# Diastereoselective synthesis of 2-methoxyimidoyloxiranes via dimethyl phosphite-mediated coupling of *α*-keto *N*-sulfinyl imidates with aldehydes

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## Supporting Information

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**General experimental information**

All reactions were performed under an argon atmosphere in flame-dried glassware with magnetic stirring. All solvents were purified according to the standard procedures. Dimethyl phosphite was distilled before use. Purification of the reaction products was carried out by flash column chromatography using 200–300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) or treatment with aqueous ceric ammonium molybdate followed by heating. High-resolution mass spectra (HRMS) were recorded on a Bruker BIO TOF Q mass spectrometer. Measurements of melting point (mp) were performed by using a BUCHI M-560 instrument. Proton and carbon magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were recorded on a Varian Inova 400 MHz ($^1$H NMR at 400 MHz and $^{13}$C NMR at 100 MHz) or 600 MHz ($^1$H NMR at 600 MHz and $^{13}$C NMR at 150 MHz) spectrometer with solvent resonance as the internal standard ($^1$H NMR: $CDCl_3$ at 7.26 ppm, $C_6D_6$ at 7.16 ppm; $^{13}$C NMR: $CDCl_3$ at 77.16 ppm, $C_6D_6$ at 128.06 ppm). $^1$H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet), coupling constant(s) in Hz, integration. Imidate **8** was prepared according to literature procedures.[1]

**General procedure for the preparation of α-keto *N*-*tert*-butylsulfinylimidate 2**

THF, imidate **8** (1 equiv) and aldehyde (1 equiv) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −78 °C. LDA (0.5 M in THF, 1.3 equiv) was added dropwise to the solution via syringe. The reaction was allowed to stir at −78 °C for 1h. 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 and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to afford alcohol **9**.

Dess-Martin periodinane (1.1 equiv) was added to a solution of alcohol **9** (1 equiv) in dry $CH_2Cl_2$ at room temperature. The solution was stirred for 1 h, then the reaction was quenched with saturated aqueous $NaHCO_3$:$NaS_2O_3$ (1:1) and extracted with $CH_2Cl_2$ (3 times). The combined

organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel to afford α-keto *N-tert*-butylsulfinylimidate **2**.[2]

**General procedure for the preparation of product 10a**

α-Keto *N-tert*-butylsulfinylimidate (0.2 mmol, 1 equiv) and dimethyl phosphite (0.2 mmol, 1 equiv) in 2.0 mL THF were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −10 °C. LHMDS (1.2 M in THF, 0.22 mmol, 1.1 equiv) was added dropwise to the solution via syringe. The reaction was allowed to stir at −10 °C for 30min. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 15 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

**General procedure for the preparation of product 7**

α-Keto *N-tert*-butylsulfinylimidate (0.26 mmol, 1.3 equiv) and dimethyl phosphite (0.26 mmol, 1.3 equiv) in 2.0 mL THF were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −10 °C. LHMDS (1.2 M in THF, 0.26 mmol, 1.3 equiv) was added dropwise to the solution via syringe. After 30 minutes, aldehyde (0.20 mmol, 1.0 equiv) in 1.0 mL THF was added dropwise to the solution via syringe. The reaction was allowed to stirred at −10 °C for 2–3 h (see Table 1) or the reaction mixture was warmed to 0 $^{o}$C for another 1h before quenching (see Table 1). Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 15 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

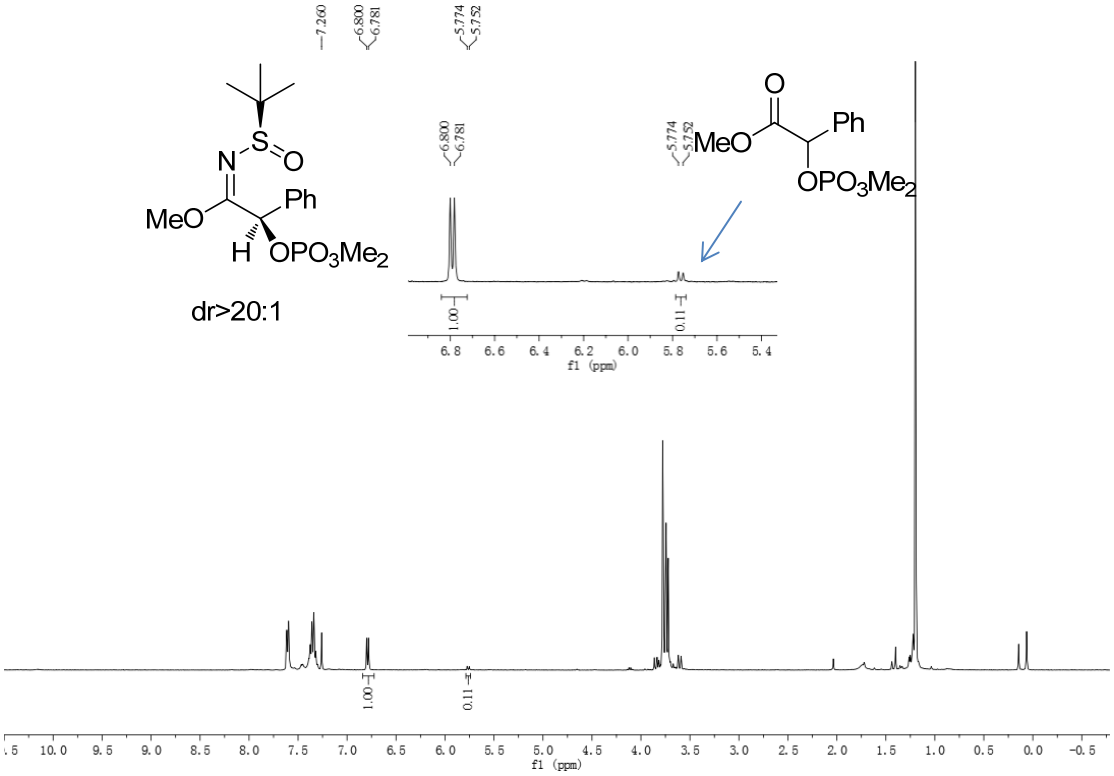
**Procedure for 1-gram scale preparation of 7c**

*α*-Keto *N-tert*-butylsulfinylimidate **2a** (1.336 g, 5.0 mmol, 1.3 equiv), dimethyl phosphite **1a** (0.5503g, 5.0 mmol, 1.3 equiv), and 24.0 mL THF were added to a flame-dried Schlenk flask

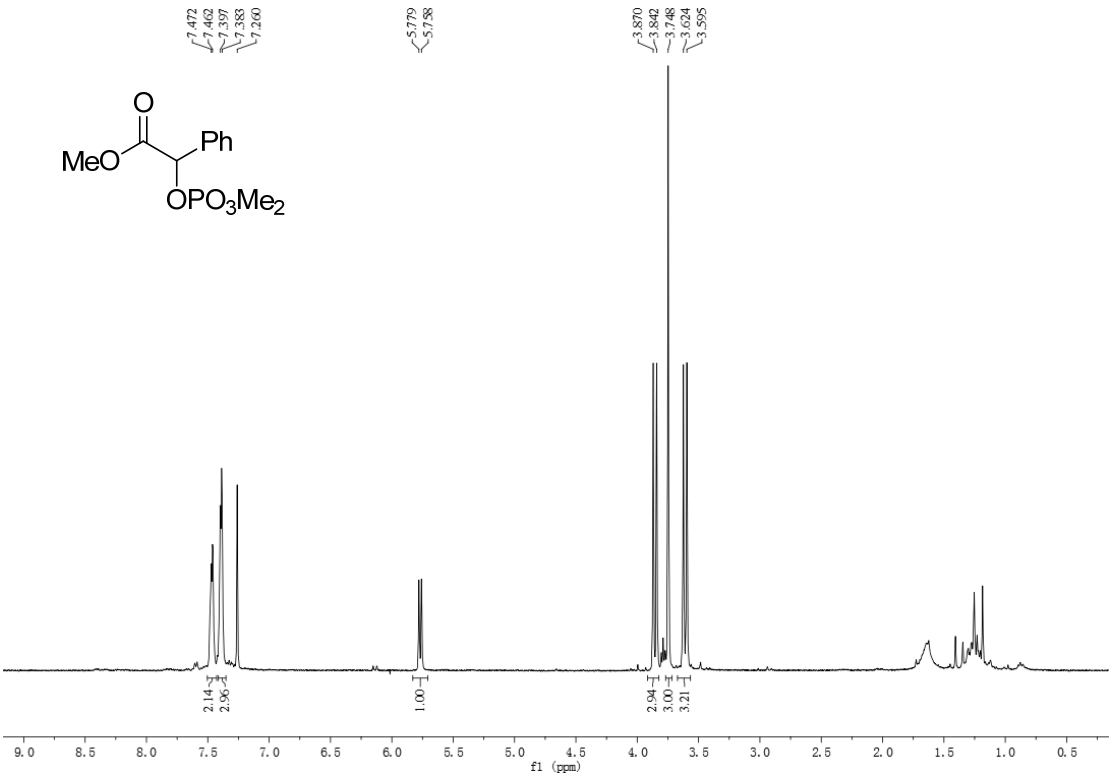
equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −10 °C. LHMDS (1.2 M in THF, 4.2 mL, 5.0 mmol, 1.3 equiv) was added dropwise to the solution via syringe. After 30 minutes, 4-bromobenzaldehyde (**5c**, 0.711 g, 3.85 mmol, 1.0 equiv) in 12.0 mL THF was added dropwise to the solution via syringe. The reaction was allowed to stir at −10 °C for 3h. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 60 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether / ethyl acetate = 6:1), achieving 1.34 g (80%) of **7c** as a white solid.

**Calculation of diastereomeric ratio and assignment of desulfinyl product**

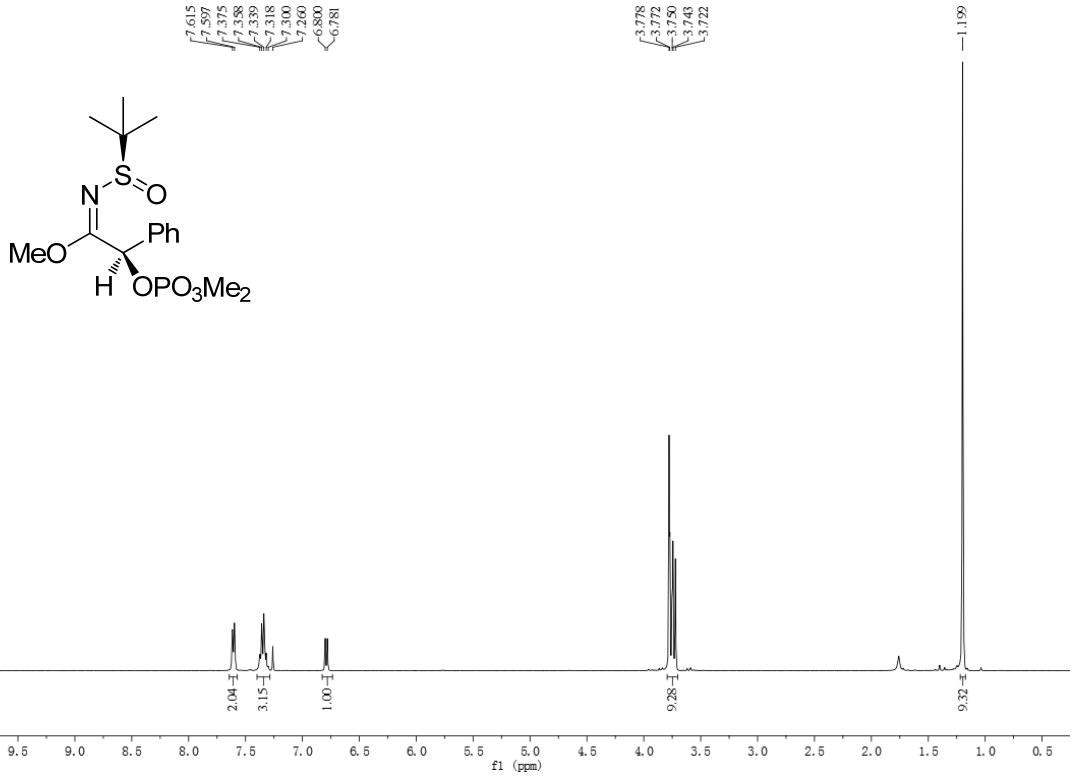
Diastereomeric ratios were determined by $^1$H NMR of the crude mixture of products. The dr determination and assignments of the corresponding desulfinyl products were presented as follows. No diastereomeric isomers were detected in the NMR spectra.



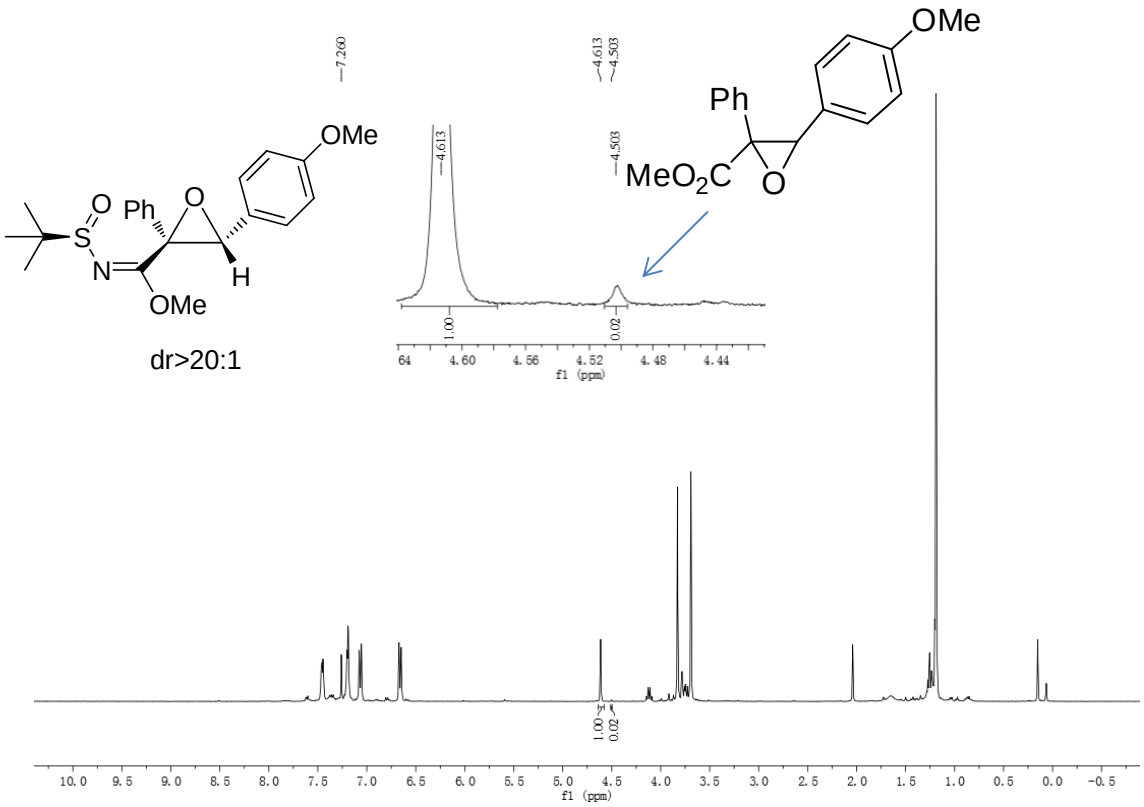

$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of the crude product (**10a**)



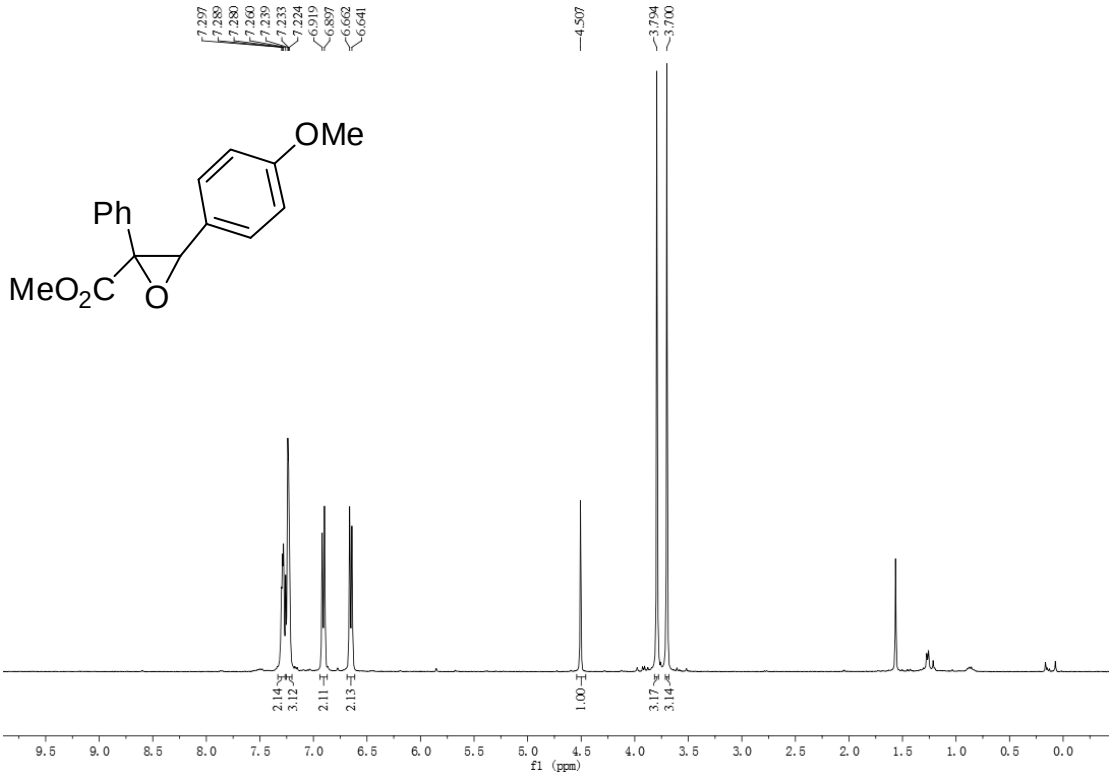

$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of the desulfinyl product **10'a**



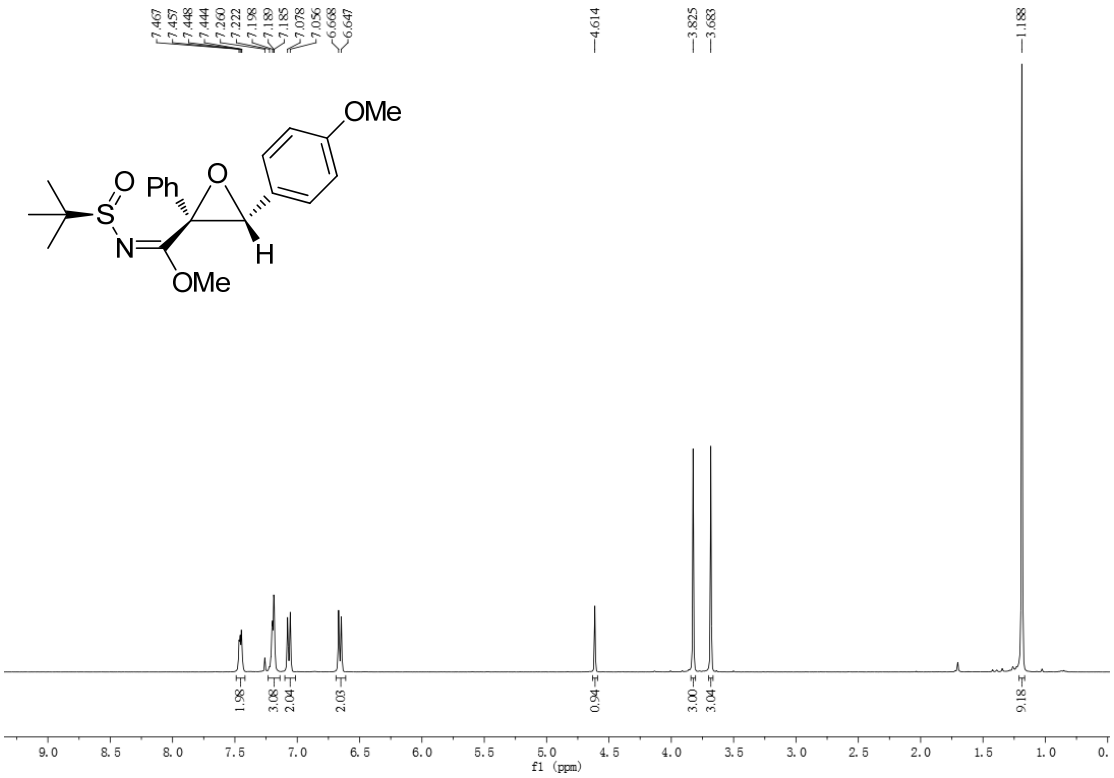

$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of product **10a**




$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of the crude product **7f**

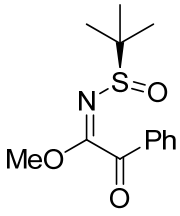



$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of desulfinyl product **7'f**

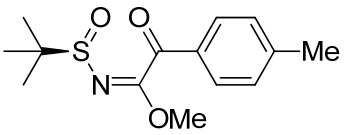



$^1$H NMR spectrum ($CDCl_3$, 400 MHz) of product **7f**

**Analytical data for *α*-keto *N-tert*-butylsulfinylimidate 2a−2g**

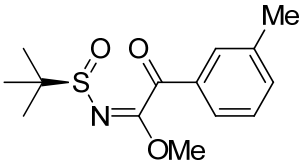


**Compound 2a:** General procedure was followed with 1.14 g imidate **8**, 0.74 g benzaldehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 1.22 g of **2a** as a pale yellow solid (65% total yield). Analytical data: $R_f$ = 0.30 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −200° (*c* = 0.10, MeOH), mp 81−82 °C; $^1$H NMR (600 MHz, $CDCl_3$): *δ* 7.85 (d, *J*= 7.8 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 3.99 (s, 3H), 1.23 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): *δ* 189.1, 165.4, 134.7, 133.5, 129.4, 129.1, 57.3, 55.3, 22.1; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{13}H_{17}NNaO_3S$ 290.0821, found 290.0820.

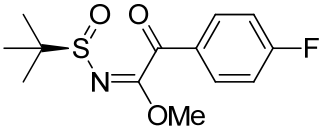


**Compound 2b:** General procedure was followed with 1.14 g imidate **8**, 0.84 g *p*-tolualdehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 1.18 g of **2b** as a pale yellow solid (60% total yield). Analytical data: $R_f$ = 0.25 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −185° (*c* = 0.10, MeOH), mp 100−101 °C; $^1$H

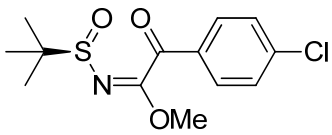
NMR (400 MHz, $CDCl_3$): $\delta$ 7.75 (d, $J$ = 8.4 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 3.99 (s, 3H), 2.42 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 188.7, 166.10, 146.1, 131.0, 129.9, 129.6, 57.2, 55.3, 22.1, 22.0; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{14}H_{19}NNaO_3S$ 304.0978, found 304.0983.



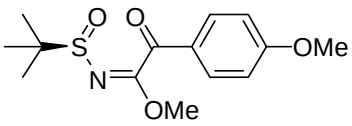

**Compound 2c:** General procedure was followed with 1.14 g imidate **8,** 0.84g *m*-tolualdehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 1.08 g of **2c** as a pale yellow solid (55% total yield). Analytical data: $R_f$ = 0.25 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −175° ($c$ = 0.10, MeOH), mp 73−74 °C; $^1$H NMR (400 MHz, $CDCl_3$):$\delta$ 7.67 (s, 1H), 7.62 (d, $J$ = 7.2 Hz, 1H), 7.40 (p, $J$ = 7.2 Hz, 2H), 3.99 (s, 3H), 2.40 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 189.2, 165.7, 139.1, 135.6, 133.4, 129.7, 128.9, 126.9, 57.2, 55.3, 22.1, 21.4; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{14}H_{19}NNaO_3S$ 304.0978, found 304.0975.




**Compound 2d:** General procedure was followed with 1.14 g imidate **8**, 0.87 g 4-fluorobenzaldehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 1.00 g of **2d** as a pale yellow solid (50% total yield). Analytical data: $R_f$ = 0.30 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −188° (c = 0.10, MeOH), mp 92−93 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 3.97 (s, 3H), 1.21 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 187.6, 166.6 (d, $J_{C\text{-}F}$ = 256 Hz), 164.8, 132.1 (d, $J_{C\text{-}F}$ = 9.7 Hz), 130.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.2 Hz), 57.3, 55.4, 22.0; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{13}H_{16}FNNaO_3S$ 308.0727, found 308.0726.

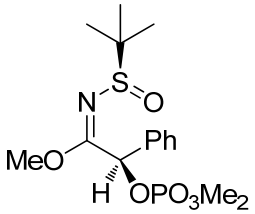



**Compound 2e:** General procedure was followed with 1.14 g imidate **8**, 0.98 g 4-chlorobenzaldehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 0.97 g of **2e** as a pale yellow solid (46% total yield). Analytical data: $R_f$ = 0.30 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −137° ($c$ = 0.10, MeOH), mp 94−95 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H),7.48 (d, $J$ = 8.4 Hz, 2H), 3.99 (s, 3H), 1.23 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 188.1, 164.5, 141.3, 132.0, 130.7, 129.5, 57.4, 55.5, 22.1; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{13}H_{16}ClNNaO_3S$ 324.0432, found 324.0422.



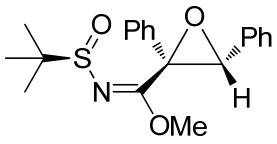
**Compound 2f:** General procedure was followed with 1.14 g imidate **8**, 0.95 g anisaldehyde, 11.1 mL LDA (0.5 M in THF), 3.26 g Dess-Martin periodinane. Column chromatography afforded 1.33 g of **2f** as a pale yellow solid (64% total yield). Analytical data: $R_f$ = 0.25 (petroleum ether / ethyl acetate = 3:1), $[\alpha]^{25}_D$ = −162° (*c* = 0.10, MeOH), mp 70−71 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.83 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H), 3.88 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 187.4, 166.6, 165.0, 132.1, 126.5, 114.6, 57.1, 55.8, 55.2, 22.1; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for C14H19NNaO$_4$S 320.0927, found 320.0934.

**Analytical data for 10a**



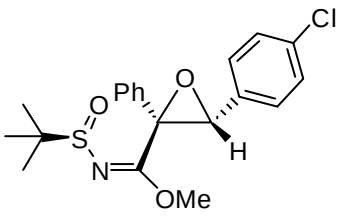
**Compound 10a:** General procedure was followed with 53.5 mg α-keto *N*-*tert*-butylsulfinylimidate **2a**, 22 mg of dimethyl phosphite **1a** . Column chromatography (petroleum ether / acetone 3:1) afforded 54.3 mg of **10a** as a colorless oil (72% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / acetone 3:1), $[\alpha]^{25}_D$ = +27° (*c* = 0.10, MeOH) ; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.61 (d, *J* = 7.2 Hz, 2H), 7.38–7.34 (m, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.78 (S, 3H), 3.76 (d, *J* = 11.6 Hz, 3H), 3.73 (d, *J* = 11.2 Hz, 3H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 168.1, 135.2, 129.0, 128.6, 127.4, 74.2, 74.2, 57.3, 54.9, 54.7, 22.2; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{12}H_{25}NNaO_6S$ 400.0954, found 400.0962.

**Analytical data for 2-methoxyimidoyloxiranes 7a-7q**

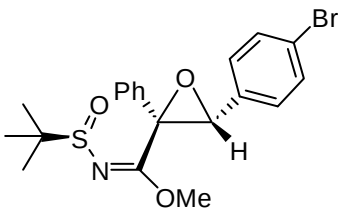


**Compound 7a:** General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 21.3 mg of benzaldehyde **5a**. Column chromatography afforded 55.8 mg of **7a** as a white solid (78% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 6:1), $[\alpha]^{25}_D$ = −84° (*c* = 0.10, MeOH), mp 122−123 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.44 (m, 2H), 7.19–7.17 (m, 5H), 7.12–7.13 (m, 3H), 4.68 (s, 1H), 3,84 (s, 3H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 169.8, 133.0, 132.2, 128.5, 128.1, 128.0, 127.8,

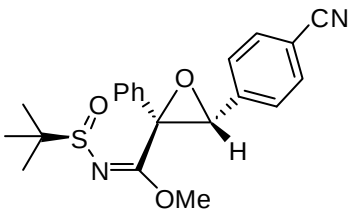
127.0, 66.8, 64.4, 56.6, 55.3, 22.0; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{20}H_{23}NNaO_3S$ 380.1291, found 380.1294.



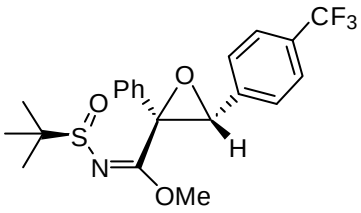
**Compound 7b:** General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 28.1 mg of 4-chlorobenzaldehyde **5b**. Column chromatography afforded 62.7 mg of **7b** as a white solid (80% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 6:1), $[\alpha]^{25}_D$ = −75° (*c* = 0.10, MeOH), mp 95−96 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.44 (m, 2H), 7.20–7.19 (m, 3H), 7.15-7.09 (m, 4H), 4.65 (s, 1H), 3,82 (s, 3H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 168.8, 134.0, 132.0, 131.6, 128.6, 128.5, 128.4, 128.1, 66.7, 64.0, 56.9, 55.3, 22.1;HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{20}H_{22}ClNNaO_3S$ 414.0901, found 414.0918.



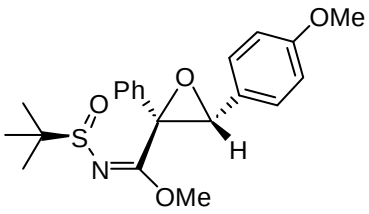
**Compound 7c:** General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenzaldehyde **5c**. Column chromatography afforded 72.4 mg of **7c** as a white solid (83% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 6:1), $[\alpha]^{25}_D$ = −58° (c = 0.10, MeOH), mp 106−107 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.46–7.44 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.20–7.19 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.63 (s, 1H), 3,82 (s, 3H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 168.8, 132.2, 131.9, 131.0, 128.8, 128.6, 128.5, 128.1, 122.3, 66.7, 64.0, 56.9, 55.3, 22.1; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{20}H_{22}BrNNaO_3S$ 458.0396, found 458.0405.



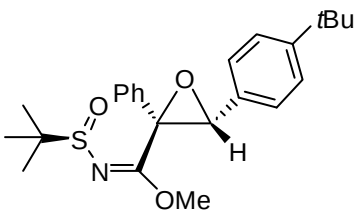
**Compound 7d:** General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 26.2 mg of 4-cyanobenzaldehyde **5d**. Column chromatography afforded 64.3 mg of **7d** as a white solid (84% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −77° (*c* = 0.10, MeOH), mp 158−159 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.46–7.36 (m, 6H), 7.19–7.18 (m, 3H), 4.74 (s, 1H), 3,81 (s, 3H), 1.23 (s, 9H); $^{13}$C NMR (100 MHz ,$CDCl_3$): *δ* 167.5, 138.6, 131.6, 131.5, 128.9, 128.5, 128.2, 128.0, 118.8, 111.9, 66.8, 63.8, 57.3, 55.4, 22.2; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{21}H_{22}BrN_2NaO_3S$ 405.1243, found 405.1253.



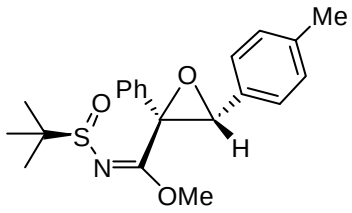
**Compound 7e:** General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 27.2 mg of 4-(trifluoromethyl)benaldehyde **5e**. Column chromatography afforded 65.5 mg of **7e** as a white solid (77% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 6:1), $[\alpha]^{25}_D$ = −63° (*c* = 0.10, MeOH), mp 80−81 °C; $^1$H NMR (400 MHz, $CDCl_3$):*δ* 7.48–7.46 (m, 2H), 7.40–7.33 (m, 4H), 7.20–7.18 (m, 2H), 4.73 (s, 1H), 3,83 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 168.3, 137.2, 131.8, 130.2 (q, $J_{C\text{-}F}$ = 30 Hz), 128.7, 128.5, 128.1, 127.5, 124.0 (q, $J_{C\text{-}F}$ = 270 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 66.8, 63.9, 57.0, 55.3, 22.1; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{21}H_{22}F_3NNaO_3S$ 448.1165, found 448.1187.



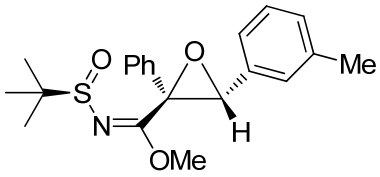
**Compound 7f**: General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 27.2 mg of anisaldehyde **5f**. Column chromatography afforded 71.3 mg of **7f** as a white solid (92% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −96° (c = 0.10, MeOH), mp 96−97 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.44 (m, 2H), 7.22–7.19 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 1H), 3,83 (s, 3H), 3.68 (s, 3H), 1.19 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 170.0, 159.5, 132.4, 128.5, 128.4, 128.3, 128.0, 125.0, 113.4, 66.8, 64.3, 56.5, 55.2, 22.0; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{21}H_{25}NNaO_4S$ 410.1397, found 410.1402.



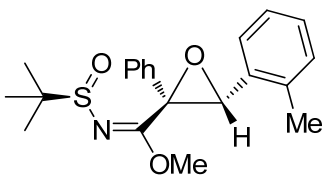
**Compound 7g**: General procedure was followed with 69.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 32.6 mg of 4-*tert*-butylbenaldehyde **5g**. Column chromatography afforded 62.9 mg of **7g** as a colorless gum (76% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −85° (*c* = 0.10, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.49–7.47 (m, 2H), 7.20–7.19 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.63 (s, 1H), 3,84 (s, 3H), 3.68 (s, 3H), 1.20 (s, 9H), 1.19 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 170.1, 151.1, 132.4, 129.9, 128.6, 128.4, 128.0, 126.9, 124.8, 66.8, 64.7, 56.6, 55.3, 34.6, 31.3, 22.1; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{24}H_{31}NNaO_3S$ 436.1917, found 436.1929.



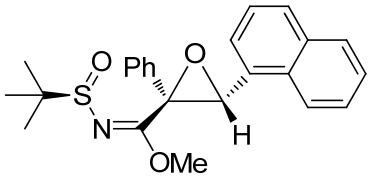
**Compound 7h:** General procedure was followed with 69.5 mg *α*-keto *N-tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 24.0 mg of *p*-tolualdehyde **5h**. Column chromatography afforded 69.1 mg of **7h** as a colorless gum (93% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −81° (*c* = 0.10, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.45 (m, 2H), 7.20–7.18 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.63 (s, 1H), 3,84 (s, 3H), 2.21 (s, 3H), 1.19 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 170.1, 137.9, 132.4, 129.9, 128.6, 128.5, 128.4, 128.0, 127.0, 66.8, 64.5, 56.5, 55.3, 22.0, 21.3; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{21}H_{25}NNaO_3S$ 394.1447, found 394.1455.



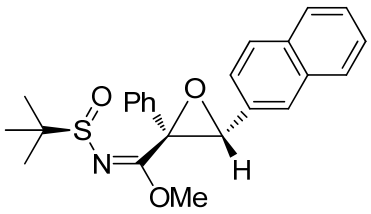
**Compound 7i:**.General procedure was followed with 69.5 mg *α*-keto *N-tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 24.0 mg of *m*-tolualdehyde **5i**. Column chromatography afforded 61.7 mg of **7i** as a pale yellow solid (83% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −86° (*c* = 0.10, MeOH), mp 111−112 °C ; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.46–7.44 (m, 2H), 7.22–7.18 (m, 3H), 7.03–6.93 (m, 4H), 4.62 (s, 1H), 3,85 (s, 3H), 2.19(s, 3H), 1.18 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 170.2, 137.4, 132.8, 132.3, 128.9, 128.4, 128.0, 127.7, 127.1, 66.8, 64.4, 56.4, 55.3, 22.0, 21,4; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{21}H_{25}NNaO_3S$ 394.1447, found 394.1448.



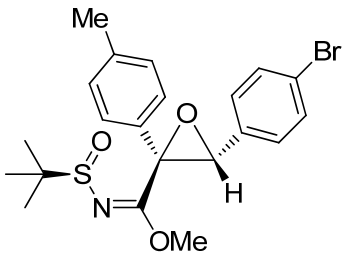
**Compound 7j:** General procedure was followed with 69.5 mg *α*-keto *N-tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 24.0 mg of 2-methylbenaldehyde **5j**. Column chromatography afforded 39.4 mg of **7j** as a white solid (53% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 4:1), $[\alpha]^{25}_D$ = −133° (*c* = 0.10, MeOH), mp 123−124 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.35–7.33 (m, 2H), 7.18–7.14 (m, 3H), 7.09–6.92 (m, 4H), 4.66 (s, 1H), 3,97 (s, 3H), 2.39 (s, 3H), 1.06 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 171.8, 136.0, 132.6, 131.1, 129.5, 128.5, 128.0, 127.9, 127.2, 126.9, 125.3, 66.7, 63.3, 55.7, 55.5, 21.7, 19.0; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{21}H_{25}NNaO_3S$ 394.1447, found 394.1460.



**Compound 7k:** General procedure was followed with 69.5 mg *α*-keto *N-tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 31.2 mg of 1-naphthaldehyde **5k**. Column chromatography afforded 51.3 mg of **7k** as a white solid (63% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −80° (*c* = 0.10, MeOH), mp 144−145 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 8.22 (d, *J* = 8.4Hz, 1H), 7.77 (d, *J* = 8.4Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.49–7.45 (m, 1H), 7.38–7.32 (m, 3H), 7.24–7.20 (m, 1H), 7.05–7.03 (m, 3H) , 5.12 (s, 1H), 4.07 (s, 3H), 1.07 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 171.9, 133.1, 132.6, 131.1, 128.7, 128.5, 128.4, 127.9, 127.1, 126.5, 125.9, 125.1, 125.0, 123.2, 67.0, 63.1 (d, *J* = 5.8 Hz ), 55.8, 55.7 (d, *J* = 1.8 Hz ), 21.7; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{24}H_{25}NNaO_3S$ 430.1447, found 430.1459.

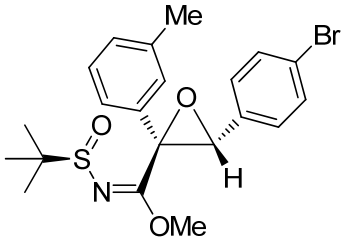


**Compound 7l:** General procedure was followed with 69.5 mg *α*-keto *N-tert*-butylsulfinylimidate **2a**, 28.6 mg of dimethyl phosphite **1a** and 31.2 mg of 2-naphthaldehyde **5l**. Column chromatography afforded 65.2 mg of **7l** as a white solid (80% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −57° (*c* = 0.10, MeOH), mp 129−130 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 8.22 (d, *J* = 8.4Hz, 1H), 7.77 (d, *J* = 8.4Hz, 1H), 7.77-7.68 (m, 3H), 7.60 (d, *J* = 8.4Hz, 1H), 7.51–7.49 (m, 2H), 7.41–7.38 (m, 2H), 7.29 (d, *J* = 8.8Hz, 1H), 7.18–7.12 (m, 3H) , 4.83 (s, 1H), 3.87 (s, 3H), 1.21 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 169.9, 133.1, 132.8, 132.2, 130.6, 128.5, 128.4, 128.1, 128.1, 128.0, 127.7, 127.6, 126.7, 126.1, 124.5, 67.1, 64.6, 56.6, 55.3, 22.0; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{24}H_{25}NNaO_3S$ 430.1447, found 430.1455.

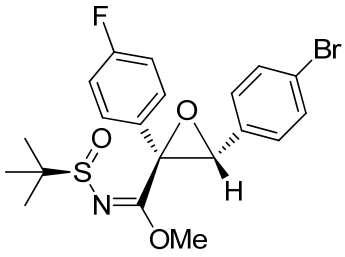


**Compound 7m:** General procedure was followed with 73.2 mg *α*-keto *N-tert*-butylsulfinylimidate **2b**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenaldehyde **5c**. Column chromatography afforded 67.6 mg of **7m** as a white solid (75% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −61° (*c* = 0.10, MeOH), mp 109−110 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 1H), 3.81 (s, 3H), 2.25(s, 3H), 1.21 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ*

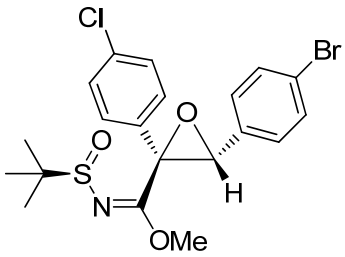
169.1, 138.5, 132.3, 131.0, 128.9 (overlap, 2C), 128.3, 122.2, 66.7, 64.0, 56.8, 55.3, 22.1, 21.4; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{21}H_{24}BrNNaO_3S$ 472.0552, found 472.0572.




**Compound 7n:** General procedure was followed with 73.2 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2c**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenaldehyde **5c**. Column chromatography afforded 54.9 mg of **7n** as a white solid (61% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 5:1), $[\alpha]^{25}_D$ = −64° (*c* = 0.10, MeOH), mp 94–95 °C; $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.28–7.22 (m, 4H), 7.09–7.06 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 4.61 (s, 1H), 3.82 (s, 3H), 2.25 (s, 3H), 1.21 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 169.0, 137.8, 132.2, 131.8, 131.0, 129.4, 128.9, 128.8, 128.0, 125.6, 122.3, 66.8, 64.0, 56.9, 55.3, 22.1, 21.5; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{21}H_{24}BrNNaO_3S$ 472.0552, found 472.0561.

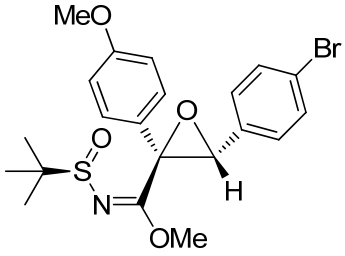



**Compound 7o:** General procedure was followed with 74.2 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2d**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenaldehyde **5c**. Column chromatography afforded 71.8 mg of **7o** as a white solid (79% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate =6:1), $[\alpha]^{25}_D$ = −54° (c = 0.10, MeOH), mp 97–98 °C; $^1$HNMR (400 MHz, $CDCl_3$): *δ* 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 8.4 Hz, 2H), 4.64 (s, 1H), 3.80 (s, H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 168.0, 162.7 (d, $J_{C\text{-}F}$ = 246 Hz), 132.0, 131.1, 130.6 (d, $J_{C\text{-}F}$ = 8.4 Hz), 128.8, 127.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 122.4, 115.2 (d, $J_{C\text{-}F}$ = 21.7 Hz), 66.0, 64.1, 57.1, 55.3, 22.2; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{20}H_{21}BrFNNaO_3S$ 476.0302, found 476.0314.




**Compound 7p:** General procedure was followed with 78.5 mg *α*-keto *N*-*tert*-butylsulfinylimidate **2e**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenaldehyde **5c**. Column chromatography afforded 57.4 mg of **7p** as a colorless gum (61% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate =6:1), $[\alpha]^{25}_D$ = −66° (*c* = 0.10, MeOH); *δ* 7.43 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.65 (s, 1H), 3.80 (s, H), 1.23 (s, 9H); $^{13}$C

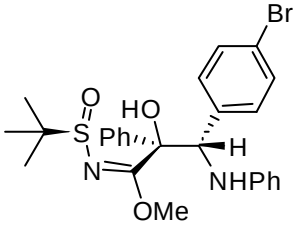
NMR: (100 MHz, $CDCl_3$):167.7, 134.7, 131.9, 131.2, 130.6, 130.1, 128.8, 128.4, 122.5, 66.1, 64.2 (d, $J$ = 2.9 Hz), 57.2, 55.3 (d, $J$ = 2.3 Hz), 22.2; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{20}H_{21}BrBrNNaO_3S$ 492.0006, found 492.0021.




**Compound 7q:** General procedure was followed with 77.3 mg $\alpha$-keto *N-tert*-butylsulfinylimidate **2f**, 28.6 mg of dimethyl phosphite **1a** and 37.0 mg of 4-bromobenaldehyde **5c**. Column chromatography afforded 68.1 mg of **7q** as a white solid (73% yield), dr > 20:1. Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 3:1), $[\alpha]^{25}_D = -98°$ ($c$ = 0.10, MeOH), mp 121−122 °C; $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.77 (d, $J$ = 8.8 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 7.10 (d, $J$ = 8.4 Hz, 2H), 6.58 (d, $J$ = 8.8 Hz, 2H), 4.68 (s, 1H), 3.21 (s, 3H), 3.05 (s, 3H), 1.12 (s, 9H); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 167.4, 160.1, 133.4, 131.1, 130.8, 129.7, 124.8, 122.4, 111.7, 66.4, 64.7, 57.1, 54.5, 54.3, 22.2; HRMS (ESI-TOF) ($m/z$) $[M + Na]^+$ calcd for $C_{21}H_{24}BrNNaO_4S$ 488.0502, found 488.0525.

**Further transformations of 2-methoxyimidoyloxirane 7c:**

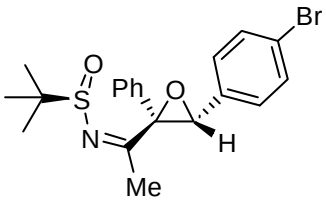
***α*-Hydroxy-*β*-amino imidate 11**: $Sc(OTf)_3$ (369 mg, 0.75 mmol, 3.0 equiv) was added to a 100 mL flame-dried round-bottomed flask equipped with a magnetic stirring bar and purged with argon. Toluene (18 mL) was added and to the resulting suspension were added aniline (336.5mg, 2.5 mmol, 10.0 equiv) and a toluene solution (1.5 mL) of 2-methoxyimidoyloxirane **7c** (109 mg, 0.25 mmol, 1.0 equiv). The reaction was heated to 60 °C with vigorous stirring and maintained for 14 h. The reaction was cooled to rt, diluted with $H_2O$ (10 mL) and EtOAc (10 mL), and the resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded 92.8 mg (70%) of **11** as white solid.




Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 12:1); $[\alpha]^{25}_D = -227°$ ($c$ = 0.10, MeOH), mp 161−162 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J$ = 7.6 Hz, 2H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.38–7.33 (m, 5H), 7.29 (d, $J$ = 7.2 Hz, 1H), 7.00 (t, $J$ = 7.6 Hz, 2H), 6.56 (t, $J$ = 7.6 Hz, 1H), 6.40 (d, $J$ = 7.6 Hz, 2H), 5.29 (s, 1H), 3.62 (s, 3H), 1.00 (s, 9H); $^{13}$C

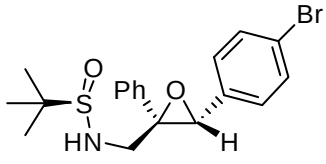
NMR (100 MHz, $CDCl_3$): $\delta$ 169.6, 146.6, 140.5, 138.6, 131.3, 131.0, 129.1, 128.5, 128.2, 126.6, 121.7, 117.2, 113.3, 82.7, 62.0, 58.2, 54.4, 22.2; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{26}H_{29}BrN_2NaO_3S$ 551.0974, found 551.0995.

**Sulfinyl ketimine 12**: 5.0 mL THF, 2-methoxyimidoyloxirane **7c** (109 mg, 0.25 mmol, 1.0 equiv) was added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The solution was cooled to −40 °C. MeMgBr (1.0 M in THF, 1.0 mL, 1.0 mmol, 4.0 equiv) was added dropwise to the solution via syringe. The reaction was allowed to stir at −40 °C for 4 h. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 15 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded 78.6 mg (75% yield) of **12** as colorless oil.



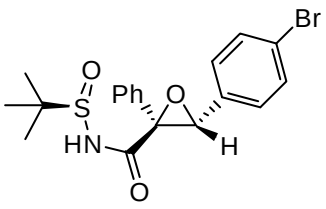

Analytical data: $R_f$ = 0.25 (petroleum ether / ethyl acetate = 6:1); $[\alpha]^{25}_D$ = +16° (*c* = 0.10, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.24 (s, 2H), 7.20 (s, 5H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 1H), 2.41 (s, 3H), 1.15 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 181.5, 132.9, 132.5, 131.2, 128.7, 128.5, 128.4, 128.0, 122.3, 71.6, 63.2, 57.4, 22.3, 18.3; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{20}H_{22}BrNNaO_2S$ 442.0447, found 442.0453.

**Sulfinyl amine 13**: 4.0 mL THF, 2-methoxyimidoyloxirane **7c** (109 mg, 0.25 mmol, 1.0 equiv) was added to a round-bottomed flask equipped with a magnetic stirring bar. $NaBH_4$ (19.5 mg, 0.5 mmol, 2 equiv) was added to the solution. The reaction was allowed to stir at rt for 2 h. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 15 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded 98.0 mg (96% yield) of **13** as a white solid.



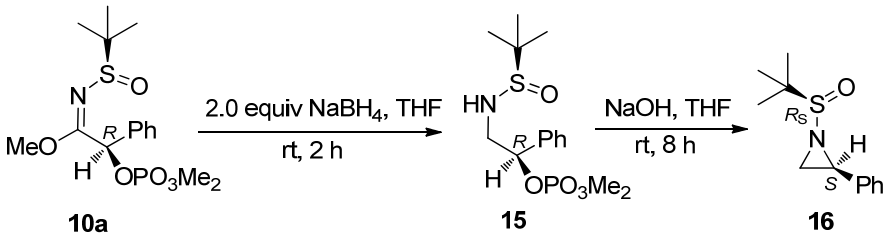

Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 2:1); $[\alpha]^{25}_D$ = −27° (*c* = 0.10, MeOH), mp 100−101 °C; $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.20 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.85–6.93 (m, 5H), 4.22 (s, 1H), 3.54–3.47 (m, 1H), 3.44–3.32 (m, 2H), 0.96 (s, 9H); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 135.3, 134.8, 131.1, 128.8, 128.7, 128.3, 128.1, 121.9, 68.1, 62.7, 55.8, 52.1, 22.5; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{19}H_{22}BrNNaO_2S$ 430.0447, found 430.0463.

**Amide 14**: 4.0 mL THF, 2-methoxyimidoyloxirane **7c** (109 mg, 0.25 mmol, 1.0 equiv) was added to a round-bottomed flask equipped with a magnetic stirring bar. $H_2SO_4$ (1.0 M, 2 mL) was added to the solution. The reaction was allowed to stir at rt for 15 h. Then, the reaction was extracted with 15 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded 96.5 mg (96%) of **14** as a white solid.



Analytical data: $R_f$ = 0.20 (petroleum ether / ethyl acetate = 3:1); $[\alpha]^{25}_D$ = −41° (*c* = 0.10, MeOH), mp 68–69 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.70 (s, 1H), 7.35–7.32 (m, 2H), 7.29–7.26 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 2H ), 4.32 (s, 1H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 169.1, 131.4, 131.3, 129.4, 129.2, 128.8, 128.5, 128.4, 123.1, 66.8, 64.1, 57.3, 22.1; HRMS (ESI-TOF) (*m*/*z*) [M + Na]$^+$ calcd for $C_{19}H_{20}BrNNaO_3S$ 444.0239, found 444.0249.

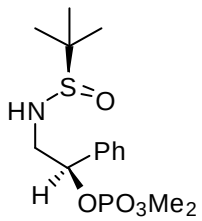
Assignment of the absolute stereochemistry of compound **10a**:




5.0 mL THF, 151 mg **10a** (0.4 mmol, 1.0 equiv) was added to a round-bottomed flask equipped with a magnetic stirring bar. $NaBH_4$ (31 mg, 0.8 mmol, 2 equiv) was added to the solution. The reaction was allowed to stir at rt for 2 h. Then, the reaction was quenched with saturated aqueous ammonium chloride and extracted with 20 mL (×3) of ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded **15** as a white solid.

3.0 mL THF, 70 mg **15** (0.2 mmol, 1.0 equiv) was added to a round-bottomed flask equipped with a magnetic stirring bar. NaOH (1.0 M, 2 mL) was added to the solution. The reaction was allowed to stir at rt for 8 h. Then, the reaction mixture was extracted with 20 mL (×3) of dichloromethane. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography afforded **16** as

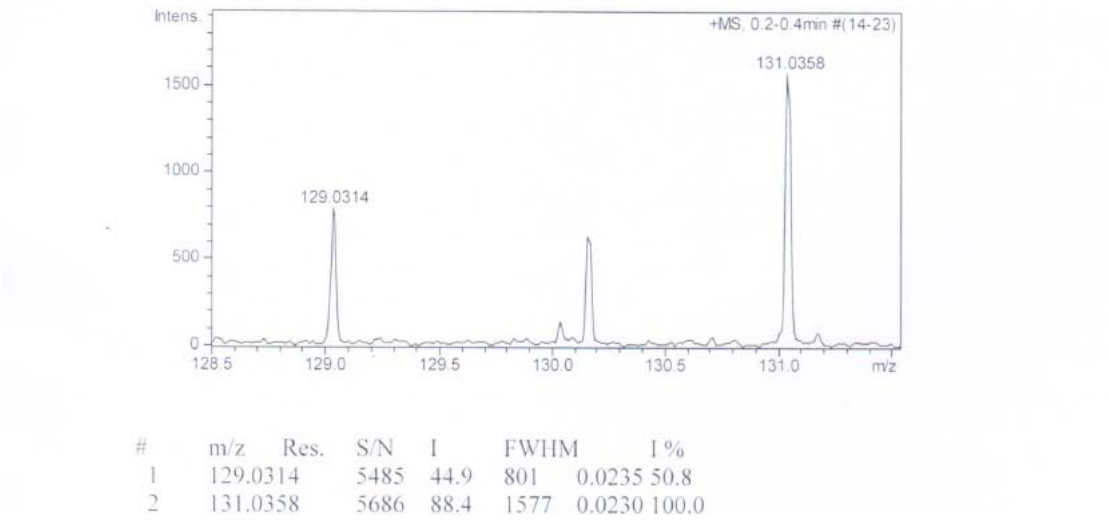
a white solid. The NMR spectra of compound **16** is identical to that of known compound (*R*s, *S*)-**16** reported in literature,[3] allowing assignment of the absolute stereochemistry of (2*R*, *R*s)-**10a**.




(**15**): Analytical data: $R_f$ = 0.20 ($CH_2Cl_2$ /MeOH = 30:1); $[\alpha]^{25}_D$ = −48° (*c* = 0.10, MeOH),mp 67–68 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.70 (s, 1H), 7.385–7.34 (m, 5H), 5.41–5.37 (m, 1H), 3.94–3.91 (m, 1H), 3.71 (d, *J* = 11.2 Hz, 3H ), 3.72–3.69 (m, 1H), 3.58 (d, *J* = 11.2 Hz, 3H ),1.20 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 137.5, 129.1, 128.9, 126.7, 80.4, 56.2, 54.6, 54.5, 51.7, 22.7; HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_{14}H_{24}NNaO_5PS$ 372.1005, found 372.1022.

**$^{18}$O labeling experiments**

$^{18}$O-Labeled benzaldehyde was prepared according to literature,[4] the $^{18}$O isotope content was 66% by mass spectral analysis:



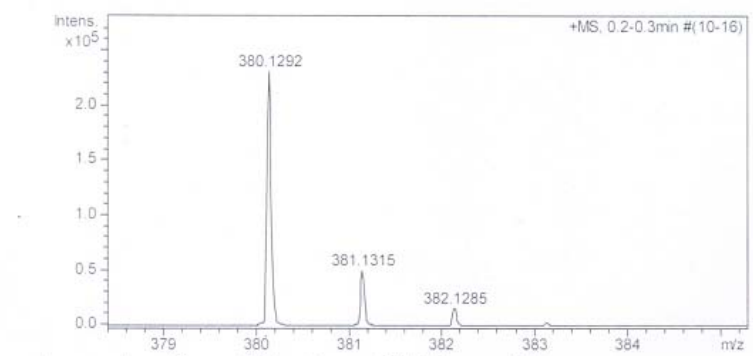

| # | m/z | Res. | S/N | I | FWHM | I % |
|---|---|---|---|---|---|---|
| 1 | 129.0314 | 5485 | 44.9 | 801 | 0.0235 | 50.8 |
| 2 | 131.0358 | 5686 | 88.4 | 1577 | 0.0230 | 100.0 |

For PhCHO: HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_7H_6NaO$ 129.0311, found 129.0314 (intensity: 50.8%)

For PhCH$^{18}$O: HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ calcd for $C_7H_6Na^{18}O$ 131.0353, found 131.0358 (intensity: 100%)

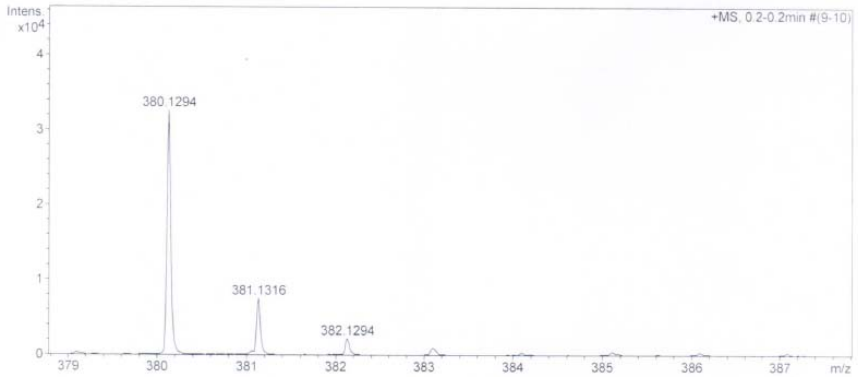
**$^{18}$O isotope content**: PhCH$^{18}$O / (PhCH$^{18}$O + PhCHO) ≈ 100 / (100 + 50.8) = 66%

HRMS of product **7a** prepared from the reaction using $^{18}$O-labeled benzaldehyde (PhCH$^{18}$O, 66% isotope content):




| # | m/z | Res. | S/N | I | FWHM | I % | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 380.1292 | 7826 | 24033.0 | 231550 | 0.0486 | 100.0 | | |
| 2 | 381.1315 | 8463 | 5304.1 | 51103 | 0.0450 | 22.1 | | |
| 3 | 382.1285 | 7998 | 1640.1 | 15802 | 0.0478 | 6.8 | | |

HRMS of product **7a** prepared from the reaction using benzaldehyde (PhCHO):




| Meas. m/z | # | Formula | m/z | err [ppm] | Mean err [ppm] | rdb | N-Rule | e⁻ Conf | mSigma | Std I | Std Mean m/z | Std I VarNorm | Std m/z Diff | Std Comb Dev |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 380.1294 | | | | | | | | | | | | | | |
| | 1 | C 20 H 23 N Na O 3 S | 380.1291 | -0.8 | -0.8 | 9.5 | ok | even | 7.52 | 0.0120 | 0.0011 | 0.0074 | 0.0030 | 0.8427 |

| # | m/z | Res. | S/N | I | FWHM | I % |
|---|---|---|---|---|---|---|
| 1 | 380.1294 | 8324 | 3694.2 | 32647 | 0.0457 | 100.0 |
| 2 | 381.1316 | 8272 | 855.9 | 7564 | 0.0461 | 23.2 |
| 3 | 382.1294 | 7695 | 248.7 | 2198 | 0.0497 | 6.7 |

HRMS (ESI-TOF) (*m*/*z*) $[M + Na]^+$ for epoxide produced from PhCH$^{18}$O and PhCHO:

| $C_{20}H_{23}NNaO_3S^+$ (mass, intensity) | | |
|---|---|---|
| calcd | Found (using **PhCH$^{18}$O**) | Found (using **PhCHO**) |
| 380.1295, 100% | 380.1292, 100% | 380.1294, 100% |
| 381.1325, 21.6% | 381.1315, 22.1% | 381.1316, 23.2% |
| 382.1249, 4.5% | 382.1285, 6.8% | 382.1294, 6.7% |
| 382.1358, 2.2% | | |
| 383.1283, 1.0% | – | – |

*Conclusion*: *Near identical HRMS results were obtained for the reaction products in the cases using PhCH$^{18}$O and PhCHO. Reaction employing $^{18}$O-labeled benzaldehyde provided product without effective incorporation of the $^{18}$O label.*

**References**

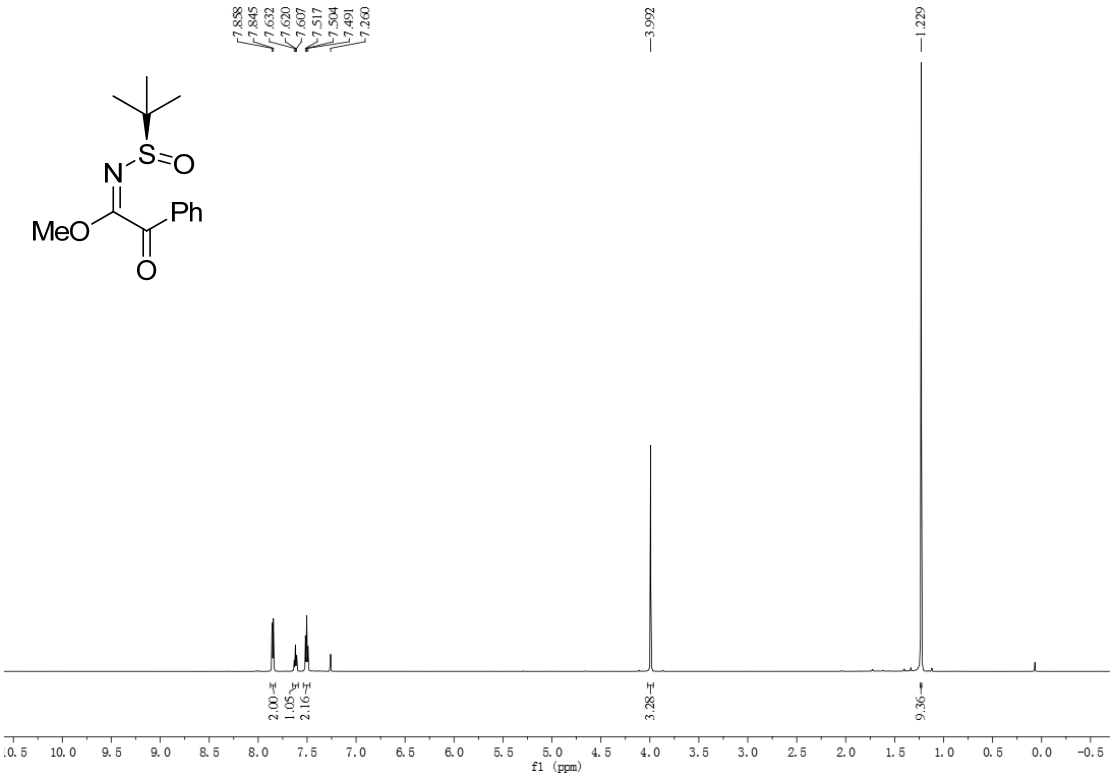
(1) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1539.

(2) Satoh, T.; Nakamura, A.; Iriuchijima, A. *Tetrahedron*. **2001**, *57*, 9689.

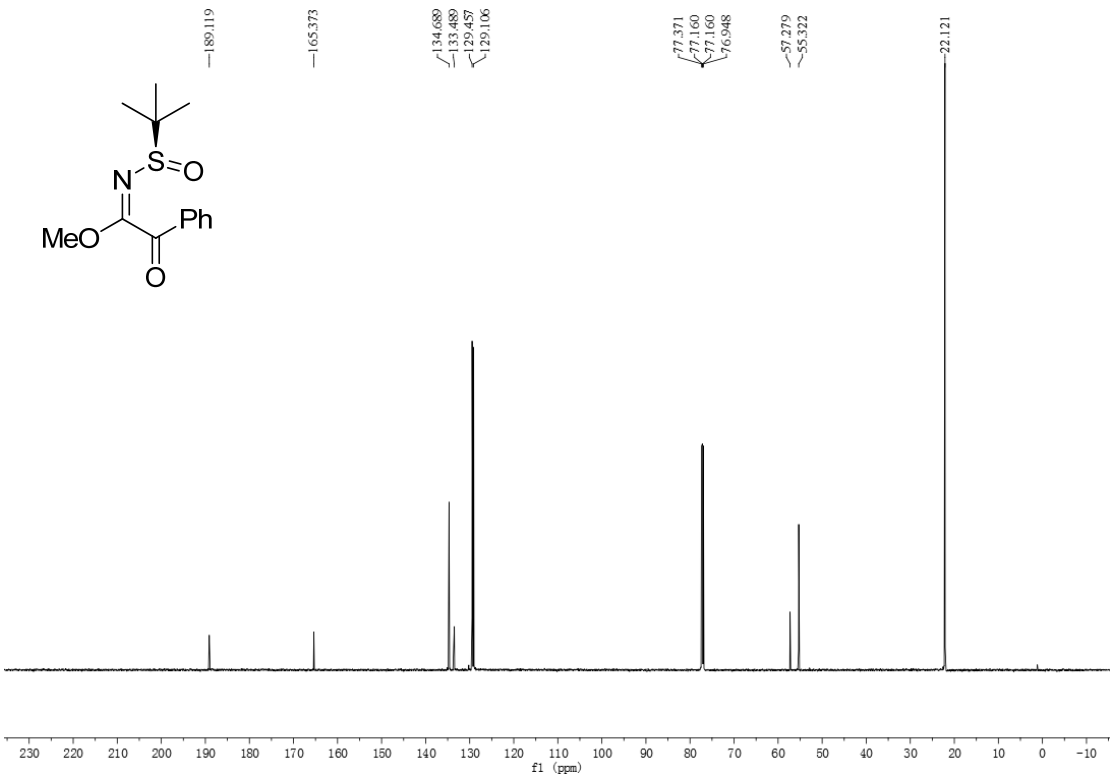
(3) Denolf, B.; Leemans, M.; Kimpe, N. D. *J. Org. Chem.* **2007**, *72*, 3211.

(4) Carlsen, P. H. J.; Ystenes, M. *Acta Chem. Scand.* **1986**, *40B*, 757.

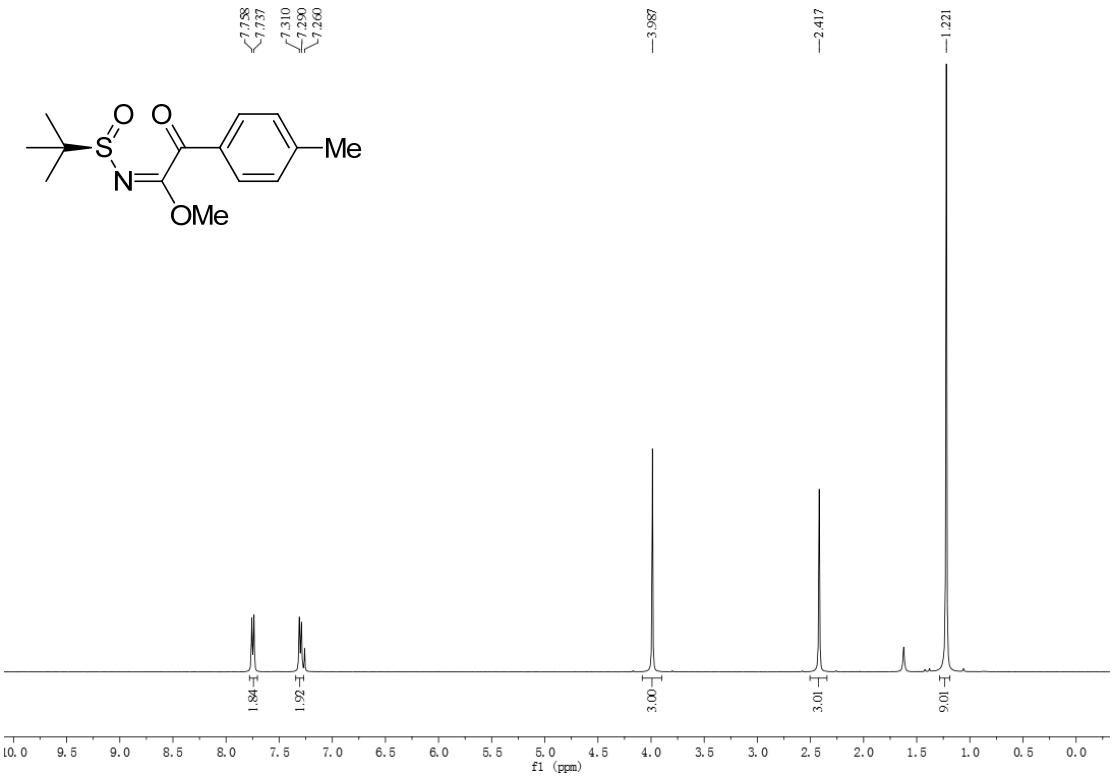
**$^{1}$H NMR and $^{13}$C NMR spectra for new compounds**



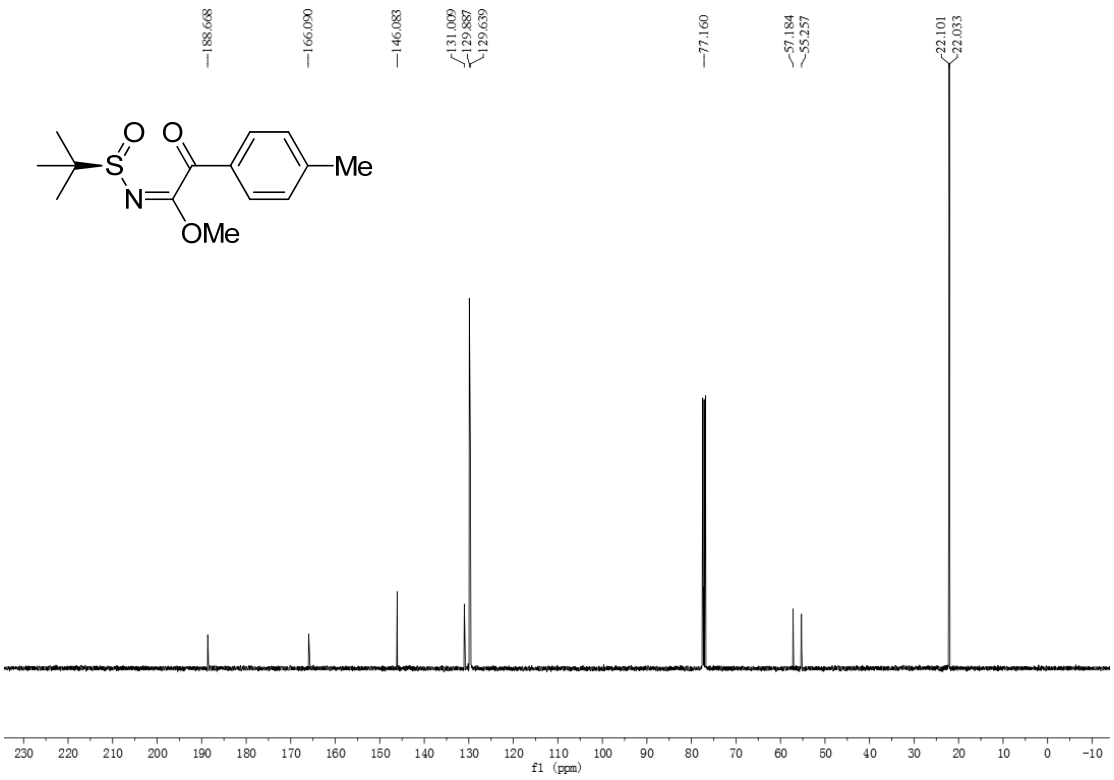

$^{1}$H NMR spectrum ($CDCl_3$, 600 MHz) of **2a**



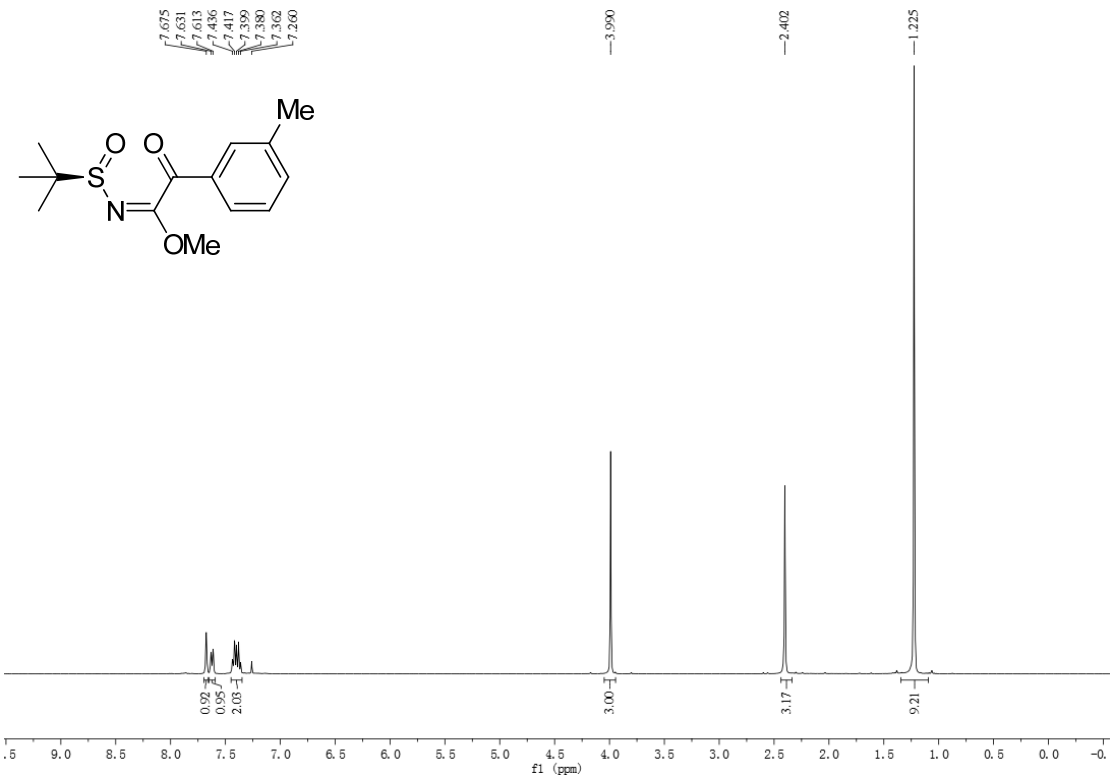

$^{13}$C NMR spectrum ($CDCl_3$, 150 MHz) of **2a**



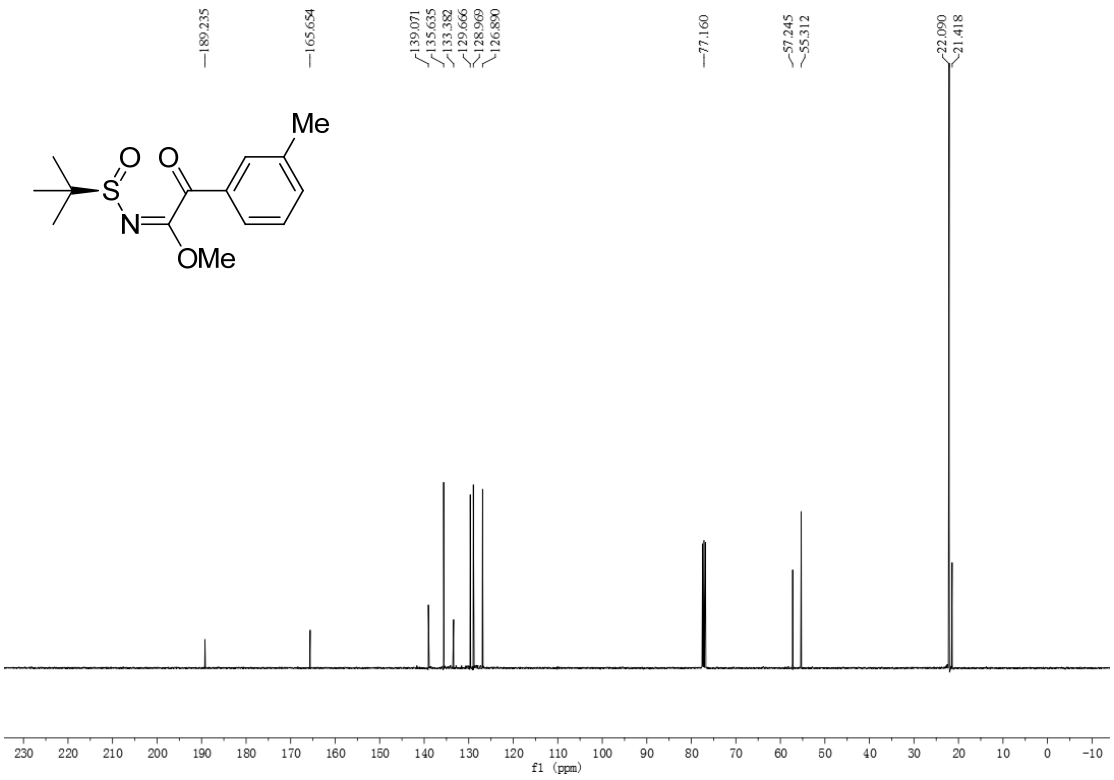

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **2b**



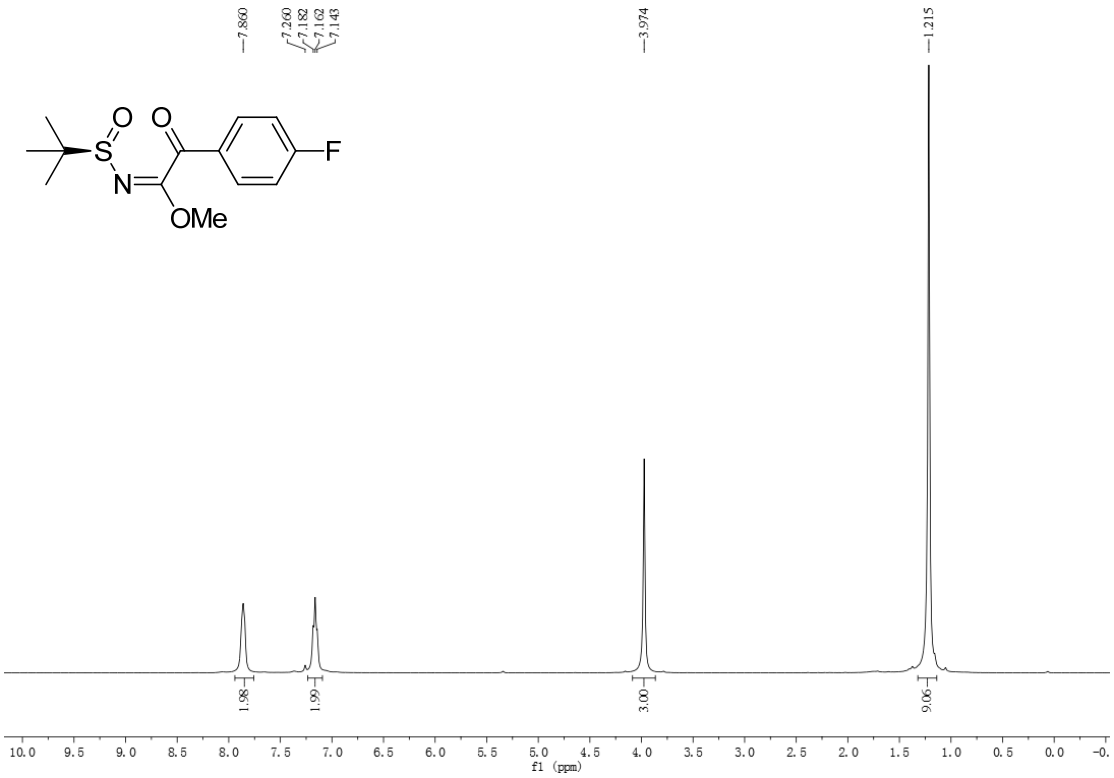

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **2b**



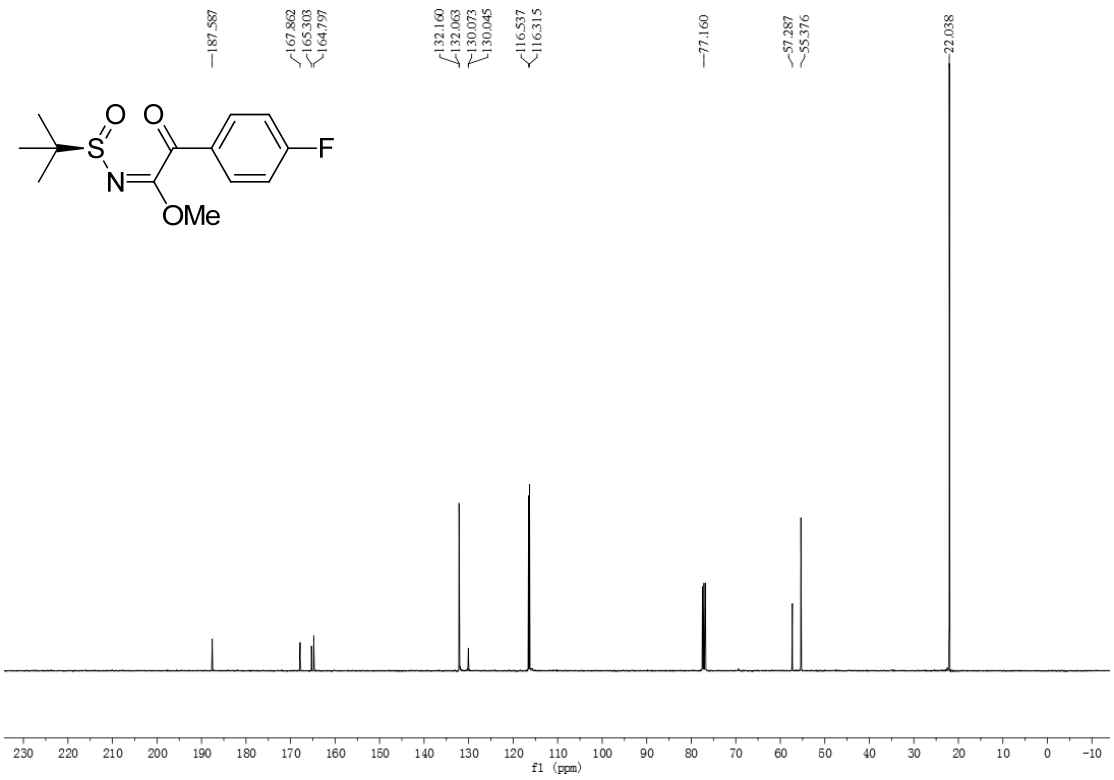

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **2c**



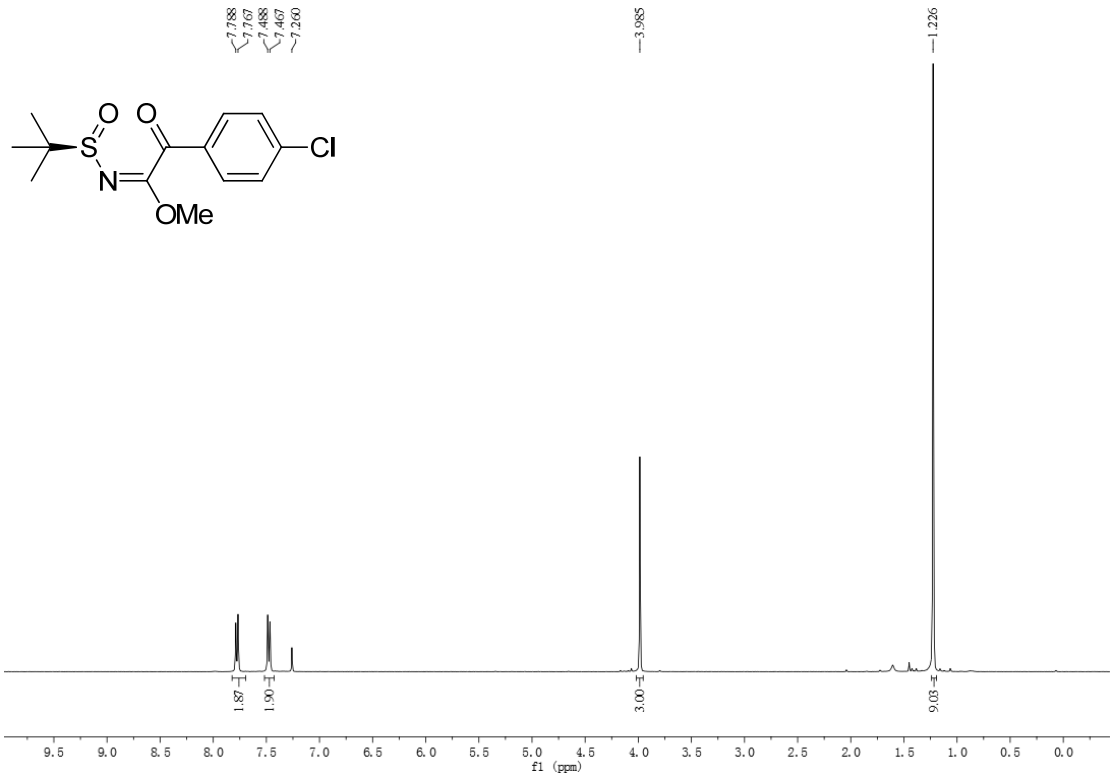

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **2c**



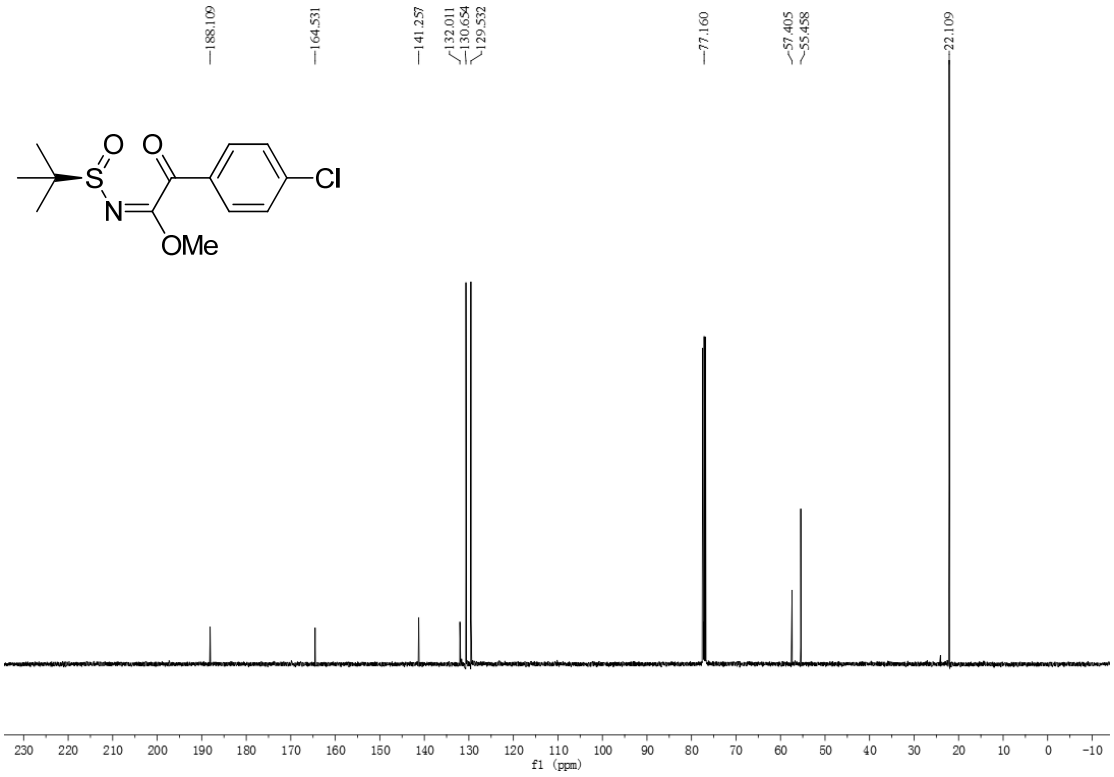

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **2d**



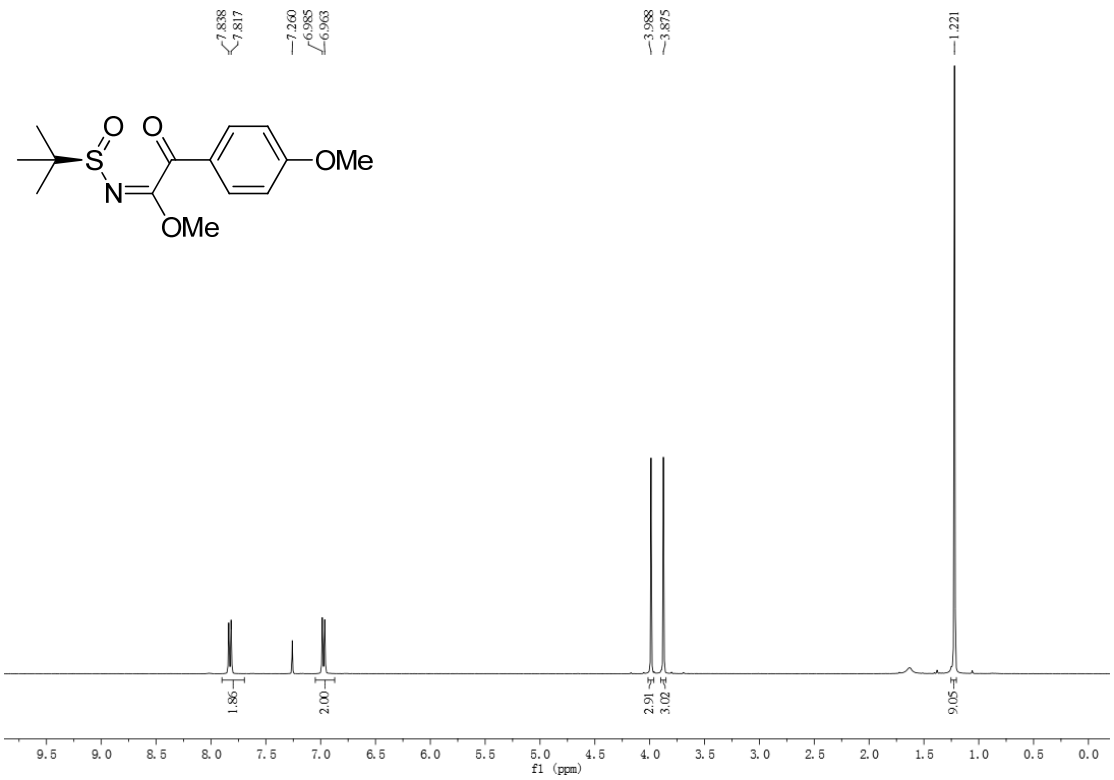

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **2d**



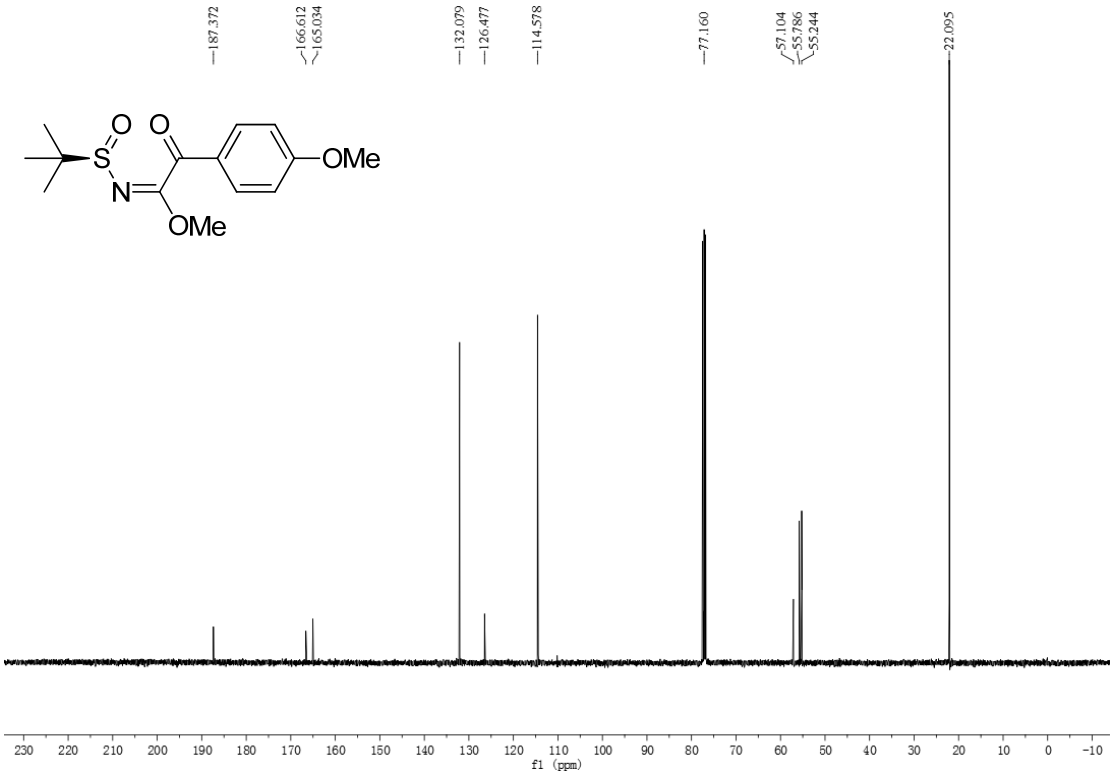

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **2e**



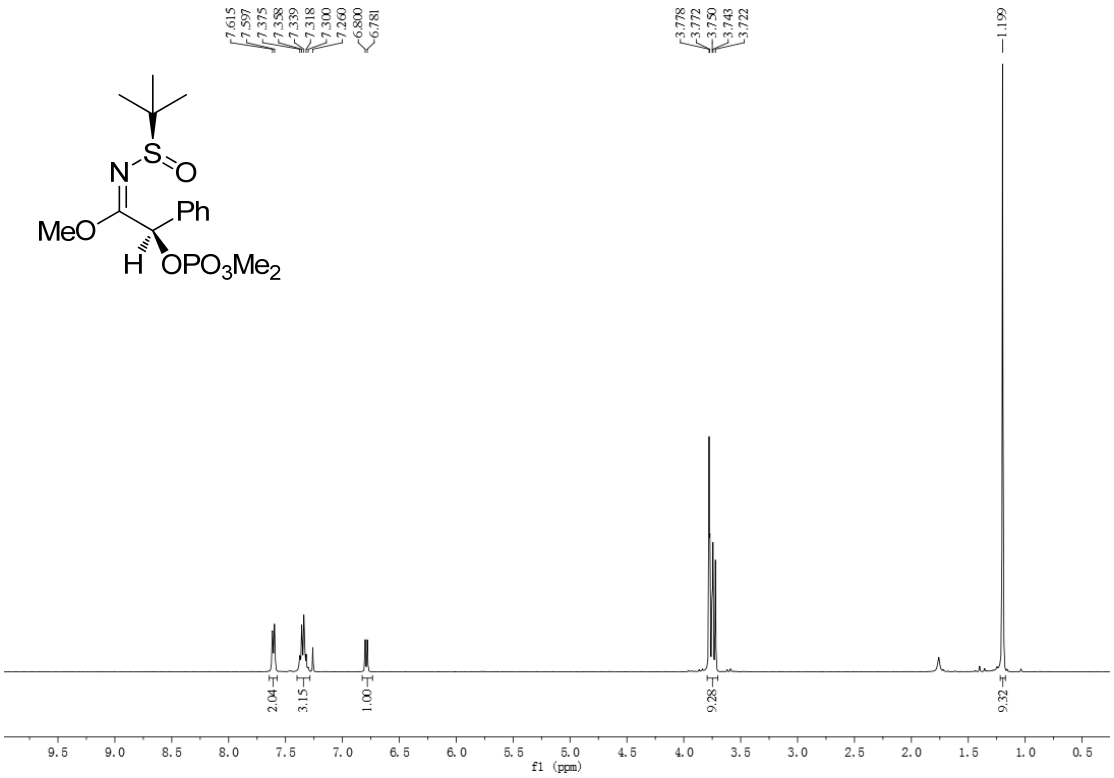

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **2e**



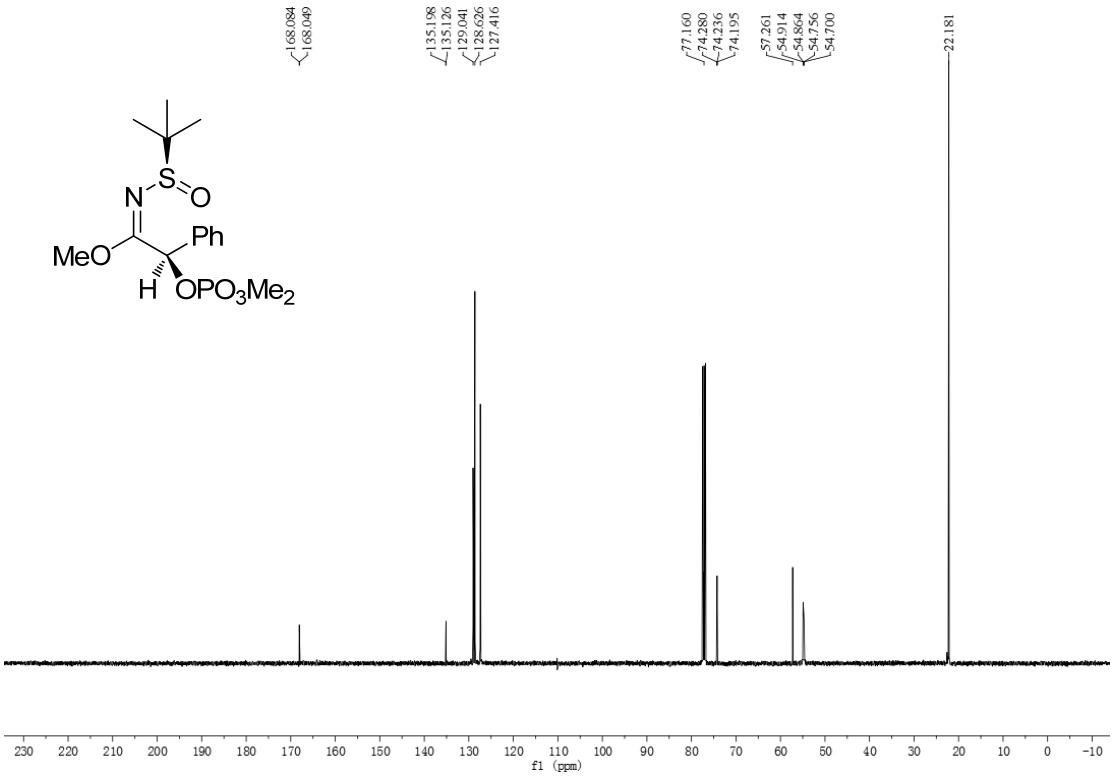

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **2f**



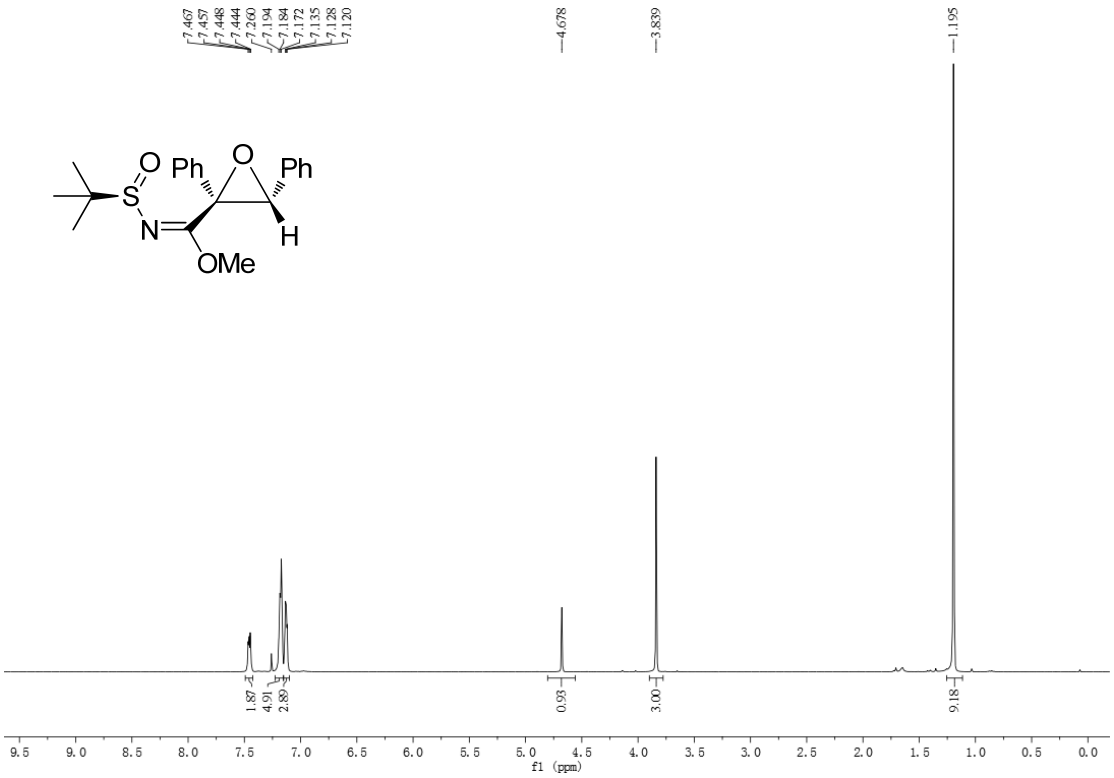

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **2f**



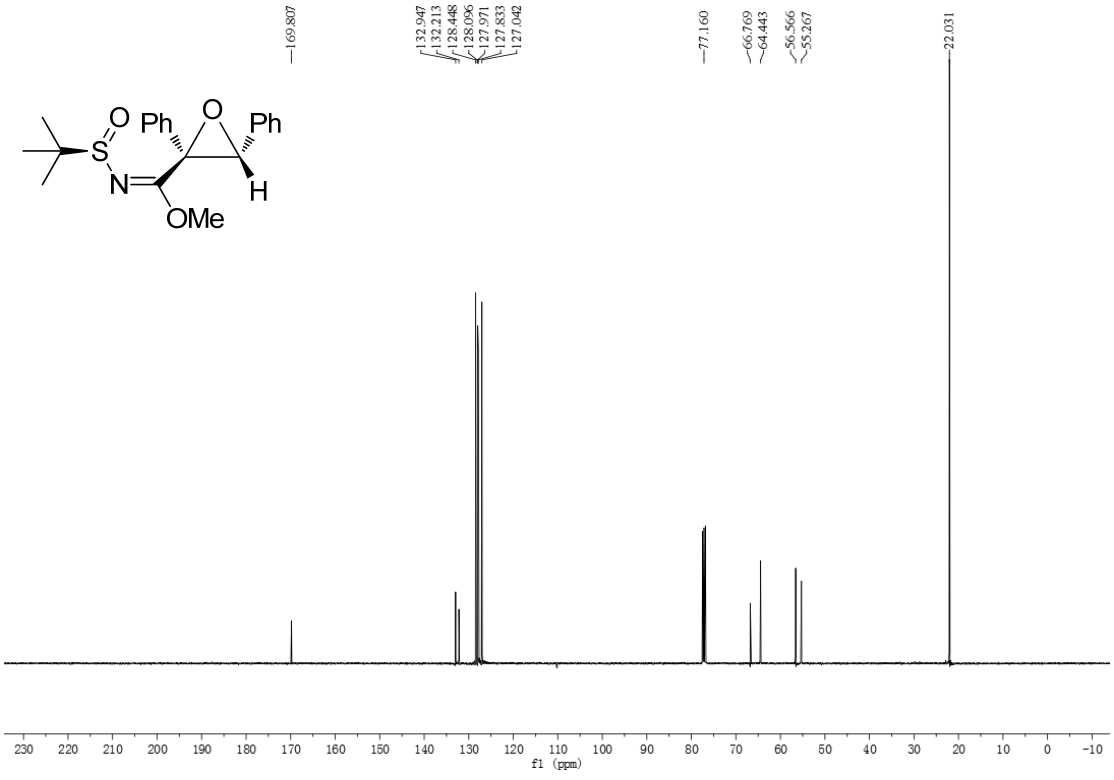

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **10a**



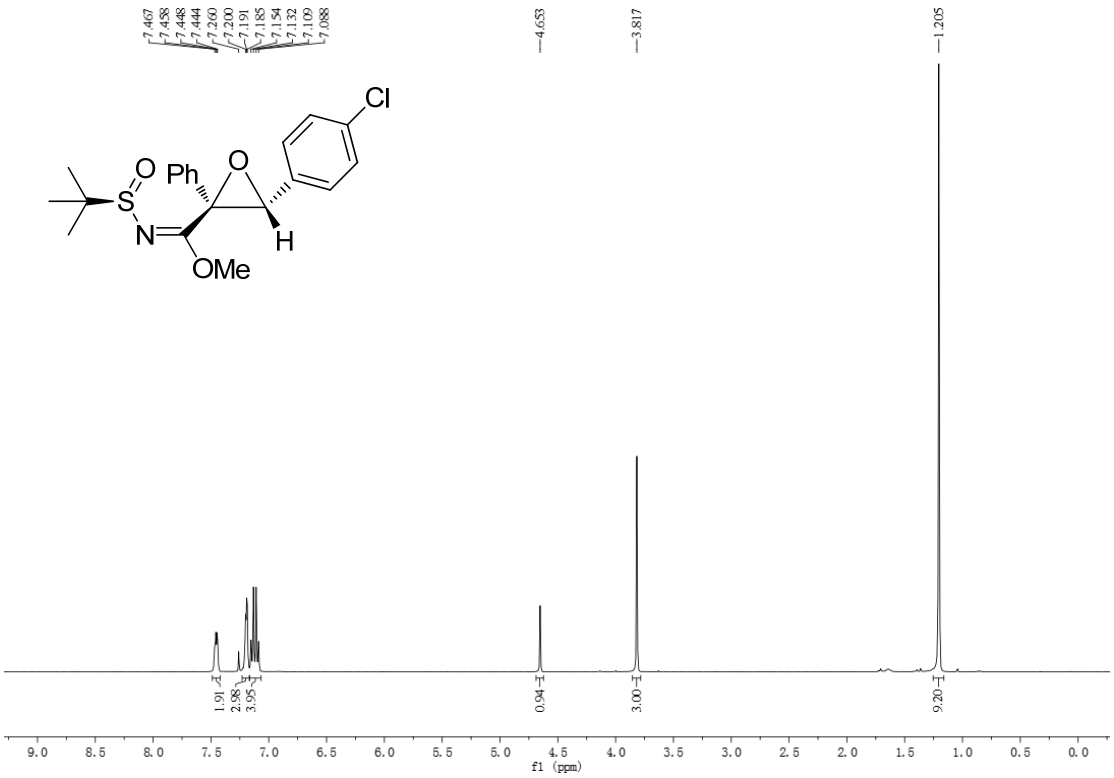

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **10a**



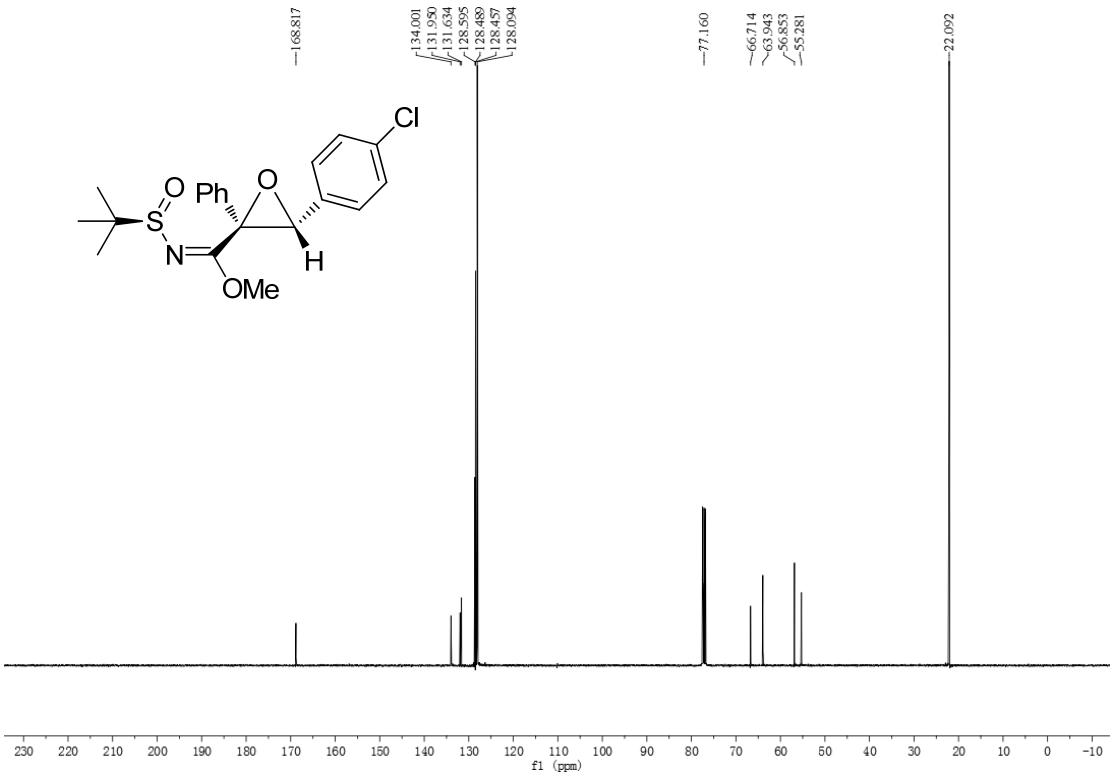

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7a**



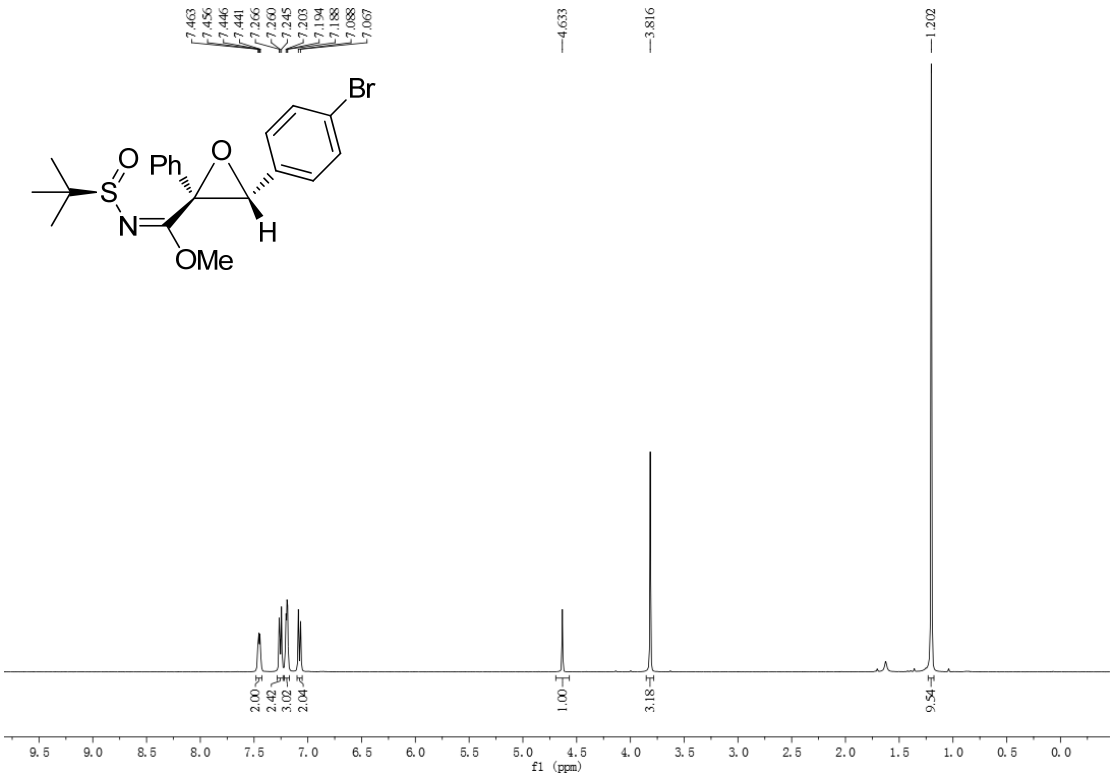

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7a**



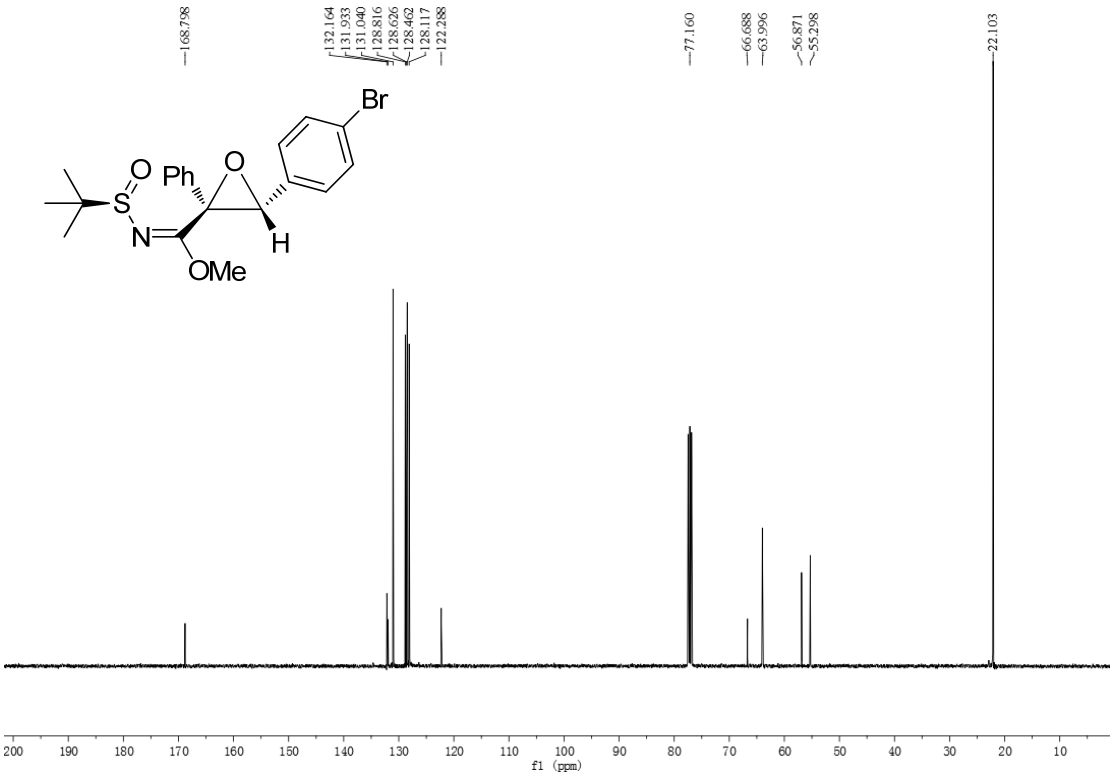

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7b**



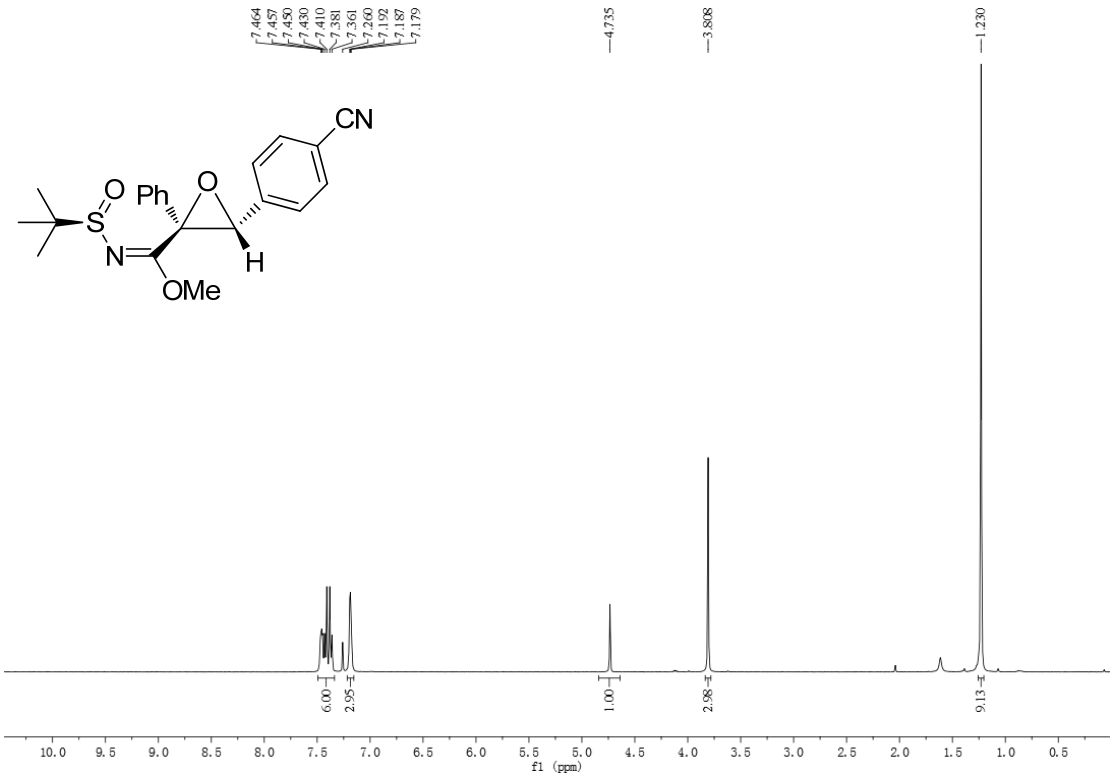

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7b**



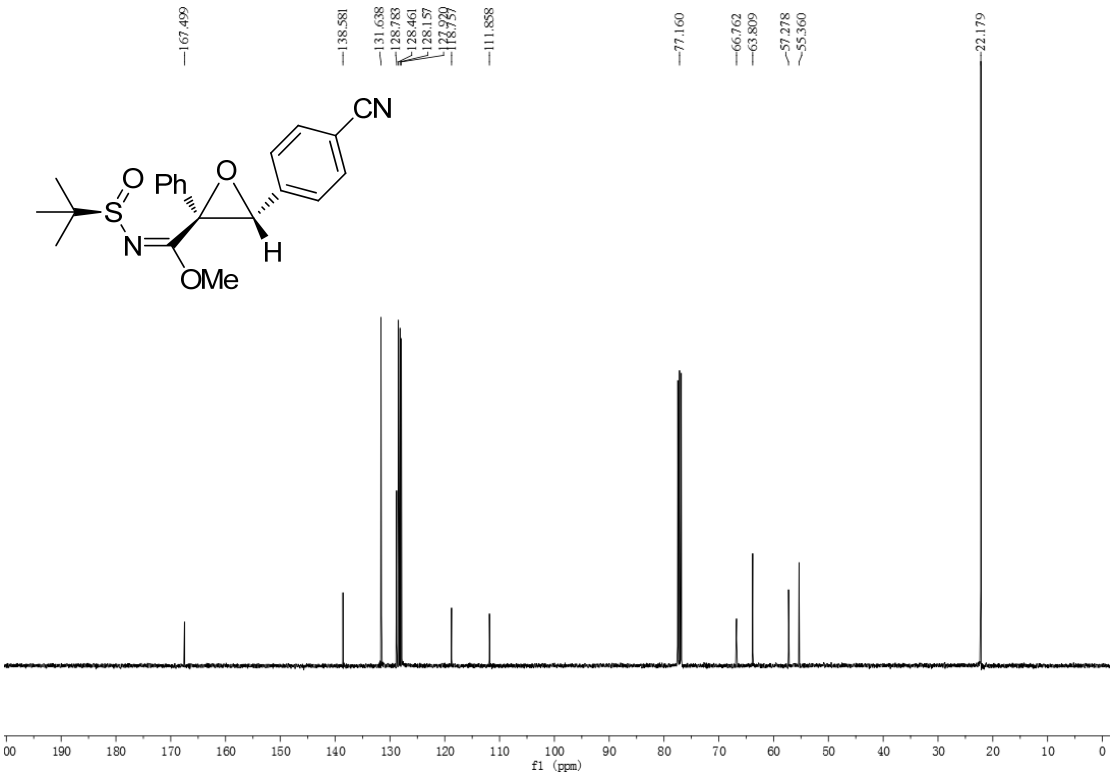

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7c**



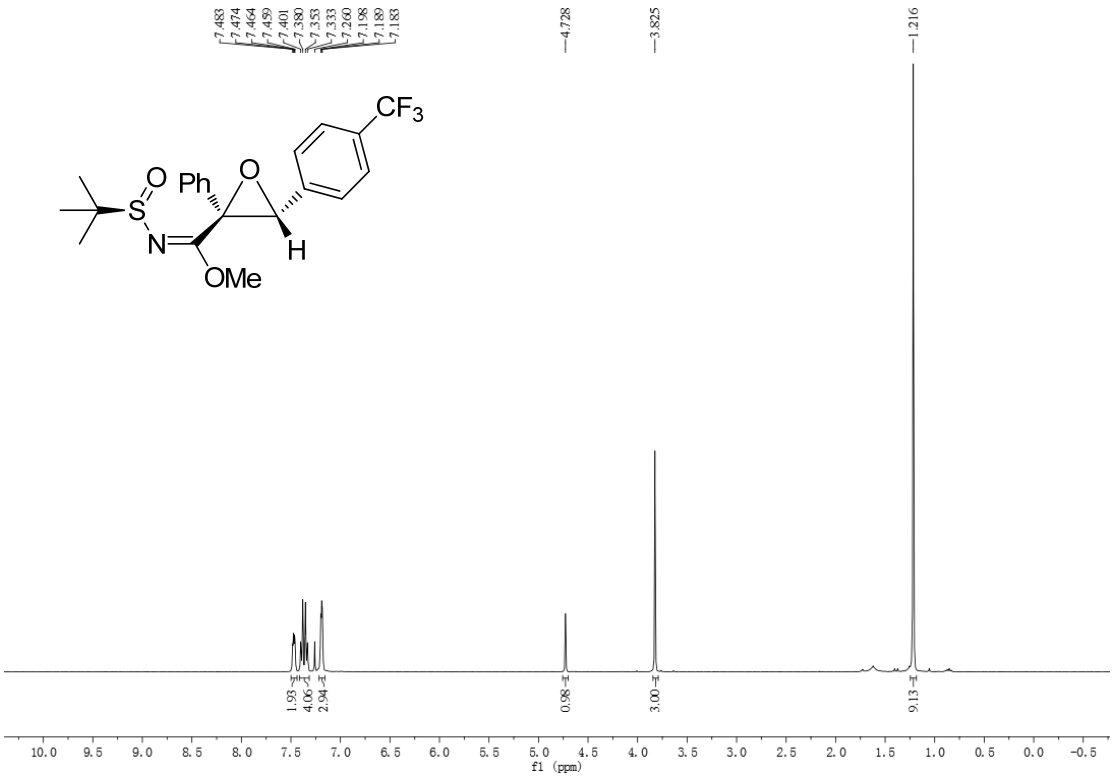

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7c**



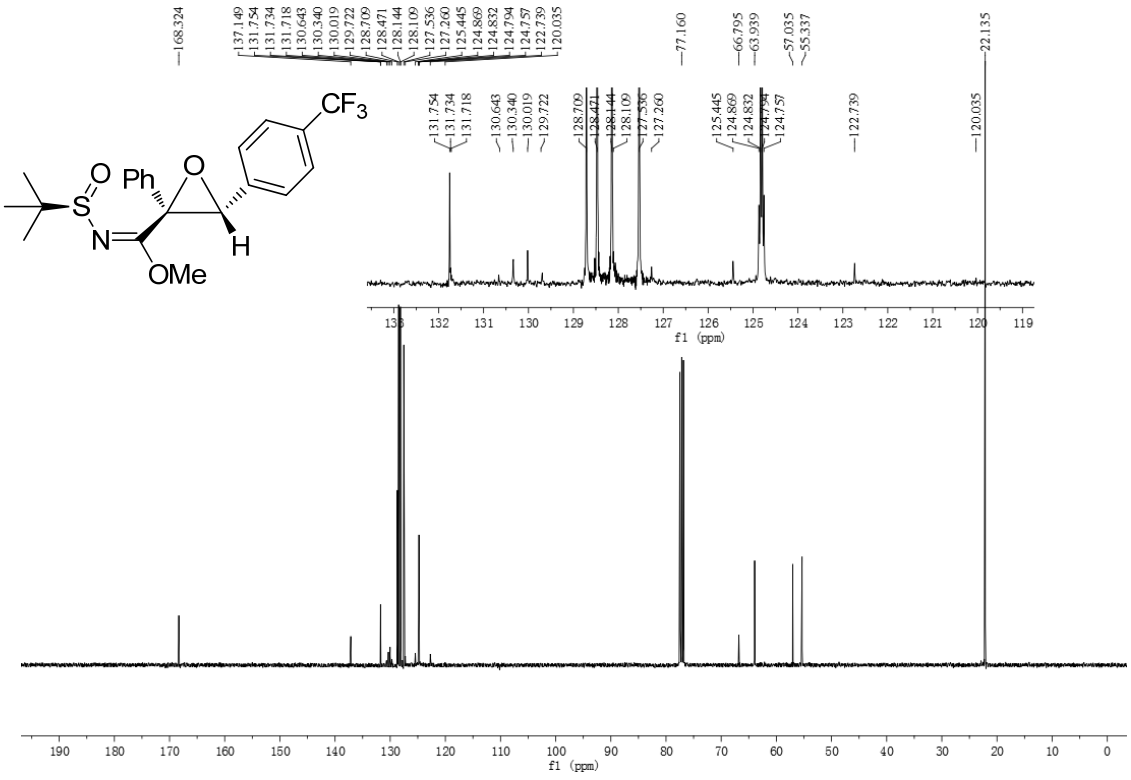

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7d**



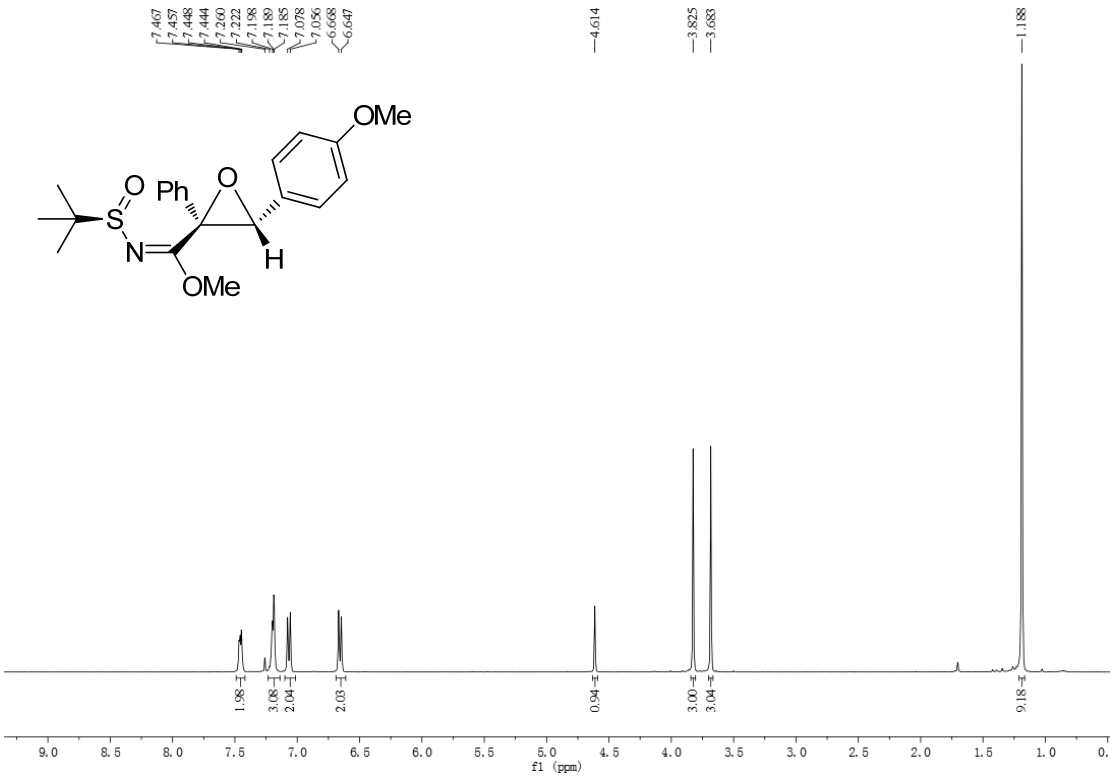

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7d**



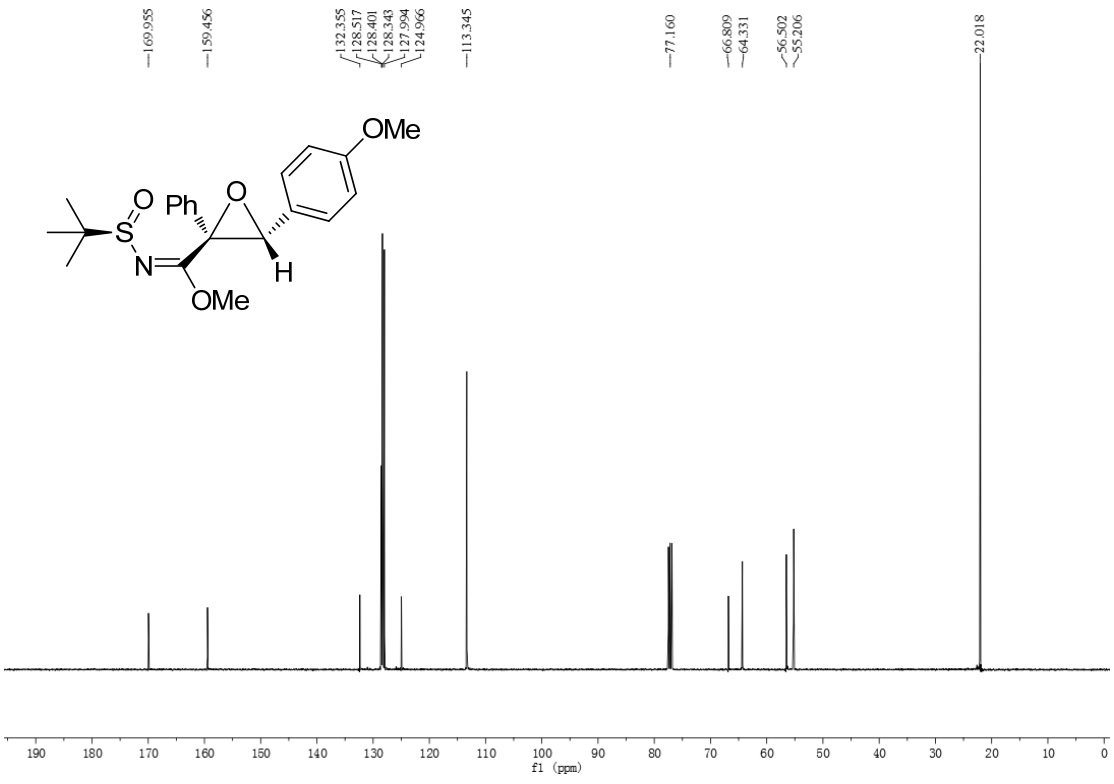

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7e**



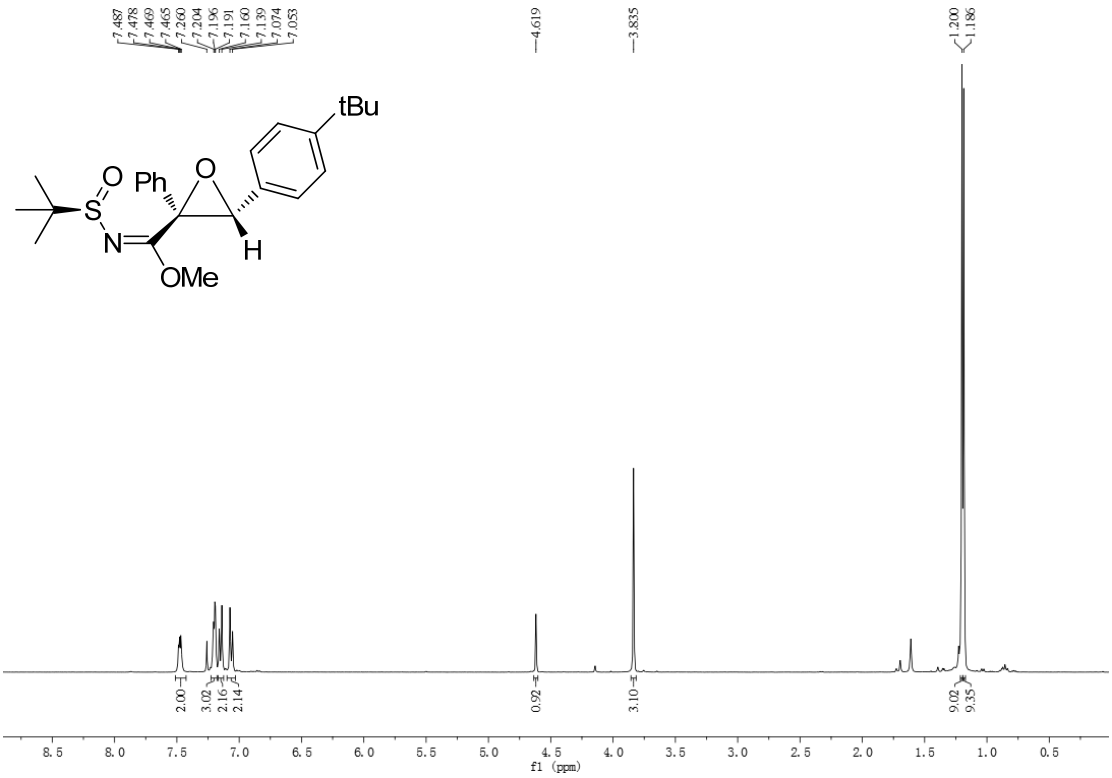

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7e**



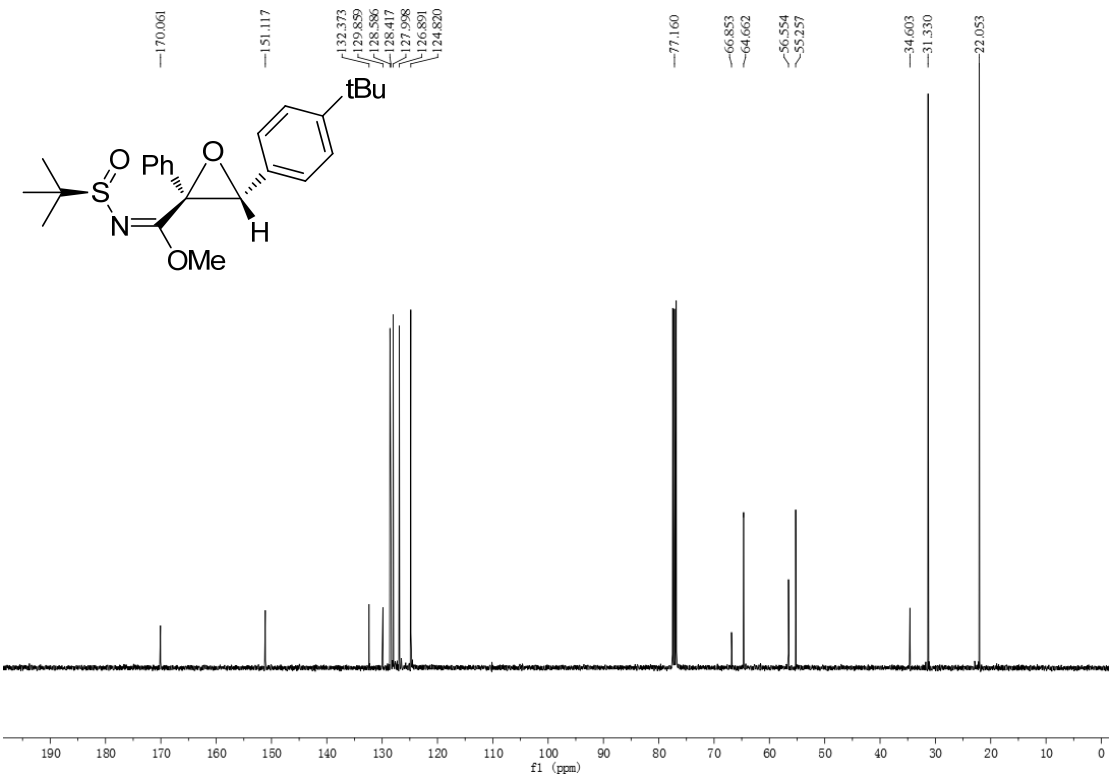

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7f**



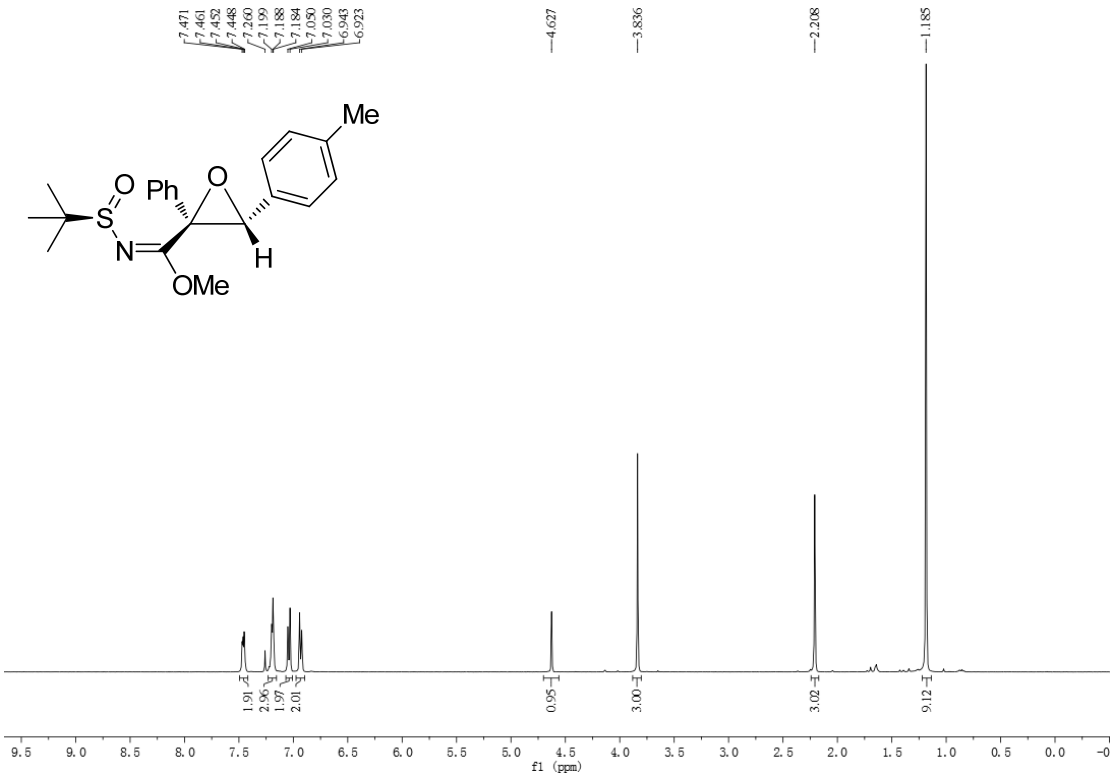

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7f**



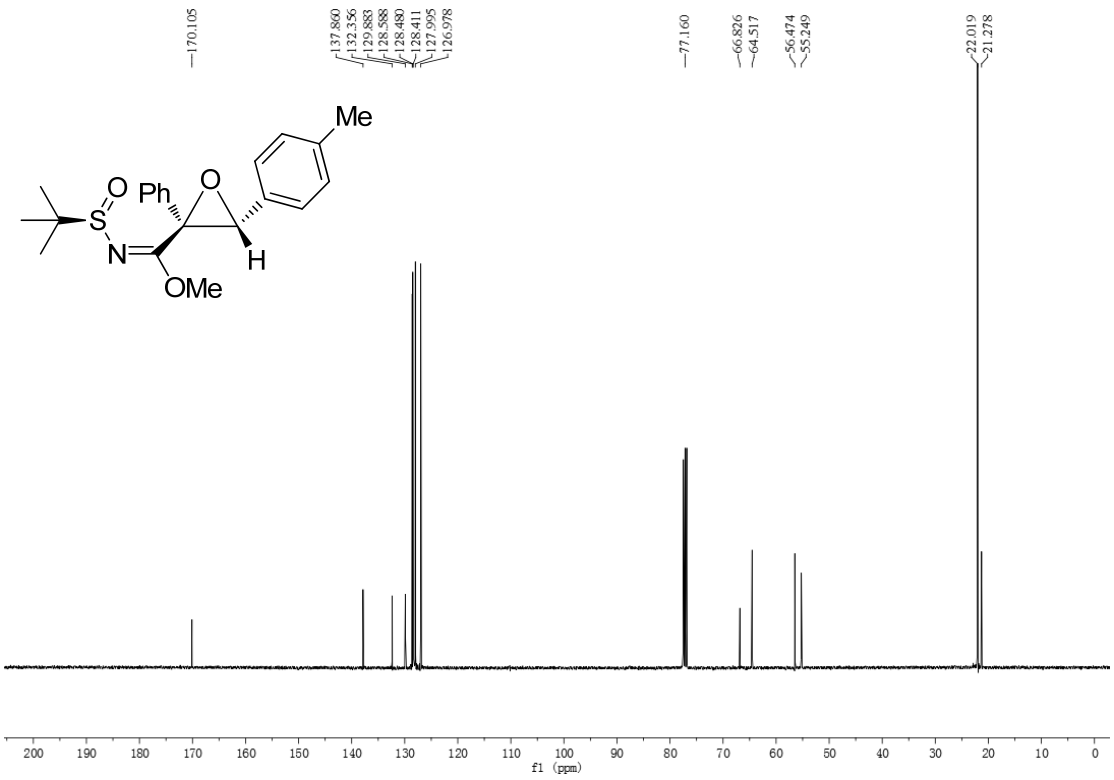

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7g**



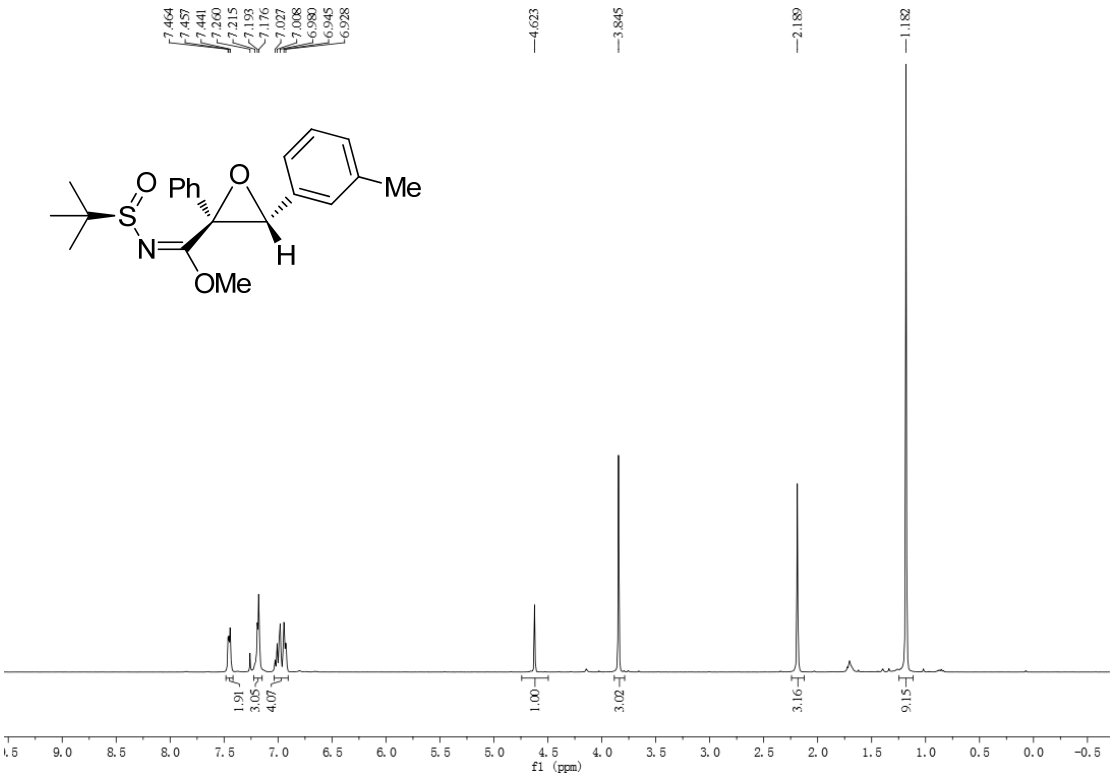

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7g**



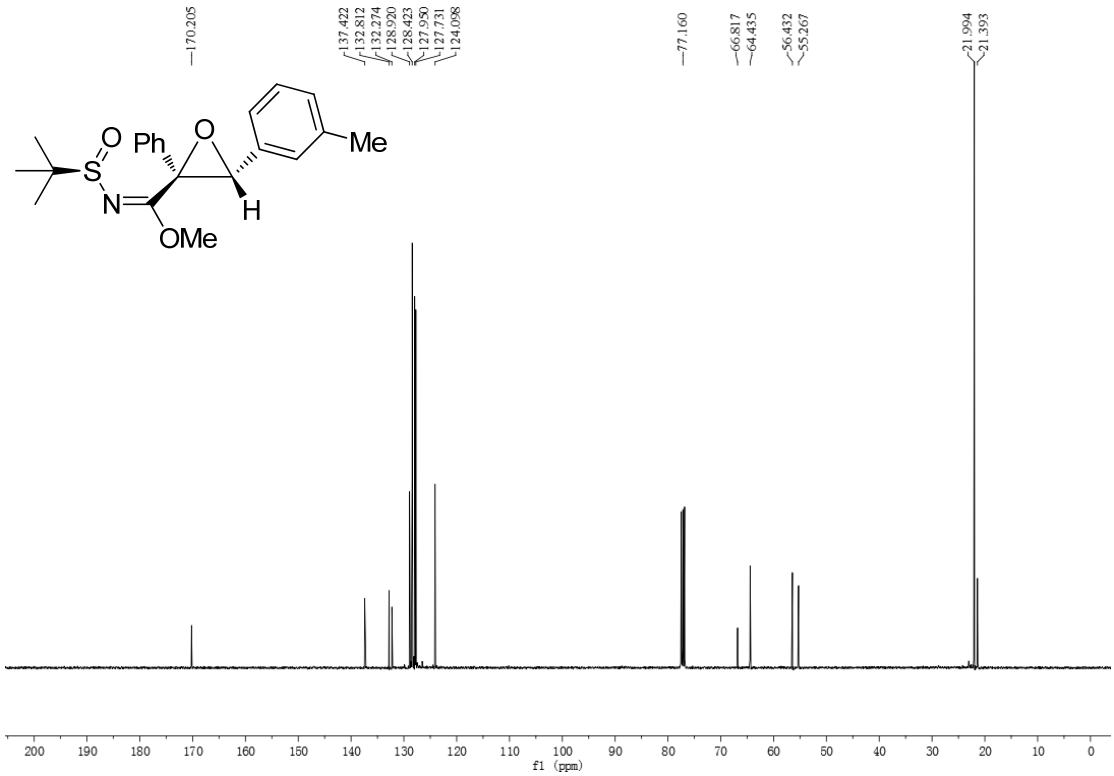

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7h**



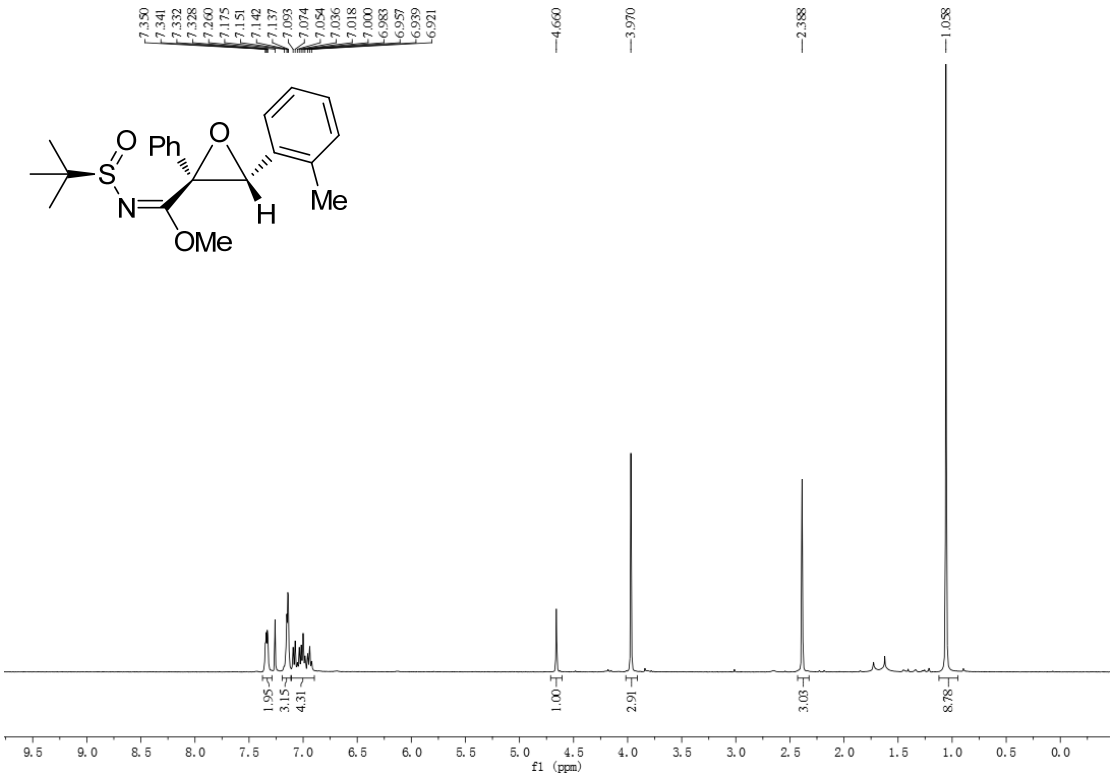

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7h**



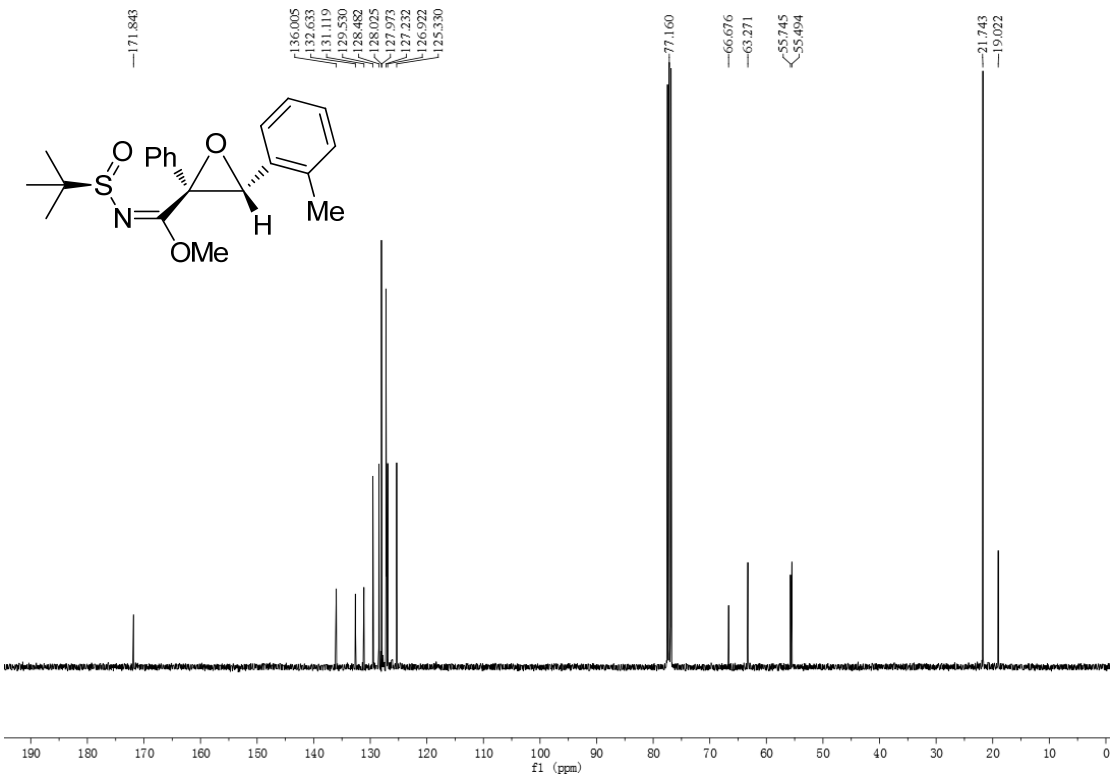

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7i**



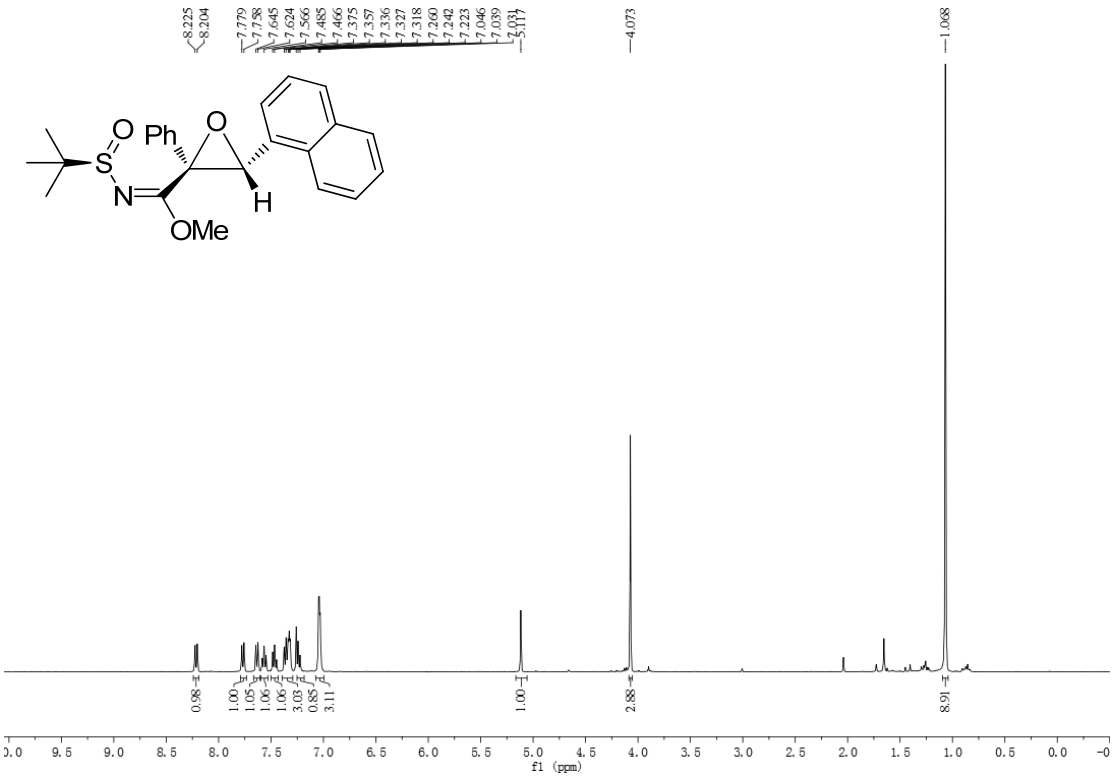

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7i**



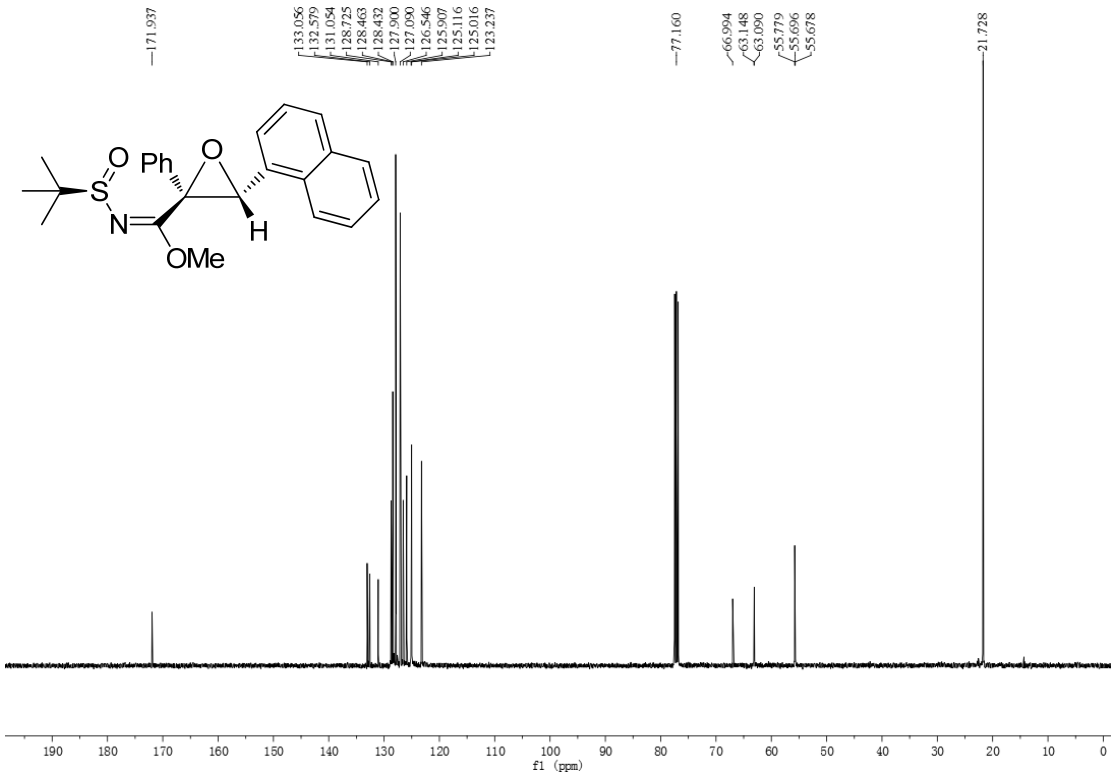

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7j**



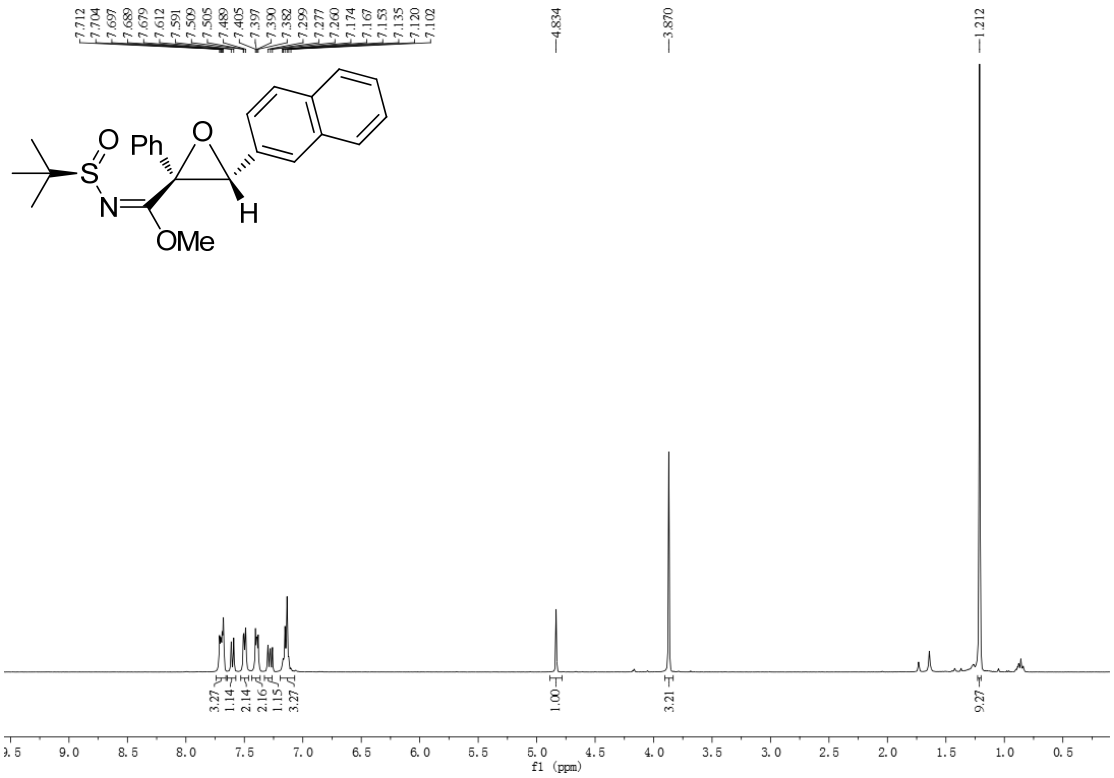

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7j**



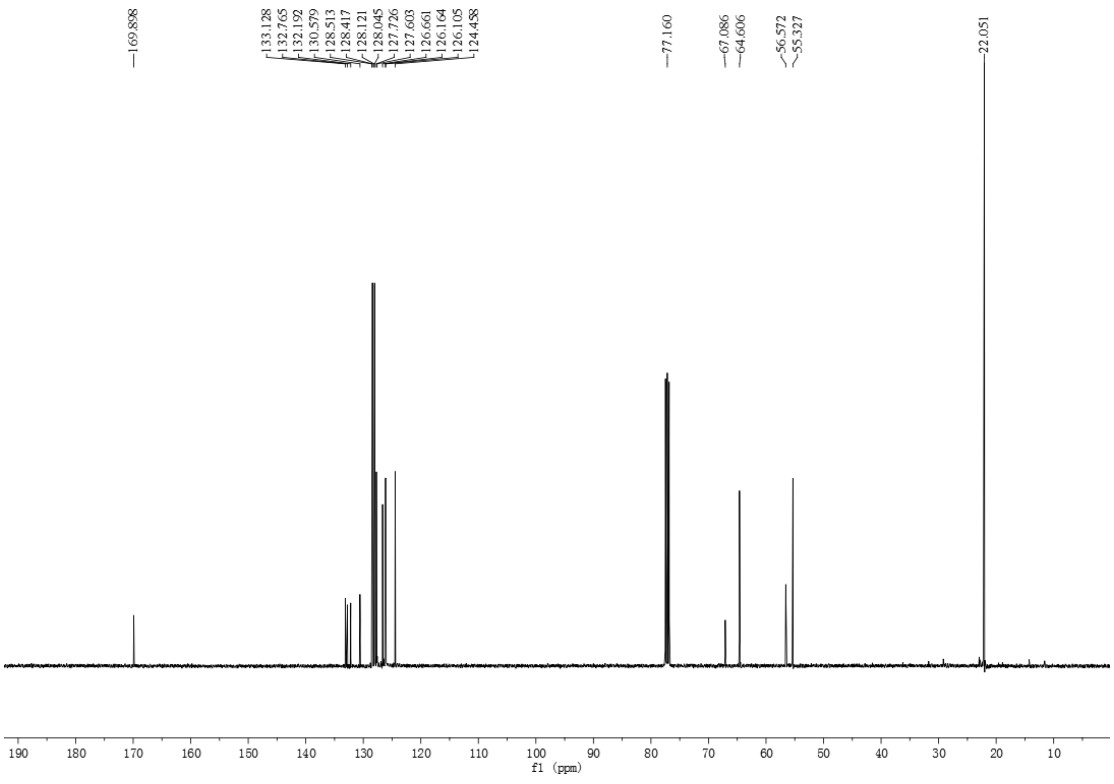

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7k**



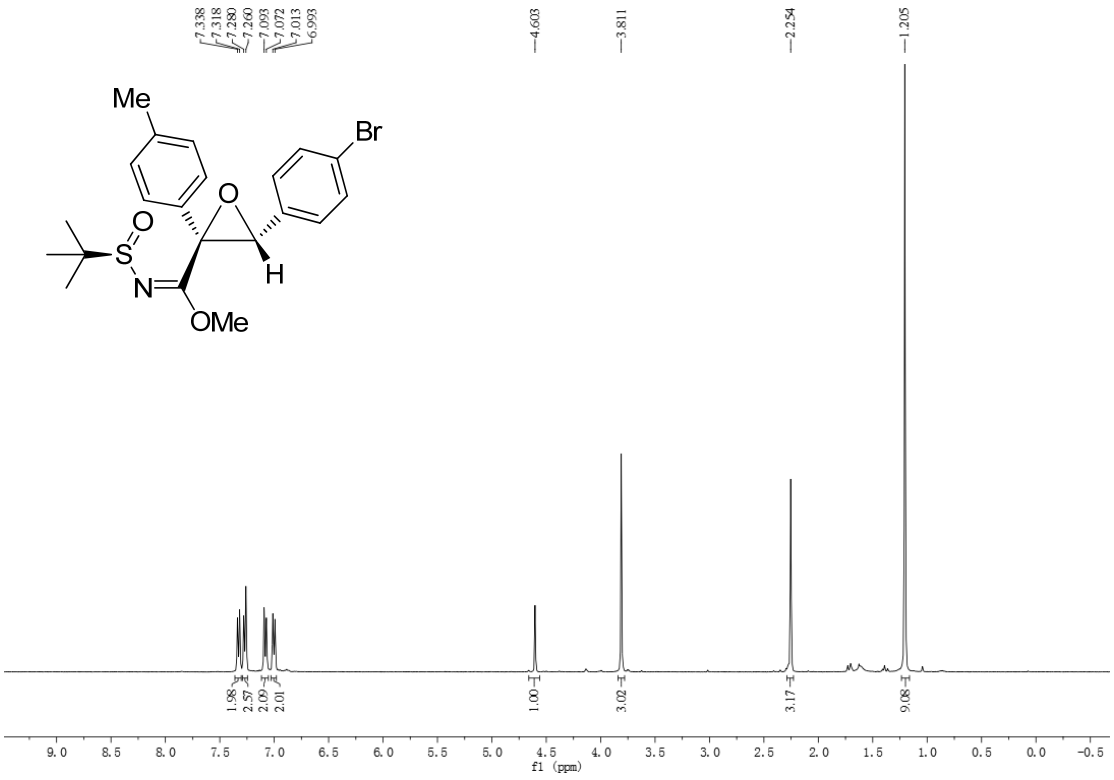

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7k**



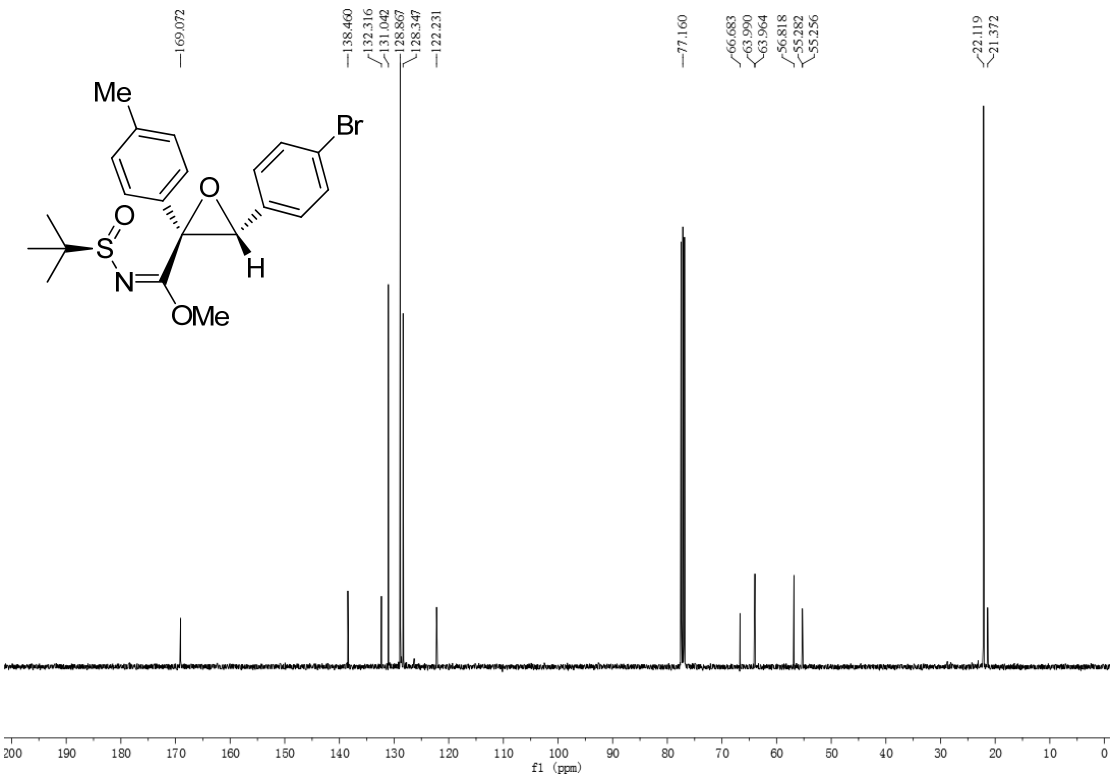

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7l**



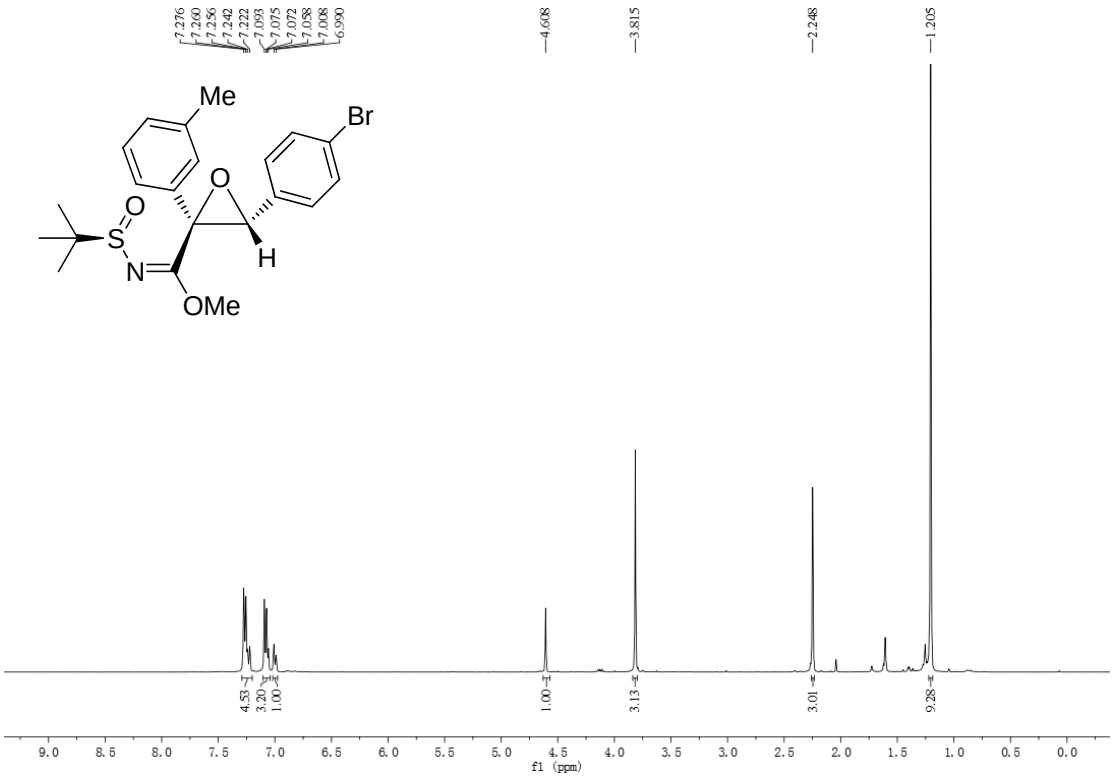

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7l**



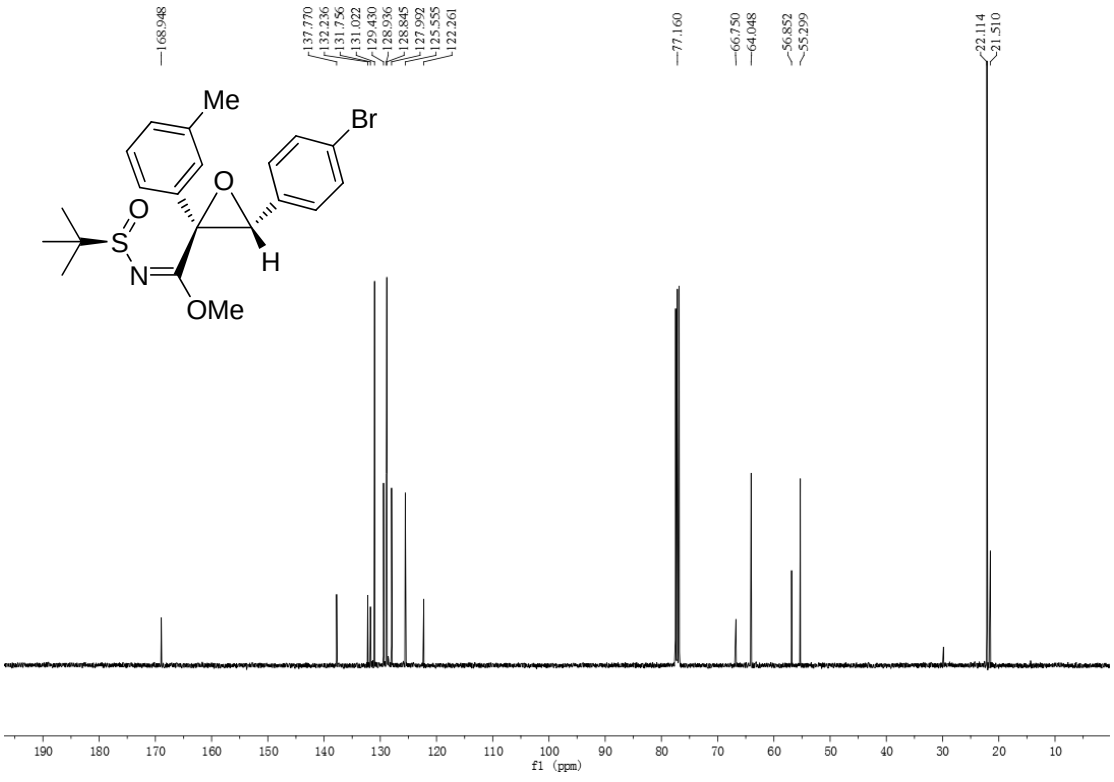

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7m**



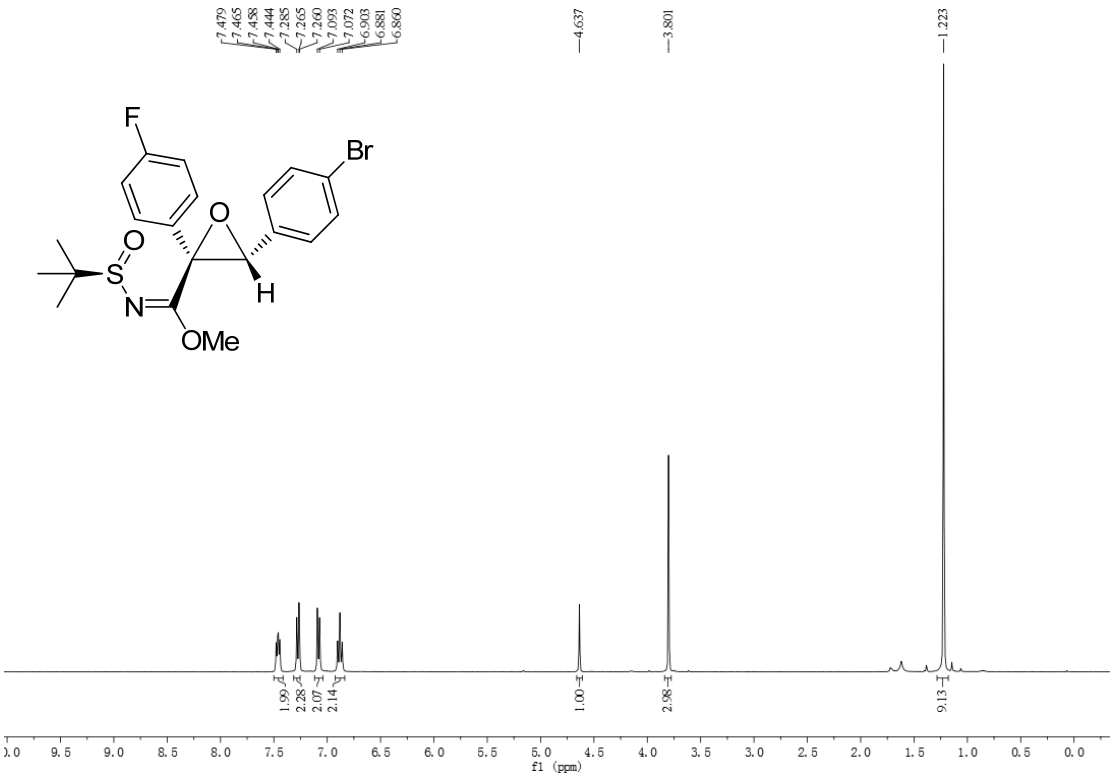

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7m**



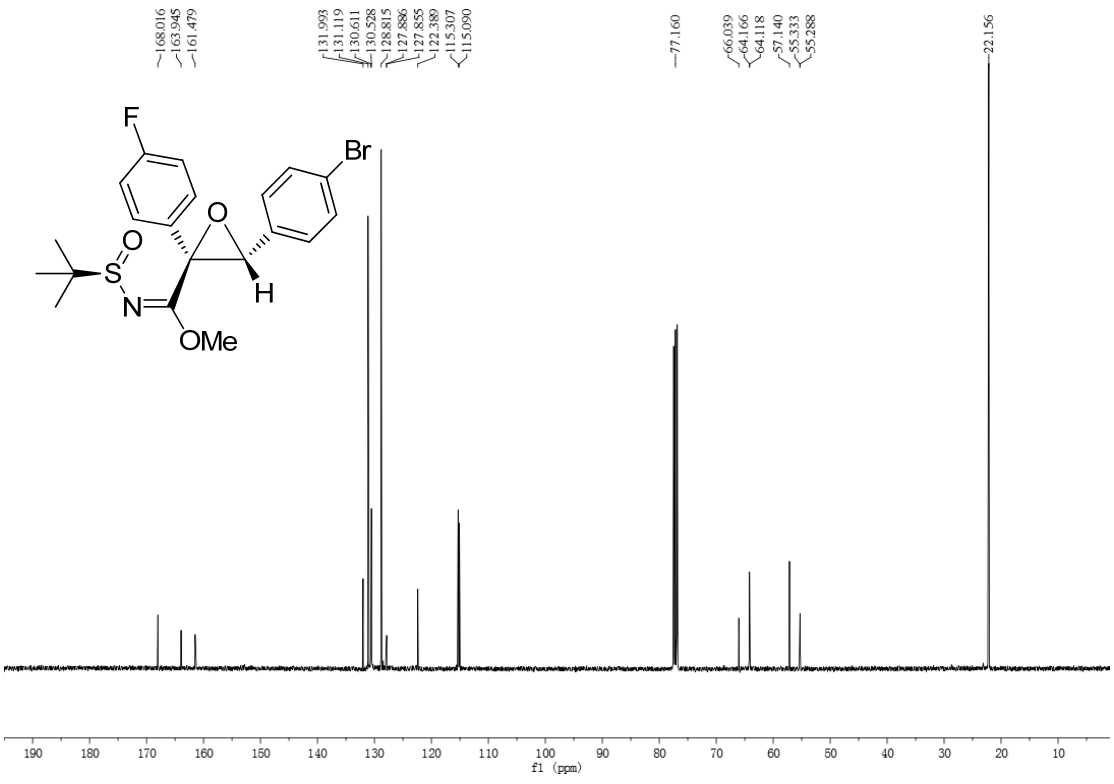

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7n**



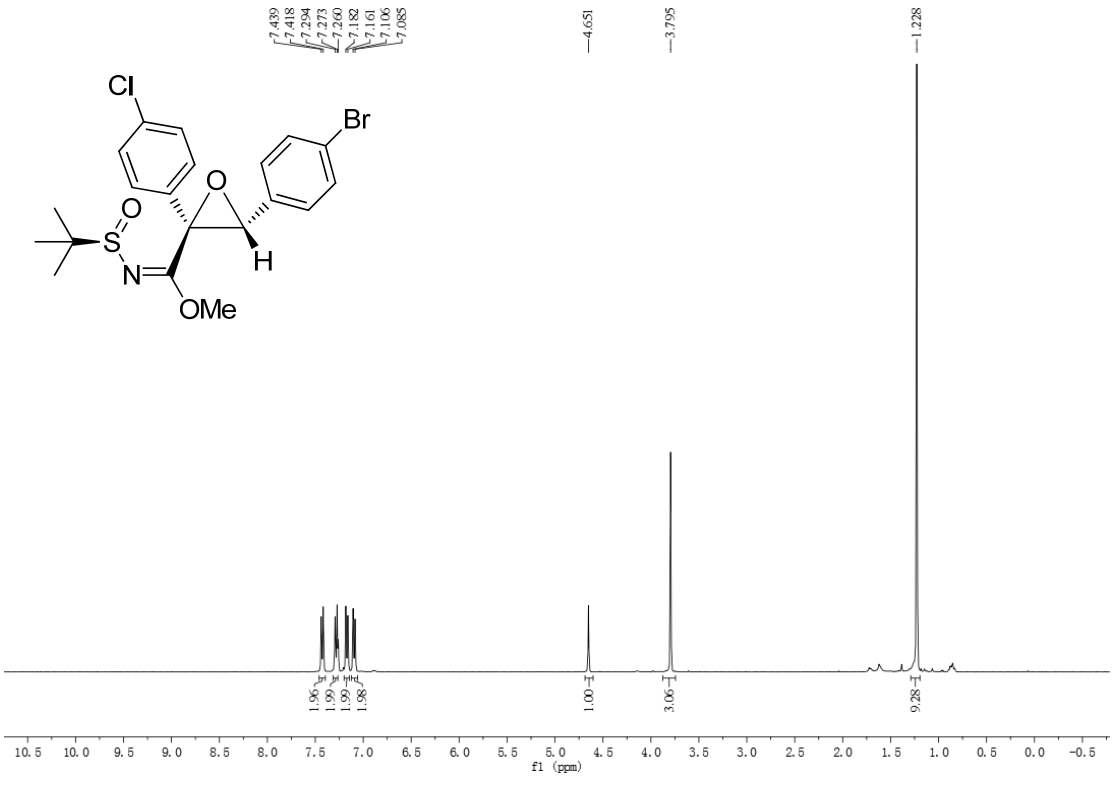

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7n**



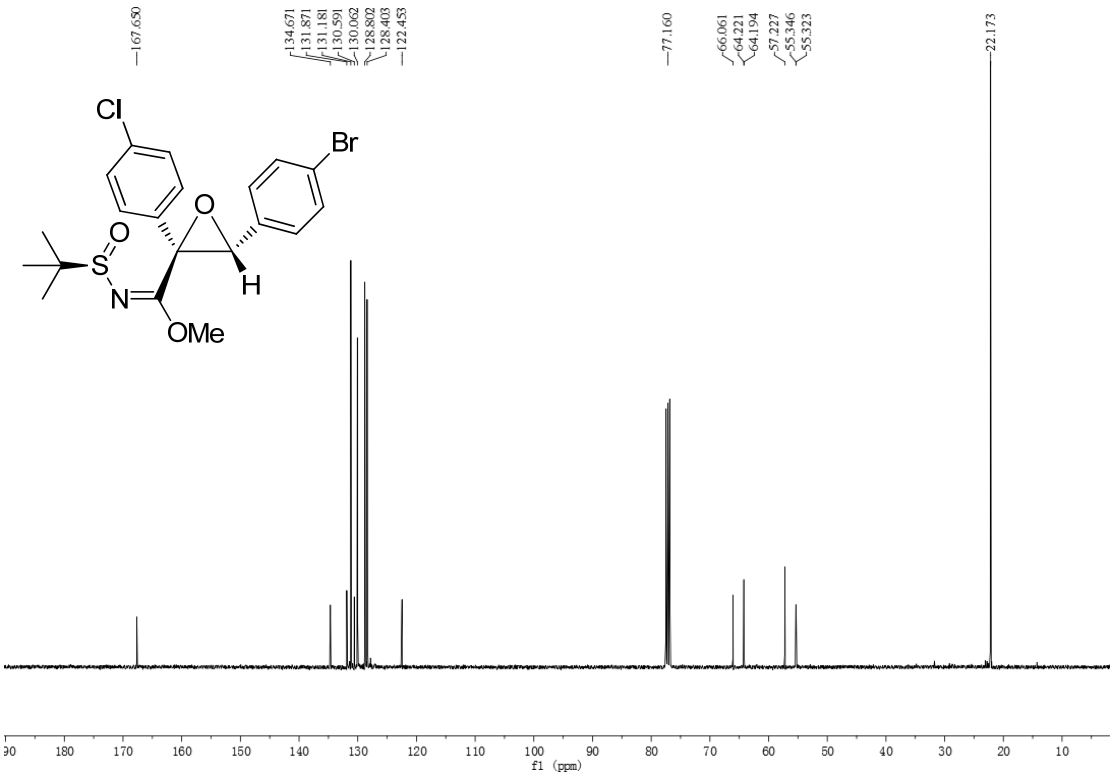

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7o**



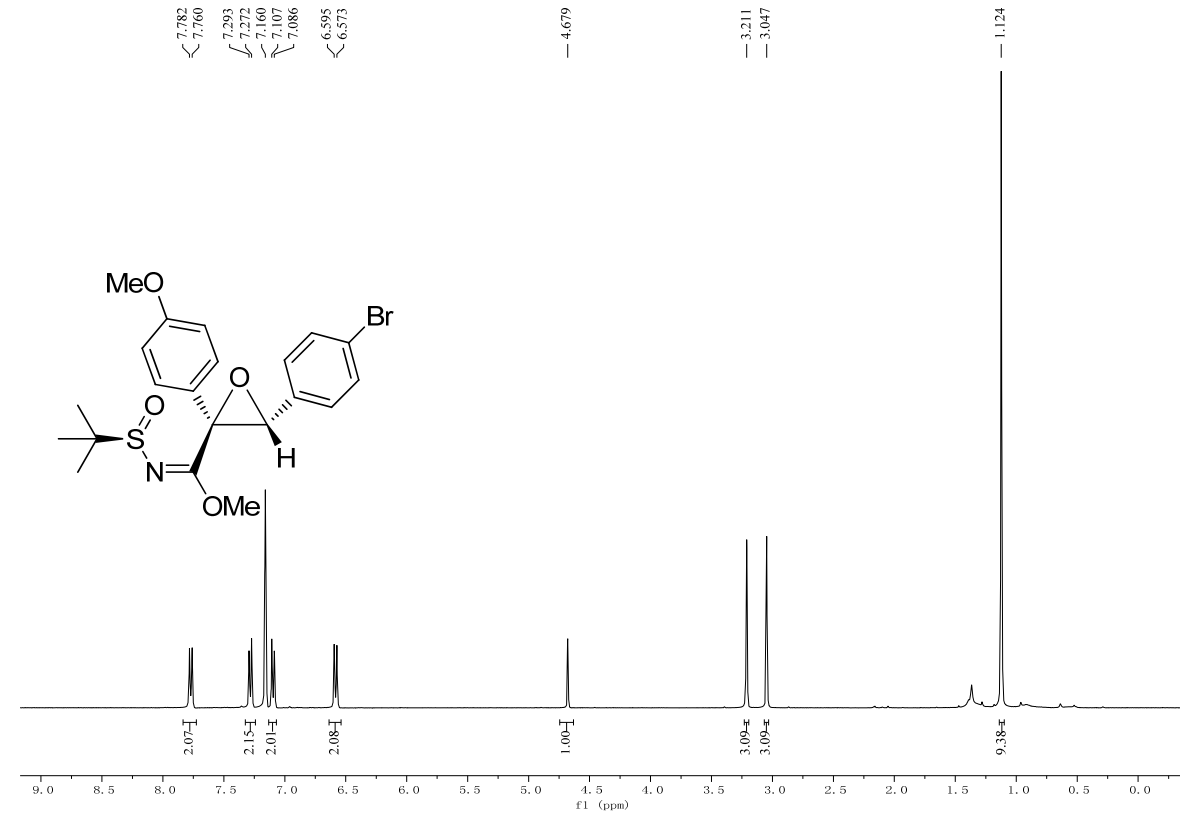

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7o**



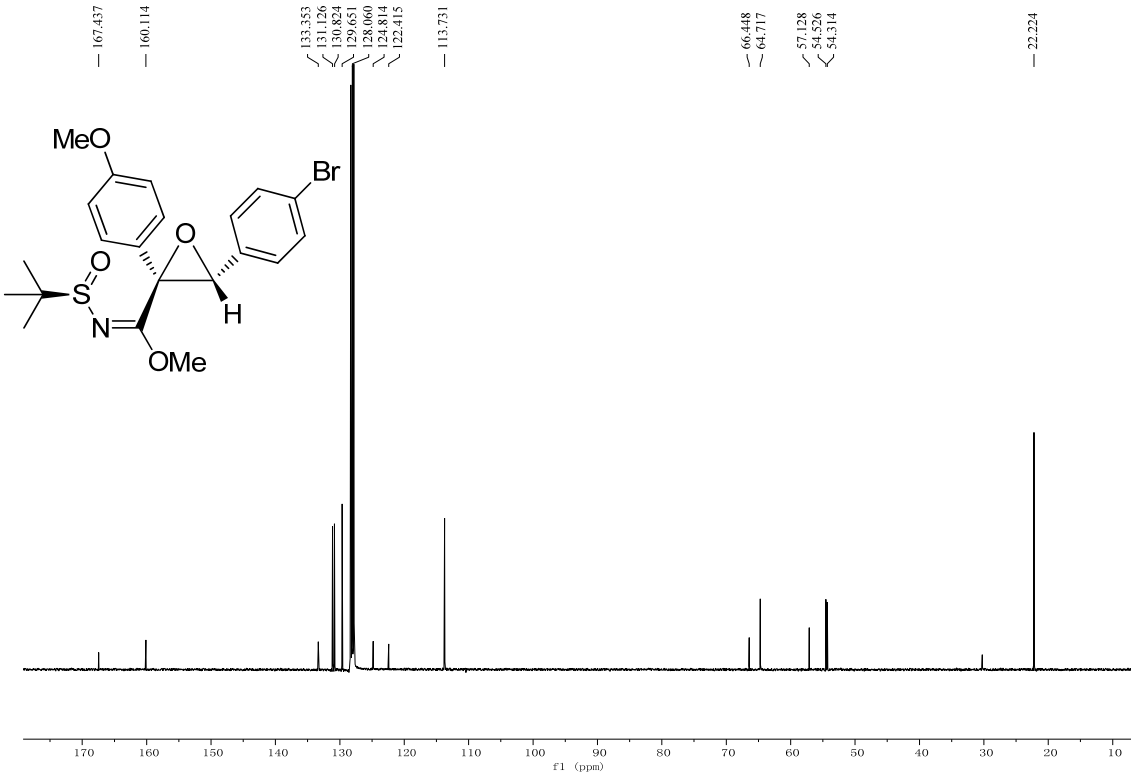

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **7p**



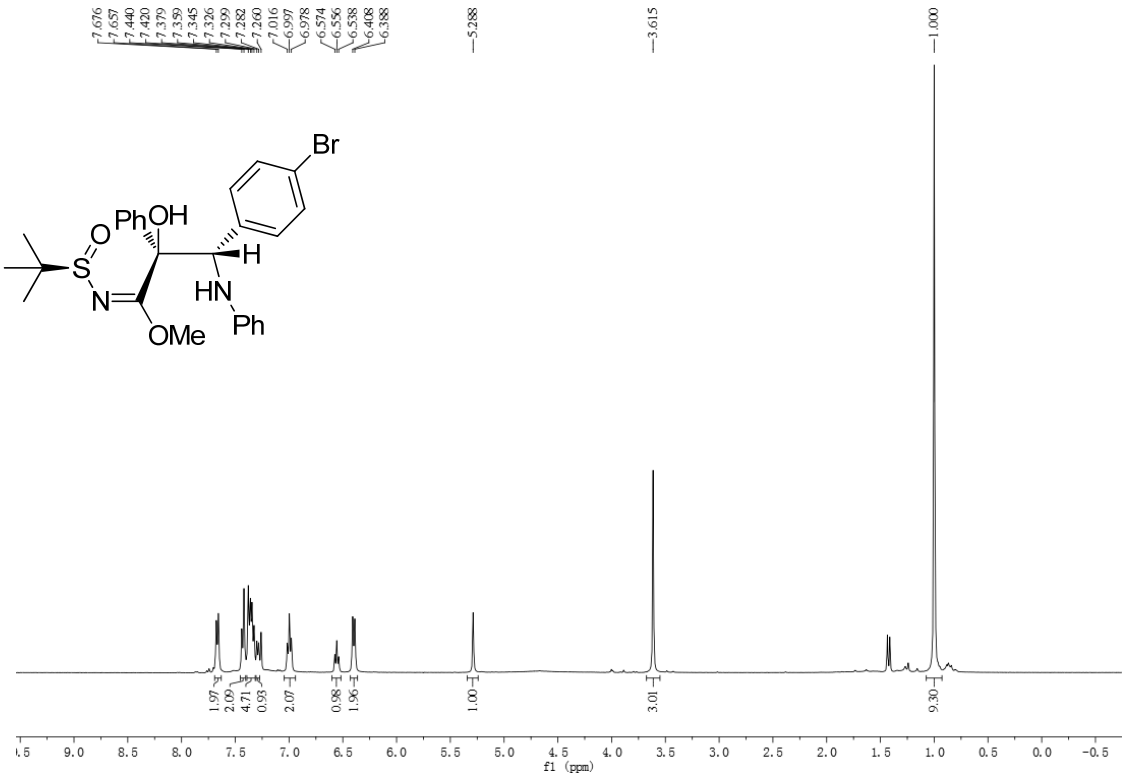

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **7p**



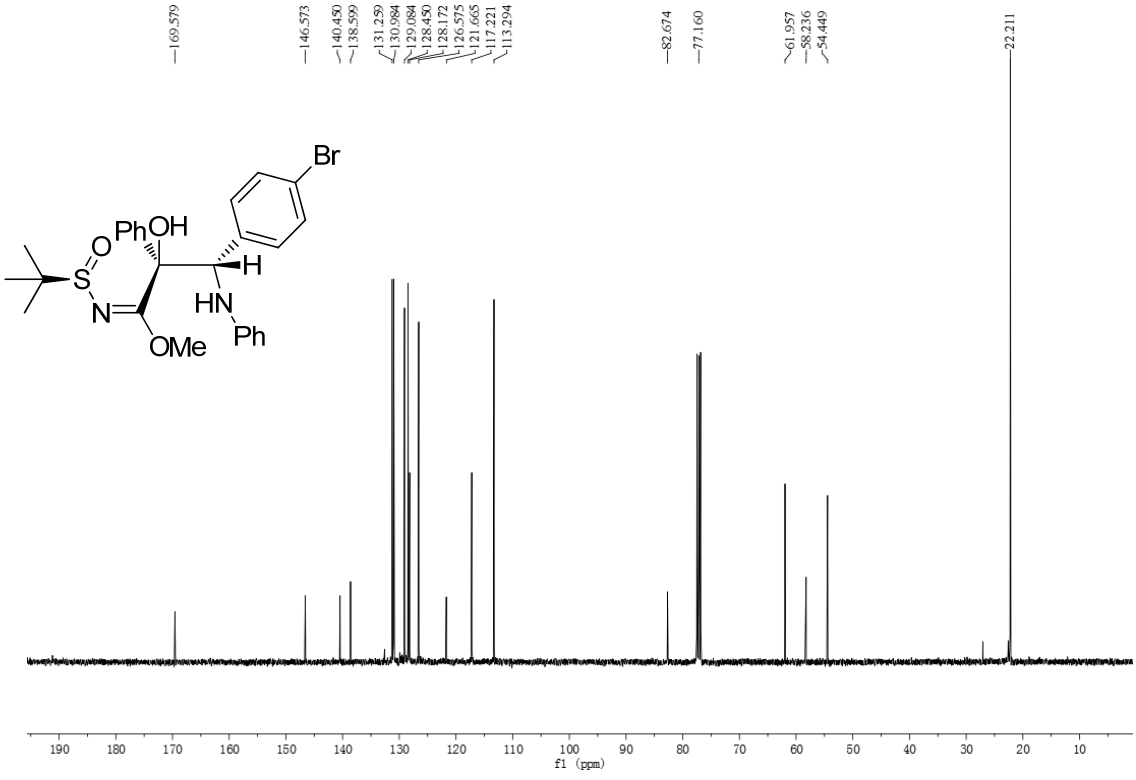

$^{1}$H NMR spectrum ($C_6D_6$, 400 MHz) of **7q**



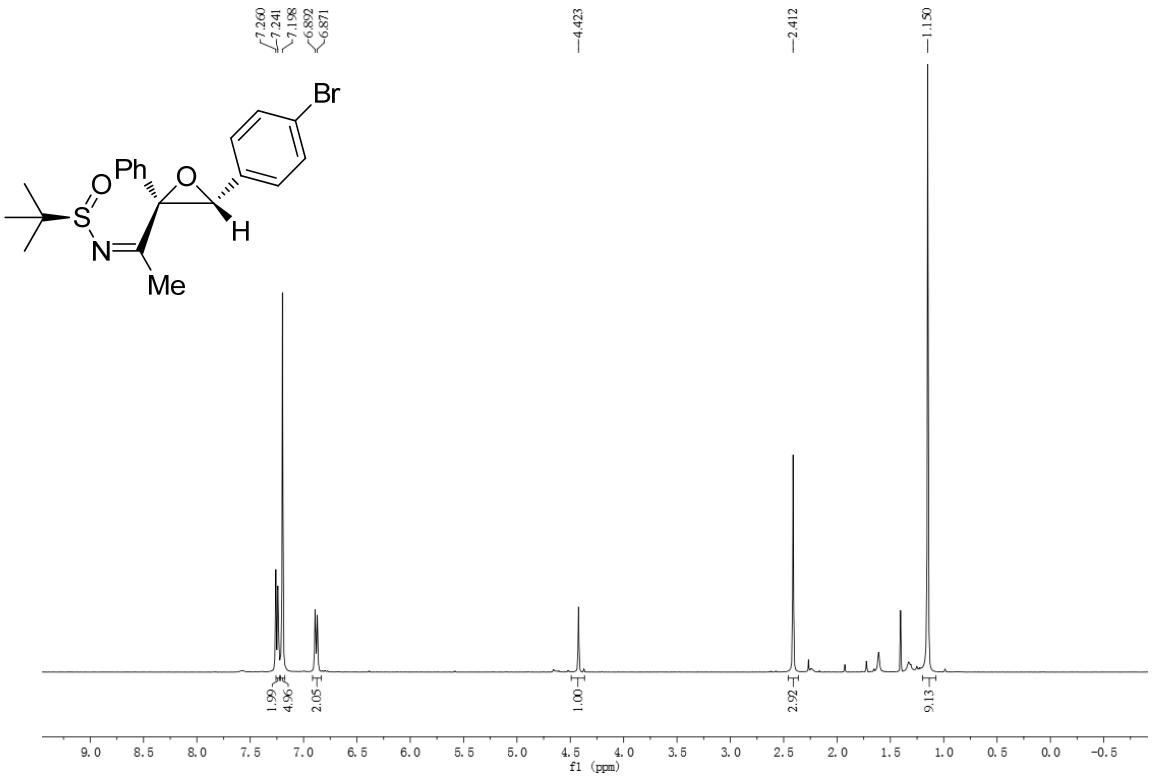

$^{13}$C NMR spectrum ($C_6D_6$, 100 MHz) of **7q**



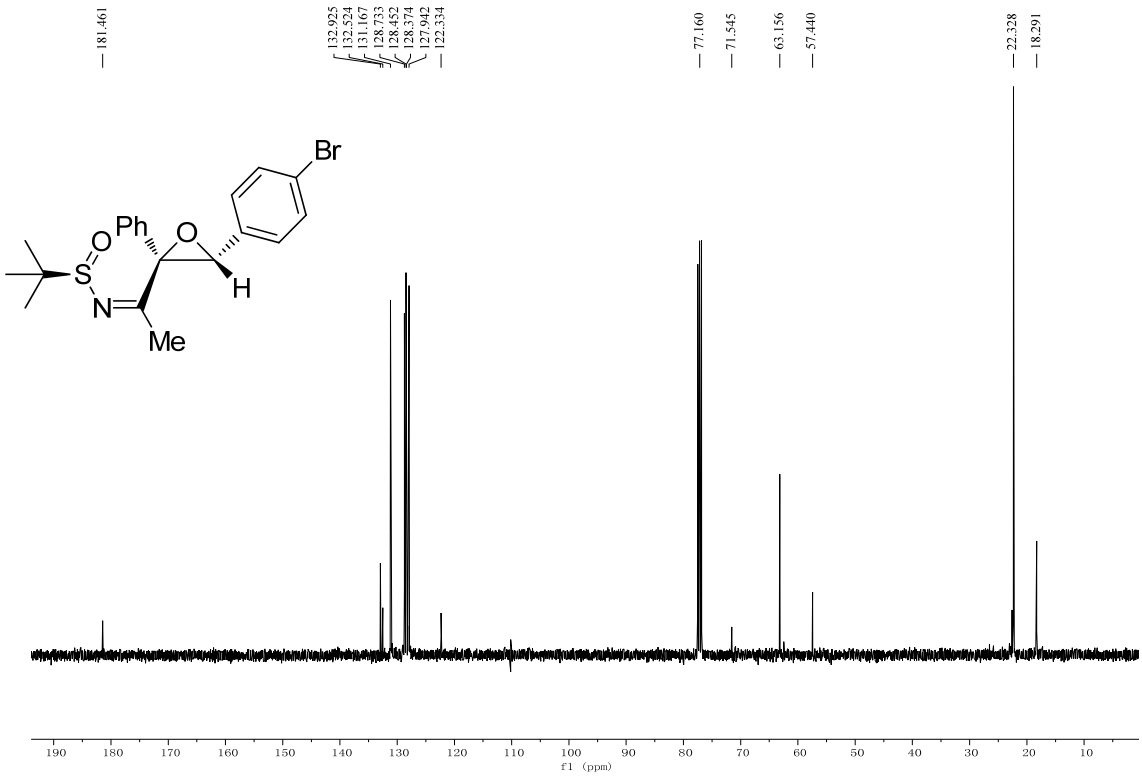

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **11**



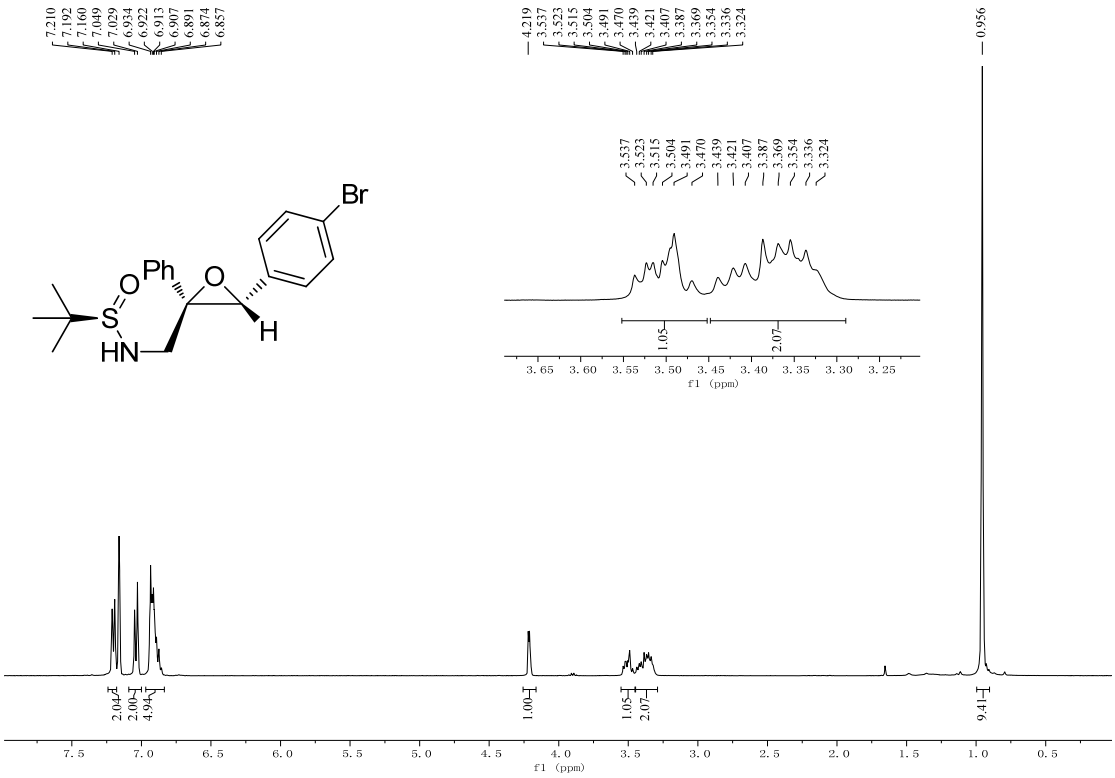

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **11**



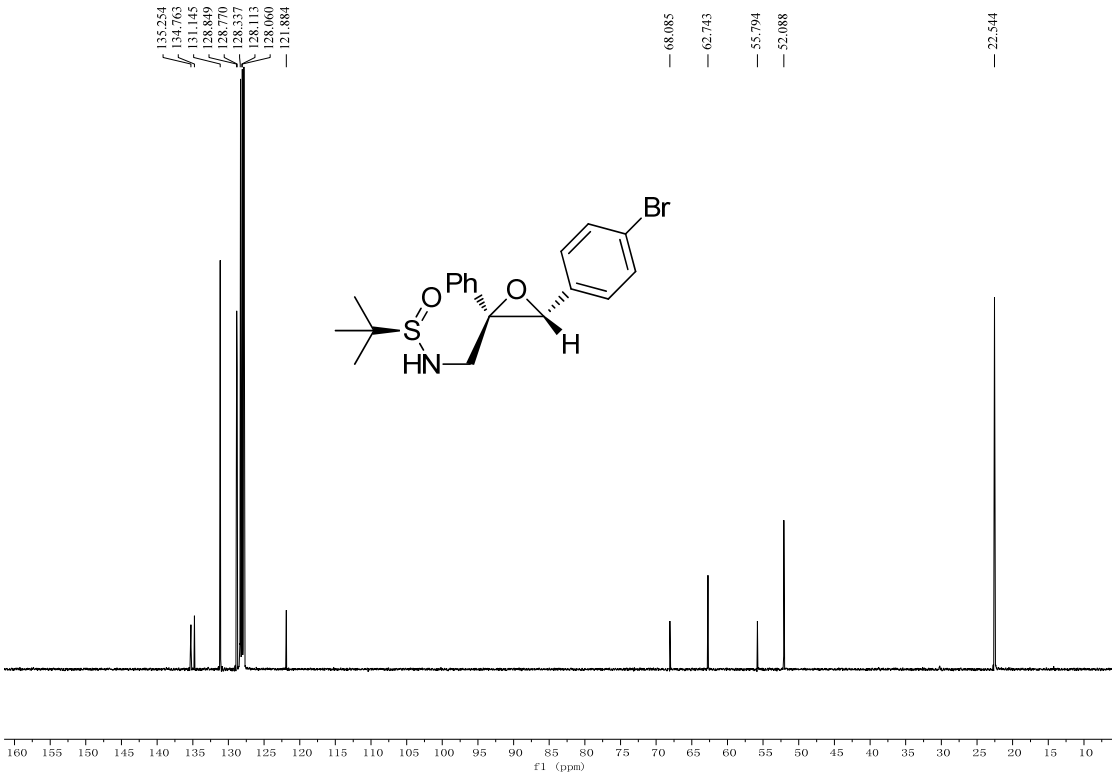

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **12**



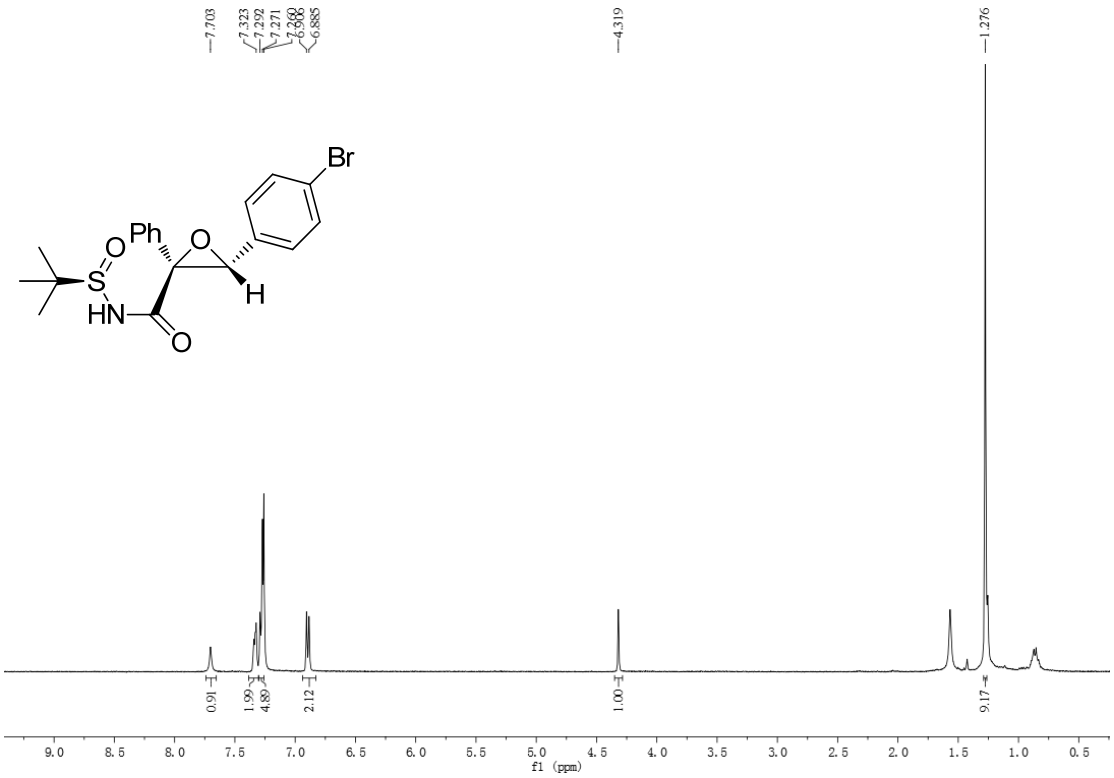

$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **12**



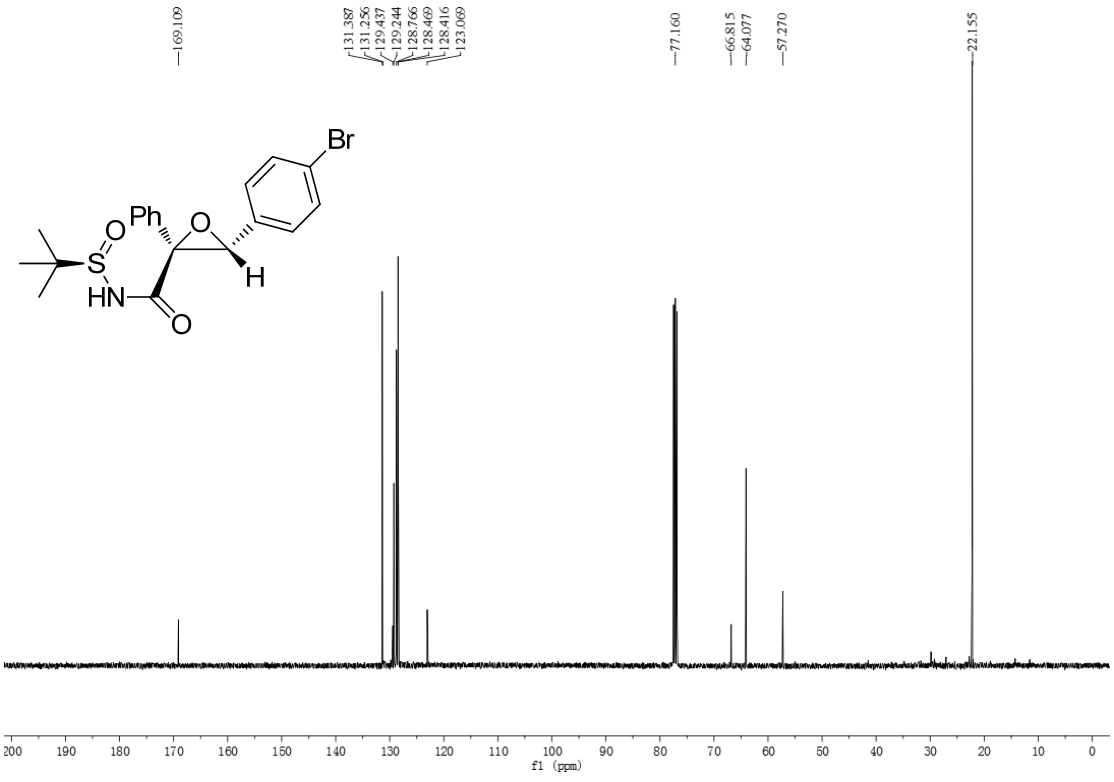

$^{1}$H NMR spectrum ($C_6D_6$, 400 MHz) of **13**



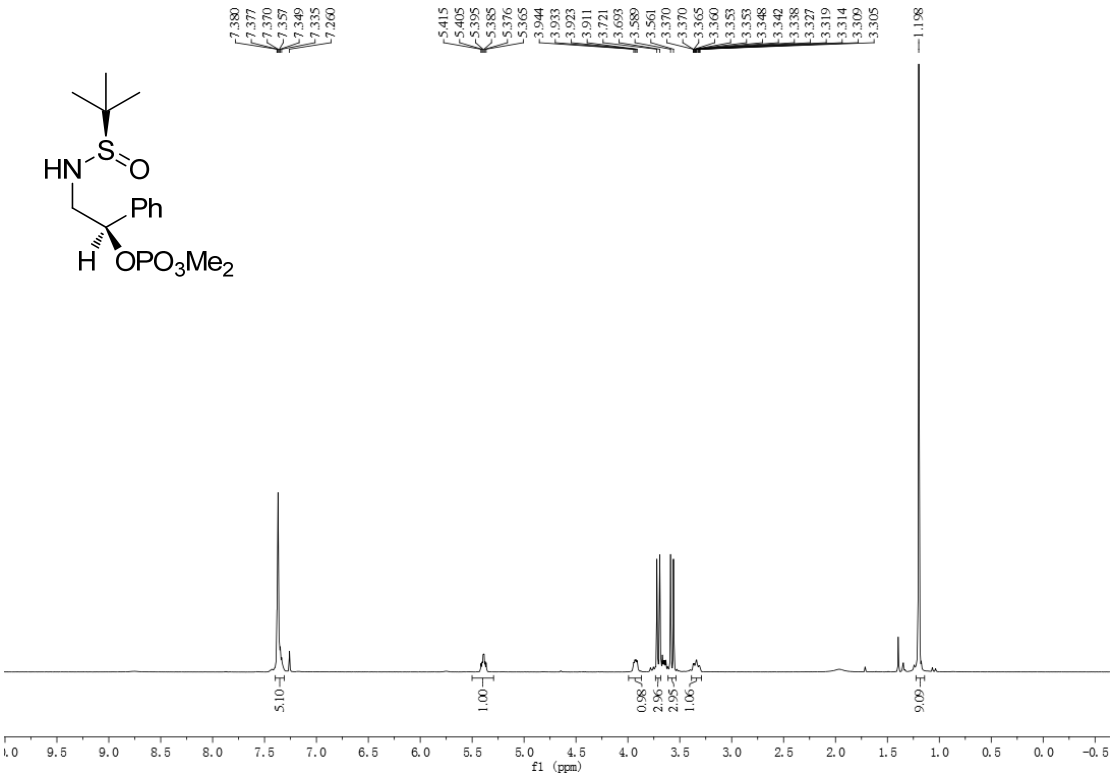

$^{13}$C NMR spectrum ($C_6D_6$, 100 MHz) of **13**



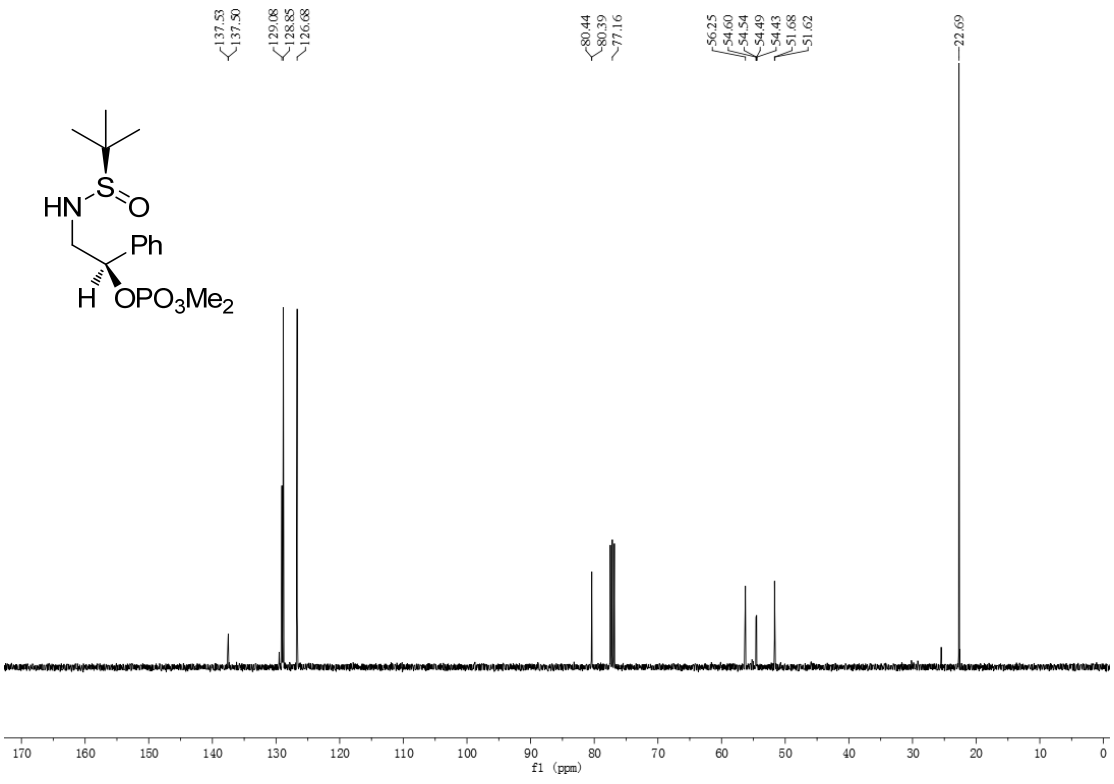

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **14**




$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **14**



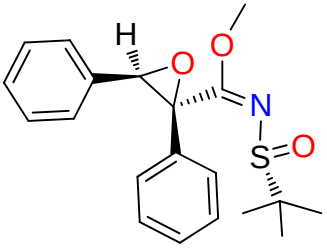

$^{1}$H NMR spectrum ($CDCl_3$, 400 MHz) of **15**




$^{13}$C NMR spectrum ($CDCl_3$, 100 MHz) of **15**

**X-Ray crystal structure of the compound 7a**

The stereochemistry of **7a** was determined by X-ray crystallography. The crystals of **7a** used in the X-ray diffraction study were grown by the slow evaporation of the ethyl acetate solution of the compound. X-Ray crystal structure (ORTEP) of this compound, with the thermal ellipsoids shown at a 50% probability level.



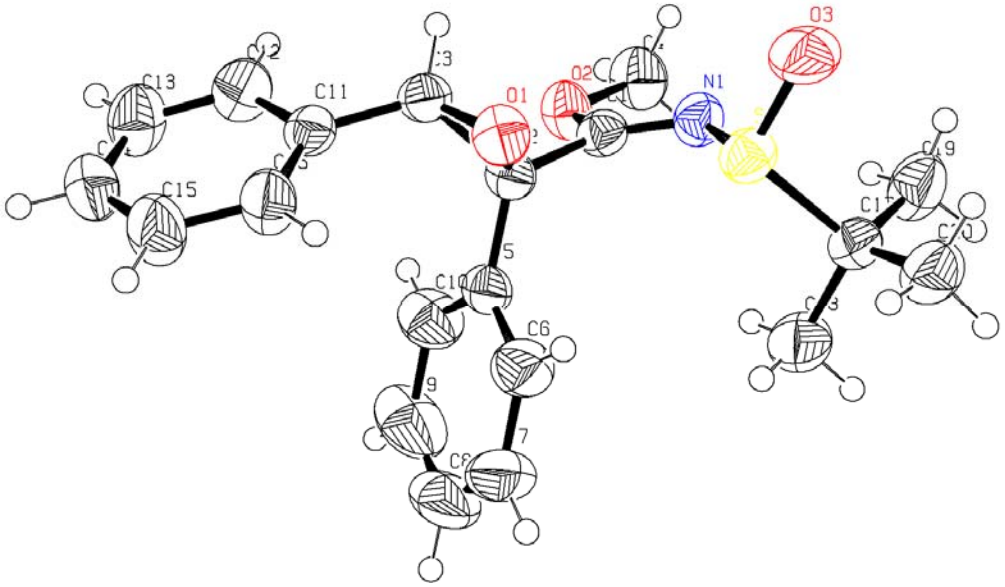




**Table 1. Crystal data and structure refinement for 7a**

| | |
|---|---|
| Identification code | 7a |
| Empirical formula | $C_{20}$ $H_{23}$ N $O_3$ S |
| Formula weight | 357.45 |
| Temperature/K | 296(2) K |
| Wavelength | 0.71073 Å |

| | |
|---|---|
| Crystal system, space group | Orthorhombic, P212121 |
| Unit cell dimensions | a = 8.3041(12) Å alpha = 90°. |
| | b = 10.2744(15)Å beta = 90°. |
| | c = 22.465(3) Å gamma = 90°. |
| Volume | 1916.7(5) $Å^3$ |
| Z, Calculated density | 4, 1.239 $Mg/m^3$ |
| Absorption coefficient | 0.186 $mm^{-1}$ |
| F(000) | 760 |
| Crystal size | 0.21 x 0.20 x 0.19 $mm^3$ |
| Theta range for data collection | 2.18 to 25.01°. |
| Limiting indices | -6<=h<=9, -9<=k<=12, -26<=l<=23 |
| Reflections collected / unique | 9795 / 3388 [R(int) = 0.0329] |
| Completeness to theta = 25.01 | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9654 and 0.9619 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3388 / 1 / 226 |
| Goodness-of-fit on F^2 | 1.030 |
| Final R indices [I>2sigma(I)] | R1 = 0.0372, wR2 = 0.0914 |
| R indices (all data) | R1 = 0.0490, wR2 = 0.0993 |
| Absolute structure parameter | -0.02(8) |
| Largest diff. peak and hole | 0.113 and -0.227 $e.Å^{-3}$ |

**Table 2. Bond lengths [Å] and angles [°] for 7a.**

| | |
|---|---|
| S(1)-O(3) | 1.4698(19) |
| S(1)-N(1) | 1.701(2) |
| S(1)-C(17) | 1.836(2) |

| | |
|---|---|
| O(1)-C(8) | 1.429(3) |
| O(1)-C(7) | 1.444(3) |
| O(2)-C(15) | 1.332(3) |
| O(2)-C(16) | 1.456(3) |
| N(1)-C(15) | 1.265(3) |
| C(1)-C(6) | 1.367(3) |
| C(1)-C(2) | 1.380(4) |
| C(1)-H(1A) | 0.9300 |
| C(2)-C(3) | 1.366(4) |
| C(2)-H(2A) | 0.9300 |
| C(3)-C(4) | 1.359(4) |
| C(3)-H(3A) | 0.9300 |
| C(4)-C(5) | 1.376(4) |
| C(4)-H(4A) | 0.9300 |
| C(5)-C(6) | 1.391(3) |
| C(5)-H(5A) | 0.9300 |
| C(6)-C(7) | 1.476(3) |
| C(7)-C(8) | 1.481(3) |
| C(7)-H(7A) | 0.9800 |
| C(8)-C(9) | 1.495(3) |
| C(8)-C(15) | 1.505(3) |
| C(9)-C(14) | 1.370(4) |
| C(9)-C(10) | 1.374(3) |
| C(10)-C(11) | 1.385(4) |
| C(10)-H(10A) | 0.9300 |
| C(11)-C(12) | 1.342(6) |
| C(11)-H(11A) | 0.9300 |

| | |
|---|---|
| C(12)-C(13) | 1.371(6) |
| C(12)-H(12A) | 0.9300 |
| C(13)-C(14) | 1.385(4) |
| C(13)-H(13A) | 0.9300 |
| C(14)-H(14A) | 0.9300 |
| C(16)-H(16A) | 0.9600 |
| C(16)-H(16B) | 0.9600 |
| C(16)-H(16C) | 0.9600 |
| C(17)-C(19) | 1.512(3) |
| C(17)-C(18) | 1.518(4) |
| C(17)-C(20) | 1.520(3) |
| C(18)-H(18A) | 0.9600 |
| C(18)-H(18B) | 0.9600 |
| C(18)-H(18C) | 0.9600 |
| C(19)-H(19A) | 0.9600 |
| C(19)-H(19B) | 0.9600 |
| C(19)-H(19C) | 0.9600 |
| C(20)-H(20A) | 0.9600 |
| C(20)-H(20B) | 0.9600 |
| C(20)-H(20C) | 0.9600 |

| | |
|---|---|
| O(3)-S(1)-N(1) | 104.95(11) |
| O(3)-S(1)-C(17) | 106.11(12) |
| N(1)-S(1)-C(17) | 96.14(10) |
| C(8)-O(1)-C(7) | 62.04(14) |
| C(15)-O(2)-C(16) | 117.5(2) |
| C(15)-N(1)-S(1) | 118.91(17) |

| | |
|---|---|
| C(6)-C(1)-C(2) | 120.3(2) |
| C(6)-C(1)-H(1A) | 119.8 |
| C(2)-C(1)-H(1A) | 119.8 |
| C(3)-C(2)-C(1) | 120.8(3) |
| C(3)-C(2)-H(2A) | 119.6 |
| C(1)-C(2)-H(2A) | 119.6 |
| C(4)-C(3)-C(2) | 119.2(3) |
| C(4)-C(3)-H(3A) | 120.4 |
| C(2)-C(3)-H(3A) | 120.4 |
| C(3)-C(4)-C(5) | 120.8(3) |
| C(3)-C(4)-H(4A) | 119.6 |
| C(5)-C(4)-H(4A) | 119.6 |
| C(4)-C(5)-C(6) | 120.1(2) |
| C(4)-C(5)-H(5A) | 119.9 |
| C(6)-C(5)-H(5A) | 119.9 |
| C(1)-C(6)-C(5) | 118.6(2) |
| C(1)-C(6)-C(7) | 122.8(2) |
| C(5)-C(6)-C(7) | 118.6(2) |
| O(1)-C(7)-C(6) | 119.12(18) |
| O(1)-C(7)-C(8) | 58.48(13) |
| C(6)-C(7)-C(8) | 122.10(19) |
| O(1)-C(7)-H(7A) | 115.1 |
| C(6)-C(7)-H(7A) | 115.1 |
| C(8)-C(7)-H(7A) | 115.1 |
| O(1)-C(8)-C(7) | 59.48(14) |
| O(1)-C(8)-C(9) | 116.43(17) |
| C(7)-C(8)-C(9) | 121.15(19) |

| | |
|---|---|
| O(1)-C(8)-C(15) | 115.50(18) |
| C(7)-C(8)-C(15) | 117.14(18) |
| C(9)-C(8)-C(15) | 115.32(18) |
| C(14)-C(9)-C(10) | 118.7(2) |
| C(14)-C(9)-C(8) | 121.2(2) |
| C(10)-C(9)-C(8) | 120.1(2) |
| C(9)-C(10)-C(11) | 120.9(3) |
| C(9)-C(10)-H(10A) | 119.6 |
| C(11)-C(10)-H(10A) | 119.6 |
| C(12)-C(11)-C(10) | 119.9(4) |
| C(12)-C(11)-H(11A) | 120.0 |
| C(10)-C(11)-H(11A) | 120.0 |
| C(11)-C(12)-C(13) | 120.3(3) |
| C(11)-C(12)-H(12A) | 119.9 |
| C(13)-C(12)-H(12A) | 119.9 |
| C(12)-C(13)-C(14) | 120.2(4) |
| C(12)-C(13)-H(13A) | 119.9 |
| C(14)-C(13)-H(13A) | 119.9 |
| C(9)-C(14)-C(13) | 120.0(3) |
| C(9)-C(14)-H(14A) | 120.0 |
| C(13)-C(14)-H(14A) | 120.0 |
| N(1)-C(15)-O(2) | 120.8(2) |
| N(1)-C(15)-C(8) | 131.2(2) |
| O(2)-C(15)-C(8) | 108.00(19) |
| O(2)-C(16)-H(16A) | 109.5 |
| O(2)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |

| | |
|---|---|
| O(2)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(19)-C(17)-C(18) | 113.1(2) |
| C(19)-C(17)-C(20) | 110.3(2) |
| C(18)-C(17)-C(20) | 110.4(2) |
| C(19)-C(17)-S(1) | 106.88(18) |
| C(18)-C(17)-S(1) | 111.43(16) |
| C(20)-C(17)-S(1) | 104.40(18) |
| C(17)-C(18)-H(18A) | 109.5 |
| C(17)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(17)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| C(17)-C(19)-H(19A) | 109.5 |
| C(17)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| C(17)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |
| C(17)-C(20)-H(20A) | 109.5 |
| C(17)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(17)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |