` *Supporting Information*

# Diastereoselective Organophotocatalytic Hydrosulfonylation of Cyclopropenes

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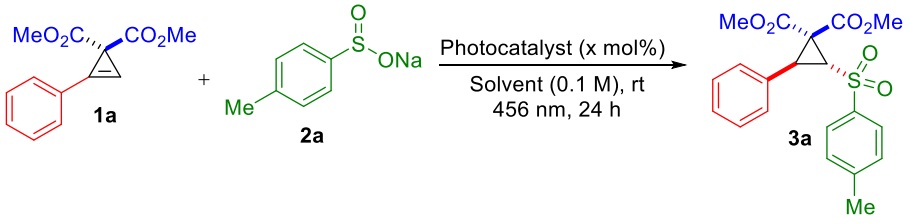
**1. General Information:** Commercial reagents were purified prior to use, following the guidelines of L.L Chai and Armarego. All NMR spectra were recorded on 400 MHz Jeol and 500 MHz Bruker spectrometers. $^{1}H$, $^{13}C$, and $^{19}F$ spectral data are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using the Jeol internal referencing procedure (edlock). Chemical shifts in ppm from tetramethylsilane (TMS) as an internal standard in $CDCl_3$. Chemical shifts (δ) are quoted in parts per million (ppm), and coupling constants (*J*) are measured in Hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, br = broad, and m = multiplet. NMR spectra were processed in Mestrenova, keeping the $CDCl_3$ residual peaks at 7.26 ppm ($^{1}H$) and 77.16 ppm ($^{13}C$). High-resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF. All fluorescence and UV−Vis spectra were recorded in a HORIBA FluoroMax Plus spectrofluorometer and a Hitachi UV−Vis spectrophotometer. X-ray diffraction data for the crystal was collected at 100 K on a SuperNova Eos diffractometer using monochromatic Cu Kα radiation (λ = 1.54184 Å). IUPAC names were obtained using the ChemDraw service. The weighing was performed with a 4-decimal place balance. All reactions of sulfonylation of cyclopropene were conducted in dried glassware with magnetic stirring under an inert atmosphere unless otherwise noted. All solvents were distilled following the guidelines of L.L Chai and Armarego purification of laboratory chemicals. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Flash column chromatography was performed over Merck silica gel (230−400 μm) using the eluent system described for each experiment. TLC was stained with an ethanolic solution of potassium permanganate ($KMnO_4$) or *p*-anisaldehyde. Erythrosin-B ($C_{20}H_8I_4O_5$, CAS number 15905-32-5, Dye content ≥95 %) purchased from sigma-Aldrich. All cyclopropenes and sodium sulfinates are synthesized from the literature. All metal catalysts were prepared from the literature, and the remaining catalysts were purchased from the TCI chemicals and used without purification unless otherwise specified. Other reagents were obtained from commercial suppliers Alfa Aesar and Spectrochem. In a general experiment, 40 W blue LEDs (456 nm) brought from Kessil with a cooling fan were used as a visible light source. The light source was placed approximately 5.0 cm from the reaction tube. The product yields were determined after purification by flash column chromatography using $SiO_2$, and $^{1}H$ NMR spectra determined the purity of compounds.

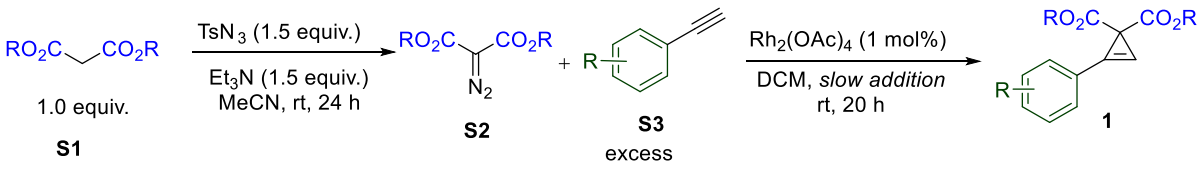
## 2. Optimization:[a]




| Entry | Photocatalyst | Solvent (2 mL) | Yield 3a (%)[b] |
|---|---|---|---|
| 1 | 2 mol% $Ru(bpy)_3Cl_2$. $6H_2O$ | DMF | 61 |
| 2 | 2 mol% $Ru(bpz)_3(PF_6)_2$ | DMF | 23 |
| 3 | 2 mol% $[Ir(ppy)_2(dtbpy)]PF_6$ | DMF | 41 |
| 4 | 2 mol% $[IrdFCF_3(ppy)_2(dtbpy)]PF_6$ | DMF | 69 |
| 5 | 5 mol% Mes.Acr.$ClO_4$ | DMF | 40 |
| 6 | 5 mol% Eosin-Y | DMF | 79 |
| 1 | 5 mol% Erythrosine-B | DMF | 87 |
| 8 | 5 mol% 4 CzIPN | DMF | 52 |
| 9 | 5 mol% 10-Phenylphenothiazine | DMF | 32 |
| 10 | 2 mol% DCA | DMF | 30 |
| 11 | 5 mol% T(*p*-Me)PPT | DMF | 47 |
| 12 | 5 mol% Rhodamine-B | DMF | 56 |
| 13 | 5 mol% Erythrosin-B | DMSO | 50 |
| 14 | 5 mol% Erythrosin-B | MeCN | 55 |
| 15 | 5 mol% Erythrosin-B | MeOH | 93 |
| 16 | 5 mol% Erythrosin-B | DCM | 49 |
| 17 | 5 mol% Erythrosin-B | EtOH | 91 |
| 18 | 5 mol% Erythrosin-B | PhMe | **09** |
| 19 | 5 mol% Erythrosin-B | DCE | 24 |
| 20 | 5 mol% Erythrosin-B | Acetone | 42 |
| 21 | 5 mol% Erythrosin-B | Benzene | Trace |
| 22 | 5 mol% Erythrosin-B | DME | 60 |
| 23 | 2 mol% Erythrosin-B | MeOH | 94 (91) |
| 24[c] | 2 mol% Erythrosin-B | MeOH | 6 |
| 25 | - | MeOH | N.R |

[a]All reactions were performed in 0.2 mmol. scale with 2.5 equiv. of **2a** and x mol% photocatalyst in 2 mL of the solvent and irradiated with 40 W 456 nm blue LEDs under Ar atm. for 24 h; [b] yields based on $^1$HNMR using 1,1,2,2-tetrachloroethane as an internal standard. [c]No light.

## 3. General Procedure for The Synthesis of Cyclopropenes:



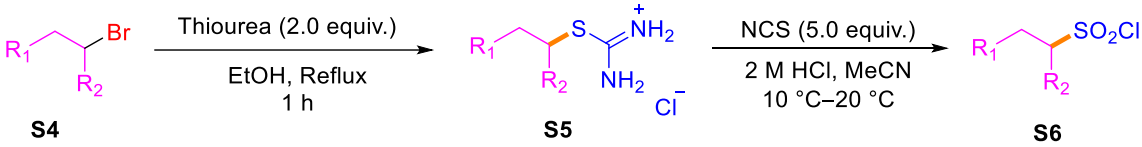

**Step 1: General Procedure for The Synthesis of Diazo Compounds from Malonates**:[1] Corresponding malonate **S1** (20.0 mmol, 1.0 equiv.), triethylamine (30.0 mmol, 1.5 equiv.), and 4-methyl benzenesulfonyl azide (24.0 mmol, 1.1 equiv.) were dissolved in 0.2M acetonitrile (100 mL) at room temperature. After stirring the resulting mixture overnight, the suspension was filtered through a cotton wool plug, and the solvent was removed under reduced pressure. The crude was dissolved in dichloromethane (200 mL) and water (200 mL). The two layers were separated, and the aqueous layer was extracted with dichloromethane (2 x 150 mL). The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure, and dried under a vacuum. Filtration through a plug of silica (AcOEt/hexane 1/1 + 1% $Et_3N$, 200

mL) afforded the corresponding diazomalonate **S5** as a yellow oil which was further purified by column chromatography on $SiO_2$ (230–400 mesh).

**Step 2: General Procedure for The Synthesis of Cyclopropenes from Diazo Compounds**:[1] Following a general procedure, the diazo compound **S5** (9.0 mmol, 1.0 equiv.) was dissolved in 0.5M DCM (18.0 mL), and the resulting solution was added *via* syringe pump to a suspension of 1 mol% $Rh_2(OAc)_4$ (0.09 mmol, 0.01 equiv.) and the corresponding acetylene **S6** (27.0 mmol, 3.0 equiv.) in 1.5M DCM (18.0 mL) at room temperature over 10 hours. After the addition, the reaction mixture was allowed to stir for another 10 hours. The reaction mixture was then filtered through a small pad of silica eluting with $CH_2Cl_2$, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on $SiO_2$ (230–400 mesh) using (EtOAc/Hexane = 20/80) as an eluent to afford the desired cyclopropenes **1** as the product.

**4. Synthesis of Sodium Sulfinates:**

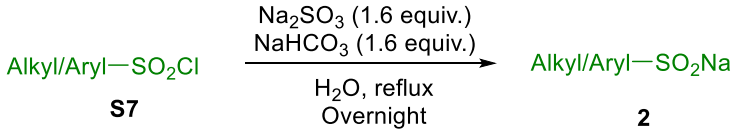
**4.1. General Procedure for The Synthesis of Sulfonyl Chlorides from Corresponding Bromides:**[2]




**S4** **S5** **S6**

A mixture of alkyl bromide **S4** (10.0 mmol, 1.0 equiv.) and 1.0 equiv. thiourea (0.77 g, 10 mmol) were refluxed together in 0.1M EtOH (10 mL) for 1 h. After removal of EtOH at reduced pressure, the obtained solid or sticky oil **S10** was slowly added to a mixture of NCS (13.4 g, 50.0 mmol), 2 M HCl (3.5 mL), and MeCN (15 mL) in a 10 °C water bath to maintain the internal temperature between 10 and 20 °C. When the reaction was completed (~15 min), $Et_2O$ (15 mL) was added, and the resulting solution was partitioned by the addition of $H_2O$ (15 mL). The organic phase was separated, dried ($Na_2SO_4$), and concentrated under reduced pressure. The residue was subjected to flash column chromatography on $SiO_2$ (230–400 mesh) using EtOAc/Hexane (5/95) to afford the desired sulfonyl chlorides **S6** as the product.

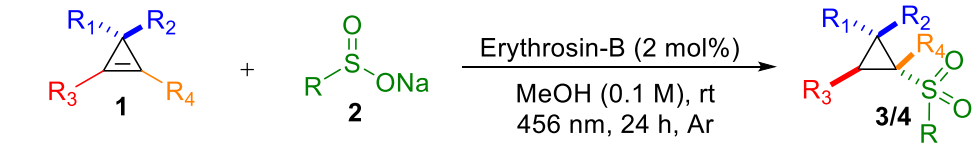
**4.2. General Procedure for The Synthesis of Sodium Sulfinates from Corresponding Sulfonyl Chlorides:**[3]




**S7** **2**

The alkyl sulfonyl chloride **S7** (10.0 mmol, 1.0 equiv.) was dissolved in 0.5 M water (20 mL). Sodium sulfite (16.0 mmol, 1.6 equiv.) and sodium bicarbonate (16.0 mmol, 1.6 equiv.) were added, and the reaction mixture was refluxed overnight. The water was evaporated, and ethanol was added to the residue. The suspension was heated for 10 min, cooled, and filtered through a Celite pad. This was repeated twice with the residue from the filtration. The ethanol fractions were combined, and the solvent evaporated under a vacuum to form a solid, which was washed with toluene. Sodium alkyl sulfinates **2** were isolated as a white powder.

**5. General Procedure for Diastereoselective Sulfonylation of Cyclopropenes:**




$R_1 = R_2$ = Aryl, EWG, F
$R_3$ = Aryl, Alkyl, H
$R_4$ = Alkyl, H

R = Aryl, Alkyl
Hetero aryl

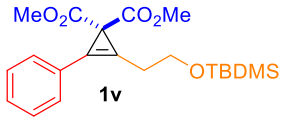
To an oven-dried borosilicate test tube equipped with a magnetic stir bar was added cyclopropene **1** (0.2 mmol, 1.0 equiv.), Sodium sulfinate salt **2** (0.5 mmol, 2.5 equiv.) and 2 mol% photocatalyst [Erythrosin-B (3.5 mg, 0.004 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 2 mL of MeOH solvent (0.1 M) was added through the septum and placed in approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After 24 h of the reaction, 10 mL of water was added, extracted with EtOAc (20 mL), and washed

with $H_2O$ (3 × 20 mL). The combined organic layer was dried over $Na_2SO_4$, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (230–400 mesh) using hexane and EtOAc as an eluent to afford the corresponding sulfonylated cyclopropane derivatives **3/4**.

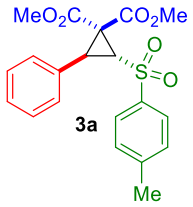
Note: All reactions are monitored by $^1H$ NMR and isolated by column chromatography using $KMnO_4$ stain.

**5.1. Characterization and Spectral Data of the Sulfonylation Products:**

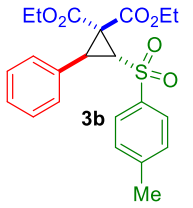
**Dimethyl-2-(2-((*tert*-butyldimethyl-silyl)-oxy)-ethyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate 1v:** Colorless oil; (Yield = 62%, 455 mg); $R_f$ = 0.5 (20% EtOAc/Hexane); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.29 (m, 2H), 3.98 (t, *J* = 6.7 Hz, 2H), 3.70 (s, 6H), 2.92 (t, *J* = 6.7 Hz, 2H), 0.89 (s, 9H), 0.09 (s, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 171.49, 129.93, 129.59, 128.85, 125.17, 106.42, 105.69, 60.59, 52.25, 34.91, 28.67, 25.98, 18.38, –5.14; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{30}NaO_5Si$: 390.1863, found: 390.1866.



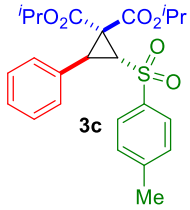

**Dimethyl-(2*S**,3*R**)-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate 3a:** White solid; (Yield = 94%, 72.9 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, *1*H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 6.8, 3.3 Hz, 3H), 7.13 (dd, *J* = 6.7, 3.0 Hz, 2H), 3.98 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.92 (d, *J* = 7.7 Hz, 1H), 3.49 (s, 3H), 2.48 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.02, 164.81, 145.39, 136.72, 131.65, 130.15, 128.62, 128.36, 128.24, 128.06, 53.71, 53.28, 48.62, 44.14, 33.88, 21.80. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{20}NaO_6S$: 411.0873, found: 411.0875.



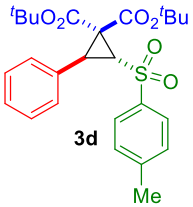

**Diethyl-(2*S**,3*R**)-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate 3b:** White solid; (Yield = 91%, 75.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.13 – 7.08 (m, 2H), 4.40 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.32 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.97 – 3.86 (m, 4H), 2.44 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 164.41, 164.33, 145.20, 136.99, 131.77, 130.06, 128.48, 128.41, 128.10, 127.97, 62.71, 62.36, 48.45, 44.43, 33.78, 21.70, 13.90, 13.71; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{22}H_{24}NaO_6S$: 439.1186, found: 439.1196.



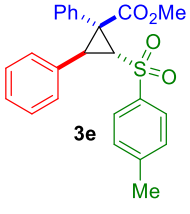

**Diisopropyl-(2*S**,3*R**)-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate 3c:** White solid; (Yield = 87%, 77.3 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.06 (dd, *J* = 6.8, 3.1 Hz, 2H), 5.23 (m, 1H), 4.75 (m, 1H), 3.89 (d, *J* = 7.7 Hz, 1H), 3.86 (d, *J* = 7.9 Hz, 1H), 2.46 (s, 3H), 1.36 (dd, *J* = 6.3, 3.6 Hz, 6H), 1.01 (d, *J* = 6.1 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 164.00, 163.96, 145.16, 137.31, 131.86, 130.14, 128.54, 128.49, 128.10, 128.01, 70.56, 70.41, 48.37, 44.87, 33.99, 21.81, 21.61, 21.60, 21.51, 21.26; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ Calcd for $C_{24}H_{32}NO_6S$: 462.1945, found: 462.1940.



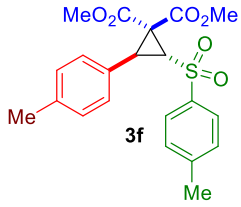

**Di-*tert*-Butyl-(2*S**,3*R**)-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate 3d:** White solid; (Yield = 97%, 91.6 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.07 (dd, *J* = 6.8, 2.7 Hz, 2H), 3.81 (d, *J* = 7.8 Hz, 1H), 3.77 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 1.58 (s, 9H), 1.17 (s, 9H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 163.47, 163.37, 145.02, 137.55, 132.11, 130.12, 128.59, 128.40, 127.95, 83.34, 83.02, 48.05, 46.46, 33.77, 27.91, 27.72, 21.83; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{26}H_{32}NaO_6S$: 495.1812, found: 495.1814.



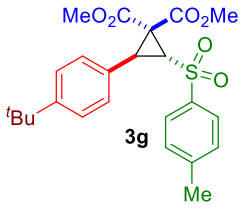

**Methyl-(1*R**,2*S**,3*R**)-1,2-diphenyl-3-tosylcyclopropane-1-carboxylate 3e:** White solid; (Yield = 83%, 67.4 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.35 (m, 5H), 7.33 – 7.23 (m, 5H), 7.18 – 7.12 (m, 2H), 4.12 (d, *J* = 6.8 Hz, 1H), 3.96 (d, *J* = 7.2 Hz, 1H), 3.32 (s, 3H), 2.46 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 168.80, 144.81, 137.69, 133.21, 132.69, 130.63, 129.94, 128.67, 128.50, 128.44, 128.01, 52.98, 48.69, 45.73, 34.99, 21.81; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{22}NaO_4S$: 429.1131, found: 429.1126.



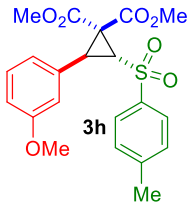
**Dimethyl-(2*S**,3*R**)-2-(*p*-tolyl)-3-tosylcyclopropane-1,1-dicarboxylate 3f**: White solid; (Yield = 86%, 69.1 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.92 (d, *J* = 7.9 Hz, 1H), 3.90 (s, 3H), 3.86 (d, *J* = 7.9 Hz, 1H), 3.49 (s, 3H), 2.46 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.47, 165.27, 145.68, 138.39, 137.24, 130.49, 129.70, 128.94, 128.60, 128.44, 54.05, 53.65, 49.09, 44.57, 34.14, 22.17, 21.58; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{22}NaO_4S$: 425.1029, found: 425.1010.



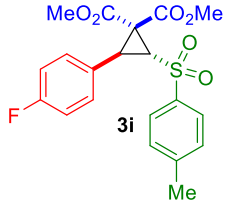

**Dimethyl-(2*S**,3*R**)-2-(4-(*tert*-butyl)phenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3g:** White solid; (Yield = 91%, 80.8 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.91 (d, J = 7.9 Hz, 1H), 3.87 (d, J = 7.8 Hz, 1H), 2.47 (s, 3H), 1.26 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.15, 164.92, 151.24, 145.32, 136.90, 130.16, 128.55, 128.07, 125.54, 53.71, 53.27, 48.73, 44.21, 34.63, 33.78, 31.32, 21.83; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{28}NaO_4S$: 467.1499, found: 467.1509.



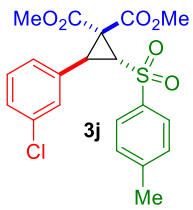

**Dimethyl-(2*S**,3*R**)-2-(3-methoxyphenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3h:** White Solid; (Yield = 76%, 63.5 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.59 (s, 1H), 3.91 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 3.86 (d, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 3.50 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.99, 164.82, 159.72, 145.35, 136.87, 133.25, 130.14, 129.68, 128.08, 120.56, 113.96, 113.93, 55.26, 53.68, 53.30, 48.80, 44.19, 33.94, 21.77; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{22}NaO_7S$: 441.0978, found: 441.0985.



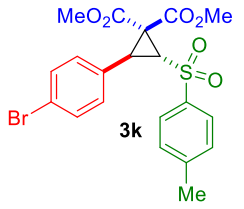

**Dimethyl-(2*S**,3*R**)-2-(4-fluorophenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3i**: White solid; (Yield = 84%, 68.2 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 8.6, 5.2 Hz, 2H), 6.98 – 6.90 (m, 2H), 3.91 (d, *J* = 7.9 Hz, s, 1H), 3.90 (s, 3H), 3.85 (d, *J* = 7.9 Hz, 1H), 3.49 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.86, 164.76, 162.57 (d, *J* = 247.6 Hz),, 145.49, 136.68, 130.21, 130.18, 130.14, 128.09, 127.51 (d, *J* = 3.2 Hz), 115.78, 115.61, 53.74, 53.38, 48.81, 44.20, 33.12, 21.82; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –113.07 - –113.36 (m); HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{19}FNaO_6S$: 429.0779, found: 429.0783.



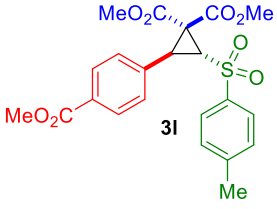

**Dimethyl-(2*S**,3*R**)-2-(3-chlorophenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3j**: White solid; (Yield = 85%, 71.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.14 (m, 2H), 7.09 (s, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 3.90 (d, *J* = 7.9 Hz, 1H).3.90 (s, 3H), 3.85 (d, *J* = 7.9 Hz, 1H), 3.51 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.74, 164.66, 145.59, 136.54, 134.54, 133.79, 130.21, 129.94, 128.68, 128.57, 128.12, 126.64, 53.80, 53.47, 48.67, 44.13, 33.18, 21.83; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{19}ClNaO_6S$: 445.0483, found: 445.0485.




**Dimethyl-(2*S**,3*R**)-2-(4-bromophenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3k**: White solid; (Yield = 93%, 86.5 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 4H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 3.88 (d, *J* = 7.9 Hz, 1H), 3.84 (d, *J* = 7.9 Hz, 1H), 3.50 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.11, 165.03, 145.87, 136.99, 132.18, 131.13, 130.54, 130.47, 128.43, 122.78, 54.11, 53.80, 48.99, 44.51, 33.61, 22.17; HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{19}BrNaO_6S$: 488.9978, found: 488.9984.

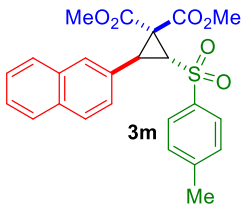



**Dimethyl-(2*S**,3*R**)-2-(4-(methoxycarbonyl)phenyl)-3-tosylcyclopropane-1,1-dicarboxylate 3l:** White solid; (Yield = 82%, 73.1 mg); $R_f$ = 0.3 (30% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.86 (dd, *J*= 8.4, 2.1 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.97 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 1H), 3.90 (d, *J* = 6.6 Hz, 1H), 3.88 (s, 3H),

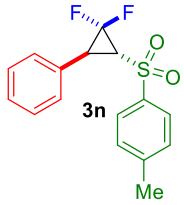


2.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.58, 164.73, 164.66, 145.57, 136.87, 136.67, 130.22, 130.19, 129.93, 128.58, 128.14, 53.80, 53.43, 52.29, 48.69, 44.28, 33.61, 21.83; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{22}BrNaO_8S$: 469.0928, found: 469.0913.

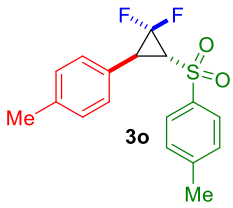
**Dimethyl-(2*S**,3*R**)-2-(naphthalen-2-yl)-3-tosylcyclopropane-1,1-dicarboxylate 3m:** White solid; (Yield = 81%, 71.0 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.69 (m, 3H), 7.56 (s, 1H), 7.51 – 7.45 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.12 (d, *J* = 7.8 Hz, 1H), 4.03 (d, *J* = 7.8 Hz, 1H), 3.94 (s, 3H), 3.44 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.08, 164.85, 145.44, 136.85, 133.15, 133.01, 130.19, 129.12, 128.52, 128.17, 127.89, 127.81, 127.63, 126.61, 126.50, 125.95, 77.41, 77.16, 76.90, 53.79, 53.36, 48.86, 44.38, 34.09, 21.85; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{22}NaO_6S$: 461.1029, found: 461.1035.



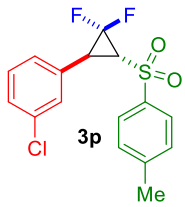

**1-(((1*R**,3*S**)-2,2-Difluoro-3-phenylcyclopropyl)sulfonyl)-4-methylbenzene 3n**: White semi-solid; (Yield = 69%, 42.5 mg); $R_f$ = 0.3 (5% EtOAc/Hexane/2% $Et_3N$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.23 (dd, *J* = 7.6, 2.1 Hz, 2H), 3.88 (ddd, *J* = 14.0, 8.0, 2.3 Hz, 1H), 3.34 (dd, *J* = 11.6, 7.9 Hz, 1H), 2.48 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.97, 137.29, 130.70, 129.96, 129.35, 128.92, 128.74, 128.37, 108.97 (dd, *J* = 294.3, 288.9 Hz), 48.27 (t, *J* = 12.0 Hz), 33.15 (dd, *J* = 11.3, 10.6 Hz), 22.19; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –131.37 (ddd, *J* = 160.8, 11.9, 2.3 Hz), –133.54 (dd, *J* = 160.8, 14.0 Hz); HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{14}F_2NaO_2S$: 331.0575, found: 331.0583.



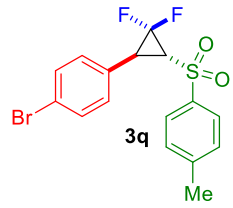

**1-(1*R**,3*S**)-2,2-Difluoro-3-(*p*-tolyl)cyclopropyl)sulfonyl)-4-methylbenzene 3o**: White semi-solid; (Yield = 75%, 48.3 mg); $R_f$ = 0.3 (5% EtOAc/Hexane/2% $Et_3N$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.13 (q, *J* = 8.3 Hz, 4H), 3.84 (ddd, *J* = 14.1, 8.0, 2.3 Hz, 1H), 3.32 (dd, *J* = 11.6, 7.9 Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.56, 138.48, 136.98, 130.32, 129.89, 129.67, 129.28, 128.22, 127.99, 127.57, 127.44, 127.29, 127.16, 126.49, 108.71 (dd, *J* = 294.3, 288.7 Hz),47.89 (t, *J* = 12.0 Hz), 32.63 (t, *J* = 12.0 Hz), 21.83, 21.23; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –131.42 (ddd, *J* = 160.7, 11.9, 2.3 Hz), –133.58 (dd, *J* = 160.8, 14.0 Hz); HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{16}F_2NaO_2S$: 345.0731, found: 345.0717.



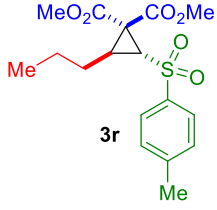

**1-Chloro-3-((1*R**,3*S**)-2,2-difluoro-3-tosylcyclopropyl)benzene 3p:** White semi-solid; (Yield = 71%, 48.6 mg); $R_f$ = 0.3 (5% EtOAc/Hexane/2% $Et_3N$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.20 (s, 1H), 7.13 (d, *J* = 9.2 Hz, 1H), 3.84 (ddd, *J* = 13.8, 8.0, 2.1 Hz, 1H), 3.34 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.48 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.17, 137.01, 135.30, 131.94, 130.76, 130.63, 129.23, 128.85, 128.39, 127.07, 108.64 (dd, *J* = 295.0, 288.8 Hz), 48.26 (t, *J* = 11.9 Hz), 32.44 (dd, *J* = 12.0, 10.1 Hz), 22.20; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -131.18 (ddd, *J* = 161.5, 11.9, 2.0 Hz), -133.69 (dd, *J* = 161.3, 13.7 Hz); HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}ClF_2NaO_2S$: 365.0185, found: 365.0190.



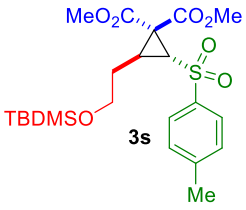

**1-Bromo-4-((1*R**,3*S**)-2,2-difluoro-3-tosylcyclopropyl)benzene 3q**: White semi-solid; (Yield = 74%, 57.0 mg); $R_f$ = 0.3 (5% EtOAc/Hexane and 2% $Et_3N$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.82 (ddd, *J* = 14.0, 8.0, 2.2 Hz, 1H), 3.31 (dd, *J* = 11.6, 7.9 Hz, 1H), 2.48 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.79, 136.74, 132.22, 130.41, 130.07, 128.72, 128.03, 122.80, 108.34 (dd, *J* = 294.8, 288.7 Hz), 47.95 (t, *J* = 11.9 Hz), 32.14 (dd, *J* = 12.0, 10.1 Hz), 21.86; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –131.30 (ddd, *J* = 161.2, 11.8, 2.0 Hz), –133.73 (dd, *J* = 161.3, 13.7 Hz); HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}BrF_2NaO_2S$: 408.9680, found: 408.9685.



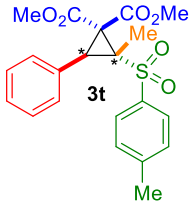

**Dimethyl-(2*S**,3*R**)-2-propyl-3-tosylcyclopropane-1,1-dicarboxylate 3r:** White solid; (dr = 1:0.4); (Yield = 63%, 44.6 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.72 (s, 3H), 3.27 (d, *J* = 7.6 Hz, 1H), 2.63 (q, *J* = 7.4 Hz, 1H), 2.44 (s, 3H), 1.55 – 1.28 (m, 2H), 1.34 – 1.21 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (126 MHz,



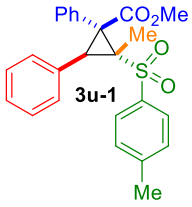
$CDCl_3$) δ 166.25, 165.44, 145.08, 137.11, 129.98, 128.02, 53.47, 53.40, 49.74, 42.38, 30.27, 27.74, 21.78, 21.70, 13.46; HRMS (ESI-TOF) m/z [M + H]$^+$ Calcd for $C_{17}H_{23}O_6S$: 355.1210, found: 355.1210.



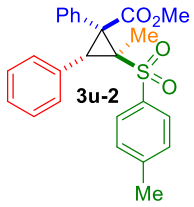

**Dimethyl-(2*S**,3*R**)-2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3-tosylcyclopropane-1,1-dicarboxylate 3s**: White solid; (Yield = 71%, 66.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 3H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.27 (d, *J* = 7.6 Hz, 1H), 2.72 (q, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 1.70 (dt, *J* = 14.0, 6.7 Hz, 1H), 1.61 (dt, *J* = 14.0, 7.0 Hz, 1H), 0.87 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 168.95, 166.24, 165.30, 145.10, 137.05, 129.99, 128.04, 61.48, 53.58, 49.33, 42.02, 29.22, 27.78, 25.99, 21.79, 18.42, –5.36, –5.39; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{34}NaO_7SSi$: 493.1687, found: 493.1692.

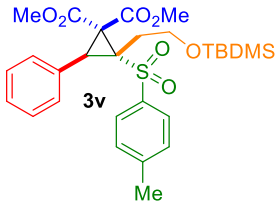



**Dimethyl-(2*S**,3*R**)-2-methyl-3-phenyl-2-tosylcyclopropane-1,1-dicarboxylate 3t**: (dr = 1:0.2); White solid; (Yield = 83%, 66.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 0.4H), 7.38 (d, *J* = 8.2 Hz, 2.4H), 7.25 (dd, *J* = 4.8, 1.9 Hz, 3.6H), 7.06 (dd, *J* = 7.2, 1.5 Hz, 0.4H), 7.00 – 6.92 (m, 2.H), 4.05 (s, 1H), 3.92 (s, 3H), 3.84 (s, 0.6H), 3.68 (s, 3H), 2.46 (s, 3.6H), 1.54 (s, 3H), 1.06 (s, 0.6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 168.18, 167.02, 165.23, 145.34, 145.00, 135.12, 134.50, 133.31, 131.08, 129.98, 129.88, 129.57, 129.21, 129.12, 128.82, 128.73, 128.68, 127.87, 54.08, 53.72, 53.08, 52.92, 49.71, 44.25, 35.06, 34.03, 31.12, 21.81, 15.78, 12.48; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{22}NaO_6S$: 425.1029, found: 425.1034.

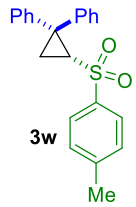



**Methyl-(1*R**,2*S**,3*R**)-2-methyl-1,3-diphenyl-2-tosylcyclopropane-1-carboxylate (*Trans*-Isomer 3u-1):** (dr 82:18); White solid; (Yield = 62%, 52.1 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 4H), 7.45 – 7.21 (m, 8H), 7.19 (dd, *J* = 5.3, 2.7 Hz, 2H), 4.04 (s, 1H), 3.51 (s, 3H), 2.44 (s, 3H), 1.55 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 168.24, 144.81, 135.91, 135.51, 132.55, 130.45, 130.06, 129.74, 129.31, 128.35, 128.29, 127.50, 52.49, 51.45, 46.78, 36.23, 21.77, 15.03; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{24}NaO_4S$: 443.1288, found: 443.1299; (***Cis*-Isomer 3u-2):** Colourless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.25 (m, 5H), 7.22 – 7.11 (m, 3H), 6.98 – 6.82 (m, 2H), 4.05 (s, 1H), 3.78 (s, 3H), 2.44 (s, 3H), 1.30 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.62, 144.87, 135.42, 132.69, 131.81, 131.68, 130.46, 129.96, 129.28, 128.57, 128.48, 128.10, 127.22, 53.45, 52.60, 47.06, 35.19, 21.79, 13.49; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{24}NaO_4S$: 4431288, found: 443.1293.



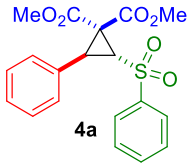




**Dimethyl-(2*S**,3*R**)-2-(2-((tert-butyl-dimethyl-silyl)-oxy)-ethyl)-3-phenyl-2-tosylcyclopropane-1,1-dicarboxylate 3v:** White solid; (Yield = 59%, 64.4 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.86 – 6.69 (m, 2H), 6.82 – 6.72 (m, 1H), 4.05 (ddd, *J* = 16.4, 10.7, 5.5 Hz, 1H), 4.00 (s, 1H), 3.93 (s, 3H), 3.69 (s, 3H), 3.52 (td, *J* = 10.1, 5.3 Hz, 1H), 2.50 (s, 3H), 2.36 – 2.19 (m, 1H), 2.02 (ddd, *J* = 15.3, 10.3, 5.0 Hz, 1H), 0.82 (s, 9H), –0.01 (s, 3H), -0.04 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.91, 165.10, 145.58, 135.33, 130.84, 130.20, 129.50, 129.02, 128.68, 127.80, 60.71, 55.77, 53.62, 53.20, 43.87, 37.72, 28.74, 26.08, 21.84, 18.44, –5.14, – 5.26; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{38}NaO_7SSi$: 569.2000, found: 569.2010.

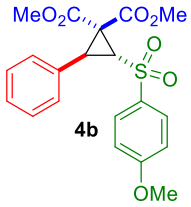



**(*R**)-(2-Tosylcyclopropane-1,1-diyl) di benzene 3w:** White solid; (Yield = 48%, 33.4 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.34 – 7.24 (m, 9H), 7.23 – 7.17 (m, 2H), 3.27 (dd, *J* = 8.7, 5.9 Hz, 1H), 2.52 (t, *J* = 5.7 Hz, 1H), 2.47 (s, 3H), 1.80 (dd, *J* = 8.7, 5.4 Hz, 1H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.27, 144.03, 138.30, 137.21, 130.14, 129.72, 128.82, 128.23, 127.99, 127.83, 127.49, 127.21, 45.79, 40.72, 21.75, 18.87. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{20}NaO_2S$: 371.1076, found: 371.1075.

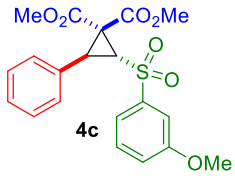
**Dimethyl-(2*S**,3*R**)-2-phenyl-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate 4a:** White solid; (Yield = 90%, 67.3 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.75 – 7.69 (m, 1H), 7.67 – 7.57 (m, 2H), 7.31 – 7.24 (m, 3H), 7.14 – 7.09 (m, 2H), 4.00 (d, *J* = 7.9 Hz, 1H), 3.94 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.49 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.96, 164.75, 139.69, 134.32, 131.57, 129.54, 128.65, 128.54, 128.33, 128.01, 53.72, 53.30, 48.52, 44.20, 33.92; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{18}NaO_6S$: 397.0716, found: 397.0711.



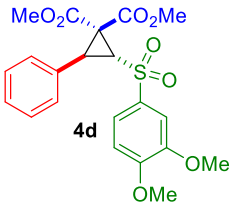

**Dimethyl-(2*S**,3*R**)-2-((4-methoxyphenyl)sulfonyl)-3-phenylcyclopro-pane-1,1-dicarboxylate:** White solid; (Yield = 91%, 73.5 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.10 (dd, *J* = 6.9, 3.1 Hz, 2H), 7.06 – 7.01 (m, 2H), 3.94 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.88 (d, *J* = 7.9 Hz, 1H), 3.46 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.12, 164.88, 164.23, 131.75, 131.23, 130.35, 128.64, 128.39, 128.23, 114.72, 55.82, 53.72, 53.26, 48.90, 44.20, 33.93; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{20}NaO_7S$: 427.0822, found: 427.0824.



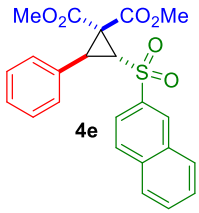

**Dimethyl-(2*S**,3*R**)-2-((3-methoxyphenyl)sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 86%, 69.5 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.29 – 7.24 (m, 3H), 7.22 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.13 (dd, *J* = 6.5, 3.2 Hz, 2H), 3.99 (d, *J* = 7.9 Hz, 1H), 3.93 (S, 3H), 3.93 (d, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 3.50 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.99, 164.76, 160.20, 140.79, 131.60, 130.62, 128.65, 128.52, 128.43, 128.34, 128.28, 120.87, 120.11, 112.39, 55.83, 53.72, 53.30, 48.56, 44.23, 33.88; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{20}NaO_7S$: 427.0822, found: 427.0827.



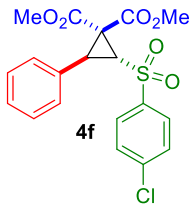

**Dimethyl-(2*S**,3*R**)-2-((3,4-dimethoxyphenyl)sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 93%, 80.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.26 (q, *J* = 4.0 Hz, 3H), 7.13 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.98 (d, *J* = 2.1 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 3.94 (s, 3H), 3.89 (d, *J* = 7.3 Hz, 1H), 3.50 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.28, 164.92, 153.90, 149.48, 131.76, 131.33, 128.69, 128.41, 128.30, 122.38, 110.97, 110.31, 56.50, 56.46, 56.43, 56.41, 56.39, 53.73, 53.69, 53.66, 53.63, 53.38, 53.35, 53.33, 53.30, 49.04, 44.29, 33.95; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{22}NaO_8S$: 457.0928, found: 457.0927.



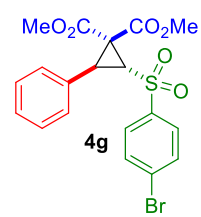

**Dimethyl-(2*S**,3*R**)-2-(naphthalen-2-ylsulfonyl)-3-phenylcyclopro-pane-1,1-dicarboxylate:** White solid; (Yield = 84%, 71.2 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.8 Hz, 1H), 8.08 – 7.89 (m, 4H), 7.79 – 7.61 (m, 2H), 7.25 – 7.21 (m, 3H), 7.14 – 7.09 (m, 2H), 4.05 (d, *J* = 7.6 Hz, 1H), 4.00 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.03, 164.81, 136.59, 135.68, 132.30, 131.65, 130.07, 129.96, 129.73, 129.65, 128.68, 128.42, 128.30, 128.19, 127.95, 122.60, 53.80, 53.33, 48.66, 44.30, 34.08; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{20}NaO_6S$: 447.0873, found: 447.0880.



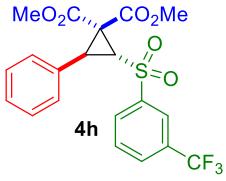

**Dimethyl-(2*S**,3*R**)-2-((4-chlorophenyl)sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate 4f:** White solid; (Yield = 87%, 70.1 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.58 – 7.53 (m, 2H), 7.25 (q, *J* = 4.0 Hz, 3H), 7.11 (dd, *J* = 6.9, 3.1 Hz, 2H), 3.97 (d, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.47 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.93, 164.66, 141.15, 138.15, 131.41, 129.91, 129.64, 128.74, 128.42, 128.37, 53.82, 53.42, 48.53, 44.32, 33.83; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{17}ClNaO_6S$: 431.0327, found: 431.0323.



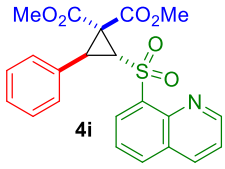

**Dimethyl-(2*S**,3*R**)-2-((4-bromophenyl)sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate 4g:** White solid; (Yield = 83%, 74.9 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.78 – 7.70 (m, 2H), 7.29 – 7.24 (m, 3H), 7.13 (dd, *J* = 6.9, 2.8 Hz, 2H), 3.98 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.89 (d, *J* = 7.4 Hz, 1H), 3.48 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.92, 164.65, 138.68,



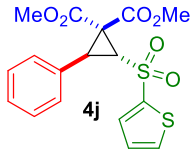
132.90, 131.40, 129.79, 129.67, 128.75, 128.43, 128.38, 53.84, 53.81, 53.44, 53.42, 48.48, 44.32, 33.82; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{17}BrNaO_6S$: 474.9821, found: 474.9830.



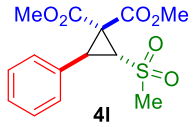

**Dimethyl-(2*S**,3*R**)-2-phenyl-3-((3-(trifluoromethyl)phenyl)-sulfonyl)cyclopropane-1,1-dicarboxylate 4h:** White solid; (Yield = 80%, 70.7 mg); $R_f$ = 0.3 (20% EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.11 (m, 2H), 4.01 (dd, *J* = 15.0, 7.9 Hz, 1H), 3.91 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.47 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.73, 164.55, 140.85, 132.33, 132.06, 131.51, 131.27, 131.00 (q, *J* = 3.5 Hz), 130.46, 128.77, 128.50, 128.38, 125.40 (q, *J* = 3.8 Hz), 123.20 (d, *J* = 273.0 Hz), 53.82, 53.47, 48.41, 44.44, 33.65; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.72 (s); HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{17}F_3NaO_6S$: 465.0590, found: 465.052.



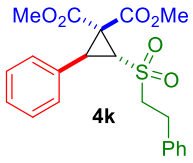

**Dimethyl-(2*S**,3*R**)-2-phenyl-3-(quinolin-8-ylsulfonyl)cyclopro-pane-1,1-dicarboxylate 4i:** White solid; (Yield = 83%, 70.6 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.37 (dd, *J* = 7.6, 1.5 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (s, 5H), 5.37 (d, *J* = 7.9 Hz, 1H), 4.09 (d, *J* = 7.9 Hz, 1H), 3.76 (s, 3H), 3.39 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.95, 164.78, 151.83, 144.16, 136.83, 136.53, 134.83, 131.91, 131.40, 129.12, 128.67, 128.47, 128.05, 125.42, 122.56, 53.39 , 53.37, 53.08, 53.05, 48.09, 44.02, 33.88.; HRMS (ESI-TOF) m/z [M + H]$^+$ Calcd for $C_{22}H_{20}O_6S$: 426.1006, found: 426.1010.



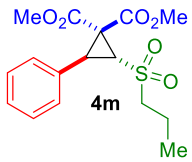

**Dimethyl-(2*S**,3*R**)-2-phenyl-3-(thiophen-2-ylsulfonyl)cyclopropane-1,1-dicarboxylate 4j:** White solid; (Yield = 79%, 60.0 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.80 – 7.75 (m, 1H), 7.28 – 7.23 (m, 3H), 7.19 (dd, *J* = 4.8, 3.7 Hz, 1H), 7.12 (dd, *J* = 6.7, 2.7 Hz, 2H), 4.01 (d, *J* = 7.9 Hz, 1H), 3.96 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 3.50 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.83, 164.70, 140.33, 134.89, 134.74, 131.50, 128.70, 128.38, 128.35, 128.23, 53.83, 53.80, 53.77, 53.73, 53.41, 53.38, 5 3.36, 53.33, 49.65, 44.66, 34.29; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{16}NNaO_6S_2$: 403.0281, found: 403.0274.



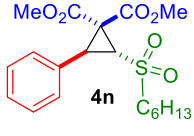

**Dimethyl-(2*S**,3*R**)-2-(methylsulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 89%, 55.5 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 5H), 3.90 (d, *J* = 7.4 Hz, 1H), 3.83 (s, 3H), 3.82 (d, *J* = 7.5 Hz, 1H), 3.51 (s, 3H), 3.12 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.07, 164.82, 131.33, 128.75, 128.59, 128.44, 53.87, 53.53, 46.26, 43.45, 41.78, 32.39; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{14}H_{16}NaO_6S$: 335.0560, found: 335.0564.




**Dimethyl-(2*S**,3*R**)-2-(phenethyl-sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 78%, 62.7 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 10H), 3.95 (d, *J* = 7.8 Hz, 1H), 3.86 (s, 3H), 3.75 (d, *J* = 7.9 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.50 (s, 3H), 3.49 – 3.44 (m, 1H) 3.23 (dd, *J* = 9.8, 7.3 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.06, 164.70, 137.54, 131.36, 129.09, 128.71, 128.61, 128.55, 128.48, 128.40, 127.24, 55.51, 53.84, 53.43, 45.10, 43.45, 32.45, 28.00; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{22}NaO_6S$: 425.1029, found: 425.1035.

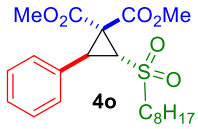



**Dimethyl-(2*S**,3*R**)-2-phenyl-3-(propyl-sulfonyl)cyclopropane-1,1-dicarboxylate:** White solid; (Yield = 72%, 49.0 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 5H), 3.90 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.78 (d, *J* = 7.4 Hz, 1H), 3.50 (s, 3H), 3.26 – 3.09 (m, 2H), 2.01 – 1.87 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.13, 164.90, 131.48, 128.73, 128.59, 128.40, 55.86, 53.82, 53.49, 44.84, 43.40, 32.32, 15.77, 13.35; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{20}NaO_6S$: 363.0873, found: 363.0879.

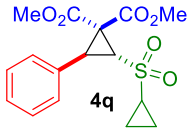



**Dimethyl-(2*S**,3*R**)-2-(hexylsulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 77%, 58.8 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 3.94 (d, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 3.81 (d, *J* = 7.7 Hz, 1H), 3.54 (s, 3H), 3.22 (qq, *J* = 14.1, 6.6 Hz, 2H), 2.03 – 1.84 (m, 2H), 1.55 – 1.39 (m, 2H), 1.39 – 1.27 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ

165.12, 164.89, 131.50, 128.71, 128.59, 128.38, 54.12, 53.82, 53.79, 53.48, 53.46, 44.84, 43.42, 32.35, 31.23, 28.22, 22.40, 21.74, 14.05; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{26}NaO_6S$: 405.1342, found: 405.1351.




**Dimethyl-(2*S**,3*R**)-2-(octylsulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate:** White solid; (Yield = 74%, 57.3 mg); $R_f$ = 0.3 (20 % EtOAc/Hexane); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 3.93 (d, J = 7.6 Hz, 1H), 3.86 (s, 3H), 3.81 (d, J = 7.6 Hz, 1H), 3.54 (s, 3H), 3.27 – 3.08 (m, 2H), 2.01 – 1.82 (m, 2H), 1.55 – 1.39 (m, 2H), 1.40 – 1.15 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.10, 164.88, 131.50, 128.70, 128.58, 128.37, 54.14, 53.79, 53.46, 44.85, 43.43, 32.36, 31.82, 29.06, 29.01, 28.56, 22.72, 21.78, 14.18; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{30}NaO_6S$: 410.1763, found: 410.1769.




**Dimethyl-(2*S**,3*R**)-2-(cyclopropyl-sulfonyl)-3-phenylcyclopropane-1,1-dicarboxylate 4q:** White solid; $R_f$ = 0.5 (20% EtOAc/Hexane); Yield (93%, 62.9 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 3.89 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.82 (d, *J* = 7.9 Hz, 1H), 3.52 (s, 3H), 2.74 – 2.63 (m, 1H), 1.48 – 1.37 (m, 1H), 1.35 – 1.21 (m, 1H), 1.20 – 1.02 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.34, 164.96, 131.58, 128.67, 128.55, 128.32, 53.78, 53.39, 45.84, 43.31, 32.77, 30.28, 5.86, 4.48; (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{18}NaO_6S$: 361.0716, found: 361.0725.

**6. Scale-up experiment:**

**Diastereoselective sulfonylation of cyclopropenes:** A 100 mL 2 neck round-bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with cyclopropene **1a** (0.93 g, 4.0 mmol), Sodium salt **2a** (1.8 g, 10 mmol), and Erythrosin-B (70.3 mg, 0.08 mmol, 2 mol %). The flask was evacuated and backfilled with nitrogen 3-5 times. MeOH (40 mL, 0.1 M) was added with a syringe under nitrogen and placed approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After the reaction (24 h, monitored by $^1$H NMR), the mixture was poured into a separatory funnel containing 50 mL of saturated NaCl solution and 50 mL of EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL) successively and then evaporated. The crude product was purified by column chromatography on silica gel (230-400 mesh), eluting with EtOAc/hexane (1/9 to 2/8) to afford the desired product **3a** in 84% yield (1.3 g).

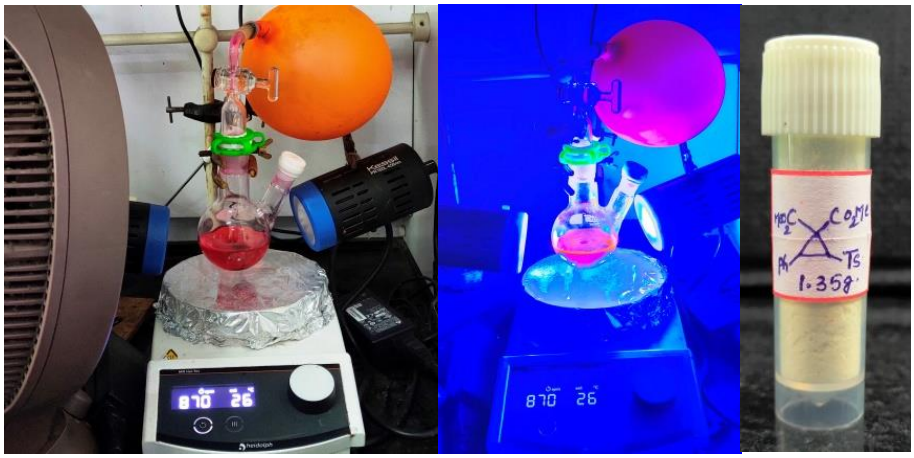
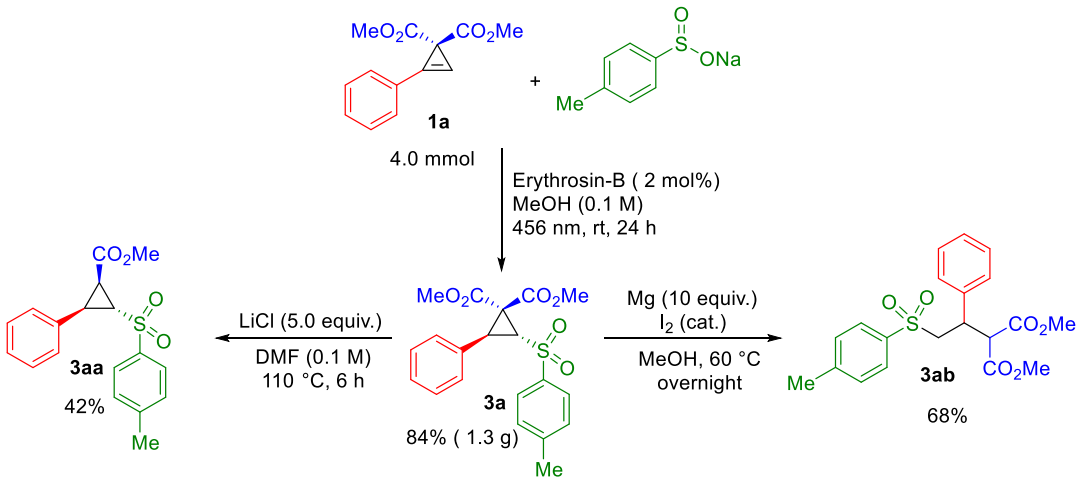
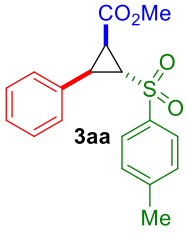


**Figure S1**: LED Setup

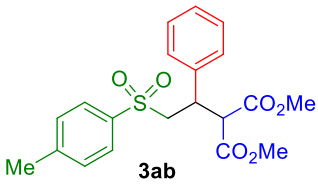
## 7. Further functionalization of final products:




**Selective removal ester group of compound 3a:** To an oven-dried borosilicate test tube equipped with a magnetic stir bar charged with **3a** (0.2 mmol, 1.0 equiv.), and LiCl (1.0 mmol, 5 equiv.) and the reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. DMF (2 mL, 0.1 M) was added with a syringe under nitrogen, placed in a preheated oil bath at 110 °C, and heated for 6 h. After the reaction, the mixture was poured into a separatory funnel containing 10 mL of saturated NaCl and 10 mL of EtOAc. The combined organic layers were washed with brine (50 mL) and evaporated. The crude product was purified by column chromatography on silica gel (230-400 mesh), eluting with EtOAc/hexane (1/9 to 2/8) to afford the desired product **3aa** in a 42% yield. **Methyl (*1S*,2R*,3R**)-2-phenyl-3-tosylcyclopropane-1-carboxylate 3aa**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.19 (m, 3H), 7.12 – 7.02 (m, 2H), 3.57 (dd, *J* = 6.4, 4.9 Hz, 1H), 3.48 (s, 3H), 3.39 (dd, *J* = 10.4, 6.5 Hz, 1H), 2.91 (dd, *J* = 10.4, 4.9 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.59, 145.18, 136.80, 132.49, 130.31, 128.77, 128.54, 127.93, 127.89, 52.40, 52.38, 44.25, 30.73, 27.48, 21.80; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{18}H_{18}NaO_4S$: 353.0818, found: 353.0820.




**Mg mediated ring opening of 3a:** To an oven-dried borosilicate test tube equipped with a magnetic stir bar charged with **3a** (0.2 mmol, 1.0 equiv.), Mg Turnings (1.0 mmol, 5.0 equiv.) $I_2$ (Cat.) and MeOH (2 mL) were added and placed in a preheated oil bath at 60 °C, which was heated for Overnight. After the reaction, the mixture was poured into a separatory funnel containing 10 mL of saturated NaCl solution and 10 mL of DCM. The combined organic layers were washed with brine (10 mL) and evaporated. The crude product was purified by column chromatography on silica gel (230-400 mesh), eluting with EtOAc/hexane (5/95 to 10/90) to afford the desired product **3ab** in 68% yields; **Dimethyl 2-(1-phenyl-2-tosylethyl)malonate 3ab**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 6.8 Hz, 5H), 7.07 (dd, *J* = 6.0, 2.3 Hz, 2H), 3.97 – 3.88 (m, 1H), 3.80 – 3.71 (m, 3H), 3.69 (s, 3H), 3.52 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 168.02, 167.54, 144.45, 137.74, 136.67, 129.71, 128.61, 128.42, 128.11, 127.76, 58.57, 57.17, 52.84, 52.69, 40.37, 21.65; HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{22}NaO_6S$: 413.1029, found: 413.1033.



**8. Luminescence quenching studies of Erythrosine-B with substrate cyclopropene 1a, sodium salt 2a:** To perform luminescence quenching studies, 2 μM of Erythrosin-B, 1 M of **1a,** and 1 M of sodium salt **2a** in MeOH were prepared as a stock solution, all other solutions with different concentration were prepared by dilution of stock solution.

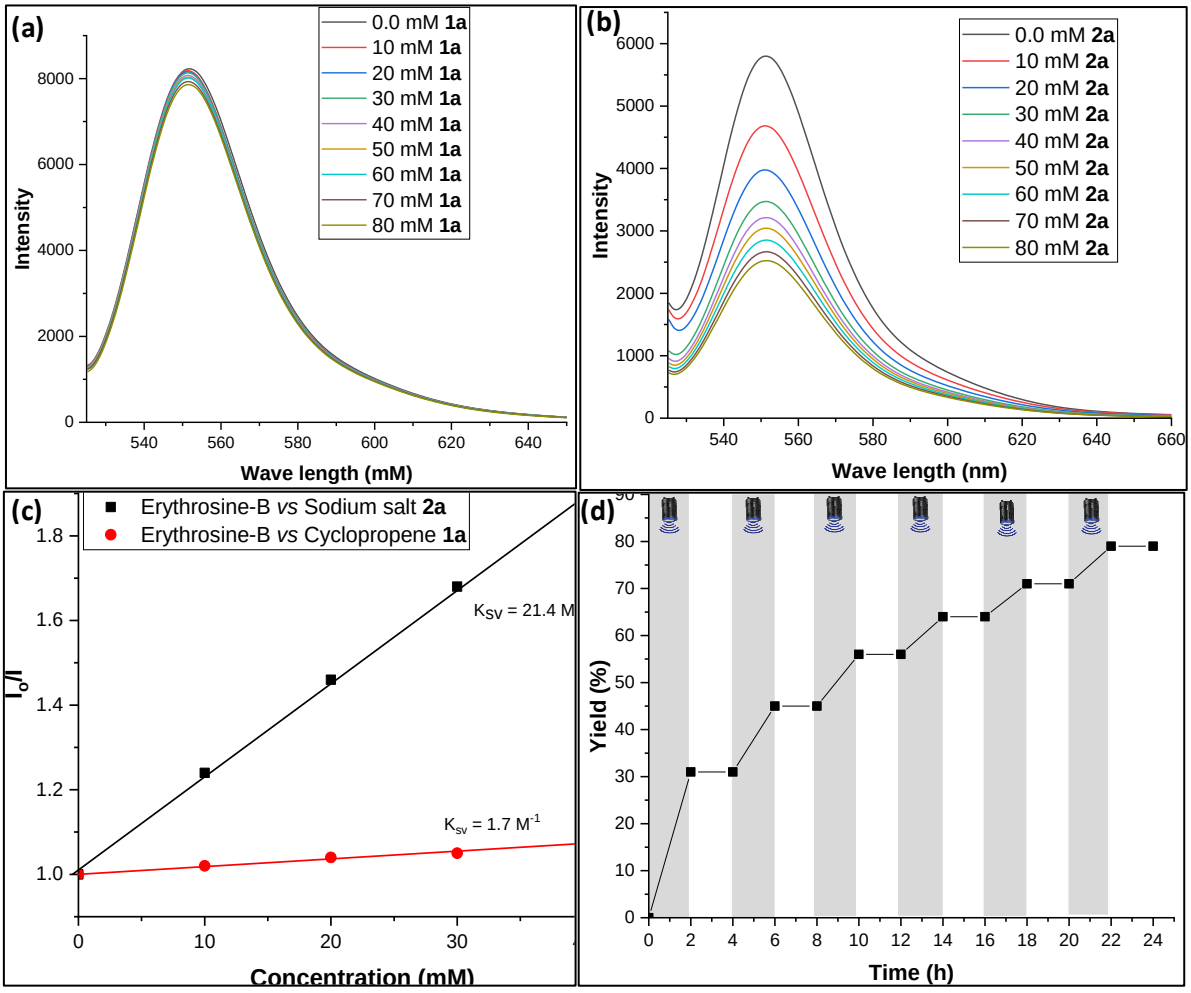


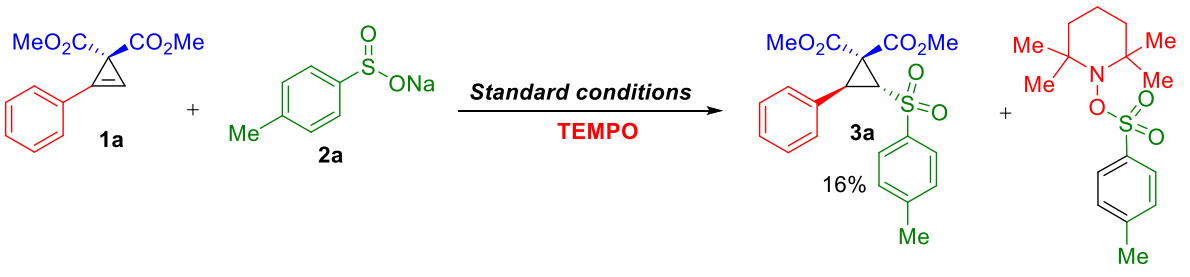

**Figure S2**. Luminescence quenching spectra of Erythrosine-B at 530 nm

In Methanol Solution: **a**) fluorescent quenching studies with 2μm Erythrosin-B with sodium sulfinate **1a** at 530 nm; **b**) fluorescent quenching studies with 2μm Erythrosin-B with sodium sulfinate **2a** at 530 nm; **c**) Stern-Volmer quenching studies with cyclopropene **1a** and **2a** with 2μm Erythrosin-B at 530 nm; **d**) Light On/Off experiment.

As expected, in the Erythrosin-B photocatalyst case, no quenching was observed with respect to **1a,** shown in Figure **S2a**. The only quenching of the Erythrosin-B photocatalyst was observed concerning substrate **2a**, as shown in Figure **S2b** and Stern-Volmer plot Figure **S2c**. Therefore, the reaction initially follows a single electron transfer (SET) pathway mechanism concerning the photoexcited state of the photocatalyst Erythrosin-B.

**9. Control Experiments:**

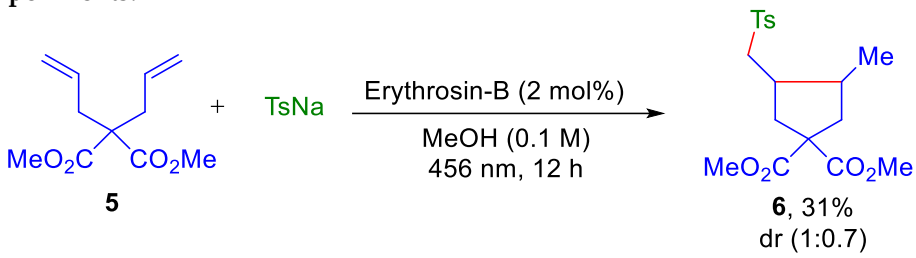
**9.1. Radical quenching experiments:**




**Reaction with TEMPO (Radical quencher):** To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar and charged with **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.5 mmol, 2.5 equiv.), Erythrosine-B (6.5 mg, 5 mol%) and TEMPO

(0.8 mmol, 2.0 equiv.) were added. The reaction tube was vacuumed and backfilled with nitrogen (3 to 4 times) and sealed with a septum. Then, 2 mL of dry MeOH (0.1 M) was added using a syringe and placed the reaction tube approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After 6 h of the reaction, 5 mL of brine solution was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure. $^1H$ NMR was recorded for the crude, which indicated the trace amount of product formation.

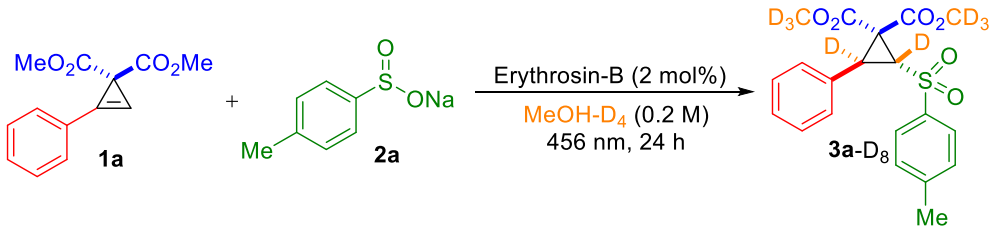
**9.2. Radical Clock Experiments**:




To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar and charged with **5** (0.1 mmol, 1.0 equiv.), **2a** (0.25 mmol, 2.5 equiv.), Erythrosin-B (1.8 mg, 2.0 mol%) were added. The reaction tube was vacuumed and backfilled with nitrogen (3 to 4 times) and sealed with a septum. Then, 2 mL of dry MeOH (0.2 M) was added using a syringe and placed the reaction tube approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After 12 h of the reaction, 5 mL of brine solution was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure. $^1H$ NMR was recorded for the crude, the formation **6** observed by comparison of the previous literature reports.[4]

This Conforms this reaction is radical reaction.

**9.3 Deuterium label experiments:**




To an oven-dried borosilicate test tube equipped with a magnetic stir bar was added cyclopropene **1** (0.05 mmol, 1.0 equiv., 11.6 mg), Sodium sulfinate salt **2** (0.15 mmol, 2.5 equiv.) and 2 mol% photocatalyst [Erythrosin-B (1.0 mg, 0.001 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.5 mL of $MeOD_4$ solvent (0.1 M) was added through the septum and placed in approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After 24 h of the reaction, the crude reaction mixture was concentrated under reduced pressure, and the crude product was passed through the silica pad (230−400 mesh) using DCM solvent. The final product analysed by $^1H$ NMR and HRMS.

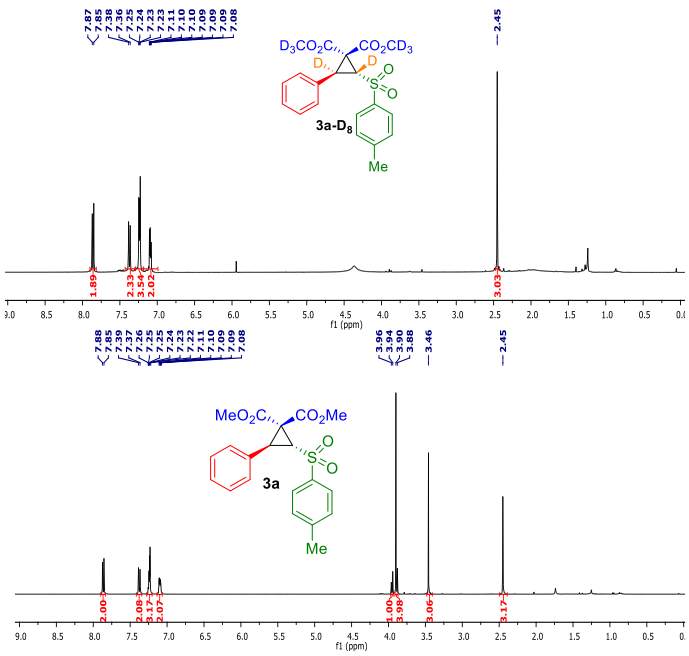


**Figure S3a:** Comparison of $^1$H NMR of **3a** and **3a**-D$_8$

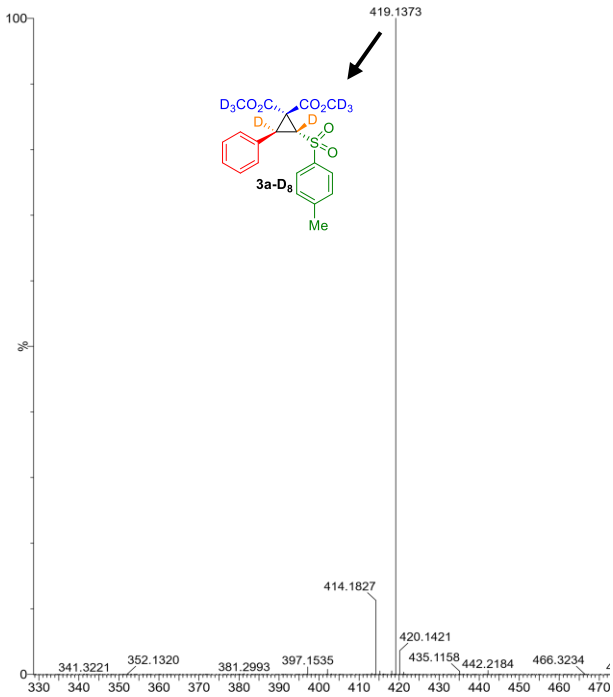
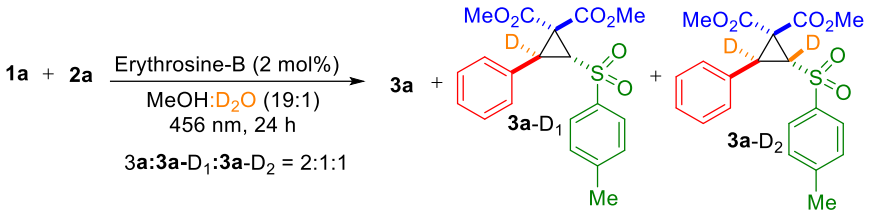


**Figure S3b:** HRMS data of **3a**-D$_8$




To an oven-dried borosilicate test tube equipped with a magnetic stir bar was added cyclopropene **1** (0.05 mmol, 1.0 equiv., 11.6 mg), Sodium sulfinate salt **2** (0.15 mmol, 2.5 equiv.) and 2 mol% photocatalyst [Erythrosin-B (1.0 mg, 0.001 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.5 mL of MeOH:D$_2$O (19:1) solvent (0.1 M) was added through the septum and placed in approximately 5 cm from the light setup (2 x Kessil 40 W 456 nm). After 24 h of the reaction, the crude reaction mixture was concentrated under reduced pressure, and the crude product was passed through the silica pad (230−400 mesh) using DCM solvent. The final product analysed by $^1$H NMR and HRMS.

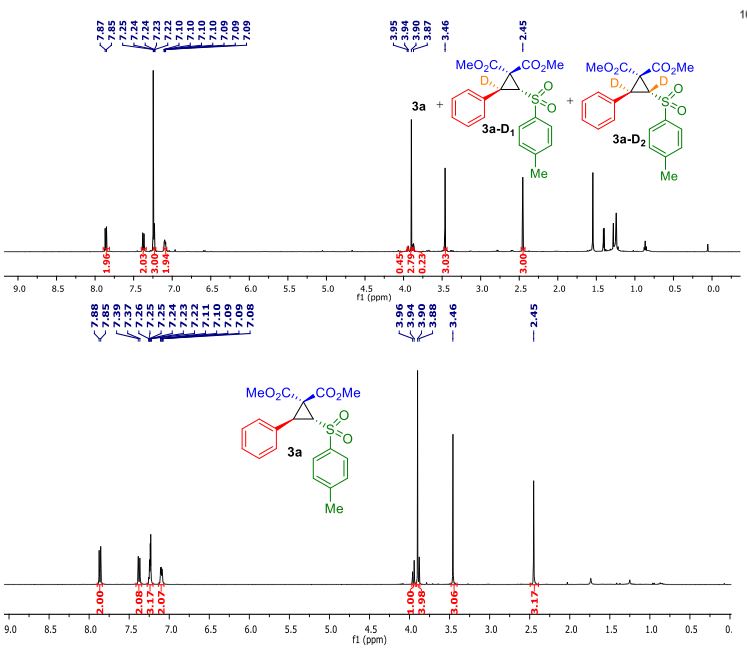


**Figure S4a:** Comparison with $^1$H NMR of **3a**

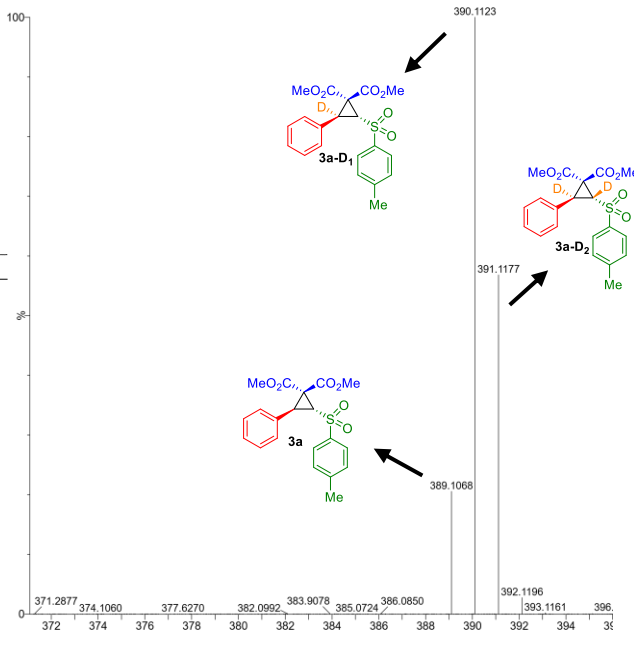


**Figure S4b:** HRMS analysis

This above deuterium labelled experiments confirms that both MeOH and trace amount $H_2O$ in the solvent are involved in the protonation step.

**10. Quantum yield measurement:**[5] To determine the photon flux of 40W-456 nm blue LED, we have followed a previously reported protocol by Yoon and co-workers. All the solutions required for ferrioxalate actinometric measurement were prepared and stored in the dark, as much as possible, away from the ambient light. The potassium ferrioxalate trihydrate, $[K_3Fe^{III}(C_2O_4)_3]\cdot 3H_2O$ ((CAS: 5936-11-8), Purity: >98.0%) was prepared following standard procedure and recrystallized in deionized water, 1,10-phenanthroline ($C_{12}H_8N_2$, (CAS: 5144-89-8), Purity: >99.0%) was recrystallized from benzene.

**Preparation of stock solution:** Potassium ferrioxalate ($[K_3Fe^{III}(C_2O_4)_3]\cdot 3H_2O$) of 1.11 g (2.26 mmol) was dissolved in 0.05 M $H_2SO_4$ (in fresh deionized water) to get a final volume of 15.0 mL with the concentration of 0.15 M with respect to potassium ferrioxalate. 2.25 gm of sodium acetate was dissolved in 0.5 M $H_2SO_4$ to get a buffer solution, and then 10.0 mg of 1,10-phenanthroline was added to get a total of 15.0 mL of buffered 1,10-phenanthroline solution. Both stock solutions were kept in the dark by rapping the volumetric fluxes with aluminum foil.

**Determination of background $Fe^{2+}$ concentration:** In a 4.0 mL clear glass vial, 2.0 mL of 0.15 M potassium ferrioxalate solution and 0.350 mL of 1,10-phenanthroline solution were added, and the mixture was kept in the dark for 1 h. Then the respective solution was transferred to a 3.0 mL cuvette, and a UV-Vis spectrum (400 nm to 600 nm) was recorded using BioTek EPOCH 2 UV-vis absorption spectrometer. The absorbance at 510 nm was measured. This process was repeated twice, and the average absorbance value was calculated.

Average value: 0.598

**Determination of photon flux:** In a 4.0 mL clear glass vial, 2.0 mL of 0.15 M potassium ferrioxalate solution was added, and the vial was irradiated with 40 W-456nm blue LED at a 5 cm distance for 10 seconds. After 10 seconds, the vial was removed from the light, and 0.350 mL 1,10-phenanthroline solution was added to it, then the mixture was kept in the dark. After 1 h, the solution was transferred into a 3.0 mL cuvette, and the UV-Vis spectrum was recorded (400 nm to 600 nm). The absorbance at 510 nm was measured. This process was repeated twice, and the average absorbance value was calculated.

Average value: 1.344

**Calculations:**

The amount of $Fe^{2+}$ formed has been calculated using the following equation

$$mol\ \ of\ \ Fe^{2+} = \frac{\mathrm{V} \times \Delta\mathrm{A}}{\mathrm{l} \times \epsilon}$$

$$mol\ \ of\ \ Fe^{2+} = \frac{\mathrm{V} \times \Delta\mathrm{A}}{\mathrm{l} \times \epsilon} = \frac{(0.00235\mathrm{L}) \times (0.746)}{(1.00\ \ \mathrm{cm}) \times (\frac{11100\ \ \mathrm{L}}{\mathrm{mol}\cdot\mathrm{cm}})} = 1.58 \times 10^{-7} mol$$

Where V is the volume of the respective sample solution analyzed (2.35 mL), ΔA is the difference between the average absorbance of irradiated and nonirradiated ferrioxalate solutions at 510 nm, l is the pathlength, and the $\epsilon$ is the molar absorptivity at 510 nm.

The following equation has calculated the fraction of light absorbed by the ferrioxalate actinometer

$$\mathrm{f} = 1 - 10^{-A}$$

A is the measured absorbance of the ferrioxalate actinometer solution at 456 nm before blue LED irradiation without 1,10-phenanthroline.

$$\mathrm{f} = 1 - 10^{-A} = 1 - 10^{-1.25} = 0.94$$

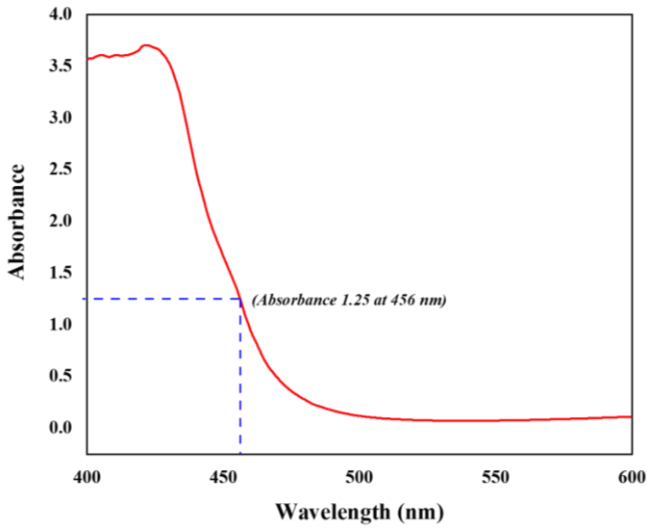
The photon flux has been calculated using the following equation

$$\text{photon flux} = \frac{mol\ \ of\ \ Fe^{2+}}{\Phi \times t \times \text{f}}$$

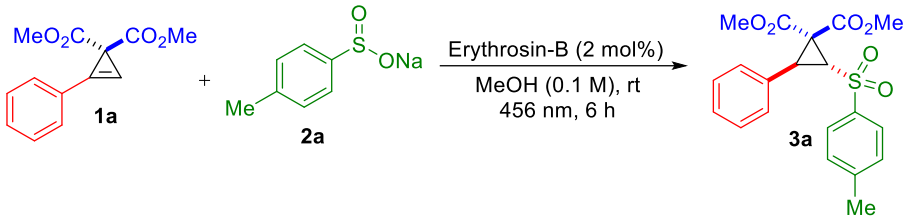
Where Φ is the quantum yield for the ferrioxalate actinometer at 456 nm, $t$ is the irradiation time and f is the fraction of light absorbed by the ferrioxalate actinometer solution.

$$\text{photon flux} = \frac{mol\ \ of\ \ Fe^{2+}}{\Phi \times t \times \text{f}} = \frac{1.58 \times 10^{-7} mol}{(0.92) \times (10\ \ \text{s}) \times (0.94)} = 1.8 \times 10^{-8}\ \ \text{einstine.s}^{-1}$$

**Determination of the fraction of light absorbed at 468 nm by the ferrioxalate solution:** The absorbance of the ferrioxalate actinometer solution at 456 nm before blue LED irradiation, without 1,10-phenanthroline, was measured at 1.25.




**Determination of the quantum yield:**




To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar, **1a** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol, 2.5 equiv.), and Erythrosin-B (0.004 mmol, 0.02 eq.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and then backfilled with nitrogen, and this cycle was repeated another four times. A rubber septum was tightly put on the top of the reaction tube, with continuous nitrogen flow. Freshly dried 2 mL of MeOH was added using a syringe. Then the reaction tube was placed on a magnetic stirrer and irradiated using a Kessil 40 W, 456 nm blue LED, keeping at ~5 cm distance between them. A cooling fan was fitted approximately 30 cm away to maintain the room temperature. After 6 h of the reaction, 10 mL of water was added and extracted with EtOAc (3×20 mL). The combined organic layer was dried over $Na_2SO_4$, and the solvent was removed under reduced pressure. Then the crude product was dissolved in $CDCl_3$, 0.4 mmol 1,1,2,2-tetrachloroethane was added as $^1$H NMR standard and crude $^1$H NMR yield was measured. The yield of the desired product **3a** is 61% with respect to the $^1$H NMR standard.

The quantum yield (Φ) has been calculated using the equation

$$\Phi = \frac{\text{mol product}}{\text{flux} \times \text{t} \times \text{f}}$$

Where $t$ is the reaction time, and f is the previously calculated fraction of light absorbed by the solution.

$$\Phi = \frac{\text{mol product}}{\text{flux} \times \text{t} \times \text{f}} = \frac{0.2 \times 0.61\ \ \times 10^{-3}}{(1.8 \times 10^{-8}\ \ \text{einstine.s}^{-1}) \times (21600\ \ \text{s}) \times (0.94)} = 0.33$$

The above results confirm the reaction, not the chain reaction.

**References:**

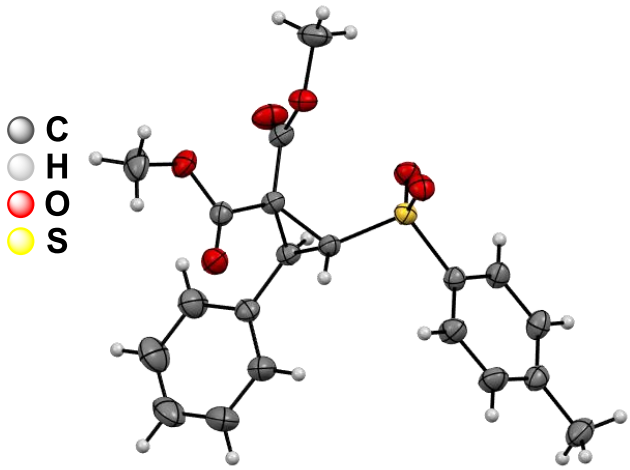

1. Muriel, B.; Waser, J. *Angew. Chem. Int. Ed.* **2021**, *60* (8), 4075–4079. https://doi.org/10.1002/anie.202013516.
2. Yang, Z.; Zhou, B.; Xu, J. *Synthesis* **2013**, *46* (02), 225–229. https://doi.org/10.1055/s-0033-1338567.
3. Skillinghaug, B.; Sköld, C.; Rydfjord, J.; Svensson, F.; Behrends, M.; Sävmarker, J.; Sjöberg, P. J. R.; Larhed, M. *J. Org. Chem.* **2014**, *79* (24), 12018–12032. https://doi.org/10.1021/jo501875n.
4. Long, T.; Pan, S.; Zhu, S.; Chu, L. *Chem. Eur. J.* **2022**, *28*, e20210408. https://doi.org/10.1002/chem.202104080.
5. Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426-5434

## 11. X-ray crystallography data

### X-ray crystallographic data of compound 3a with 50% ellipsoid contour probability:

**Table 1 Crystal data and structure refinement for Compound 3a.**

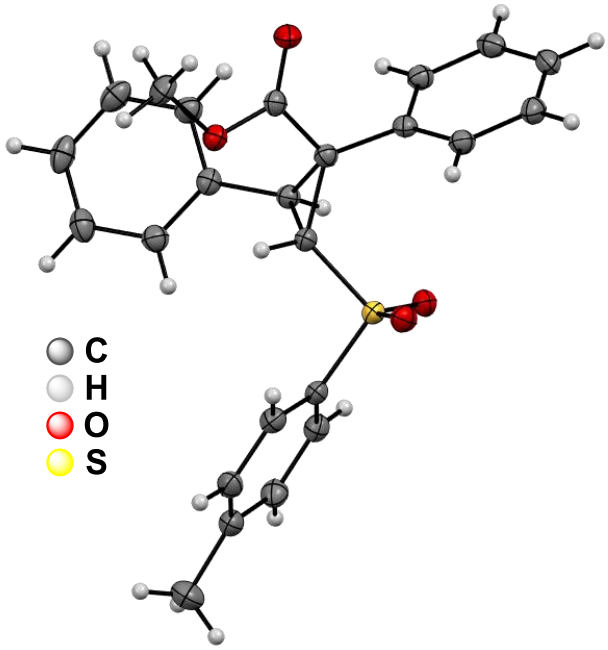
| | |
|---|---|
| Identification code | Compound **3a** |
| CCDC Number | 2285742 |
| Empirical formula | $C_{20}H_{20}O_6S$ |
| Formula weight | 388.42 |
| Temperature/K | 293(2) |
| Crystal system | orthorhombic |
| Space group | Pbcn |
| a/Å | 13.84590(10) |
| b/Å | 10.37070(10) |
| c/Å | 26.6399(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 3825.27(6) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.349 |
| μ/mm$^{-1}$ | 1.800 |
| F(000) | 1632.0 |
| Crystal size/mm$^3$ | 0.3 × 0.2 × 0.2 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.636 to 136.33 |
| Index ranges | $-11 \le h \le 16$, $-12 \le k \le 12$, $-32 \le l \le 32$ |
| Reflections collected | 21551 |
| Independent reflections | 3480 [$R_{int}$ = 0.0389, $R_{sigma}$ = 0.0237] |
| Data/restraints/parameters | 3480/0/247 |
| Goodness-of-fit on F$^2$ | 1.073 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0382, $wR_2$ = 0.1069 |
| Final R indexes [all data] | $R_1$ = 0.0432, $wR_2$ = 0.1114 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.35 |



## X-ray crystallographic data of compound 3e with 50% ellipsoid contour probability:

**Table 1 Crystal data and structure refinement for Compound 3e.**

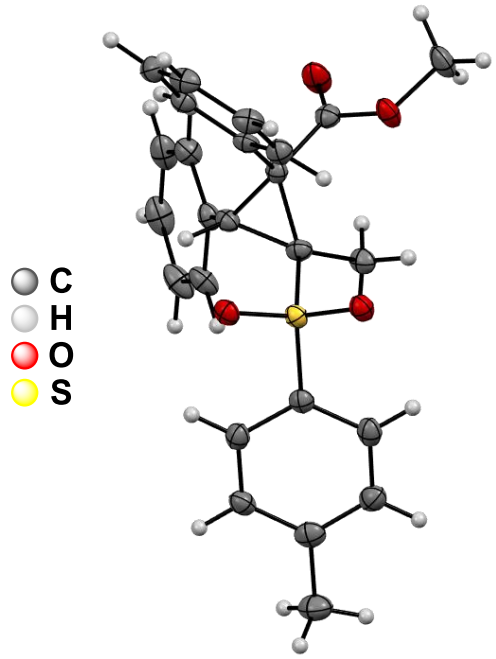
| | |
|---|---|
| Identification code | Compound **3e** |
| CCDC number | 2285745 |
| Empirical formula | $C_{24}H_{25}O_4S$ |
| Formula weight | 384.55 |
| Temperature/K | 100(5) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 12.50680(10) |
| b/Å | 10.94440(10) |
| c/Å | 15.01980(10) |
| α/° | 90 |
| β/° | 99.8670(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 2025.49(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.261 |
| μ/mm$^{-1}$ | 1.648 |
| F(000) | 769.0 |
| Crystal size/mm$^3$ | 0.3 × 0.2 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.516 to 136.316 |
| Index ranges | $-11 \le h \le 15$, $-13 \le k \le 13$, $-18 \le l \le 17$ |
| Reflections collected | 20242 |
| Independent reflections | 3664 [$R_{int}$ = 0.0521, $R_{sigma}$ = 0.0256] |
| Data/restraints/parameters | 3664/0/265 |
| Goodness-of-fit on F$^2$ | 1.054 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0331, $wR_2$ = 0.0907 |
| Final R indexes [all data] | $R_1$ = 0.0344, $wR_2$ = 0.0919 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.45/-0.35 |



## X-ray crystallographic data of compound 3u-1 with 50% ellipsoid contour probability:

**Table 1 Crystal data and structure refinement for Compound 3u-1.**

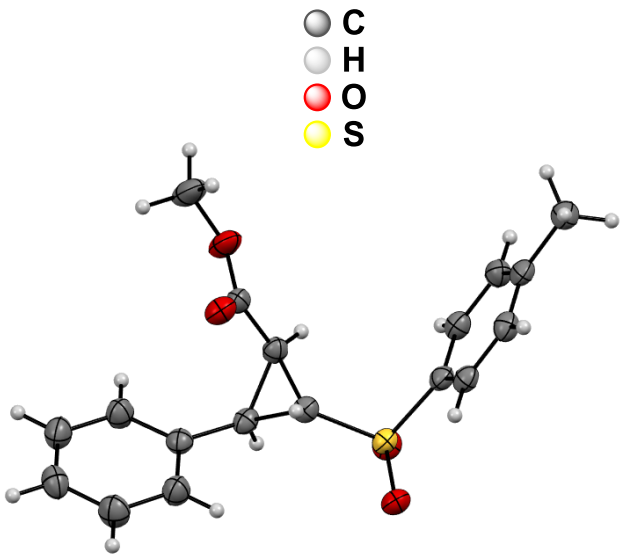
| | |
|---|---|
| Identification code | Compound **3u-1** |
| CCDC number | 2285744 |
| Empirical formula | $C_{25}H_{24}O_4S$ |
| Formula weight | 420.50 |
| Temperature/K | 100.00(13) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.6633(5) |
| b/Å | 10.4825(5) |
| c/Å | 11.2824(7) |
| α/° | 84.233(4) |
| β/° | 68.850(5) |
| γ/° | 83.784(4) |
| Volume/Å$^3$ | 1057.28(11) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.321 |
| μ/mm$^{-1}$ | 1.598 |
| F(000) | 444.0 |
| Crystal size/mm$^3$ | 0.6 × 0.1 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.422 to 136.4 |
| Index ranges | -11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -13 ≤ l ≤ 13 |
| Reflections collected | 11810 |
| Independent reflections | 3800 [$R_{int}$ = 0.0564, $R_{sigma}$ = 0.0421] |
| Data/restraints/parameters | 3800/0/275 |
| Goodness-of-fit on F$^2$ | 1.104 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0784, $wR_2$ = 0.2295 |
| Final R indexes [all data] | $R_1$ = 0.0807, $wR_2$ = 0.2302 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.95/-0.44 |



## X-ray crystallographic data of compound 3aa with 50% ellipsoid contour probability:

**Table 1 Crystal data and structure refinement for Compound 3aa.**

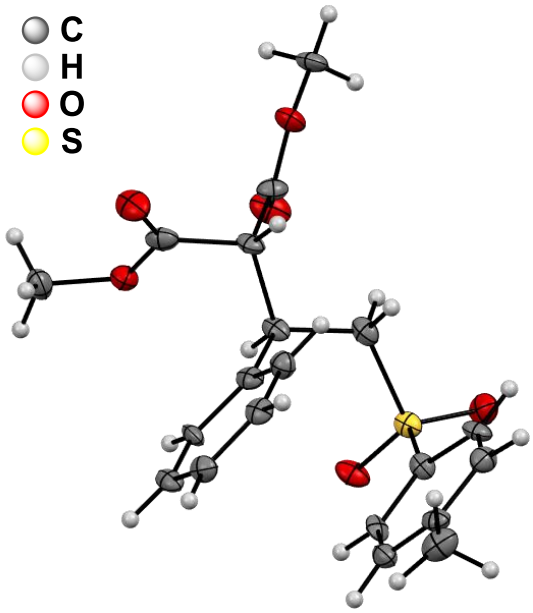
| | |
|---|---|
| Identification code | Compound **3aa** |
| CCDC number | 2285751 |
| Empirical formula | $C_{36}H_{36}O_8S_2$ |
| Formula weight | 660.77 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 19.6119(2) |
| b/Å | 16.7818(2) |
| c/Å | 10.16150(10) |
| α/° | 90 |
| β/° | 92.9420(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 3339.98(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.314 |
| μ/mm$^{-1}$ | 1.872 |
| F(000) | 1392.0 |
| Crystal size/mm$^3$ | 0.5 × 0.2 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 4.512 to 136.306 |
| Index ranges | $-22 \le h \le 23$, $-20 \le k \le 12$, $-11 \le l \le 12$ |
| Reflections collected | 21443 |
| Independent reflections | 5962 [$R_{int}$ = 0.0461, $R_{sigma}$ = 0.0278] |
| Data/restraints/parameters | 5962/0/419 |
| Goodness-of-fit on $F^2$ | 1.132 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0589, $wR_2$ = 0.1577 |
| Final R indexes [all data] | $R_1$ = 0.0709, $wR_2$ = 0.1691 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.41/-0.43 |



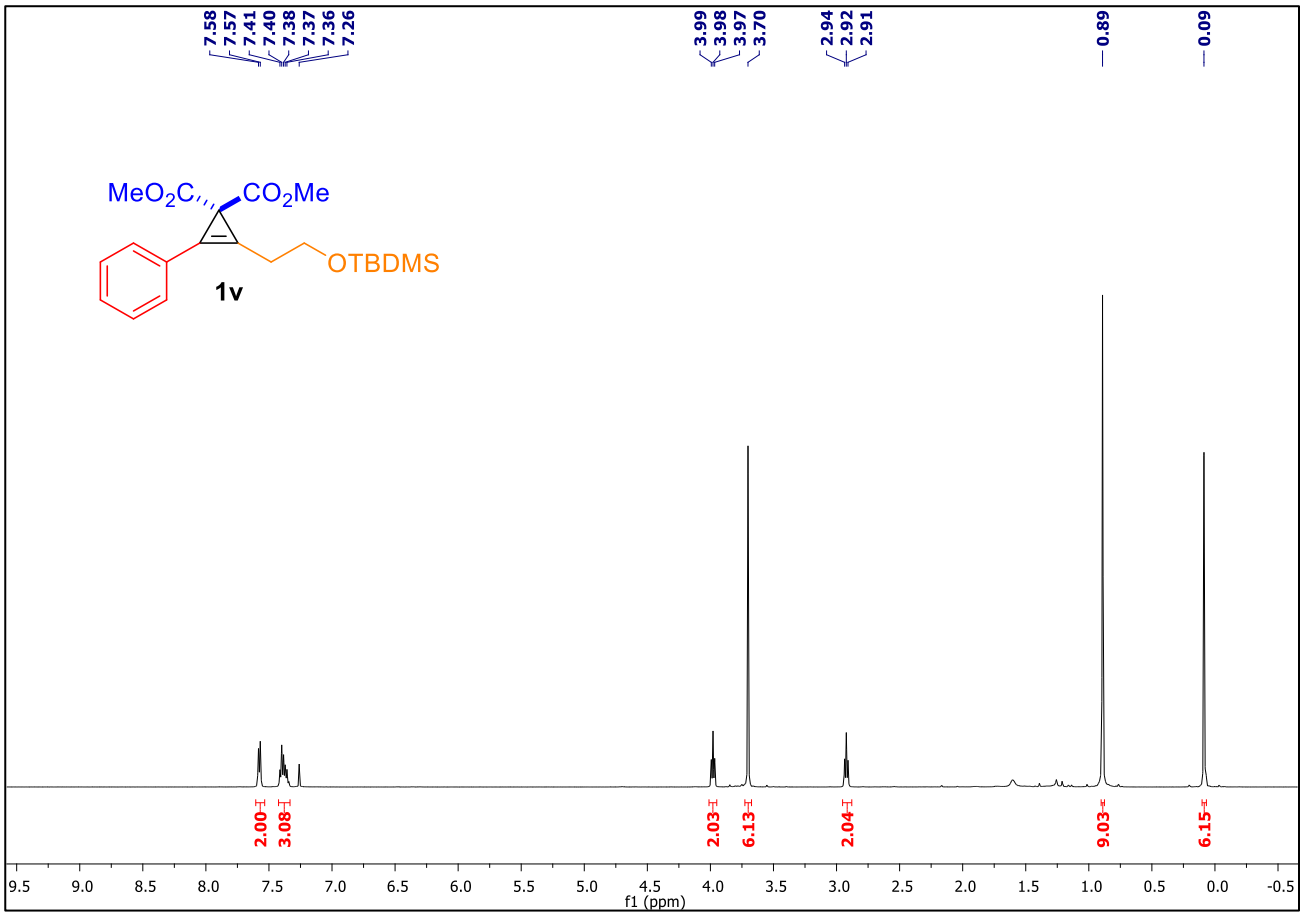
## X-ray crystallographic data of compound 3ab with 50% ellipsoid contour probability:

**Table 1 Crystal data and structure refinement for Compound 3ab.**

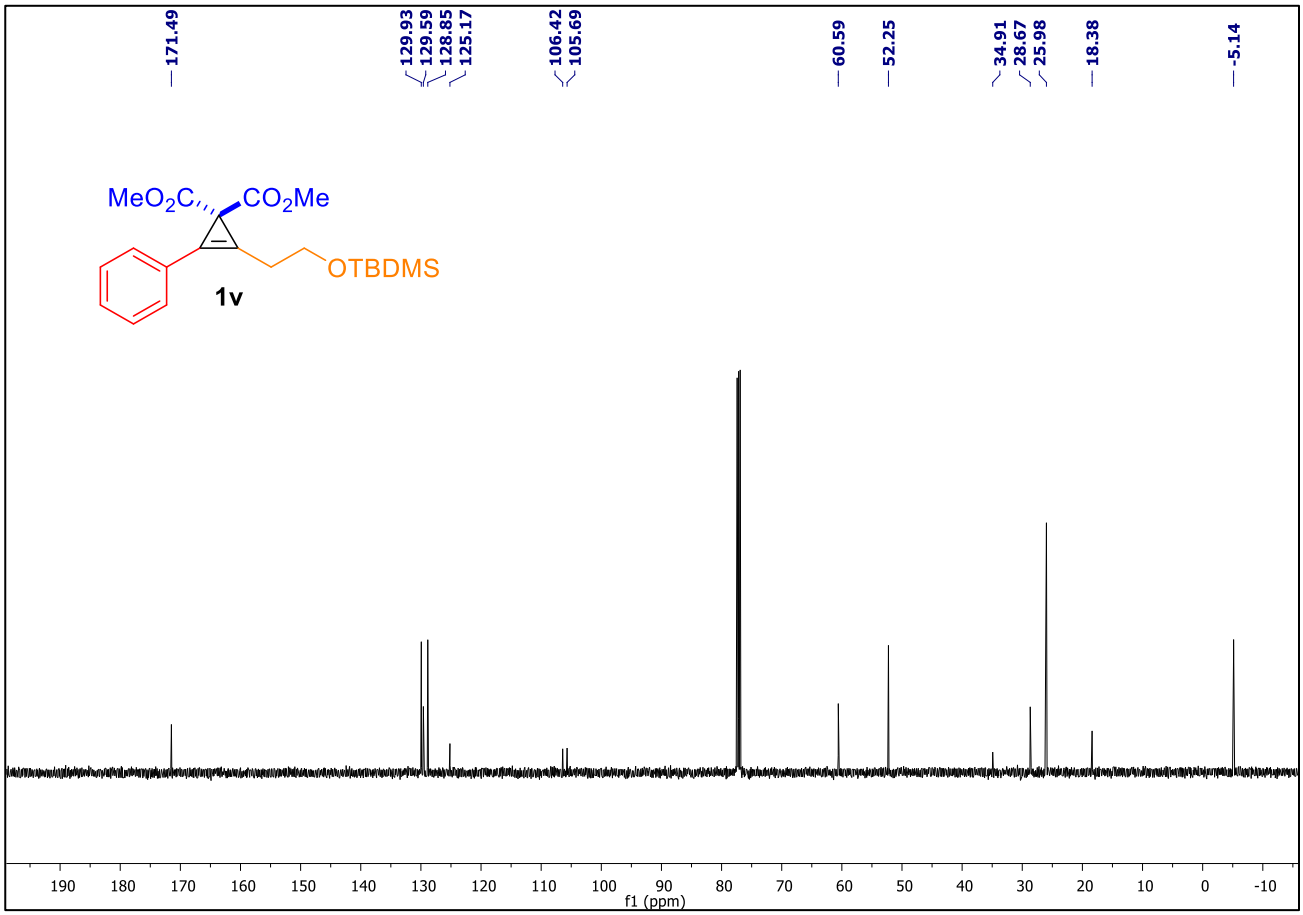
| | |
|---|---|
| Identification code | Compound **3ab** |
| CCDC number | 2285747 |
| Empirical formula | $C_{40}H_{44}O_{12}S_2$ |
| Formula weight | 780.87 |
| Temperature/K | 100(5) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 5.7239(2) |
| b/Å | 16.0544(4) |
| c/Å | 20.5787(7) |
| α/° | 94.727(2) |
| β/° | 94.995(3) |
| γ/° | 90.152(2) |
| Volume/Å$^3$ | 1877.37(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.381 |
| μ/mm$^{-1}$ | 0.207 |
| F(000) | 824.0 |
| Crystal size/mm$^3$ | 0.7 × 0.2 × 0.1 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.988 to 54.262 |
| Index ranges | -7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -25 ≤ l ≤ 25 |
| Reflections collected | 25421 |
| Independent reflections | 7374 [$R_{int}$ = 0.0456, $R_{sigma}$ = 0.0537] |
| Data/restraints/parameters | 7374/0/494 |
| Goodness-of-fit on F$^2$ | 1.103 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1794, $wR_2$ = 0.4517 |
| Final R indexes [all data] | $R_1$ = 0.1966, $wR_2$ = 0.4613 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.31/-0.84 |



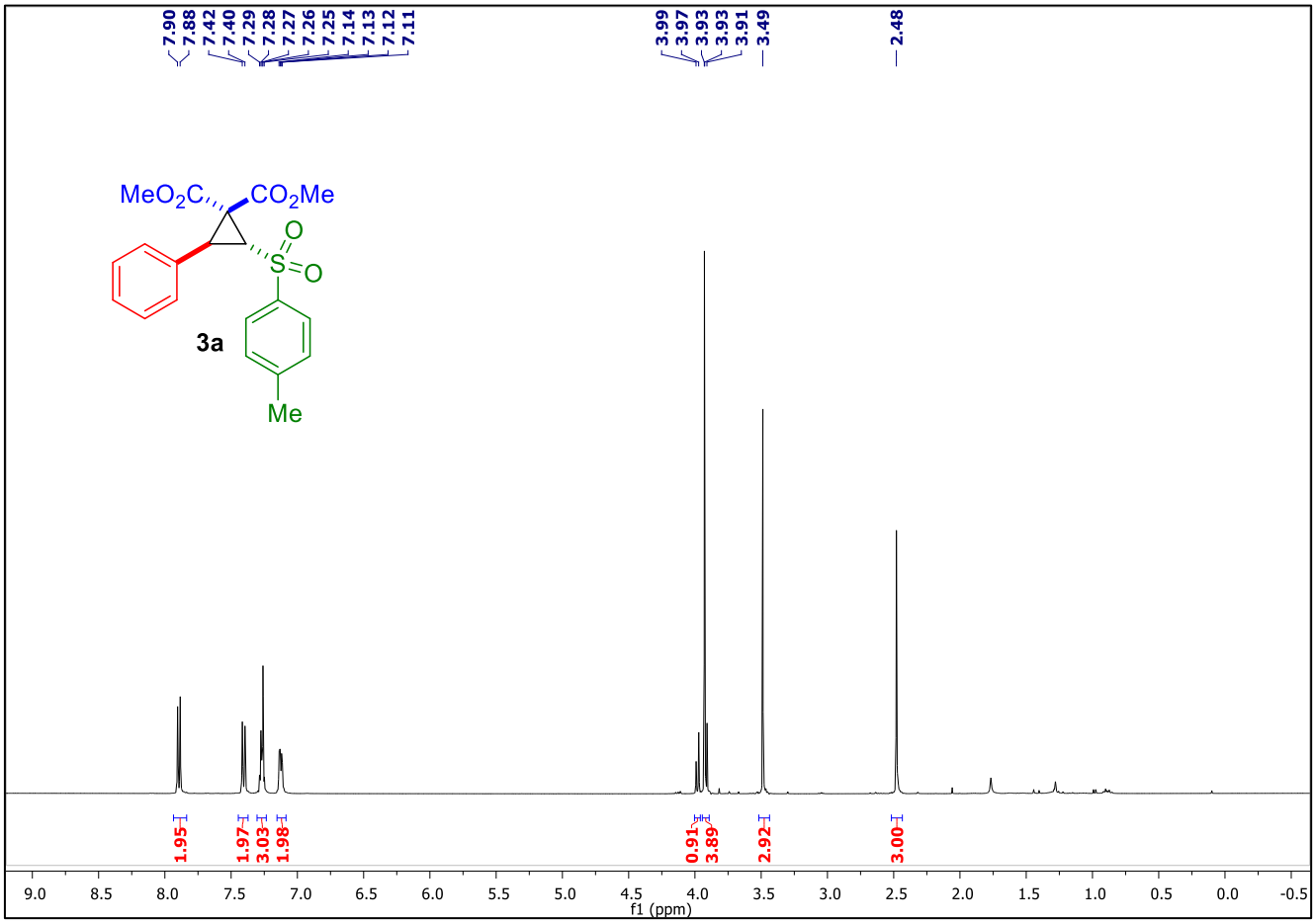
**12. Spectral data of the products:**



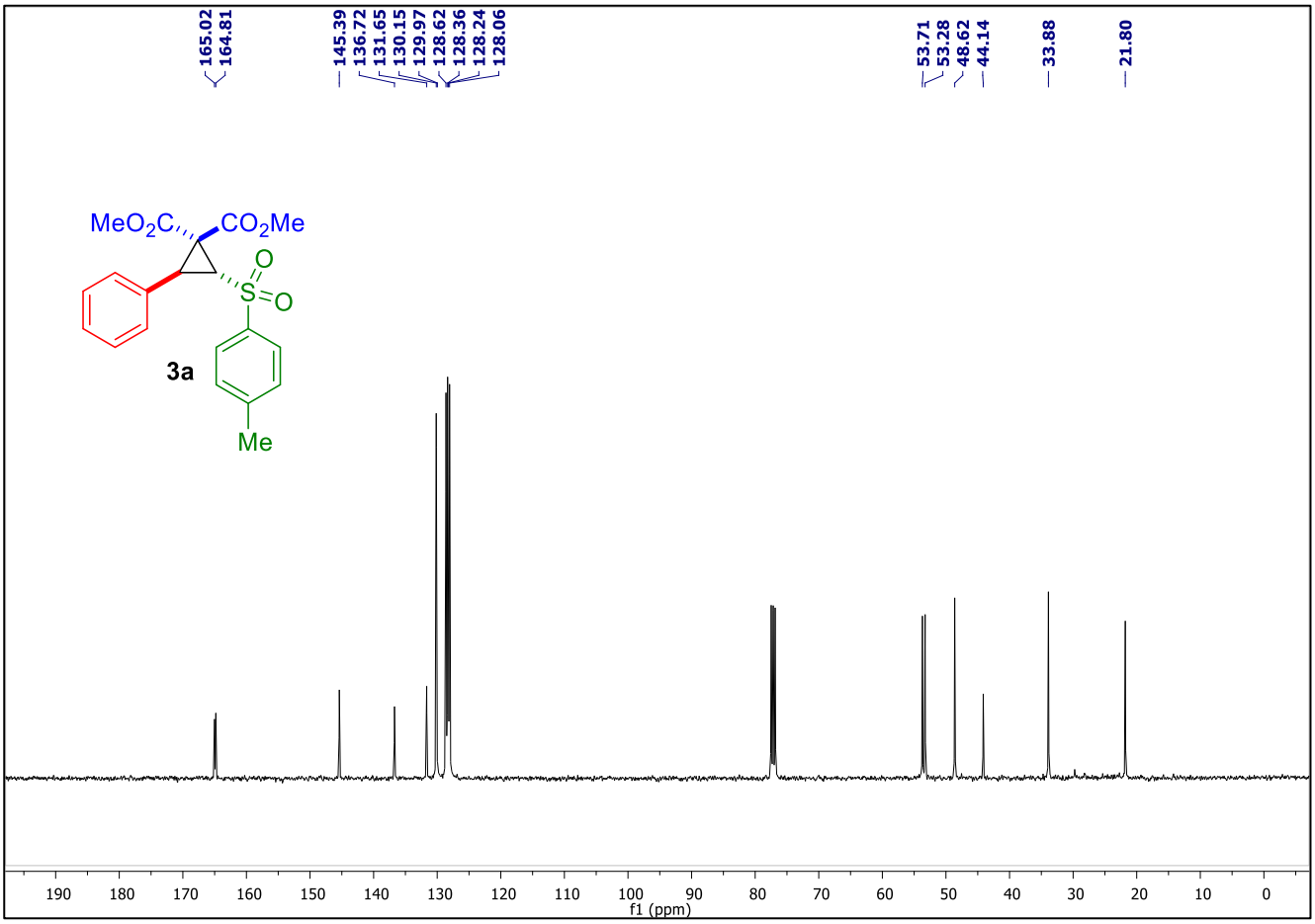

$^{1}$H NMR of Compound **1v** (500 MHz, $CDCl_3$)



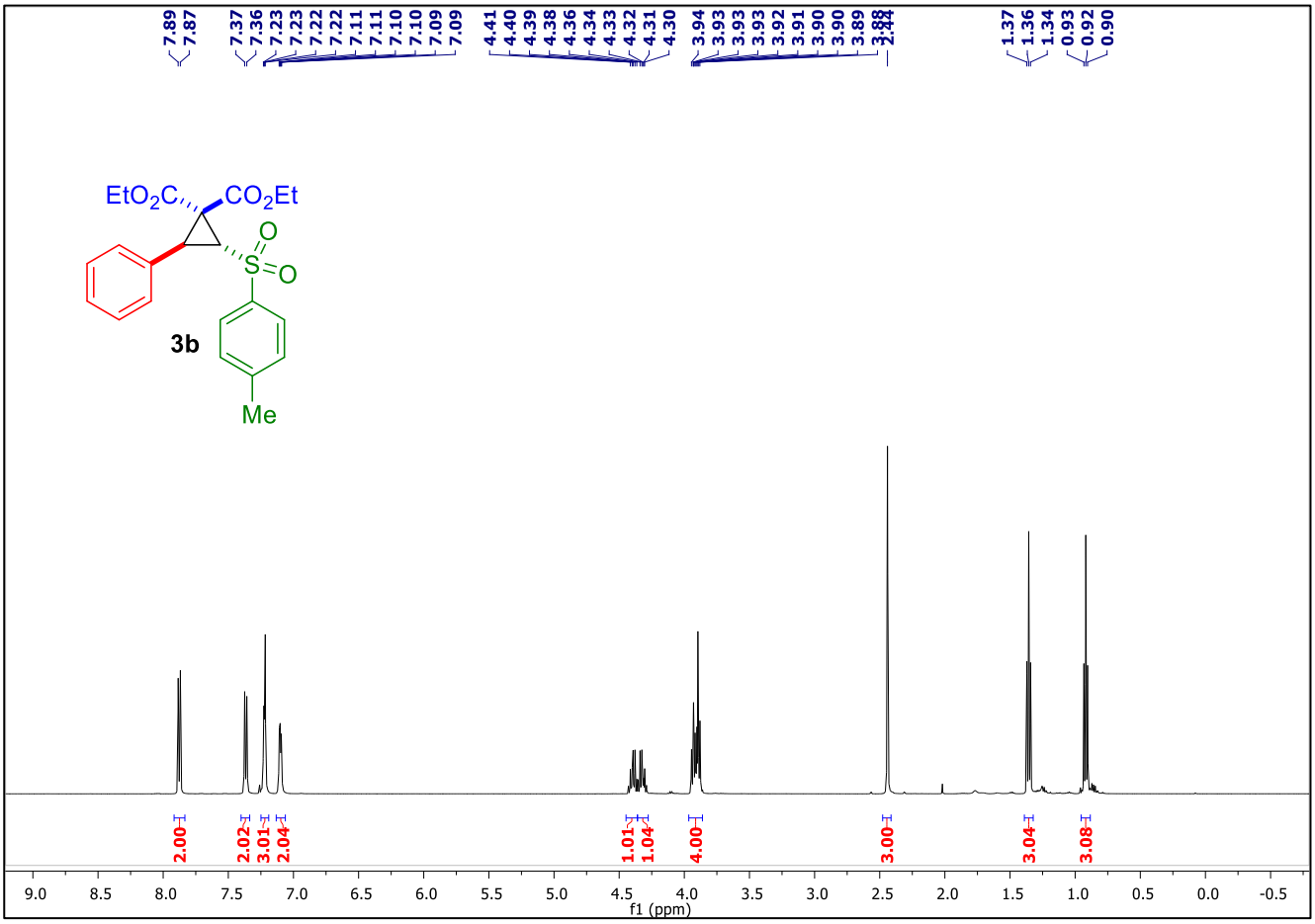

$^{13}$C NMR of Compound **1v** (126 MHz, $CDCl_3$)



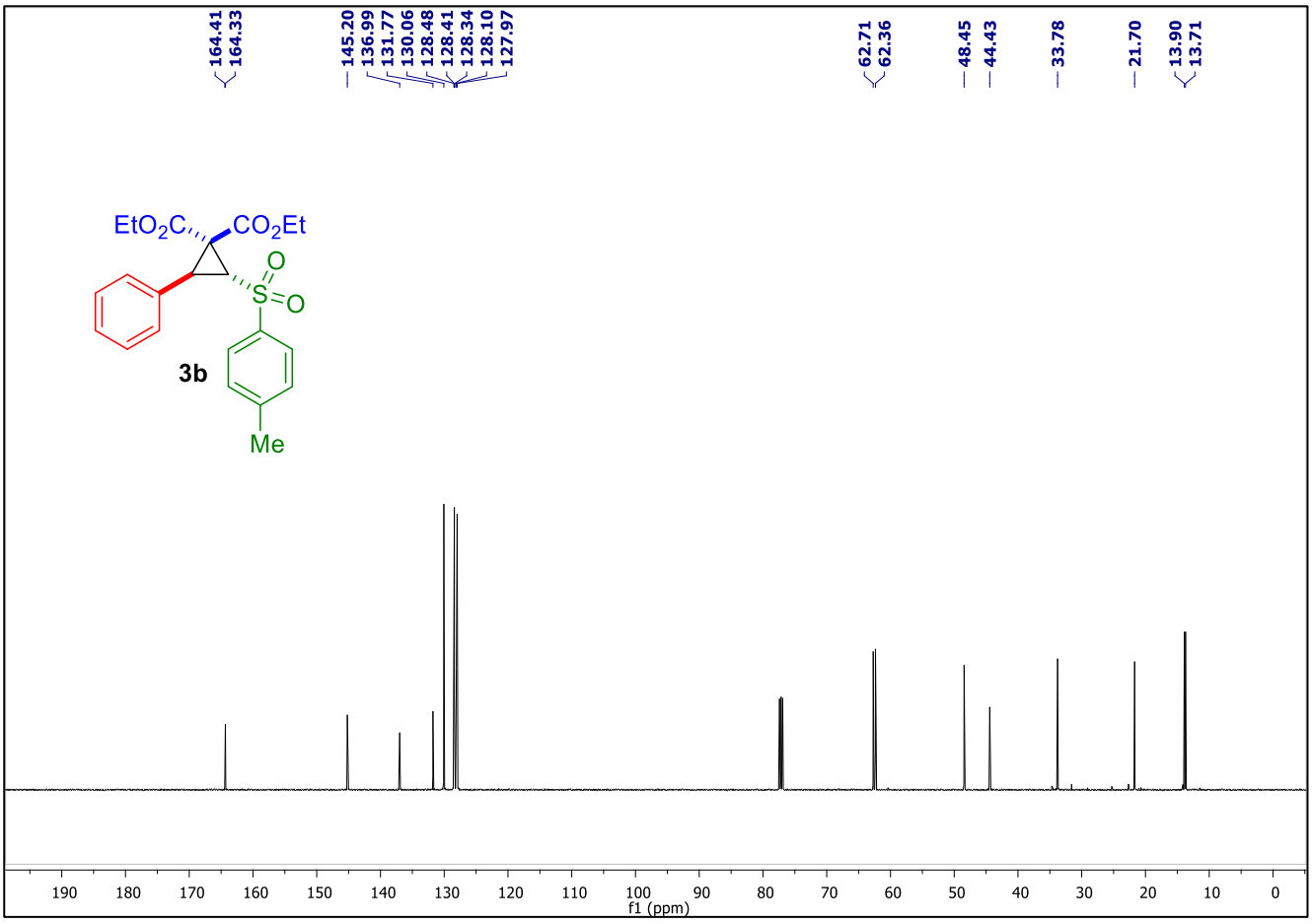

$^{1}$H NMR of Compound **3a** (400 MHz, $CDCl_3$)



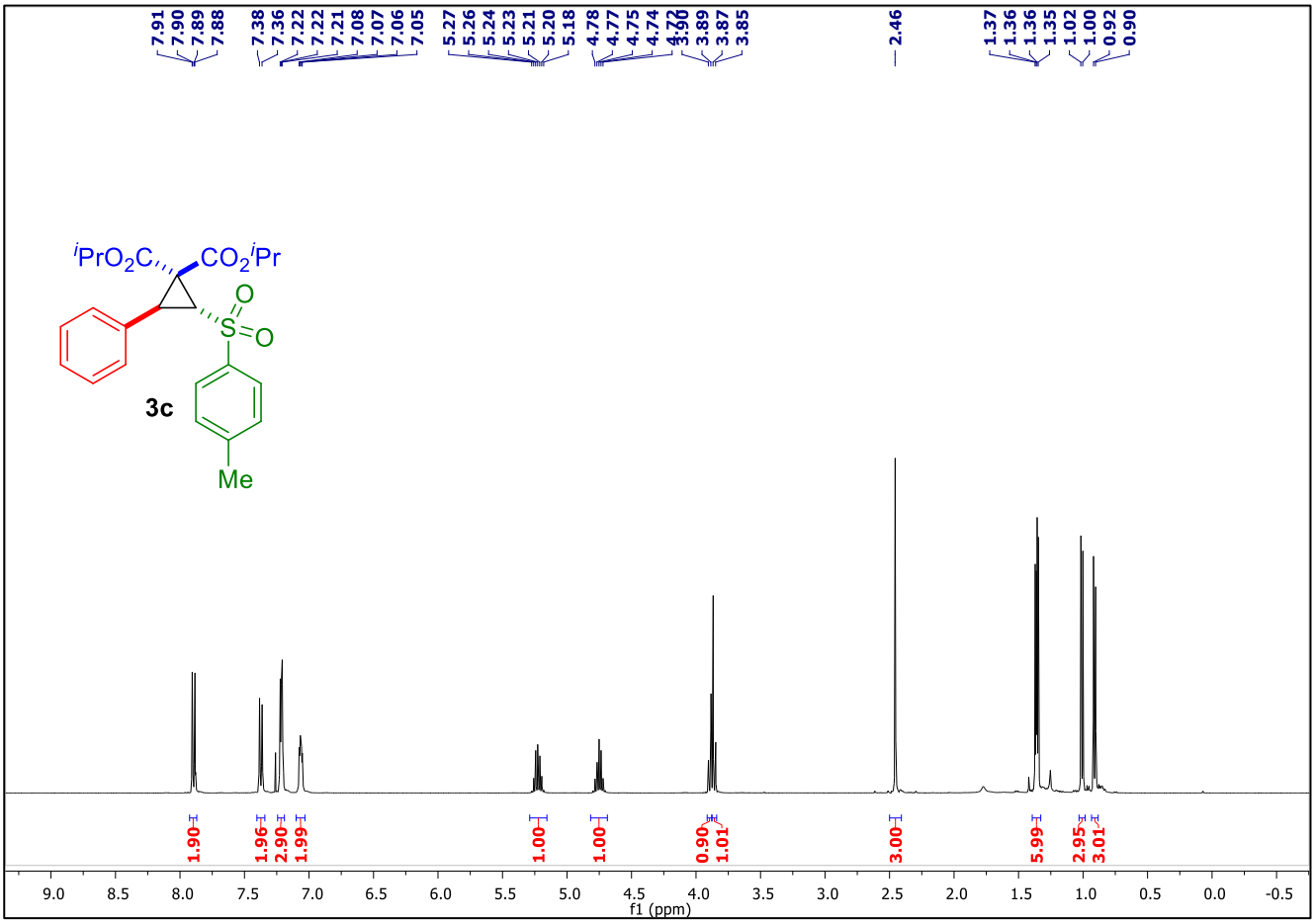

$^{13}$C NMR of Compound **3a** (101 MHz, $CDCl_3$)



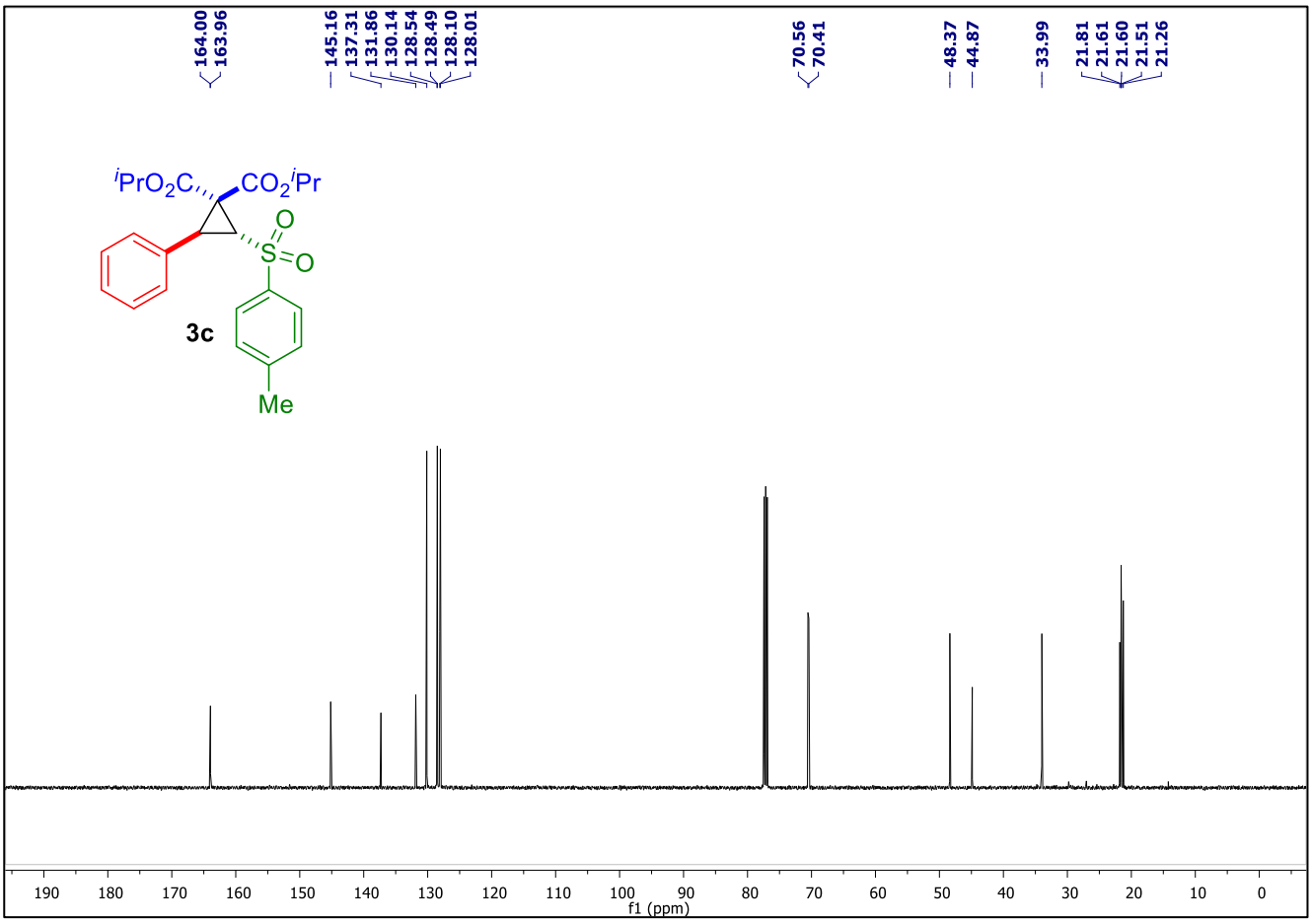

$^{1}$H NMR of Compound **3b** (500 MHz, $CDCl_3$)



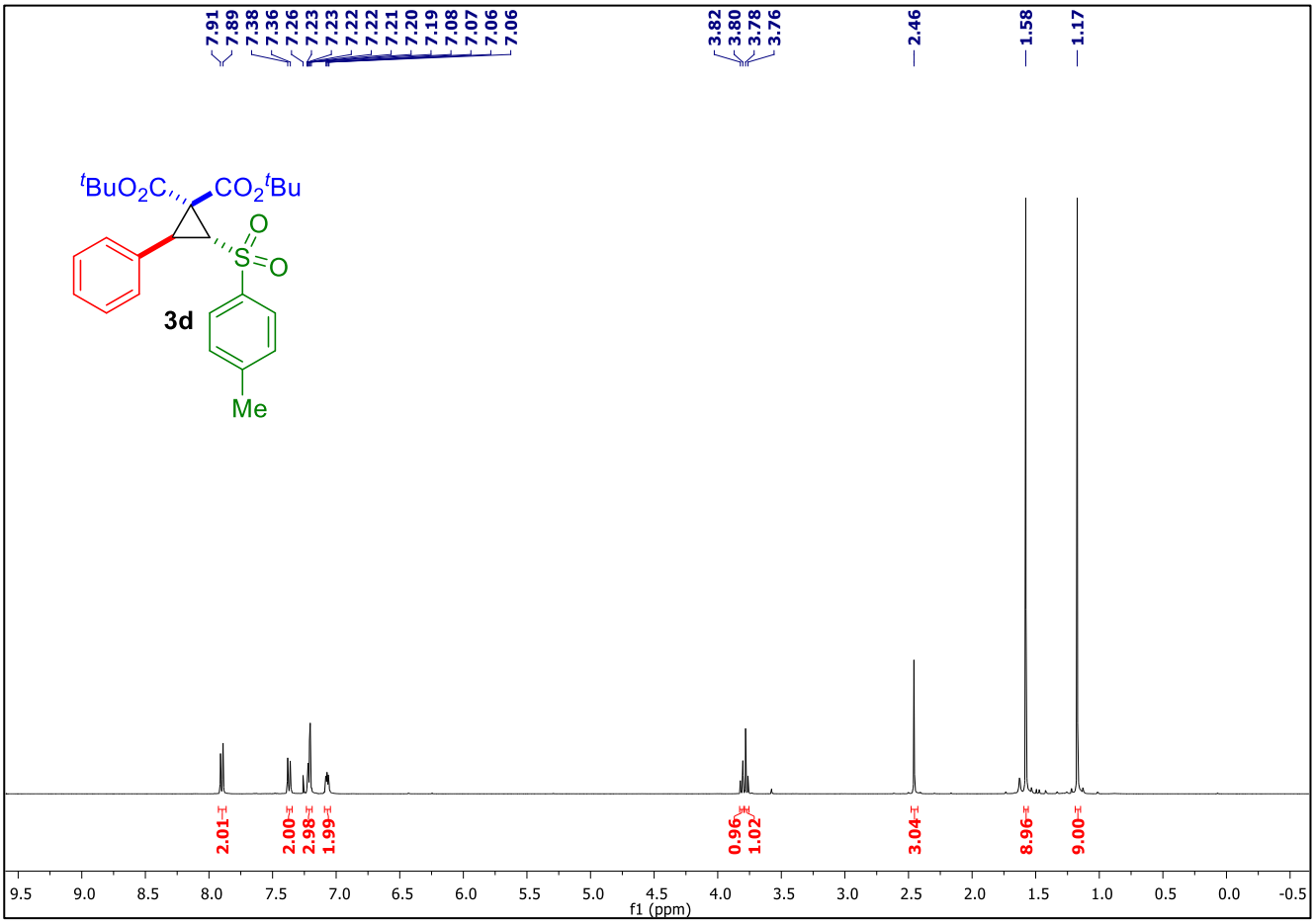

$^{13}$C NMR of Compound **3b** (126 MHz, $CDCl_3$)



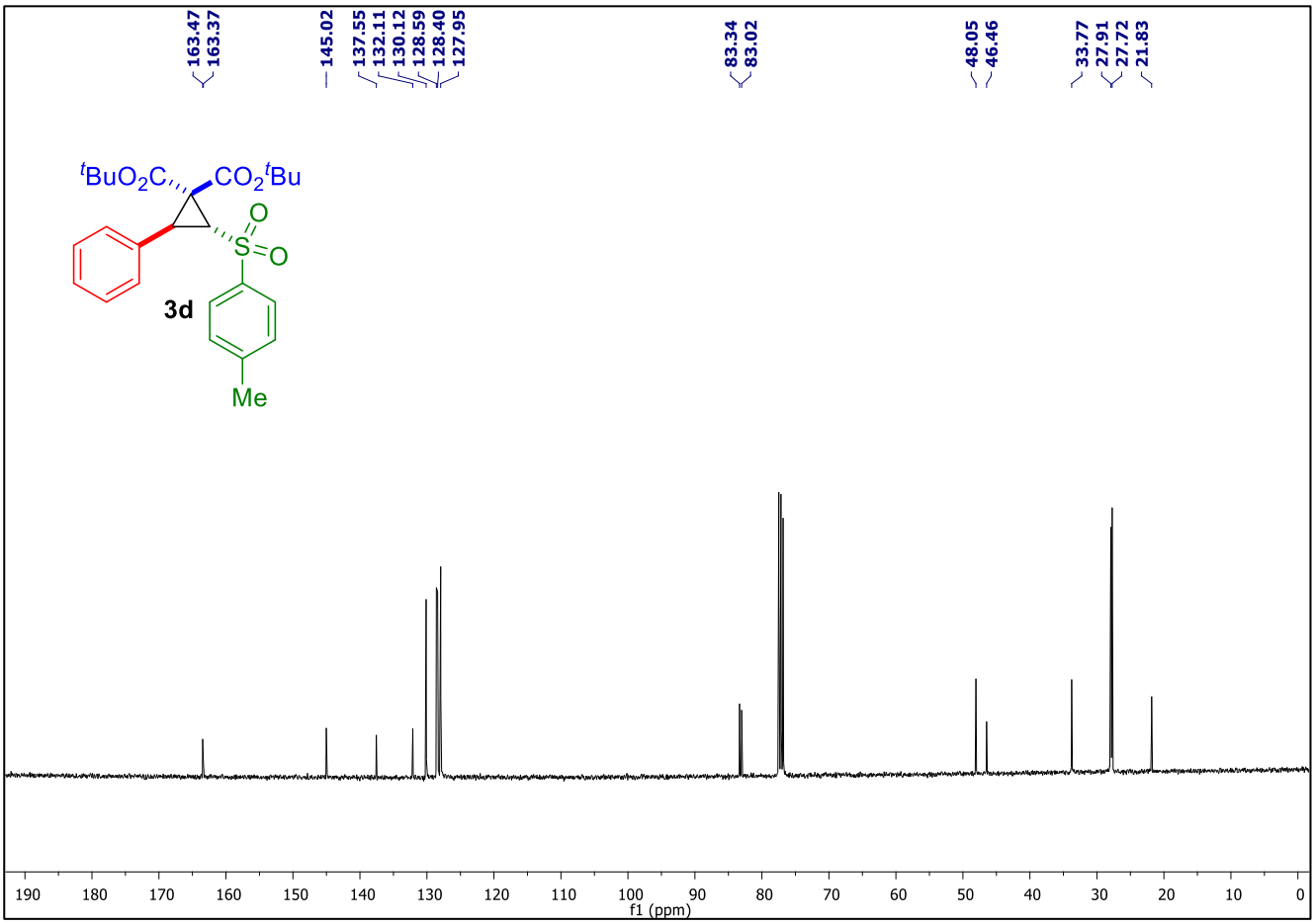

$^{1}$H NMR of Compound **3c** (400 MHz, $CDCl_3$)



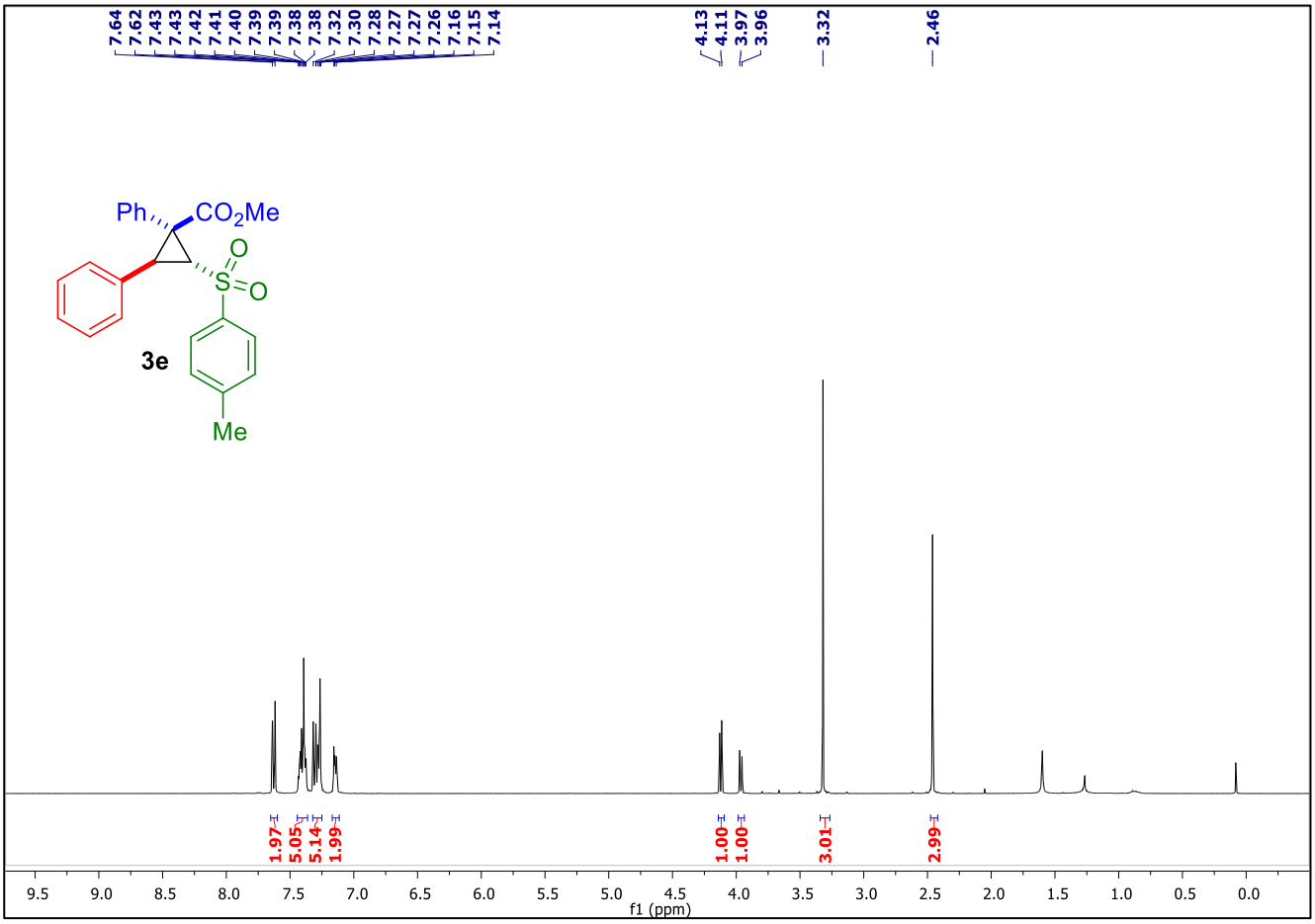

$^{13}$C NMR of Compound **3c** (126 MHz, $CDCl_3$)



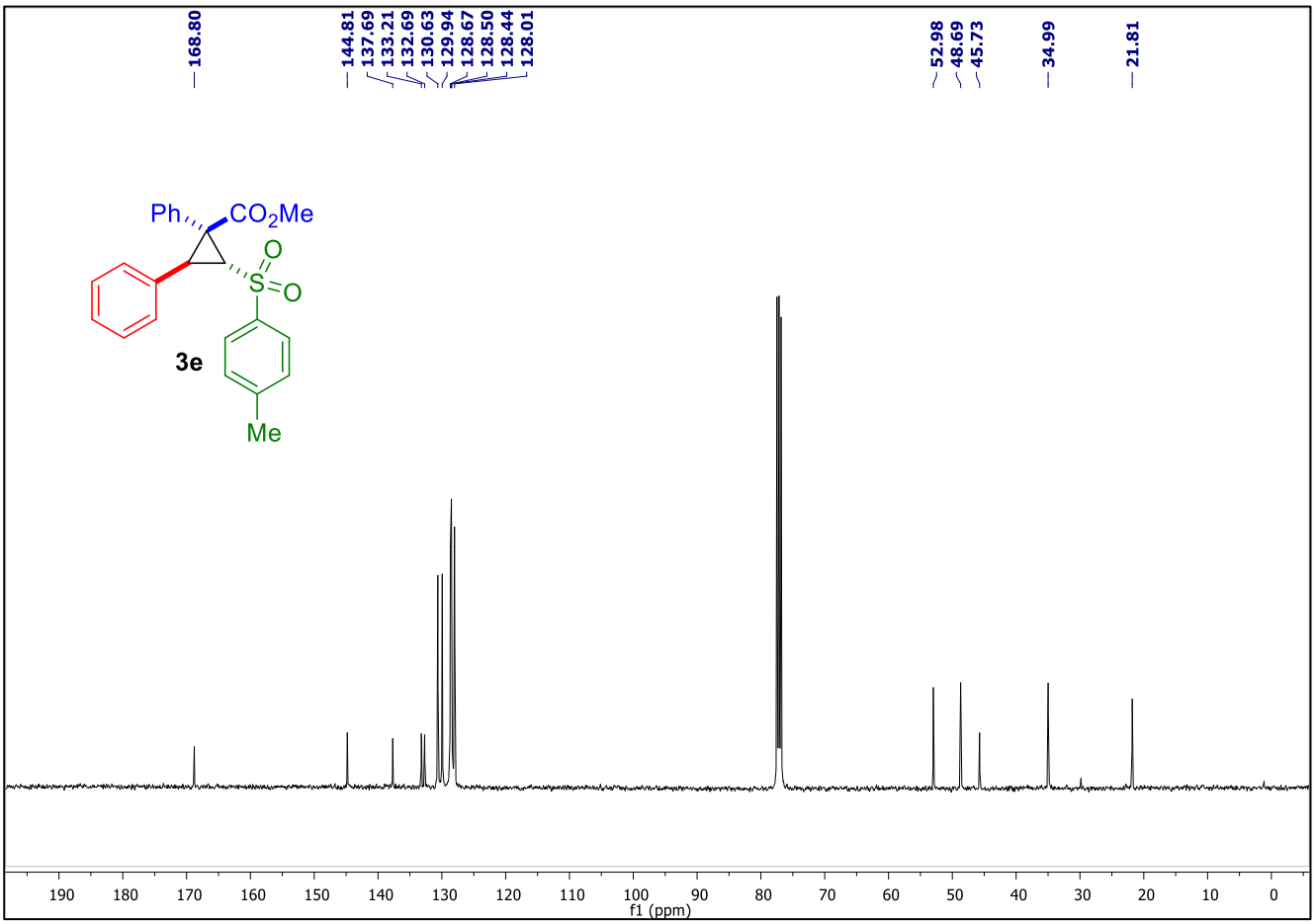

$^{1}$H NMR of Compound **3d** (400 MHz, $CDCl_3$)



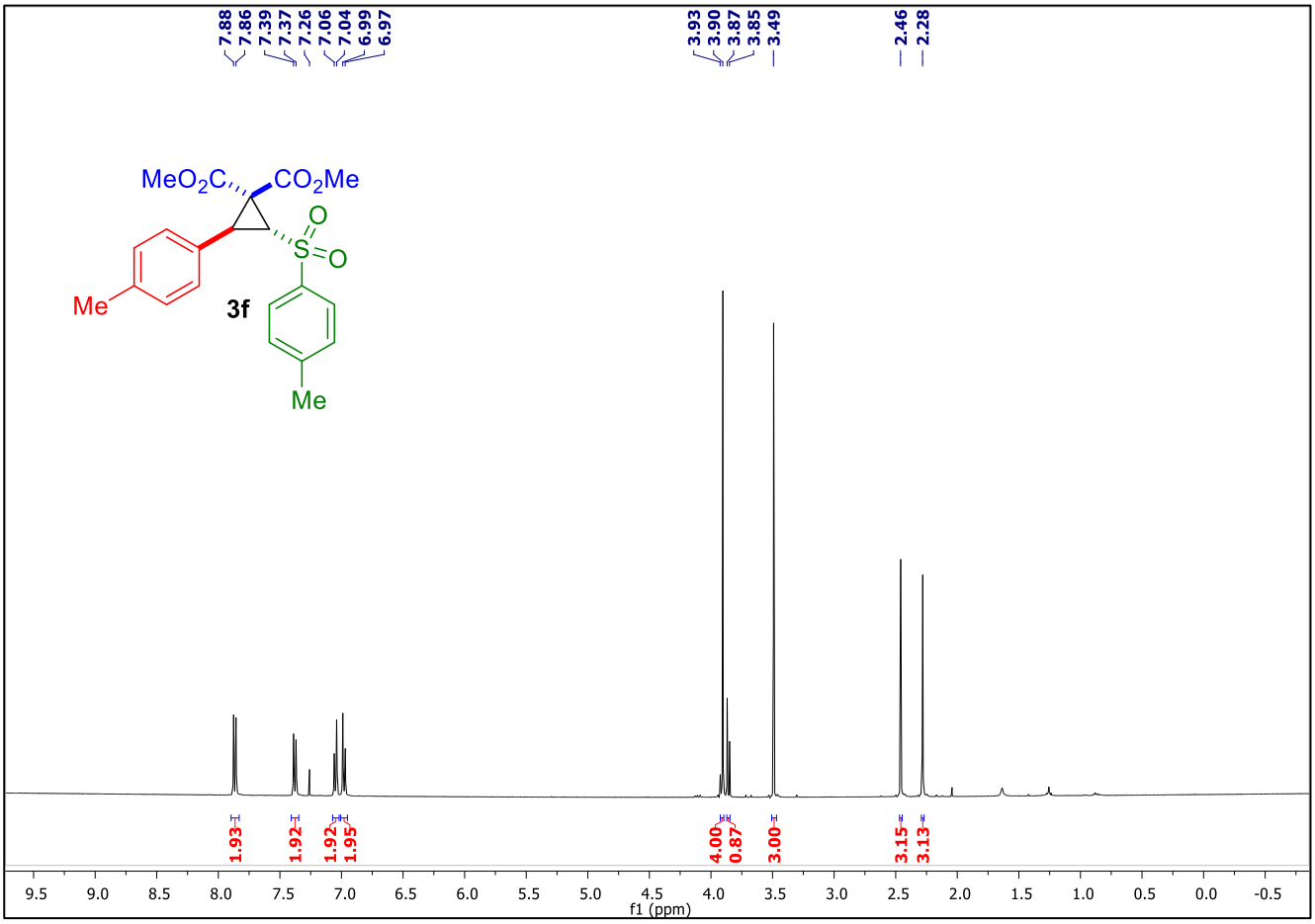

$^{13}$C NMR of Compound **3d** (101 MHz, $CDCl_3$)



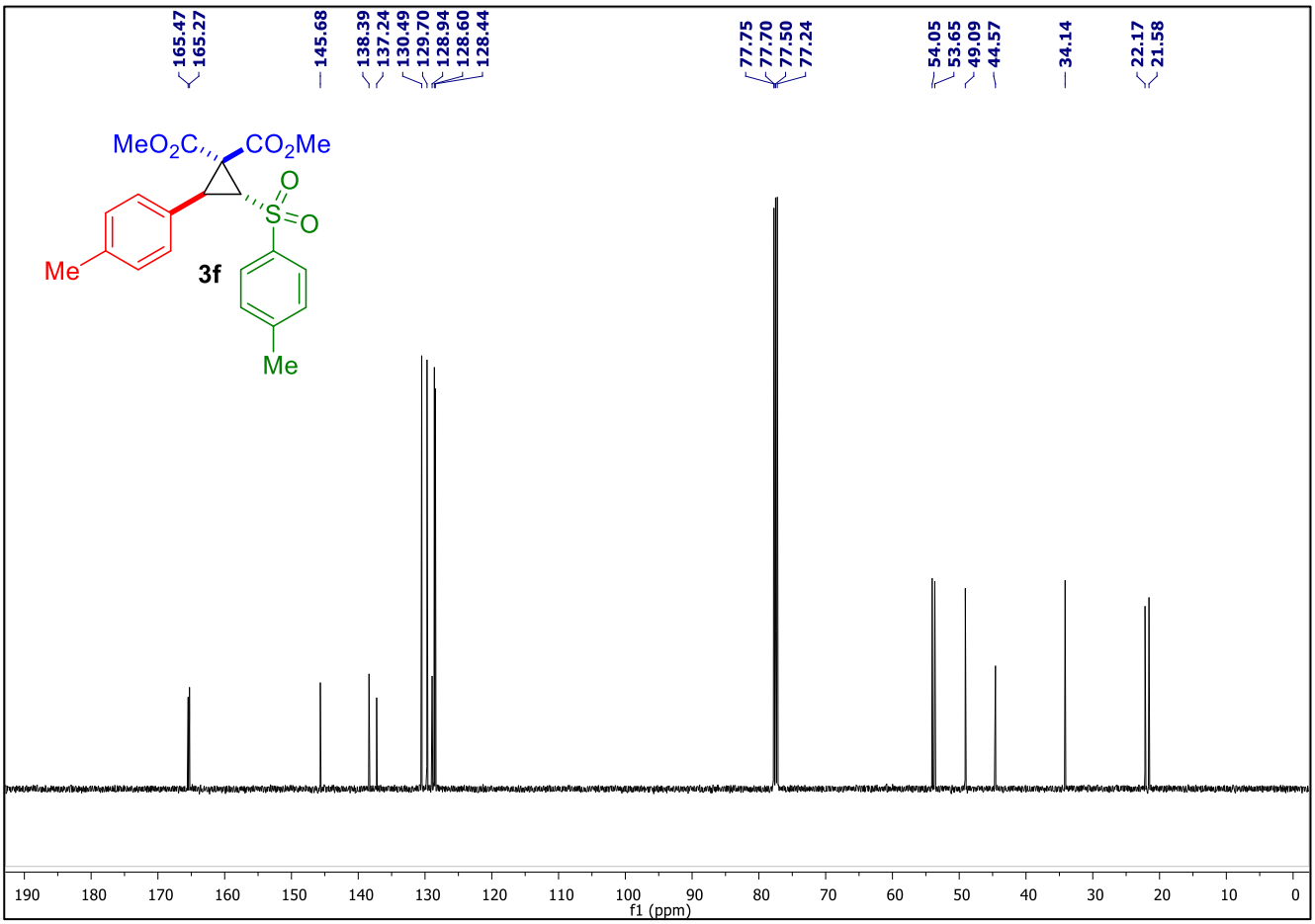

$^{1}$H NMR of Compound **3e** (400 MHz, $CDCl_3$)



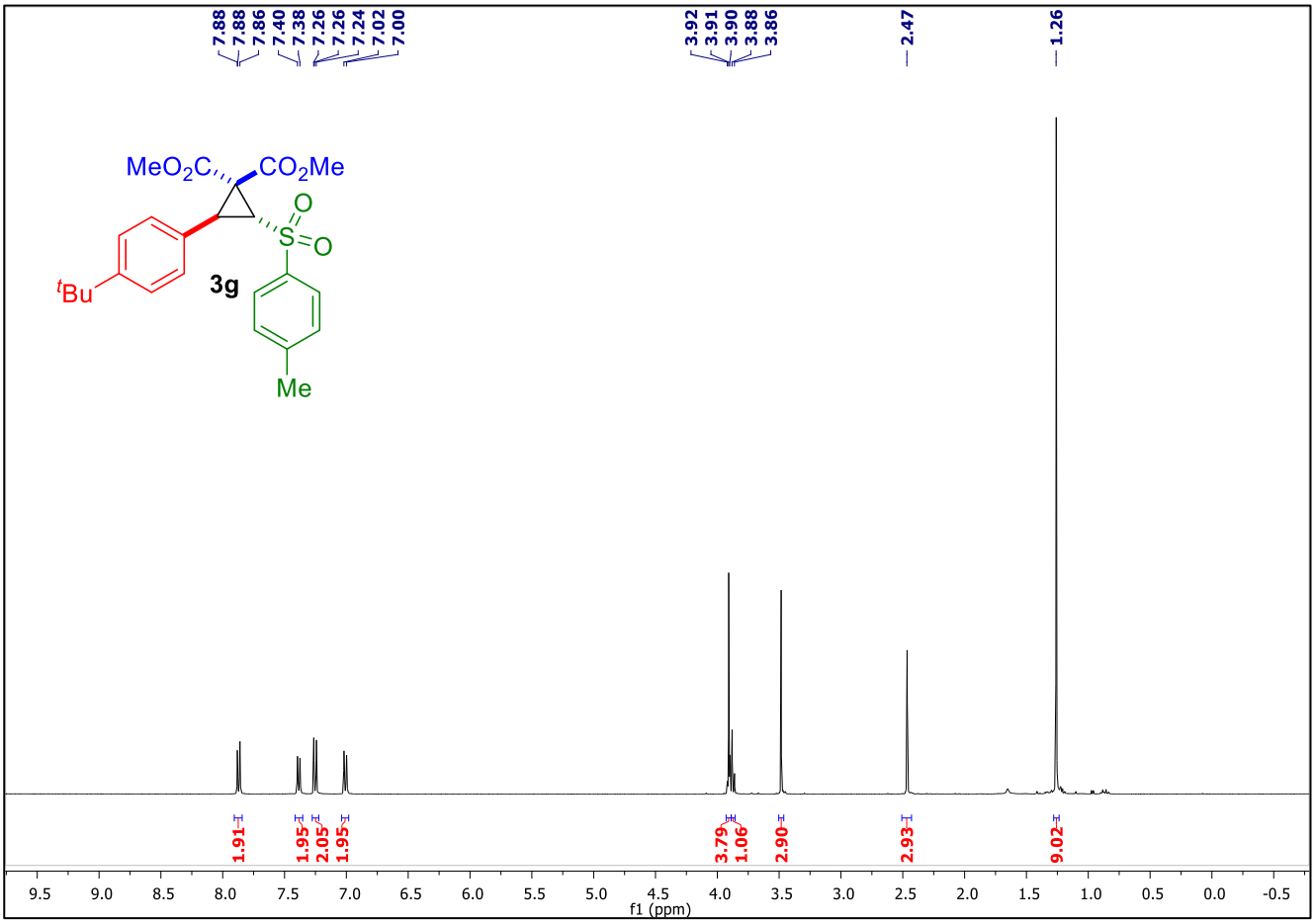

$^{13}$C NMR of Compound **3e** (101 MHz, $CDCl_3$)



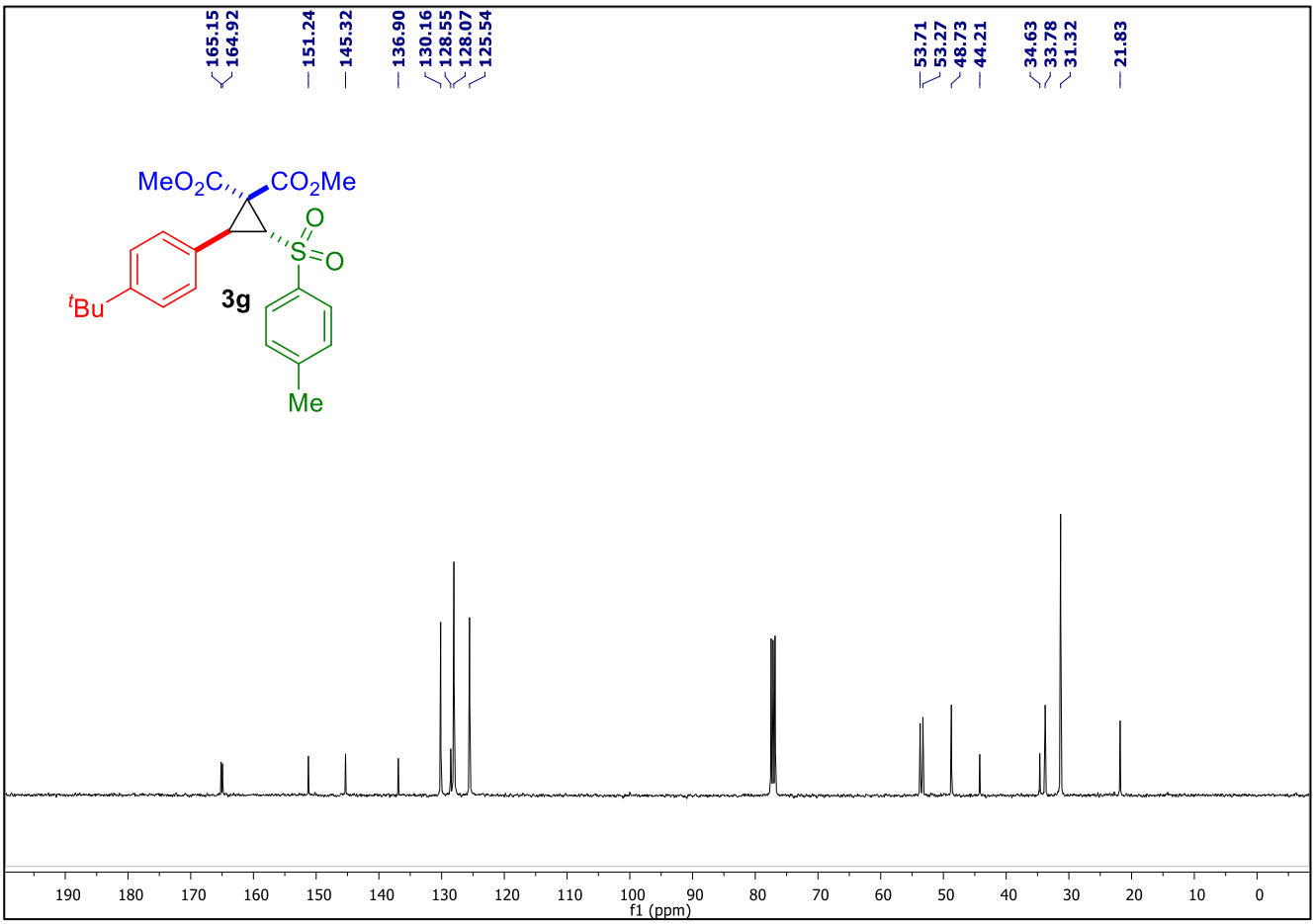

$^{1}$H NMR of Compound **3f** (400 MHz, $CDCl_3$)



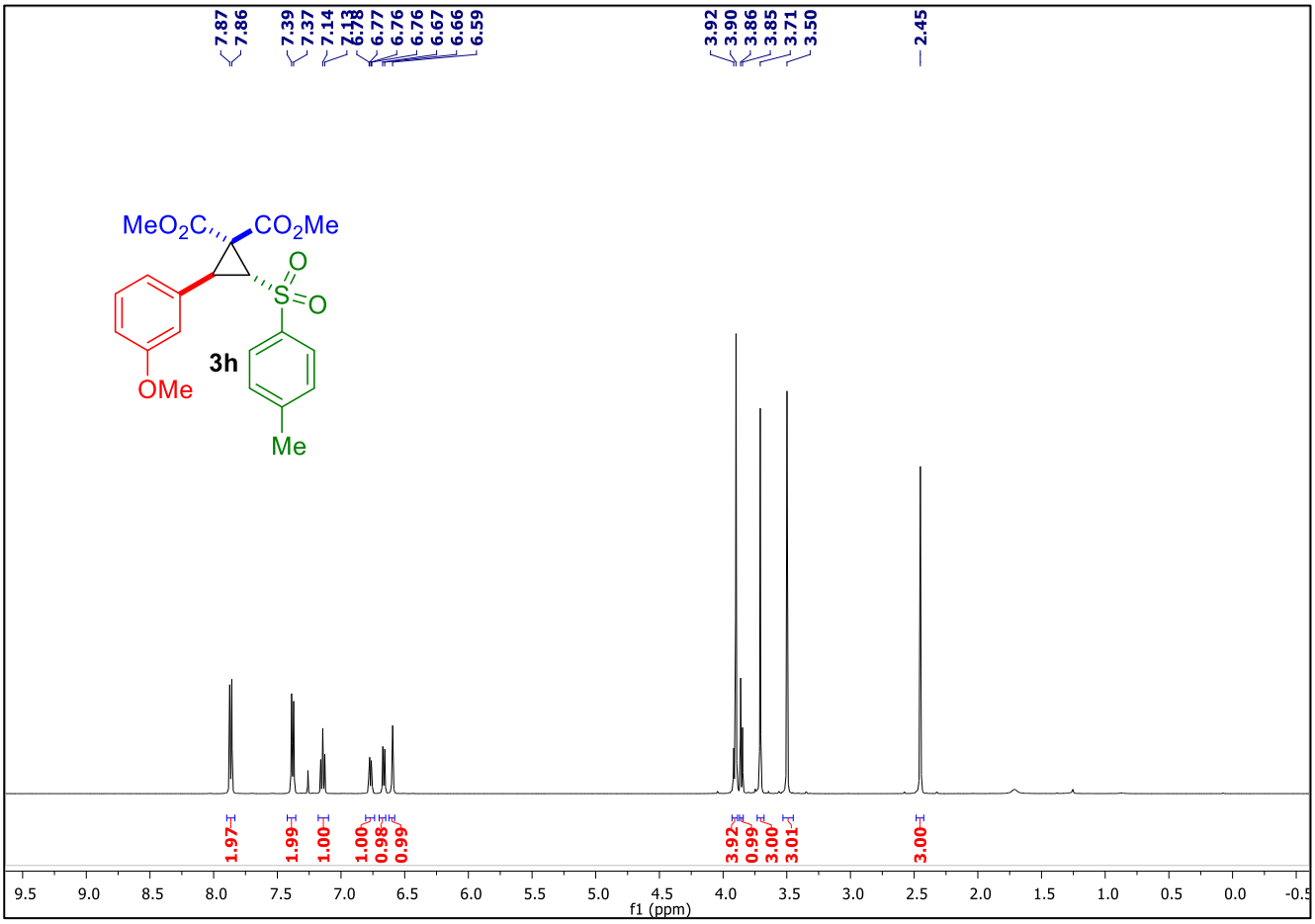

$^{13}$C NMR of Compound **3f** (126 MHz, $CDCl_3$)



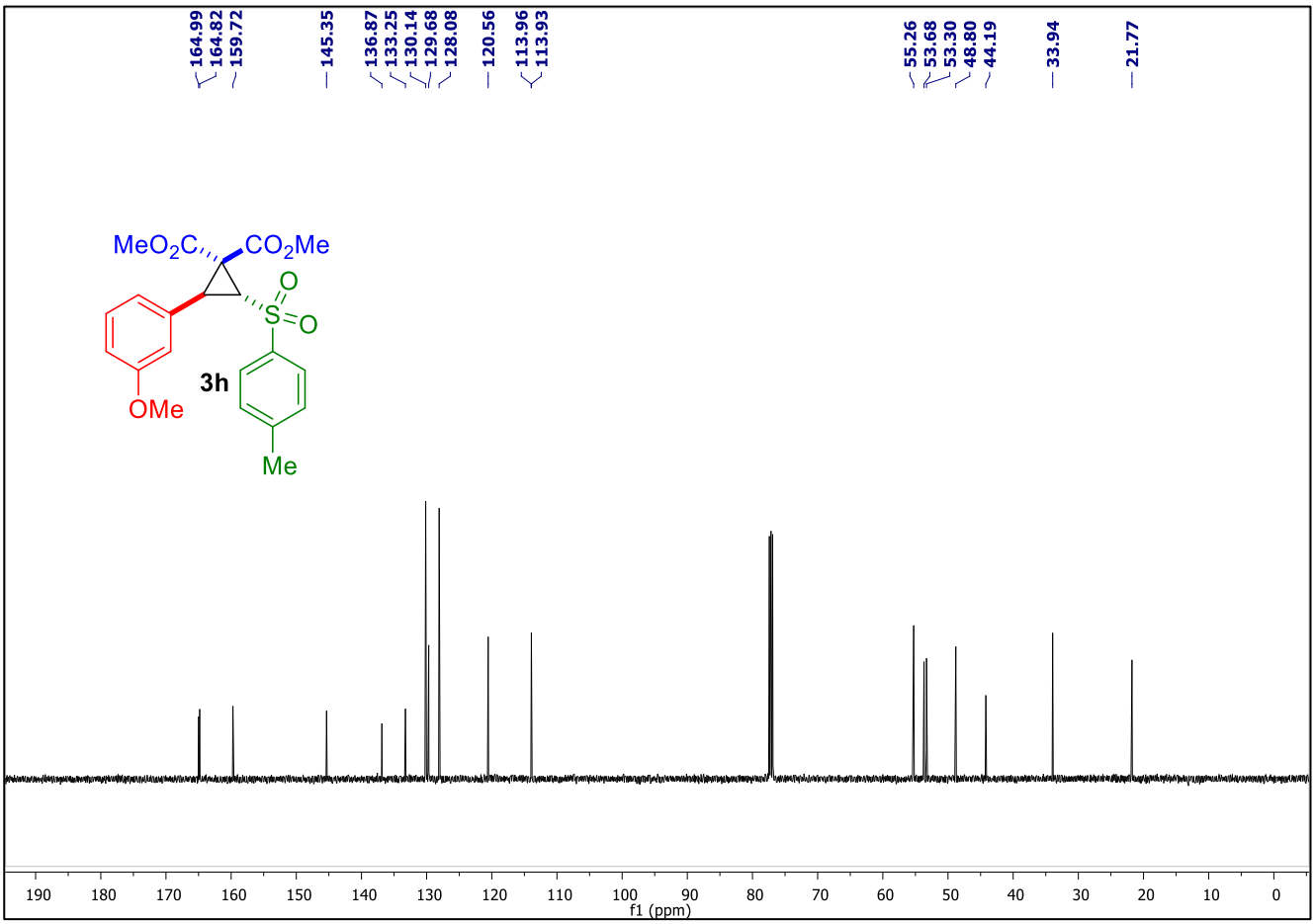

$^{1}$H NMR of Compound **3g** (400 MHz, $CDCl_3$)



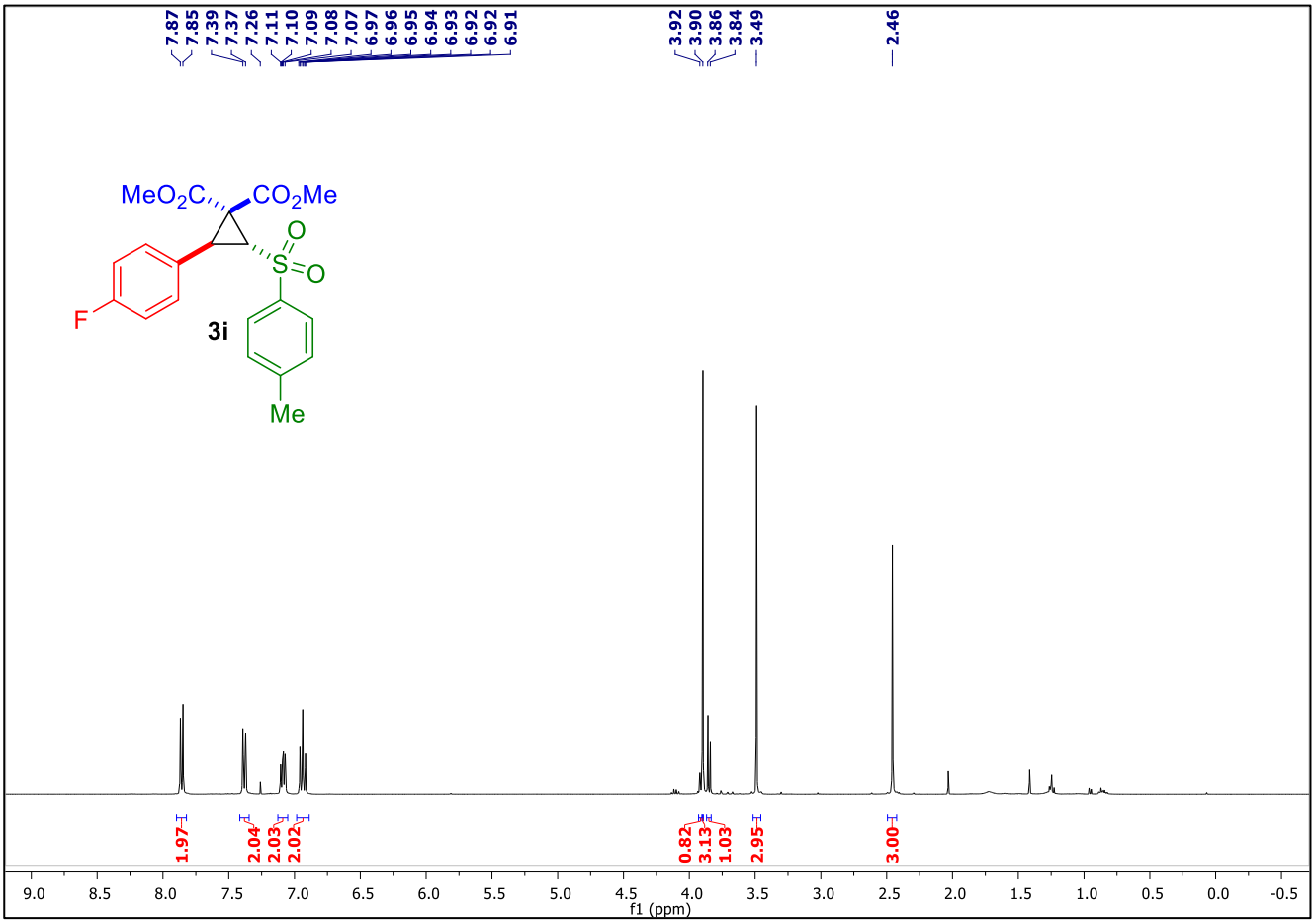

$^{13}$C NMR of Compound **3g** (101 MHz, $CDCl_3$)



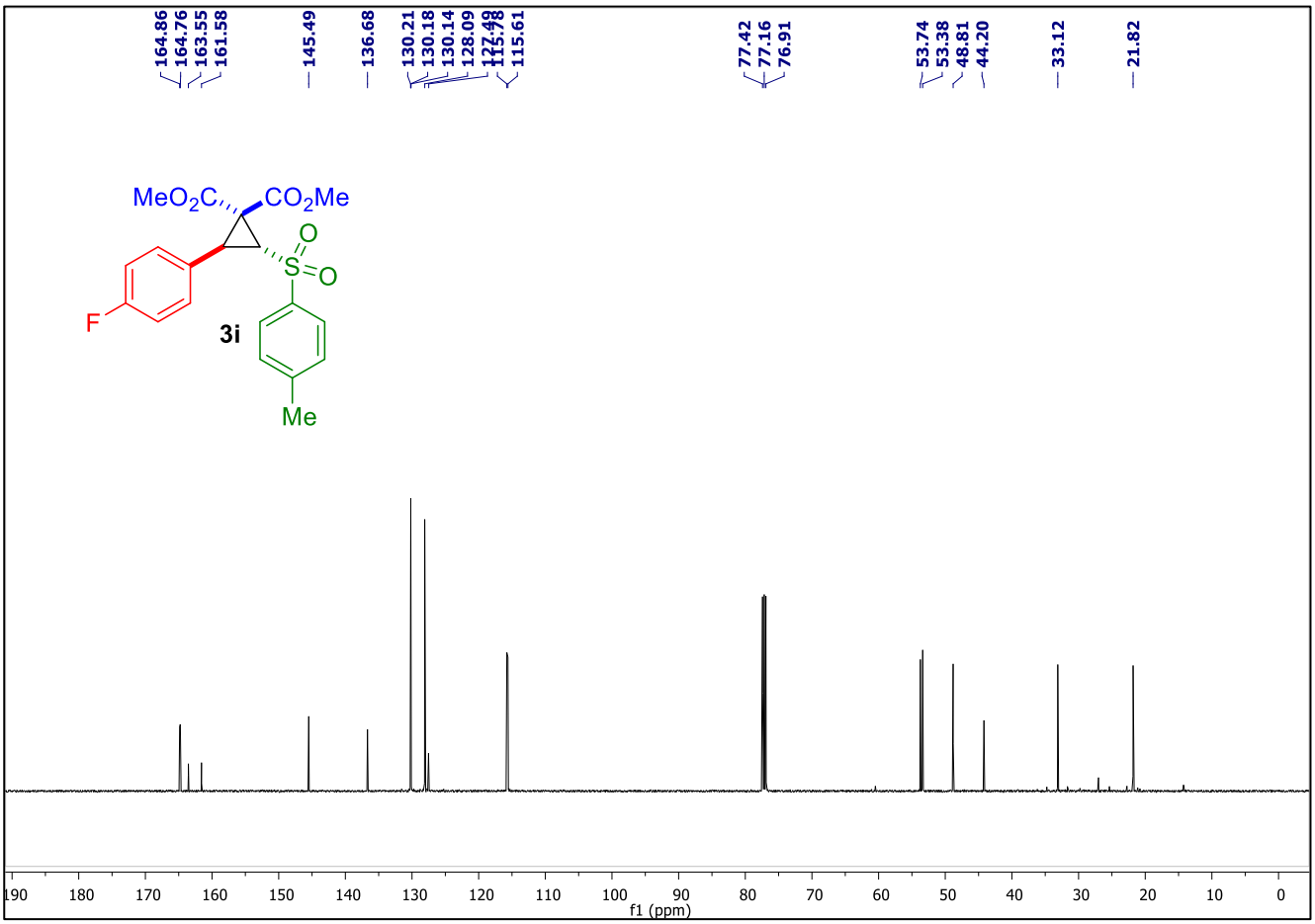

$^{1}$H NMR of Compound **3h** (400 MHz, $CDCl_3$)



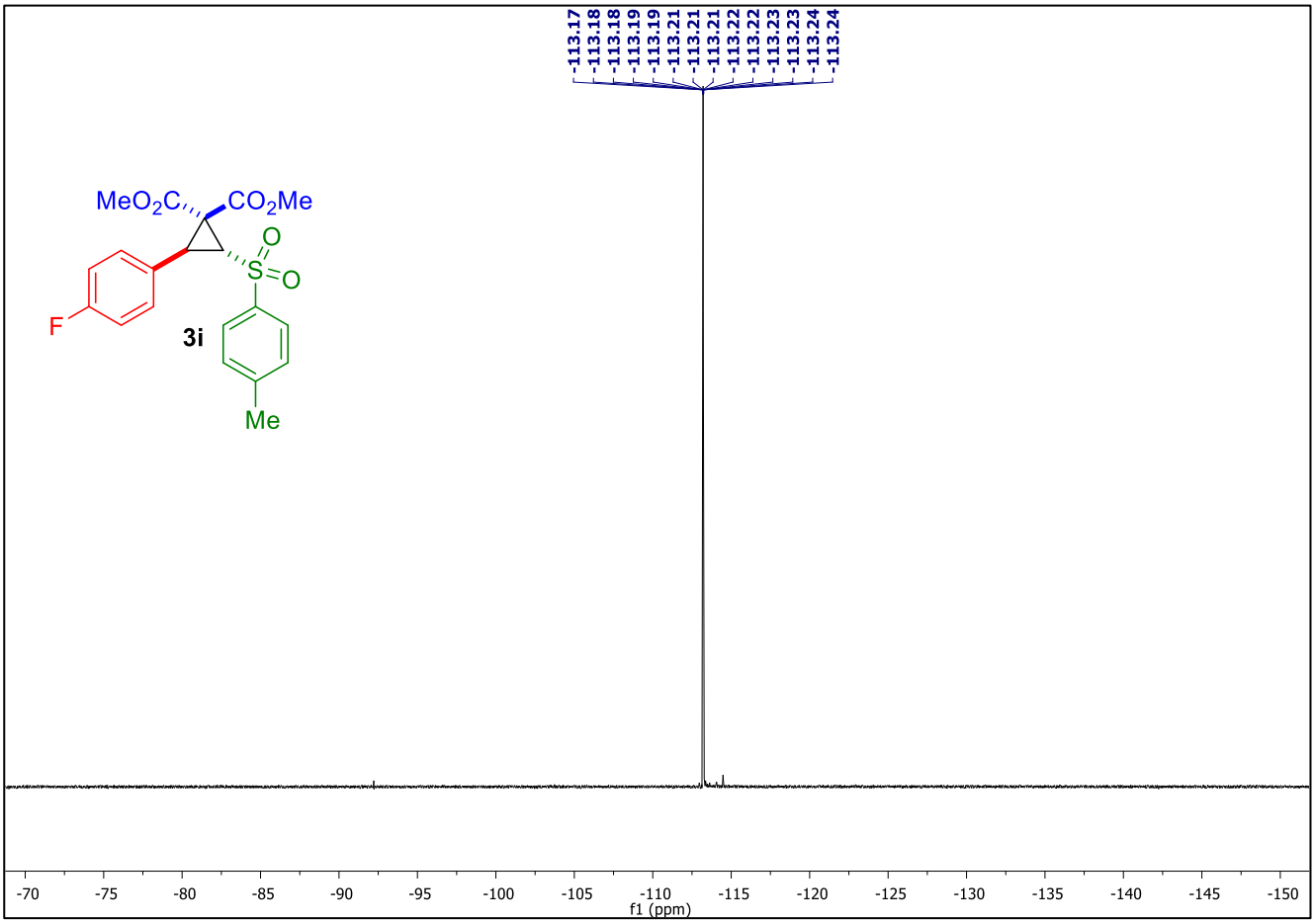

$^{13}$C NMR of Compound **3h** (126 MHz, $CDCl_3$)



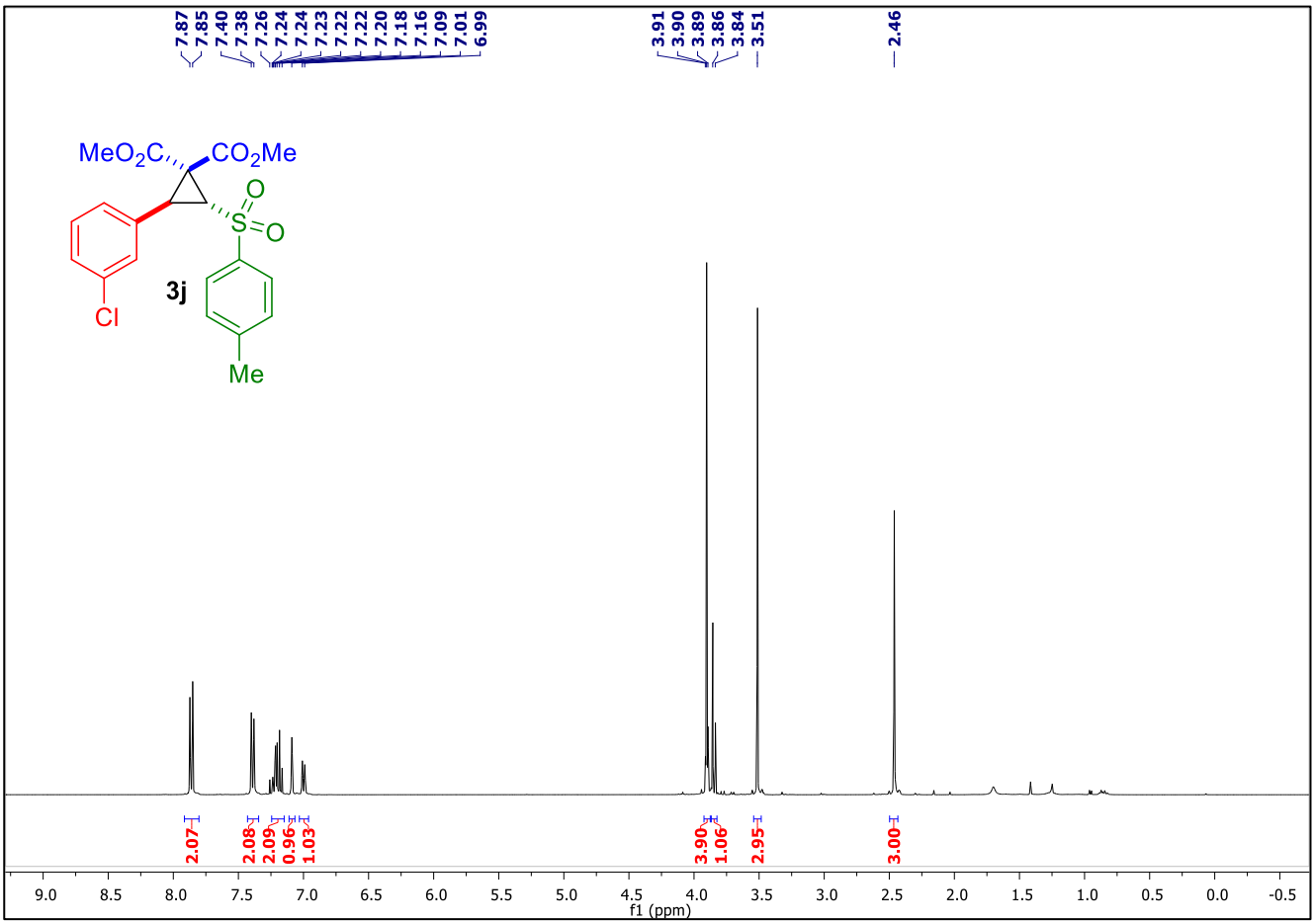

$^{1}$H NMR of Compound **3i** (400 MHz, $CDCl_3$)



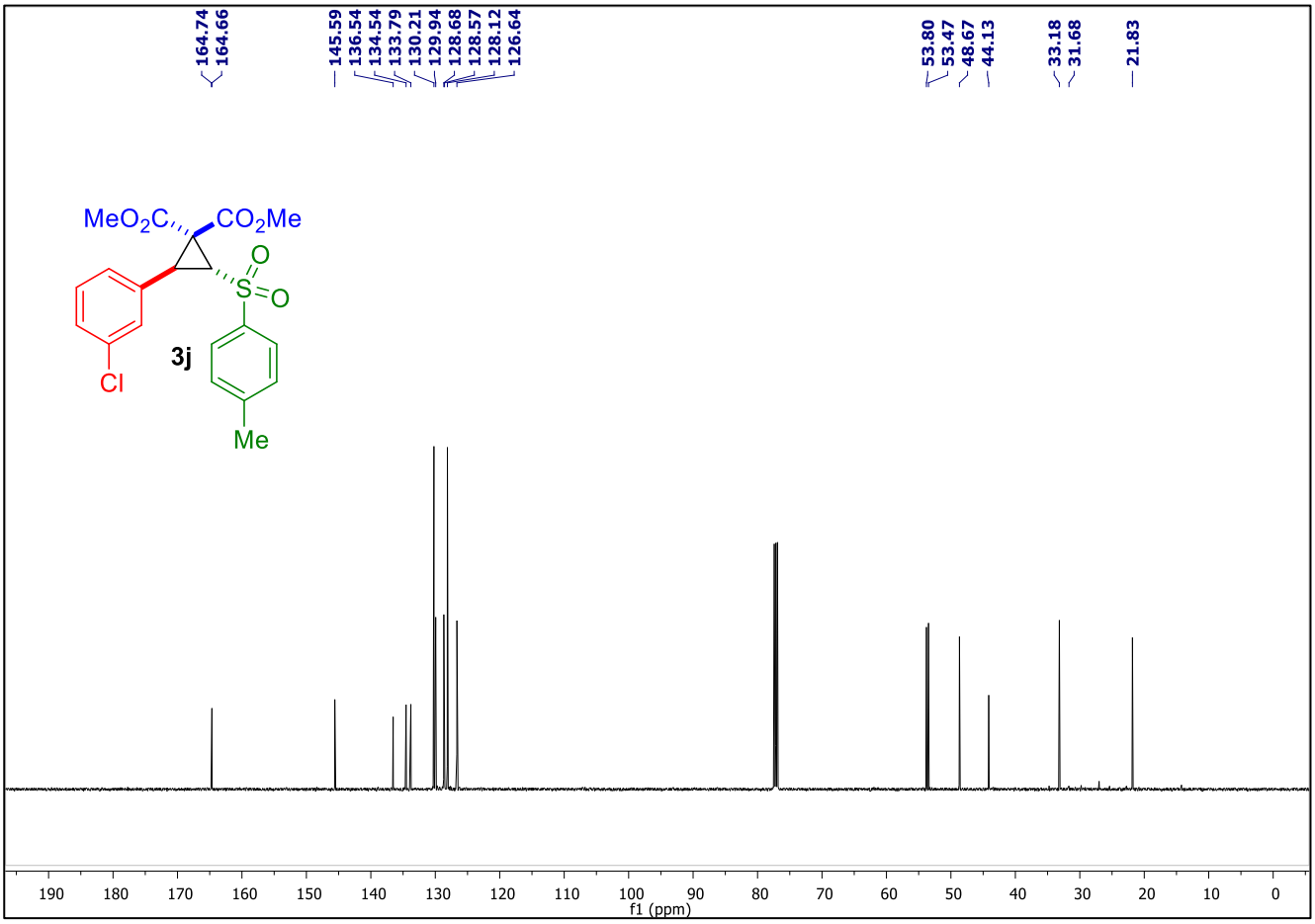

$^{13}$C NMR of Compound **3i** (126 MHz, $CDCl_3$)



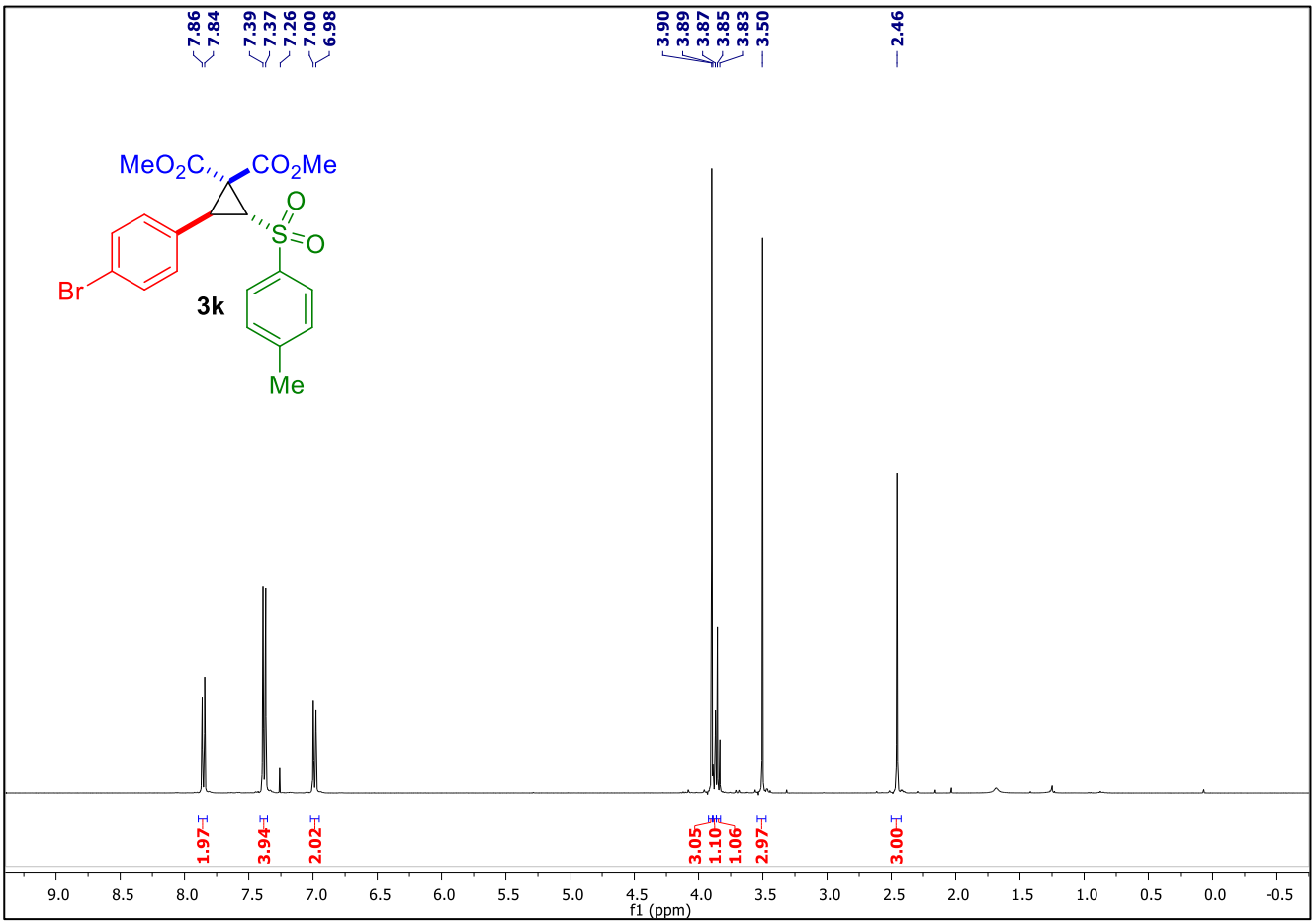

$^{19}$F NMR of Compound **3i** (376 MHz, $CDCl_3$)



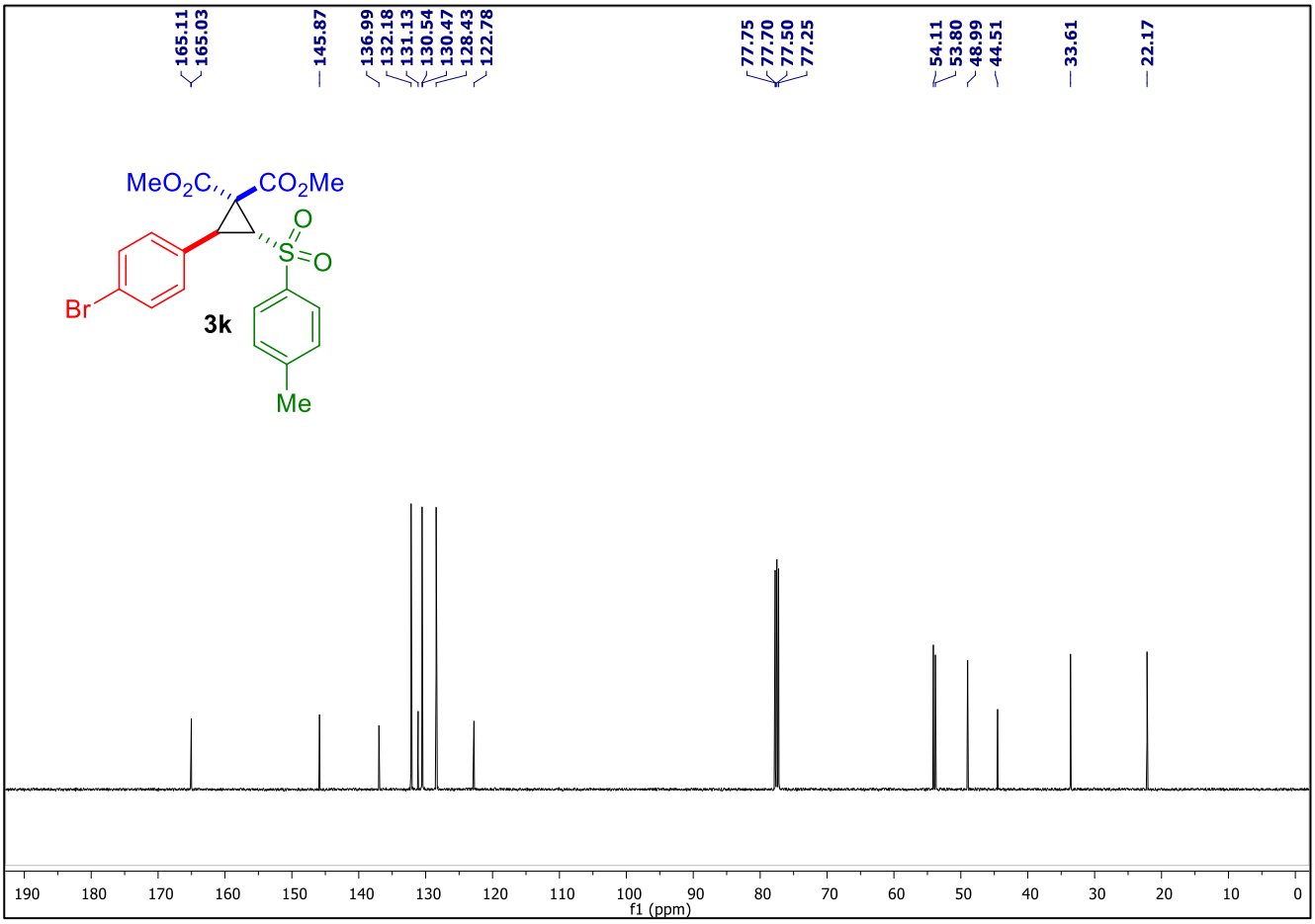

$^{1}$H NMR of Compound **3j** (400 MHz, $CDCl_3$)



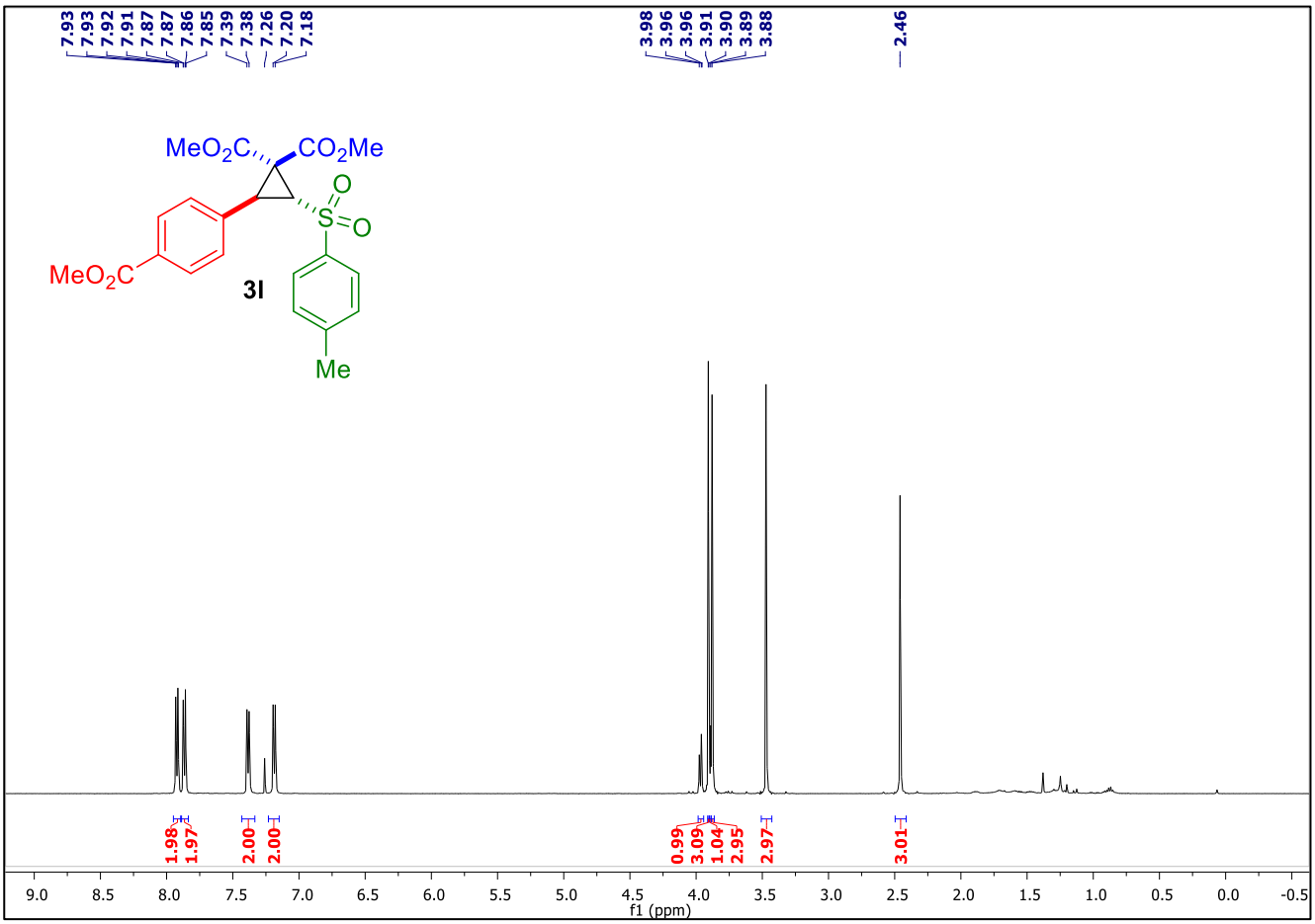

$^{13}$C NMR of Compound **3j** (126 MHz, $CDCl_3$)



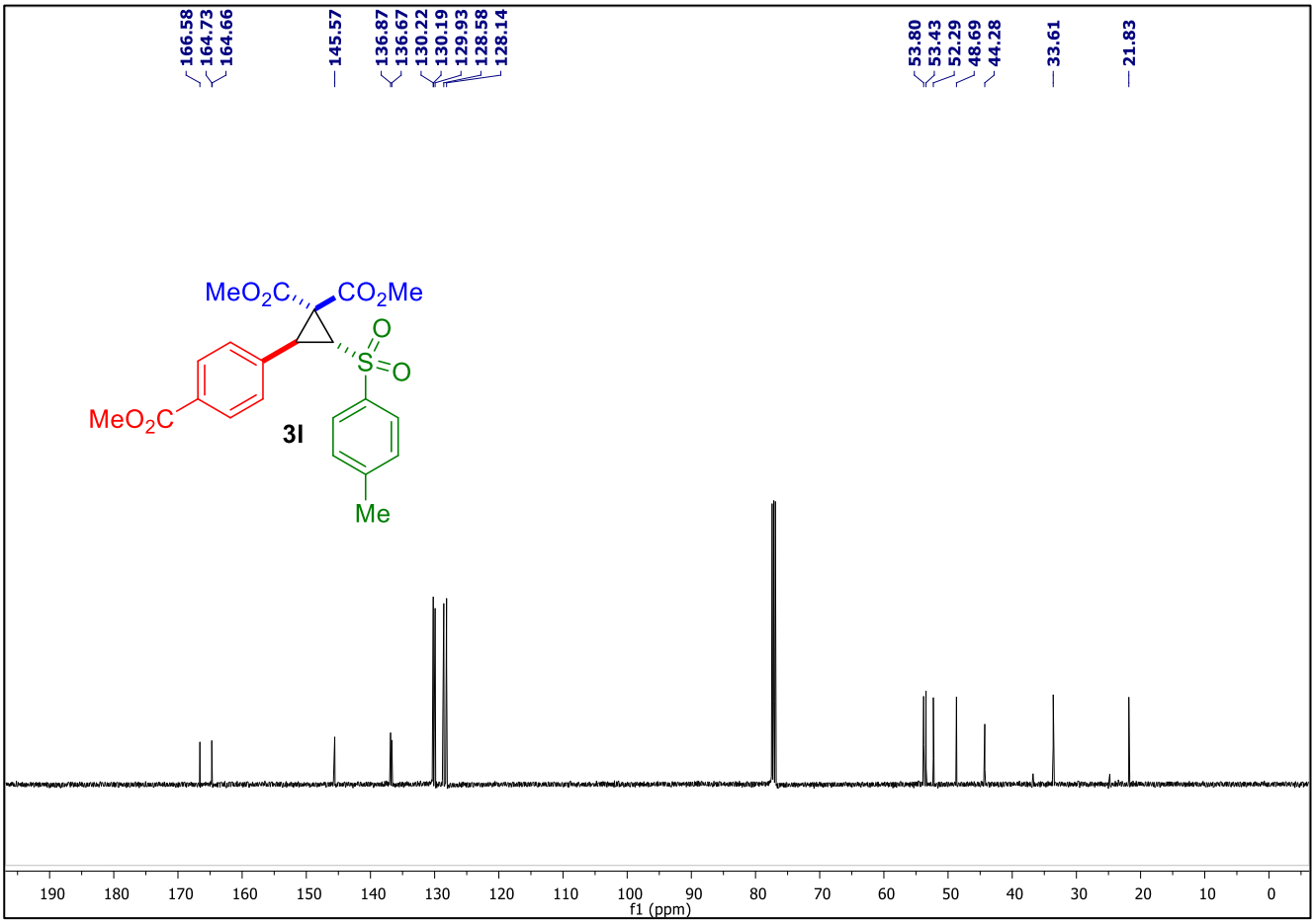

$^{1}$H NMR of Compound **3k** (400 MHz, $CDCl_3$)



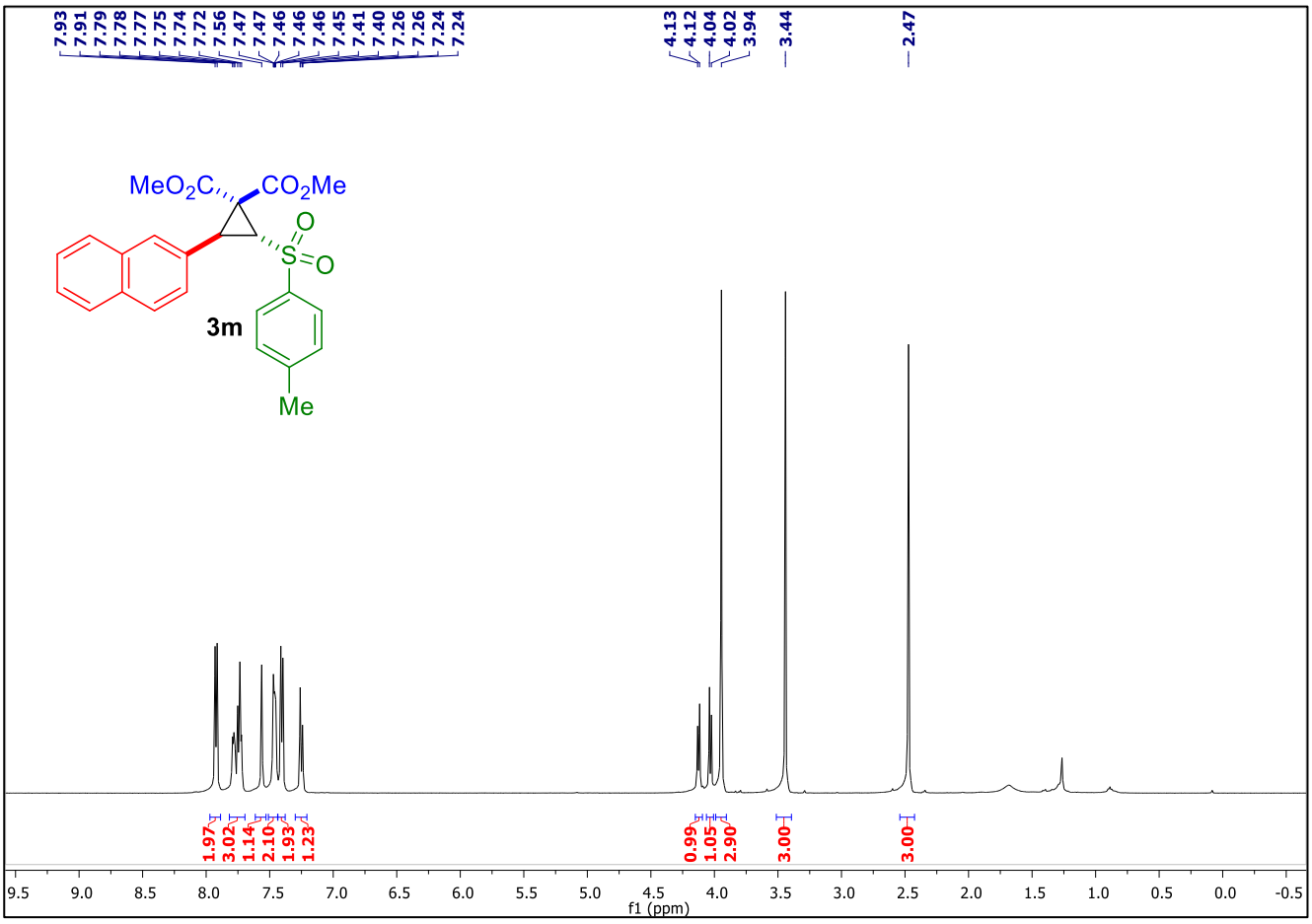

$^{13}$C NMR of Compound **3k** (126 MHz, $CDCl_3$)



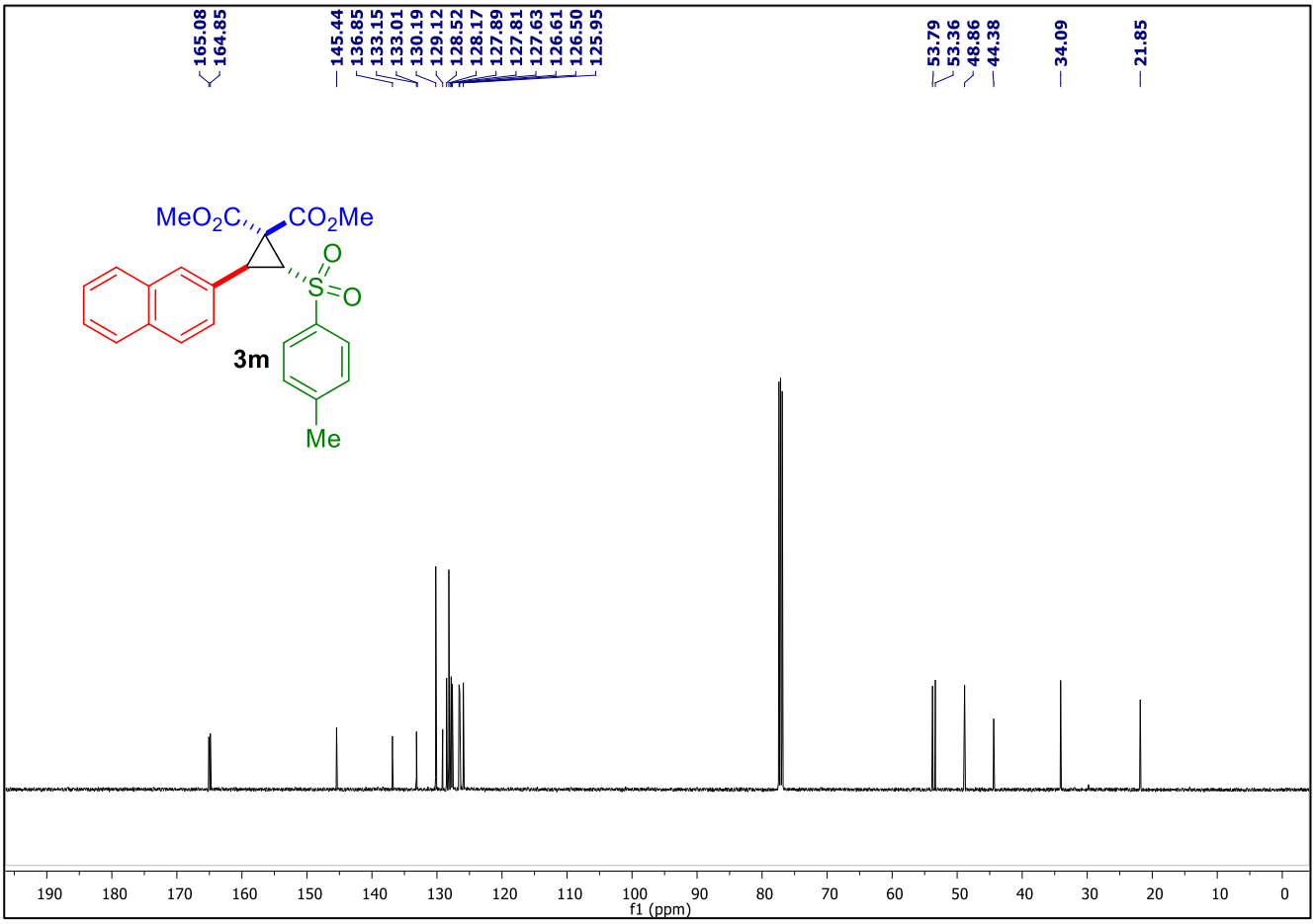

$^{1}$H NMR of Compound **3l** (400 MHz, $CDCl_3$)



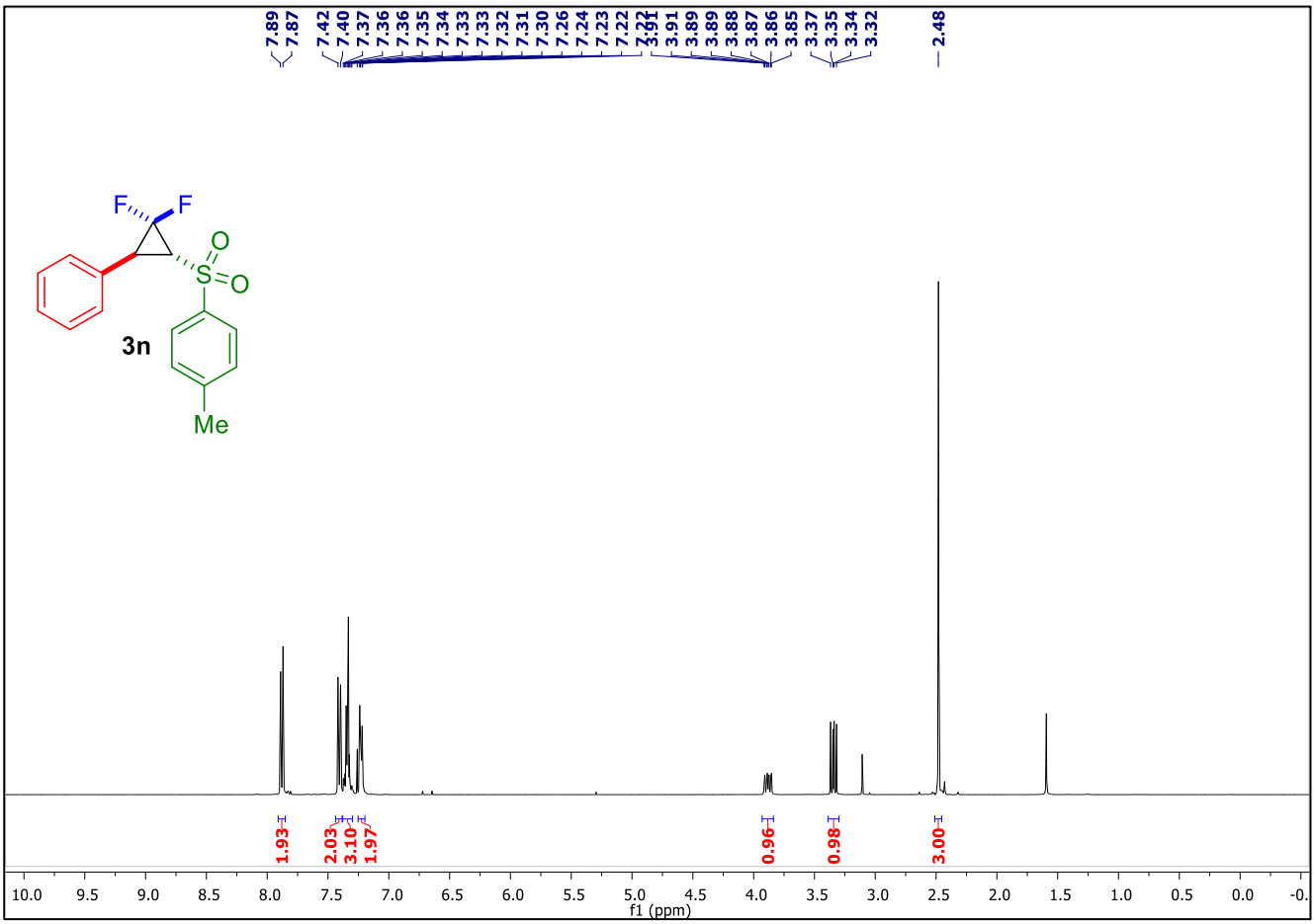

$^{13}$C NMR of Compound **3l** (126 MHz, $CDCl_3$)



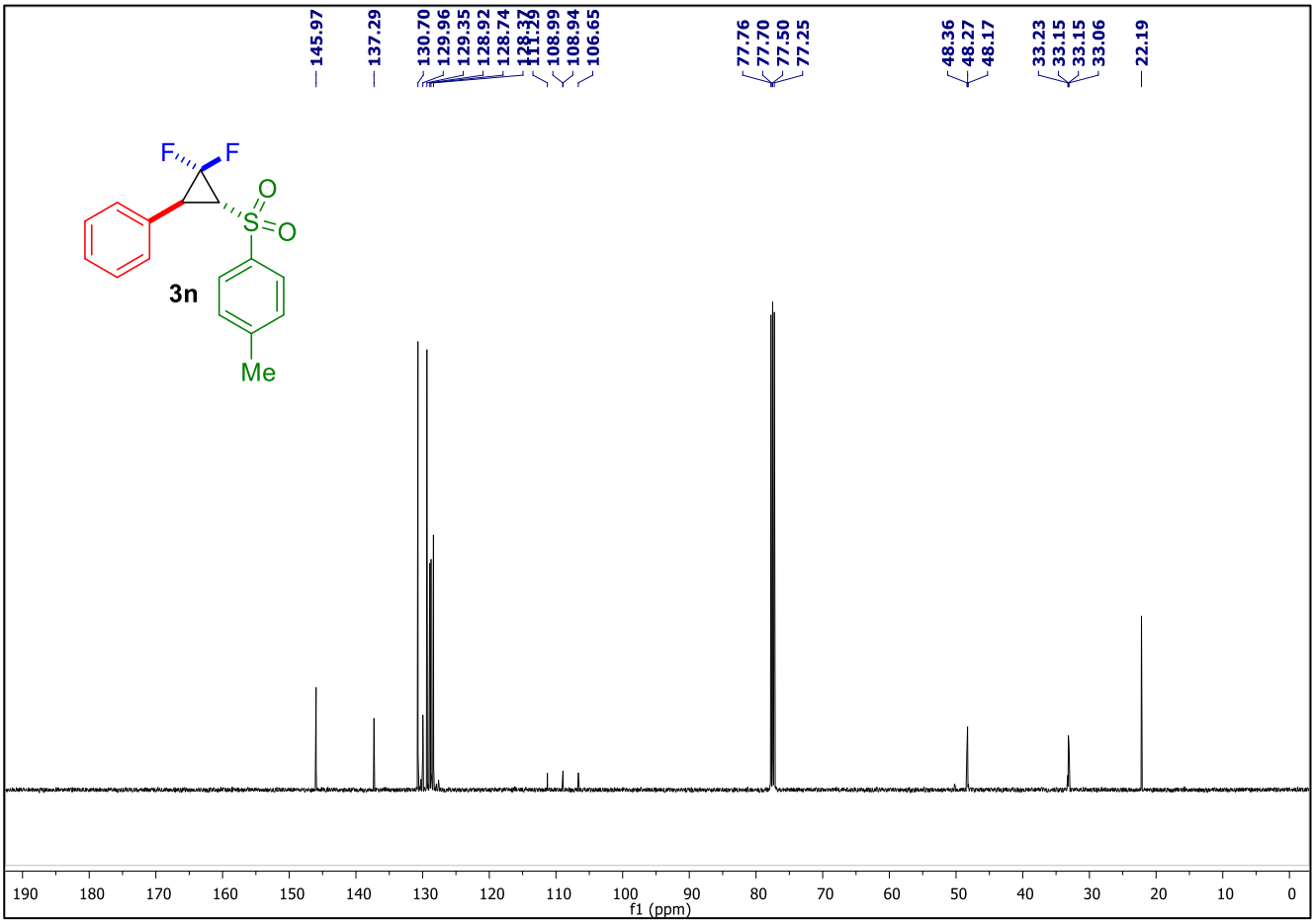

$^{1}$H NMR of Compound **3m** (400 MHz, $CDCl_3$)



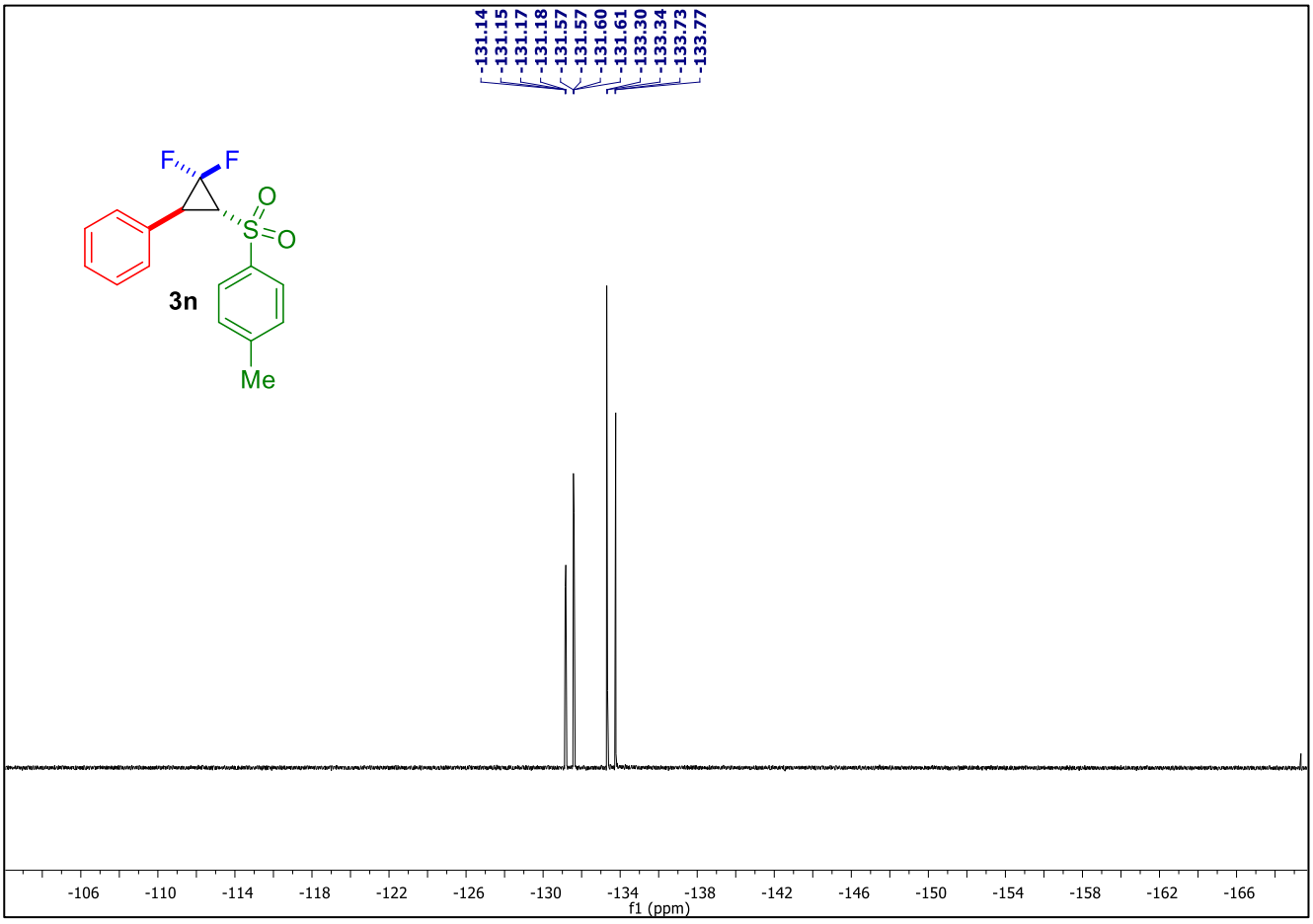

$^{13}$C NMR of Compound **3m** (126 MHz, $CDCl_3$)



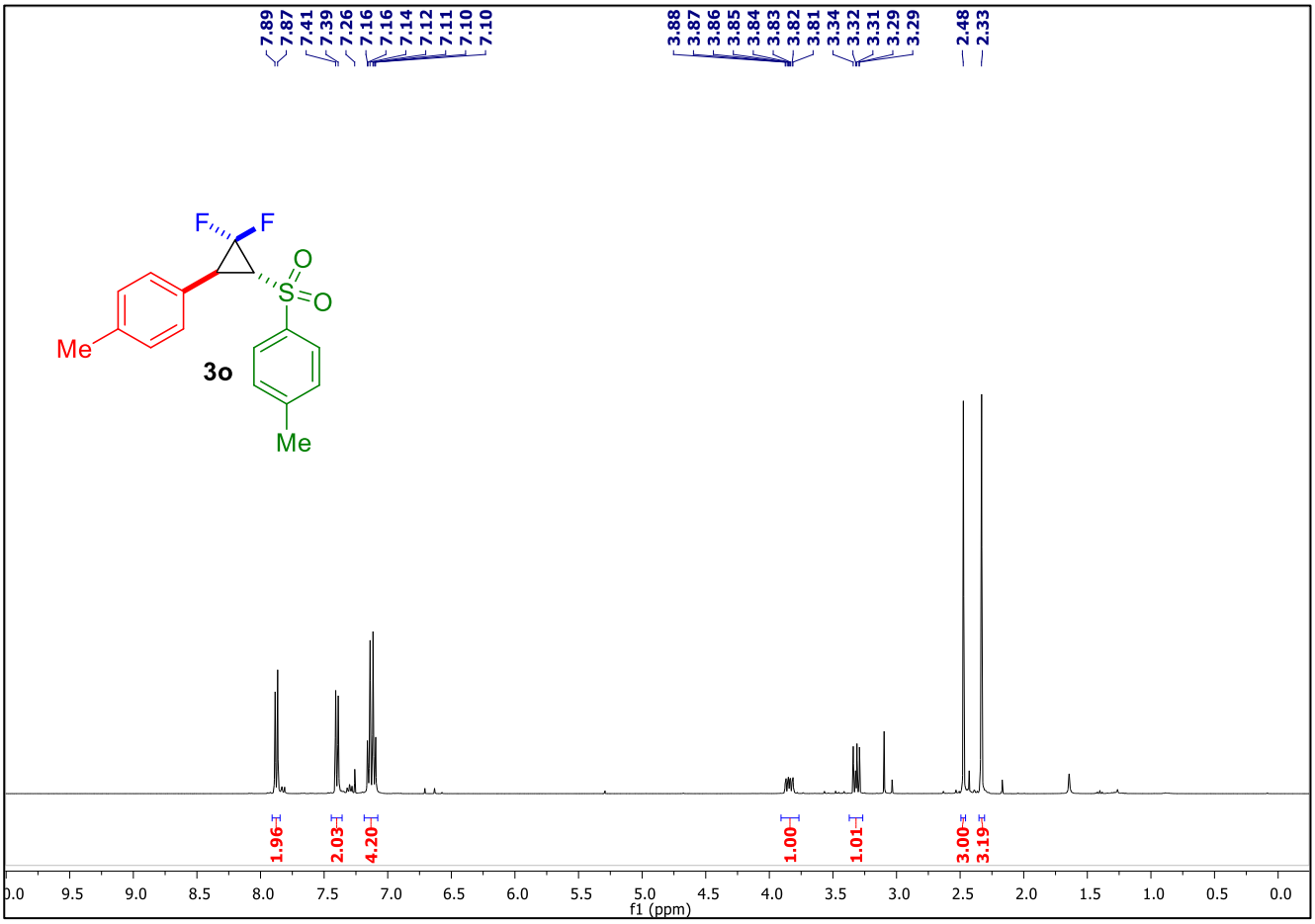

$^{1}$H NMR of Compound **3n** (400 MHz, $CDCl_3$)



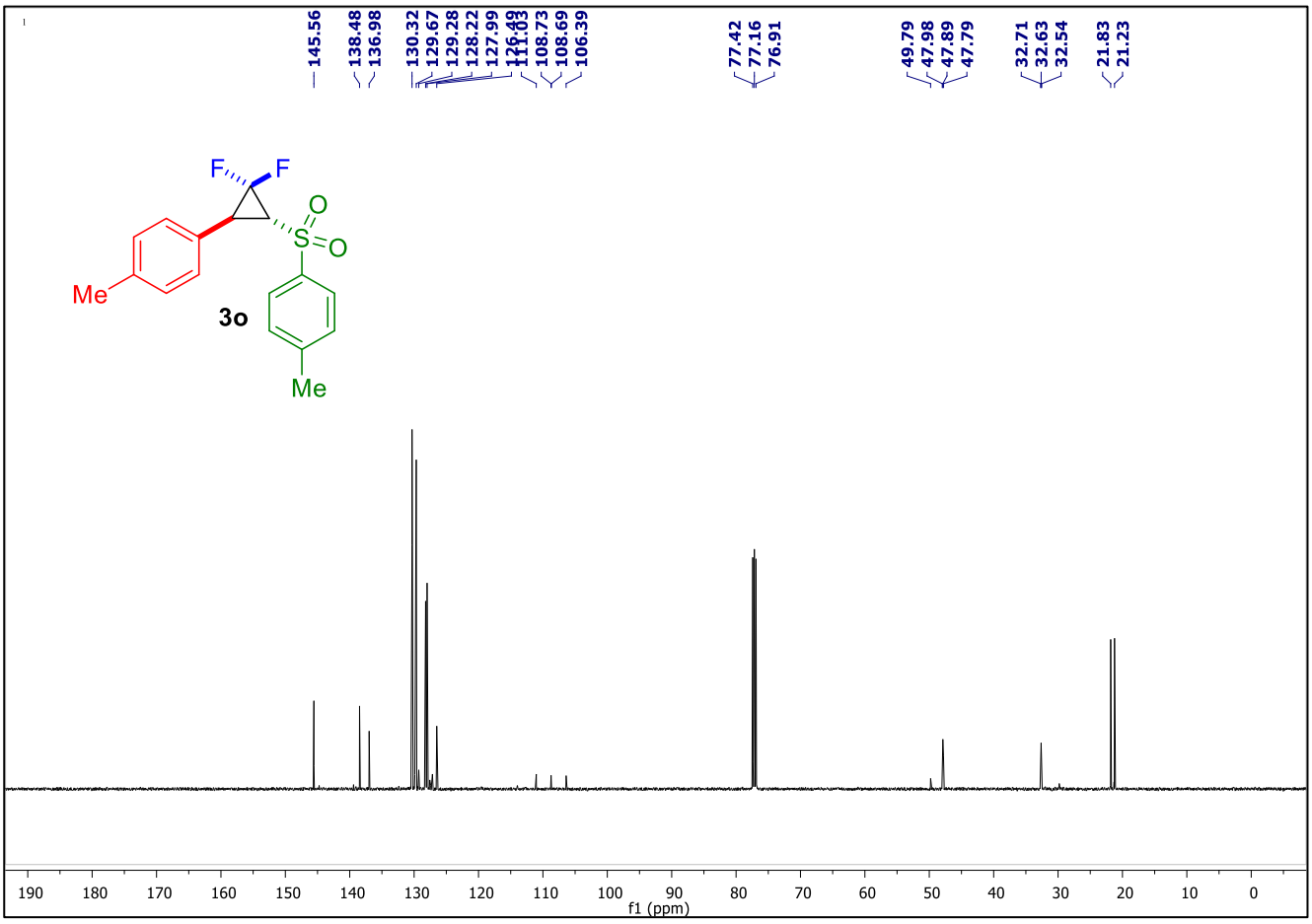

$^{13}$C NMR of Compound **3n** (126 MHz, $CDCl_3$)



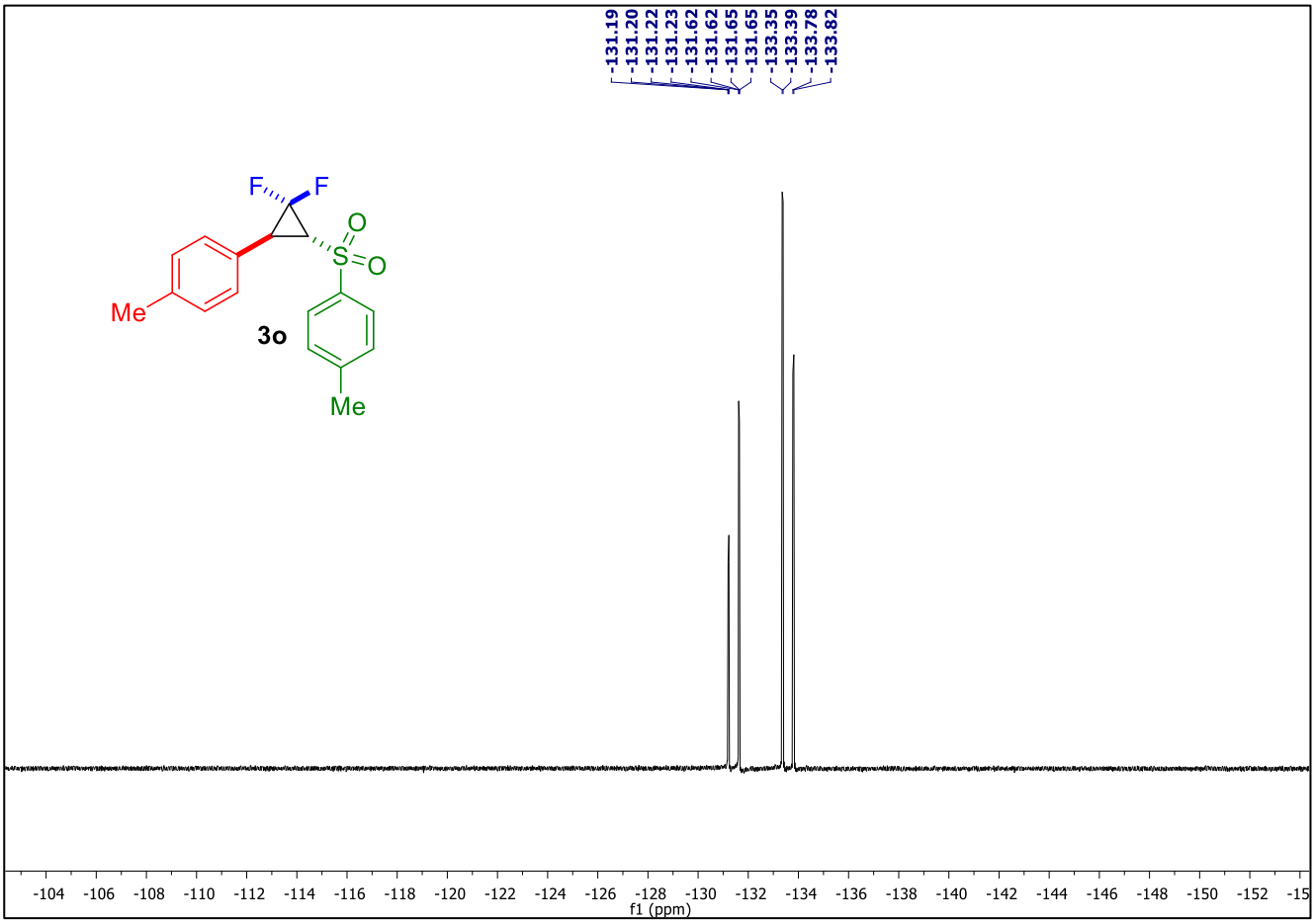

$^{19}$F NMR of Compound **3n** (376 MHz, $CDCl_3$)



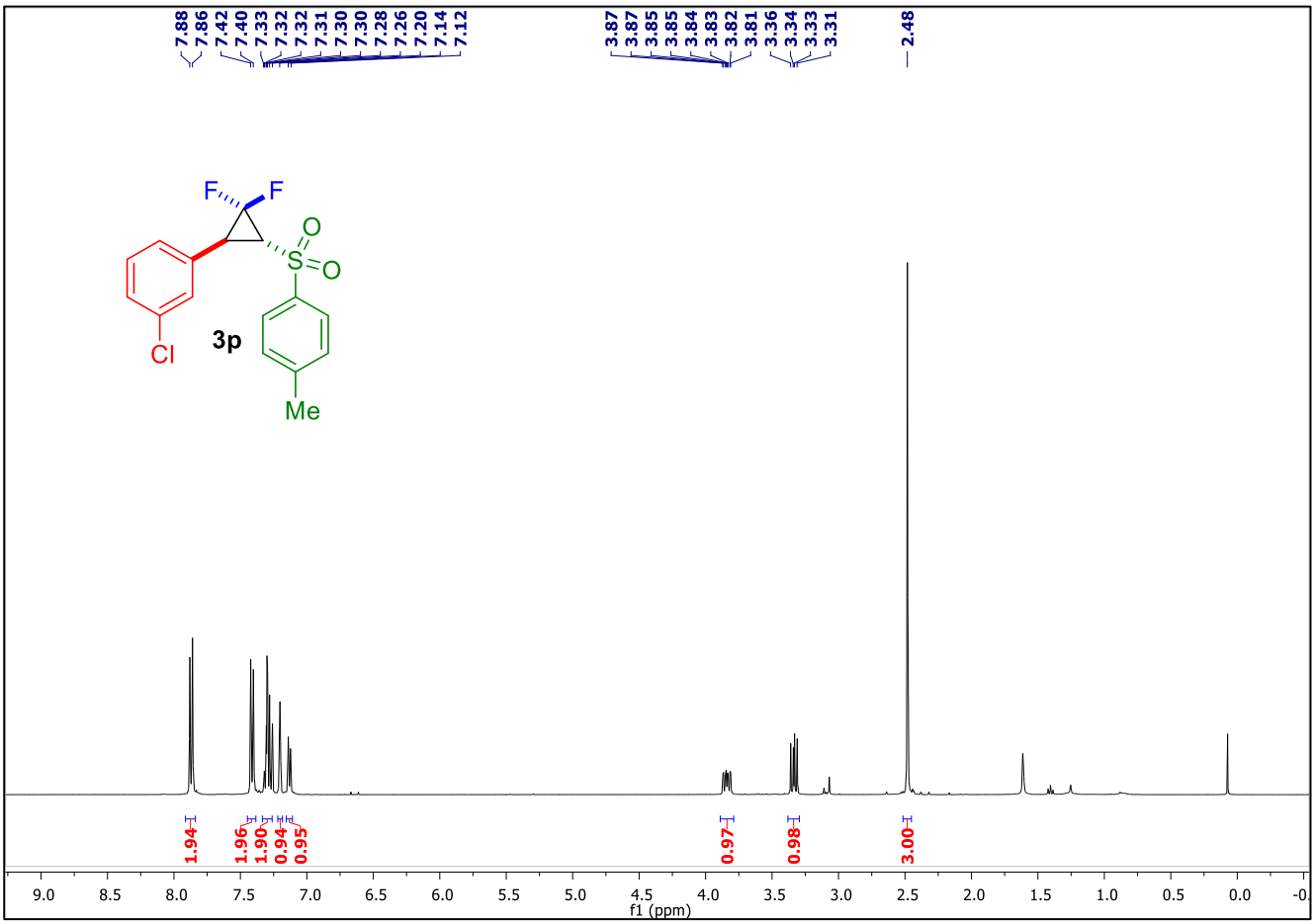

$^{1}$H NMR of Compound **3o** (400 MHz, $CDCl_3$)



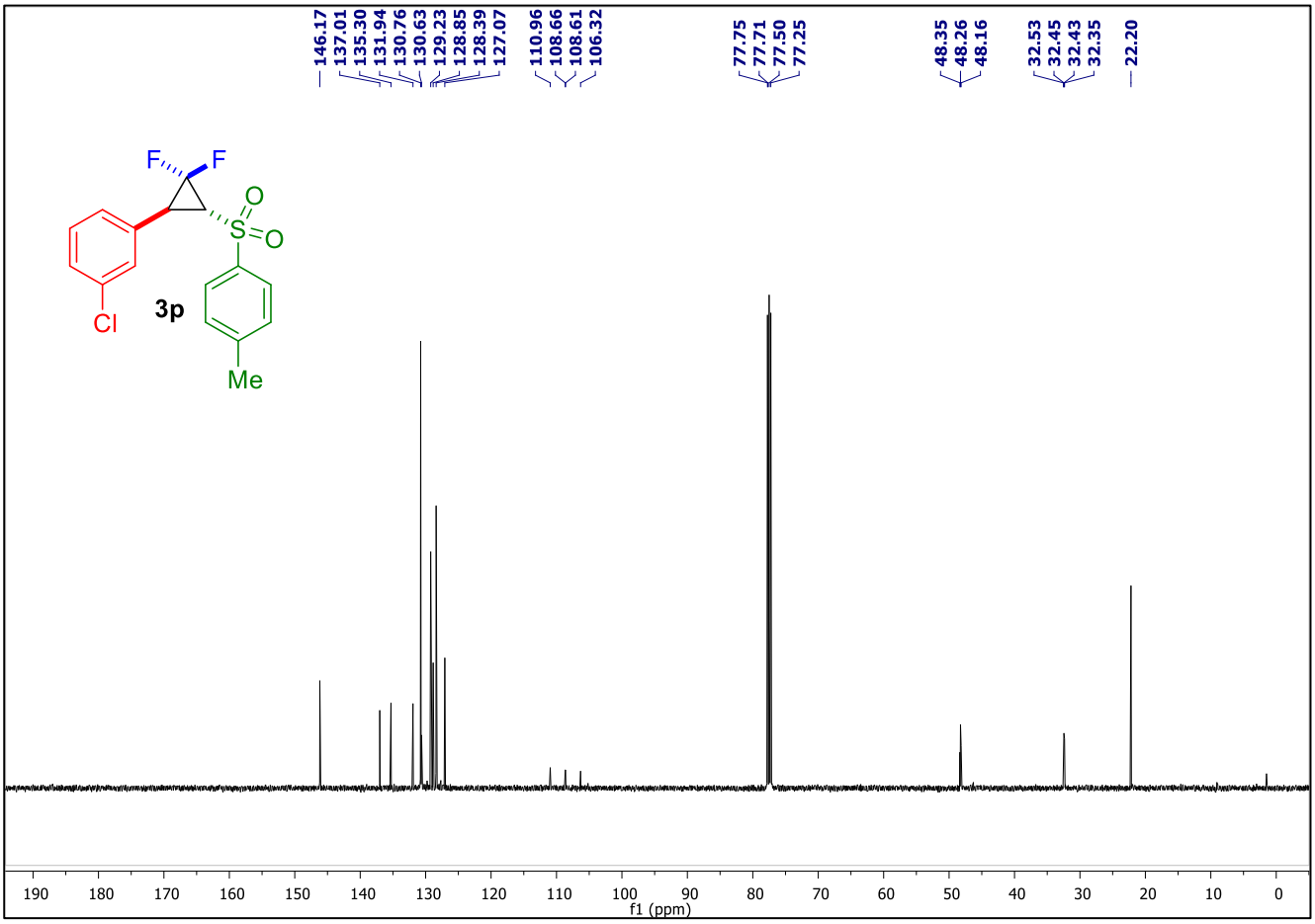

$^{13}$C NMR of Compound **3o** (126 MHz, $CDCl_3$)



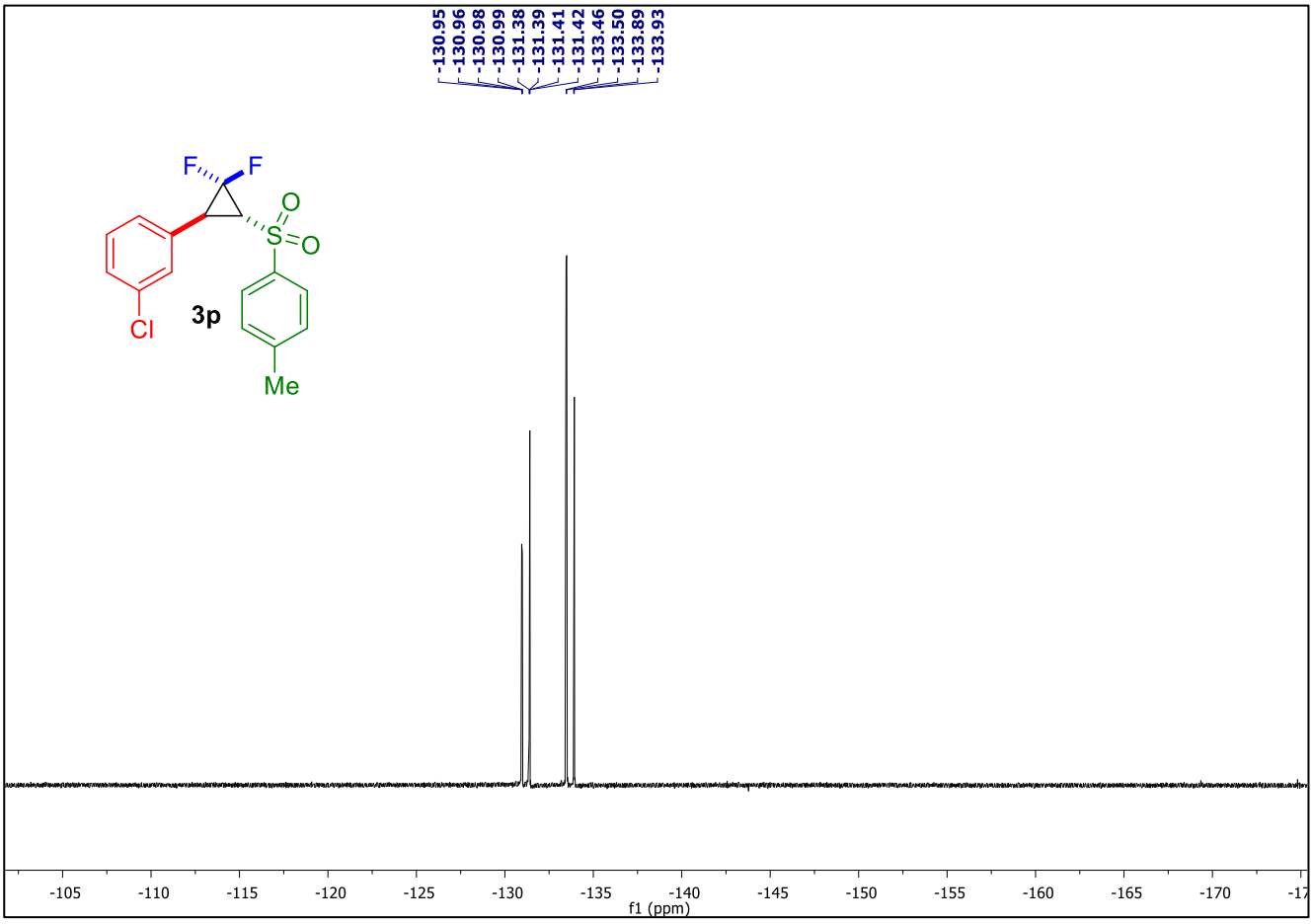

$^{19}$F NMR of Compound **3o** (376 MHz, $CDCl_3$)



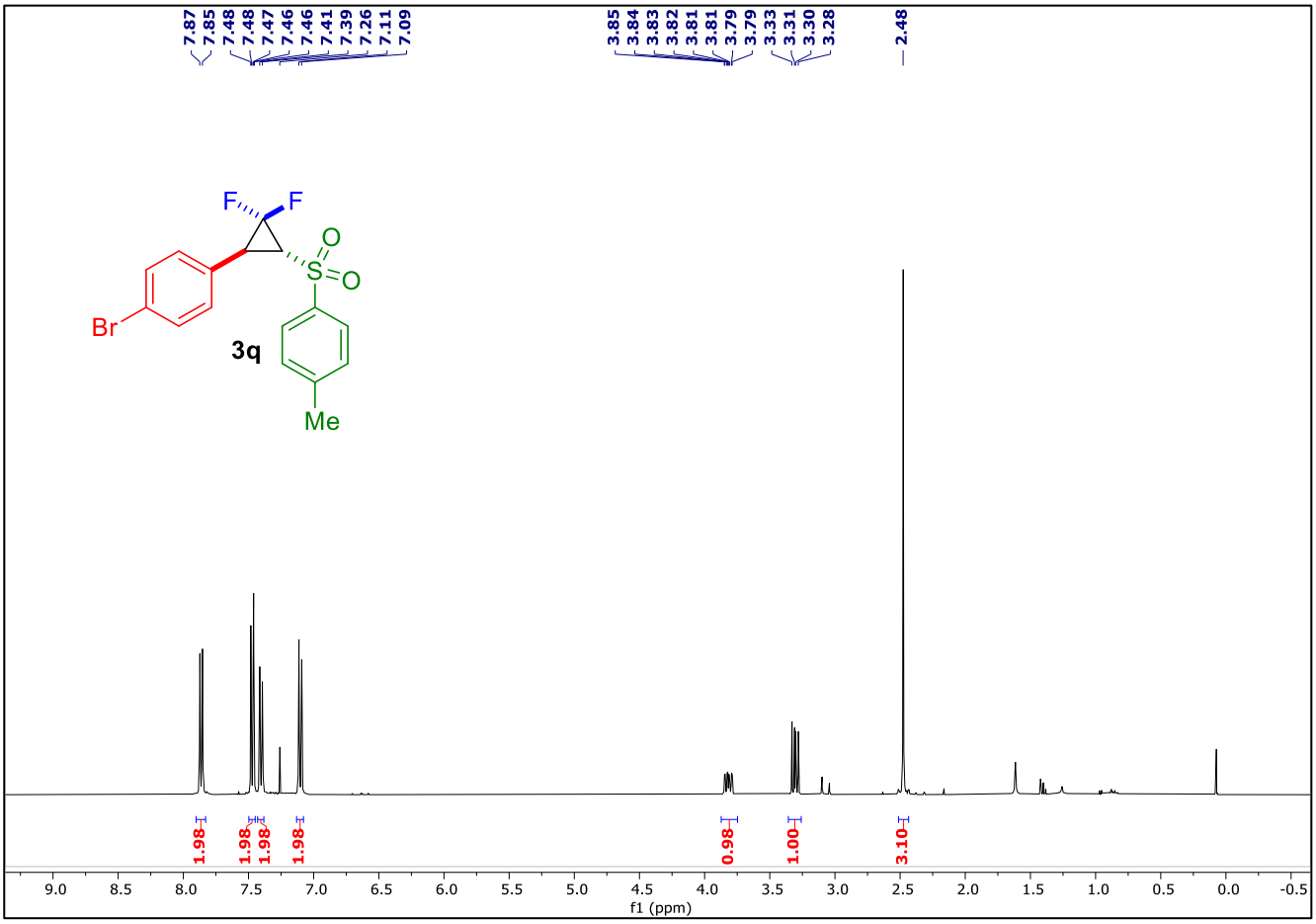

$^{1}$H NMR of Compound **3p** (400 MHz, $CDCl_3$)



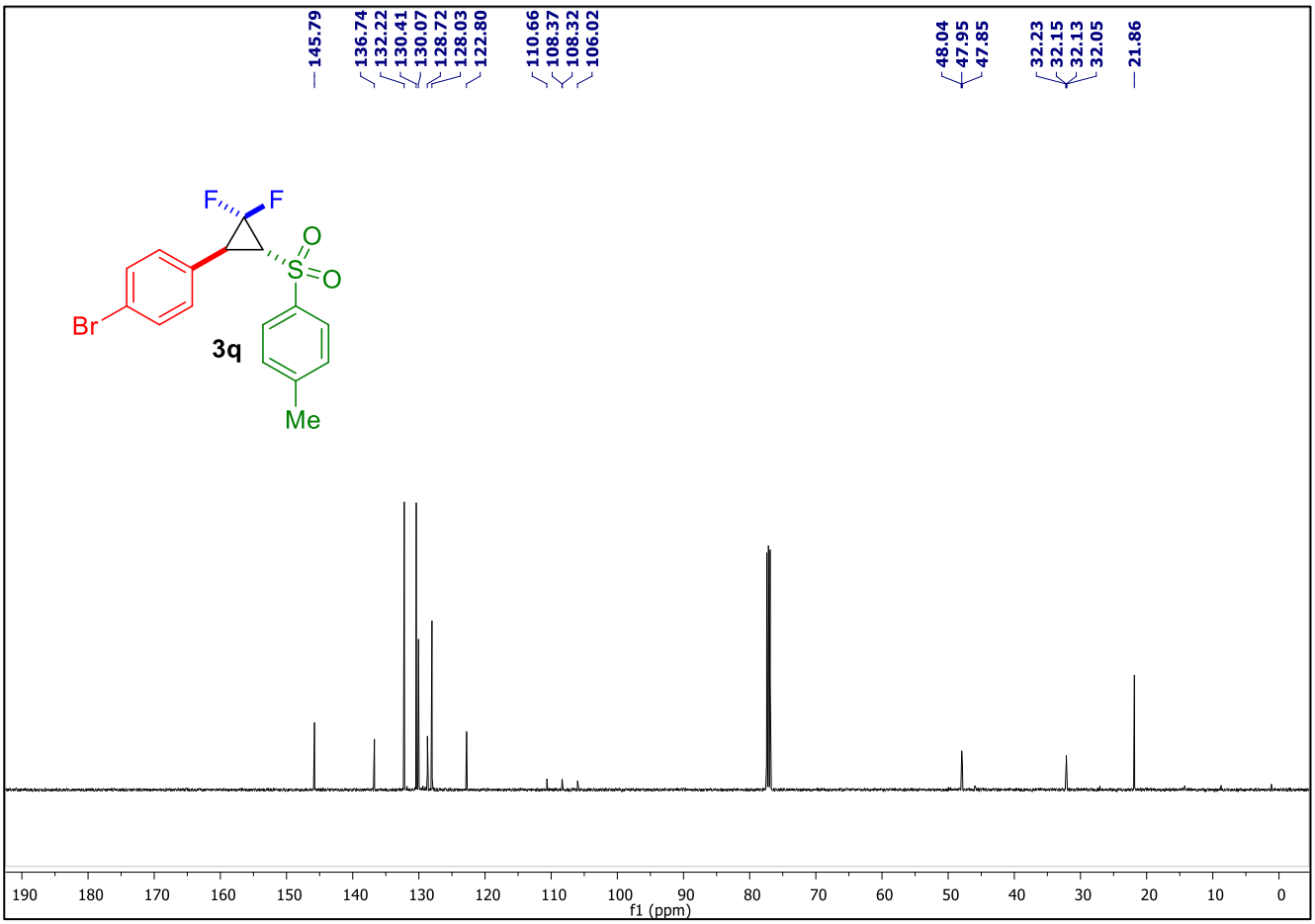

$^{13}$C NMR of Compound **3p** (126 MHz, $CDCl_3$)



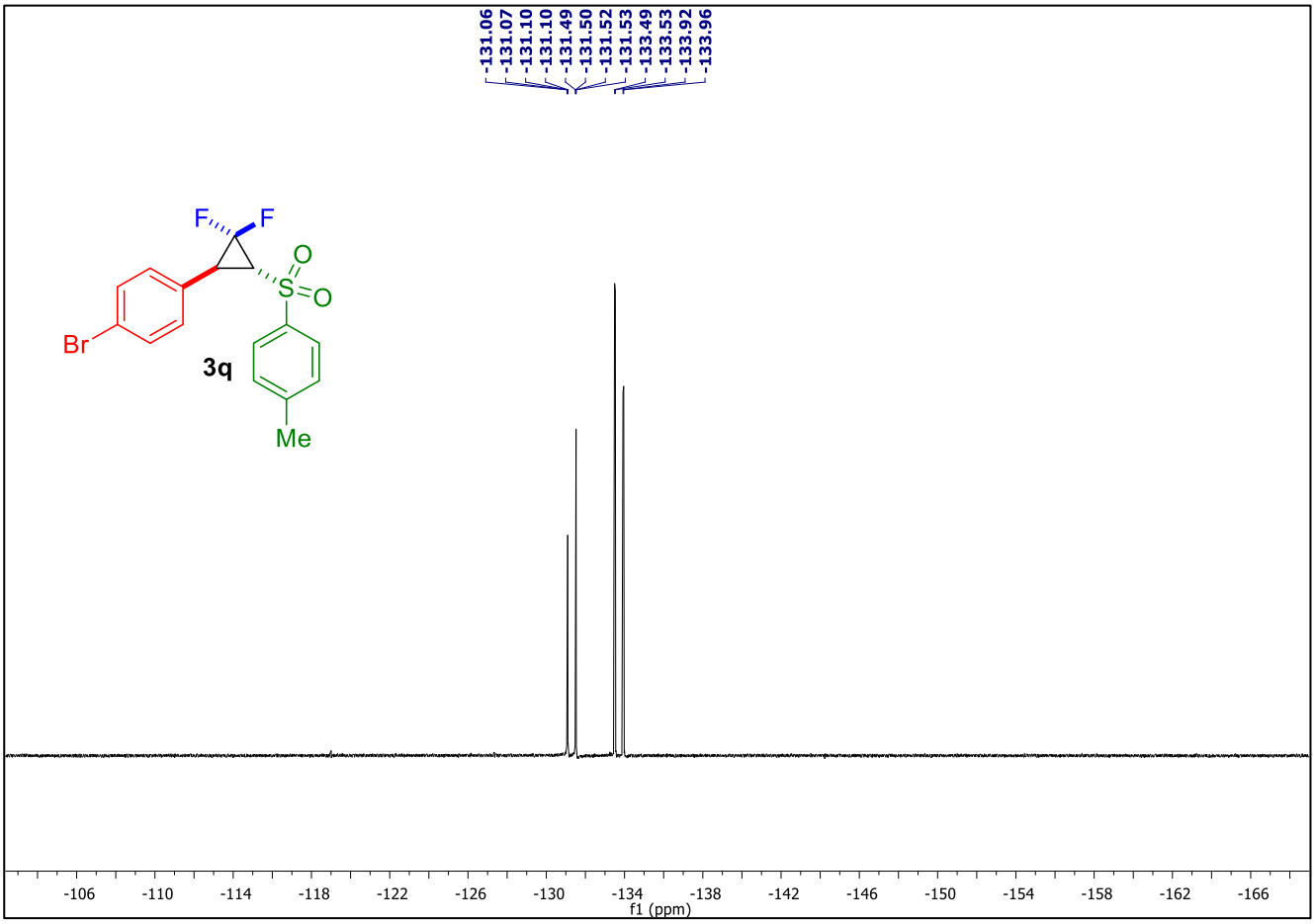

$^{19}$F NMR of Compound **3p** (376 MHz, $CDCl_3$)



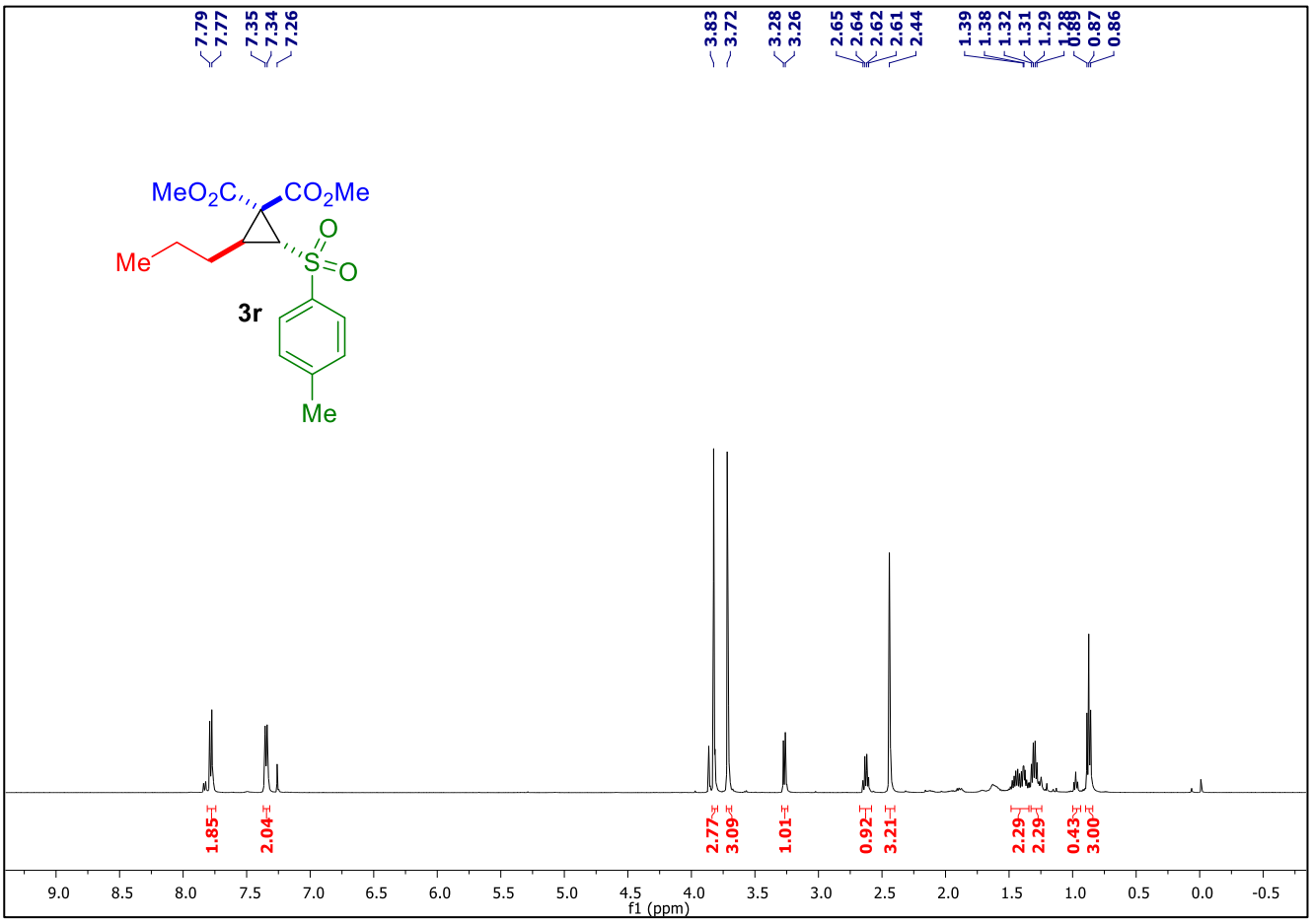

$^{1}$H NMR of Compound **3q** (400 MHz, $CDCl_3$)



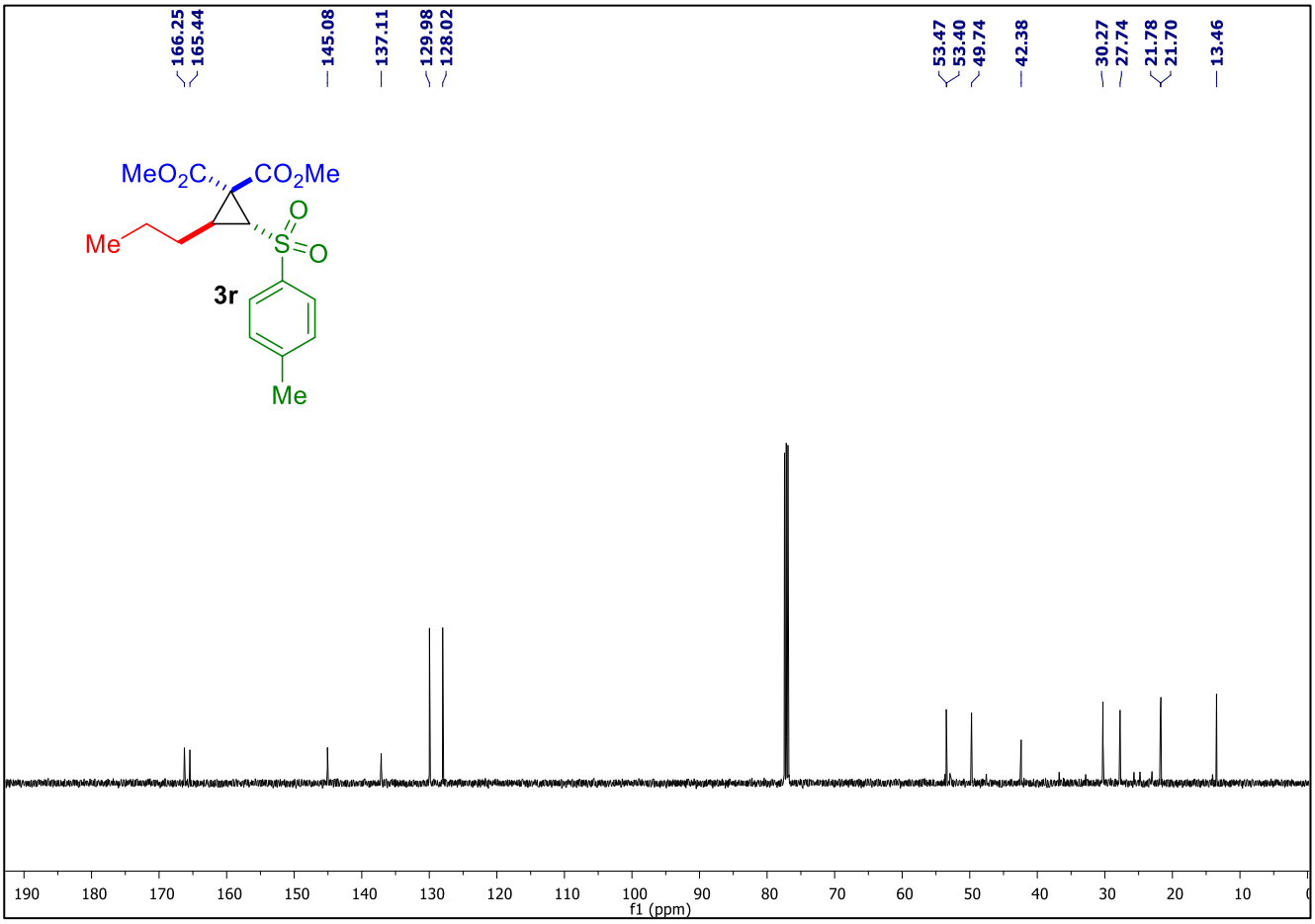

$^{13}$C NMR of Compound **3q** (126 MHz, $CDCl_3$)



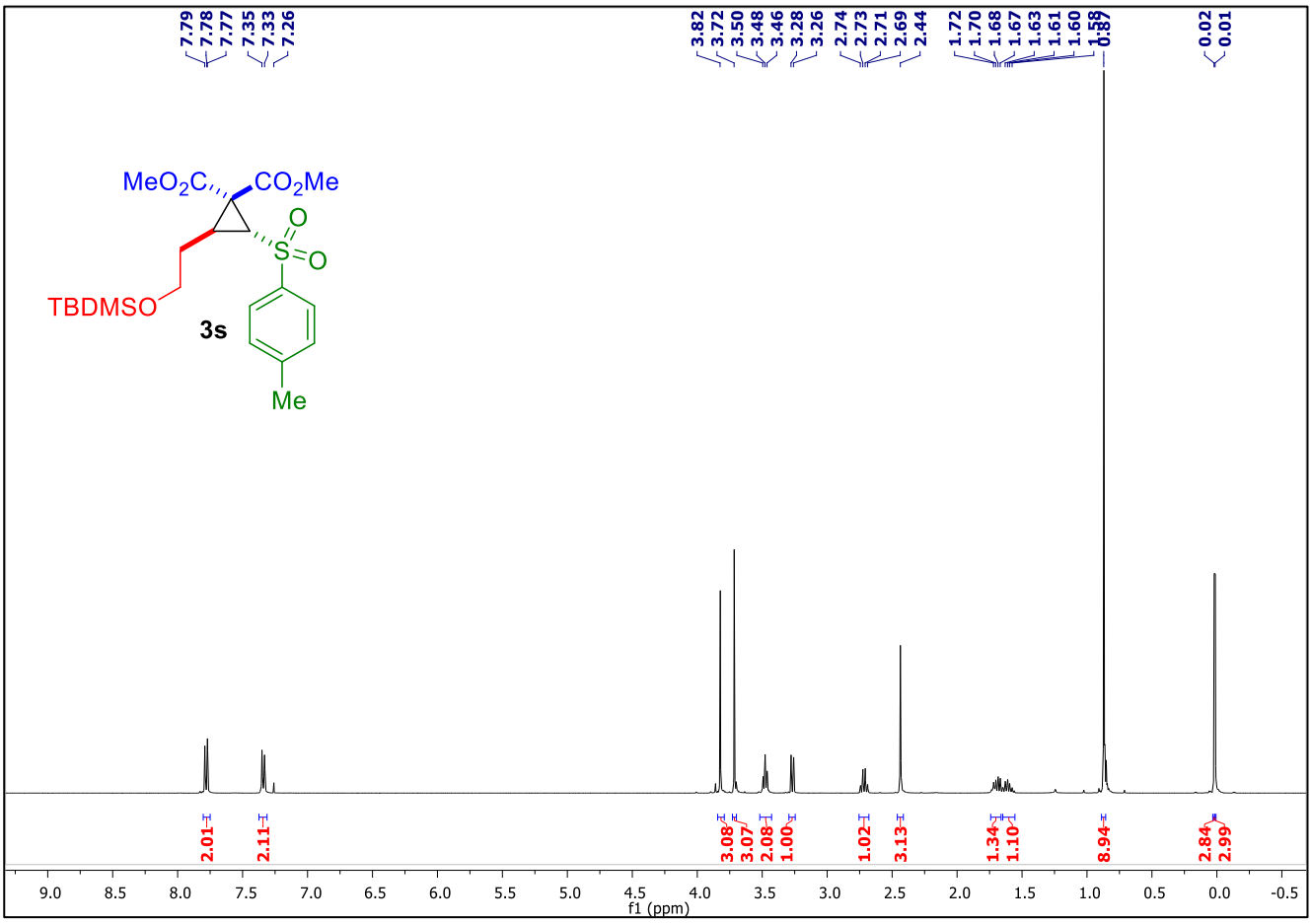

$^{19}$F NMR of Compound **3q** (376 MHz, $CDCl_3$)



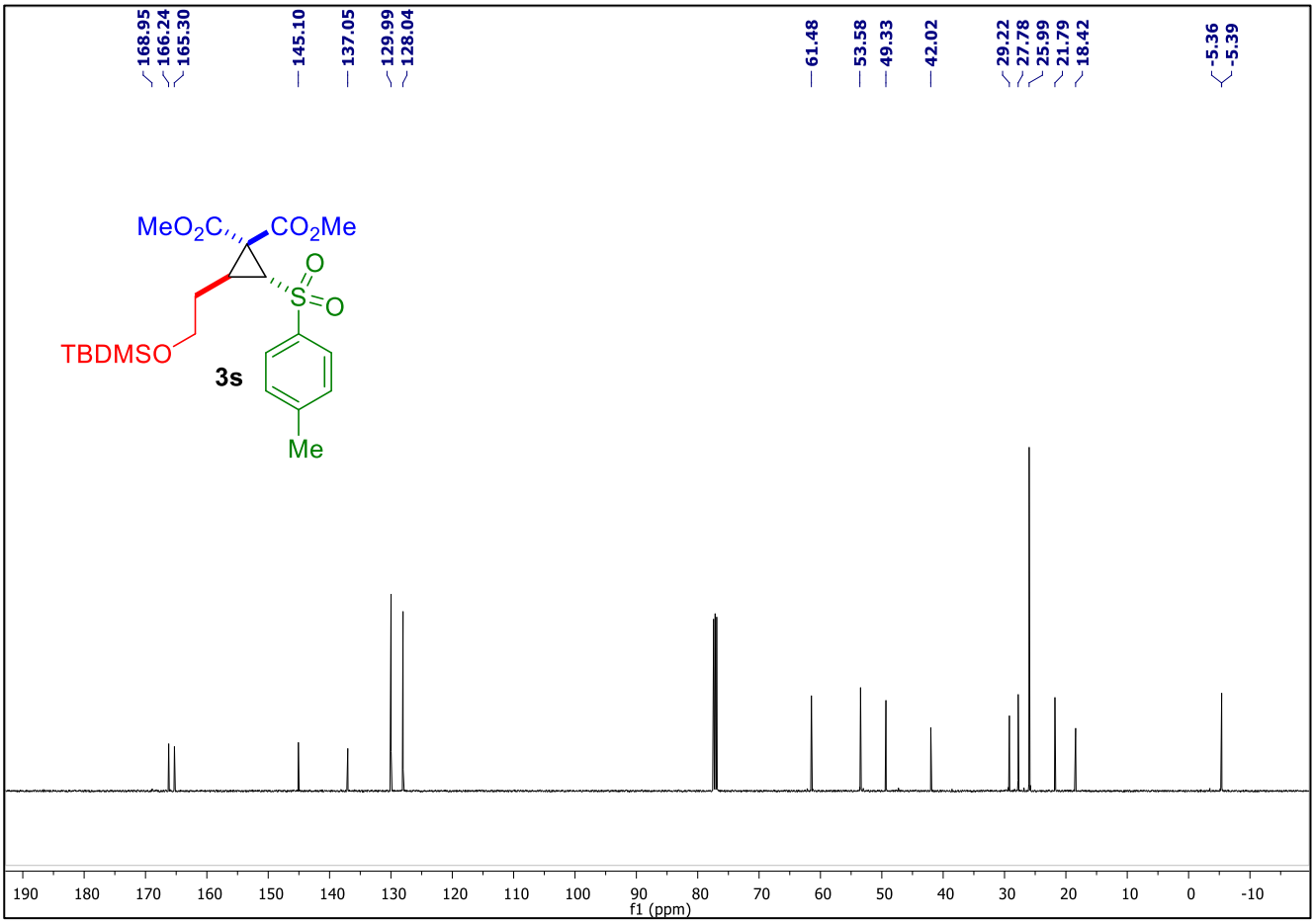

$^{1}$H NMR of Compound **3r** (500 MHz, $CDCl_3$) (dr = 1:0.4)



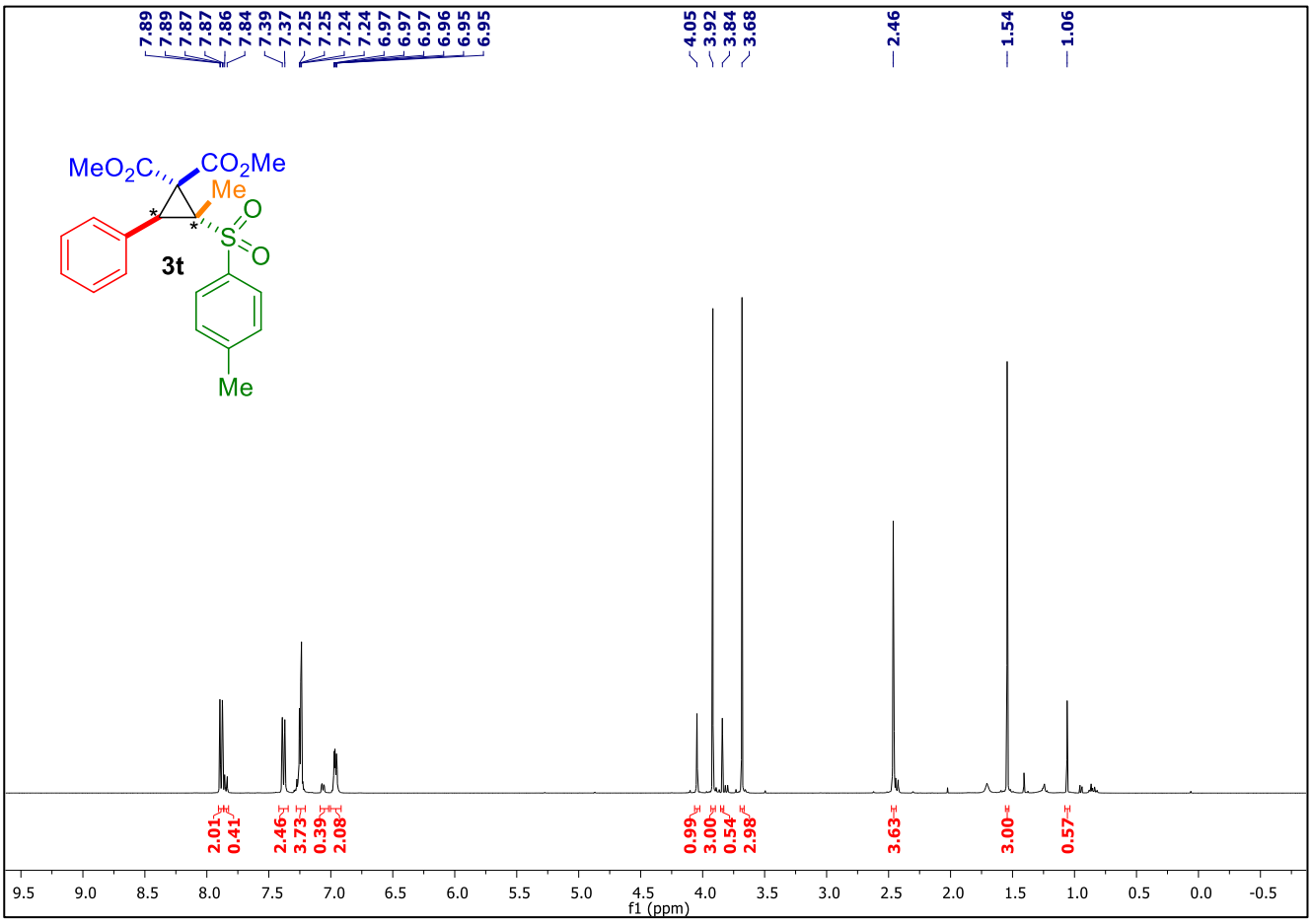

$^{13}$C NMR of Compound **3r** (126 MHz, $CDCl_3$) (dr = 1:0.4)



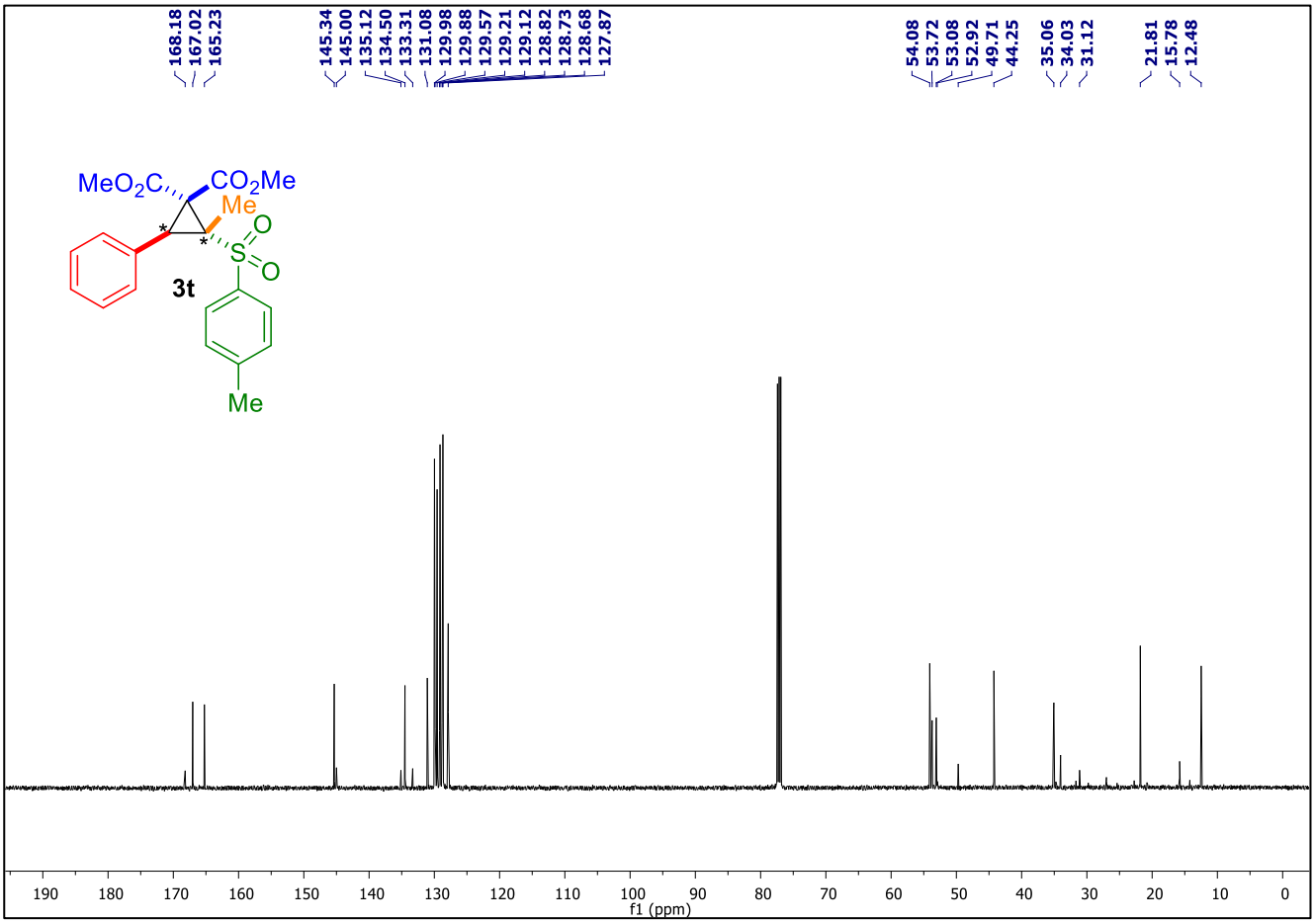

$^{1}$H NMR of Compound **3s** (400 MHz, $CDCl_3$)



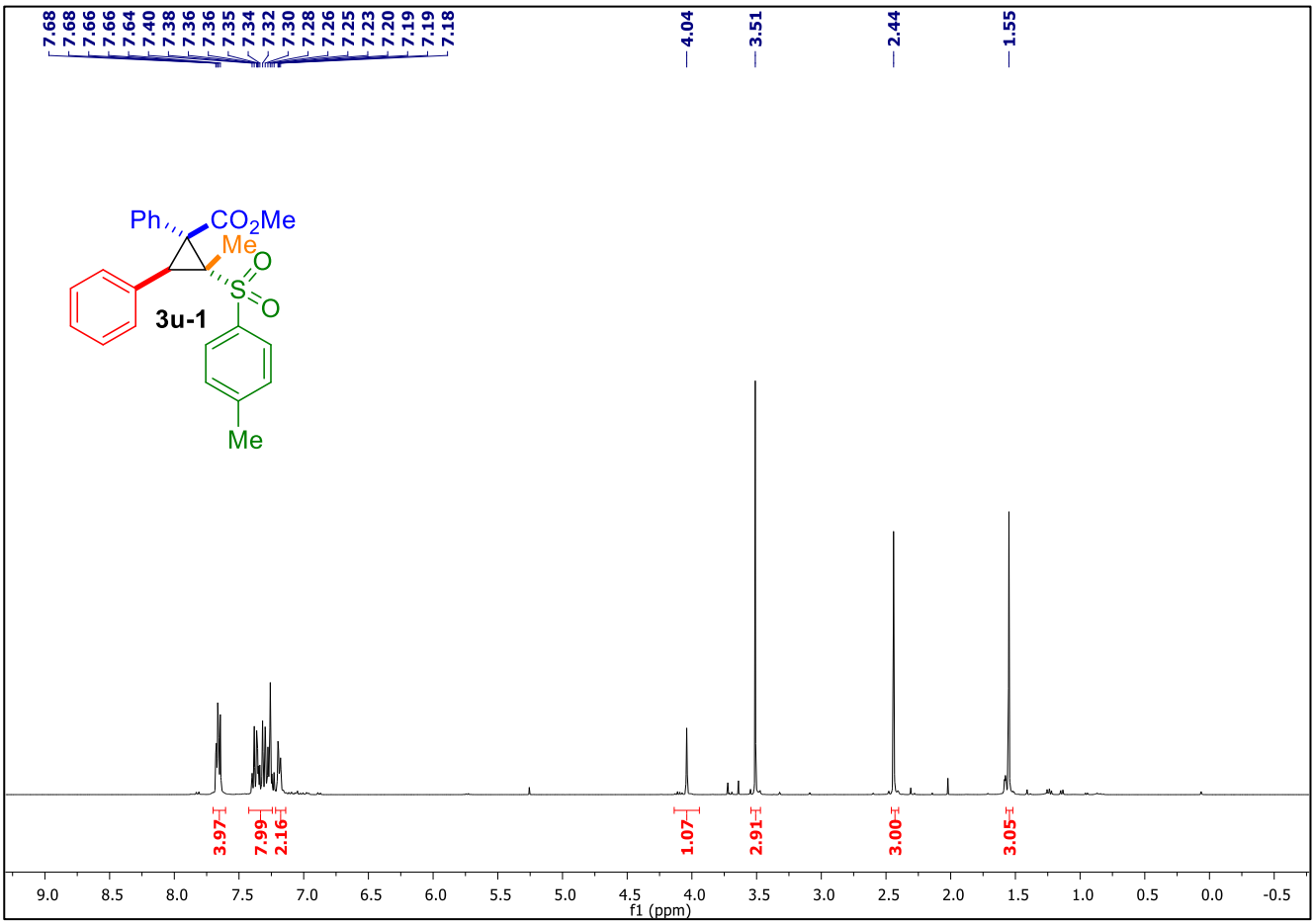

$^{13}$C NMR of Compound **3s** (126 MHz, $CDCl_3$)



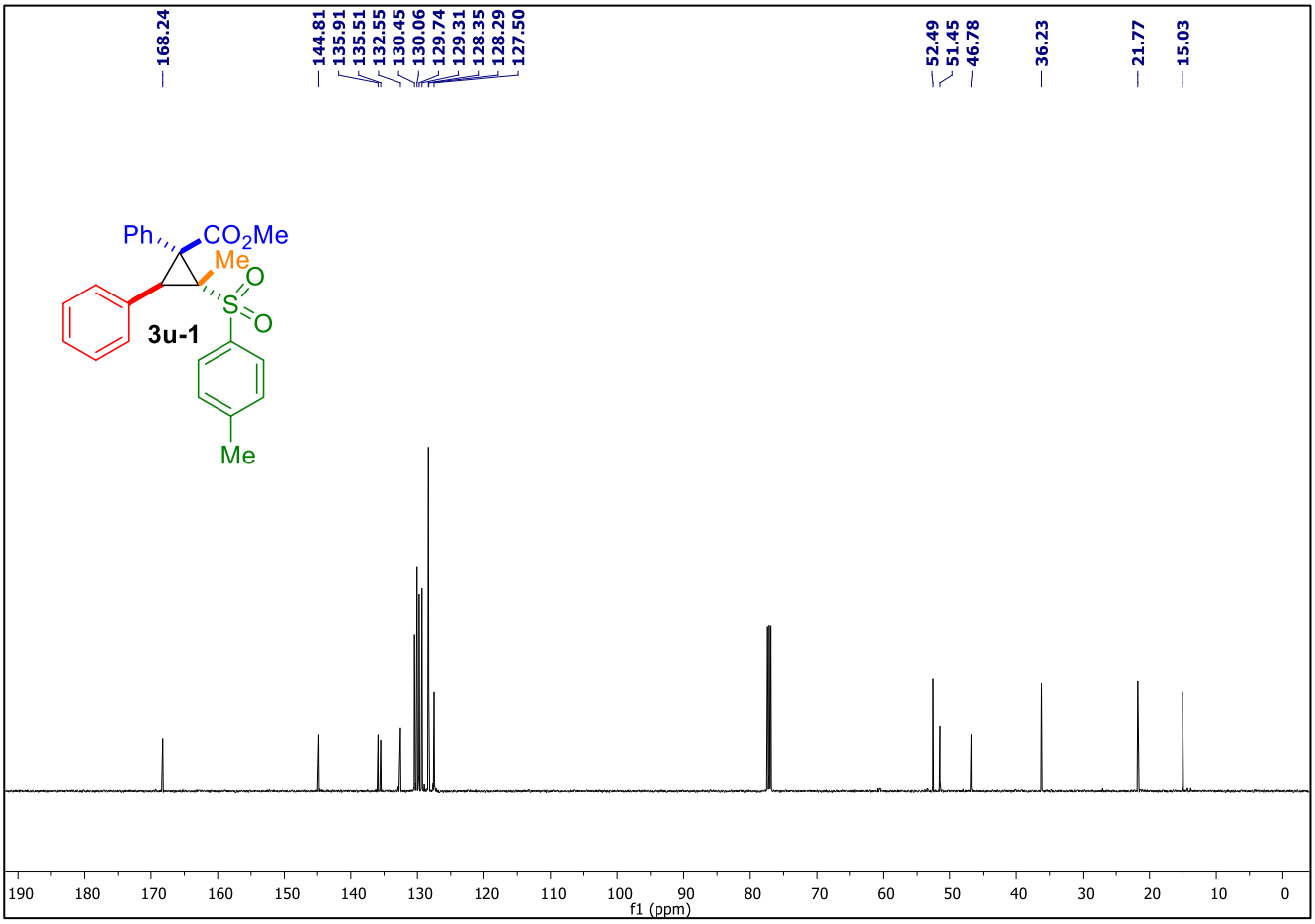

$^{1}$H NMR of Compound **3t** (400 MHz, $CDCl_3$)



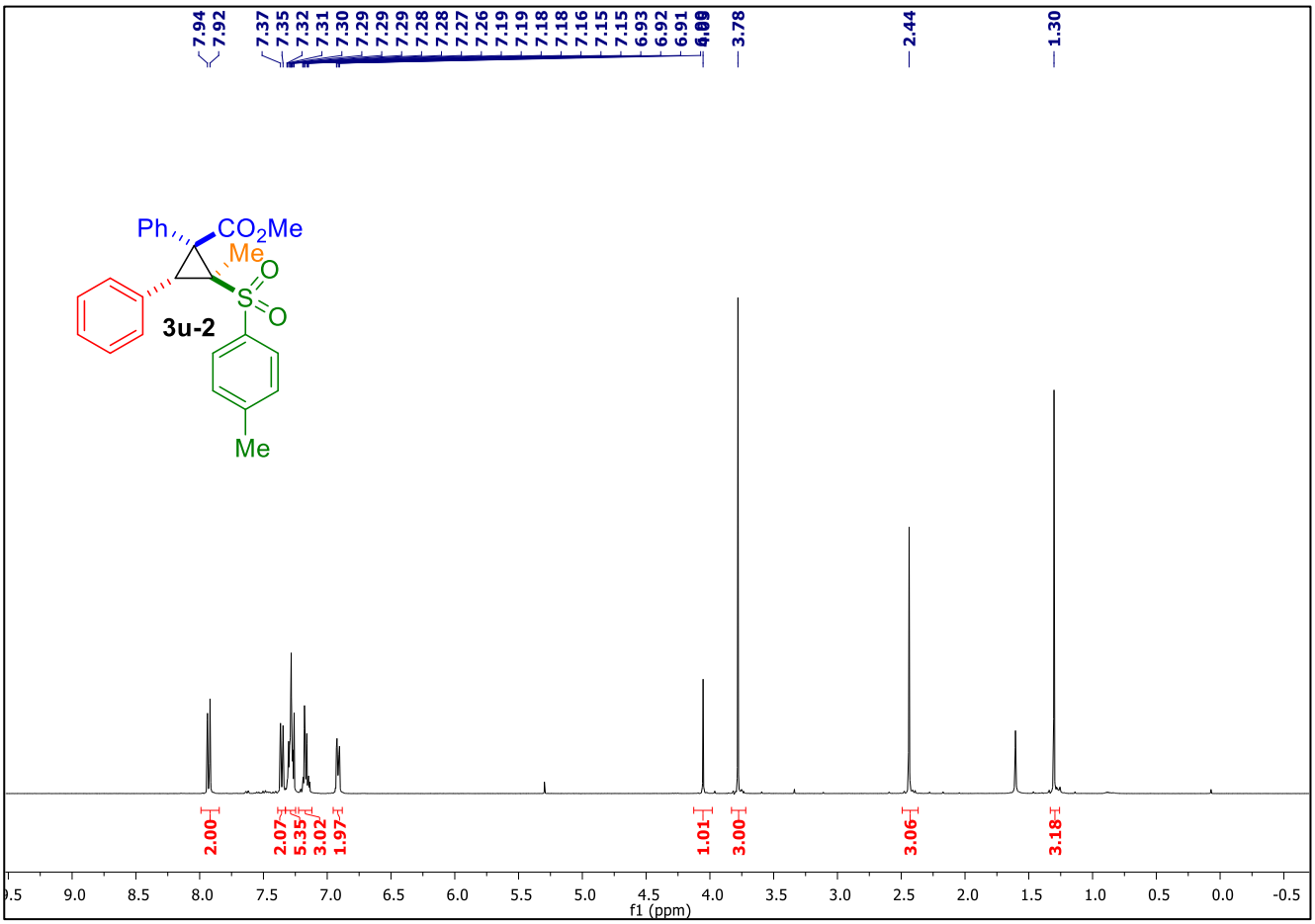

$^{13}$C NMR of Compound **3t** (126 MHz, $CDCl_3$)



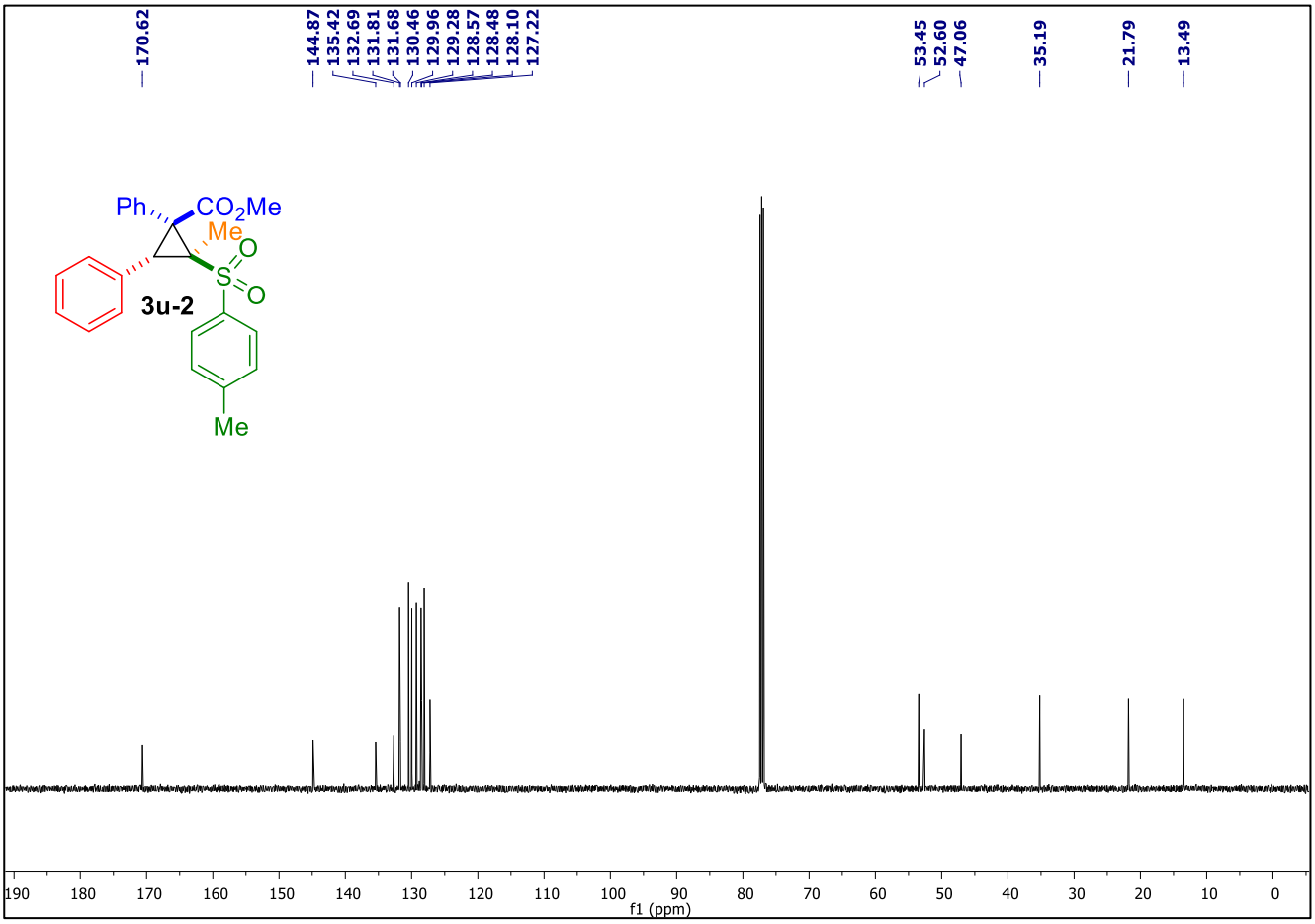

$^{1}$H NMR of Compound **3u-1** (400 MHz, $CDCl_3$)



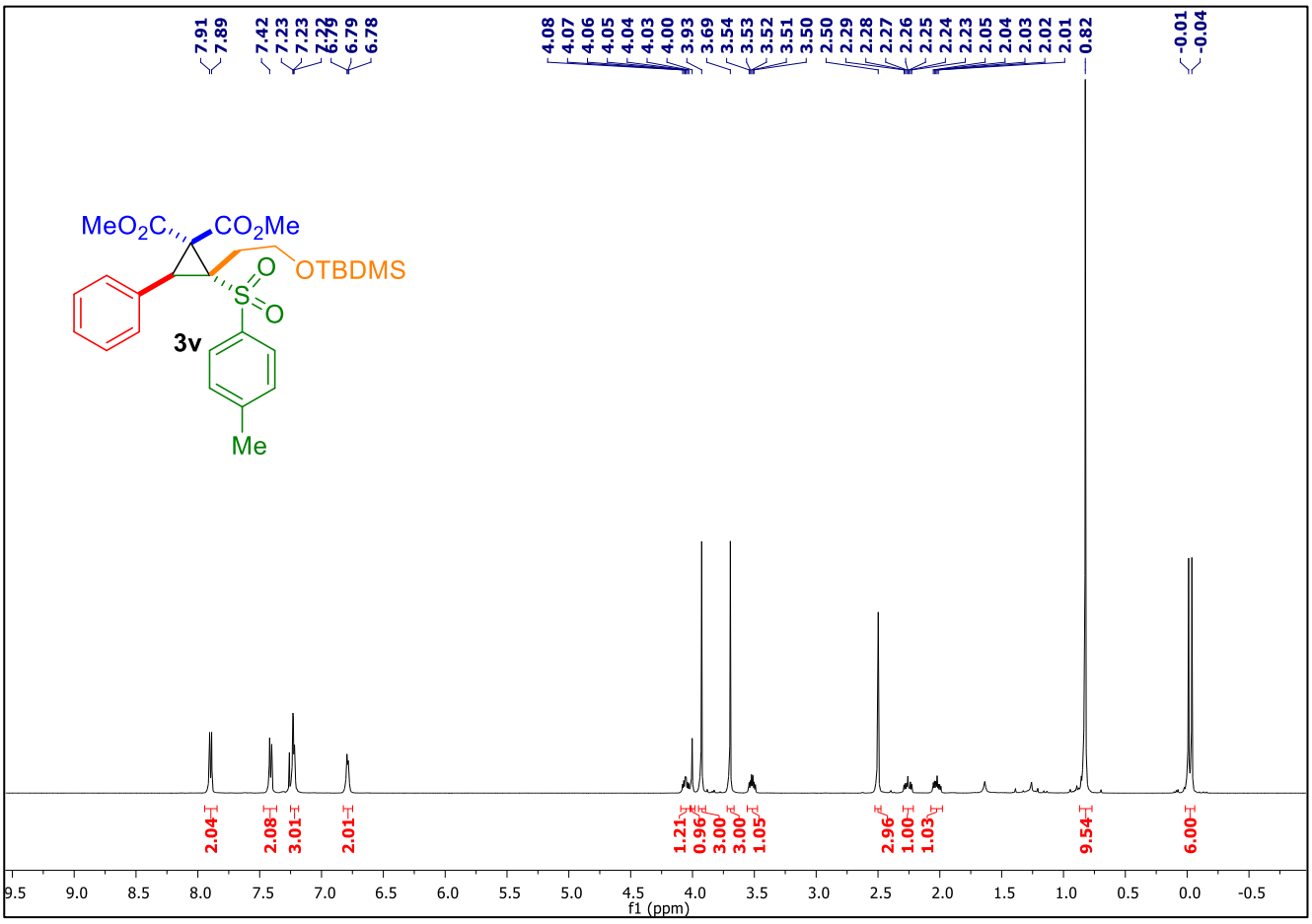

$^{13}$C NMR of Compound **3u-1** (126 MHz, $CDCl_3$)



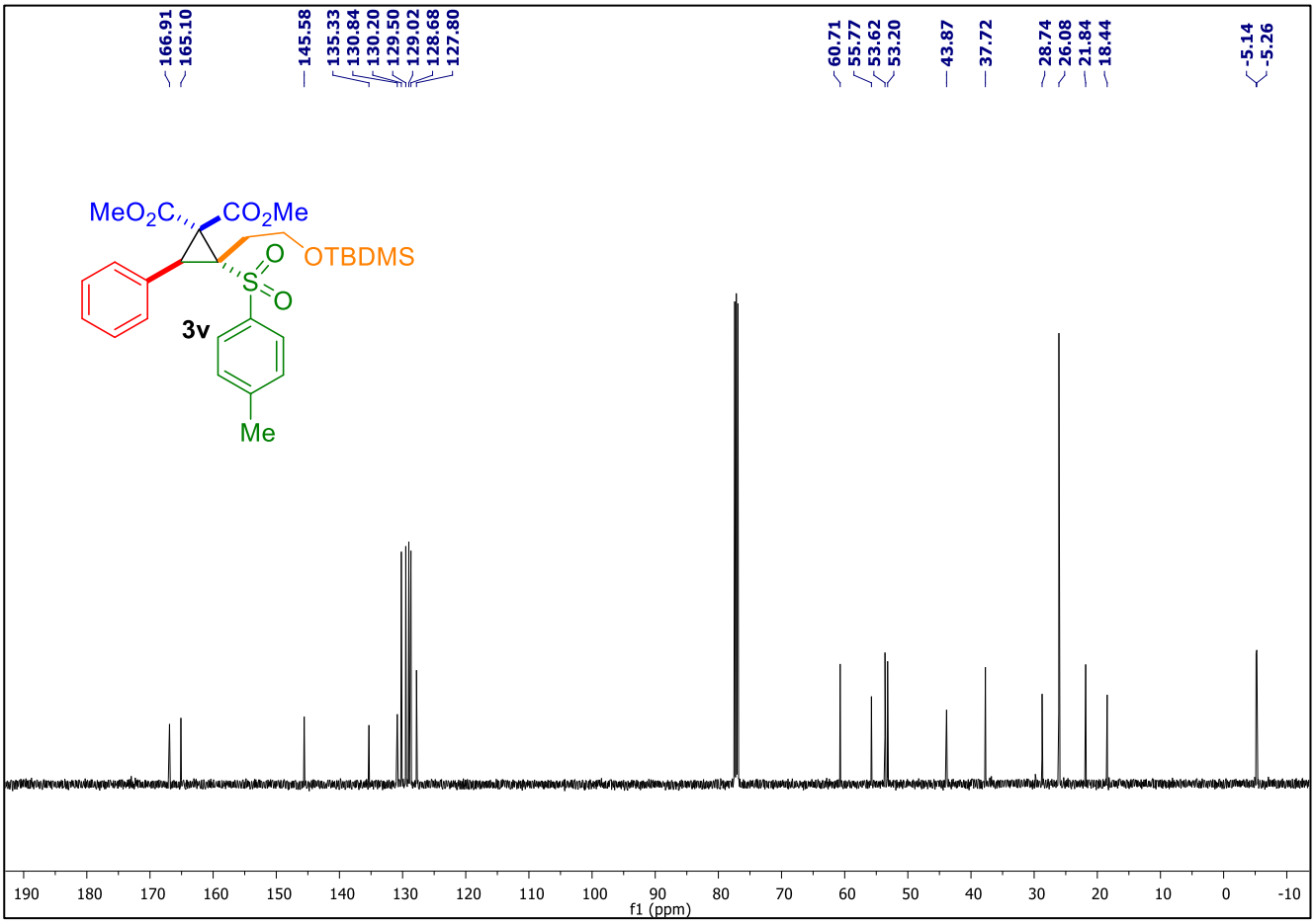

$^{1}$H NMR of Compound **3u-2** (400 MHz, $CDCl_3$)



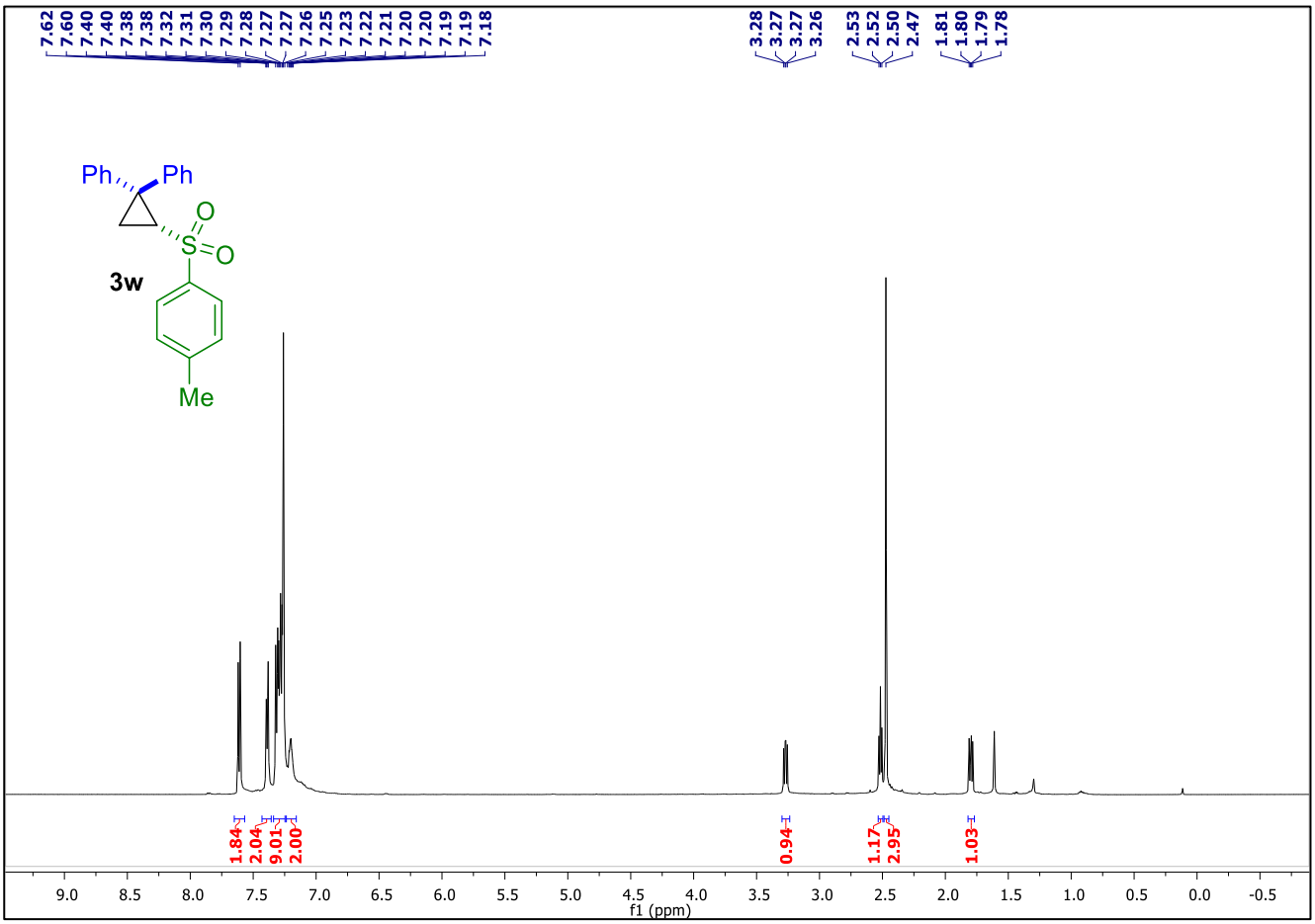

$^{13}$C NMR of Compound **3u-2** (126 MHz, $CDCl_3$)



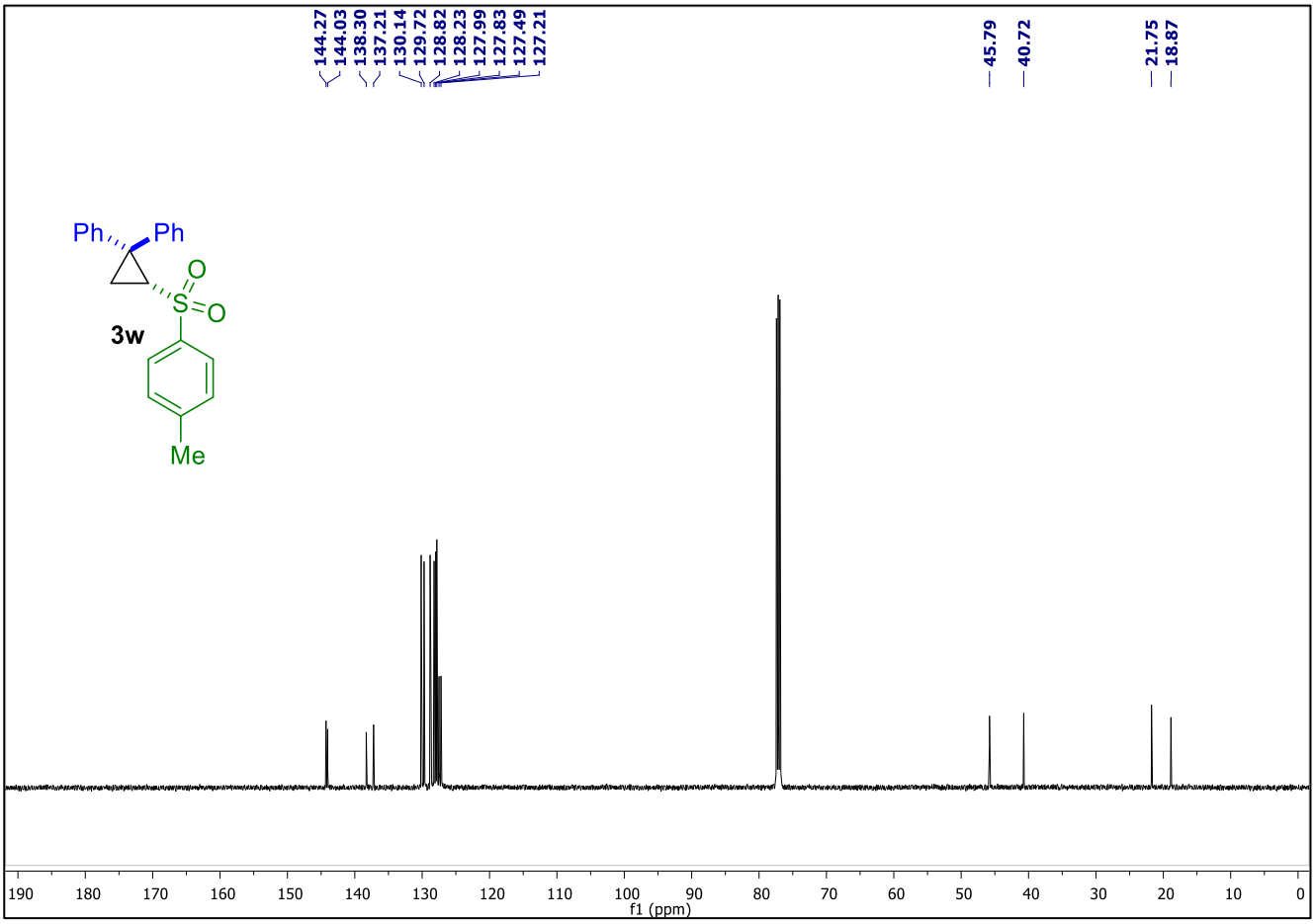

$^{1}$H NMR of Compound **3v** (500 MHz, $CDCl_3$)



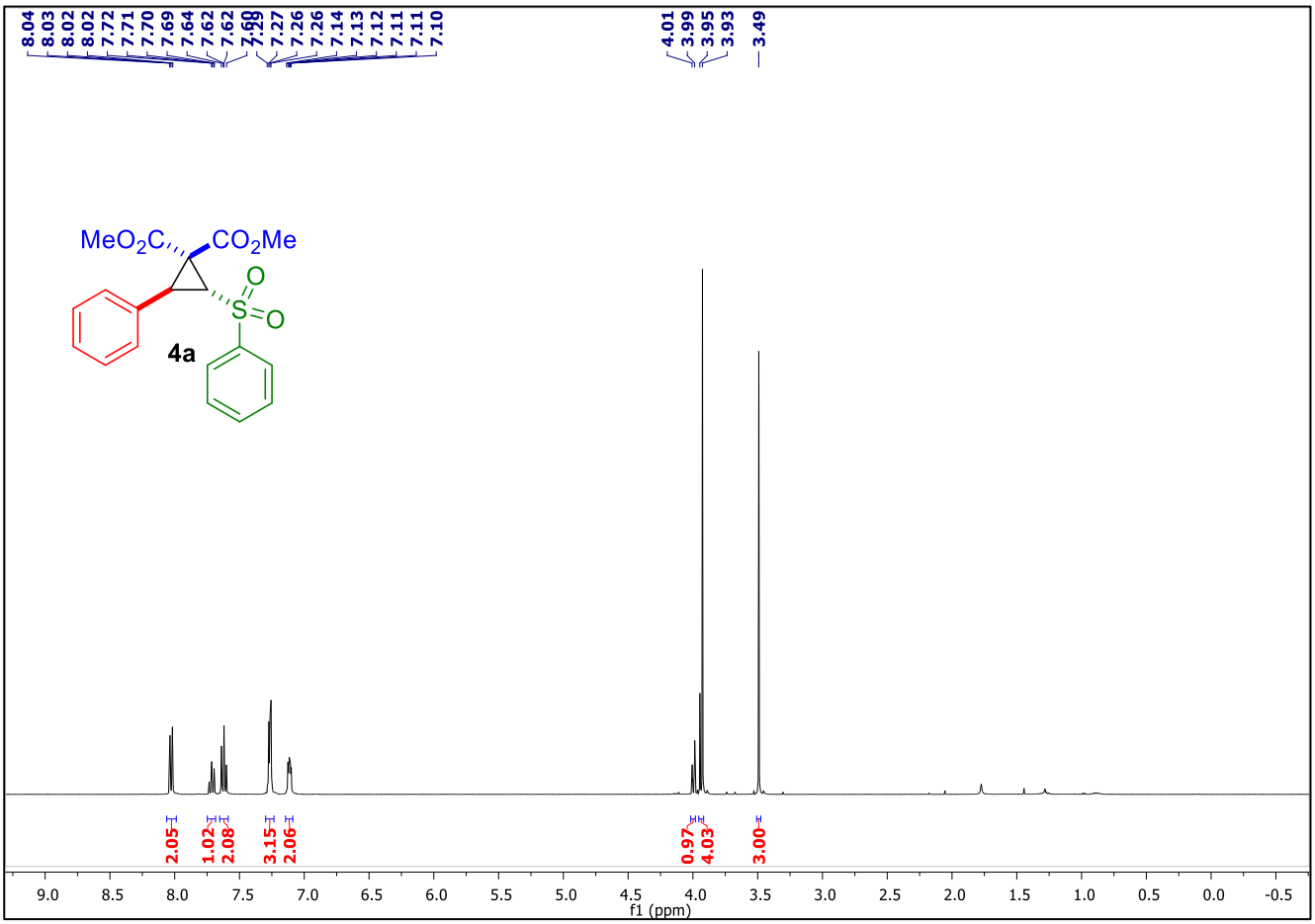

$^{13}$C NMR of Compound **3v** (126 MHz, $CDCl_3$)



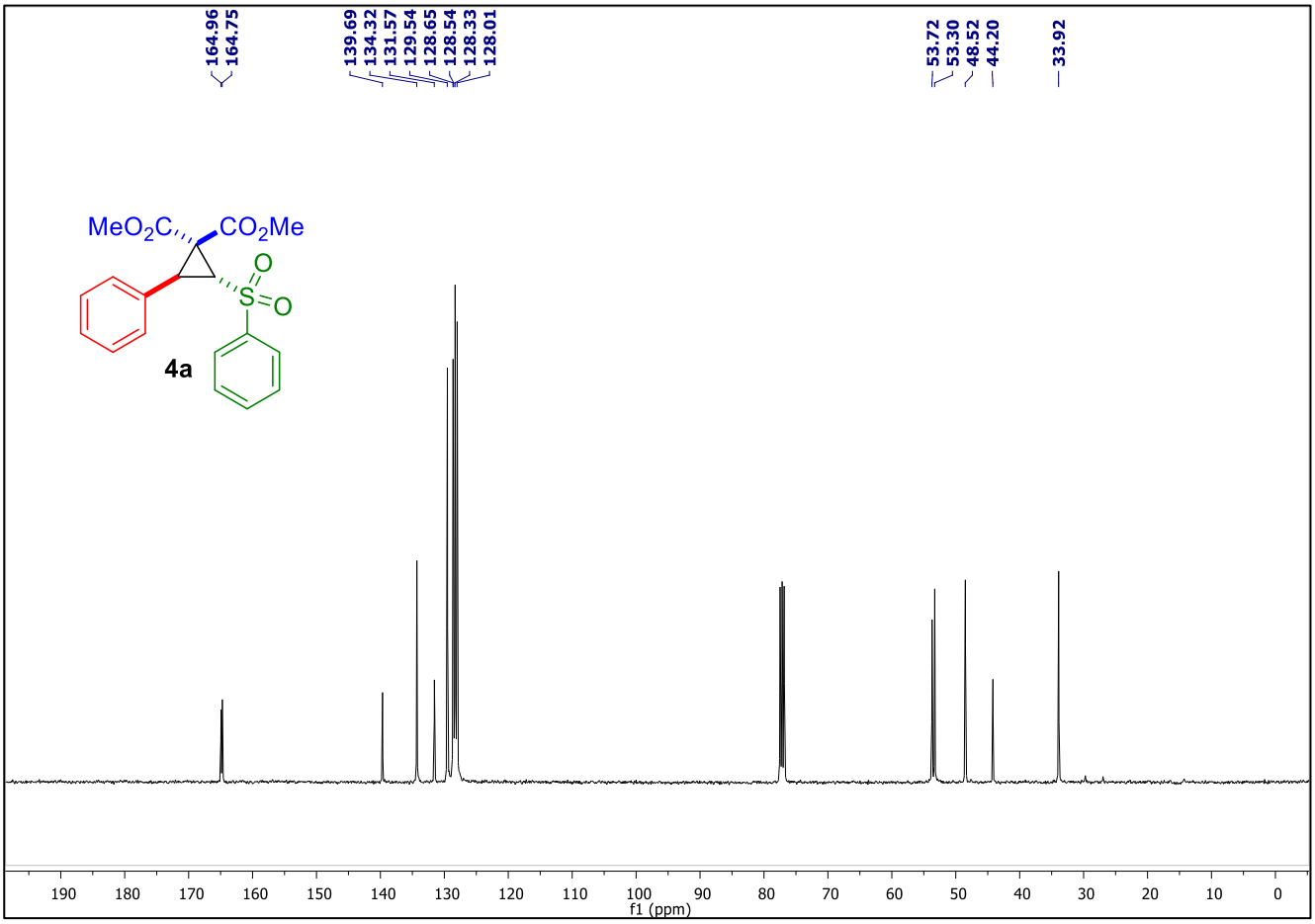

$^{1}$H NMR of Compound **3w** (400 MHz, $CDCl_3$)



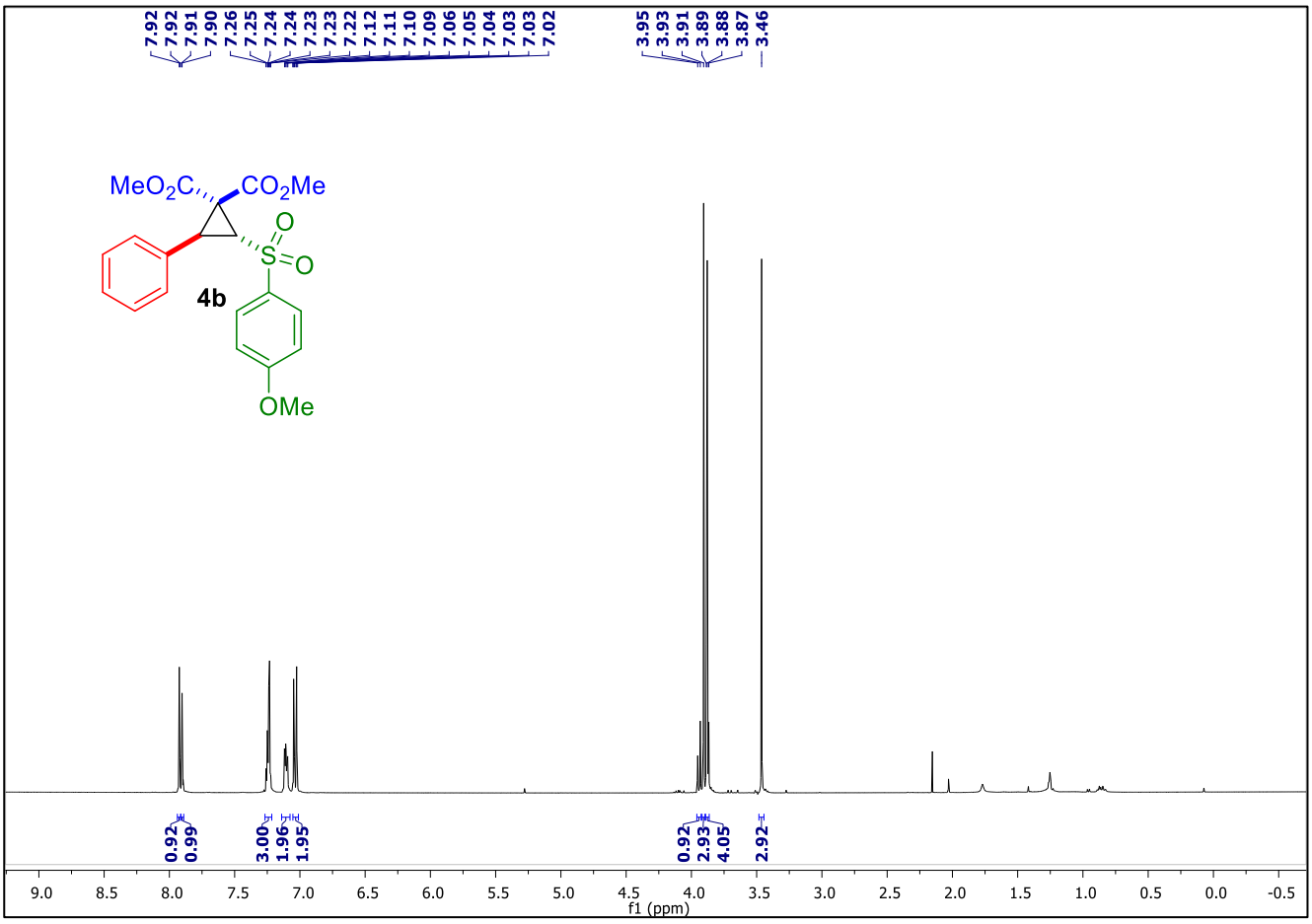

$^{13}$C NMR of Compound **3w** (126 MHz, $CDCl_3$)



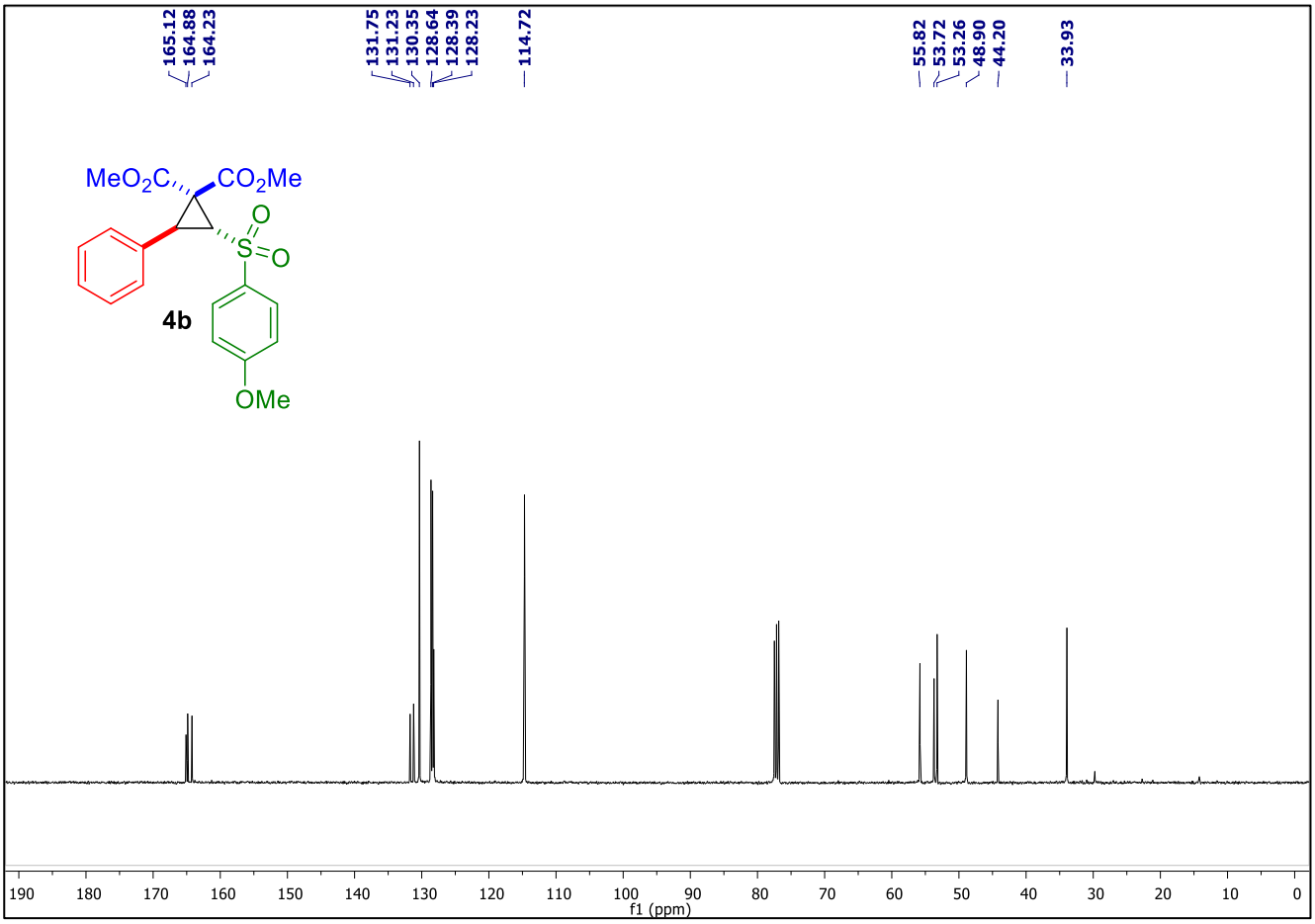

$^{1}$H NMR of Compound **4a** (400 MHz, $CDCl_3$)



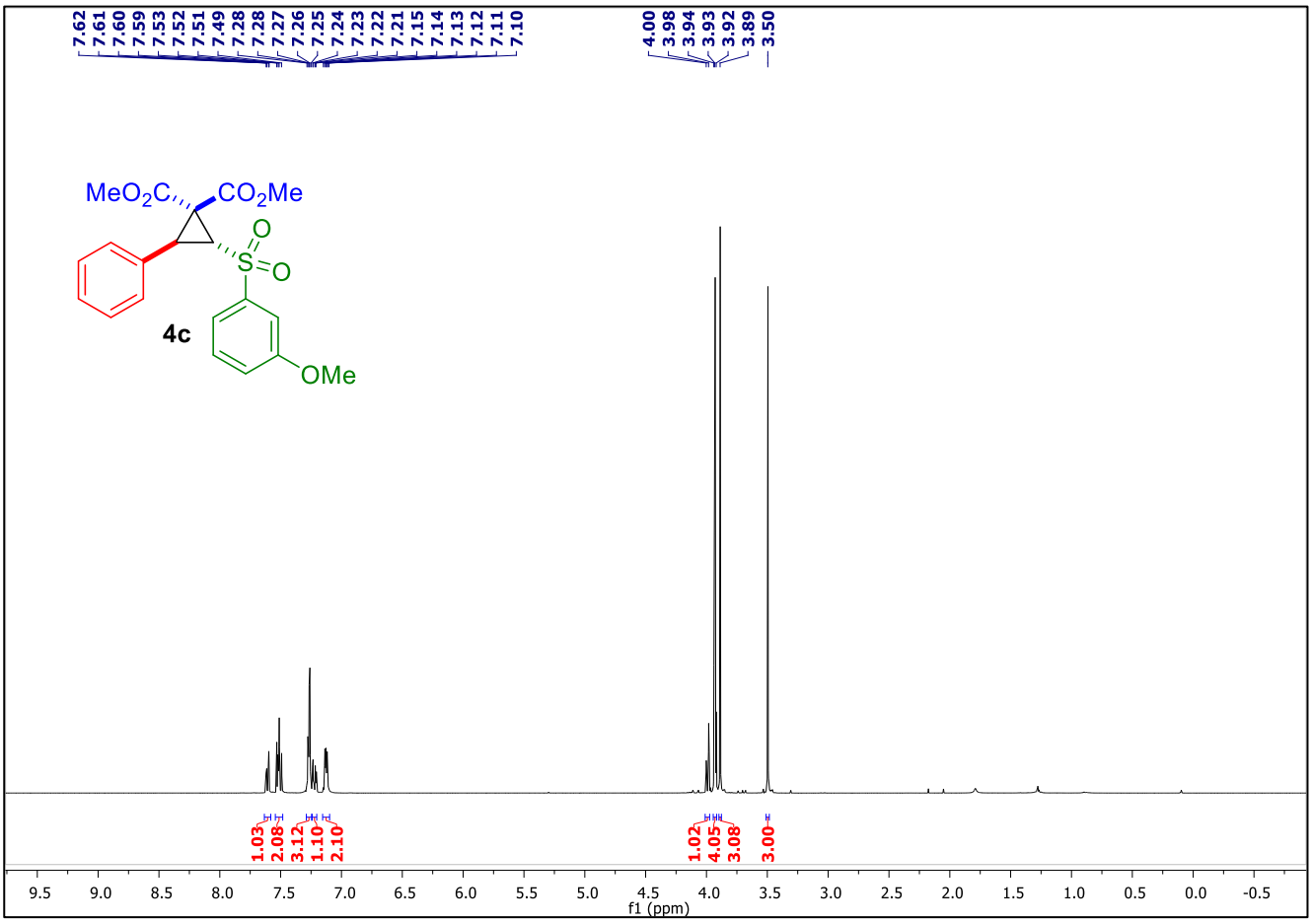

$^{13}$C NMR of Compound **4a** (101 MHz, $CDCl_3$)



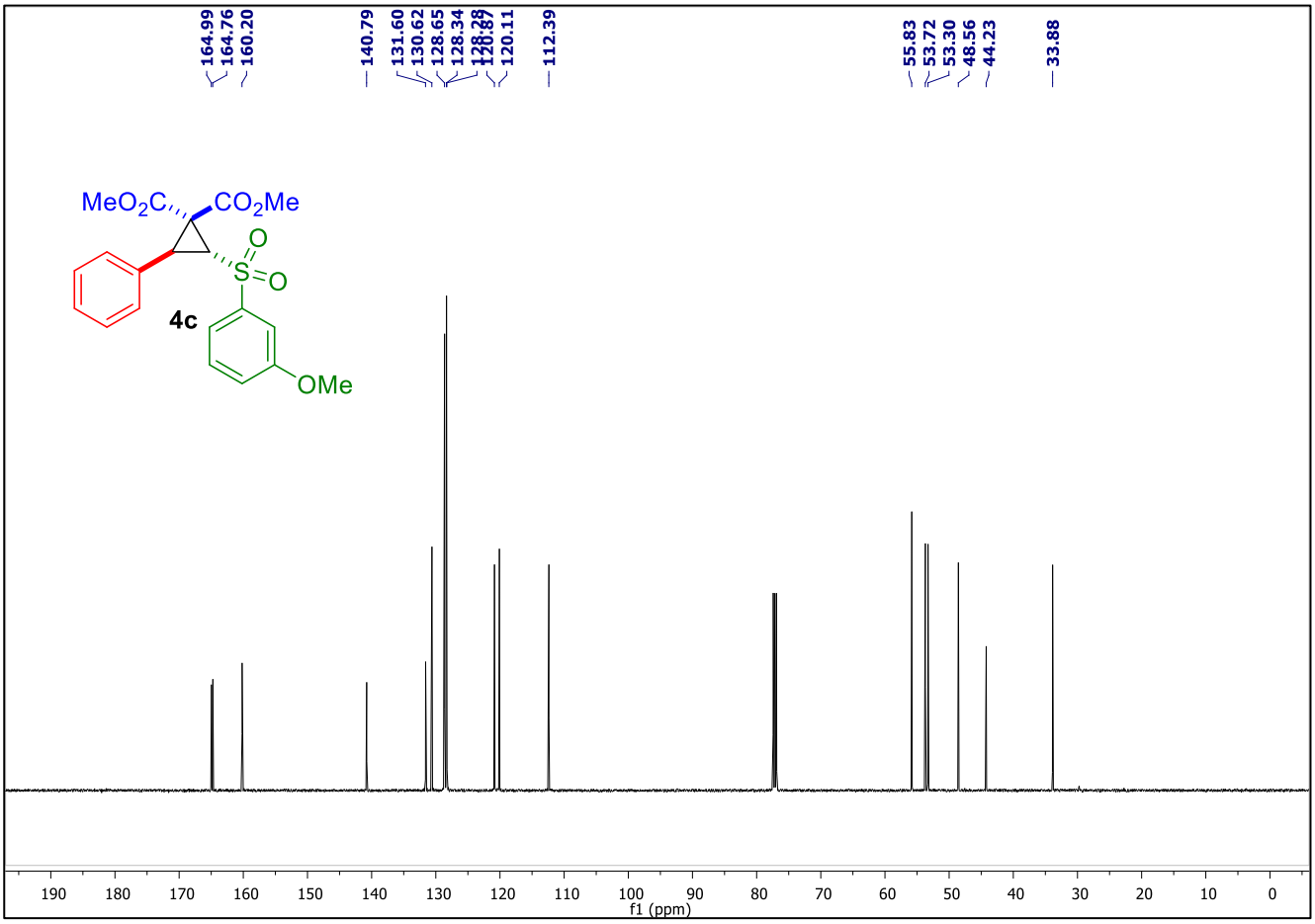

$^{1}$H NMR of Compound **4b** (400 MHz, $CDCl_3$)



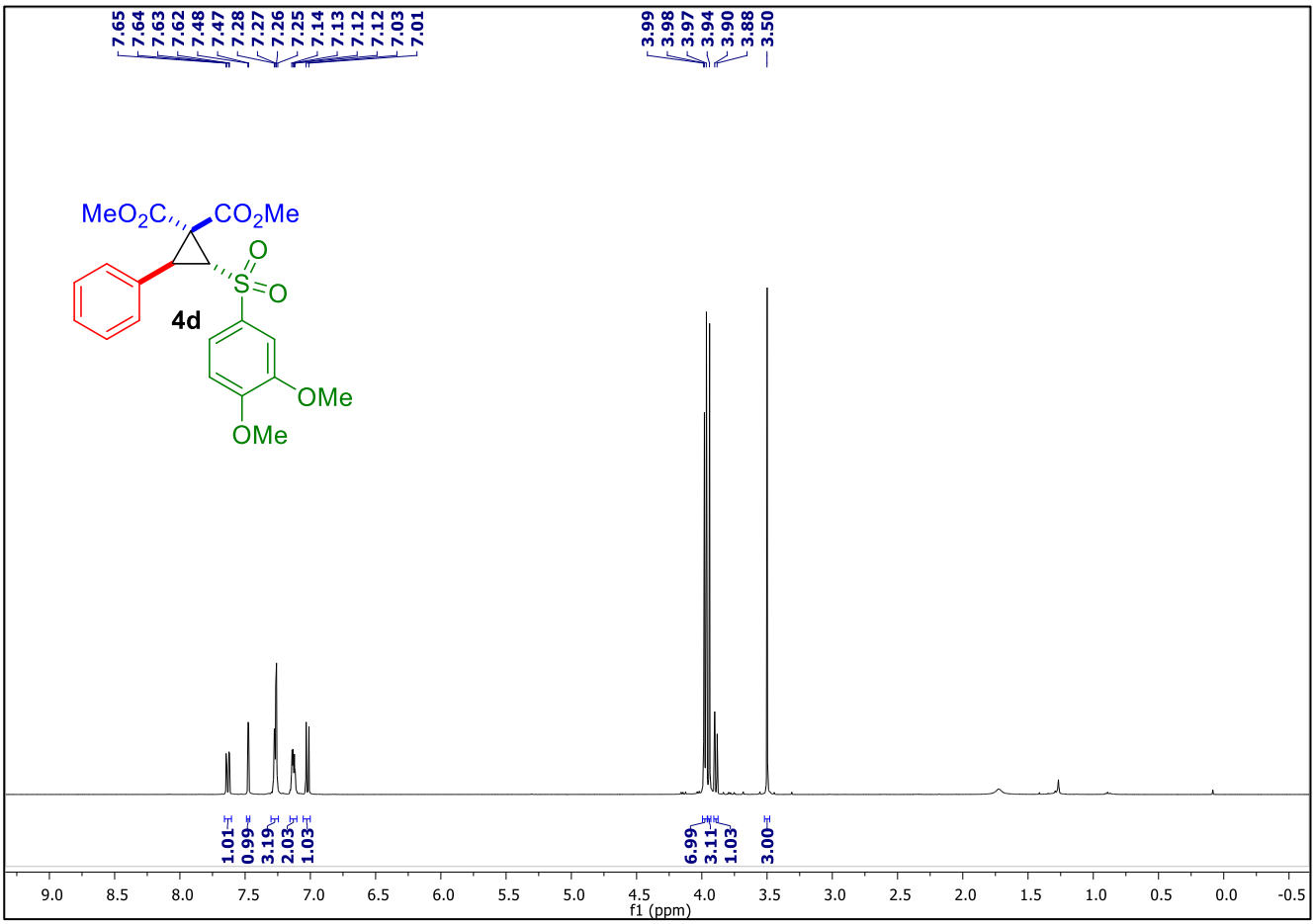

$^{13}$C NMR of Compound **4b** (101 MHz, $CDCl_3$)



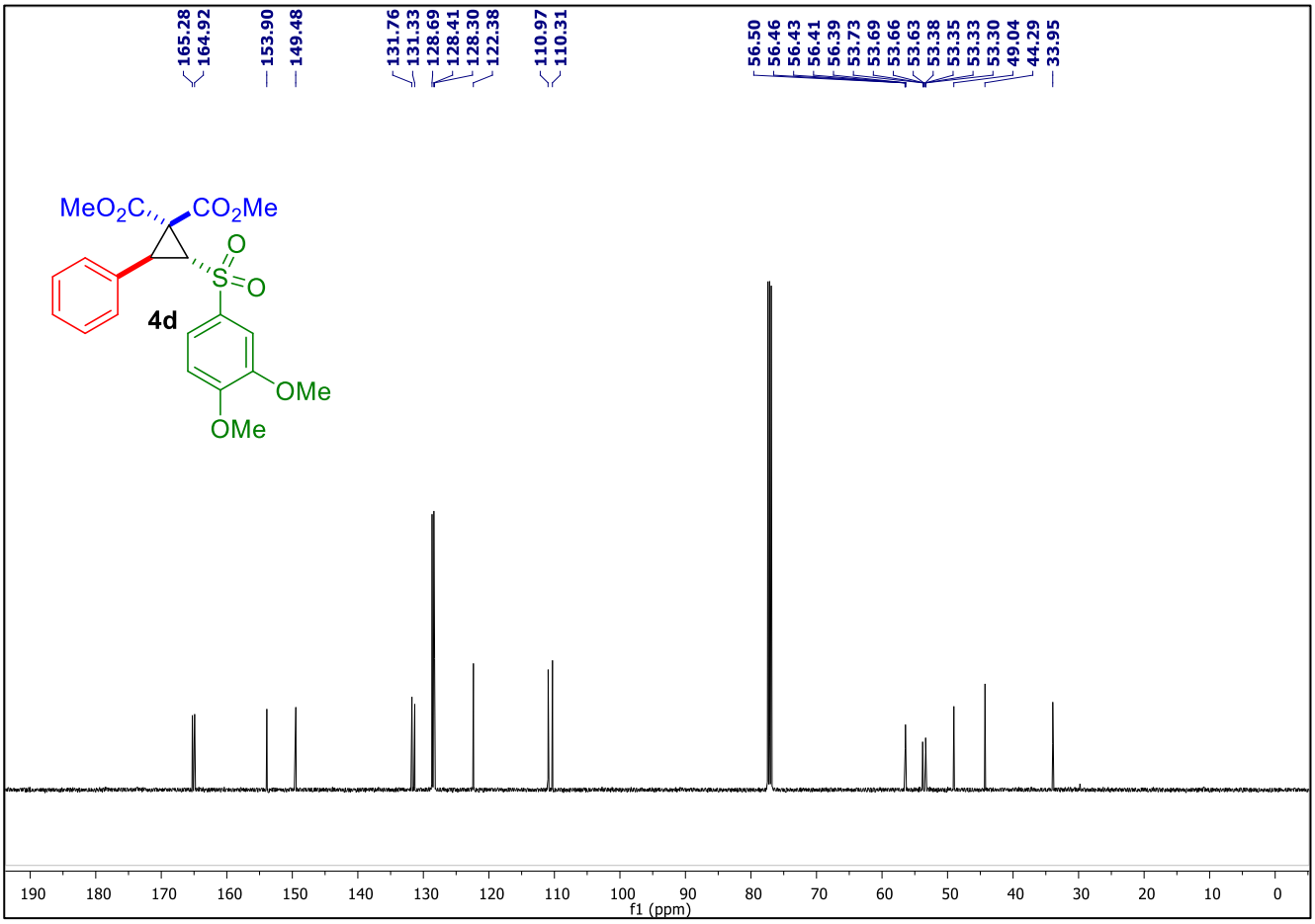

$^{1}$H NMR of Compound **4c** (400 MHz, $CDCl_3$)



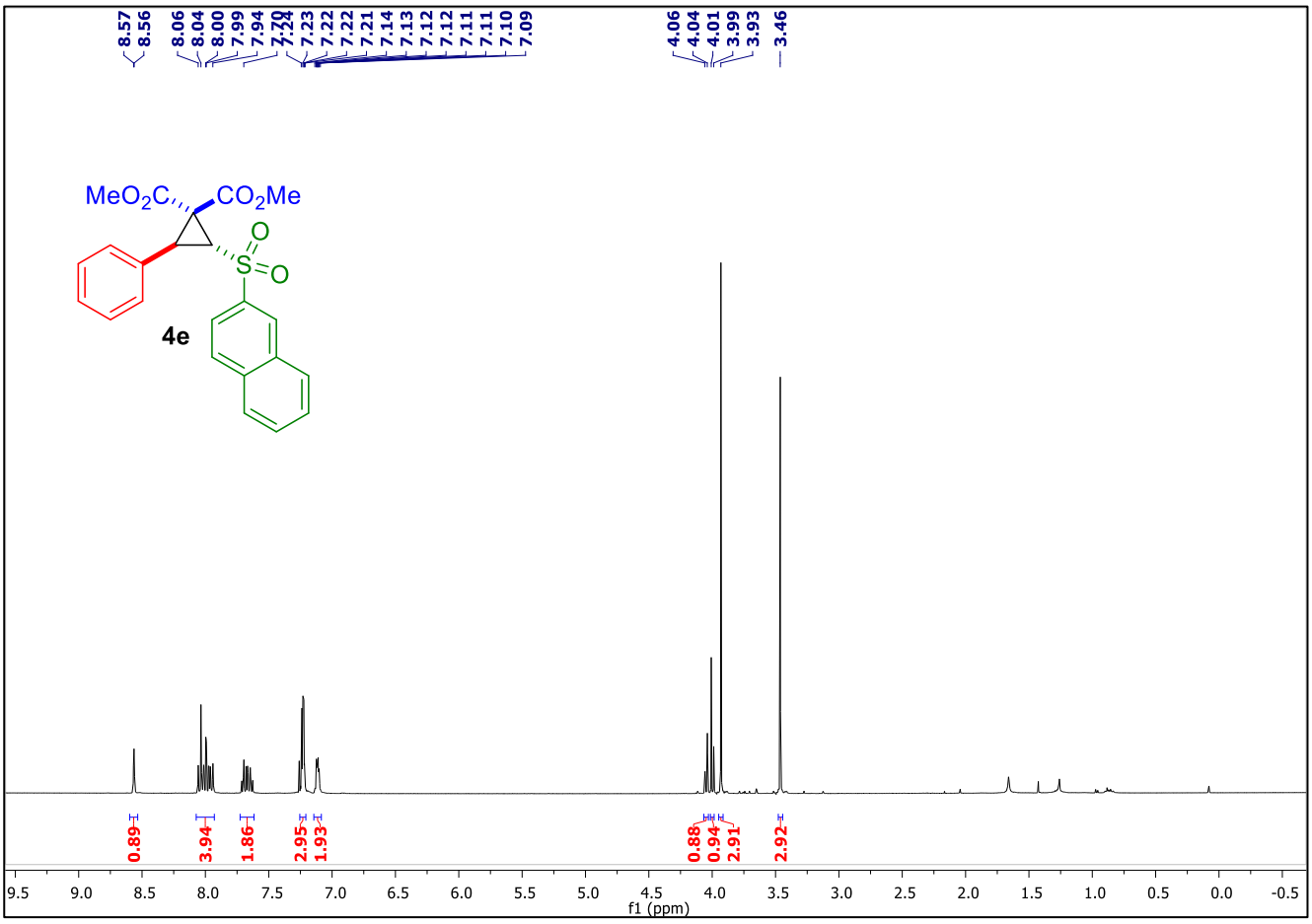

$^{13}$C NMR of Compound **4c** (126 MHz, $CDCl_3$)



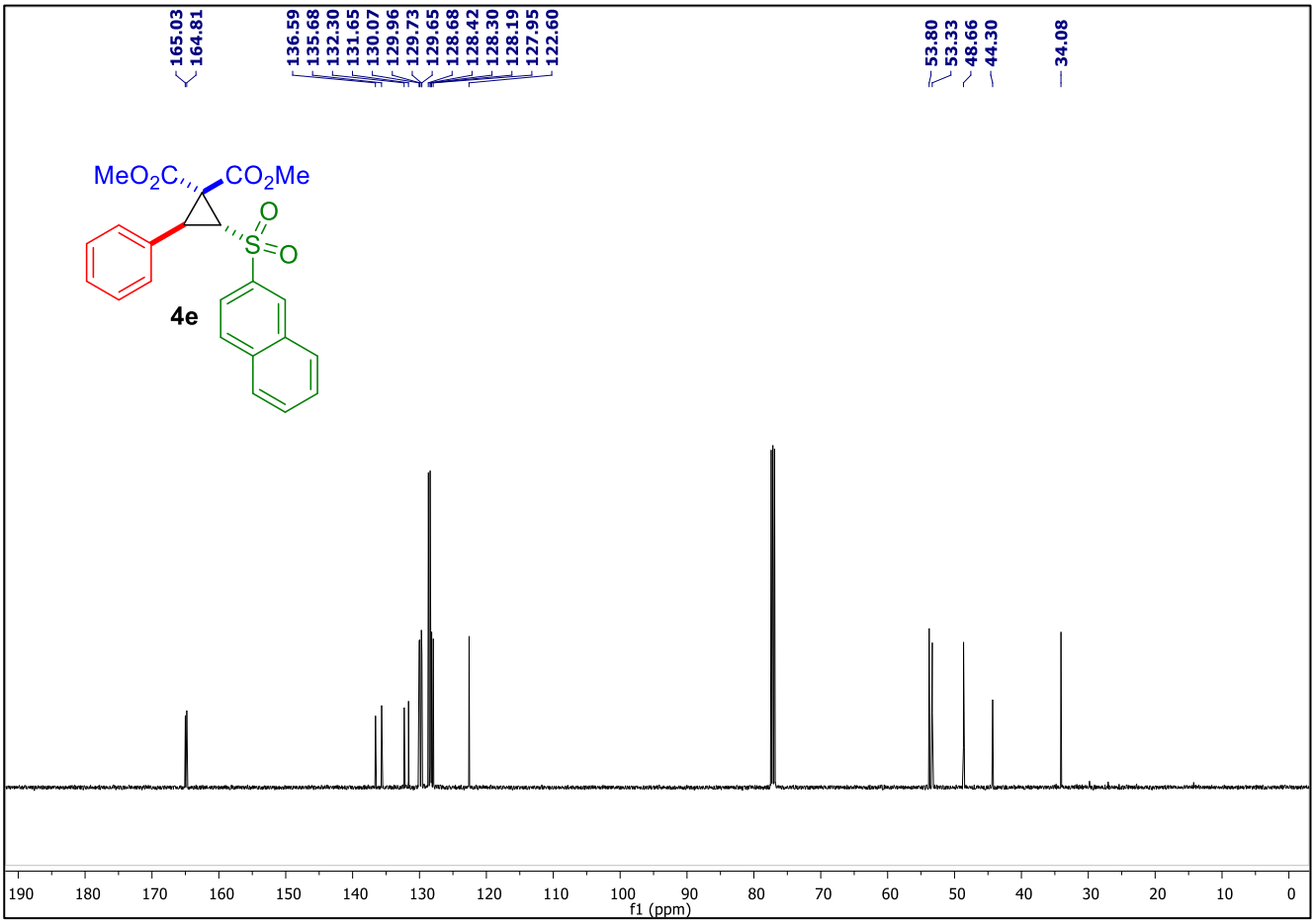

$^{1}$H NMR of Compound **4d** (400 MHz, $CDCl_3$)



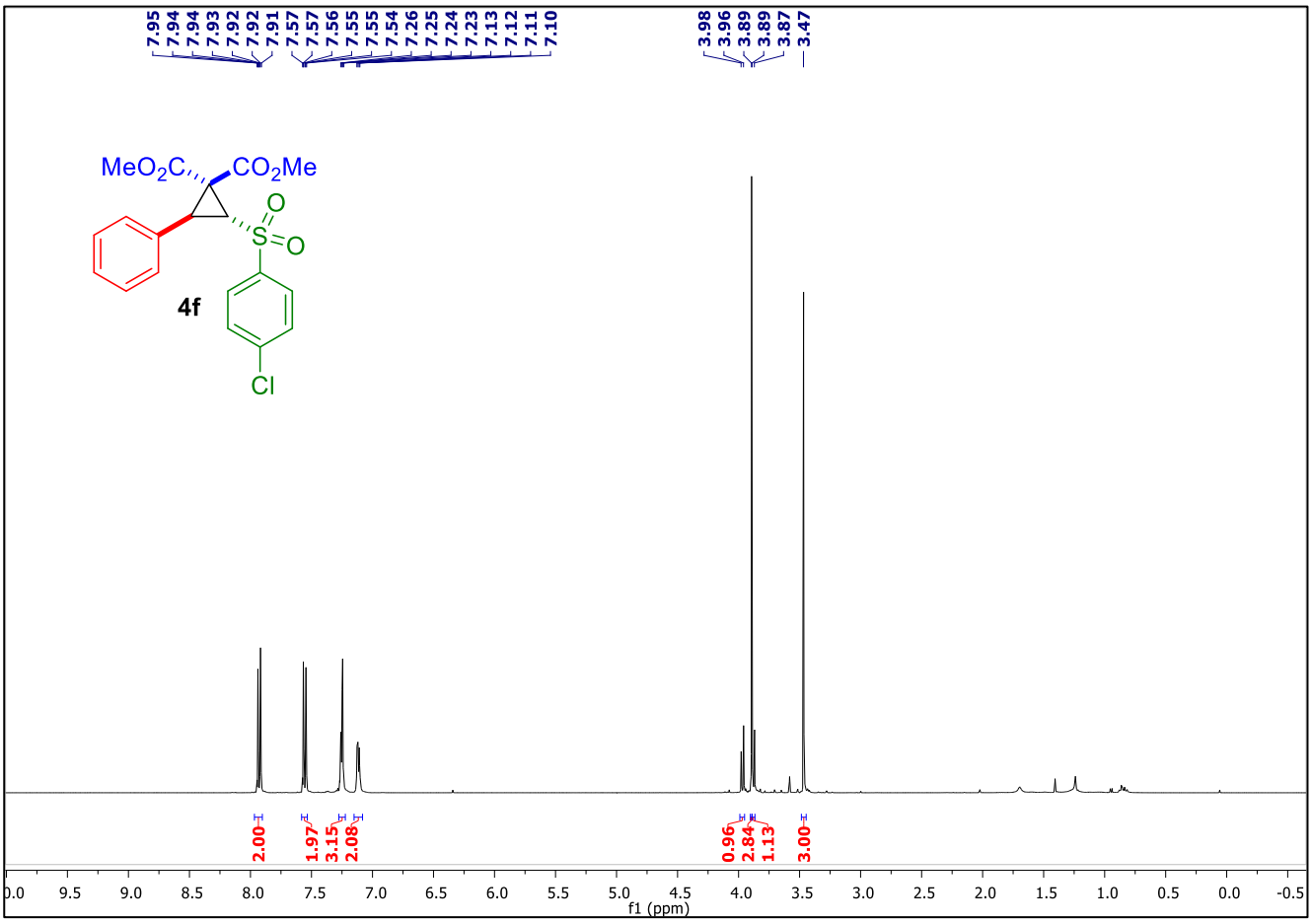

$^{13}$C NMR of Compound **4d** (126 MHz, $CDCl_3$)



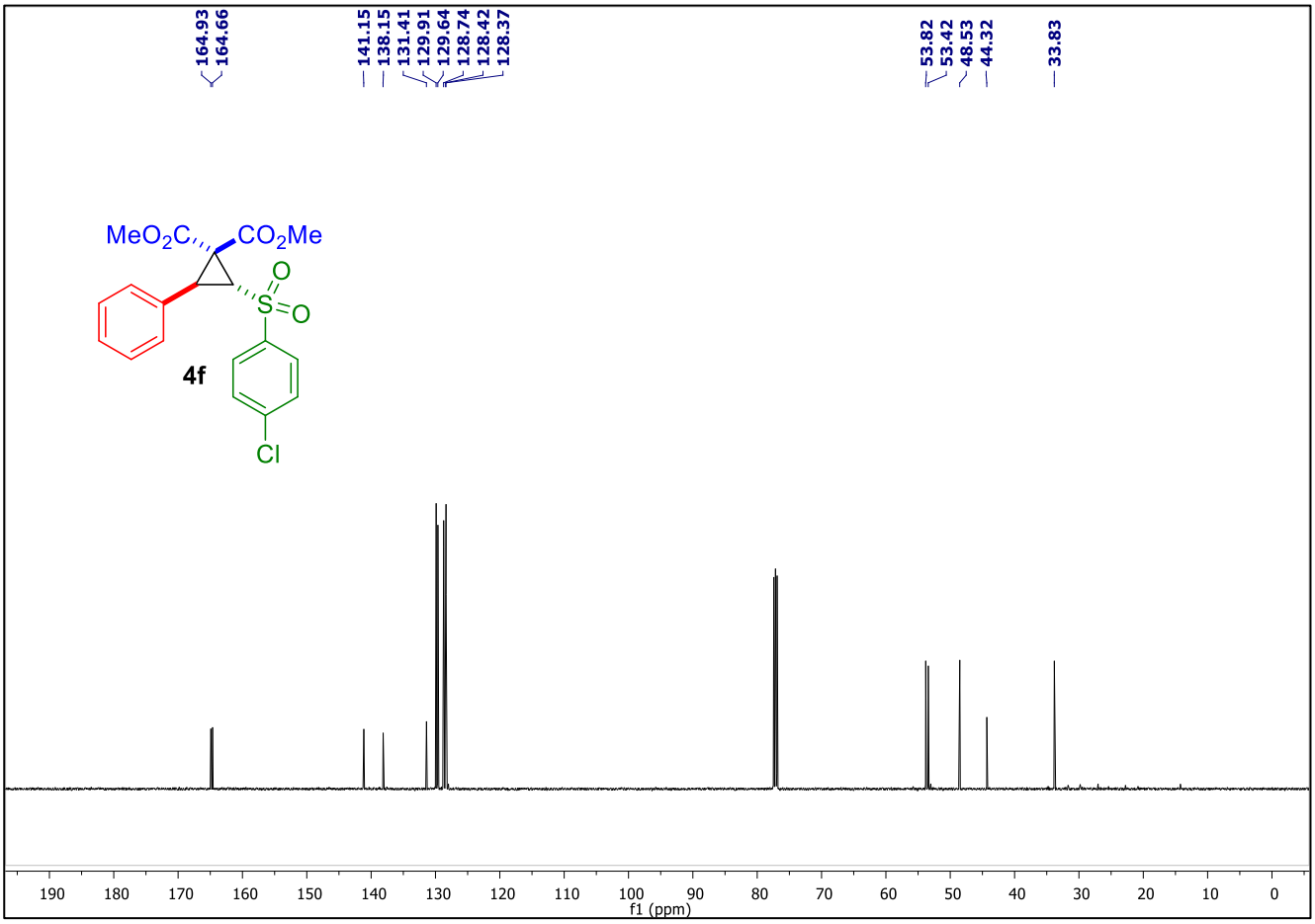

$^{1}$H NMR of Compound **4e** (400 MHz, $CDCl_3$)



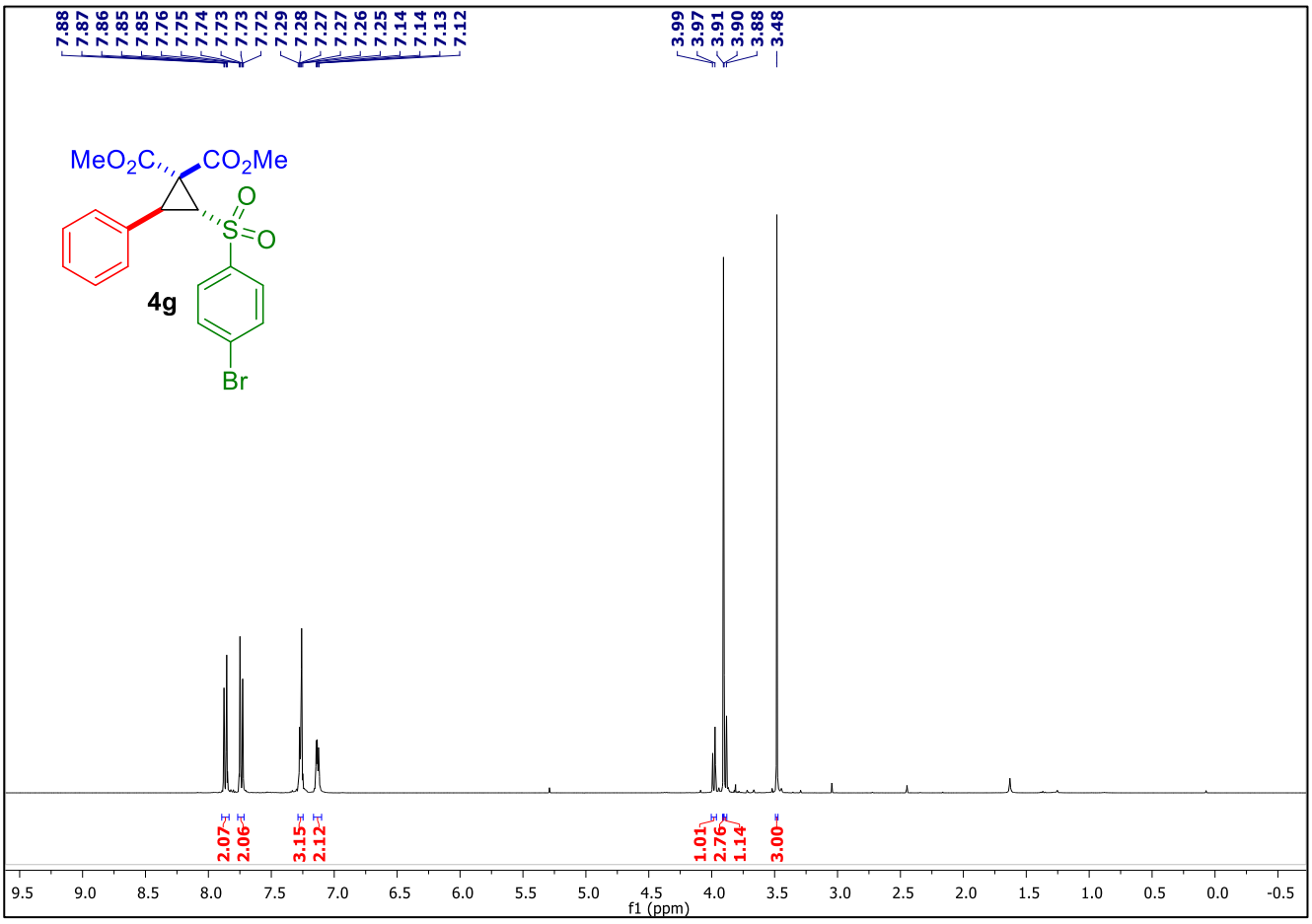

$^{13}$C NMR of Compound **4e** (126 MHz, $CDCl_3$)



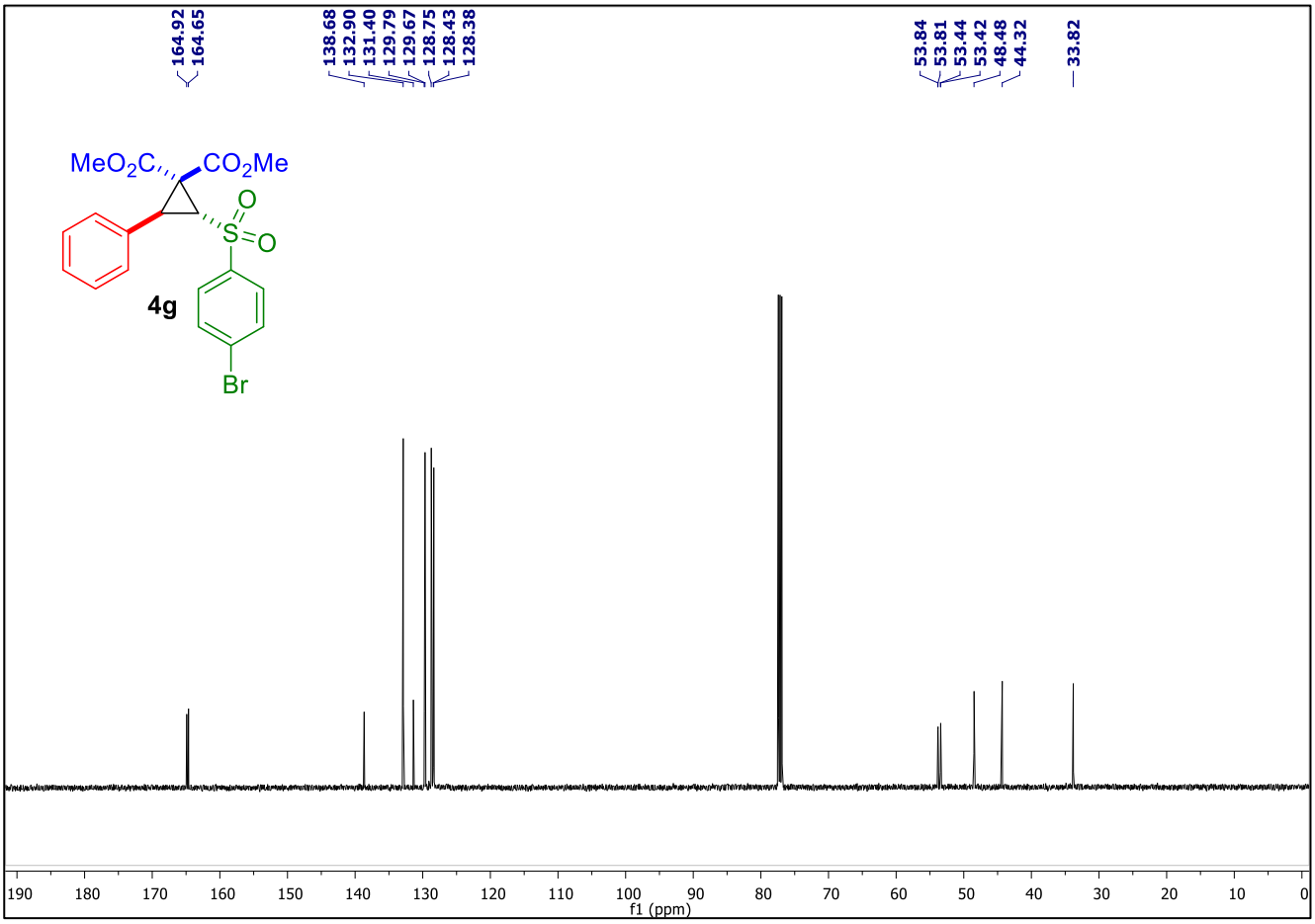

$^{1}$H NMR of Compound **4f** (400 MHz, $CDCl_3$)



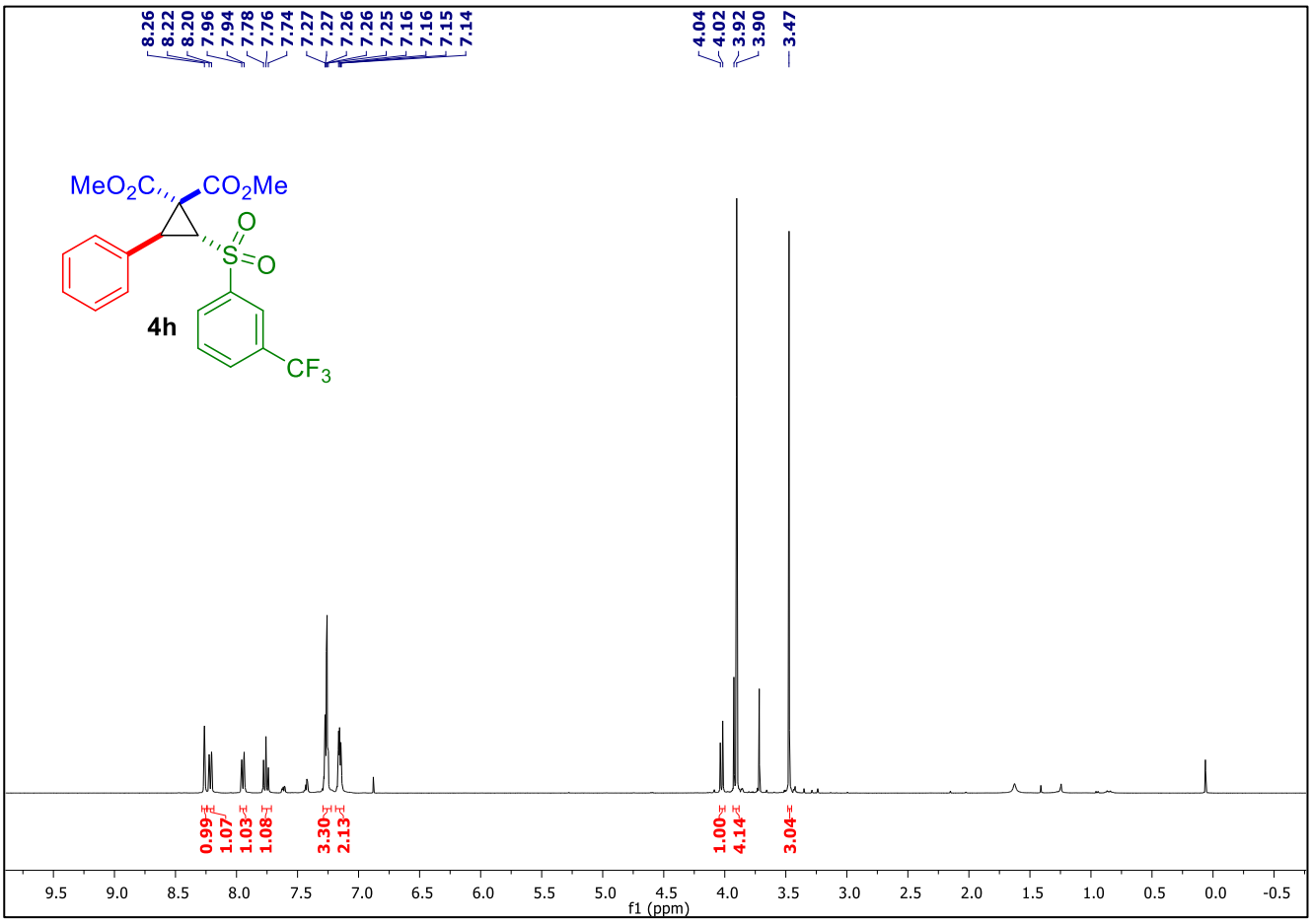

$^{13}$C NMR of Compound **4f** (126 MHz, $CDCl_3$)



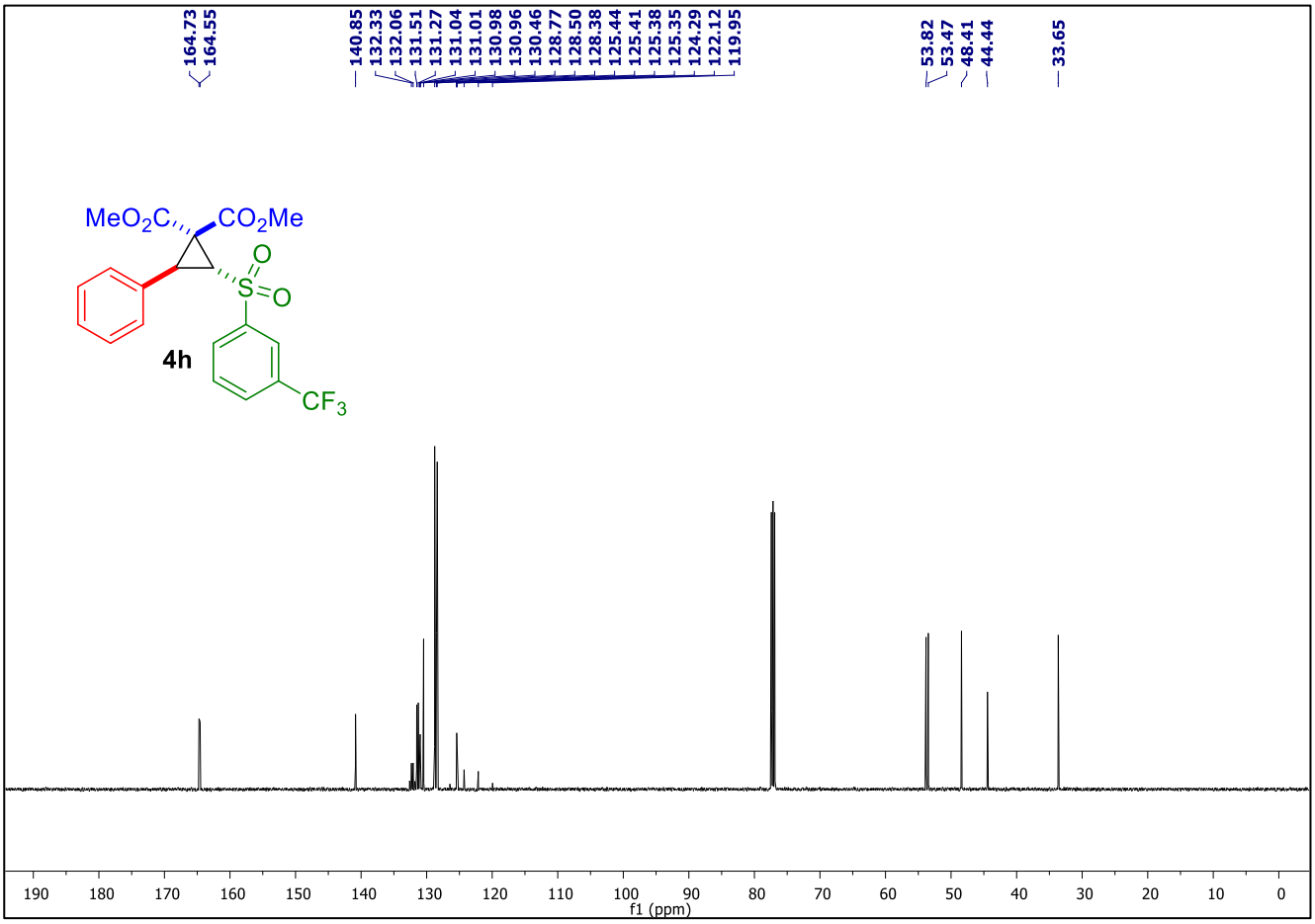

$^{1}$H NMR of Compound **4g** (400 MHz, $CDCl_3$)



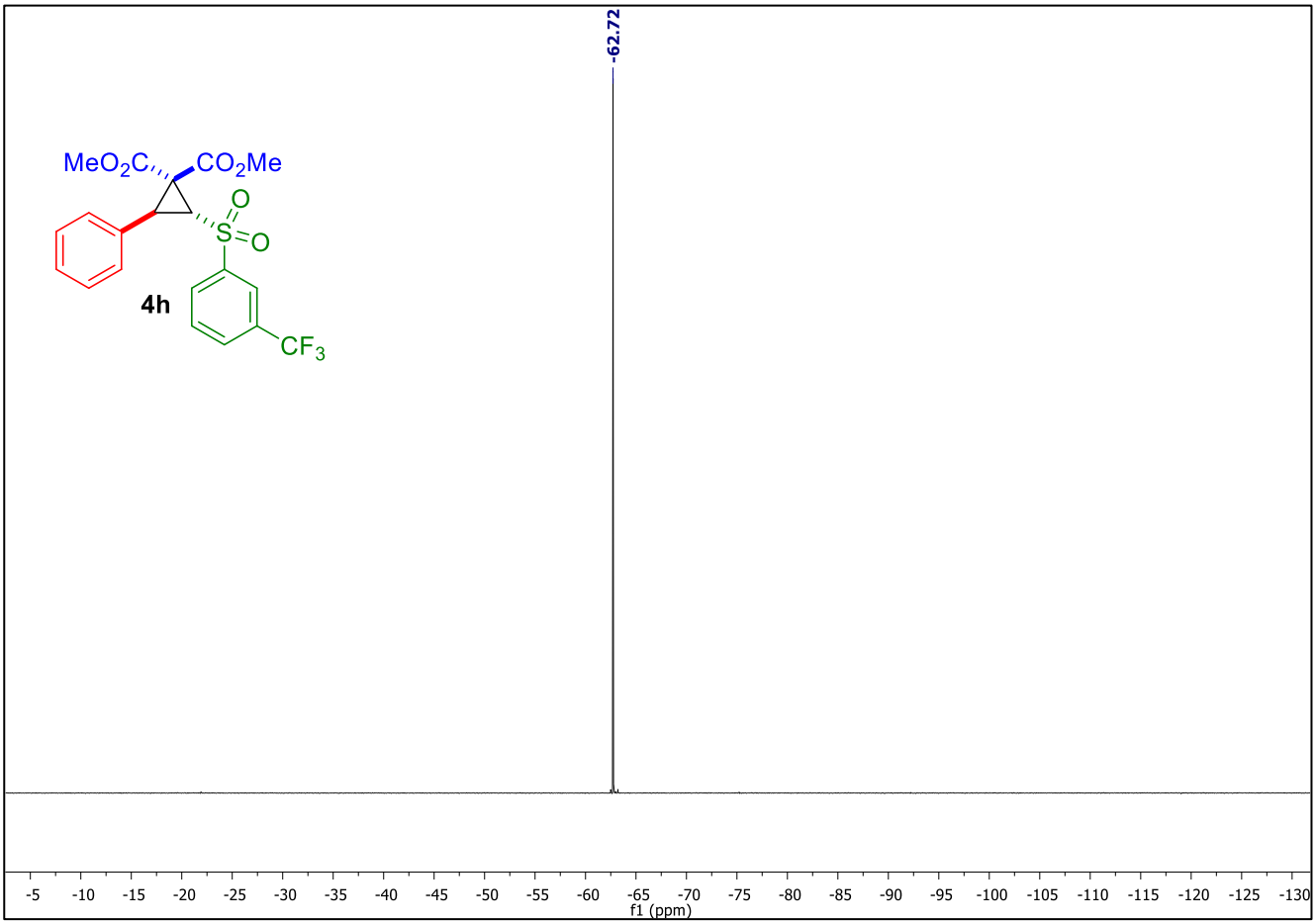

$^{13}$C NMR of Compound **4g** (126 MHz, $CDCl_3$)



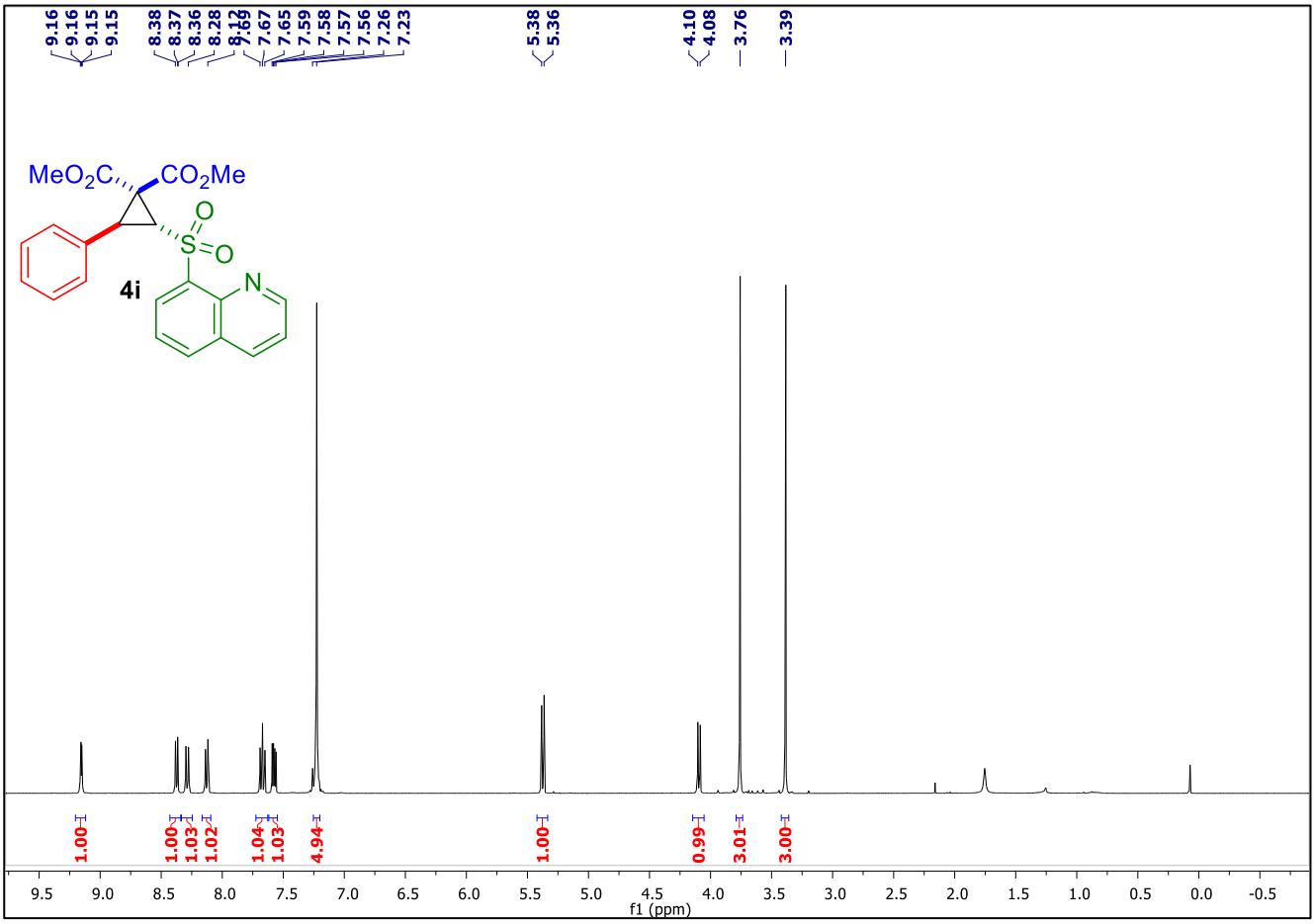

$^{1}$H NMR of Compound **4h** (400 MHz, $CDCl_3$)



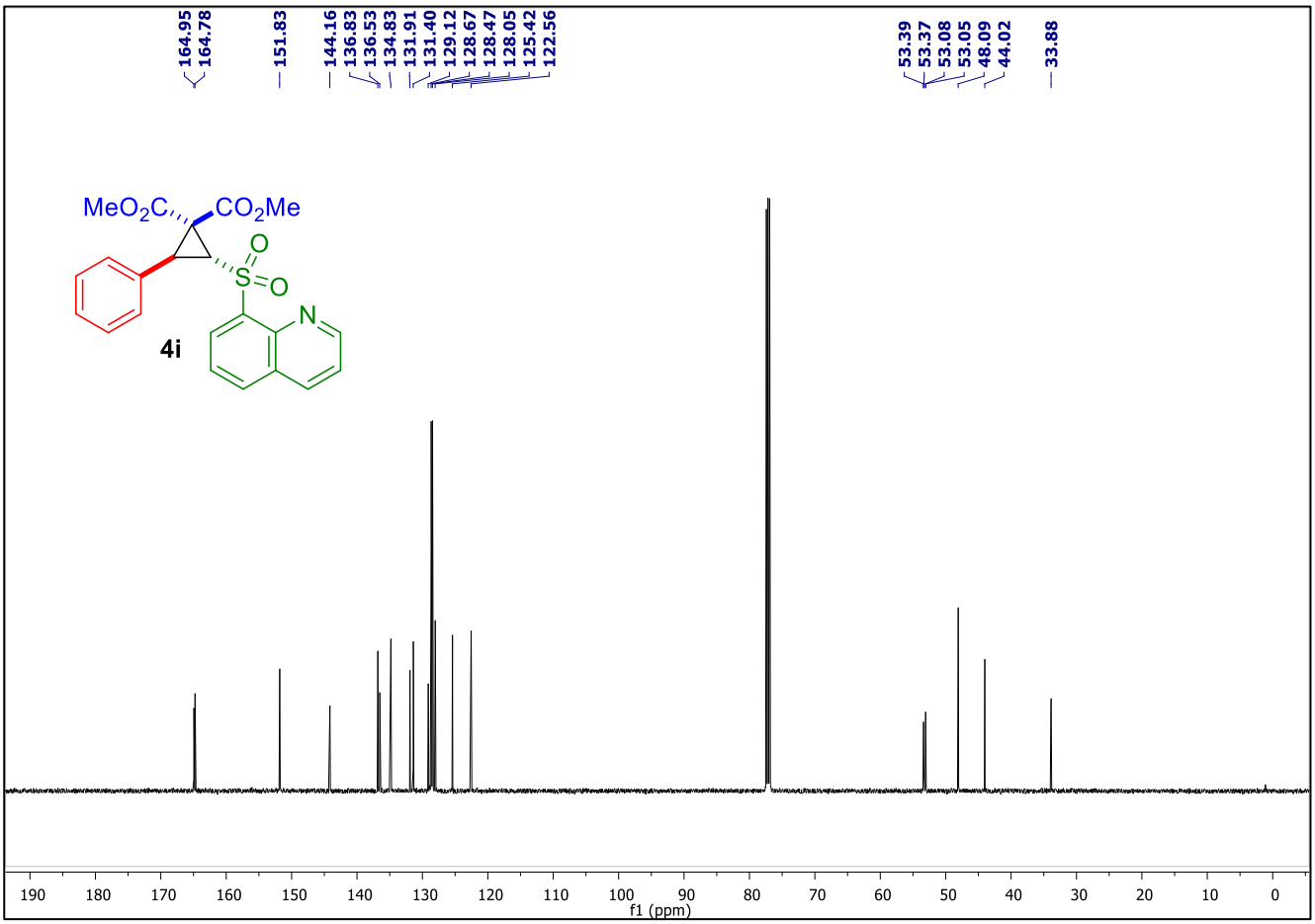

$^{13}$C NMR of Compound **4h** (126 MHz, $CDCl_3$)



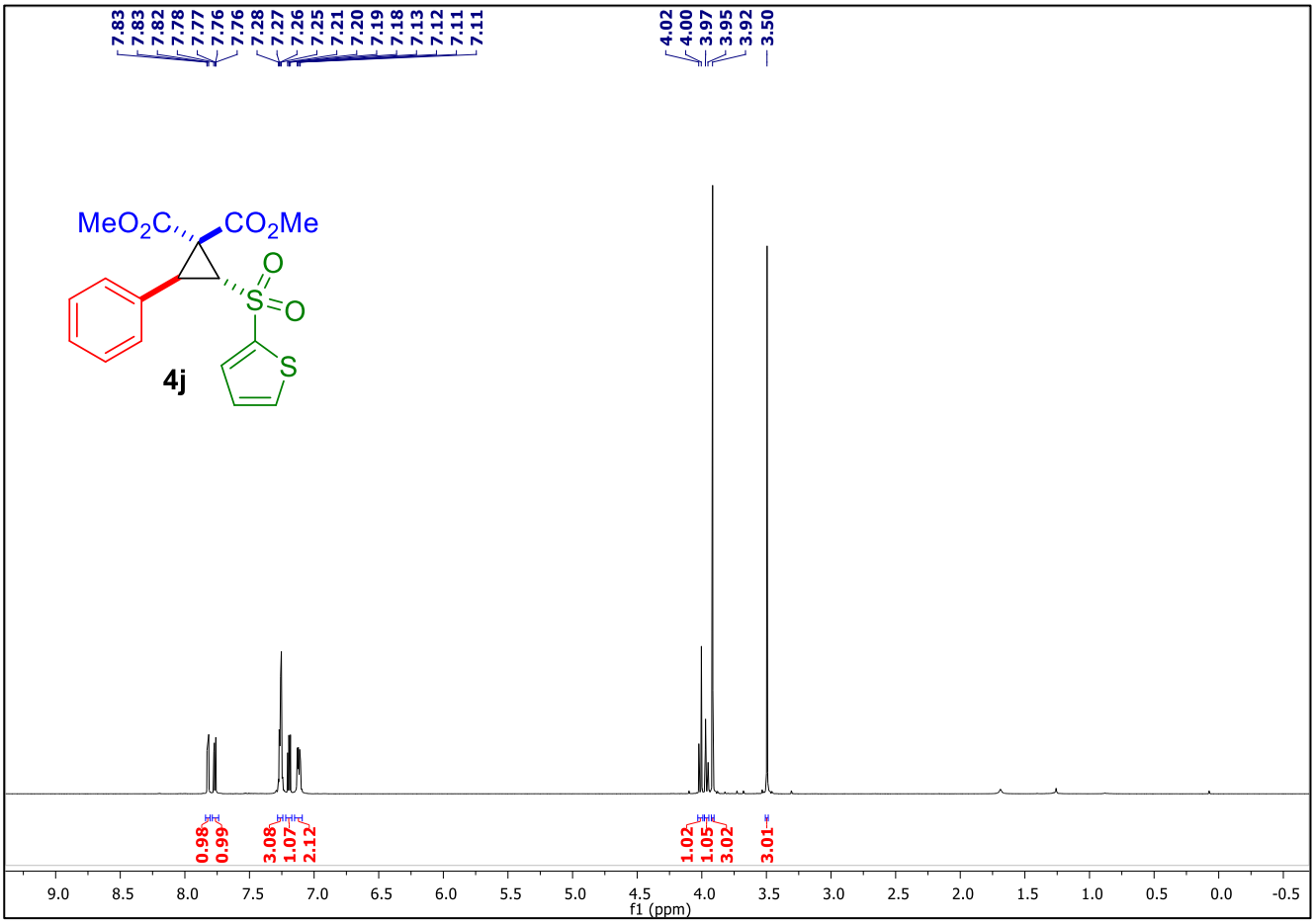

$^{19}$F NMR of Compound **4h** (376 MHz, $CDCl_3$)



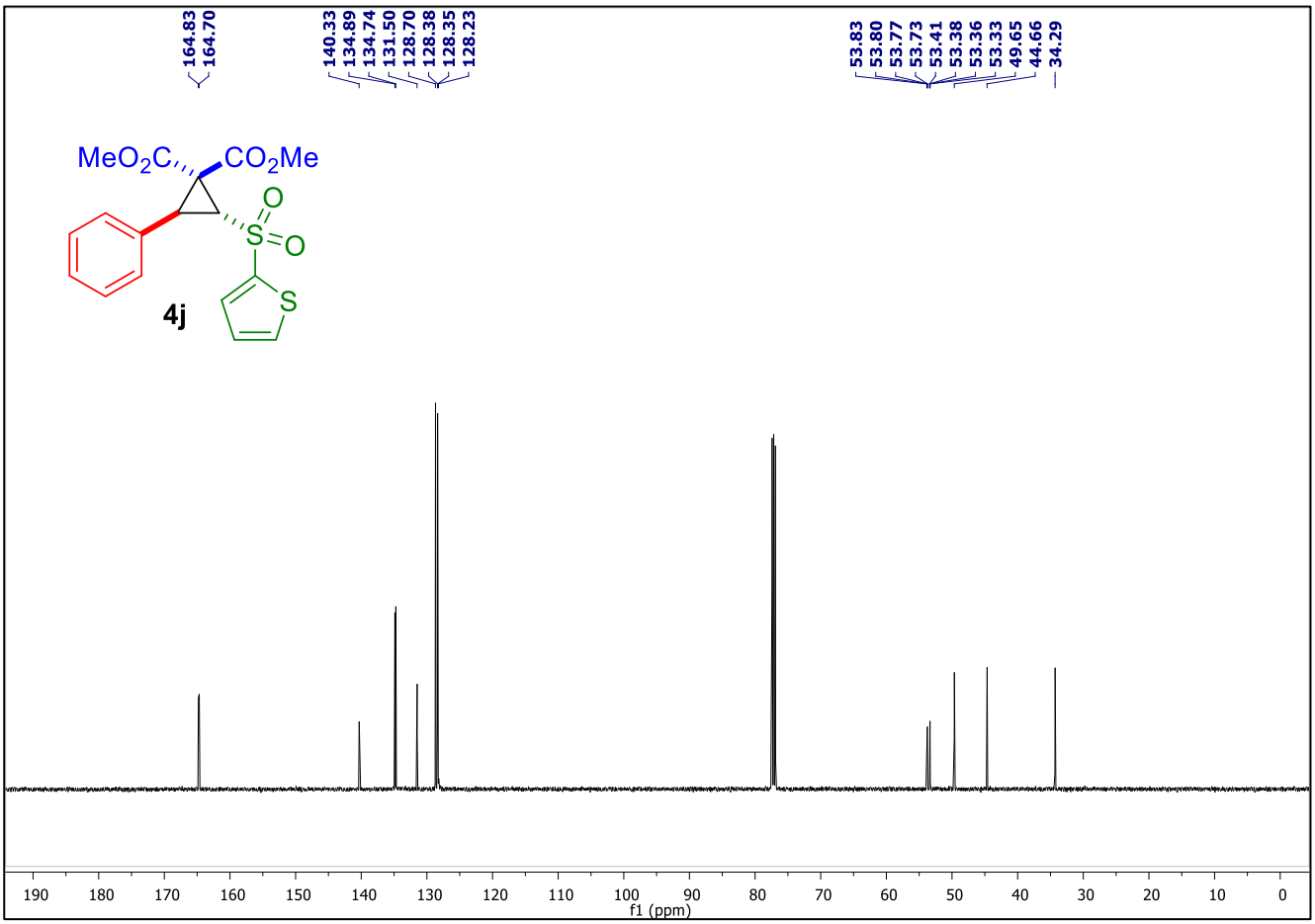

$^{1}$H NMR of Compound **4i** (400 MHz, $CDCl_3$)



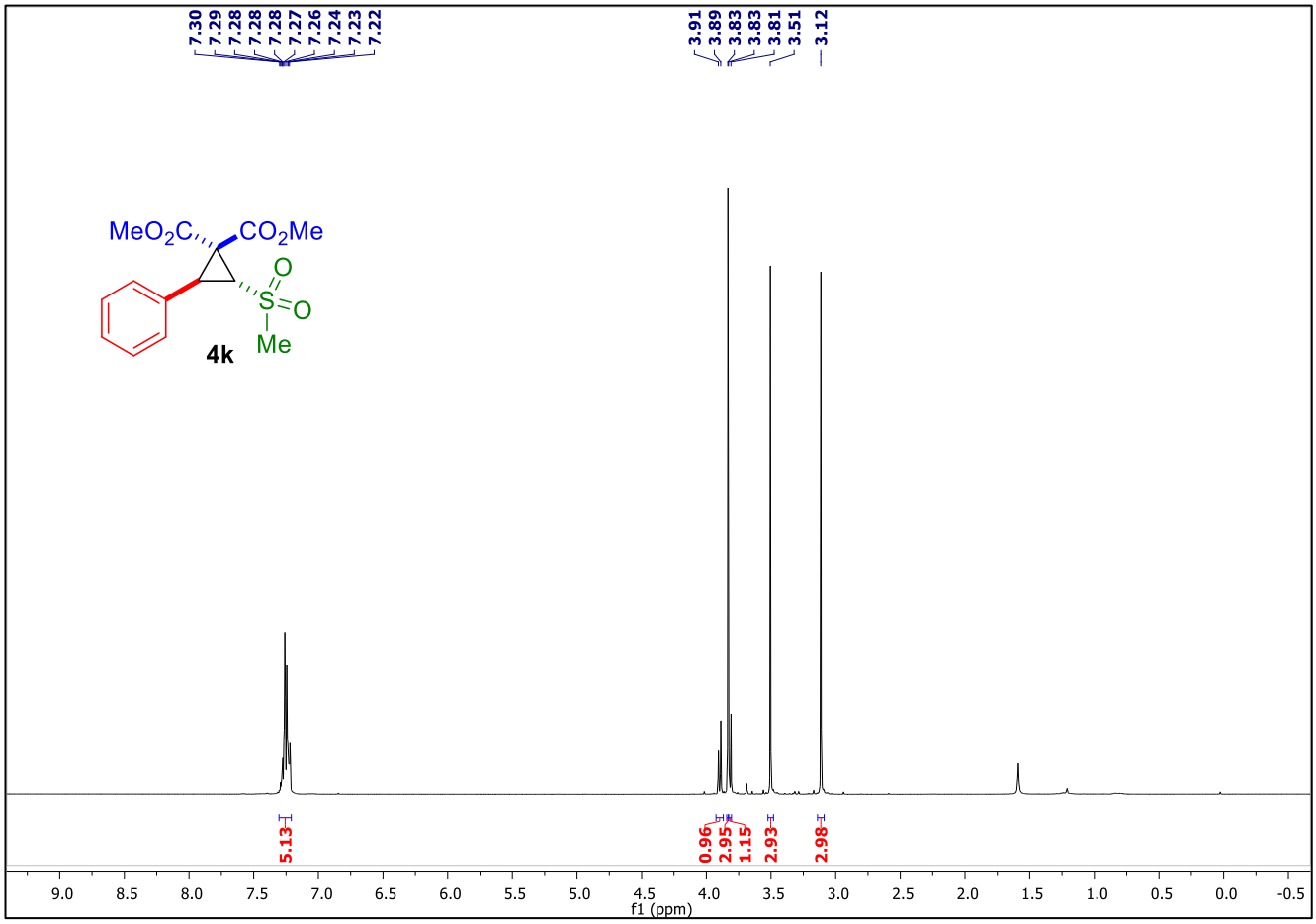

$^{13}$C NMR of Compound **4i** (126 MHz, $CDCl_3$)



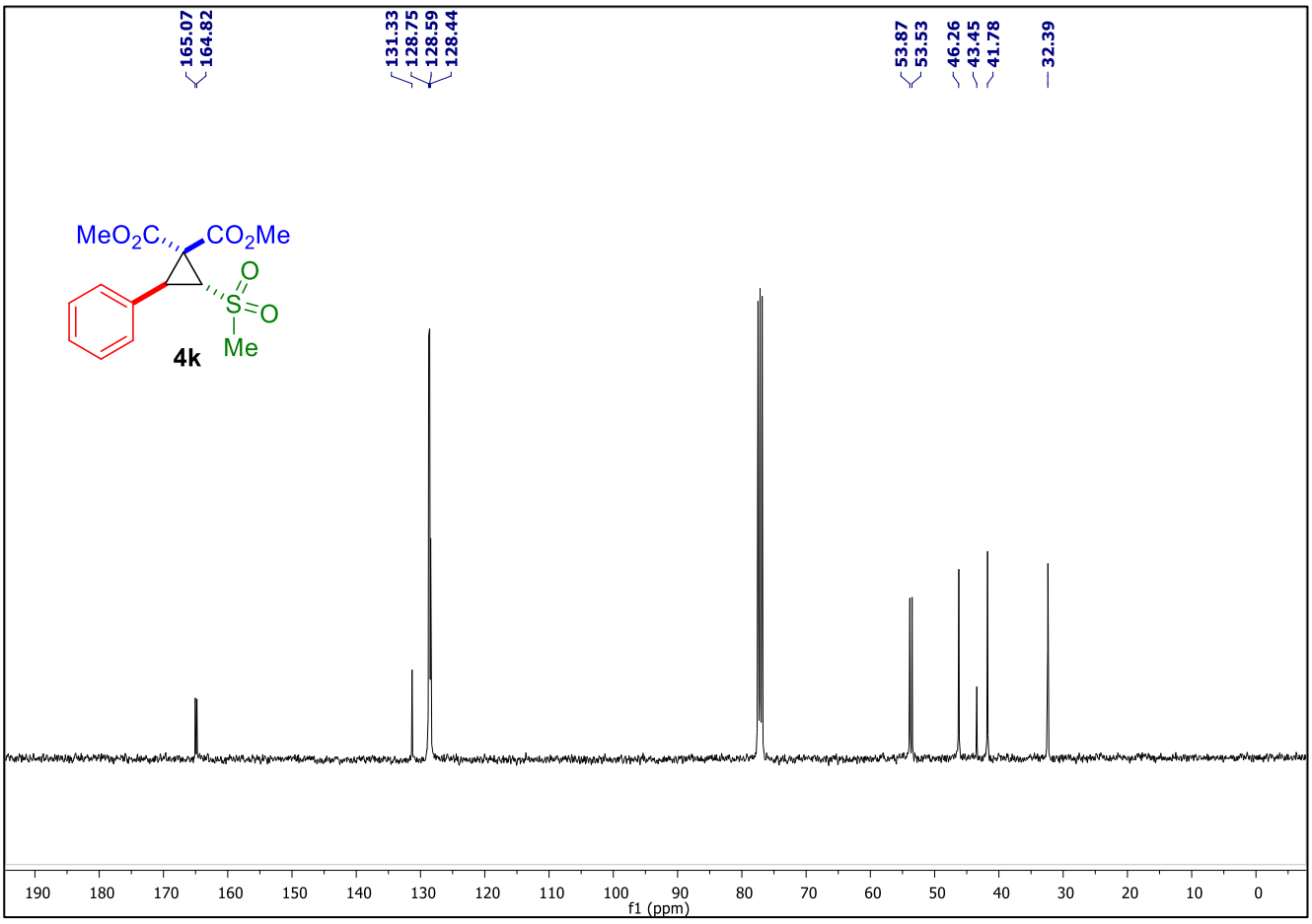

$^{1}$H NMR of Compound **4j** (400 MHz, $CDCl_3$)



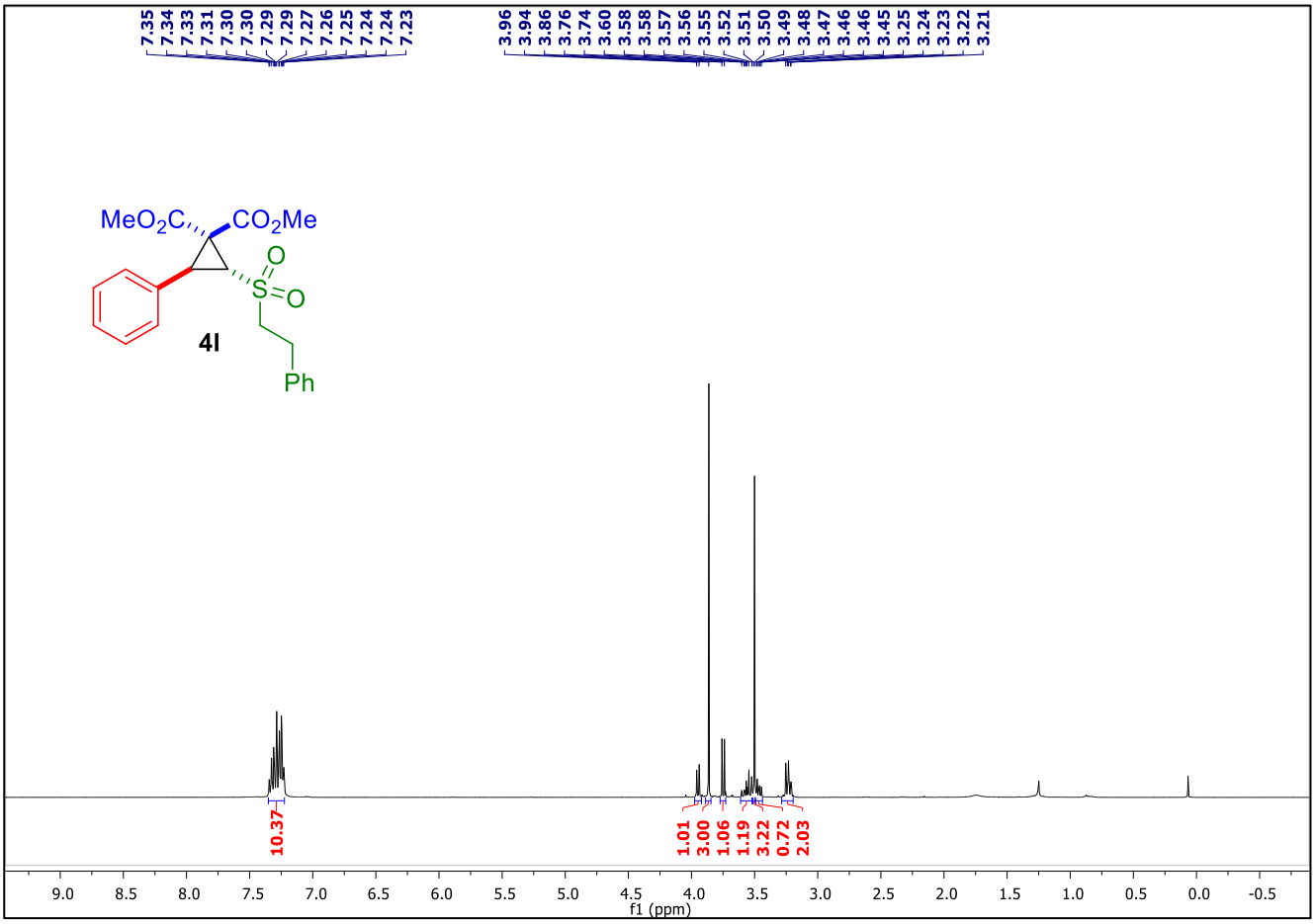

$^{13}$C NMR of Compound **4j** (126 MHz, $CDCl_3$)



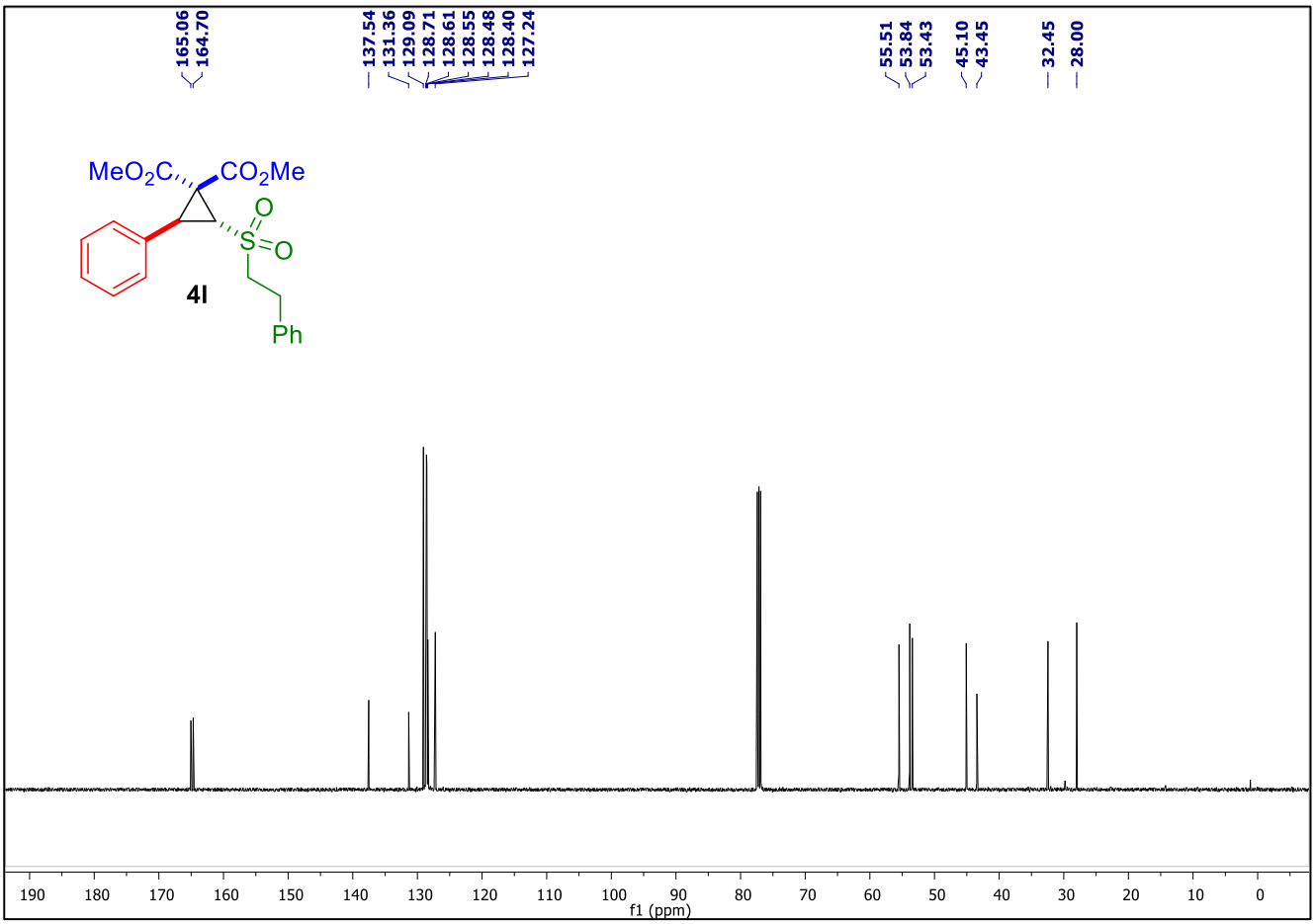

$^{1}$H NMR of Compound **4k** (400 MHz, $CDCl_3$)



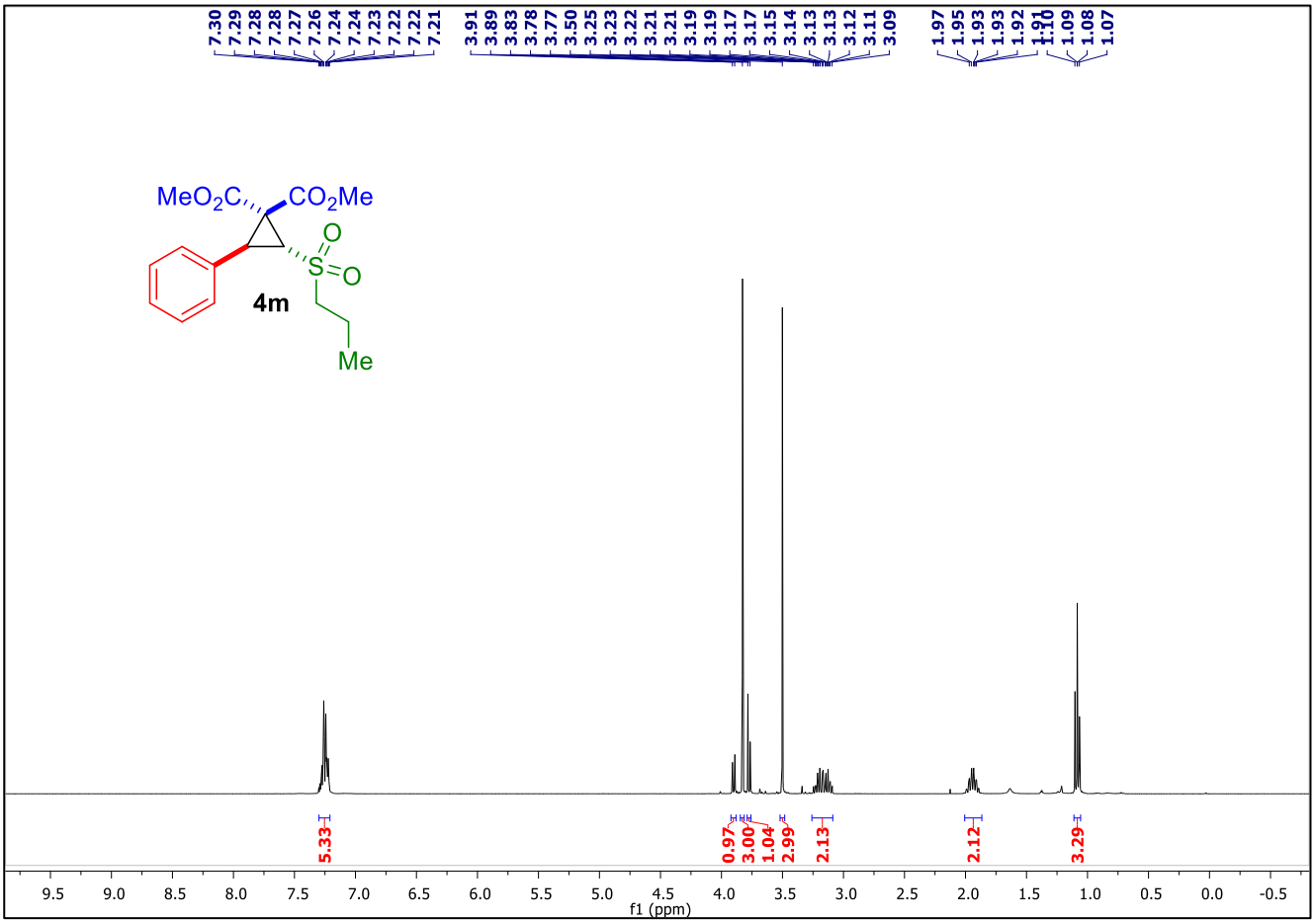

$^{13}$C NMR of Compound **4k** (101 MHz, $CDCl_3$)



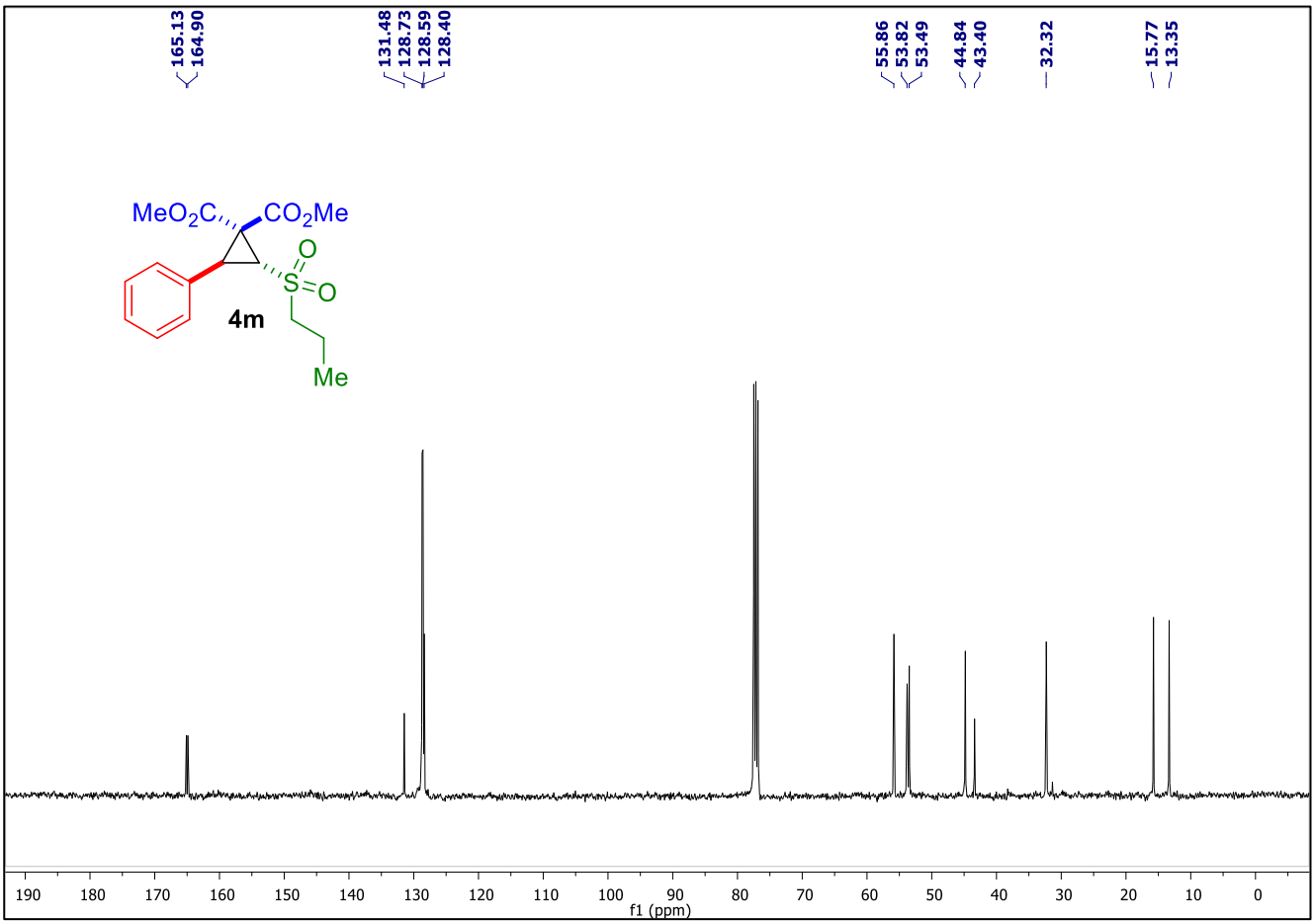

$^{1}$H NMR of Compound **4l** (400 MHz, $CDCl_3$)



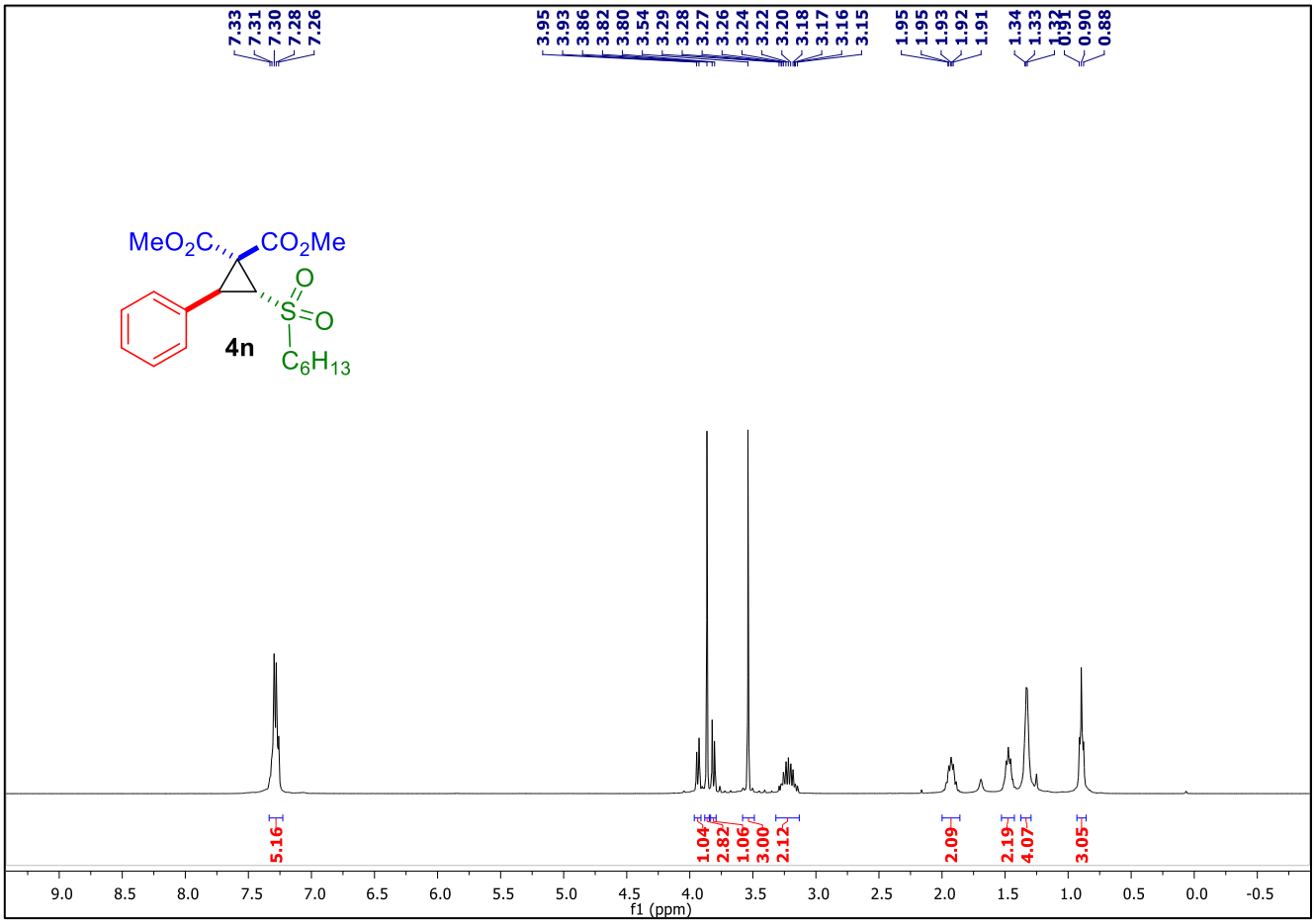

$^{13}$C NMR of Compound **4l** (126 MHz, $CDCl_3$)



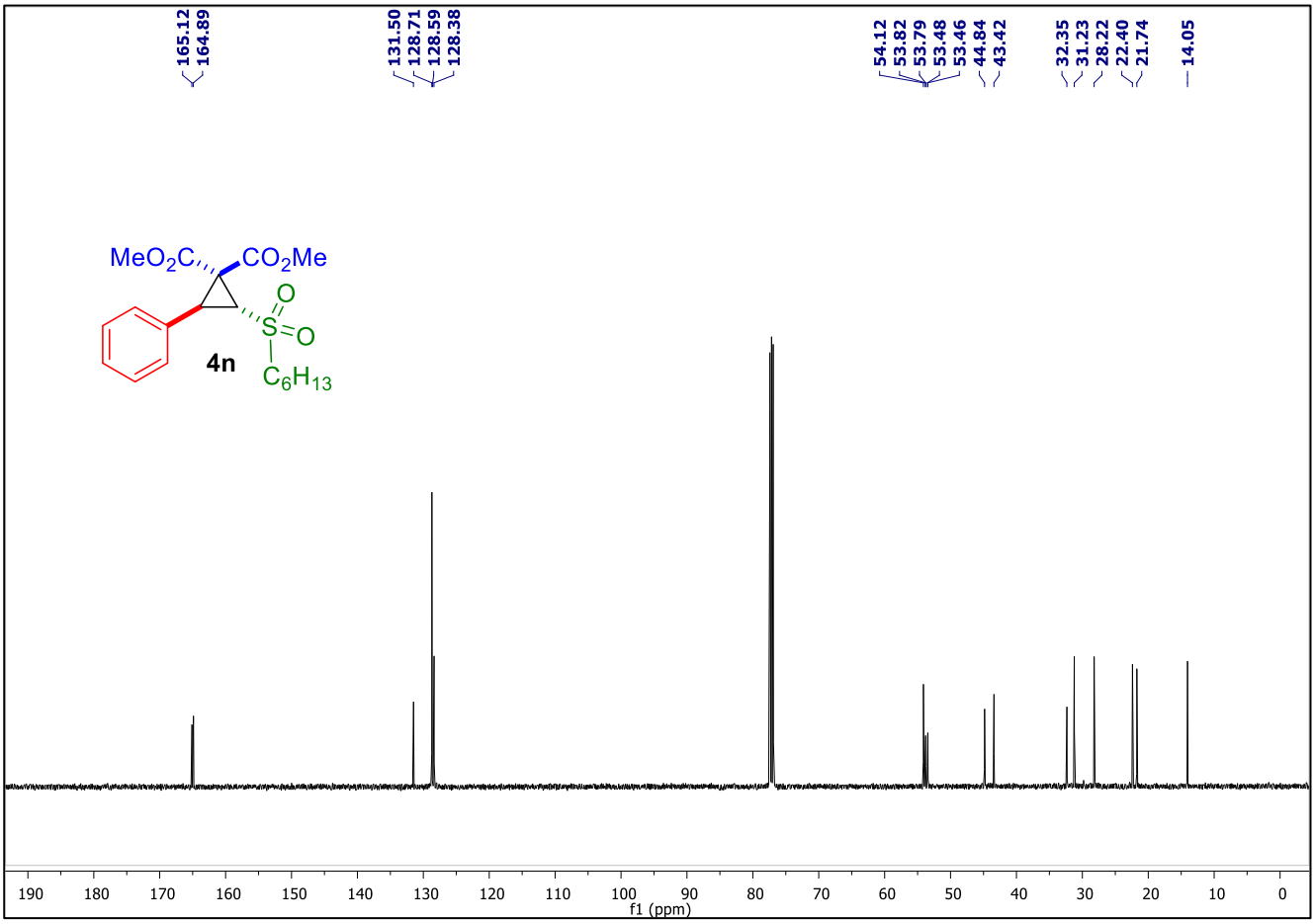

$^{1}$H NMR of Compound **4m** (400 MHz, $CDCl_3$)



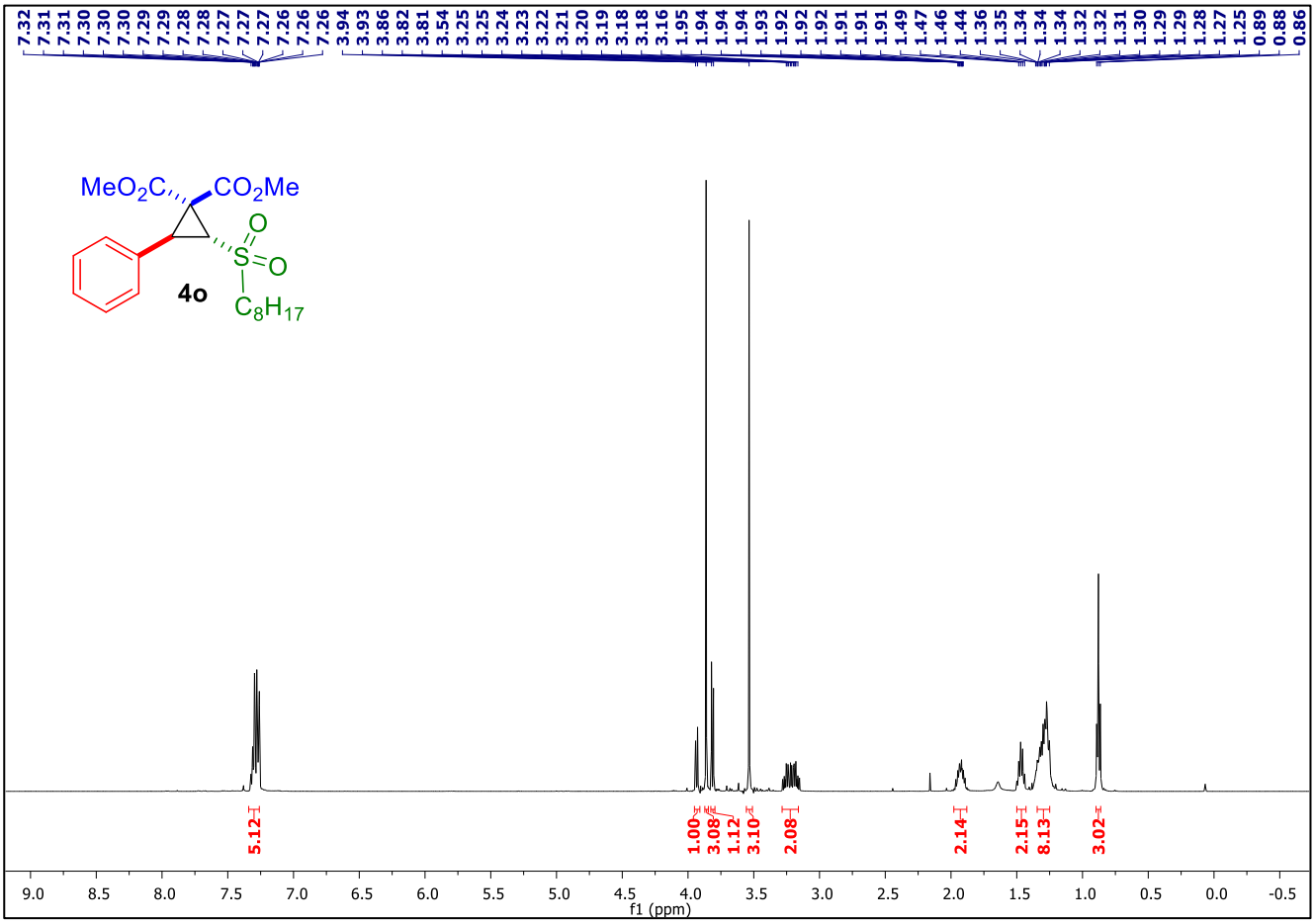

$^{13}$C NMR of Compound **4m** (101 MHz, $CDCl_3$)



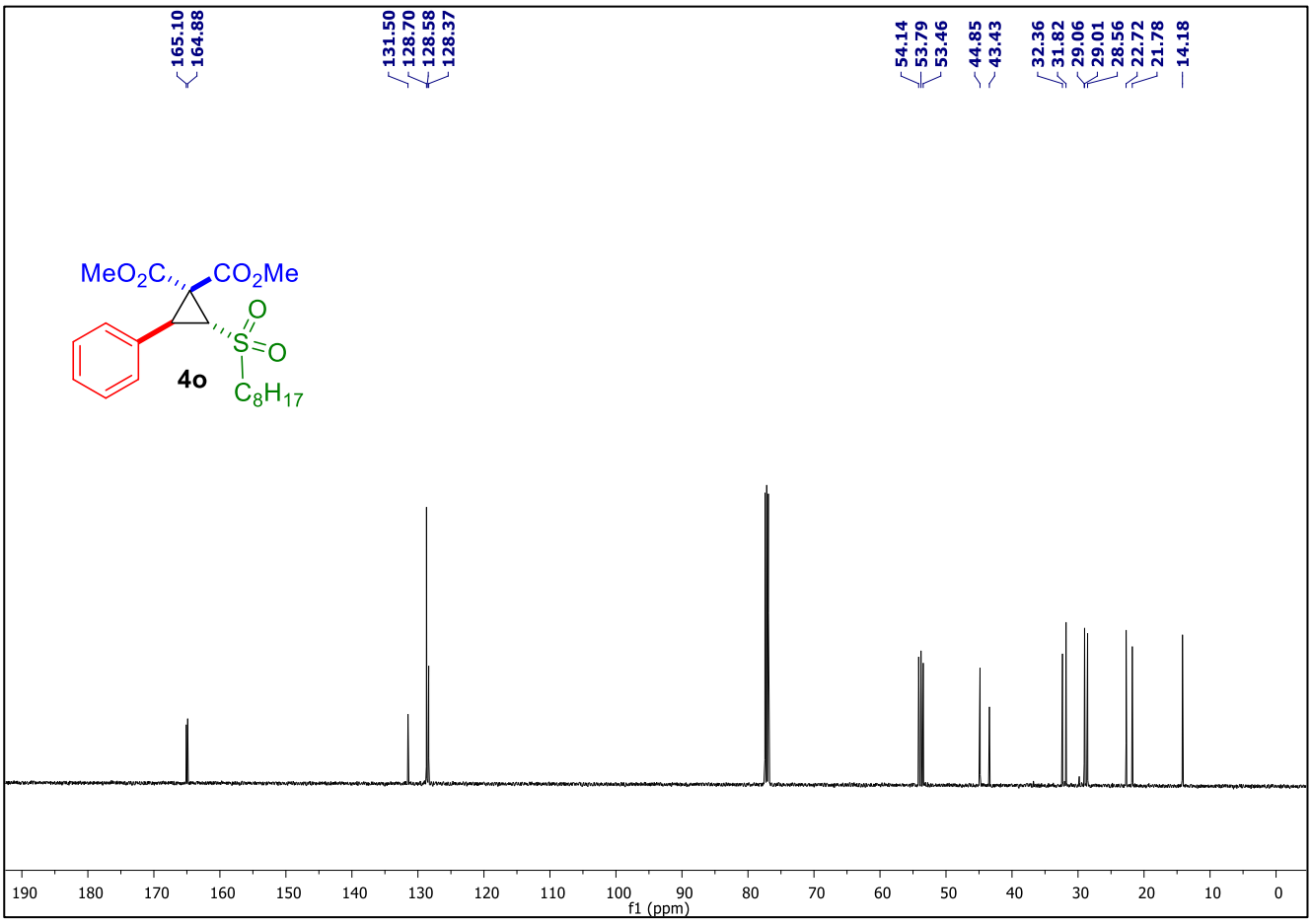

$^{1}$H NMR of Compound **4n** (400 MHz, $CDCl_3$)



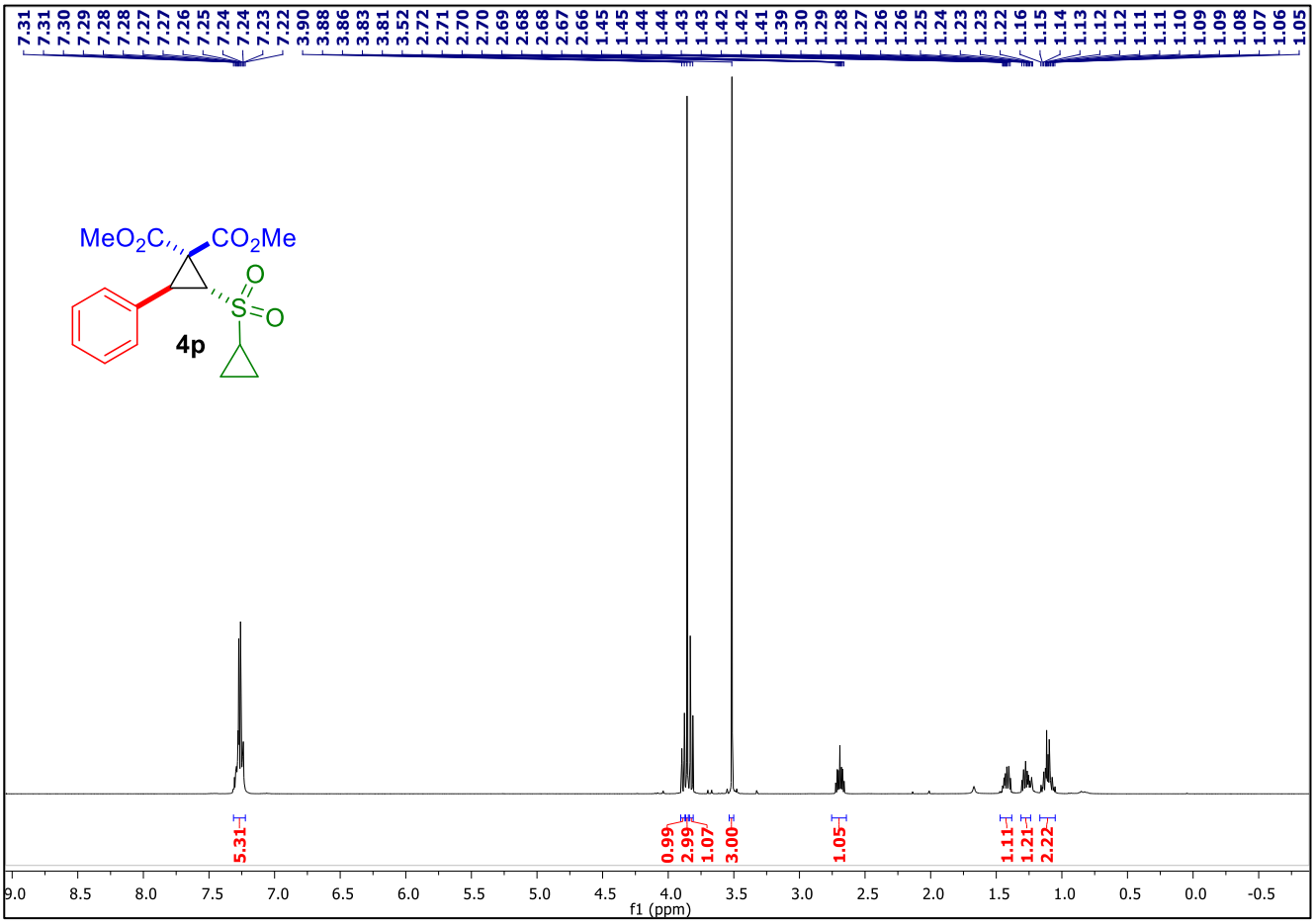

$^{13}$C NMR of Compound **4n** (126 MHz, $CDCl_3$)



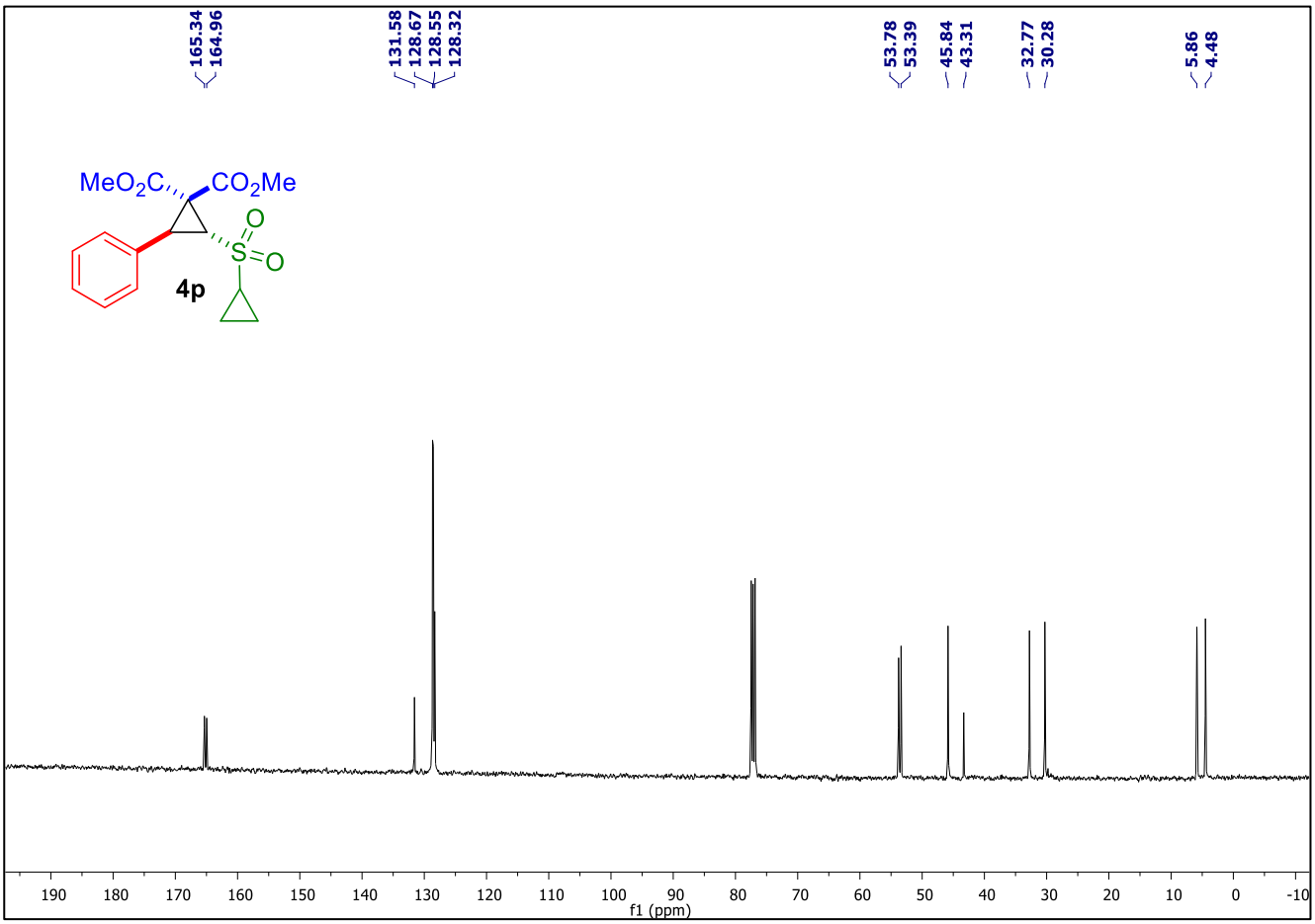

$^{1}$H NMR of Compound **4o** (500 MHz, $CDCl_3$)



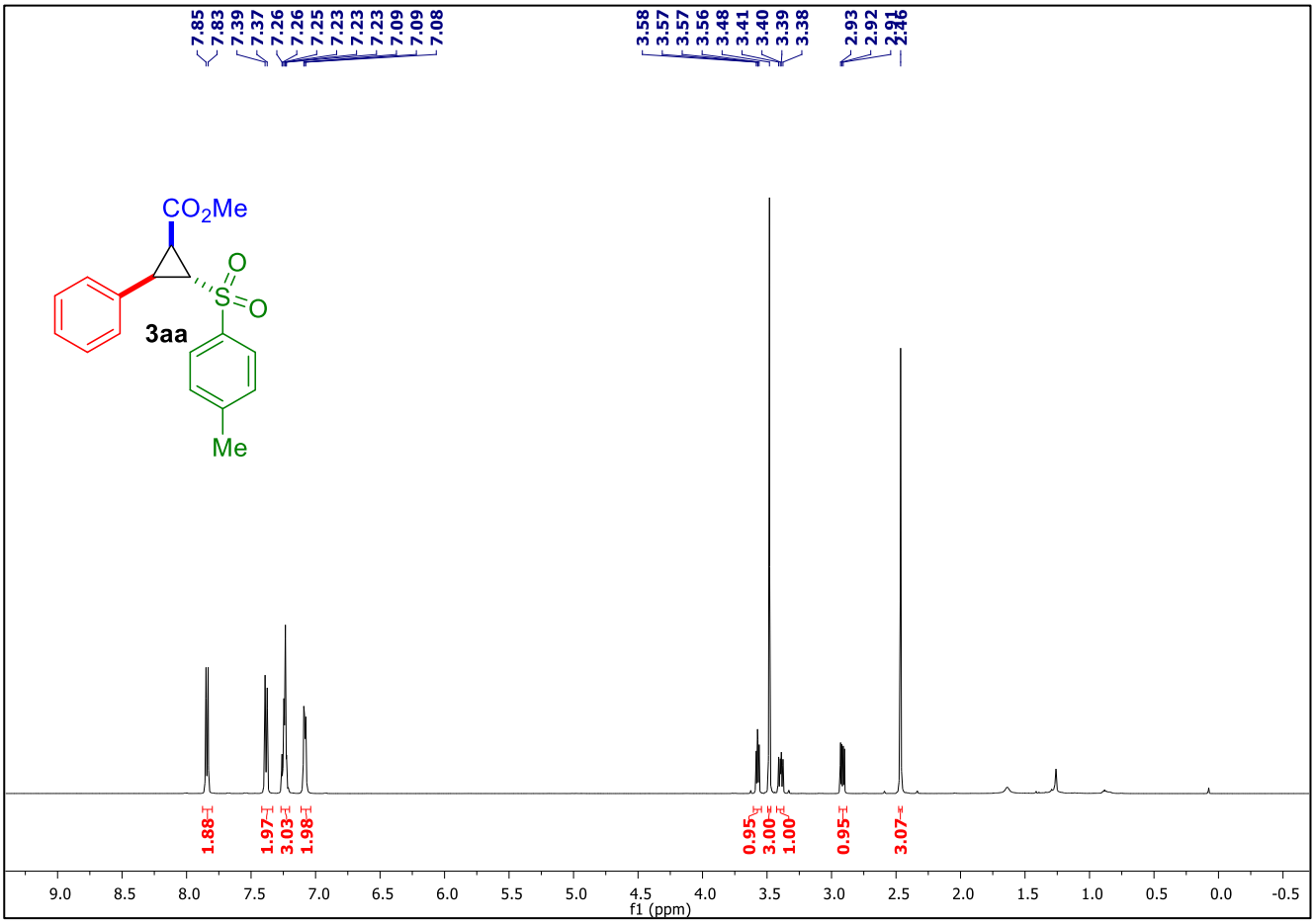

$^{13}$C NMR of Compound **4o** (126 MHz, $CDCl_3$)



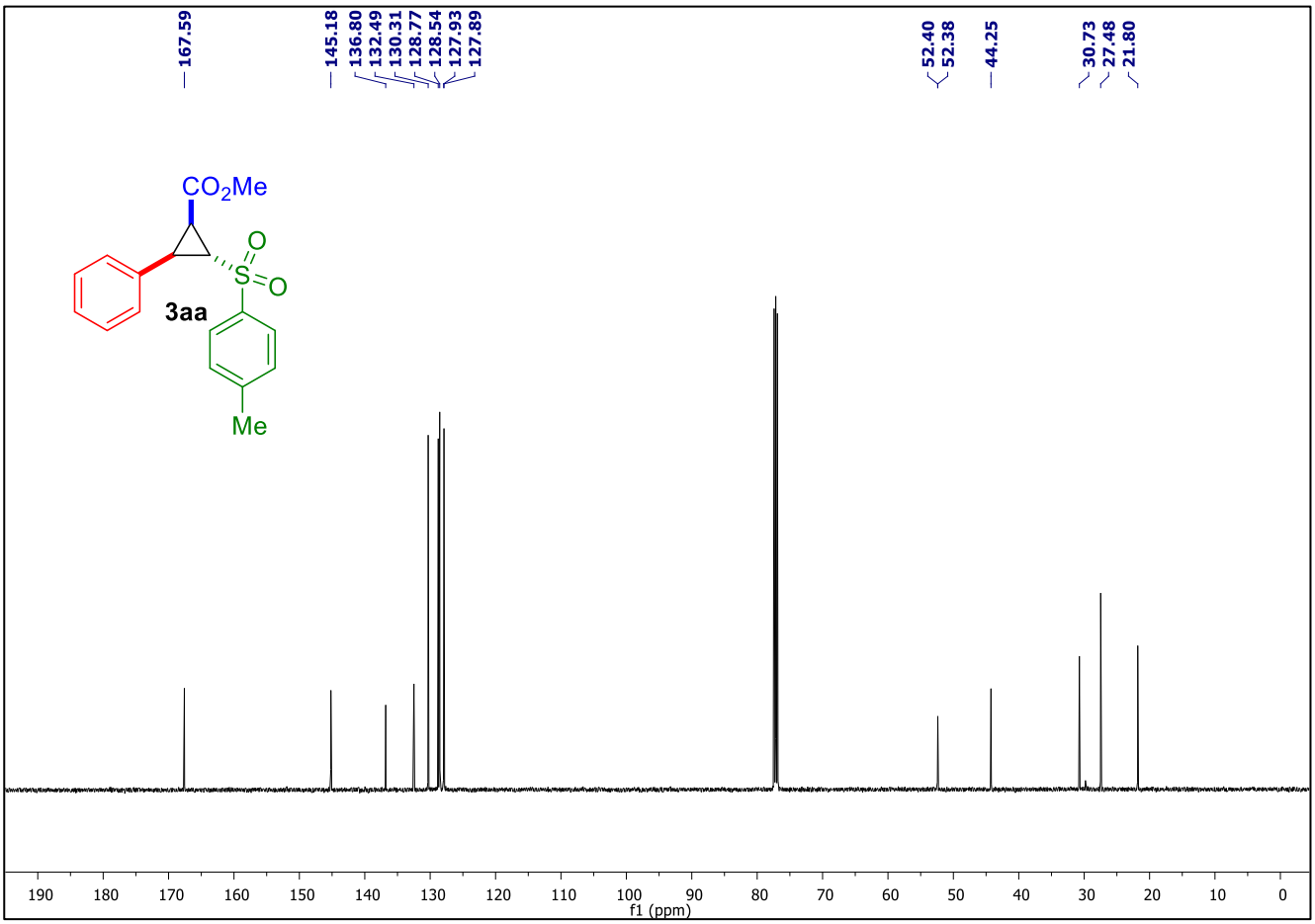

$^{1}$H NMR of Compound **4p** (400 MHz, $CDCl_3$)



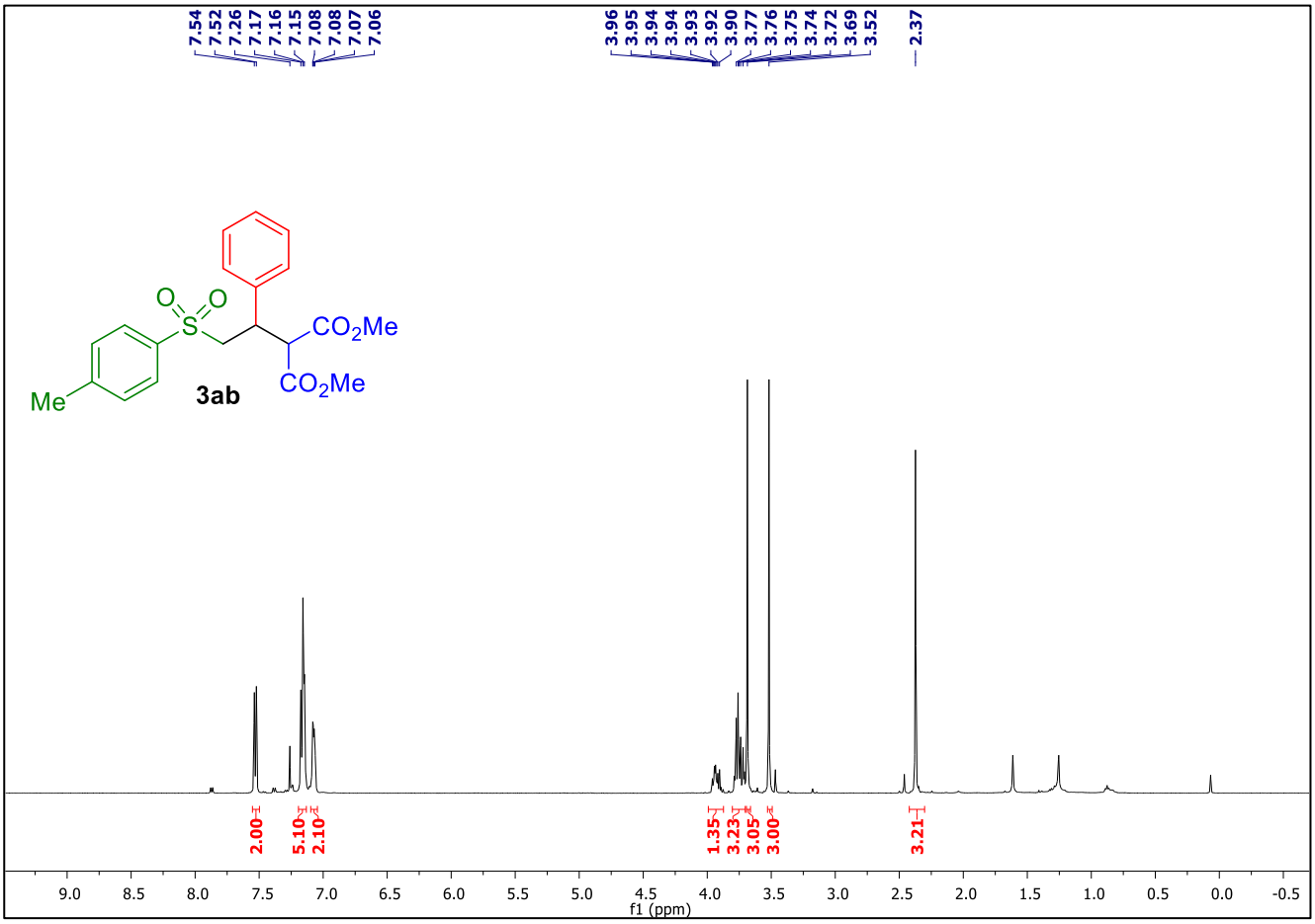

$^{13}$C NMR of Compound **4p** (101 MHz, $CDCl_3$)



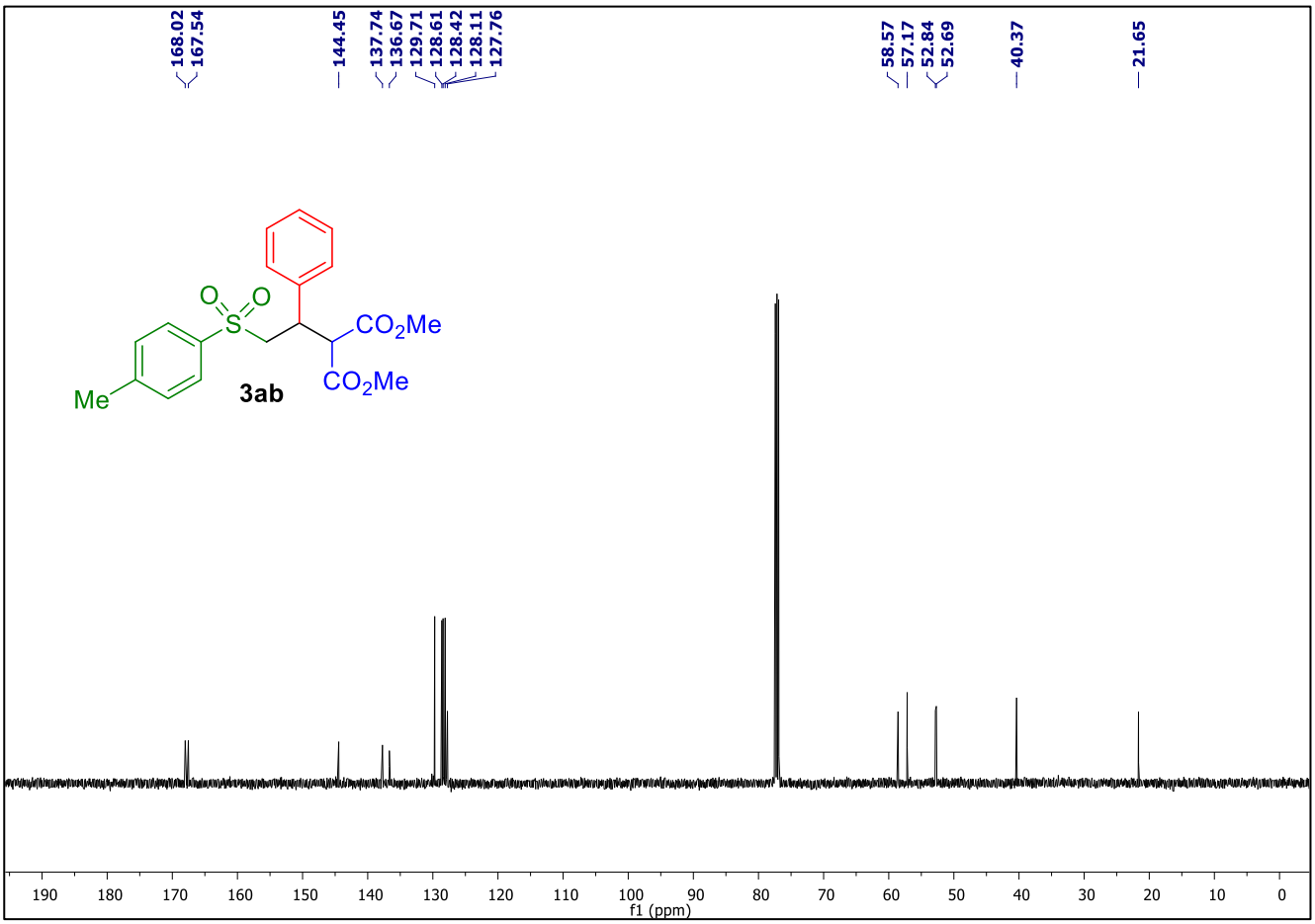

$^{1}$H NMR of Compound **3aa** (400 MHz, $CDCl_3$)




$^{13}$C NMR of Compound **3aa** (126 MHz, $CDCl_3$)




$^{1}$H NMR of Compound **3ab** (500 MHz, $CDCl_3$)



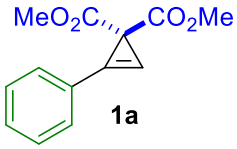

$^{13}$C NMR of Compound **3ab** (126MHz, $CDCl_3$)

## 13. Structural, energetic, and spectroscopic calculated parameters for all species

Calculated geometries (in cartesian coordinates) with their respective energies (in Hartree), charge, multiplicity, stoichiometry, number of imaginary frequencies

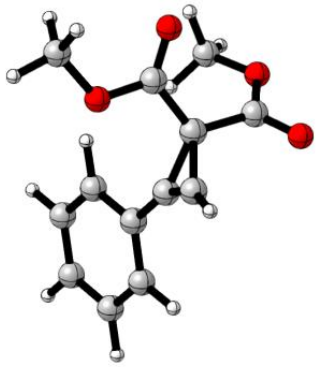
**Compound 1a**:

| | |
|---|---|
| Charge = | 0 |
| Multiplicity = | 1 |
| Stoichiometry= | $C_{13}H_{12}O_4$ |
| Number of Basis Functions = | 298 |
| Electronic Energy (Eh) = | - 802.514939 |
| Sum of electronic and zero-point Energies= | - 802.288018 |
| Sum of electronic and thermal Energies= | - 802.271889 |
| Sum of electronic and thermal Enthalpies= | - 802.270945 |
| Sum of electronic and thermal Free Energies= | - 802.333349 |
| Number of Imaginary Frequencies= | 0 |
| Mean of alpha and beta Electrons= | 61 |



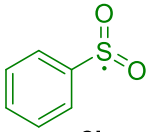
**1a**

| | | | |
|---|---|---|---|
| C | -0.468493000 | -0.434504000 | -1.960481000 |
| C | 0.360466000 | -0.255547000 | -0.985717000 |
| C | -1.091290000 | -0.383832000 | -0.592238000 |
| H | -0.732650000 | -0.559117000 | -3.003739000 |
| C | 1.683687000 | -0.066974000 | -0.414649000 |
| C | 1.839483000 | 0.682547000 | 0.758873000 |
| C | 2.810196000 | -0.616183000 | -1.042314000 |
| C | 3.107214000 | 0.877592000 | 1.300060000 |
| H | 0.960627000 | 1.132669000 | 1.224358000 |
| C | 4.074477000 | -0.423246000 | -0.493844000 |
| H | 2.681261000 | -1.202125000 | -1.953403000 |
| C | 4.224722000 | 0.321832000 | 0.676940000 |
| H | 3.224443000 | 1.466812000 | 2.210404000 |
| H | 4.948528000 | -0.858288000 | -0.980224000 |
| H | 5.217284000 | 0.470386000 | 1.104527000 |
| C | -1.890172000 | 0.822911000 | -0.196636000 |
| C | -1.618236000 | -1.727429000 | -0.090469000 |
| C | -1.436294000 | -0.982275000 | 2.205640000 |
| H | -0.539832000 | -0.420329000 | 1.903880000 |
| H | -2.256143000 | -0.286322000 | 2.421131000 |
| H | -1.193910000 | -1.562991000 | 3.103358000 |
| C | -2.032525000 | 3.151033000 | -0.287110000 |
| H | -3.011630000 | 3.127356000 | -0.783564000 |
| H | -2.194445000 | 3.255408000 | 0.794180000 |
| H | -1.428866000 | 3.980700000 | -0.666834000 |
| O | -1.303686000 | 1.965617000 | -0.569627000 |
| O | -2.945387000 | 0.782071000 | 0.379145000 |
| O | -1.823648000 | -1.913793000 | 1.217169000 |
| O | -1.809039000 | -2.626358000 | -0.856987000 |



**Radical 2ba**:

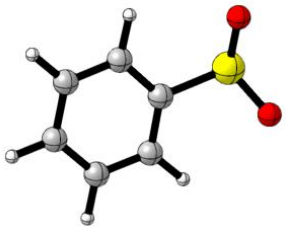
| | |
|---|---|
| Charge = | 0 |
| Multiplicity = | 2 |
| Stoichiometry= | $C_{13}H_{12}O_4$ |
| Number of Basis Functions = | 155 |
| Electronic Energy (Eh) = | - 779.611093 |
| Sum of electronic and zero-point Energies= | - 779.511448 |
| Sum of electronic and thermal Energies= | - 779.503911 |
| Sum of electronic and thermal Enthalpies= | - 779.502967 |
| Sum of electronic and thermal Free Energies= | - 779.545134 |
| Number of Imaginary Frequencies= | 0 |
| Mean of alpha and beta Electrons= | 36.5 |



**2ba**

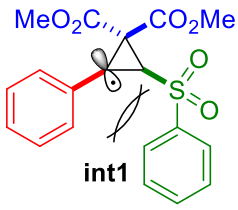
| | | | |
|---|---|---|---|
| C | -2.148012000 | -1.213508000 | 0.034979000 |
| C | -0.757970000 | -1.225727000 | -0.059563000 |

| | | | |
|---|---|---|---|
| C | -0.096545000 | 0.000047000 | -0.090960000 |
| C | -0.758006000 | 1.225873000 | -0.059750000 |
| C | -2.147971000 | 1.213518000 | 0.034912000 |
| C | -2.837360000 | -0.000007000 | 0.080688000 |
| H | -2.693174000 | -2.157601000 | 0.073789000 |
| H | -0.200170000 | -2.162647000 | -0.093810000 |
| H | -0.200123000 | 2.162724000 | -0.094290000 |
| H | -2.693281000 | 2.157534000 | 0.073815000 |
| H | -3.926308000 | 0.000088000 | 0.151973000 |
| S | 1.686908000 | 0.000027000 | -0.255017000 |
| O | 2.200052000 | 1.279628000 | 0.270605000 |
| O | 2.199663000 | -1.279841000 | 0.270264000 |

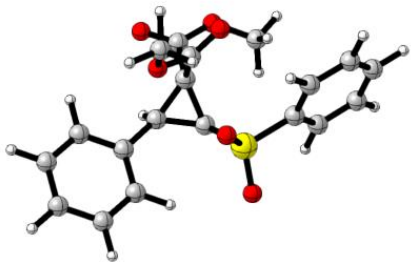


**Int1**:

| | |
|---|---|
| \| Charge = | 0 |
| \| Multiplicity = | 2 |
| \| Stoichiometry= | $C_{19}H_{17}SO_6$ |
| \| Number of Basis Functions = | 453 |
| \| Electronic Energy (Eh) = | -1582.145320 |
| \| Sum of electronic and zero-point Energies= | -1581.815042 |
| \| Sum of electronic and thermal Energies= | -1581.791237 |
| \| Sum of electronic and thermal Enthalpies= | -1581.790293 |
| \| Sum of electronic and thermal Free Energies= | -1581.869781 |
| \| Number of Imaginary Frequencies= | 0 |
| \| Mean of alpha and beta Electrons= | 97.5 |



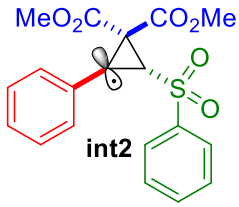

| | | | |
|---|---|---|---|
| C | -1.412026000 | 0.428153000 | -1.023170000 |
| C | -0.100206000 | -0.225261000 | -1.088562000 |
| C | -0.248685000 | 1.127783000 | -0.395175000 |
| C | -2.718816000 | -0.206922000 | -0.665715000 |
| C | -2.870408000 | -1.593804000 | -0.617867000 |
| C | -3.818154000 | 0.625515000 | -0.421587000 |
| C | -4.122842000 | -2.145803000 | -0.341818000 |
| H | -2.017900000 | -2.248634000 | -0.809283000 |
| C | -5.063211000 | 0.070519000 | -0.138604000 |
| H | -3.685101000 | 1.709576000 | -0.455652000 |
| C | -5.217929000 | -1.317728000 | -0.100585000 |
| H | -4.238663000 | -3.230670000 | -0.314024000 |
| H | -5.917594000 | 0.722486000 | 0.052021000 |
| H | -6.194807000 | -1.753102000 | 0.117390000 |
| C | -0.106847000 | 1.288877000 | 1.106814000 |
| C | 0.081102000 | 2.467305000 | -1.069105000 |
| C | -1.209458000 | 1.178911000 | 3.160728000 |
| C | 2.391728000 | 1.821122000 | -1.293809000 |
| H | -0.853692000 | 2.166414000 | 3.481140000 |
| H | -2.236559000 | 1.011891000 | 3.497572000 |
| H | -0.544978000 | 0.395862000 | 3.550613000 |
| H | 3.295669000 | 2.369609000 | -1.578765000 |
| H | 2.503373000 | 1.428925000 | -0.276155000 |
| H | 2.206647000 | 1.018140000 | -2.019076000 |
| O | 1.330022000 | 2.777065000 | -1.348688000 |
| O | -0.802686000 | 3.253228000 | -1.289323000 |
| O | -1.248574000 | 1.107983000 | 1.732441000 |
| O | 0.925473000 | 1.627398000 | 1.630321000 |
| S | 0.573486000 | -1.512733000 | -0.059806000 |
| C | 2.304163000 | -1.185569000 | 0.052363000 |
| C | 3.083237000 | -1.386985000 | -1.087833000 |
| C | 2.840849000 | -0.775908000 | 1.270608000 |
| C | 4.446297000 | -1.118437000 | -1.009804000 |
| H | 2.630223000 | -1.733712000 | -2.019291000 |
| C | 4.210886000 | -0.523736000 | 1.332457000 |
| H | 2.200707000 | -0.647746000 | 2.143749000 |
| C | 5.004278000 | -0.683421000 | 0.195895000 |



| | | | |
|---|---|---|---|
| H | 5.076289000 | -1.254309000 | -1.889814000 |
| H | 4.657662000 | -0.199255000 | 2.273119000 |
| H | 6.074141000 | -0.474946000 | 0.250688000 |
| O | 0.397665000 | -2.778014000 | -0.776698000 |
| O | -0.027141000 | -1.373087000 | 1.270789000 |
| H | -1.573019000 | 0.938956000 | -1.989437000 |

**Int2**:

| | |
|---|---|
| \| Charge = | 0 |
| \| Multiplicity = | 2 |
| \| Stoichiometry= | $C_{19}H_{17}SO_6$ |
| \| Number of Basis Functions = | 453 |
| \| Electronic Energy (Eh) = | -1582.156280 |
| \| Sum of electronic and zero-point Energies= | -1581.826481 |
| \| Sum of electronic and thermal Energies= | -1581.802746 |
| \| Sum of electronic and thermal Enthalpies= | -1581.801801 |
| \| Sum of electronic and thermal Free Energies= | -1581.881290 |
| \| Number of Imaginary Frequencies= | 0 |
| \| Mean of alpha and beta Electrons= | 97.5 |




| | | | |
|---|---|---|---|
| C | 1.395426000 | -0.169842000 | -0.849026000 |
| C | 0.068789000 | -0.753259000 | -0.673895000 |
| C | 0.562202000 | 0.292608000 | 0.314518000 |
| C | 0.034971000 | 1.714901000 | 0.413686000 |
| C | 0.998502000 | -0.116295000 | 1.718608000 |
| C | 0.335418000 | 3.938169000 | -0.225325000 |
| C | -0.938462000 | -1.511648000 | 2.118621000 |
| H | 0.332385000 | 4.307732000 | 0.808170000 |
| H | 1.052974000 | 4.499148000 | -0.831028000 |
| H | -0.673072000 | 4.018060000 | -0.653458000 |
| H | -1.318447000 | -1.805570000 | 3.104019000 |
| H | -1.512407000 | -0.648724000 | 1.757604000 |
| H | -1.023841000 | -2.362331000 | 1.431336000 |
| O | 0.437051000 | -1.162407000 | 2.312743000 |
| O | 1.866306000 | 0.496595000 | 2.283282000 |
| O | 0.767412000 | 2.576101000 | -0.262333000 |
| O | -0.881060000 | 2.014528000 | 1.139391000 |
| S | -1.335386000 | -0.115796000 | -1.638985000 |
| C | -2.738898000 | -0.402647000 | -0.599526000 |
| C | -3.159928000 | -1.722335000 | -0.424335000 |
| C | -3.390026000 | 0.678716000 | -0.010500000 |
| C | -4.246419000 | -1.963558000 | 0.411054000 |
| H | -2.645254000 | -2.544879000 | -0.925615000 |
| C | -4.483959000 | 0.418103000 | 0.814388000 |
| H | -3.043834000 | 1.697236000 | -0.186928000 |
| C | -4.900857000 | -0.895553000 | 1.031293000 |
| H | -4.588404000 | -2.986666000 | 0.572793000 |
| H | -5.010815000 | 1.246975000 | 1.288936000 |
| H | -5.752823000 | -1.091176000 | 1.684700000 |
| O | -1.458620000 | -0.969481000 | -2.822094000 |
| O | -1.157760000 | 1.324911000 | -1.826746000 |
| H | -0.083175000 | -1.801804000 | -0.389056000 |
| C | 2.779643000 | -0.490179000 | -0.566286000 |
| C | 3.614006000 | 0.498733000 | -0.006499000 |
| C | 3.324303000 | -1.748912000 | -0.891677000 |
| C | 4.948461000 | 0.214472000 | 0.252554000 |
| H | 3.197645000 | 1.480796000 | 0.221277000 |
| C | 4.657017000 | -2.030706000 | -0.609208000 |
| H | 2.684035000 | -2.504618000 | -1.351323000 |
| C | 5.471388000 | -1.049828000 | -0.038640000 |
| H | 5.589559000 | 0.983496000 | 0.686641000 |
| H | 5.066152000 | -3.015235000 | -0.842171000 |
| H | 6.519417000 | -1.267315000 | 0.175059000 |