Divergent synthesis of polysubstituted cyclopropanes and β-silyoxy imidates via switchable additions of *N-tert*-butanesulfinylimidates to acylsilanes

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1. General experimental information

All reactions were carried out under a positive pressure of argon atmosphere in flame-dried glass ware with magnetic stirring using standard Schlenk techniques. THF and toluene were freshly distilled from sodium/benzophenone under argon. CH_2Cl_2 was distilled from CaH_2 prior to use. Other solvents and commercial reagents were used without additional purification otherwise stated. Purification of the reaction products was carried out by flash column chromatography using 200-300 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 or aqueous $KMnO_4$ 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 recorded with an Agilent 6210 ESI-TOF mass spectrometer. Optical rotations were measured on an Autopol IV (Rudolph Research Analytical). Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on either a Varian Inova 400 MHz (^{13}C NMR at 100 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.2 ppm). ^{1}H NMR data are reported as follows: chemical shifts, multiplicity (brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constants (Hz) and integration.

All *N*-*tert*-butanesulfinyl imidates were prepared from the enantioenriched *tert*-butanesulfinamide (*ee* > 99.0%)[S1] according to the reported procedure.[S2] Acylsilanes were prepared according to the reported procedure.[S3]

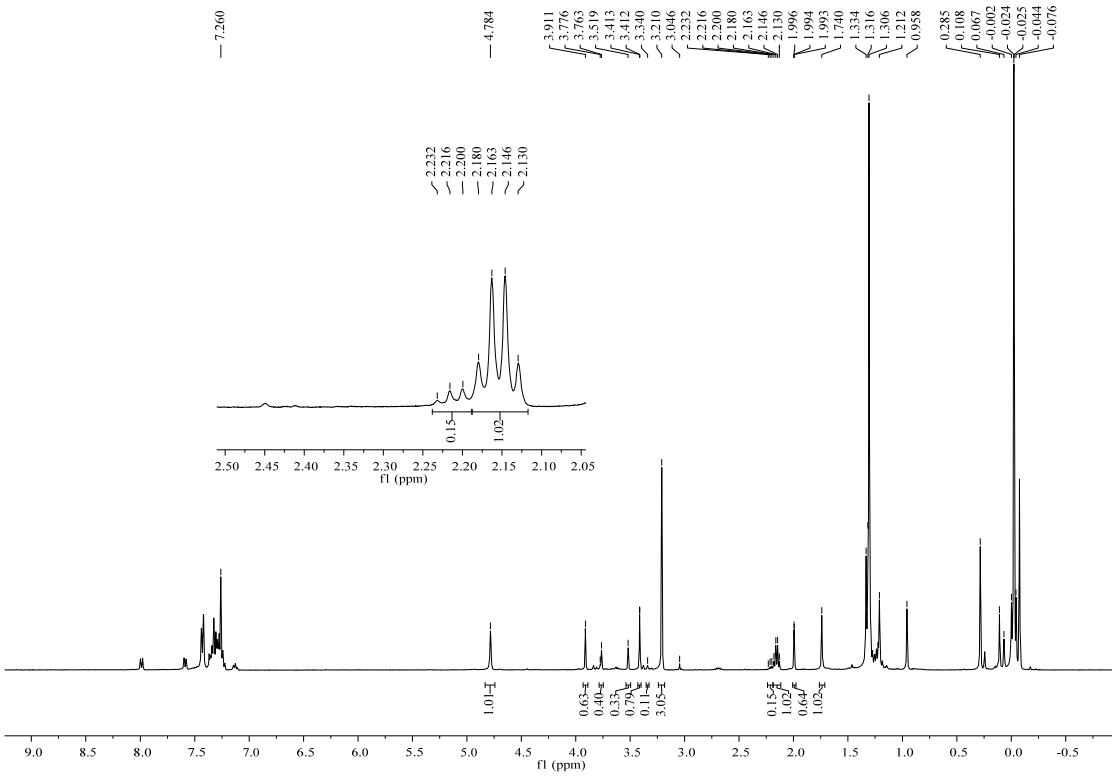
References

(S1) The enantiomeric excess of the starting *tert*-butylsulfinamide was checked by chiral HPLC: Daicel Chiralpak AD, 25 cm × 0.46 cm; 93:7 *n*-hexane:*i*-PrOH, 1 mL/min; 220 nm; (*R*) RT = 8.86; (*S*) RT = 11.55.

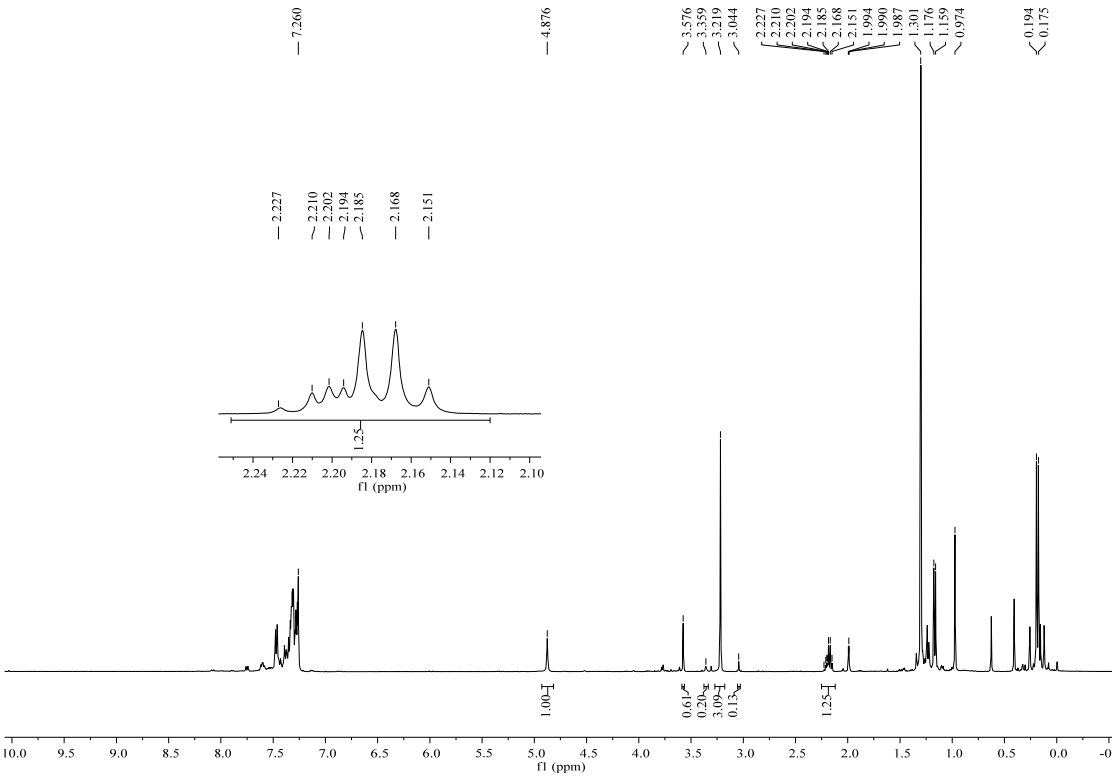
(S2) (a) Owens, T. D.; Souers, A. J.; Ellman, J. A. *J. Org. Chem.* **2003**, *68*, 3. (b) Colpaert, F.; Mangelinckx, S.; Verniest, G.; DeKimpe, N. *J. Org. Chem.* **2009**, *74*, 3792. (c) Kochi, T.; Ellman, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 15652. (d) Huang, H.-X.; Wang, H.-J.; Tan, L.; Wang, S.-Q.; Tang, P.; Song, H.; Liu, X.-Y.; Qin, Y. *J. Org. Chem.* **2016**, *81*, 10506−10516. (e) Ma, P.-J.; Liu, H.; Xu, Y.-J.; Aisa, H. A.; Lu, C.-D. *Org. Lett.* **2018**, *20*, 1236− 1239.

(S3) Linghu, X.; Nicewicz, D. A.; Johnson, J. S. *Org. Lett*. **2002**, *4*, 2957.

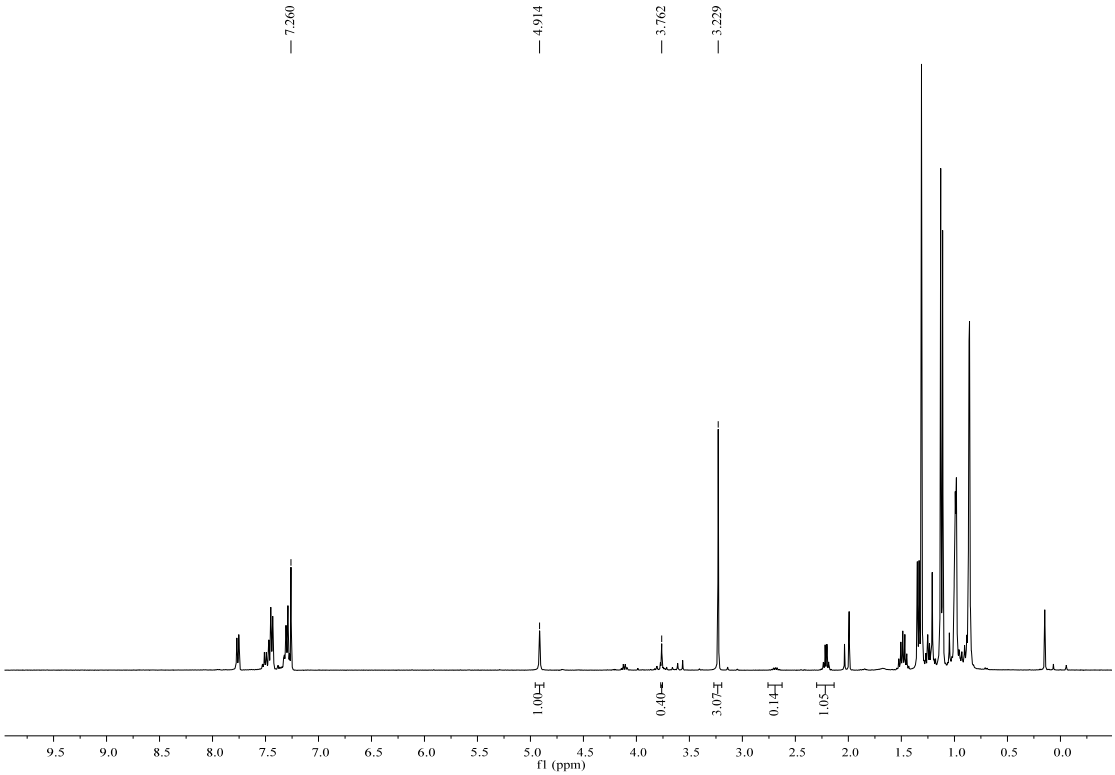
2. Calculation of diastereomeric ratio



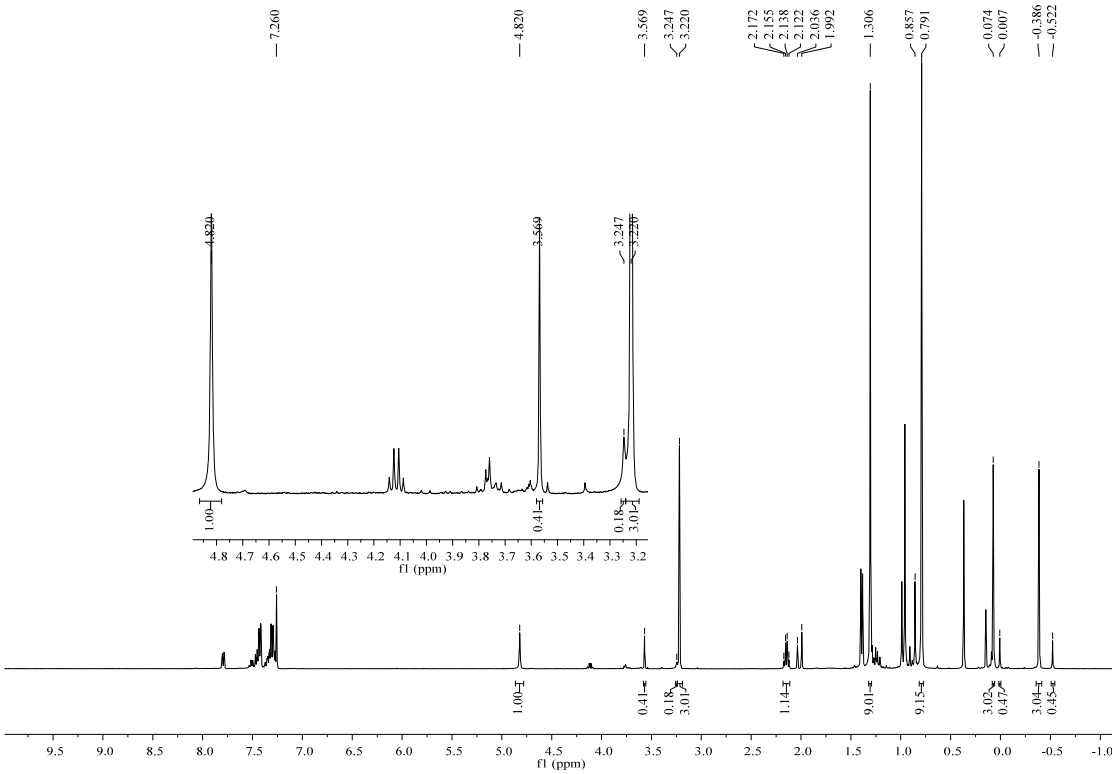
Crude ^{1}H NMR of **3aa** (Table 1, entry 1, dr ~ 7:1)



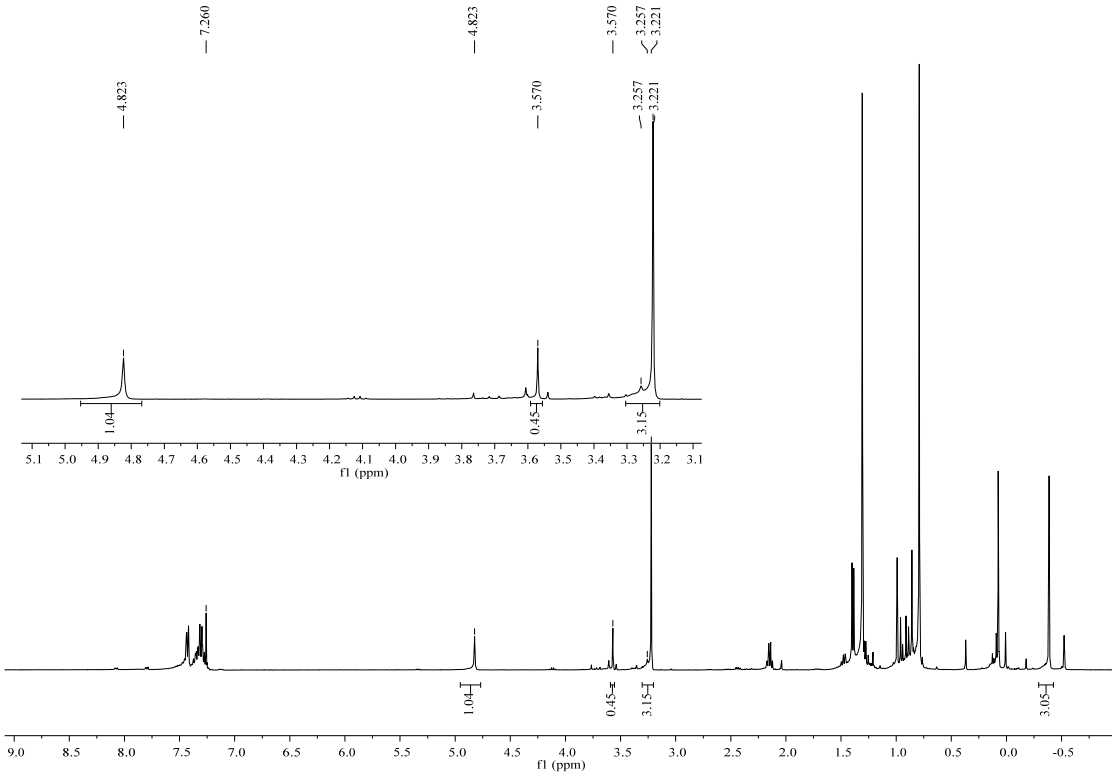
Crude ^{1}H NMR of **3ab** (Table 1, entry 2, dr ~ 4:1)



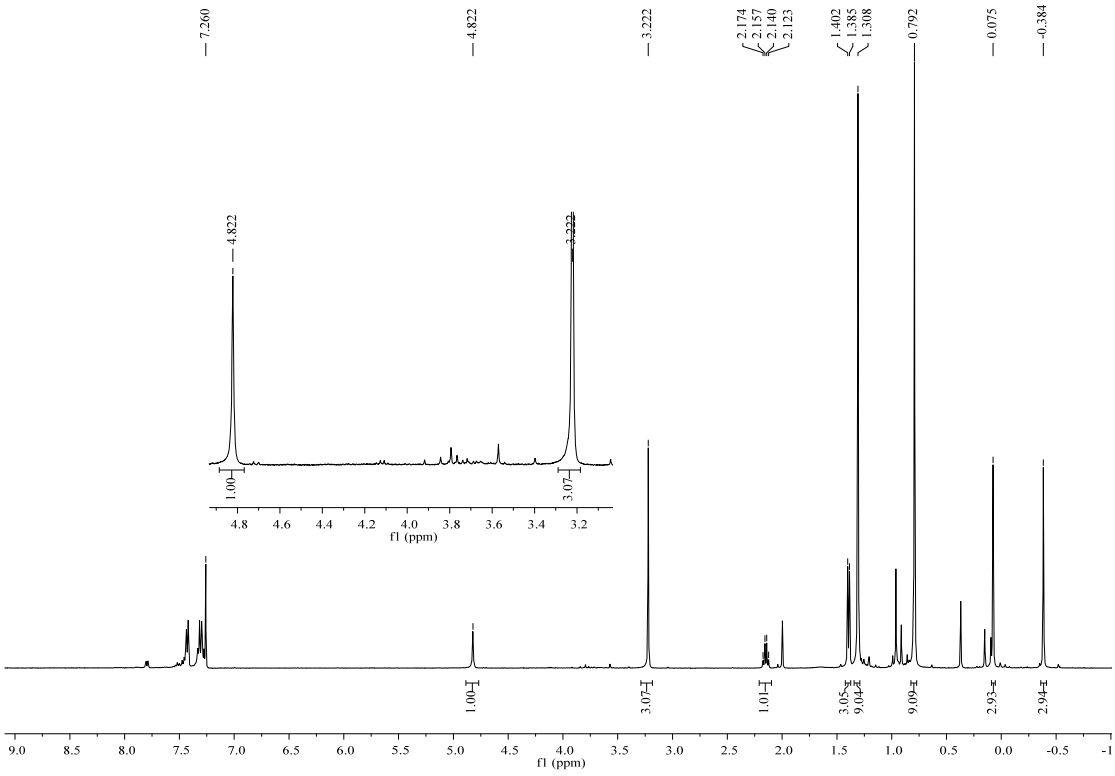
Crude ^{1}H NMR of **3ac** (Table 1, entry 3, dr ~ 7.5:1)



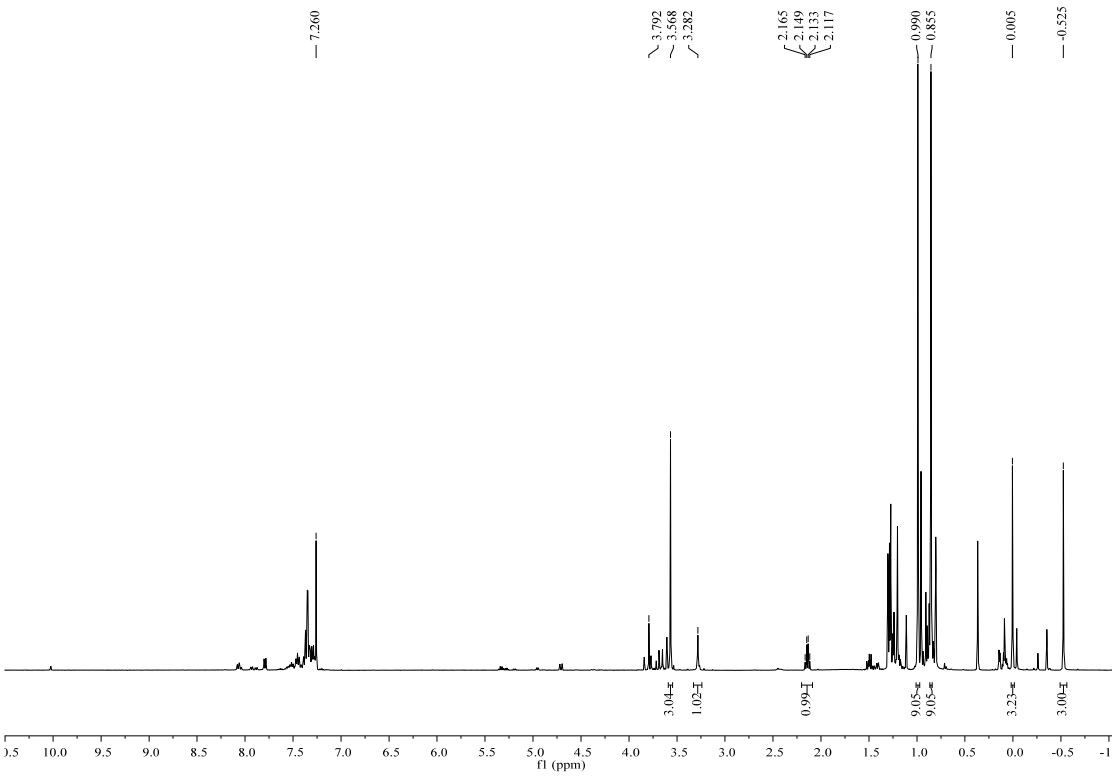
Crude ^{1}H NMR of **3ad** (Table 1, entry 4, dr ~ 7:1)



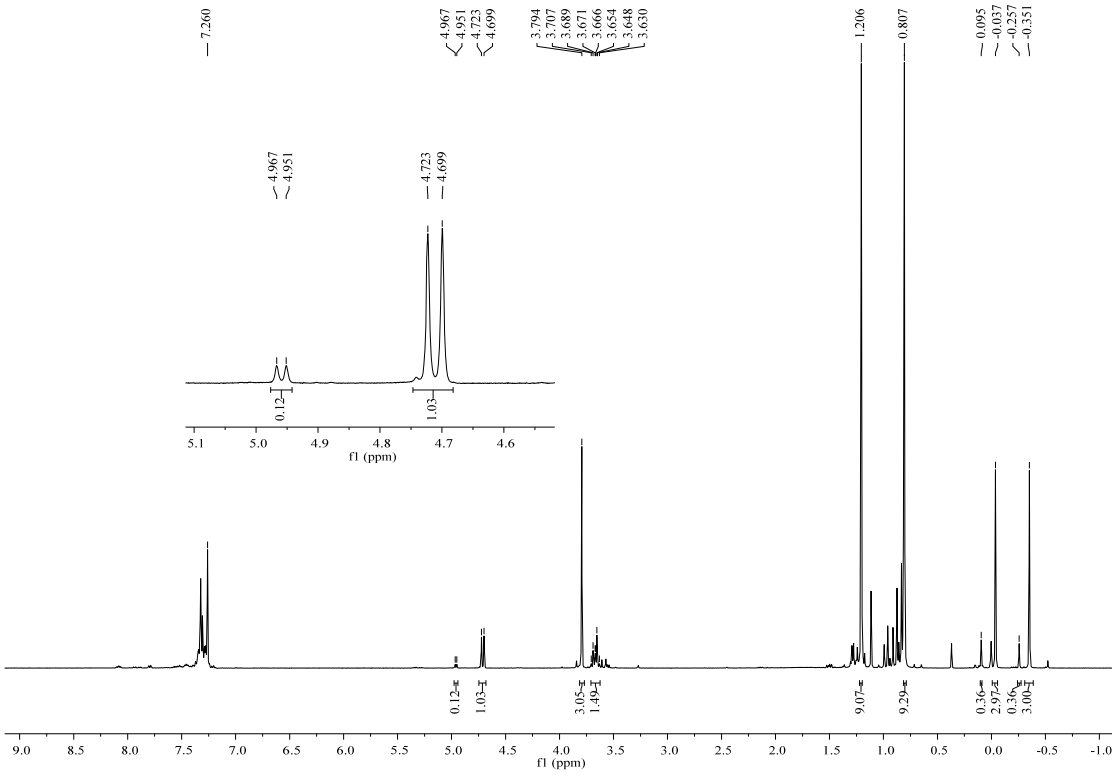
Crude ^{1}H NMR of **3ad** (Table 1, entry 5, dr ~ 7:1)



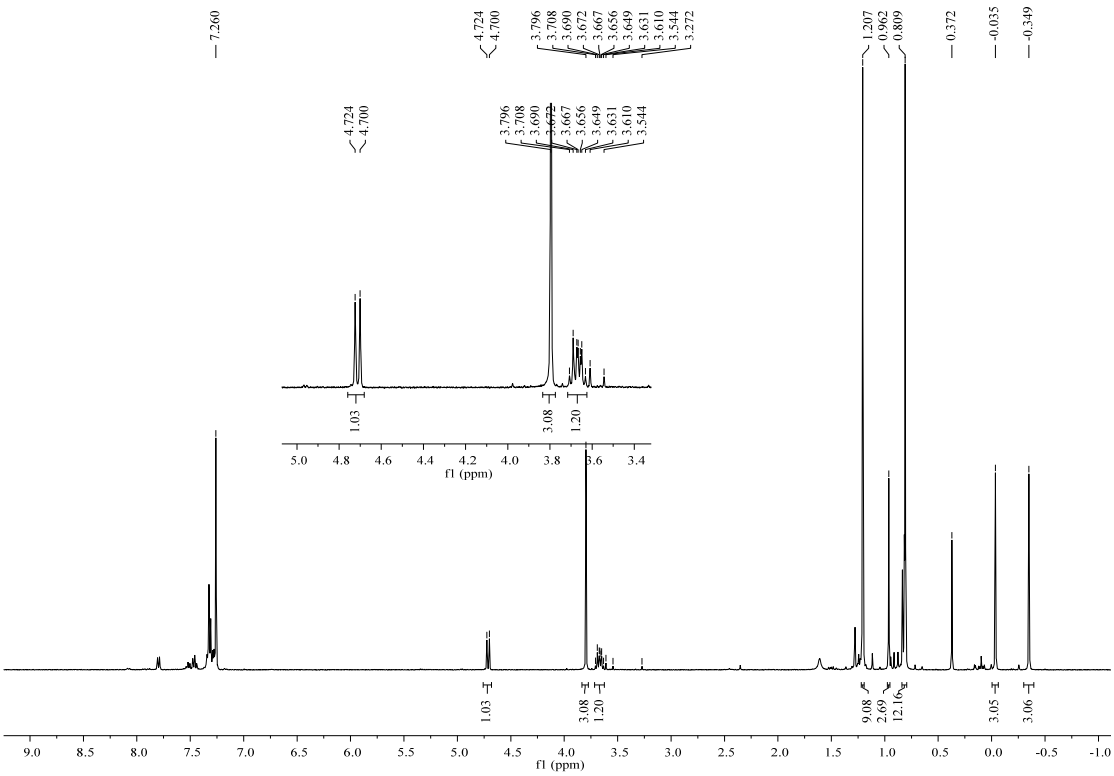
Crude ^{1}H NMR of **3ad** (Table 1, entry 6, dr > 20:1)



Crude ^{1}H NMR of **4a** (Table 1, entry 7, dr > 20:1)



Crude ^{1}H NMR of **5a** (Table 1, entry 8, dr ~ 8:1)



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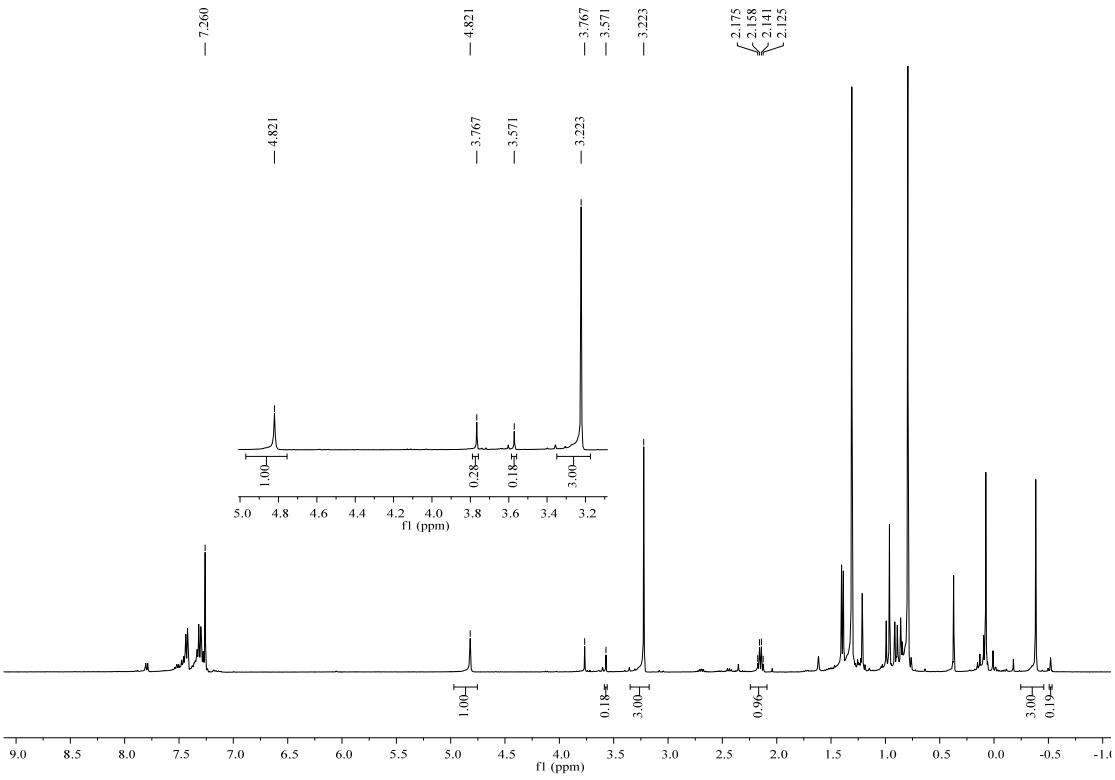
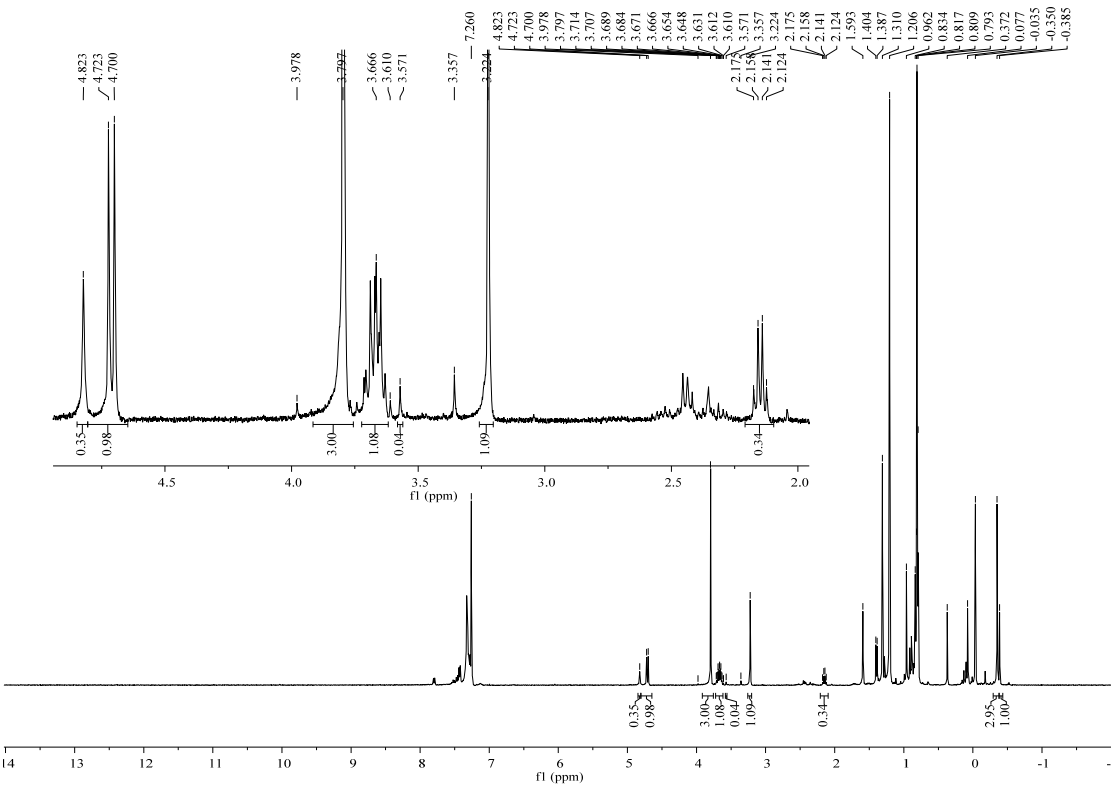


Crude ^{1}H NMR of **3ad** (Table 1, entry 10, dr ~ 17:1)



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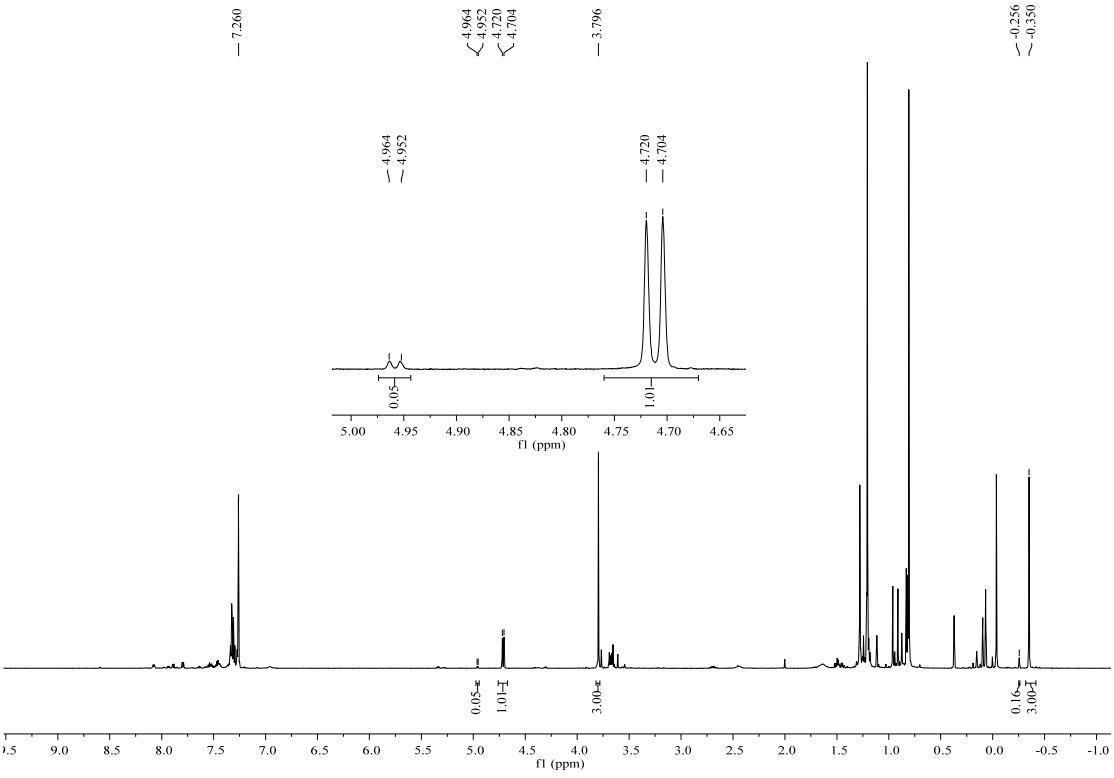

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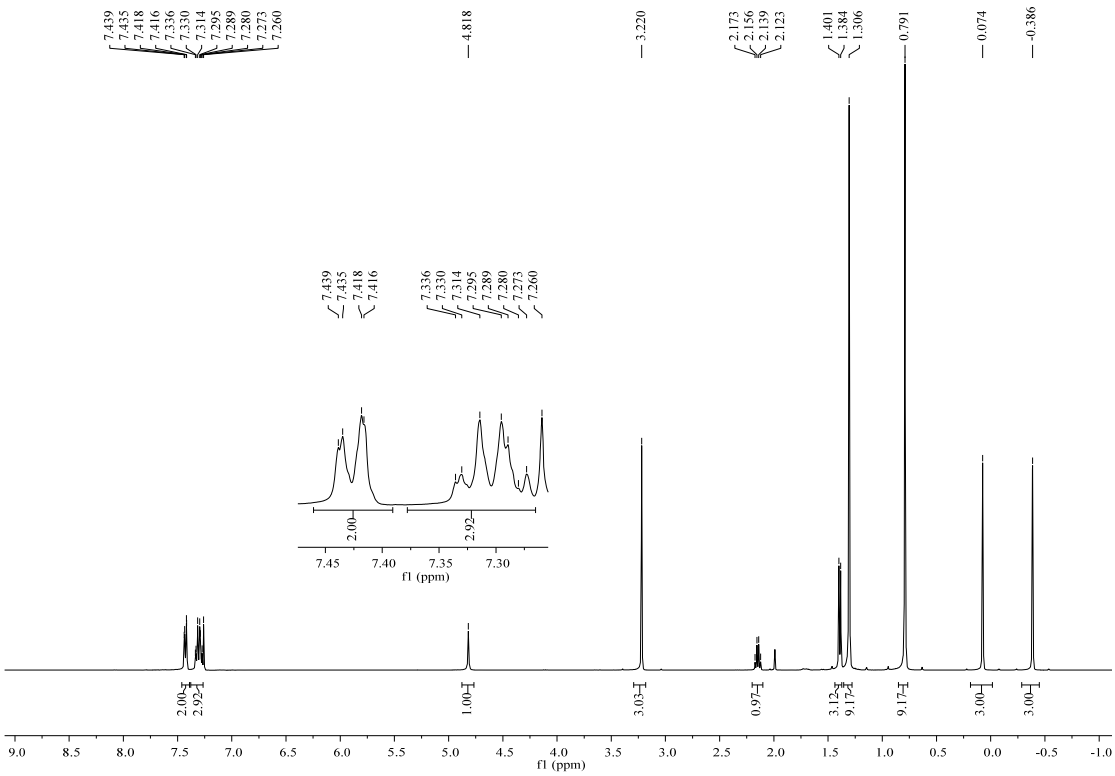
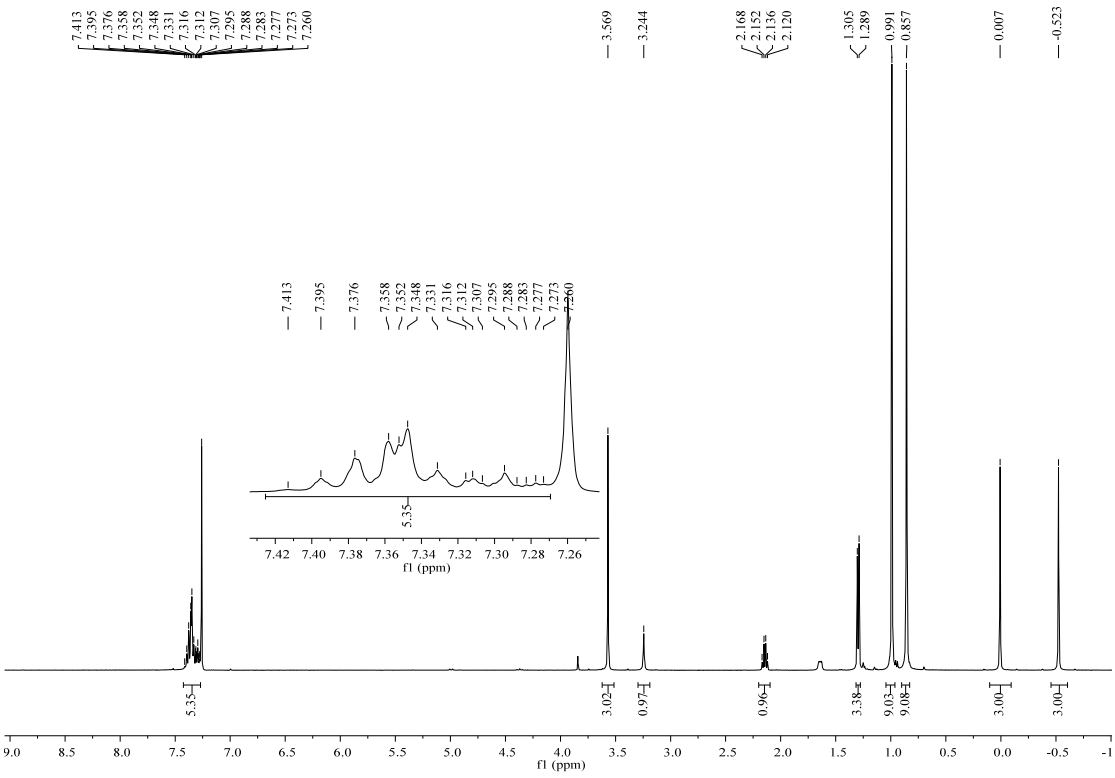
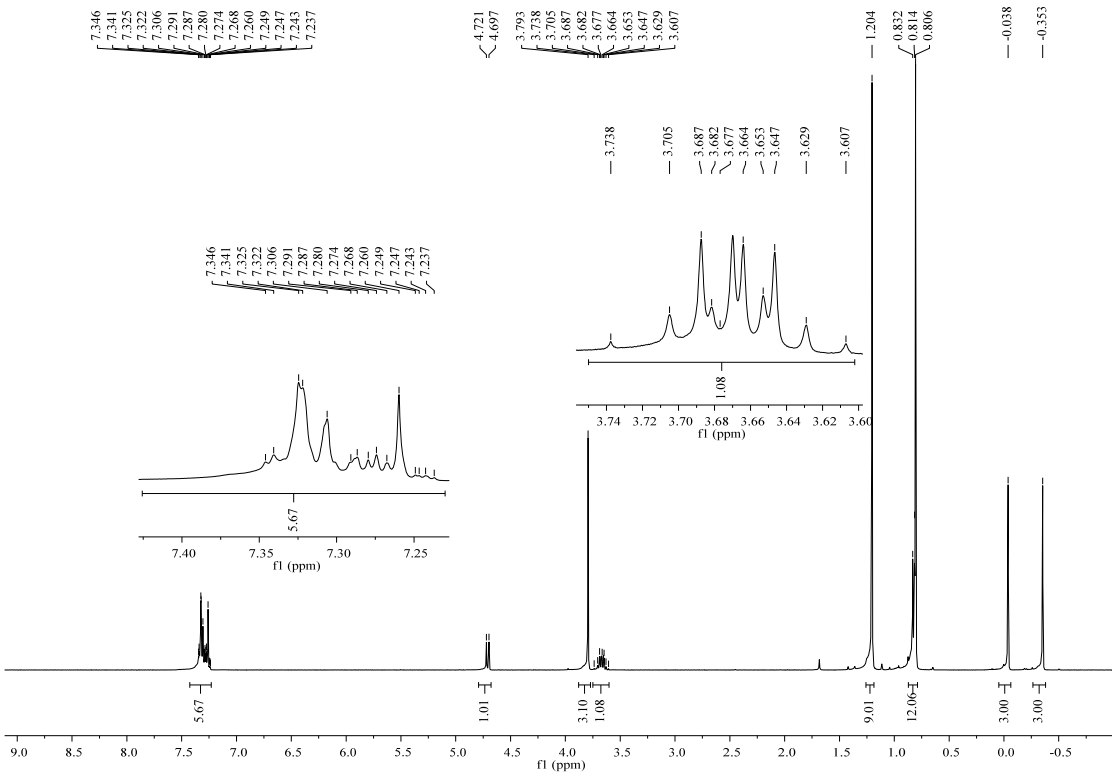


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ad**



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

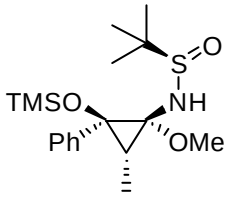


^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5a**

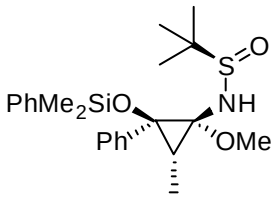
3. Procedure for preparation of cyclopropane products 3ad and 3b–3r

A solution of *N*-*tert*-butanesulfinylimidate (0.30 mmol, 1.0 equiv) in 2.0 mL THF was added to a flame-dried schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to –78 °C. Then, NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) was added dropwise to the solution by syringe. After the reaction mixture was stirred for 30 min at –78 °C, the solution of acylsilane (0.39 mmol, 1.3 equiv) in 2.0 mL THF was added to the reaction mixture via syringe. The reaction mixture was stirred for 1 h at -78 ^{o}C. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

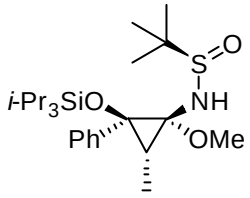
Analytical data for cyclopropane products 3



(**3aa**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), LiHMDS (1.2 M in THF, 0.30 mL, 0.36 mmol, 1.2 equiv) and acylsilane **2a** (69.5 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 85.4 mg (69 %) of **3aa** as a white solid. Analytical data for **3aa**: m.p. 131–133 ^{o}C; R_f = 0.30 (petroleum/ ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –25.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.34–7.27 (m, 3H), 4.78 (s, 1H), 3.21 (s, 3H), 2.15 (q, J = 6.8 Hz, 1H), 1.32 (d, J = 6.4 Hz, 3H), 1.30 (s, 9H), -0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 130.5, 128.1, 127.7, 75.6, 64.9, 56.4, 53.8, 32.2, 22.7, 10.5, 0.81; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{18}H_{32}NO_3SSi$ 370.1867, found 370.1865.

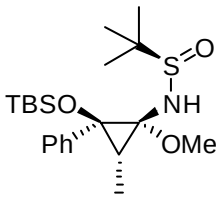


(**3ab**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), LiHMDS (1.2 M in THF, 0.30 mL, 0.36 mmol, 1.2 equiv) and acylsilane **2b** (93.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 93.2 mg (72 %) of **3ab** as a white amorphous solid. Analytical data for **3ab**: R_f = 0.27 (petroleum/ ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –8.1 (c 0.31, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.37–7.31 (m, 5H), 7.29–7.26 (m, 3H), 4.87 (s, 1H), 3.22 (s, 3H), 2.18 (q, J = 6.8 Hz, 1H), 1.30 (s, 9H), 1.17 (d, J = 6.8 Hz, 3H), 0.20 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.1, 133.9, 131.0, 129.7, 128.0, 127.9, 127.7, 75.4, 56.5, 53.9, 32.4, 22.7, 10.8, -0.63, -0.91; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{33}NNaO_3SSi$ 454.1843, found 454.1838.

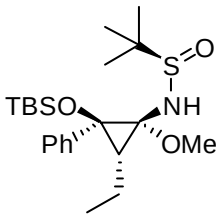


(**3ac**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), LiHMDS (1.2 M in THF, 0.30 mL, 0.36 mmol, 1.2 equiv) and acylsilane **2c** (102.4 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 91.2 mg (67 %) of **3ac** as a white amorphous

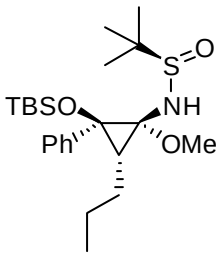
solid. Analytical data for **3ac**: R_f = 0.54 (petroleum / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –16.9 (c 0.54, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.33–7.27 (m, 3H), 4.91 (s, 1H), 3.23 (s, 3H), 2.21 (q, J = 6.8 Hz, 1H), 1.34 (d, J = 6.8 Hz, 3H), 1.31 (s, 9H), 1.00–0.98 (m, 9H), 0.86–0.85 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 131.5, 128.1, 127.9, 75.6, 65.1, 56.6, 53.9, 32.5, 22.8, 18.3, 18.0, 13.0, 11.6; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{24}H_{43}NNaO_3SSi$ 476.2625, found 476.2621.



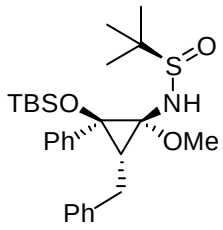
(**3ad**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 121.1 mg (98%) of **3ad** as a white solid. Analytical data for **3ad**: m.p. 62–64 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –33.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.34–7.27 (m, 3H), 4.82 (s, 1H), 3.22 (s, 3H), 2.15 (q, J = 6.8 Hz, 1H), 1.39 (d, J = 6.8 Hz, 3H), 1.31 (s, 9H), 0.79 (s, 9H), 0.07 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 131.1, 128.0, 127.9, 75.1, 64.7, 56.4, 53.8, 32.2, 25.8, 22.7, 18.0, 11.3, -4.0, -4.2; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{37}NNaO_3SSi$ 434.2156, found 434.2151.



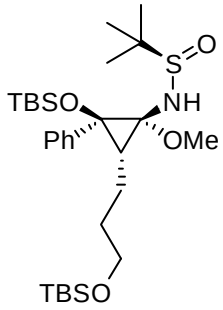
(**3b**) The title compound was prepared using imidate **1b** (61.6 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 127.6 mg (99%) of **3b** as a white solid. Analytical data for **3b**: m.p. 52–54 °C; R_f = 0.51 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –38.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.31–7.24 (m, 3H), 4.68 (s, 1H), 3.14 (s, 3H), 2.03–1.93 (m, 2H), 1.74–1.62 (m, 1H), 1.29 (s, 9H), 1.20 (t, J = 6.8 Hz, 3H), 0.81 (s, 9H), 0.09 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 130.7, 127.8, 75.4, 64.9, 56.1, 52.9, 39.9, 25.8, 22.6, 19.8, 18.0, 15.0, -4.0, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{39}NNaO_3SSi$ 448.2312, found 448.2316.



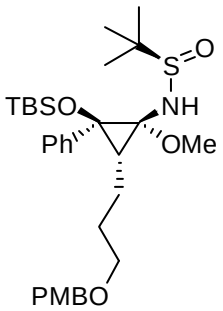
(**3c**) The title compound was prepared using imidate **1c** (65.8 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 128.0 mg (97%) of **3c** as a white solid. Analytical data for **3c**: m.p. 51–52 °C; R_f = 0.62 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –46.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.32–7.24 (m, 3H), 4.68 (s, 1H), 3.13 (s, 3H), 2.08–2.04 (m, 1H), 1.94–1.85 (m, 1H), 1.70–1.60 (m, 3H), 1.29 (s, 9H), 1.01 (t, J = 7.2 Hz, 3H), 0.82 (s, 9H), 0.09 (s, 3H), -0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 130.6, 127.79, 127.77, 75.4, 64.7, 56.1, 52.8, 38.2, 28.6, 25.9, 23.8, 22.7, 18.0, 14.3, -4.0, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{41}NNaO_3SSi$ 462.2469, found 462.2465.



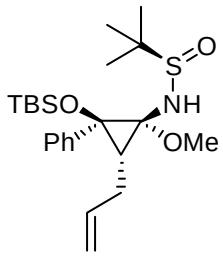
(**3d**) The title compound was prepared using imidate **1d** (80.2 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 122.8 mg (84%) of **3d** as a colorless oil. Analytical data for **3d**: R_f = 0.41 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –55.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.0, 2.0 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.36–7.31 (m, 5H), 7.21 (t, J = 7.2 Hz, 1H), 4.79 (s, 1H), 3.23 (dd, J = 15.2, 5.6 Hz, 1H), 3.14 (s, 3H), 3.00 (dd, J = 15.2, 8.8 Hz, 1H), 2.53 (dd, J = 8.8, 5.6 Hz, 1H), 1.27 (s, 9H), 0.81 (s, 9H), 0.04 (s, 3H), -0.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.7, 131.0, 128.6, 128.5, 128.03, 127.97, 126.1, 75.3, 65.2, 56.3, 53.5, 37.5, 32.0, 25.8, 22.6, 18.0, -3.9, -4.2 ; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{27}H_{41}NNaO_3SSi$ 510.2469, found 510.2465.



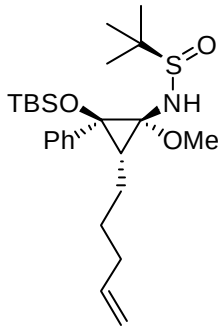
(**3e**) The title compound was prepared using imidate **1e** (104.9 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 164.2 mg (96%) of **3e** as a colorless oil. Analytical data for **3d**: R_f = 0.61 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –37.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.47 (m, 2H), 7.32–7.24 (m, 3H), 4.68 (s, 1H), 3.78–3.65 (m, 2H), 3.13 (s, 3H), 2.12–2.02 (m, 2H), 1.86–1.79 (m, 2H), 1.69–1.61 (m, 1H), 1.29 (s, 9H), 0.90 (s, 9H), 0.82 (s, 9H), 0.09 (s, 3H), 0.06 (s, 6H), -0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 130.7, 127.83, 127.80, 75.4, 64.8, 63.0, 56.2, 52.8, 37.9, 33.6, 26.2, 25.9, 22.74, 22.68, 18.5, 18.0, -3.9, -4.1, -5.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{29}H_{55}NNaO_4SSi_2$ 592.3283, found 592.3289.



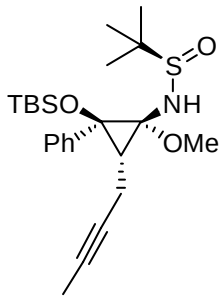
(**3f**) The title compound was prepared using imidate **1f** (106.6 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 150.3 mg (87%) of **3f** as a colorless oil. Analytical data for **3f**: R_f = 0.32 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –40.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.32–7.28 (m, 5H), 6.89–6.85 (m, 2H), 4.68 (s, 1H), 4.46 (s, 2H), 3.80 (s, 3H), 3.61–3.52 (m, 2H), 3.14 (s, 3H), 2.15–2.04 (m, 2H), 1.98–1.86 (m, 2H), 1.73–1.65 (m, 1H), 1.30 (s, 9H), 0.82 (s, 9H), 0.08 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.3, 131.1, 130.8, 129.4, 127.9, 113.9, 110.2, 75.3, 72.6, 69.9, 64.8, 56.2, 55.4, 52.8, 37.8, 30.5, 25.9, 23.1, 22.7, 18.0, -3.9, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{31}H_{49}NNaO_5SSi$ 598.2993, found 598.2988.



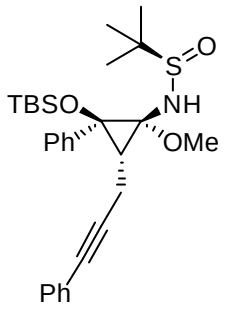
(**3g**) The title compound was prepared using imidate **1g** (65.2 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 111.7 mg (85%) of **3g** as a white solid. Analytical data for **3g**: m.p. 56–57 ^{o}C; R_f = 0.32 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –50.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.34–7.28 (m, 3H), 6.05 (m, 1H), 5.26 (dd, J = 17.2, 1.6 Hz, 1H), 5.13 (dd, J = 10.4, 1.6 Hz, 1H), 4.77 (s, 1H), 3.19 (s, 9H), 2.67–2.60 (m, 1H), 2.46–2.38 (m, 1H), 2.17 (dd, J = 8.8, 6.0 Hz, 1H), 1.31 (s, 9H), 0.81 (s, 9H), 0.08 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.7, 130.9, 128.03, 127.96, 115.9, 77.4, 75.1, 64.9, 56.4, 53.5, 36.7, 30.5, 25.8, 22.7, 18.0, -3.9, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^{+}$ calcd for $C_{23}H_{39}NNaO_3SSi$ 460.2312, found 460.2305.



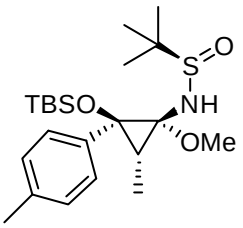
(**3h**) The title compound was prepared using imidate **1h** (73.6 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 123.0 mg (88%) of **3h** as a white solid. Analytical data for **3h**: m.p. 84–86 ^{o}C; R_f = 0.60 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –43.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.33–7.27 (m, 3H), 5.91–5.81 (m, 1H), 5.05–5.02 (m, 1H), 4.98–4.94 (m, 1H), 4.68 (s, 1H), 3.14 (s, 3H), 2.21–2.16 (m, 2H), 2.07–2.03 (m, 1H), 1.99–1.92 (m, 1H), 1.75–1.62 (m, 3H), 1.30 (s, 9H), 0.82 (s, 9H), 0.09 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.4, 130.7, 127.9, 114.7, 75.4, 64.8, 56.2, 52.8, 38.0, 33.9, 29.9, 29.7, 25.9, 22.7, 18.0, -4.0, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^{+}$ calcd for $C_{25}H_{43}NNaO_3SSi$ 488.2625, found 488.2619.



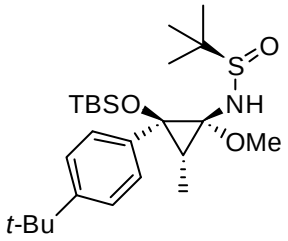
(**3i**) The title compound was prepared using imidate **1i** (68.8 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 113.1 mg (84%) of **3i** as a white solid. Analytical data for **4i**: m.p. 76–78 ^{o}C; R_f = 0.26 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –108.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.36–7.28 (m, 3H), 4.76 (s, 1H), 3.20 (s, 3H), 2.69–2.62 (m, 1H), 2.42–2.33 (m, 1H), 2.30 (dd, J = 10.0, 4.4 Hz, 1H), 1.85 (t, J = 2.4 Hz, 3H), 1.31 (s, 9H), 0.80 (s, 9H), 0.17 (s, 3H), -0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 131.0, 128.2, 128.1, 78.3, 77.7, 74.6, 65.1, 56.5, 53.5, 36.4, 25.8, 22.7, 18.0, 16.7, 3.7, -4.2, -4.3; HRMS (ESI-TOF) *m/z* [M + Na]$^{+}$ calcd for $C_{24}H_{39}NNaO_3SSi$ 472.2312, found 472.2314.



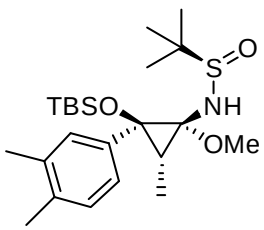
(**3j**) The title compound was prepared using imidate **1j** (87.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 130.2 mg (85%) of **3j** as a colorless oil. Analytical data for **3j**: R_f = 0.47 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –112.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.66 (m, 2H), 7.48–7.45 (m, 2H), 7.37–7.30 (m, 6H), 4.80 (s, 1H), 3.24 (s, 3H), 2.97 (dd, *J* = 17.6, 4.8 Hz, 1H), 2.65 (dd. *J* = 17.6, 10.0 Hz, 1H), 2.44 (dd, *J* = 10.4, 4.8 Hz, 1H), 1.32 (s, 9H), 0.81 (s, 9H), 0.21 (s, 3H), -0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 131.7, 131.0, 128.4, 128.3, 128.2, 127.8, 124.0, 89.2, 82.5, 74.6, 65.2, 56.5, 53.5, 35.8, 25.8, 22.7, 18.0, 17.4, -4.0, -4.2; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{29}H_{41}NNaO_3SSi$ 534.2469, found 534.2461.



(**3k**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2e** (91.4 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 119.8 mg (94%) of **3k** as a white amorphous solid. Analytical data for **3k**: R_f = 0.30 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –31.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 4.82 (s, 1H), 3.23 (s, 3H), 2.34 (s, 3H), 2.12 (q, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.30 (s, 9H), 0.80 (s, 9H), 0.07 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 133.6, 131.0, 128.7, 75.2, 64.5, 56.4, 53.8, 32.1, 25.9, 22.7, 21.4, 18.0, 11.3, -4.0, -4.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{39}NNaO_3SSi$ 448.2312, found 448.2307.

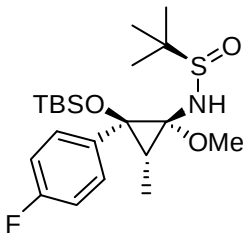


(**3l**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2f** (107.8 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 126.1 mg (90%) of **3l** as a white solid. Analytical data for **3l**: m.p. 134–136 ^{o}C; R_f = 0.29 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –29.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H), 4.82 (s, 1H), 3.24 (s, 3H), 2.12 (q, *J* = 6.8 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H), 0.78 (s, 9H), 0.05 (s, 3H), -0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 133.5, 130.8, 124.9, 75.2, 64.5, 56.4, 53.8, 34.7, 32.1, 31.5, 25.8, 22.7, 18.0, 11.3, -4.1, -4.3; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{25}H_{45}NNaO_3SSi$ 490.2782, found 490.2786.

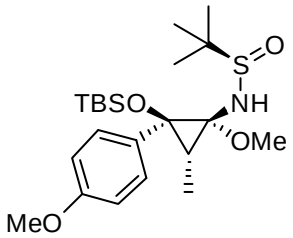


(**3m**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2g** (96.9 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 127.8 mg (97%) of **3m** as a white solid. Analytical data for **3m**: m.p. 68–70 ^{o}C; R_f = 0.31 (petroleum ether / ethyl

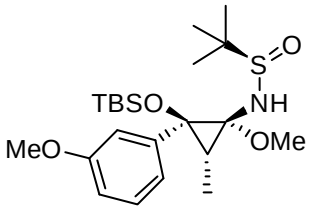
acetate = 8:1); $[\alpha]_D^{20}$ = –34.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 1.6 Hz, 1H), 7.14 (dd, J = 8.0, 1.6 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 4.82 (s, 1H), 3.23 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H), 2.11 (q, J = 6.8 Hz, 1H), 1.38 (d, J = 6.8 Hz, 3H), 1.31 (s, 9H), 0.80 (s, 9H), 0.06 (s, 3H), -0.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 136.0, 133.9, 132.4, 129.2, 128.5, 75.2, 64.5, 56.4, 32.1, 25.9, 22.7, 19.9, 19.7, 18.0, 11.3, -4.0, -4.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{41}NNaO_3SSi$ 462.2469, found 462.2461.



(**3n**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2h** (93.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 128.7 mg (99%) of **3n** as a white solid. Analytical data for **3n**: m.p. 49–51 °C; R_f = 0.18 (petroleum ether / ethyl acetate = 8:1); $[\alpha]_D^{20}$ = –33.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.05–6.98 (m, 2H), 4.81 (s, 1H), 3.22 (s, 3H), 2.15 (q, J = 6.8 Hz, 1H), 1.36 (d, J = 6.8 Hz, 3H), 1.31 (s, 9H), 0.79 (s, 9H), 0.07 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 245.5 Hz), 132.8 (d, J = 8.1 Hz), 132.66 (d, J = 3.3 Hz), 115.0 (d, J = 21.0 Hz), 75.0, 64.1, 56.5, 53.9, 32.2, 25.8, 22.7, 18.0, 11.3, -3.9, -4.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{21}H_{37}FNNaO_3SSi$ 452.2061, found 452.2068.

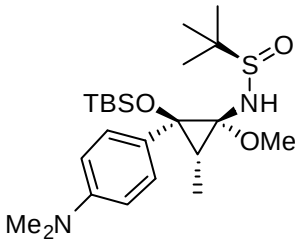


(**3o**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2i** (97.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 131.2 mg (99%) of **3o** as a white solid. Analytical data for **3o**: m.p. 95–97 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –26.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 2H), 6.87–6.83 (m, 2H), 4.82 (s, 1H), 3.81 (s, 3H), 3.24 (s, 3H), 2.11 (q, J = 6.8 Hz, 1H), 1.36 (d, J = 6.8 Hz, 3H), 1.30 (s, 9H), 0.80 (s, 9H), 0.07 (s, 3H), -0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 132.4, 128.8, 113.4, 75.2, 64.3, 56.4, 55.3, 53.9, 32.2, 25.9, 22.7, 18.0, 11.4, -4.02, -4.04; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2268.

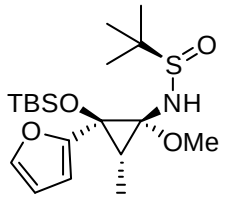


(**3p** + **3p'**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2j** (97.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 107.3 mg (81%) of **3p** as a white solid and 21.2 mg (16%) of **3p'** as a white solid. Analytical data for **3p** (major diastereoisomer): m.p. 66–68 °C; R_f = 0.27 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –32.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 2.0 Hz, 1H), 6.83 (dd, J = 8.0, 2.4 Hz, 1H), 4.79 (s, 1H), 3.81 (s, 3H), 3.22 (s, 3H), 2.13 (q, J = 6.8 Hz, 1H), 1.41 (d, J = 6.8 Hz, 3H), 1.31 (s, 9H), 0.81 (s, 9H), 0.08 (s, 3H), -0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.2, 128.9, 123.6, 117.0,

113.2, 75.2, 64.5, 56.5, 55.4, 53.7, 32.3, 25.9, 22.7, 18.0, 11.2, -4.0, -4.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2265. Analytical data for **3p'** (minor diastereoisomer): m.p. 70–71 °C; R_f = 0.29 (petroleum ether / ethyl acetate = 3:1); $[\alpha]_D^{20}$ = –24.0 (c 0.05, MeOH);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 2.0 Hz, 1H), 6.83 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.81 (s, 3H), 3.55 (s, 3H), 3.31 (s, 1H), 2.11 (q, *J* = 6.4 Hz, 1H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.01 (s, 9H), 0.86 (s, 9H), 0.02 (s, 3H), -.0.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 139.4, 130.1, 122.1, 115.6, 113.9, 74.1, 67.6, 55.7, 55.5, 54.0, 27.4, 26.1, 22.3, 18.5, 7.6, -3.4, -3.6; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2256.



(**3q**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2k** (102.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 65.5 mg (48%) of **3q** as a white solid. Analytical data for **3q**: m.p. 68–70 °C; R_f = 0.39 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –13.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.8, 2H), 4.83 (s, 1H), 3.25 (s, 3H), 2.95 (s, 6H), 2.07 (q, *J* = 6.8 Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.30 (s, 9H), 0.81 (s, 9H), 0.06 (s, 3H), -0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 132.1, 123.9, 111.7, 75.3, 64.5, 56.4, 53.9, 40.5, 32.1, 25.9, 22.8, 18.0, 11.4, -4.0, -4.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{43}N_2O_3SSi$ 455.2758, found 455.2762.



(**3r**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), NaHMDS (2.0 M in THF, 180 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2l** (82.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 120.3 mg (99%) of **3r** as a light yellow oil. Analytical data for **3r**: R_f = 0.48 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –2.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.41 (m, 1H), 6.37–6.34 (m, 2H), 4.86 (s, 1H), 3.21 (s, 3H), 2.07 (q, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.28 (s, 9H), 0.85 (s, 9H), 0.08 (s, 3H), -0.25 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 141.8, 111.1, 110.6, 75.6, 59.0, 56.3, 53.6, 33.0, 25.8, 22.6, 17.9, 10.0, -4.6, -4.9; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{35}NNaO_4SSi$ 424.1948, found 424.1955.

Procedure for 1-gram scale preparation of 3ad

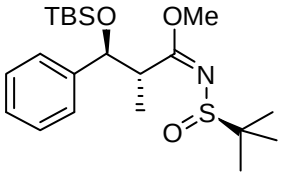
A solution of *N*-*tert*-butanesulfinylimidate **1a** (956.5 mg, 5.0 mmol, 1.0 equiv) in 50 mL THF was added to a flame-dried schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to –78 °C. Then, NaHMDS (2.0 M in THF, 3.0 mL, 6.0 mmol, 1.2 equiv) was added dropwise to the solution by syringe. After the reaction mixture was stirred for 30 min at –78 °C, the solution of acylsilane **2d** (1432.5 mg, 6.5 mmol, 1.3 equiv) in 20 mL THF was added to the reaction mixture via syringe. The reaction mixture was stirred for 1 h at –78 °C. Then,

the reaction was quenched with 10.0 mL saturated aqueous ammonium chloride and extracted with ethyl acetate (50 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

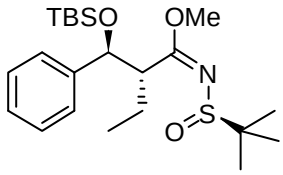
4. Procedure for preparation of product 5

To a solution of *N*-*tert*-butanesulfinylimidate (0.30 mmol, 1.0 equiv) and acylsilane (0.39 mmol, 1.3 equiv) in 4.0 mL toluene was added *t*-BuOK (1.0 M in THF, 360μL, 0.36 mmol, 1.2 equiv) at –78 °C. After the reaction mixture was stirred for 60 min at –78 °C, the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

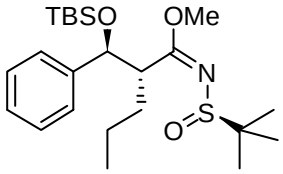
Analytical data for β-silyloxy imidates 5



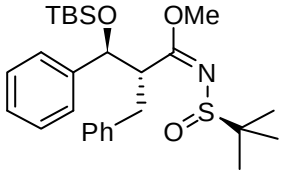
(**5a**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 116.2 mg (94%) of **5a** as a white solid. Analytical data for **5a**: m.p. 78–80 ^oC; R_f = 0.33 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –105.0 (c 0.20, MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 5H), 4.71 (d, J = 9.6 Hz, 1H), 3.79 (s, 3H), 3.71–3.63 (m, 1H), 1.20 (s, 9H), 0.82 (d, J = 7.2 Hz, 3H), 0.81 (s, 9H), -0.04 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.6, 128.3, 128.0, 127.5, 55.9, 54.1, 46.3, 25.8, 22.2, 18.1, 14.2, -4.5, -5.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{21}H_{37}NNaO_3SSi$ 434.2156, found 434.2151.



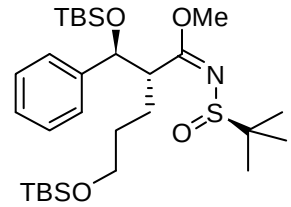
(**5b**) The title compound was prepared using imidate **1b** (61.6 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 108.4 mg (85%) of **5b** as a colorless oil. Analytical data for **5b**: R_f = 0.33 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –119.0 (c 0.10, MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 4.70 (d, J = 9.2 Hz, 1H), 3.76 (s, 3H), 3.73–3.70 (m, 1H), 1.45–1.36 (m, 1H), 1.23 (s, 9H), 1.15–1.00 (m, 3H), 0.79 (s, 9H), 0.74 (t, J = 7.2 Hz, 3H), -0.06 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 143.1, 128.2, 127.9, 127.6, 76.9, 56.0, 53.8, 51.9, 31.3, 25.8, 22.4, 20.7, 18.1, 14.3, -4.6, -5.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_3SSi$ 448.2312, found 448.2319.



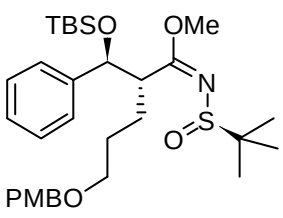
(**5c**) The title compound was prepared using imidate **1c** (65.8 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 126.6 mg (96%) of **5c** as a colorless oil. Analytical data for **5c**: R_f = 0.57 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –138.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 4.70 (d, J = 9.2 Hz, 1H), 3.75 (s, 3H), 3.73–3.70 (m, 1H), 1.45–1.36 (m, 1H), 1.23 (s, 9H), 1.14–1.02 (m, 3H), 0.79 (s, 9H), 0.73 (t, J = 7.2 Hz, 3H), -0.06 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 143.1, 128.2, 127.9, 127.6, 76.9, 56.0, 53.8, 51.9, 31.3, 25.8, 22.4, 20.7, 18.1, 14.3, -4.6, -5.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{41}NNaO_3SSi$ 462.2469, found 462.2466.



(**5d**) The title compound was prepared using imidate **1d** (80.2 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 145.9 mg (99%) of **5d** as a colorless oil. Analytical data for **5d**: R_f = 0.20 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –102.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 2H), 7.37–7.28 (m, 3H), 7.17–7.07 (m, 3H), 6.99–6.93 (m, 2H), 4.85 (d, J = 8.8 Hz, 1H), 4.02–3.96 (m, 1H), 3.72 (s, 3H), 2.72–2.66 (m, 1H), 2.49 (dd, J = 13.2, 4.0 Hz, 1H), 0.89 (s, 9H), 0.82 (s, 9H), -0.01 (s, 3H), -0.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 142.8, 138.7, 129.1, 128.5, 128.4, 128.1, 127.6, 126.5, 76.8, 55.4, 54.3, 53.6, 35.0, 25.8, 21.9, 18.2, -4.6, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{41}NNaO_3SSi$ 510.2469, found 510.2461.

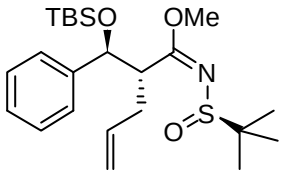


(**5e**) The title compound was prepared using imidate **1e** (104.9 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 155.5 mg (91%) of **5e** as a colorless oil. Analytical data for **5e**: R_f = 0.38 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –95.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 4.72 (d, J = 8.8 Hz, 1H), 3.76 (s, 3H), 3.73–3.65 (m, 1H), 3.46–3.37 (m, 2H), 1.61–1.59 (m, 1H), 1.49–1.39 (m, 1H), 1.33–1.27 (m, 1H), 1.23 (s, 9H), 1.19–1.13 (m, 1H), 0.80 (s, 18H), -0.05 (s, 3H), -0.06 (s, 6H), -0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 143.0, 128.3, 127.9, 127.6, 76.8, 62.9, 56.1, 53.9, 51.8, 30.8, 26.0, 25.8, 25.5, 22.4, 18.4, 18.1, -4.5, -5.1, -5.2; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{29}H_{55}NNaO_4SSi_2$ 592.3283, found 592.3281.

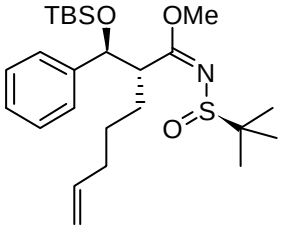


(**5f**) The title compound was prepared using imidate **1f** (106.6 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 155.2 mg (90%) of **5f** as a colorless oil. Analytical data for **5f**: R_f = 0.19 (petroleum ether / ethyl acetate =

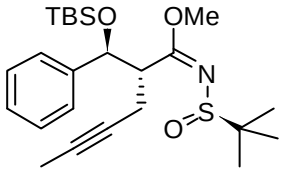
10:1); $[\alpha]_D^{20}$ = –89.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.22 (m, 5H), 7.12 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.71 (d, J = 9.2 Hz, 1H), 4.28 (s, 2H), 3.78 (s, 3H), 3.76–3.71 (m, 4H), 3.29–3.19 (m, 1H), 1.53–1.30 (m, 3H), 1.26–1.13 (m, 10H), 0.78 (s, 9H), -0.07 (s, 3H), -0.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 159.2, 143.0, 130.7, 129.3, 128.3, 127.9, 127.6, 113.8, 76.8, 72.5, 69.8, 56.2, 55.4, 53.9, 51.6, 27.6, 25.8, 25.7, 22.4, 18.1, -4.6, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{31}H_{49}NNaO_5SSi$ 598.2993, found 598.2998.



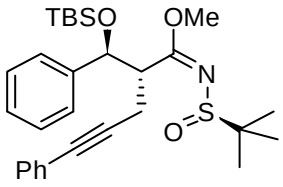
(**5g**) The title compound was prepared using imidate **1g** (65.2 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 115.4 mg (88%) of **5g** as a colorless oil. Analytical data for **5g**: R_f = 0.20 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –132.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 5.60–5.49 (m,1H), 4.89 (t, J = 9.2 Hz, 2H), 4,76 (d, J = 9.2 Hz, 1H), 3.87–3.81 (m, 1H), 3.74 (s, 3H), 2.17–2.08 (m, 1H), 1.94–1.88 (m, 1H), 1.22 (s, 9H), 0.80 (s, 9H), -0.04 (s, 3H), -0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.6, 135.2, 128.3, 128.1, 127.6, 117.1, 76.6, 56.1, 53.8, 51.7, 33.7, 25.8, 22.5, 18.1, -4.6, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{39}NNaO_3SSi$ 460.2312, found 460.2314.



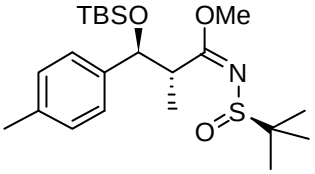
(**5h**) The title compound was prepared using imidate **1h** (73.6 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 125.6 mg (90%) of **5h** as a colorless oil. Analytical data for **5h**: R_f = 0.30 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –118.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.22 (m, 5H), 5.66–5.56 (m, 1H), 4.87–4.82 (m, 2H), 4.69 (d, J = 9.2 Hz, 1H), 3.75 (s, 3H), 3.73–3.69 (m, 1H), 1.94–1.78 (m, 2H), 1.48–1.38 (m, 1H), 1.22 (s, 9H), 1.19–1.08 (m, 3H), 0.78 (s, 9H), -0.07 (s, 3H), -0.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 143.1, 138.3, 128.2, 127.9, 127.6, 114.7, 76.8, 56.1, 53.8, 51.8, 33.7, 28.6, 26.7, 25.8, 22.4, 18.1, -4.5, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{43}NNaO_3SSi$ 488.2625, found 488.2629.



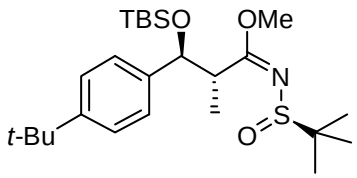
(**5i**) The title compound was prepared using imidate **1i** (68.8 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 124.9 mg (93%) of **5i** as a white solid. Analytical data for **5i**: m.p. 63–65 ^{o}C; R_f = 0.35 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –157.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.25 (m, 5H), 4.74 (d, J = 8.8 Hz, 1H), 3.89 (ddd, J = 10.4, 8.8, 4.4 Hz, 1H), 3.77 (s, 3H), 2.26–2.18 (m, 1H), 2.04–1.97 (m, 1H), 1.64 (t, J = 2.4 Hz, 3H), 1.24 (s, 9H), 0.80 (s, 9H), -0.03 (s, 3H), -0.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 142.1, 128.4, 128.2, 127.4, 76.1, 75.8, 56.0, 54.0, 51.0, 25.8, 22.4, 18.8, 18.2, 3.6, -4.6, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{39}NNaO_3SSi$ 472.2312, found 472.2308.



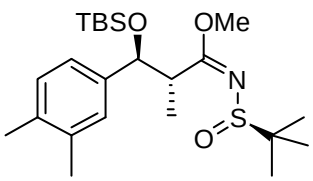
(**5j**) The title compound was prepared using imidate **1j** (87.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 136.3 mg (89%) of **5j** as a white solid. Analytical data for **5j**: m.p. 64–66 ^{o}C; R_f = 0.38 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –152.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 3H), 7.32–7.30 (m, 2H), 7.29–7.28 (m, 2H), 7.26–7.24 (m, 3H), 4.88 (d, J = 8.8 Hz, 1H), 4.04 (ddd, J = 9.6, 9.2, 4.4 Hz, 1H), 3.79 (s, 3H), 2.49 (dd, J = 16.8, 10.0 Hz, 1H), 2.34 (dd, J = 16.8, 4.4 Hz, 1H), 1.21 (s, 9H), 0.83 (s, 9H), 0.00 (s, 3H), -0.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 141.9, 131.6, 128.4, 128.3, 127.9, 127.7, 127.4, 123.7, 86.7, 82.3, 75.9, 56.2, 54.1, 50.7, 29.9, 25.8, 22.4, 19.4, 18.2, -4.6, -5.0; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{29}H_{41}NNaO_3SSi$ 534.2469, found 534.2473.



(**5k**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2e** (91.4 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 103.3 mg (81%) of **5k** as a white solid. Analytical data for **5k**: m.p. 80–82 ^{o}C; R_f = 0.22 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –109.0 (c 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 4.67 (d, J = 9.2 Hz, 1H), 3.79 (s, 3H), 3.67–3.60 (m, 1H), 2.33 (s, 3H), 1.20 (s, 9H), 0.82–0.81 (m, 12H), -0.05, -0.35; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 139.6, 137.6, 128.9, 127.4, 55.9, 54.0, 46.3, 25.8, 22.2, 21.3, 18.1, 14.2, -4.5, -5.1; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_3SSi$ 448.2312, found 448.2305.

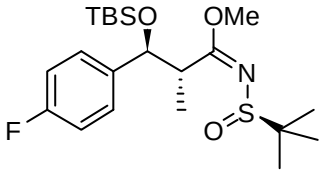


(**5l**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2f** (107.8 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 95.6 mg (68%) of **5l** as a white solid. Analytical data for **5l**: m.p. 95–97 ^{o}C; R_f = 0.50 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –116.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.67 (d, J = 9.6 Hz, 1H), 3.80 (s, 3H), 3.68–3.60 (m, 1H), 1.30 (s, 9H), 1.20 (s, 9H), 0.83–0.81 (m, 12H), -0.05 (s, 3H), -0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 150.9, 139.4, 127.1, 125.0, 55.8, 54.0, 46.3, 34.7, 31.5, 25.8, 22.2, 18.1, 14.3, -4.5, -5.2; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{45}NNaO_3SSi$ 490.2782, found 490.2779.

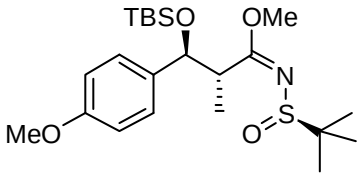


(**5m**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2g** (96.9 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 96.3 mg (73%) of **5m** as a white solid. Analytical data for **5m**: m.p. 96–98 ^{o}C; R_f = 0.33 (petroleum ether / ethyl acetate =

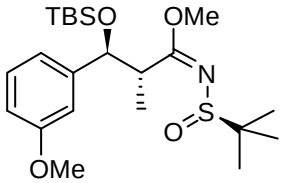
10:1); $[\alpha]_D^{20}$ = –107.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–7.01 (m, 3H), 4.64 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.65–3.57 (m, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 1.20 (s, 9H), 0.82–0.81 (m, 12H), -0.05 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 139.9, 136.3, 136.1, 129.4, 128.6, 125.0, 55.8, 54.1, 46.3, 25.8, 22.2, 19.9, 19.7, 18.1, 14.3, -4.4, -5.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{41}NNaO_3SSi$ 462.2469, found 462.2476.



(**5n**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2h** (93.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 117.3 mg (91%) of **5n** as a white solid. Analytical data for **5n**: m.p. 87–88 °C; R_f = 0.44 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –102.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.4, 5.6 Hz, 2H), 7.00 (t, J = 8.8 Hz, 2H), 4.72 (d, J = 9.6 Hz, 1H), 3.77 (s, 3H), 3.68–3.59 (m, 1H), 1.20 (s, 9H), 0.82 (d, J = 6.8 Hz, 3H), 0.80 (s, 9H), -0.04 (s, 3H), -0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 162.5 (d, J = 244.4), 138.5 (d, J = 3.2 Hz), 129.0 (d, J = 8.0 Hz), 15.2 (d, J = 21.2 Hz), 76.6, 56.0, 54.1, 46.3, 25.8, 22.2, 18.0, 14.0, -4.5, -5.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{36}FNNaO_3SSi$ 452.2061, found 452.2058.



(**5o** + **5o'**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2i** (97.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 51.4 mg (39%) of **5o** as a colorless oil and 10.3 mg (8%) of **5o'** as a colorless oil. Analytical data for **5o** (major diastereoisomer): R_f = 0.33 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ = –114.6 (c 0.37, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.66 (d, J = 9.6 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.66–3.59 (m, 1H), 1.20 (s, 9H), 0.82–0.80 (m, 12H), -0.05 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ176.3, 159.4, 134.8, 128.5, 113.6, 77.0, 55.9, 55.3, 54.0, 46.4, 25.8, 22.2, 18.1, 14.2, -4.5, -5.1; HRMS (ESI-TOF) *m/z* [M +]$^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2255. Analytical data for **5o'** (minor diastereoisomer): R_f = 0.31 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = +10.2 (c 0.24, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 4.88 (d, J = 6.6 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.57–3.51 (m, 1H), 1.19 (d, J = 7.2 Hz, 3H), 0.86 (s, 9H), -0.01 (s, 3H), -0.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 158.9, 134.9, 127.8, 113.3, 75.9, 55.9, 55.1, 53.7, 46.4, 25.7, 22.0, 18.1, 13.1, -4.6, -5.2; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2259.



(**5p**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), *t*-BuOK (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2j** (97.7 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 121.8 mg (92%) of **5p** as a white solid. Analytical data for **5p**: m.p. 86–88 °C; R_f = 0.14 (petroleum ether / ethyl acetate = 10:1); $[\alpha]_D^{20}$ =

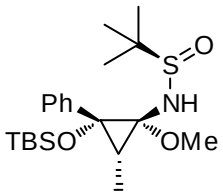
–102.0 (c 0.20, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 8.4 Hz, 1H), 6.96–6.90 (m, 2H), 6.82–6.79 (m, 1H), 4.69 (d, J = 9.6 Hz,, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.66–3.59 (m, 1H), 1.20 (s, 9H), 0.84–0.82 (m, 12H), -0.03 (s, 3H), -0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 159.6, 144.2, 129.2, 120.0, 113.6, 112.7, 55.9, 55.4, 54.1, 46.2, 25.8, 22.2, 18.1, 14.3, -4.5, -5.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{39}NNaO_4SSi$ 464.2261, found 464.2266.

Procedure for 1-gram scale preparation of 5a

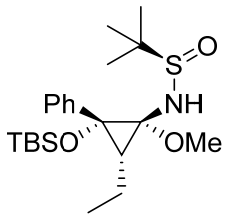
To a solution of *N-tert*-butanesulfinylimidate **1a** (956.5 mg, 5.0 mmol, 1.0 equiv) and **3a** (1432.5 mg, 6.5 mmol, 1.3 equiv) in 60 mL toluene was added *t*-BuOK (1.0 M in THF, 6.0 mL, 6.0 mmol, 1.2 equiv) at –78 °C. After the reaction mixture was stirred for 60 min at –78 °C, the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (50 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

5. General procedure for preparation of cyclopropane products 4a-c

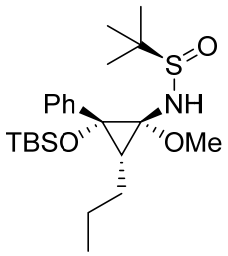
A solution of *N-tert*-butanesulfinylimidate (0.30 mmol, 1.0 equiv) in 2.0 mL THF was added to a flame-dried schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to –78 °C. Then, KHMDS (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) was added dropwise to the solution by syringe. After the reaction mixture was stirred for 30 min at –78 °C, the solution of acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv) in 2.0 mL THF was added to the reaction mixture via syringe. The reaction mixture was stirred for 1 h at –78 °C. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.



(**4a**) The title compound was prepared using imidate **1a** (57.4 mg, 0.30 mmol, 1.0 equiv), KHMDS (1.0 M in THF, 360 μL, 0.36 mmol, 1.2 equiv) and acylsilane **2d** (86.0 mg, 0.39 mmol, 1.3 equiv). Column chromatography afforded 86.5 mg (70%) of **4a** as a white solid. Analytical data for **4a**: m.p. 94–96 ^{o}C; R_f = 0.34 (petroleum ether / ethyl acetate = 3:1); $[\alpha]_D^{20}$ = –32.6 (c 0.46, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.27 (m, 5H), 3.57 (s, 3H), 3.24 (s, 1H), 2.15 (q, J = 6.4 Hz, 1H), 1.30 (d, J = 6.4 Hz, 3H), 0.99 (s, 9H), 0.86 (s, 9H), 0.01 (s, 3H), -0.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 129.8, 129.0, 128.6, 74.1, 67.6, 55.7, 54.1, 27.2, 26.1, 22.2, 18.5, 7.6, -3.4, -3.6; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{37}NNaO_3SSi$ 434.2156, found 434.2158.

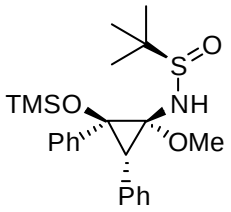


(**4b**) The title compound was prepared using imidate **1b** (41.1 mg, 0.20 mmol, 1.0 equiv), KHMDS (1.0 M in THF, 240 μL, 0.24 mmol, 1.2 equiv) and acylsilane **2d** (57.3 mg, 0.26 mmol, 1.3 equiv). Column chromatography afforded 59.0 mg (69%) of **4b** as a colorless oil. Analytical data for **4b**: R_f = 0.2 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –37.6 (c 0.49, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 3.55 (s, 3H), 3.21 (s, 1H), 2.01–1.98 (m, 1H), 1.80–1.60 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H), 1.00 (s, 9H), 0.84 (s, 9H), -0.02 (s, 3H), -0.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 129.9, 129.0, 128.6, 74.4, 68.0, 55.6, 54.0, 35.0, 26.1, 22.3, 18.5, 16.4, 14.0, -3.4, -3.5; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{39}NNaO_3SSi$ 448.2312, found 448.2307.



(**4c**) The title compound was prepared using imidate **1c** (43.9 mg, 0.20 mmol, 1.0 equiv), KHMDS (1.0 M in THF, 240 μL, 0.24 mmol, 1.2 equiv) and acylsilane **2d** (57.3 mg, 0.26 mmol, 1.3 equiv). Column chromatography afforded 58.7 mg (67%) of **4c** as a colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –35.2 (c 0.21, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5H), 3.56 (s, 3H), 3.21 (s, 1H), 2.06–2.02 (m, 1H), 1.76–1.68 (m, 1H), 1.65–1.52 (m, 3H), 1.03 (t, J = 7.2 Hz, 3H), 1.00 (s, 9H), 0.85 (s, 9H), -0.02 (s, 3H), -0.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 129.9, 129.0, 128.6, 74.4, 67.9, 55.6, 54.0, 33.2, 26.1, 25.3, 22.8, 22.3, 18.5, 14.5, -3.4, -3.5; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{41}NNaO_3SSi$ 462.2469, found 462.2461.

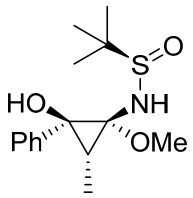
6. Procedure for preparation of cyclopropane products 3s



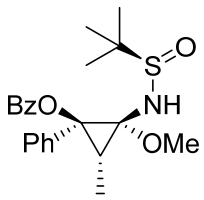
A solution of *N-tert*-butanesulfinylimidate **1k** (76.0 mg, 0.30 mmol, 1.0 equiv) in 2.0 mL THF was added to a flame-dried schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to –78 °C. Then, LiHMDS (1.2 M in THF, 300 μL, 0.36 mmol, 1.2 equiv) was added dropwise to the solution by syringe. After the reaction mixture was stirred for 30 min at –78 °C, the solution of acylsilane **2a** (69.5 mg, 0.39 mmol, 1.3 equiv) in 2.0 mL THF was added to the reaction mixture via syringe. The reaction mixture was stirred for 1 h at –78 °C and was gradually warmed to –60 °C. At which time, the reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and

concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to give 98.3 mg (76%) of **3s** as a white solid. Analytical data for **3s**: m.p. 136–138 °C; R_f = 0.45 (petroleum ether / ethyl acetate = 5:1); $[\alpha]_D^{20}$ = –79.8 (c 0.36, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 5H), 7.18–7.13 (m, 5H), 4.85 (s, 1H), 3.42 (s, 1H), 2.97 (s, 3H), 1.34 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.8, 130.4, 129.9, 128.0, 127.5, 127.3, 126.4, 77.9, 66.4, 56.5, 53.7, 42.6, 22.6, 1.1; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{34}NO_3SSi$ 432.2023, found 432.2028.

7. Procedure for the manipulations of cyclopropane product 3ad



Preparation of alcohol **6** via desilylation of **3ad**: Cyclopropane **3ad** (411.7 mg, 1.0 mmol, 1.0 equiv) was dissolved in 10.0 mL of anhydrous THF and placed under stirring in an ice bath, 189.8 mg (5.0 mmol, 5.0 equiv) of $LiAlH_4$ were added in batches. The reaction was checked by TLC examination of an aliquot which was separately hydrolyzed. After ~10 min, the reaction was hydrolyzed with saturated potassium sodium tartrate aqueous solution (5.0 mL) and extracted with ethyl acetate. The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to yield 277.4 mg (93%) of **6** as a white solid. Analytical data for compound **6**: Analytical data for **6**: m.p. 86–87 °C; R_f = 0.1 (petroleum ether/ethyl acetate = 2:1); $[\alpha]_D^{20}$ = +22.4 (c 0.21, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.37–7.33 (m, 2H), 7.31–7.28 (m, 1H), 4.93 (s, 1H), 3.77 (s, 1H), 3.30 (s, 3H), 2.06 (q, *J* = 6.8 Hz, 1H), 1.33 (s, 9H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 130.0, 128.2, 127.7, 78.3, 64.1, 56.8, 54.0, 30.9, 22.9, 9.6. HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{23}NNaO_3S$ 320.1291, found 320.1296.



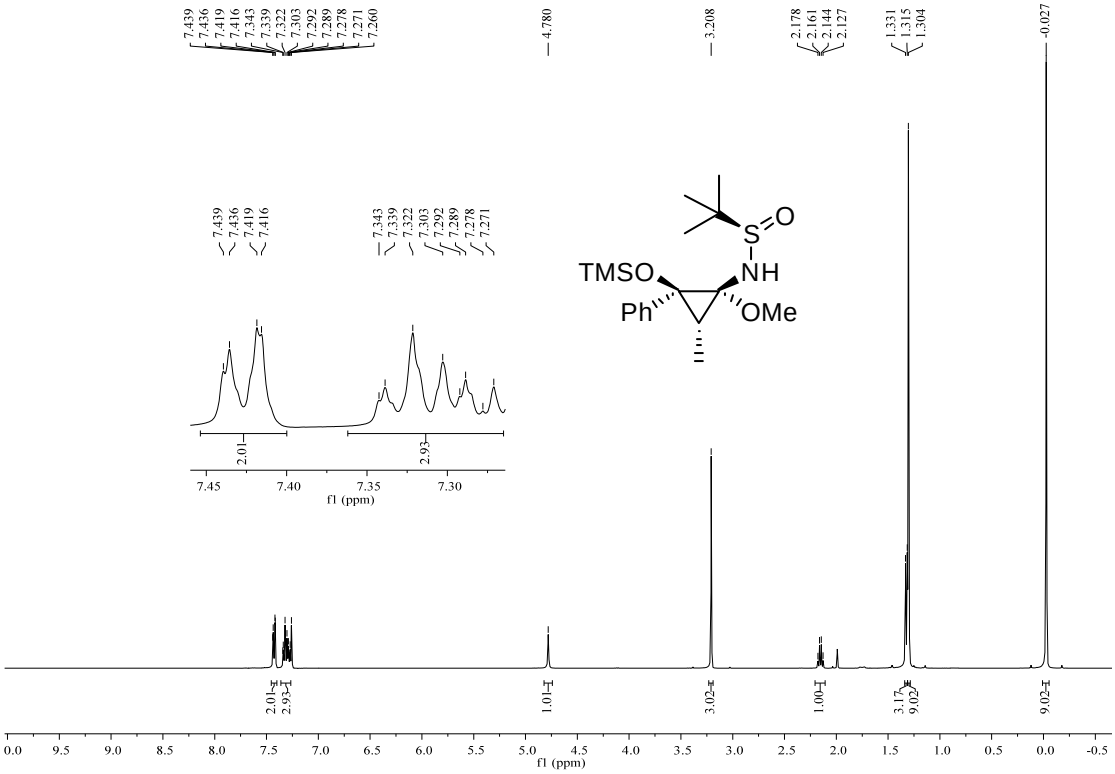
Preparation of benzoic ester **7** via benzoylation of **6**: To a stirred solution of **6** (59.5 mg, 0.20 mmol, 1.0 equiv) in 5.0 mL CH_2Cl_2 at 0 °C was added 4–dimethylaminopyridine (48.9 mg, 0.40 mmol, 2.0 equiv), followed by benzoyl chloride (30 μL, 0.26 mmol, 1.3 equiv). The resultant solution was stirred at 0 °C for 5 min and then warmed to room temperature. When the starting material was completely consumed, the reaction mixture was quenched with 5.0 mL saturated aqueous

$NaHCO_3$. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with 1.0 M HCl aqueous solution and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to yield 78.9 mg (98%) of **7** as a white solid. Analytical data for compound **7**: m.p. 150–151 ^oC; R_f = 0.2 (petroleum ether/ethyl acetate = 2:1); $[\alpha]_D^{20}$ = +46.3 (c 0.18, MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–7.95 (m, 2H), 7.65–7.62 (m, 2H), 7.53–7.48 (m, 1H), 7.39–7.27 (m, 5H), 5.10 (s, 1H), 3.37 (s, 3H), 2.51 (q, J = 6.8 Hz, 1H), 1.22 (s, 9H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 133.3, 132.9, 131.6, 130.2, 129.9, 128.4, 128.3, 128.0, 77.7, 68.1, 56.8, 53.7, 29.8, 22.9, 9.6. HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{27}NNaO_4S$ 424.1553, found 424.1557.

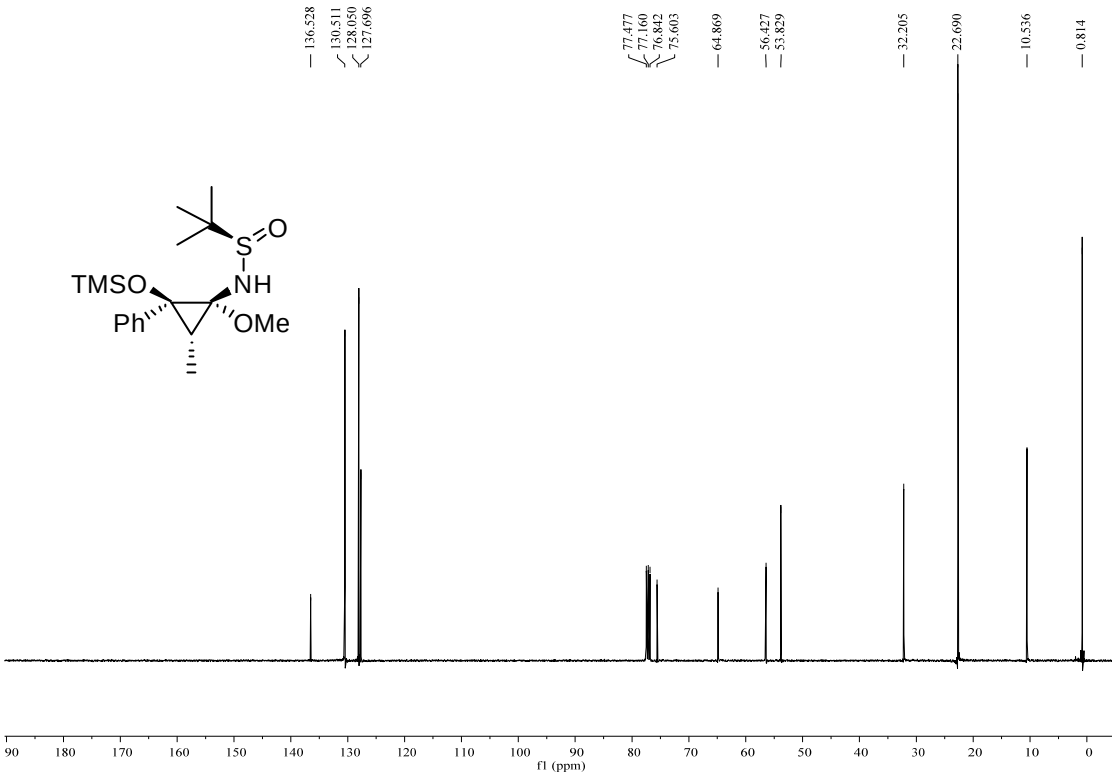
Procedure for ring-opening reaction of cyclopropane **3ad** with L-selectride: To the cyclopropane **3ad** (41.2 mg, 0.10 mmol, 1.0 equiv) in THF (2.0 mL) was added L-selectride (0.40 mL, 1.0 M in THF, 0.40 mmol, 4.0 equiv) at -40 ^oC. The resulting solution was gradually allowed to warm to 0 ^oC. Then the solution was quenched with saturated aqueous ammonium chloride and diluted with ethyl acetate. The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to yield 24.4 mg (59%) of **5a** as a white solid. For characterization data of compound **5a**, see page 18.

Procedure for ring-opening reaction of cyclopropane **3ad** with LiHMDS: Cyclopropane **3ad** (41.2 mg, 0.10 mmol, 1.0 equiv) was dissolved in THF (2.0 mL). The solution was cooled to -78 ^oC and LiHMDS (1.2 M in THF, 0.10 mL, 0.12 mmol, 1.2 equiv) was then added to the solution. The reaction mixture was stirred for 30 min at -78 ^oC and then gradually warmed up to room temperature. When the starting material was completely consumed, the reaction mixture was quenched with saturated aqueous ammonium chloride and diluted with ethyl acetate. The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to yield 37.4 mg (91%) of **5a** as a white solid. For characterization data of compound **5a**, see page 18.

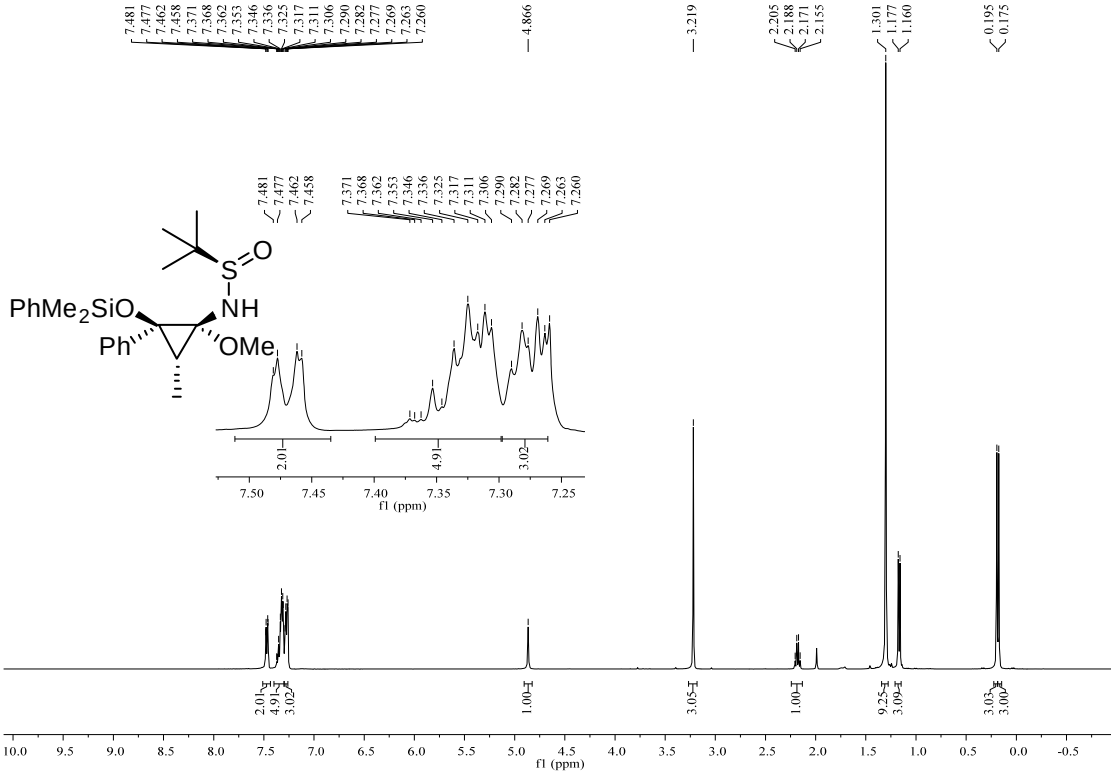
8. ^{1}H NMR and ^{13}C NMR spectra for all new compounds



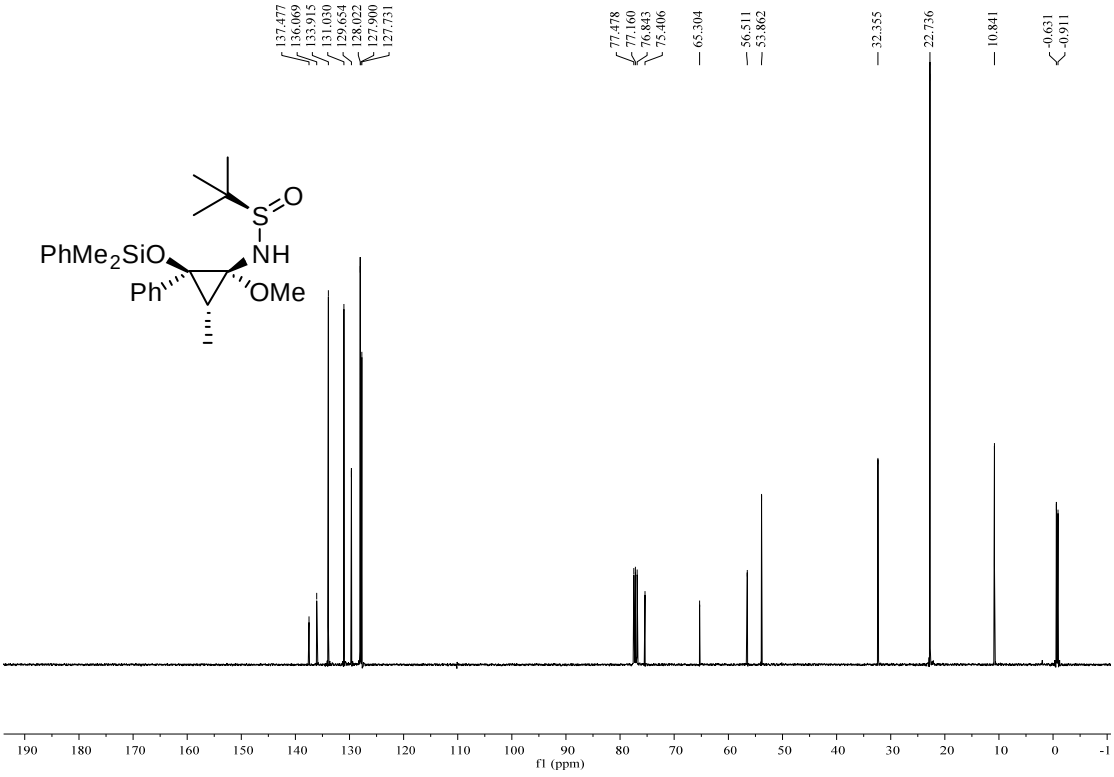
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3aa**



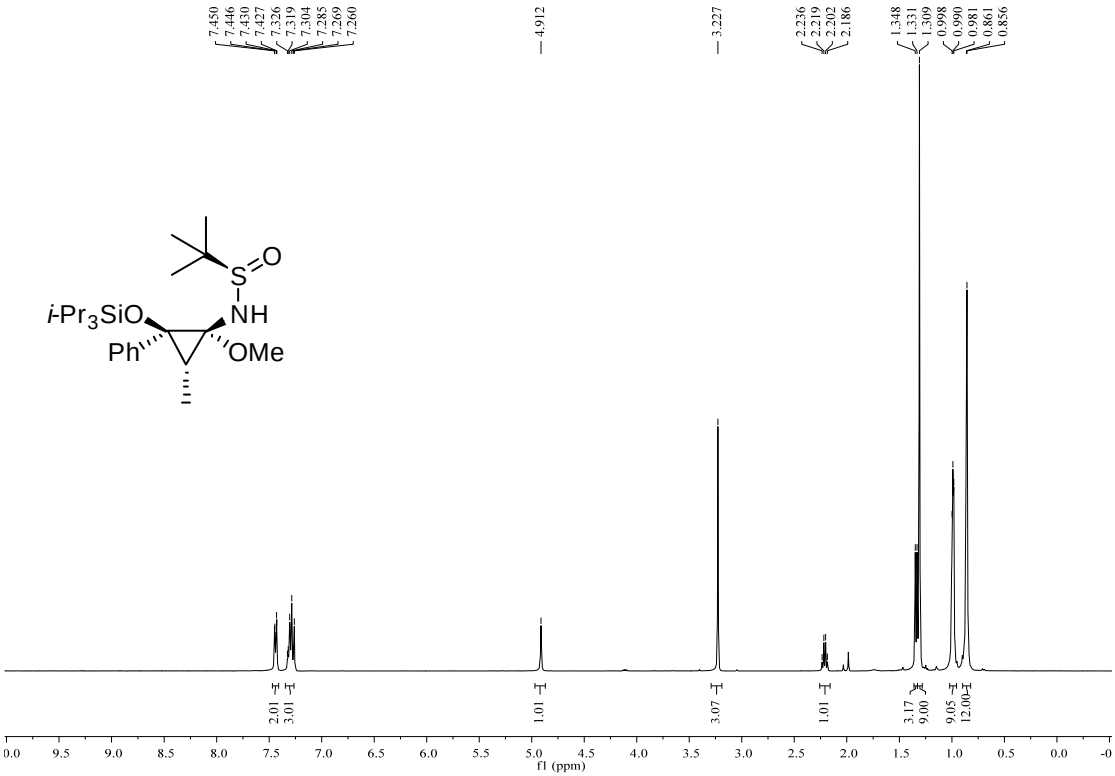
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3aa**



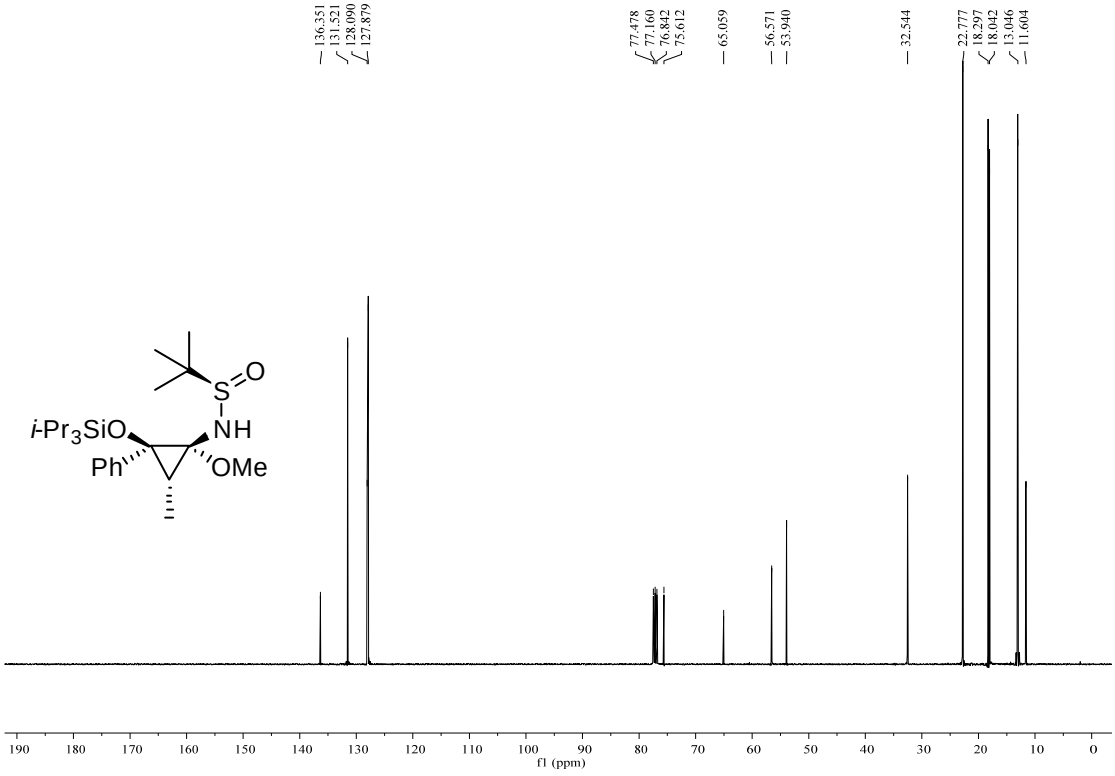
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ab**



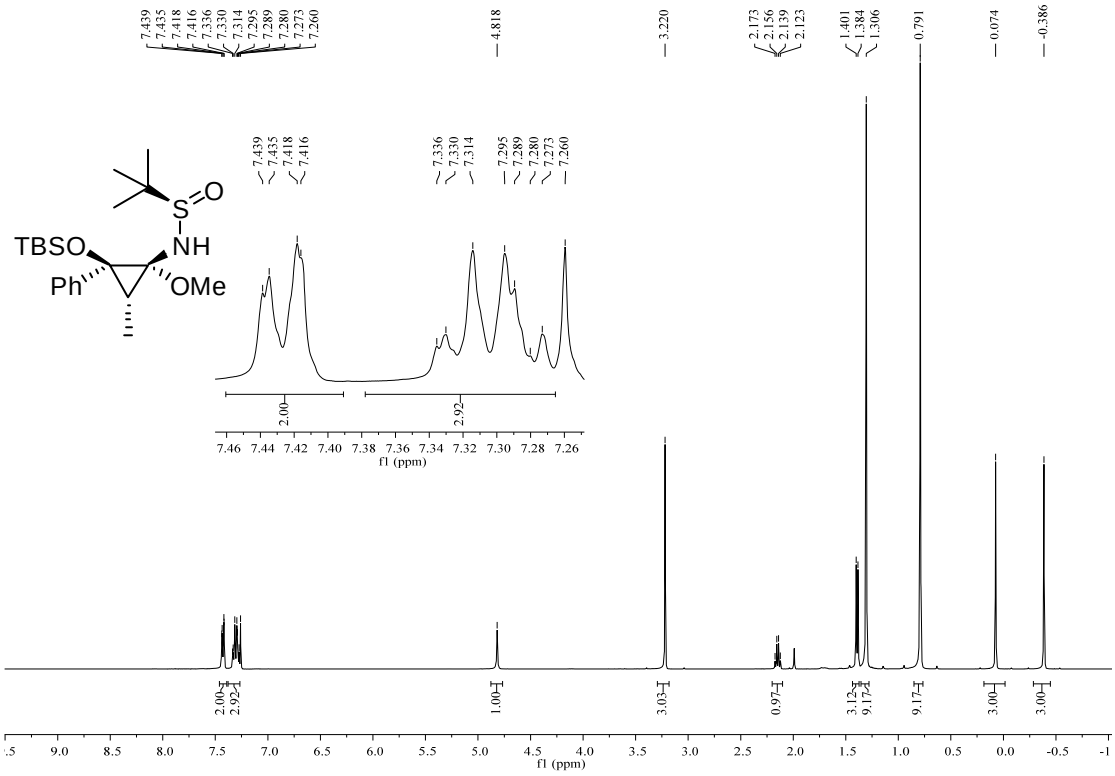
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ab**



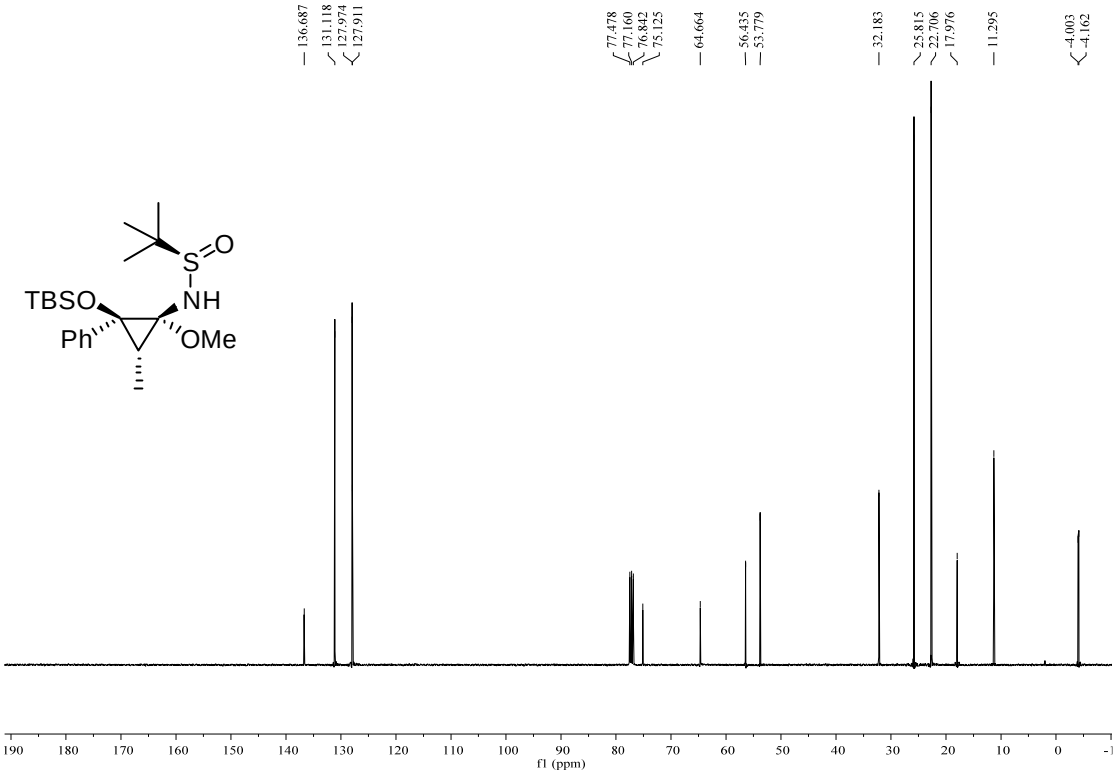
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ac**



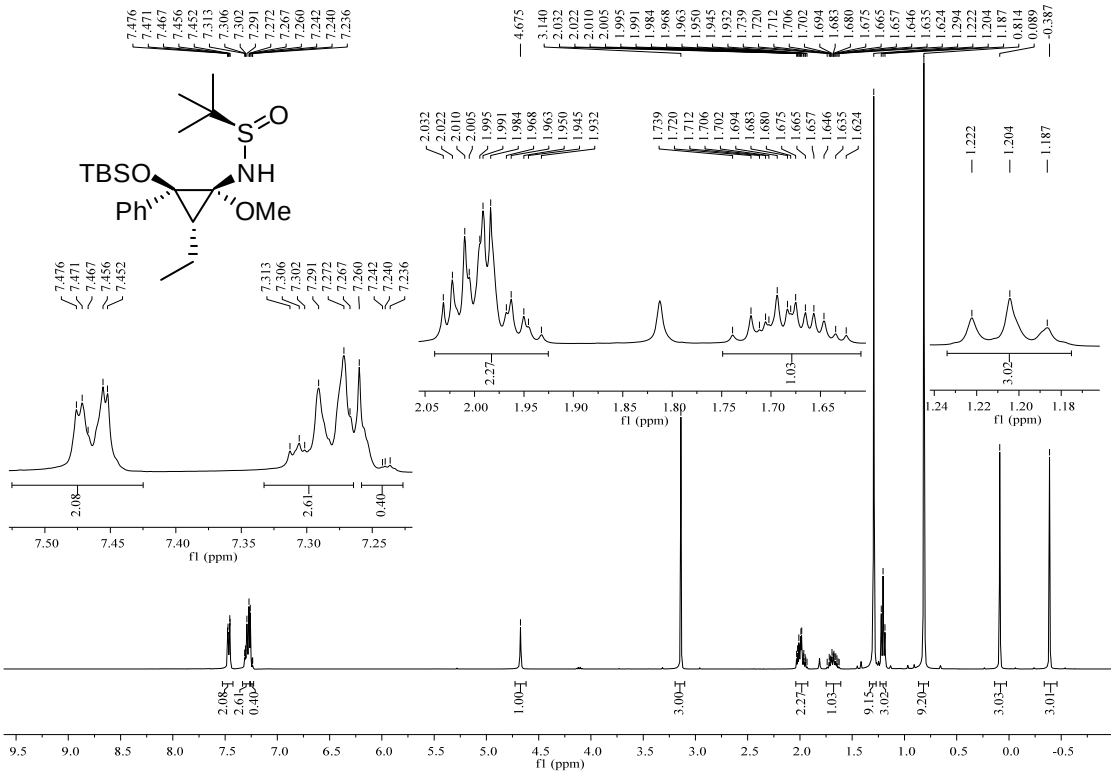
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ac**



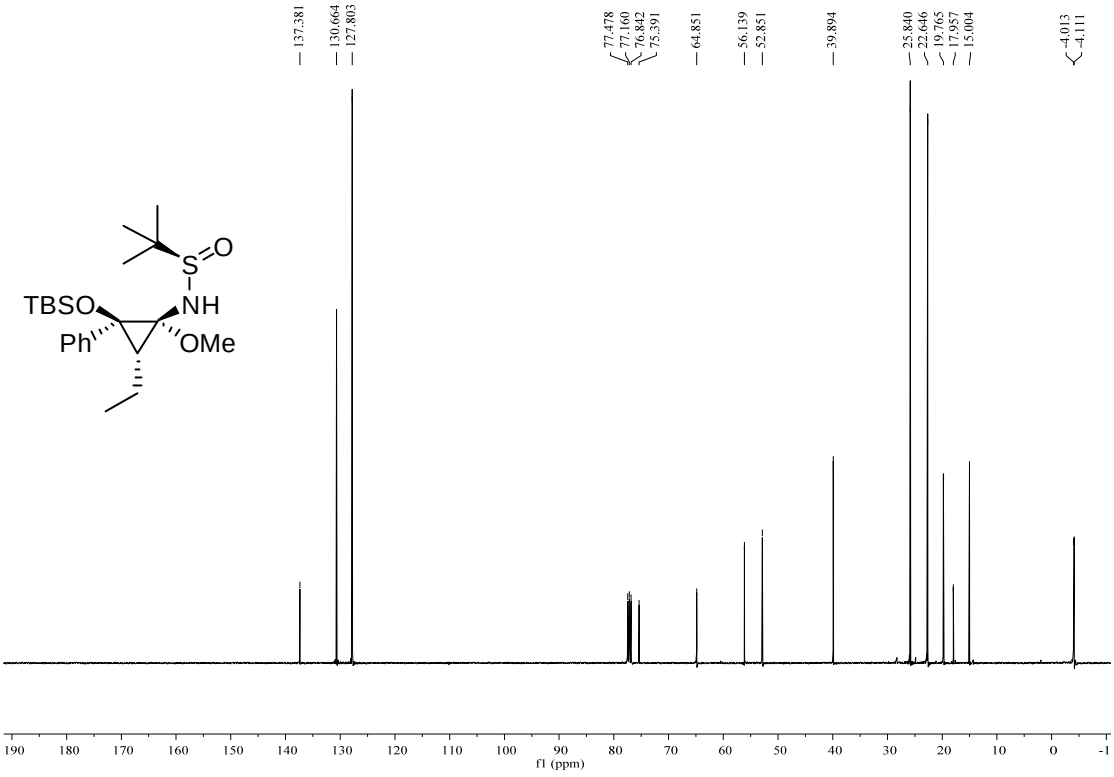
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ad**



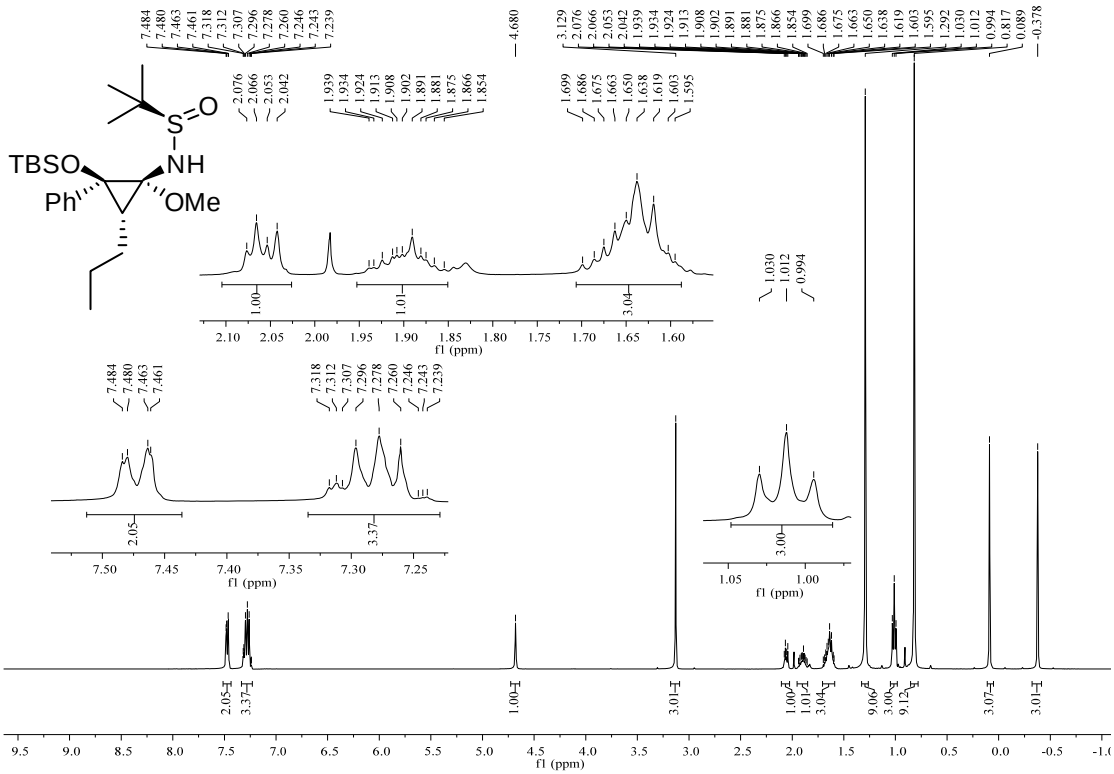
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ad**



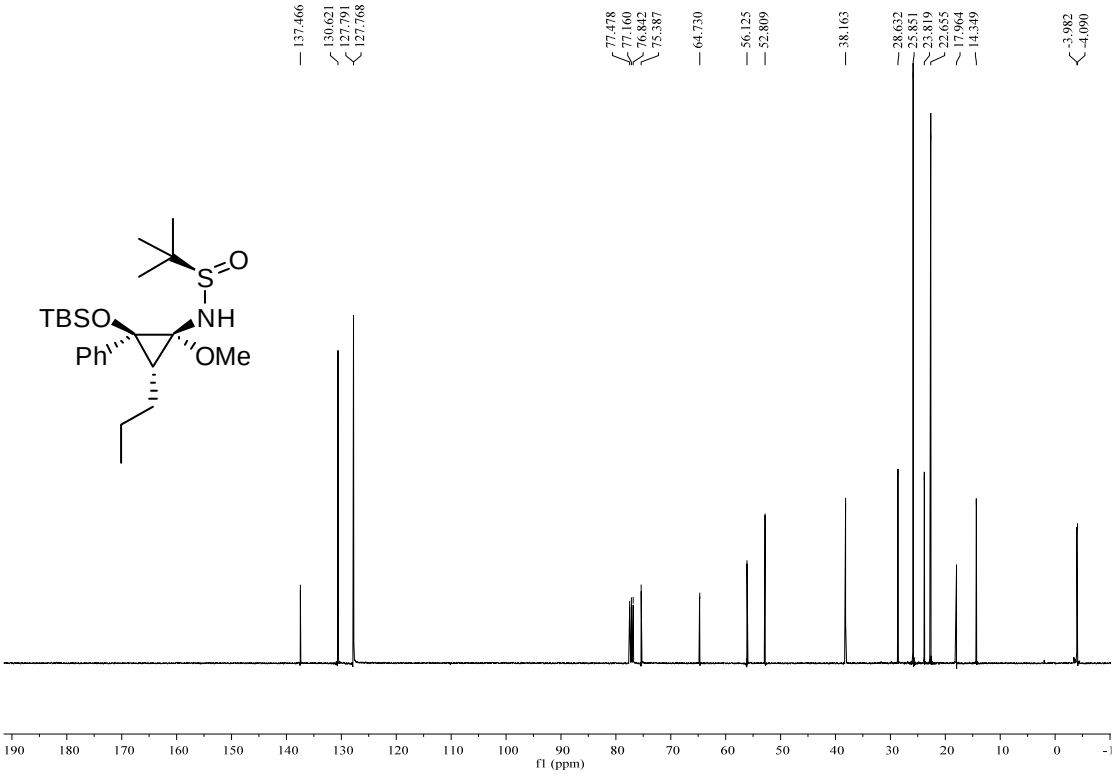
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3b**



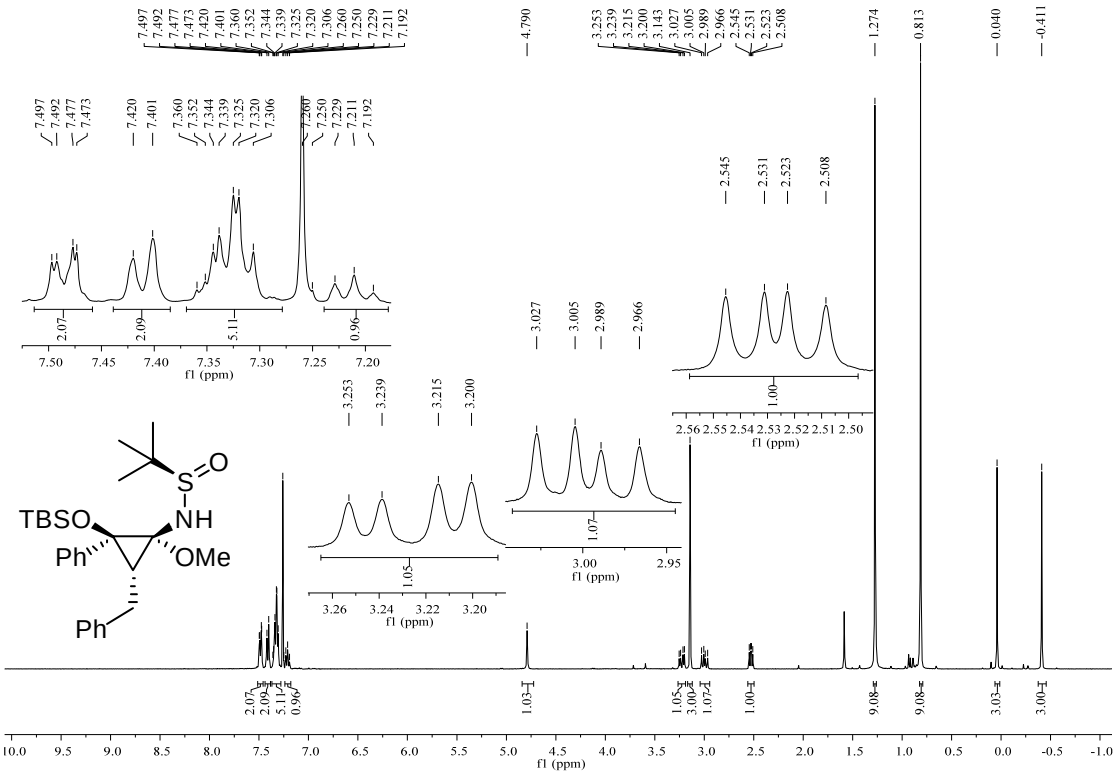
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3b**



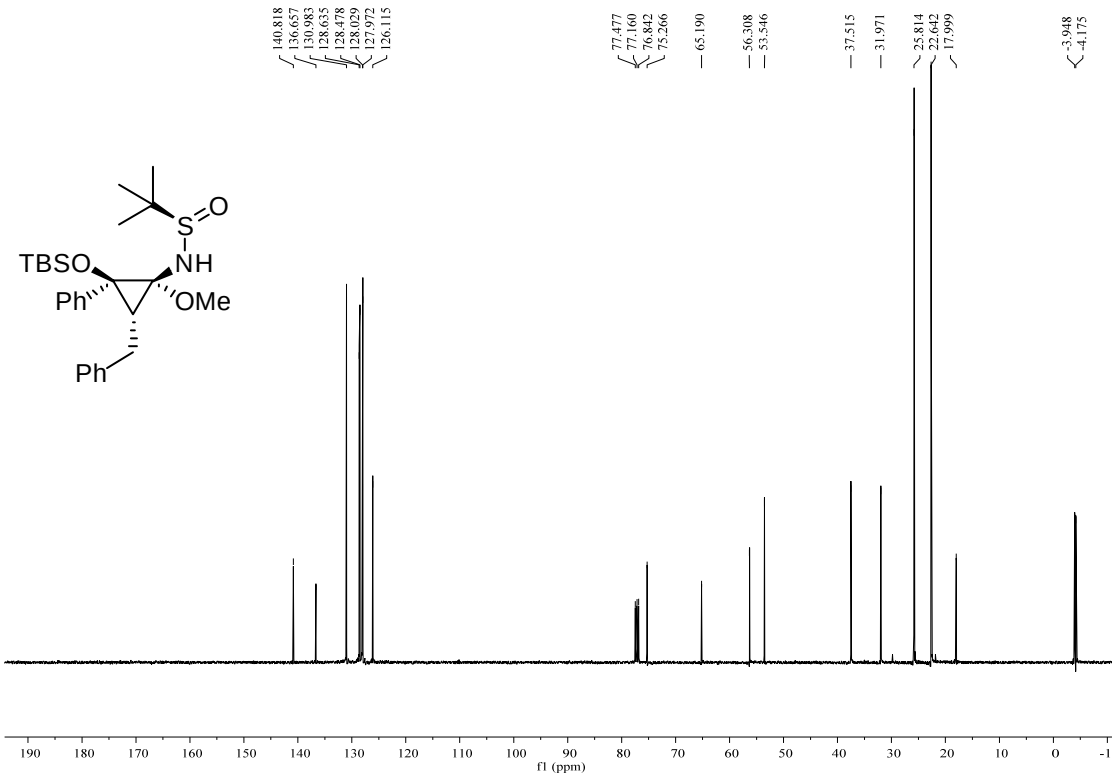
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3c**



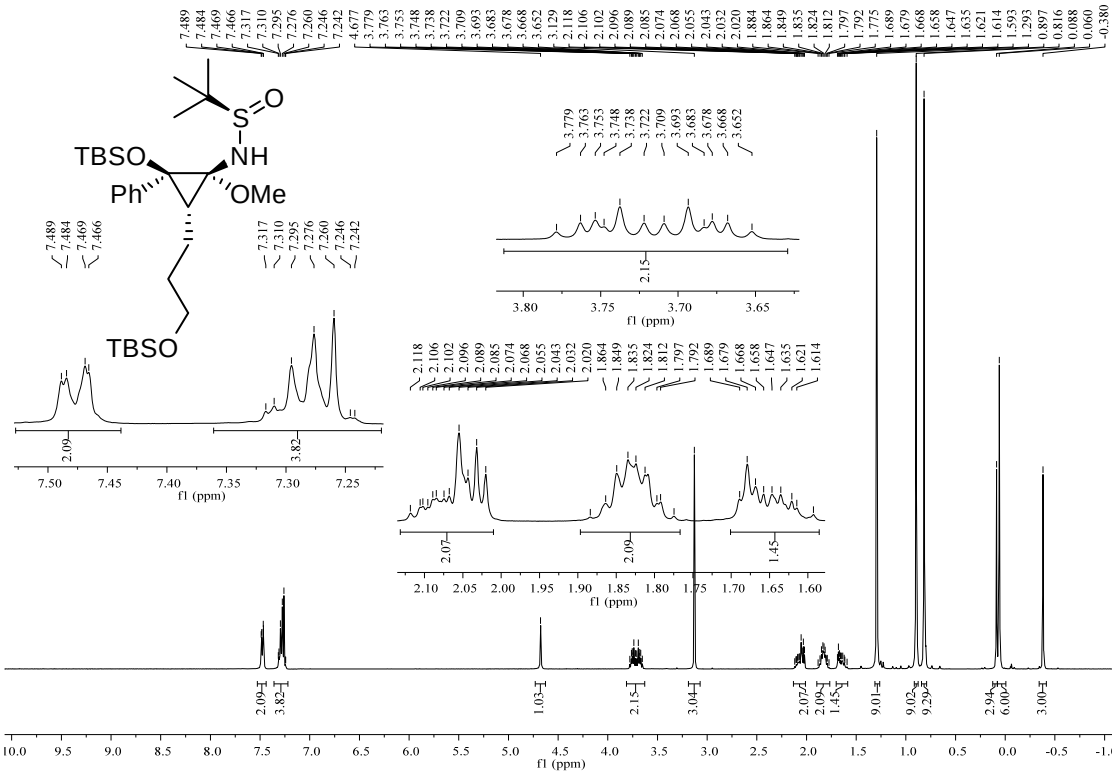
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3c**



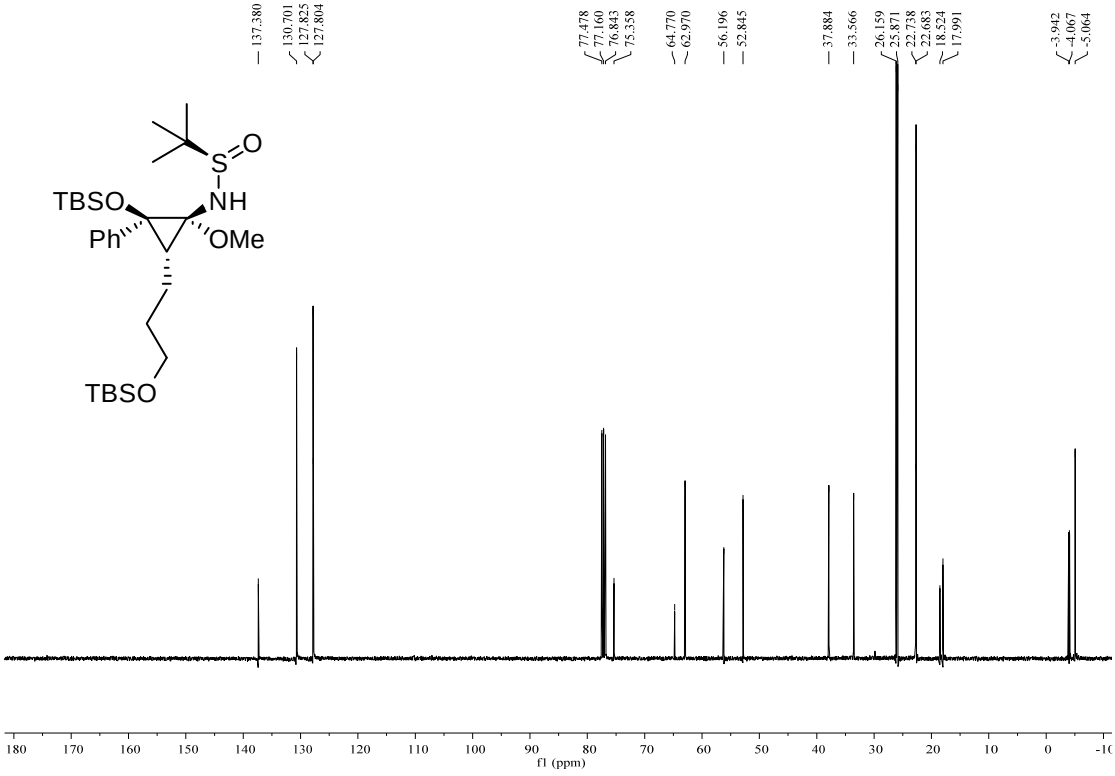
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3d**



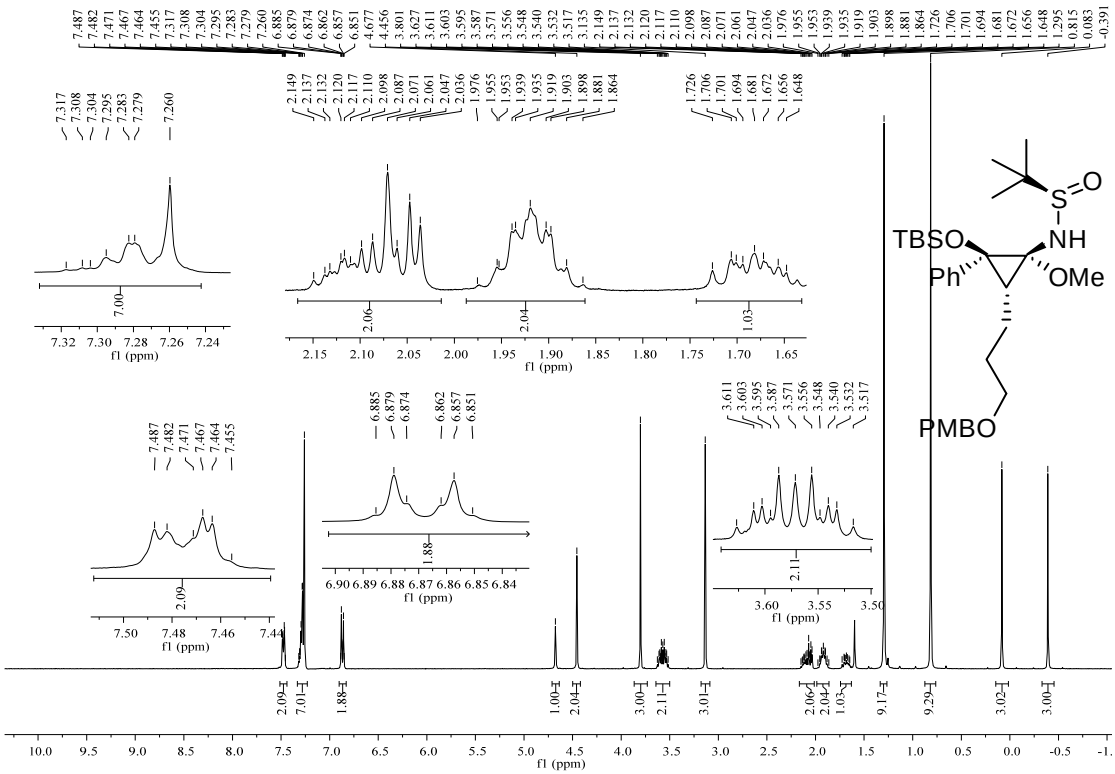
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3d**



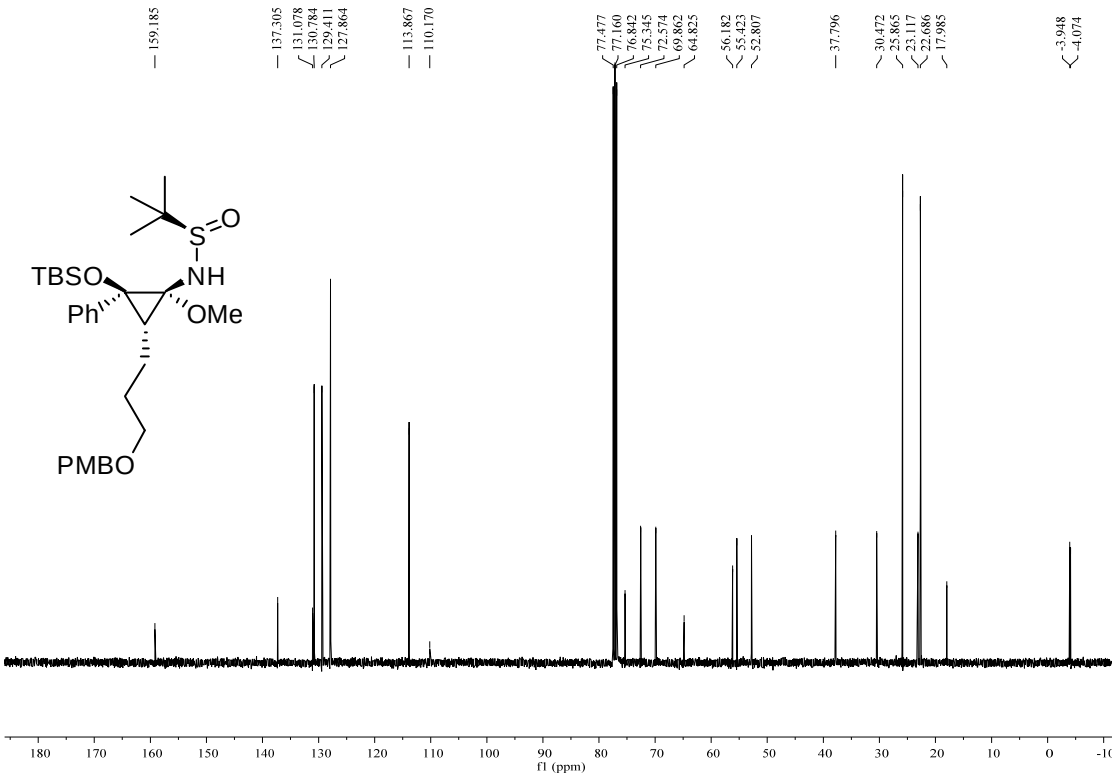
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3e**



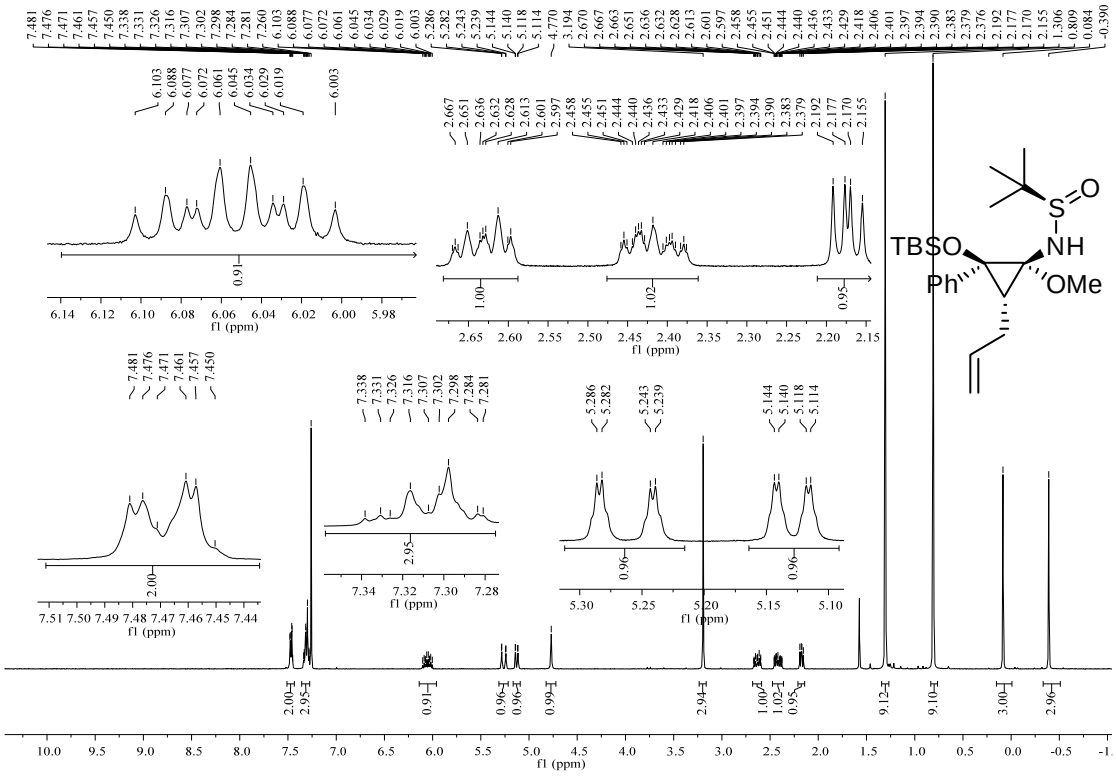
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3e**



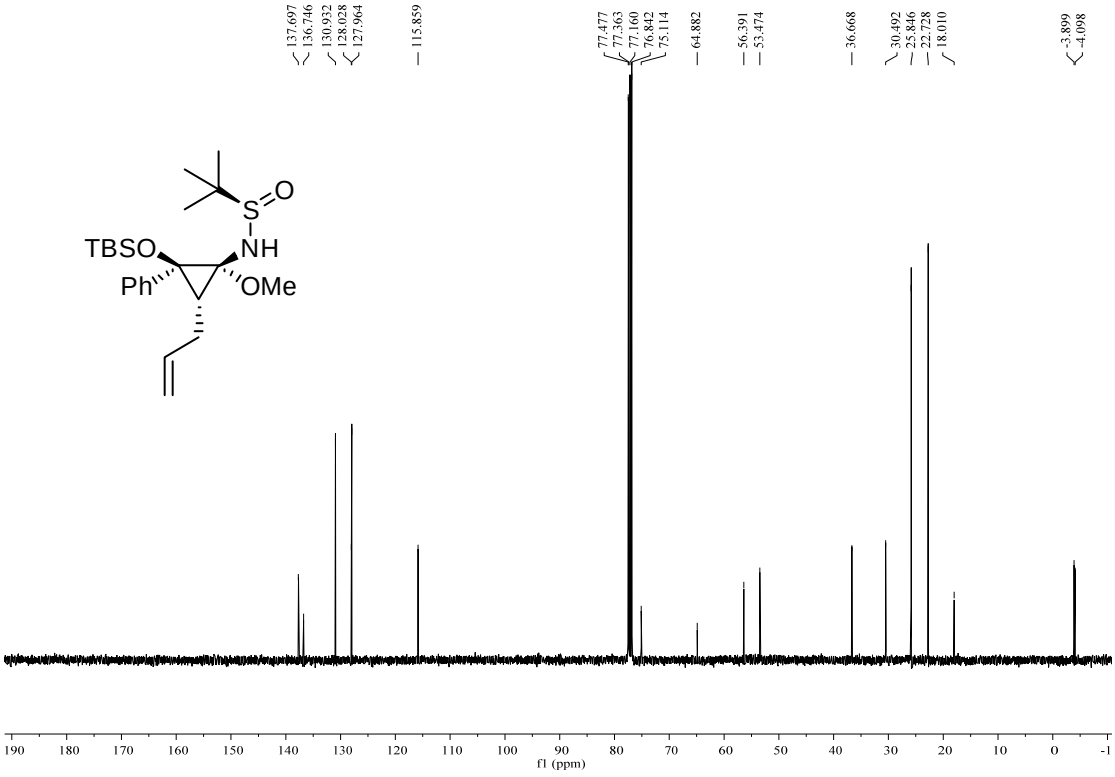
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3f**



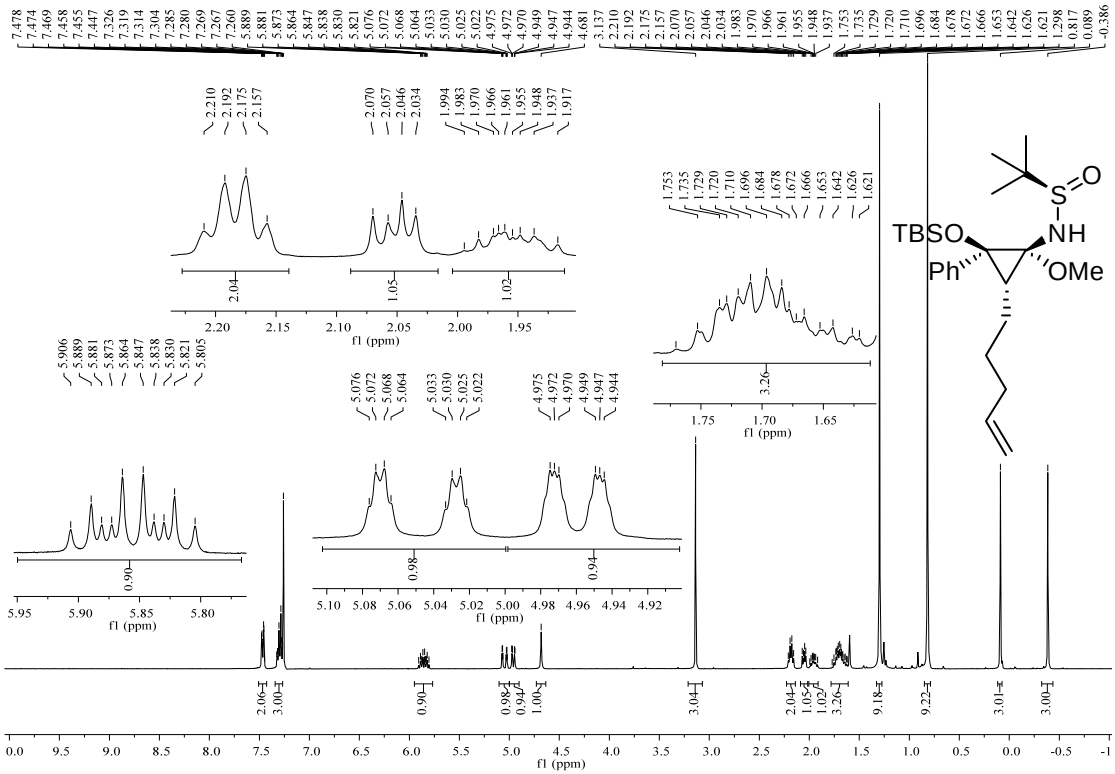
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3f**



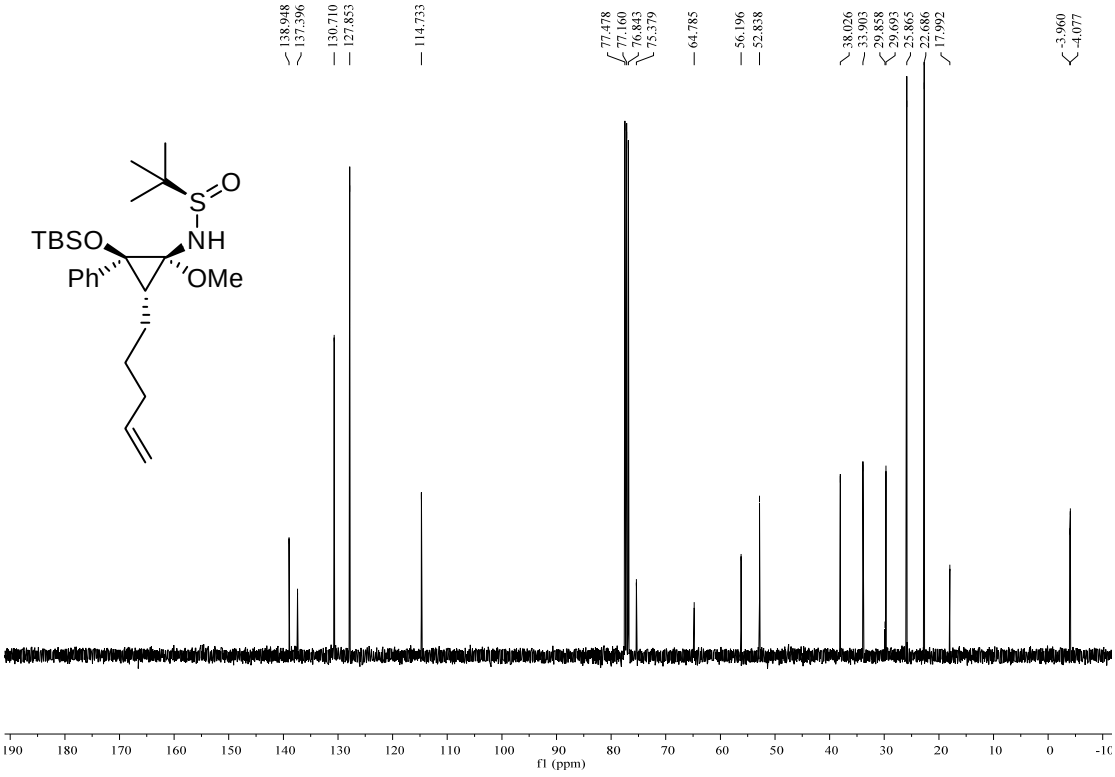
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3g**



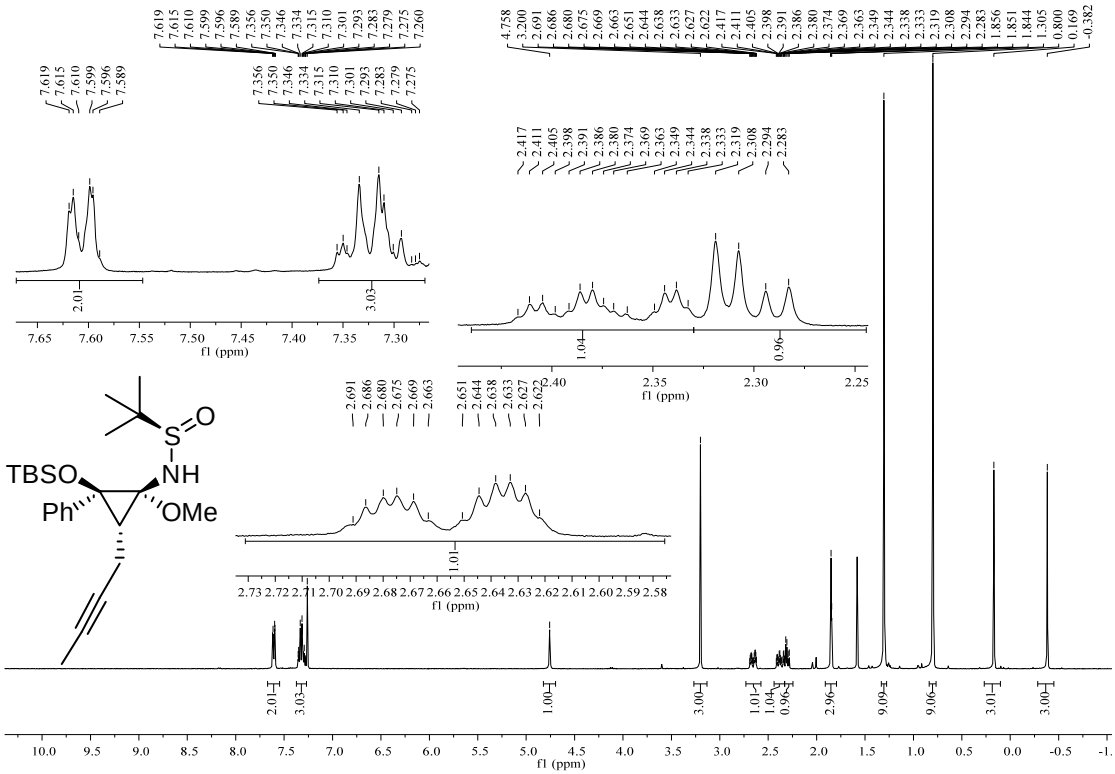
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3g**



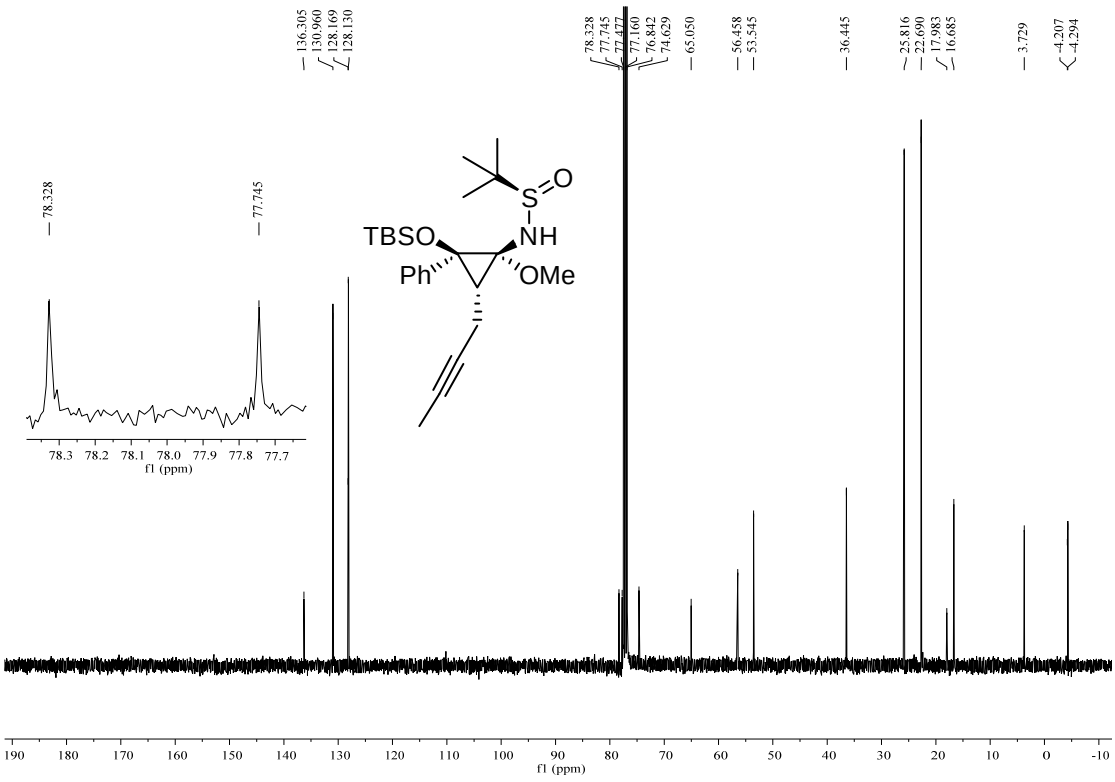
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3h**



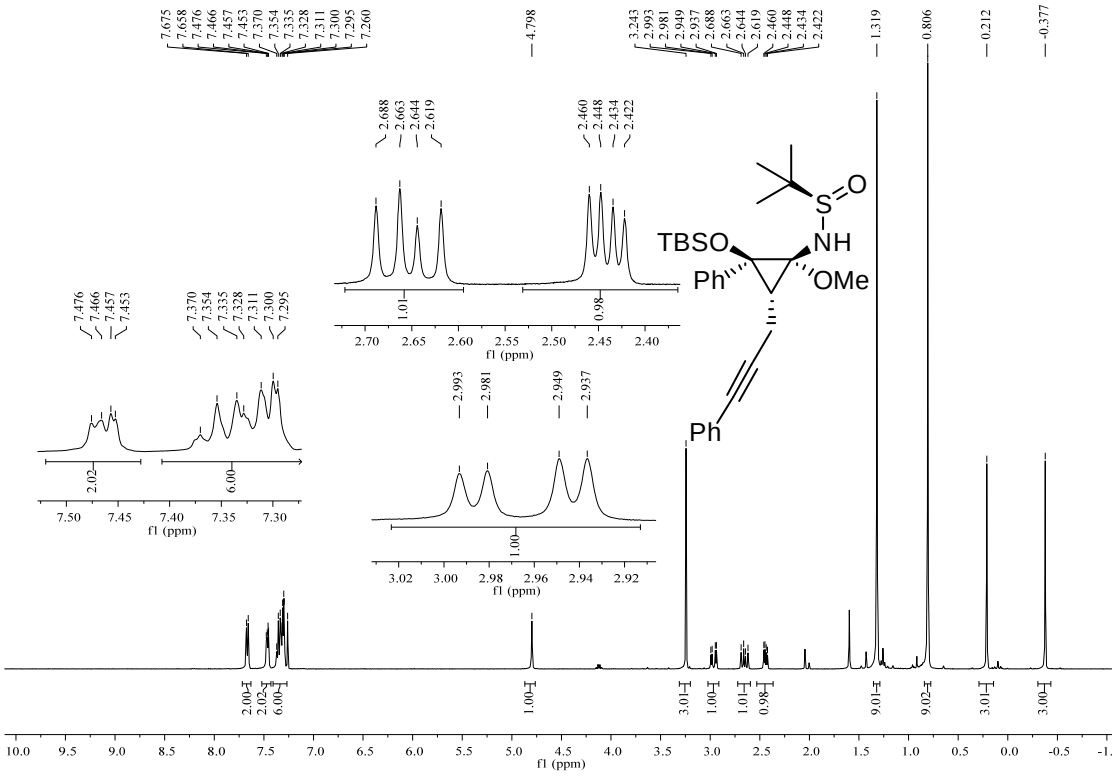
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3h**



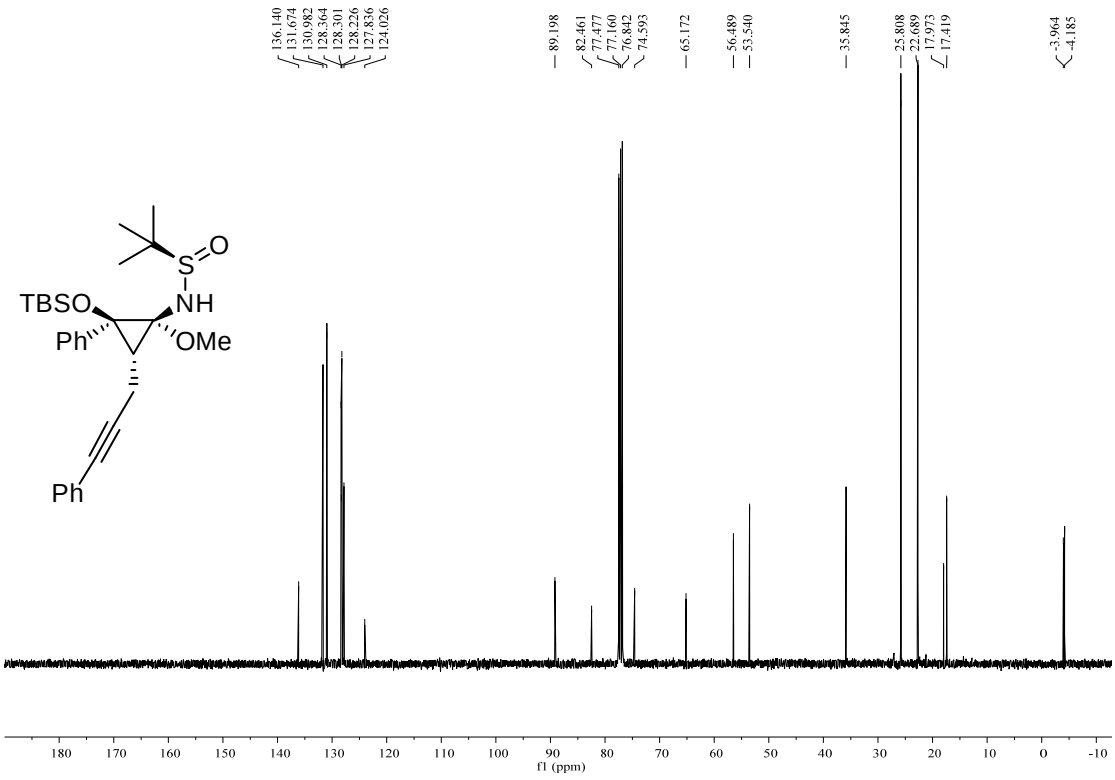
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3i**



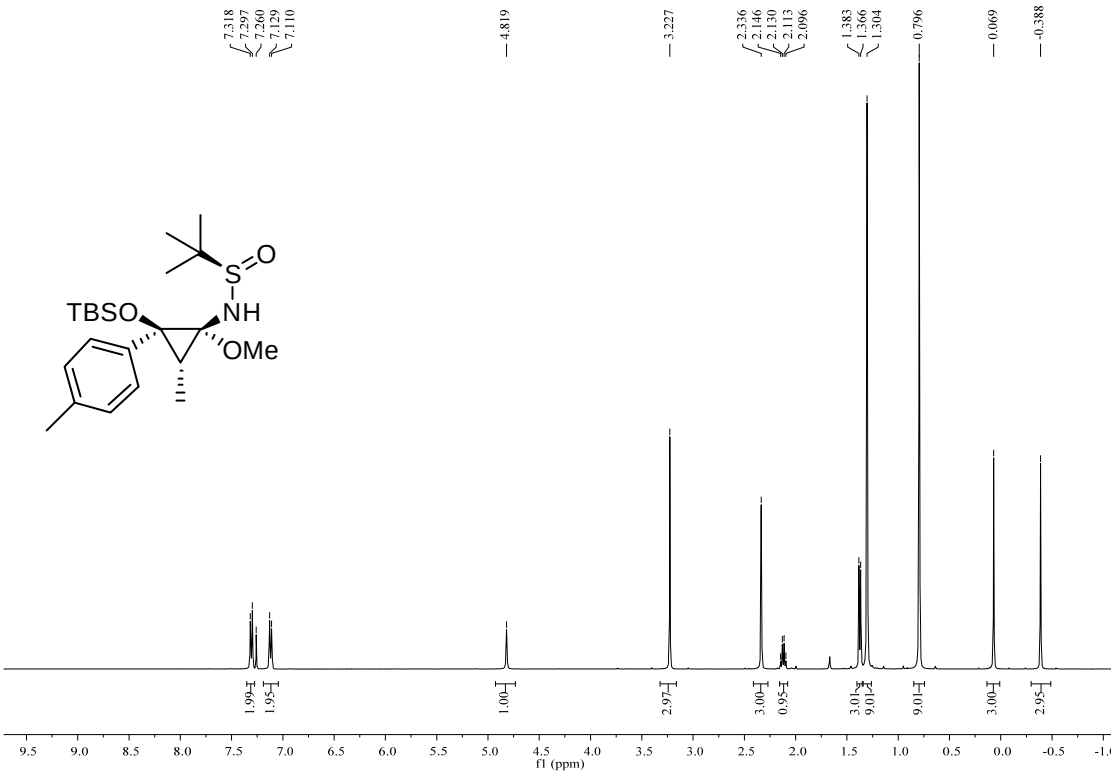
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3i**



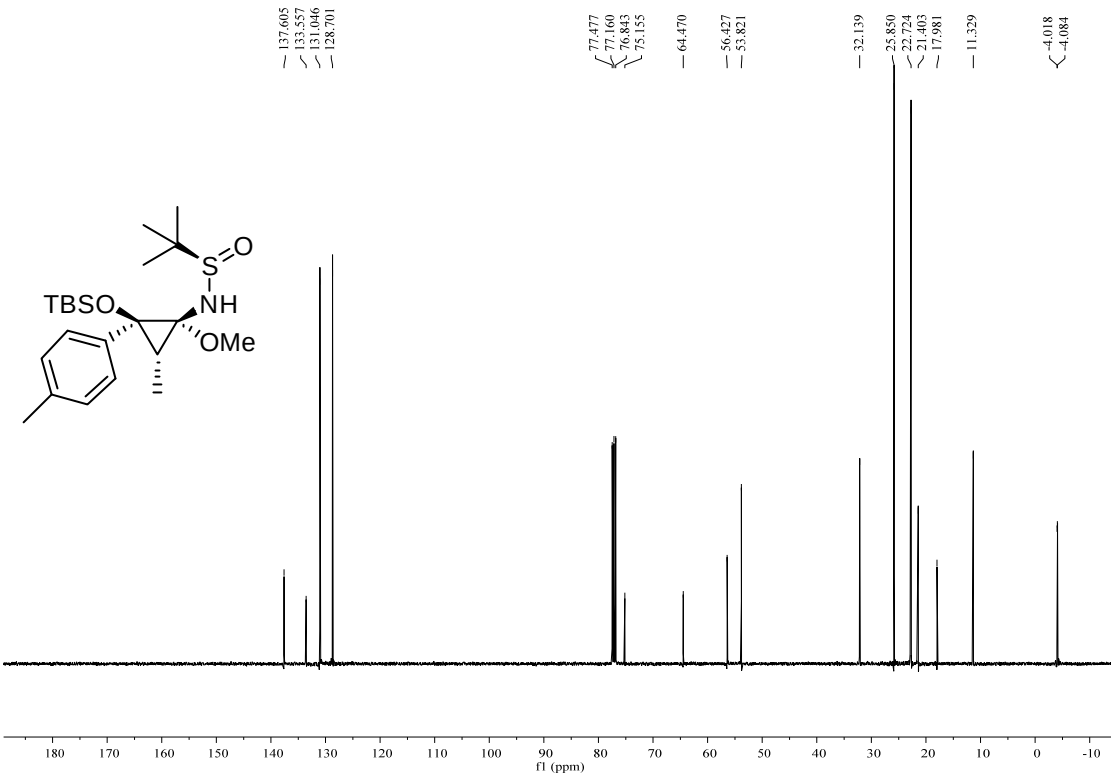
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3j**



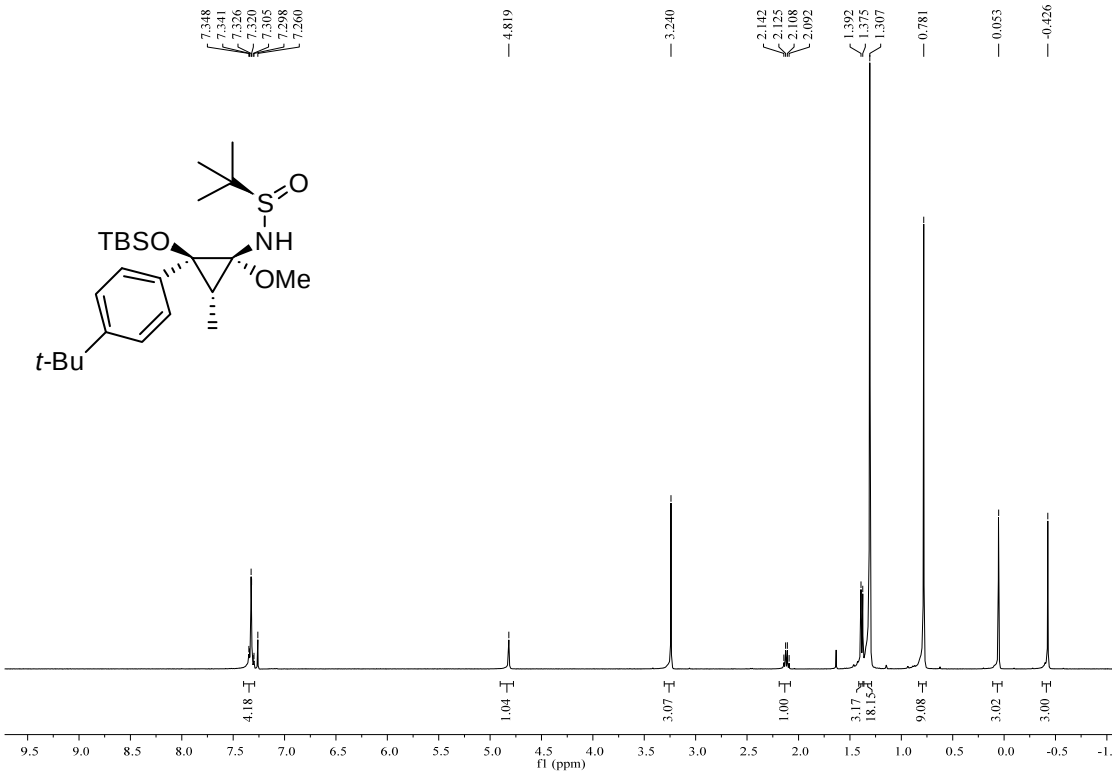
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3j**



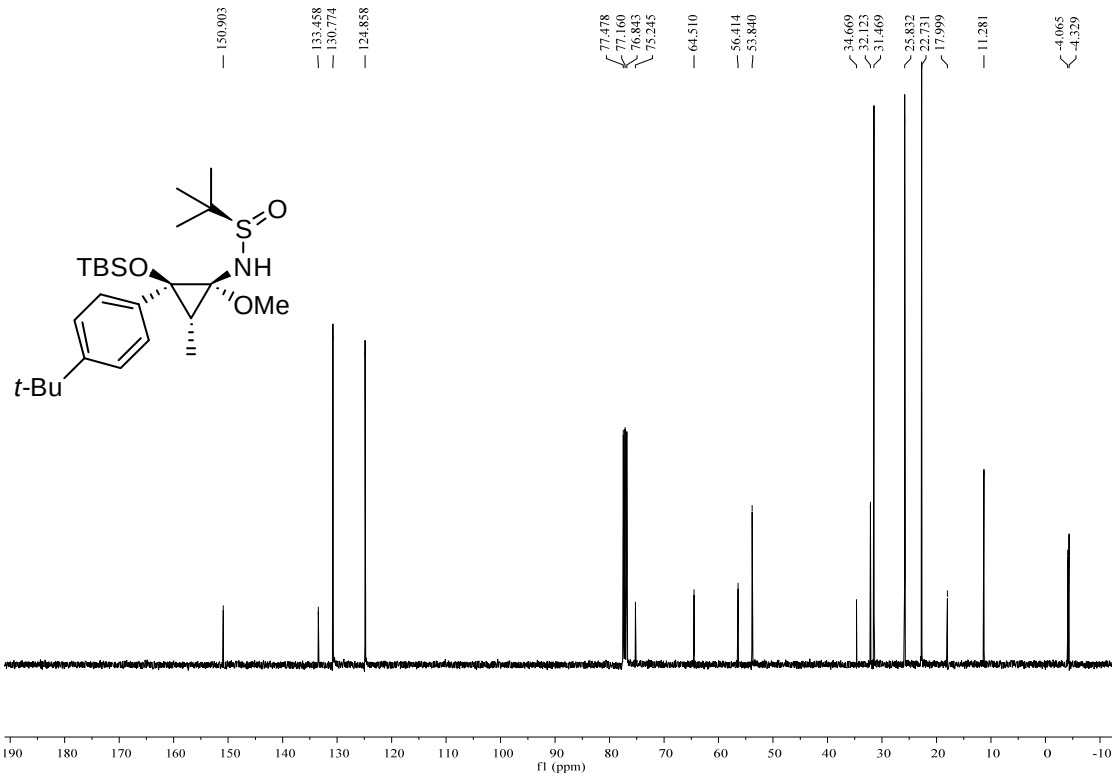
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3k**



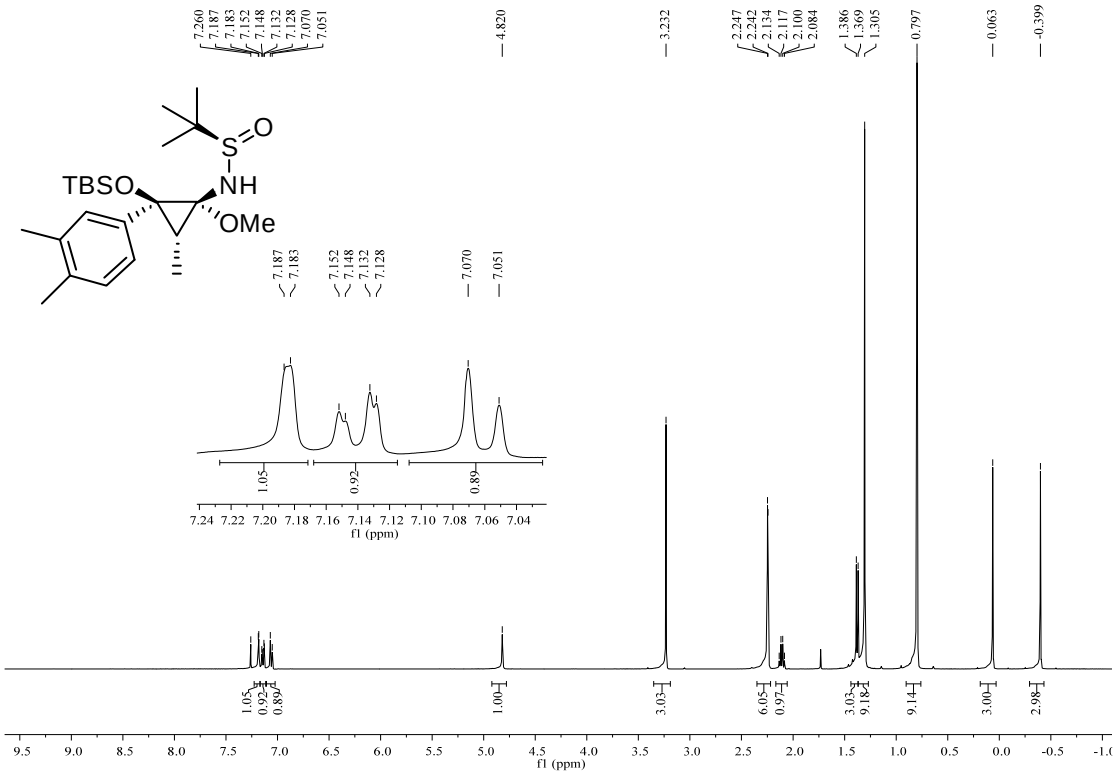
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3k**



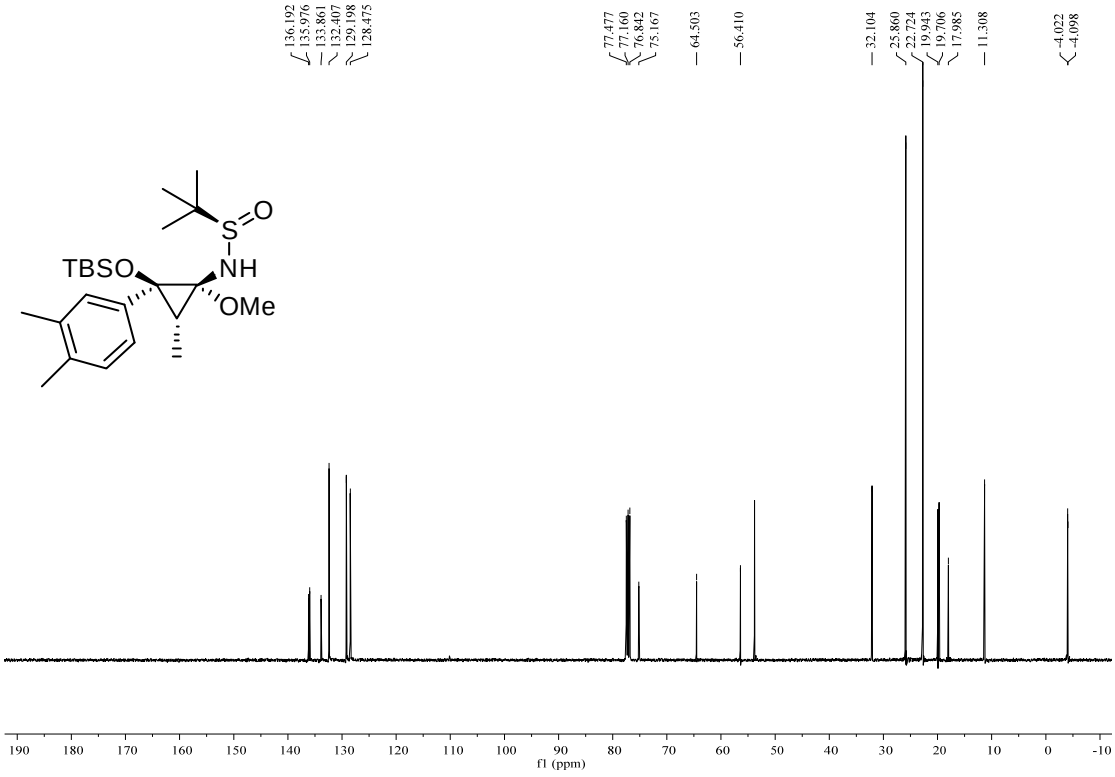
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3l**



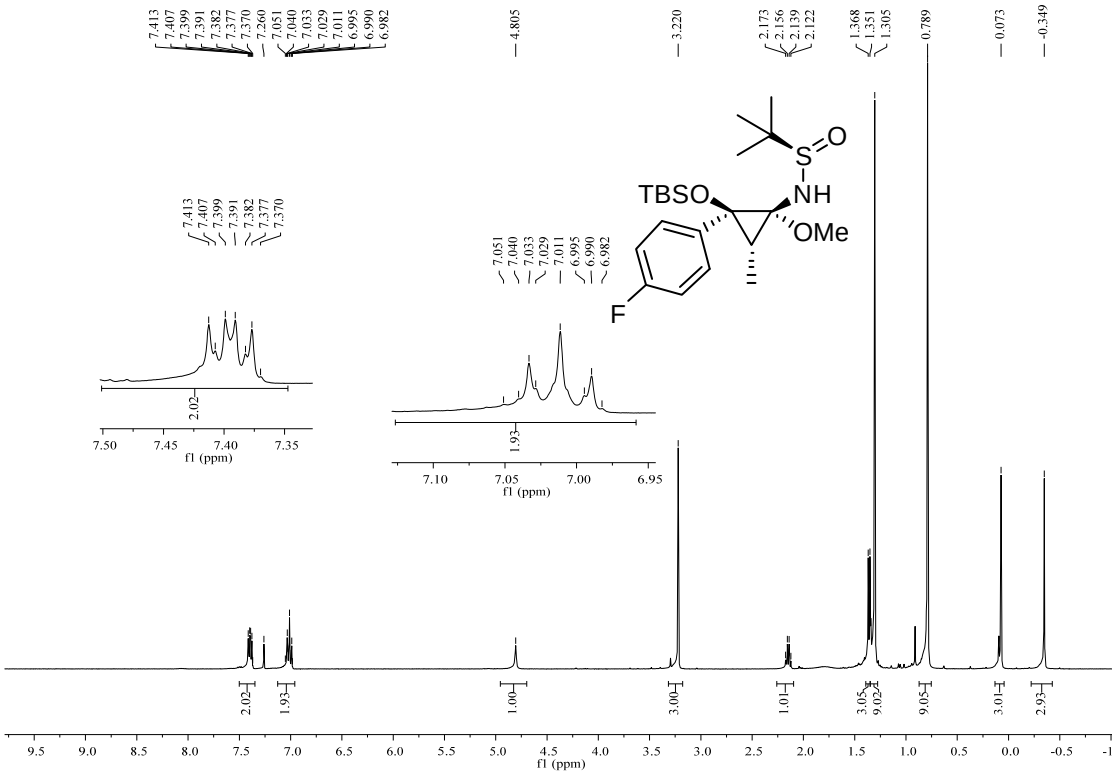
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3l**



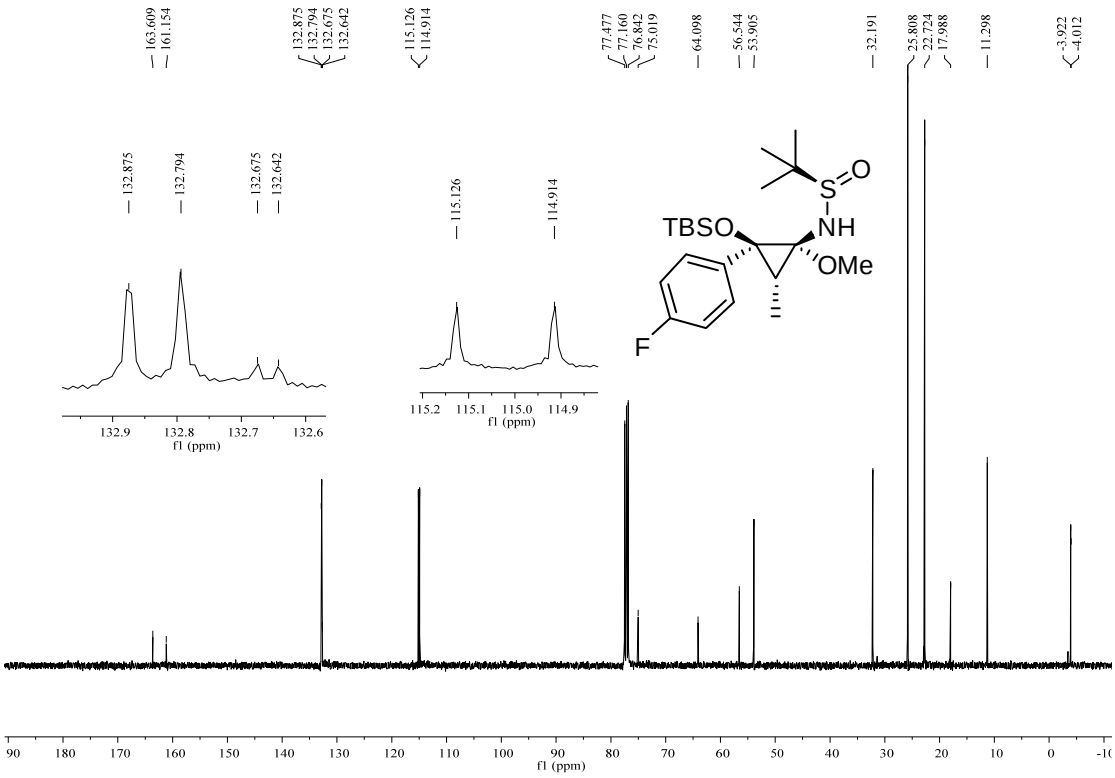
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3m**



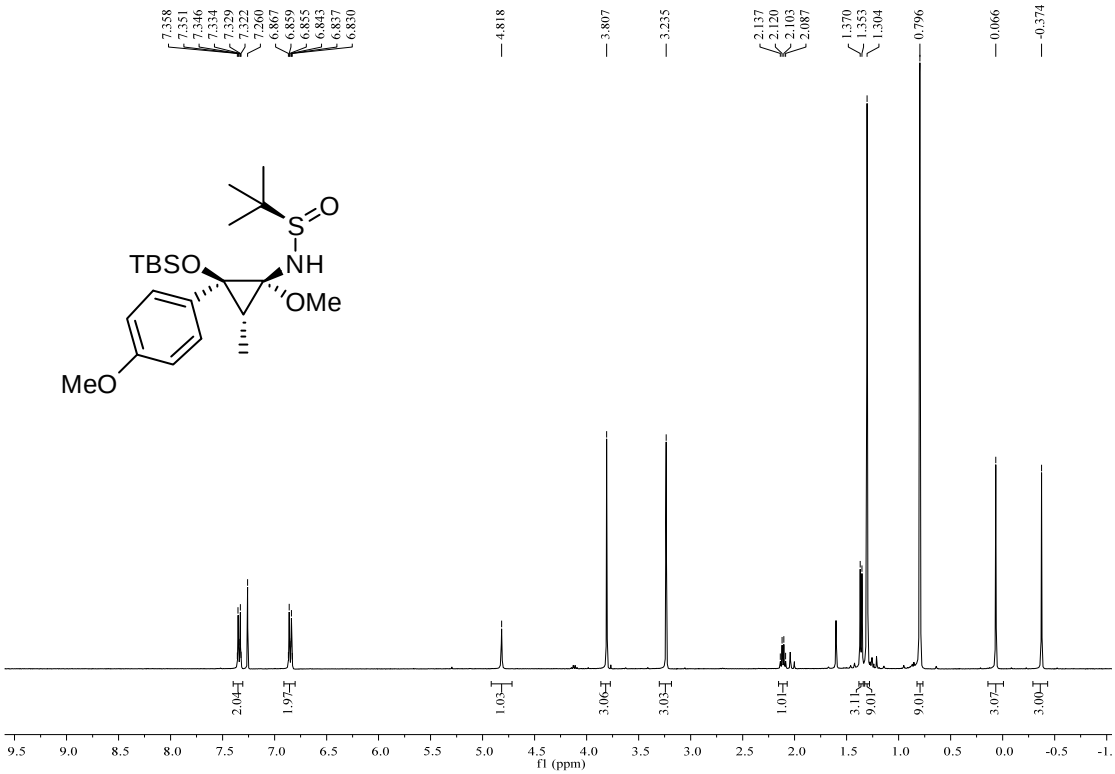
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3m**



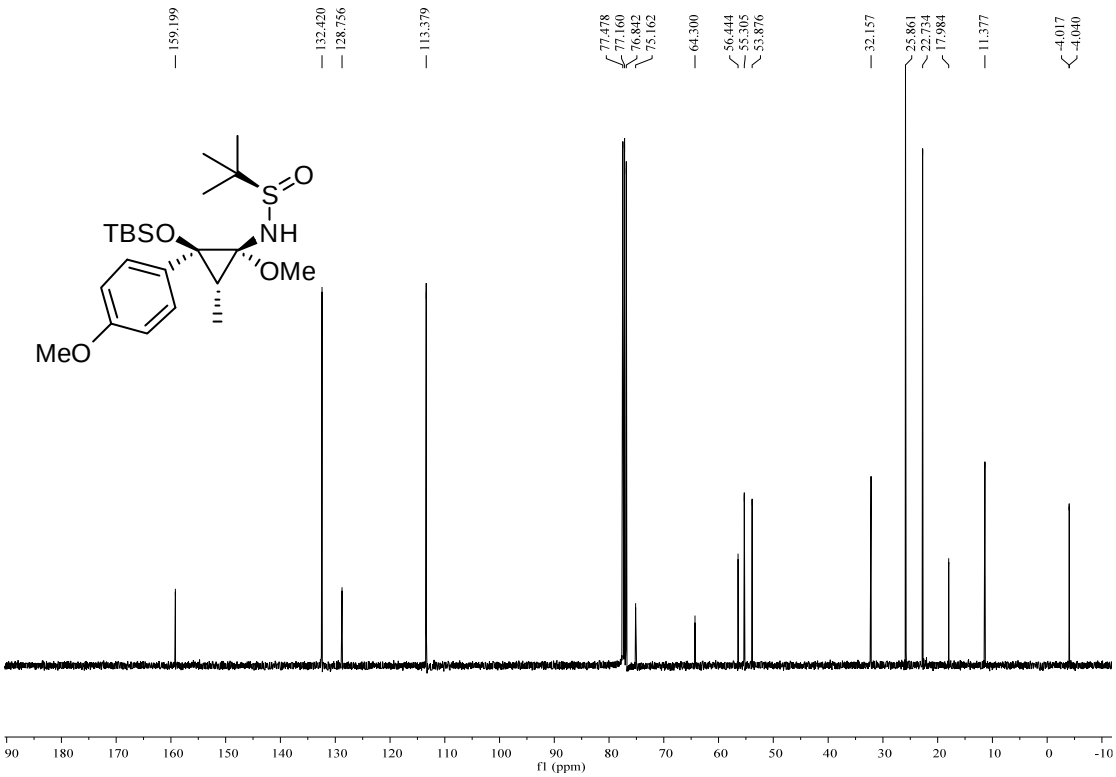
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3n**



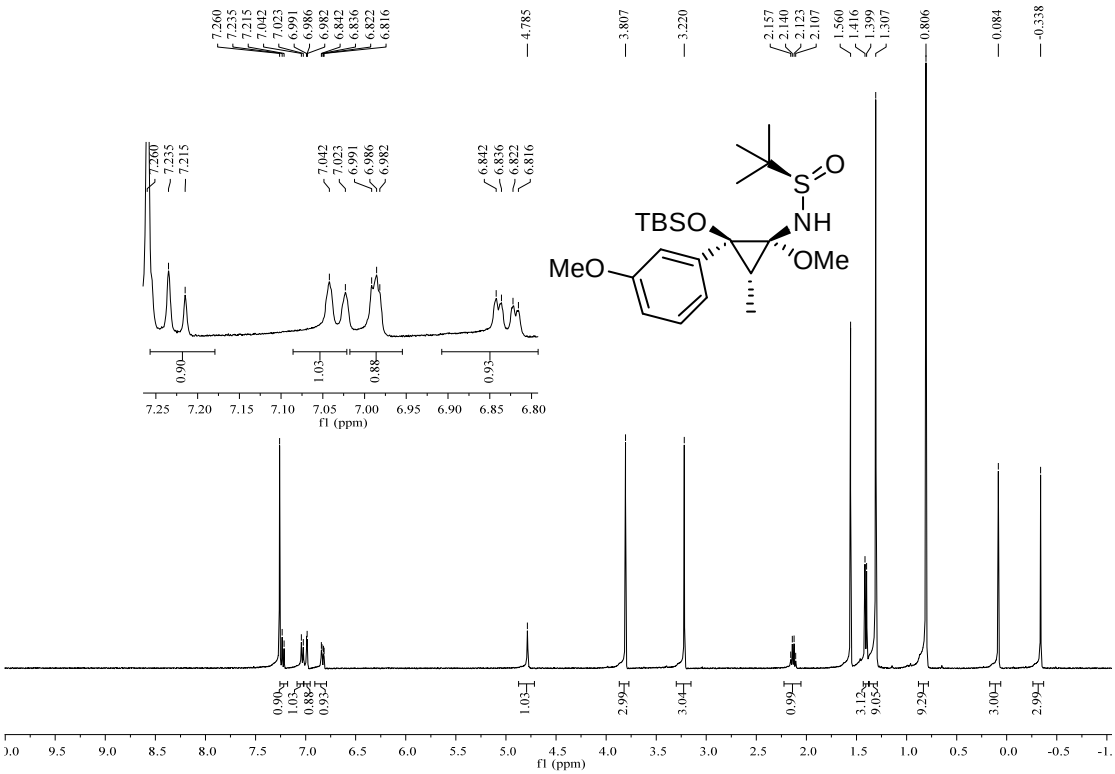
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3n**



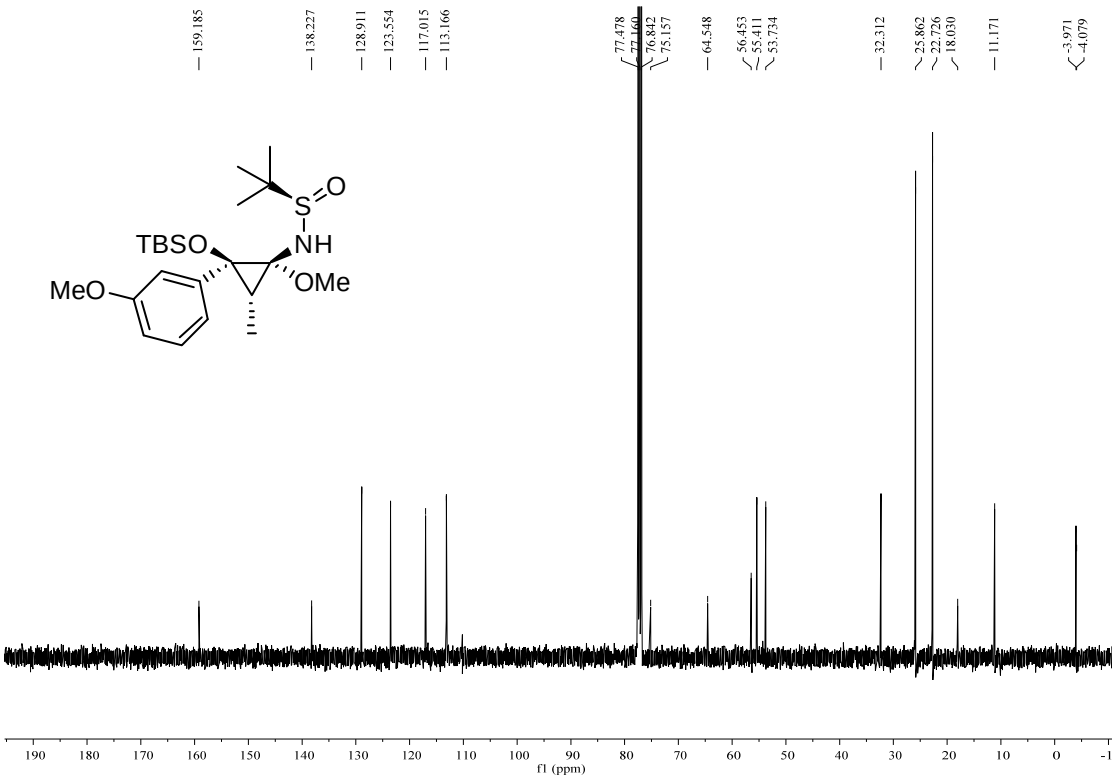
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3o**



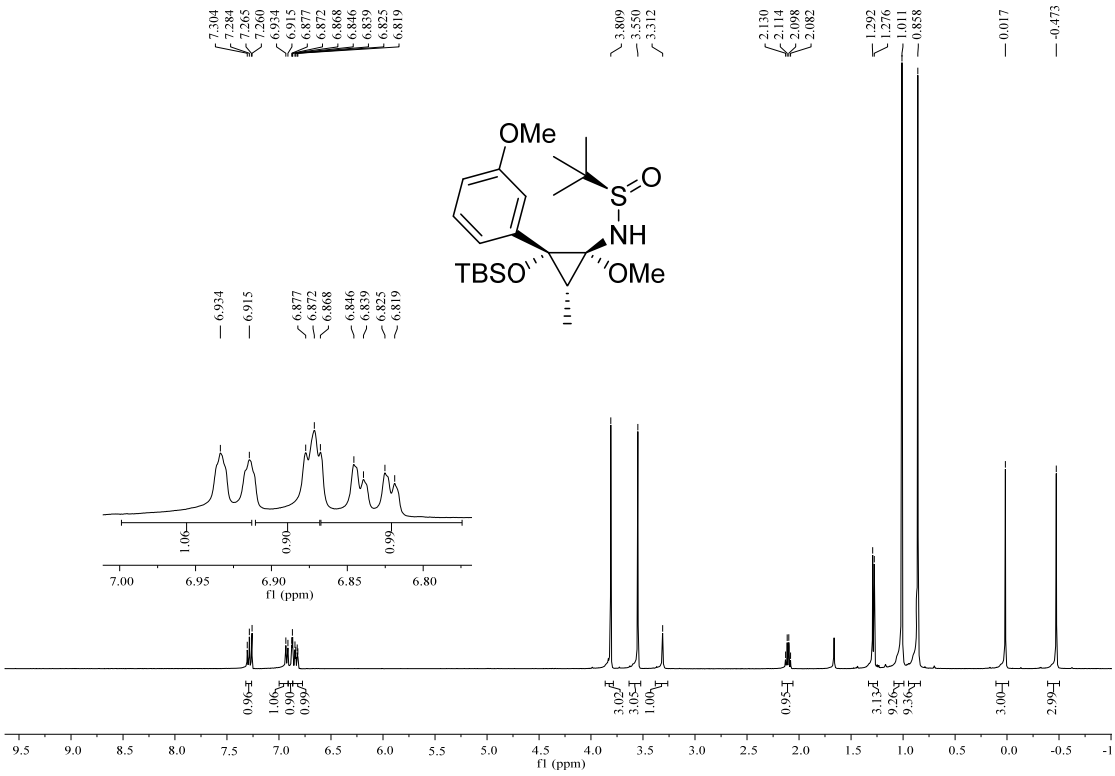
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3o**



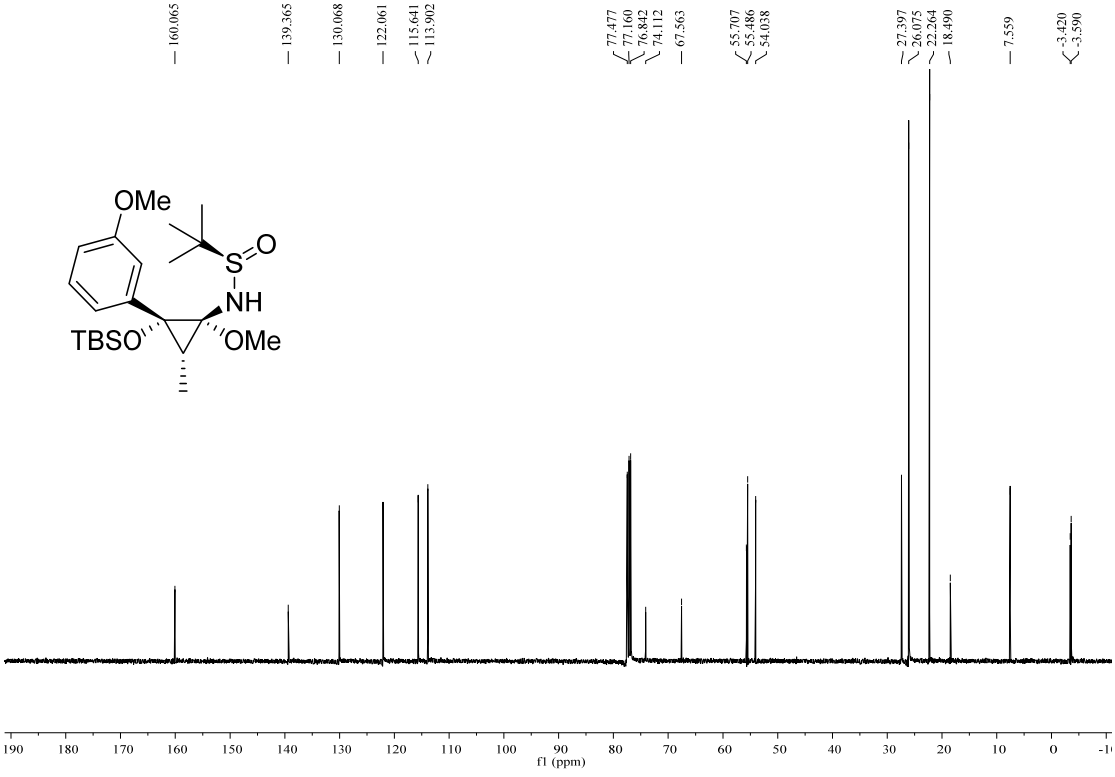
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3p** (major diastereomer)



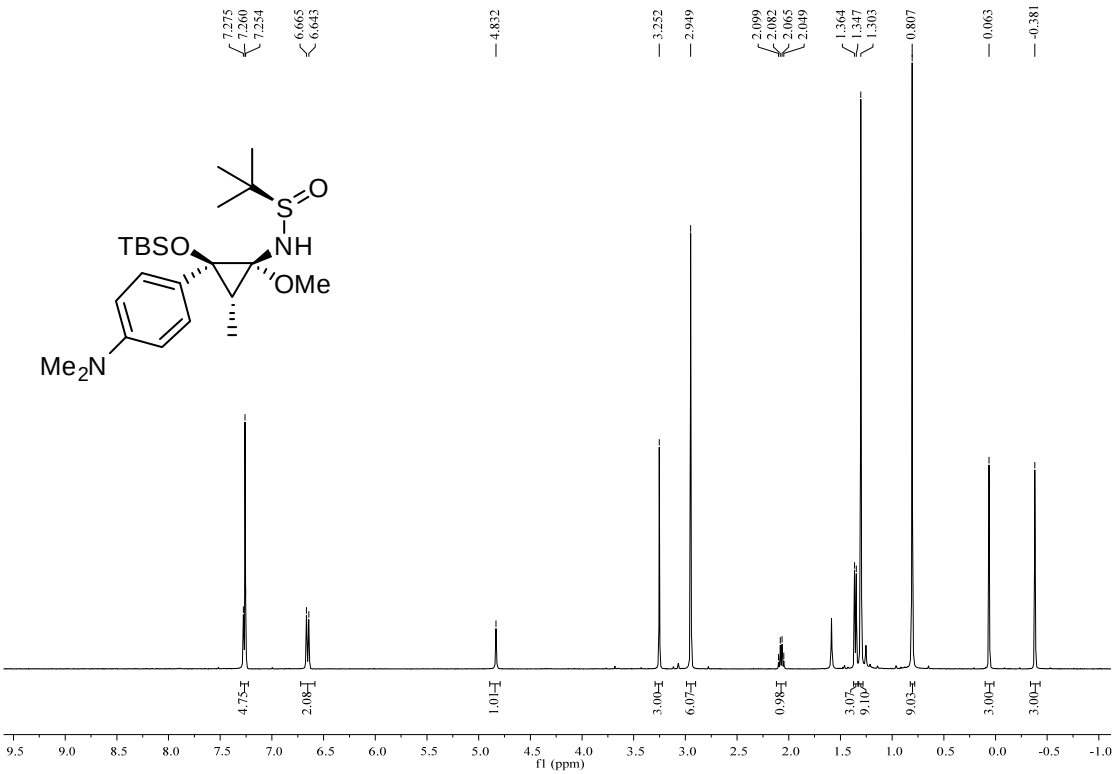
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3p** (major diastereomer)



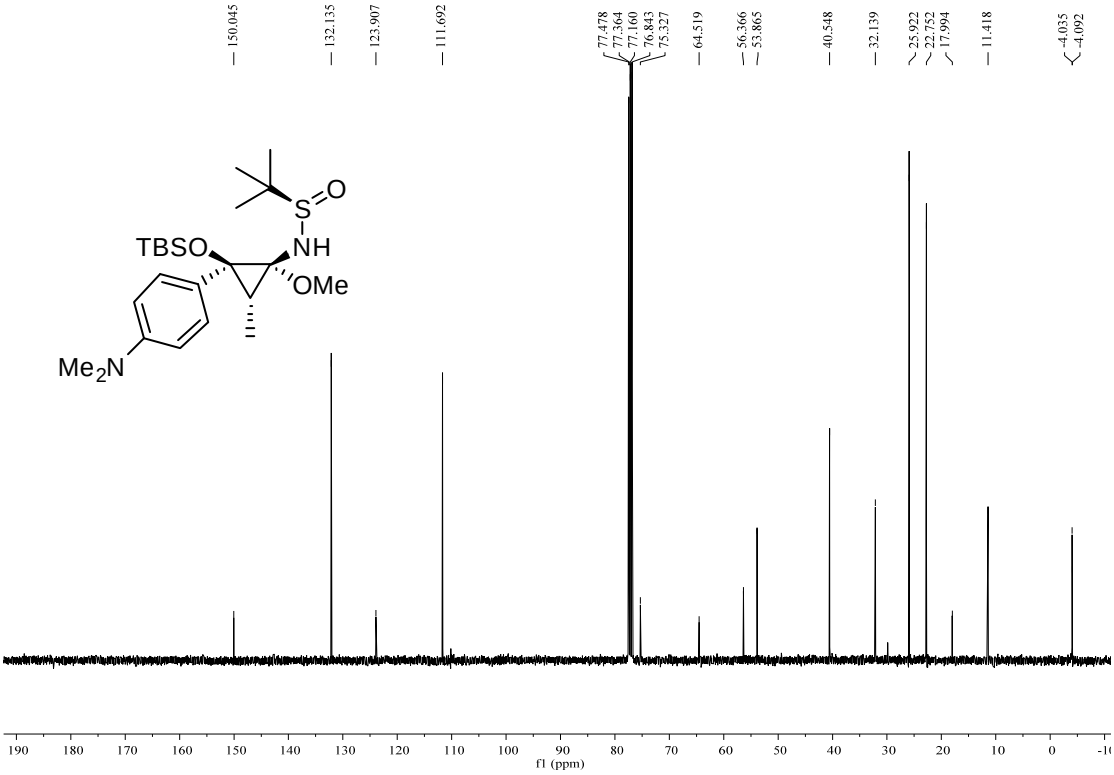
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3p'** (minor diastereomer)



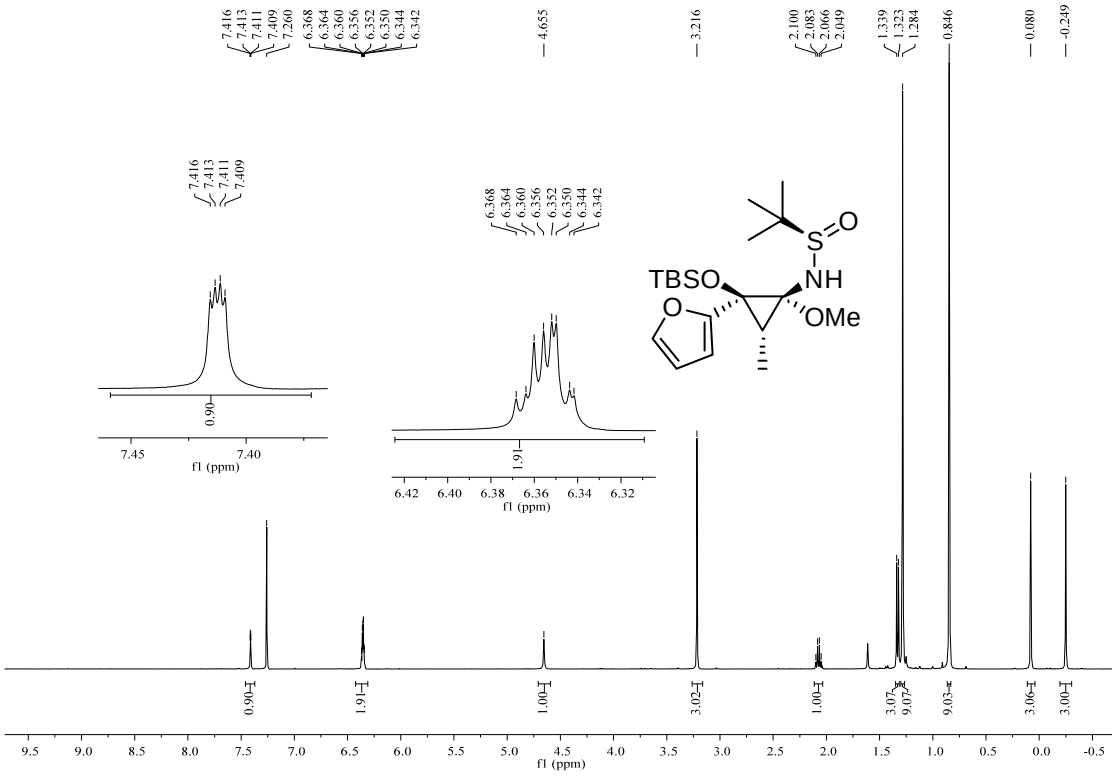
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3p'** (minor diastereomer)



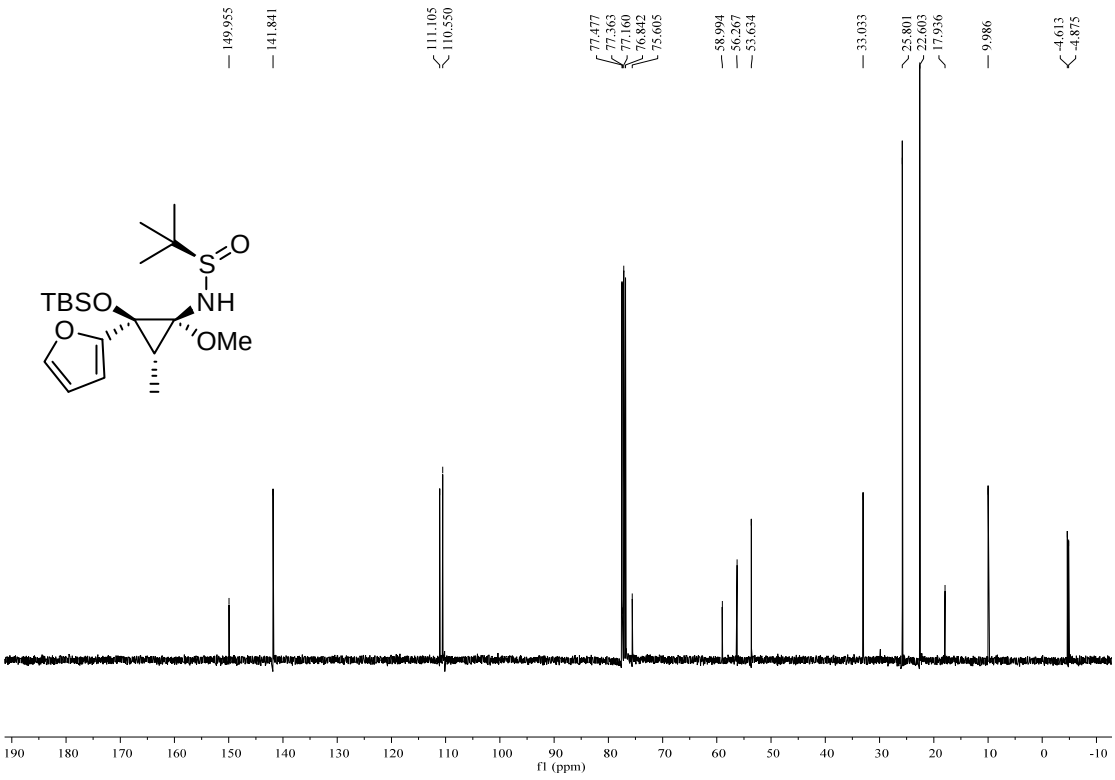
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3q**



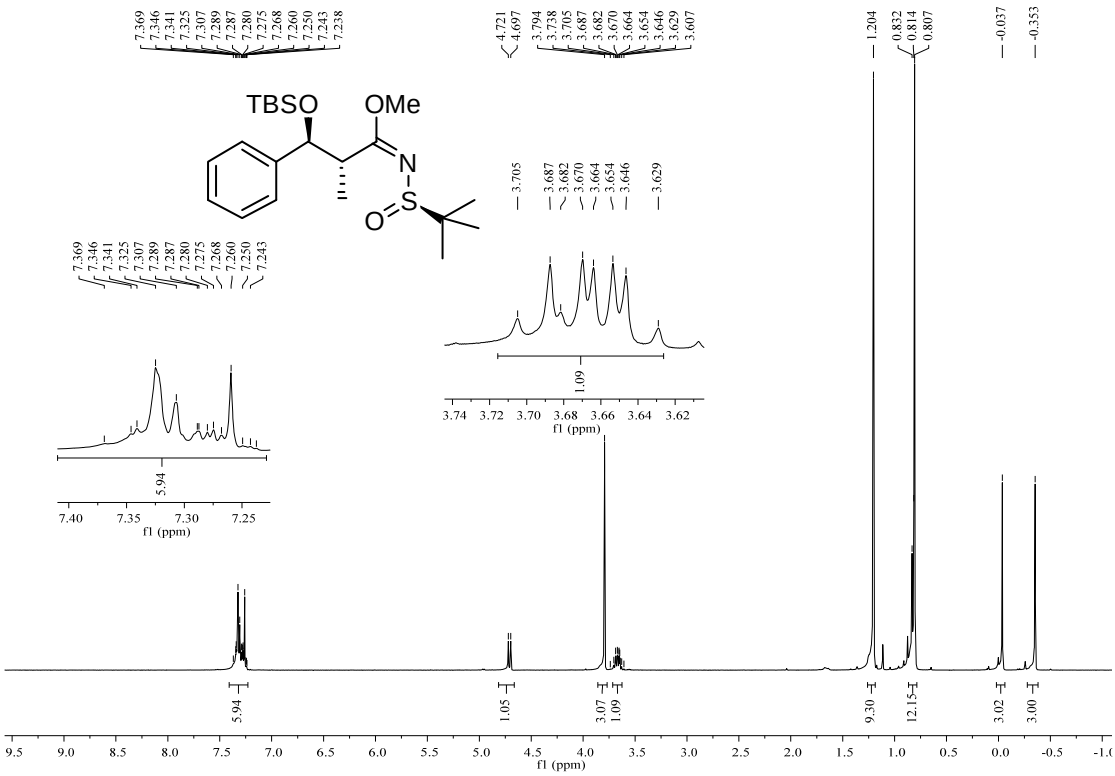
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3q**



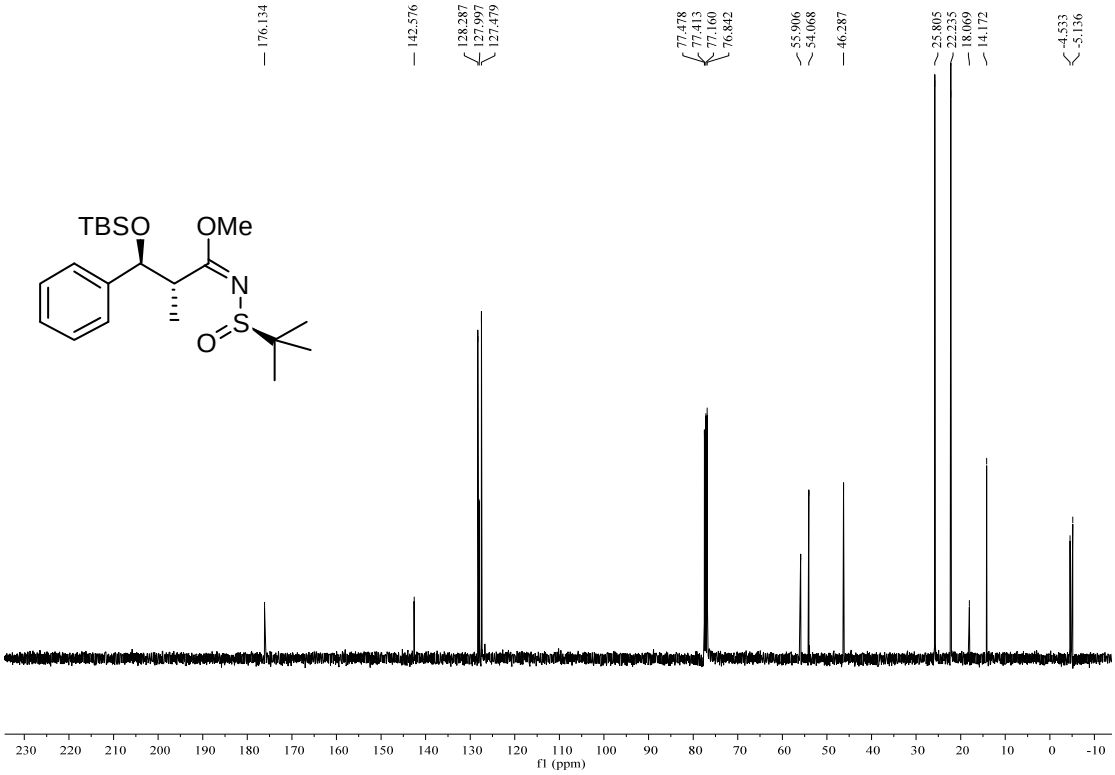
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3r**



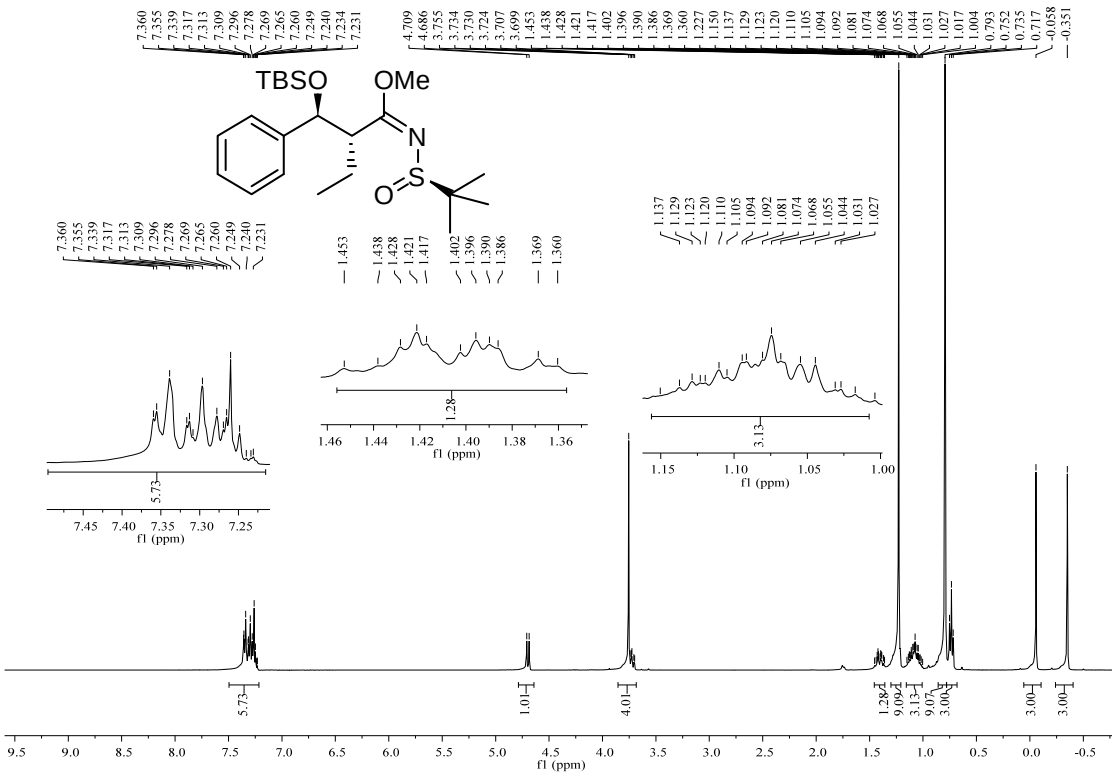
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3r**



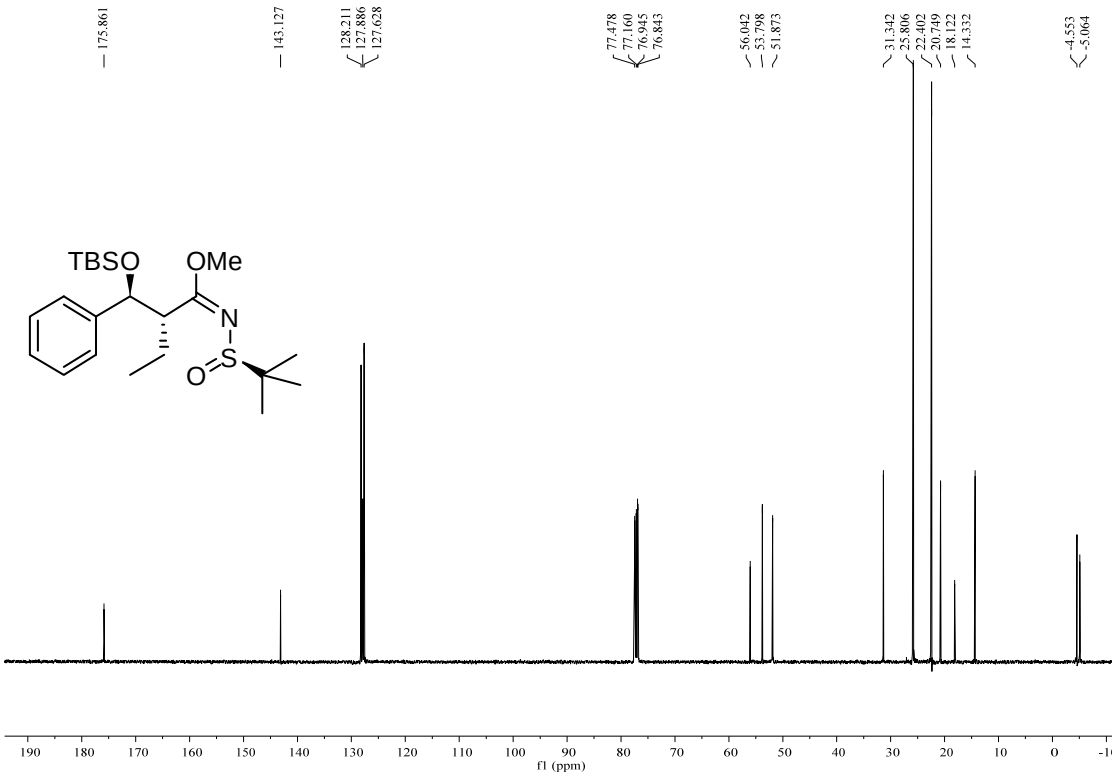
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5a**



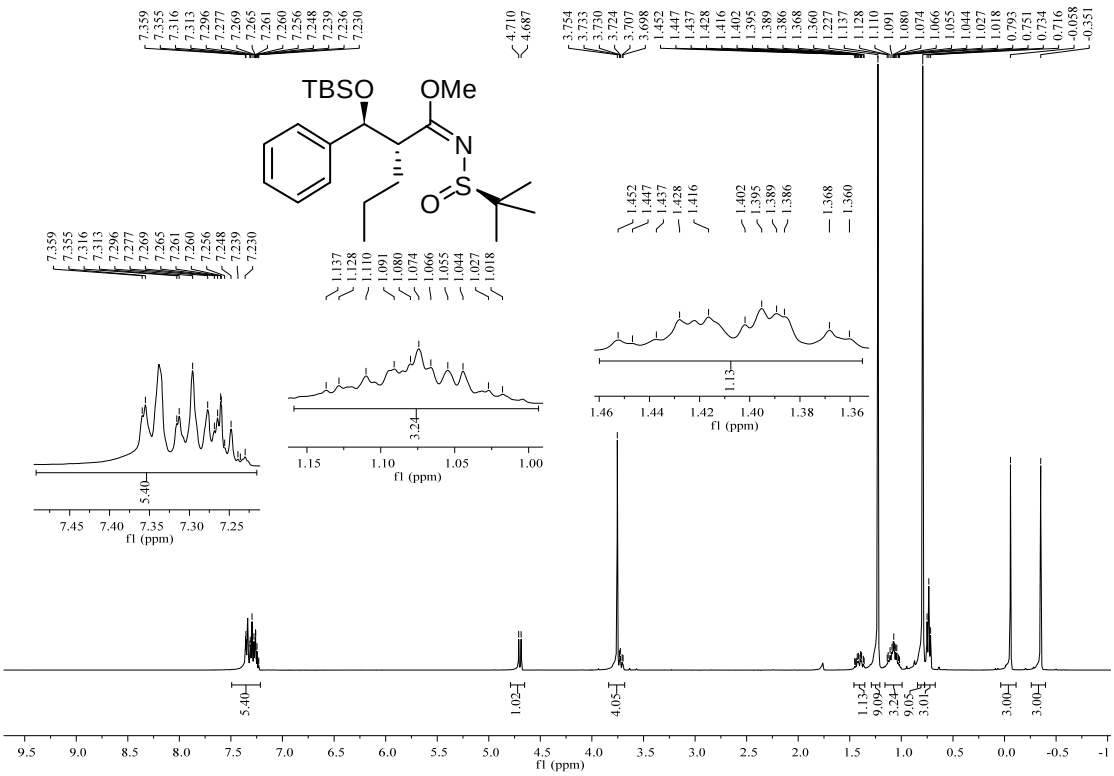
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5a**



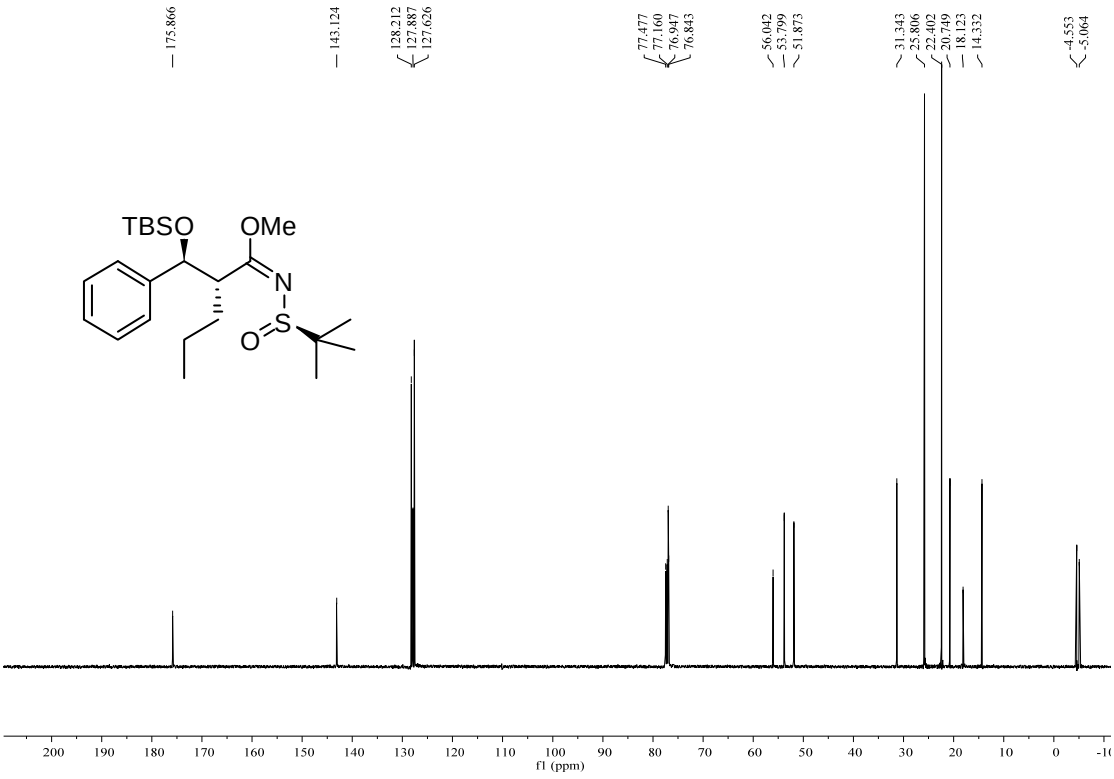
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5b**



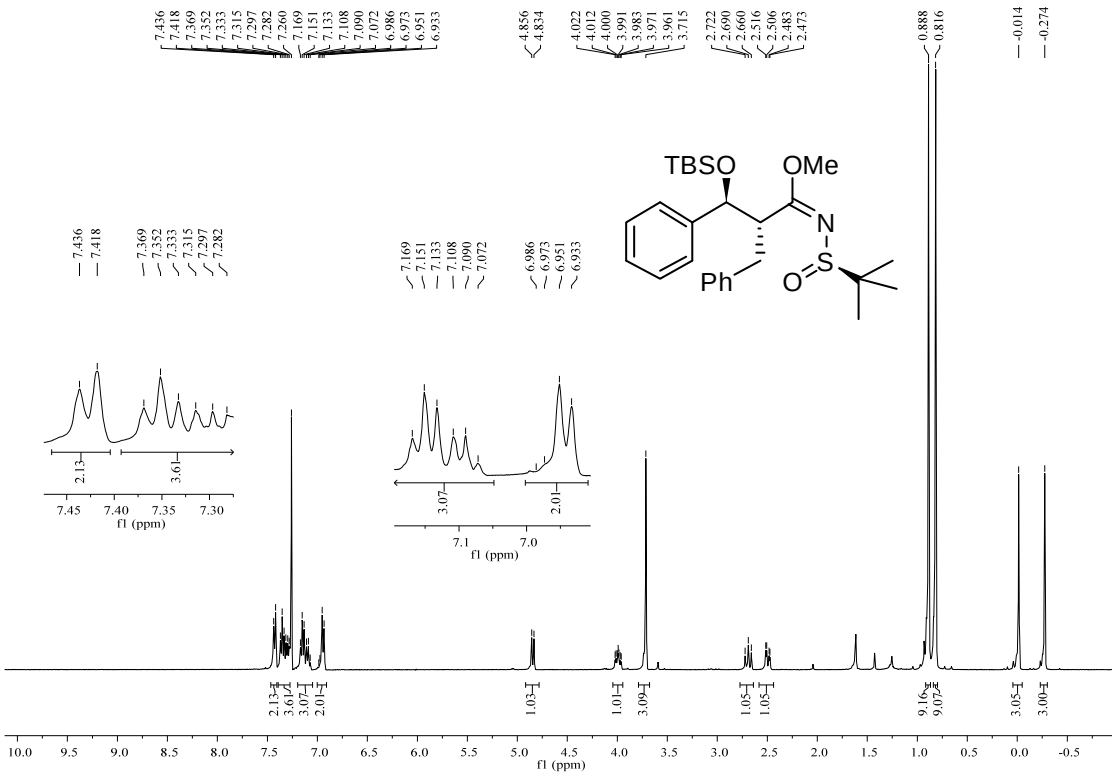
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5b**



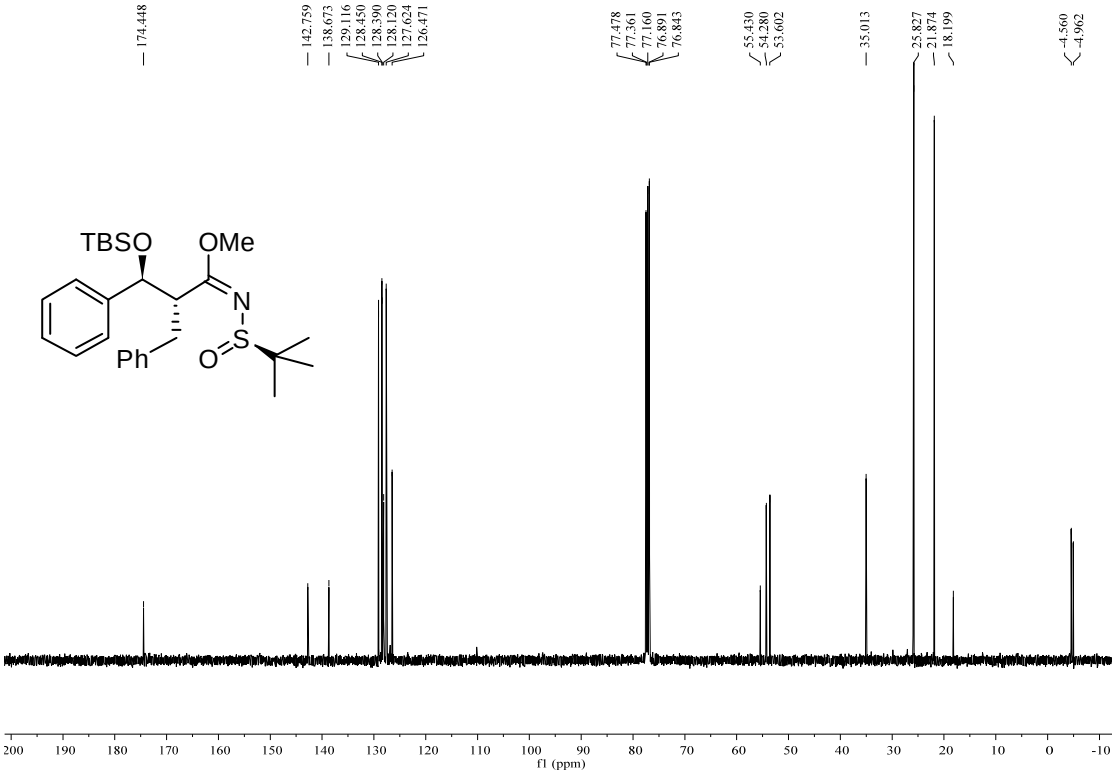
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5c**



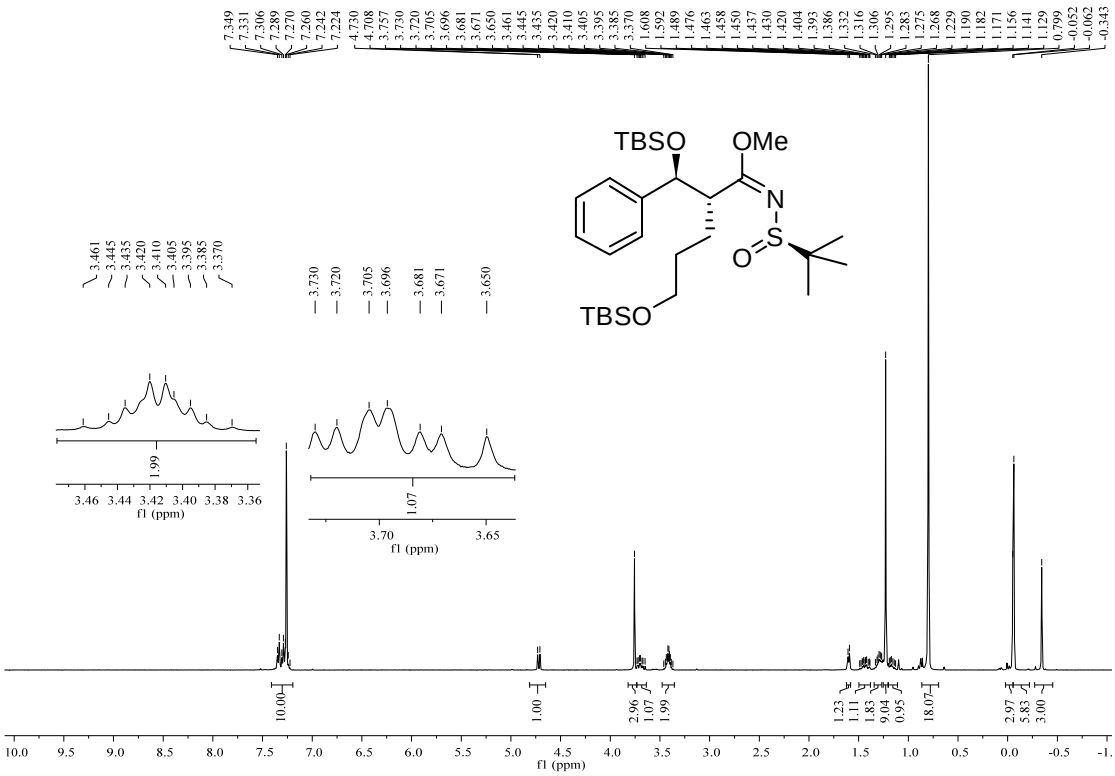
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5c**



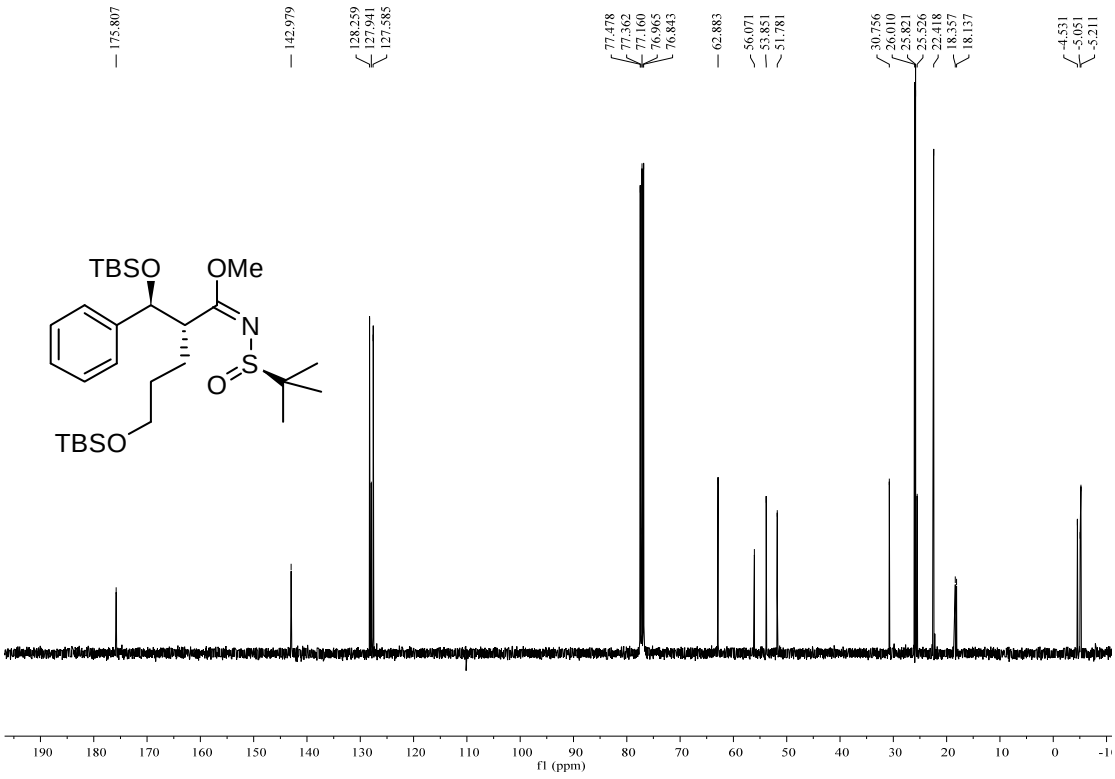
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5d**



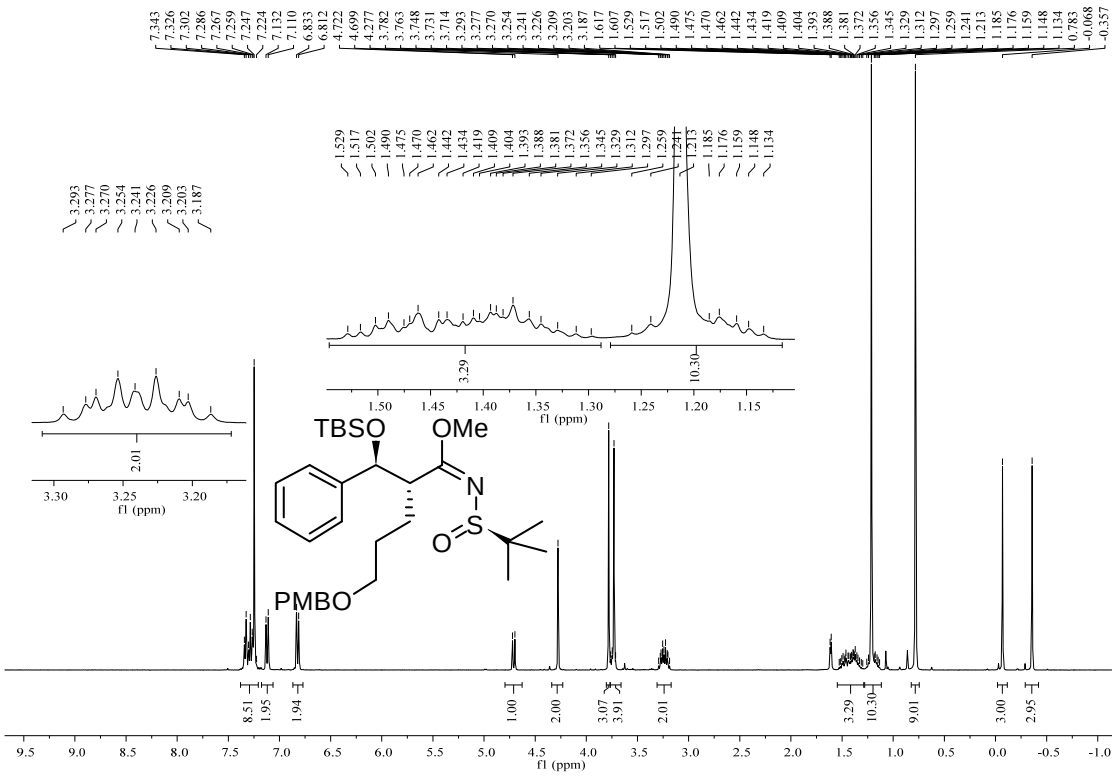
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5d**



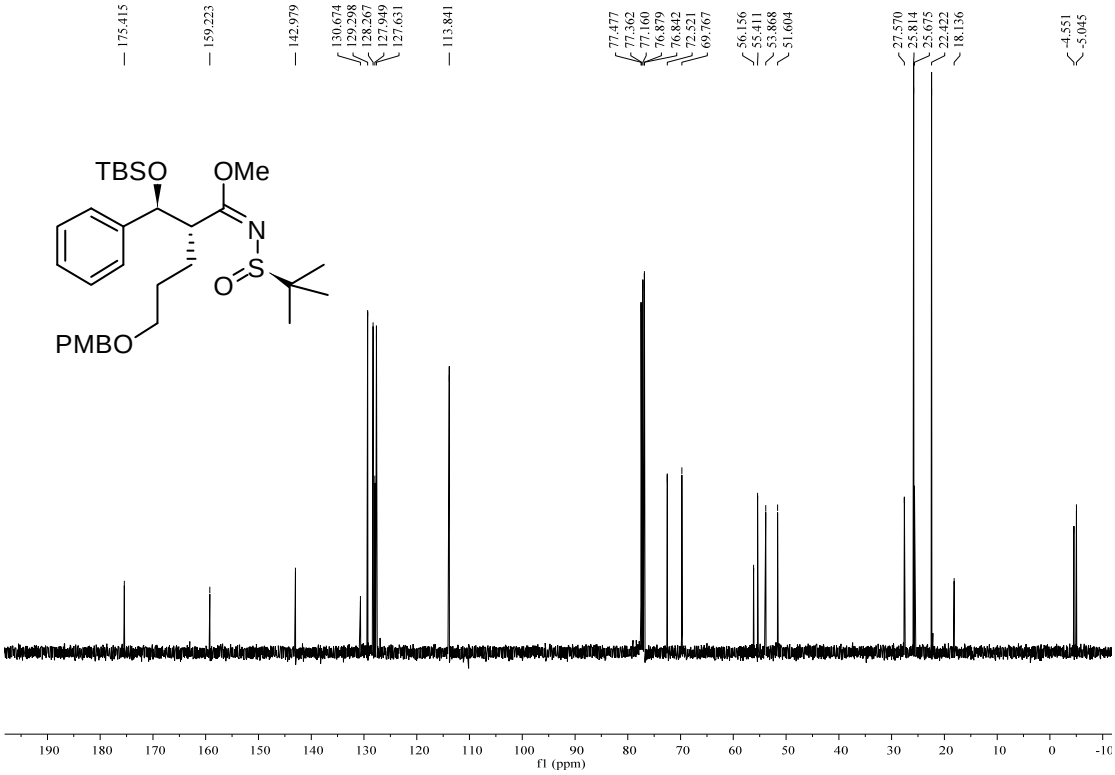
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5e**



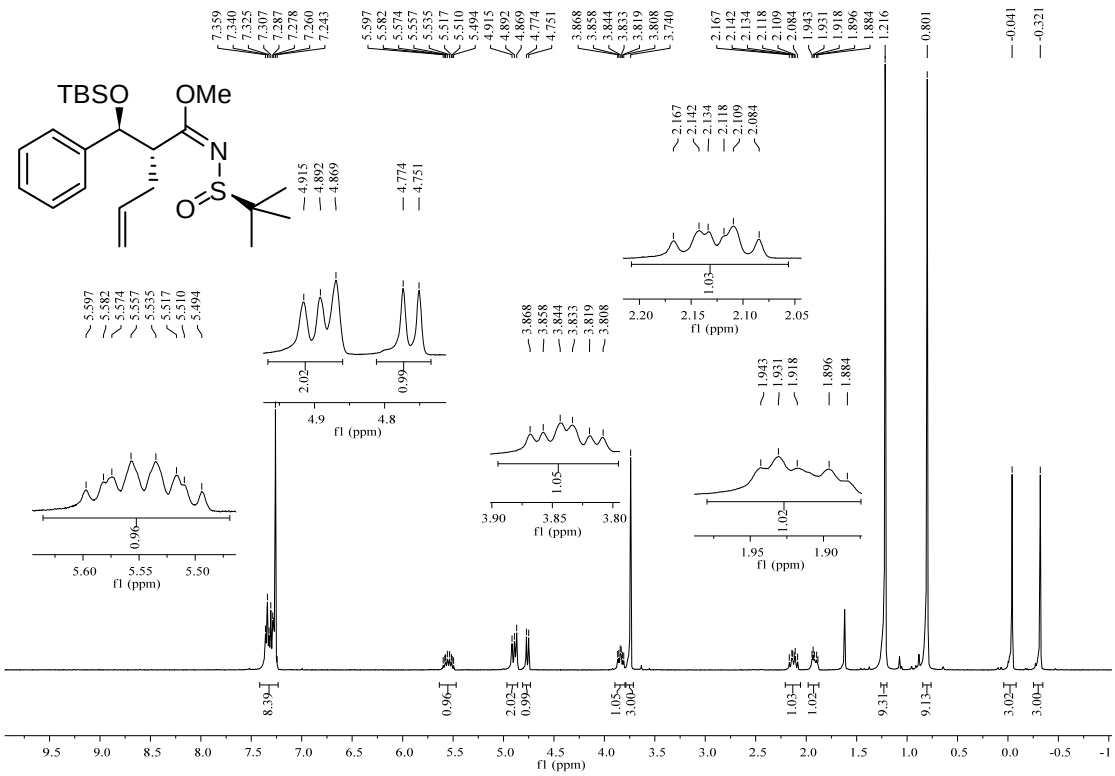
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5e**



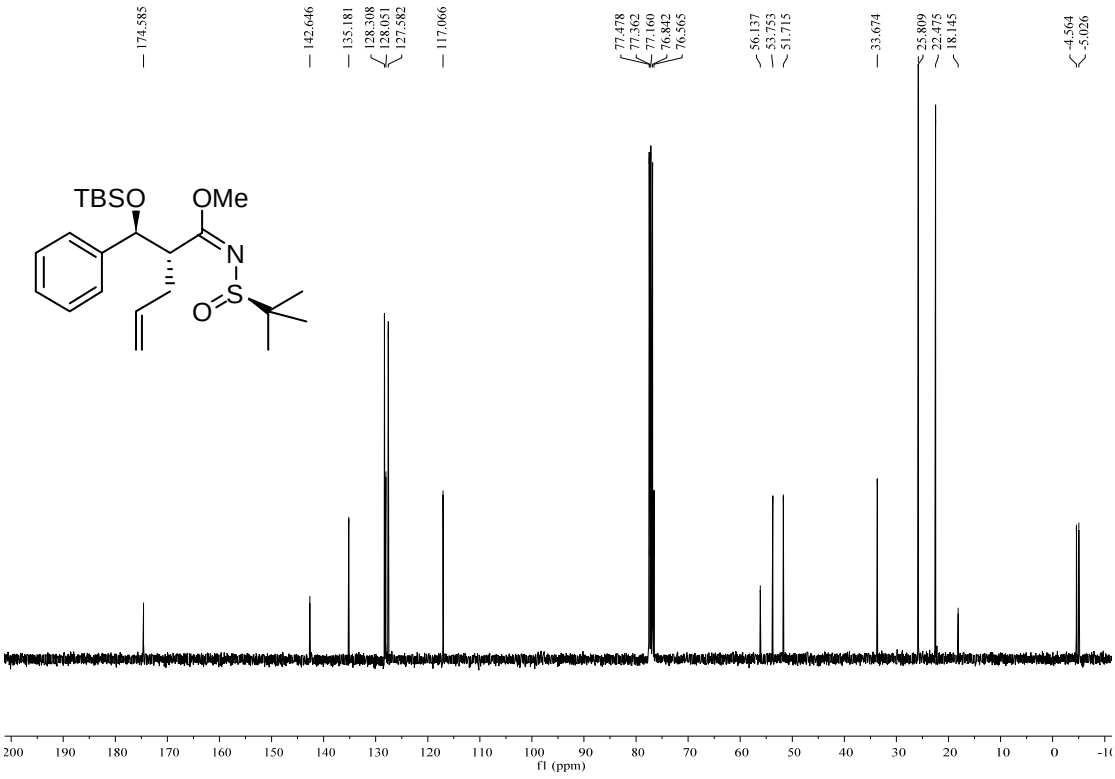
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5f**



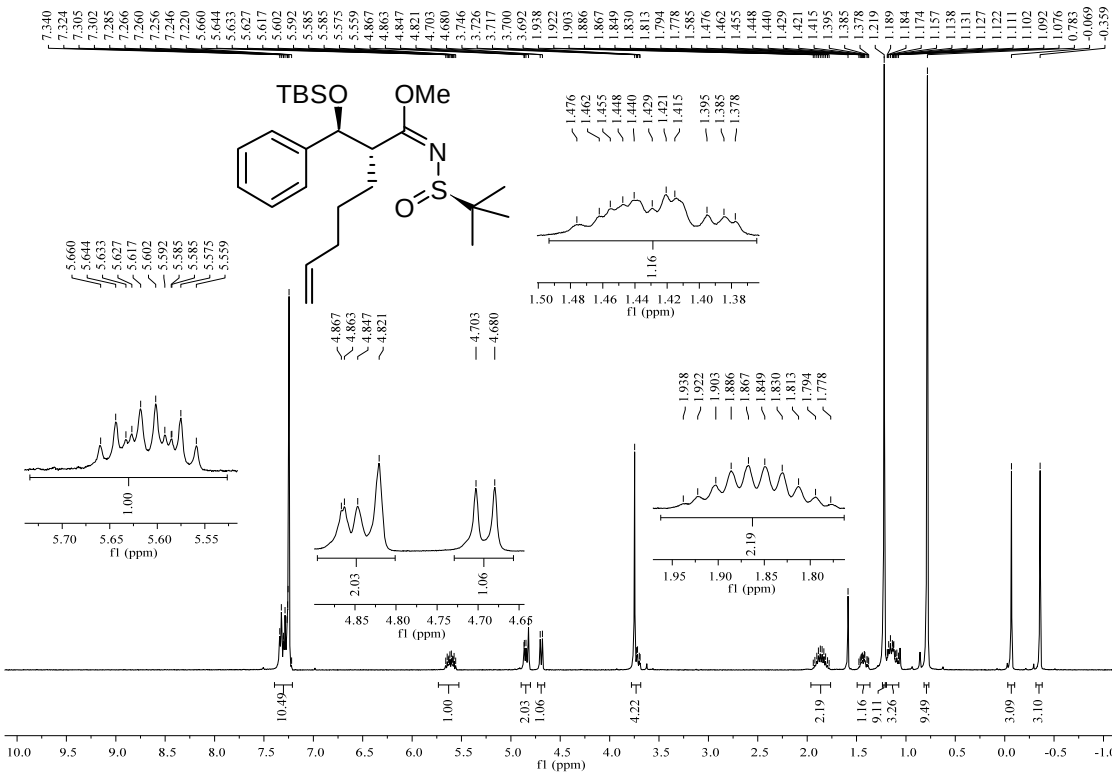
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5f**



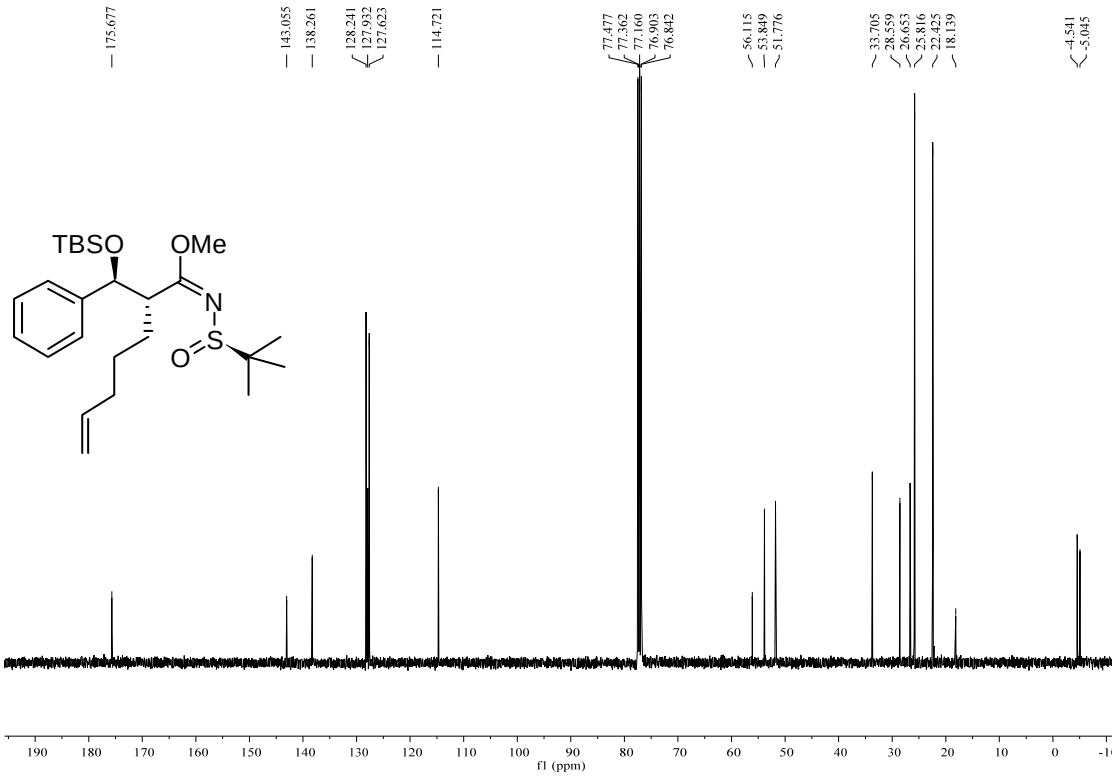
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5g**



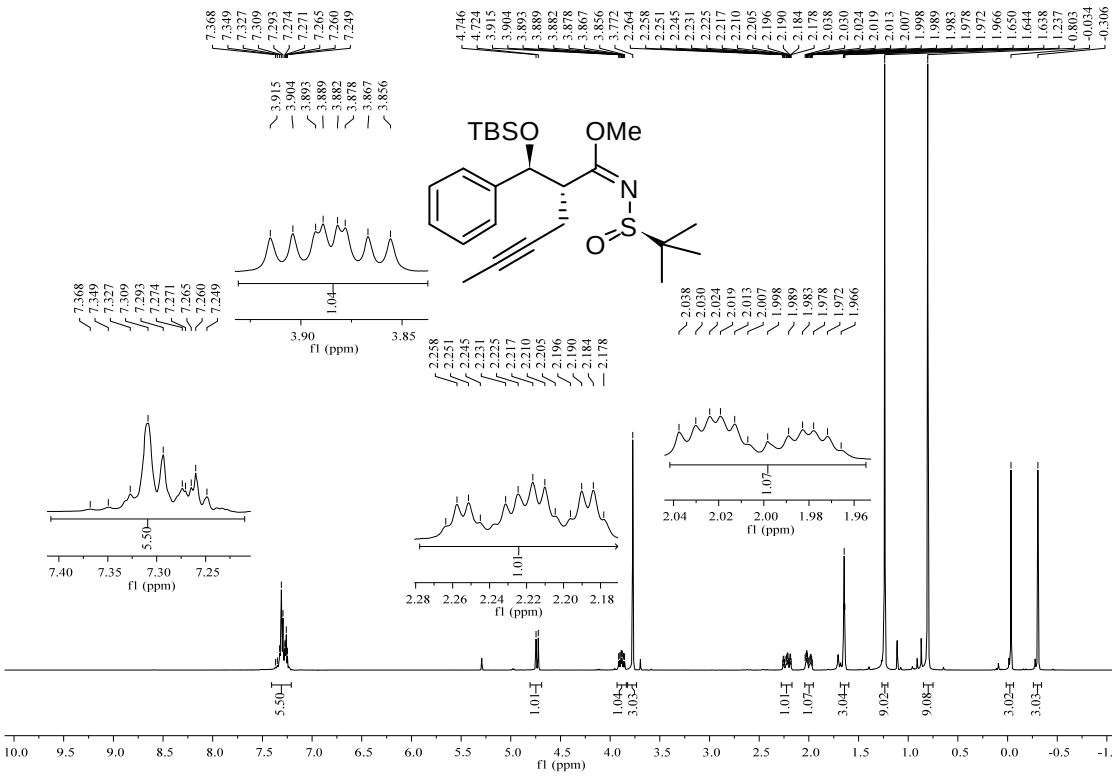
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5g**



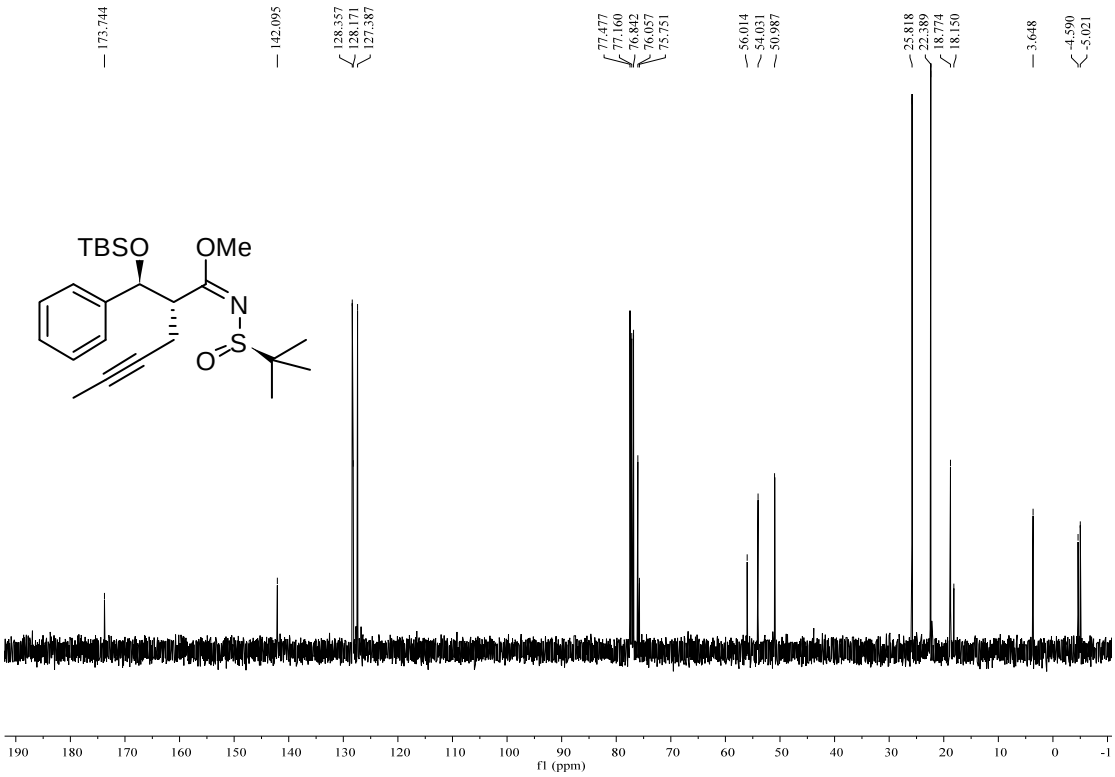
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5h**



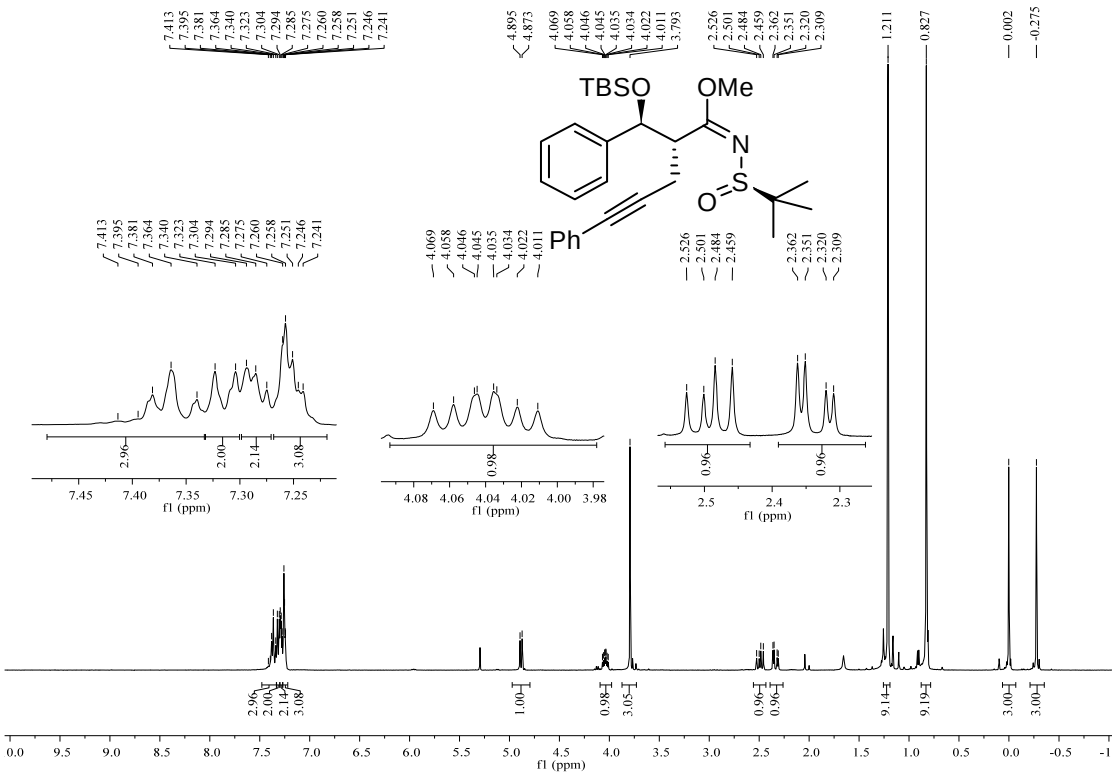
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5h**



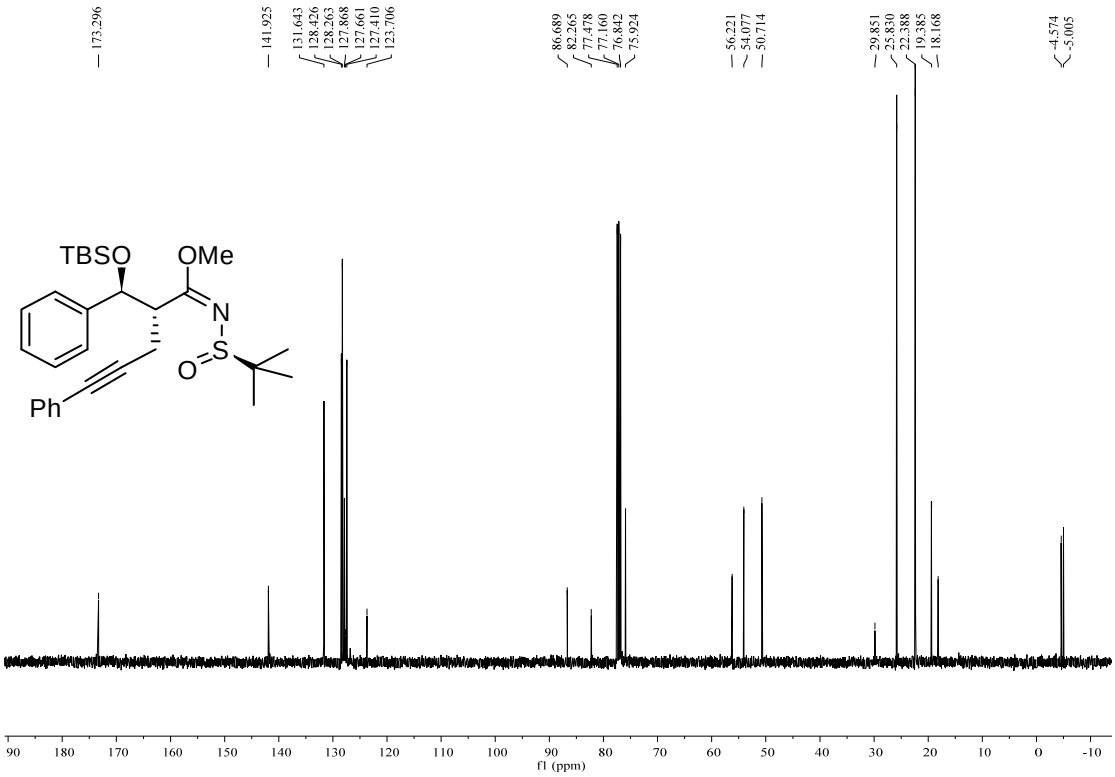
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5i**



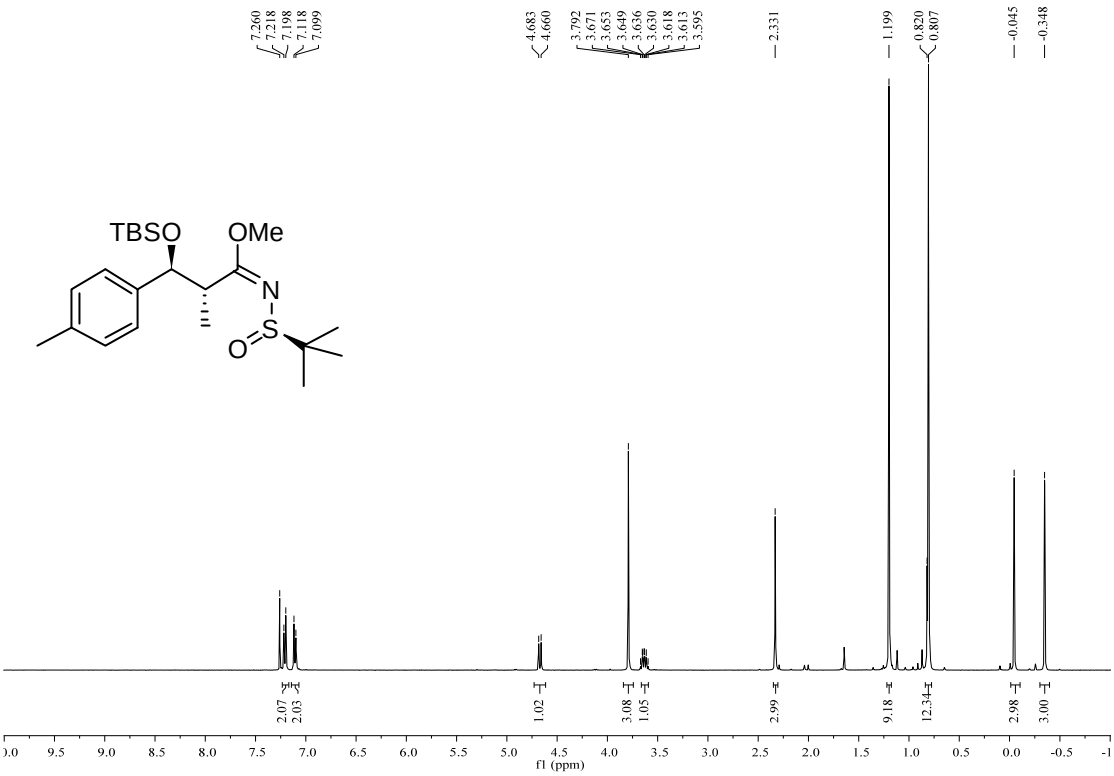
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5i**



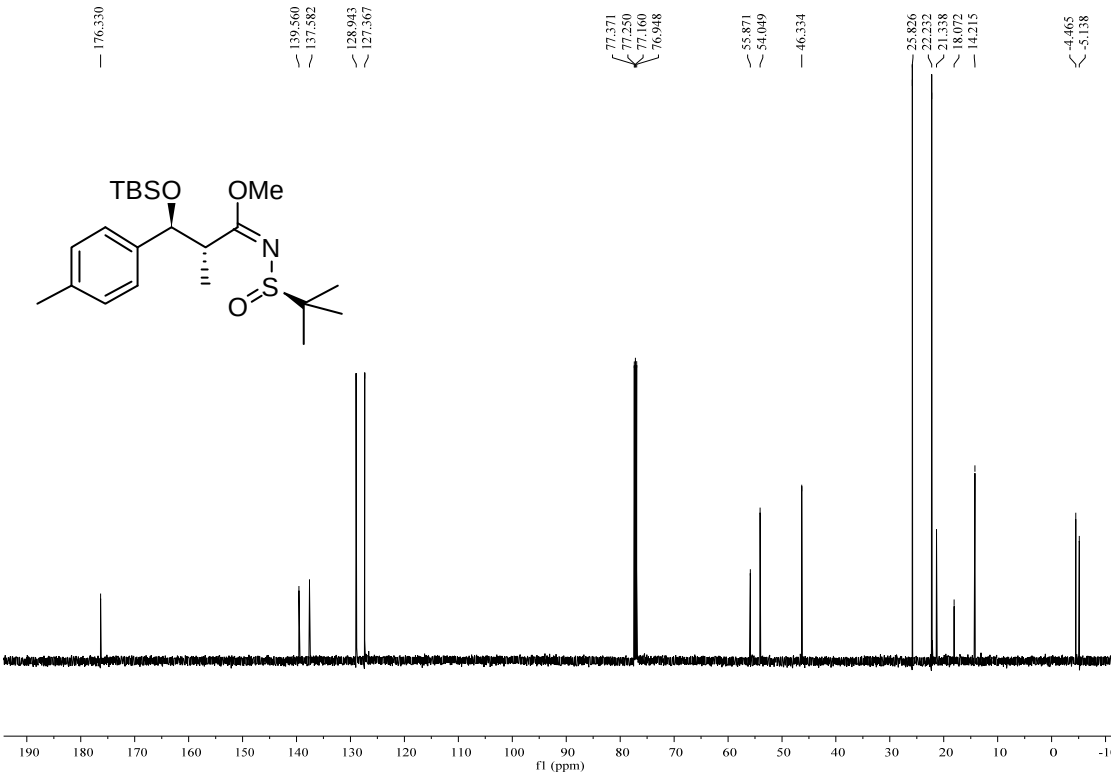
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5j**



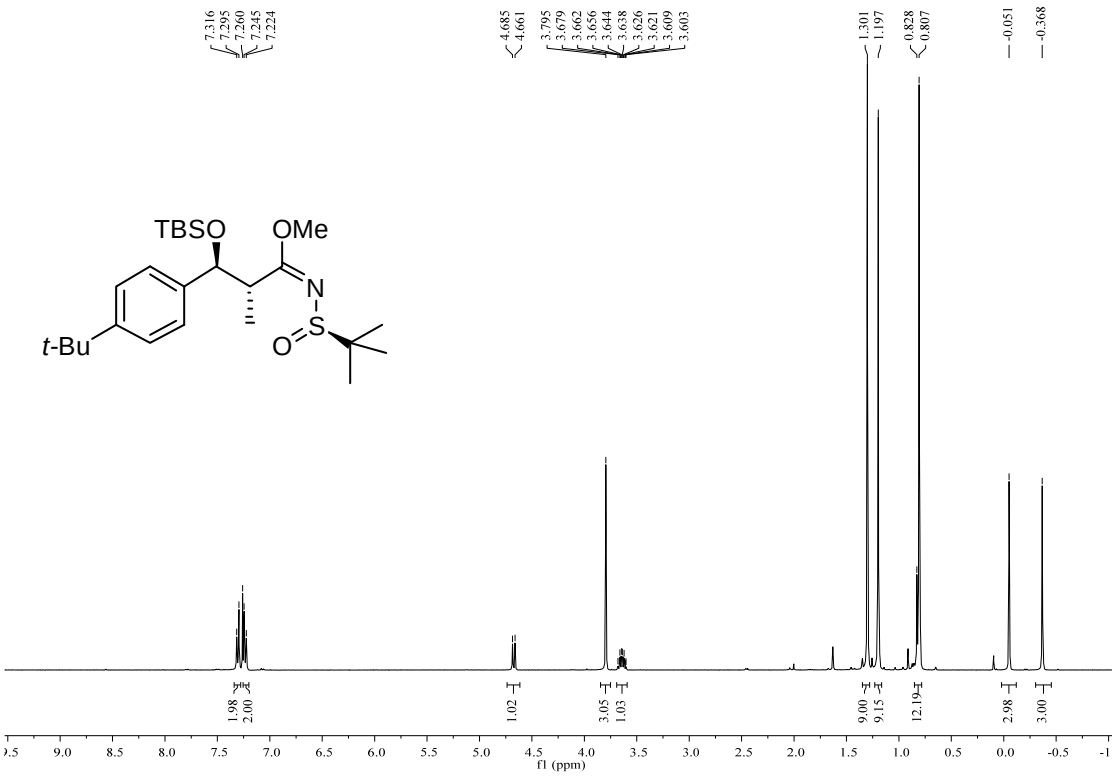
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5j**



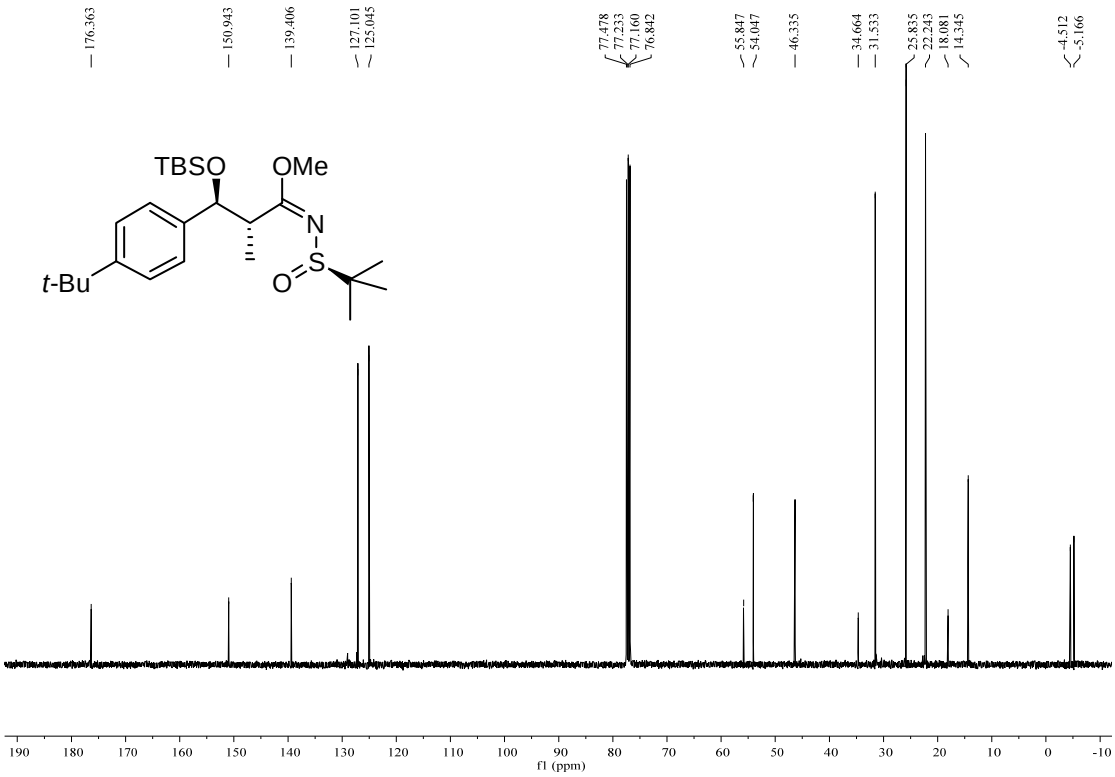
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5k**



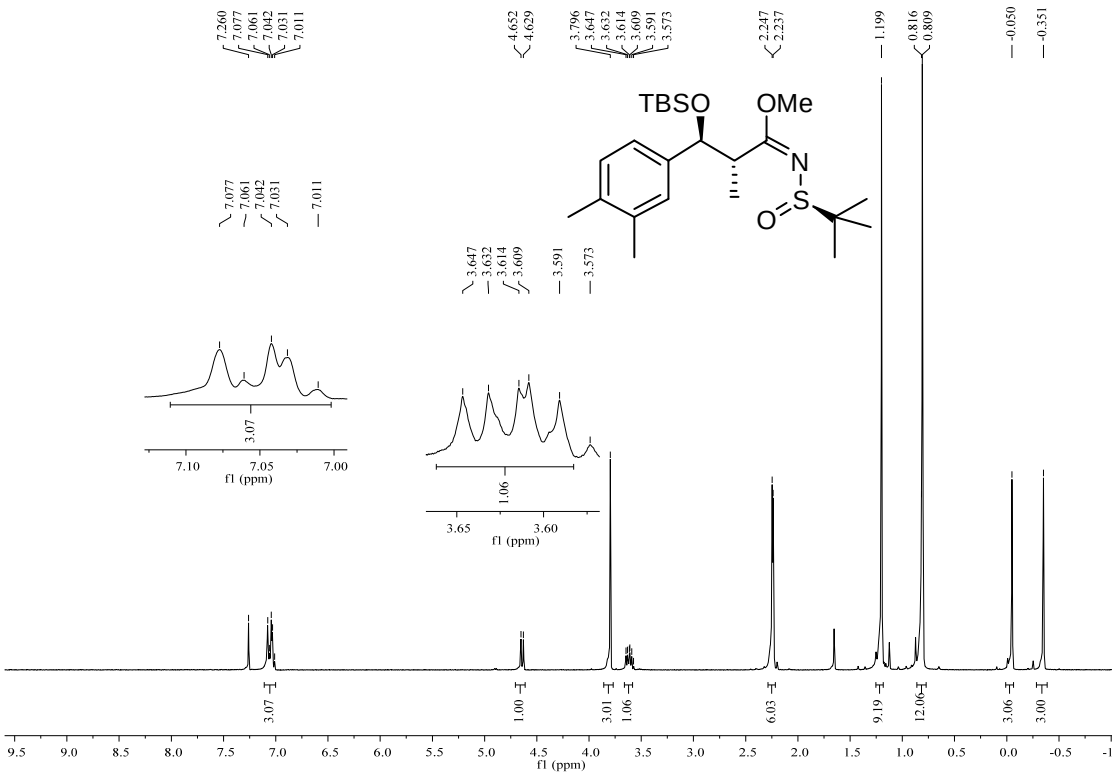
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5k**



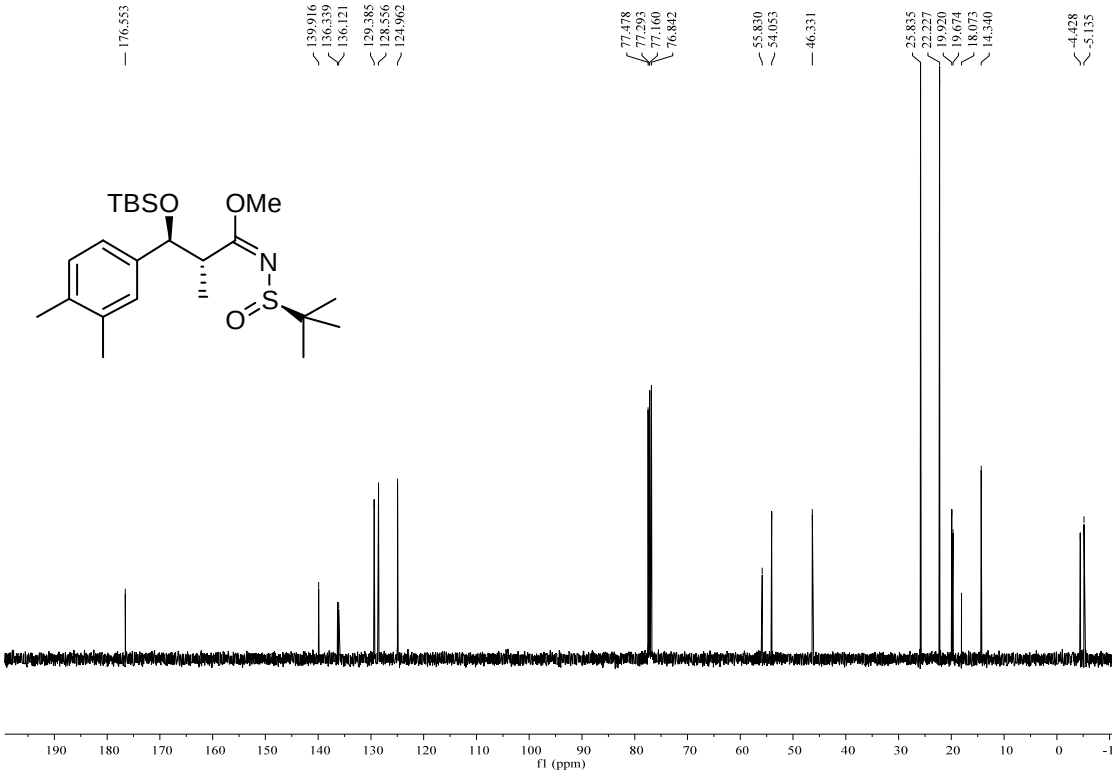
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5l**



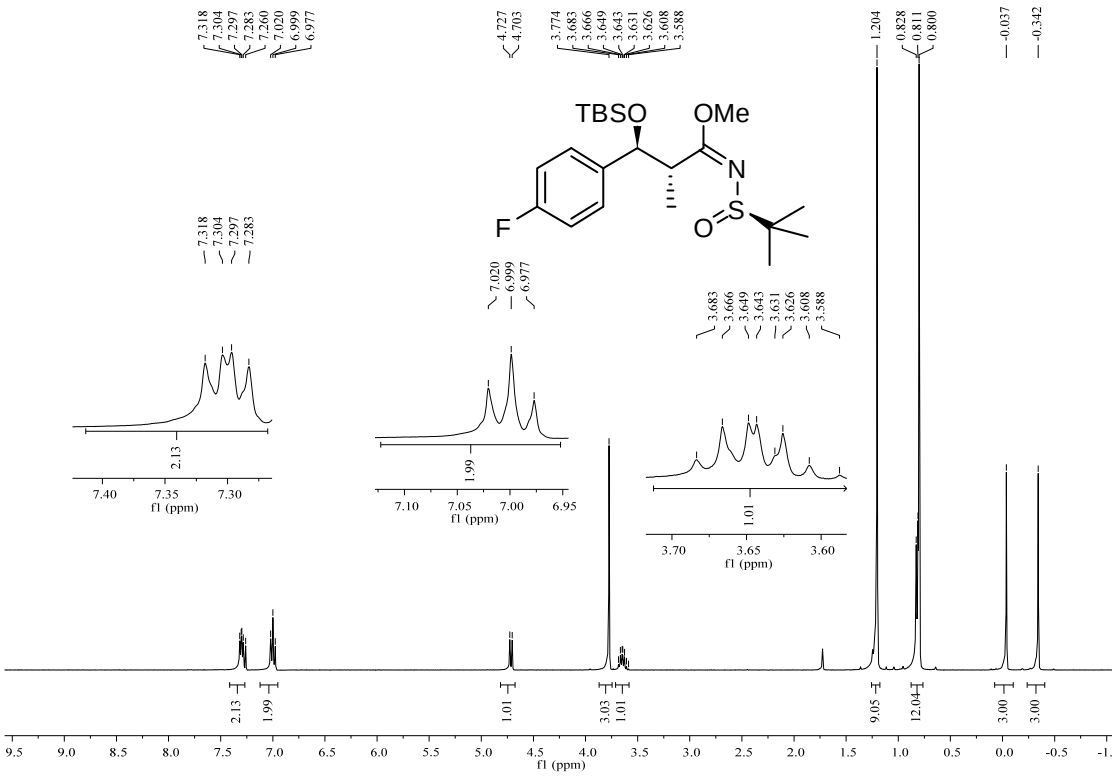
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5l**



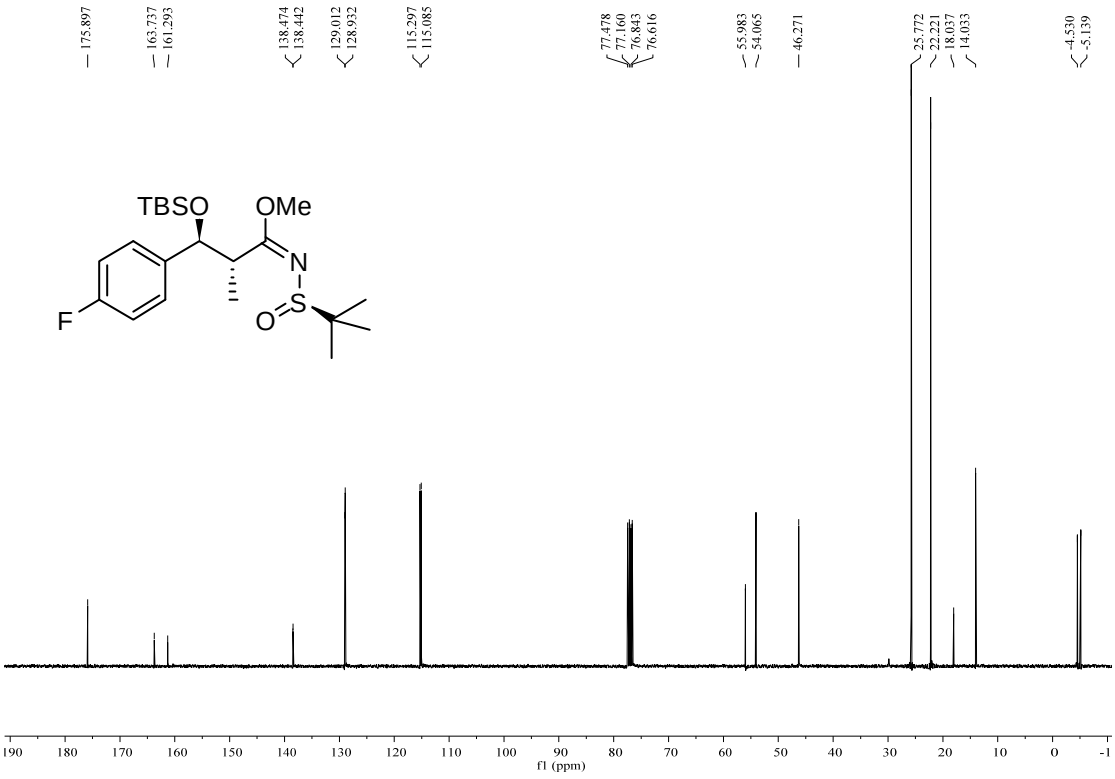
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5m**



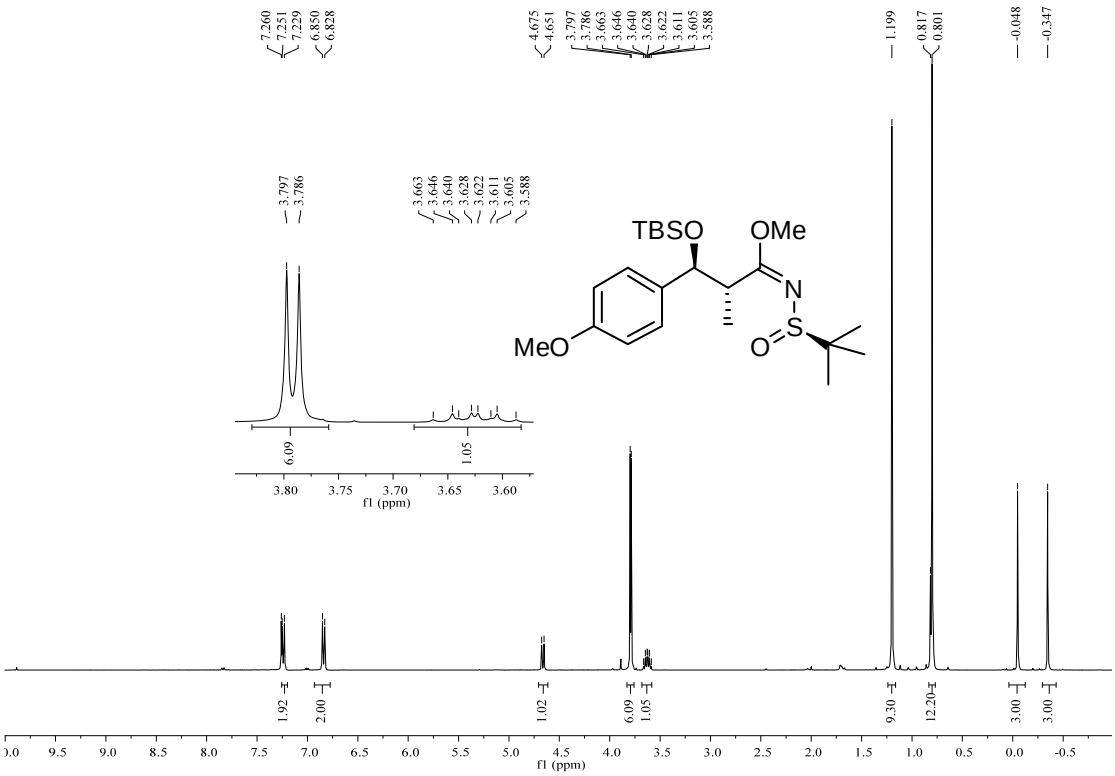
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5m**



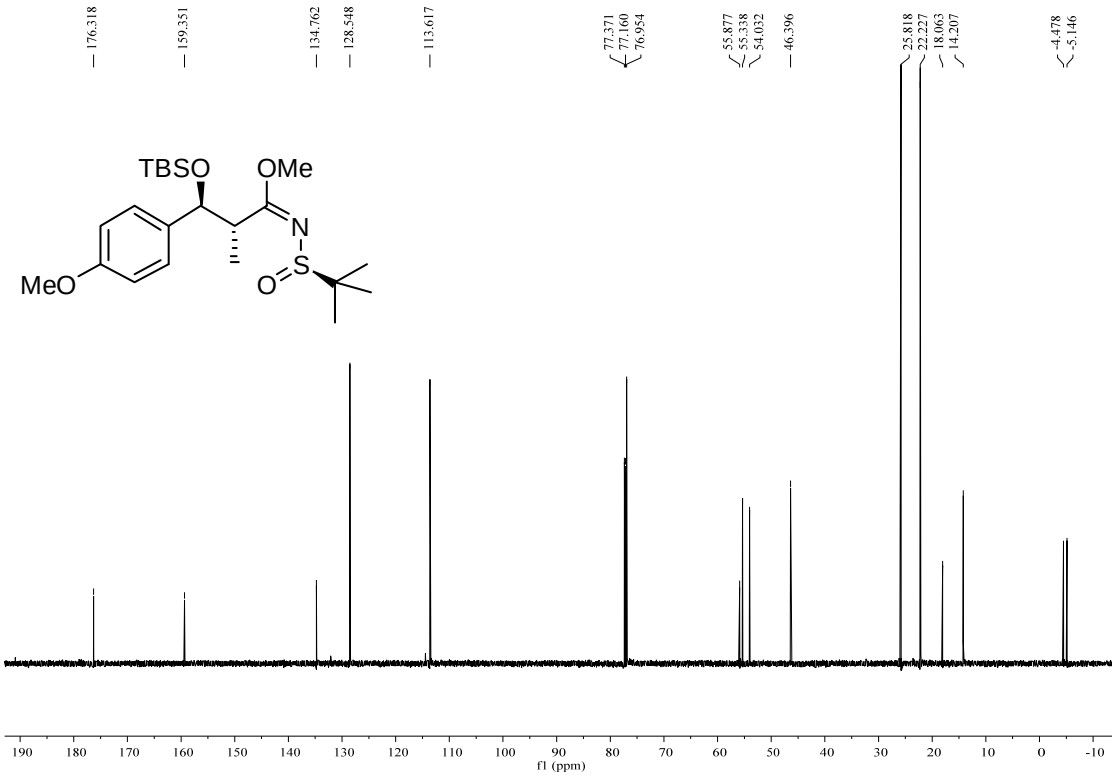
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5n**



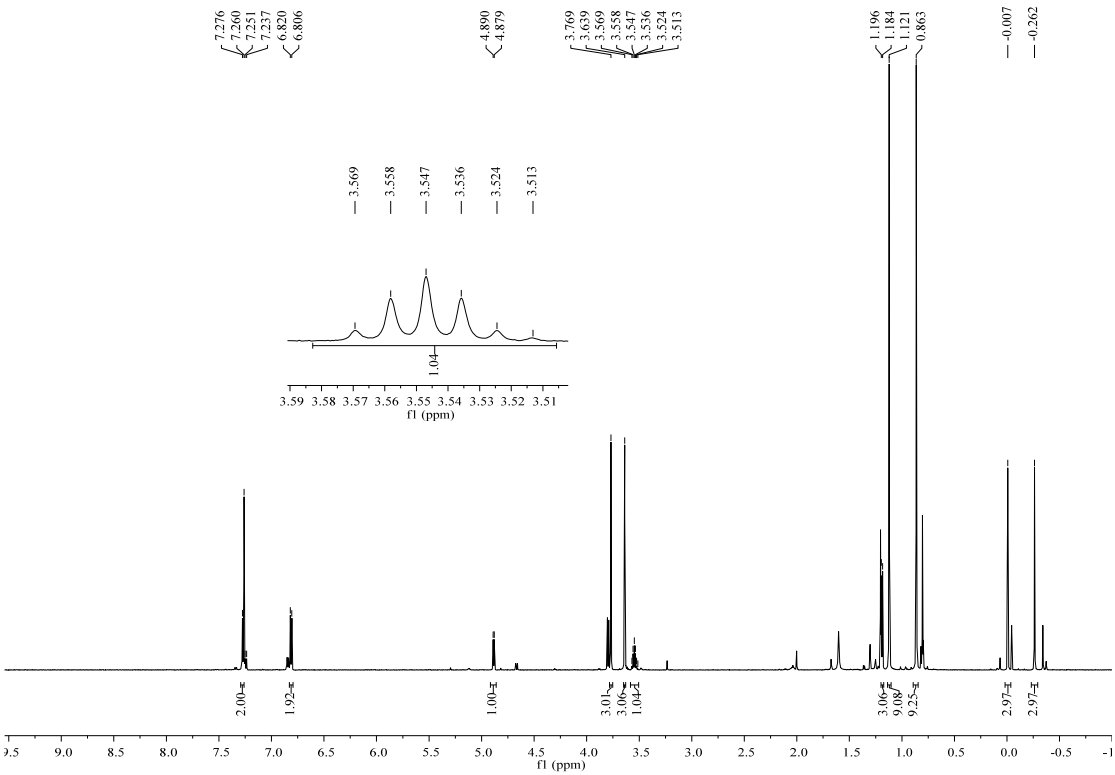
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5n**



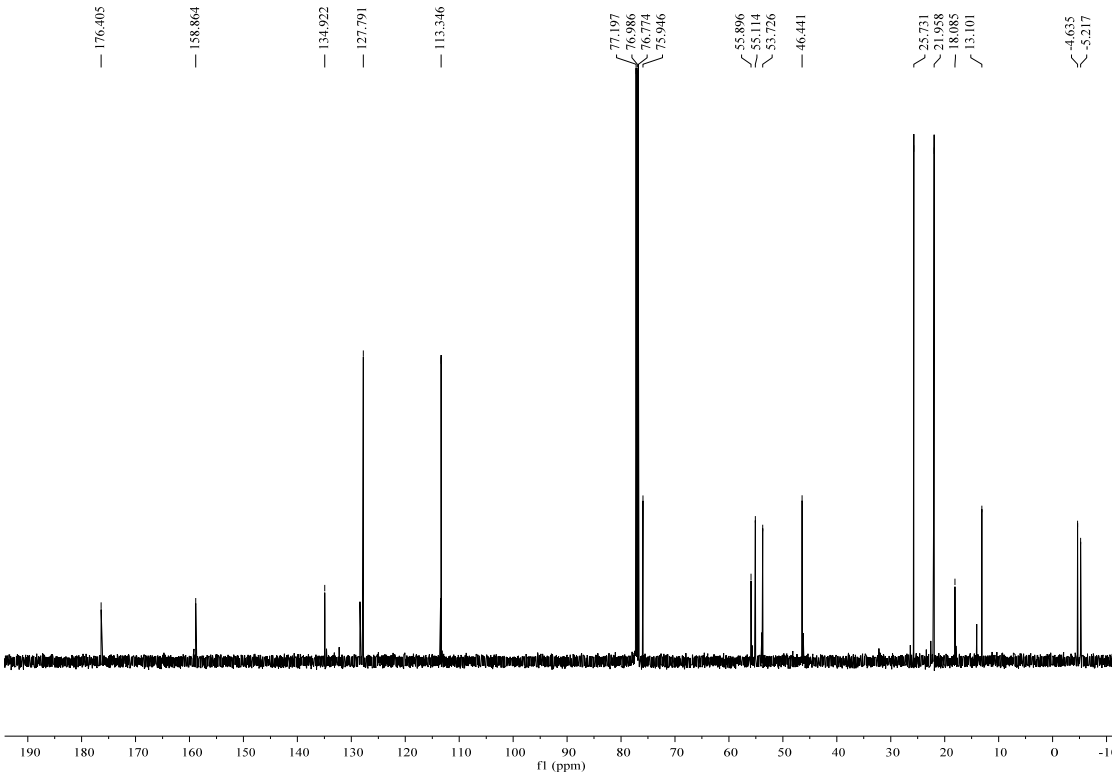
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5o** (major diastereomer)



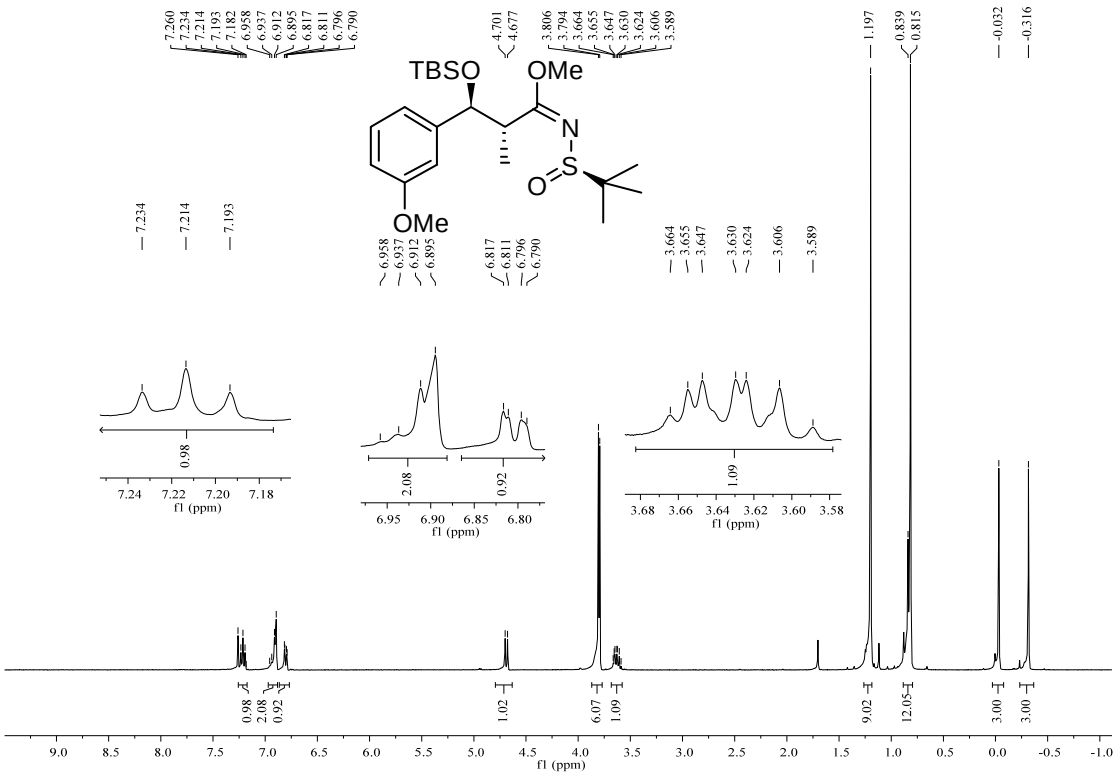
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5o** (major diastereomer)



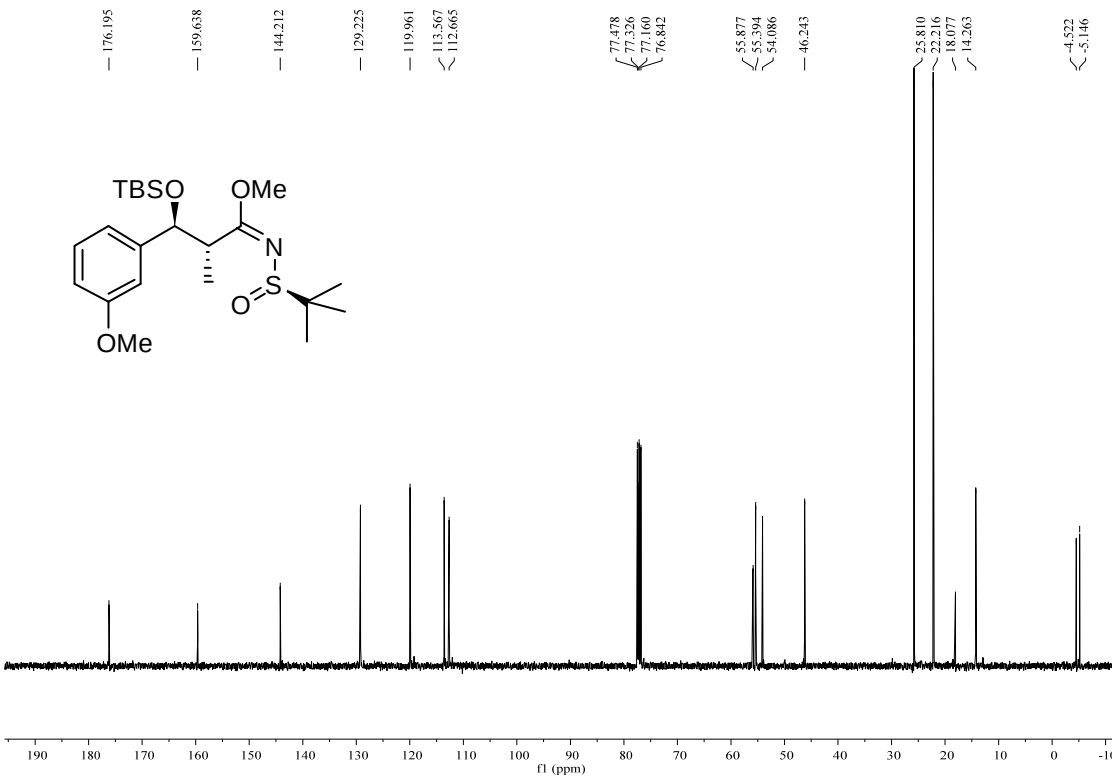
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5o'** (minor diastereomer)



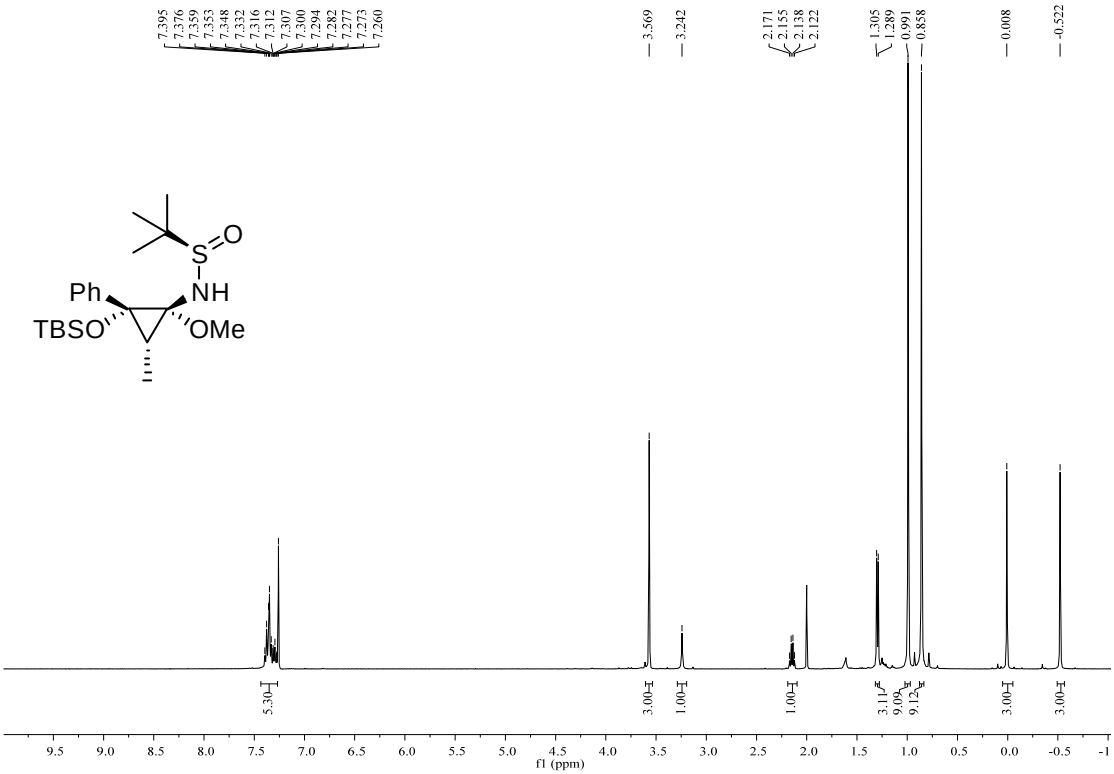
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5o'** (minor diastereomer)



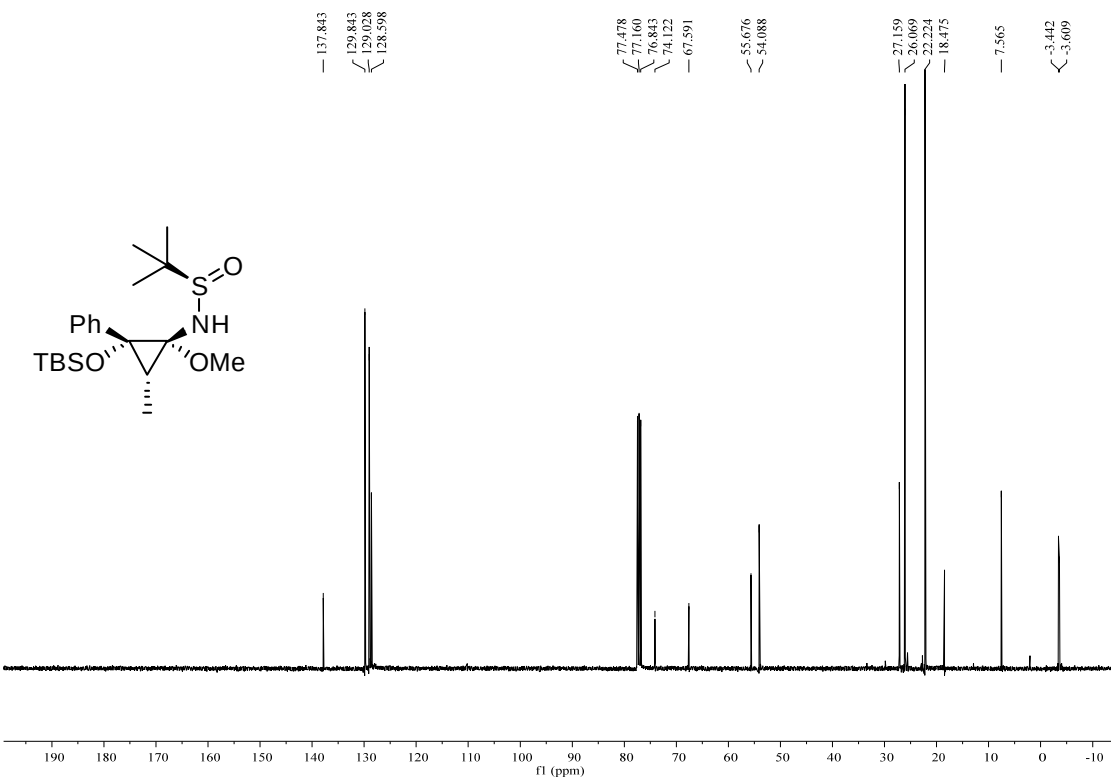
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5p**



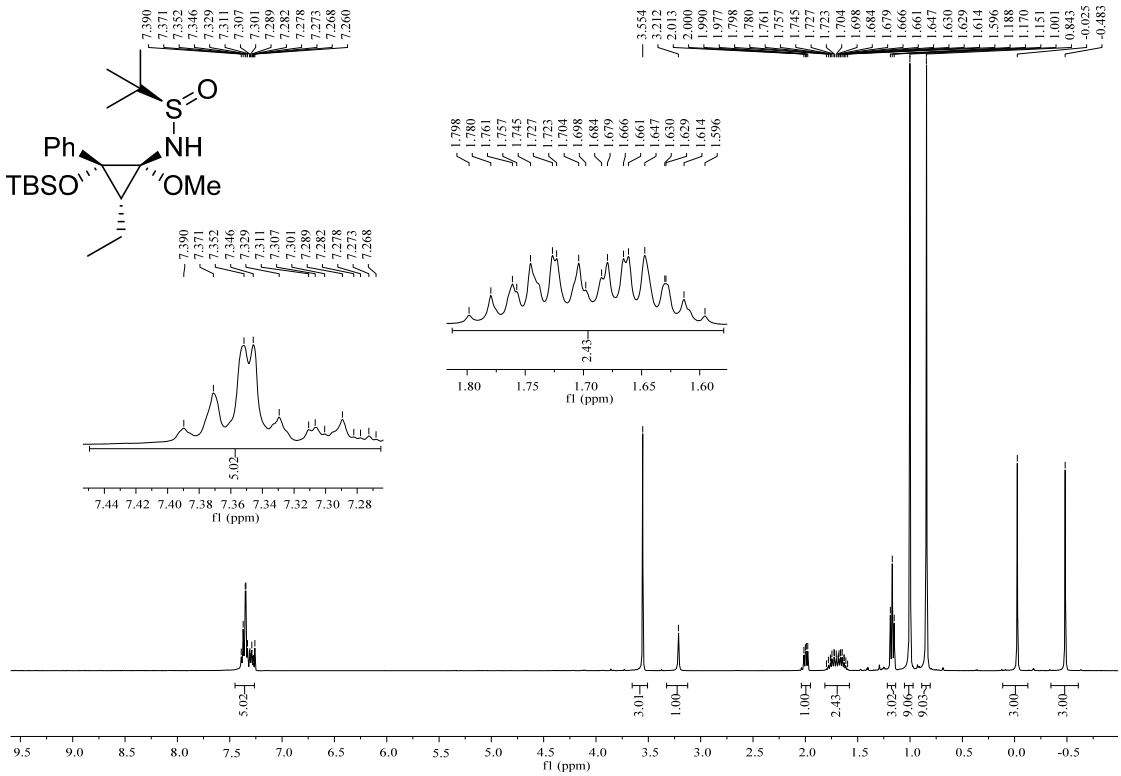
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **5p**



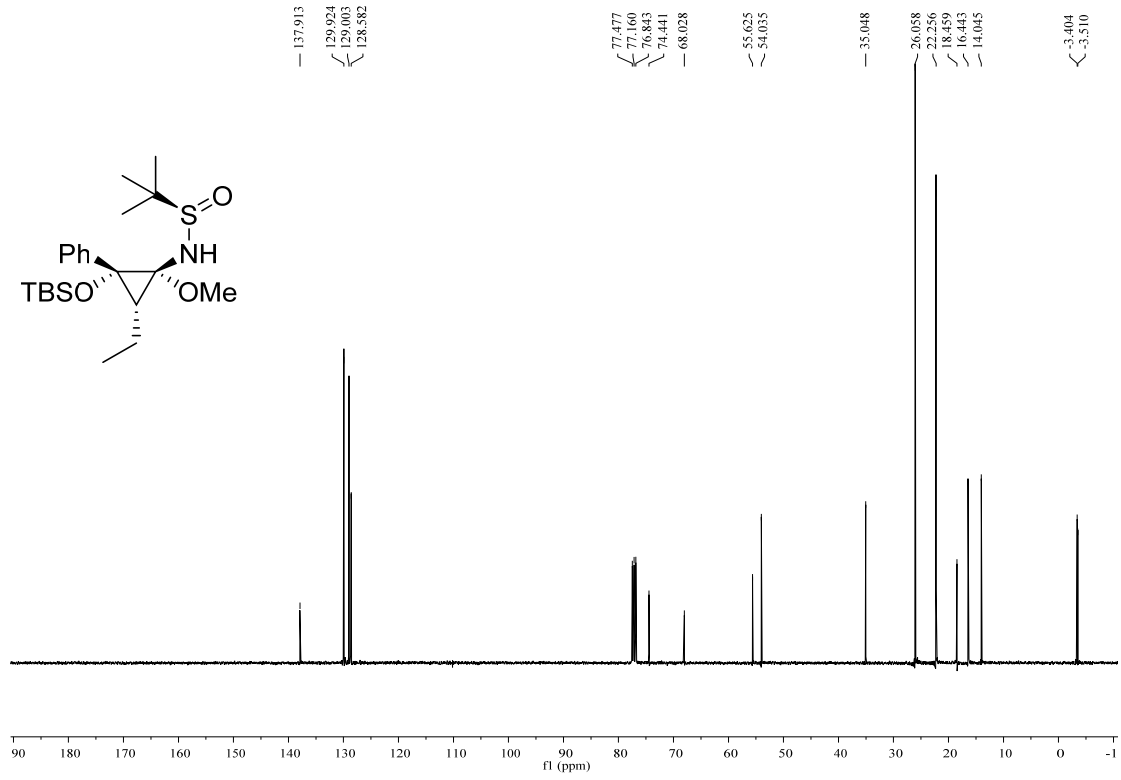
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4a**



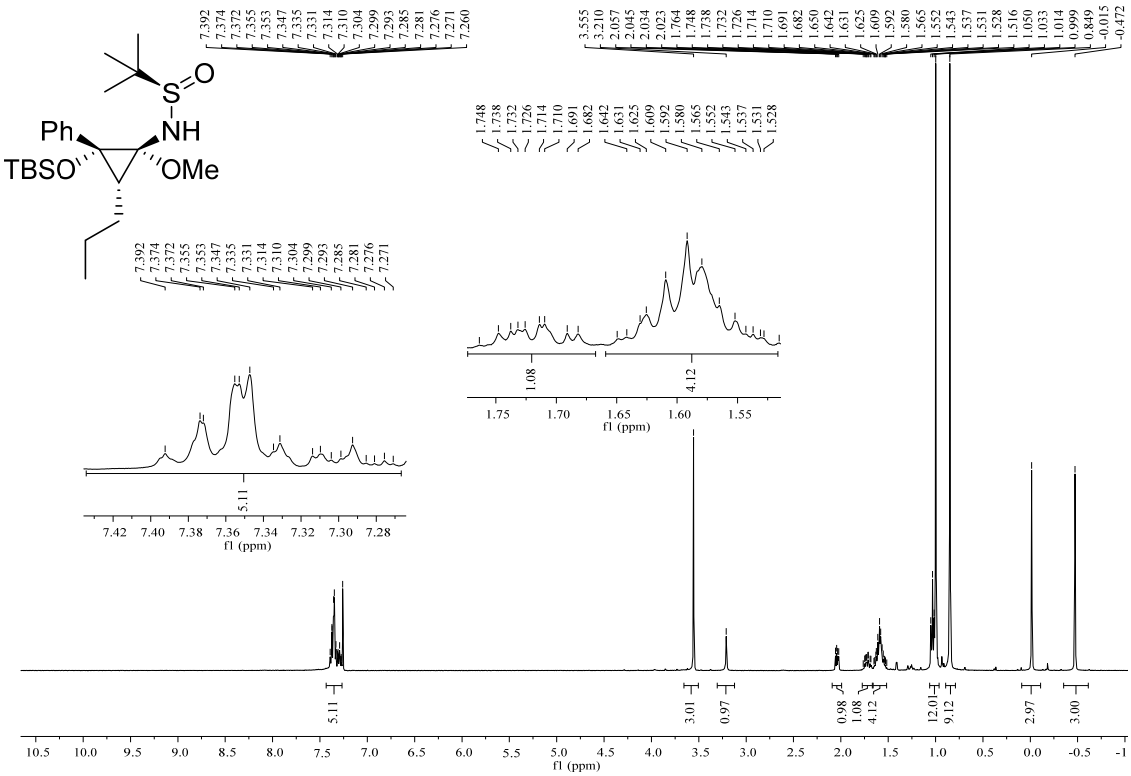
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4a**



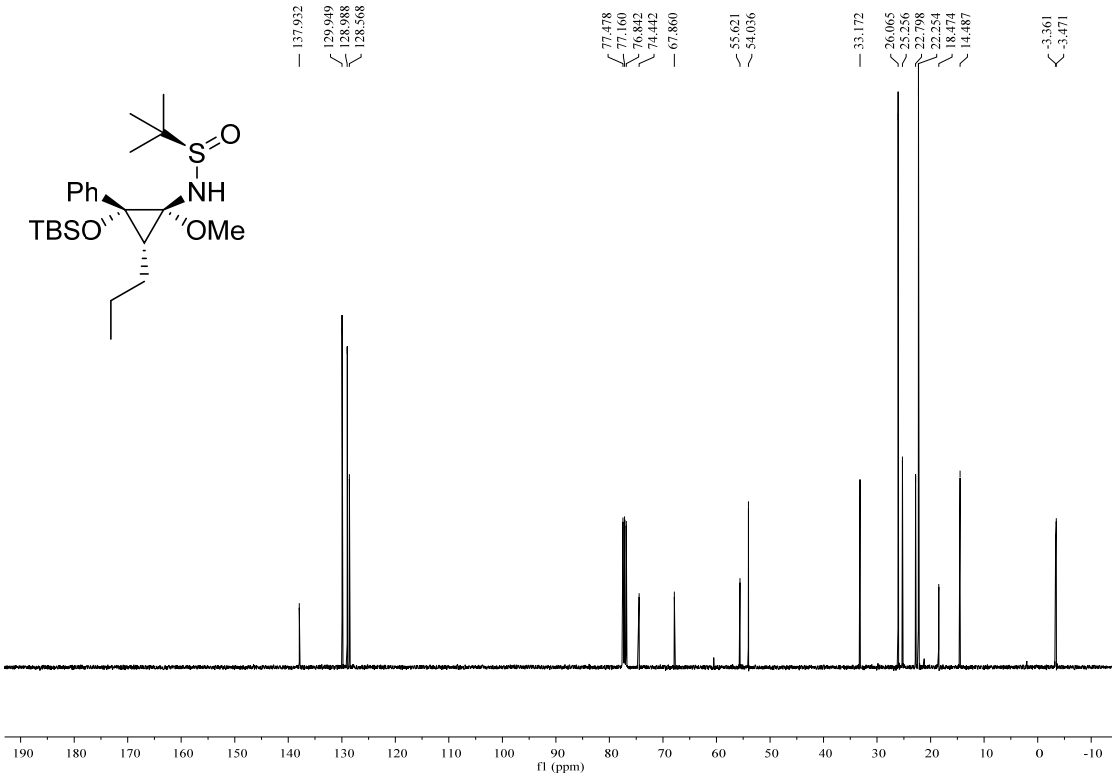
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4b**



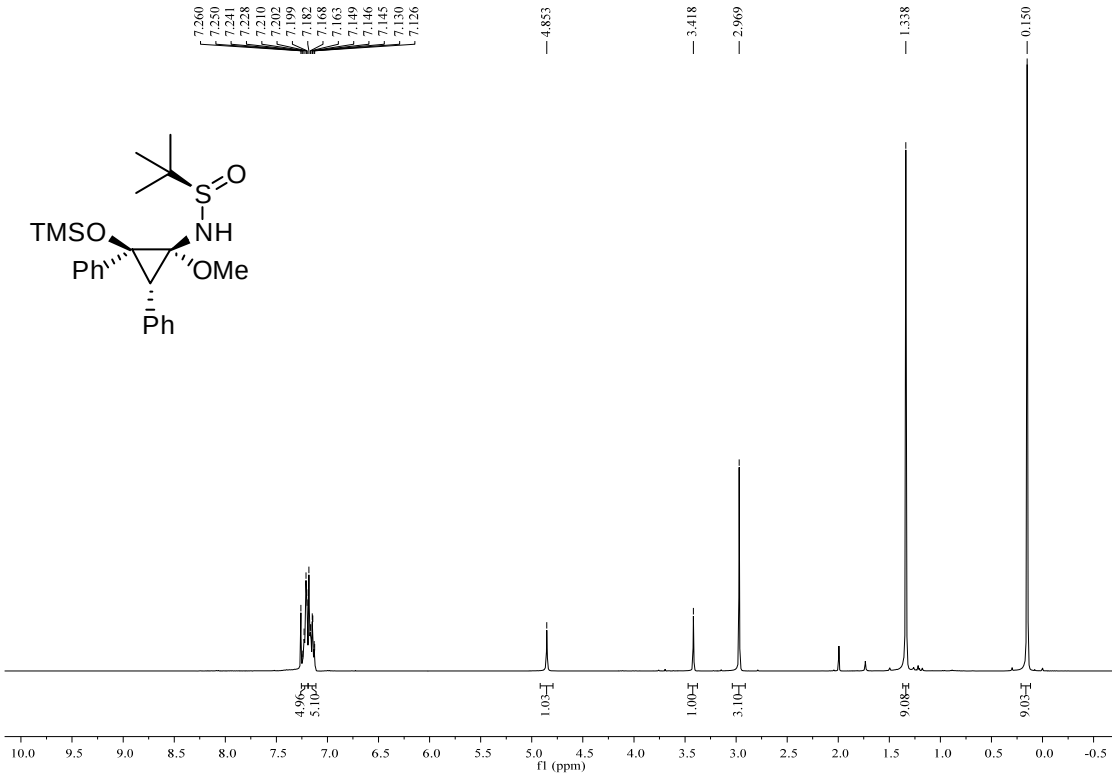
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4b**



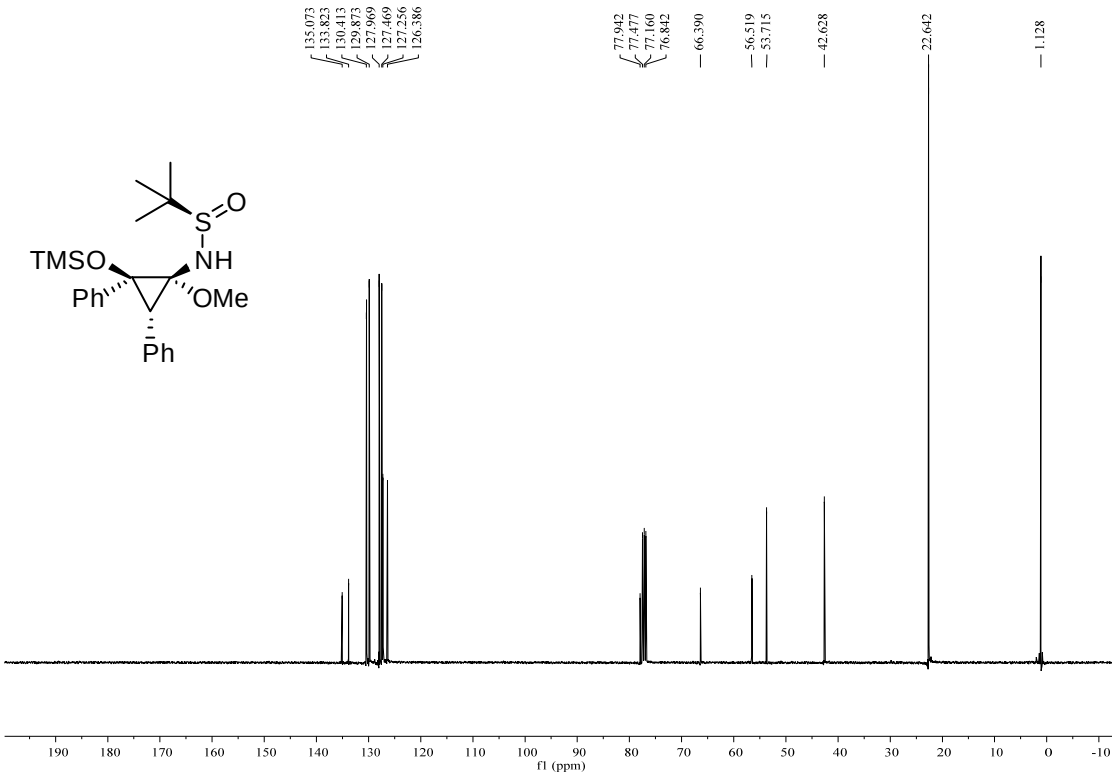
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4c**



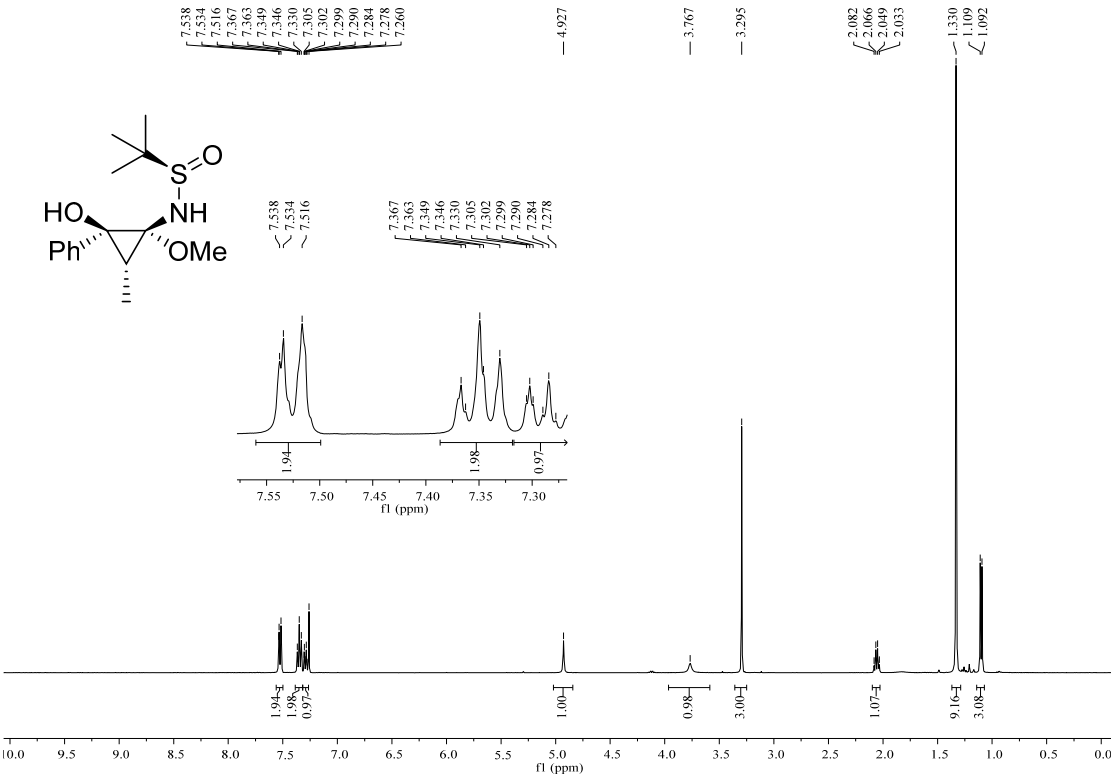
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4c**



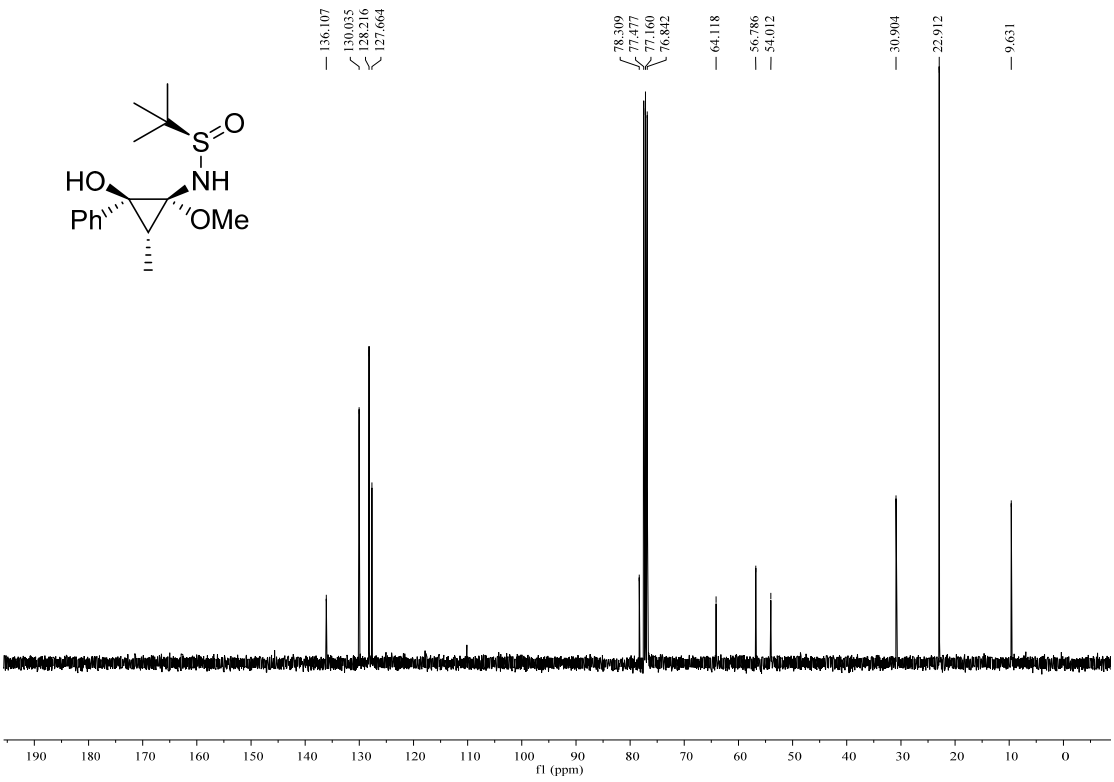
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3s**



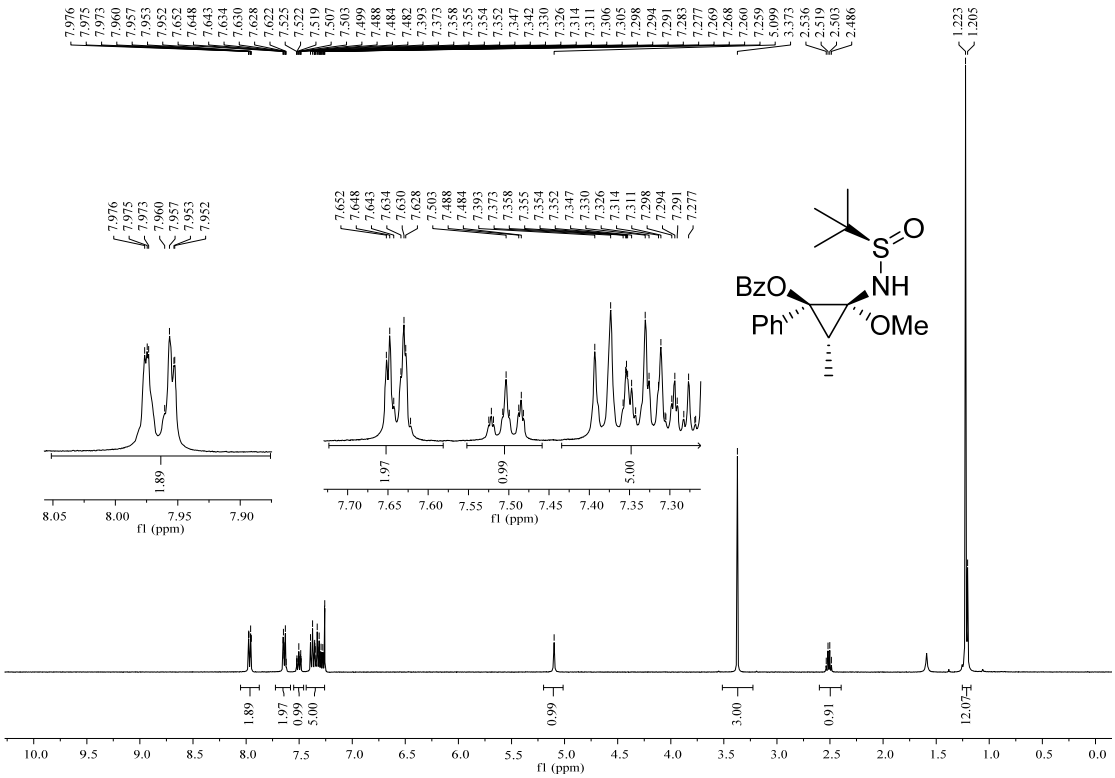
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3s**



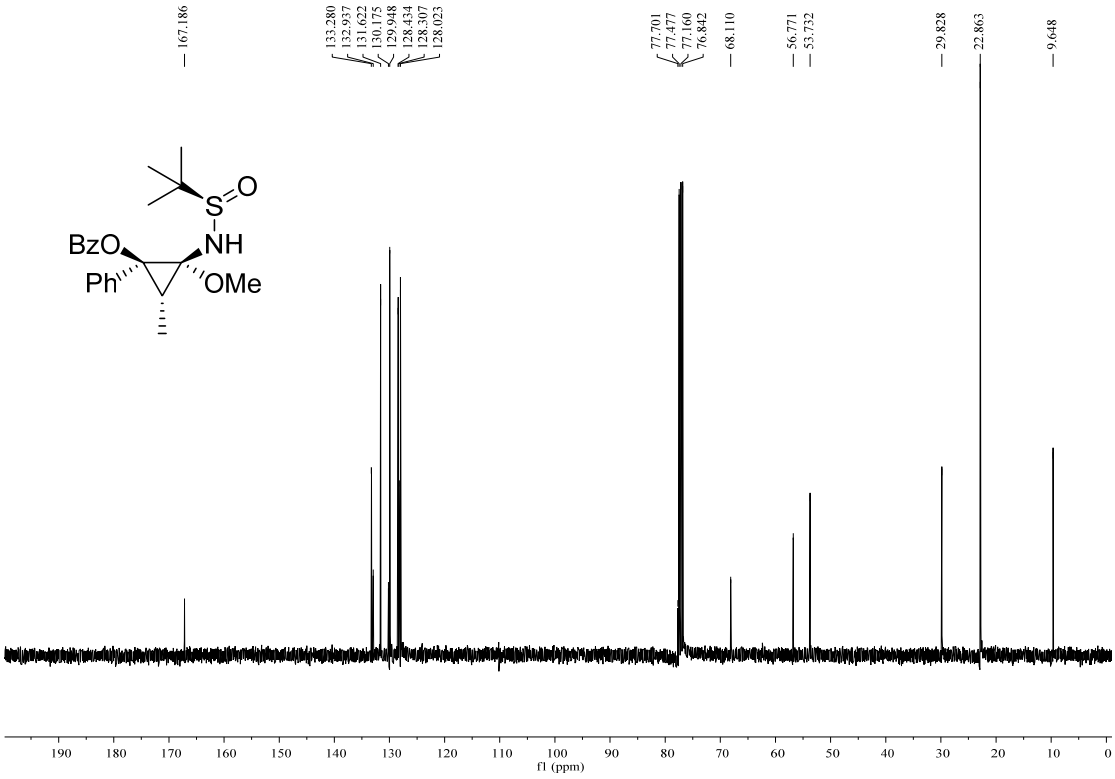
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6**



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **7**

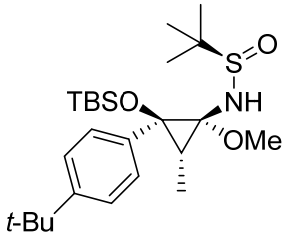


^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **7**

9. X-Ray crystal structures of products

Figure S1. X-Ray crystal structure of the compound 3l

The single crystals of compound **3l** for X-ray structure studies were obtained by evaporation its solution of CH_2Cl_2/petroleum ether (1:6, v/v) at room temperature. X-Ray crystal structure (ORTEP) of compound **3l** with the thermal ellipsoids shown at a 50% probability level.



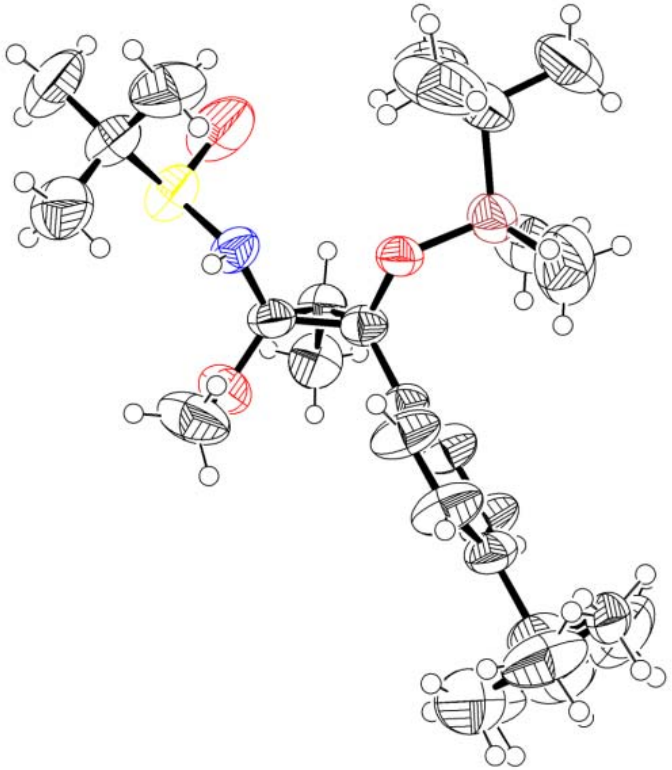


Table S1 Crystal data and structure refinement for 3l

Identification code	**3l**
Empirical formula	$C_{25}H_{45}NO_3SSi$
Formula weight	467.77
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.328(5)
b/Å	12.879(6)
c/Å	10.995(5)
α/°	90
β/°	96.809(7)
γ/°	90
Volume/Å^3	1452.1(11)
Z	2
ρ_{calc}g/cm^3	1.070
μ/mm^{-1}	0.176
F(000)	512.0
Crystal size/mm^3	0.272 × 0.184 × 0.117
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.078 to 55.01
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 14$, $-7 \le l \le 14$
Reflections collected	8972
Independent reflections	6082 [R_{int} = 0.0409, R_{sigma} = 0.0907]
Data/restraints/parameters	6082/1/293
Goodness-of-fit on F^2	0.969
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1389
Final R indexes [all data]	R_1 = 0.1407, wR_2 = 0.1777
Largest diff. peak/hole / e Å^{-3}	0.25/-0.22
Flack parameter	0.16(9

Table S2 Bond Lengths for 3l

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	N1	1.678(5)	C3AA	C9	1.372(8)
S1	O15	1.481(6)	C7	C8	1.362(9)

S1	C18	1.818(7)	C7	C12	1.373(9)
Si2	O17	1.639(4)	C7	C14	1.534(9)
Si2	C16	1.838(8)	C9	C12	1.387(9)
Si2	C24	1.844(9)	C10	C11	1.501(8)
Si2	C26	1.833(8)	C10	C13	1.503(8)
O17	C1AA	1.423(6)	C14	C23	1.484(11)
O16	C11	1.392(6)	C14	C2	1.523(13)
O16	C20	1.400(8)	C14	C4	1.473(13)
C1AA	C3AA	1.490(8)	C16	C25	1.540(10)
C1AA	C10	1.516(8)	C16	C1	1.523(13)
C1AA	C11	1.513(8)	C16	C3	1.554(13)
N1	C11	1.426(7)	C17	C18	1.550(10)
C2AA	C3AA	1.362(8)	C18	C19	1.479(10)
C2AA	C8	1.387(9)	C18	C21	1.518(10)

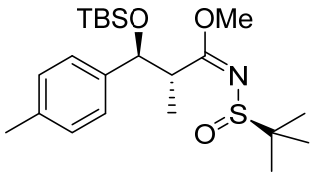
Table S3 Bond Angles for 3l

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	S1	C18	98.1(3)	C11	C10	C13	121.5(5)
O15	S1	N1	108.6(3)	C13	C10	C1AA	126.1(5)
O15	S1	C18	105.8(3)	O16	C11	C1AA	119.1(5)
O17	Si2	C16	105.7(3)	O16	C11	N1	115.7(5)
O17	Si2	C24	106.8(4)	O16	C11	C10	112.9(5)
O17	Si2	C26	111.4(3)	N1	C11	C1AA	116.2(5)
C16	Si2	C24	110.3(5)	N1	C11	C10	121.5(5)
C26	Si2	C16	113.6(4)	C10	C11	C1AA	60.4(4)
C26	Si2	C24	108.8(5)	C7	C12	C9	123.0(6)
C1AA	O17	Si2	127.8(3)	C23	C14	C7	108.5(6)
C11	O16	C20	114.6(5)	C23	C14	C2	106.1(9)
O17	C1AA	C3AA	113.1(5)	C2	C14	C7	112.1(6)
O17	C1AA	C10	114.6(4)	C4	C14	C7	109.8(7)
O17	C1AA	C11	111.4(4)	C4	C14	C23	115.0(10)
C3AA	C1AA	C10	125.9(5)	C4	C14	C2	105.3(9)
C3AA	C1AA	C11	121.6(5)	C25	C16	Si2	110.8(6)
C11	C1AA	C10	59.4(4)	C25	C16	C3	109.4(8)
C11	N1	S1	116.6(4)	C1	C16	Si2	110.7(6)

C3AA	C2AA	C8	122.3(6)	C1	C16	C25	109.6(8)
C2AA	C3AA	C1AA	119.6(5)	C1	C16	C3	107.9(10)
C2AA	C3AA	C9	117.0(5)	C3	C16	Si2	108.3(6)
C9	C3AA	C1AA	123.3(5)	C17	C18	S1	103.1(5)
C8	C7	C12	116.0(6)	C19	C18	S1	112.8(5)
C8	C7	C14	123.0(6)	C19	C18	C17	110.4(7)
C12	C7	C14	120.9(6)	C19	C18	C21	112.9(7)
C7	C8	C2AA	121.5(7)	C21	C18	S1	106.9(5)
C3AA	C9	C12	120.2(6)	C21	C18	C17	110.3(7)
C11	C10	C1AA	60.2(4)				

Figure S2. X-Ray crystal structure of the compound 5k

The single crystals of compound **5k** for X-ray structure studies were obtained by evaporation its solution of CH_2Cl_2/petroleum ether (1:4, v/v) at room temperature. X-Ray crystal structure (ORTEP) of compound **5k** with the thermal ellipsoids shown at a 50% probability level.



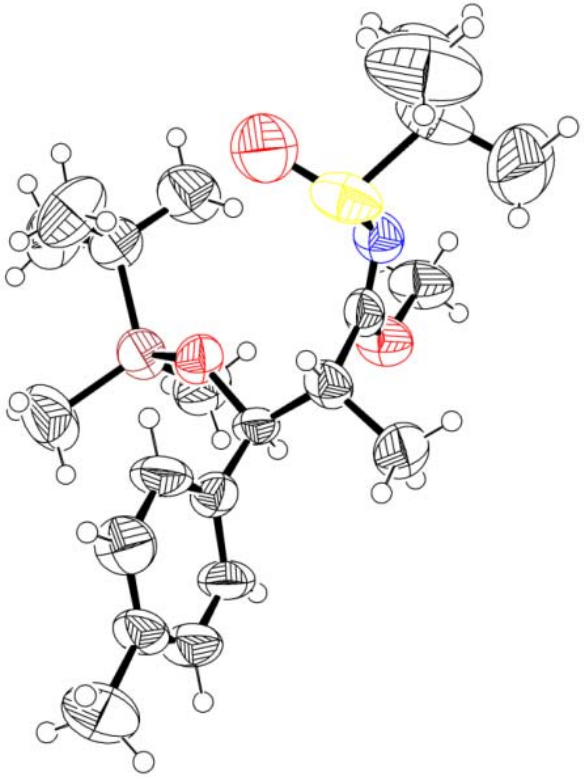


Table S4 Crystal data and structure refinement for 5k

Identification code	**5k**
Empirical formula	$C_{22}H_{39}NO_3SSi$
Formula weight	425.69
Temperature/K	296.15
Crystal system	triclinic
Space group	P1
a/Å	7.182(8)
b/Å	9.354(10)
c/Å	10.768(11)
α/°	108.471(14)
β/°	90.746(16)
γ/°	107.794(15)
Volume/Å^3	648.4(12)
Z	1
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	0.191
F(000)	232.0
Crystal size/mm^3	0.207 × 0.198 × 0.128
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.858 to 54.448
Index ranges	$-8 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 11$
Reflections collected	3863
Independent reflections	3317 [R_{int} = 0.0367, R_{sigma} = 0.1025]
Data/restraints/parameters	3317/6/264
Goodness-of-fit on F^2	0.974
Final R indexes [I>=2σ (I)]	R_1 = 0.0828, wR_2 = 0.2133
Final R indexes [all data]	R_1 = 0.1590, wR_2 = 0.2894
Largest diff. peak/hole / e Å^{-3}	0.39/-0.29
Flack parameter	-0.10(19)

Table 5 Bond Lengths for 5k

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	O15	1.657(7)	C6	C7	1.392(14)

Si1	C16	1.846(15)	C6	C11	1.355(14)
Si1	C19	1.880(14)	C7	C10	1.359(15)
Si1	C22	1.850(15)	C8	C13	1.549(16)
S2	N1	1.707(10)	C9	C11	1.348(16)
S2	O14	1.502(11)	C9	C12	1.306(19)
S2	C1	1.787(15)	C9	C24	1.559(17)
O15	C5	1.442(11)	C10	C12	1.419(15)
O2	C4	1.333(13)	C17	C1	1.526(17)
O2	C15	1.463(11)	C18	C19	1.569(17)
N1	C4	1.219(14)	C19	C20	1.512(17)
C4	C8	1.510(13)	C19	C23	1.481(19)
C5	C7	1.481(12)	C21	C1	1.540(15)
C5	C8	1.580(14)	C1	C2	1.555(17)

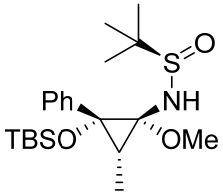
Table 6 Bond Angles for 5k

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O15	Si1	C16	109.4(6)	C4	C8	C5	109.2(8)
O15	Si1	C19	103.0(5)	C4	C8	C13	110.3(9)
O15	Si1	C22	109.3(6)	C13	C8	C5	109.0(9)
C16	Si1	C19	113.4(6)	C11	C9	C24	117.6(14)
C16	Si1	C22	110.4(9)	C12	C9	C11	115.6(10)
C22	Si1	C19	111.1(7)	C12	C9	C24	126.8(14)
N1	S2	C1	94.5(6)	C7	C10	C12	118.1(11)
O14	S2	N1	108.0(6)	C9	C11	C6	124.2(11)
O14	S2	C1	106.8(7)	C9	C12	C10	124.6(13)
C5	O15	Si1	124.1(7)	C18	C19	Si1	108.2(11)
C4	O2	C15	116.7(9)	C20	C19	Si1	109.8(9)
C4	N1	S2	119.1(7)	C20	C19	C18	107.7(10)
O2	C4	C8	111.1(11)	C23	C19	Si1	111.4(9)
N1	C4	O2	120.8(9)	C23	C19	C18	109.4(12)
N1	C4	C8	128.0(11)	C23	C19	C20	110.4(14)
O15	C5	C7	112.0(8)	C17	C1	S2	110.4(11)
O15	C5	C8	102.7(7)	C17	C1	C21	114.8(16)
C7	C5	C8	110.1(7)	C17	C1	C2	108.6(18)

C11	C6	C7	119.5(11)	C21	C1	S2	111.4(11)
C6	C7	C5	120.1(10)	C21	C1	C2	104.7(16)
C10	C7	C5	122.3(10)	C2	C1	S2	106.3(15)
C10	C7	C6	117.6(9)				

Figure S3. X-Ray crystal structure of the compound 4a

The single crystals of compound **4a** for X-ray structure studies were obtained by evaporation its solution of CH_2Cl_2/petroleum ether (1:8, v/v) at room temperature. X-Ray crystal structure (ORTEP) of compound **4a** with the thermal ellipsoids shown at a 50% probability level.



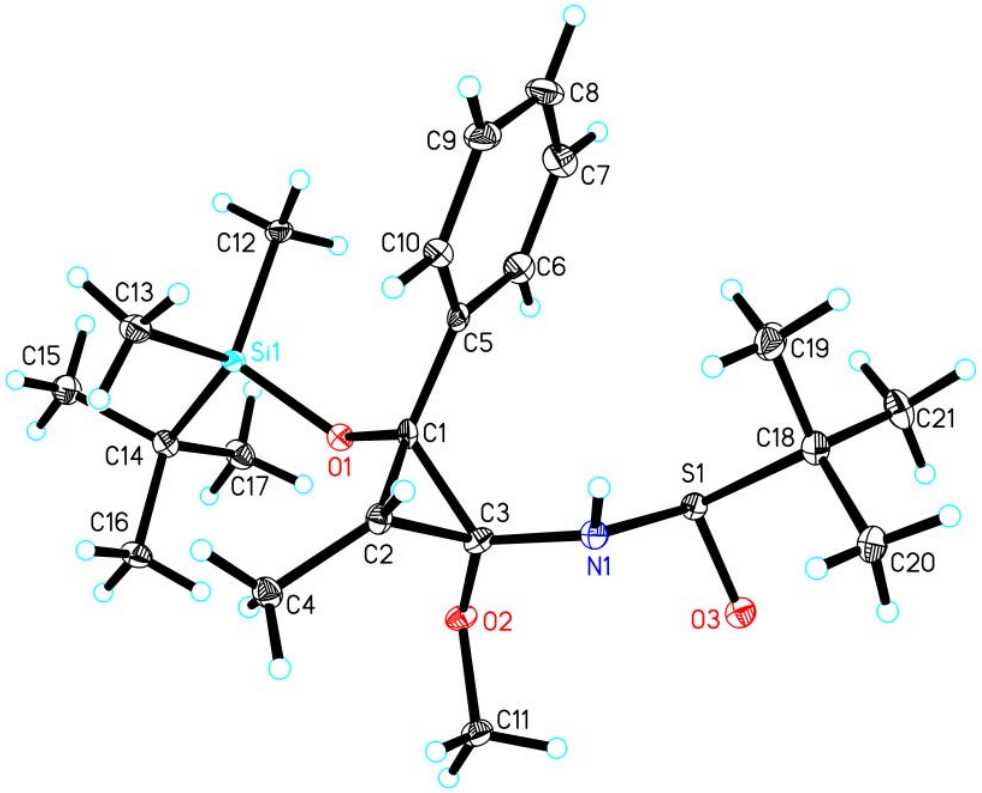


Table S7 Crystal data and structure refinement for 4a

Identification code	**4a**
Empirical formula	$C_{21}H_{39}NO_4SSi$
Formula weight	429.68
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.2420(5)
b/Å	6.4724(3)
c/Å	14.3242(5)
α/°	90
β/°	92.113(3)
γ/°	90
Volume/Å^3	1226.86(8)
Z	2
ρ_{calc}g/cm^3	1.163
μ/mm^{-1}	1.833
F(000)	468.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.174 to 147.848
Index ranges	$-16 \le h \le 16$, $-7 \le k \le 7$, $-17 \le l \le 17$
Reflections collected	9985
Independent reflections	4600 [R_{int} = 0.0439, R_{sigma} = 0.0498]
Data/restraints/parameters	4600/1/266
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1695
Final R indexes [all data]	R_1 = 0.0634, wR_2 = 0.1701
Largest diff. peak/hole / e Å^{-3}	0.96/-0.49
Flack parameter	0.027(16)

Table S8 Bond Lengths for 4a

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(001)	O(3)	1.504(5)	C(5)	C(6)	1.401(9)

S(001)	N(1)	1.661(5)	C(1)	C(3)	1.512(8)
S(001)	C(18)	1.859(6)	C(1)	C(2)	1.535(8)
Si(02)	O(1)	1.663(4)	C(3)	C(2)	1.507(9)
Si(02)	C(12)	1.874(6)	C(6)	C(7)	1.379(9)
Si(02)	C(14)	1.896(6)	C(9)	C(8)	1.400(11)
Si(02)	C(13)	1.870(7)	C(16)	C(14)	1.535(8)
O(1)	C(1)	1.384(7)	C(17)	C(14)	1.536(10)
O(2)	C(3)	1.405(7)	C(7)	C(8)	1.380(11)
O(2)	C(11)	1.426(7)	C(4)	C(2)	1.505(8)
N(1)	C(3)	1.429(8)	C(14)	C(15)	1.522(9)
C(10)	C(5)	1.388(9)	C(18)	C(19)	1.515(9)
C(10)	C(9)	1.395(9)	C(18)	C(20)	1.498(9)
C(5)	C(1)	1.509(8)	C(18)	C(21)	1.532(10)

Table S9 Bond Angles for 4a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O(3)	S(001)	N(1)	110.5(3)	O(2)	C(3)	C(2)	118.4(5)
O(3)	S(001)	C(18)	104.3(3)	N(1)	C(3)	C(1)	120.2(5)
N(1)	S(001)	C(18)	100.2(3)	N(1)	C(3)	C(2)	115.1(5)
O(1)	Si(02)	C(12)	111.1(3)	C(2)	C(3)	C(1)	61.1(4)
O(1)	Si(02)	C(14)	103.9(2)	C(7)	C(6)	C(5)	119.6(7)
O(1)	Si(02)	C(13)	111.0(3)	C(10)	C(9)	C(8)	118.7(6)
C(12)	Si(02)	C(14)	110.8(3)	C(6)	C(7)	C(8)	121.2(7)
C(13)	Si(02)	C(12)	108.0(3)	C(3)	C(2)	C(1)	59.6(4)
C(13)	Si(02)	C(14)	112.1(3)	C(4)	C(2)	C(1)	122.3(5)
C(1)	O(1)	Si(02)	129.0(4)	C(4)	C(2)	C(3)	122.7(5)
C(3)	O(2)	C(11)	113.1(5)	C(7)	C(8)	C(9)	120.0(6)
C(3)	N(1)	S(001)	116.2(4)	C(16)	C(14)	Si(02)	109.7(4)
C(5)	C(10)	C(9)	121.3(6)	C(16)	C(14)	C(17)	109.5(5)
C(10)	C(5)	C(1)	121.9(6)	C(17)	C(14)	Si(02)	109.4(4)
C(10)	C(5)	C(6)	119.2(6)	C(15)	C(14)	Si(02)	109.8(4)
C(6)	C(5)	C(1)	118.7(6)	C(15)	C(14)	C(16)	109.2(5)
O(1)	C(1)	C(5)	114.4(5)	C(15)	C(14)	C(17)	109.2(6)
O(1)	C(1)	C(3)	114.5(5)	C(19)	C(18)	S(001)	108.6(4)

O(1)	C(1)	C(2)	117.9(5)	C(19)	C(18)	C(21)	110.4(6)
C(5)	C(1)	C(3)	120.0(5)	C(20)	C(18)	S(001)	110.4(5)
C(5)	C(1)	C(2)	119.7(5)	C(20)	C(18)	C(19)	113.2(7)
C(3)	C(1)	C(2)	59.3(4)	C(20)	C(18)	C(21)	110.8(6)
O(2)	C(3)	N(1)	117.2(5)	C(21)	C(18)	S(001)	103.0(5)
O(2)	C(3)	C(1)	113.1(5)				