1.65 (m, 1H), 1.38 (s, 3H), 1.24 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.2, 137.9, 135.7, 131.5, 129.9, 127.9, 127.6, 127.1, 124.0, 118.4, 56.5, 53.7, 29.4, 22.2, 21.7, 20.1, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_2OS$ 331.1839; Found 331.1836.



5d

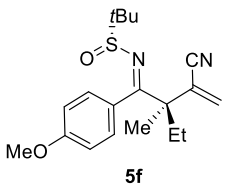
(*R*)-*N*-((*R*,*Z*)-3-cyano-2-ethyl-2-methyl-1-(o-tolyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5d**): According to the general procedure C, reaction was performed using enesulfinamide **1d** (28.0 mg, 0.101 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.121 mmol, 1.2 equiv), **4a** (41.8 mg,

0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5d** as a white solid (29.0 mg, 88%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 96:4), HPLC (IG-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.5 min (major), 15.9 min (minor). Analytical data for **5d** (mixture of imino *Z*/*E* isomers): R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 76–77 °C; $[\alpha]^{25}_D$ = –146.7 (*c* 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 1H), 7.25–7.13 (m, 2H), 7.06–6.87 (m, 1H), 6.15 (d, *J* = 1.6 Hz, 1H), 5.84 (d, *J* = 10.4 Hz, 1H), 2.28 (d, *J* = 11.2 Hz, 3H), 2.11–1.98 (m, 1H), 1.83–1.61 (m, 1H), 1.35 (s, 3H), 1.24 (d, *J* = 11.2 Hz, 9H), 0.92–0.81 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.6, 186.5, 136.2, 135.2, 134.9, 133.6, 131.8, 131.6, 130.7, 130.4, 129.2, 129.1, 127.9, 127.7, 127.4, 126.1, 125.2, 125.0, 118.6, 118.3, 56.9, 56.8, 54.3, 53.5, 30.6, 28.9, 22.4, 22.2, 21.5, 20.5, 20.4, 19.6, 8.4, 8.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_2OS$ 331.1839; Found 331.1837.



5e

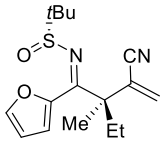
(*R*)-*N*-((*R*,*E*)-1-(4-chlorophenyl)-3-cyano-2-ethyl-2-methylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5e**): According to the general procedure C, reaction was performed using enesulfinamide **1e** (29.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (42.0 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5e** as a white solid (29.5 mg, 84%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5e**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 107–108 °C; $[\alpha]^{25}_D$ = –166.6 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.01 (s, 1H), 5.68 (s, 1H), 1.91–1.75 (m, 1H), 1.69–1.56 (m, 1H), 1.25 (s, 3H), 1.14 (s, 9H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.6, 135.4, 133.9, 131.7, 128.4, 128.2, 127.4, 118.1, 57.1, 53.8, 29.3, 22.3, 20.2, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{24}ClN_2OS$ 351.1292; Found 351.1291.



5f

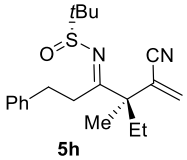
(*R*)-*N*-((*R*,*E*)-3-cyano-2-ethyl-1-(4-methoxyphenyl)-2-methylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5f**): According to the general procedure C, reaction was performed using enesulfinamide **1f** (29.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (42.0 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column

chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5f** as a pale yellow oil (24.6 mg, 71%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5f**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –111.0 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–6.98 (m, 2H), 6.94–6.86 (m, 2H), 6.10 (s, 1H), 5.79 (s, 1H), 3.82 (s, 3H), 1.96–1.85 (m, 1H), 1.79–1.69 (m, 1H), 1.37 (s, 3H), 1.23 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.0, 160.0, 131.4, 128.4, 128.0, 127.8, 118.4, 113.5, 56.6, 55.3, 53.9, 29.5, 22.3, 20.4, 8.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_2O_2S$ 347.1788; Found 347.1785.



5g

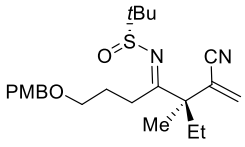
(*R*)-*N*-((*R*,*Z*)-3-cyano-2-ethyl-1-(furan-2-yl)-2-methylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5g**): According to the general procedure C, reaction was performed using enesulfinamide **1g** (29.5 mg, 0.115 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 140 μL, 0.138 mmol, 1.2 equiv), **4a** (47.6 mg, 0.230 mmol, 2.0 equiv), DBU (70.1 mg, 0.460 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5g** as a pale yellow oil (28.9 mg, 82%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5g**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –218.2 (*c* 0.11, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 1H), 7.24–7.22 (m, 1H), 6.53–6.49 (m, 1H), 6.04 (s, 1H), 5.78 (s, 1H), 2.13–2.01 (m, 1H), 1.97–1.86 (m, 1H), 1.48 (s, 3H), 1.30 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2, 146.4, 144.6, 130.6, 128.9, 120.0, 118.0, 112.0, 57.5, 53.1, 30.2, 22.5, 22.4, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{23}N_2O_2S$ 307.1475; Found 307.1472.



5h

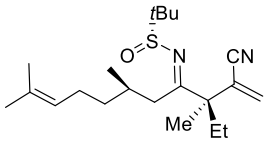
(*R*)-*N*-((*R*,*E*)-5-cyano-4-ethyl-4-methyl-1-phenylhex-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5h**): According to the general procedure D, reaction was performed using enesulfinamide **1h** (29.4 mg, 0.101 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (66.5 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded as a pale yellow oil (23.0 mg, 67%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 97:3), HPLC (IC-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 13.8 min (minor), 19.7 min (major). Analytical data for **5h**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1);

$[\alpha]^{25}_{D}$ = –178.4 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 7.24–7.16 (m, 1H), 6.12 (s, 1H), 5.85 (s, 1H), 3.30–3.19 (m, 1H), 3.19–3.10 (m, 1H), 2.84–2.74 (m, 1H), 2.68–2.59 (m, 1H), 1.99–1.80 (m, 2H), 1.35 (s, 3H), 1.33 (s, 9H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.3, 140.6, 131.2, 128.7, 128.5, 128.3, 126.5, 117.9, 58.1, 54.6, 34.0, 33.8, 28.9, 22.9, 20.1, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{29}N_2OS$ 345.1995; Found 345.1994.



5i

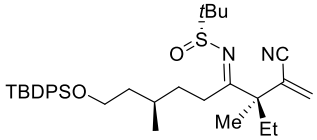
(*R*)-*N*-((*R*,*E*)-2-cyano-3-ethyl-7-((4-methoxybenzyl)oxy)-3-methylhept-1-en-4-ylidene)-2-methylpropane-2-sulfinamide (**5i**): According to the general procedure D, reaction was performed using enesulfinamide **1i** (36.7 mg, 0.101 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (66.5 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **5i** as a pale yellow oil (28.8 mg, 69%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 97:3), HPLC (ID-3, *n*-hexane/*i*PrOH = 87/13, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.6 min (minor), 15.7 min (major). Analytical data for **5i**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_{D}$ = –42.6 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.19 (m, 2H), 6.92–6.80 (m, 2H), 6.07 (s, 1H), 5.81 (s, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.56–3.42 (m, 2H), 2.98–2.86 (m, 1H), 2.57–2.44 (m, 1H), 2.15–1.96 (m, 1H), 1.92–1.78 (m, 3H), 1.32 (s, 3H), 1.27 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ^{13}C 185.9, 159.3, 131.1, 130.6, 129.4, 128.3, 118.0, 113.9, 72.7, 69.8, 57.8, 55.4, 54.6, 28.8, 28.7, 28.4, 22.8, 20.0, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{35}N_2O_3S$ 419.2363; Found 419.2356.



5j

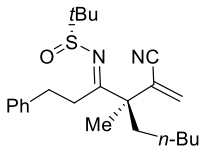
(*R*)-*N*-((3*R*,6*R*,E)-2-cyano-3-ethyl-3,6,10-trimethylundeca-1,9-dien-4-ylidene)-2-methylpropane-2-sulfinamide (**5j**): According to the general procedure D, reaction was performed using enesulfinamide **1j** (31.3 mg, 0.101 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (66.5 mg, 0.202 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **5j** as a pale yellow oil (27.7 mg, 76%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 97:3), HPLC (IF-3, *n*-hexane/*i*PrOH = 98/02, flow rate = 1.0 mL/min, l = 254 nm) t_R = 15.2 min (major), 16.4 min (minor). Analytical data for **5j**: R_f = 0.20

(petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_{D}$ = –138.9 (*c* 0.14, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.79 (s, 1H), 5.09–5.01 (m, 1H), 3.17–3.08 (m, 1H), 2.42–2.34 (m, 1H), 2.18–2.06 (m, 1H), 2.06–1.81 (m, 4H), 1.67 (s, 3H), 1.59 (s, 3H), 1.39–1.33 (m, 1H), 1.32 (s, 3H), 1.26 (s, 9H), 1.24–1.18 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.8, 131.9, 130.7, 128.8, 124.2, 118.1, 57.7, 54.6, 38.2, 37.6, 32.0, 29.4, 25.9, 25.7, 22.7, 20.7, 19.7, 17.9, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{37}N_2OS$ 365.2621; Found 365.2620.



5k

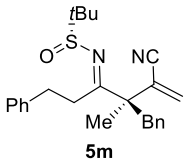
(*R*)-*N*-((3*R*,7*R*,*E*)-9-((tert-butyldiphenylsilyl)oxy)-2-cyano-3-ethyl-3,7-dimethylnon-1-en-4-ylidene)-2-methylpropane-2-sulfinamide (**5k**): According to the general procedure D, reaction was performed using enesulfinamide **1k** (26.5 mg, 0.051 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 60 μL, 0.060 mmol, 1.2 equiv), **4b** (33.4 mg, 0.102 mmol, 2.0 equiv), DBU (31.0 mg, 0.204 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5k** as a pale yellow oil (21.8 mg, 74%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 94:6), HPLC (ID-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 5.0 min (minor), 5.2 min (major). Analytical data for **5k**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_{D}$ = –85.6 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.57 (m, 4H), 7.47–7.31 (m, 6H), 6.05 (s, 1H), 5.79 (s, 1H), 3.78–3.60 (m, 2H), 3.06–2.93 (m, 1H), 2.34–2.20 (m, 1H), 1.91–1.74 (m, 2H), 1.65–1.54 (m, 2H), 1.50–1.33 (m, 3H), 1.31 (s, 3H), 1.27 (s, 9H), 1.04 (s, 9H), 0.91–0.82 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.6, 135.7, 134.1, 130.9, 129.7, 128.5, 127.7, 118.0, 62.1, 57.6, 54.6, 39.2, 34.2, 30.4, 29.4, 28.9, 27.0, 22.7, 20.0, 19.3, 19.2, 8.6; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{34}H_{51}N_2O_2SSi$ 579.3435; Found 579.3429.



5l

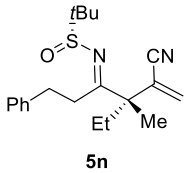
(*R*)-*N*-((*R*,*E*)-4-(1-cyanovinyl)-4-methyl-1-phenylnonan-3-ylidene)-2-methylpropane-2-sulfinamide (**5l**): According to the general procedure D, reaction was performed using enesulfinamide **1l** (25.5 mg, 0.076 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 90 μL, 0.091 mmol, 1.2 equiv), **4b** (49.7 mg, 0.152 mmol, 2.0 equiv), DBU (46.9 mg, 0.308 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5l** as a pale yellow oil (24.1 mg, 82%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture

(dr > 20:1). Analytical data for **5l**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –118.6 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 4H), 7.24–7.15 (m, 1H), 6.10 (s, 1H), 5.84 (s, 1H), 3.29–3.07 (m, 2H), 2.87–2.73 (m, 1H), 2.69–2.56 (m, 1H), 1.88–1.66 (m, 2H), 1.37 (s, 3H), 1.32 (s, 9H), 1.31–1.15 (m, 6H), 0.92–0.83 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.4, 140.6, 130.8, 128.71, 128.66, 128.5, 126.5, 118.0, 58.1, 54.3, 36.2, 34.0, 33.8, 32.3, 23.9, 22.9, 22.6, 20.7, 14.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{23}H_{35}N_2OS$ 387.2465; Found 387.2460.



5m

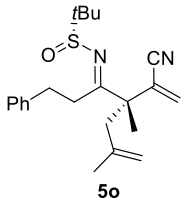
(*R*)-*N*-((*R*,*E*)-4-benzyl-5-cyano-4-methyl-1-phenylhex-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5m**): According to the general procedure D, reaction was performed using enesulfinamide **1m** (35.5 mg, 0.100 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (49.7 mg, 0.200 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5m** as a pale yellow oil (31.3 mg, 77%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5m**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –168.4 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.06 (m, 10H), 6.04 (s, 1H), 5.63 (s, 1H), 3.39–3.28 (m, 1H), 3.28–3.17 (m, 1H), 3.15–3.04 (m, 2H), 2.79–2.69 (m, 1H), 2.68–2.59 (m, 1H), 1.27 (s, 9H), 1.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.0, 140.5, 135.7, 132.0, 130.7, 128.7, 128.6, 128.3, 127.5, 127.1, 126.6, 118.2, 58.5, 55.4, 42.1, 34.0, 33.6, 23.0, 20.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{31}N_2OS$ 407.2152; Found 407.2147.



5n

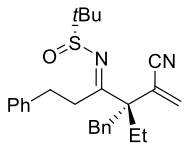
(*R*)-*N*-((*S*,*E*)-5-cyano-4-ethyl-4-methyl-1-phenylhex-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5n**): According to the general procedure D, reaction was performed using enesulfinamide **1n** (29.3 mg, 0.100 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (65.4 mg, 0.200 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5n** as a pale yellow oil (26.5 mg, 77%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 94.5:5.5), HPLC (IC-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 13.4 min (major), 19.6 min (minor). Analytical data for **5n**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –177.0 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 4H), 7.24–7.15

(m, 1H), 6.13 (s, 1H), 5.86 (s, 1H), 3.17–3.04 (m, 2H), 2.92–2.82 (m, 1H), 2.76–2.67 (m, 1H), 1.96–1.88 (m, 2H), 1.36 (s, 3H), 1.33 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 184.4, 140.7, 131.2, 128.7, 128.5, 128.2, 126.5, 118.0, 58.1, 54.7, 34.4, 34.3, 29.0, 22.9, 20.6, 8.7; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{20}H_{29}N_2OS$ 345.1995; Found 345.1992.



5o

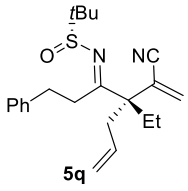
(*R*)-*N*-((*S*,*E*)-4-(1-cyanovinyl)-4,6-dimethyl-1-phenylhept-6-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5o**): According to the general procedure D, reaction was performed using enesulfinamide **1o** (32.0 mg, 0.102 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (66.7 mg, 0.204 mmol, 2.0 equiv), DBU (61.2 mg, 0.404 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5o** as a pale yellow oil (25.9 mg, 70%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 97.5:2.5), HPLC (AD-3, *n*-hexane/*i*PrOH = 95/05, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.0 min (minor), 14.2 min (major). Analytical data for **5o**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –146.5 (*c* 0.15, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H), 7.24–7.16 (m, 1H), 6.15 (s, 1H), 5.91 (s, 1H), 5.01–4.90 (m, 1H), 4.79–4.75 (m, 1H), 3.12–2.91 (m, 3H), 2.85–2.74 (m, 1H), 2.74–2.57 (m, 2H), 1.75 (s, 3H), 1.41 (s, 3H), 1.35 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 184.4, 140.7, 140.5, 131.5, 128.7, 128.55, 128.48, 126.6, 118.2, 116.9, 58.1, 54.0, 44.3, 34.9, 24.7, 22.9, 21.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{31}N_2OS$ 371.2152; Found 371.2147.



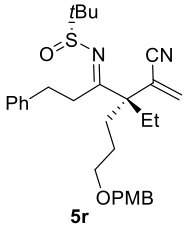
5p

(*R*)-*N*-((*S*,*E*)-4-benzyl-5-cyano-4-ethyl-1-phenylhex-5-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5p**): According to the general procedure D, reaction was performed using enesulfinamide **1p** (36.9 mg, 0.100 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (65.4 mg, 0.200 mmol, 2.0 equiv), DBU (60.9 mg, 0.400 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5p** as a colorless solid (28.6 mg, 68%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr = 20:1). Analytical data for **5p**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); mp 110–111 °C; $[\alpha]^{25}_D$ = –87.7 (*c* 0.19, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 1H), 7.26–7.22 (m, 5H), 7.22–7.14 (m, 2H), 7.14–7.09 (m, 2H), 6.15 (s, 1H), 5.69 (s, 1H), 3.25–3.06 (m, 4H), 2.93–2.81 (m, 1H), 2.67–2.53 (m, 1H), 1.82–1.69 (m, 1H), 1.69 – 1.59 (m, 1H), 1.34

(s, 9H), 0.99 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.3, 140.7, 136.2, 132.6, 130.4, 128.7, 128.5, 128.3, 127.1, 126.9, 126.5, 118.2, 59.0, 58.0, 37.6, 35.0, 34.0, 23.7, 23.0, 8.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{26}H_{33}N_2OS$ 421.2308; Found 421.2299.

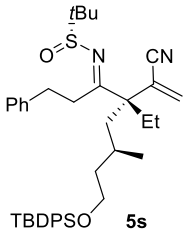


(*R*)-*N*-((*S*,*E*)-4-(1-cyanovinyl)-4-ethyl-1-phenylhept-6-en-3-ylidene)-2-methylpropane-2-sulfinamide (**5q**): According to the general procedure D, reaction was performed using enesulfinamide **1q** (32.0 mg, 0.102 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (66.7 mg, 0.204 mmol, 2.0 equiv), DBU (61.2 mg, 0.404 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5q** as a pale yellow oil (29.6 mg, 80%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 95:5), HPLC (AD-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 8.4 min (minor), 11.0 min (major). Analytical data for **5q**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –147.5 (*c* 0.19, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 4H), 7.24–7.13 (m, 1H), 6.22 (s, 1H), 5.91 (s, 1H), 5.64–5.47 (m, 1H), 5.21–5.10 (m, 2H), 3.25–3.08 (m, 2H), 2.88–2.75 (m, 1H), 2.69–2.53 (m, 3H), 2.01–1.84 (m, 1H), 1.83–1.70 (m, 1H), 1.35 (s, 9H), 0.85 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.8, 140.7, 132.2, 132.1, 128.7, 128.5, 127.1, 126.5, 119.6, 117.7, 58.1, 57.6, 36.1, 34.4, 33.8, 24.8, 23.0, 8.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{31}N_2OS$ 371.2152; Found 371.2149.



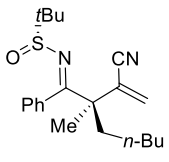
(*R*)-*N*-((*S*,*E*)-4-(1-cyanovinyl)-4-ethyl-7-((4-methoxybenzyl)oxy)-1-phenylheptan-3-ylidene)-2-methylpropane-2-sulfinamide (**5r**): According to the general procedure D, reaction was performed using enesulfinamide **1r** (45.7 mg, 0.100 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4b** (65.4 mg, 0.200 mmol, 2.0 equiv), DBU (60.8 mg, 0.400 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5r** as a pale yellow oil (41.0 mg, 81%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (ID-3, *n*-hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 19.5 min (major), 23.5 min (minor). Analytical data for **5r**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –137.6 (*c* 0.13, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 1H), 7.25–7.16 (m, 6H), 6.89–6.82 (m, 2H), 6.19 (s, 1H), 5.92 (s, 1H), 4.43 (s, 2H), 3.79 (s, 3H), 3.52–3.37 (m, 2H), 3.25–3.08 (m, 2H), 2.88–2.71 (m, 1H), 2.65–2.52 (m, 1H),

2.05–1.88 (m, 2H), 1.86–1.72 (m, 2H), 1.51–1.40 (m, 2H), 1.34 (s, 9H), 0.82 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 183.0, 159.3, 140.8, 132.3, 130.5, 129.4, 128.7, 128.5, 127.4, 126.4, 117.9, 113.9, 72.9, 69.7, 58.2, 57.8, 55.4, 34.3, 33.7, 27.9, 25.2, 24.4, 23.0, 8.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{30}H_{41}N_2O_3S$ 509.2832; Found 509.2823.



5s

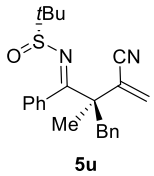
(*R*)-*N*-((4*S*,6*R*,*E*)-8-((tert-butyldiphenylsilyl)oxy)-4-(1-cyanovinyl)-4-ethyl-6-methyl-1-phenyloctan-3-ylidene)-2-methylpropane-2-sulfinamide (**5s**): According to the general procedure D, reaction was performed using enesulfinamide **1s** (30.2 mg, 0.051 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 60 μL, 0.062 mmol, 1.2 equiv), **4b** (33.0 mg, 0.102 mmol, 2.0 equiv), DBU (31.0 mg, 0.204 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5s** as a pale yellow oil (24.0 mg, 72%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 99:1), HPLC (ID-3, *n*-hexane/*i*PrOH = 95/05, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.2 min (minor), 9.9 min (major). Analytical data for **5s**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = – 77.2 (*c* 0.18, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67–7.58 (m, 4H), 7.43–7.32 (m, 6H), 7.26–7.13 (m, 5H), 6.18 (s, 1H), 5.89 (s, 1H), 3.74–3.55 (m, 2H), 3.23–2.98 (m, 2H), 2.90–2.77 (m, 1H), 2.71–2.57 (m, 1H), 2.01–1.80 (m, 2H), 1.74–1.51 (m, 4H), 1.31 (s, 9H), 1.28–1.19 (m, 1H), 1.02 (s, 9H), 0.90–0.74 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 183.4, 140.9, 135.64, 135.63, 133.90, 133.88, 131.9, 129.8, 128.7, 128.5, 128.3, 127.8, 126.5, 61.5, 58.2, 58.1, 41.6, 38.9, 34.6, 34.3, 27.0, 25.1, 25.0, 23.0, 21.1, 19.3, 8.7; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{40}H_{55}N_2O_2SSi$ 655.3748; Found 655.3735.



5t

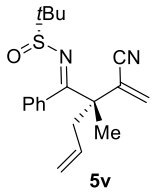
(*R*)-*N*-((*R*,*E*)-2-(1-cyanovinyl)-2-methyl-1-phenylheptylidene)-2-methyl-propane-2-sulfinamide (**5t**): According to the general procedure C, reaction was performed using enesulfinamide **1t** (30.7 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5t** as a yellow oil (29.4 mg, 82%). Diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5t**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = – 189.2 (*c* 0.14, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.32 (m, 3H), 7.18–7.06 (m, 2H), 6.09 (s, 1H), 5.79 (s, 1H), 1.91–1.76 (m, 1H), 1.72–1.56

(m, 1H), 1.39 (s, 3H), 1.35–1.08 (m, 15H), 0.86 (t, J = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 186.6, 135.7, 131.3, 129.2, 128.1, 128.0, 126.8, 118.4, 56.7, 53.4, 36.6, 32.2, 23.8, 22.6, 22.3, 20.9, 14.1 ; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{21}H_{31}N_2OS$ 359.2152; Found 359.2149.



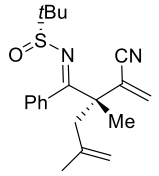
5u

(*R*)-*N*-((*R*,*E*)-2-benzyl-3-cyano-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methyl-propane-2-sulfinamide (**5u**): According to the general procedure C, reaction was performed using enesulfinamide **1u** (32.7 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5u** as a pale yellow oil (29.1 mg, 77%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 99:1), HPLC (IG-3, *n*-hexane/*i*PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 8.2 min (major), 12.8 min (minor). Analytical data for **5u**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –82.2 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 3H), 7.26 (s, 1H), 7.26–7.21 (m, 2H), 7.21–7.12 (m, 4H), 6.02 (s, 1H), 5.51 (s, 1H), 3.34 (d, J = 13.6 Hz, 1H), 2.96 (d, J = 13.6 Hz, 1H), 1.29 (s, 9H), 1.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 185.8, 135.7, 135.5, 132.2, 130.8, 129.2, 128.20, 128.17, 127.1, 126.9, 126.8, 119.0, 57.1, 54.7, 42.7, 22.4, 20.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{23}H_{27}N_2OS$ 379.1839 ; Found 379.1833.



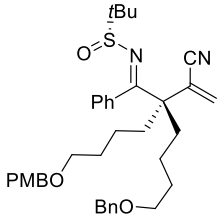
5v

(*R*)-*N*-((*S*,*E*)-2-(1-cyanovinyl)-2-methyl-1-phenylpent-4-en-1-ylidene)-2-methyl-propane-2-sulfinamide (**5v**): According to the general procedure C, reaction was performed using enesulfinamide **1v** (27.7 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **5v** as a colorless oil (25.3 mg, 78%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5v**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –79.7 (*c* 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.32 (m, 3H), 7.18–7.09 (m, 2H), 6.09 (s, 1H), 5.77–5.63 (m, 2H), 5.30–5.06 (m, 2H), 2.86–2.77 (m, 1H), 2.74–2.63 (m, 1H), 1.28 (s, 3H), 1.24 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 185.5, 135.4, 132.3, 132.2, 129.2, 128.0, 127.0, 126.9, 120.0, 118.0, 56.7, 53.0, 41.0, 22.3, 21.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{25}N_2OS$ 329.1682; Found 329.1677.



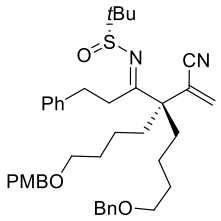
5w

(*R*)-*N*-((*S*,*E*)-2-(1-cyanovinyl)-2,4-dimethyl-1-phenylpent-4-en-1-ylidene)-2-methylpropane-2-sulfinamide (**5w**): According to the general procedure C, reaction was performed using enesulfinamide **1w** (29.1 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.12 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.401 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded **5w** as a colorless oil (30.1 mg, 88%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5w**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = – 272.2 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.33 (m, 3H), 7.16–7.09 (m, 2H), 6.09 (s, 1H), 5.73 (s, 1H), 4.97–4.92 (m, 1H), 4.83–4.79 (m, 1H), 2.92–2.71 (m, 2H), 1.77 (s, 3H), 1.29 (s, 3H), 1.25 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.1, 140.8, 135.5, 132.3, 129.2, 128.0, 127.8, 127.0, 118.3, 116.9, 56.6, 53.1, 44.3, 24.8, 22.2, 21.0; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{27}N_2OS$ 343.1839; Found 343.1835.



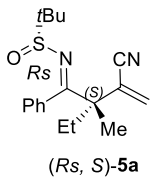
5x

(*R*)-*N*-((*E*)-6-(benzyloxy)-2-(1-cyanovinyl)-2-(4-((4-methoxybenzyl)oxy)butyl)-1-phenylhexylidene)-2-methylpropane-2-sulfinamide (**5x**): According to the general procedure C, reaction was performed using enesulfinamide **1x** (45.0 mg, 0.081 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 100 μL, 0.097 mmol, 1.2 equiv), **4a** (33.5 mg, 0.162 mmol, 2.0 equiv), DBU (49.2 mg, 0.324 mmol, 4.0 equiv). Column chromatography (35% ethyl acetate/petroleum ether as eluent) afforded **5x** as a colorless oil (40.3 mg, 79%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 98:2), HPLC (IC-3, *n*-hexane/*i*PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 29.0 min (minor), 30.4min (major). Analytical data for **5x**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = – 285.1 (*c* 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 8H), 7.24 (s, 2H), 7.14–7.07 (m, 2H), 6.90–6.84 (m, 2H), 6.11 (s, 1H), 5.69 (s, 1H), 4.47 (s, 2H), 4.41 (s, 2H), 3.79 (s, 3H), 3.50–3.38 (m, 4H), 2.01–1.78 (m, 2H), 1.74–1.57 (m, 6H), 1.42–1.27 (m, 4H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.3, 159.2, 138.5, 135.6, 132.9, 130.7, 129.4, 129.2, 128.5, 128.0, 127.8, 127.7, 126.9, 126.7, 118.1, 113.9, 73.1, 69.8, 69.5, 56.9, 56.6, 55.4, 31.9, 31.6, 30.0, 22.4, 20.6, 20.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{38}H_{49}N_2O_4S$ 629.3408; Found 629.3395.



5y

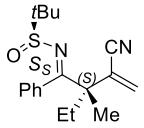
(*R*)-*N*-((*E*)-8-(benzyloxy)-4-(1-cyanovinyl)-4-(4-((4-methoxybenzyl)oxy)butyl)-1-phenyloctan-3-ylidene)-2-methylpropane-2-sulfinamide (**5y**): According to the general procedure D, reaction was performed using enesulfinamide **1y** (48.4 mg, 0.080 mmol, 1.0 equiv), lithium bis(trimethylsilyl)amide in THF (1.0 M, 100 μL, 0.096 mmol, 1.2 equiv), **4b** (52.4 mg, 0.160 mmol, 2.0 equiv), DBU (48.7 mg, 0.321 mmol, 4.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether as eluent) afforded **5y** as a pale yellow oil (38.8 mg, 74%). Diastereomeric ratio was determined by HPLC analysis of the crude reaction mixture (dr = 95.5:4.5), HPLC (IG-3, *n*-hexane/*i*PrOH = 85/15, flow rate = 1.0 mL/min, l = 254 nm) t_R = 34.7 min (minor), 35.9min (major). Analytical data for **5y**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = –248.1 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 7.29–7.27 (m, 4H), 7.25 (s, 1H), 7.23–7.17 (m, 2H), 6.90–6.83 (m, 2H), 6.17 (s, 1H), 5.87 (s, 1H), 4.47 (s, 2H), 4.41 (s, 2H), 3.79 (s, 3H), 3.48–3.39 (m, 4H), 3.20–3.10 (m, 2H), 2.84–2.74 (m, 1H), 2.66–2.58 (m, 1H), 1.93–1.74 (m, 4H), 1.68–1.59 (m, 4H), 1.34 (s, 9H), 1.28–1.19 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.1, 159.2, 140.7, 138.5, 132.0, 130.6, 129.3, 128.7, 128.49, 128.45, 127.7, 127.6, 127.5, 126.5, 117.9, 113.8, 73.0, 72.7, 69.8, 69.5, 58.2, 57.6, 55.3, 34.2, 34.0, 32.2, 31.8, 30.1, 23.0, 20.62, 20.58; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{40}H_{53}N_2O_4S$ 657.3721; Found 657.3717.



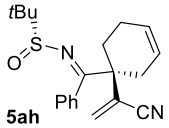
(*Rs, S*)-**5a**

(*R*)-*N*-((*S*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*R*$_S$, *S*)-**5a**): According to the general procedure C, reaction was performed using *N-tert*-Butanesulfinyl ketimine (*R*$_S$, *S*)-**1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*R*$_S$, *S*)-**5a** as a white solid (29.1 mg, 92%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*R*$_S$, *2S*)-**5a**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 60–61 °C; $[\alpha]^{25}_D$ = –104.2 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.33 (m, 3H), 7.17–7.07 (m, 2H), 6.10 (s, 1H), 5.74 (s, 1H), 2.12–1.91 (m, 2H), 1.29 (s, 3H), 1.24 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.5, 135.7, 131.5, 129.1, 128.1, 127.6, 126.8, 118.3, 56.7,

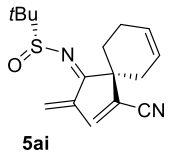
53.7, 29.4, 22.3, 20.2, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1680.


(*Ss, S*)-**5a**

(*S*)-*N*-((*S*,*E*)-3-cyano-2-ethyl-2-methyl-1-phenylbut-3-en-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*$_S$, *S*)-**5a**): According to the general procedure C, reaction was performed using *N*-*tert*-Butanesulfinyl ketimine (*S*$_S$, *S*)-**1a** (26.5 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether as eluent) afforded (*S*$_S$, *S*)-**5a** as a white solid (26.6 mg, 84%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for (*S*$_S$, *S*)-**5a**: R$_f$ = 0.25 (petroleum ether/ethyl acetate = 3/1); mp 56–57 °C; $[\alpha]^{25}_D$ = +140.8 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 3H), 7.16–7.07 (m, 2H), 6.11 (s, 1H), 5.79 (s, 1H), 2.00–1.86 (m, 1H), 1.79–1.66 (m, 1H), 1.37 (s, 3H), 1.23 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.5, 135.7, 131.6, 129.1, 128.1, 127.5, 126.7, 118.3, 56.7, 53.7, 29.4, 22.2, 20.1, 8.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{18}H_{25}N_2OS$ 317.1682; Found 317.1680.

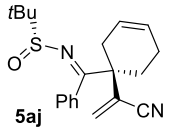

5ah

(*R*)-*N*-((*E*)-((*R*)-1-(1-cyanovinyl)cyclohex-3-en-1-yl)(phenyl)methylene)-2-methylpropane-2-sulfinamide (**5ah**): According to the general procedure C, reaction was performed using *N*-*tert*-Butanesulfinyl ketimine (*R*$_S$, *R*)-**1ah** (28.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5ah** as a colorless oil (29.3 mg, 86%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 20:1). Analytical data for **5ah** R$_f$ = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –145.2 (*c* 0.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.32 (m, 3H), 7.15–7.09 (m, 2H), 6.14 (s, 1H), 5.73 (s, 1H), 5.72–5.64 (m, 1H), 5.60–5.53 (m, 1H), 2.51–2.38 (m, 1H), 2.34–2.14 (m, 4H), 2.07–1.93 (m, 1H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.5, 135.7, 133.5, 129.6, 128.3, 128.0, 127.2, 125.0, 123.0, 118.1, 56.9, 52.2, 31.9, 29.1, 22.9, 22.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{25}N_2OS$ 341.1682; Found 341.1678.



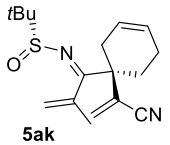
5ai

(*R*)-*N*-((*E*)-1-((*R*)-1-(1-cyanovinyl) cyclohex-3-en-1-yl)-2-methylallylidene)-2-methylpropane-2-sulfinamide (**5ai**): According to the general procedure C, reaction was performed using *N*-*tert*-Butanesulfinyl ketimine (R_S, *R*)-**1ai** (25.3 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5ai** as a colorless oil (25.7 mg, 83%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr = 12:1). Analytical data for **5ai** R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –194.3(*c* 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1H) (6.12), 5.84 (s, 1H), 5.70–5.59 (m, 2H), 5.18 (s, 1H), 4.83 (s, 1H), 2.59–2.33 (m, 2H), 2.25–2.05 (m, 3H), 1.97 (s, 4H), 1.25 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.9, 141.2, 132.7 (132.3), 127.4 (127.2), 125.1, 122.9 (123.2), 117.8, 117.1, 56.7, 51.1, 31.5, 28.6, 24.5, 22.5, 22.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{17}H_{25}N_2OS$ 305.1682; Found 305.1677.



5aj

(*R*)-*N*-((*E*)-((*S*)-1-(1-cyanovinyl)cyclohex-3-en-1-yl)(phenyl)methylene)-2-methylpropane-2-sulfinamide (**5aj**): According to the general procedure C, reaction was performed using *N*-*tert*-Butanesulfinyl ketimine (R_S, *S*)-**1aj** (28.9 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201 mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5aj** as a colorless oil (28.6 mg, 84%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5aj** R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –216.7 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 3H), 7.18–7.09 (m, 2H), 6.14 (s, 1H), 5.79 (s, 1H), 5.70–5.57 (m, 2H), 2.58–2.48 (m, 1H), 2.37–2.27 (m, 1H), 2.23–2.07 (m, 2H), 2.06–1.90 (m, 2H), 1.24 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.7, 135.4, 132.6, 129.2, 128.0, 127.1, 126.8, 124.9, 123.1, 118.0, 57.0, 52.0, 31.6, 28.8, 22.4, 22.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{25}N_2OS$ 341.1682; Found 341.1676.



5ak

(*R*)-*N*-((*E*)-1-((*S*)-1-(1-cyanovinyl)cyclohex-3-en-1-yl)-2-methylallylidene)-2-methylpropane-2-sulfinamide (**5ak**): According to the general procedure C, reaction was performed using *N*-*tert*-Butanesulfinyl ketimine (R_S, *S*)-**1ak** (25.3 mg, 0.100 mmol, 1.0 equiv), *t*BuOK in THF (1.0 M, 120 μL, 0.120 mmol, 1.2 equiv), **4a** (41.6 mg, 0.201

mmol, 2.0 equiv), DBU (60.9 mg, 0.402 mmol, 4.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether as eluent) afforded **5ak** as a colorless oil (25.9 mg, 85%). Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (dr > 20:1). Analytical data for **5ak** R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = –270.6 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.85 (s, 1H), 5.65 (s, 2H), 5.18 (s, 1H), 4.85 (s, 1H), 2.57–2.48 (m, 1H), 2.44–2.35 (m, 1H), 2.21–2.10 (m, 1H), 2.11–2.03 (m, 2H), 1.98 (s, 4H), 1.25 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.6, 141.2, 132.3, 127.2, 125.2, 123.2, 117.9, 116.8, 56.8, 51.0, 31.6, 28.7, 24.3, 22.44, 22.41; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{25}N_2OS$ 305.1682; Found 305.1678.

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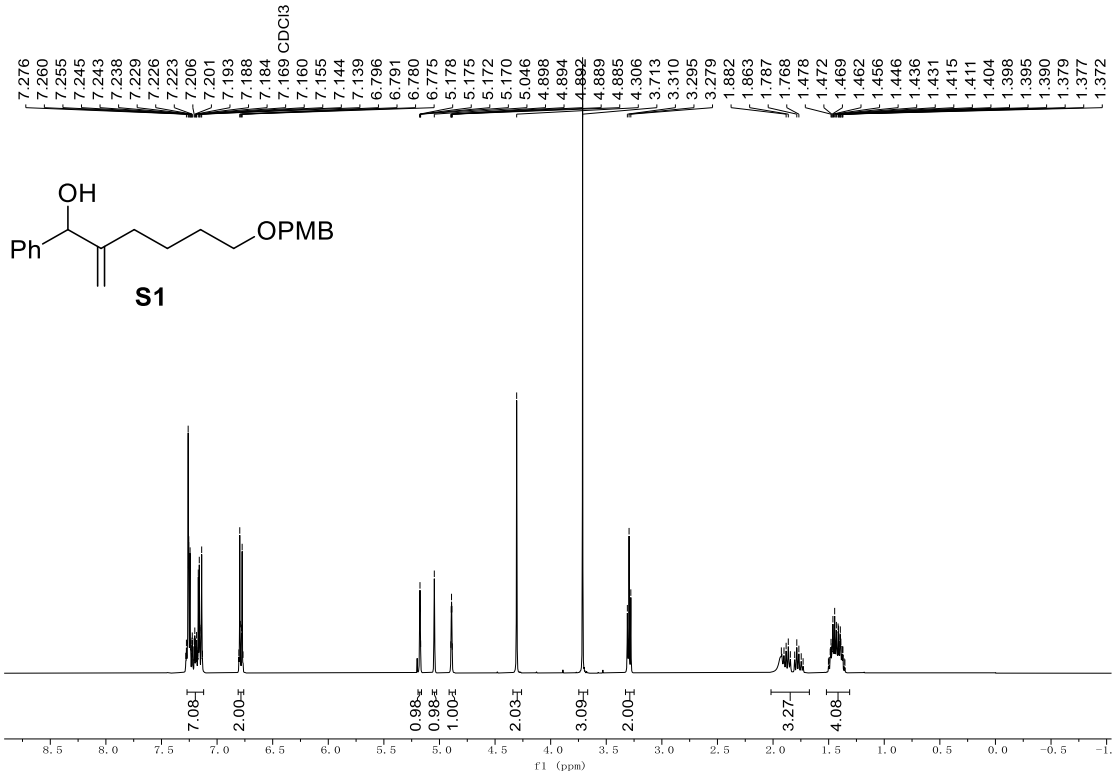
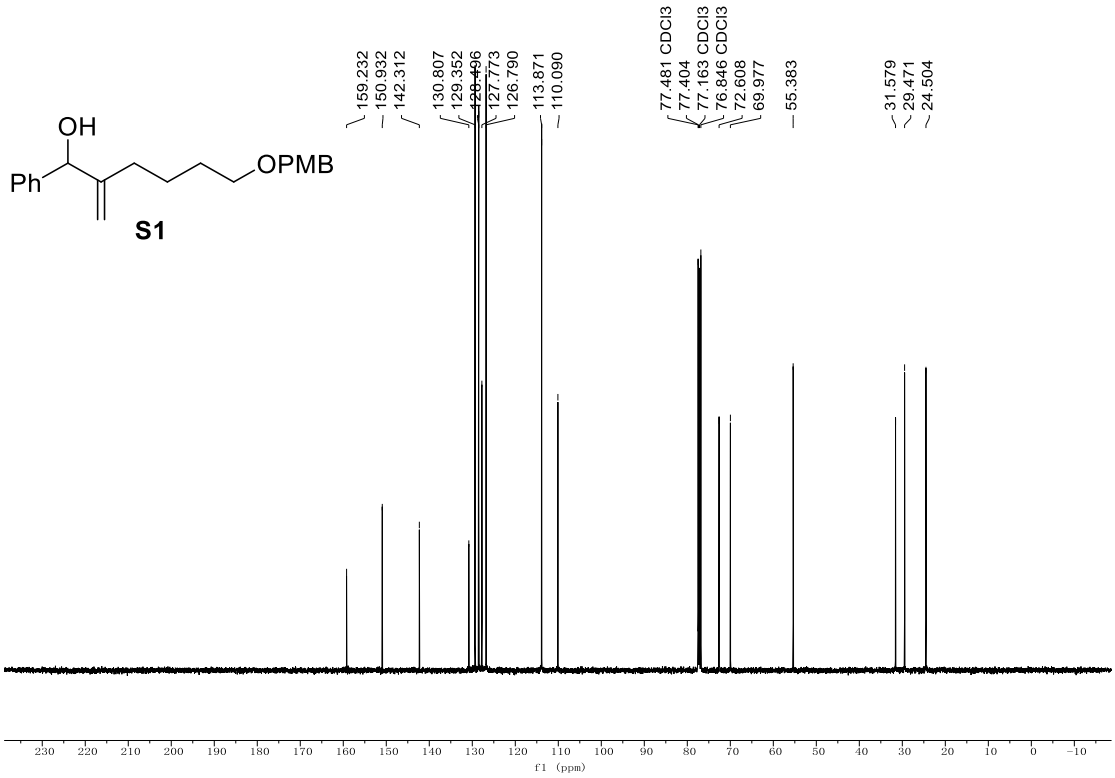
(S6) Sheng, S.-R.; Zhou, W.; Zhong, M.-H.; Liu, X.-L.; Song, C.-S. Facile Method for Solid-Phase Synthesis of Vinyl Sulfones Using Polystyrene-Supported Selenomethyl Aryl Sulfone. *Synth. Commun.* **2005**, *35*, 815.

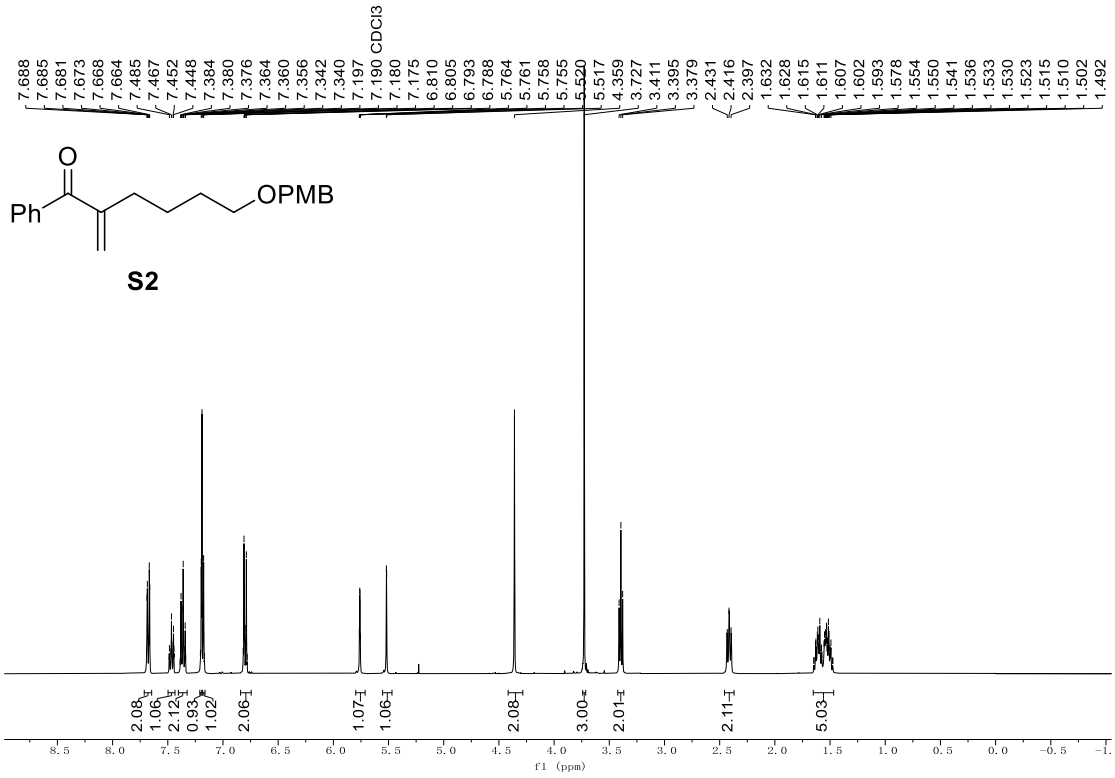
^{1}H and ^{13}C NMR spectra for S1-S6



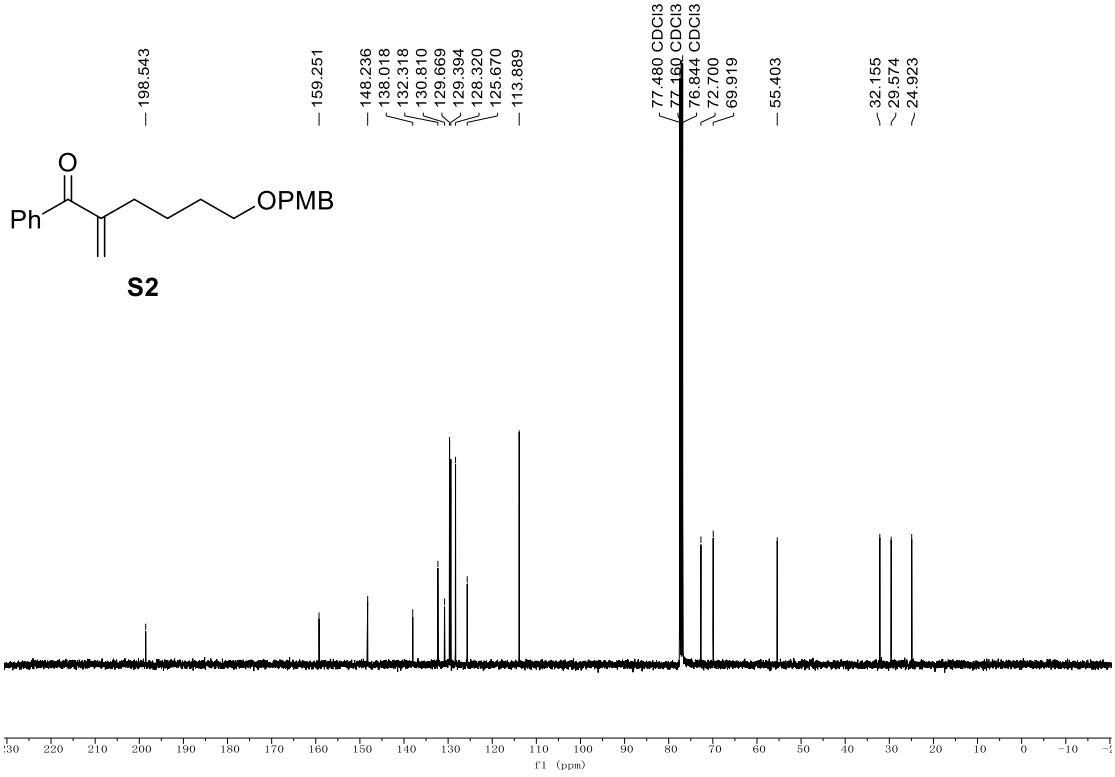
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S1**



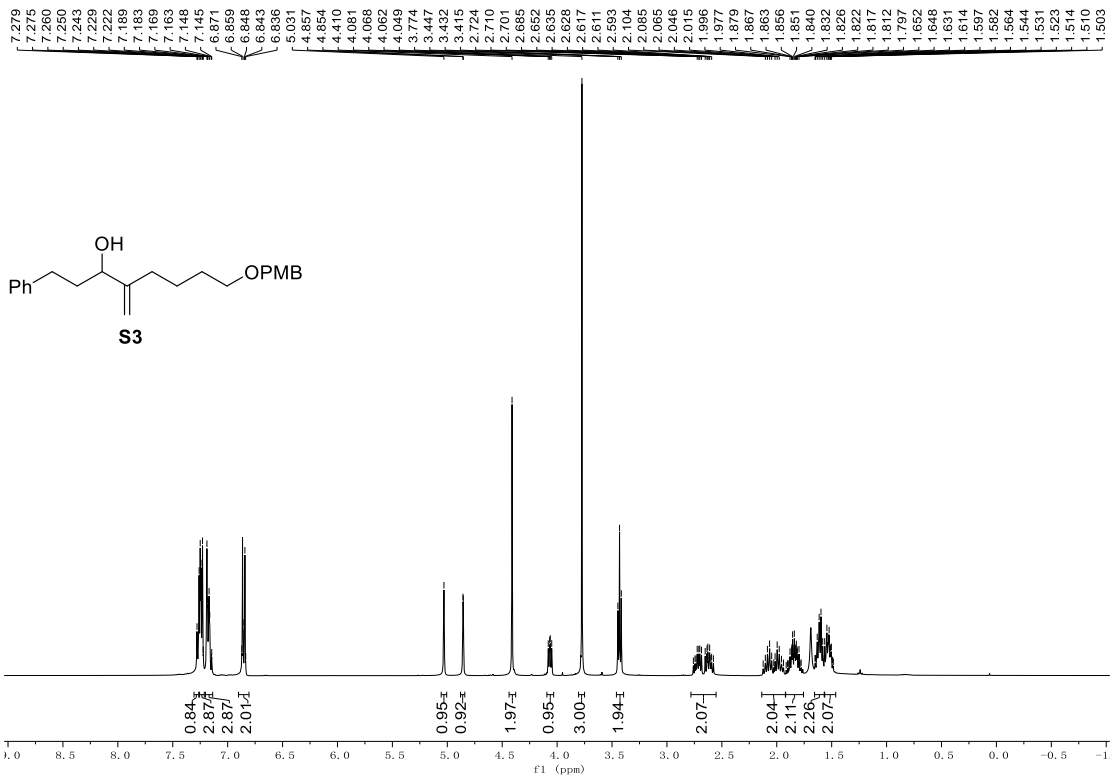
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S1**



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S2**



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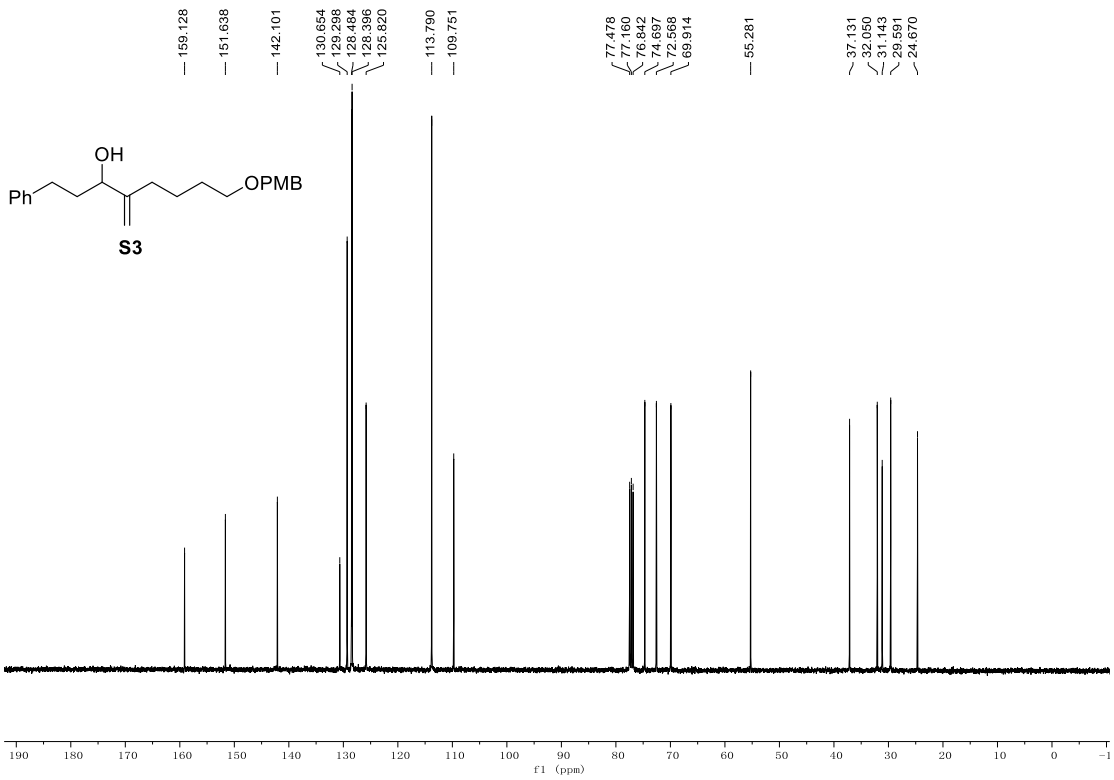

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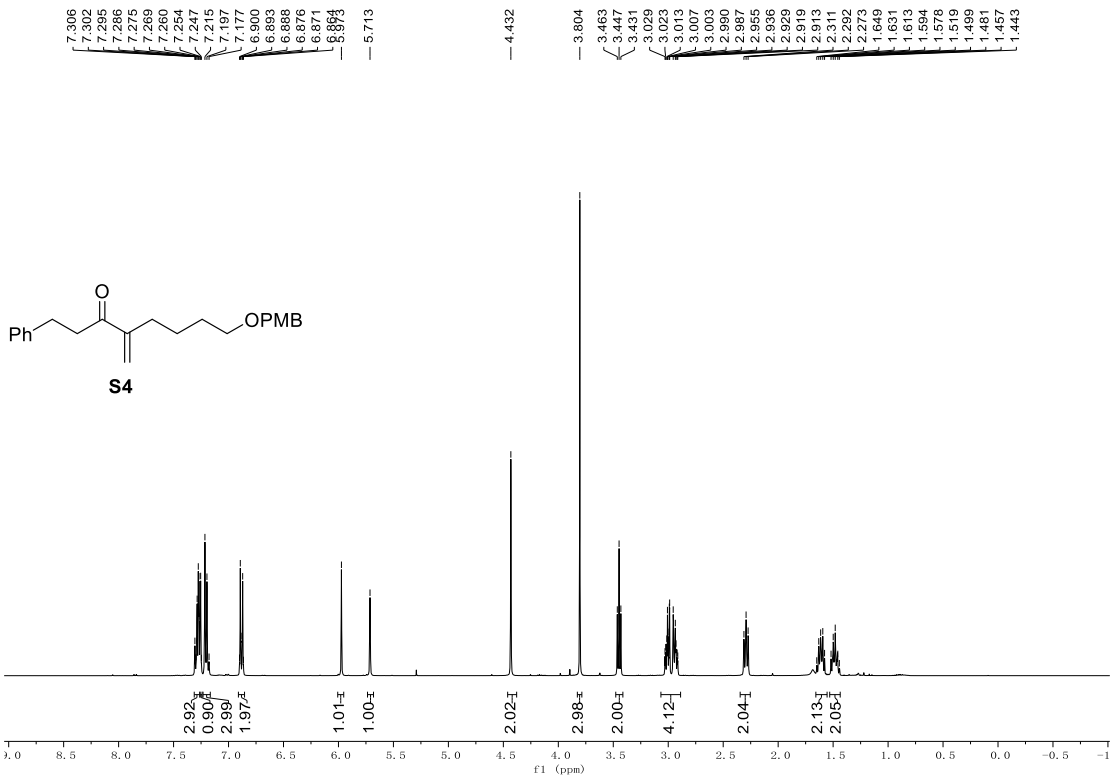
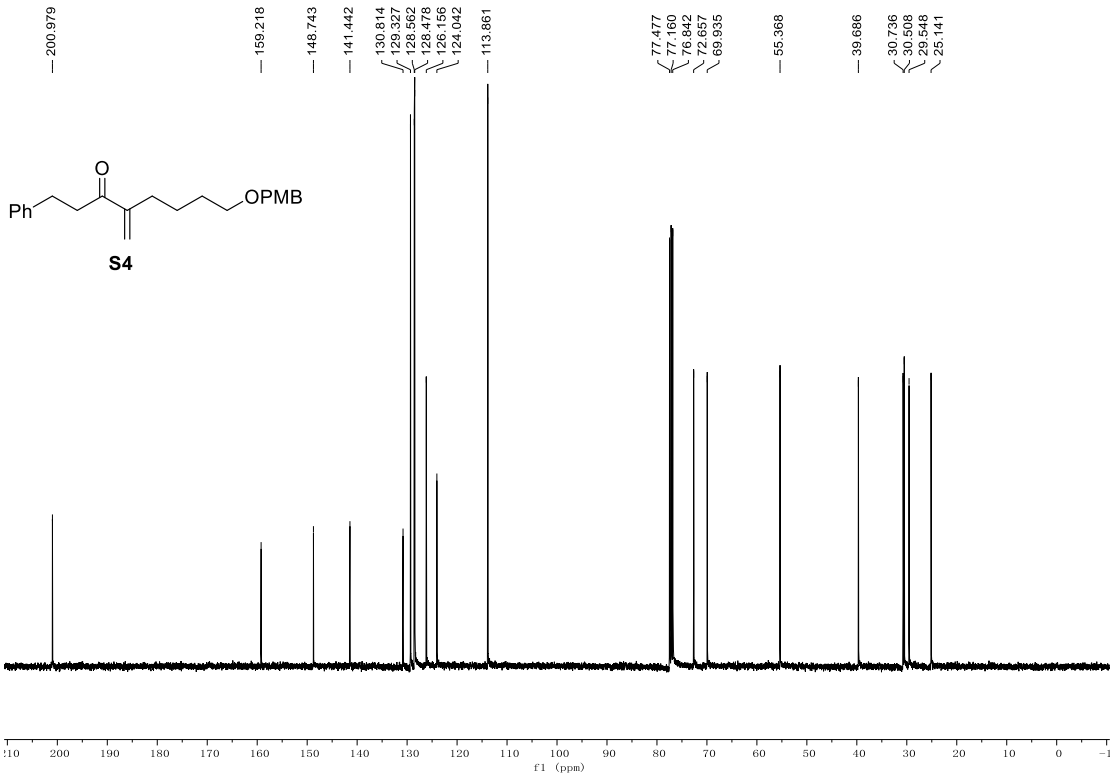
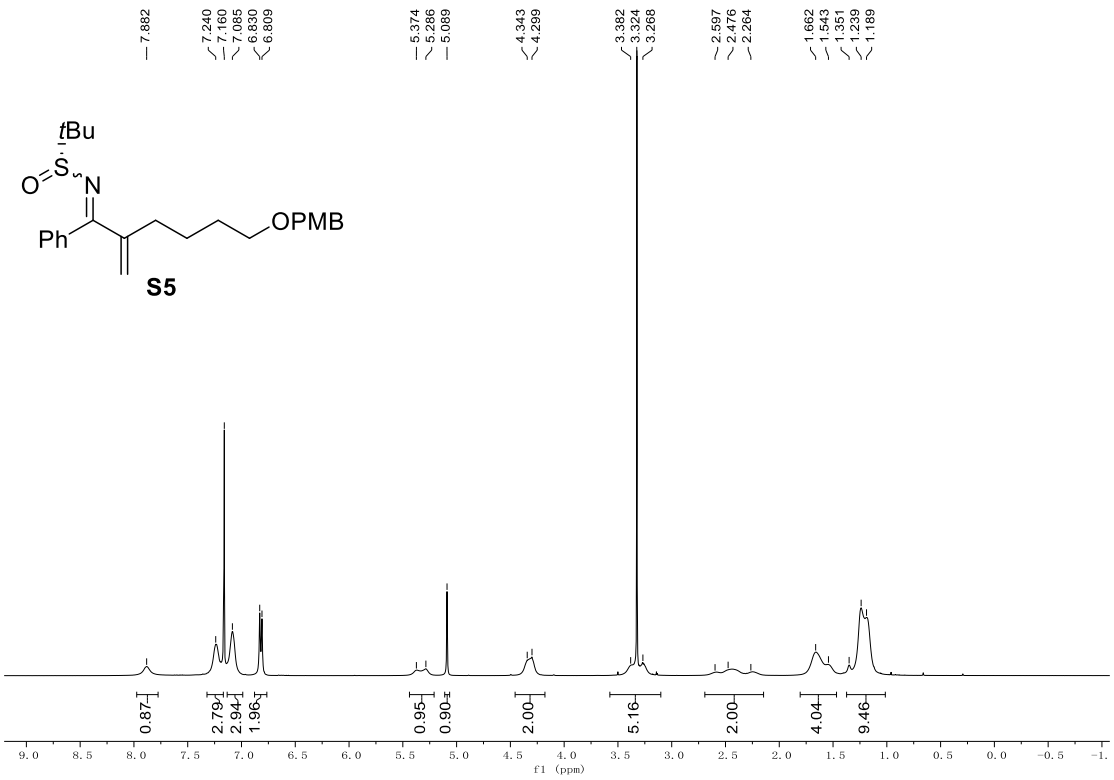


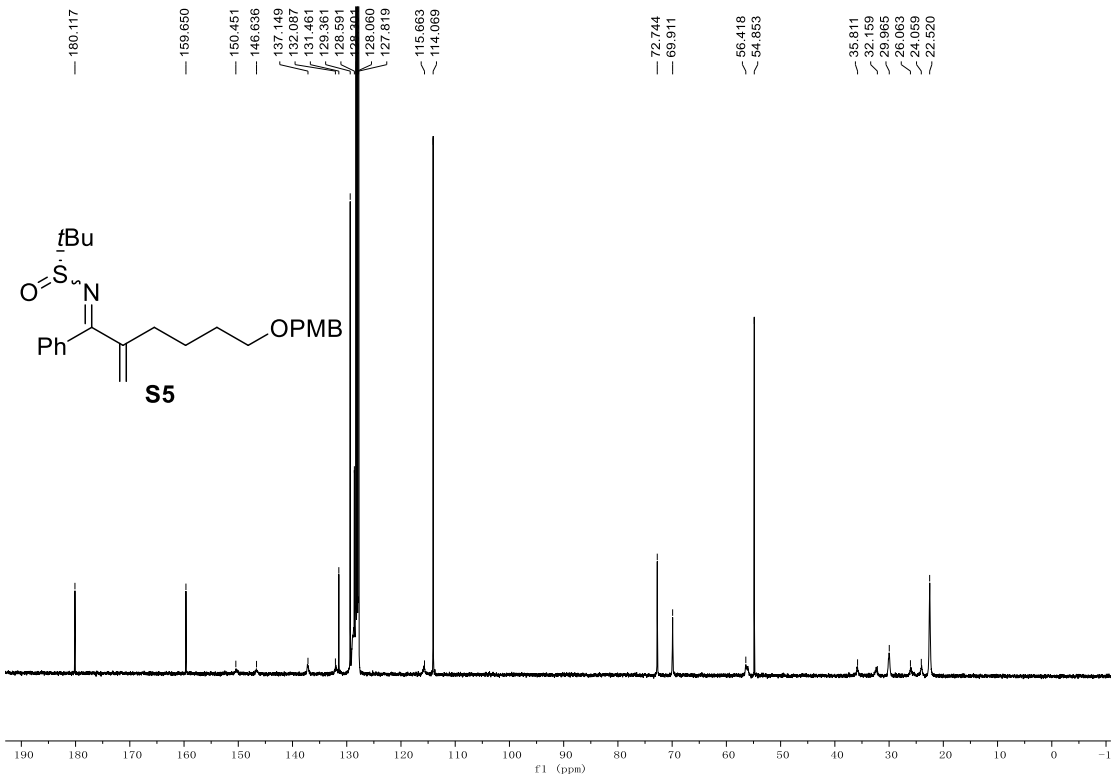
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S4**



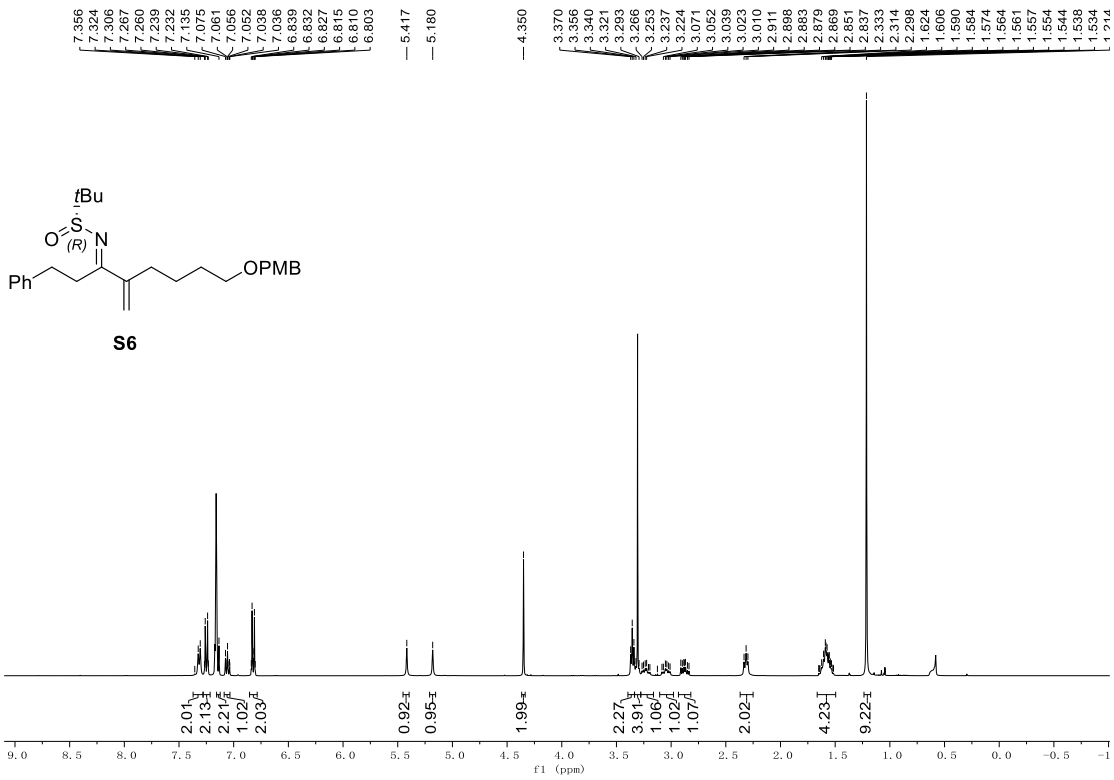
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S4**



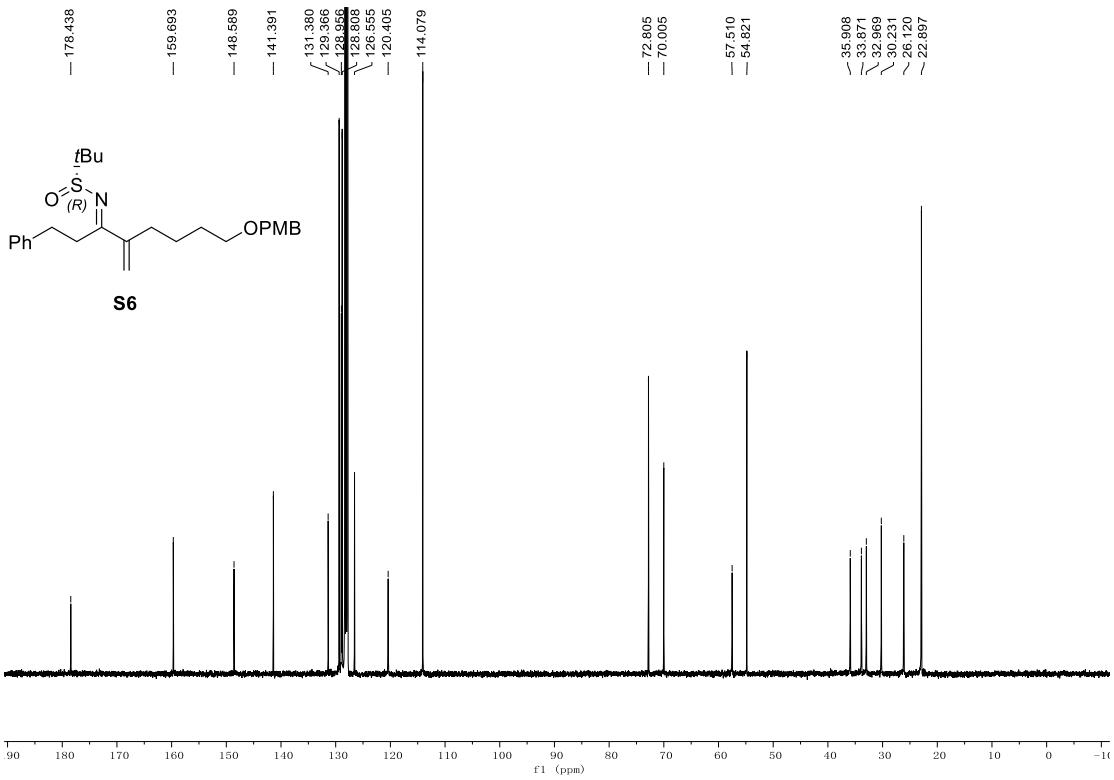
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **S5** (mixture of imino *Z*/*E* isomers)



^{13}C NMR spectrum (C_6D_6, 100 MHz) of **S5** (mixture of imino *Z*/*E* isomers)

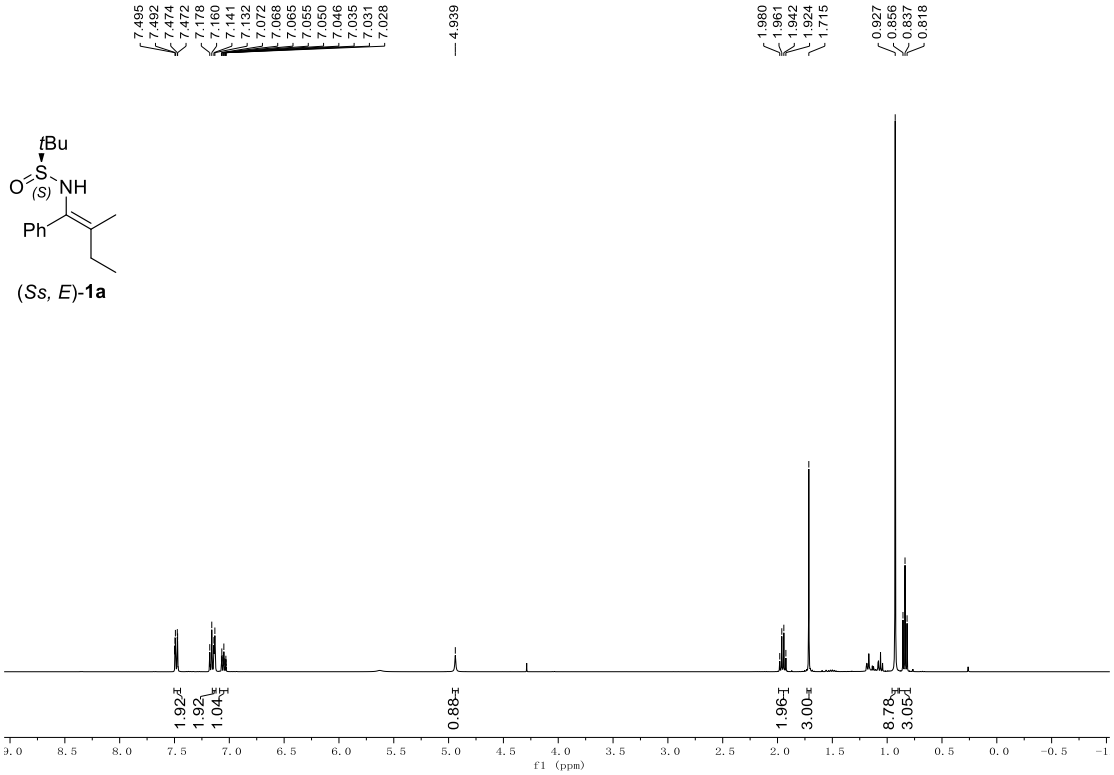


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S6**

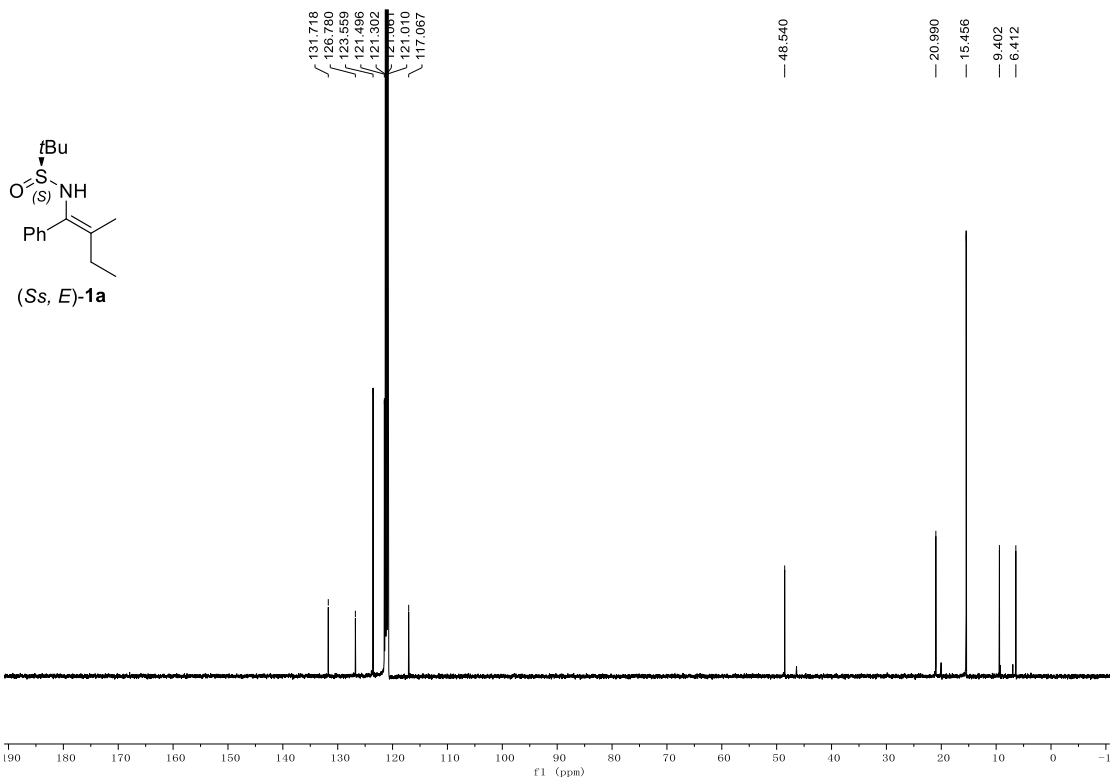


^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S6**

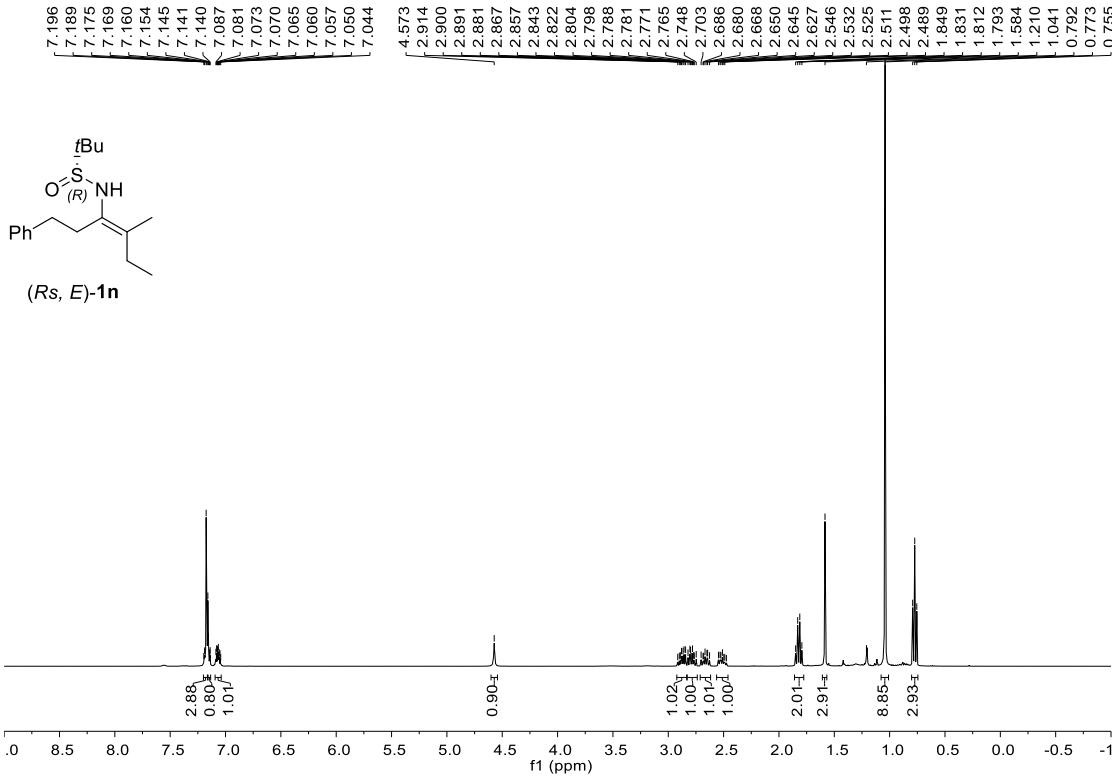
^{1}H and ^{13}C NMR spectra for enesulfinamides (S*s, E*)-1a, (*Rs, E*)-1n, 1x, 1y



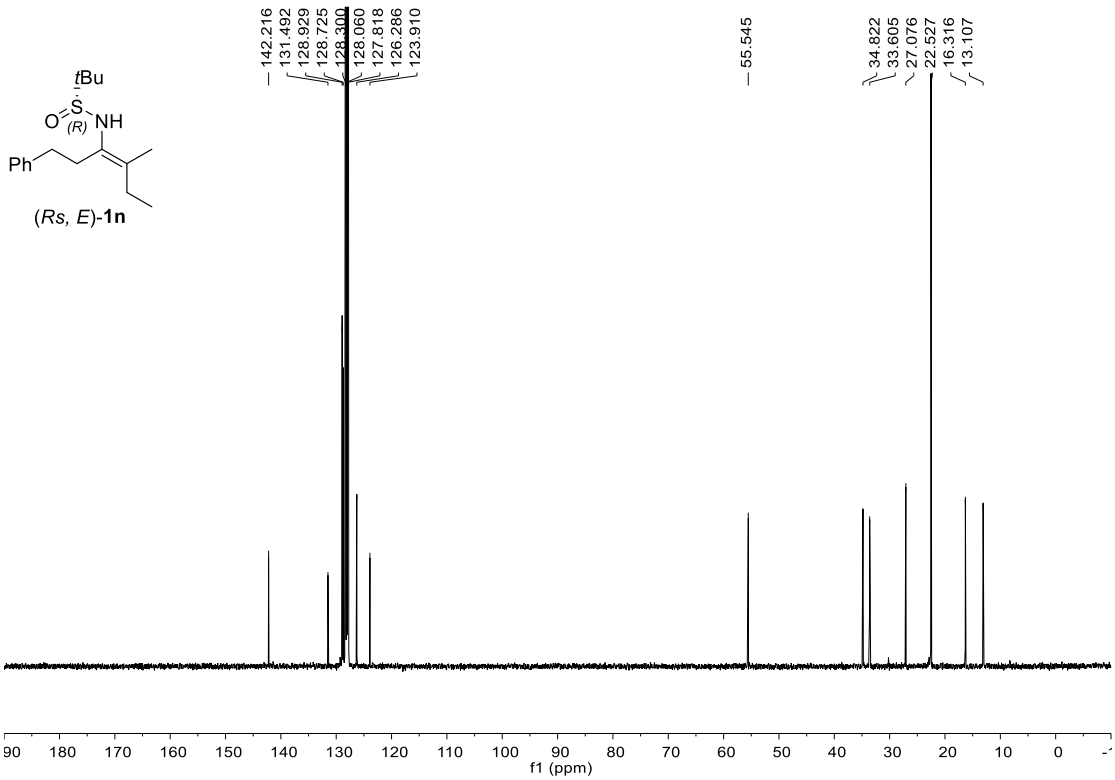
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Ss, E*)-**1a**



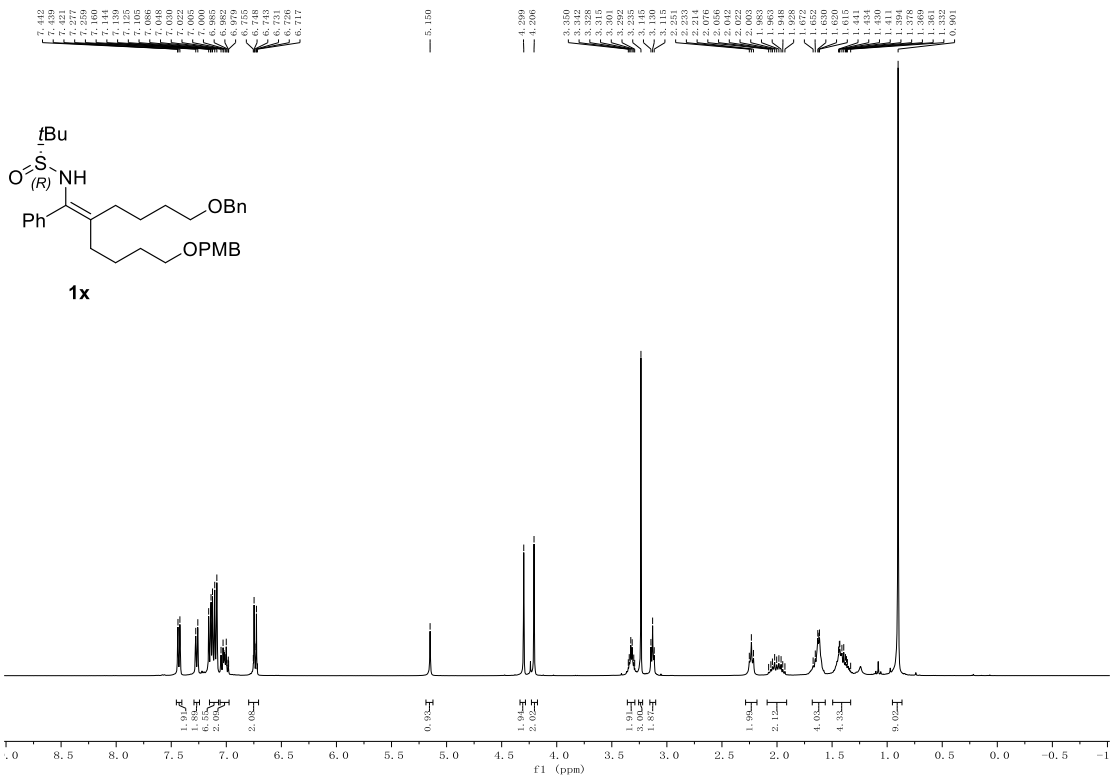
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Ss, E*)-**1a**



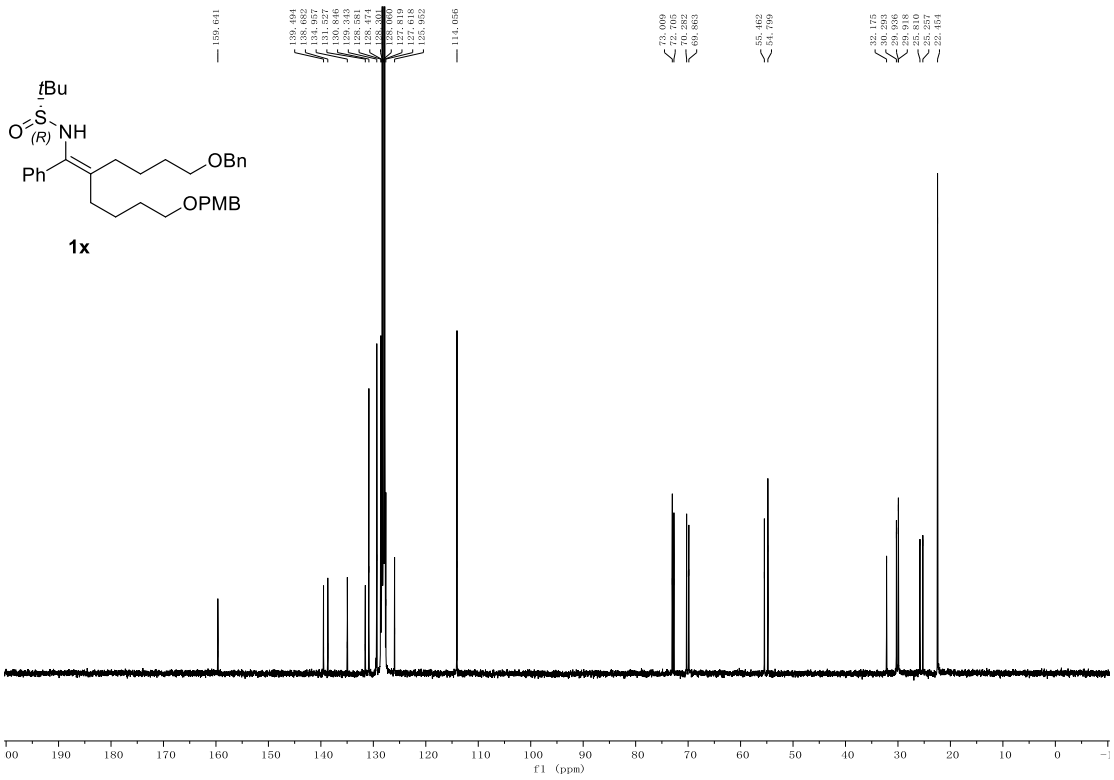
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Rs, E*)-**1n**



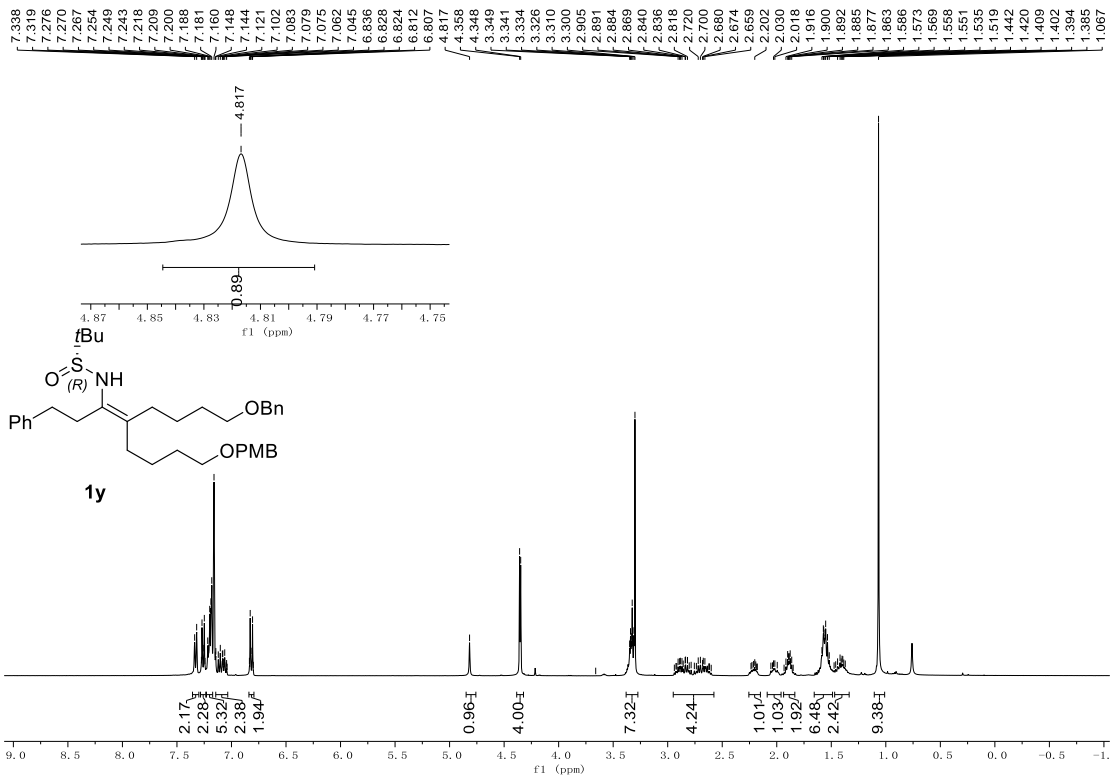
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Rs, E*)-**1n**



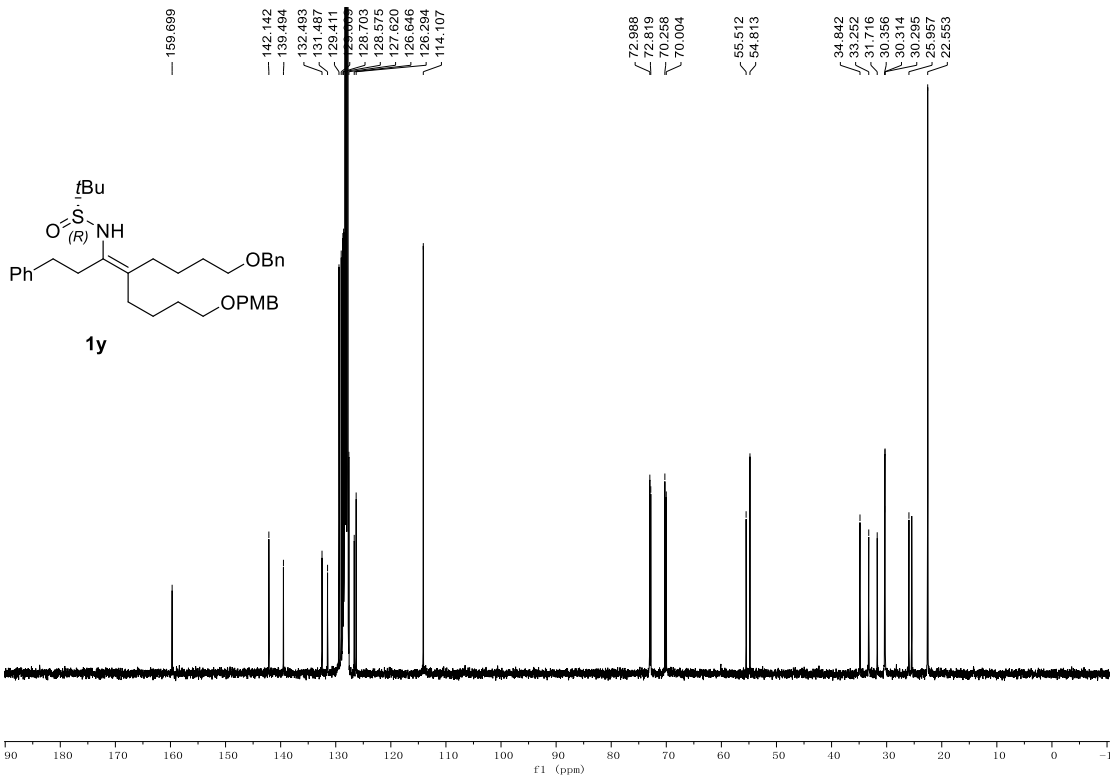
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **1x**



^{13}C NMR spectrum (C_6D_6, 100 MHz) of **1x**

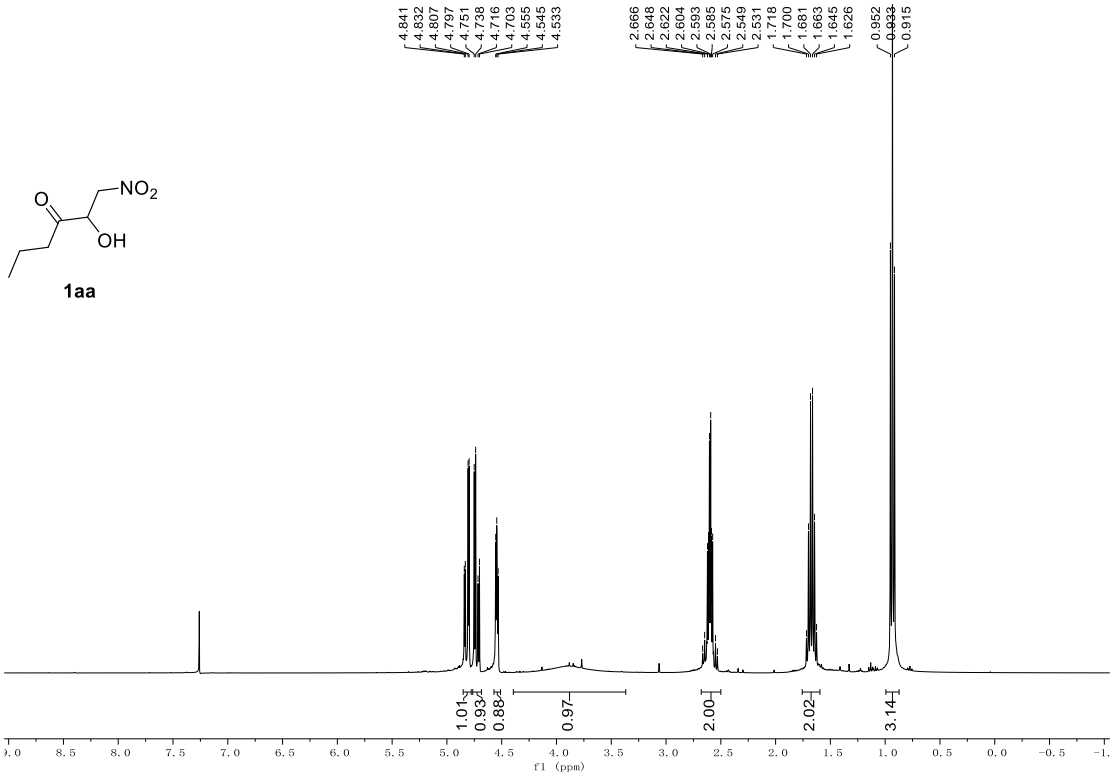


^{1}H NMR spectrum (C_6D_6, 400 MHz) of **1y**

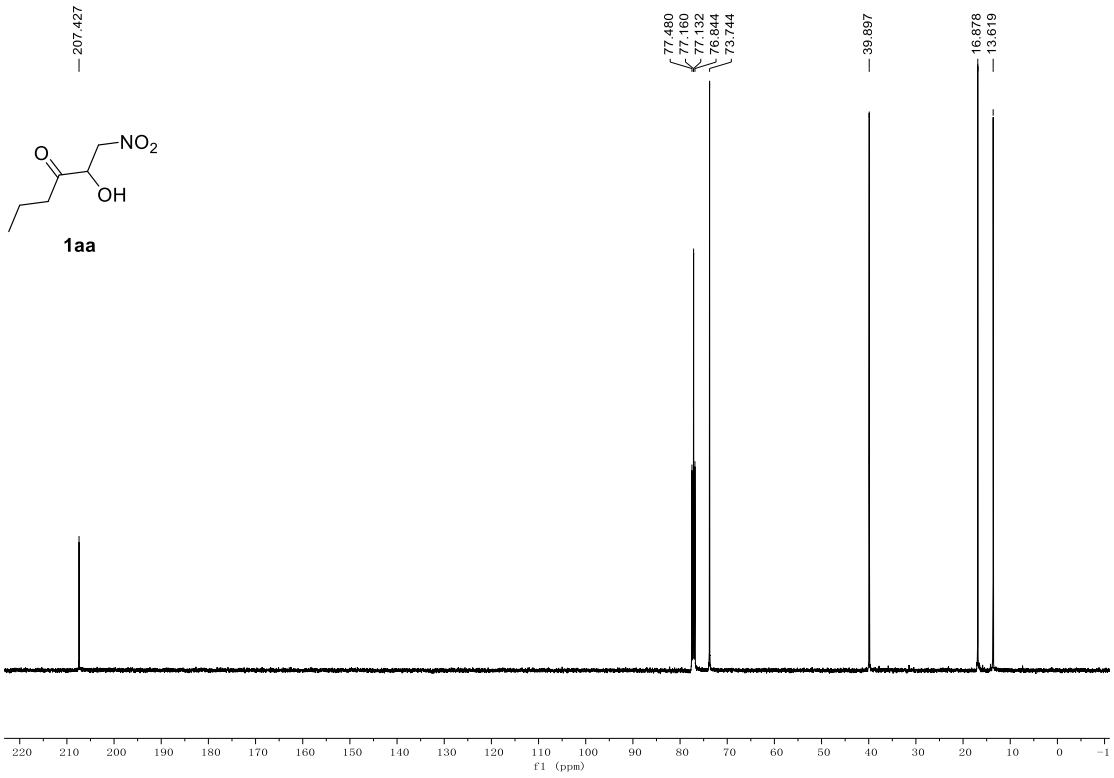


^{13}C NMR spectrum (C_6D_6, 100 MHz) of **1y**

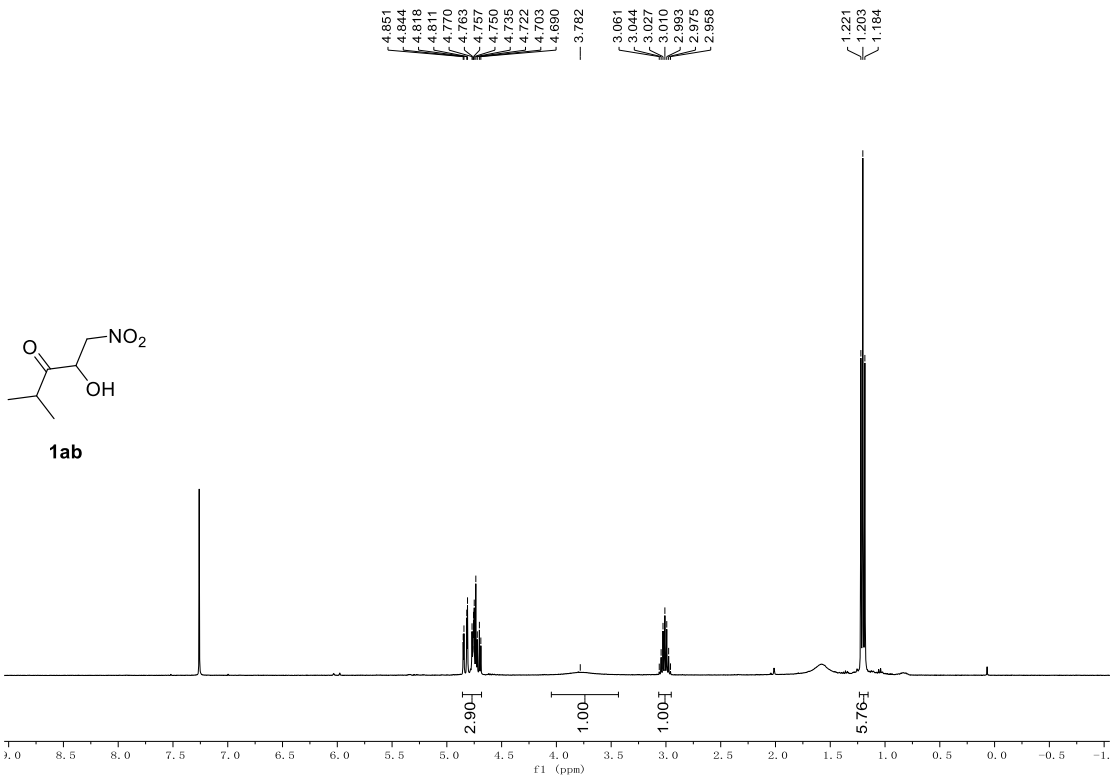
^{1}H and ^{13}C NMR spectra for compounds 1aa–1ab, 2g–2h



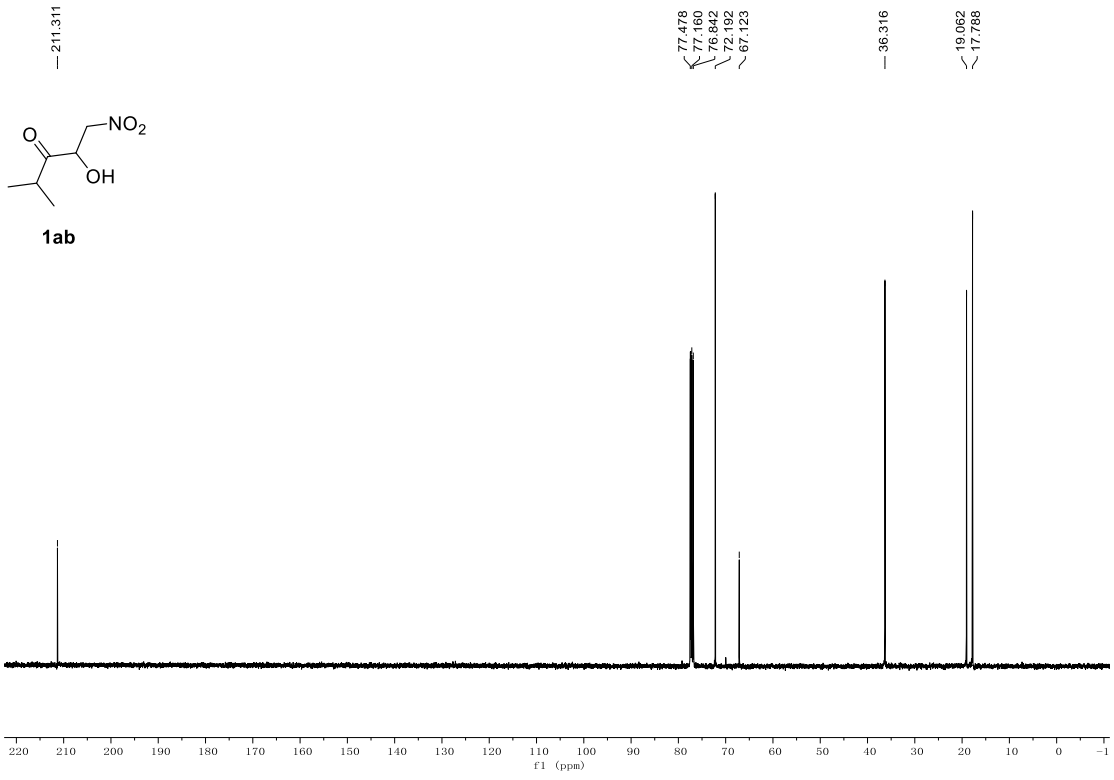
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1aa**



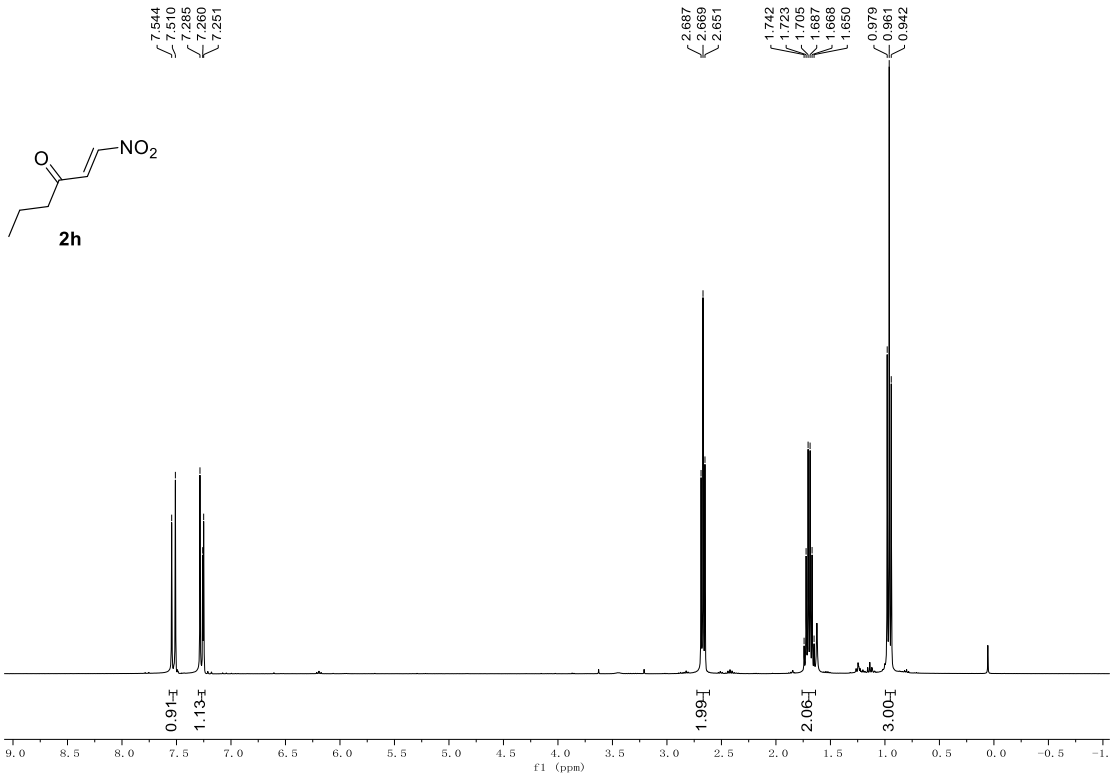
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1aa**



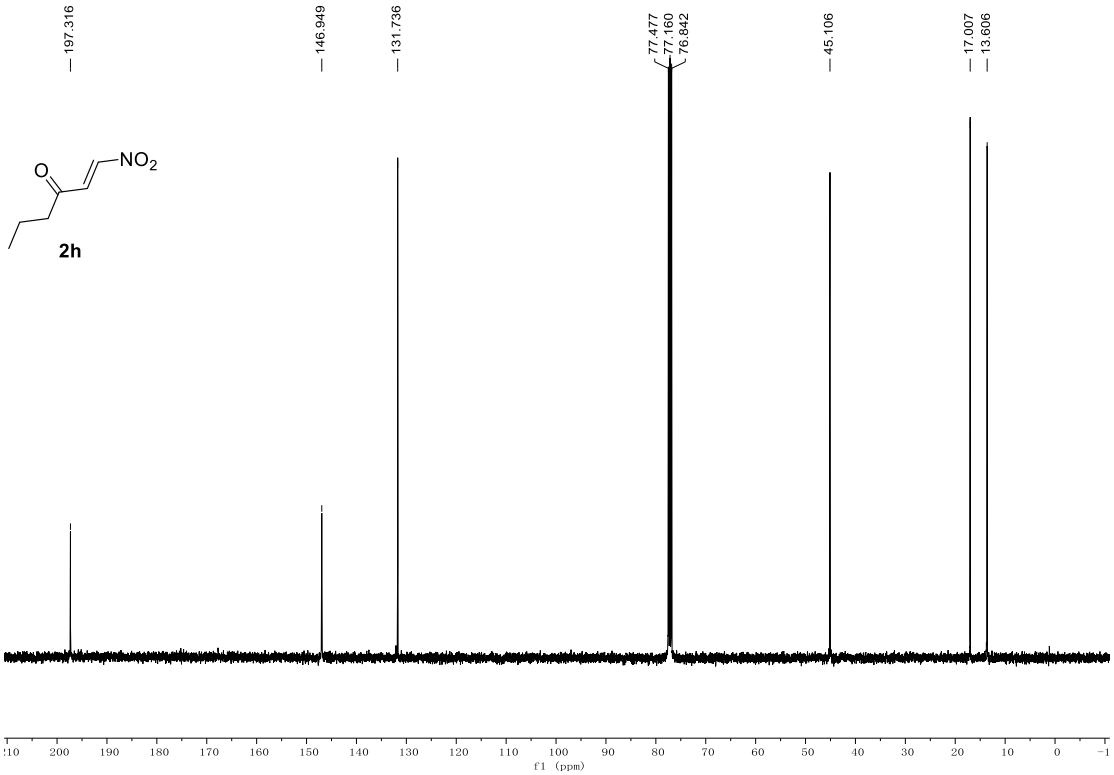
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1ab**



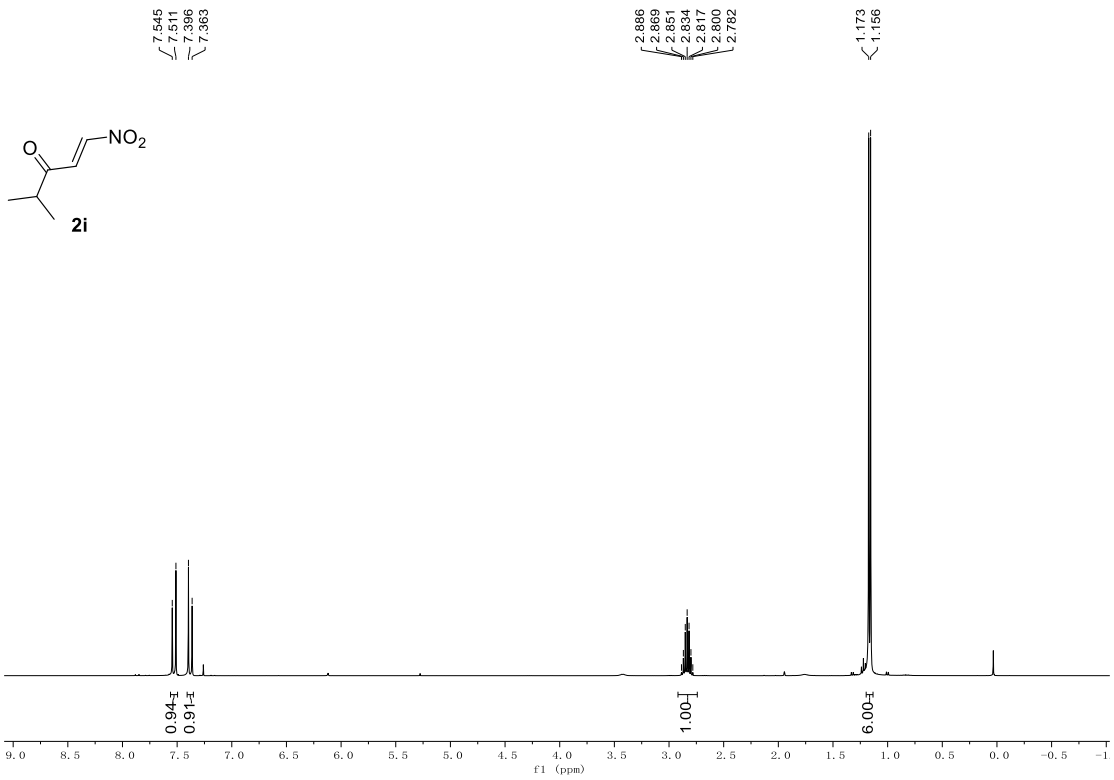
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1ab**



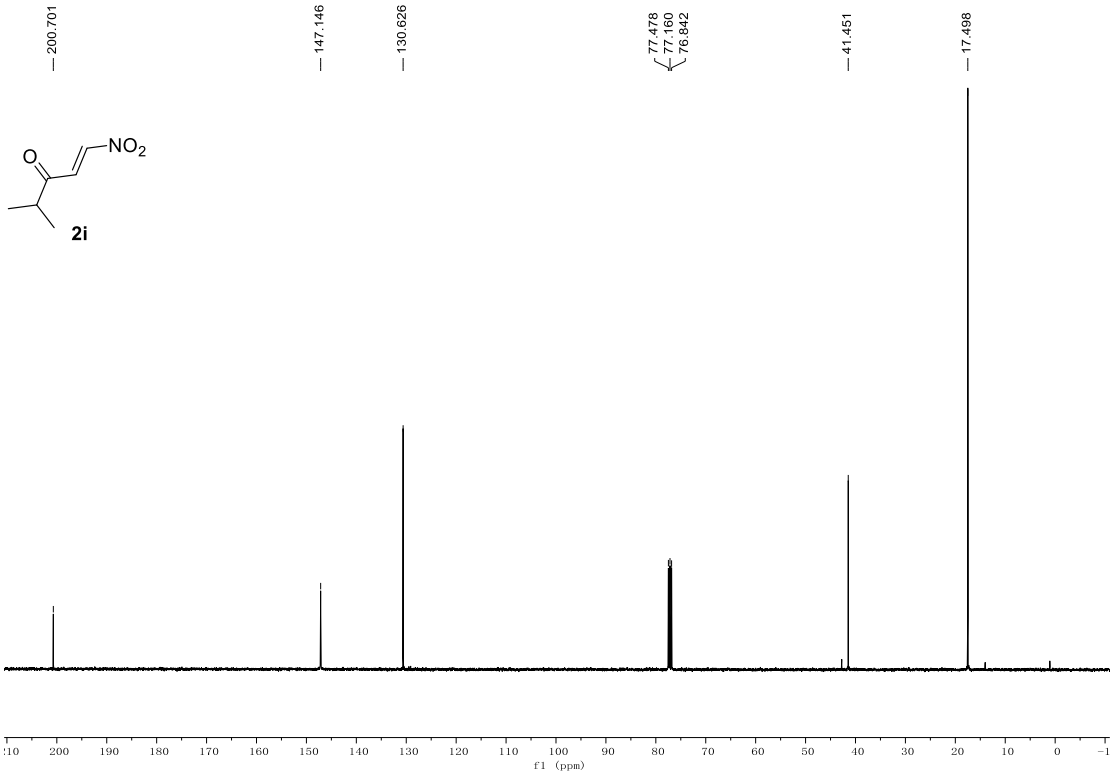
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2h**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2h**

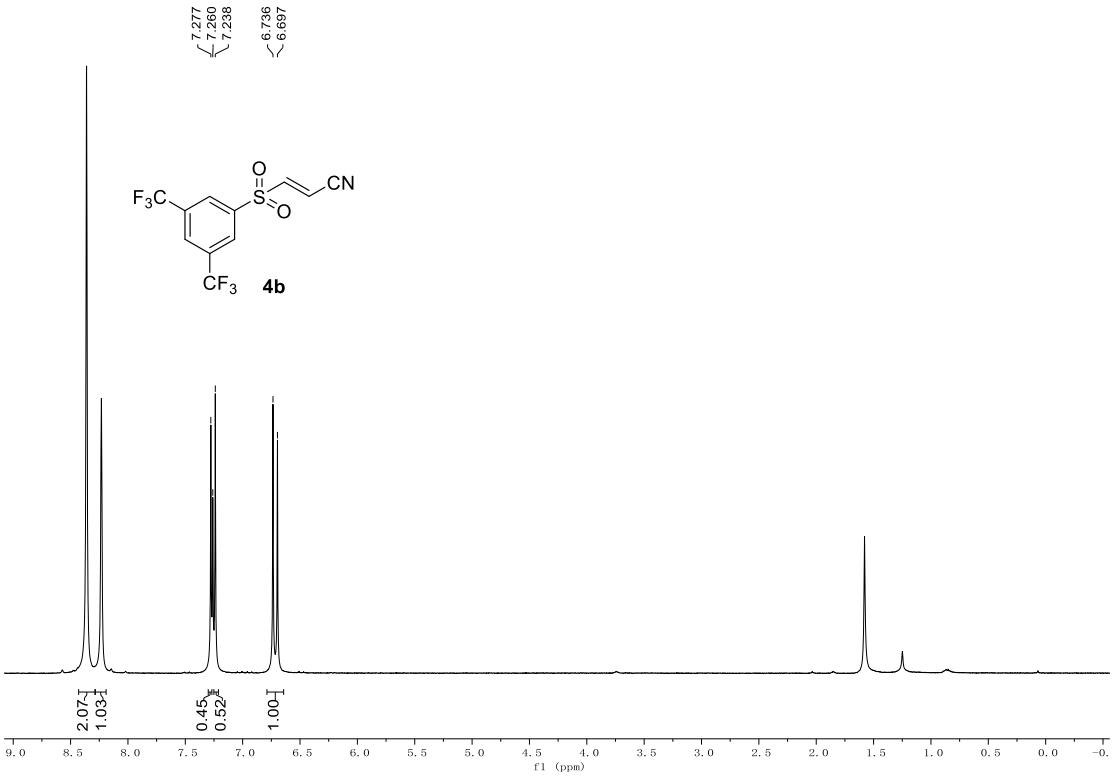


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2i**

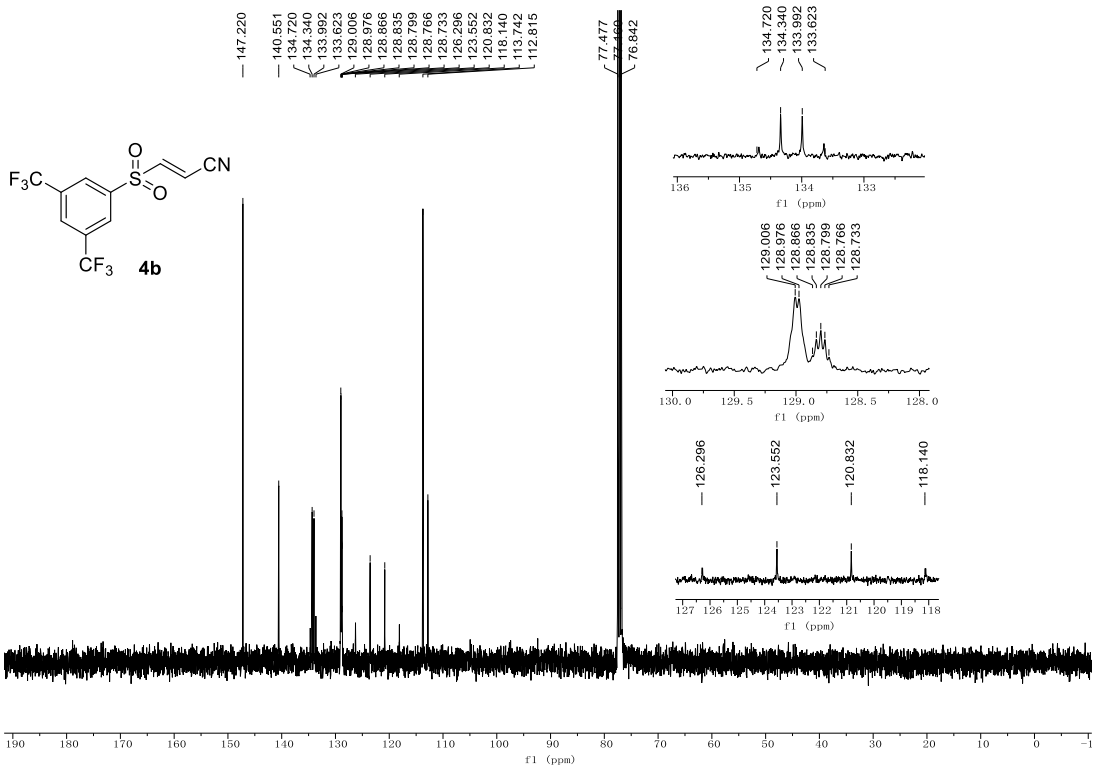


^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2i**

^{1}H and ^{13}C NMR spectra for β-sulfonyl acrylonitrile 4b

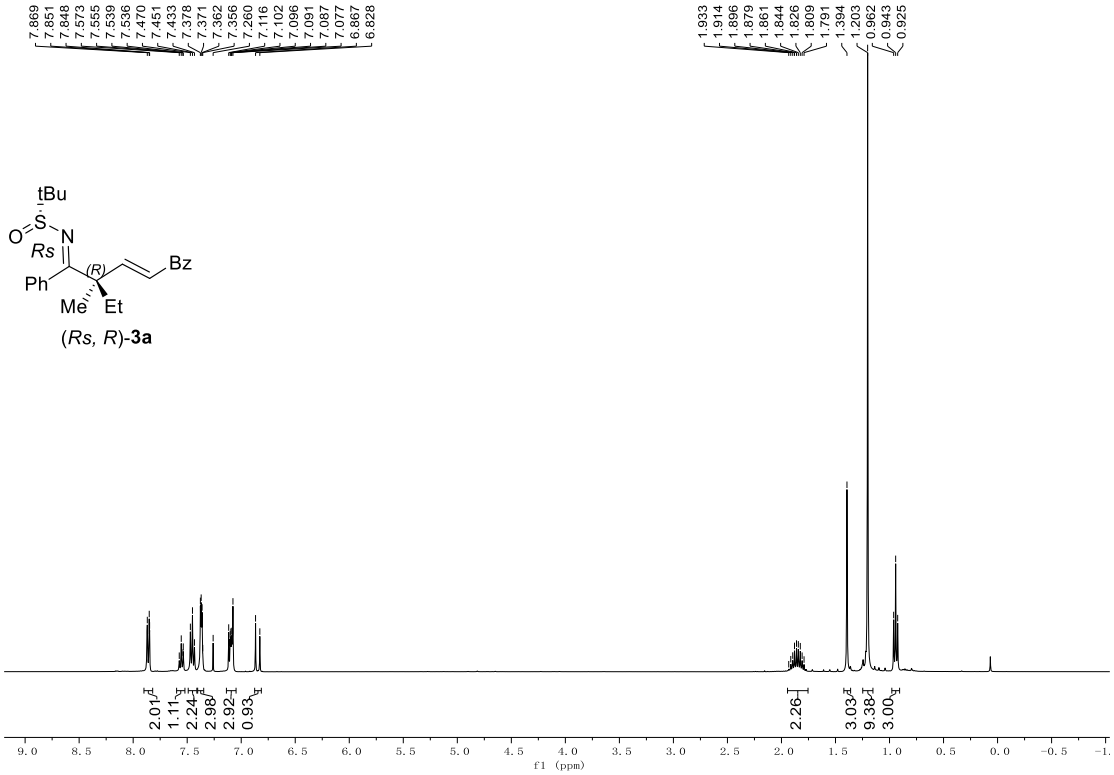


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4b**

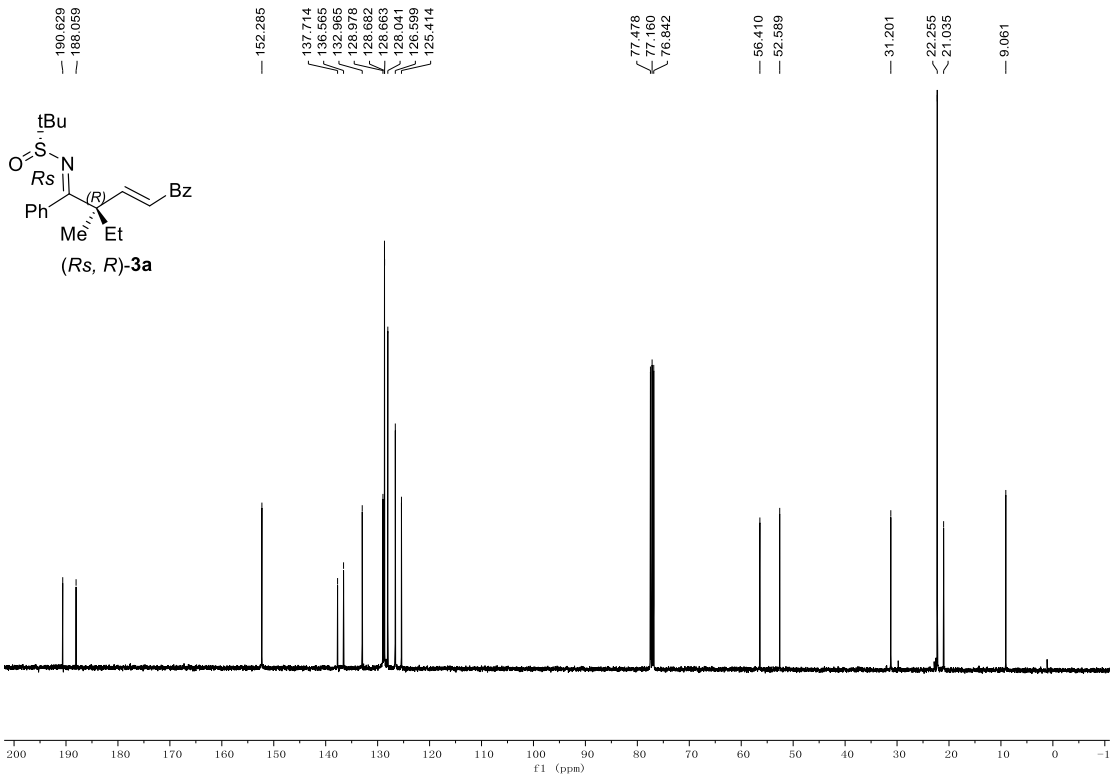


^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4b**

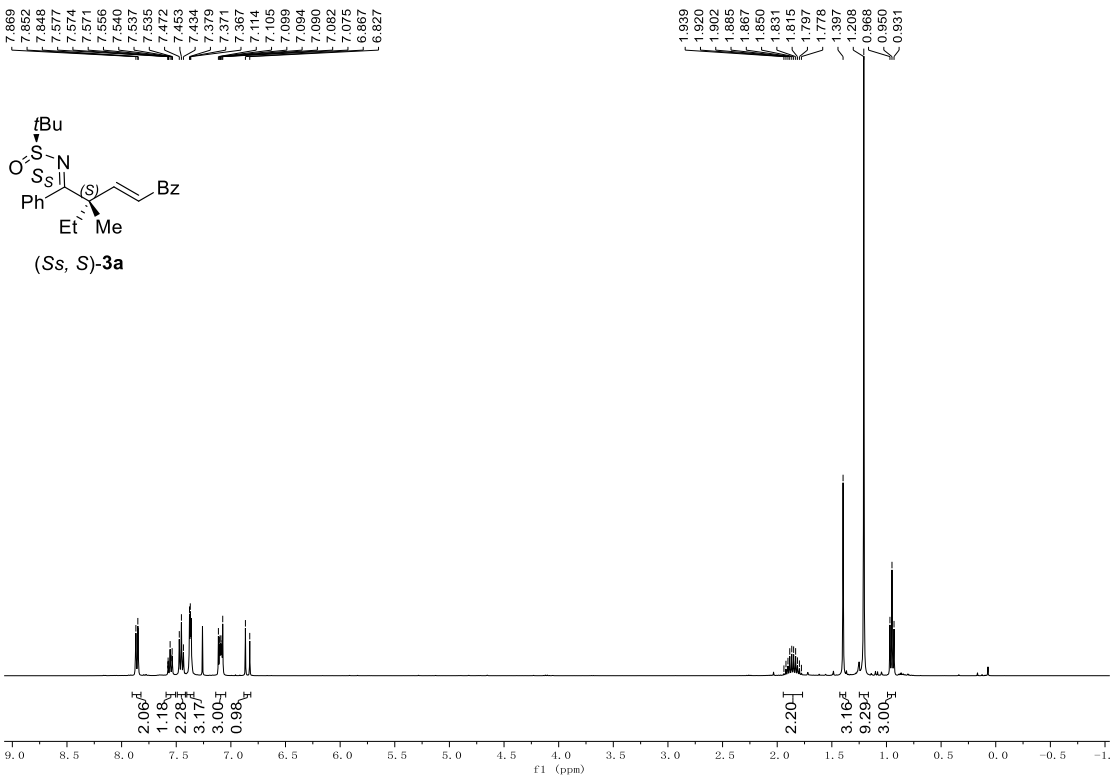
^{1}H and ^{13}C NMR spectra of 1,5- and 1,4-dicarbonyl derivatives



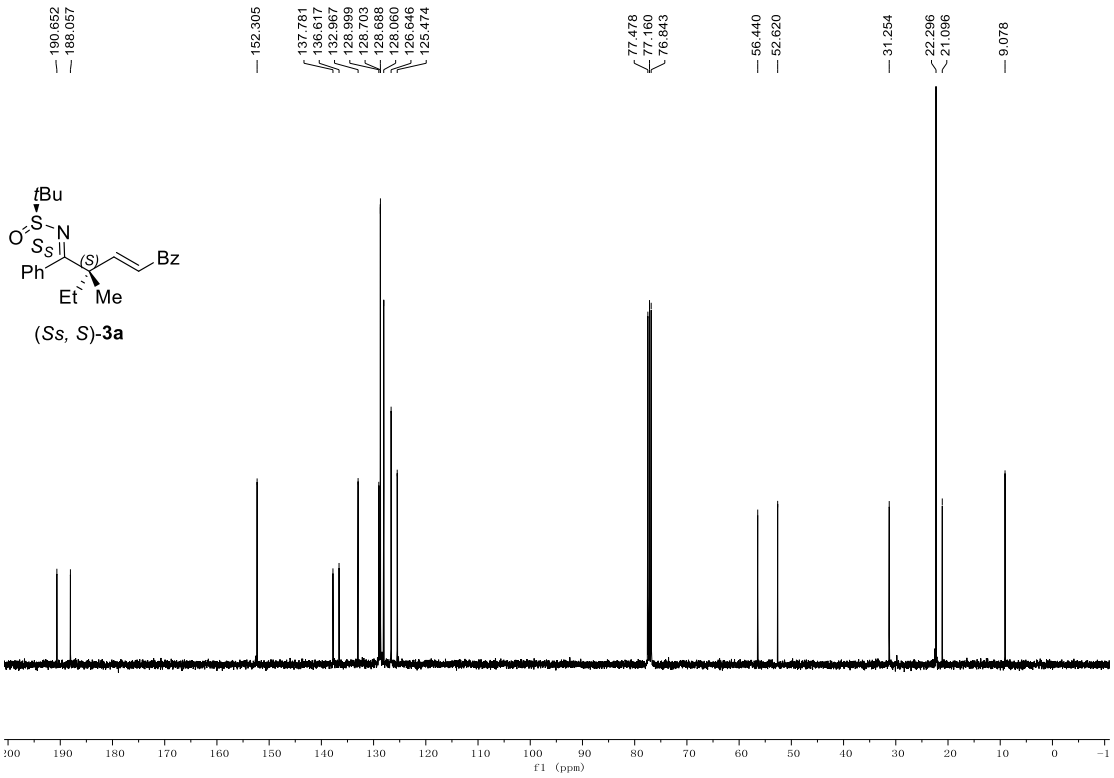
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *R*)-**3a**



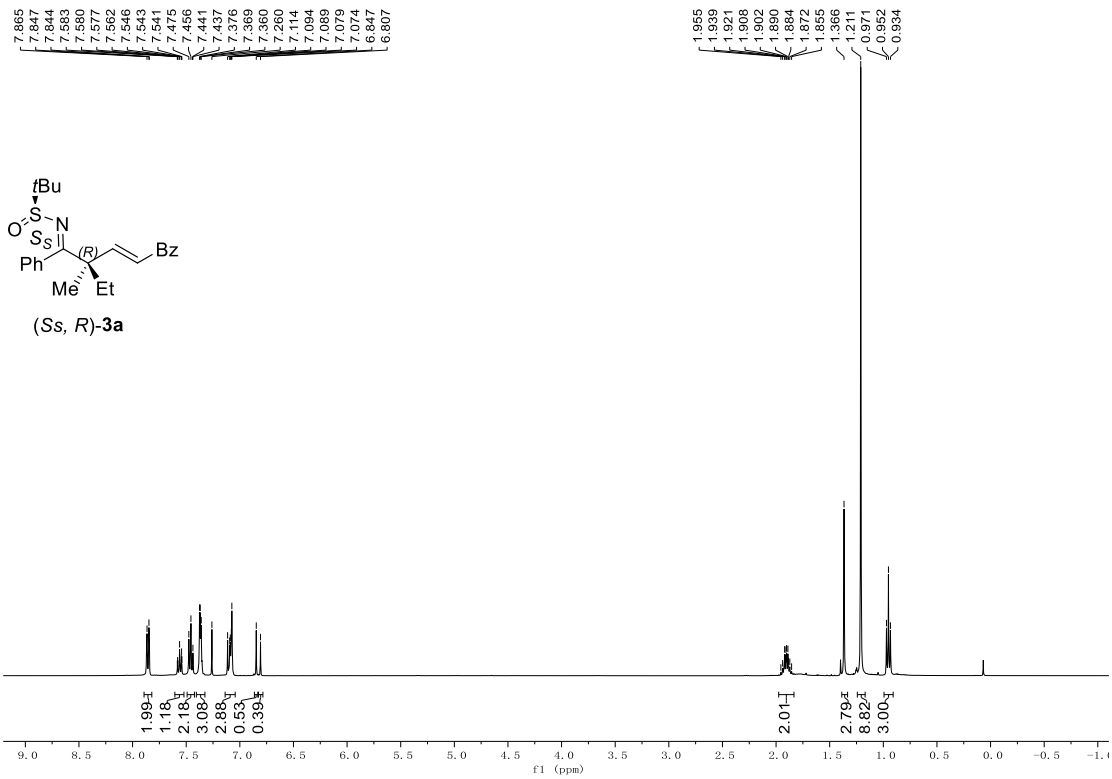
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *R*)-**3a**



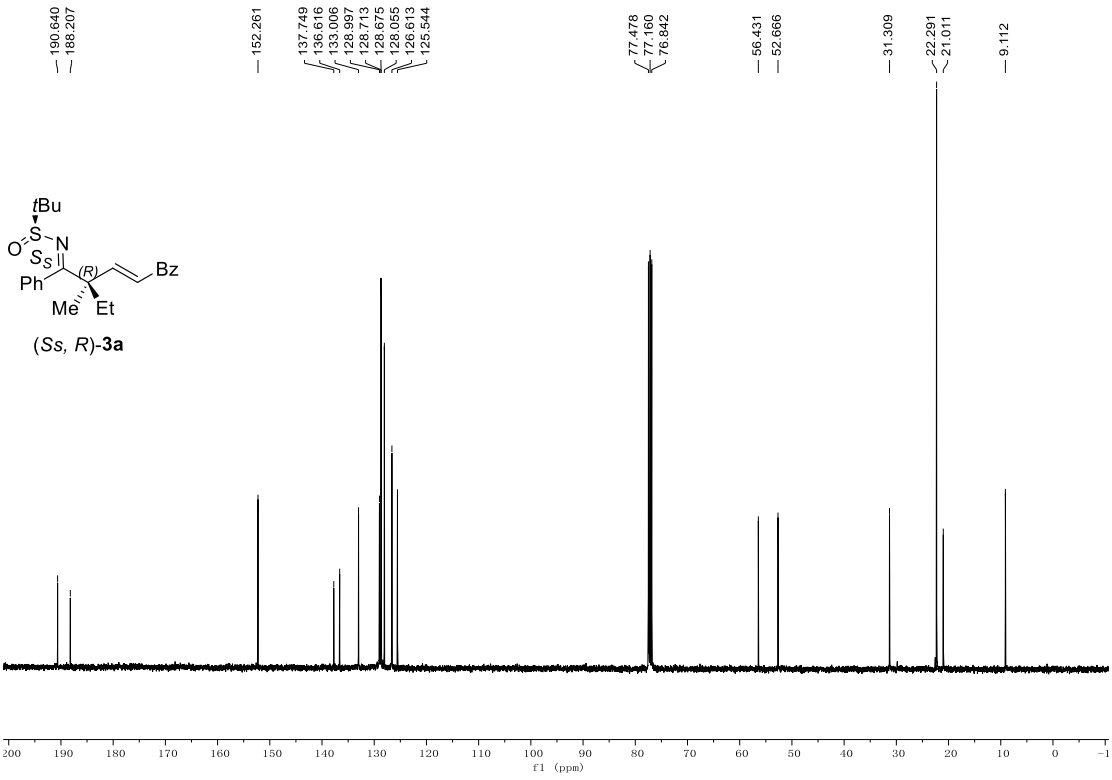
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *S*)-**3a**



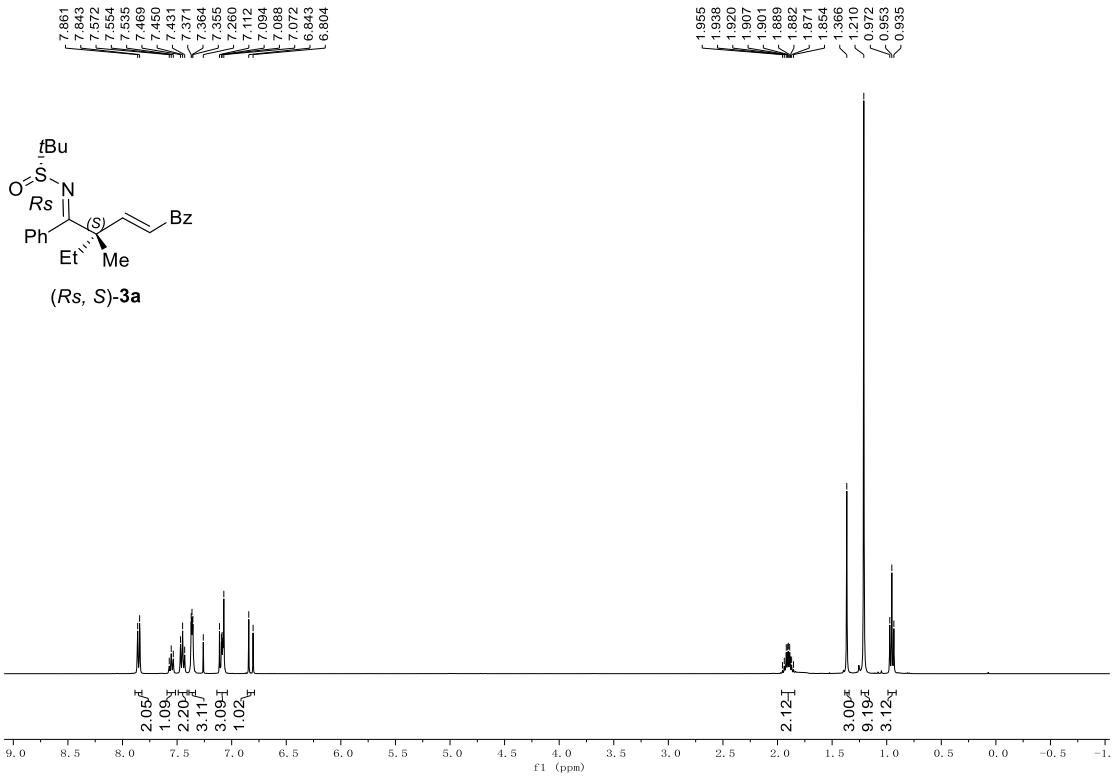
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *S*)-**3a**



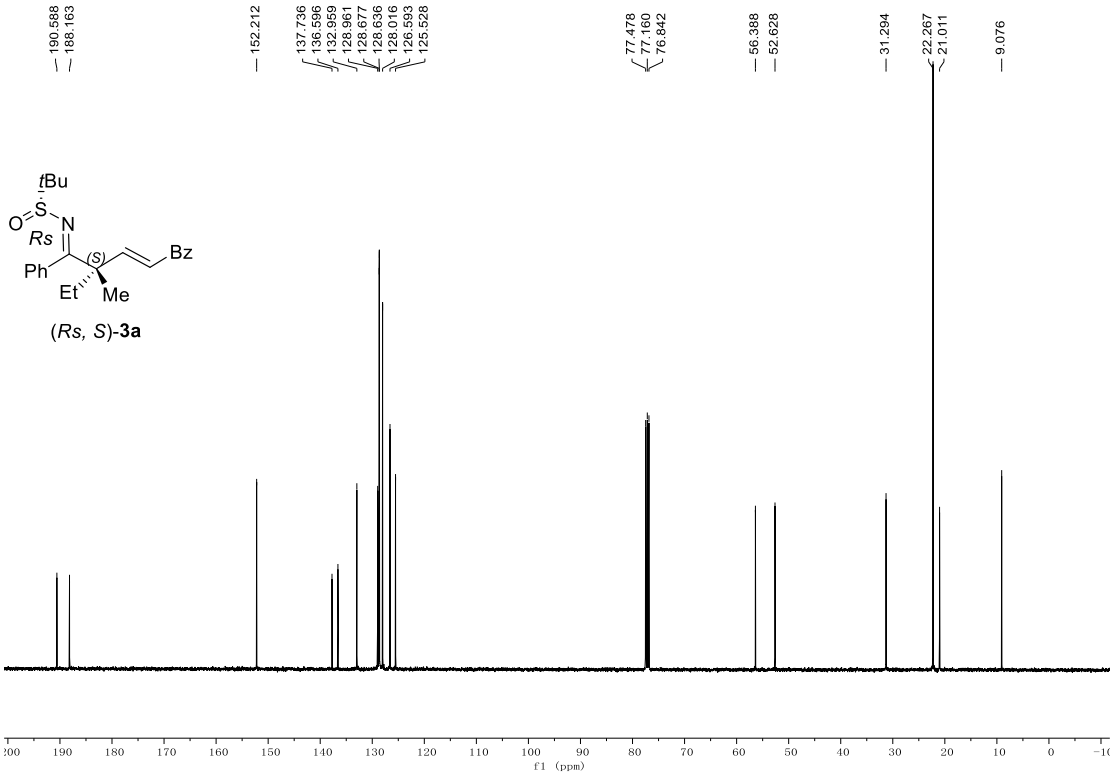
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *R*)-**3a**



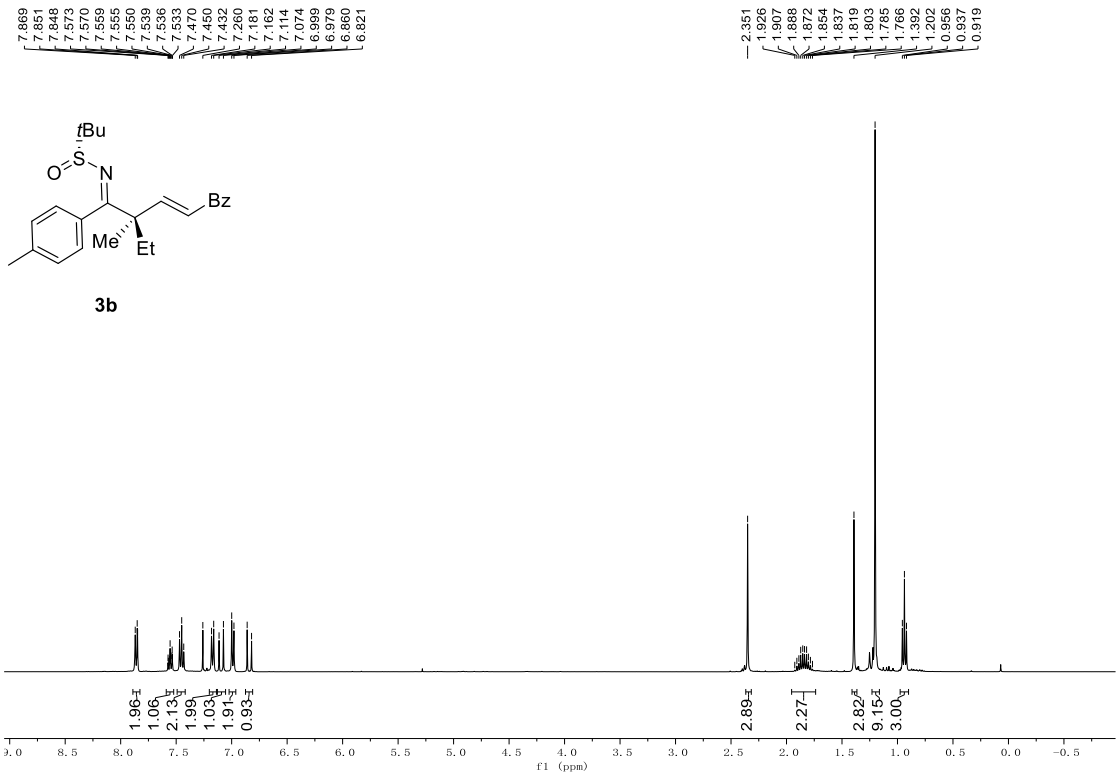
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *R*)-**3a**



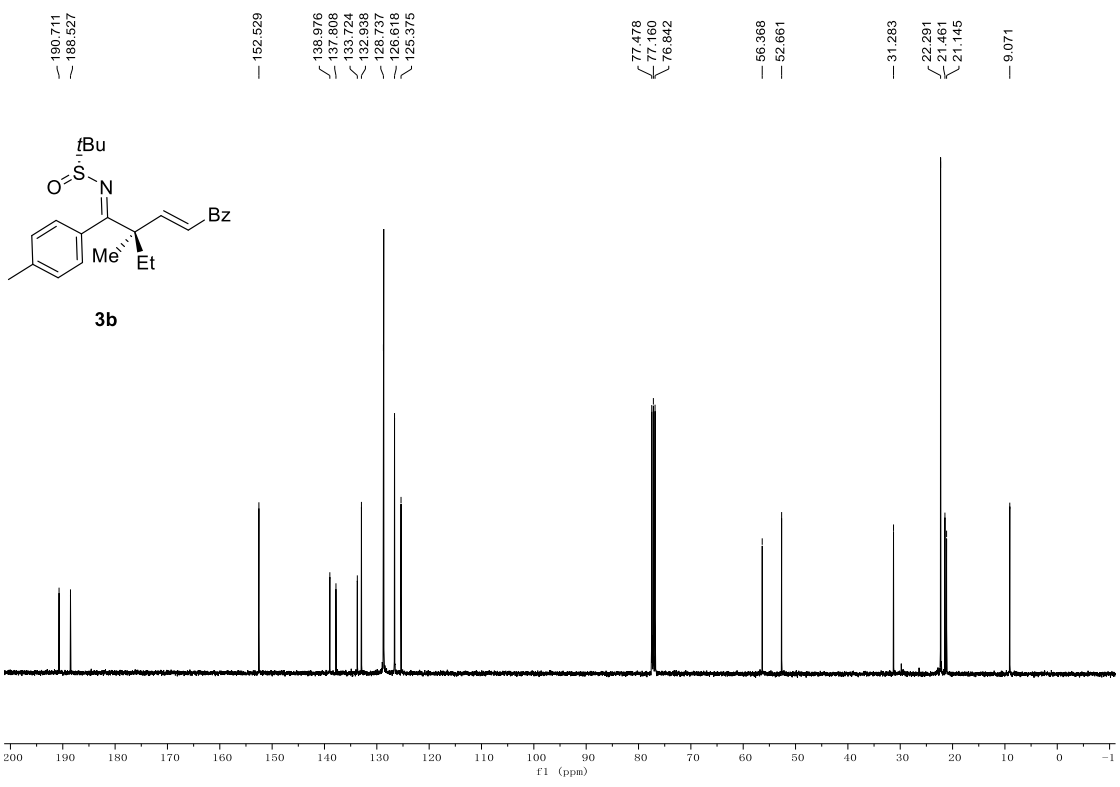
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *S*)-**3a**



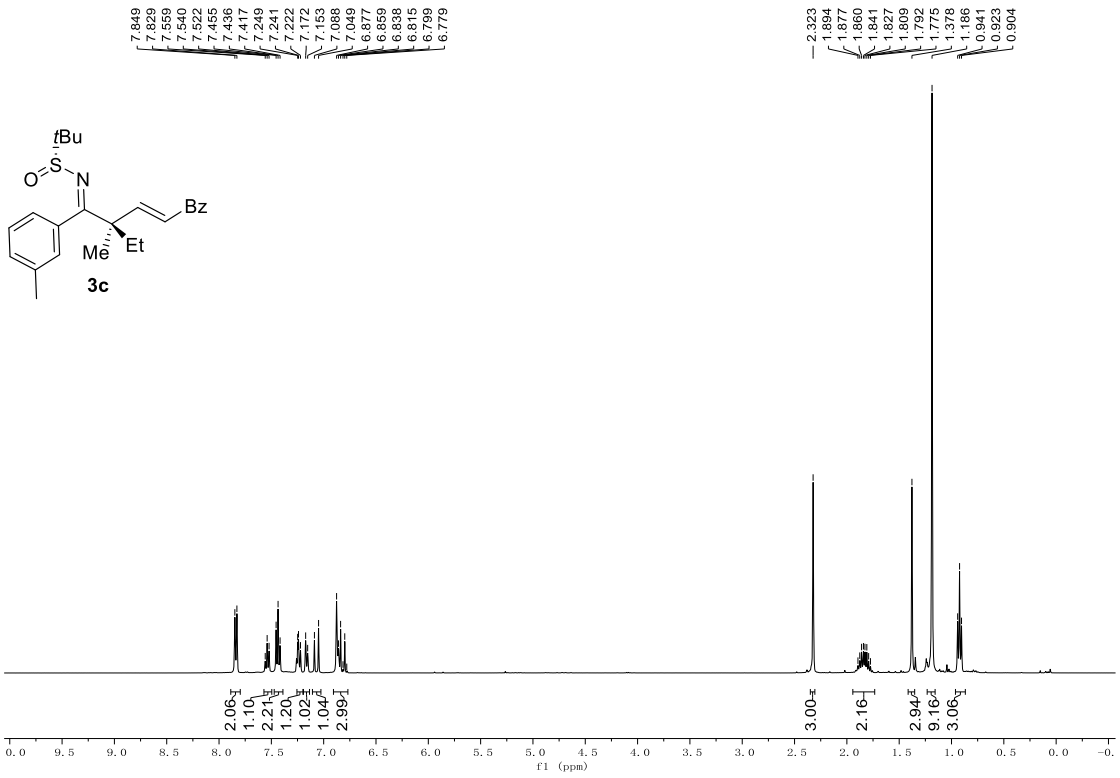
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *S*)-**3a**



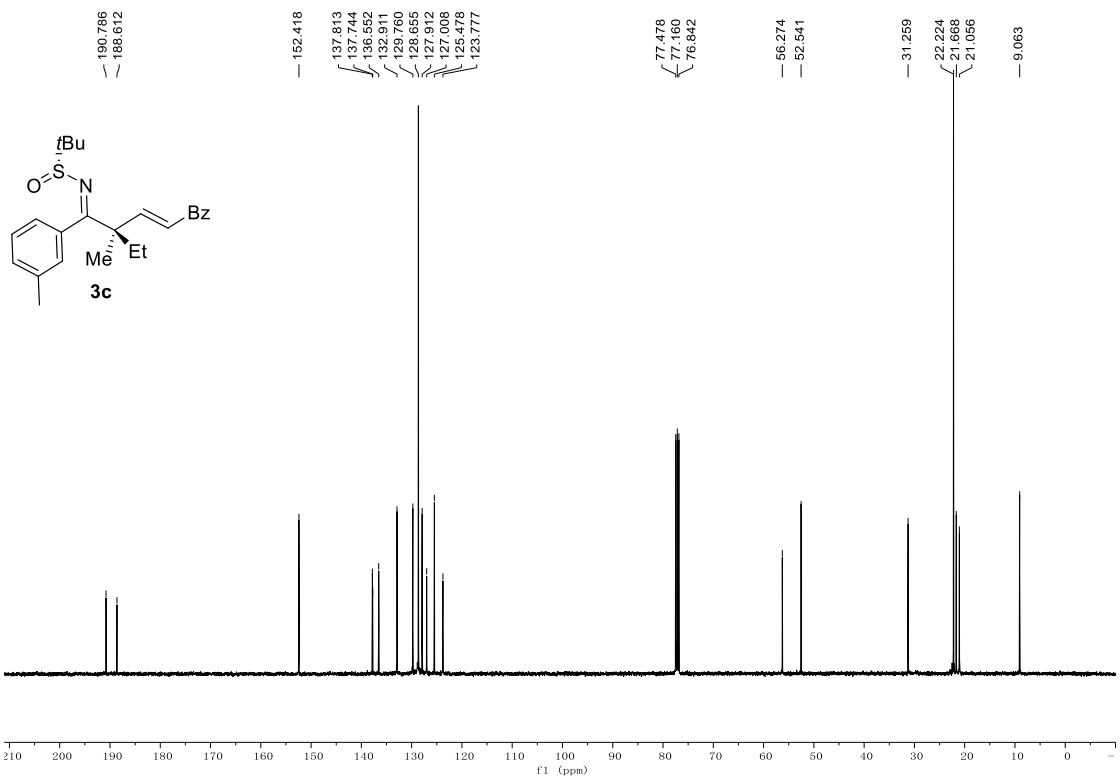
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3b**



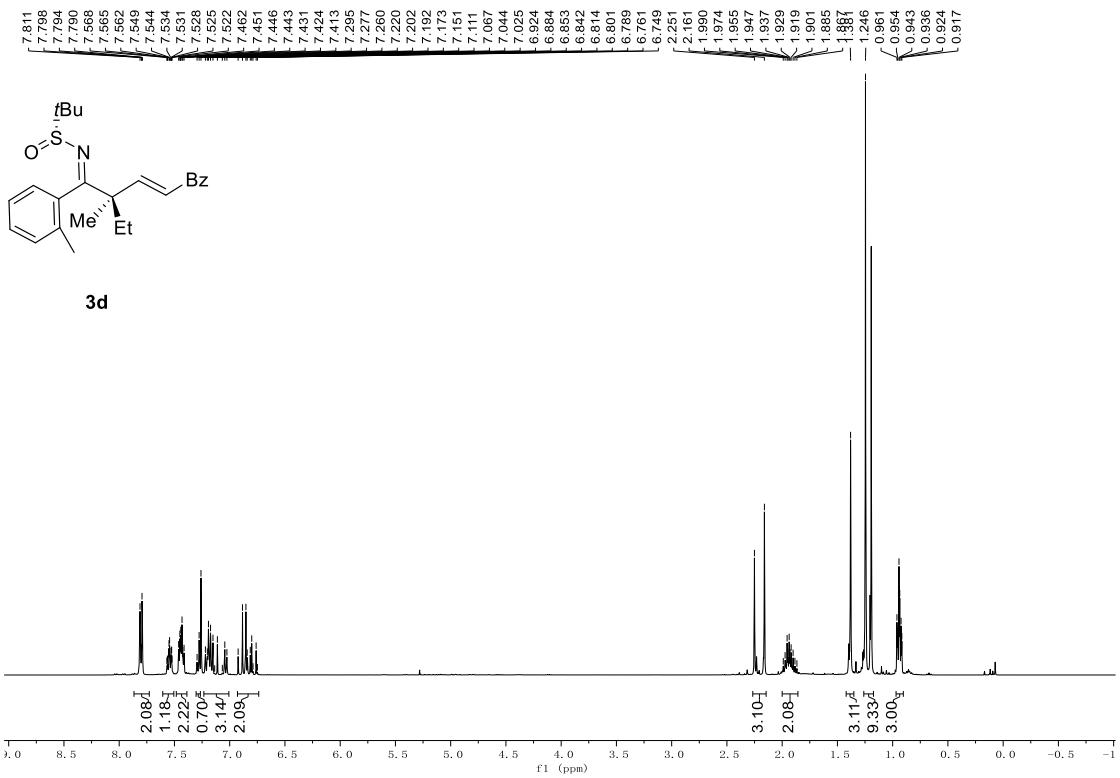
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3b**



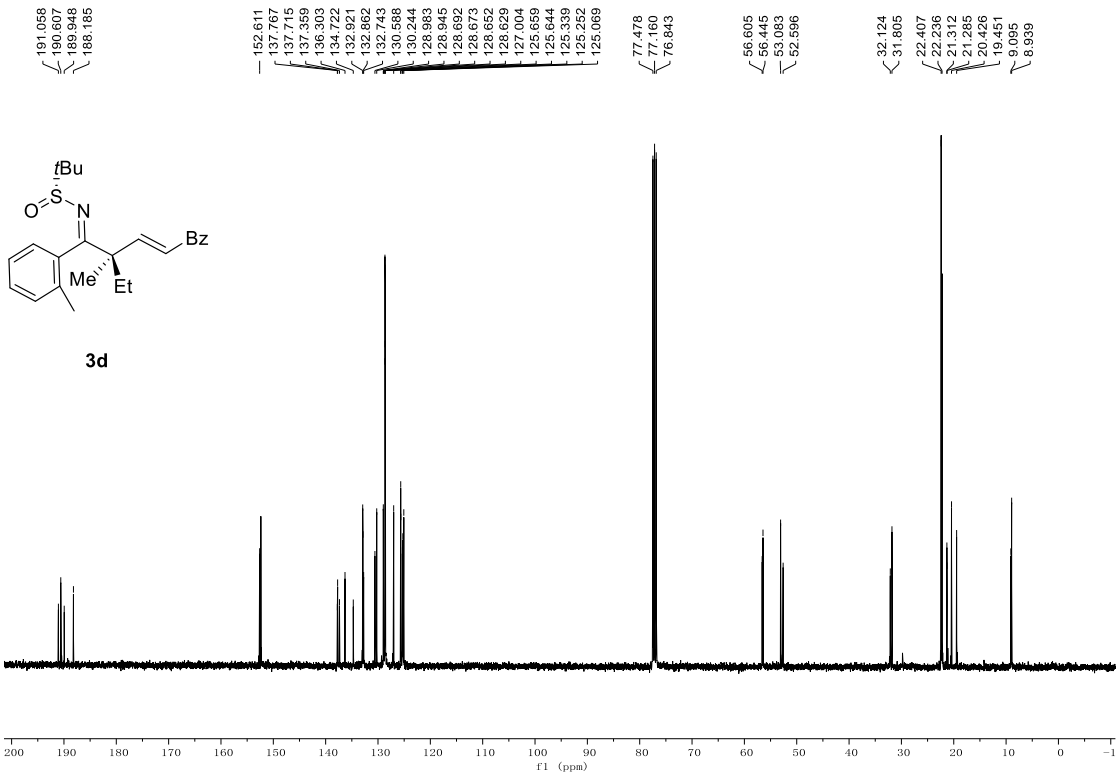
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3c**



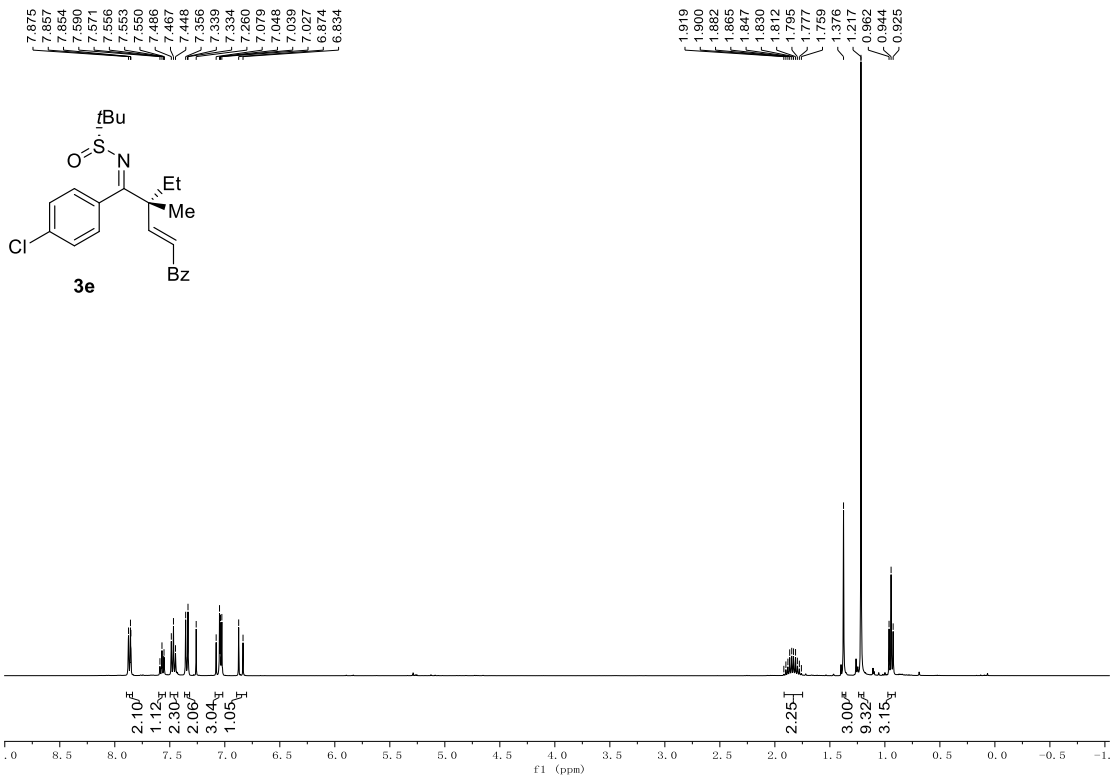
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3c**



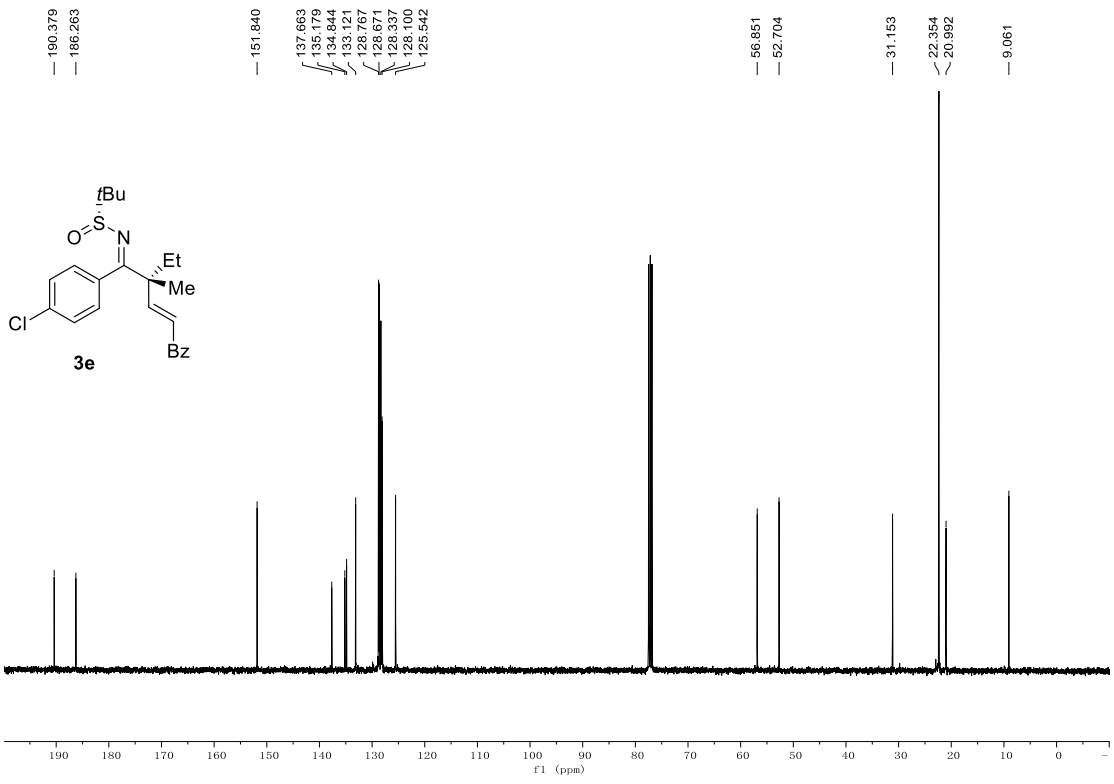
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3d** (mixture of imino *Z*/*E* isomers)



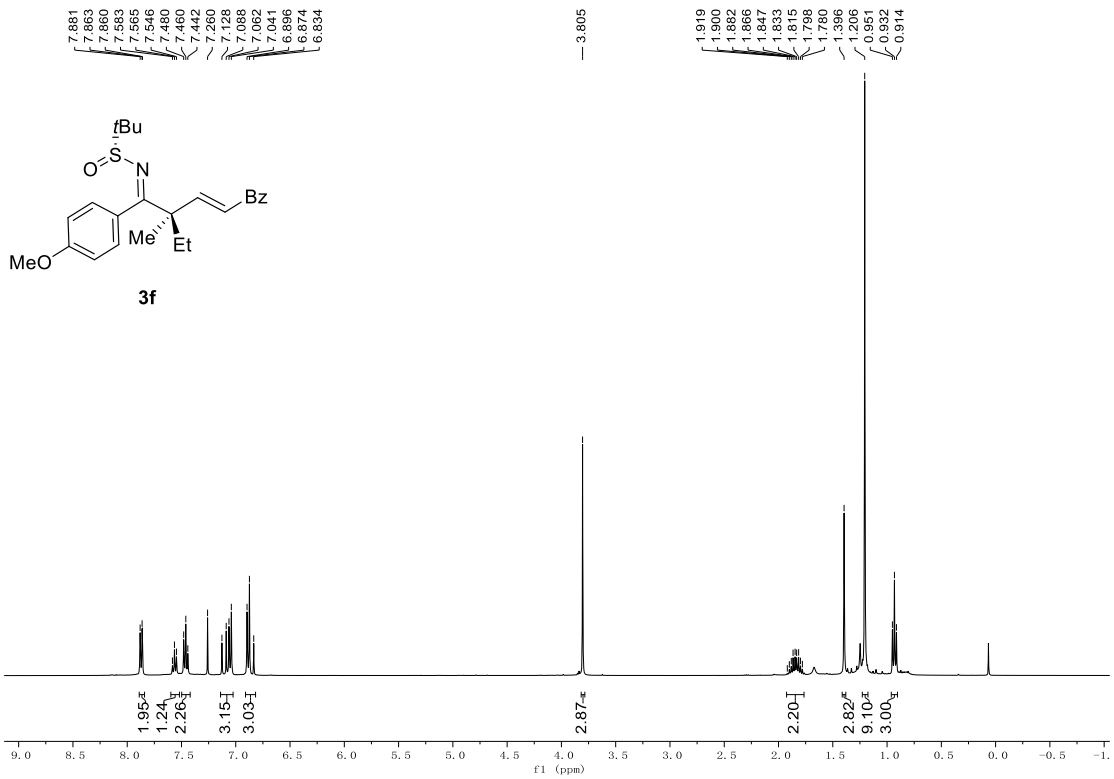
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3d** (mixture of imino *Z*/*E* isomers)



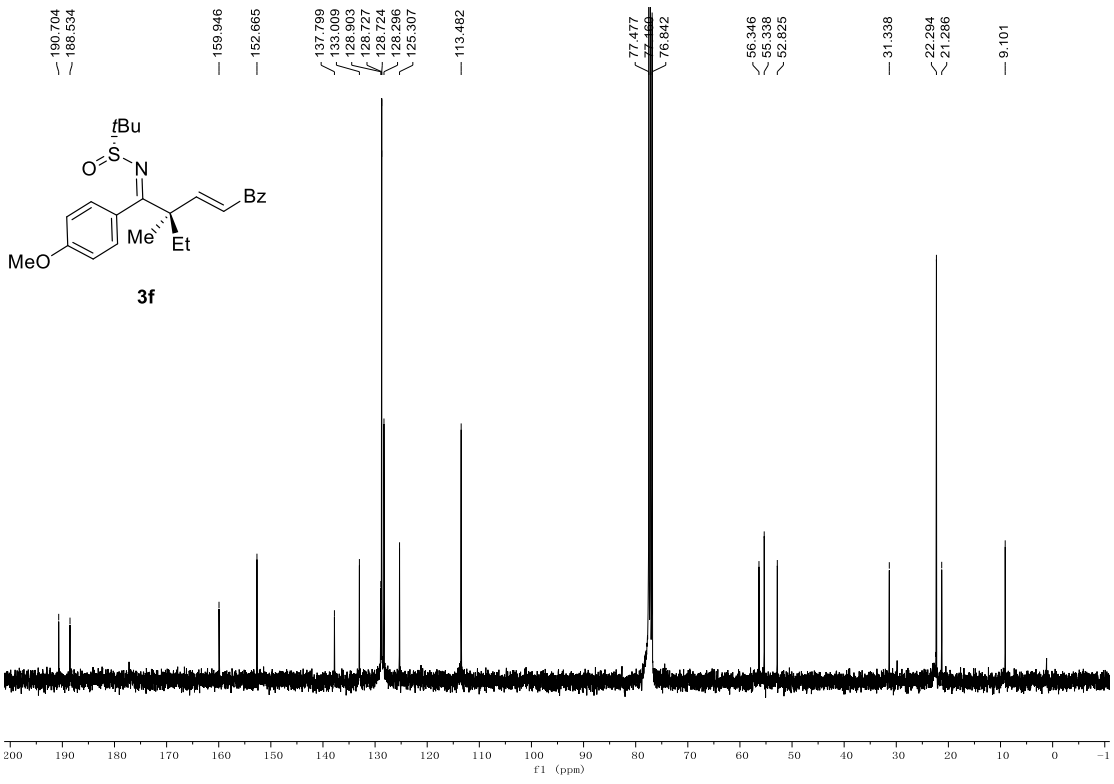
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3e**



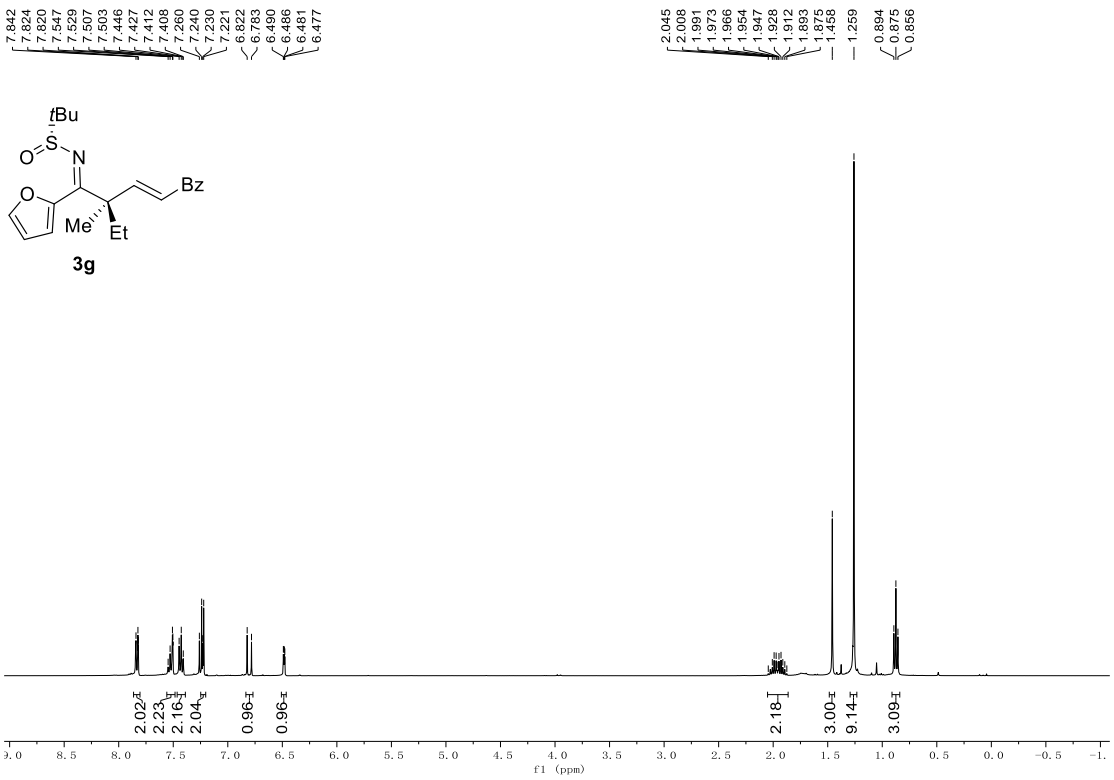
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3e**



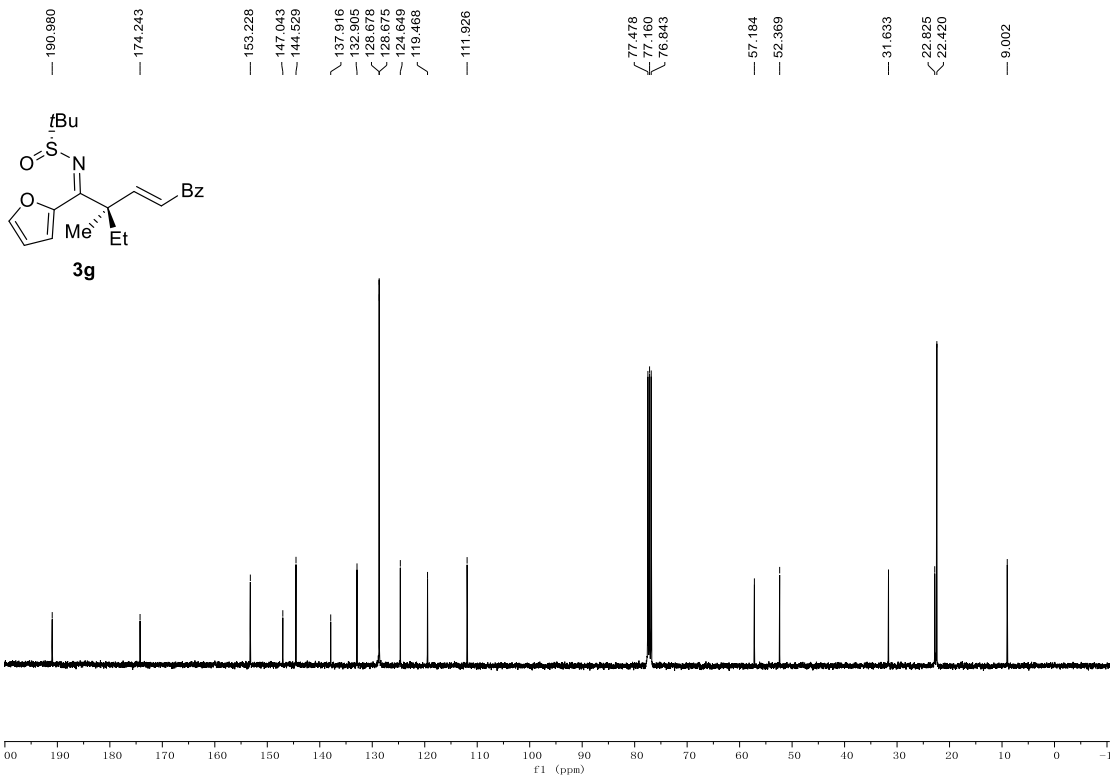
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3f**



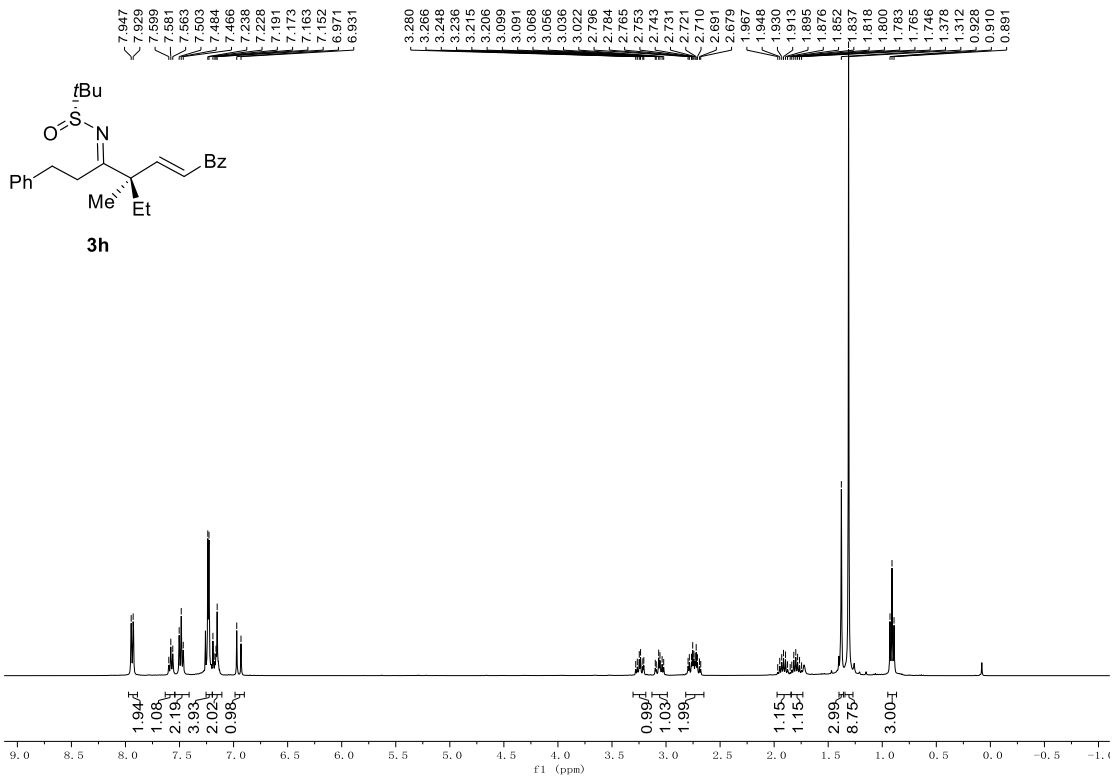
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3f**



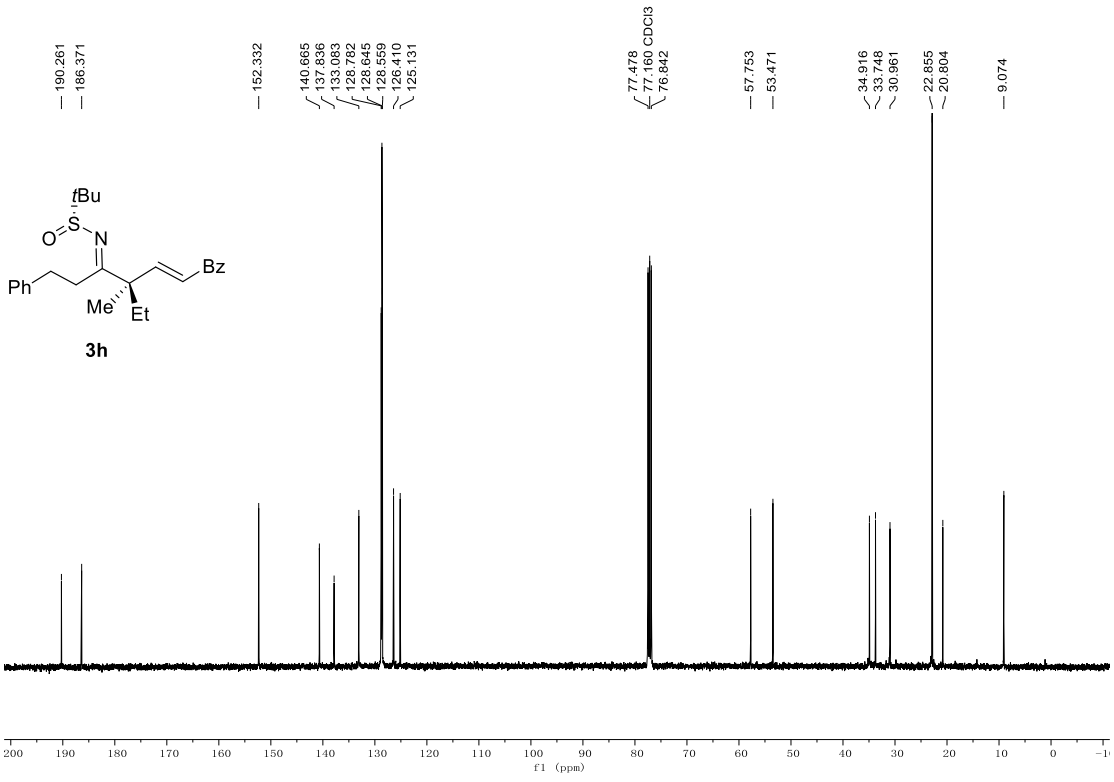
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3g**



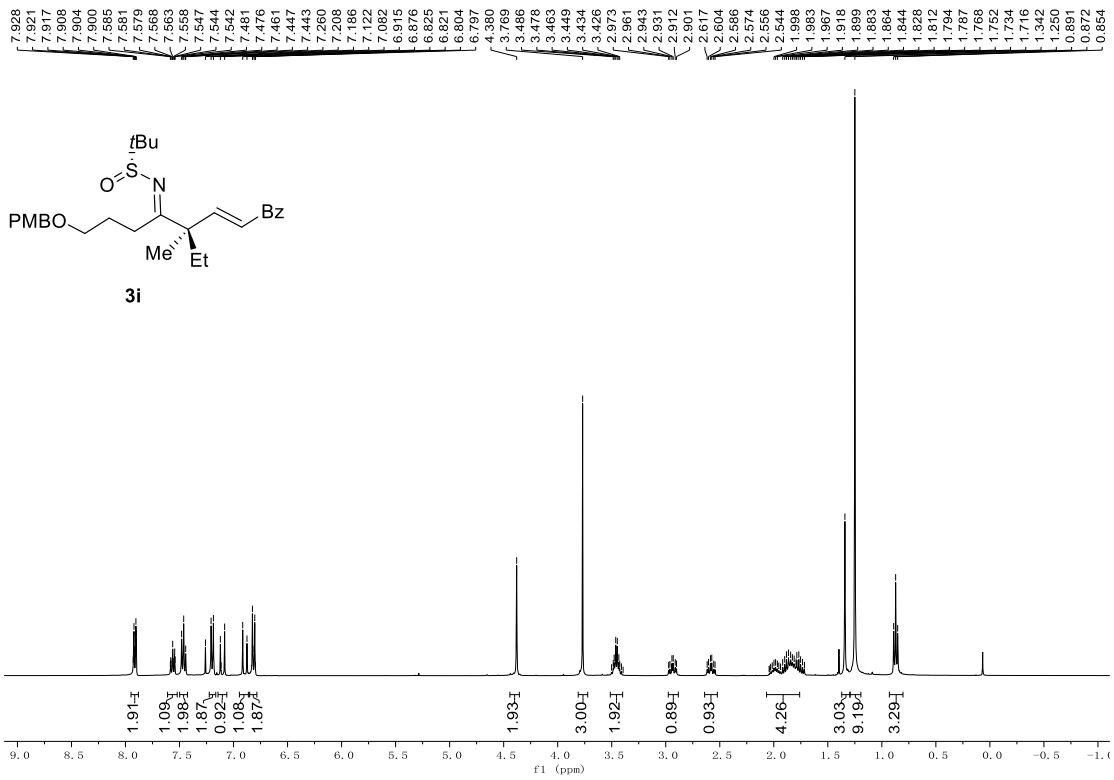
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3g**



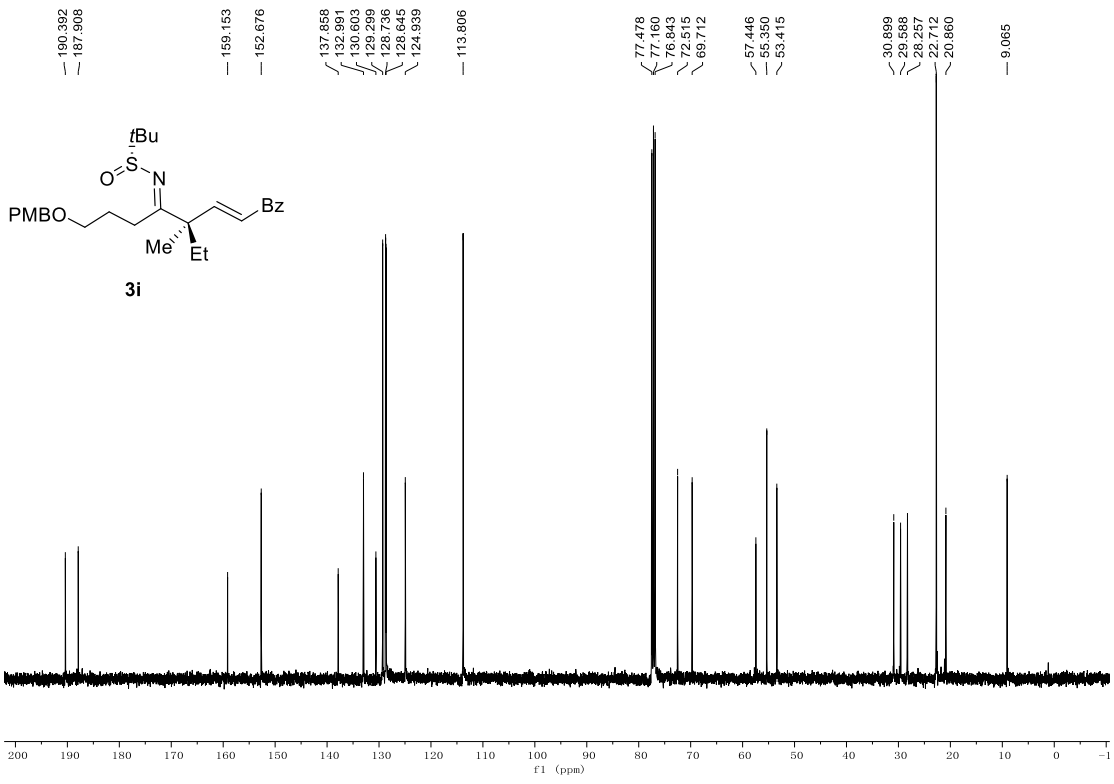
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3h**



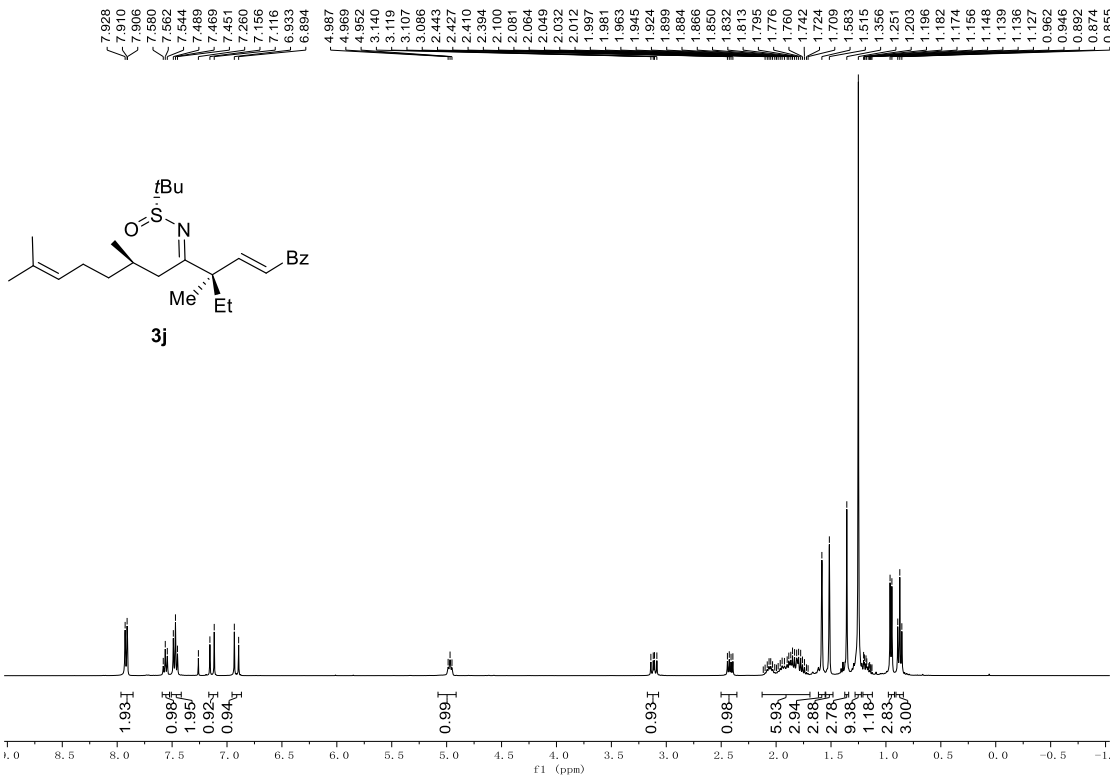
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3h**



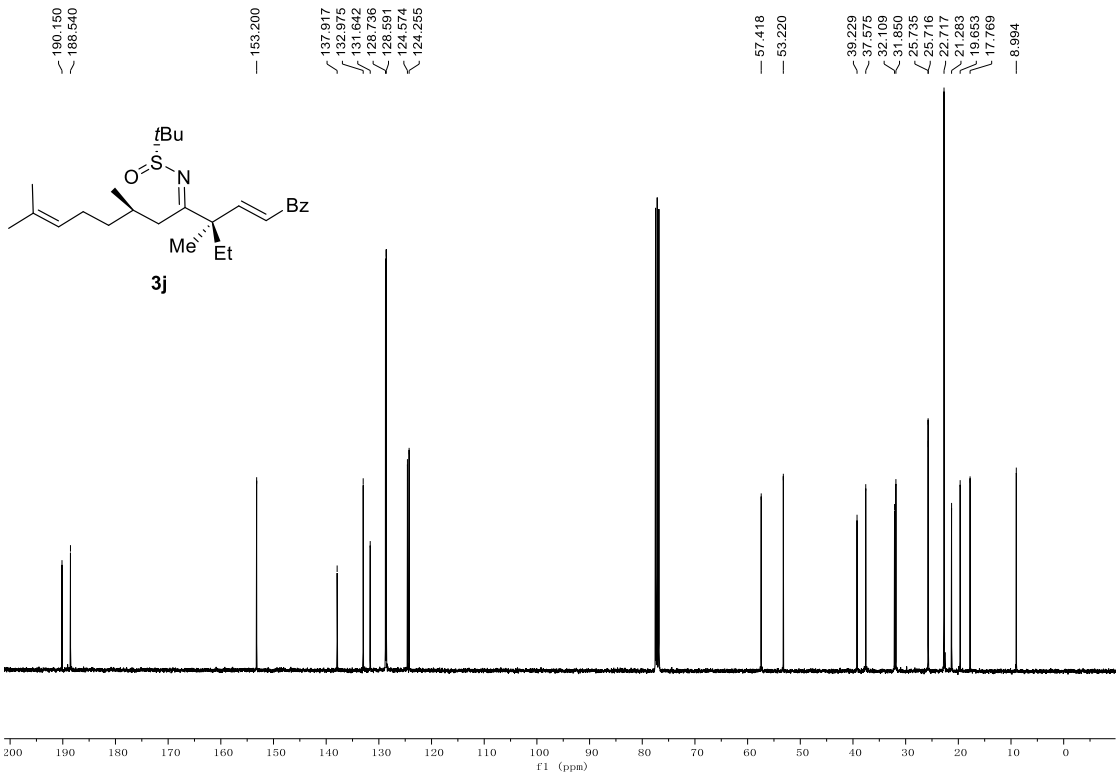
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3i**



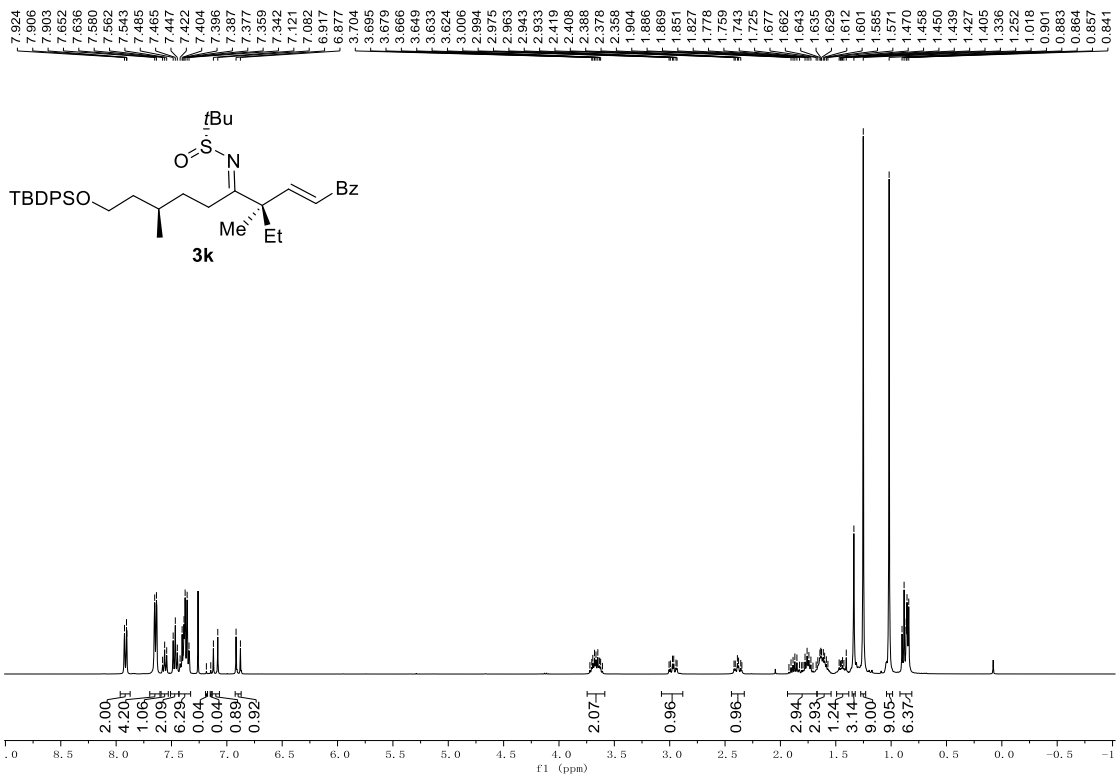
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3i**



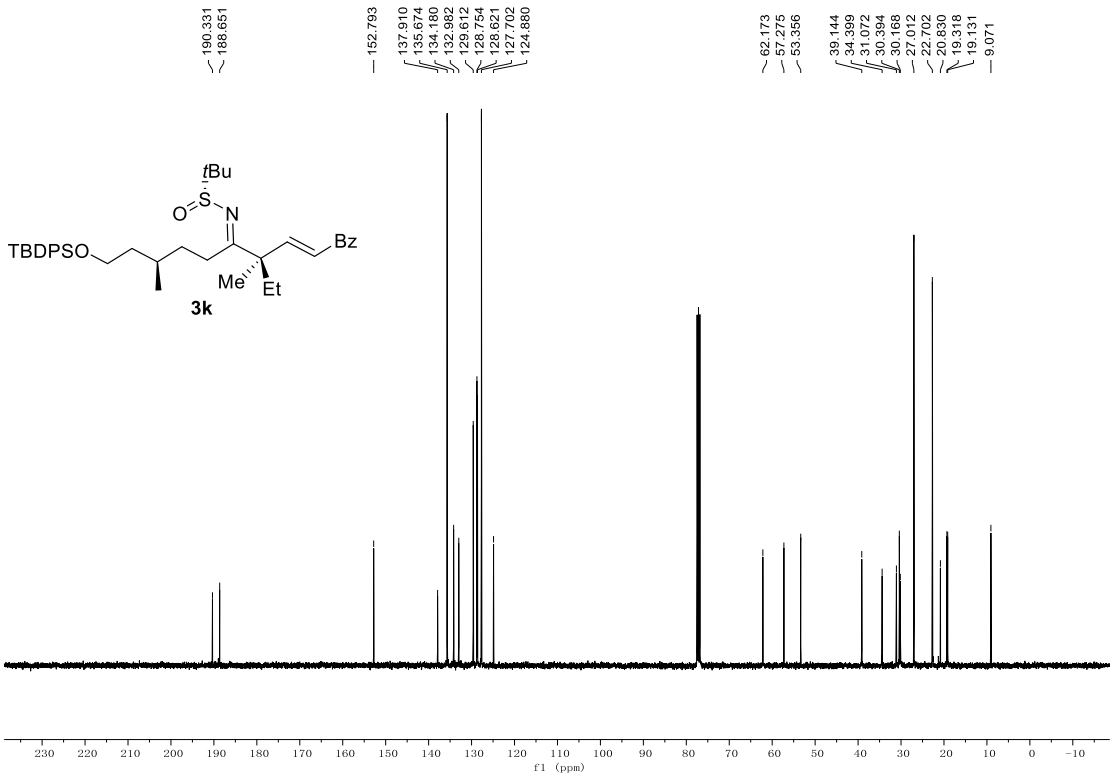
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3j**



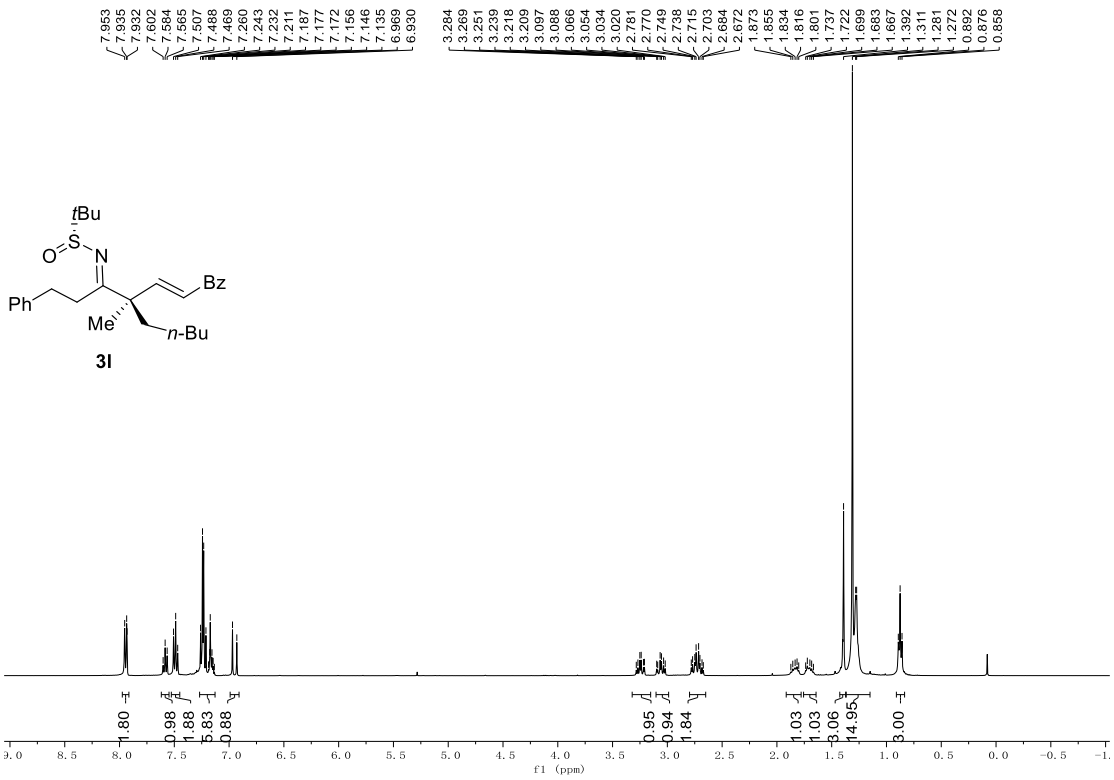
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3j**



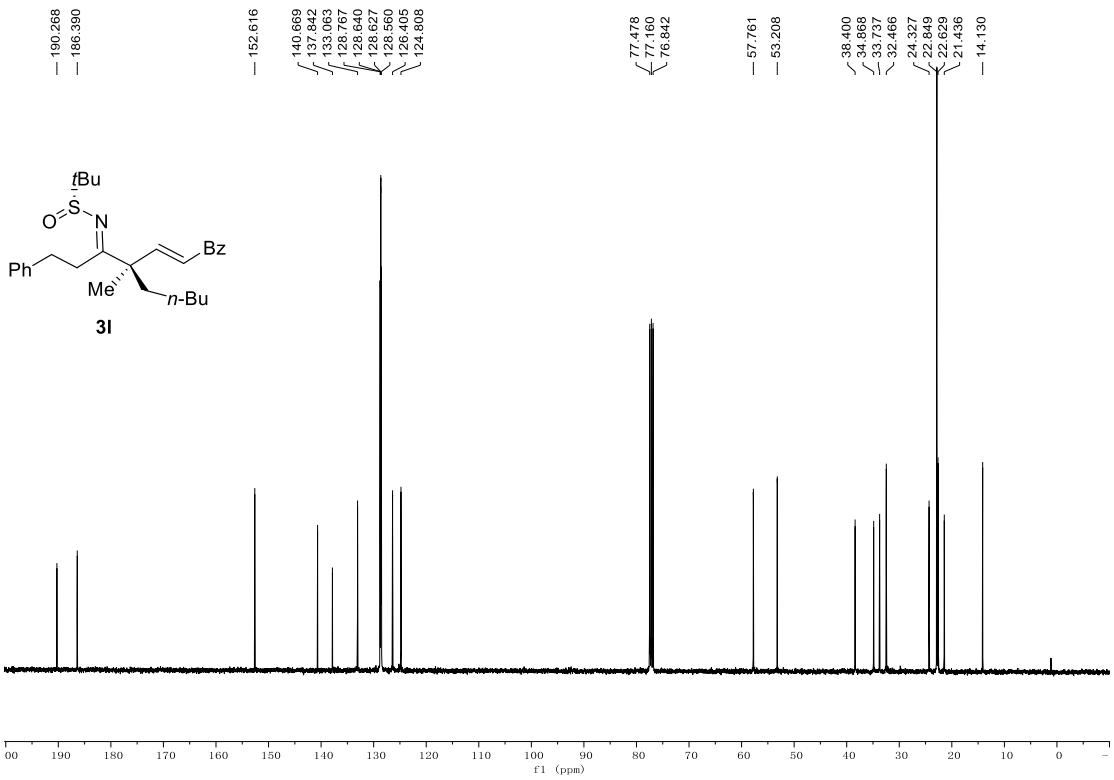
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3k**



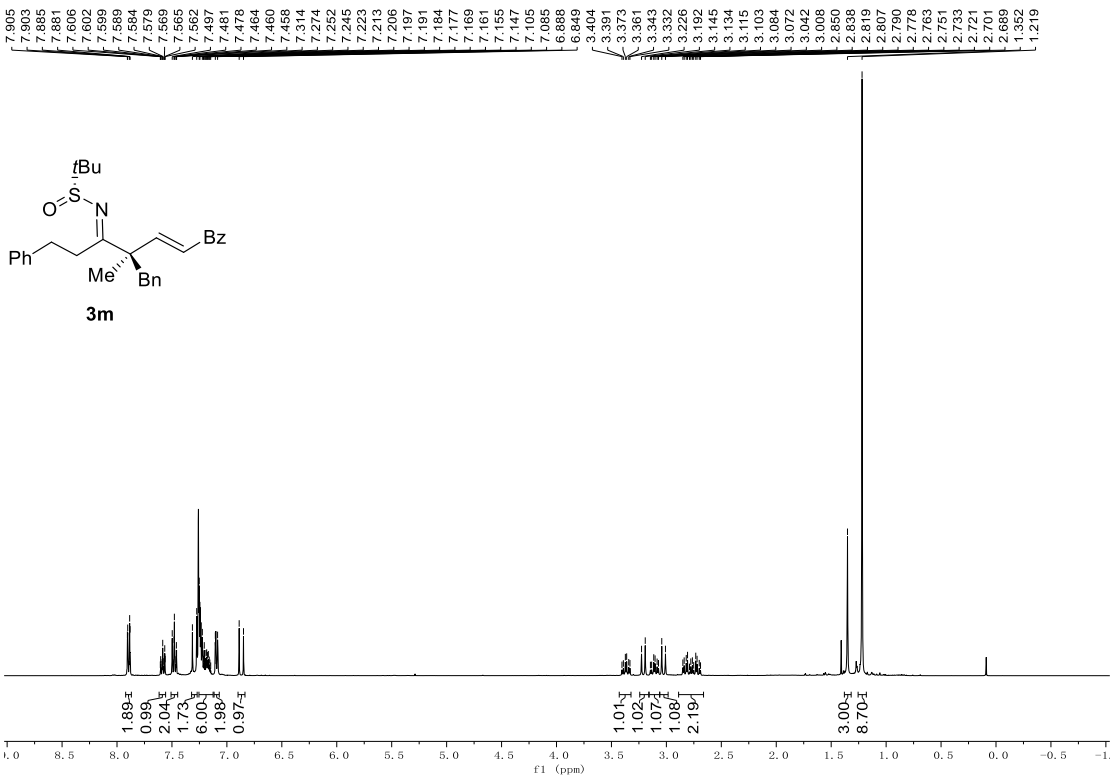
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3k**



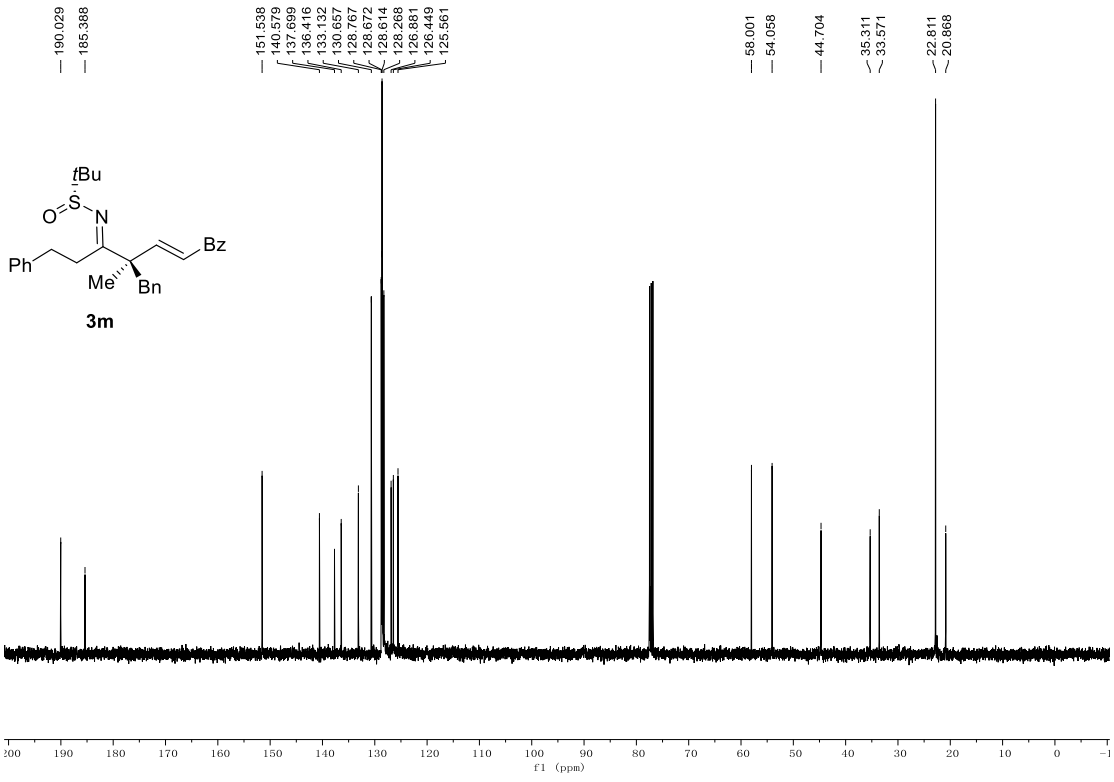
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3l**



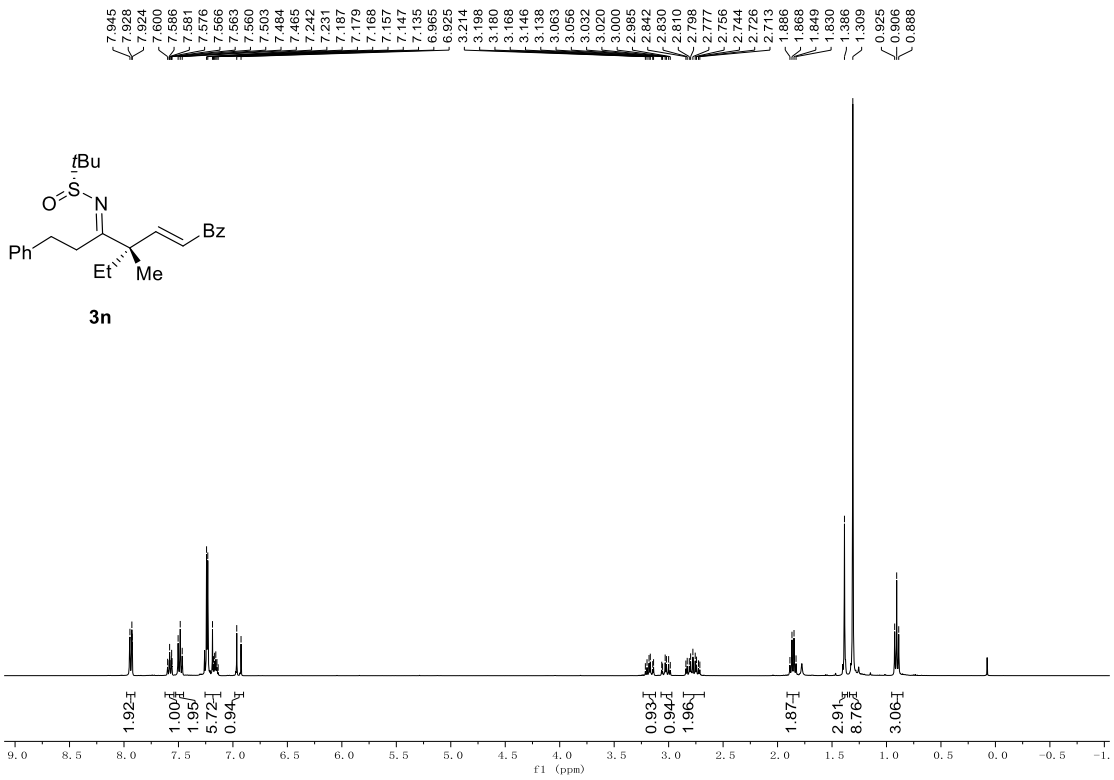
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3l**



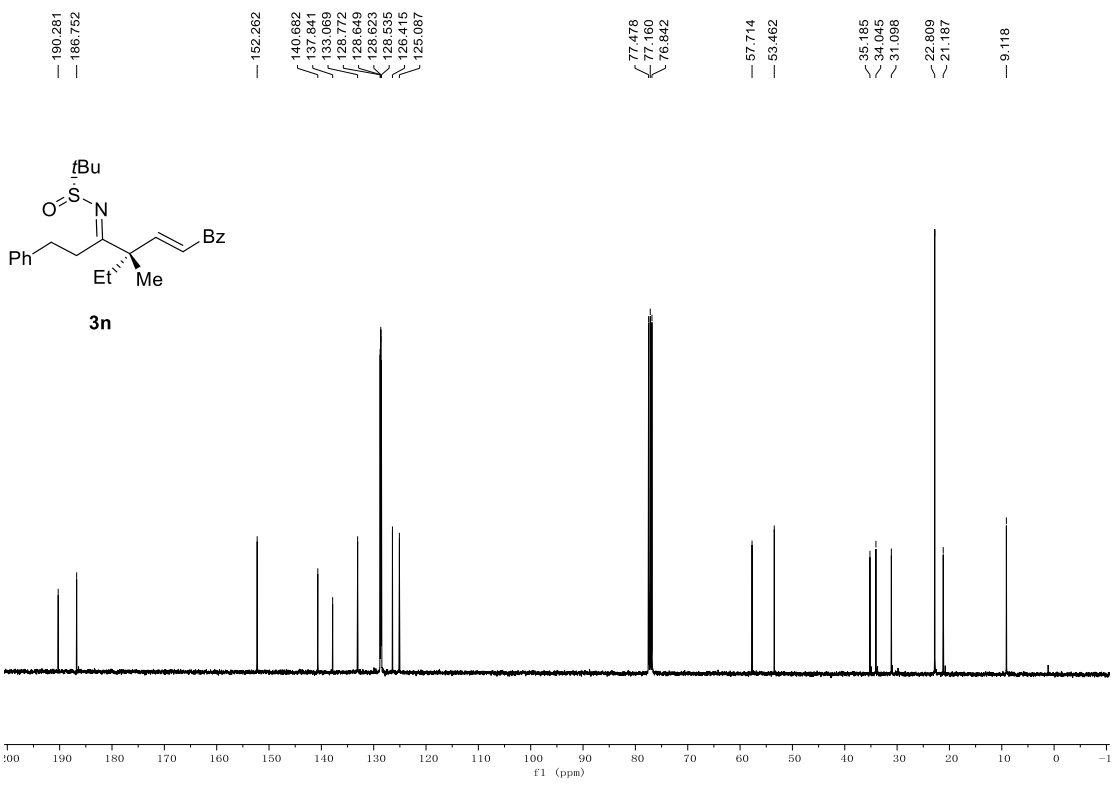
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3m**



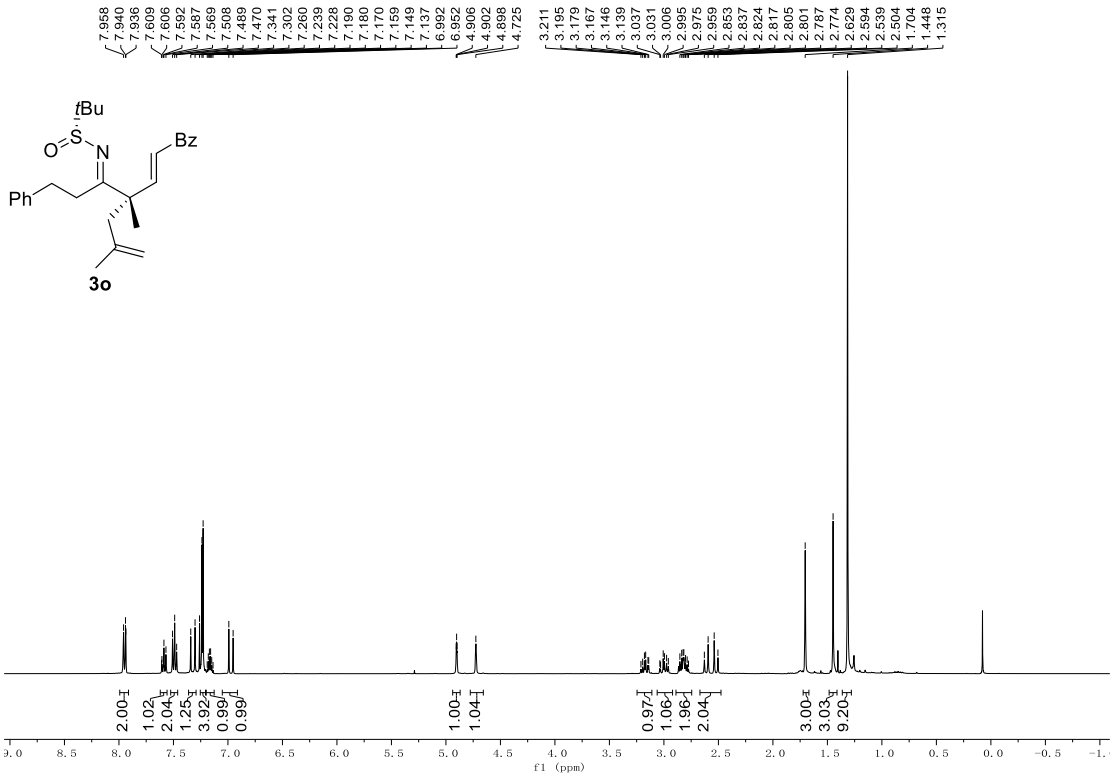
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3m**



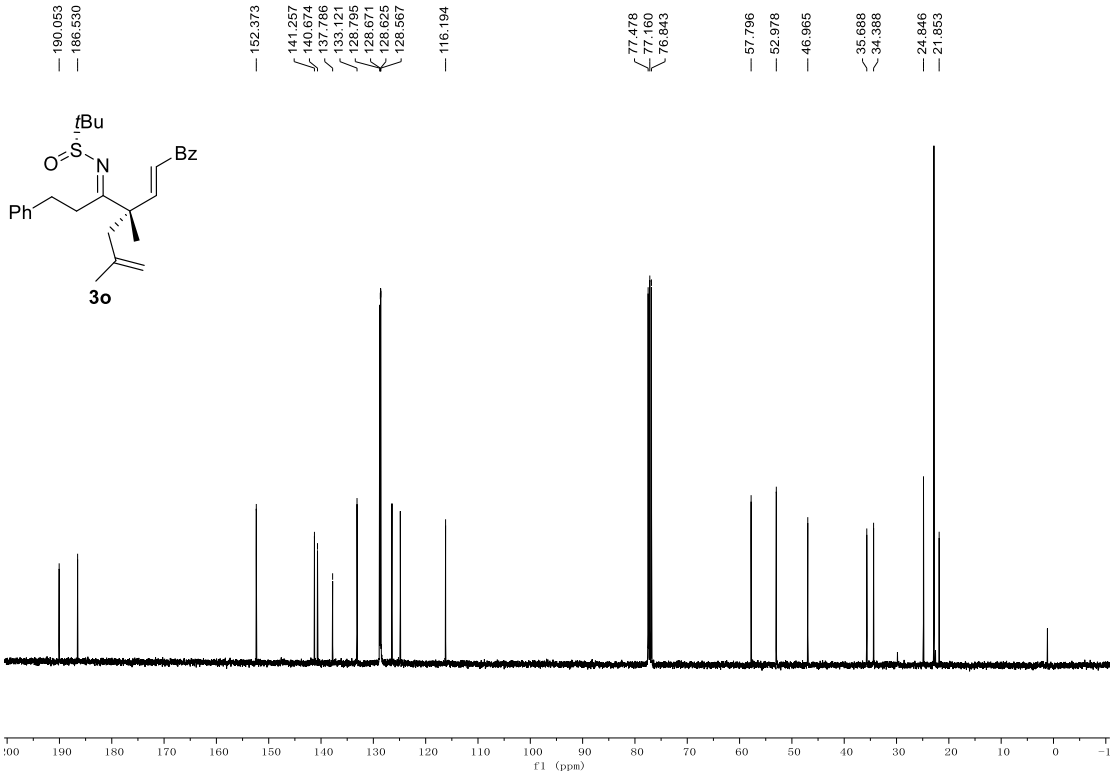
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3n**



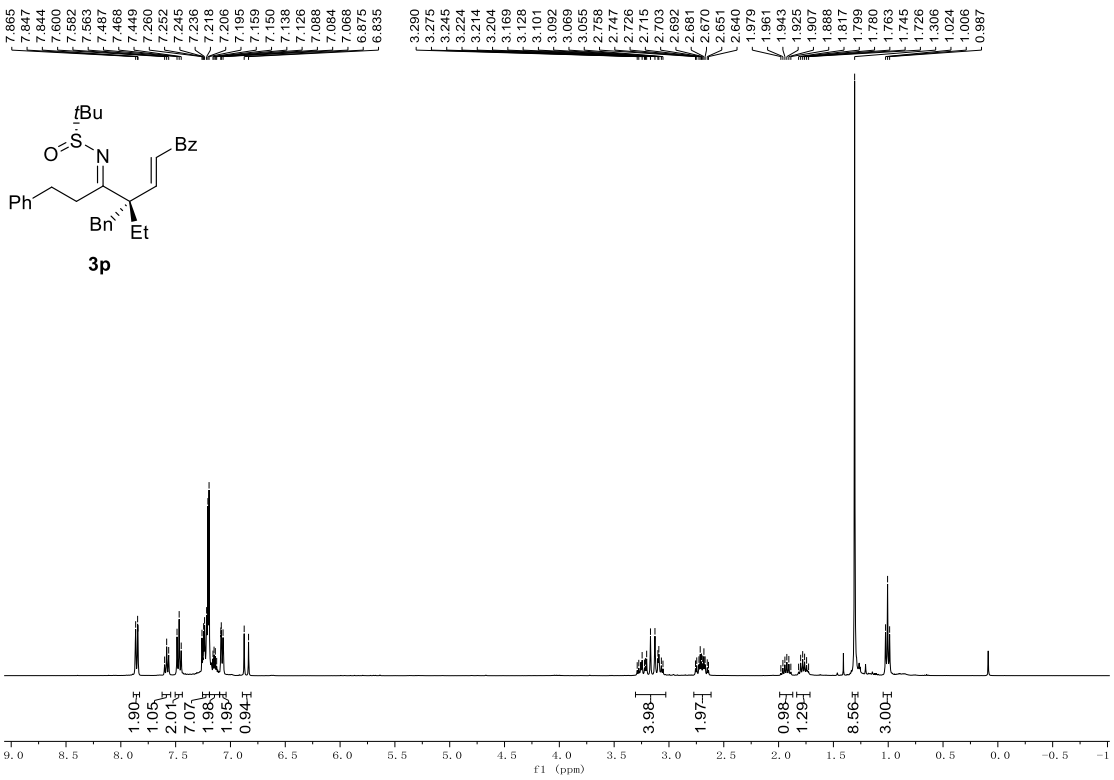
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3n**



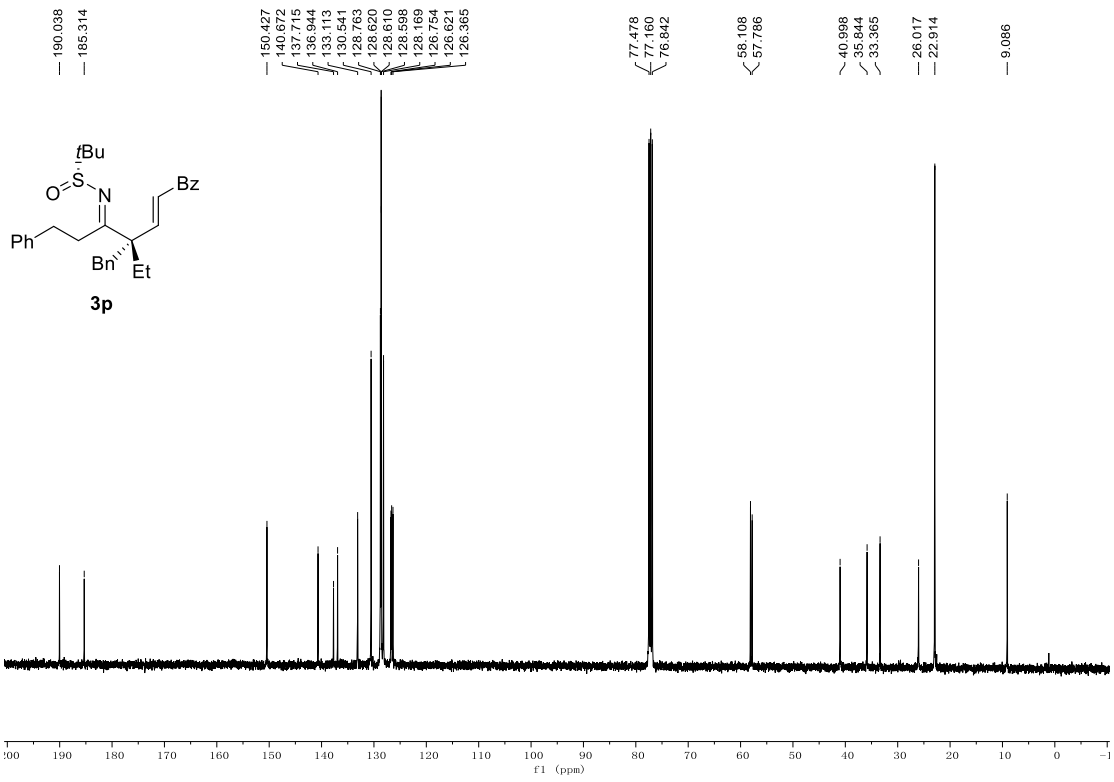
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3o**



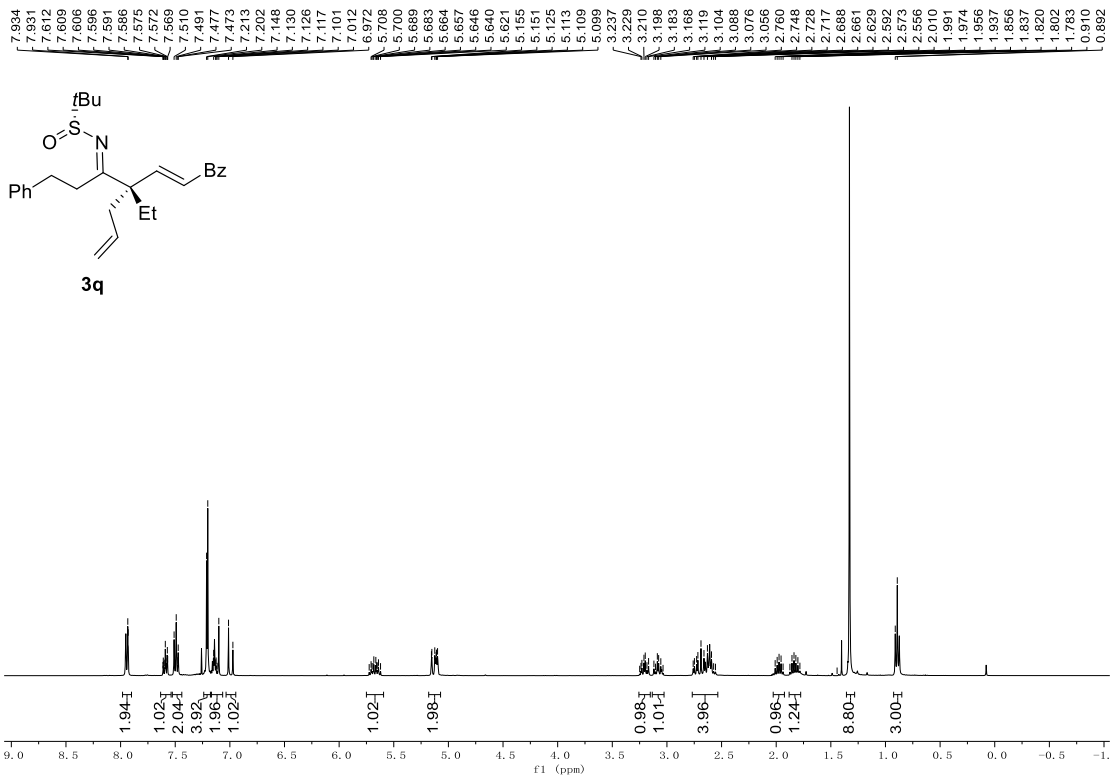
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3o**



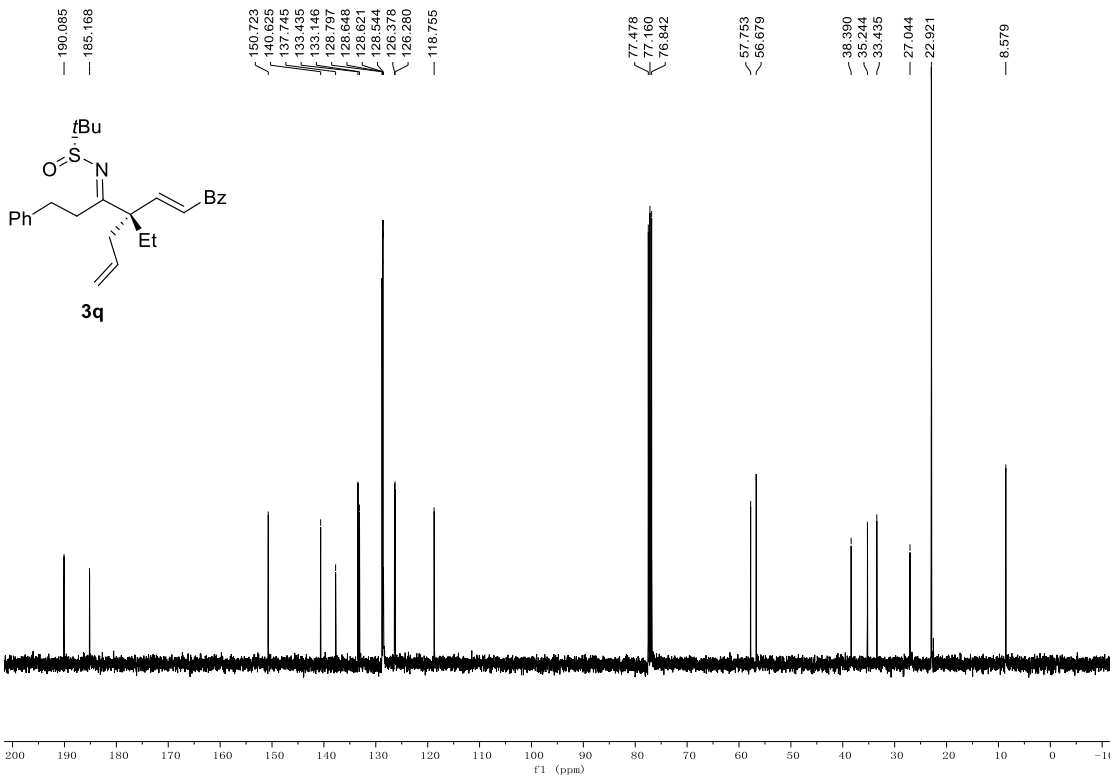
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3p**



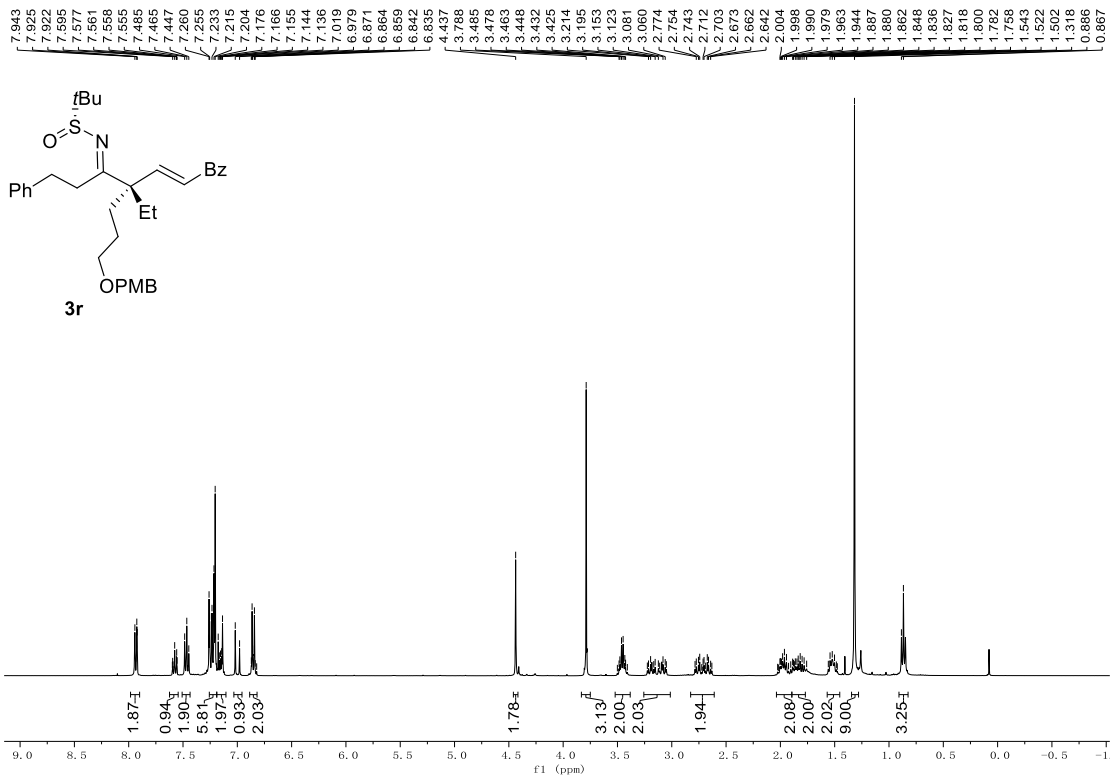
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3p**



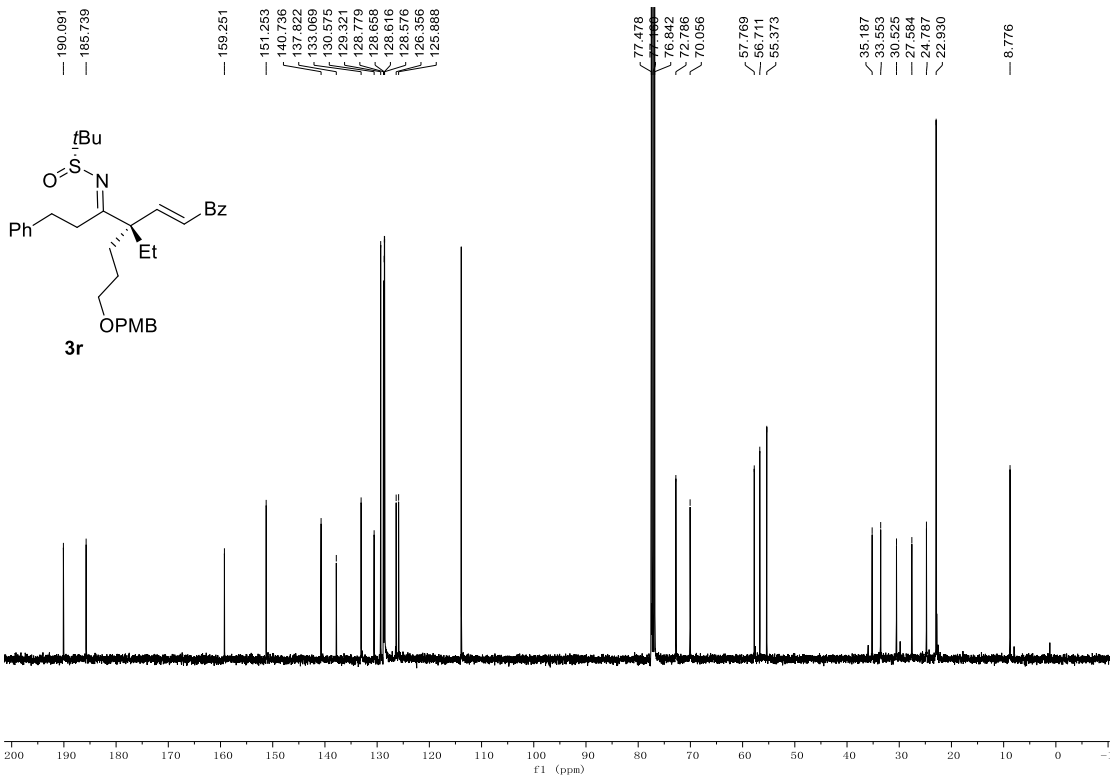
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3q**



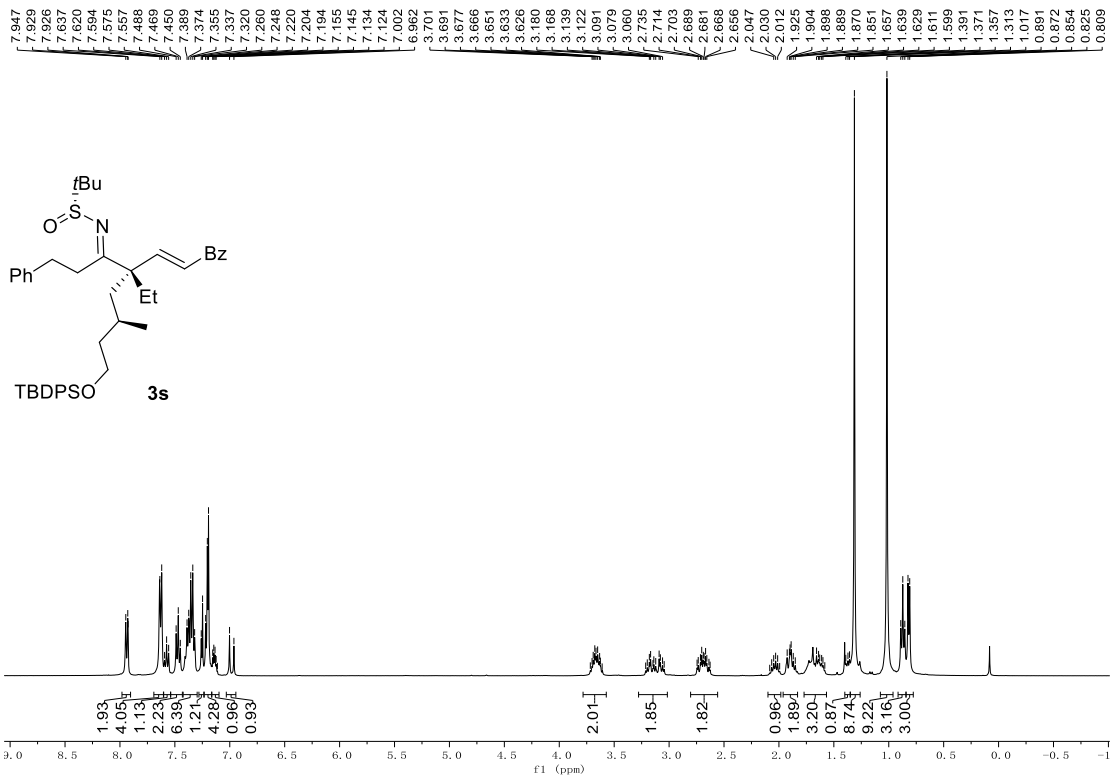
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3q**



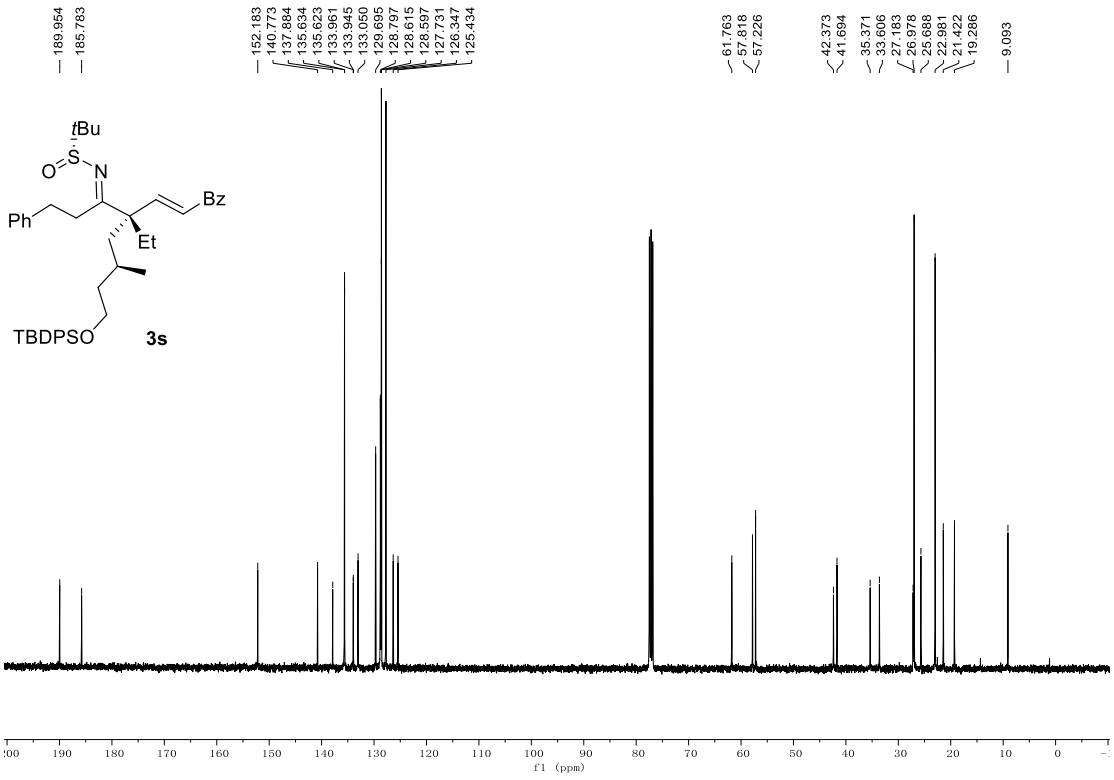
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3r**



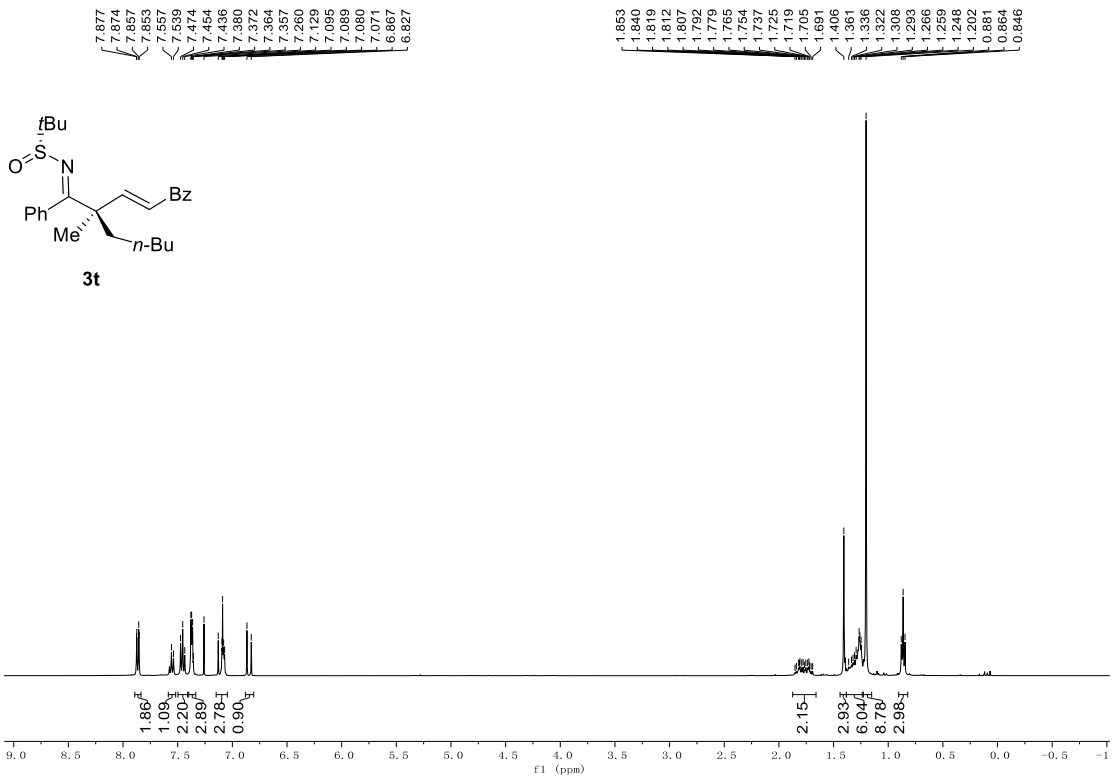
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3r**



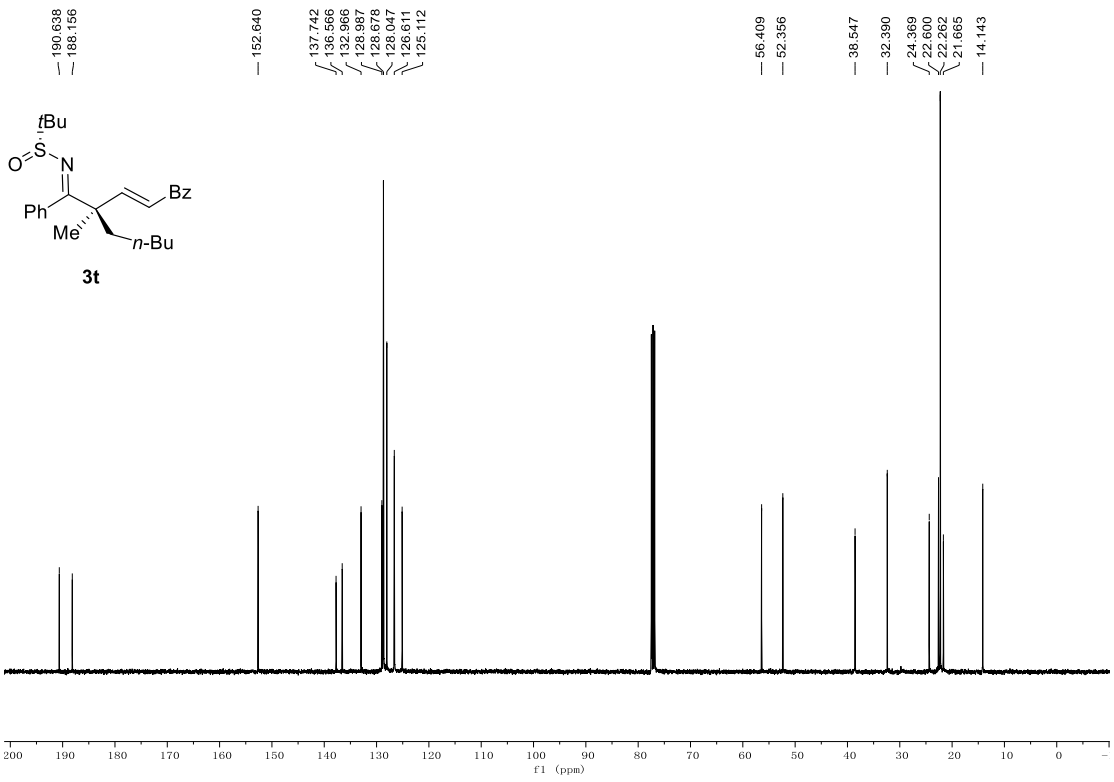
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3s**



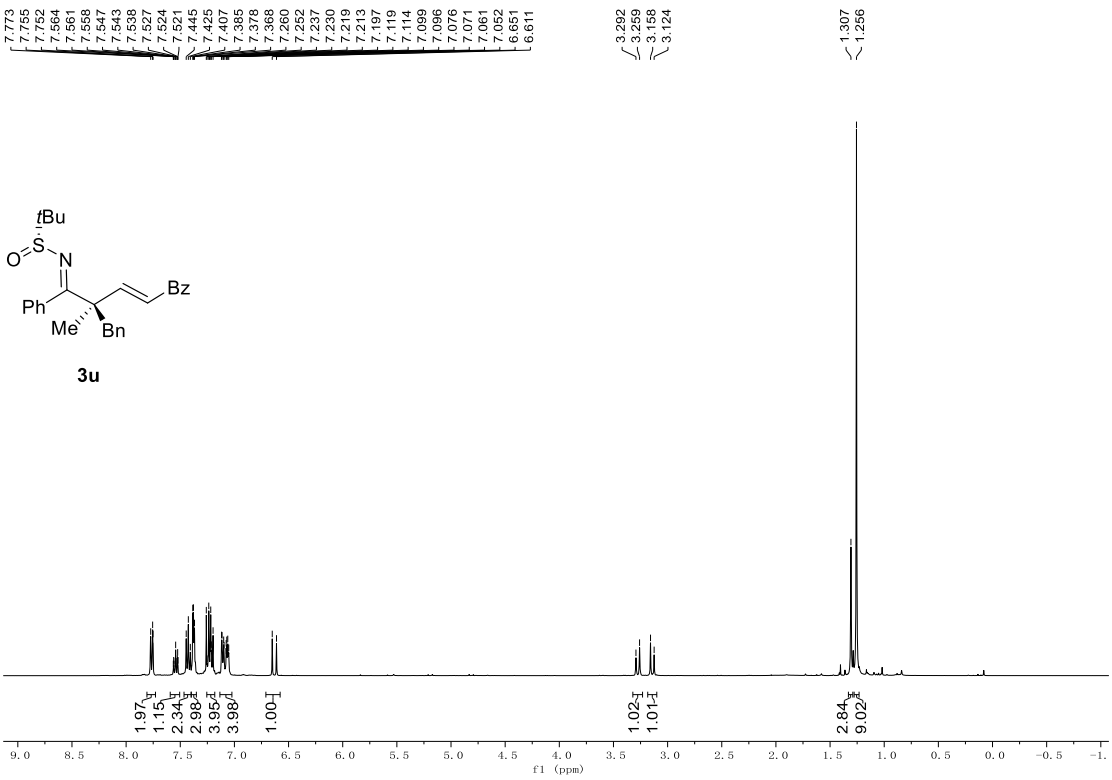
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3s**



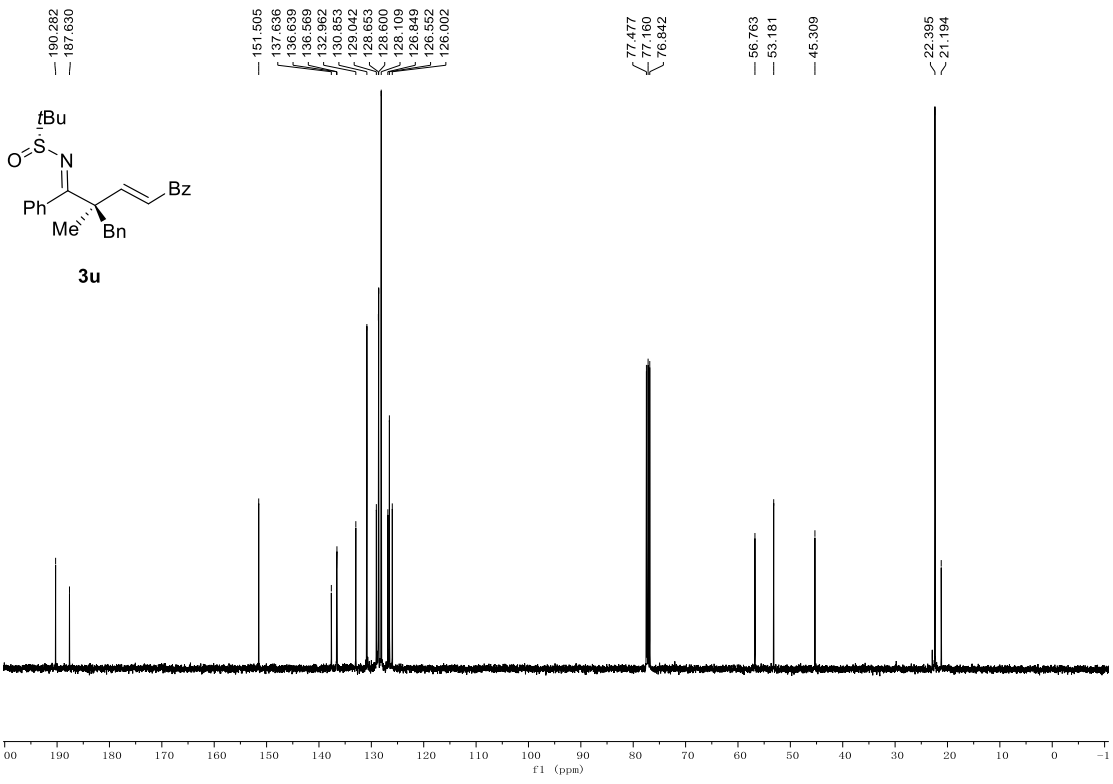
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3t**



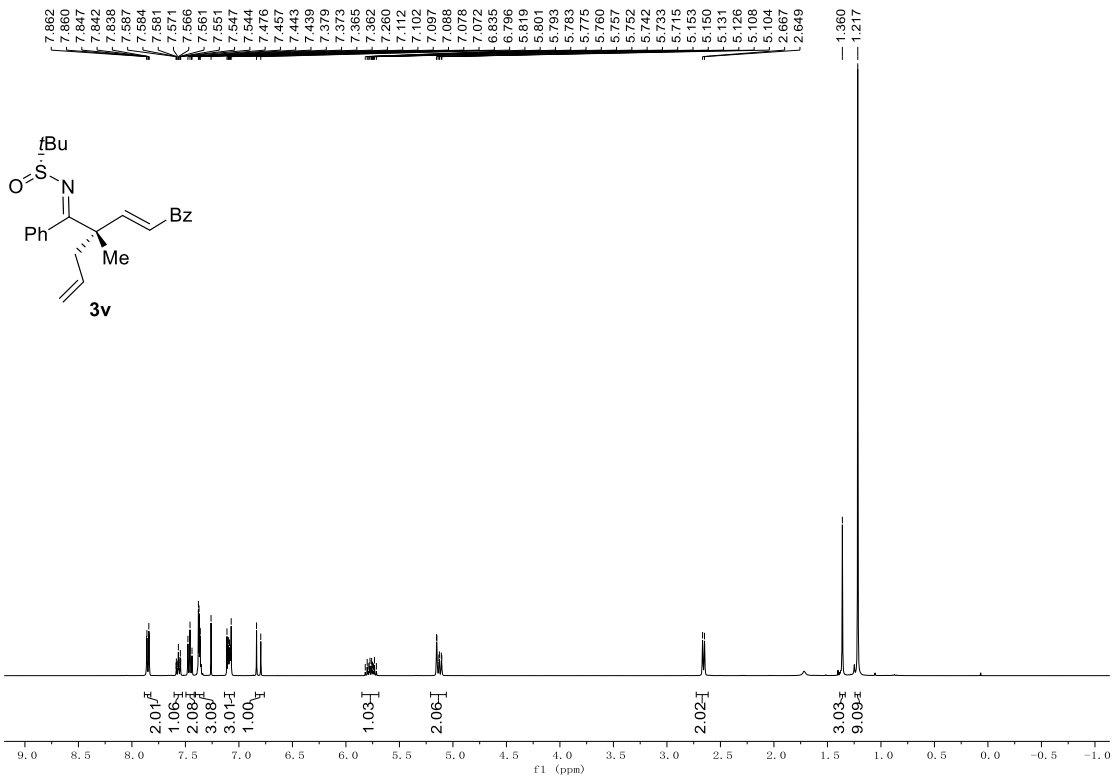
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3t**



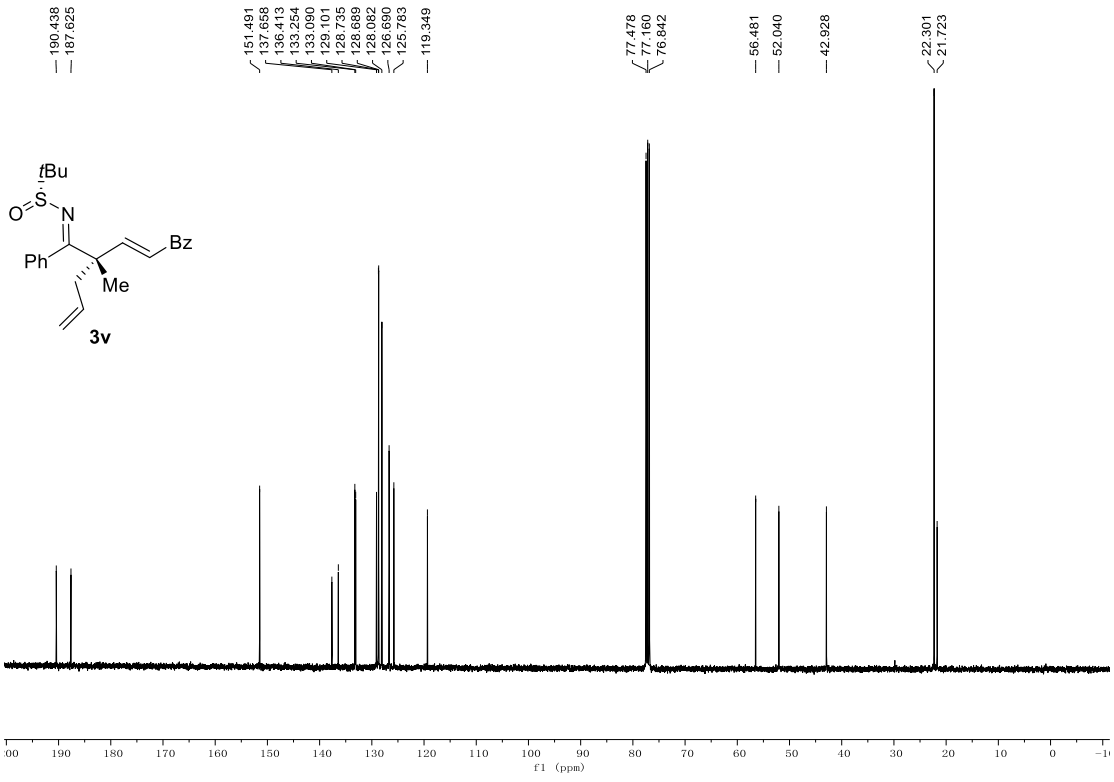
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3u**



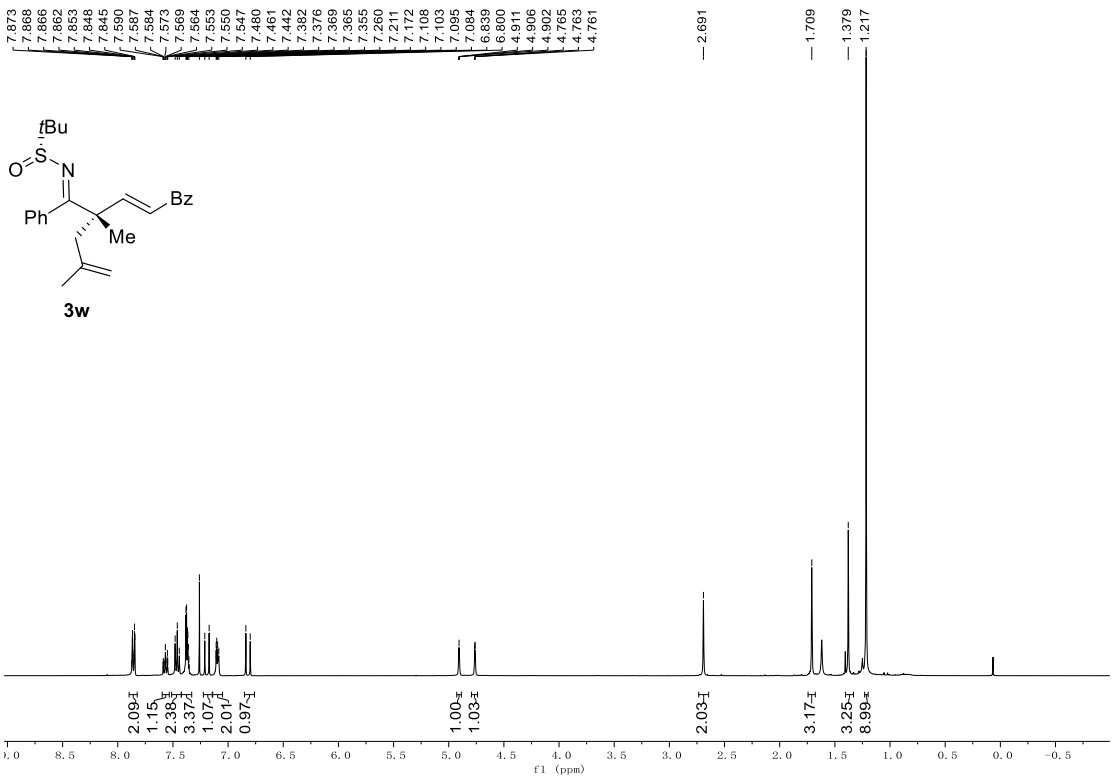
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3u**



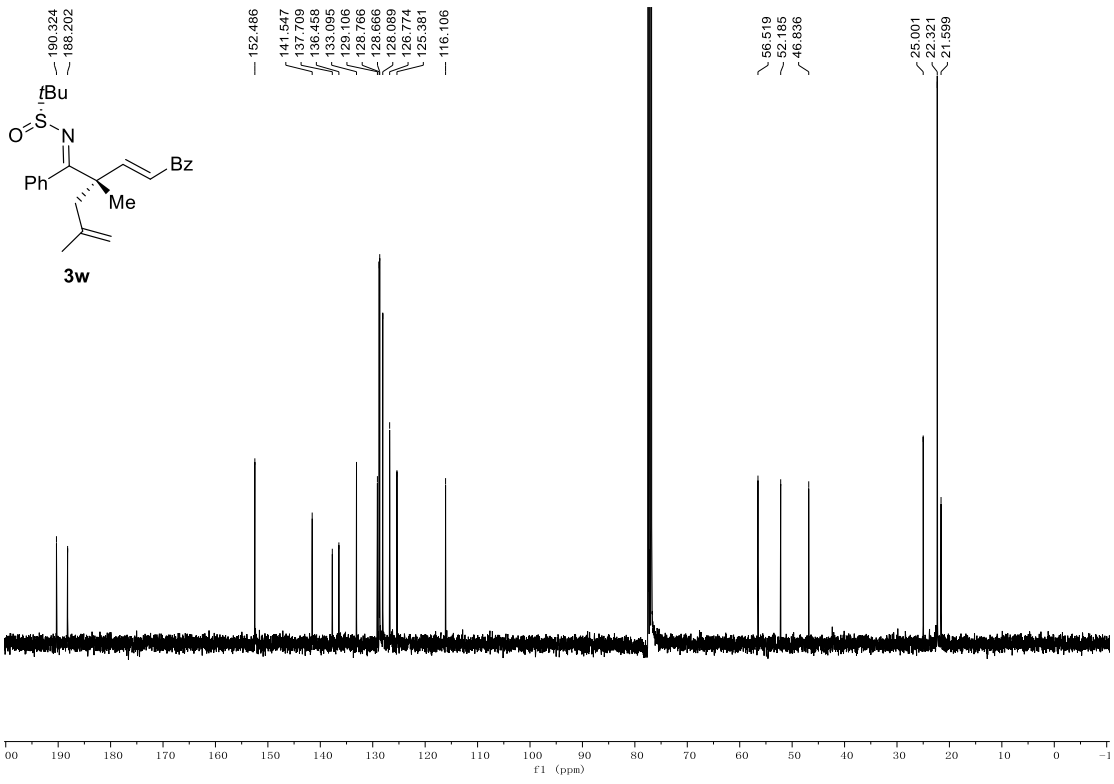
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3v**



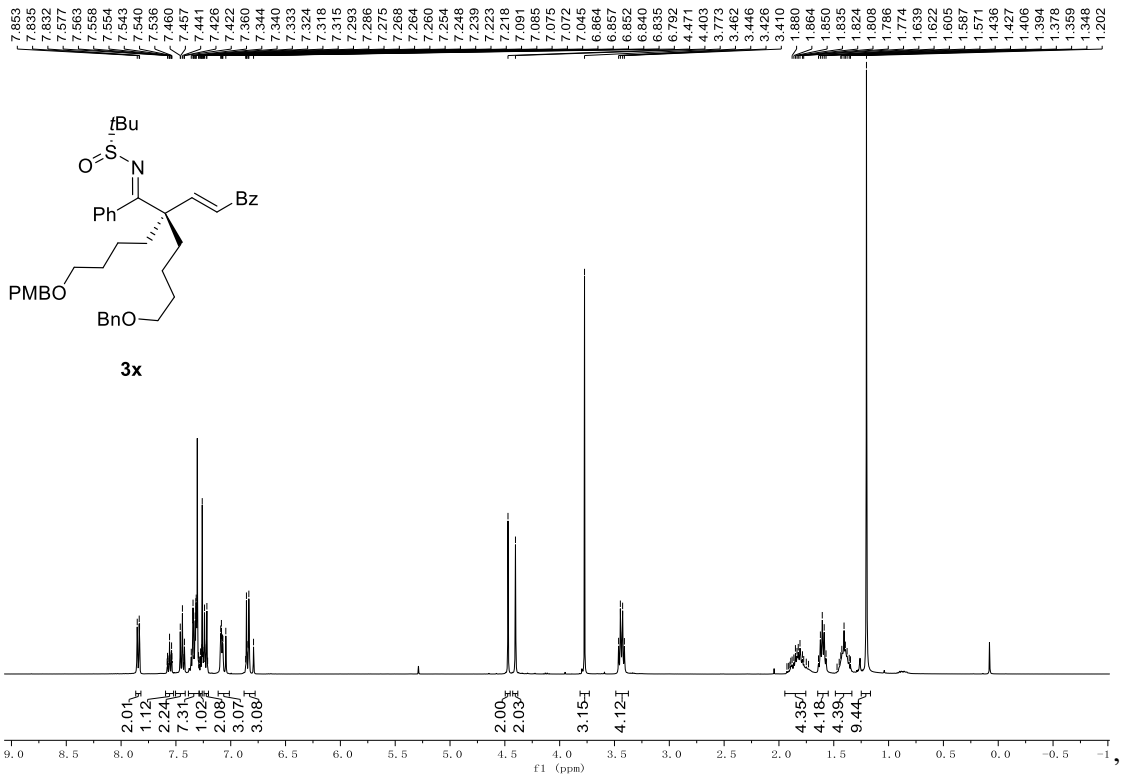
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3v**



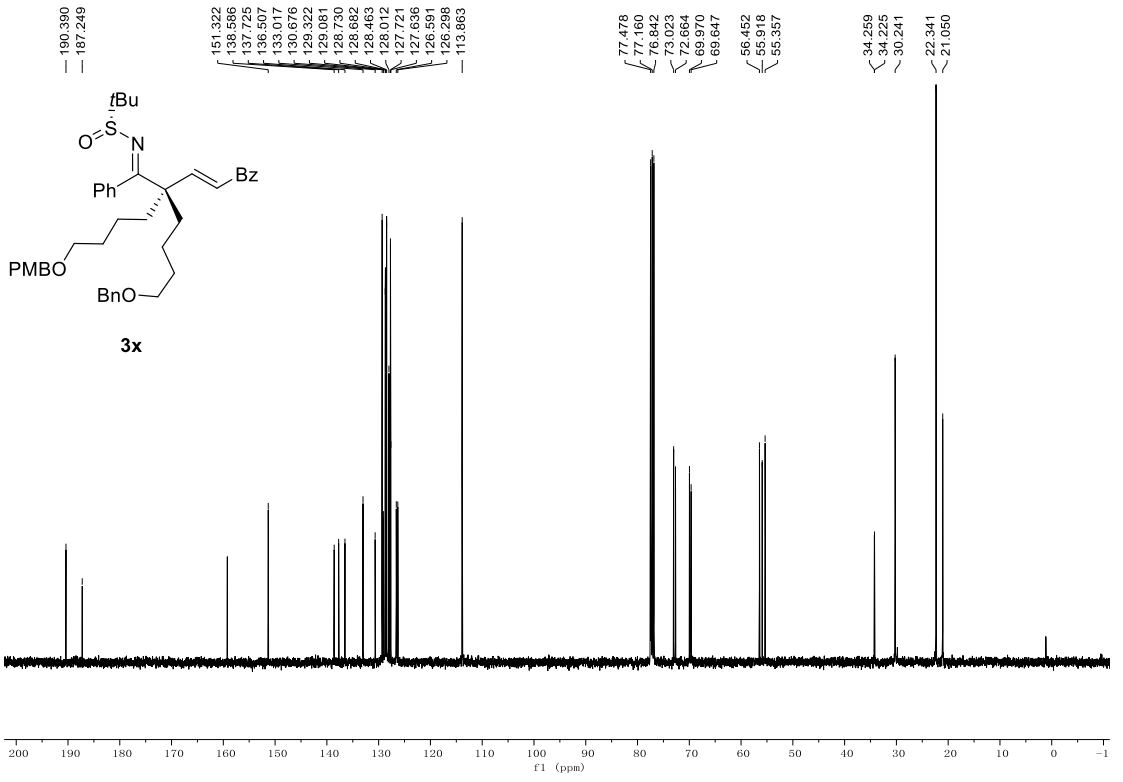
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3w**



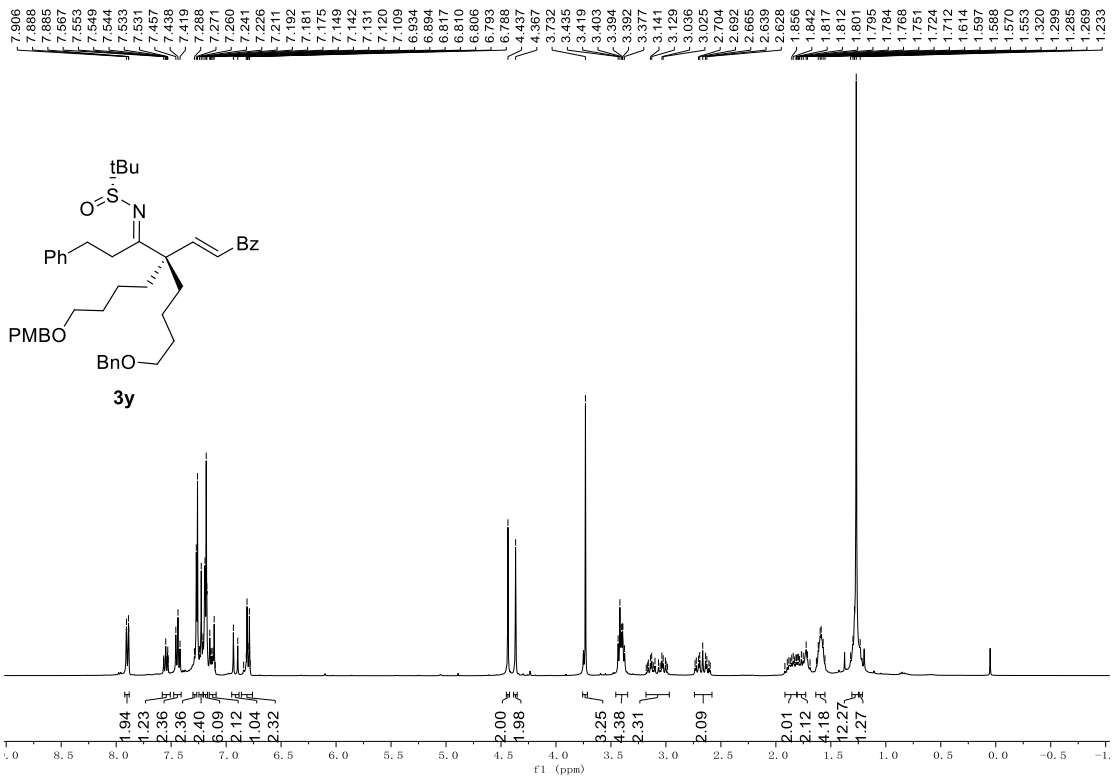
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3w**



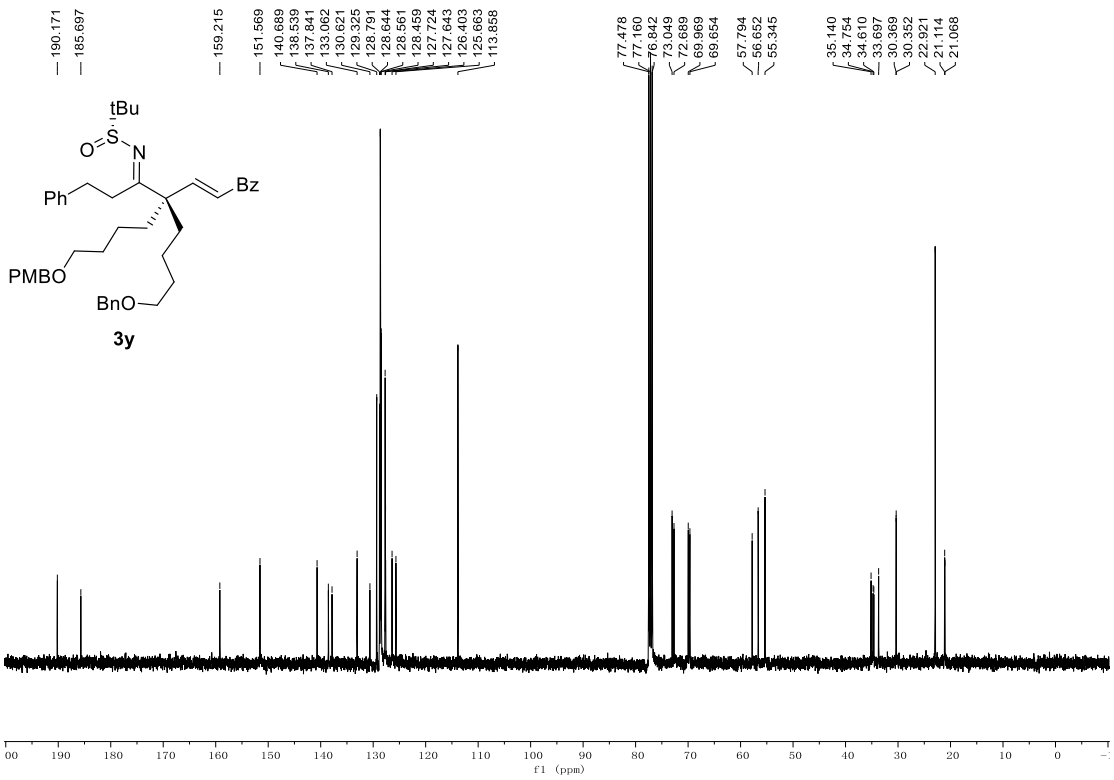
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3x**



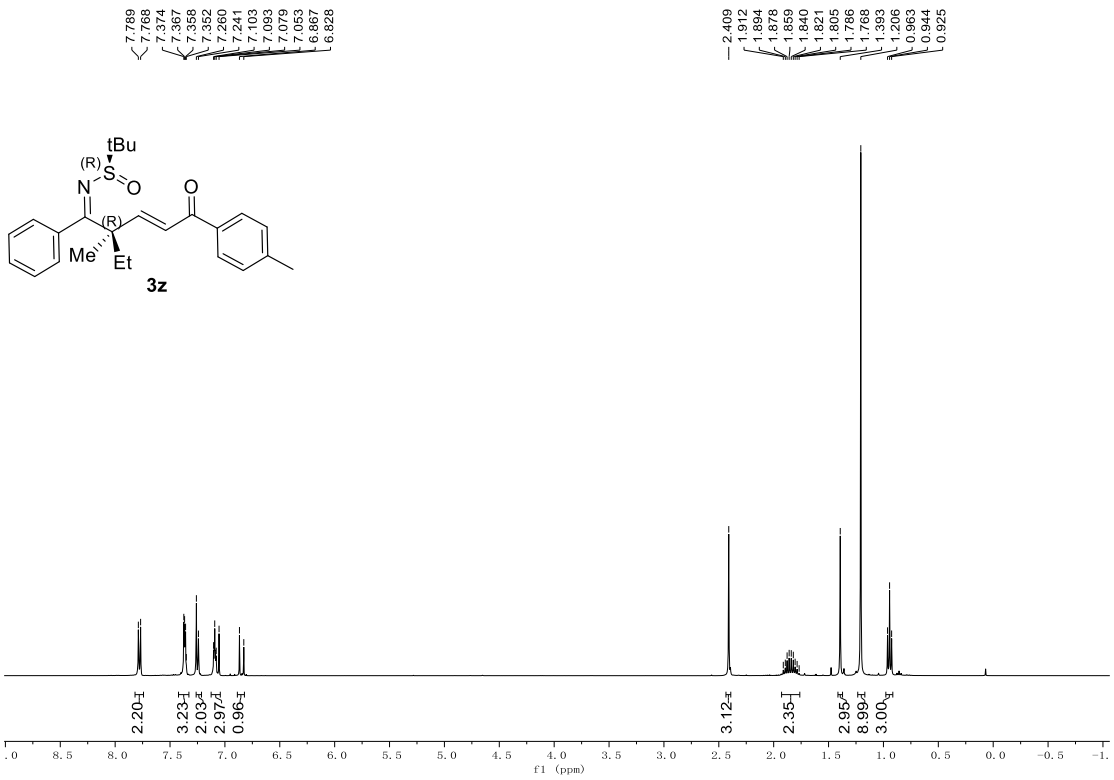
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3x**



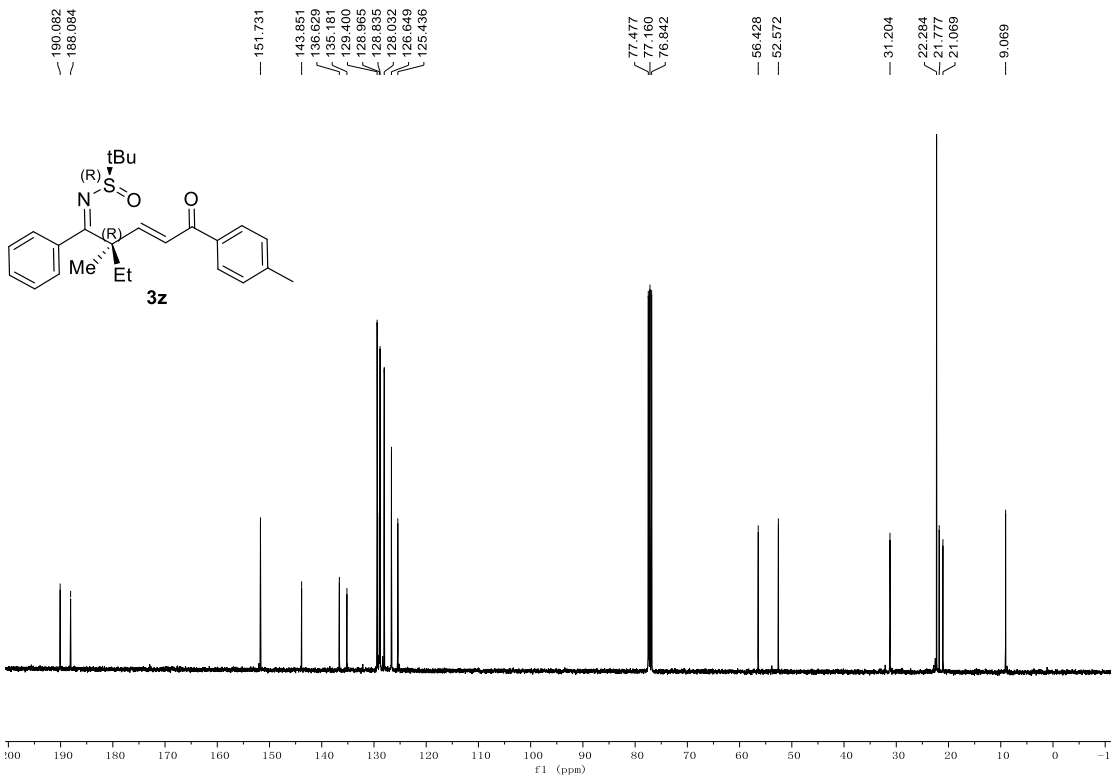
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3y**



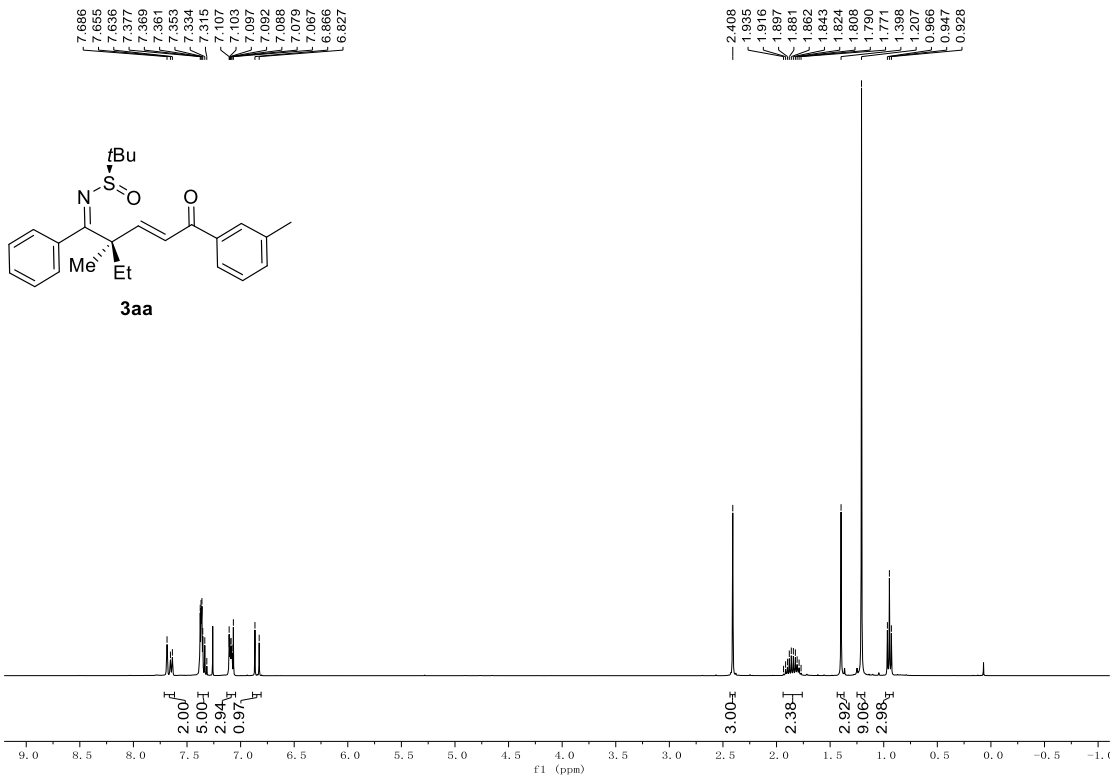
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3y**



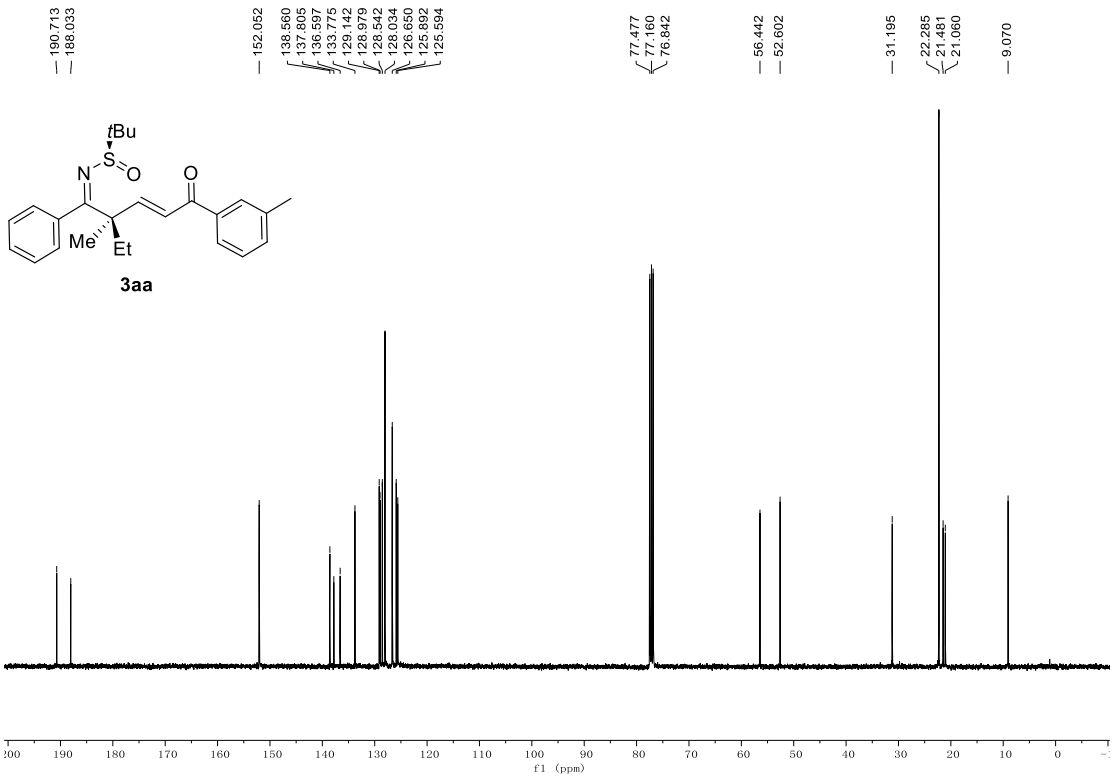
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3z**



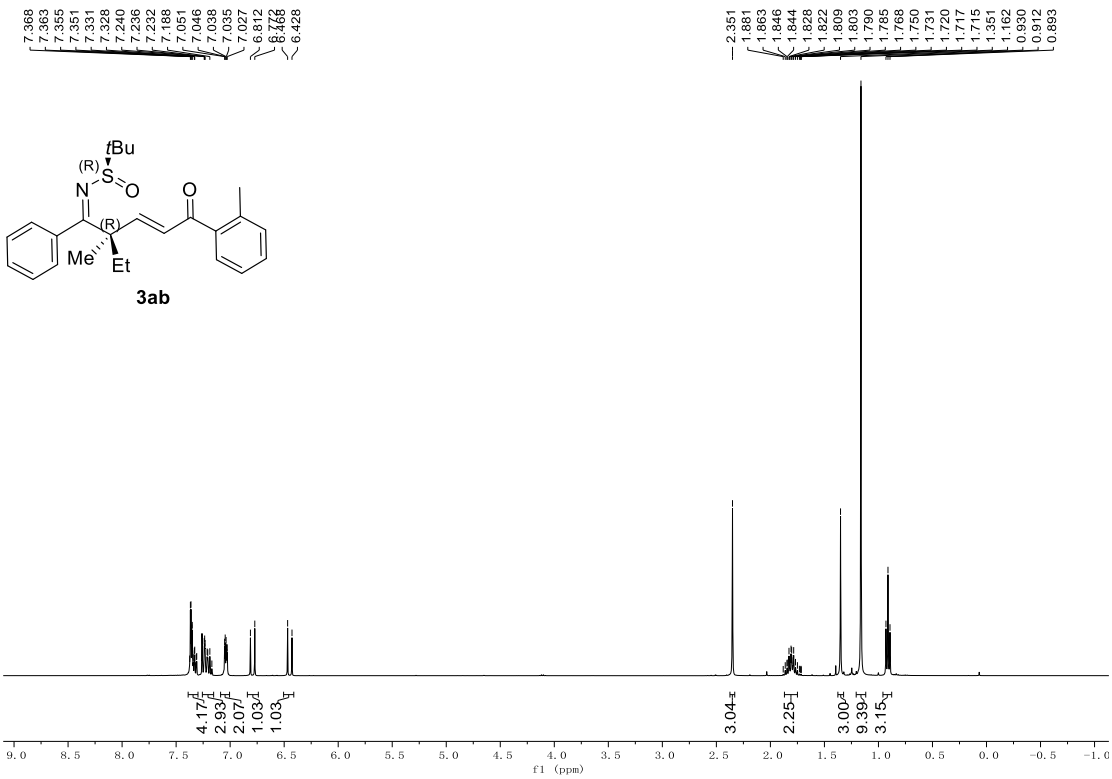
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3z**



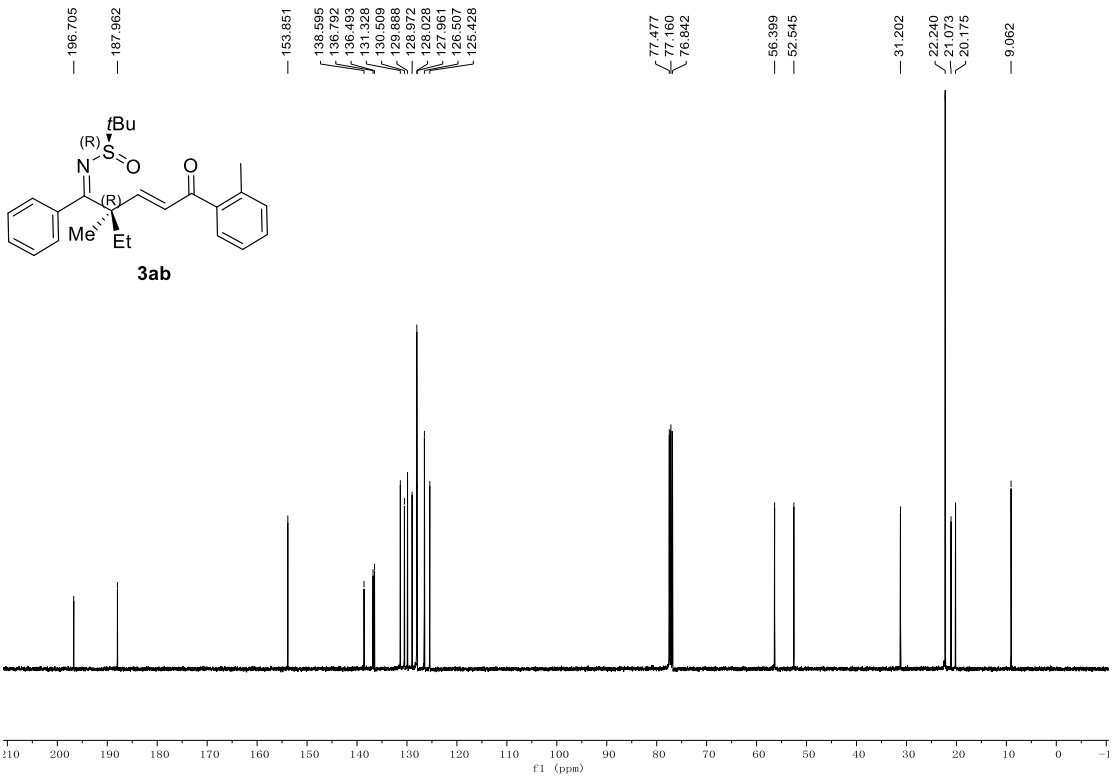
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3aa**



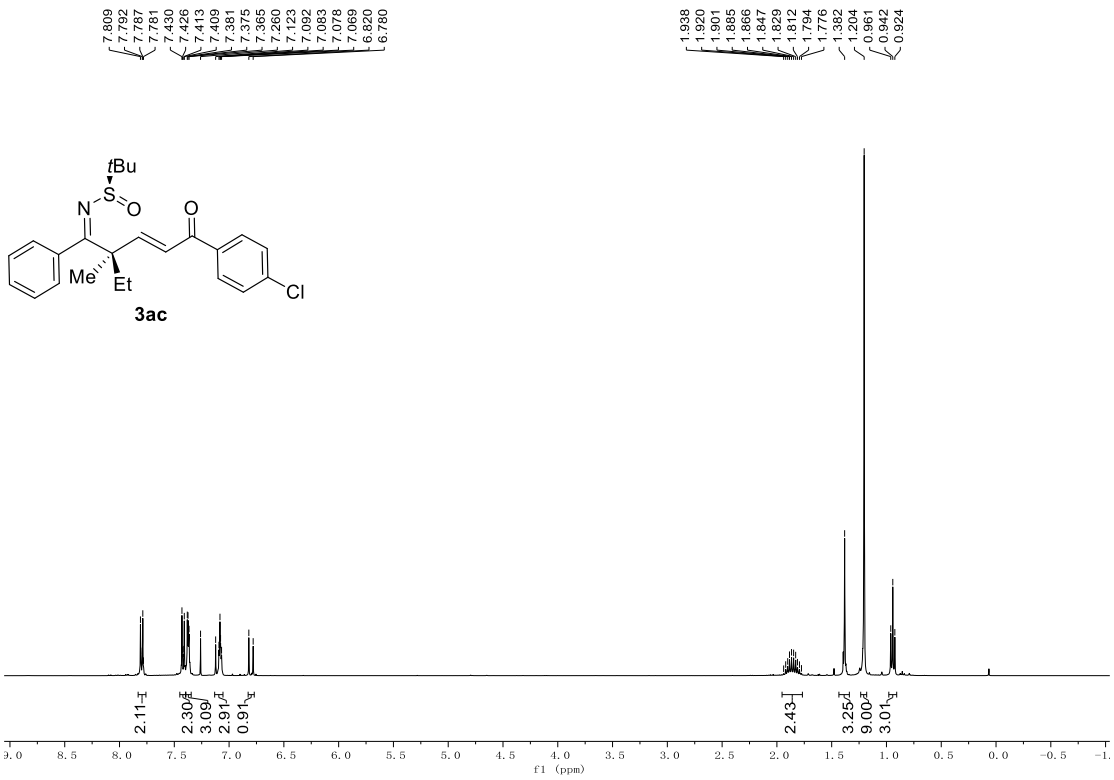
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *2R*)-**3aa**



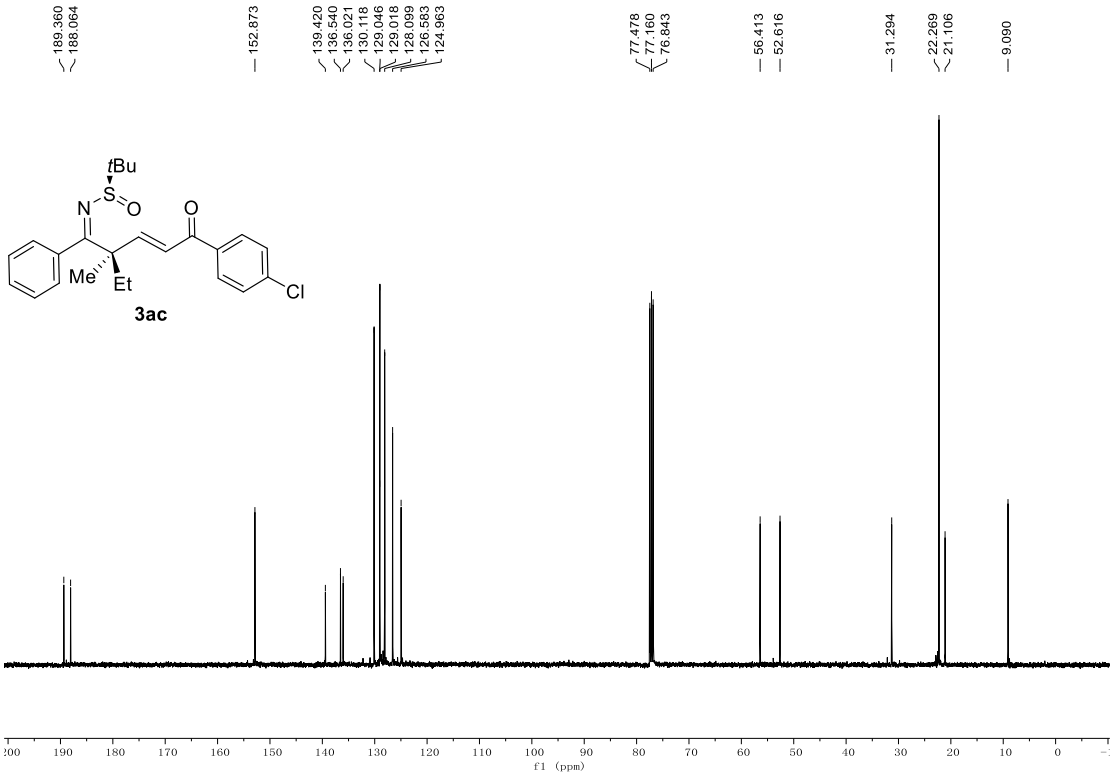
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ab**



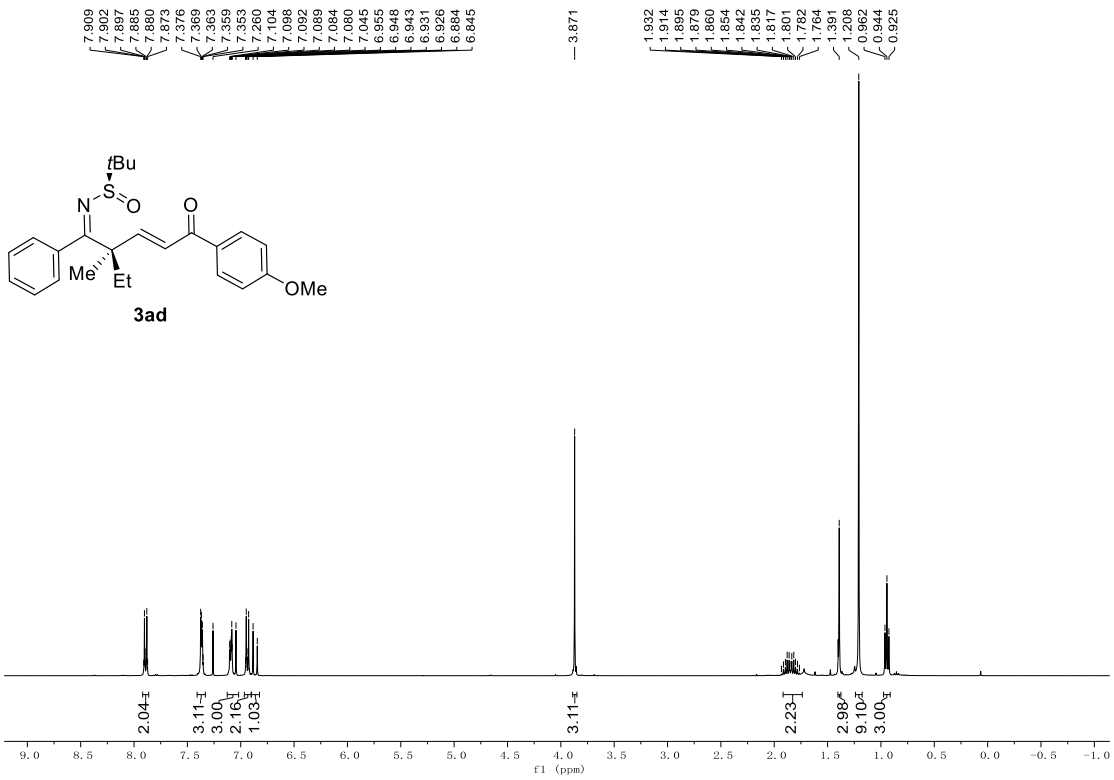
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ab**



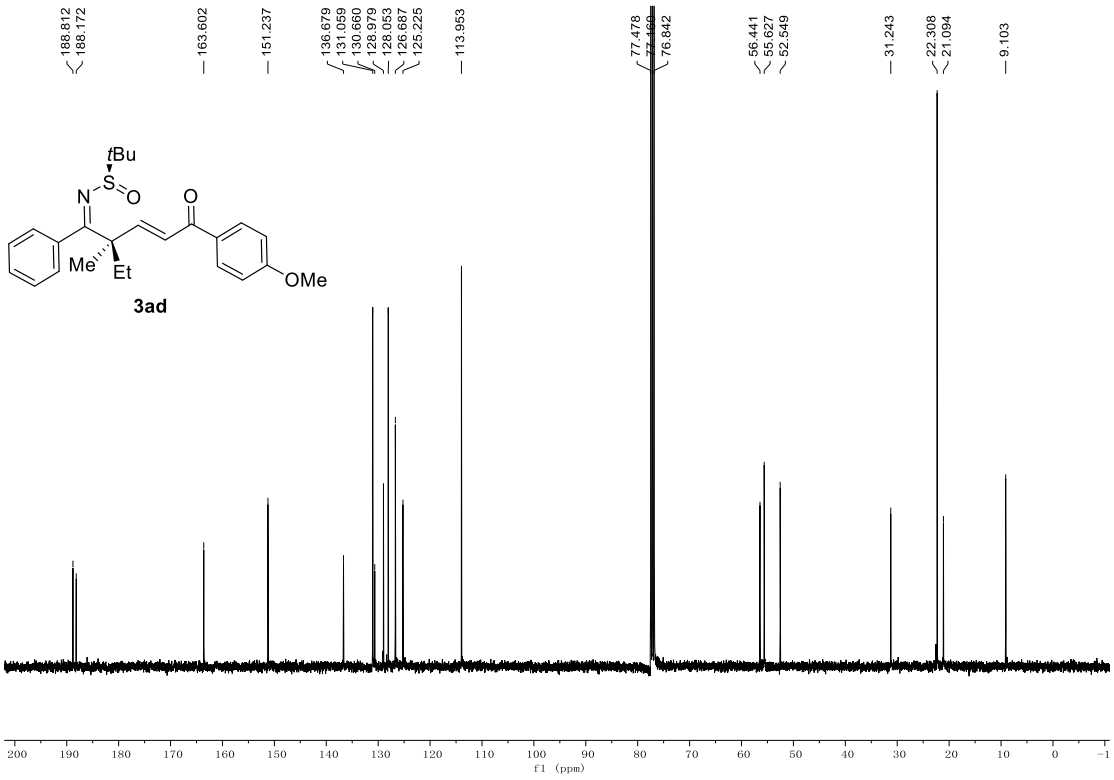
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ac**



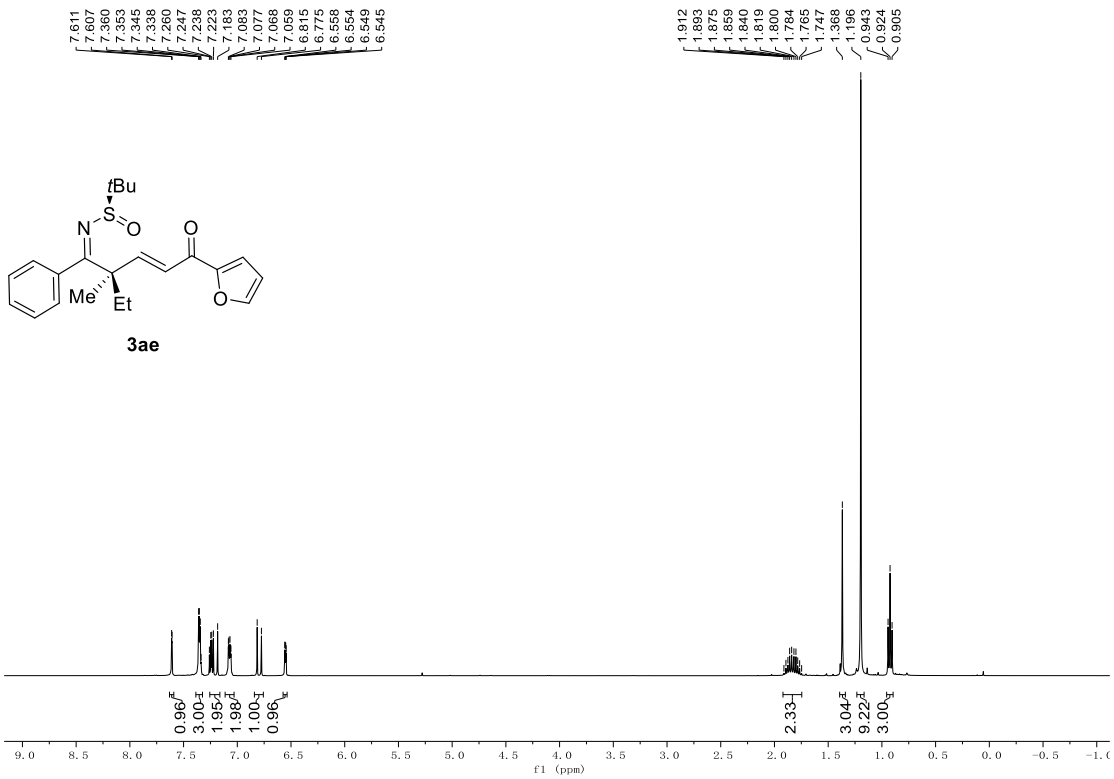
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ac**



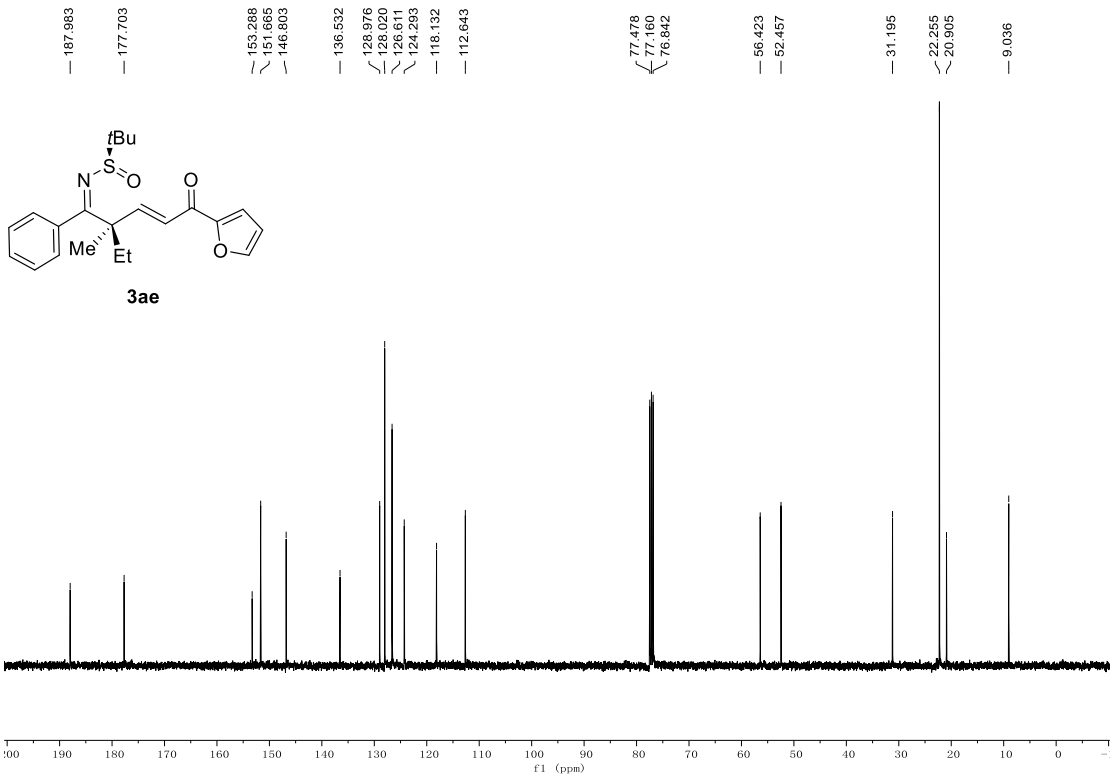
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ad**



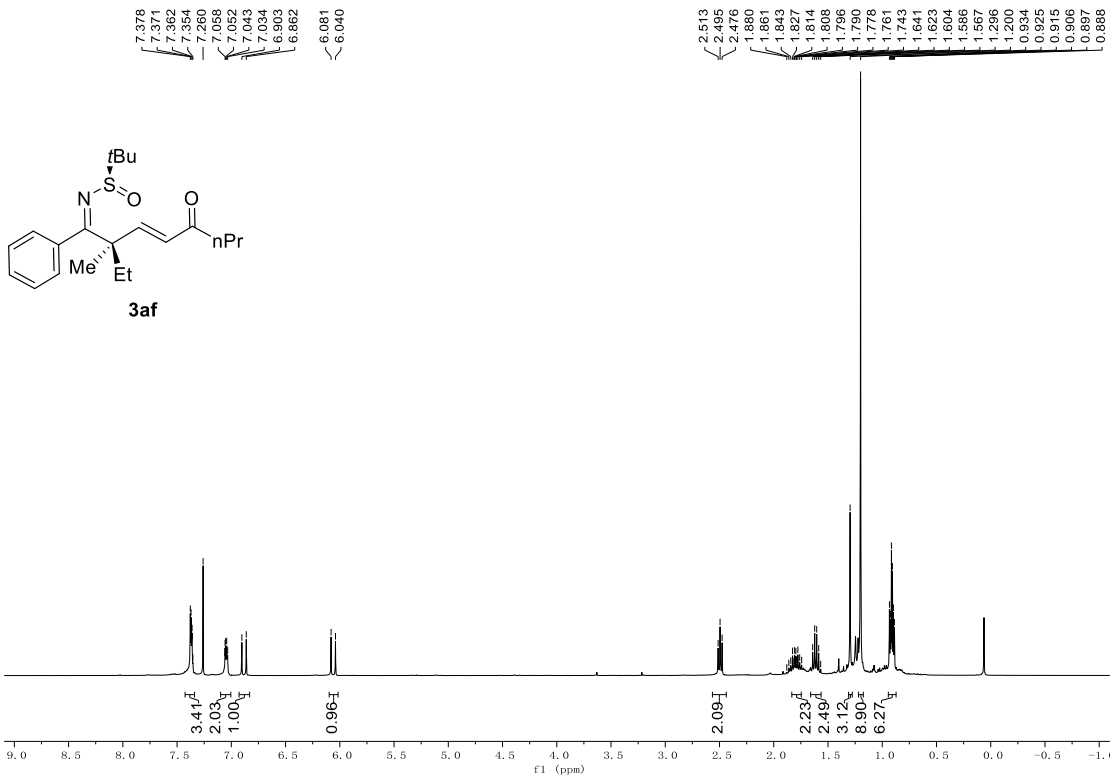
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ad**



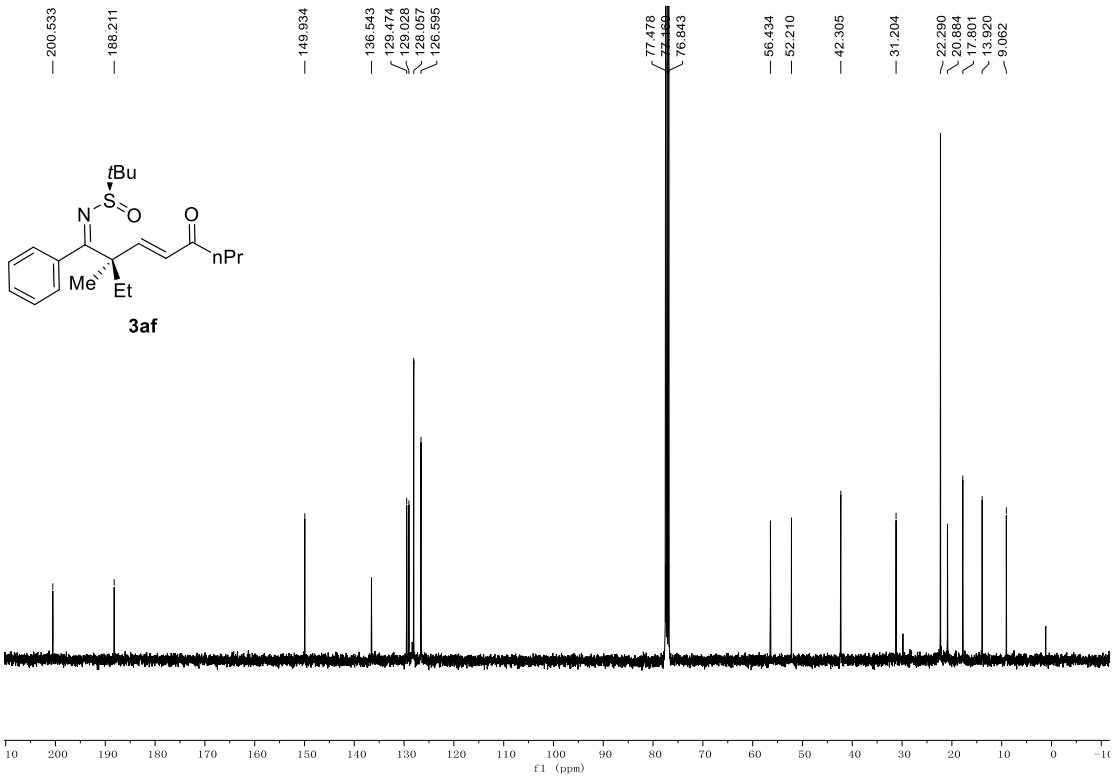
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ae**



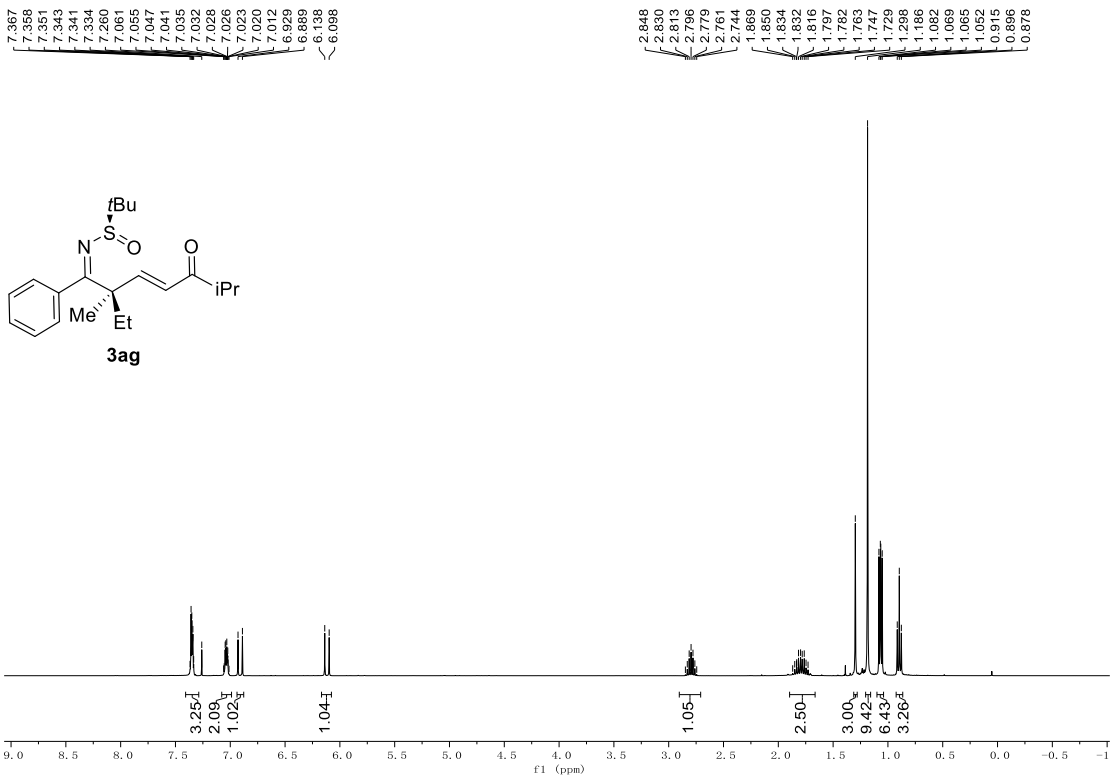
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ae**



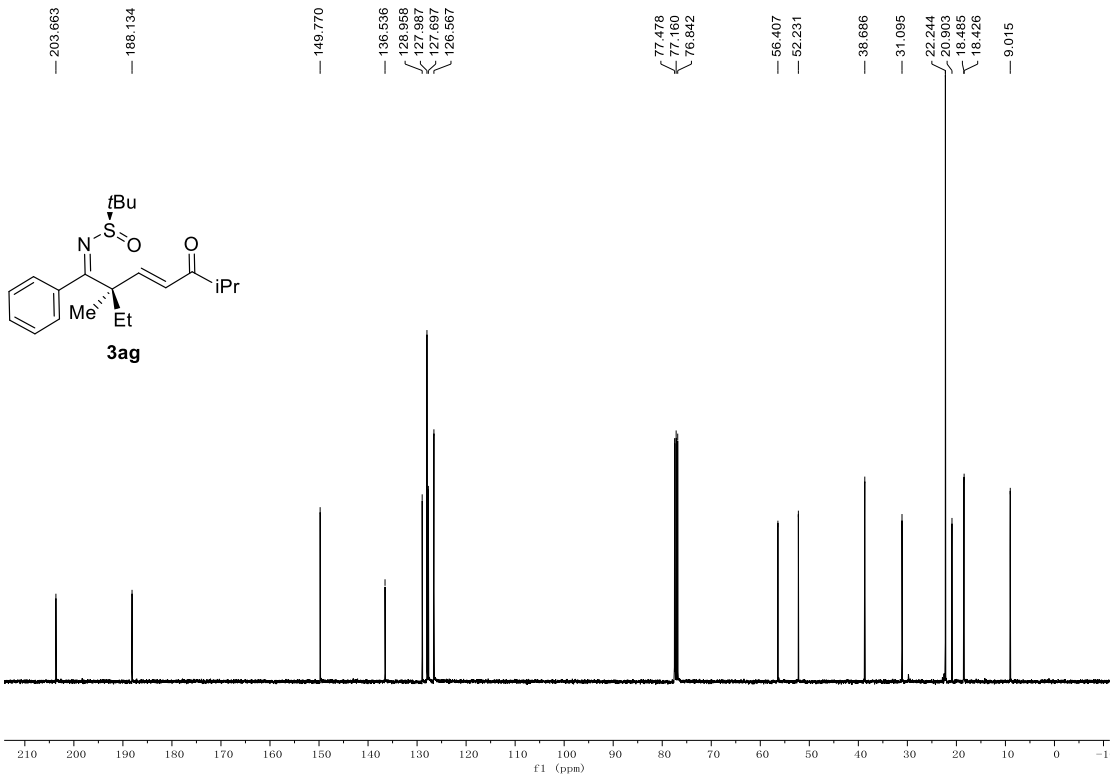
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3af**



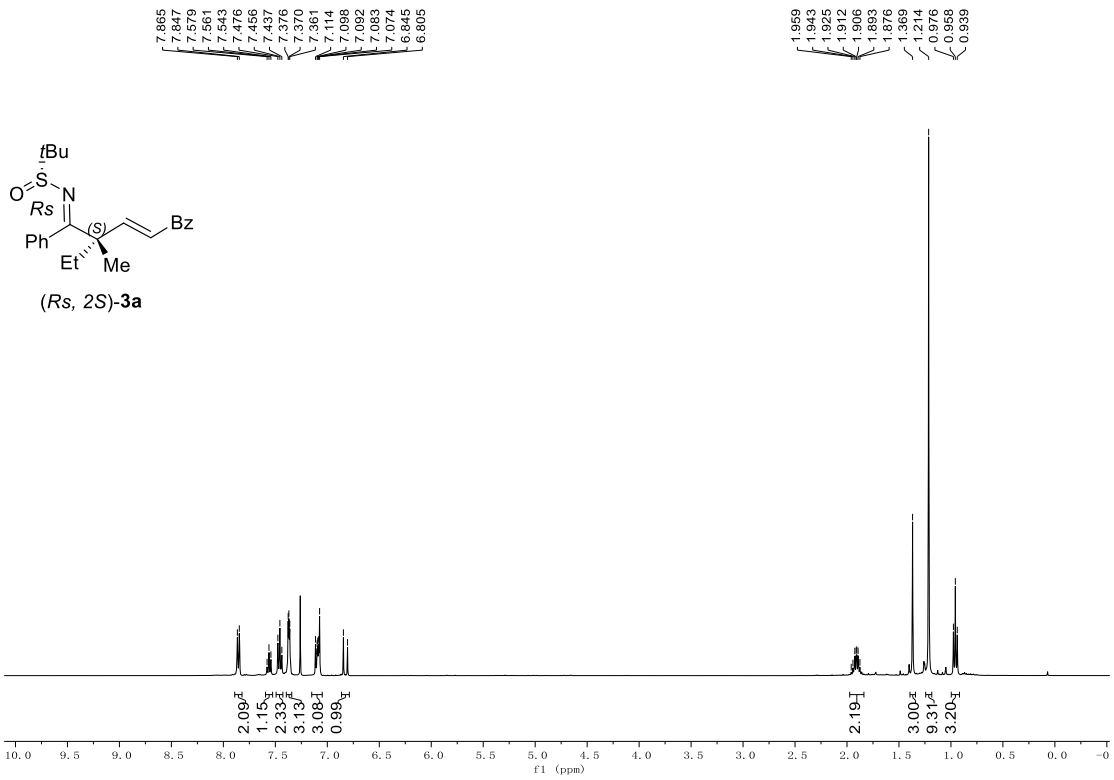
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3af**



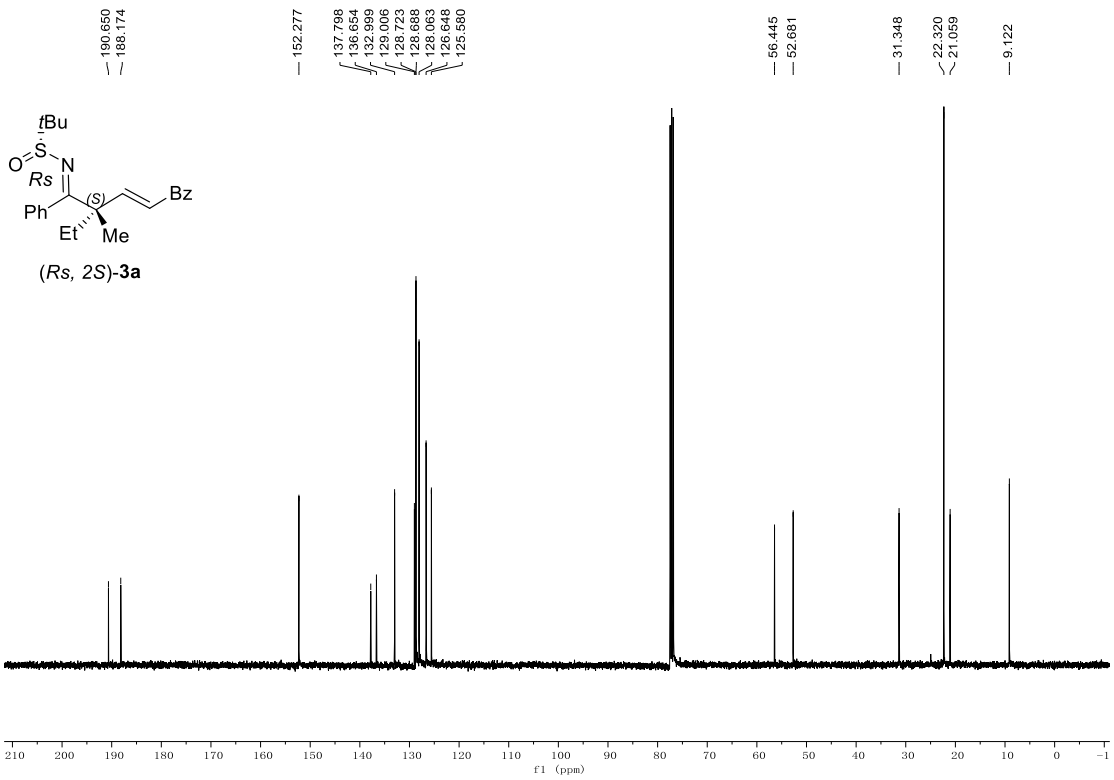
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ag**



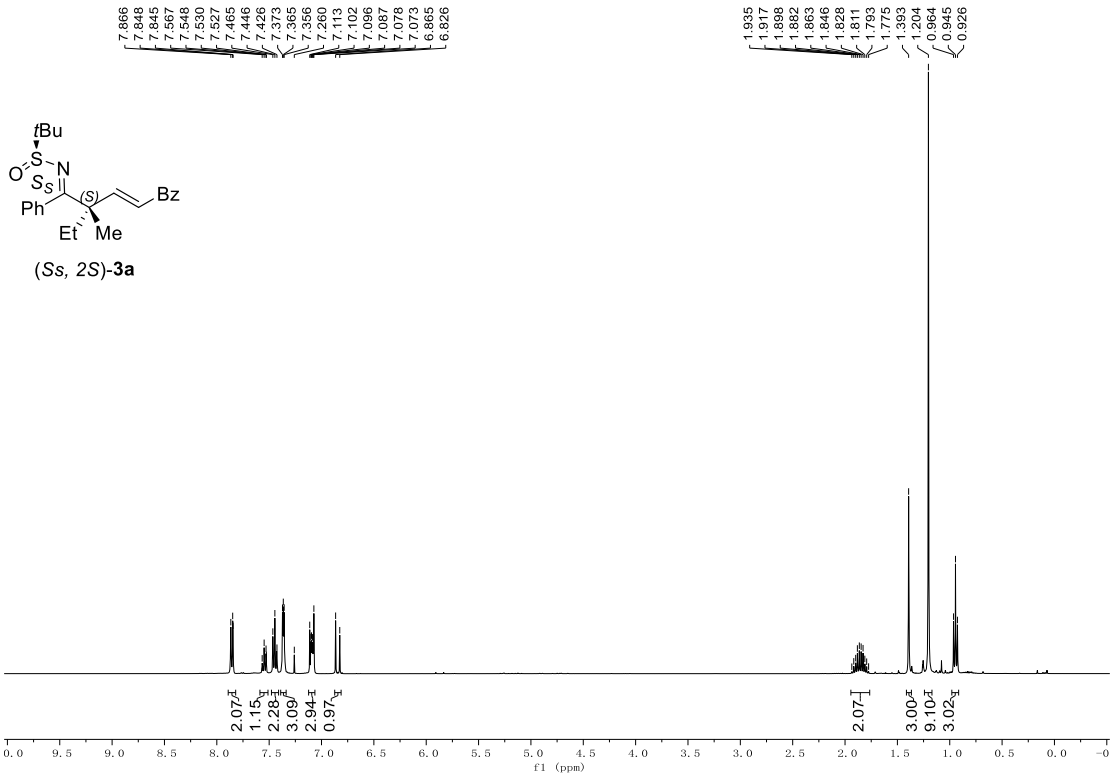
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ag**



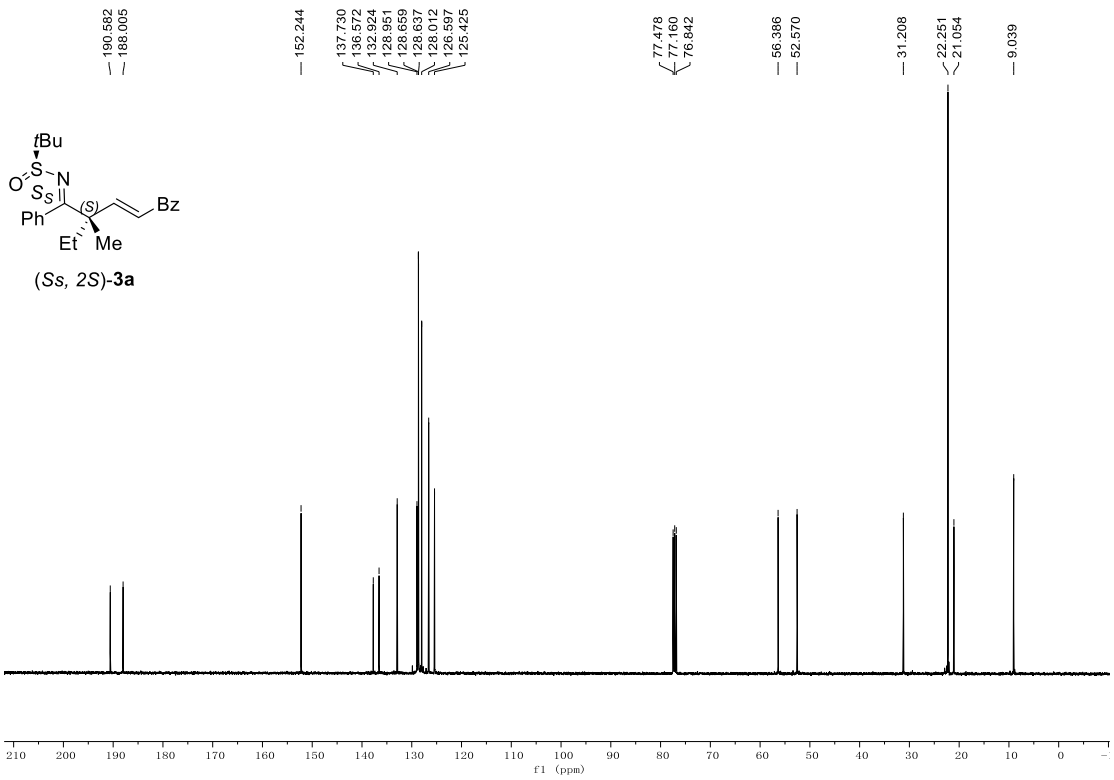
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *2S*)-**3a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



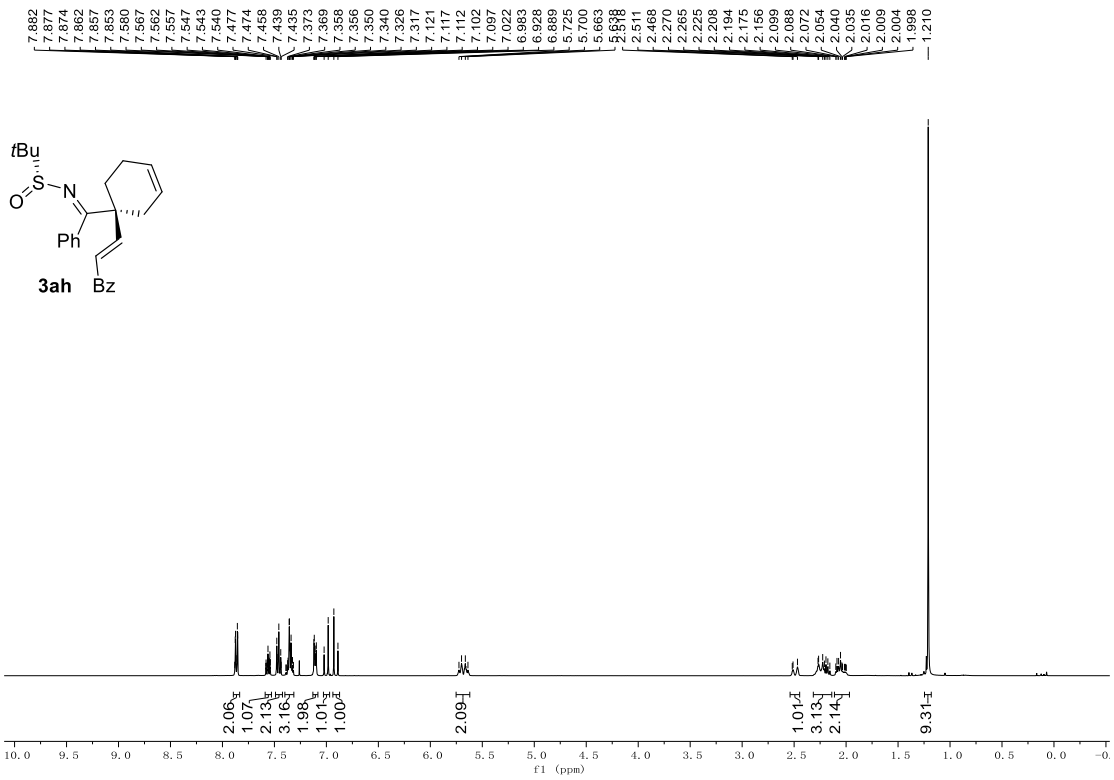
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *2S*)-**3a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



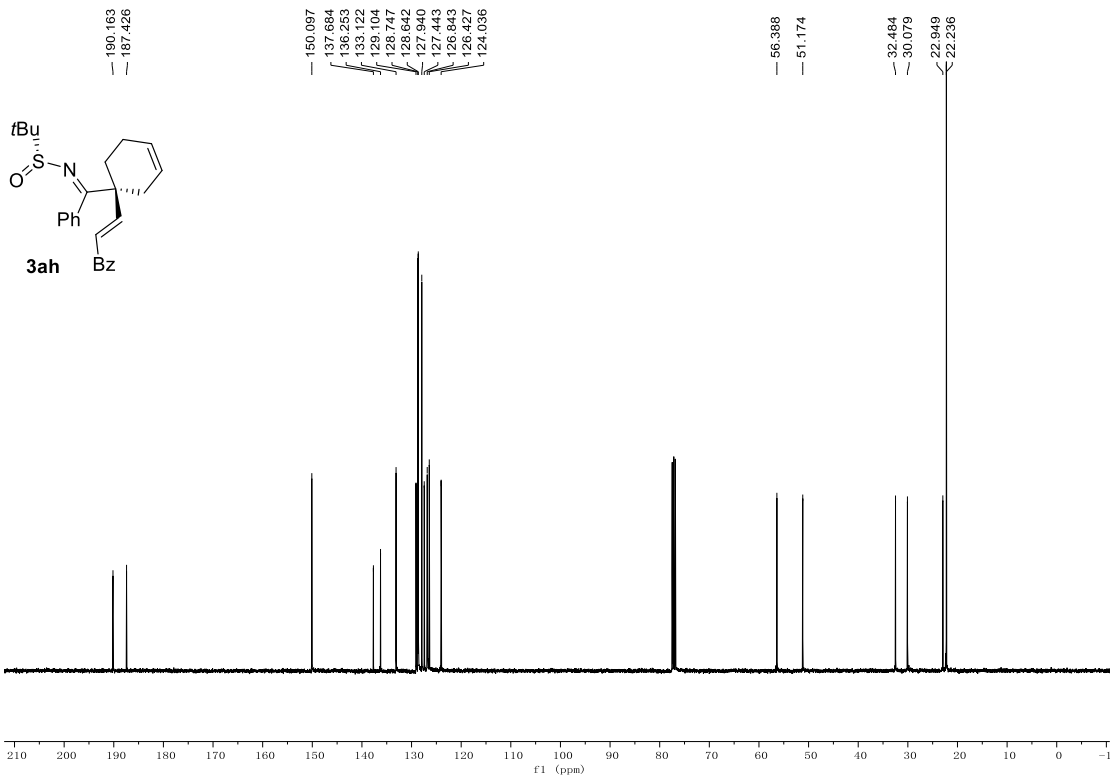
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *2S*)-**3a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



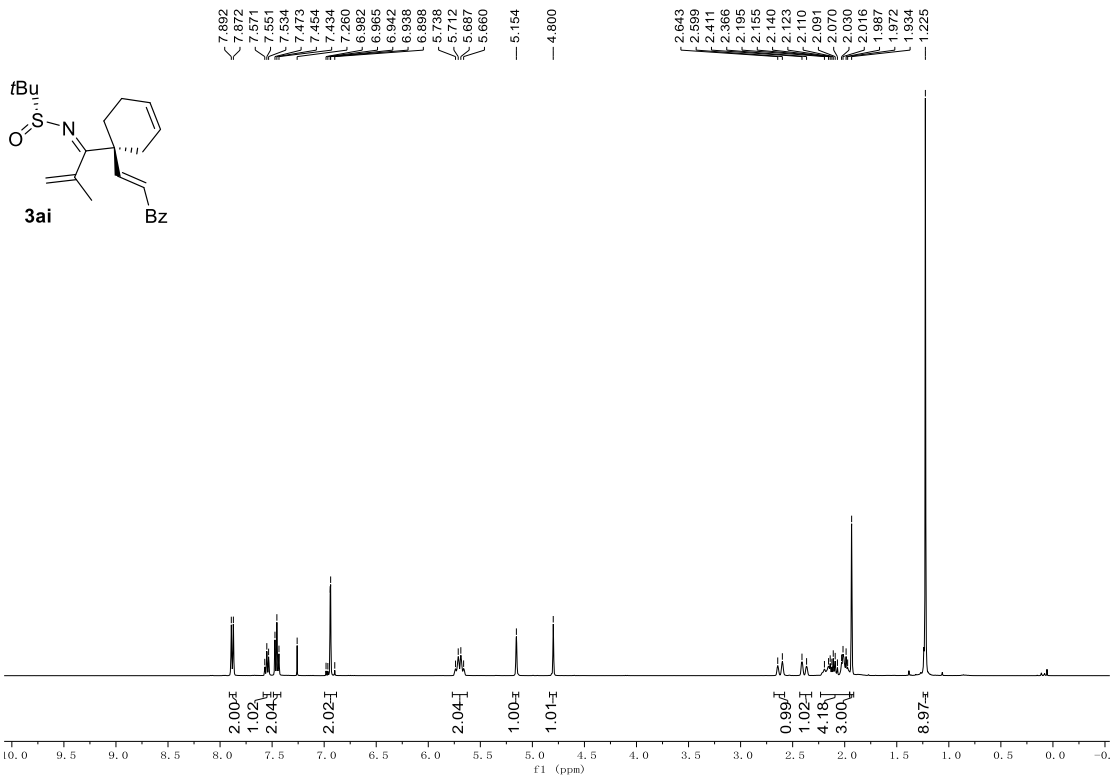
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *2S*)-**3a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



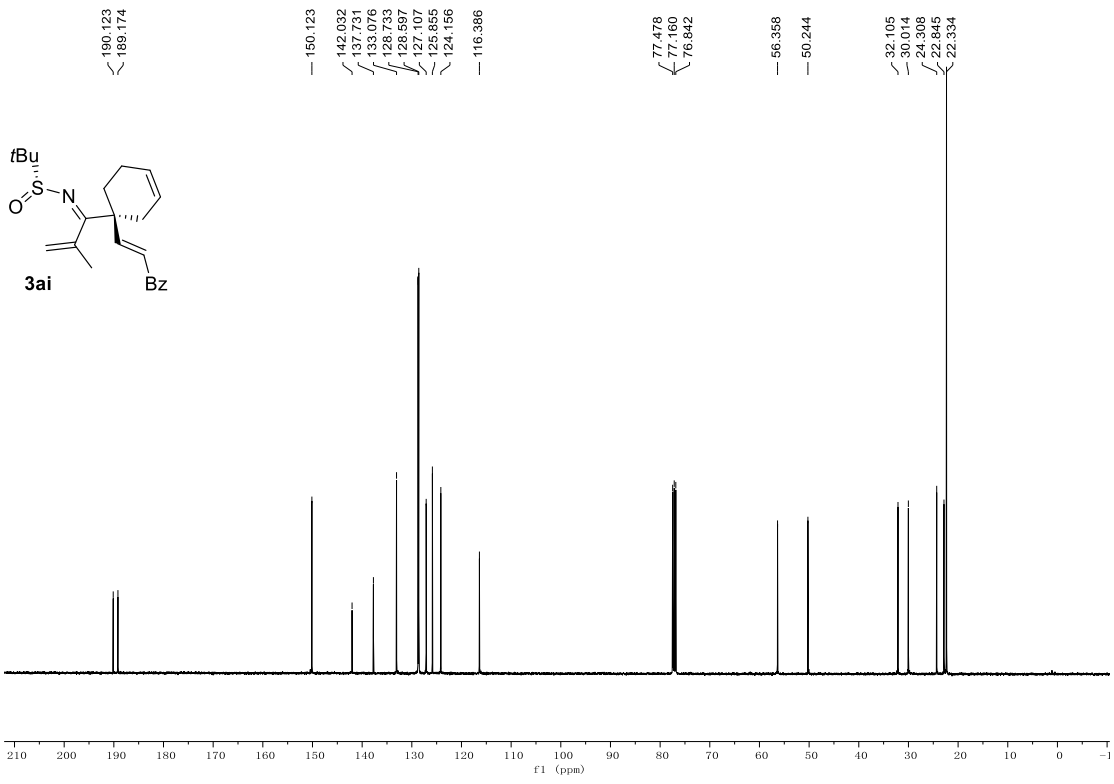
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ah**



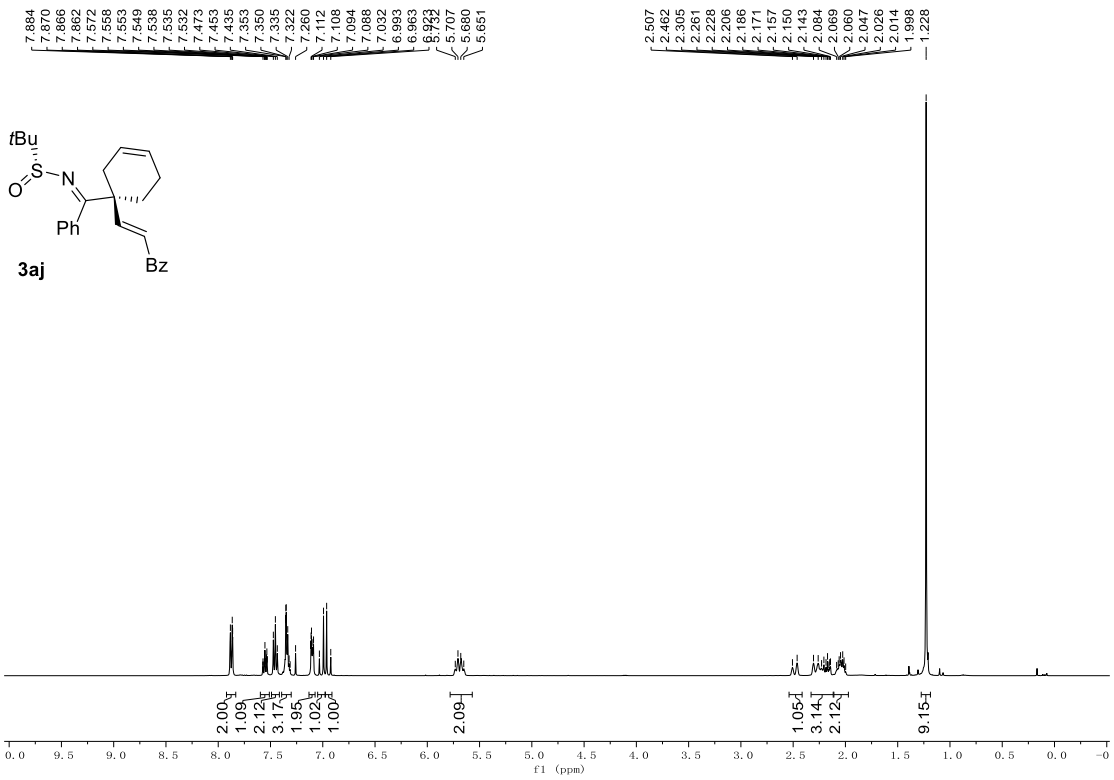
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ah**



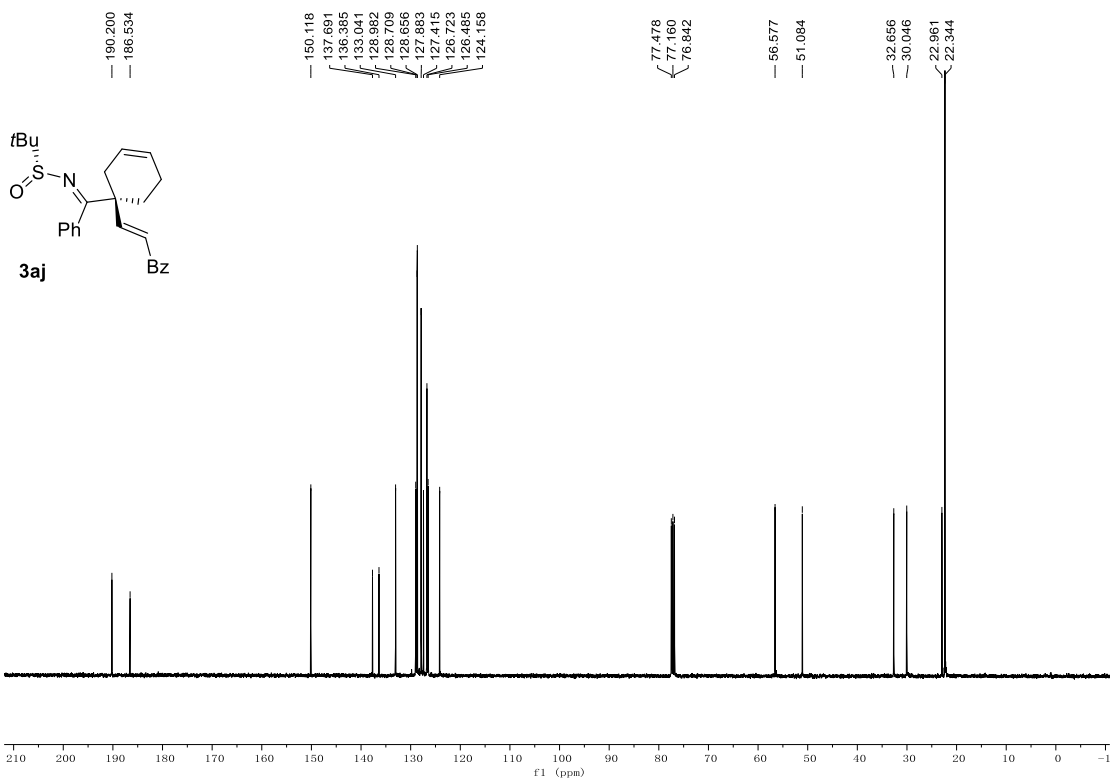
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ai**



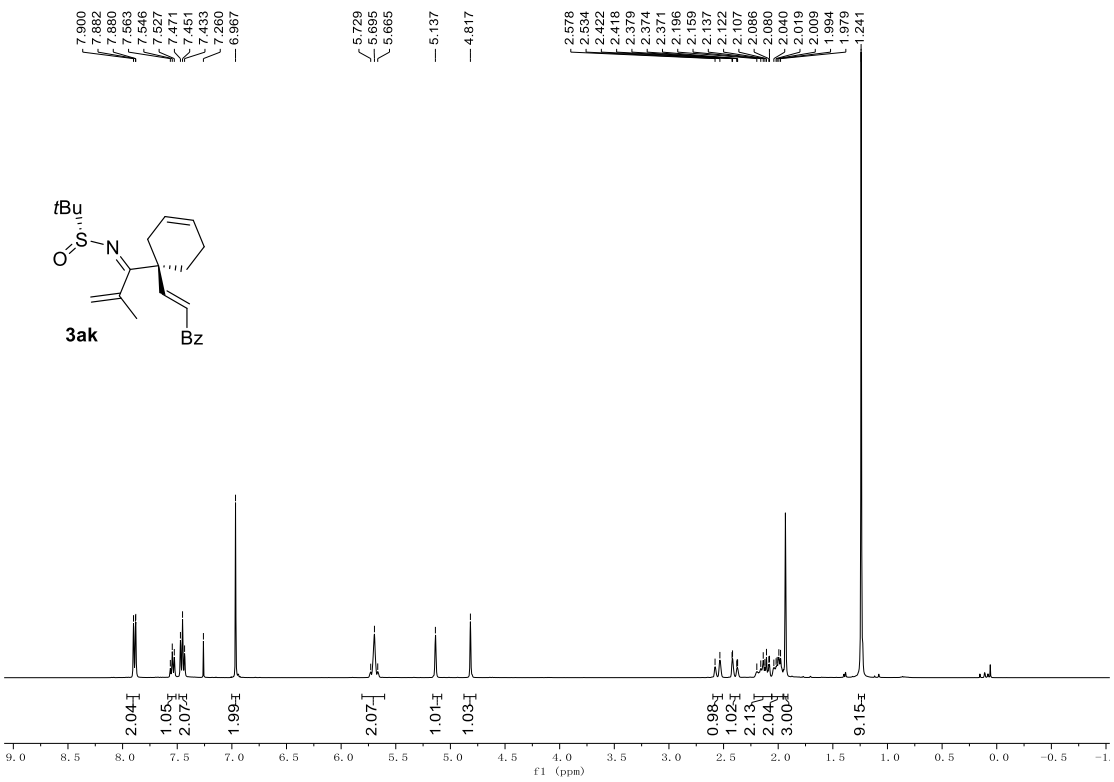
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ai**



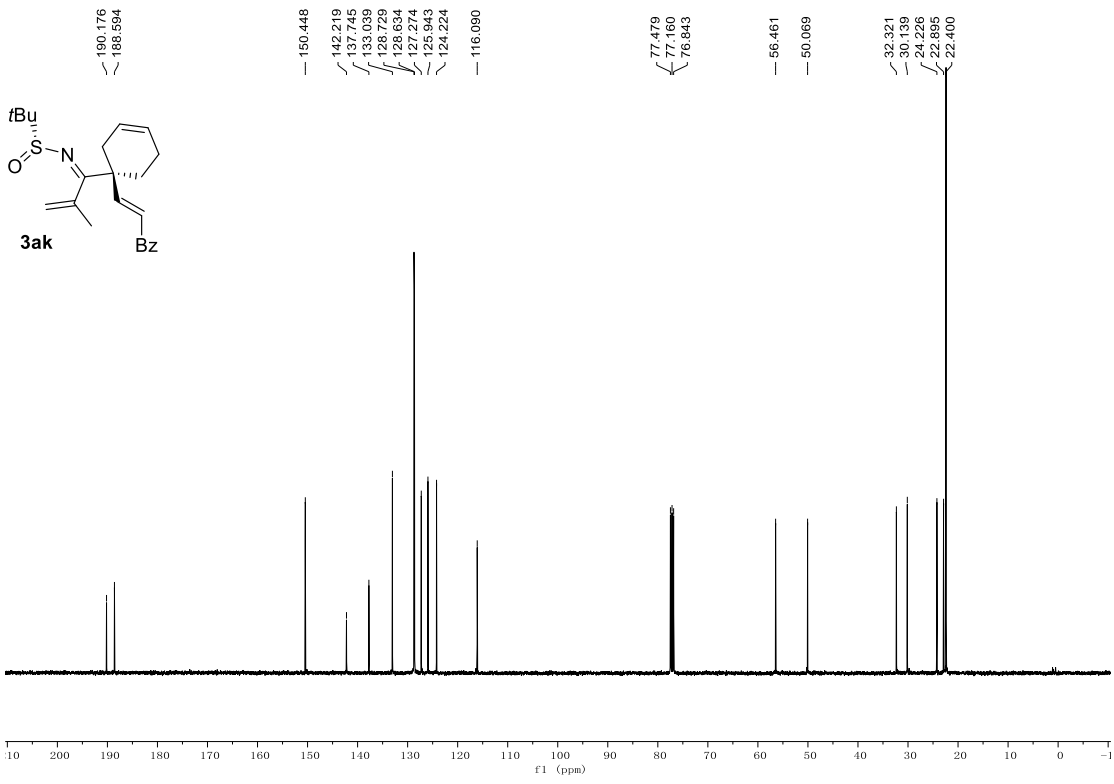
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3aj**



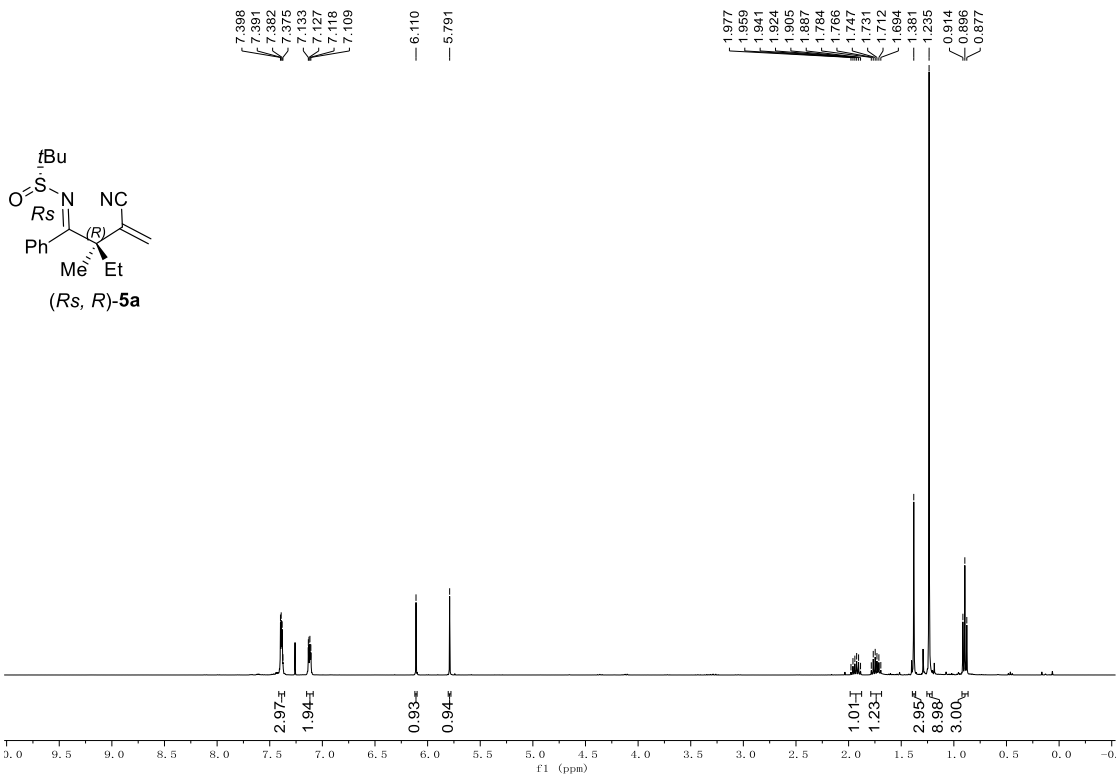
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3aj**



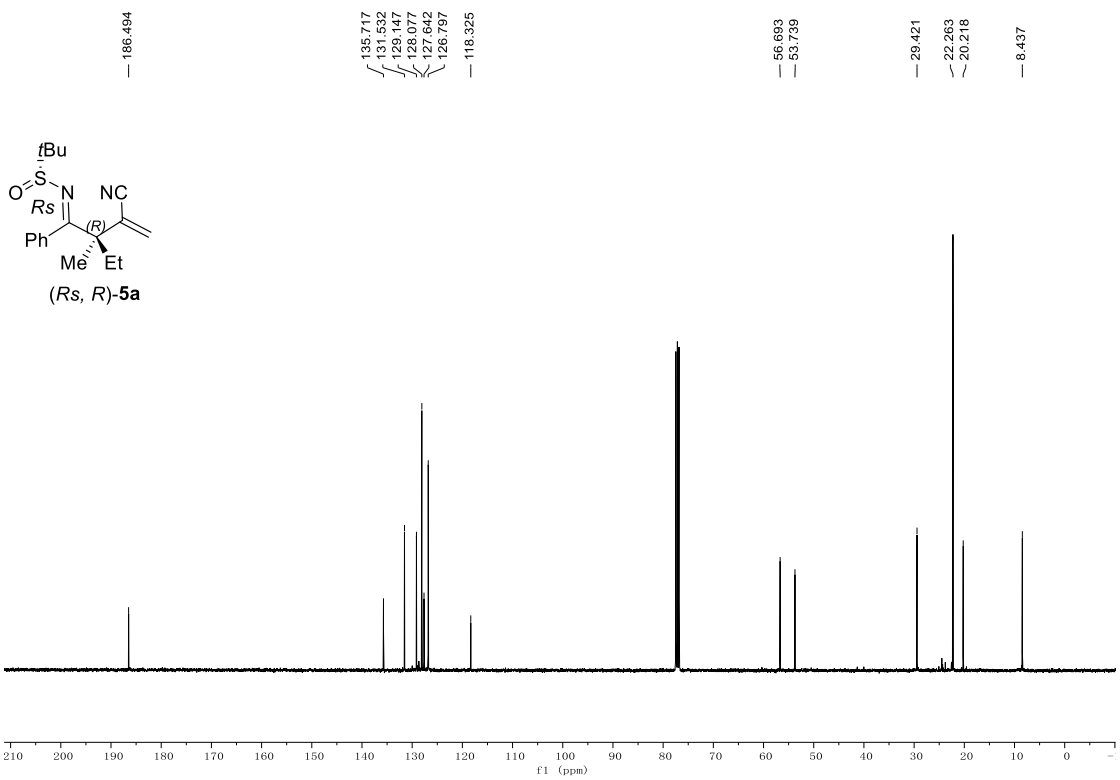
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ak**



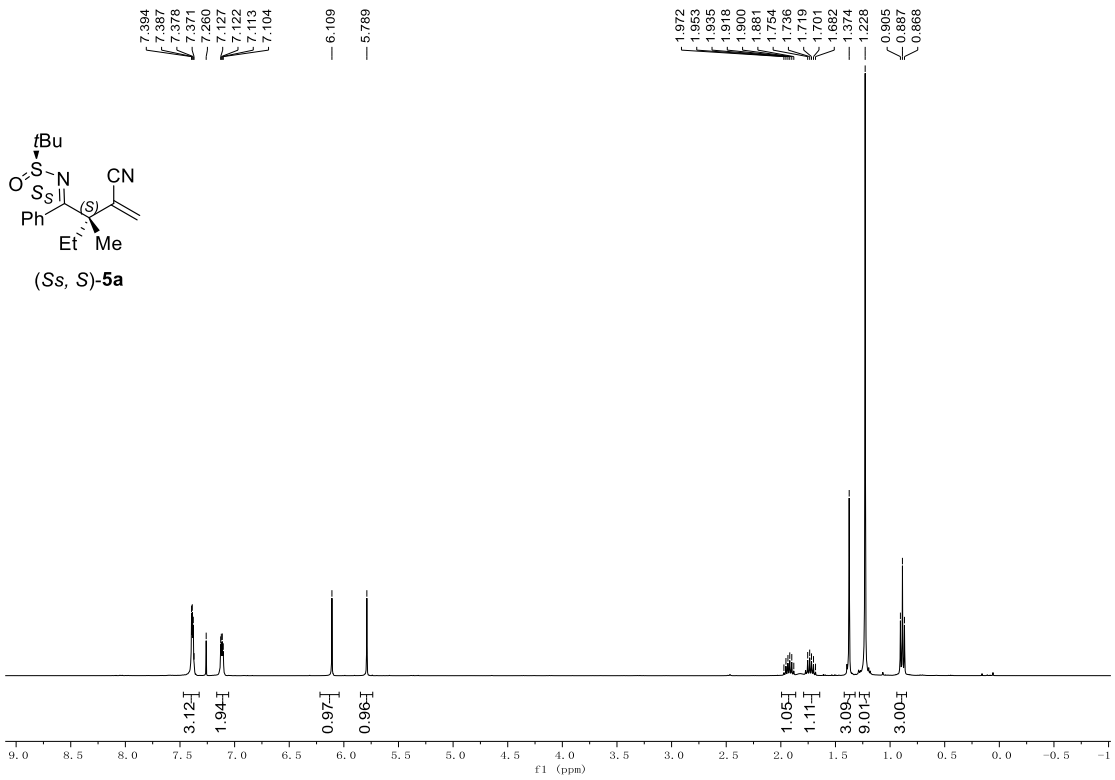
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *2S*)-**3ak**



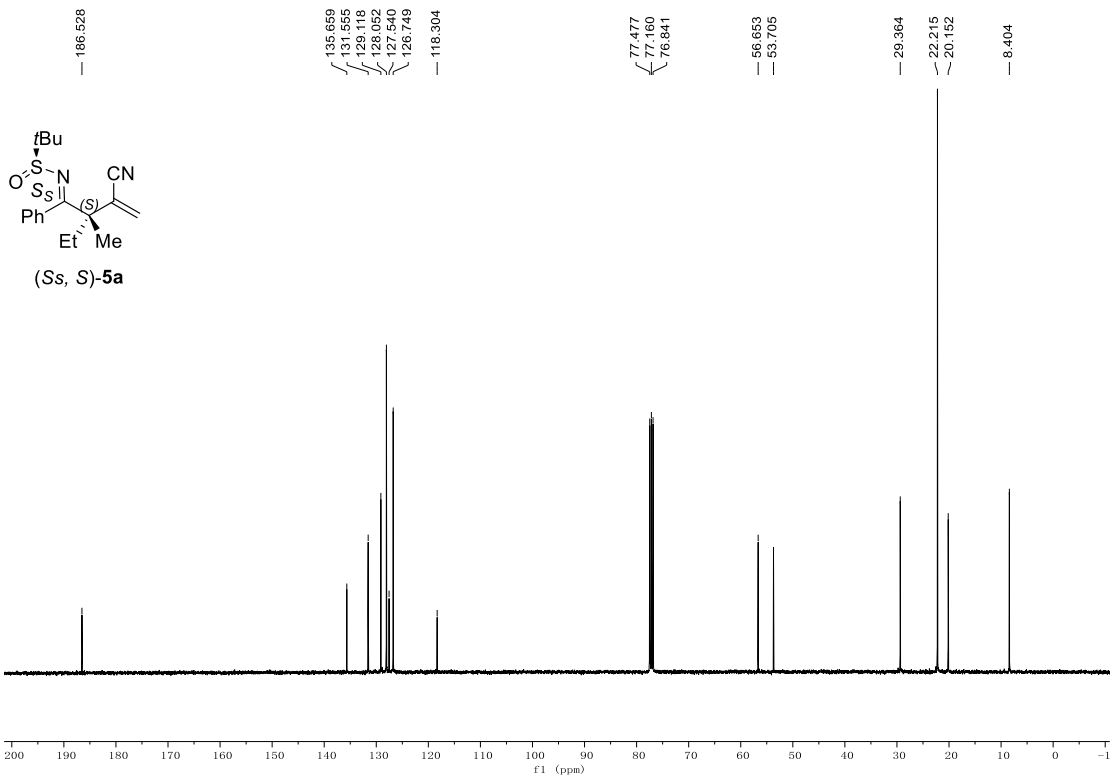
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *R*)-**5a**



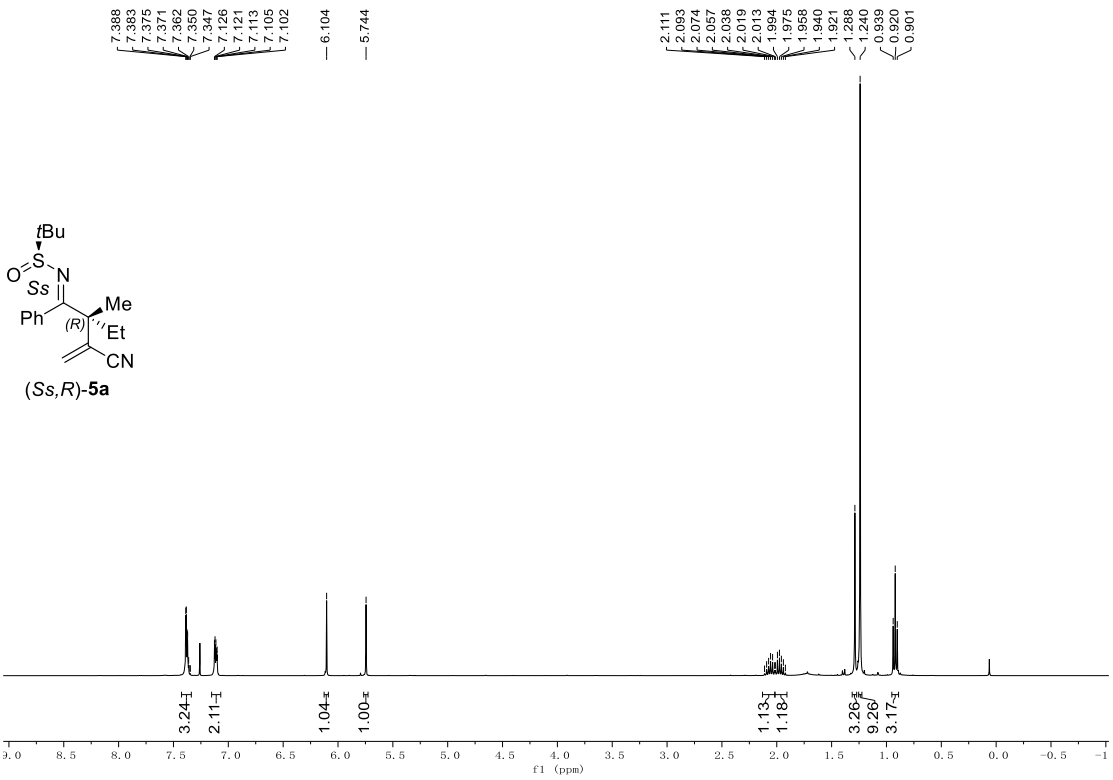
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *R*)-**5a**



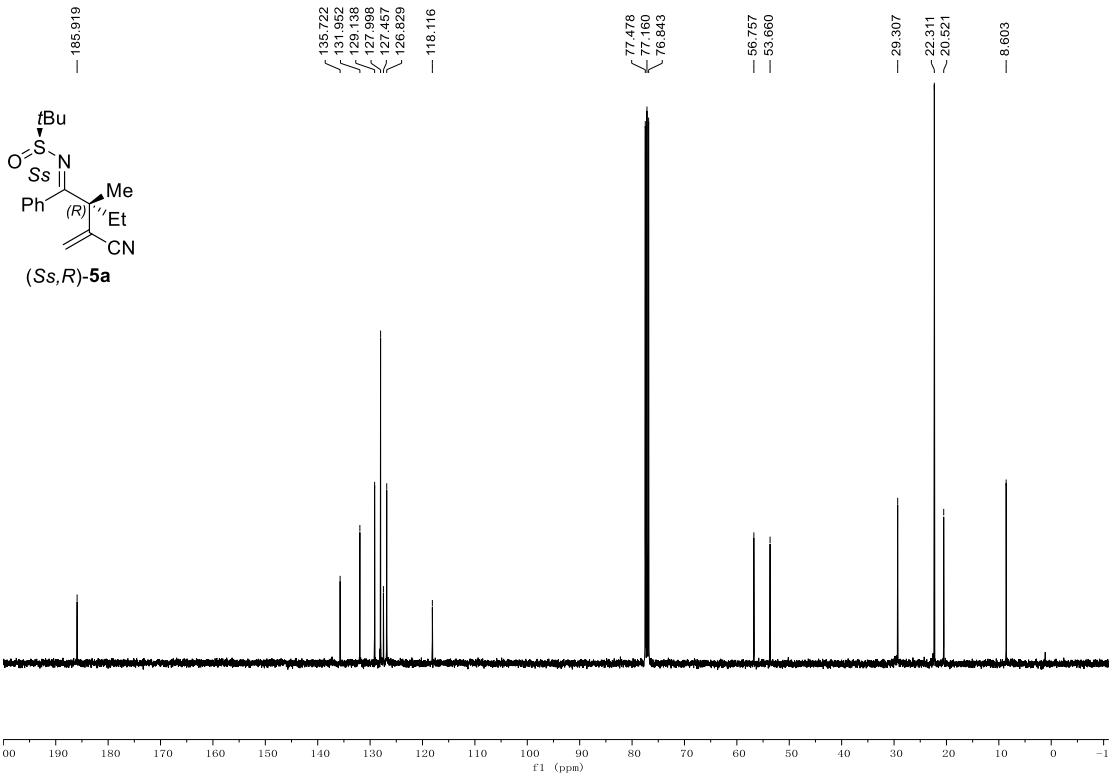
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *S*)-**5a**



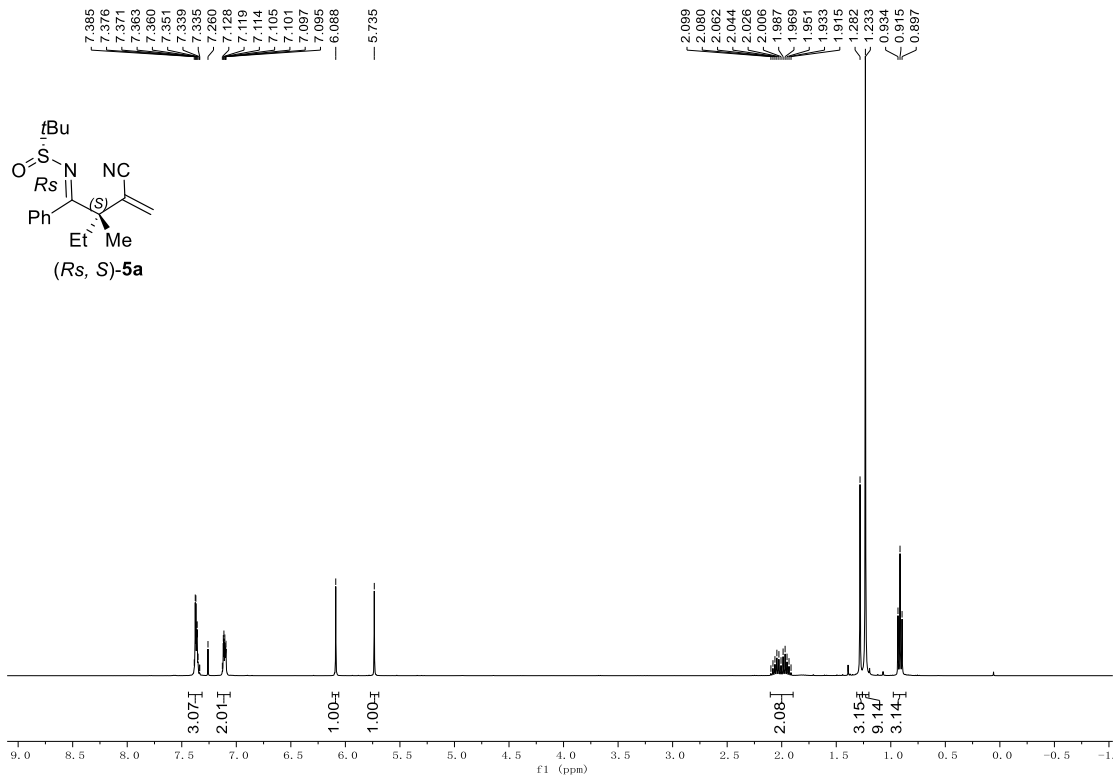
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *S*)-**5a**



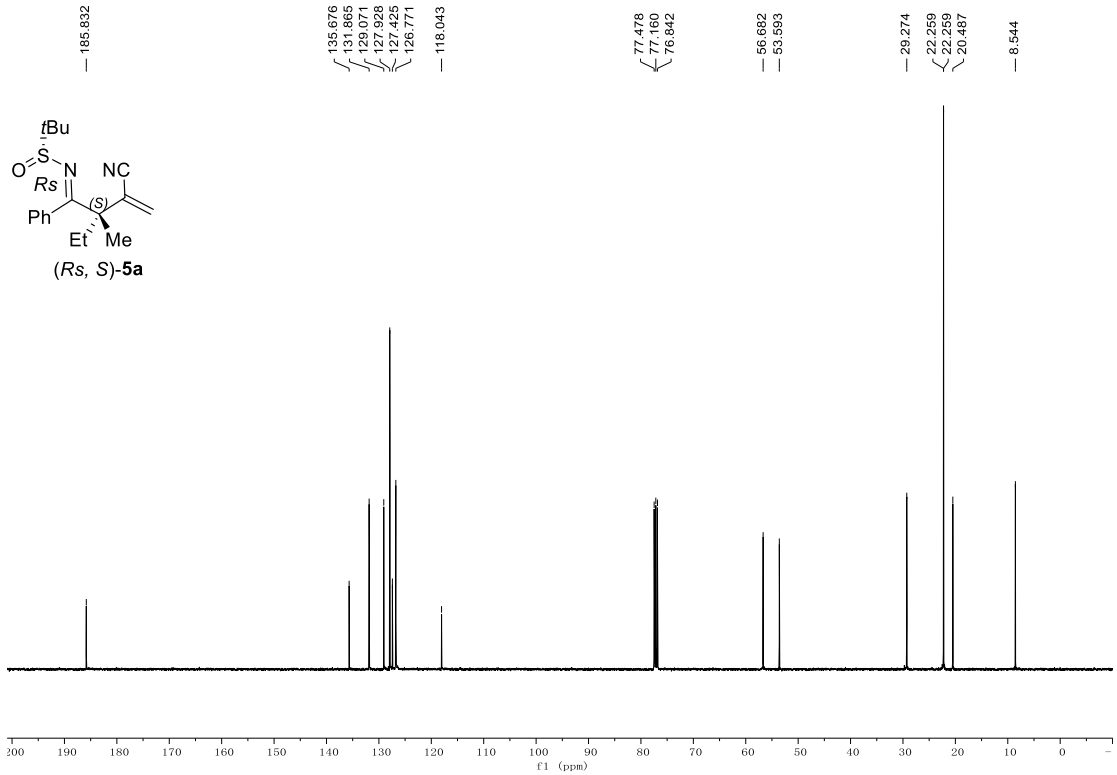
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *R*)-**5a**



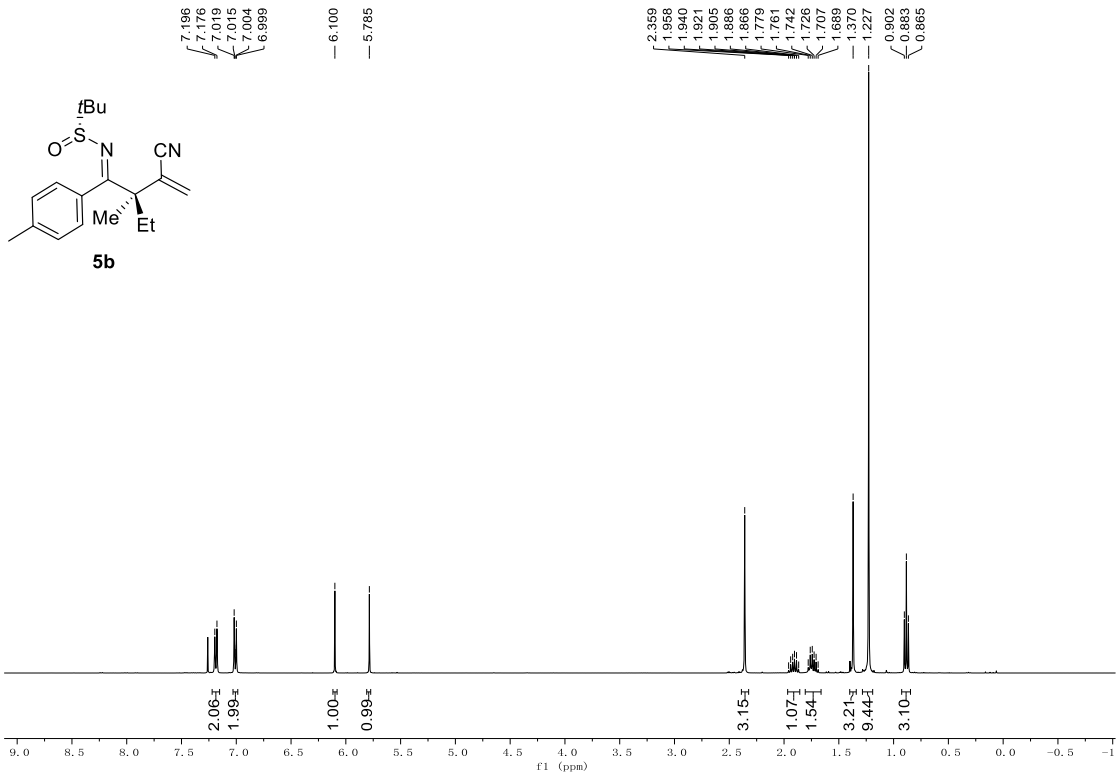
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *R*)-**5a**



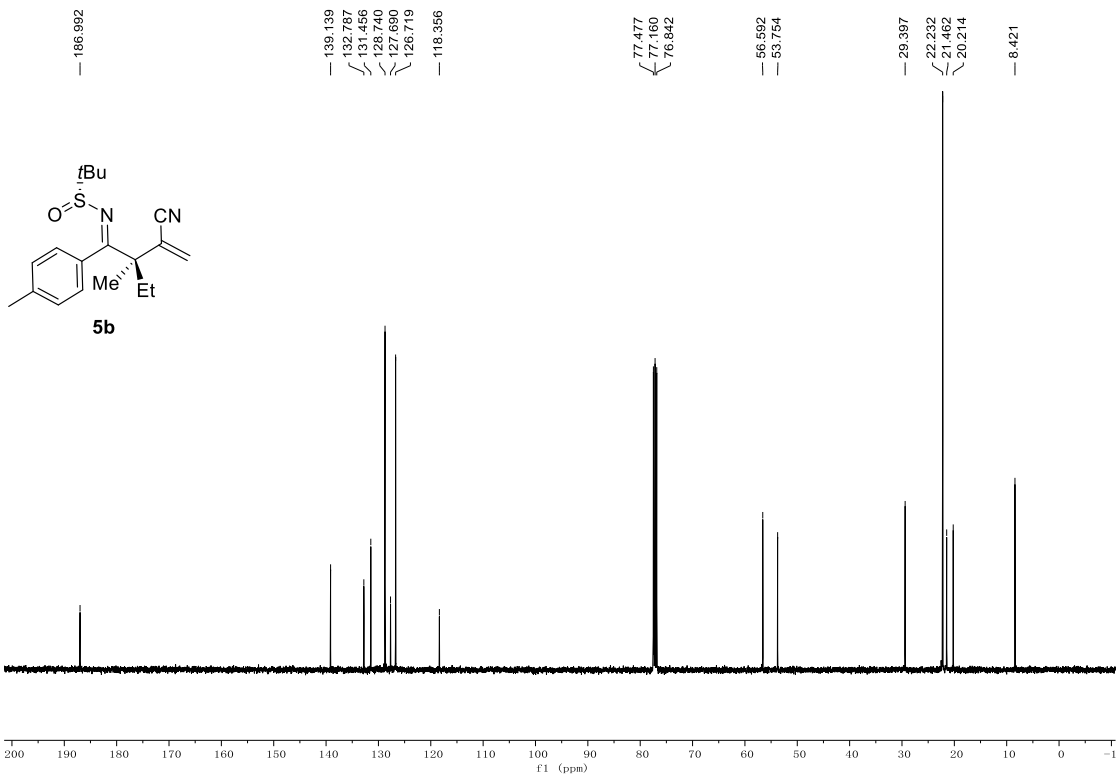
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *S*)-**5a**



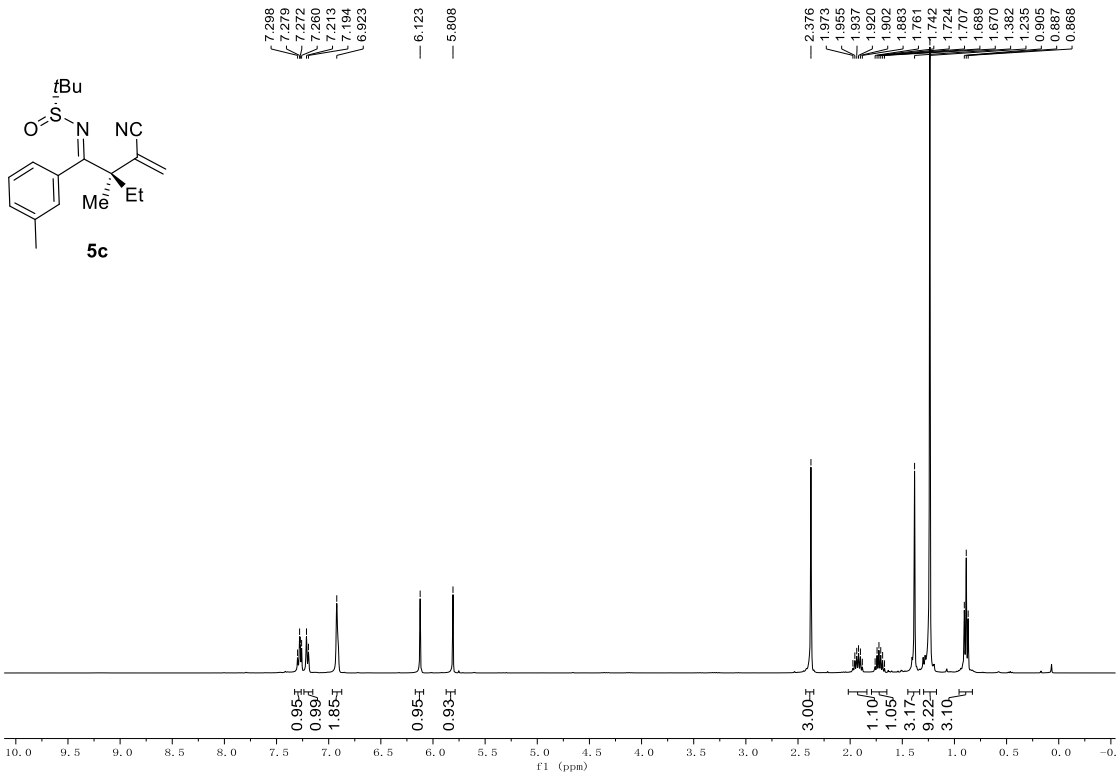
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *S*)-**5a**



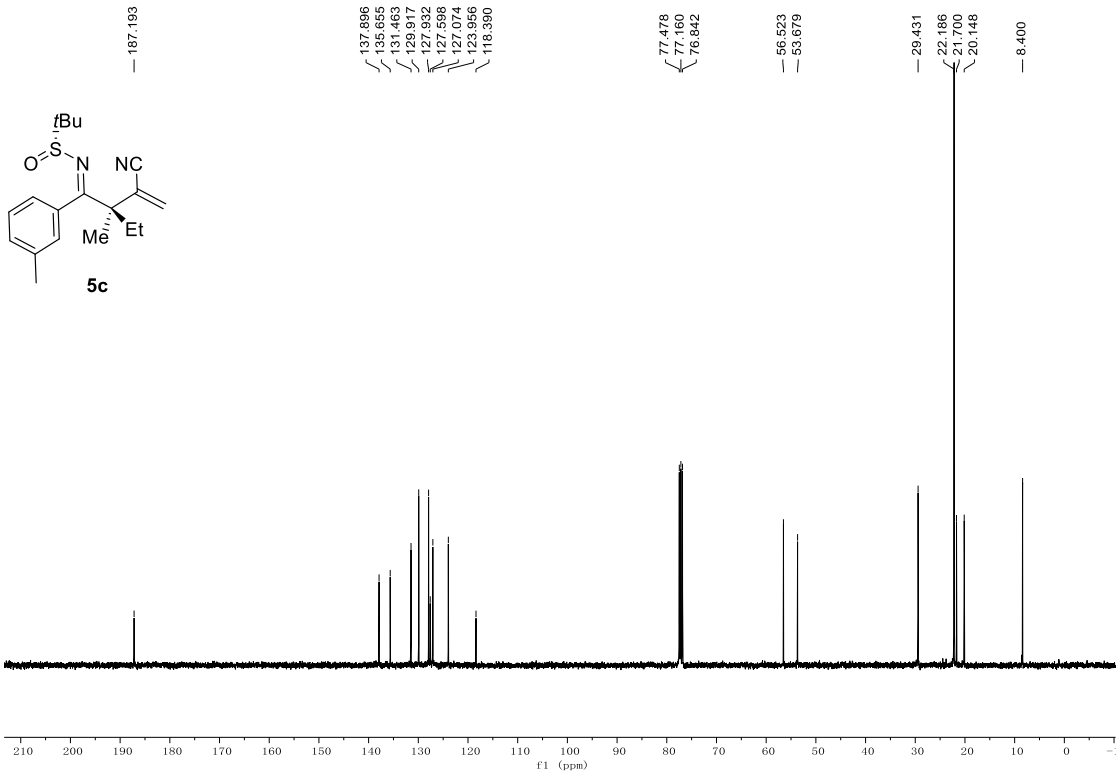
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5b**



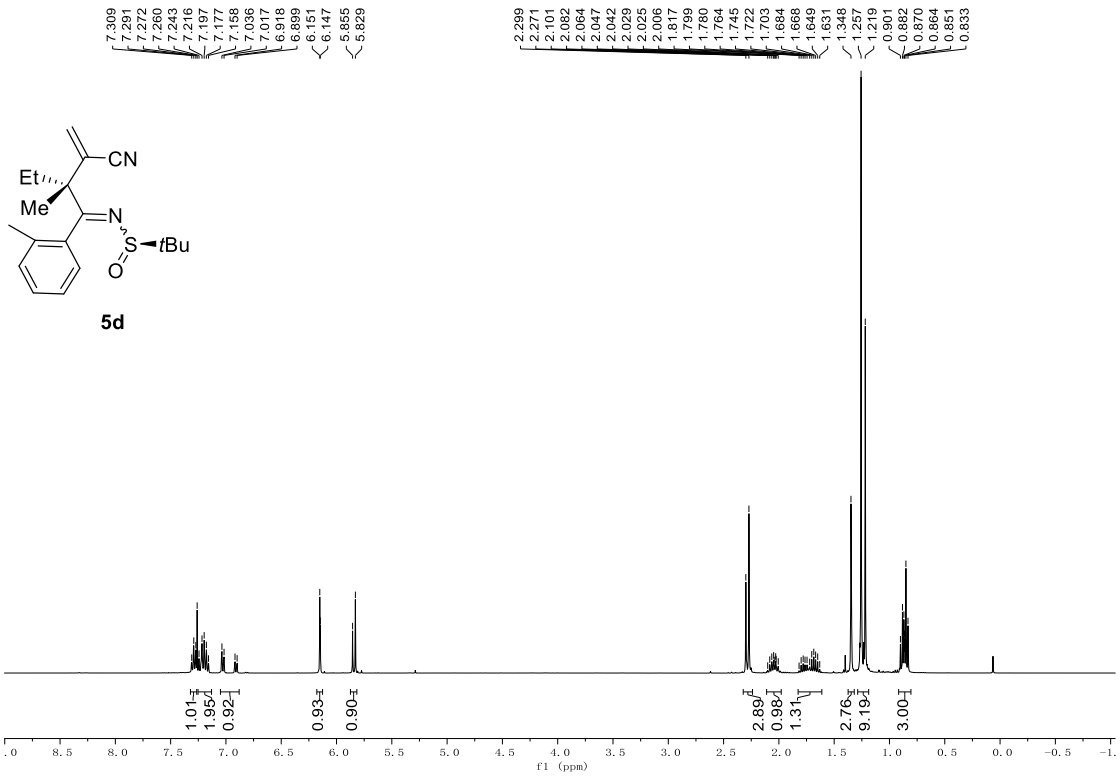
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5b**



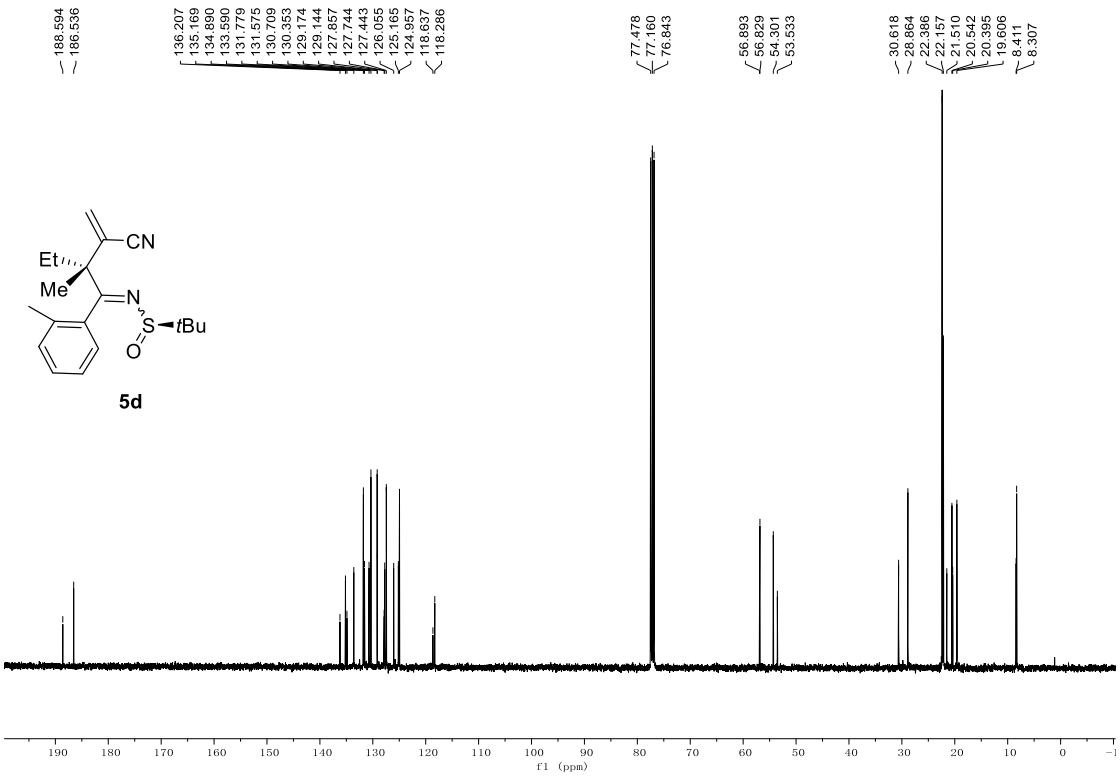
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5c**



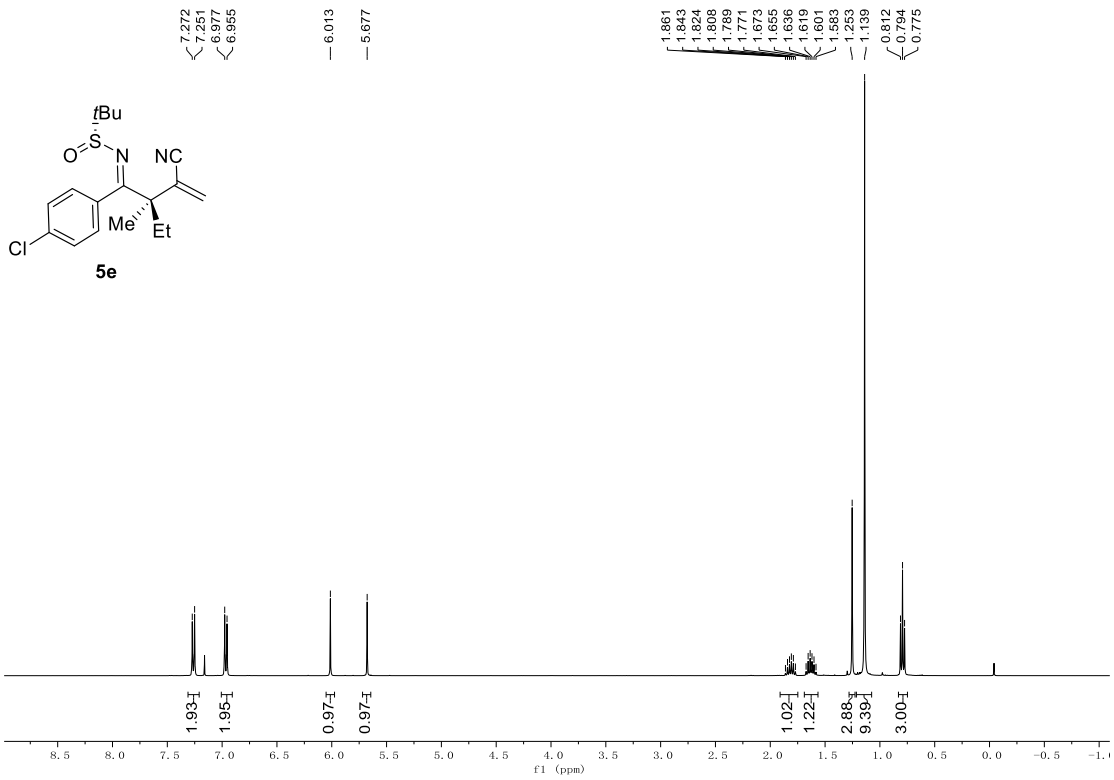
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5c**



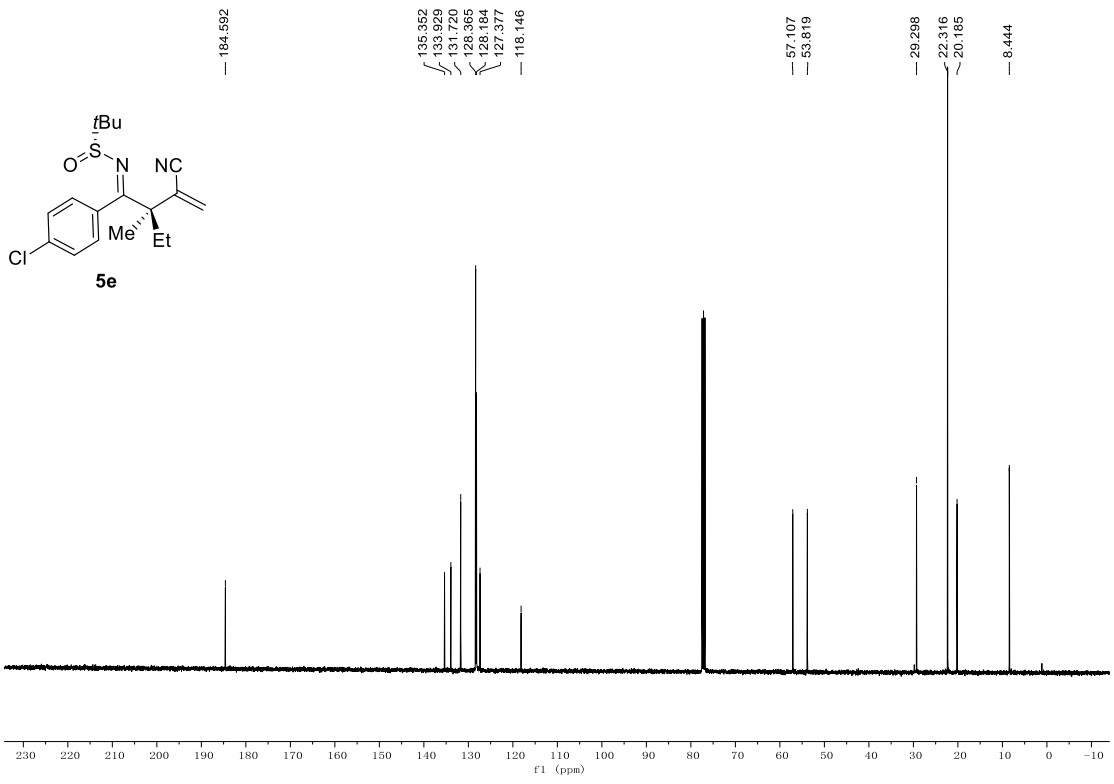
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5d** (mixture of imino *Z*/*E* isomers)



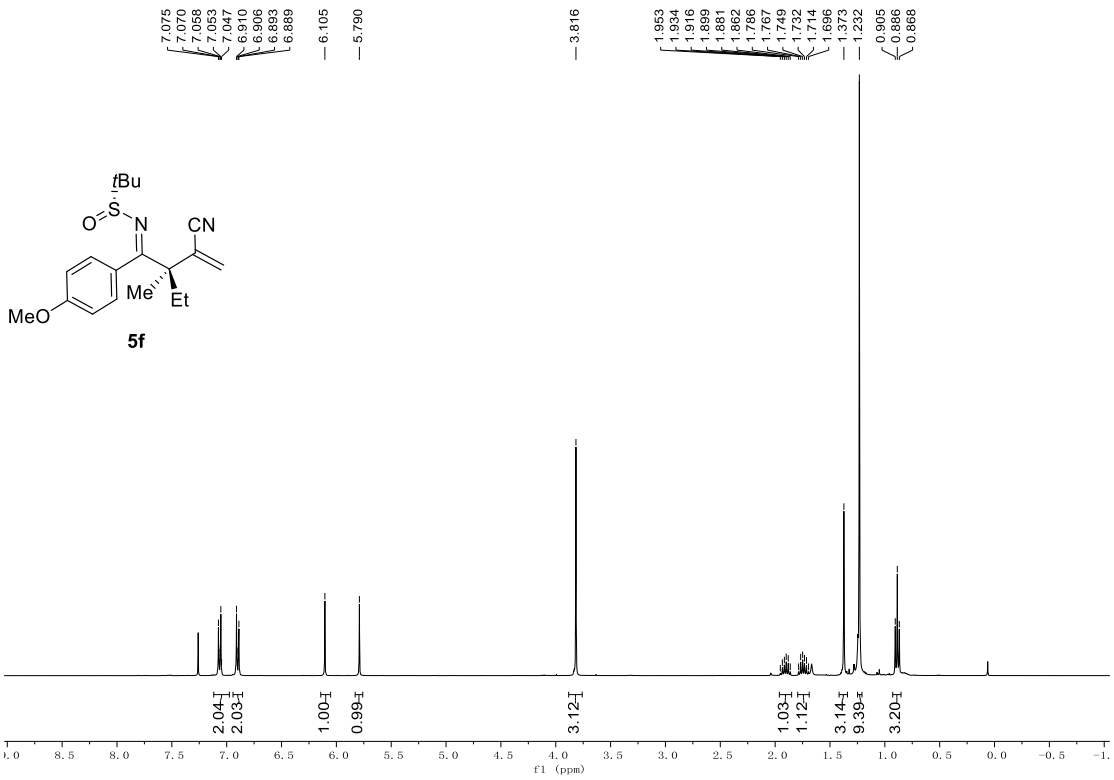
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5d** (mixture of imino *Z*/*E* isomers)



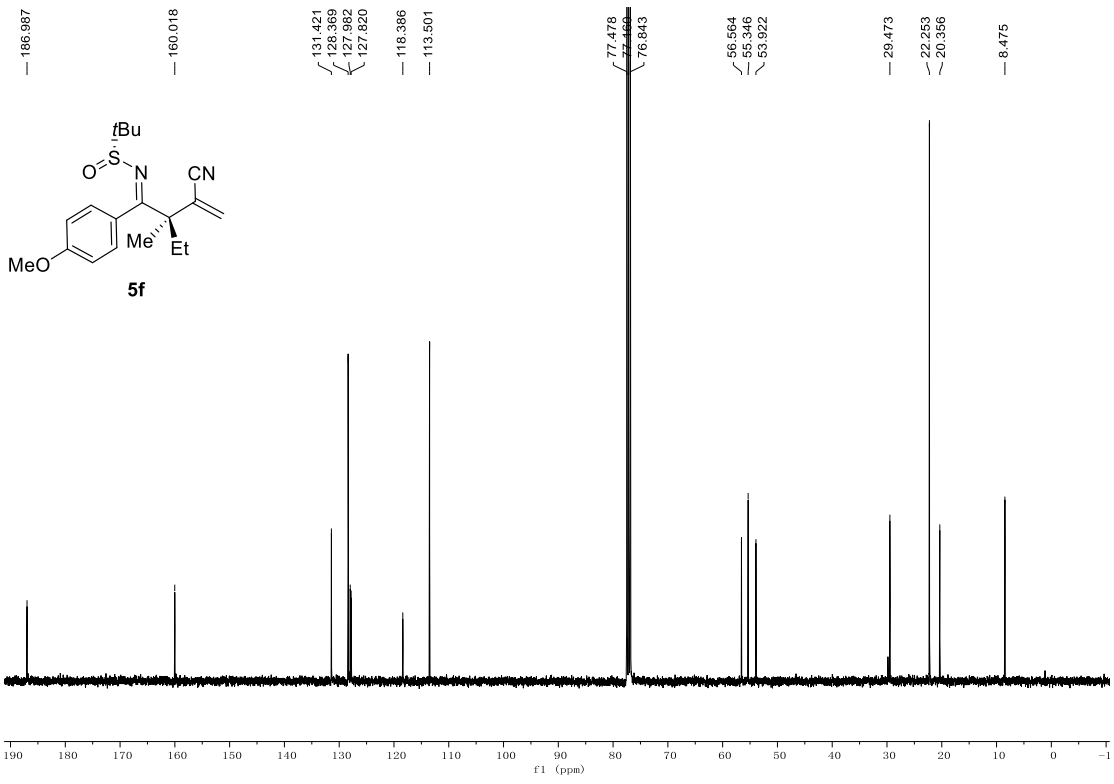
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5e**



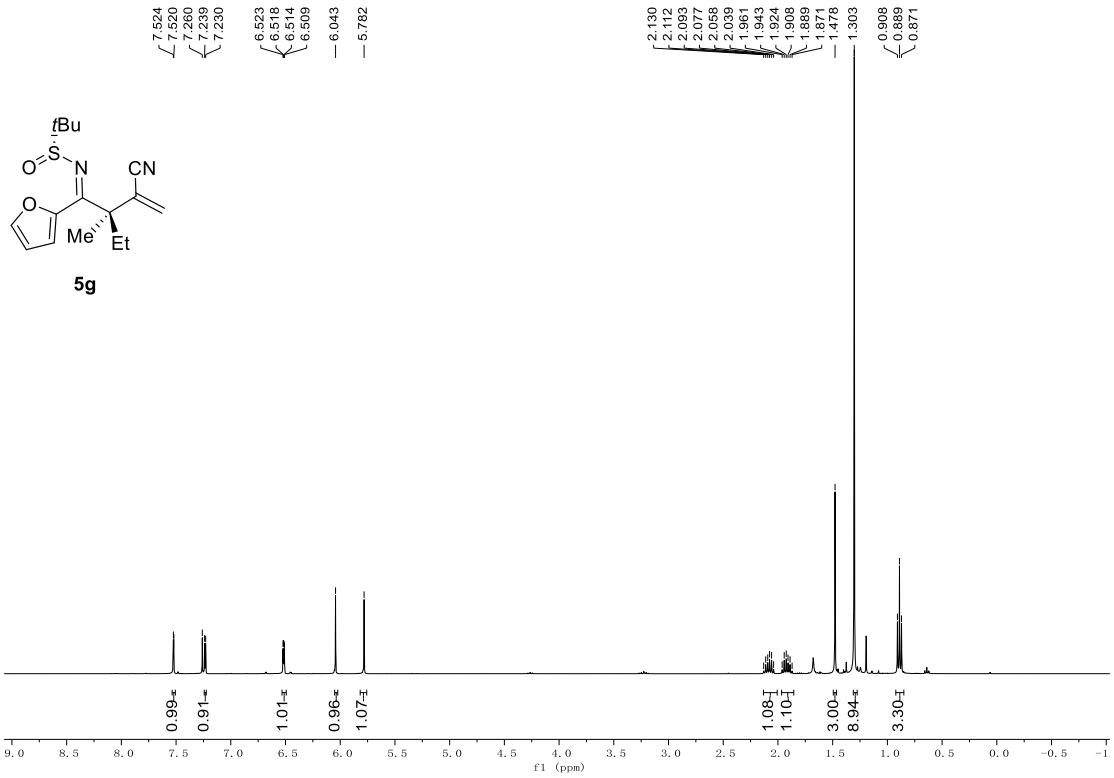
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5e**



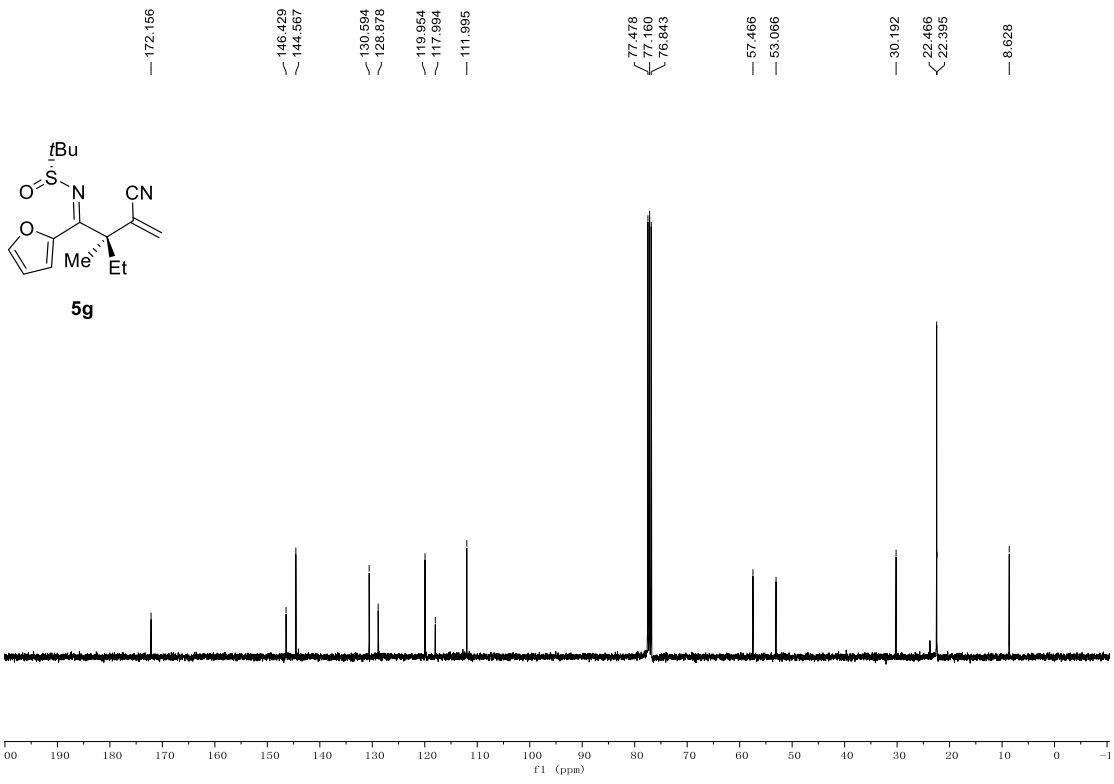
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5f**



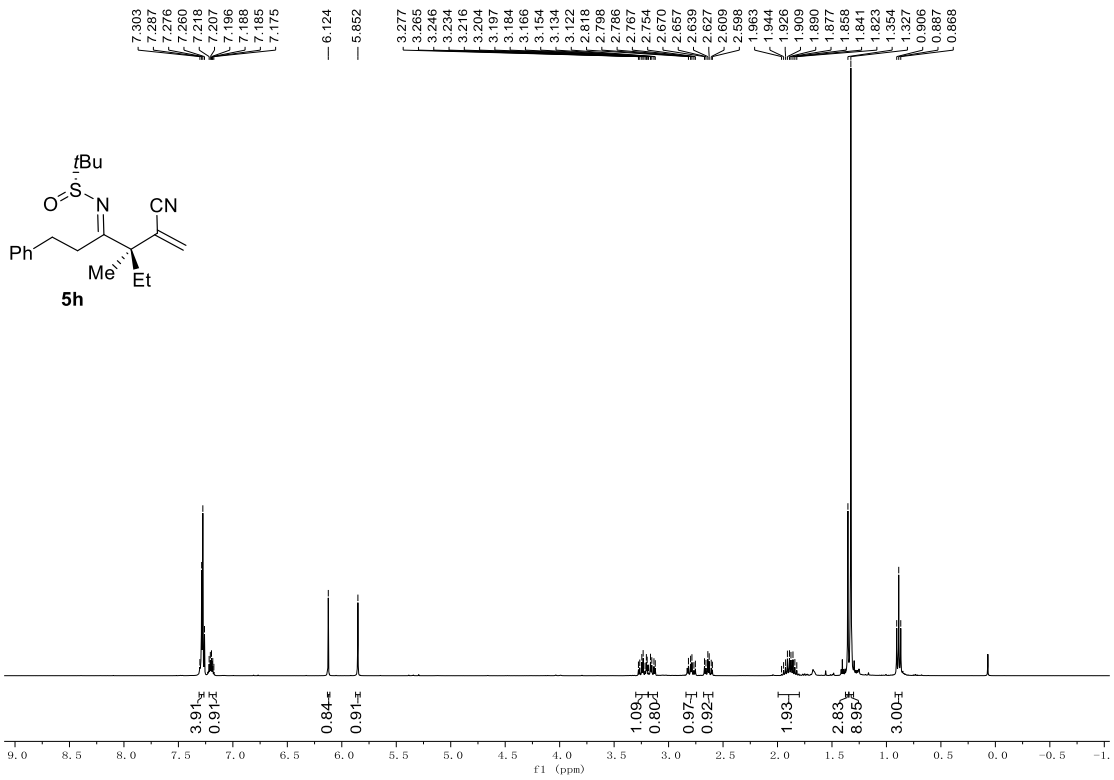
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5f**



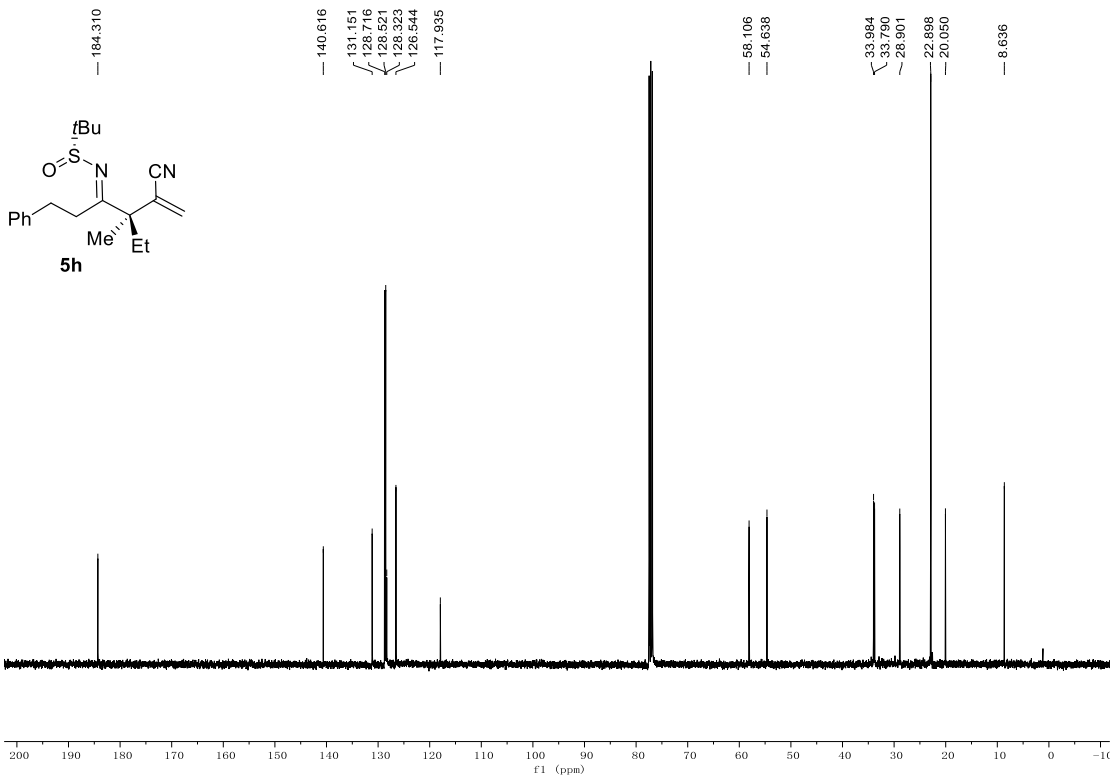
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5g**



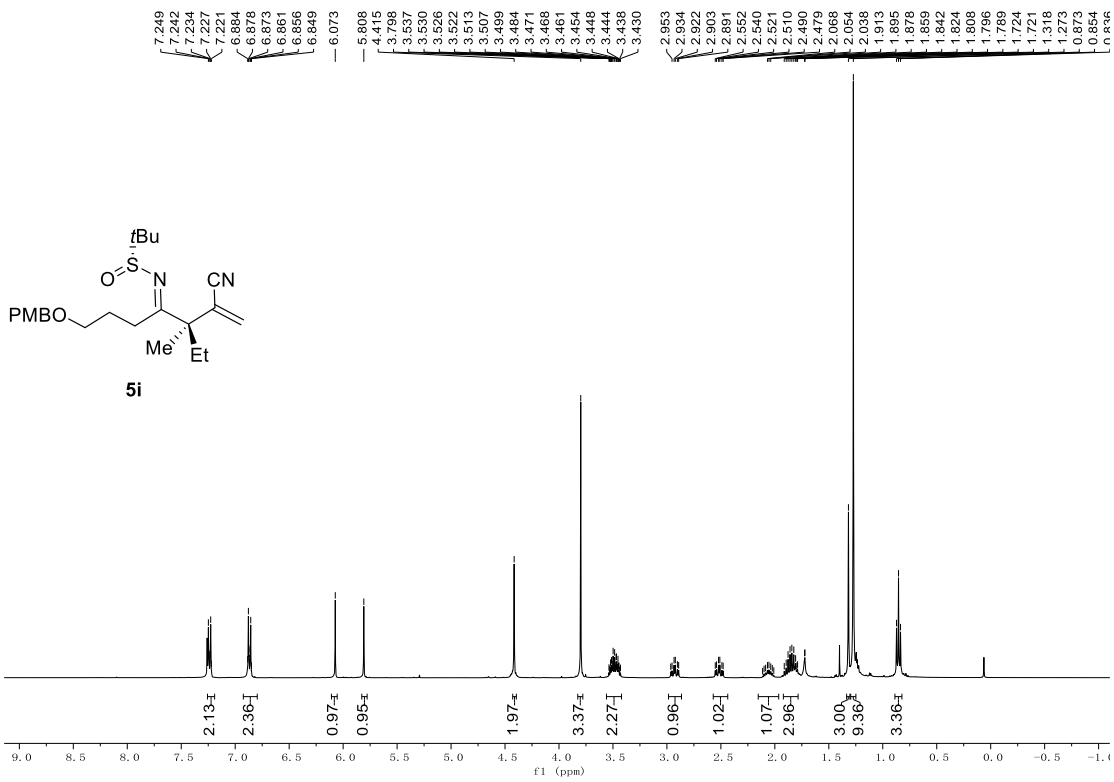
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5g**



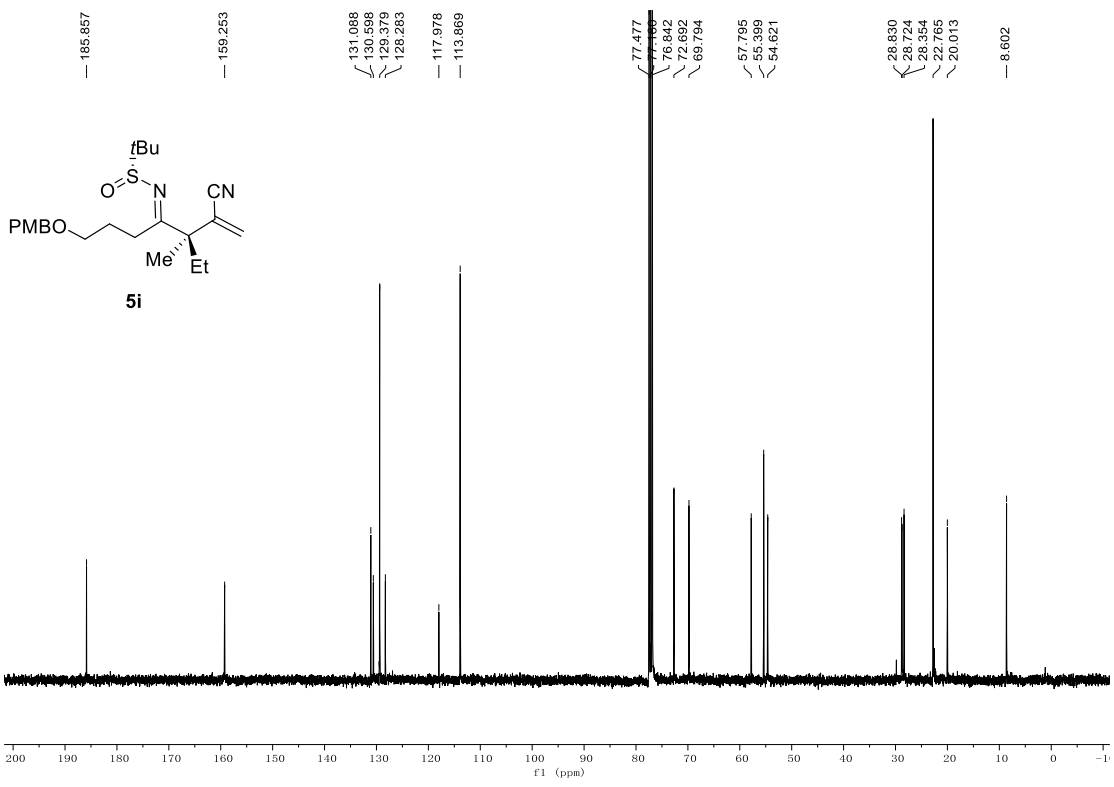
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5h**



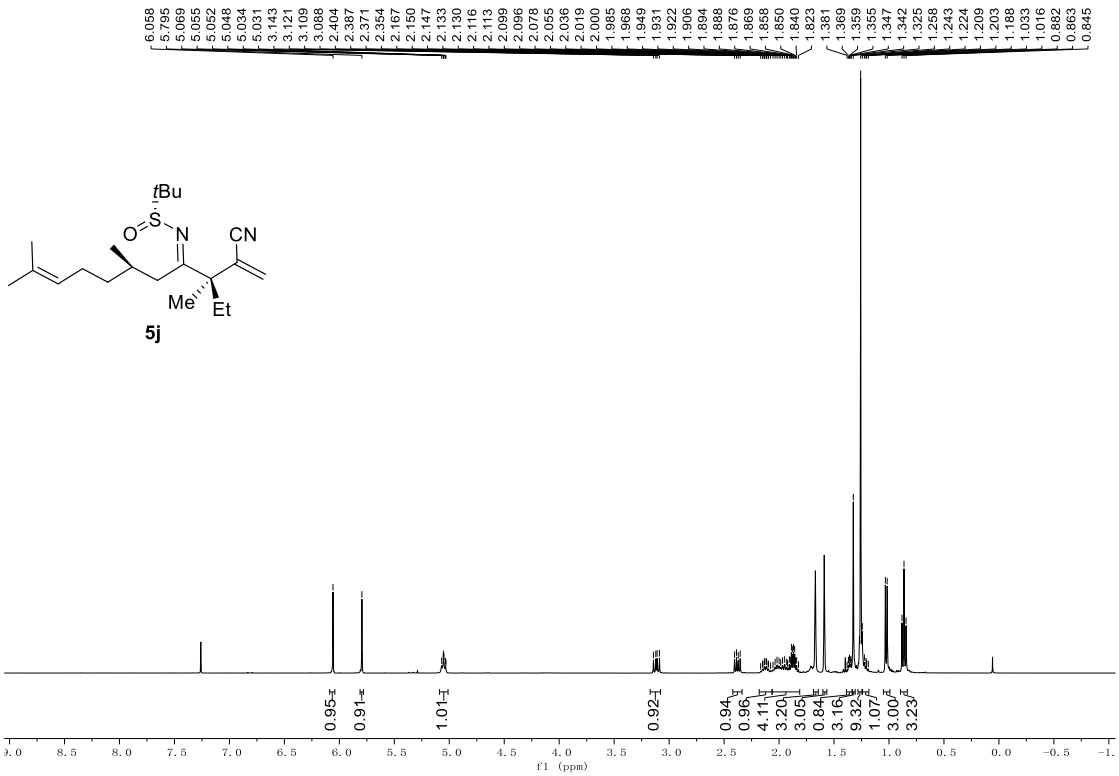
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5h**



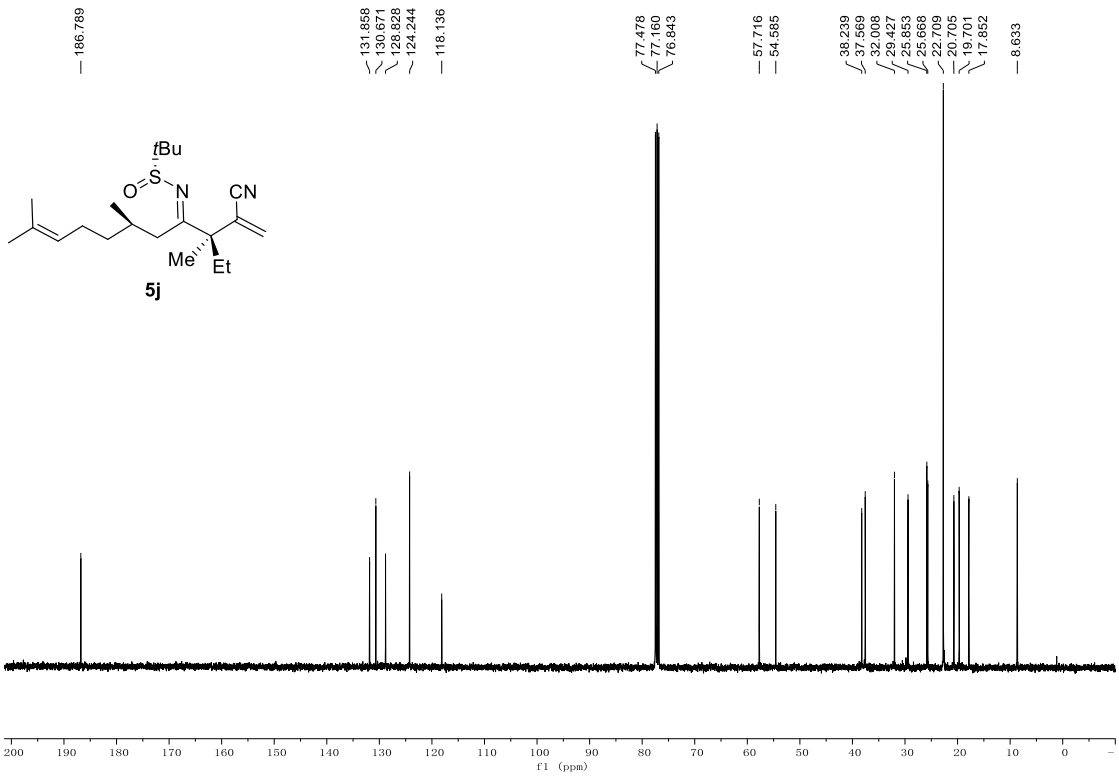
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5i**



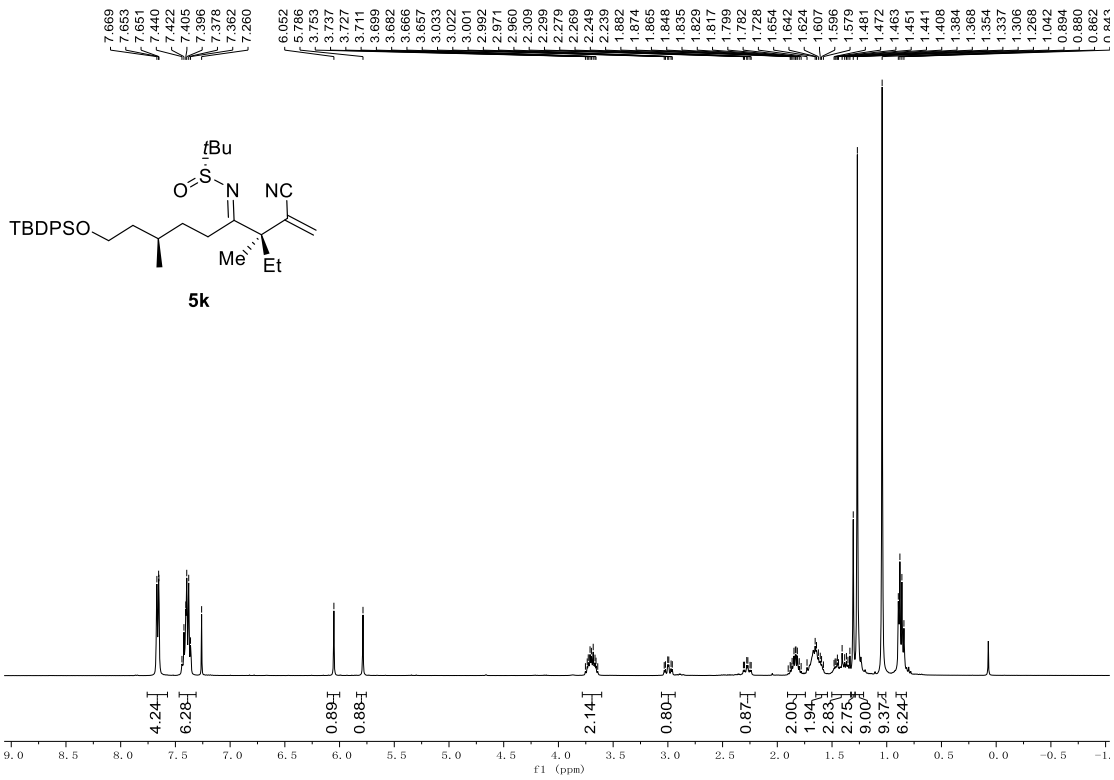
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5i**



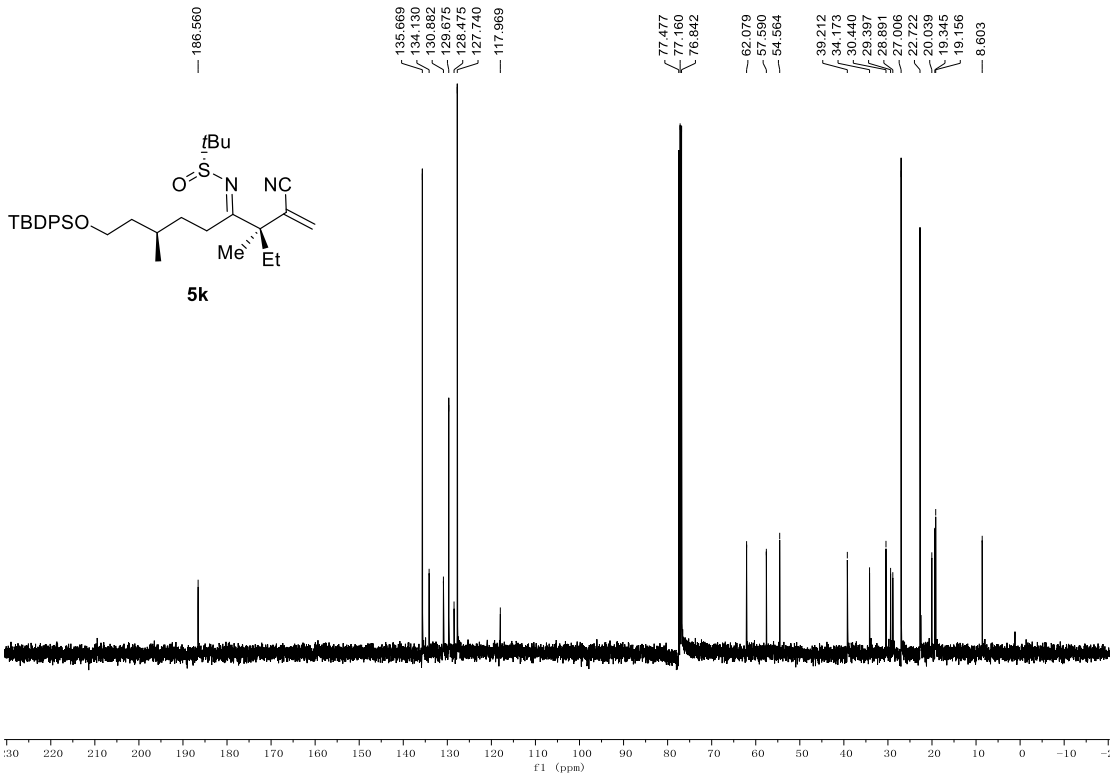
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5j**



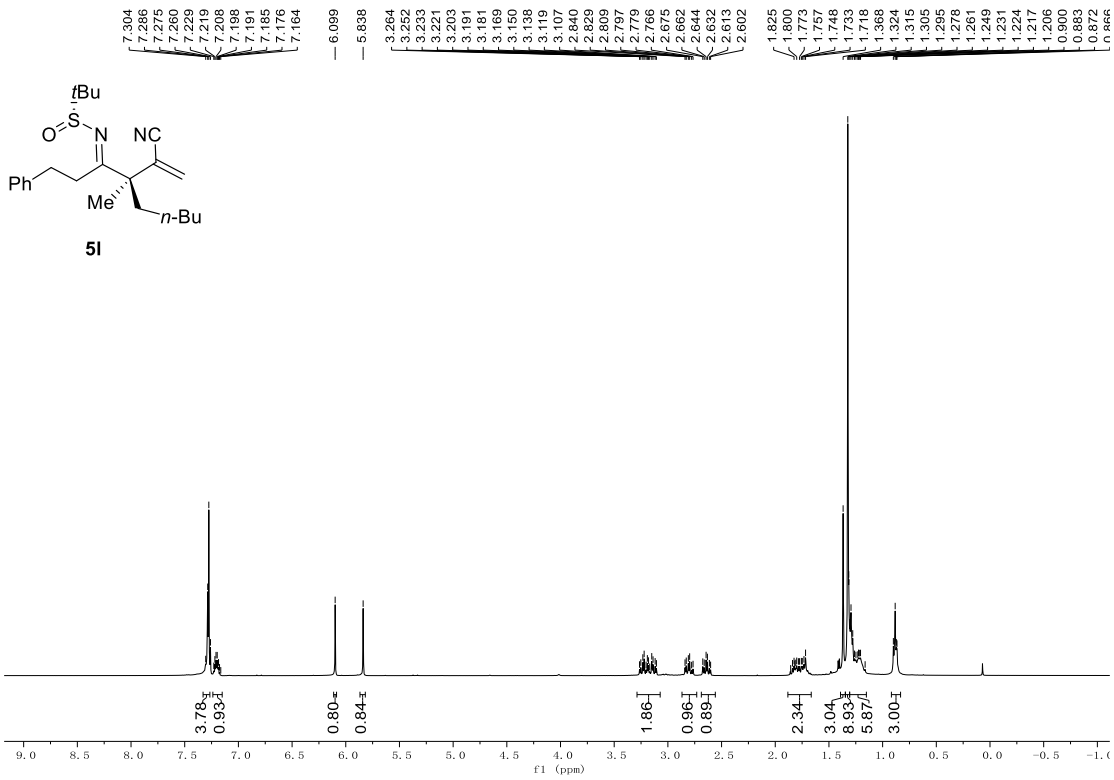
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5j**



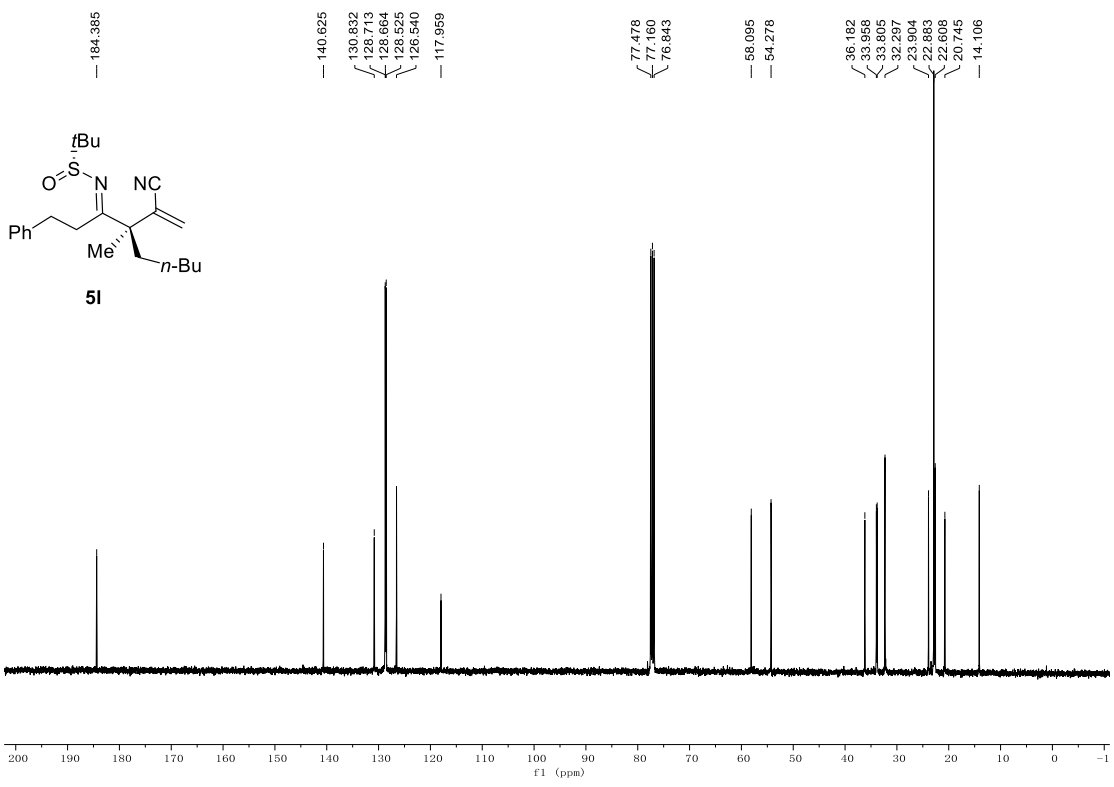
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5k**



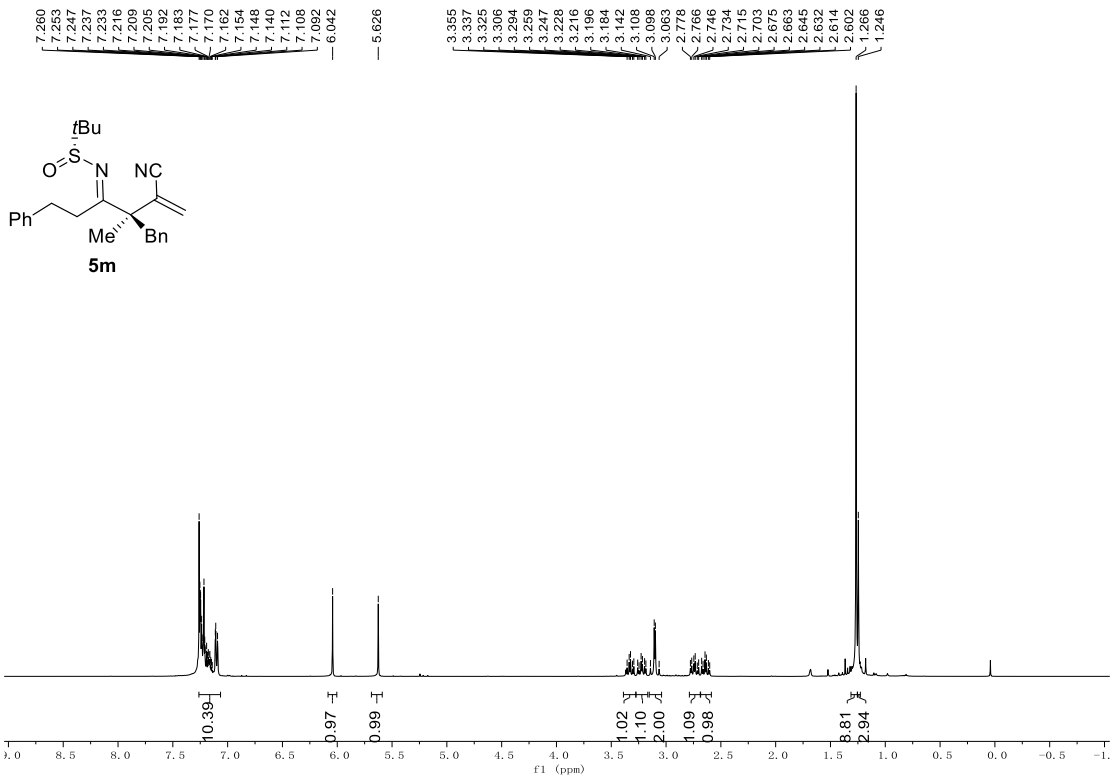
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5k**



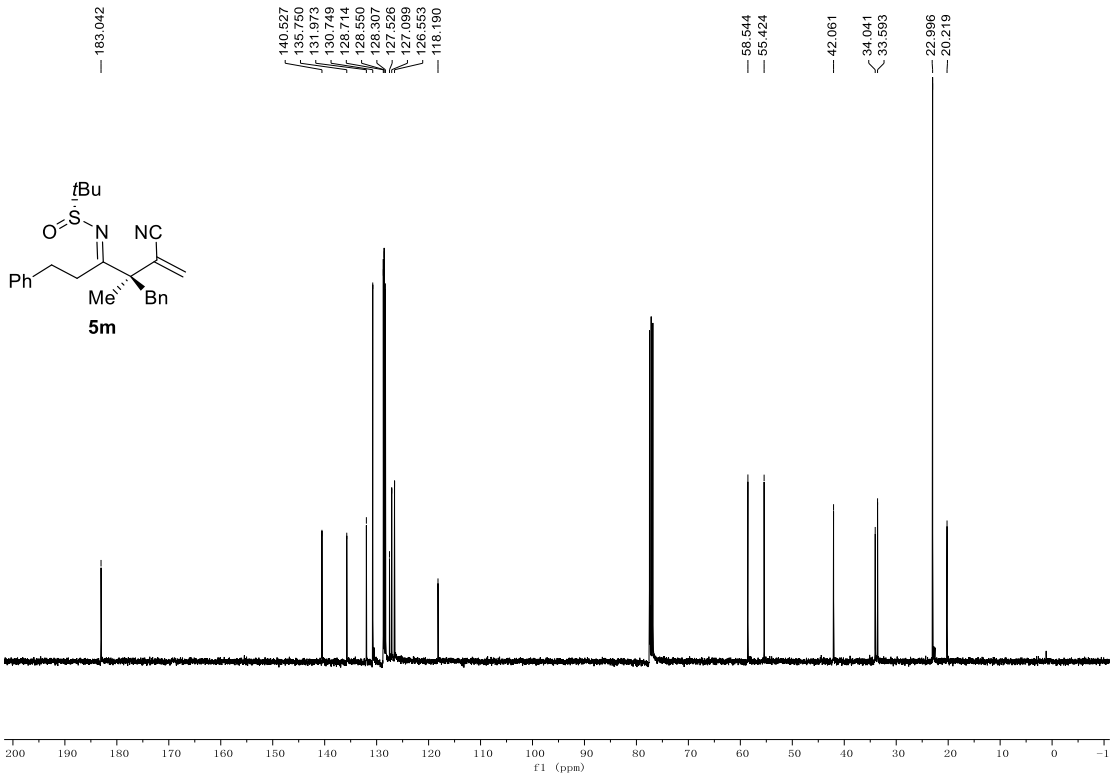
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5l**



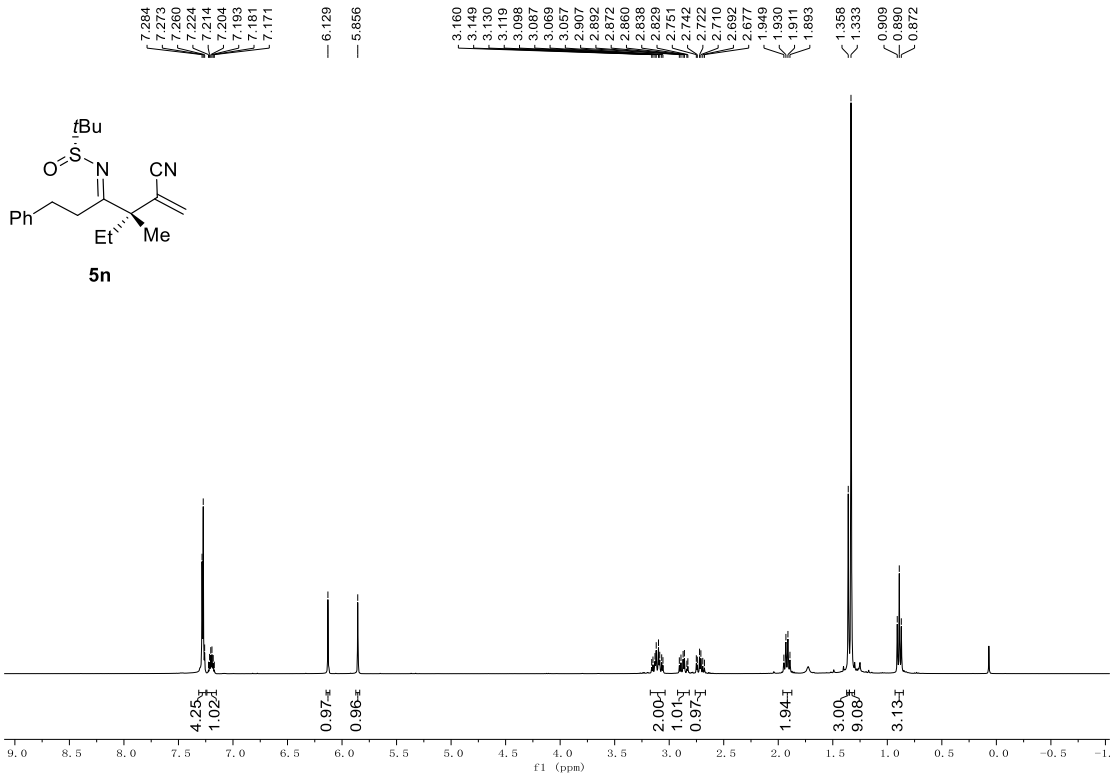
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5l**



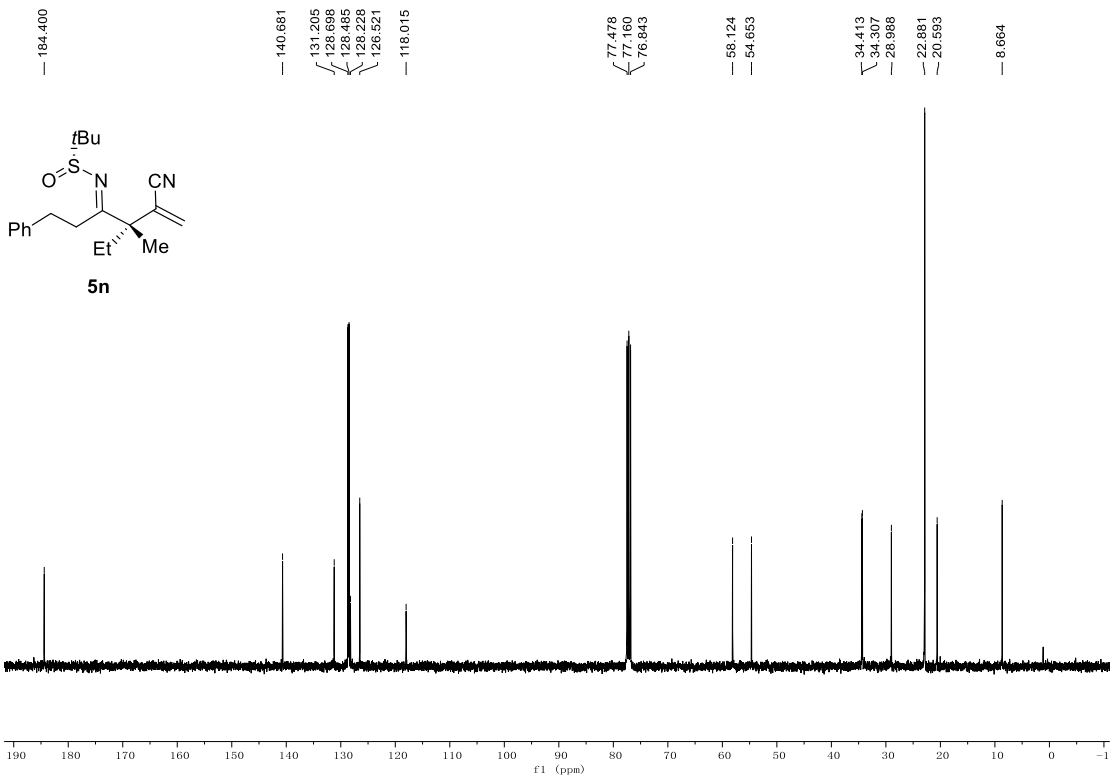
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5m**



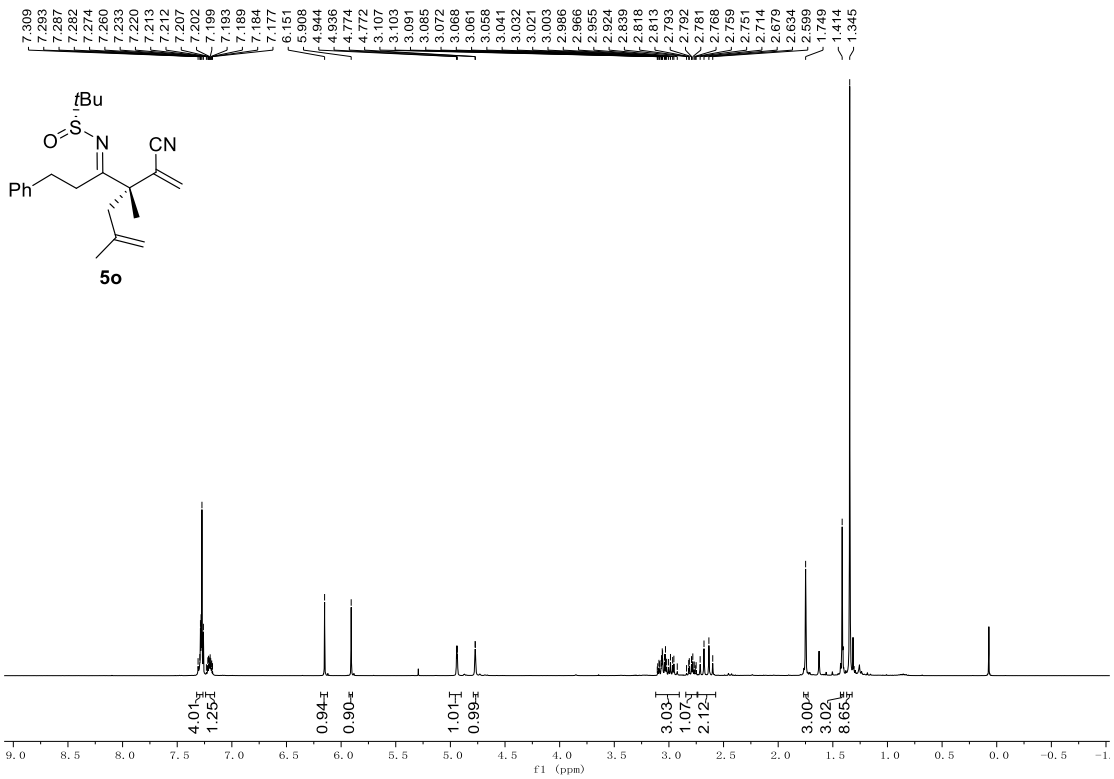
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5m**



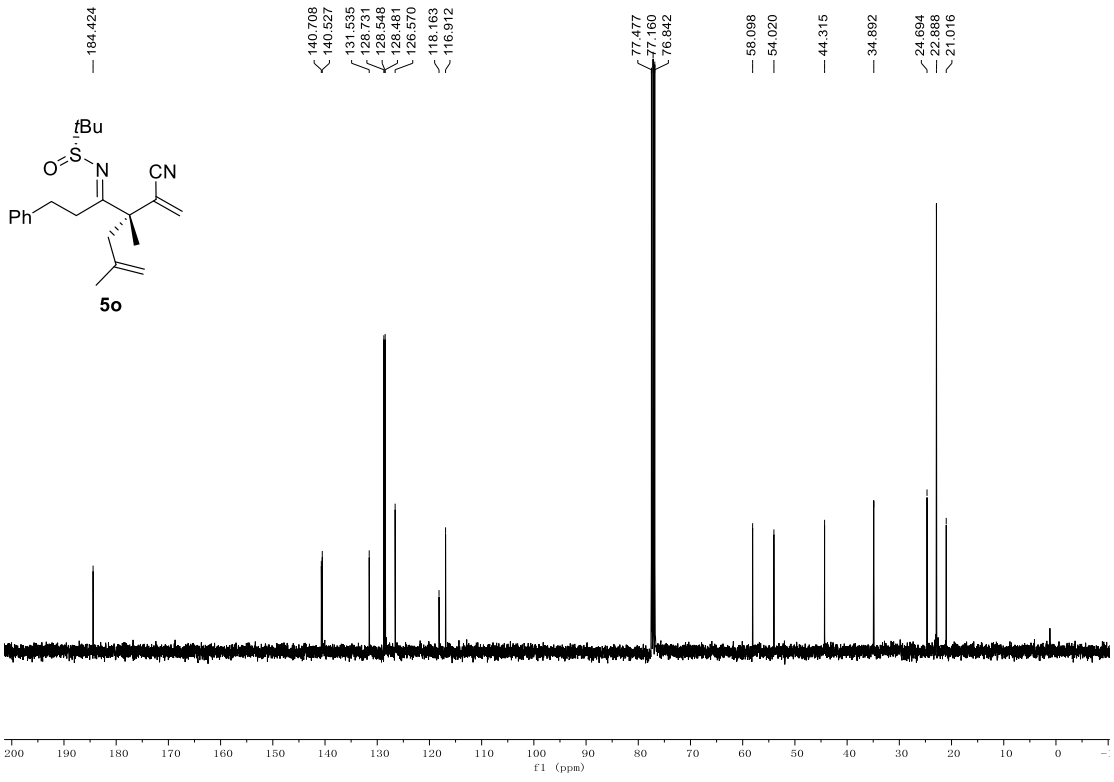
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5n**



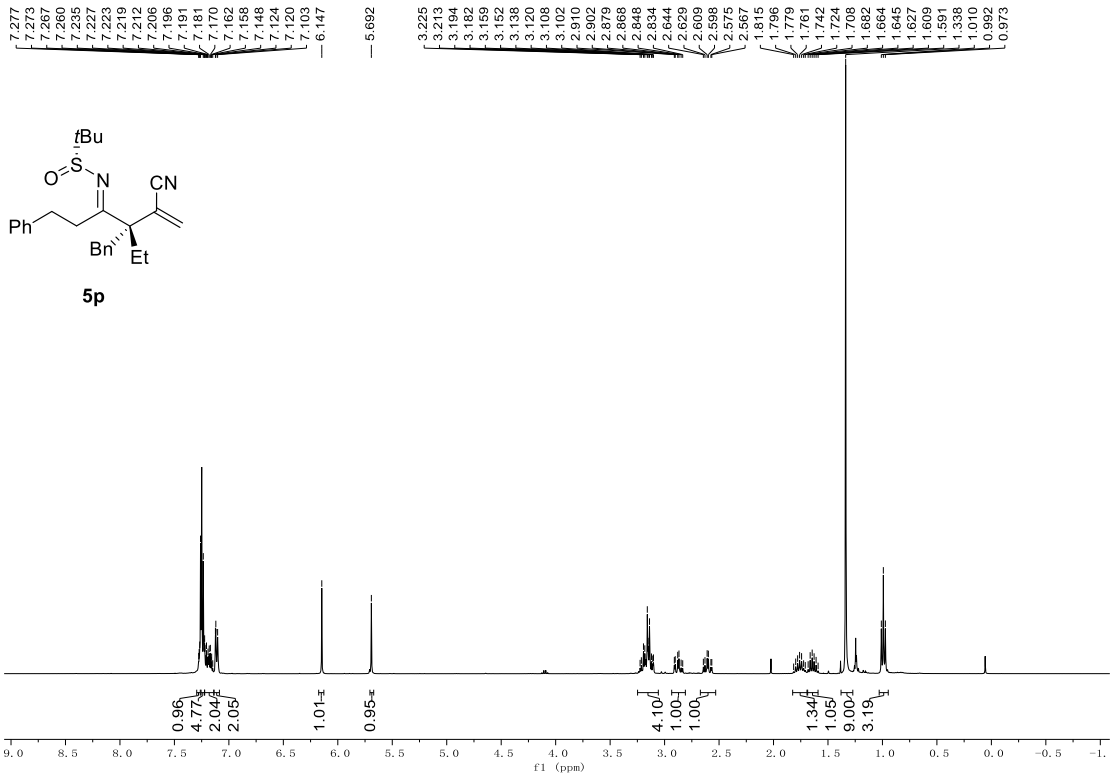
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5n**



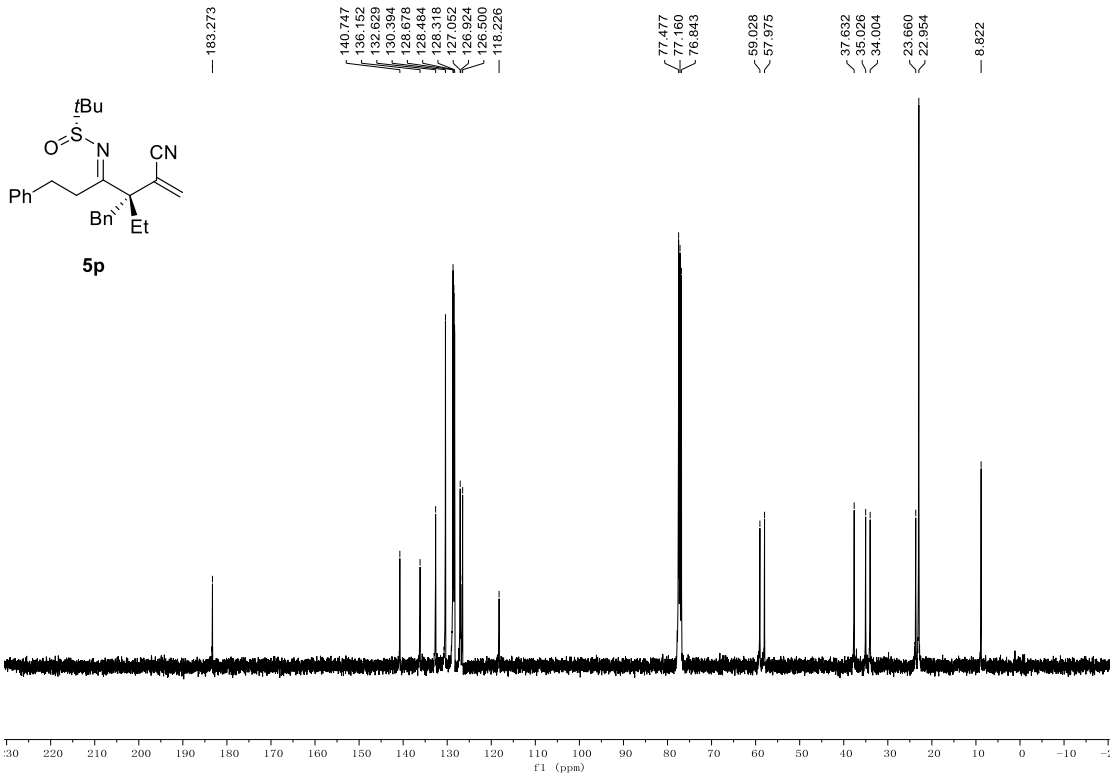
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5o**



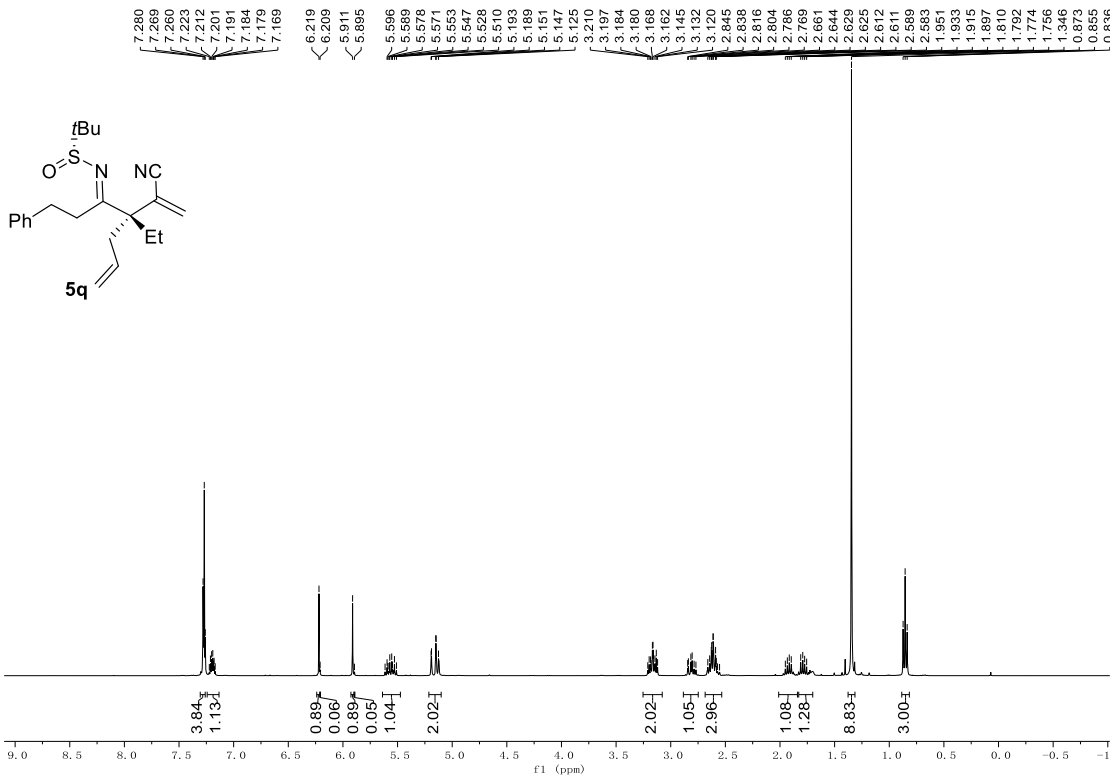
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5o**



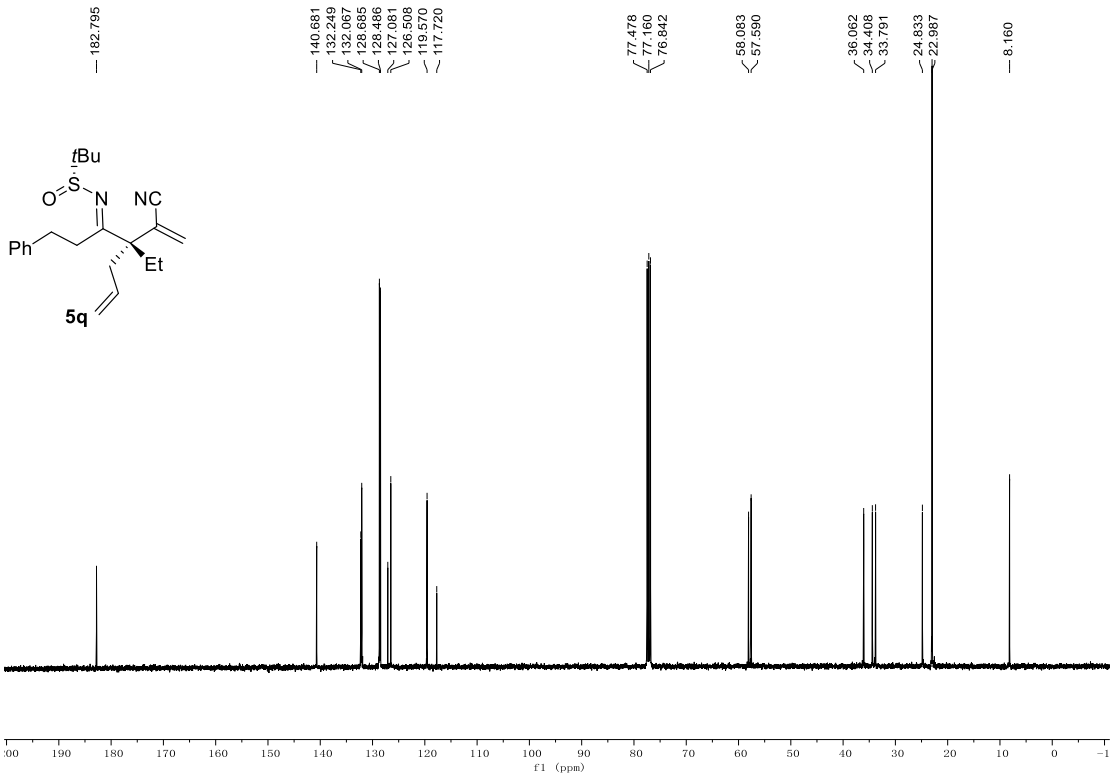
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5p**



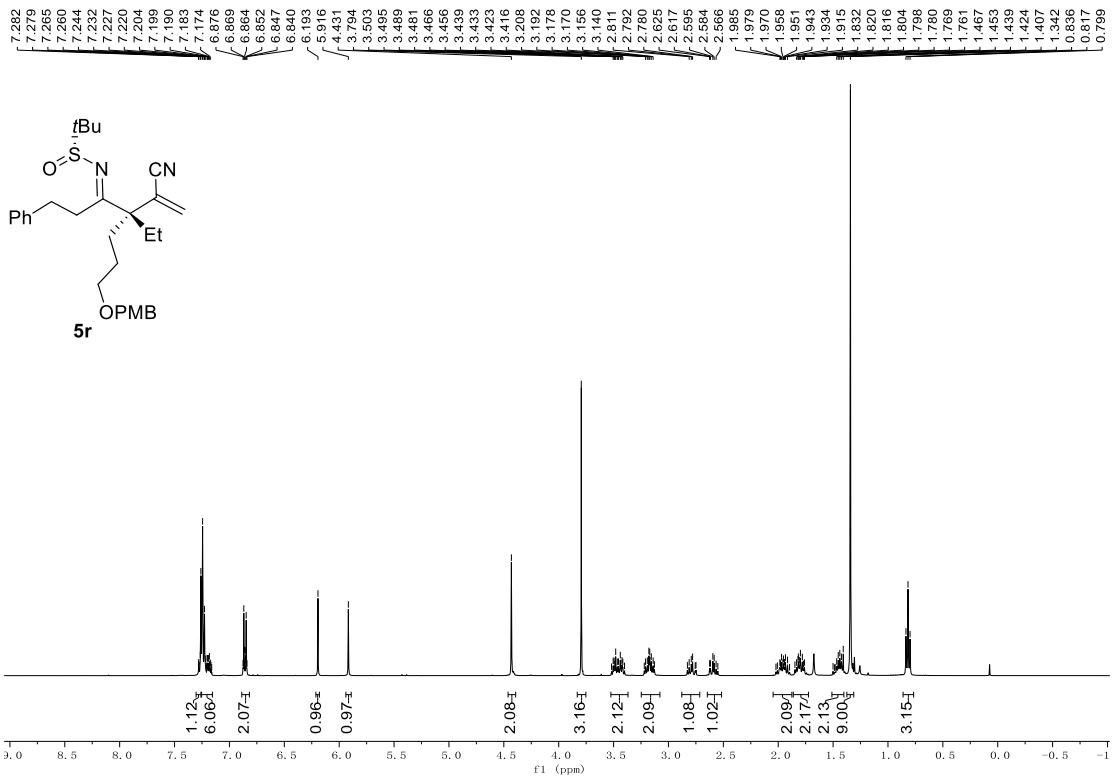
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5p**



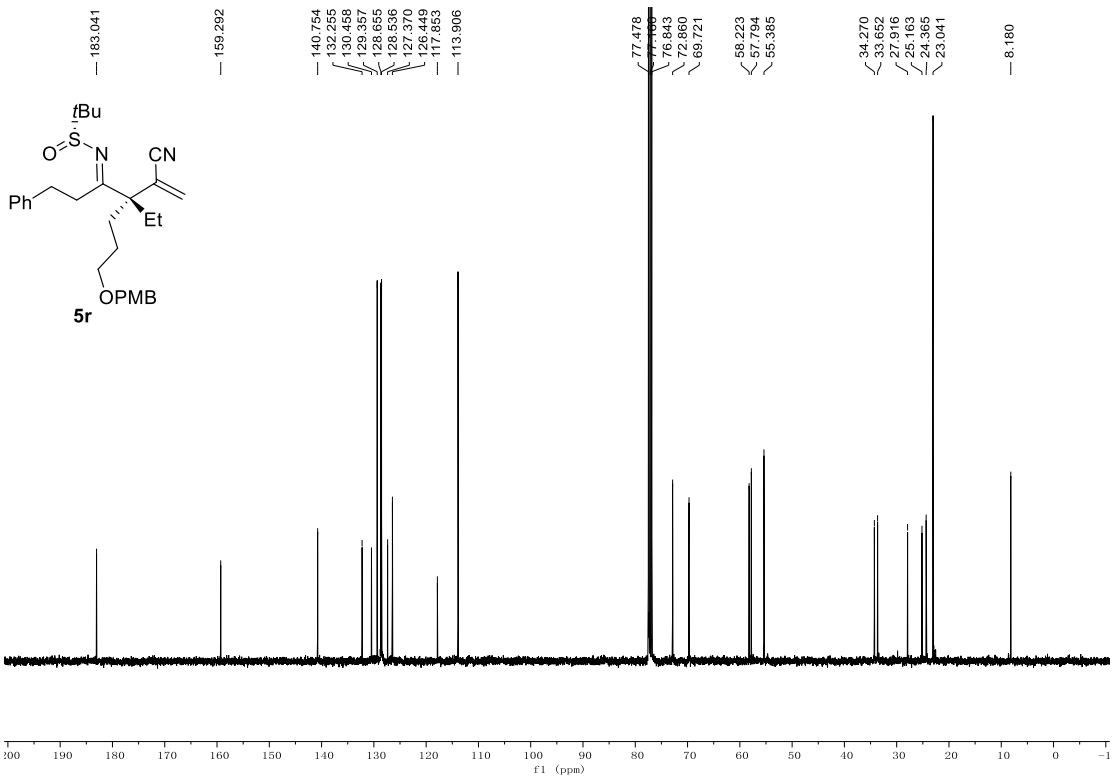
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5q**



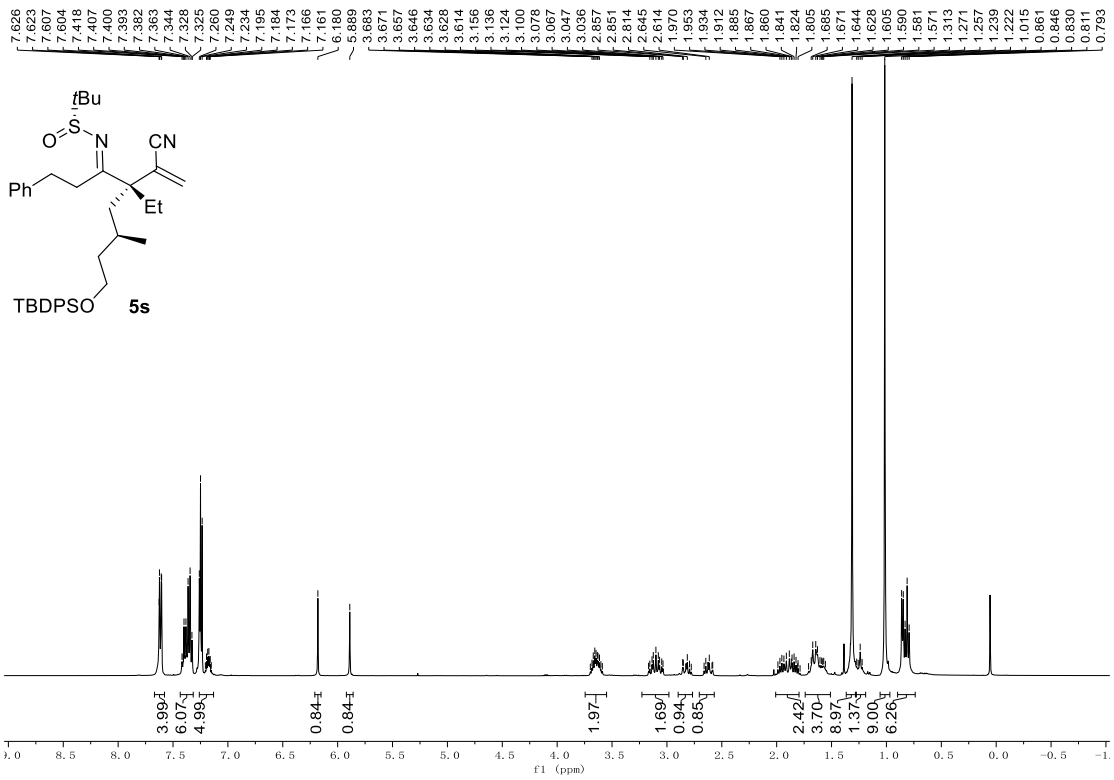
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5q**



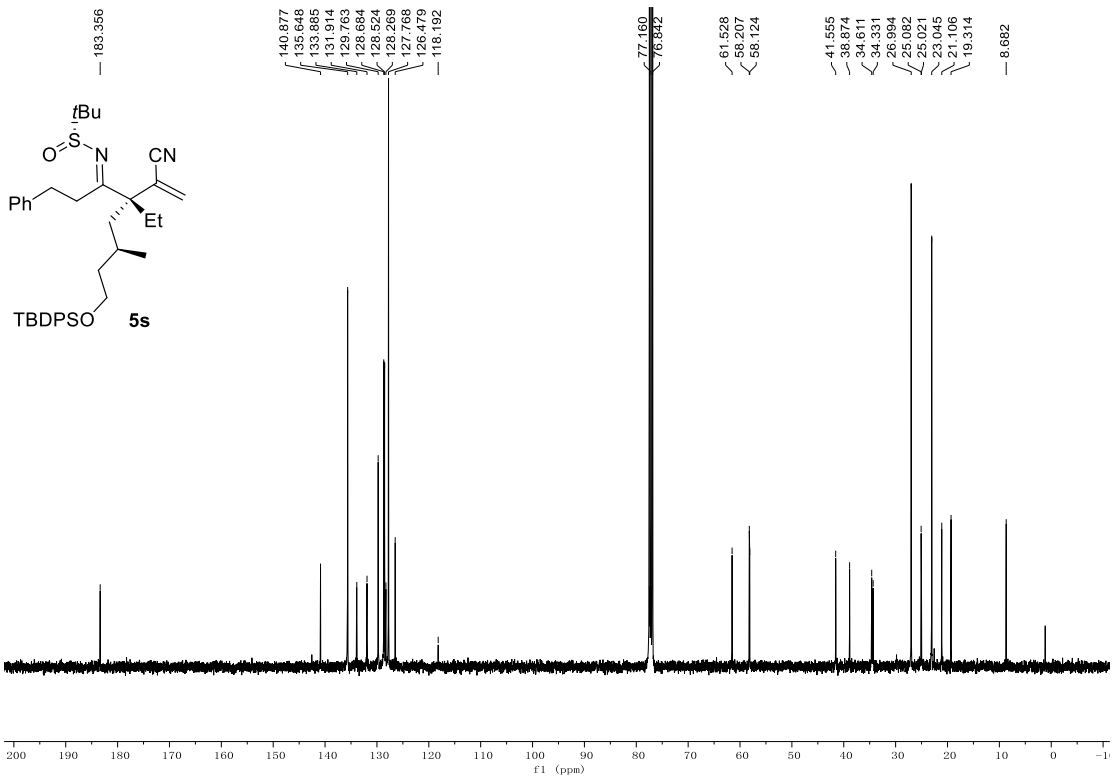
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5r**



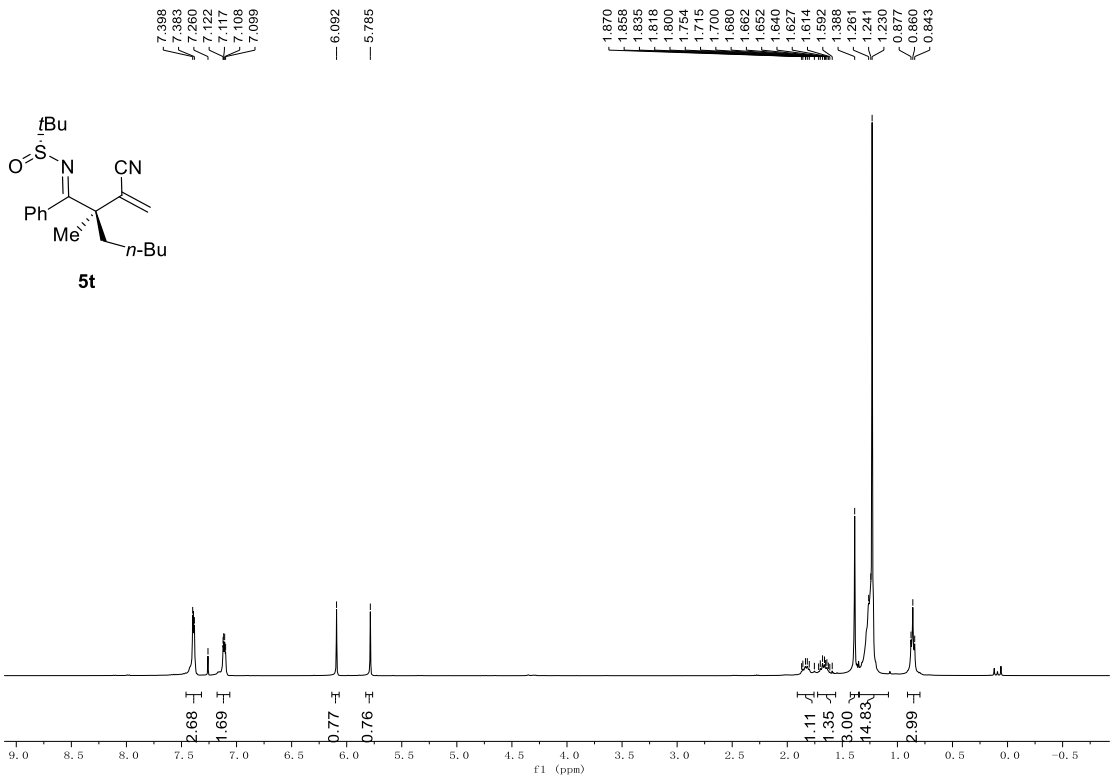
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5r**



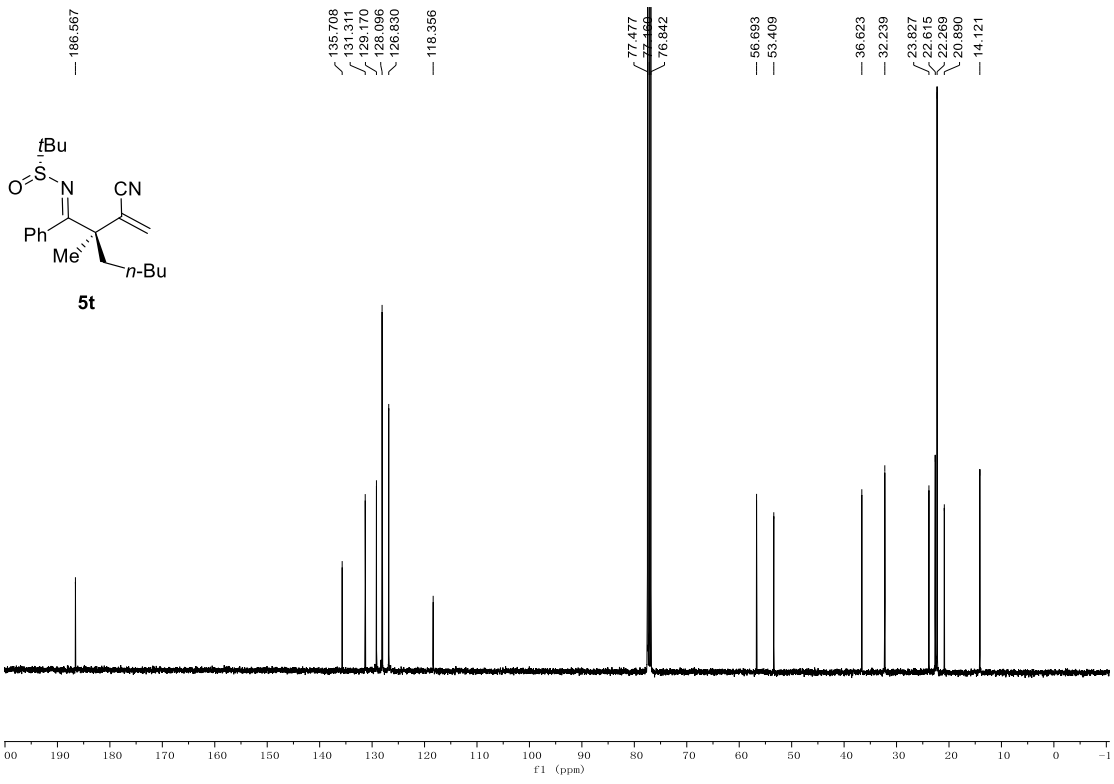
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5s**



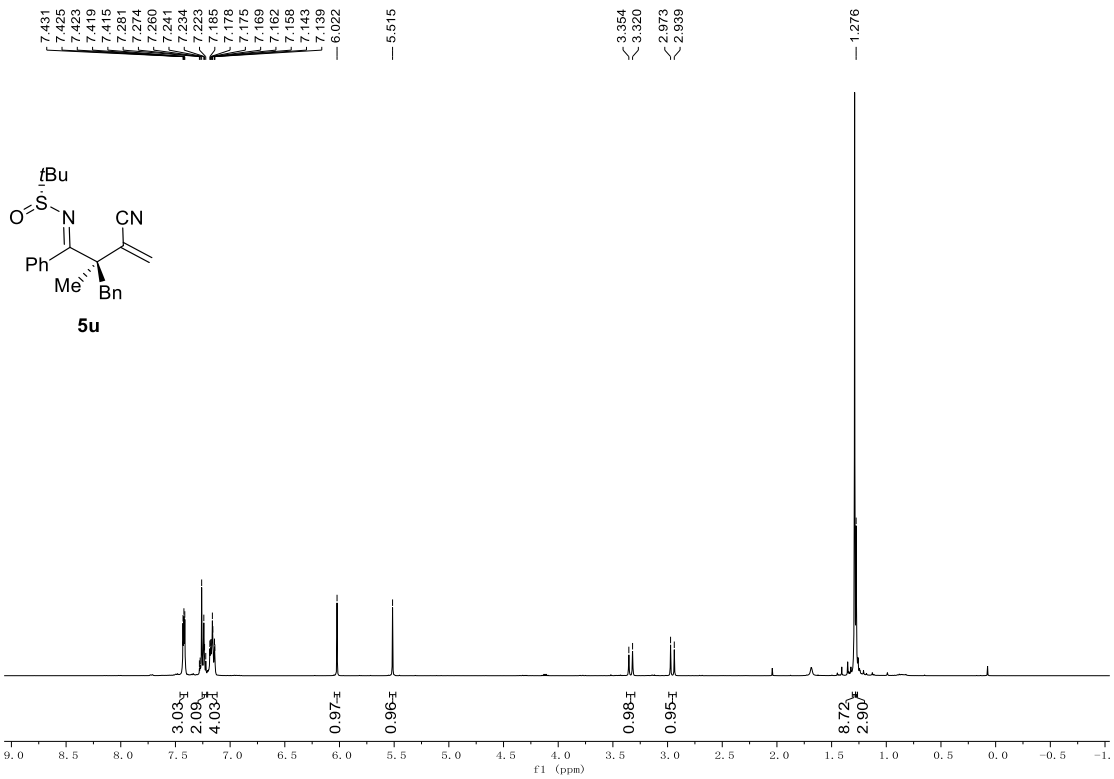
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5s**



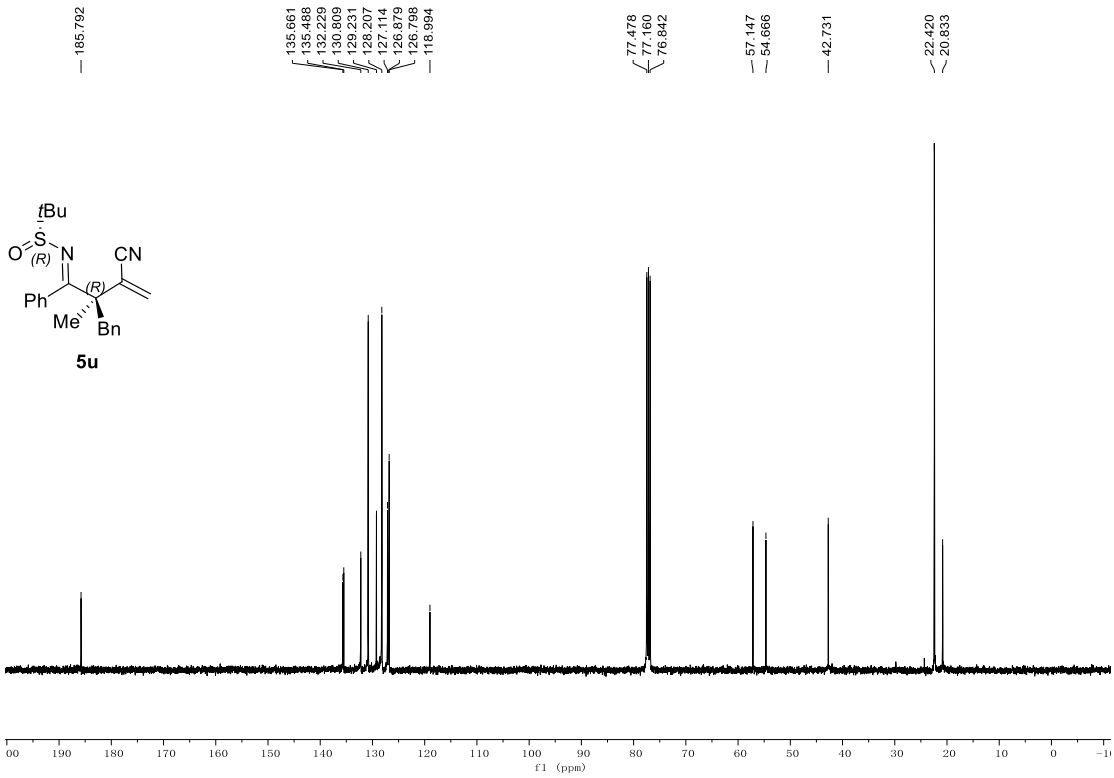
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5t**



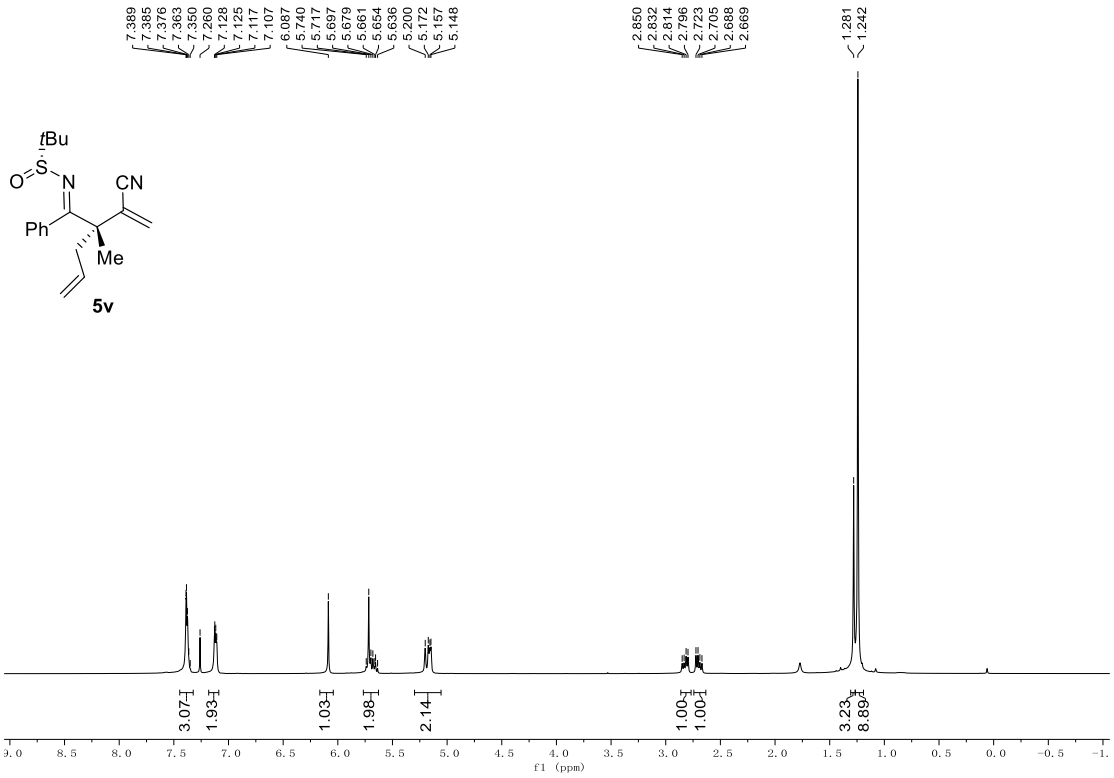
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5t**



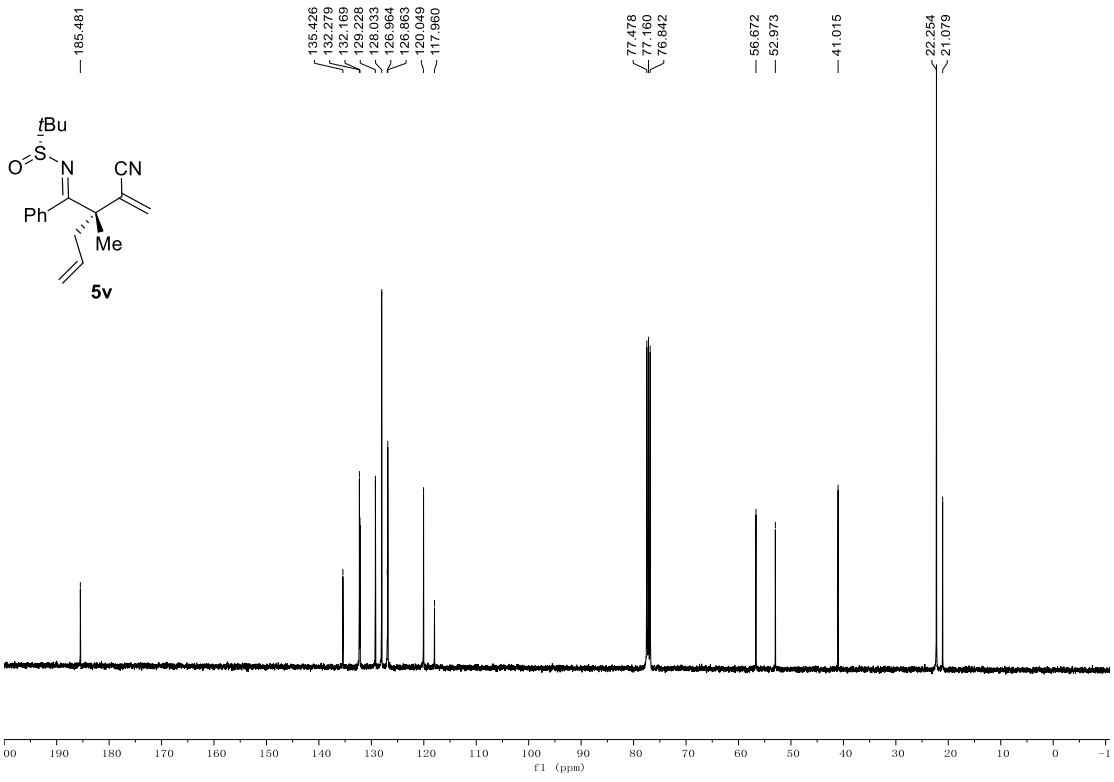
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5u**



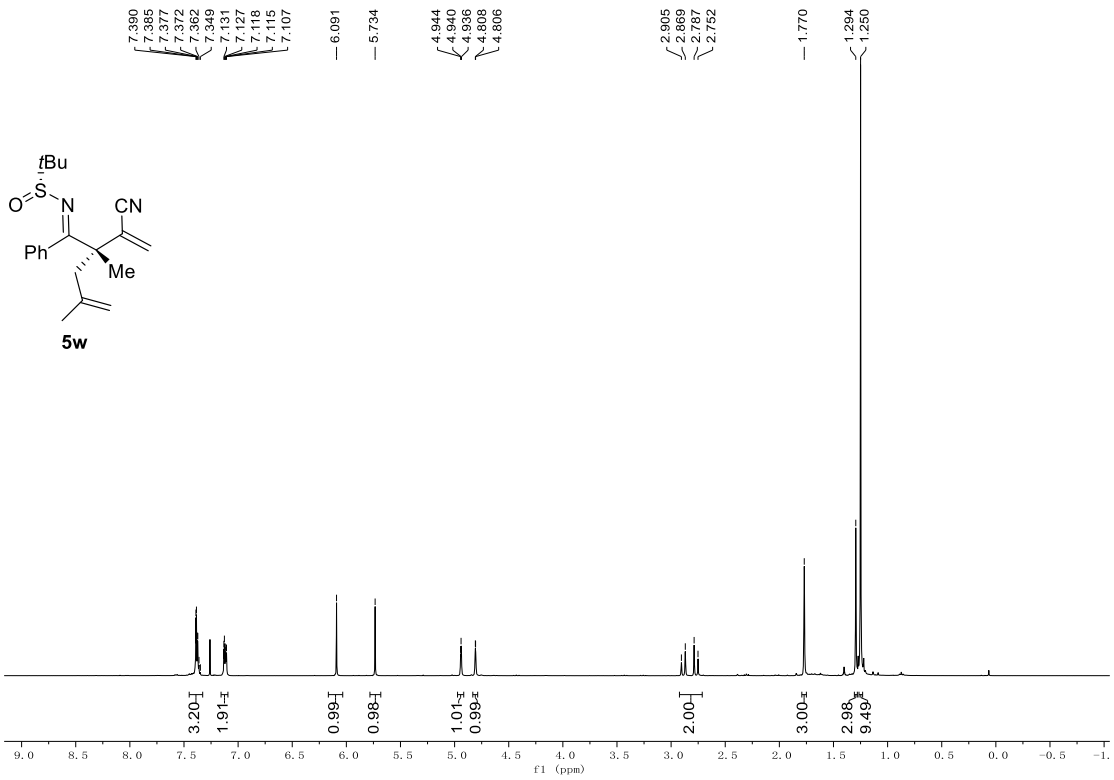
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5u**



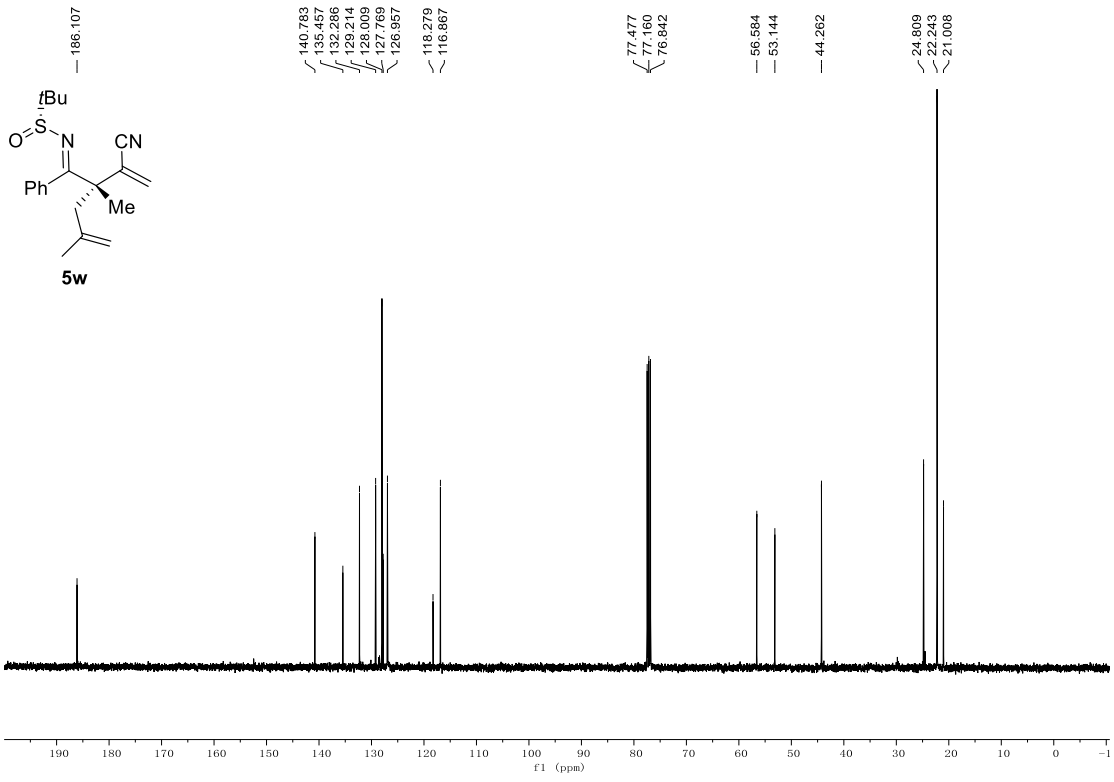
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5v**



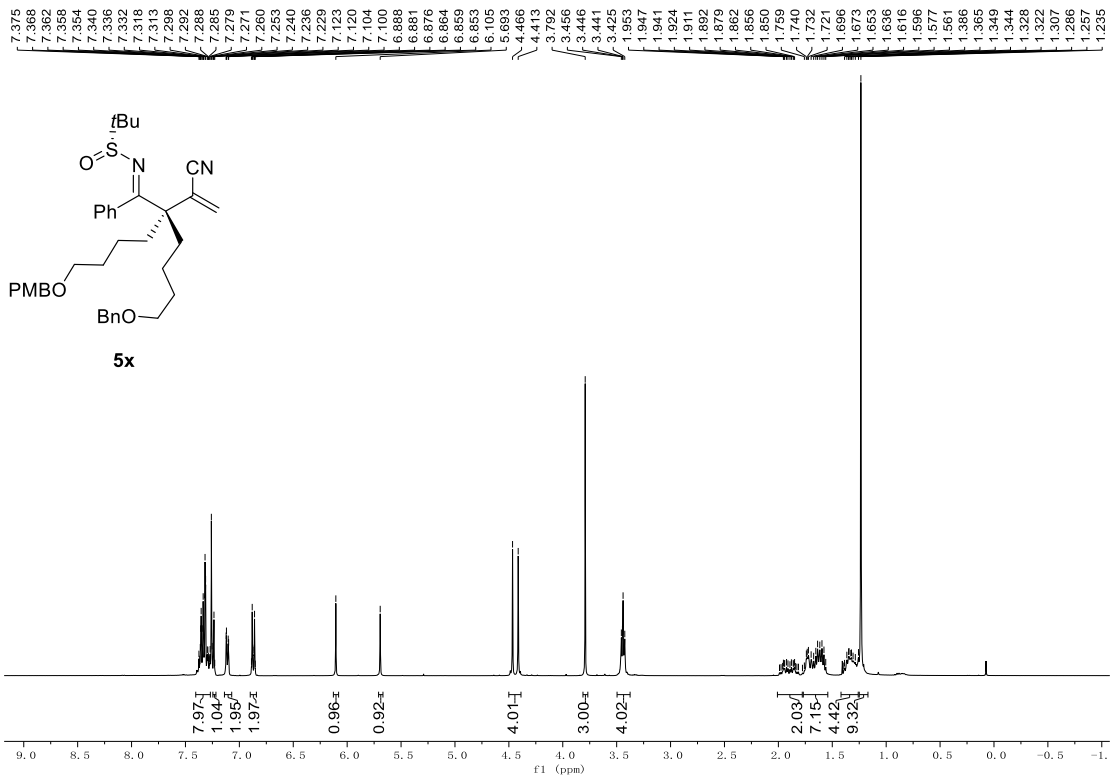
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5v**



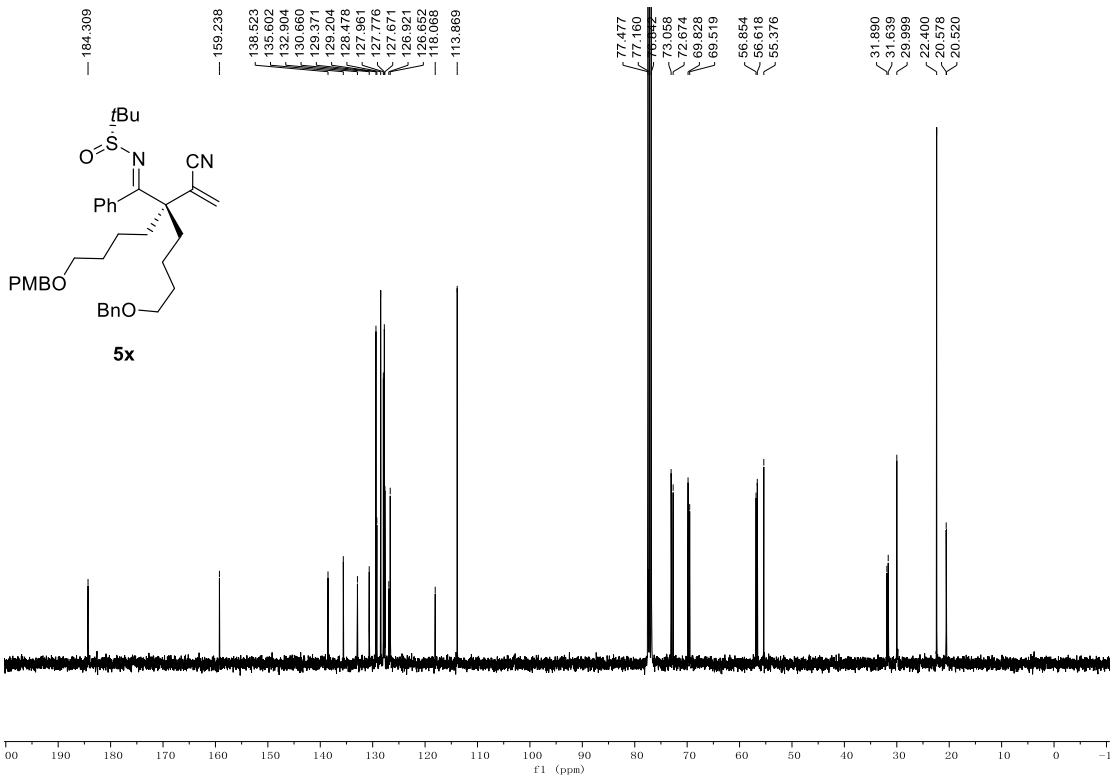
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5w**



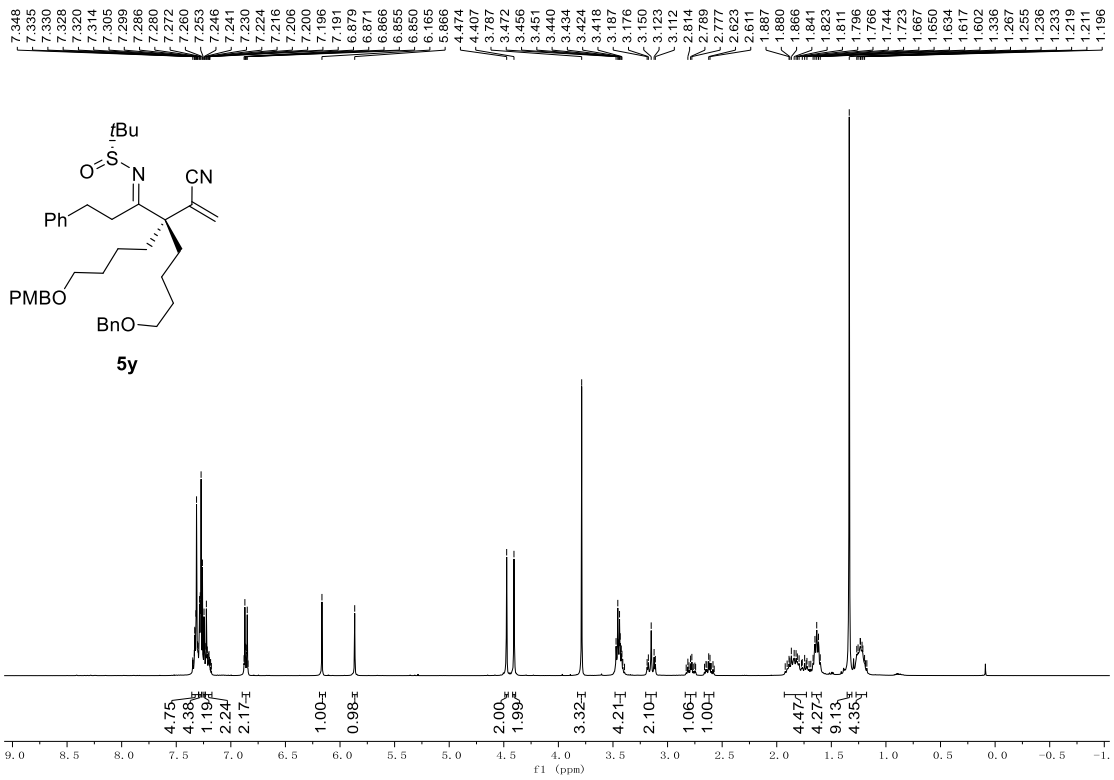
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5w**



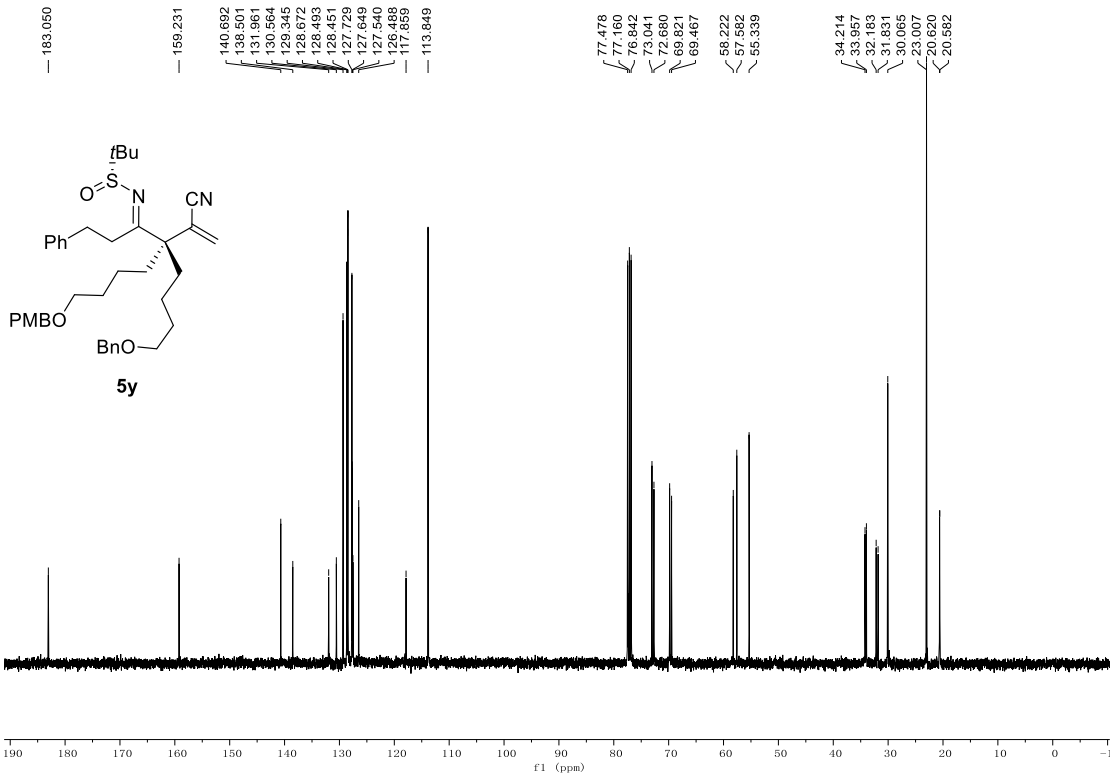
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5x**



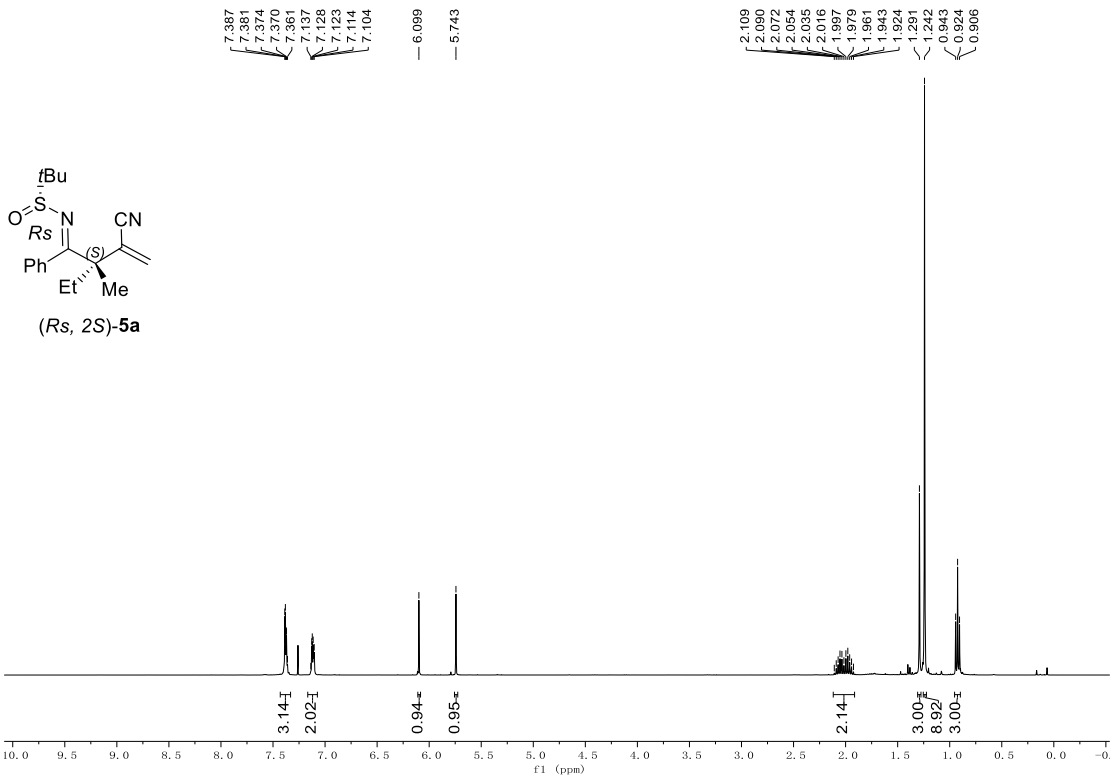
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5x**



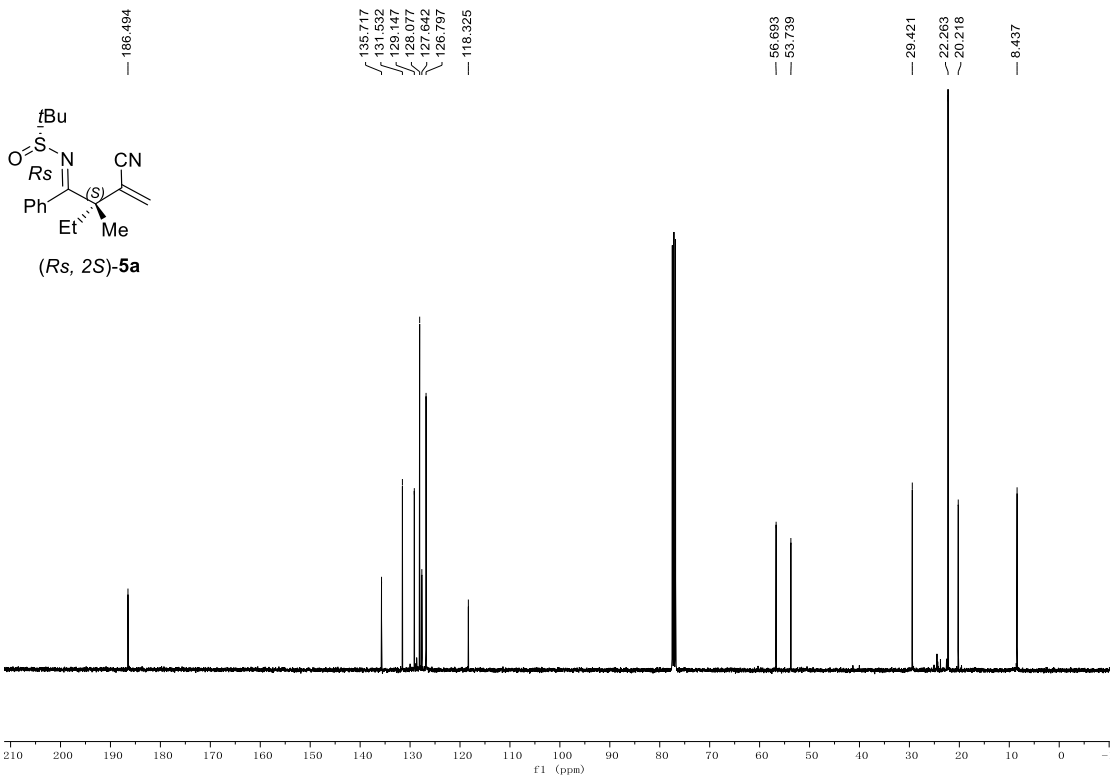
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5y**



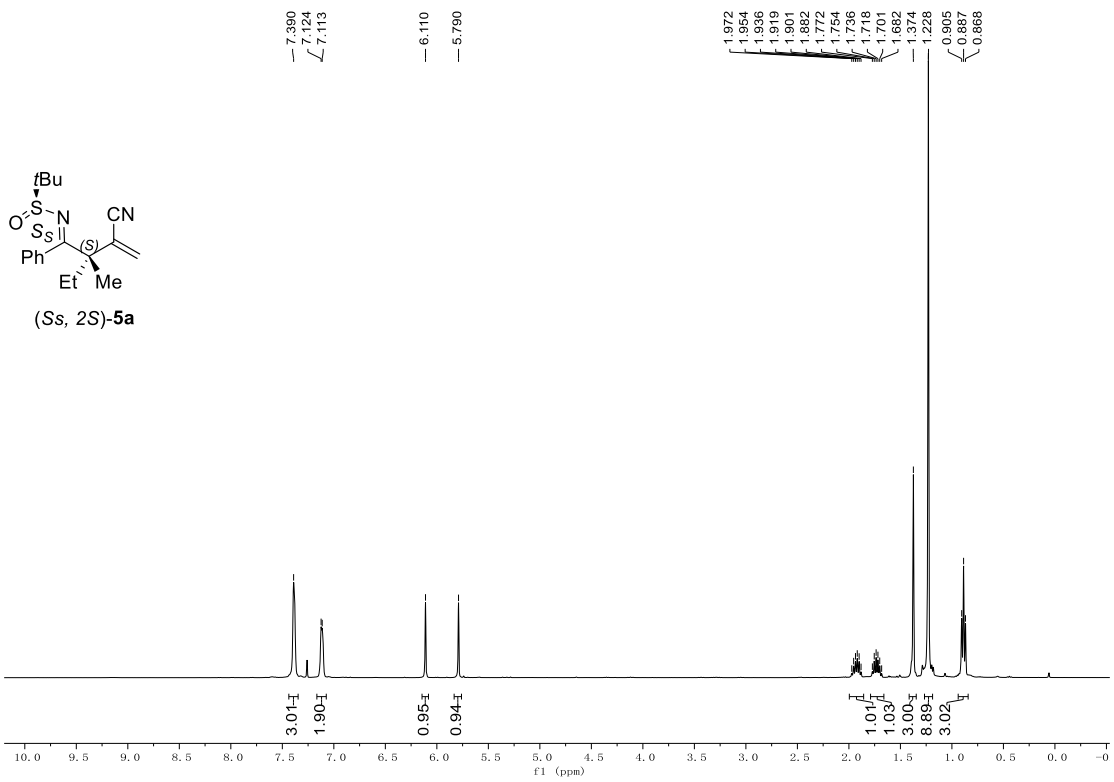
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5y**



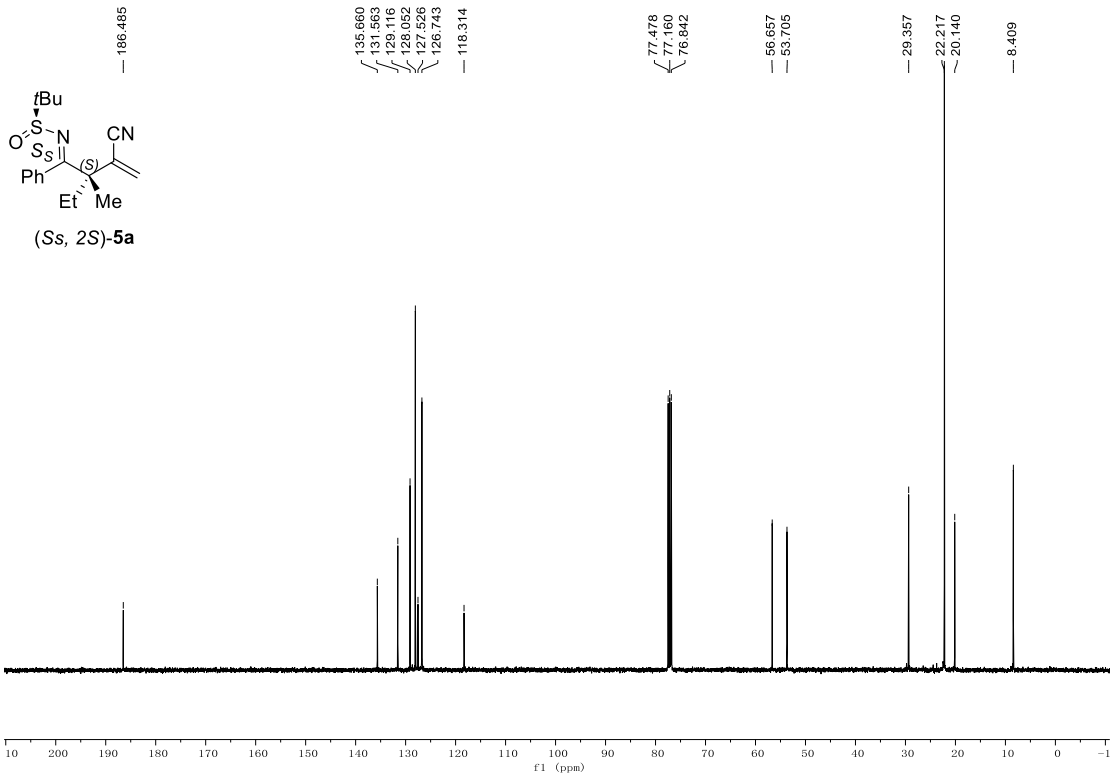
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*, *2S*)-**5a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



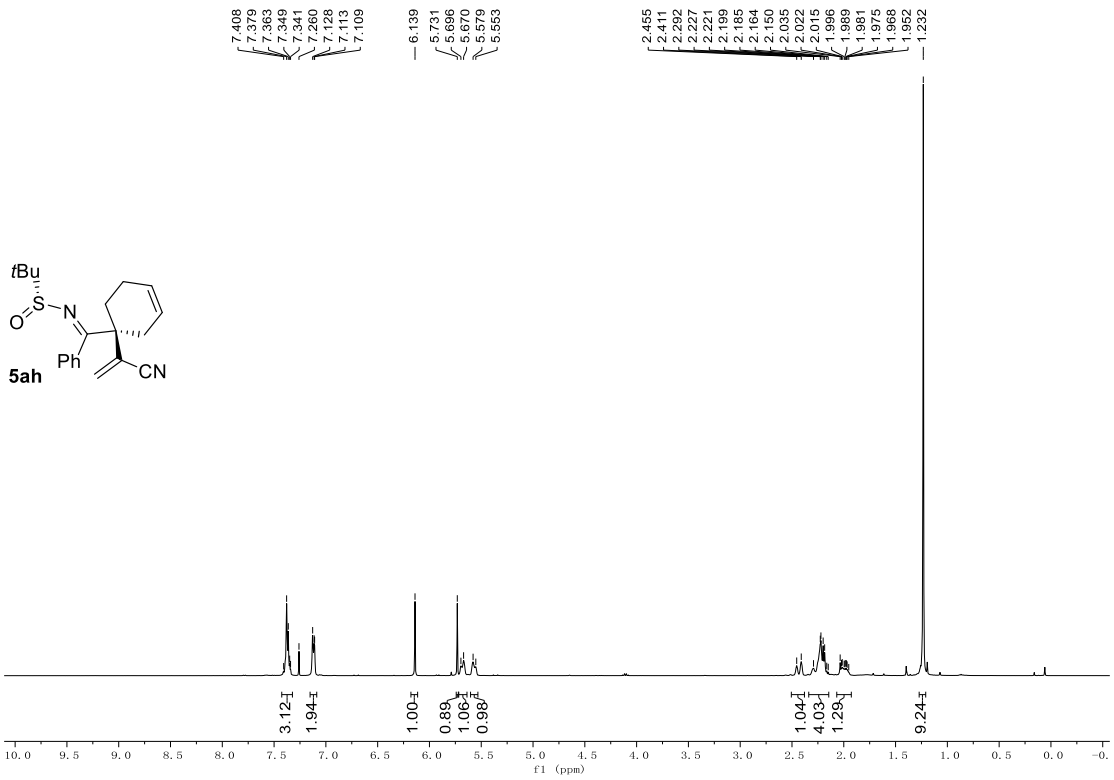
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Rs*, *2S*)-**5a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



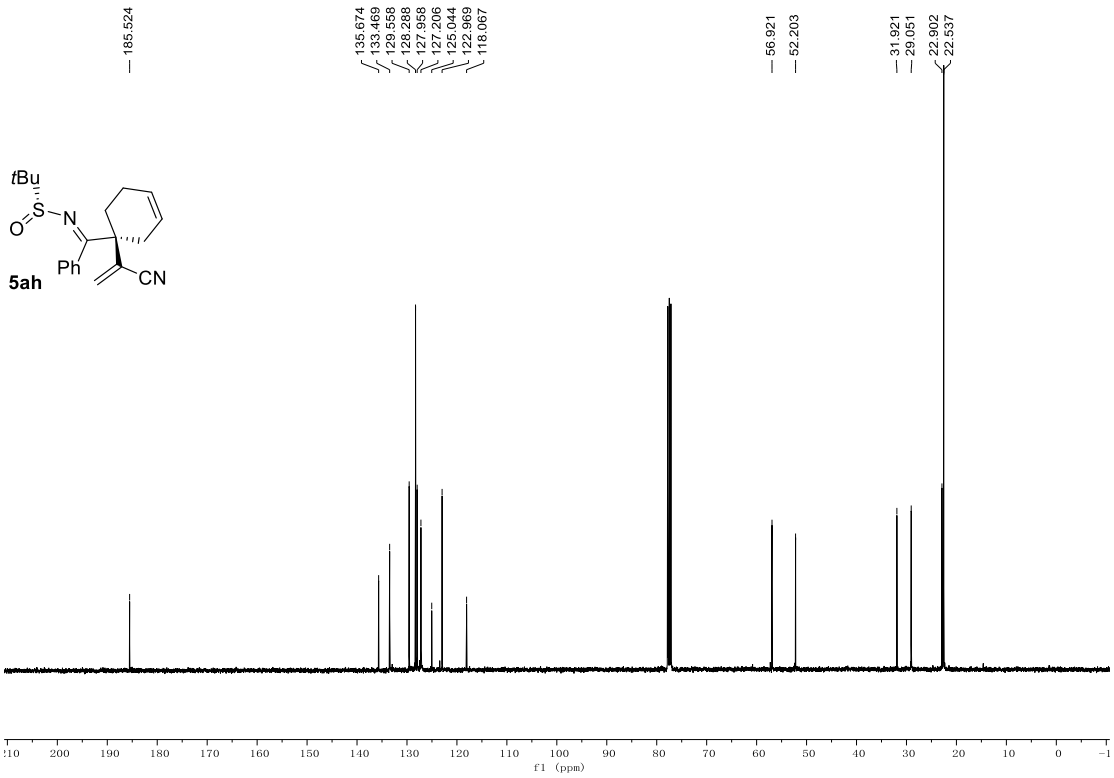
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*, *2S*)-**5a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



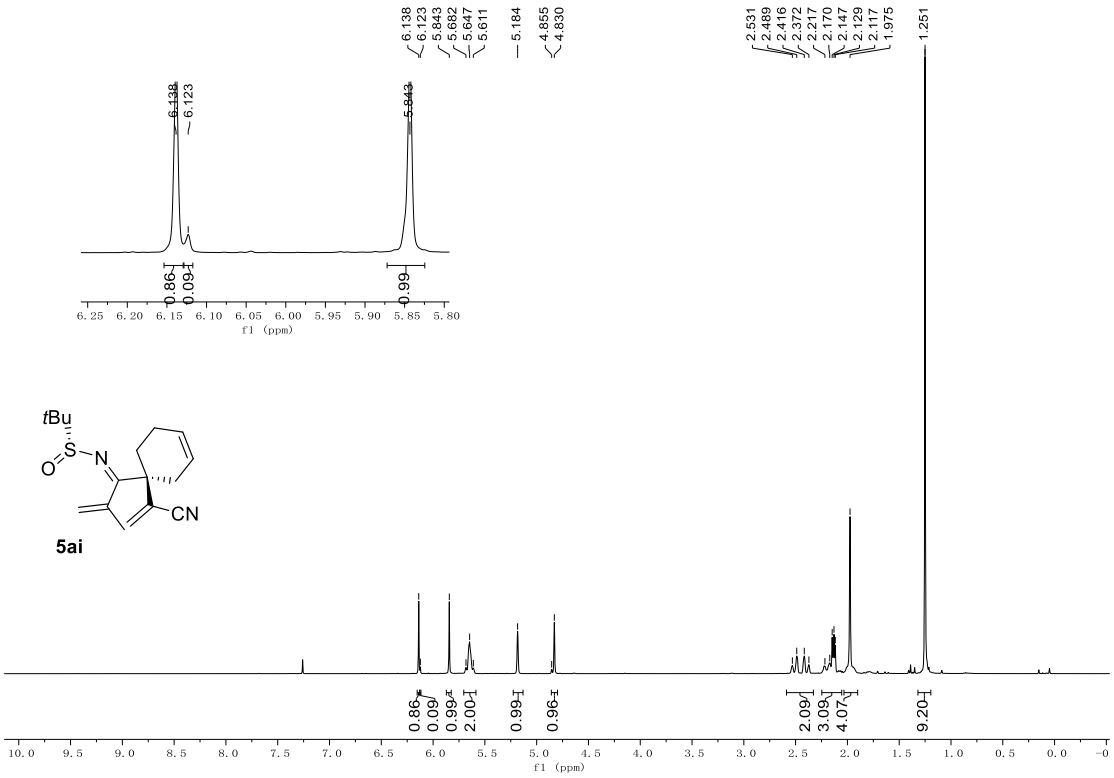
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of (*Ss*, *2S*)-**5a** prepared from α-alkenylation of enantioenriched ketimines (Scheme 5)



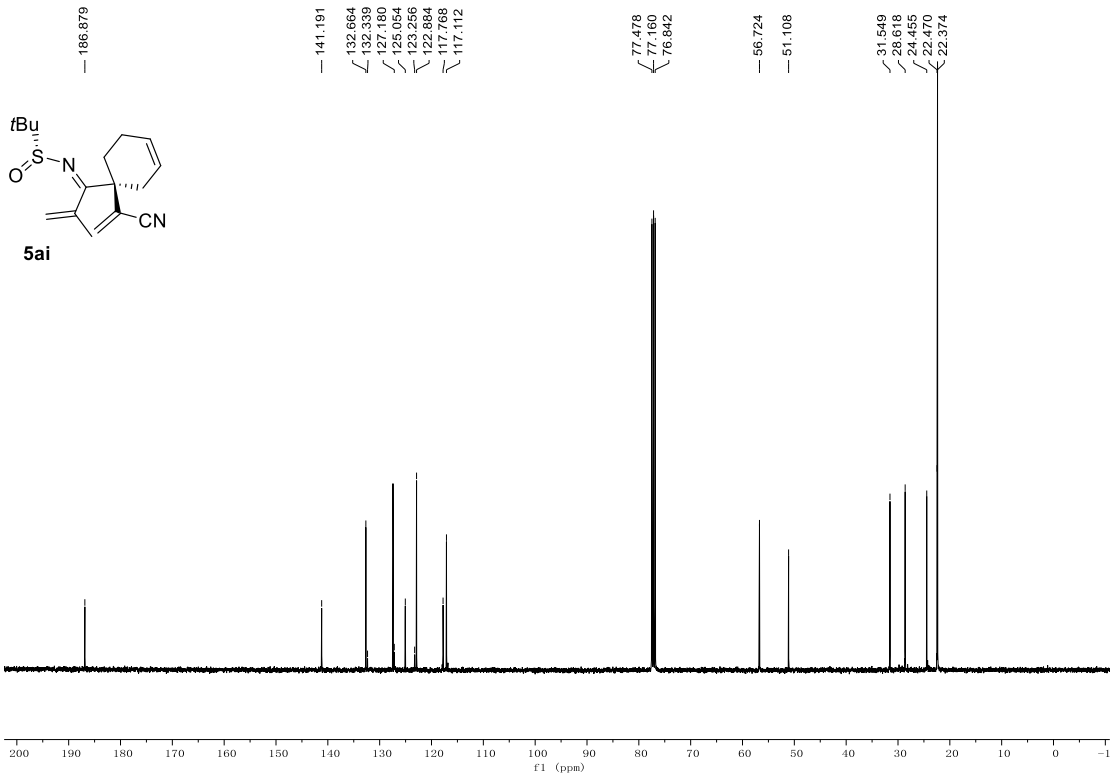
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5ah**



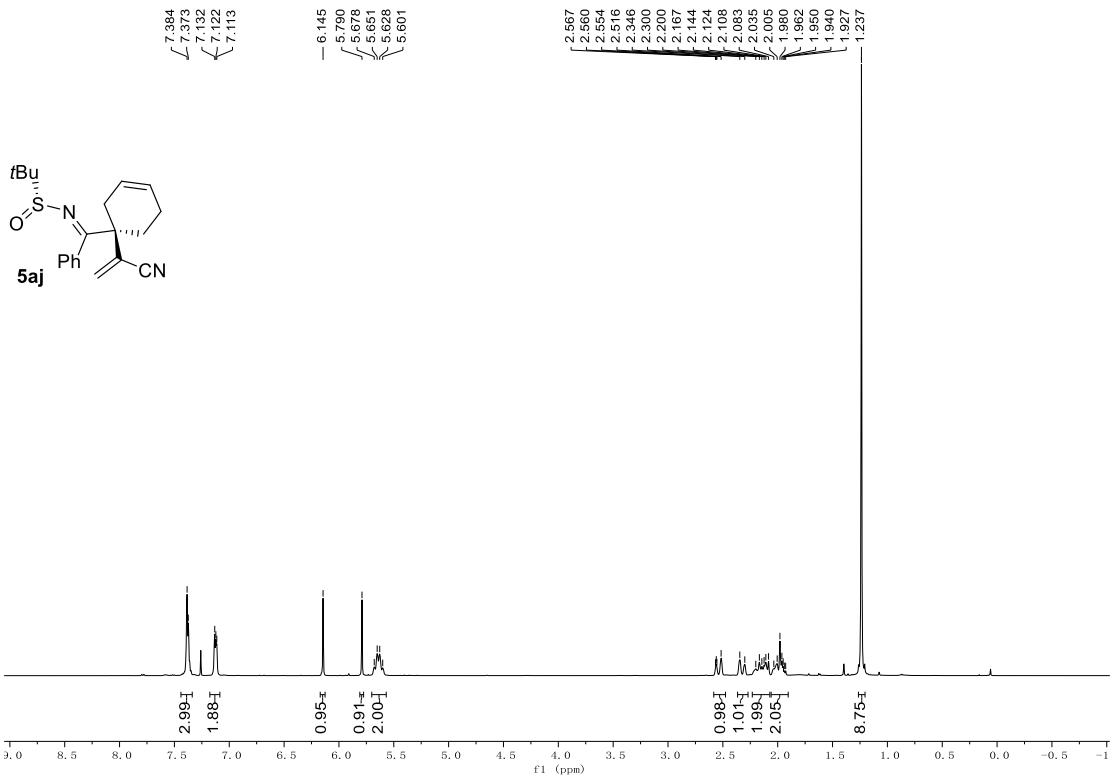
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5ah**



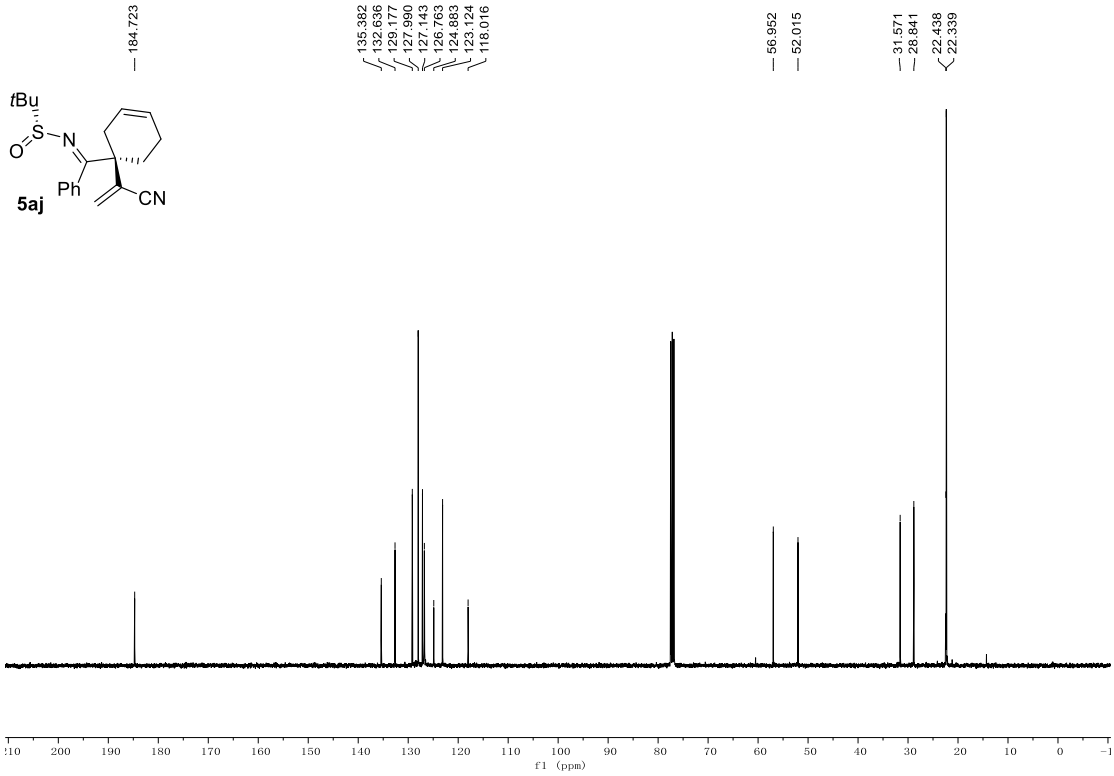
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5ai**



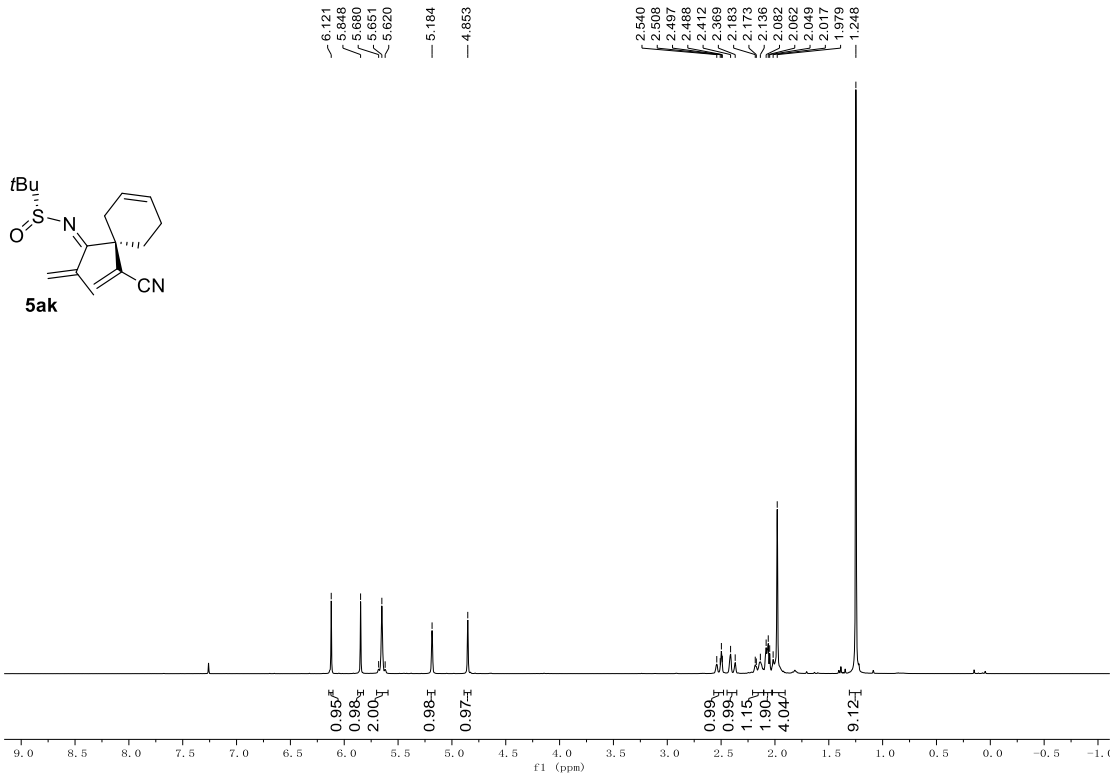
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5ai**



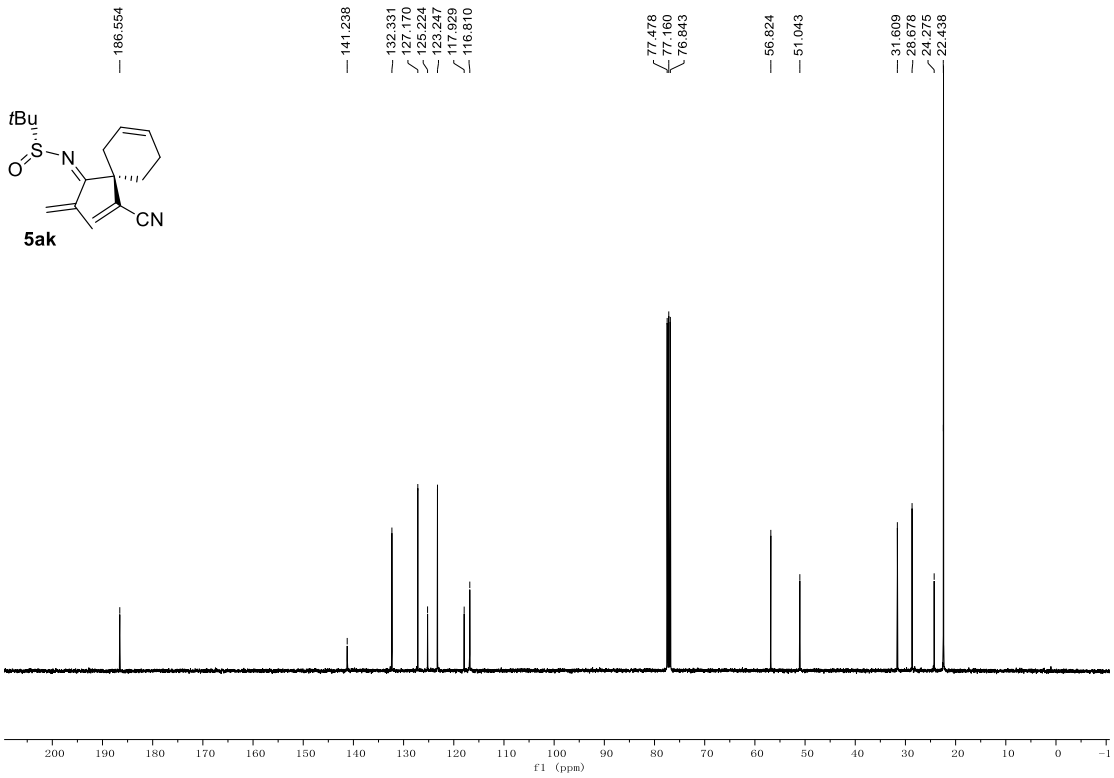
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5aj**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5aj**



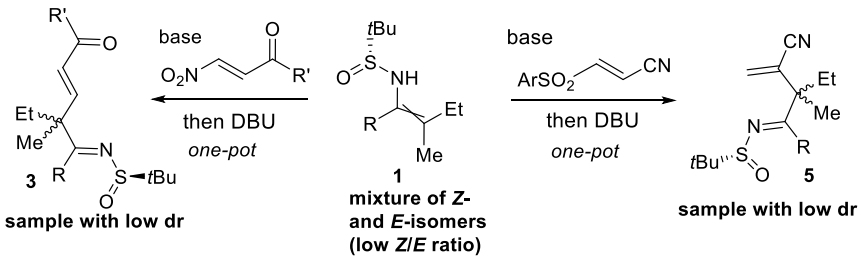
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5ak**



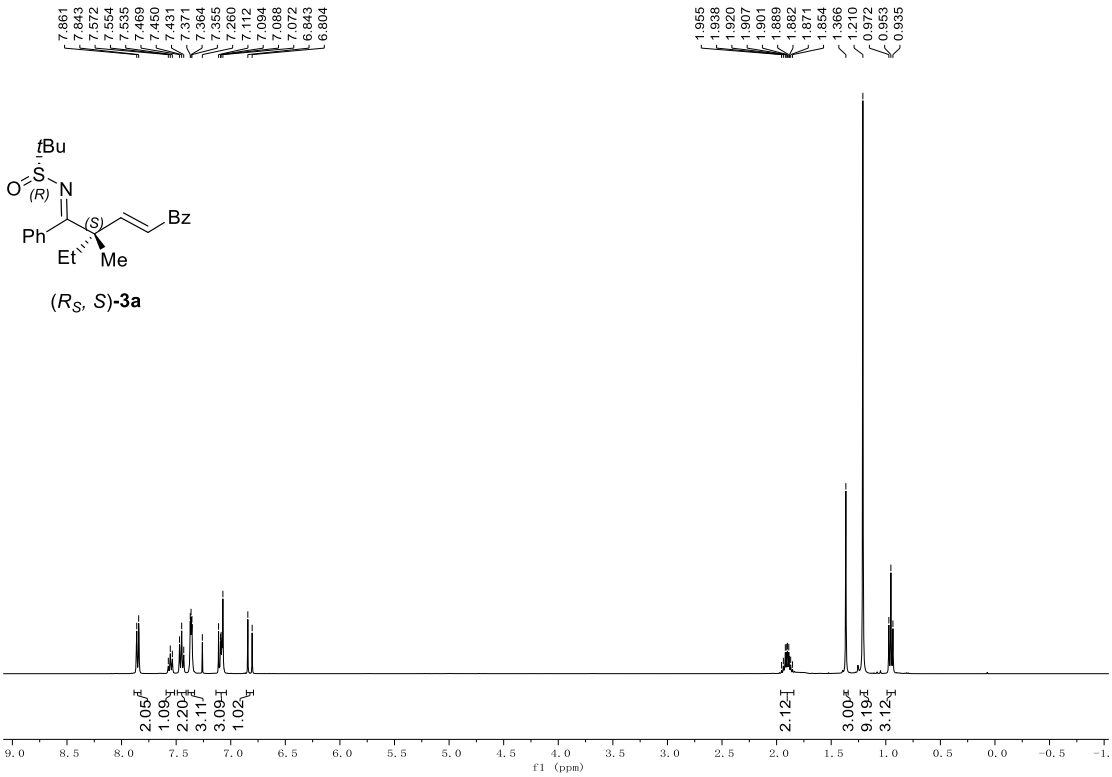
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5ak**

Determination of dr by ^{1}H NMR or HPLC analysis of the crude products

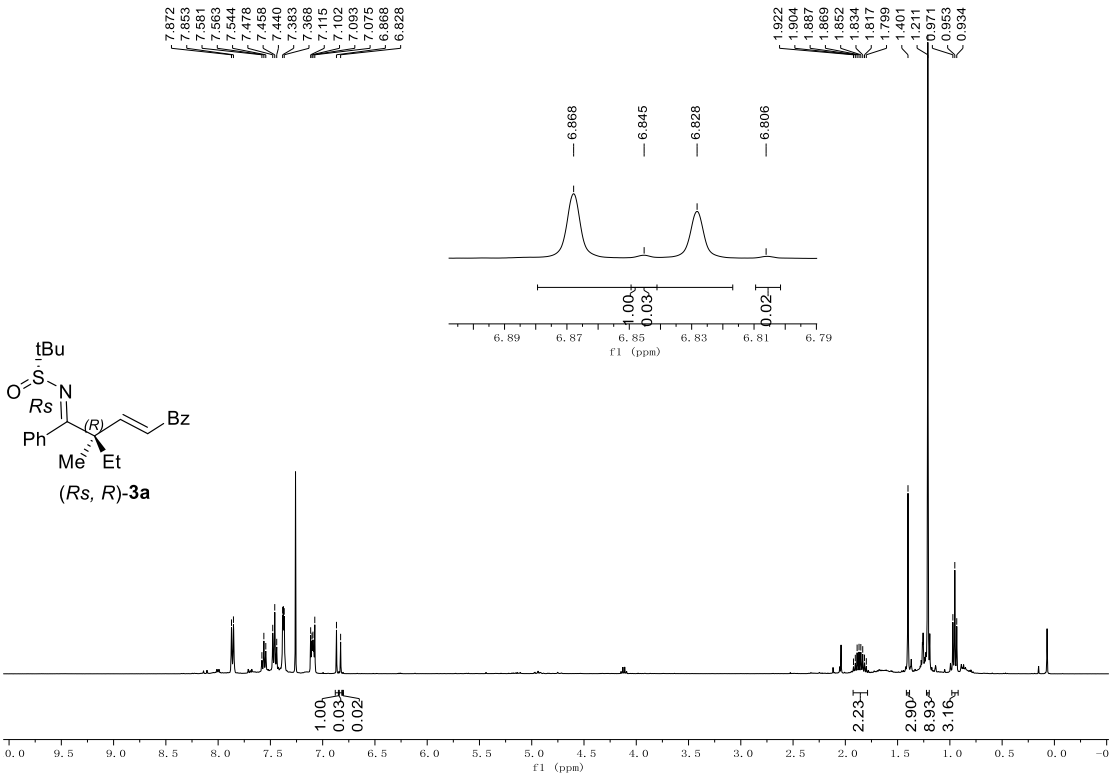
Note: In most cases, in order to identify the diagnostic peak(s) for the minor diastereomer from the ^{1}H NMR spectrum of the crude reaction mixture generated from the reaction using one geometric isomer (*Z*/*E* or *Z*/*E* > 100:1) of the enesulfinamides as the starting material, reaction were intentionally performed under identical conditions using the enesulfinamides with low ratio of geometric isomer (for details of preparing ensulfinamides with high or low ratio of geometric isomers, see ref S2), which gave a pair of diastereomers of the alkenylation products with low dr. The ^{1}H NMR spectra of the alkenylation product with low dr was recorded and used as a reference spectrum.



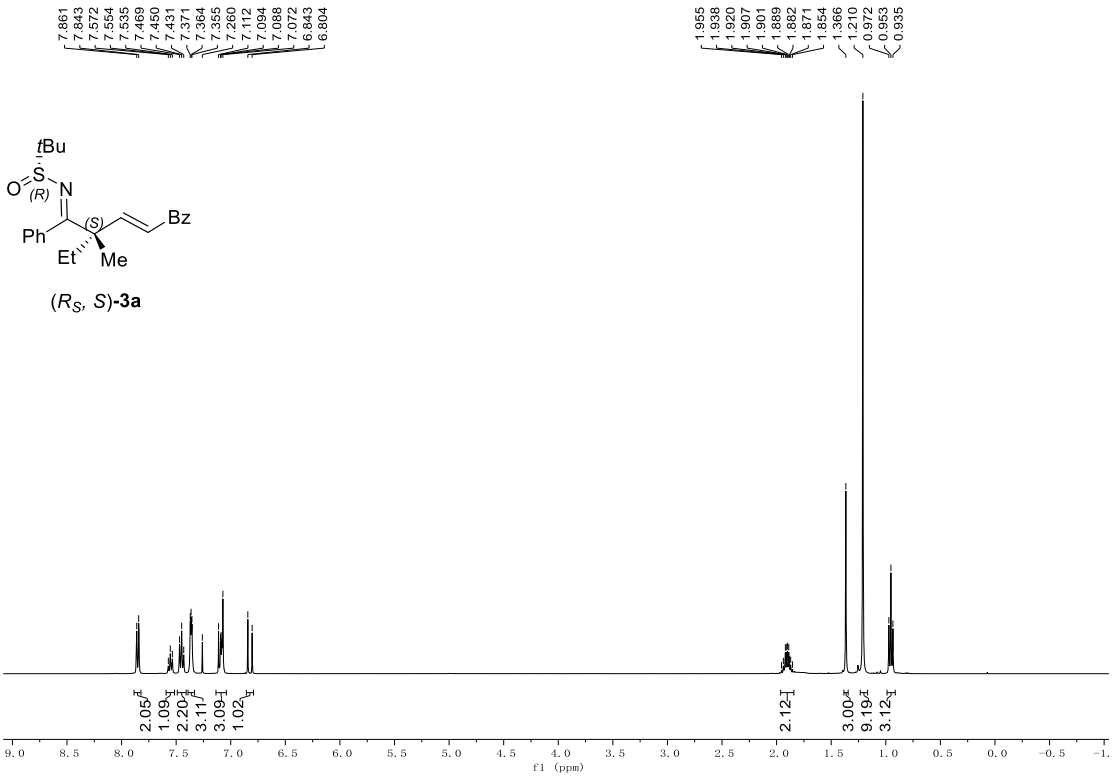
In some cases, determination of dr with ^{1}H NMR spectrum of the crude reaction mixture was not possible since the ^{1}H NMR spectra of the diastereomers in these cases are nearly identical. Instead, HPLC analysis of the crude reaction mixture was used to determine dr. For details, please see the pages S147–S224.



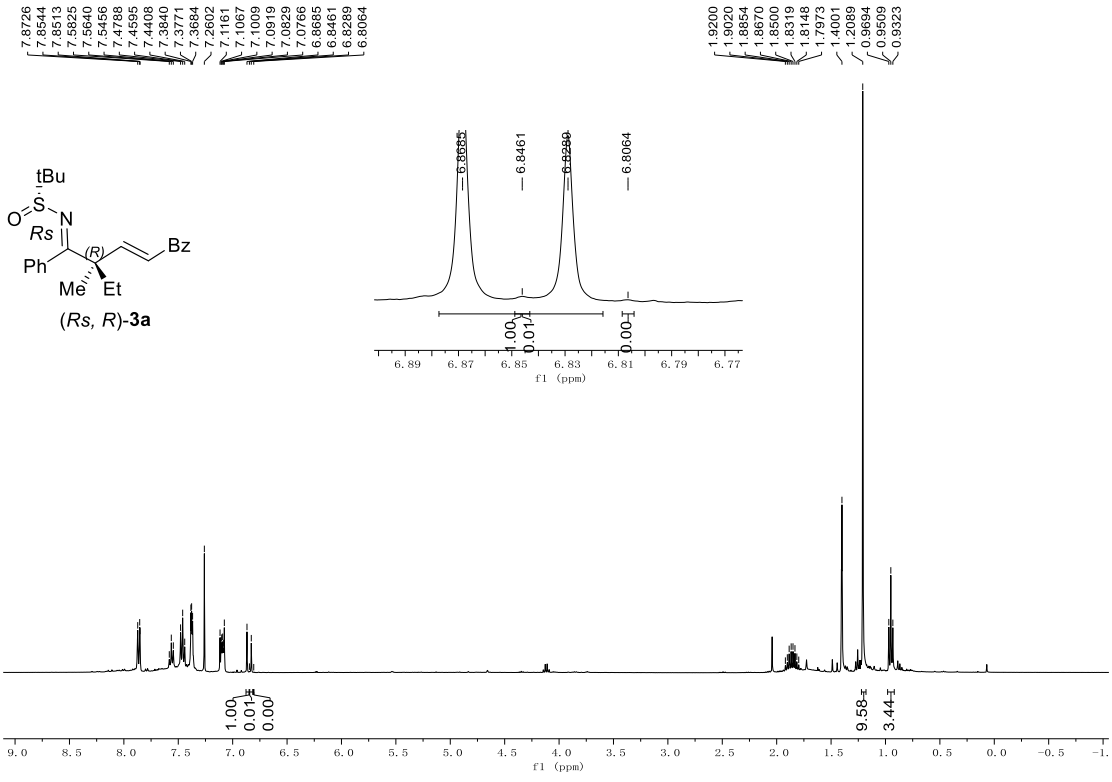
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs, S*)-**3a** that was used to identify the diagnostic peak(s) of the minor diastereomer

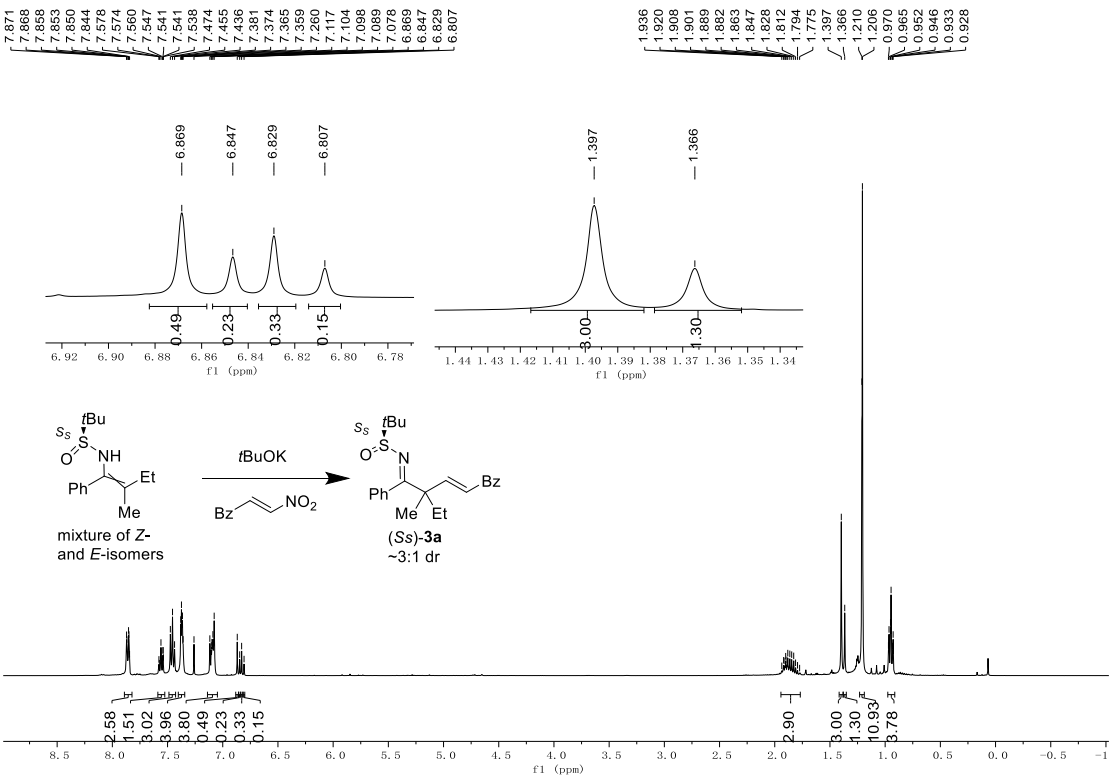


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *R*)-**3a** (dr > 20:1; 1 gram scale reaction)

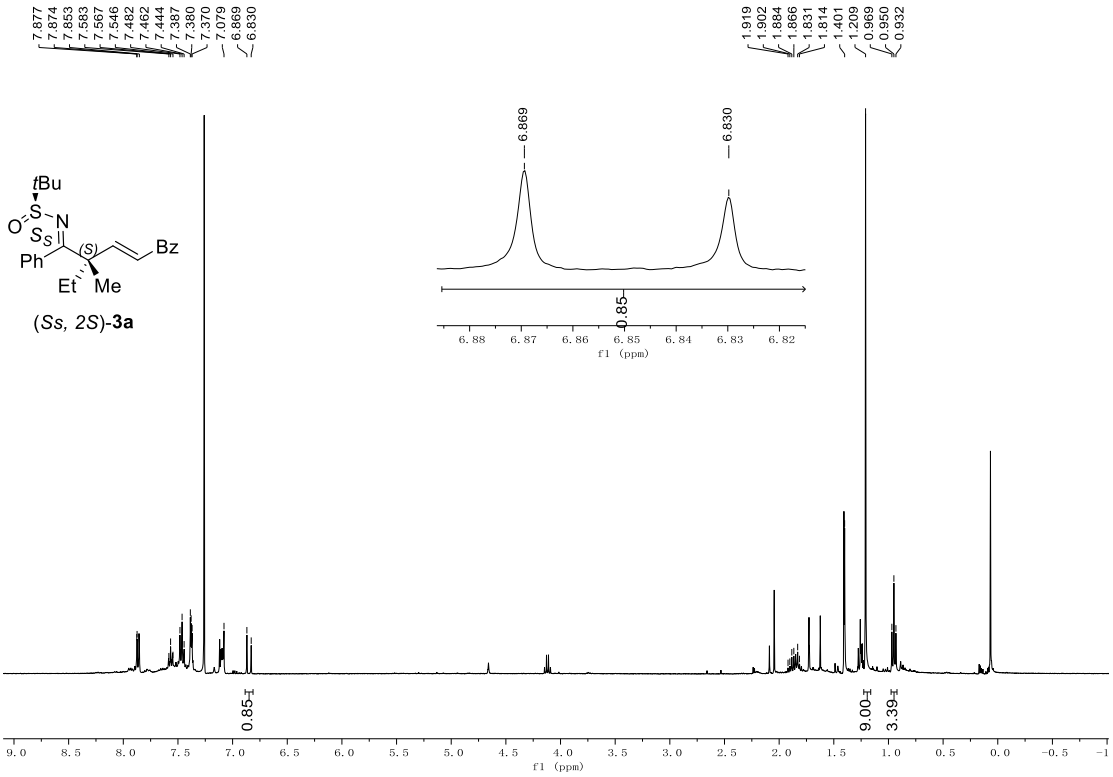


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs, S*)-**3a** that was used to identify the diagnostic peak(s) of the minor diastereomer



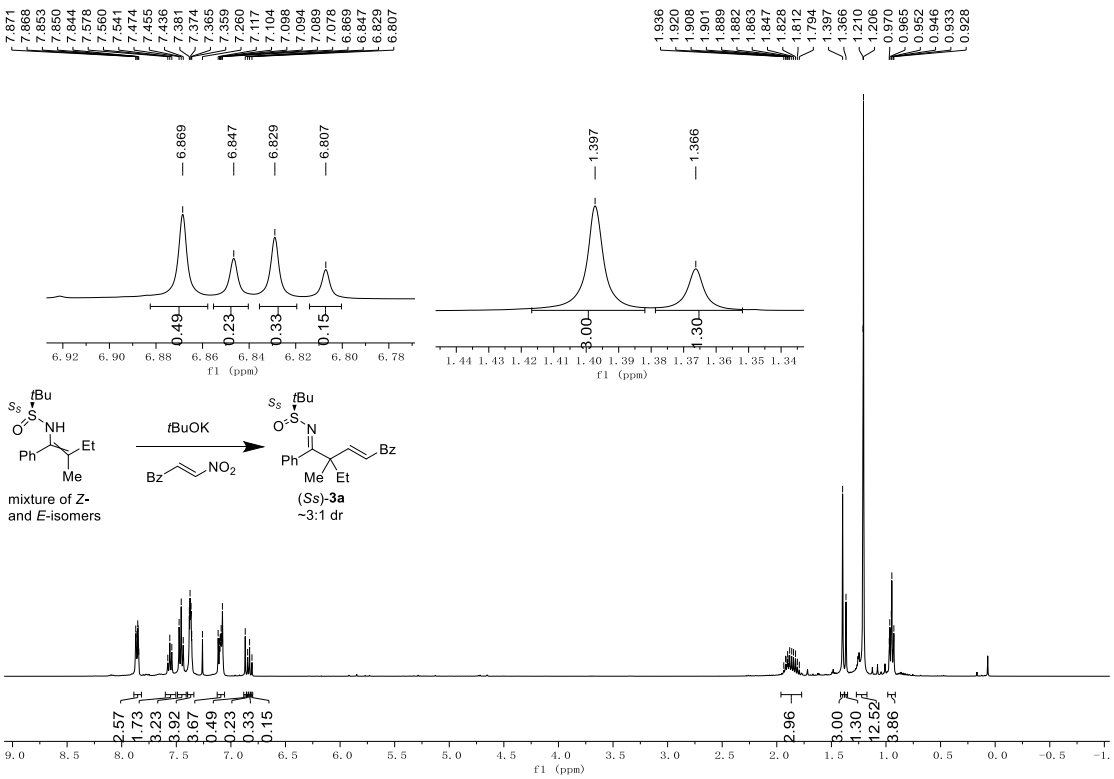


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*)-**3a** with low diastereoselectivity (dr ~ 3:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio

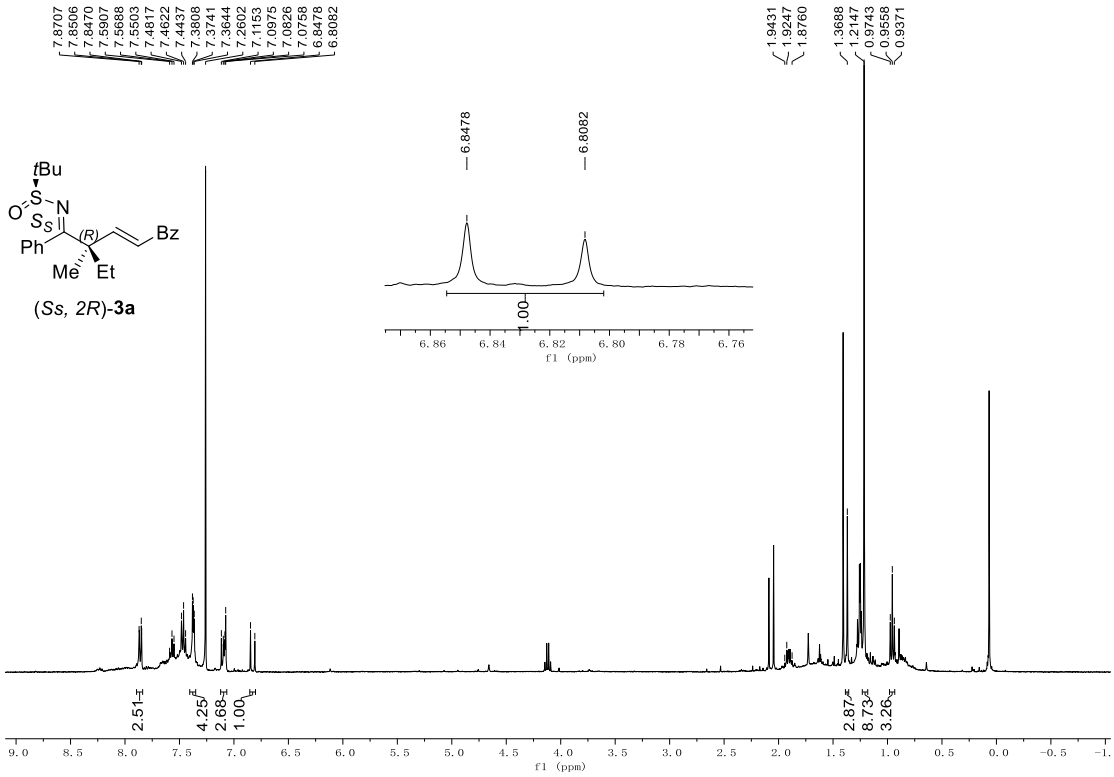


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *S*)-**3a** (dr > 20:1)

(No observable presence of the minor diastereomer)

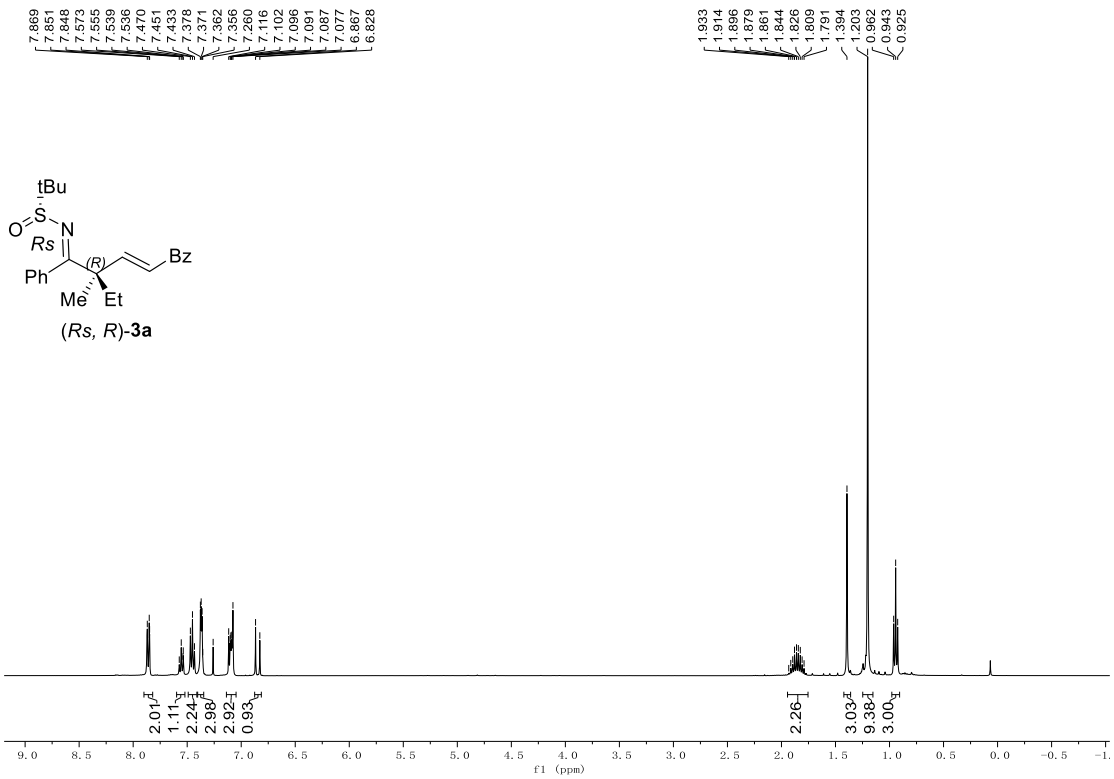


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*)-**3a** with low diastereoselectivity (dr ~ 3:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio

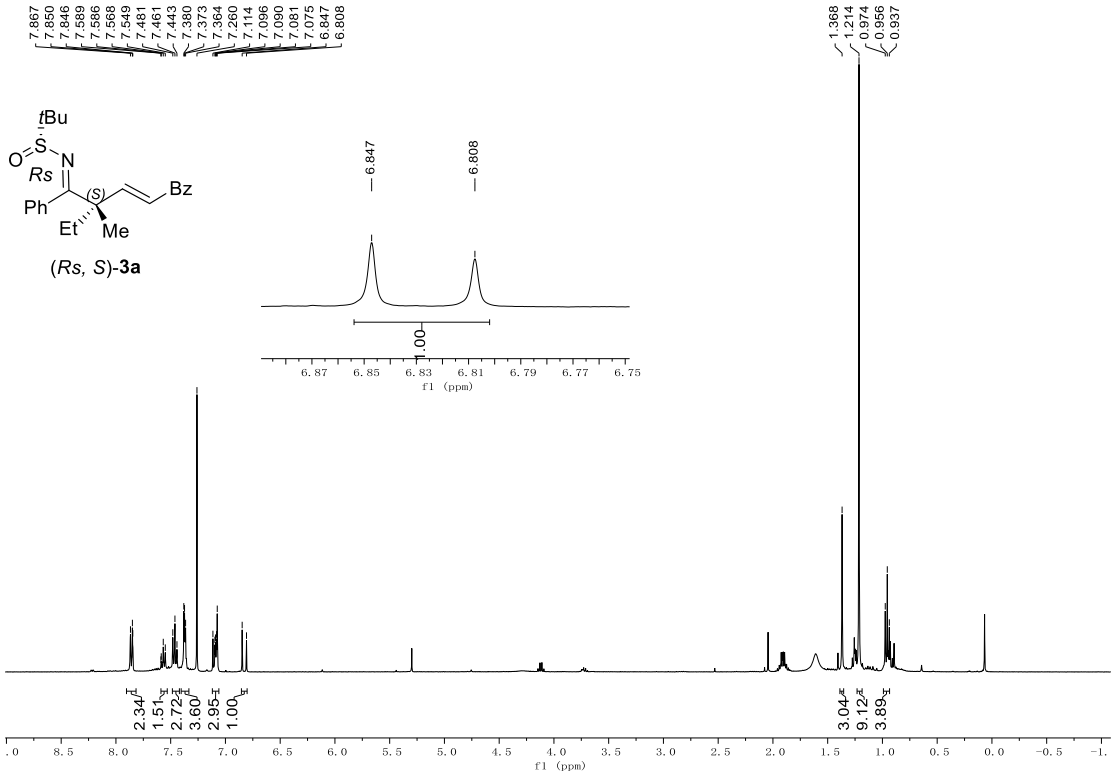


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *R*)-**3a** (dr >20:1)

(No observable presence of the minor diastereomer)

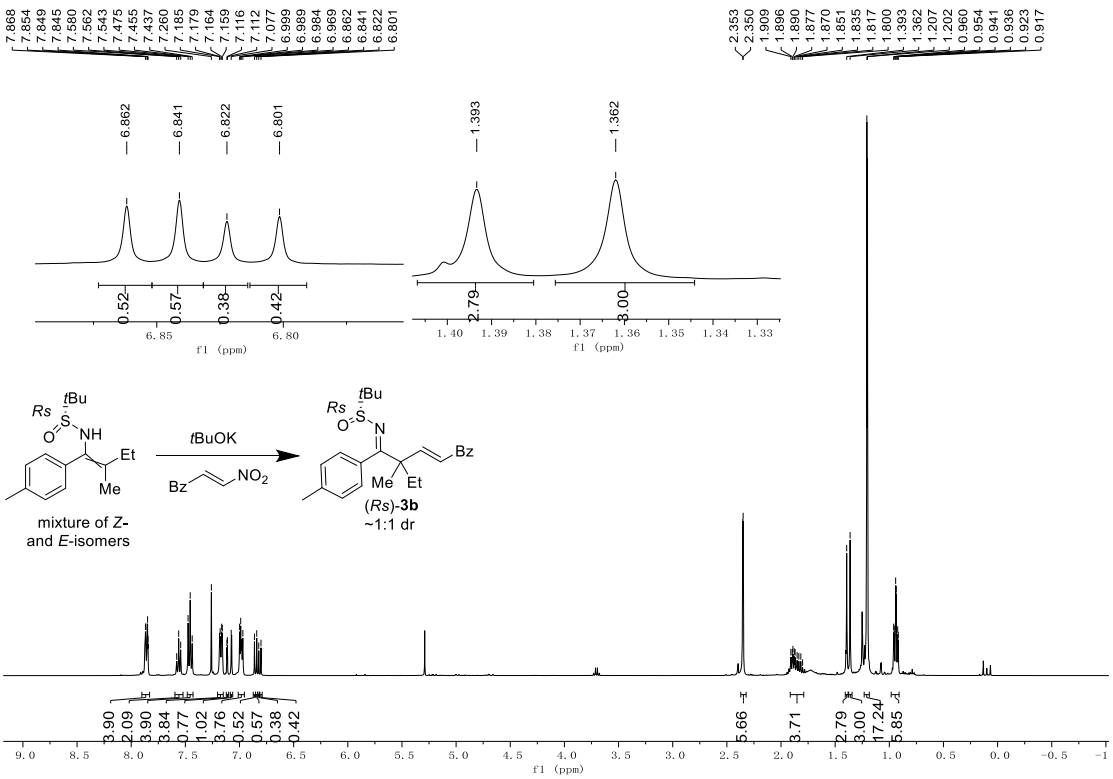


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs*, *R*)-**3a** that was used to identify the diagnostic peak(s) of the minor diastereomer

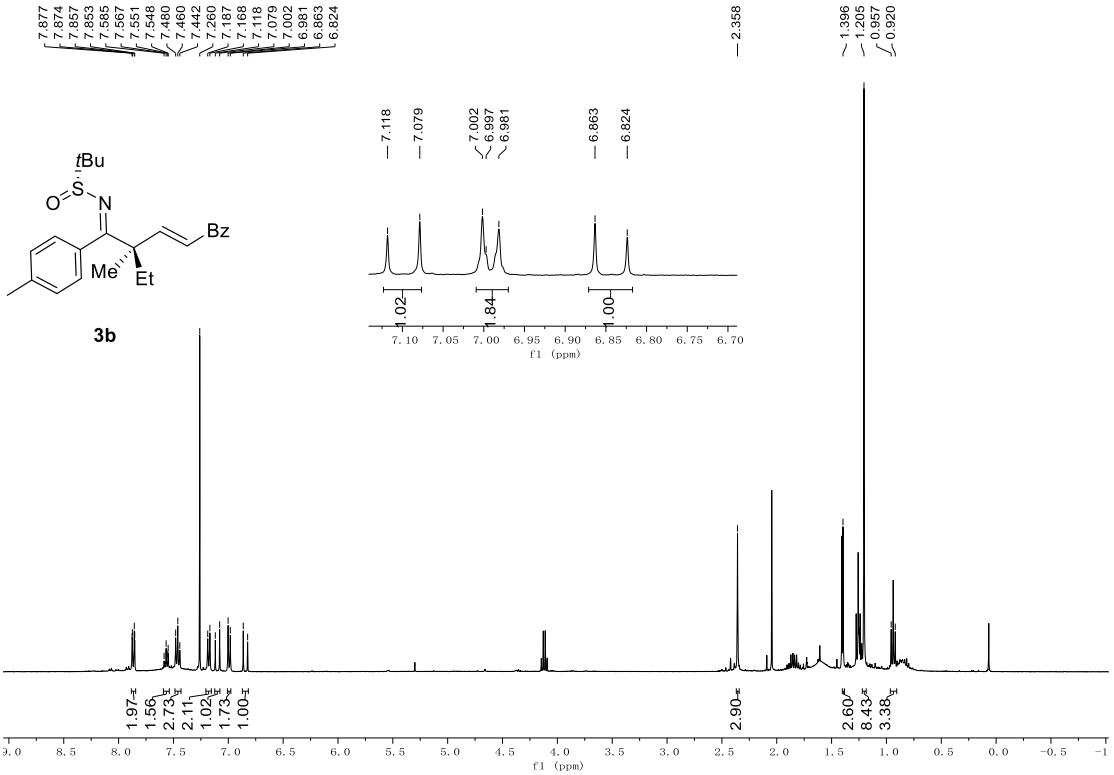


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *S*)-**3a** (dr > 20:1)

(No observable presence of the minor diastereomer)

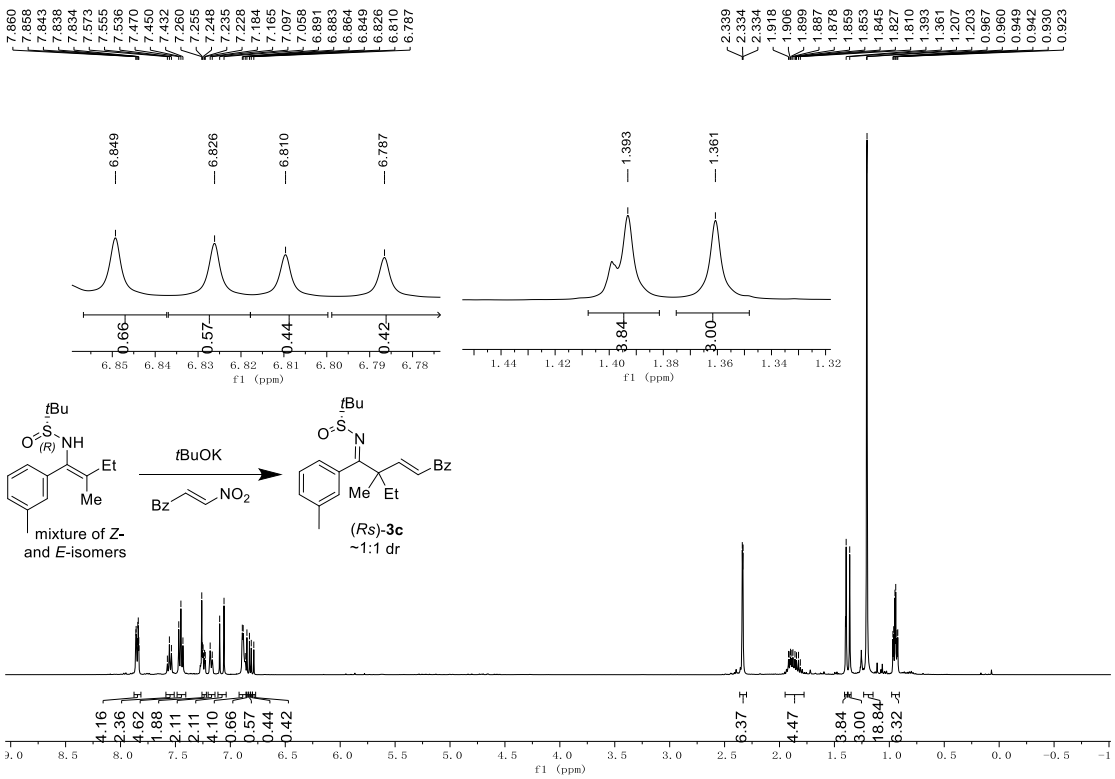


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3b** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

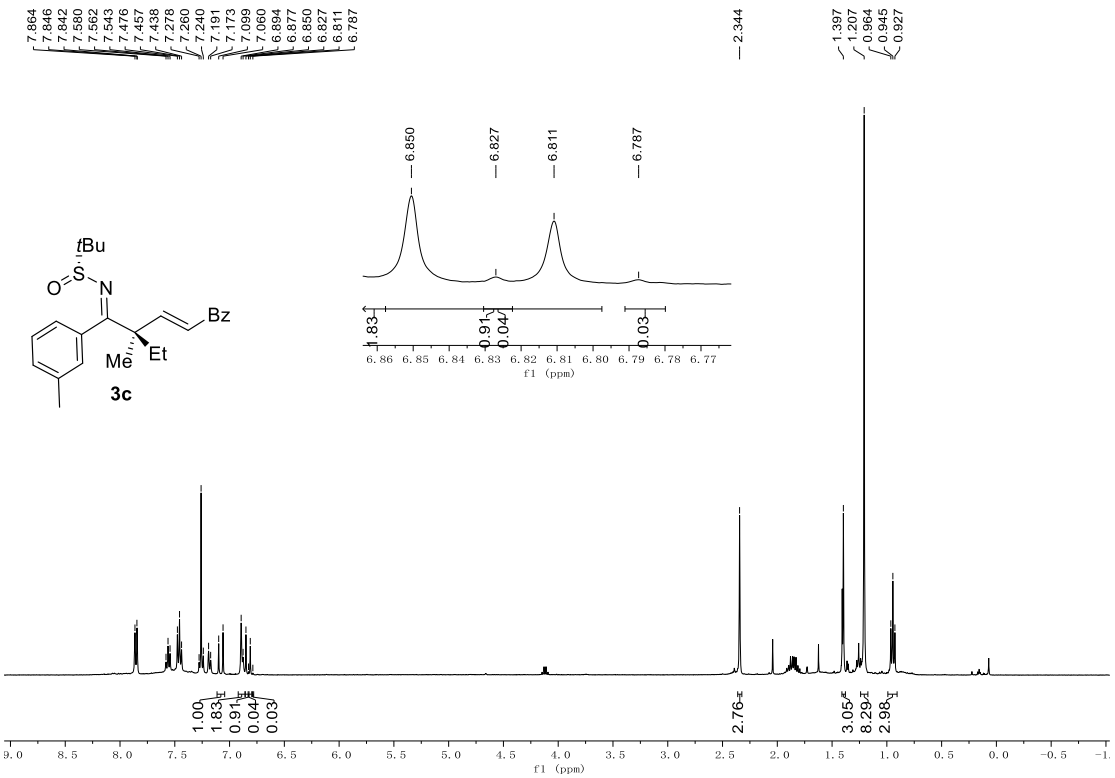


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3b** (dr > 20:1)

(No observable presence of the minor diastereomer)

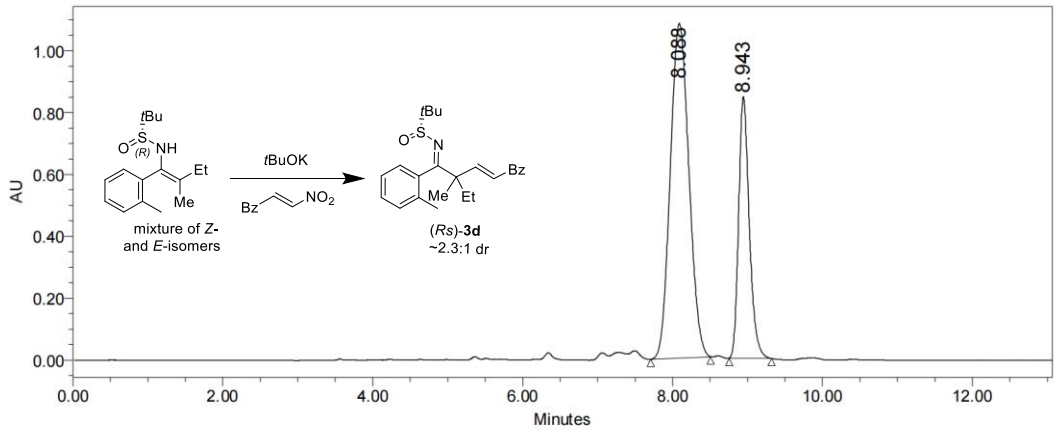


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3c** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3c** (dr = 20:1)

(*Rs*)-**3d**: HPLC conditions: Daicel Chiralcel IA-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

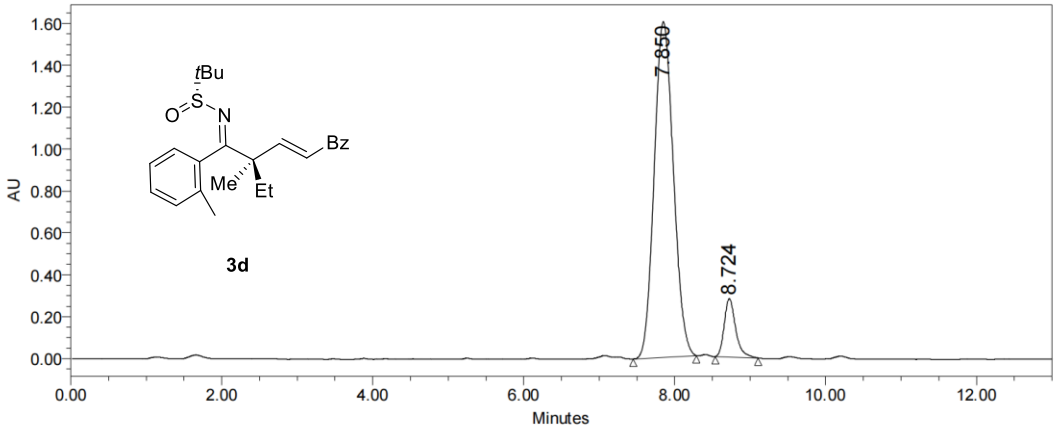


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1596; Processing Method: H230615AP XX 90 10 254 40 IA

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.088	18718381	69.19	1082313
2	W2489 ChA 254nm	8.943	8334701	30.81	846234

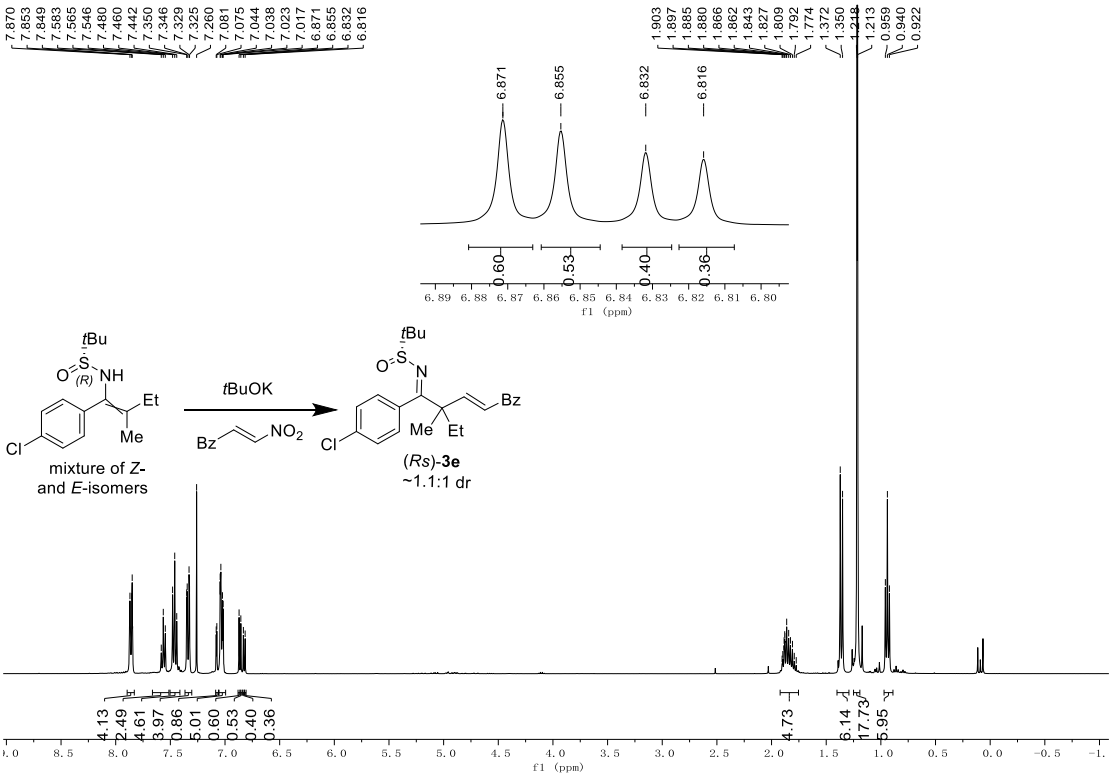
HPLC chromatogramfor dr determination of crude **3d**



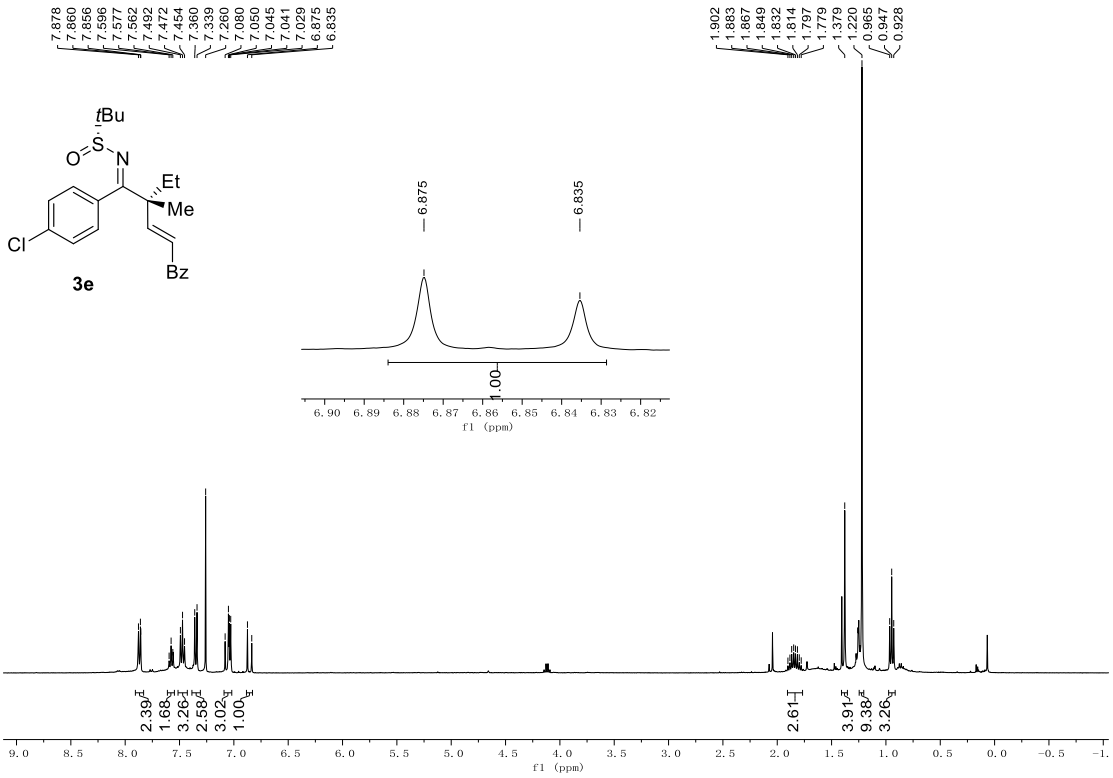
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1598; Processing Method: H230616G SX 90 10 254 40 IA

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.850	28296789	90.66	1602552
2	W2489 ChA 254nm	8.724	2916232	9.34	278385

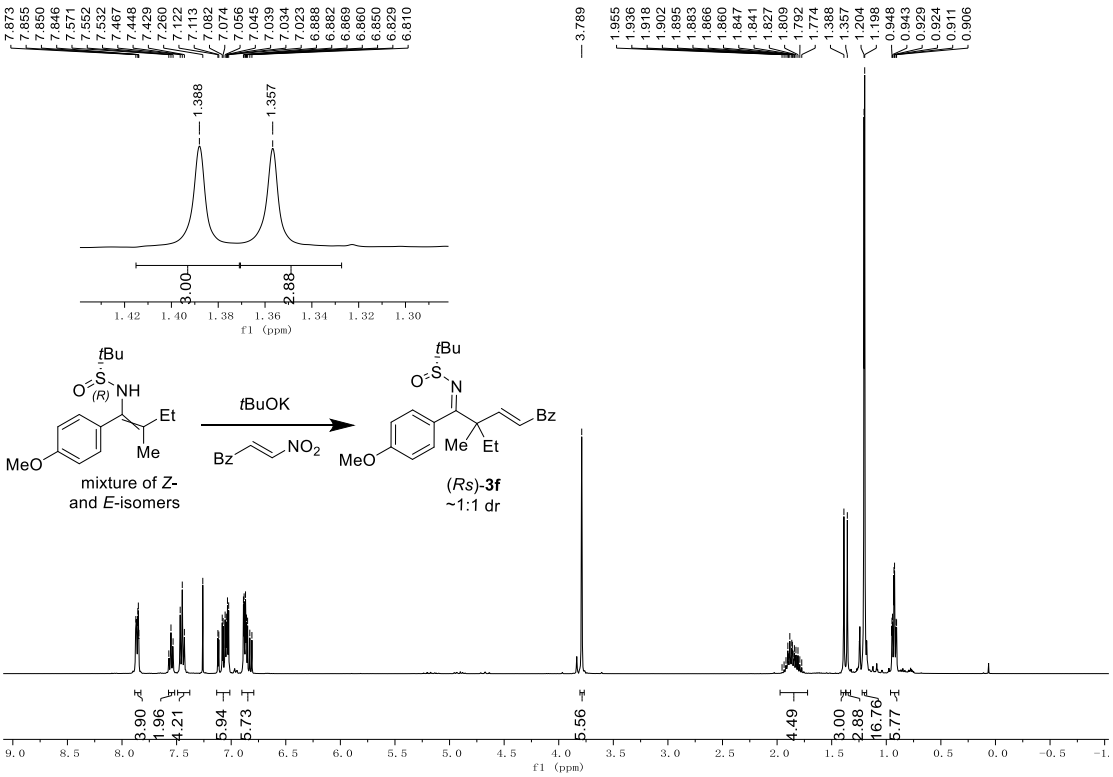


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3e** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio

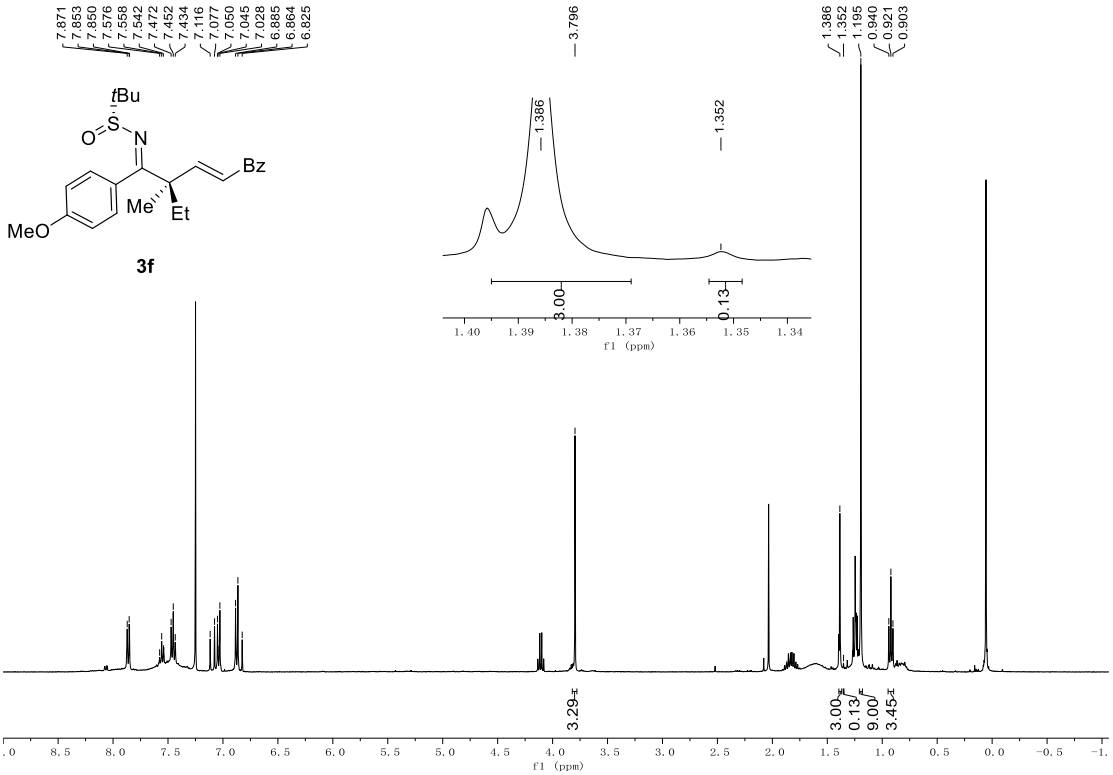


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3e** (dr > 20:1)

(No observable presence of the minor diastereomer)

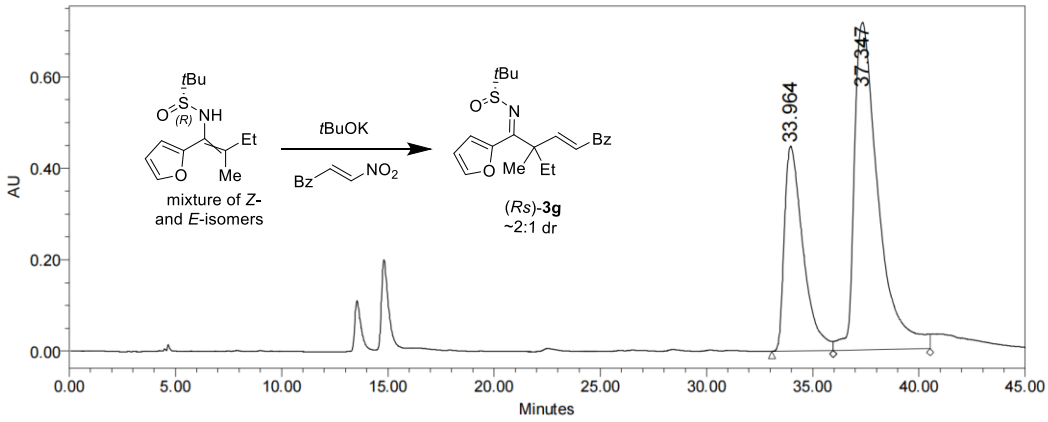


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3f** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3f** (dr > 20:1)

(*Rs*)-**3g**: HPLC conditions: Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 97:03 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

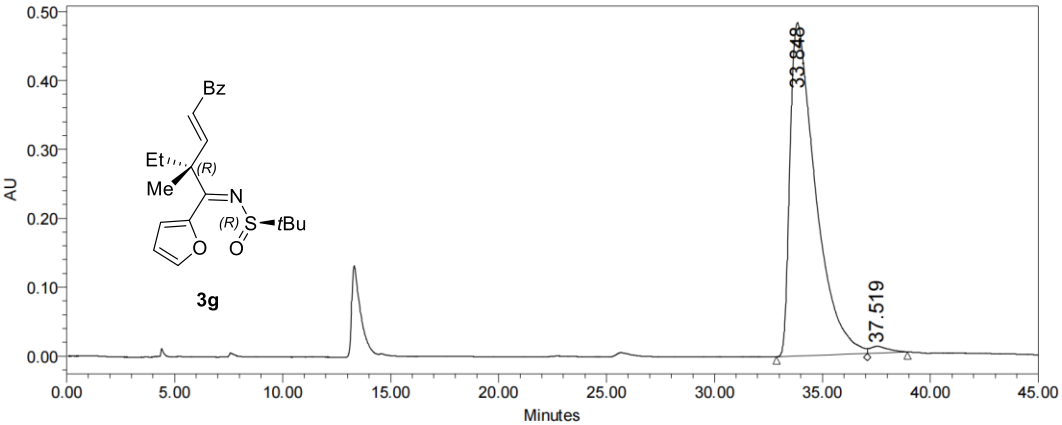


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1808; Processing Method: H230628AP XX 97 03 254 40 AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	33.964	27404928	32.84	448143
2	W2489 ChA 254nm	37.347	56043033	67.16	715746

HPLC chromatogramfor dr determination of crude **3g**

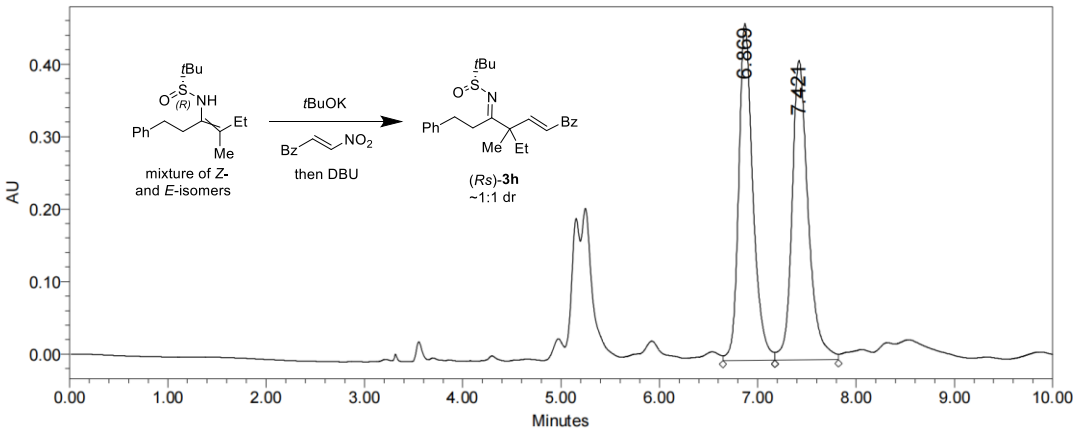


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1826; Processing Method: H230629A SX 97 03 254 40 AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	33.848	39705255	98.54	483948
2	W2489 ChA 254nm	37.519	590316	1.46	9938

(*Rs*)-**3h**: HPLC conditions: Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:03 (v/v), 1.0 mL/min, 254 nm, 40 °C.

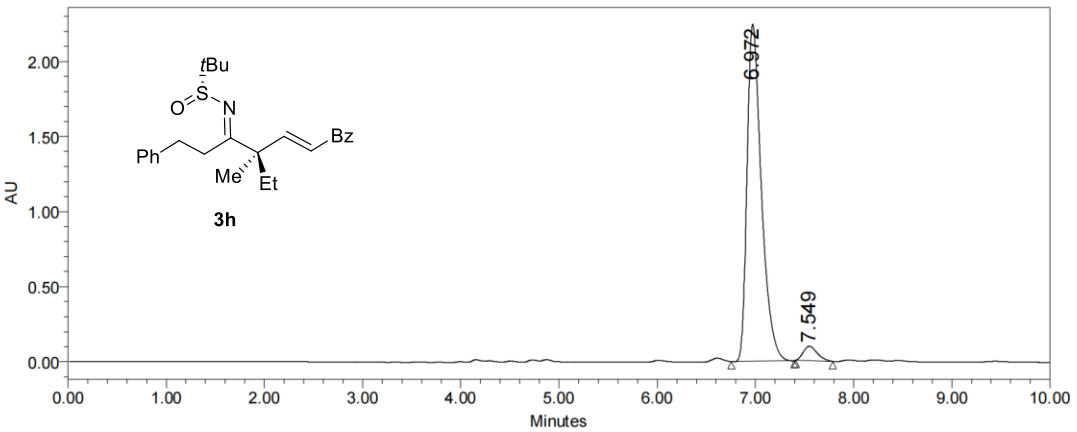


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1257; Processing Method: H230505AP XX 97 03 254 40 OD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.869	4665458	49.58	464550
2	W2489 ChA 254nm	7.421	4744107	50.42	413481

HPLC chromatogramfor dr determination of crude **3h**

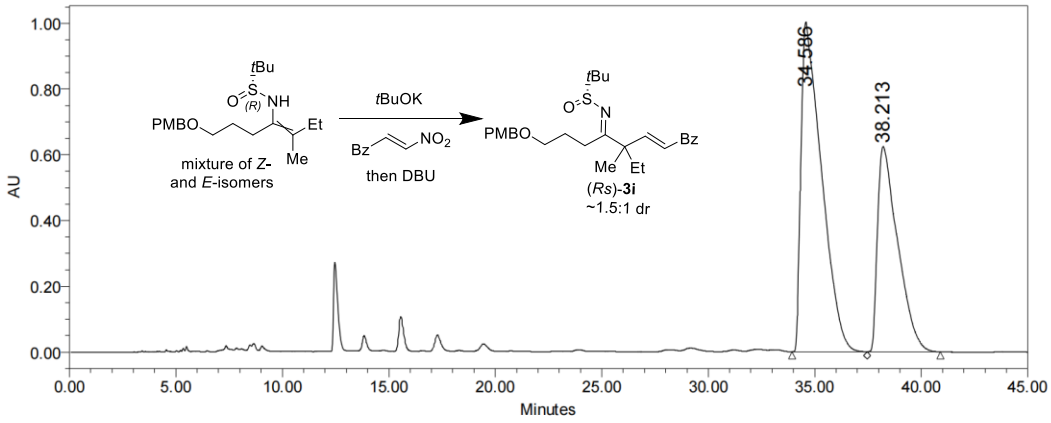


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1271; Processing Method: H230508A SX 97 03 254 40 OD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.972	22781264	95.99	2243967
2	W2489 ChA 254nm	7.549	951011	4.01	95930

(*Rs*)-**3i**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

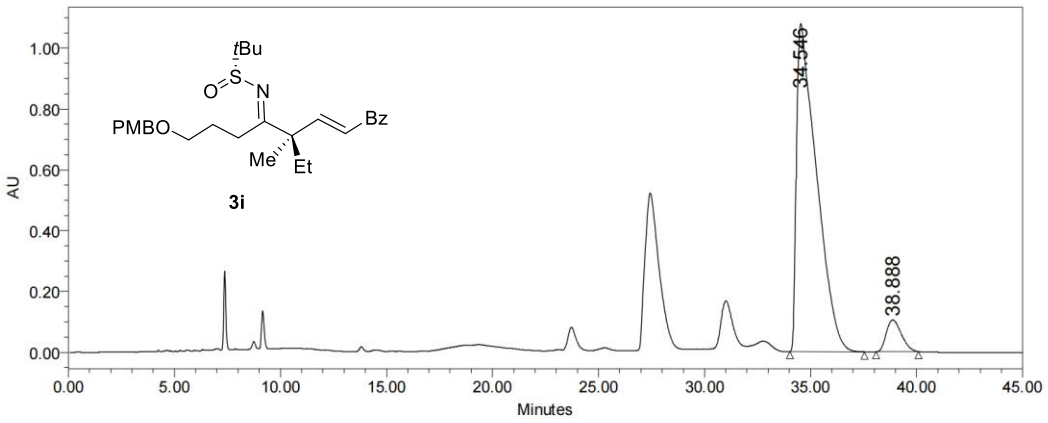


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1801; Processing Method: H230630CP 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	34.586	67372425	62.13	1002943
2	W2489 ChA 254nm	38.213	41072719	37.87	624617

HPLC chromatogramfor dr determination of crude **3i**

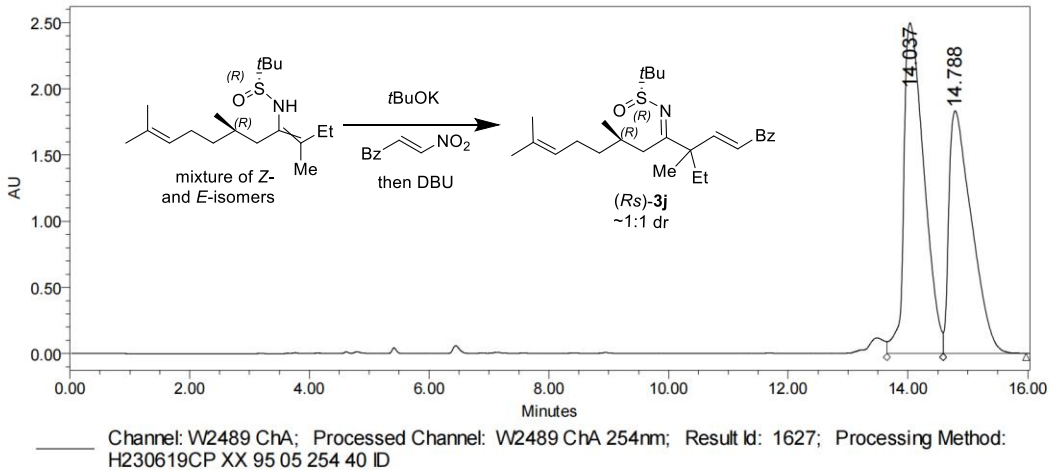


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1822; Processing Method: H230718D SX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	34.546	70732758	93.17	1078581
2	W2489 ChA 254nm	38.888	5185740	6.83	104414

(*Rs*)-**3j**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 95:05 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

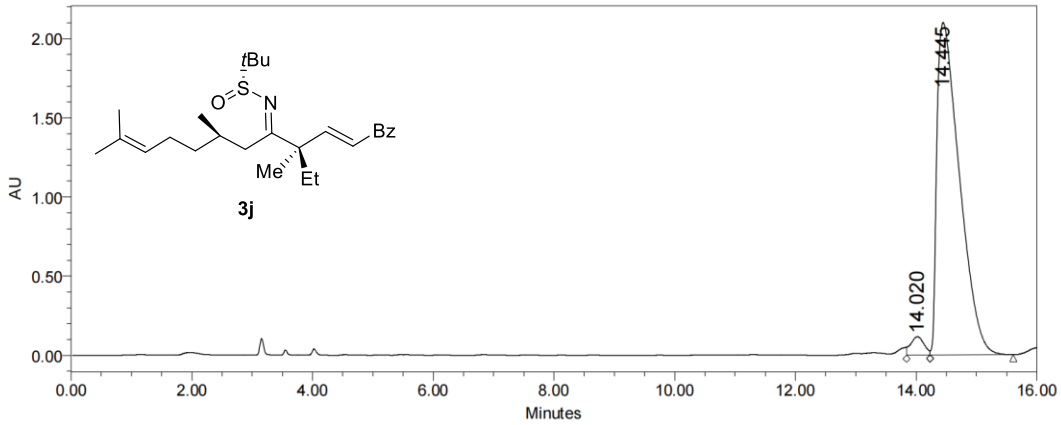


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1627; Processing Method: H230619CP XX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.037	58265034	54.70	2497014
2	W2489 ChA 254nm	14.788	48261397	45.30	1831398

HPLC chromatogramfor dr determination of crude **3j**

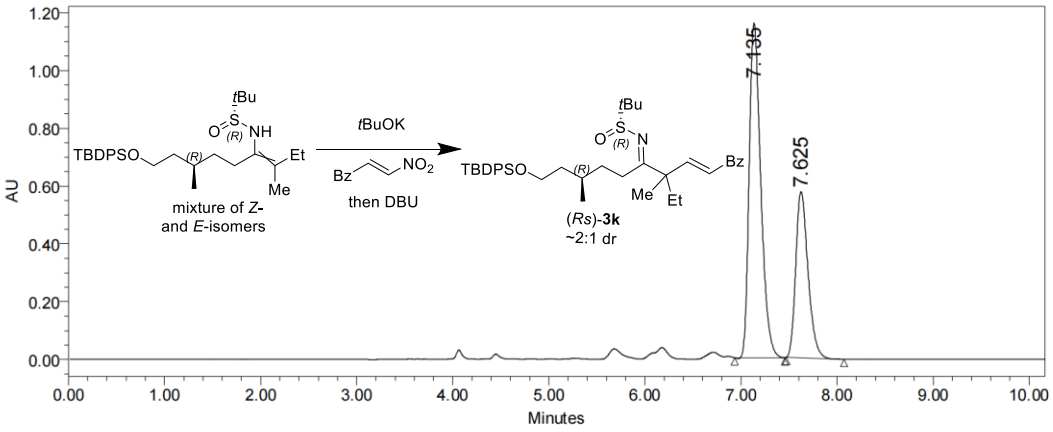


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1632; Processing Method: H230619A SX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.020	1776660	3.17	115850
2	W2489 ChA 254nm	14.445	54300303	96.83	2099257

(*Rs*)-**3k**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

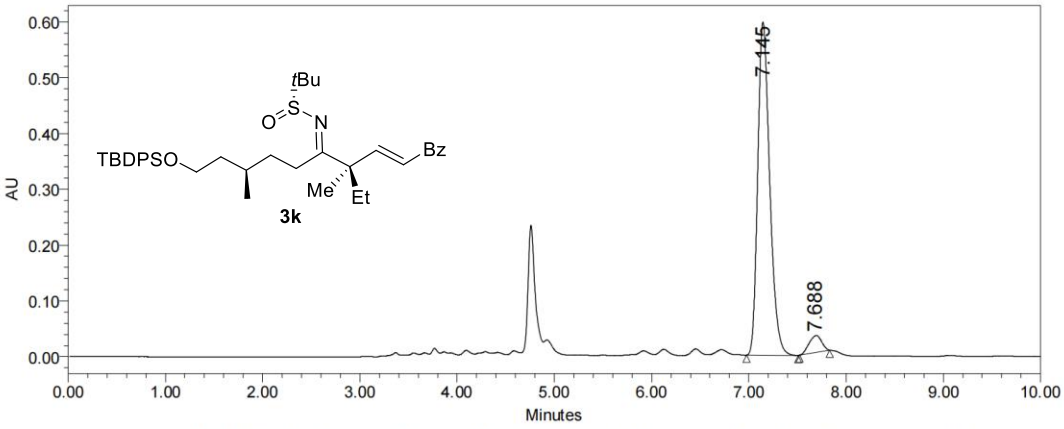


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1345; Processing Method: H230516CP XX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.135	9717386	65.57	1157529
2	W2489 ChA 254nm	7.625	5102397	34.43	575379

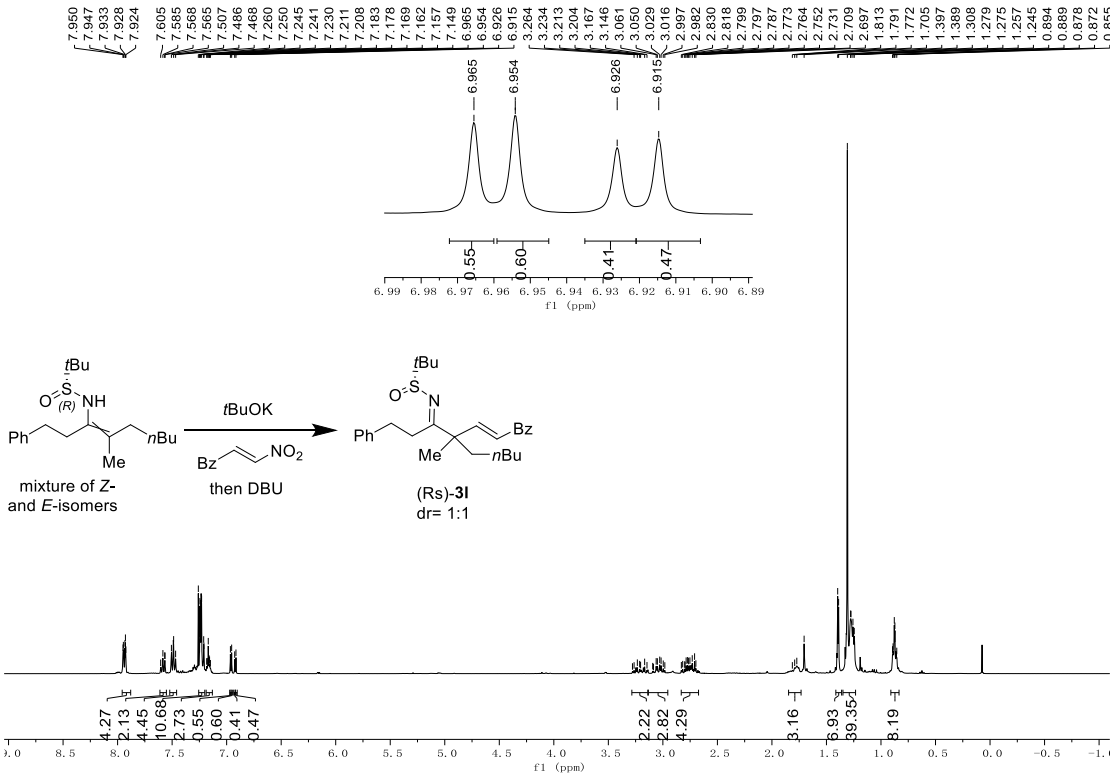
HPLC chromatogramfor dr determination of crude **3k**



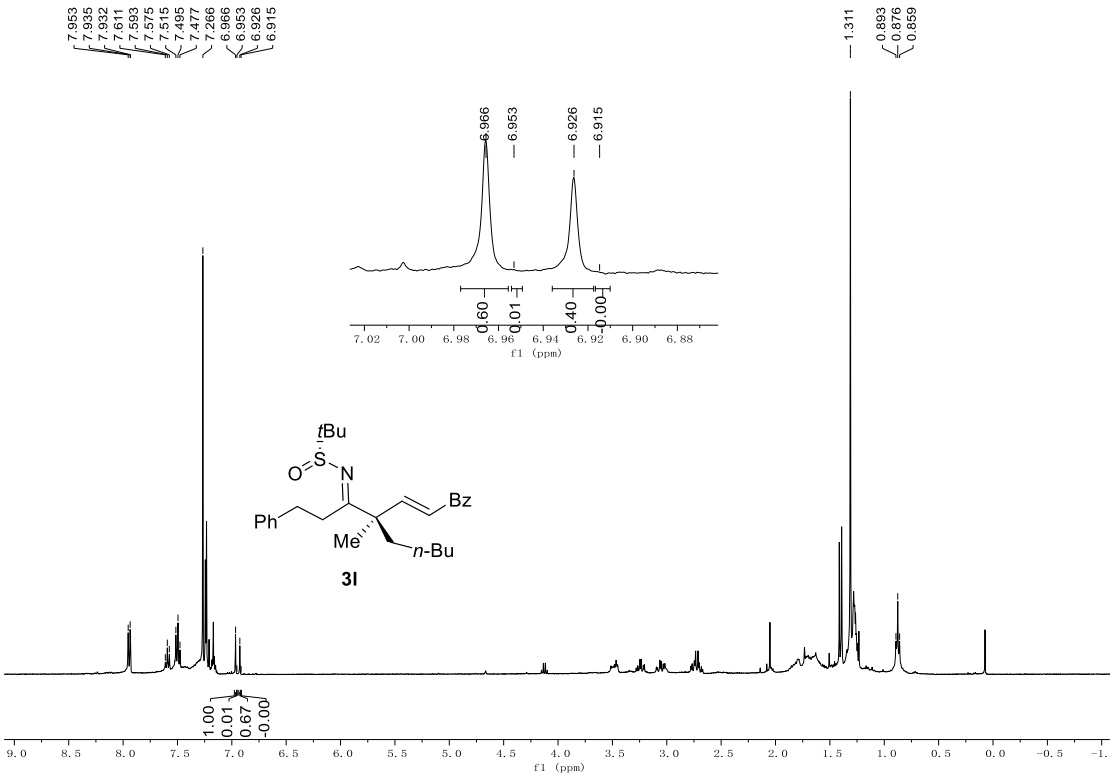
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1480; Processing Method: H2305115B SX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

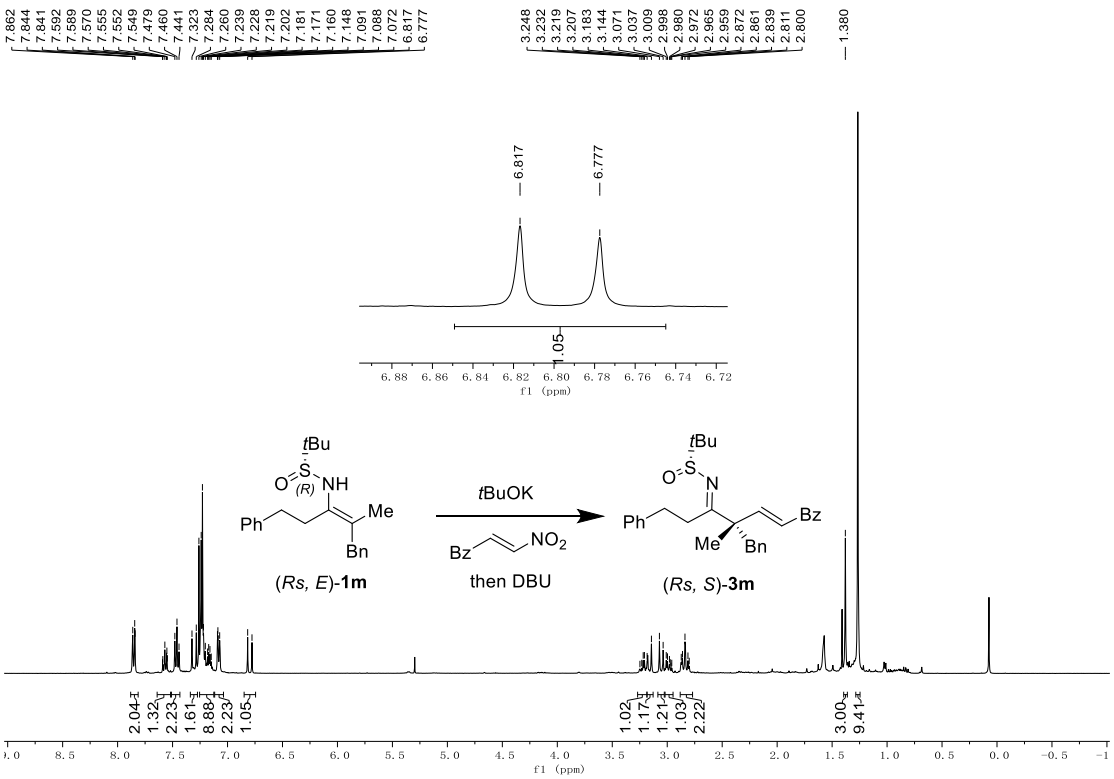
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.145	5092515	94.94	596983
2	W2489 ChA 254nm	7.688	271569	5.06	30151



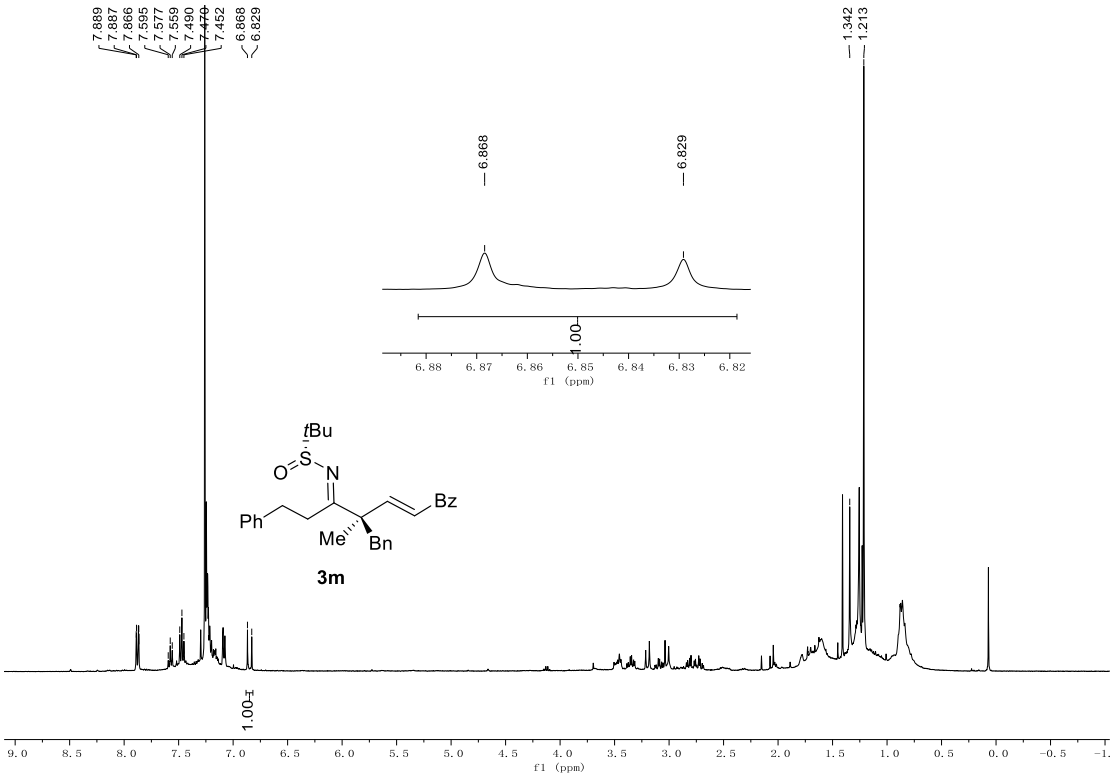
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3l** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3l** (dr > 20:1)



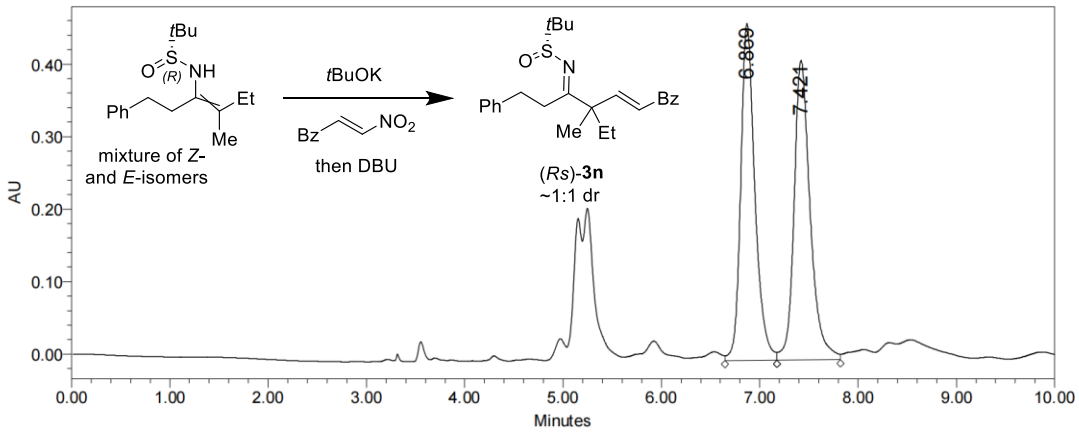
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs, S*)-**3m** that was intentionally prepared by using geometric isomer (*Rs, E*)-**1m** and was used to identify the diagnostic peak(s) of the minor diastereomer



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3m** (dr > 20:1)

(No observable presence of the minor diastereomer)

(*Rs*)-**3n**: HPLC conditions: Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:03 (v/v), 1.0 mL/min, 254 nm, 40 °C.

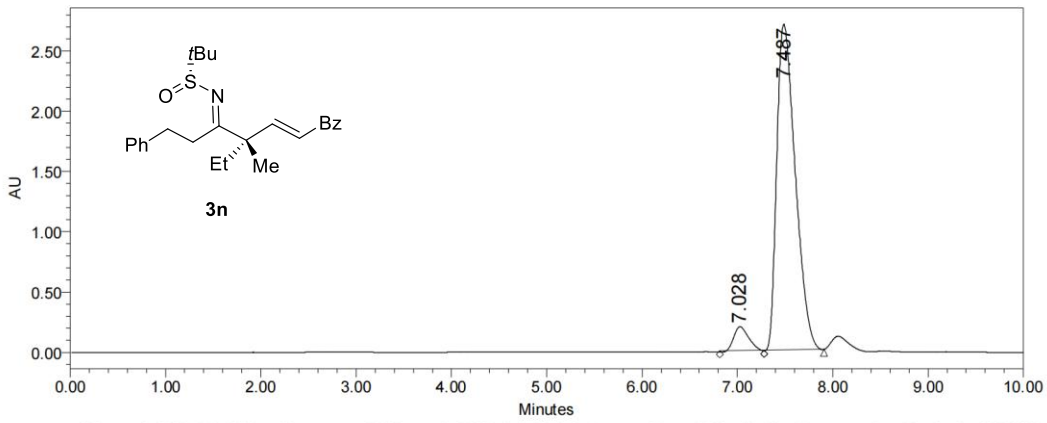


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1257; Processing Method: H230505AP XX 97 03 254 40 OD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.869	4665458	49.58	464550
2	W2489 ChA 254nm	7.421	4744107	50.42	413481

HPLC chromatogramfor dr determination of crude **3n**

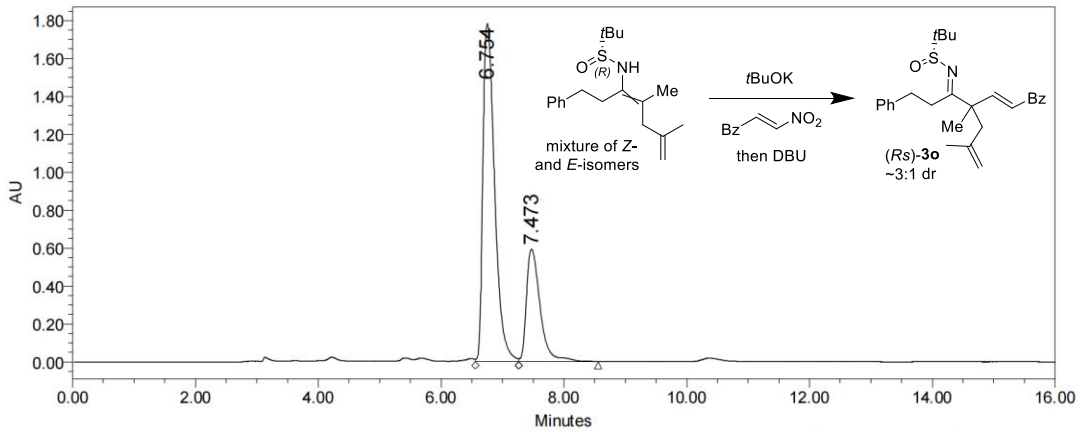


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1913; Processing Method: 3N SX 97 03 254 40 OD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.028	2120601	5.50	197684
2	W2489 ChA 254nm	7.487	36444628	94.50	2701408

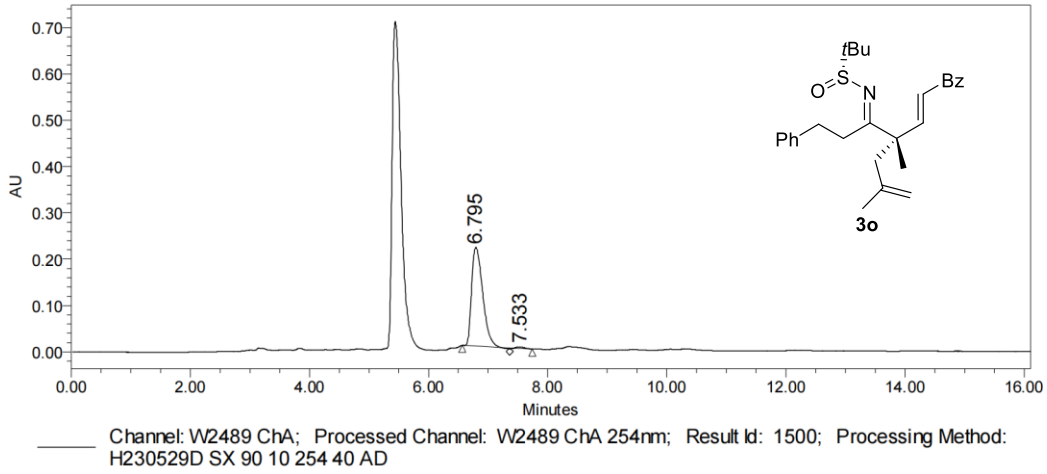
(*Rs*)-**3o**: HPLC conditions: Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.



Processed Channel Descr.: W2489 ChA 254nm

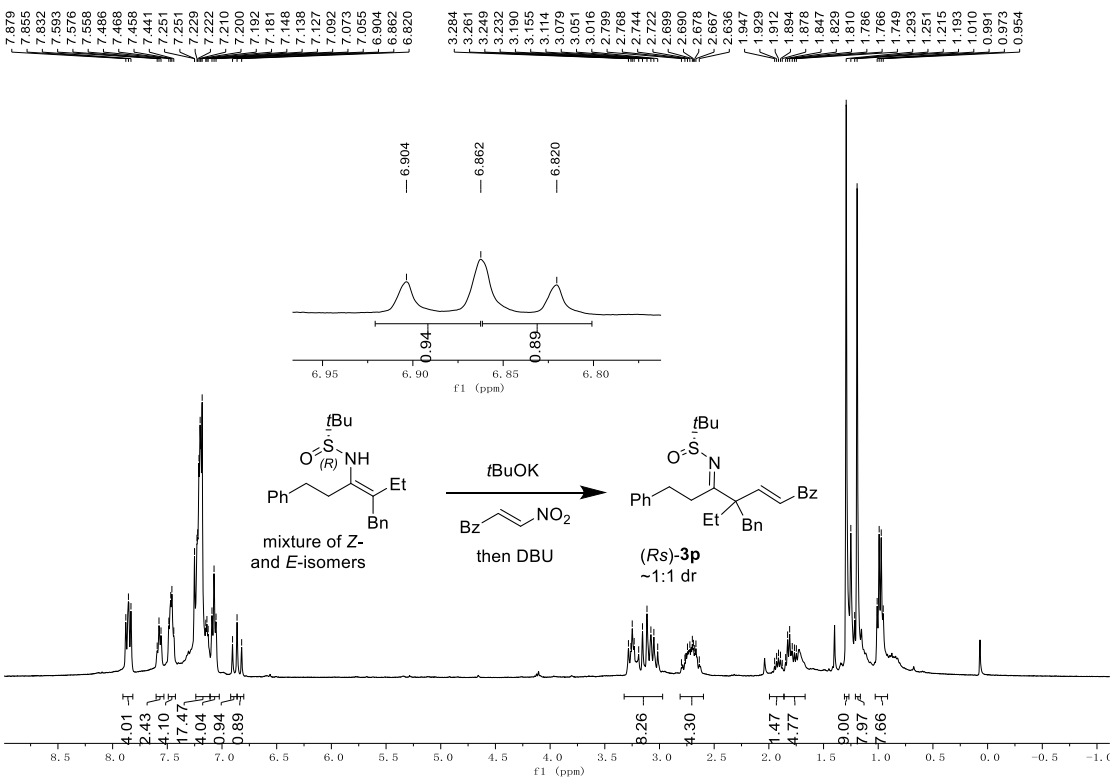
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.754	23634556	72.01	1781222
2	W2489 ChA 254nm	7.473	9184699	27.99	592447

HPLC chromatogramfor dr determination of crude **3o**

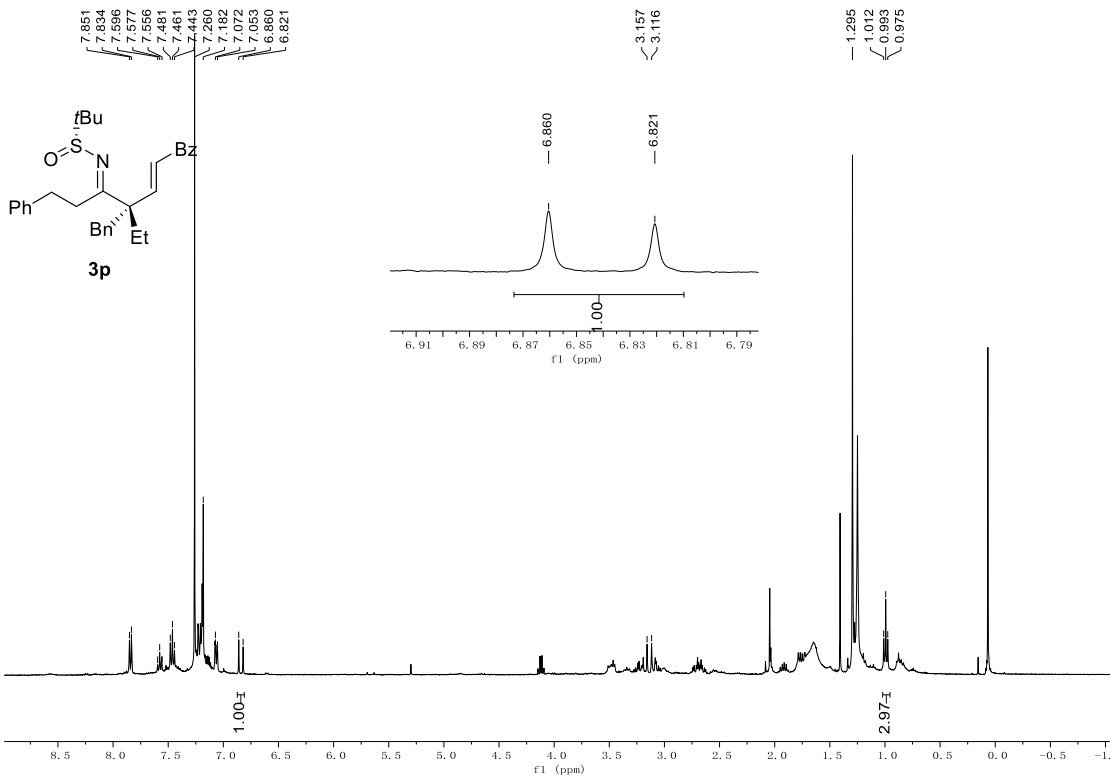


Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.795	2764927	98.74	212762
2	W2489 ChA 254nm	7.533	35204	1.26	3009



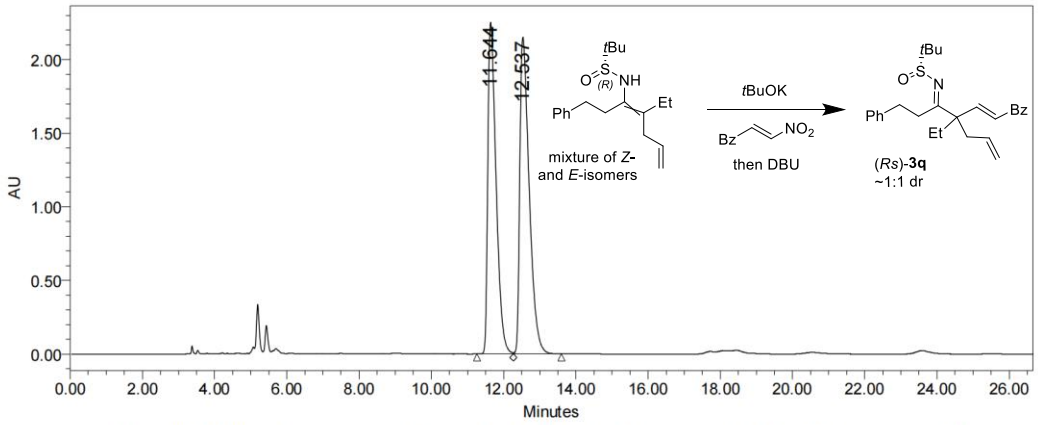
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3p** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3p** (dr > 20:1)

(No observable presence of the minor diastereomer)

(*Rs*)-**3q**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

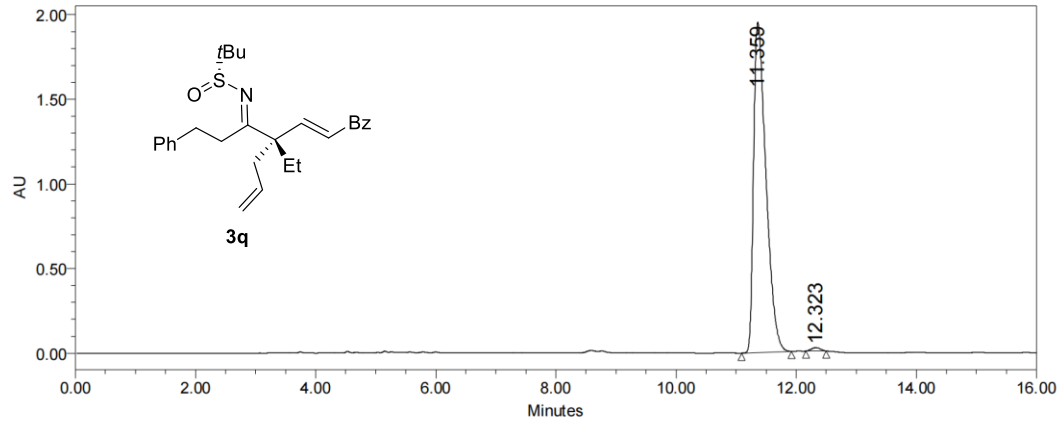


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1474; Processing Method: H23602CP XX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.644	35558727	47.88	2251228
2	W2489 ChA 254nm	12.537	38711202	52.12	2149453

HPLC chromatogramfor dr determination of crude **3q**

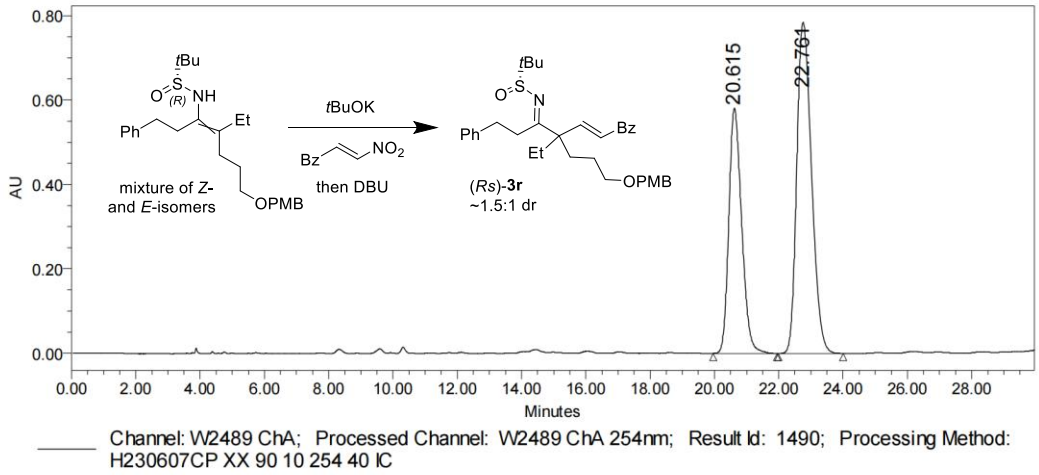


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1525; Processing Method: H230612D SX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.359	27865196	99.25	1951325
2	W2489 ChA 254nm	12.323	209629	0.75	19716

(*Rs*)-**3r**: HPLC conditions: Daicel Chiralcel IC-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

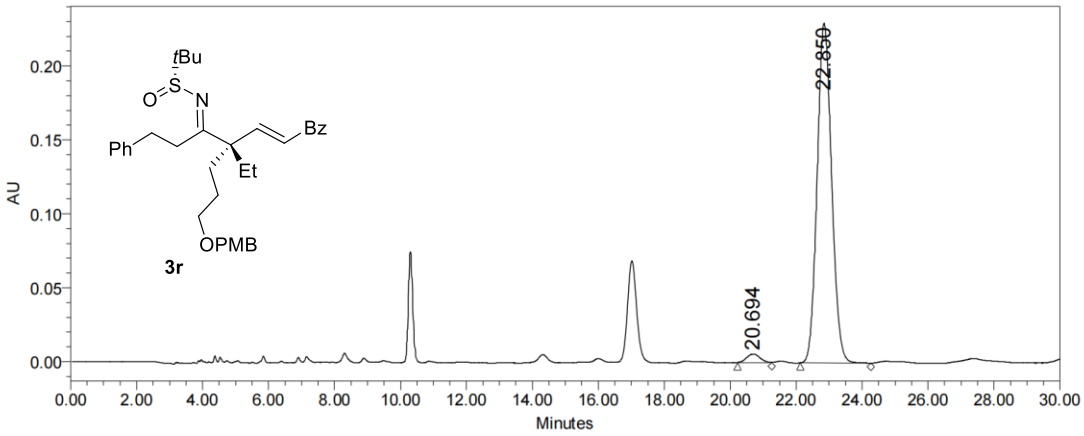


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1490; Processing Method: H230607CP XX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.615	16122603	39.12	581275
2	W2489 ChA 254nm	22.761	25091919	60.88	784680

HPLC chromatogramfor dr determination of crude **3r**

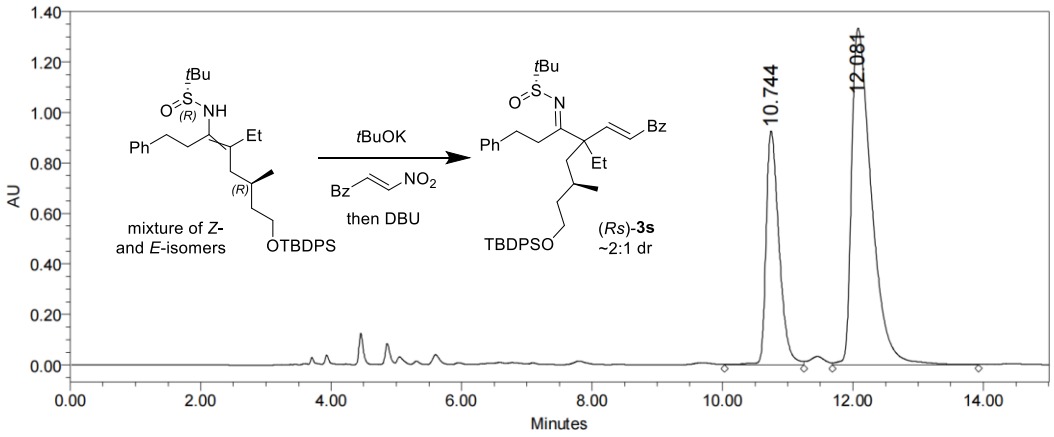


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1492; Processing Method: H230601A SX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.694	162096	2.27	5814
2	W2489 ChA 254nm	22.850	6990685	97.73	229591

(*Rs*)-**3s**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 95:05 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

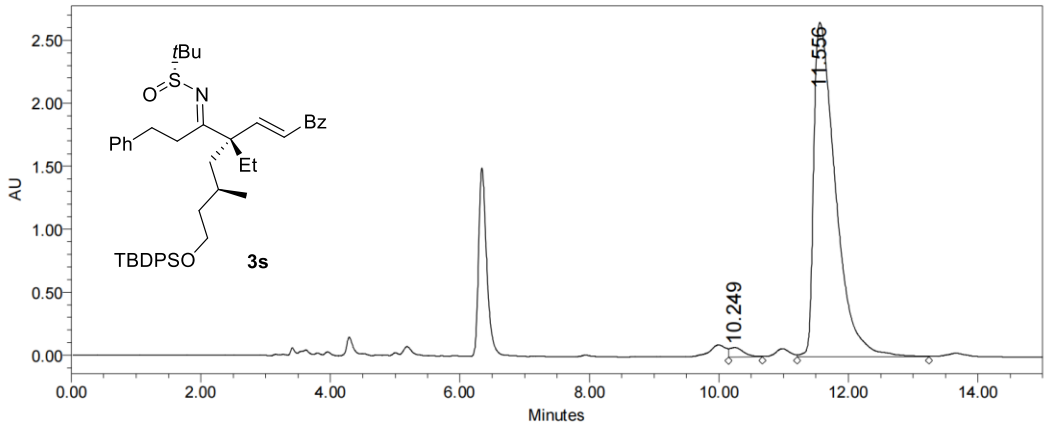


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1540; Processing Method: H230613CP XX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.744	12816803	31.28	926091
2	W2489 ChA 254nm	12.081	28156608	68.72	1332575

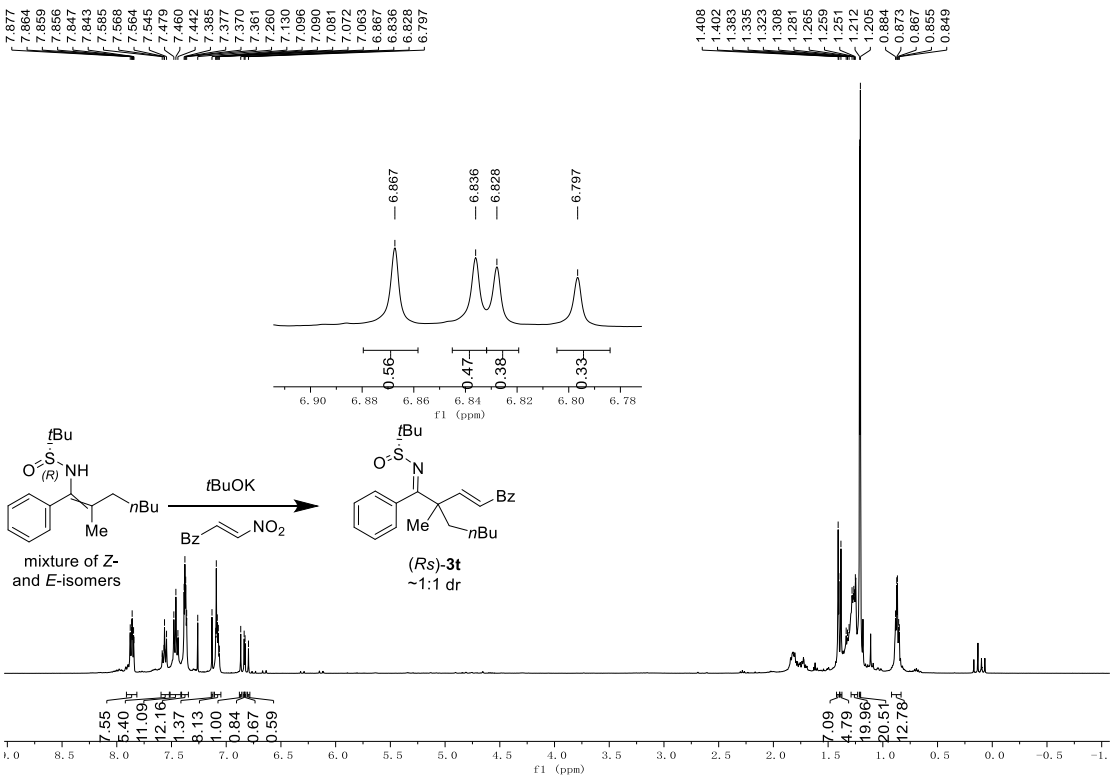
HPLC chromatogramfor dr determination of crude **3s**



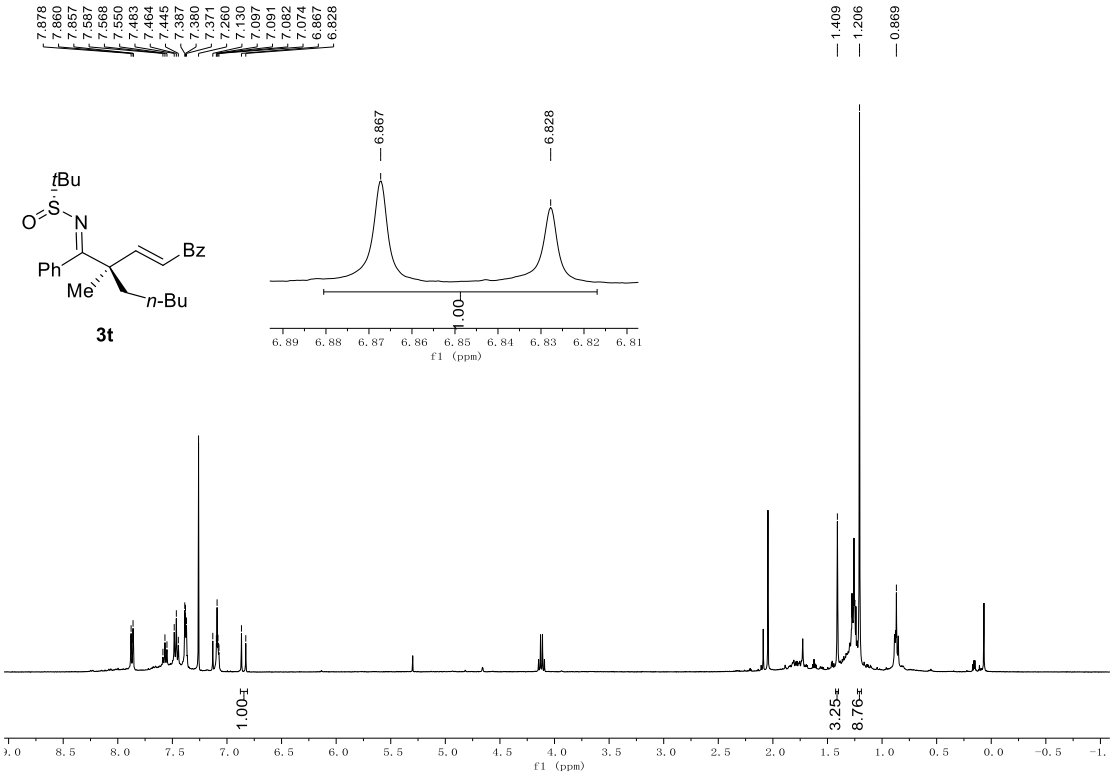
Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 1556; Processing Method: H230429A 95 05 220 40 ID

Processed Channel Descr.: W2489 ChA 220nm

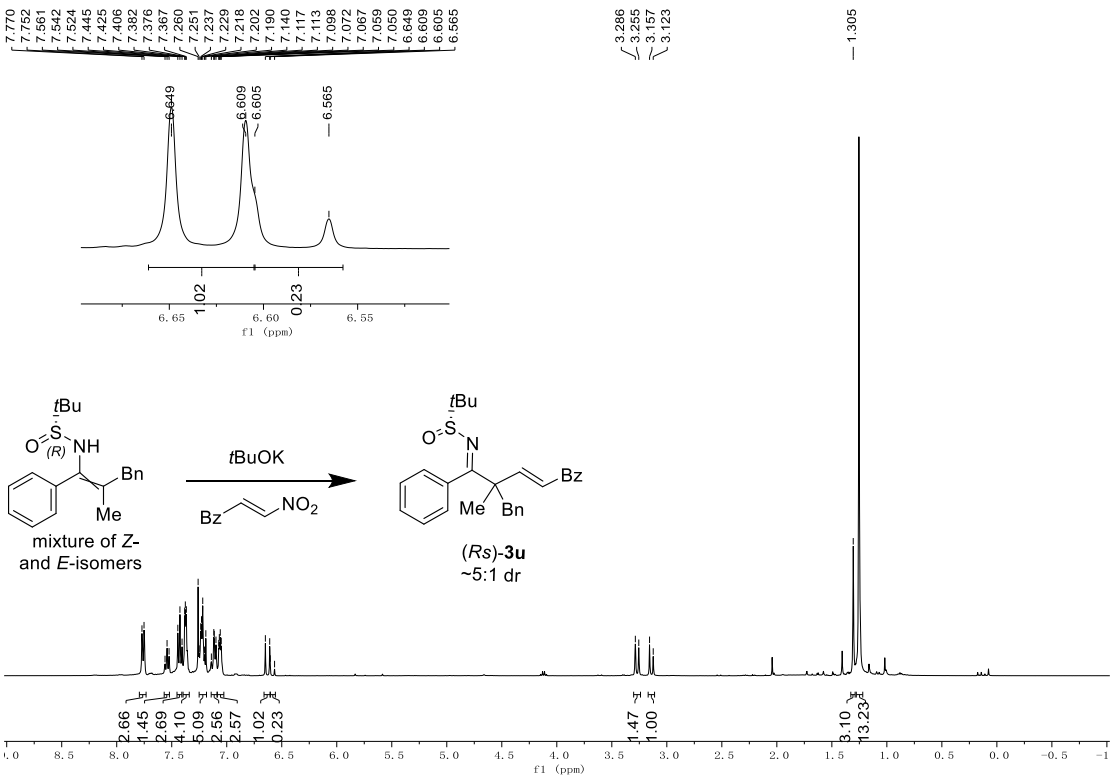
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 220nm	10.249	1133145	1.79	74088
2	W2489 ChA 220nm	11.556	62236139	98.21	2654860



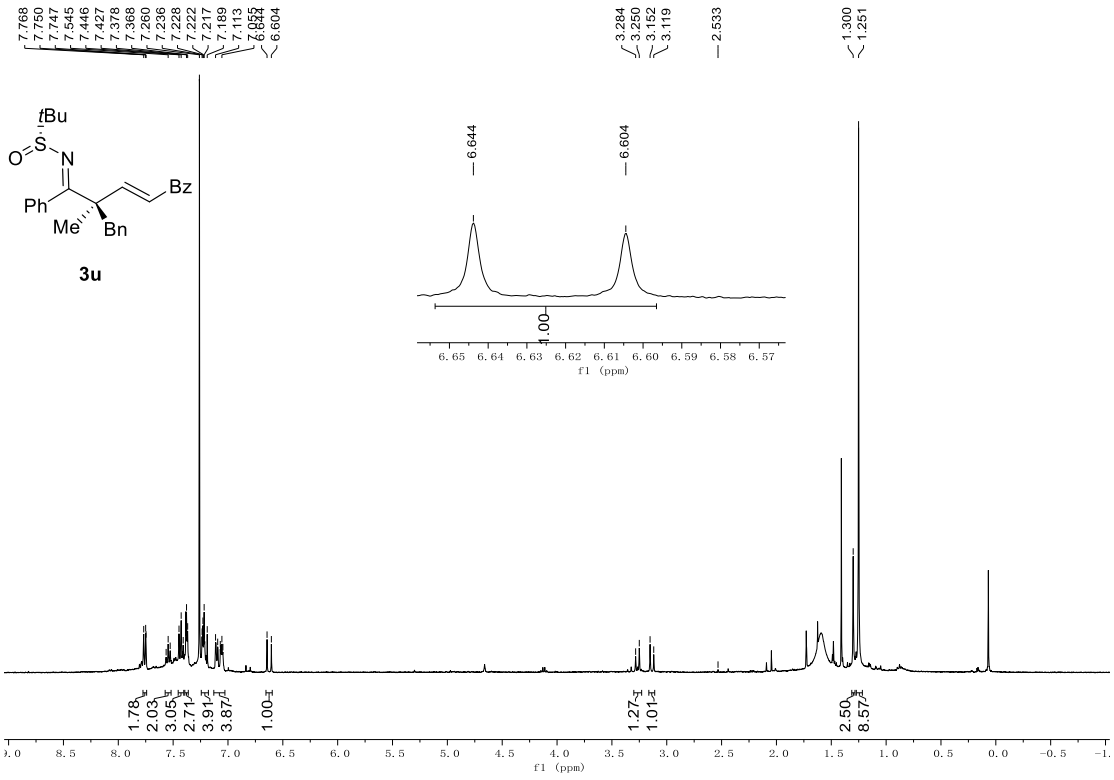
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3t** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3t** (dr = 20:1)

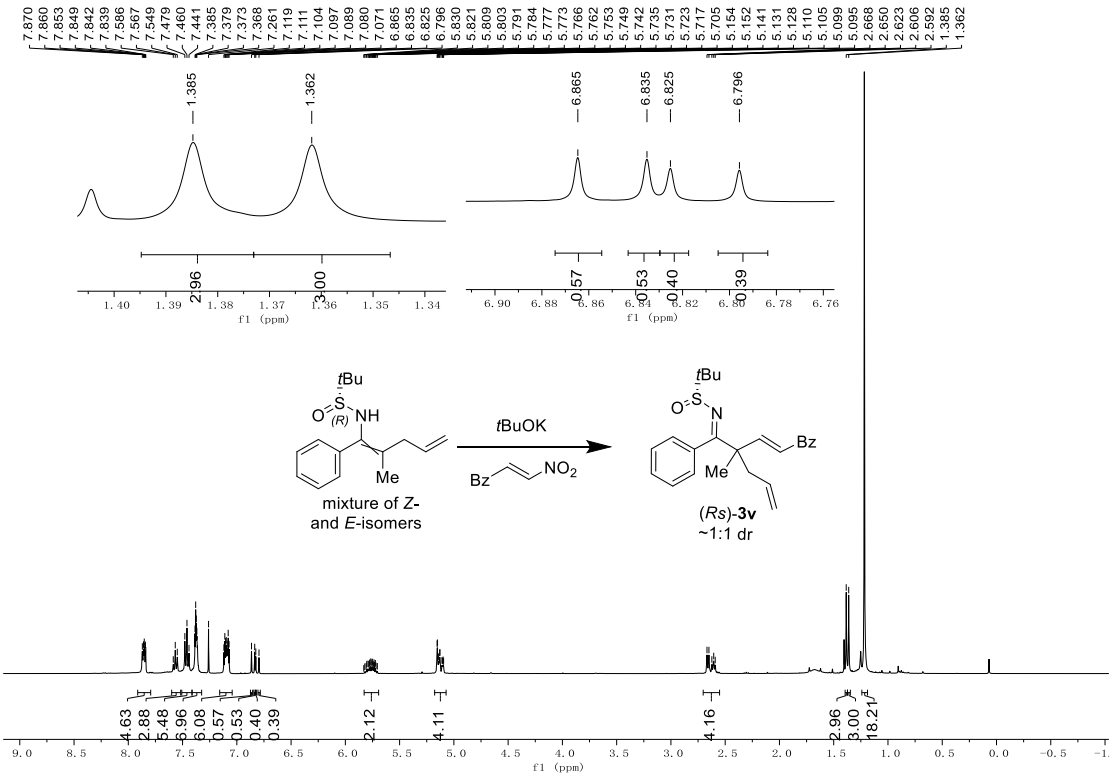


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3u** with low diastereoselectivity (dr ~ 5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

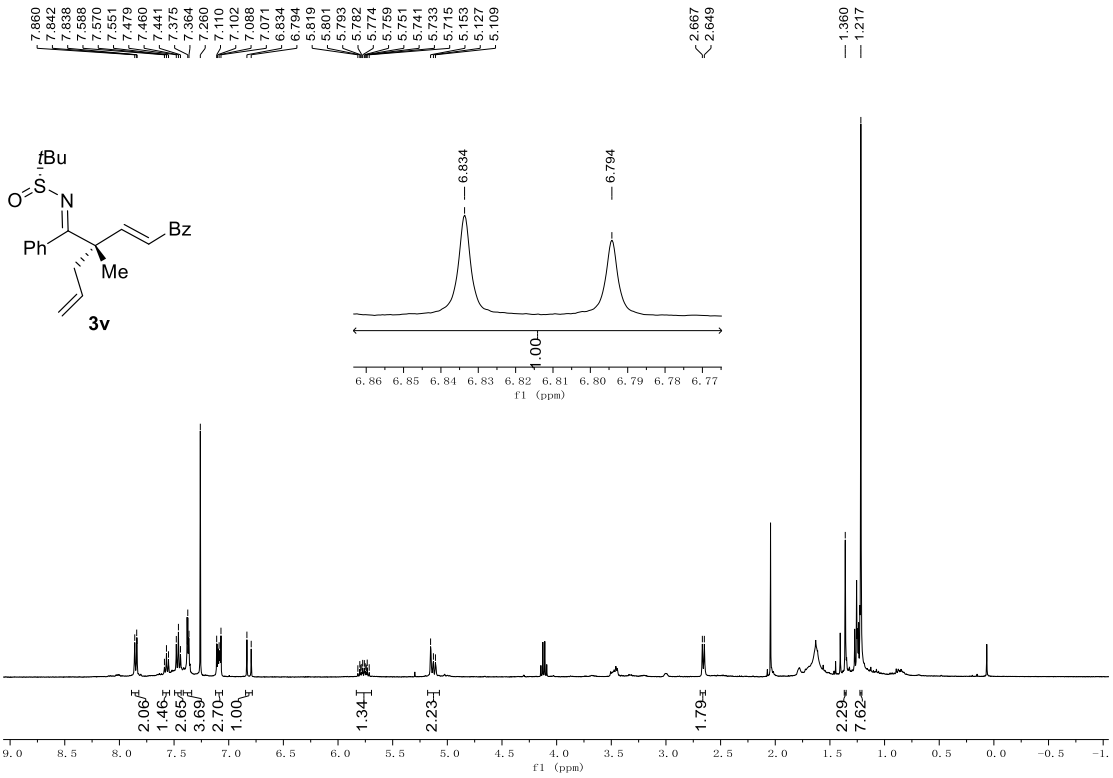


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3u** (dr > 20:1)

(No observable presence of the minor diastereomer)

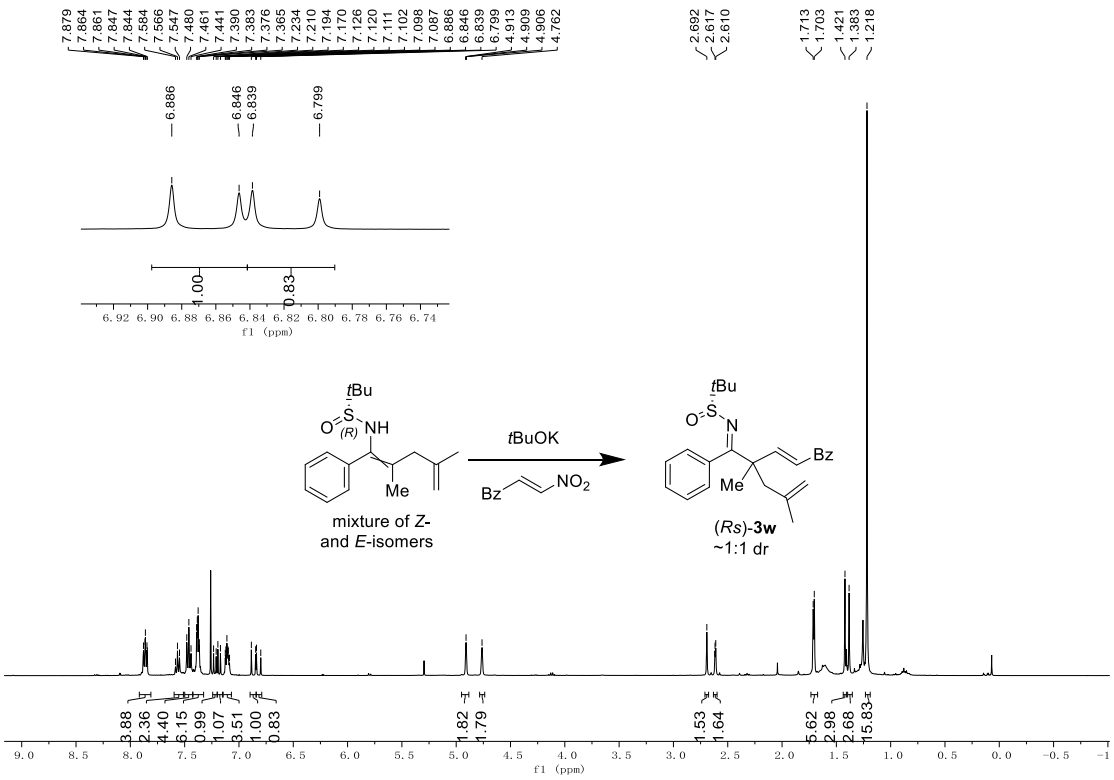


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3v** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

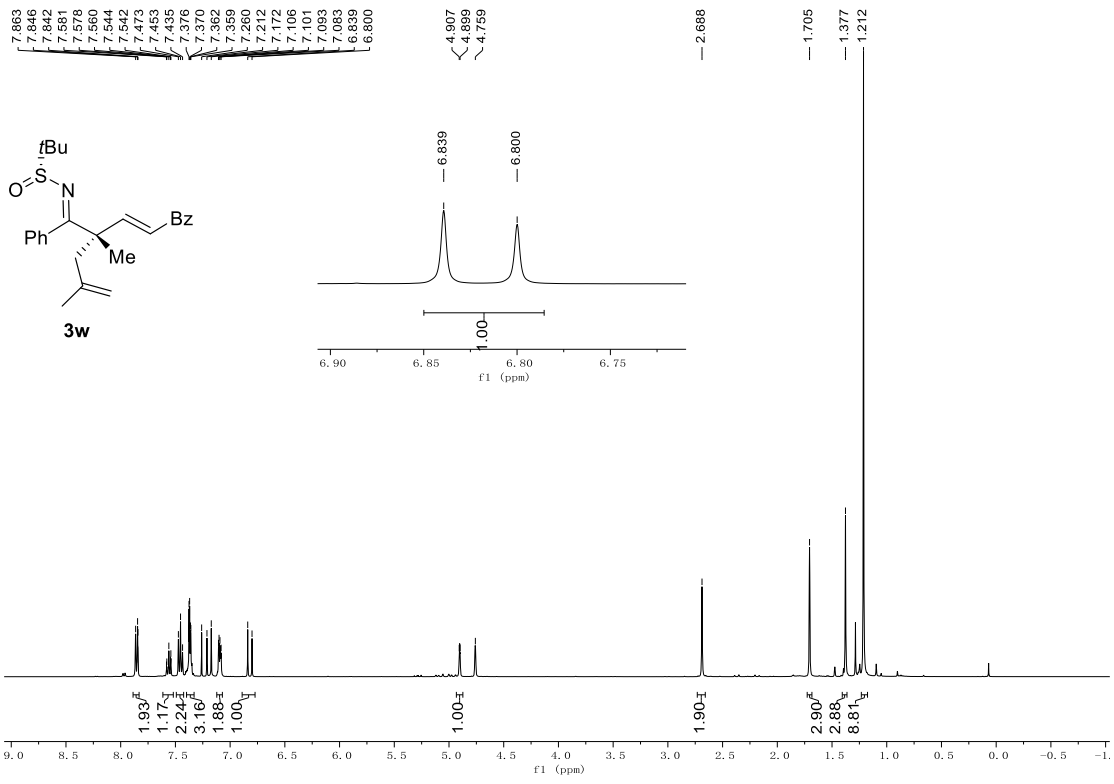


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3v** (dr > 20:1)

(No observable presence of the minor diastereomer)



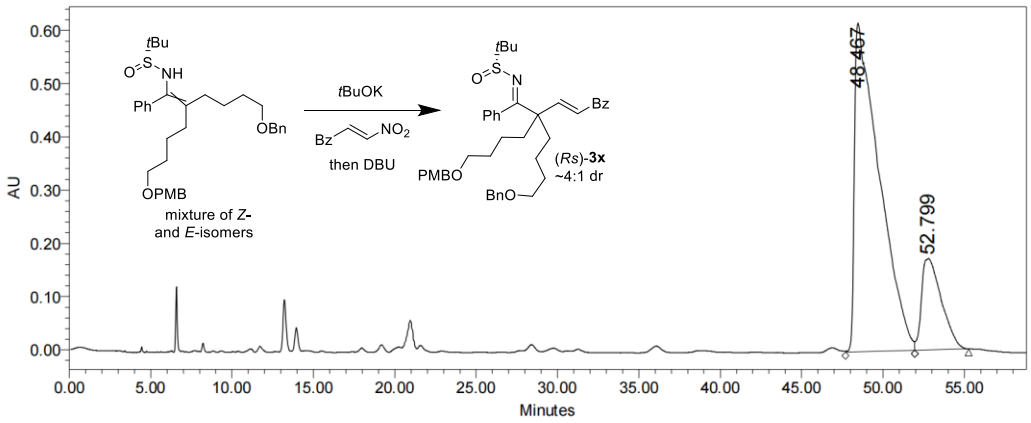
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3w** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3w** (dr > 20:1)

(No observable presence of the minor diastereomer)

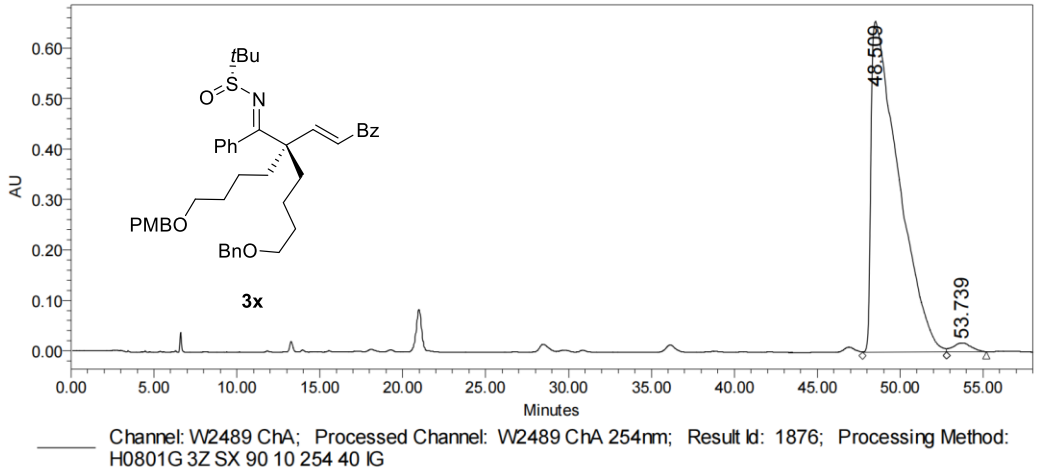
(*Rs*)-**3x**: HPLC conditions: Daicel Chiralcel IF-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 °C.



Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	48.467	65035468	81.72	617112
2	W2489 ChA 254nm	52.799	14547216	18.28	171377

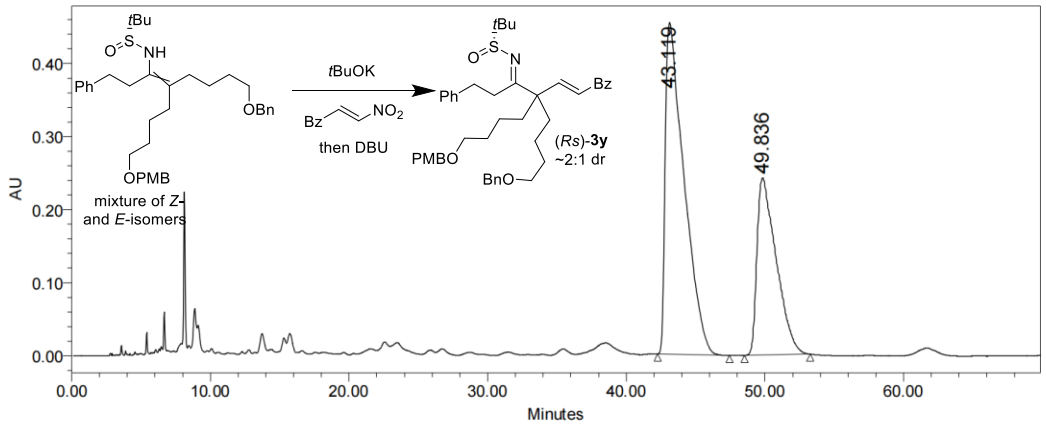
HPLC chromatogramfor dr determination of crude **3x**



Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	48.509	75171454	98.26	655263
2	W2489 ChA 254nm	53.739	1332882	1.74	17637

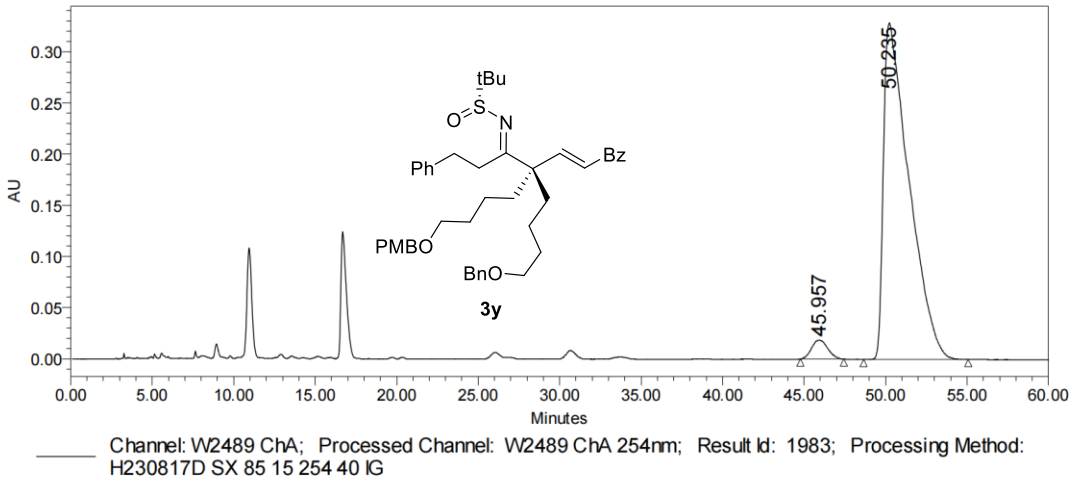
(*Rs*)-**3y**: HPLC conditions: Daicel Chiralcel IG-3 column, *n*-hexane/2-propanol = 85:15 (v/v), 1.0 mL/min, 254 nm, 40 °C



Processed Channel Descr.: W2489 ChA 254nm

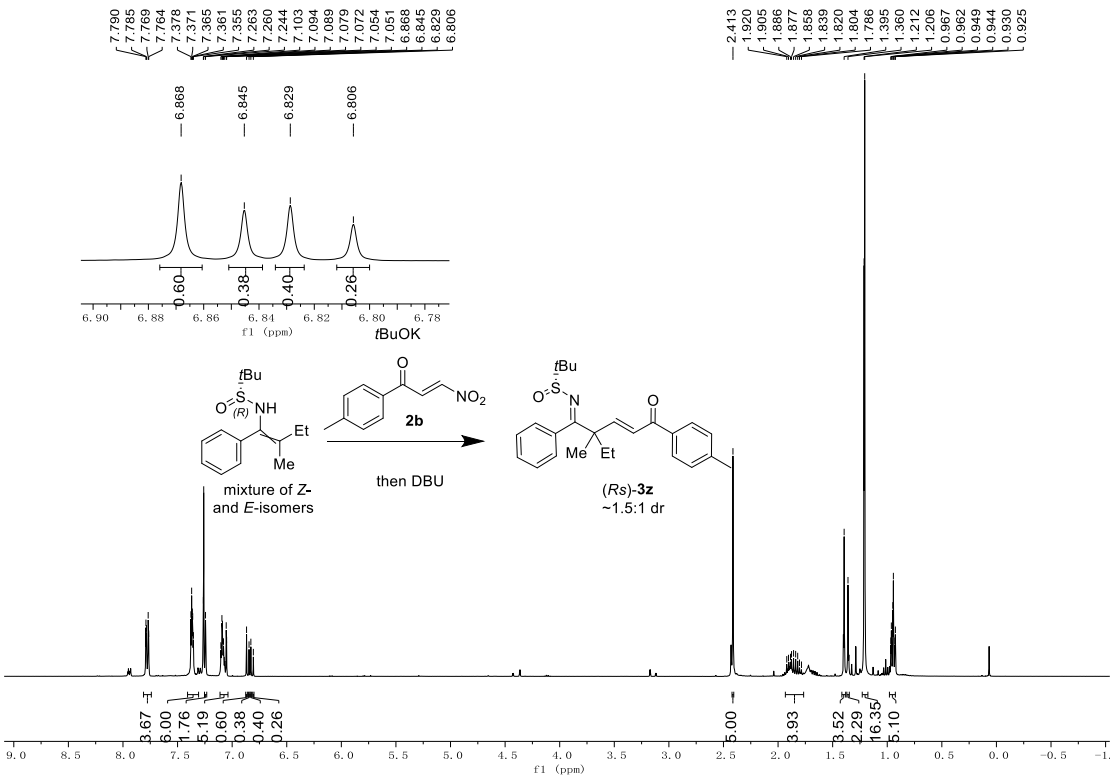
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	43.119	42708450	64.57	453901
2	W2489 ChA 254nm	49.836	23431287	35.43	242546

HPLC chromatogramfor dr determination of crude **3y**

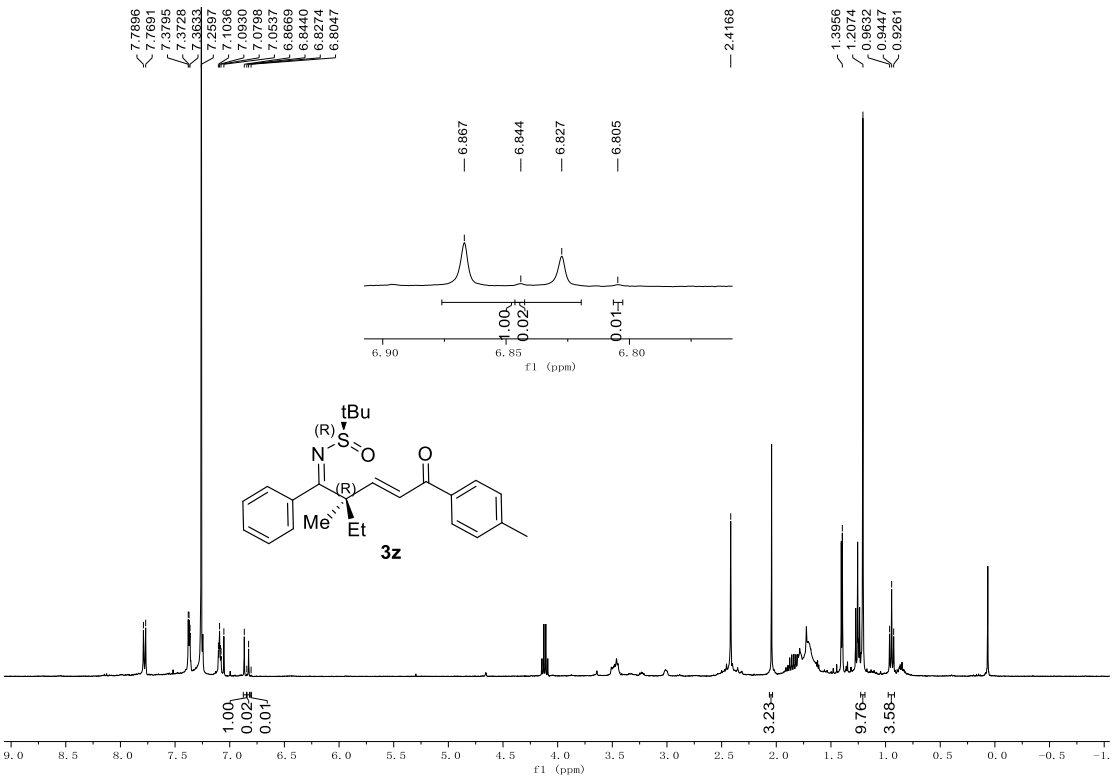


Processed Channel Descr.: W2489 ChA 254nm

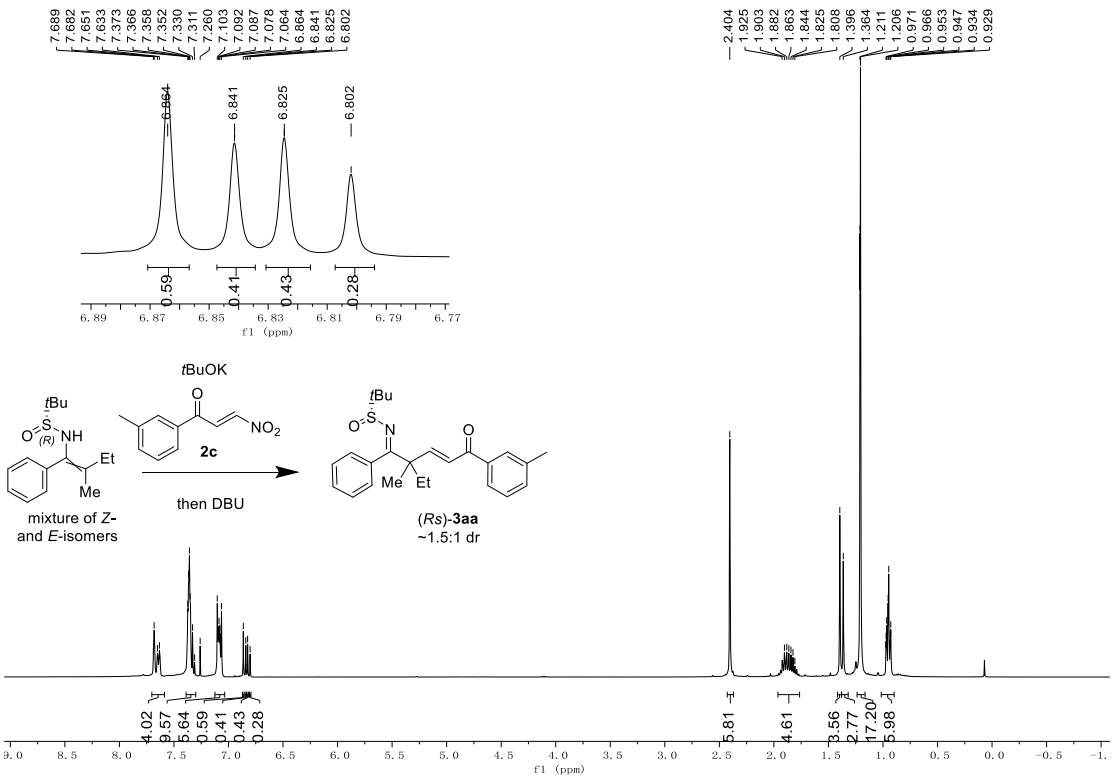
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	45.957	1269176	3.42	18305
2	W2489 ChA 254nm	50.235	35797760	96.58	328886



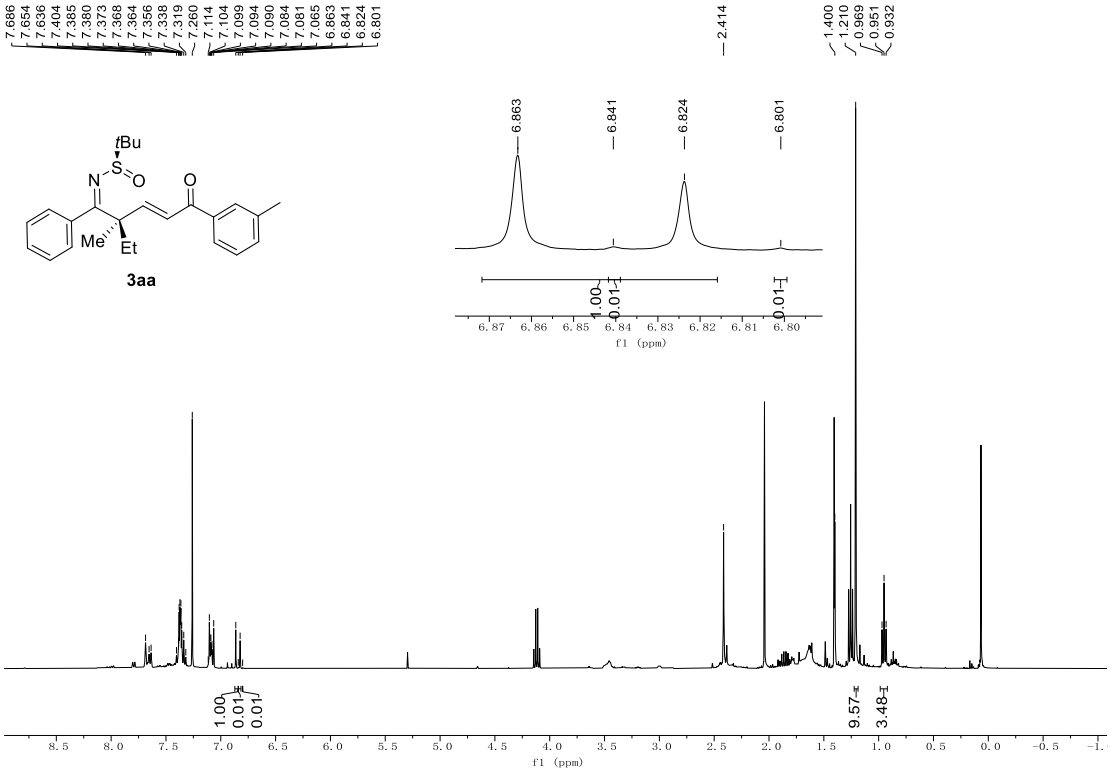
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3z** with low diastereoselectivity (dr ~ 1.5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio



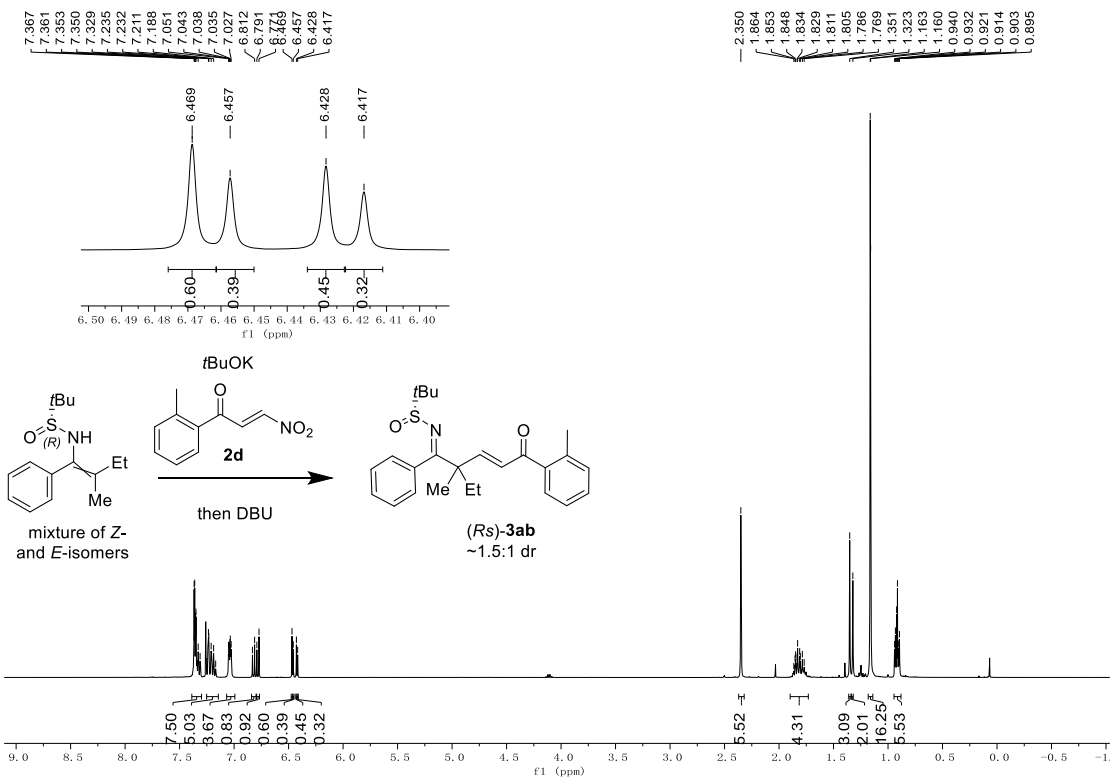
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3z** (dr ~ 33:1)



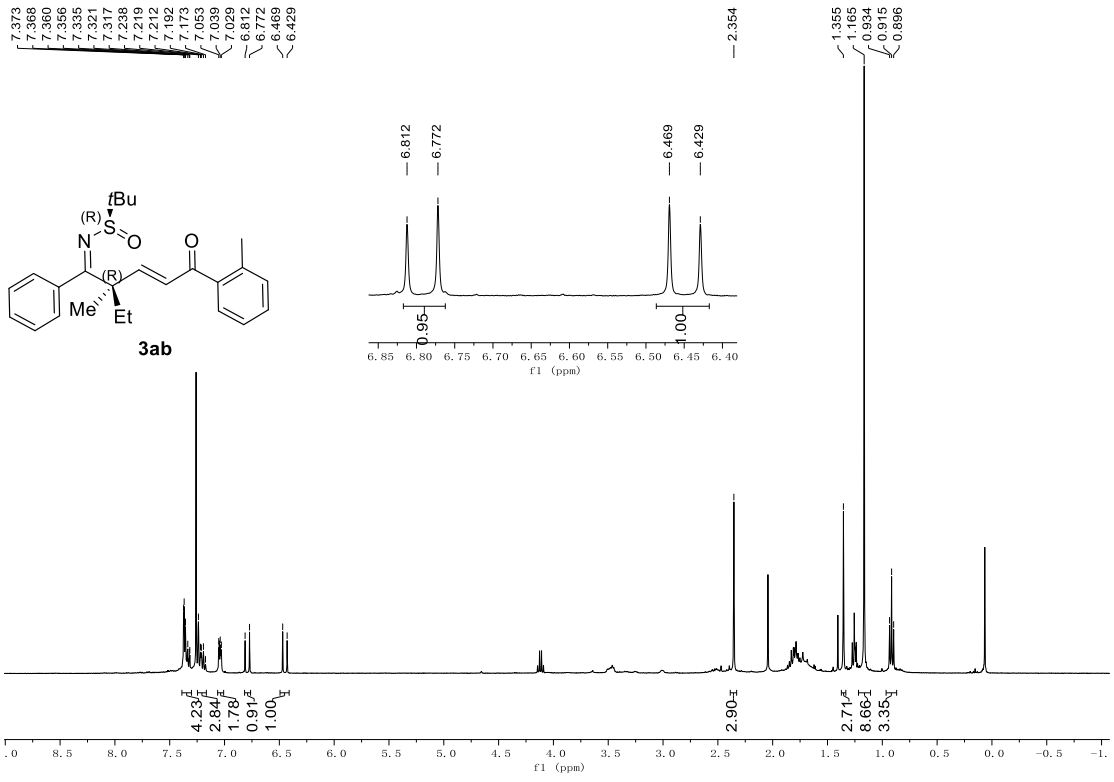
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3aa** with low diastereoselectivity (dr ~ 1.5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3aa** (dr = 50:1)

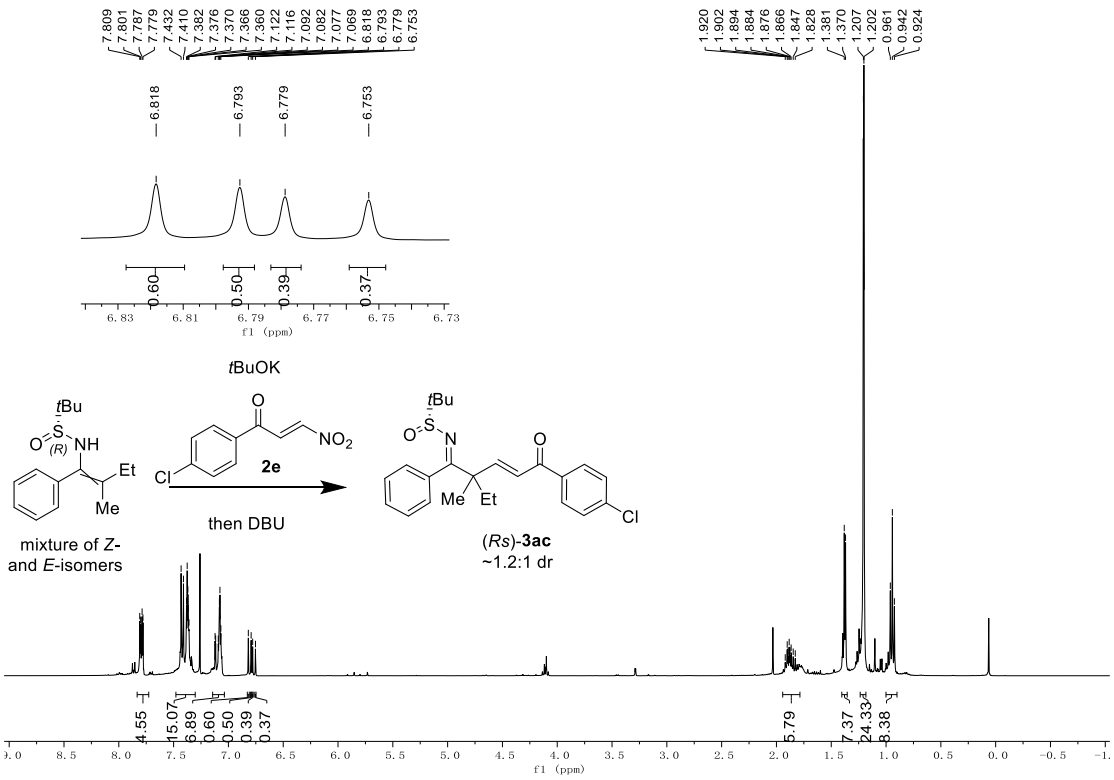


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3ab** with low diastereoselectivity (dr ~ 1.5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

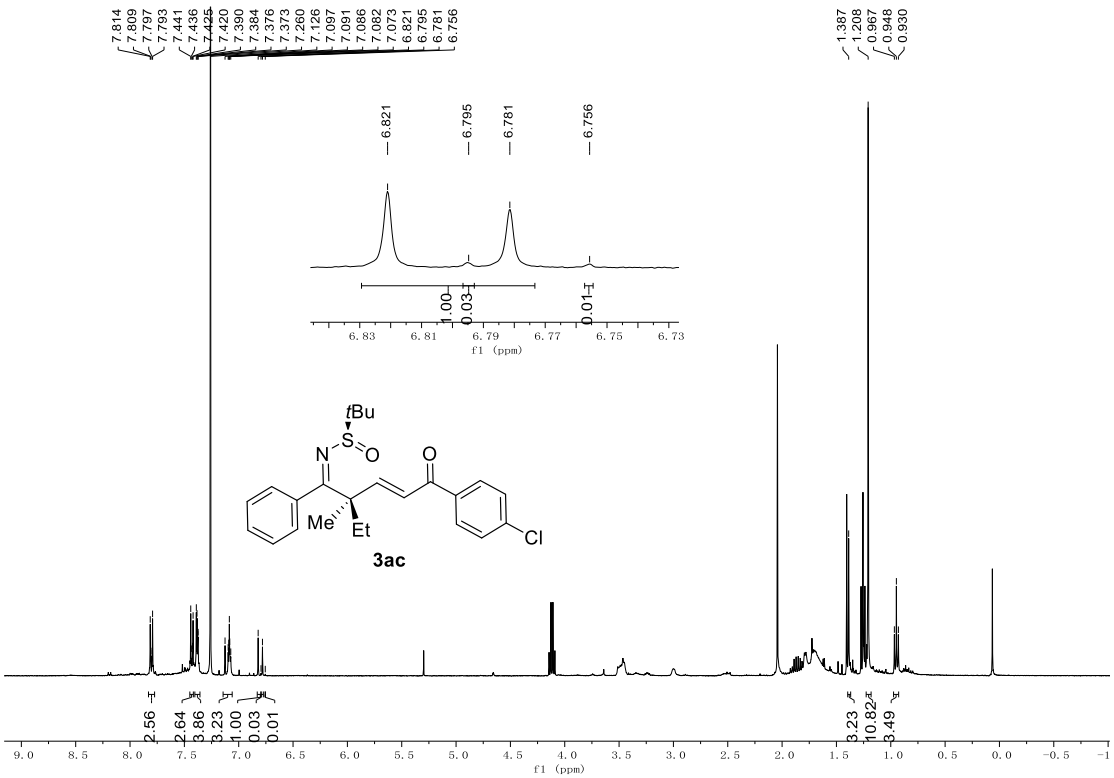


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ab** (dr > 20:1)

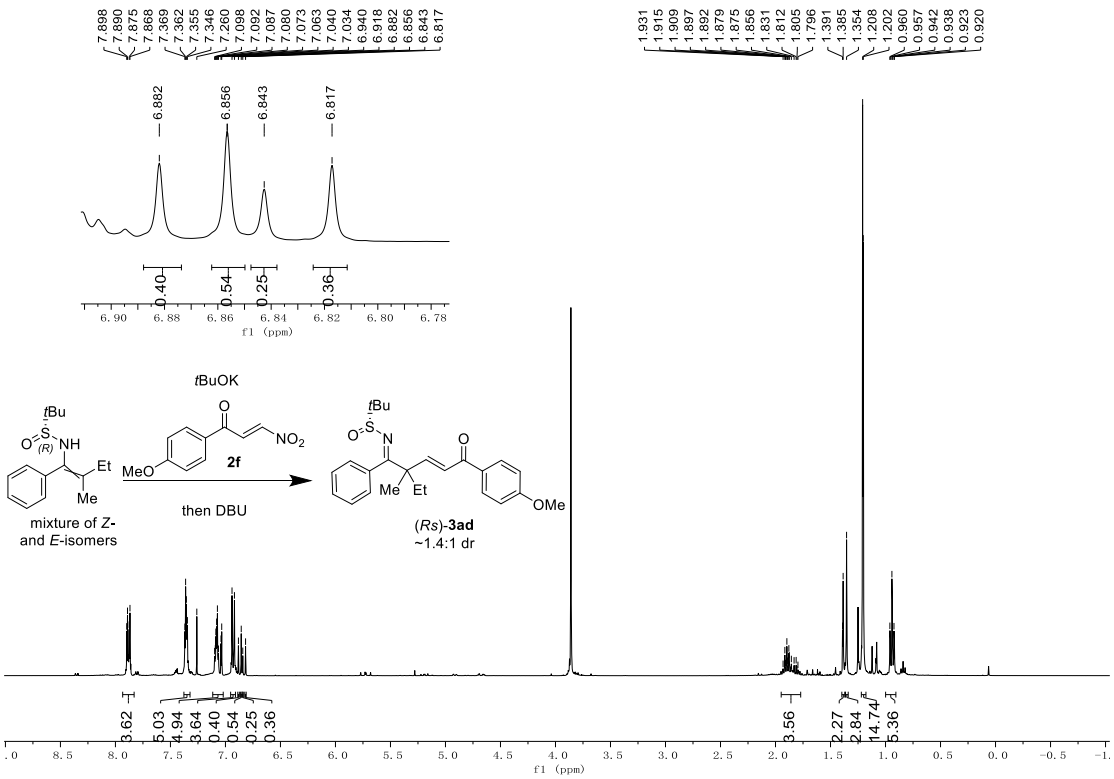
(No observable presence of the minor diastereomer)



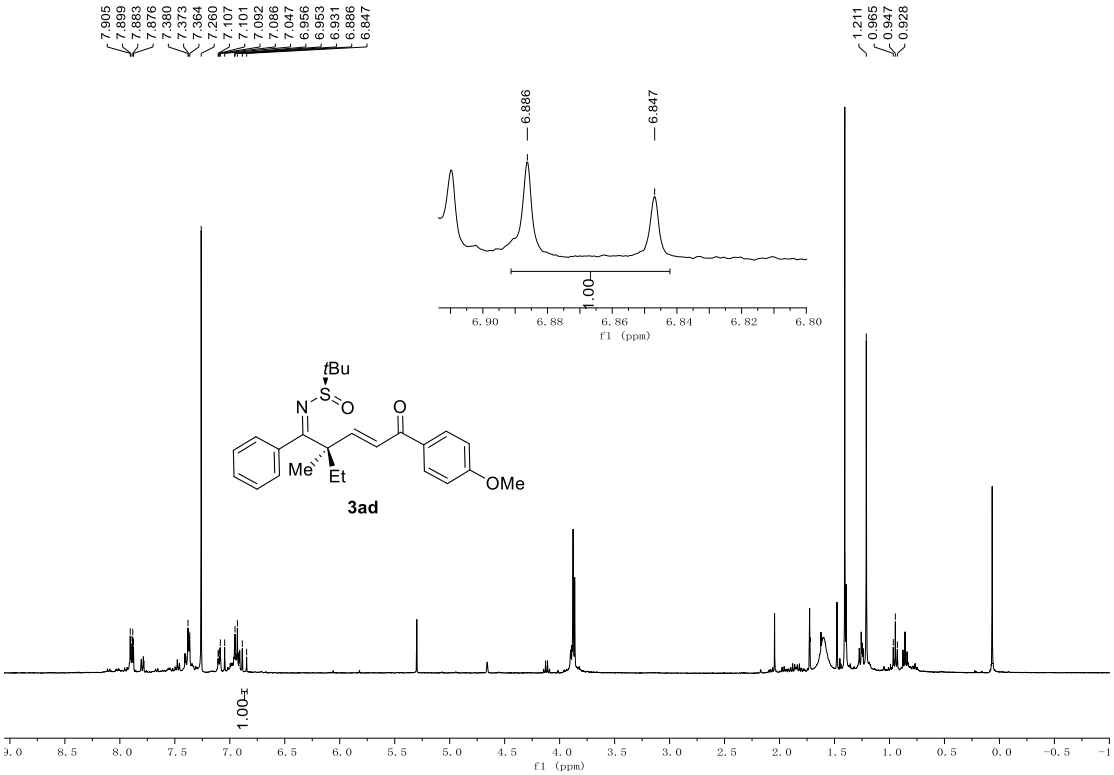
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3ac** with low diastereoselectivity (dr ~ 1.2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



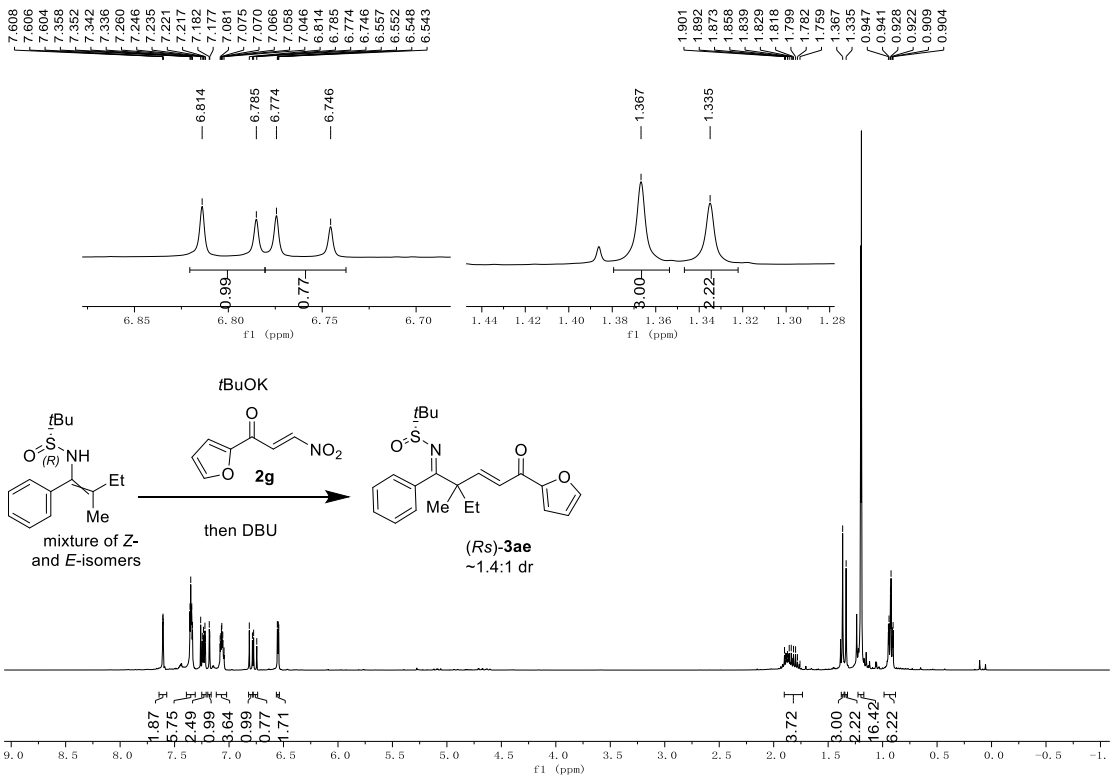
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ac** (dr = 25:1)



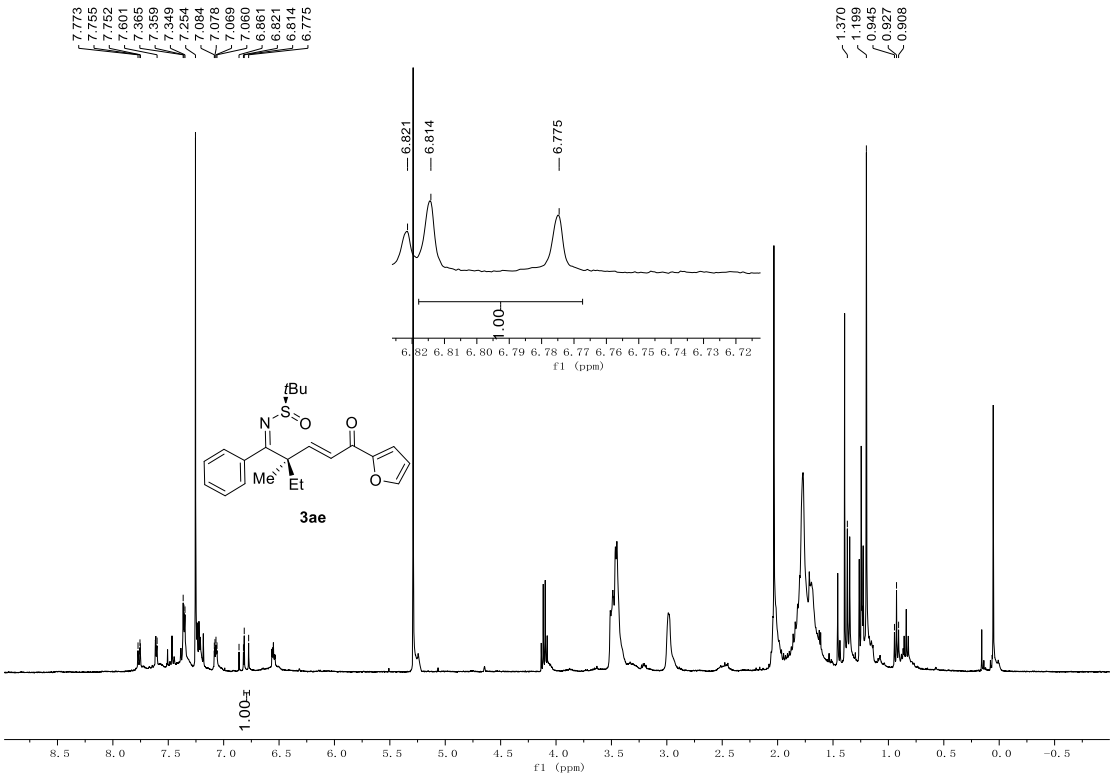
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3ad** with low diastereoselectivity (dr ~ 1.4:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



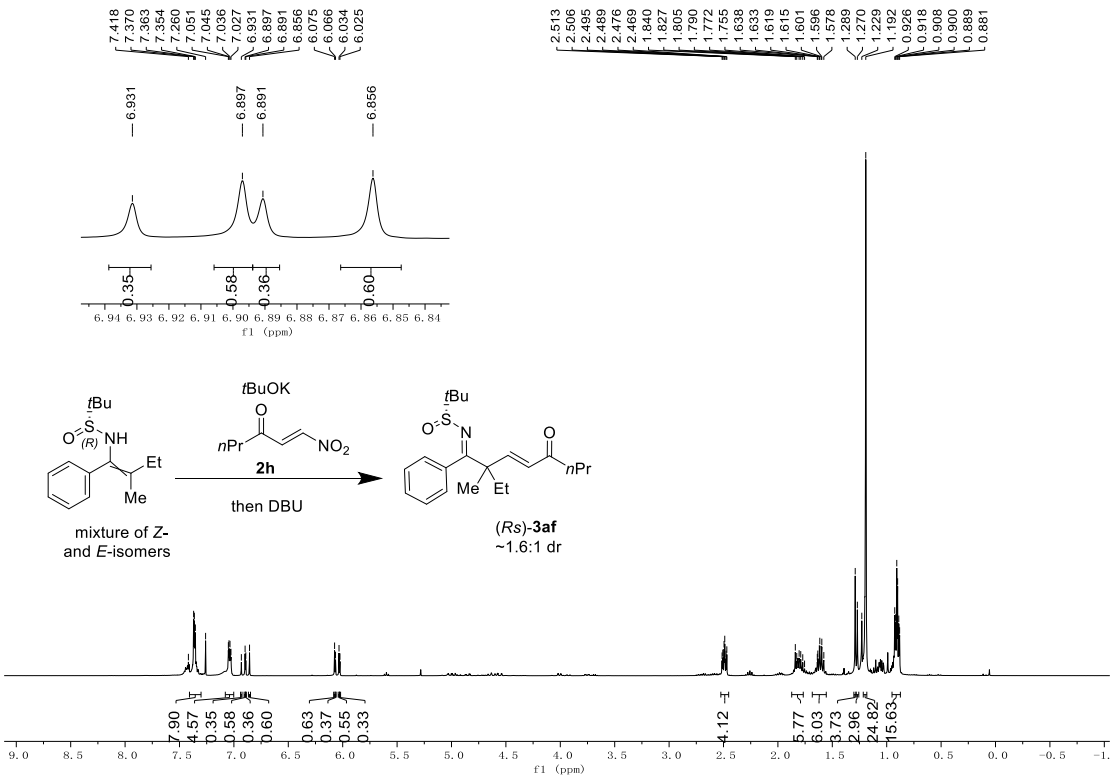
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ad** (dr > 20:1)



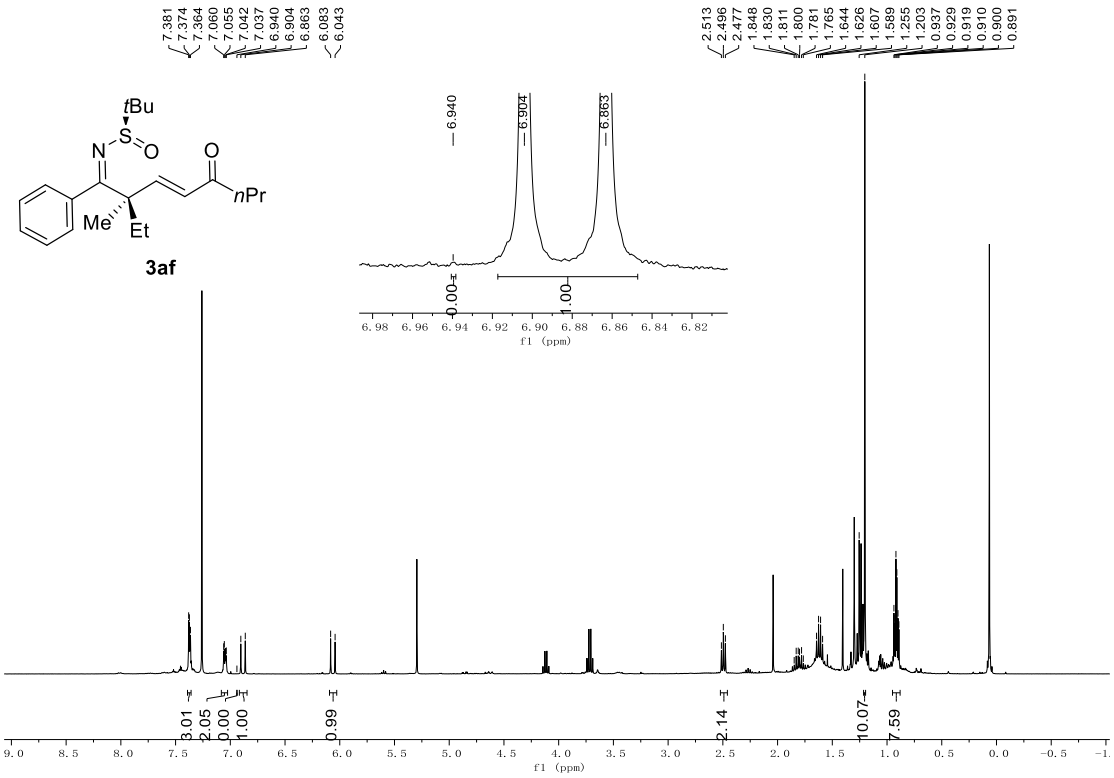
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3ae** with low diastereoselectivity (dr ~ 1.4:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



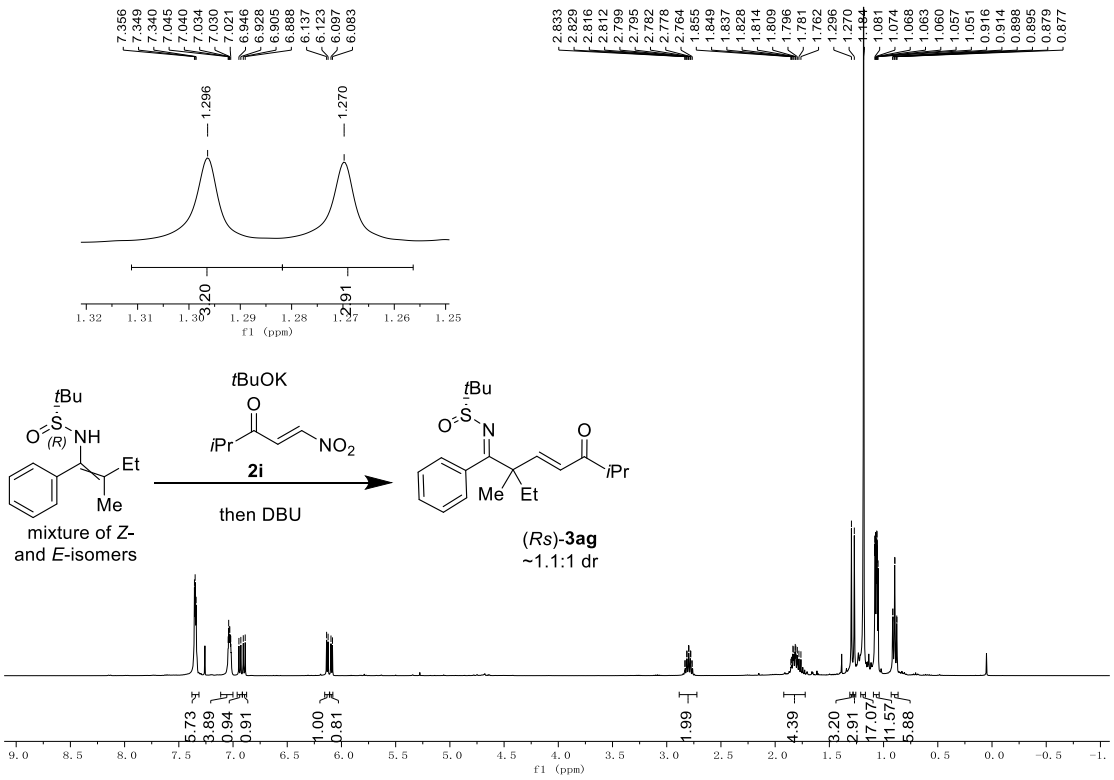
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ae** (dr > 20:1)



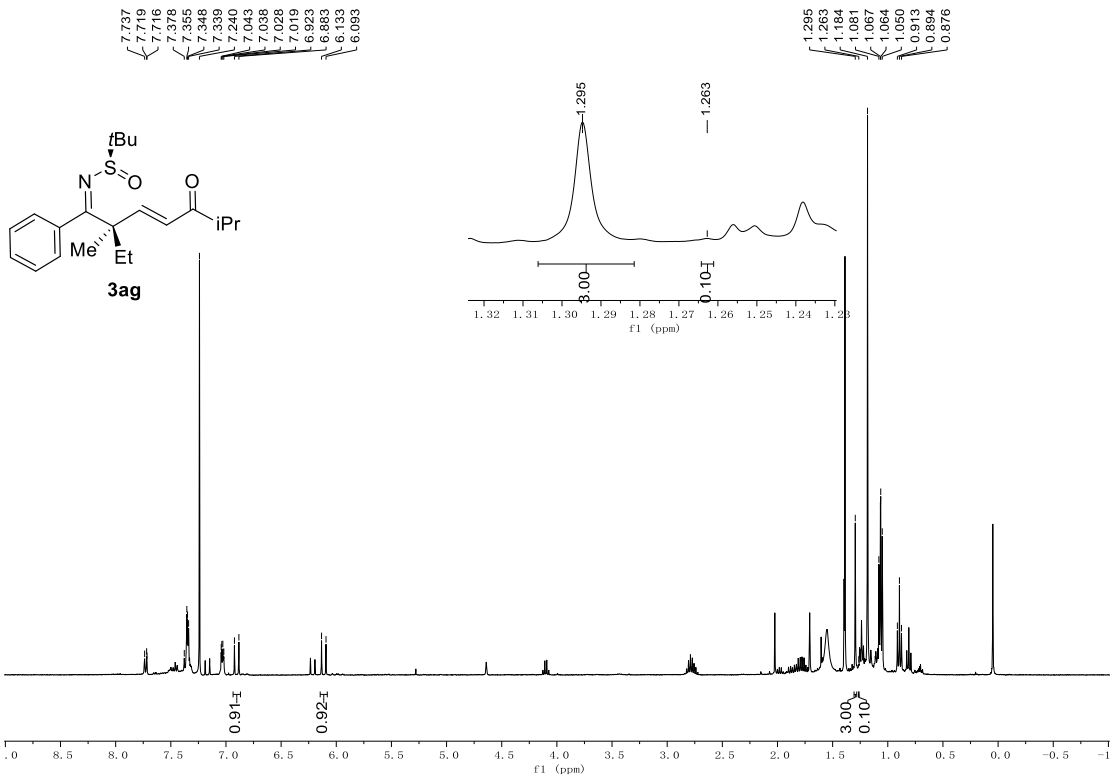
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3af** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



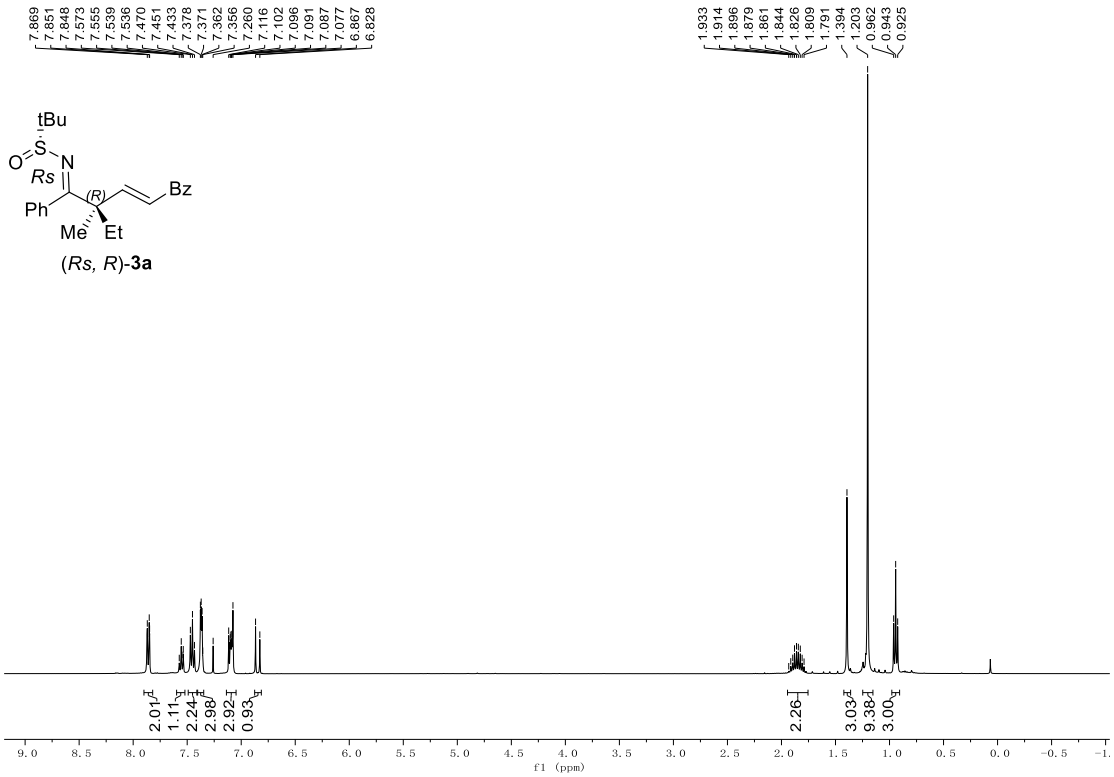
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3af** (dr > 20:1)



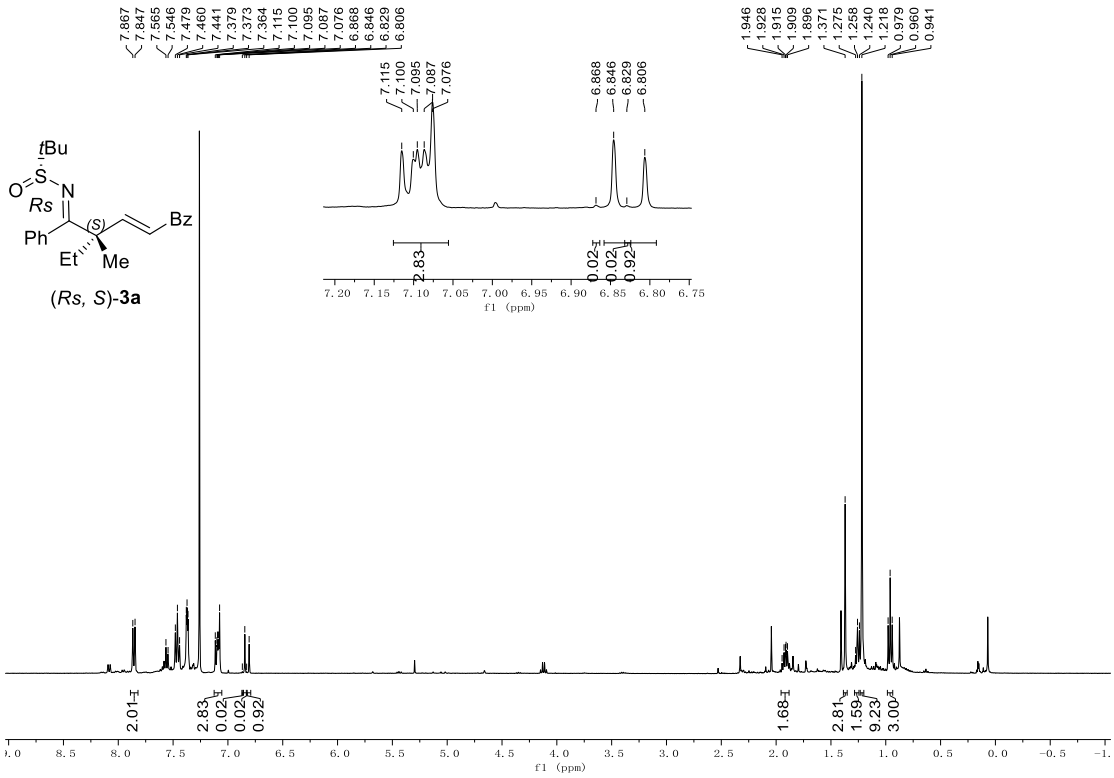
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**3ag** with low diastereoselectivity (dr ~ 1.1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



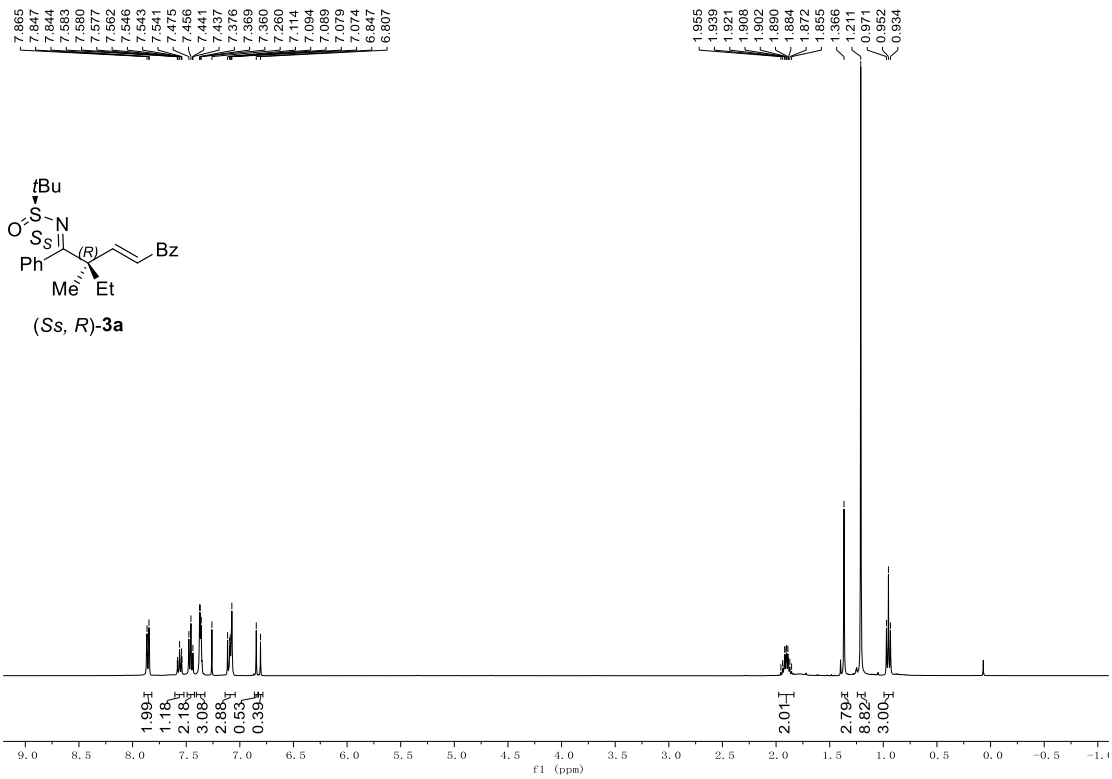
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ag** (dr ~ 30:1)



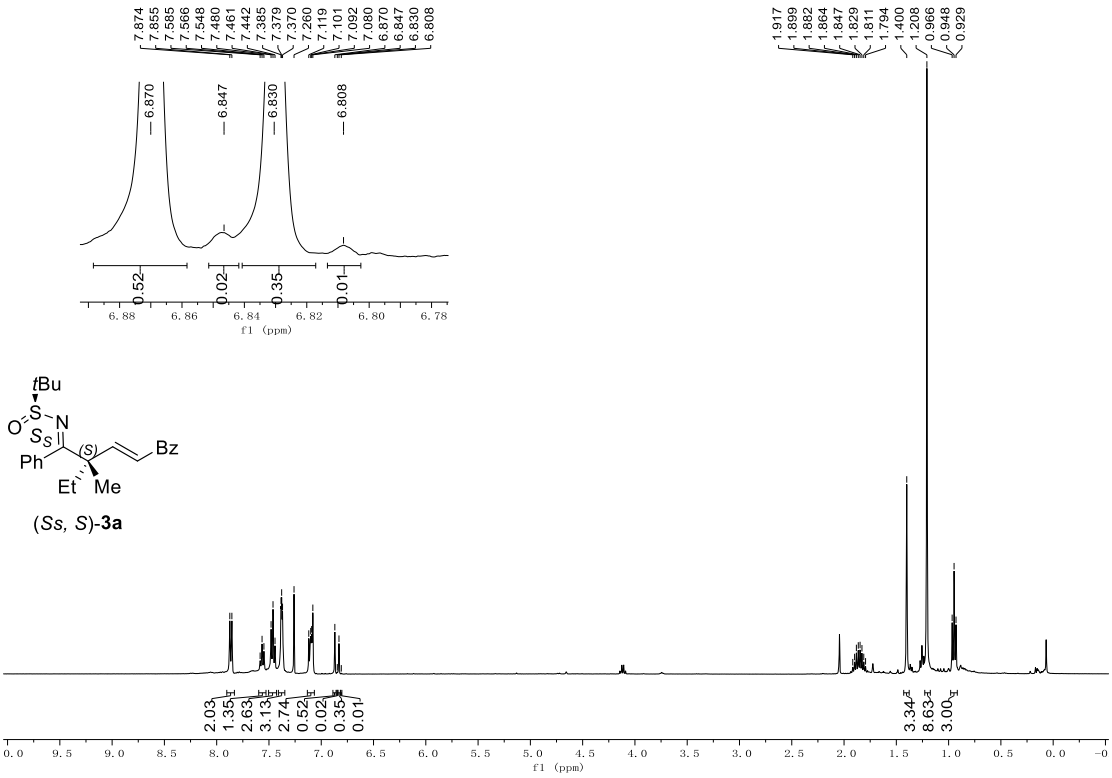
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs*, *R*)-**3a** that was used to identify the diagnostic peak(s) of the minor diastereomer



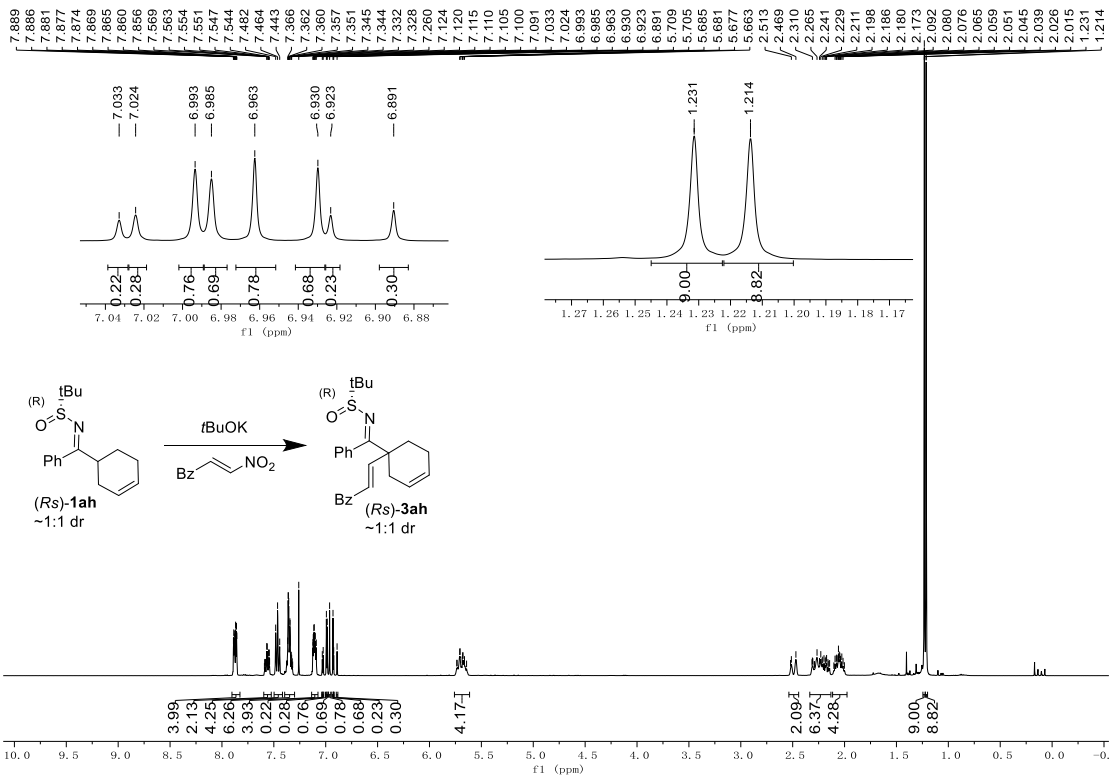
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *S*)-**3a** (dr >20:1; Scheme 5)



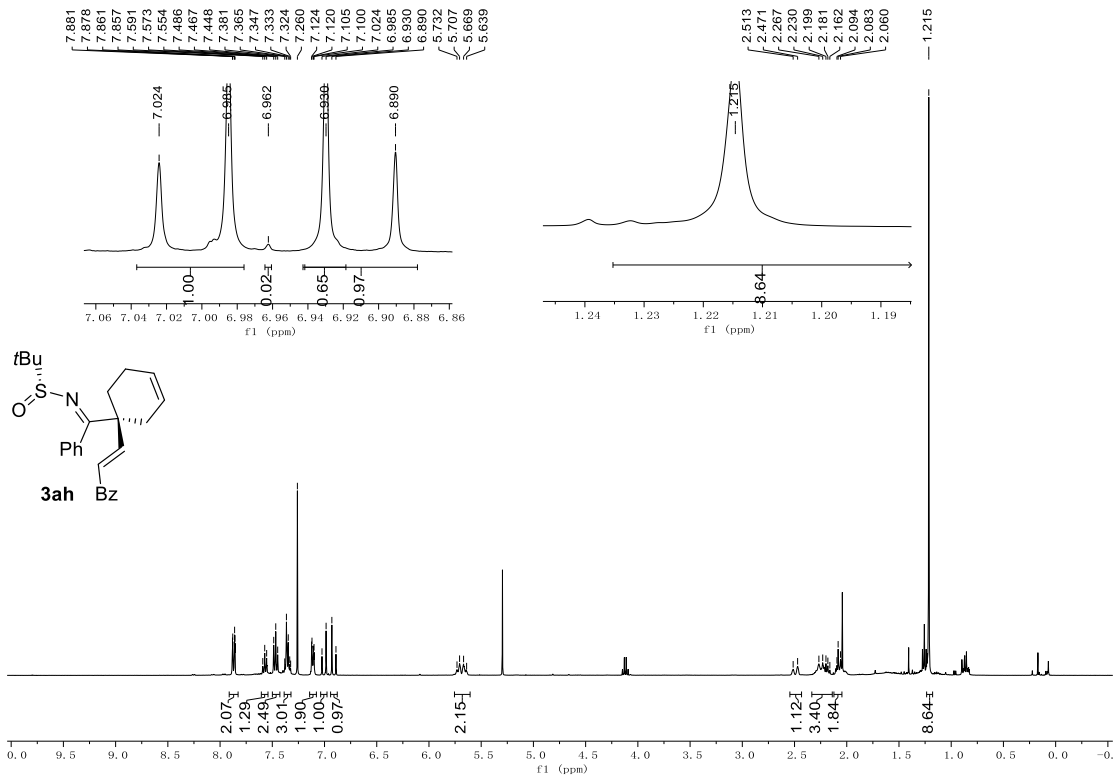
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Ss, R*)-**3a** that was used to identify the diagnostic peak(s) of the minor diastereomer



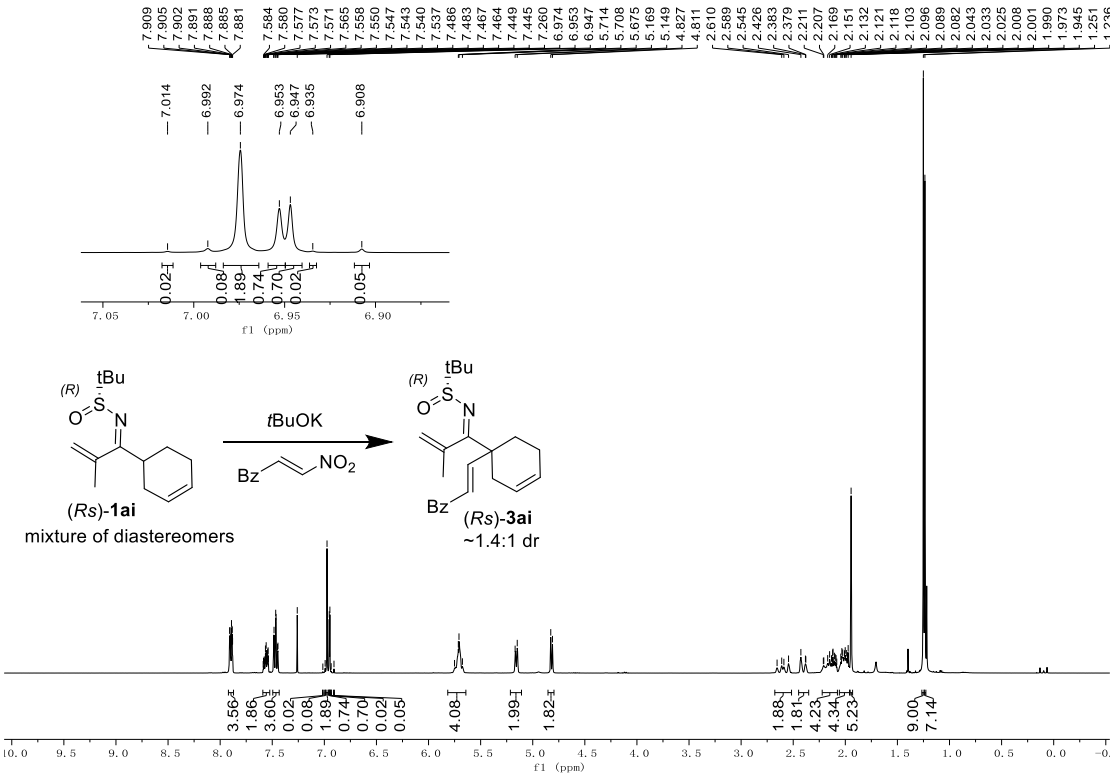
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *S*)-**3a** (dr > 20:1; Scheme 5)



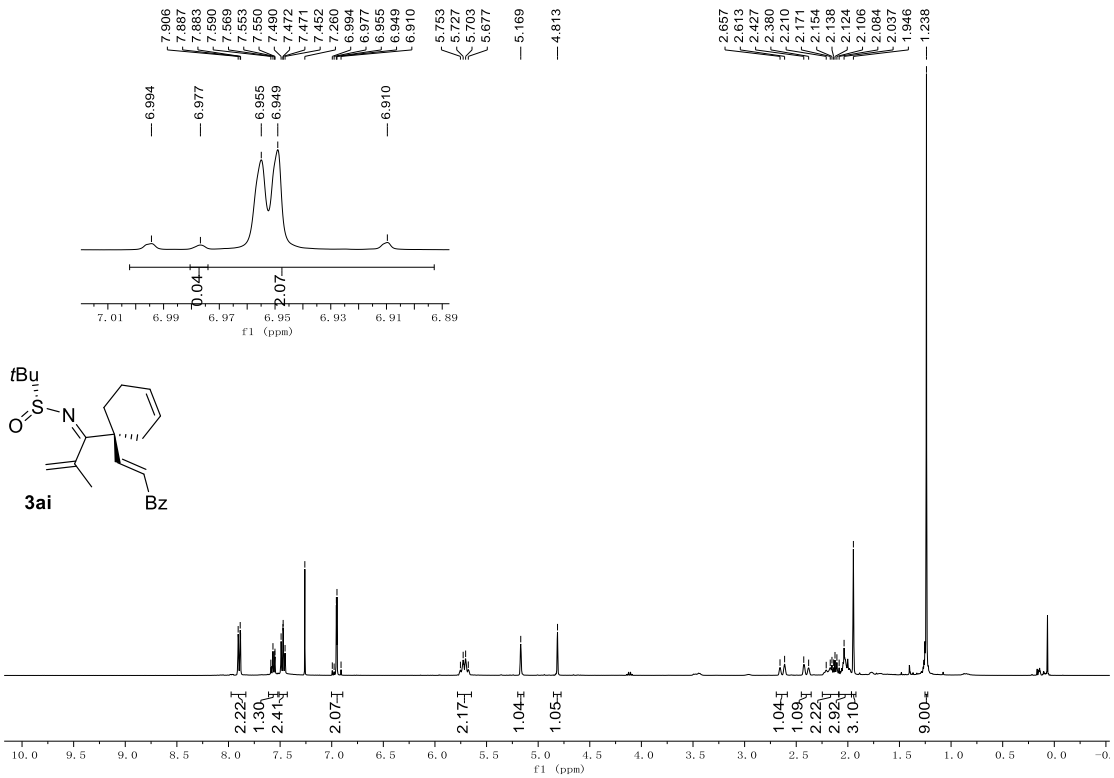
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**3ah** and (R_S, 2*R*)-**3ah** (~1:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ah** and (*Rs*,2*R*)-**1ah** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis)



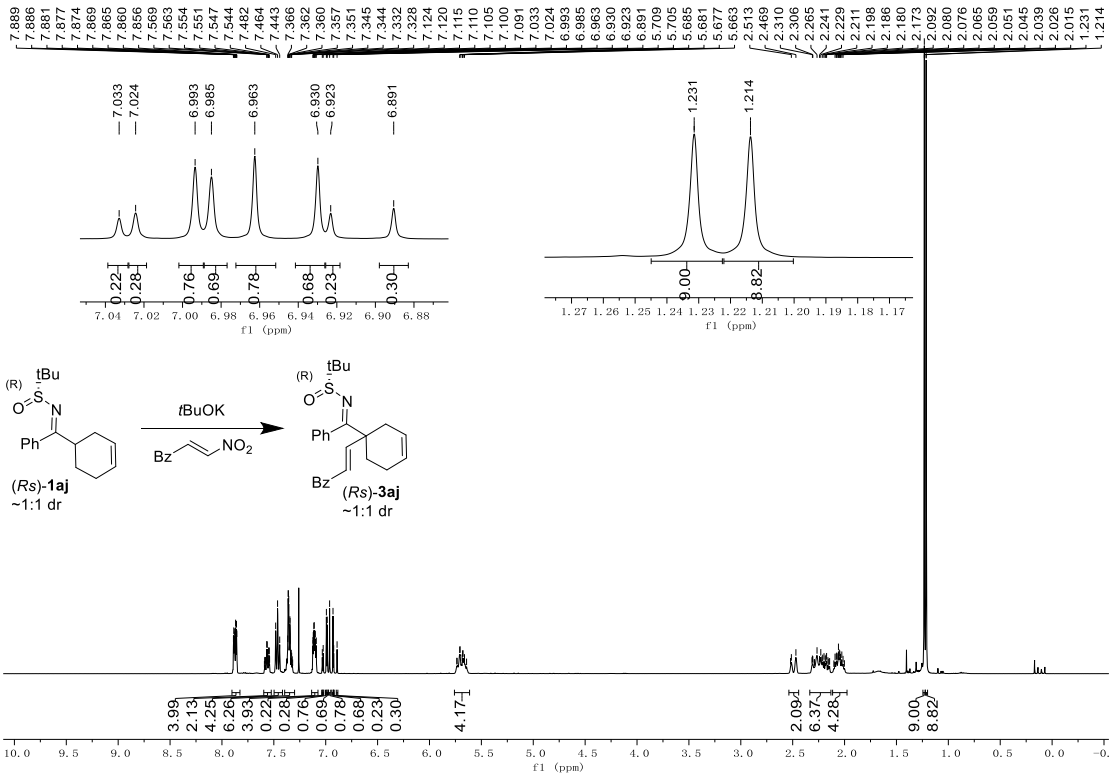
^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of the crude reaction mixture of **3ah** (dr ~ 30:1)



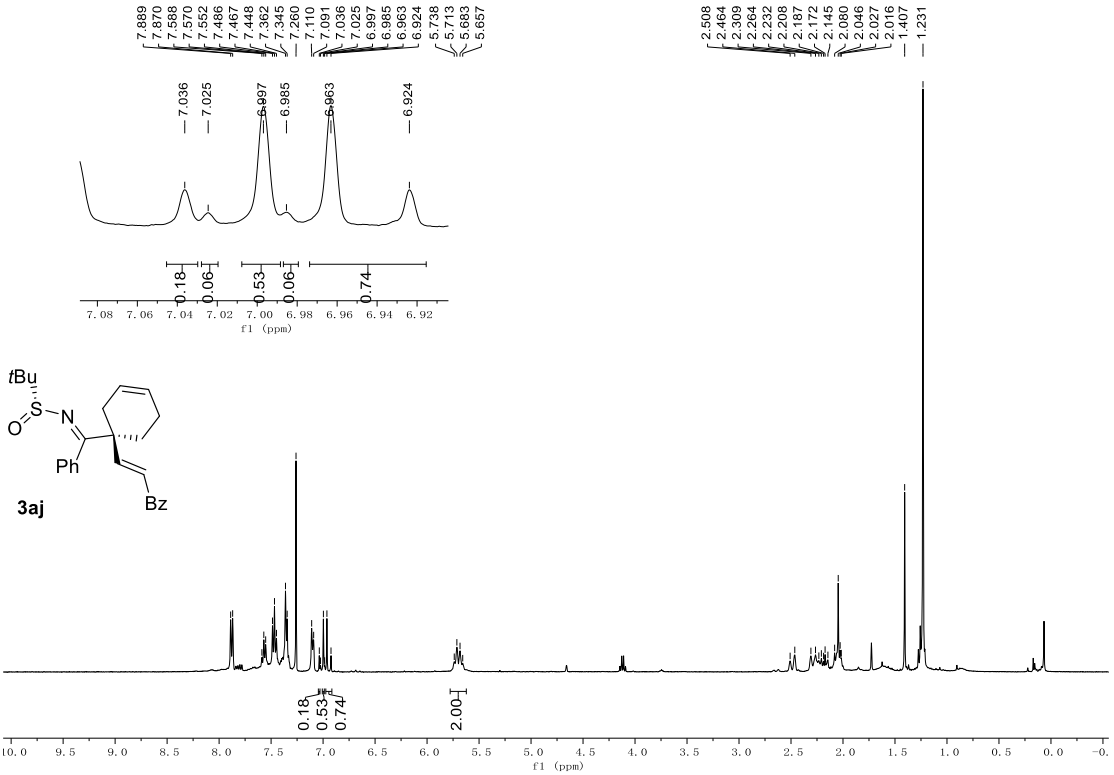
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**3ai** and (R_S, 2*R*)-**3ai** (~1.4:1 dr) (this low dr sample was intentionally prepared by using diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ai** and (*Rs*,2*R*)-**1ai** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis)



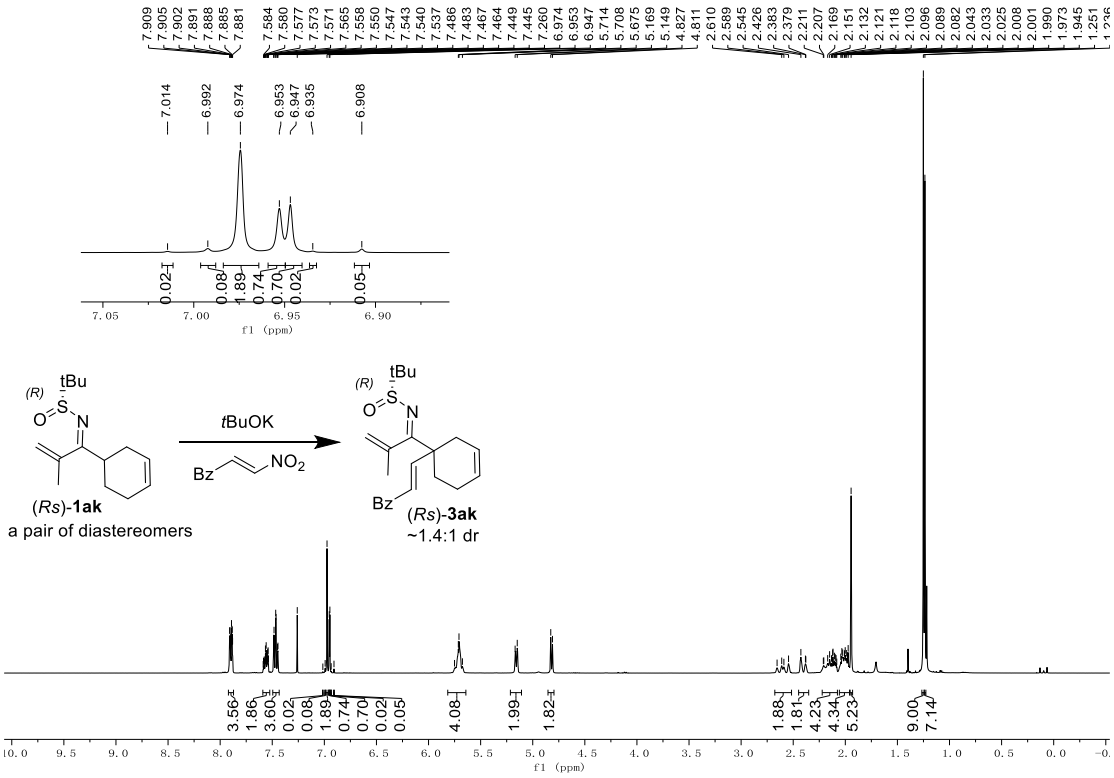
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ai** (dr > 20:1)



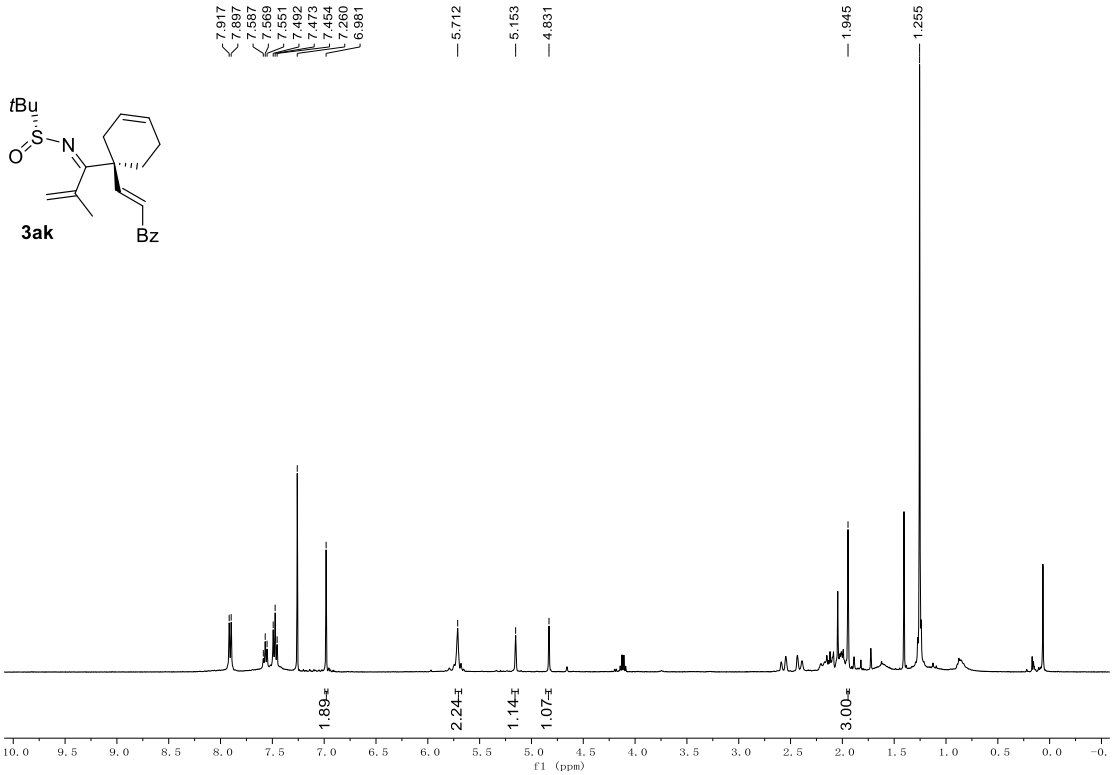
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**3aj** and (R_S, 2*R*)-**3aj** (~1:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1aj** and (*Rs*,2*R*)-**1aj** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis; note: **3ah** and **3aj** is a pair of diastereomers, see Scheme 5)



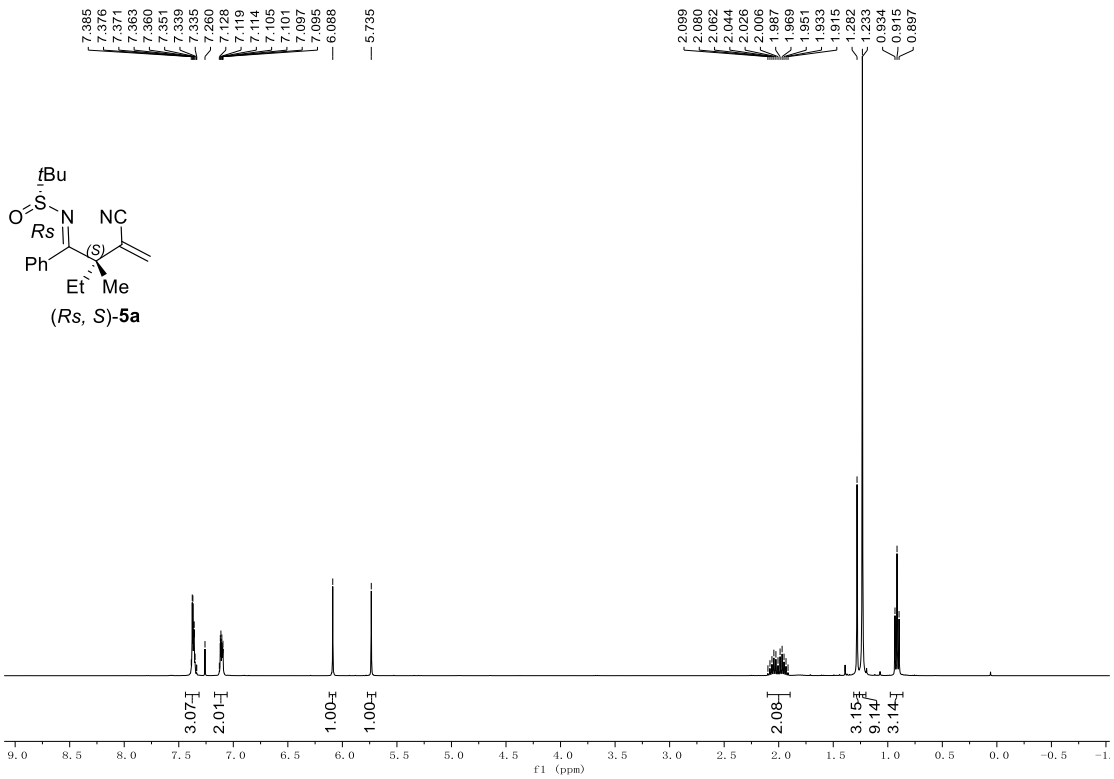
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3aj** (dr > 20:1)



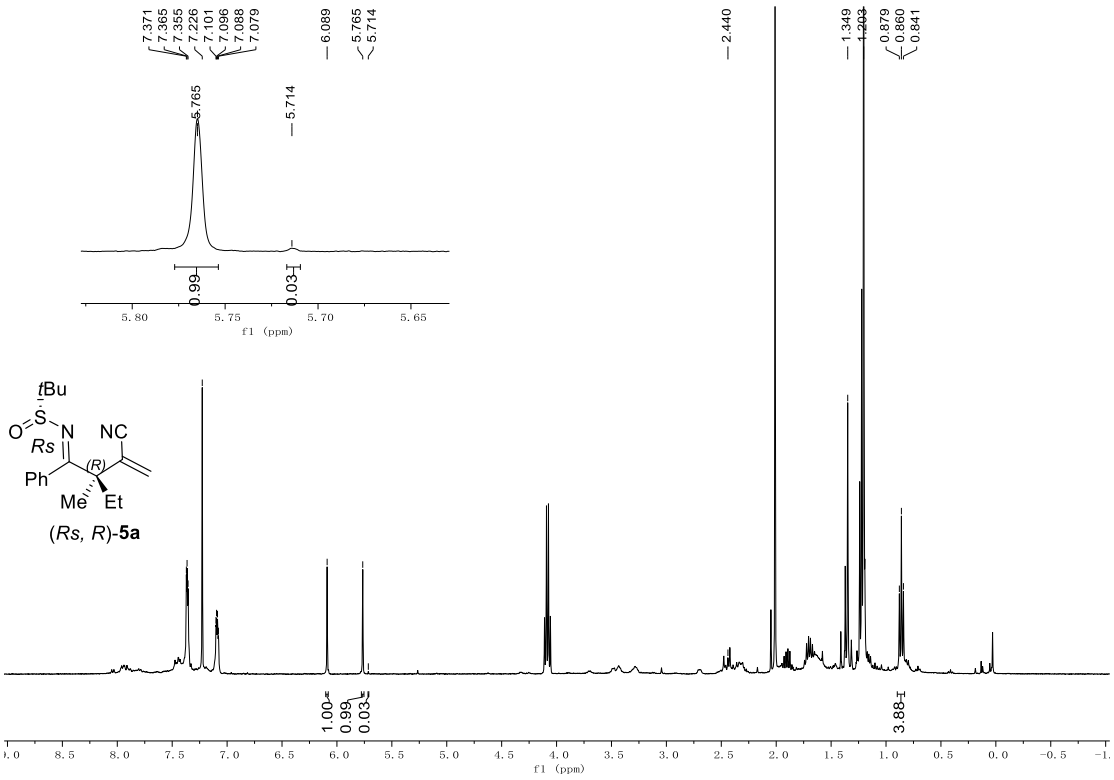
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**3ak** and (R_S, 2*R*)-**3ak** (~1.4:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ak** and (*Rs*,2*R*)-**1ak** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis; note: **3ai** and **3ak** is a pair of diastereomers, see Scheme 5)



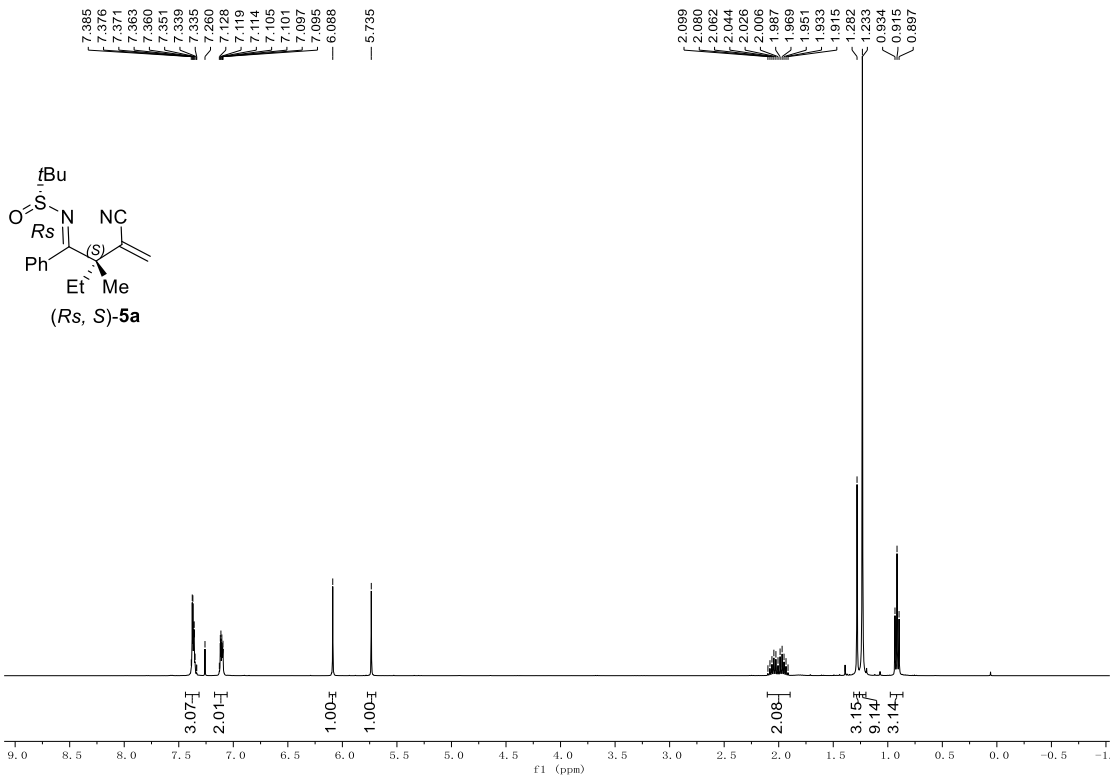
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3ak** (dr > 20:1)



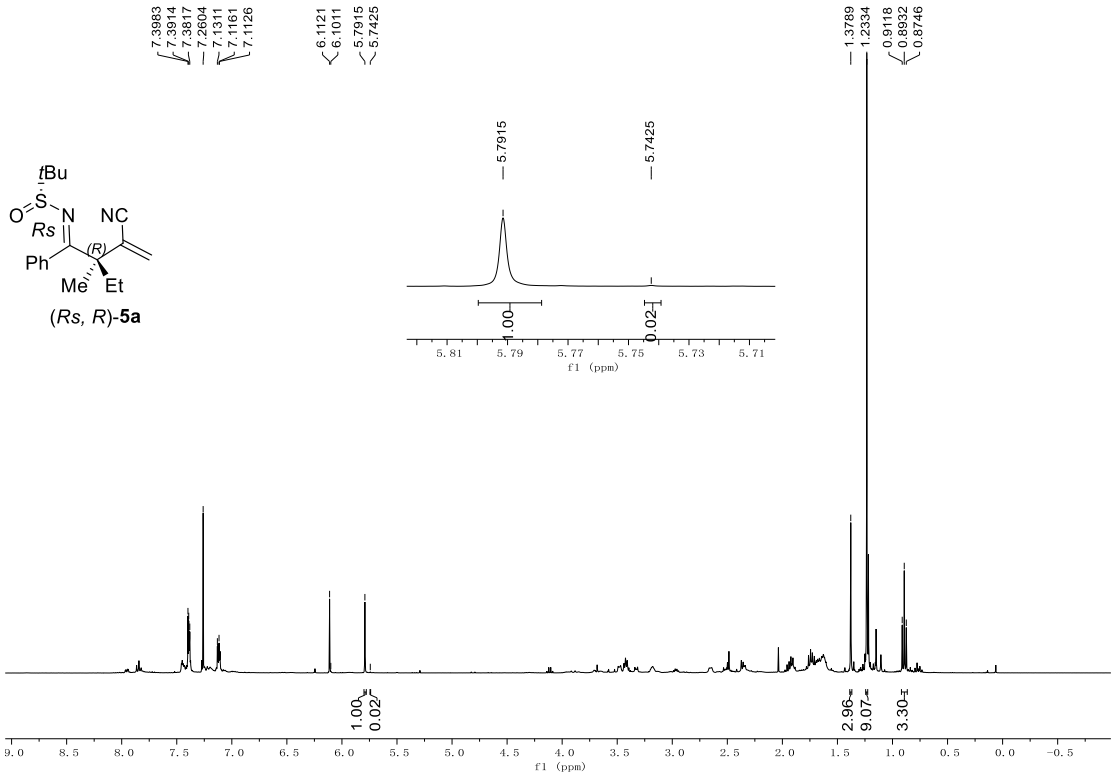
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs, S*)-**5a** that was used as a control sample to identify the diagnostic peak(s) of the minor diastereomer



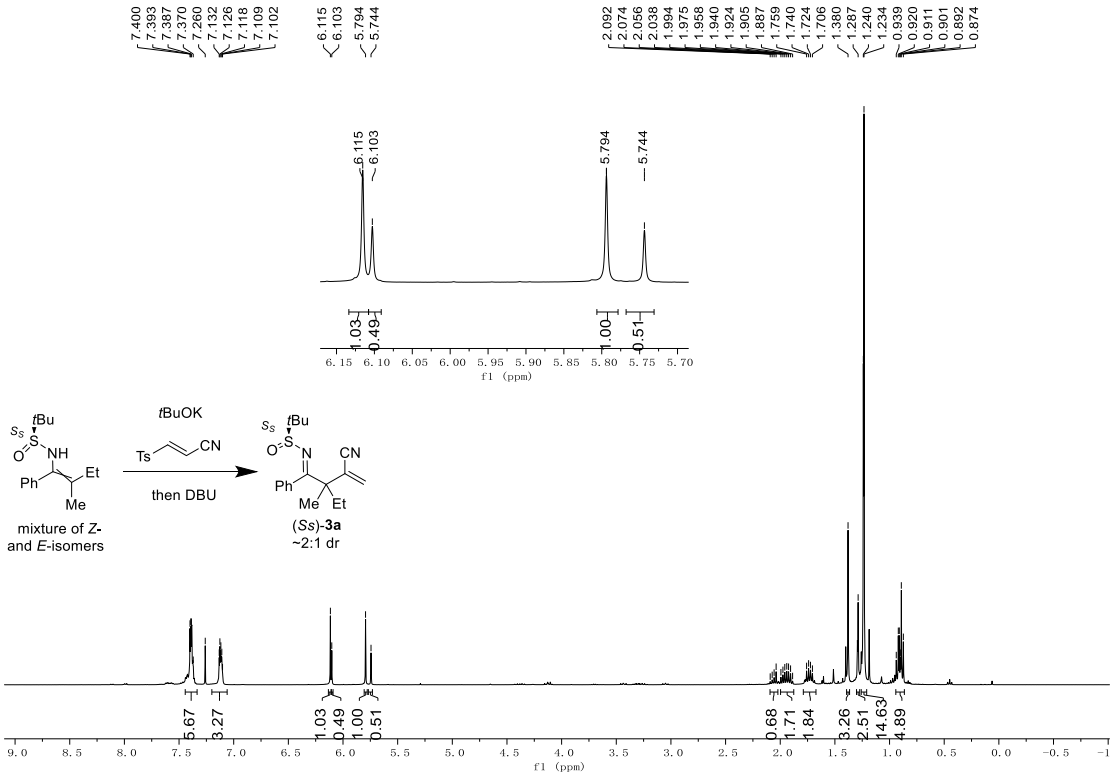
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *R*)-**5a** (dr > 20:1; 0.1 mmol scale)



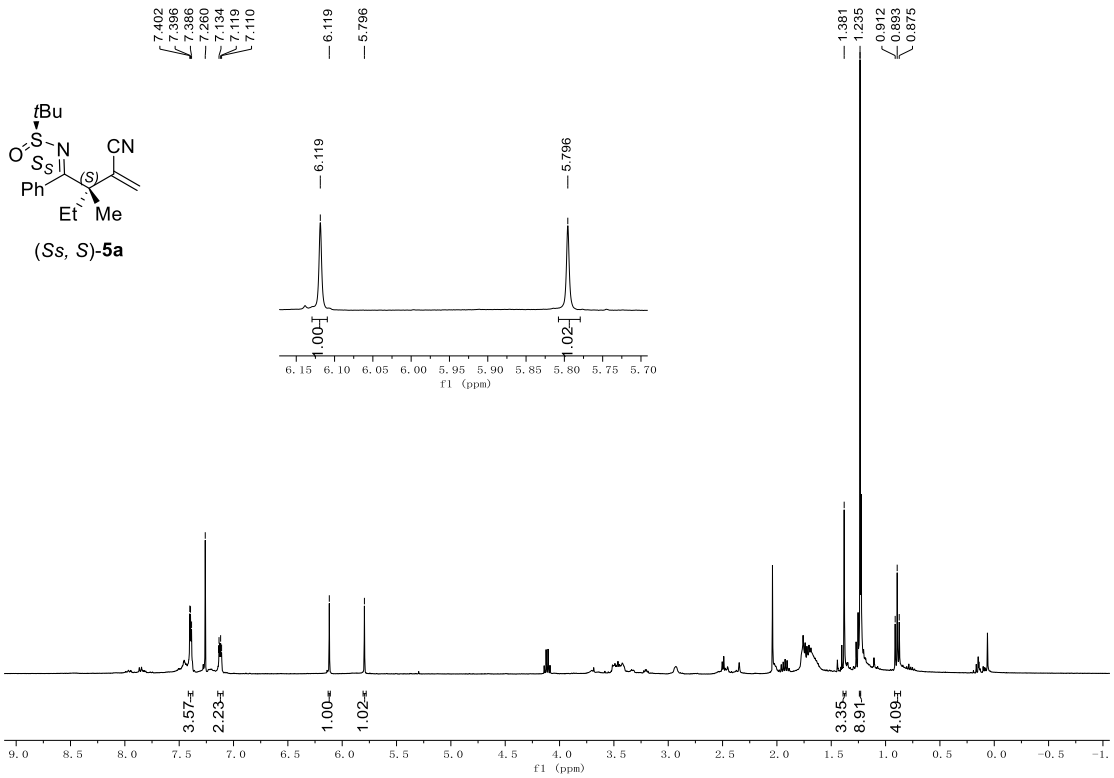
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs*, *S*)-**5a** that was used as a control sample to identify the diagnostic peak(s) of the minor diastereomer



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *R*)-**5a** (dr > 20:1; 1 gram scale)

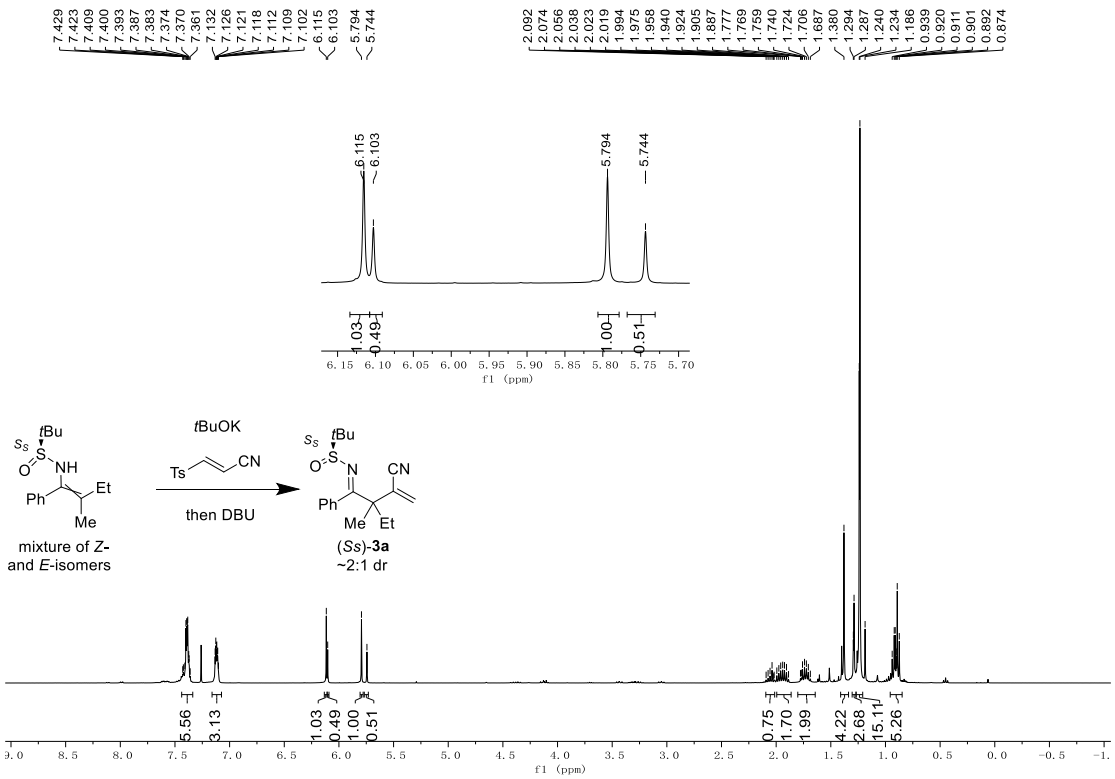


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*)-**5a** with low diastereoselectivity (dr ~ 2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio

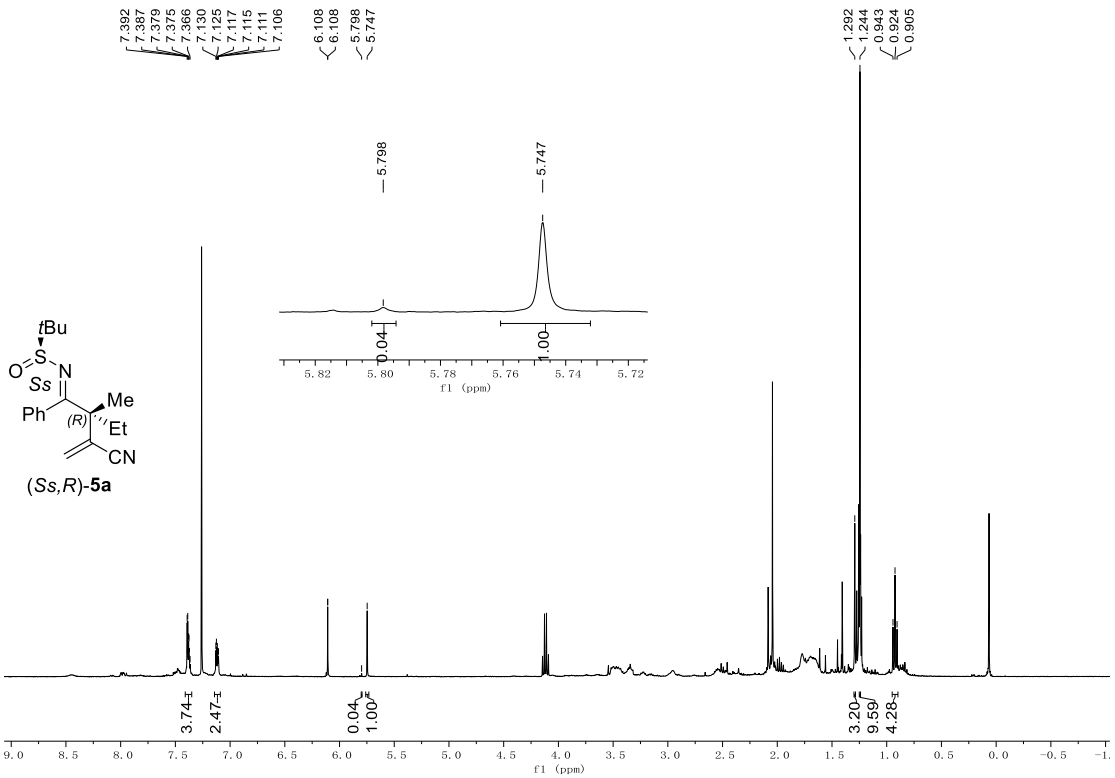


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *S*)-**5a** (dr > 20:1)

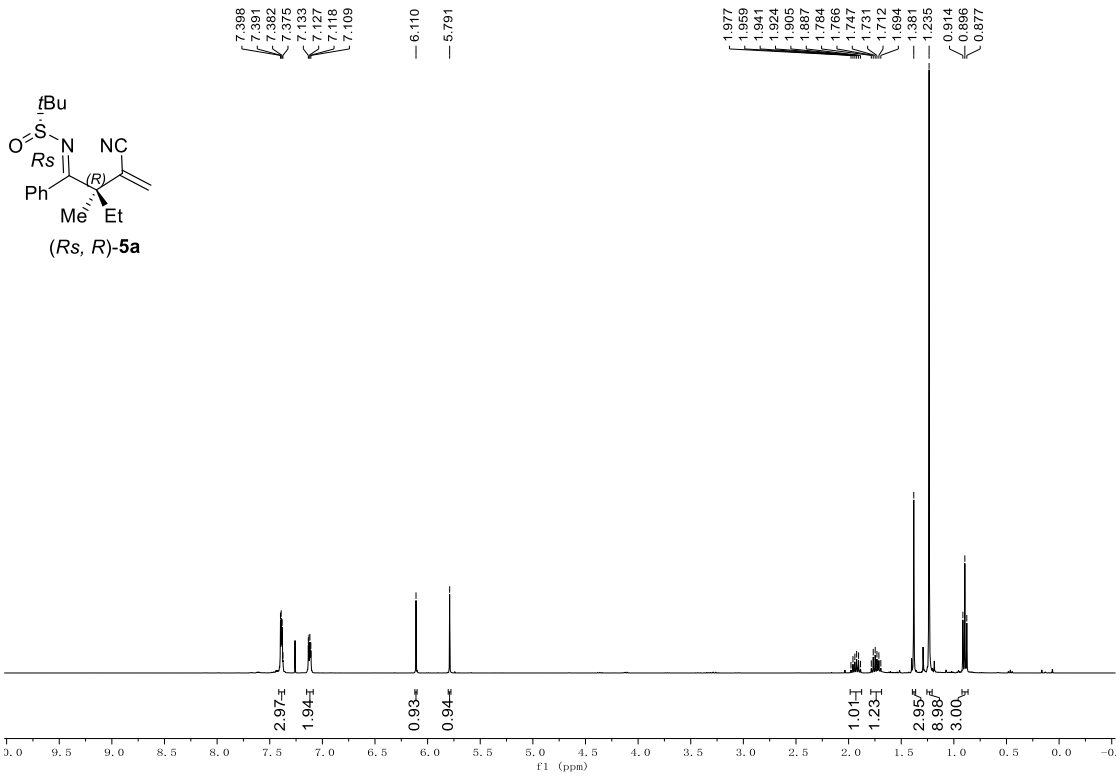
(No observable presence of the minor diastereomer)



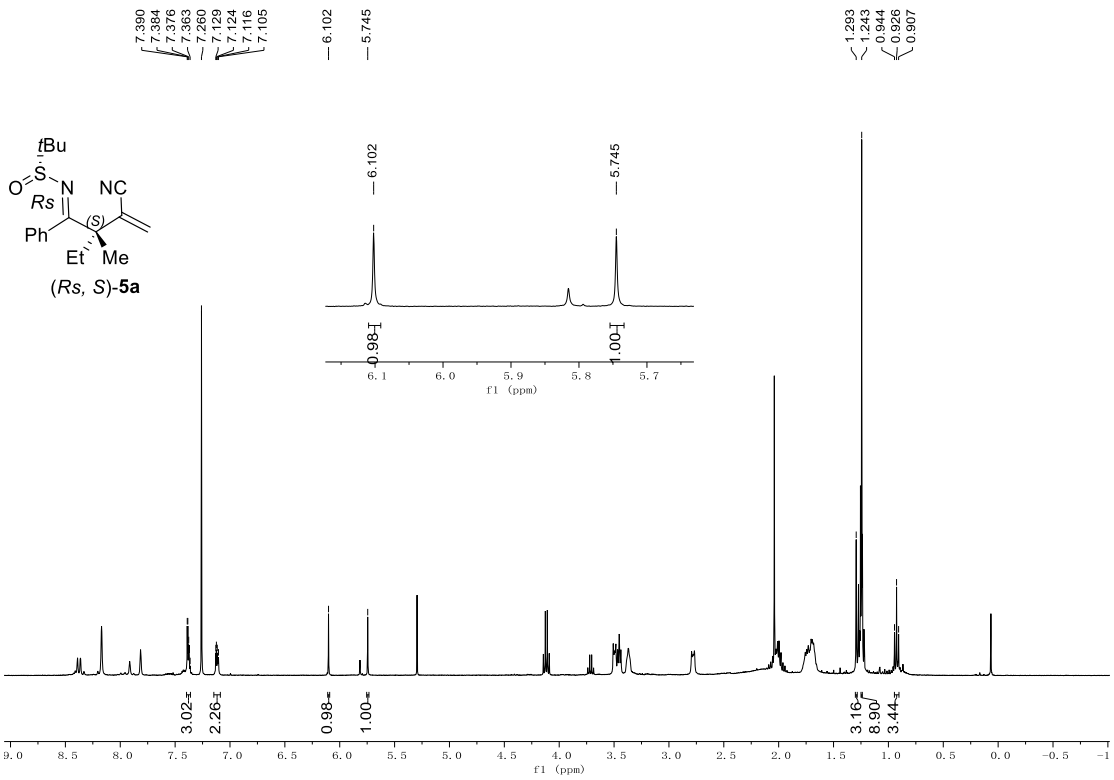
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Ss*)-**5a** with low diastereoselectivity(dr ~ 2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *R*)-**5a** (dr = 25:1)

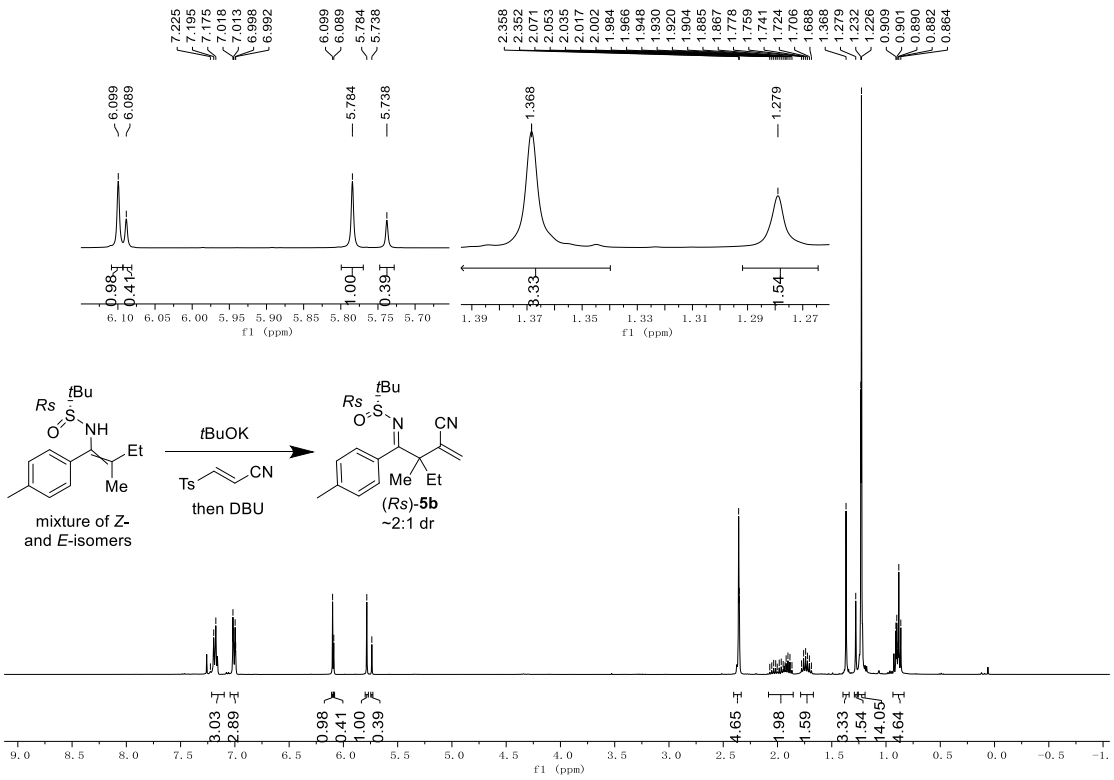


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs*, *R*)-**5a** that was used to identify the diagnostic peak(s) of the minor diastereomer

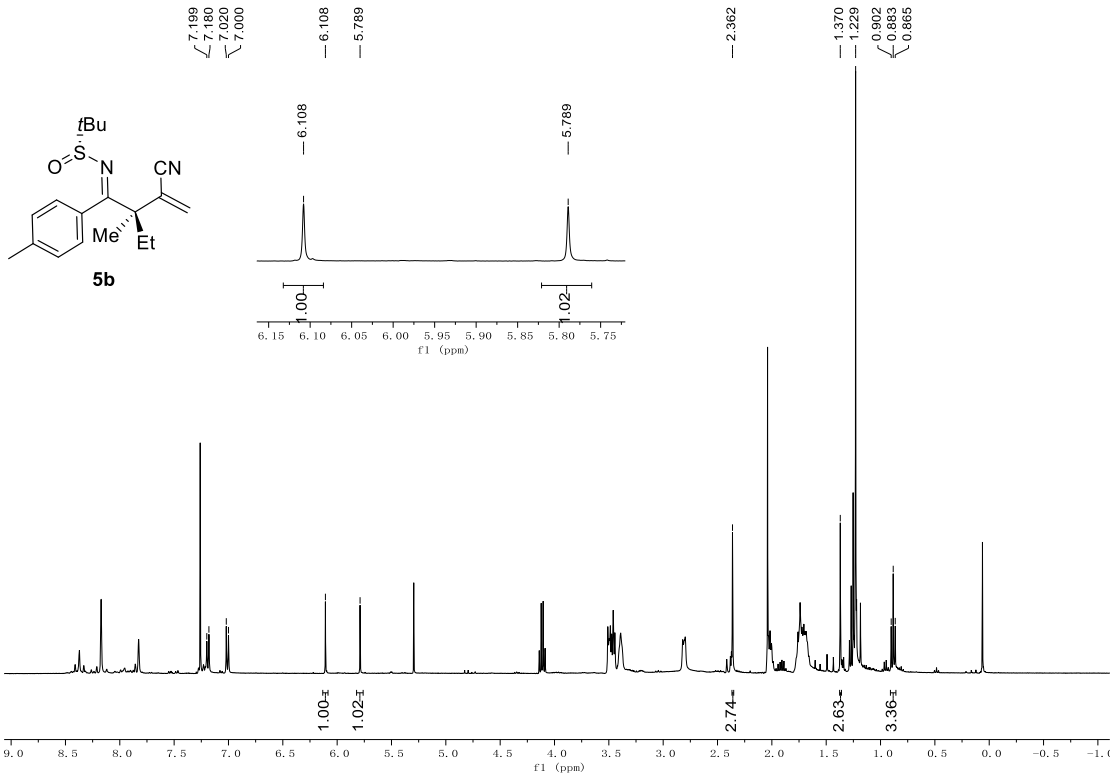


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *S*)-**5a** (dr > 20:1)

(No observable presence of the minor diastereomer)

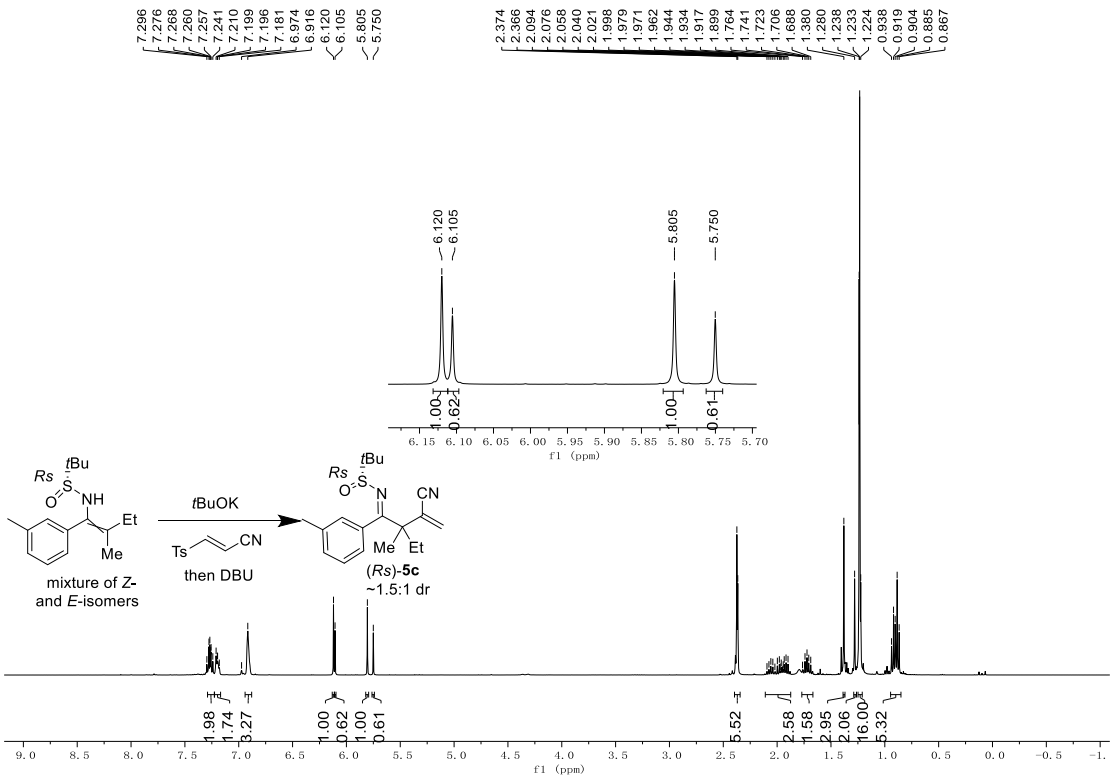


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5b** with low diastereoselectivity (dr ~ 2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

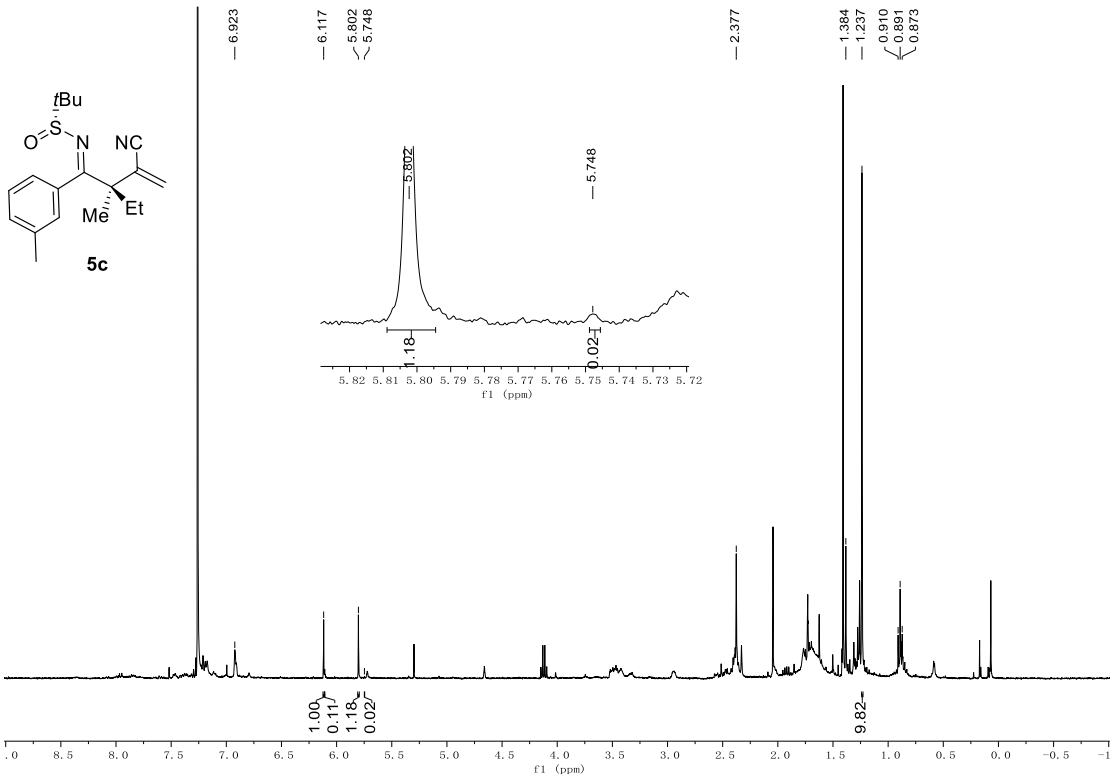


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **3b** (dr > 20:1)

(No observable presence of the minor diastereomer)

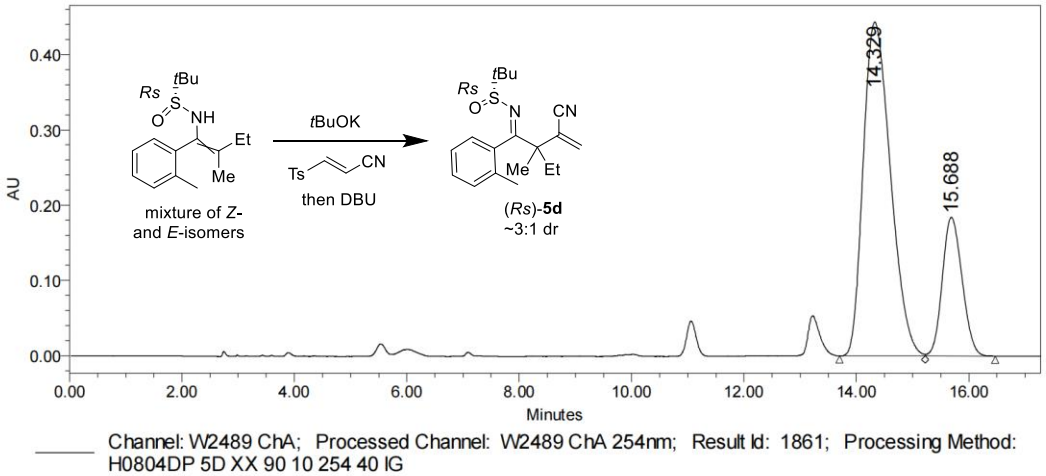


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5c** with low diastereoselectivity (dr ~ 1.5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5c** (dr > 20:1)

(*Rs*)-**5d**: HPLC conditions: Daicel Chiralcel IG-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

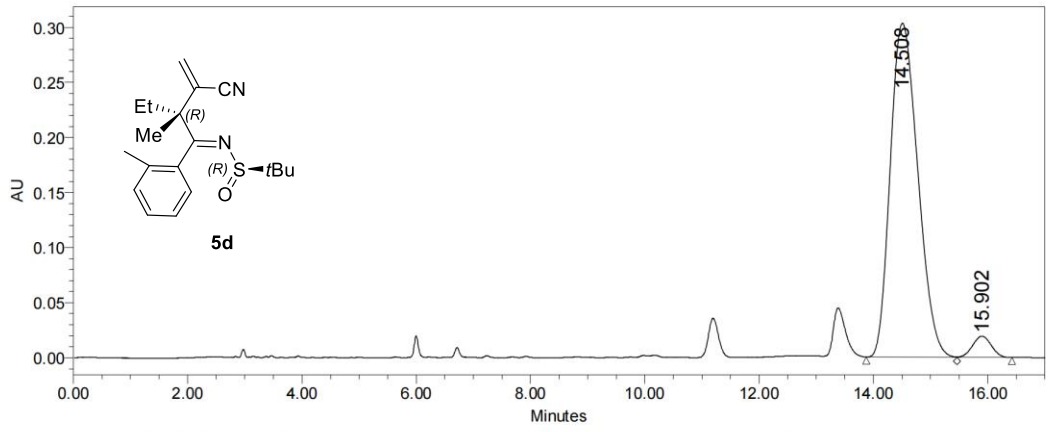


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1861; Processing Method: H0804DP 5D XX 90 10 254 40 IG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.329	14924120	76.82	443408
2	W2489 ChA 254nm	15.688	4503073	23.18	184372

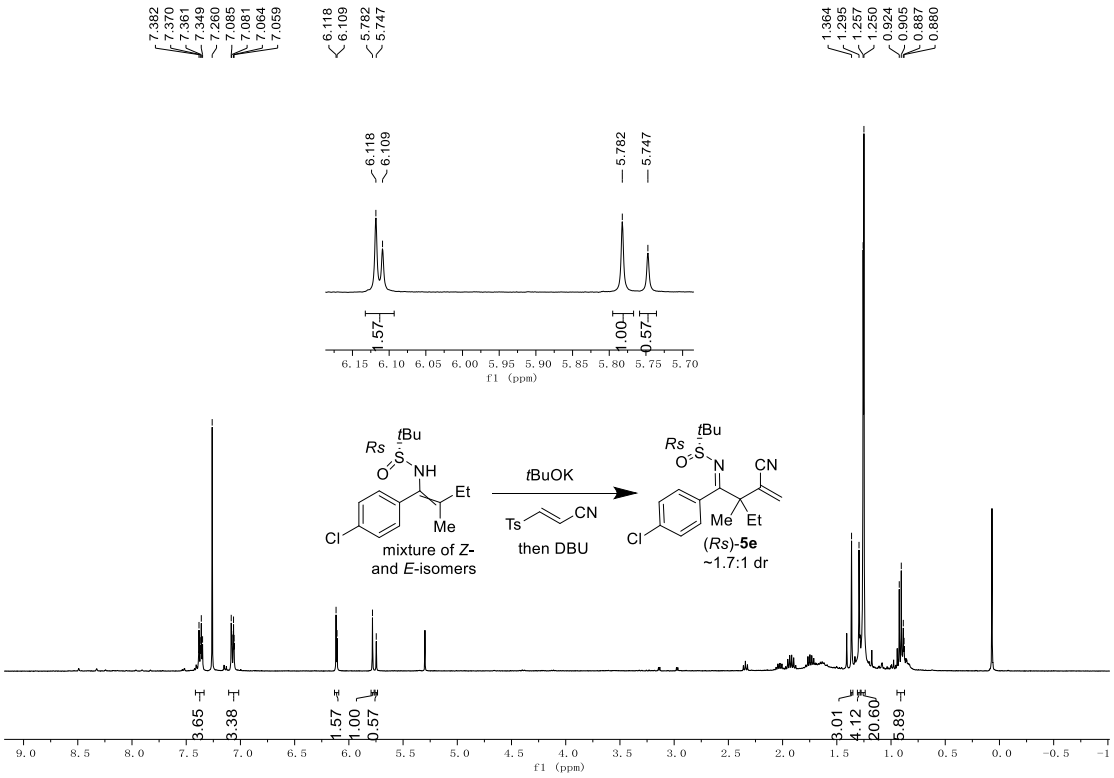
HPLC chromatogramfor dr determination of crude **5d**



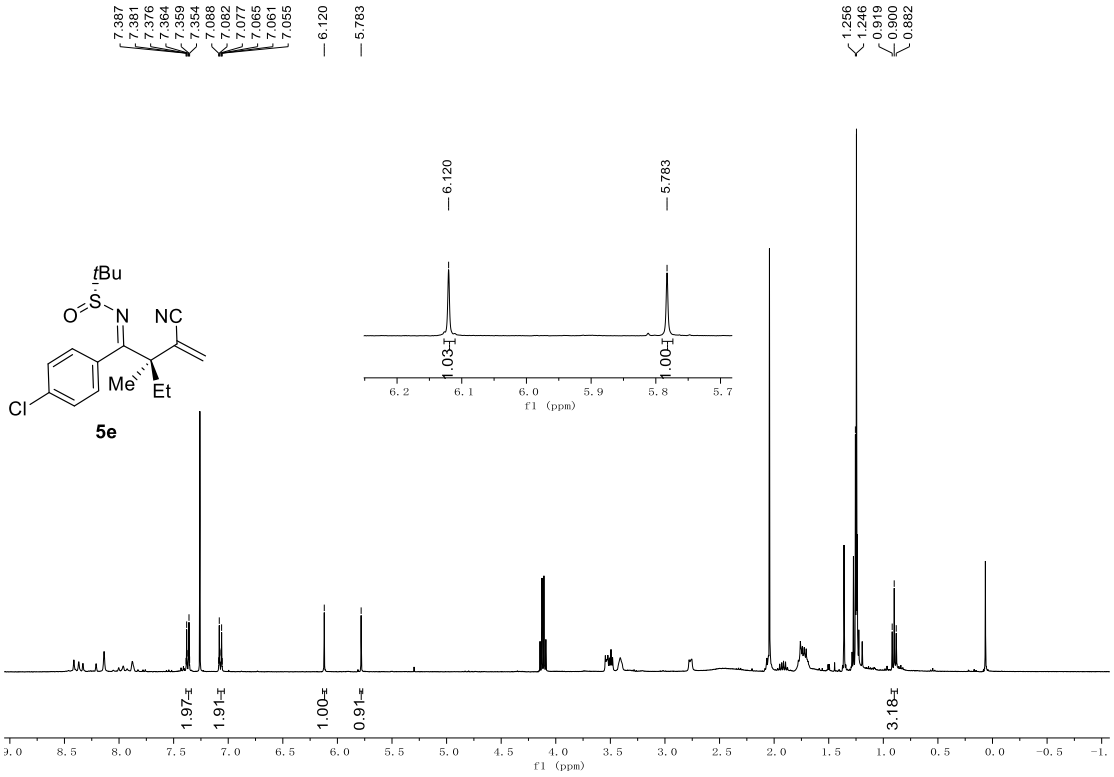
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1863; Processing Method: H0715F 5D SX 90 10 254 40 IG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.508	10138355	95.82	303077
2	W2489 ChA 254nm	15.902	441889	4.18	19360

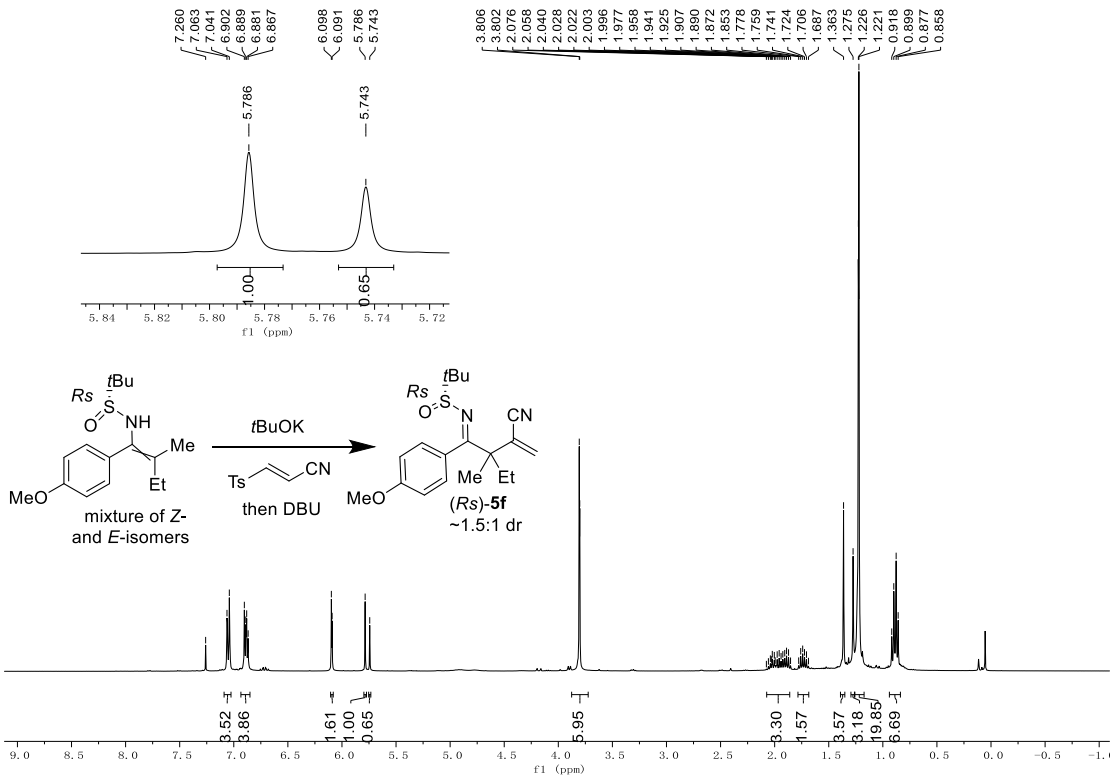


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5e** with low diastereoselectivity (dr ~ 2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

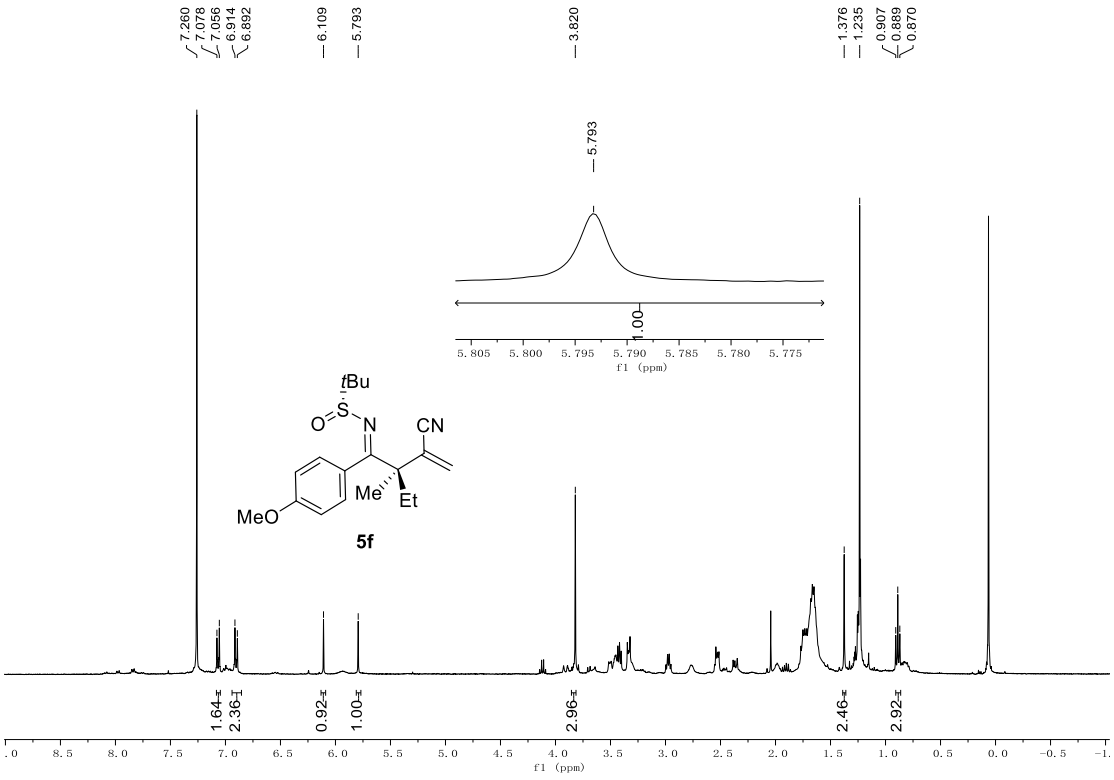


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5e** (dr > 20:1)

(No observable presence of the minor diastereomer)

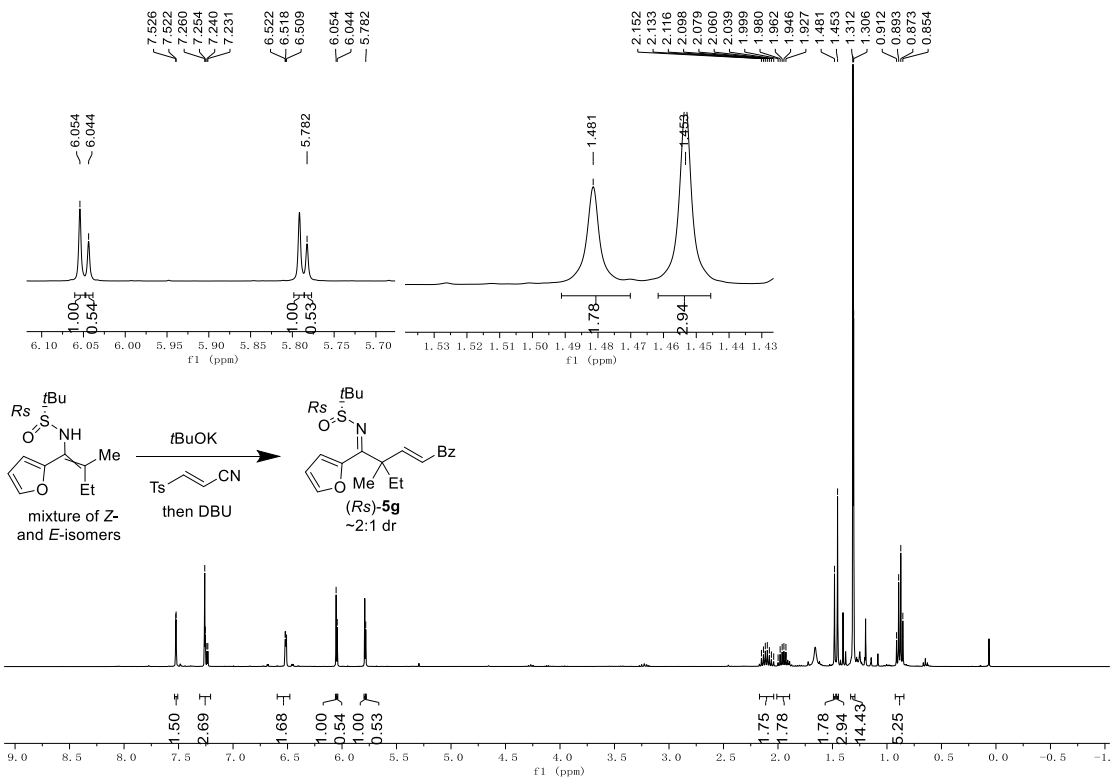


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5f** with low diastereoselectivity (dr ~ 1.5.:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

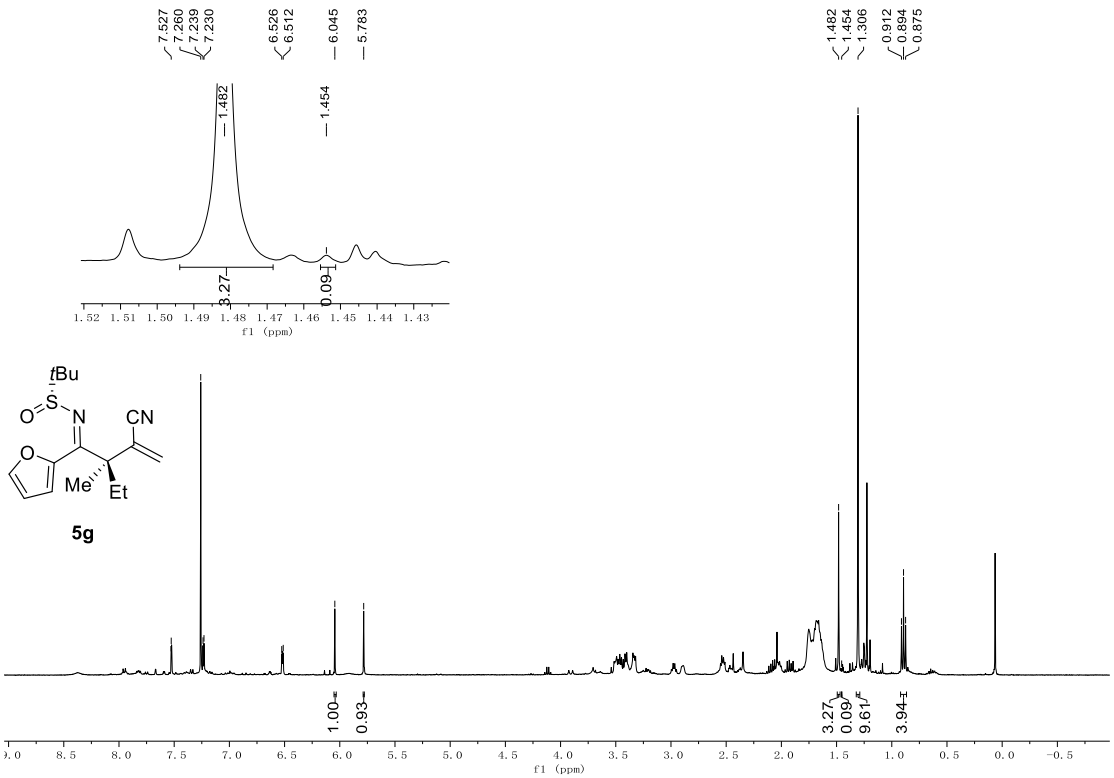


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5f** (dr > 20:1)

(No observable presence of the minor diastereomer)

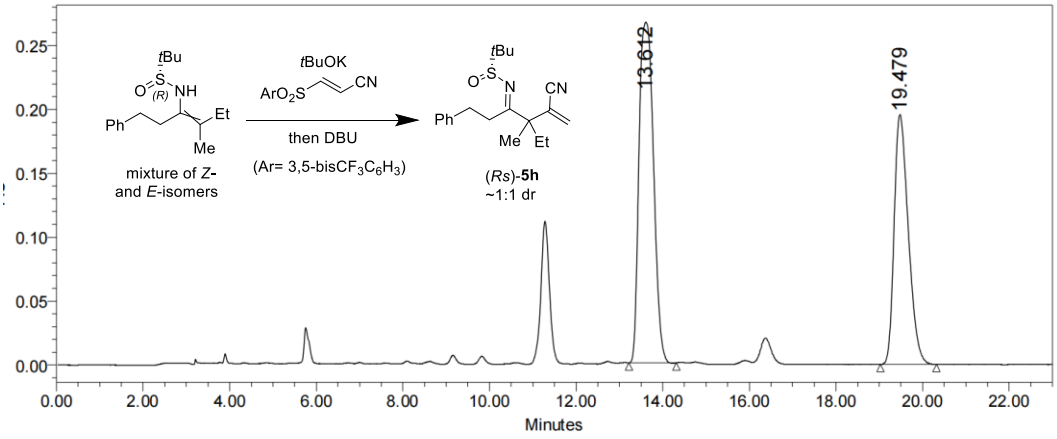


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5g** with low diastereoselectivity (dr ~ 2.:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5g** (dr ~ 33:1)

(*Rs*)-**5h**: HPLC conditions: Daicel Chiralcel IC-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

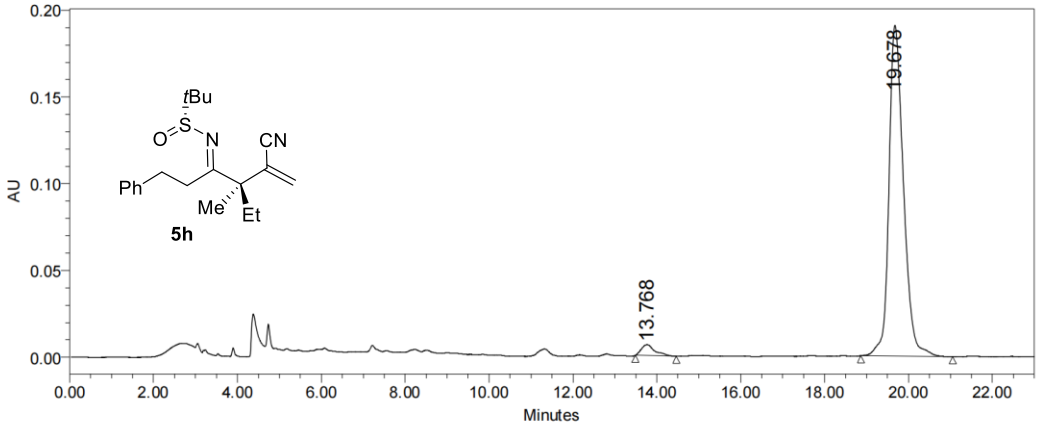


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1281; Processing Method: H230511EP XX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.612	6192435	58.32	266555
2	W2489 ChA 254nm	19.479	4425000	41.68	195473

HPLC chromatogramfor dr determination of crude **5h**

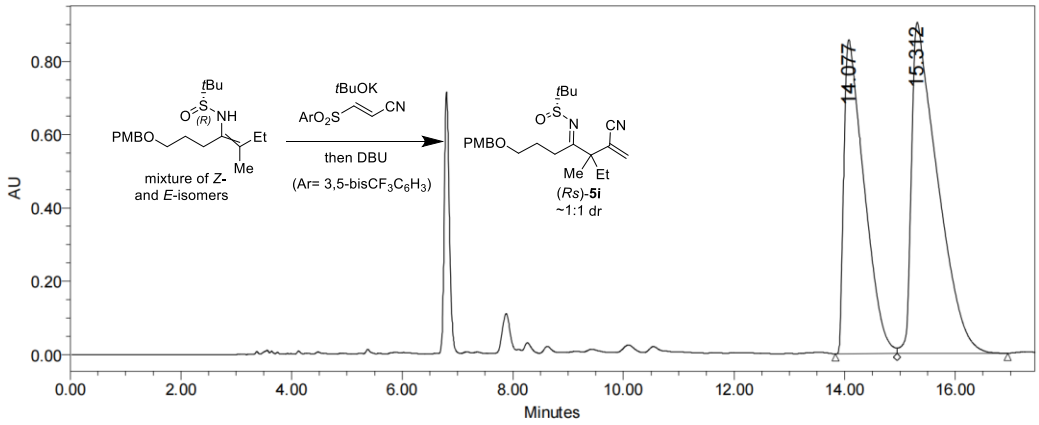


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1293; Processing Method: H230510A SX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.768	139726	2.97	6328
2	W2489 ChA 254nm	19.678	4570911	97.03	190528

(*Rs*)-**5i**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 87:13 (v/v), 1.0 mL/min, 254 nm, 40 °C.

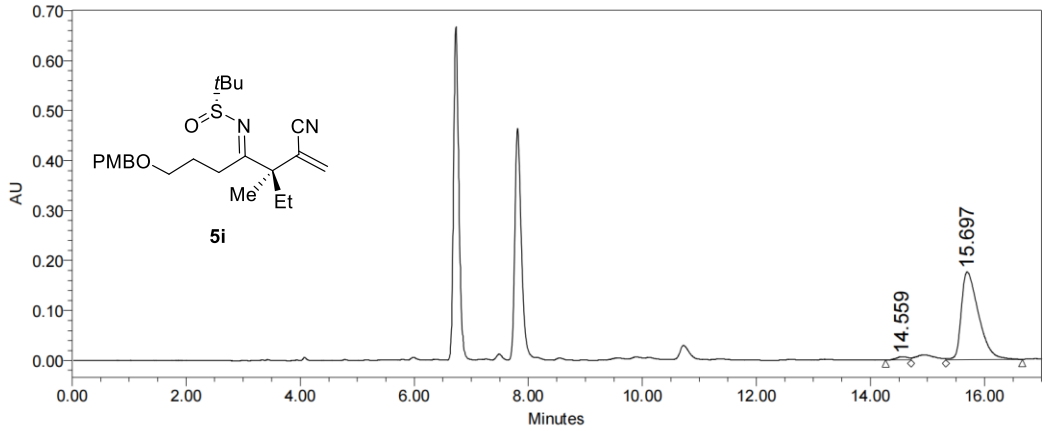


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1803; Processing Method: H230630DP 87 13 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.077	21795480	42.41	856224
2	W2489 ChA 254nm	15.312	29602331	57.59	902896

HPLC chromatogramfor dr determination of crude **5i**

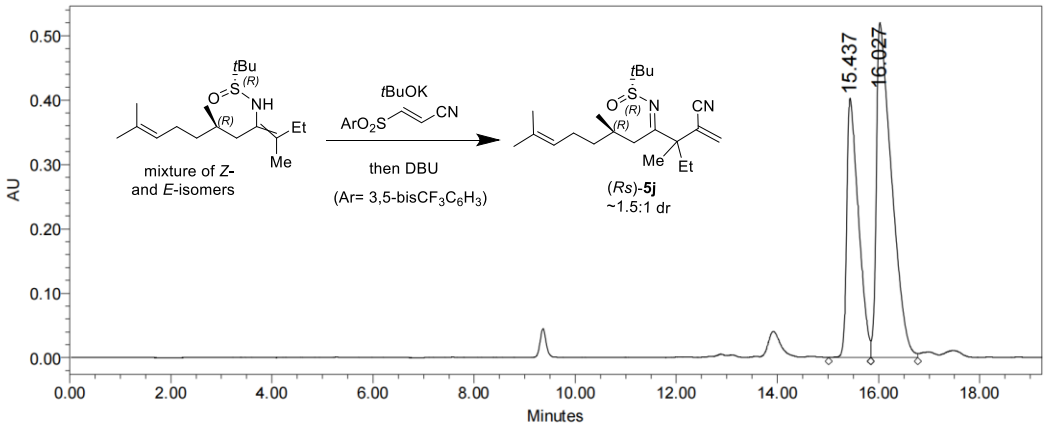


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1820; Processing Method: H230718E SX 87 13 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.559	91885	2.45	6258
2	W2489 ChA 254nm	15.697	3662140	97.55	175507

(*Rs*)-**5j**: HPLC conditions: Daicel Chiralcel IF-3 column, *n*-hexane/2-propanol = 98:02 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

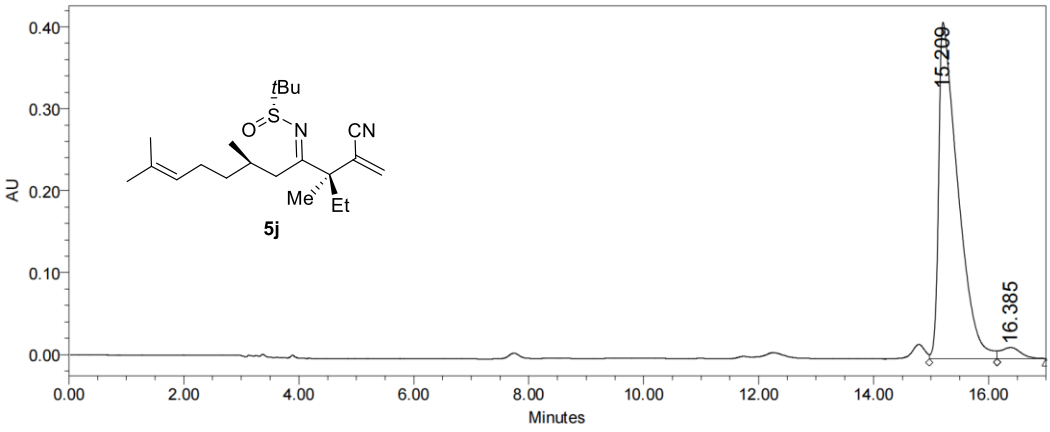


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5444; Processing Method: H230619DP XX 98 02 254 40 IF

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.437	6465505	37.28	402728
2	W2489 ChA 254nm	16.027	10879156	62.72	519789

HPLC chromatogramfor dr determination of crude **5j**

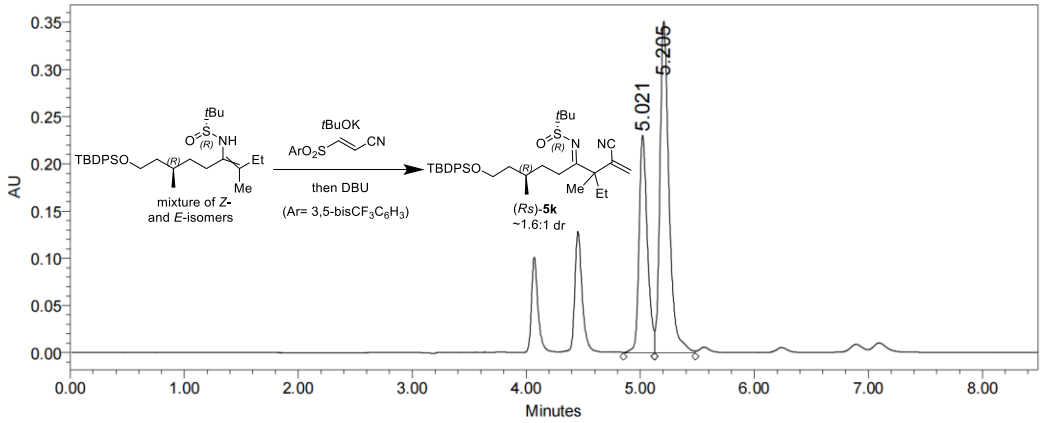


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1653; Processing Method: H230619B SX 98 02 254 40 IF

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.209	9461237	96.64	410186
2	W2489 ChA 254nm	16.385	329344	3.36	13585

(*Rs*)-**5k**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 95:05 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

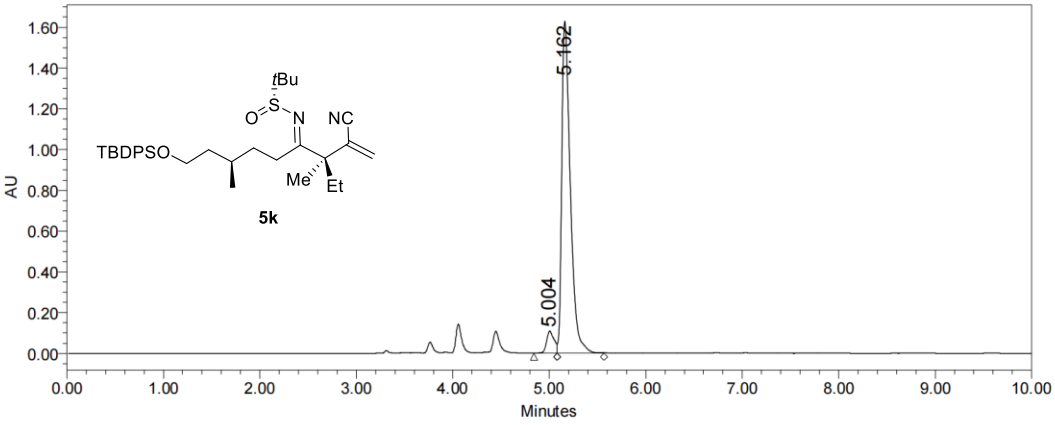


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1343; Processing Method: H230516DP XX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.021	1160745	37.30	230475
2	W2489 ChA 254nm	5.205	1950781	62.70	350999

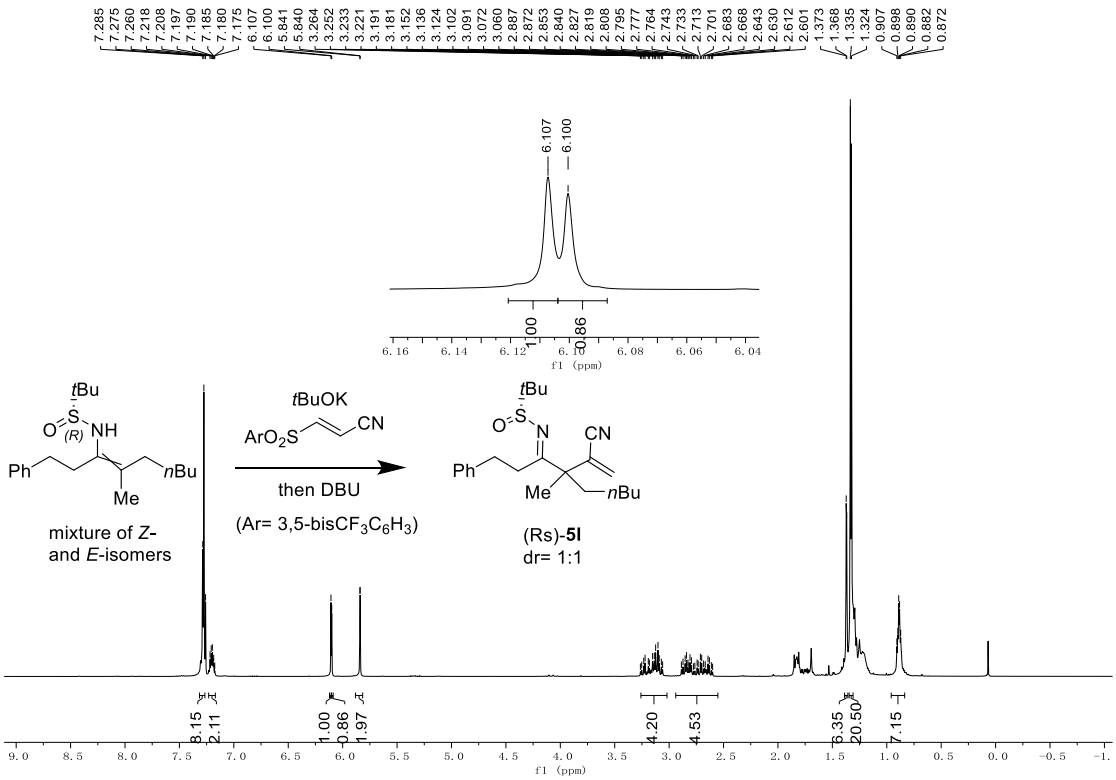
HPLC chromatogramfor dr determination of crude **5k**



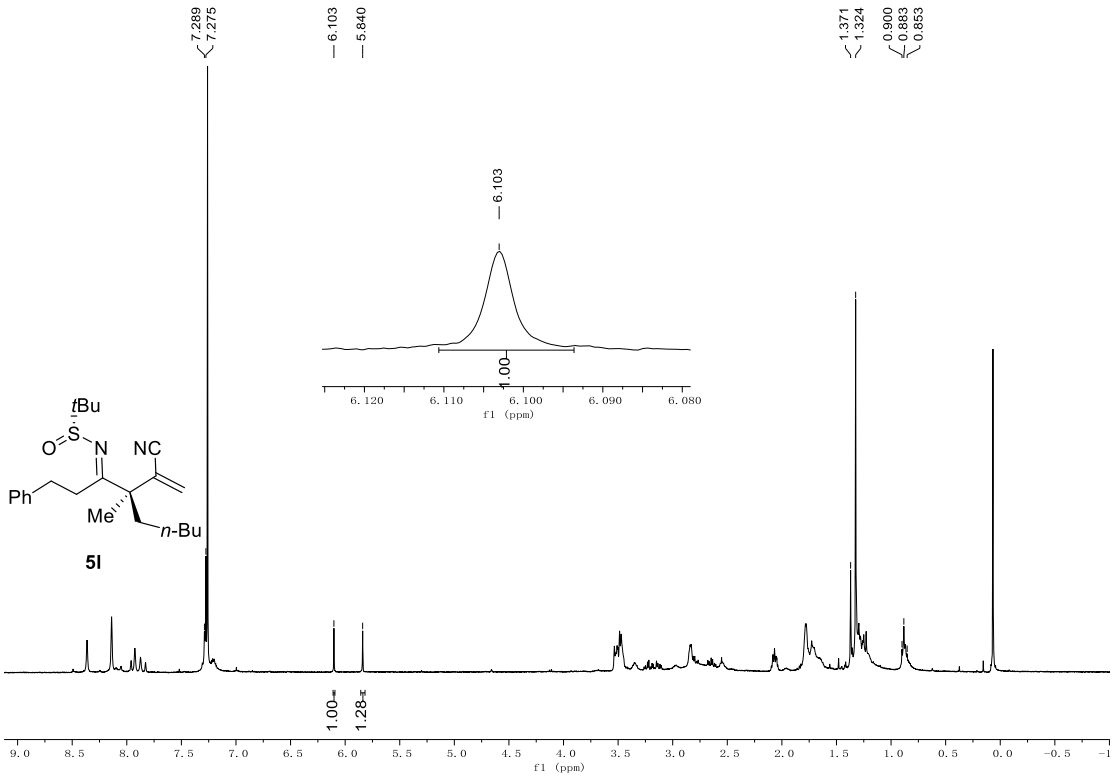
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1488; Processing Method: H0515C SX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.004	592618	5.60	108175
2	W2489 ChA 254nm	5.162	9994755	94.40	1627822

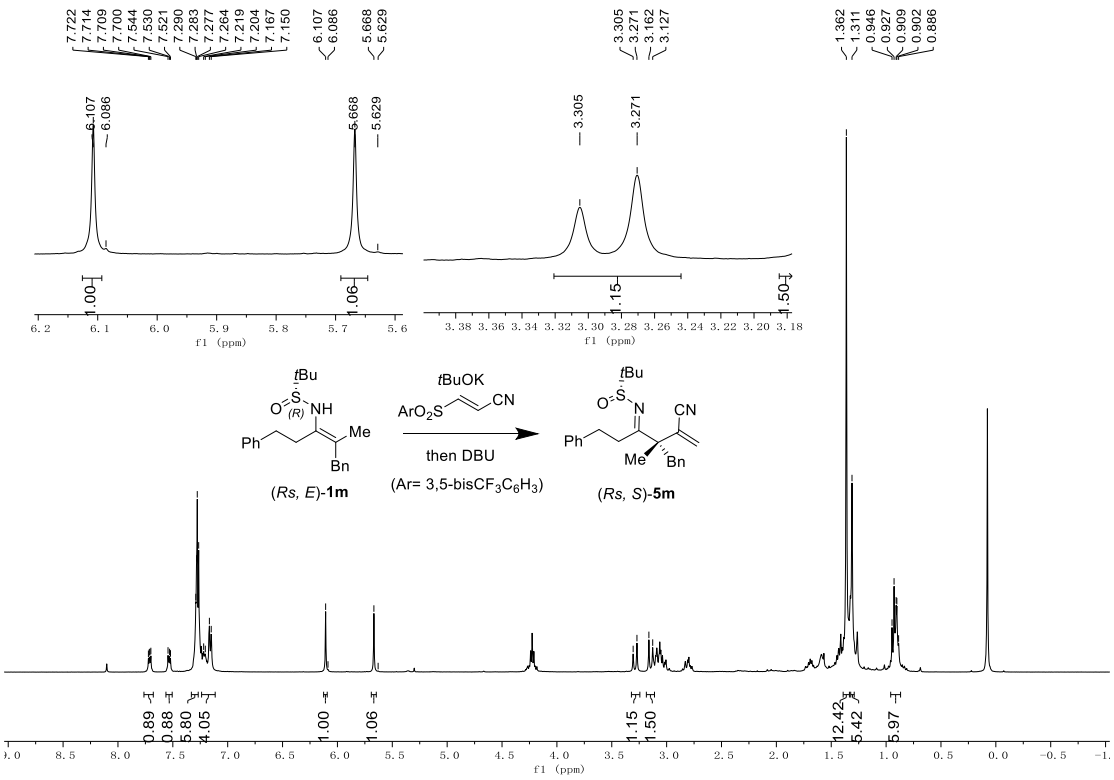


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5l** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio

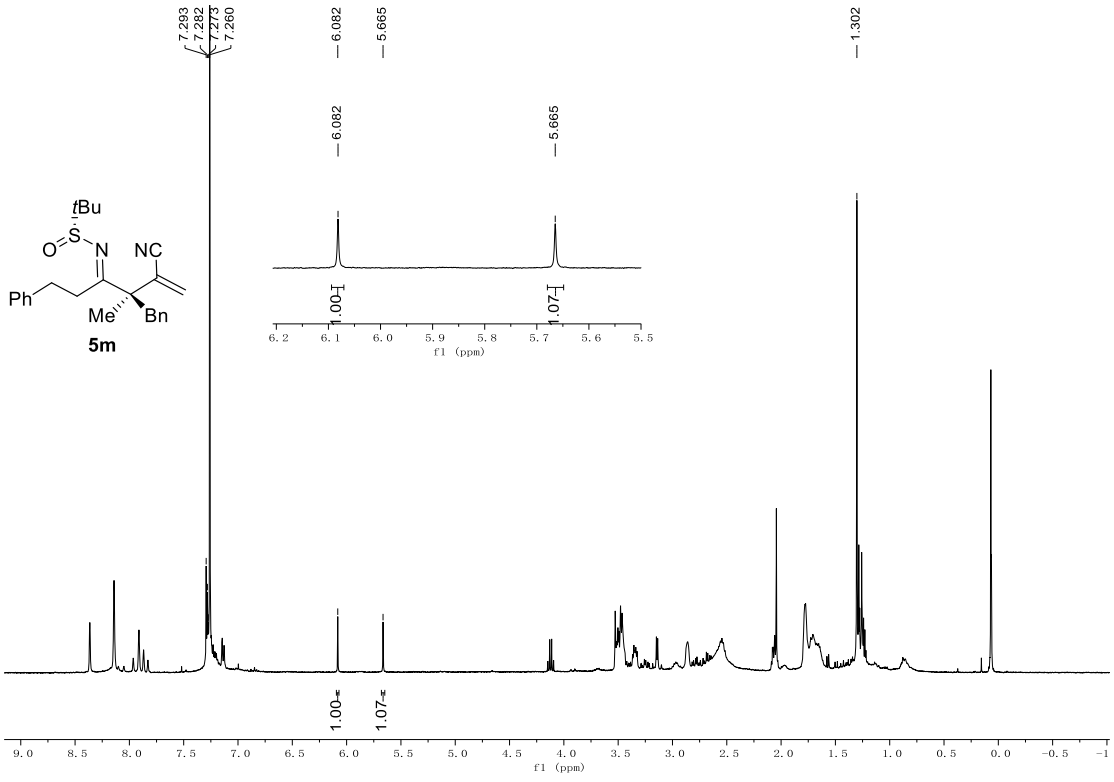


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5l** (dr > 20:1)

(No observable presence of the minor diastereomer)



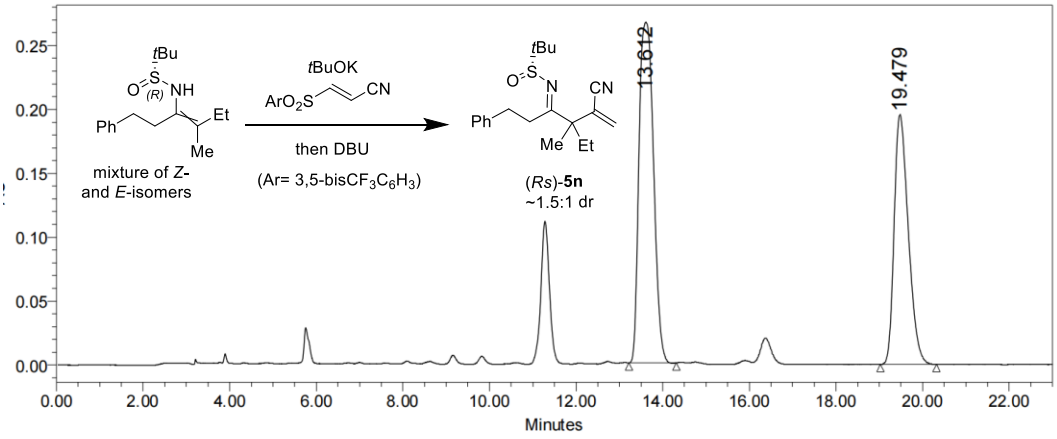
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs, S*)-**5m** that was intentionally prepared by using geometric isomer (*Rs, E*)-**1m** and was used to identify the diagnostic peak(s) of the minor diastereomer



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5m** (dr > 20:1)

(No observable presence of the minor diastereomer)

(*Rs*)-**5n**: HPLC conditions: Daicel Chiralcel IC-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

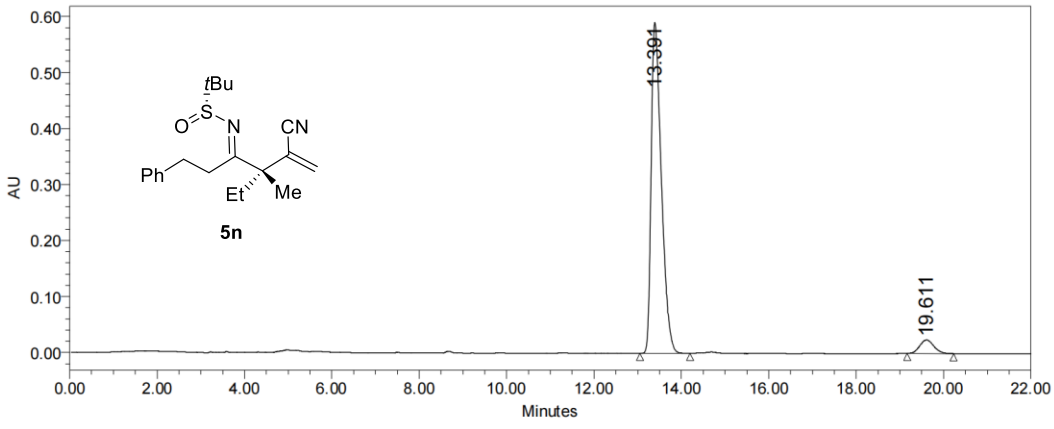


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1281; Processing Method: H230511EP XX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.612	6192435	58.32	266555
2	W2489 ChA 254nm	19.479	4425000	41.68	195473

HPLC chromatogramfor dr determination of crude **5n**

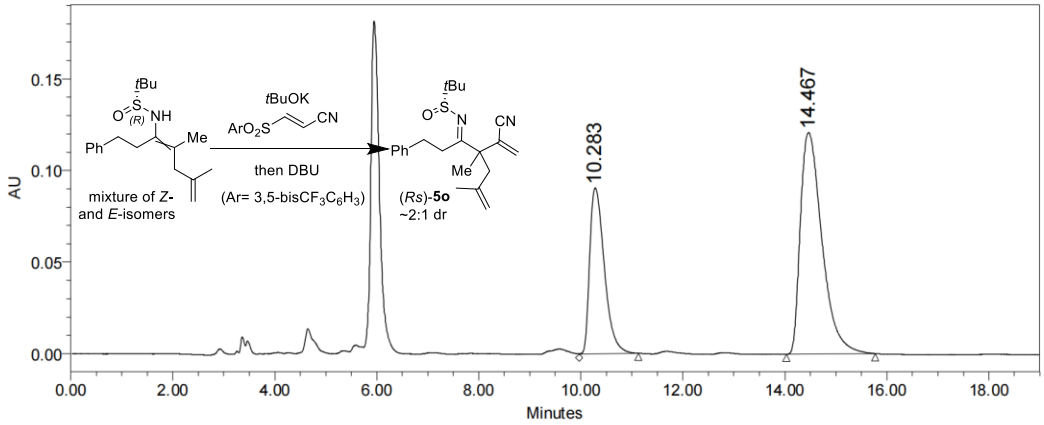


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1918; Processing Method: 5N SX 90 10 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.391	9558275	94.60	590574
2	W2489 ChA 254nm	19.611	545500	5.40	24224

(*Rs*)-**5o**: HPLC conditions: Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 95:05 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

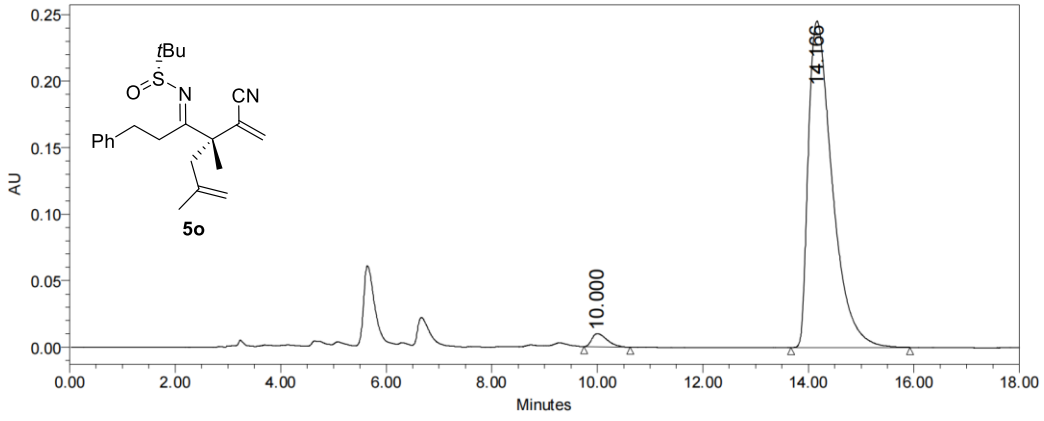


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1506; Processing Method: H0529GP XX 95 05 254 40 AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.283	1798889	33.55	90458
2	W2489 ChA 254nm	14.467	3563376	66.45	120912

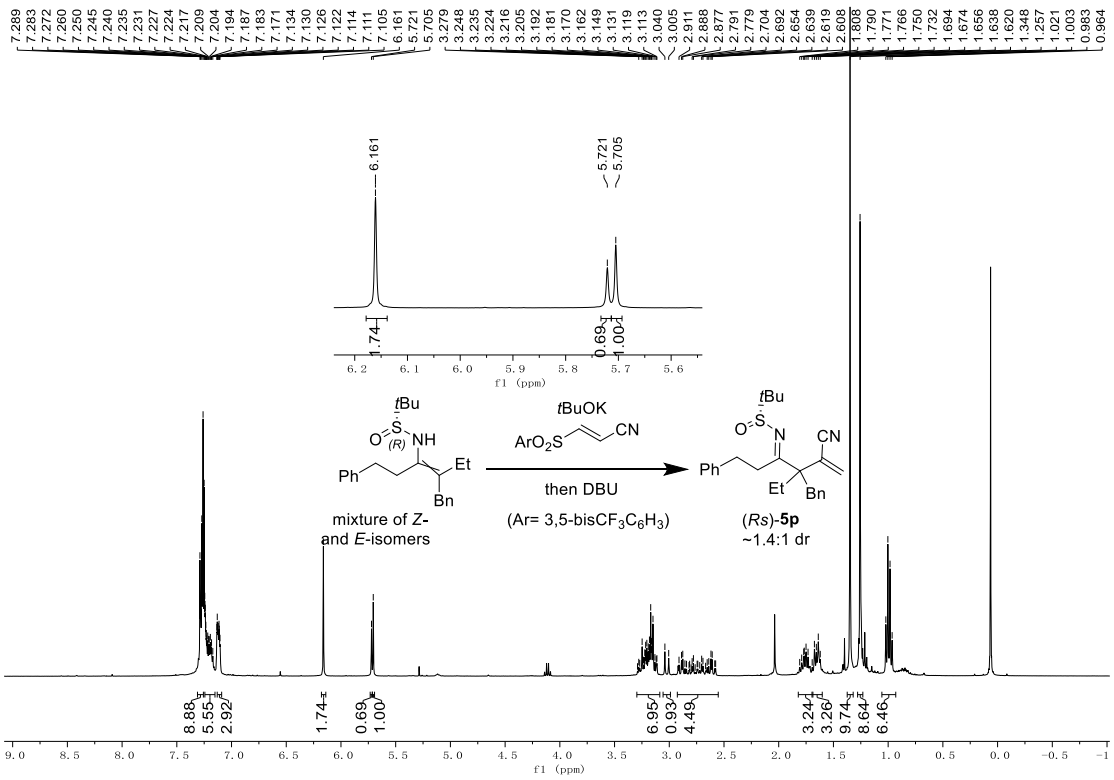
HPLC chromatogramfor dr determination of crude **5o**



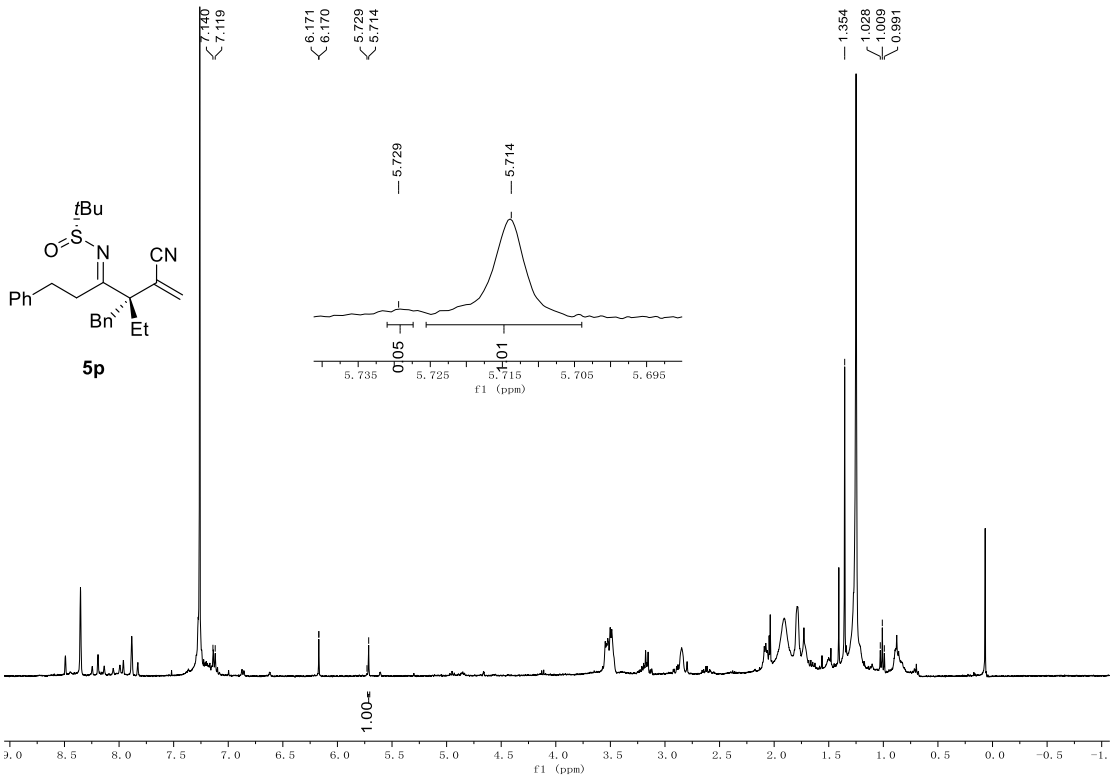
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1610; Processing Method: H230529EP SX 95 05 254 40 AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.000	199039	2.51	9912
2	W2489 ChA 254nm	14.166	7728592	97.49	245373

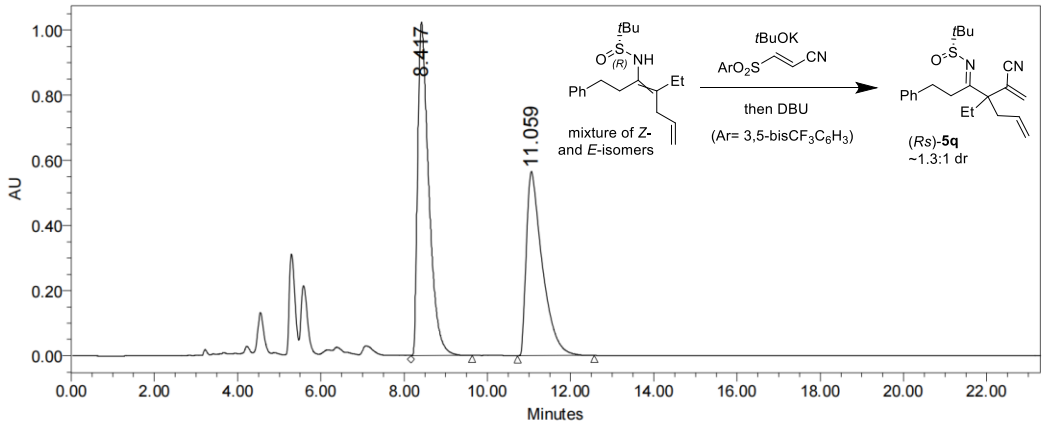


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5p** with low diastereoselectivity (dr ~ 1.4:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5p** (dr = 20:1)

(*Rs*)-**5q**: HPLC conditions: Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

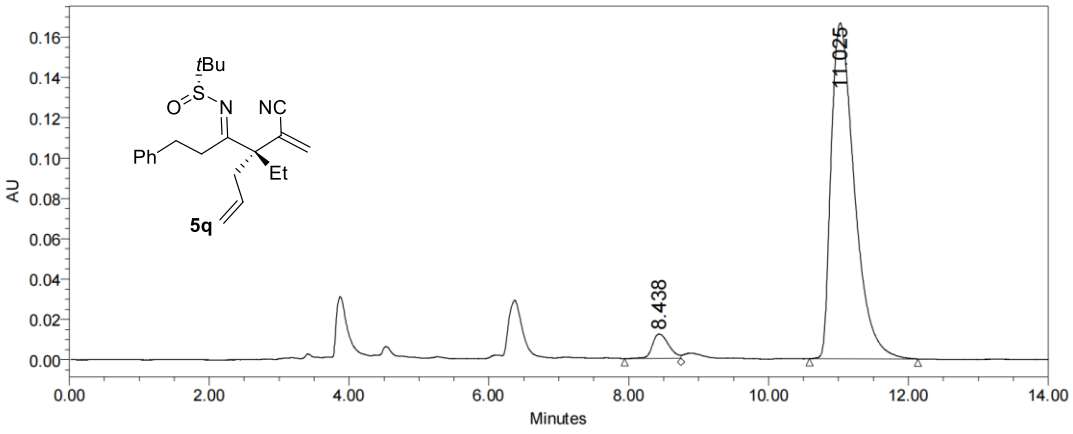


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1472; Processing Method: H23602DP XX 90 10 254 40 AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.417	19192606	56.14	1022940
2	W2489 ChA 254nm	11.059	14997089	43.86	564974

HPLC chromatogramfor dr determination of crude **5q**

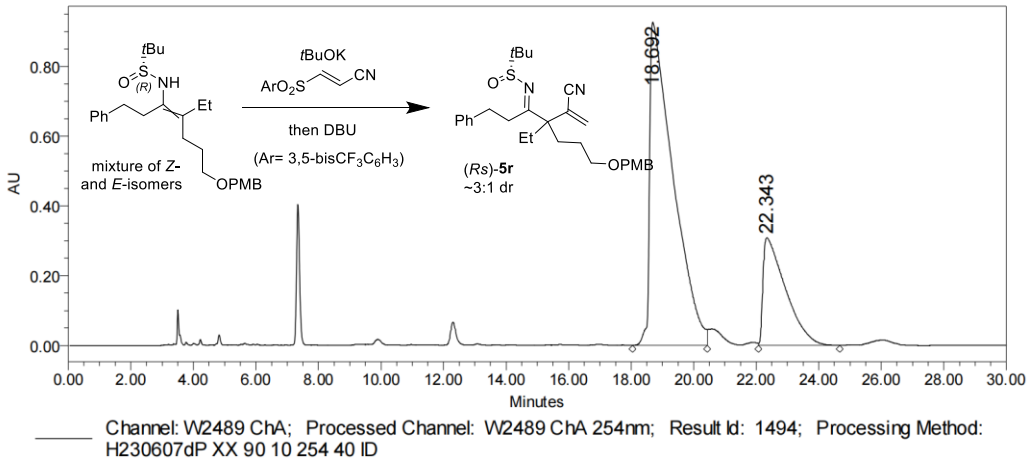


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1523; Processing Method: H230612E SX 90 10 254 40AD

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.438	196470	4.86	12085
2	W2489 ChA 254nm	11.025	3849597	95.14	166444

(*Rs*)-**5r**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

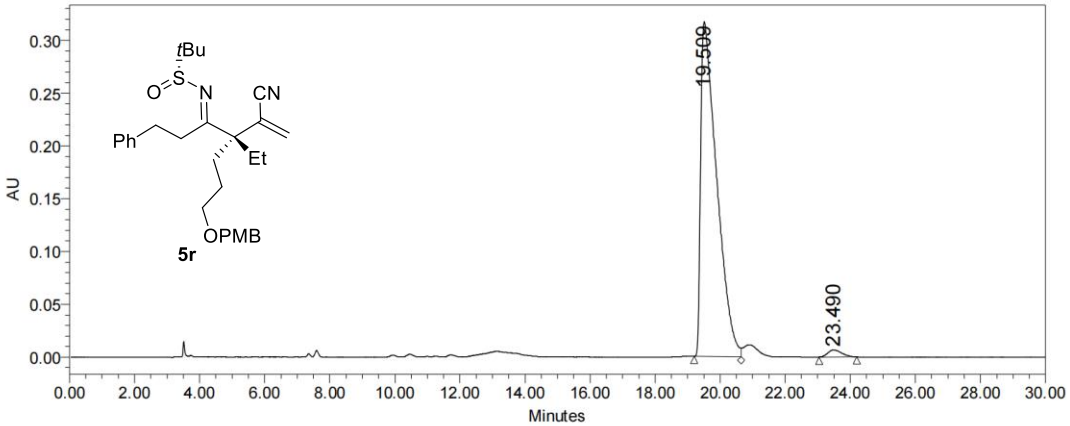


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1494; Processing Method: H230607dP XX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	18.692	48187808	75.80	925777
2	W2489 ChA 254nm	22.343	15384539	24.20	308430

HPLC chromatogramfor dr determination of crude **5r**

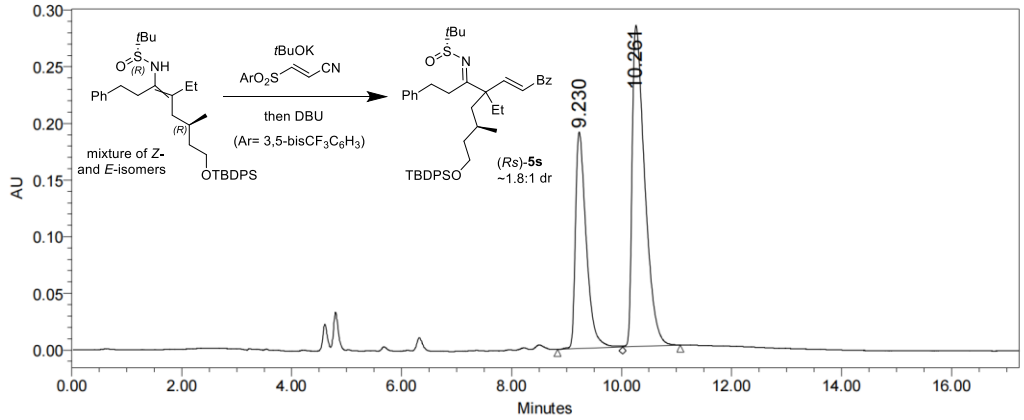


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1496; Processing Method: H230601B SX 90 10 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.509	10825118	98.20	316809
2	W2489 ChA 254nm	23.490	198249	1.80	6679

(*Rs*)-**5s**: HPLC conditions: Daicel Chiralcel ID-3 column, *n*-hexane/2-propanol = 95:05 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

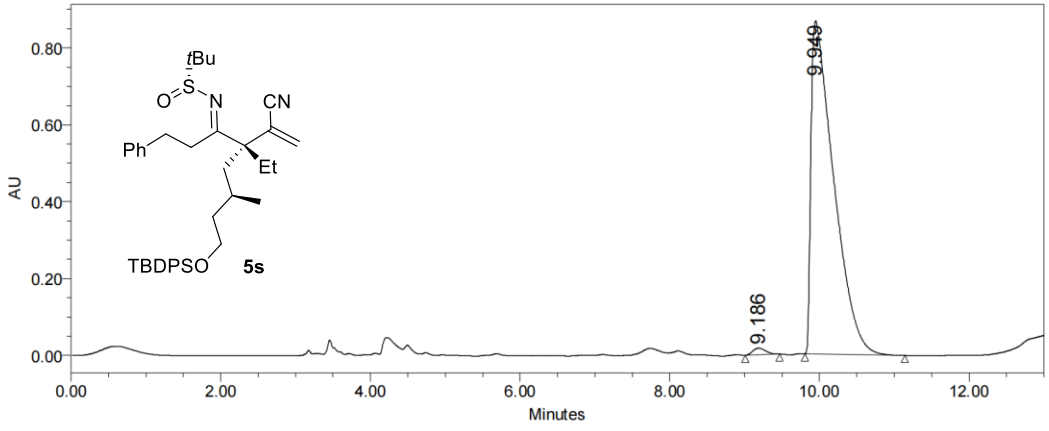


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1806; Processing Method: H230613DP XX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.230	2605796	36.71	191229
2	W2489 ChA 254nm	10.261	4492220	63.29	283530

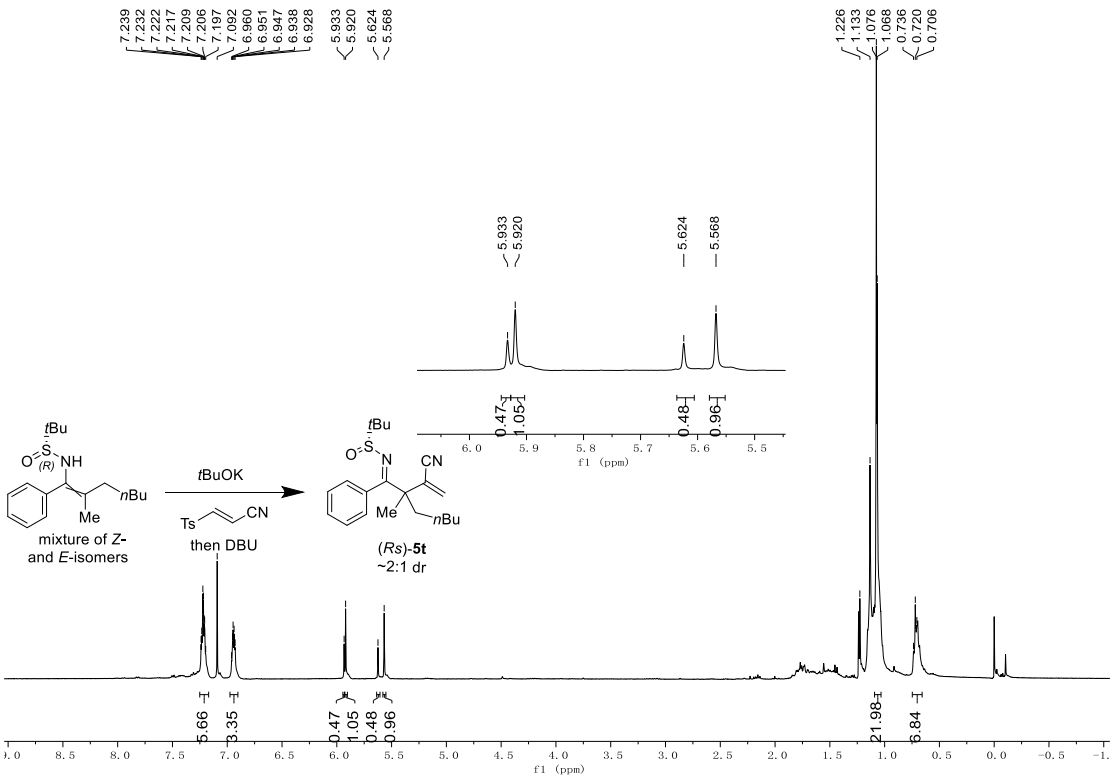
HPLC chromatogramfor dr determination of crude **5s**



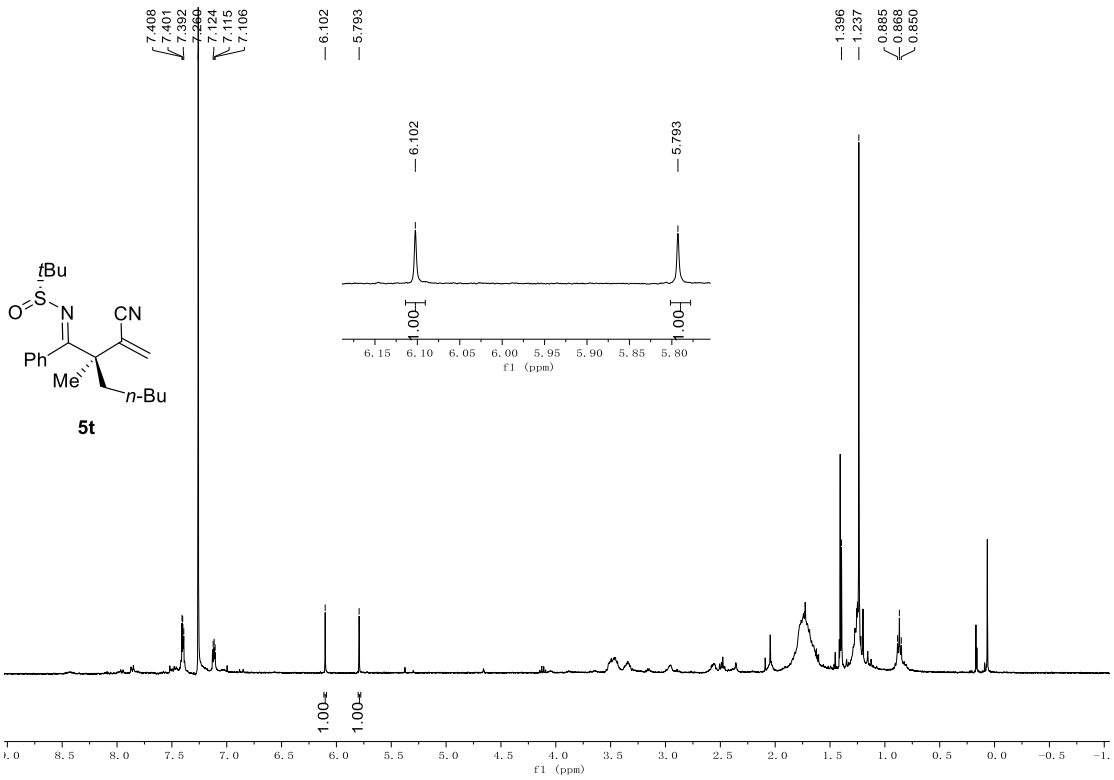
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1824; Processing Method: H230616D SX 95 05 254 40 ID

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.186	203648	1.10	17127
2	W2489 ChA 254nm	9.949	18252508	98.90	865368



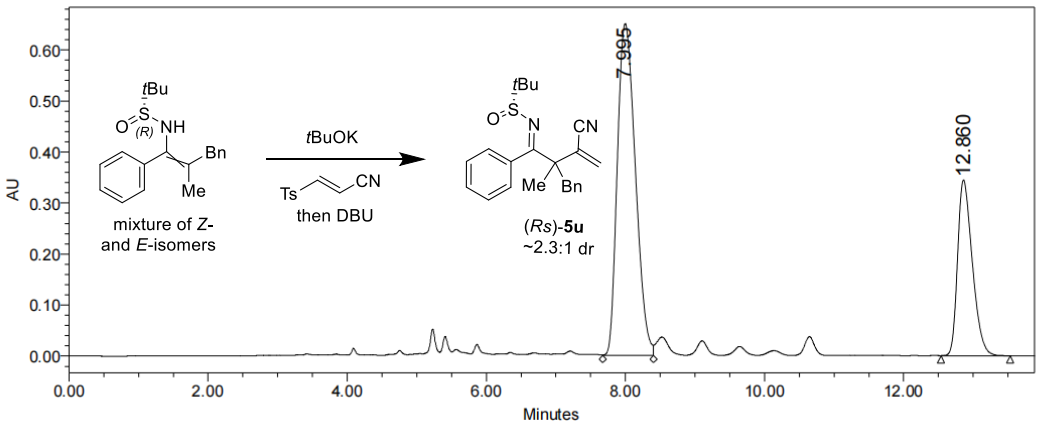
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5t** with low diastereoselectivity (dr ~ 2:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z*/*E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5t** (dr > 20:1)

(No observable presence of the minor diastereomer)

(*Rs*)-**5u**: HPLC conditions: Daicel Chiralcel IG-3 column, *n*-hexane/2-propanol = 80:20 (v/v), 1.0 mL/min, 254 nm, 40 °C.

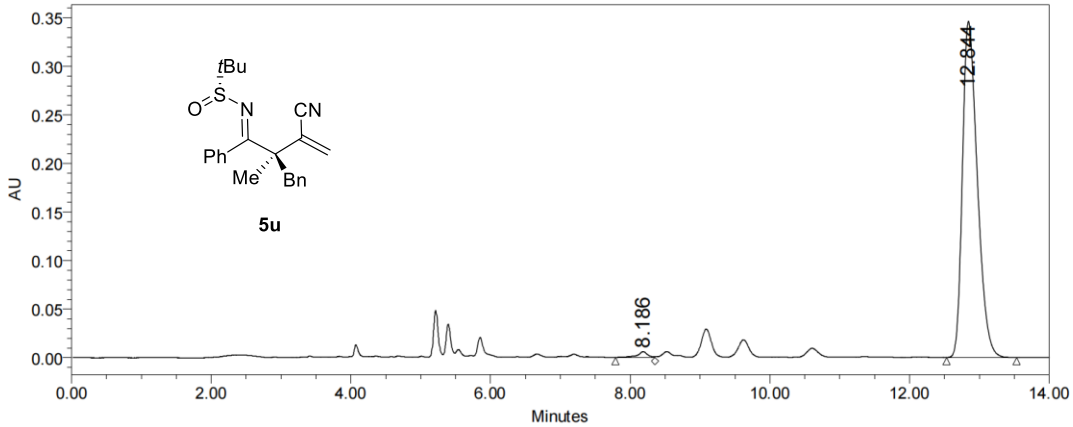


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2005; Processing Method: 0628BP XX 5U 80 20 254 40 IG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.995	11714063	69.84	650327
2	W2489 ChA 254nm	12.860	5059252	30.16	344580

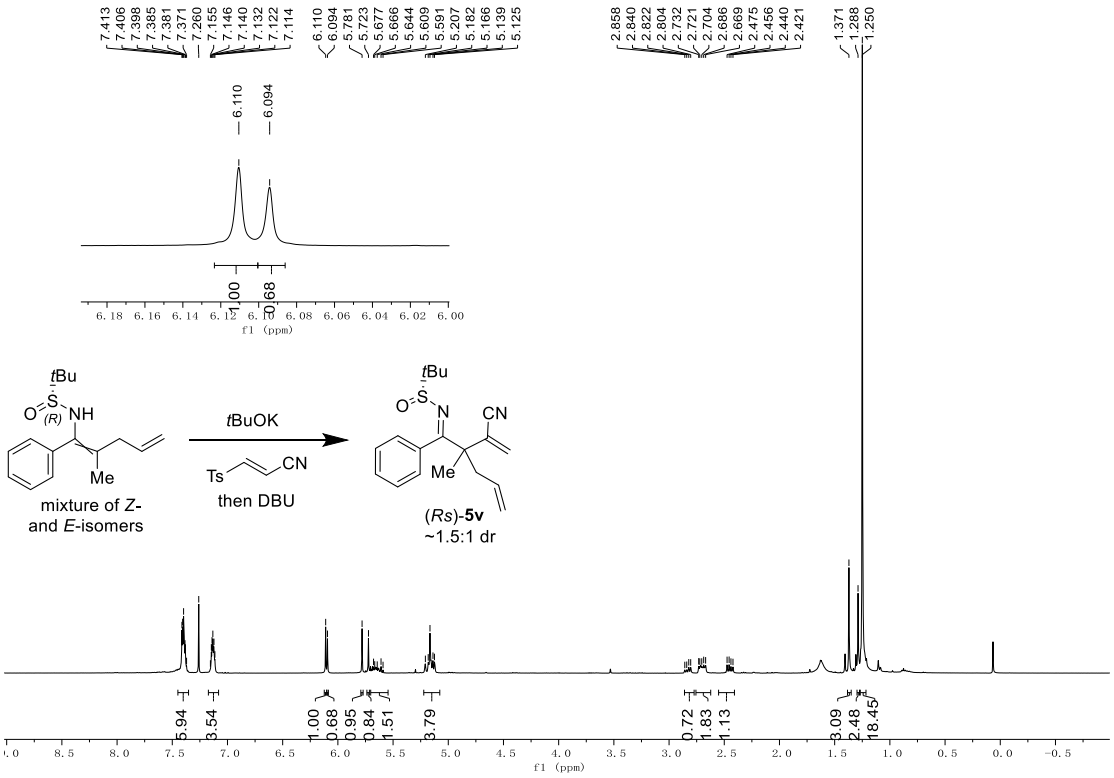
HPLC chromatogramfor dr determination of crude **5u**



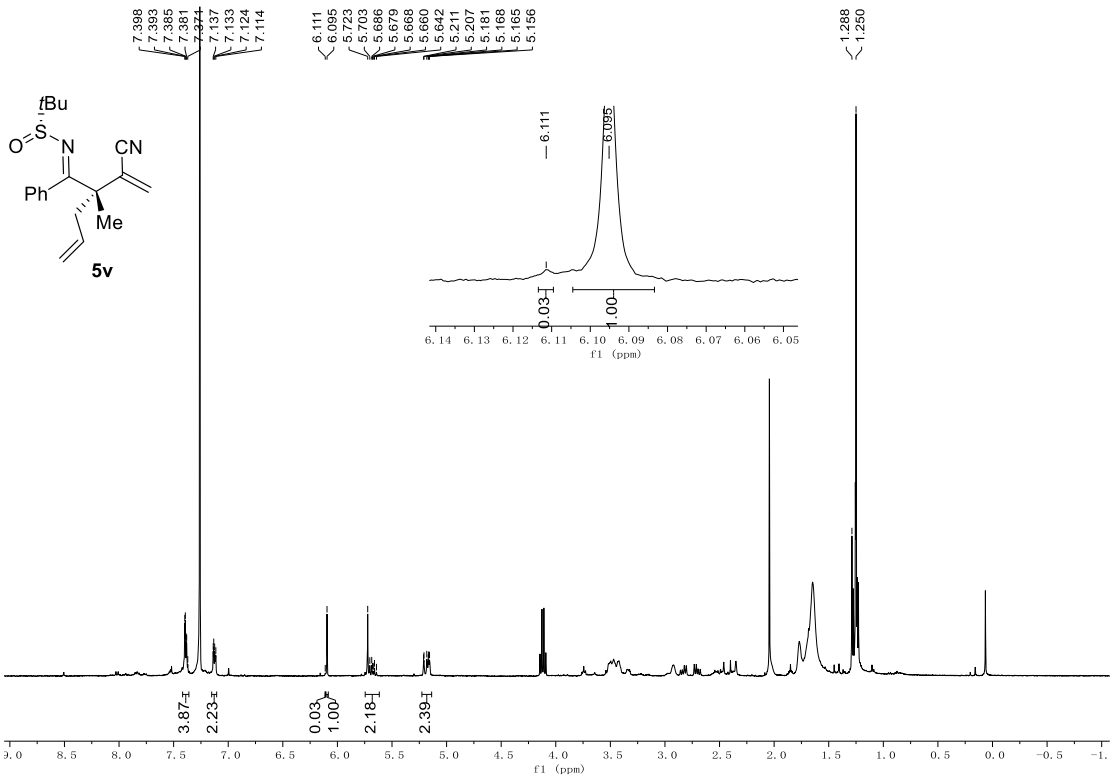
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1998; Processing Method: SX 5U 80 20 254 40 IG

Processed Channel Descr.: W2489 ChA 254nm

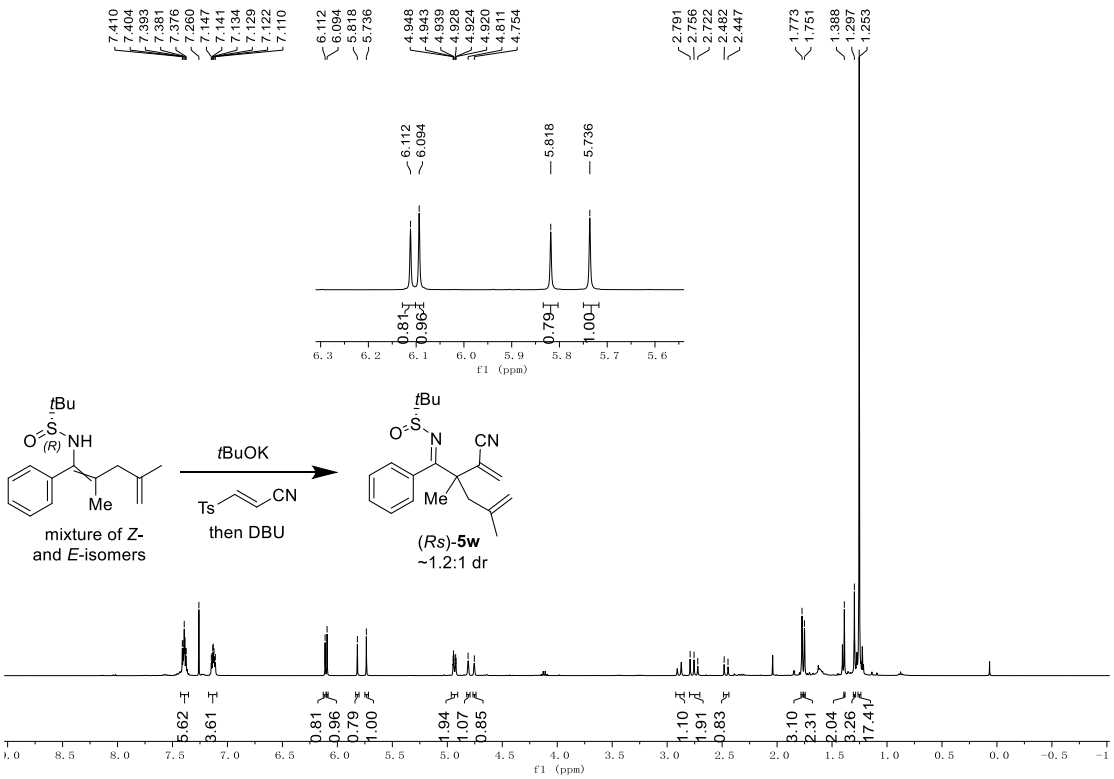
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.186	62358	1.20	5904
2	W2489 ChA 254nm	12.844	5117052	98.80	346247



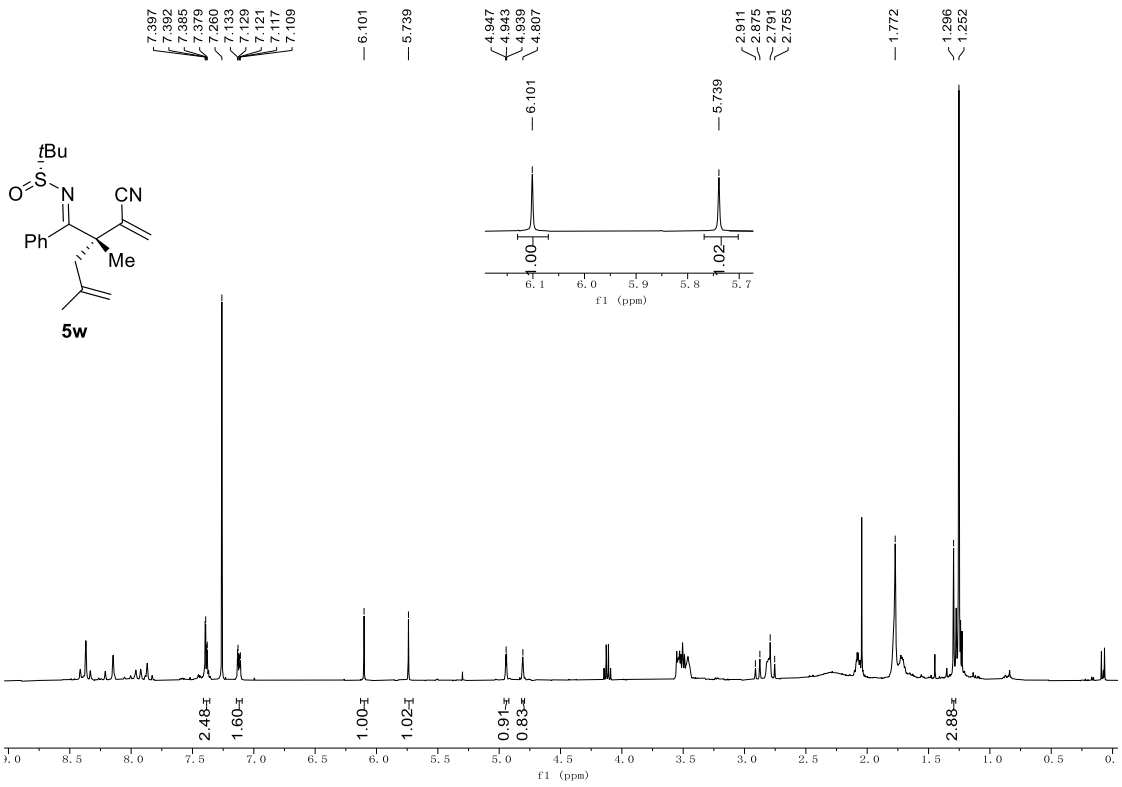
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5v** with low diastereoselectivity (dr ~ 1.5:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5v** (dr > 20:1)



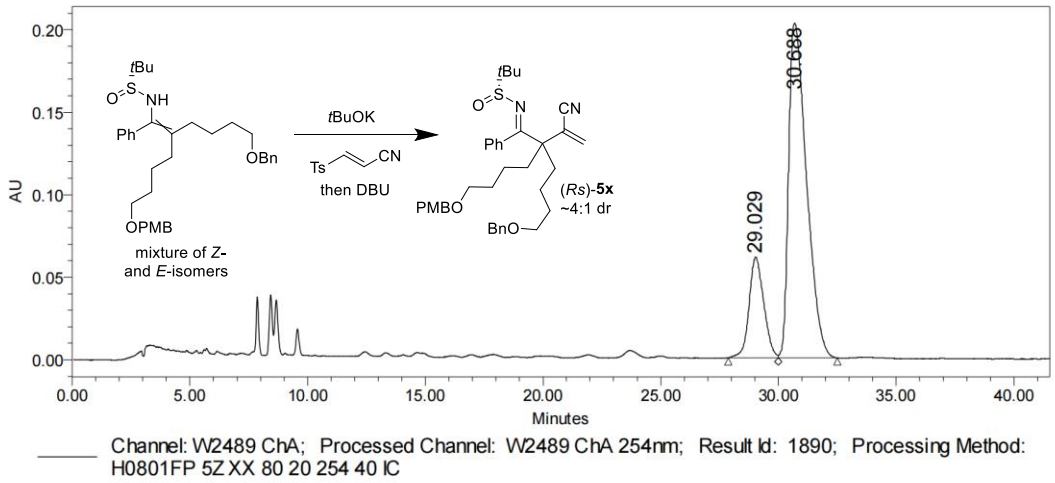
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (*Rs*)-**5w** with low diastereoselectivity (dr ~ 1:1) intentionally prepared using the corresponding enesulfinamide sample with low *Z/E* ratio



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5w** (dr > 20:1)

(No observable presence of the minor diastereomer)

(*Rs*)-**5x**: HPLC conditions: Daicel Chiralcel IC-3 column, *n*-hexane/2-propanol = 80:20 (v/v), 1.0 mL/min, 254 nm, 40 ºC.

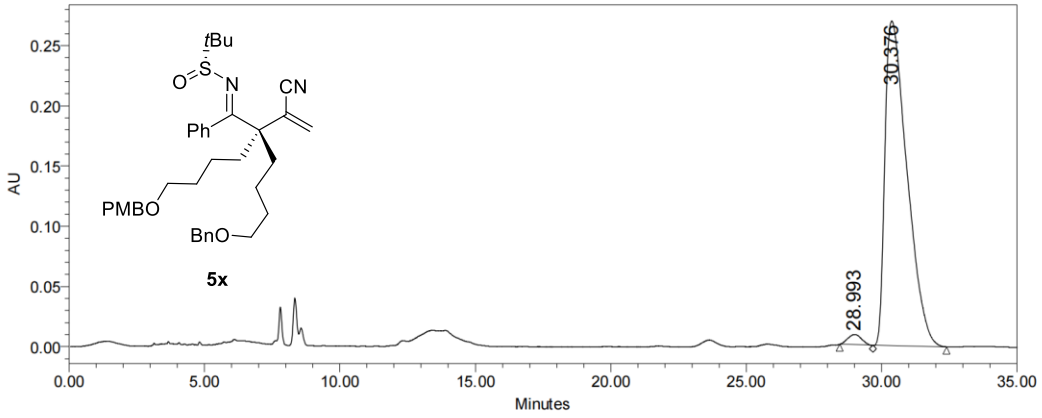


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1890; Processing Method: H0801FP 5Z XX 80 20 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	29.029	2644107	19.69	61055
2	W2489 ChA 254nm	30.688	10783573	80.31	202690

HPLC chromatogram for dr determination of crude **5x**

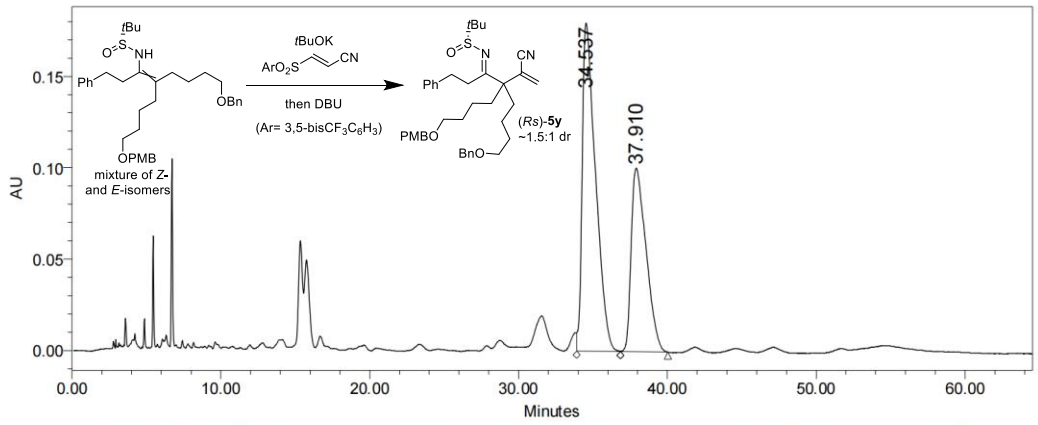


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1892; Processing Method: H0801HP 5Z SX 80 20 254 40 IC

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	28.993	296685	1.91	8444
2	W2489 ChA 254nm	30.376	15225628	98.09	269446

(*Rs*)-**5y**: HPLC conditions: Daicel Chiralcel IG-3 column, *n*-hexane/2-propanol = 85:15 (v/v), 1.0 mL/min, 254 nm, 40 °C

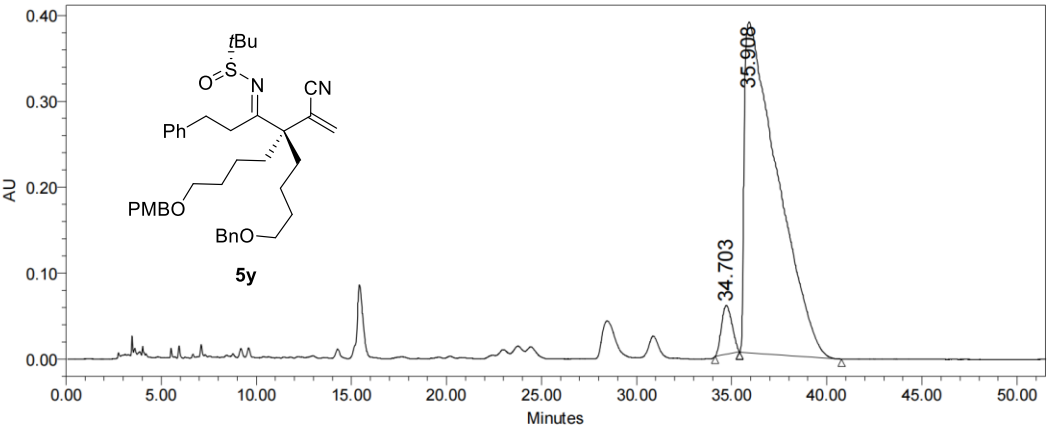


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1814; Processing Method: H230754DP XX 85 15 254 40 IG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	34.537	11172218	61.48	179531
2	W2489 ChA 254nm	37.910	6999961	38.52	100506

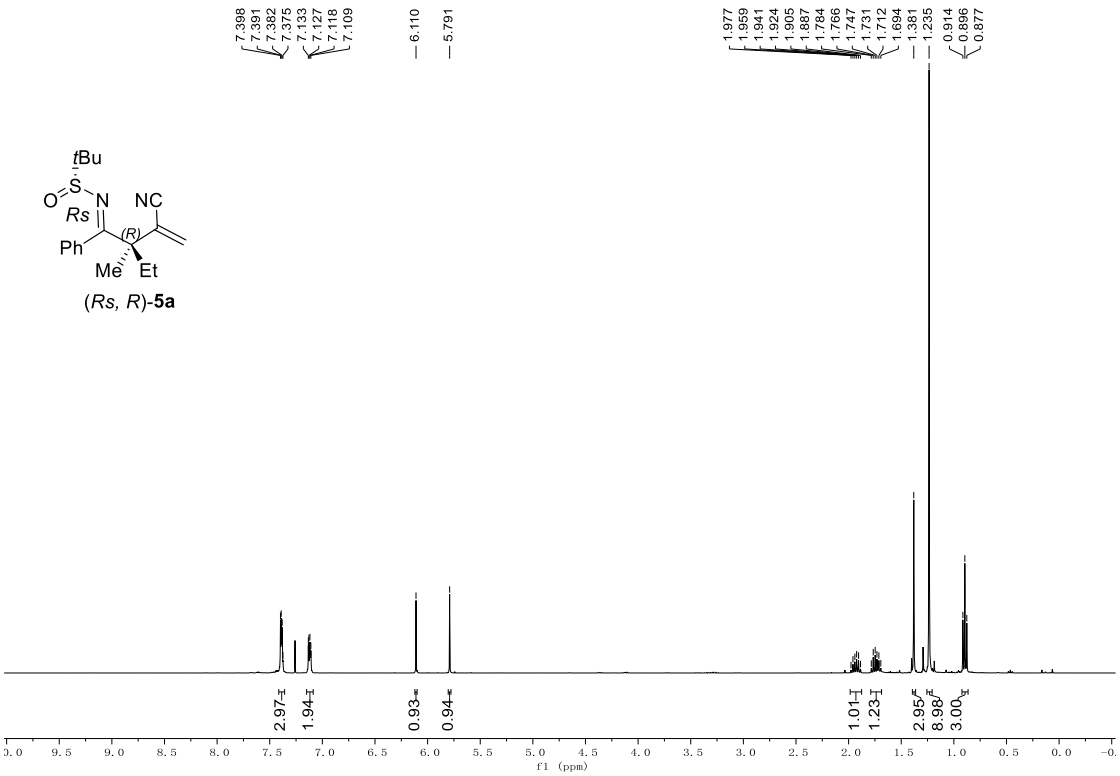
HPLC chromatogramfor dr determination of crude **5y**



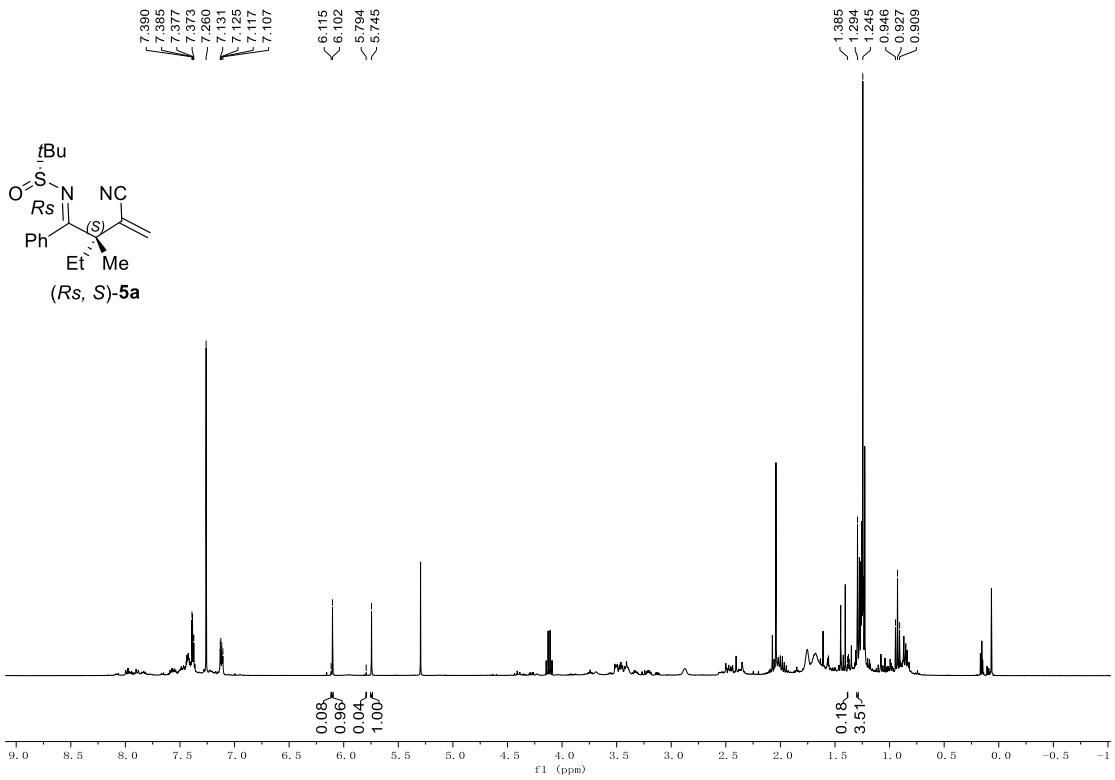
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2012; Processing Method: 5Y 85 15 254 40 IG 955 45

Processed Channel Descr.: W2489 ChA 254nm

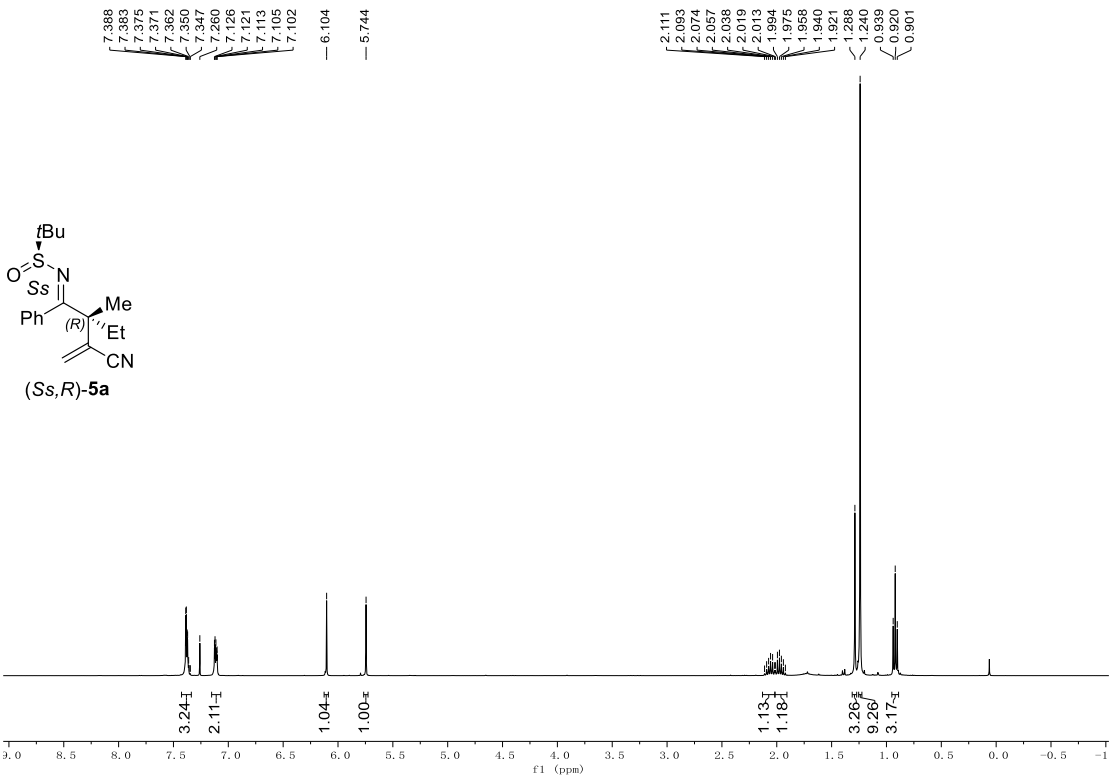
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	34.703	2207891	4.52	56966
2	W2489 ChA 254nm	35.908	46612978	95.48	384710



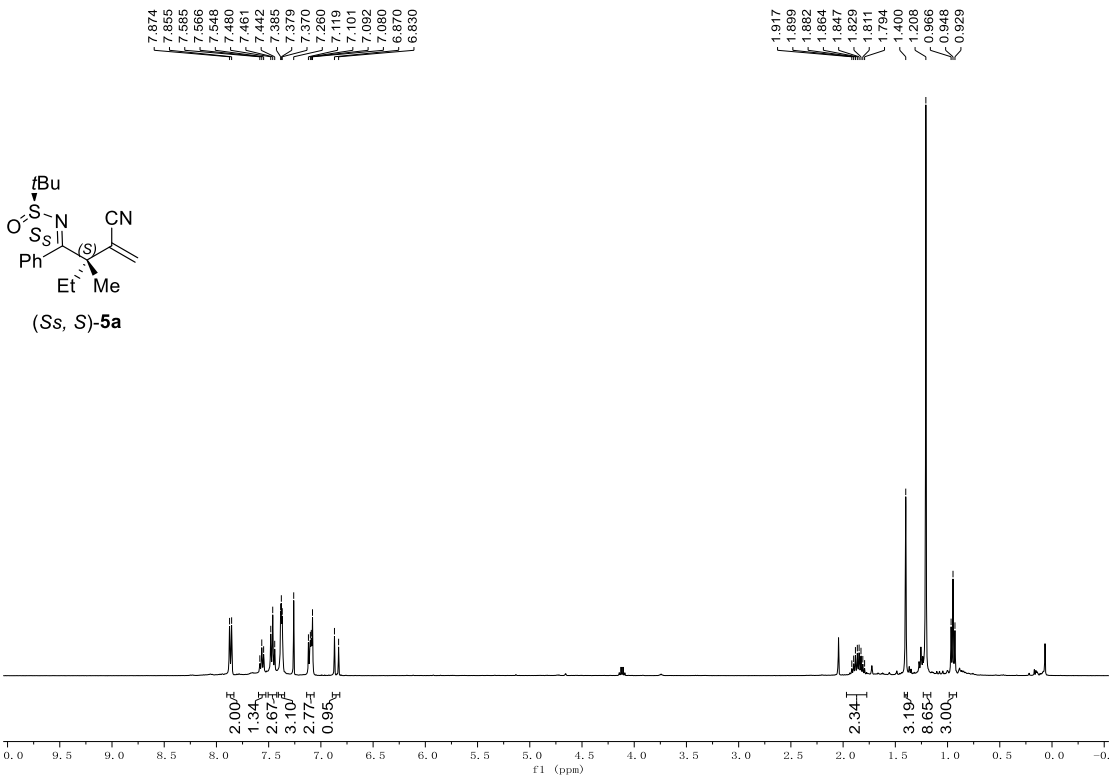
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Rs*, *R*)-**5a** that was used to identify the diagnostic peak(s) of the minor diastereomer



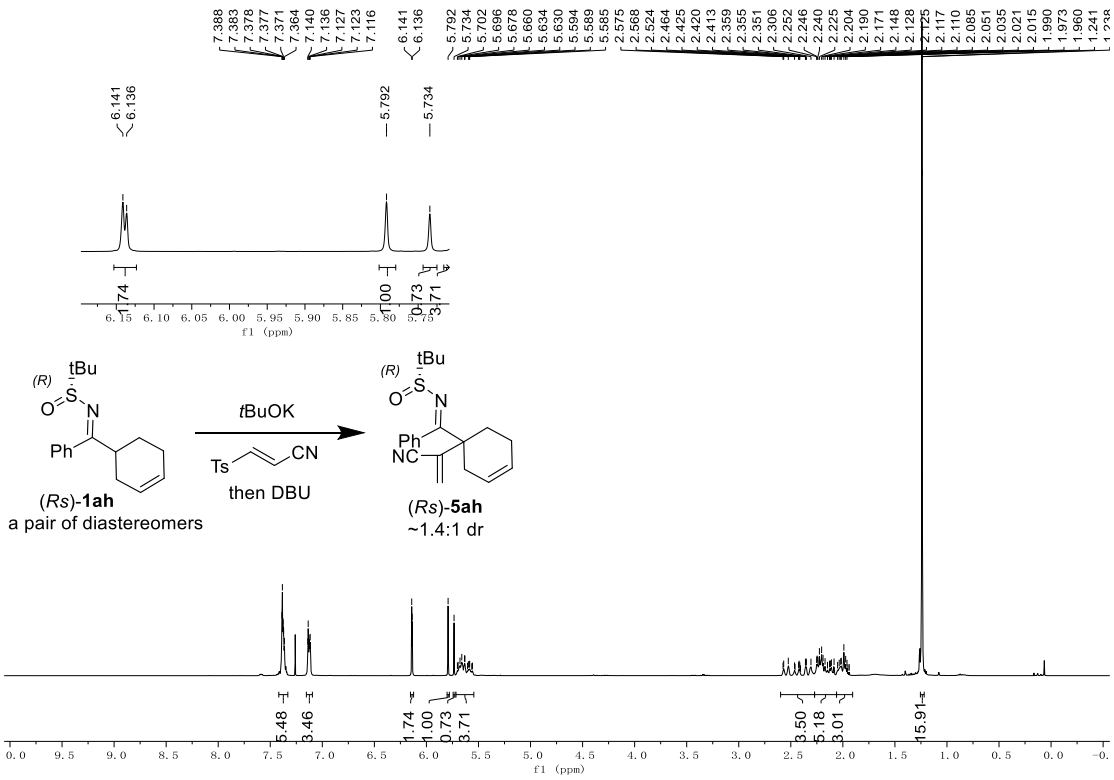
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Rs*, *S*)-**5a** (dr >20:1; Scheme 5)



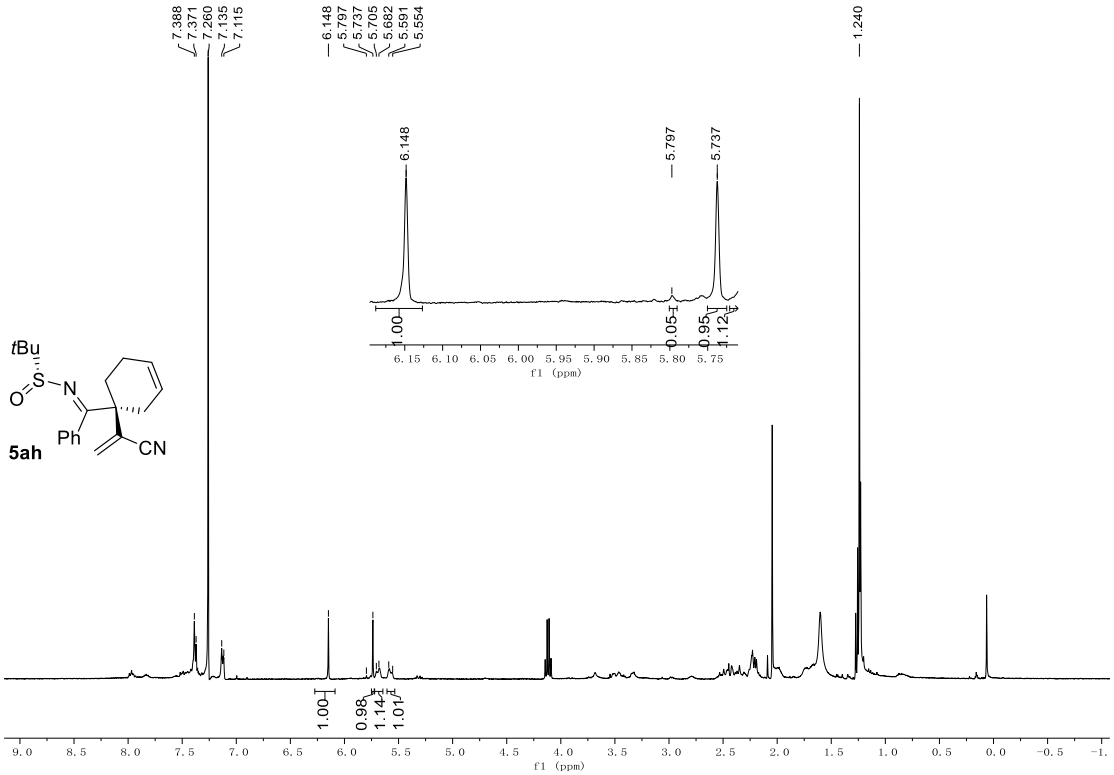
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the diastereomer (*Ss, R*)-**5a** that was used to identify the diagnostic peak(s) of the minor diastereomer



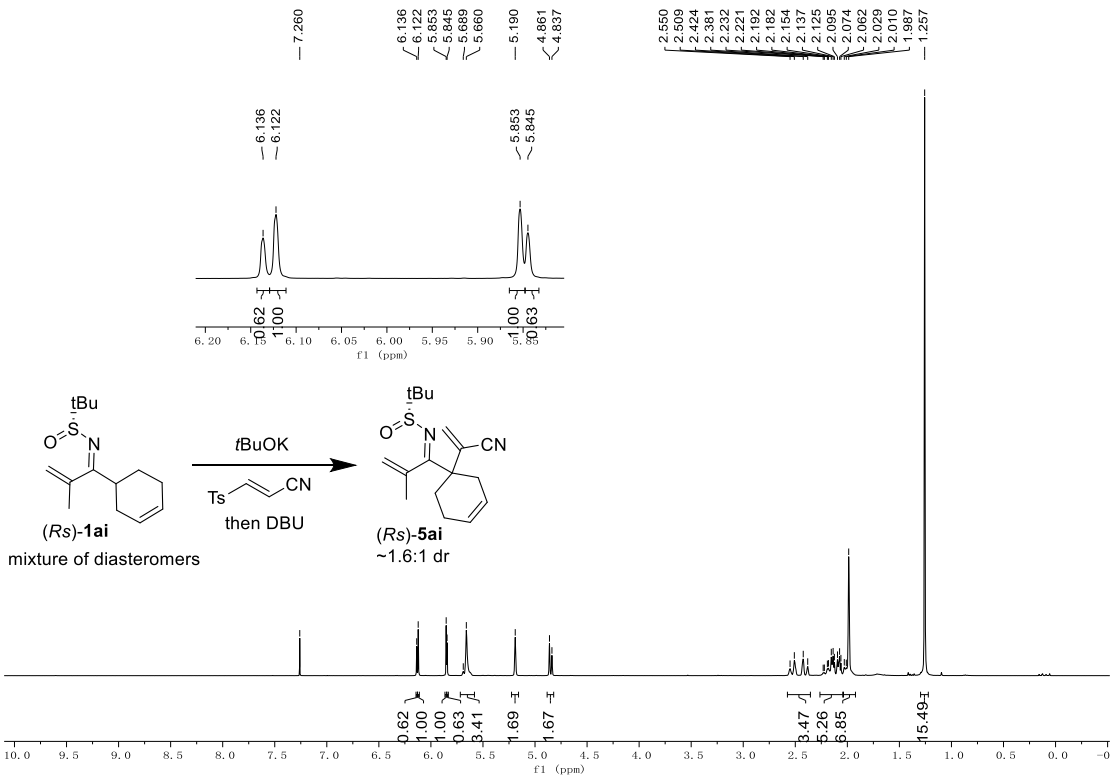
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of (*Ss*, *S*)-**5a** (dr > 20:1, Scheme 5)



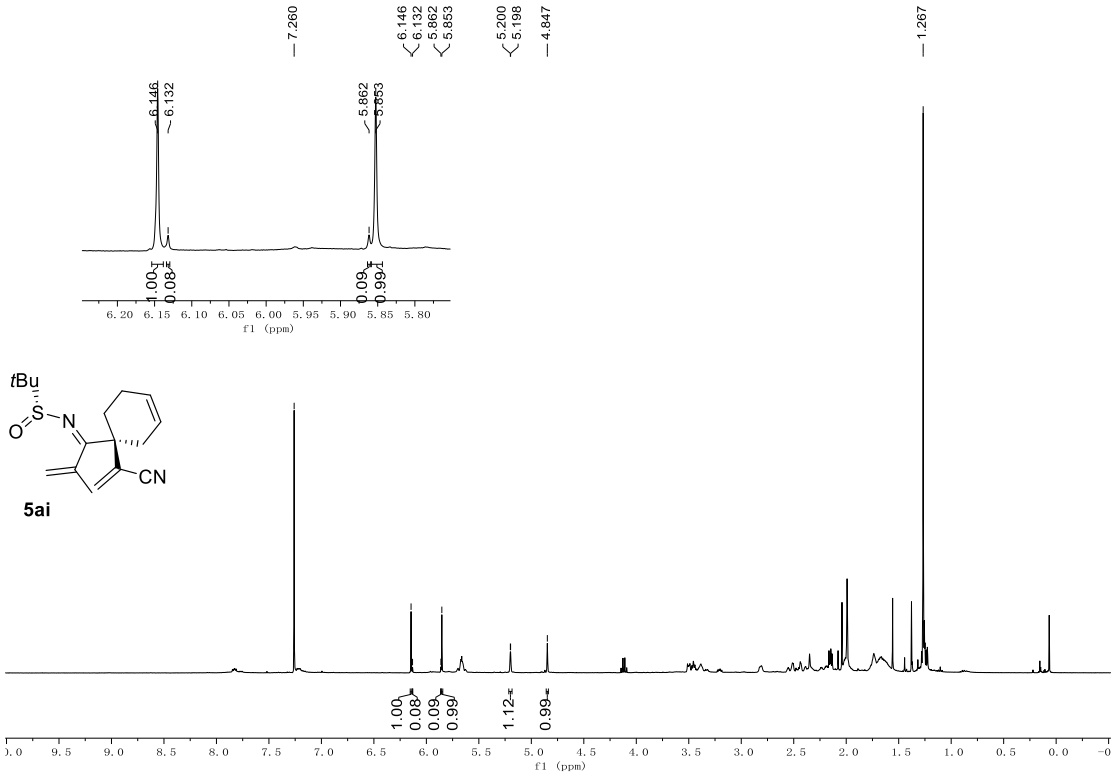
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**5ah** and (R_S, 2*R*)-**5ah** (~1.4:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ah** and (*Rs*,2*R*)-**1ah** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis)



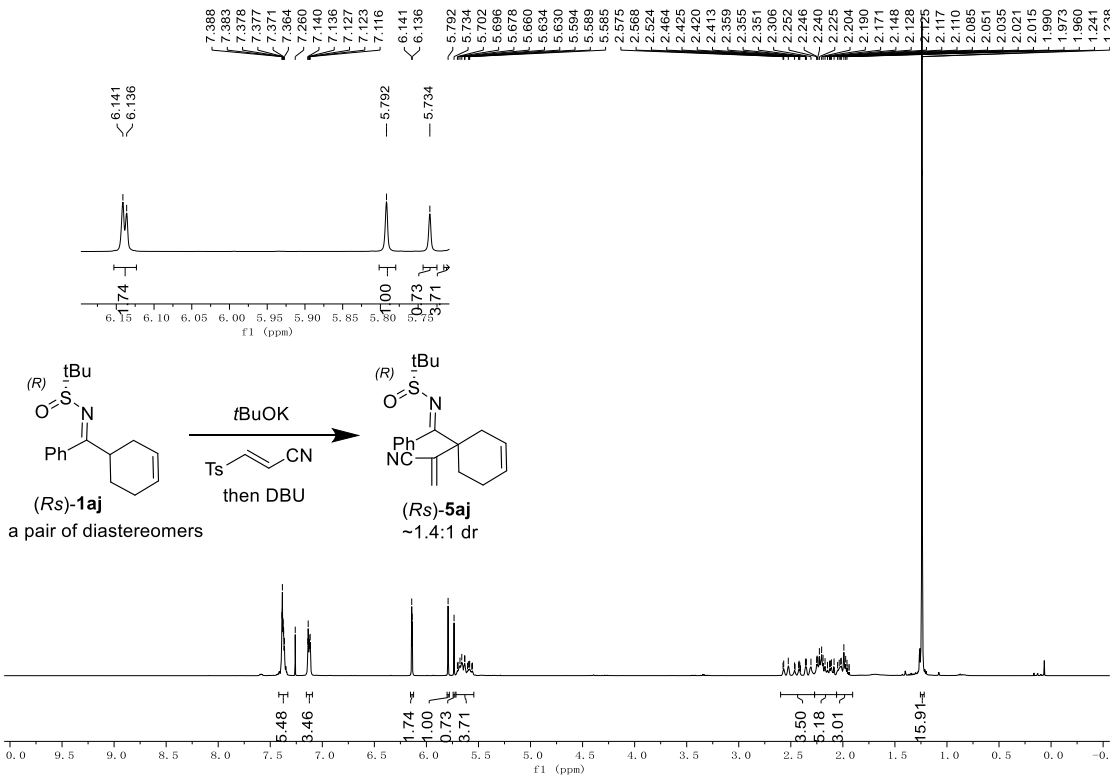
^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of the crude reaction mixture of **5ah** (dr = 20:1)



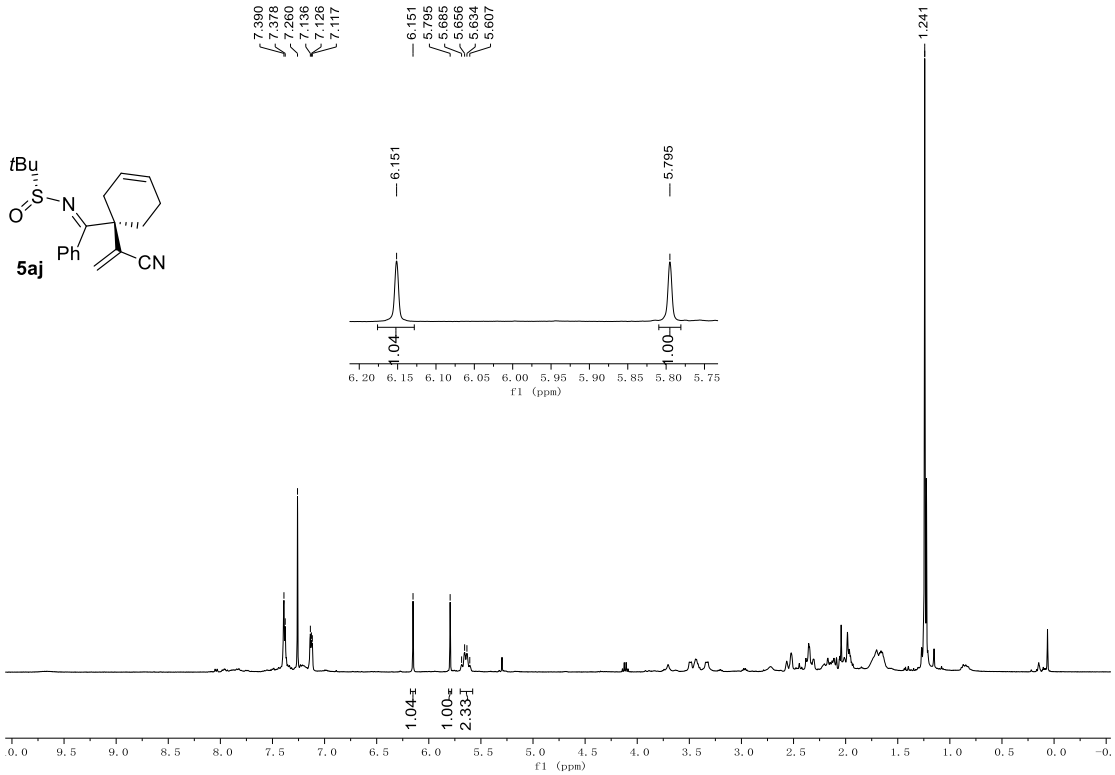
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**5ai** and (R_S, 2*R*)-**5ai** (~1.6:1 dr) (this low dr sample was intentionally prepared by using diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ai** and (*Rs*,2*R*)-**1ai** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis)



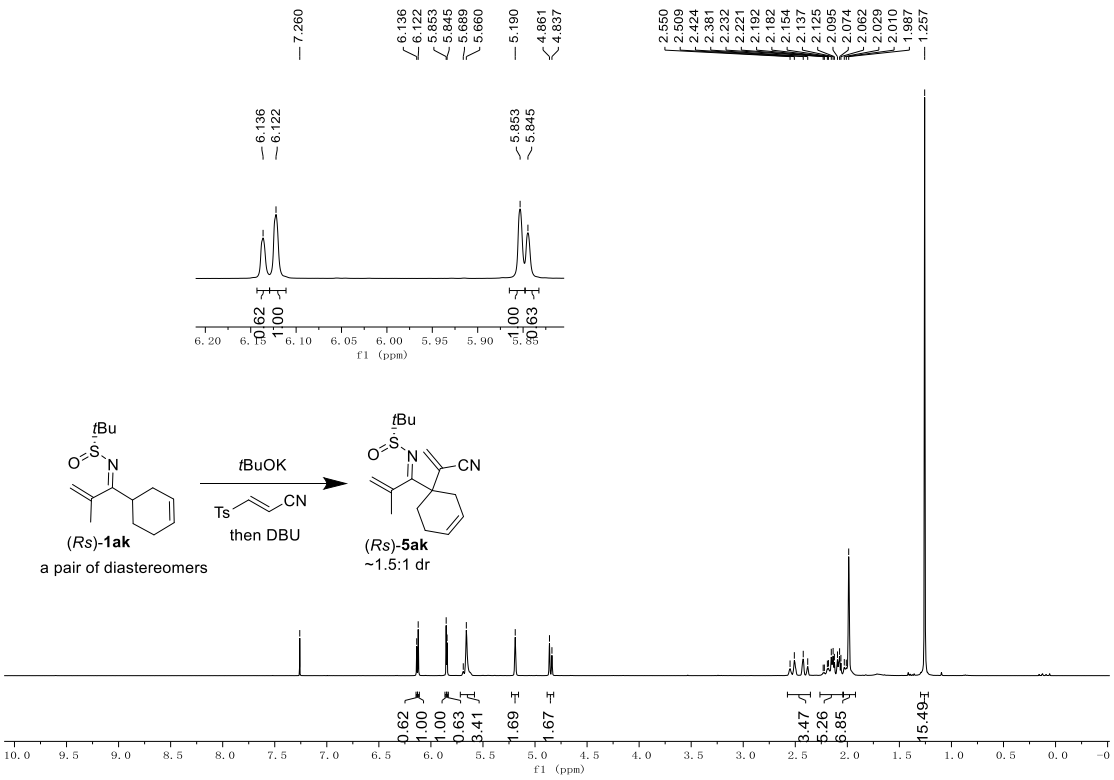
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5ai** (dr = 12:1)



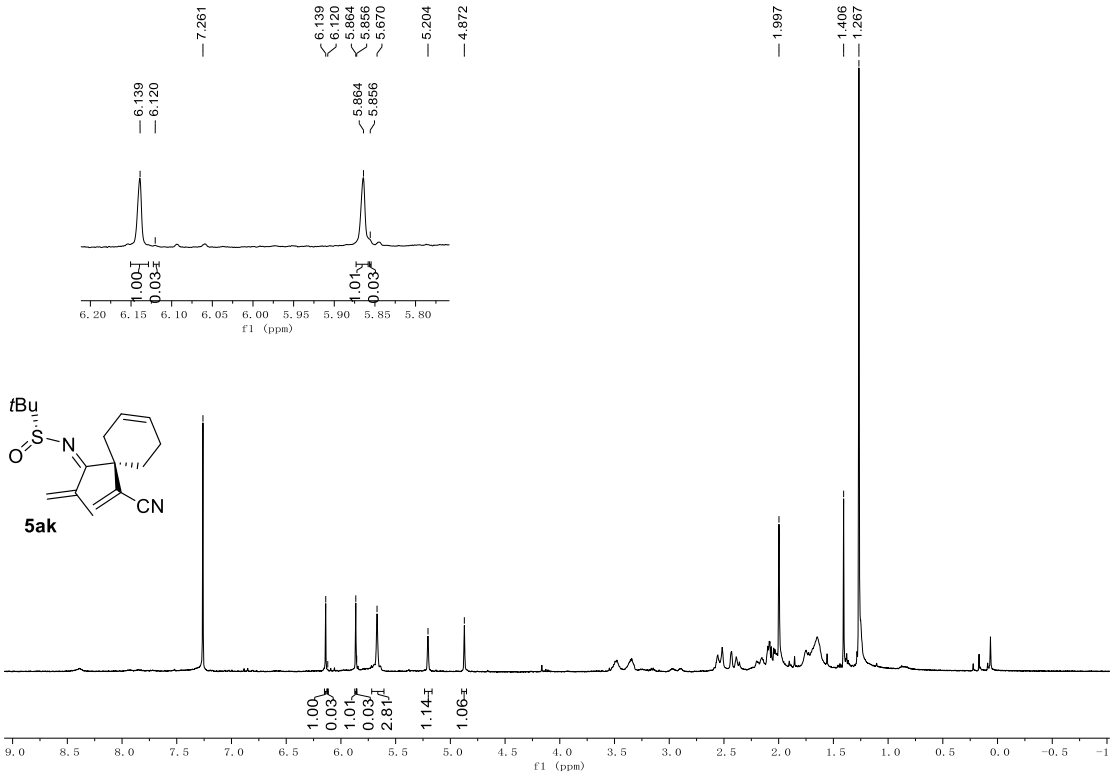
^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**5aj** and (R_S, 2*R*)-**5aj** (~1.4:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1aj** and (*Rs*,2*R*)-**1aj** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis; note: **5ah** and **5aj** is a pair of diastereomers, see Scheme 5)



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the crude reaction mixture of **5aj** (dr > 20:1)



^{1}H NMR spectrum of the purified mixture of inseparable diastereomers of (R_S, 2*S*)-**5ak** and (R_S, 2*R*)-**5ak** (~1.5:1 dr) (this low dr sample was intentionally prepared by using ~1:1 diastereomeric mixture of *N*-*t*BS ketimine (*Rs*,2*S*)-**1ak** and (*Rs*,2*R*)-**1ak** as the starting material in order to identify the diagnostic peak(s) of the minor diastereomer by ^{1}H NMR analysis; note: **5ai** and **5ak** is a pair of diastereomers, see Scheme 5)



^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of the crude reaction mixture of **5ak** (dr ~ 30:1)

X-Ray crystal structure of the compound 3z

The crystal of compound **3z** was grown by the slow evaporation of its solution in acetone/MeOH at room temperature. X-Ray crystal structure (ORTEP) of compound **3z** with the thermal ellipsoids shown at a 50% possibility level.

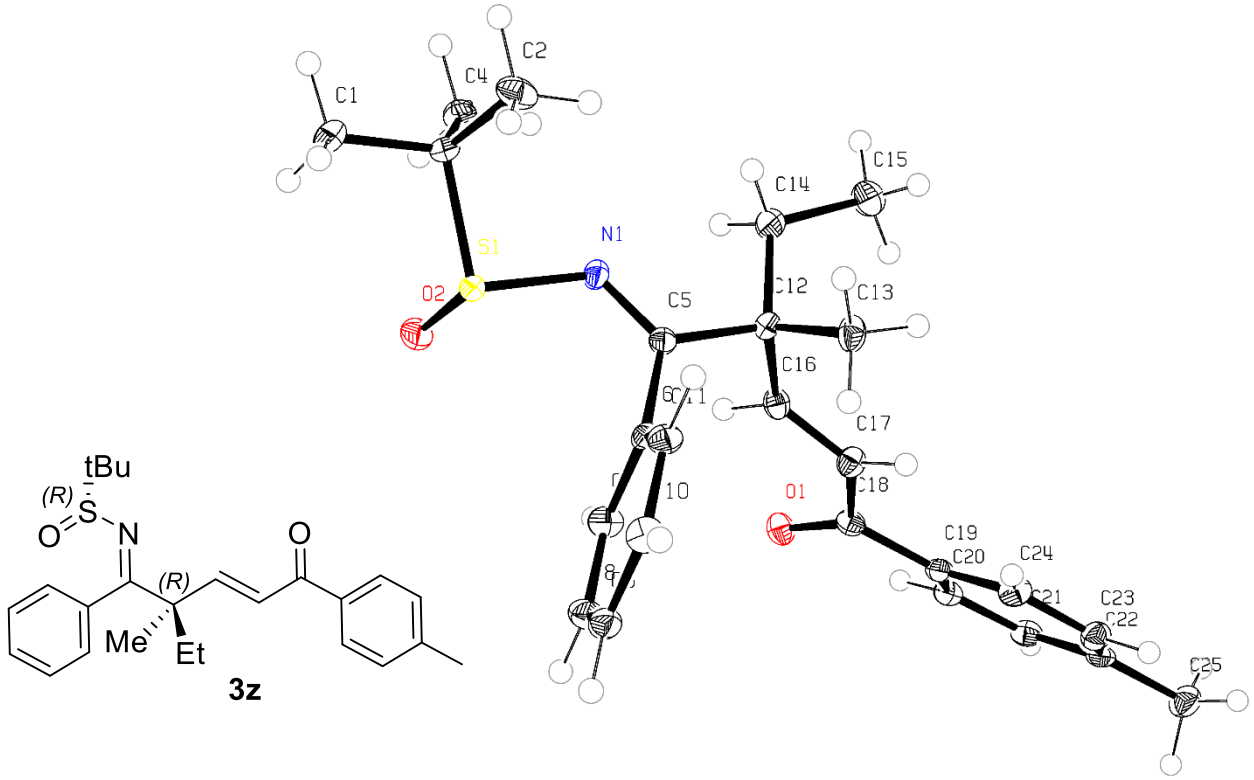


Table S1 Crystal data and structure refinement for 3z

Identification code	**3z**
Empirical formula	$C_{25}H_{31}NO_2S$
Formula weight	409.57
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.7335(11)
b/Å	6.0074(4)
c/Å	14.8867(12)
α/°	90
β/°	112.483(3)
γ/°	90
Volume/Å^3	1134.84(15)
Z	2
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	0.163
F(000)	440.0
Crystal size/mm^3	0.28 × 0.24 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.132 to 56.904
Index ranges	$-18 \leq h \leq 18$, $-8 \leq k \leq 7$, $-19 \leq l \leq 19$
Reflections collected	5650
Independent reflections	5650 [R_{int} = 0.0568, R_{sigma} = 0.0407]
Data/restraints/parameters	5650/1/268
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0676
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.0704
Largest diff. peak/hole / e Å^{-3}	0.24/-0.22
Flack parameter	0.02(2)

Table S2 Bond Lengths for 3z

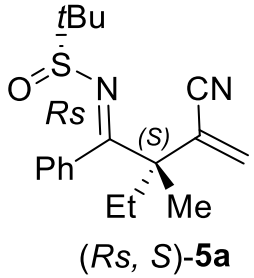
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.4888(15)	C10	C11	1.394(3)
S1	N1	1.7366(16)	C12	C13	1.534(3)
S1	C3	1.8380(17)	C12	C14	1.551(3)
O1	C18	1.227(2)	C12	C16	1.514(3)
N1	C5	1.277(2)	C14	C15	1.527(3)
C1	C3	1.530(3)	C16	C17	1.328(3)
C2	C3	1.528(3)	C17	C18	1.493(3)
C3	C4	1.522(3)	C18	C19	1.491(3)
C5	C6	1.502(2)	C19	C20	1.403(3)
C5	C12	1.544(2)	C19	C24	1.396(3)
C6	C7	1.395(3)	C20	C21	1.385(3)
C6	C11	1.396(3)	C21	C22	1.396(3)
C7	C8	1.394(3)	C22	C23	1.388(3)
C8	C9	1.388(3)	C22	C25	1.510(3)
C9	C10	1.388(3)	C23	C24	1.393(3)

Table S3 Bond Angles for 3z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O(2)	S(1)	N(1)	105.36(8)	C(13)	C(12)	C(5)	109.41(15)
O(2)	S(1)	C(3)	106.41(8)	C(13)	C(12)	C(14)	110.65(16)
N(1)	S(1)	C(3)	93.89(8)	C(16)	C(12)	C(5)	106.95(14)
C(5)	N(1)	S(1)	118.22(13)	C(16)	C(12)	C(13)	112.45(15)
C(1)	C(3)	S(1)	105.19(12)	C(16)	C(12)	C(14)	107.91(16)
C(2)	C(3)	S(1)	107.39(12)	C(15)	C(14)	C(12)	114.81(16)
C(2)	C(3)	C(1)	110.58(16)	C(17)	C(16)	C(12)	127.17(17)
C(4)	C(3)	S(1)	109.72(12)	C(16)	C(17)	C(18)	120.41(17)
C(4)	C(3)	C(1)	110.87(16)	O(1)	C(18)	C(17)	121.02(18)
C(4)	C(3)	C(2)	112.75(16)	O(1)	C(18)	C(19)	120.76(17)
N(1)	C(5)	C(6)	125.17(16)	C(19)	C(18)	C(17)	118.17(16)
N(1)	C(5)	C(12)	116.46(16)	C(20)	C(19)	C(18)	118.18(16)
C(6)	C(5)	C(12)	118.31(14)	C(24)	C(19)	C(18)	122.98(17)
C(7)	C(6)	C(5)	119.33(16)	C(24)	C(19)	C(20)	118.83(17)
C(7)	C(6)	C(11)	119.68(17)	C(21)	C(20)	C(19)	120.28(17)
C(11)	C(6)	C(5)	120.98(16)	C(20)	C(21)	C(22)	121.09(18)
C(8)	C(7)	C(6)	120.31(17)	C(21)	C(22)	C(25)	120.66(17)
C(9)	C(8)	C(7)	119.95(17)	C(23)	C(22)	C(21)	118.40(17)
C(8)	C(9)	C(10)	119.85(17)	C(23)	C(22)	C(25)	120.93(17)
C(9)	C(10)	C(11)	120.66(17)	C(22)	C(23)	C(24)	121.23(18)
C(10)	C(11)	C(6)	119.55(17)	C(23)	C(24)	C(19)	120.13(18)
C(5)	C(12)	C(14)	109.36(14)				

X-Ray crystal structure of the compound (*Rs, S*)**-5a**

The crystal of (*Rs, S*)**-5a** was grown by the slow evaporation of its solution in dichloromethane/petroleum ether at room temperature. X-Ray crystal structure (ORTEP) of compound (*Rs, S*)**-5a** with the thermal ellipsoids shown at a 50% possibility level.



(*Rs, S*)-**5a**

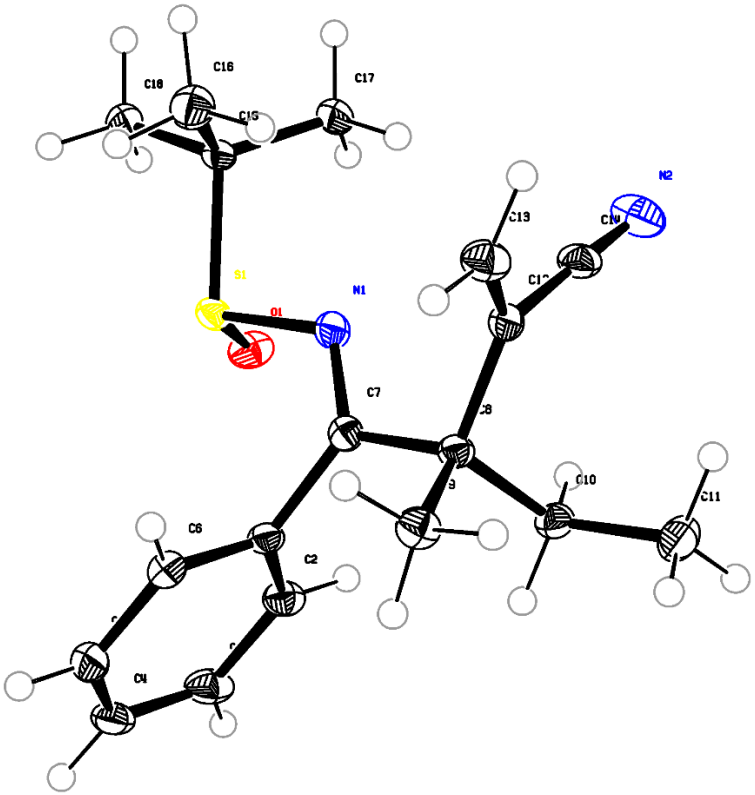


Table S4 Crystal data and structure refinement for (*Rs, S*)-5a

Identification code	(*Rs, S*)-**5a**
Empirical formula	$C_{18}H_{24}N_2OS$
Formula weight	316.45
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.0440(6)
b/Å	15.6224(10)
c/Å	21.9085(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3437.7(4)
Z	8
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	0.192
F(000)	1360.0
Crystal size/mm^3	0.25 × 0.23 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.462 to 56.642
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -28 ≤ l ≤ 29
Reflections collected	46595
Independent reflections	8541 [R_{int} = 0.0586, R_{sigma} = 0.0419]
Data/restraints/parameters	8541/0/407
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0339, wR_2 = 0.0707
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.0752
Largest diff. peak/hole / e Å^{-3}	0.22/-0.23
Flack parameter	-0.02(2)

Table S5 Bond Lengths for (*Rs, S*)-5a

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.4859(16)	S2	O2	1.4884(17)
S1	N1	1.7355(18)	S2	N3	1.7347(18)
S1	C15	1.838(2)	S2	C33	1.840(2)
N1	C7	1.278(3)	N3	C25	1.279(3)
N2	C14	1.149(3)	N4	C32	1.148(3)
C1	C2	1.391(3)	C19	C20	1.391(3)
C1	C6	1.399(3)	C19	C24	1.401(3)
C1	C7	1.505(3)	C19	C25	1.504(3)
C2	C3	1.393(3)	C20	C21	1.391(3)
C3	C4	1.381(3)	C21	C22	1.380(3)
C4	C5	1.387(3)	C22	C23	1.384(3)
C5	C6	1.387(3)	C23	C24	1.389(3)
C7	C8	1.533(3)	C25	C26	1.538(3)
C8	C9	1.534(3)	C26	C27	1.533(3)
C8	C10	1.551(3)	C26	C28	1.556(3)
C8	C12	1.532(3)	C26	C30	1.531(3)
C10	C11	1.528(3)	C28	C29	1.527(3)
C12	C13	1.327(3)	C30	C31	1.327(3)
C12	C14	1.446(3)	C30	C32	1.446(3)
C15	C16	1.522(3)	C33	C34	1.528(3)
C15	C17	1.527(3)	C33	C35	1.523(3)
C15	C18	1.528(3)	C33	C36	1.529(3)

Table S6 Bond Angles for (*Rs, S*)-5a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	108.38(9)	O2	S2	N3	106.12(10)
O1	S1	C15	106.86(10)	O2	S2	C33	107.11(10)
N1	S1	C15	94.15(9)	N3	S2	C33	95.03(9)
C7	N1	S1	116.72(14)	C25	N3	S2	116.75(15)
C2	C1	C6	119.70(19)	C20	C19	C24	118.90(19)
C2	C1	C7	120.18(18)	C20	C19	C25	121.16(18)
C6	C1	C7	120.03(18)	C24	C19	C25	119.95(18)
C1	C2	C3	120.0(2)	C21	C20	C19	120.2(2)
C4	C3	C2	120.2(2)	C22	C21	C20	120.5(2)
C3	C4	C5	119.9(2)	C21	C22	C23	119.9(2)
C6	C5	C4	120.6(2)	C22	C23	C24	120.0(2)
C5	C6	C1	119.6(2)	C23	C24	C19	120.4(2)
N1	C7	C1	123.89(19)	N3	C25	C19	125.04(19)
N1	C7	C8	117.10(17)	N3	C25	C26	116.66(18)
C1	C7	C8	118.99(18)	C19	C25	C26	118.29(17)
C7	C8	C9	110.17(17)	C25	C26	C28	107.91(17)
C7	C8	C10	108.32(16)	C27	C26	C25	110.27(17)
C9	C8	C10	110.05(17)	C27	C26	C28	109.98(18)
C12	C8	C7	108.57(17)	C30	C26	C25	108.48(17)
C12	C8	C9	109.95(17)	C30	C26	C27	110.97(18)
C12	C8	C10	109.74(17)	C30	C26	C28	109.16(17)
C11	C10	C8	113.32(18)	C29	C28	C26	114.25(19)
C13	C12	C8	124.84(19)	C31	C30	C26	126.1(2)
C13	C12	C14	117.7(2)	C31	C30	C32	117.3(2)
C14	C12	C8	117.44(18)	C32	C30	C26	116.59(18)
N2	C14	C12	178.0(3)	N4	C32	C30	177.1(2)
C16	C15	S1	107.69(15)	C34	C33	S2	104.17(14)
C16	C15	C17	112.67(18)	C34	C33	C36	110.50(18)
C16	C15	C18	110.99(19)	C35	C33	S2	110.21(15)
C17	C15	S1	109.66(15)	C35	C33	C34	111.57(18)
C17	C15	C18	110.96(18)	C35	C33	C36	112.54(18)
C18	C15	S1	104.49(14)	C36	C33	S2	107.44(15)