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Stereodivergent Conjugate Reduction of α-Substituted α,β-Unsaturated *N*-Sulfinyl Ketimines: Flexible Access to Challenging Acyclic β,β-Disubstituted Enesulfinamides

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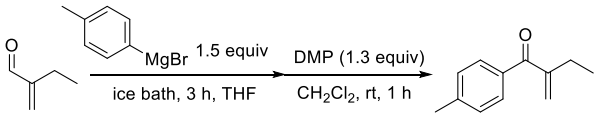
General experimental information

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. Melting point (m.p.) 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).

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), 500 MHz (^{1}H NMR at 500 MHz and ^{13}C{^{1}H} NMR at 125 MHz) or 600 MHz (^{1}H NMR at 600 MHz and ^{13}C{^{1}H} NMR at 150 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.

Materials: Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Diethyl ether was distilled from sodium/benzophenone ketyl. All commercially available reagents were used without further purification unless otherwise noted. All *N*-*tert*-butanesulfinyl ketimines were prepared from the purchased enantioenriched *tert*-butanesulfinamide (*ee* > 99.0%).

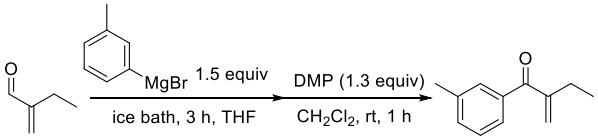
Procedures for the preparation of compounds S1–S17



S1

To a solution of ethylacrolein (1.00 g, 11.89 mmol, 1.0 equiv) in freshly distilled THF (50 mL) at 0 °C was added *p*-tolylmagnesium bromide (1 M in THF, 17.8 mL, 17.83 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 (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (50 mL) and DMP (6.55 g, 15.45 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (40 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 (5%–10% ethyl acetate/petroleum ether) to give **S1** (1.82 g, 88% for two steps) as a colorless oil. Analytical data for **S1**: R_f = 0.40 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J*=8.0, 2H), 7.23 (d, *J*=7.6, 2H), 5.78–5.75 (m, 1H), 5.55–5.52 (m, 1H), 2.48 (q, *J*=7.6, 2H), 2.41 (s, 3H), 1.12 (t, *J*=7.6, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.5, 150.0, 143.1, 135.3, 129.9, 129.0, 123.3, 25.5, 21.7, 12.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{12}H_{15}O$ 175.1117; Found 175.1120.

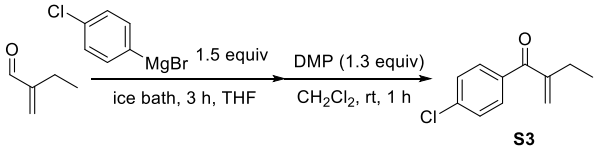


S2

To a solution of ethylacrolein (2.00 g, 23.78 mmol, 1.0 equiv) in freshly distilled THF (80 mL) at 0 °C was added *m*-tolylmagnesium bromide (1 M in THF, 35.7 mL, 35.67 mmol, 1.5 equiv) dropwise under argon atmosphere. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (40 mL) was added carefully and the mixture was extracted with ethyl acetate (40 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 (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (80 mL) and DMP (13.11 g, 30.91 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (50 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (80 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×50 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 (5%–10% ethyl acetate/petroleum ether) to give **S2** (3.70 g, 89% for two steps) as a colorless oil. Analytical data for **S2**: R_f = 0.40 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.37–7.28 (m, 2H), 5.82–5.79 (m, 1H), 5.58–5.56 (m, 1H), 2.48 (q, J = 7.4 Hz, 2H), 2.40 (s, 3H), 1.12 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.9, 149.9, 138.1, 133.0, 130.1, 128.1, 126.9, 124.2, 25.4, 21.5, 12.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{12}H_{15}O$ 175.1117; Found 175.1120.

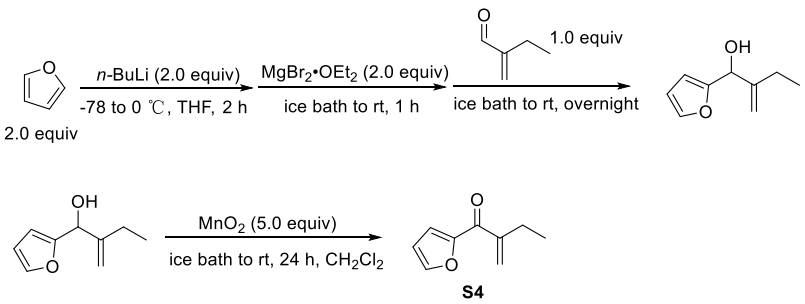


S3

To a solution of ethylacrolein (1.64 g, 19.50 mmol, 1.0 equiv) in freshly distilled THF (50 mL) at 0 °C was added 4-chlorophenylmagnesium bromide (1 M in THF, 29.3 mL, 29.24 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 (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (70 mL) and DMP (10.67 g, 25.35 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (40 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 (5%–10% ethyl acetate/petroleum

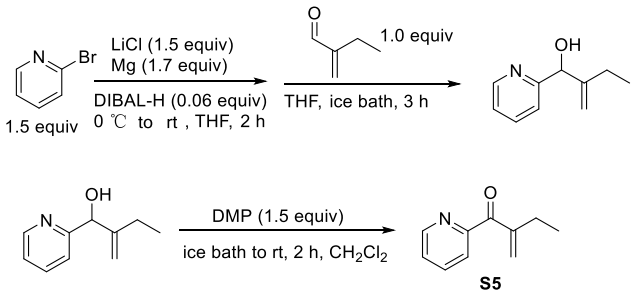
ether) to give **S3** (3.12 g, 82% for two steps) as a colorless oil. Analytical data for **S3**: R_f = 0.40 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 5.81 (s, 1H), 5.54 (s, 1H), 2.46 (q, J = 7.4 Hz, 2H), 1.10 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.3, 149.6, 138.7, 136.3, 131.0, 128.6, 124.4, 25.3, 12.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{11}H_{12}ClO$ 195.0571; Found 195.0576.



Furan (2.91 g, 42.80 mmol, 2.0 equiv) was dissolved in anhydrous THF (100 mL) in a flame-dried 250 mL round-bottomed flask under argon atmosphere, and the solution was cooled to −78 °C. *n*-BuLi (2.5 M in hexane, 17.1 mL, 42.80 mmol, 2.0 equiv) was added, and the mixture was stirred for 2 h while warming to 0 °C. The resulting solution was mixed with a slurry of $MgBr_2 \cdot Et_2O$ (11.14 g, 42.80 mmol, 2.0 equiv) in anhydrous THF (20 mL) at 0 °C and stirred at rt for 1 h until all solids were dissolved. Then it was cooled to ice bath, ethylacrolein (1.80 g, 21.40 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (40 mL) was added carefully and the mixture was extracted with ethyl acetate (50 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 (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (80 mL) and MnO_2 (9.30 g, 106.99 mmol, 5.0 equiv) was added portionwise. After stirring for 24 h at rt, the mixture was filtered through a pad of celite, thoroughly washed with CH_2Cl_2, and concentrated under reduced pressure. The residue was purified by column chromatography (5%–10% ethyl acetate/petroleum ether) to give **S4** (1.55 g, 48% for two steps) as a colorless oil. Analytical data for **S4**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 1.5, 0.5 Hz, 1H), 7.13 (dd, J = 3.5, 0.5 Hz, 1H), 6.52 (dd, J = 3.5, 1.5 Hz, 1H), 5.91–5.88 (m, 1H), 5.74–5.70 (m, 1H), 2.46 (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.6, 152.2, 149.5,

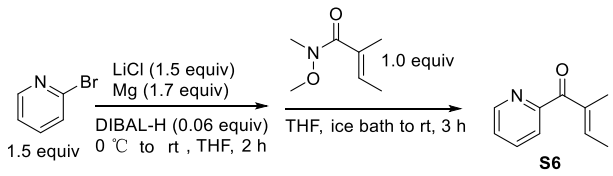
147.1, 122.3, 119.9, 112.0, 25.2, 12.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_9H_{11}O_2$ 151.0754; Found 151.0756.



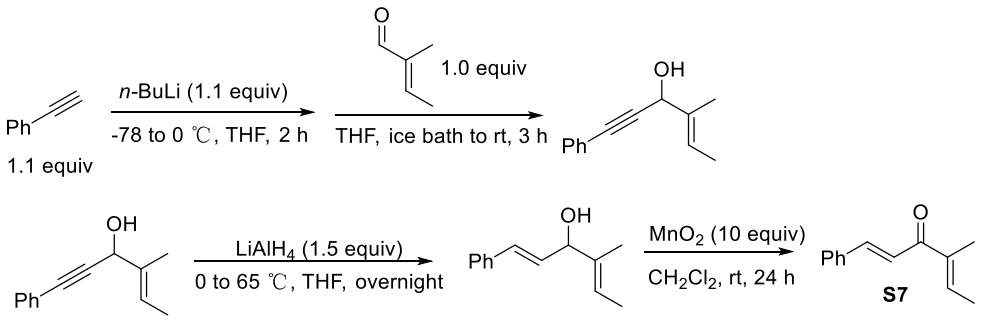
A flame-dried 250 mL round-bottomed flask was charged with Mg turnings (1.69 g, 69.32 mmol, 1.7 equiv) and LiCl (2.59 g, 61.16 mmol, 1.5 equiv) in anhydrous THF (100 mL), which was followed by addition of diisobutylaluminum hydride (DIBAL-H) (1 M, 2.45 mL, 2.45 mmol, 0.06 equiv). The resulting suspension was stirred at RT for 5 min. To the resulting mixture was added 2-bromopyridine (9.66 g, 61.16 mmol, 1.5 equiv) in dry THF (80 mL), which was stirred at RT until all Mg had disappeared. Then it was cooled with ice bath, ethylacrolein (3.43 g, 40.78 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (40 mL) was added carefully and the mixture was extracted with ethyl acetate (50 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 (40% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (100 mL) and DMP (22.32 g, 53.00 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (80 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (80 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×80 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 (20% ethyl acetate/petroleum ether) to give **S5** (3.75 g, 57% for two steps) as a colorless oil. Analytical data for **S5**: R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67–8.65 (m, 1H), 7.85–7.81 (m, 2H), 7.44–7.40 (m, 1H), 5.99–5.98 (m, 1H), 5.98–5.96 (m, 1H), 2.51 (qt, J = 7.4, 1.2 Hz, 2H), 1.14 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.1, 155.8, 148.7, 148.6, 137.0, 127.7, 125.9, 124.1, 24.9, 12.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{10}H_{12}NO$

162.0913; Found 162.0913.



A flame-dried 100 mL round-bottomed flask was charged with Mg turnings (0.834 g, 34.31 mmol, 1.7 equiv) and LiCl (1.28 g, 30.28 mmol, 1.5 equiv) in anhydrous THF (50 mL), which was followed by addition of diisobutylaluminum hydride (DIBAL-H) (1 M, 1.21 mL, 1.21 mmol, 0.06 equiv). The resulting suspension was stirred at RT for 5 min. To the resulting mixture was added 2-bromopyridine (4.78 g, 30.28 mmol, 1.5 equiv) in dry THF (10 mL) and the mixture was stirred at RT until all Mg had disappeared. Then it was cooled to ice bath, Weinreb amide (2.89 g, 20.18 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. After the amide 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 (20% ethyl acetate/petroleum ether) to give **S6** (2.21 g, 68%) as a colorless oil. Analytical data for **S6**: R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37–8.30 (m, 2H), 7.58–7.49 (m, 1H), 7.43–7.37 (m, 2H), 7.14–7.06 (m, 2H), 6.49–6.40 (m, 1H), 1.72–1.67 (m, 3H), 1.61 (d, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.3, 156.1, 147.8, 144.0, 136.4, 136.3, 124.7, 123.4, 14.6, 11.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{10}H_{12}NO$ 162.0913; Found 162.0916.

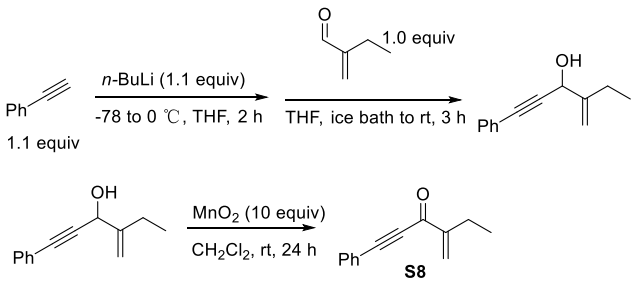


To a solution of phenylacetylene (1.56 g, 15.30 mmol, 1.1 equiv) in dry THF (50 mL) was added *n*BuLi (2.5 M in hexane, 6.2 mL, 15.30 mmol, 1.1 equiv) dropwise at –78 ºC under argon atmosphere. The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h, after which aldehyde (1.17 g, 13.91 mmol, 1.0 equiv) was added dropwise at 0 ºC. 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 (20% ethyl acetate/petroleum ether).

To a solution of $LiAlH_4$ (0.792 g, 20.86 mmol, 1.5 equiv) in dry THF (50 mL) at 0 ºC was added the alcohol obtained above in THF (5 mL). The resulting mixture was heated at 65 ºC in a heating mantle for 24 h. Then the mixture was cooled to 0 ºC, and quenched with saturated aqueous ammonium chloride (20 mL) very carefully. Saturated aqueous solution of potassium sodium tartrate was added and stirred vigorously at rt for 2 h before 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 (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (50 mL) and MnO_2 (12.09 g, 139.10 mmol, 10.0 equiv) was added portionwise. After stirring for 24 h at rt, the mixture was filtered through a pad of celite, thoroughly washed with CH_2Cl_2, and concentrated under reduced pressure. The residue was purified by column chromatography (5%–10% ethyl acetate/petroleum ether) to give **S7** (1.49 g, 58% for three steps) as a colorless oil. Analytical data for **S7**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 15.6 Hz, 1H), 7.58–7.55 (m, 2H), 7.41–7.34 (m, 3H), 7.30 (d, J = 15.6 Hz, 1H), 6.87–6.80 (m, 2H), 1.93–1.89 (m, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 191.9, 142.7, 139.4, 137.5, 135.4, 130.1, 128.9, 128.2, 121.9, 15.0, 11.7; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{15}O$ 187.1117; Found 187.1119.

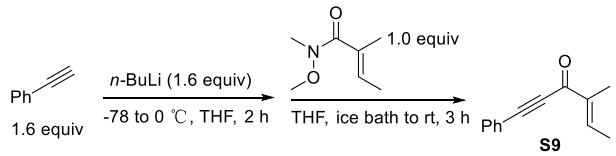


S8

To a solution of phenylacetylene (2.64 g, 25.89 mmol, 1.1 equiv) in dry THF (80 mL) was added *n*BuLi (2.5 M in hexane, 10.4 mL, 25.89 mmol, 1.1 equiv) dropwise at –78 ºC under argon atmosphere. The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h, after which

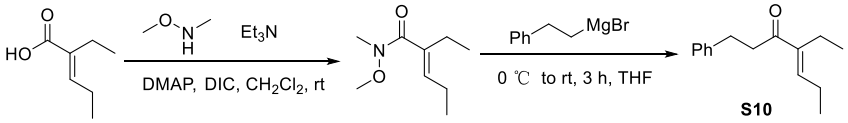
aldehyde (1.98 g, 23.54 mmol, 1.0 equiv) was added dropwise at 0 ºC. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (20 mL) was added carefully and the mixture was extracted with ethyl acetate (30 mL×3). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20% ethyl acetate/petroleum ether).

The alcohol obtained above was dissolved in CH_2Cl_2 (80 mL) and MnO_2 (10.23 g, 117.69 mmol, 5.0 equiv) was added portionwise. After stirring for 24 h at rt, the mixture was filtered through a pad of celite, thoroughly washed with CH_2Cl_2, and concentrated under reduced pressure. The residue was purified by column chromatography (5%–10% ethyl acetate/petroleum ether) to give **S8** (3.33 g, 77% for two steps) as a colorless oil. Analytical data for **S8**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.49–7.42 (m, 1H), 7.39 (t, J = 7.2 Hz, 2H), 6.59 (s, 1H), 6.04 (s, 1H), 2.39 (q, J = 7.2 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.1, 151.0, 133.0, 130.6, 129.4, 128.7, 120.4, 91.3, 86.4, 22.7, 12.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{13}H_{13}O$ 185.0961; Found 185.0962.



To a solution of phenylacetylene (3.38 g, 33.08 mmol, 1.6 equiv) in dry THF (80 mL) was added *n*BuLi (2.5 M in hexane, 13.2 mL, 33.08 mmol, 1.6 equiv) dropwise at –78 ºC under argon atmosphere. After the reaction mixture had been allowed to warm to 0 ºC and stirred for 2 h, Weinreb amide (2.96 g, 20.67 mmol, 1.0 equiv) was added dropwise at 0 ºC. After the amide was consumed completely, saturated aqueous ammonium chloride (40 mL) was added carefully and the mixture was extracted with ethyl acetate (40 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 (20% ethyl acetate/petroleum ether) to give **S9** (2.81 g, 74%) as a colorless oil. Analytical data for **S9**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.39–7.34 (m, 1H), 7.34–7.27 (m, 3H), 1.93–1.89 (m, 3H), 1.82–1.78 (m, 3H); ^{13}C{^{1}H} NMR

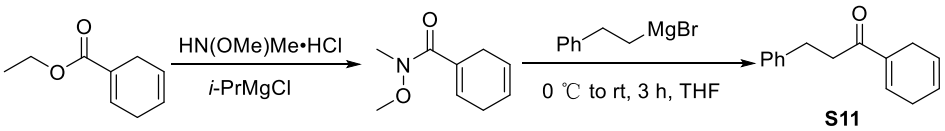
(125 MHz, $CDCl_3$) δ 180.0, 145.2, 139.4, 132.6, 130.2, 128.5, 120.4, 90.8, 86.0, 15.1, 10.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{13}O$ 185.0961; Found 185.0965.



S10

To a suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (5.88 g, 60.23 mmol, 4.0 equiv) in anhydrous CH_2Cl_2 (100 mL), triethylamine (9.14 g, 90.35 mmol, 6.0 equiv), (*E*)-2-ethylpent-2-enoic acid (1.93 g, 15.06 mmol, 1.0 equiv), a solution of 4-dimethylaminopyridine (DMAP, 3.68 g, 30.12 mmol, 2.0 equiv) in CH_2Cl_2 (10 mL), and diisopropylcarbodiimide (3.80 g, 30.12 mmol, 2.0 equiv) were added successively. After stirring for 48 h at rt, the suspension was diluted with CH_2Cl_2 (100 mL). After washing with water (4×50 mL), the organic layer was dried over anhydrous sodium sulfate and the solvent was removed in vacuum. The residue was purified by silica gel chromatography (15% ethyl acetate/petroleum ether).

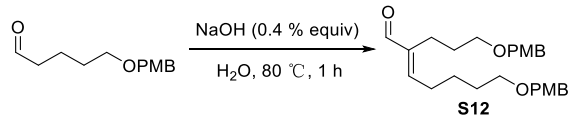
To a solution of Weinreb amide obtained above in freshly distilled THF (50 mL) at 0 °C was added phenethylmagnesium bromide (~0.5 M, 60.2 mL, 30.12 mmol, 2.0 equiv) (which was freshly prepared using Mg turnings (0.732 g, 30.12 mmol, 2.0 equiv) and (2-bromoethyl)benzene (5.57 g, 30.12 mmol, 2.0 equiv) in dry THF (60 mL) at 50 °C for 3 h) dropwise under argon atmosphere. After the amide 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 (5-10% ethyl acetate/petroleum ether) to afford **S10** (2.17 g, 67% for two steps) as colorless oil. Analytical data for **S10**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.23–7.16 (m, 3H), 6.53 (t, J = 7.4 Hz, 1H), 3.00–2.88 (m, 4H), 2.34–2.20 (m, 4H), 1.05 (t, J = 7.6 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.6, 144.0, 142.8, 141.7, 128.5, 126.0, 39.2, 30.9, 22.1, 18.9, 14.0, 13.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{21}O$ 217.1587; Found 217.1590.



S11

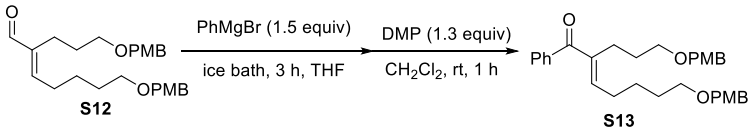
To a solution of *N,O*-dimethylhydroxylamine hydrochloride (8.72 g, 89.36 mmol, 4.0 equiv) in anhydrous THF (50 mL) was added a solution of ethyl cyclohexa-1,4-diene-1-carboxylate (3.40 g, 22.34 mmol, 1.0 equiv) in anhydrous THF (10 mL). The reaction mixture was then cooled to -15 °C and *i*-PrMgCl (1 M, 44.7 mL, 44.68 mmol, 2.0 equiv) was added steadily dropwise in 30 min. The reaction mixture was stirred at −15 °C for 2 h. After full conversion, saturated aqueous ammonium chloride (30 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 (20% ethyl acetate/petroleum ether).

To a solution of Weinreb amide obtained above in freshly distilled THF (50 mL) at 0 ^{o}C was added phenethylmagnesium bromide (~0.5 M, 89.4 mL, 44.68 mmol, 2.0 equiv) (which was freshly prepared using Mg turnings (1.086 g, 44.68 mmol, 2.0 equiv) and (2-bromoethyl)benzene (8.27 g, 44.68 mmol, 2.0 equiv) in dry THF (90 mL) at 50 ^{o}C for 3 h) dropwise under argon atmosphere. After the amide 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 (5–10% ethyl acetate/petroleum ether) to afford **S11** (2.03 g, 43% for two steps) as a white solid, which contained inseparable oxidized impurity 1,3-diphenylpropan-1-one (see S27). The prepared keteone **S11** containing impurity could be used for condensation with *t*BSNH$_2$. Analytical data for **S11**: R_f = 0.50 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.23–7.18 (m, 3H), 6.91–6.82 (m, 1H), 5.84–5.78 (m, 1H), 5.70–5.62 (m, 1H), 3.03–2.85 (m, 8H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 199.8, 141.6, 136.7, 136.4, 128.6, 128.5, 126.1, 124.9, 122.0, 38.9, 30.5, 27.3, 24.3; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{17}O$ 213.1274; Found 213.1276.



S12

Sodium hydroxide (5.9 mg, 0.148 mmol, 0.4% equiv) in water (1 mL) was added to neat aldehyde 5-((4-methoxybenzyl)oxy)pentanal (8.20 g, 36.89 mmol, 1.0 equiv), and the mixture was heated at 80 ℃ in an oil bath with magnetic stirring for 1 h. The mixture was diluted with ethyl acetate (50 mL), and washed with brine (30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20% ethyl acetate/petroleum ether) to afford **S12** (8.0 g, 99%) as a clear oil. Analytical data for **S12**: R_f = 0.30 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.26–7.23 (m, 4H), 6.90–6.84 (m, 4H), 6.46 (t, J = 7.4 Hz, 1H), 4.41 (d, J = 6.5 Hz, 4H), 3.83–3.77 (m, 6H), 3.49–3.37 (m, 4H), 2.43–2.24 (m, 4H), 1.69–1.58 (m, 5H), 1.57–1.52 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.1, 159.14, 159.08, 155.3, 143.2, 130.6, 130.5, 129.20, 129.18, 113.74, 113.70, 72.6, 72.4, 69.5, 69.4, 55.2, 29.4, 28.6, 28.5, 25.4, 20.7; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{26}H_{34}NaO_5$ 449.2298; Found 449.2304.

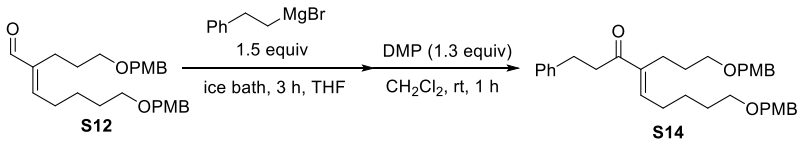


S12 **S13**

To a solution of **S12** (4.20 g, 9.85 mmol, 1.0 equiv) in freshly distilled THF (40 mL) at 0 °C was added phenylmagnesium bromide (2.8 M, 5.3 mL, 14.77 mmol, 1.5 equiv) dropwise under argon atmosphere. After full conversion, 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).

The alcohol obtained above was dissolved in CH_2Cl_2 (50 mL) and DMP (5.43 g, 12.80 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at RT, the mixture was diluted with CH_2Cl_2 (40 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 (20% ethyl

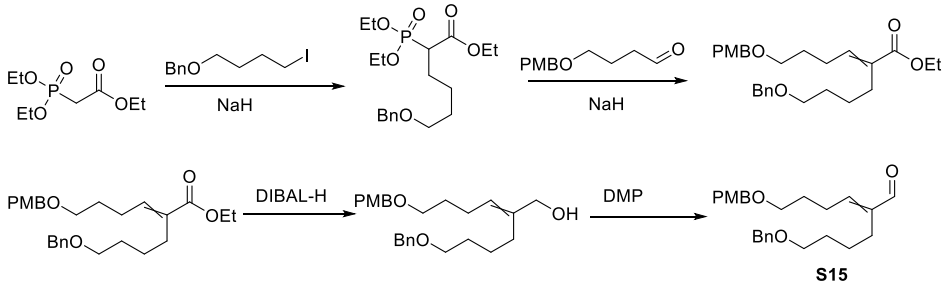
acetate/petroleum ether) to give **S13** (2.87 g, 58% for two steps) as a colorless oil. Analytical data for **S13**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.57 (m, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.26–7.21 (m, 4H), 6.86 (d, J = 8.0 Hz, 4H), 6.20 (t, J = 7.3 Hz, 1H), 4.41 (d, J = 4.0 Hz, 4H), 3.79 (s, 6H), 3.47 (t, J = 6.4 Hz, 2H), 3.42 (t, J = 6.4 Hz, 2H), 2.58–2.52 (m, 2H), 2.30 (q, J = 7.4 Hz, 2H), 1.79–1.70 (m, 2H), 1.64–1.58 (m, 2H), 1.53–1.45 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 159.1, 146.1, 140.7, 138.9, 131.4, 130.6, 130.5, 129.33, 129.27, 129.22, 128.0, 113.74, 113.71, 72.6, 72.5, 69.61, 69.56, 55.2, 29.5, 28.9, 28.6, 25.7, 23.4; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{32}H_{38}NaO_5$ 525.2611; Found 525.2614.



To a solution of **S12** (2.10 g, 4.92 mmol, 1.0 equiv) in freshly distilled THF (30 mL) at 0 °C was added freshly prepared phenethylmagnesium bromide (~0.5 M, 14.8 mL, 7.38 mmol, 1.5 equiv) dropwise under argon atmosphere. After full conversion, 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).

The alcohol obtained above was dissolved in CH_2Cl_2 (40 mL) and DMP (2.71 g, 6.40 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (40 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 (20% ethyl acetate/petroleum ether) to give **S14** (1.50 g, 57% for two steps) as a colorless oil. Analytical data for **S14**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.6 Hz, 3H), 7.26–7.22 (m, 3H), 7.21–7.15 (m, 3H), 6.90–6.83 (m, 6H), 6.56 (t, J = 7.2 Hz, 1H), 4.44–4.37 (m, 4H), 3.79 (s, 6H), 3.43 (t, J = 6.4 Hz, 2H), 3.39 (t, J = 6.6 Hz, 2H), 2.98–2.86 (m, 4H), 2.38–2.31 (m, 2H), 2.24 (q, J = 7.2 Hz, 2H), 1.65–1.58 (m, 4H), 1.55–1.47 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

200.4, 159.1, 159.0, 143.0, 141.3, 130.7, 130.5, 129.2, 129.1, 128.37, 128.36, 125.9, 113.70, 113.66, 72.5, 72.3, 69.6, 55.1, 39.1, 30.7, 29.5, 29.1, 28.6, 25.6, 22.4; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{34}H_{42}NaO_5$ 553.2924; Found 553.2927.



S15

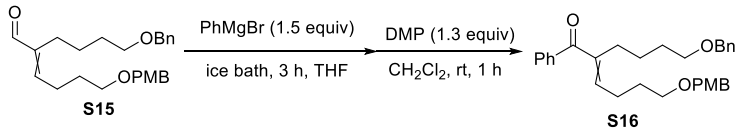
Ethyl 2-(diethoxyphosphoryl)acetate (1.16 g, 5.17 mmol, 1.0 equiv) was added dropwise over 30 min to a suspension of sodium hydride (248 mg, 6.21 mmol, 1.2 equiv, 60% oil dispersion) in DMSO (10 mL) at 0 ℃. The mixture was stirred at 0 ℃ for 60 min and then a solution of ((4-iodobutoxy)methyl)benzene (2.25 g, 7.76 mmol, 1.5 equiv) in DMSO (5 mL) was added. The mixture was allowed to warm to room temperature over 14 h, before being quenched with water (10 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and then evaporated in vacuo. The residue was purified by silica gel column chromatography (30% ethyl acetate/petroleum ether) to afford the phosphonate (1.52 g, 76%) as a pale yellow oil.

Ethyl 6-(benzyloxy)-2-(diethoxyphosphoryl)hexanoate (1.50 g, 3.88 mmol, 1.2 equiv) obtained above was added dropwise towards a stirring suspension of NaH (60% in mineral oil, 155 mg, 3.88 mmol, 1.2 equiv) in THF (20 mL) at 0 °C. Stirring was continued for 30 min followed by the addition of aldehyde 4-((4-methoxybenzyl)oxy)butanal (0.674 g, 3.23 mmol, 1.0 equiv). Saturated aqueous ammonium solution (20 mL) was added after 16 h to quench the reactants and the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous sodium sulfate and evaporated in vacuo to dryness to give the crude. The crude was purified by column chromatography (5–10% ethyl acetate/petroleum ether) to yield the desired α,β-unsaturated ester (1.17 g, 82%).

To a solution of α,β-unsaturated ester (900 mg, 2.04 mmol, 1.0 equiv) obtained above in CH_2Cl_2 (30 mL) was dropwise added diisobutylaluminum hydride (1.0 M in hexane, 6.33 ml, 6.33 mmol, 3.1 equiv) at -78 °C under an argon atmosphere. After stirring for 2 h at -78 °C, the reaction

mixture was allowed warming up to 0 °C and kept stirring for 1 h. Then the reaction mixture was diluted with CH_2Cl_2 (30 mL) and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 40 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (20% ethyl acetate/petroleum ether) to afford the primary alcohol (780 mg, 96%) as a clear oil.

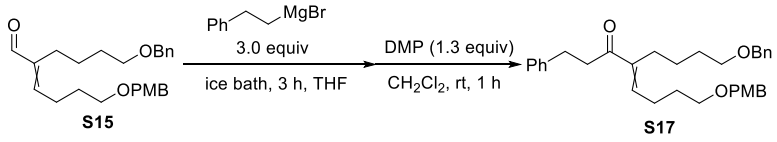
The primary alcohol (750 mg, 1.88 mmol, 1.0 equiv) obtained above was dissolved in CH_2Cl_2 (30 mL) and DMP (1.04 g, 2.45 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (30 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (40 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×20 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 **S15** (720 mg, 96%, mixture of *Z/E* isomers) as a colorless oil. Analytical data for **S15**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.30–7.26 (m, 2H), 7.26–7.24 (m, 2H), 7.23–7.15 (m, 3H), 6.81 (d, J = 8.8 Hz, 2H), 6.42–6.33 (m, 2H), 4.44–4.40 (m, 2H), 4.37–4.33 (m, 2H), 3.75–3.71 (m, 3H), 3.42–3.36 (m, 4H), 2.64–2.33 (m, 2H), 2.23–2.06 (m, 2H), 1.78–1.66 (m, 2H), 1.58–1.48 (m, 2H), 1.44–1.32 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.3, 191.2, 159.3, 154.9, 148.9, 143.9, 140.6, 138.7, 130.5, 130.4, 129.5, 129.4, 128.5, 127.7, 127.6, 113.9, 73.0, 72.83, 72.80, 70.3, 70.2, 69.1, 68.6, 55.4, 30.0, 29.8, 29.7, 29.6, 28.9, 25.9, 25.5, 25.4, 23.5; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{25}H_{32}NaO_4$ 419.2193; Found 419.2196.



To a solution of **S15** (1.80 g, 4.54 mmol, 1.0 equiv) in freshly distilled THF (40 mL) at 0 °C was added phenylmagnesium bromide (2.8 M, 2.43 mL, 6.81 mmol, 1.5 equiv) dropwise under argon atmosphere. After full conversion, 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).

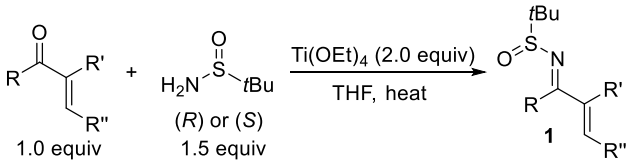
The alcohol obtained above was dissolved in CH_2Cl_2 (50 mL) and DMP (2.50 g, 5.90 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (40 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (50 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×20 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 (20% ethyl acetate/petroleum ether) to give **S16** (1.62 g, 75% for two steps; ~1:1 mixture of *Z/E* isomers) as a colorless oil. Analytical data for **S16**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.89 (m, 2H), 7.65–7.60 (m, 2H), 7.59–7.54 (m, 1H), 7.52–7.43 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.36–7.30 (m, 8H), 7.30–7.26 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.90–6.82 (m, 4H), 6.20 (t, *J* = 7.4 Hz, 1H), 5.68 (t, *J* = 7.6 Hz, 1H), 4.49 (s, 2H), 4.47 (s, 2H), 4.42 (s, 2H), 4.34 (s, 2H), 3.79 (s, 6H), 3.49 (t, *J* = 6.6 Hz, 2H), 3.44 (td, *J* = 6.4, 1.6 Hz, 4H), 3.33 (t, *J* = 6.6 Hz, 2H), 2.55–2.49 (m, 2H), 2.42–2.30 (m, 4H), 1.94 (q, *J* = 7.6 Hz, 2H), 1.76–1.67 (m, 4H), 1.67–1.59 (m, 4H), 1.53 (ddd, *J* = 15.7, 9.8, 6.6 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.5, 198.9, 159.3, 159.2, 145.4, 141.4, 140.5, 139.0, 138.73, 138.69, 137.1, 133.4, 131.6, 131.1, 130.7, 130.5, 129.5, 129.38, 129.36, 129.3, 128.8, 128.5, 128.1, 127.7, 127.6, 113.9, 113.8, 73.01, 72.97, 72.8, 72.5, 70.3, 70.1, 69.3, 69.2, 55.4, 35.2, 29.9, 29.6, 29.4, 29.1, 26.61, 26.59, 25.8, 25.7, 25.0; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{31}H_{36}NaO_4$ 495.2506; Found 495.2506.



To a solution of **S15** (0.67 g, 1.69 mmol, 1.0 equiv) in freshly distilled THF (20 mL) at 0 °C was added freshly prepared phenethylmagnesium bromide (~0.5 M, 10.1 mL, 5.07 mmol, 3.0 equiv) dropwise under argon atmosphere. After full conversion, 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).

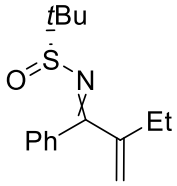
The alcohol obtained above was dissolved in CH_2Cl_2 (30 mL) and DMP (0.93 g, 2.20 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (20 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (30 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×20 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 (20% ethyl acetate/petroleum ether) to give **S17** (0.71 g, 84% for two steps) as a colorless oil. Analytical data for **S17**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 8H), 7.33–7.25 (m, 10H), 7.21 (dd, J = 7.0, 4.6 Hz, 6H), 6.89 (dd, J = 8.6, 1.8 Hz, 4H), 6.58 (t, J = 7.4 Hz, 1H), 5.56 (t, J = 7.6 Hz, 1H), 4.53–4.49 (m, 4H), 4.46–4.42 (m, 4H), 3.82–3.78 (m, 6H), 3.51–3.41 (m, 8H), 3.01–2.91 (m, 6H), 2.89–2.83 (m, 2H), 2.40–2.31 (m, 4H), 2.24 (q, J = 7.6 Hz, 4H), 1.79–1.67 (m, 4H), 1.67–1.57 (m, 4H), 1.48–1.36 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.9, 200.5, 159.2, 159.1, 142.5, 142.0, 141.6, 141.5, 141.2, 138.7, 138.6, 134.5, 130.6, 130.4, 129.29, 129.27, 128.5, 128.38, 128.36, 127.6, 127.54, 127.48, 126.1, 126.0, 113.79, 113.77, 72.9, 72.7, 72.5, 70.3, 70.0, 69.3, 69.2, 55.3, 44.0, 39.2, 34.2, 30.8, 29.8, 29.2, 29.0, 26.2, 25.9, 25.8, 25.5; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{33}H_{40}NaO_4$ 523.2819; Found 523.2820.

General procedure A for the synthesis of α,β-unsaturated *N*-sulfinyl ketimines

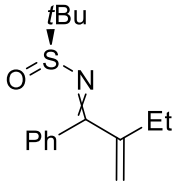


To a stirring solution of α-substituted α,β-unsaturated ketone (1.0 equiv) in dry THF (~1 M) in flame-dried round-bottom flask equipped with a magnetic stirring bar was added *N-tert*-butanesulfinamide (1.5 equiv) and $Ti(OEt)_4$ (tech. grade, ~20% Ti; 2.0 equiv). Then the flask was heated in a heating mantle at 76 °C. Conversion was followed by TLC, and the flask 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 vigorous stirring. The resulting suspension was filtered through a plug of celite and the filter cake was thoroughly washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The

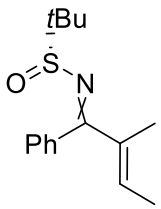
brine layer was extracted once with a small volume of EtOAc, and the combined organic portions were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by silica gel chromatography.



1a: The title compound was prepared according to the general procedure A using 2-methylene-1-phenylbutan-1-one (4.90 g, 30.58 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (5.56 g, 45.88 mmol, 1.5 equiv), and titanium ethoxide (12.82 mL, 61.17 mmol, 2.0 equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1a** (6.28 g, 78%) as an oil. Analytical data for **1a** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −147.2 (*c* = 0.24, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.98–7.71 (m, 1H), 7.32–7.18 (m, 1H), 7.13–7.01 (m, 3H), 5.41–5.15 (m, 1H), 5.06 (s, 1H), 2.62–2.07 (m, 2H), 1.23 (s, 9H), 1.09–0.89 (m, 3H); ^{13}C{^{1}H} NMR (10 MHz, C_6D_6) δ 180.0, 151.9, 148.0, 137.2, 132.0, 128.9, 128.7, 128.5, 128.2, 127.9, 127.0, 114.5, 56.4, 55.9, 29.1, 25.4, 22.6, 22.4, 13.3, 11.3; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{22}NOS$ 264.1417; Found 264.1415.

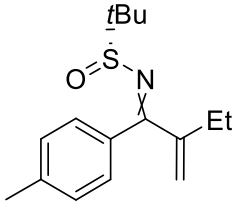


ent-**1a**: The title compound was prepared according to the general procedure A using 2-methylene-1-phenylbutan-1-one (1.80 g, 11.23 mmol, 1.0 equiv), *(S)-N-tert*-butanesulfinamide (2.04 g, 16.85 mmol, 1.5 equiv), and titanium ethoxide (4.71 mL, 22.47 mmol, 2.0 equiv). Column chromatography (10-15% ethyl acetate/petroleum ether) afforded *ent*-**1a** (2.19 g, 74%) as an oil. Analytical data for *ent*-**1a** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = +149.3 (*c* = 0.28, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.57–7.35 (m, 3H), 7.25–7.15 (m, 1H), 5.83–5.40 (m, 1H), 5.33–5.10 (m, 1H), 2.69–2.18 (m, 2H), 1.37–1.07 (m, 12H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 181.3, 180.7, 151.4, 147.3, 136.4, 132.3, 128.9, 128.5, 127.9, 115.2, 56.4, 28.7, 24.9, 22.3, 12.9, 11.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{22}NOS$ 264.1417; Found 264.1422.

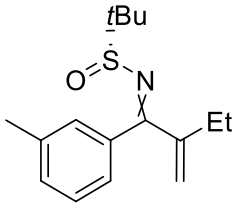


1a′: The title compound was prepared according to the general procedure A using 2-methylene-1-phenylbutan-1-one (2.00 g, 12.48 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.27 g, 18.72 mmol, 1.5 equiv), and titanium ethoxide (5.23 mL, 24.97 mmol, 2.0 equiv). Column chromatography (10-15% ethyl acetate/petroleum ether) afforded **1a′** (2.41 g, 73%) as an oil. Analytical data for **1a′**

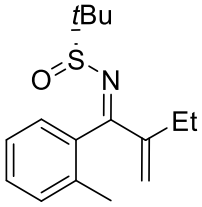
(mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −183.7 (*c* = 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.33 (m, 4H), 7.18 (s, 1H), 6.04–5.55 (m, 1H), 2.02 (s, 3H), 1.82 (d, *J* = 6.8 Hz, 3H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.1, 142.6, 139.2, 136.6, 128.7, 127.9, 127.8, 55.9, 22.1, 15.3, 12.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{22}NOS$ 264.1417; Found 264.1420.



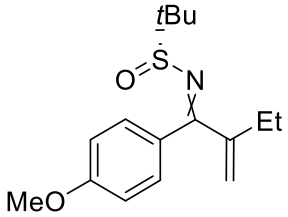
1b: The title compound was prepared according to the general procedure A using 2-methylene-1-(*p*-tolyl)butan-1-one **S1** (3.06 g, 17.56 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (3.19 g, 26.34 mmol, 1.5 equiv), and titanium ethoxide (11.05 mL, 52.69 mmol, 2.0 equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1b** (3.95 g, 81%) as an oil. Analytical data for **1b** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −135.3 (*c* = 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.71 (m, 1H), 7.24–7.09 (m, 3H), 5.85–5.37 (m, 1H), 5.35–5.04 (m, 1H), 2.64–2.22 (m, 5H), 1.36–1.18 (m, 9H), 1.18–1.07 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 181.2, 151.6, 147.3, 143.1, 139.0, 133.6, 129.2, 128.9, 128.8, 128.5, 128.0, 127.3, 115.0, 66.3, 56.3, 28.7, 24.9, 22.3, 21.5, 12.9, 11.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{24}NOS$ 278.1573; Found 278.1578.



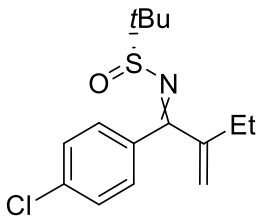
1c: The title compound was prepared according to the general procedure A using 2-methylene-1-(*m*-tolyl)butan-1-one **S2** (2.60 g, 14.92 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.71 g, 22.38 mmol, 1.5 equiv), and titanium ethoxide (6.26 mL, 29.84 mmol, 2.0 equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1c** (3.38 g, 82%) as an oil. Analytical data for **1c** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −154.7 (*c* = 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.35–7.27 (m, 1H), 7.26–7.19 (m, 1H), 7.03 (s, 1H), 5.82–5.38 (m, 1H), 5.30–5.10 (m, 1H), 2.64–2.22 (m, 5H), 1.39–1.19 (m, 9H), 1.14 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 181.4, 181.2, 151.5, 147.3, 138.2, 137.6, 136.4, 133.1, 129.8, 129.2, 128.3, 127.7, 126.2, 125.1, 115.1, 56.3, 28.7, 24.8, 22.3, 21.5, 12.9, 11.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{24}NOS$ 278.1573; Found 278.1574.



1d: The title compound was prepared according to the general procedure A using 2-methylene-1-(*o*-tolyl)butan-1-one (1.30 g, 7.46 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.36 g, 11.19 mmol, 1.5 equiv), and titanium ethoxide (3.13 mL, 14.92 mmol, 2.0 equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1d** (1.10 g, 53%) as an oil. Analytical data for **1d** (mixture of rotamers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −236.4 (*c* = 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 1H), 7.25–6.88 (m, 3H), 5.69 (s, 1H), 5.20 (s, 1H), 2.64–2.51 (m, 2H), 2.25–2.09 (m, 3H), 1.26–1.21 (m, 9H), 1.18 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.3, 180.6, 151.0, 150.9, 137.3, 136.3, 135.5, 133.7, 130.1, 129.8, 129.0, 128.9, 128.7, 126.7, 125.2, 56.5, 56.0, 24.7, 22.3, 19.9, 19.6, 13.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{24}NOS$ 278.1573; Found 278.1581.

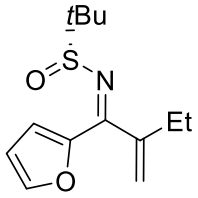


1e: The title compound was prepared according to the general procedure A using 1-(4-methoxyphenyl)-2-methylenebutan-1-one (2.40 g, 12.62 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.29 g, 18.92 mmol, 1.5 equiv), and titanium ethoxide (5.29 mL, 25.23 mmol, 2.0 equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1e** (2.95 g, 80%) as an oil. Analytical data for **1e** (mixture of imino *Z*/*E* isomers): R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −112.7 (*c* = 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.67 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.88–5.37 (m, 1H), 5.35–5.03 (m, 1H), 3.85 (s, 3H), 2.65–2.19 (m, 2H), 1.28 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 181.0, 163.2, 147.3, 131.0, 128.9, 115.1, 113.9, 56.23, 56.19, 55.48, 55.47, 28.9, 22.3, 11.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{24}NO_2S$ 294.1522; Found 294.1529.

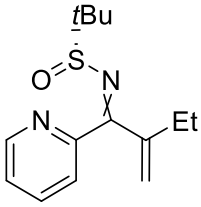


1f: The title compound was prepared according to the general procedure A using 1-(4-chlorophenyl)-2-methylenebutan-1-one **S3** (3.00 g, 15.41 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.80 g, 23.12 mmol, 1.5 equiv), and titanium ethoxide (6.46 mL, 30.82 mmol, 2.0

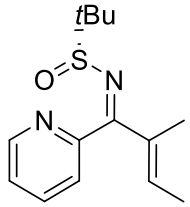
equiv). Column chromatography (10–15% ethyl acetate/petroleum ether) afforded **1f** (3.28 g, 71%) as an oil. Analytical data for **1f** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −124.7 (*c* = 0.27, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 5.83–5.38 (m, 1H), 5.18 (s, 1H), 2.67–2.18 (m, 2H), 1.29 (s, 9H), 1.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.9, 151.3, 146.9, 138.5, 134.8, 130.1, 129.4, 128.8, 128.1, 127.4, 115.5, 67.9, 56.6, 28.7, 25.6, 24.8, 22.3, 12.8, 11.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{21}ClNOS$ 298.1027; Found 298.1033.



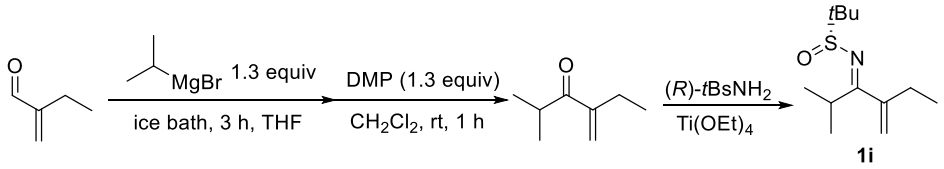
1g: The title compound was prepared according to the general procedure A using 1-(furan-2-yl)-2-methylenebutan-1-one **S4** (1.55 g, 10.32 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.88 g, 15.48 mmol, 1.5 equiv), and titanium ethoxide (4.33 mL, 20.64 mmol, 2.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded **1g** (2.01 g, 77%) as an oil. Analytical data for **1g**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = −148.0 (*c* = 0.26, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.56 (m, 1H), 6.95 (d, *J* = 3.6 Hz, 1H), 6.49 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.38 (s, 1H), 5.16 (s, 1H), 2.50–2.38 (m, 2H), 1.27 (s, 9H), 1.10 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 184.8, 172.7, 168.9, 147.0 , 118.6, 115.8, 112.3, 57.0, 28.8, 22.4, 11.8; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{13}H_{19}NNaO_2S$ 276.1029; Found 276.1033.



1h: The title compound was prepared according to the general procedure A using 2-methylene-1-(pyridin-2-yl)butan-1-one **S5** (3.75 g, 23.26 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (4.23 g, 34.89 mmol, 1.5 equiv), and titanium ethoxide (9.75 mL, 46.52 mmol, 2.0 equiv). Column chromatography (40% ethyl acetate/petroleum ether) afforded **1h** (3.94 g, 64%) as an oil. Analytical data for **1h** (mixture of imino *Z*/*E* isomers): R_f = 0.20 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{20}_D$ = −314.2 (*c* = 0.16, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.2 Hz, 1H), 7.69 (s, 1H), 7.41–7.13 (m, 2H), 5.76–5.37 (m, 1H), 5.13 (s, 1H), 2.62–2.29 (m, 2H), 1.21 (s, 9H), 1.16–1.06 (m, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 175.2, 155.2, 150.1, 149.0, 135.6, 126.4, 123.6, 123.5, 57.4, 24.9, 22.5, 12.7; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{21}N_2OS$ 265.1369; Found 265.1373.



1h′: The title compound was prepared according to the general procedure A using (*E*)-2-methyl-1-(pyridin-2-yl)but-2-en-1-one **S6** (1.70 g, 10.55 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.92 g, 15.82 mmol, 1.5 equiv), and titanium ethoxide (4.42 mL, 21.09 mmol, 2.0 equiv). Column chromatography (40% ethyl acetate/petroleum ether) afforded **1h′** (2.23 g, 80%) as an oil. Analytical data for **1h′**: R_f = 0.20 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{20}_D = -287.6$ (*c* = 0.28, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.68 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29–7.20 (m, 2H), 5.81–5.71 (m, 1H), 1.98 (s, 3H), 1.78 (d, *J* = 7.2 Hz, 3H), 1.19 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.9, 155.5, 149.0, 141.5, 138.3, 135.6, 123.7, 123.3, 57.0, 22.4, 15.3, 12.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{21}N_2OS$ 265.1369; Found 265.1374.

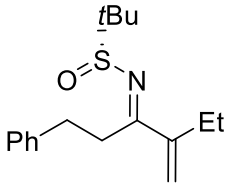


To a solution of ethylacrolein (1.60 g, 19.02 mmol, 1.0 equiv) in freshly distilled THF (40 mL) at 0 °C was added isopropylmagnesium bromide (1 M in THF, 24.7 mL, 24.73 mmol, 1.3 equiv) dropwise under argon atmosphere. After the aldehyde was consumed completely, saturated aqueous ammonium chloride (30 mL) was added carefully and the aqueous phase was extracted with CH_2Cl_2 (30 mL×3). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by silica gel column chromatography (15% ethyl acetate/petroleum ether), and the eluent was concentrated to 30 mL before used to next step.

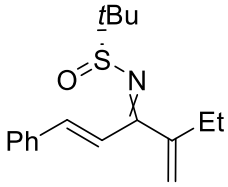
To the alcohol obtained above with solvent was added CH_2Cl_2 (100 mL) and DMP (10.49 g, 24.73 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (50 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (80 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to 30 mL. The crude ketone was used to next step without further purification.

According to the general procedure A, **1i** was prepared using crude ketone obtained above,

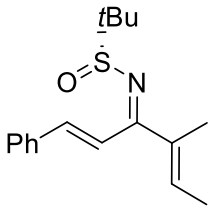
(R)-N-tert-butanesulfinamide (4.61 g, 38.04 mmol, 2.0 equiv), and titanium ethoxide (11.96 mL, 57.06 mmol, 3.0 equiv) in a seal tube. Column chromatography (10% ethyl acetate/petroleum ether) afforded **1i** (1.40 g, 32% for three steps) as an oil. Analytical data for **1i**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −168.5 (*c* = 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (s, 1H), 4.94 (s, 1H), 2.66 (s, 1H), 2.29–2.15 (m, 2H), 1.18 (s, 9H), 1.15–1.09 (m, 6H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.5, 148.9, 113.4, 55.8, 38.2, 27.7, 22.2, 20.0, 19.8, 11.4; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{12}H_{24}NOS$ 230.1573; Found 230.1578.



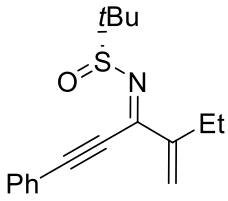
1j: The title compound was prepared according to the general procedure A using 4-methylene-1-phenylhexan-3-one (2.70 g, 14.34 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.61 g, 21.51 mmol, 1.5 equiv), and titanium ethoxide (6.01 mL, 28.68 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1j** (3.10 g, 74%) as a white solid. Analytical data for **1j**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); mp 55–56 °C; $[\alpha]^{20}_D$ = −216.0 (*c* = 0.31, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 4H), 7.22–7.17 (m, 1H), 5.79 (s, 1H), 5.57 (s, 1H), 3.41–3.28 (m, 1H), 3.24–3.12 (m, 1H), 3.00–2.87 (m, 2H), 2.36 (q, *J* = 7.4 Hz, 2H), 1.28 (s, 9H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 179.4, 149.9, 140.8, 128.51, 128.46, 126.3, 119.9, 57.4, 35.2, 33.9, 25.5, 22.7, 13.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{26}NOS$ 292.1730; Found 292.1735.



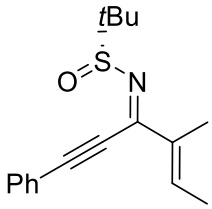
1k: The title compound was prepared according to the general procedure A using (*E*)-4-methylene-1-phenylhex-1-en-3-one (1.70 g, 9.13 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.66 g, 13.69 mmol, 1.5 equiv), and titanium ethoxide (3.83 mL, 18.25 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1k** (3.10 g, 74%) as an oil. Analytical data for **1k** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −411.7 (*c* = 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.4 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.44–7.29 (m, 3H), 7.11–6.85 (m, 1H), 5.57–4.96 (m, 2H), 2.53–2.27 (m, 2H), 1.28 (s, 9H), 1.13 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.1, 149.4, 142.4, 135.4, 129.9, 129.0, 128.1, 122.5, 119.7, 115.0, 58.0, 27.5, 22.7, 22.5, 12.6; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{24}NOS$ 290.1573; Found 290.1580.



1k′: The title compound was prepared according to the general procedure A using **S7** (1.37 g, 7.36 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.34 g, 11.03 mmol, 1.5 equiv), and titanium ethoxide (3.08 mL, 14.71 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1k′** (1.71 g, 81%) as an oil. Analytical data for **1k′**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −380.6 (*c* = 0.26, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.45 (m, 3H), 7.38–7.28 (m, 3H), 6.86 (d, *J* = 15.5 Hz, 1H), 6.28 (s, 1H), 1.94 (s, 3H), 1.84 (d, *J* = 6.0 Hz, 3H), 1.26 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 178.6, 140.8, 137.1, 135.5, 135.4, 129.5, 128.9, 127.8, 122.8, 57.3, 22.5, 14.8, 14.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{24}NOS$ 290.1573; Found 290.1578.

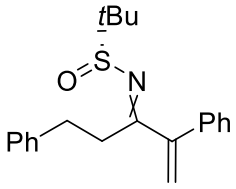


1l: The title compound was prepared according to the general procedure A using **S8** (3.27 g, 17.75 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (3.23 g, 26.62 mmol, 1.5 equiv), and titanium ethoxide (7.44 mL, 35.50 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1l** (4.10 g, 80%) as an oil. Analytical data for **1l**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −405.9 (*c* = 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.46–7.36 (m, 3H), 6.36–6.34 (m, 1H), 5.81–5.78 (m, 1H), 2.54–2.46 (m, 2H), 1.30 (s, 9H), 1.14 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 149.4, 132.6, 130.5, 128.7, 125.5, 120.9, 102.8, 82.2, 57.7, 24.2, 22.6, 12.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{22}NOS$ 288.1417; Found 288.1423.

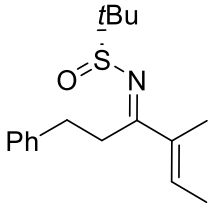


1l′: The title compound was prepared according to the general procedure A using **S9** (2.70 g, 14.65 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.66 g, 21.98 mmol, 1.5 equiv), and titanium ethoxide (6.15 mL, 29.31 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1l′** (3.30 g, 83%) as a yellow solid. Analytical data for **1l′**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); mp 126–127 °C; $[\alpha]^{20}_D$ = −353.0 (*c* = 0.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.8 Hz, 2H), 7.46–7.35 (m, 3H), 7.10–7.02 (m, 1H), 2.00–1.94 (m, 6H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 140.5, 137.3, 132.4,

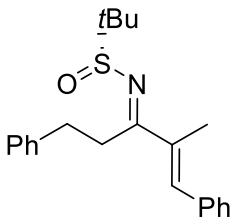
130.3, 128.6, 120.9, 102.6, 81.7, 57.3, 22.3, 15.3, 11.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{22}NOS$ 288.1417; Found 288.1423.



1r: The title compound was prepared according to the general procedure A using 2,5-diphenylpent-1-en-3-one (1.75 g, 7.41 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.35 g, 11.11 mmol, 1.5 equiv), and titanium ethoxide (3.11 mL, 14.81 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1r** (2.20 g, 88%) as an oil. Analytical data for **1r** (mixture of imino *Z*/*E* isomers): R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −63.4 (*c* = 0.24, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.29 (m, 3H), 7.29–7.26 (m, 2H), 7.26–7.20 (m, 3H), 7.18 (t, *J* = 7.0 Hz, 2H), 5.90–5.72 (m, 1H), 5.70–5.23 (m, 1H), 3.45–3.16 (m, 1H), 3.07–2.82 (m, 3H), 1.26–1.12 (m, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 185.4, 180.2, 149.7, 146.9, 140.5, 140.3, 138.8, 135.7, 128.8, 128.7, 128.4, 127.9, 127.7, 126.2, 126.1, 121.1, 115.2, 57.6, 55.6, 42.4, 34.7, 34.3, 31.3, 22.5, 22.0; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{21}H_{25}NNaOS$ 362.1549; Found 362.1555.

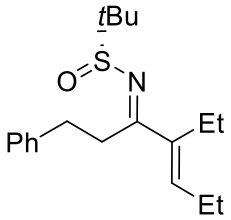


1s: The title compound was prepared according to the general procedure A using (*E*)-4-methyl-1-phenylhex-4-en-3-one (2.86 g, 15.19 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.76 g, 22.79 mmol, 1.5 equiv), and titanium ethoxide (6.40 mL, 30.38 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1s** (3.40 g, 77%) as a white solid. Analytical data for **1s**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); mp 71–72 °C; $[\alpha]^{20}_D$ = −196.2 (*c* = 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 3H), 7.26–7.23 (m, 1H), 7.19 (t, *J* = 6.6 Hz, 1H), 6.55–6.43 (m, 1H), 3.39–3.25 (m, 1H), 3.21–3.10 (m, 1H), 2.99–2.82 (m, 2H), 1.87 (d, *J* = 6.8 Hz, 3H), 1.84 (s, 3H), 1.27 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 180.4, 140.8, 137.4, 133.3, 128.44, 128.39, 126.2, 57.0, 35.4, 33.3, 22.5, 15.1, 12.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{26}NOS$ 292.1730; Found 292.1735.

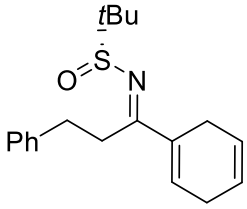


1t: The title compound was prepared according to the general procedure A using (*E*)-2-methyl-1,5-diphenylpent-1-en-3-one (2.20 g, 8.79 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.60 g, 13.18 mmol, 1.5 equiv), and titanium ethoxide (3.68 mL, 17.58 mmol, 2.0 equiv). Column

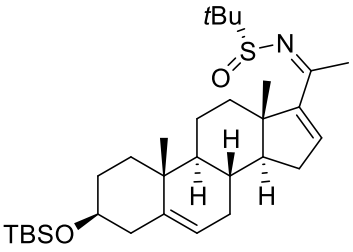
chromatography (10% ethyl acetate/petroleum ether) afforded **1t** (2.65 g, 85%) as an oil. Analytical data for **1t**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −58.3 (*c* = 0.49, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.36–7.32 (m, 3H), 7.31–7.27 (m, 5H), 7.24–7.18 (m, 1H), 3.57–3.41 (m, 1H), 3.39–3.24 (m, 1H), 3.11–2.94 (m, 2H), 2.08 (s, 3H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.9, 140.9, 137.7, 136.7, 135.8, 129.7, 128.7, 128.6, 128.5, 128.2, 126.5, 57.6, 35.5, 33.7, 22.8, 15.0; HRMS (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd for $C_{22}H_{27}NNaOS$ 376.1706; Found 376.1712.



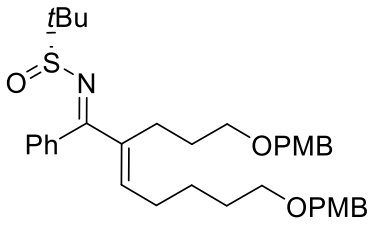
1u: The title compound was prepared according to the general procedure A using **S10** (2.70 g, 12.48 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (2.27 g, 18.72 mmol, 1.5 equiv), and titanium ethoxide (5.23 mL, 24.96 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1u** (3.40 g, 85%) as an oil. Analytical data for **1u**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = −178.8 (*c* = 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 7.22–7.17 (m, 1H), 6.28 (t, *J* = 7.0 Hz, 1H), 3.39–3.26 (m, 1H), 3.22–3.10 (m, 1H), 2.99–2.81 (m, 2H), 2.39 (q, *J* = 7.4 Hz, 2H), 2.27 (p, *J* = 7.4 Hz, 2H), 1.28 (s, 9H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.2, 141.8, 140.9, 140.4, 128.5, 126.3, 56.9, 35.4, 33.4, 22.6, 22.3, 20.1, 13.9, 13.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{30}NOS$ 320.2043; Found 320.2050.



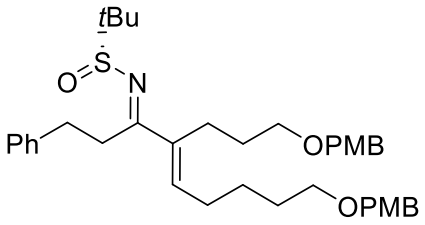
1v: The title compound was prepared according to the general procedure A using **S11** (1.70 g, 8.01 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.46 g, 12.01 mmol, 1.5 equiv), and titanium ethoxide (3.36 mL, 16.02 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1v** (2.28 g, 90%) as a white solid. Analytical data for **1u**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); mp 127–128 °C; $[\alpha]^{20}_D$ = −150.1 (*c* = 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 4H), 7.23–7.17 (m, 1H), 6.65 (s, 1H), 5.86–5.77 (m, 1H), 5.73–5.64 (m, 1H), 3.39–3.28 (m, 1H), 3.22–3.12 (m, 1H), 3.01–2.85 (m, 6H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 178.8, 140.9, 135.5, 133.0, 128.6, 128.5, 126.4, 125.1, 122.0, 57.3, 35.5, 33.1, 27.8, 25.9, 22.7; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{26}NOS$ 316.1730; Found 316.1734.



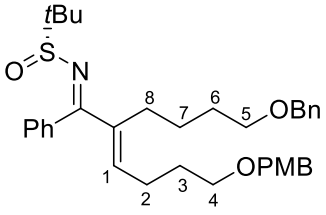
1w: The title compound was prepared according to the general procedure A using TBS-protected 16-dehydropregnenolone (1.20 g, 2.80 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (0.51 g, 4.20 mmol, 1.5 equiv), and titanium ethoxide (1.17 mL, 5.60 mmol, 2.0 equiv). Column chromatography (10% ethyl acetate/petroleum ether) afforded **1w** (1.15 g, 77%) as a white solid. Analytical data for **1w**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); mp 157–158 °C; $[\alpha]^{20}_D$ = +3.4 (*c* = 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55–6.51 (m, 1H), 5.33 (d, *J* = 5.2 Hz, 1H), 3.53–3.43 (m, 1H), 2.51–2.39 (m, 4H), 2.34–2.23 (m, 2H), 2.22–2.14 (m, 1H), 2.07–1.97 (m, 2H), 1.83–1.77 (m, 1H), 1.75–1.68 (m, 2H), 1.67–1.61 (m, 1H), 1.59–1.48 (m, 3H), 1.46–1.41 (m, 1H), 1.39–1.34 (m, 1H), 1.27 (s, 9H), 1.13–1.02 (m, 4H), 1.02–0.95 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.4, 155.9, 142.2, 141.4, 120.8, 72.7, 57.0, 56.7, 50.6, 46.9, 42.9, 37.4, 36.9, 35.4, 32.3, 32.2, 31.6, 30.3, 26.1, 22.6, 21.0, 20.4, 19.5, 18.4, 16.0, -4.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{31}H_{54}NO_2SSi$ 532.3639; Found 532.3638.



1x: The title compound was prepared according to the general procedure A using **S13** (2.27 g, 4.52 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (0.82 g, 6.77 mmol, 1.5 equiv), and titanium ethoxide (1.89 mL, 9.03 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded **1x** (1.91 g, 70%) as an oil. Analytical data for **1x**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{20}_D$ = −80.5 (*c* = 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.35 (m, 3H), 7.31–7.08 (m, 6H), 6.95–6.80 (m, 4H), 5.86–5.72 (m, 1H), 4.49–4.29 (m, 4H), 3.84–3.74 (m, 6H), 3.59–3.32 (m, 4H), 2.80–2.44 (m, 2H), 2.32–2.18 (m, 2H), 1.92–1.68 (m, 2H), 1.61–1.33 (m, 4H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.9, 159.12, 159.09, 148.5, 142.3, 136.7, 130.7, 130.6, 129.21, 129.19, 128.9, 128.0, 127.9, 113.8, 113.7, 72.52, 72.50, 69.7, 69.6, 55.9, 55.3, 29.5, 29.2, 25.6, 23.5, 22.2; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{36}H_{47}NNaO_5S$ 628.3067; Found 628.3071.

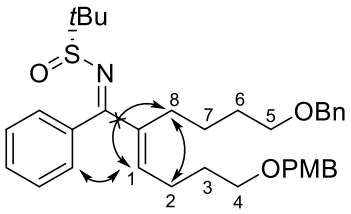


1y: The title compound was prepared according to the general procedure A using **S14** (1.50 g, 2.83 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (0.51 g, 4.24 mmol, 1.5 equiv), and titanium ethoxide (1.19 mL, 5.65 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded **1y** (1.40 g, 78%) as an oil. Analytical data for **1y**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{20}_D$ = −88.0 (*c* = 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 8H), 7.20–7.15 (m, 1H), 6.90–6.78 (m, 4H), 6.32 (t, *J* = 6.8 Hz, 1H), 4.42 (s, 2H), 4.40 (s, 2H), 3.77 (s, 6H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 3.35–3.24 (m, 1H), 3.18–3.07 (m, 1H), 2.96–2.76 (m, 2H), 2.49–2.36 (m, 2H), 2.26 (q, *J* = 7.2 Hz, 2H), 1.70–1.57 (m, 4H), 1.56–1.45 (m, 2H), 1.24 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.4, 159.23, 159.17, 140.8, 140.3, 139.8, 130.8, 130.7, 129.3, 129.2, 128.6, 128.5, 126.3, 113.9, 113.8, 72.7, 72.6, 69.9, 69.8, 57.0, 55.4, 35.4, 33.5, 29.7, 29.3, 29.1, 26.0, 23.8, 22.7; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{38}H_{51}NNaO_5S$ 656.3380; Found 656.3383.

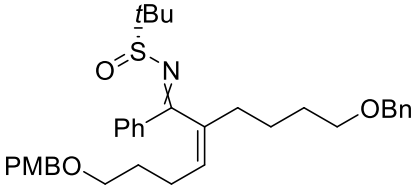


(2*E*)-**1z**: The title compound was prepared according to the general procedure A using **S16** (1.70 g, 3.60 mmol, 1.0 equiv; *Z*/*E* mixture), *(R)-N-tert*-butanesulfinamide (1.31 g g, 10.79 mmol, 3.0 equiv), and titanium ethoxide (6.03 mL, 28.78 mmol, 8.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded **1z** (mixture of 2*Z* and 2*E*, partially separable via column chromatography) (1.24 g, 60%; 0.41 g of **S16** was recovered) as an oil. Analytical data for (2*E*)-**1z**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −79.6 (*c* = 0.19, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.36 (m, 3H), 7.35–7.33 (m, 3H), 7.31–7.26 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.75 (t, *J* = 7.5 Hz, 1-*CH*, 1H), 4.50 (s, 2H), 4.36 (s, 2H), 3.79 (s, 3H), 3.49 (t, *J* = 6.6 Hz, 5-CH_2, 2H), 3.33 (q, *J* = 6.0 Hz, 4-CH_2, 2H), 2.74–2.66 (m, 8-CH_2, 1H), 2.49–2.43 (m, 8-CH_2, 1H), 2.33–2.25 (m, 2-CH_2, 2H), 1.73–1.68 (m, 6-CH_2, 2H), 1.61–1.53 (m, 3-CH_2, 7-CH_2, 4H), 1.17 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 182.1, 159.2, 147.9, 143.1, 138.6, 136.8, 130.5, 129.4, 129.0, 128.4, 128.0, 127.9, 127.7, 127.6, 113.8, 73.0, 72.7, 70.4, 69.1, 56.0, 55.4, 30.2, 29.0, 26.6, 26.3, 26.0, 22.2; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{35}H_{45}NNaO_4S$ 598.2962; Found 598.2966.

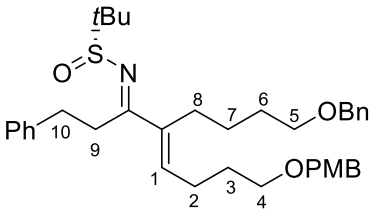
Table S1. NOESY ($CDCl_3$, 600 MHz) for (2*E*)-**1z.**



entry	NOE observed between		conclusion
1	H2 (2.25–2.33 ppm)	H8 (2.43–2.49 ppm) H8 (2.66–2.74 ppm)	H2 and H8 are *cis*



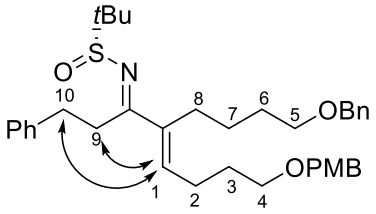
(2*Z*)-**1z**: Analytical data for (2*Z*)-**1z** (mixture of imino *Z*/*E* isomers): R_f = 0.23 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −47.0 (*c* = 0.14, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96–7.84 (m, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35–7.27 (m, 5H), 7.20–7.16 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.76–5.58 (m, 1H), 4.47 (s, 2H), 4.34 (s, 2H), 3.79 (s, 3H), 3.44 (t, *J* = 6.0 Hz, 2H), 3.41–3.32 (m, 2H), 2.42–2.18 (m, 2H), 2.11–1.88 (m, 2H), 1.76–1.70 (m, 1H), 1.68–1.56 (m, 5H), 1.33–1.28 (m, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 181.9, 180.8, 159.1, 138.7, 138.5, 137.9, 136.4, 135.9, 135.6, 132.7, 132.3, 130.7, 130.6, 130.4, 129.42, 129.36, 129.3, 129.0, 128.7, 128.6, 128.5, 127.74, 127.66, 127.6, 127.2, 113.8, 73.0, 72.9, 72.5, 70.3, 70.1, 69.8, 69.6, 56.5, 56.1, 55.4, 36.0, 35.8, 29.73, 29.69, 29.2, 27.3, 26.9, 24.2, 24.0, 22.7, 22.5, 22.3; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{35}H_{45}NNaO_4S$ 598.2962; Found 598.2962.



(2*E*)-**1aa**: The title compound was prepared according to the general procedure A using **S17** (2.10 g, 4.19 mmol, 1.0 equiv), *(R)-N-tert*-butanesulfinamide (1.53 g g, 12.58 mmol, 3.0 equiv), and titanium ethoxide (4.40 mL, 20.97 mmol, 5.0 equiv). Column chromatography (25% ethyl acetate/petroleum ether) afforded **1aa** (mixture of 2*Z* and 2*E*, partially separable via column chromatography) (1.68 g, 66%) as an oil. Analytical data for (2*E*)-**1aa**: R_f = 0.25 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −88.3 (*c* = 0.21, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.26–7.24 (m, 1H), 7.23–7.15 (m, 8H), 7.13 (t, *J* =

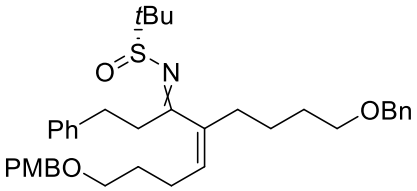
7.2 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.27 (t, *J* = 7.2 Hz, 1-*CH*, 1H), 4.41 (s, 2H), 4.36 (s, 2H), 3.70 (s, 3H), 3.41–3.36 (m, 4-CH_2, 5-CH_2, 4H), 3.21 (td, *J* = 12.0, 6.0 Hz, 9-CH_2, 1H), 3.06 (td, *J* = 12.0, 5.4 Hz, 9-CH_2, 1H), 2.83 (td, *J* = 11.4, 5.4 Hz, 10-CH_2, 1H), 2.74 (td, *J* = 11.4, 5.4 Hz, 10-CH_2, 1H), 2.37–2.32 (m, 8-CH_2, 1H), 2.32–2.26 (m, 2-CH_2, 8-CH_2, 3H), 1.68 (p, *J* = 6.6 Hz, 3-CH_2, 2H), 1.59–1.53 (m, 6-CH_2, 2H), 1.35 (p, *J* = 7.8 Hz, 7-CH_2, 2H), 1.19 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 180.4, 159.3, 141.0, 140.9, 139.1, 138.7, 130.5, 129.4, 128.59, 128.55, 128.4, 127.7, 127.6, 126.4, 113.9, 73.0, 72.8, 70.4, 69.3, 57.0, 55.3, 35.4, 33.6, 30.2, 29.4, 26.9, 26.2, 26.0, 22.6; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{37}H_{49}NNaO_4S$ 626.3275; Found 626.3270.

Table S2. NOESY ($CDCl_3$, 600 MHz) for (2*E*)-**1aa.**



(2*E*)-**1aa**

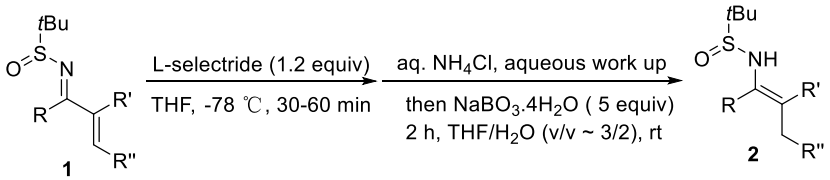
entry	NOE observed between		conclusion
1	H1 (6.27 ppm)	H9 (3.21 ppm) H9 (3.06 ppm)	H1 and H9 are *cis*
2	H1 (6.27 ppm)	H10 (2.83 ppm) H10 (2.74 ppm)	H1 and H10 are *cis*



(2*Z*)-**1aa**: Analytical data for (2*Z*)-**1aa** (mixture of imino *Z*/*E* isomers): R_f = 0.23 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D = -57.4$ (*c* = 0.19, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 4H), 7.31–7.16 (m, 8H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.52–5.20 (m, 1H), 4.51 (s, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.56–3.36 (m, 4H), 3.28–2.62 (m, 4H), 2.38–1.87 (m, 4H), 1.85–1.44 (m, 6H), 1.22 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 188.7, 187.3, 159.1, 141.1, 138.6, 130.6, 129.3, 128.53, 128.45, 128.4, 127.7, 127.6 , 126.2 , 125.1 , 113.8 , 73.0 , 72.5 , 70.2 , 70.1 , 69.6 , 69.3 , 59.0 , 55.7 , 55.3 , 42.4 , 35.3 , 35.1, 34.8, 31.0, 29.6, 29.3, 27.0, 26.5, 24.4, 24.3, 22.5, 22.2; HRMS (ESI-Orbitrap) *m/z:*

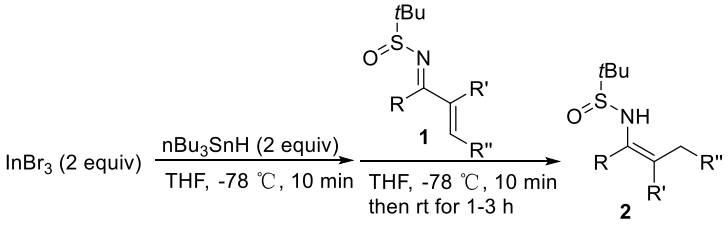
$[M + Na]^+$ Calcd for $C_{37}H_{49}NNaO_4S$ 626.3275; Found 626.3271.

General procedure B for the 1,4-reduction using Li(*s*-Bu)$_3$BH (L-Selectride)



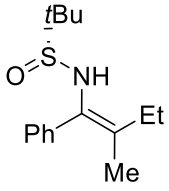
A solution of α-substituted α,β-unsaturated *N*-sulfinyl ketamine **1** (1.0 equiv) in freshly distilled THF (0.1 M) was added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon atmosphere via syringe. The solution was cooled to –78 °C and L-Selectride (1.0 M in THF, 1.2 equiv) was added dropwise to the solution by syringe. The reaction progress was monitored by TLC. Upon completion (usually 15–60 min), the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ^oC water bath). To the residue was added THF/H_2O (0.1 M, v/v~3/2) and sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$) (5.0 equiv) at rt. The mixture was stirred vigorously for 2 hours and then extracted with CH_2Cl_2 (×3), dried, filtered and concentrated under reduced pressure (in ≤ 25 ^oC water bath). The residue was purified by column chromatography to afford enesulfinamide **2** (solvent was removed under reduced pressure in ≤ 37 ^oC water bath).

General procedure C for the 1,4-reduction using InBr$_3$/*n*Bu$_3$SnH

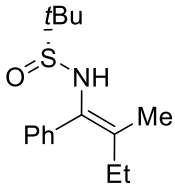


Anhydrous indium tribromide ($InBr_3$) (2.0 equiv) was placed in a flame-dried schlenk flask equipped with a magnetic stirring bar and heated with a heat gun in vacuo for 2 min. The indium salt was dissolved with freshly distilled THF (0.1 M) at rt under an argon atmosphere. The solution turned to a white suspension upon cooling to –78 ˚C. Tributyltin hydride (nBu$_3$SnH) (2.0 equiv) was then added dropwise to the suspension at –78 ˚C. The mixture was then stirred for 10 min. Then a solution of α-substituted α,β-unsaturated *N*-sulfinyl ketamine **1** (1.0 equiv) in dry

THF was added to the mixture, and stirred for 10 more min at –78 ˚C before warmed to rt. The reaction progress was monitored by TLC. Upon completion (usually 1–2 h), the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (×3). The combined organic extracts were washed with aqueous solution of sodium hydroxide (1.0 M) once, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford enesulfinamide **2** (solvent was removed under reduced pressure in ≤ 37 °C water bath).



(*Z*)-**2a** (Table 1 entry 1): The title compound was prepared according to the general procedure B using **1a** (34.0 mg, 0.129 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 155 μL, 0.155 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (99.3 mg, 0.645 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2a** (27.8 mg, 81%) as a white solid. Analytical data for (*Z*)-**2a**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); *Z*/*E* > 40:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.52 (dd, J = 8.2, 1.2 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 4.96 (s, 1H), 2.31–2.15 (m, 2H), 1.60 (s, 3H), 1.05 (t, J = 7.6 Hz, 3H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 139.0, 133.2, 130.9, 128.4, 127.9, 124.7, 55.5, 26.4, 22.4, 18.8, 12.5; The spectral data were in agreement with our previously reported.[S1]



(*E*)-**2a** (Table 1 entry 2): The title compound was prepared according to the general procedure B using **1a′** (41.5 mg, 0.158 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 189 μL, 0.189 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (121.2 mg, 0.788 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2a** (34.9 mg, 83%) as a white solid. Analytical data for (*E*)-**2a**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +69.6 (c = 0.29, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.53 (dd, J = 8.2, 1.0 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 5.01 (s, 1H), 1.99 (q, J = 7.6 Hz, 2H), 1.76 (s, 3H), 0.98 (s, 9H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.8, 133.9, 130.6, 128.5, 128.0, 124.0, 55.5, 28.0, 22.5, 16.4, 13.4; HRMS

(ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{15}H_{23}NNaOS$ 288.1393; Found 288.1400.

Table 1 entry 3: According to the general procedure B, the reaction using **1a** (32.0 mg, 0.121 mmol, 1.0 equiv)/$LiEt_3BH$ (0.146 mL, 0.146 mmol, 1.2 equiv) afforded (*Z*)-**2a** (21.5 mg, 67%) with >30:1 *Z/E* (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture).

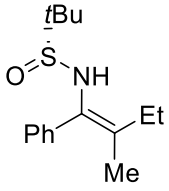
Table 1 entry 4: To a solution of **1a** (30.0 mg, 0.114 mmol, 1.0 equiv) in ethanol (2.0 mL) at –20 ˚C was added $NaBH_4$ (8.6 mg, 0.228 mmol, 2.0 equiv), and stirred for 4 h until full conversion. The reaction mixture was quenched with saturated aqueous ammonium chloride (3.0 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford (*Z*)-**2a** (23.8 mg, 79%) with >30:1 *Z/E* (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture).

Table 1 entry 6: To a solution of **1a′** (1.0 equiv) in ethanol at –40 ˚C was added $NiCl_2·6H_2O$ (2.0 equiv) and $NaBH_4$ (2.0 equiv) successively. It was stirred for 1 h until full conversion. The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath) and afforded (*E*)-**2a** with 1:6 *Z/E* (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture).

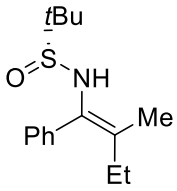
Table 1 entry 7: To a solution of **1a′** (1.0 equiv) in methanol at –40 ˚C was added $CoCl_2$ (2.0 equiv) and $NaBH_4$ (2.0 equiv) successively. It was stirred for 0.5 h until full conversion. The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). and afforded **2a** with 1:1 *Z/E* (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture).

Table 1 entry 9: According to the reported literature,[S2] to a solution of ATPH (0.40 mmol, ~3.4 equiv) in toluene (3.0 mL) was added **1a′** (30.8 mg, 0.117 mmol, 1.0 equiv) at –78 ˚C and the resulting mixture was treated with DIBAL-*n*BuLi (0.40 mmol, ~3.4 equiv) in THF/toluene (v/v = 1:1). Upon completion (~30 min), the reaction mixture was quenched with saturated aqueous ammonium chloride (3.0 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford

(*E*)-**2a** (22.6 mg, 73%) with <1:20 *Z/E* (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).



(*Z*)-**2a** (Table 1 entry 10): The title compound was prepared according to the general procedure C using **1a′** (60.0 mg, 0.228 mmol, 1.0 equiv), $InBr_3$ (161.5 mg, 0.456 mmol, 2.0 equiv), and *n*Bu_3SnH (132.6 mg, 0.456 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2a** (51.2 mg, 85%) as a white solid. Analytical data for (*Z*)-**2a**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.96 (s, 1H), 2.32–2.14 (m, 2H), 1.60 (s, 3H), 1.05 (t, *J* = 7.6 Hz, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 139.0, 133.3, 130.9, 128.4, 124.7, 55.5, 26.4, 22.5, 18.8, 12.5; the spectral data were in agreement with our previously reported.[S1]

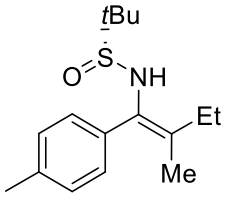


(*E*)-**2a** (Table 1 entry 11): The title compound was prepared according to the general procedure C using **1a** (60.0 mg, 0.228 mmol, 1.0 equiv), $InBr_3$ (161.5 mg, 0.456 mmol, 2.0 equiv), and *n*Bu_3SnH (132.6 mg, 0.456 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2a** (52.7 mg, 87%) as a white solid. Analytical data for (*E*)-**2a**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 4.89 (s, 1H), 1.99 (q, *J* = 7.4 Hz, 2H), 1.75 (s, 3H), 0.97 (s, 9H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.8, 133.9, 130.6, 128.5, 128.0, 123.9, 55.6, 28.0, 22.5, 16.4, 13.4; the spectral data were in agreement with (*E*)-**2a**.

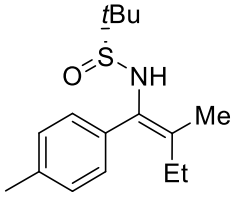
Table 1 entry 12: To a solution of $InBr_3$ (44.4 mg, 0.125 mmol, 1.1 equiv) in dry THF (3.0 mL) under argon atmosphere was added $(Et_2SiH)_2O$ (30.6 mg, 0.228 mmol, 2.0 equiv) and **1a** (30.0 mg, 0.114 mmol, 1.0 equiv) in THF (1.0 mL) at 0 ˚C successively. Then it was allowed to warm to rt and stirred for 4 h until full conversion. The reaction mixture was quenched with saturated aqueous ammonium chloride (3.0 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined

organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford (*E*)-**2a** (17.6 mg, 58%) with <1:20 *Z/E* (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

Table 1 entry 13: To a solution of **1a** (1.0 equiv) in dry THF under argon atmosphere at rt was added $PhSiH_3$ (2.0 equiv) and Stryker's reagent (5% equiv) successively. It was stirred for 24 h at rt (about ~50% conversion). The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath) and afforded (*E*)-**2a** with 1:3 *Z/E* (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

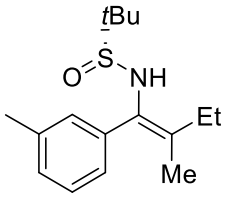


(*Z*)-**2b**: The title compound was prepared according to the general procedure B using **1b** (52.6 mg, 0.190 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 228 μL, 0.228 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (145.9 mg, 0.948 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2b** (41.9 mg, 79%) as a white solid. Analytical data for (*Z*)-**2b**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.45 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 5.00 (s, 1H), 2.33–2.15 (m, 2H), 2.10 (s, 3H), 1.64 (s, 3H), 1.06 (t, J = 7.6 Hz, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 137.4, 136.1, 133.3, 130.8, 129.1, 123.9, 55.4, 26.4, 22.5, 21.2, 18.8, 12.5; The spectral data were in agreement with our previously reported.[S1]

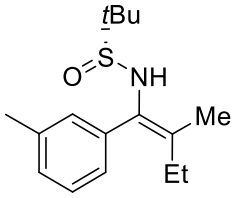


(*E*)-**2b**: The title compound was prepared according to the general procedure C using **1b** (61.0 mg, 0.220 mmol, 1.0 equiv), $InBr_3$ (155.9 mg, 0.440 mmol, 2.0 equiv), and nBu$_3$SnH (128.0 mg, 0.440 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2b** (51.1 mg, 83%) as a white solid. Analytical data for (*E*)-**2b**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 93–94 °C; $[\alpha]^{25}_D$ = +75.7 (c = 0.38, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E*

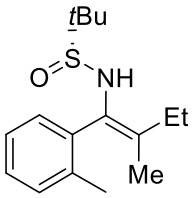
ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.47 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 4.91 (s, 1H), 2.09 (s, 3H), 2.08–2.01 (m, 2H), 1.76 (s, 3H), 0.99 (s, 9H), 0.90 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 137.5, 135.8, 133.9, 130.5, 129.2, 123.2, 55.5, 28.0, 22.5, 21.2, 16.4, 13.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{26}NOS$ 280.1730; Found 280.1733.



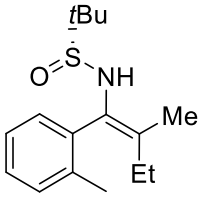
(*Z*)-**2c**: The title compound was prepared according to the general procedure B using **1c** (62.8 mg, 0.226 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 271 μL, 0.271 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (173.9 mg, 1.130 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2c** (51.4 mg, 81%) as a clear oil. Analytical data for (*Z*)-**2c**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.39–7.33 (m, 2H), 7.14–7.11 (m, 1H), 6.93 (d, J = 7.2 Hz, 1H), 5.00 (s, 1H), 2.31–2.16 (m, 2H), 2.14 (s, 3H), 1.62 (s, 3H), 1.06 (t, J = 7.6 Hz, 3H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.9, 137.8, 133.4, 131.6, 128.6, 124.1, 55.5, 26.3, 22.5, 21.4, 18.8, 12.5; The spectral data were in agreement with our previously reported.[S1]



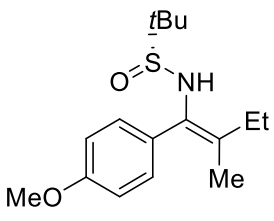
(*E*)-**2c**: The title compound was prepared according to the general procedure C using **1c** (65.0 mg, 0.234 mmol, 1.0 equiv), $InBr_3$ (166.1 mg, 0.469 mmol, 2.0 equiv), and nBu$_3$SnH (136.4 mg, 0.469 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2c** (58.4 mg, 89%) as an oil. Analytical data for (*E*)-**2c**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +53.2 (c = 0.39, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (d, J = 8.8 Hz, 2H), 7.15–7.12 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 4.91 (s, 1H), 2.15 (s, 3H), 2.08–1.97 (m, 2H), 1.76 (s, 3H), 0.98 (s, 9H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.7, 137.9, 134.0, 131.3, 128.8, 128.4, 127.7, 123.4, 55.5, 28.0, 22.5, 21.5, 16.4, 13.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{26}NOS$ 280.1730; Found 280.1733.



(*Z*)-**2d**: The title compound was prepared according to the general procedure B using **1d** (64.0 mg, 0.231 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 277 μL, 0.277 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (177.5 mg, 1.153 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2d** (52.2 mg, 81%) as a clear oil. Analytical data for (*Z*)-**2d**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); mixture of inseparable rotamers (~1:1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.45–7.40 (m, 1H), 7.36–7.32 (m, 1H), 7.13–7.05 (m, 6H), 5.24 (s, 1H), 5.16 (s, 1H), 2.44 (s, 3H), 2.25 (s, 3H), 2.20–1.96 (m, 5H), 1.42–1.38 (m, 6H), 1.06–1.00 (m, 6H), 0.93 (s, 9H), 0.91 (s, 8H); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ 138.1, 137.8, 137.3, 137.1, 132.6, 131.9, 131.7, 130.9, 130.4, 130.3, 128.4, 128.3, 126.2, 126.0, 121.4, 120.9, 55.4, 54.8, 25.5, 25.3, 22.4, 22.3, 19.8, 19.5, 18.2, 18.0, 12.43, 12.37; The spectral data were in agreement with our previously reported.[S1]

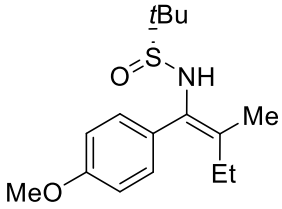


(*E*)-**2d**: The title compound was prepared according to the general procedure C using **1d** (65.0 mg, 0.234 mmol, 1.0 equiv), $InBr_3$ (166.1 mg, 0.469 mmol, 2.0 equiv), and nBu$_3$SnH (136.4 mg, 0.469 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2d** (50.7 mg, 77%) as a white solid. Analytical data for (*E*)-**2d**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 101–102 °C; $[\alpha]^{25}_D = -3.9$ (c = 0.32, CH_2Cl_2); *Z/E* < 1:30 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); mixture of inseparable rotamers (~1:1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.48–7.43 (m, 1H), 7.32–7.28 (m, 1H), 7.14–7.04 (m, 6H), 5.13 (s, 1H), 5.06 (s, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 1.87–1.69 (m, 4H), 1.64–1.61 (m, 6H), 0.96–0.90 (m, 18H), 0.82–0.75 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 138.1, 137.5, 137.2, 137.0, 133.1, 132.4, 131.8, 131.1, 130.3, 128.5, 126.1, 126.0, 120.6, 119.2, 55.5, 54.8, 27.8, 27.6, 22.4, 22.3, 20.1, 19.7, 15.2, 15.1, 13.2, 12.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{26}NOS$ 280.1730; Found 280.1734.

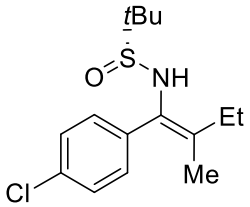


(*Z*)-**2e**: The title compound was prepared according to the general procedure B using **1e** (67.5 mg, 0.230 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 276 μL, 0.276 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$

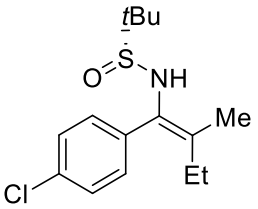
(177.0 mg, 1.150 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2e** (57.9 mg, 85%) as a clear oil. Analytical data for (*Z*)-**2e**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D6) δ 7.45 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.00 (s, 1H), 3.29 (s, 3H), 2.35 – 2.17 (m, 2H), 1.66 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) *δ* 159.7, 133.0, 132.1, 131.1, 123.6, 113.9, 55.4, 54.8, 26.4, 22.5, 18.8, 12.6; The spectral data were in agreement with our previously reported.[S1]



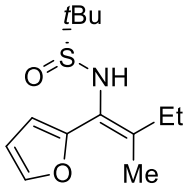
(*E*)-**2e**: The title compound was prepared according to the general procedure C using **1e** (61.0 mg, 0.208 mmol, 1.0 equiv), $InBr_3$ (147.4 mg, 0.416 mmol, 2.0 equiv), and nBu$_3$SnH (121.0 mg, 0.416 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2e** (51.8 mg, 83%) as a clear oil. Analytical data for (*E*)-**2e**: R_f = 0.15 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +71.8 (*c* = 0.16, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (600 MHz, C_6D_6) *δ* 7.45 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.04 (s, 1H), 3.30 (s, 3H), 2.04 (qd, *J* = 7.2, 1.8 Hz, 2H), 1.78 (s, 3H), 1.01 (s, 9H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) *δ* 159.8, 133.6, 131.8, 130.9, 122.9, 114.0, 55.5, 54.8, 28.1, 22.5, 16.4, 13.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{26}NO_2S$ 296.1679; Found 296.1683.



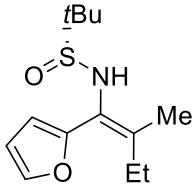
(*Z*)-**2f**: The title compound was prepared according to the general procedure B using **1f** (62.0 mg, 0.208 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 250 μL, 0.250 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (160.1 mg, 1.041 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2f** (52.4 mg, 84%) as a white solid. Analytical data for (*Z*)-**2f**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) *δ* 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 4.87 (s, 1H), 2.26–2.08 (m, 2H), 1.49 (s, 3H), 1.01 (t, *J* = 7.6 Hz, 3H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) *δ* 137.3, 133.7, 132.2, 132.1, 128.6, 125.7, 55.5, 26.4, 22.4, 18.6, 12.4; The spectral data were in agreement with our previously reported.[S2]



(*E*)-**2f**: The title compound was prepared according to the general procedure C using **1f** (61.0 mg, 0.205 mmol, 1.0 equiv), $InBr_3$ (145.2 mg, 0.410 mmol, 2.0 equiv), and nBu$_3$SnH (119.2 mg, 0.416 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2f** (46.1 mg, 75%) as an oil. Analytical data for (*E*)-**2f**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +74.8 (*c* = 0.24, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.87 (s, 1H), 1.92–1.83 (m, 2H), 1.70 (s, 3H), 0.96 (s, 9H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 137.1, 133.9, 132.7 , 131.9, 128.7, 125.0, 55.6, 27.9, 22.4, 16.4, 13.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{15}H_{23}ClNOS$ 300.1183; Found 300.1189.

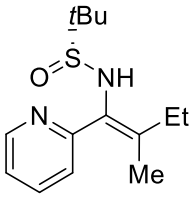


(*Z*)-**2g**: The title compound was prepared according to the general procedure B using **1g** (48.5 mg, 0.191 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 230 μL, 0.230 mmol, 1.2 equiv), and $NaBO_3{\cdot}4H_2O$ (147.3 mg, 0.957 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2g** (43.9 mg, 90%) as a white solid. Analytical data for (*Z*)-**2g**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.08 (t, *J* = 1.6, 0.8 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 6.13 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.57 (s, 1H), 2.35–2.25 (m, 1H), 2.24–2.14 (m, 1H), 1.84 (s, 3H), 1.03 (s, 9H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 153.3, 141.9, 131.3, 124.2, 111.3, 55.9, 27.1, 22.5, 18.4, 12.5; The spectral data were in agreement with our previously reported.[S1]

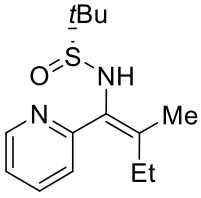


(*E*)-**2g**: The title compound was prepared according to the general procedure C using **1g** (65.0 mg, 0.257 mmol, 1.0 equiv), $InBr_3$ (181.9 mg, 0.513 mmol, 2.0 equiv), and nBu$_3$SnH (149.3 mg, 0.513 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2g** (57.7 mg, 88%) as a white solid. Analytical data for (*E*)-**2g**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 117–118 ^{o}C; $[\alpha]^{25}_D$ = +44.3 (*c* = 0.13, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was

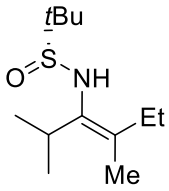
determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (600 MHz, C_6D_6) δ 7.08 (d, J = 1.8 Hz, 1H), 6.65 (d, J = 3.6 Hz, 1H), 6.13 (dd, J = 3.6, 1.8 Hz, 1H), 4.52 (s, 1H), 2.37–2.30 (m, 1H), 2.20–2.13 (m, 1H), 1.77 (s, 3H), 1.04–1.01 (m, 12H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 153.1, 142.1, 131.0, 124.5, 111.3, 110.9, 55.8, 27.9, 22.5, 17.7, 13.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{22}NO_2S$ 256.1366; Found 256.1372.



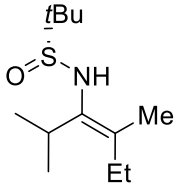
(*Z*)-**2h**: The title compound was prepared according to the general procedure B using **1h** (56.0 mg, 0.212 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 254 μL, 0.254 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (162.9 mg, 1.059 mmol, 5.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*Z*)-**2h** (46.4 mg, 82%) as an oil. Analytical data for (*Z*)-**2h**: R_f = 0.20 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{25}_D$ = −80.7 (*c* = 0.47, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 8.45 (d, J = 4.4 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.06 (td, J = 7.6, 1.6 Hz, 1H), 6.55 (td, J = 7.6, 4.8 Hz, 1H), 5.72 (s, 1H), 2.51–2.40 (m, 1H), 2.35–2.24 (m, 1H), 1.75 (s, 3H), 1.13–1.04 (m, 12H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 158.1, 149.0, 135.8, 132.5, 131.7, 124.9, 121.9, 56.0, 27.2, 22.6, 18.7, 12.6; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{23}N_2OS$ 267.1526; Found 267.1531.



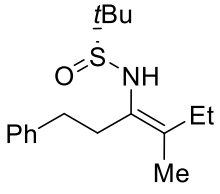
(*E*)-**2h**: The title compound was prepared according to the general procedure B using **1h′** (61.0 mg, 0.231 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 277 μL, 0.277 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (177.5 mg, 1.154 mmol, 5.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*E*)-**2h** (54.1 mg, 88%) as an oil. Analytical data for (*E*)-**2h**: R_f = 0.20 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{20}_D$ = −63.6 (*c* = 0.25, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 8.43 (d, J = 4.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.13 (td, J = 7.7, 2.0 Hz, 1H), 6.62–6.58 (m, 1H), 5.62 (s, 1H), 2.22–2.08 (m, 2H), 1.89 (s, 3H), 1.07 (s, 9H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 158.1, 149.2, 136.0, 133.0, 130.8, 124.7, 122.0, 56.0, 28.0, 22.6, 17.7, 13.3; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{23}N_2OS$ 267.1526; Found 267.1530.



(*Z*)-**2i**: The title compound was prepared according to the general procedure B using **1i** (47.0 mg, 0.205 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 246 μL, 0.246 mmol, 1.2 equiv), and $NaBO_3·4H_2O$ (157.6 mg, 1.024 mmol, 5.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*Z*)-**2i** (36.7 mg, 77%) as an oil. Analytical data for (*Z*)-**2i**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −52.2 (*c* = 0.34, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 4.38 (s, 1H), 2.78 (p, *J* = 6.8 Hz, 1H), 2.39–2.29 (m, 1H), 2.19–2.09 (m, 1H), 1.56 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H), 1.07 (s, 9H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 135.9, 127.2, 56.1, 30.0, 26.8, 22.7, 20.42, 20.38, 16.8, 12.9; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{12}H_{25}NNaOS$ 254.1549; Found 254.1544.

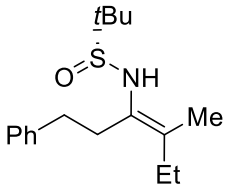


(*E*)-**2i**: The title compound was prepared according to the general procedure C using **1i** (61.0 mg, 0.266 mmol, 1.0 equiv), $InBr_3$ (188.6 mg, 0.532 mmol, 2.0 equiv), and *n*Bu_3SnH (154.8 mg, 0.532 mmol, 2.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*E*)-**2i** (41.2 mg, 67%) as a white solid. Analytical data for (*E*)-**2i**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); mp 64–65 °C; $[\alpha]^{25}_D$ = −75.1 (*c* = 0.23, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 4.35 (s, 1H), 2.79 (p, *J* = 7.0 Hz, 1H), 1.94 (qd, *J* = 7.6, 2.8 Hz, 2H), 1.77 (s, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 9H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 136.3, 126.8, 56.1, 29.5, 26.9, 22.7, 21.0, 20.8, 18.1, 13.3; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{12}H_{25}NNaOS$ 254.1549; Found 254.1554.

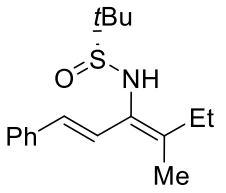


(*Z*)-**2j**: The title compound was prepared according to the general procedure B using **1j** (44.5 mg, 0.153 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 183 μL, 0.183 mmol, 1.2 equiv), and $NaBO_3·4H_2O$ (117.5 mg, 0.763 mmol, 5.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*Z*)-**2j** (32.6 mg, 73%) as an oil. Analytical data for (*Z*)-**2j**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR

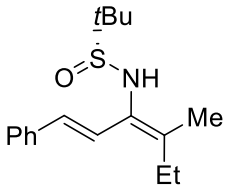
analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.16–7.14 (m, 4H), 7.09–7.04 (m, 1H), 4.54 (s, 1H), 2.89–2.71 (m, 2H), 2.66–2.57 (m, 1H), 2.56–2.47 (m, 1H), 2.17–2.07 (m, 1H), 2.00–1.89 (m, 1H), 1.37 (s, 3H), 1.04 (s, 9H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 142.1, 130.9, 129.0, 128.6, 126.3, 124.8, 55.5, 34.2, 34.0, 26.0, 22.5, 17.1, 12.6; The spectral data were in agreement with our previously reported.[S1]



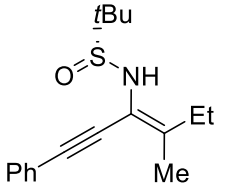
(*E*)-**2j**: The title compound was prepared according to the general procedure C using **1j** (62.0 mg, 0.213 mmol, 1.0 equiv), $InBr_3$ (150.8 mg, 0.425 mmol, 2.0 equiv), and nBu$_3$SnH (123.8 mg, 0.425 mmol, 2.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*E*)-**2j** (46.8 mg, 75%) as an oil. Analytical data for (*E*)-**2j**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −37.6 (c = 0.23, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.20–7.17 (m, 3H), 7.16–7.14 (m, 1H), 7.09–7.04 (m, 1H), 4.56 (s, 1H), 2.93–2.83 (m, 1H), 2.84–2.74 (m, 1H), 2.72–2.62 (m, 1H), 2.57–2.46 (m, 1H), 1.82 (q, J = 7.6 Hz, 2H), 1.59 (s, 3H), 1.05 (s, 9H), 0.77 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 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 294.1889.



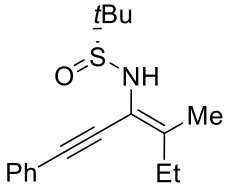
(*Z*)-**2k**: The title compound was prepared according to the general procedure B using **1k** (55.0 mg, 0.184 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 228 μL, 0.228 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (146.2 mg, 0.950 mmol, 5.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*Z*)-**2k** (49.1 mg, 89%) as a white solid. Analytical data for (*Z*)-**2k**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); mp 83–84 °C; $[\alpha]^{25}_D$ = +100.8 (c = 0.17, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.40 (d, J = 7.6 Hz, 2H), 7.15–7.10 (m, 3H), 7.09–7.02 (m, 2H), 4.61 (s, 1H), 2.42–2.31 (m, 1H), 2.22–2.12 (m, 1H), 1.63 (s, 3H), 1.09 (s, 9H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.2, 134.3, 130.8, 130.7, 129.0, 127.7, 127.0, 125.4, 56.1, 27.3, 22.7, 17.5, 12.7; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{17}H_{26}NOS$ 292.1730; Found 292.1733.



(*E*)-**2k**: The title compound was prepared according to the general procedure B using **1k′** (53.0 mg, 0.183 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 220 μL, 0.220 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (140.9 mg, 0.916 mmol, 5.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*E*)-**2k** (46.8 mg, 88%) as an oil. Analytical data for (*E*)-**2k**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = +83.8 (*c* = 0.14, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.16–7.09 (m, 4H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.53 (s, 1H), 2.15–2.02 (m, 2H), 1.83 (s, 3H), 1.09 (s, 9H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 138.2, 134.3, 131.1, 130.5, 129.0, 127.7, 127.0, 124.8, 56.1, 27.4, 22.7, 18.4, 13.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{26}NOS$ 292.1730; Found 292.1738.

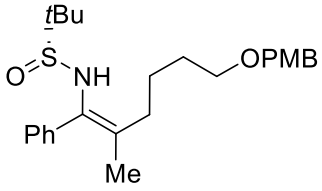


(*Z*)-**2l**: The title compound was prepared according to the general procedure B using **1l** (51.0 mg, 0.177 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 213 μL, 0.213 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (136.5 mg, 0.887 mmol, 5.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*Z*)-**2l** (42.7 mg, 83%) as an oil. Analytical data for (*Z*)-**2l**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −79.8 (*c* = 0.43, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.52–7.47 (m, 2H), 7.01–6.93 (m, 3H), 4.64 (s, 1H), 2.12–1.98 (m, 2H), 1.91 (s, 3H), 1.06 (s, 9H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 136.5, 131.8, 128.6, 128.4, 123.8, 117.5, 94.2, 86.9, 56.0, 25.7, 22.5, 19.7, 12.1; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{24}NOS$ 290.1573; Found 290.1581.

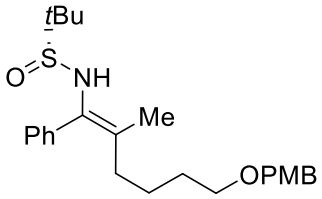


(*E*)-**2l**: The title compound was prepared according to the general procedure B using **1l′** (62.0 mg, 0.216 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 259 μL, 0.259 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (165.9 mg, 1.079 mmol, 5.0 equiv). Note: purification using silica gel column chromatography caused isomerization from *E* to *Z* isomer. Purification using basic silica gel column chromatography caused tautomerization to corresponding branched imine. Crude product

(*E*)-**2l** (73.7 mg, 118%) was obtained as an oil. Proton and carbon NMR spectra were recorded using crude product. Analytical data for (*E*)-**2k**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.51–7.46 (m, 2H), 7.00–6.92 (m, 3H), 4.79 (s, 1H), 2.47–2.33 (m, 2H), 1.61 (s, 3H), 1.08 (s, 9H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 135.8, 131.8, 128.6, 128.3, 123.7, 117.6, 94.1, 86.2, 55.9, 29.6, 22.5, 16.2, 12.7; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{17}H_{24}NOS$ 290.1573; Found 290.1578.

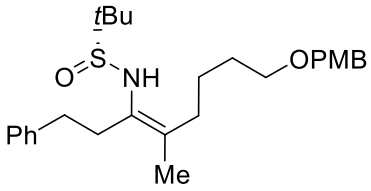


(*Z*)-**2m**: The title compound was prepared according to the general procedure B using **1m** (48.7 mg, 0.114 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 137 μL, 0.137 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (87.6 mg, 0.569 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2m** (41.7 mg, 85%) as an oil. Analytical data for (*Z*)-**2m**: R_f = 0.30 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +44.1 (*c* = 0.34, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.53–7.49 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.20–7.17 (m, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 5.12 (s, 1H), 4.39 (s, 2H), 3.44–3.38 (m, 2H), 3.30 (s, 3H), 2.34–2.25 (m, 2H), 1.73–1.64 (m, 4H), 1.62 (s, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 159.7, 139.0, 133.9, 131.4, 130.9, 129.4, 128.4, 127.9, 123.0, 114.1, 72.8, 70.0, 55.5, 54.8, 33.1, 30.1, 24.9, 22.5, 19.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{36}NO_3S$ 430.2410; Found 430.2418.

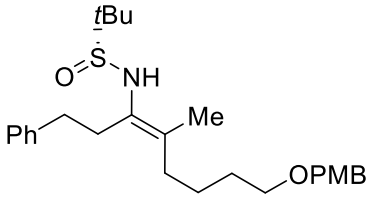


(*E*)-**2m**: The title compound was prepared according to the general procedure C using **1m** (60.0 mg, 0.140 mmol, 1.0 equiv), $InBr_3$ (99.5 mg, 0.281 mmol, 2.0 equiv), and *n*Bu_3SnH (81.7 mg, 0.281 mmol, 2.0 equiv). Column chromatography (15% ethyl acetate/petroleum ether) afforded (*E*)-**2m** (51.8 mg, 86%) as an oil. Analytical data for (*E*)-**2m**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +39.6 (*c* = 0.16, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 (d, J = 6.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 7.20–7.16 (m, 2H), 7.07 (t, J = 7.5 Hz,

1H), 6.81 (d, J = 8.5 Hz, 2H), 4.96 (s, 1H), 4.28 (s, 2H), 3.32 (s, 3H), 3.20 (t, J = 5.6 Hz, 2H), 2.14–2.06 (m, 1H), 2.04–1.97 (m, 1H), 1.79 (s, 3H), 1.52–1.37 (m, 4H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 159.6, 138.8, 134.5, 131.5, 130.7, 129.3, 128.5, 128.0, 122.6, 114.1, 72.7, 69.8, 55.5, 54.8, 34.6, 29.7, 25.5, 22.5, 16.9; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{25}H_{35}NNaO_3S$ 452.2230; Found 452.2234.

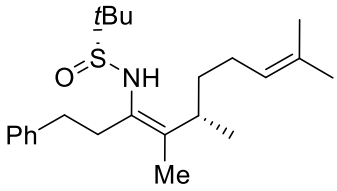


(*Z*)-**2n**: The title compound was prepared according to the general procedure B using **1n** (54.6 mg, 0.120 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 144 μL, 0.144 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (92.2 mg, 0.599 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2n** (42.9 mg, 78%) as an oil. Analytical data for (*Z*)-**2n**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −21.6 (*c* = 0.36, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (400 MHz, C_6D_6) δ 7.27 (d, J = 8.8 Hz, 2H), 7.17–7.16 (m, 2H), 7.16–7.15 (m, 2H), 7.10–7.04 (m, 1H), 6.83 (d, J = 8.4 Hz, 2H), 4.72 (s, 1H), 4.36 (s, 2H), 3.39–3.33 (m, 2H), 3.30 (s, 3H), 2.89–2.73 (m, 2H), 2.68–2.50 (m, 2H), 2.25–2.16 (m, 1H), 2.04–1.94 (m, 1H), 1.62–1.47 (m, 4H), 1.39 (s, 3H), 1.06 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 159.7, 142.1, 131.7, 131.4, 129.4, 129.0, 128.6, 126.2, 122.9, 114.1, 72.8, 70.0, 55.5, 54.8, 34.3, 33.9, 32.8, 30.1, 25.0, 22.5, 17.6; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{27}H_{39}NNaO_3S$ 480.2543; Found 480.2548.

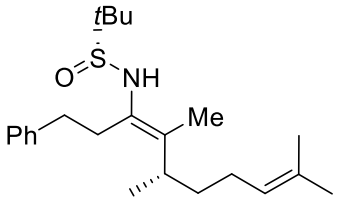


(*E*)-**2n**: The title compound was prepared according to the general procedure C using **1n** (60.0 mg, 0.132 mmol, 1.0 equiv), $InBr_3$ (93.4 mg, 0.263 mmol, 2.0 equiv), and $n$$Bu_3SnH$ (76.7 mg, 0.263 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2n** (48.8 mg, 81%) as an oil. Analytical data for (*E*)-**2n**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = −25.4 (*c* = 0.31, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (600 MHz, C_6D_6) δ 7.25 (d, J = 8.4 Hz, 2H), 7.21–7.16 (m, 3H), 7.16–7.14 (m, 1H), 7.06 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 4.56 (s, 1H), 4.35 (s, 2H), 3.33–3.30 (m, 5H), 2.93–2.87 (m,

1H), 2.86–2.79 (m, 1H), 2.75–2.68 (m, 1H), 2.59–2.52 (m, 1H), 1.88 (t, J = 7.8 Hz, 2H), 1.61 (s, 3H), 1.52 (p, J = 7.2 Hz, 2H), 1.42–1.37 (m, 1H), 1.33–1.28 (m, 1H), 1.05 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ 159.7, 142.3, 132.2, 131.5, 129.4, 128.9, 128.7, 126.3, 122.4, 114.1, 72.8, 70.0, 55.5, 54.8, 34.8, 33.9, 33.7, 30.2, 25.4, 22.5, 16.8; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{27}H_{39}NNaO_3S$ 480.2543; Found 480.2546.

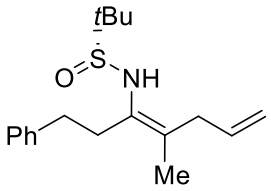


(*Z*)-**2o**: The title compound was prepared according to the general procedure B using **1o** (53.5 mg, 0.143 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 172 μL, 0.172 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (110.2 mg, 0.716 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2o** (47.3 mg, 88%) as an oil. Analytical data for (*Z*)-**2o**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −72.6 (*c* = 0.50, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (400 MHz, C_6D_6) δ 7.21–7.16 (m, 3H), 7.15–7.13 (m, 1H), 7.08–7.03 (m, 1H), 5.29–5.20 (m, 1H), 4.47 (s, 1H), 2.99–2.92 (m, 1H), 2.88–2.80 (m, 2H), 2.72–2.62 (m, 1H), 2.57–2.48 (m, 1H), 2.07–1.97 (m, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.48–1.38 (m, 1H), 1.35–1.25 (m, 4H), 1.04 (s, 9H), 0.93 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 142.1, 131.9, 131.5, 129.1, 128.7, 127.3, 126.3, 125.5, 55.7, 35.2, 35.0, 34.2, 33.5, 26.5, 26.0, 22.5, 19.0, 17.9, 11.6; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{23}H_{37}NNaOS$ 398.2488; Found 398.2495.

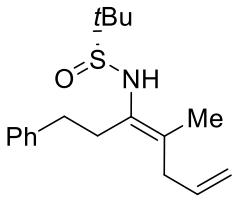


(*E*)-**2o**: The title compound was prepared according to the general procedure C using **1o** (60.0 mg, 0.161 mmol, 1.0 equiv), $InBr_3$ (113.9 mg, 0.321 mmol, 2.0 equiv), and nBu$_3$SnH (93.5 mg, 0.321 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2o** (50.1 mg, 83%) as a white solid. Analytical data for (*E*)-**2o**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 85–86 °C; $[\alpha]^{25}_D$ = −31.1 (*c* = 0.44, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (500 MHz, C_6D_6) δ 7.23 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 5.17 (t, J = 7.0 Hz, 1H), 4.55 (s, 1H), 2.99–2.91 (m, 1H), 2.89–2.81 (m, 1H), 2.78–2.70 (m, 1H), 2.65–2.58 (m, 1H), 2.52 (q, J = 7.0 Hz, 1H), 1.93–1.86 (m, 2H), 1.68 (s, 3H), 1.57

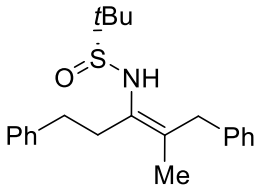
(s, 3H), 1.55 (s, 3H), 1.30–1.24 (m, 2H), 1.05 (s, 9H), 0.89 (d, J = 6.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) δ 142.3, 132.3, 131.3, 128.9, 128.8, 126.3, 125.8, 125.3, 55.6, 35.5, 35.2, 35.0, 33.7, 26.8, 25.9, 22.5, 19.3, 17.9, 11.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{23}H_{38}NOS$ 376.2669; Found 376.2673.



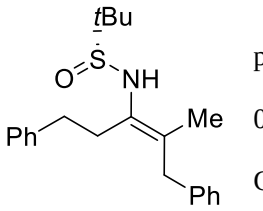
(*Z*)-**2p**: The title compound was prepared according to the general procedure B using **1p** (45.4 mg, 0.150 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 180 μL, 0.180 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (115.1 mg, 0.748 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2p** (37.1 mg, 81%) as an oil. Analytical data for (*Z*)-**2p**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D = -15.3$ (c = 0.32, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (400 MHz, C_6D_6) δ 7.18–7.17 (m, 1H), 7.15–7.11 (m, 3H), 7.09–7.03 (m, 1H), 5.74–5.62 (m, 1H), 4.99 (dt, J = 3.3, 1.7 Hz, 1H), 4.97–4.94 (m, 1H), 4.87 (s, 1H), 3.11 (dd, J = 16.0, 6.8 Hz, 1H), 2.88–2.79 (m, 1H), 2.78–2.71 (m, 1H), 2.67–2.58 (m, 1H), 2.58–2.48 (m, 2H), 1.38 (s, 3H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 142.0, 135.7, 133.2, 129.0, 128.6, 126.3, 119.9, 115.3, 55.5, 37.7, 34.3, 33.6, 22.5, 18.2; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{18}H_{28}NOS$ 306.1886; Found 306.1893.



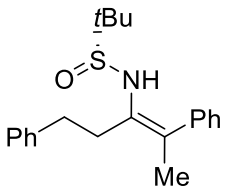
(*E*)-**2p**: The title compound was prepared according to the general procedure C using **1p** (61.0 mg, 0.201 mmol, 1.0 equiv), $InBr_3$ (142.5 mg, 0.402 mmol, 2.0 equiv), and nBu$_3$SnH (117.1 mg, 0.402 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2p** (51.0 mg, 83%) as an oil. Analytical data for (*E*)-**2o**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 85–86 °C; $[\alpha]^{25}_D = -39.7$ (c = 0.28, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^1H NMR analysis of the crude reaction mixture); ^1H NMR (500 MHz, C_6D_6) δ 7.17–7.16 (m, 2H), 7.16–7.15 (m, 2H), 7.09–7.05 (m, 1H), 5.57–5.46 (m, 1H), 5.02–4.92 (m, 2H), 4.56 (s, 1H), 2.90–2.84 (m, 1H), 2.84–2.77 (m, 1H), 2.71–2.63 (m, 1H), 2.57–2.50 (m, 3H), 1.60 (s, 3H), 1.03 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) δ 142.1, 136.3, 133.3, 128.9, 128.7, 126.3, 119.2, 115.6, 55.6, 38.4, 34.7, 33.6, 22.5, 16.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{18}H_{28}NOS$ 306.1886; Found 306.1889.



(*Z*)-**2q**: The title compound was prepared according to the general procedure B using **1q** (53.0 mg, 0.150 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 180 μL, 0.180 mmol, 1.2 equiv), and $NaBO_3·4H_2O$ (115.3 mg, 0.750 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2q** (43.5 mg, 82%) as an oil. Analytical data for (*Z*)-**2q**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.19–7.16 (m, 2H), 7.15–7.13 (m, 4H), 7.12–7.03 (m, 4H), 4.80 (s, 1H), 3.55 (d, *J* = 15.6 Hz, 1H), 3.31 (d, *J* = 15.6 Hz, 1H), 2.90–2.74 (m, 2H), 2.73–2.64 (m, 1H), 2.63–2.54 (m, 1H), 1.40 (s, 3H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 141.9, 139.8, 133.2, 129.1, 128.9, 128.8, 128.7, 126.5, 126.3, 121.6, 55.5, 38.8, 34.1, 33.6, 22.5, 18.4; The spectral data were in agreement with our previously reported.[S1]

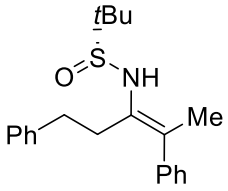


(*E*)-**2q**: The title compound was prepared according to the general procedure C using **1q** (60.0 mg, 0.170 mmol, 1.0 equiv), $InBr_3$ (120.3 mg, 0.339 mmol, 2.0 equiv), and nBu$_3$SnH (98.8 mg, 0.339 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2q** (51.0 mg, 85%) as an oil. Analytical data for (*E*)-**2q**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D = -38.6$ (*c* = 0.27, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.16–7.12 (m, 6H), 7.10–7.03 (m, 4H), 4.74 (s, 1H), 3.16 (s, 2H), 2.96–2.89 (m, 1H), 2.89–2.75 (m, 2H), 2.68–2.60 (m, 1H), 1.56 (s, 3H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 142.0, 140.2, 133.8, 129.0, 128.83, 128.78, 126.4, 126.3, 120.2, 55.6, 39.6, 34.7, 33.7, 22.5, 17.0; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{30}NOS$ 356.2043; Found 356.2046.

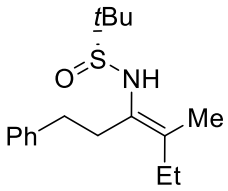


(*Z*)-**2r**: The title compound was prepared according to the general procedure B using **1r** (60.0 mg, 0.177 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 212 μL, 0.212 mmol, 1.2 equiv), and $NaBO_3·4H_2O$ (136.0 mg, 0.884 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2r** (46.6 mg, 77%) as an oil. Analytical data for (*Z*)-**2r**: R_f =

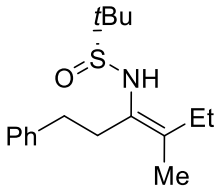
0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_{D}$ = +34.0 (*c* = 0.49, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.40–7.36 (m, 2H), 7.21–7.17 (m, 6H), 7.13–7.08 (m, 1H), 7.05–6.99 (m, 1H), 5.51 (s, 1H), 2.92–2.83 (m, 3H), 2.72–2.62 (m, 1H), 1.63 (s, 3H), 0.88 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 141.7, 141.3, 132.9, 129.7, 129.2, 129.1, 128.6, 127.1, 126.4, 119.2, 55.2, 34.2, 31.1, 22.4, 19.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{28}NOS$ 342.1886; Found 342.1892.



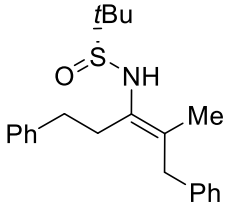
(*E*)-**2r**: The title compound was prepared according to the general procedure C using **1r** (60.0 mg, 0.177 mmol, 1.0 equiv), $InBr_3$ (125.3 mg, 0.353 mmol, 2.0 equiv), and *n*Bu_3SnH (102.9 mg, 0.353 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2r** (48.9 mg, 81%) as an oil. Analytical data for (*E*)-**2r**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_{D}$ = −13.8 (*c* = 0.28, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.14–6.99 (m, 8H), 6.96–6.91 (m, 2H), 4.94 (s, 1H), 2.93–2.81 (m, 2H), 2.70–2.57 (m, 2H), 1.90 (s, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 143.6, 141.9, 134.7, 128.9, 128.8, 128.7, 128.5, 126.7, 126.2, 122.5, 55.8, 34.9, 33.9, 22.5, 19.7; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{28}NOS$ 342.1886; Found 342.1888.



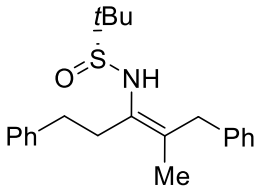
(*E*)-**2s**: The title compound was prepared according to the general procedure B using **1s** (36.5 mg, 0.125 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 150 μL, 0.150 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (96.3 mg, 0.626 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2s** (33.9 mg, 92%) as an oil. Analytical data for (*E*)-**2s**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_{D}$ = −37.6 (*c* = 0.23, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H 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), 1.82 (q, *J* = 7.6 Hz, 2H), 1.58 (s, 3H), 1.04 (s, 9H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} 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; The spectral data were in agreement with (*E*)-**2j**.



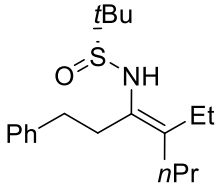
(*Z*)-**2s**: The title compound was prepared according to the general procedure C using **1s** (60.0 mg, 0.206 mmol, 1.0 equiv), $InBr_3$ (146.0 mg, 0.412 mmol, 2.0 equiv), and nBu_3SnH (119.8 mg, 0.412 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2s** (49.6 mg, 82%) as an oil. Analytical data for (*Z*)-**2s**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.17–7.16 (m, 2H), 7.16–7.14 (m, 2H), 7.10–7.05 (m, 1H), 4.60 (s, 1H), 2.88–2.81 (m, 1H), 2.80–2.72 (m, 1H), 2.61 (dt, *J* = 16.1, 8.1 Hz, 1H), 2.55–2.47 (m, 1H), 2.17–2.08 (m, 1H), 1.99–1.91 (m, 1H), 1.37 (s, 3H), 1.05 (s, 9H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 142.1, 131.0, 129.0, 128.6, 126.2, 124.8, 55.4, 34.2, 34.1, 26.0, 22.5, 17.1, 12.6; The spectral data were in agreement with our previously reported.[S1]



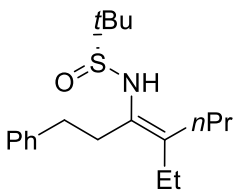
(*E*)-**2t**: To a solution of **1t** (51.9 mg, 0.147 mmol, 1.0 equiv) in ethanol (2.0 mL) at –40 ˚C was added $NiCl_2·6H_2O$ (69.8 mg, 0.294 mmol, 2.0 equiv) and $NaBH_4$ (11.1 mg, 0.294 mmol, 2.0 equiv) successively. It was stirred for 1 h until full conversion. The reaction mixture was quenched with saturated aqueous ammonium chloride (3.0 mL) and extracted with CH_2Cl_2 (15 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ^{o}C water bath). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2t** (39.3 mg, 75%) as an oil. Analytical data for (*E*)-**2t**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); −38.6 (*c* = 0.27, CH_2Cl_2); *Z/E* ~ 1:8 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.16–7.11 (m, 5H), 7.11–7.02 (m, 5H), 4.70 (s, 1H), 3.16 (s, 2H), 2.96–2.84 (m, 2H), 2.82–2.74 (m, 1H), 2.68–2.59 (m, 1H), 1.55 (s, 3H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 142.0, 140.2, 133.7, 129.0, 128.83, 128.79, 126.42, 126.36, 120.2, 55.6, 39.6, 34.7, 33.7, 22.5, 16.9; The spectral data were in agreement with (*E*)-**2q**. HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{30}NOS$ 356.2043; Found 356.2048.



(*Z*)-**2t**: The title compound was prepared according to the general procedure C using **1t** (63.0 mg, 0.178 mmol, 1.0 equiv), $InBr_3$ (126.4 mg, 0.356 mmol, 2.0 equiv), and nBu$_3$SnH (103.7 mg, 0.356 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2t** (39.0 mg, 62%) as an oil. Analytical data for (*Z*)-**2t**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.21–7.16 (m, 5H), 7.14–7.13 (m, 1H), 7.12–7.03 (m, 4H), 4.79 (s, 1H), 3.56 (d, J = 15.2 Hz, 1H), 3.31 (d, J = 15.6 Hz, 1H), 2.91–2.75 (m, 2H), 2.75–2.64 (m, 1H), 2.63–2.54 (m, 1H), 1.40 (s, 3H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 141.9, 139.8, 133.2, 129.1, 128.9, 128.8, 128.7, 126.5, 126.3, 121.6, 55.4, 38.8, 34.1, 33.6, 22.5, 18.4; The spectral data were in agreement with our previously reported.[S1]

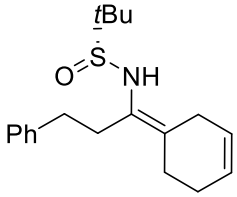


(*E*)-**2u**: The title compound was prepared according to the general procedure B using **1u** (56.0 mg, 0.175 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 210 μL, 0.210 mmol, 1.2 equiv), and $NaBO_3{\cdot}4H_2O$ (134.8 mg, 0.876 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2u** (44.8 mg, 80%) as an oil. Analytical data for (*E*)-**2u**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −36.1 (*c* = 0.40, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.20–7.17 (m, 3H), 7.16–7.13 (m, 1H), 7.10–7.04 (m, 1H), 4.66 (s, 1H), 2.94–2.86 (m, 1H), 2.84–2.76 (m, 1H), 2.74–2.57 (m, 2H), 2.19–2.07 (m, 1H), 2.03–1.91 (m, 1H), 1.87–1.76 (m, 2H), 1.29–1.18 (m, 2H), 1.05 (s, 9H), 0.97 (t, J = 7.6 Hz, 3H), 0.81 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 142.2, 132.0, 129.0, 128.7, 128.2, 126.3, 55.4, 34.8, 33.6, 33.3, 23.5, 22.5, 22.3, 14.4, 13.1; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{32}NOS$ 322.2199; Found 322.2204.

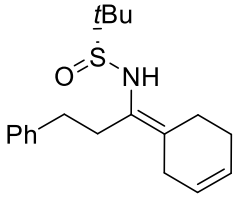


(*Z*)-**2u**: The title compound was prepared according to the general procedure C using **1u** (61.0 mg, 0.191 mmol, 1.0 equiv), $InBr_3$ (135.4 mg, 0.382 mmol, 2.0 equiv), and nBu$_3$SnH (111.1 mg, 0.382 mmol, 2.0 equiv).

Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2u** (55.3 mg, 90%) as an oil. Analytical data for (*Z*)-**2u**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = −34.8 (*c* = 0.28, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (500 MHz, C_6D_6) δ 7.18–7.16 (m, 2H), 7.16–7.14 (m, 2H), 7.09–7.04 (m, 1H), 4.74 (s, 1H), 2.91–2.84 (m, 1H), 2.83–2.75 (m, 1H), 2.70–2.55 (m, 2H), 2.14–2.05 (m, 1H), 1.98–1.91 (m, 1H), 1.82 (p, *J* = 7.4 Hz, 2H), 1.47–1.39 (m, 1H), 1.37–1.29 (m, 1H), 1.07 (s, 9H), 0.87 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 142.1, 132.0, 129.0, 128.7, 128.1, 126.3, 55.4, 34.9, 33.2, 32.3, 24.9, 22.5, 22.0, 14.6, 13.6; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{32}NOS$ 322.2199; Found 322.2206.

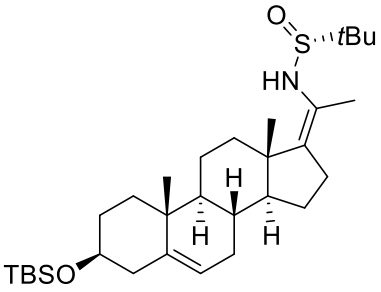


(*Z*)-**2v**: The title compound was prepared according to the general procedure B using **1v** (57.5 mg, 0.182 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 219 μL, 0.219 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (140.2 mg, 0.911 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2v** (30.5 mg, 53%) as an oil. Analytical data for (*Z*)-**2v**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{25}_D$ = −23.4 (*c* = 0.26, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.19–7.16 (m, 1H), 7.16–7.12 (m, 3H), 7.09–7.03 (m, 1H), 5.72–5.62 (m, 1H), 5.60–5.51 (m, 1H), 4.45 (s, 1H), 3.01–2.91 (m, 1H), 2.90–2.72 (m, 2H), 2.71–2.61 (m, 2H), 2.54–2.43 (m, 1H), 2.16–2.06 (m, 1H), 2.01–1.91 (m, 1H), 1.89–1.71 (m, 2H), 1.02 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 142.1, 130.0, 129.0, 128.7, 127.4, 126.3, 126.0, 123.0, 55.6, 34.5, 33.8, 28.6, 26.5, 26.4, 22.5; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{28}NOS$ 318.1886; Found 318.1891.

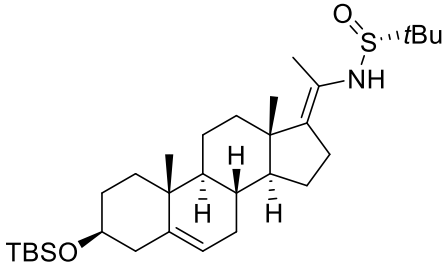


(*E*)-**2v**: The title compound was prepared according to the general procedure C using **1v** (60.0 mg, 0.190 mmol, 1.0 equiv), $InBr_3$ (134.9 mg, 0.380 mmol, 2.0 equiv), and *n*Bu_3SnH (110.7 mg, 0.380 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*E*)-**2v** (30.8 mg, 51%) as a white solid. Analytical data for (*E*)-**2v**: R_f = 0.20 (petroleum ether/ethyl acetate = 4/1); mp 62–63 °C; $[\alpha]^{25}_D$ = −49.6 (*c* = 0.20, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E*

ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.16–7.12 (m, 4H), 7.10–7.03 (m, 1H), 5.71–5.63 (m, 1H), 5.56–5.48 (m, 1H), 4.48 (s, 1H), 2.88–2.79 (m, 1H), 2.78–2.69 (m, 1H), 2.65–2.52 (m, 2H), 2.48–2.38 (m, 3H), 2.35–2.25 (m, 1H), 2.16–1.98 (m, 2H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 142.1, 130.0, 129.0, 128.7, 127.2, 126.3, 126.2, 124.5, 55.5, 34.6, 34.1, 29.4, 26.7, 25.6, 22.5; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{28}NOS$ 318.1886; Found 318.1888.

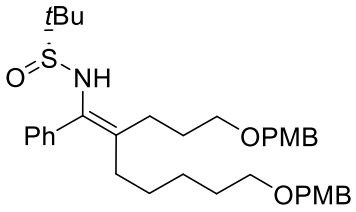


(*Z*)-**2w**: The title compound was prepared according to the general procedure B using **1w** (50.0 mg, 0.094 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 113 μL, 0.113 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (72.3 mg, 0.470 mmol, 5.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Z*)-**2w** (46.8 mg, 93%) as a white solid. Analytical data for (*Z*)-**2w**: R_f = 0.30 (petroleum ether/ethyl acetate = 8/1); mp 148–149 °C; $[\alpha]^{25}_D$ = +6.7 (*c* = 0.15, CH_2Cl_2); *Z/E* > 50:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 5.51 (s, 1H), 5.37 (d, *J* = 4.8 Hz, 1H), 3.69–3.58 (m, 1H), 2.51 (t, *J* = 13.6 Hz, 1H), 2.44–2.32 (m, 2H), 2.22 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.10–2.00 (m, 1H), 1.96–1.88 (m, 1H), 1.84–1.76 (m, 4H), 1.73–1.63 (m, 2H), 1.62–1.51 (m, 3H), 1.50–1.34 (m, 4H), 1.12 (s, 9H), 1.10–1.06 (m, 4H), 1.04 (s, 9H), 1.01–0.91 (m, 2H), 0.89 (s, 3H), 0.13 (d, *J* = 3.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 141.5, 131.9, 125.4, 121.4, 72.9, 56.7, 55.1, 50.3, 44.3, 43.5, 38.3, 37.6, 36.9, 32.7, 32.1, 31.5, 29.7, 26.2, 24.9, 22.6, 21.8, 19.5, 18.43, 18.38, 17.8, -4.3; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{31}H_{56}NO_2SSi$ 534.3796; Found 534.3803.

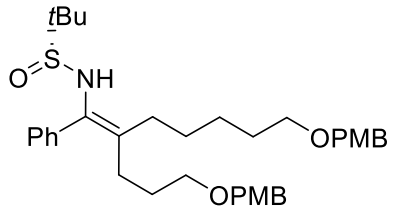


(*E*)-**2w**: The title compound was prepared according to the general procedure C using **1w** (50.0 mg, 0.094 mmol, 1.0 equiv), $InBr_3$ (66.7 mg, 0.188 mmol, 2.0 equiv), and *n*Bu_3SnH (54.7 mg, 0.188 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum

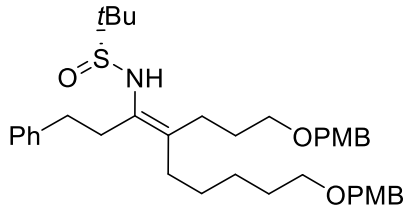
ether) afforded (*E*)-**2w** (47.6 mg, 95%) as a white solid. Analytical data for (*E*)-**2w**: R_f = 0.20 (petroleum ether/ethyl acetate = 8/1); mp 151–152 °C; $[\alpha]^{25}_D$ = −62.8 (*c* = 0.18, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (600 MHz, C_6D_6) δ 5.42–5.37 (m, 1H), 4.69 (s, 1H), 3.68–3.61 (m, 1H), 2.54–2.47 (m, 1H), 2.43–2.38 (m, 1H), 2.26–2.18 (m, 1H), 2.13–2.07 (m, 1H), 2.07–2.04 (m, 1H), 2.03–2.01 (m, 3H), 1.95–1.88 (m, 1H), 1.85–1.80 (m, 1H), 1.74–1.63 (m, 2H), 1.58–1.45 (m, 3H), 1.44–1.33 (m, 3H), 1.08 (s, 9H), 1.03 (s, 11H), 0.95 (s, 3H), 0.94–0.91 (m, 1H), 0.77 (s, 3H), 0.13 (d, *J* = 3.0 Hz, 6H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 141.6, 132.3, 125.2, 121.5, 72.9, 56.4, 55.2, 50.2, 43.7, 43.5, 37.9, 37.6, 36.9, 32.7, 32.2, 31.7, 28.3, 26.2, 24.5, 22.5, 21.7, 19.5, 18.4, 17.0, 16.6, -4.3; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{31}H_{55}NNaO_2SSi$ 556.3615; Found 556.3613.



(*Z*)-**2x**: The title compound was prepared according to the general procedure B using **1x** (52.0 mg, 0.086 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 172 μL, 0.172 mmol, 2.0 equiv), and $NaBO_3 \cdot 4H_2O$ (105.6 mg, 0.687 mmol, 8.0 equiv) (Note: After 30 min stirring at –78 ˚C, the reaction mixture was moved to rt for 10 min for full conversion). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*Z*)-**2x** (43.9 mg, 84%) as an oil. Analytical data for (*Z*)-**2x**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +11.3 (*c* = 0.52, CH_2Cl_2); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.26–7.19 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.89–6.80 (m, 4H), 6.22 (s, 1H), 4.45 (q, *J* = 11.6 Hz, 2H), 4.33 (s, 2H), 3.39–3.33 (m, 2H), 3.33–3.30 (m, 6H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.64–2.53 (m, 1H), 2.45–2.35 (m, 1H), 1.95 (t, *J* = 7.8 Hz, 2H), 1.82–1.73 (m, 1H), 1.71–1.62 (m, 1H), 1.54–1.46 (m, 2H), 1.42–1.33 (m, 2H), 1.26 (q, *J* = 7.2 Hz, 2H), 1.02 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 159.9, 159.7, 138.7, 135.9, 131.6, 130.9, 130.8, 129.9, 129.3, 128.4, 123.7, 114.2, 114.1, 72.73, 72.68, 70.1, 68.4, 55.7, 54.83, 54.81, 32.1, 30.0, 29.2, 27.8, 26.7, 26.2, 22.6; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{36}H_{49}NNaO_5S$ 630.3224; Found 630.3228.

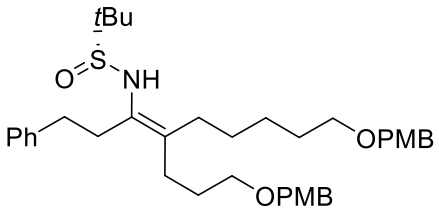


(*E*)-**2x**: The title compound was prepared according to the general procedure C using **1x** (49.0 mg, 0.081 mmol, 1.0 equiv), $InBr_3$ (57.3 mg, 0.162 mmol, 2.0 equiv), and nBu$_3$SnH (47.1 mg, 0.162 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*E*)-**2x** (41.9 mg, 85%) as an oil. Analytical data for (*E*)-**2x**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +22.0 (*c* = 0.29, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.21–7.17 (m, 4H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.86–6.78 (m, 4H), 5.15 (s, 1H), 4.39 (s, 2H), 4.24 (s, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 3.32–3.29 (m, 6H), 3.25–3.16 (m, 2H), 2.34–2.13 (m, 4H), 1.77–1.63 (m, 5H), 1.58–1.47 (m, 3H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 159.7, 159.6, 138.7, 134.9, 131.5, 131.4, 130.8, 129.4, 129.3, 128.5, 126.0, 114.1, 114.0, 72.8, 72.6, 70.1, 69.9, 55.5, 54.80, 54.78, 30.3, 30.2, 29.5, 29.3, 28.3, 27.0, 22.5; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{36}H_{49}NNaO_5S$ 630.3224; Found 630.3230.

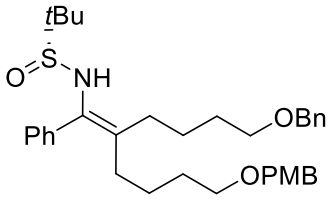


(*Z*)-**2y**: The title compound was prepared according to the general procedure B using **1y** (47.0 mg, 0.074 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 148 μL, 0.148 mmol, 2.0 equiv), and $NaBO_3 \cdot 4H_2O$ (91.3 mg, 0.593 mmol, 8.0 equiv) (Note: After 30 min stirring at –78 ˚C, the reaction mixture was moved to rt for 10 min for full conversion). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*Z*)-**2y** (37.9 mg, 81%) as an oil. Analytical data for (*Z*)-**2y**: R_f = 0.30 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −22.8 (*c* = 0.23, CH_2Cl_2); *Z*/*E* > 30:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.31–7.22 (m, 6H), 7.20–7.17 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.87–6.80 (m, 4H), 5.88 (s, 1H), 4.44–4.34 (m, 4H), 3.34 (t, *J* = 6.4 Hz, 2H), 3.31 (s, 3H), 3.31 (s, 3H), 3.26–3.19 (m, 2H), 2.98–2.88 (m, 2H), 2.84–2.75 (m, 1H), 2.74–2.65 (m, 1H), 2.53–2.45 (m, 1H), 2.21–2.10 (m, 1H), 1.89–1.74 (m, 2H), 1.64–1.54 (m, 3H), 1.53–1.45 (m, 1H), 1.38–1.24 (m, 4H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 159.9, 159.7, 142.3, 133.5, 131.5, 130.8, 129.9, 129.4, 129.0,

128.7, 126.3, 123.7, 114.15, 114.09, 72.8, 72.6, 70.2, 68.1, 55.7, 54.8, 35.0, 32.8, 31.3, 30.2, 29.1, 27.7, 26.9, 26.3, 22.7; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{38}H_{53}NNaO_5S$ 658.3537; Found 658.3542.

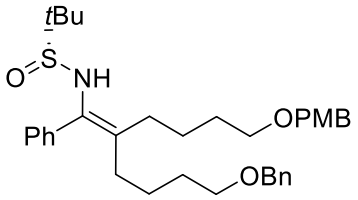


(*E*)-**2y**: The title compound was prepared according to the general procedure C using **1y** (50.0 mg, 0.079 mmol, 1.0 equiv), $InBr_3$ (55.9 mg, 0.158 mmol, 2.0 equiv), and nBu$_3$SnH (45.9 mg, 0.158 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*E*)-**2y** (43.4 mg, 87%) as an oil. Analytical data for (*E*)-**2y**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −19.7 (*c* = 0.29, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (t, *J* = 8.6 Hz, 4H), 7.22–7.17 (m, 4H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.86–6.80 (m, 4H), 4.81 (s, 1H), 4.37 (s, 2H), 4.33 (s, 2H), 3.37 (t, *J* = 6.4 Hz, 2H), 3.32 (s, 3H), 3.31–3.29 (m, 5H), 2.96–2.76 (m, 3H), 2.73–2.63 (m, 1H), 2.23–2.10 (m, 2H), 2.08–1.97 (m, 2H), 1.67–1.57 (m, 4H), 1.54–1.47 (m, 1H), 1.45–1.35 (m, 3H), 1.08 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ 159.7, 142.2, 132.8, 131.5, 131.4, 129.5, 129.4, 129.0, 128.7, 128.3, 126.2, 126.1, 114.10, 114.08, 72.83, 72.78, 70.1, 69.5, 55.5, 54.8, 34.9, 33.2, 30.4, 30.2, 29.3, 28.5, 28.3, 28.2, 27.0, 22.5; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{38}H_{53}NNaO_5S$ 658.3537; Found 658.3538.

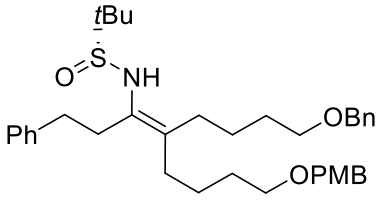


(*E*)-**2z**: The title compound was prepared according to the general procedure B using **1z** (29.0 mg, 0.050 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 101 μL, 0.101 mmol, 2.0 equiv), and $NaBO_3 \cdot 4H_2O$ (62.0 mg, 0.403 mmol, 8.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*E*)-**2z** (23.1 mg, 80%) as an oil. Analytical data for (*E*)-**2z**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +31.5 (*c* = 0.35, CH_2Cl_2); *Z/E* < 1:20 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.25–7.17 (m, 6H), 7.13–7.05 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.22 (s, 1H), 4.38 (s, 2H), 4.28 (s, 2H), 3.43–3.37 (m, 2H), 3.31 (s, 3H), 3.21 (t, *J* = 5.8 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.15–2.00 (m,

2H), 1.77–1.66 (m, 4H), 1.55–1.42 (m, 4H), 0.98 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 159.7, 139.5, 138.7, 135.0, 131.5, 130.9, 129.3, 128.6, 128.5, 128.0, 127.6, 125.9, 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:* $[M + Na]^+$ Calcd for $C_{35}H_{47}NNaO_4S$ 600.3118; Found 600.3124; The spectral data were in agreement with our previously reported.[S3]

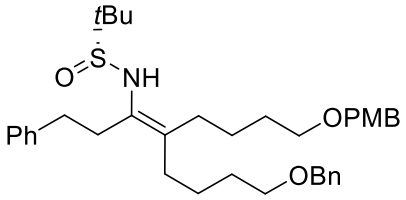


(*Z*)-**2z**: The title compound was prepared according to the general procedure C using **1z** (50.0 mg, 0.087 mmol, 1.0 equiv), $InBr_3$ (61.6 mg, 0.174 mmol, 2.0 equiv), and nBu$_3$SnH (50.5 mg, 0.174 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*Z*)-**2z** (42.2 mg, 84%) as an oil. Analytical data for (*Z*)-**2z**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = +19.1 (*c* = 0.33, CH_2Cl_2); *Z/E* > 20:1 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 4H), 7.21–7.18 (m, 3H), 7.12–7.04 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 1H), 4.39 (s, 2H), 4.27 (s, 2H), 3.47–3.39 (m, 2H), 3.30 (s, 3H), 3.18 (t, *J* = 6.0 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.15–1.99 (m, 2H), 1.78–1.68 (m, 4H), 1.54–1.40 (m, 4H), 0.98 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6) δ 159.7, 139.6, 138.7, 135.0, 131.4, 130.9, 129.5, 128.54, 128.47, 128.0, 127.7, 127.5, 125.9, 114.1, 72.9, 72.8, 70.2, 70.0, 55.5, 54.8, 32.2, 30.3, 30.0, 29.9, 25.8, 25.3, 22.5; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{35}H_{47}NNaO_4S$ 600.3118; Found 600.3126.

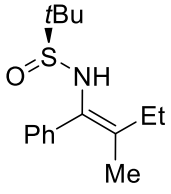


(*E*)-**2aa**: The title compound was prepared according to the general procedure B using **1aa** (40.0 mg, 0.066 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 132 μL, 0.132 mmol, 2.0 equiv), and $NaBO_3 \cdot 4H_2O$ (81.5 mg, 0.530 mmol, 8.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*E*)-**2aa** (34.4 mg, 86%) as an oil. Analytical data for (*E*)-**2aa**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_D$ = −24.8 (*c* = 0.22, CH_2Cl_2); *Z/E* < 1:20 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.22–7.17 (m, 5H), 7.15–7.14 (m, 1H), 7.13–7.04 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 1H),

4.36 (s, 2H), 4.35 (s, 2H), 3.34 (dt, *J* = 9.5, 6.1 Hz, 4H), 3.30 (s, 3H), 2.93–2.79 (m, 2H), 2.76–2.60 (m, 2H), 2.26–2.16 (m, 1H), 2.06–1.96 (m, 1H), 1.93–1.84 (m, 2H), 1.60–1.50 (m, 6H), 1.45–1.36 (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, 70.2, 70.0, 55.5, 54.8, 34.8, 33.2, 31.7, 30.34, 30.30, 30.28, 25.9, 25.4, 22.5; The spectral data were in agreement with our previously reported.[S3]

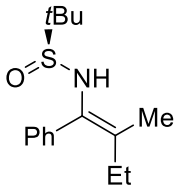


(*Z*)-**2aa**: The title compound was prepared according to the general procedure C using **1aa** (49.0 mg, 0.081 mmol, 1.0 equiv), $InBr_3$ (57.5 mg, 0.162 mmol, 2.0 equiv), and nBu$_3$SnH (47.2 mg, 0.162 mmol, 2.0 equiv). Column chromatography (30% ethyl acetate/petroleum ether) afforded (*Z*)-**2aa** (40.4 mg, 82%) as an oil. Analytical data for (*Z*)-**2aa**: R_f = 0.20 (petroleum ether/ethyl acetate = 3/1); $[\alpha]^{25}_{D}$ = −22.3 (*c* = 0.34, CH_2Cl_2); *Z*/*E* > 20:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (600 MHz, C_6D_6) δ 7.32 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.21–7.17 (m, 5H), 7.16–7.14 (m, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.85 (s, 1H), 4.36 (s, 2H), 4.35 (s, 2H), 3.40–3.34 (m, 2H), 3.32 (s, 3H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.92–2.86 (m, 1H), 2.85–2.79 (m, 1H), 2.74–2.67 (m, 1H), 2.67–2.61 (m, 1H), 2.26–2.18 (m, 1H), 2.06–1.99 (m, 1H), 1.92–1.84 (m, 2H), 1.62–1.57 (m, 3H), 1.55–1.50 (m, 3H), 1.44–1.35 (m, 2H), 1.08 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6) δ 159.7, 142.1, 139.5, 132.5, 131.4, 129.4, 129.0, 128.7, 128.6, 127.8, 127.6, 126.6, 126.3, 114.1, 73.0, 72.8, 70.3, 69.9, 55.5, 54.8, 34.8, 33.2, 31.7, 30.35, 30.31, 30.25, 25.9, 25.5, 22.6; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{37}H_{51}NNaO_4S$ 628.3431; Found 628.3437.



ent-(*Z*)-**2a**: The title compound was prepared according to the general procedure B using *ent*-**1a** (42.0 mg, 0.159 mmol, 1.0 equiv), L-Selectride (1.0 M in THF, 191 μL, 0.191 mmol, 1.2 equiv), and $NaBO_3 \cdot 4H_2O$ (122.7 mg, 0.797 mmol, 8.0 equiv). Column chromatography (15-20% ethyl acetate/petroleum ether) afforded *ent*-(*Z*)-**2a** (35.3 mg, 83%) as a white solid. Analytical data for *ent*-(*Z*)-**2a**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR

analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.54–7.50 (m, 2H), 7.21–7.17 (m, 2H), 7.07 (t, J = 7.4 Hz, 1H), 4.95 (s, 1H), 2.32–2.13 (m, 2H), 1.60 (s, 3H), 1.05 (t, J = 7.6 Hz, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 139.0, 133.3, 130.9, 128.4, 127.9, 124.7, 55.5, 26.4, 22.5, 18.8, 12.5; The spectral data were in agreement with our previously reported.[S1]



ent-(*E*)-**2a**: The title compound was prepared according to the general procedure C using *ent*-**1a** (60.0 mg, 0.228 mmol, 1.0 equiv), $InBr_3$ (161.5 mg, 0.456 mmol, 2.0 equiv), and nBu$_3$SnH (132.6 mg, 0.456 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded *ent*-(*E*)-**2a** (52.6 mg, 87%) as a white solid. Analytical data for *ent*-(*E*)-**2a**: R_f = 0.20 (petroleum ether/ethyl acetate = 5/1); mp 103–104 °C; $[\alpha]^{25}_D$ = −68.8 (c = 0.34, CH_2Cl_2); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 7.54 (d, J = 6.8 Hz, 2H), 7.21–7.17 (m, 2H), 7.08 (t, J = 7.4 Hz, 1H), 4.90 (s, 1H), 1.99 (q, J = 7.2 Hz, 2H), 1.75 (s, 3H), 0.97 (s, 9H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 138.8, 133.9, 130.6, 128.5, 128.0, 124.0, 55.5, 28.0, 22.5, 16.4, 13.4; HRMS (ESI-Orbitrap) *m/z:* [M + Na]$^+$ Calcd for $C_{15}H_{23}NNaOS$ 288.1393; Found 288.1398.

Procedure for gram scale preparation of 2a

(*Z*)-**2a** (Table 1 entry 1): A solution of **1a** (1.75 g, 6.64 mmol, 1.0 equiv) in freshly distilled THF (50 mL) was added to a flame-dried 100 mL schlenk flask equipped with a magnetic stirring bar under argon atmosphere via syringe. The solution was cooled to –78 °C and L-Selectride (1.0 M in THF, 7.97 mL, 7.97 mmol, 1.2 equiv) was added dropwise to the solution by syringe. The reaction progress was monitored by TLC. Upon completion (within 30 min), the reaction mixture was quenched with saturated aqueous ammonium chloride (15.0 mL) carefully. To the mixture was added water (30.0 mL) and separated via a funnel. The aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). To the residue was added THF/H_2O (30 mL/20 mL, v/v ~3/2) and sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$) (5.11 g, 33.22 mmol, 5.0 equiv) at rt. The mixture was stirred vigorously for 2 hours before separated via a

funnel and the aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were dried, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford (*Z*)-**2a** (1.54 g, 87%) as a white solid (eluent was removed under reduced pressure in ≤ 37 °C water bath); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

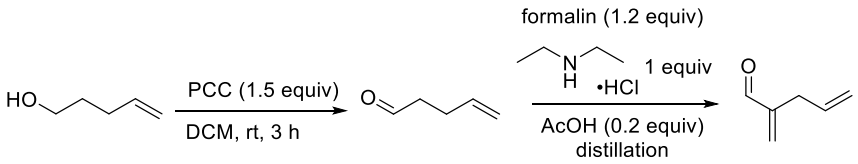
(*E*)-**2a** (Table 1 entry 2): A solution of **1a′** (1.53 g, 5.81 mmol, 1.0 equiv) in freshly distilled THF (50 mL) was added to a flame-dried 100 mL schlenk flask equipped with a magnetic stirring bar under argon atmosphere via syringe. The solution was cooled to –78 °C and L-Selectride (1.0 M in THF, 6.97 mL, 6.97 mmol, 1.2 equiv) was added dropwise to the solution by syringe. The reaction progress was monitored by TLC. Upon completion (within 30 min), the reaction mixture was quenched with saturated aqueous ammonium chloride (15.0 mL) carefully. To the mixture was added water (30.0 mL) and separated via a funnel. The aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). To the residue was added THF/H_2O (30 mL/20 mL, v/v~3/2) and sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$) (4.47 g, 29.04 mmol, 5.0 equiv) at rt. The mixture was stirred vigorously for 2 hours before separated via a funnel and the aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were dried, filtered and concentrated under reduced pressure (in ≤ 25 °C water bath). The residue was purified by column chromatography to afford (*E*)-**2a** (1.34 g, 87%) as a white solid (eluent was removed under reduced pressure in ≤ 37 °C water bath); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

(*Z*)-**2a** (Table 1 entry 10): Anhydrous indium tribromide ($InBr_3$) (4.04 g, 11.39 mmol, 2.0 equiv) was placed in a flame-dried 100 mL schlenk flask equipped with a magnetic stirring bar and heated with a hair dryer in vacuo for 5 min. The indium salt was dissolved with freshly distilled THF (50.0 mL) at rt under an argon atmosphere. The solution turned to a white suspension upon cooling to –78 ˚C. Tributyltin hydride (nBu$_3$SnH) (3.32 g, 11.39 mmol, 2.0 equiv) was then added dropwise to the suspension at –78 ˚C. The mixture was stirred for 10 min to prepare dibromoindium hydride. Then a solution of **1a′** (1.50 g, 5.69 mmol, 1.0 equiv) in dry THF (5.0 mL)

was added to the flask. The flask containing the imine solution was rinsed once with 5.0 mL of THF and the resulting solution was added by syringe to the reaction flask. It was stirred for 10 more min at –78 ˚C before warmed to rt. The reaction progress was monitored by TLC. Upon completion (1 h), the reaction mixture was quenched with saturated aqueous ammonium chloride (15.0 mL). To the mixture was added water (30.0 mL) and separated via a funnel. The aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were washed with aqueous solution of sodium hydroxide (1.0 M, 40.0 mL) once, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ºC water bath). The residue was purified by column chromatography to afford (*Z*)-**2a** (1.31 g, 87%) (eluent was removed under reduced pressure in ≤ 37 ºC water bath); *Z*/*E* > 50:1 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

(*E*)-**2a** (Table 1 entry 11): Anhydrous indium tribromide ($InBr_3$) (4.12 g, 11.62 mmol, 2.0 equiv) was placed in a flame-dried 100 mL schlenk flask equipped with a magnetic stirring bar and heated with a hair dryer in vacuo for 5 min. The indium salt was dissolved with freshly distilled THF (50.0 mL) at rt under an argon atmosphere. The solution turned to a white suspension upon cooling to –78 ˚C. Tributyltin hydride (nBu$_3$SnH) (3.38 g, 11.62 mmol, 2.0 equiv) was then added dropwise to the suspension at –78 ˚C. The mixture was stirred for 10 min to prepare dibromoindium hydride. Then a solution of **1a** (1.53 g, 5.81 mmol, 1.0 equiv) in dry THF (5.0 mL) was added to the flask. The flask containing the imine solution was rinsed once with 5.0 mL of THF and the resulting solution was added by syringe to the reaction flask. It was stirred for 10 more min at –78 ˚C before warmed to rt. The reaction progress was monitored by TLC. Upon completion (1 h), the reaction mixture was quenched with saturated aqueous ammonium chloride (15.0 mL). To the mixture was added water (30.0 mL) and separated via a funnel. The aqueous phase was extracted with CH_2Cl_2 (20 mL×3). The combined organic extracts were washed with aqueous solution of sodium hydroxide (1.0 M, 40.0 mL) once, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure (in ≤ 25 ºC water bath). The residue was purified by column chromatography to afford (*E*)-**2a** (1.32 g, 86%) (eluent was removed under reduced pressure in ≤ 37 ºC water bath); *Z*/*E* < 1:50 (the *Z*/*E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

Asymmetric synthesis of (−)-daucene



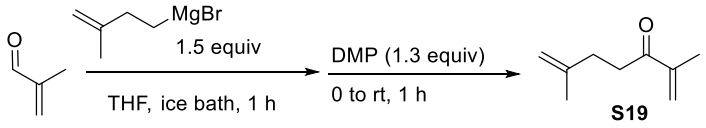
Pyridinium chlorochromate (13.14 g, 60.95 mmol, 1.5 equiv) was suspended in dichloromethane (100 mL) at rt, to which was added 4-Penten-1-ol (3.50 g, 40.64 mmol, 1.0 equiv), and the reaction was left for 3 h, monitoring by TLC. The mixture was filtered through silica and celite (layered, 3:1 ratio), then concentrated in vacuo (200 hPa, in ≤ 15 °C water bath) to leave pent-4-enal as a colorless oil. It was used for next step without further purification.

To a solution of formalin (37%, 4.1 mL, 48.76 mmol, 1.2 equiv) and Et_2NH (4.2 mL, 40.64 mmol, 1.0 equiv) was added glacial acetic acid (2.4 mL, 40.64 mmol, 1.0 equiv) at 0 °C. The pH of the solution was 6–7 (slight excess of AcOH should be used. Otherwise, excess Et_2NH will be distilled out with the product.). The mixture was heated to 72 °C. 4-Pentenal obtained above was added dropwise via an addition funnel over 30 min. After completion of the addition, the mixture was stirred for a further 30 min. The product was collected by distillation (b.p. 115–118 °C at 606 mmHg; atmosphere pressure at Kunming city). The aq. layer in the receiving flask was saturated with solid NaCl. The organic layer was washed with aqeous 2N HCl (saturated with NaCl, 2 × 2 mL) and brine (2 × 2 mL), dried over activated 4Å MS (20 mg) and stored at −20°C. Colorless oil (2.8 g, 72% yield), R_f = 0.8 (20:1 hexanes/AcOEt).

In a flame-dried flask fitted with reflux condenser and magnetic stirring bar was placed Mg (1.52 g, 62.42 mmol, 1.5 equiv). This was covered with 5 mL of dry THF, and a few drops of 4-bromo-2-methylbut-1-ene were added. Initiation was proceeded easily, and the reaction was diluted with 40 mL of THF. The remainder of the halide (9.30 g, 62.42 mmol, 1.5 equiv) was added to the flask dropwise over 1 h. The flask containing the halide was rinsed with an additional 5 mL of THF. The solution was heated at reflux for 2 h and then cooled. The reaction mixture was

cooled with an ice bath and was added 2-methylenepent-4-enal (4.0 g, 41.61 mmol, 1.0 equiv), and stirred for 1 h until full conversion. 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 (10−20% ethyl acetate/petroleum ether).

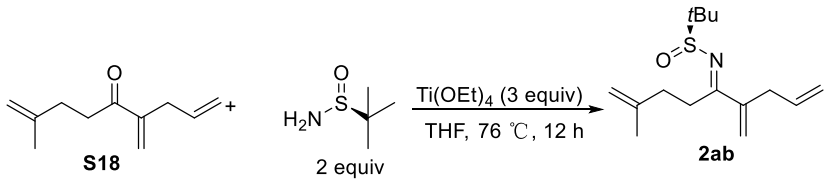
The alcohol obtained above was dissolved in CH_2Cl_2 (200 mL) and DMP (22.9 g, 54.09 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (100 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (100 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×50 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 (5%−10% ethyl acetate/petroleum ether) to give **S18** (5.74 g, 84% for two steps) as a colorless oil. Analytical data for **S18**: R_f = 0.40 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.87–5.75 (m, 2H), 5.08 (s, 1H), 5.07–5.02 (m, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 3.03 (d, J = 6.8 Hz, 2H), 2.84 (t, J = 7.8 Hz, 2H), 2.32 (t, J = 7.8 Hz, 2H), 1.75 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.8, 147.1, 144.8, 135.5, 124.6, 116.8, 110.2, 36.0, 35.0, 32.1, 22.8; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{11}H_{17}O$ 165.1274; Found 165.1277.



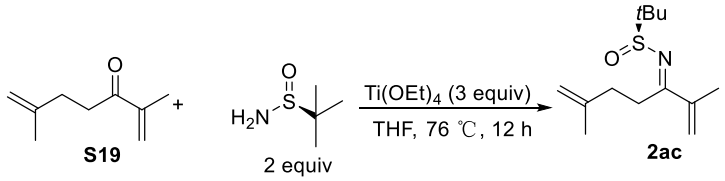
In a flame dried 100 mL flask fitted with reflux condenser and magnetic stirring was placed Mg (1.04 g, 42.80 mmol, 1.5 equiv). This was covered with 5 mL of dry THF, and a few drops of 4-bromo-2-methylbut-1-ene were added. Initiation was proceeded easily, and the reaction was diluted with 40 mL of THF. The remainder of the halide (6.38 g, 42.80 mmol, 1.5 equiv) was added to the flask dropwise over 1 h. The flask containing the halide was rinsed with an additional 5 mL of THF. The solution was heated at reflux for 2 h and then cooled in an ice bath. To the solution of Grignard reagent was added methacrylaldehyde (2.0 g, 28.53 mmol, 1.0 equiv), and stirred for 1 h until full conversion. 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 (10-20% ethyl acetate/petroleum ether).

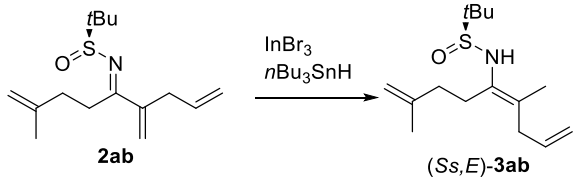
The alcohol obtained above was dissolved in CH_2Cl_2 (200 mL) and DMP (15.73 g, 37.09 mmol, 1.3 equiv) was added portionwise. After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2 (100 mL) and washed twice with 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution (100 mL, v/v = 1/1). The aqueous layer was extracted with CH_2Cl_2 (3×50 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 (5%-10% ethyl acetate/petroleum ether) to give **S19** (3.10 g, 79% for two steps) as a colorless oil. Analytical data for **S19**: R_f = 0.40 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 5.80–5.75 (m, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 2.87–2.80 (m, 2H), 2.32 (t, J = 7.8 Hz, 2H), 1.88 (s, 3H), 1.75 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.5, 144.8, 144.5, 124.4, 110.1, 35.7, 32.2, 22.7, 17.7; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_9H_{15}O$ 139.1117; Found 139.1117.



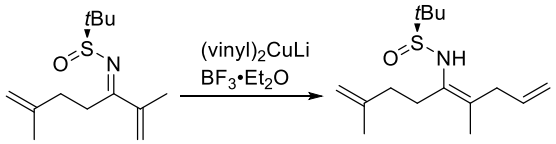
According to the general procedure A, **2ab** was prepared using **S18** (2.50 g, 15.31 mmol, 1.0 equiv), *(S)-N-tert*-butanesulfinamide (3.71 g, 30.63 mmol, 2.0 equiv), and titanium ethoxide (9.63 mL, 45.94 mmol, 3.0 equiv). Column chromatography (10-15% ethyl acetate/petroleum ether) afforded **2ab** (3.49 g, 85%) as an oil. Analytical data for **2ab**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = +181.9 (c = 0.18, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91–5.78 (m, 2H), 5.60 (s, 1H), 5.08 (s, 1H), 5.05 (d, J = 5.2 Hz, 1H), 4.74 (d, J = 4.8 Hz, 2H), 3.25–3.13 (m, 1H), 3.13–2.96 (m, 3H), 2.36–2.22 (m, 2H), 1.78 (s, 3H), 1.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 179.7, 146.7, 144.4, 136.1, 121.8, 116.5, 110.8, 57.4, 36.8, 36.6, 30.3, 22.6, 22.4; HRMS (ESI-Orbitrap) *m/z:* [M + H]$^+$ Calcd for $C_{15}H_{26}NOS$ 268.1730; Found 268.1732.



According to the general procedure A, **2ac** was prepared using **S19** (1.50 g, 10.85 mmol, 1.0 equiv), *(S)-N-tert*-butanesulfinamide (2.63 g, 21.71 mmol, 2.0 equiv), and titanium ethoxide (6.83 mL, 32.56 mmol, 3.0 equiv). Column chromatography (10-15% ethyl acetate/petroleum ether) afforded **2ac** (2.15 g, 82%) as an oil. Analytical data for **2ac**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); $[\alpha]^{20}_D$ = +209.2 (*c* = 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 1H), 5.59 (s, 1H), 4.74 (d, *J* = 4.8 Hz, 2H), 3.24–3.11 (m, 1H), 3.06–2.95 (m, 1H), 2.37–2.23 (m, 2H), 1.93 (s, 3H), 1.77 (s, 3H), 1.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.3, 144.4, 144.2, 121.5, 110.7, 57.2, 36.9, 30.0, 22.6, 22.3, 19.8; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{24}NOS$ 242.1573; Found 242.1575.



According to the general procedure C, (*Ss,E*)-**3ab** was prepared using **2ab** (500.0 mg, 1.87 mmol, 1.0 equiv), $InBr_3$ (1.33 g, 3.739 mmol, 2.0 equiv), and nBu$_3$SnH (1.09 g, 3.739 mmol, 2.0 equiv). Column chromatography (20% ethyl acetate/petroleum ether) afforded (*Ss,E*)-**3ab** (388.0 mg, 77%) as an oil. Analytical data for (*Ss,E*)-**3ab**: R_f = 0.25 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = +20.1 (*c* = 0.25, CH_2Cl_2); *Z/E* < 1:50 (the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, C_6D_6) δ 5.75–5.59 (m, 1H), 5.08–4.96 (m, 2H), 4.84 (s, 1H), 4.80 (s, 1H), 4.66 (s, 1H), 2.66 (d, *J* = 6.0 Hz, 2H), 2.60–2.50 (m, 1H), 2.45–2.31 (m, 2H), 2.29–2.19 (m, 1H), 1.68 (s, 3H), 1.63 (s, 3H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 145.7, 136.3, 134.0, 118.8, 115.6, 110.7, 55.5, 38.4, 36.7, 30.0, 22.6, 22.5, 16.9; HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{28}NOS$ 270.1886; Found 270.1889.

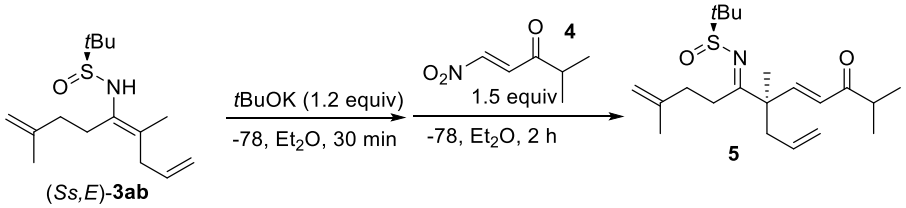


2ac **3ac**

Z/E~2.5-5:1

To a flame dried 10 mL Schlenk tube placed tetravinyltin (36.3 mg, 0.16 mmol, 1.0 equiv) at rt was added *n*BuLi (2.5 M in hexane, 0.216 mL, 0.54 mmol, 3.4 equiv) under argon atmosphere. After 1 h stirring, it was diluted with dry THF to prepare vinyllithium solution.

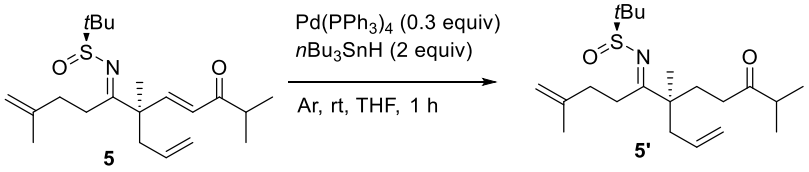
To a separate 10 mL Schlenk flask containing anhydrous CuCN (flame dried and backfilled with argon) (23.5 mg, 0.262 mmol, 1.6 equiv) was added freshly distilled THF (1.6 mL). This suspension was cooled to −78 °C and vinyllithium prepared above was transferred via syringe to this flask. Then it was warmed to 0 °C and stirred for 10 min to form a clear solution. The solution was cooled back to −78 °C before $BF_3{\cdot}OEt_2$ (32 μL, 0.262 mmol, 1.6 equiv) was added. After 10 min, a solution of **2ac** (38.0 mg, 0.16 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 30 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 °C water bath). *Z/E* ~ 2.5:1 (with $BF_3{\cdot}OEt_2$ as additive. The *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); *Z/E* ~ 5:1 (in absence of $BF_3{\cdot}OEt_2$; the *Z/E* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).



(*Ss,E*)-**3ab**

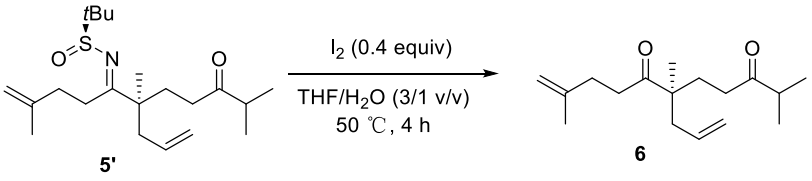
Enesulfinamide (*Ss,E*)-**3ab** (360 mg, 1.336 mmol, 1.0 equiv) in freshly distilled Et_2O (30 mL) was added to a flame dried Schlenk tube equipped with magnetic stirring bar under argon. The resulting clear solution was then cooled to −78 °C and a solution of potassium *tert*-butoxide in THF (1.0 M, 1.60 mL, 1.603 mmol, 1.2 equiv) was added dropwise to the mixture via syringe. After 30 min, β-nitroenone **4** (286.9 mg, 2.004 mmol, 1.5 equiv) in dry Et_2O (10 mL) was added

dropwise by syringe at −78 ℃. The reaction progress was monitored by TLC analysis. After 2 h, the reaction mixture was quenched with saturated aqueous ammonium chloride (10 mL). The resulting mixture was extracted with ethyl acetate (30 mL×3) 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 (10% ethyl acetate/petroleum ether) to afford **5** (397.0 mg, 81%) as an oil. Analytical data for **5**: R_f = 0.4 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{20}_D$ = +135.6 (*c* = 0.23, CH_2Cl_2); dr > 20:1 (The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 16.0 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 5.71–5.57 (m, 1H), 5.10 (s, 1H), 5.09–5.04 (m, 1H), 4.71 (s, 1H), 4.67 (s, 1H), 2.98 (td, *J* = 12.4, 4.4 Hz, 1H), 2.82 (p, *J* = 6.8 Hz, 1H), 2.59–2.41 (m, 3H), 2.34 (td, *J* = 13.4, 4.4 Hz, 1H), 2.18 (td, *J* = 13.1, 4.6 Hz, 1H), 1.72 (s, 3H), 1.30 (s, 3H), 1.26 (s, 9H), 1.11 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.3, 187.2, 149.0, 144.1, 133.2, 127.6, 119.0, 110.9, 57.4, 52.5, 42.7, 39.0, 35.4, 31.4, 22.6, 22.1, 21.6, 18.5, 18.3; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{21}H_{35}NNaO_2S$ 388.2281; Found 388.2279.



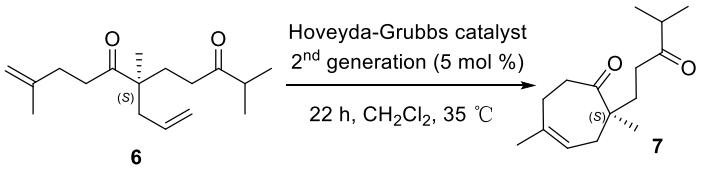
To a 50 mL flame dried Schlenk tube was added $Pd(PPh_3)_4$ (350.9 mg, 0.304 mmol, 0.3 equiv), followed by adding a solution of **5** (370.0 mg, 1.012 mmol, 1.0 equiv) in anhydrous THF (25 mL) under argon atmosphere. Then to the reaction mixture was added tributyltin hydride (589.2 mg, 2.024 mmol, 2.0 equiv) in one portion. The resulting mixture was stirred at room temperature for 1 h, and then saturated ammonium chloride (5 ml) was added to quench the reaction. The aqueous phase was extracted with ethyl acetate (2 × 15 mL). The combined organic phases were washed by 1 M aqueous sodium hydroxide and dried over anhydrous sodium sulfate, filtered and followed by concentrating in vacuum. The residue was purified by column chromatography on silica gel (10% ethyl acetate/petroleum ether) to afford **5′** (349.8 mg, 94%) as an oil. Analytical data for **5′**: R_f = 0.4 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{20}_D$ = +155.1 (*c* = 0.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73–5.62 (m, 1H), 5.07 (s, 1H), 5.04 (d, *J* = 4.0 Hz, 1H), 4.77–4.70 (m, 2H), 3.03 (td, *J*

= 12.3, 4.5 Hz, 1H), 2.59–2.51 (m, 2H), 2.43–2.38 (m, 1H), 2.37–2.30 (m, 3H), 2.28–2.16 (m, 2H), 1.96–1.89 (m, 1H), 1.76 (s, 3H), 1.73–1.67 (m, 1H), 1.24 (s, 9H), 1.11 (s, 3H), 1.06 (d, J = 2.5 Hz, 3H), 1.05 (d, J = 2.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 214.1, 190.0, 144.4, 133.8, 118.5, 110.9, 57.1, 49.2, 43.7, 41.1, 35.5, 35.0, 31.8, 30.2, 22.7, 22.3, 21.9, 18.5; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{21}H_{37}NNaO_2S$ 390.2437; Found 390.2437.



5' **6**

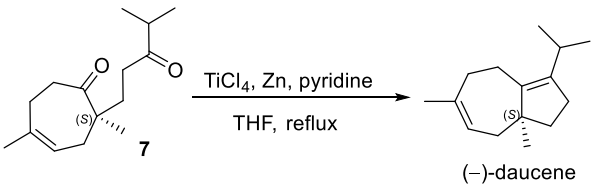
To a solution of **6** (320 mg, 0.871 mmol, 1.0 equiv) in THF (12.0 mL), was added H_2O (4.0 mL) and I_2 (88.4 mg, 0.348 mmol, 0.4 equiv) successively at rt. The resulting mixture was stirred at 50 ℃ in a heating mantle for 4 h. Then the reaction mixture was cooled to rt, diluted with CH_2Cl_2 (30 mL), washed with saturated sodium thiosulfate, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by silica gel chromatography (2-5% ethyl acetate/petroleum ether) to afford **6** (216 mg, 94%) as an oil. Analytical data for **6**: R_f = 0.4 (petroleum ether/ethyl acetate = 20/1); $[\alpha]^{20}_D$ = +7.0 (c = 0.27, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 5.69–5.59 (m, 1H), 5.07 (s, 1H), 5.05–5.02 (m, 1H), 4.71 (s, 1H), 4.65 (s, 1H), 2.60–2.53 (m, 3H), 2.37 (dd, J = 14.0, 7.0 Hz, 1H), 2.33–2.28 (m, 2H), 2.24–2.17 (m, 3H), 1.92–1.84 (m, 1H), 1.77–1.70 (m, 4H), 1.12 (s, 3H), 1.06 (d, J = 7.0 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 214.1, 213.9, 145.0, 133.7, 118.5, 110.3, 50.5, 42.5, 41.1, 35.9, 35.4, 31.6, 31.5, 22.8, 21.1, 18.4; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{17}H_{28}NaO_2$ 287.1982; Found 287.1983.



6 **7**

To a flame-dried 50 mL Schlenk flask equipped with a magnetic stirring was added dione **6** (50.0 mg, 0.189 mmol, 1.00 equiv) in dry CH_2Cl_2 (10 mL) via syringe under argon atmosphere. The flask was charged with additional CH_2Cl_2 (20 mL) and Hoveyda–Grubbs 2nd generation catalyst (5.9 mg, 0.0095 mmol, 5.0 mol %), generating a pale green solution. The flask was rinsed

with CH_2Cl_2 (5 mL) and lowered into a preheated heating mantle (35 °C). After 22 h, the reaction was quenched with ethyl vinyl ether (1.5 mL), removed from the oil bath, and allowed to cool to room temperature. The reaction contents were filtered through a short silica gel plug, rinsing with TBME, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (2−5% ethyl acetate/petroleum ether) to afford dione **7** (43.9 mg, 98% yield) as a clear oil. Analytical data for **7**: R_f = 0.35 (petroleum ether/ethyl acetate = 20/1); $[\alpha]^{20}_D$ = +53.9 (*c* = 0.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.44–5.39 (m, 1H), 2.96–2.90 (m, 1H), 2.54 (hept, *J* = 6.9 Hz, 1H), 2.48–2.39 (m, 2H), 2.39–2.34 (m, 2H), 2.32–2.26 (m, 1H), 2.23–2.16 (m, 1H), 2.01 (dd, *J* = 15.6, 7.8 Hz, 1H), 1.81–1.75 (m, 1H), 1.66–1.59 (m, 4H), 1.0– 1.01 (m, 6H), 1.00 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 216.2, 214.4, 137.1, 121.3, 53.2, 41.0, 37.5, 35.7, 35.4, 32.2, 32.0, 25.3, 21.7, 18.4, 18.3; HRMS (ESI-Orbitrap) *m/z:* $[M + Na]^+$ Calcd for $C_{15}H_{24}NaO_2$ 259.1669; Found 259.1664.



At 0 °C, titanium(IV) chloride (0.42 mL, 0.722 g, 3.808 mmol, 10.0 equiv) was injected dropwise by syringe to dry THF (30 mL) to afford a yellowish suspension. After 20 min. of stirring, activated Zn powder (498 mg, 7.616 mmol, 20.0 equiv) and anhyd. pyridine (77 μL, 75.3 mg, 0.952 mmol, 2.5 equiv) were added successively at 0 °C to the $TiCl_4$·THF complex. The resulting suspension was refluxed (oil bath temp. 80 °C) for 1.5 h, and then a solution of diketone **7** (90 mg, 0.381 mmol, 1.0 equiv) in dry THF (15 mL) was added dropwise using a syringe pump over 32 h. After refluxing for additional 30 min., the grey-black suspension was allowed to cool to rt, and quenched by dropwise addition of aq. K_2CO_3 (10%, 20 mL). The insoluble material was removed by suction filtration, and thoroughly washed with Et_2O. The aqueous layer was extracted with Et_2O (2 × 20 mL), and the combined organic extracts were washed with brine (1×50 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The resulting crude oil was purified by silica gel column chromatography (silica was impregnated with silver nitrate (10%) before use,[S4] 0−2% MTBE/pentane) to afford (–)-daucene (53.0 mg, 68% yield) as a clear oil. Analytical data

for (–)-daucene: R_f = ~1.0 (pentane); $[\alpha]^{25}_D$ = –30.49 (*c* = 1.37, CH_3Cl) (reported value: $[\alpha]^{25}_D$ = –24.95 (*c* = 1.37, CH_3Cl)[S5]); ^1H NMR (600 MHz, $CDCl_3$) δ 5.45–5.40 (m, 1H), 2.66 (h, *J* = 6.8 Hz, 1H), 2.42–2.37 (m, 1H), 2.17 (td, *J* = 8.0, 6.9, 2.3 Hz, 2H), 2.08–2.00 (m, 3H), 1.94 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.86–1.79 (m, 1H), 1.74 (s, 3H), 1.62–1.56 (m, 1H), 1.56–1.51 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.91 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 142.0, 139.9, 138.8, 122.9, 49.7, 40.5, 38.7, 33.7, 27.3, 26.6, 26.1, 23.7, 22.7, 22.0, 21.4 (the NMR spectra are in agreement with the reported[S5]); HRMS (ESI-Orbitrap) *m/z:* $[M + H]^+$ Calcd for $C_{15}H_{25}$ 205.1951; Found 205.1952.

References

(S1) Yisimayili, N.; Zhu, C.-L.; Liu, T.; Yao, Y.; Lu, C.-D. Stereoselective Construction of Acyclic beta,beta-Disubstituted Enesulfinamides via Conjugate Addition of Organocuprates to alpha-Substituted alpha,beta-Unsaturated N-Sulfinyl Ketimines. *Org. Lett.* **2023**, *25*, 5536-5541. DOI: 10.1021/acs.orglett.3c02060.

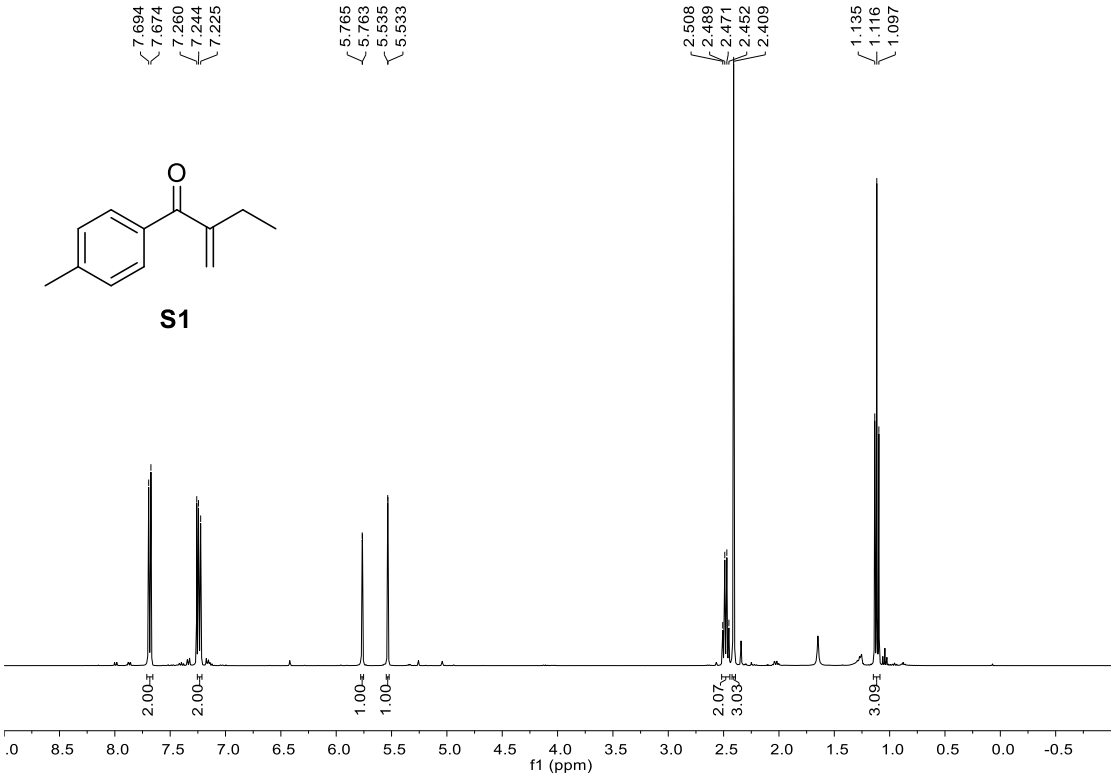
(S2) Saito, S.; Yamamoto, H. Efficient Conjugate Reduction of alpha,beta-Unsaturated Carbonyl Compounds by Complexation with Aluminum Tris(2,6-diphenylphenoxide). *J. Org. Chem.* **1996**, *61*, 2928-2929. DOI: 10.1021/jo960161e.

(S3) Zhu, C.-L.; Lu, C.-D. Stereoselective formal alkenylation of β,β-disubstituted enesulfinamides for constructing 1,5-and 1,4-dicarbonyl derivatives bearing less-accessible acyclic α-quaternary stereocenters. *Org. Chem. Front.* **2023**, *10*, 5490-5495. DOI: 10.1039/d3qo01381b.

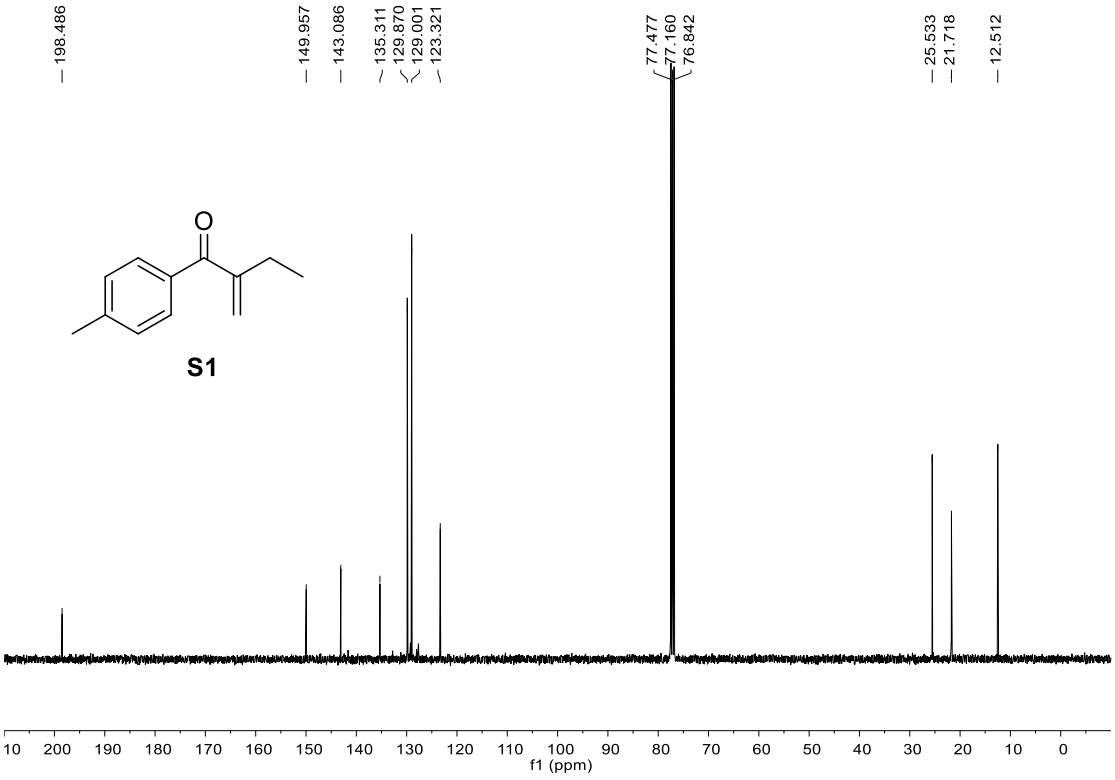
(S4) Li, T.-S.; Li, J.-T. L.; H.-Z. Modified and convenient preparation of silica impregnated with silver nitrate and its application to the separation of steroids and triterpenes. *J. Chromatogr. A* **1995**, *715*, 372-375. DOI: 10.1016/0021-9673(95)00619-X.

(S5) Bennett, N. B.; Stoltz, B. M. A unified approach to the daucane and sphenolobane bicyclo[5.3.0]decane core: enantioselective total syntheses of daucene, daucenal, epoxydaucenal B, and 14-para-anisoyloxydauc-4,8-diene. *Chem.–Eur. J.* **2013**, *19*, 17745-17750. DOI: 10.1002/chem.201302353.

^{1}H and ^{13}C NMR spectra of the compounds S1−S17



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



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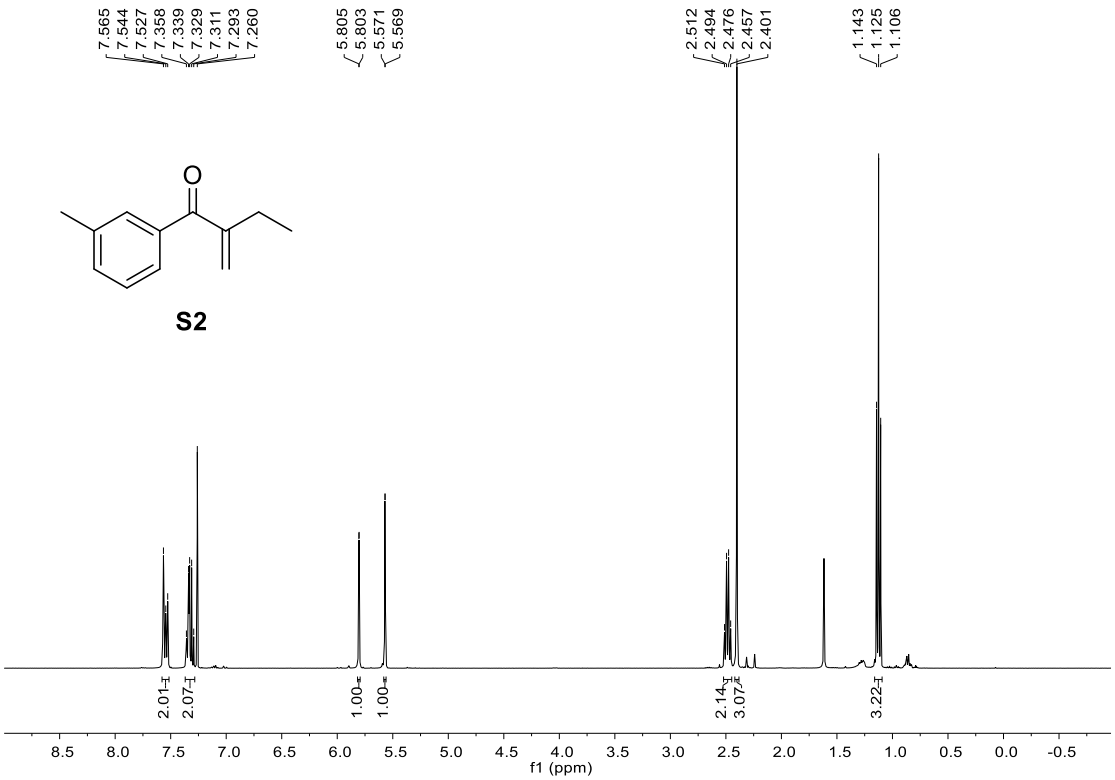
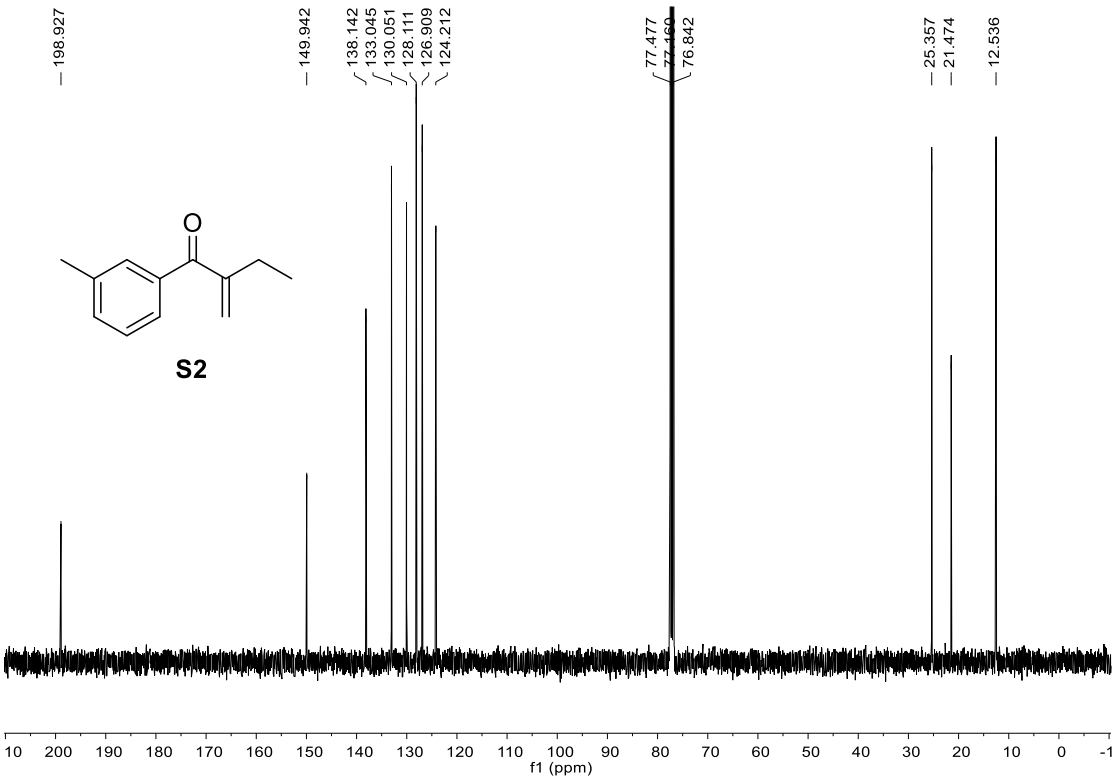
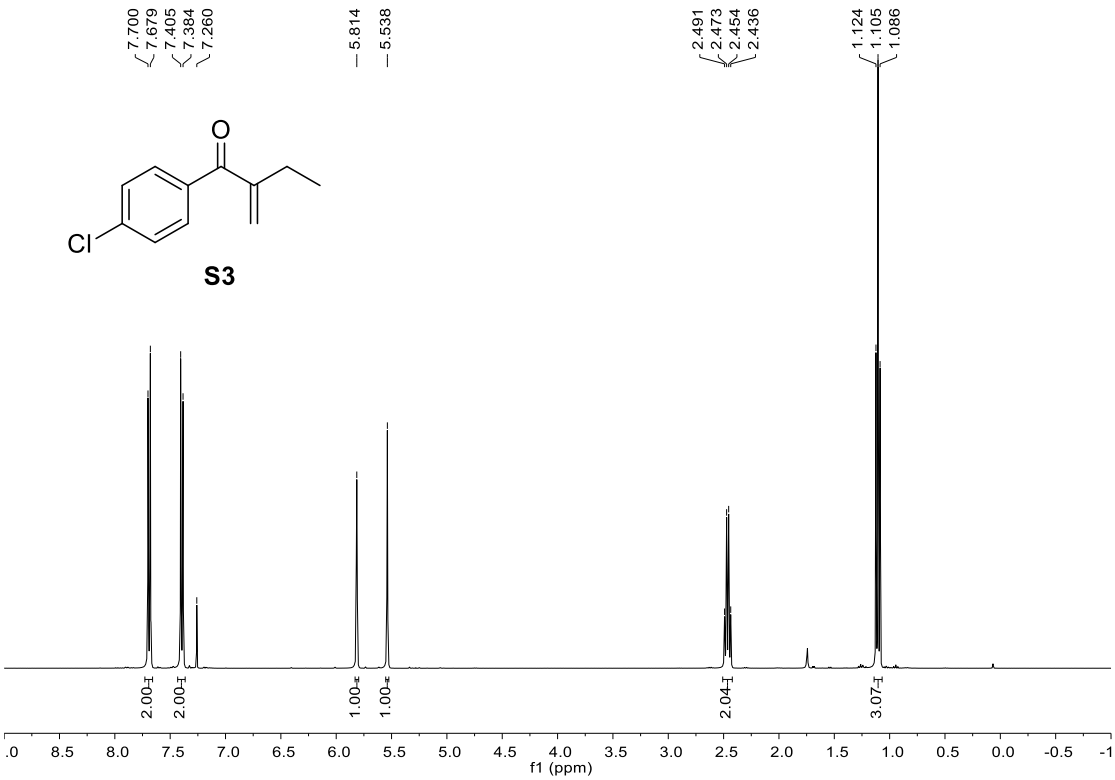


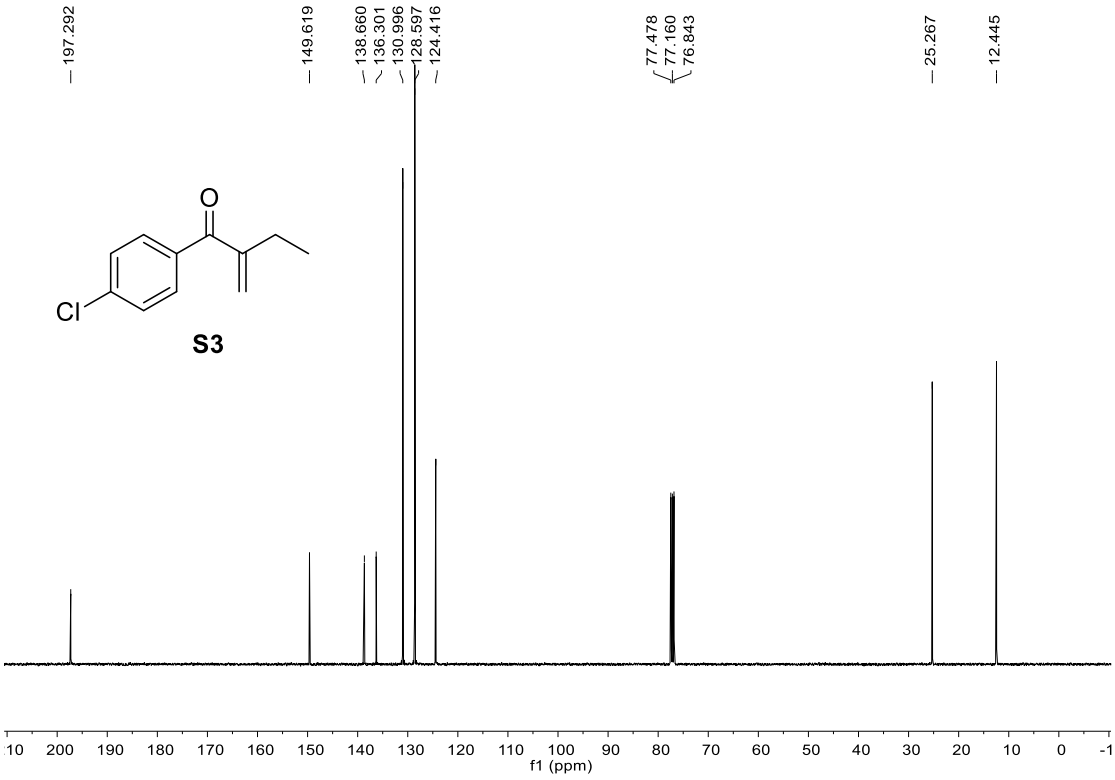
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2**



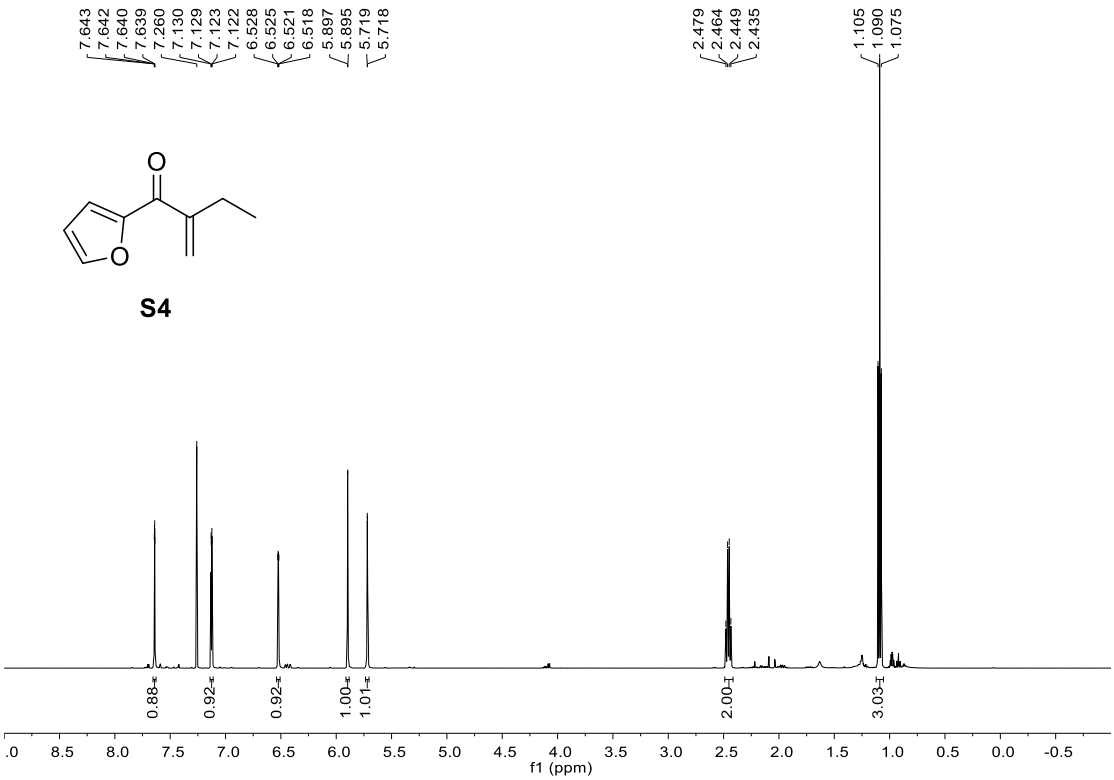
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S2**



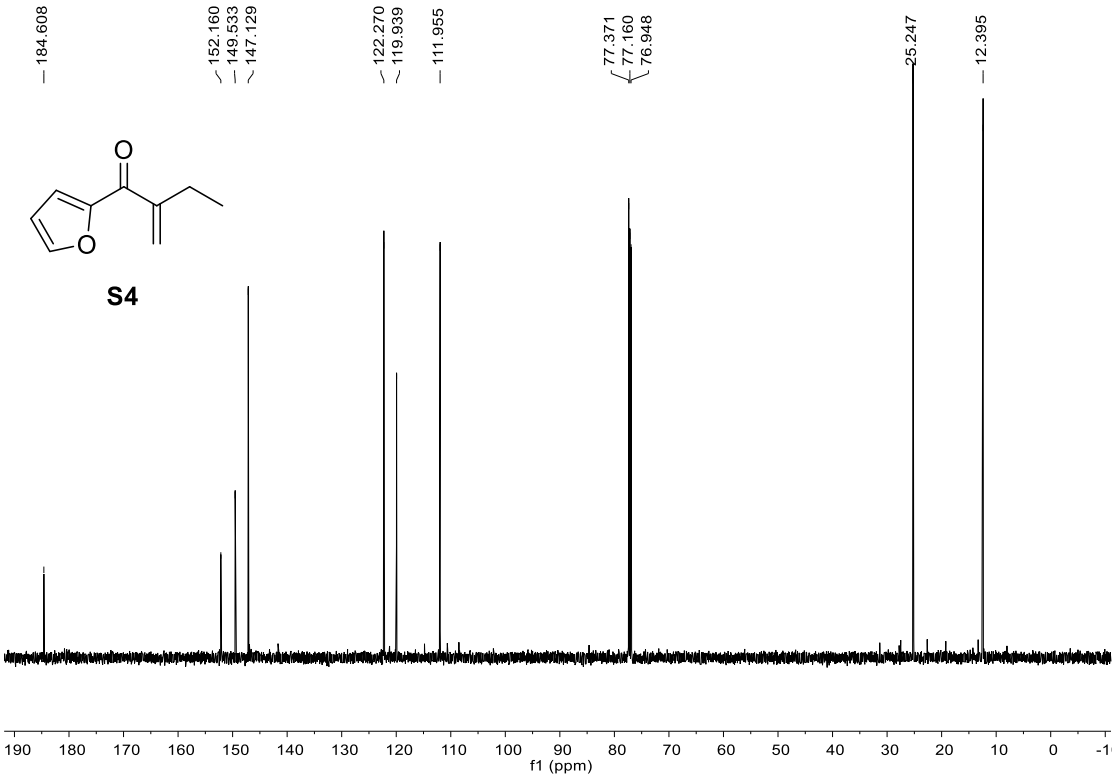
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S3**



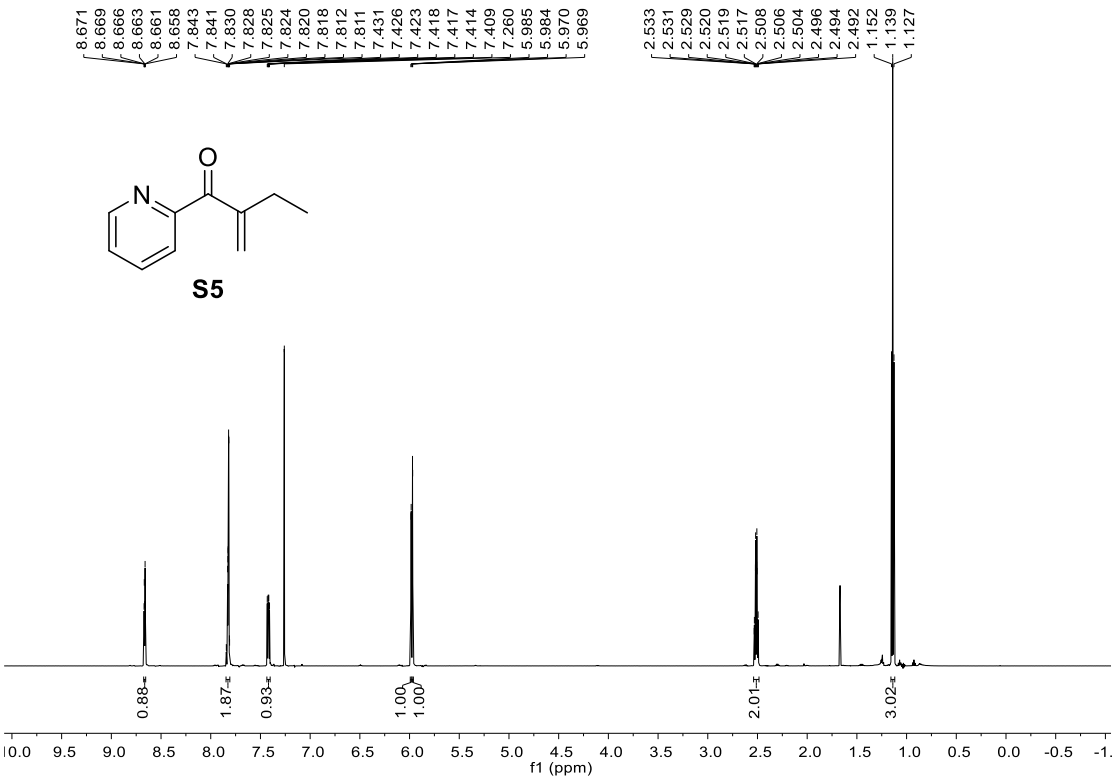
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S3**



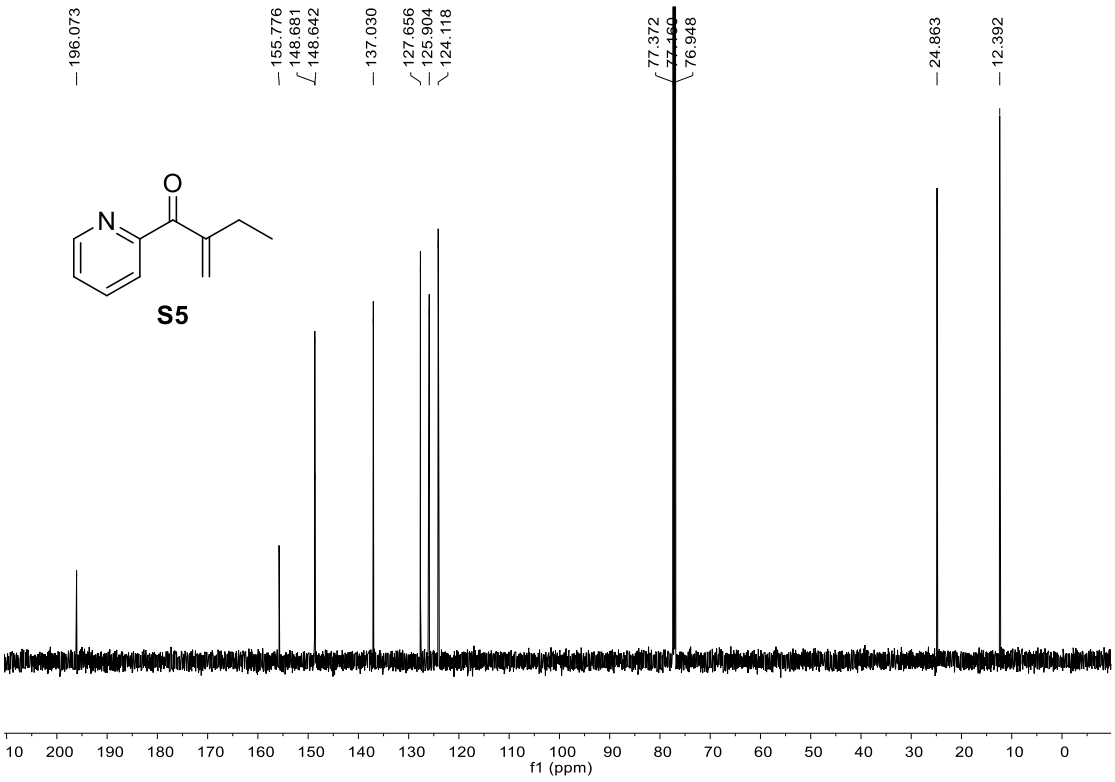
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S4**



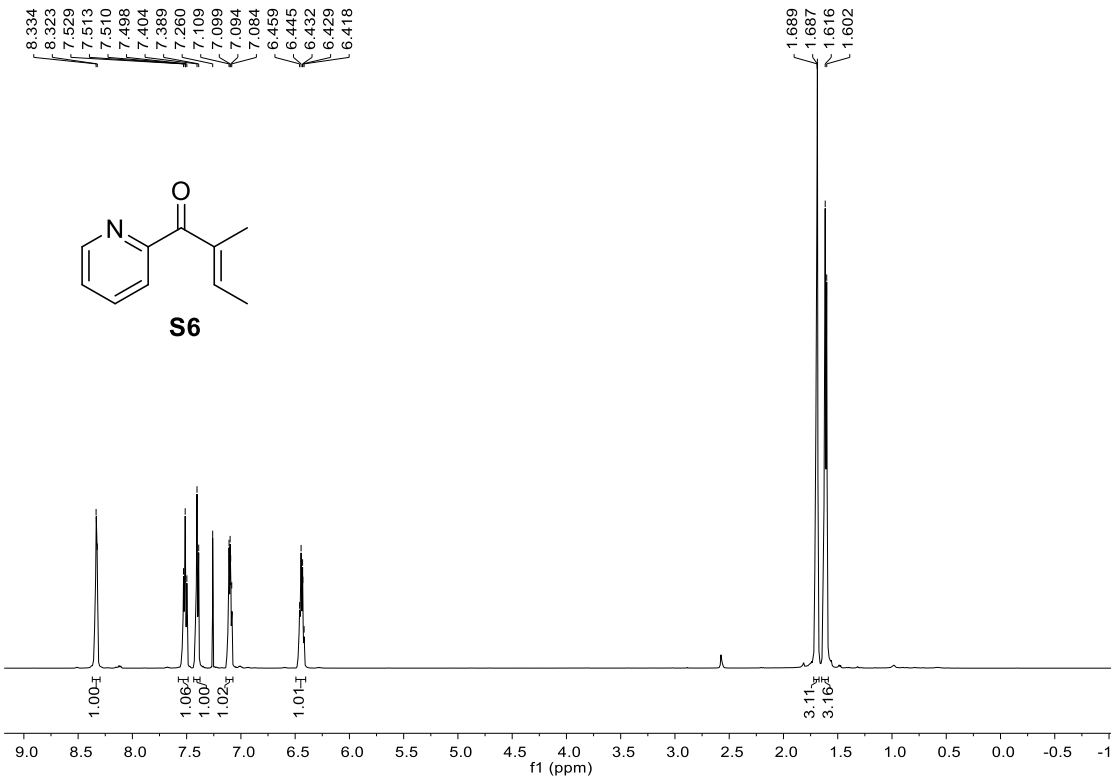
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **S4**



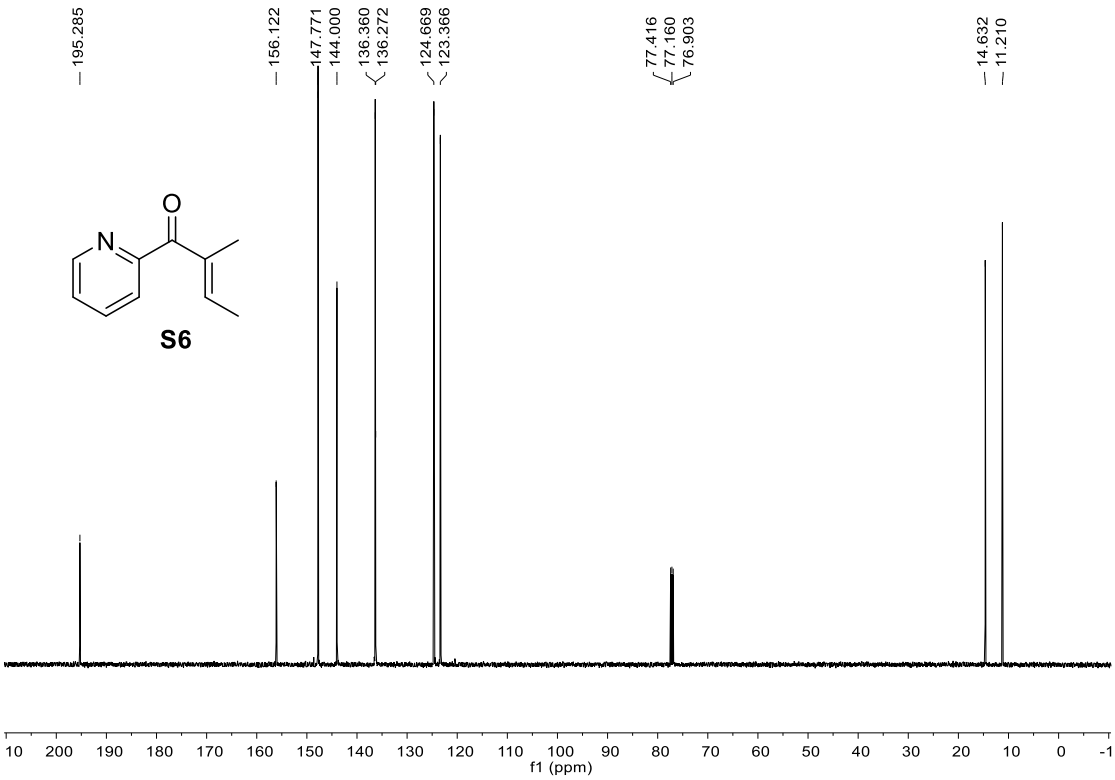
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **S5**



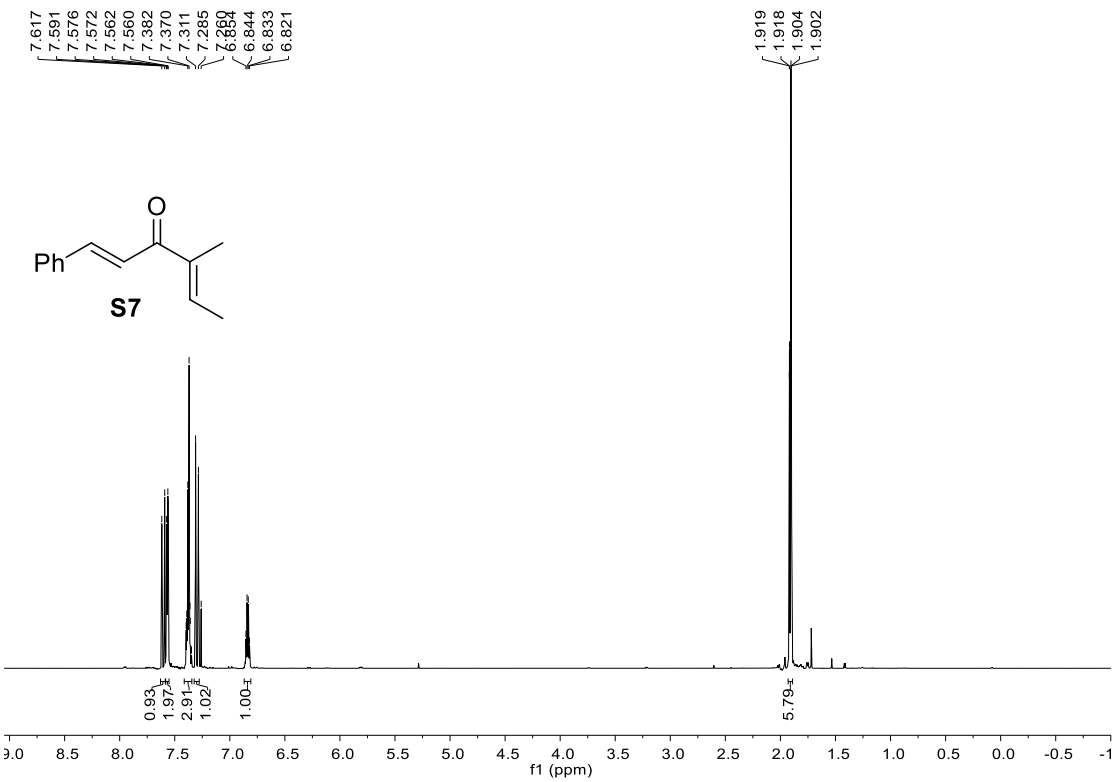
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **S5**



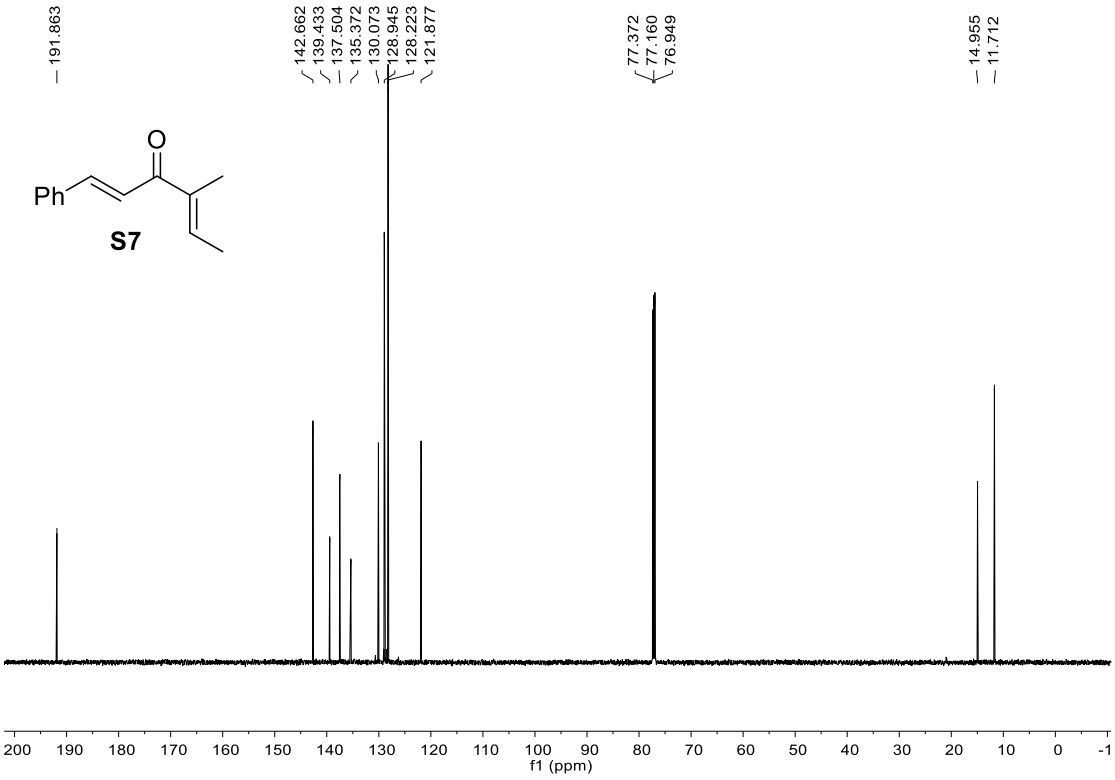
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S6**



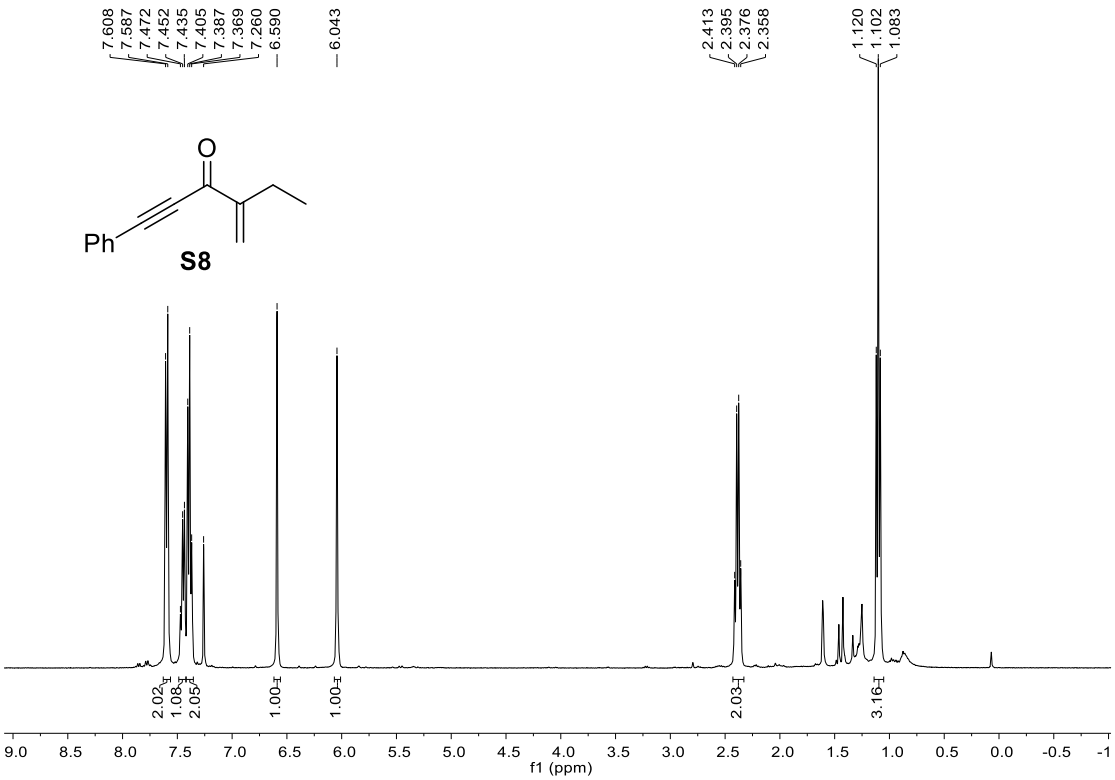
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S6**



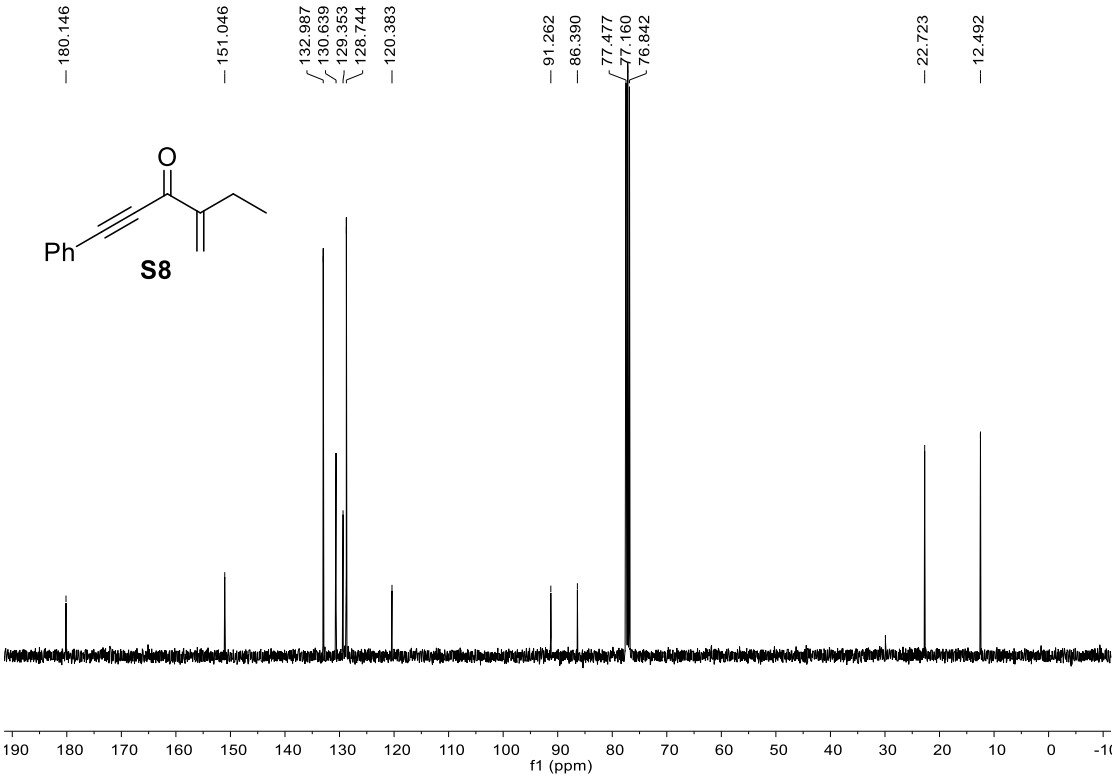
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **S7**



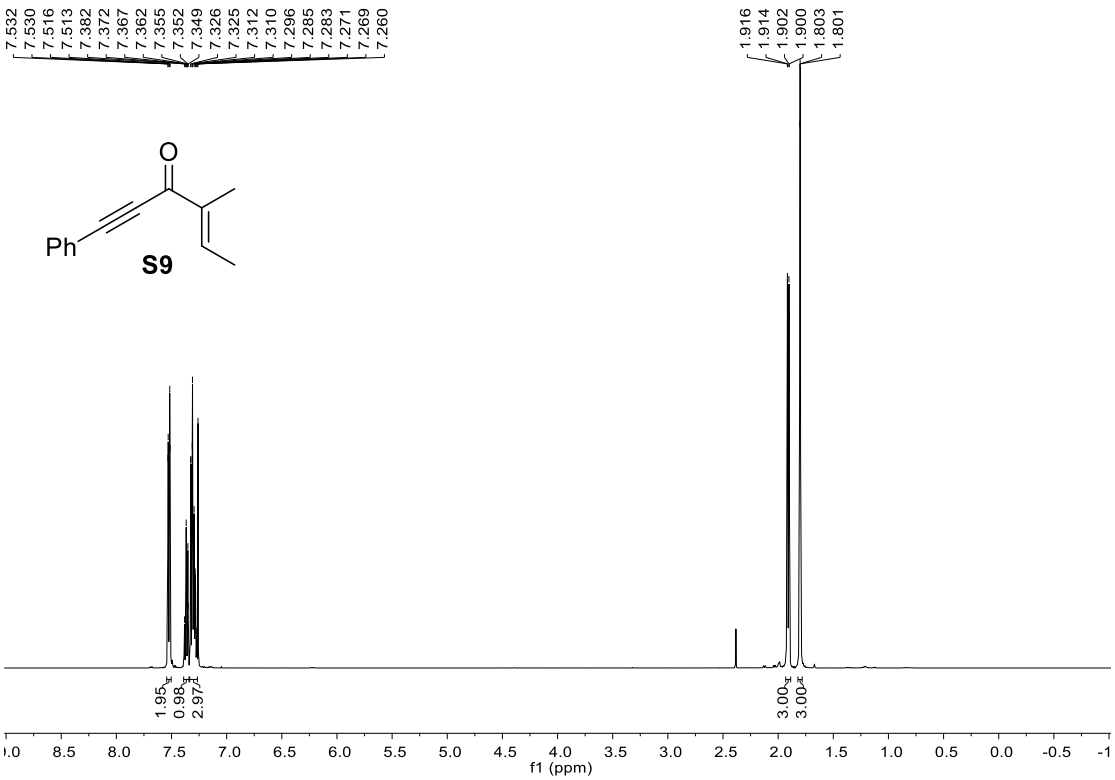
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **S7**



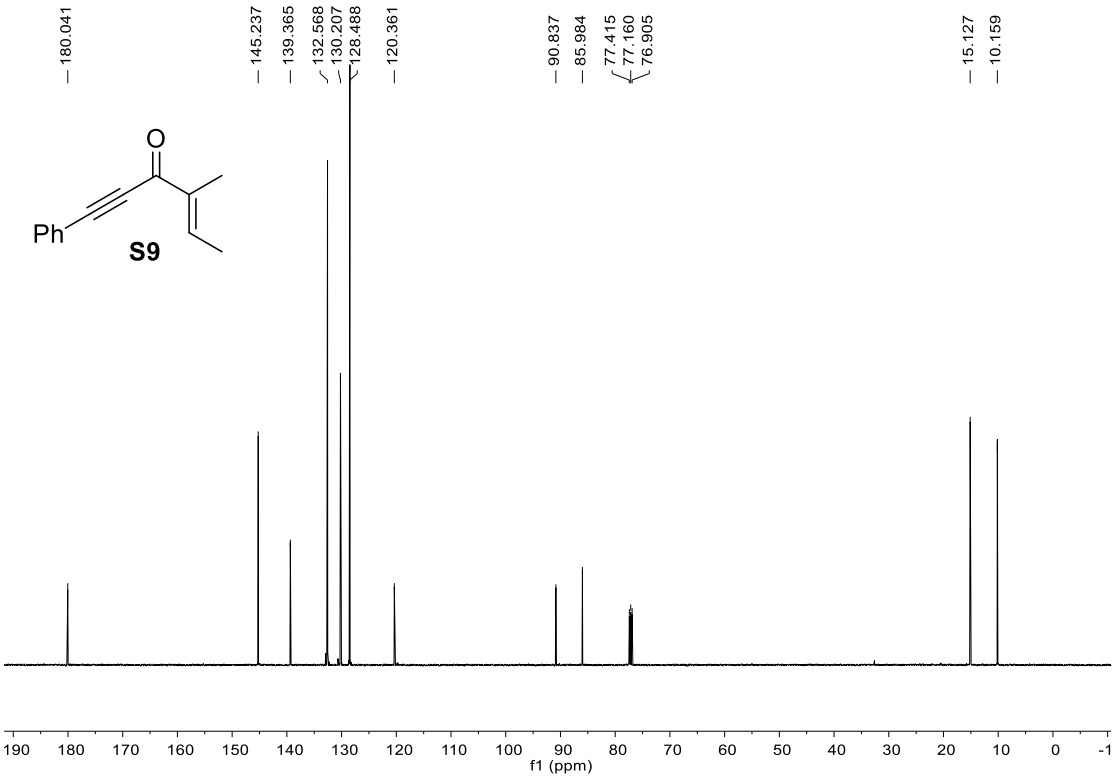
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S8**



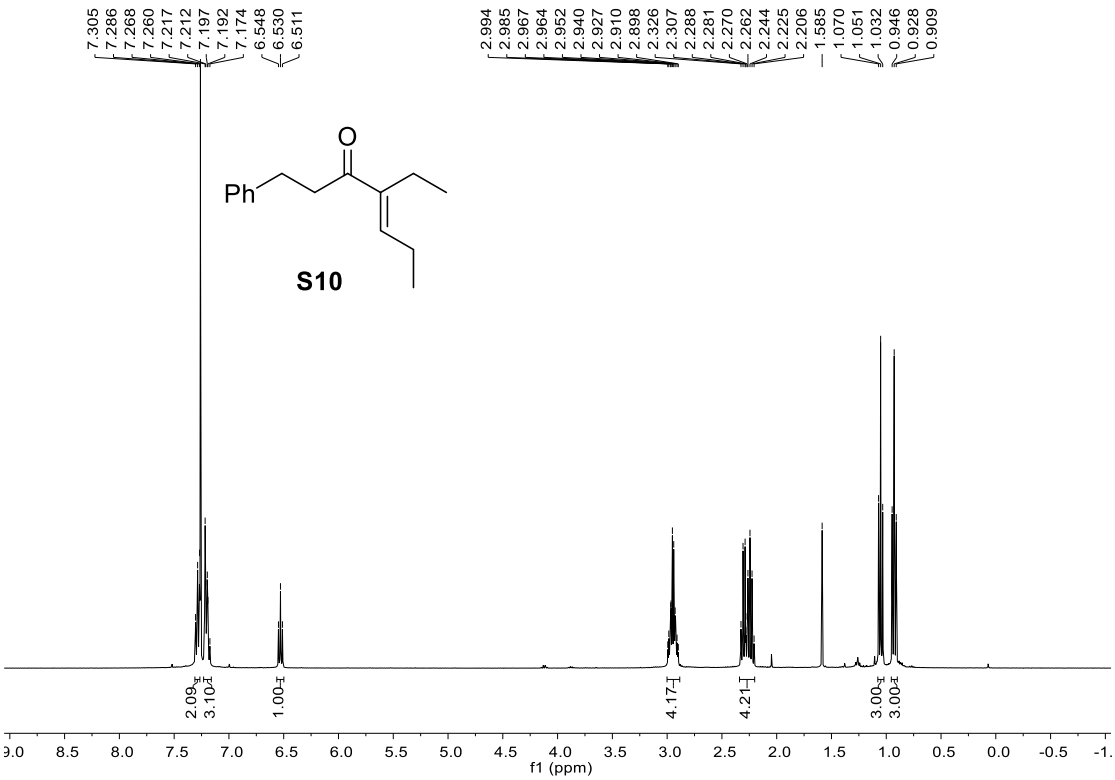
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S8**



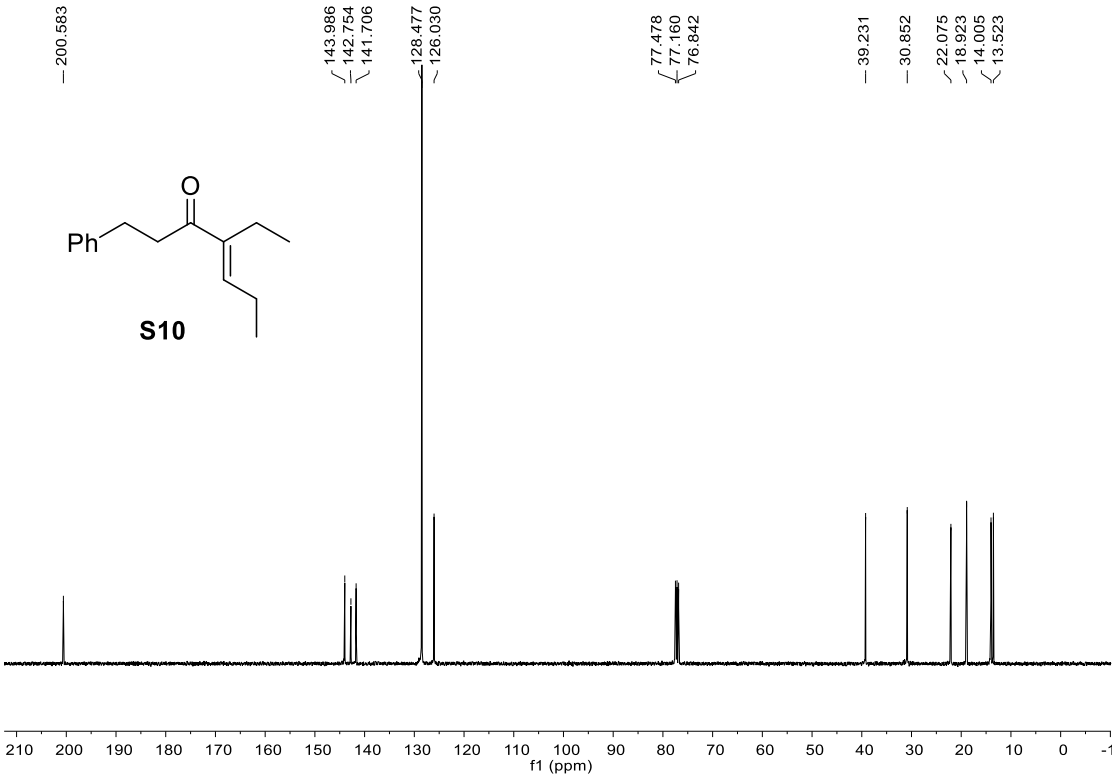
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S9**



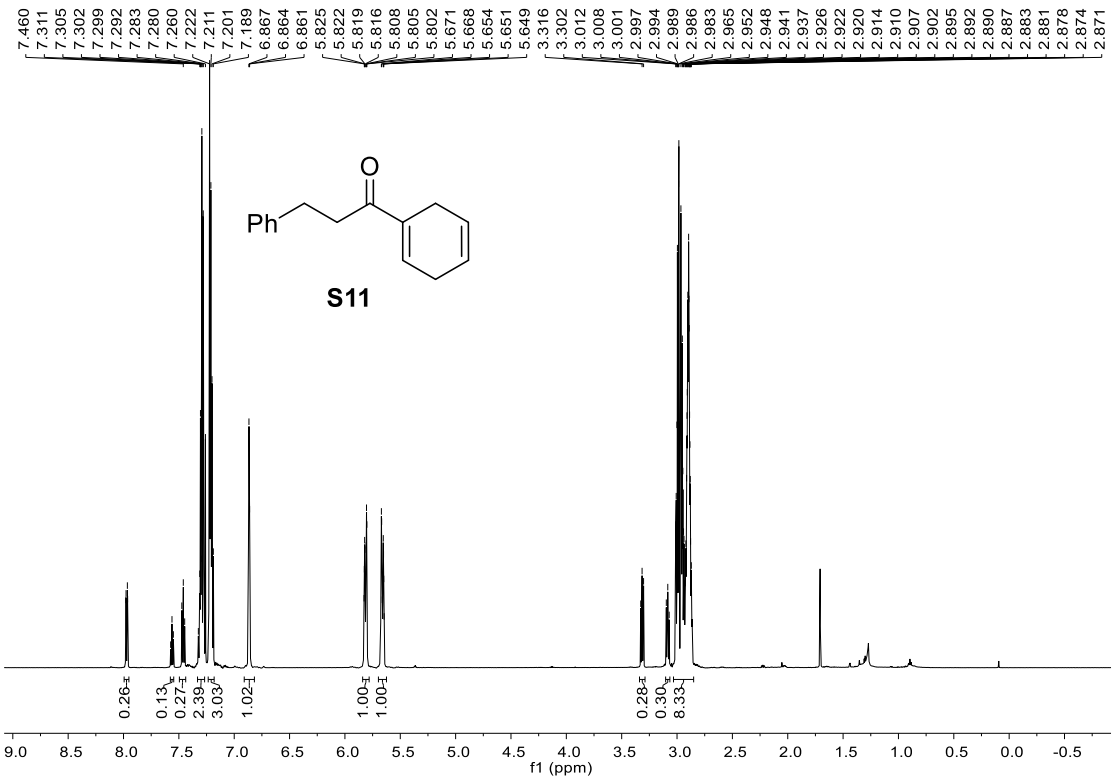
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S9**



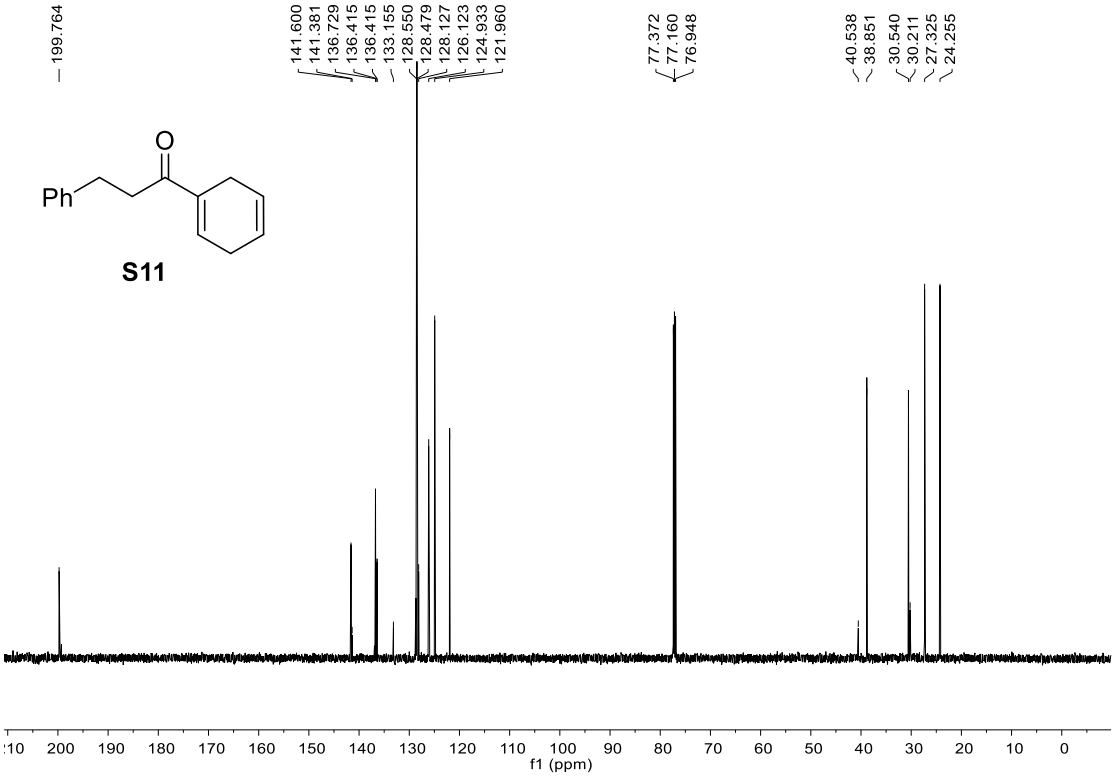
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S10**



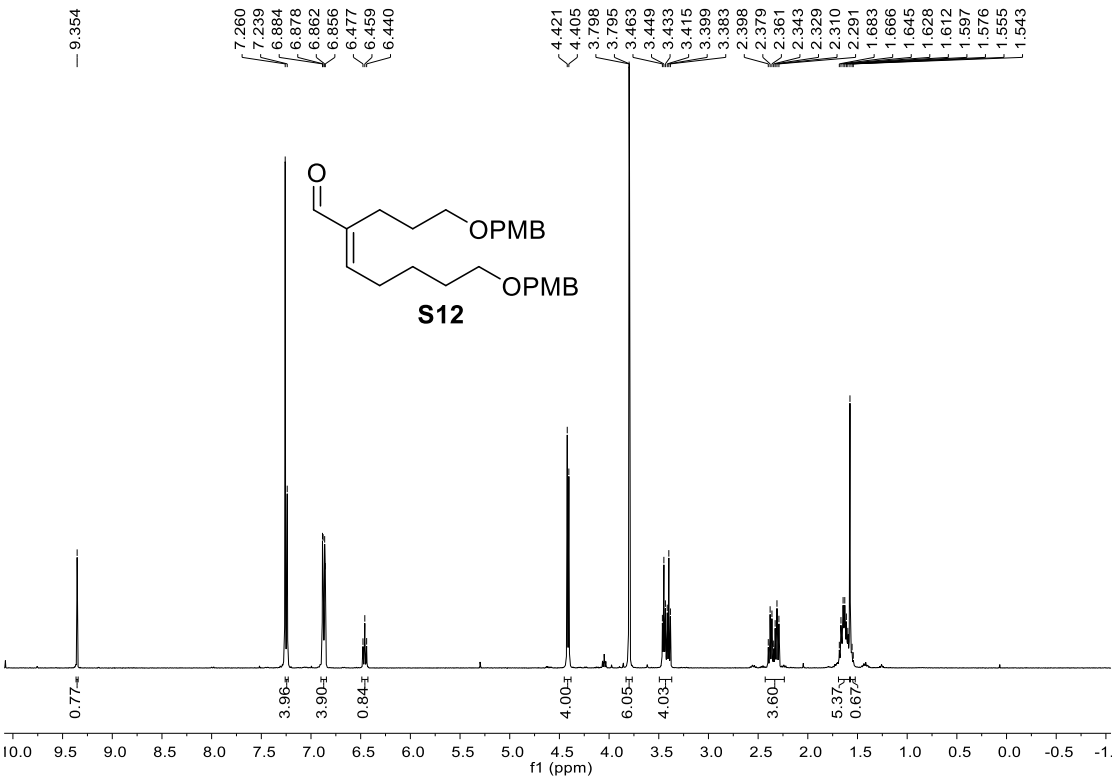
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S10**



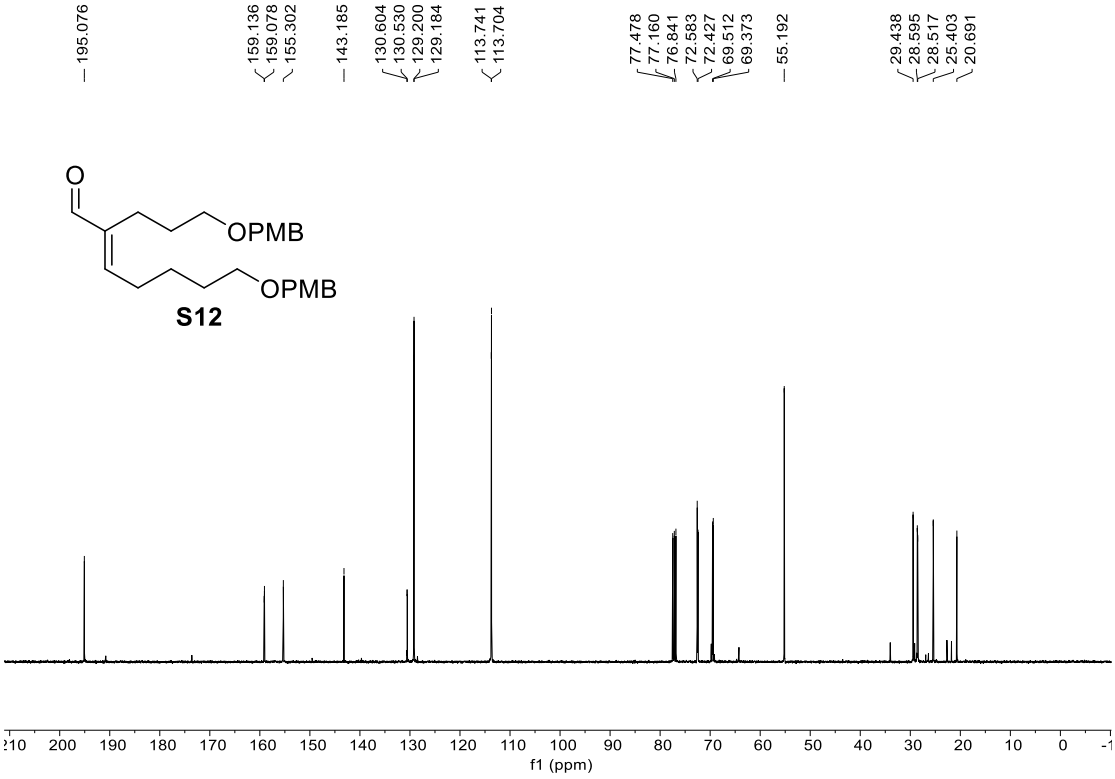
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **S11** (containing inseparable oxidized impurity: 1,3-diphenylpropan-1-one)



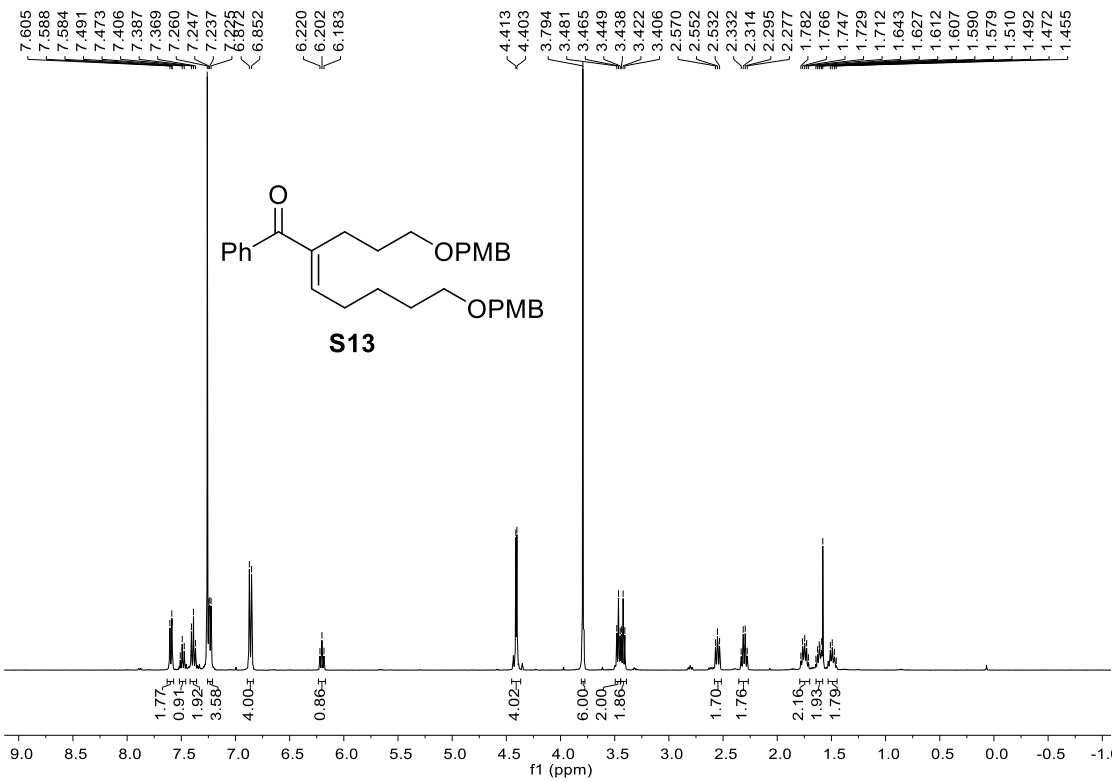
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **S11** (containing inseparable oxidized impurity: 1,3-diphenylpropan-1-one)



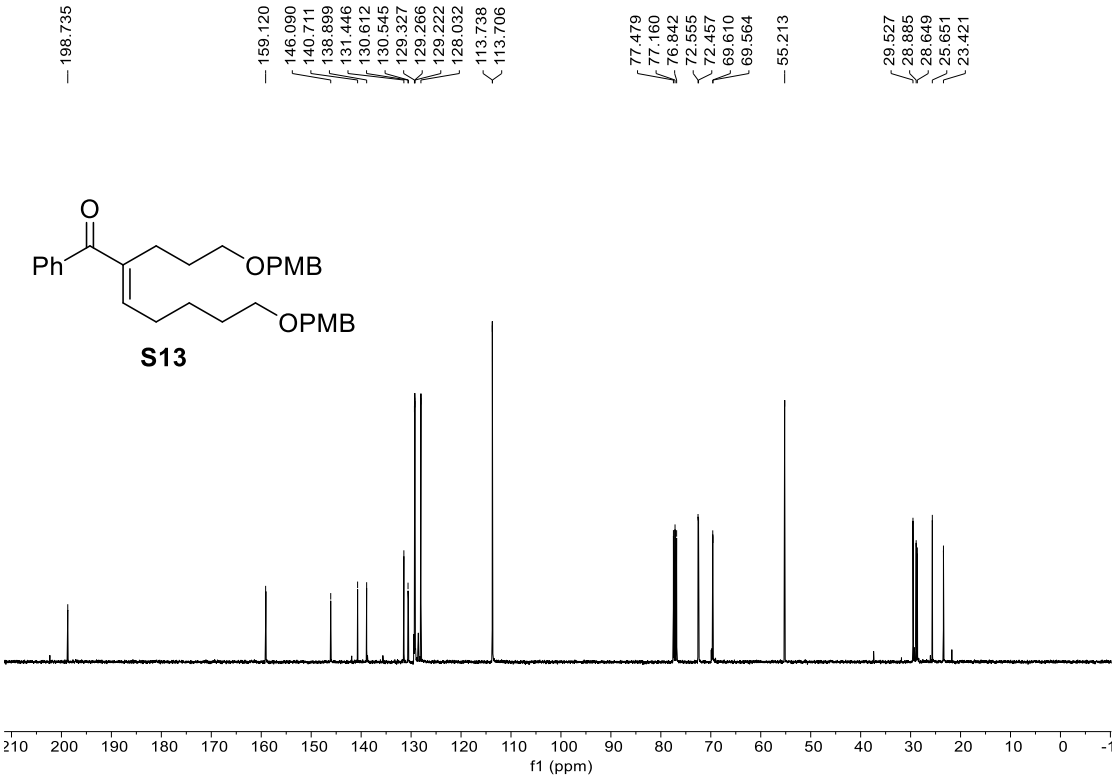
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S12**



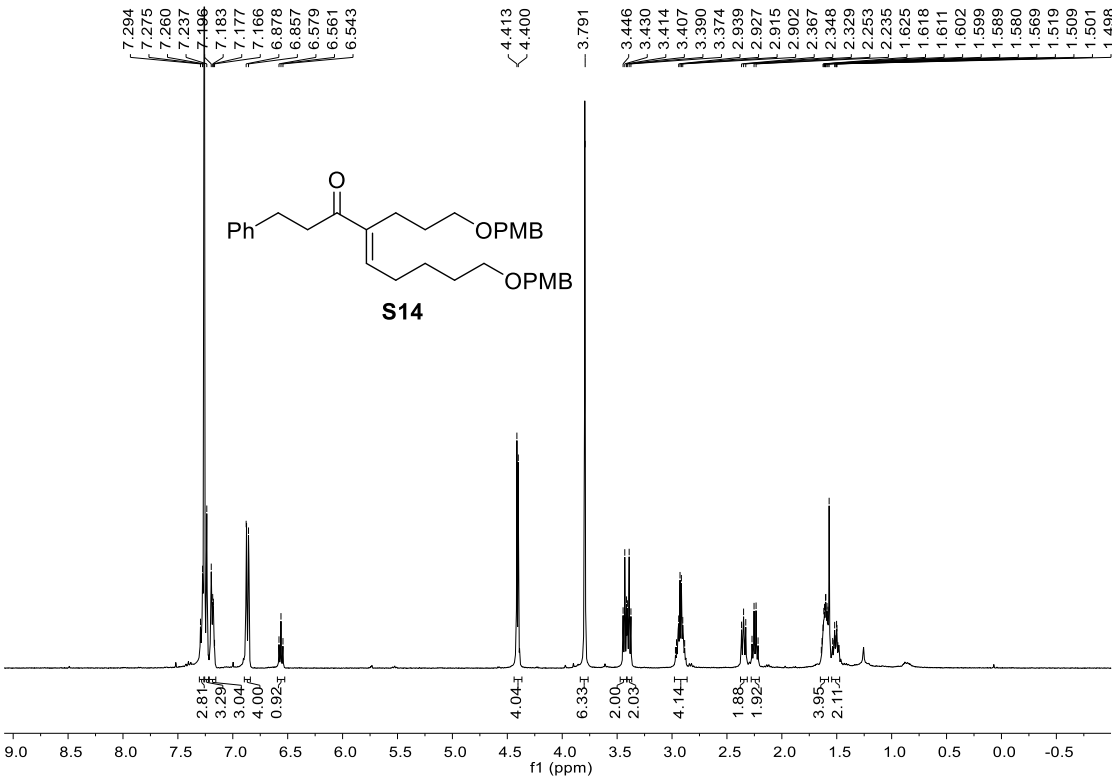
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S12**



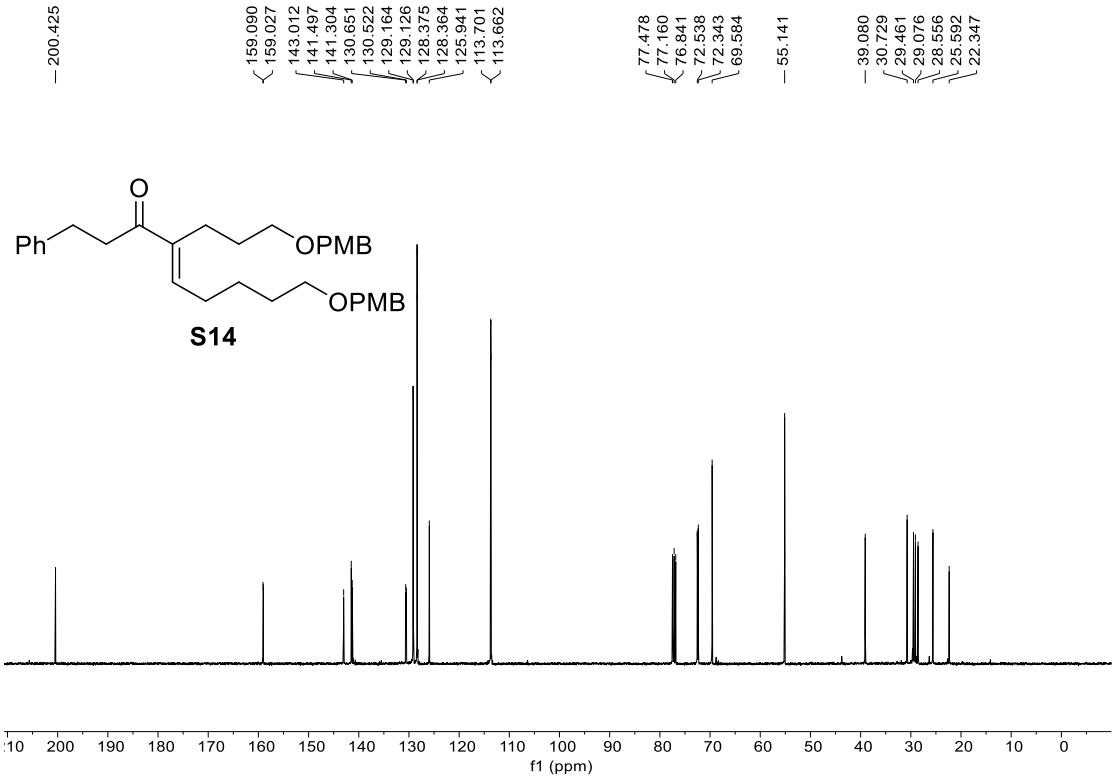
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S13**



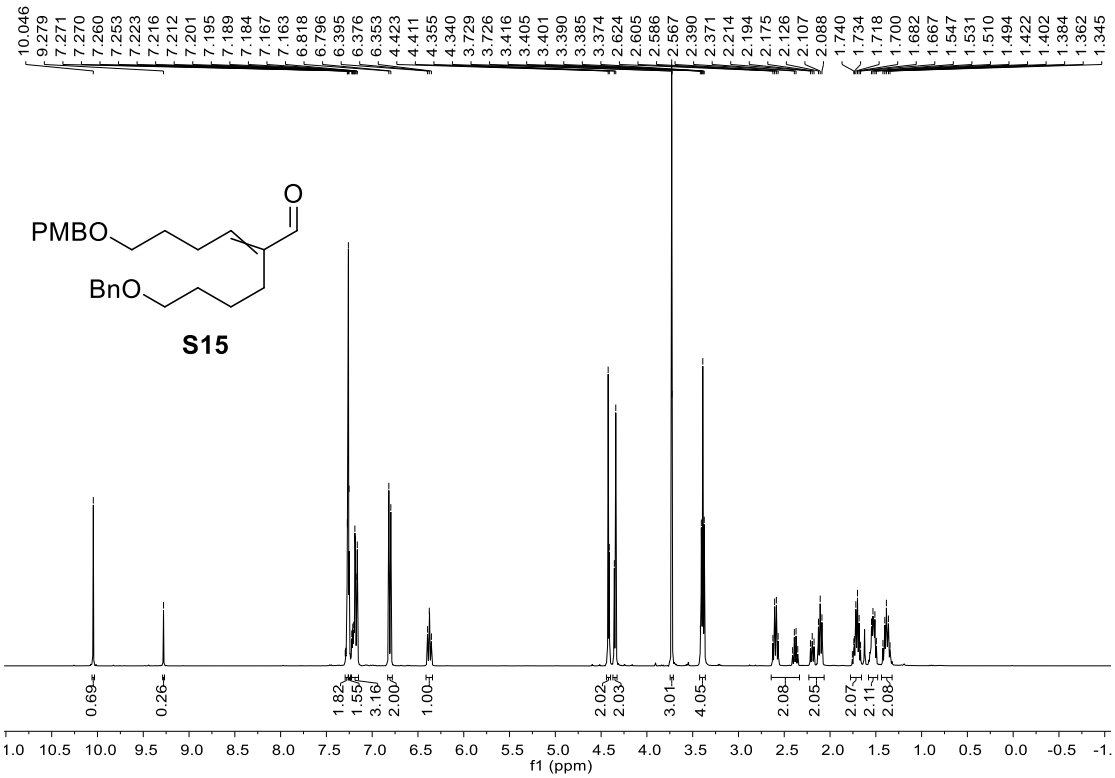
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S13**



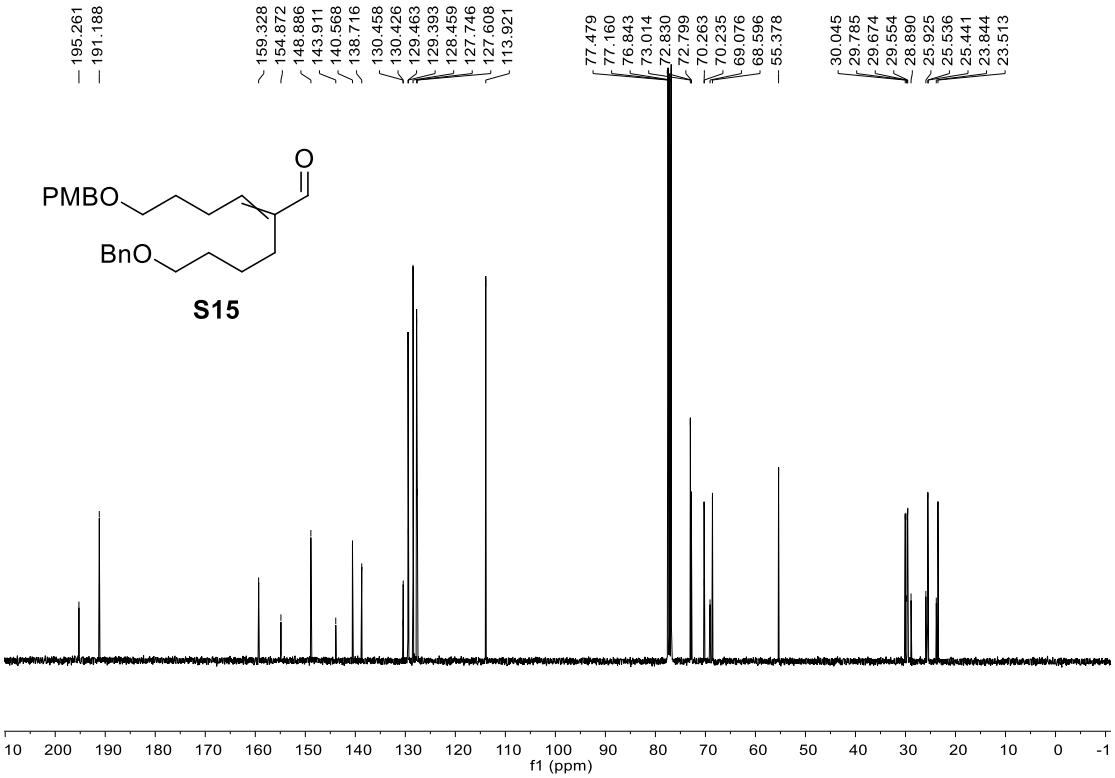
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S14**



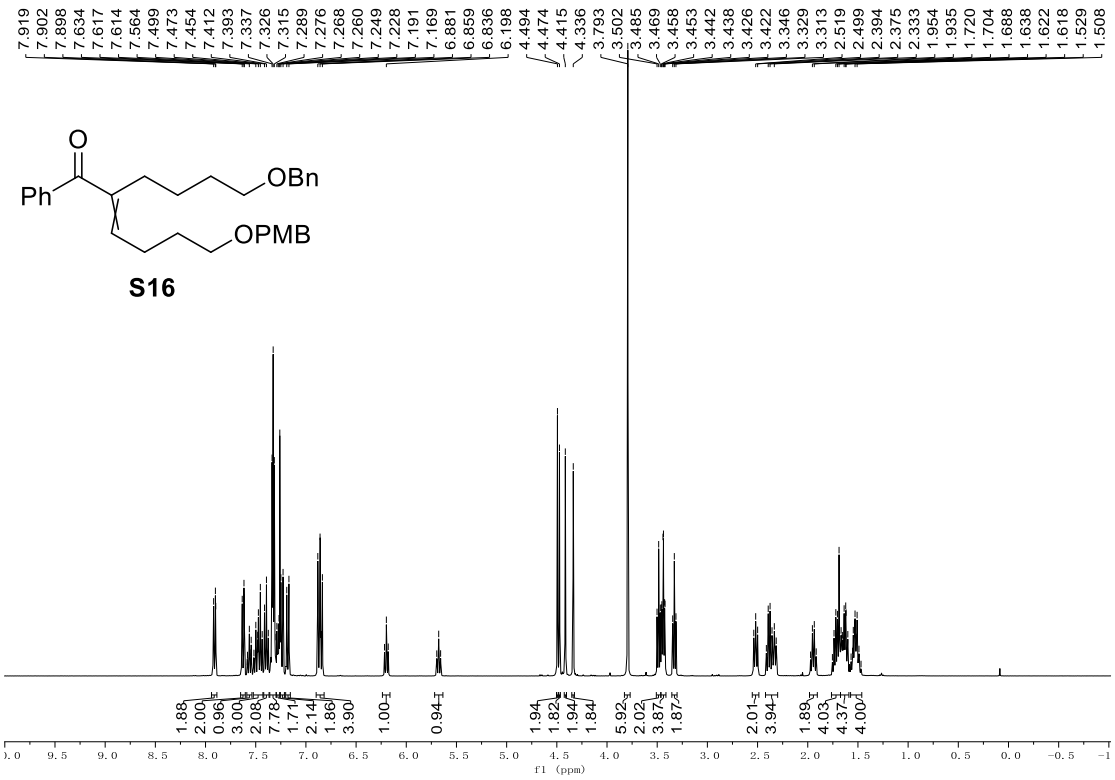
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S14**



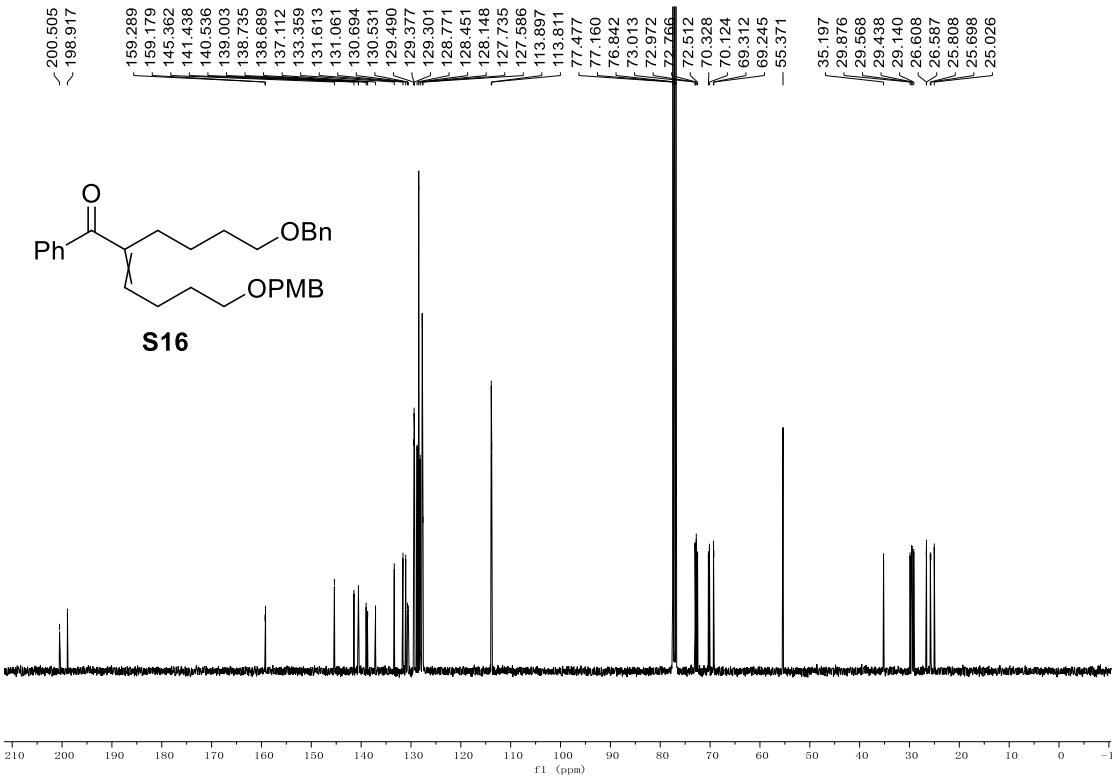
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S15** (mixture of *Z/E* isomers)



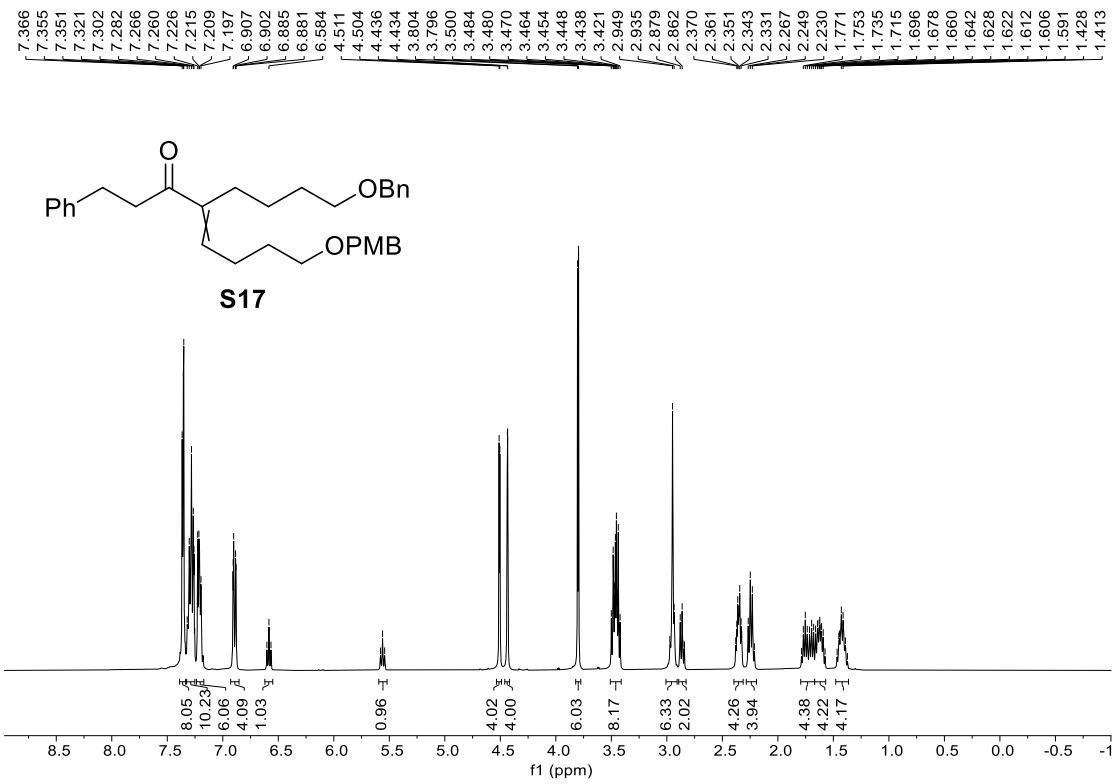
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S15** (mixture of *Z/E* isomers)



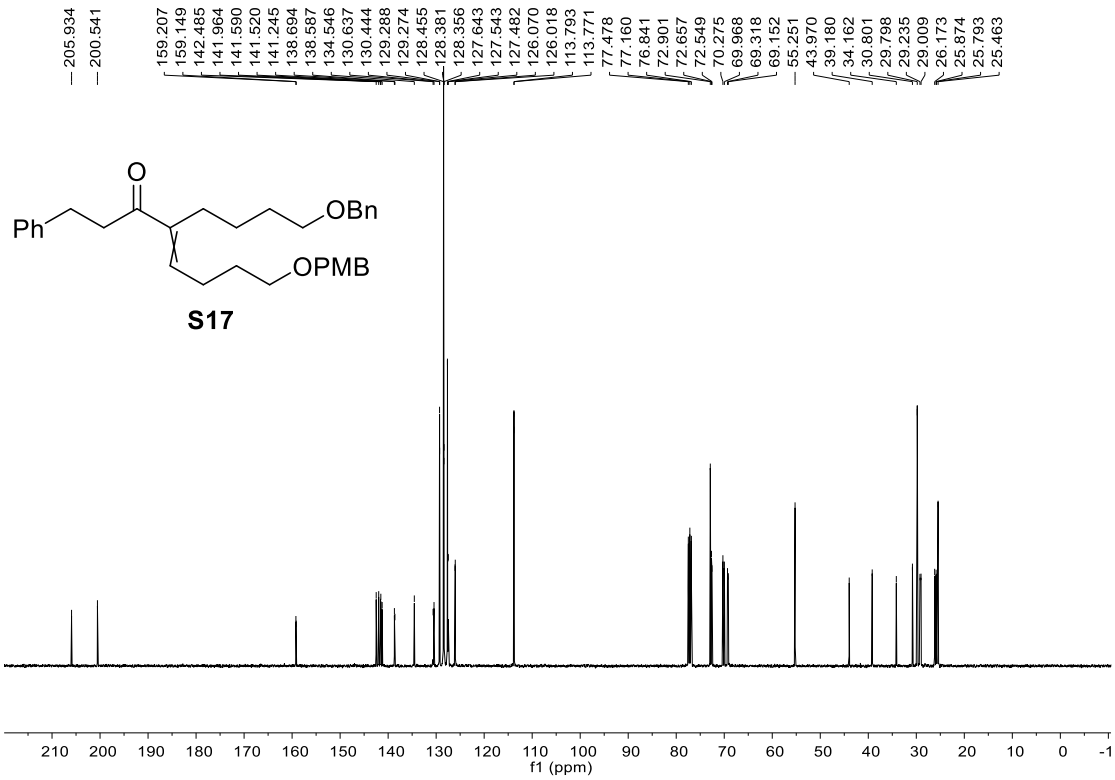
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S16** (mixture of *Z/E* isomers)



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S16** (~1:1 mixture of *Z/E* isomers)

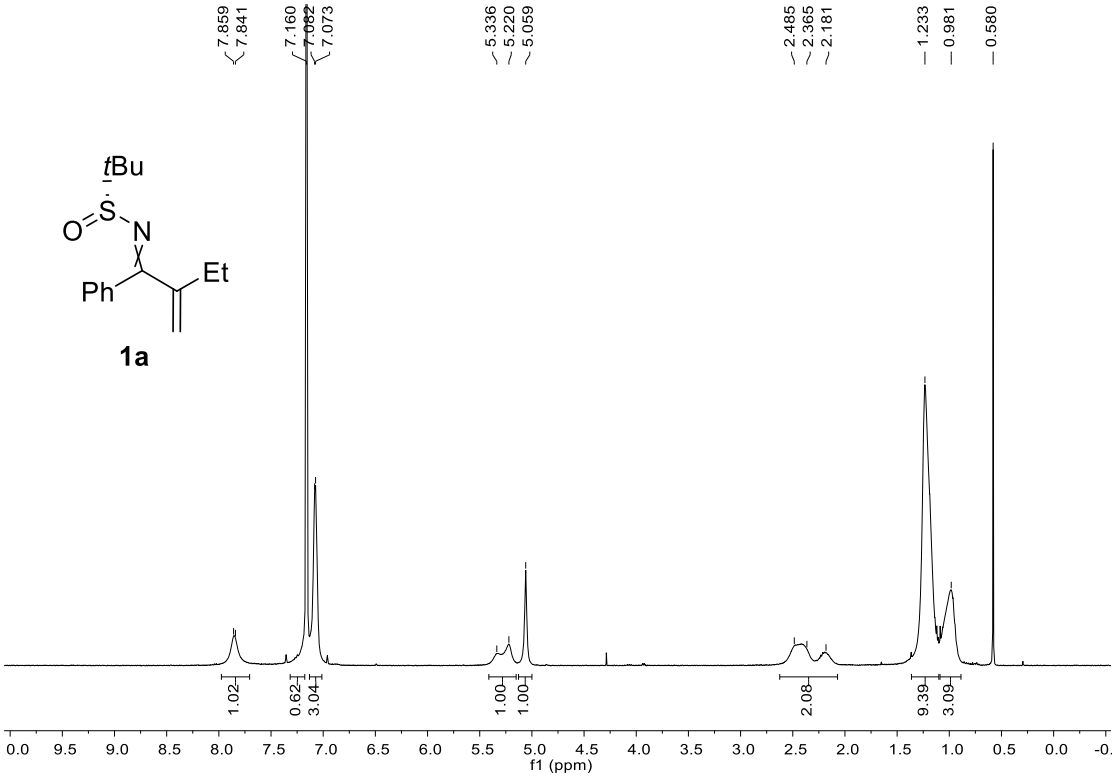


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S17** (mixture of *Z/E* isomers)

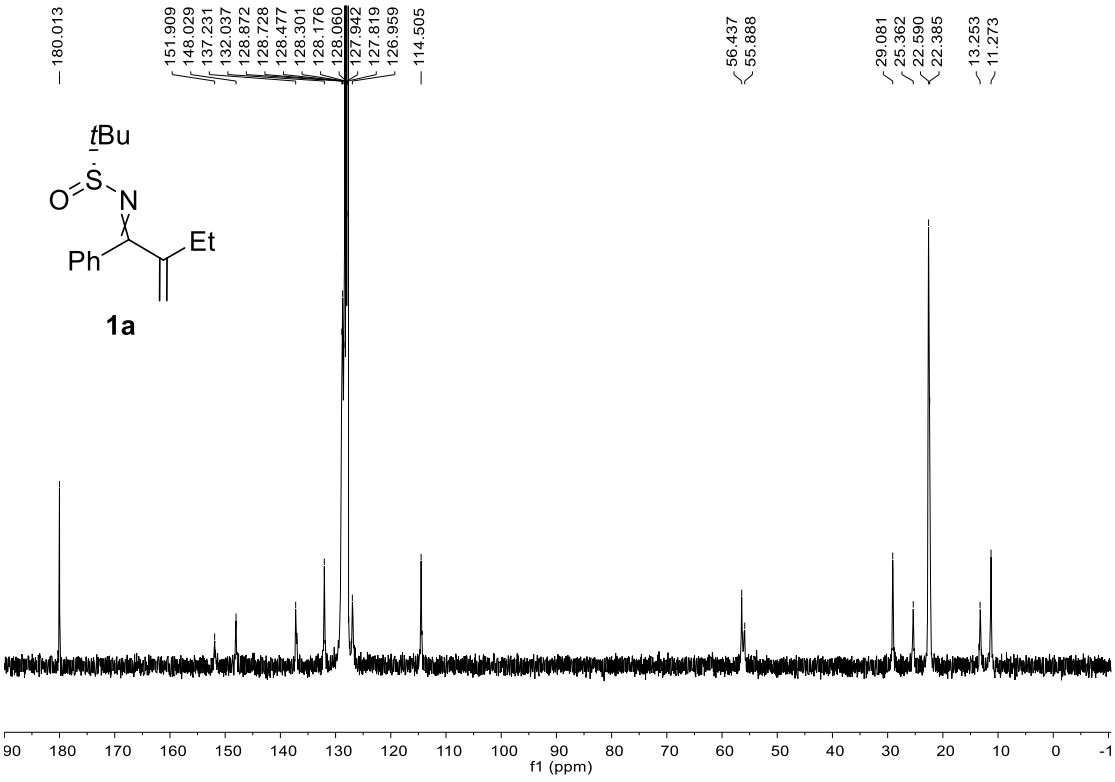


^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S17** (mixture of *Z/E* isomers)

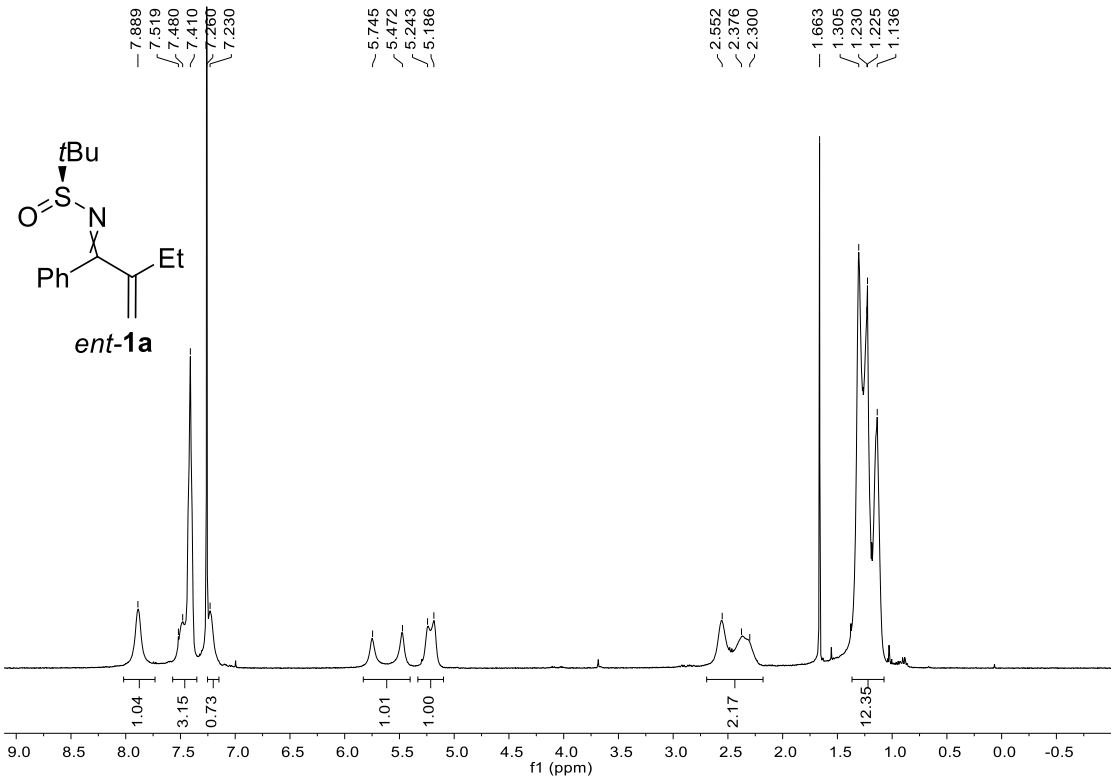
^{1}H and ^{13}C NMR spectra of α,β-unsaturated *N*-sulfinyl ketimines



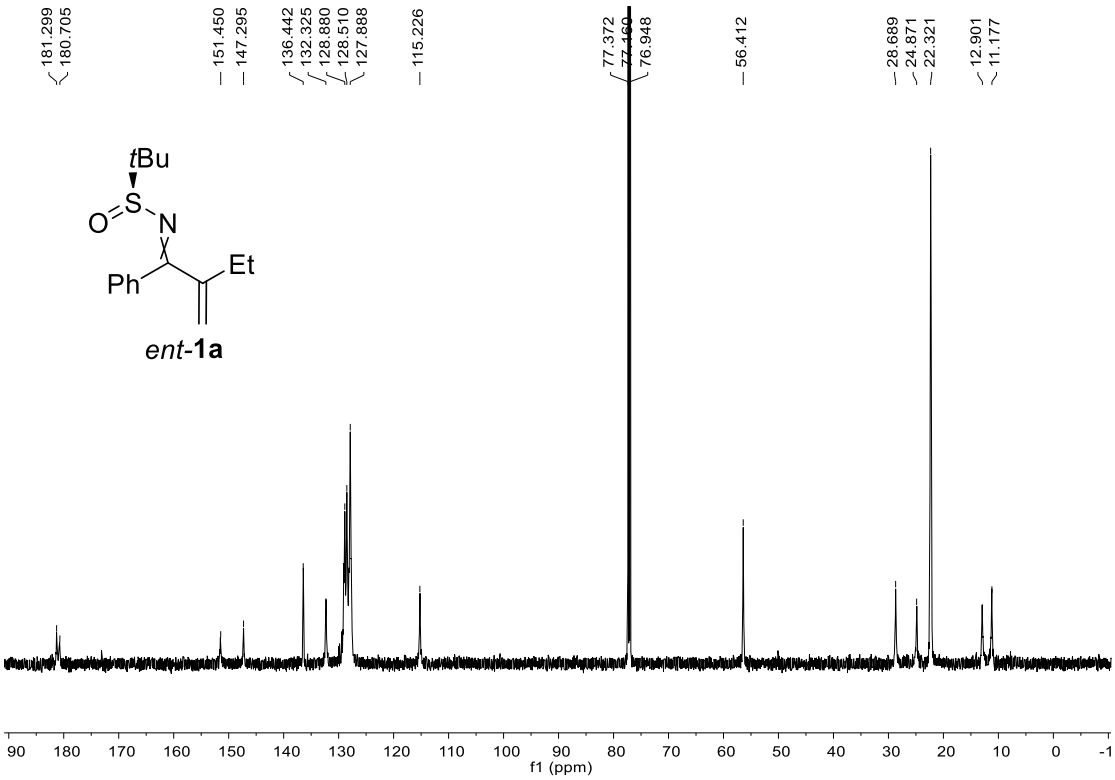
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **1a** (mixture of imino *Z/E* isomers)



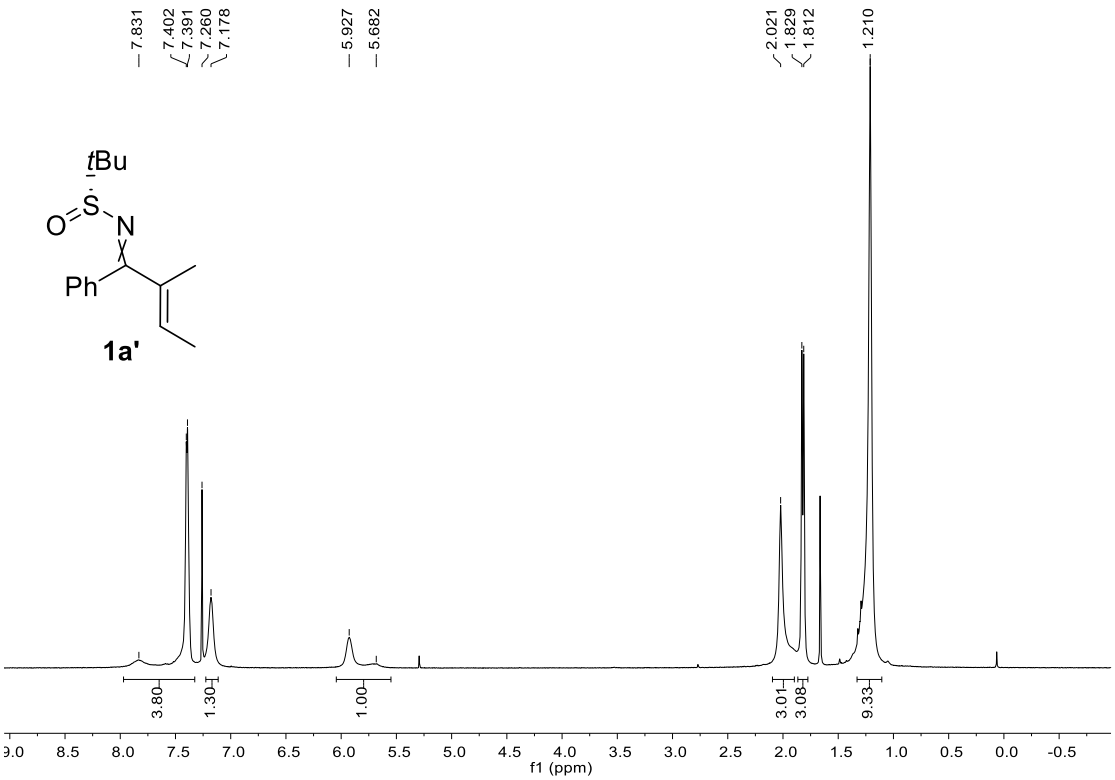
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **1a** (mixture of imino *Z/E* isomers)



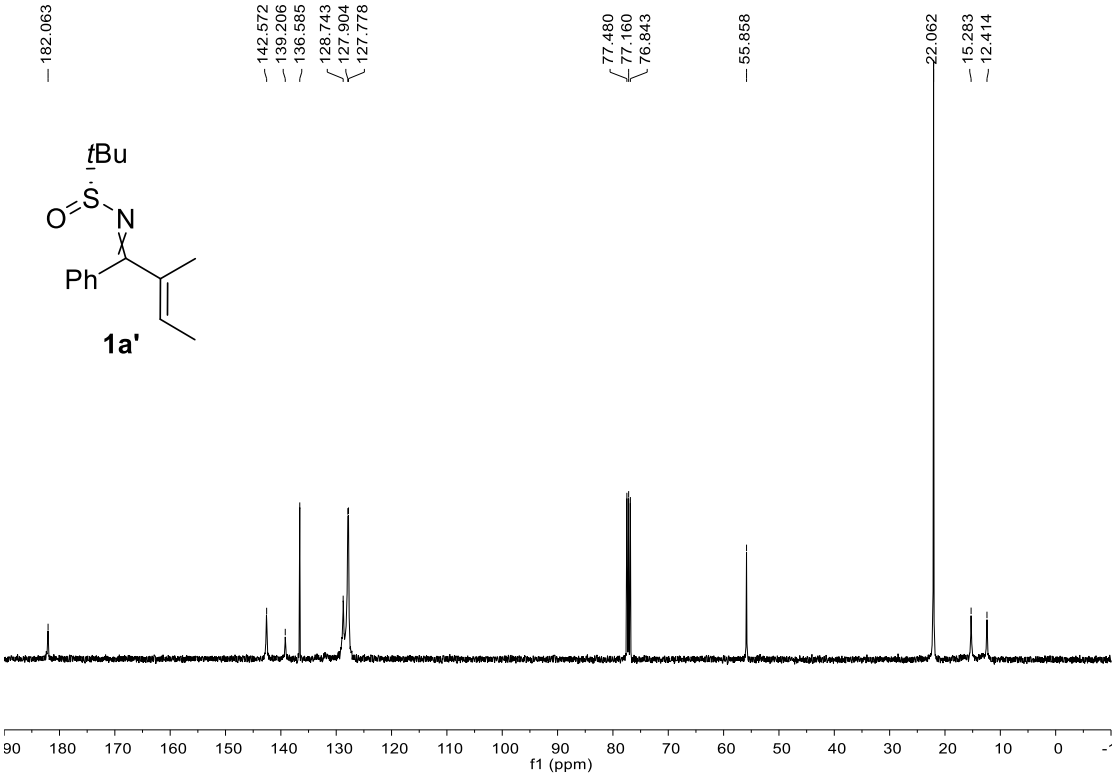
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *ent*-**1a** (mixture of imino *Z/E* isomers)



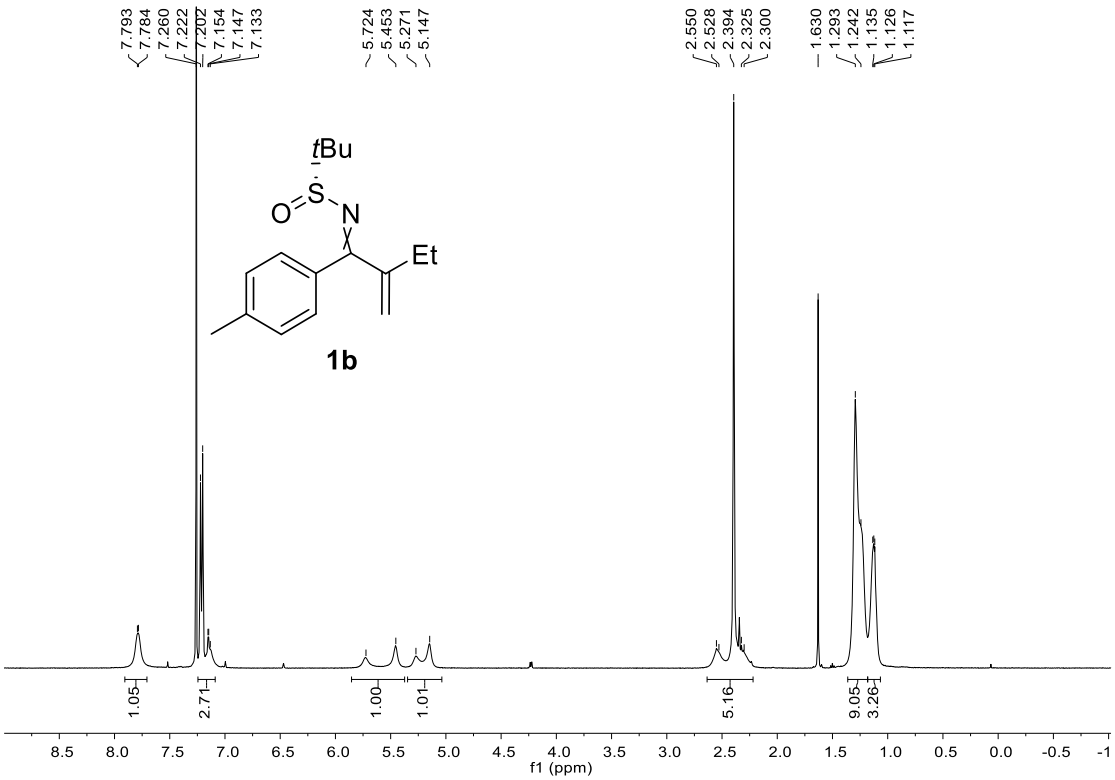
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of *ent*-**1a** (mixture of imino *Z/E* isomers)



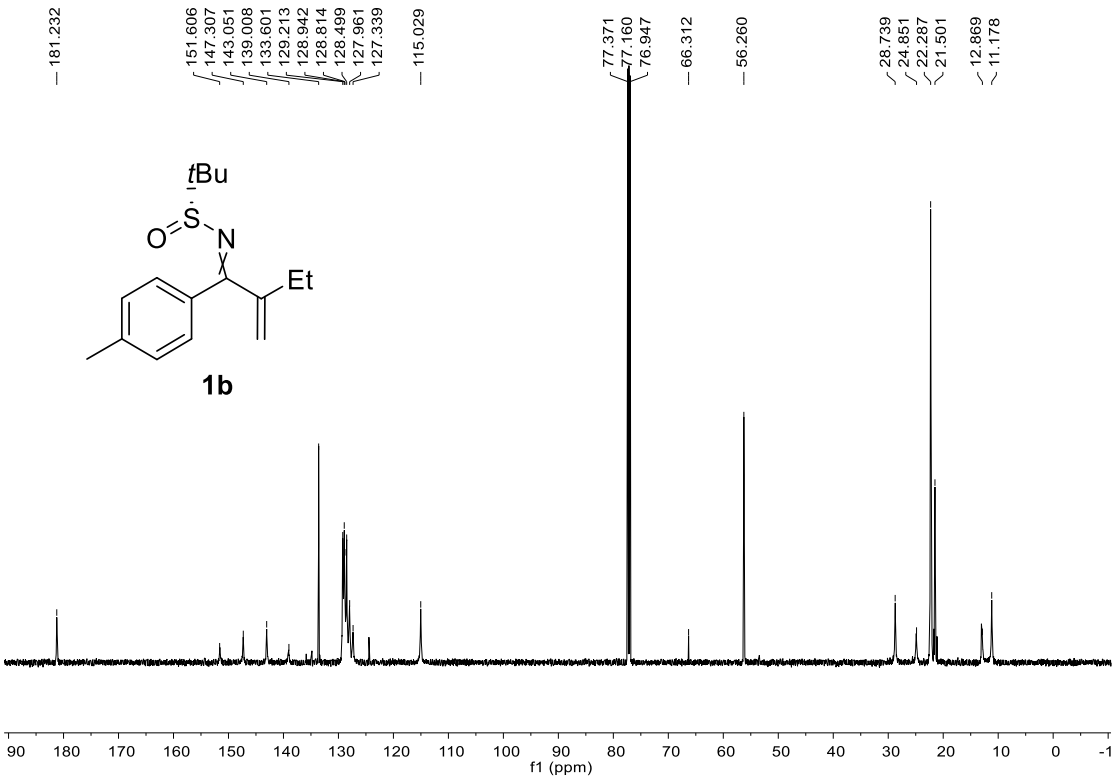
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1a′** (mixture of imino *Z/E* isomers)



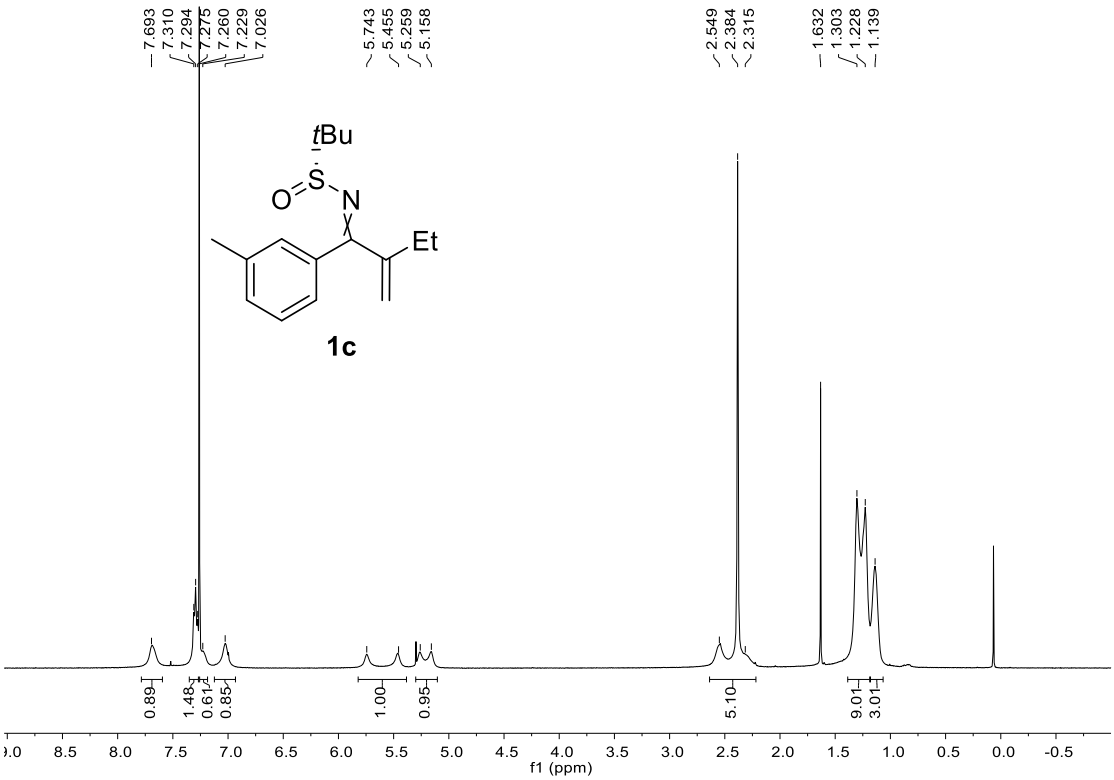
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1a′** (mixture of imino *Z/E* isomers)



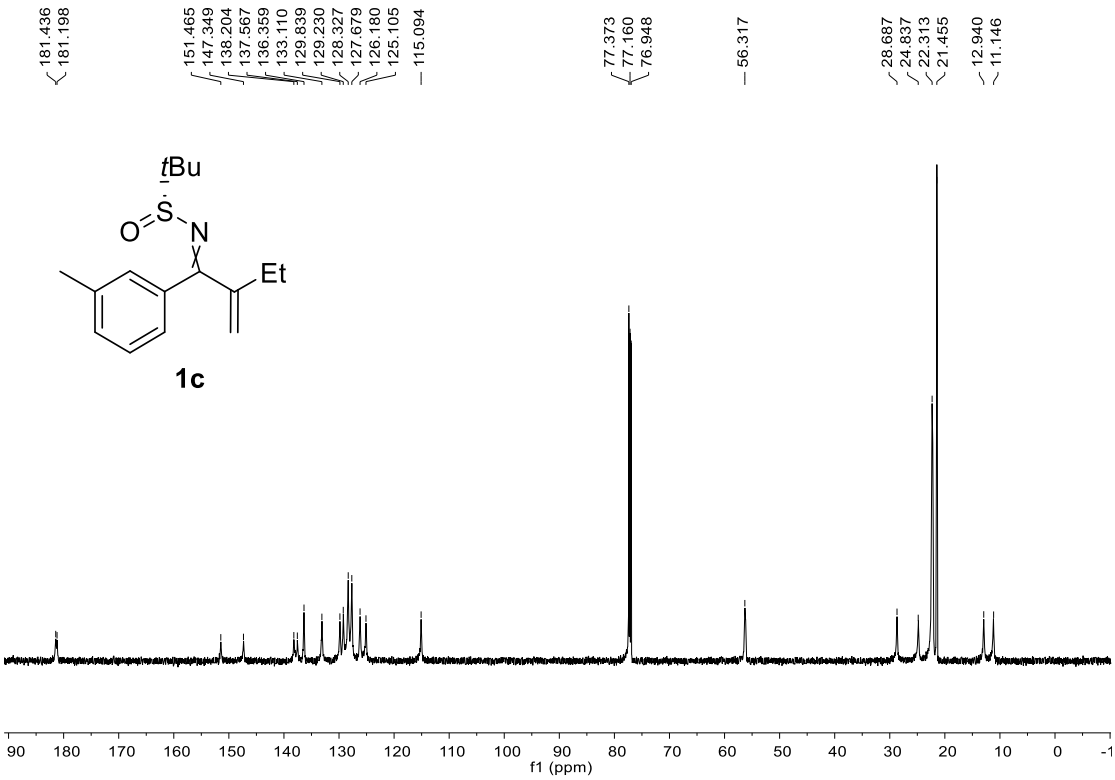
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1b** (mixture of imino *Z/E* isomers)



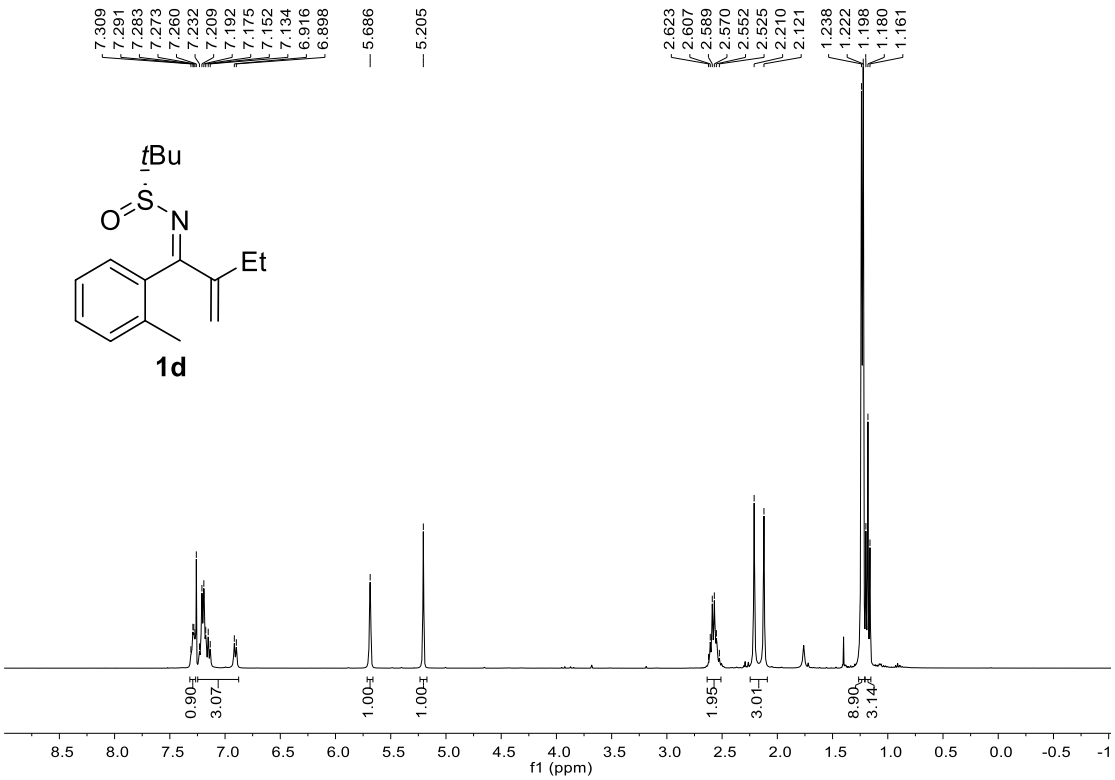
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **1b** (mixture of imino *Z/E* isomers)



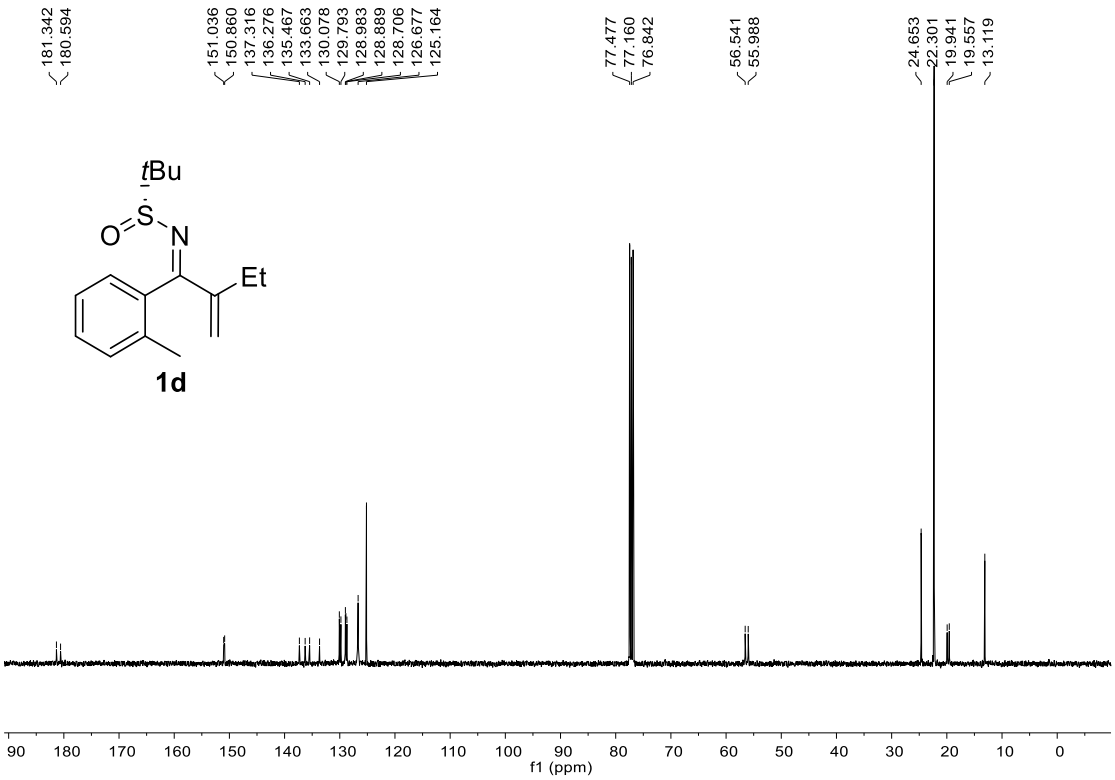
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1c** (mixture of imino *Z/E* isomers)



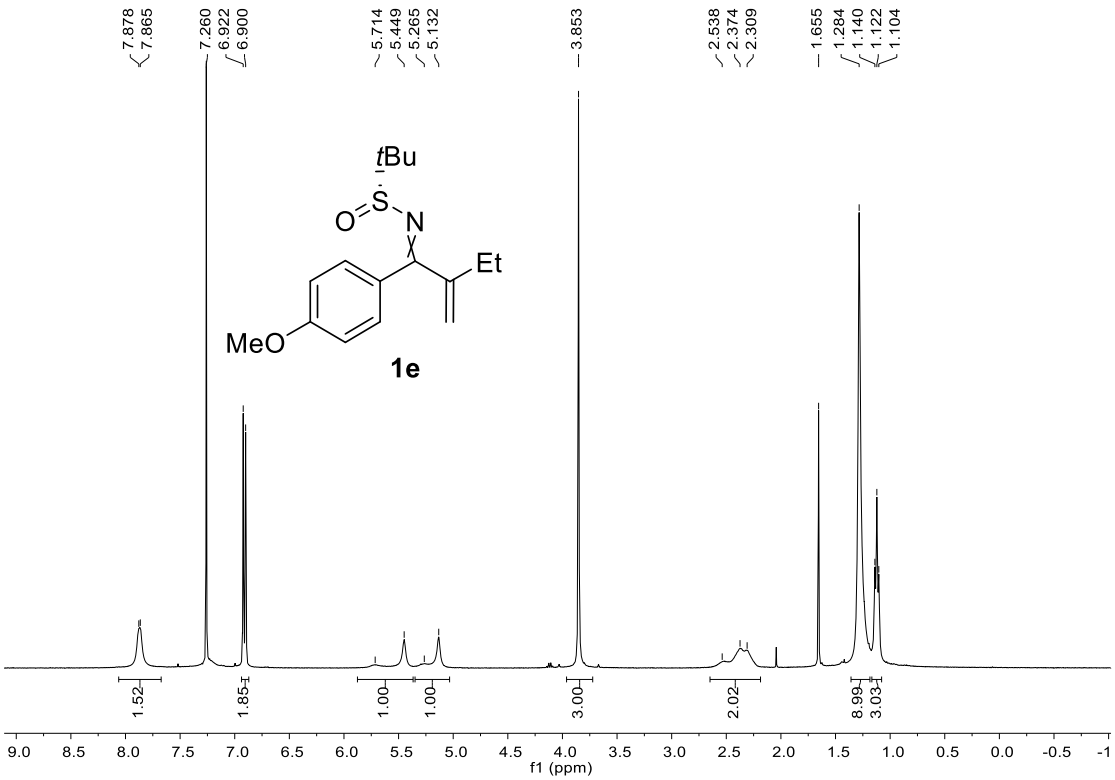
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **1c** (mixture of imino *Z/E* isomers)



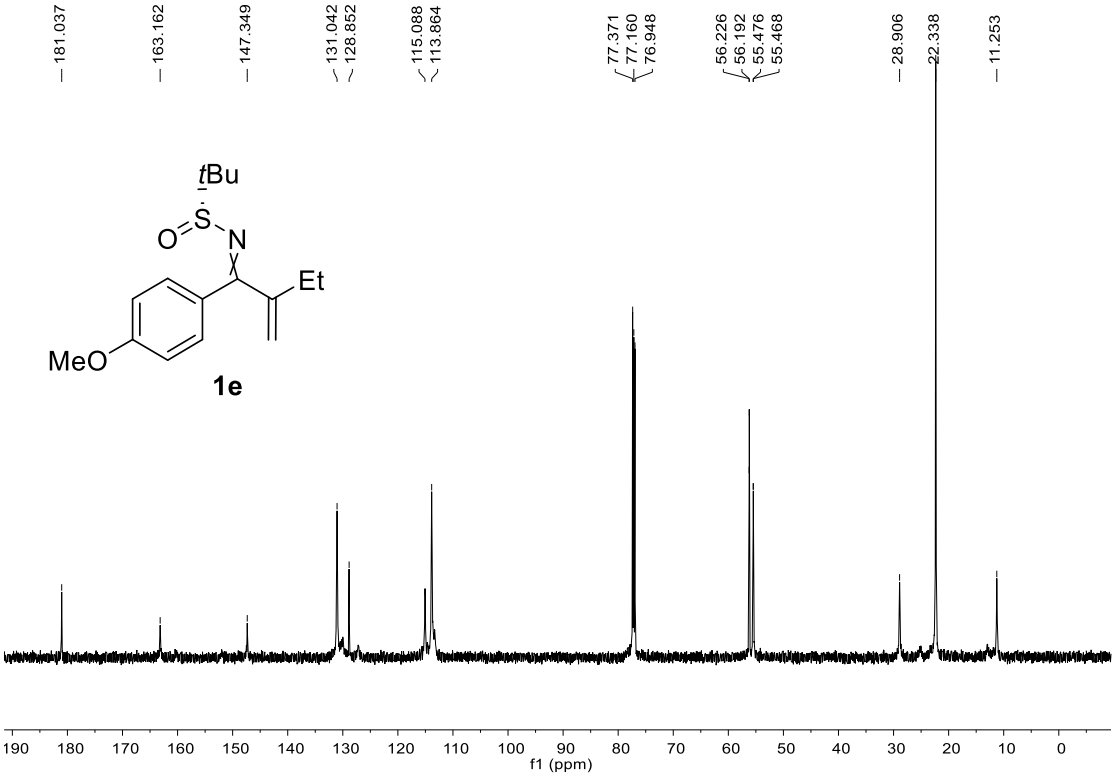
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1d** (mixture of rotamers)



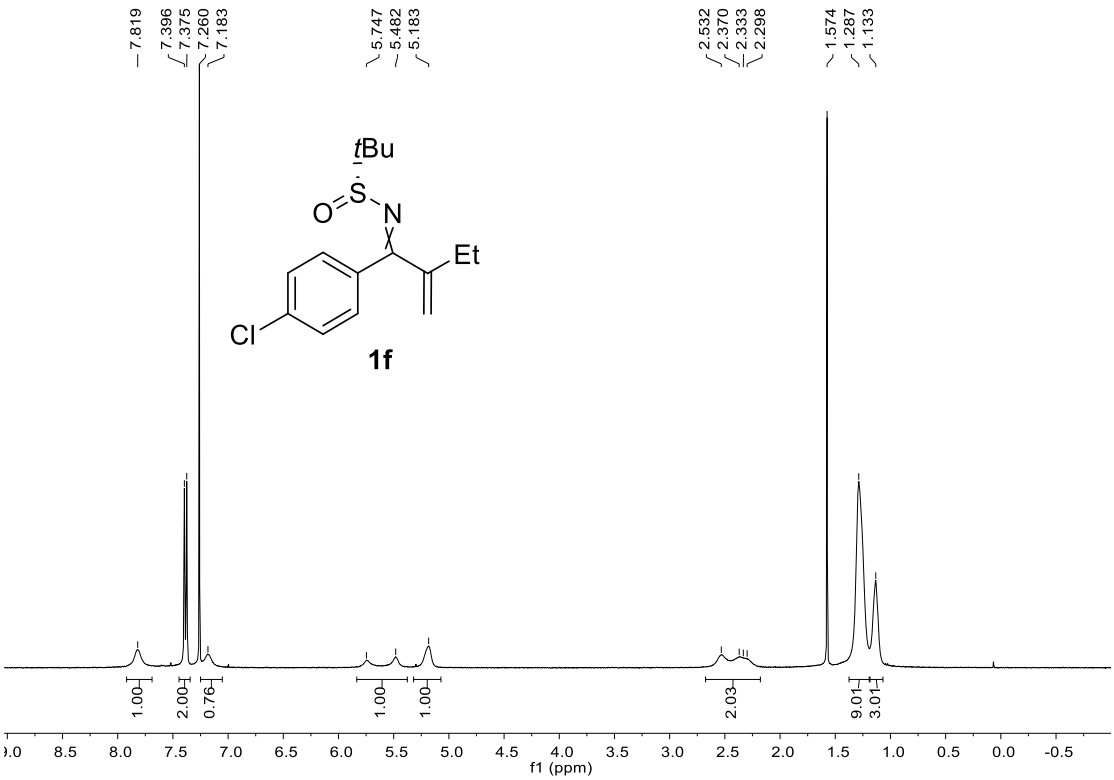
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1d** (mixture of rotamers)



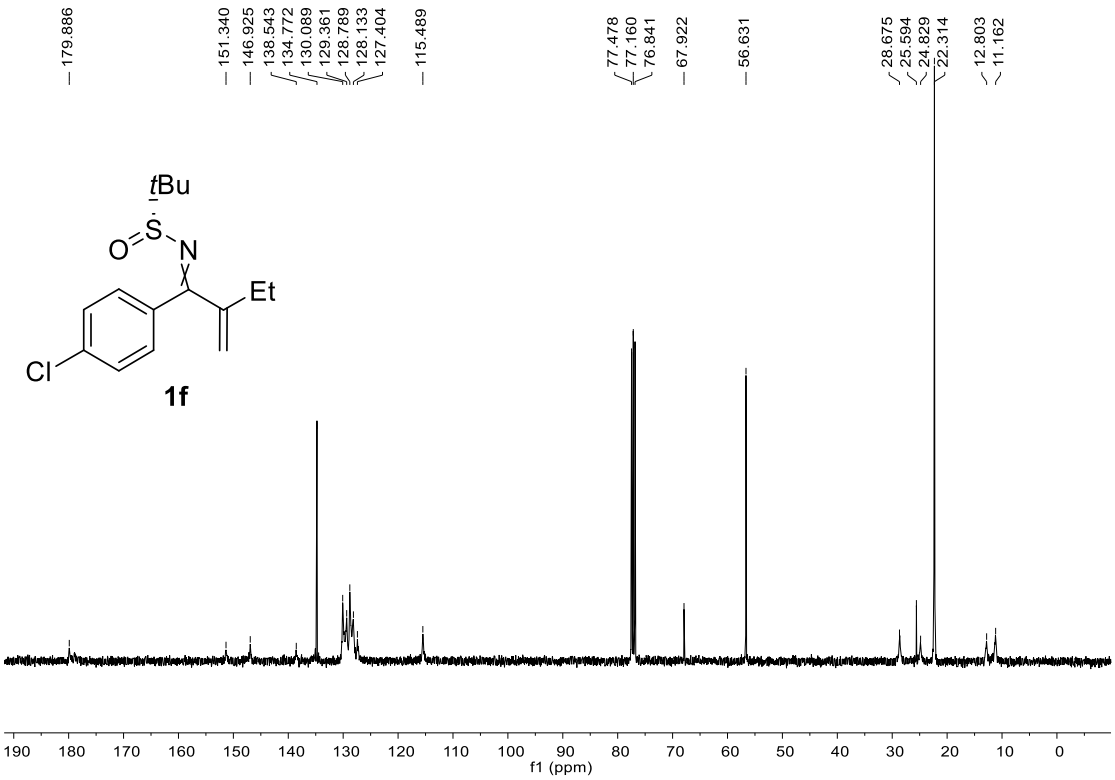
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1e** (mixture of imino *Z/E* isomers)



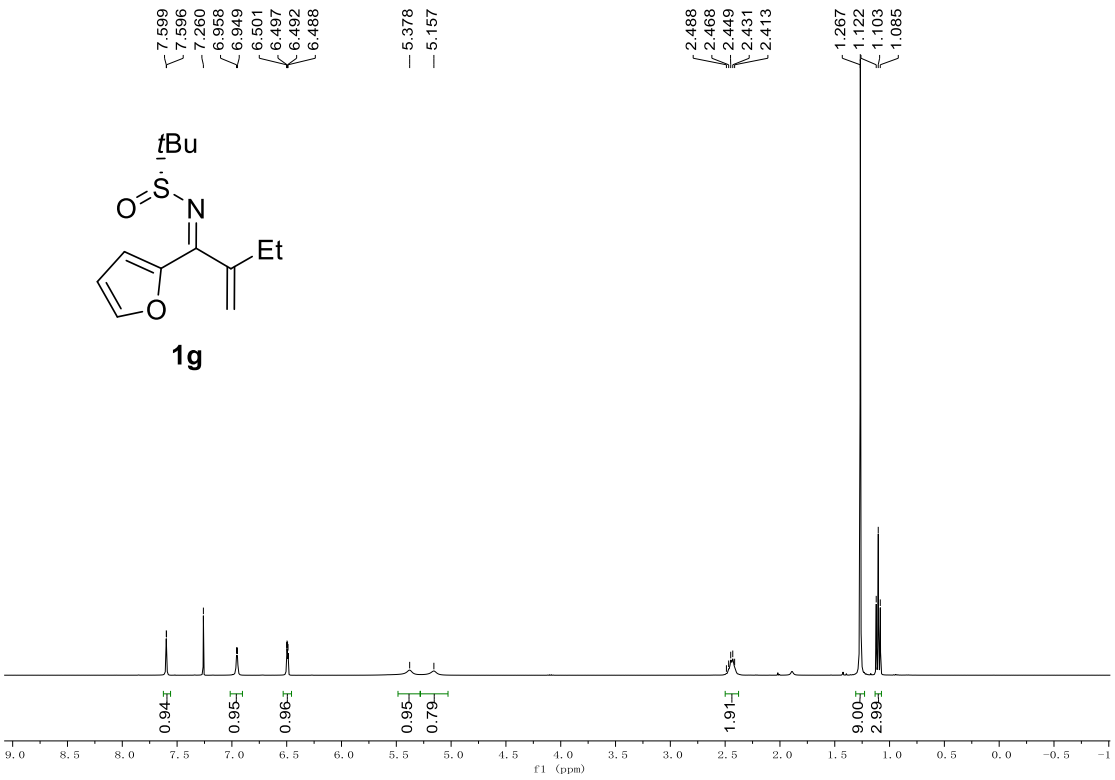
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **1e** (mixture of imino *Z/E* isomers)



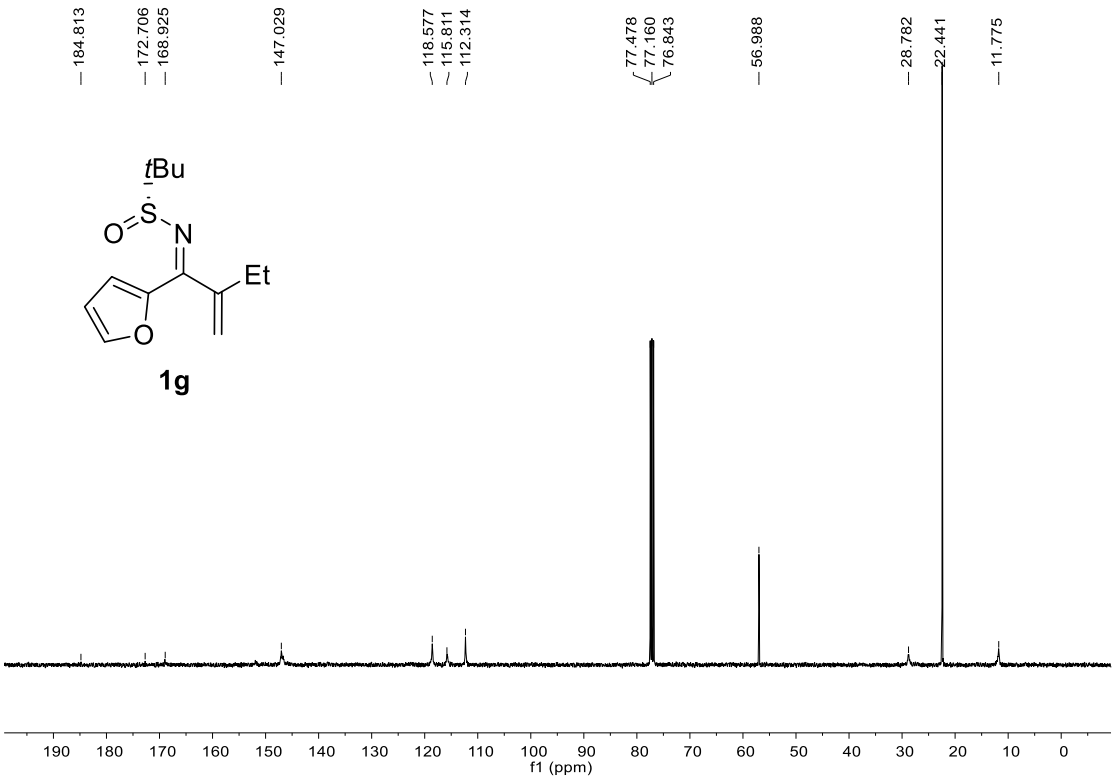
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1f** (mixture of imino *Z/E* isomers)



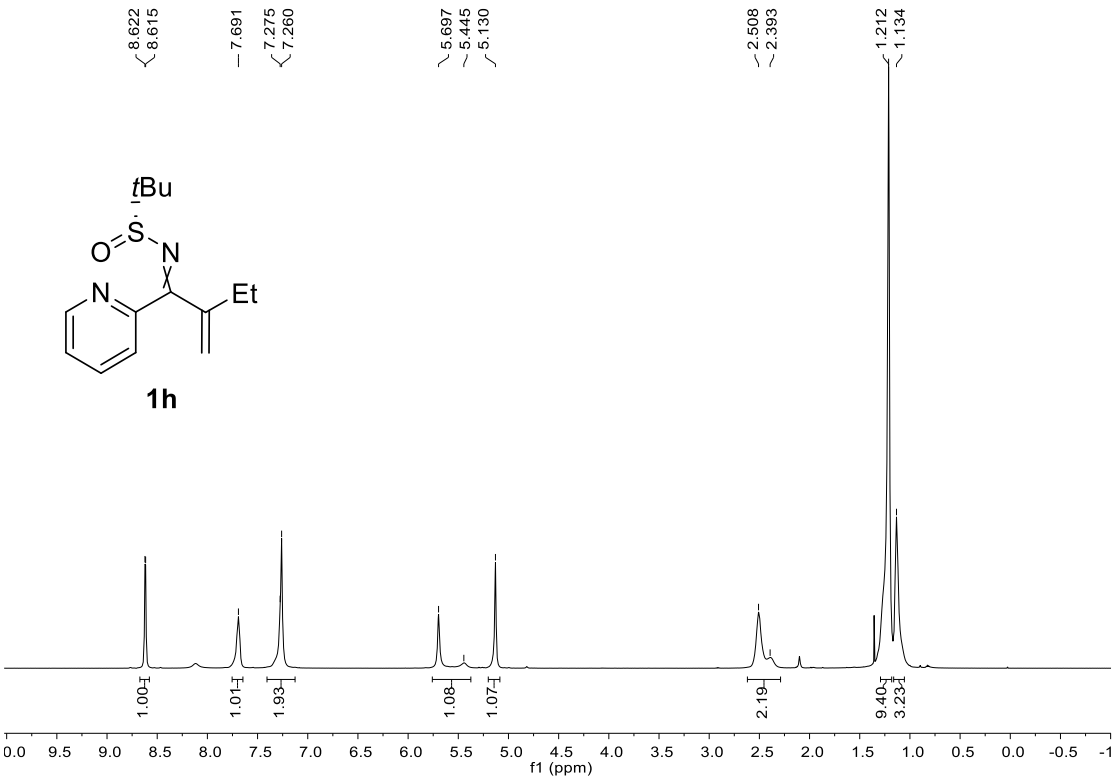
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1f** (mixture of imino *Z/E* isomers)



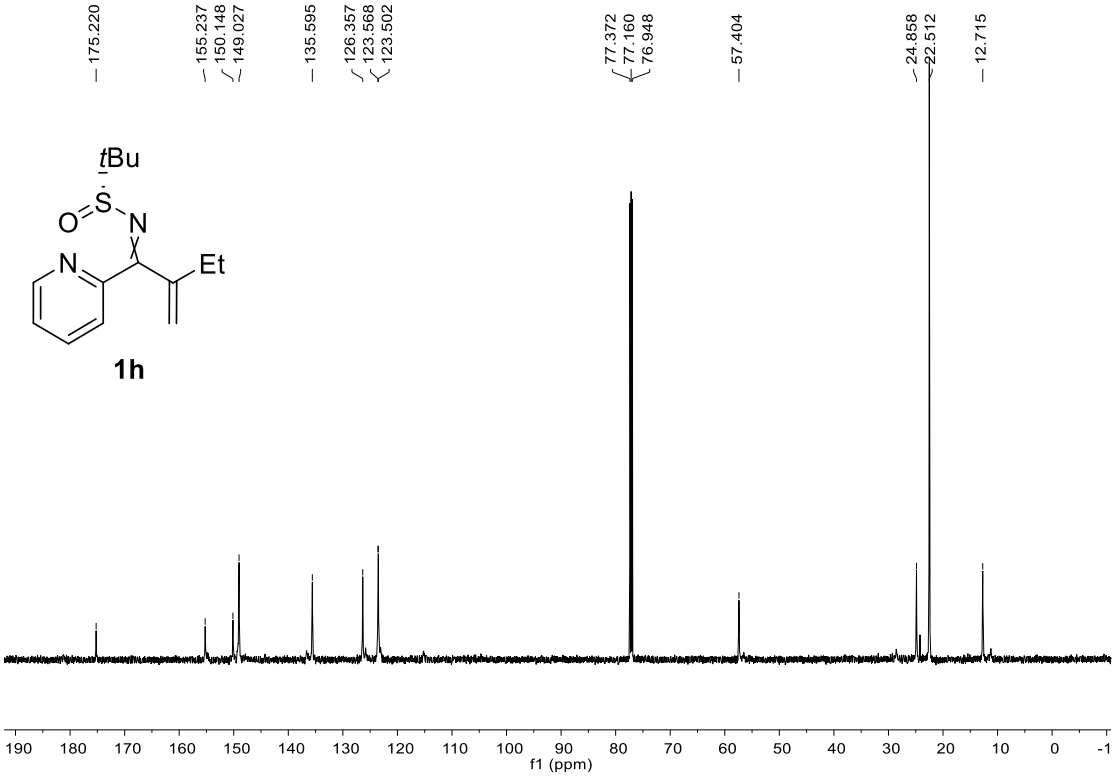
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1g**



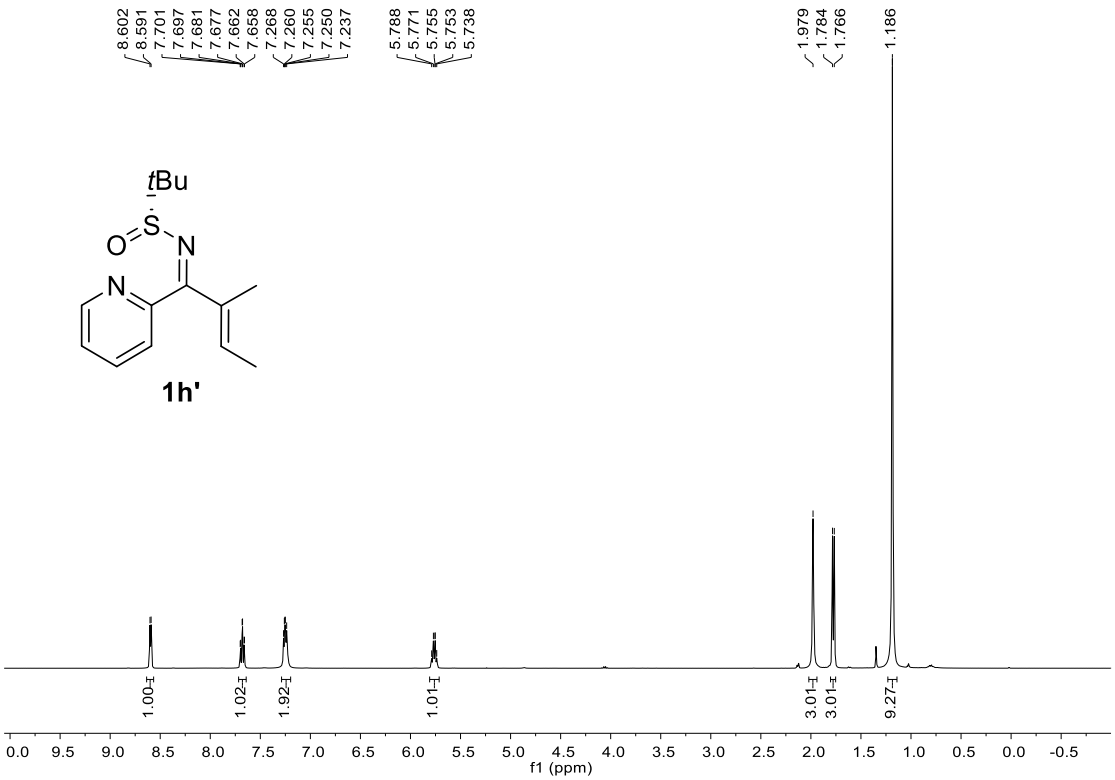
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1g**



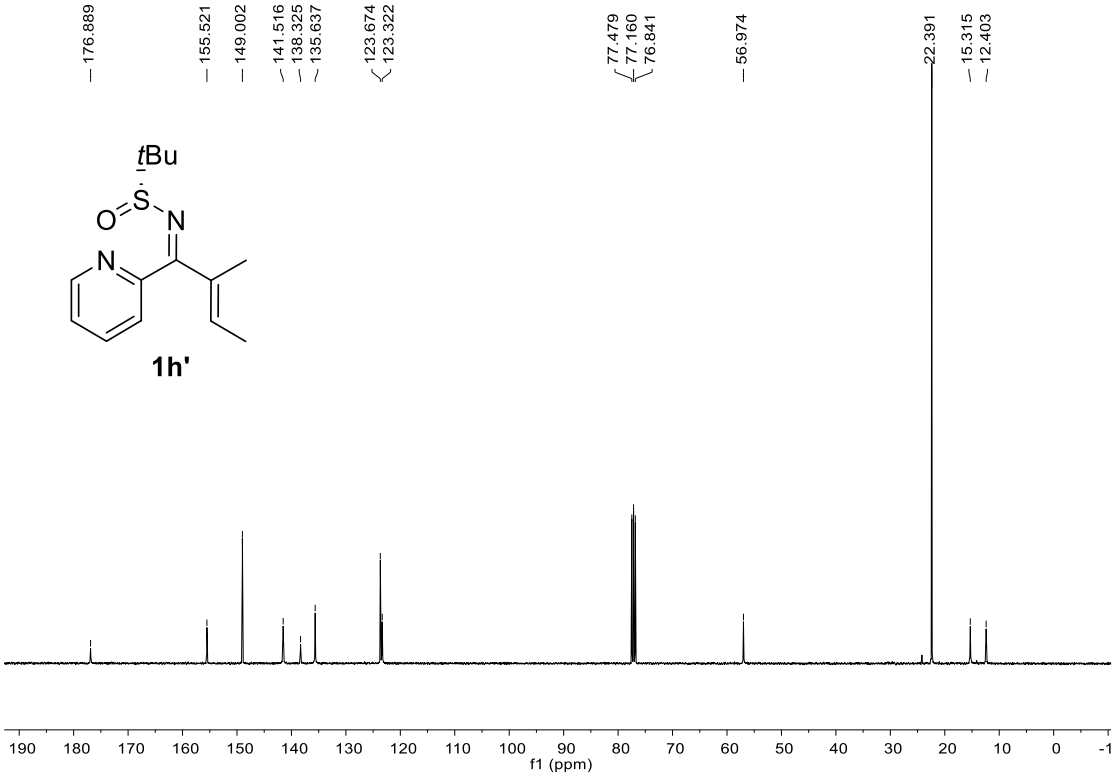
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1h** (mixture of imino *Z/E* isomers)



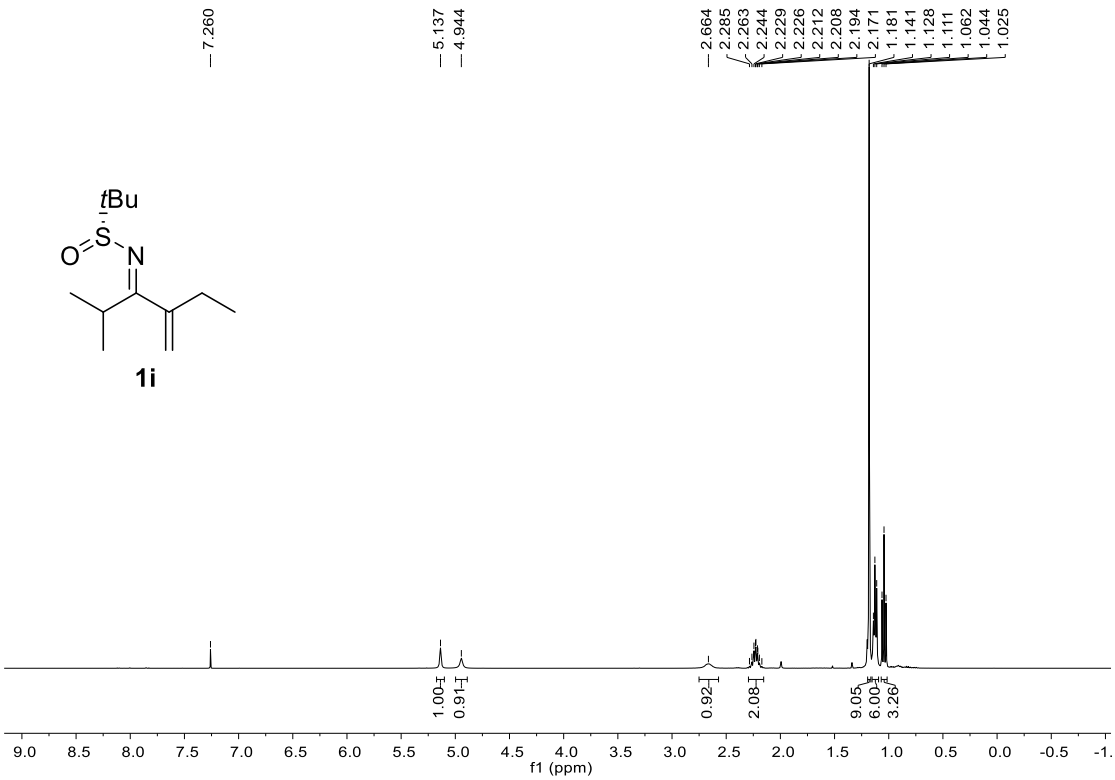
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **1h** (mixture of imino *Z/E* isomers)



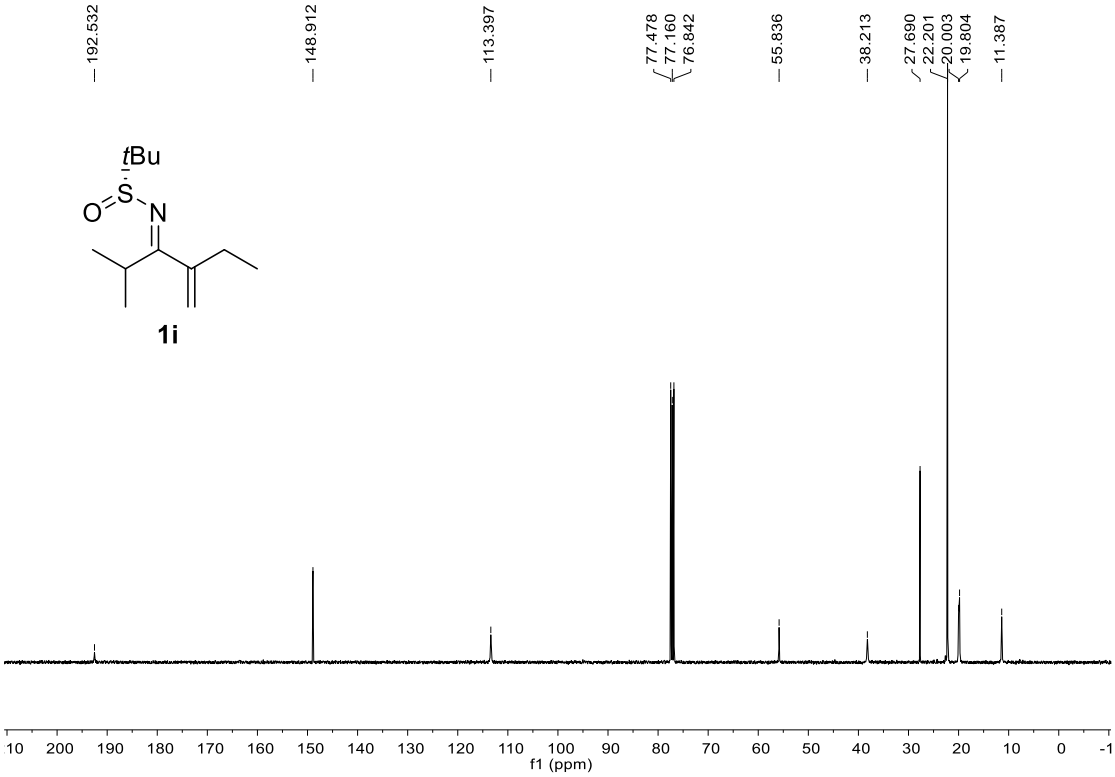
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1h′**



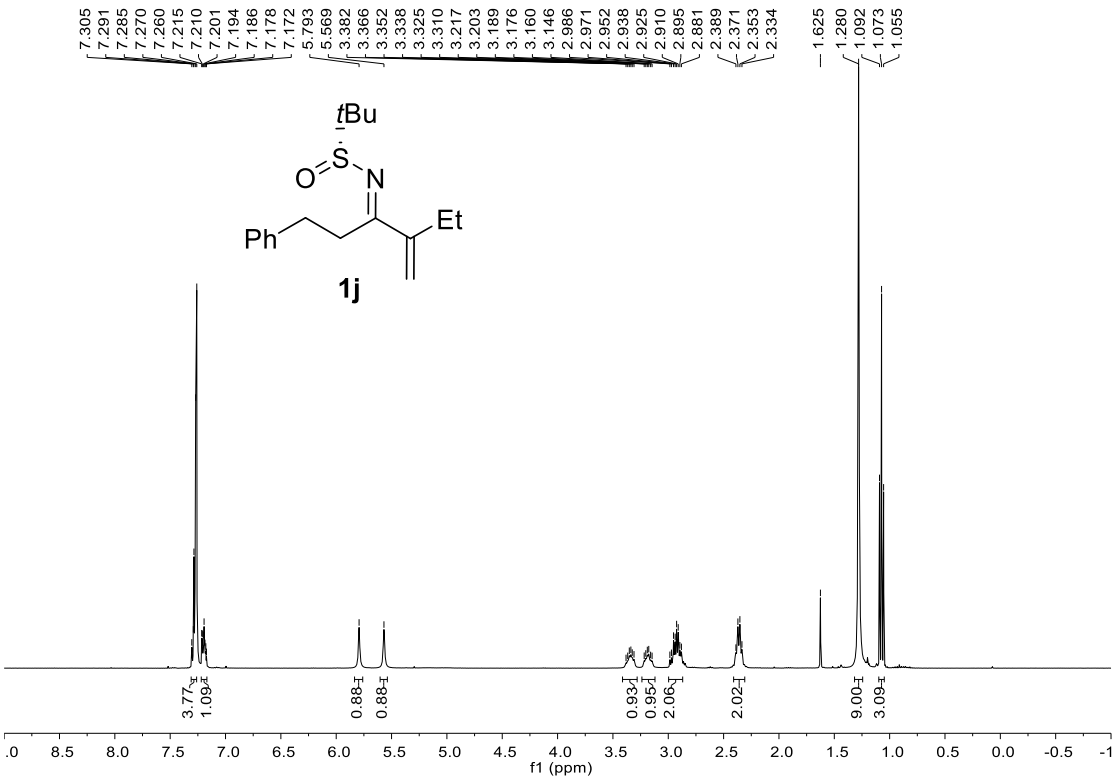
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1h′**



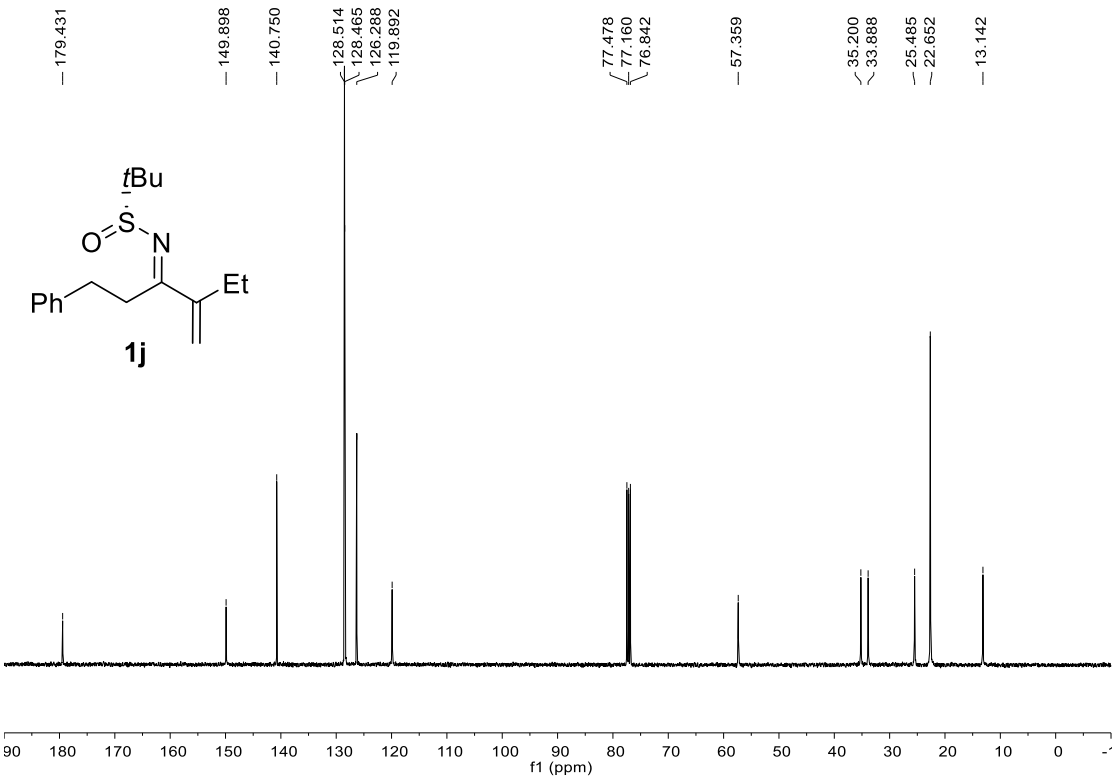
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1i**



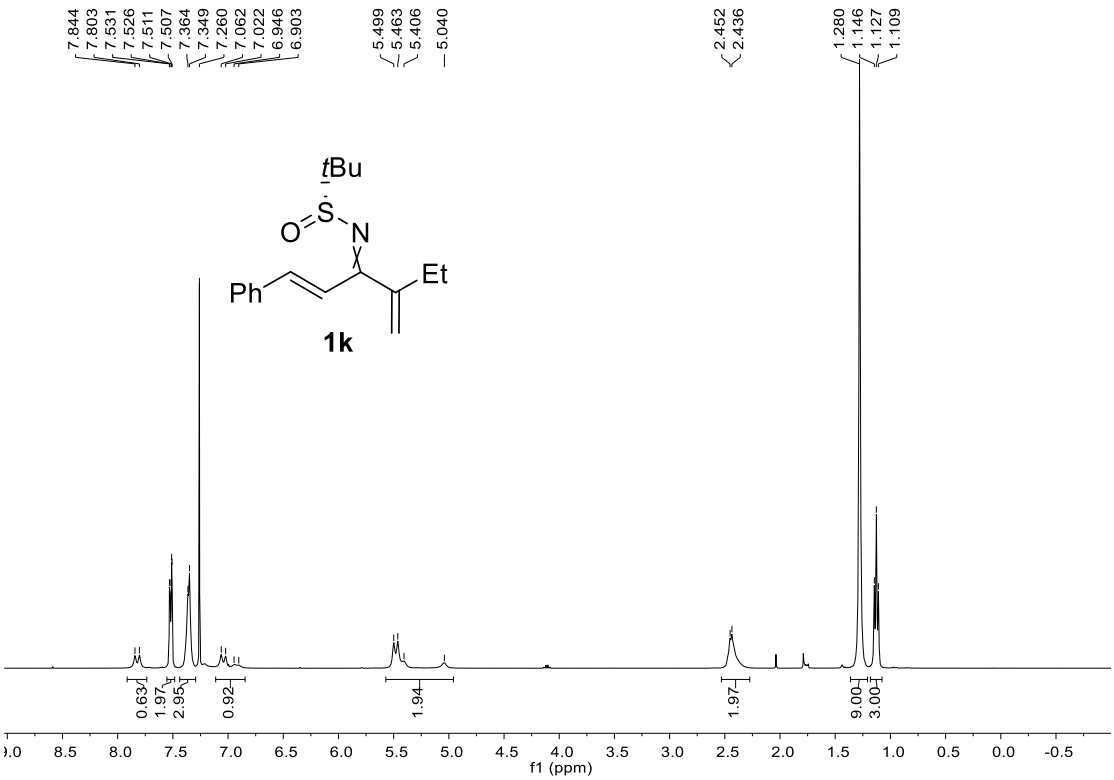
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1i**



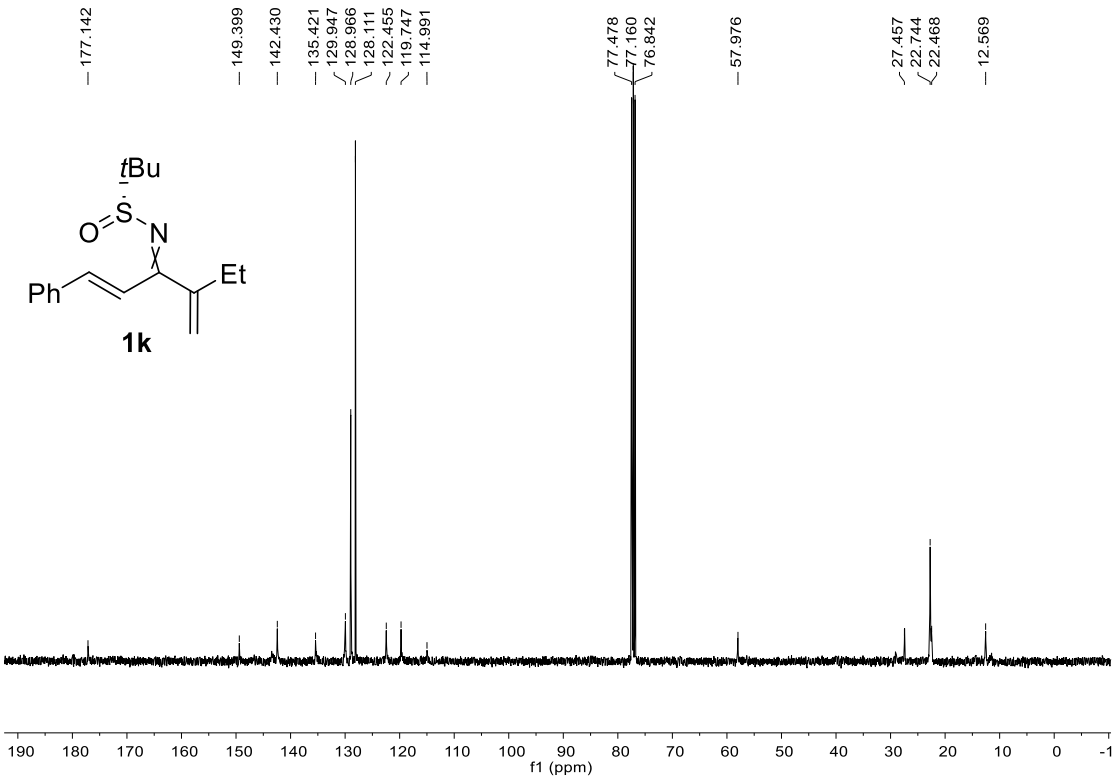
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1j**



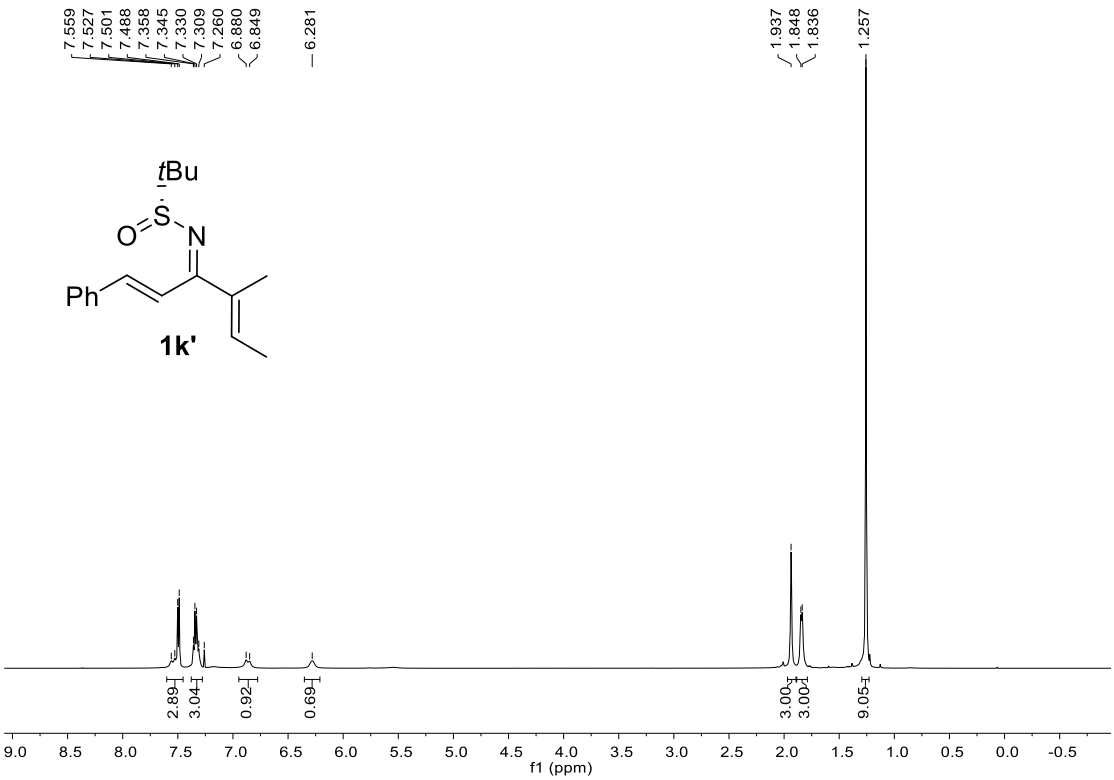
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1j**



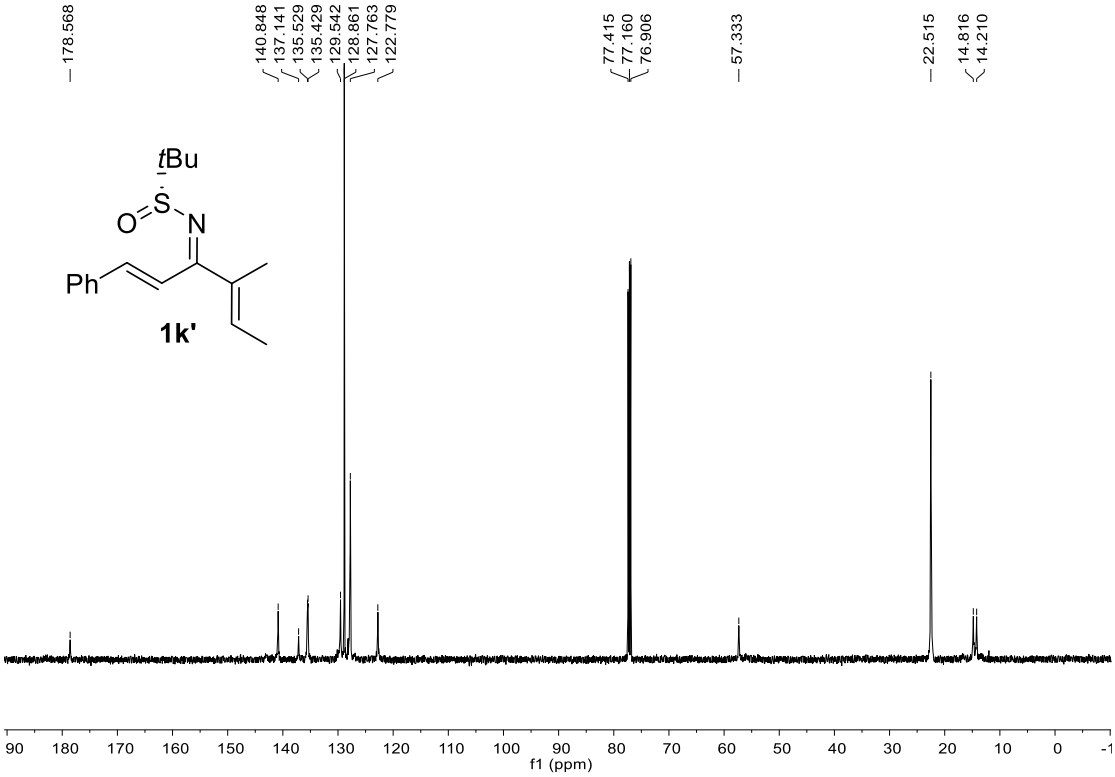
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1k** (mixture of imino *Z/E* isomers)



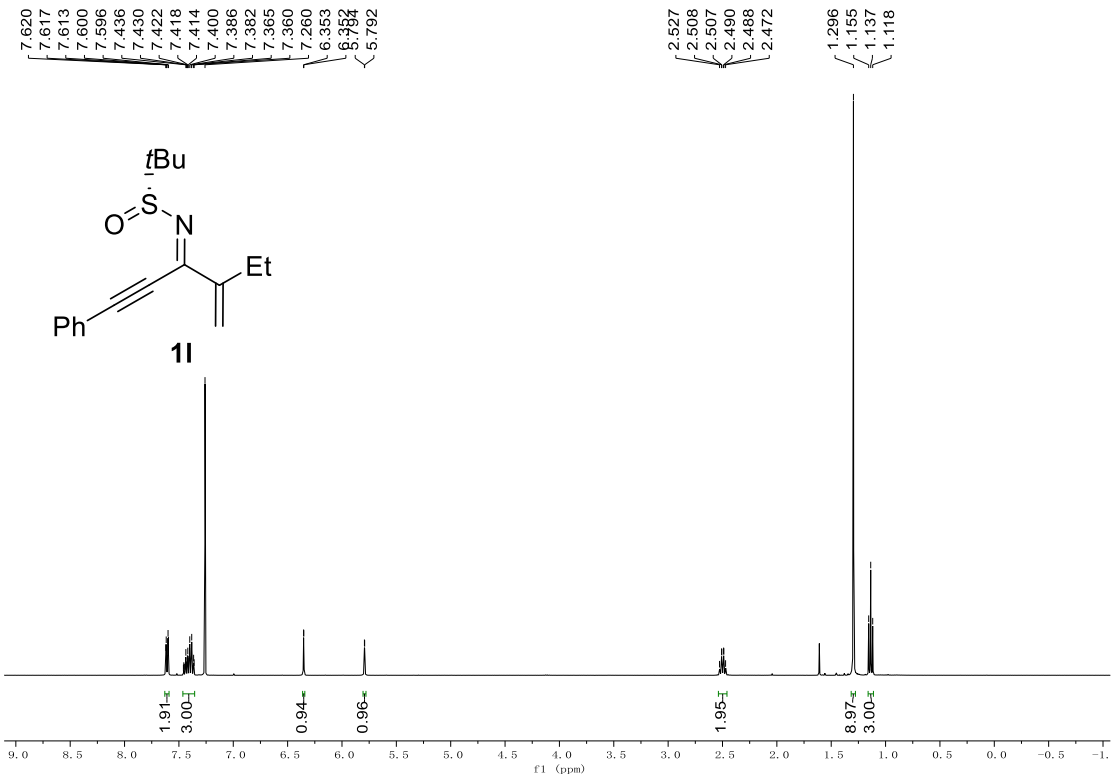
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1k** (mixture of imino *Z/E* isomers)



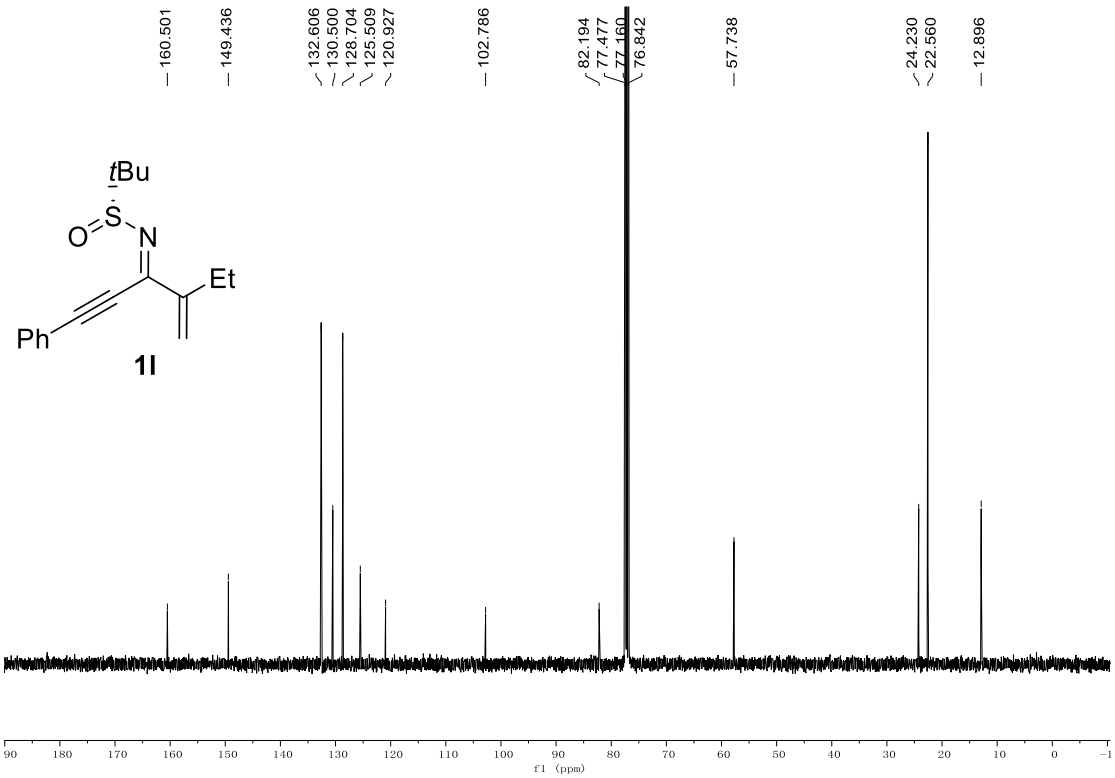
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **1k′**



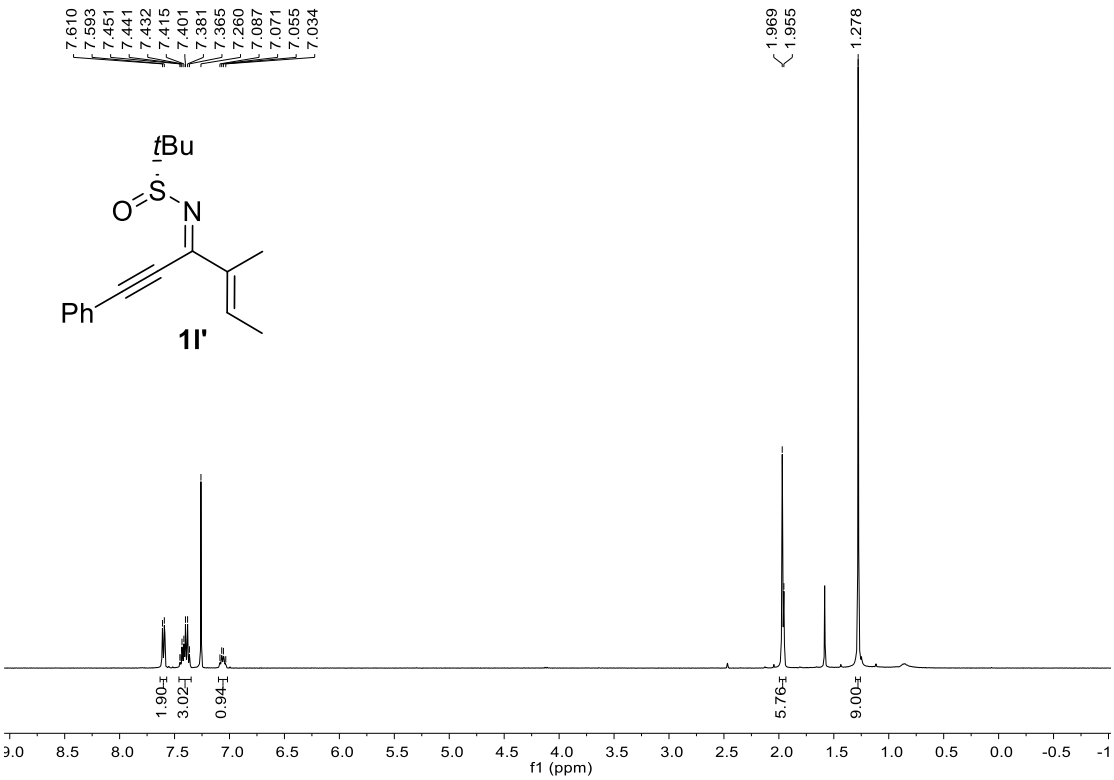
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **1k′**



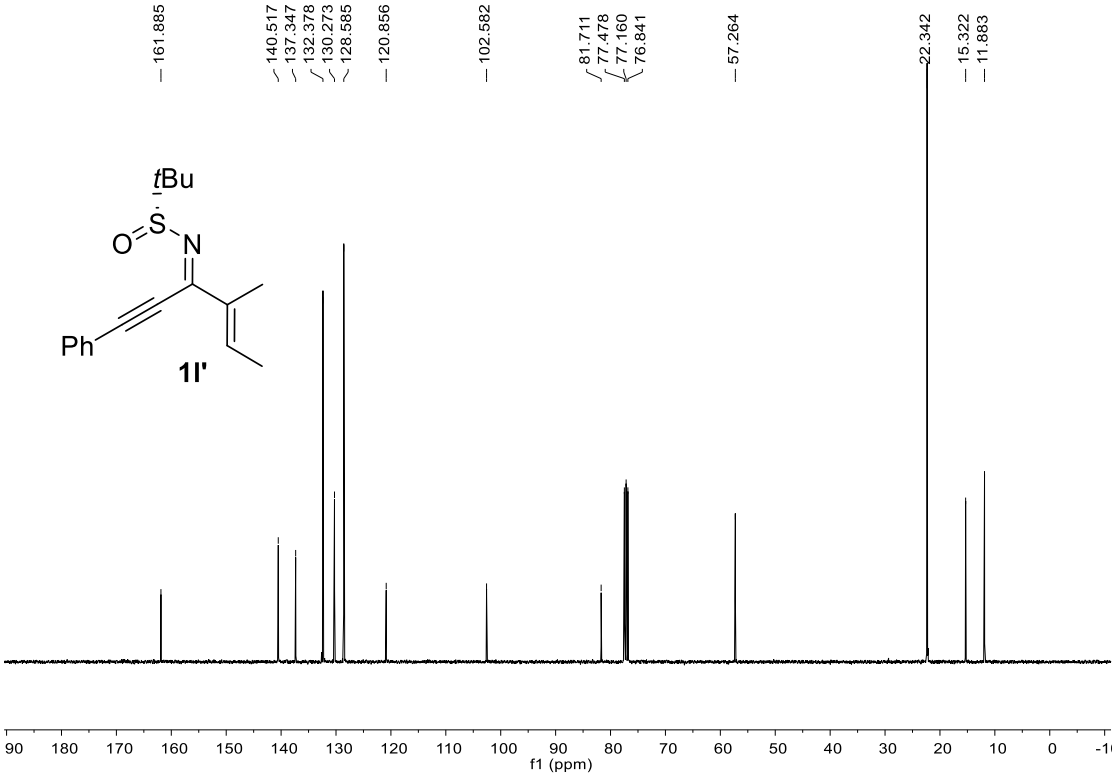
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1l**



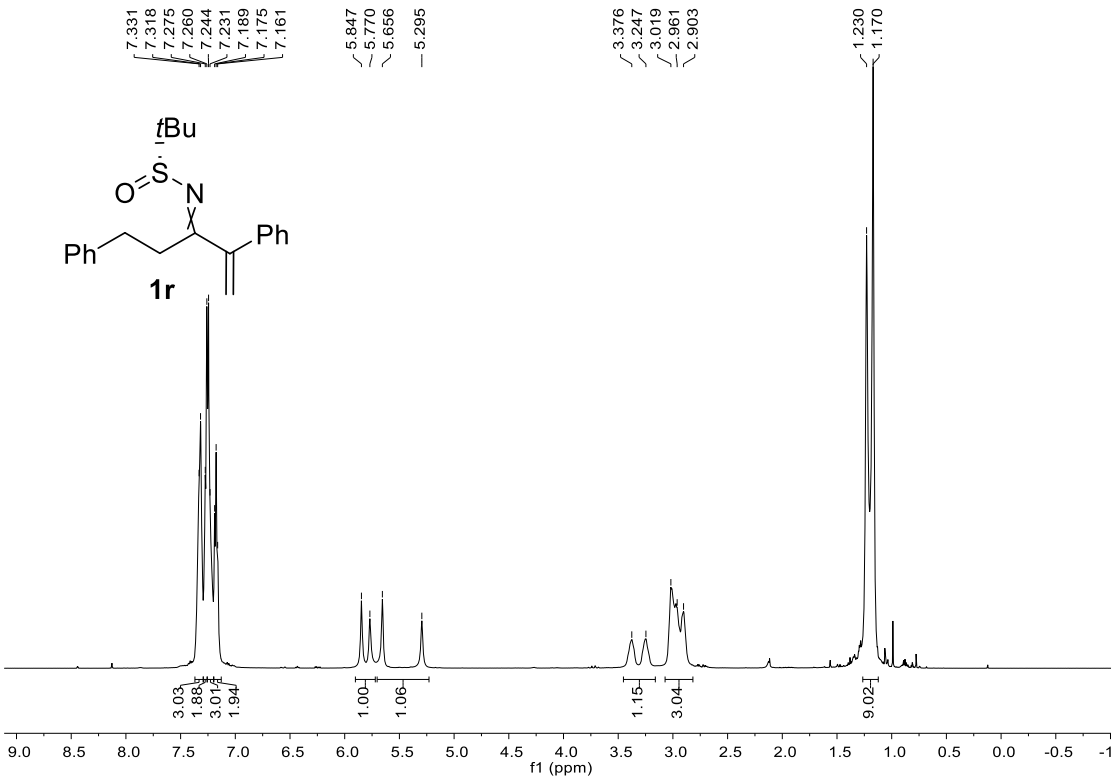
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1l**



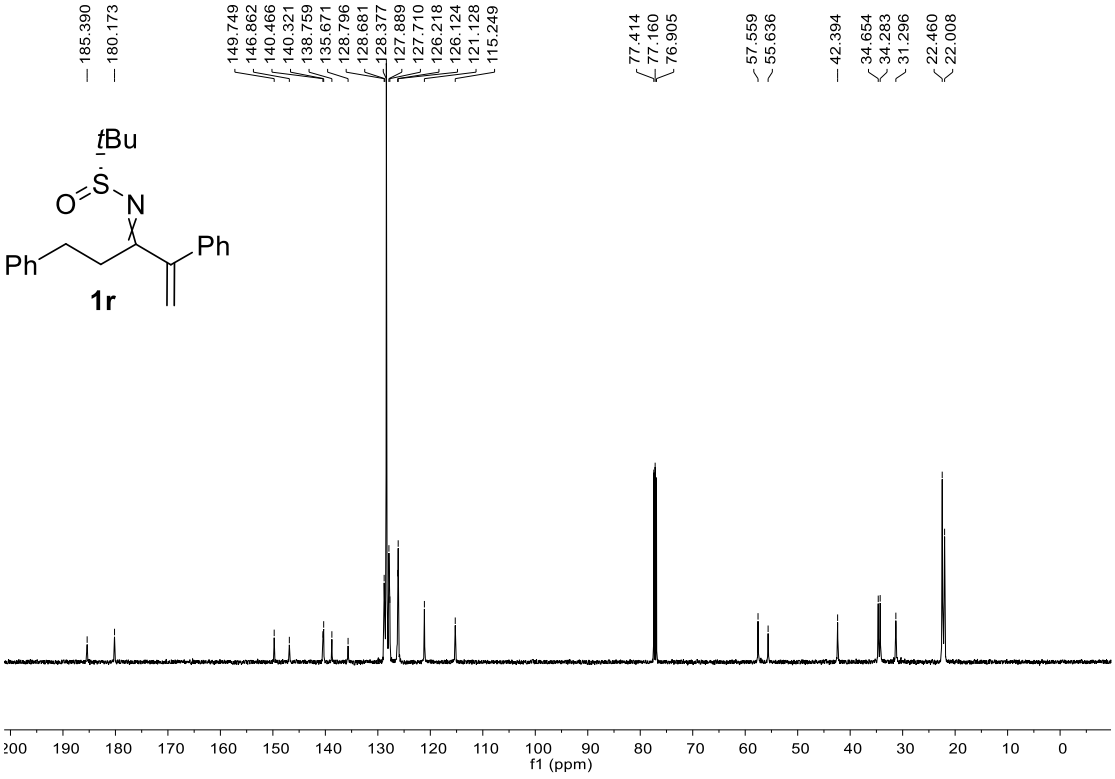
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1l′**



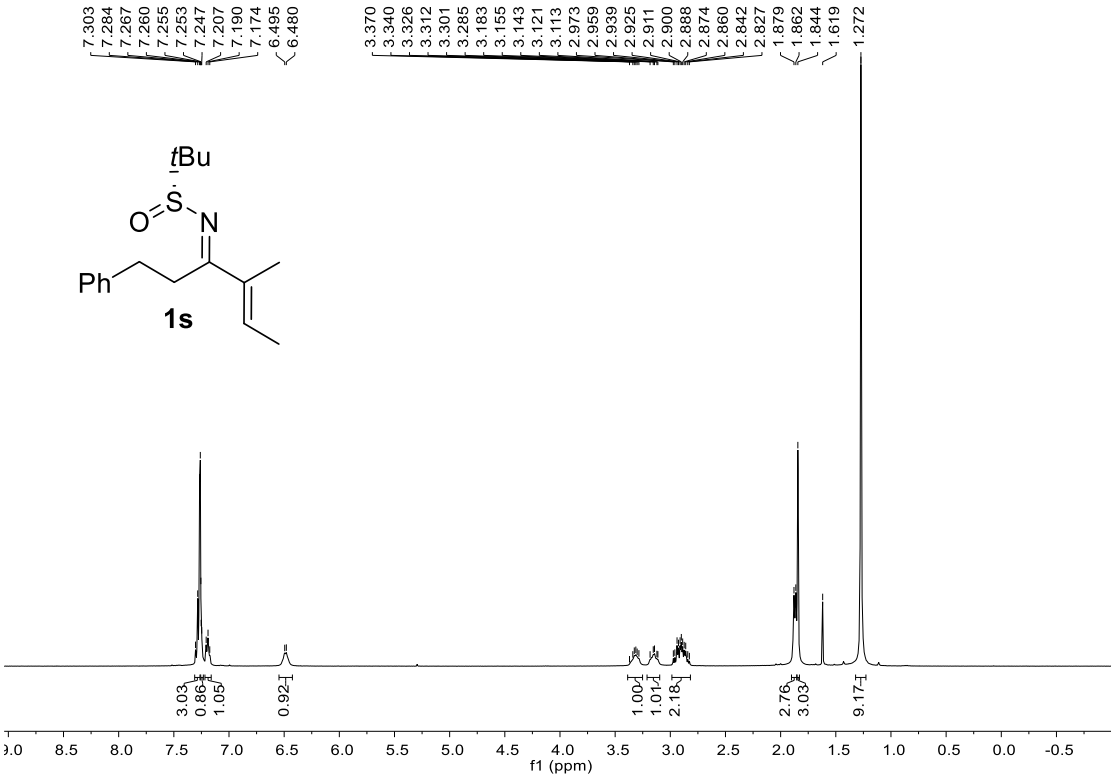
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1l′**



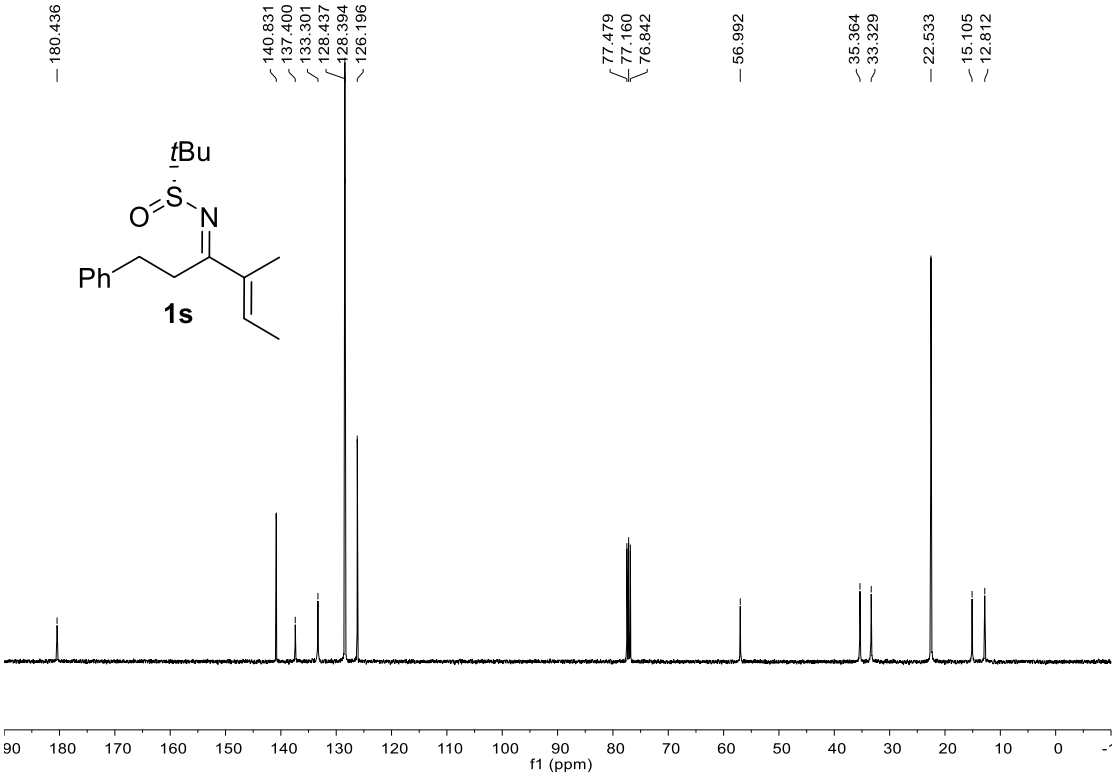
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **1r** (mixture of imino *Z/E* isomers)



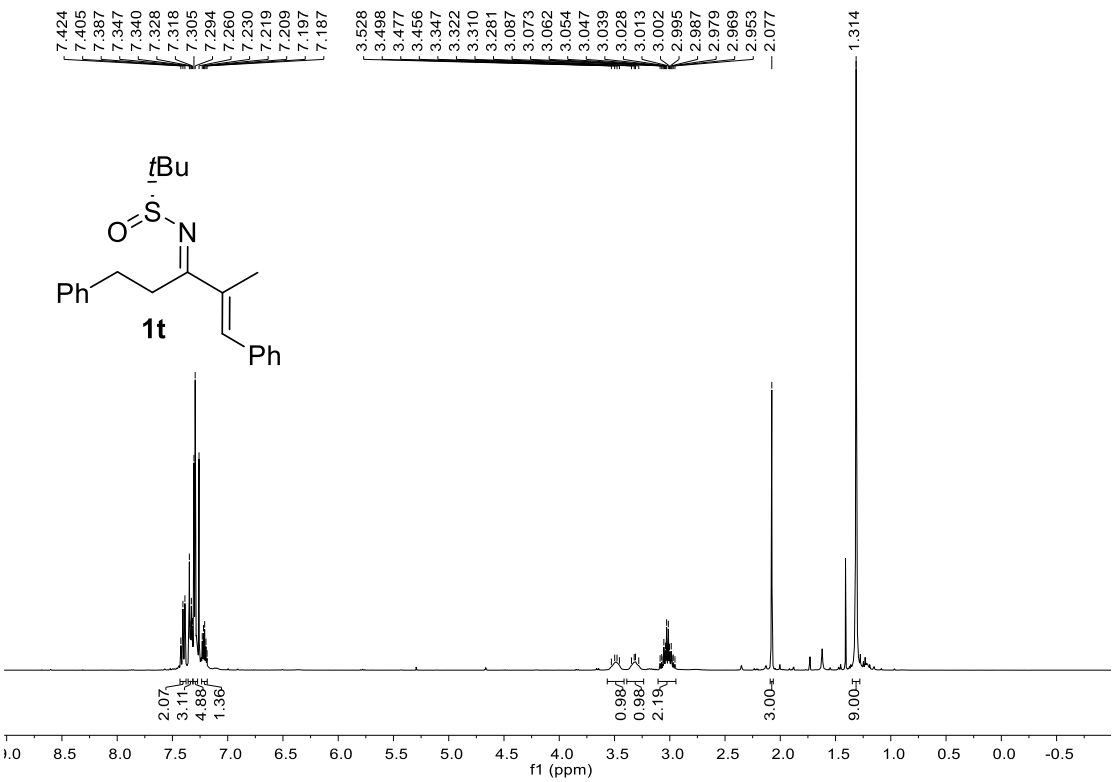
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **1r** (mixture of imino *Z/E* isomers)



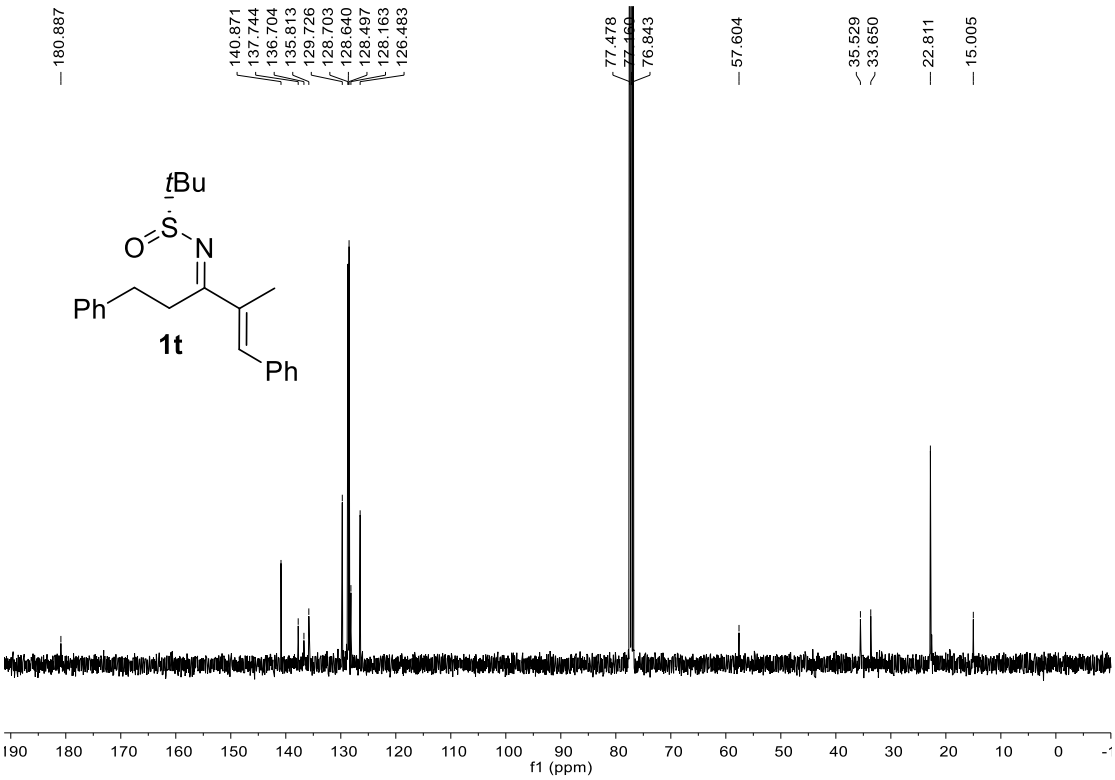
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1s**



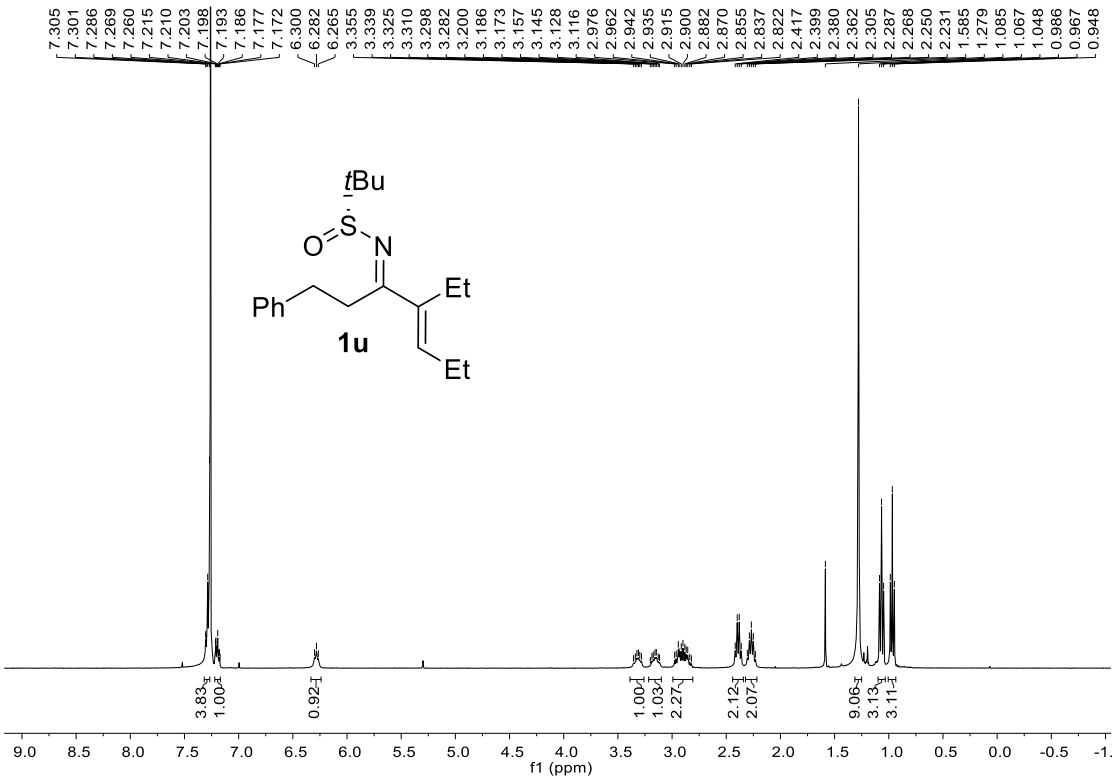
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1s**



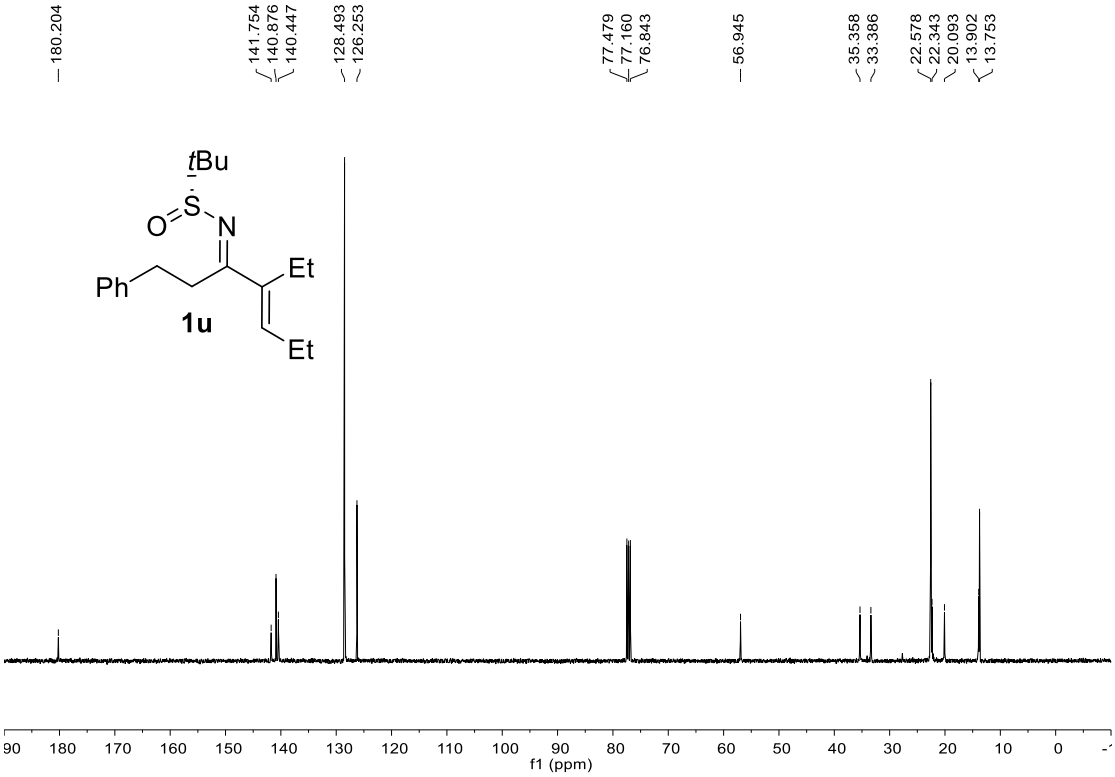
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1t**



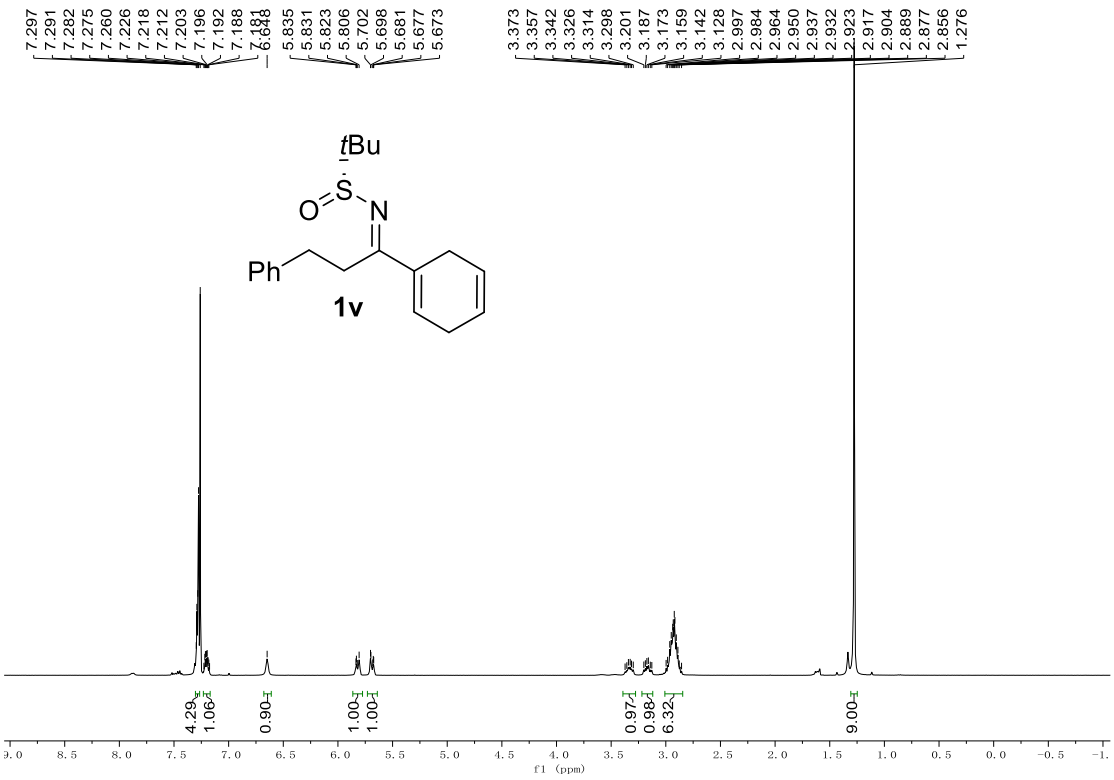
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1t**



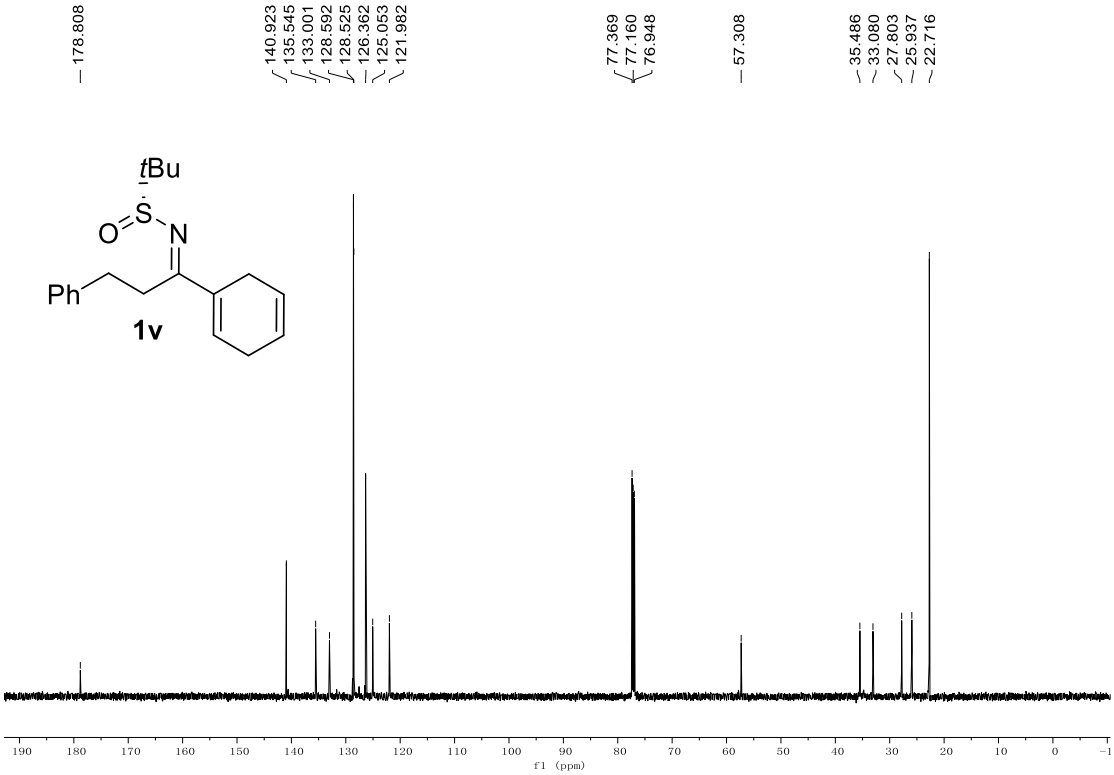
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1u**



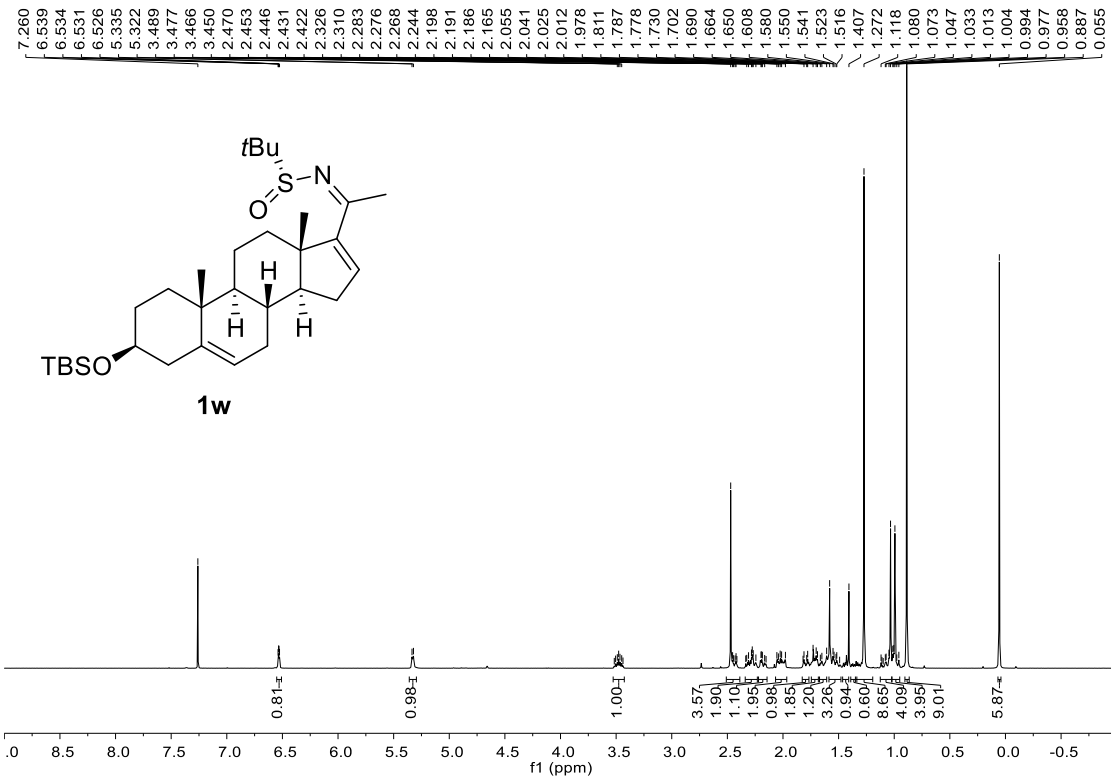
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1u**



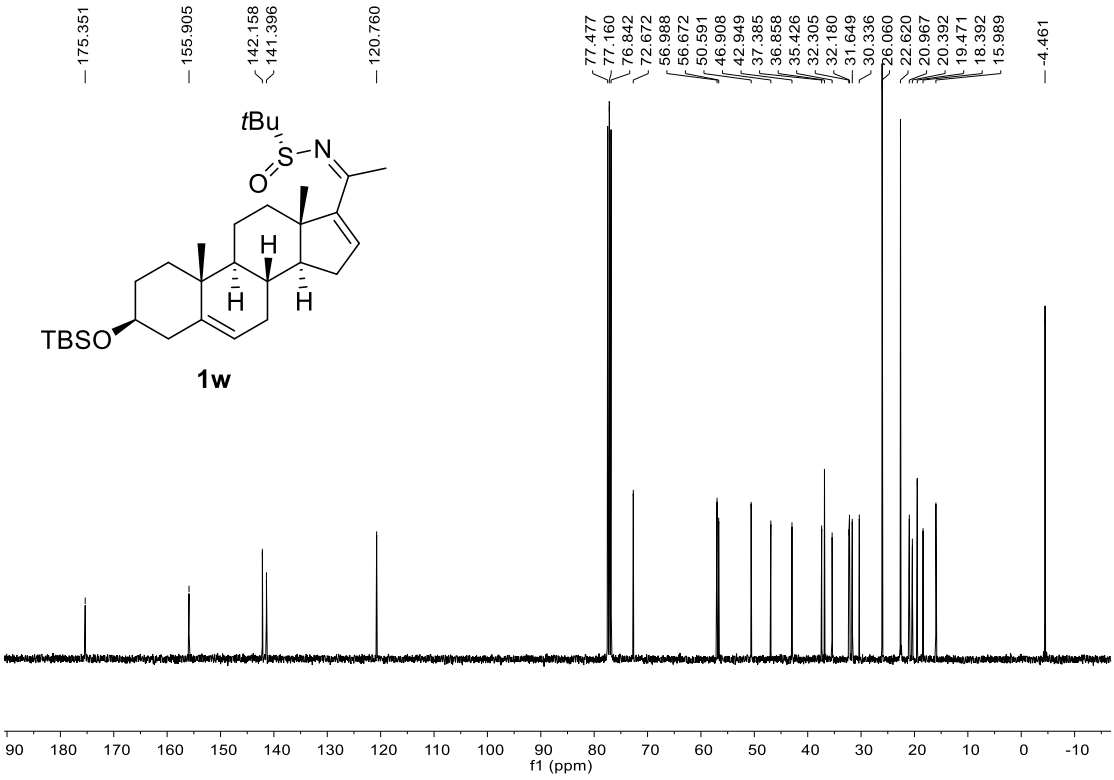
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1v**



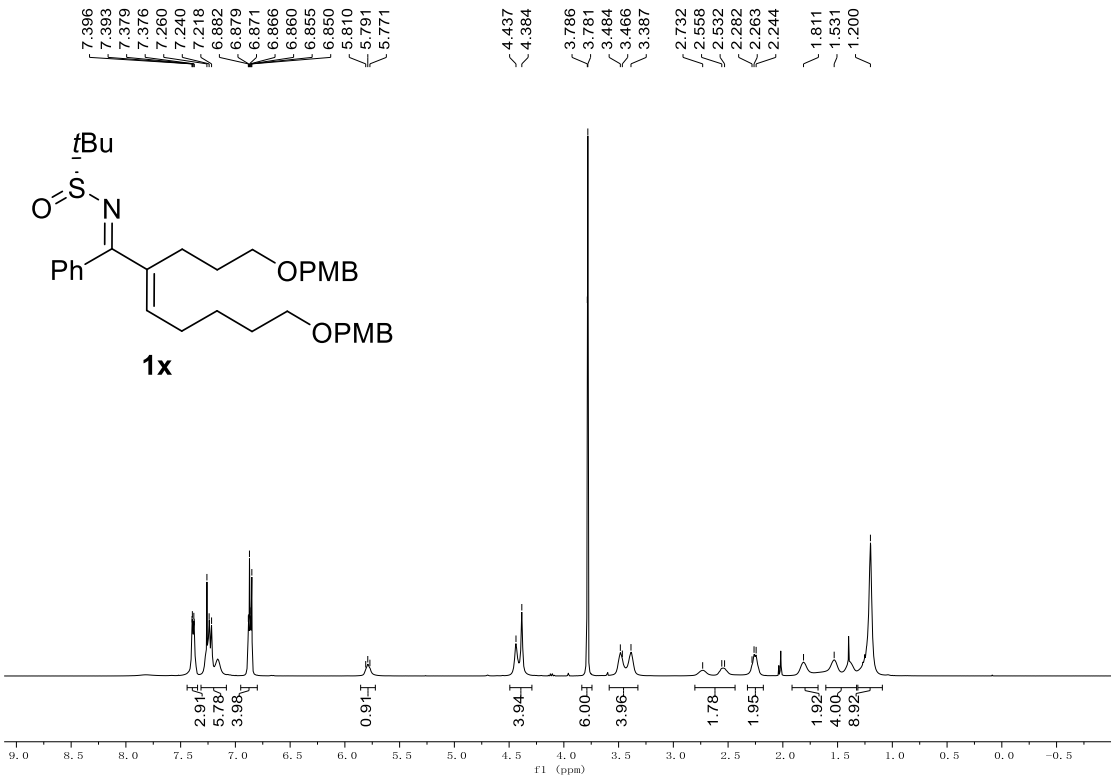
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **1v**



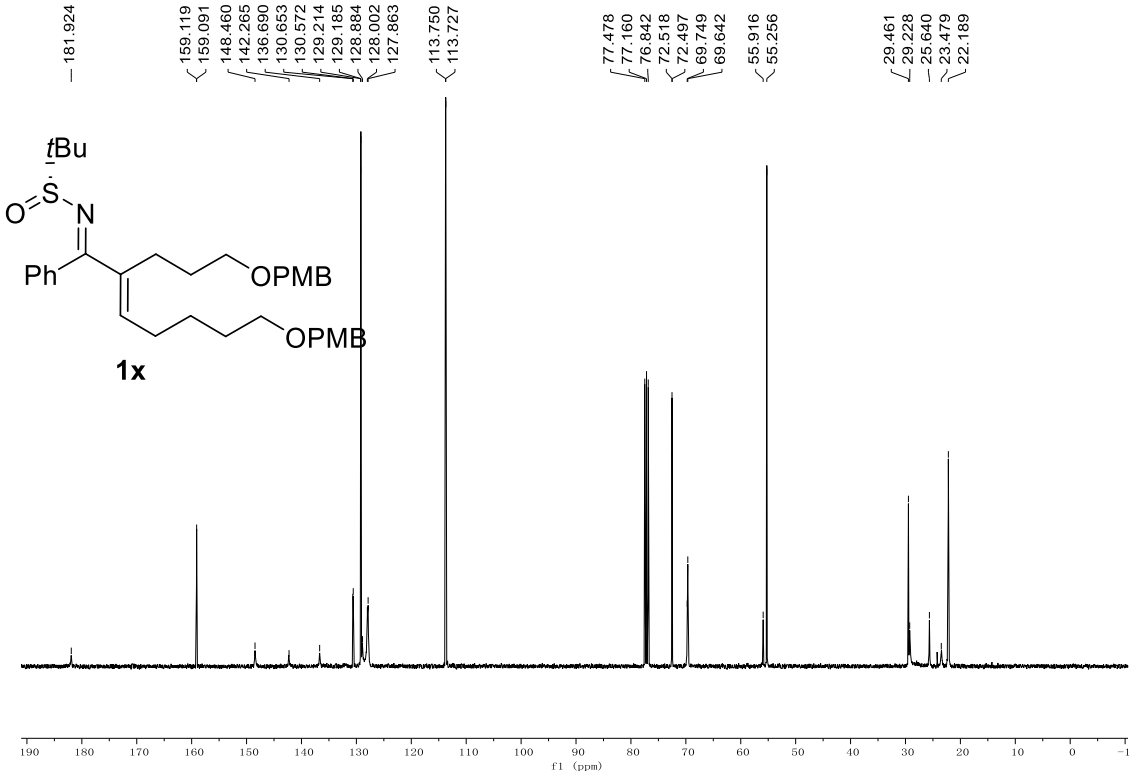
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1w**



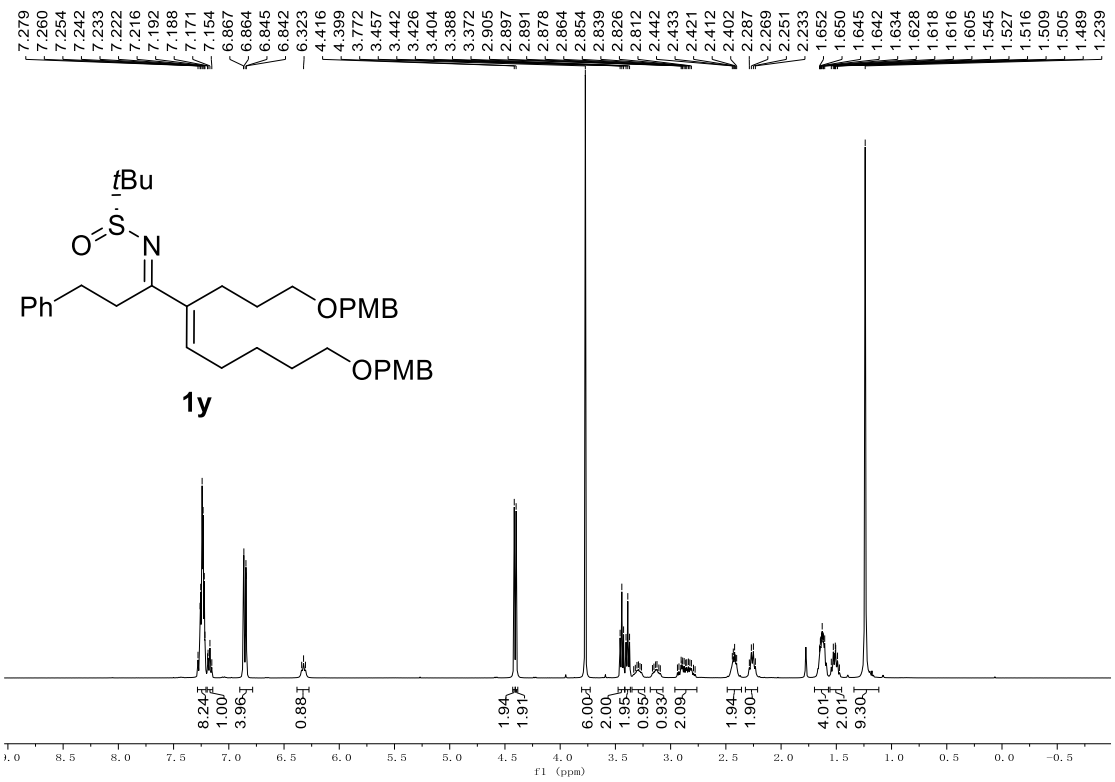
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1w**



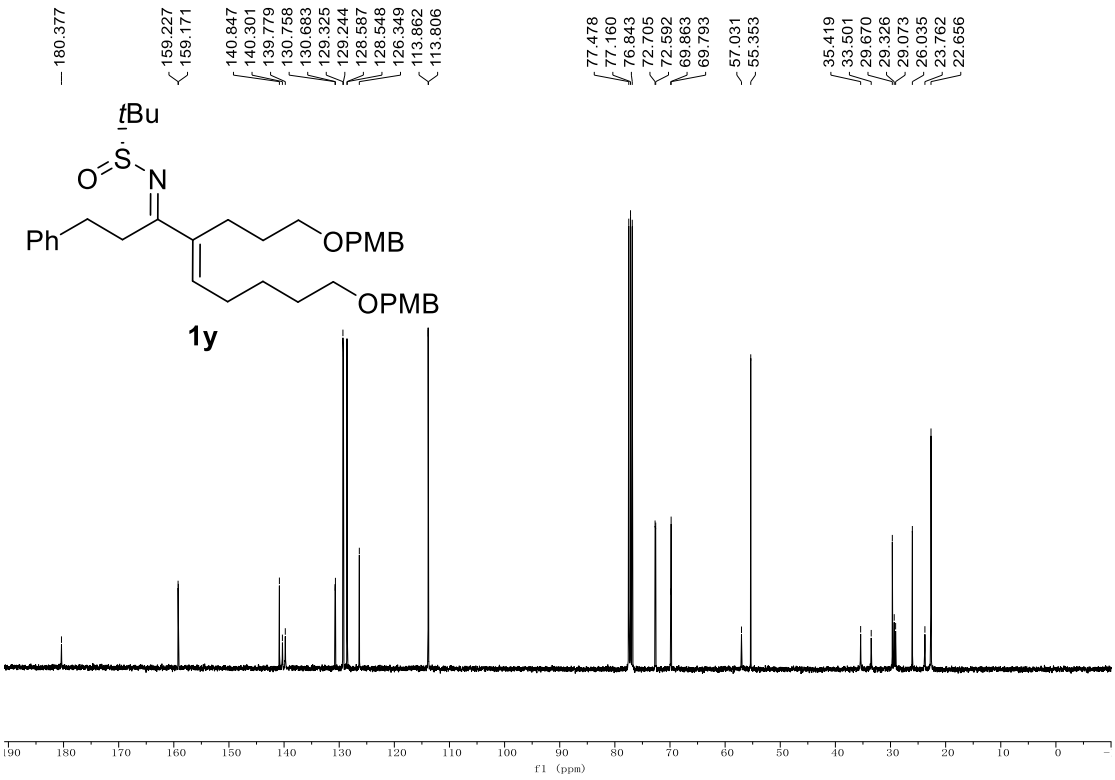
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1x**



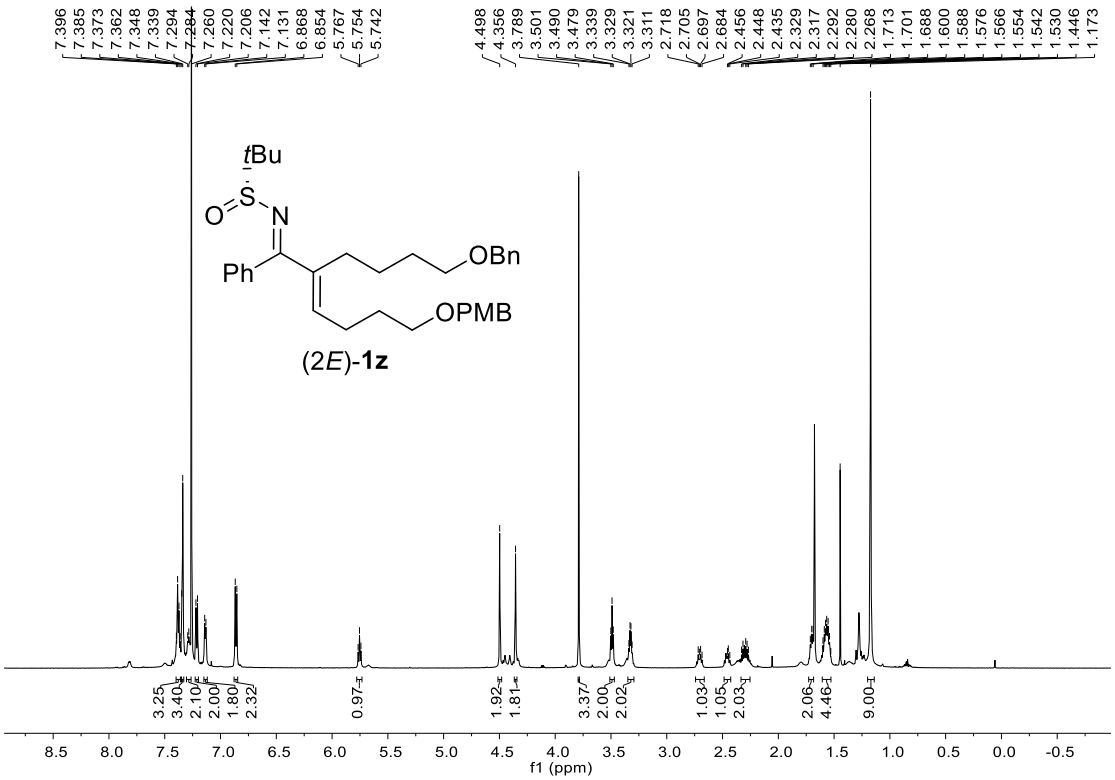
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1x**



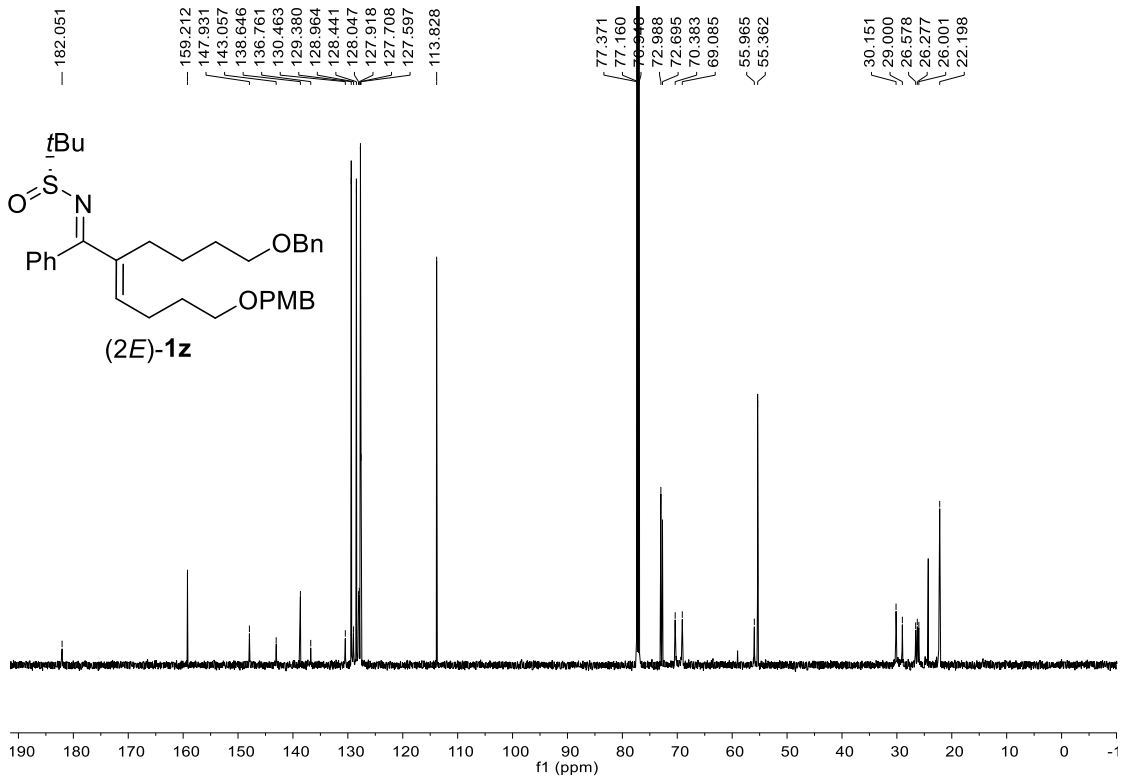
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1y**



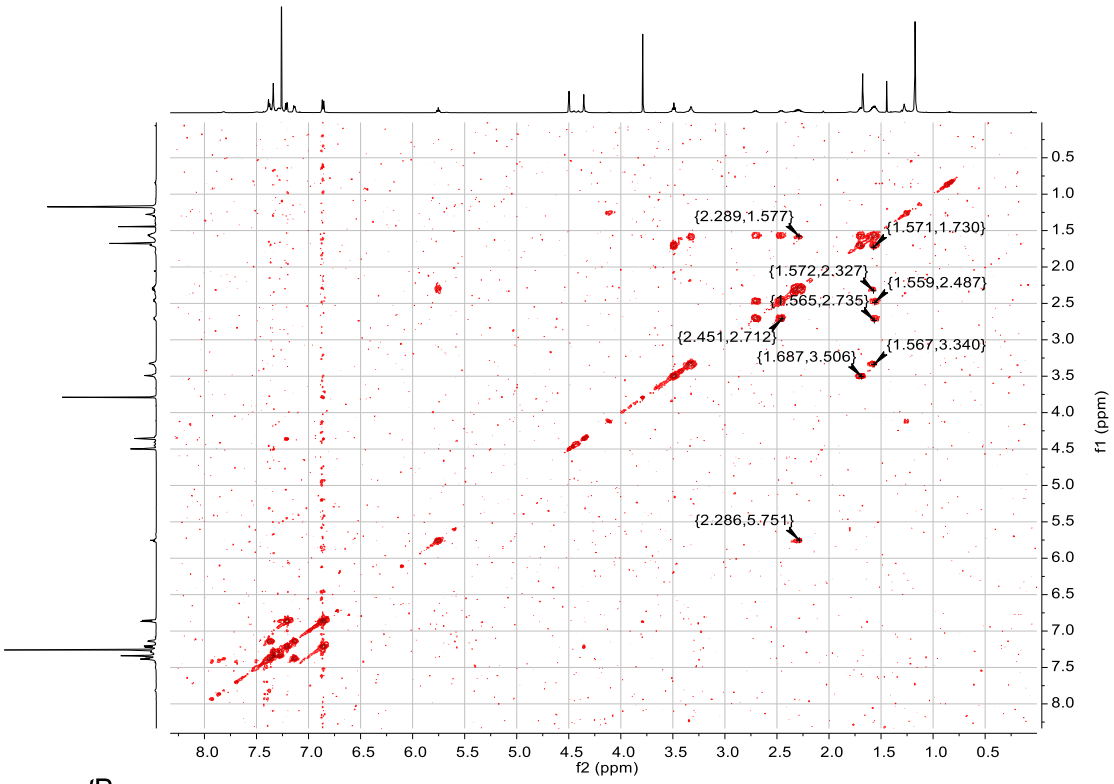
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1y**



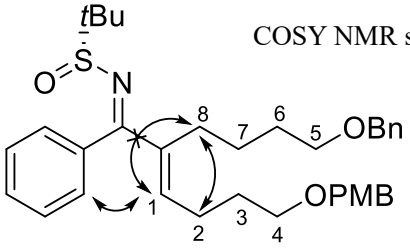
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1z**



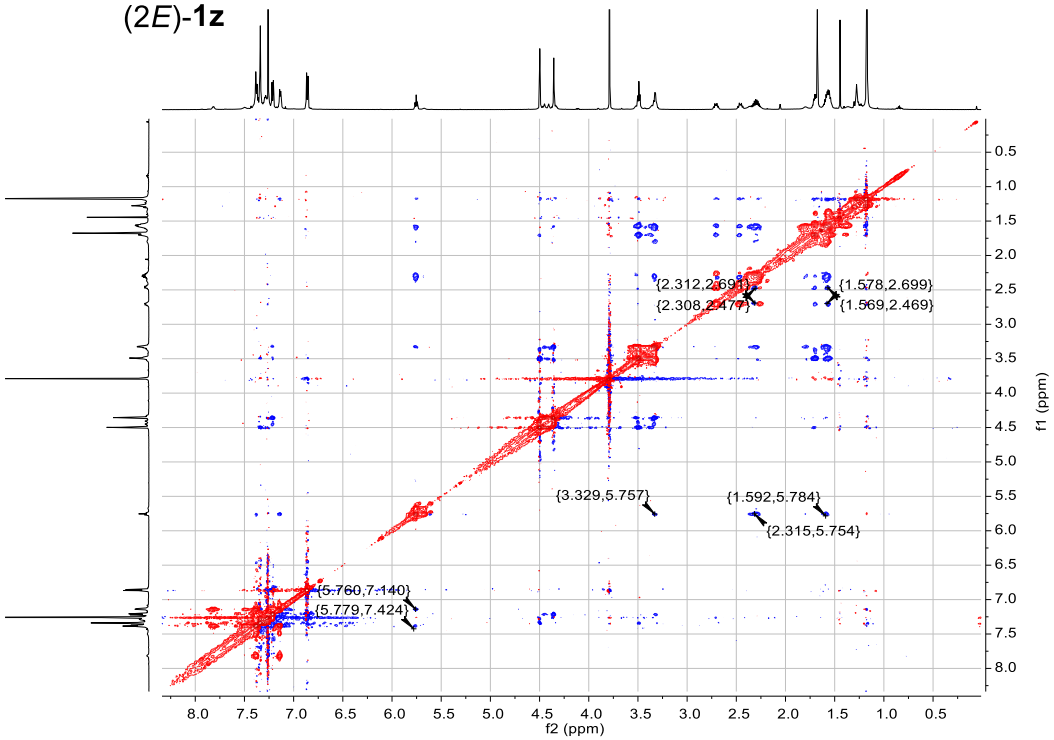
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of (2*E*)-**1z**



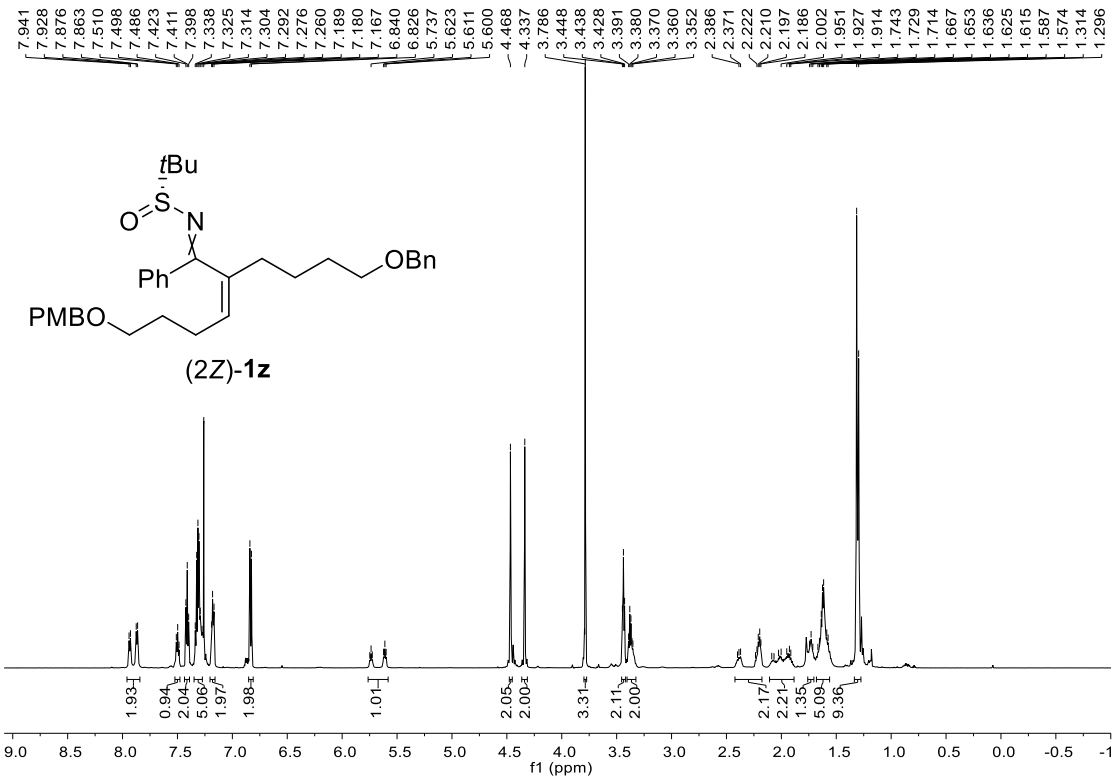
COSY NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1z**



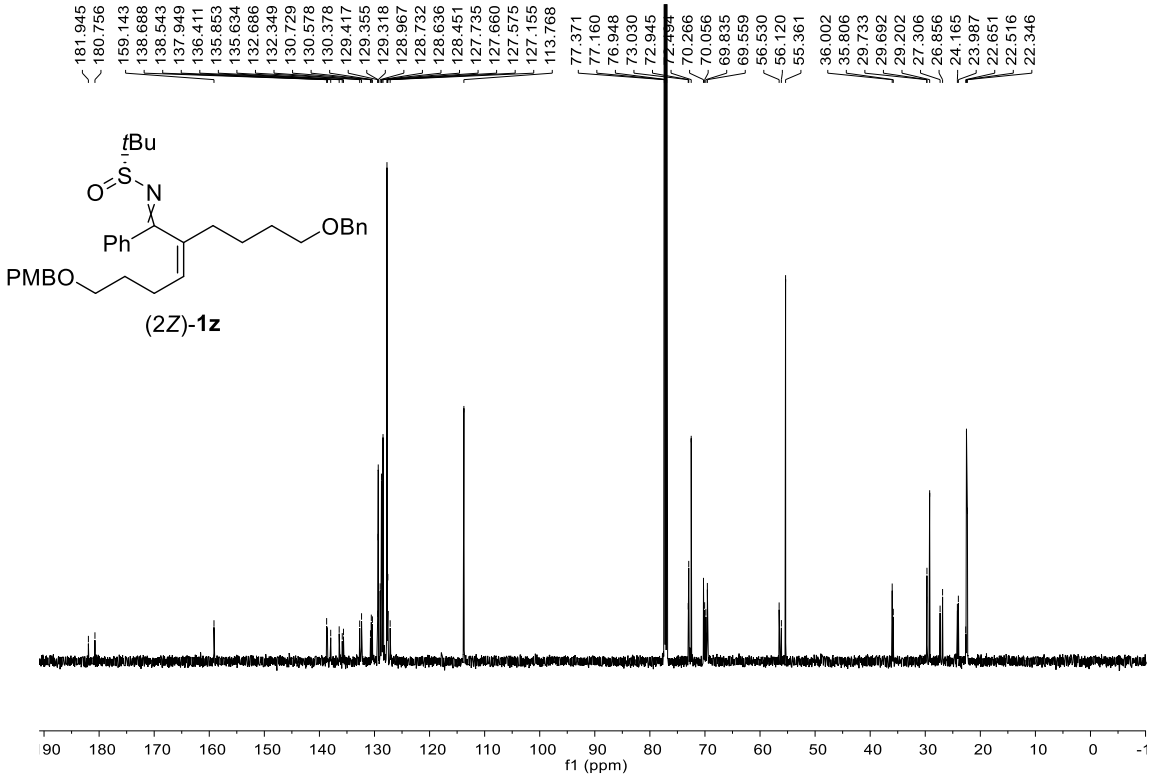
(2*E*)-**1z**



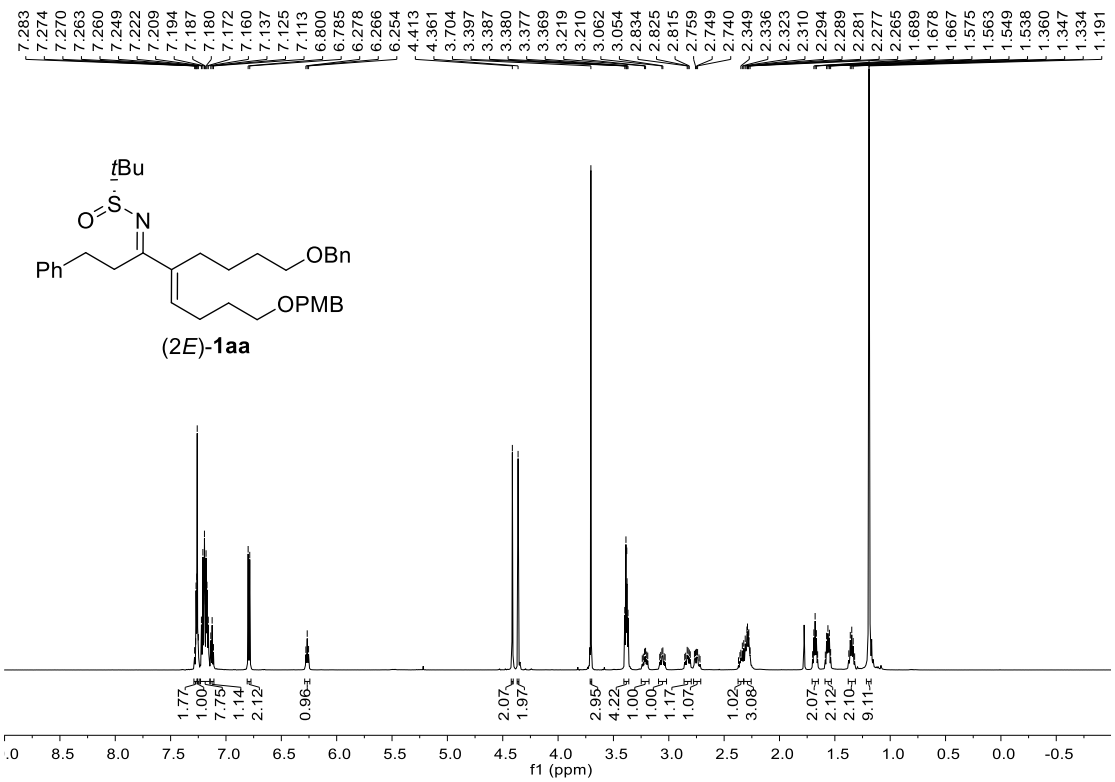
NOESY NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1z**



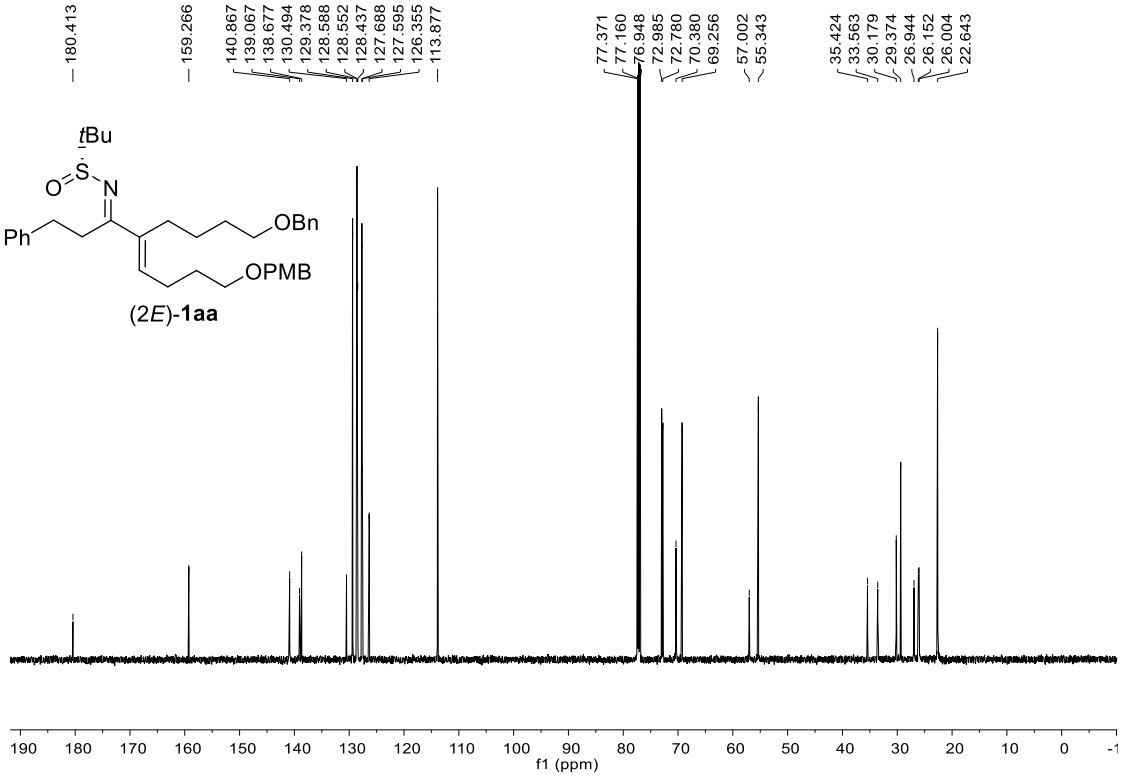
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of (2*Z*)-**1z** (mixture of imino *Z*/*E* isomers)



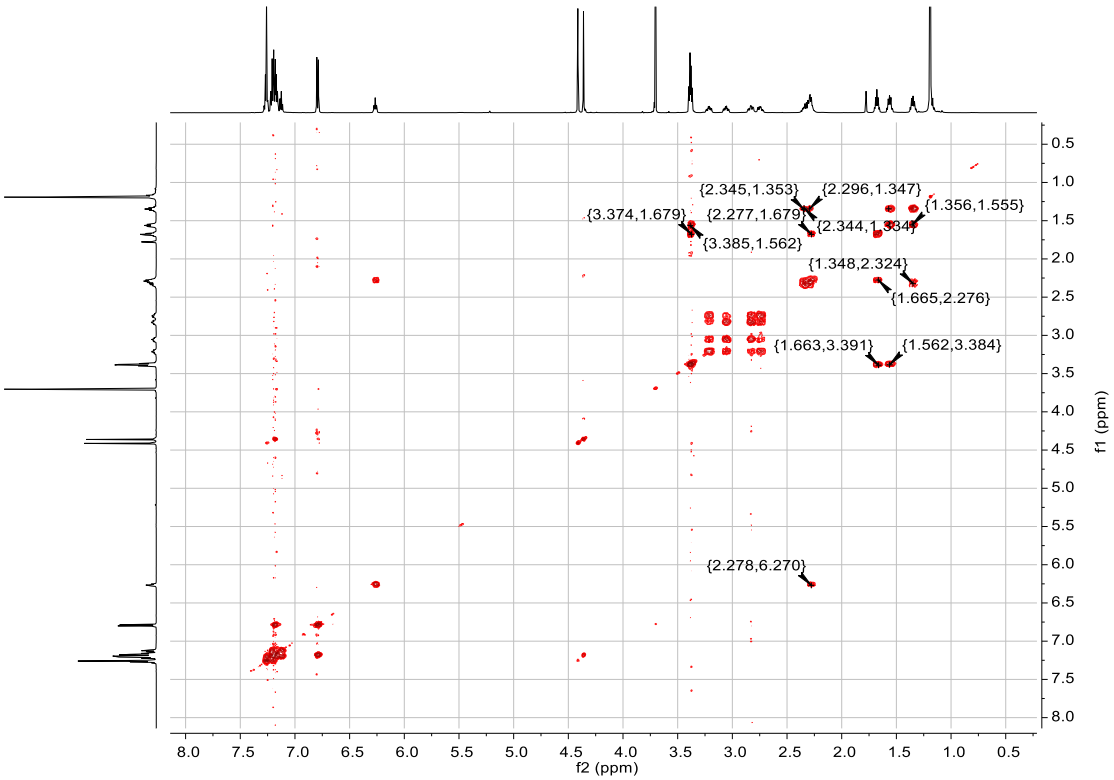
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of (2*Z*)-**1z** (mixture of imino *Z*/*E* isomers)



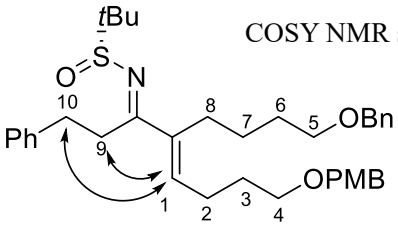
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1aa**



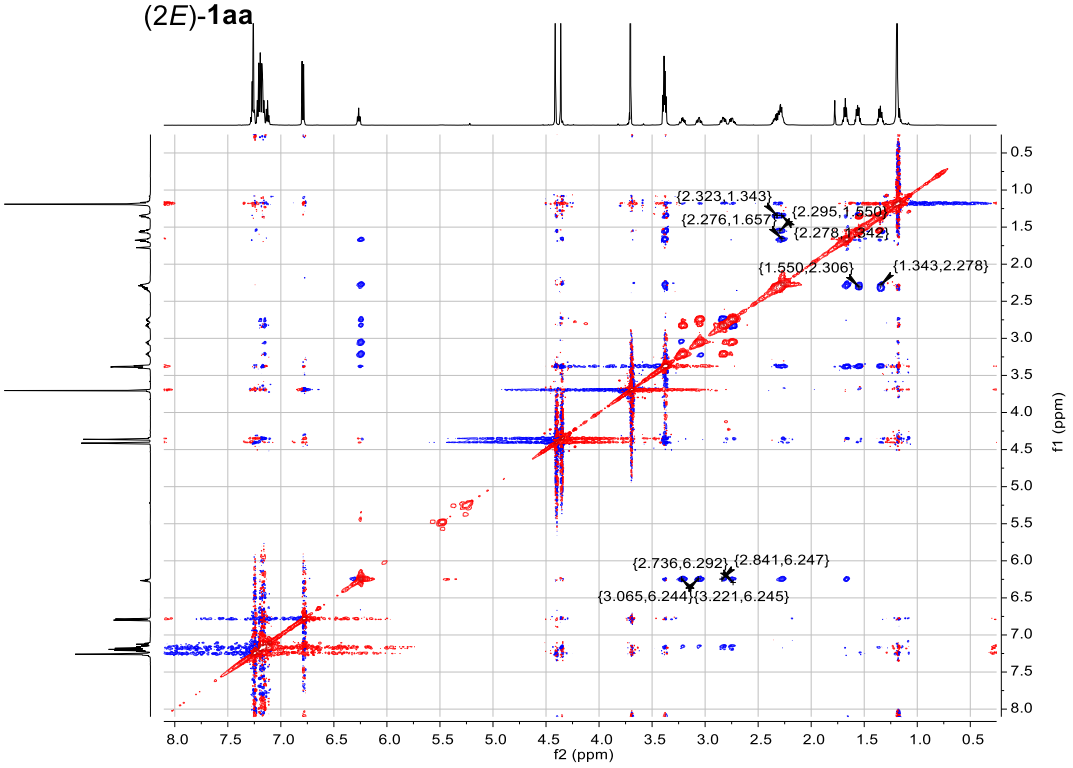
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of (2*E*)-**1aa**



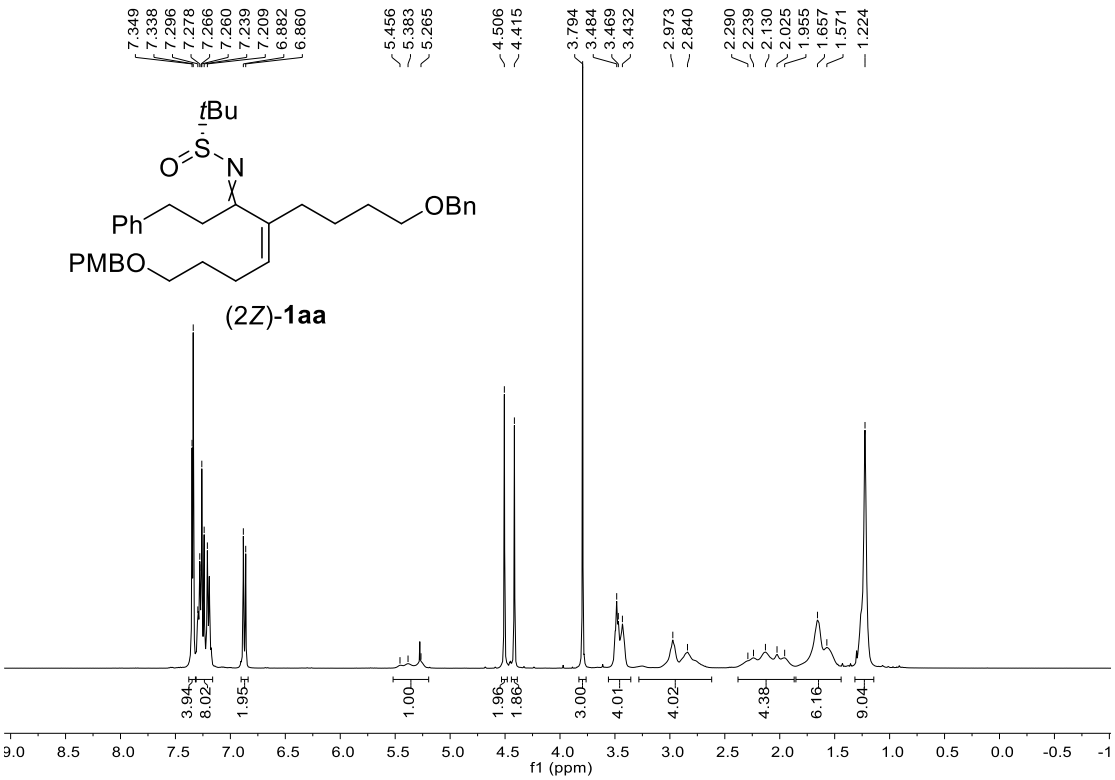
COSY NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1aa**



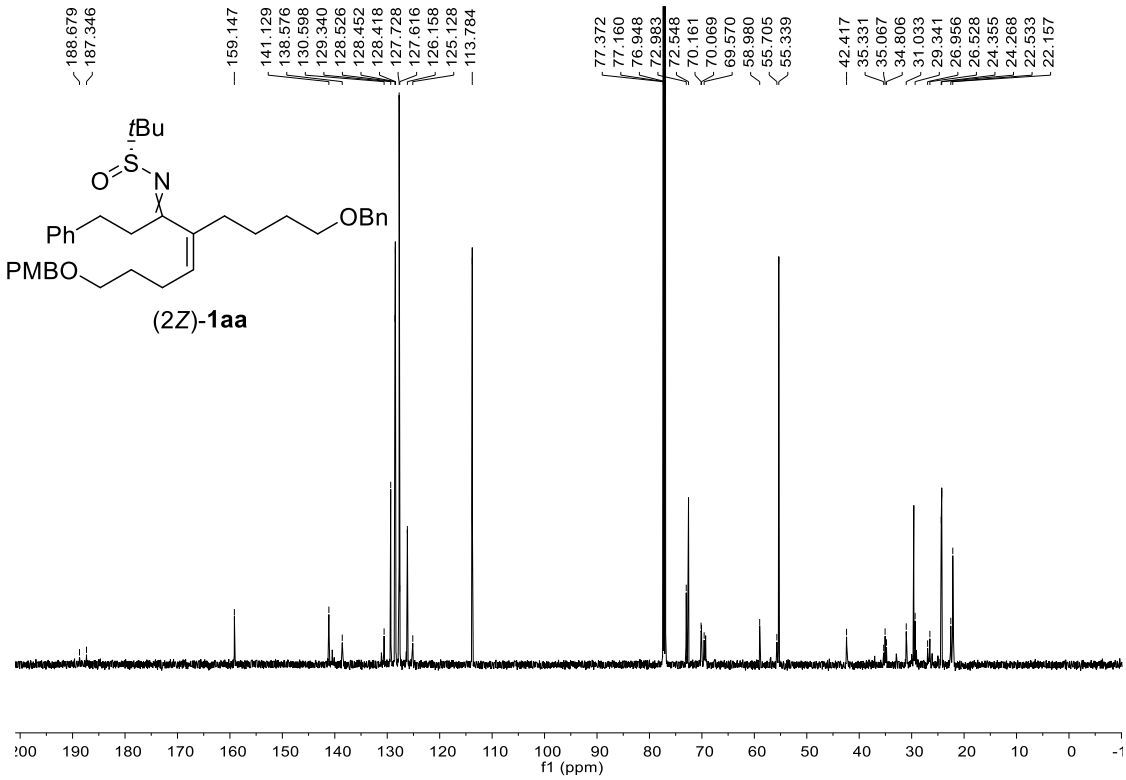
(2*E*)-**1aa**



NOESY NMR spectrum ($CDCl_3$, 600 MHz) of (2*E*)-**1aa**

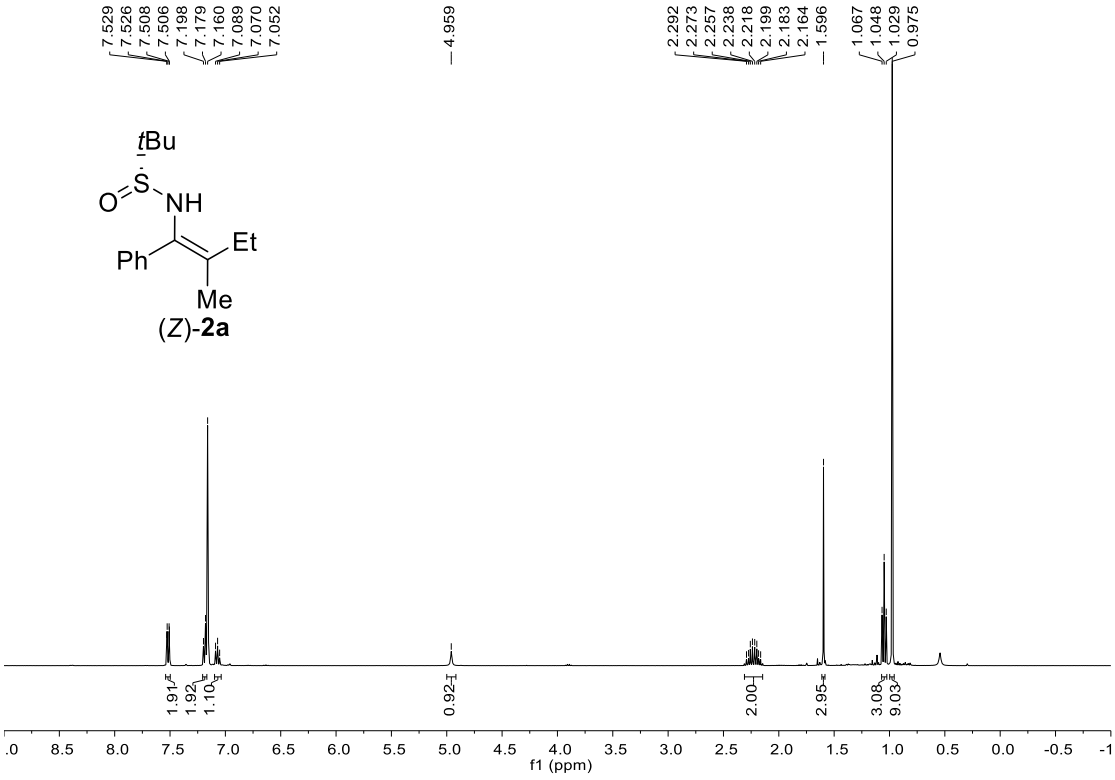


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (2*Z*)-**1aa** (mixture of imino *Z/E* isomers)

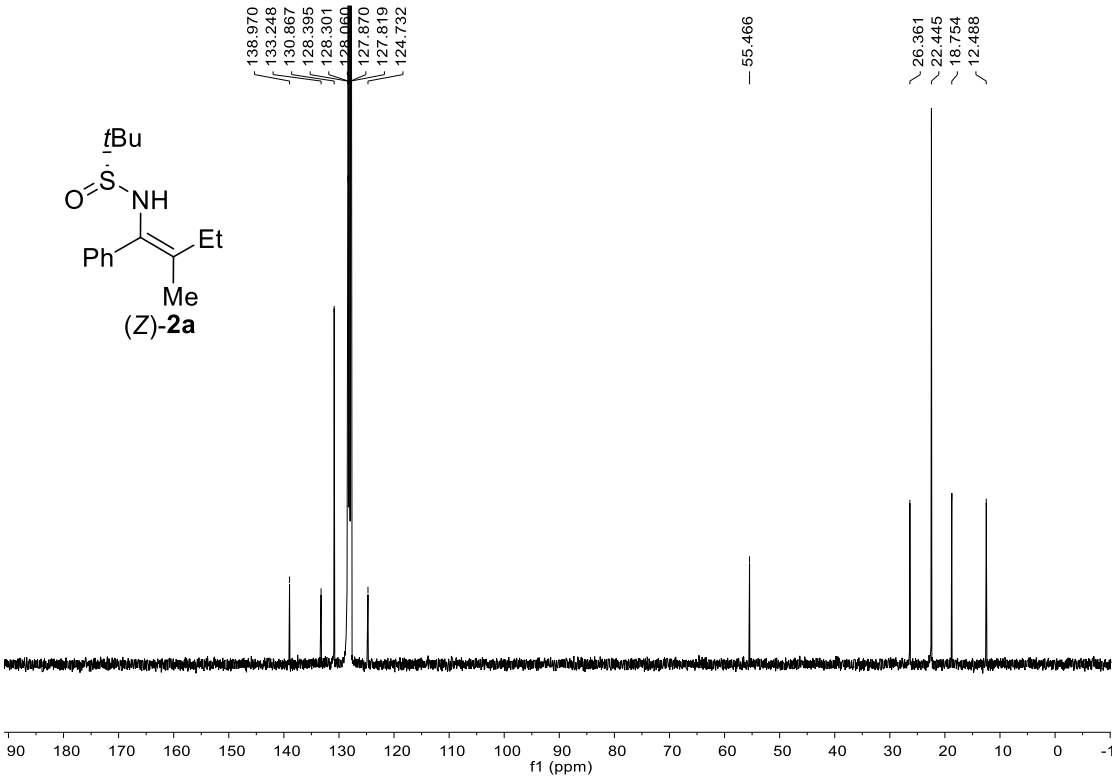


^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of (2*Z*)-**1aa** (mixture of imino *Z/E* isomers)

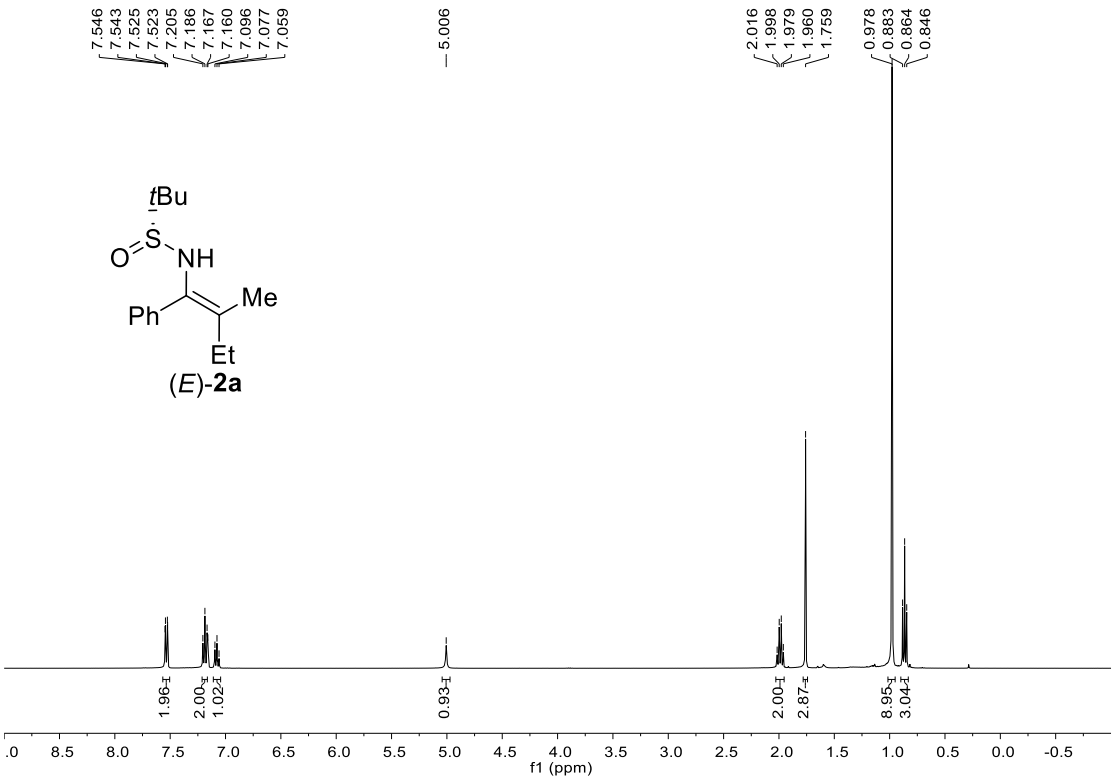
^{1}H and ^{13}C NMR spectra of enesulfinamides



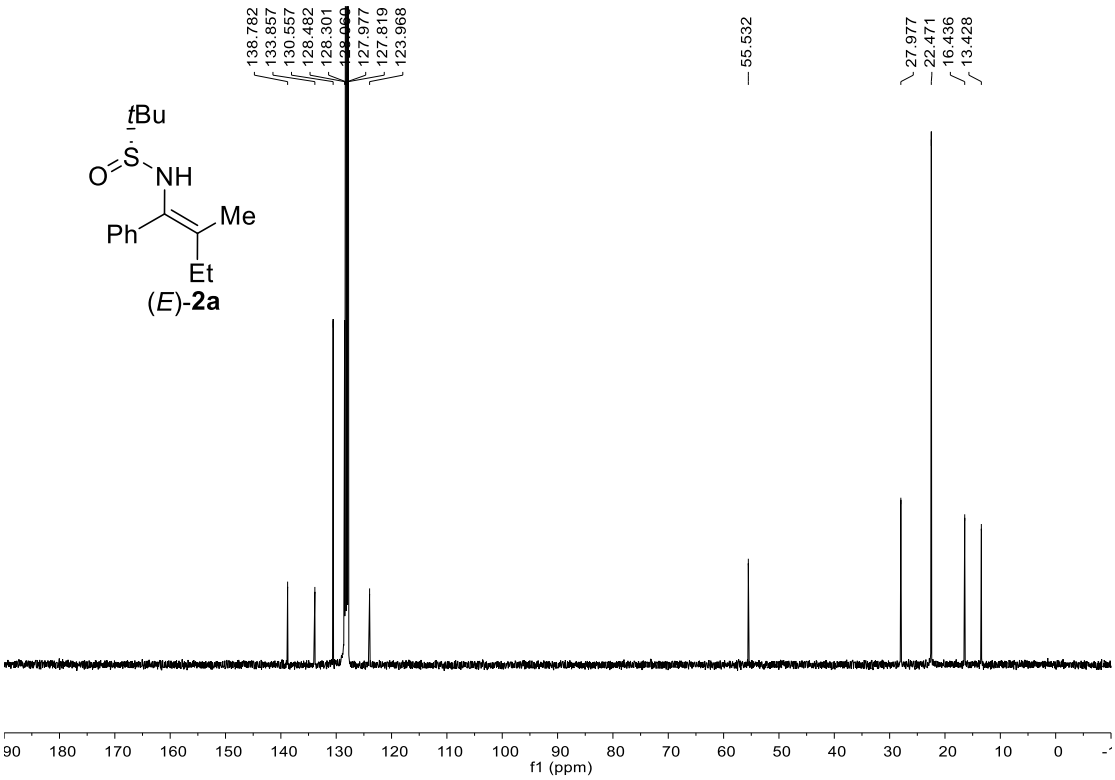
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2a** (Table 1 entry 1)



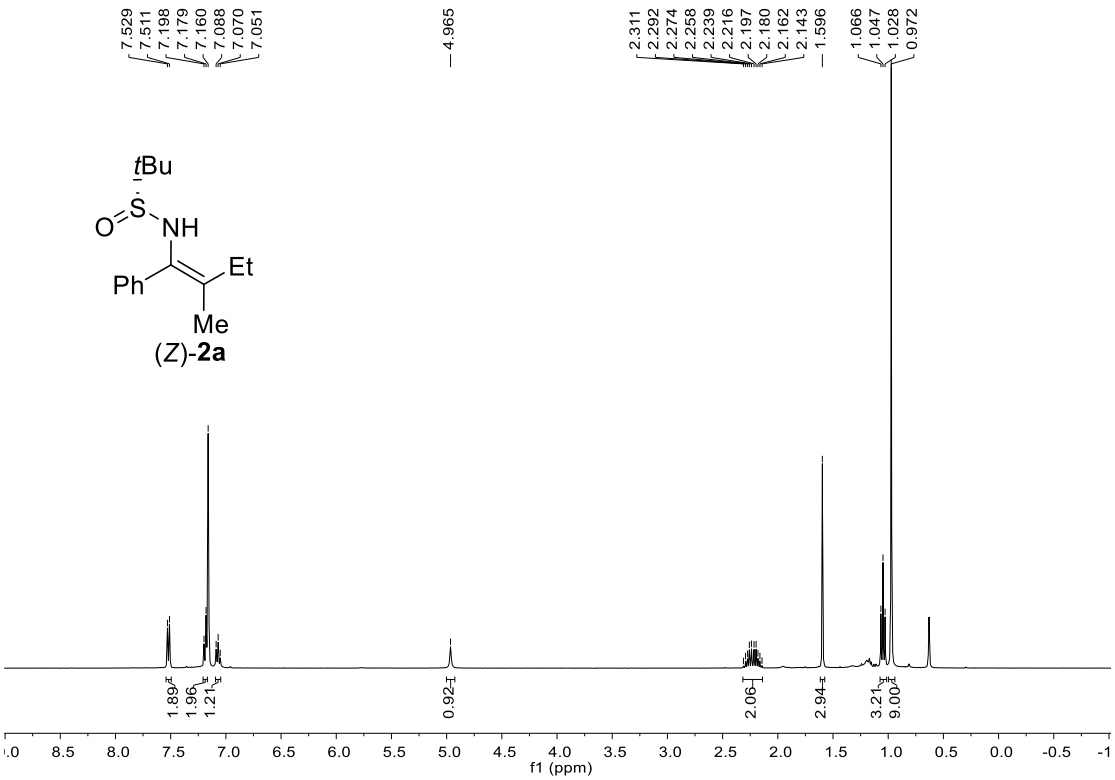
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2a** (Table 1 entry 1)



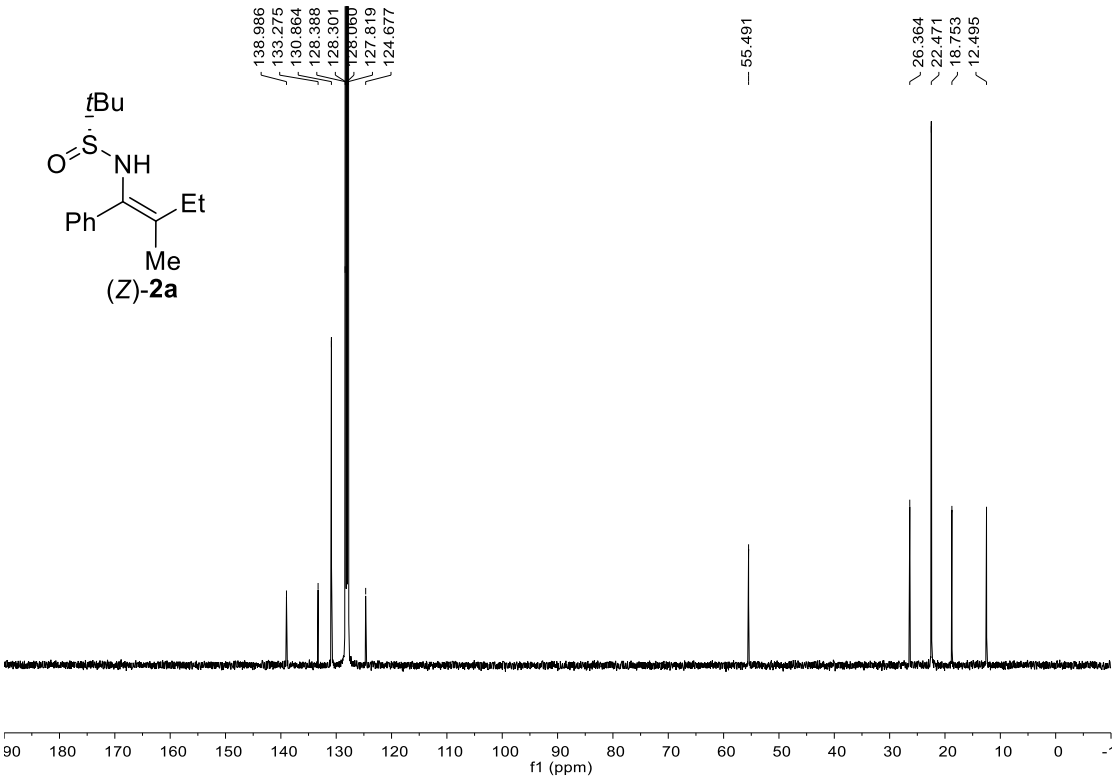
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2a** (Table 1 entry 2)



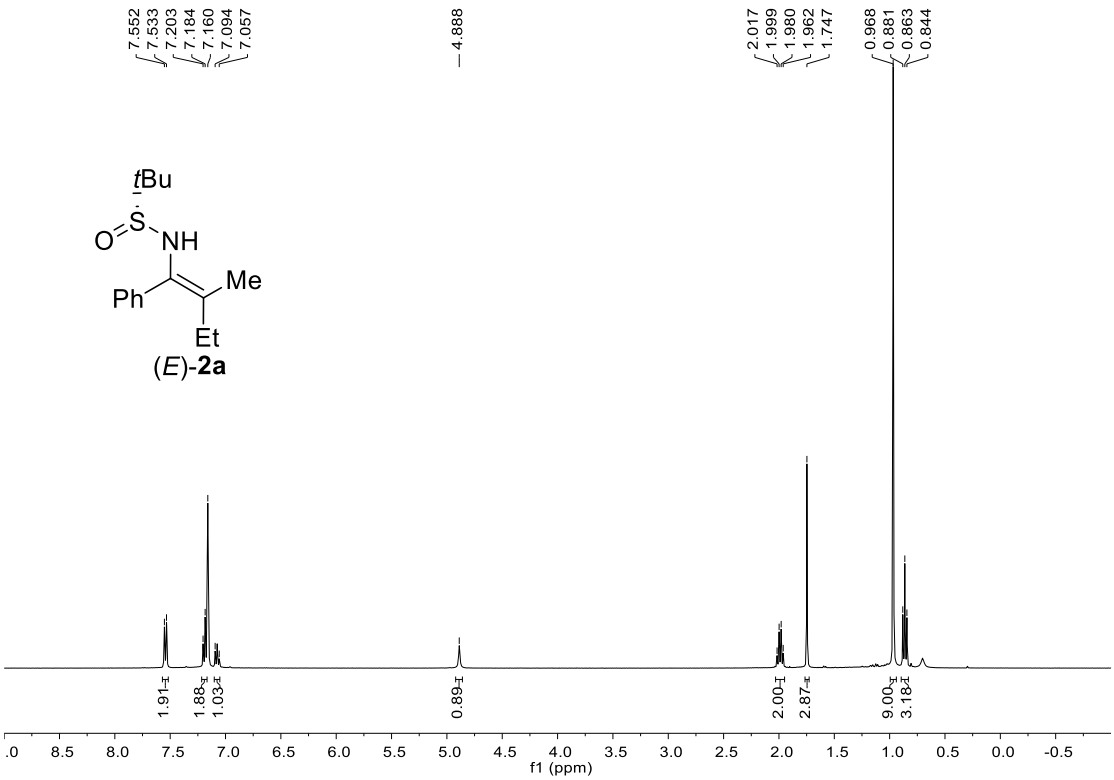
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2a** (Table 1 entry 2)



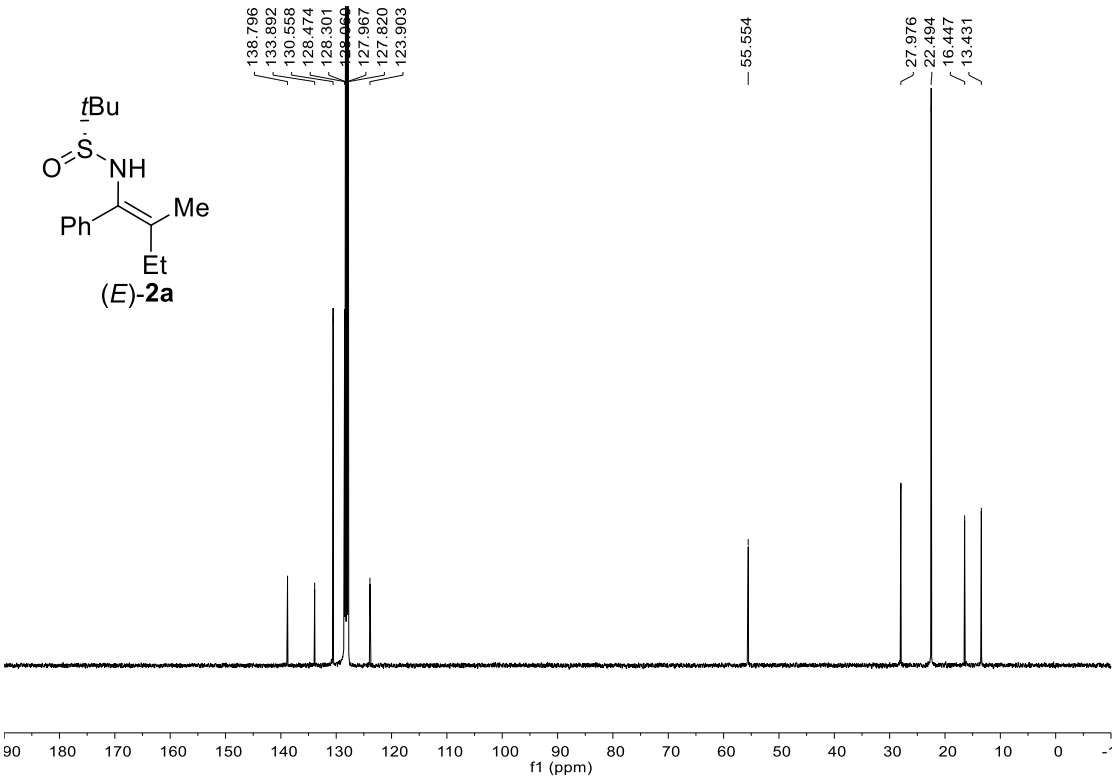
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2a** (Table 1 entry 10)



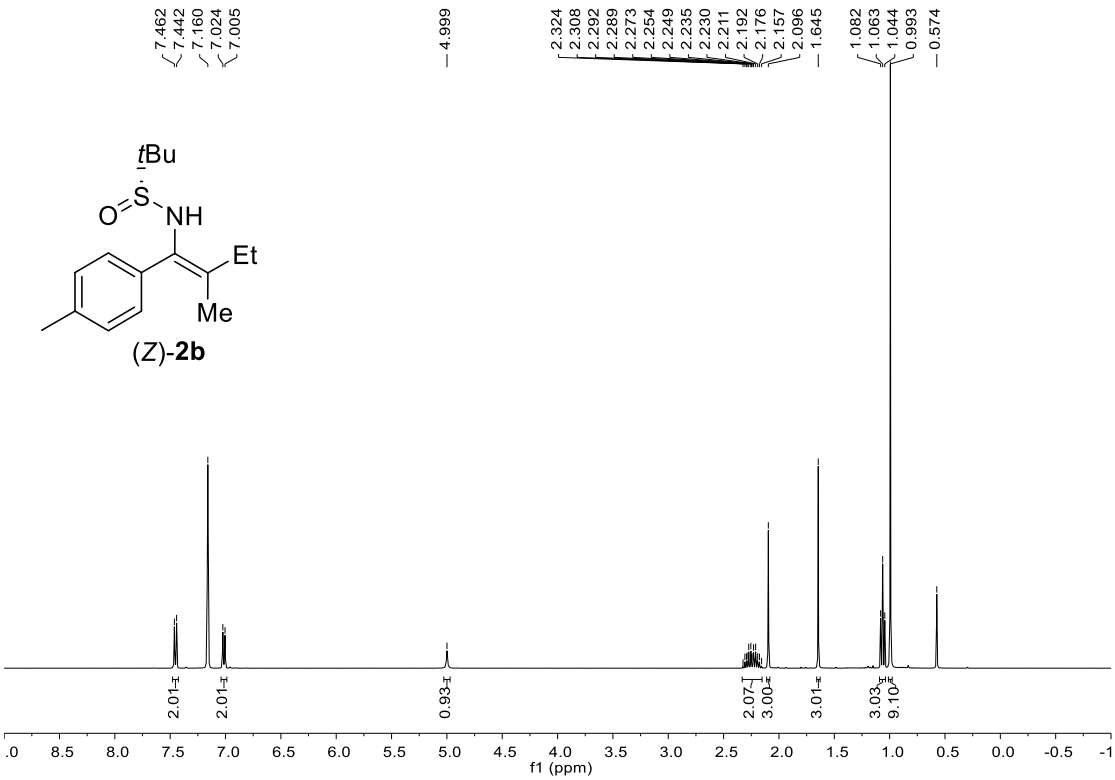
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2a** (Table 1 entry 10)



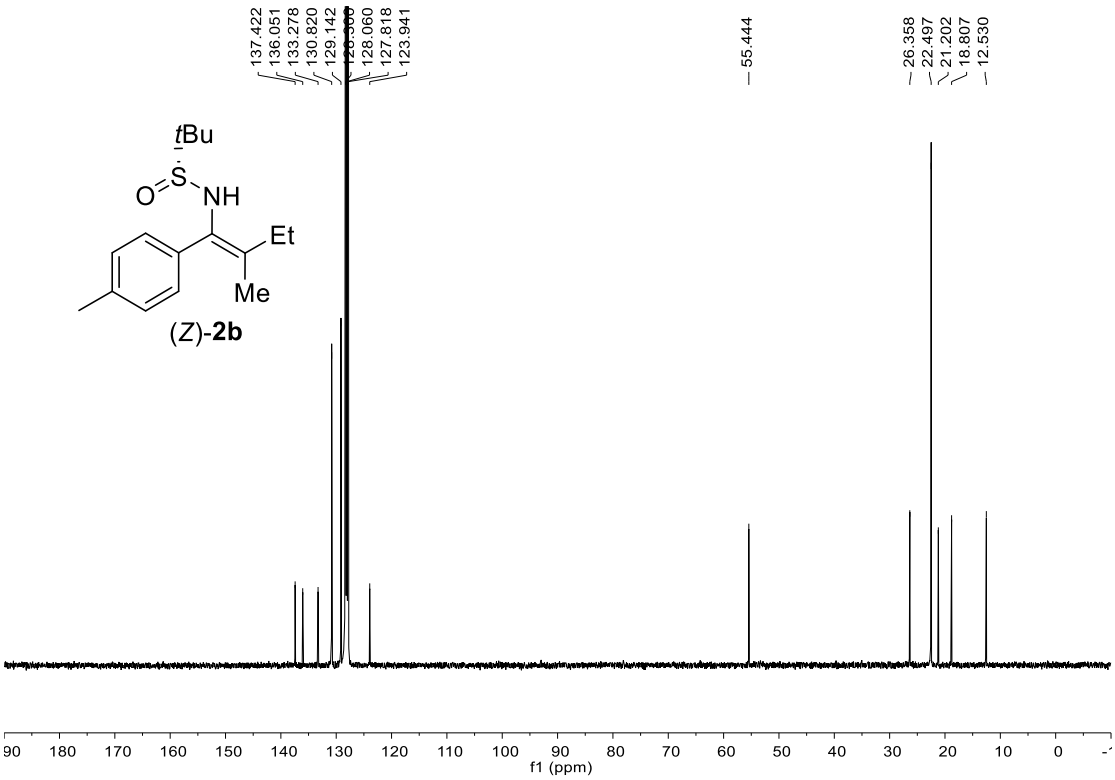
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2a** (Table 1 entry 11)



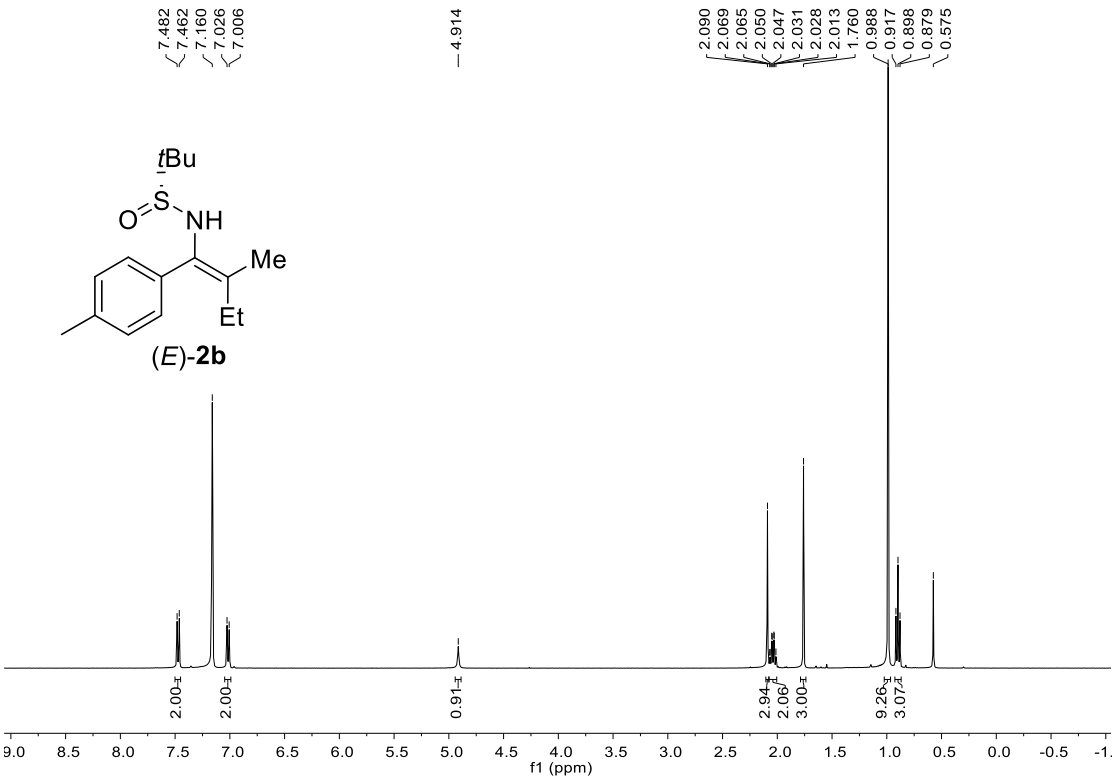
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2a** (Table 1 entry 11)



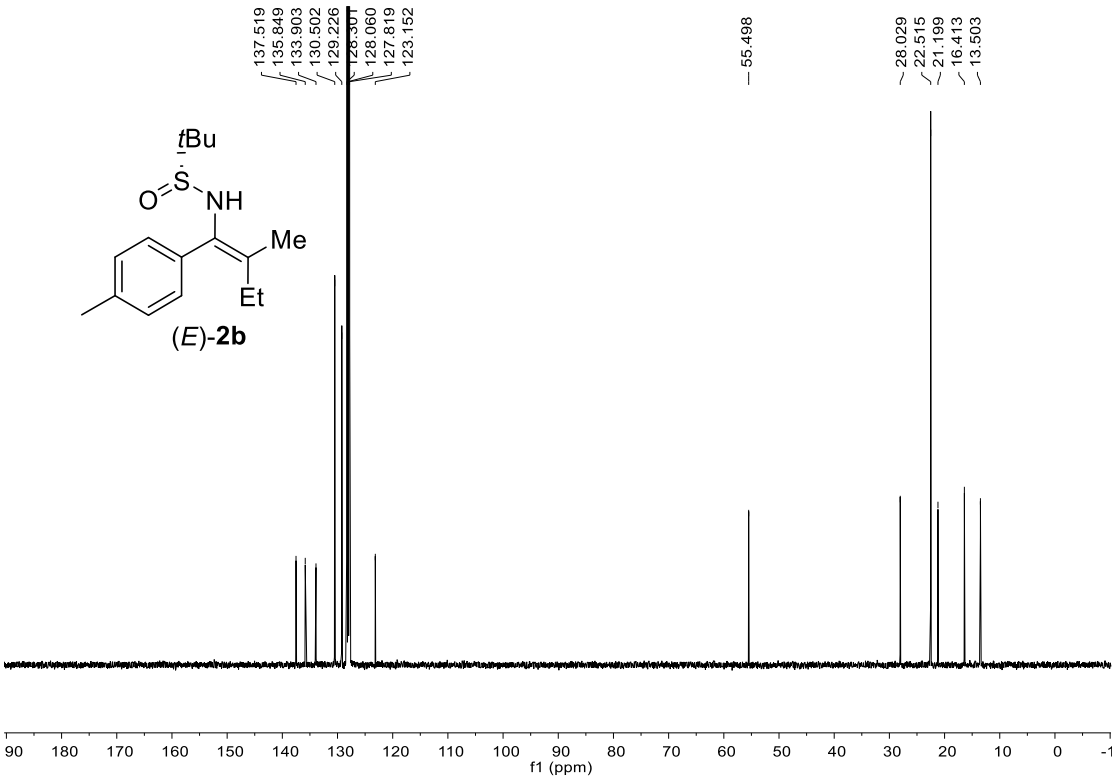
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2b**



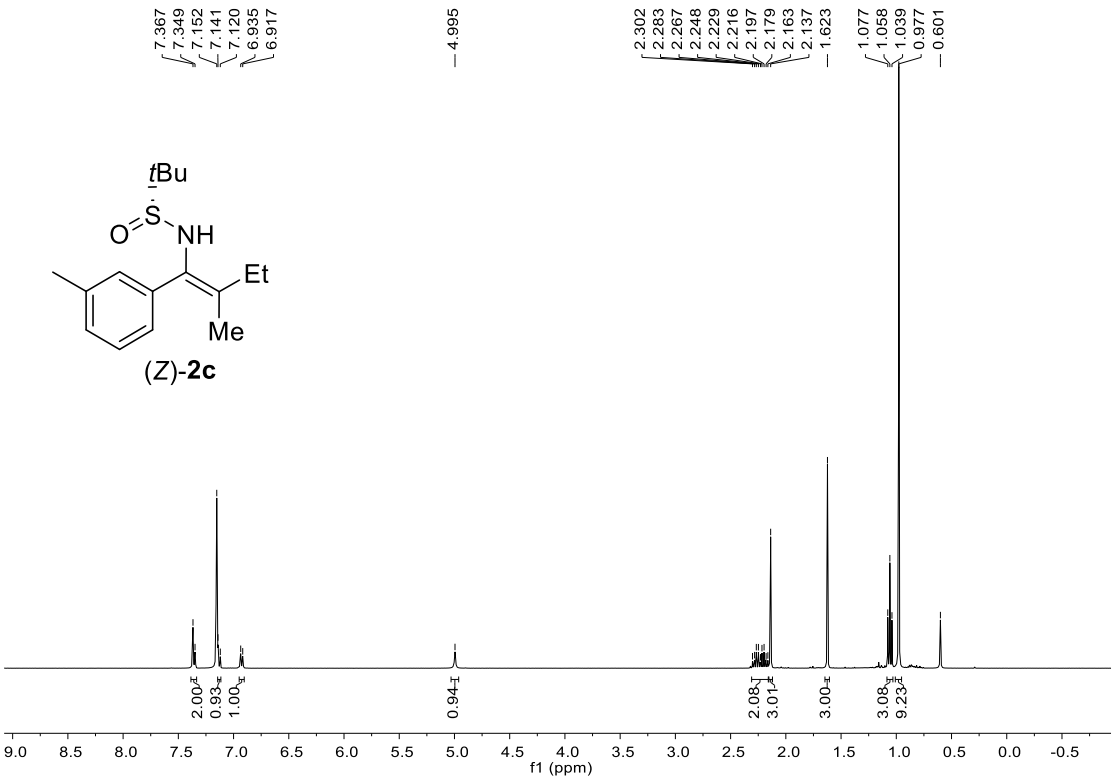
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2b**



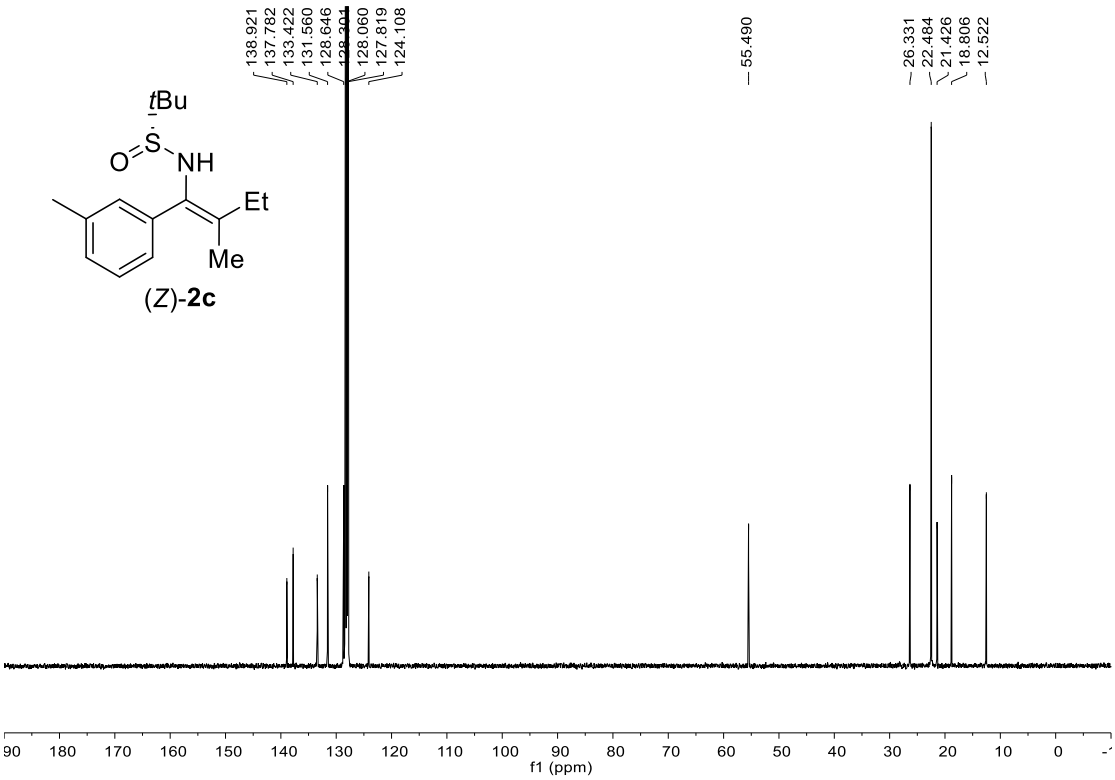
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2b**



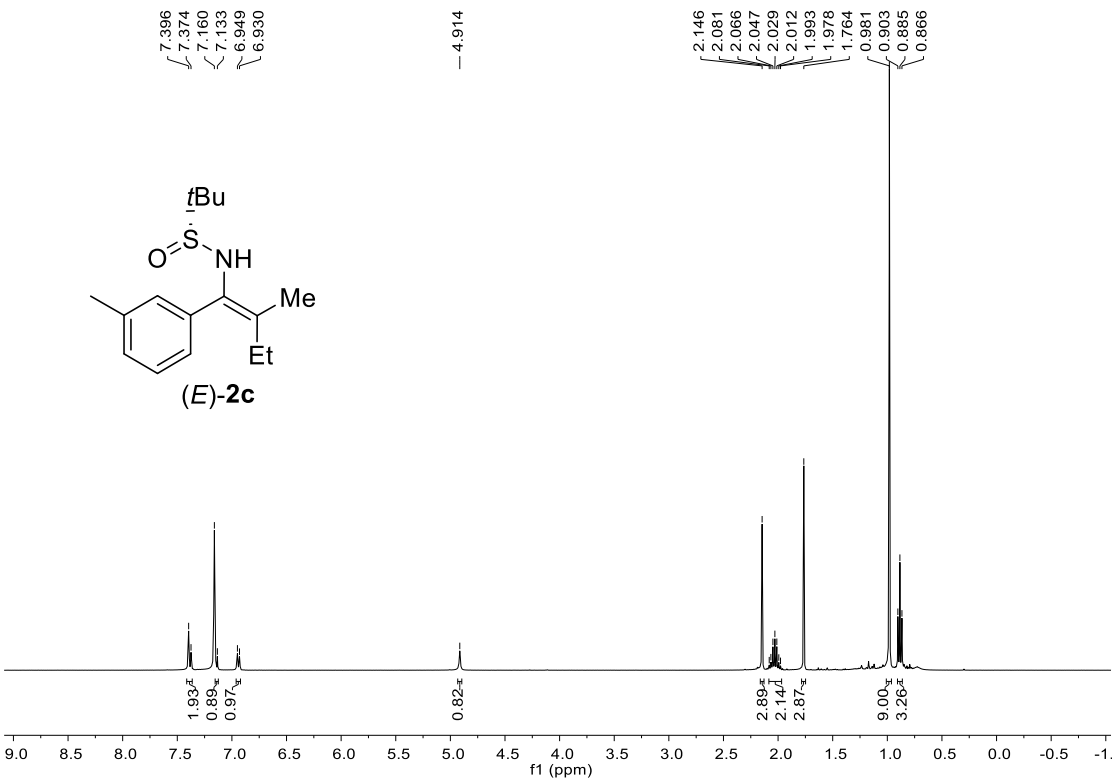
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2b**



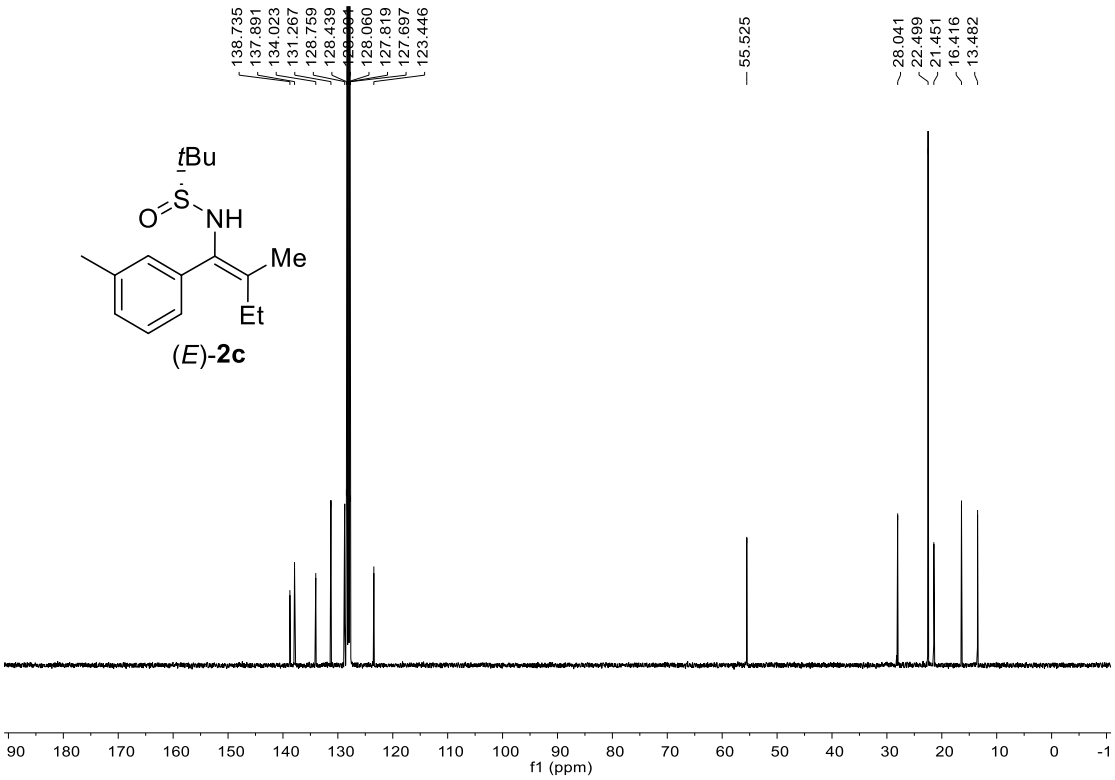
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2c**



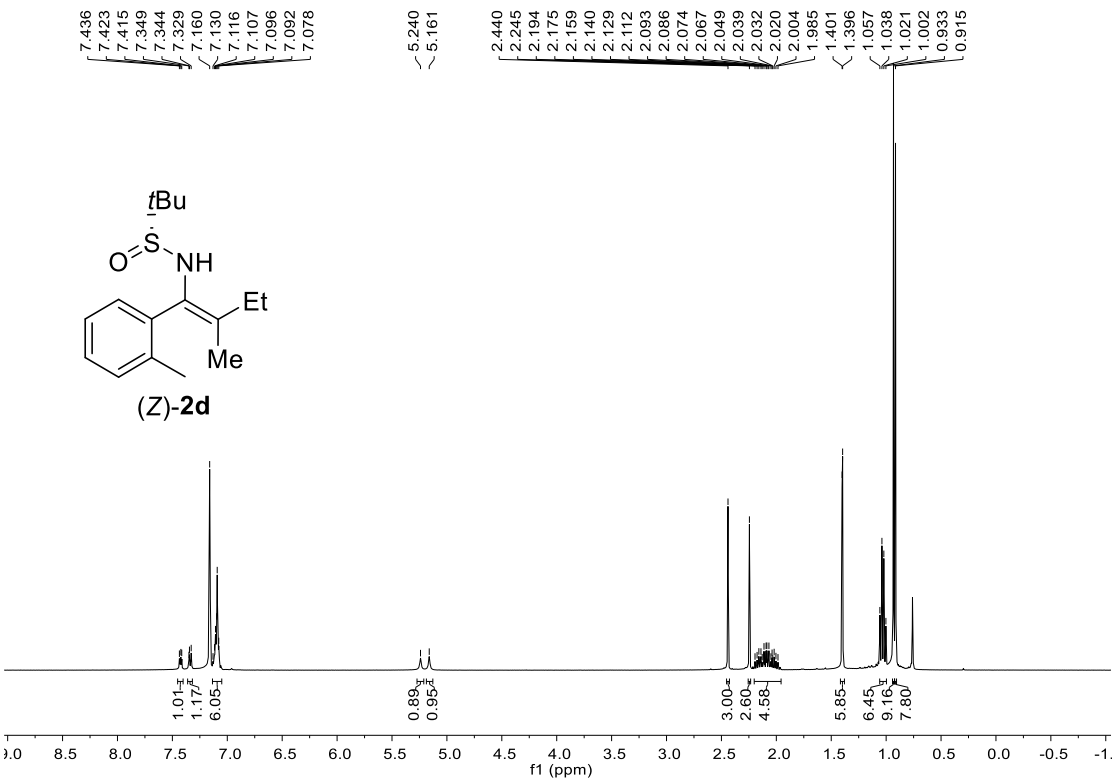
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2c**



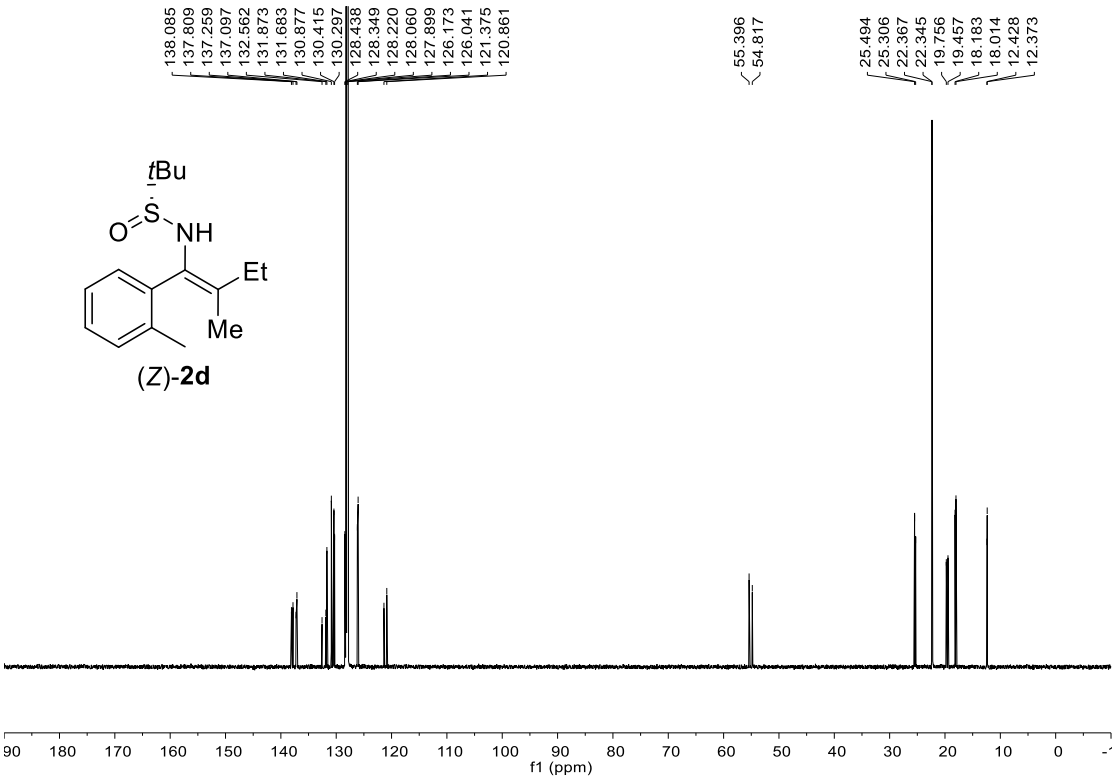
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2c**



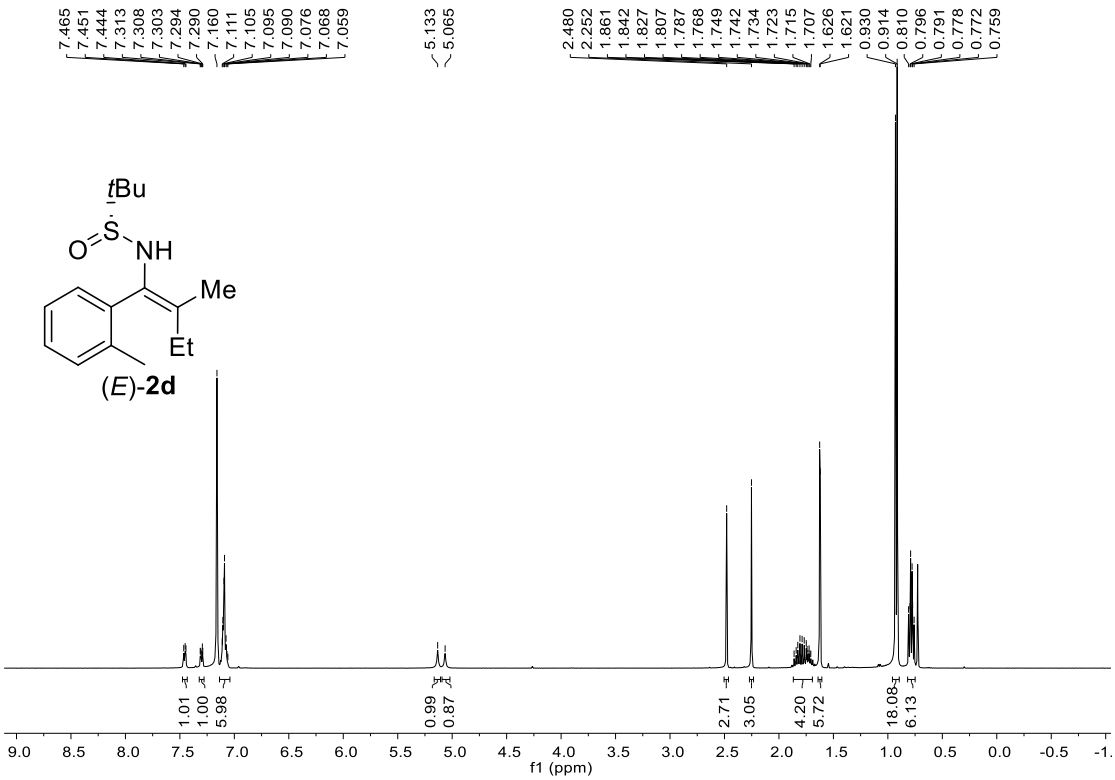
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2c**



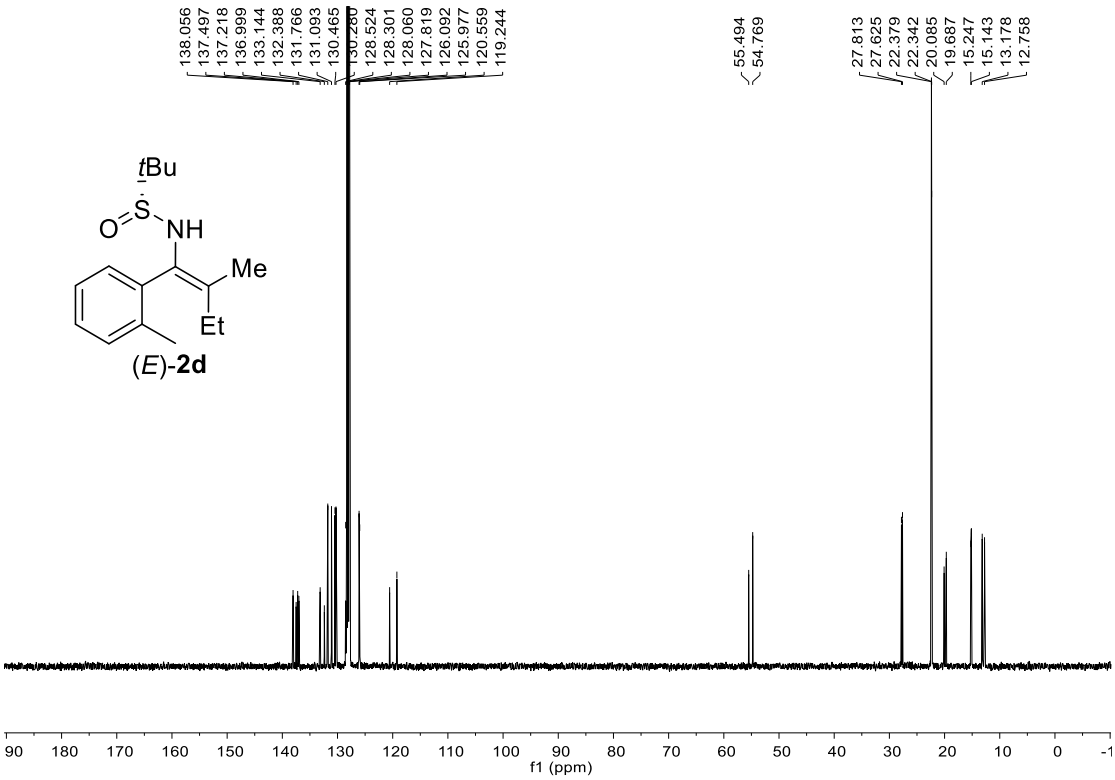
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2d** (mixture of rotamers)



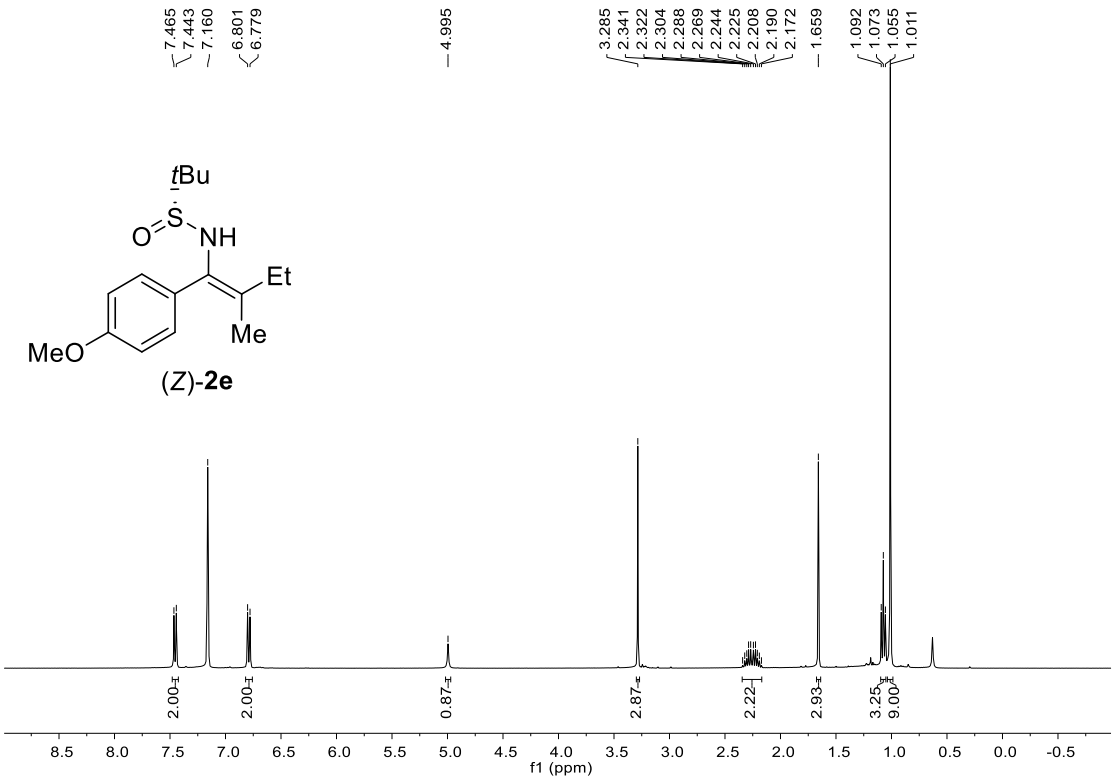
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*Z*)-**2d** (mixture of rotamers)



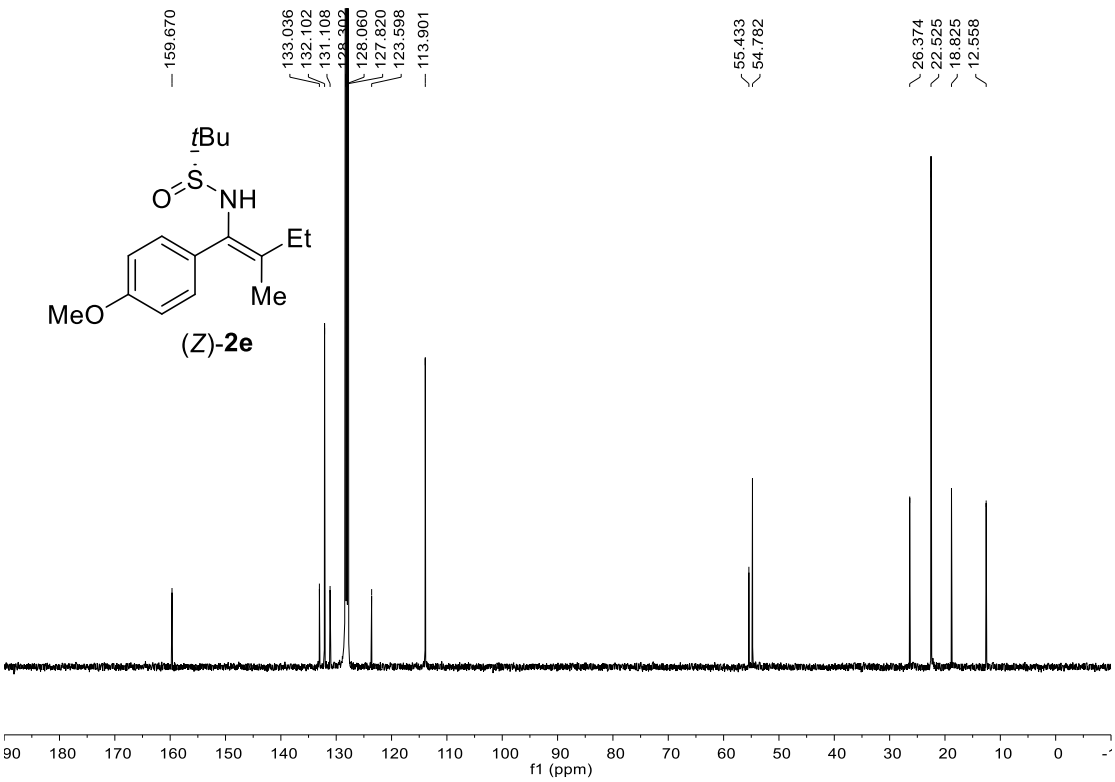
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2d** (mixture of rotamers)



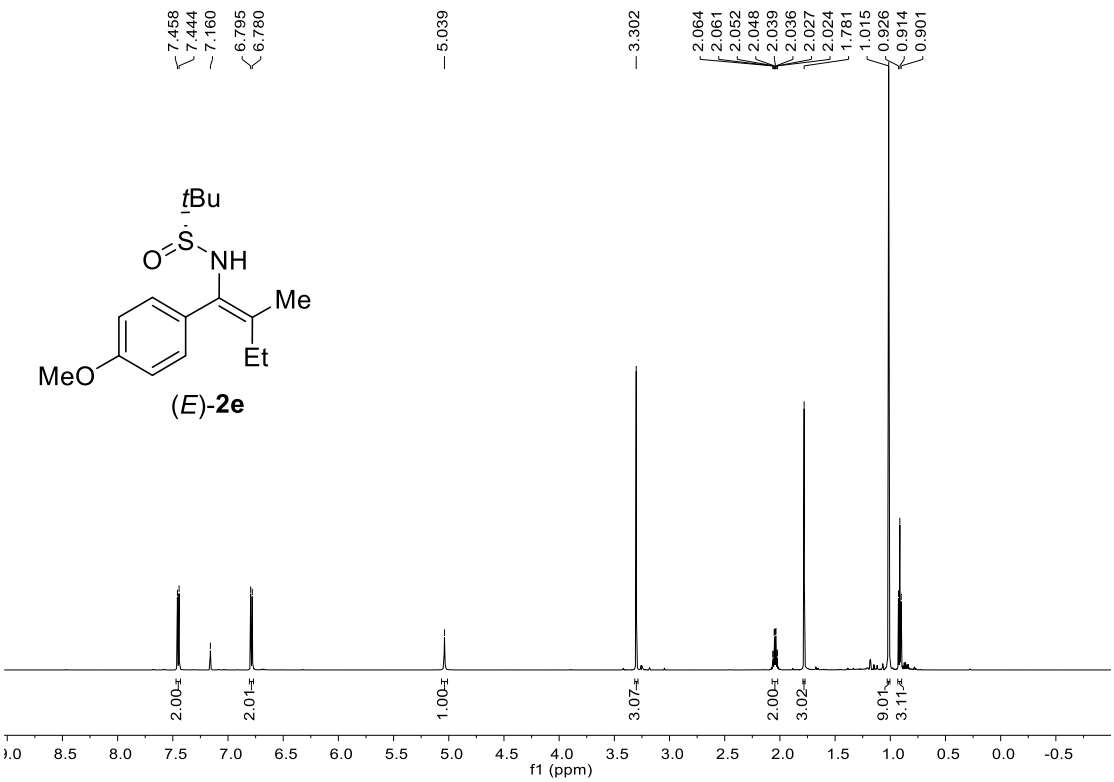
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2d** (mixture of rotamers)



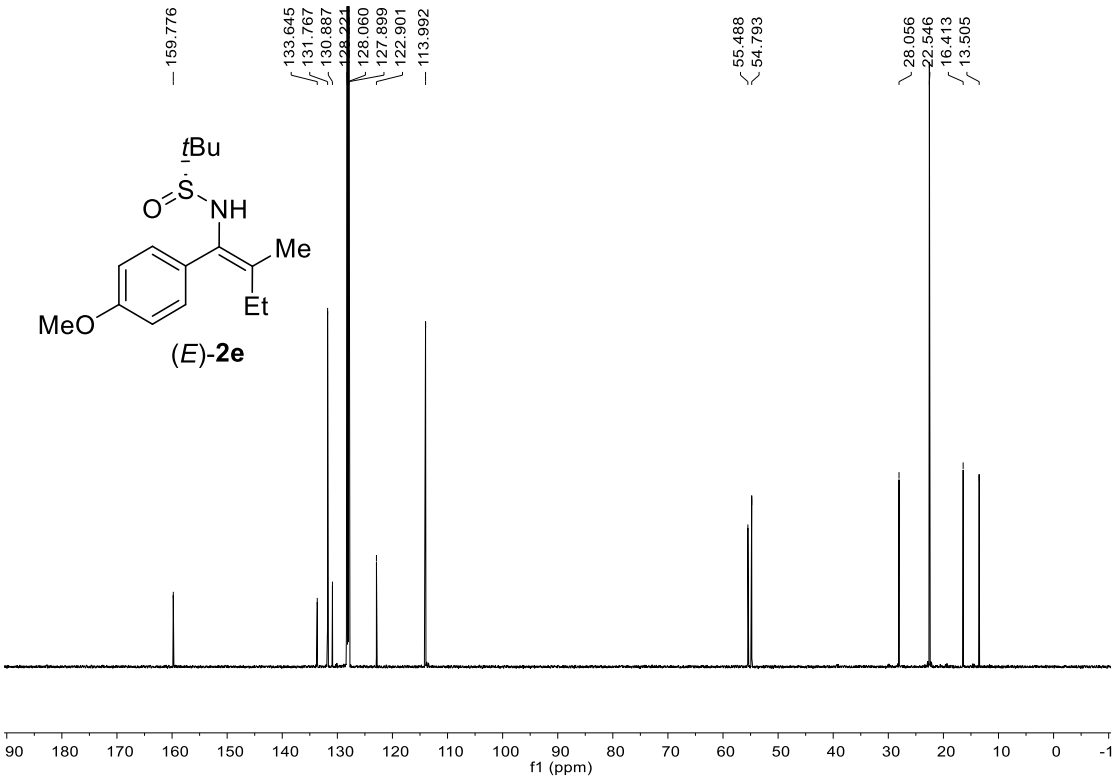
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2e**



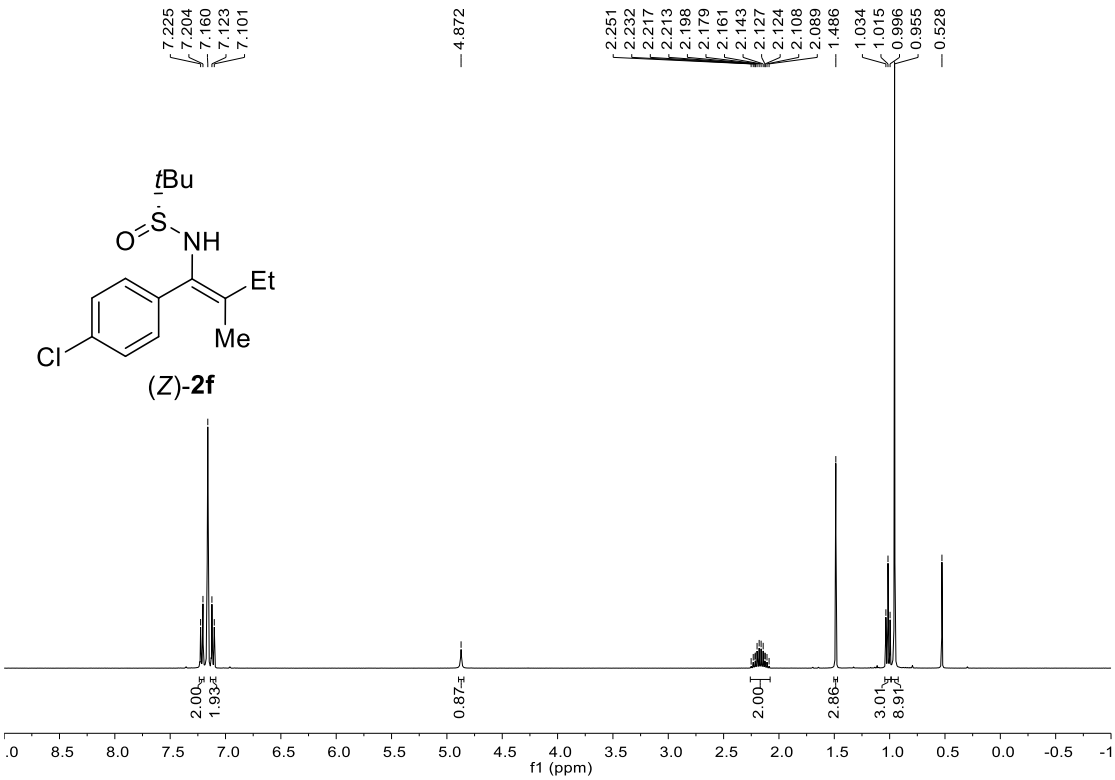
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2e**



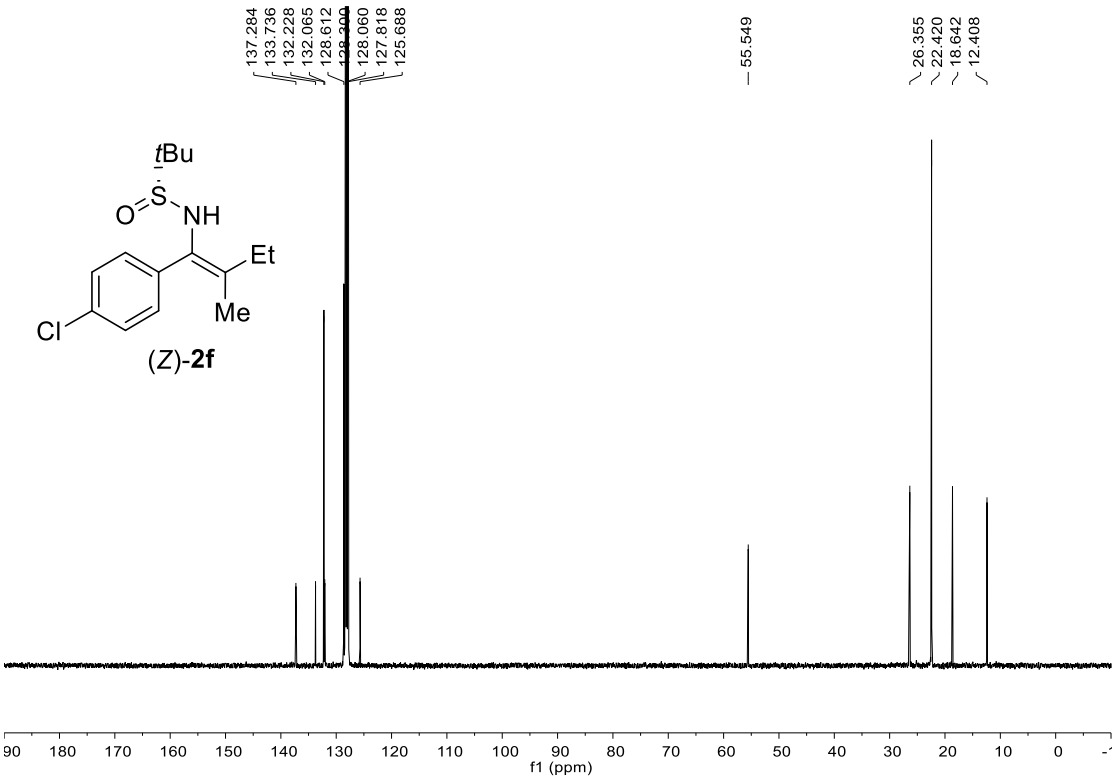
^{1}H NMR spectrum (C_6D_6, 600 MHz) of (*E*)-**2e**



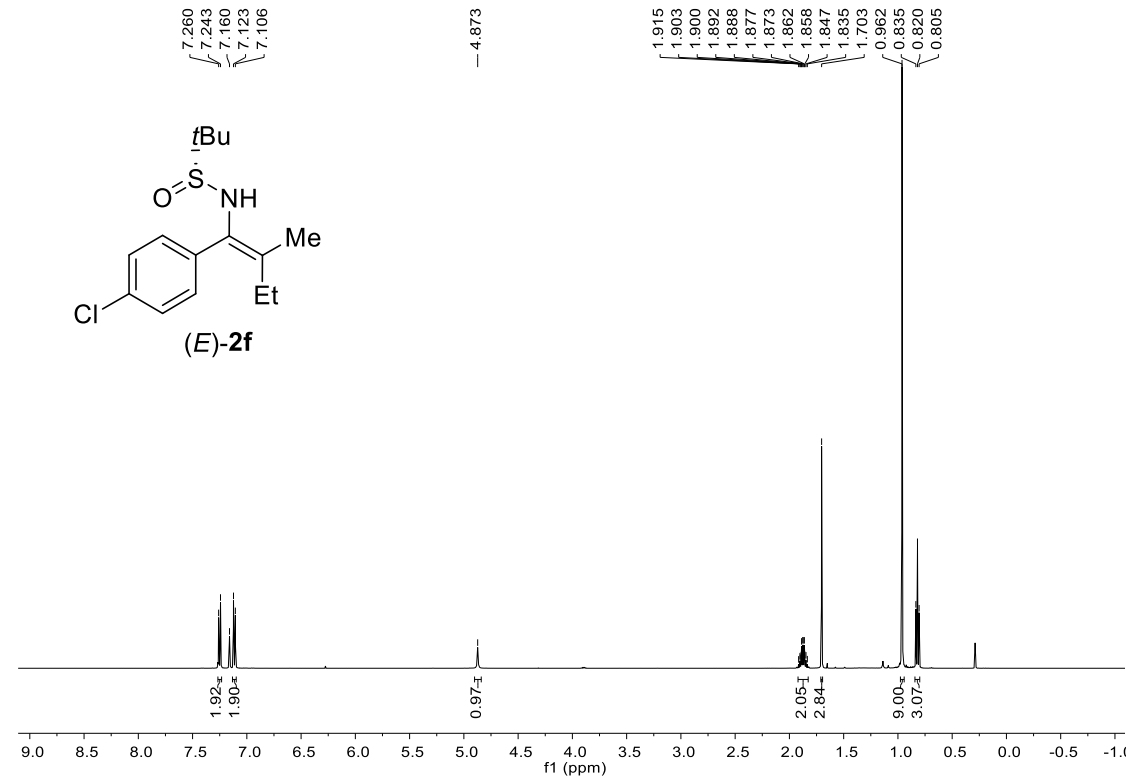
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2e**



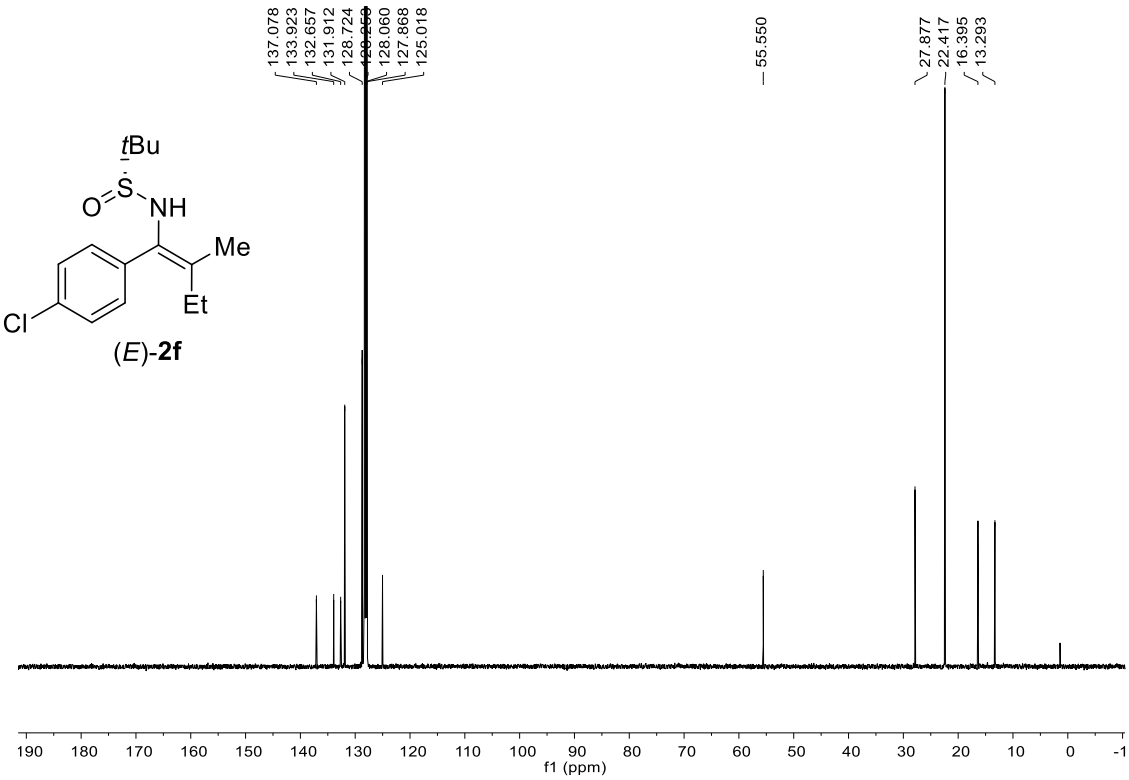
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2f**



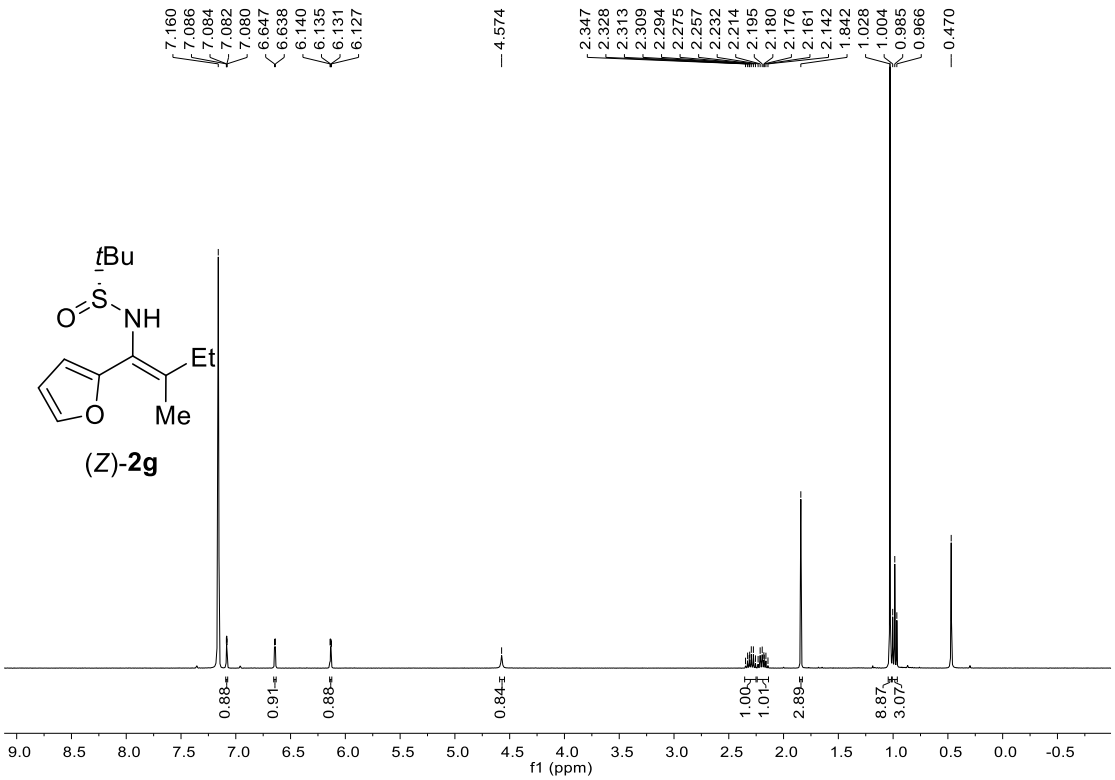
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2f**



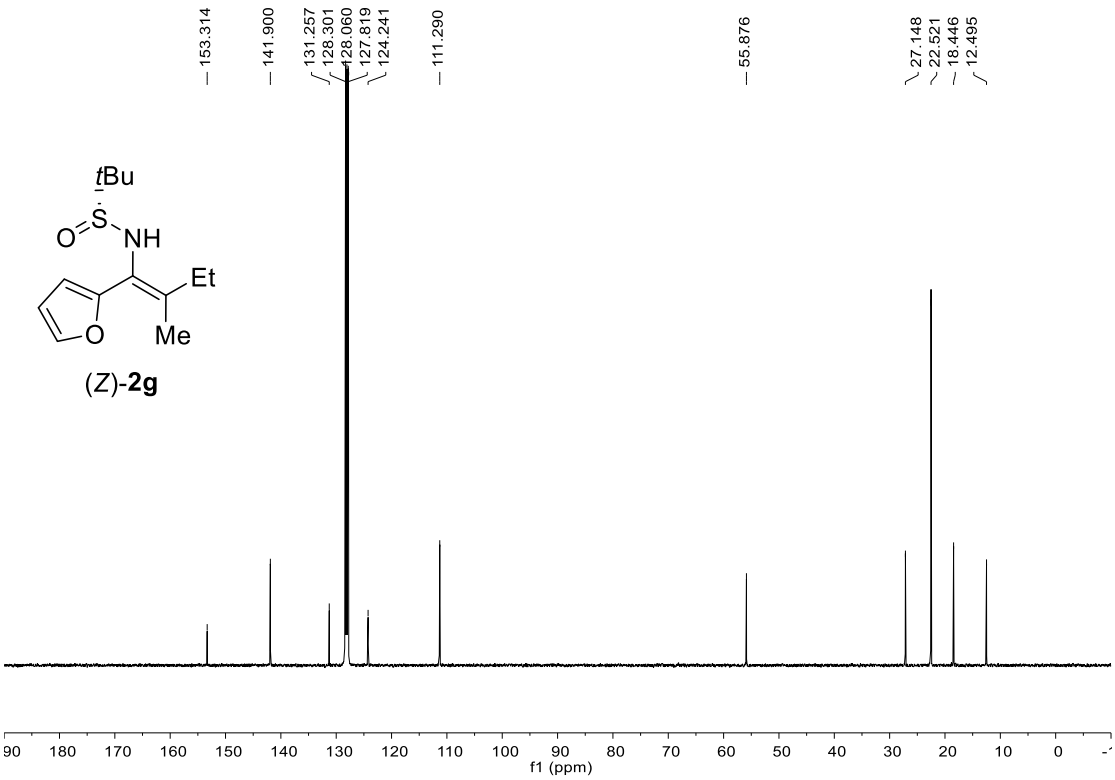
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2f**



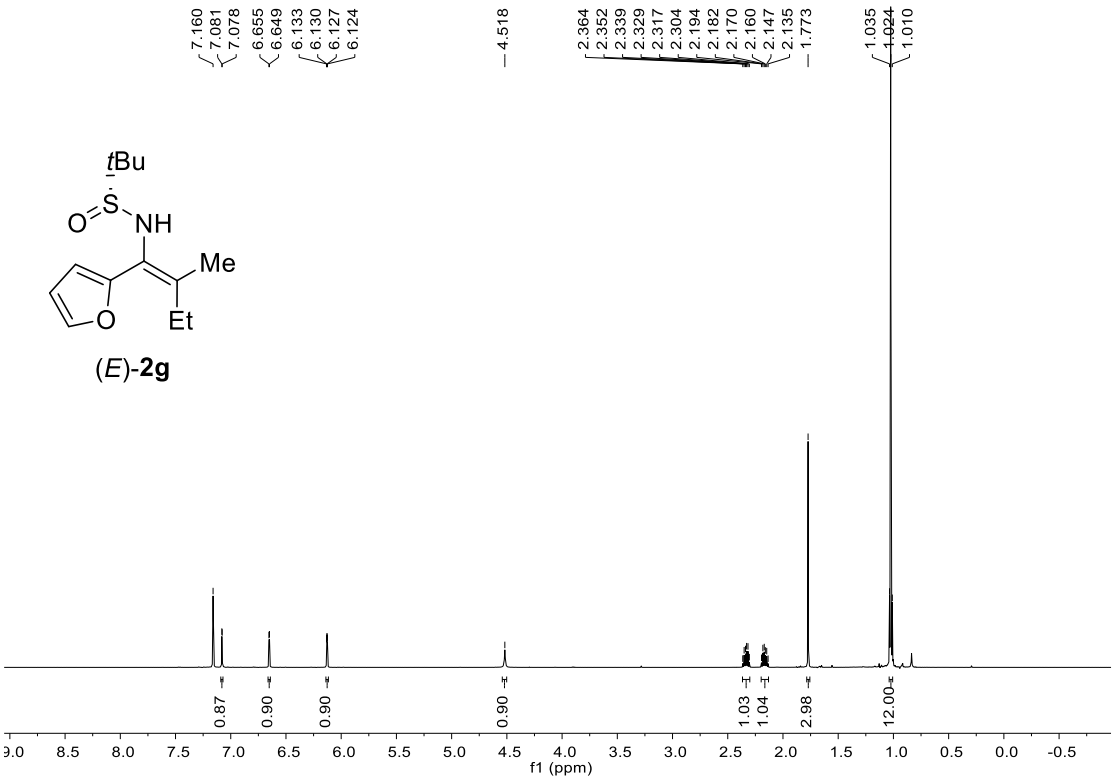
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2f**



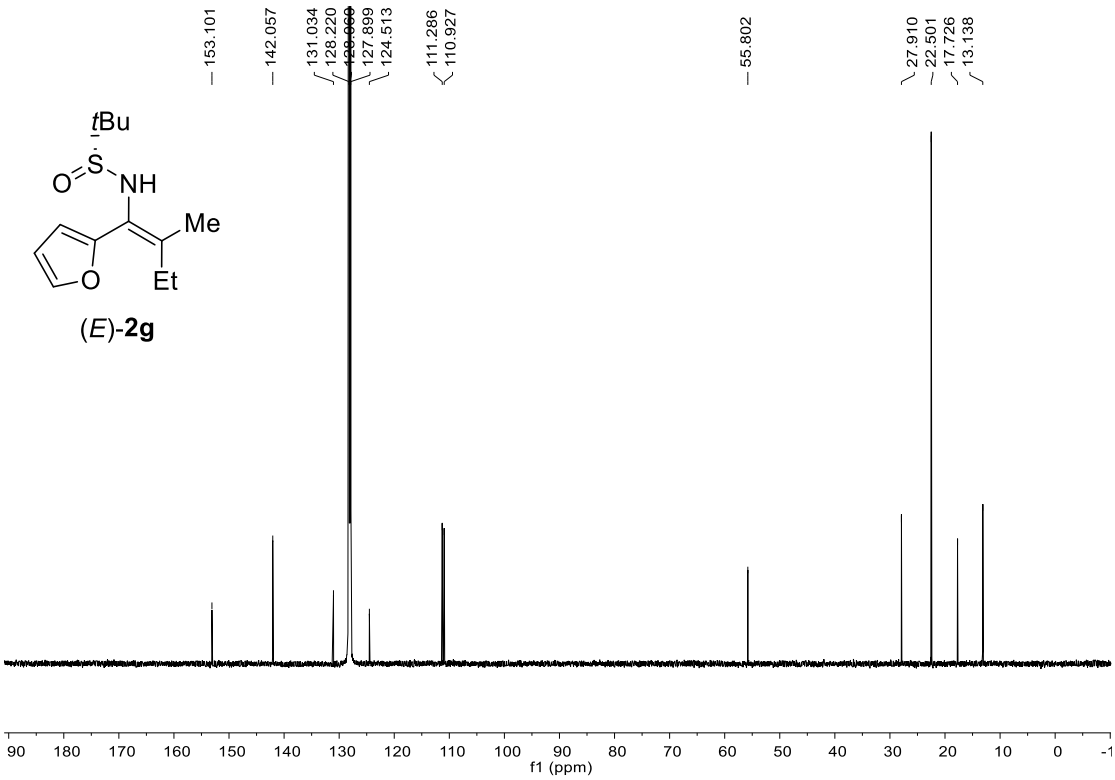
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2g**



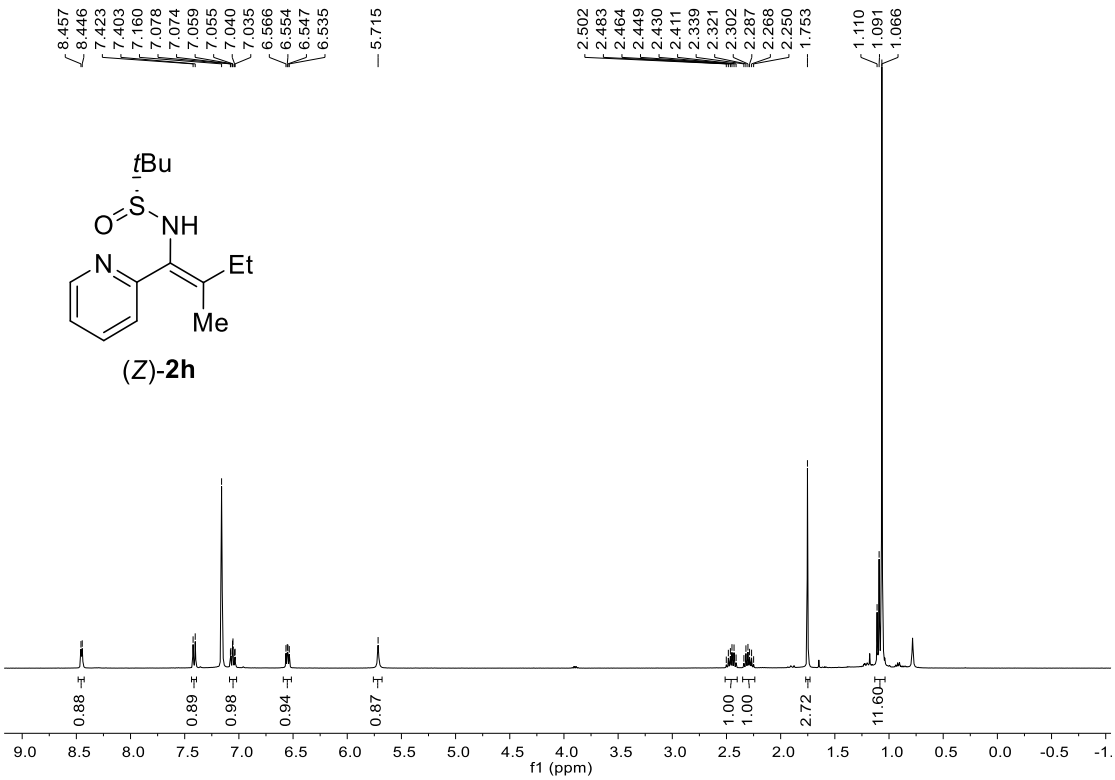
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2g**



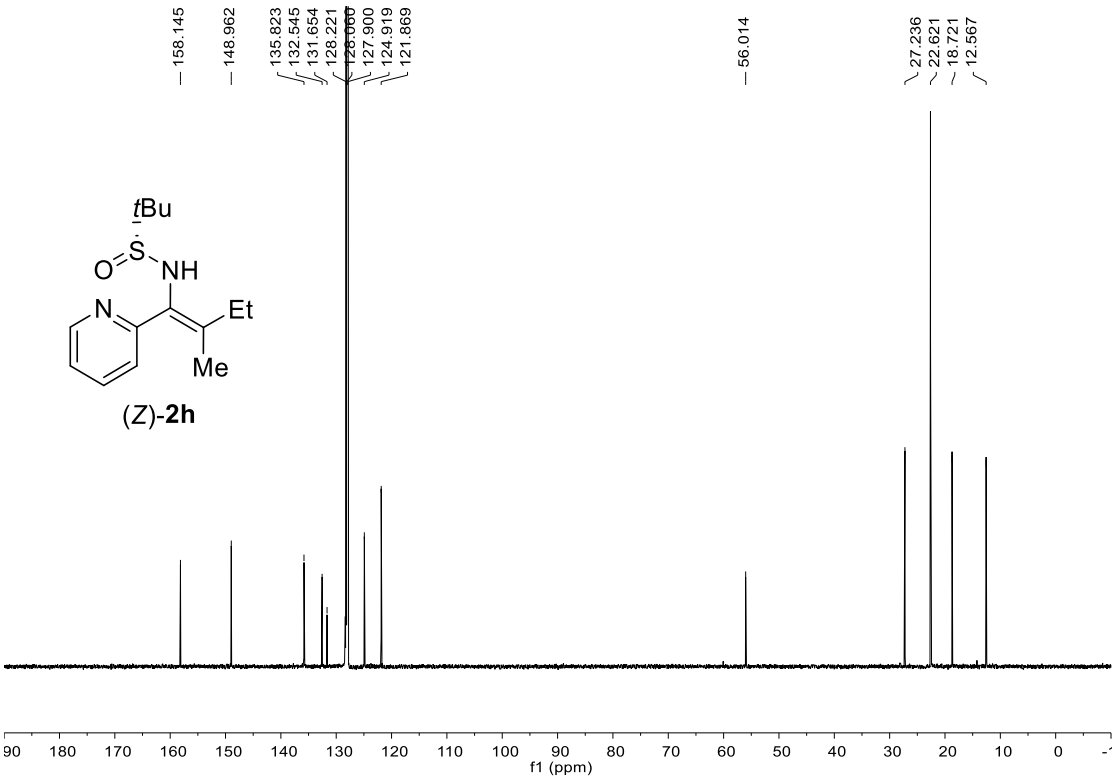
^{1}H NMR spectrum (C_6D_6, 600 MHz) of (*E*)-**2g**



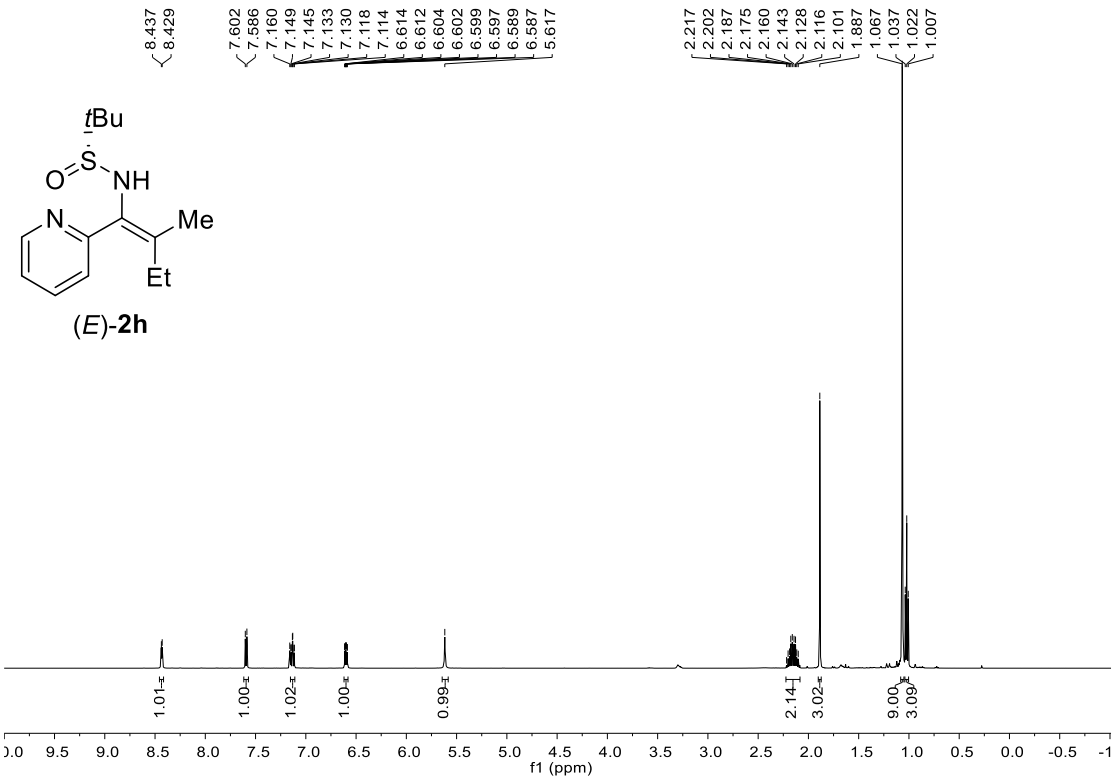
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2g**



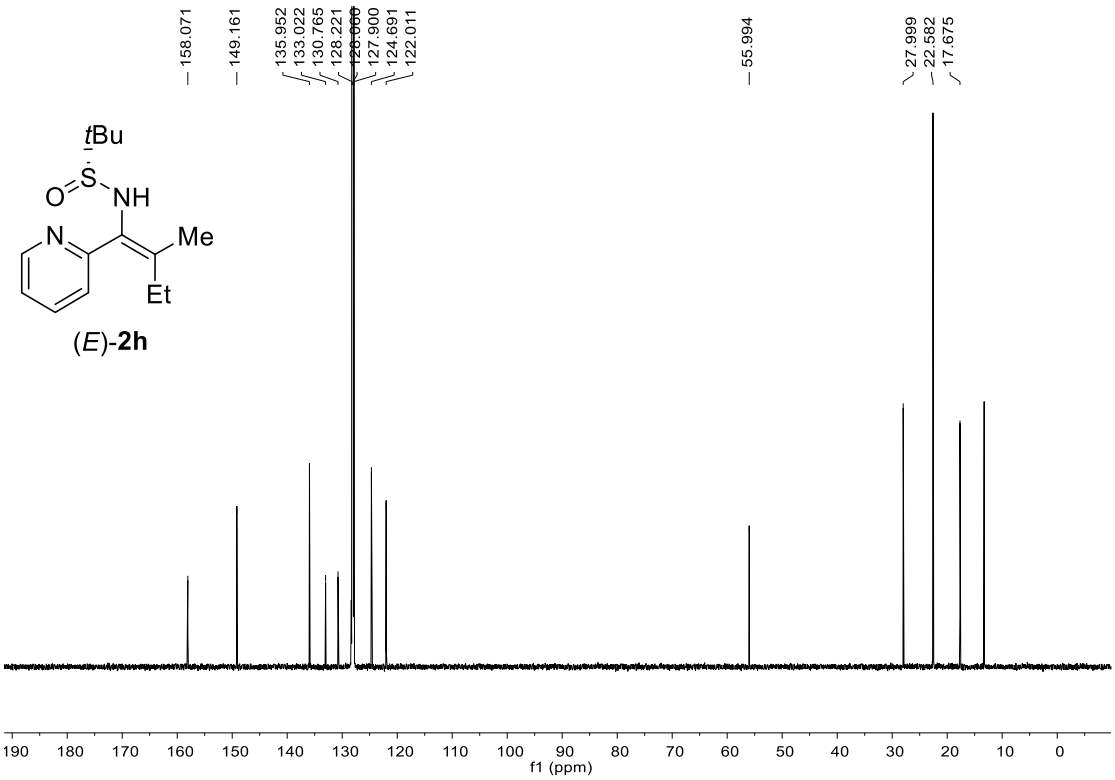
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2h**



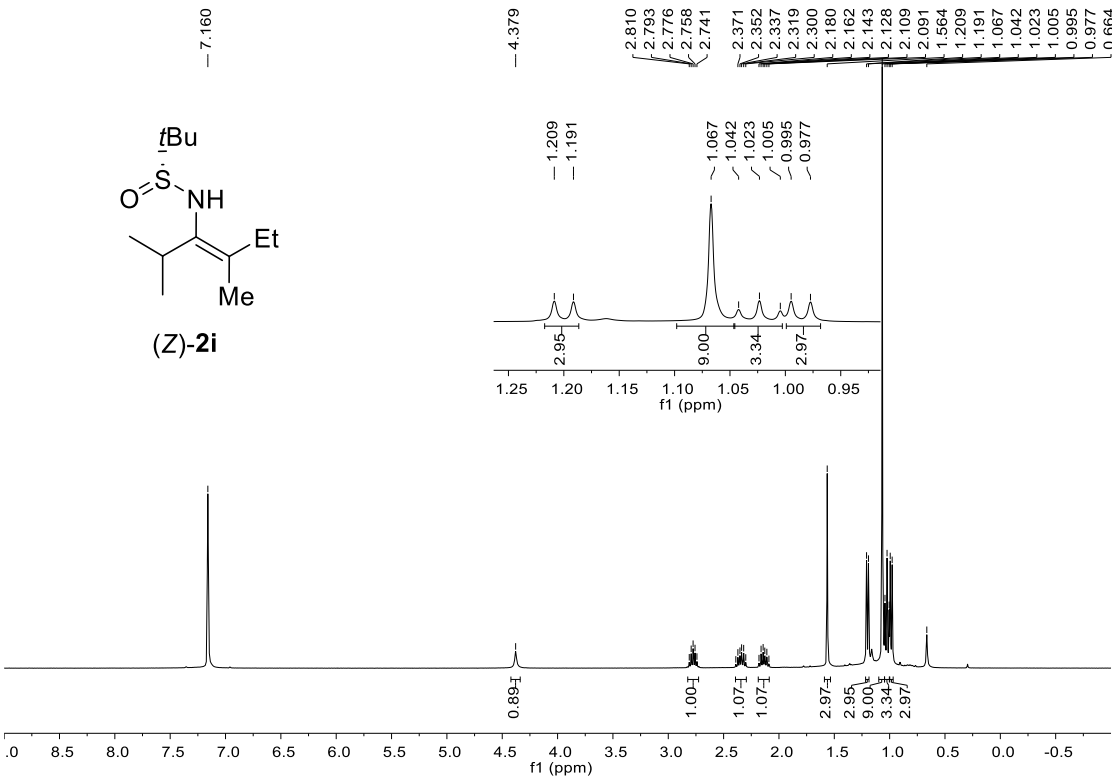
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*Z*)-**2h**



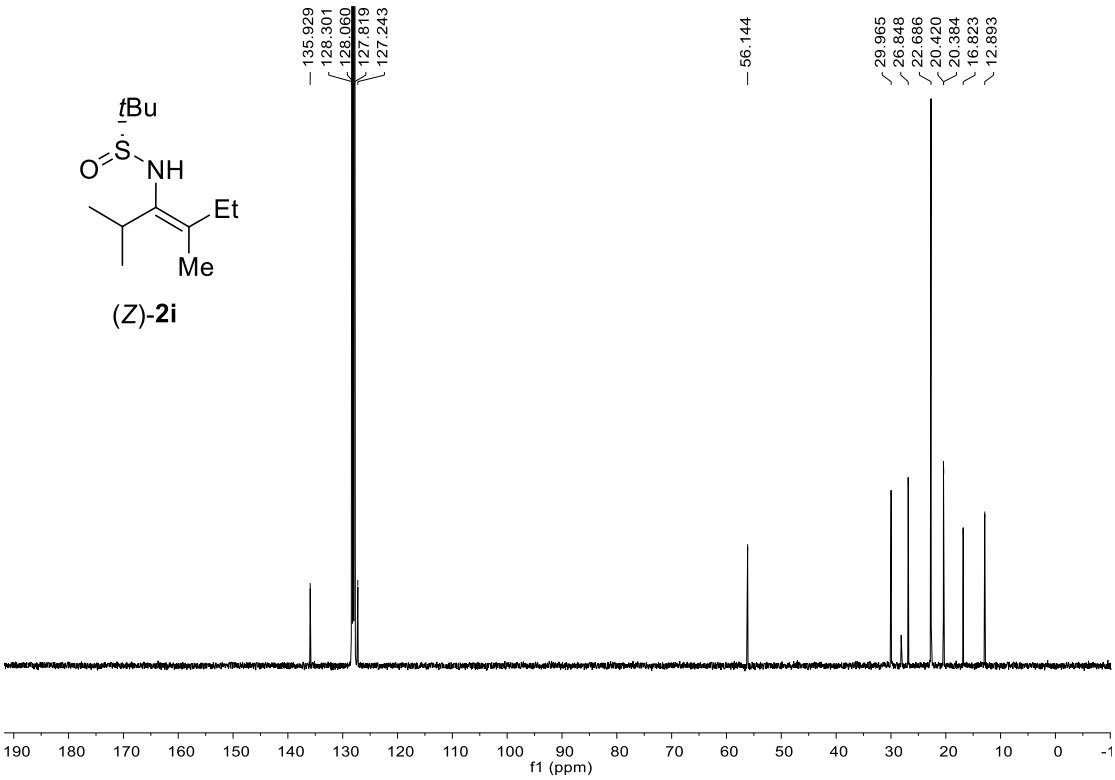
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2h**



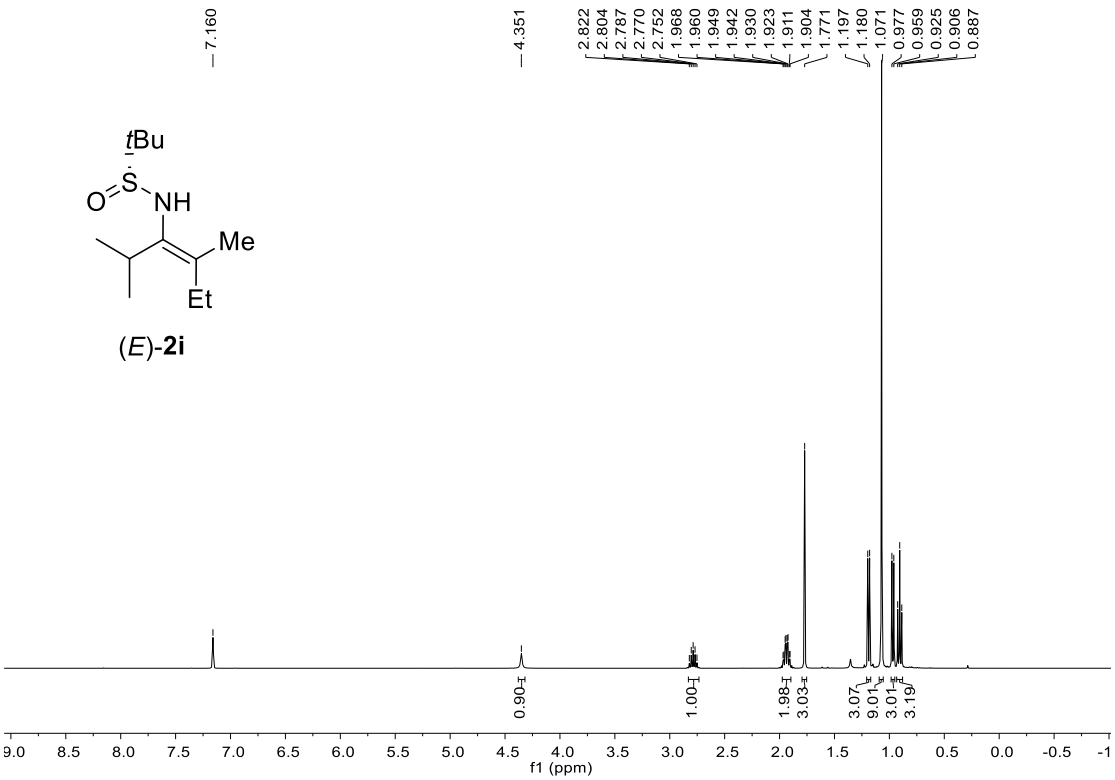
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2h**



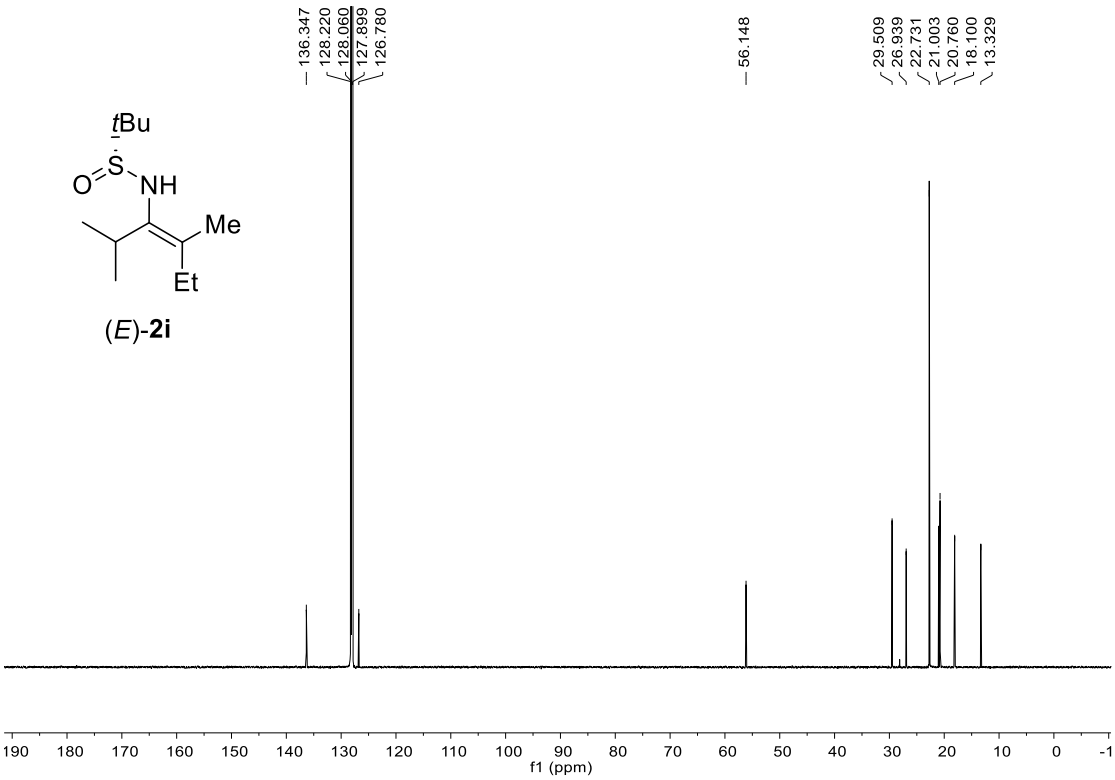
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2i**



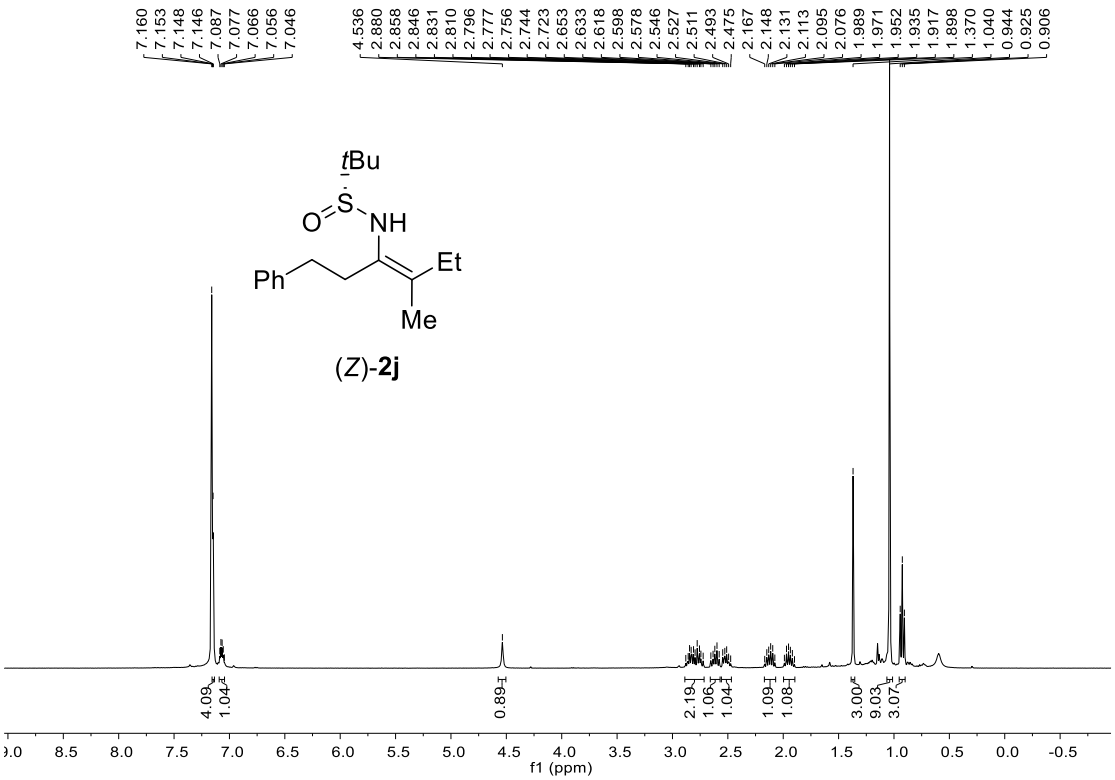
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2i**



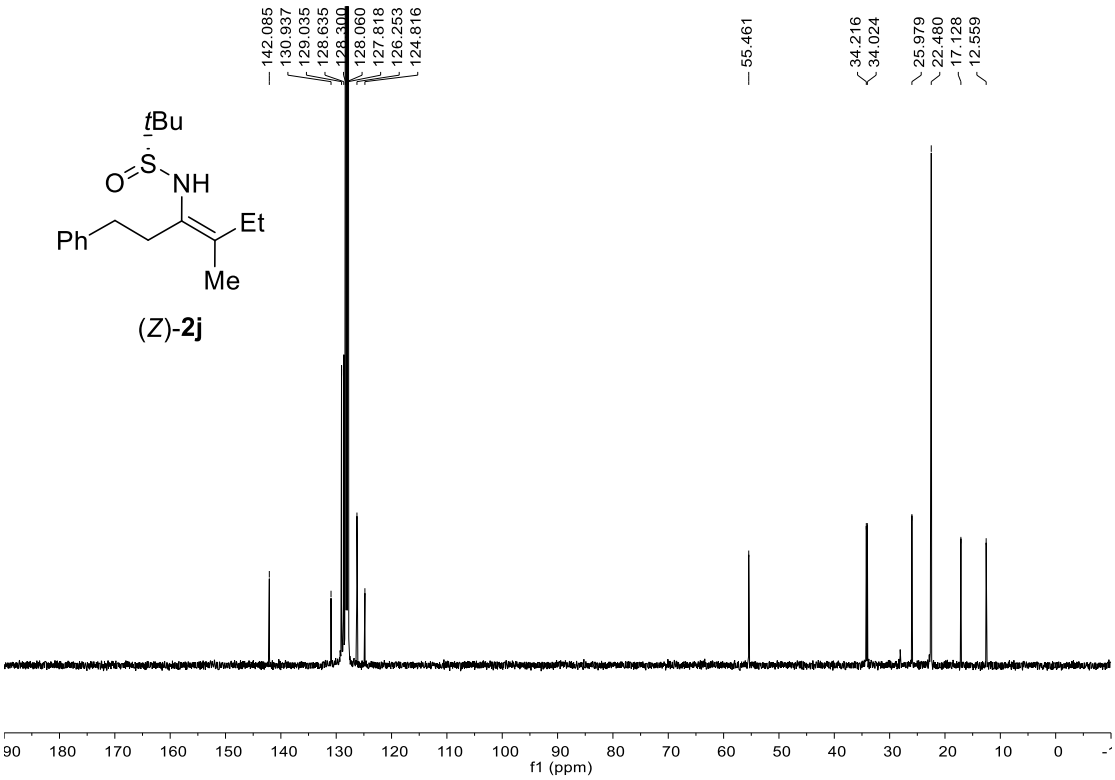
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2i**



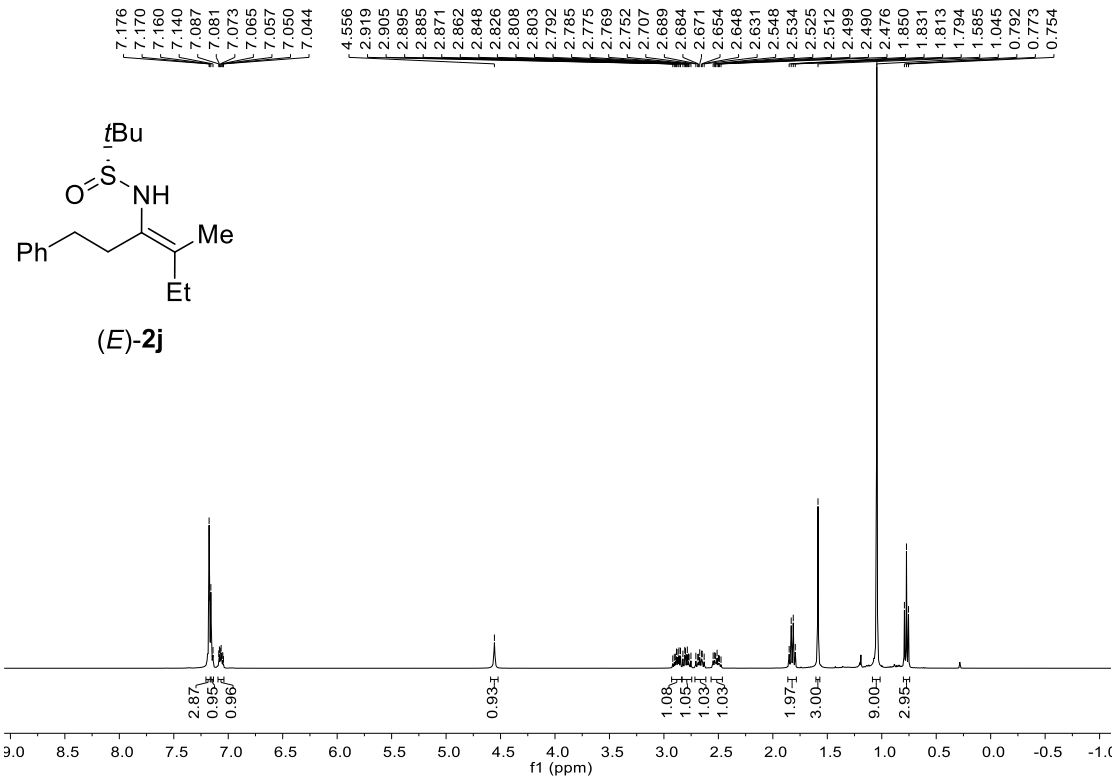
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2i**



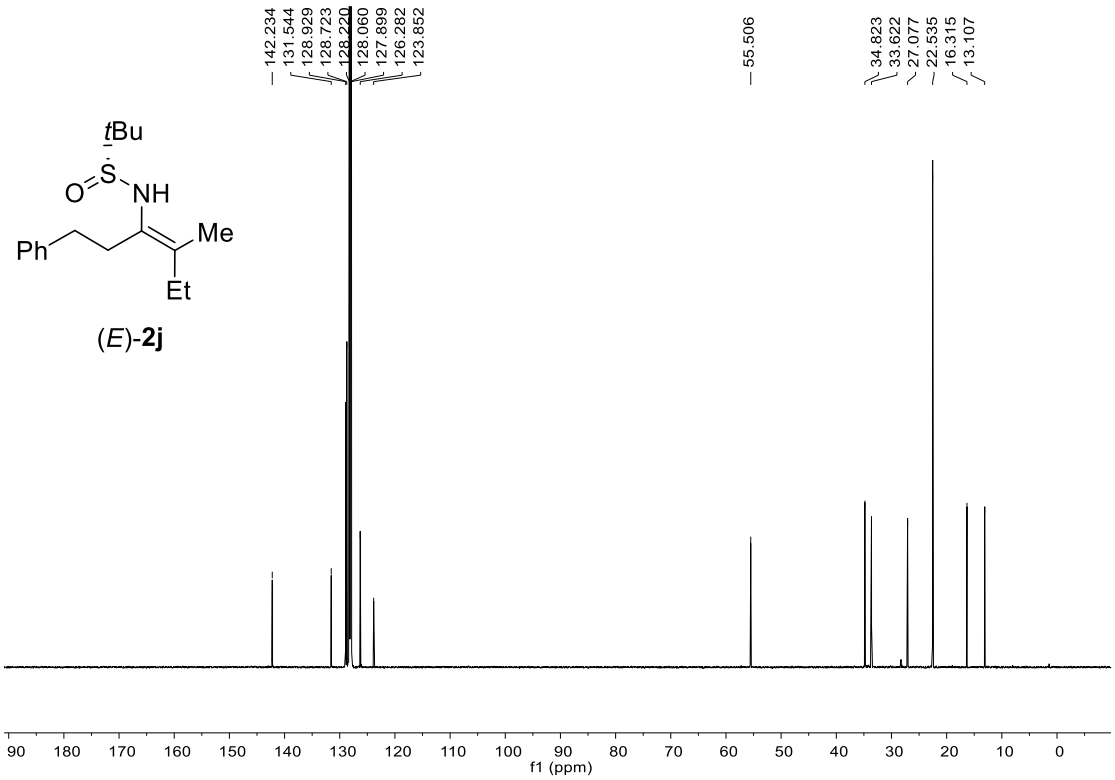
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2j**



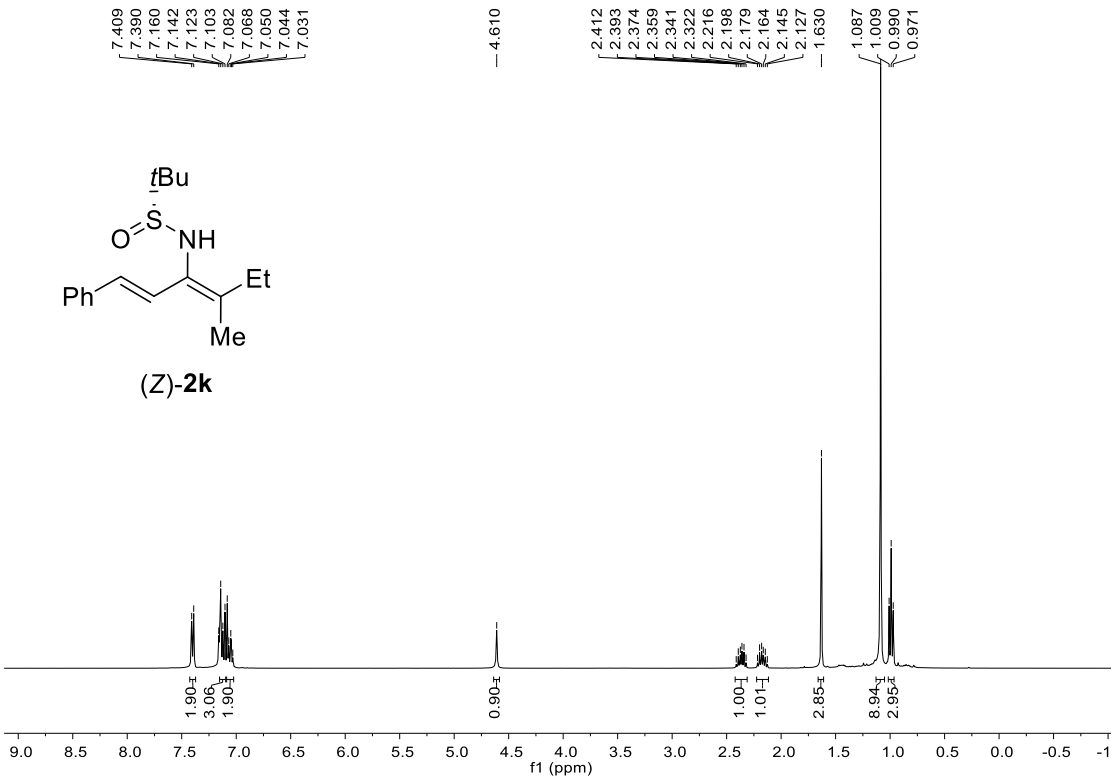
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2j**



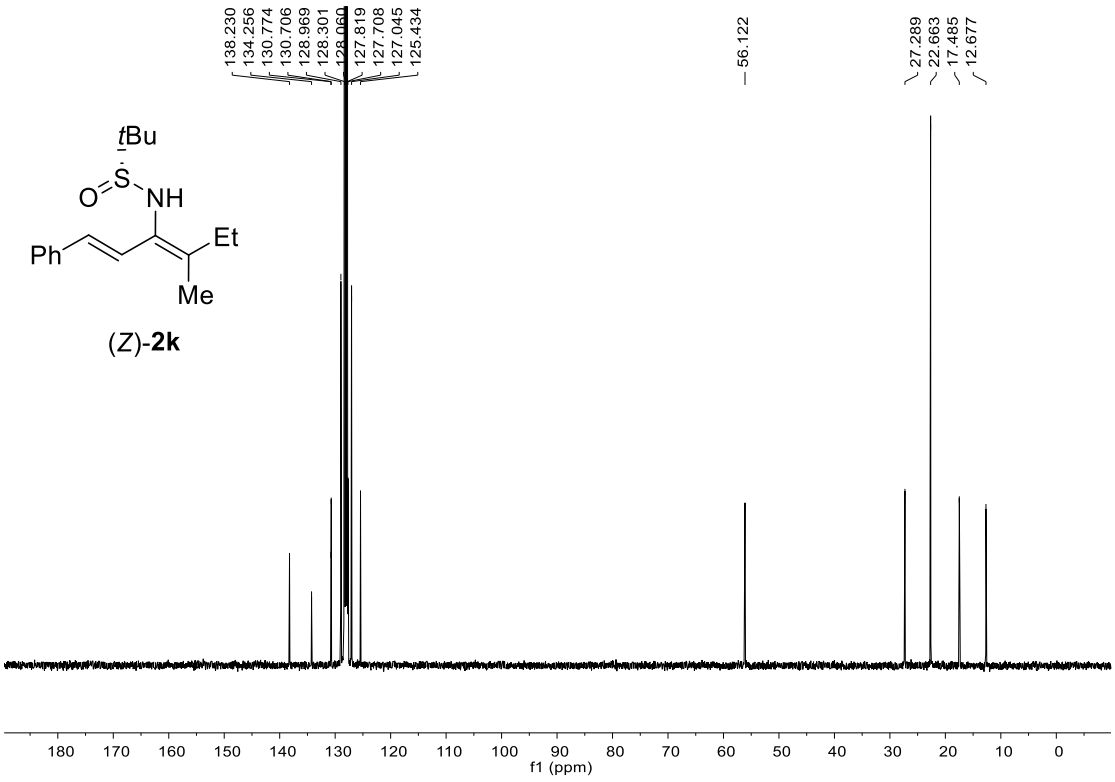
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2j**



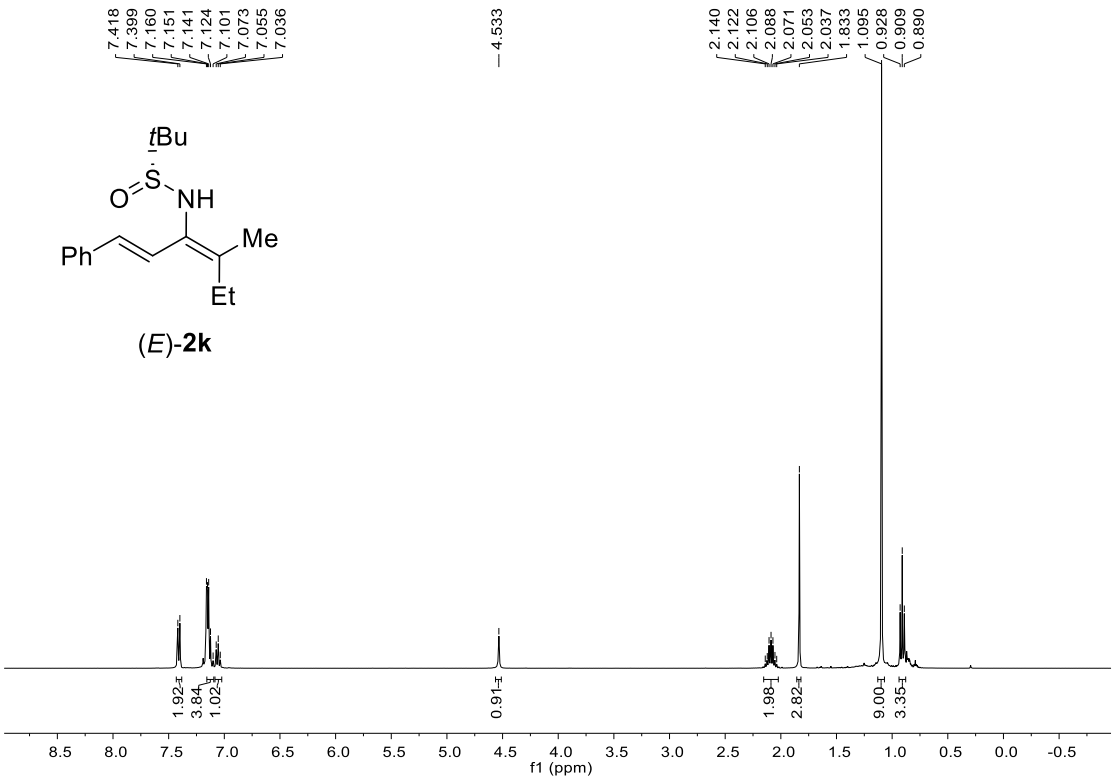
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2j**



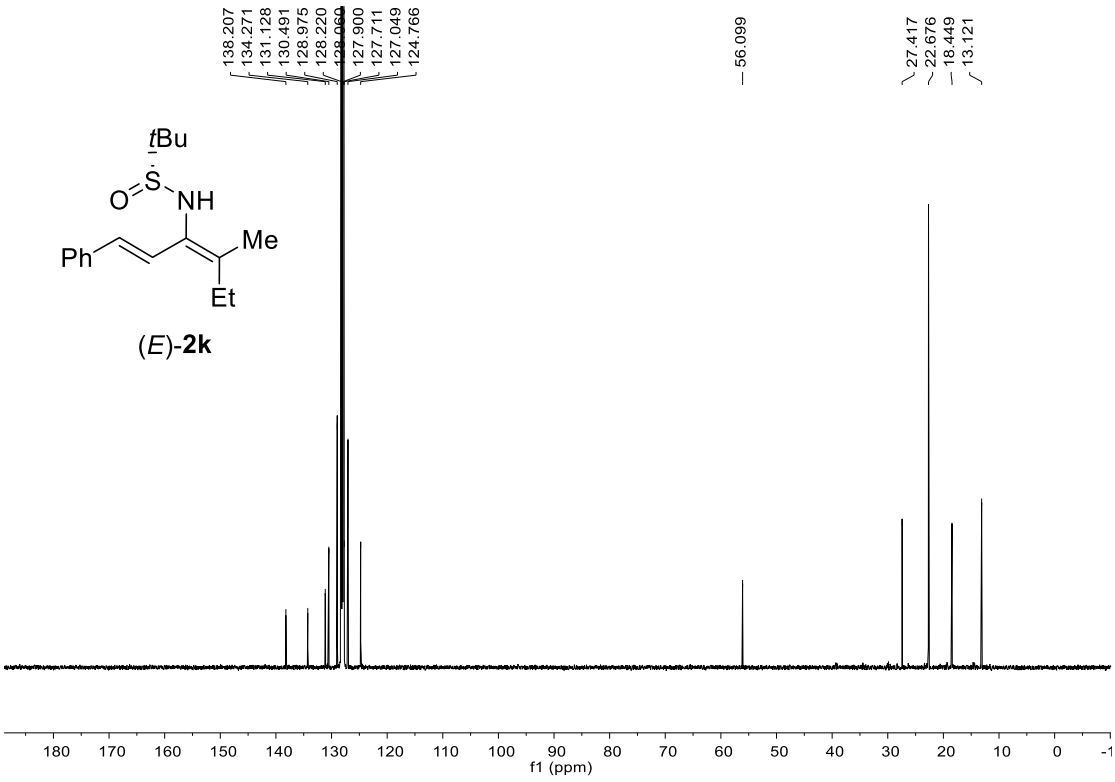
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2k**



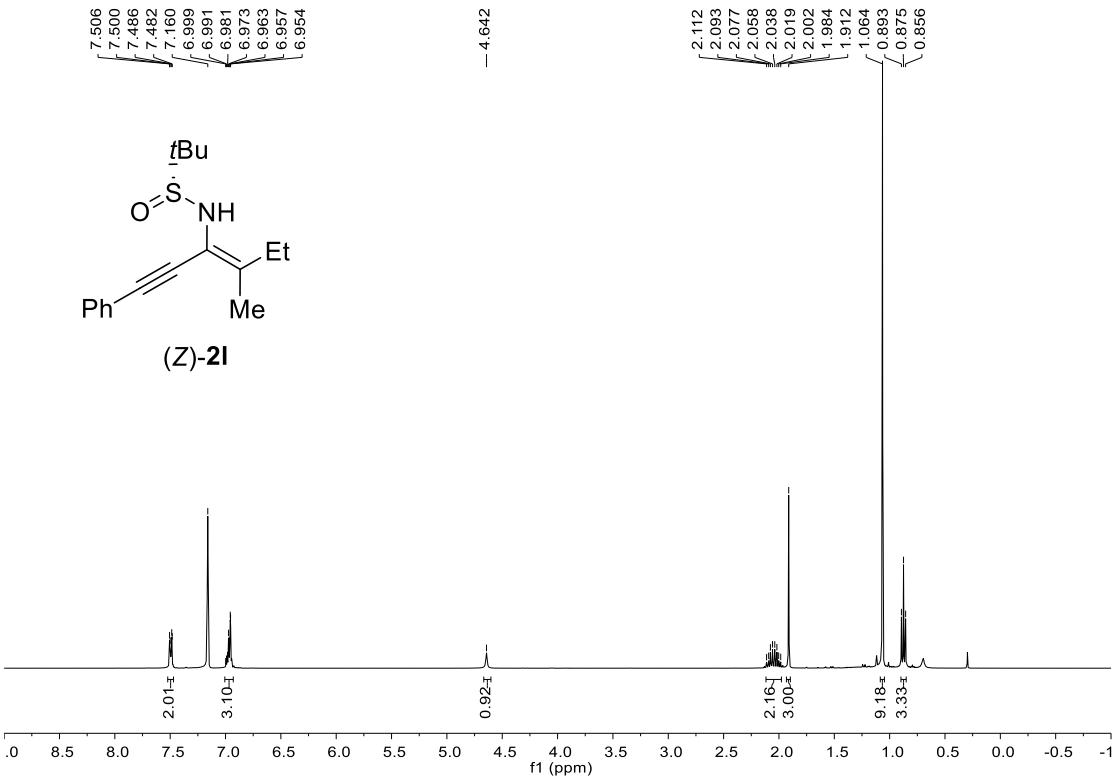
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2k**



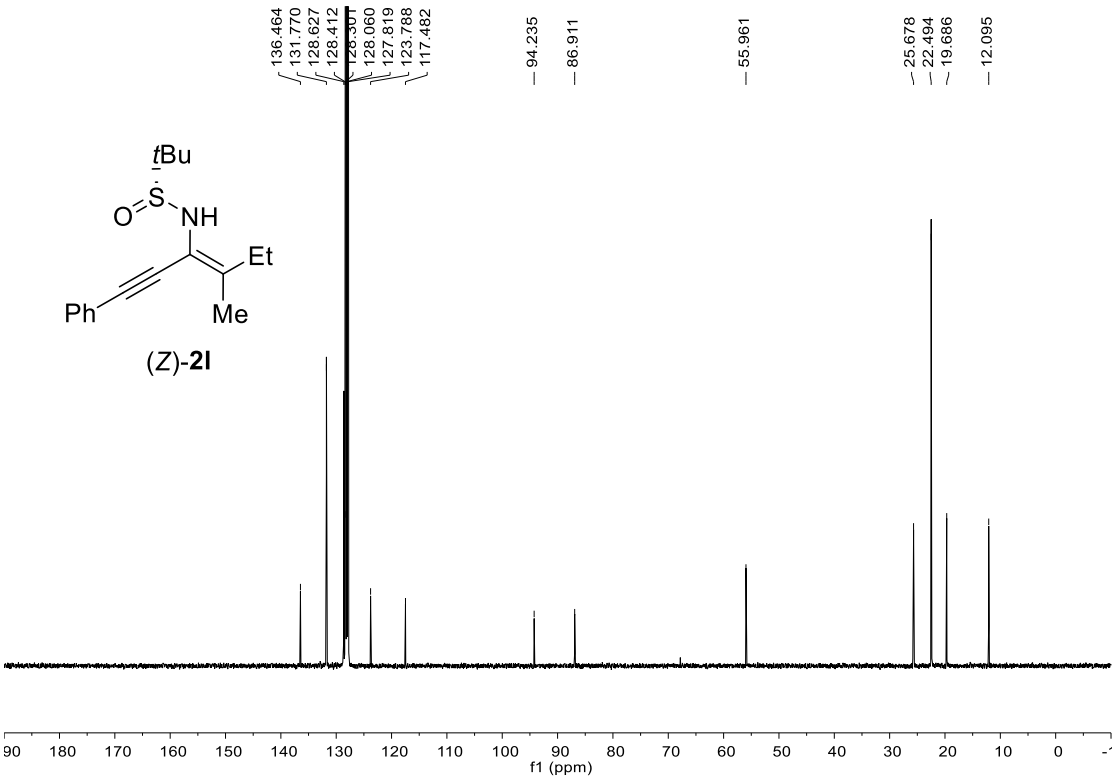
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2k**



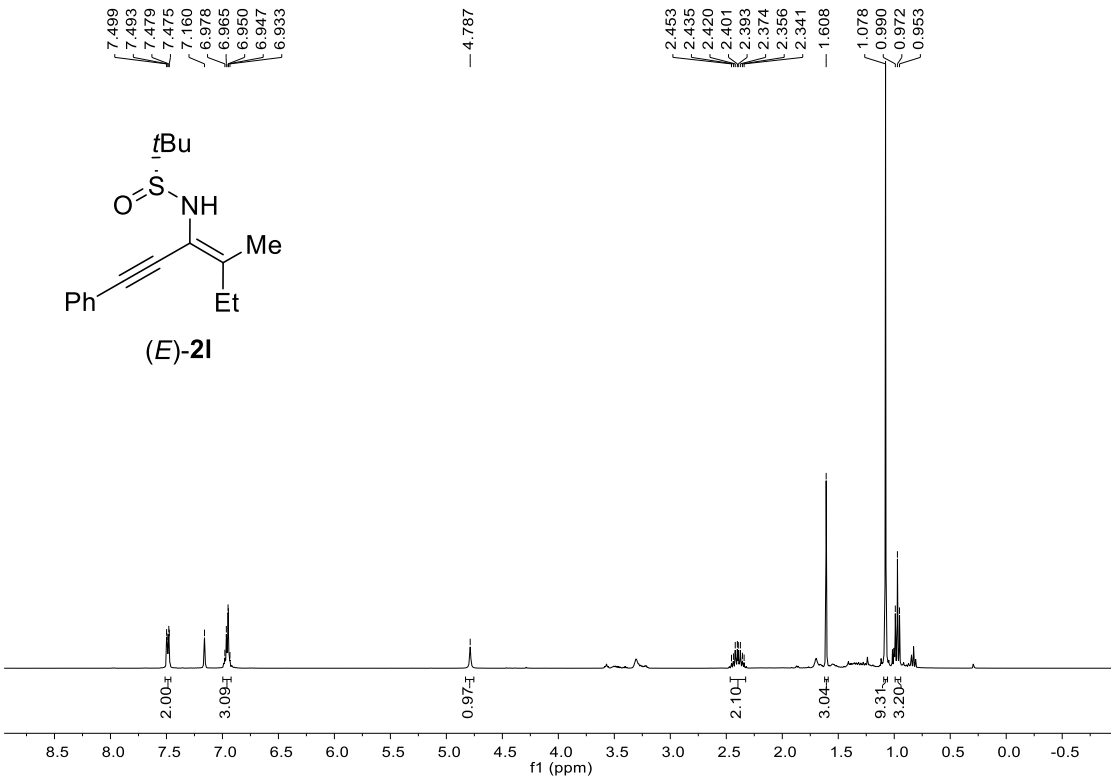
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2k**



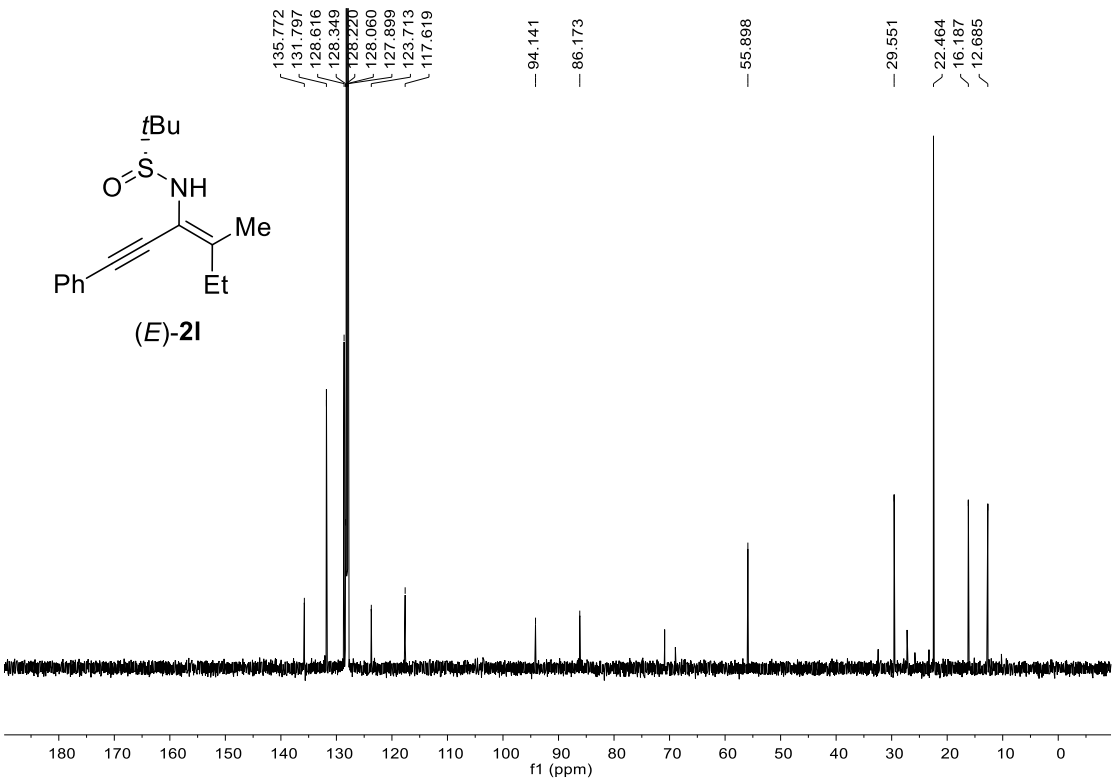
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2l**



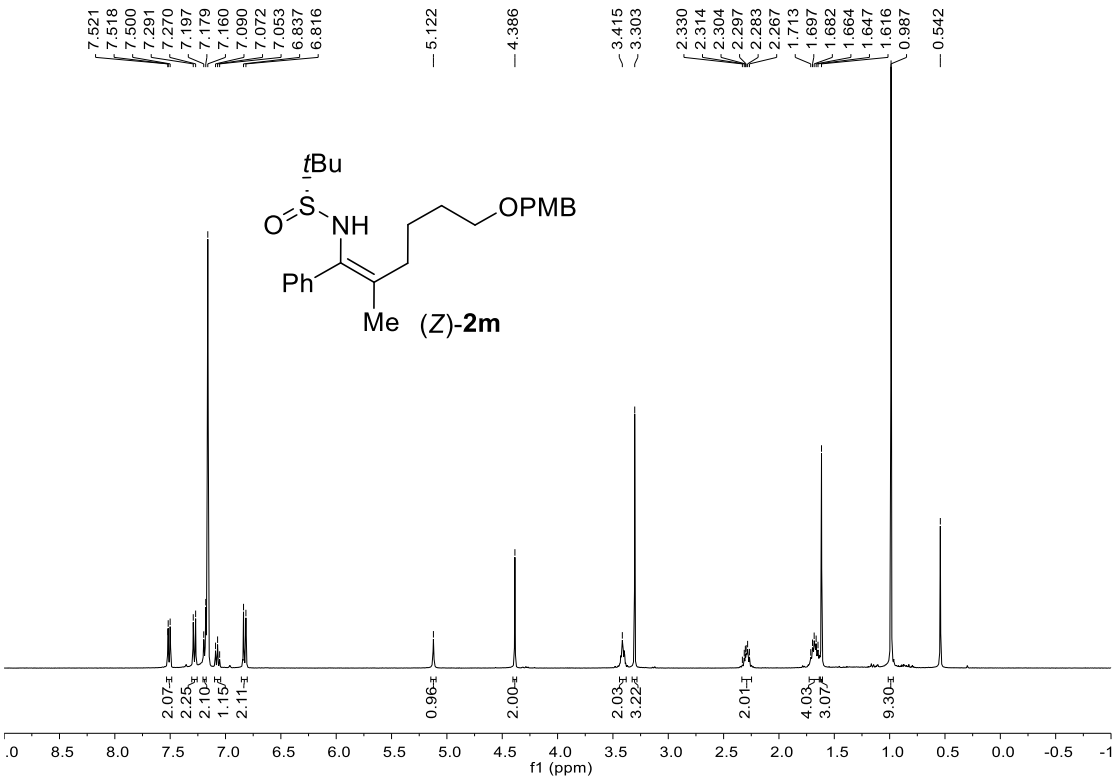
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2l**



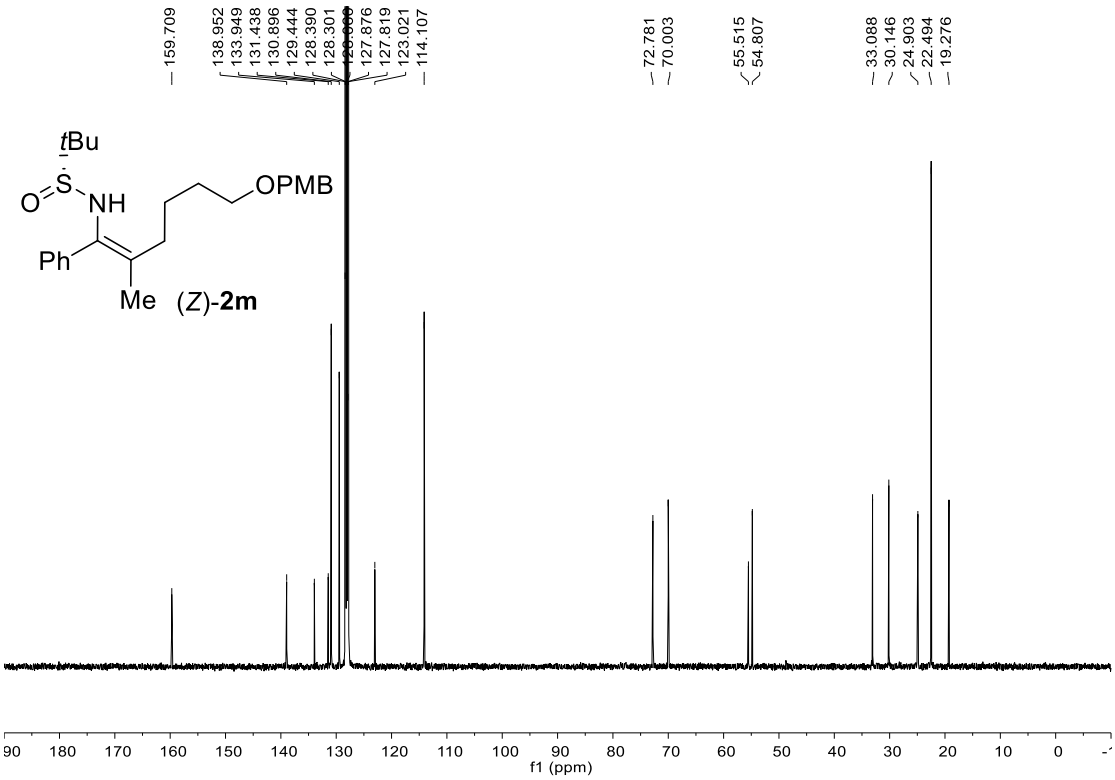
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2l**



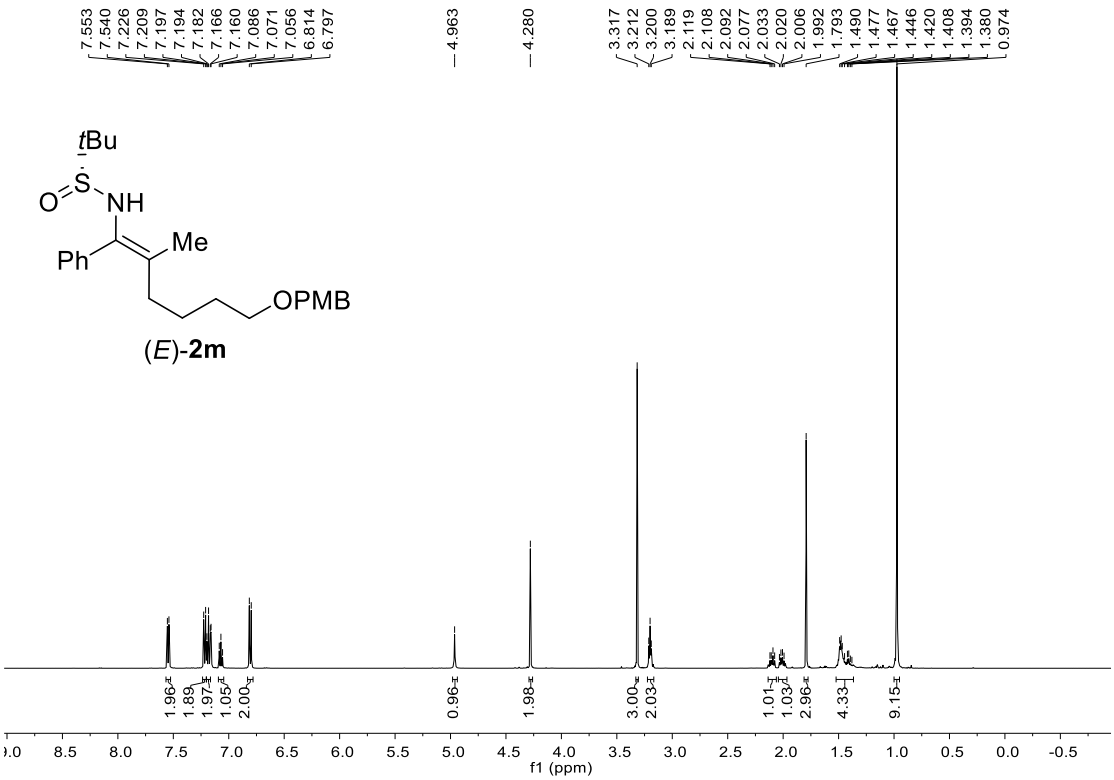
^{13}C NMR spectrum (C_6D_6, 150 MHz) of the crude reaction mixture of (*E*)-**2l**



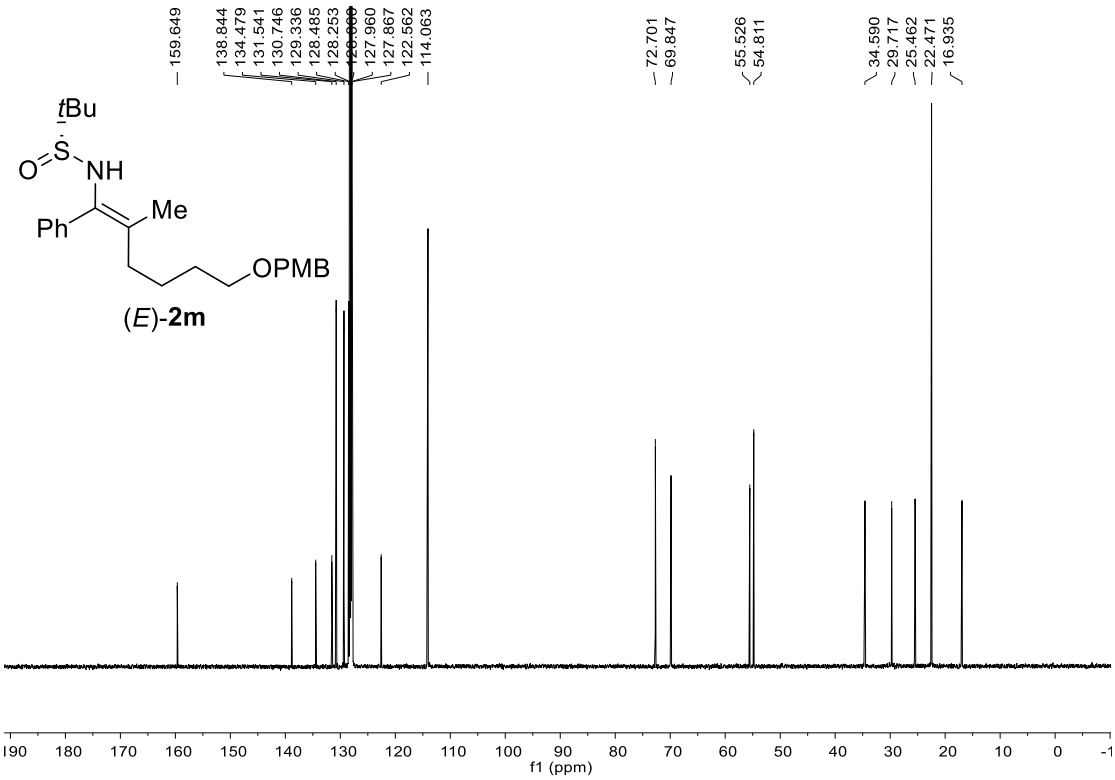
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2m**



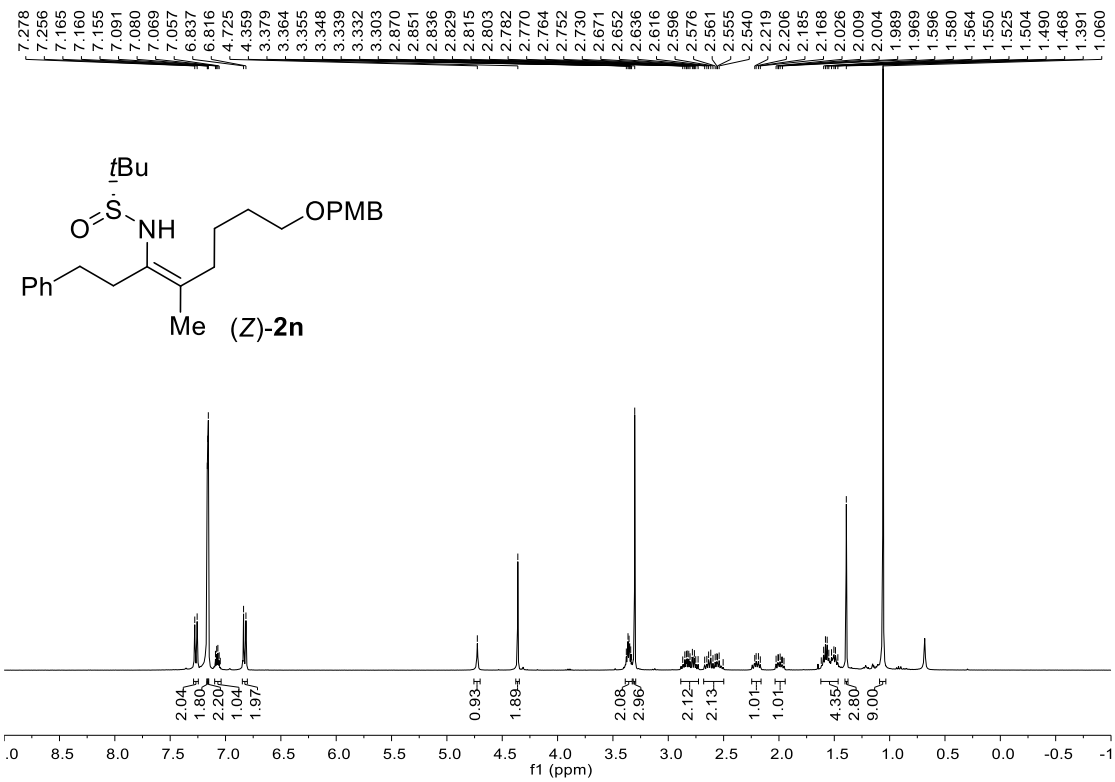
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2m**



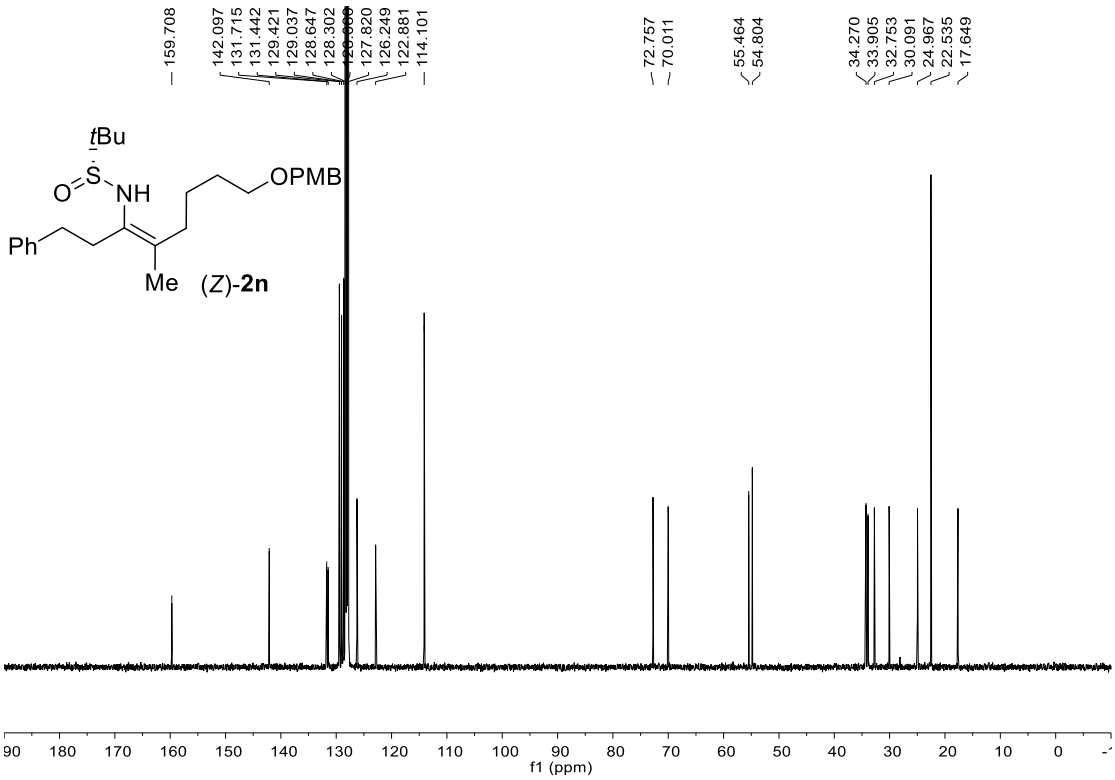
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2m**



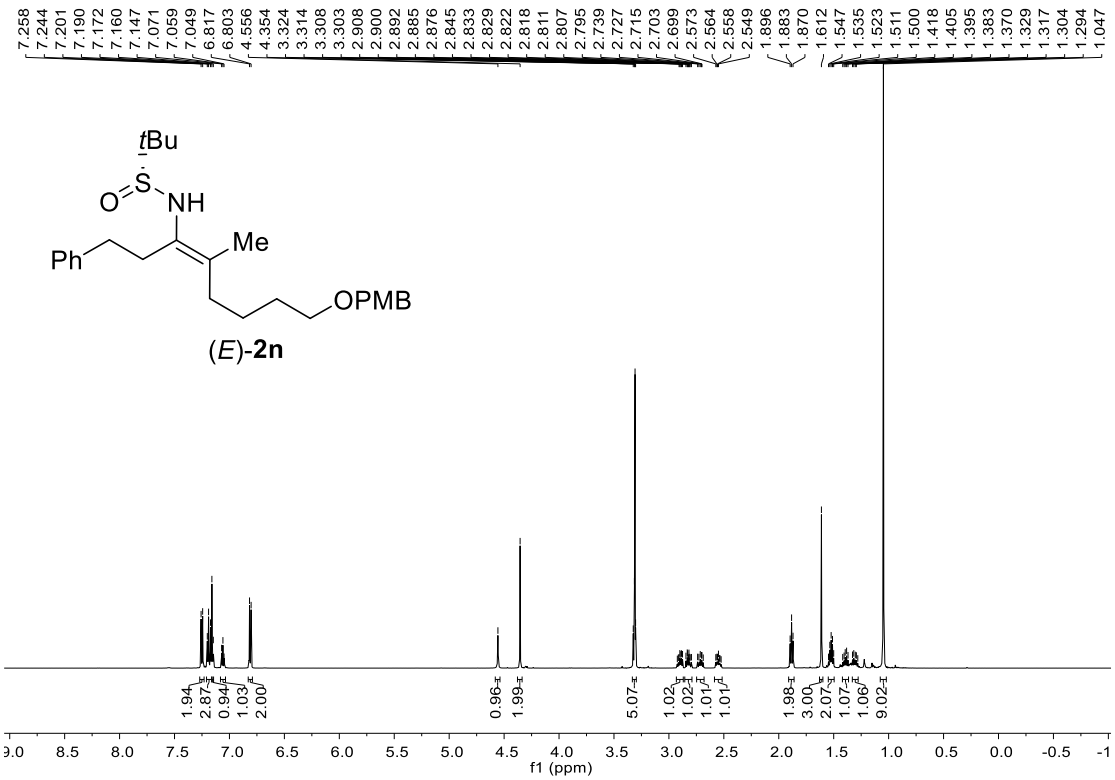
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2m**



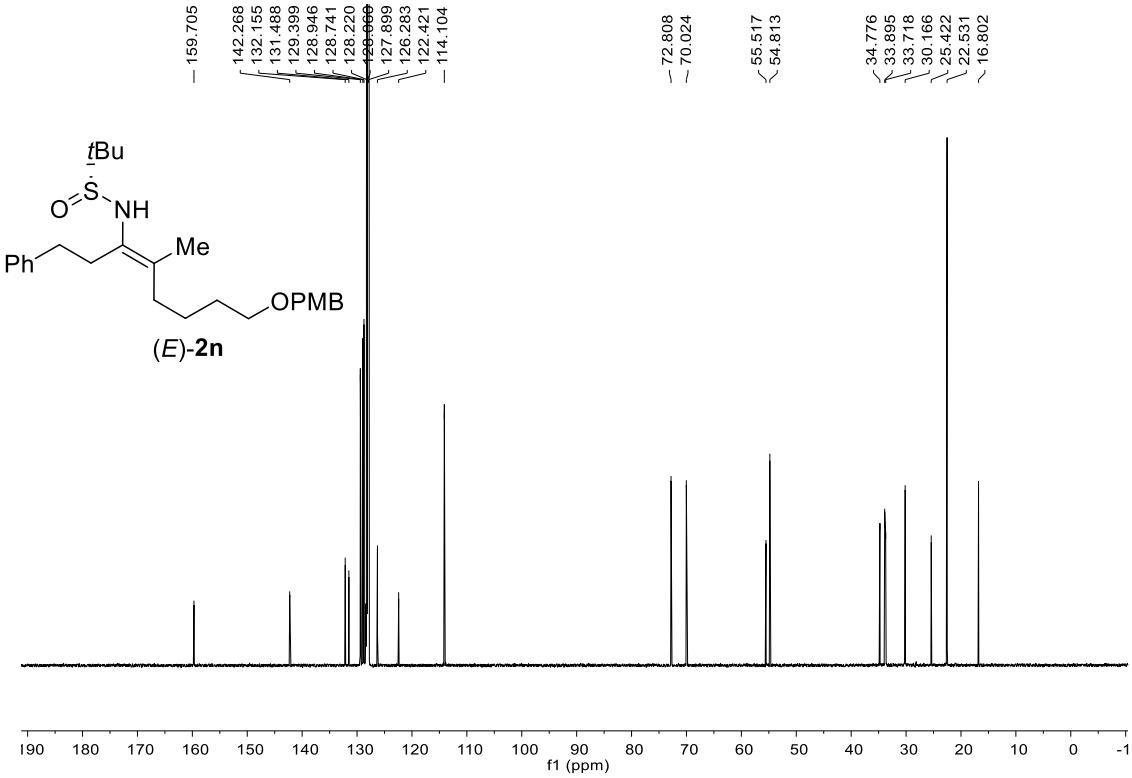
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2n**



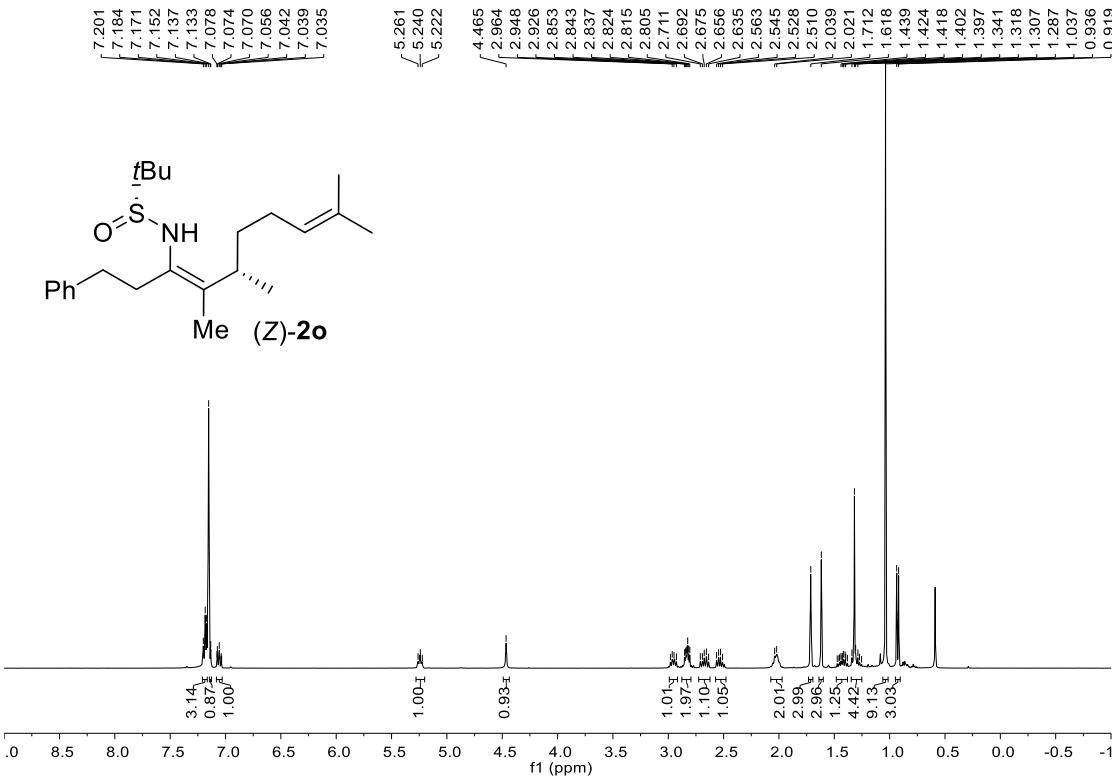
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2n**



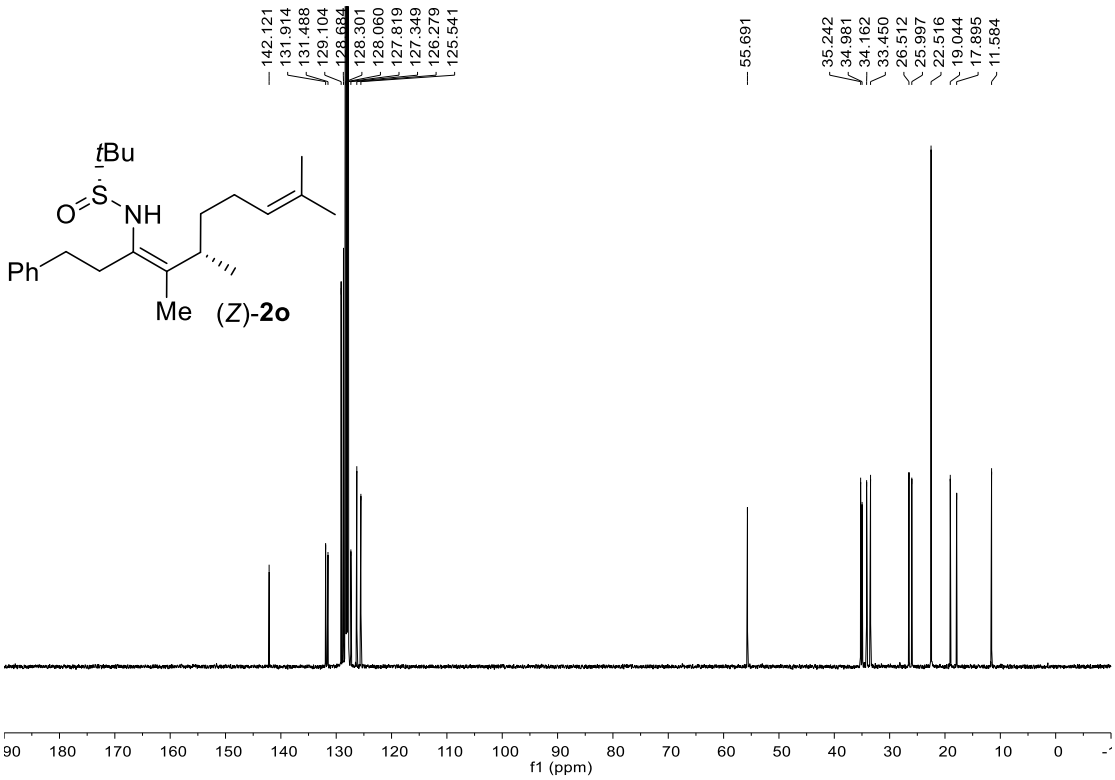
^{1}H NMR spectrum (C_6D_6, 600 MHz) of (*E*)-**2n**



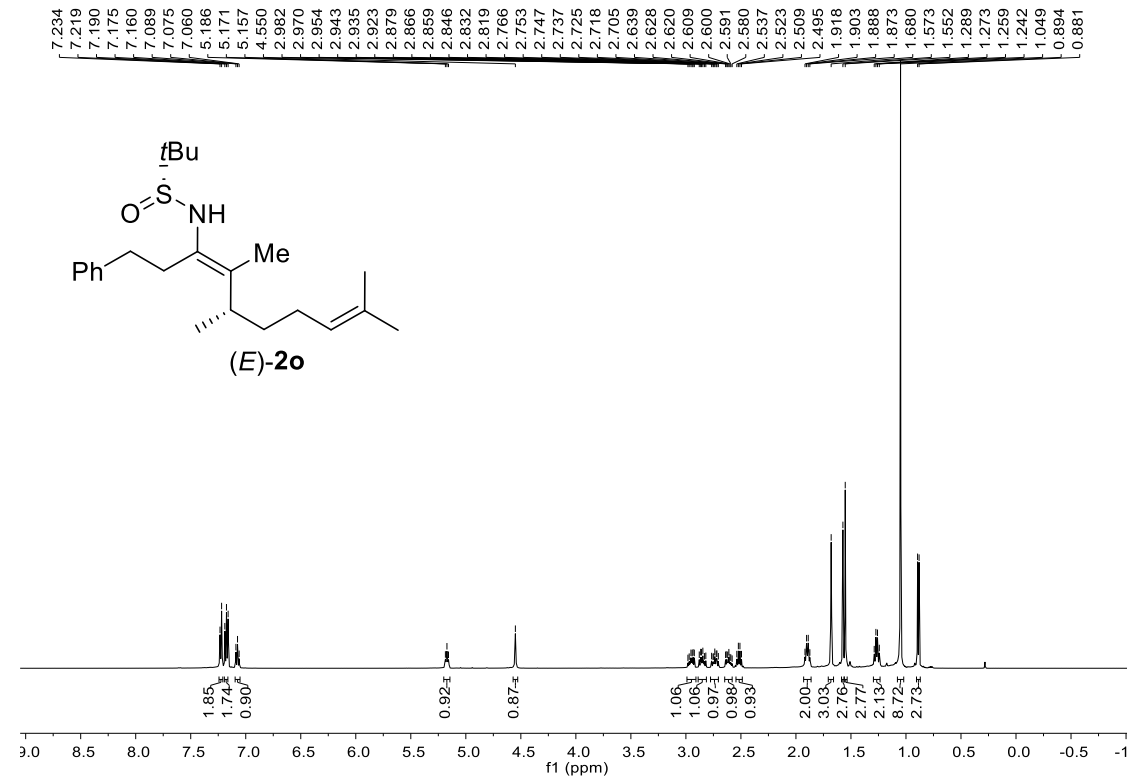
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2n**



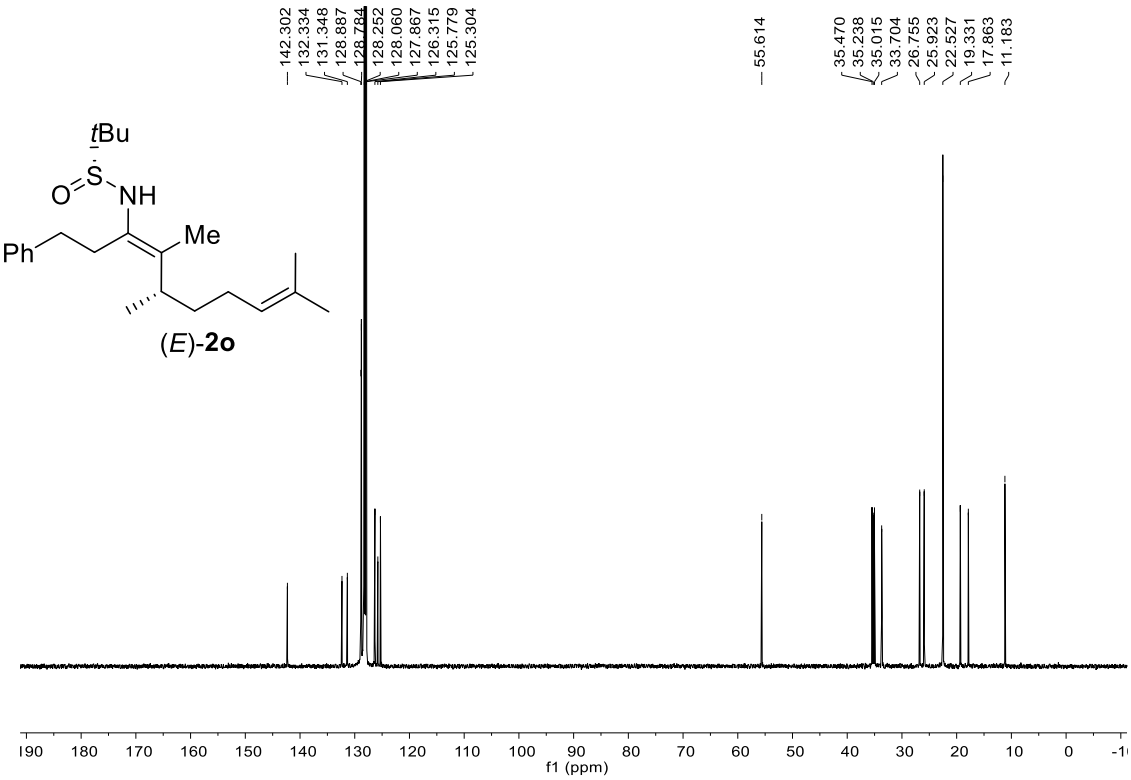
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2o**



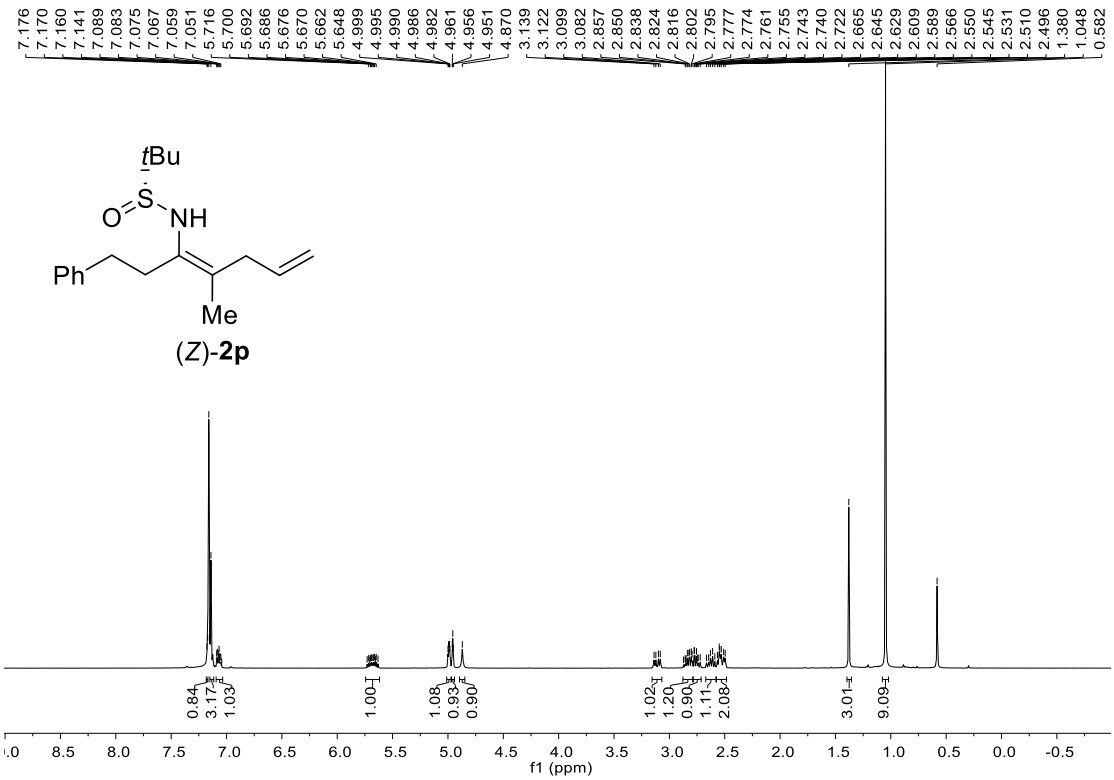
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2o**



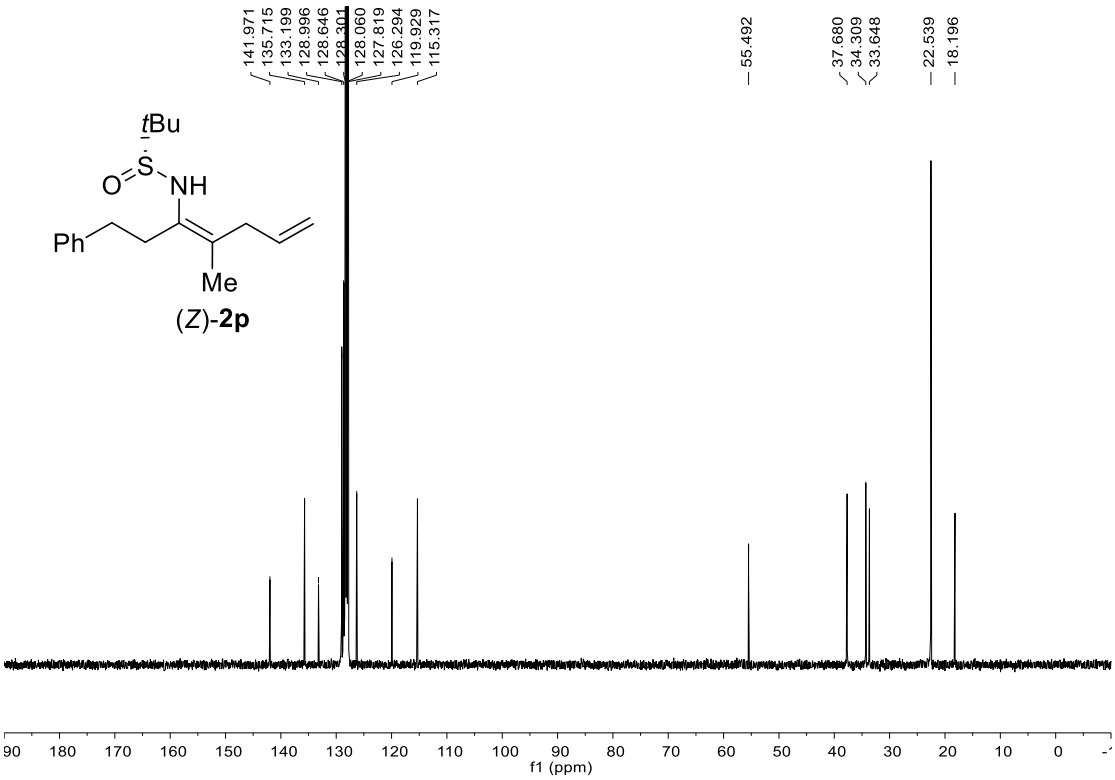
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2o**



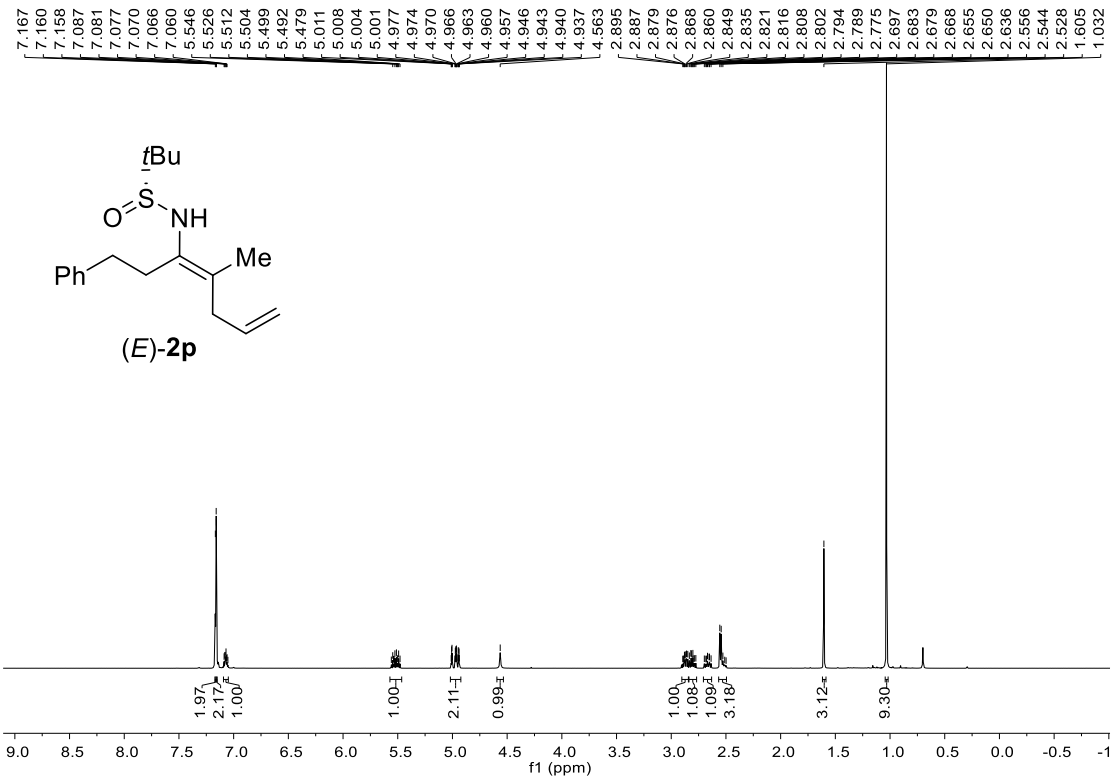
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2o**



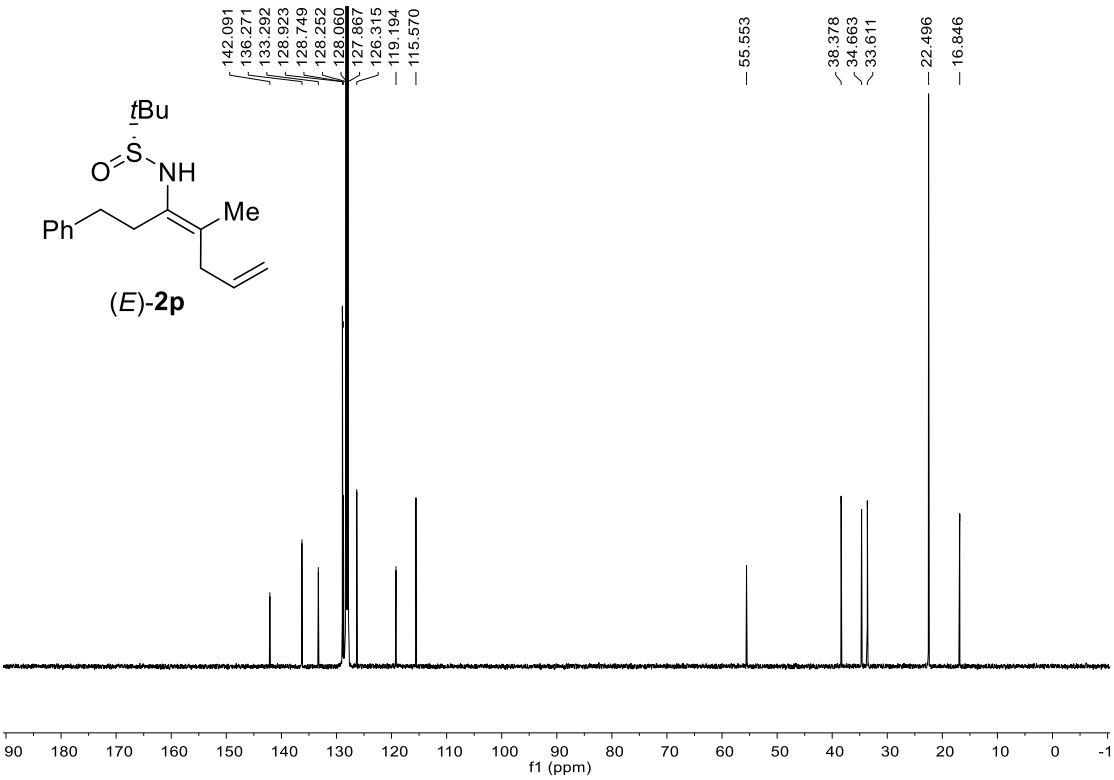
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2p**



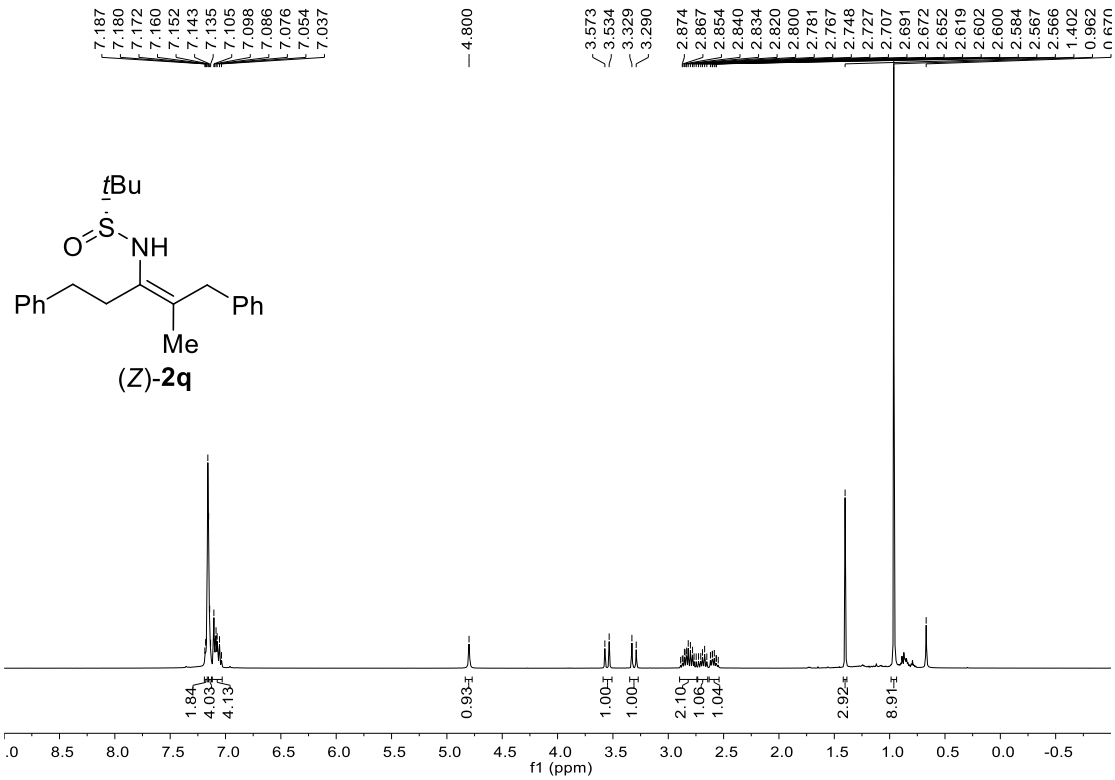
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2p**



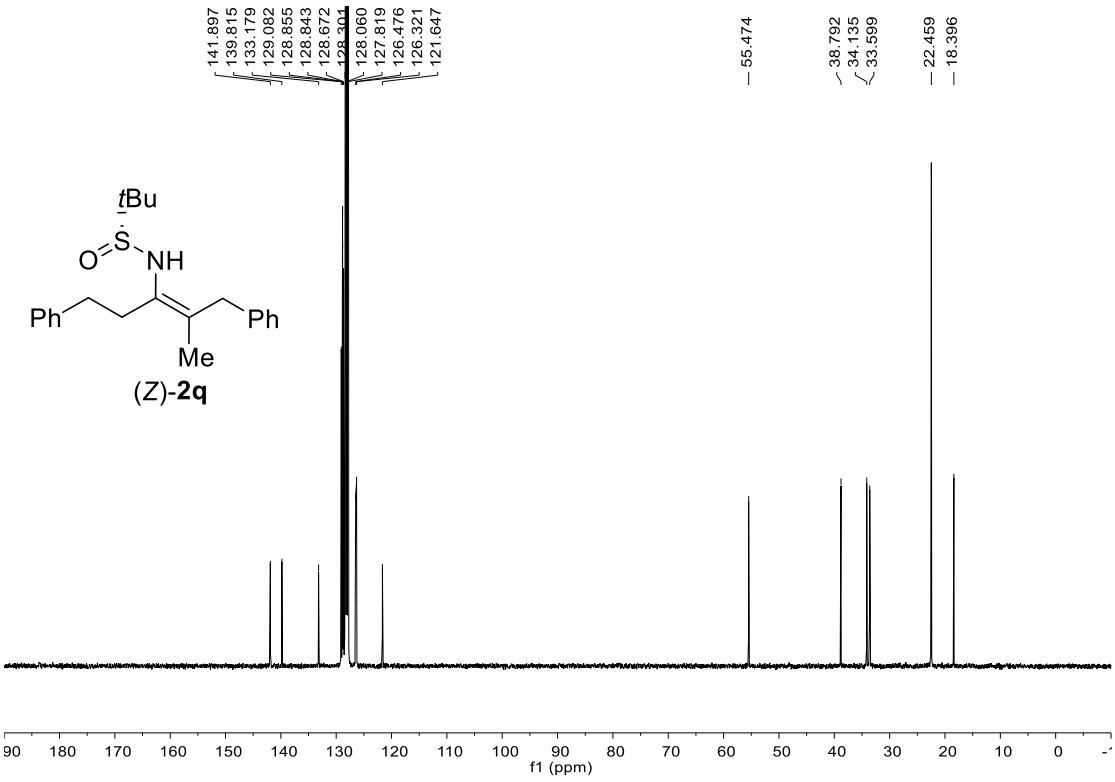
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2p**



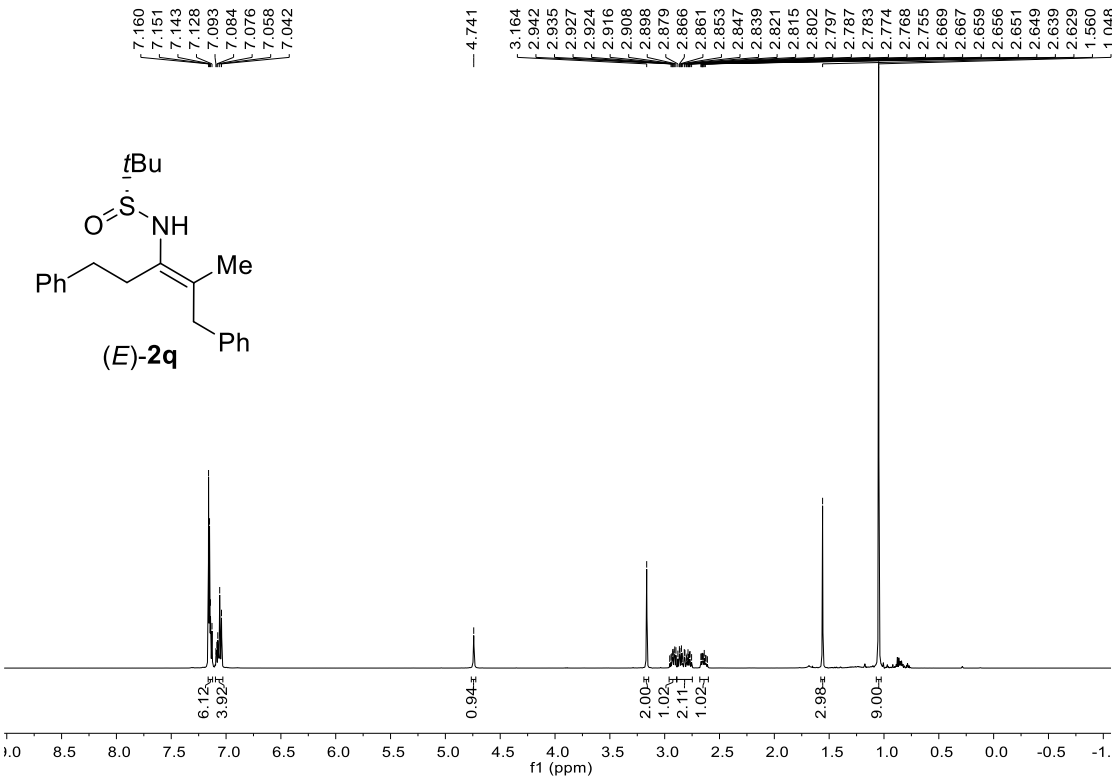
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2p**



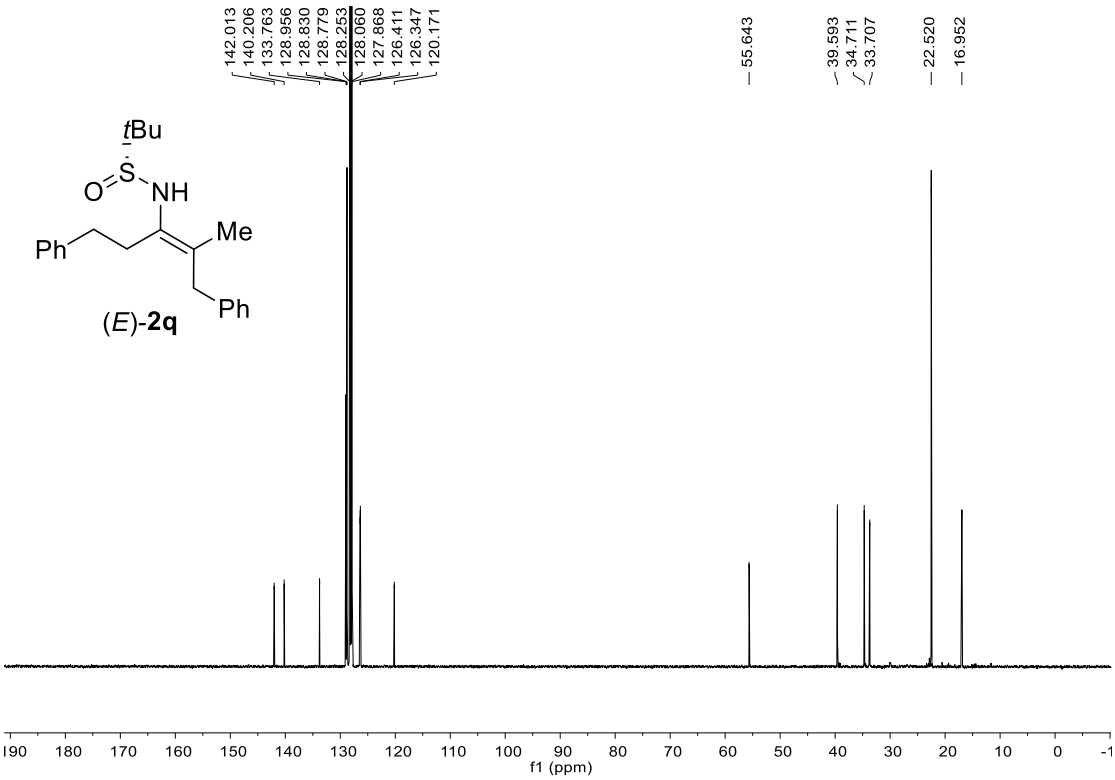
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2q**



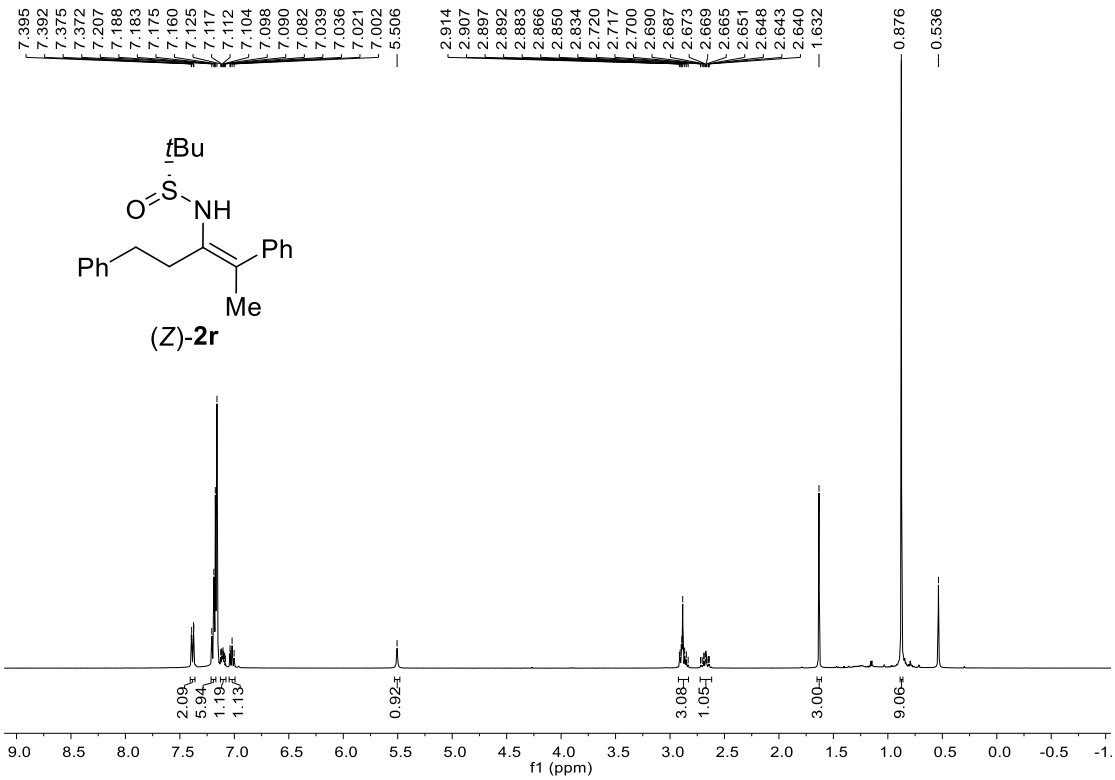
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2q**



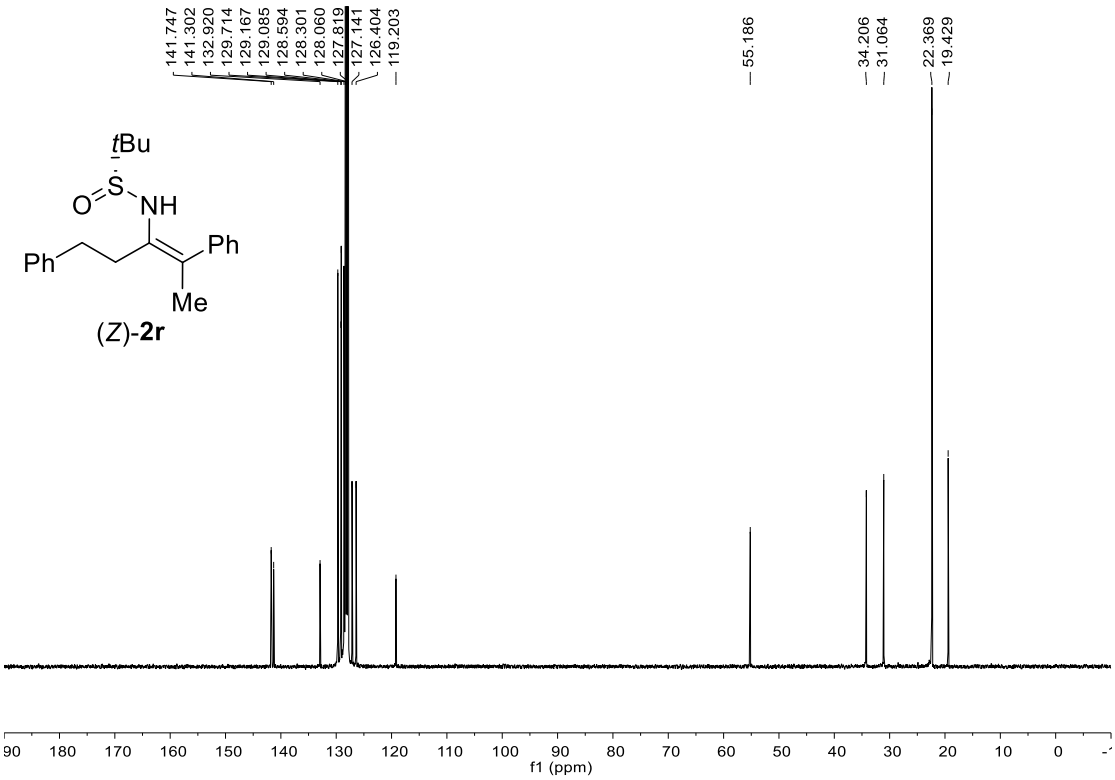
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2q**



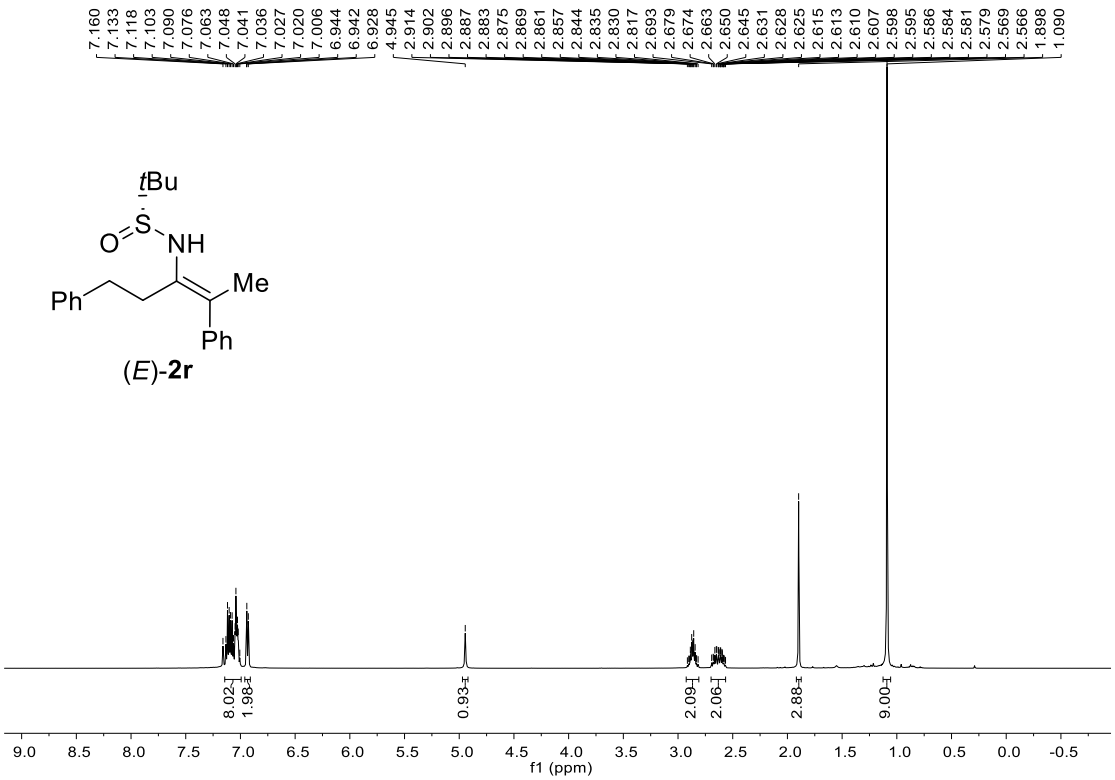
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2q**



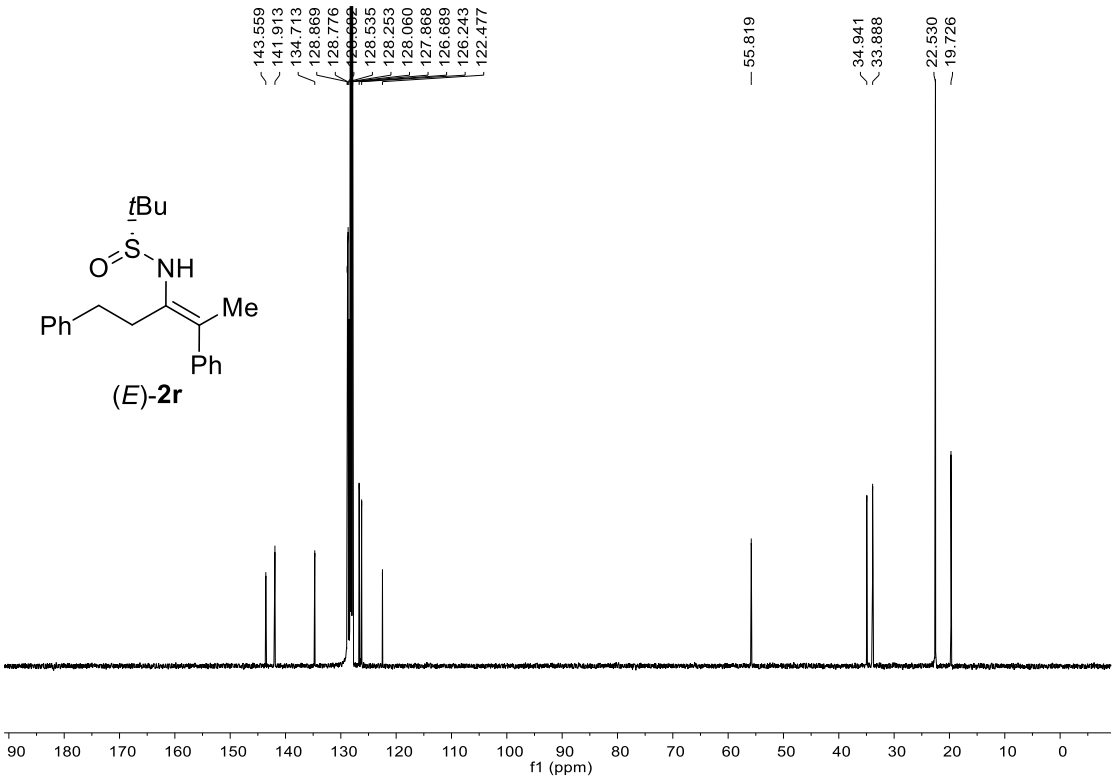
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2r**



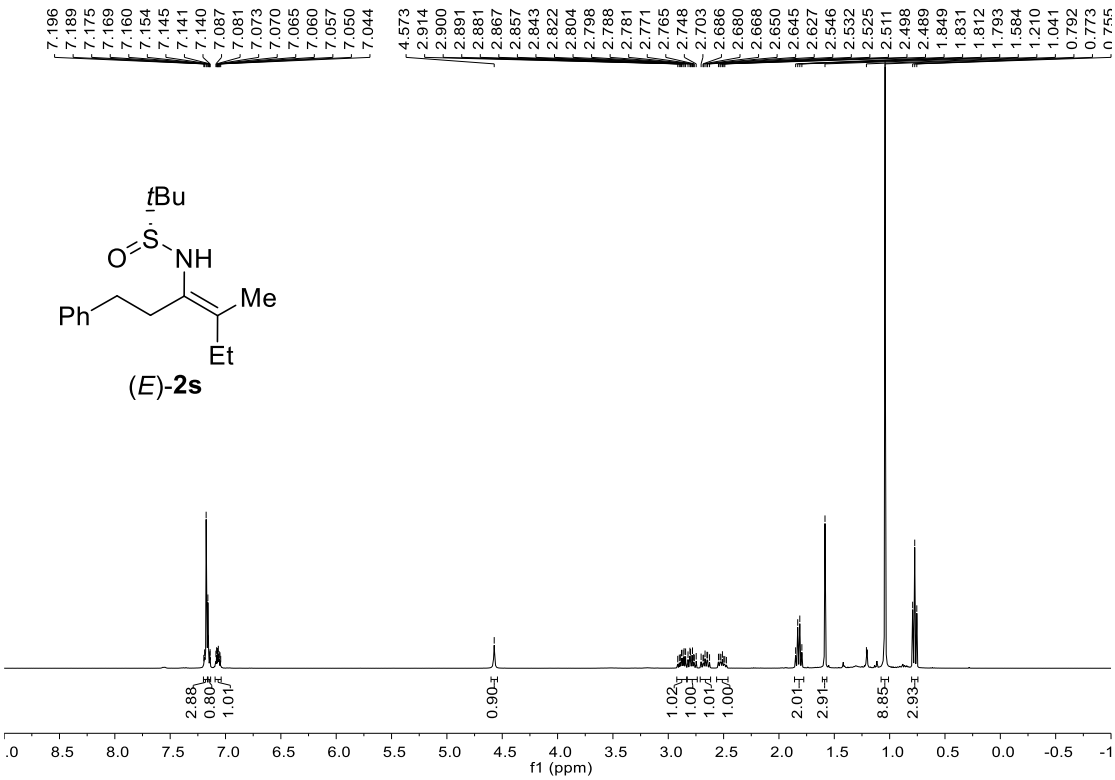
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2r**



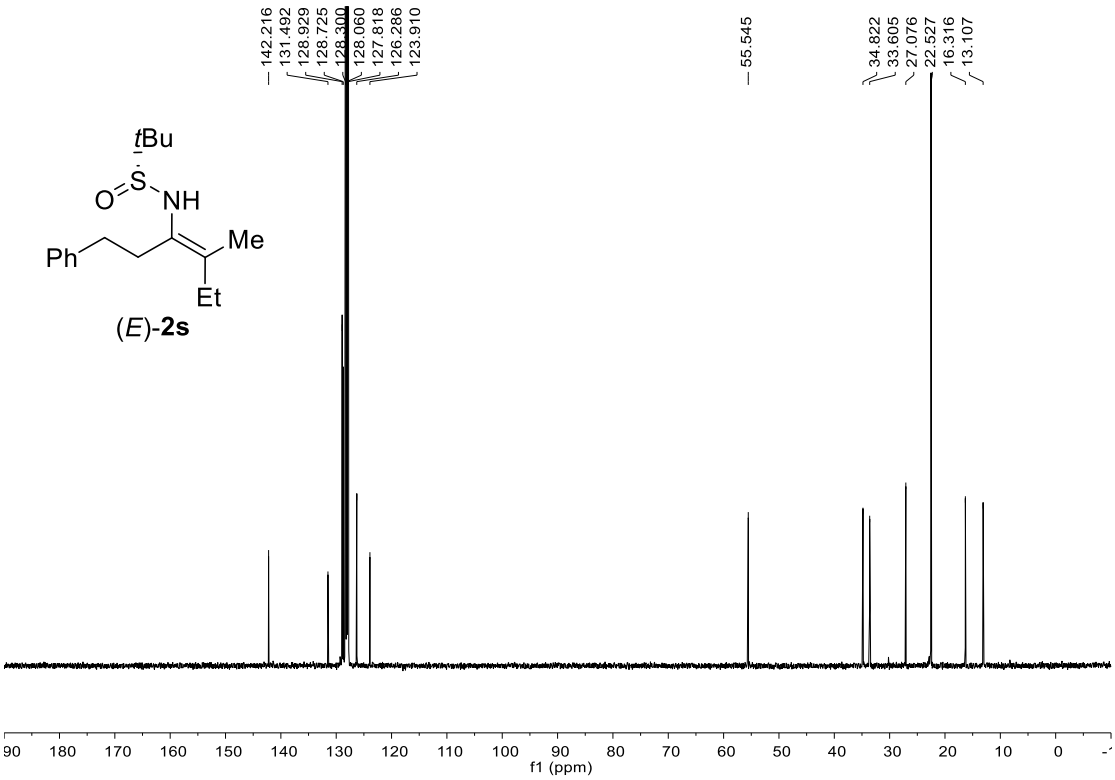
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*E*)-**2r**



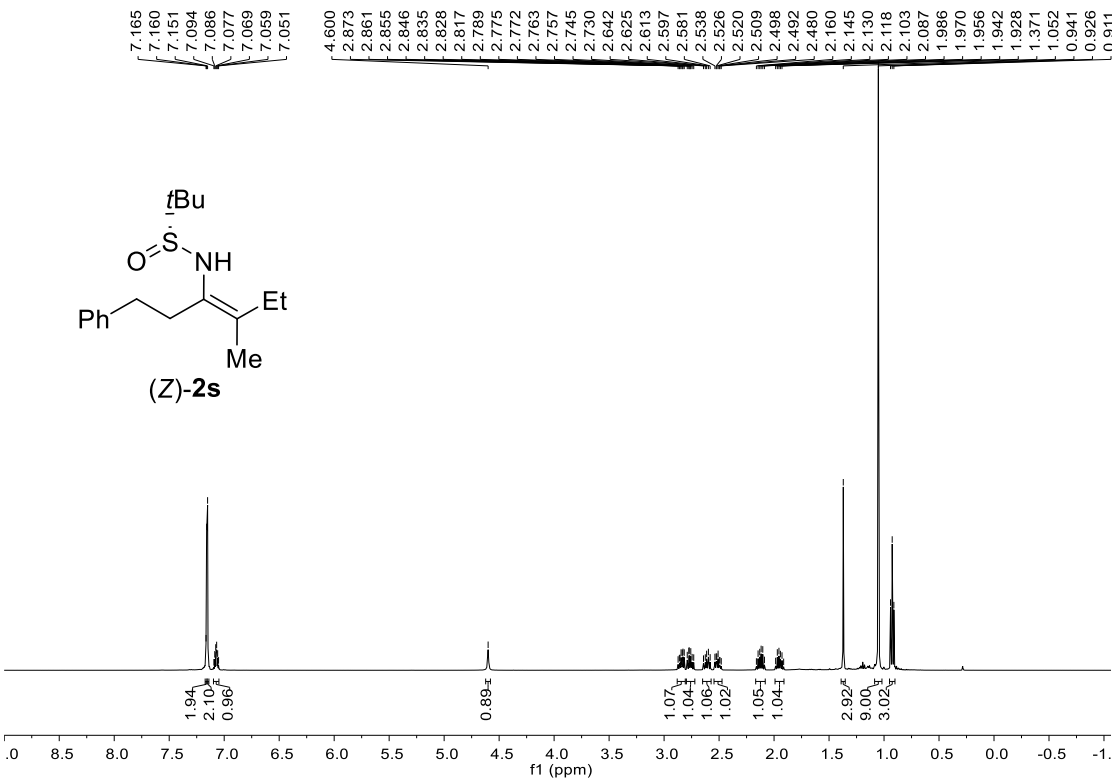
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*E*)-**2r**



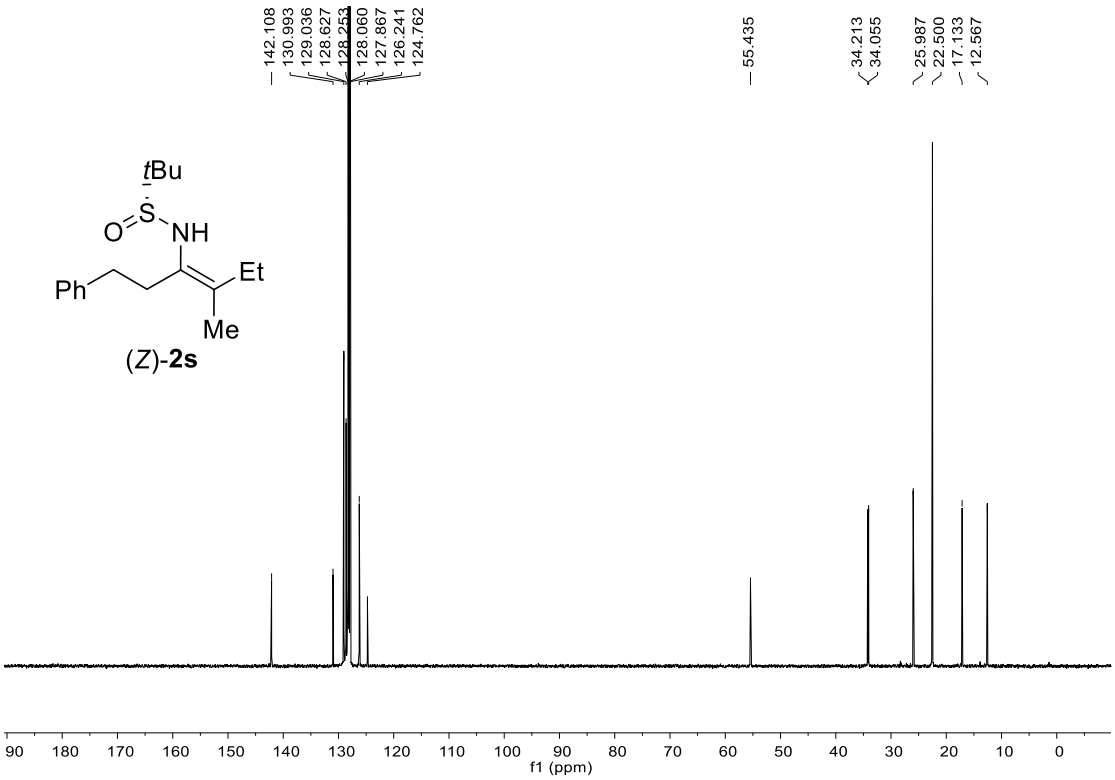
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2s**



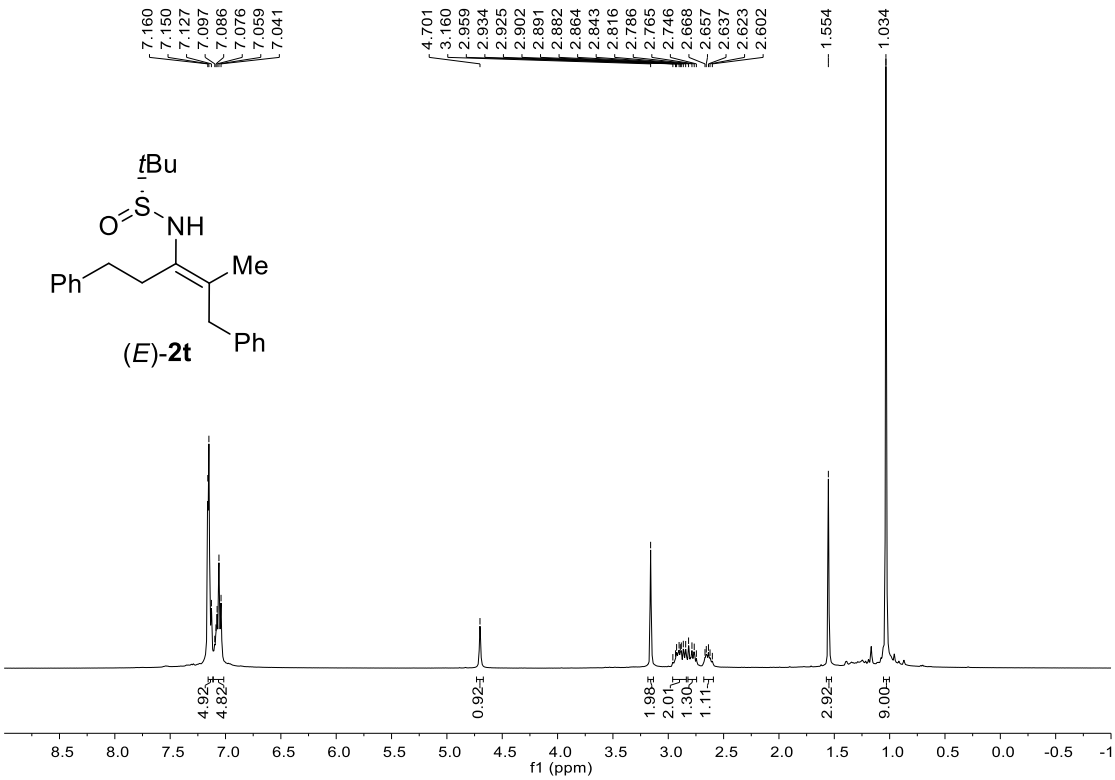
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2s**



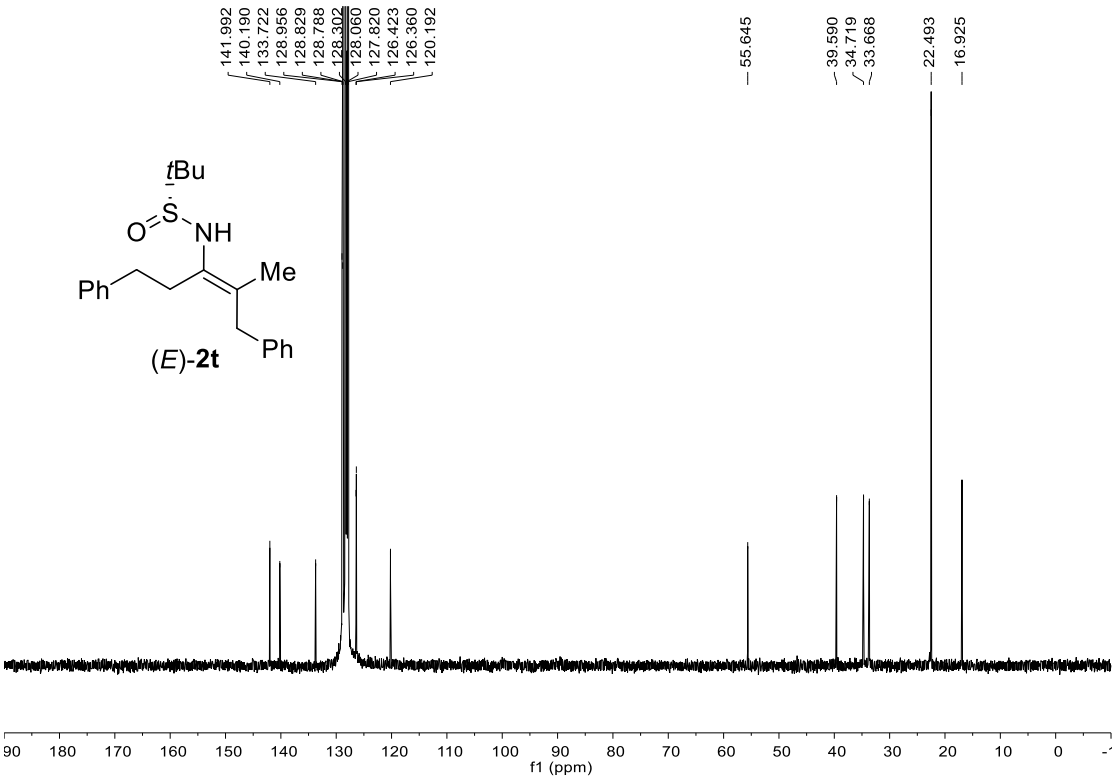
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*Z*)-**2s**



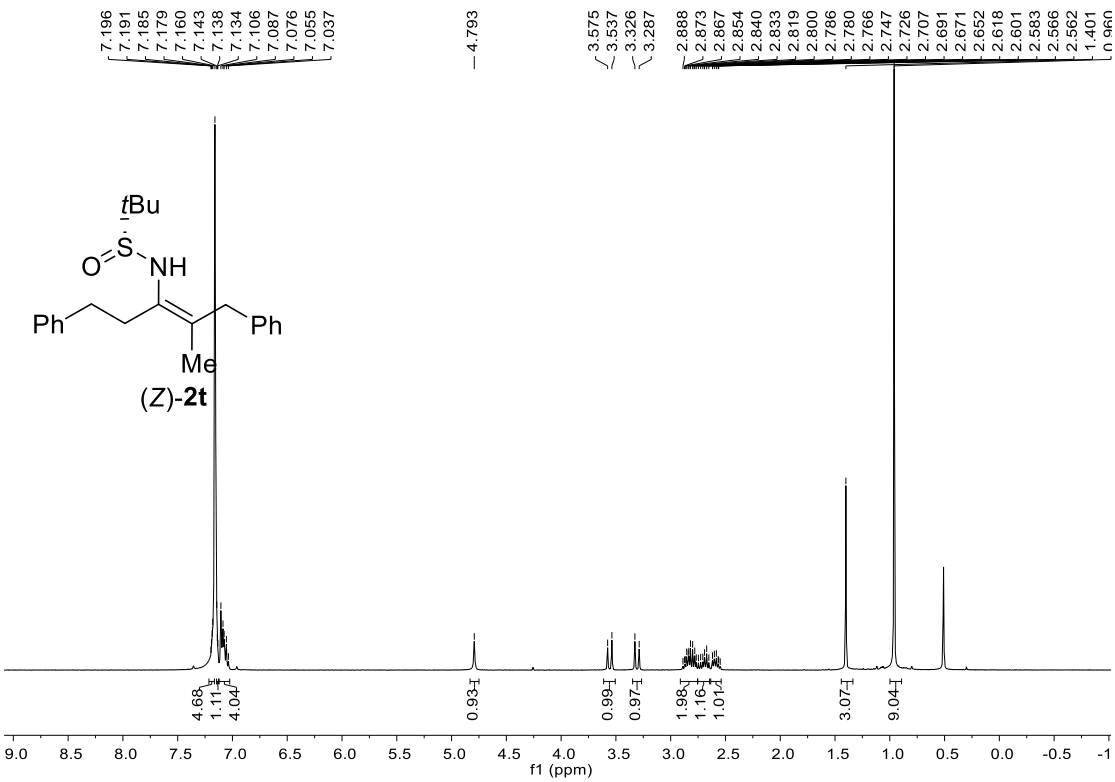
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*Z*)-**2s**



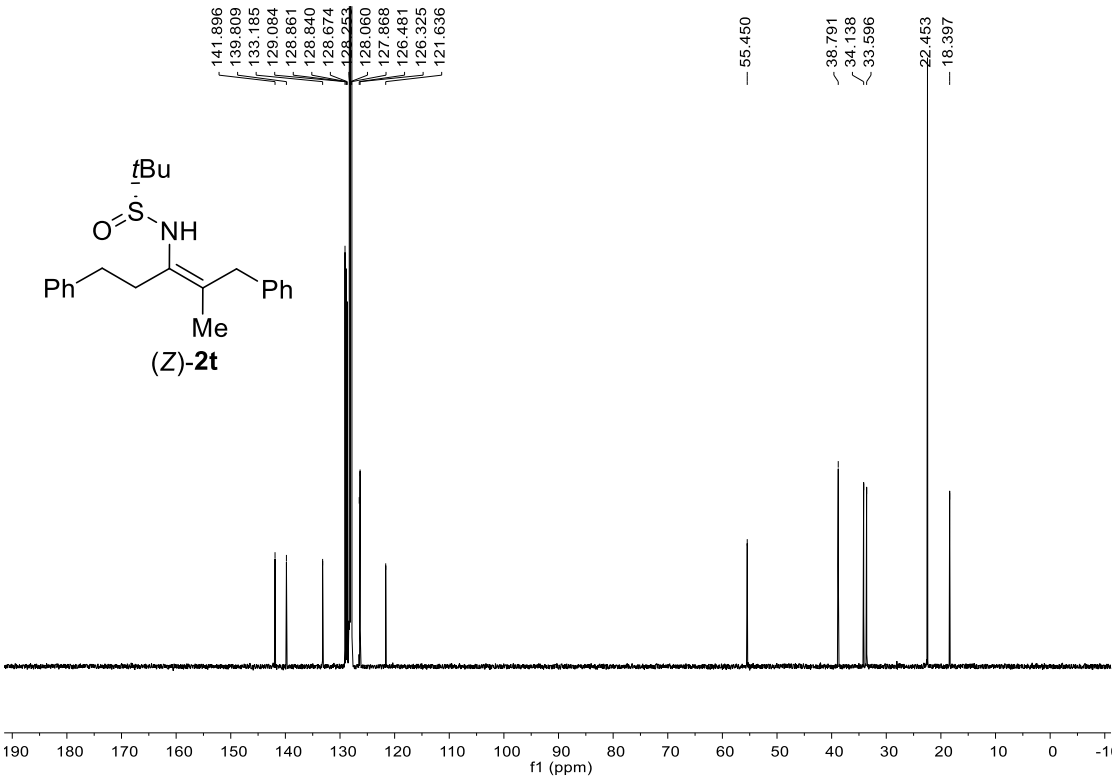
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2t**



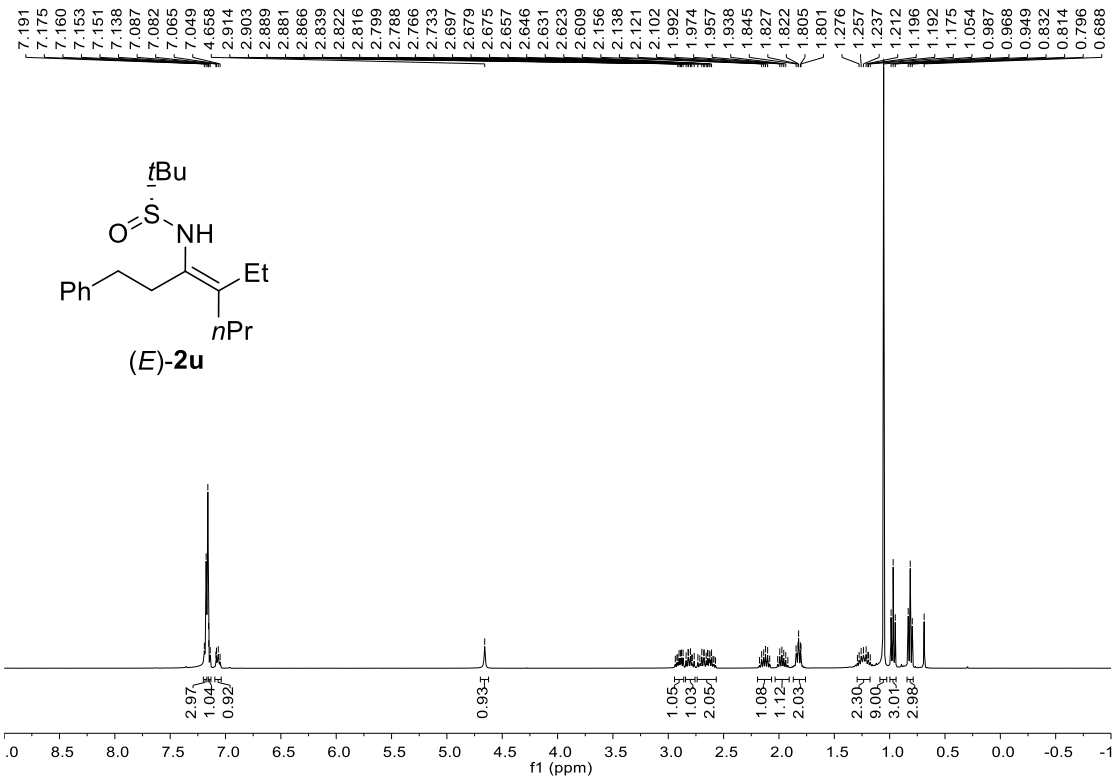
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2t**



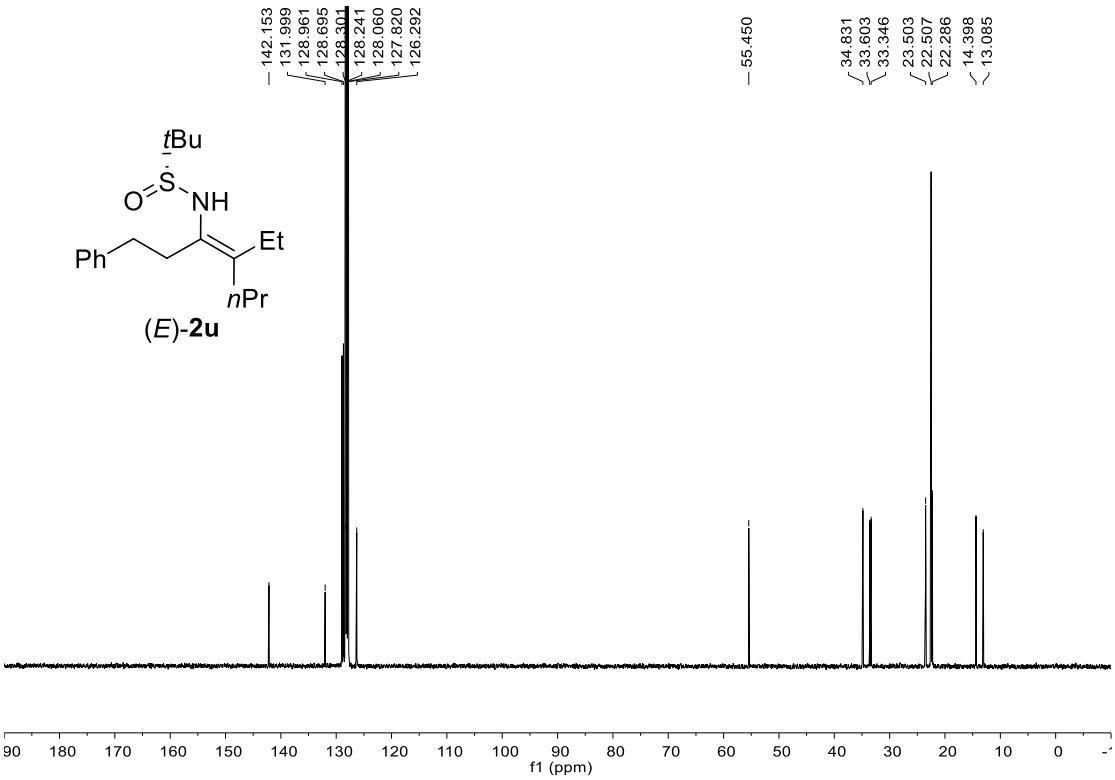
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2t**



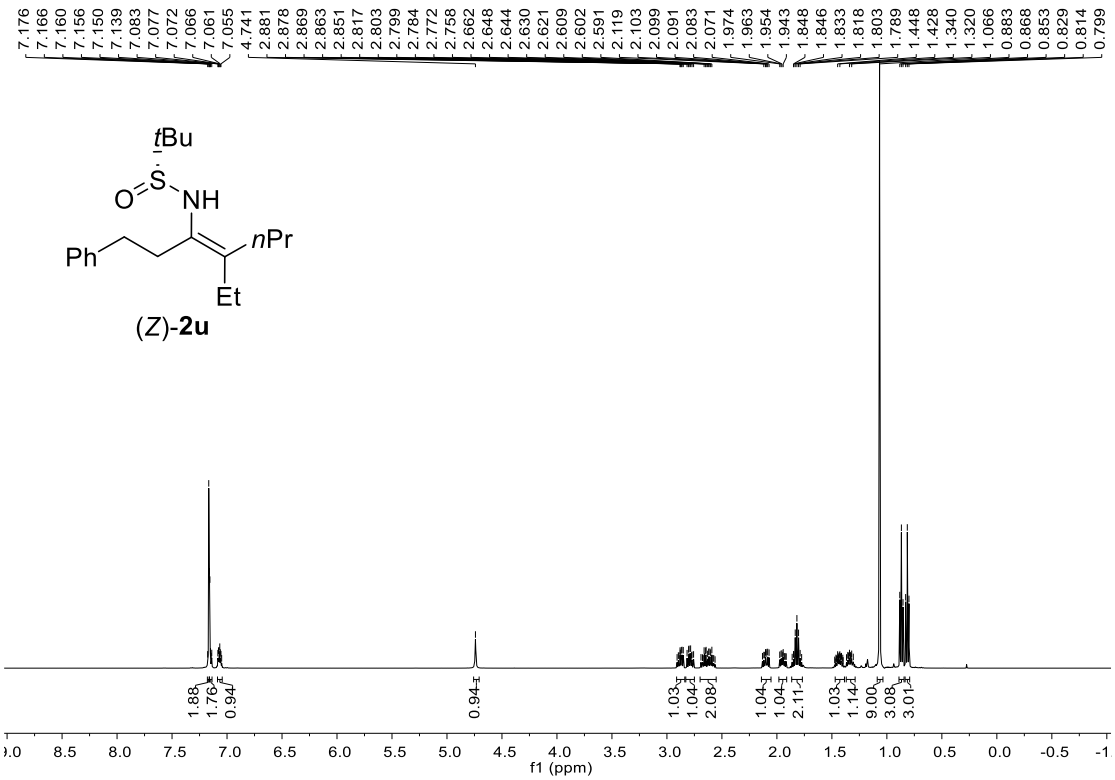
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*Z*)-**2t**



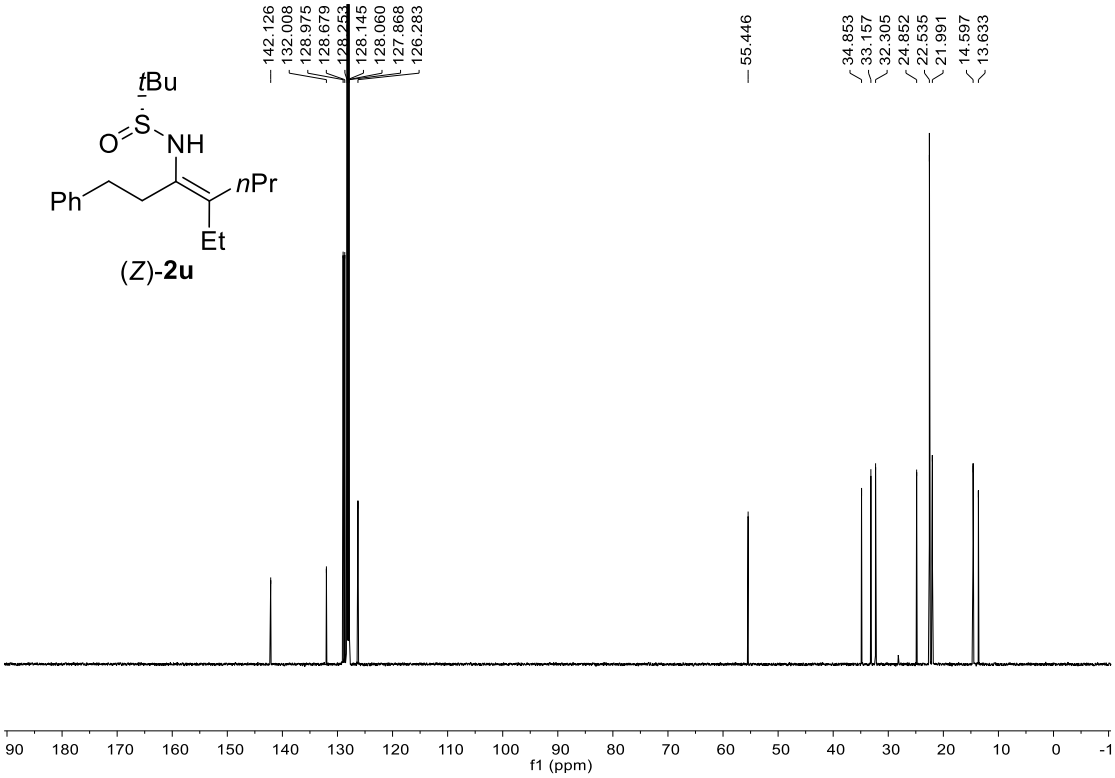
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2u**



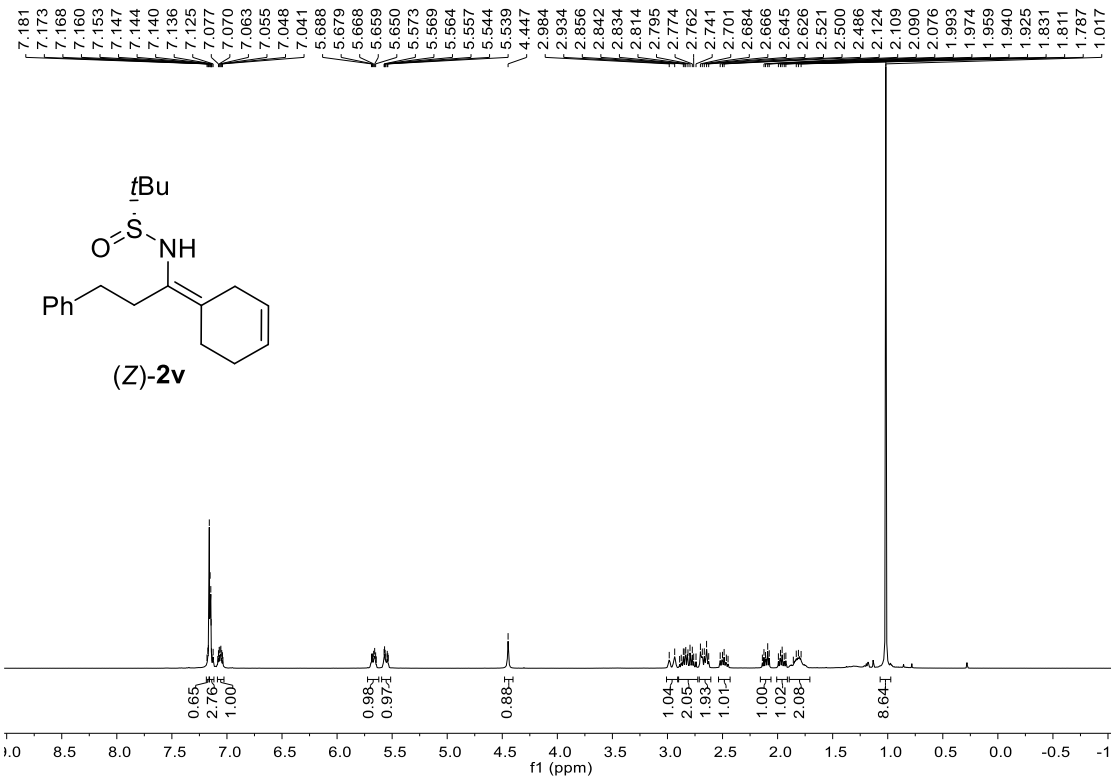
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2u**



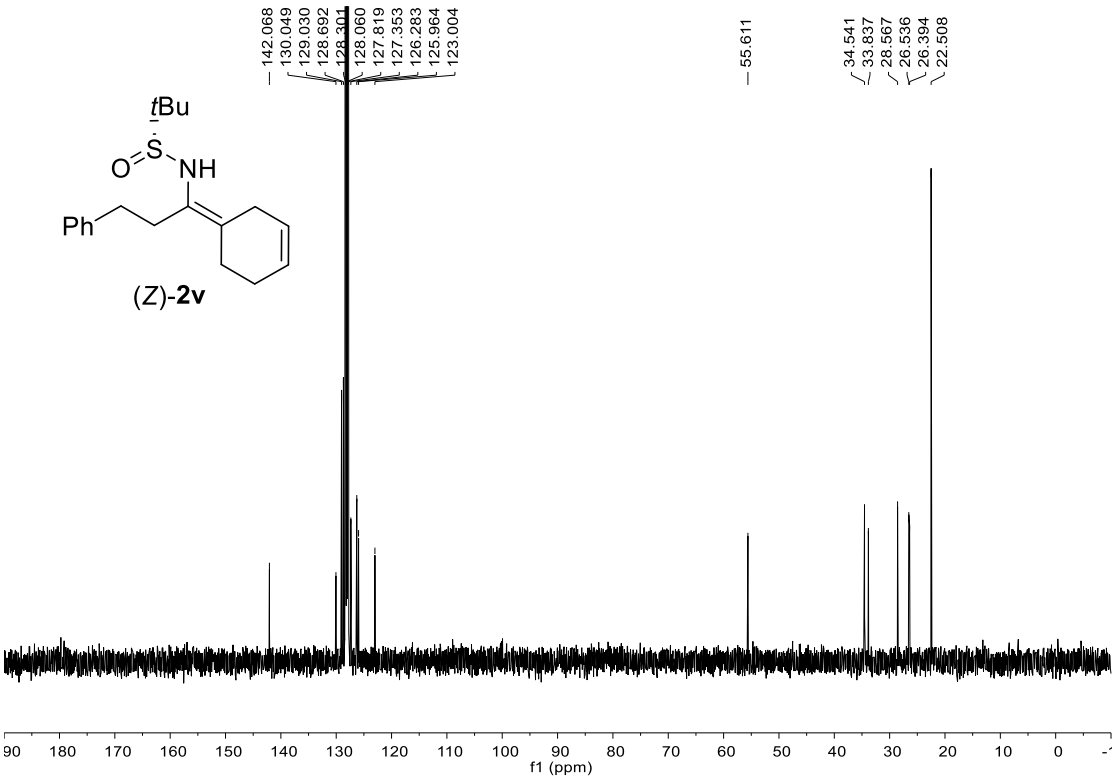
^{1}H NMR spectrum (C_6D_6, 500 MHz) of (*Z*)-**2u**



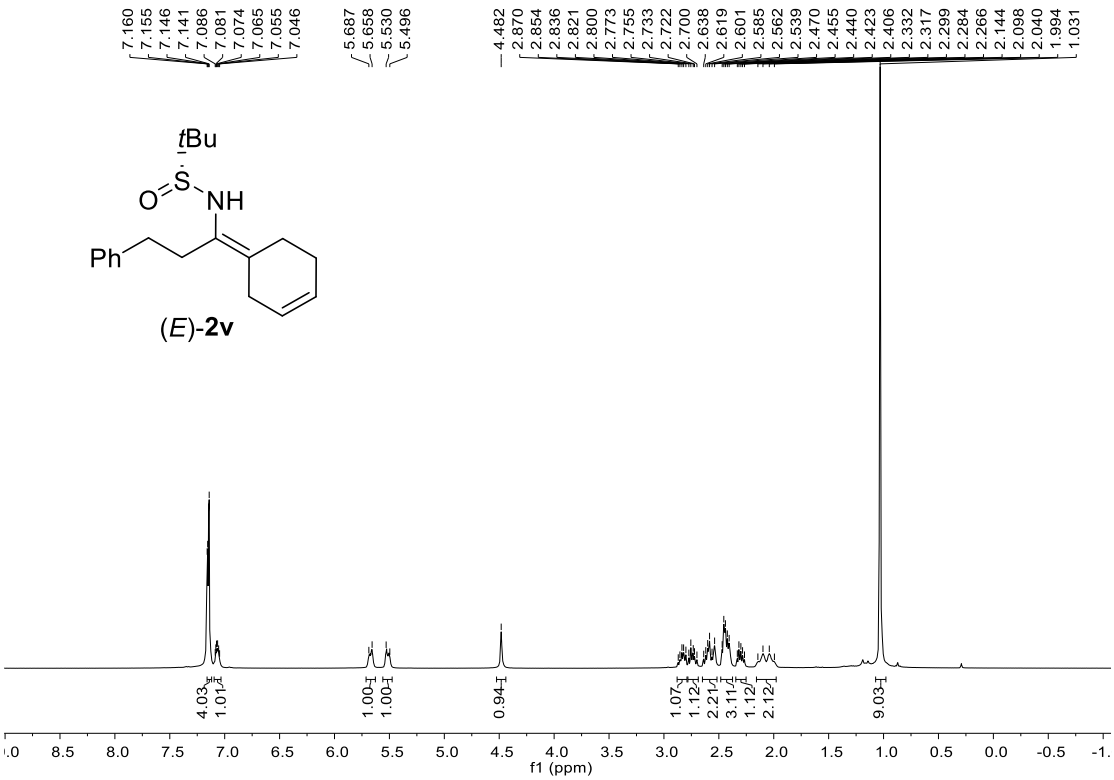
^{13}C NMR spectrum (C_6D_6, 125 MHz) of (*Z*)-**2u**



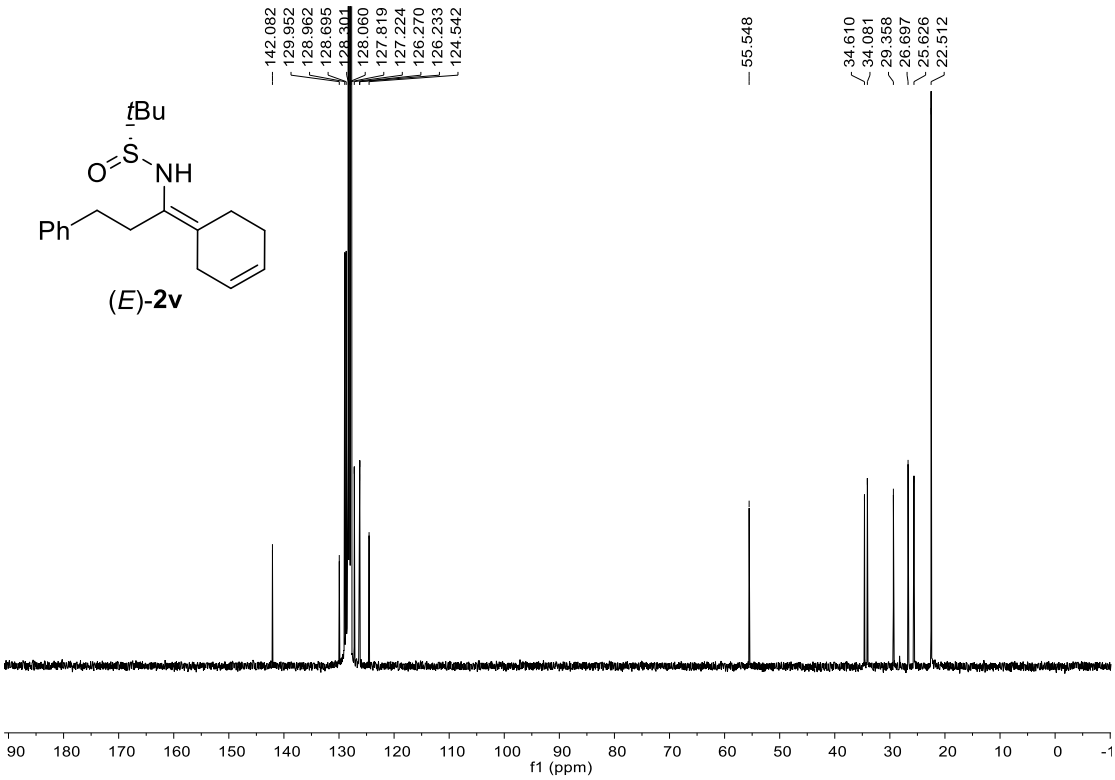
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2v**



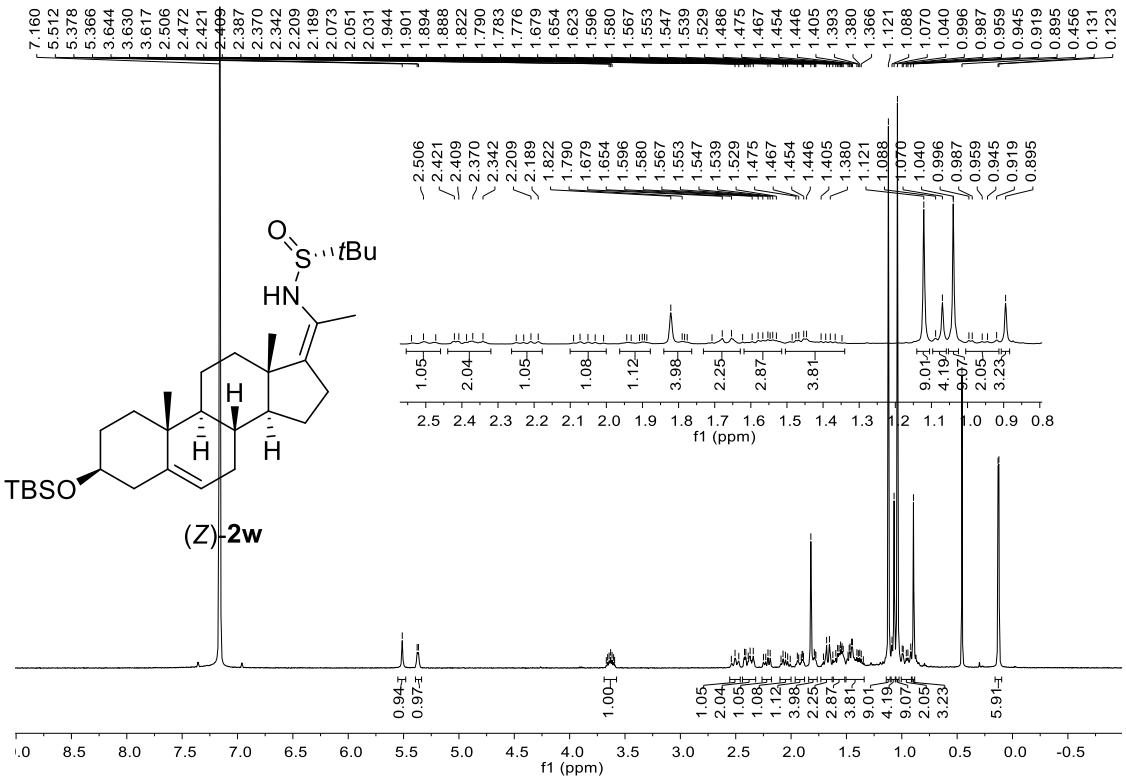
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2v**



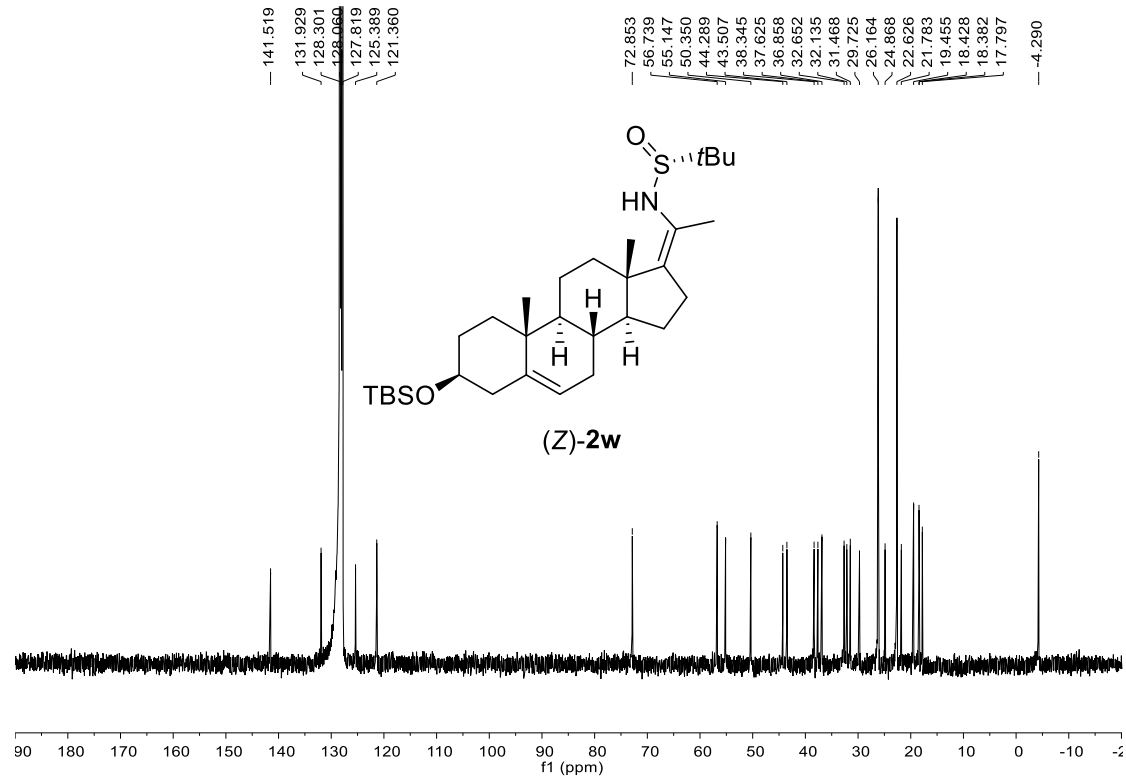
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2v**



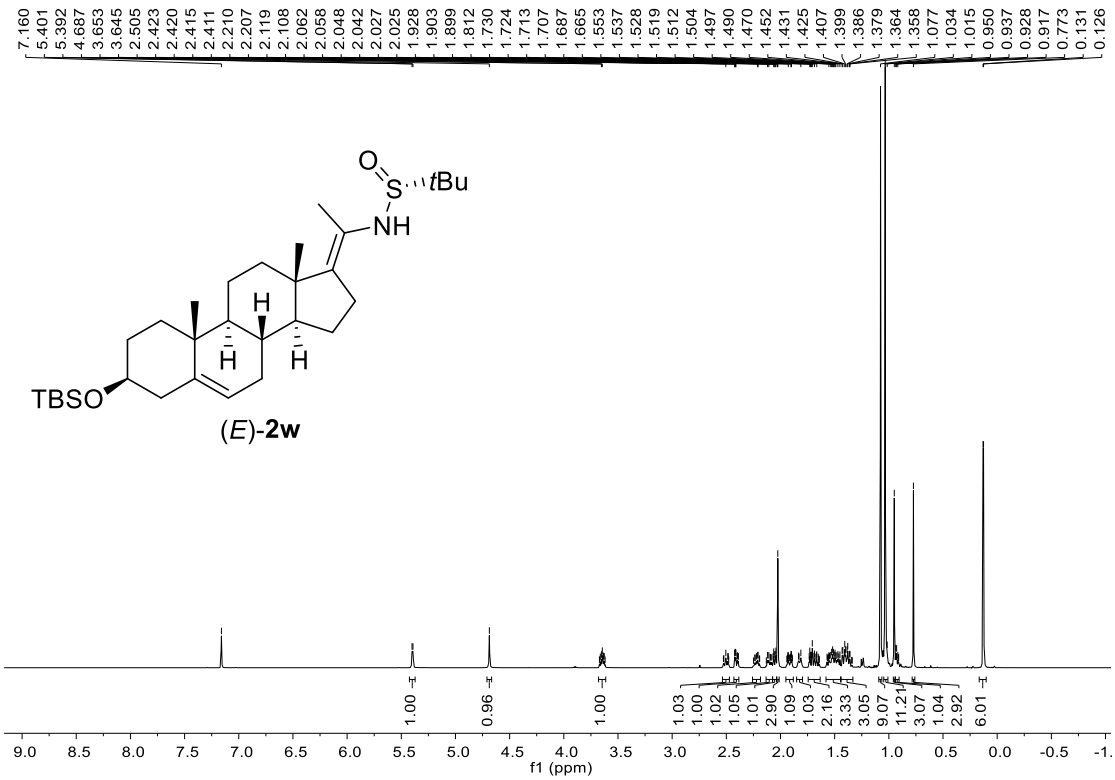
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2v**



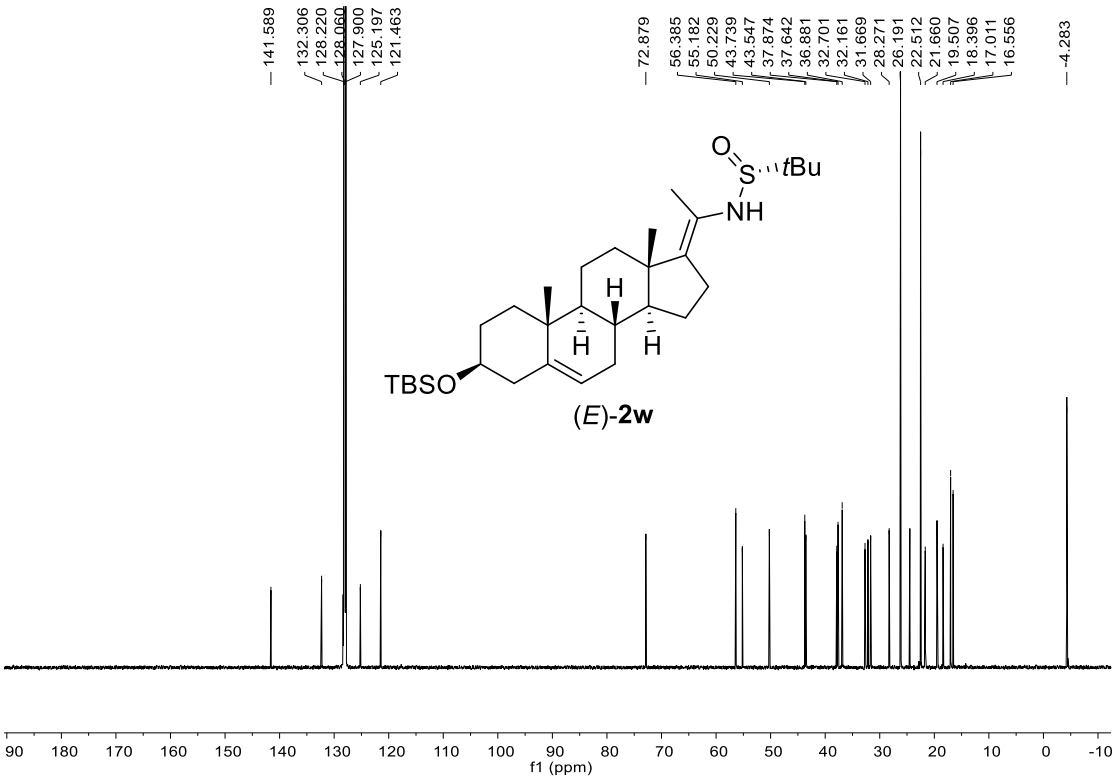
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2w**



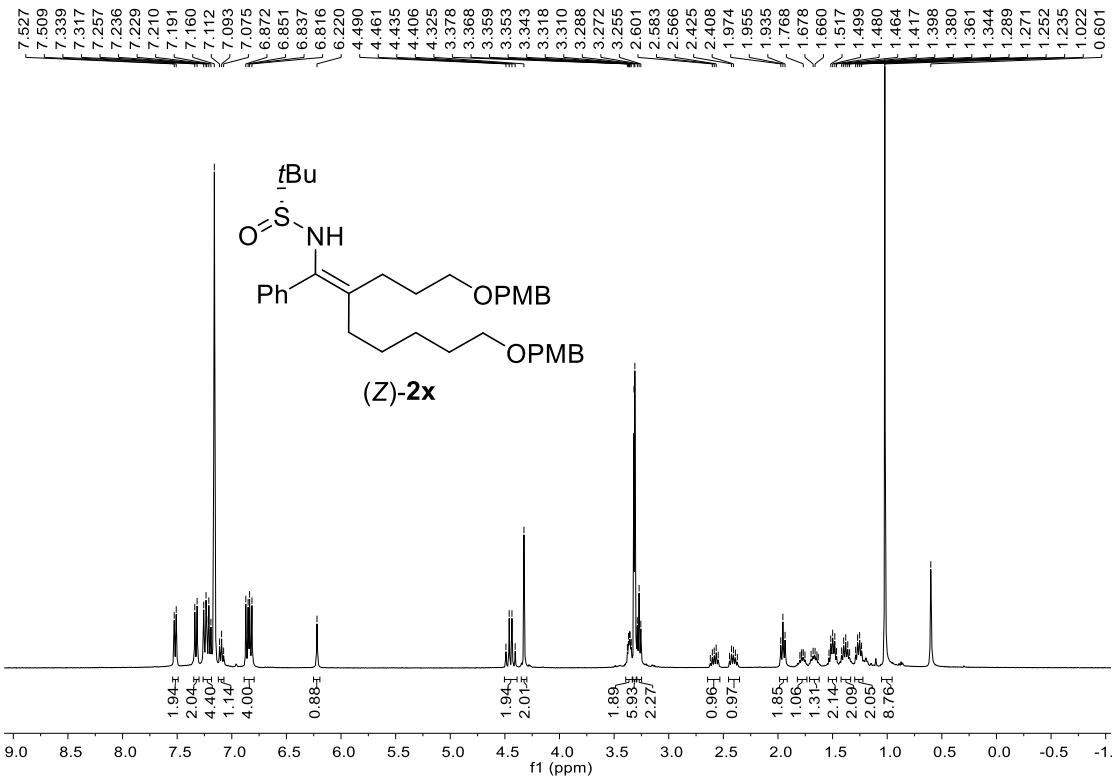
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2w**



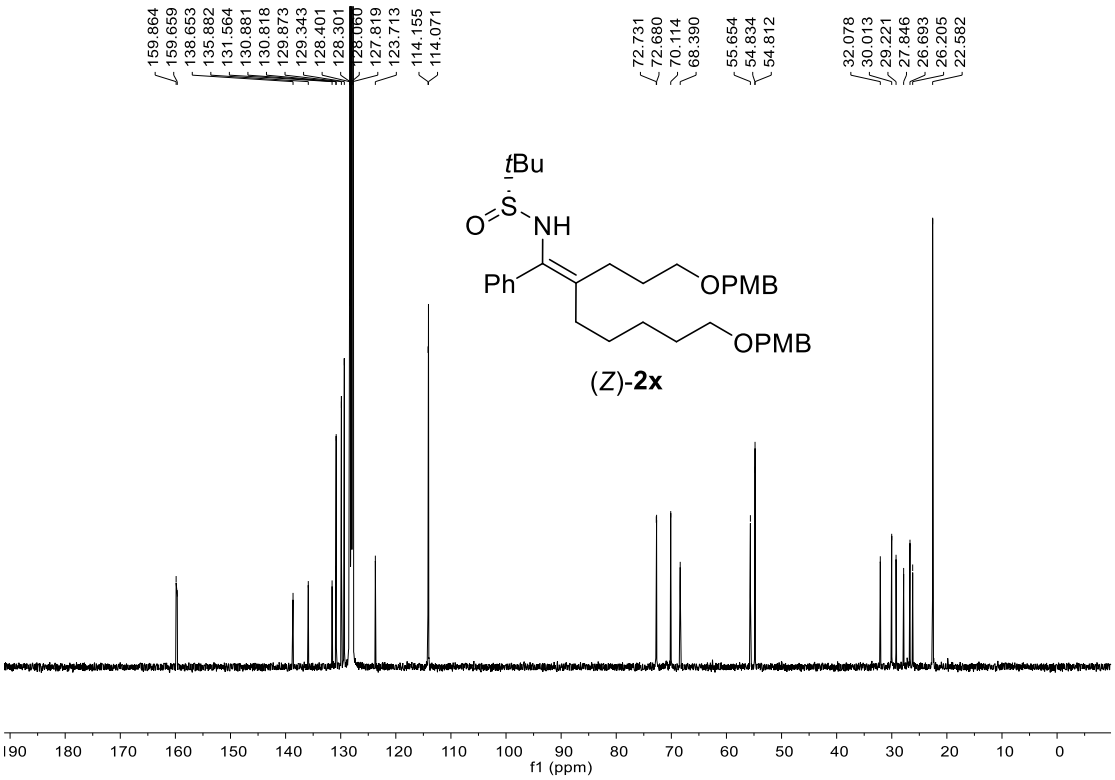
^{1}H NMR spectrum (C_6D_6, 600 MHz) of (*E*)-**2w**



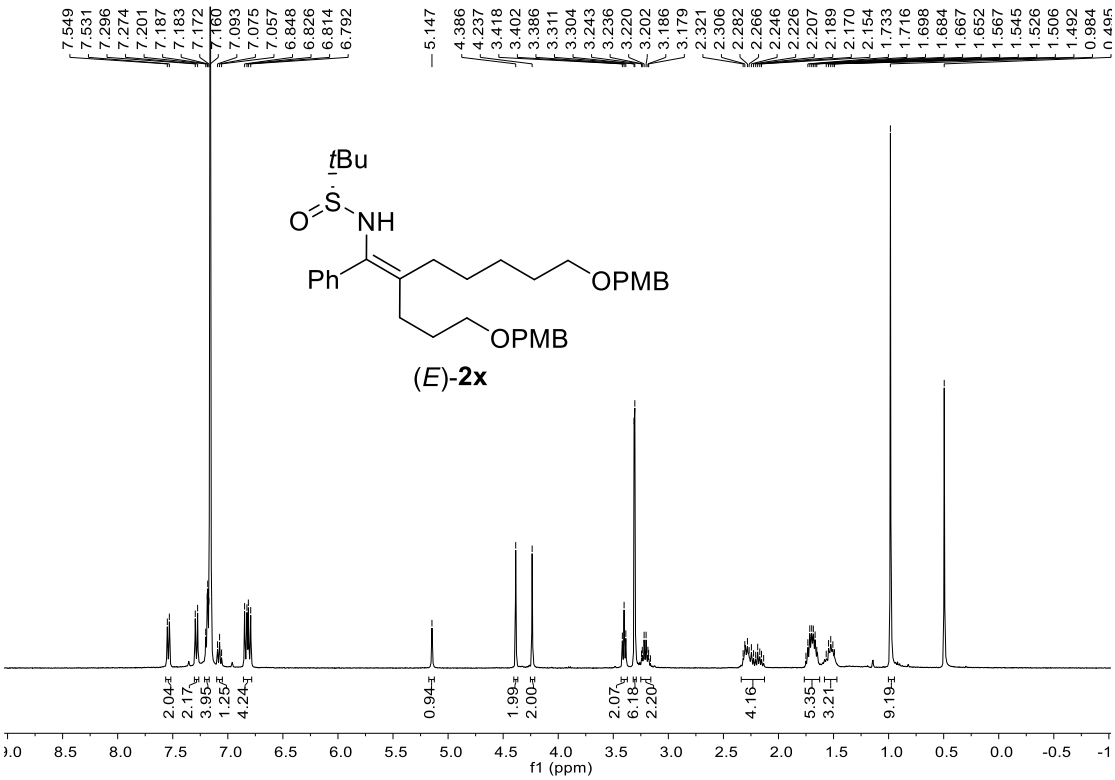
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2w**



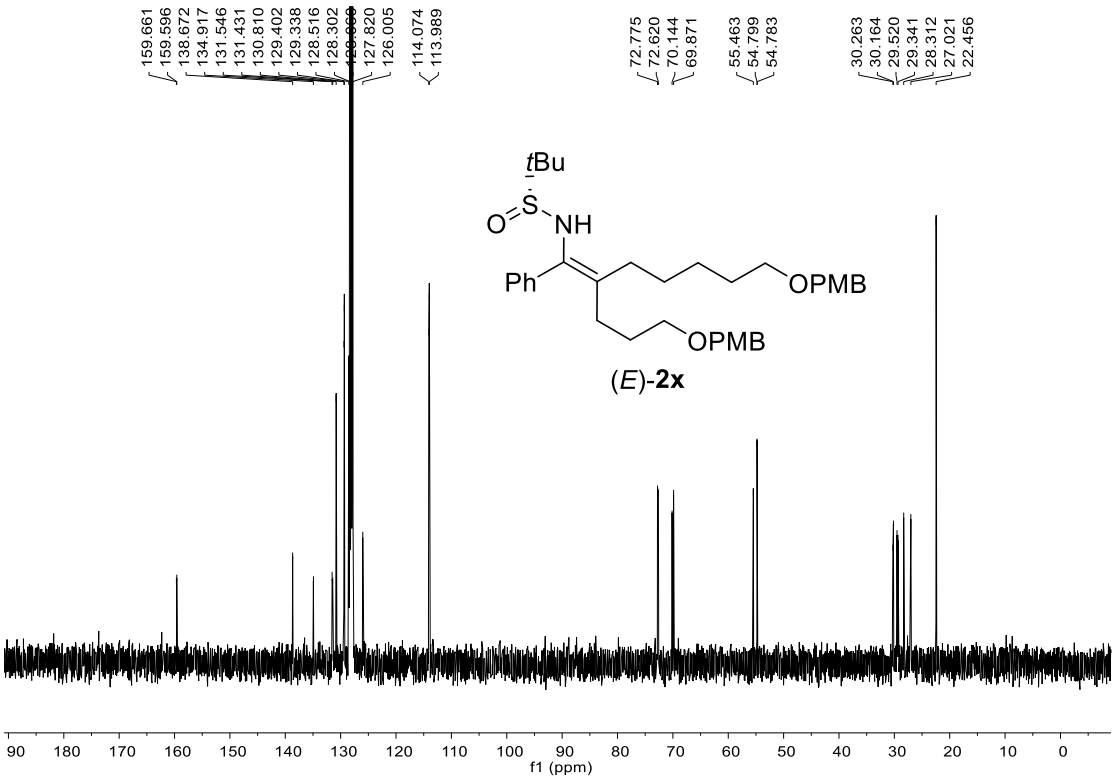
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2x**



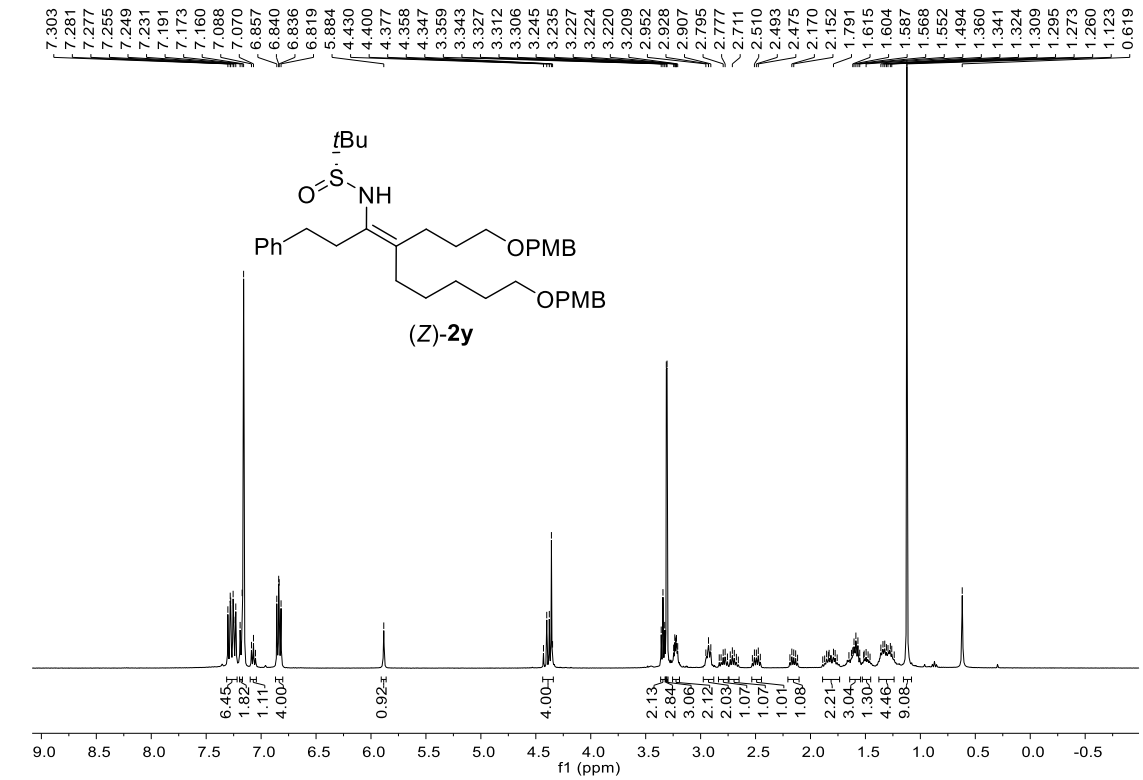
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2x**



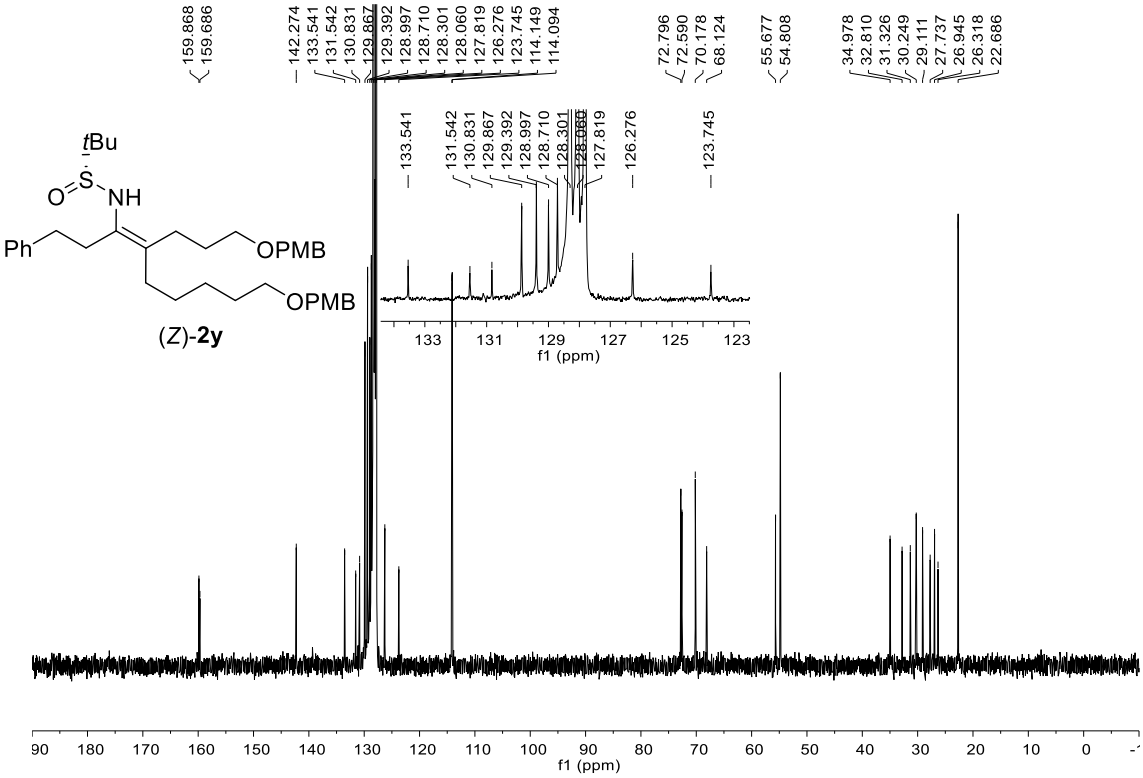
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2x**



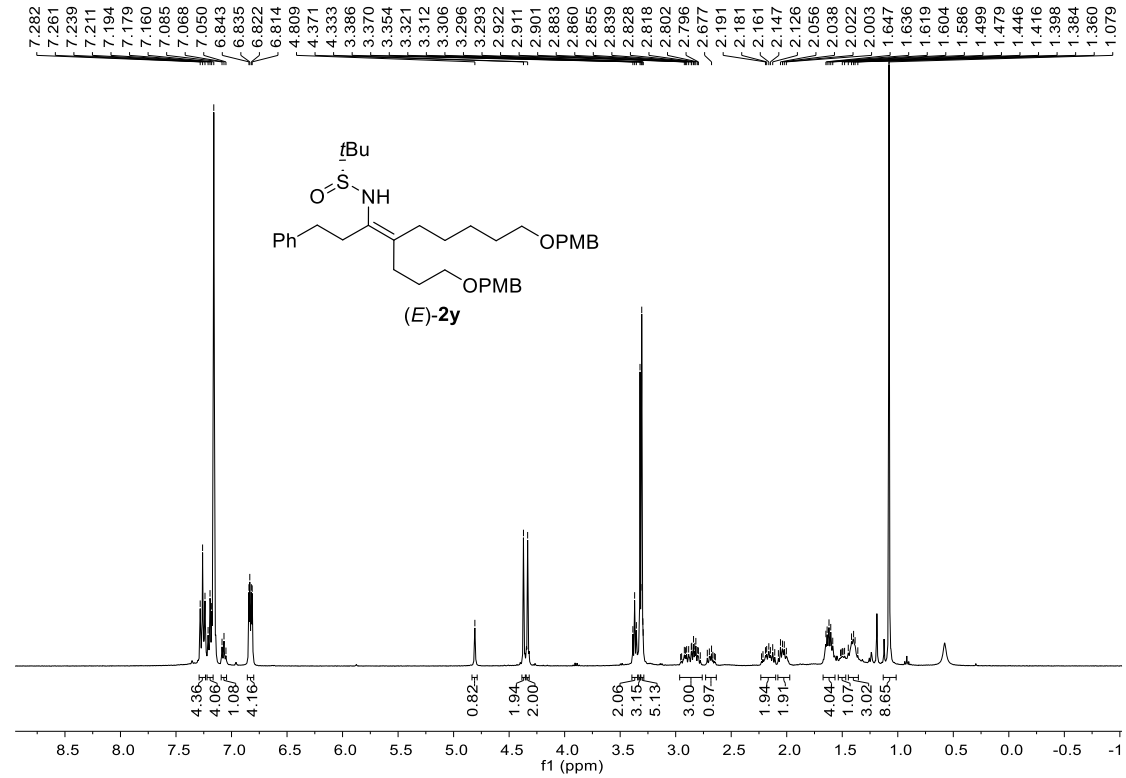
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2x**



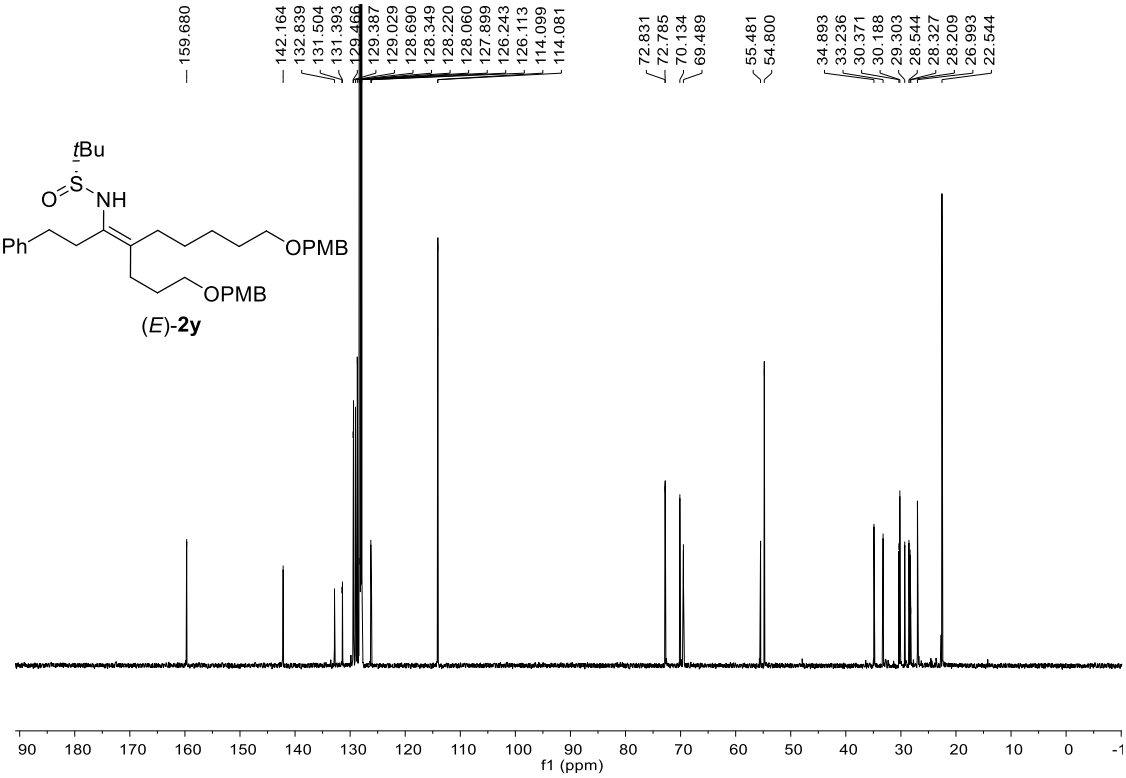
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2y**



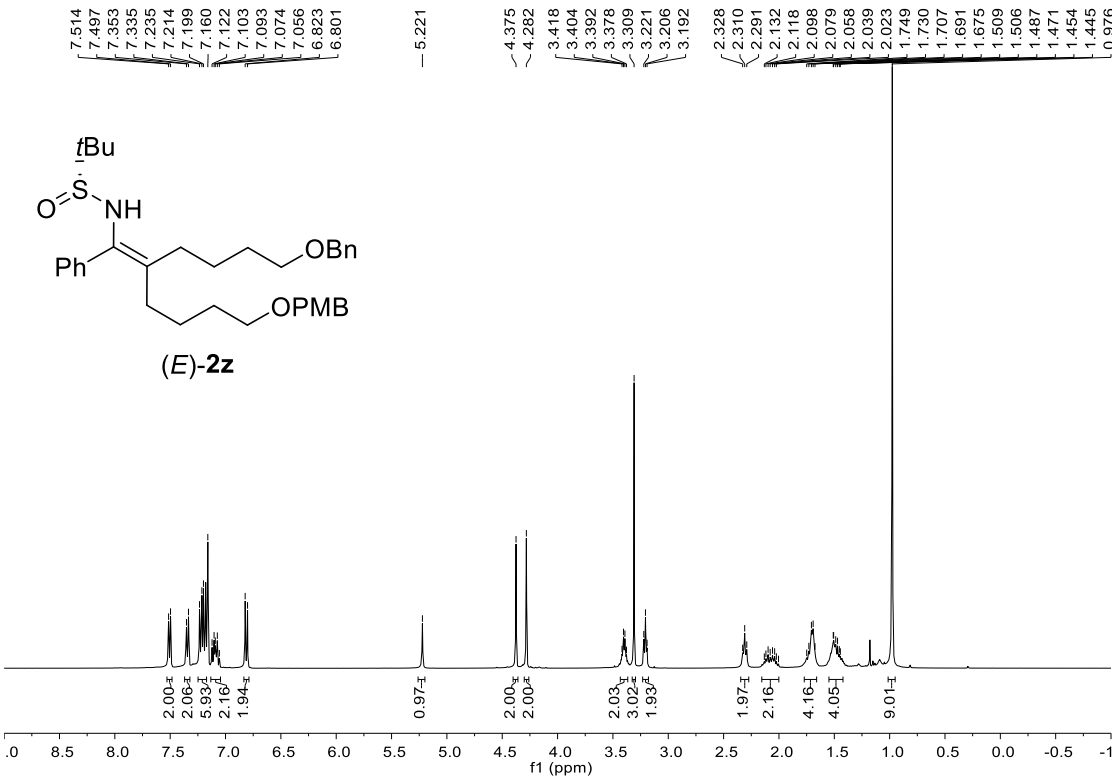
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Z*)-**2y**



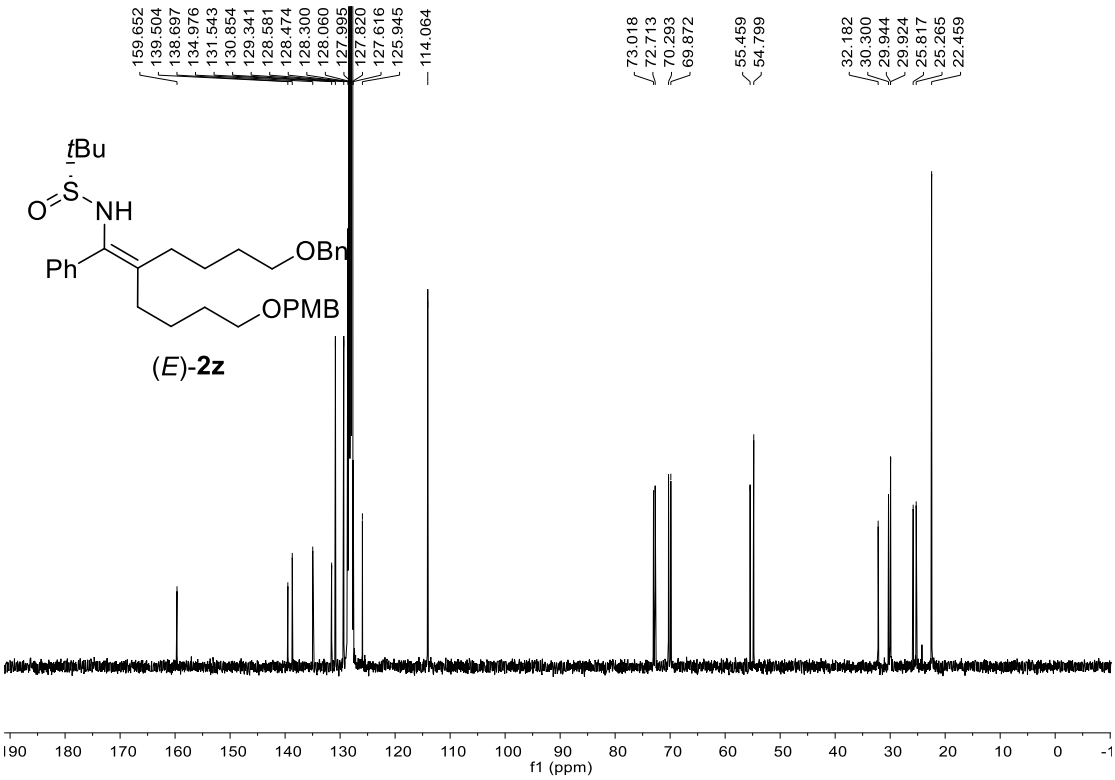
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2y**



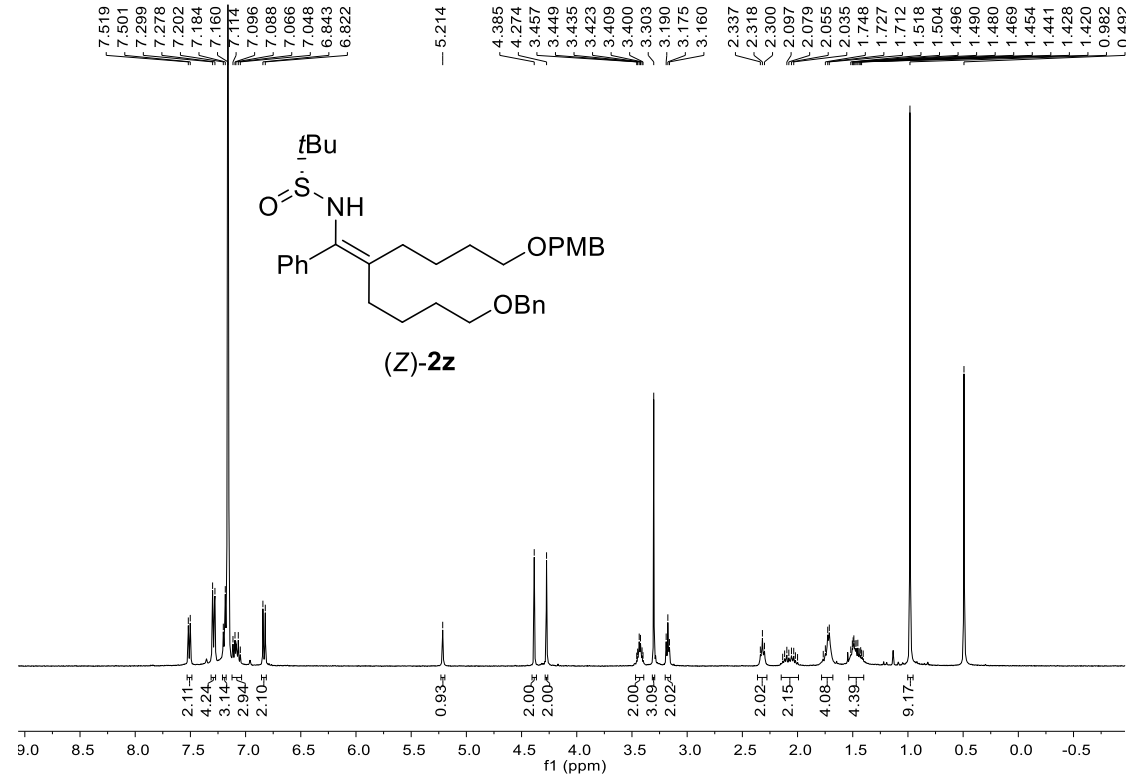
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*E*)-**2y**



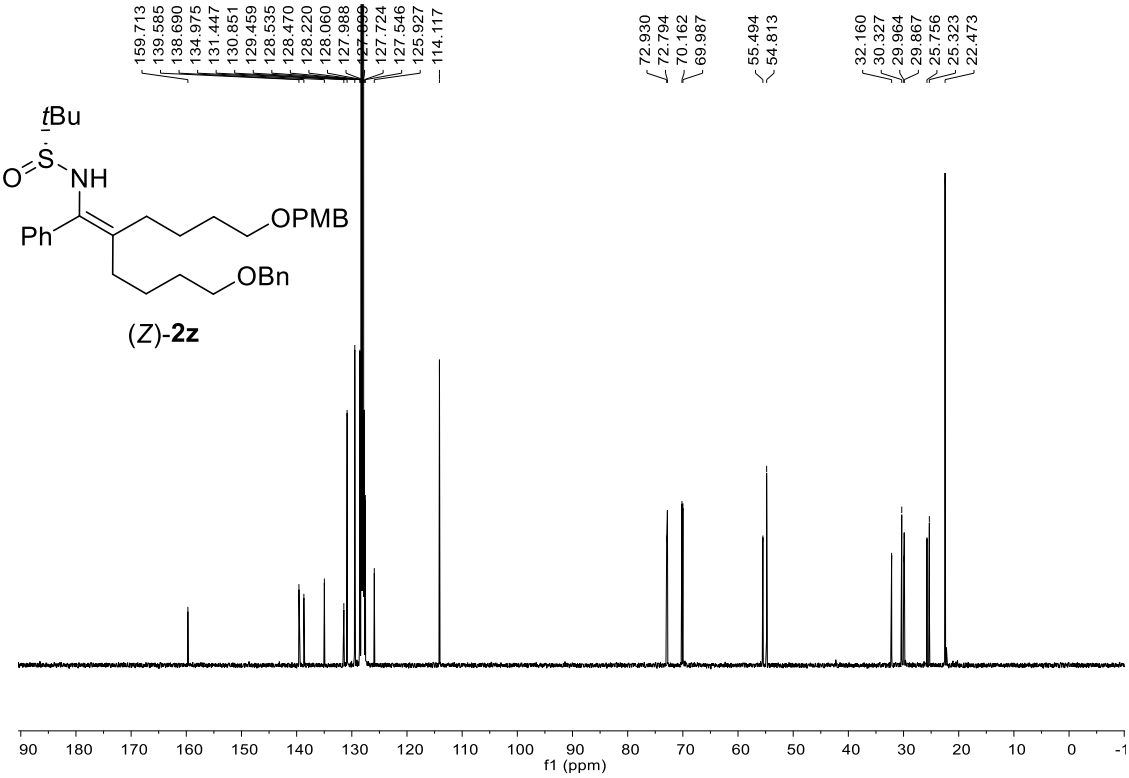
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2z**



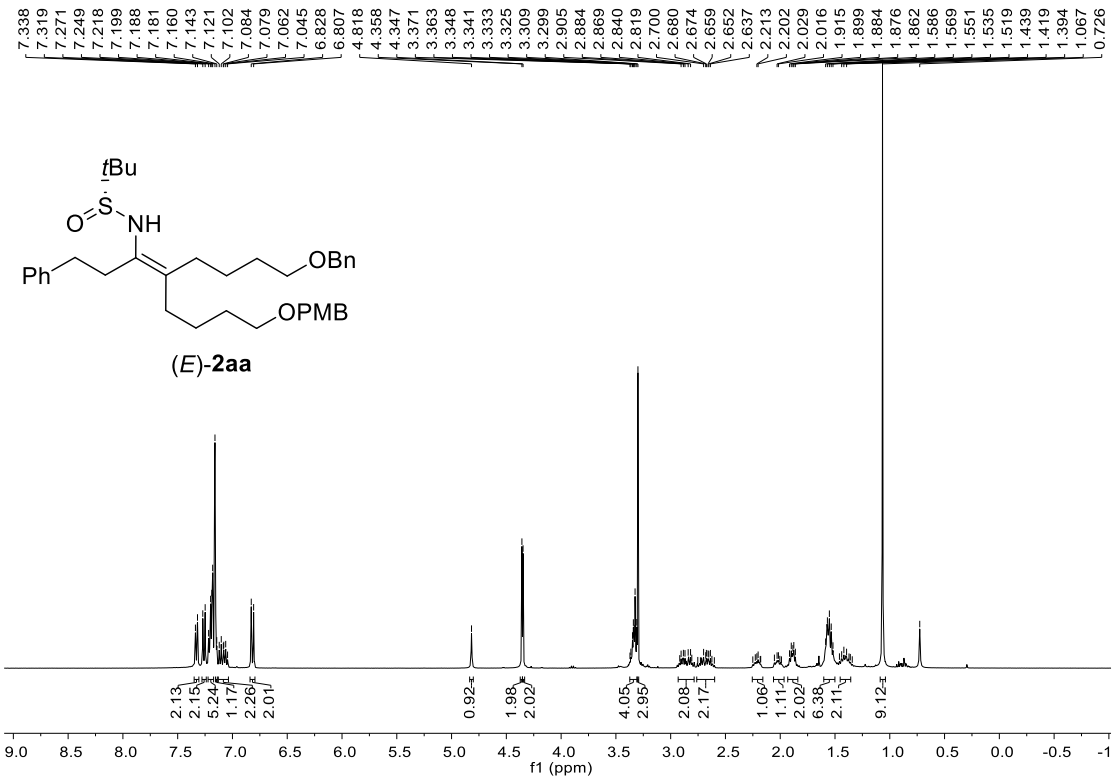
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2z**



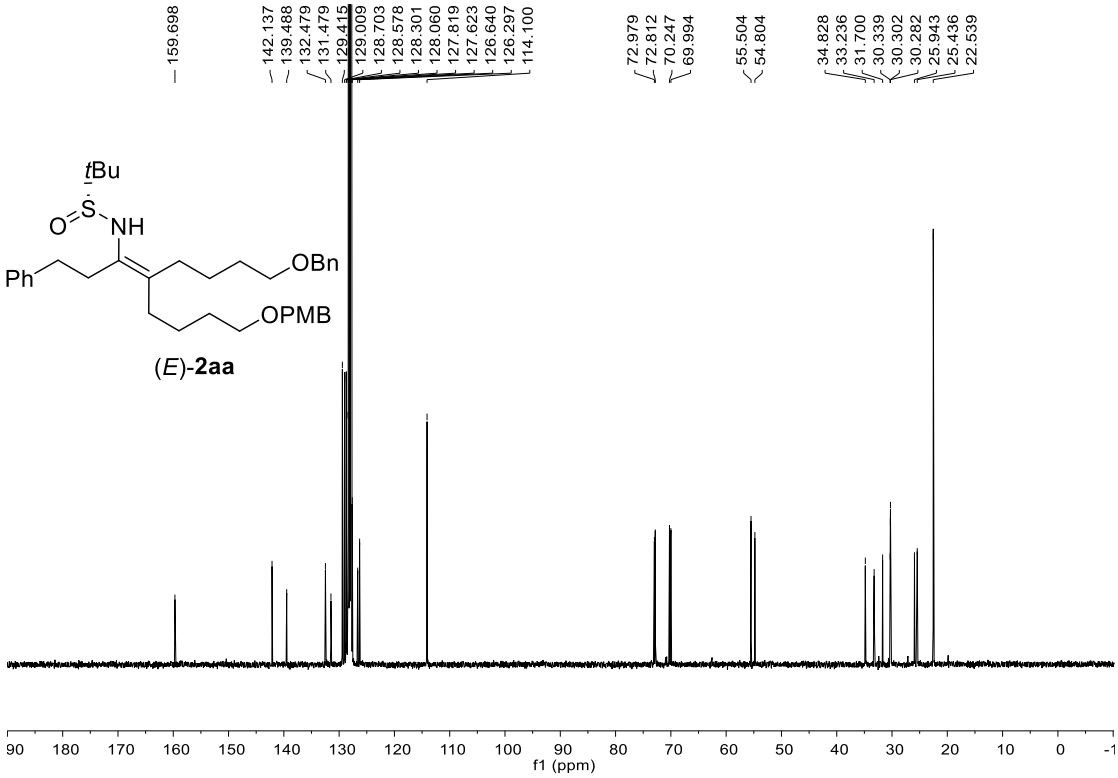
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Z*)-**2z**



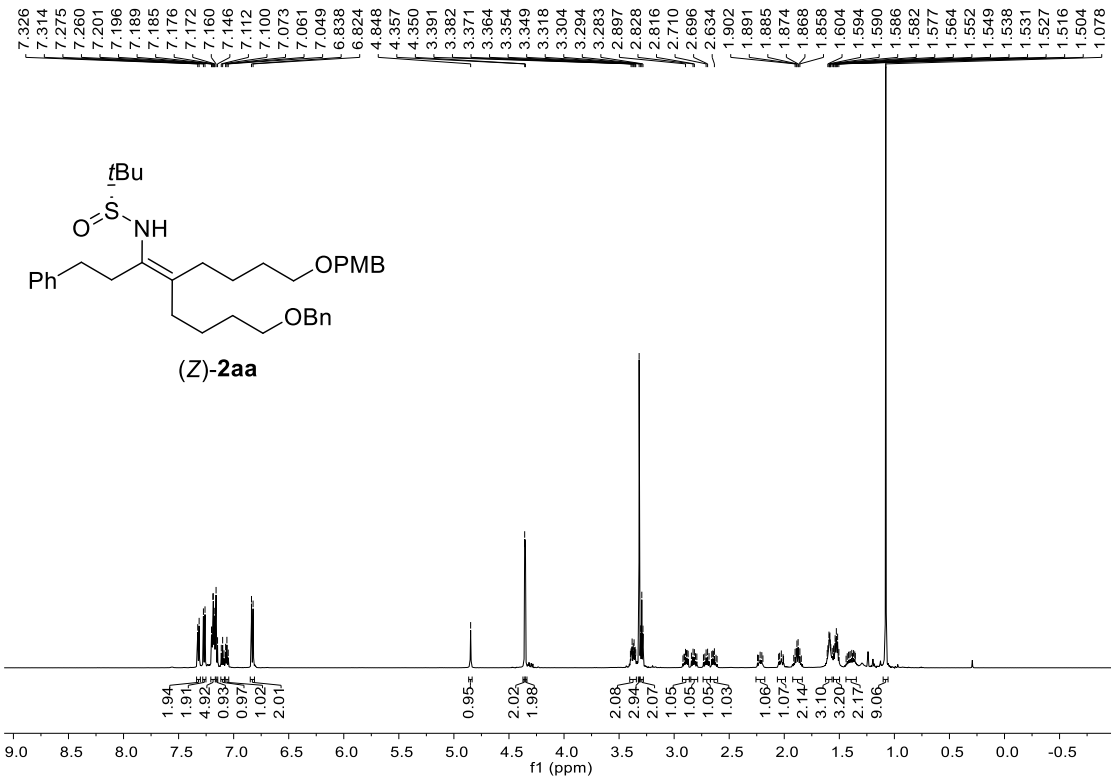
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*Z*)-**2z**



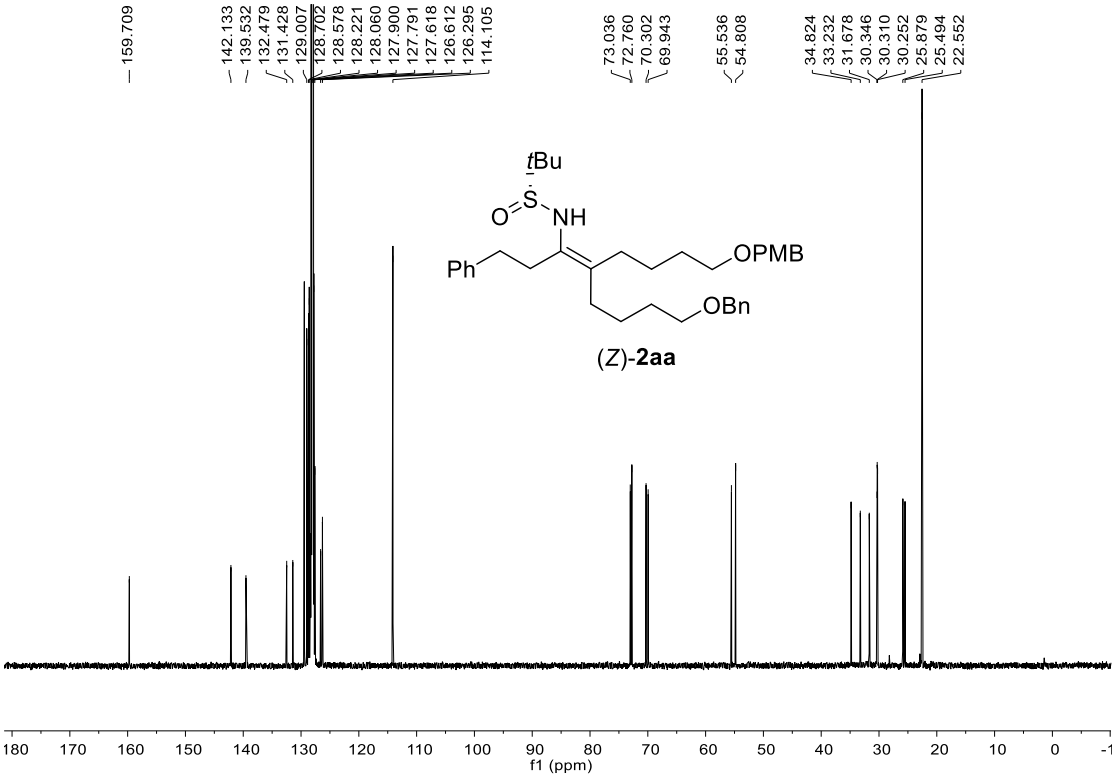
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*E*)-**2aa**



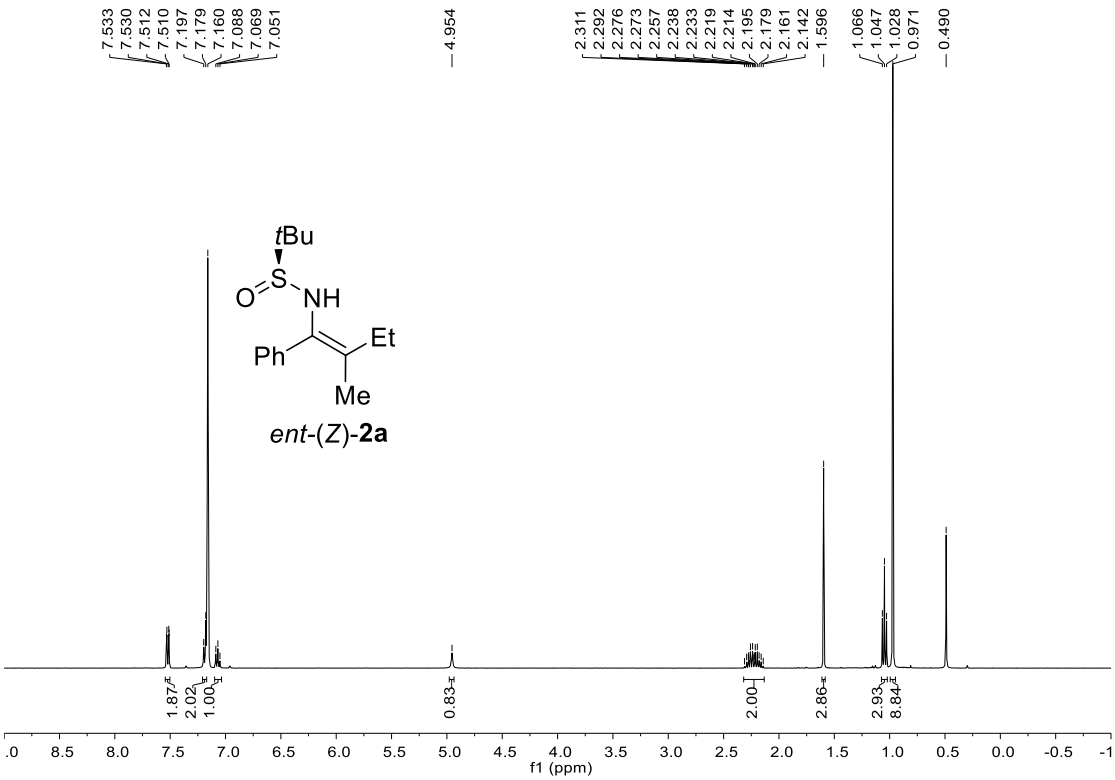
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*E*)-**2aa**



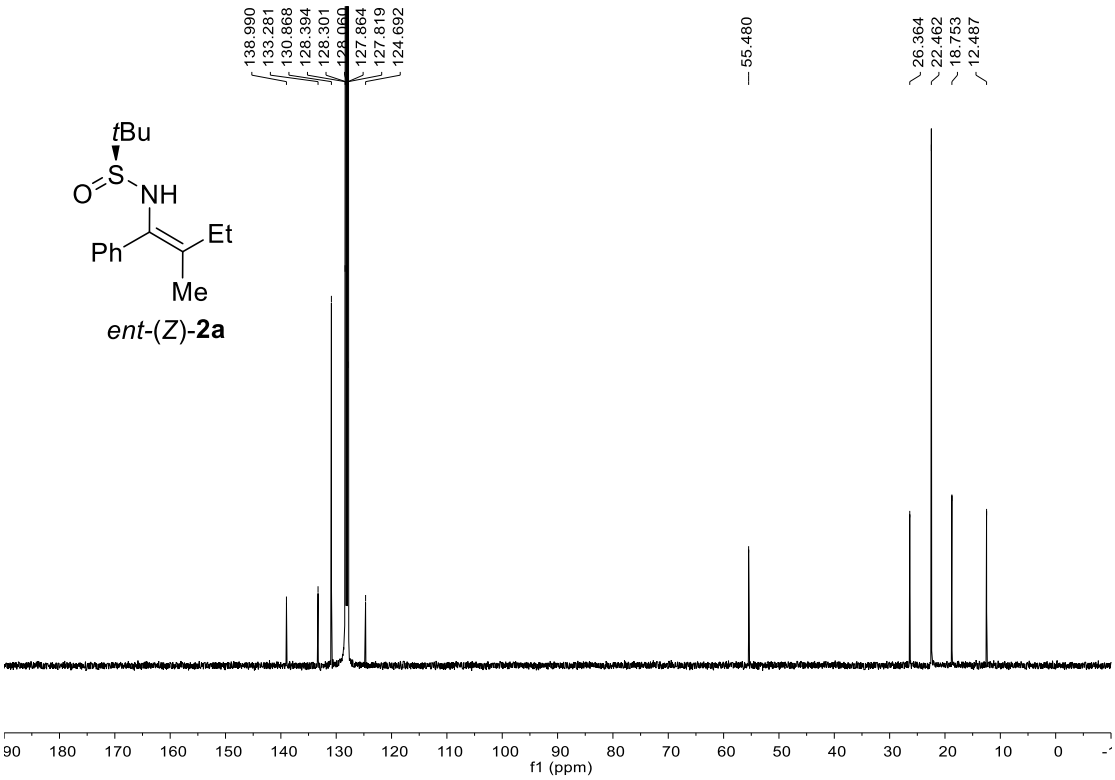
^{1}H NMR spectrum (C_6D_6, 600 MHz) of (*Z*)-**2aa**



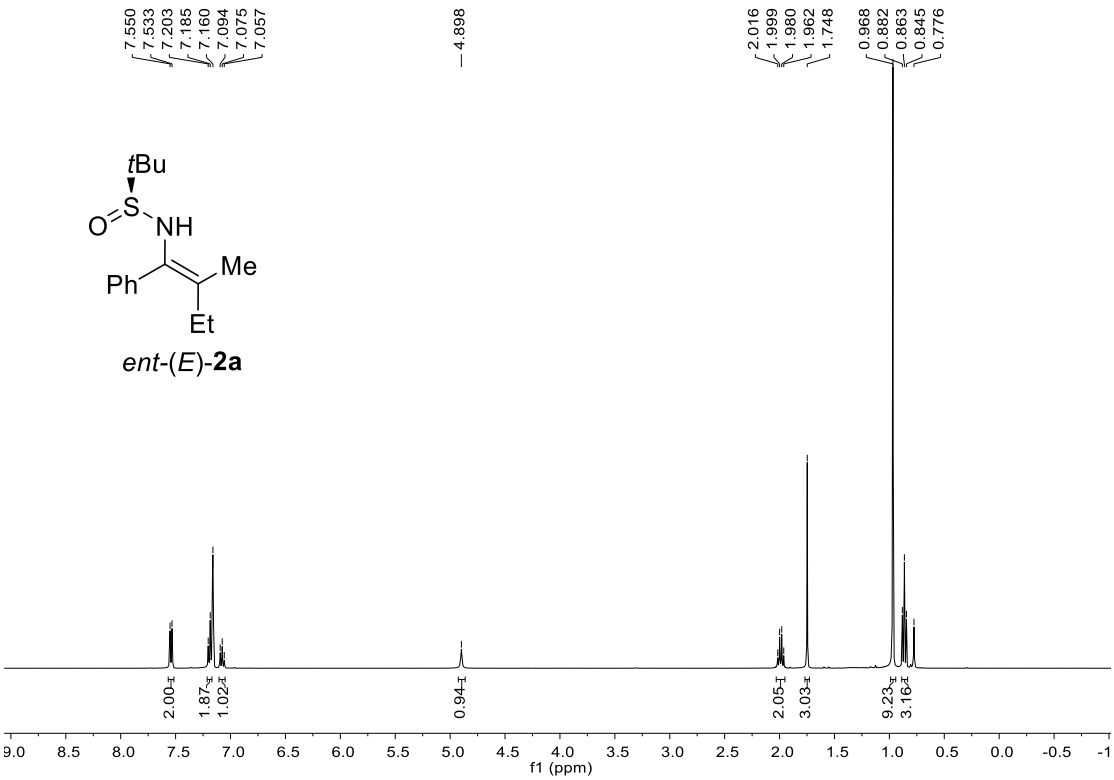
^{13}C NMR spectrum (C_6D_6, 150 MHz) of (*Z*)-**2aa**



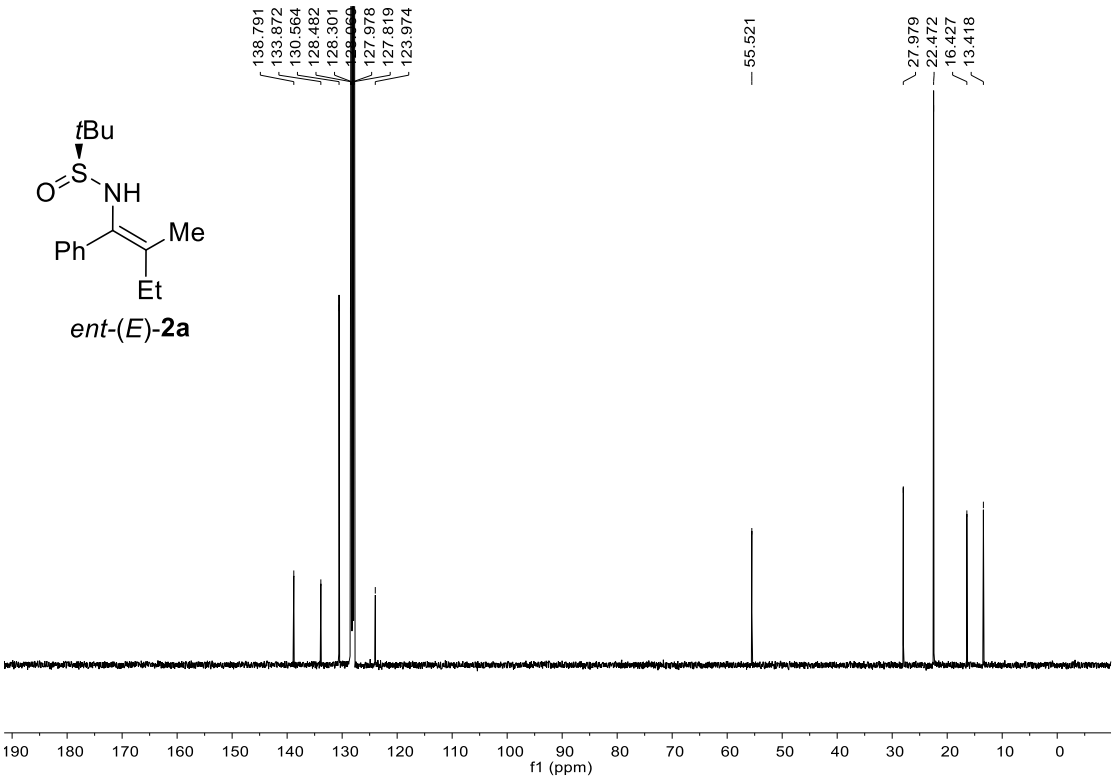
^{1}H NMR spectrum (C_6D_6, 400 MHz) of *ent*-(*Z*)-**2a**



^{13}C NMR spectrum (C_6D_6, 100 MHz) of *ent*-(*Z*)-**2a**

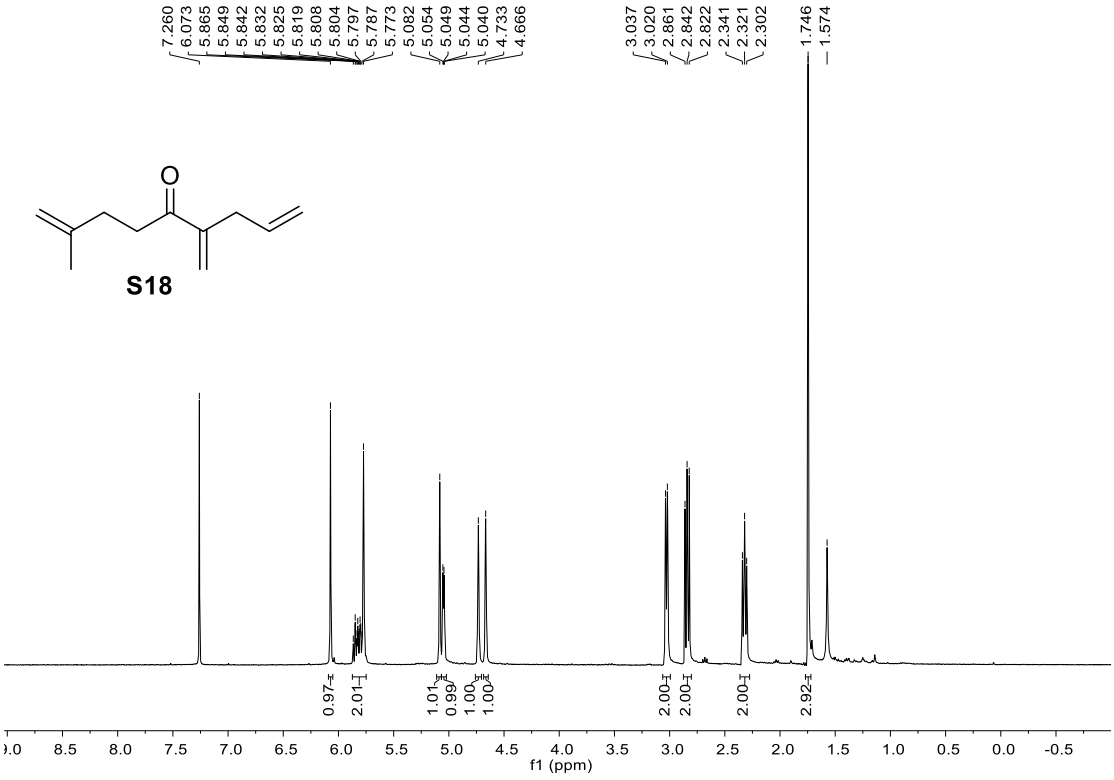


^{1}H NMR spectrum (C_6D_6, 400 MHz) of *ent*-(*E*)-**2a**

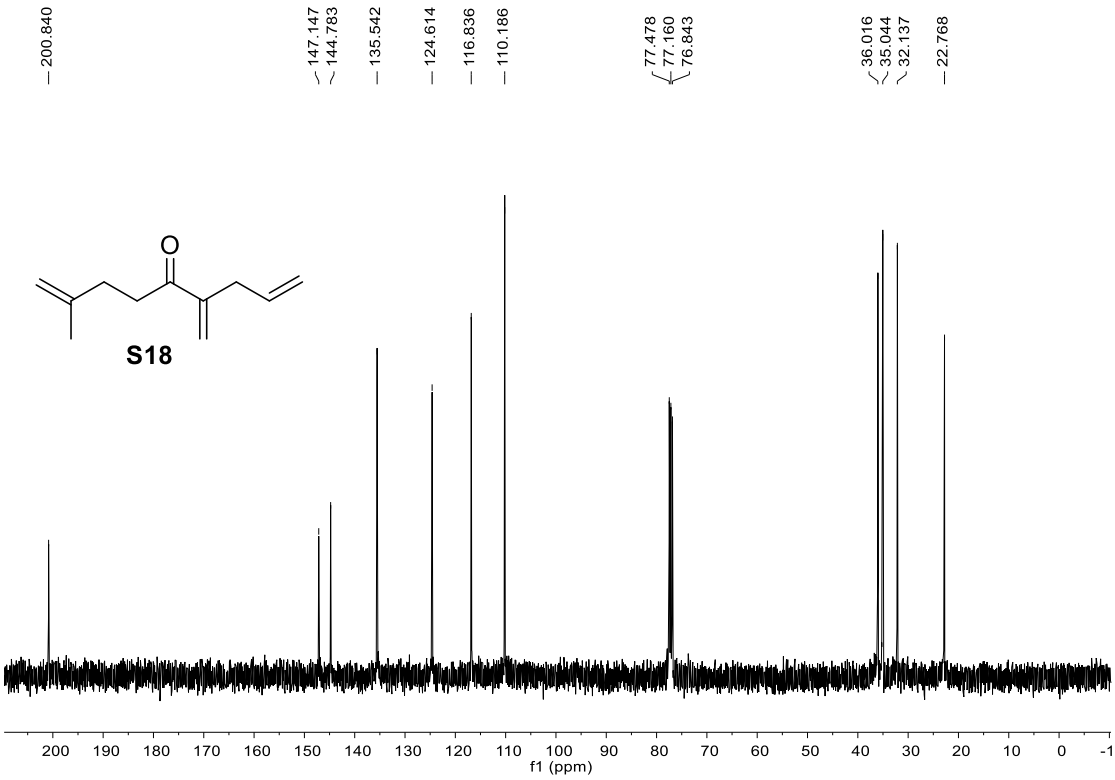


^{13}C NMR spectrum (C_6D_6, 100 MHz) of *ent*-(*E*)-**2a**

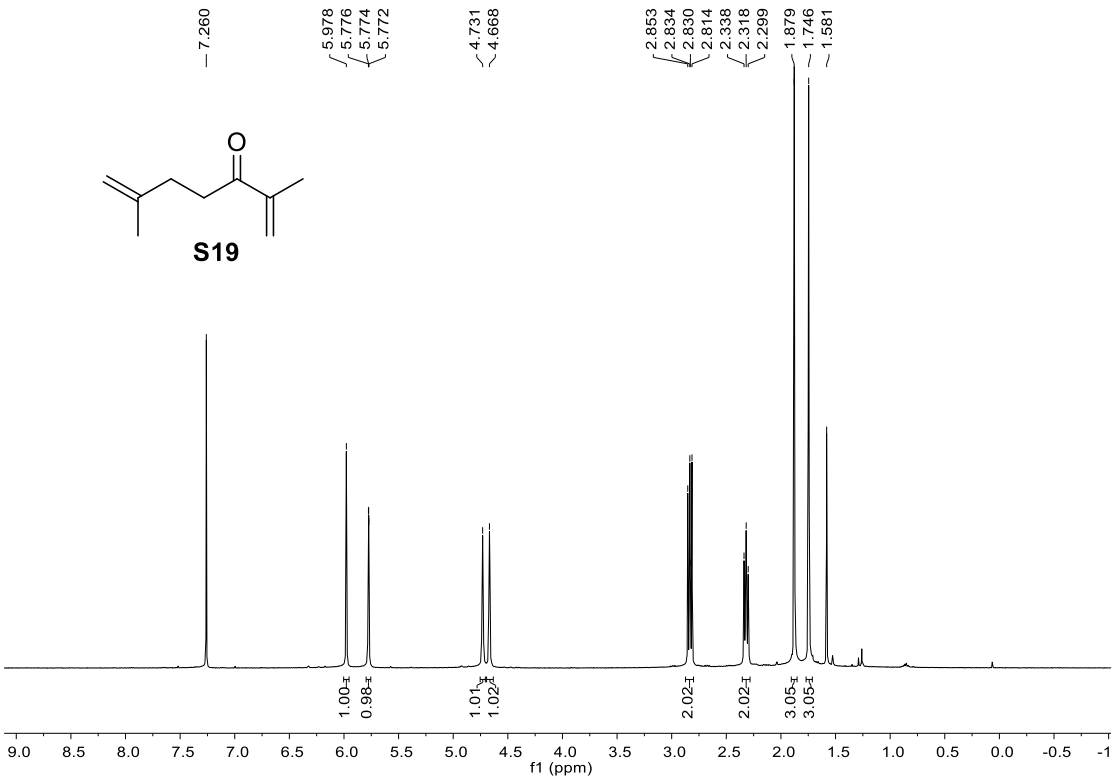
^{1}H and ^{13}C NMR spectra of synthetic intermediates for preparation of (–)-Daucene



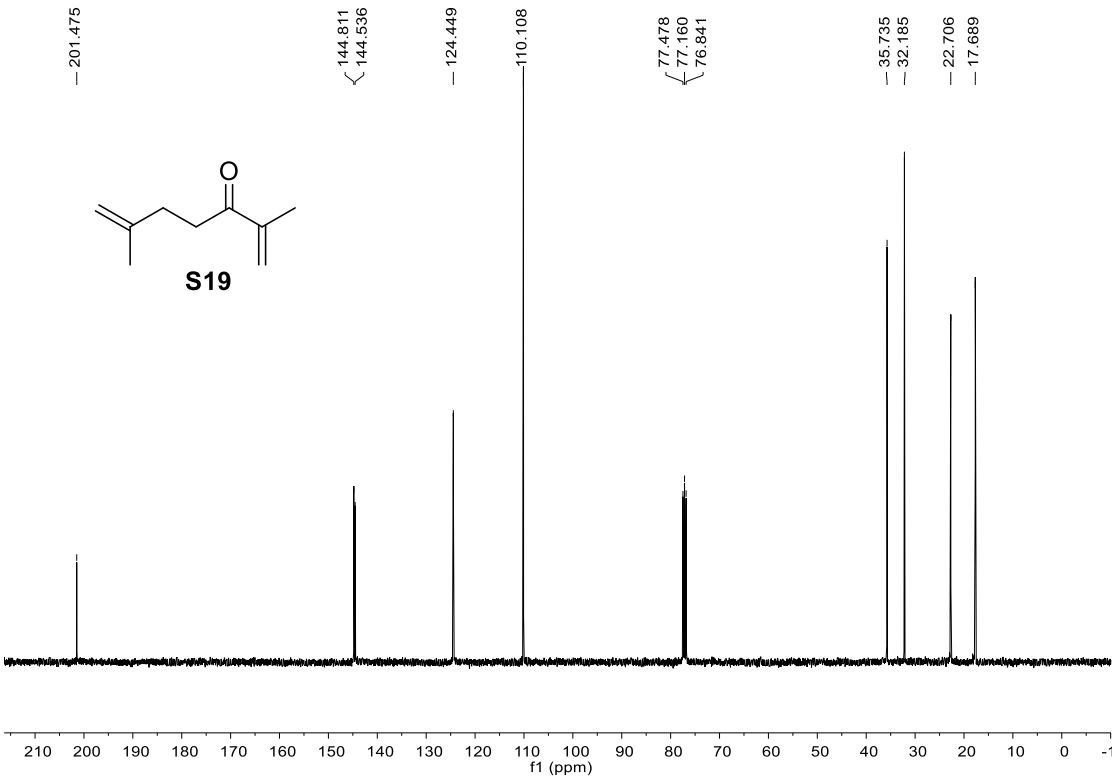
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S18**



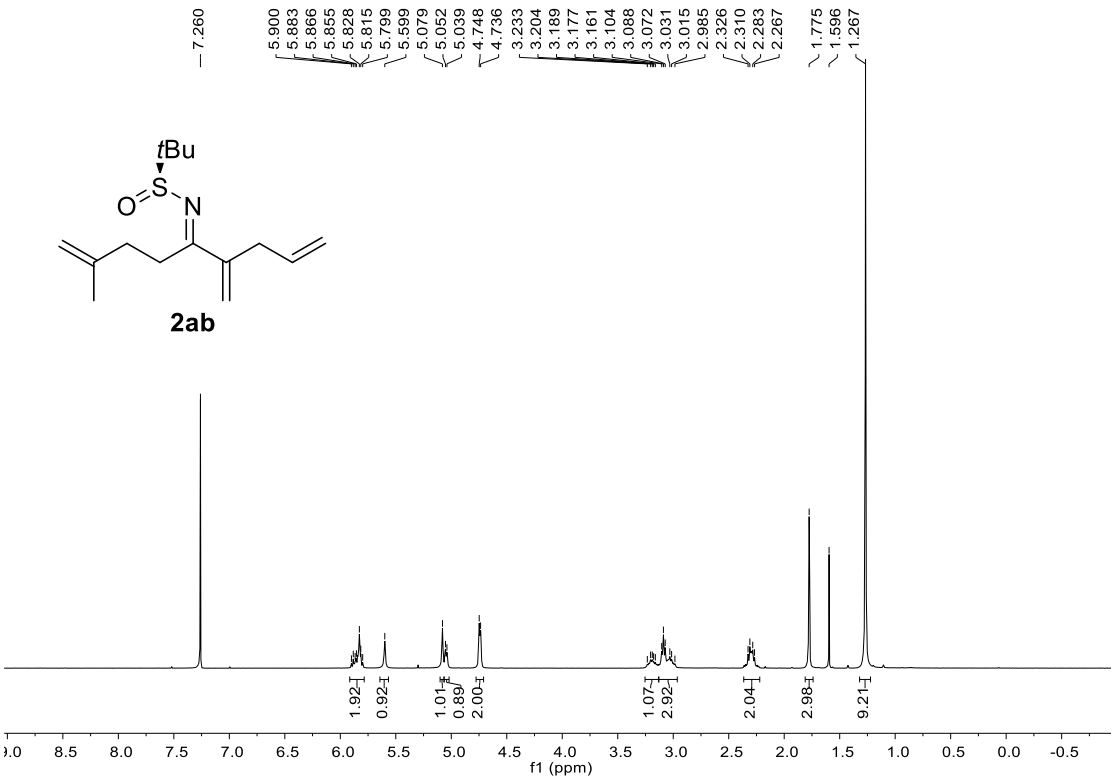
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S18**



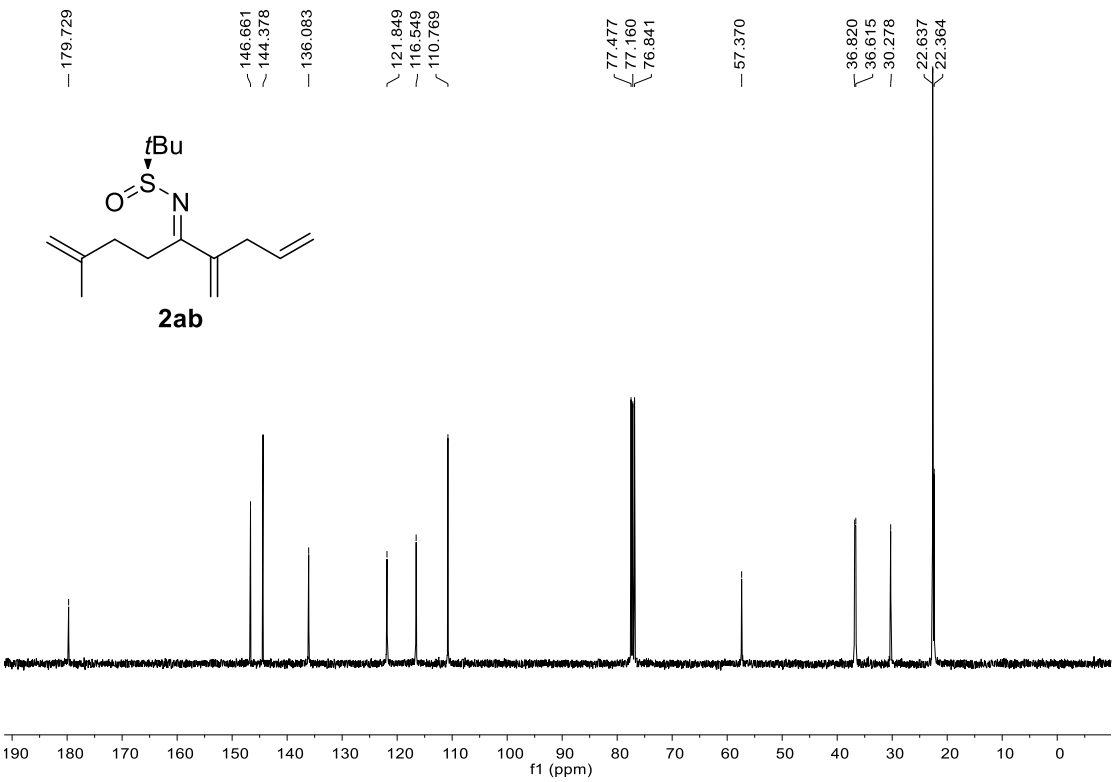
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S19**



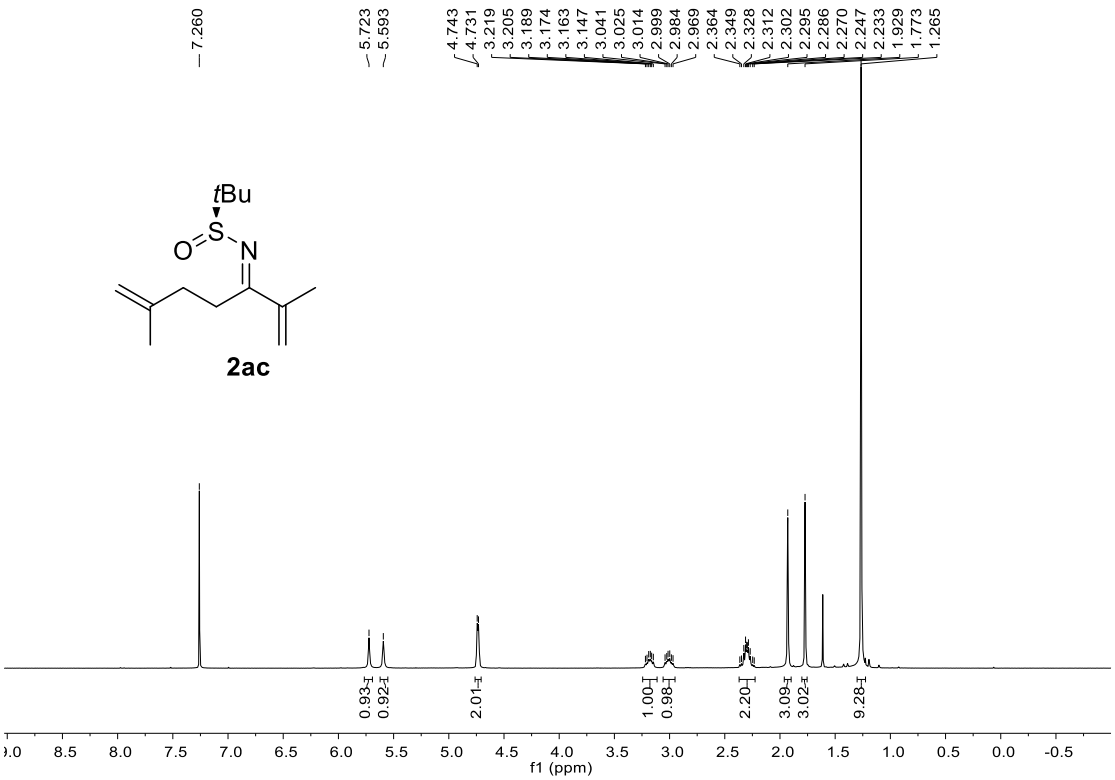
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S19**



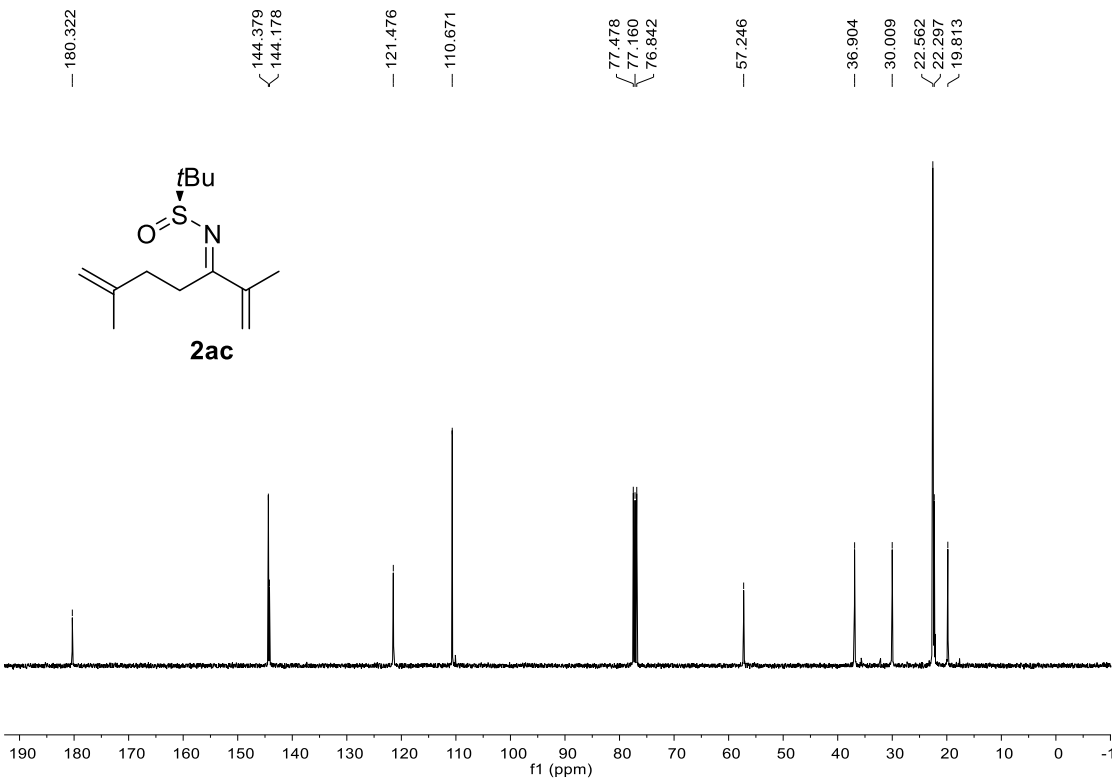
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2ab**



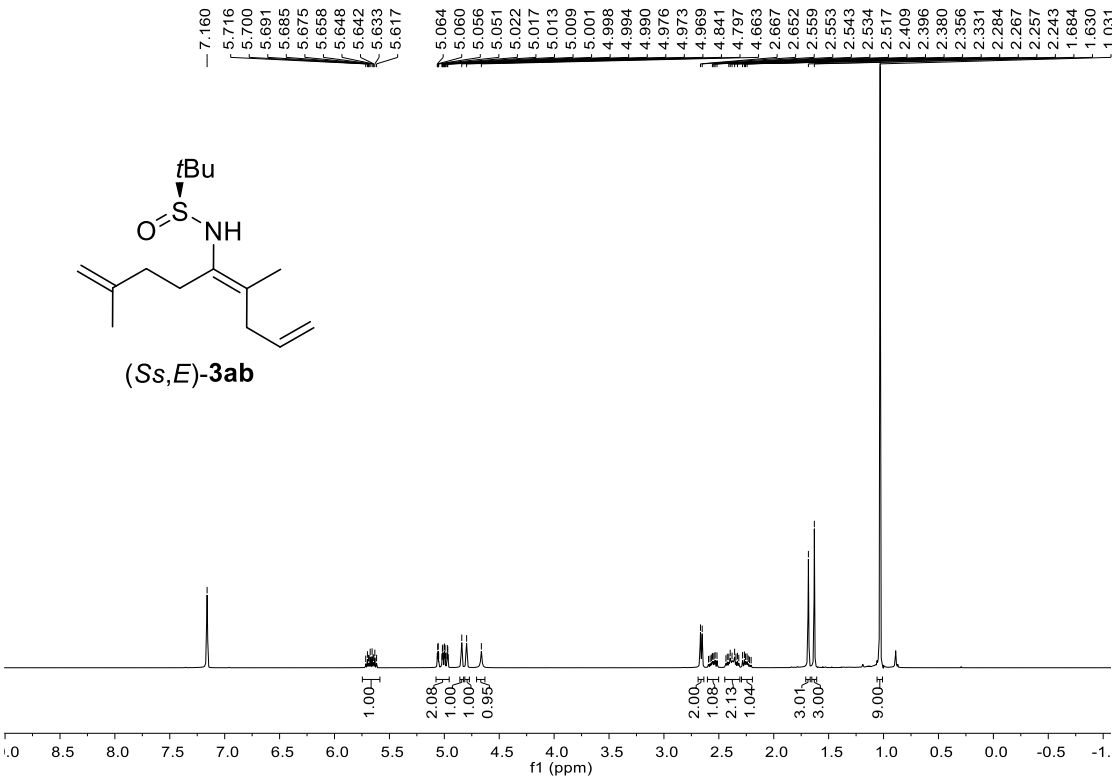
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2ab**



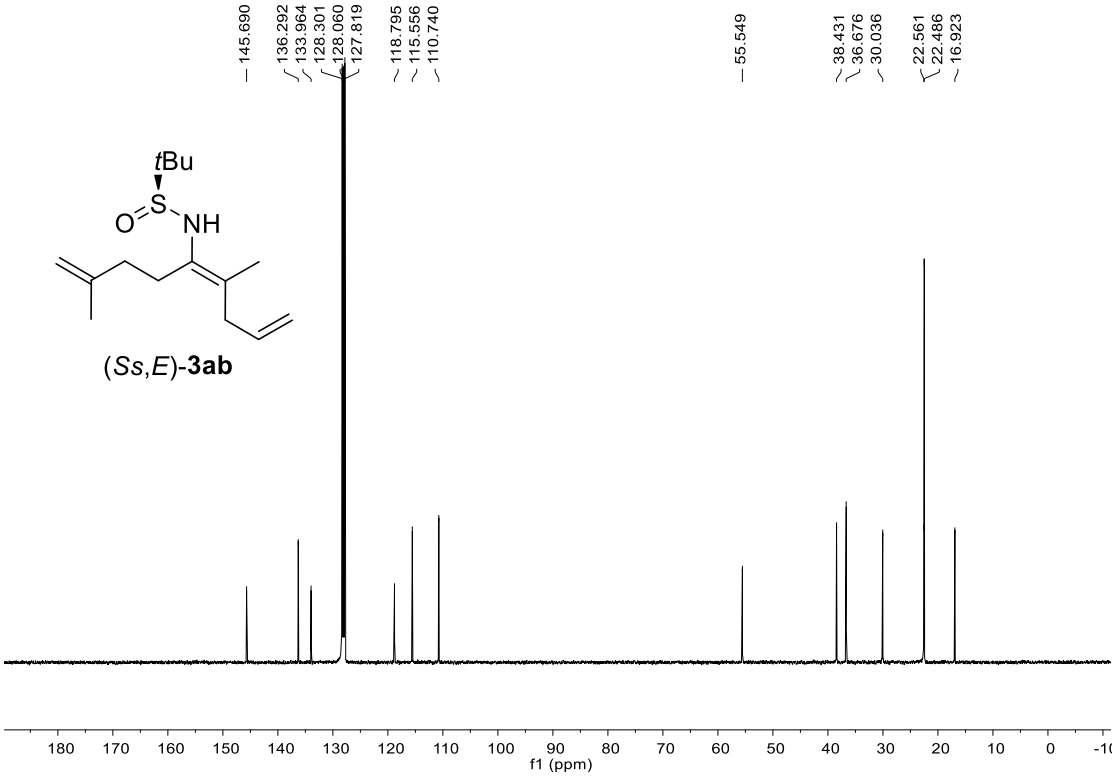
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2ac**



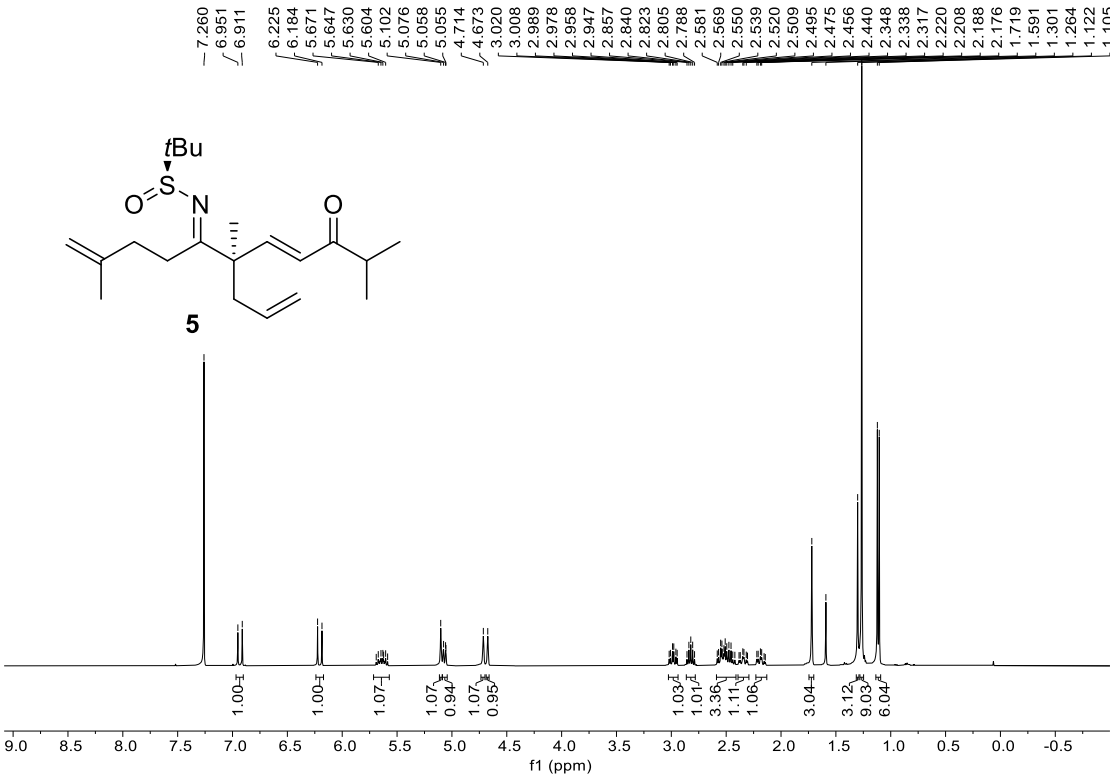
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2ac**



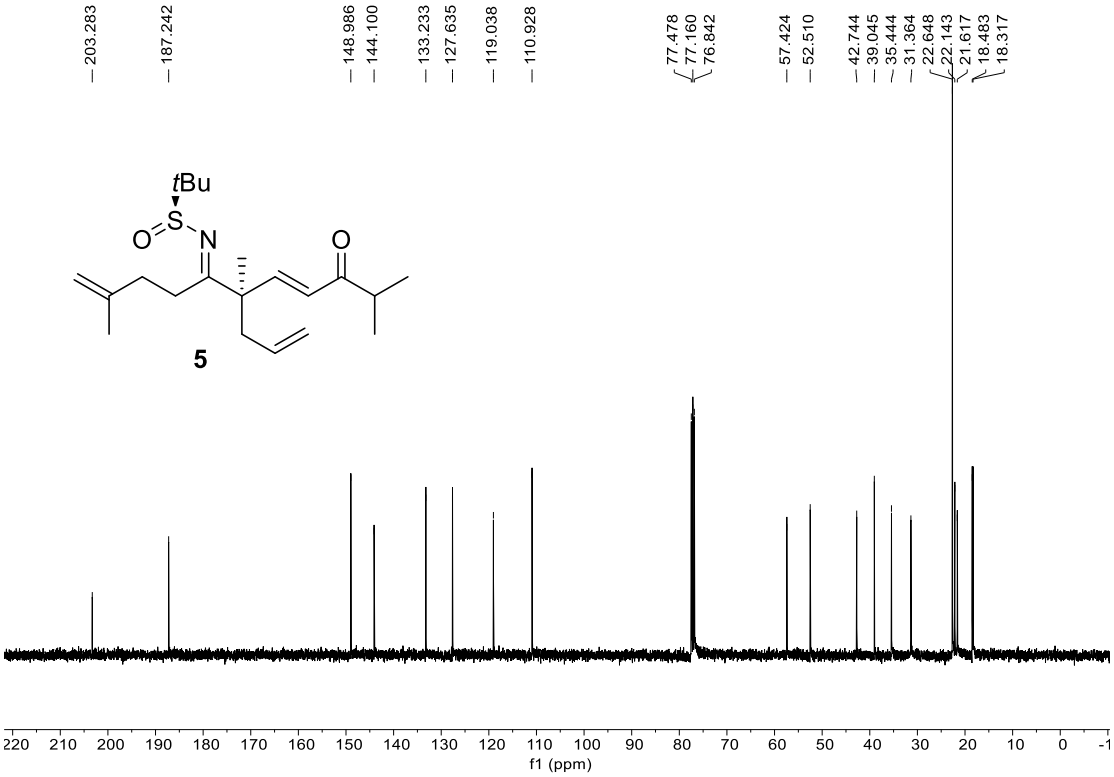
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (*Ss*,*E*)-**3ab**



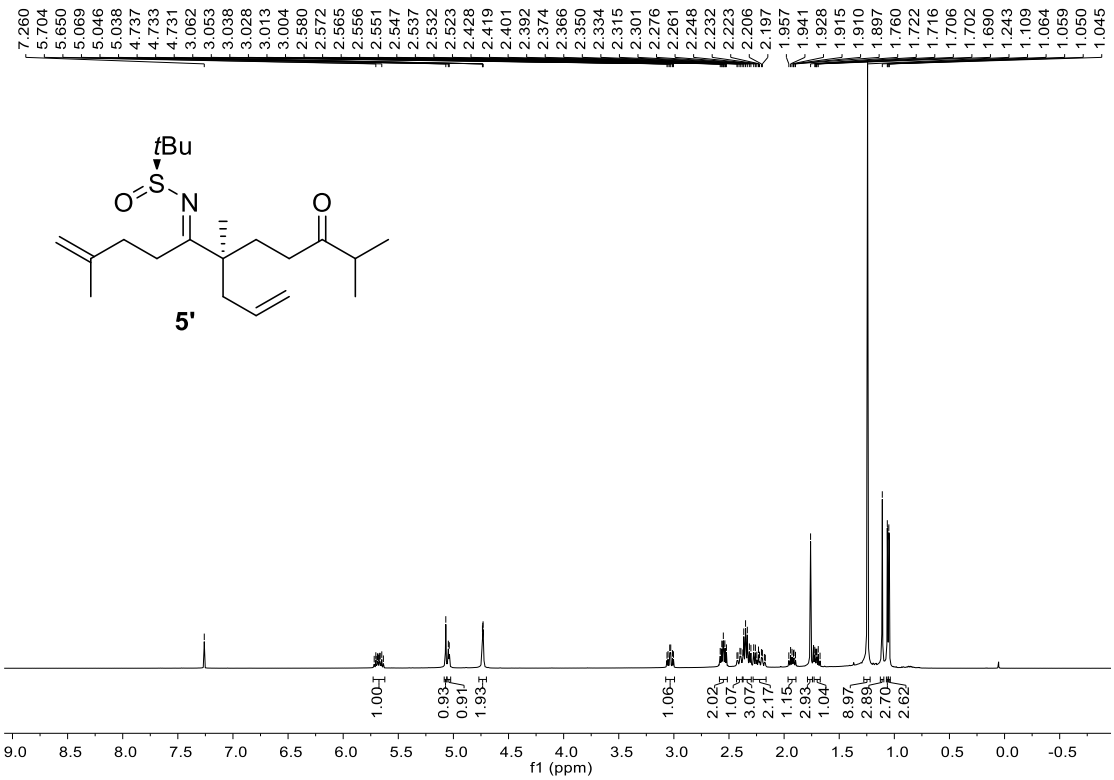
^{13}C NMR spectrum (C_6D_6, 100 MHz) of (*Ss*,*E*)-**3ab**



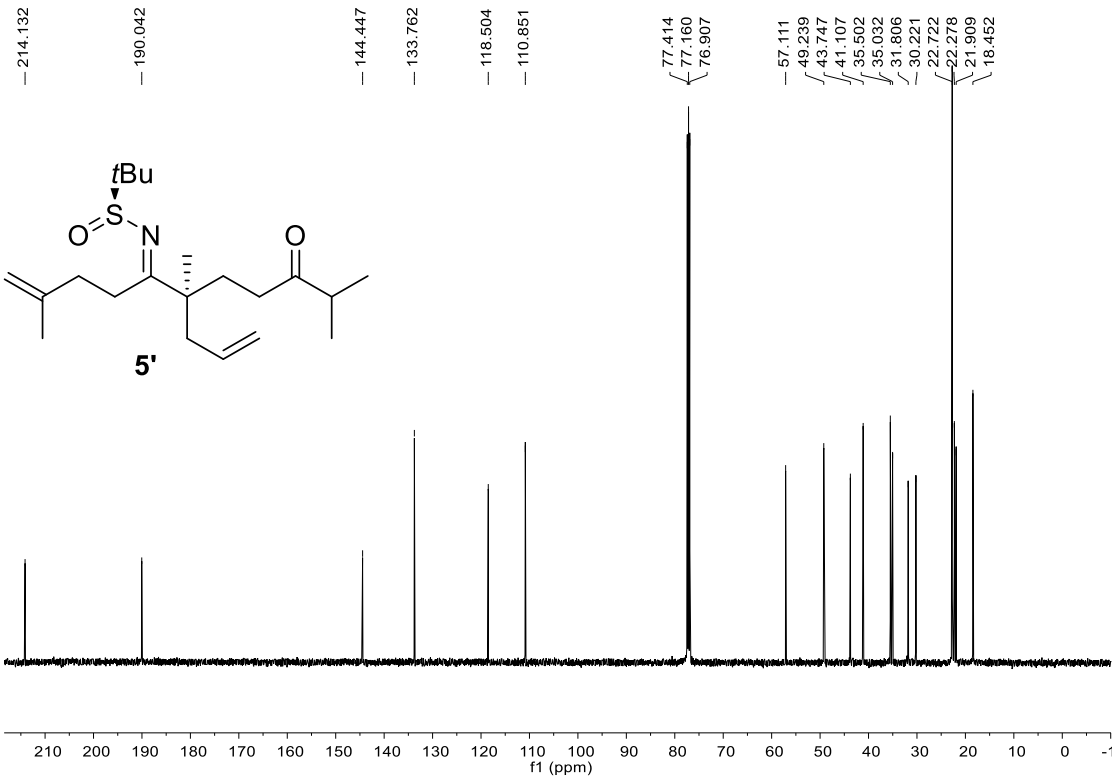
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5**



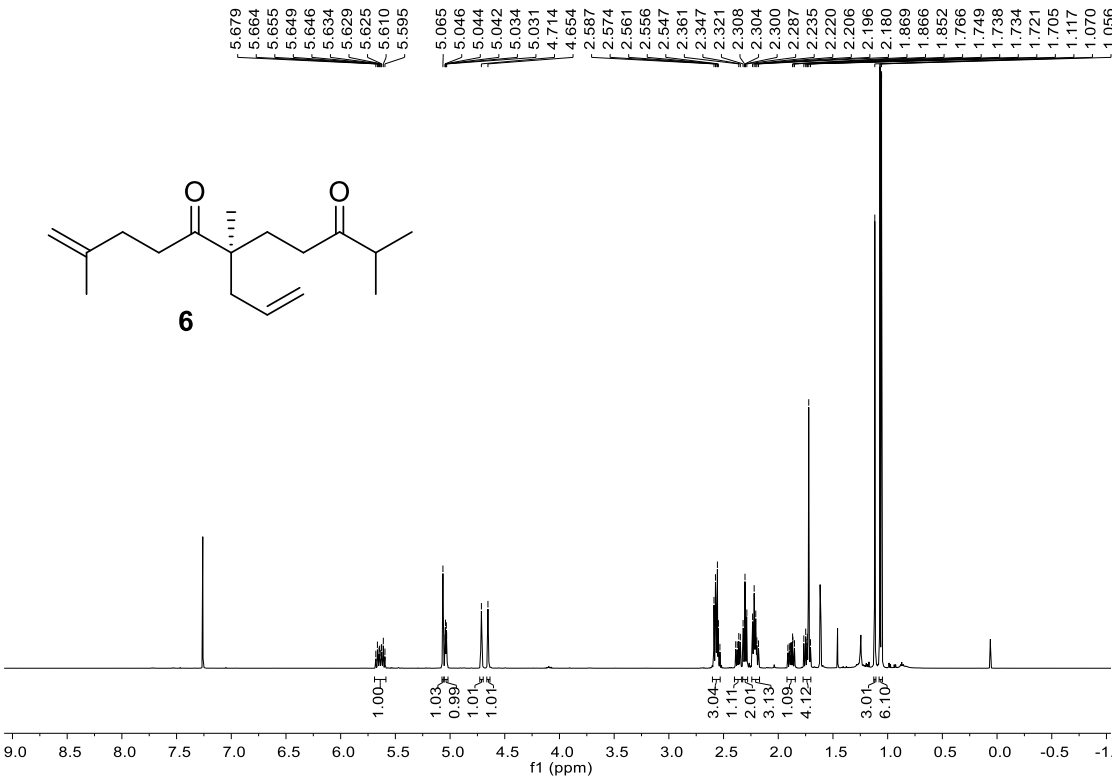
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5**



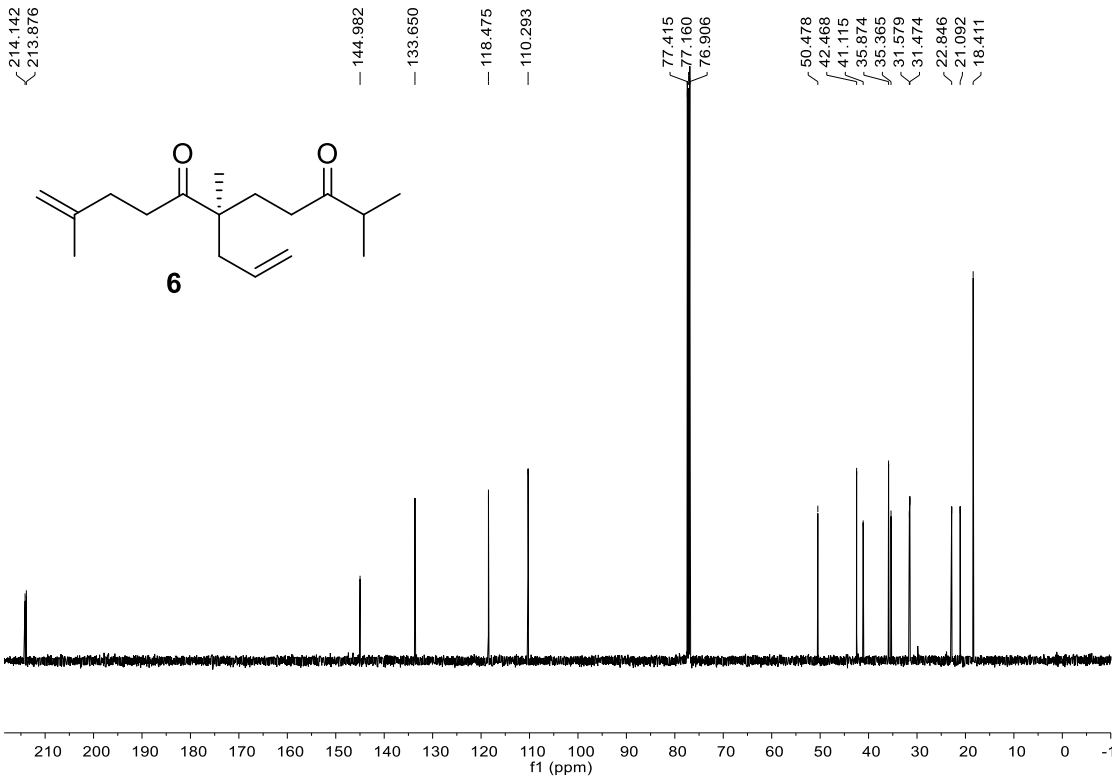
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **5′**



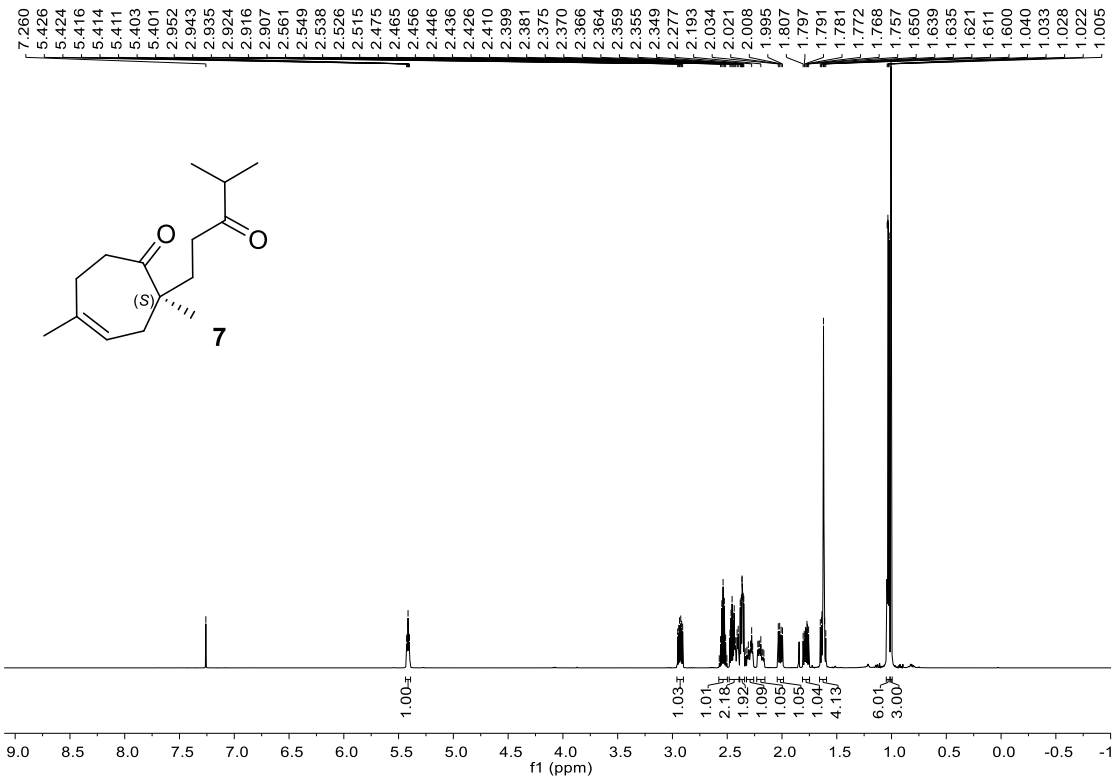
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **5′**



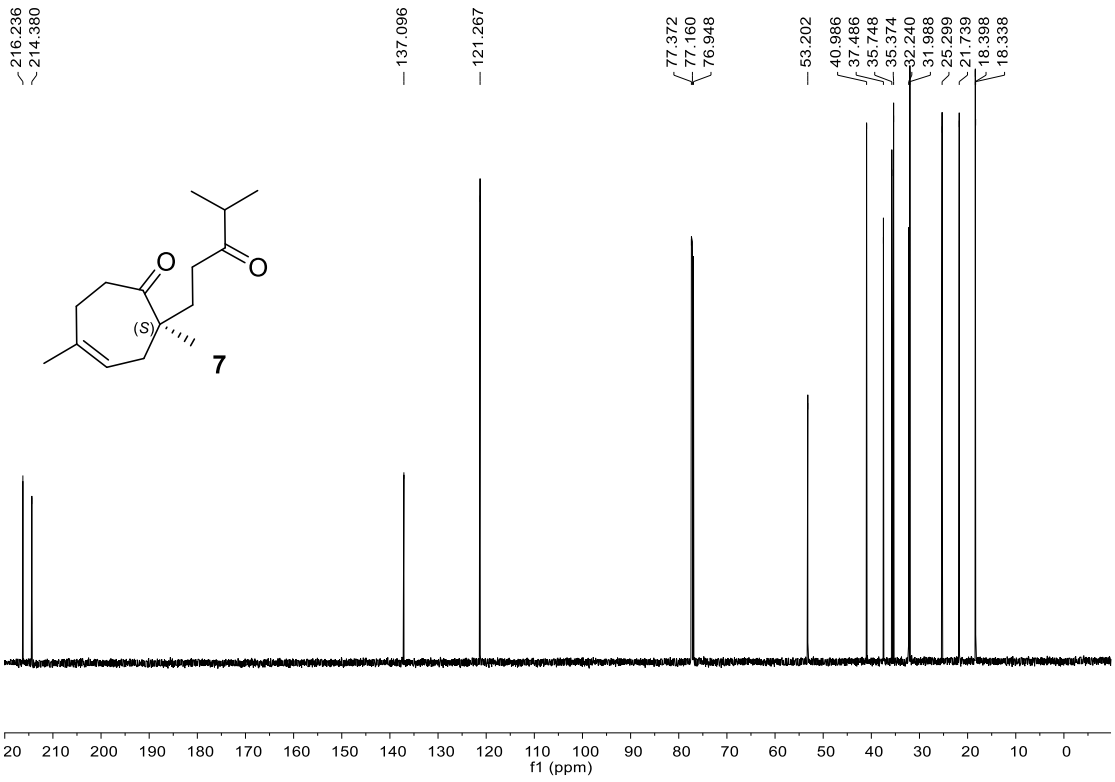
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **6**



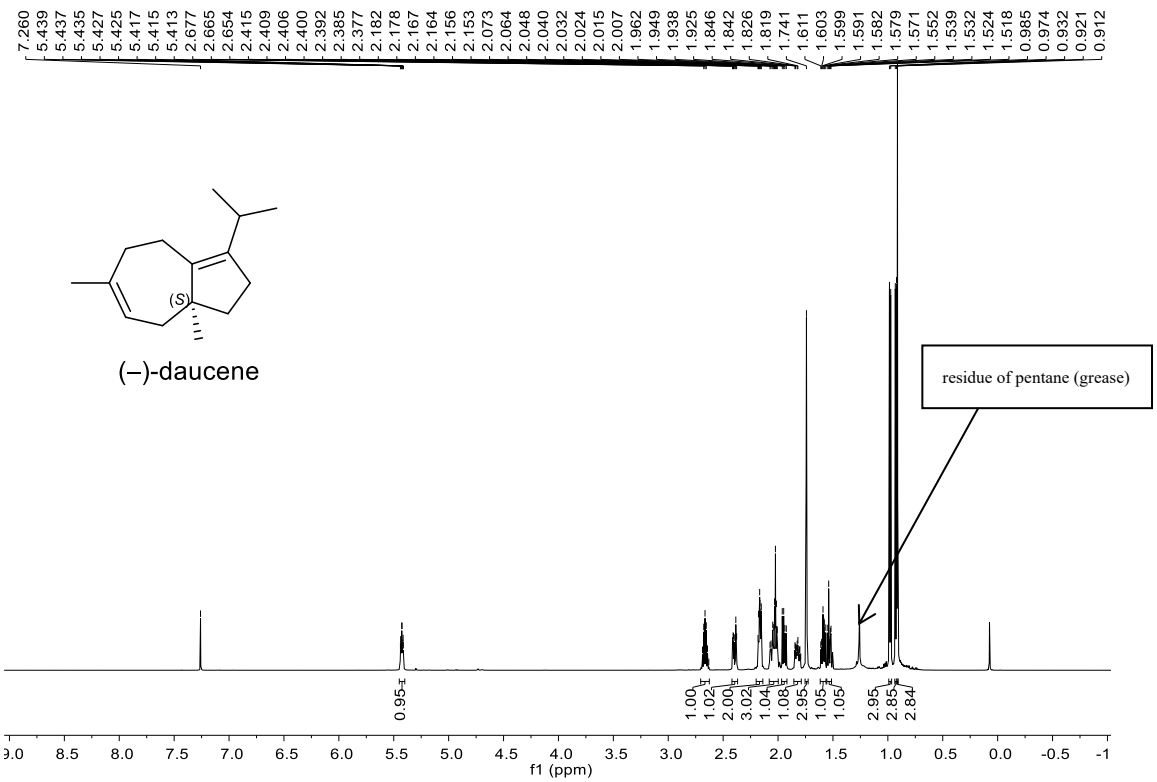
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **6**



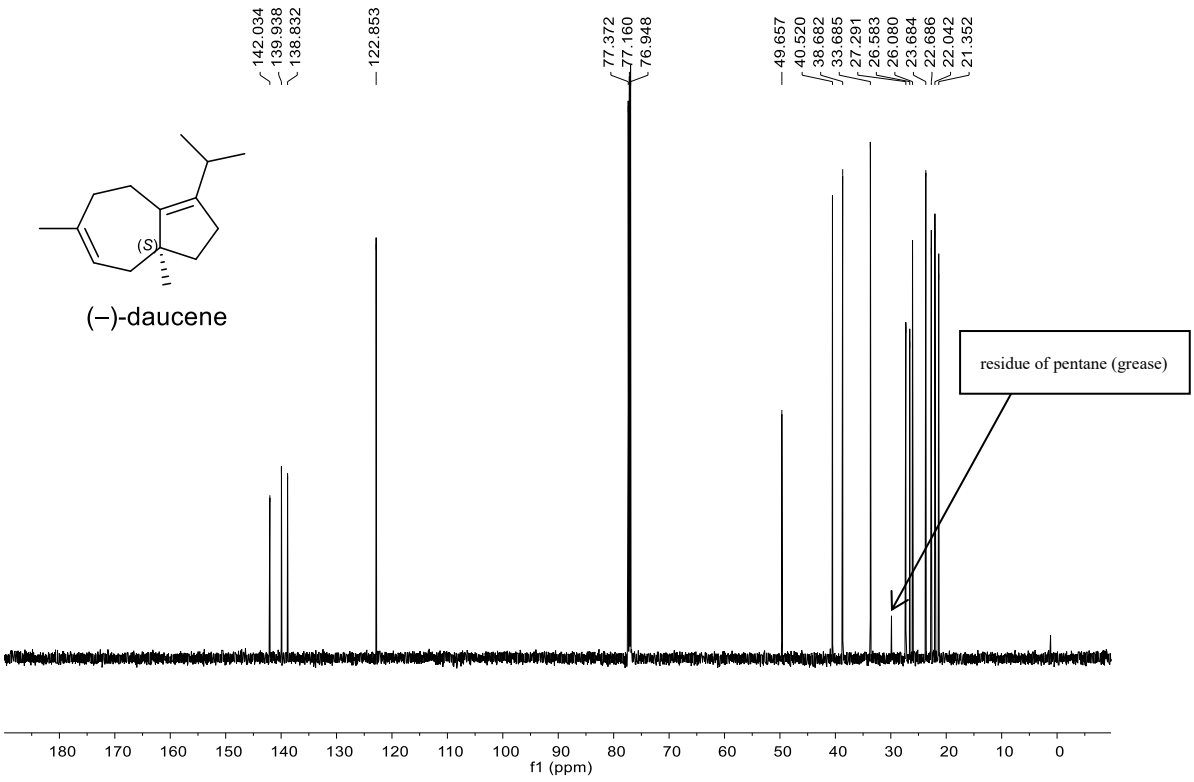
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **7**



^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **7**

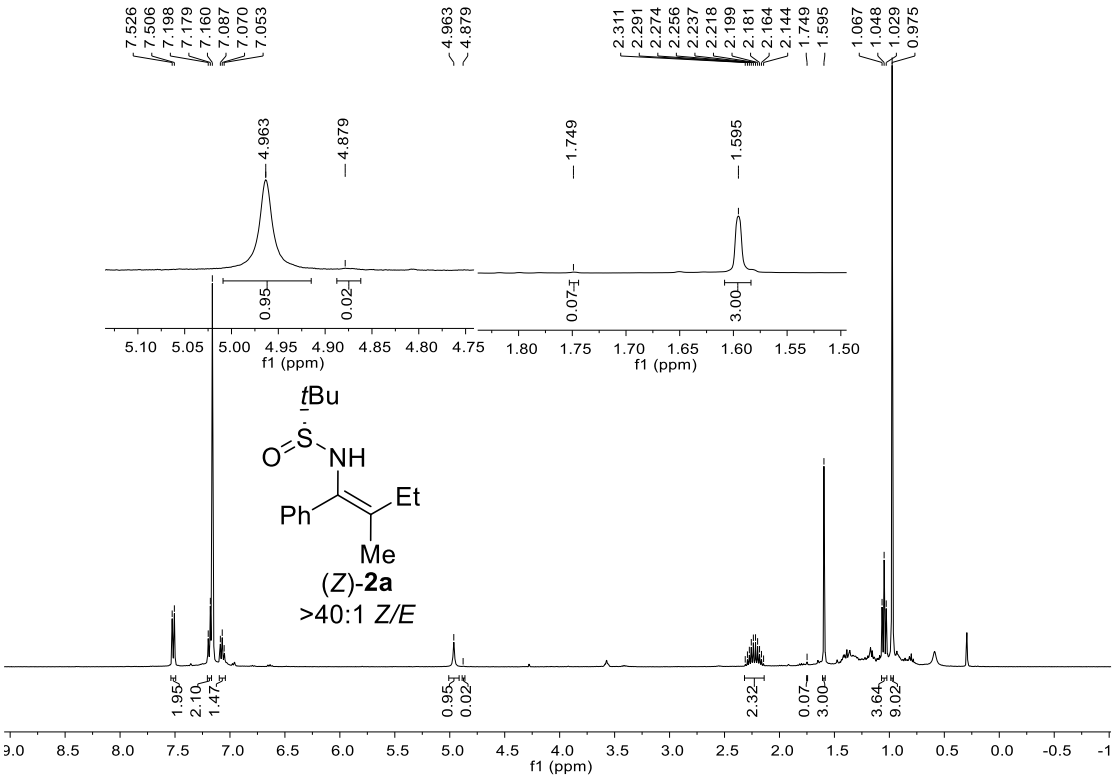


^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of (–)-daucene

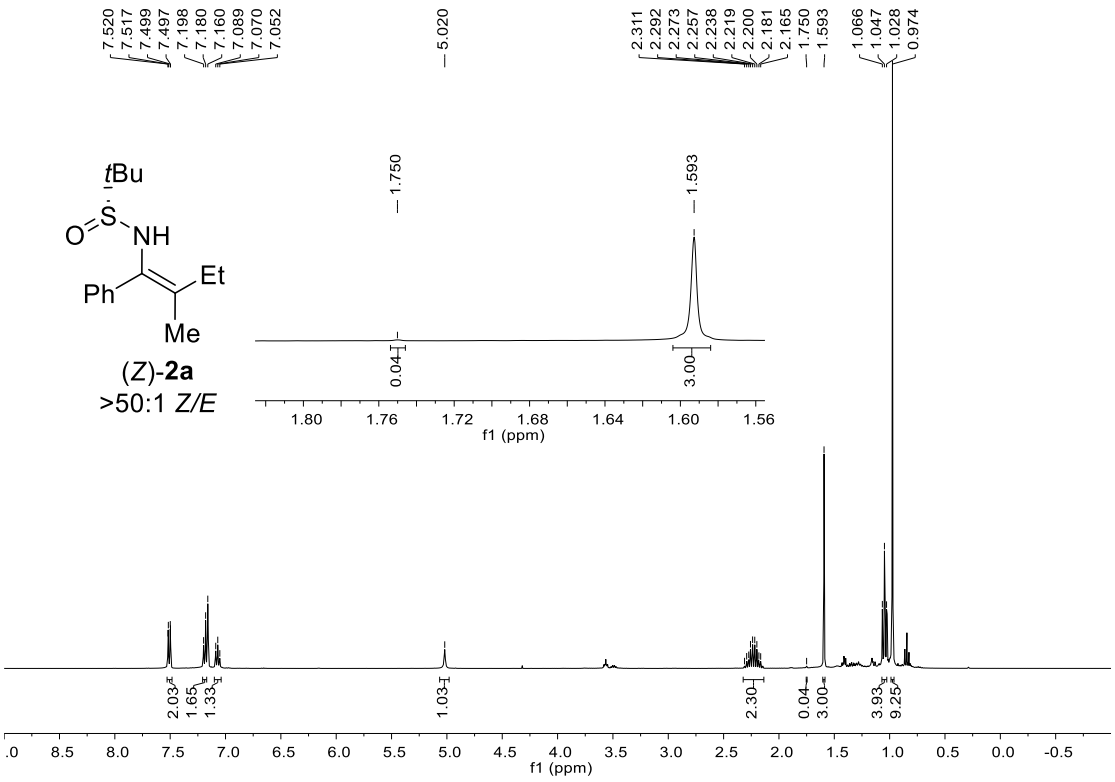


^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of (–)-daucene

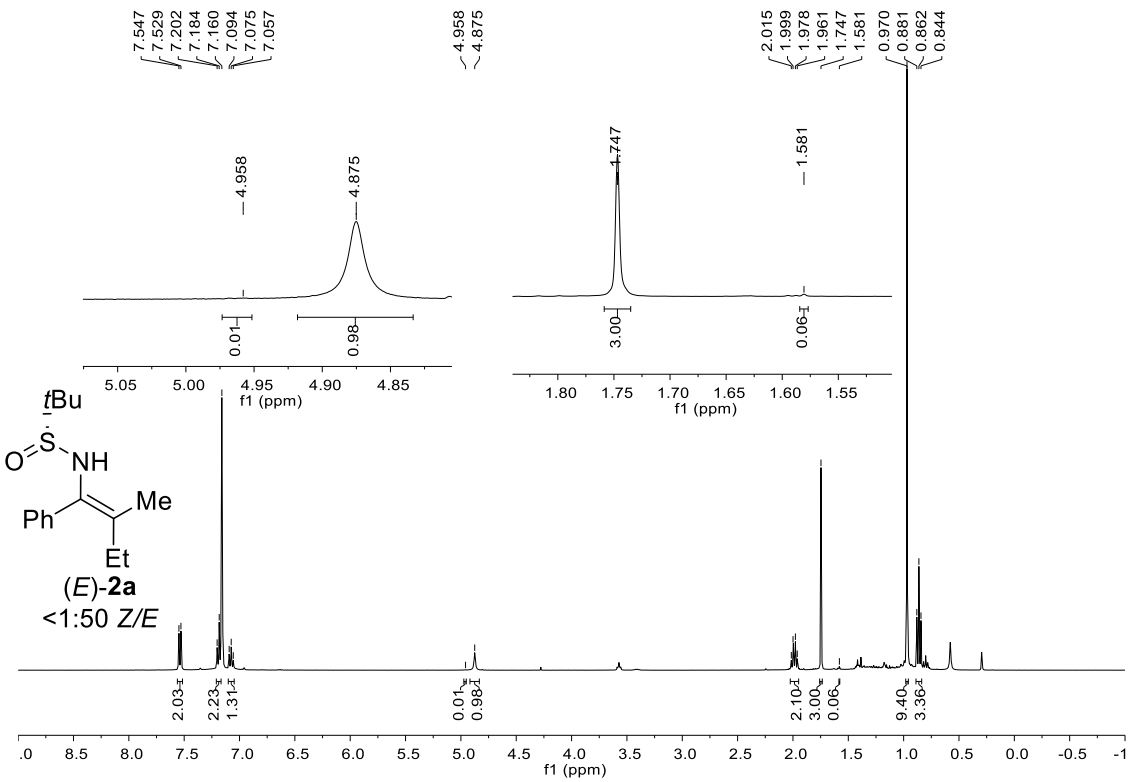
^{1}H NMR spectra of the crude reaction mixture for determination of *Z*/*E* ratio



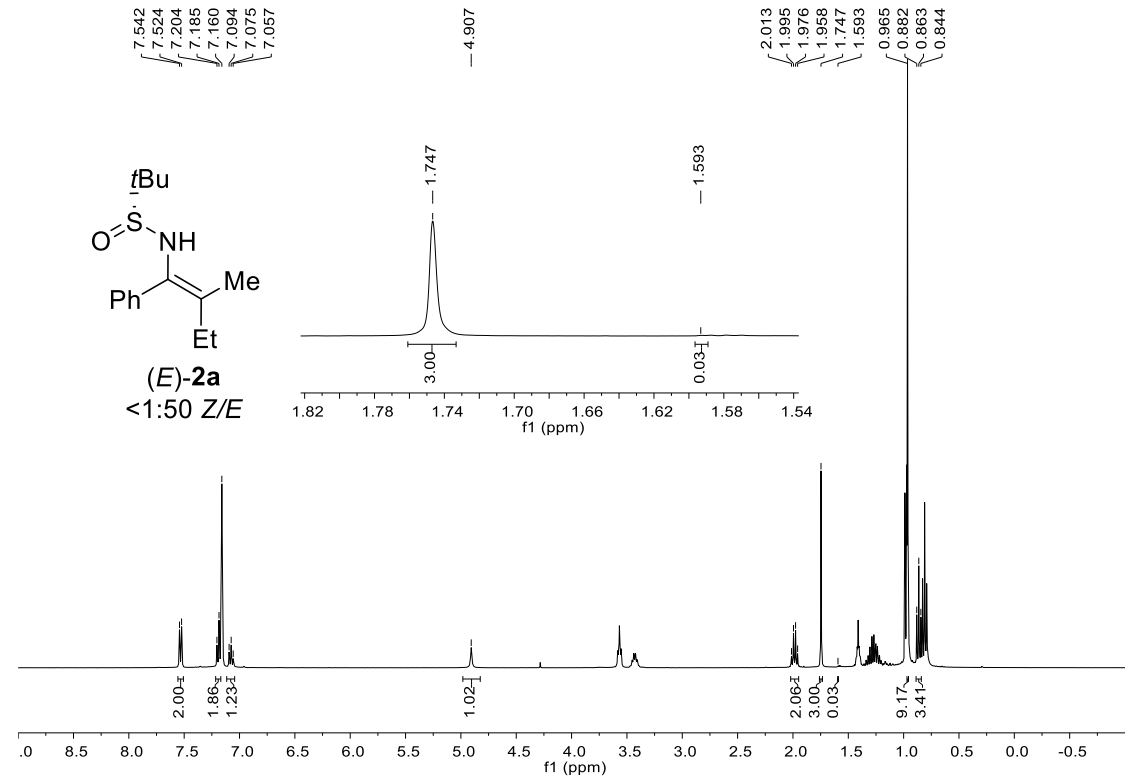
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2a** prepared using **1a**/L-Selectride (Table 1, entry 1) (> 40:1 *Z*/*E*)



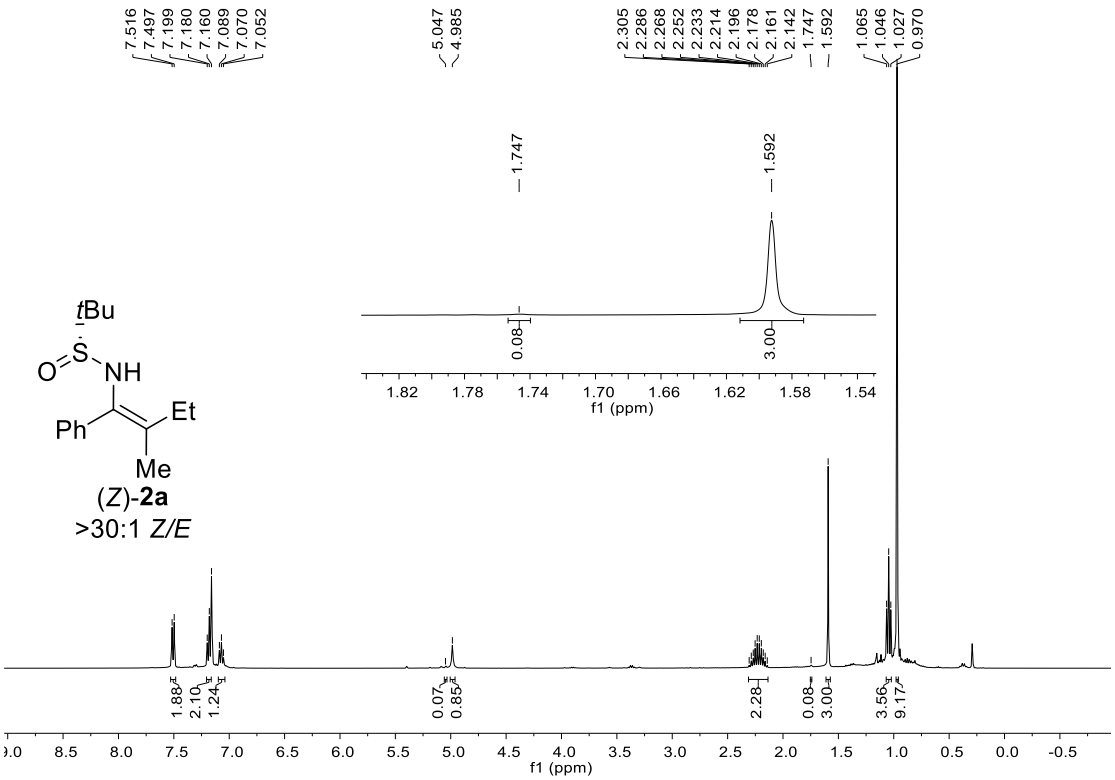
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of gram scale (*Z*)-**2a** prepared using **1a**/L-Selectride (Table 1, entry 1) (> 50:1 *Z*/*E*)



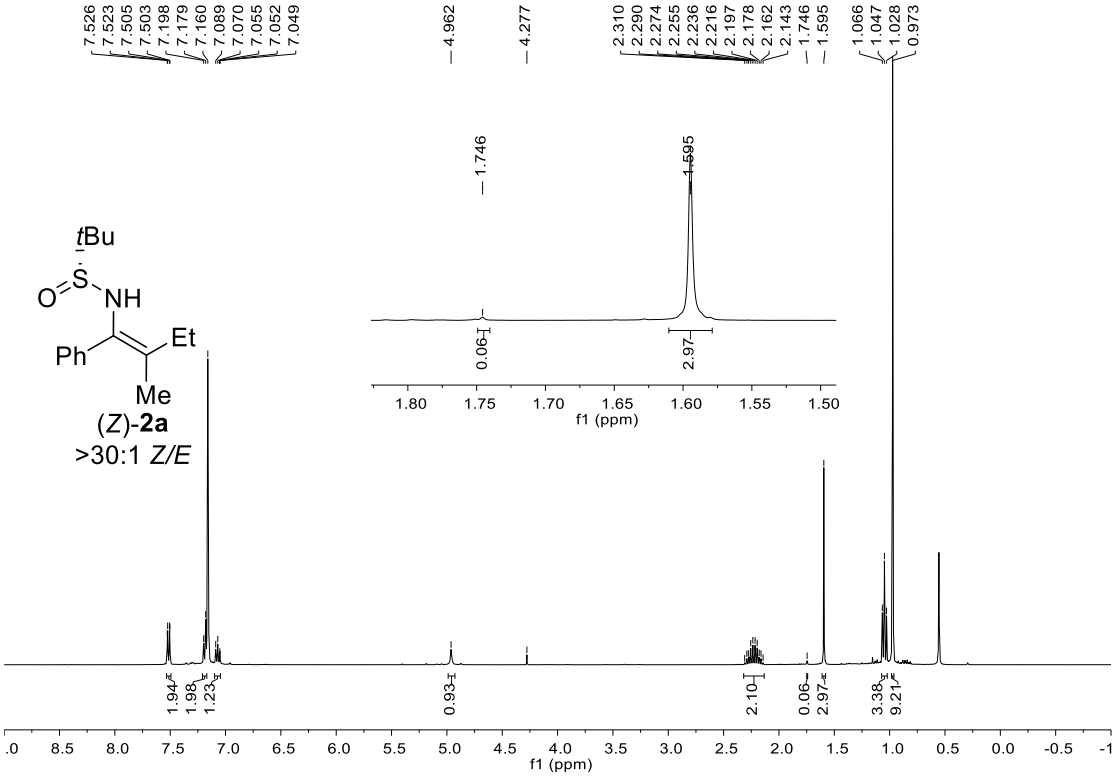
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a′**/L-Selectride (Table 1, entry 2) (< 1:50 *Z*/*E*)



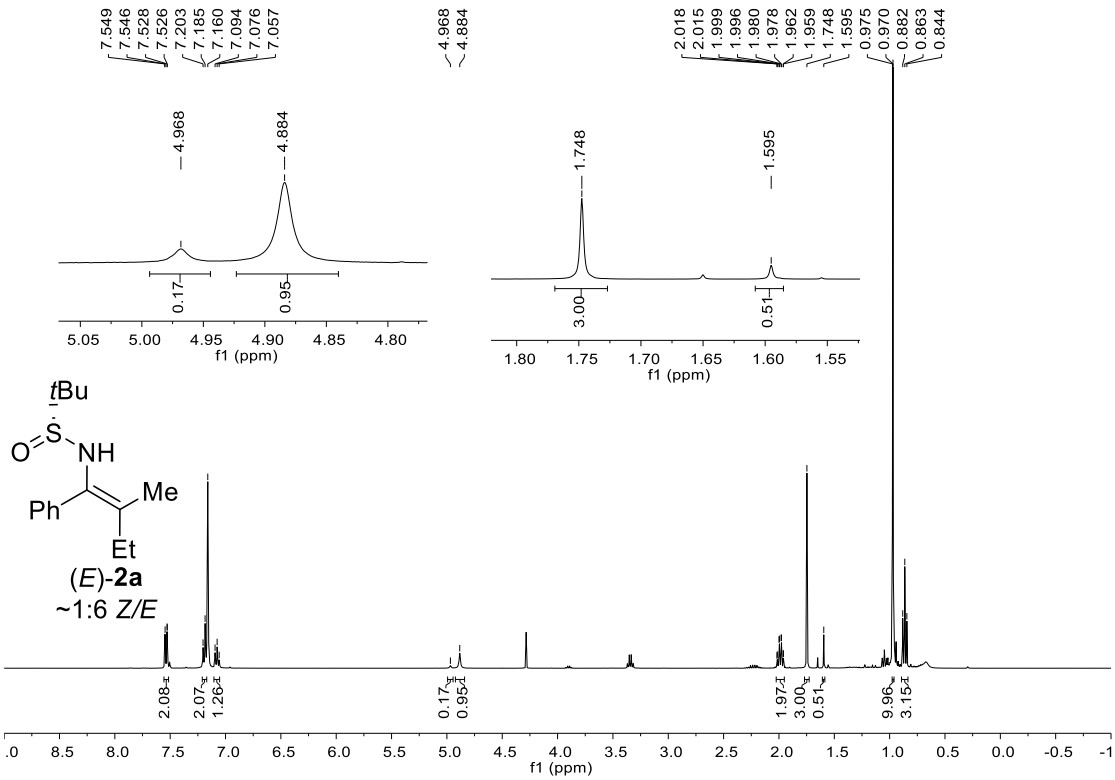
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of gram scale (*E*)-**2a** prepared using **1a′**/L-Selectride (Table 1, entry 2) (< 1:50 *Z*/*E*)



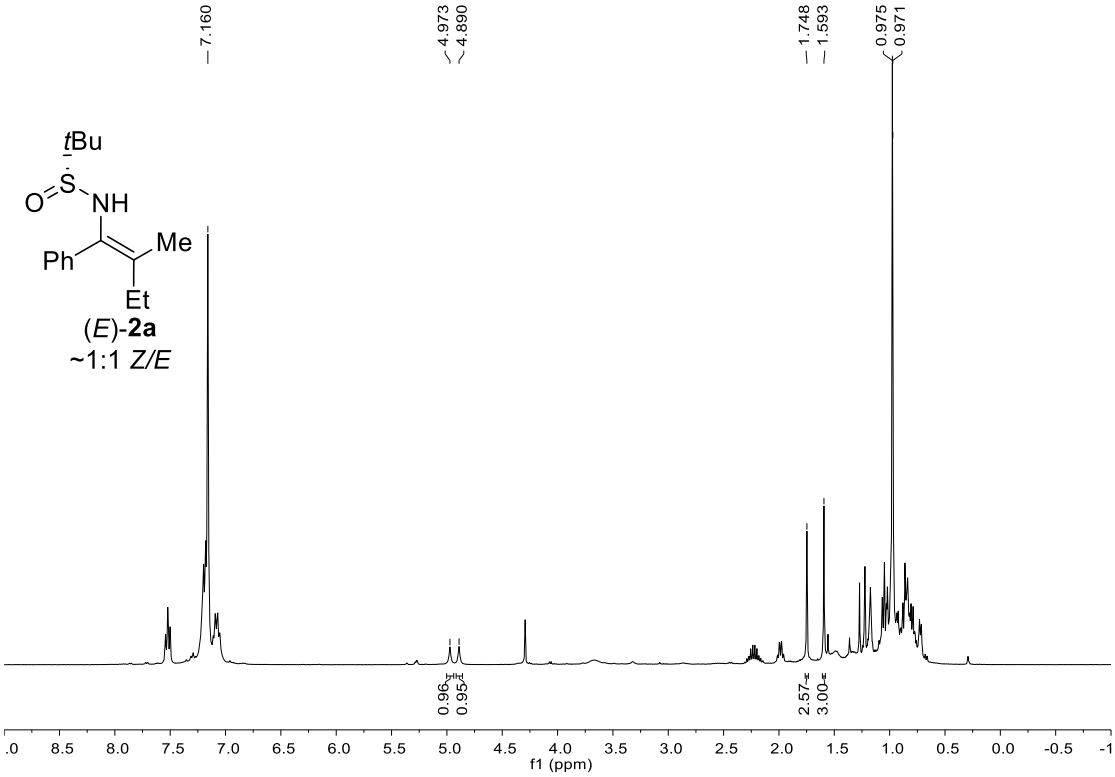
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2a** prepared using **1a**/$LiEt_3BH$ (Table 1, entry 3) (> 30:1 *Z/E*)



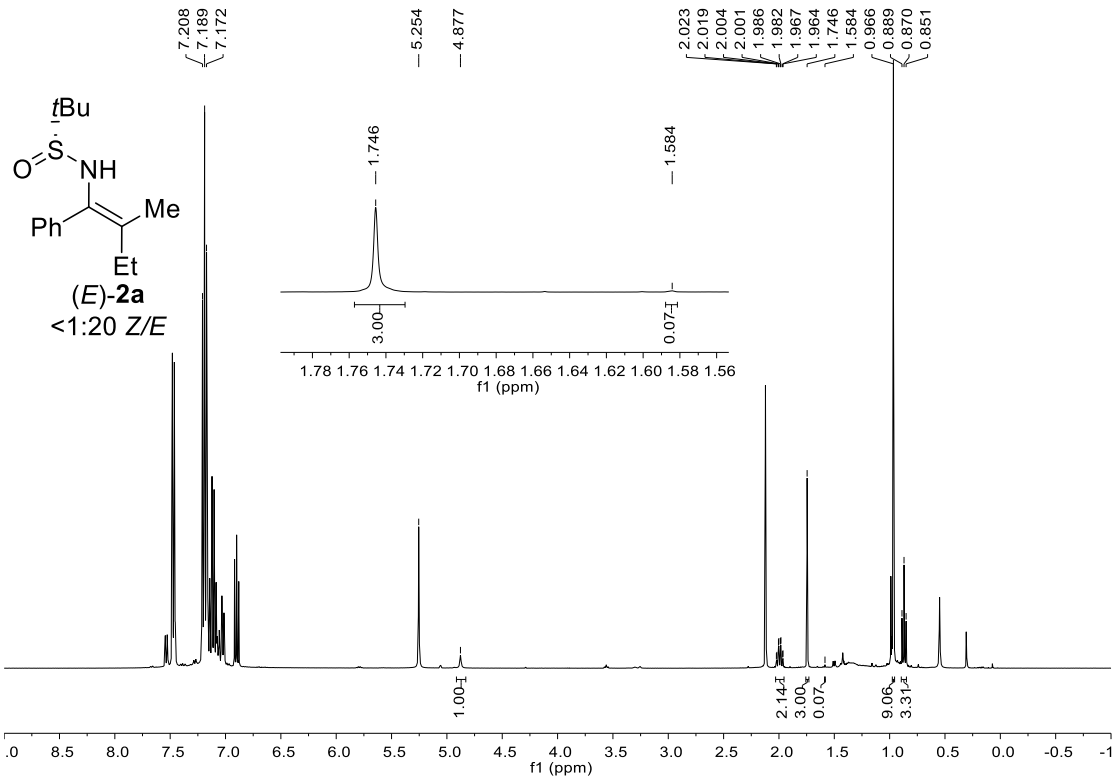
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2a** prepared using **1a**/$NaBH_4$ (Table 1, entry 4) (> 30:1 *Z/E*)



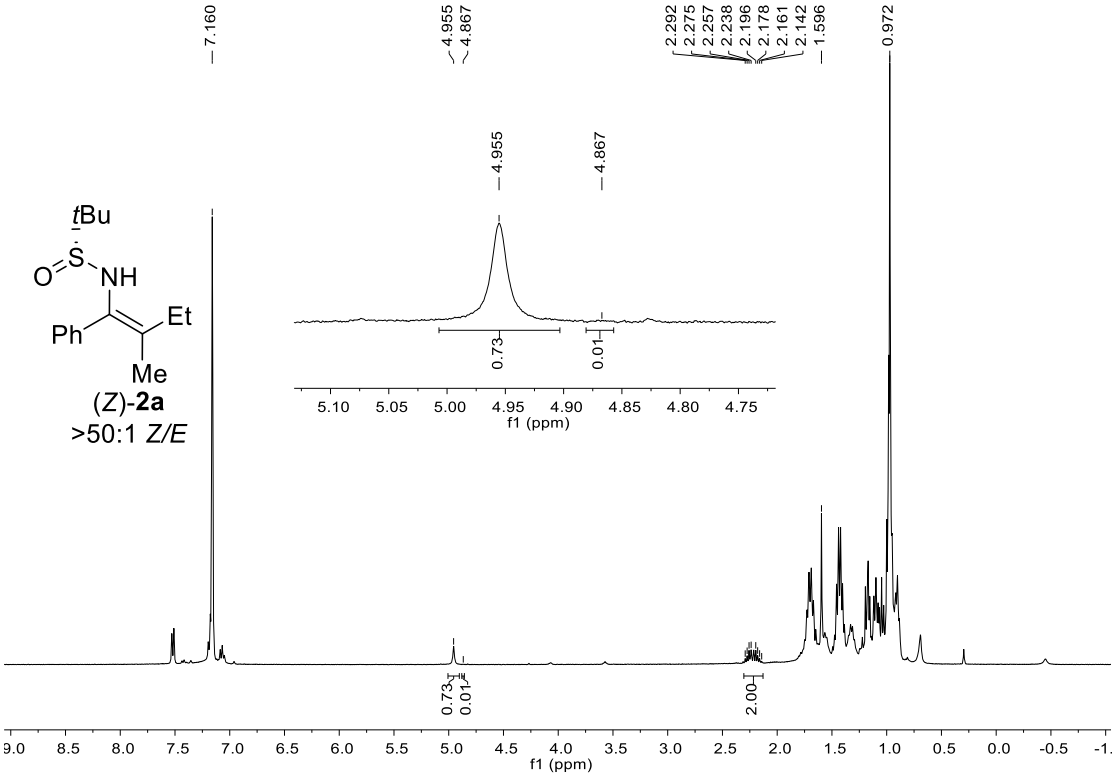
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a′**/$NiCl_2$/$NaBH_4$ (Table 1, entry 6) (~ 1:6 *Z*/*E*)



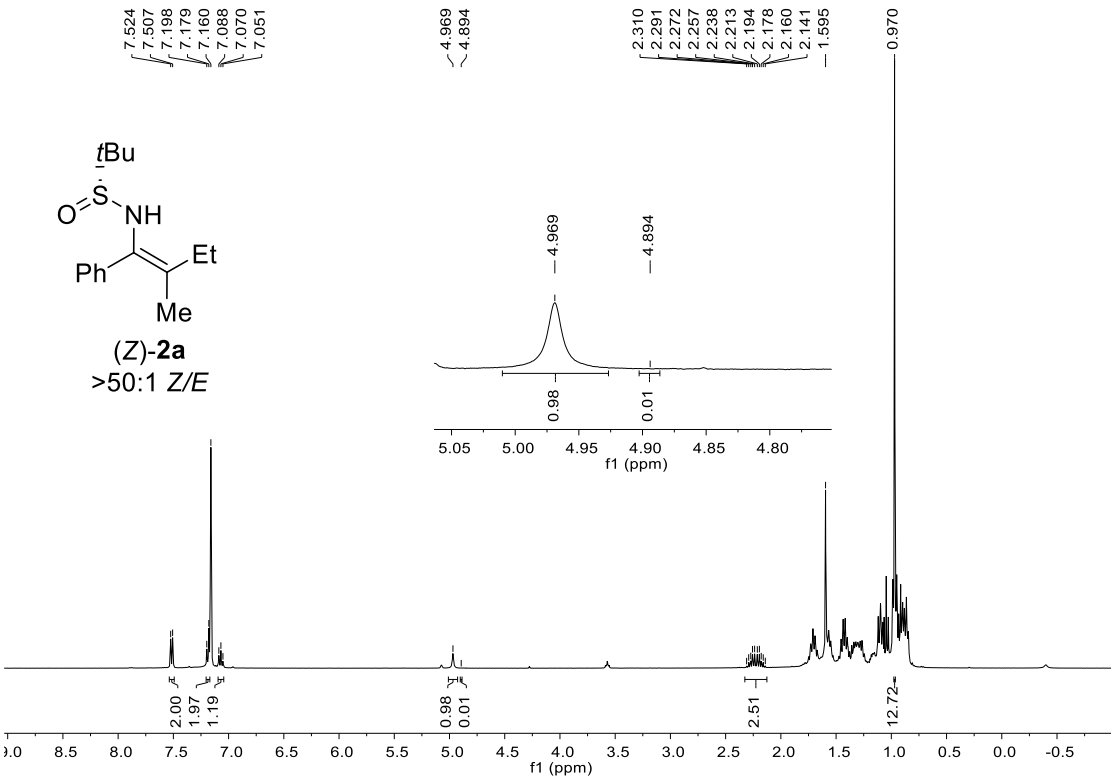
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of **2a** prepared using **1a′**/$CoCl_2$/$NaBH_4$ (Table 1, entry 7) (~ 1:1 *Z*/*E*)



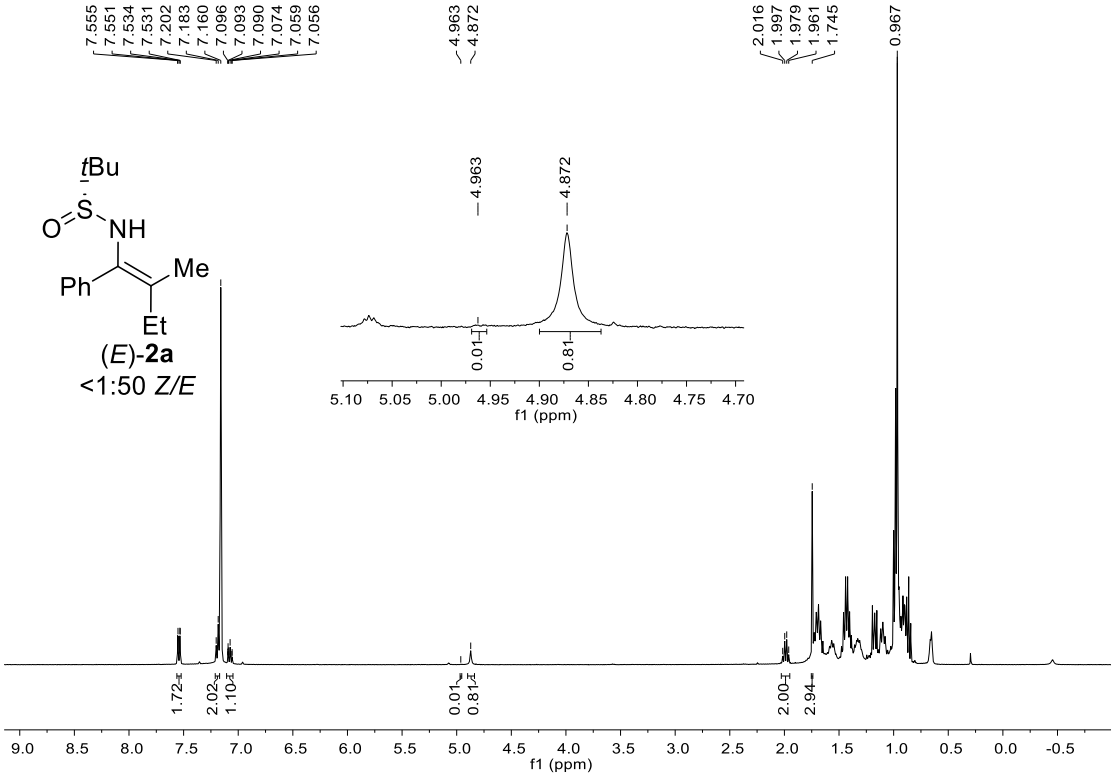
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a′**/ATPH/DIBAL-nBuLi (Table 1, entry 9) (< 1:20 *Z*/*E*)



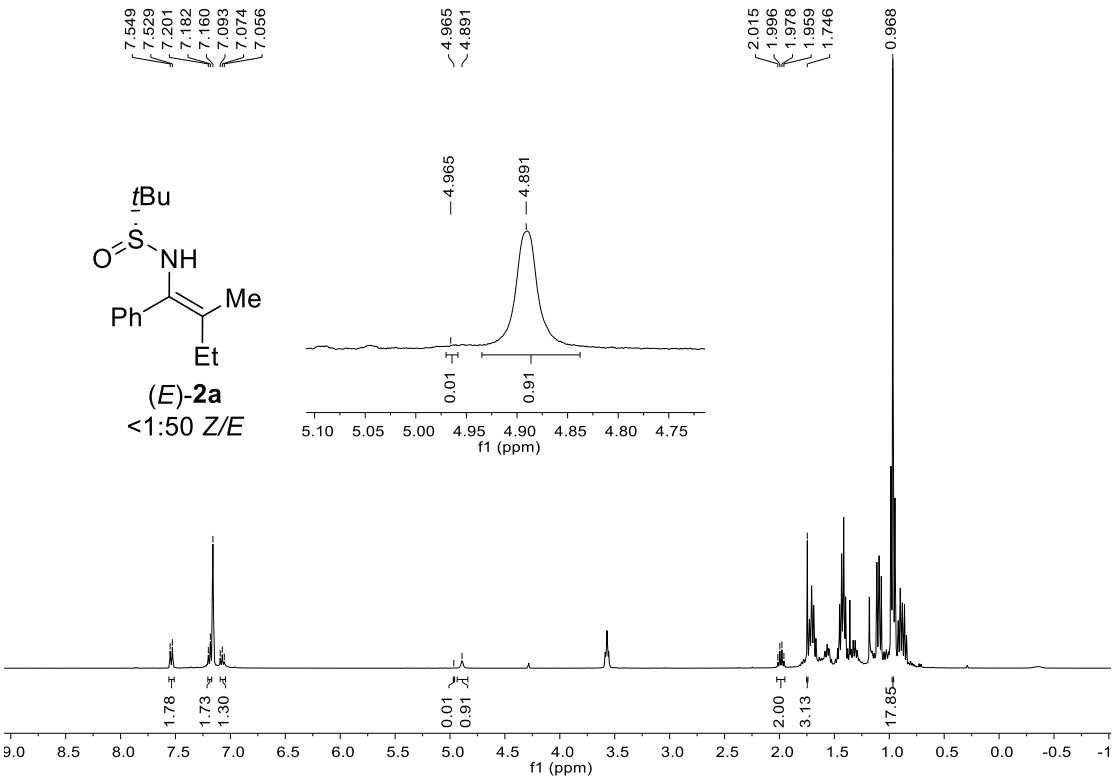
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2a** prepared using **1a′**/$InBr_3$/nBu_3SnH (Table 1, entry 10) (> 50:1 *Z*/*E*)



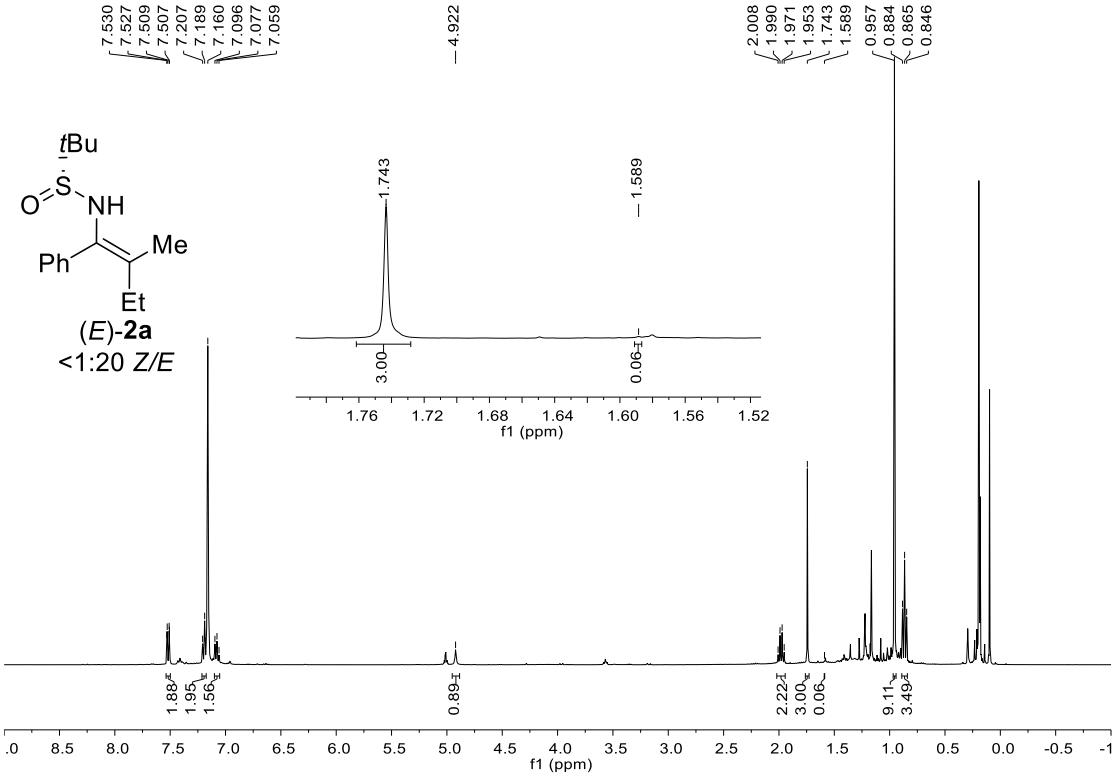
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of gram scale (*Z*)-**2a** prepared using **1a′**/$InBr_3$/*n*Bu_3SnH (Table 1, entry 10) (> 50:1 *Z*/*E*)



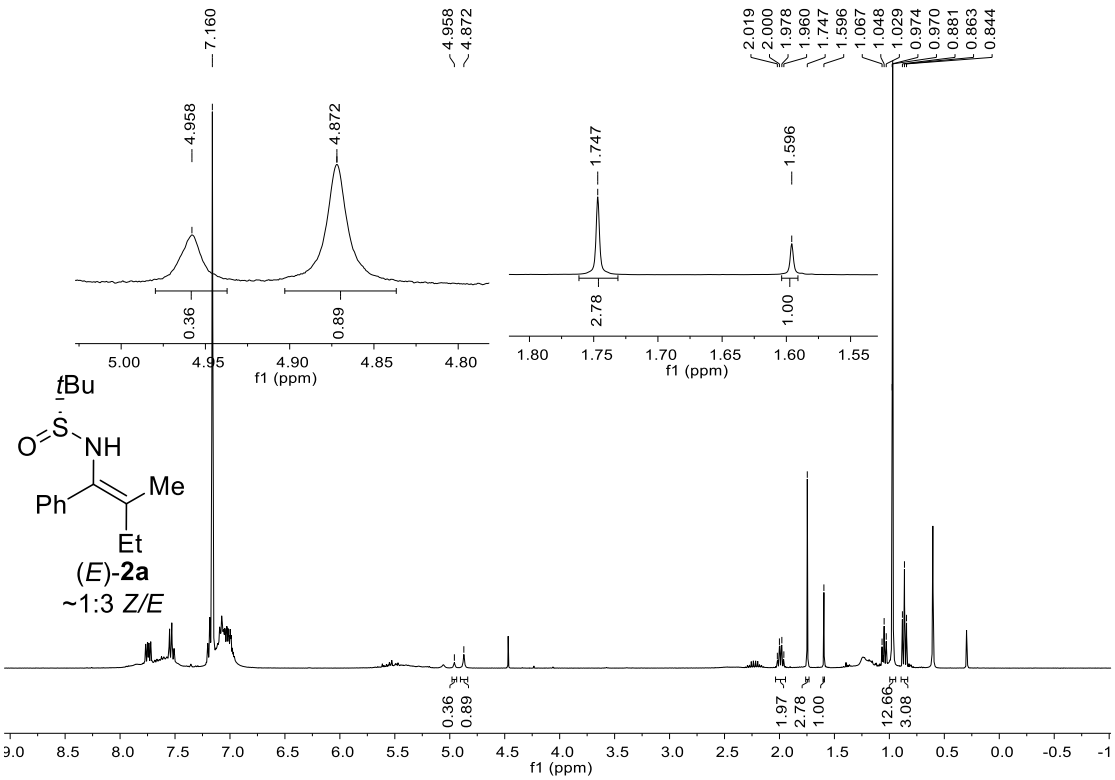
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a**/$InBr_3$/*n*Bu_3SnH (Table 1, entry 11) (< 1:50 *Z*/*E*)



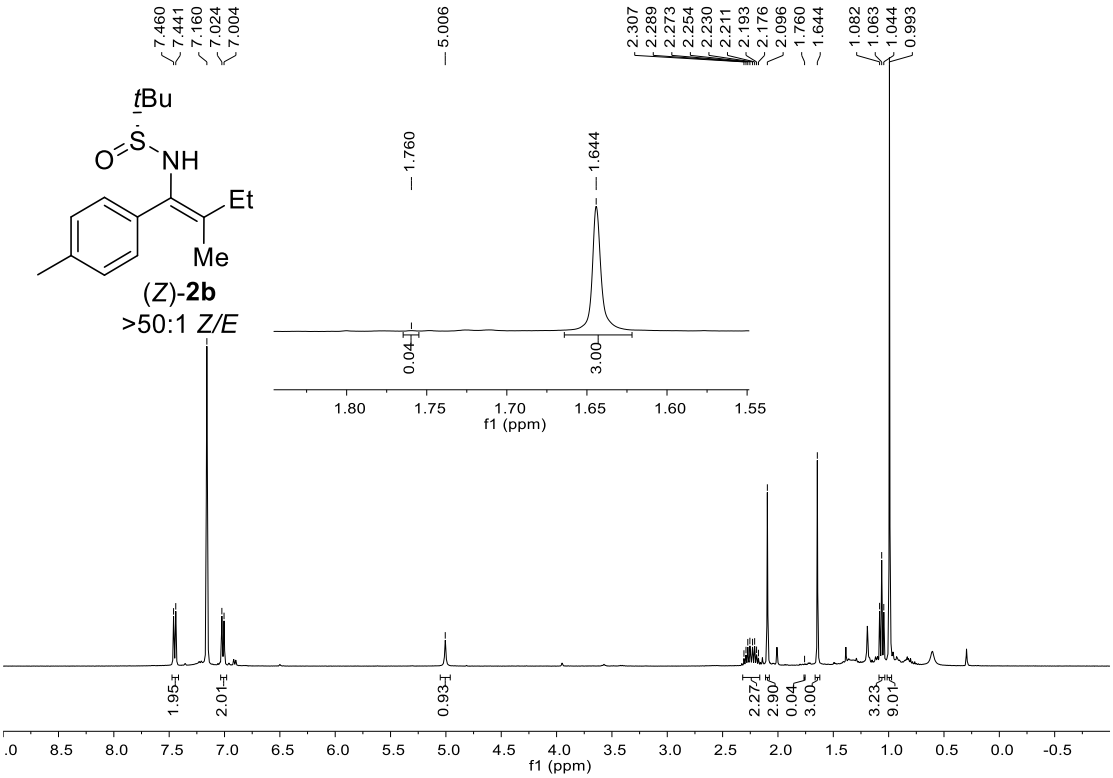
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of gram scale (*E*)-**2a** prepared using **1a**/$InBr_3$/*n*Bu_3SnH (Table 1, entry 11) (< 1:50 *Z*/*E*)



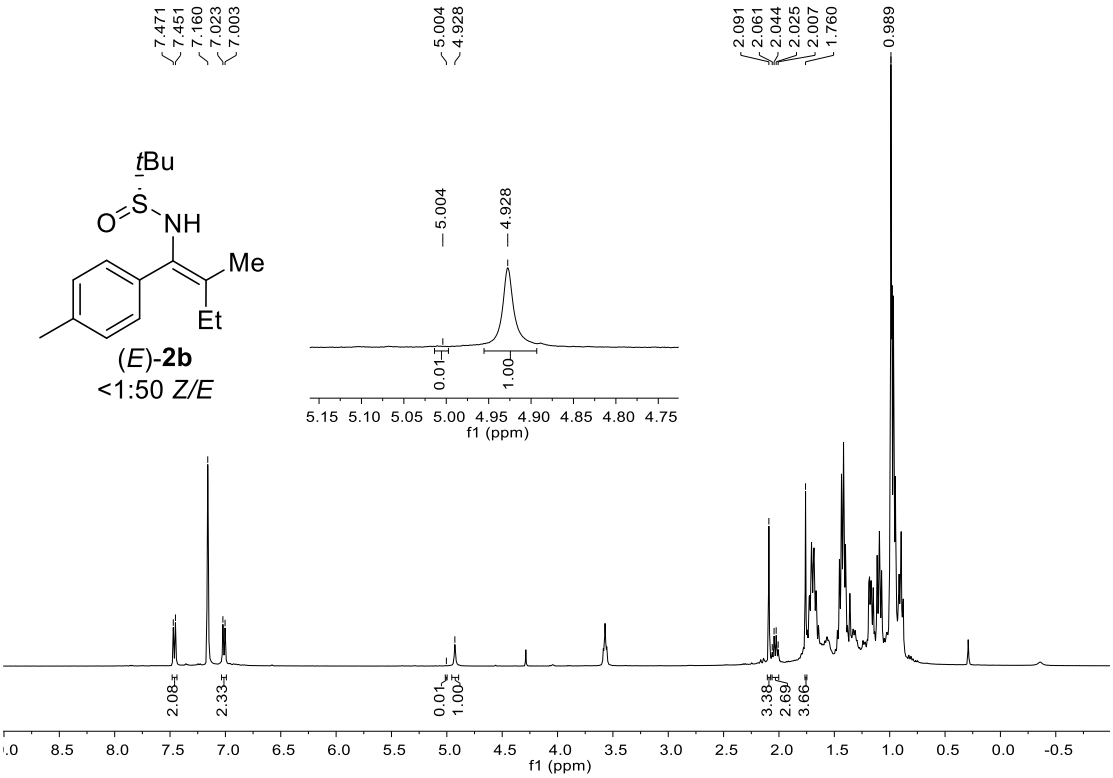
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a**/$InBr_3$/$(Et_2SiH)_2O$ (Table 1, entry 12) (< 1:20 *Z*/*E*)



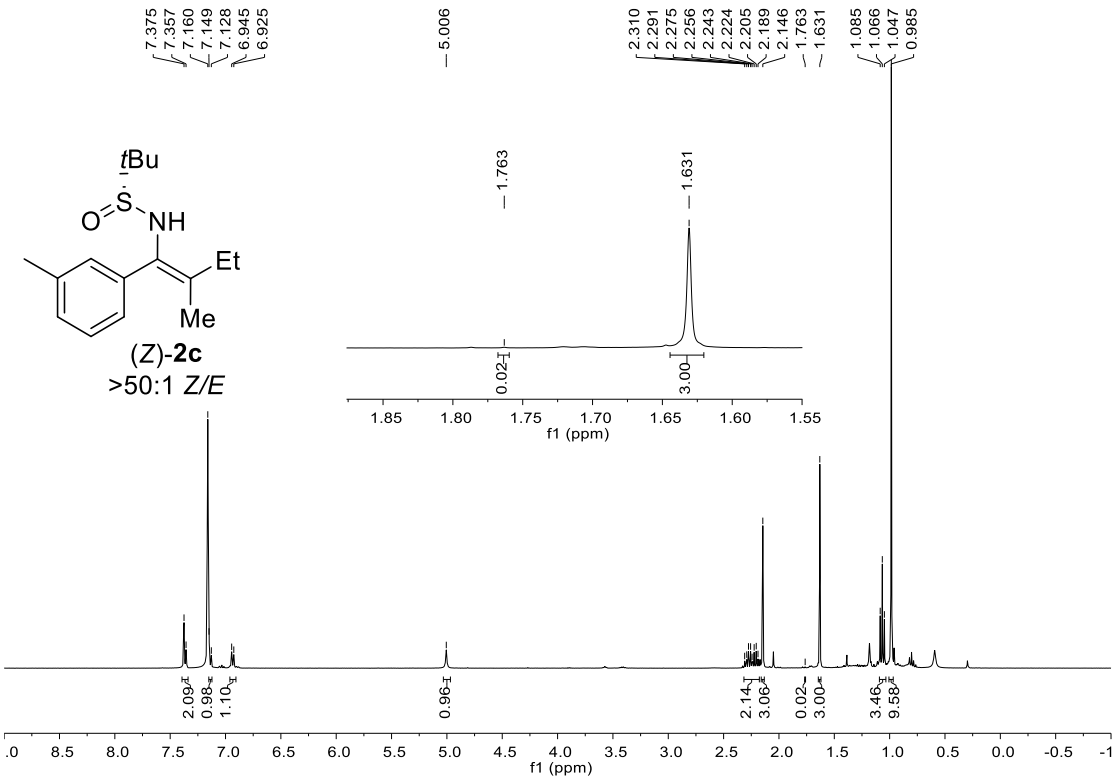
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2a** prepared using **1a**/$PhSiH_3$/Stryker' reagent (Table 1, entry 13) (~ 1:3 *Z*/*E*)



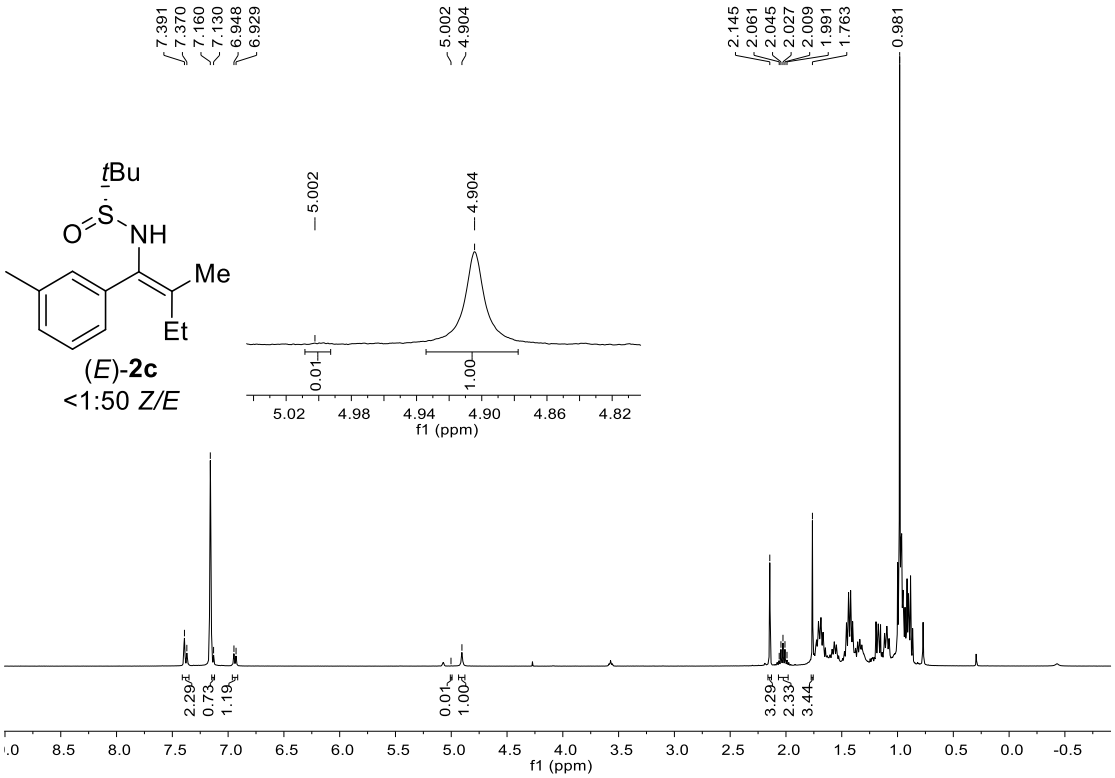
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2b** prepared using **1b**/L-Selectride (> 50:1 *Z*/*E*)



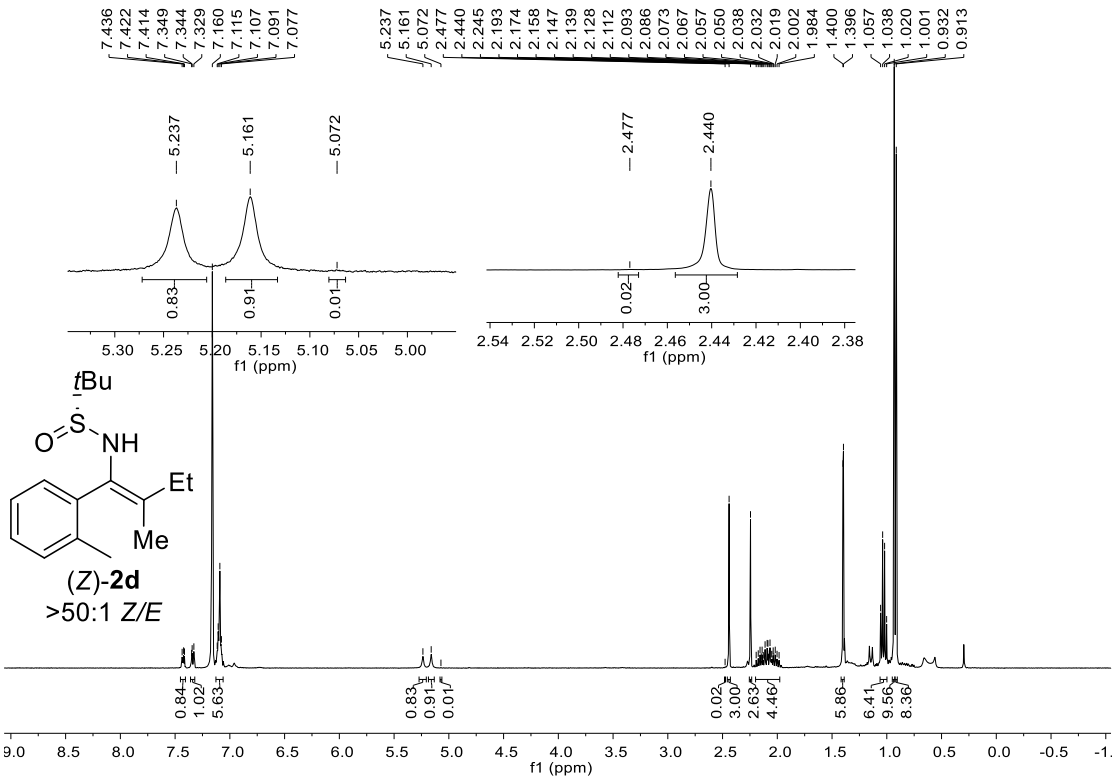
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2b** prepared using **1b**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



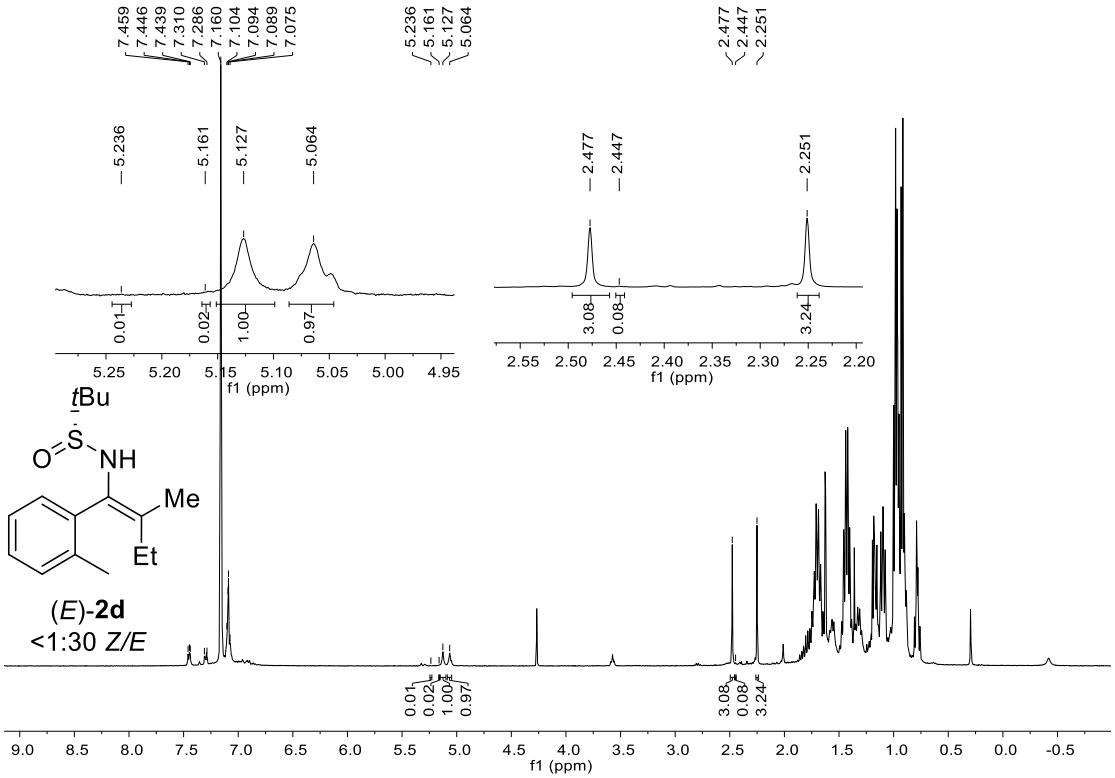
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2c** prepared using **1c**/L-Selectride (> 50:1 *Z/E*)



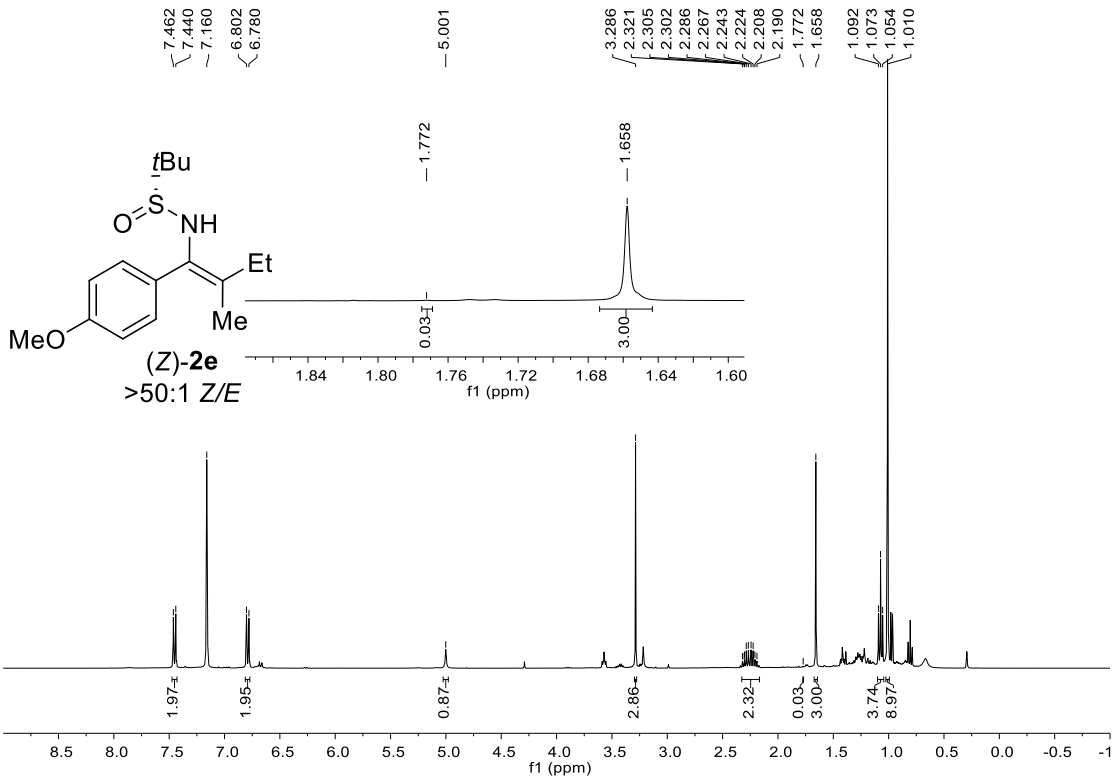
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2c** prepared using **1c**/$InBr_3$/nBu_3SnH (< 1:50 *Z/E*)



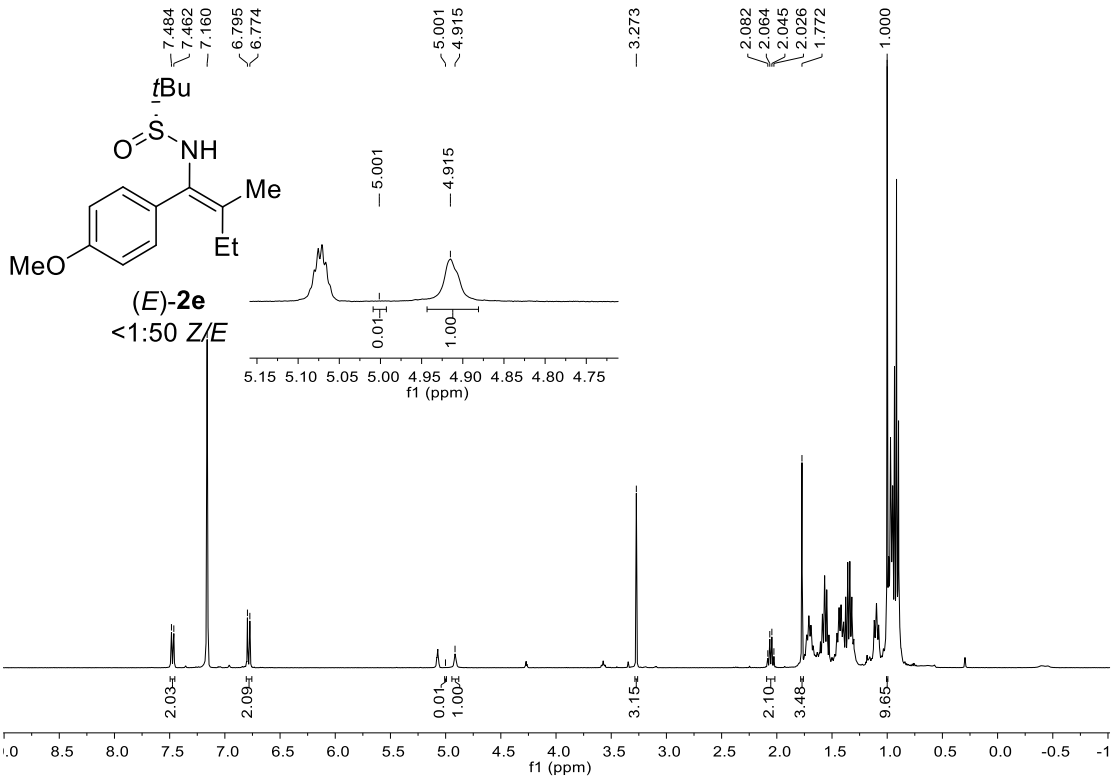
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2d** prepared using **1d**/L-Selectride (> 50:1 *Z*/*E*)



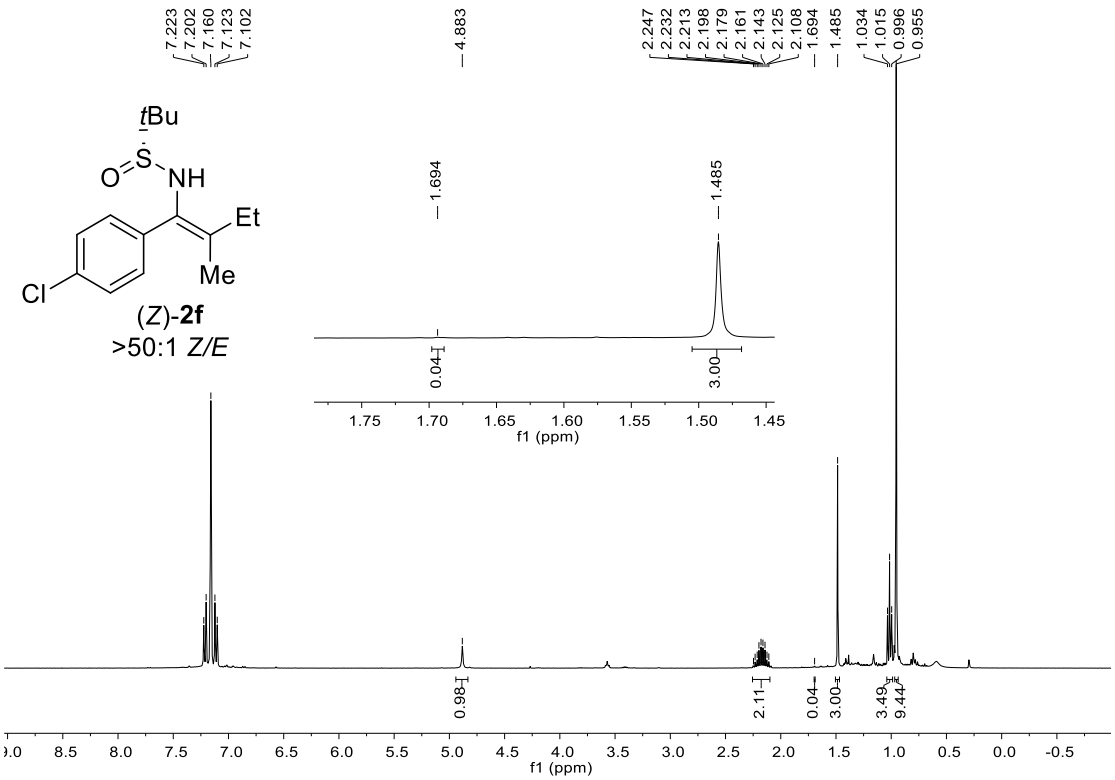
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2d** prepared using **1d**/$InBr_3$/$n$$Bu_3SnH$ (< 1:30 *Z*/*E*)



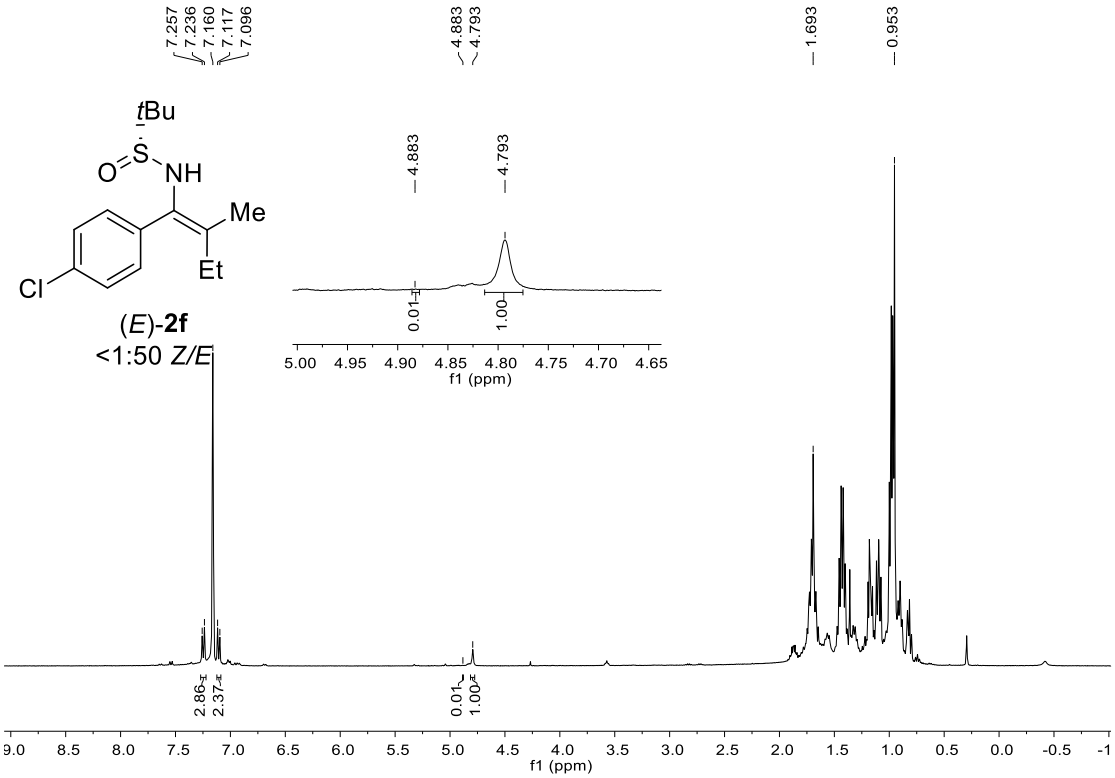
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2e** prepared using **1e**/L-Selectride (> 50:1 *Z*/*E*)



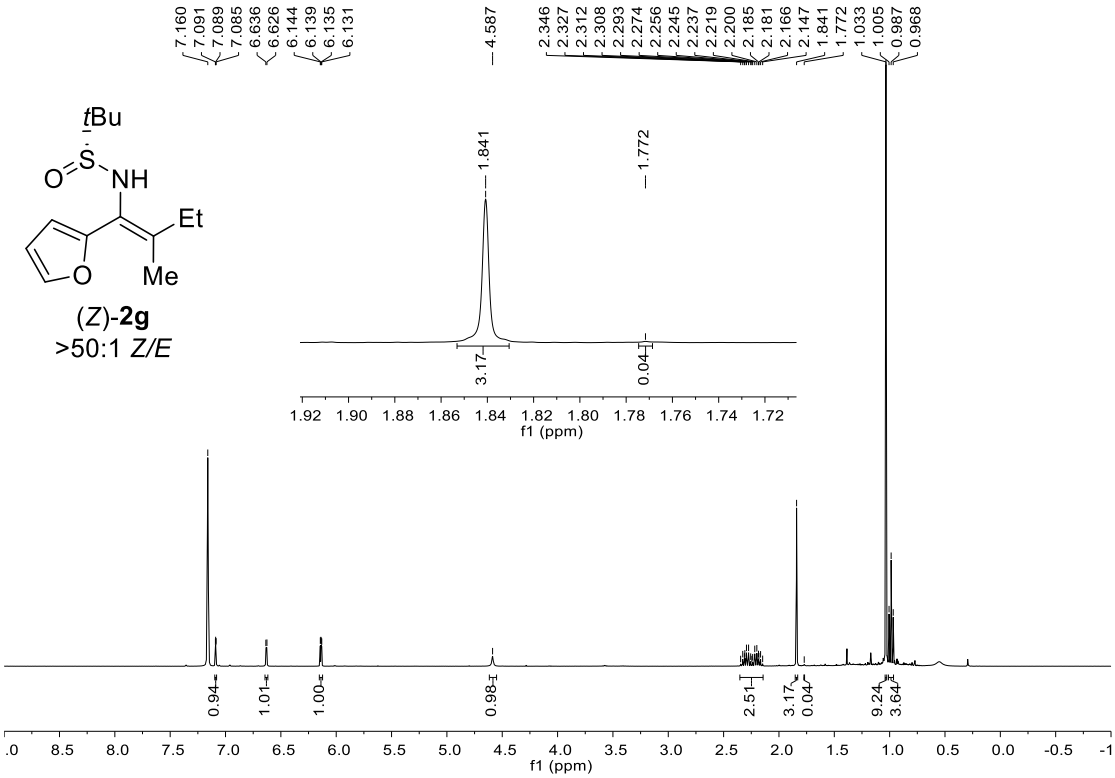
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2e** prepared using **1e**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z*/*E*)



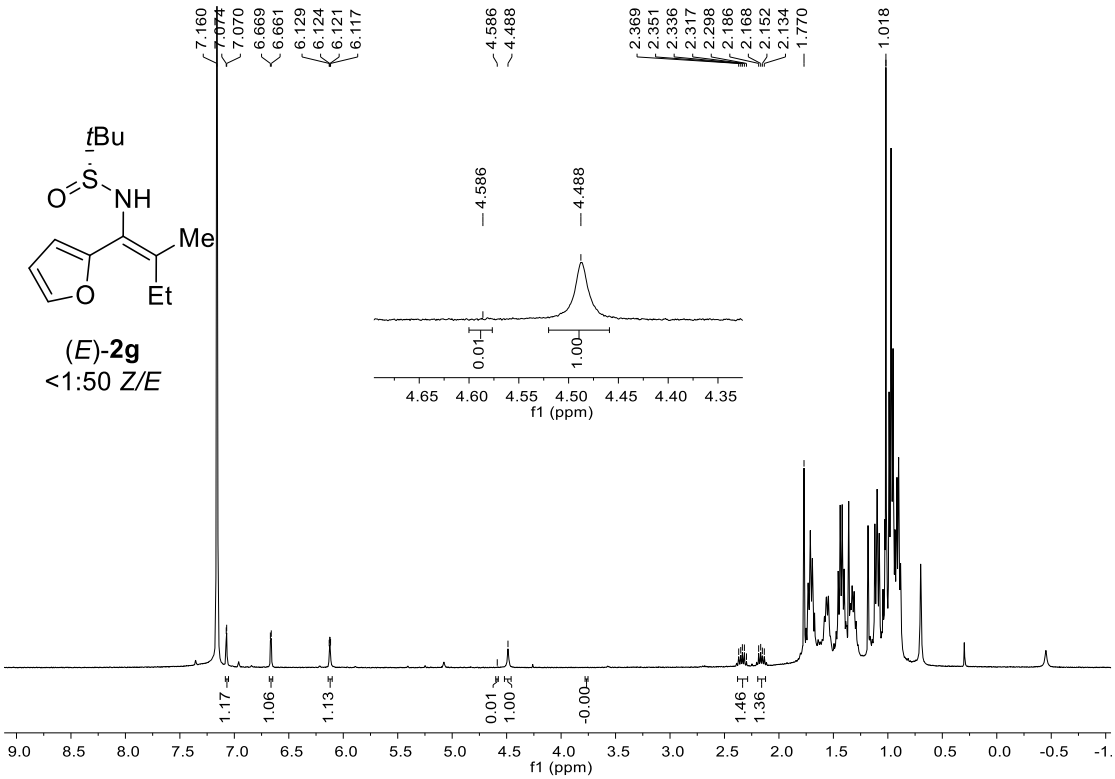
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2f** prepared using **1f**/L-Selectride (> 50:1 *Z*/*E*)



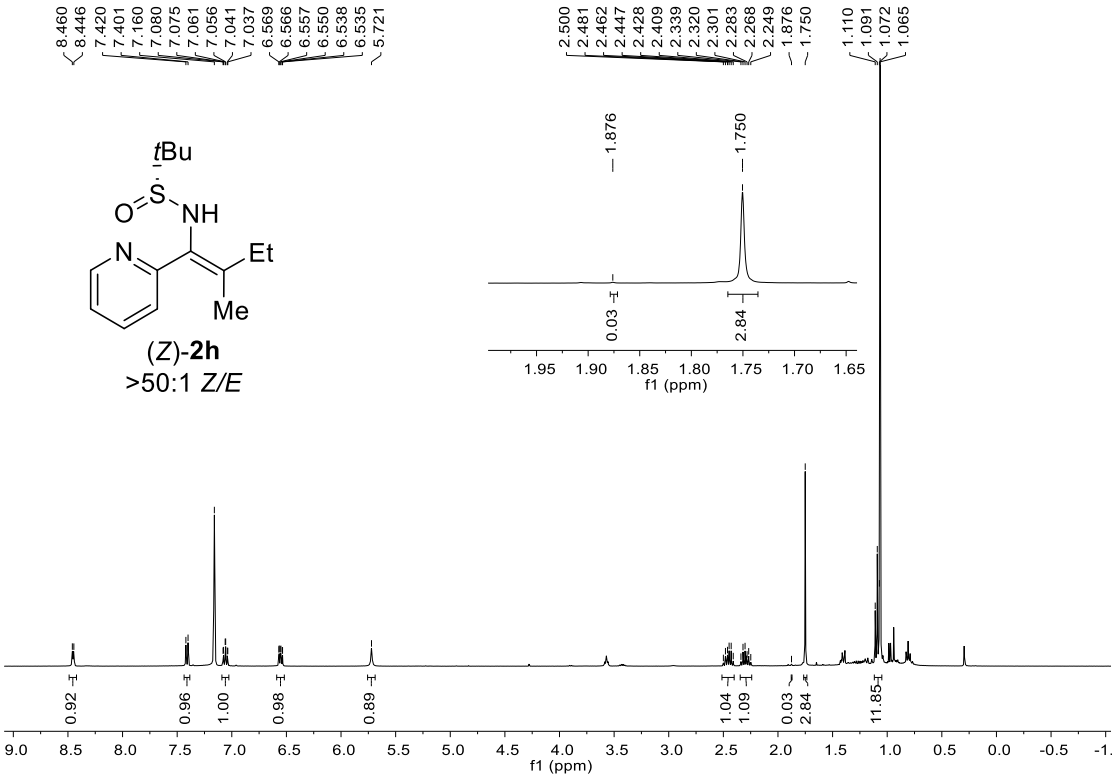
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2f** prepared using **1f**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



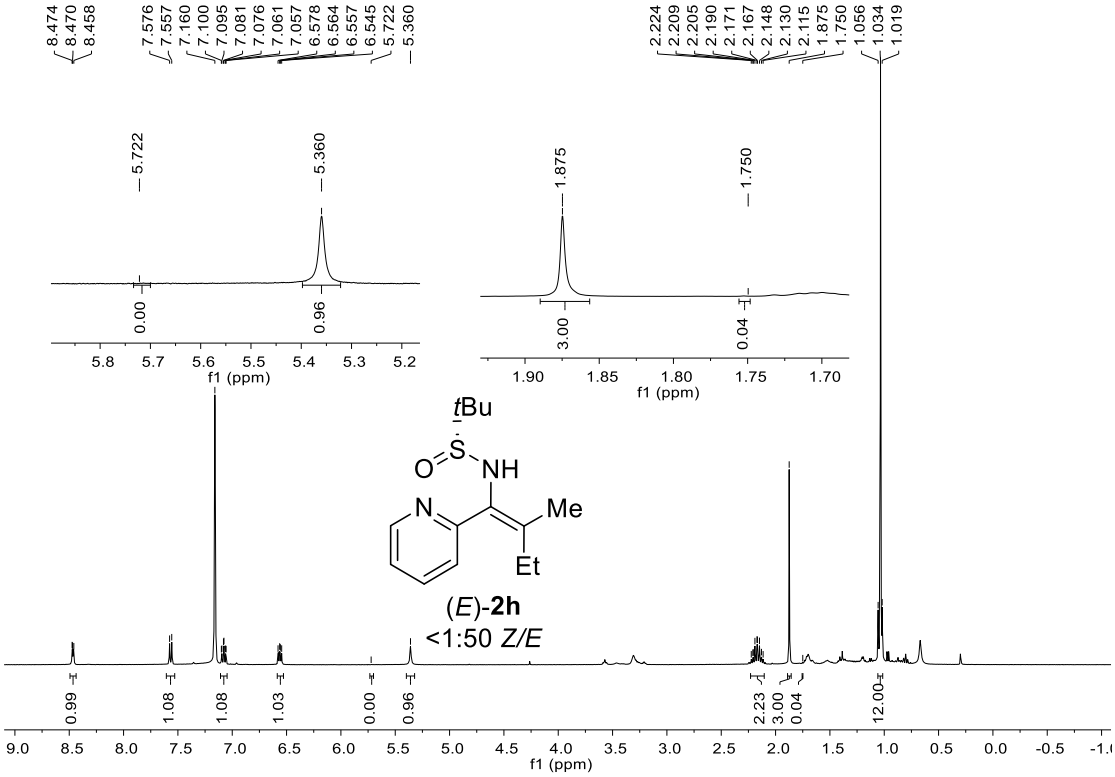
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2g** prepared using **1g**/L-Selectride (> 50:1 *Z*/*E*)



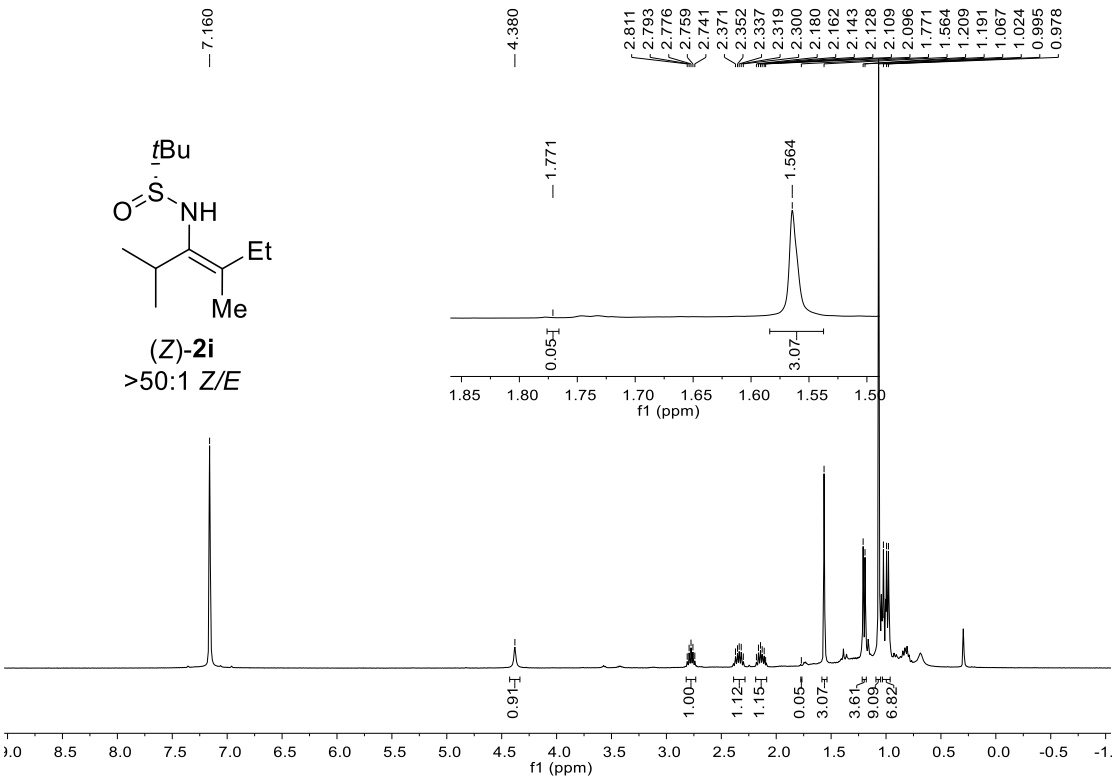
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2g** prepared using **1g**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



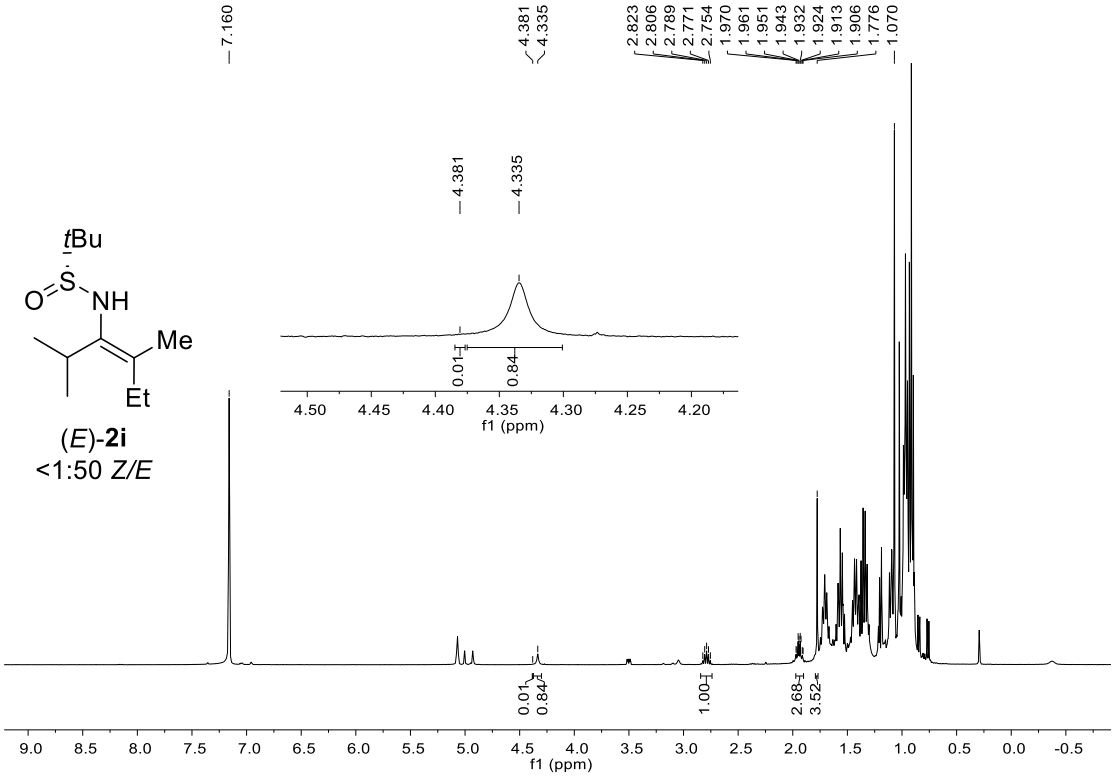
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2h** prepared using **1h**/L-Selectride (> 50:1 *Z*/*E*)



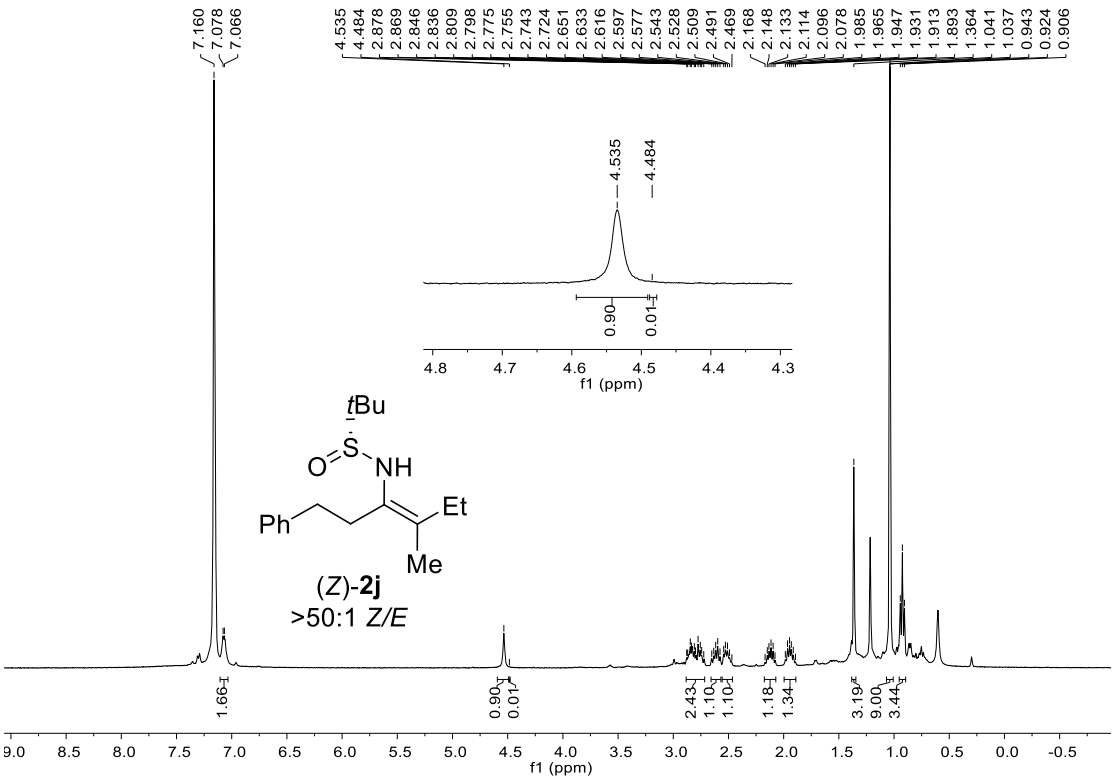
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2h** prepared using **1h′**/L-Selectride (< 1:50 *Z*/*E*)



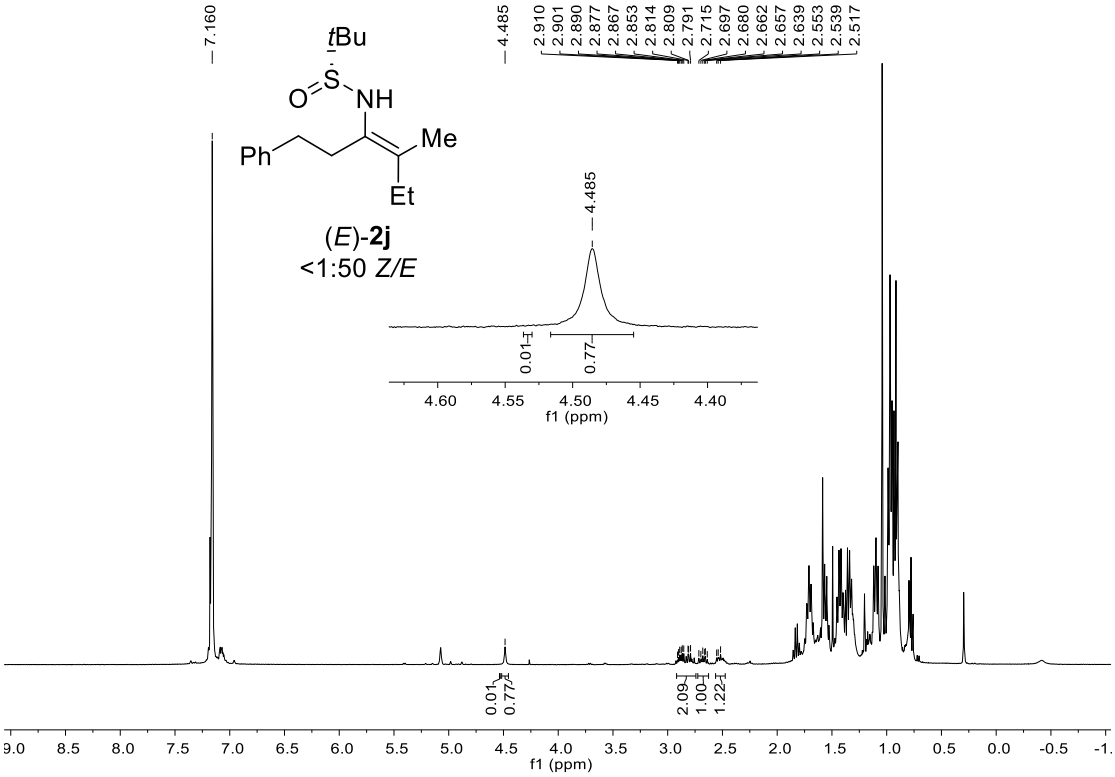
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2i** prepared using **1i**/L-Selectride (> 50:1 *Z*/*E*)



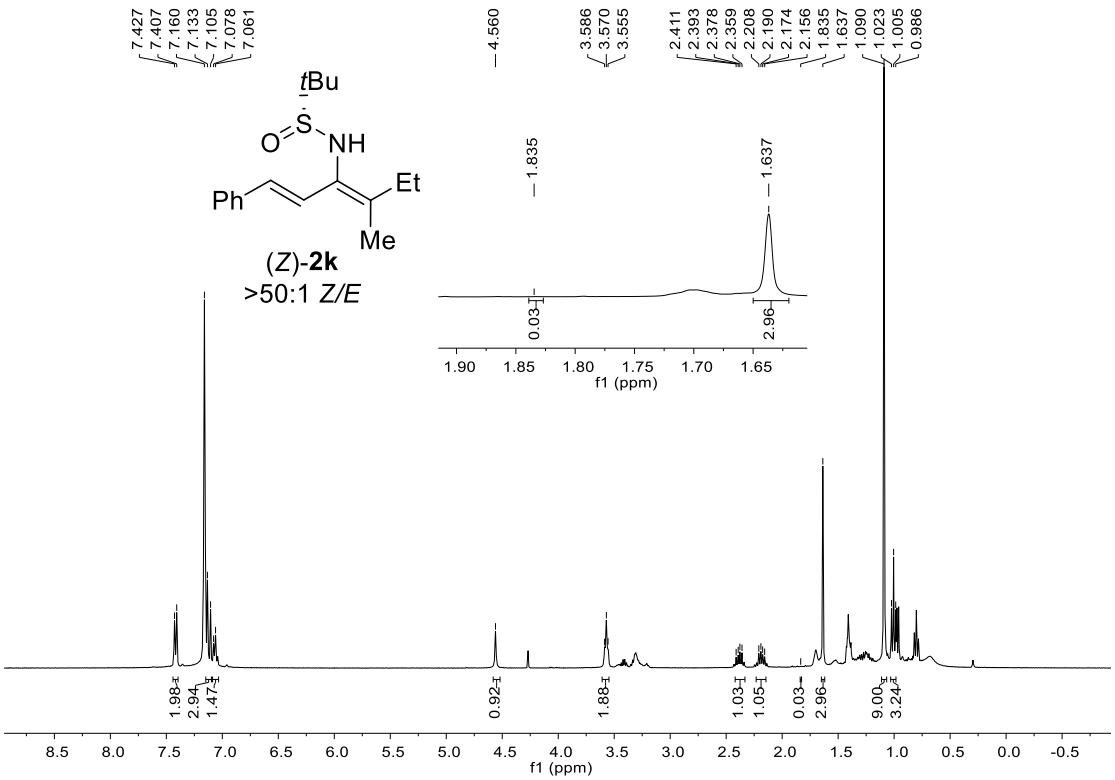
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2i** prepared using **1i**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



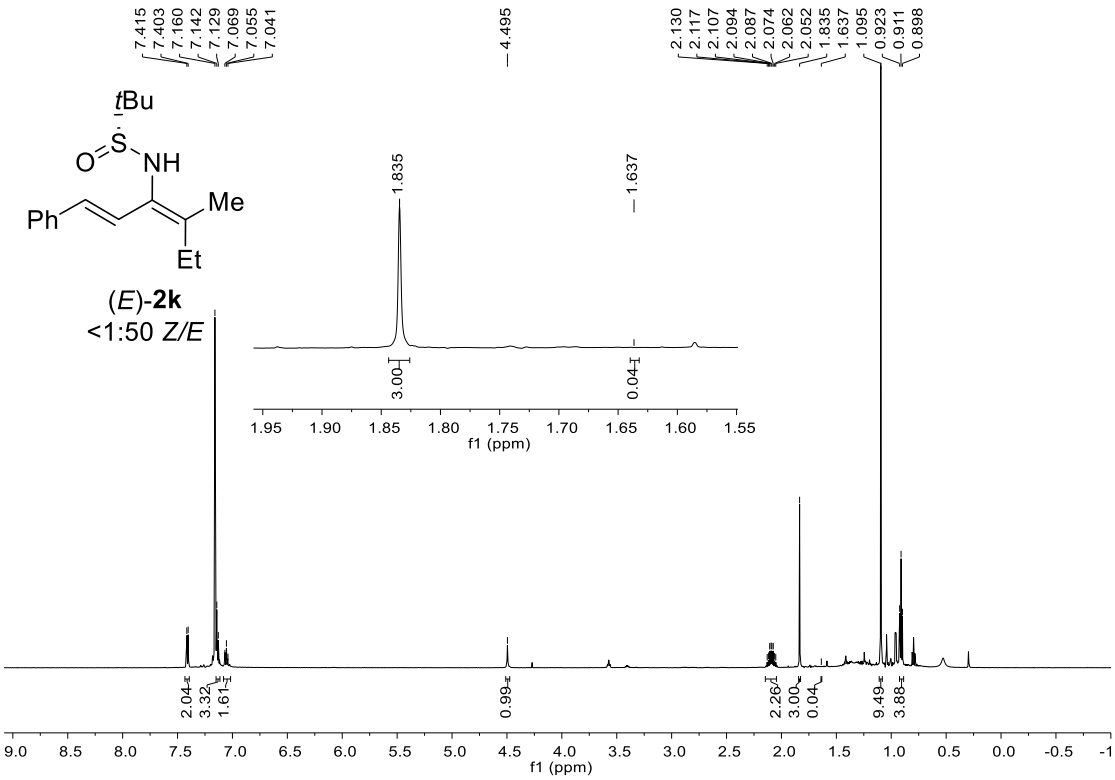
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2j** prepared using **1j**/L-Selectride (> 50:1 *Z/E*)



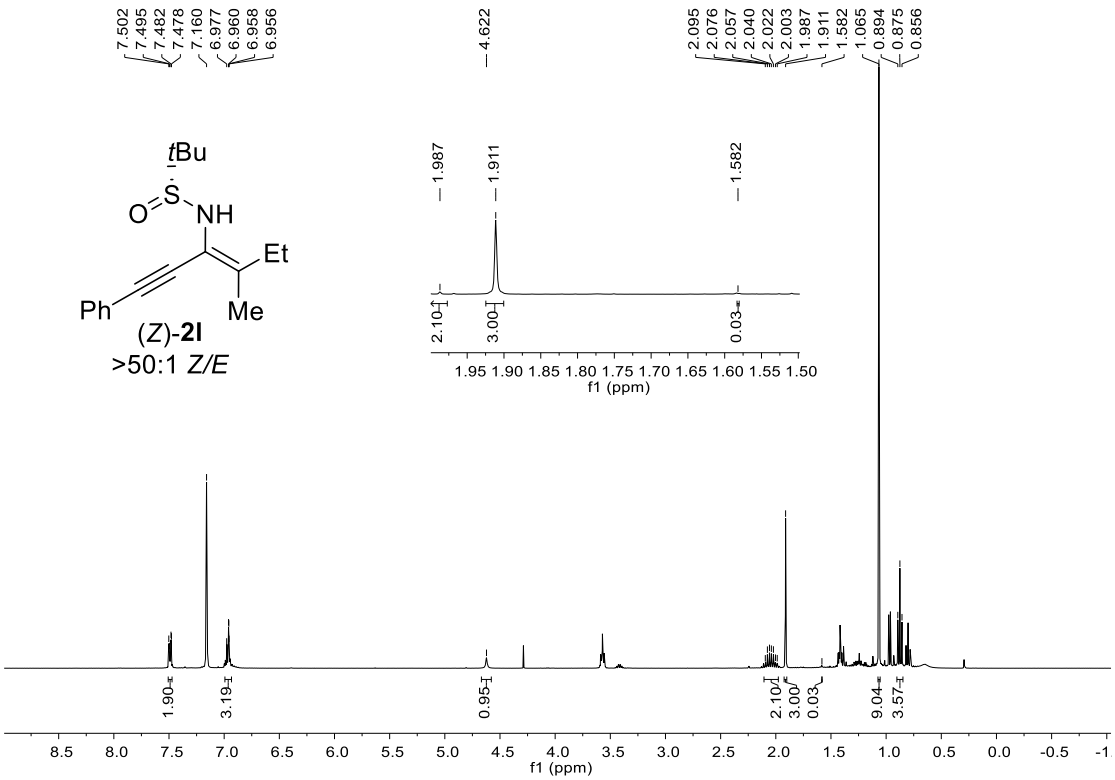
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2j** prepared using **1j**/$InBr_3$/nBu_3SnH (< 1:50 *Z/E*)



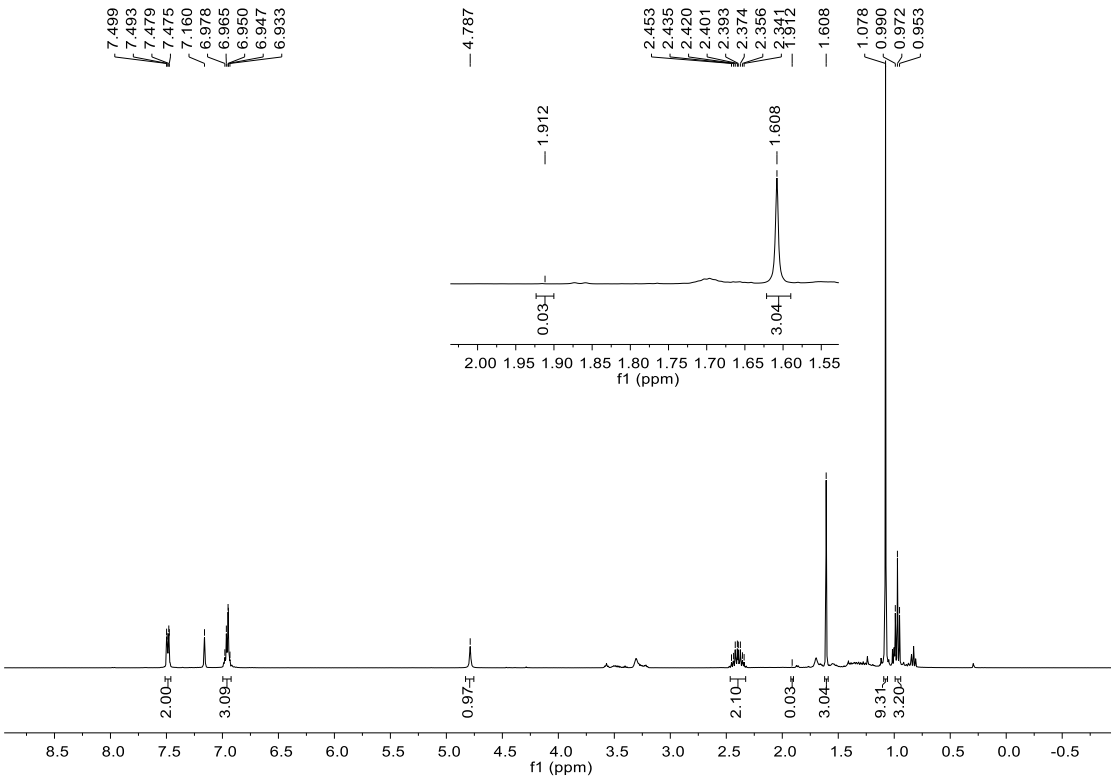
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2k** prepared using **1k**/L-Selectride (> 50:1 *Z*/*E*)



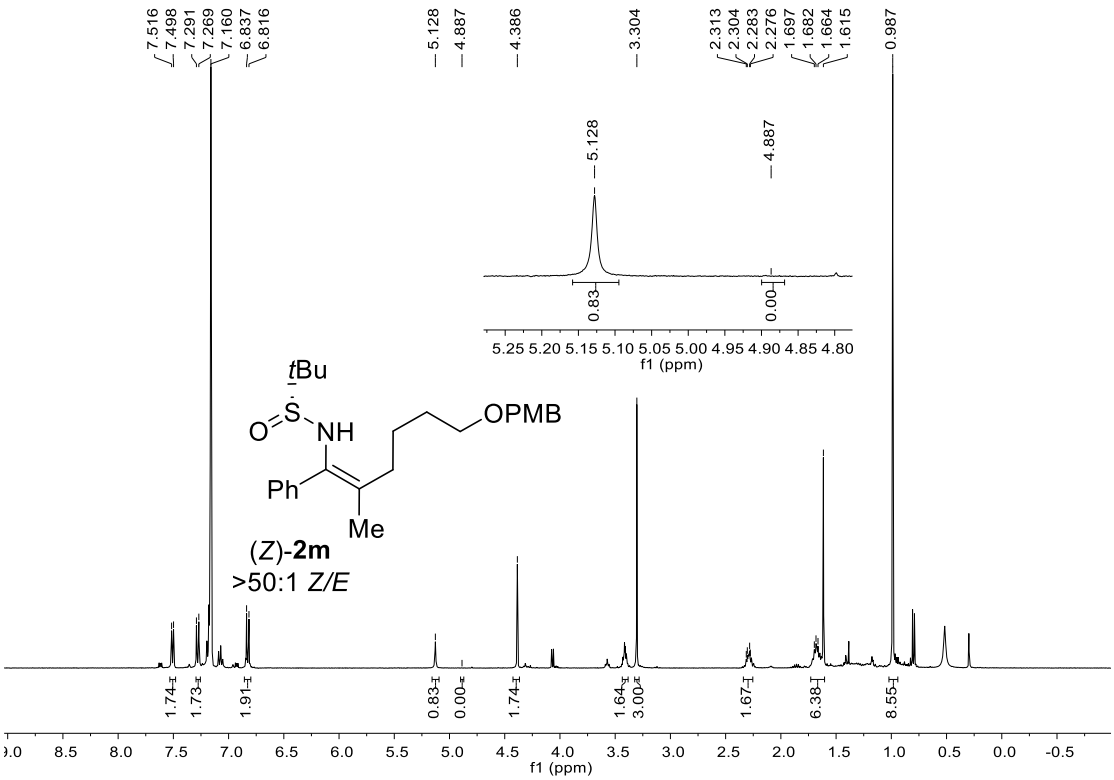
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2k** prepared using **1k′**/L-Selectride (< 1:50 *Z*/*E*)



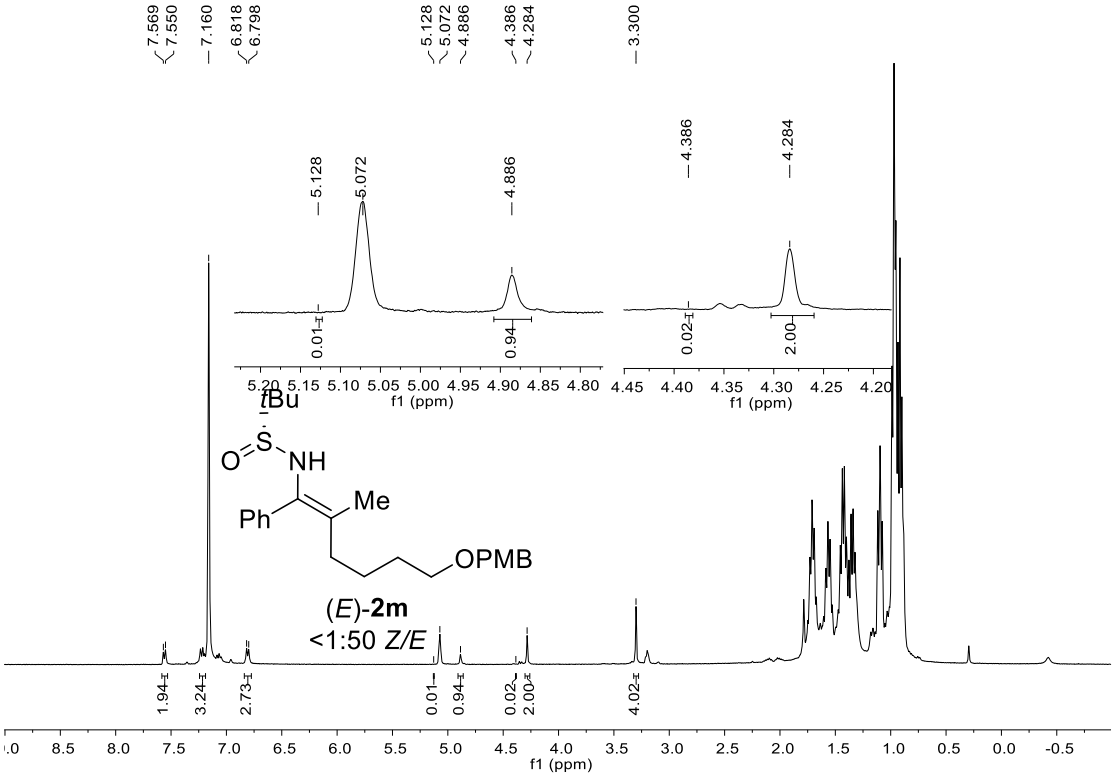
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2l** prepared using **1l**/L-Selectride (> 50:1 *Z*/*E*)



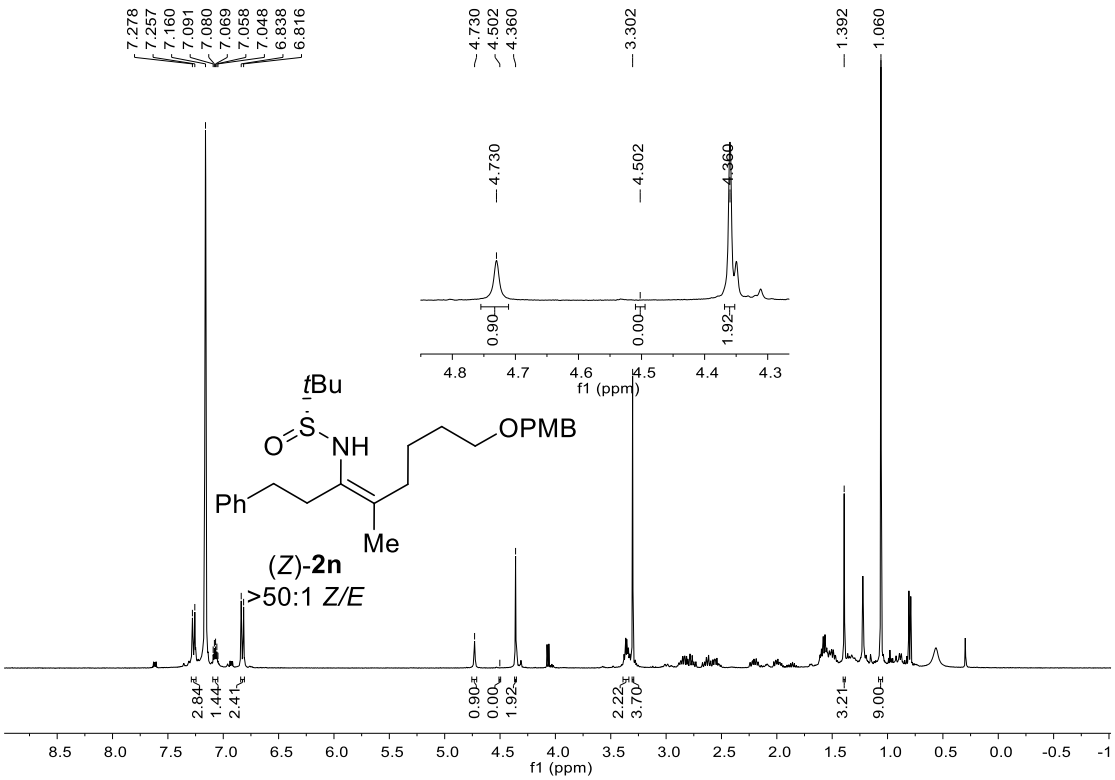
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2l** prepared using **1l′**/L-Selectride (< 1:50 *Z*/*E*)



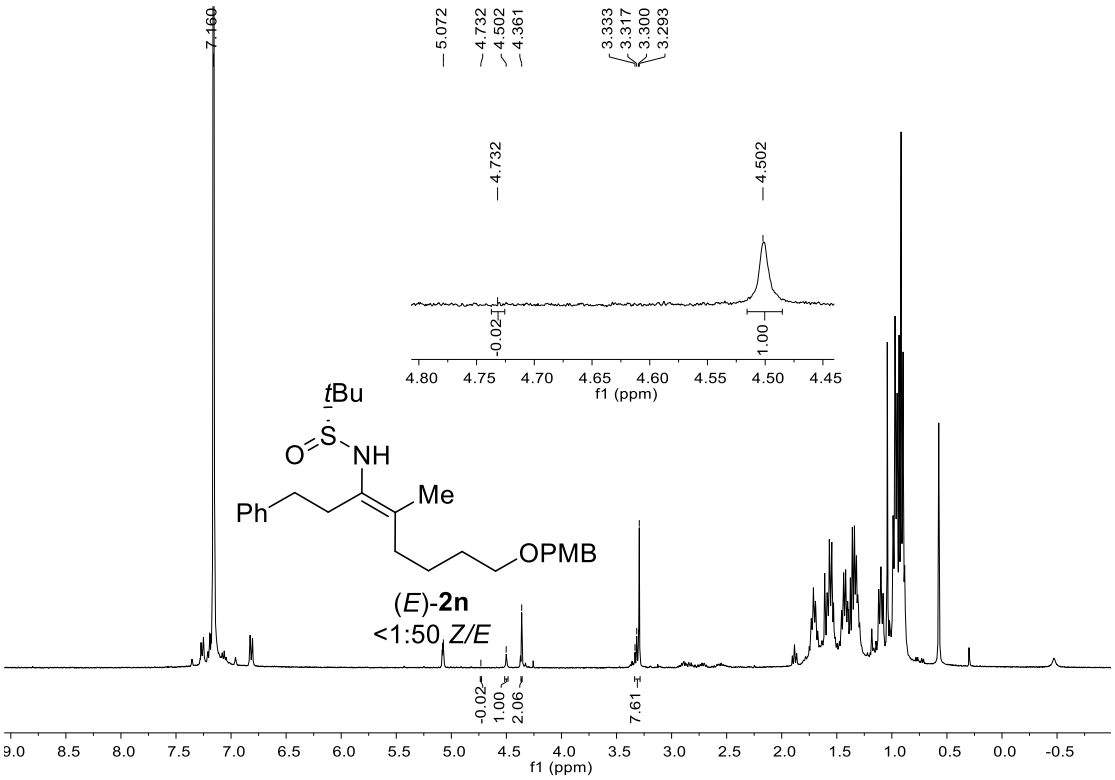
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2m** prepared using **1m**/L-Selectride (> 50:1 *Z*/*E*)



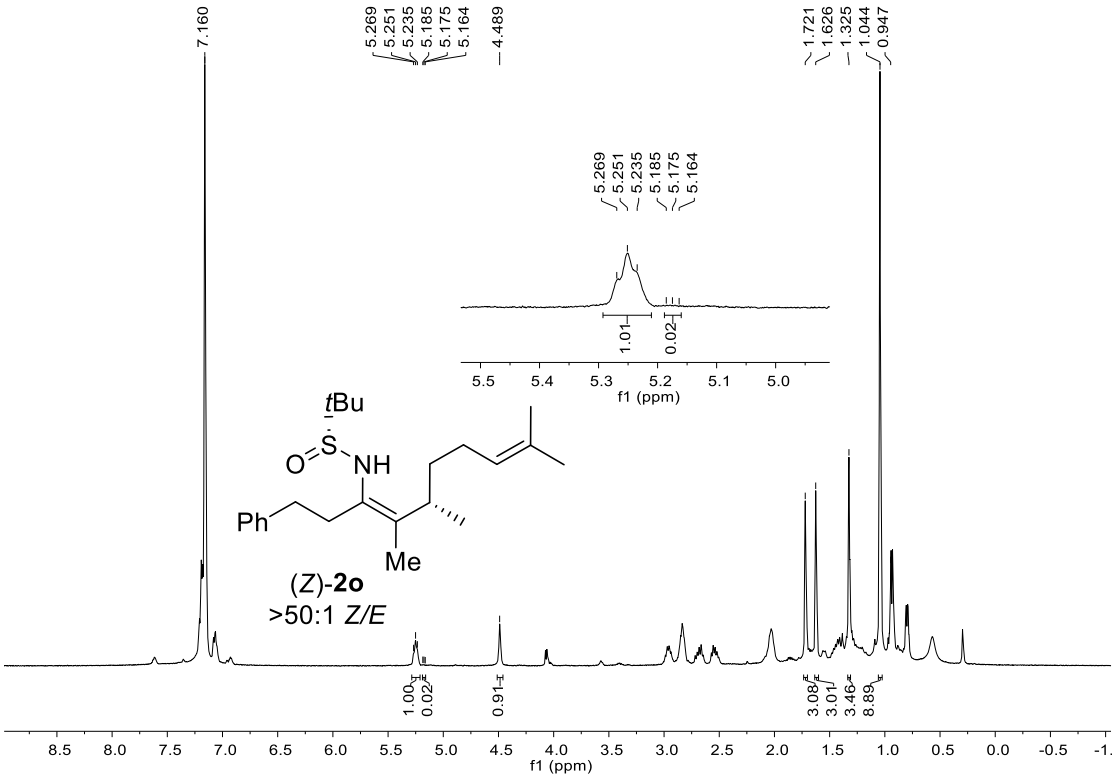
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2m** prepared using **1m**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



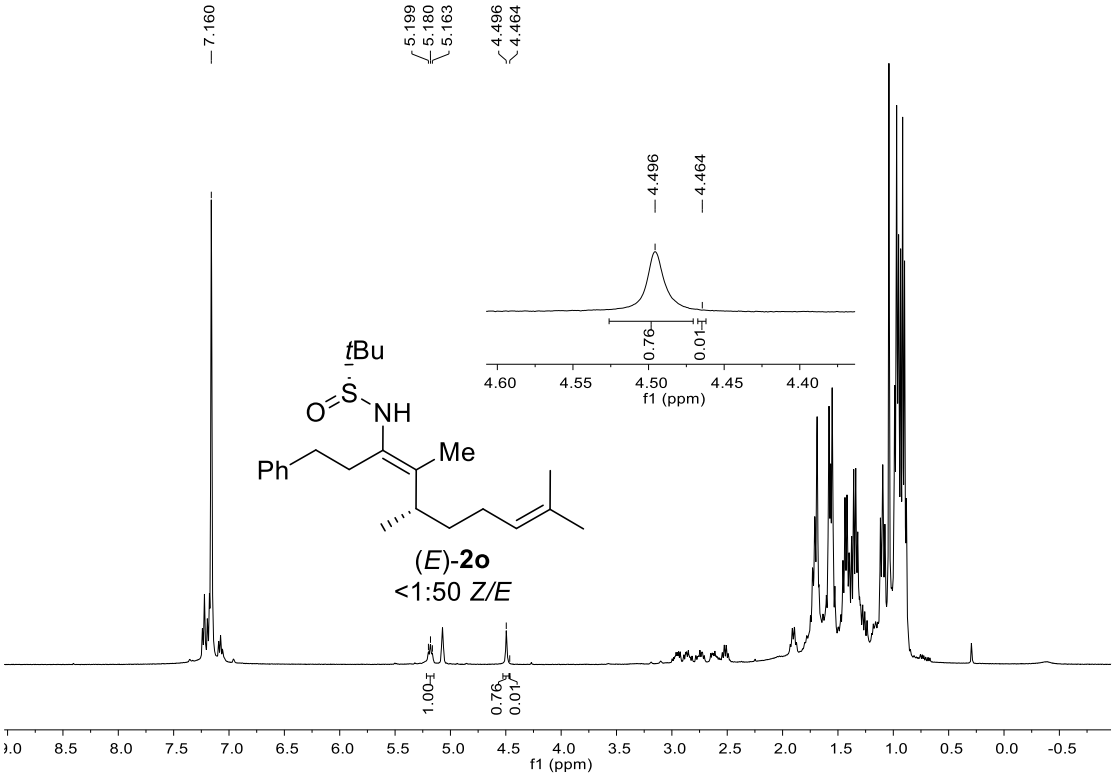
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2n** prepared using **1n**/L-Selectride (> 50:1 *Z/E*)



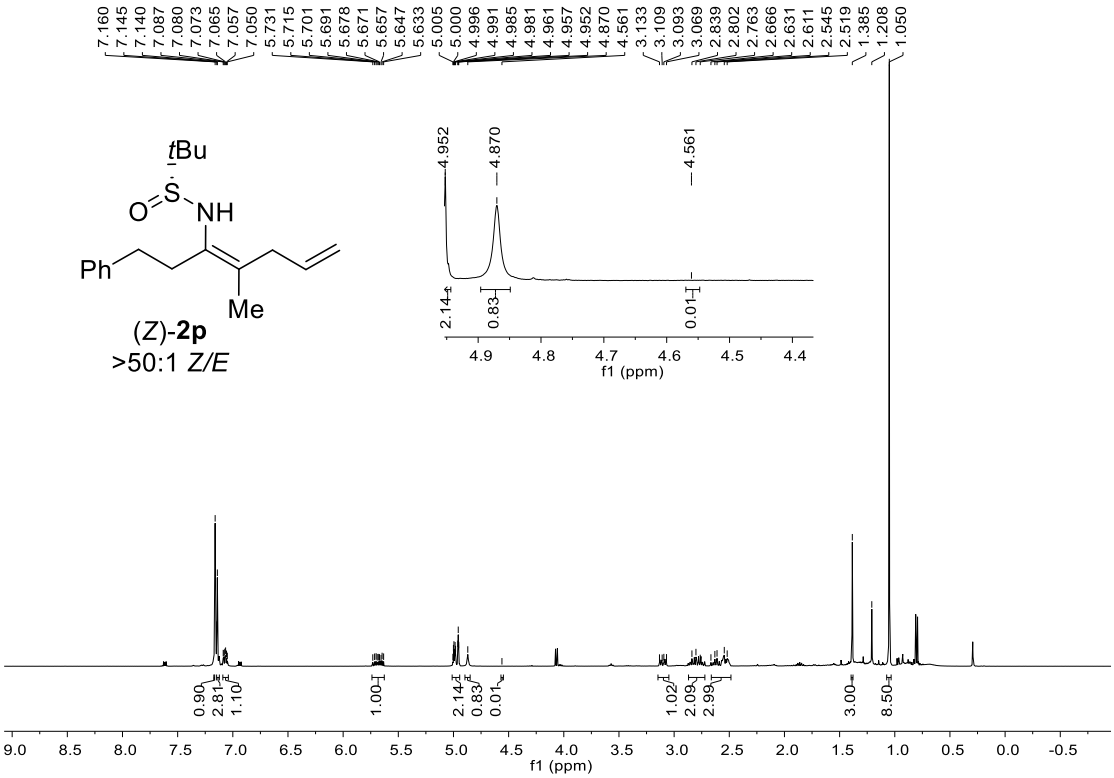
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2n** prepared using **1n**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z/E*)



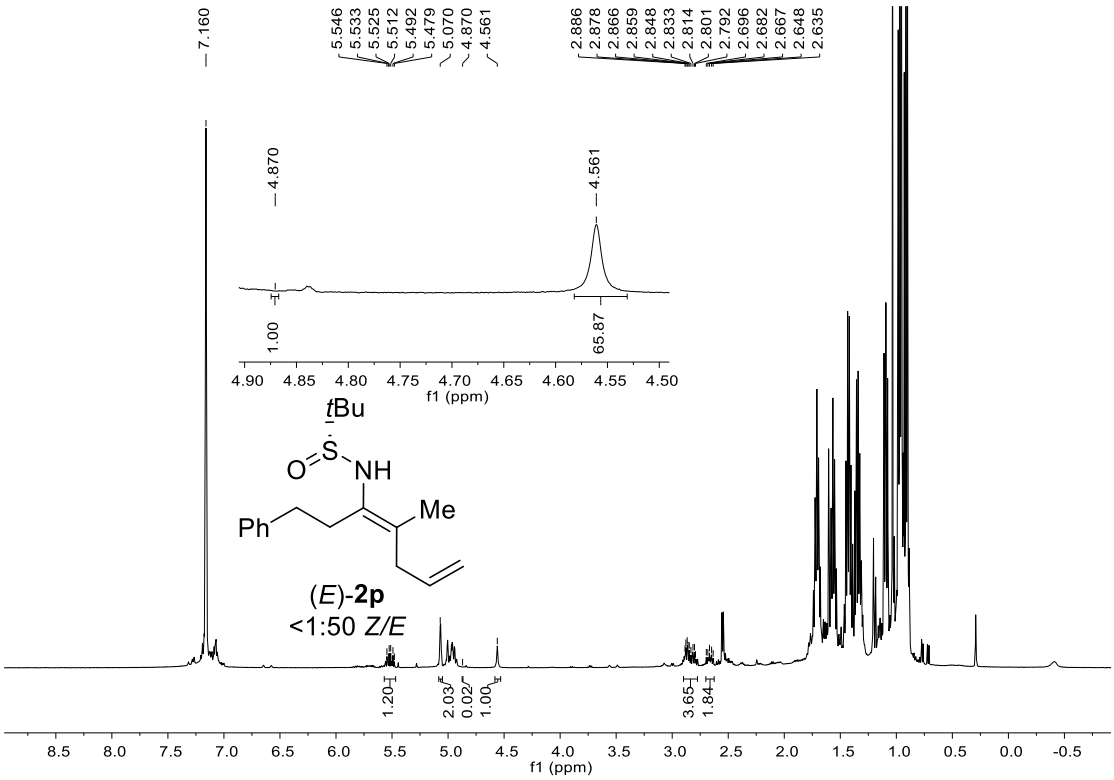
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2o** prepared using **1o**/L-Selectride (> 50:1 *Z*/*E*)



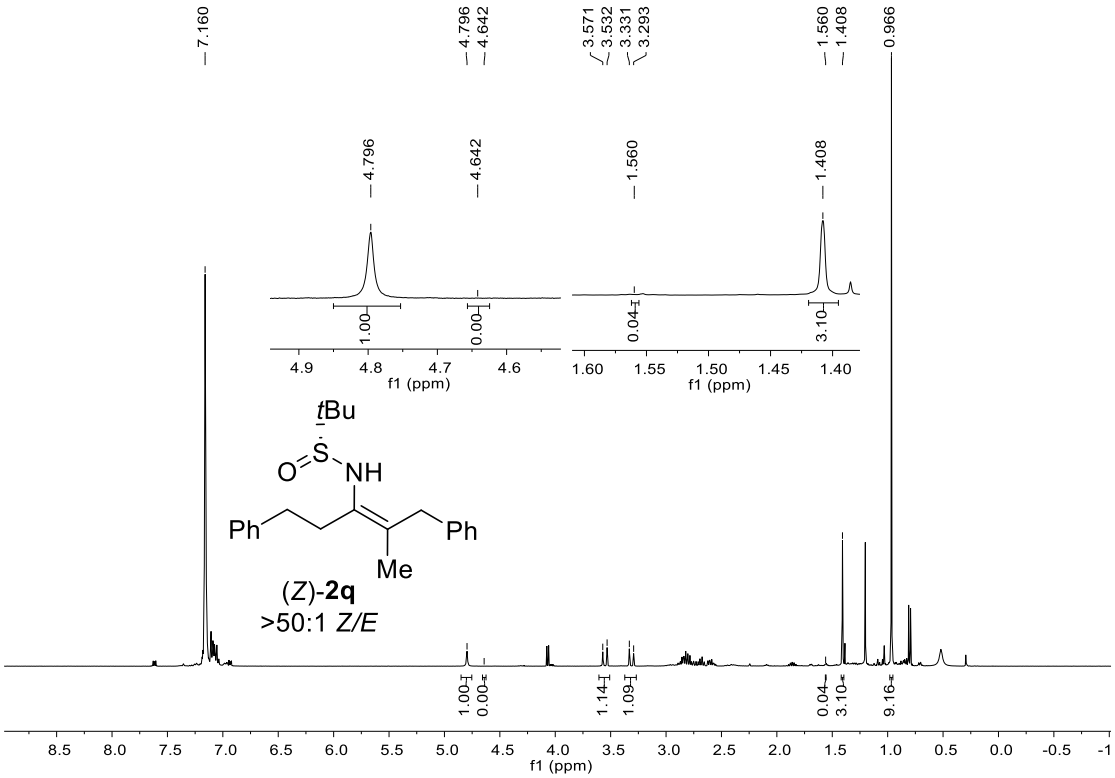
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2o** prepared using **1o**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



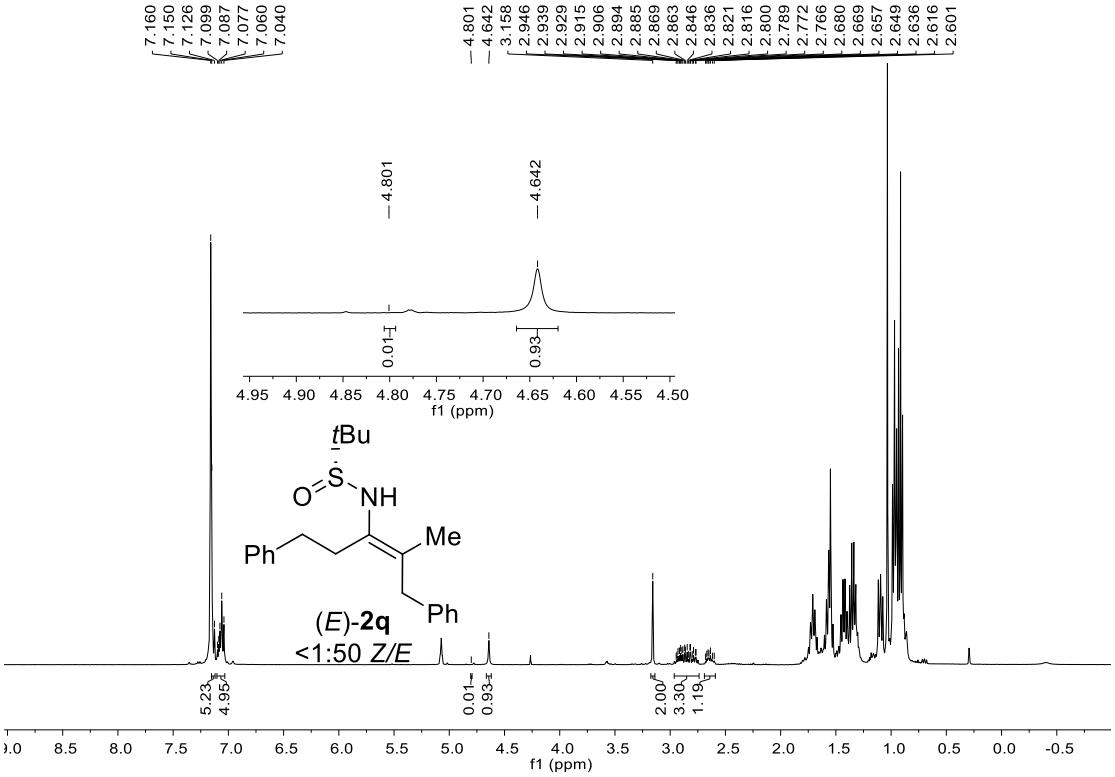
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2p** prepared using **1p**/L-Selectride (> 50:1 *Z/E*)



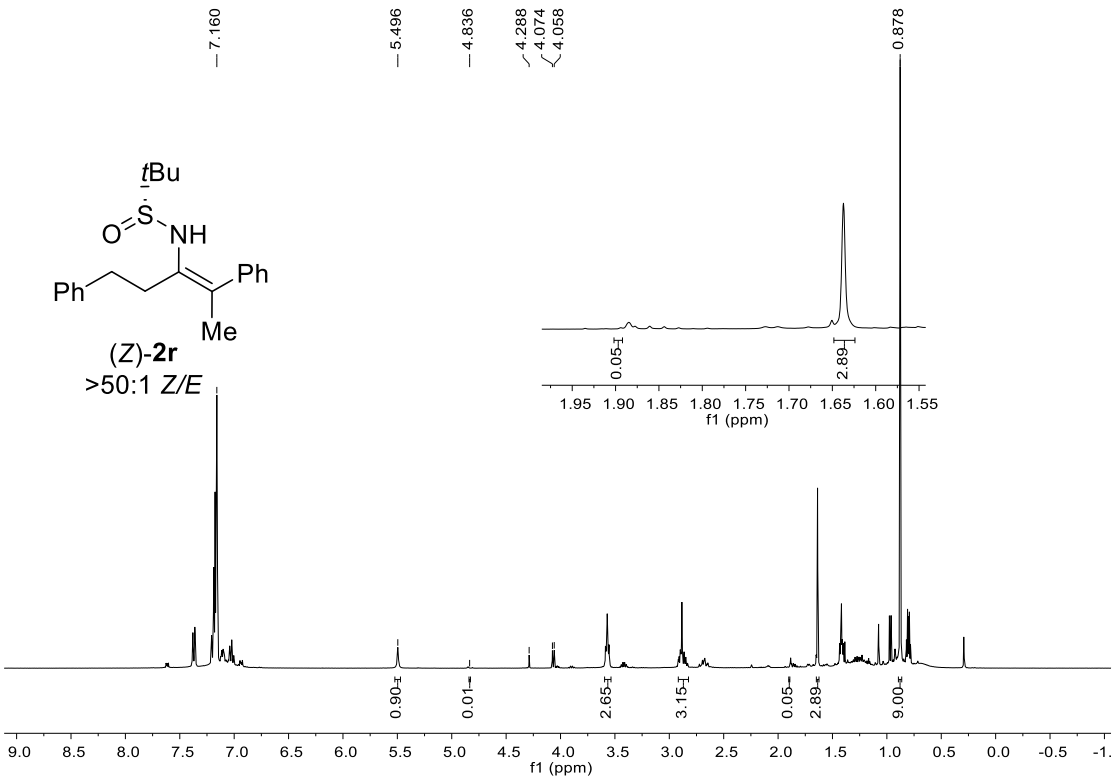
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2p** prepared using **1p**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z/E*)



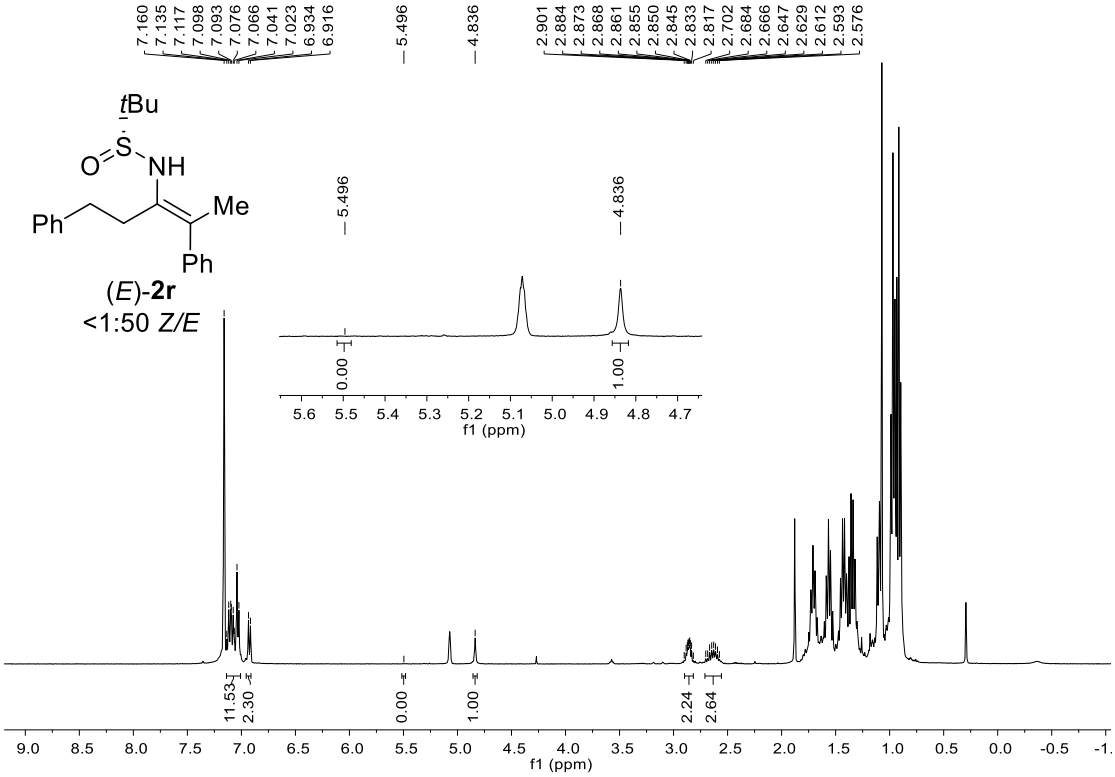
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2q** prepared using **1q**/L-Selectride (> 50:1 *Z*/*E*)



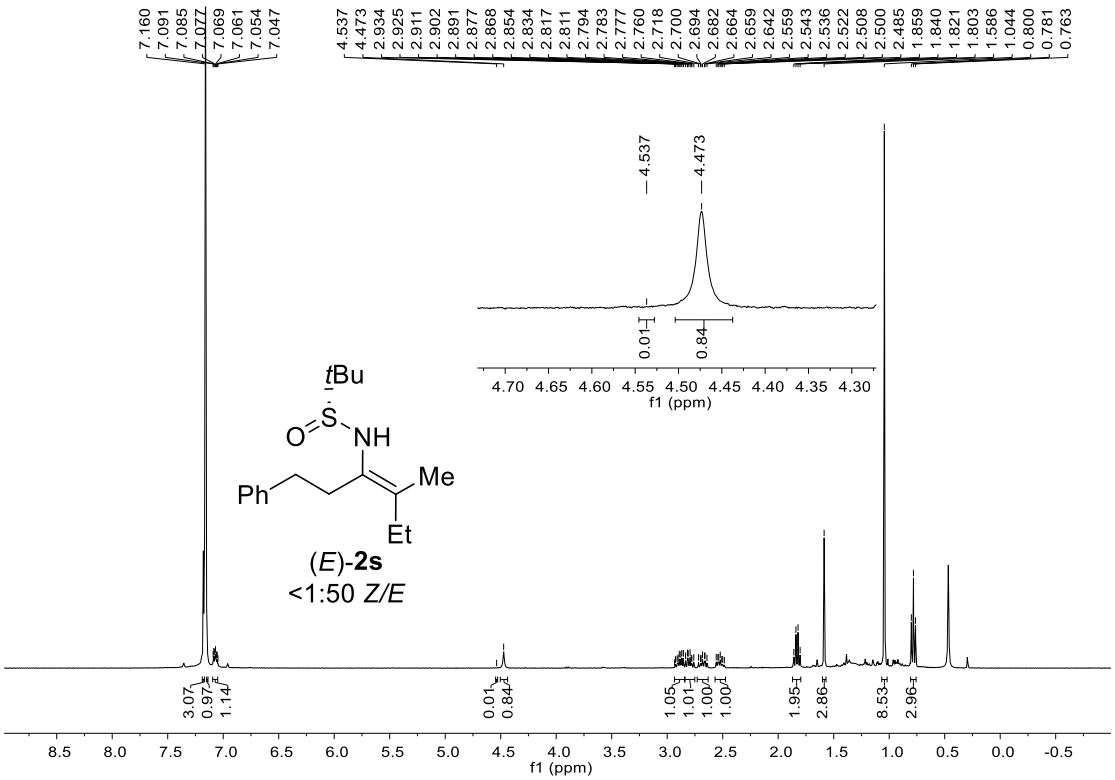
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2q** prepared using **1q**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z*/*E*)



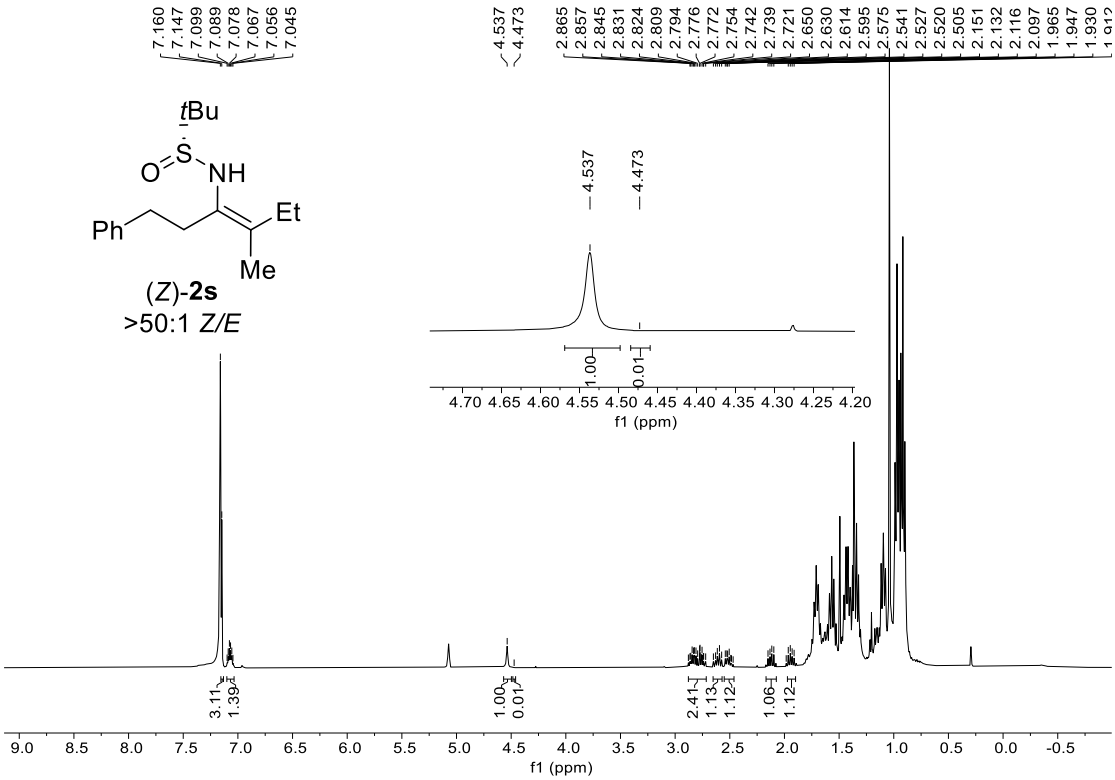
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2r** prepared using **1r**/L-Selectride (> 50:1 *Z/E*)



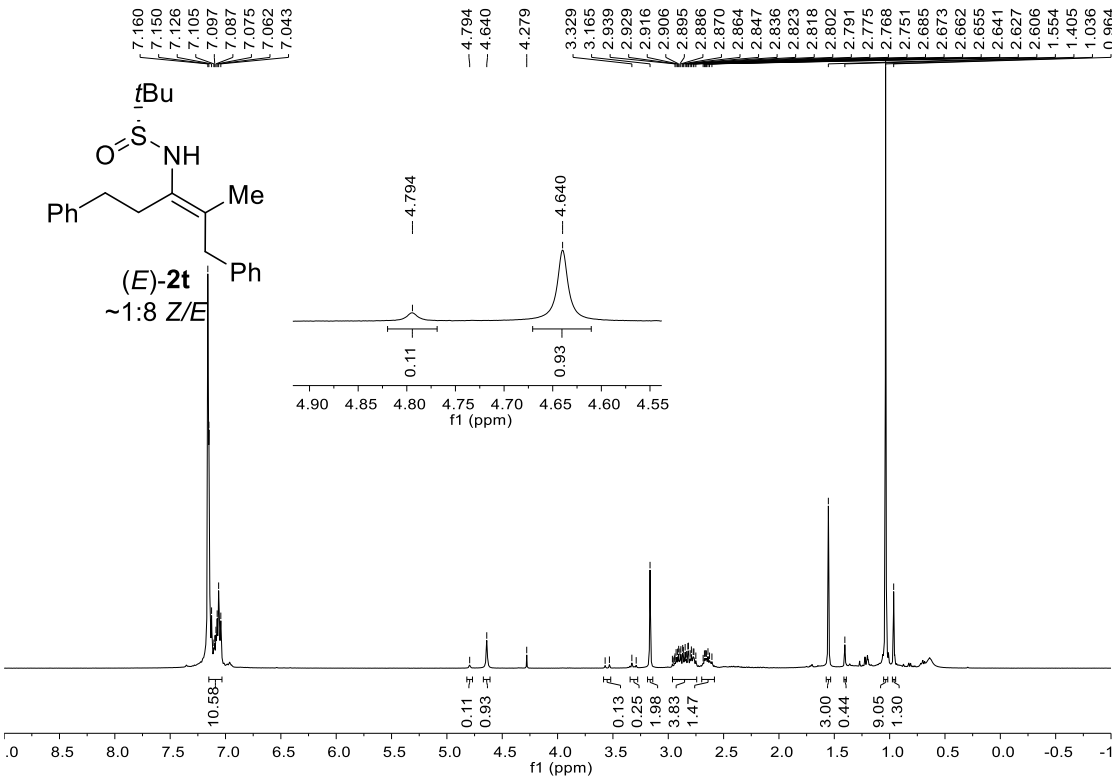
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2r** prepared using **1r**/$InBr_3$/nBu_3SnH (< 1:50 *Z/E*)



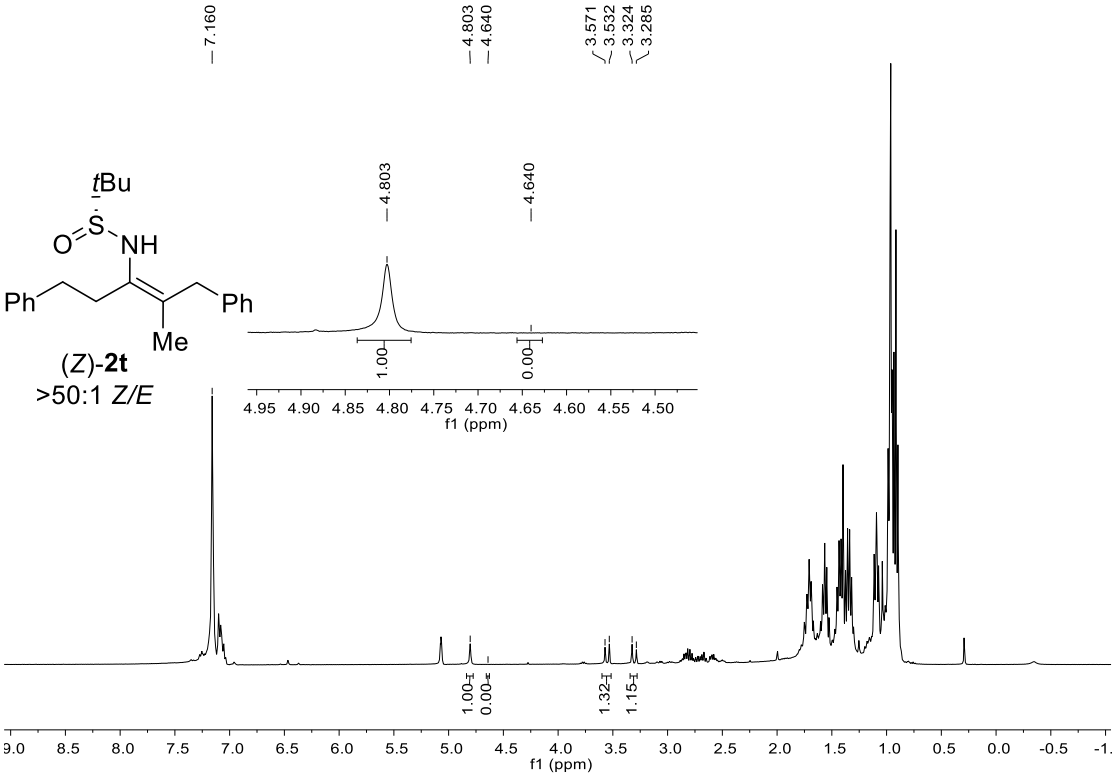
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2s** prepared using **1s**/L-Selectride (< 1:50 *Z*/*E*)



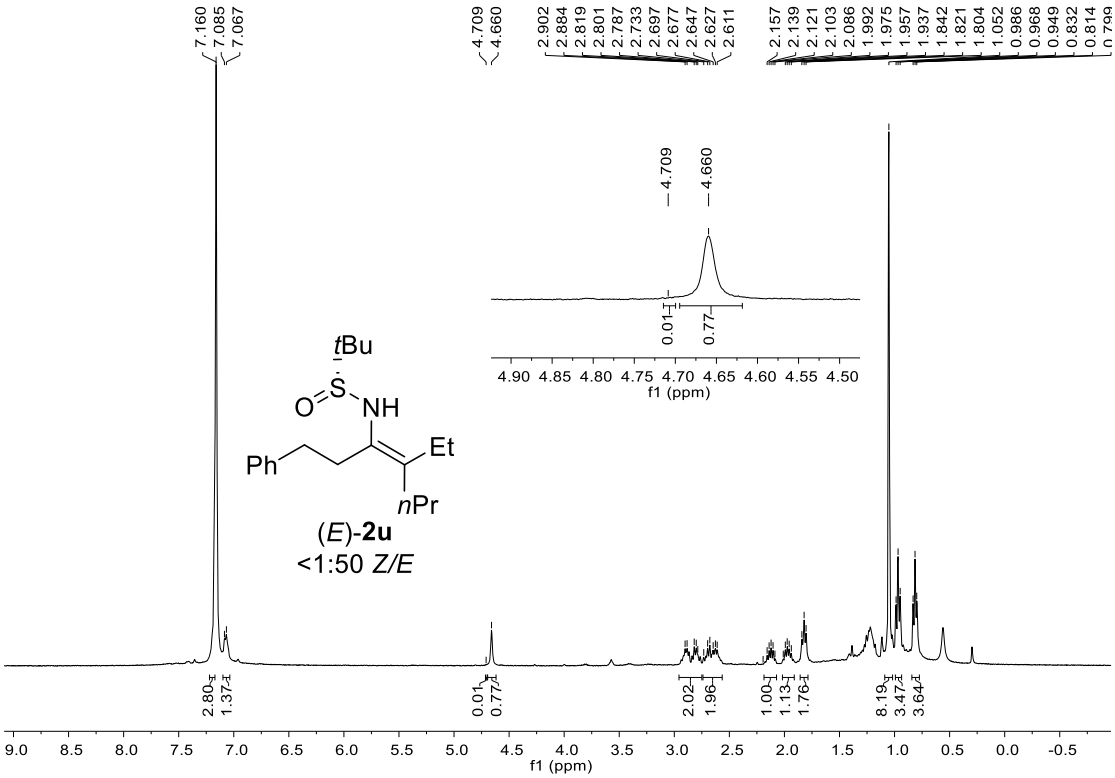
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2s** prepared using **1s**/$InBr_3$/nBu_3SnH (> 50:1 *Z*/*E*)



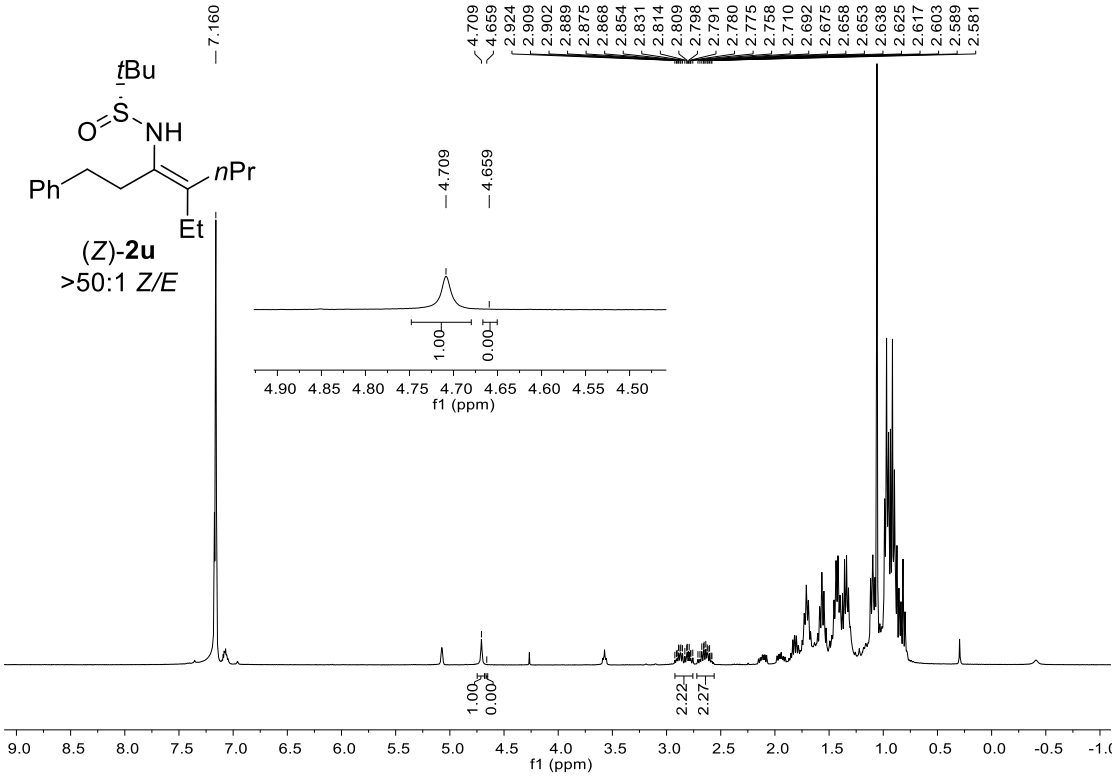
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2t** prepared using **1t**/$NiCl_2$/$NaBH_4$ (~ 1:8 *Z/E*)



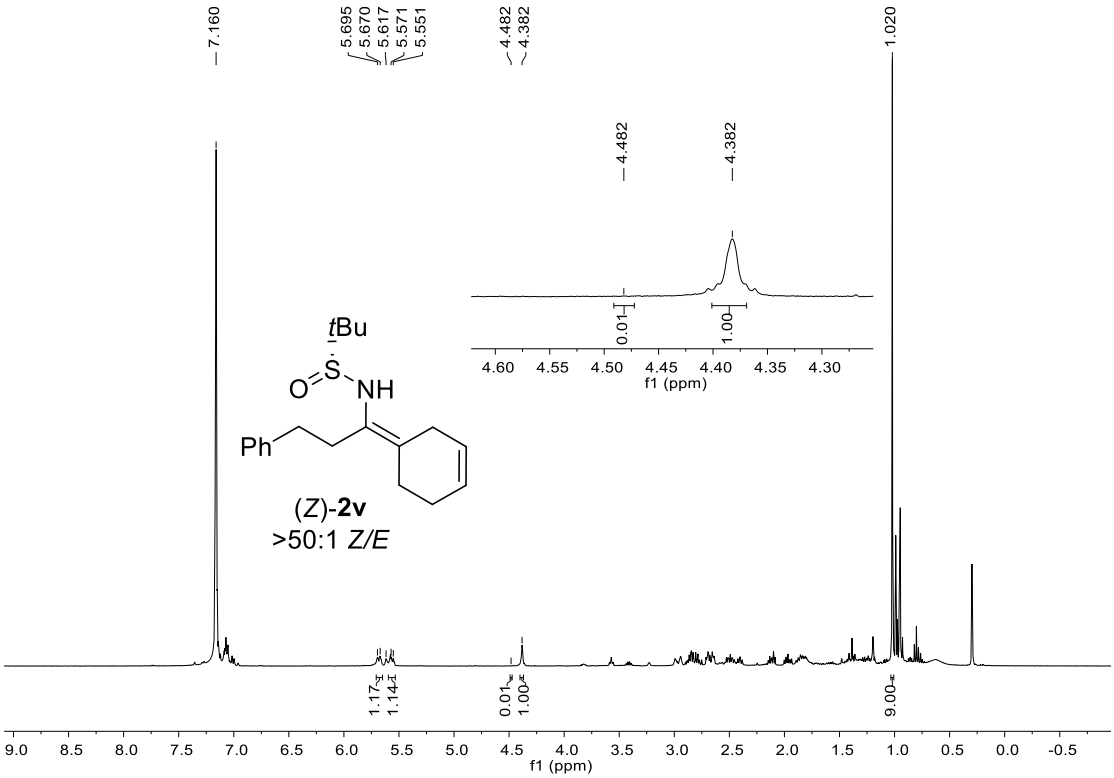
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2t** prepared using **1t**/$InBr_3$/$n$$Bu_3SnH$ (> 50:1 *Z/E*)



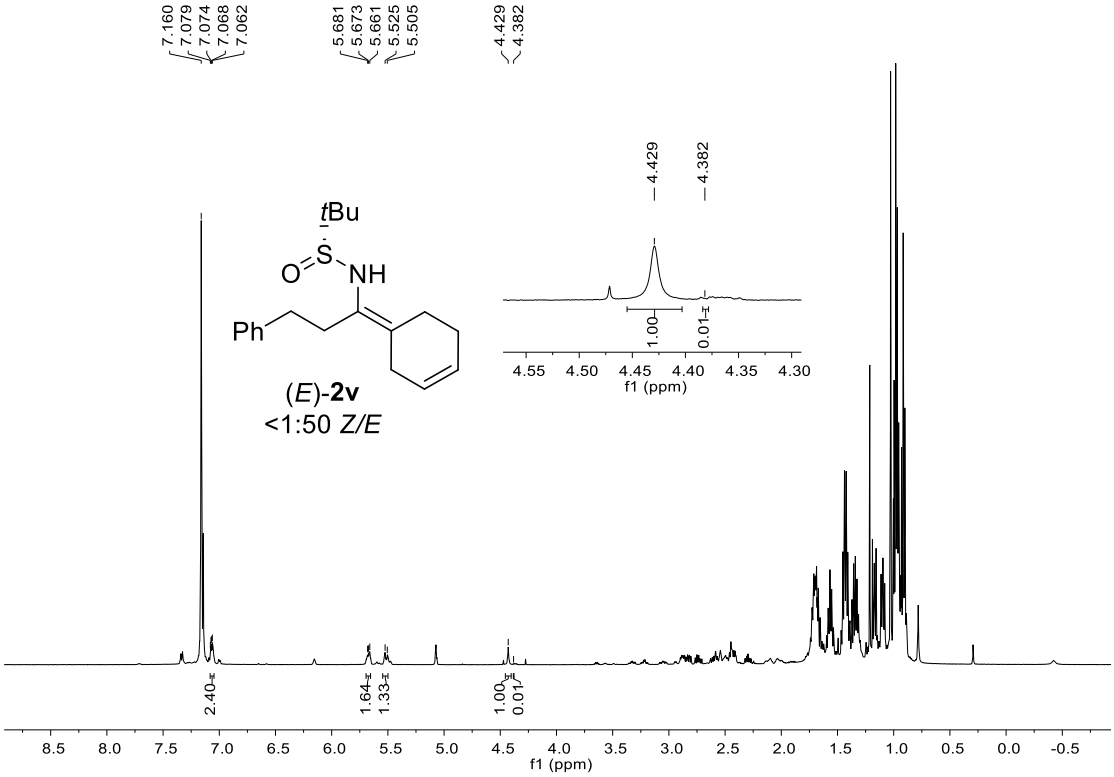
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2u** prepared using **1u**/L-Selectride (< 1:50 *Z*/*E*)



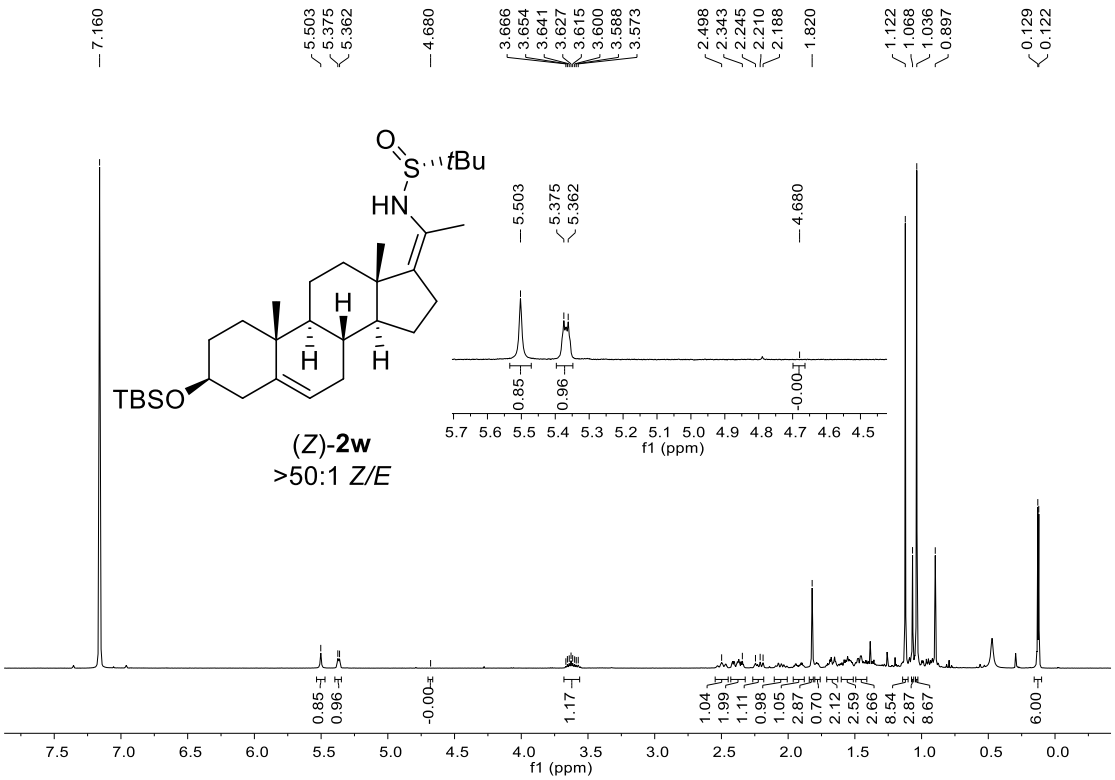
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2u** prepared using **1u**/$InBr_3$/$n$$Bu_3SnH$ (> 50:1 *Z*/*E*)



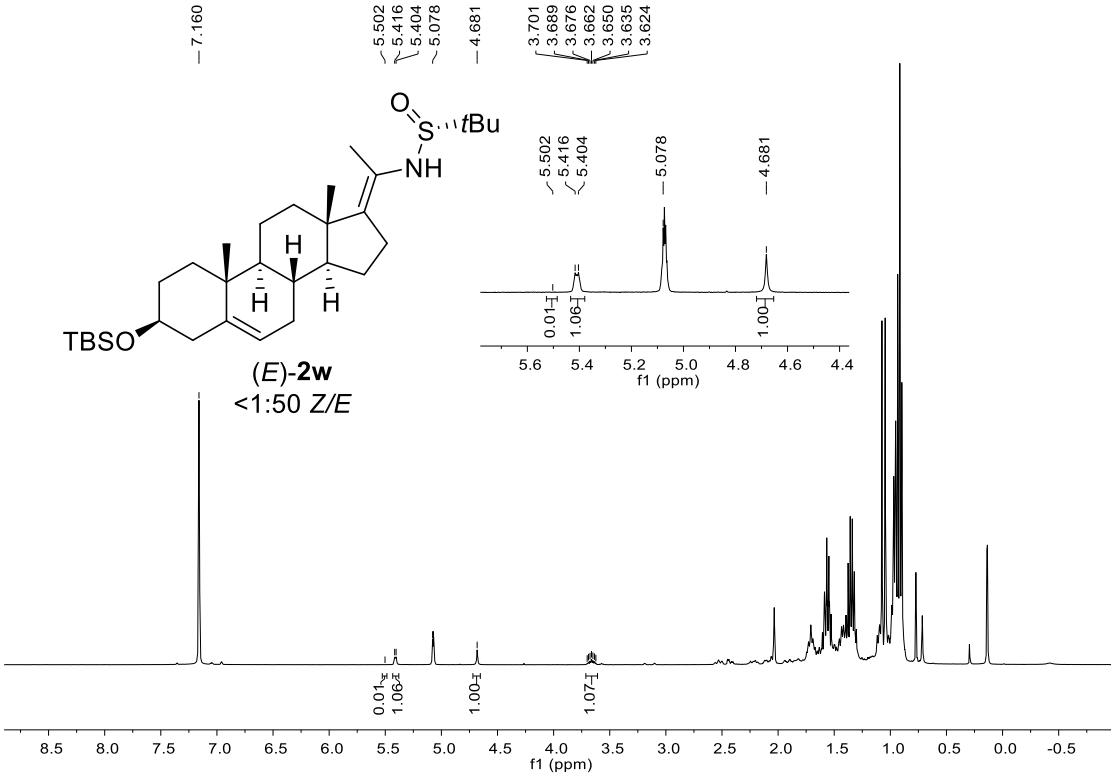
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2v** prepared using **1v**/L-Selectride (> 50:1 *Z*/*E*)



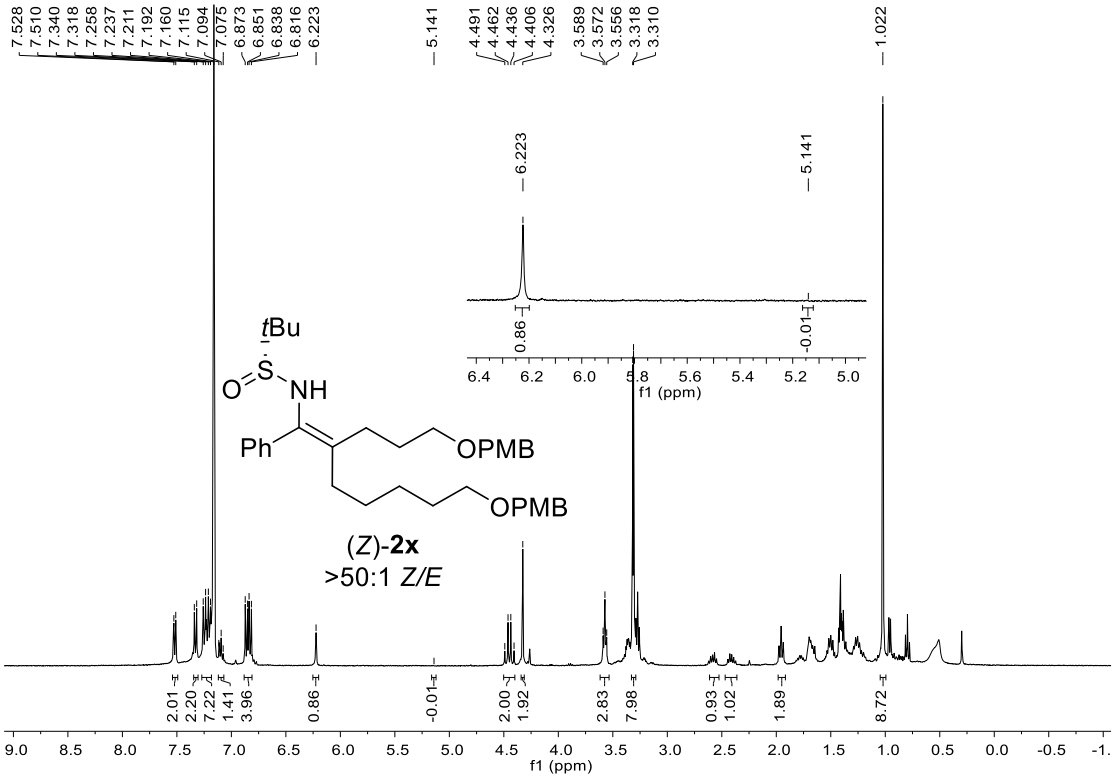
^{1}H NMR spectrum (C_6D_6, 500 MHz) of the crude reaction mixture of (*E*)-**2v** prepared using **1v**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z*/*E*)



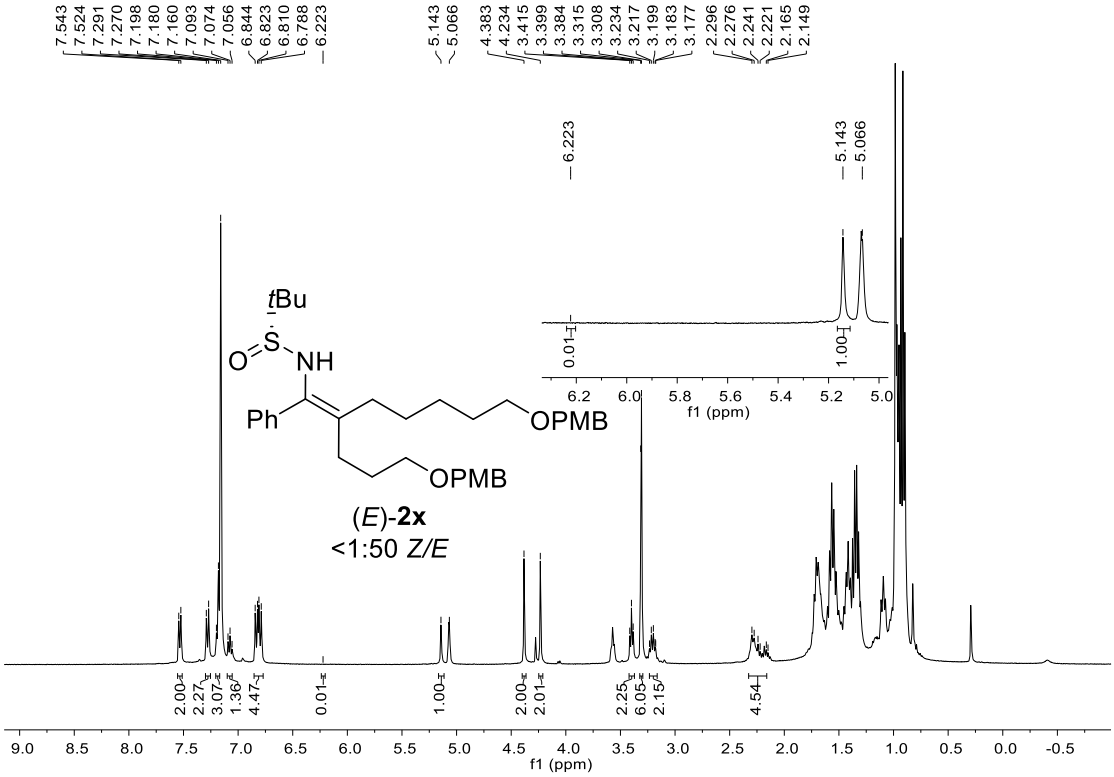
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2w** prepared using **1w**/L-Selectride (> 50:1 *Z/E*)



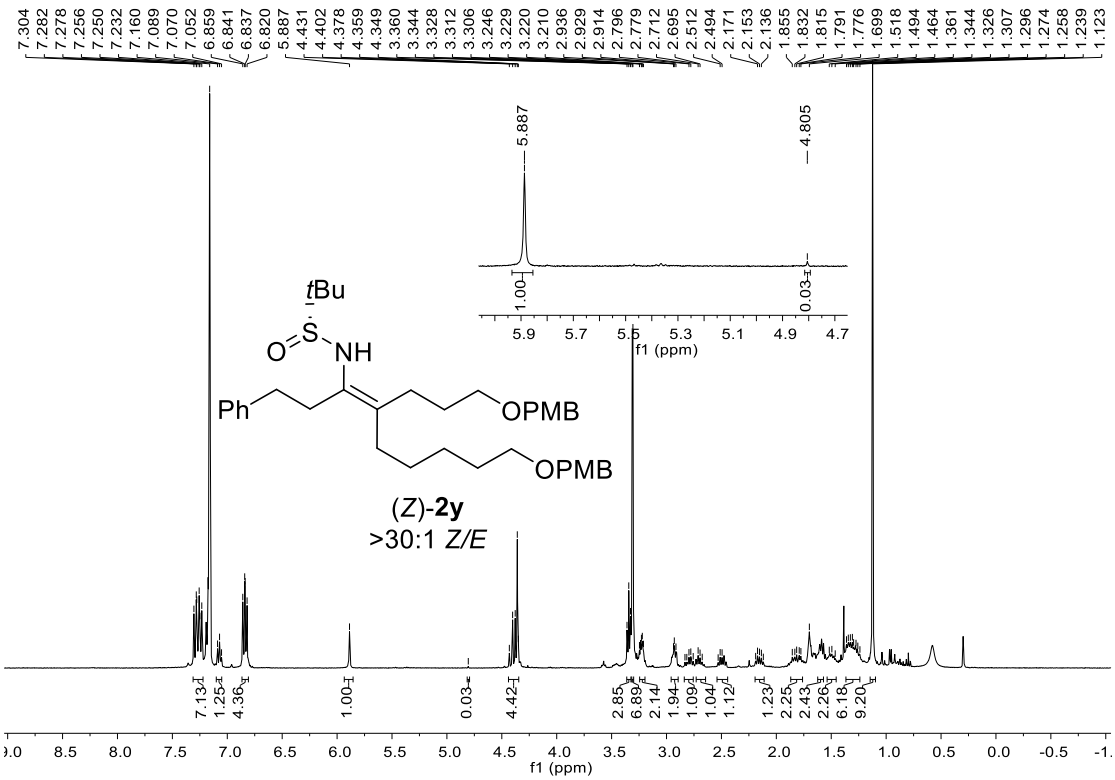
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2w** prepared using **1w**/$InBr_3$/nBu_3SnH (< 1:50 *Z/E*)



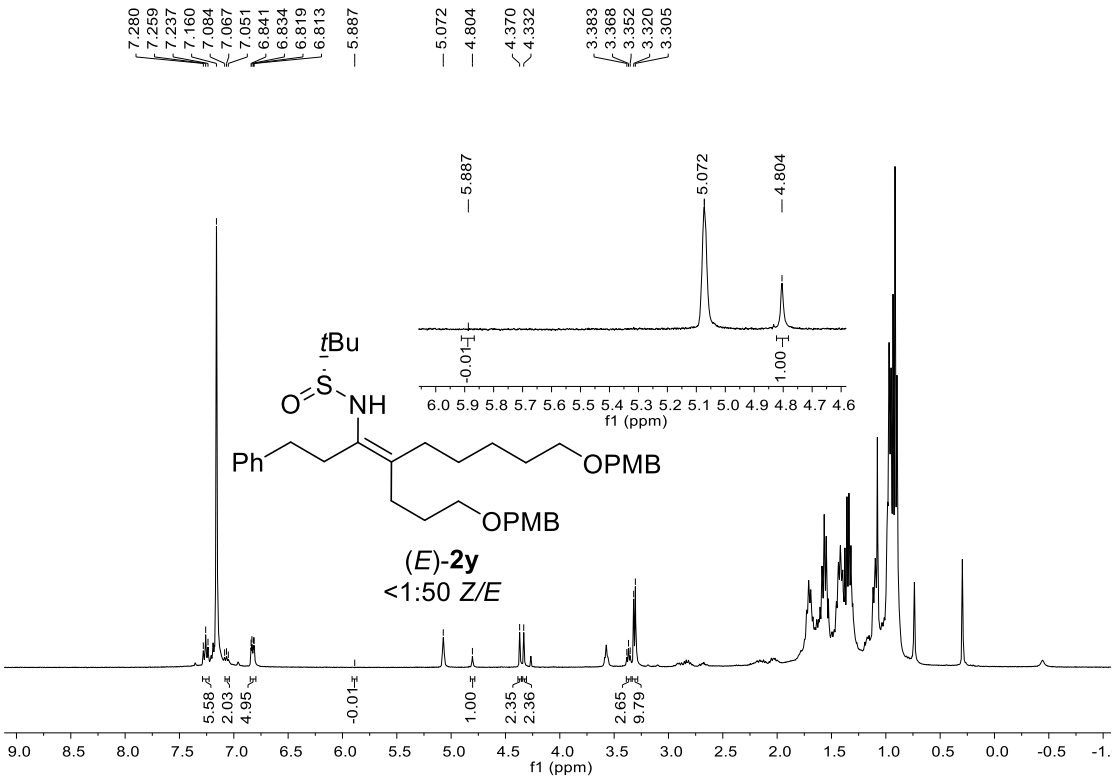
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2x** prepared using **1x**/L-Selectride (> 50:1 *Z*/*E*)



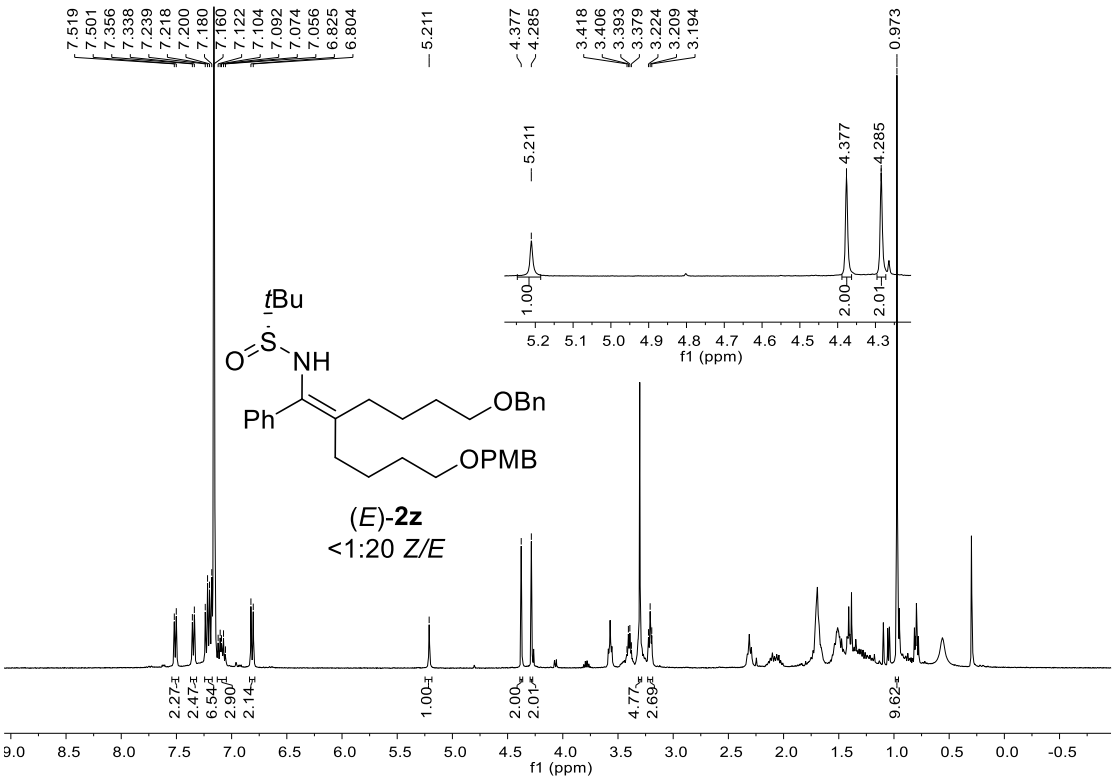
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2x** prepared using **1x**/$InBr_3$/$n$$Bu_3SnH$ (< 1:50 *Z*/*E*)



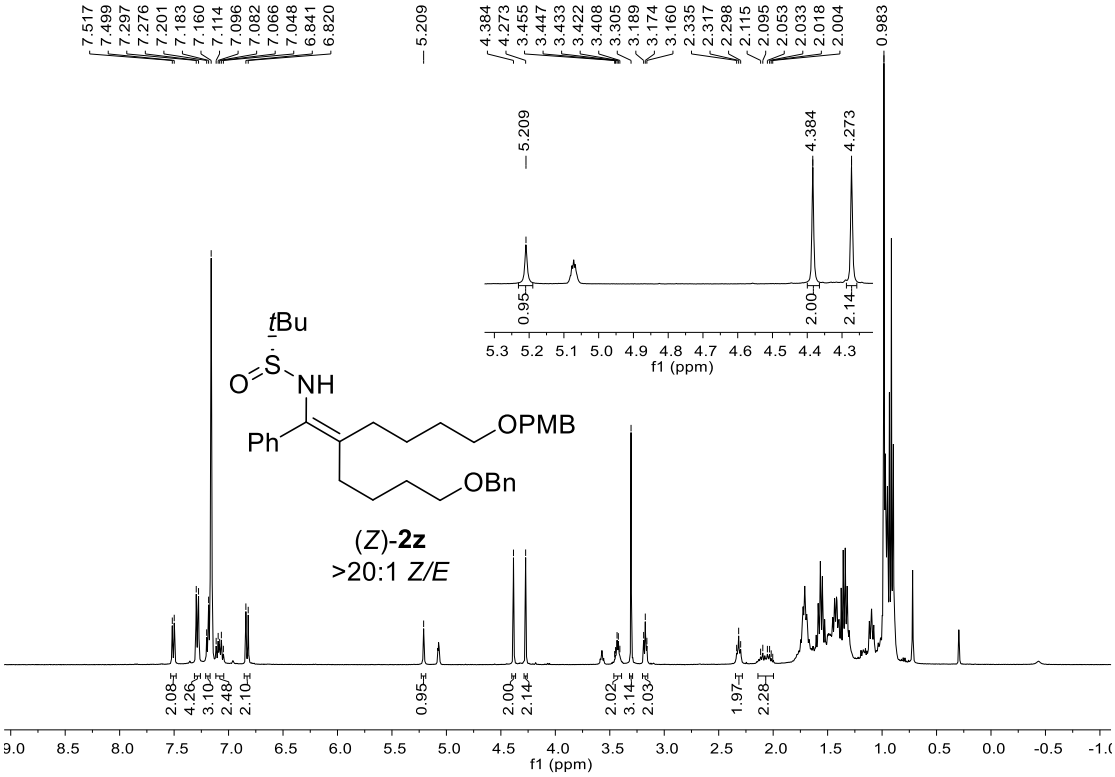
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2y** prepared using **1y**/L-Selectride (> 30:1 *Z*/*E*)



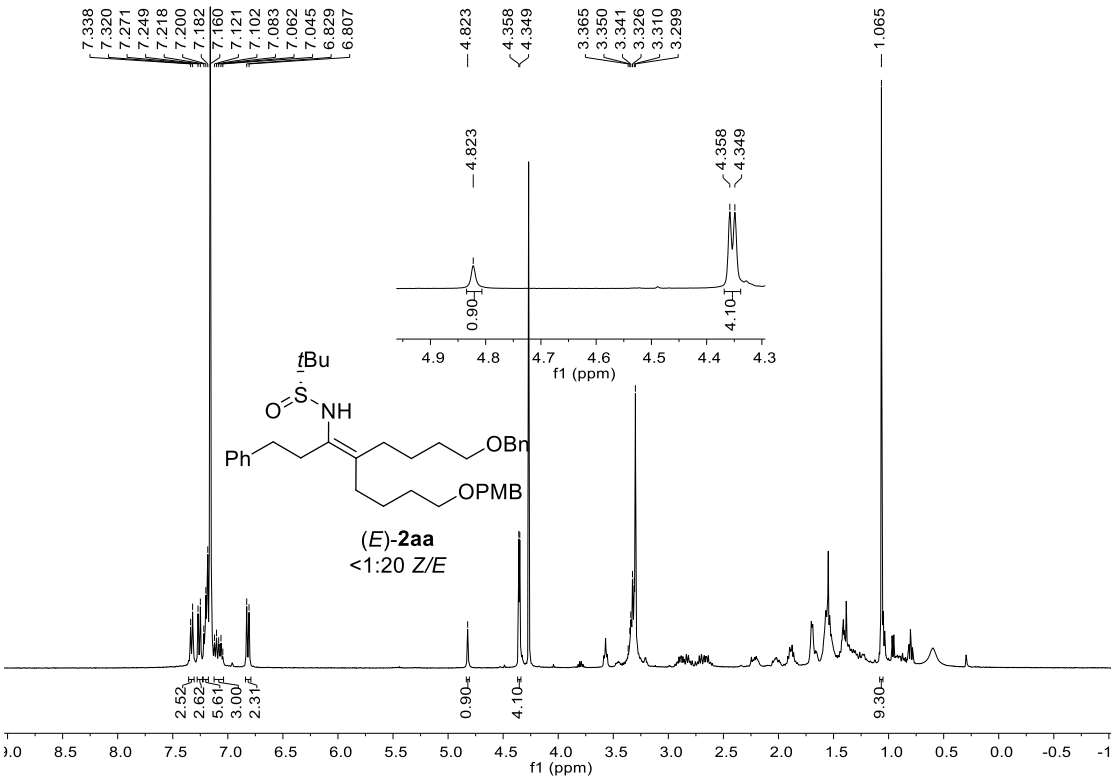
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2y** prepared using **1y**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



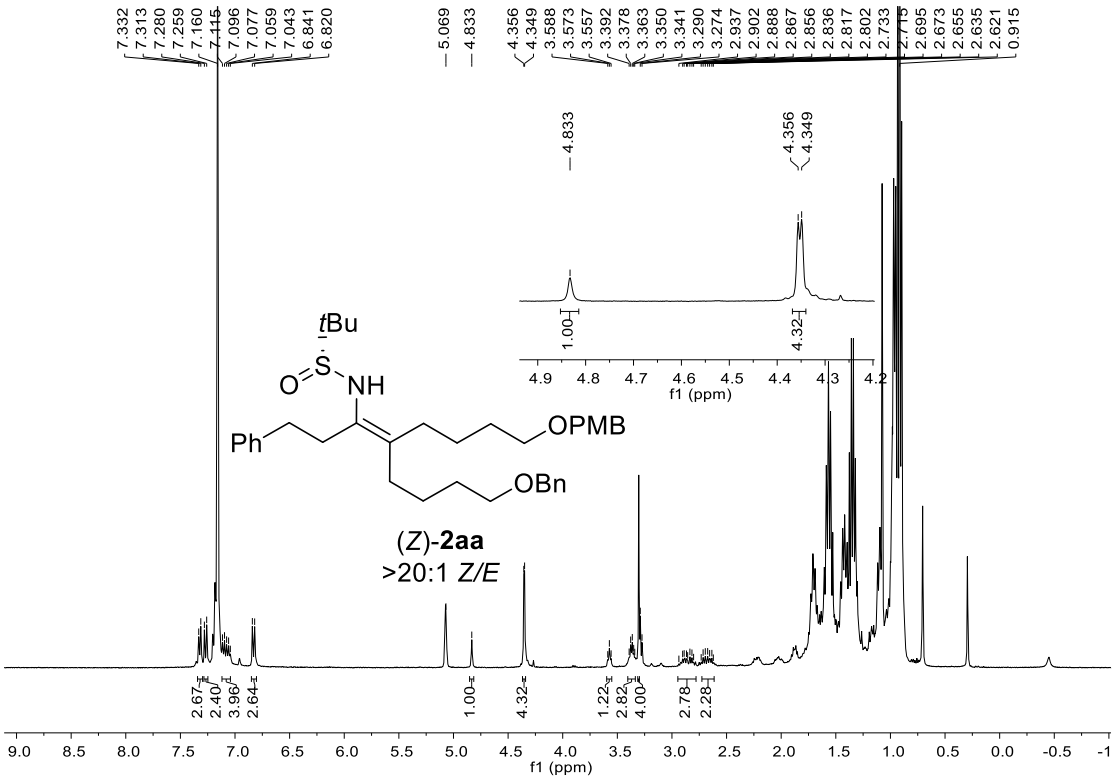
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2z** prepared using **1z**/L-Selectride (< 1:20 *Z*/*E*)



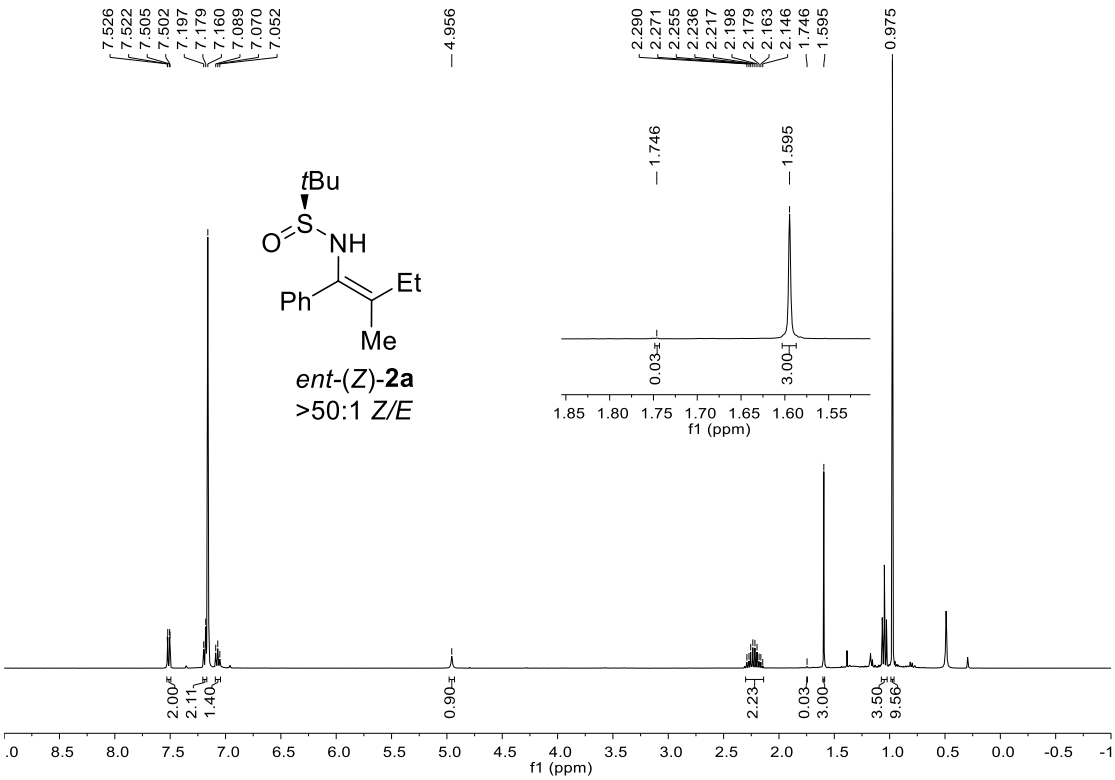
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2z** prepared using **1z**/$InBr_3$/nBu_3SnH (> 20:1 *Z*/*E*)



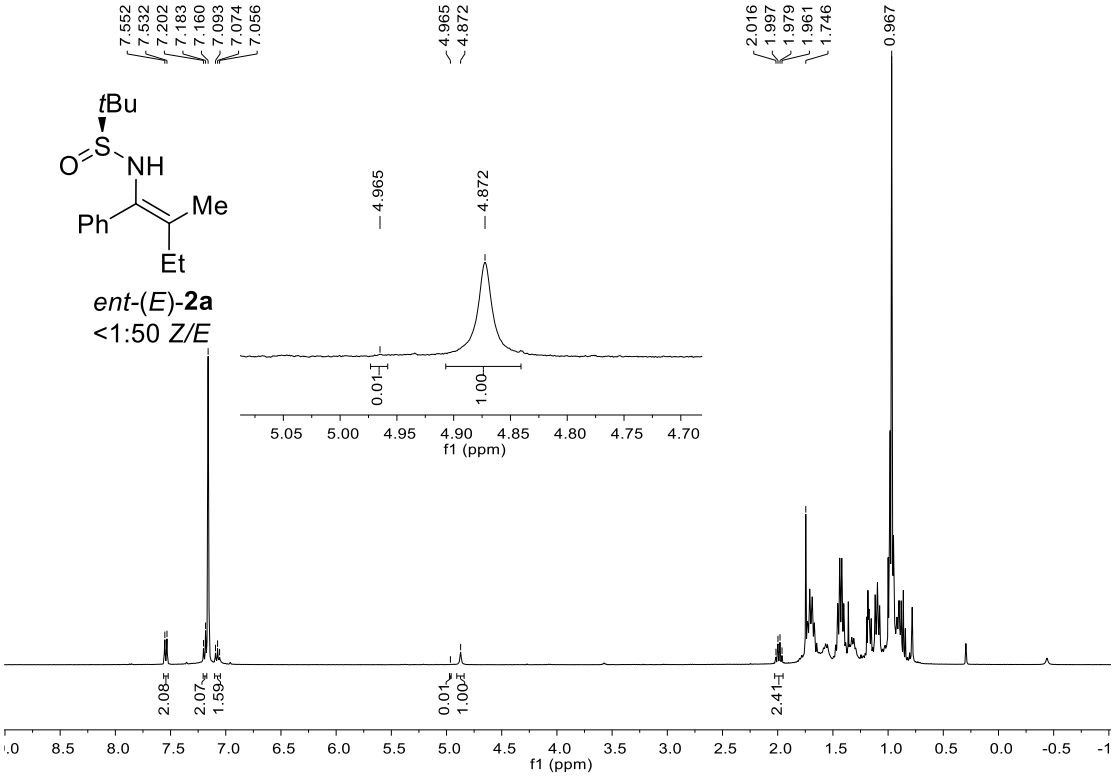
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*E*)-**2aa** prepared using **1aa**/L-Selectride (< 1:20 *Z*/*E*)



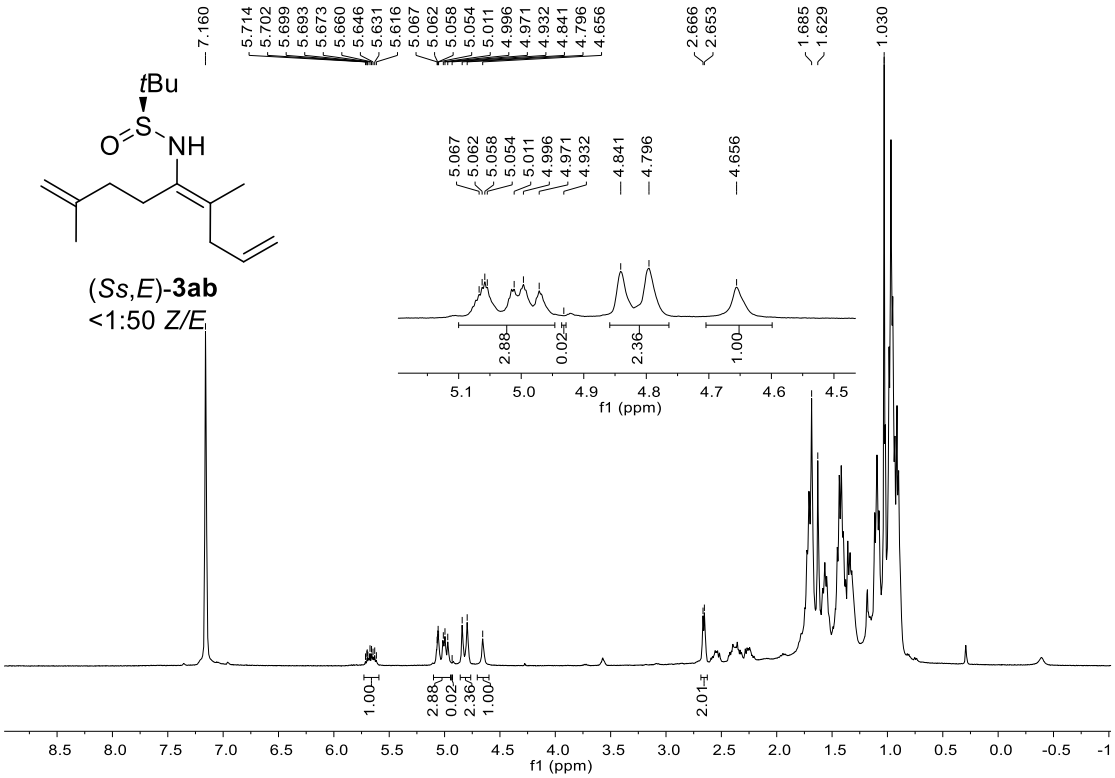
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (*Z*)-**2aa** prepared using **1aa**/$InBr_3$/nBu_3SnH (> 20:1 *Z*/*E*)



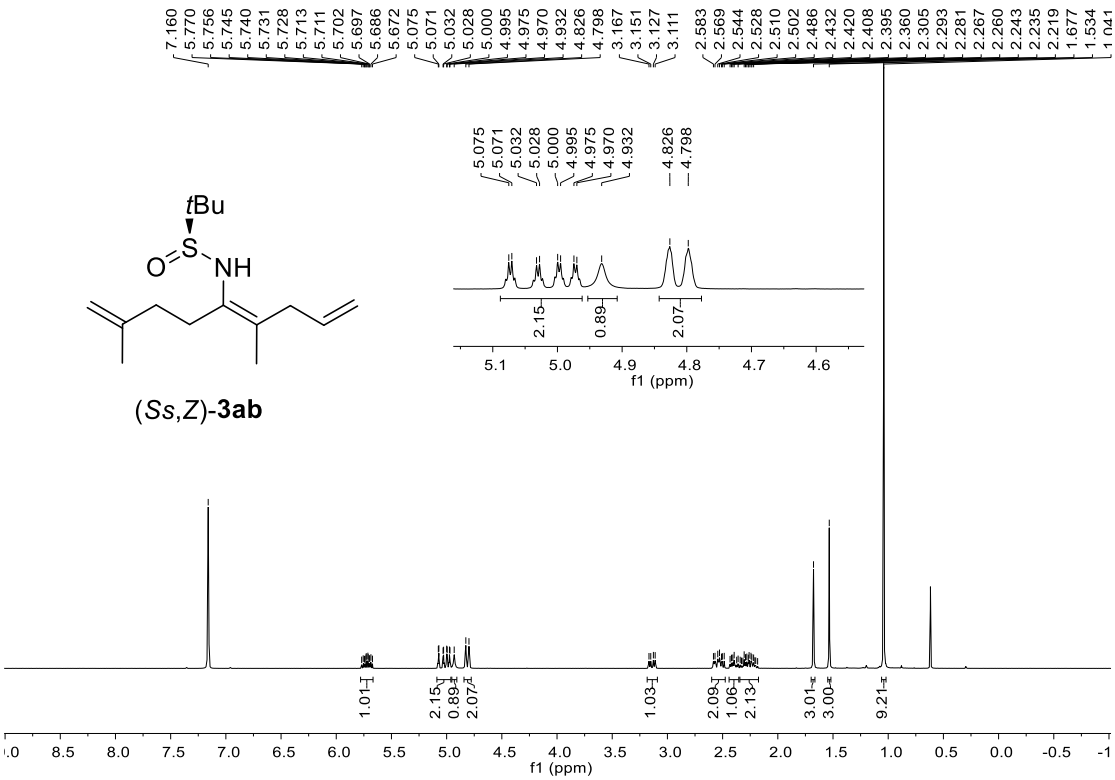
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of *ent*-(*Z*)-**2a** prepared using *ent*-**1a**/L-Selectride (> 50:1 *Z*/*E*)



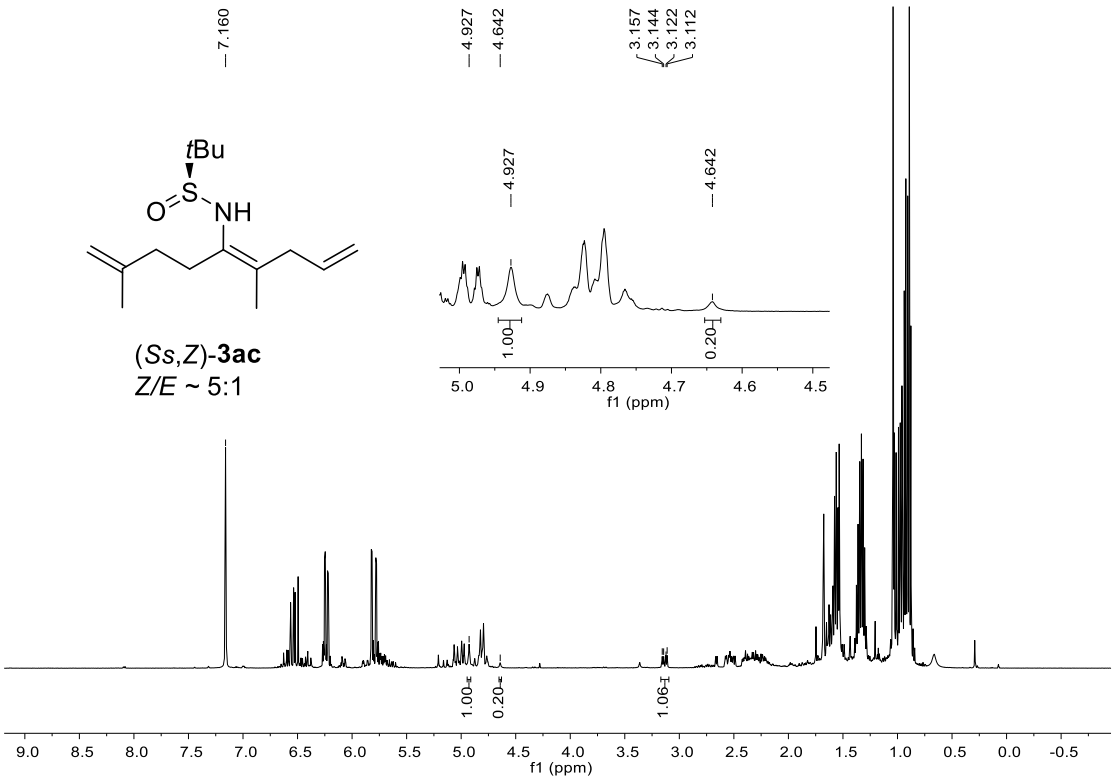
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of *ent*-(*E*)-**2a** prepared using *ent*-**1a**/$InBr_3$/nBu_3SnH (< 1:50 *Z*/*E*)



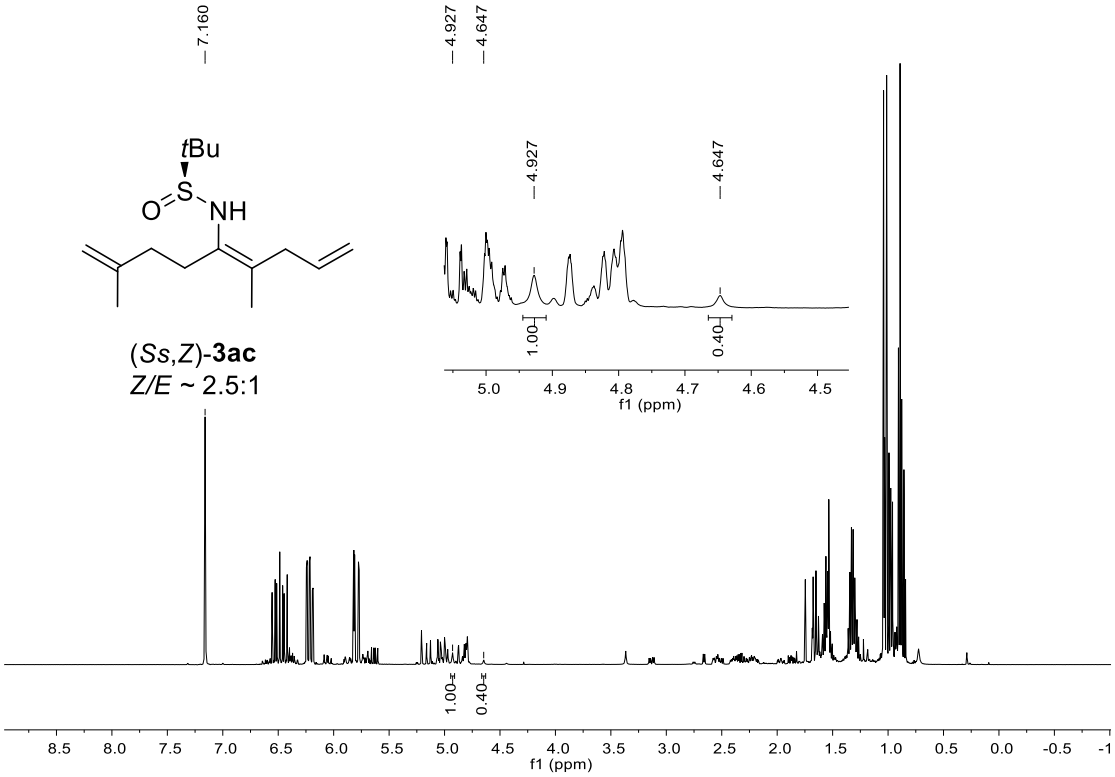
^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (Ss,*E*)-**3ab** prepared using **2ab**/$InBr_3$/*n*Bu_3SnH (< 1:50 *Z*/*E*)



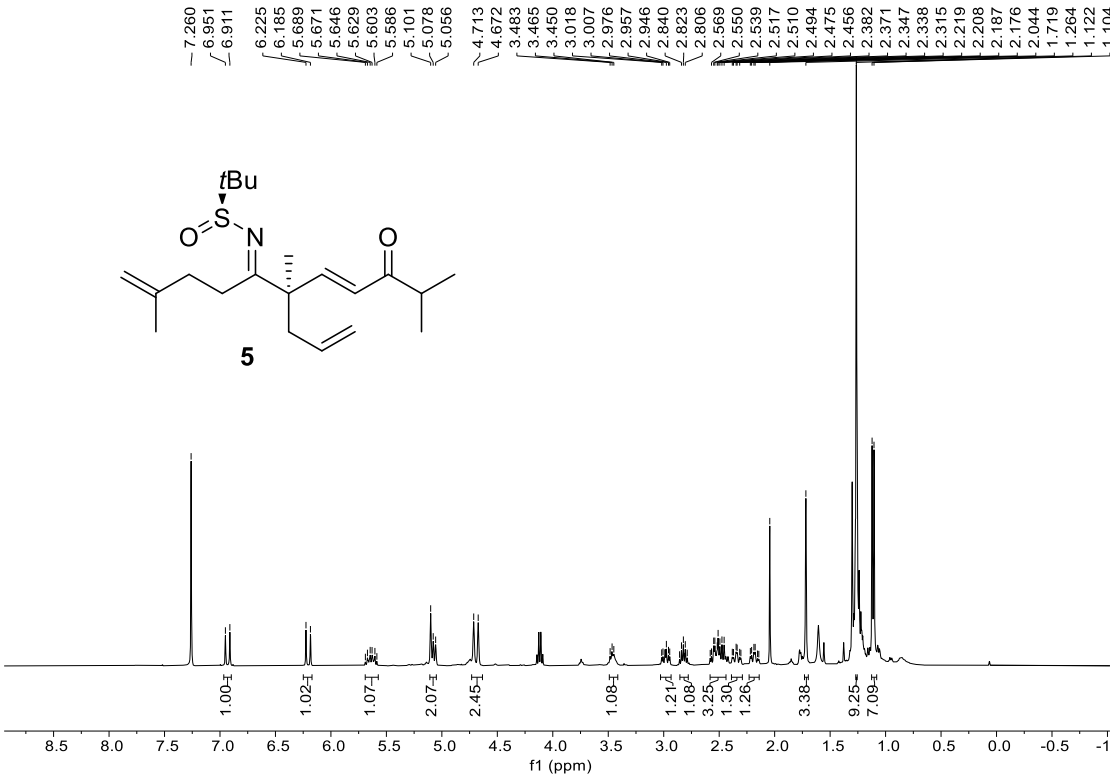
^{1}H NMR spectrum (C_6D_6, 400 MHz) of (Ss,*Z*)-**3ab** prepared using **2ab**/L-Selectride



^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (Ss,*Z*)-**3ac** prepared using **2ac**/Vinylcuprate (~ 5:1 *Z/E*)



^{1}H NMR spectrum (C_6D_6, 400 MHz) of the crude reaction mixture of (Ss,*Z*)-**3ac** prepared using **2ac**/Vinylcuprate/$BF_3.OEt_2$ (~ 2.5:1 *Z/E*)



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