Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for

Facile synthesis of 1,2-aminoalcohols *via* α-C−H aminoalkylation of alcohols by photoinduced hydrogen-atom transfer catalysis

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Table of Contents

1. General Information

Materials

Dry solvents were purchased and used as received: dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), diethyl ether (Et_2O), acetone were purchased as "Super Dehydrated" grade from FUJIFILM Wako Pure Chemical Co., Inc. Dichloromethane (CH_2Cl_2) and acetonitrile (MeCN) were purchased as "Dehydrated -Super^2-" and "Dehydrated -Super-" grade respectively from Kanto Chemical Co., Inc. Commercially available reagents were purchased from TCI, FUJIFILM Wako, Merck Sigma-Aldrich, Nacalai tesque, Combi-Blocks or BLDpharm, and used as received for the reactions unless otherwise noted.

Methods

^{1}H-NMR spectra were recorded on a JEOL JNM-ECA500 (500 MHz) or JEOL JNM-FX400 (400 MHz) spectrometer. Data for ^{1}H-NMR are reported as follows: chemical shifts in ppm relative to tetramethylsilane as an internal standard (0.00 ppm) in $CDCl_3$ or DMSO-d_6, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C-NMR spectra were recorded on a JEOL JNM-ECA500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts for ^{13}C-NMR are reported in ppm relative to the residual solvent as an internal standard: $CDCl_3$ (77.16 ppm), DMSO-d_6 (39.52 ppm). ^{19}F-NMR spectra were recorded on a JEOL JNM-ECA500 (471 MHz) or JEOL JNM-FX400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts for ^{19}F-NMR are reported in ppm from benzotrifluoride (–63.7 ppm) resonance as an external standard. High-resolution mass spectrometry (HRMS) was performed on a Thermo Exactive plus (ESI) spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Silica gel 60 F_{254}) were used, and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved mainly by basic aqueous $KMnO_4$ solution stain or phosphomolybdic acid stain (PMA). The products were purified by flash column chromatography on neutral silica gel (Kanto Chemical Co. Inc., Silica gel 60N, particle size 40–50 μm). Further purification by preparative thin layer chromatography (PLC) was performed using Merck PLC plates (PLC silica gel 60 F_{254}, 0.5 mm) if necessary.

Diastereomeric ratios were determined by high-performance liquid chromatography (HPLC) analysis using Shimadzu 20A instruments, and chiral column [DAICEL, CHIRALPAK IC-3, ϕ 4.6 mm x 250

mm] with hexane and 2-propanol (*i*PrOH) mixture as an eluent. Cyclic voltammetry was performed on an electrochemical analyzer ALS model 760D (BAS Inc.). Stern-Volmer quenching experiments were conducted on a Shimadzu RF-6000 spectrofluorophotometer.

Photochemical Reaction Set-up

Unless otherwise noted, the photochemical reactions were run using a stick-type blue LED (Techno-Sigma PER-448, λ_{max} = 448 nm, radiant flux = 0.68 W), which was inserted into a reaction vessel (Schlenk tube with three-way stopcock on side, 18 × 125 mm) and connected with a light source device (Techno-Sigma PER-AMP-N4) (**Figure S1**). The reaction vessel was kept in a temperature-controlled reactor (Techno-Sigma, UCR-80 Nh) and the temperature was set to 25 ˚C during the reaction.

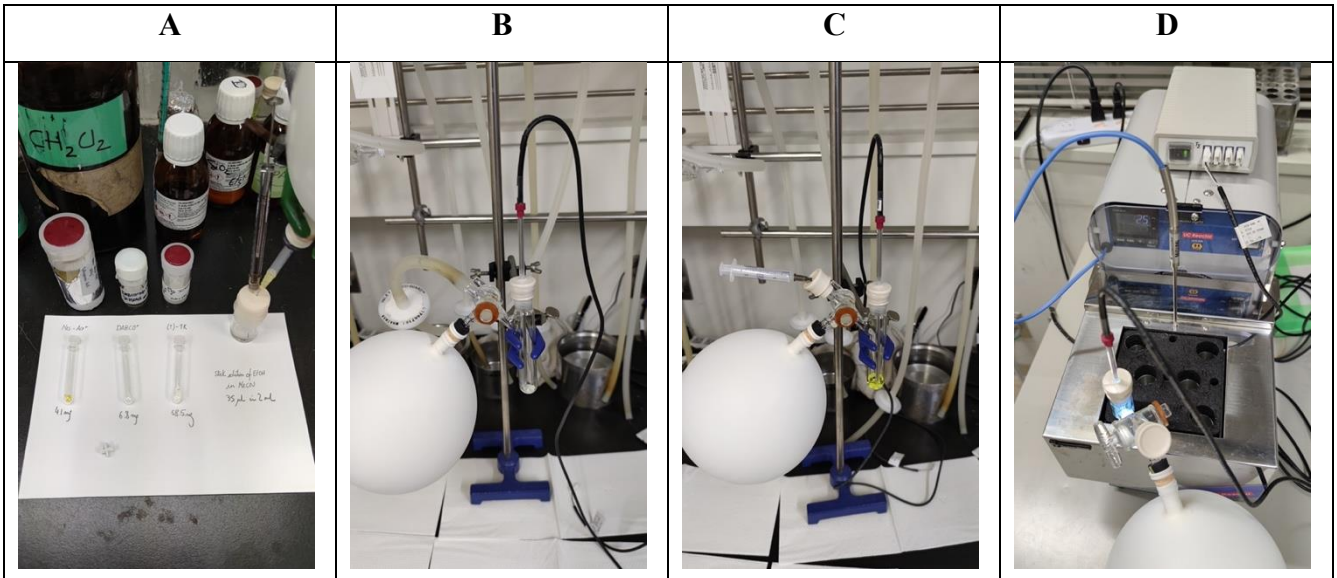
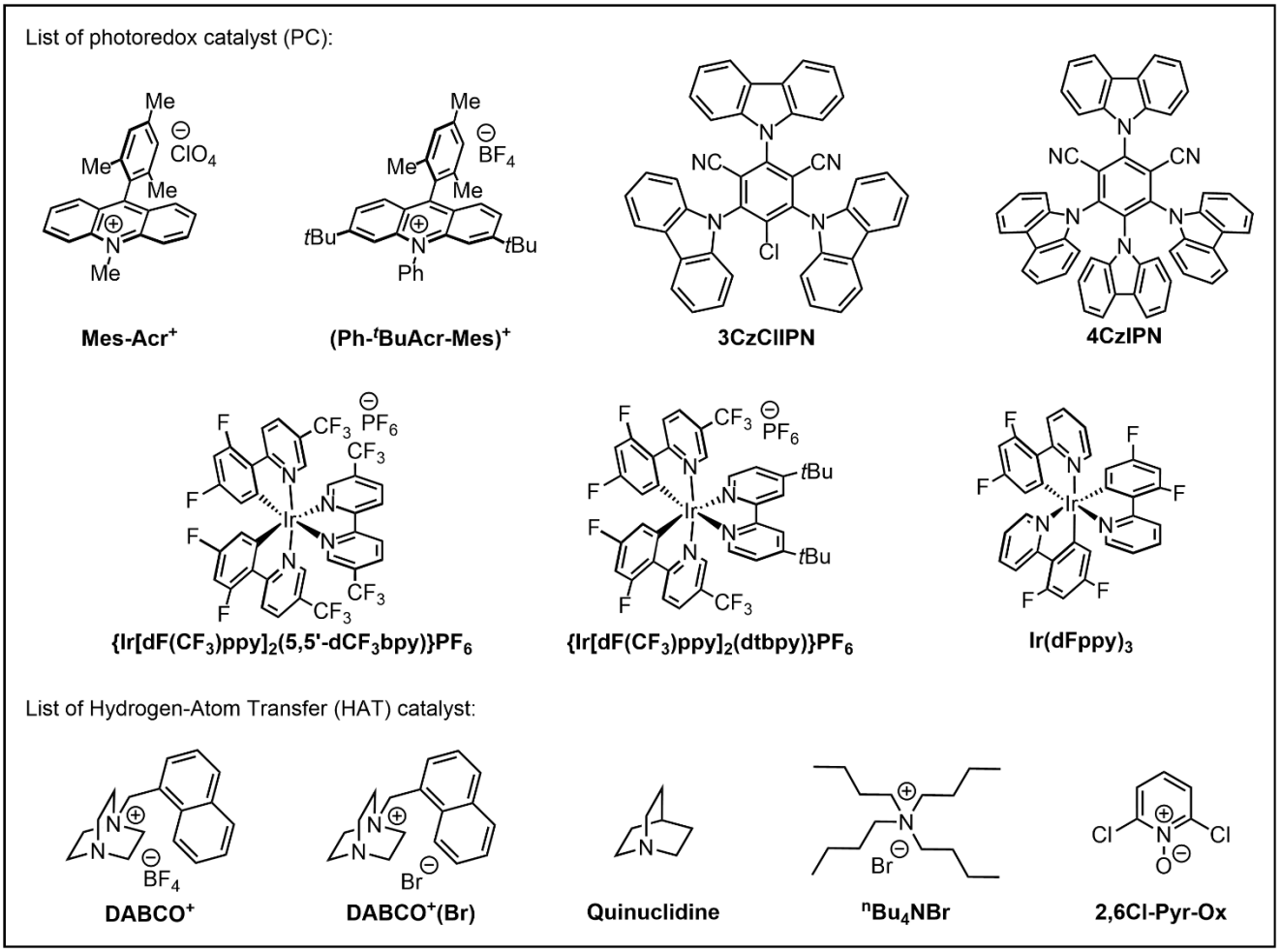


Figure S1. A) Solid reagents were weighed in microtubes and liquid reagents were dissolved in the solvent under argon atmosphere in a separated vial. **B)** Solids and a magnetic stirring bar (crosshead type) were placed in a Schlenk tube with a three-way stopcock on side and a LED light source (Techno-Sigma, PER-448 on NMR tube) was inserted into a Schlenk tube, which was capped with a rubber septum and covered with parafilm. The Schlenk tube was degassed via vacuum evacuation and subsequent backfill with argon for three times through the three-way stopcock *(under vacuum in the snapshot)*. **C)** The solution of liquid reagent in the solvent was transferred via syringe to the Schlenk tube through a septum equipped in the three-way stopcock under positive argon pressure. **D)** The reaction mixture was irradiated in a temperature-controlled reactor equipped with an aluminum block at 25 ˚C.

2. Preparation of Catalysts and Substrates

2.1. Photoredox Catalysts and Hydrogen-Atom Transfer (HAT) Catalysts

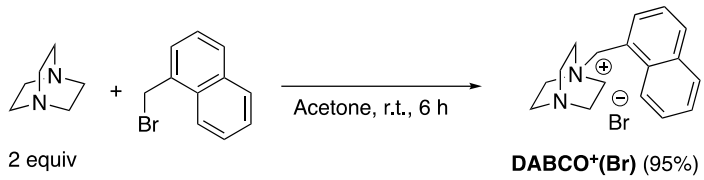
All photoredox catalysts and hydrogen-atom transfer catalysts are commercially available or made by known methods:



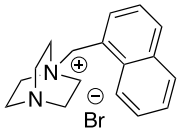
Commercially available: **Mes-Acr**$^{+}$, **{Ir[dF(CF$_3$)ppy]$_2$(dtbpy)}PF$_6$**, **Ir(dFppy)$_3$**, **Quinuclidine**, **(^{n}Bu)$_4$NBr**.

The following compounds were synthesized according to previously reported methods: **(Ph-^{t}BuAcr-Mes)**$^{+}$,[1] **4CzIPN**,[2] **DABCO**$^{+}$,[3] **DABCO**$^{+}$**(Br)**,[3] **2,6-Cl$_2$-Pyr-Ox**.[4]

1-(Naphthalen-1-ylmethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium tetrafluoroborate (DABCO$^+$(Br))



To a solution of 1-(bromomethyl)naphthalene (1.15 g, 5.2 mmol) in acetone (20 mL) was added 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.19 g, 10.5 mmol) in one portion at r.t., and the mixture was stirred vigorously for 6 h under argon atmosphere. The resultant white solid was filtered, triturated repeatedly with Et_2O and EtOAc to remove the excess amount of DABCO, and dried under vacuum. The process furnished 1.55 g (95% yield) of **DABCO$^+$(Br)** as a white solid.



DABCO$^+$(Br), new compound.

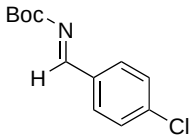
^{1}H-NMR (500 MHz, DMSO-d$_6$) δ 8.47 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.81–7.79 (m, 1H), 7.70–7.61 (m, 3H), 5.07 (s, 2H), 3.42 (t, *J* = 7.4 Hz, 6H), 2.99 (t, *J* = 7.4 Hz, 6H).

^{13}C-NMR (126 MHz, DMSO-d$_6$) δ 133.8, 133.7, 132.9, 131.3, 129.0, 127.3, 126.3, 125.3, 124.1, 123.4, 62.8, 51.7, 44.8.

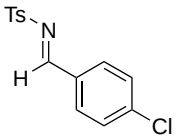
HRMS ESI [M–Br]$^+$ calculated for $C_{17}H_{21}N_2^+$: 253.1699, found 253.1699.

2.2. Imines (Radical Acceptors)

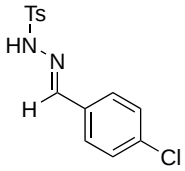
Imines (other than *N*-sulfinyl α-iminoesters) used in the initial screening:



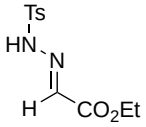
1a



1b



1c



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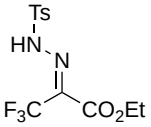
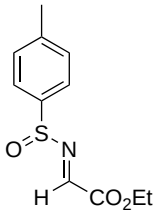
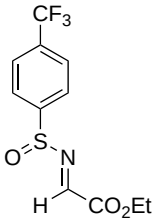


1e

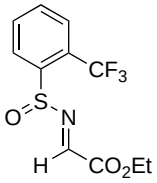
(±)-*N*-Sulfinyl α-iminoesters used in this work:



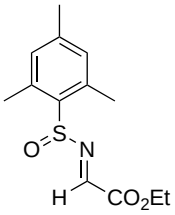
(±)-**1f**



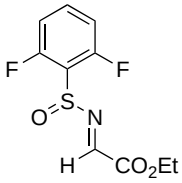
(±)-**1g**



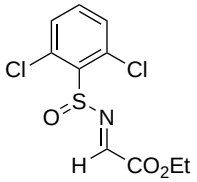
(±)-**1h**



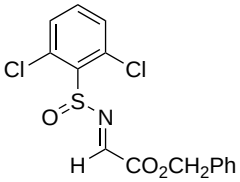
(±)-**1i**



(±)-**1j**



(±)-**1k**



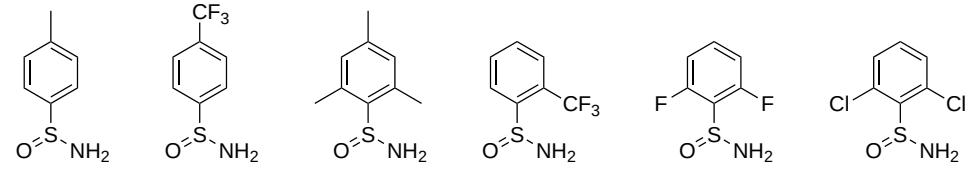
(±)-**1l**

The following compounds were synthesized according to previously reported methods: **1a**,[5] **1b**,[6] **1c**,[7] **1d**,[8] **1e**.[9]

Racemic *N*-sulfinyl α-iminoesters were synthesized from the corresponding racemic sulfinamides according to the reported method:[10] (±)-**1f**, (±)-**1g**, (±)-**1h**, (±)-**1i**, (±)-**1j**, (±)-**1k**, (±)-**1l**.

2.2.1. Racemic Sulfinamides ((±)-**s1**-**6**) as Precursors for *N*-Sulfinyl α-Iminoesters

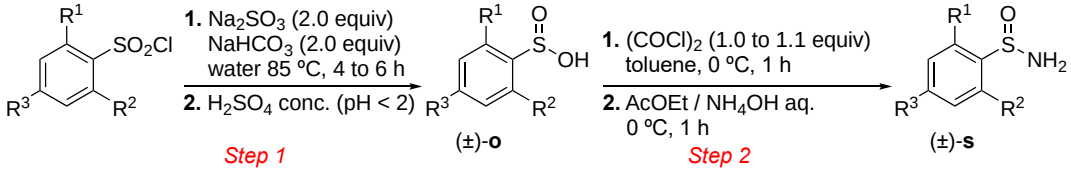
(±)-Sulfinamides prepared in this work for the synthesis of *N*-sulfinyl α-iminoesters:



(±)-**s1** (±)-**s2** (±)-**s3** (±)-**s4** (±)-**s5** (±)-**s6**

Racemic sulfinamides were prepared according to the reported methods for the reduction of aromatic sulfonyl chlorides with Na_2SO_3 (**Method A**)[11] or $NaBH_4$ (**Method B**)[12] to give the corresponding sulfinic acids ((±)-**o**), followed by the condensation with ammonia via the sulfinyl chloride intermediates:[13]

Method A



Step 1:[11a] Sodium sulfinate (20 mmol, 2 equiv.) and sodium bicarbonate (20 mmol, 2 equiv.) were dissolved in distilled water (10 mL) and the corresponding aryl sulfonyl chloride (10 mmol, 1 equiv.) was added. The reaction mixture was stirred for 4 to 6 h at 85 °C. After cooling down to r.t., the mixture was cooled at 0 °C and conc. H_2SO_4 was added to adjust the pH < 2. After 1 h at 0 °C (*a white precipitate of sulfinic acid was formed*), 30 mL of CH_2Cl_2 were added, and after decantation, the aqueous phase was extracted with CH_2Cl_2 and Et_2O several times. The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure using a rotary evaporator to furnish the desired sulfinic acid (±)-**o** as a colorless powder, which was used without further purification in the next step.

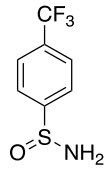
Step 2:[13] Aryl sulfinic acid ((±)-**o**, 1 equiv.) was suspended in toluene at 0 ºC (0.5 M). DMF (few drops) and oxalyl chloride (1.05 equiv.) were added dropwise sequentially. After 10 min at 0 ºC the reaction mixture was stirred at r.t. for 1 h. The freshly prepared solution of sulfinic chloride was transferred dropwise (*using a syringe*) to 1:1 mixture of EtOAc/25 w/w% ammonia aq. (2.5 mL/mmol of initial (±)-

o) at 0 ºC. After 10 min at 0 ºC the reaction mixture was stirred at r.t. for 2 h and then diluted with EtOAc. After decantation, the organic phase was washed with brine and the combined aqueous phase was extracted with CH_2Cl_2 and/or $CHCl_3$ several times. The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure using a rotary evaporator to afford the desired aryl sulfinamide (±)-**s**.

(±)-4-(Trifluoromethyl)benzenesulfinamide ((±)-**s2**) [CAS: 2282706-55-0]

Method A, Step 1: 4-(Trifluoromethyl)benzenesulfonyl chloride (2.48 g, 10.0 mmol) provided 1.41 g (61% yield) of (±)-4-(trifluoromethyl)benzenesulfinic acid ((±)-**o2**) as a white solid.

Method A, Step 2: (±)-4-(Trifluoromethyl)benzenesulfinic acid ((±)-**o2**, 626 mg, 3.0 mmol) furnished 534 mg (86% yield) of (±)-**s2** as a white solid.

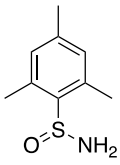


(±)-**s2** is a known compound in literature and its spectral data are in good agreement with literature values.[14]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 4.46 (br s, 2H). **^{19}F-NMR (471 MHz, $CDCl_3$)** δ –62.7.

(±)-2,4,6-Trimethylbenzenesulfinamide ((±)-**s3**) [CAS: 137280-49-0]

Method A: Step 1: 2-Mesitylenesulfonyl chloride (2.20 g, 10.0 mmol) provided 1.32 g (71% overall yield) of (±)-2,4,6-trimethylenzenesulfinic acid ((±)-**o3**) as a white solid.

Method A: Step 2: (±)-2,4,6-trimethylenzenesulfinic acid ((±)-**o3**, 1.29 g, 7.0 mmol) furnished 1.06 g (83% yield) of (±)-**s3** as a white solid.

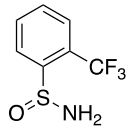


(±)-**s3** is a known compound in literature and its spectral data are in good agreement with literature values.[15]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.49 (br s, 2H), 2.59 (s, 6H), 2.28 (s, 3H).

(±)-2-(Trifluoromethylbenzenesulfinamide ((±)-**s4**)

Method A, Step 1: 2-(Trifluoromethyl)-benzenesulfonyl chloride (1.55 mL, 10.0 mmol) provided 1.84 g (88% yield) of (±)-2-(trifluoromethyl)benzenesulfinic acid ((±)-**o4**) as a white solid.

Method A, Step 2: (±)-2-(Trifluoromethyl)benzenesulfinic acid ((±)-**o4**, 1.27 g, 6.0 mmol) furnished 1.15 g (91% yield) of (±)-**s4** as a white solid.



(±)-**s4**, new compound.

^{1}H-NMR (500 MHz, DMSO-d$_6$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 6.31 (s, 2H).

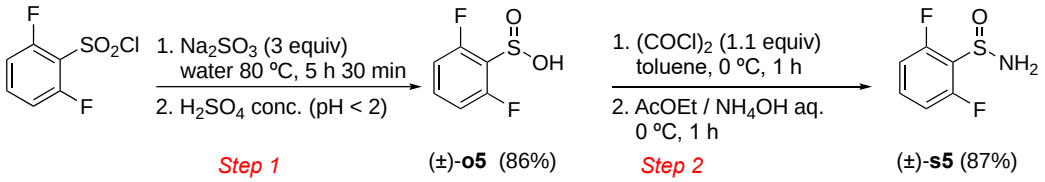
^{13}C-NMR (126 MHz, DMSO-d$_6$) δ 147.9, 133.3, 131.0, 126.3 (q, $J_{C\text{-}F}$ = 5.6 Hz), 124.9 (q, $J_{C\text{-}F}$ = 32.4 Hz), 124.4, 123.7 (q, $J_{C\text{-}F}$ = 275.1 Hz).

^{19}F-NMR (471 MHZ, DMSO-d$_6$) δ –56.2.

HRMS ESI [M+Na]$^+$ calculated for $C_7H_6F_3NNaOS^+$: 232.0014, found 232.0013.

(±)-2,6-Difluorobenzenesulfinamide ((±)-**s5**)

The target sulfinamide was prepared according to **Method A** with slight modifications in **Step 1**.



Step 1:[11b] Sodium sulfinate (4.54 g, 36 mmol, 3 equiv.) was dissolved in distilled water (24 mL) and 2,6-difluorobenzenesulfonyl chloride (1.6 mL, 12 mmol, 1 equiv.) was added. Then, the reaction mixture was stirred for 5.5 h at 80 °C. After cooling down to r.t., the mixture was cooled at 0 °C and conc. H_2SO_4 was added to adjust the pH < 2. After 1 h at 0 °C (*a white precipitate of* (±)-**o5** *was formed*), 30 mL of CH_2Cl_2 was added, and after decantation, the aqueous phase was extracted with CH_2Cl_2 and Et_2O several times. The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure using a rotary evaporator to provide 2.14 g (86% yield) of (±)-**o5** as an off-white solid, which was used without further purification in the next step.

Step 2:[13] Same as described in **Method A**. (±)-2,6-Difluorobenzesulfinic acid ((±)-**o5**, 1.80 g, 10.1 mmol) furnished 1.79 g (87% yield) of (±)-**s5** as a white solid.

(±)-**s5**, new compound.

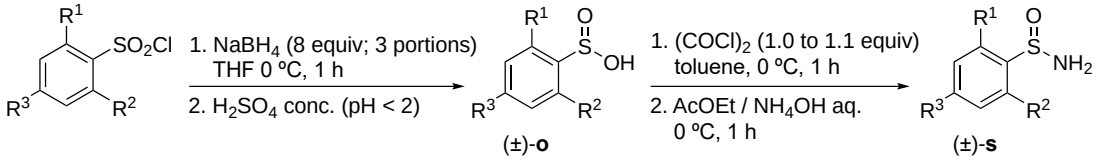
^{1}H-NMR (500 MHz, DMSO-d$_6$) δ 7.58–7.52 (m, 1H), 7.20 (t, *J* = 8.6 Hz), 6.70 (s, 2H).

^{13}C-NMR (126 MHz, DMSO-d$_6$) δ 158.8 (dd, $J_{C\text{-}F}$ = 250.7, 7.2 Hz), 133.1 (t, $J_{C\text{-}F}$ = 10.8 Hz), 124.9 (t, $J_{C\text{-}F}$ = 19.2 Hz), 112.9 (dd, $J_{C\text{-}F}$ = 20.4, 3.6 Hz).

^{19}F-NMR (377 MHZ, DMSO-d$_6$) δ –113.5.

HRMS ESI [M+H]$^+$ calculated for $C_6H_6F_2NOS^+$: 178.0133, found 178.0132.

Method B



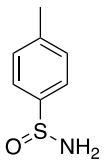
Step 1:[12] The corresponding aryl sulfonyl chloride (1 equiv.) was dissolved in THF (0.17 M) at 0 ºC. $NaBH_4$ (8 equiv.) was added in 3 portions over 15 min and the reaction mixture was stirred at 0 ºC for 1 h. After removal of THF under reduced pressure using a rotary evaporator, water (2 mL/mmol) was added carefully at 0 ºC. The mixture was then quenched with HCl aq. (1N) and the pH was adjusted to < 2 with conc. H_2SO_4 at 0 ºC. The acidic solution was extracted with $CHCl_3$ and/or Et_2O several times and the combined organic layers were dried with Na_2SO_4. The solvent was removed under reduced pressure using a rotary evaporator to furnish the desired sulfinic acid ((±)-**o**) as a white powder, which was used without further purification in the next step.

Step 2:[13] Same as described in **Method A**.

(±)-4-Methylbenzenesulfinamide ((±)-**s1**) [CAS: 6873-55-8]

Method B, Step 1: 4-methylbenzenesulfonyl chloride (1.09 g, 5.7 mmol) provided 720 mg (81% yield) of (±)-4-methylenzenesulfinic acid ((±)-**o1**) as a white solid.

Method B, Step 2: (±)-4-methylenzenesulfinic acid ((±)-**o1**, 703 mg, 4.5 mmol) furnished 560 mg (80% yield) of (±)-**s1**.

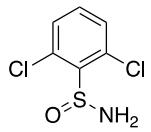


(±)-**s1** is a known compound in literature and its spectral data are in good agreement with literature values.[16]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8,3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.35 (br s, 2H), 2.42 (s, 3H).

(±)-2,6-Dichlorobenzenesulfinamide ((±)-**s6**)

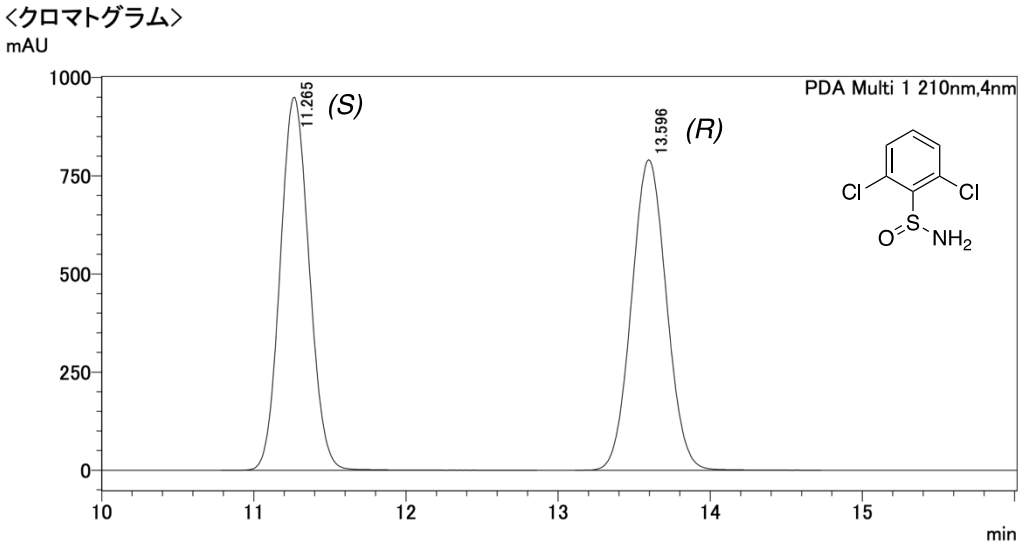
Method B, Step 1: 2,6-Dichlorobenzenesulfonyl chloride (1.03 g, 4.2 mmol) provided 712 mg (81% yield) of (±)-2,6-dichlorobenzenesulfinic acid ((±)-**o6**) as a colorless solid.

Method B, Step 2: (±)-2,6-Dichlorobenzenesulfinic acid ((±)-**o6**, 680 mg, 3.2 mmol) furnished 501 mg (74% yield) of (±)-**s6** as an off-white solid.



(±)-**s6**, new compound.
^{1}H-NMR (500 MHz, DMSO-d$_6$) δ 7.54-7.52 (m, 2H), 7.48–7.46 (m, 1H), 6.60 (s, 2H).
^{13}C-NMR (126 MHz, DMSO-d$_6$) δ 141.8, 132.2, 132.0, 130.2.
HRMS ESI [M+Na]$^+$ calculated for $C_6H_5Cl_2NNaOS^+$: 231.9361, found 231.9361.
Chiral HPLC (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:20, 40 °C, flow rate: 1.5 mL/min, λ =210 nm): Retention time = 11.3 min ((*S*)-**s6**, 50.0%), 13.6 min ((*R*)-**s6**, 50.0%).

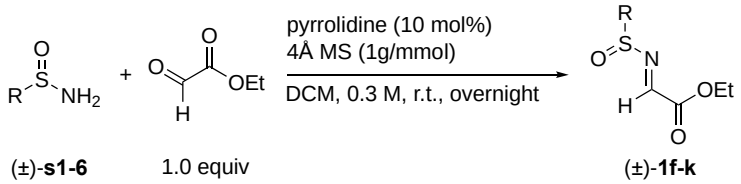
Chromatogram of (±)-**s6**:



Entry	Retention time (min)	Area	Area (%)
1	11.265	12592005	49.958
2	13.596	12613403	50.042
Total		25205409	100

2.2.2. Racemic *N*-Sulfinyl α-Iminoesters

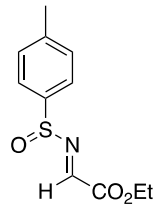
Method C[10]



In a round bottom flask, 4Å MS (1 g/mmol of (±)-**s**) was activated by heating with a heat gun. After cooling at r.t., sulfinamide ((±)-**s**, 1 equiv.) and CH_2Cl_2 (0.3 M) were added under argon atmosphere. Ethyl glyoxylate (1 equiv., 47 w/w% solution in toluene) and pyrrolidine (10 mol%) were added to the solution via syringe and the mixture was stirred overnight. Then, the reaction solution was filtered through a short pad of Celite® and the solvent was removed under reduced pressure using a rotary evaporator. The residue was purified by flash column chromatography on silica-gel (hexanes/EtOAc 95:5 to 8:2) to afford the desired compound.

(±)-Ethyl (*E*)-2-((tolylsulfinyl)imino)acetate ((±)-**1f**) [CAS: 1533401-88-5]

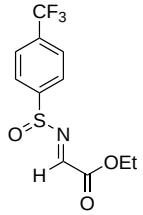
Method C: (±)-4-Toluenesulfinamide ((±)-**s1**, 466 mg, 3.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 630 µL) provided 718 g (77% yield) of (±)-**1f** as an off-white solid.



(±)-**1f** is a known compound in literature and its spectral data are in good agreement with literature values.[10]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.35 (qd, *J* = 7.1, 3.2 Hz, 2H), 2.41 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 161.4, 153.2, 142.7, 139.3, 130.2, 124.8, 62.7, 21.6, 14.1.

(±)-Ethyl (*E*)-2-(((4-(trifluoromethyl)phenyl)sulfinyl)imino)acetate ((±)-**1g**)

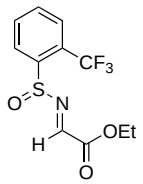
Method C: (±)-4-(Trifluoromethyl)benzenesulfinamide ((±)-**s2**, 420 mg, 2.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 400 µL) provided 282 mg (48% yield) of (±)-**1g** as a colorless solid.



(±)-**1g**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 4.41–4.32 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 161.0, 154.1, 146.4, 134.0 (q, J_{C-F} = 32.8 Hz), 126.0 (q, J_{C-F} = 32.8 Hz), 125.5, 123.5 (q, J_{C-F} = 272.3 Hz, *only the two main peaks are observed*), 63.0, 14.1. **^{19}F-NMR (377 MHZ, $CDCl_3$)** δ –62.9. **HRMS ESI $[M+H]^+$** calculated for $C_{11}H_{11}F_3NO_3S^+$: 294.0406, found 294.0404.

(±)-Ethyl (*E*)-2-(((4-(trifluoromethyl)phenyl)sulfinyl)imino)acetate ((±)-**1h**)

Method C: (±)-2-(Trifluoromethyl)benzenesulfinamide ((±)-**s4**, 419 mg, 2.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 400 µL) provided 324 mg (55% yield) of (±)-**1h** as a yellowish wax-oil.



(±)-**1h**, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.76 (m, 2H), 7.65 (t, J = 7.7 Hz, 1H), 4.33 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H).

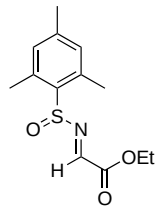
^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.1, 153.9, 141.7, 133.3, 132.0, 128.0 (q, $J_{C\text{-}F}$ = 33.2 Hz), 126.8 (q, $J_{C\text{-}F}$ = 5.2 Hz), 123.3 (q, $J_{C\text{-}F}$ = 274.7 Hz), 62.6, 13.8.

^{19}F-NMR (471 MHZ, $CDCl_3$) δ –56.9.

HRMS ESI [M+H]$^+$ calculated for $C_{11}H_{11}F_3NO_3S^+$: 294.0406, found 294.0405.

(±)-Ethyl (*E*)-2-((mesitylsulfinyl)imino)acetate ((±)-**1i**) [CAS: 2549158-51-0]

Method C: (±)-2,4,6-Trimethylbenzenesulfinamide ((±)-**s3**, 916 mg, 5.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 1.0 mL) provided 1.01 g (76% yield) of (±)-**1i** as a colorless solid.



(±)-**1i** has a CAS RN.

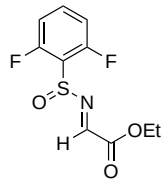
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 6.86 (s, 2H), 4.40–4.35 (m, 2H), 2.46 (s, 6H), 2.28 (s, 3H), 1.39–1.35 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.5, 154.0, 142.6, 138.9, 133.1, 131.2, 62.7, 21.2, 19.0, 14.2.

HRMS ESI [M+H]$^+$ calculated for $C_{13}H_{18}F_3NO_3S^+$: 268.1002, found 268.0998.

(±)-Ethyl (*E*)-2-(((2,6-difluorophenyl)sulfinyl)imino)acetate ((±)-**1j**)

Method C: (±)-2,6-Difluorobenzenesulfinamide ((±)-**s5**, 357 mg, 2.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 400 µL) provided 279 mg (53% yield) of (±)-**1j** as an off-white solid.



(±)-**1j**, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.54–7.48 (m, 1H), 7.01–6.98 (m, 2H), 4.45–4.38 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H).

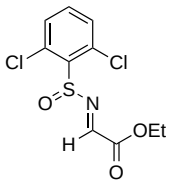
^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.0, 160.9 (dd, $J_{C\text{-}F}$ = 257.3, 5.4 Hz), 156.1, 119.1 (t, $J_{C\text{-}F}$ = 18.0 Hz), 113.1 (dd, $J_{C\text{-}F}$ = 21.6, 3.6 Hz), 63.0, 14.2.

^{19}F-NMR (471 MHZ, $CDCl_3$) δ –110.5.

HRMS ESI [M+H]$^+$ calculated for $C_{10}H_{10}F_2NO_3S^+$: 262.0344, found 262.0340.

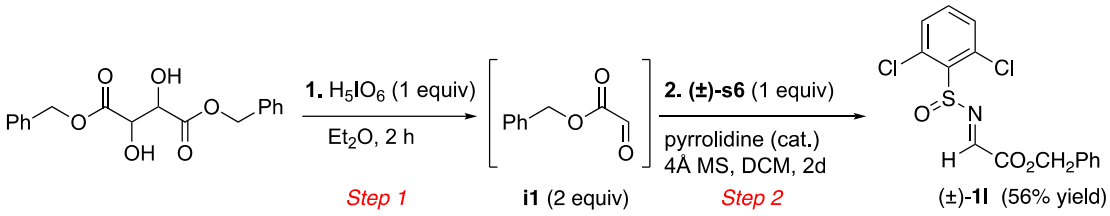
(±)-Ethyl (*E*)-2-(((2,6-dichlorophenyl)sulfinyl)imino)acetate ((±)-**1k**)

Method C: (±)-2,6-Dichlorobenzenesulfinamide ((±)-**s6**, 1.470 g, 7.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 1.5 mL) provided 1.38 g (67% yield) of (±)-**1k** as a colorless solid.



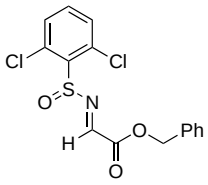
(±)-**1k**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.37 (br s, 3H), 4.46–4.36 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H).
^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.1, 156.5, 136.1, 135.3, 133.6, 130.6, 63.0, 14.2.
HRMS ESI [M+H]$^+$ calculated for $C_{10}H_{10}Cl_2NO_3S^+$: 293.9753, found 293.9754.

(±)-Benzyl (*E*)-2-(((2,6-dichlorophenyl)sulfinyl)imino)acetate ((±)-**1l**)



Step 1:[17] To an oven-dried, 2-neck 50 mL round bottom flask equipped with a magnetic stir bar was added dibenzyl L-tartrate (661 mg, 2.0 mmol, 1 equiv.), followed by 15 mL of Et_2O under argon atmosphere. Once dissolved, H_5IO_6 (456 mg, 2.0 mmol, 1 equiv.) was added in one portion at r.t. The reaction was complete in 2 h as judged by TLC (Hexanes/EtOAc 1:1). The reaction mixture was filtered over Celite® and the residue was washed with extra Et_2O. The filtrate was concentrated under reduced pressure using a rotary evaporator to give the crude residue of **i1**, which was used without further purification in the next step.

Step 2: The crude residue of **i1** was transferred to a 50 mL round bottom flask together with 2 g of 4Å MS. After purge and backfill with argon, dry CH_2Cl_2 (7 mL), **s6** (420 mg, 2.0 mmol, 1 equiv.), and pyrrolidine (9 mol%, 15 μL) were sequentially added. The resulting mixture was stirred for 2 days at r.t., and the solution was filtered over Celite®. The filter cake was washed several times with CH_2Cl_2 until the desired product was not detected by TLC. The combined organic phases were concentrated under reduced pressure using a rotary evaporator, and the crude oil was purified by flash column chromatography on silica-gel (hexanes/EtOAc 95:5 to 8:2) to afford the desired compound (±)-**1l** (400 mg, 56% yield) as a white solid.



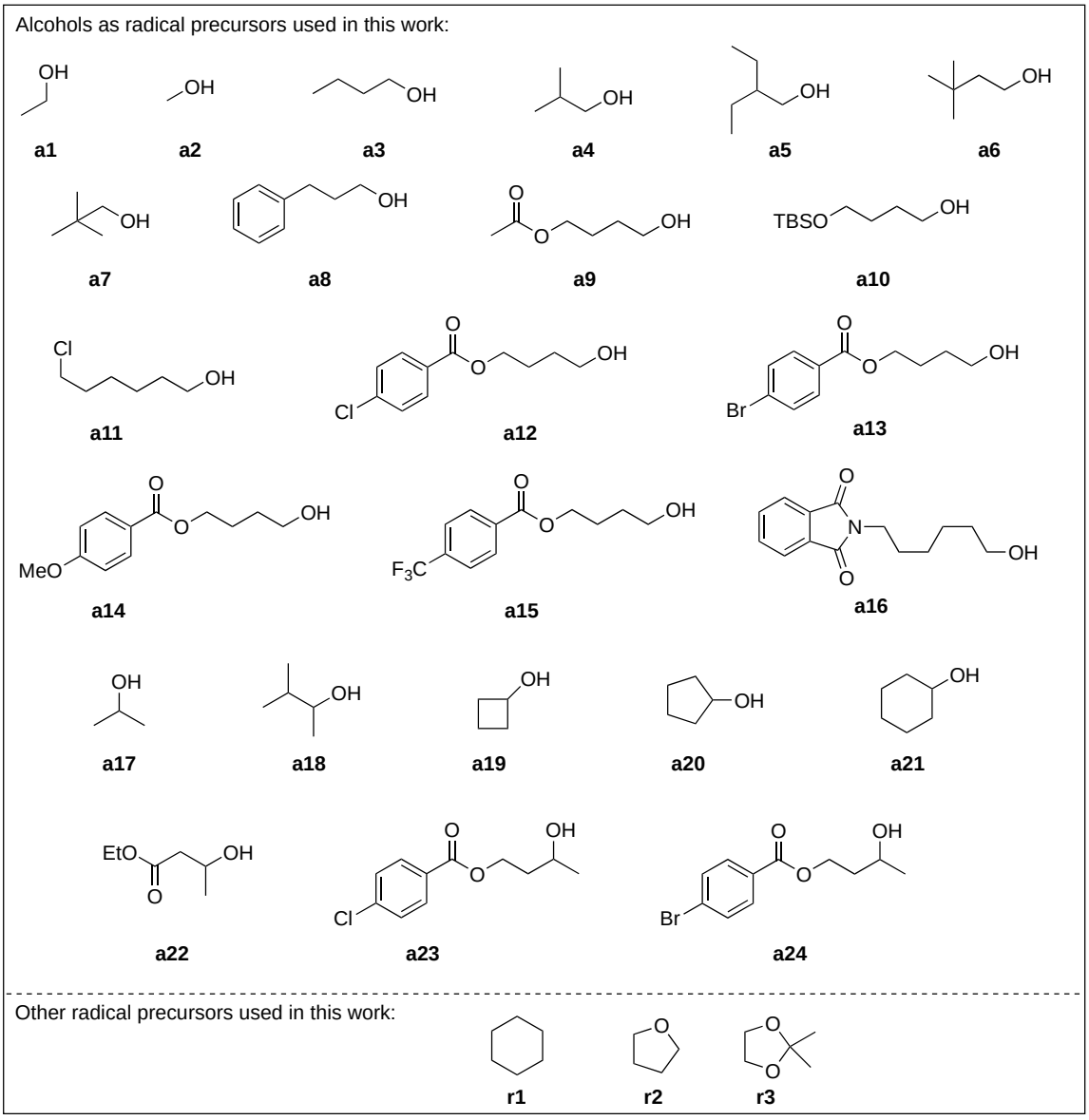
(±)-**1l**, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.42–7.35 (m, 8H), 5.36 (dd, *J* = 17.6, 12.2 Hz, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 160.9, 156.2, 136.0, 135.2, 134.5, 133.6, 130.6, 129.0, 128.9, 128.8, 68.5.

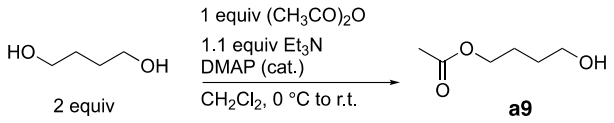
HRMS ESI $[M+H]^+$ calculated for $C_{15}H_{12}Cl_2NO_3S^+$: 355.9909, found 355.9912.

2.3. Alcohols (Substrates)

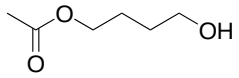


Commercially available: **a1**, **a2**, **a3**, **a4**, **a5**, **a6**, **a7**, **a8**, **a9**, **a12**, **a18**, **a19**, **a20**, **a21**, **a22**, **a23**, **r1**, **r2, r3**. The following compounds were synthesized and/or characterized according to previous literatures: **a9**, **a10**, **a12**, **a13**, **a14**, **a15**, **a16**, **a23**, **a24**.

4-Hydroxybutyl acetate (**a9**) [CAS: 35435-68-8]

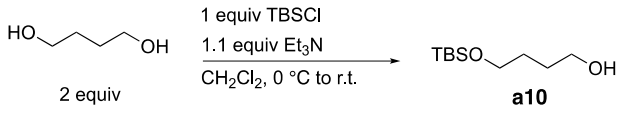


To a stirred solution of 1,4-butanediol (1.8 mL, 20 mmol, 2 equiv.) in CH_2Cl_2 (40 mL) at 0 °C was added Et_3N (1.4 mL, 10 mmol, 1 equiv.). After 10 min, $(CH_3CO)_2O$ (950 μL, 10 mmol, 1 equiv.) and DMAP (60 mg, 0.5 mmol, cat.) were added to the solution, and the resultant mixture was stirred at r.t. overnight. The reaction was quenched with NH_4Cl aq., and after decantation, the organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. Purification of the crude residue by flash chromatography on silica-gel (hexanes/EtOAc 75:25 to 50:50) afforded 830 mg (63% yield) of the title compound **a9** as a colorless oil.

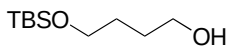


a9 is a known compound in literature, and its spectral data are in good agreement with literature values.[18]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.11 (t, *J* = 6.4 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.06 (s, 3H), 1.77–1.69 (m, 2H), 1.68–1.62 (m, 2H), 1.56–1.36 (br s, 1H).

4-((*tert*-Butylsilyl)oxy)butan-1-ol (**a10**) [CAS: 87184-99-4]

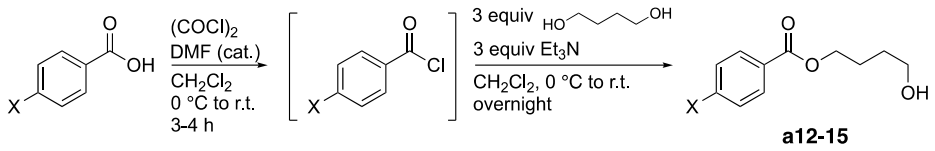


To a stirred solution of 1,4-butanediol (1.8 mL, 20 mmol, 2 equiv.) and *tert*-butyldimethylsilyl chloride (1.51 g, 10.0 mmol, 1 equiv.) in CH_2Cl_2 (35 mL) at 0 °C was added Et_3N (1.4 mL, 10.0 mmol, 1 equiv.). The reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched with NH_4Cl aq., and after decantation, the organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. Purification of the residue by flash chromatography on silica-gel (hexanes/EtOAc 90:10) afforded 1.84 g (90% yield) of the title compound **a10** as a colorless oil.



a10 is a known compound in literature, and its spectral data are in good agreement with literature values.[19]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.69–3.63 (m, 4H), 2.52 (br s, 1H, O**H**), 1.67–1.62 (m, 4H), 0.91 (s, 9H), 0.08 (s, 6H).

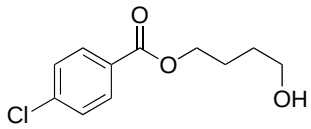
Method D



To a solution of *p*-substituted benzoic acid (10 mmol, 1 equiv.) in CH_2Cl_2 (20 mL) at 0 °C were added DMF (50 µL, cat.) and oxalyl chloride (1.0 mL, 12 mmol, 1.2 equiv.). The reaction mixture was allowed to warm at r.t. and stirred for 3 to 4 h. The freshly prepared solution of the corresponding *p*-substituted benzoyl chloride was transferred dropwise to a solution of 1,4-butanediol (2.6 mL, 30 mmol, 3 equiv.) and Et_3N (4 mL, 28 mmol, 2.8 equiv.) in CH_2Cl_2 (15 mL) at 0 °C using a syringe. After 15 min, the reaction mixture was stirred at r.t. overnight. The reaction was quenched with NH_4Cl aq., and after decantation, the organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. The residue was purified by flash column chromatography on silica-gel (hexanes/EtOAc 75:25 to 50:50) to furnish the corresponding alcohol.

4-Hydroxybutyl 4-chlorobenzoate (**a12**) [CAS: 356070-05-8]

Method D: 4-Chlorobenzoic acid (1.57 g, 10.0 mmol) provided 1.33 g (58% yield) of **a12** as a colorless oil.

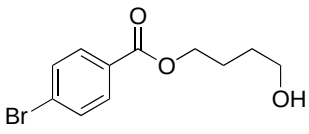


a12 is a known compound in literature and its spectral data ware in good agreement with literature values.[20]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 9.1, 2.1 Hz, 2H), 7.41 (dt, *J* = 9.0, 2.2 Hz, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.73 (dd, *J* = 10.5, 6.2 Hz, 2H), 1.90–1.84 (m, 2H), 1.75–1.70 (m, 2H), 1.47 (br s, 1H).

4-Hydroxybutyl 4-bromobenzoate (**a13**) [CAS: 1009630-64-1]

Method D: 4-Bromobenzoic acid (2.01 g, 10.0 mmol) provided 1.62 g (59% yield) of **a13** as a yellowish oil.

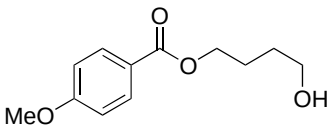
a13 is a known compound in literature and its spectral data are in good agreement with literature values.[21]



^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.90–7.86 (m, 2H), 7.58–7.54 (m, 2H), 4.37–4.33 (m, 2H), 3.73–3.70 (m, 2H), 1.89–1.83 (m, 2H), 1.95 (br s, 1H, O**H**), 1.74–1.68 (m, 2H).

4-Hydroxybutyl 4-methoxybenzoate (**a14**) [CAS: 616236-46-5]

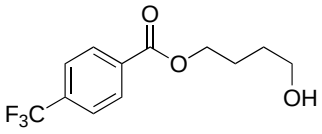
Method D: *p*-Anisic acid (1.55 g, 10.0 mmol) provided 1.2 g (52% yield) of **a14** as a colorless solid.



a14 has a CAS RN.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 9.5, 2.4 Hz, 2H), 6.92 (dt, *J* = 9.4, 2.4 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 3.73 (dd, *J* = 11.6, 6.4 Hz, 2H), 1.89–1.83 (m, 2H), 1.76–1.70 (m, 2H), 1.43 (br s, 1H, O**H**). **^{13}C-NMR(126MHz,CDCl3)** δ 166.6, 163.4, 131.7, 122.7, 113.7, 64.6, 55.5, 29.4, 25.4. **HRMS ESI $[M+Na]^+$** calculated for $C_{12}H_{16}NaO_4^+$: 247.0941, found 247.0939.

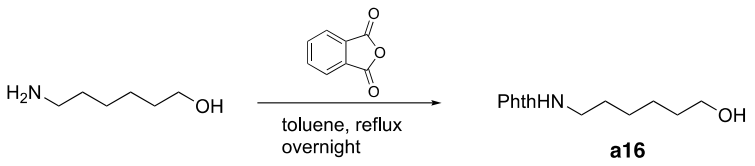
4-Hydroxybutyl 4-(trifluoromethyl)benzoate (**a15**)

Method D: 4-(Trifluoromethyl)benzoic acid (1.88 g, 10.0 mmol) provided 1.78 g (68% yield) of **a15** as a pale yellowish oil.

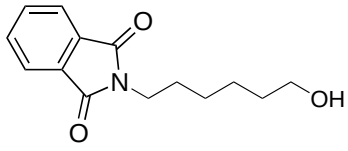


a15, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.17–8.15 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 4.41 (t, *J* = 6.6 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 1.93–1.87 (m, 2H), 1.77–1.71 (m, 2H), 1.35–1.64 (1H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 164.6, 133.5 (q, J_{C-F} = 32.8 Hz), 132.6, 129.0, 124.5 (q, J_{C-F} = 3.6 Hz) 122.7 (q, J_{C-F} = 272.9 Hz), 64.5, 61.3, 28.2, 24.3. **^{19}F-NMR (471 MHz, $CDCl_3$)** δ –63.0. **HRMS ESI $[M+Na]^+$** calculated for $C_{12}H_{13}F_3NaO_3^+$: 285.0709, found 285.0709.

1-Phthalimido-6-hexanol, (**a16**) [CAS: 63945-11-9]

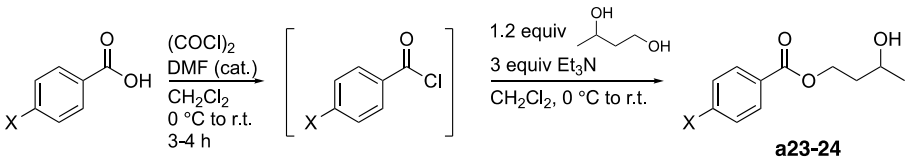


6-Amino-1-hexanol (1.18 g, 10 mmol, 1 equiv.) and phthalic anhydride (1.48 g, 10 mmol, 1 equiv.) were refluxed overnight in toluene (35 mL) with a Dean Stark water trap. The reaction mixture was cooled at r.t., diluted with EtOAc, washed with water and brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure using a rotary evaporator, the crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 1:1) to furnish 2.23 g (90% yield) of **a16** as a white solid.



a16 is a known compound in literature and its spectral data are in good agreement with literature values.[22]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.86–7.82 (m, 2H), 7.73–7.69 (m, 2H), 3.70–3.68 (m, 2H), 3.63 (t, *J* = 6.3 Hz, 2H), 1.73–1.67 (m, 2H), 1.60–1.54 (m, 2H), 1.50 (br s, 1H, O**H**), 1.45–1.34 (m, 4H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 168.6, 134.0, 132.3, 123.3, 62.8, 38.0, 32.7, 28.7, 26.6, 25.3

<u>Method E</u>

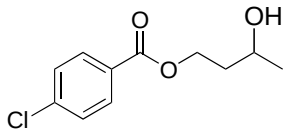


To a solution of *p*-substituted benzoic acid (10 mmol, 1 equiv.) in CH_2Cl_2 (20 mL) at 0 °C were added DMF (50 µL, cat.) and oxalyl chloride (1.0 mL, 12 mmol, 1.2 equiv.). The reaction mixture was allowed to warm at r.t. and stirred for 3 to 4 h. The freshly prepared solution of the corresponding *p*-substituted benzoyl chloride was transferred dropwise to a solution of 1,3-butanediol (1.1 mL, 12 mmol, 3 equiv.) and Et_3N (4 mL, 28 mmol, 2.8 equiv.) in CH_2Cl_2 (10 mL) at 0 °C using a syringe. After 15 min, the reaction mixture was stirred at r.t. overnight. The reaction was quenched with NH_4Cl aq., and after decantation, the organic phase was washed with brine, dried over Na_2SO_4, and concentrated under

reduced pressure using a rotary evaporator. The residue was purified by flash column chromatography on silica-gel (hexanes/EtOAc 75:25 to 50:50) to furnish the desired compound.

3-Hydroxybutyl 4-chlorobenzoate, (**a23**) [CAS: 1808114-86-4]

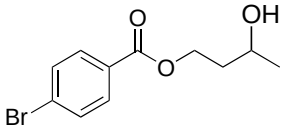
Method E: 4-Chlorobenzoic acid (1.58 g, 10.0 mmol) provided 1.87 g (82% yield) of **a23** as a colorless oil.



a23 is a known compound in literature and its spectral data are in good agreement with literature values.[23]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.98 (dt, *J* = 8.8, 2.1 Hz, 2H), 7.43 (dt, *J* = 8.9, 2.1 Hz, 2H), 4.63–4.58 (m, 1H), 4.42–4.37 (m, 1H), 3.99–3.96 (m, 1H), 1.98 (d, *J* = 4.6 Hz, 1H, O**H**), 1.97–1.91 (m, 1H), 1.88–1.82 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 3H).

3-Hydroxybutyl 4-bromobenzoate, (**a24**) [CAS: 2821895-18-3]

Method E: 4-Bromobenzoic acid (1.55 g, 10.0 mmol) provided 1.91 g (70% yield) of **a24** as a colorless oil.



a24 is a known compound in literature, and its spectral data are in good agreement with literature values.[23]
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.91–7.88 (m, 2H), 7.60–7.57 (m, 2H), 4.61–4.56 (m, 1H), 4.41–4.36 (m, 1H), 3.98–3.95 (m, 1H), 2.00 (br s, 1H, O**H**), 1.94–1.91 (m, 1H), 1.87–1.81 (m, 1H), 1.27 (d, *J* = 6.3 Hz, 3H).

3. Investigations on Reaction Conditions

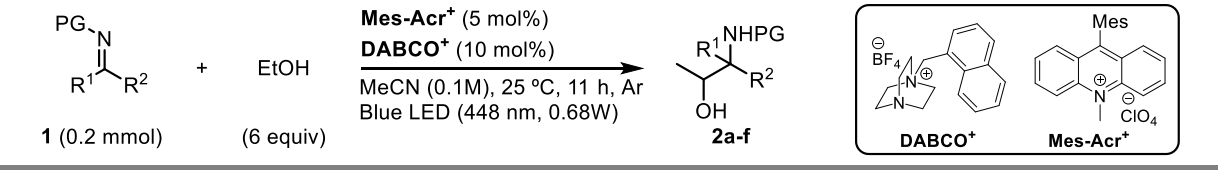
Optimization Procedure

To an oven-dried three-way key Schlenk tube equipped with a magnetic stir bar were added **Mes-Acr**$^+$ (4.1 mg, 10 μmol), **DABCO**$^+$ (6.8 mg, 20 μmol), and imine **1** (0.2 mmol, 1 equiv.). The tube was capped with a rubber septum equipped with LED light source (Techno-Sigma, PER-AMP, 448 nm). The cap was sealed with parafilm, and the tube was degassed via vacuum evacuation and subsequent backfill with argon for three times. Then, a solution of EtOH (70 μL, 1.2 mmol, 6 equiv.) in 2 mL of MeCN was added under argon via syringe through the three-way key. The tube was set to an aluminum block in a temperature-controlled reactor (Techno-Sigma, UCR-80 Nh) and the reaction solution was stirred under irradiation of blue LED while keeping the temperature at 25 ºC. After being stirred for the indicated time, the solvent was removed under reduced pressure using a rotary evaporator. The conversion and yield were calculated based on the integration of ^{1}H NMR spectra ($CDCl_3$, 500 MHz) using 1,1,2,2-tetrachloroethane as an internal standard. The *syn*/*anti* ratio of 1,2-aminoalcohol product **2** was evaluated based on its α-CH or β-CH proton if possible, or the NH proton if not possible.

3.1. Screening of Imines

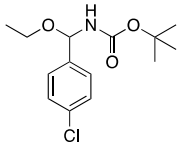
Reactions were carried out according to the **Optimization Procedure** using imines **1a-f** for 11 h.

Table S1. Screening of imines.[a]



1a	1b	1c	1d	1e	(±)-1f
conv: 80% **2a**: N.D. **2a'**: 68%	conv: 35% **2b**: N.D.	conv: 40% **2c**: N.D.	conv: >90% **2d**: < 10%	conv: >95% **2e**: 75%	conv: >95% **2f**: 74%

2a': tert-butyl ((4-chlorophenyl)(ethoxy)methyl)carbamate:

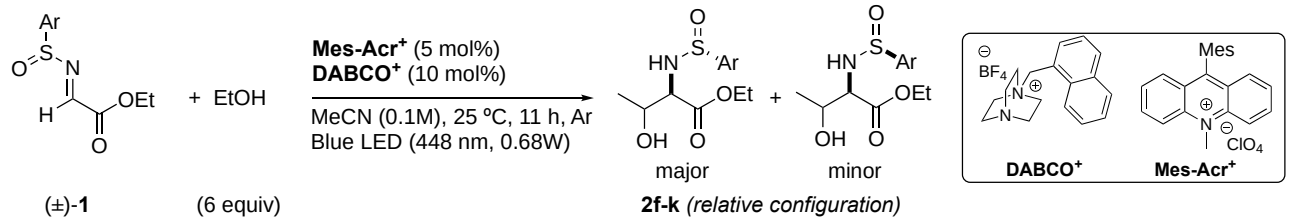


[a] Conversions and yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. N.D. = Not Detected.

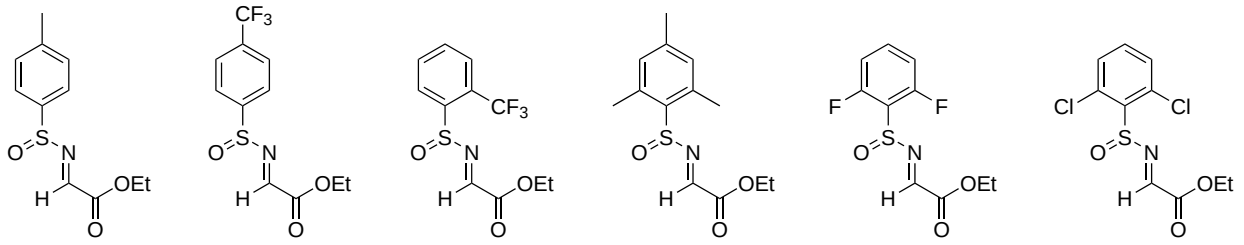
3.2. Screening of *N*-Sulfinyl α-Iminoesters

Reactions were carried out according to the **Optimization Procedure** using imines (±)-**1f-k** for 11 h.

Table S2. Screening of *N*-sulfinyl α-iminoesters.[a]



(±)-**1** (6 equiv) **2f-k** *(relative configuration)*



(±)-**1f** (±)-**1g** (±)-**1h** (±)-**1i** (±)-**1j** (±)-**1k**

entry	(±)-1	conv. of (±)-1 (%)	2 (%)	*major* : *minor*
1	(±)-**1f**	96	74	<3:1[b]
2	(±)-**1g**	>98	70	1.9:1
3	(±)-**1h**	>98	85	1.4:1
4	(±)-**1i**	48	34	>19:1
5	(±)-**1j**	>99	93	7.3:1
6	(±)-**1k**	>99	70 (67)	>19:1

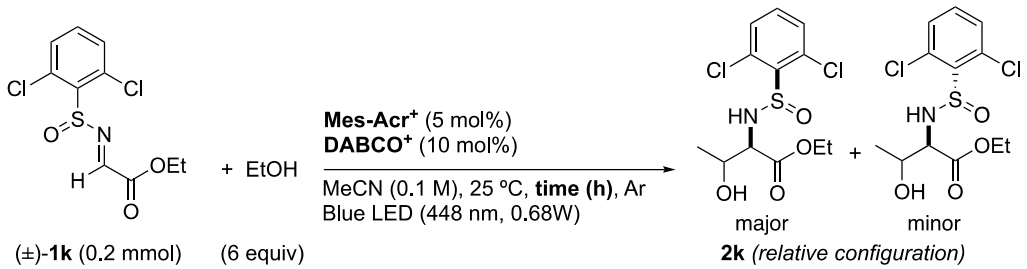
[a] Conversions, yields, and the ratios of isomers were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yield was shown in parentheses. ***Syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was <1.3:1 in all cases.**

[b] The peaks of different isomers partially overlap.

3.3. Screening of Reaction Time

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** for different reaction times.

Table S3. Screening of reaction time.[a]



(±)-**1k** (0.2 mmol) (6 equiv) **2k** *(relative configuration)*

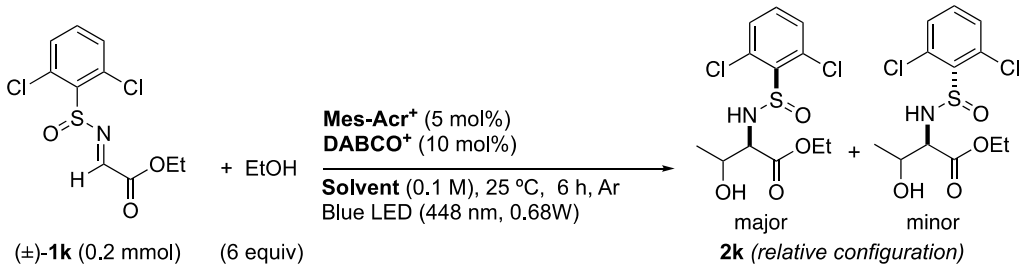
entry	time (h)	conv. of (±)-1k (%)	2k (%)	*major* : *minor*
1	11	>99	70 (67)	>19:1
2	6	>99	84 (83)	>19:1
3	3	85	62	>19:1

[a] Conversions, yields, and the ratios of isomers were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields were shown in parentheses**.** ***Syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was <1.3:1 in all cases.**

3.4. Screening of Solvents

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** for 6 h in the indicated solvent.

Table S4. Screening of solvents.[a]



(±)-**1k** (0.2 mmol) (6 equiv) **2k** *(relative configuration)*

entry	solvent	conv. of (±)-1k (%)	2k (%)	*major* : *minor*
1	Acetone	96	64	>19:1
2	MeCN	>99	84 (83)	>19:1
3	CH_2Cl_2	70	41	>19:1
4	DMA	69	34	N.D.
5	DMF	67	23	N.D.

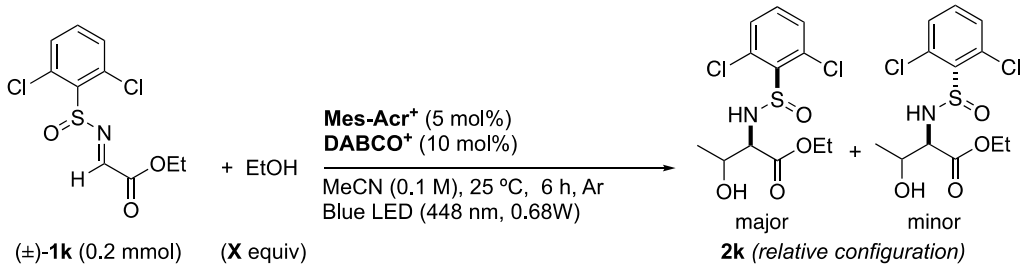
6	DMSO	17	trace	N.D.

[a] Conversions, yields, and the ratios of isomers were determined by ^{1}H NMR using 1,1,2,2-teterachloroethane as an internal standard. Isolated yield was shown in parentheses**.** ***Syn*/*anti*** **selectivity of the 1,2-aminoalcohol moiety was <1.3:1 in all cases.** N.D. = N**ot D**etected**.**

3.5. Screening of Equivalents of EtOH

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** for 6 h with different amounts of EtOH.

Table S5. Screening of equivalents of EtOH.[a]



(±)-**1k** (0.2 mmol) (**X** equiv) **2k** *(relative configuration)*

entry	X equiv.	conv. of (±)-1k (%)	2k (%)	*major* : *minor*
1	12	>99	70	>19:1
2	6	>99	84 (83)	>19:1
3	3	99	83 (82)	>19:1
4[b]	3	82	47	>19:1
5	1.5	87	45	>19:1

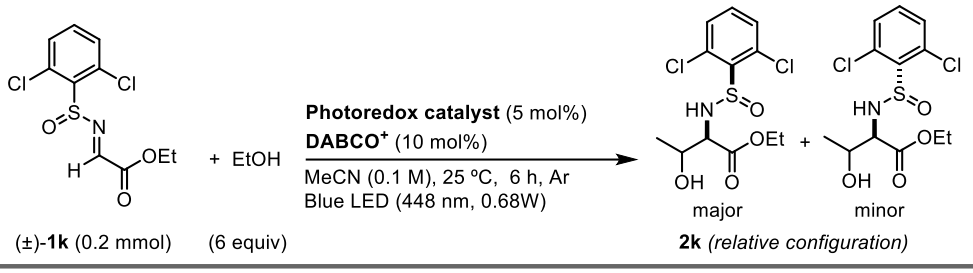
[a] Conversions, yields, and the ratios of isomers were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields were shown in parentheses**.** ***Syn*/*anti*** **selectivity of the 1,2-aminoalcohol moiety was <1.3:1 in all cases.**

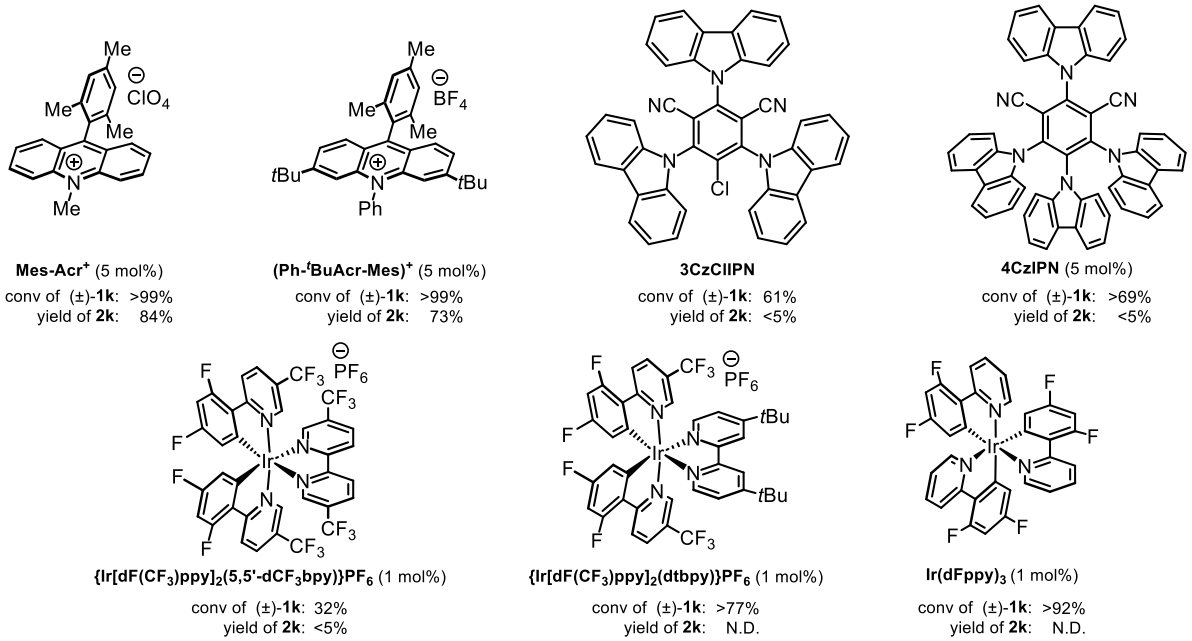
[b] The reaction was run for 3 h.

3.6. Screening of Photoredox Catalysts

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** and the indicated photoredox catalyst instead of **Mes-Acr**$^+$ for 6 h. For Iridium photoredox catalyst, the amount was 1 mol% instead of 5 mol%.

Table S6. Screening of photoredox catalysts.[a]



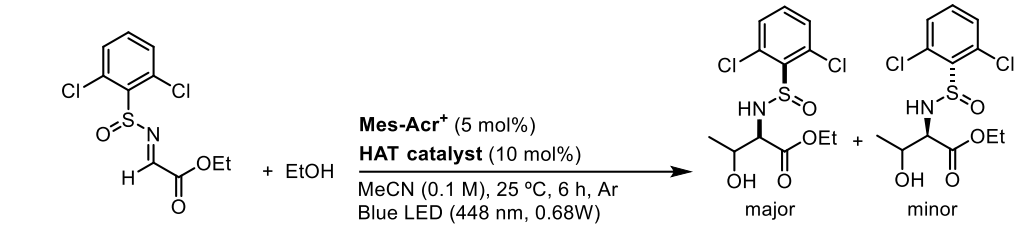


[a] Conversions and yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. N.D. = Not Detected.

3.7. Comparison with Other Hydrogen Atom Transfer (HAT) Catalysts

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** and the indicated HAT catalyst instead of **DABCO**$^+$ for 6 h.

Table S7. Comparison with other HAT catalysts.[a]



DABCO$^+$	DABCO$^+$(Br)	(^{n}Bu)$_4$NBr	Quinuclidine	2,6-Cl$_2$-Pyr-Ox
conv of **1**: >99% yield of **2**: 84%	conv of **1**: >21% yield of **2**: 7%	conv of **1**: >54% yield of **2**: N.D.	conv of **1**: >93% yield of **2**: <5%	conv of **1**: >29% yield of **2**: <5%

[a] Conversions and yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. N.D. = Not Detected.

3.8. Comparison with Other Conditions

Reactions were carried out according to other conditions for radical addition to imine derivatives via HAT catalysis.[24]–[26]

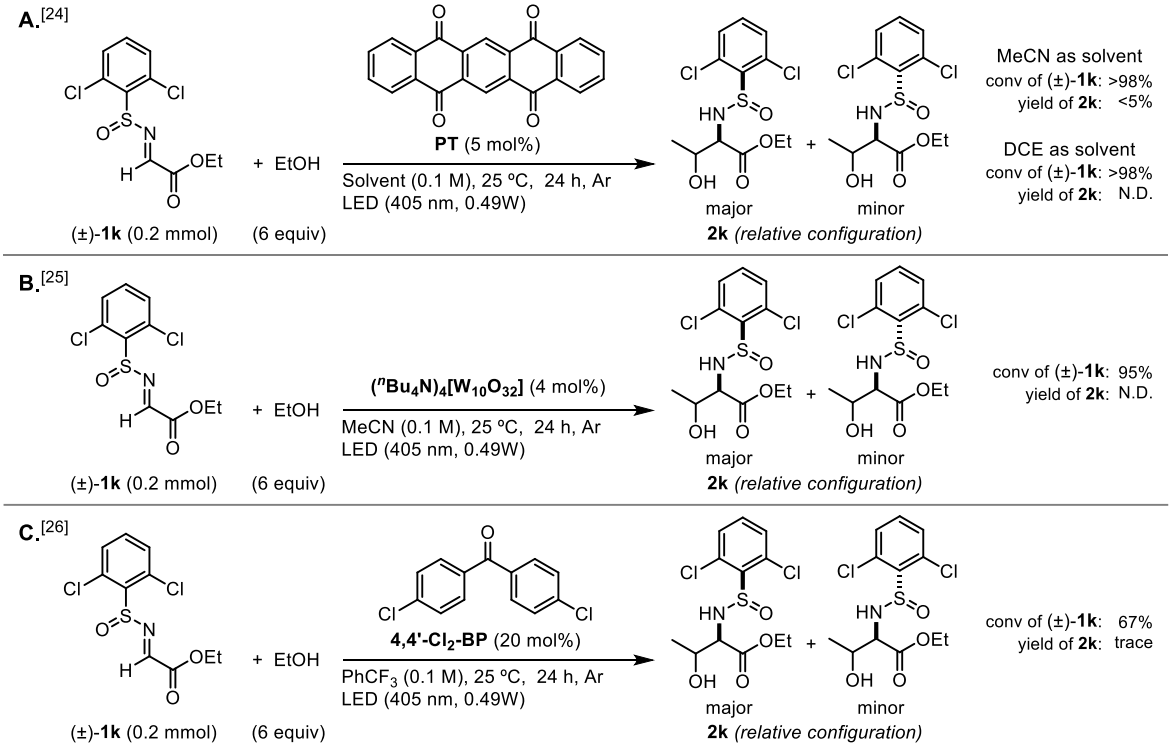
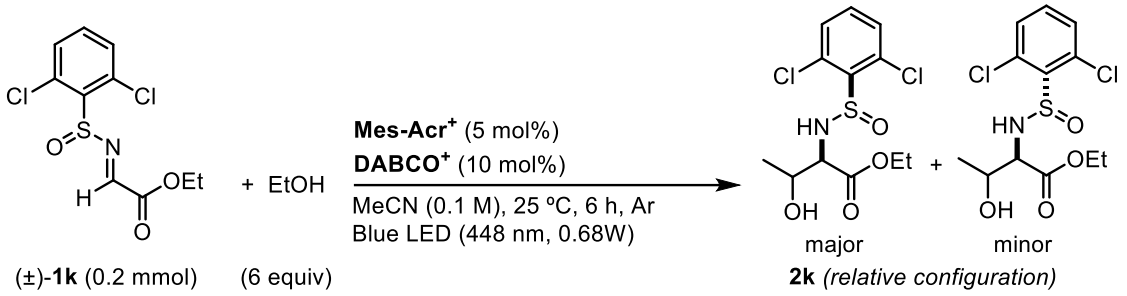


Figure S2. Reactions under other HAT catalysis conditions.

3.9. Control Experiments

Reactions were carried out according to the **Optimization Procedure** using imine (±)-**1k** for 6 h without one of the key components. The dark reaction was performed in a Schlenk tube covered with aluminum foil to avoid the incidence of ambient light.

Table S8. Control experiments.[a]



entry	variations from standard conditions	conv. of (±)-1k (%)	yield of 2k (%)
1	none	>99	84 (83)
2	without **Mes-Acr**$^+$	11	N.D.
3	without **DABCO**$^+$	32	N.D.
4	without light	3	N.D.

[a] Conversions **and** yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yield was shown in parentheses. N.D. = Not Detected.

4. General Procedure for Synthesis of 1,2-Aminoalcohols

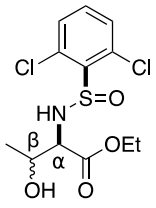
General Procedure

To an oven-dried three-way key Schlenk tube equipped with a magnetic stir bar were added **Mes-Acr**$^+$ (4.1 mg, 10 μmol), **DABCO**$^+$ (6.8 mg, 20 μmol), and (±)-**1** (0.2 mmol, 1 equiv.). The tube was capped with a rubber septum equipped with LED light source (Techno-Sigma, PER-AMP, 448 nm). The cap was sealed with parafilm, and the tube was degassed via vacuum evacuation and subsequent backfill with argon for three times. Then, a solution of alcohol (3 or 6 equiv.) in 2 mL of MeCN was added under argon via syringe through the three-way key. The Schlenk tube was set to an aluminum block in a temperature-controlled reactor (Techno-Sigma, UCR-80 Nh) and the reaction solution was stirred under irradiation of blue LED while keeping the temperature at 25 ºC. After being stirred for 6 h, the solvent was removed under reduced pressure. The conversions, yields, and ratios of isomers were calculated based on the integration of ^{1}H NMR spectra ($CDCl_3$, 500 MHz) using 1,1,2,2-tetrachloroethane as an internal standard. The solvent was removed once again under reduced pressure and the crude product was purified by flash column chromatography on silica-gel (hexanes/EtOAc) to afford the desired 1,2-aminoalcohol product.

NOTE: The stereochemistry of the α-carbon relative to the chiral sulfur center in the product was fully controlled in all cases (*major*: *minor* >19:1), whereas the *syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was low (< 2.6:1).

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxybutanoate (2k)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.5 mg, 0.2 mmol) and ethanol (**a1**, 35 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **2k** (55.6 mg, 82% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.

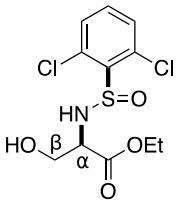


2k, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.36 (m, 2H), 7.35–7.30 (m, 1H), 6.12 (d, *J* = 7.5 Hz, 0.57H, N**H**), 6.05 (d, *J* = 7.5 Hz, 0.43H, N**H**), 4.28–4.21 (m, 2H), 4.20–4.15 (m, 0.43H), 4.15–4.11 (m, 1H), 3.96 (dd, *J* = 8.0 Hz, 3.5 Hz, 0.57H), 2.45 (br s, 0.43H, O**H**), 2.28 (br s, 0.57H, O**H**), 1.33–1.24 (m, 4.7H), 1.18 (d, *J* = 6.0 Hz, 1.3H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.0, 170.6, 140.0, 139.7, 133.7, 133.6, 132.3, 130.4, 130.3, 68.8, 68.6, 63.2, 63.1, 62.4, 62.3, 19.9, 18.7, 14.2. **HRMS ESI [M+H]$^+$** calculated for $C_{12}H_{16}Cl_2NO_4S^+$: 340.0172, found 340.0180.

Ethyl (((2,6-dichlorophenyl)sulfinyl)amino)-3-propioate (**3**)

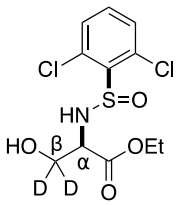
The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.6 mg, 0.2 mmol) and methanol (**a2**, 50 μL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **3** (43.7 mg, 67% yield) as a colorless oil.



3, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.34–7.30 (m, 1H), 6.10 (d, *J* = 6.3 Hz, 1H, N**H**), 4.27–4.21 (m, 3H), 3.96 (dd, *J* = 11.3, 3.3 Hz, 1H), 3.90 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.51 (br s, 1H, O**H**), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 170.4, 139.5, 133.8, 132.3, 130.4, 63.8, 62.5, 59.3, 14.2. **HRMS ESI [M+K]$^+$** calculated for $C_{11}H_{13}Cl_2KNO_4S^+$: 363.9574, found 363.9579.

Ethyl (((2,6-dichlorophenyl)sulfinyl)amino)-3-propioate-3,3-*d_2* (3-d_2)

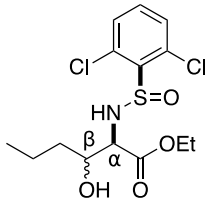
The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.6 mg, 0.2 mmol) and methanol-d_3 (**a2-d_3**, 50 μL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 75:25 to 40:60) to yield the title compound **3-d_2** (41.7 mg, 64% yield) as a colorless waxy solid.



3-d_2, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.34–7.28 (m, 1H), 6.09 (d, *J* = 6.3 Hz, 1H, N**H**), 4.27-4.21 (m, 3H), 2.44 (bs, 1H, O**H**), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 170.4, 139.5, 133.8, 132.3, 130.4, 62.5, 59.2, 14.2, (1C missed, -***C***D_2-). **HRMS ESI [M+Na]$^+$** calculated for $C_{11}H_{13}Cl_2NNaO_4S^+$: 349.9960, found 349.9967.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxyhexanoate (**4**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.6 mg, 0.2 mmol) and 1-butanol (**a3**, 110 μL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **4** (55.8 mg, 73% yield, *syn*/*anti* ratio = 1.1:1) as a colorless oil.



4, new compound.

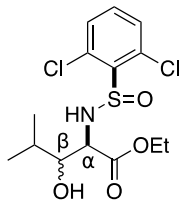
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.35 (m, 2H), 7.32 (m, 1H), 6.13 (d, *J* = 7.4 Hz, 0.53H, N**H**), 6.05 (d, *J* = 8.0 Hz, 0.47H, N**H**), 4.28–4.18 (m, 2H), 4.14 (dd, *J* = 8.0, 4.5 Hz, 0.53H), 4.05 (dd, *J* = 7.4, 2.9 Hz, 0.47H), 4.02–3.98 (m, 0.53H), 3.91–3.88 (m, 0.47H), 2.33 (br s, 0.47H, O**H**), 2.13 (br s 0.53H, O**H**), 1.58–1.35 (m, 4H), 1.34–1.20 (m, 3H), 0.96–0.90 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.2, 170.7, 140.1, 139.7, 133.8, 133.6, 132.21, 132.19, 130.33, 130.28, 72.7, 72.2, 62.3, 62.2, 61.6, 35.9, 35.0, 18.9, 18.8, 14.2, 14.0, 13.9.

HRMS ESI $[M+Na]^+$ calculated for $C_{14}H_{19}Cl_2NNaO_4S^+$: 390.0304, found 390.0309.

Ethyl 2-((-(2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-4-methylpentanoate (**5**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.6 mg, 0.2 mmol) and 2-ethylpropanol (**a4**, 55 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **5** (44.9 mg, 61% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.



5, new compound.

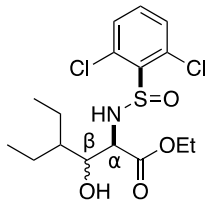
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.30 (m, 3H), 6.10 (d, *J* = 8.0 Hz, 0.57H, N**H**), 6.07 (d, *J* = 8.6 Hz, 0.43H, N**H**), 4.28–4.17 (m, 3H), 3.61–3.58 (m, 0.67H), 3.58–3.49 (m, 0.37H), 2.34 (d, *J* = 7.4 Hz, 0.36H, O**H**), 2.08 (d, *J* = 6.9 Hz, 0.63H, O**H**), 1.86–1.76 (m, 1H), 1.30 (m, 3H), 1.03–0.98 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.6, 171.4, 140.2, 139.9, 133.7, 133.6, 132.2, 130.33, 130.30, 78.9, 78.1, 62.4, 62.2, 60.1, 59.9, 30.6, 19.4, 19.1, 18.6, 17.8, 14.21, 14.16.

HRMS ESI [M+Na]$^+$ calculated for $C_{14}H_{19}Cl_2NNaO_4S^+$: 390.0304, found 390.0309.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-4-ethyl-3-hydroxyhexanoate (**6**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.7 mg, 0.2 mmol) and 2-ethyl-butanol (**a5**, 150 μL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **6** (45.7 mg, 58% yield, *syn*/*anti* ratio = 1.2:1) as a colorless oil.

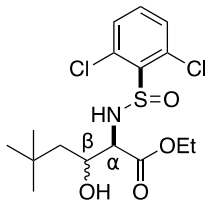


6, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.29 (m, 3H), 6.12 (d, *J* = 8.0 Hz, 0.55H, N**H**), 6.06 (d, *J* = 8.9 Hz, 0.45H, N**H**), 4.27–4.19 (m, 3H), 3.85–3.81 (m, 0.55H), 3.74–3.70 (m, 0.45H), 2.23 (d, *J* = 7.7 Hz, 0.45H, O**H**), 2.00 (d, *J* = *7.2* Hz, 0.55H, OH), 1.62–1.33 (m, 5H), 1.32–1.25 (m, 3H), 0.91–0.86 (m, 6H). **^{13}C-NMR (126 MHz, $CDCl_3$)** *(mixture of syn/anti isomers)* δ 171.8, 171.7, 140.2, 140.0, 133.70, 133.66, 132.23, 132.18, 130.3, 75.3, 74.1, 62.3, 62.1, 60.0, 59.9, 42.4, 42.0, 21.7, 21.1, 20.4, 20.1, 14.22, 14.17, 10.9, 10.8, 10.5, 10.4. **HRMS ESI [M+Na]$^+$** calculated for $C_{16}H_{23}Cl_2NNaO_4S^+$: 418.0617, found 418.0623.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-5,5-dimethylhexanoate (**7**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (59.1 mg, 0.2 mmol) and 3,3-dimethyl-1-butanol (**a6**, 75 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **7** (56.8 mg, 71% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.

7, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.35 (m, 2H), 7.34–7.30 (m, 1H), 6.14 (d, *J* = 7.4 Hz, 0.57H, N**H**), 6.02 (d, *J* = 8.0 Hz, 0.43H, N**H**), 4.30–4.17 (m, 2H), 4.15–4.08 (m, 1H), 4.05 (br s, 0.43H), 3.98 (dd, *J* = 7.4, 3.5 Hz, 0.57H), 2.23 (br s, 0.43H, O**H**), 2.07 (br s, 0.57H, O**H**), 1.53–1.42 (m, 1H), 1.35–1.20 (m, 4H), 0.97 (s, 5H), 0.93 (s, 4H).

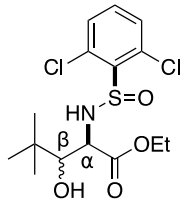


^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.0, 170.7, 140.2, 139.7, 133.8, 133.6, 132.2, 130.4, 130.3, 70.6, 70.4, 63.8, 63.6, 62.4, 62.2, 47.6, 46.4, 30.3, 30.2, 30.1, 30.0, 29.8, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{16}H_{23}Cl_2NNaO_4S^+$: 418.0617, found 418.0622.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-4,4-dimethylpentanoate (**8**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (59.1 mg, 0.2 mmol) and 2,2-dimethyl-1-propanol (**a7**, 54.8 mg, 0.3 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **8** (40.7 mg, 53% yield, *syn*/*anti* ratio = 2.6:1) as a colorless oil.



8, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.35 (m, 2H), 7.33–7.29 (m, 1H), 6.12 (d, *J* = 10.3 Hz, 0.28H, N**H**), 6.07 (d, *J* = 9.2 Hz, 0.72H, N**H**), 4.28–4.16 (m, 3H), 3.61 (dd, *J* = 7.4 Hz, 2.3 Hz, 0.72H), 3.49 (dd, *J* = 9.5, 4.0 Hz, 0.28H), 2.70 (d, *J* = 9.5 Hz, 0.28H, O**H**), 2.26 (d, *J* = 7.4 Hz, 0.72H, O**H**), 1.31–1.28 (m, 3H), 0.98 (s, 6.5H), 0.96 (s, 2.5H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 172.4, 134.0, 133.7, 132.3, 132.2, 130.3, 82.1, 78.6, 62.3, 62.1, 59.0, 58.7, 35.6, 35.4, 26.4, 26.2, 14.2, 14.0.

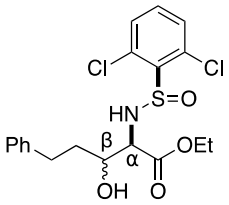
HRMS ESI [M+Na]$^+$ calculated for $C_{15}H_{21}Cl_2NNaO_4S^+$: 404.0461, found 404.0467.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-5-phenylpentanoate (**9**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (59.1 mg, 0.2 mmol) and 3-phenyl-1-propanol (**a8**, 83 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **9** (44.7 mg, 52% yield, *syn*/*anti* ratio = 1.1:1) as a colorless oil.

9, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.36 (m, 2H), 7.33–7.25 (m, 3H), 7.21–7.15 (m, 3H), 6.13 (d, *J* = 7.4 Hz, 0.52H, N**H**), 6.03 (d,



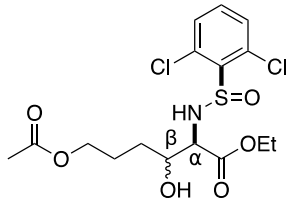
J = 7.7 Hz, 0.48H, N**H**), 4.26–4.14 (m, 2.48H), 4.08 (dd, *J* = 7.4, 3.2 Hz, 0.52H), 4.00 (br s, 0.52H), 3.90 (br s, 0.48H), 2.87–2.80 (m, 1H), 2.76–2.67 (m, 1H), 2.37 (d, *J* = 7.4 Hz, 0.48H, O**H**), 2.17 (d, *J* = 5.7 Hz, 0.52H, O**H**), 1.92–1.88 (m, 1H), 1.78–1.73 (m, 1H), 1.30–1.20 (m, 3H).

^{13}C-NMR (126 MHz, CDCl$_3$) *(mixture of syn/anti isomers)* δ 171.1, 170.6, 141.33, 141.30, 140.0, 139.6, 133.8, 133.7, 132.3, 130.4, 130.3, 128.6, 128.5, 126.2, 72.1, 71.8, 62.5, 62.4, 62.3, 61.7, 35.4, 34.5, 31.8, 14.19, 14.17.

HRMS ESI [M+Na]$^+$ calculated for $C_{19}H_{21}Cl_2NNaO_4S^+$: 452.0461, found 452.0465.

Ethyl 6-acetoxy-2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxyhexanoate (**10**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-hydroxybutyl acetate (**a9**, 79.6 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **10** (54.5 mg, 64% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.



10, new compound.

^{1}H-NMR (500 MHz, CDCl$_3$) *(mixture of syn/anti isomers*) δ 7.39–7.36 (m, 2H), 7.35–7.31 (m, 1H), 6.13 (d, *J* = 7.4 Hz, 0.56H, N**H**), 6.05 (d, *J* = 7.7 Hz, 0.44H, N**H**), 4.28–4.20 (m, 2H), 4.13 (dd, *J* = 7.9, 4.4 Hz, 0.56H), 4.11–4.02 (m, 3H), 3.93–3.89 (m, 0.44H), 2.62 (d, *J* = 7.7 Hz, 0.44H, O**H**), 2.40 (d, *J* = 6.9 Hz, 0.56H, O**H**), 2.04 (s, 1.8H), 2.02 (s, 1.2H), 1.89–1.48 (m, 4H), 1.32–1.23 (m, 3H).

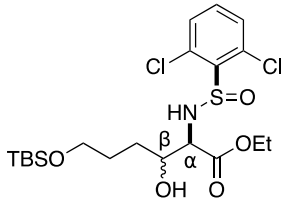
^{13}C-NMR (126 MHz, CDCl$_3$) *(mixture of syn/anti isomers)* δ 171.24, 171.23, 171.0, 170.5, 139.9, 139.5, 133.8, 133.6, 132.3, 130.4, 130.3, 72.6, 72.0, 64.21, 64.16, 62.4, 62.34, 62.32, 61.8, 30.4, 29.3, 25.0, 24.9, 21.0, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{16}H_{21}Cl_2NNaO_6S^+$: 448.0359, found 448.0366.

Ethyl 6-((*tert*-butyldimethylsilyl)oxy)-2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxyhexanoate (**11**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-((*tert*-butyldimethylsilyl)oxy)butan-1-ol (**a10**, 124.3 mg, 0.6 mmol, 3 equiv.). The crude mixture was

purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **11** (29.8 mg, 30% yield, *syn*/*anti* ratio = 1.2:1) as a colorless oil.



11, new compound.

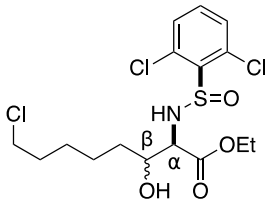
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.35 (m, 2H), 7.32–7.29 (m, 1H), 6.13 (d, *J* = 7.7 Hz, 0.54H, N**H**), 6.03 (d, *J* = 8.3 Hz, 0.46H, N**H**), 4.27–4.21 (m, 2H), 4.13–4.03 (m, 1.54H), 3.88–3.85 (m, 0.43H), 3.70–3.60 (m, 2H), 3.26 (d, *J* = 6.6 Hz, 0.46H, O**H**), 3.10 (d, *J* = 5.2 Hz, 0.54H, O**H**), 1.73–1.65 (m, 4H), 1.31–1.24 (m, 3H), 0.90–0.86 (m, 9H), 0.07 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.2, 171.0, 140.3, 140.1, 133.8, 133.7, 132.12, 132.09, 130.33, 130.29, 73.2, 72.4, 63.3, 62.6, 62.3, 62.1, 31.4, 30.5, 29.1, 29.0, 26.01, 26.99, 18.40, 18.38, 14.2, –5.3.

HRMS ESI [M+Na]$^+$ calculated for $C_{20}H_{33}Cl_2NNaO_5SSi^+$: 520.1118, found 520.1125.

Ethyl 8-chloro-2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxyoctanoate (12)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.7 mg, 0.2 mmol) and 6-chloro-1-hexanol (**a11**, 85 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **12** (54.5 mg, 63% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.



12, new compound.

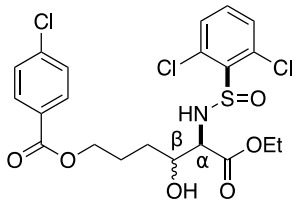
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.40–7.35 (m, 2H), 7.34–7.30 (m, 1H), 6.13 (d, *J* = 7.4 Hz, 0.57H, N**H**), 6.04 (d, *J* = 7.7 Hz, 0.43H, N**H**), 4.29–4.20 (m, 2H), 4.14 (dd, *J* = 7.7, 4.3 Hz, 0.43H), 4.05 (dd, *J* = 7.4, 2.9 Hz, 0.57H), 3.99 (br s, 0.57H), 3.90 (br s, 0.43H), 3.55–3.51 (m, 2H), 2.32 (br s, 0.43H, O**H**), 2.08 (br s, 0.57H, O**H**), 1.82–1.73 (m, 2H), 1.60–1.38 (m, 6H), 1.32–1.28 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.1, 170.6, 140.1, 139.6, 133.8, 133.6, 132.3, 130.40, 130.36, 72.8, 72.4, 62.5, 62.3, 61.7, 45.0, 33.7, 32.7, 32.5, 26.8, 26.7, 25.0, 24.9, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{16}H_{22}Cl_3NNaO_4S^+$: 452.0227, found 452.0235.

5-(((2,6-Dichlorophenyl)sulfinyl)amino)-6-ethoxy-4-hydroxy-6-oxohexyl 4-chlorobenzoate (**13**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-hydroxybutyl 4-chlorobenzoate (**a12**, 137.9 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **13** (71.9 mg, 69% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.

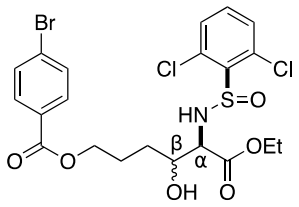


13, new compound.
^{1}H-NMR (500 MHz, CDCl$_3$) *(mixture of syn/anti isomers)* δ 7.96–7.92 (m, 2H), 7.41–7.38 (m, 2H), 7.36–7.29 (m, 3H), 6.14 (d, *J* = 7.4 Hz, 0.56H, N**H**), 6.05 (d, *J* = 8.0 Hz, 0.44H, N**H**), 4.36–4.30 (m, 2H), 4.26–4.18 (m, 2H), 4.15 (dd, *J* = 8.0, 4.6 Hz, 0.56H), 4.09–4.05 (m, 1H), 3.99–3.93 (m, 0.44H), 2.66 (br s, 0.44, O**H**), 2.43 (br s, 0.56H, O**H**), 2.04–1.95 (m, 1H), 1.92–1.83 (m, 1H), 1.75–1.71 (m, 1H), 1.65–1.57 (m, 1H), 1.30–1.24 (m, 3H). **^{13}C-NMR (126 MHz, CDCl$_3$)** *(mixture of syn/anti isomers)* δ 170.9, 170.5, 165.81, 165.79, 139.9, 139.5, 139.4, 133.8, 133.6, 132.28, 132.26, 131.1, 131.0, 130.4, 130.3, 128.8, 128.7, 72.5, 72.1, 64.94, 64.87, 62.5, 62.39, 62.37, 61.9, 30.4, 29.3, 25.1, 25.0, 14.2. **HRMS ESI [M+Na]$^+$** calculated for $C_{21}H_{22}Cl_3NNaO_6S^+$: 544.0126, found 544.0131.

5-(((2,6-Dichlorophenyl)sulfinyl)amino)-6-ethoxy-4-hydroxy-6-oxohexyl 4-bromobenzoate (**14**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-hydroxybutyl 4-bromobenzoate (**a13**, 164.7 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **14** (74.6 mg, 66% yield, *syn*/*anti* ratio = 1.4:1) as a colorless oil.

14, new compound.
^{1}H-NMR (500 MHz, CDCl$_3$) *(mixture of syn/anti isomers)* δ 7.90–7.84 (m, 2H), 7.59–7.55 (m, 2H), 7.36–7.28 (m, 3H), 6.14 (d, *J* = 7.4 Hz, 0.58H, N**H**), 6.05 (d *J* = 8.0 Hz, 0.42H, N**H**), 4.36–4.31 (m, 2H), 4.26–4.18 (m, 2H), 4.17–



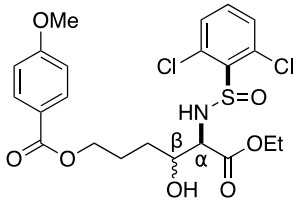
4.14 (m, 0.58H), 4.08–4.06 (m, 1H), 3.98–3.94 (m, 0.42H), 2.67 (br s, 0.42H, O**H**), 2.44 (br s, 0.58H, O**H**), 2.04–1.94 (m, 1H), 1.92–1.82 (m, 1H), 1.75–1.69 (m, 1H), 1.68–1.56 (m, 1H), 1.30–1.24 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 170.9, 170.5, 165.93, 165.91, 139.9, 139.4, 133.7, 133.6, 132.27, 132.25, 131.8, 131.2, 131.1, 130.4, 130.3, 129.2, 128.1, 72.5, 72.1, 65.0, 64.9, 62.5, 62.4, 61.9, 30.4, 29.3, 25.1, 25.0, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{21}H_{22}BrCl_2NNaO_6S^+$: 587.9620 found 587.9623.

5-(((2,6-Dichlorophenyl)sulfinyl)amino)-6-ethoxy-4-hydroxy-6-oxohexyl 4-methoxybenzoate (**15**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-hydroxybutyl 4-methoxybenzoate (**a14**, 134.6 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **15** (55.1 mg, 53% yield, *syn*/*anti* ratio = 1.6:1) as a colorless oil.



15, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.99–7.94 (m, 2H), 7.36–7.28 (m, 3H), 6.92–6.89 (m, 2H), 6.14 (d, *J* = 7.4 Hz, 0.61H, N**H**), 6.06 (d, *J* = 8.0 Hz, 0.39H, N**H**), 4.34–3.96 (m, 6H), 3.864 (s, 1.8H), 3.859 (s, 1.2H), 2.61 (d, *J* = 7.7 Hz, 0.39H, O**H**), 2.39 (d, *J* = 6.3 Hz, 0.61H, O**H**), 2.04–1.56 (m, 4H), 1.30–1.25 (m, 3H).

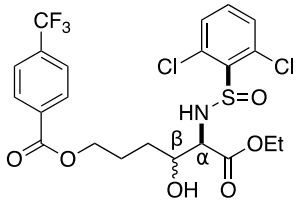
^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.0, 170.6, 166.5, 166.4, 163.5, 140.0, 139.6, 133.8, 133.6, 132.26, 132.24, 131.7, 131.6, 130.4, 130.3, 122.7, 113.7, 72.6, 72.1, 64.4, 64.3, 62.47, 62.44, 62.37, 61.9, 55.5, 30.5, 29.4, 25.2, 25.1, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{22}H_{25}Cl_2NNaO_7S^+$: 540.0621, found 540.0624.

5-(((2,6-Dichlorophenyl)sulfinyl)amino)-6-ethoxy-4-hydroxy-6-oxohexyl 4-(trifluoromethyl)benzoate (**16**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 4-hydroxybutyl 4-(trifluoromethyl)benzoate (**a15**, 153.6 mg, 0.6 mmol, 3 equiv.). The crude mixture was

purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **16** (67.7 mg, 61% yield, *syn*/*anti* ratio = 1.8:1) as a colorless oil.



16, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 8.15–8.10 (m, 2H), 7.71–7.68 (m, 2H), 7.36–7.30 (m, 3H), 6.14 (d, *J* = 7.4 Hz, 0.65H, N**H**), 6.04 (d, *J* = 7.7 Hz, 0.35H, N**H**), 4.43–4.35 (m, 2H), 4.28–4.22 (m, 2H), 4.16 (dd, *J* = 7.9, 4.7 Hz, 0.35H), 4.11–4.06 (m, 1.3H), 3.99–3.96 (m, 0.35H), 2.09–1.84 (m, 2H), 1.76–1.55 (m, 2H), 1.30–1.25 (m, 3H).

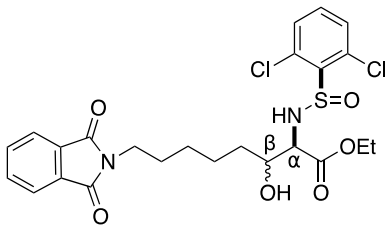
^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 170.9, 170.5, 165.48, 165.46, 139.9, 139.5, 134.9, 134.7, 134.4, 134.2, 133.8, 133.63, 133.56, 132.3, 130.41, 130.36, 130.11, 130.06, 125.55, 125.52, 124.8, 122.7, 72.5, 72.1, 65.3, 65.2, 62.6, 62.5, 62.4, 61.9, 30.4, 29.4, 25.15, 25.06, 14.2.

^{19}F-NMR (376 MHZ, $CDCl_3$) δ –63.0 ppm.

HRMS ESI $[M+Na]^+$ calculated for $C_{22}H_{22}Cl_2F_3NNaO_6S^+$: 578.0389, found 578.0395.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-8-(1,3-dioxoisoindolin-2-yl)-3-hydroxyoctanoate (17)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and 2-(6-hydroxyhexyl)isoindoline-1,3-dione (**a16**, 148.8 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **17** (65.9 mg, 61% yield, *syn*/*anti* ratio = 1.3:1) as a colorless oil.



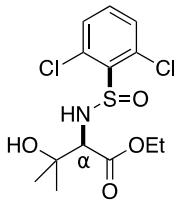
17, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.86–7.79 (m, 2H), 7.74–7.70 (m, 2H), 7.40–7.25 (m, 3H), 6.13 (d, *J* = 7.4 Hz, 0.56H, N**H**), 6.04 (d, *J* = 8.0 Hz, 0.44H, N**H**), 4.29–4.19 (m, 2H), 4.13 (dd, *J* = 8.0, 4.5 Hz, 0.44H), 4.04 (dd, *J* = 7.6, 3.0 Hz, 0.56H), 4.01–3.96 (m, 0.56H), 3.90–3.85 (m, 0.44H), 3.69–3.64 (m, 2H), 2.45 (d, *J* = 8.0 Hz, 0.44H), 2.27 (d, *J* = 6.9 Hz, 0.56H), 1.73–1.63 (m, 2H), 1.59–1.49 (m, 2H), 1.48–1.20 (m, 7H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.1, 170.6, 168.5,140.1, 139.7, 134.0, 133.7, 133.5, 132.2, 130.31, 130.25, 123.3, 72.8, 72.3, 62.4, 62.3, 62.2, 61.7, 37.9, 37.8, 33.6, 32.7, 28.5, 26.68, 26.66, 25.2, 25.0, 14.2. **HRMS ESI [M+Na]$^+$** calculated for $C_{24}H_{26}Cl_2N_2NaO_6S^+$: 563.0781, found 563.0786.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-3-methylbutanoate (**18**)

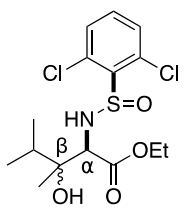
The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and isopropyl alcohol (**a17**, 92.5 µL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **18** (39.5 mg, 56% yield) as a pale-yellow oil.



18, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.34–7.31 (m, 1H), 6.11 (d, *J* = 9.2 Hz, 1H, N**H**), 4.32–4.22 (m, 2H), 3.91 (d, *J* = 9.2 Hz, 1H), 2.62 (s, 1H, O**H**), 1.34–1.31 (m, 3H), 1.29–1.24 (m, 6H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 171.4, 140.0, 133.7, 132.6, 130.3, 72.0, 66.3, 62.2, 26.3, 26.1, 14.2. **HRMS ESI [M+Na]$^+$** calculated for $C_{13}H_{17}Cl_2NNaO_4S^+$: 376.0148, found 376.0152.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-3,4-dimethylpentanoate (**19**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and 3-methyl-2-butanol (**a18**, 130 µL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **19** (32.2 mg, 42% yield, syn/anti ratio = ca. 1.2:1, overlap) as a colorless oil.

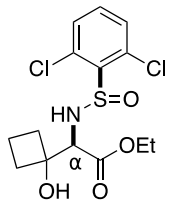


19, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.29 (m, 3H), 6.02–5.99 (m, 1H, N**H**), 4.30–4.20 (m, 2H), 4.09–4.05 (m, 1H), 2.45 (s, 0.55H, O**H**), 2.41 (s, 0.45H, O**H**), 2.02–1.99 (m, 0.5H), 1.67–1.65 (m, 0.5H, *H_2O overlaps*), 1.32–1.30 (m, 3H), 1.080 (s, 1.5H), 1.076 (s, 1.5H), 1.00–0.90 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 172.5, 172.4, 140.18, 140.15, 133.7, 132.2, 132.1, 130.3, 77.1, 76.0, 63.7, 63.0, 62.1, 35.2, 32.8, 19.1, 17.9, 17.7, 17.6, 16.9, 16.4, 14.2, 14.1. **HRMS ESI $[M+Na]^+$** calculated for $C_{15}H_{21}Cl_2NNaO_4S^+$: 404.0461, found 404.0462.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclobutyl)acetate (**20**)

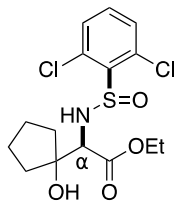
The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and cyclobutanol (**a19**, 50 µL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **20** (43.9 mg, 60% yield) as an off-white solid.



20, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.32–7.29 (m, 1H), 6.14 (d, *J* = 8.3 Hz, 1H, N**H**), 4.30–4.17 (m, 2H), 4.14 (d, *J* = 8.3 Hz, 1H), 2.69 (br s, 1H, O**H**), 2.40–2.29 (m, 2H), 2.11–1.99 (m, 2H), 1.94–1.86 (m, 1H), 1.70–1.63 (m, 1H), 1.30 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 170.1, 140.0, 133.7, 132.1, 130.3, 76.4, 62.9, 62.2, 33.3, 32.9, 14.2, 12.2. **HRMS ESI $[M+Na]^+$** calculated for $C_{14}H_{17}Cl_2NNaO_4S^+$: 388.0148, found 388.0150.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclopentyl)acetate (**21**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and cyclopentanol (**a20**, 110 µL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **21** (38.5 mg, 51% yield) as an off-white solid.

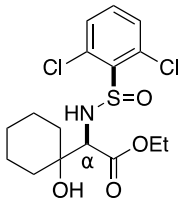


21, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.33–7.29 (m, 1H), 6.19 (d, *J* = 8.6 Hz, 1H, N**H**), 4.29–4.19 (m, 2H), 3.99 (d, *J* = 8.6 Hz, 1H), 2.39 (s, 1H, O**H**), 1.87–1.59 (m, 8H), 1.32–1.28 (m, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 171.6, 140.2, 133.7, 132.1, 130.3, 83.5, 64.6, 62.2, 37.9, 37.4, 24.2, 23.6, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{15}H_{19}Cl_2NNaO_4S^+$: 402.0304, found 402.0308.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclohexyl)acetate (22)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and cyclohexanol (**a21**, 125 μL, 1.2 mmol, 6 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **22** (29.7 mg, 38% yield) as a white solid.



22, new compound.

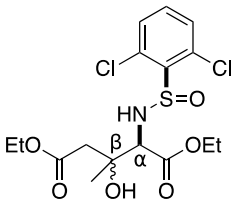
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.32–7.29 (m, 1H), 6.03 (d, *J* = 9.7 Hz, 1H, N**H**), 4.31–4.18 (m, 2H), 3.94 (d, *J* = 9.7 Hz, 1H), 2.28 (s, 1H, O**H**), 1.68–1.46 (m, 9H), 1.35–1.23 (m, 4H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.7, 140.1, 133.7, 132.1, 130.3, 73.0, 65.2, 62.1, 34.7, 34.0, 25.5, 21.69, 21.67, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{16}H_{21}Cl_2NNaO_4S^+$: 416.0461, found 416.0462.

Diethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxy-3-methylpentanedioate (23)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.5 mg, 0.2 mmol) and ethyl-DL-3-hydroxybutyrate (**a22**, 80 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **23** (55.2 mg, 65% yield, *syn*/*anti* ratio = 1.1:1) as a colorless oil.



23, new compound.

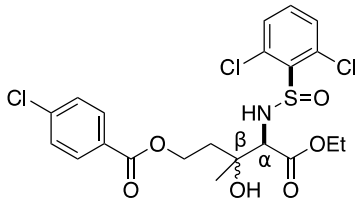
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.36 (m, 2H), 7.35–7.30 (m, 1H), 6.13 (d, *J* = 9.5 Hz, 0.52H, N**H**), 6.08 (d, *J* = 9.2 Hz, 0.48H, N**H**), 4.30–4.21 (m, 2H), 4.19–4.07 (m, 3H), 4.01 (s, 0.48H, O**H**), 3.92 (s, 0.52H, O**H**), 2.76–2.68 (m, 1H), 2.55–2.48 (m, 1H), 1.34–1.24 (m, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 172.21, 172.17, 140.1, 140.0, 133.7, 132.23, 132.18, 130.31, 130.29, 72.9, 72.8, 64.8, 64.5, 62.3, 61.1, 61.0, 42.1, 41.8, 24.8, 23.8, 14.2, 14.1.

HRMS ESI [M+Na]$^+$ calculated for $C_{16}H_{21}Cl_2NNaO_6S^+$: 448.0359, found 448.0362.

4-(((2,6-Dichlorophenyl)sulfinyl)amino)-5-ethoxy-3-hydroxy-3-methyl-5-oxopentyl 4-chlorobenzoate (24)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and 3-hydroxybutyl 4-chlorobenzoate (**a23**, 137.8 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **24** (35.6 mg, 34% yield, *syn/anti* ratio = ca. 1.0:1) as a colorless oil.



24, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.97–7.93 (m, 2H), 7.42–7.32 (m, 5H), 6.13–6.09 (m, 1H, N**H**), 4.55–4.50 (m, 2H), 4.33–4.21 (m, 2H), 4.03 (d, *J* = 8.9 Hz, 0.5H), 4.00 (d, *J* = 9.0 Hz, 0.5H), 2.80 (s, 0.5H, O**H**), 2.77 (s, 0.5H, O**H**), 2.13–2.03 (m, 1H), 1.98–1.95 (m, 1H), 1.34–1.24 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 170.97, 170.93, 165.60, 165.57, 139.7, 139.6, 139.5, 139.4, 133.63, 133.59, 132.2, 130.9, 130.3, 128.7, 128.6, 128.5, 73.0, 72.6, 65.8, 65.3, 62.5, 62.4, 61.1, 36.8, 36.6, 23.9, 23.2, 14.0.

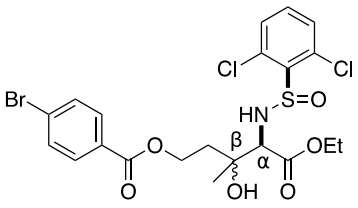
HRMS ESI $[M+Na]^+$ calculated for $C_{21}H_{22}Cl_3NNaO_6S^+$: 544.0126, found 544.0128.

4-(((2,6-Dichlorophenyl)sulfinyl)amino)-5-ethoxy-3-hydroxy-3-methyl-5-oxopentyl 4-bromobenzoate (25)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.6 mg, 0.2 mmol) and 3-hydroxybutyl 4-bromobenzoate (**a24**, 166.3 mg, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **25** (42.3 mg, 37% yield, *syn/anti* ratio = ca. 1.0:1) as a colorless oil.

25, new compound.

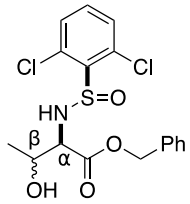
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.88–7.85 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.30–7.38 (m, 3H), 6.09–6.13 (m, 1H, N**H**), 4.52 (q, *J* = 6.7 Hz, 2H), 4.32–4.20 (m, 2H), 4.04–3.99 (m, 1H), 2.82 (s, 0.5H, O**H**), 2.79 (s, 0.5H, O**H**), 2.13–2.02 (m, 1H), 1.98–1.95 (m, 1H), 1.33–1.24 (m, 6H).



^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.09, 171.06, 165.87, 165.85, 139.8, 139.7, 133.8, 133.7, 132.4, 131.9, 131.2, 130.4, 129.2, 129.1, 128.3, 128.2, 73.1, 72.7, 66.0, 65.4, 62.6, 62.5, 61.25, 37.0, 36.8, 24.0, 23.4, 14.2.
HRMS ESI [M+Na]$^+$ calculated for $C_{21}H_{22}BrCl_2NNaO_6S^+$: 587.9621, found 587.9618.

Benzyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxyhexanoate (**26**)

The reaction was conducted according to the **General Procedure** using (±)-**1l** (71.3 mg, 0.2 mmol) and ethanol (**a1**, 35 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **26** (53.6 mg, 67% yield, *syn/anti* ratio = 1.2:1) as a colorless oil.

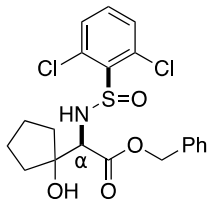


26, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.28 (m, 8H), 6.12 (d, *J* = 7.7 Hz, 0.54H, N**H**), 6.05 (d, *J* = 8.0 Hz, 0.46H, N**H**), 5.27–5.12 (m, 2H), 4.21–4.17 (m, 1H), 4.10–4.14 (m, 0.46H), 4.01 (dd, *J* = 8.0, 3.5 Hz, 0.54H), 2.4–2.0 (br s, 1H, O**H**), 1.26 (d, *J* = 6.6 Hz, 1.5H), 1.11 (d, *J* = 6.3 Hz, 1.5H). **^{13}C-NMR (126 MHz, $CDCl_3$)** *(mixture of syn/anti isomers)* δ 170.9, 170.5, 140.0, 139.7, 135.0, 134.9, 133.8, 133.7, 132.3, 130.4, 130.3, 128.80, 128.77, 128.7, 128.6, 68.9, 68.6, 68.1, 68.0, 63.4, 63.2, 19.9, 18.7. **HRMS ESI [M+Na]$^+$** calculated for $C_{17}H_{17}Cl_2NNaO_4S^+$: 424.0148, found 424.0144.

Benzyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclopentyl)acetate (**27**)

The reaction was conducted according to the **General Procedure** using (±)-**1l** (71.2 mg, 0.2 mmol) and cyclopentanol (**a20**, 55 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **27** (38.1 mg, 43% yield) as a colorless oil.

27, new compound.



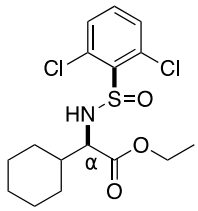
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.28 (m, 8H), 6.19 (d, *J* = 8.9 Hz, 1H, N**H**), 5.26 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.04 (d, *J* = 9.2 Hz, 1H), 2.30 (br s, 1H, O**H**), 1.82–1.52 (m, 8H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.6, 140.1, 134.9, 133.7, 132.2, 130.3, 128.8, 83.6, 68.0, 64.8, 37.9, 37.5, 24.2, 23.6.

HRMS ESI $[M+Na]^+$ calculated for $C_{20}H_{21}Cl_2NNaO_3S^+$: 464.0461, found 464.0463.

Ethyl 2-cyclohexyl-2-(((2,6-dichlorophenyl)sulfinyl)amino)acetate (**28**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.8 mg, 0.2 mmol) and cyclohexane (**r1**, 65 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **28** (57.9 mg, 77% yield) as a colorless oil.



28, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.33–7.28 (m, 1H), 5.92 (d, *J* = 8.6 Hz, 1H, N**H**), 4.28–4.18 (m, 2H), 3.87 (dd, *J* = 8.4 Hz, 5.3 Hz, 1H), 1.79–1.70 (m, 3H), 1.65–1.61 (m, 2H), 1.60–1.54 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27–1.00 (m, 5H).

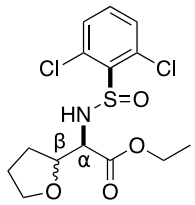
^{13}C-NMR (126 MHz, $CDCl_3$) δ 172.4, 140.6, 133.5, 132.0, 130.2, 63.4, 61.8, 41.8, 29.5, 27.6, 26.02, 26.00, 25.9, 14.3.

HRMS ESI $[M+Na]^+$ calculated for $C_{16}H_{21}Cl_2NNaO_3S^+$: 400.0512, found 400.512.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(tetrahydrofuran-2-yl)acetate (**29**)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and tetrahydrofuran (**r2**, 50 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **29** (59.2 mg, 81% yield, *syn/anti* ratio = 1.0:1) as a colorless oil.

29, new compound.



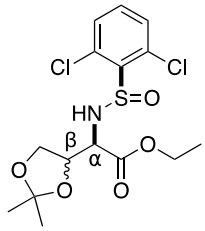
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.36 (m, 2H), 7.32–7.29 (m, 1H), 6.09 (d, *J* = 6.9 Hz, 0.49H, N**H**), 6.01 (d, *J* = 8.6 Hz, 0.51H, N**H**), 4.34 (td, *J* = 7.2, 2.6 Hz, 0.51H), 4.27–4.19 (m, 3H), 4.10 (dd, *J* = 8.6 Hz, 2.6 Hz, 0.49H), 3.81–3.66 (m, 2H), 2.04–1.77 (m, 4H), 1.31–1.26 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 170.7, 170.6, 140.6, 140.2, 133.55, 133.51, 132.0, 130.2, 79.9, 79.3, 69.5, 69.1, 62.1, 60.7, 60.6, 28.1, 27.2, 26.0, 25.8, 14.19, 14.15.

HRMS ESI [M+Na]$^+$ calculated for $C_{14}H_{17}Cl_2NNaO_4S^+$: 388.0148, found 388.0147.

Ethyl 2-(((2,6-dichlorophenyl)sulfinyl)amino)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)acetate (30)

The reaction was conducted according to the **General Procedure** using (±)-**1k** (58.9 mg, 0.2 mmol) and 2,2-dimethyl-1,3-dioxolane (**r3**, 65 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 8:2 to 1:1) to yield the title compound **30** (61.9 mg, 77% yield, *syn/anti* ratio = 1.0:1) as a colorless oil.



30, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.38–7.36 (m, 2H), 7.33–7.30 (m, 1H), 6.03 (d, *J* = 8.9 Hz, 0.5H, N**H**), 5.98 (d, *J* = 9.0 Hz, 0.5H), 4.50 (td, *J* = 6.4 Hz, 3.2 Hz, 0.5H), 4.31–4.20 (m, 2.5H), 4.14–4.07 (m, 1.5H), 4.02–4.01 (m, 1H), 3.92 (dd, *J* = 8.3 Hz, 6.3 Hz, 0.5H), 1.42 (s, 1.5H), 1.32–1.26 (m, 7.5H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 170.6, 169.9, 140.3, 140.0, 133.7, 133.5, 132.3, 132.1, 130.3, 110.6, 110.2, 76.1, 66.3, 66.1, 62.4, 62.2, 60.3, 58.9, 26.7, 26.1, 25.2, 14.2.

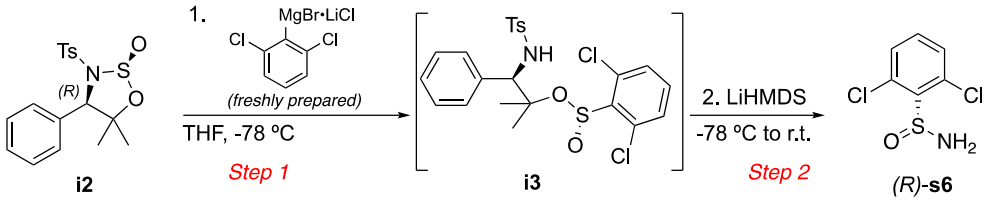
HRMS ESI [M+H]$^+$ calculated for $C_{15}H_{19}Cl_2NNaO_4S^+$: 418.0254, found 418.0256.

5. Reactions of Enantiomerically Enriched *N*-Sulfinyl α-Iminoesters

5.1. Preparation of Enantiomerically Enriched *N*-Sulfinyl α-Iminoesters

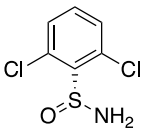
Both enantiomers of 2,6-dichlorobenzenesulfinamide (**s6**) were prepared according to Senanayake's method.[27]

(*R*)-2,6-Dichlorobenzenesulfinamide ((*R*)-s6)



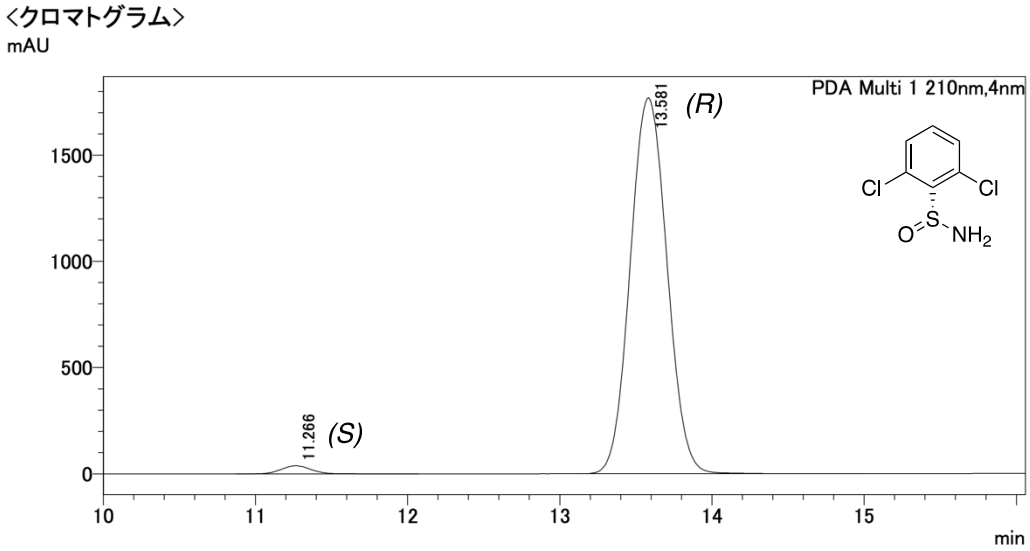
Step 1: To a stirred solution of **i2**[27a] (1.05 g, 4.8 mmol, 98:2 d.r.) in dry THF (6.5 mL) at –78 °C was added a freshly prepared 0.5 M solution of (2,6-dichlorophenyl)magnesium bromide•LiCl[28] (12 mL, 6 mmol, 1 equiv.) in THF dropwise over 40 min. The conversion of **i2** was monitored by TLC. The reaction was quenched with sat. $NaHCO_3$ aq. and the solution was diluted with 40 mL of EtOAc. The mixture was allowed to warm at r.t. and the organic phase was washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure using a rotary evaporator while keeping the temperature below 30 °C. The residue was passed through a pad of silica-gel (washed with hexanes/EtOAc 75:25 to 10:90) and the solution was concentrated under reduced pressure to afford intermediate **i3** as a solid, which was used without further purification in the next step.

Step 2: To a two-neck 50 mL round bottom flask were added **i3** and dry THF (20 mL), and the mixture was cooled at –78 °C. 1.3 M of lithium bis(trimethylsilyl)amide (10 mL, ca. 13 mmol, 3 equiv.) in THF was added dropwise to the solution. Upon completion of the addition, the reaction mixture was allowed to warm slowly to ambient temperature and the reaction was monitored by TLC. After 6 h, the reaction was quenched with water (10 mL), and the mixture was diluted with EtOAc (40 mL) and allowed to warm at r.t. The liquid layers were collected and the sticky solid generated was washed several times with EtOAc and water. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 0:100) to afford the title compound (*R*)-**s6** (495 mg, 49 % overall yield, 98:2 e.r.).



(*R*)-**s6**, new compound.
Chiral HPLC (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:20, 40 °C, flow rate: 1.5 mL/min, λ =210 nm): Retention time = 11.3 min ((*S*)-**s6**, 1.7%), 13.6 min ((*R*)-**s6**, 98.3%). **HRMS ESI [M+Na]$^+$** calculated for $C_6H_5Cl_2NOSNa^+$: 231.9361, found 231.9363.

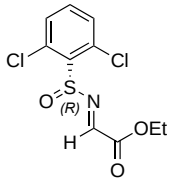
Chromatogram of (*R*)-**s6**



Entry	Retention time (min)	Area	Area (%)
1	11.266	509229	1.682
2	13.581	29767911	98.318
Total		30277140	100

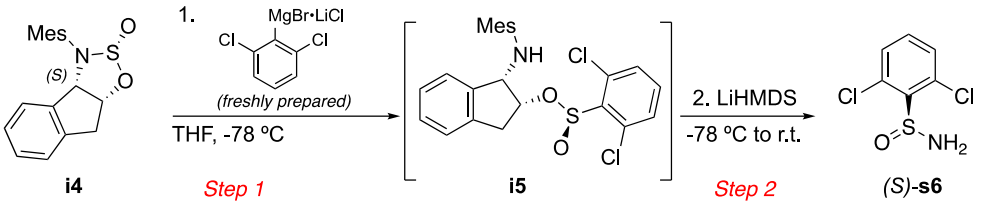
Ethyl (*R*,*E*)-2-(((2,6-dichlorophenyl)sulfinyl)imino)acetate ((*R*)-**1k**)

Method C: (*R*)-2,6-Dichlorobenzenesulfinamide ((*R*)-**s6**), 420 mg, 2.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 410 μL) provided 388 mg (66% yield) of (*R*)-**1k** as a colorless solid.



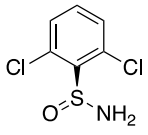
(*R*)-**1k**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.37 (t, *J* = 2.1 Hz, 3H), 4.46–4.36 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 161.1, 156.5, 136.0, 135.3, 133.6, 130.6, 63.0, 14.2. **HRMS ESI [M+H]$^+$** calculated for $C_{10}H_{10}Cl_2NO_3S^+$: 293.9753, found 293.9753.

(*S*)-2,6-Dichlorobenzenesulfinamide ((*S*)-s6)



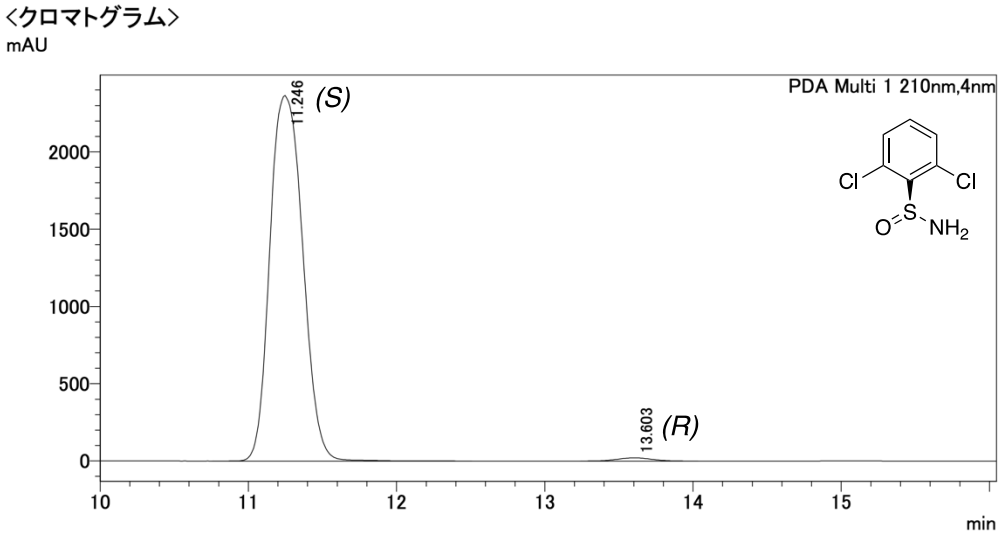
Step 1: To a stirred solution of **i4**[27b] (3.77 g, 10.0 mmol) in dry THF (20 mL) at –78 °C was added a freshly prepared 0.53 M solution of (2,6-dichlorophenyl)magnesium bromide•LiCl[28] (20 mL, 10.5 mmol, 1.05 equiv.) in THF dropwise over a 10 min. The reaction was stirred at –78 °C for 3.5 h and quenched at the same temperature by addition of sat. $NaHCO_3$ aq. (20 mL), and the mixture was diluted with EtOAc (25 mL). The phases were separated, and the aqueous phase was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator while keeping the temperature below 30 °C. The crude mixture was passed through a pad of silica-gel (washed with hexanes/EtOAc 80:20 to 50:50) and the solution was concentrated under reduced pressure to afford intermediate **i5** (ca. 65% yield, containing 8% of (1*S*,2*R*)-1-(mesitylamino)-2,3-dihydro-1*H*-inden-2-ol), which was used without further purification in the next step.

Step 2: To a two-neck 100 mL round bottom flask were added **i5** (ca. 4.8 mmol) and dry THF (20 mL), and the mixture was cooled at –78 °C. 1.9 M of sodium bis(trimethylsilyl)amide (7.6 mL, 14.4 mmol, ca. 3 equiv.) in THF was added dropwise over 10 min. Upon completion of the addition, the reaction mixture was allowed to warm slowly to –30 °C and the reaction was monitored by TLC. After 6 h, the reaction was quenched with water (10 mL), and the mixture was diluted with EtOAc (40 mL) and allowed to warm at r.t. The liquid layers were collected and the sticky solid generated was washed several times with EtOAc and water. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 0:100) to afford the title compound (*S*)-**s6** (530 mg, 53% yield, 99:1 e.r.).



(*S*)-**s6**, new compound.
Chiral HPLC DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:20, 40 °C, flow rate: 1.5 mL/min, λ =210 nm): Retention time = 11.3 min ((*S*)-**s6**, 99.1%), 13.6 min ((*R*)-**s6**, 0.9%).
HRMS ESI [M+Na]$^+$ calculated for $C_6H_5Cl_2NOSNa^+$: 231.9361, found 231.9362.

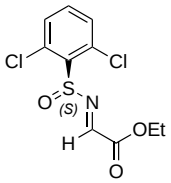
Chromatogram of (*S*)-**s6**



Entry	Retention time (min)	Area	Area (%)
1	11.246	36464316	99.086
2	13.603	336209	0.914
Total		36800525	100

(*S*)-Ethyl-(*E*)-2-(((2,6-dichlorophenyl)sulfinyl)imino)acetate ((*S*)-**1k**)

Method C: (*S*)-2,6-Dichlorobenzenesulfinamide ((*S*)-**s6**, 421.0 g, 2.0 mmol) and ethyl glyoxylate (47 w/w% solution in toluene, 420 μL) provided 383 mg (65% yield) of (*S*)-**1k** as a colorless solid.



(*S*)-**1k**, new compound.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.37 (t, *J* = 2.3 Hz, 3H), 4.46–4.36 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H).

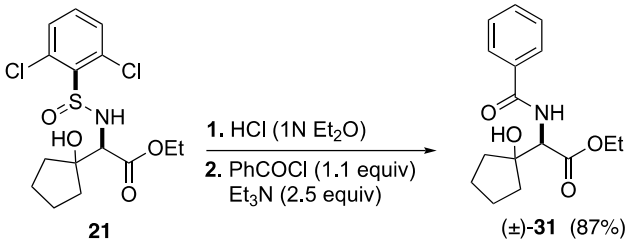
^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.1, 156.5, 136.0, 135.3, 133.6, 130.6, 63.0, 14.2.

HRMS ESI $[M+H]^+$ calculated for $C_{10}H_{10}Cl_2NO_3S^+$: 293.9753, found 293.9754.

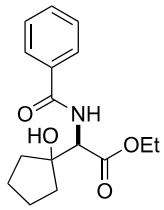
5.2. Reactions of (*R*)-**1k** and (*S*)-**1k** with Cyclopentanol

5.2.1. Preparation of ethyl 2-benzamido-2-(1-hydroxycyclopentyl)acetate ((±)-**31**)

Method F

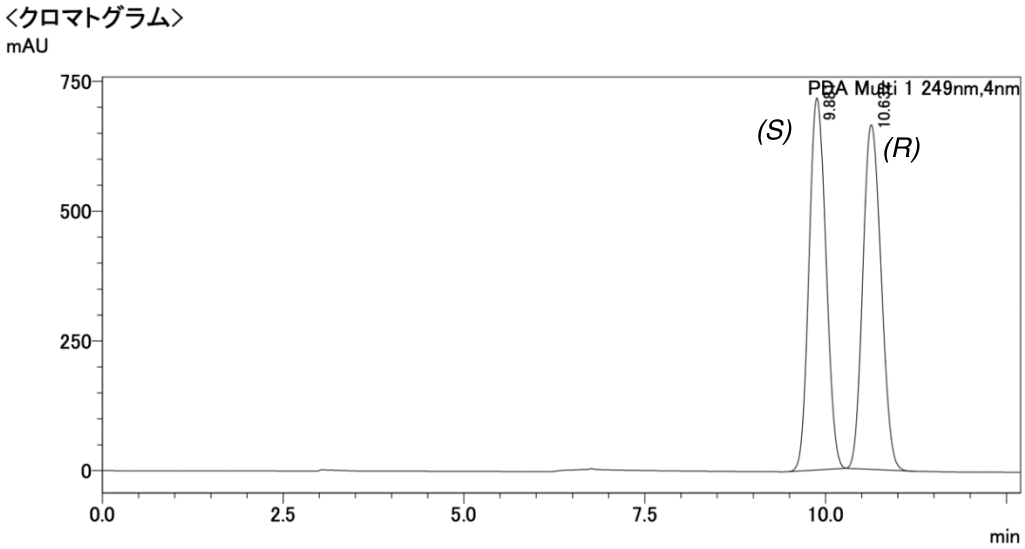


To a stirred solution of **21** (31.2 mg, 82 μmol) in MeOH (2 mL) at 0 °C was added 450 μL of HCl (1N in Et_2O). The mixture was stirred for 10 min, and then allowed to warm at r.t. After being stirred for additional 3 h, the volatiles were removed under reduced pressure. The residue was dissolved in dry CH_2Cl_2 and the solution was cooled to 0 °C. To this solution were sequentially added Et_3N (30 μL, 2.5 equiv.) and benzoyl chloride (12 μL, 1.1 equiv.) dropwise. The reaction was warmed to r.t. and stirred for 4 h at the same temperature. After solvent removal under reduced pressure using a rotary evaporator, the residue was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 50:50) to furnish the desired compound (±)-**31** (17.9 mg, 87% yield) as a colorless oil.



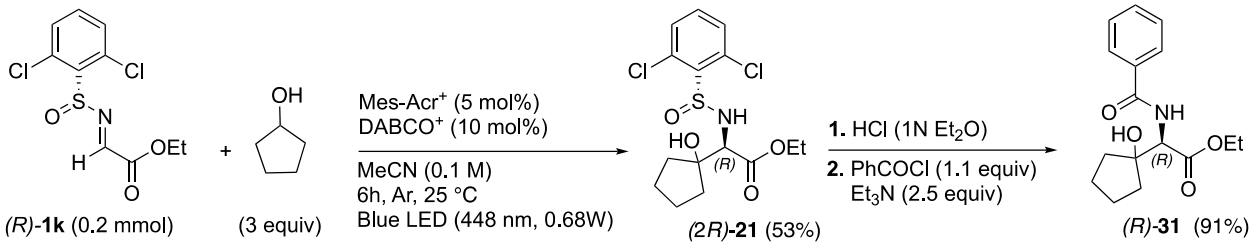
(±)-**31**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.76 (d, *J* = 8.6 Hz, 1H), 4.31–4.19 (m, 2H), 1.93–1.65 (m, 8H), 1.31 (t, *J* = 7.2 Hz, 3H). **HRMS ESI [M+H]$^+$** calculated for $C_{16}H_{21}NNaO_4^+$: 314.1363, found 314.1370. **Chiral HPLC** DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 85:15, 40 °C, flow rate: 1.0 mL/min, λ = 249 nm): Retention time = 9.9 min ((*S*)-**31**, 99.1%), 10.6 min ((*R*)-**31**, 0.9%).

Chromatogram of (±)-**31**



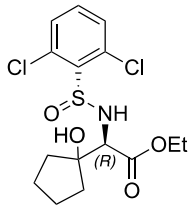
Entry	Retention time (min)	Area	Area (%)
1	9.881	11673098	50.019
2	10.632	11664455	49.981
Total		23337553	100

5.2.2. Preparation of ethyl (*R*)-2-benzamido-2-(1-hydroxycyclopentyl) acetate ((*R*)-**31**)



Ethyl (*R*)-2-(((*R*)-2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclopentyl)acetate ((2*R*)-21)

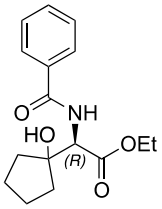
The reaction was conducted following the **General Procedure** using (*R*)-**1k** (58.8 mg, 0.2 mmol) and cyclopentanol (**a21**, 55 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 50:50) to yield the title compound (2*R*)-**21** (40.4 mg, 53% yield) as an off-white solid.



(*2R*)-**21**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.31 (m, 1H), 6.19 (d, *J* = 8.6 Hz, 1H), 4.31–4.18 (m, 2H), 3.99 (d, *J* = 8.9 Hz, 1H), 2.24–2.52 (1H), 1.90–1.57 (m, 8H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 171.7, 140.2, 133.7, 132.2, 130.4, 83.5, 64.6, 62.2, 37.9, 37.5, 24.3, 23.6, 14.2. **HRMS ESI [M+Na]$^+$** calculated for $C_{15}H_{19}Cl_2NNaO_4S^+$: 402.0305, found 402.0304.

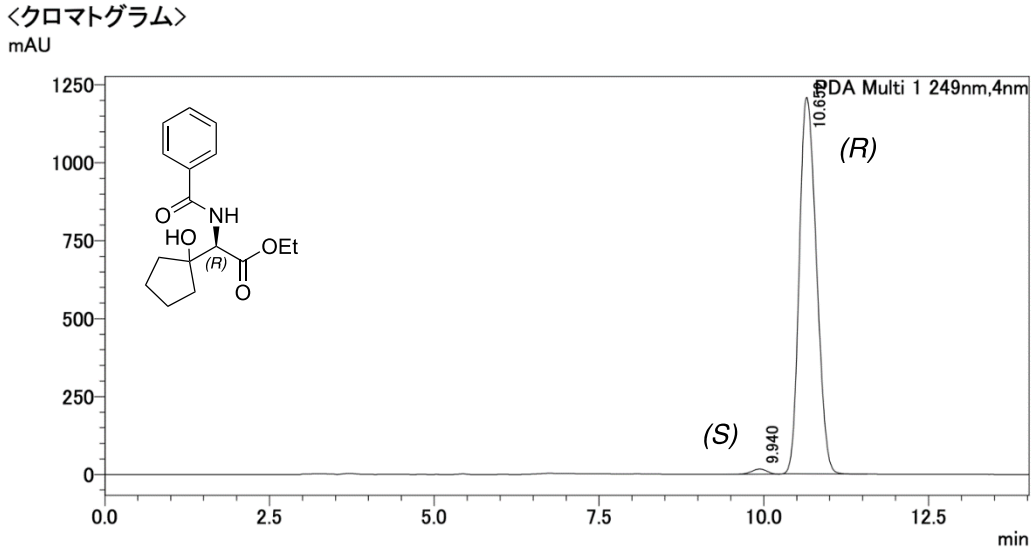
Ethyl (*R*)-2-benzamido-2-(1-hydroxycyclopentyl)acetate ((*R*)-**31**)

Method F: (*R*)-**21** (33.1 mg, 87 μmol) furnished the desired compound (*R*)-**31** (23.1 mg, 91% yield) as a colorless oil.



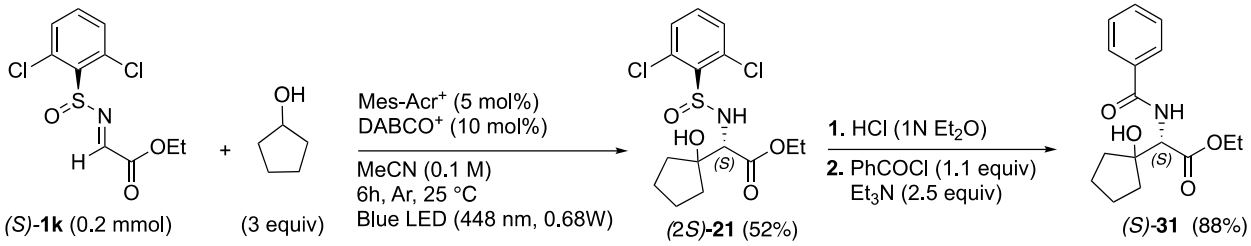
(*R*)-**31**, new compound.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.53–7.50 (m, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 4.75 (d, *J* = 8.6 Hz, 1H), 4.32–4.19 (m, 2H), 1.93–1.62 (m, 8H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 172.0, 167.5, 133.9, 132.0, 128.7, 127.3, 83.4, 61.8, 59.5, 38.2, 37.9, 24.1, 23.5, 14.3. **HRMS ESI [M+H]$^+$** calculated for $C_{16}H_{21}NNaO_4^+$: 314.1363, found 314.1371. **Chiral HPLC** (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 85:15, 40 °C, flow rate: 1.0 mL/min, λ =249 nm): Retention time = 9.9 min ((*S*)-**31**, 1.2%), 10.7 min ((*R*)-**31**, 98.8%).

Chromatogram of (*R*)-**31**



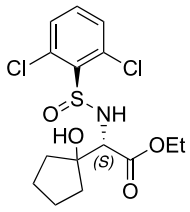
Entry	Retention time (min)	Area	Area (%)
1	9.940	268197	1.211
2	10.652	21876086	98.789
Total		22144283	100

5.2.3. Asymmetric synthesis of ethyl (*S*)-2-benzamido-2-(1-hydroxycyclopentyl)acetate ((*S*)-**31**)



Ethyl (*S*)-2-(((*S*)-2,6-dichlorophenyl)sulfinyl)amino)-2-(1-hydroxycyclopentyl)acetate ((2*S*)-**21**)

The reaction was conducted following the **General Procedure** using (*S*)-**1k** (58.8 mg, 0.2 mmol) and cyclopentanol (**a21**, 55 µL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 50:50) to yield the title compound (2*S*)-**21** (39.6 mg, 52% yield) as an off-white solid.



(2*S*)-**21**, new compound.

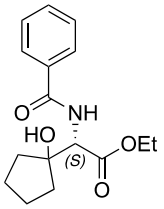
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.31 (m, 1H), 6.19 (d, *J* = 8.6 Hz, 1H, N**H**), 4.31–4.18 (m, 2H), 3.99 (d, *J* = 8.9 Hz, 1H), 2.35 (br s, 1H, O**H**), 1.90–1.57 (m, 8H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.6, 140.1, 133.7, 132.1, 130.3, 83.5, 64.6, 62.2, 37.9, 37.4, 24.2, 23.5, 14.2.

HRMS ESI [M+Na]$^+$ calculated for $C_{15}H_{19}Cl_2NNaO_4S^+$: 402.0305, found 402.0306.

Ethyl (*S*)-2-benzamido-2-(1-hydroxycyclopentyl)acetate ((*S*)-**31**)

Method F: (*2S*)-**21** (30.1 mg, 110 μmol) furnished the desired compound (*S*)-**31** (16.8 mg, 85% yield) as an off-white solid.



(*S*)-**31**, new compound.

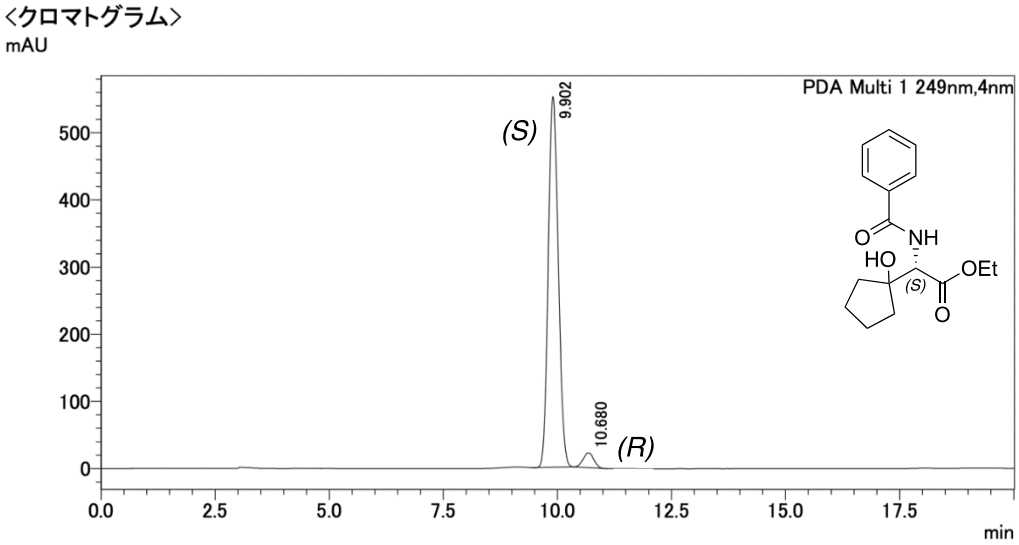
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.53–7.50 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 1H), 4.74 (d, *J* = 8.9 Hz, 1H), 4.32–4.19 (m, 2H), 1.92–1.62 (m, 8H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 172.0, 167.5, 133.9, 132.0, 128.7, 127.3, 83.4, 61.8, 59.4, 38.2, 37.9, 24.1, 23.5, 14.3.

HRMS ESI [M+H]$^+$ calculated for $C_{16}H_{21}NNaO_4^+$: 314.1363, found 314.1371.

Chiral HPLC (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 85:15, 40 °C, flow rate: 1.0 mL/min, λ =249 nm): Retention time = 9.9 min ((*S*)-**31**, 95.9%), 10.7 min ((*R*)-**31**, 4.1%).

Chromatogram of (*S*)-**31**



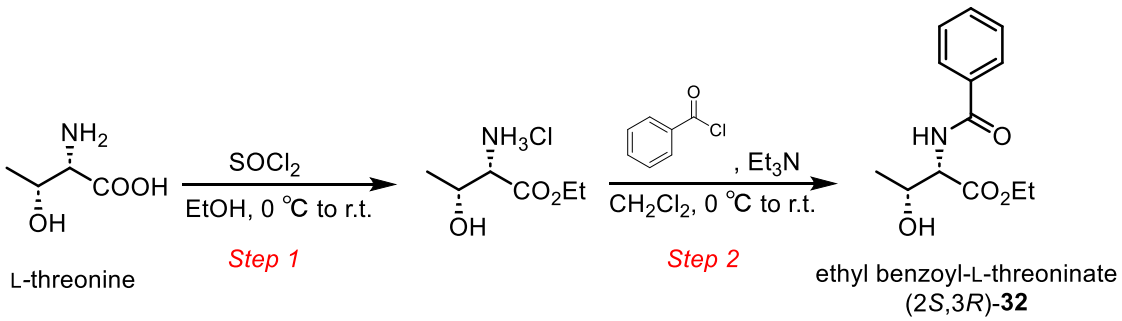
Entry	Retention time (min)	Area	Area (%)
1	9.902	8421906	95.942
2	10.680	356201	4.058
Total		8778106	100

5.3. Reactions of (*R*)-**1k** and (*S*)-**1k** with Ethanol

5.3.1. Preparation of authentic samples of threonine derivatives (**32**) for HPLC analysis

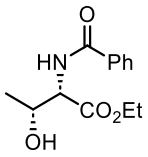
Ethyl benzoyl-L-threoninate ((2*S*,3*R*)-**32**) [CAS: 23161-25-3]

Method G



Step 1:[29] $SOCl_2$ (4.5 mL, 62 mmol, 5 equiv.) was added dropwise to EtOH (60 mL) at 0 °C. After the addition was complete, L-threonine (1.51 g, 12.7 mmol) was added in one portion and the reaction was stirred for 1 h at 0 °C and 20 h at r.t. The reaction solution was concentrated under reduced pressure using a rotary evaporator, and the obtained residue was triturated with cold Et_2O to give ethyl L-threoninate hydrochloride as a white solid, which was used without further purification in the next step.

Step 2: Benzoyl chloride (680 μL, 5.8 mmol, 1.1 equiv.) was added dropwise to a mixture of ethyl L-threoninate hydrochloride (972 mg, 5.3 mmol) and triethylamine (1.85 mL, 13.2 mmol, 2.5 equiv.) in CH_2Cl_2 (21 mL) at 0 °C. After being stirred for 4 h, the reaction was quenched with water. After warming to r.t., the organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure using a rotary evaporator to give a dense oil. The residue was purified by flash column chromatography on silica-gel (hexanes/EtOAc 1:1) to afford the desired compound **32**.



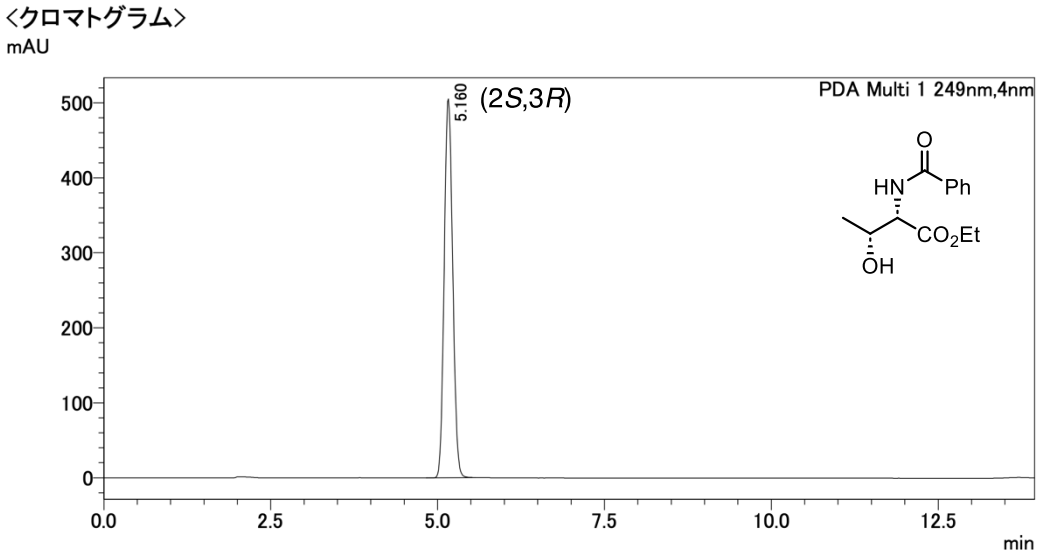
(2*S*,3*R*)-**32** has a CAS RN.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.85–7.84 (m, 2H), 7.54–7.43 (m, 3H), 7.02 (d, *J* = 33.5 Hz, 1H, N**H**), 4.82–4.80 (m, 1H, αC**H**), 4.46–4.43 (m, 1H, βC**H**), 4.27–4.23 (m, 2H), 2.95–2.35 (br s, 1H, O**H**), 1.32–1.26 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.3, 168.1, 133.9, 132.0, 128.7, 127.3, 68.5, 62.0, 57.8, 20.2, 14.3.

Chiral HPLC (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:20, 40 °C, flow rate: 1.5 mL/min, λ =249 nm): Retention time = 5.2 min (100%).

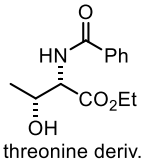
Chromatogram of (2*S*,3*R*)-**32**



Entry	Retention time (min)	Area	Area (%)
1	5.160	4466052	100
Total		4466052	100

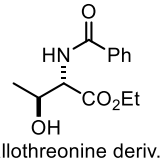
Ethyl benzoyl-DL-threoninate ((2*S*,3*R*)-**32** + (2*R*,3*S*)-**32**) and **Ethyl benzoyl-DL-allothreoninate** ((2*S*,3*S*)-**32** + (2*R*,3*R*)-**32**)

These authentic samples were prepared from a mixture of DL-threonine (containing ca. 22% of DL-allothreonine) via **Method G**.



threonine deriv.

+



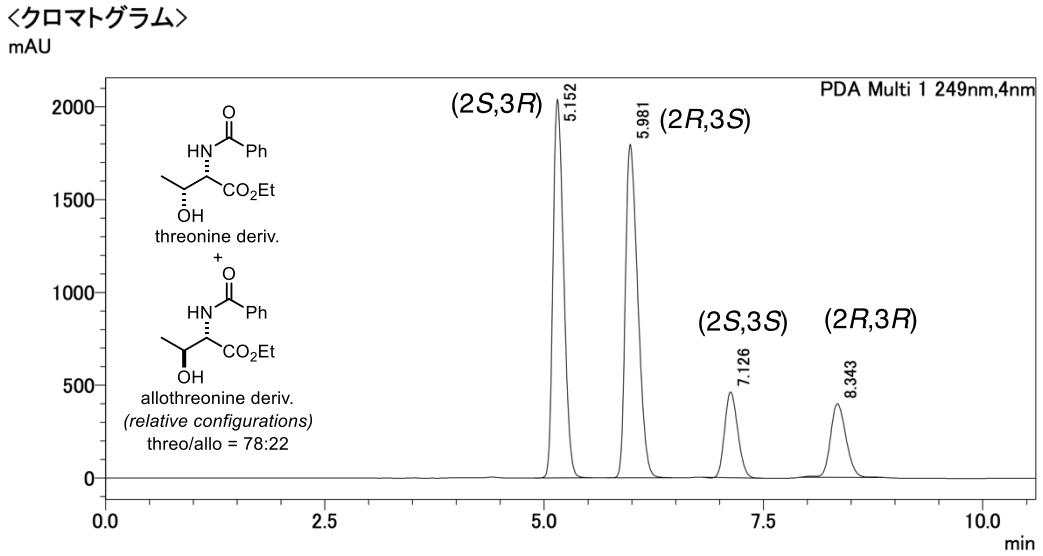
allothreonine deriv.

(relative configurations)

threo/allo = 78:22

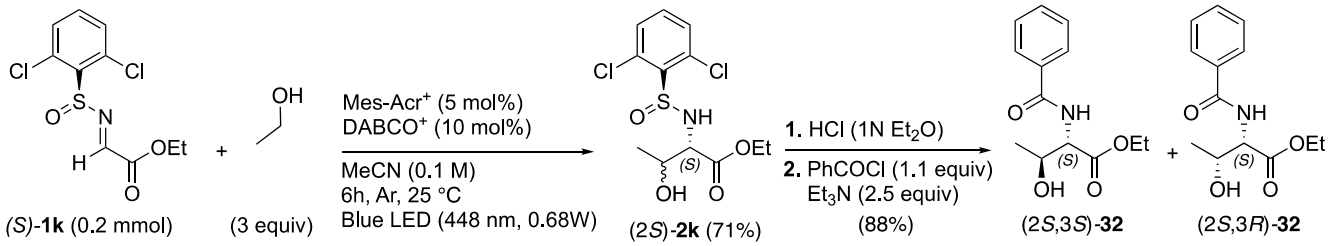
(2*S*,3*R*)-**32**, (2*R*,3*S*)-**32**, (2*S*,3*S*)-**32**, and (2*R*,3*R*)-**32** (mixture of DL-threonine deriv. + DL-allothreonine deriv.)
^{1}H-NMR (400 MHz, $CDCl_3$) *(mixture of four isomers)* δ 7.86–7.83 (m, 2H), 7.56–7.42 (m, 3H), 7.16 (br s, 0.2H, N**H**), 6.98 (br s, 0.8H, N**H**), 4.89–4.86 (m, 0.2H, αC**H**), 4.83–4.78 (m, 0.8H, αC**H**), 4.47–4.43 (m, 0.8H, βC**H**), 4.32–4.23 (m, 2.2H), 1.35–1.22 (m, 6H). **Chiral HPLC** (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:20, 40 °C, flow rate: 1.5 mL/min, λ =249 nm): Retention time = 5.2 min ((2*S*,3*R*)-**32**: 38.5%), 6.0 min ((2*R*,3*S*)-**32**: 39.6%), 7.1 min ((2*S*,3*S*)-**32**: 10.8%), 8.3 min ((2*S*,3*S*)-**32**: 11.1%).

Chromatogram of (2*S*,3*R*)-**32**, (2*R*,3*S*)-**32**, (2*S*,3*S*)-**32**, and (2*R*,3*R*)-**32** ([DL-threonine deriv.]:[DL-allothreonine deriv.] = 78:22)



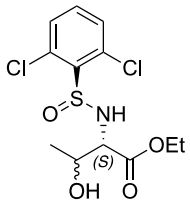
Entry	Retention time (min)	Area	Area (%)
1	5.152	17158940	38.536
2	5.981	17621273	39.574
3	7.126	4800410	10.781
4	8.343	4946544	11.109
Total		44527166	100

5.3.2. Asymmetric synthesis of ethyl (2*S*)-2-benzamido-3-hydroxybutanoate ((*2S*)-**32**)



Ethyl (2*S*)-2-(((*S*)-(2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxybutanoate ((2*S*)-2k)

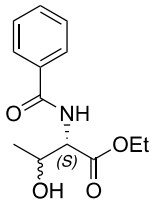
The reaction was conducted following the **General Procedure** using (*S*)-**1k** (58.8 mg, 0.2 mmol) and ethanol (**a1**, 35 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 50:50) to yield the title compound (2*S*)-**2k** (48.5 mg, 71% yield, *syn*/*anti* ratio = 1:1.3) as a colorless oil.



(2*S*)-**2k**. Mixture of *syn*/*anti* isomers ((2*S*,3*R*)-**2k** + (2*S*,3*S*)-**2k**); *syn*/*anti* = 1:1.3.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.39–7.36 (m, 2H), 7.34–7.31 (m, 1H), 6.12 (d, *J* = 7.7 Hz, 0.52H, N**H**), 6.06 (d, *J* = 7.4 Hz, 0.45H, N**H**), 4.29–4.10 (m, 3.6H), 3.96 (dd, *J* = 7.5, 3.5 Hz, 0.54H), 2.46 (br s, 0.45H, O**H**), 2.31 (d, 0.50H, O**H**), 1.32–1.28 (m, 4.6H), 1.17 (d, *J* = 6.0 Hz, 1.4H). **^{13}C-NMR (126 MHz, $CDCl_3$)** *(mixture of syn/anti isomers)* δ 171.0, 170.5, 140.0, 139.7, 133.7, 133.6, 132.3, 130.4, 130.3, 68.8, 68.6, 63.2, 63.0, 62.4, 62.3, 19.9, 18.7, 14.2. **HRMS ESI [M+H]$^+$** calculated for $C_{12}H_{15}Cl_2NNaO_4S^+$: 361.9991, found 361.9991.

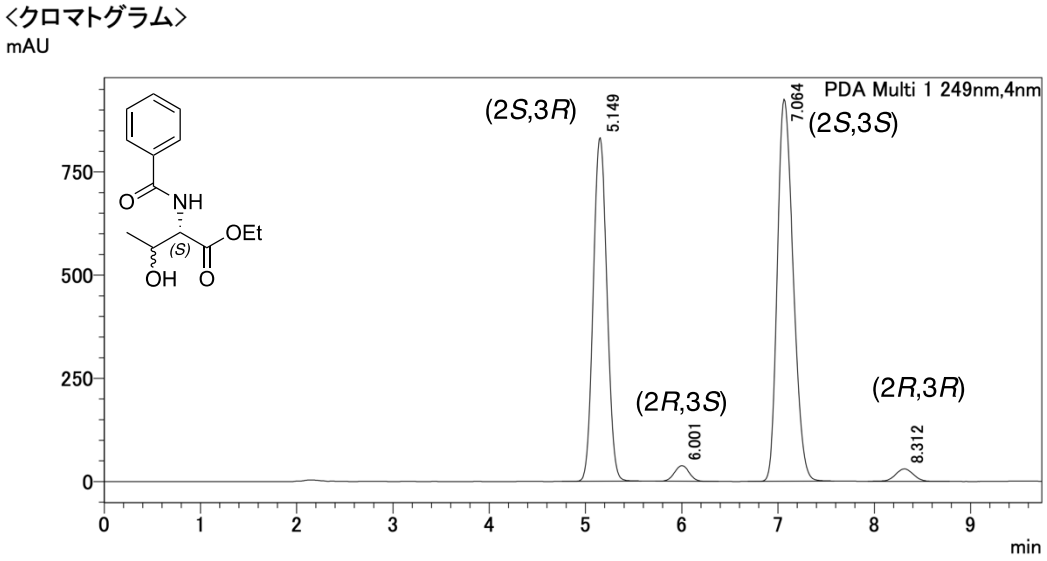
Ethyl (2*S*)-2-benzamido-3-hydroxybutanoate ((2*S*)-**32**)

Method F: (*S*)-**2k** (37.4 mg, 110 μmol) furnished the desired compound (*2S*)-**32** (24.3 mg, 88% yield, *syn*/*anti* ratio = 1:1.3) as a colorless oil.



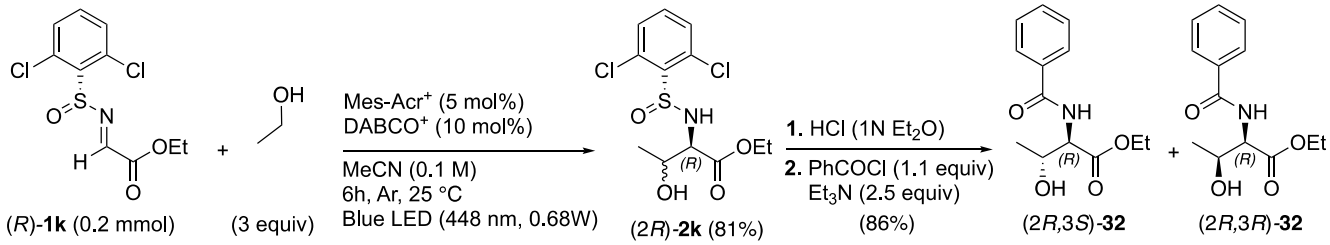
(2*S*)-**32**. Mixture of *syn*/*anti* isomers ((2*S*,3*R*)-**32** + (2*S*,3*S*)-**32**); *syn*/*anti* = 1:1.3.
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.85–7.83 (m, 2H), 7.56–7.51 (m, 1H), 7.48–7.43 (m, 2H), 7.19 (d, *J* = 6.0 Hz, 0.55H, N**H**), 7.00 (d, *J* = 8.6 Hz, 0.45H, N**H**), 4.87 (dd, *J* = 7.0, 3.5 Hz, 0.55H, αC**H**), 4.81 (dd, *J* = 8.7, 2.4 Hz, 0.45H, αC**H**), 4.47–4.43 (m, 0.46H, βC**H**), 4.34–4.23 (m, 2.6H), 3.76 (br s, 0.55H, O**H**), 2.85–2.24 (br s, 0.45**H**), 1.37–1.22 (m, 6H). **^{13}C-NMR (126 MHz, $CDCl_3$)** *(mixture of syn/anti isomers)* δ 171.3, 170.4, 168.5, 168.0, 133.9, 133.4, 132.3, 132.0, 128.8, 128.7, 127.4, 127.3, 69.5, 68.5, 62.3, 62.0, 59.1, 57.8, 20.3, 18.8, 14.3. **HRMS ESI [M+H]$^+$** calculated for $C_{13}H_{17}NNaO_4^+$ 274.1050, found 274.1050. **Chiral HPLC** (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:10, 40 °C, flow rate: 1.5 mL/min, λ =249 nm): Retention time = 5.1 min (2*S*,3*R*-**32**: 42.0%), 6.0 min (2*R*,3*S*-**32**: 2.0%), 7.1 min (2*S*,3*S*-**32**: 54.0%), 8.3 min (2*S*,3*S*-**32**: 2.0%).

Chromatogram of (2*S*)-**32**



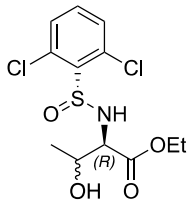
Entry	Retention time (min)	Area	Area (%)
1	5.149	8215791	41.954
2	6.001	399553	2.040
3	7.064	10579302	54.023
4	8.312	388397	1.983
Total		19583043	100

5.3.3. Asymmetric synthesis of ethyl (2*R*)-2-benzamido-3-hydroxybutanoate ((2*R*)-**32**)



Ethyl (2*R*)-2-(((*R*)-(2,6-dichlorophenyl)sulfinyl)amino)-3-hydroxybutanoate ((2*R*)-**2k**)

The reaction was conducted following the **General Procedure** using (*R*)-**1k** (58.9 mg, 0.2 mmol) and ethanol (**a1**, 35 μL, 0.6 mmol, 3 equiv.). The crude mixture was purified by flash column chromatography on silica-gel (hexanes/EtOAc 80:20 to 50:50) to yield the title compound (2*R*)-**2k** (54.9 mg, 81% yield, *syn*/*anti* ratio = 1:1.3) as an off-white solid.



(2*R*)-**2k**. Mixture of *syn*/*anti* isomers ((2*R*,3*S*)-**2k** + (2*R*,3*R*)-**2k**); *syn*/*anti* = 1:1.3.

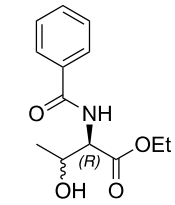
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.40–7.37 (m, 2H), 7.34–7.31 (m, 1H), 6.12 (d, *J* = 7.4 Hz, 0.52H, N**H**), 6.05 (d, *J* = 7.4 Hz, 0.45H, N**H**), 4.29–4.13 (m, 3.56H), 3.96 (q, *J* = 3.7 Hz, 0.54H), 2.38 (d, *J* = 7.2 Hz, 0.45H, O**H**), 2.22 (d, *J* = 6.0 Hz, 0.52H, O**H**), 1.32–1.26 (m, 6H), 1.17 (d, J = 6.0 Hz, 1.4H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.0, 170.5, 140.0, 139.7, 133.8, 133.7, 132.3, 130.4, 130.3, 68.8, 68.6, 63.2, 63.1, 62.4, 62.3, 19.9, 18.7, 14.2.

HRMS ESI [M+H]$^+$ calculated for $C_{12}H_{15}Cl_2NNaO_4S^+$: 361.9991, found 361.9990.

Ethyl (2*R*)-2-benzamido-3-hydroxybutanoate ((2*R*)-32)

Method F: (*R*)-**2k** (30.3 mg, 89 μmol) furnished the desired compound (2*R*)-**32** (18.3 mg, 86% yield, *syn*/*anti* ratio = 1:1.3) as a colorless oil.



(2*R*)-**32**. Mixture of *syn*/*anti* isomers ((2*R*,3*S*)-**32** + (2*R*,3*R*)-**32**); *syn*/*anti* = 1:1.3.

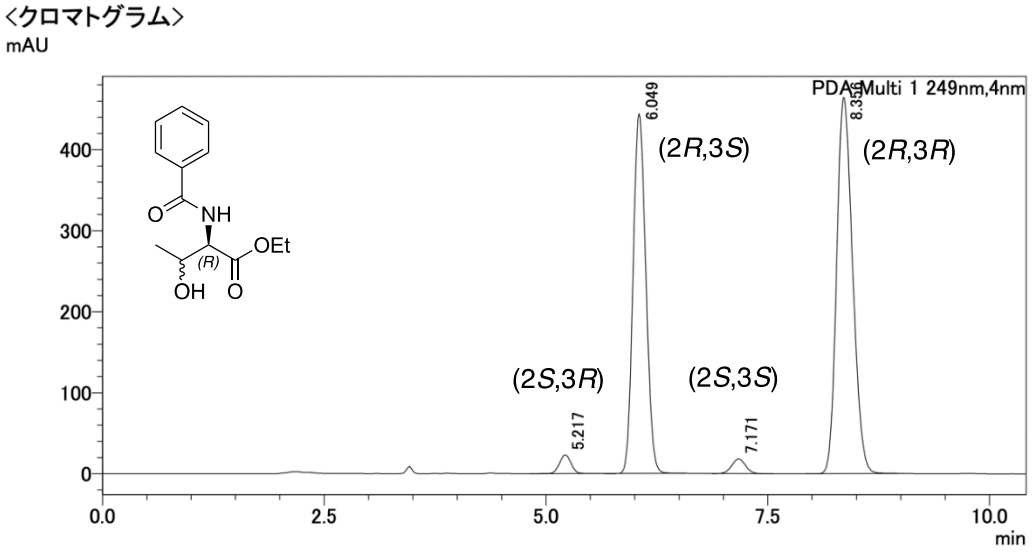
^{1}H-NMR (500 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 7.85–7.83 (m, 2H), 7.56–7.51 (m, 1H), 7.48–7.43 (m, 2H), 7.18 (d, *J* = 6.3 Hz, 0.55H, N**H**), 6.98 (d, *J* = 8.6 Hz, 0.45H, N**H**), 4.87 (dd, *J* = 7.0, 3.5 Hz, 0.55H, αC**H**), 4.81 (dd, *J* = 8.7, 2.4 Hz, 0.45H, αC**H**), 4.47–4.43 (m, 0.45H, βC**H**), 4.34–4.23 (m, 2.55H), 3.73 (br s, 0.55H, O**H**), 2.48 (br s, 0.45**H**), 1.37–1.22 (m, 4.6H).

^{13}C-NMR (126 MHz, $CDCl_3$) *(mixture of syn/anti isomers)* δ 171.3, 170.4, 168.5, 168.0, 133.9, 133.4, 132.3, 132.0, 128.8, 128.7, 127.4, 127.3, 77.4, 77.2, 76.9, 69.5, 68.5, 62.3, 62.0, 59.1, 57.8, 20.3, 18.8, 14.3.

HRMS ESI [M+H]$^+$ calculated for $C_{13}H_{17}NNaO_4^+$ 274.1050, found 274.1049.

Chiral HPLC (DAICEL CHIRALPAK IC-3, ϕ 4.6 mm x 250 mm. Isocratic: Hexanes/*i*PrOH 80:10, 40 °C, flow rate: 1.5 mL/min, λ =249 nm): Retention time = 5.2 min (2*S*,3*R*-**32**: 2.0%), 6.0 min (2*R*,3*S*-**32**: 41.7%), 7.2 min (2*S*,3*S*-**32**: 1.8%), 8.4 min (2*S*,3*S*-**32**: 54.5%).

Chromatogram of (2*R*)-**32**



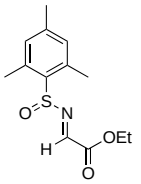
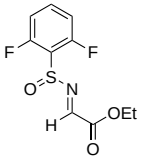
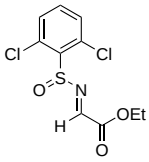
Entry	Retention time (min)	Area	Area (%)
1	5.217	211583	1.985
2	6.049	4439707	41.660
3	7.171	197257	1.851
4	8.356	5808483	54.504
Total		10657030	100

6. Mechanistic Studies

6.1. Cyclic Voltammetry

The redox potentials of *N*-sulfinyl α-iminoesters were measured by cyclic voltammetry using an electrochemical analyzer ALS model 760D (BAS Inc.) with a Ag/Ag^+ reference electrode, a platinum counter electrode, and a glassy carbon disk working electrode. For each sample, $^nBu_4NPF_6$ (195 mg, 0.5 mmol), analyte (0.01 mmol), and degassed MeCN (5 mL) were placed in a cell, and the solution was purged with argon for 5 min before the measurement. Voltammograms were taken at r.t. with the scan rate set to 100 mV/s. Ferrocene was added to the solution as an internal standard at the end of the measurements. The obtained values referenced to Ag/Ag^+ were converted to the SCE couple according to the literature.[30]

Table S9. Summary of redox potentials of *N*-sulfinyl α-iminoesters.

	(±)-1i	(±)-1j	(±)-1k
			
$E_{p/2,c}$ (V vs SCE)	–1.29	–1.17	–1.18

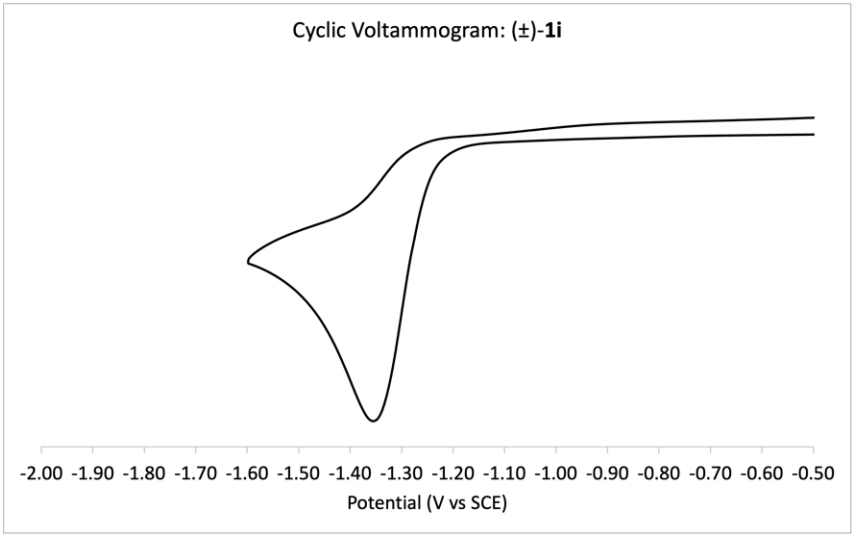


Figure S3. Cyclic voltammogram of (±)-**1i**.

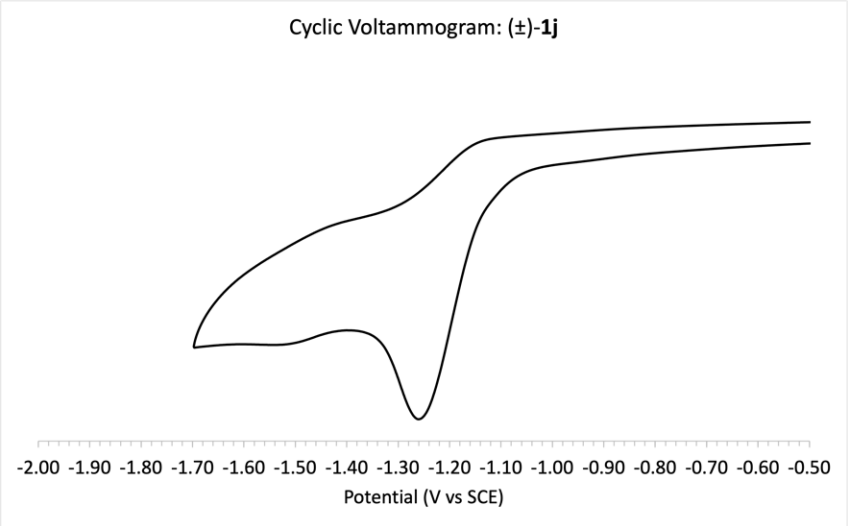


Figure S4. Cyclic voltammogram of (±)-**1j**.

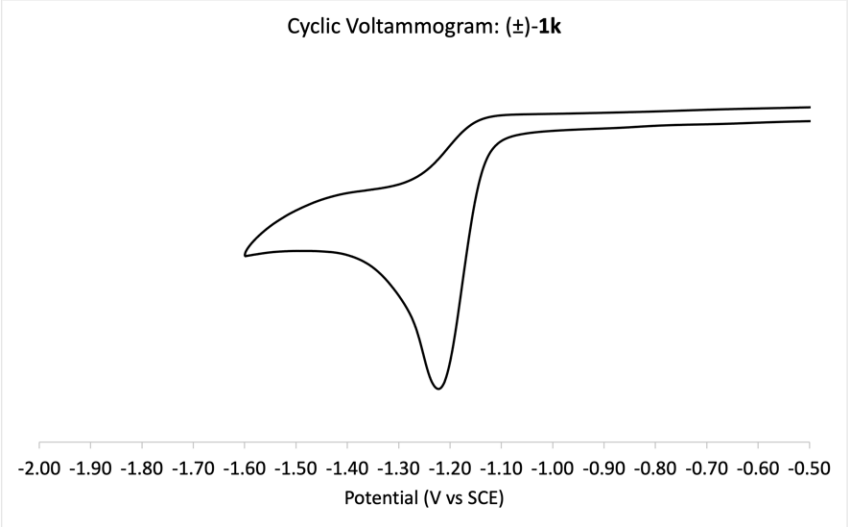


Figure S5. Cyclic voltammogram of (±)-**1k**.

6.2. Fluorescence Quenching Studies

The emission spectra were recorded using a Shimadzu RF-6000 spectrofluorophotometer. All sample solutions were prepared using dry MeCN and measured immediately after bubbling with argon at r.t. For each experiment, a sample solution was prepared by adding 100 μL of a catalyst solution (10 mM in MeCN) and an indicated amount (0, 100, 200, 300, and 500 μL) of quencher solution (**DABCO**$^+$ or *N*-sulfinyl α-iminoester (±)-**1k**, 0.10 M in MeCN) to a 5 mL volumetric flask, followed by addition of dry MeCN to the mark. The solution was then transferred to a 1 cm^2 quartz quvette. The sample solution was excited at 430 nm and the fluorescence intensity was measured at 582 nm.

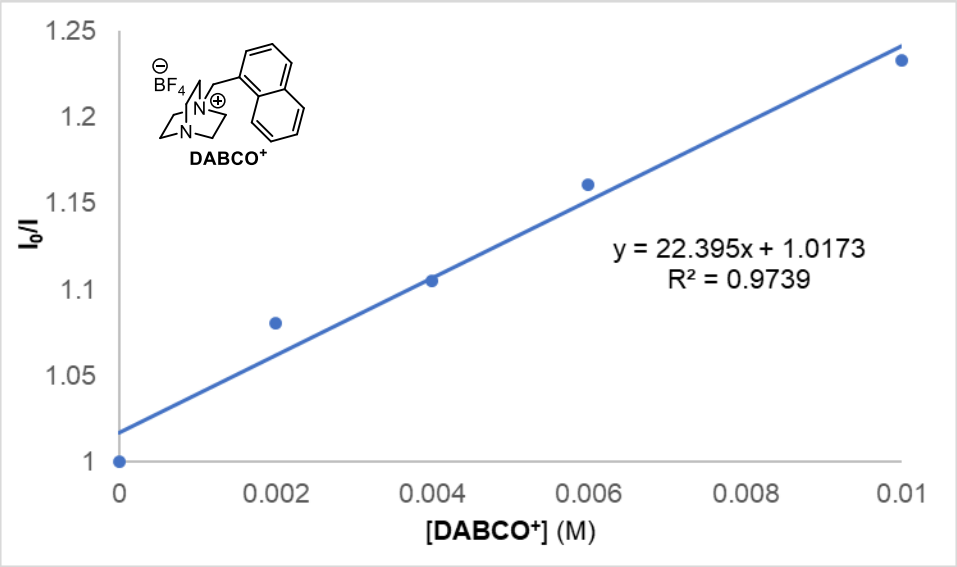


Figure S6. Stern-Volmer Plot with **DABCO**$^+$ as a quencher.

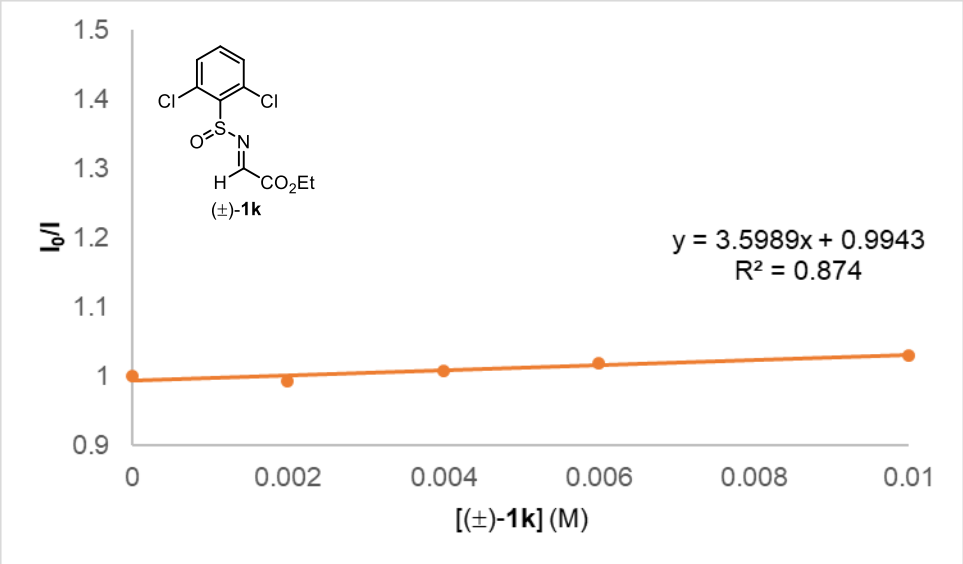


Figure S6. Stern-Volmer Plot with (±)-**1k** as a quencher.

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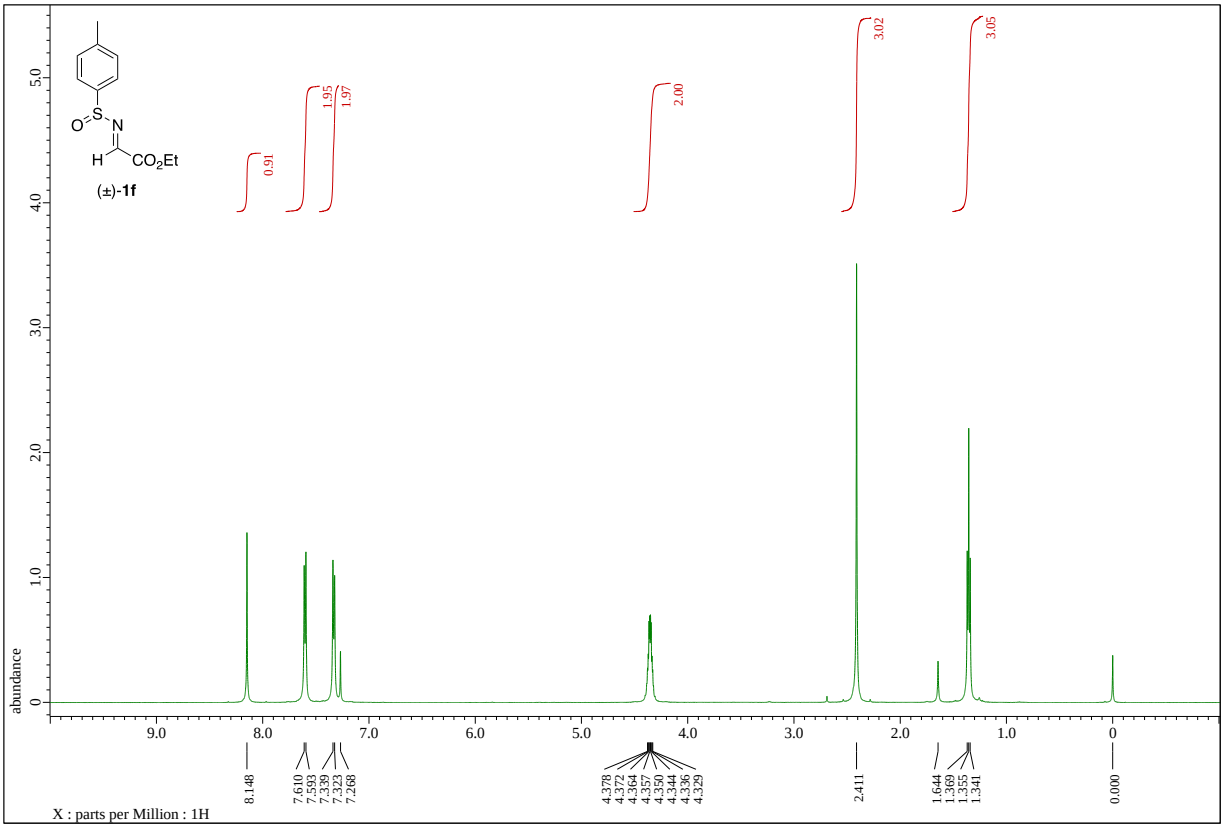
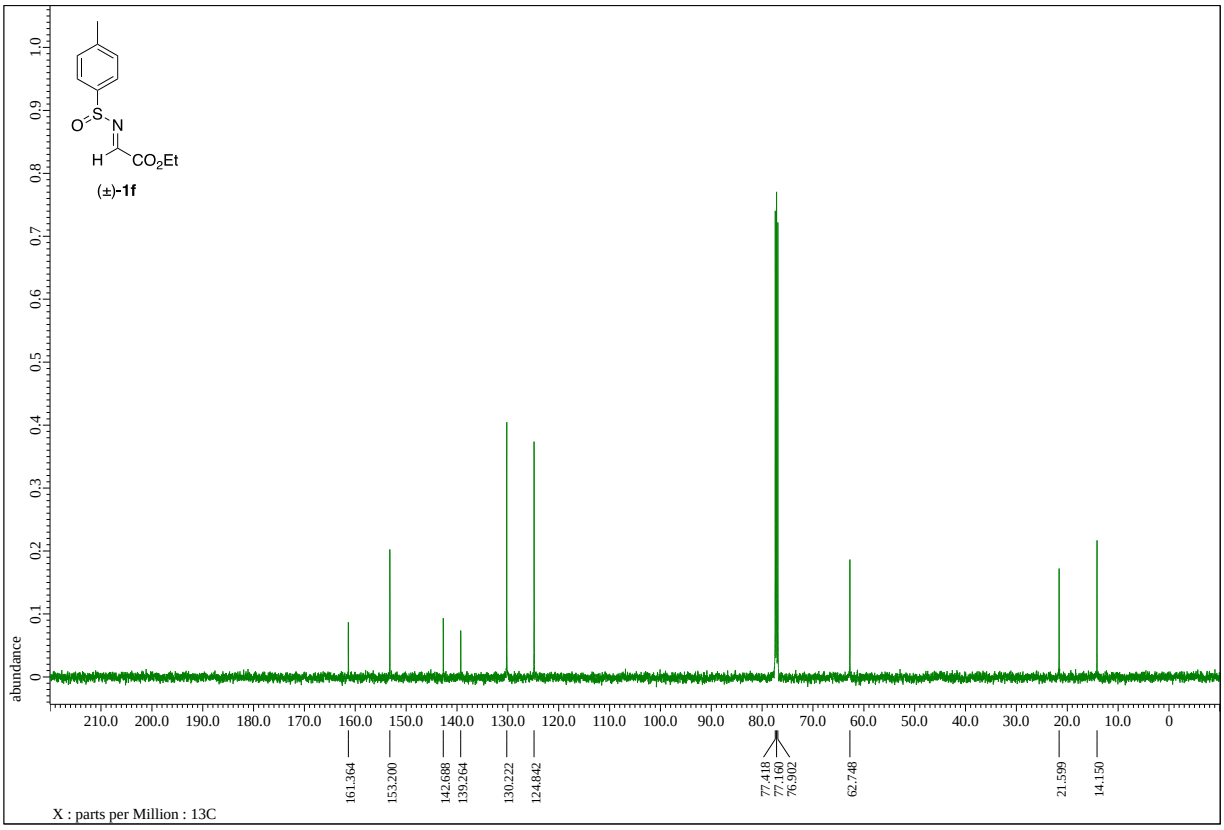
8. Spectral data collection

^{1}H-NMR spectra of (±)-**1f** (500 MHz, $CDCl_3$)



^{13}C-NMR spectra of (±)-**1f** (126 MHz, $CDCl_3$)



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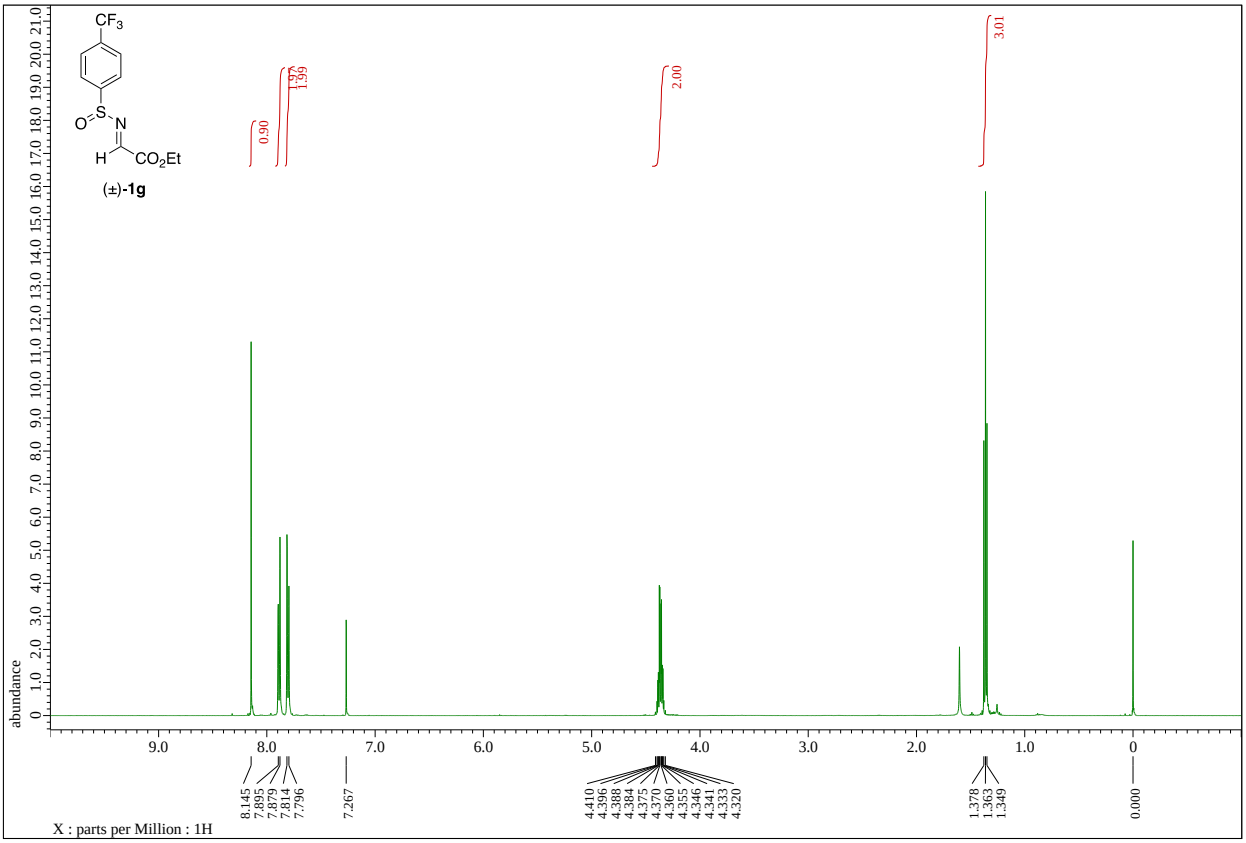

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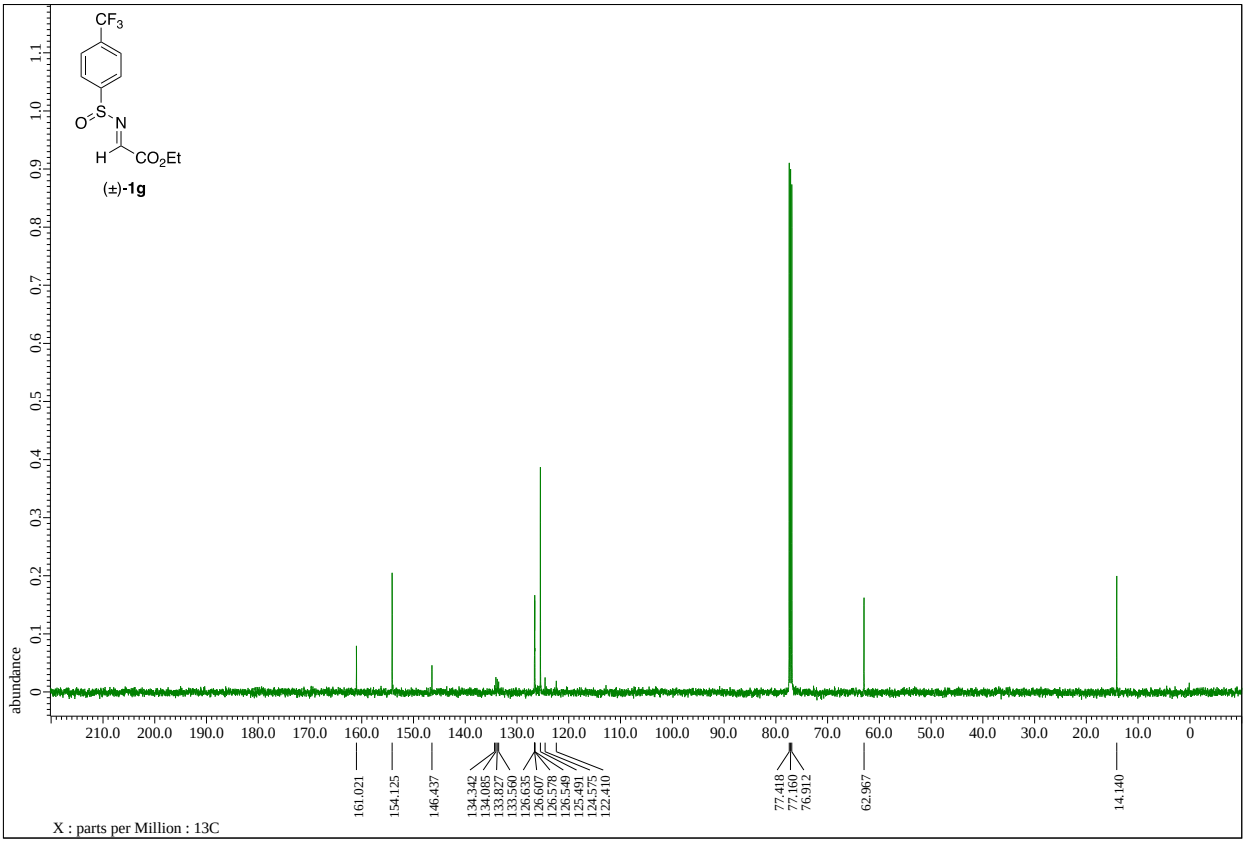
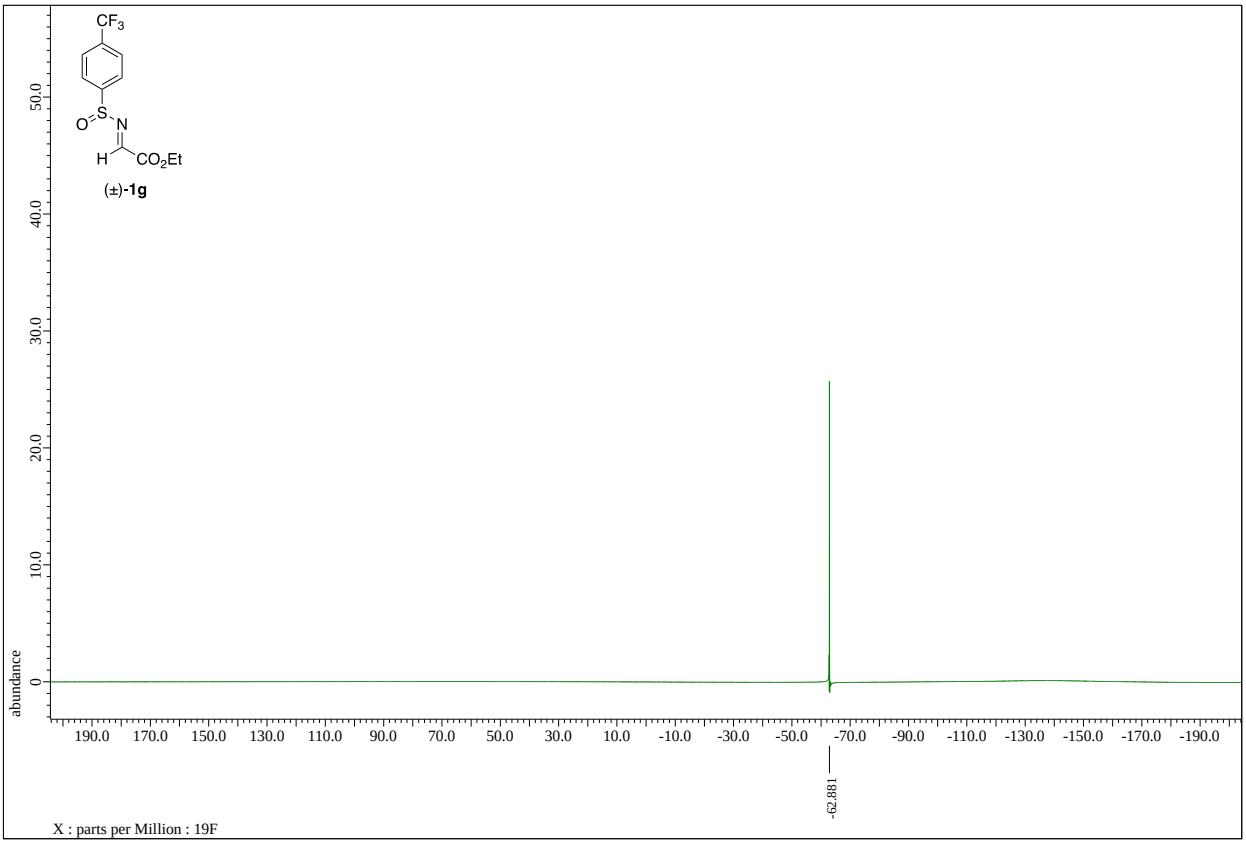


^{19}F-NMR spectra of (±)-**1g** (471 MHz, $CDCl_3$)



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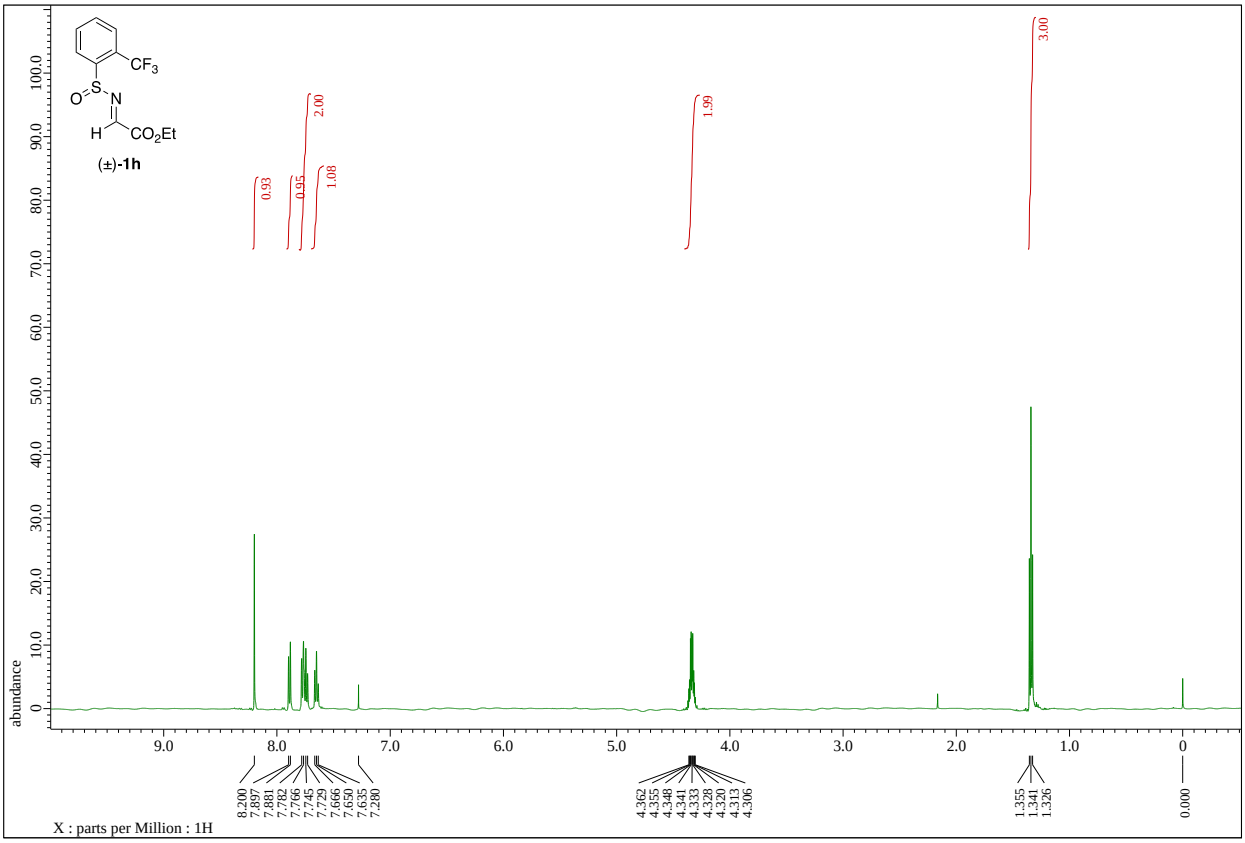

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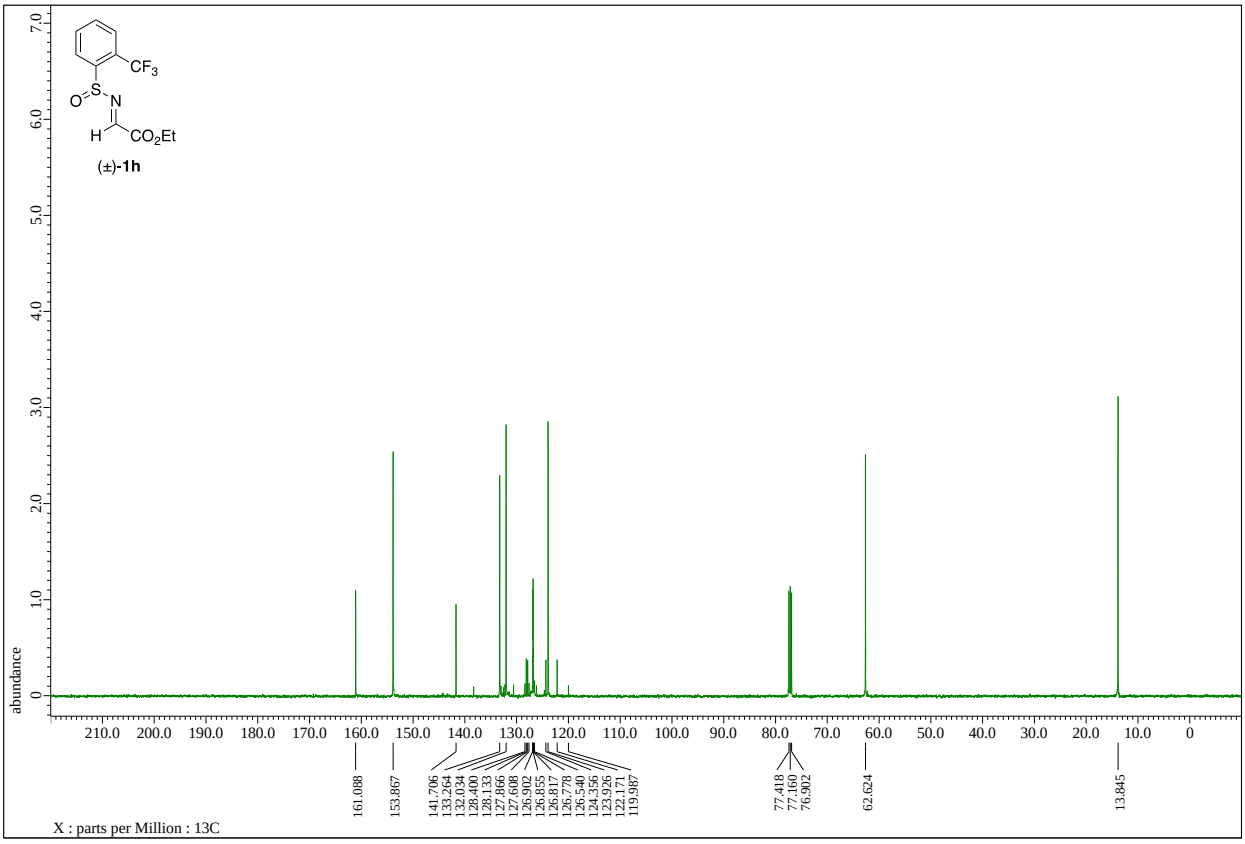

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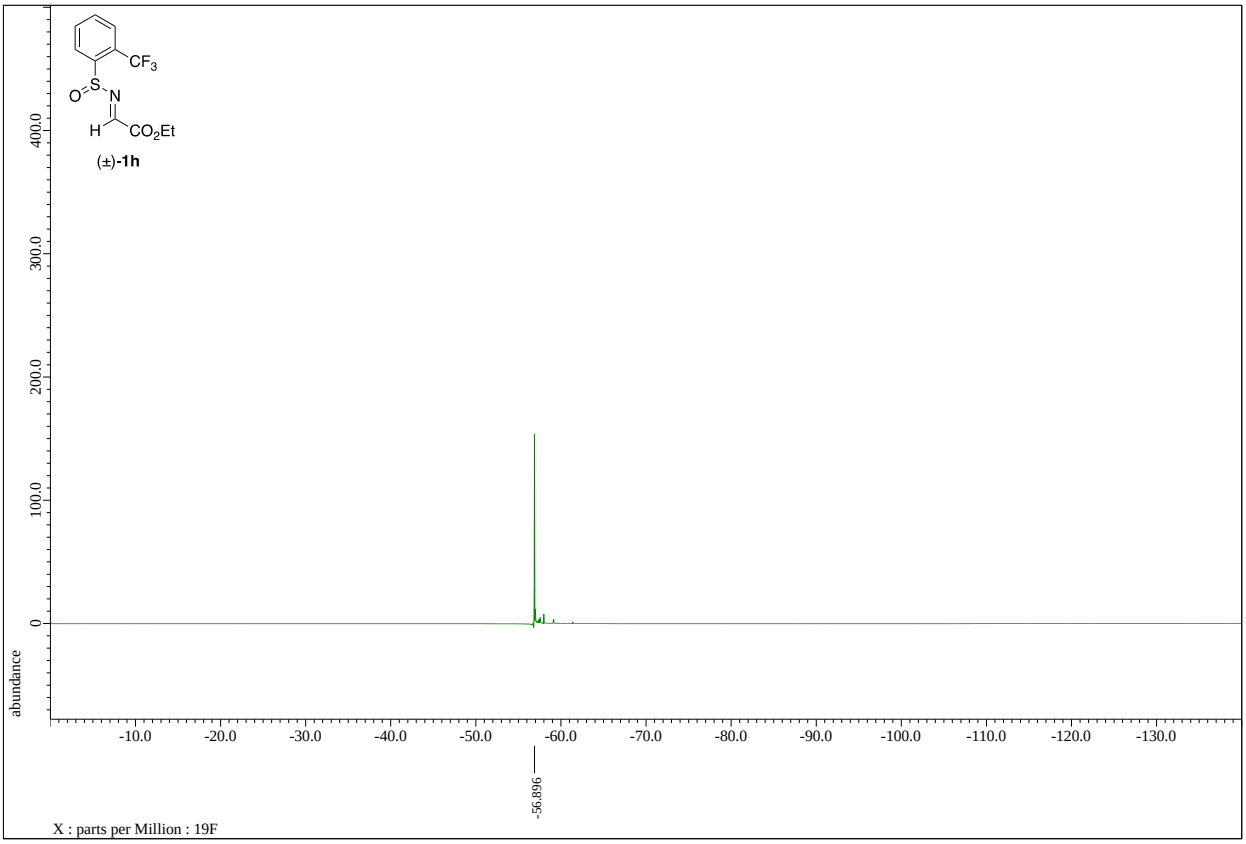
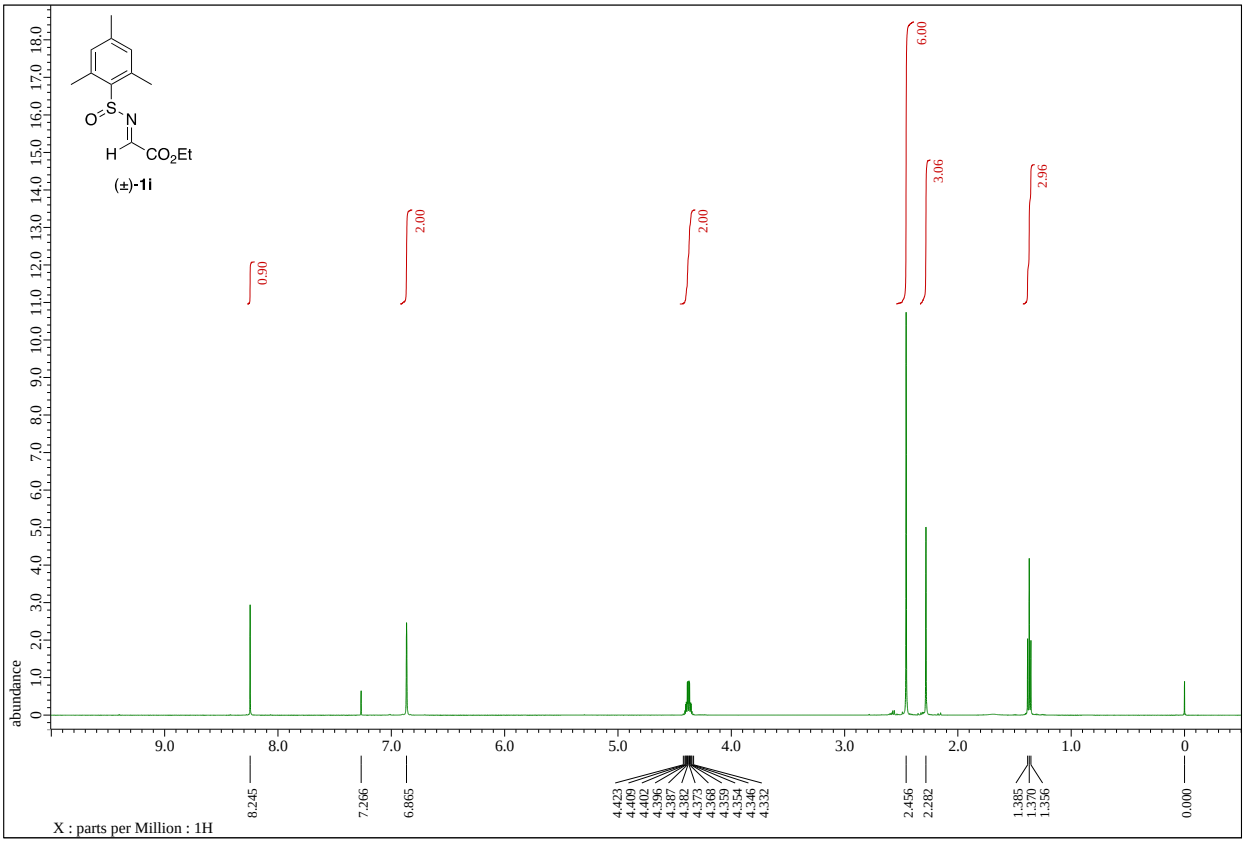


^{1}H-NMR spectra of (±)-**1i** (500 MHz, $CDCl_3$)



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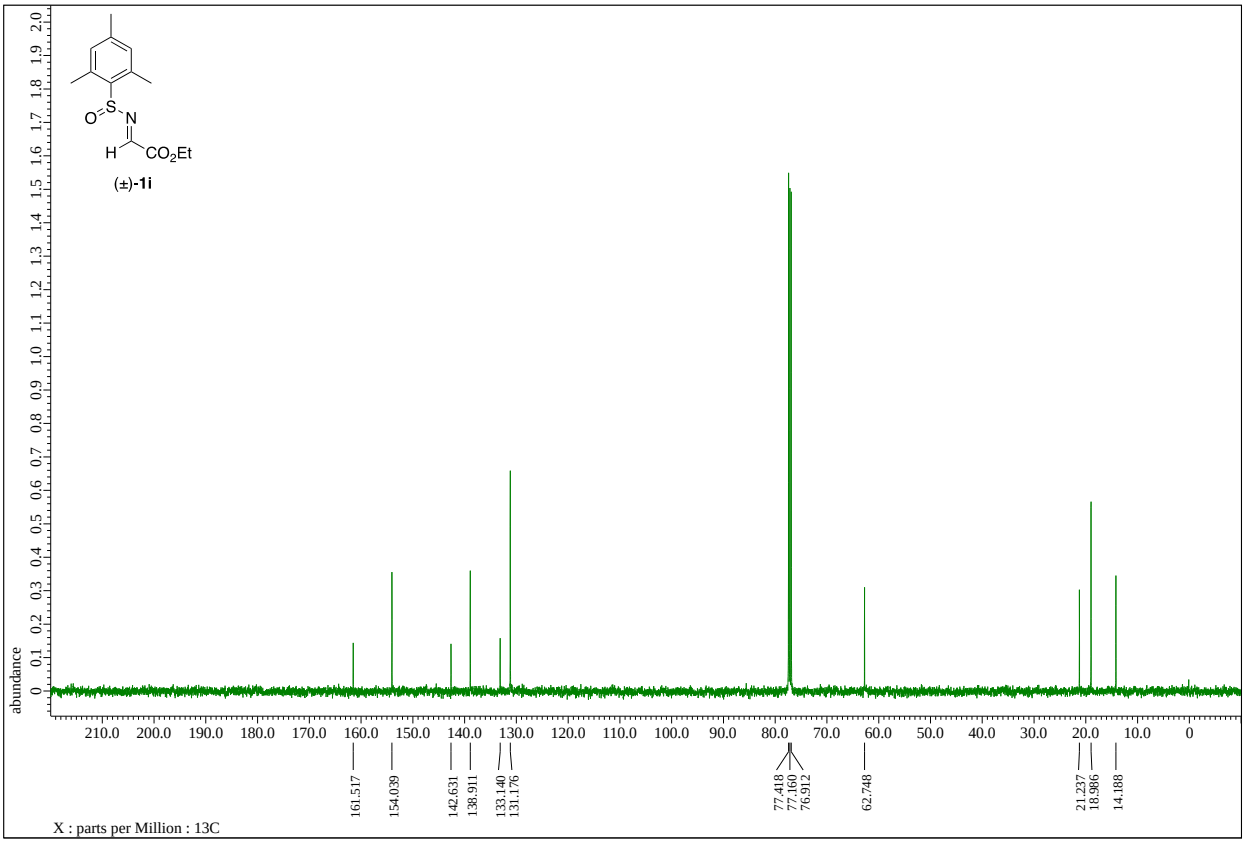

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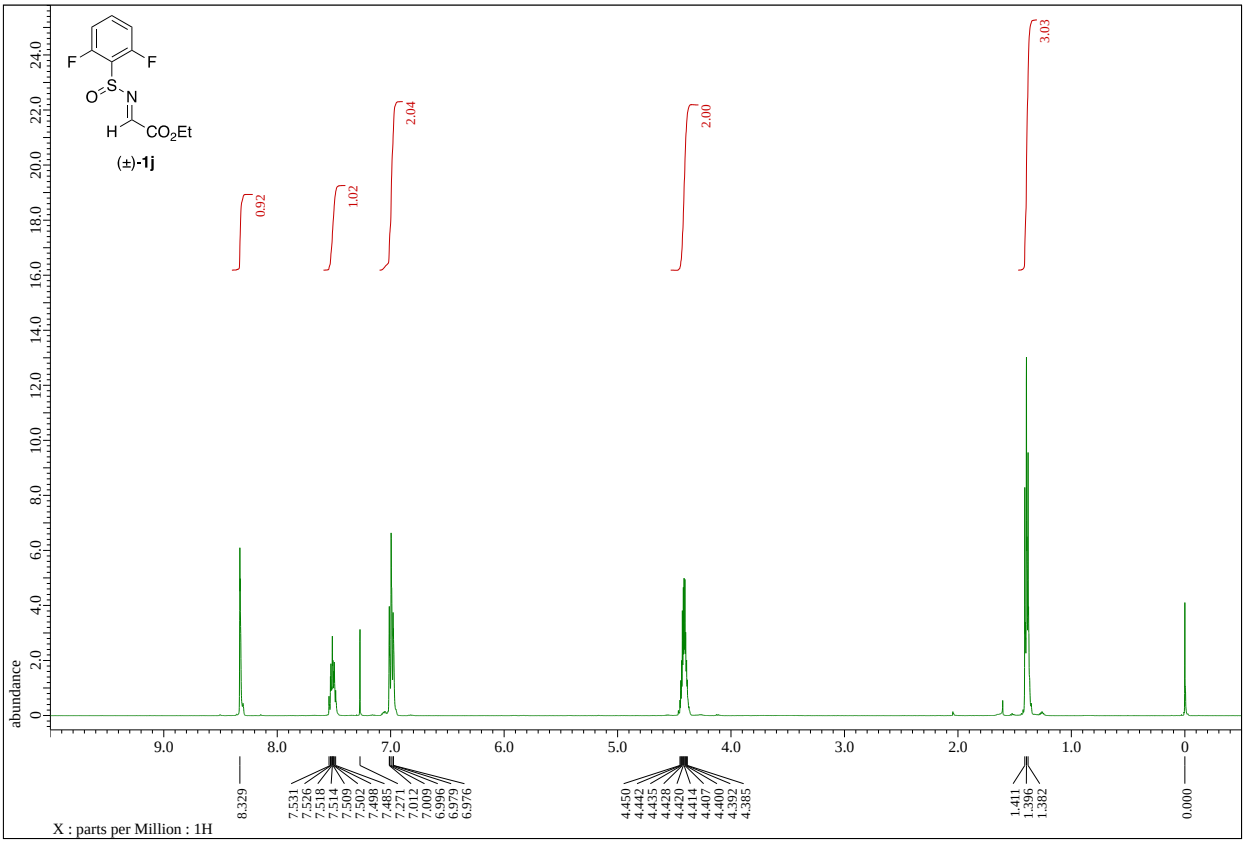

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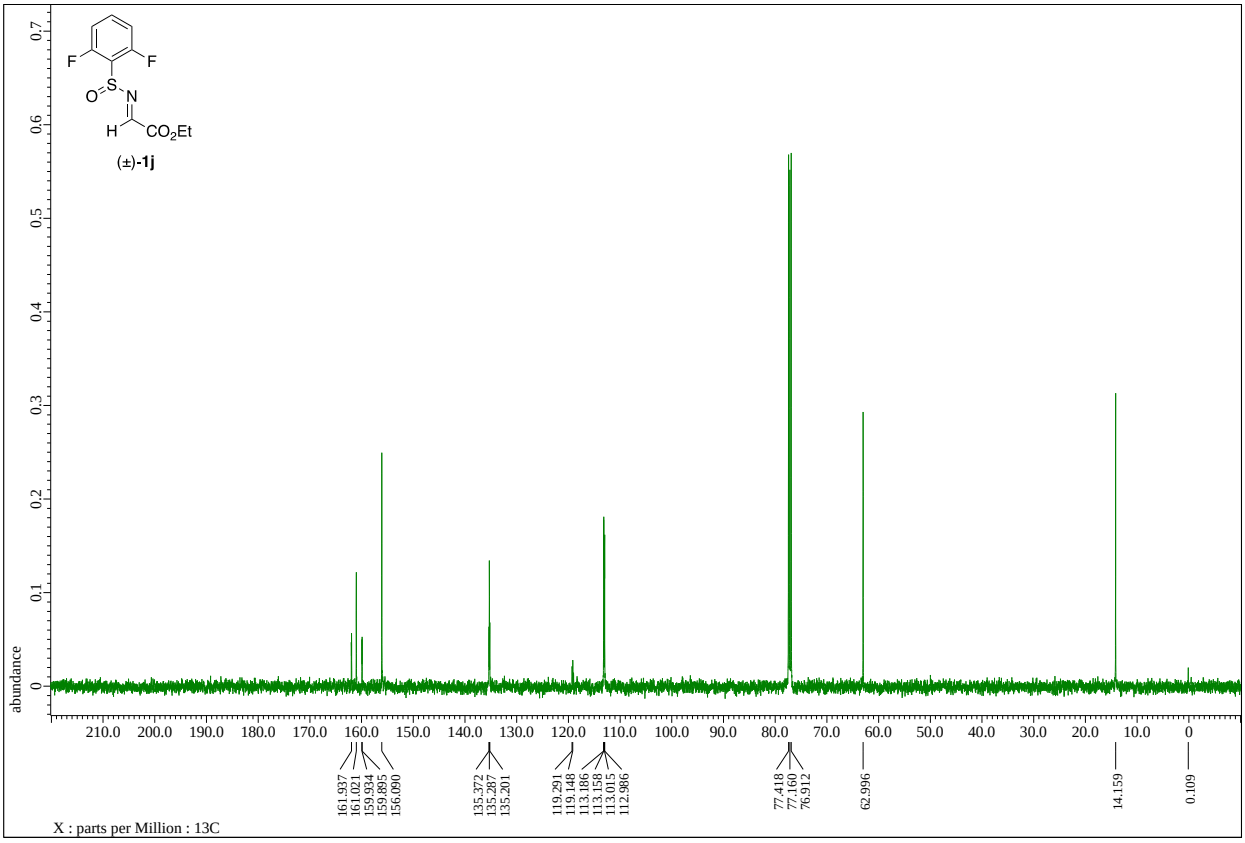

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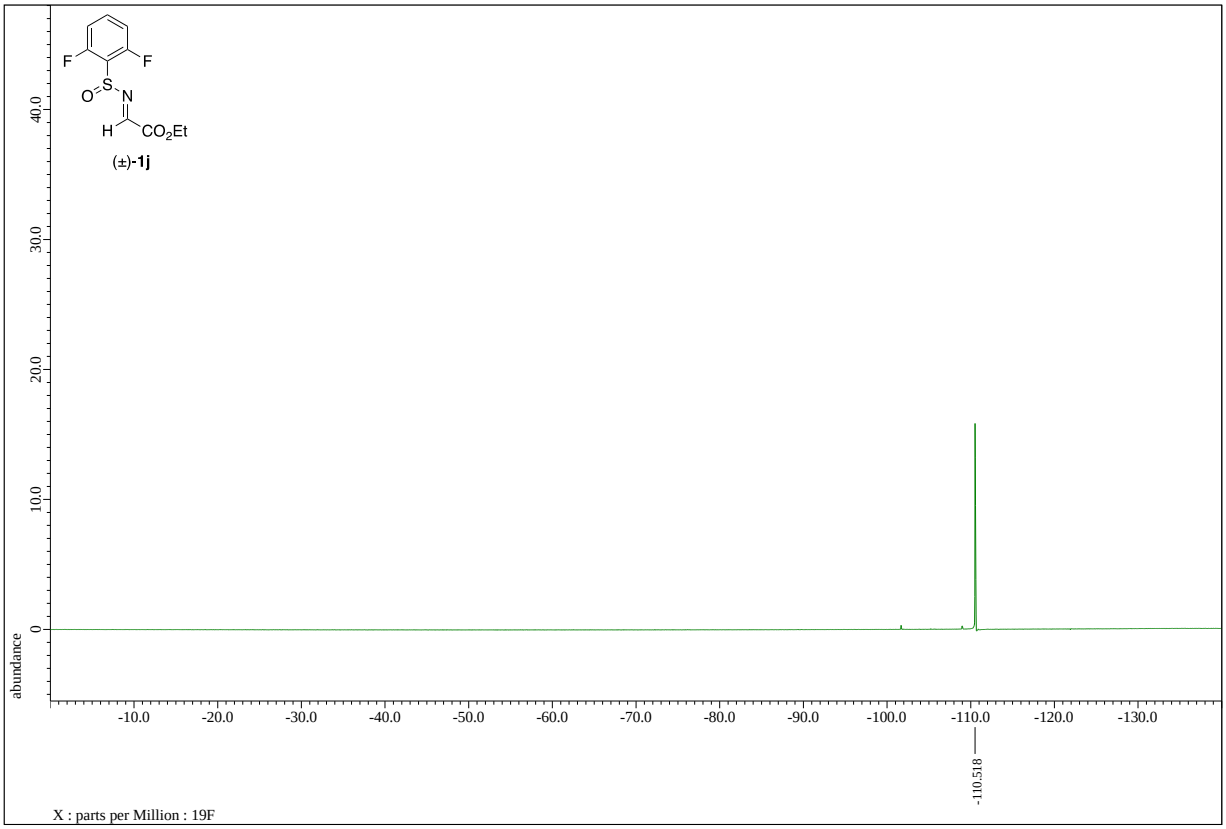
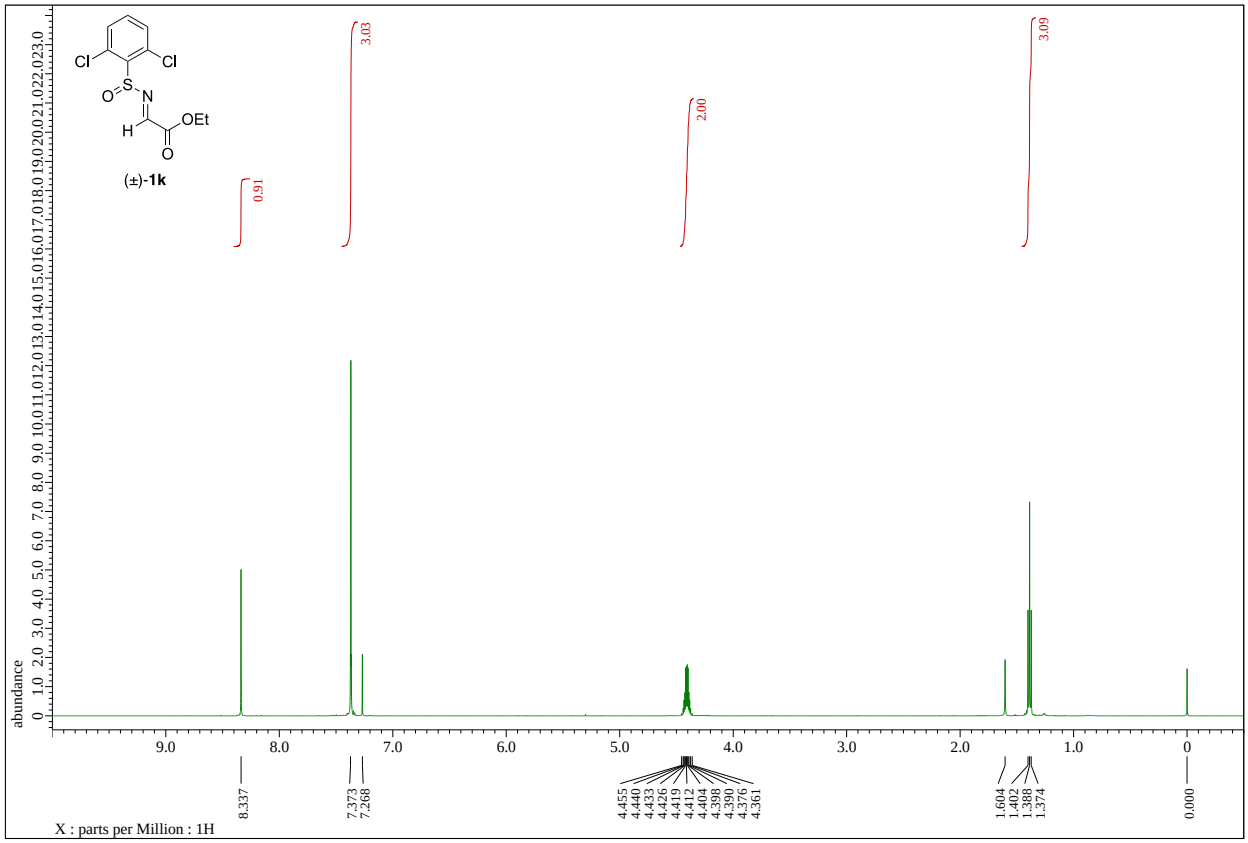


^{1}H-NMR spectra of (±)-**1k** (500 MHz, $CDCl_3$)



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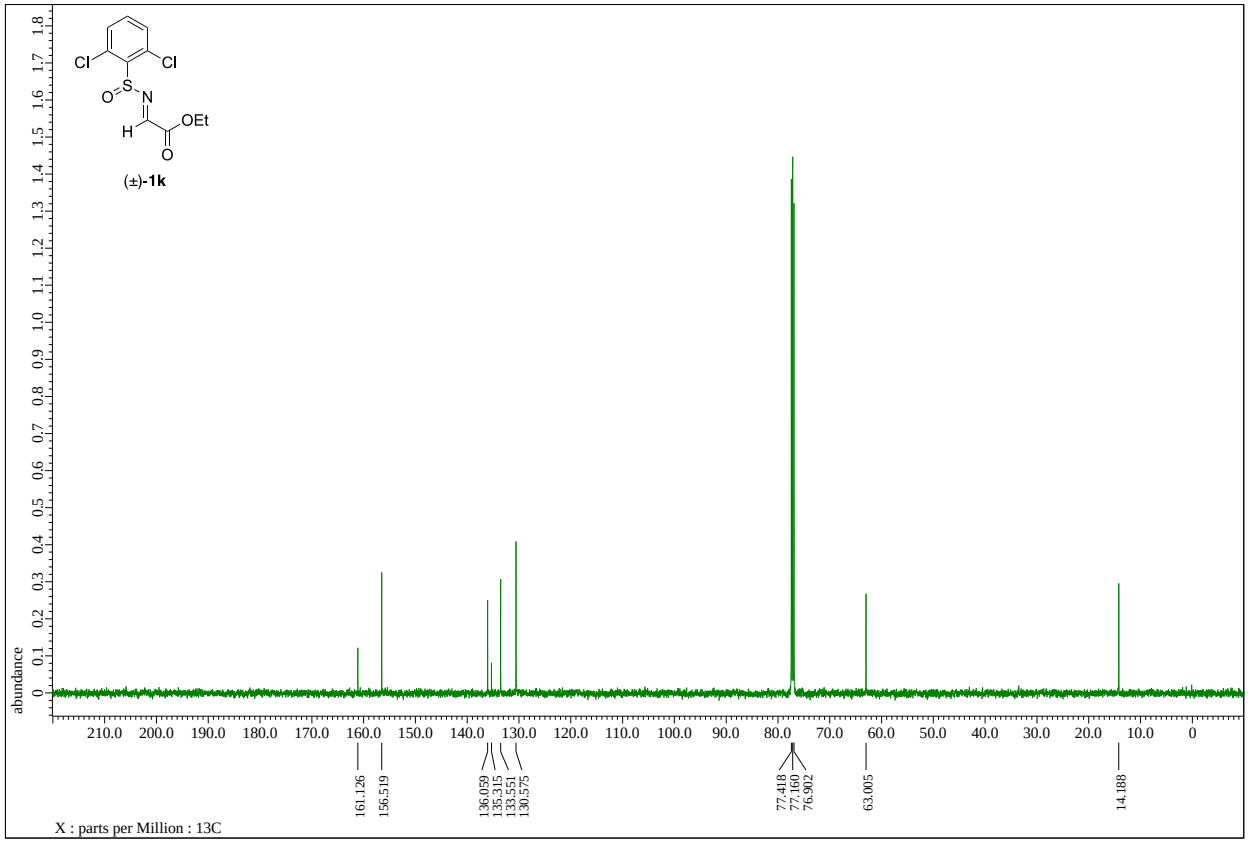

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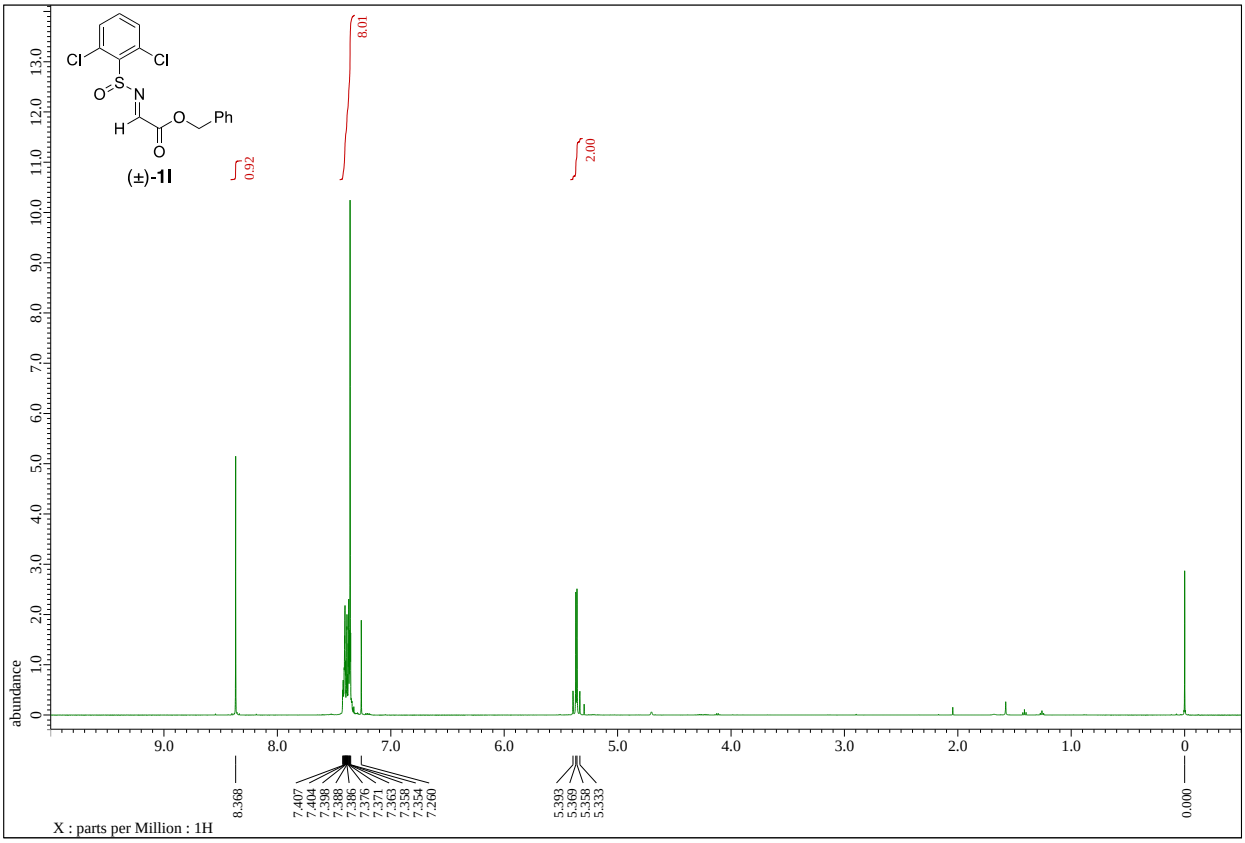

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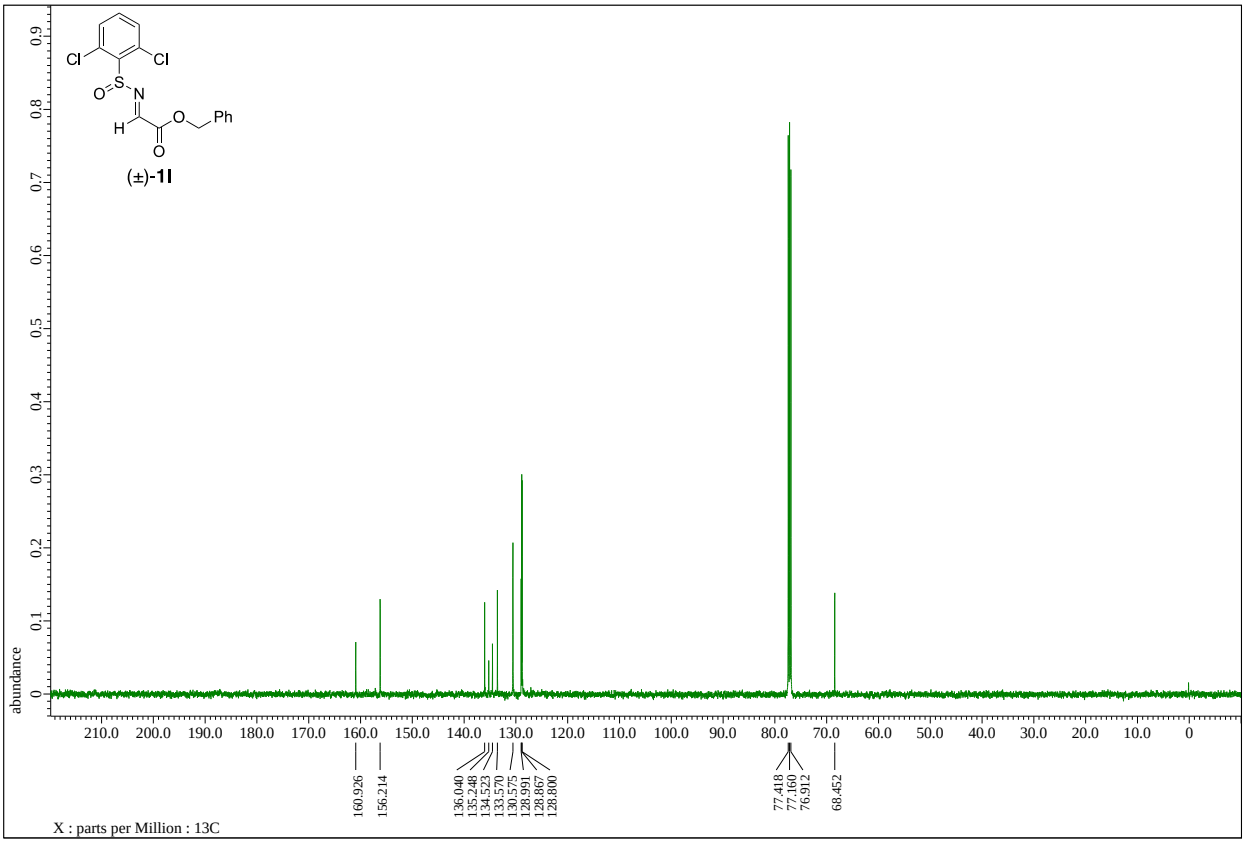
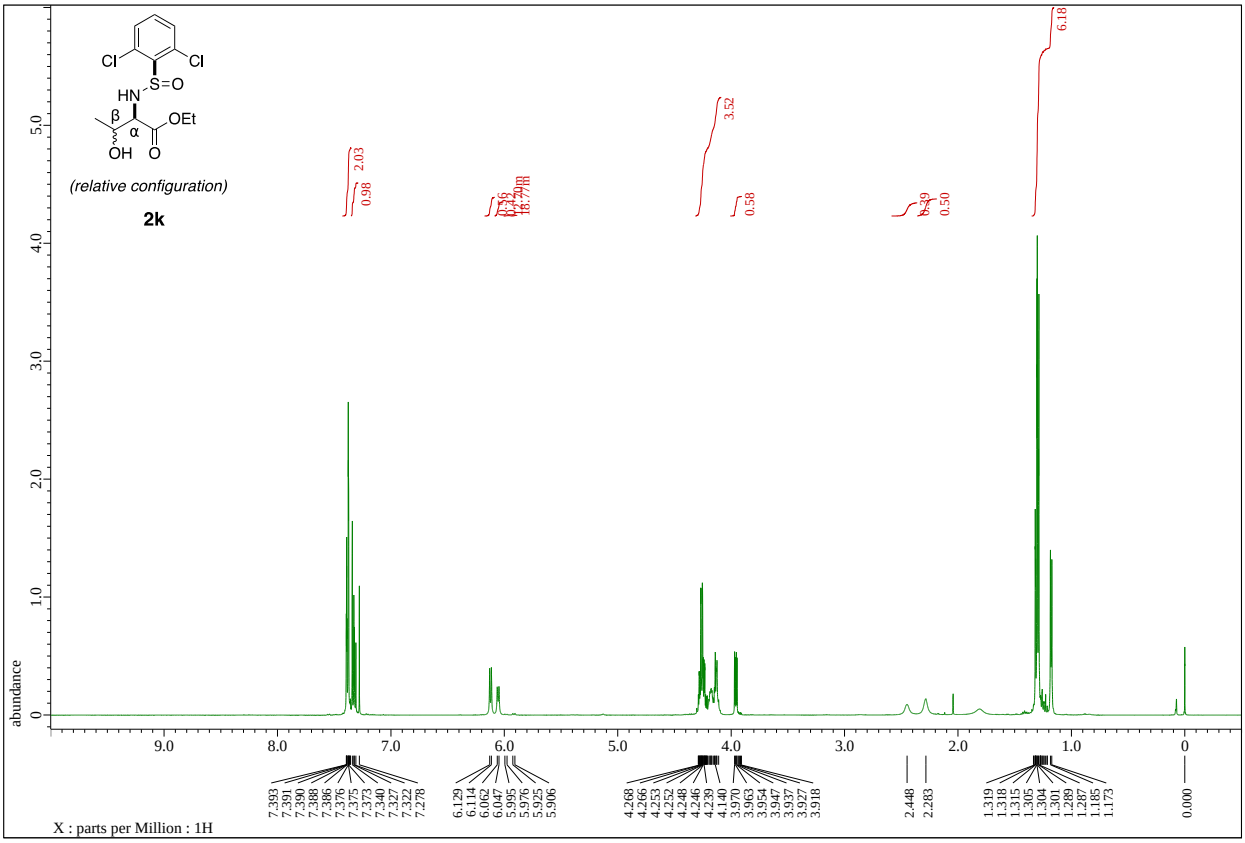


^{1}H-NMR spectra of **2k** (500 MHz, $CDCl_3$)



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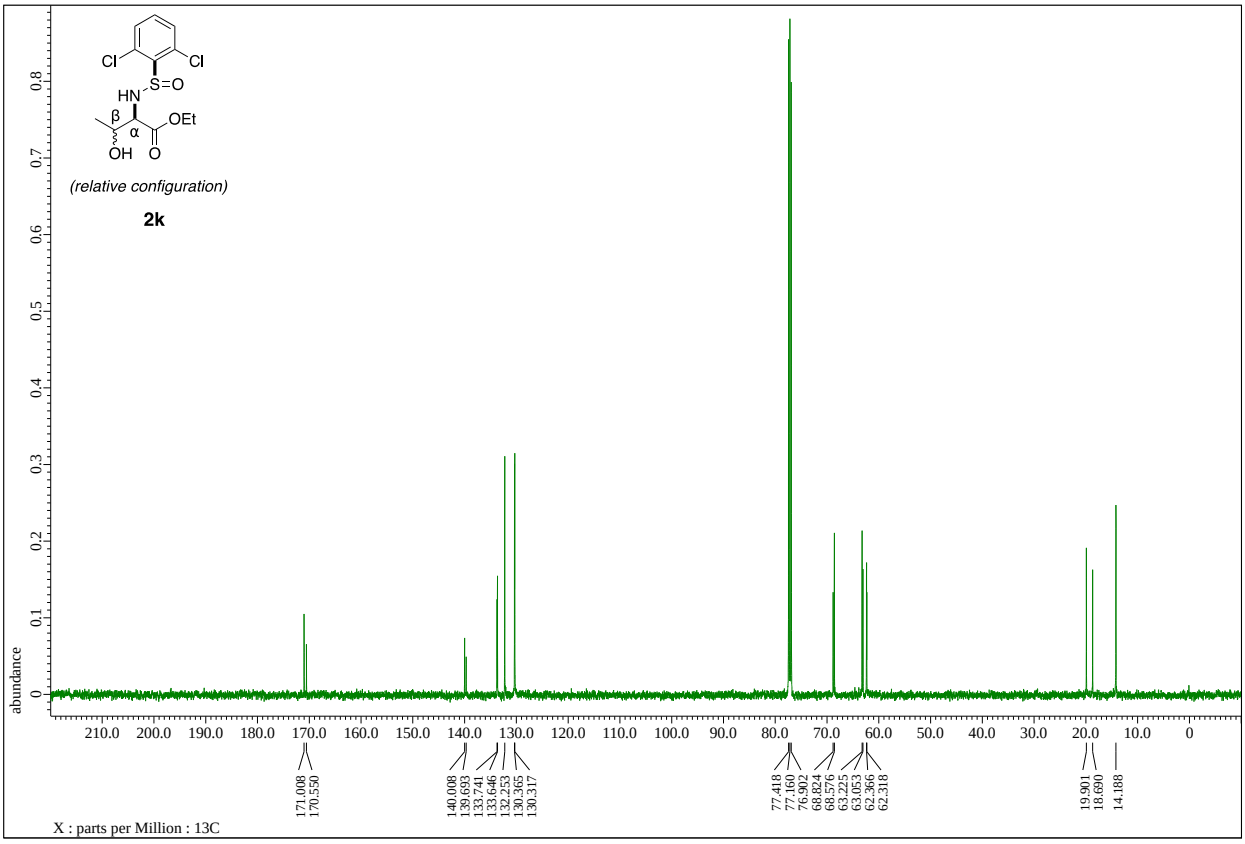

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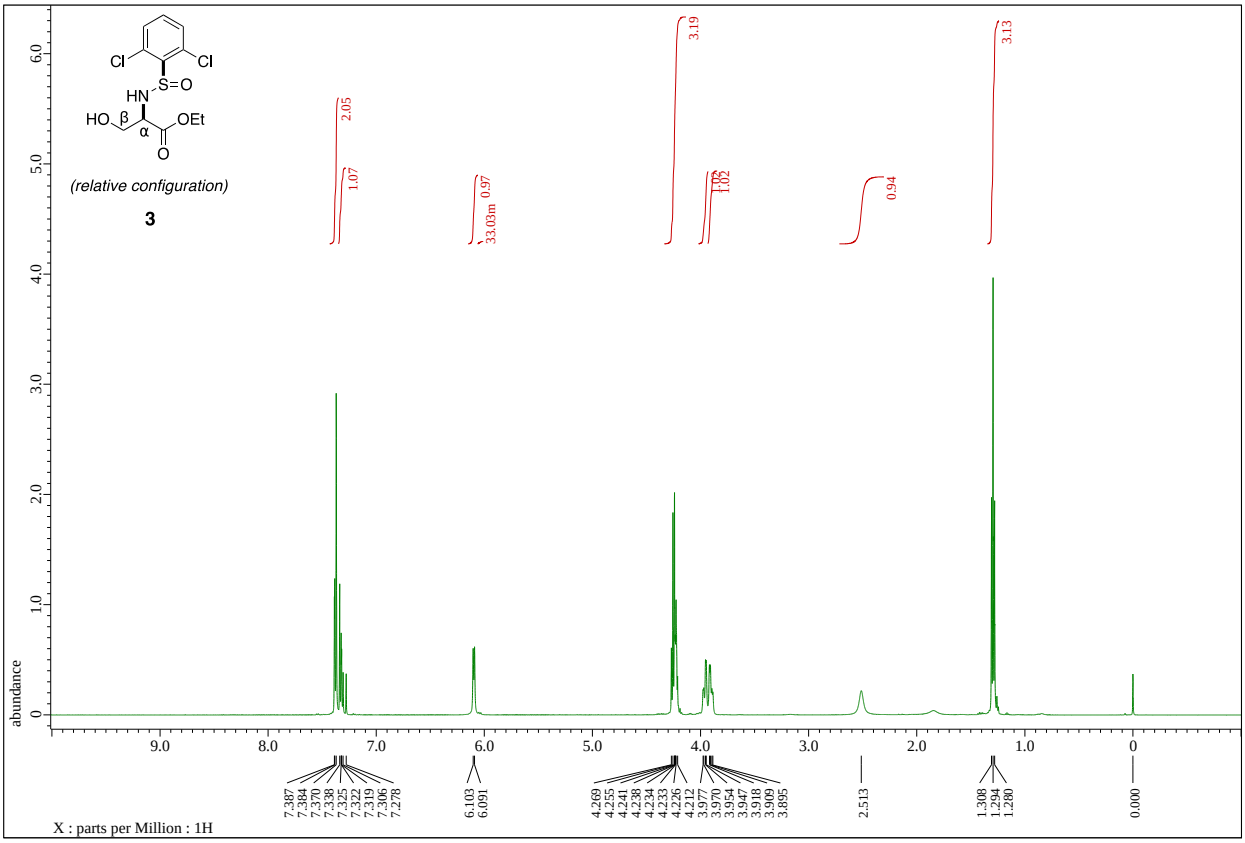
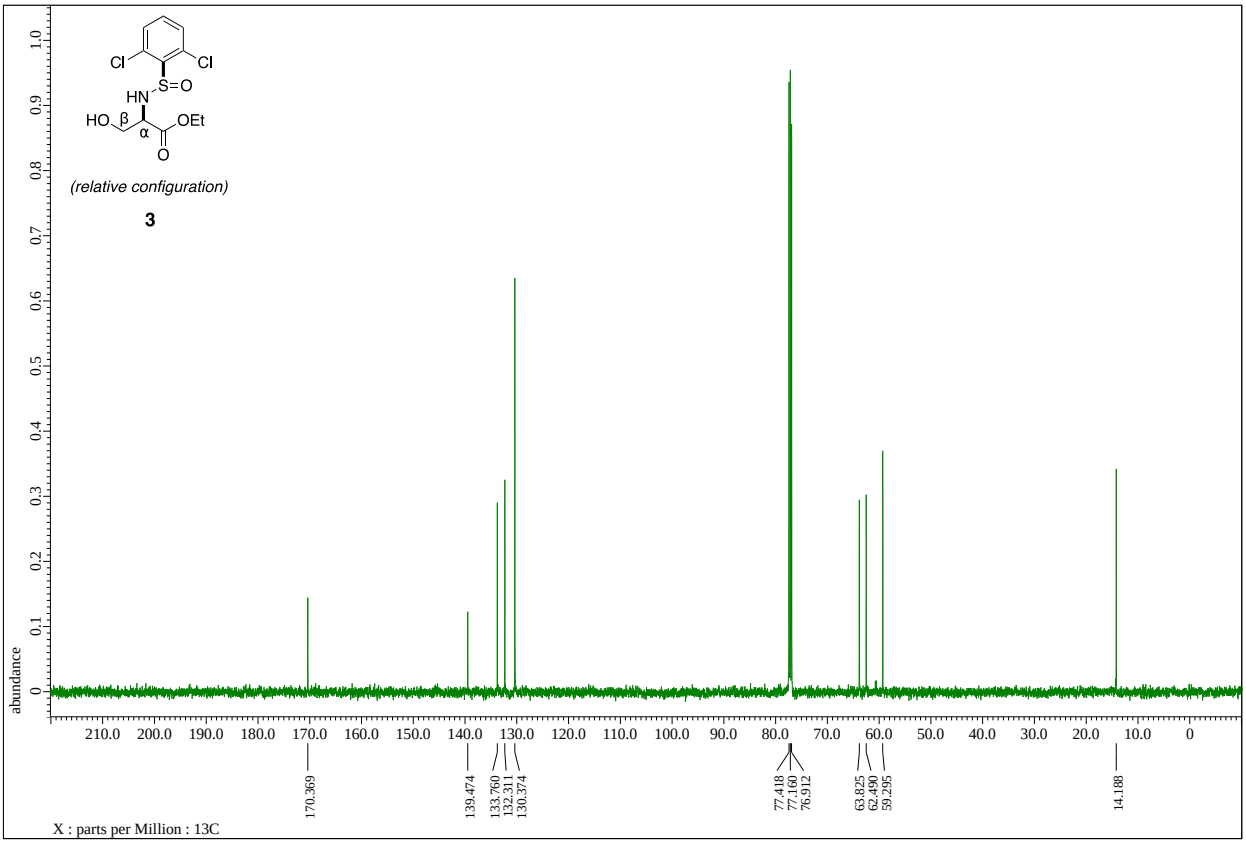
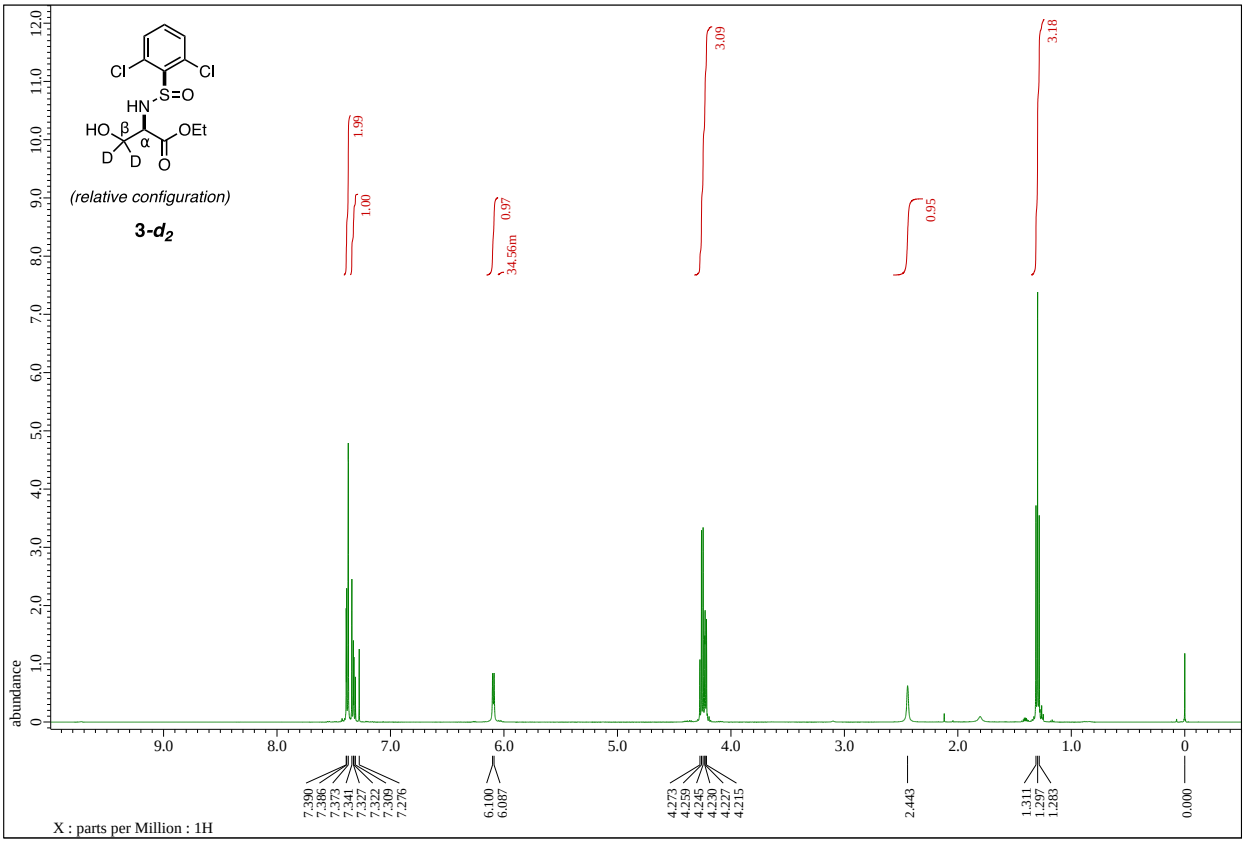


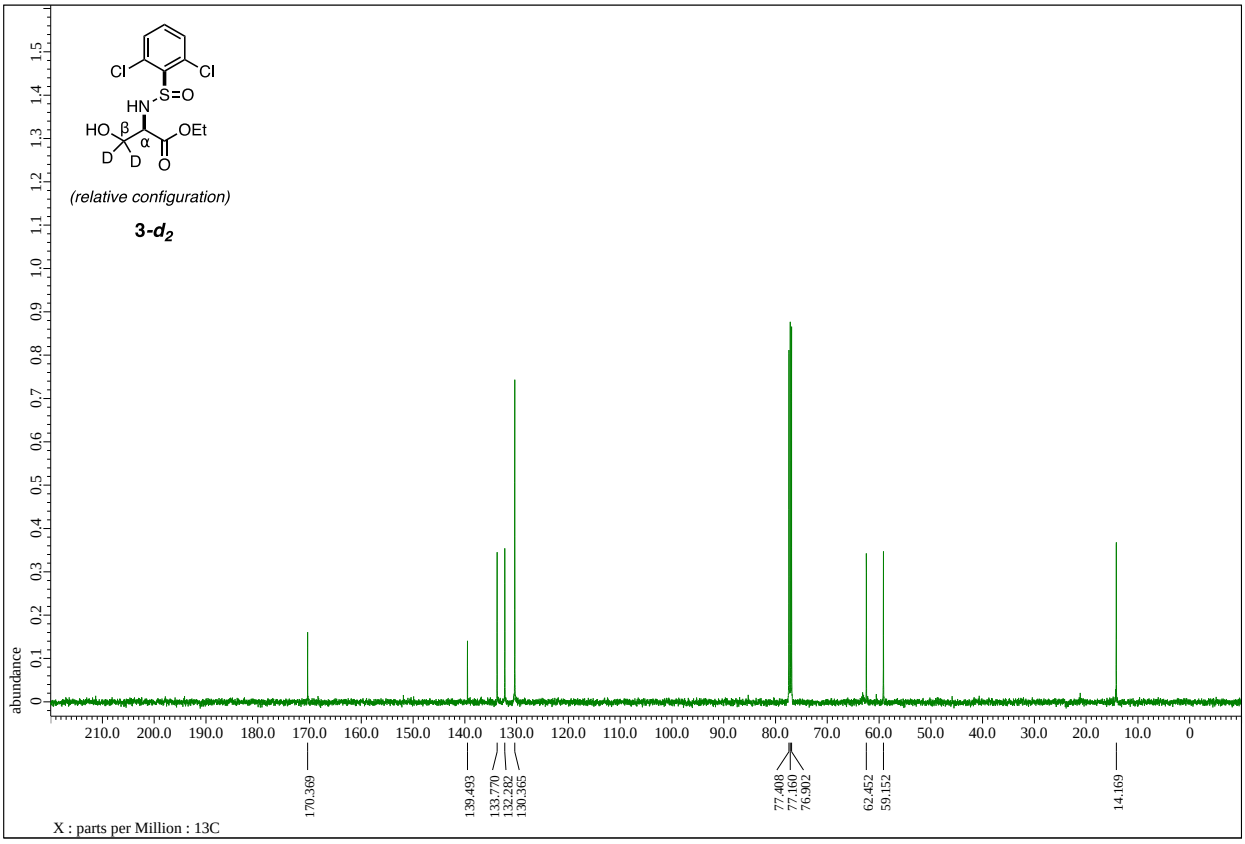
^{13}C-NMR spectra of **3** (126 MHz, $CDCl_3$)



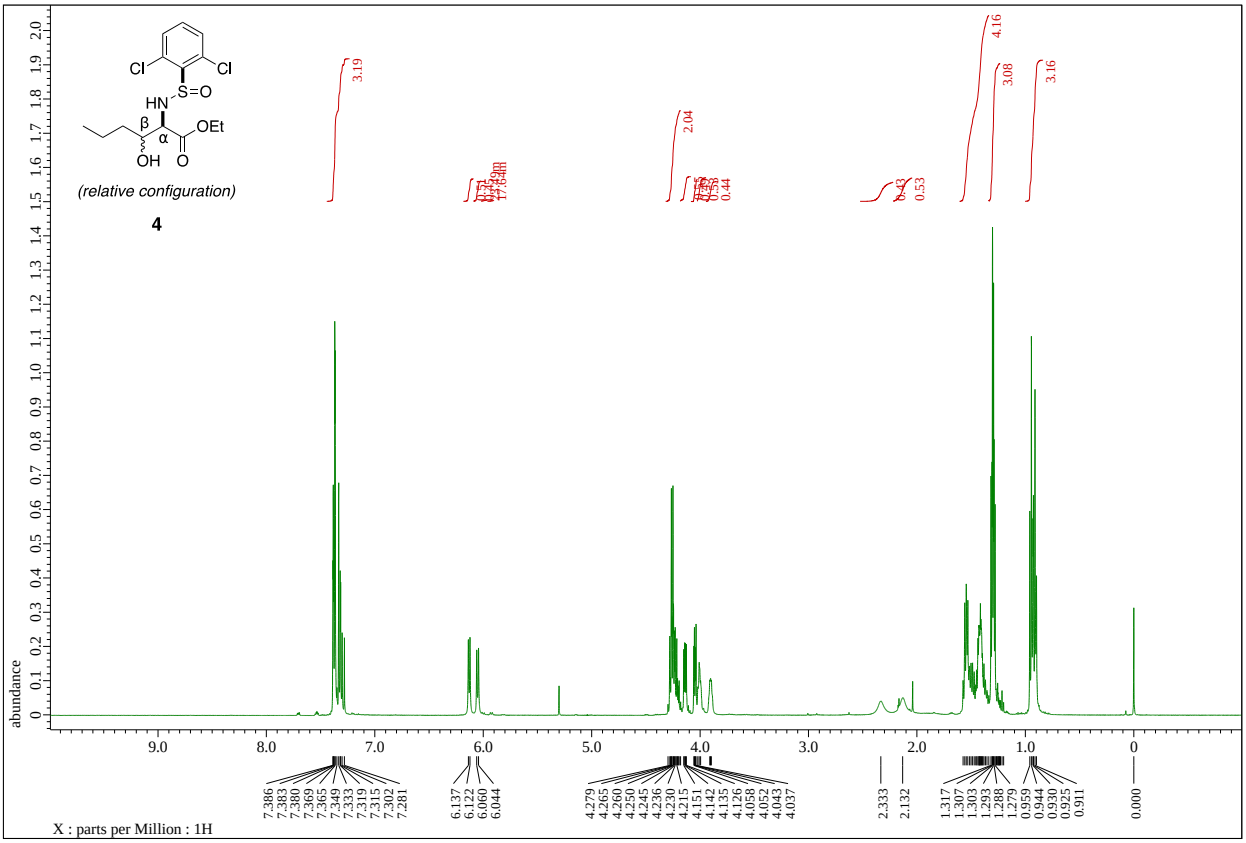
^{1}H-NMR spectra of **3-d$_2$** (500 MHz, $CDCl_3$)



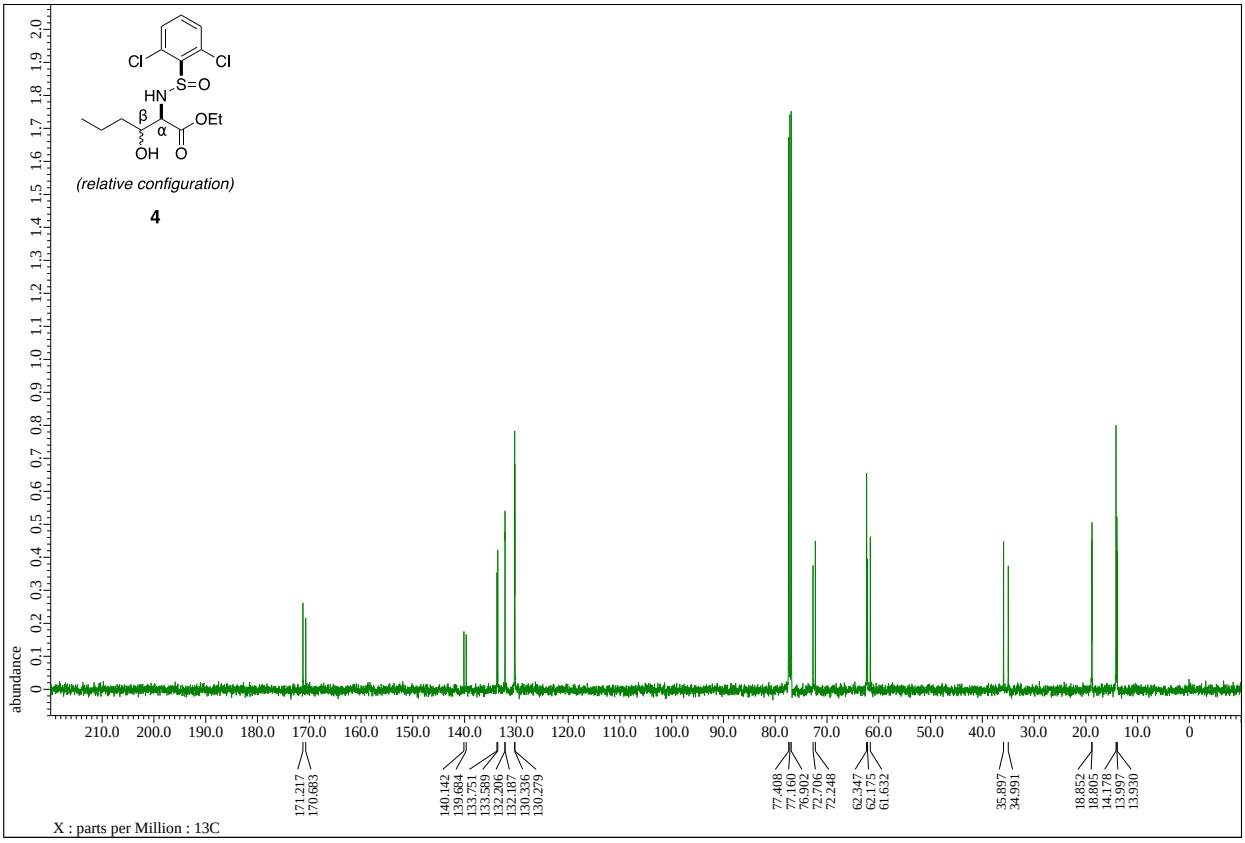
^{13}C-NMR spectra of **3-d$_2$** (126 MHz, $CDCl_3$)



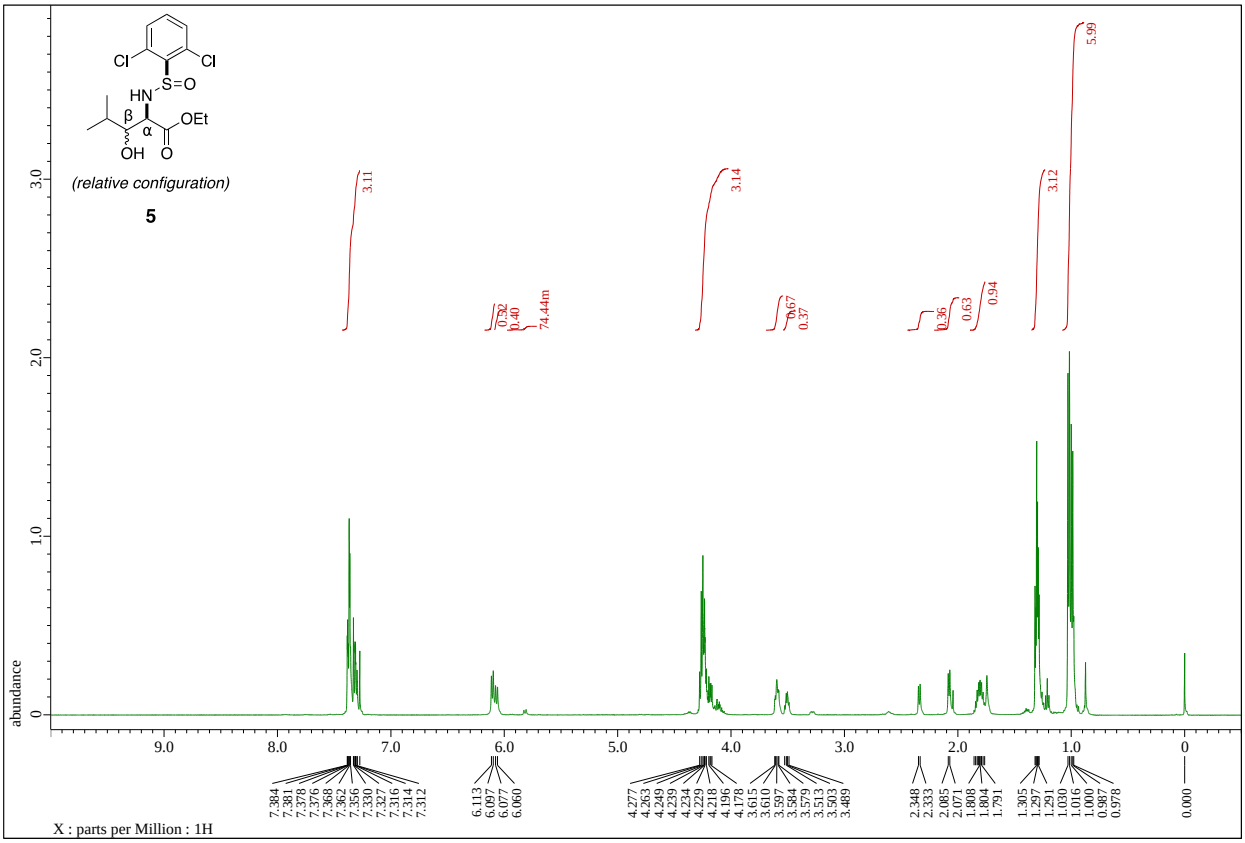
^{1}H-NMR spectra of **4** (500 MHz, $CDCl_3$)



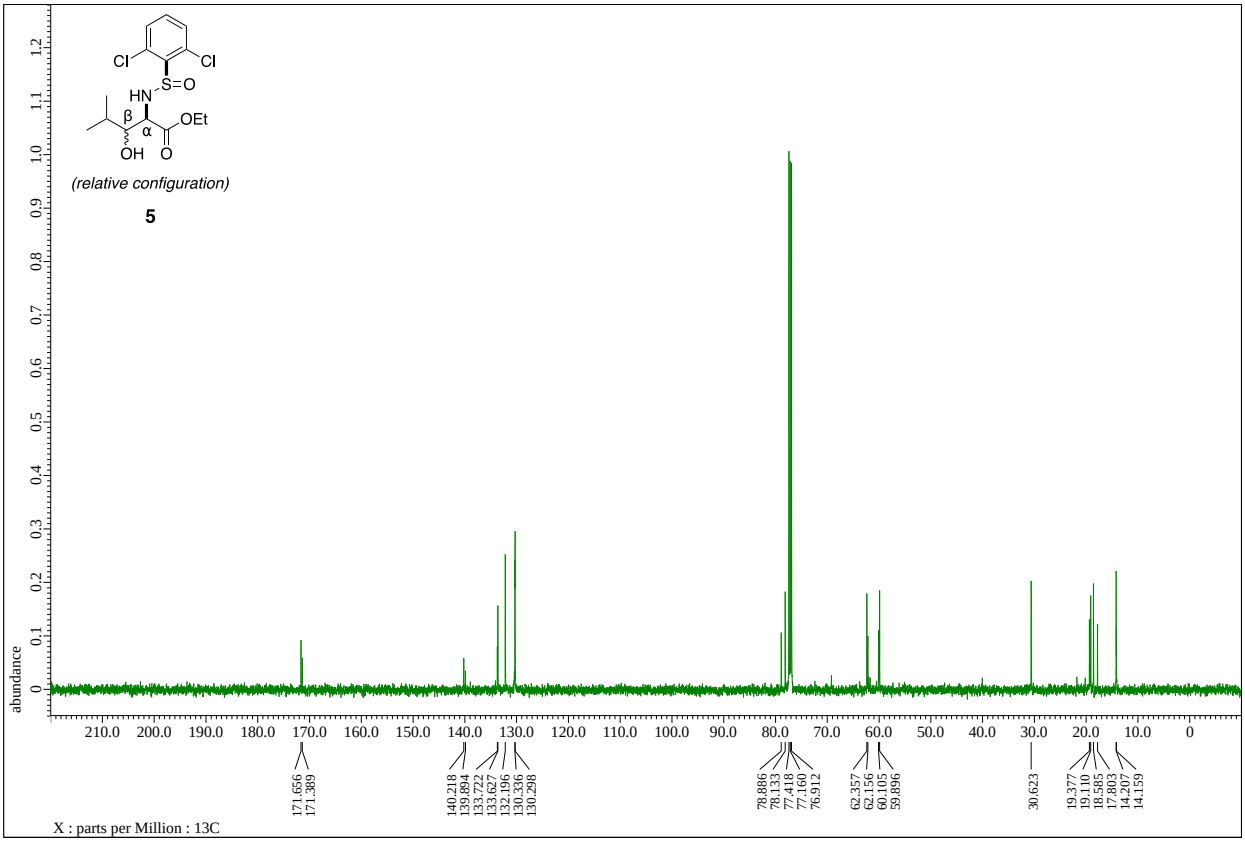
^{13}C-NMR spectra of **4** (126 MHz, $CDCl_3$)



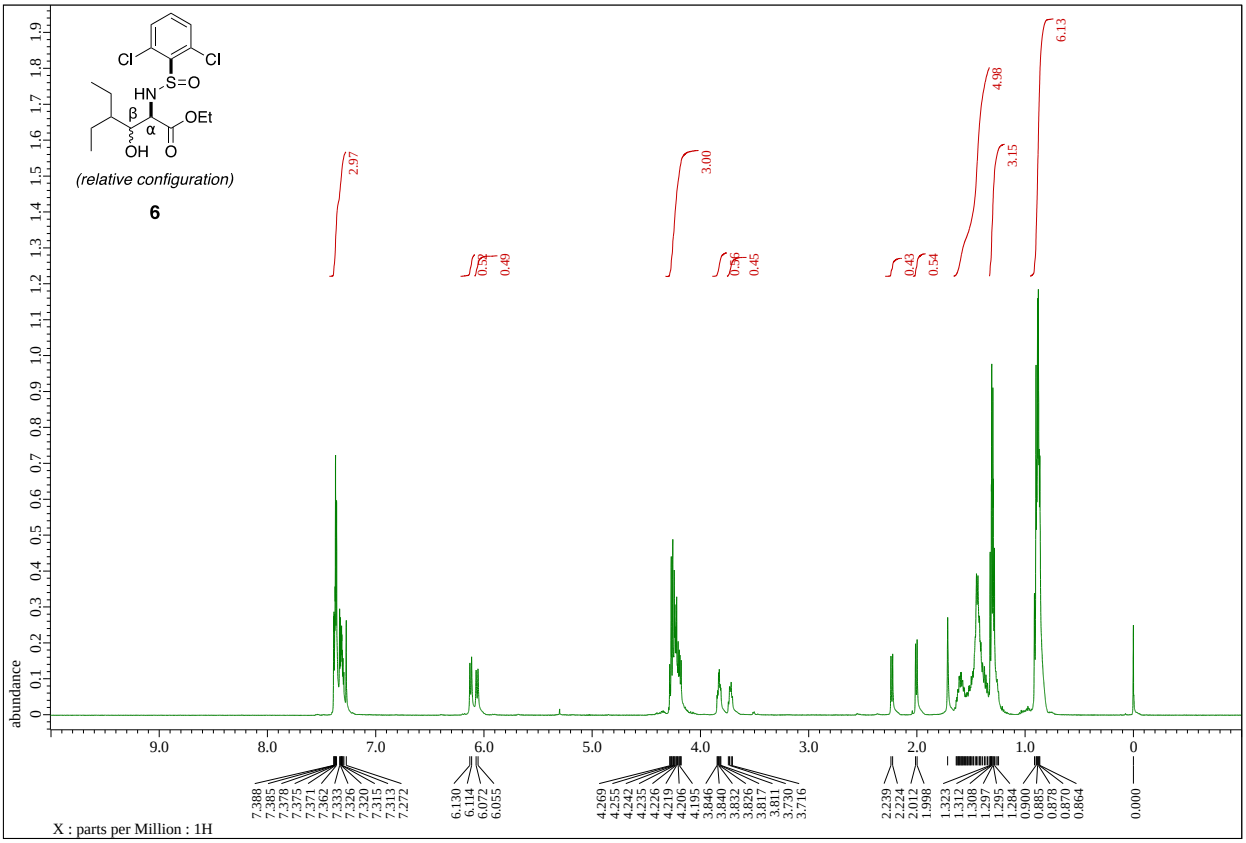
^{1}H-NMR spectra of **5** (500 MHz, $CDCl_3$)



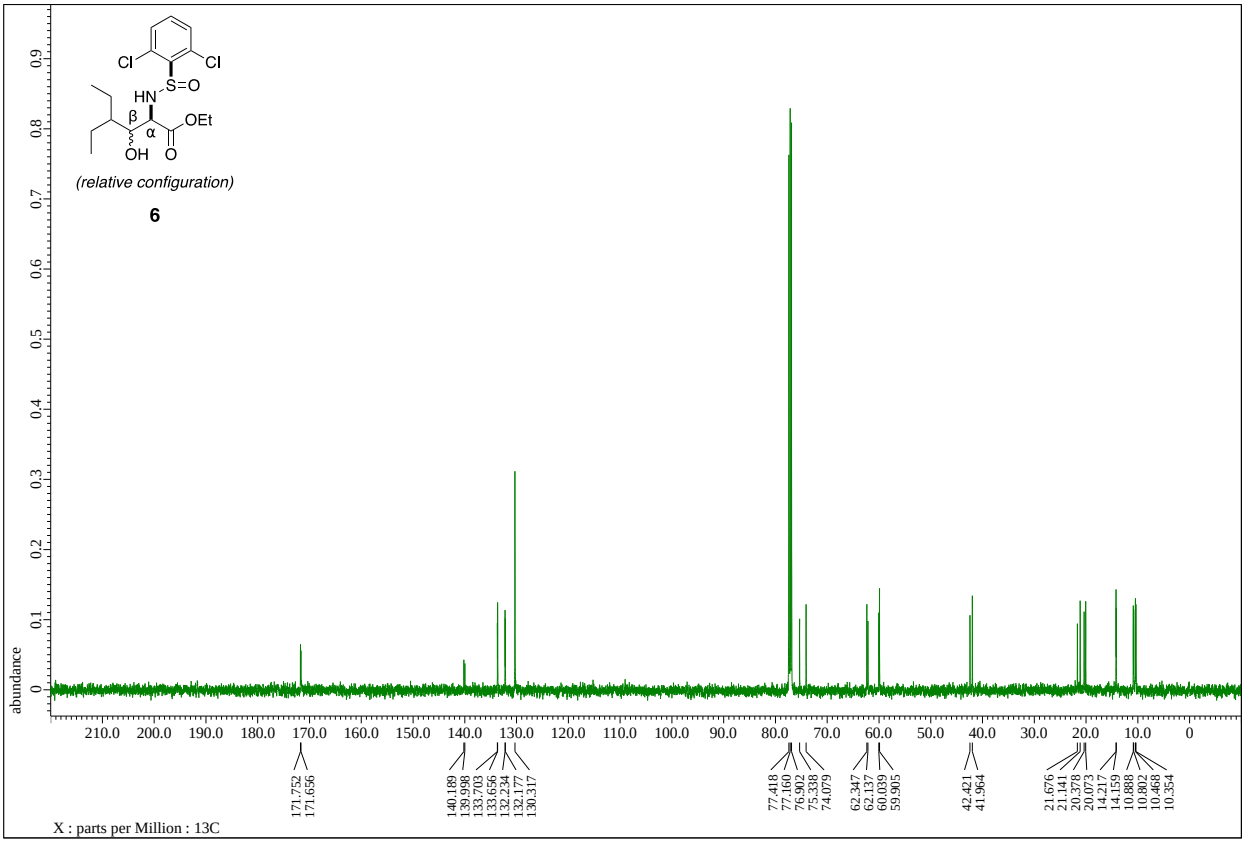
^{13}C-NMR spectra of **5** (126 MHz, $CDCl_3$)



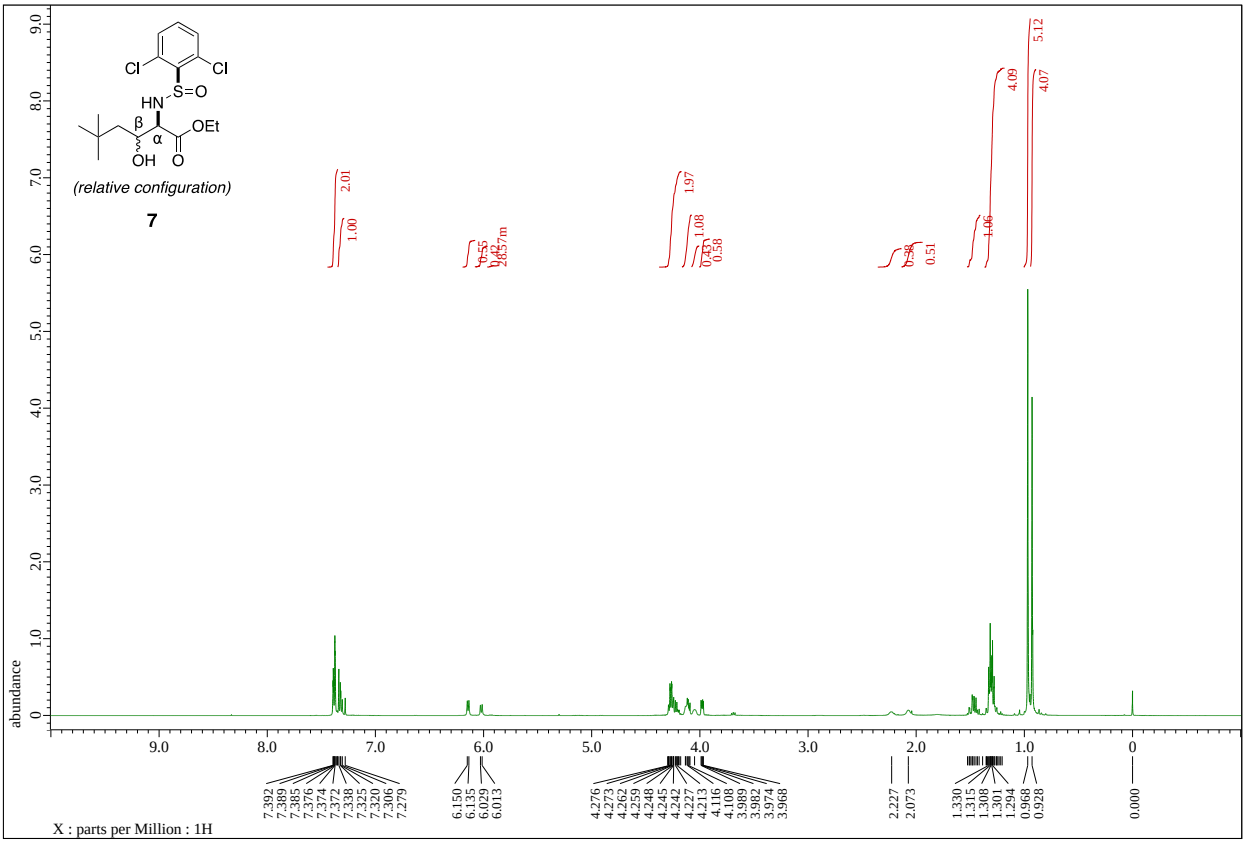
^{1}H-NMR spectra of **6** (500 MHz, $CDCl_3$)



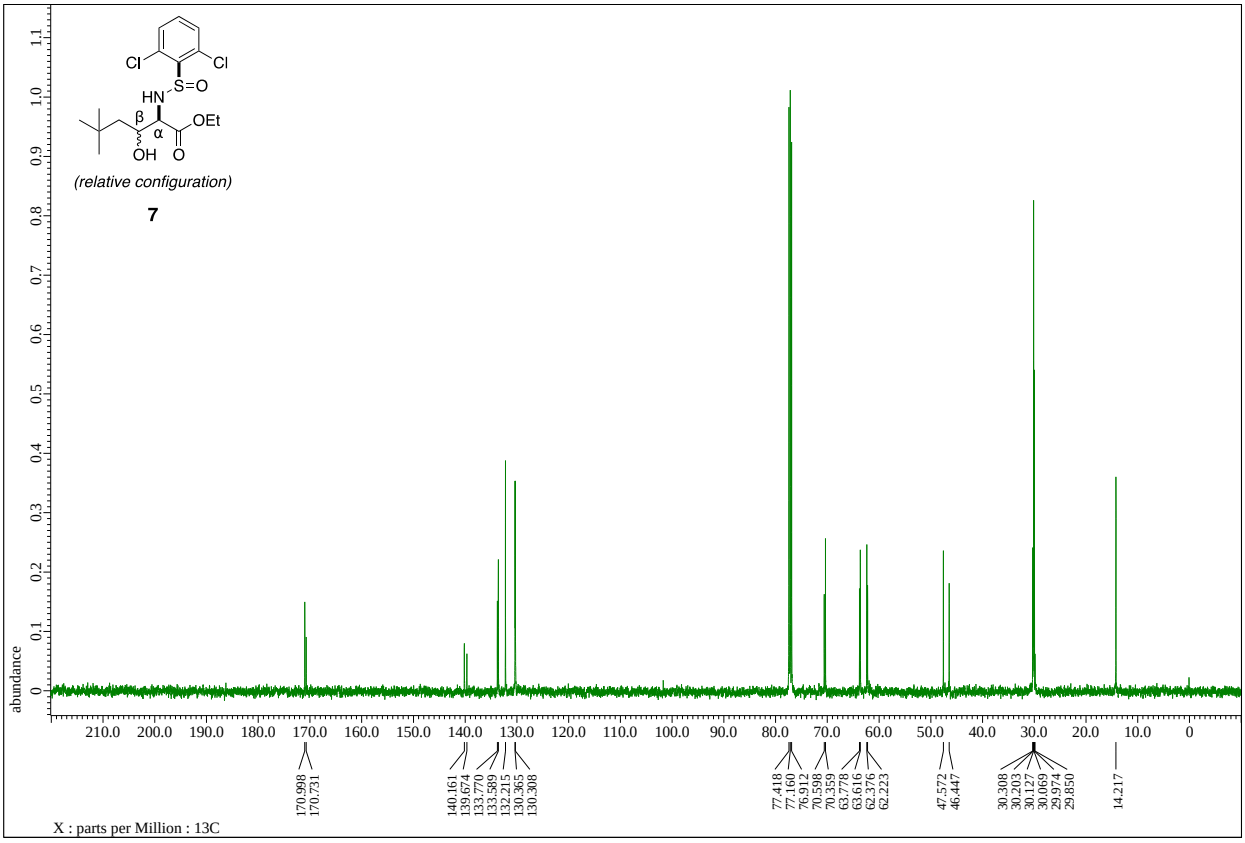
^{13}C-NMR spectra of **6** (126 MHz, $CDCl_3$)



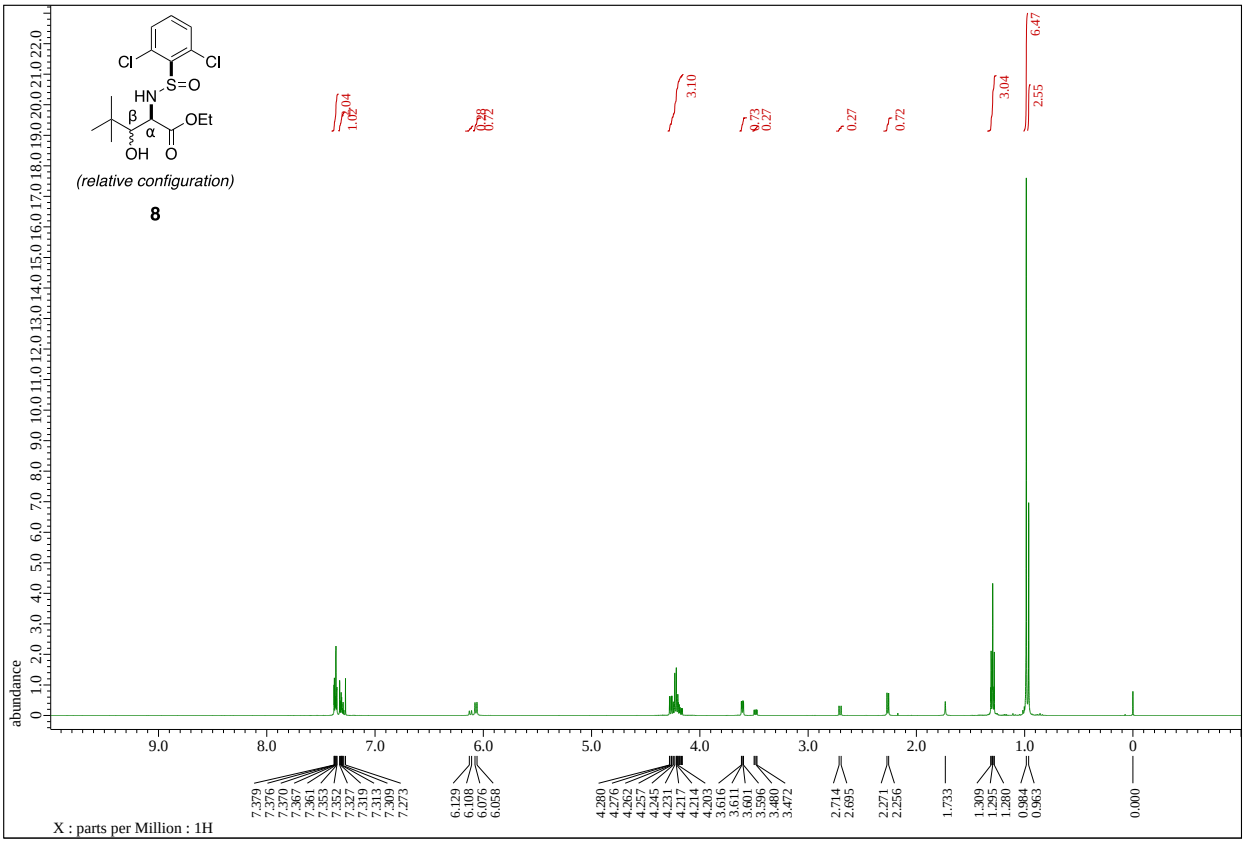
^{1}H-NMR spectra of **7** (500 MHz, $CDCl_3$)



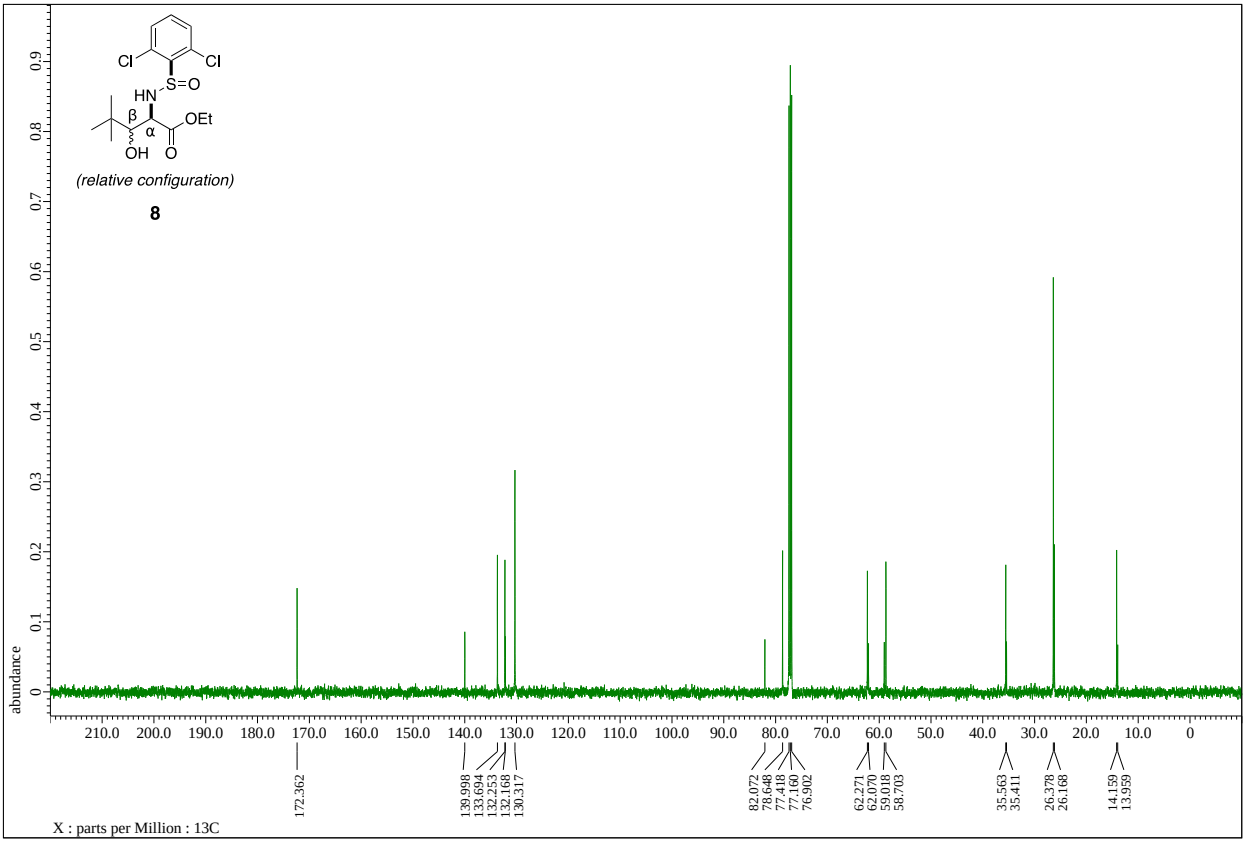
^{13}C-NMR spectra of **7** (126 MHz, $CDCl_3$)



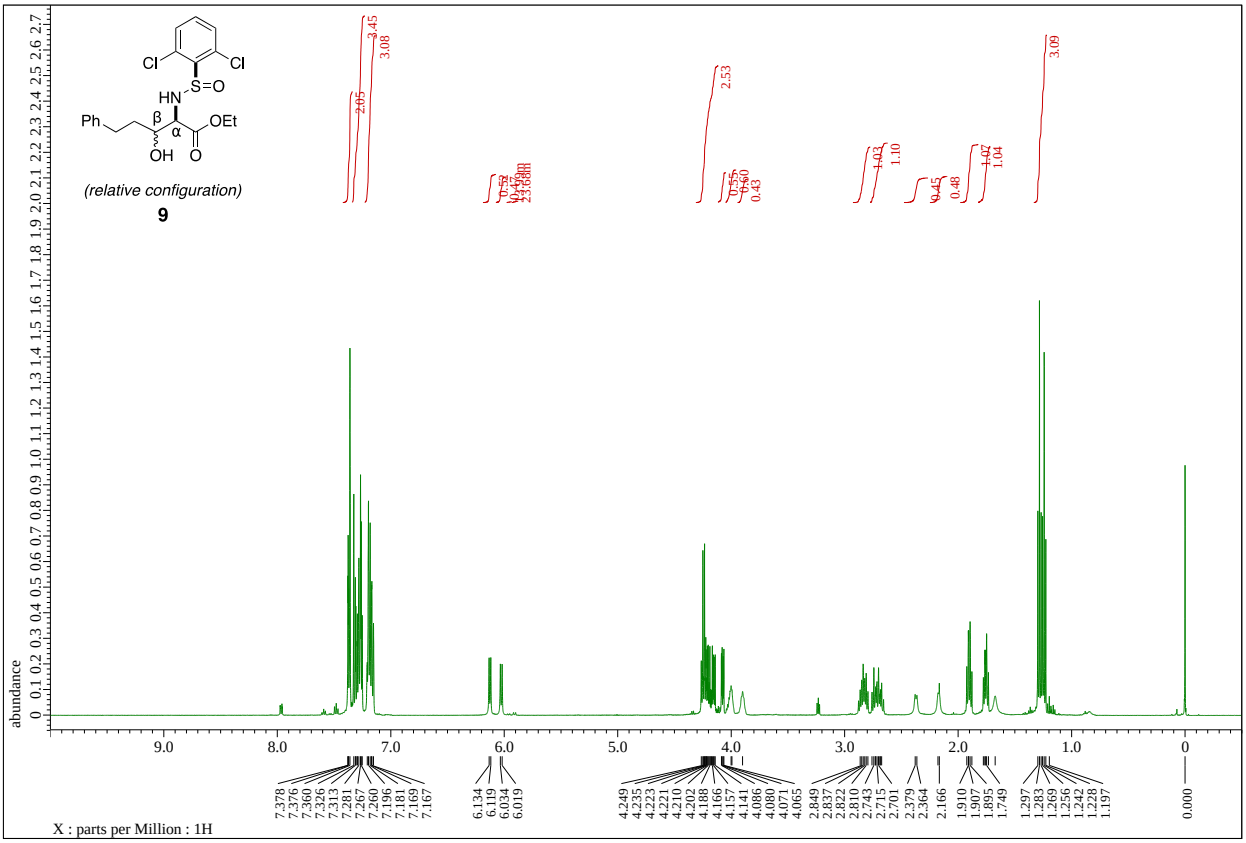
^{1}H-NMR spectra of **8** (500 MHz, $CDCl_3$)



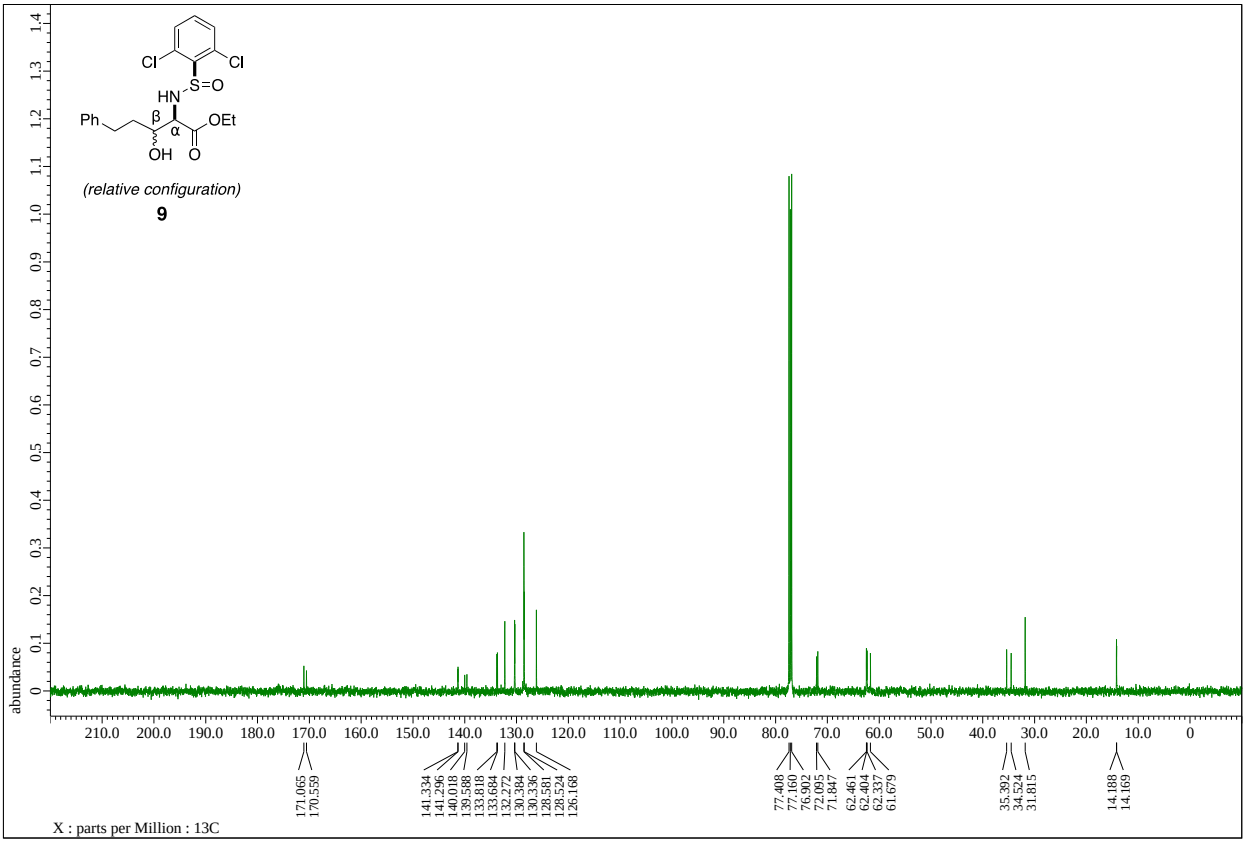
^{13}C-NMR spectra of **8** (126 MHz, $CDCl_3$)



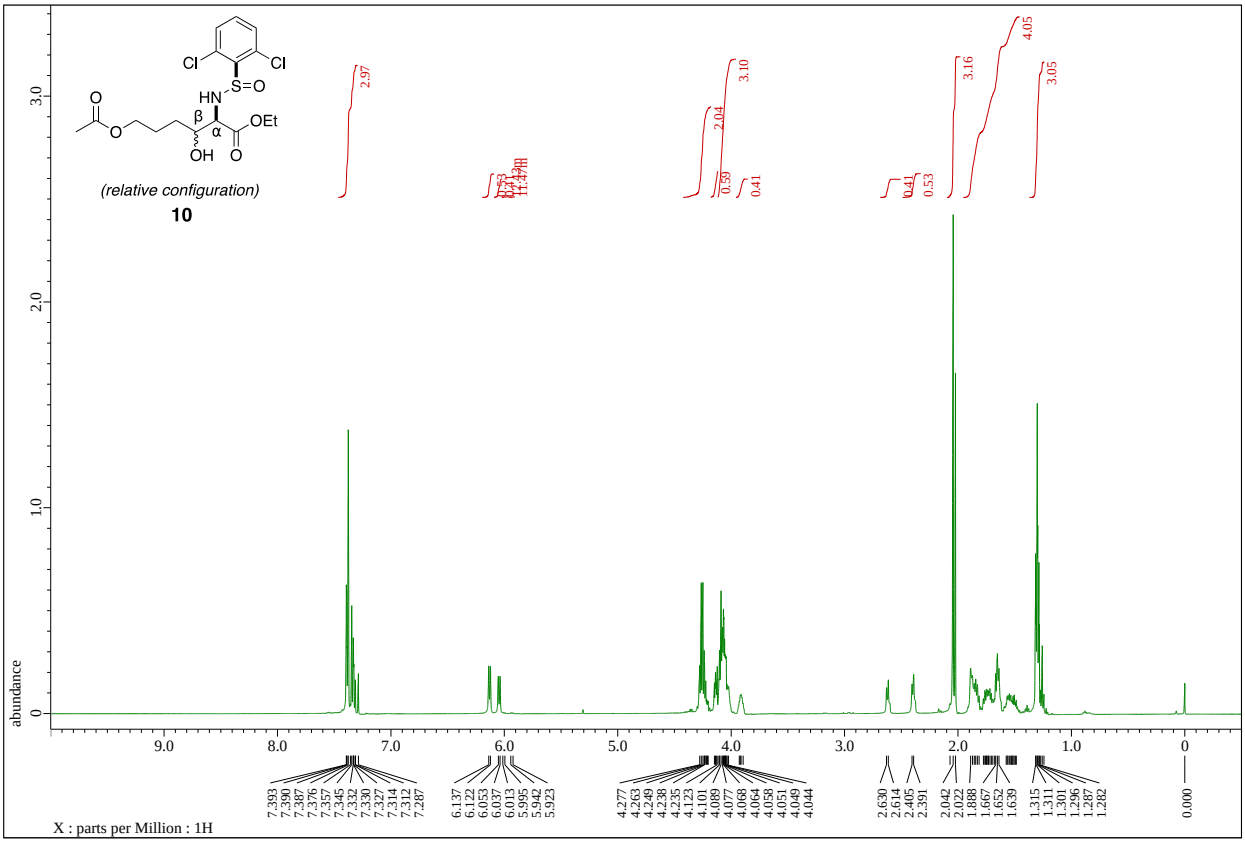
^{1}H-NMR spectra of **9** (500 MHz, $CDCl_3$)



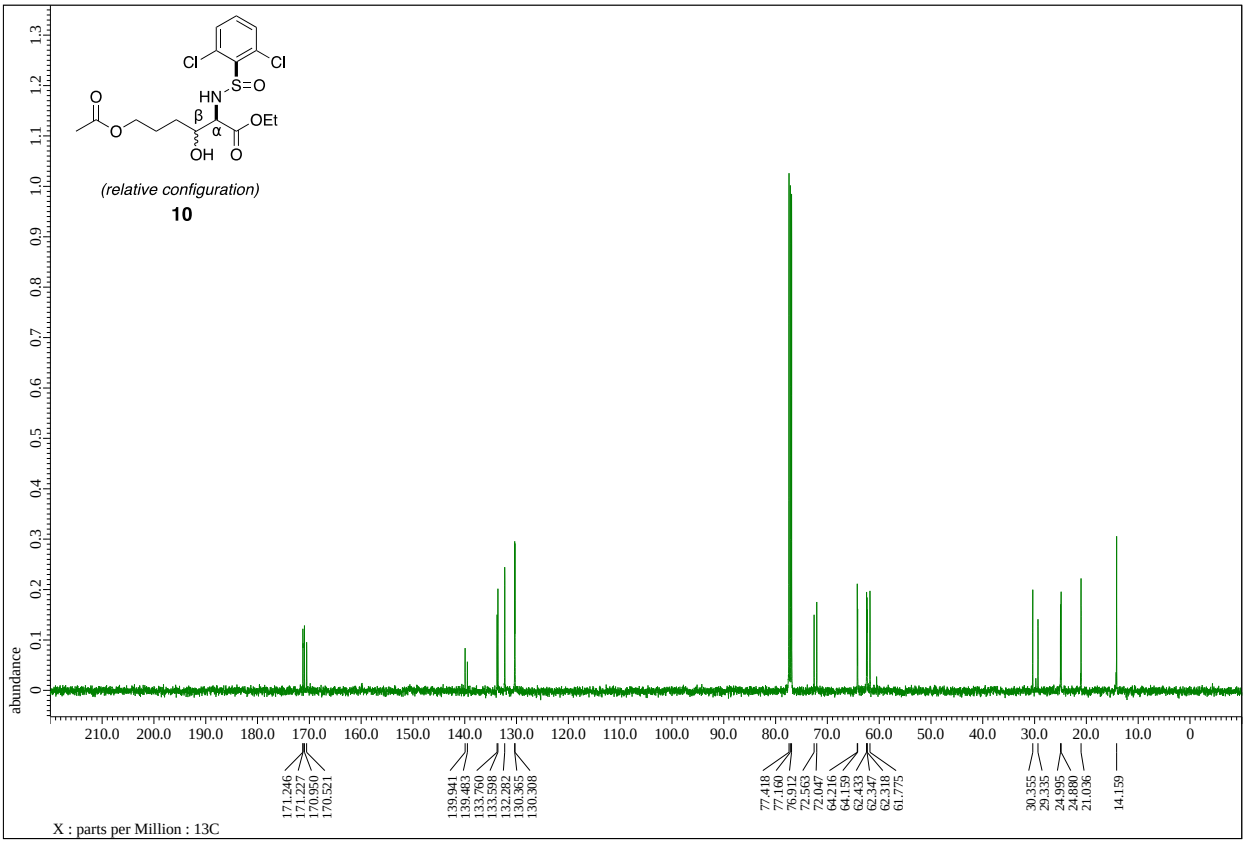
^{13}C-NMR spectra of **9** (126 MHz, $CDCl_3$)



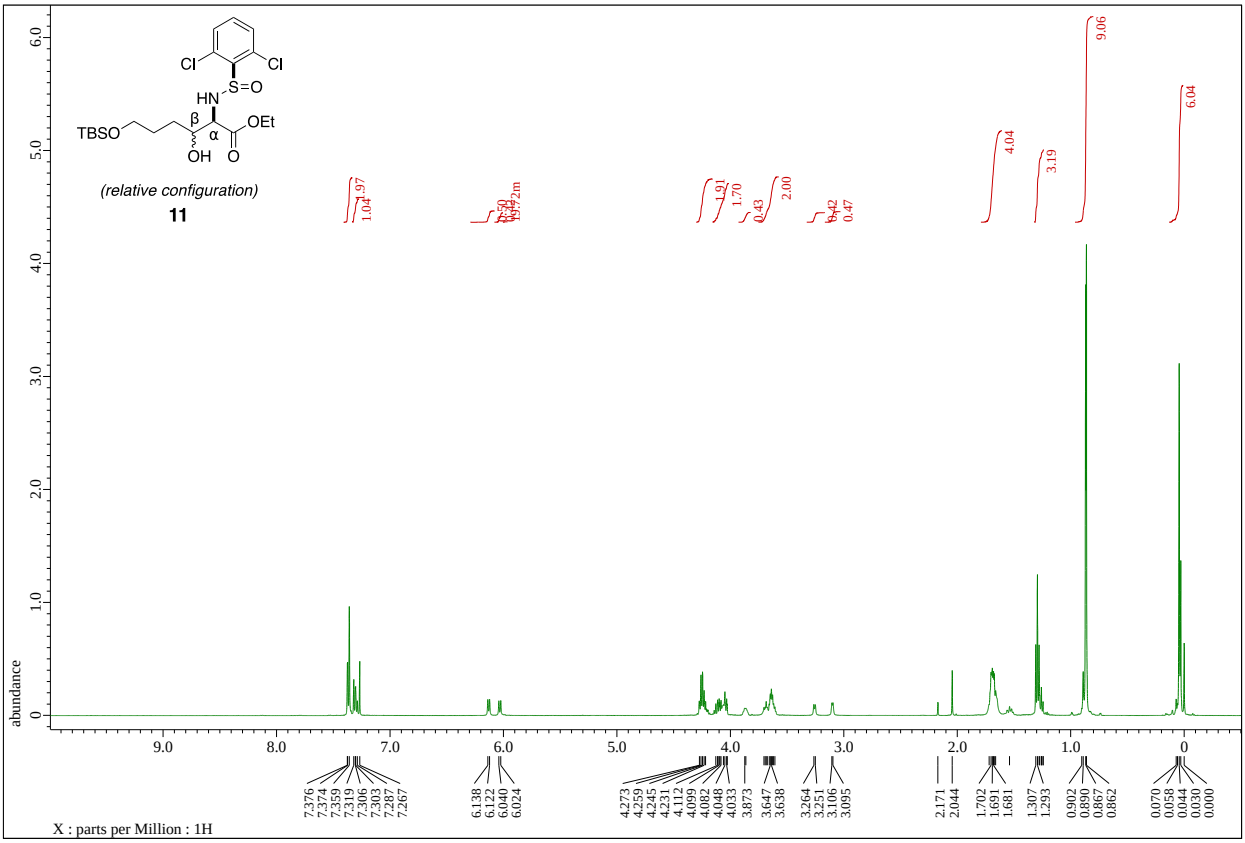
^{1}H-NMR spectra of **10** (500 MHz, $CDCl_3$)



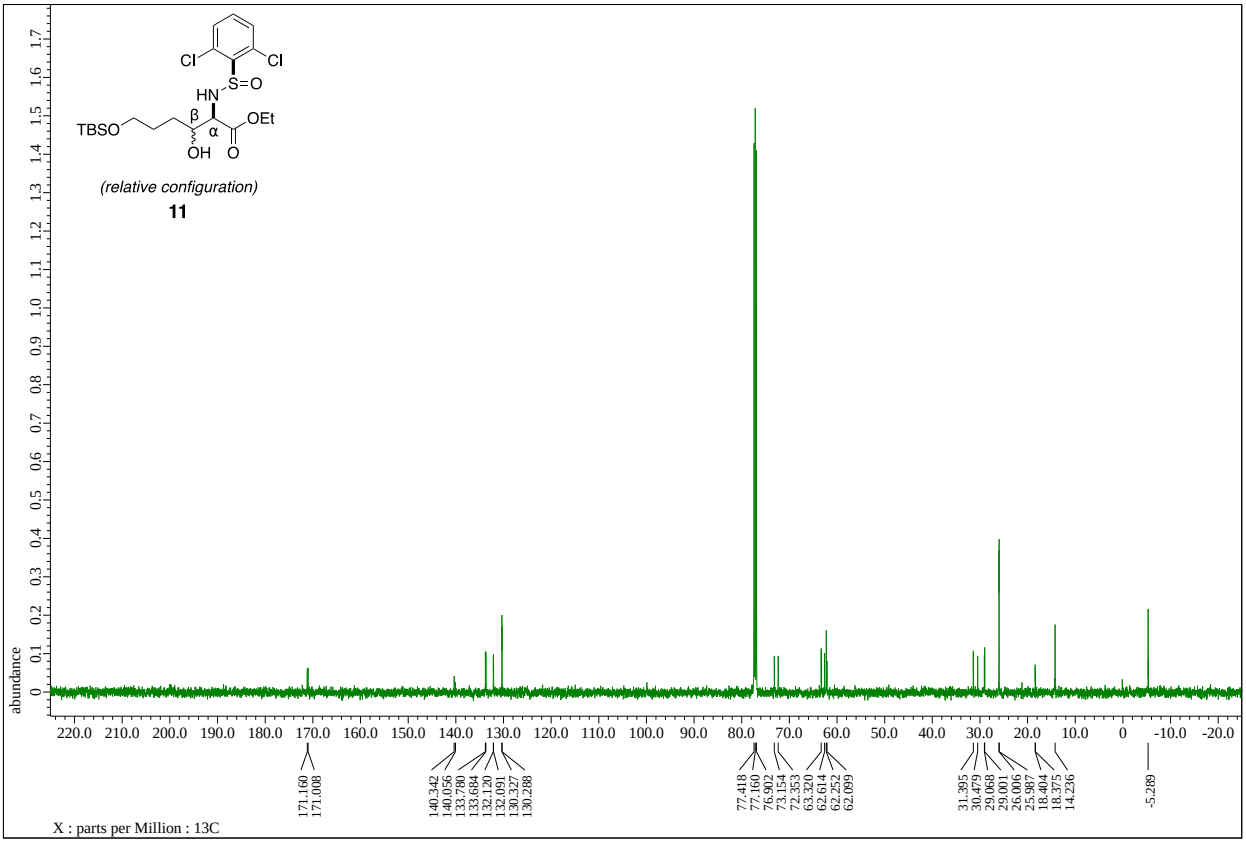
^{13}C-NMR spectra of **10** (126 MHz, $CDCl_3$)



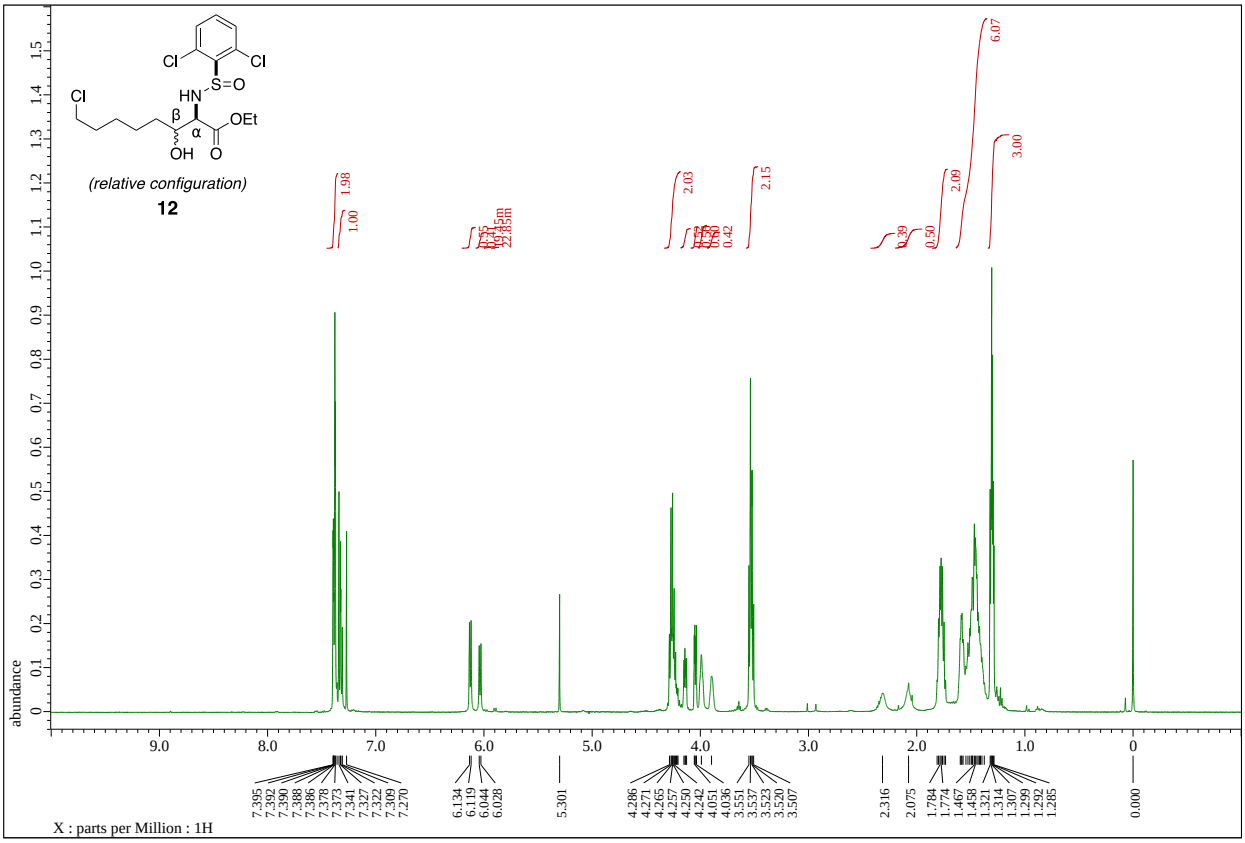
^{1}H-NMR spectra of **11** (500 MHz, $CDCl_3$)



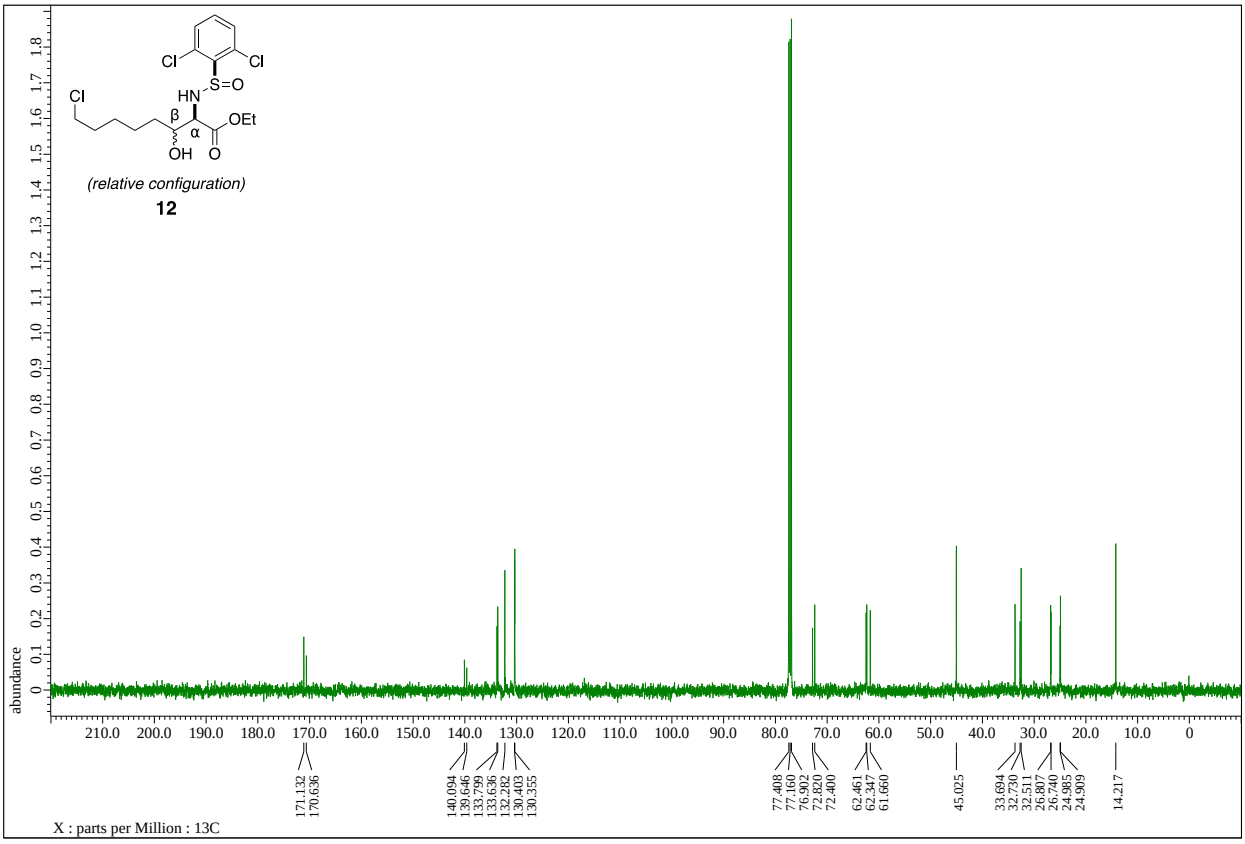
^{13}C-NMR spectra of **11** (126 MHz, $CDCl_3$)



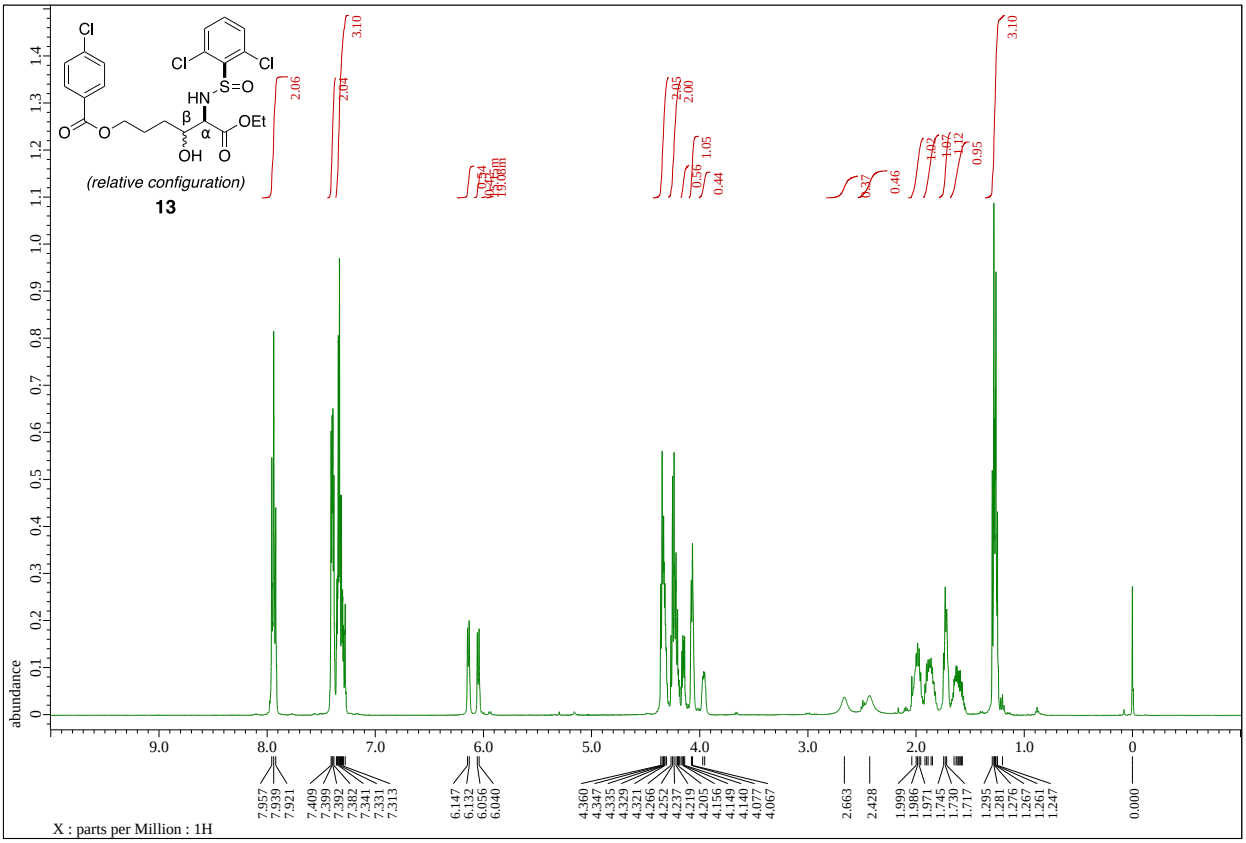
^{1}H-NMR spectra of **12** (500 MHz, $CDCl_3$)



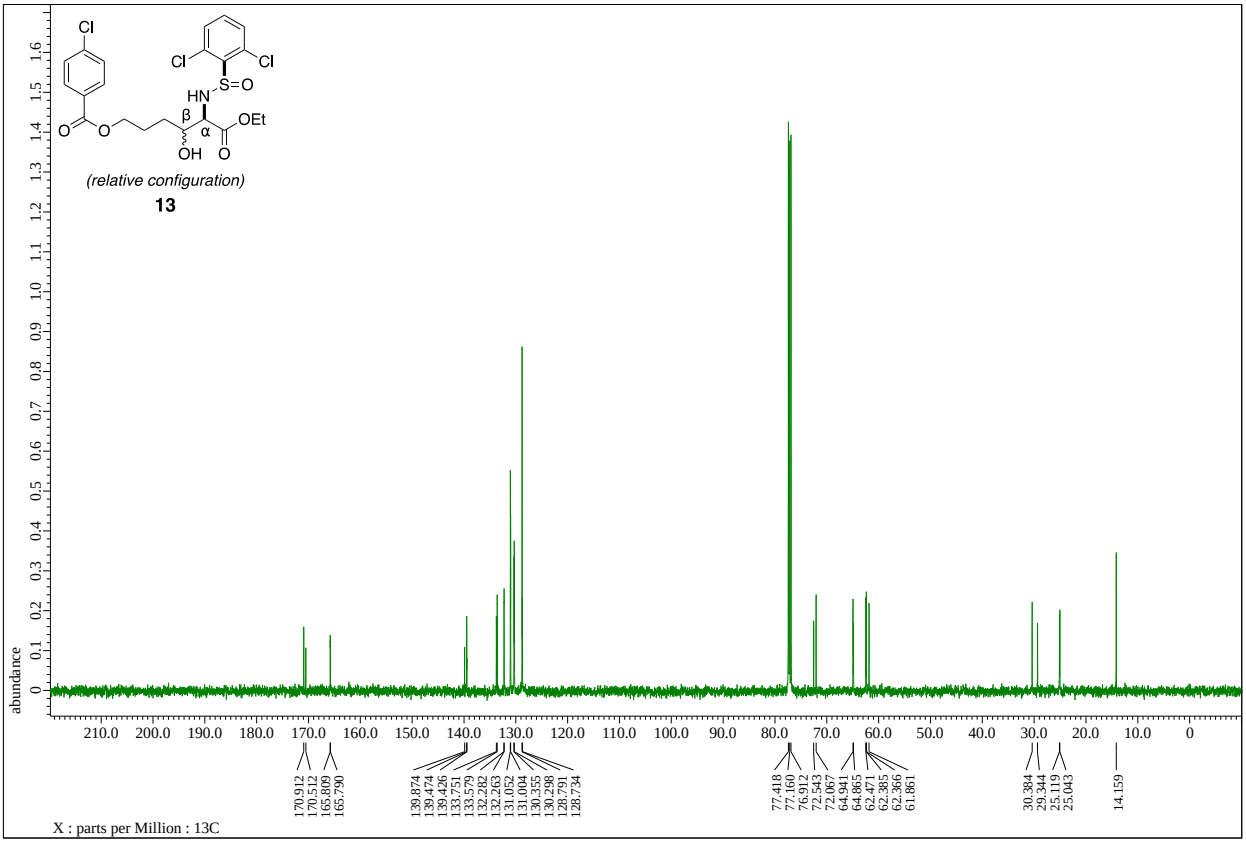
^{13}C-NMR spectra of **12** (126 MHz, $CDCl_3$)



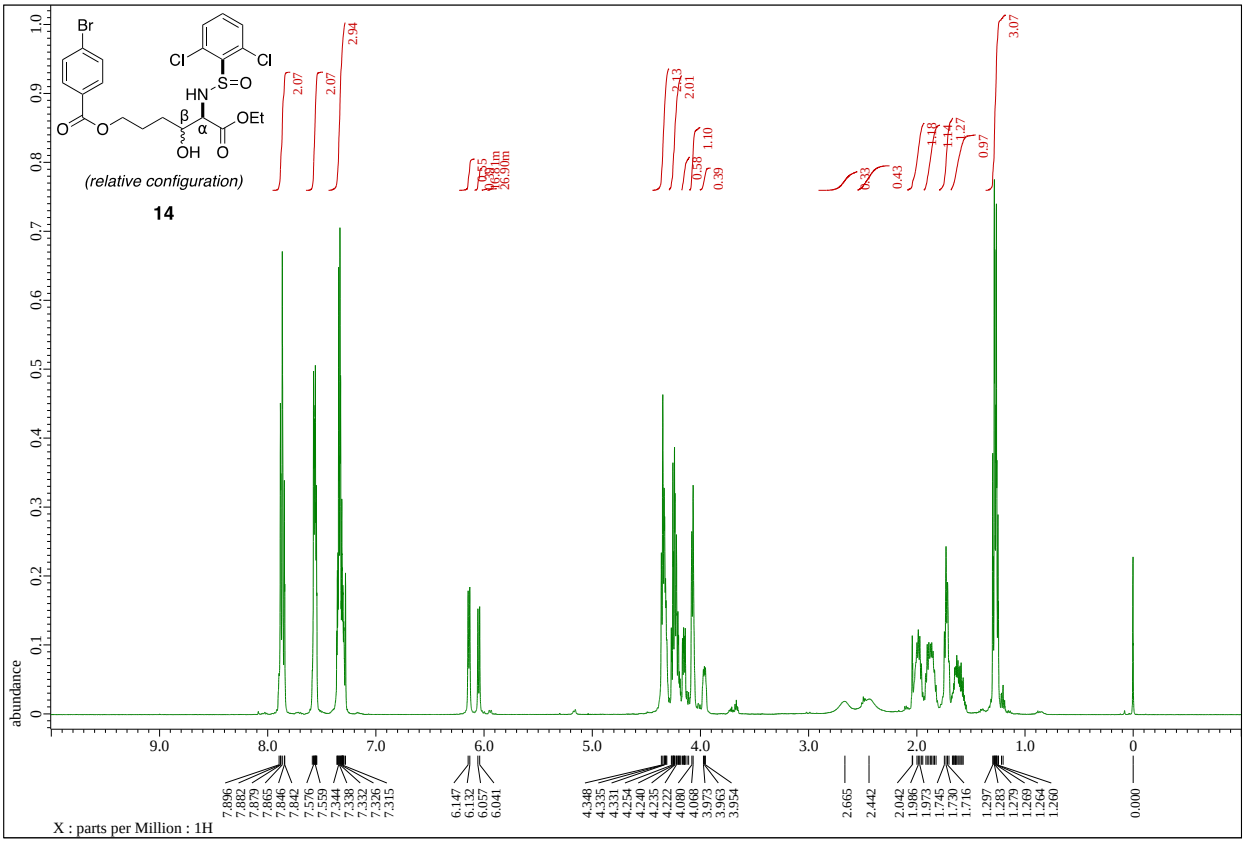
^{1}H-NMR spectra of **13** (500 MHz, $CDCl_3$)



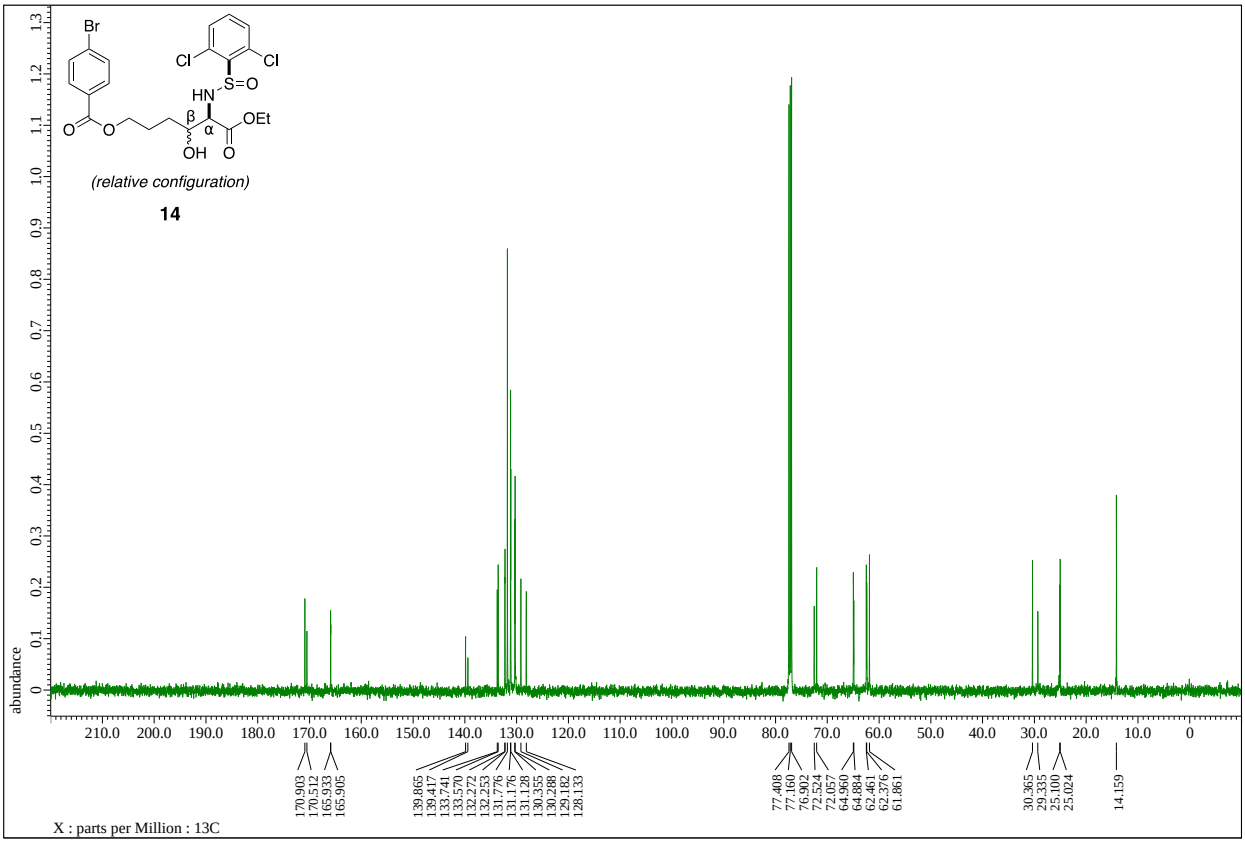
^{13}C-NMR spectra of **13** (126 MHz, $CDCl_3$)



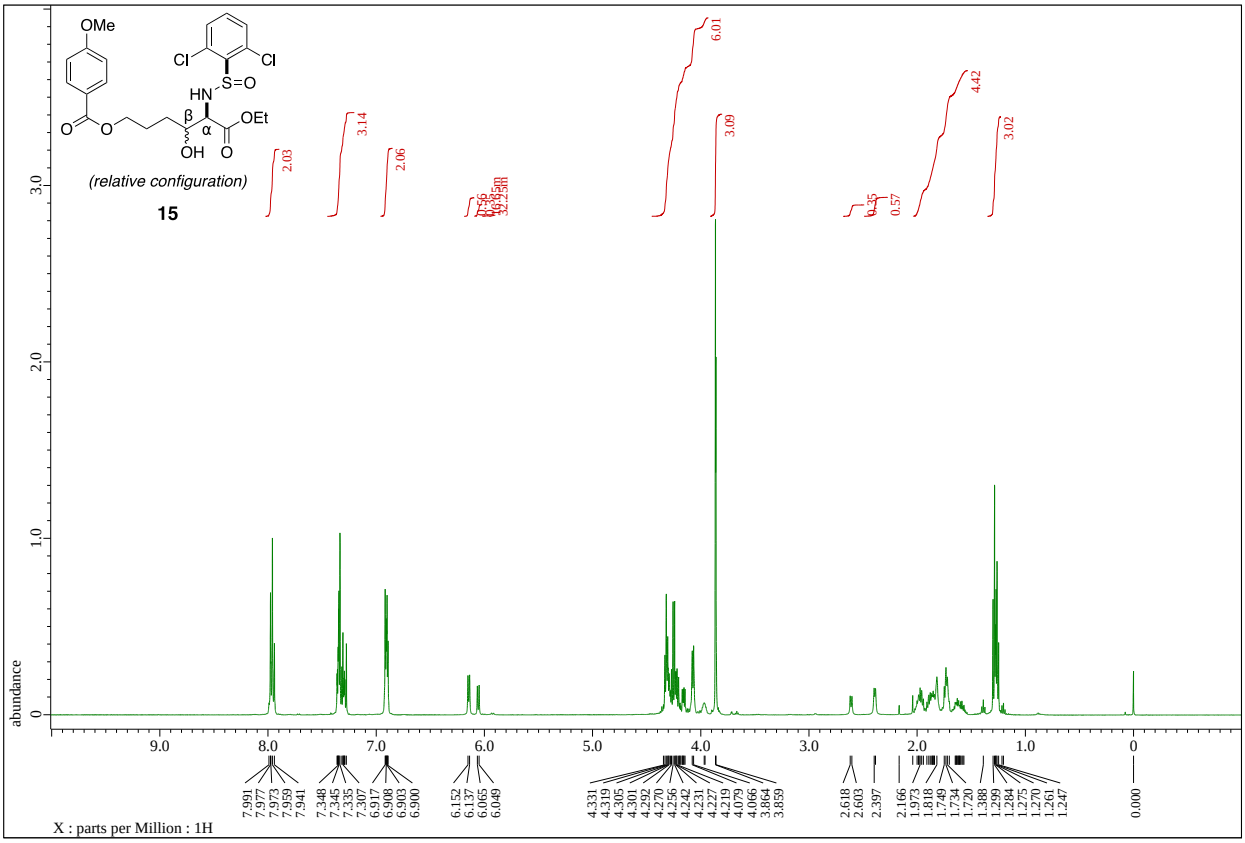
^{1}H-NMR spectra of **14** (500 MHz, $CDCl_3$)



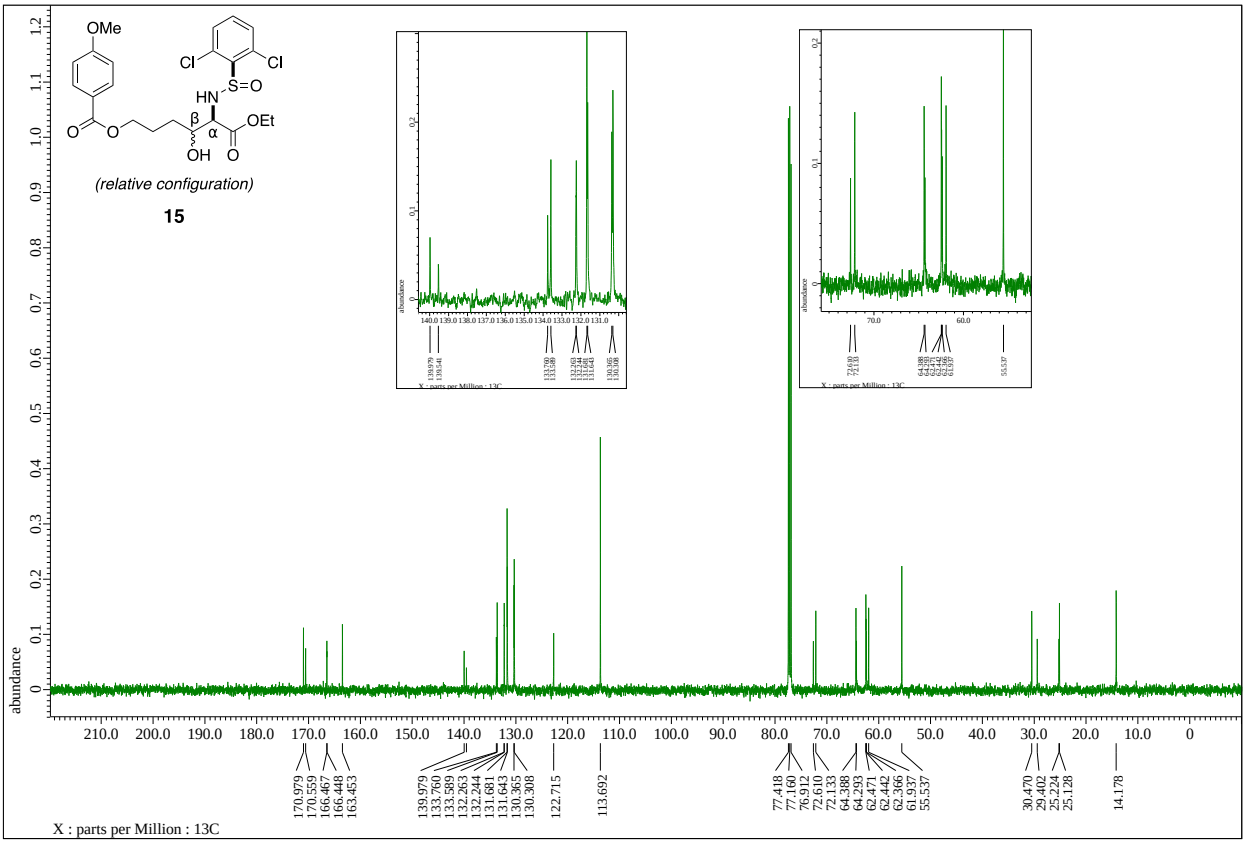
^{13}C-NMR spectra of **14** (126 MHz, $CDCl_3$)



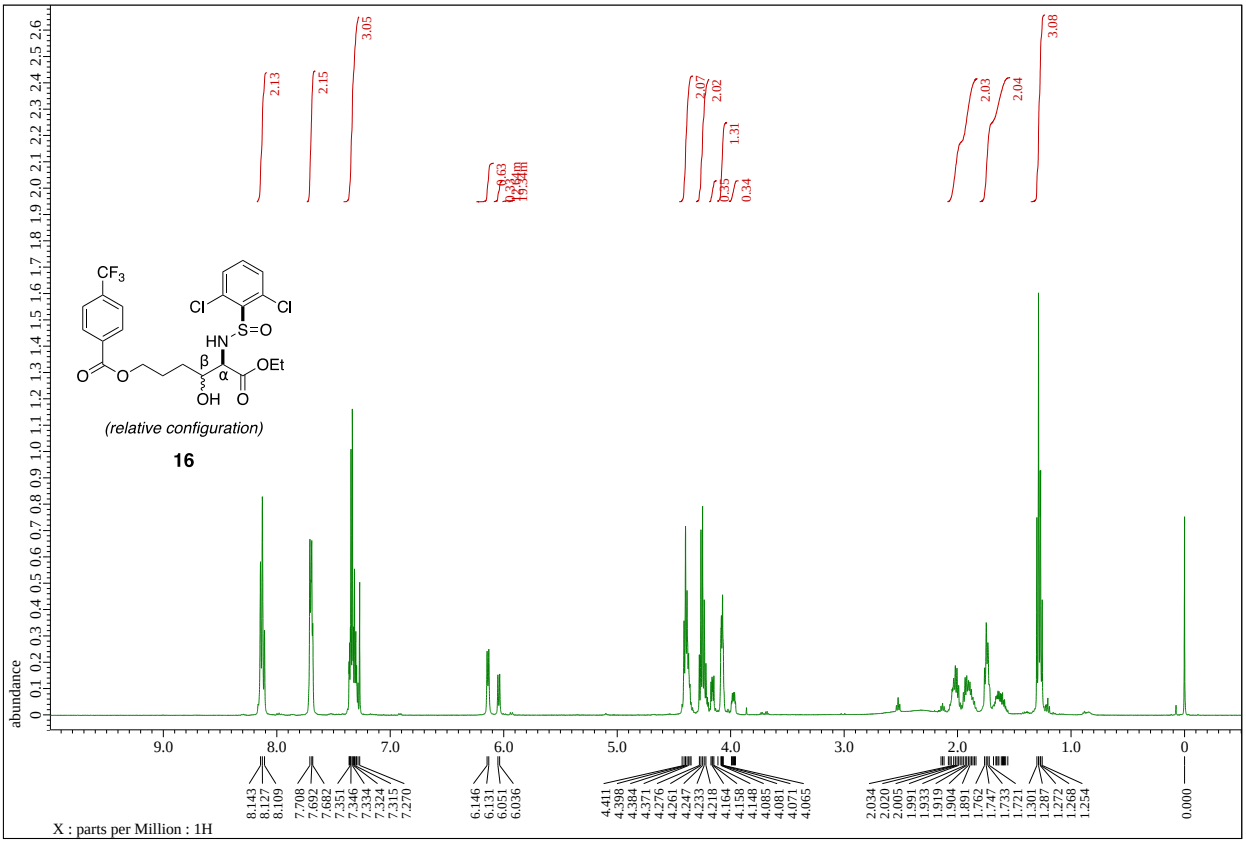
^{1}H-NMR spectra of **15** (500 MHz, $CDCl_3$)



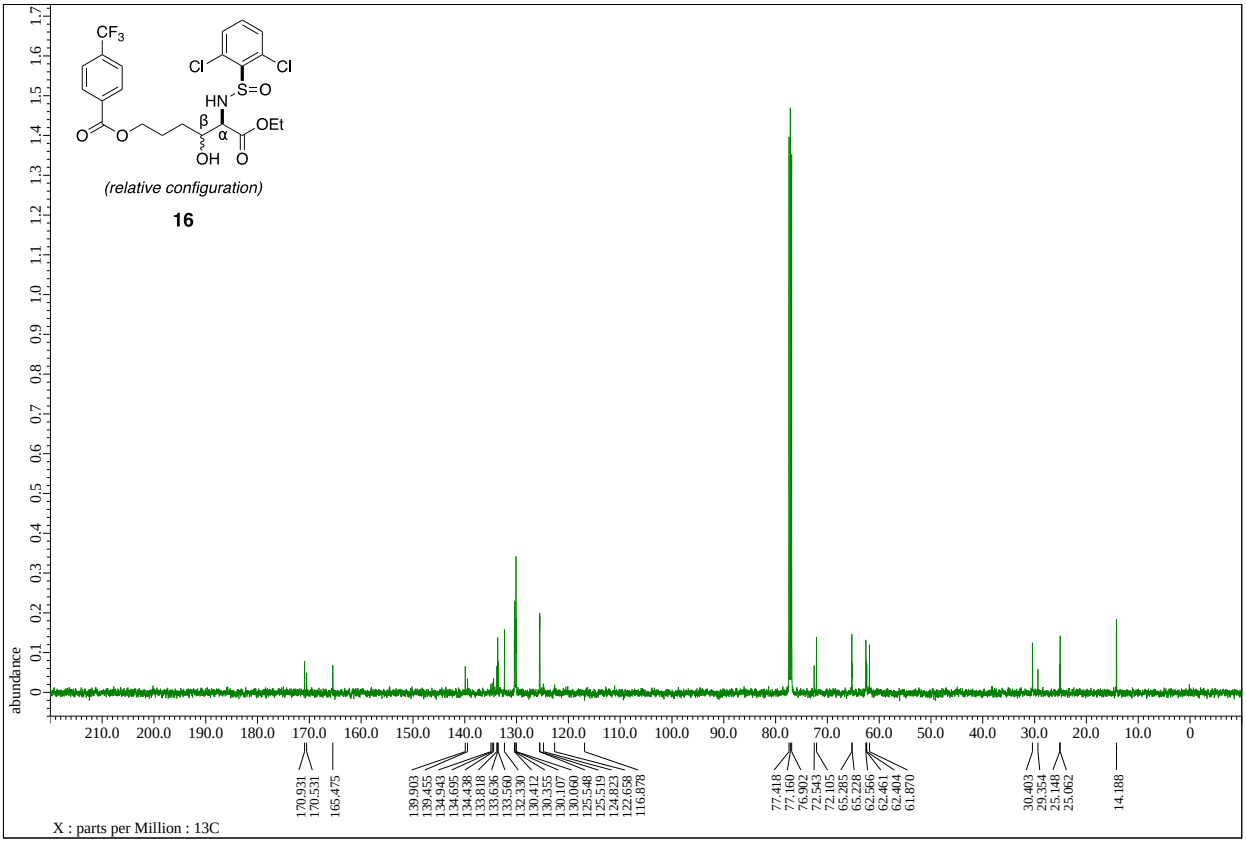
^{13}C-NMR spectra of **15** (126 MHz, $CDCl_3$)



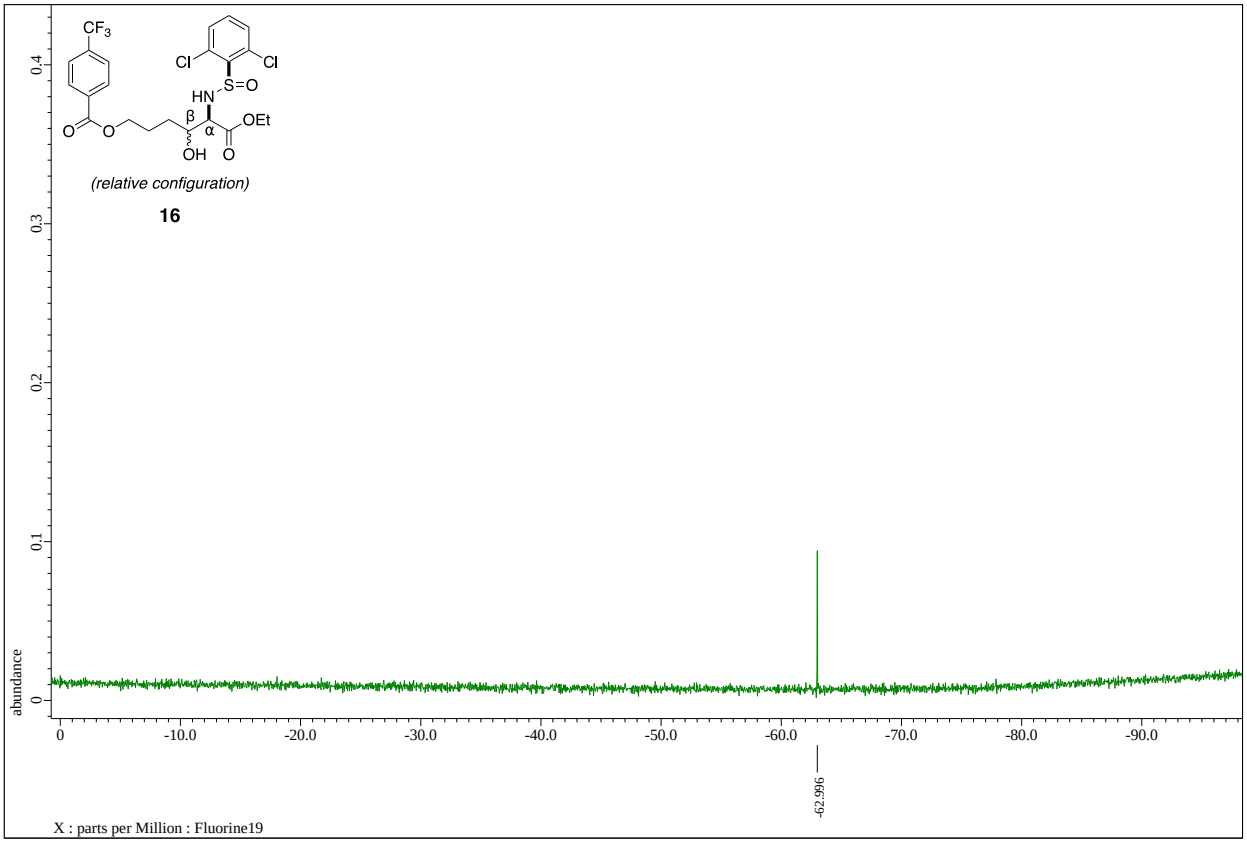
^{1}H-NMR spectra of **16** (500 MHz, $CDCl_3$)



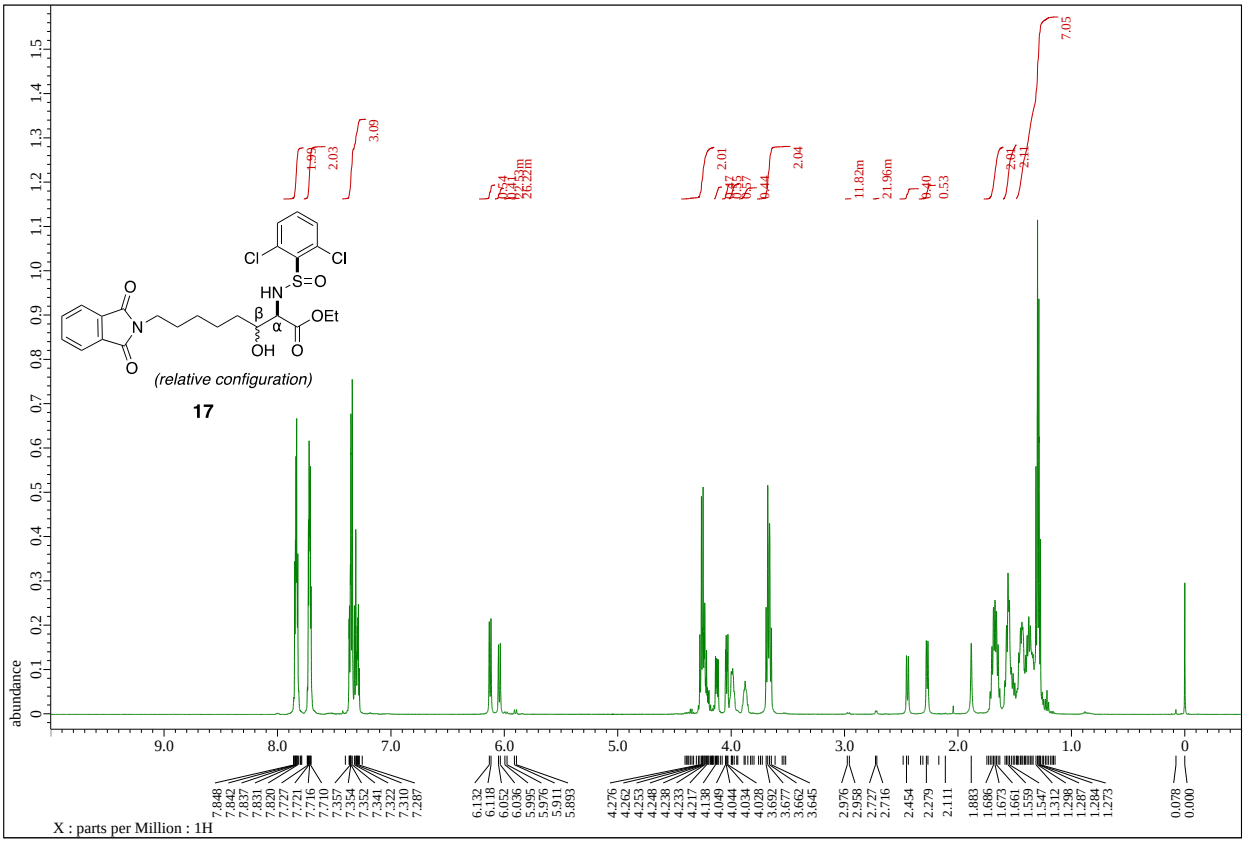
^{13}C-NMR spectra of **16** (126 MHz, $CDCl_3$)



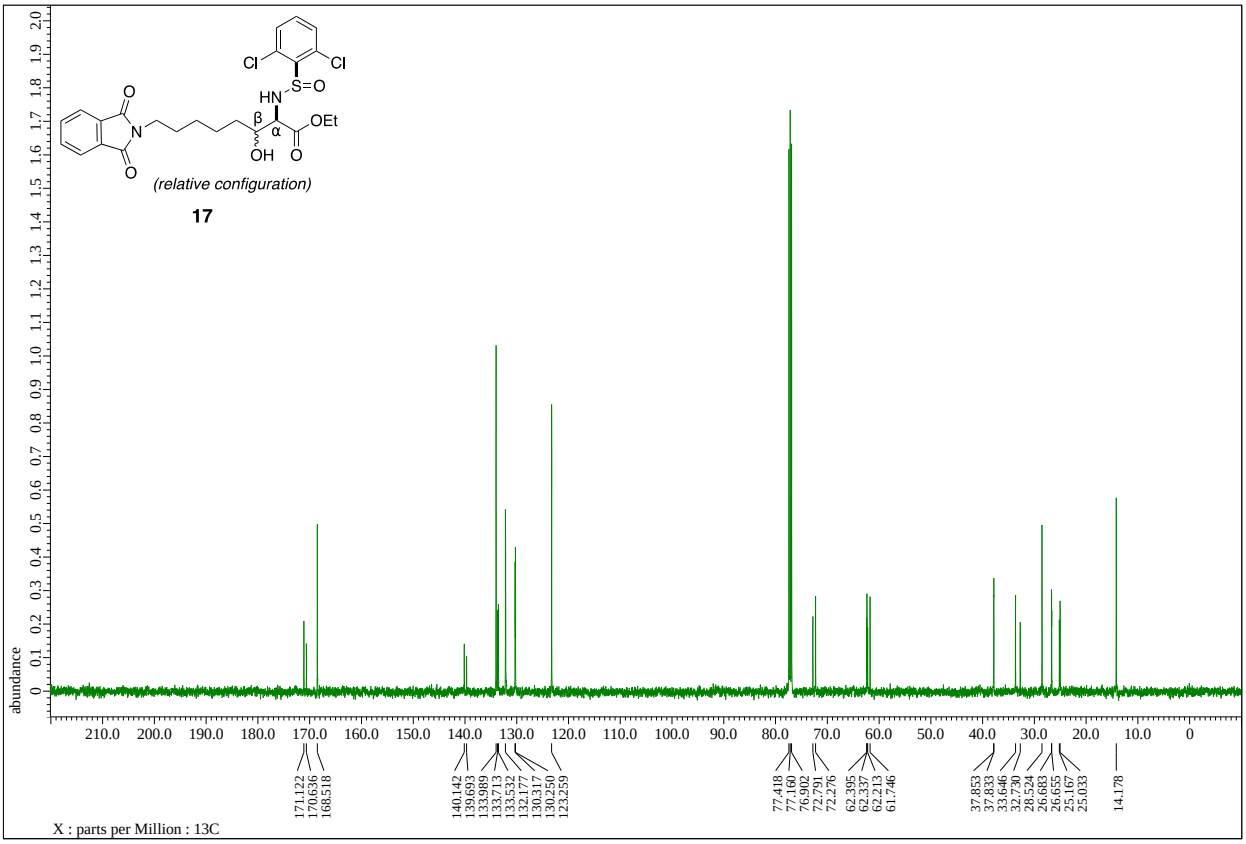
^{19}F-NMR spectra of **16** (376 MHz, $CDCl_3$)



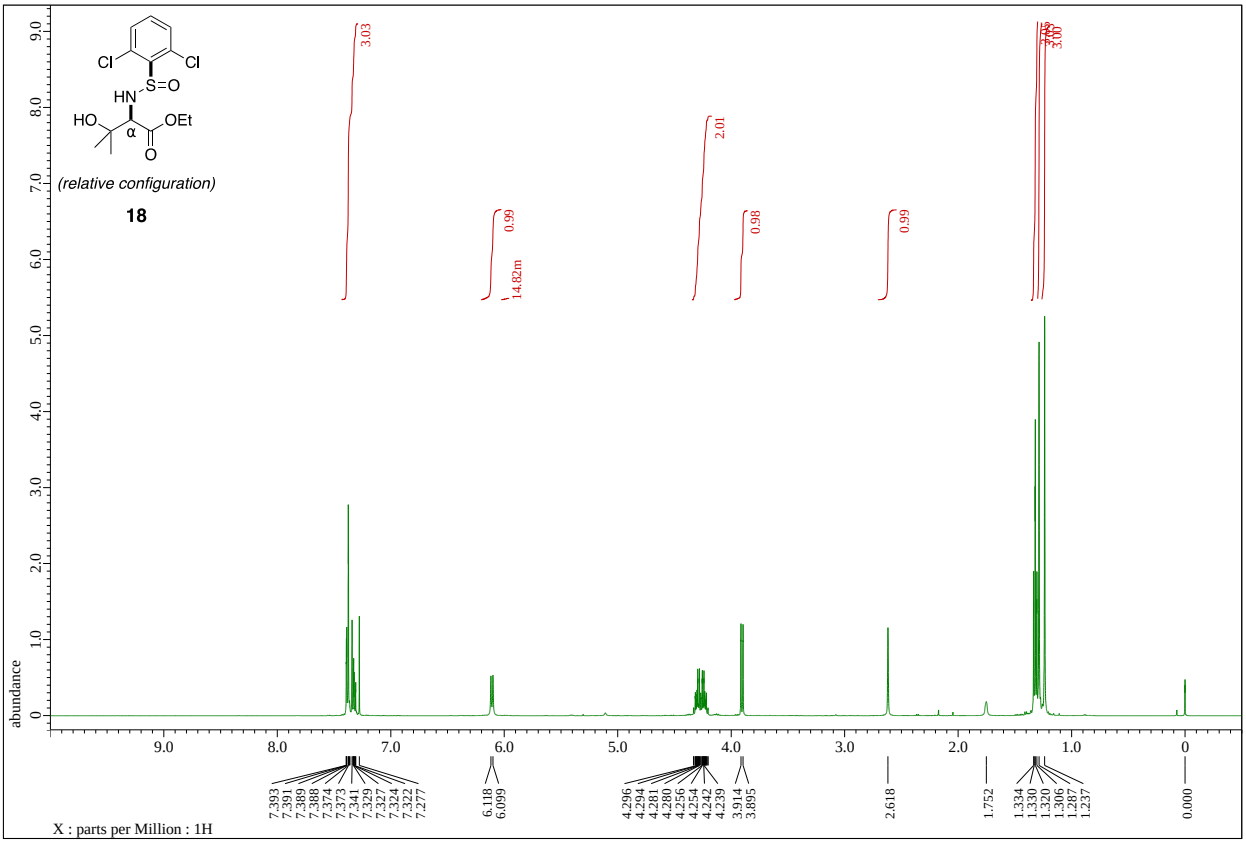
^{1}H-NMR spectra of **17** (500 MHz, $CDCl_3$)



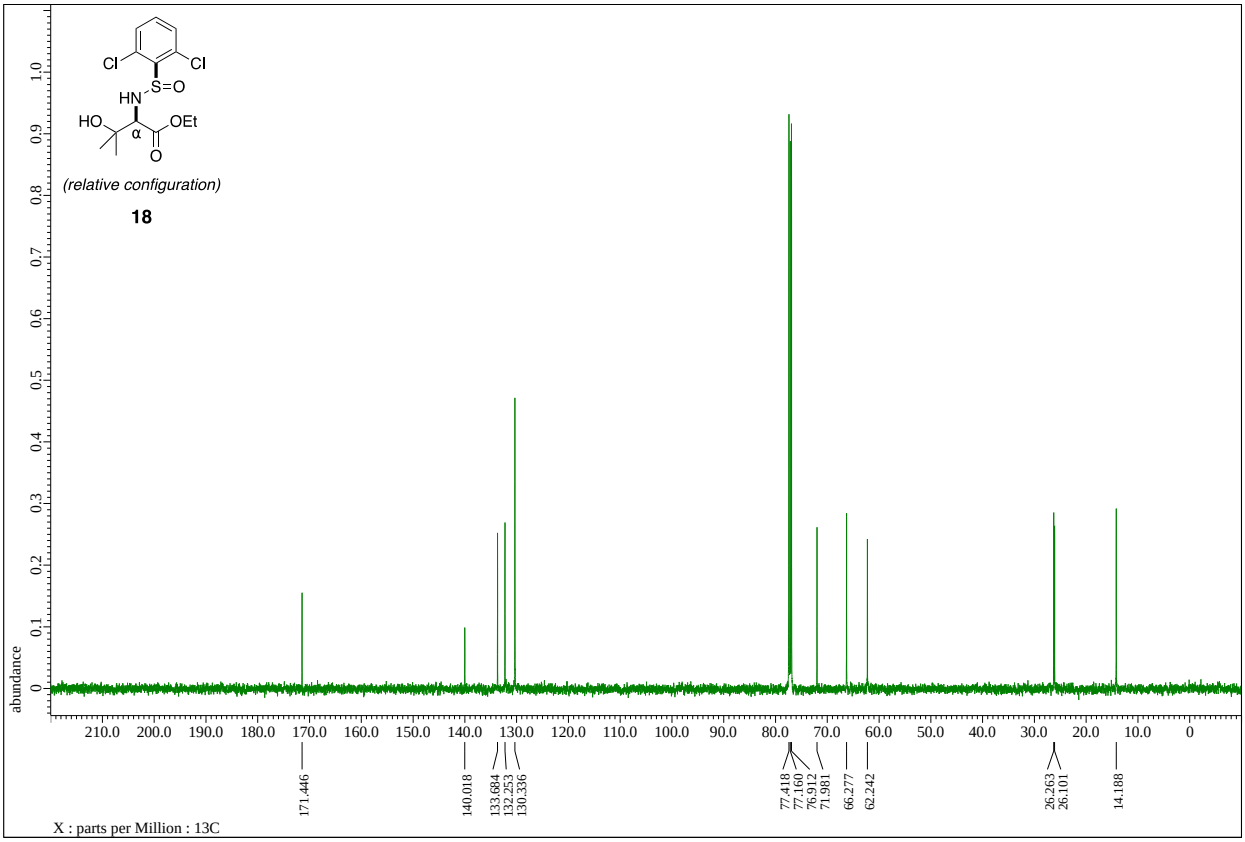
^{13}C-NMR spectra of **17** (126 MHz, $CDCl_3$)



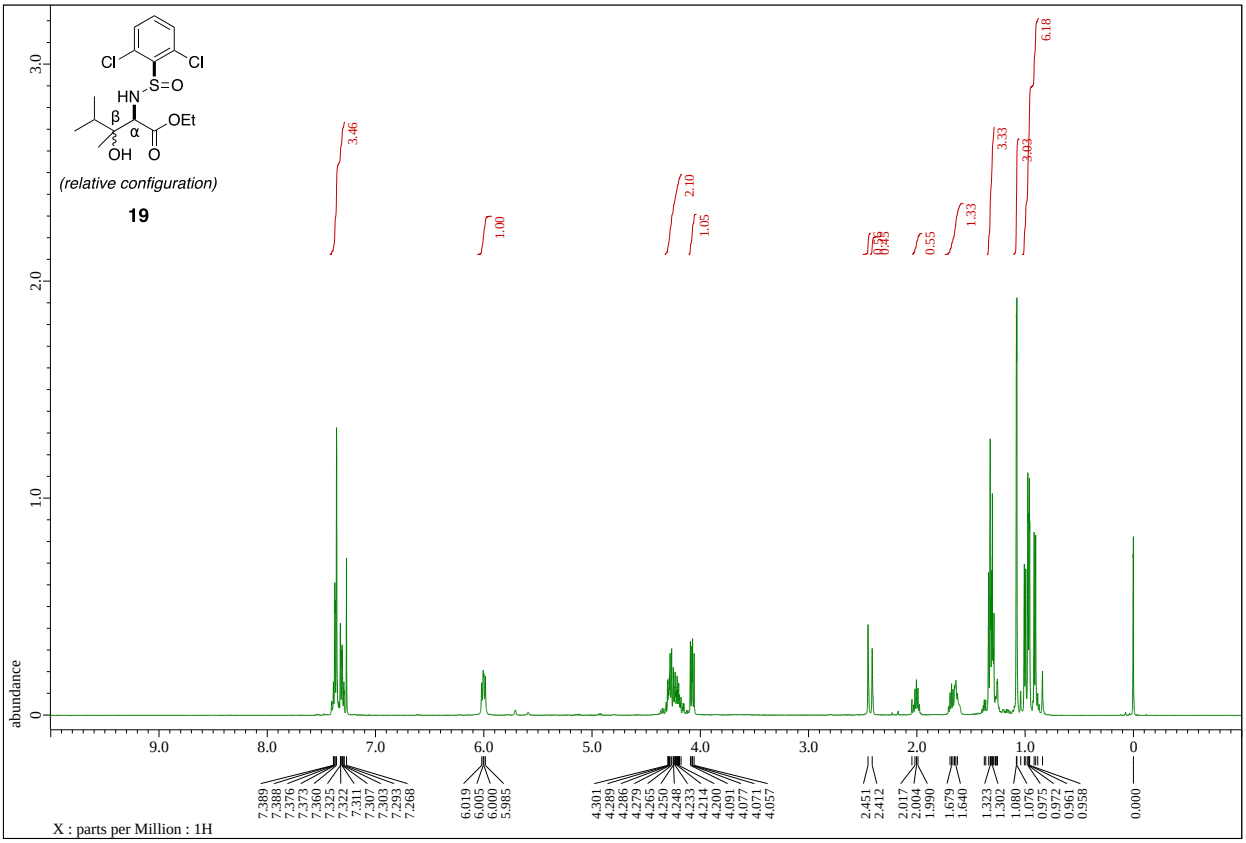
^{1}H-NMR spectra of **18** (500 MHz, $CDCl_3$)



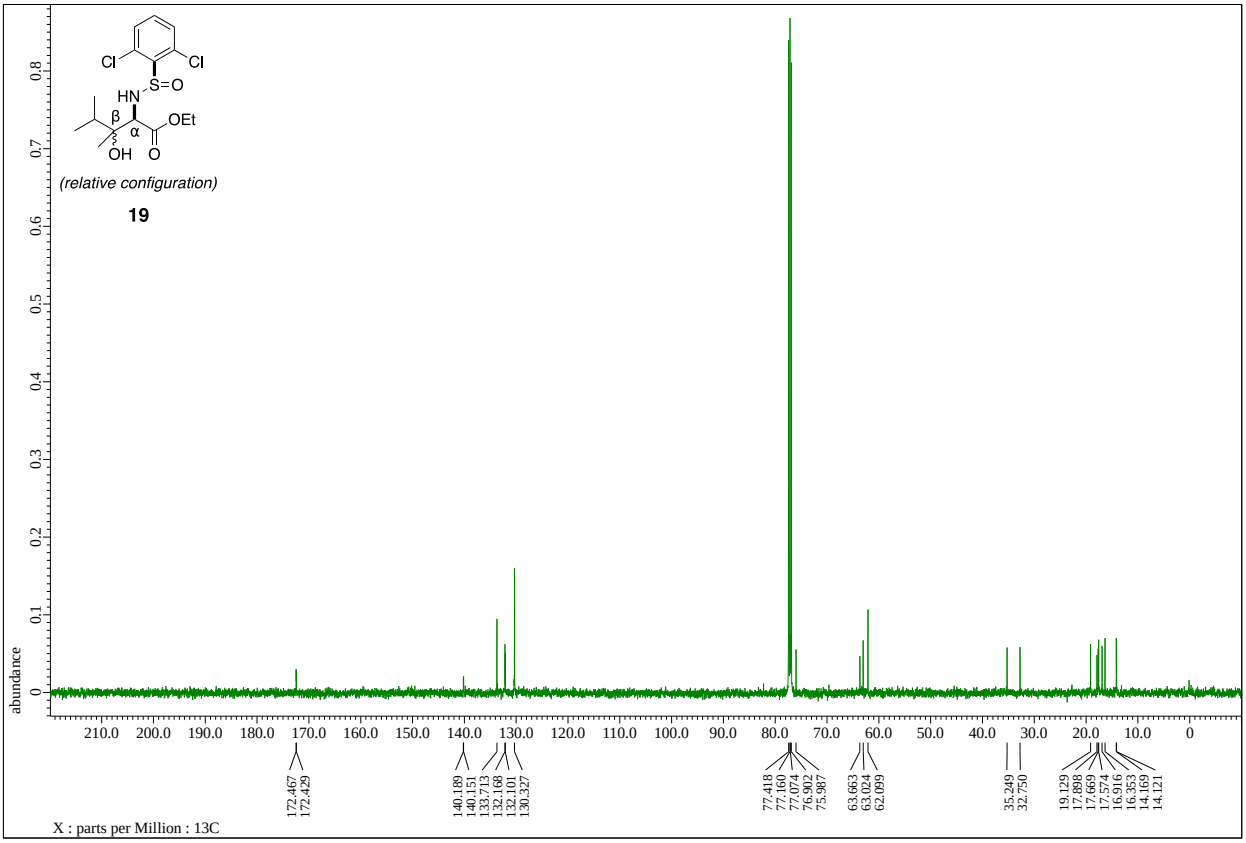
^{13}C-NMR spectra of **18** (126 MHz, $CDCl_3$)



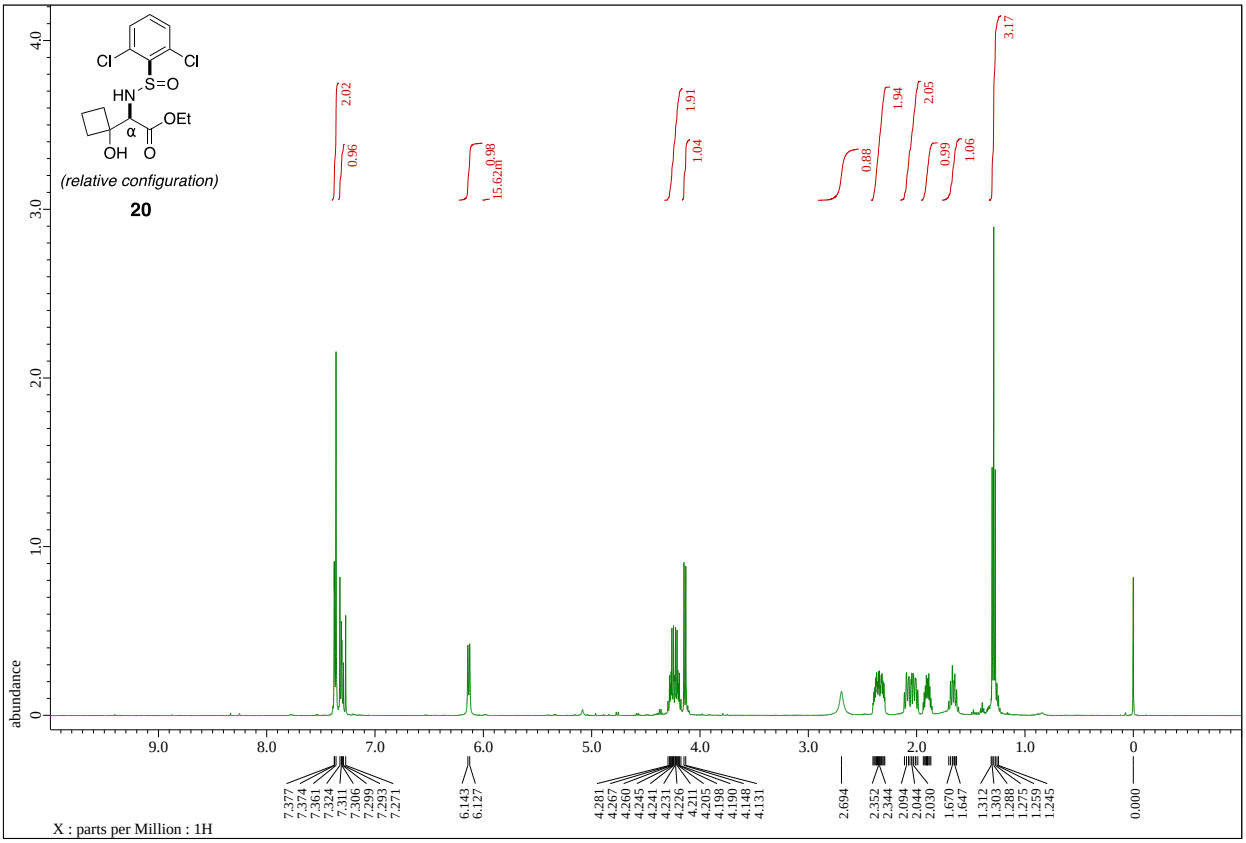
^{1}H-NMR spectra of **19** (500 MHz, $CDCl_3$)



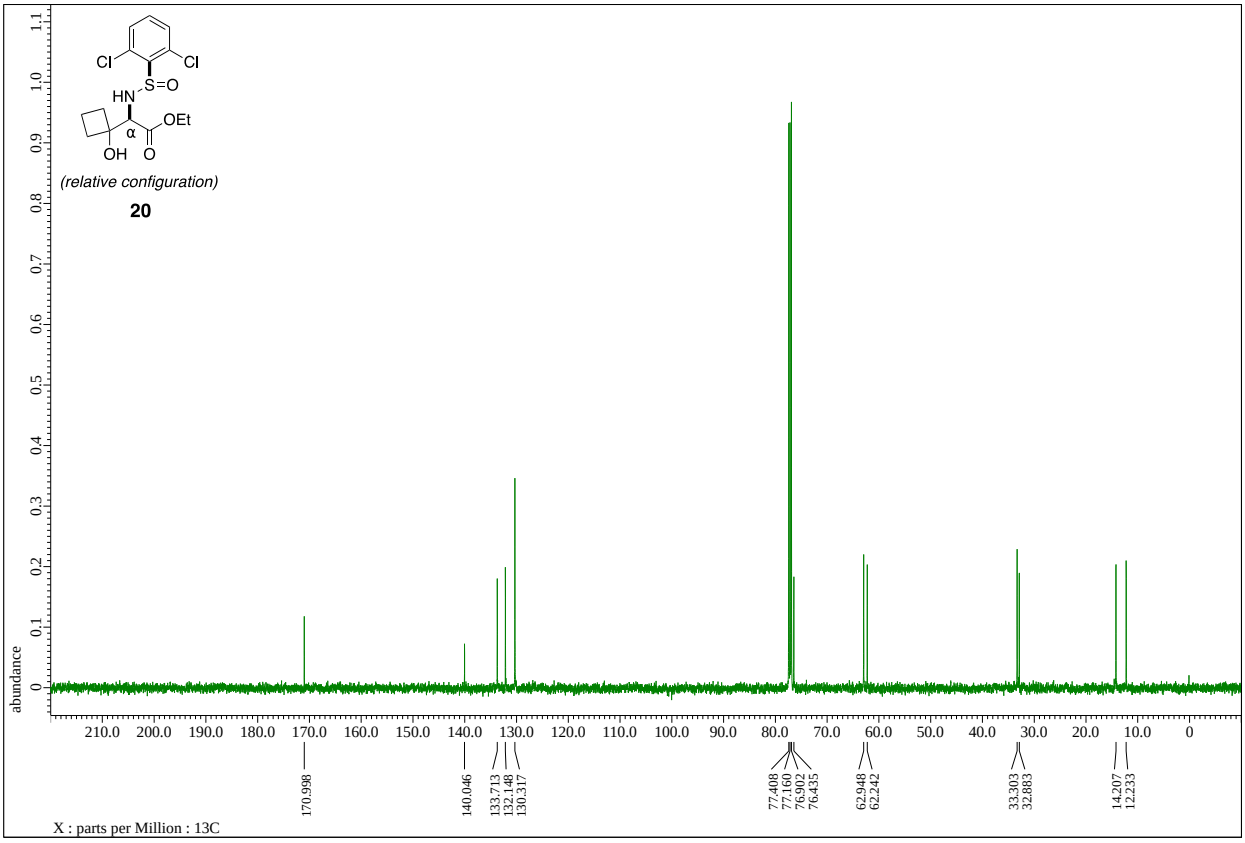
^{13}C-NMR spectra of **19** (126 MHz, $CDCl_3$)



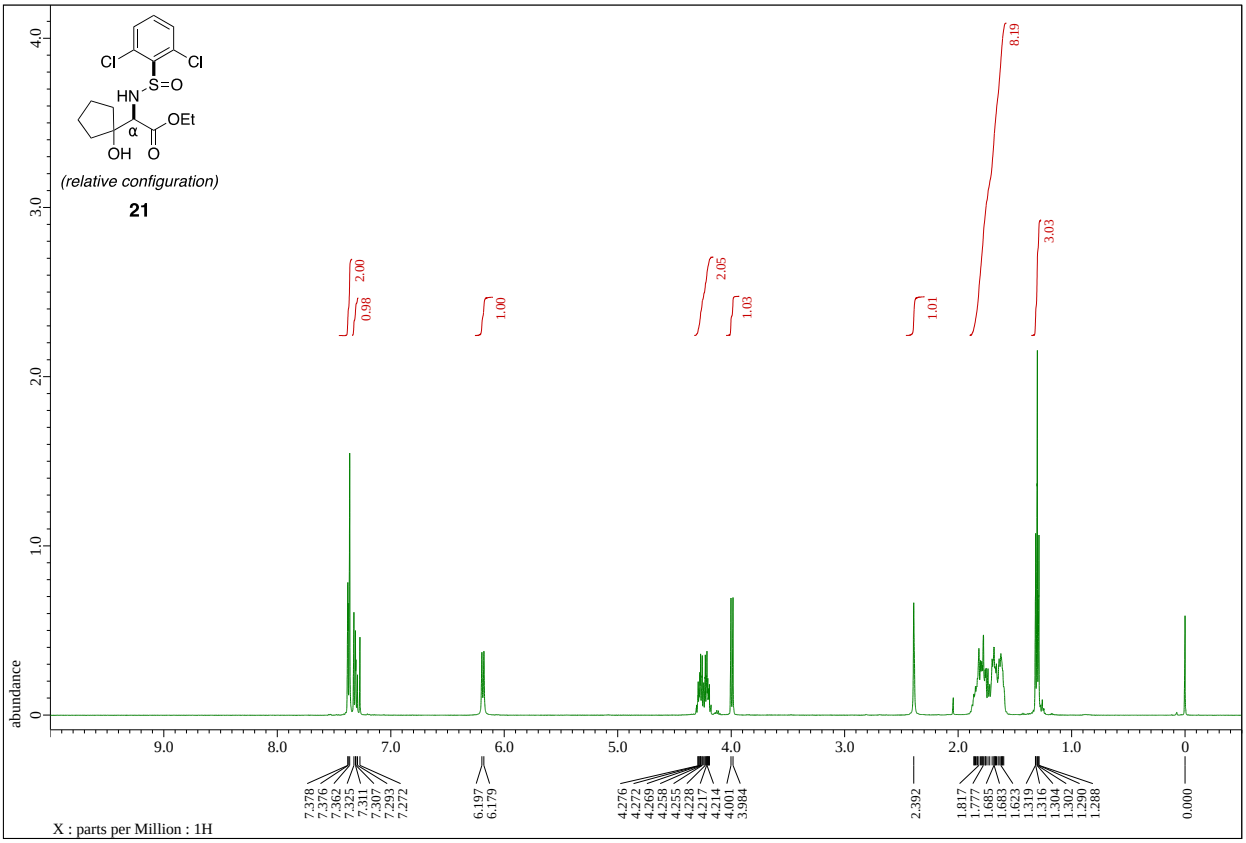
^{1}H-NMR spectra of **20** (500 MHz, $CDCl_3$)



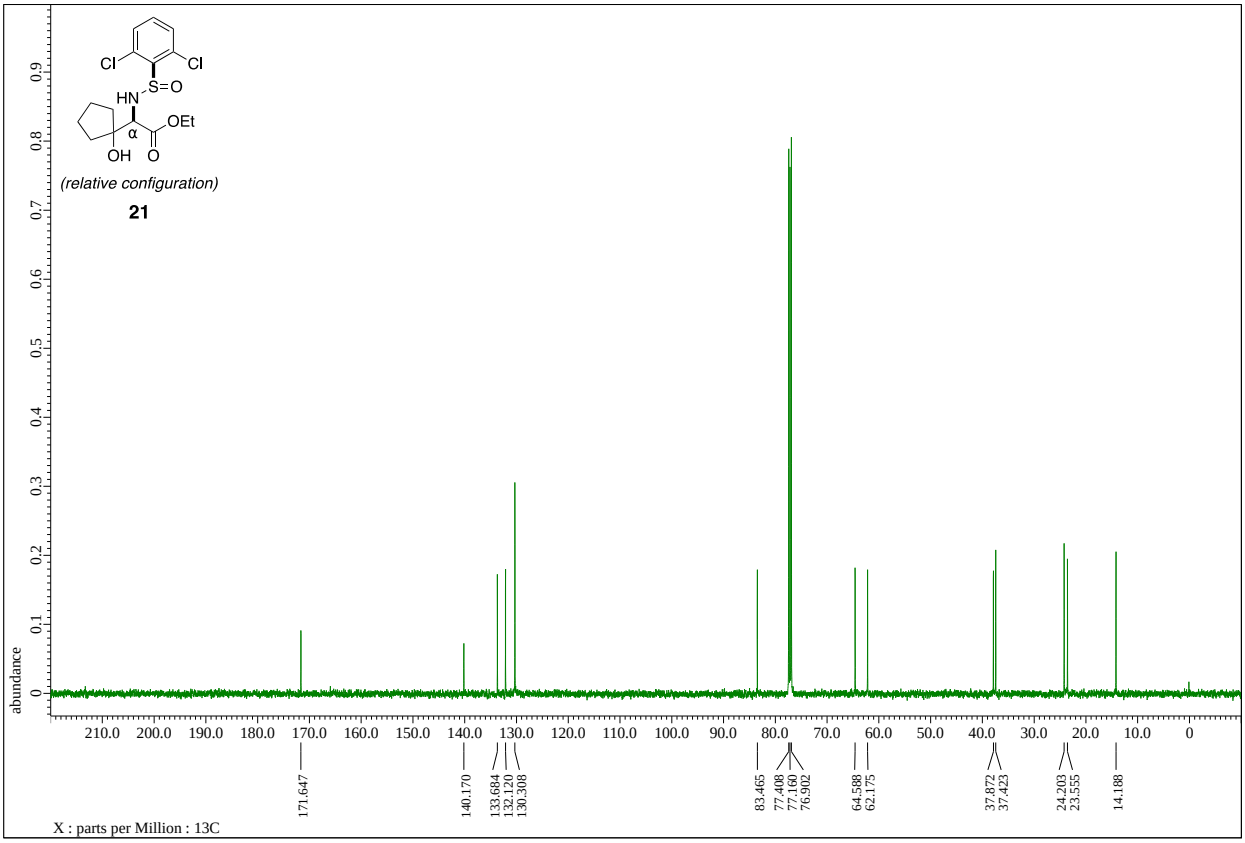
^{13}C-NMR spectra of **20** (126 MHz, $CDCl_3$)



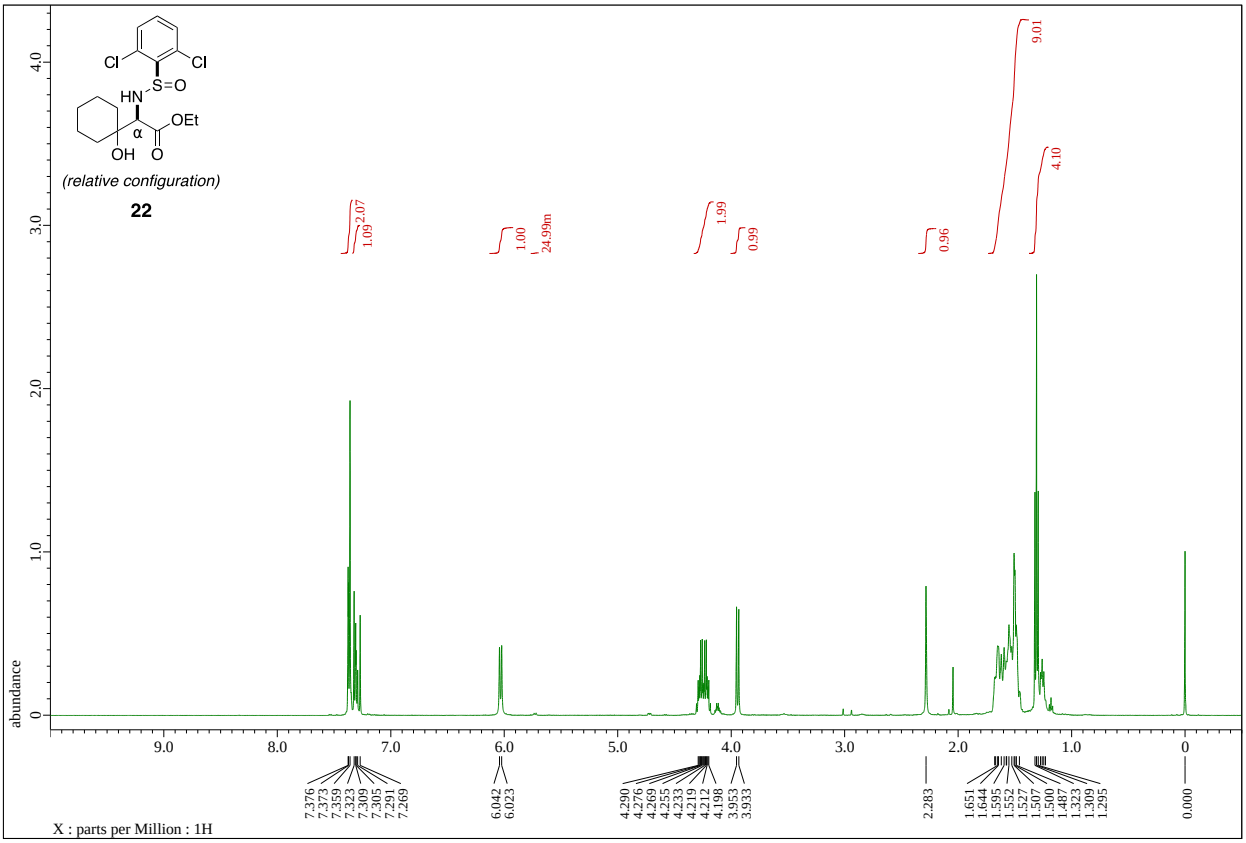
^{1}H-NMR spectra of **21** (500 MHz, $CDCl_3$)



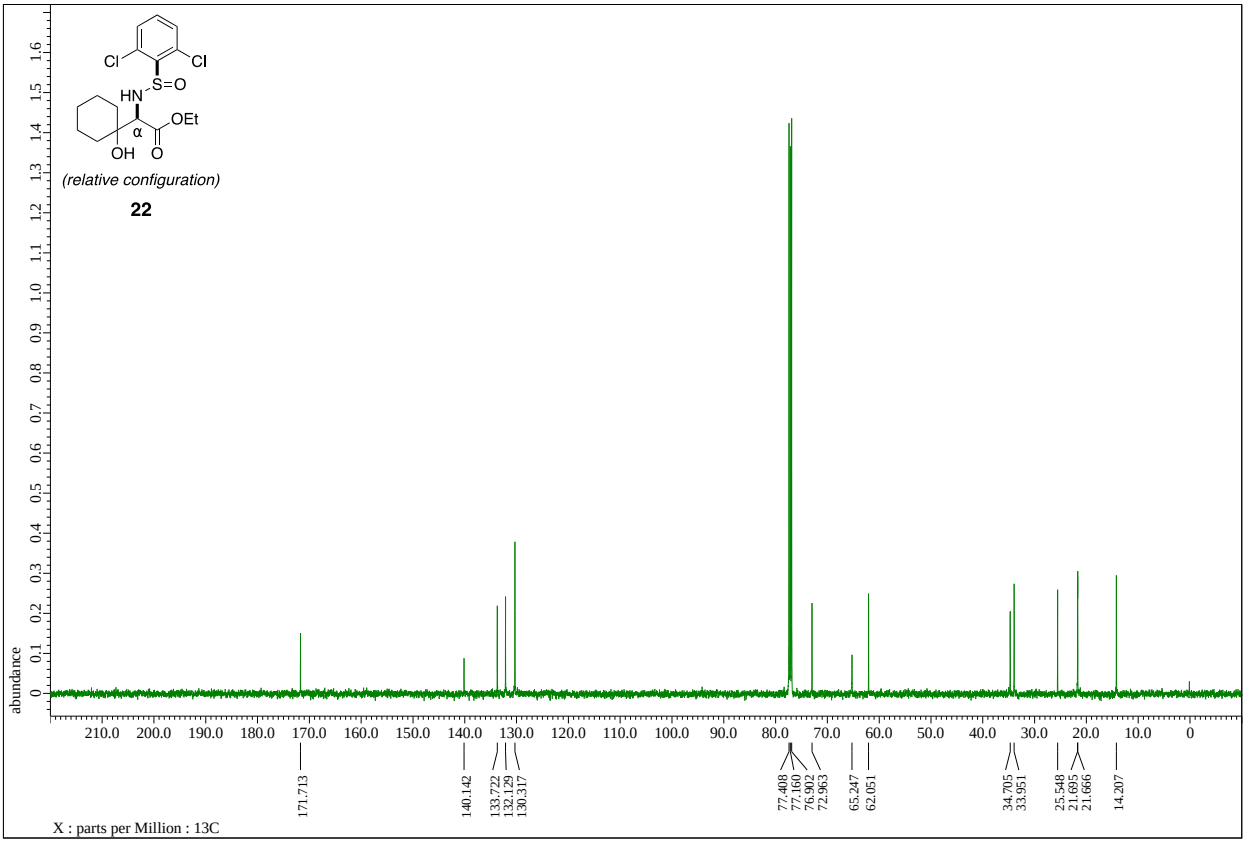
^{13}C-NMR spectra of **21** (126 MHz, $CDCl_3$)



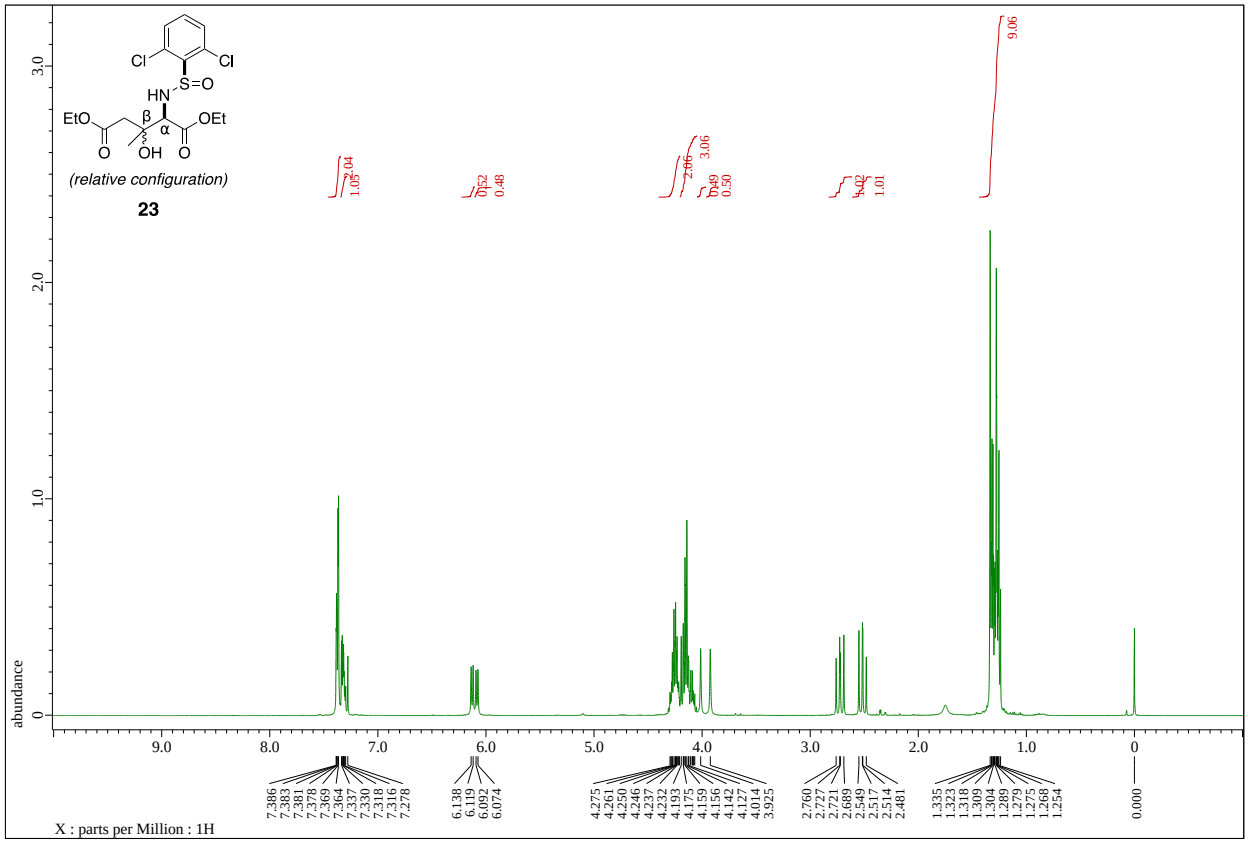
^{1}H-NMR spectra of **22** (500 MHz, $CDCl_3$)



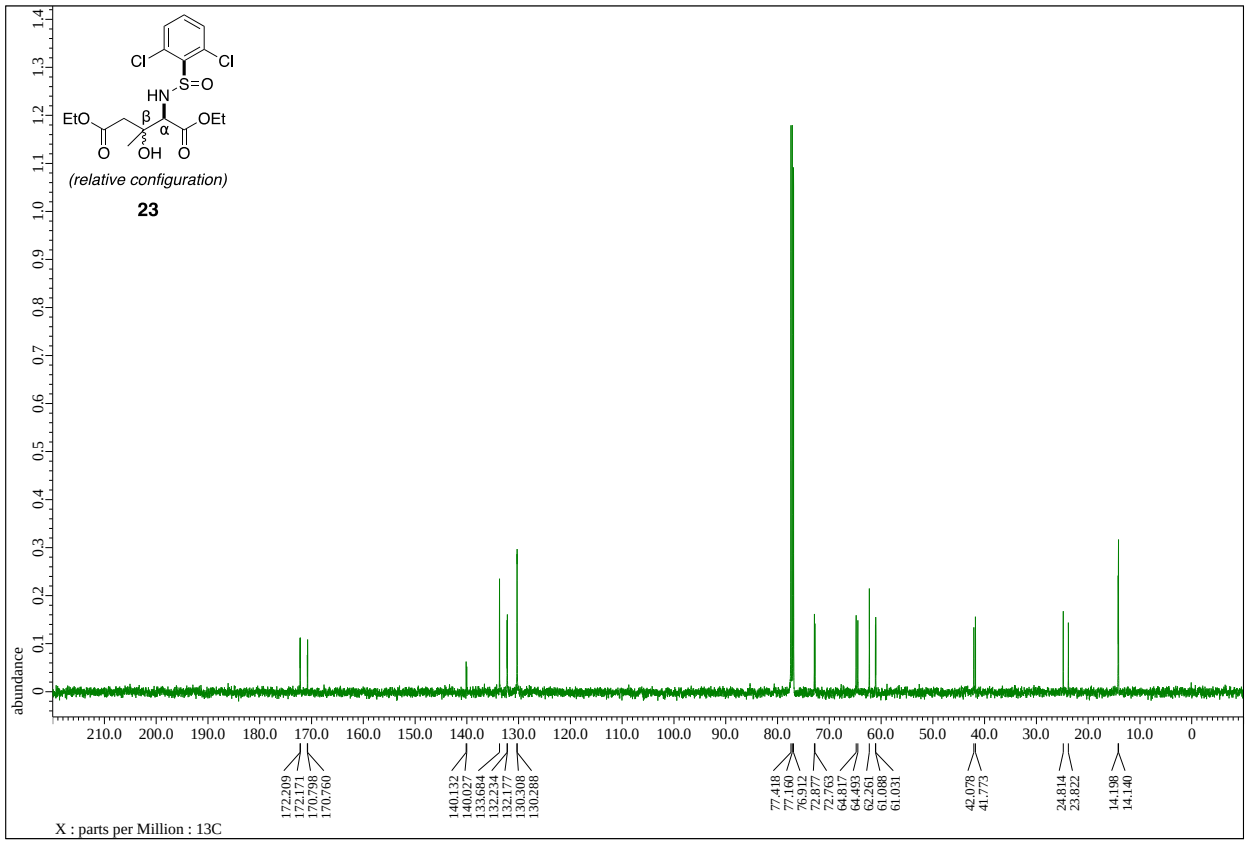
^{13}C-NMR spectra of **22** (126 MHz, $CDCl_3$)



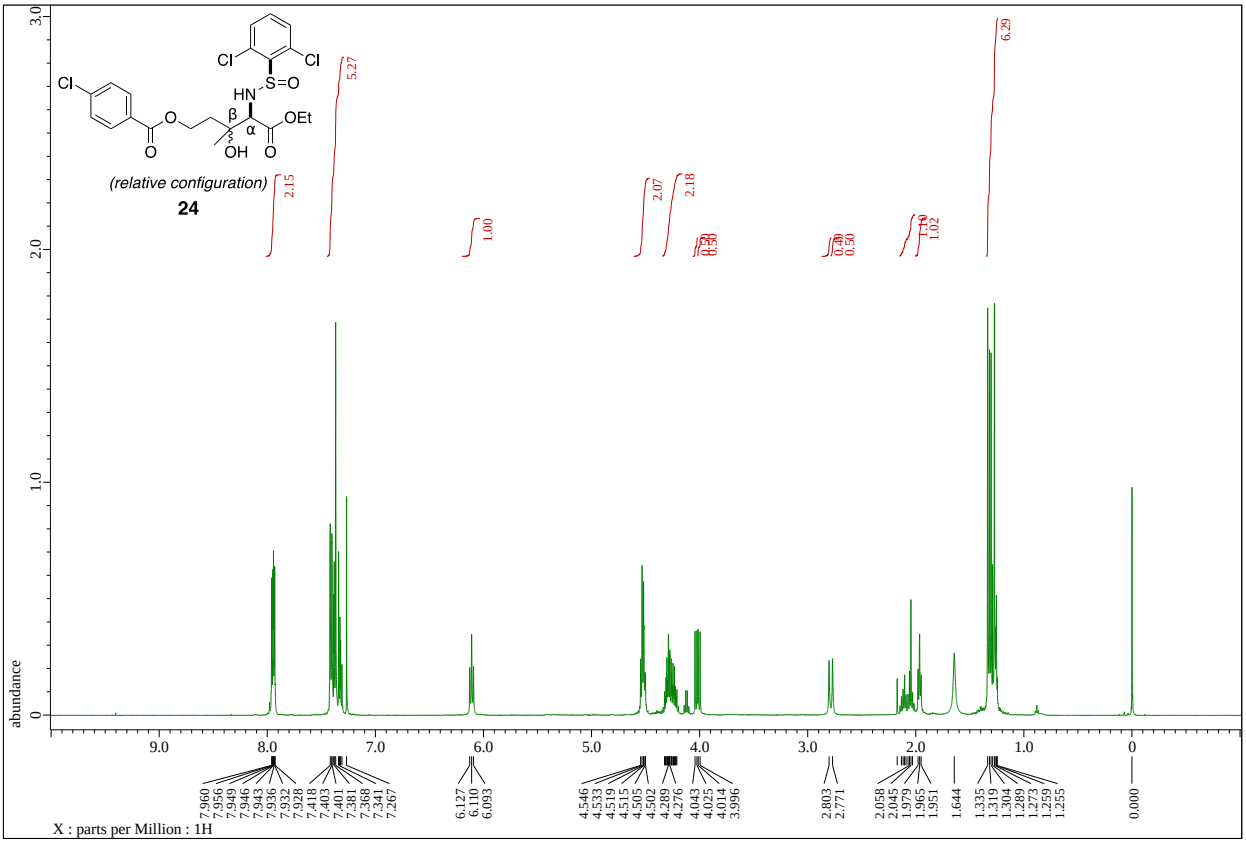
^{1}H-NMR spectra of **23** (500 MHz, $CDCl_3$)



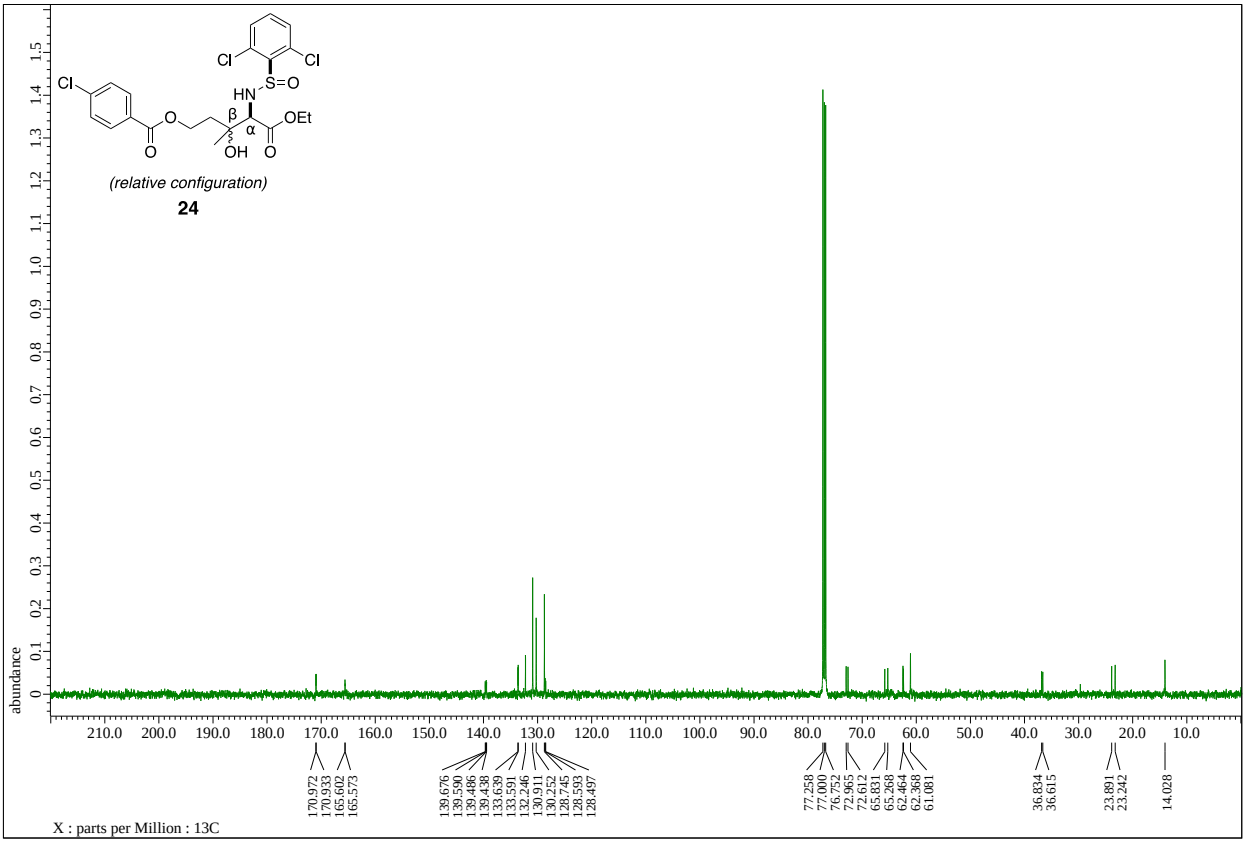
^{13}C-NMR spectra of **23** (126 MHz, $CDCl_3$)



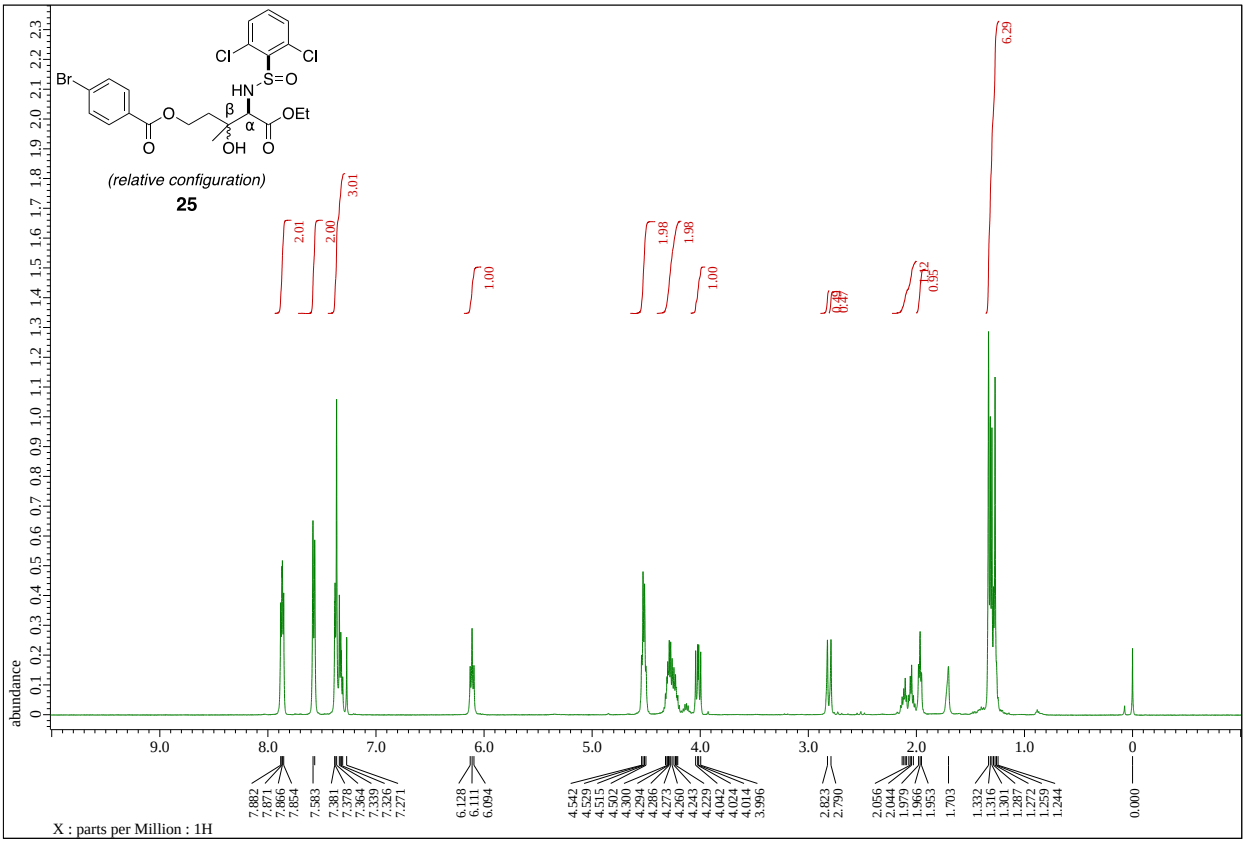
^{1}H-NMR spectra of **24** (500 MHz, $CDCl_3$)



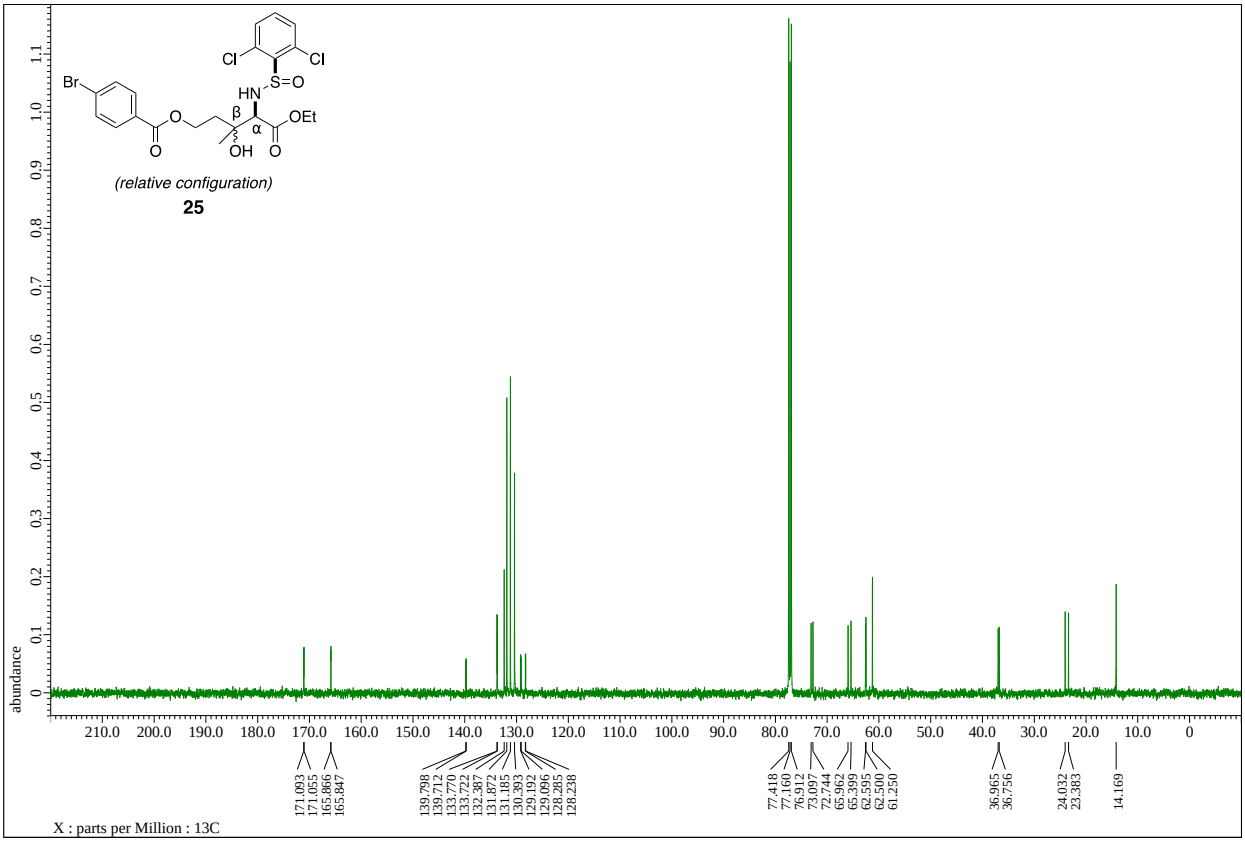
^{13}C-NMR spectra of **24** (126 MHz, $CDCl_3$)



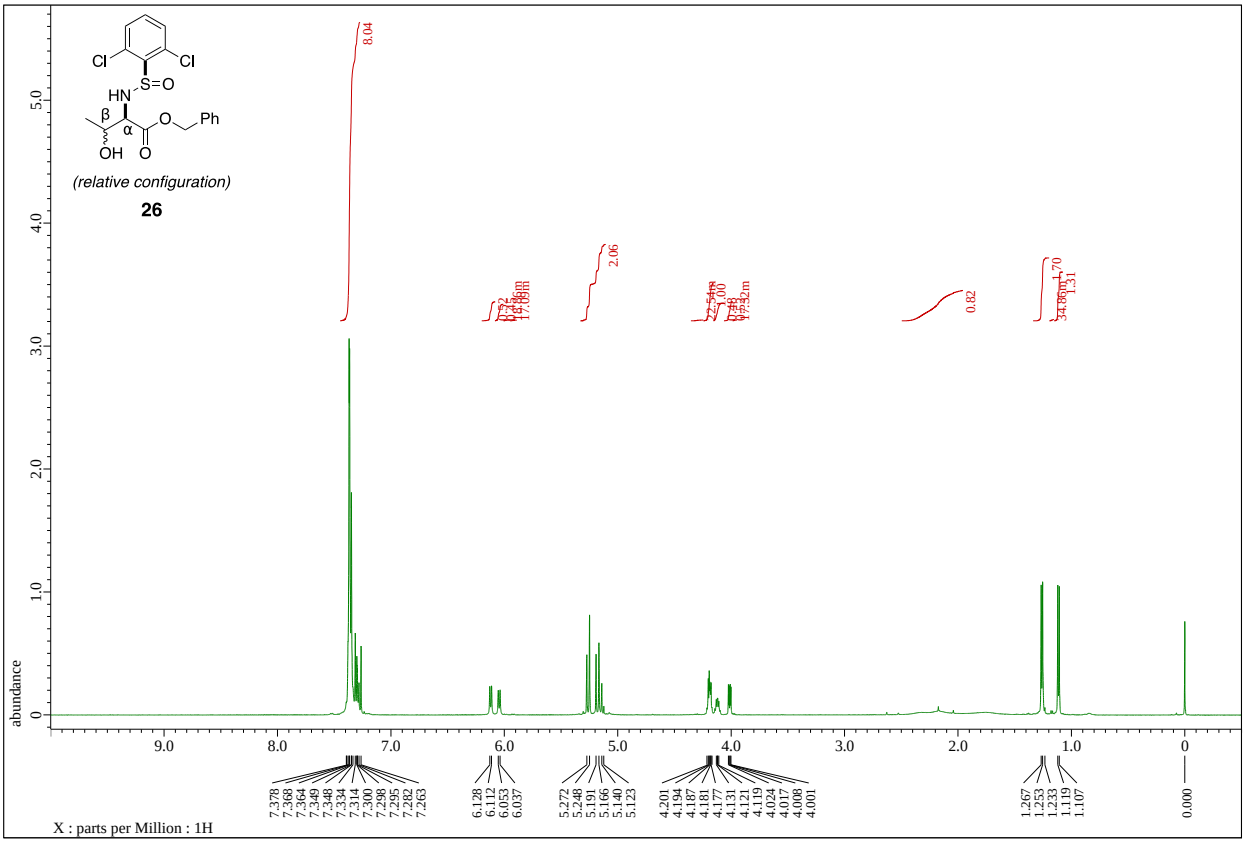
^{1}H-NMR spectra of **25** (500 MHz, $CDCl_3$)



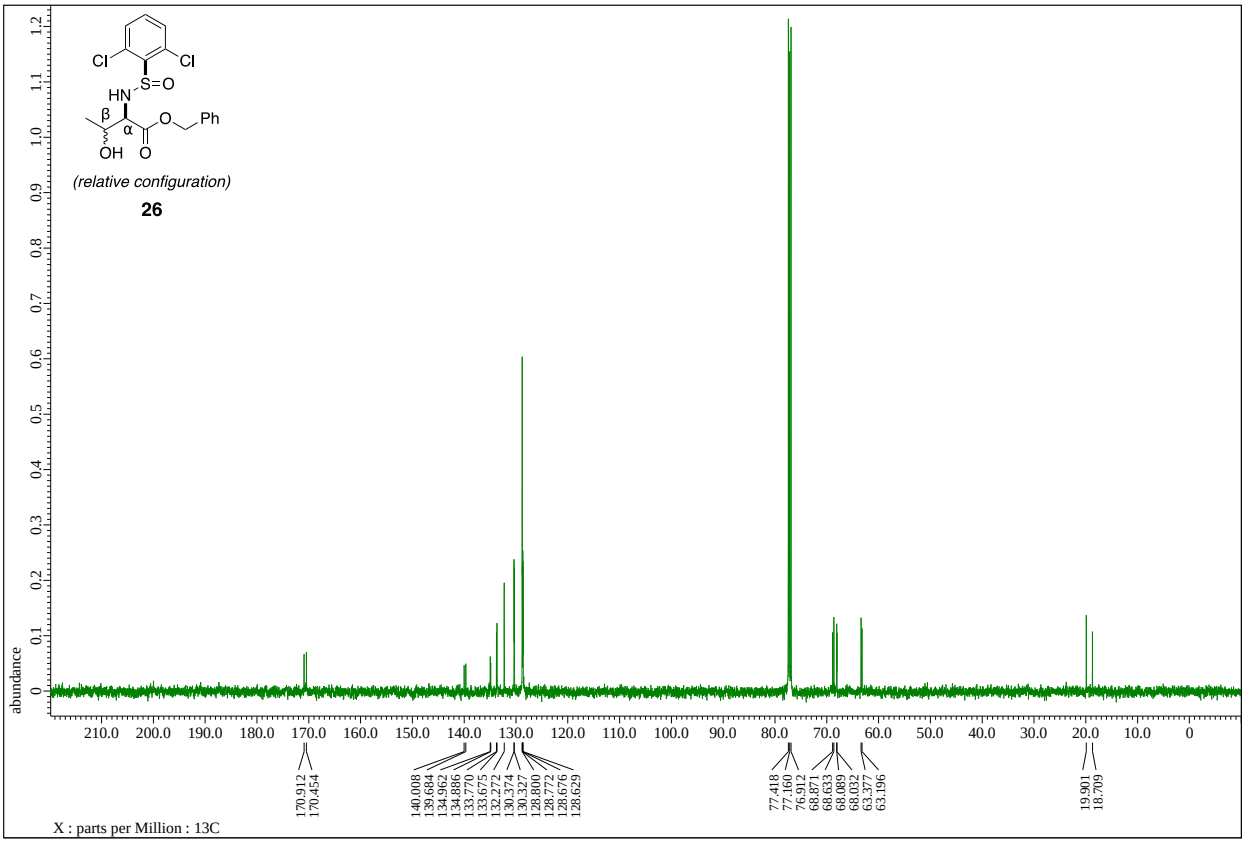
^{13}C-NMR spectra of **25** (126 MHz, $CDCl_3$)



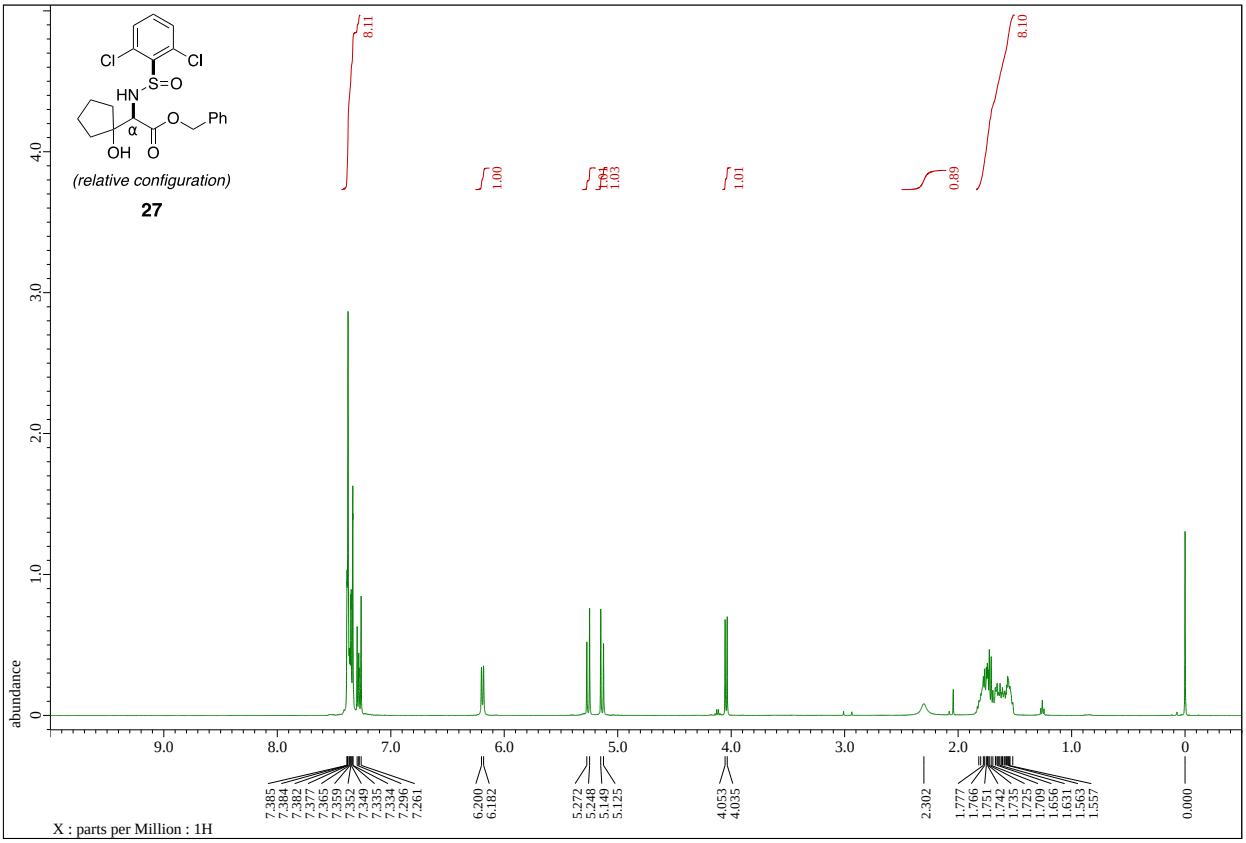
^{1}H-NMR spectra of **26** (500 MHz, $CDCl_3$)



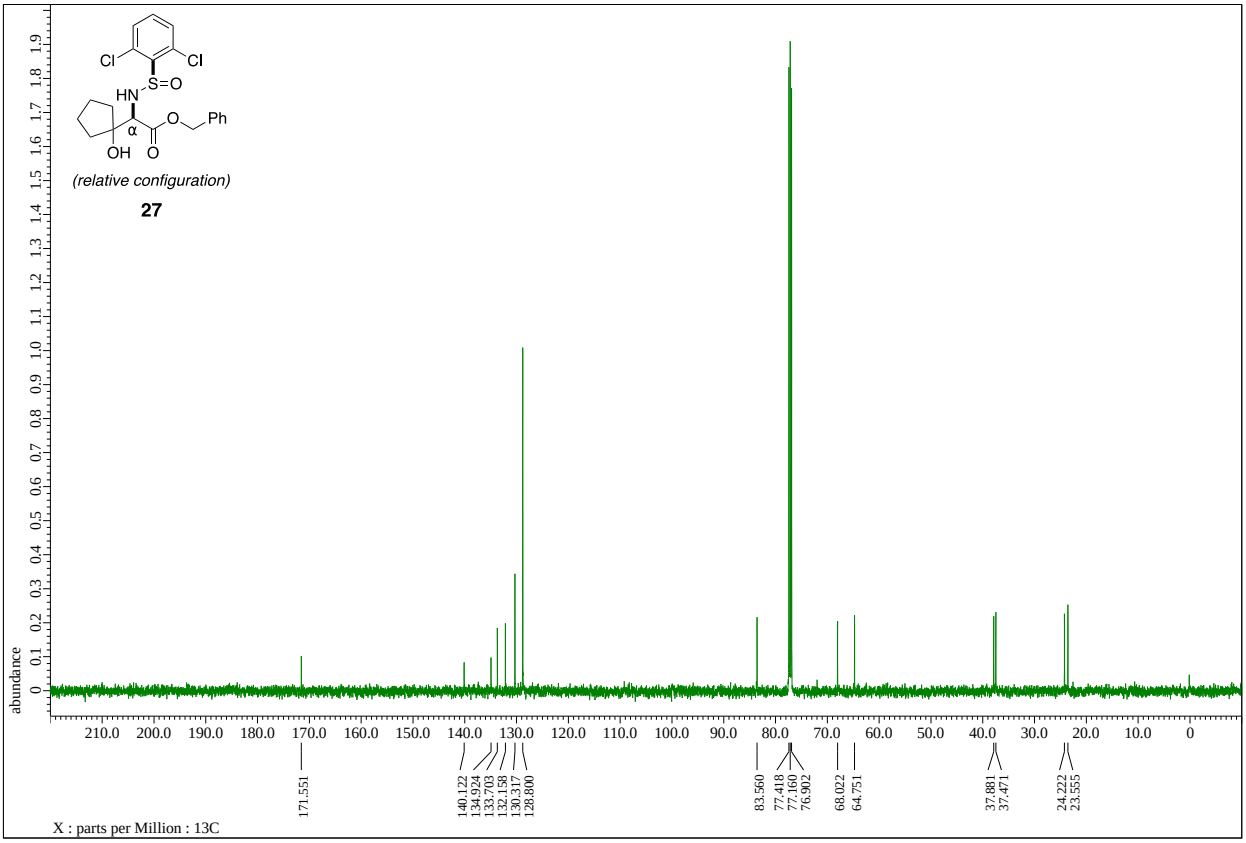
^{13}C-NMR spectra of **26** (126 MHz, $CDCl_3$)



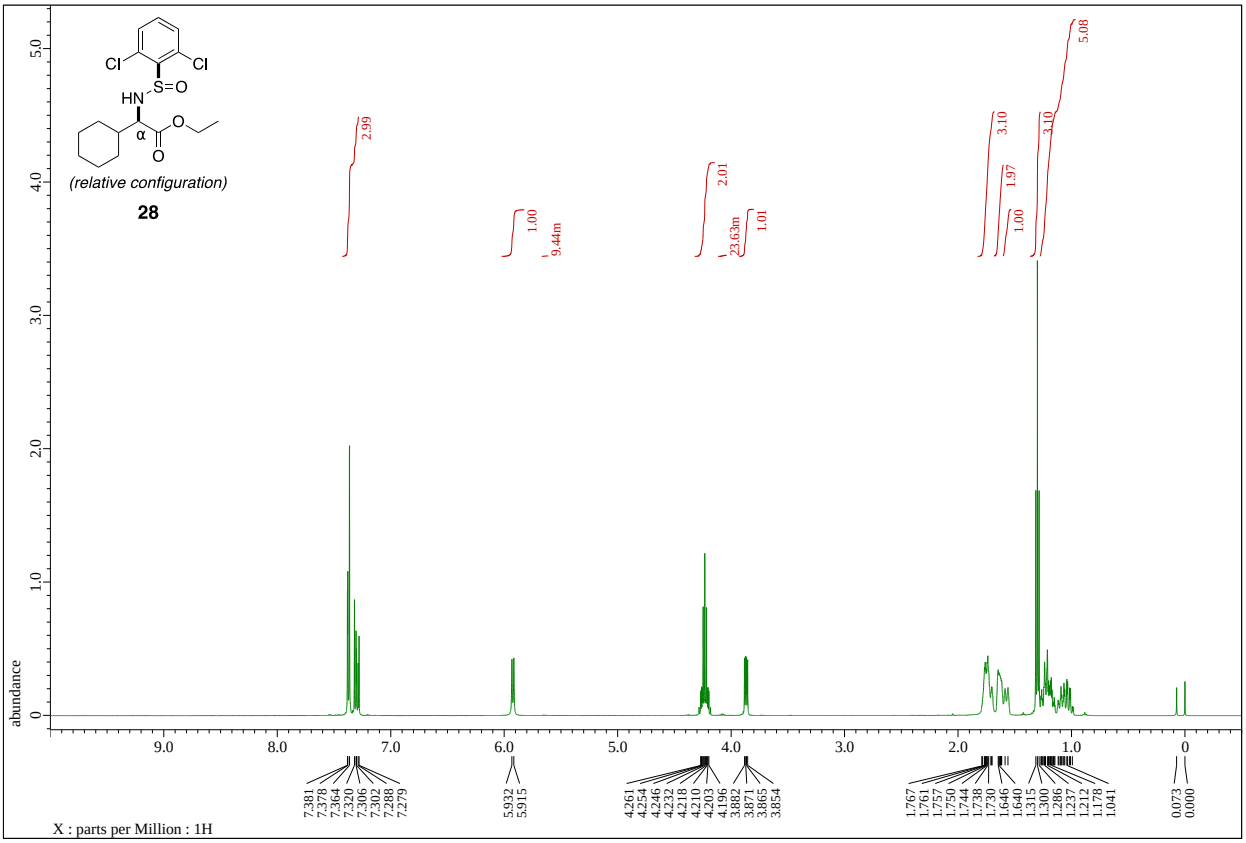
^{1}H-NMR spectra of **27** (500 MHz, $CDCl_3$)



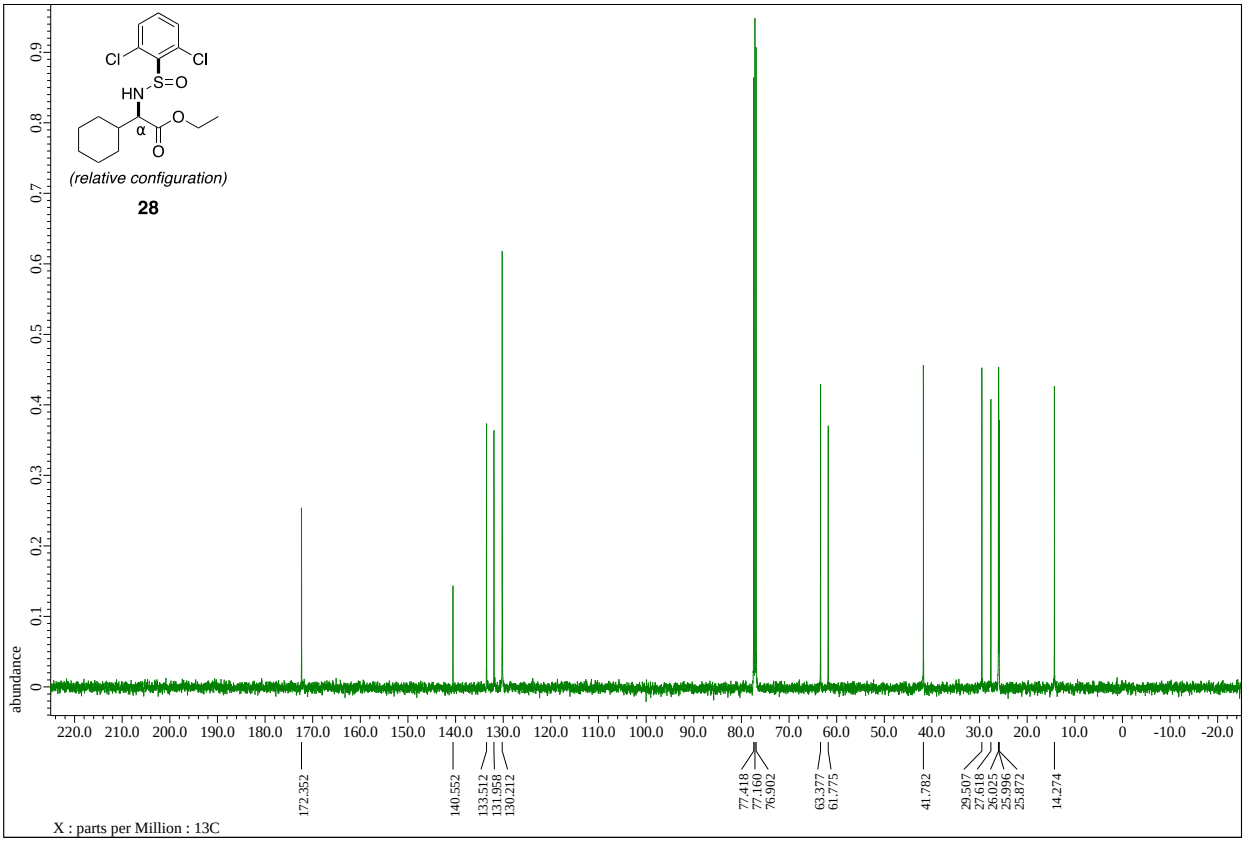
^{13}C-NMR spectra of **27** (126 MHz, $CDCl_3$)



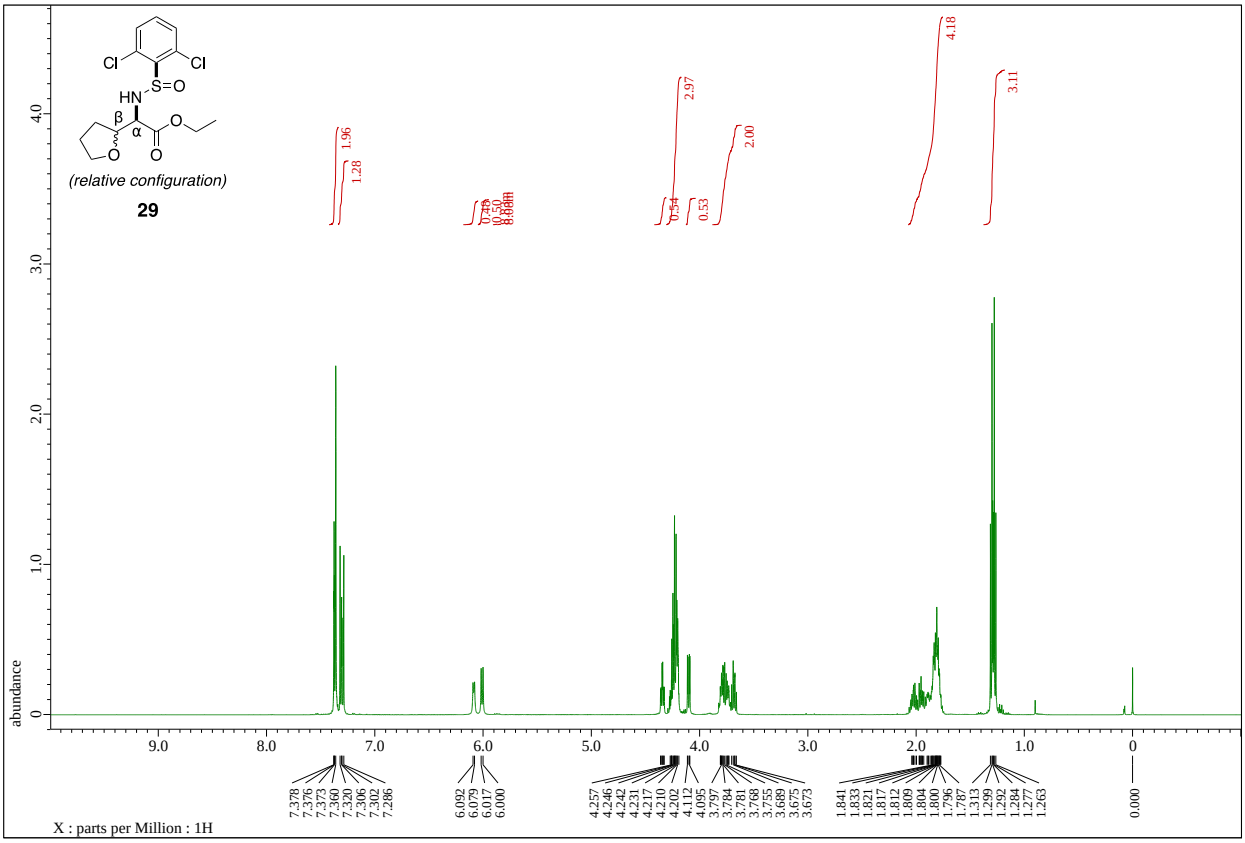
^{1}H-NMR spectra of **28** (500 MHz, $CDCl_3$)



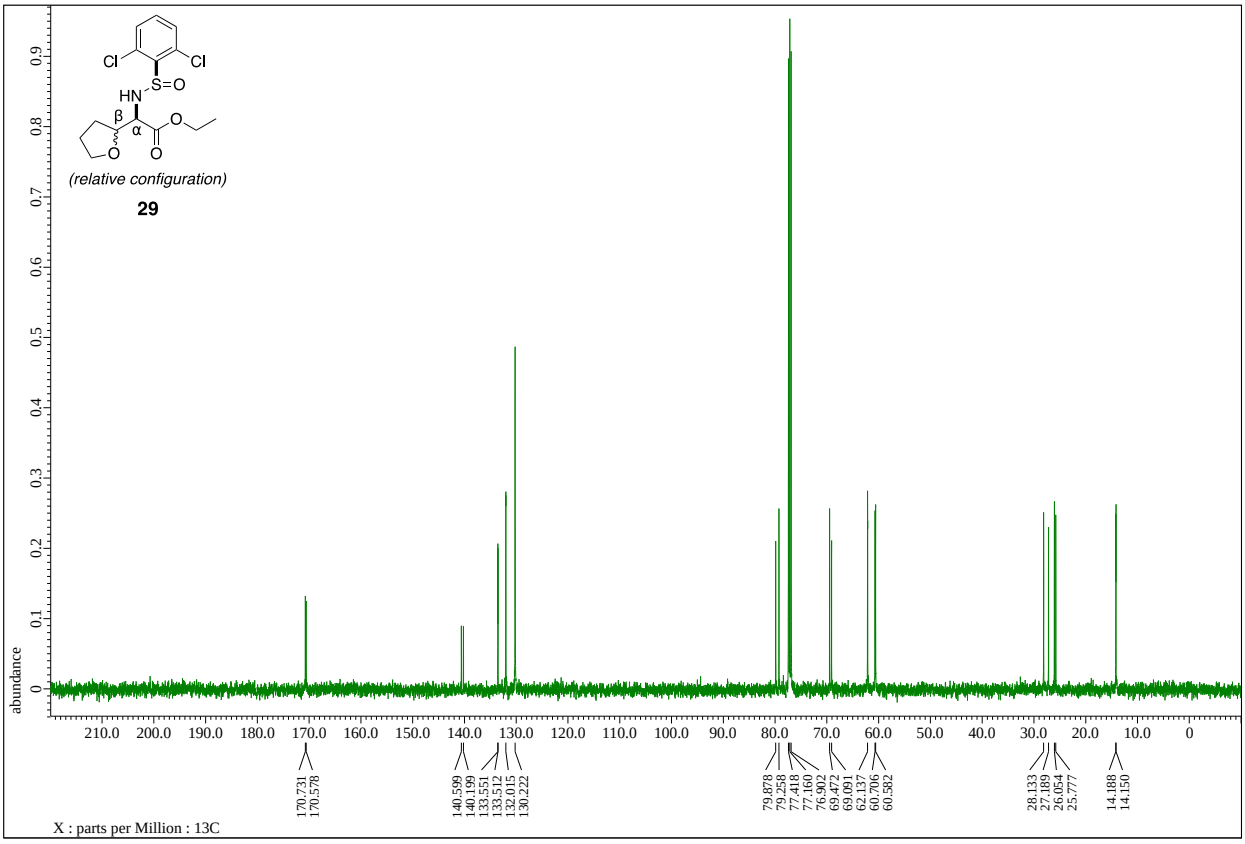
^{13}C-NMR spectra of **28** (126 MHz, $CDCl_3$)



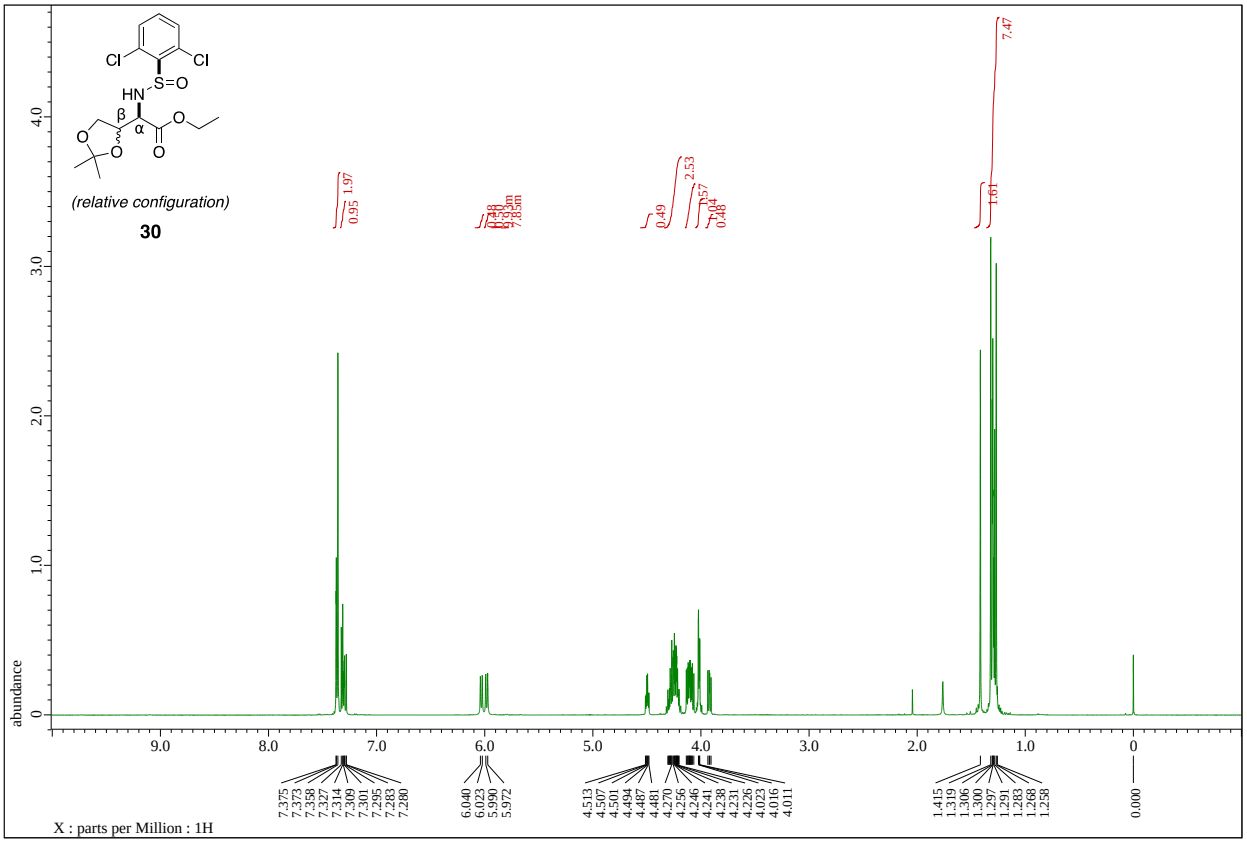
^{1}H-NMR spectra of **29** (500 MHz, $CDCl_3$)



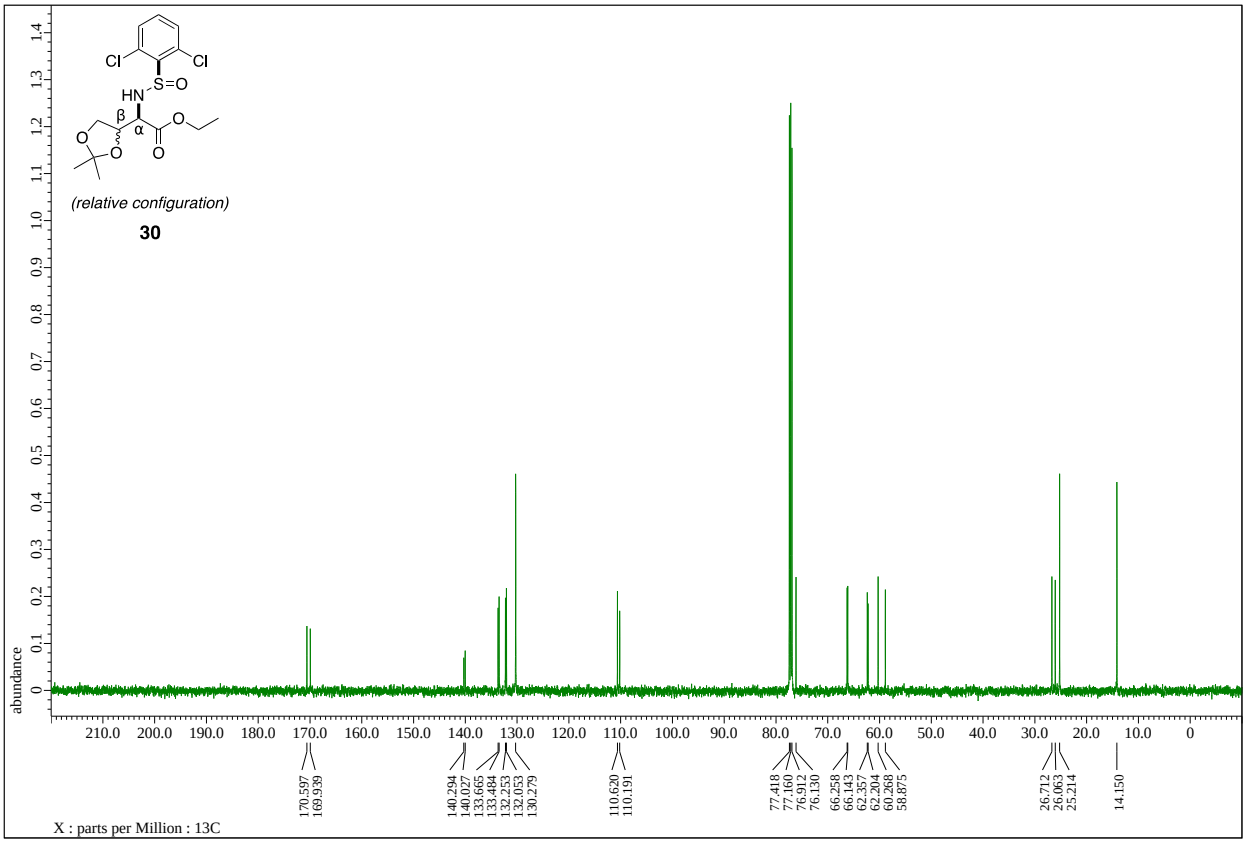
^{13}C-NMR spectra of **29** (126 MHz, $CDCl_3$)



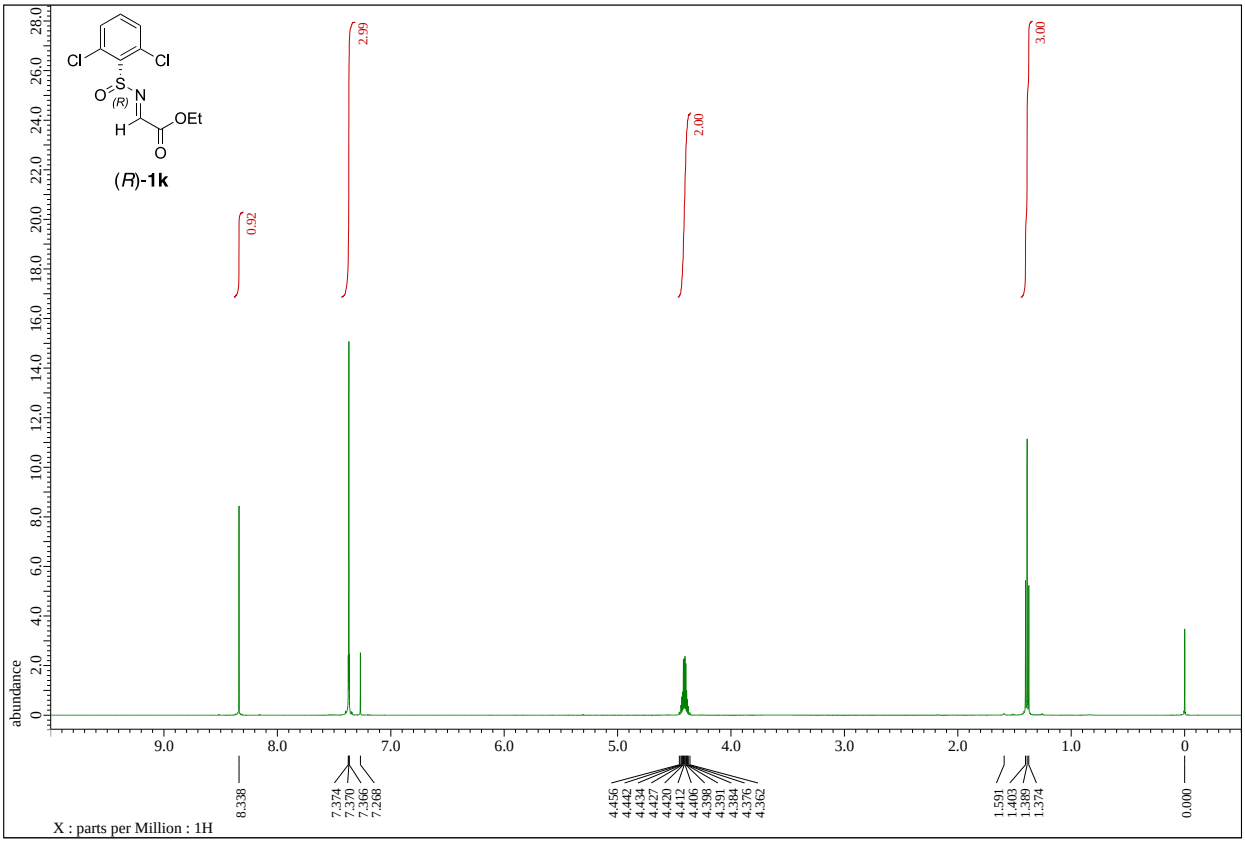
^{1}H-NMR spectra of **30** (500 MHz, $CDCl_3$)



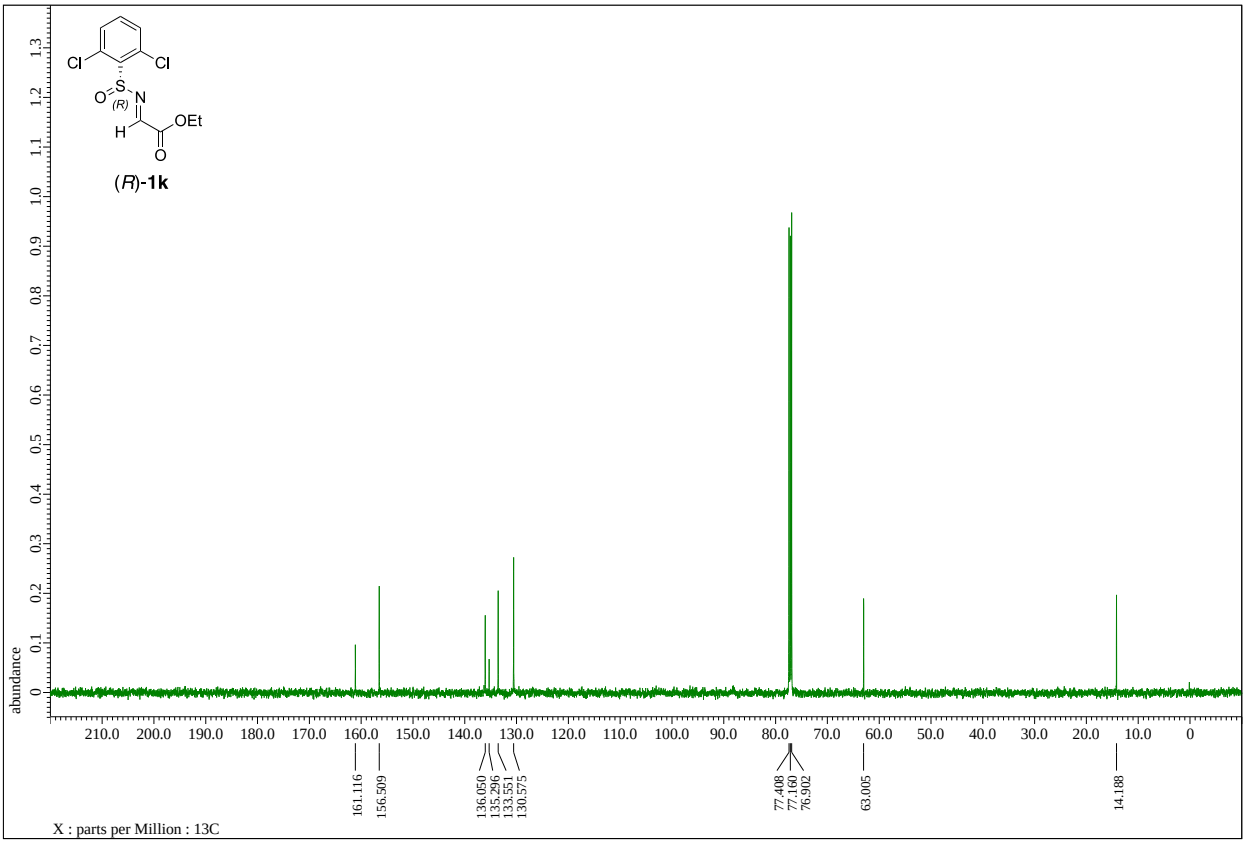
^{13}C-NMR spectra of **30** (126 MHz, $CDCl_3$)



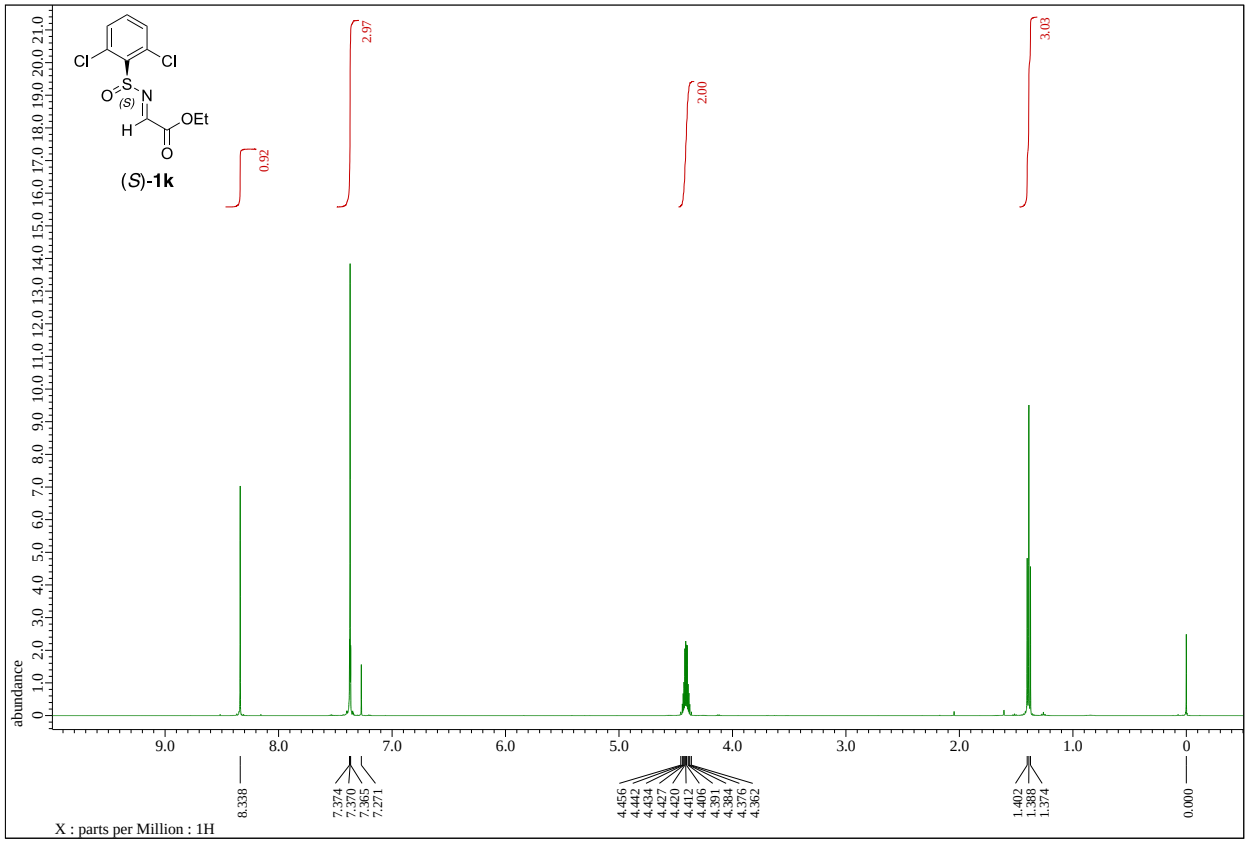
^{1}H-NMR spectra of (*R*)-**1k** (500 MHz, $CDCl_3$)



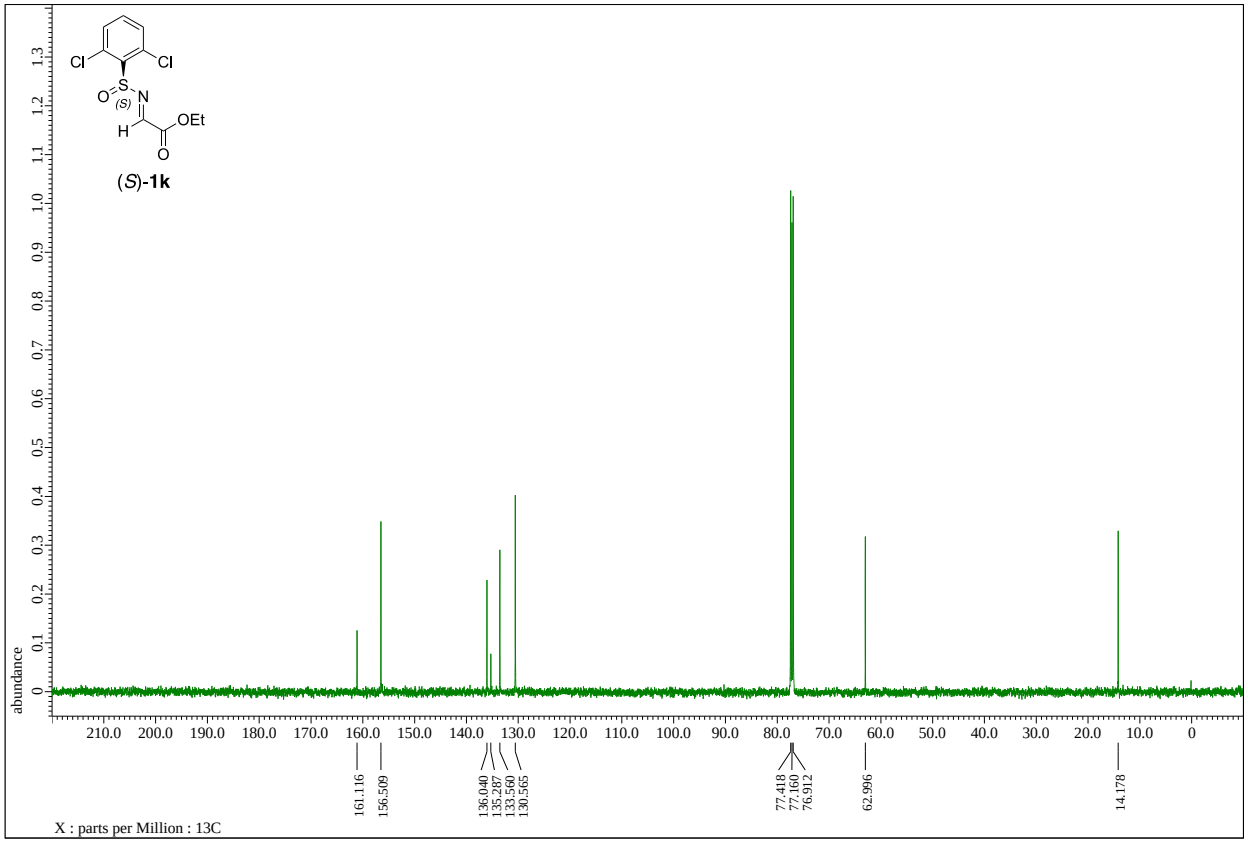
^{13}C-NMR spectra of (*R*)-**1k** (126 MHz, $CDCl_3$)



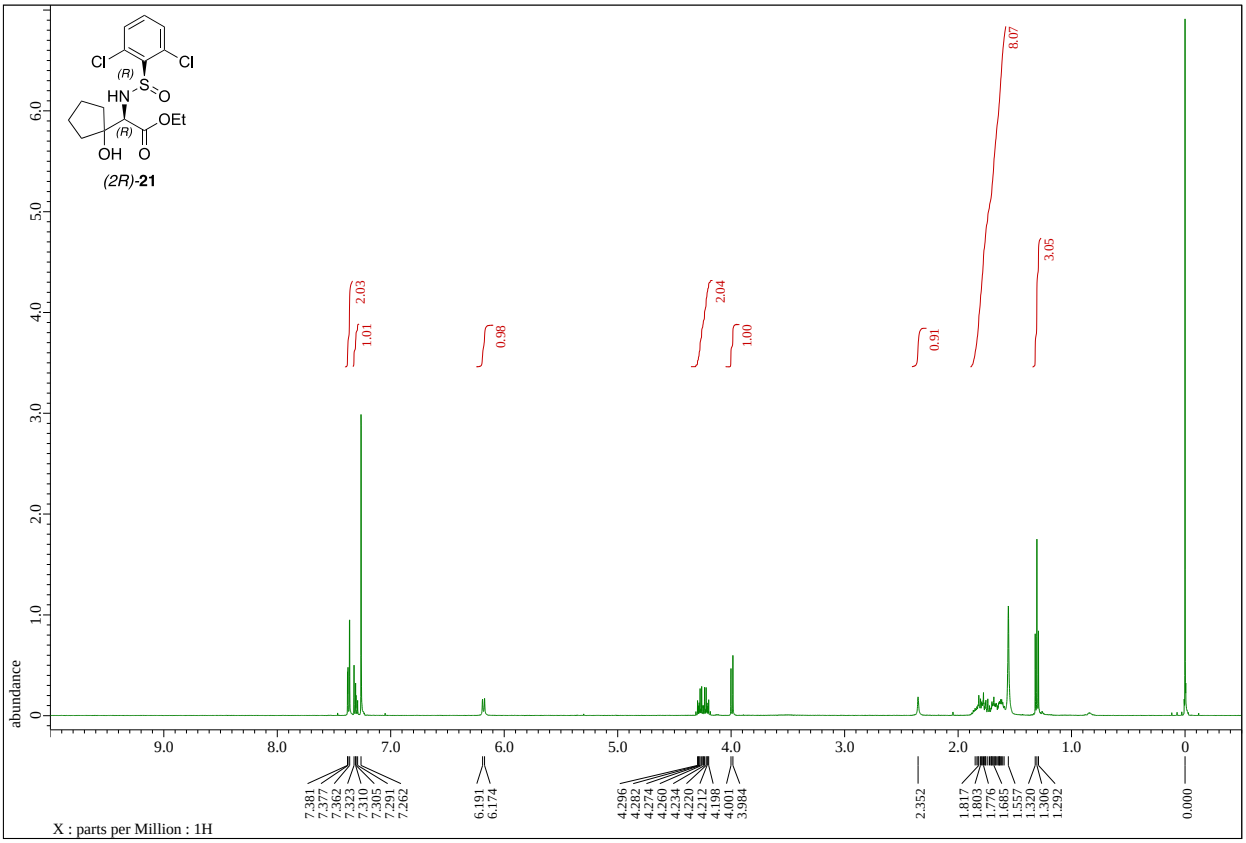
^{1}H-NMR spectra of (*S*)-**1k** (500 MHz, $CDCl_3$)



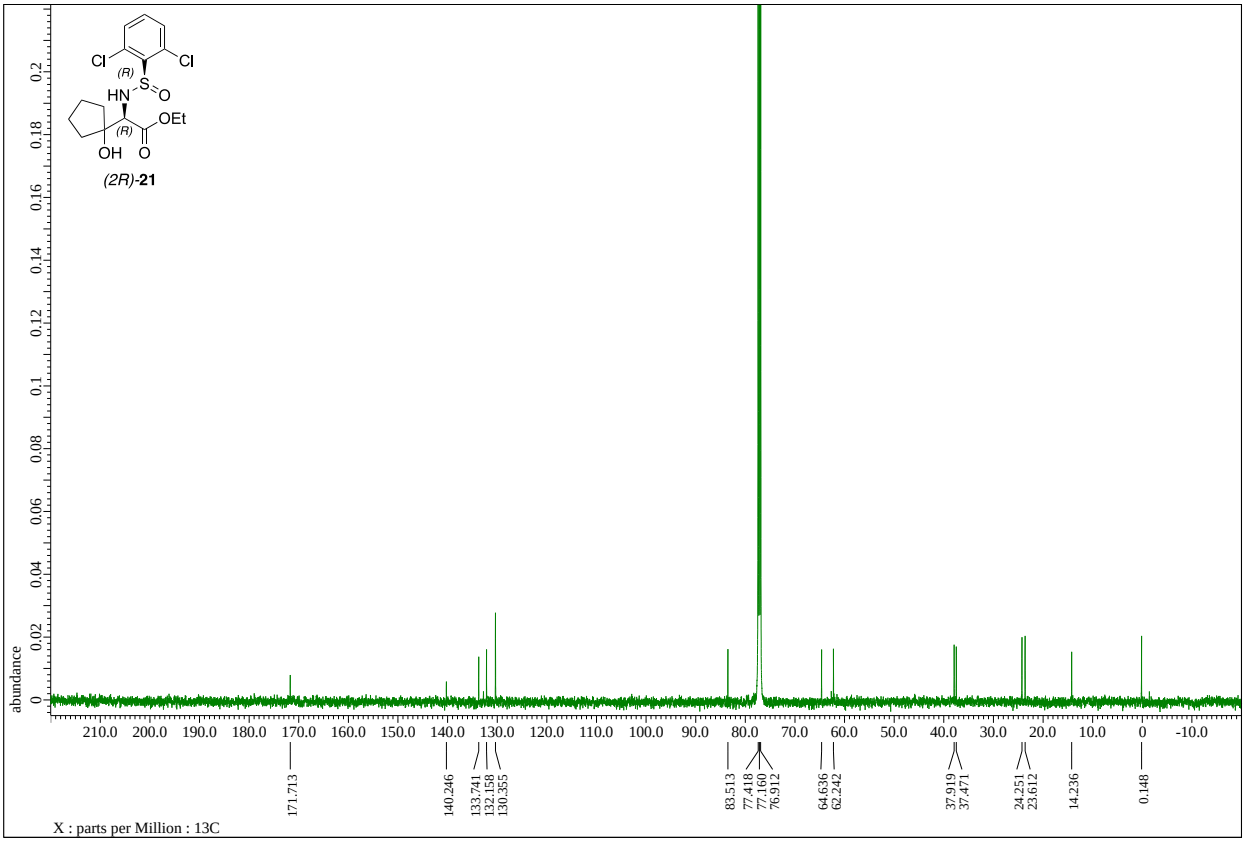
^{13}C-NMR spectra of (*S*)-**1k** (126 MHz, $CDCl_3$)



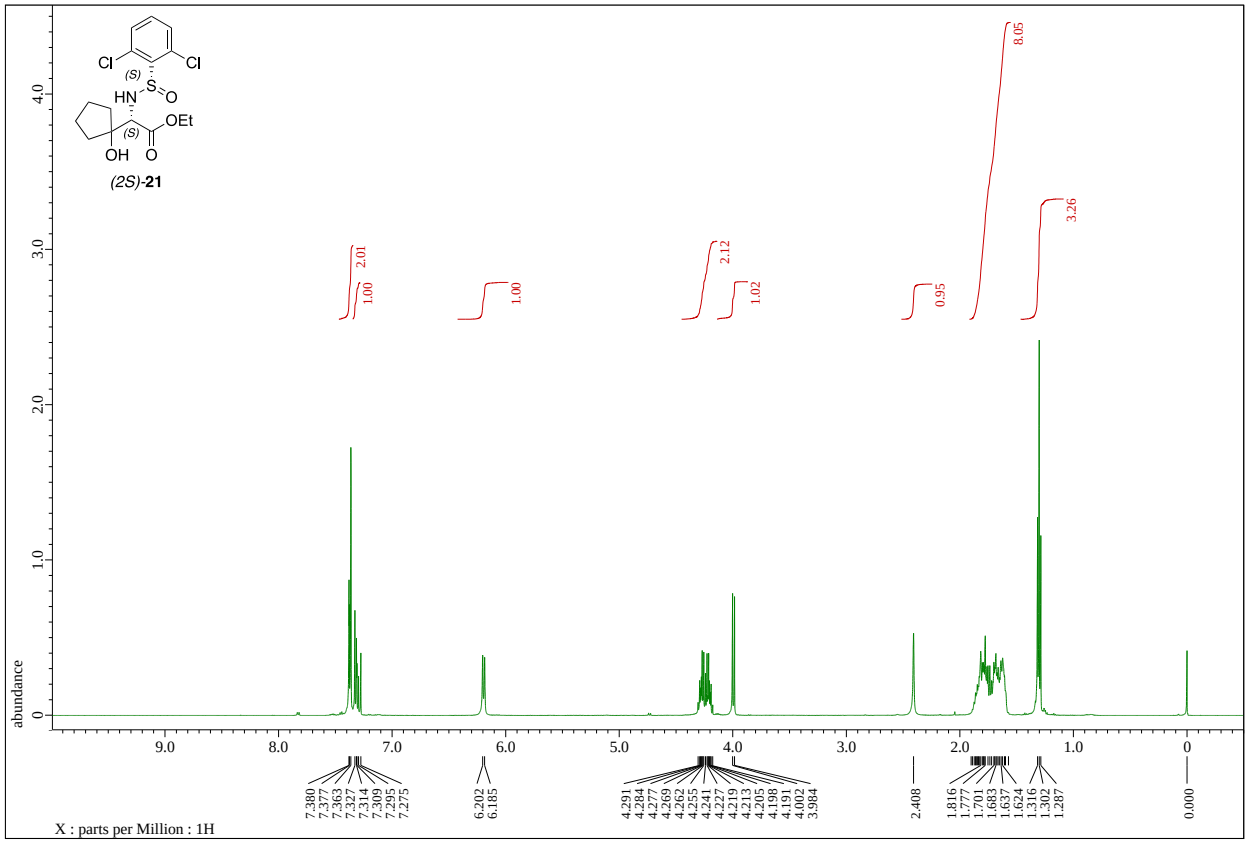
^{1}H-NMR spectra of (2*R*)-**21** (500 MHz, $CDCl_3$)



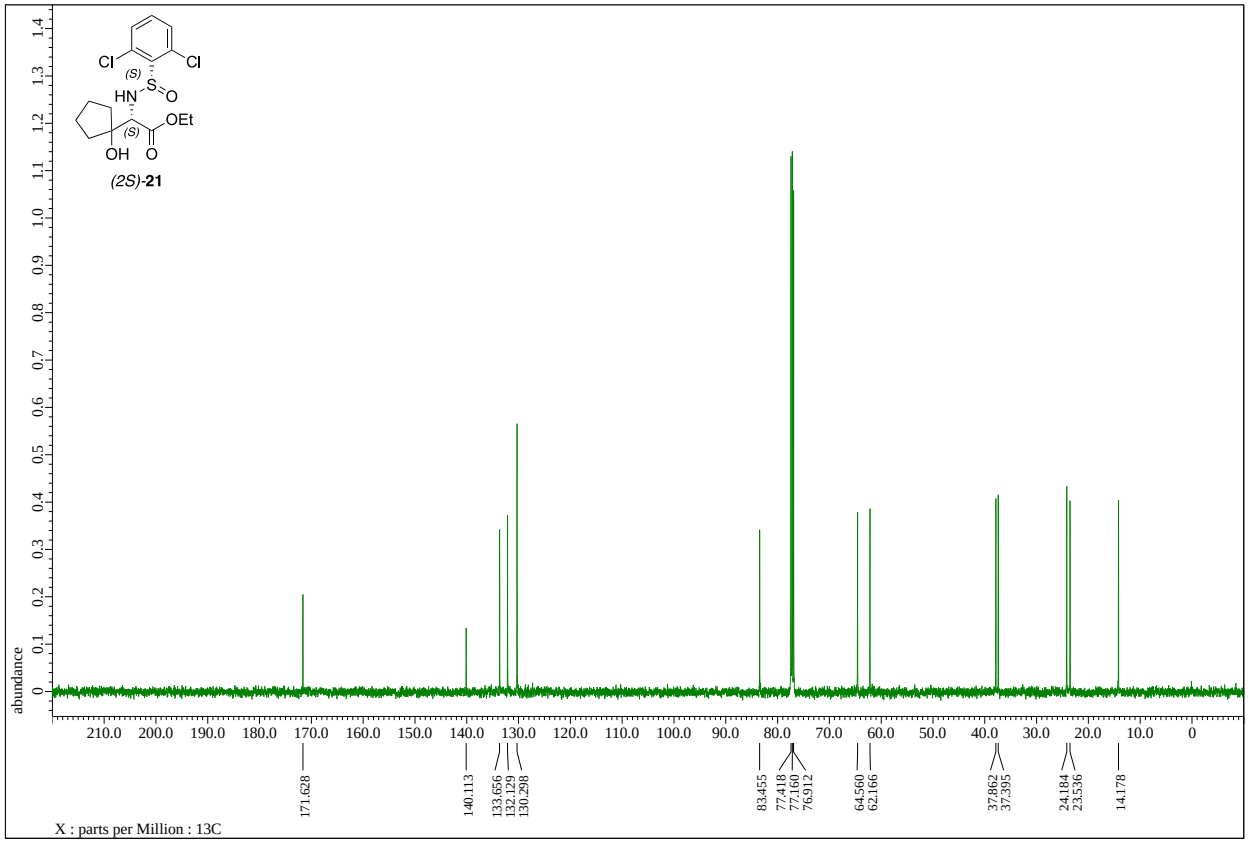
^{13}C-NMR spectra of (2*R*)-**21** (126 MHz, $CDCl_3$)



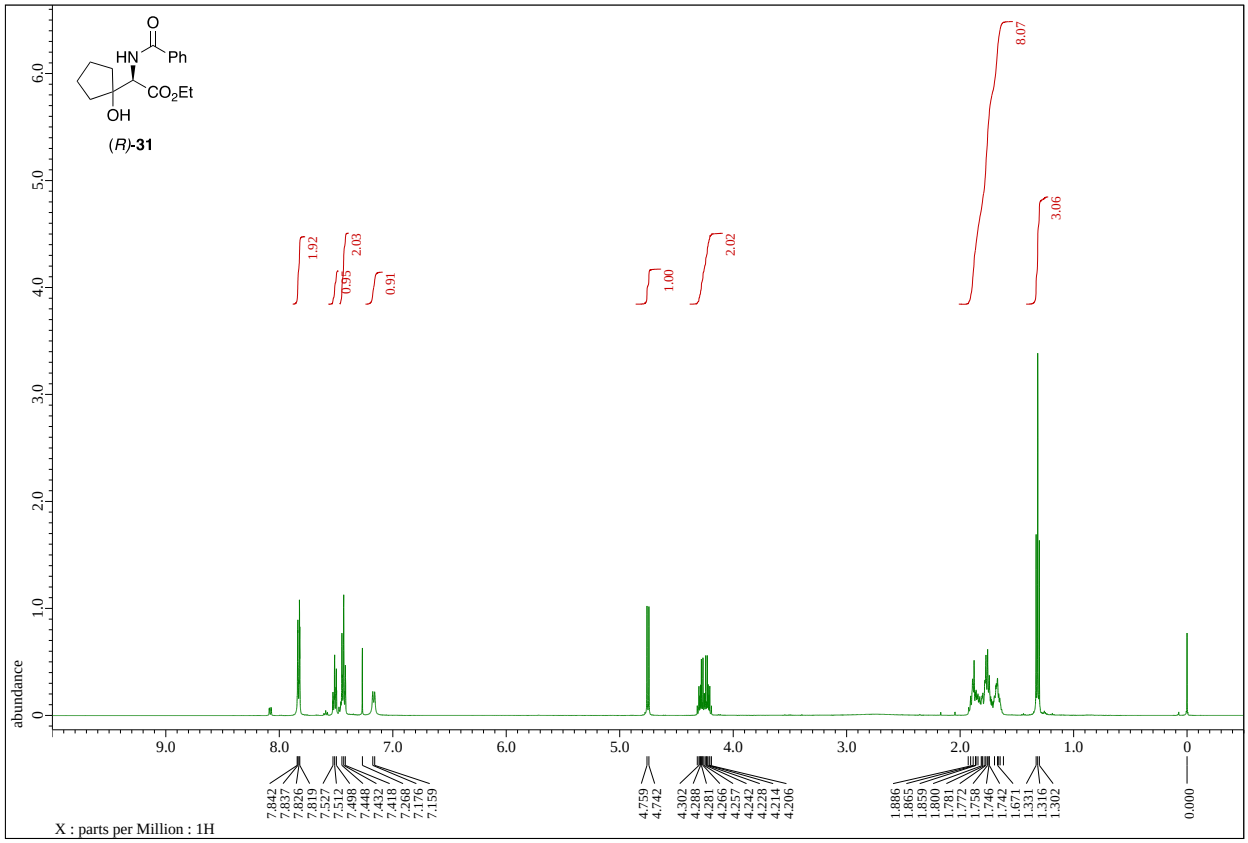
^{1}H-NMR spectra of (2*S*)-**21** (500 MHz, $CDCl_3$)



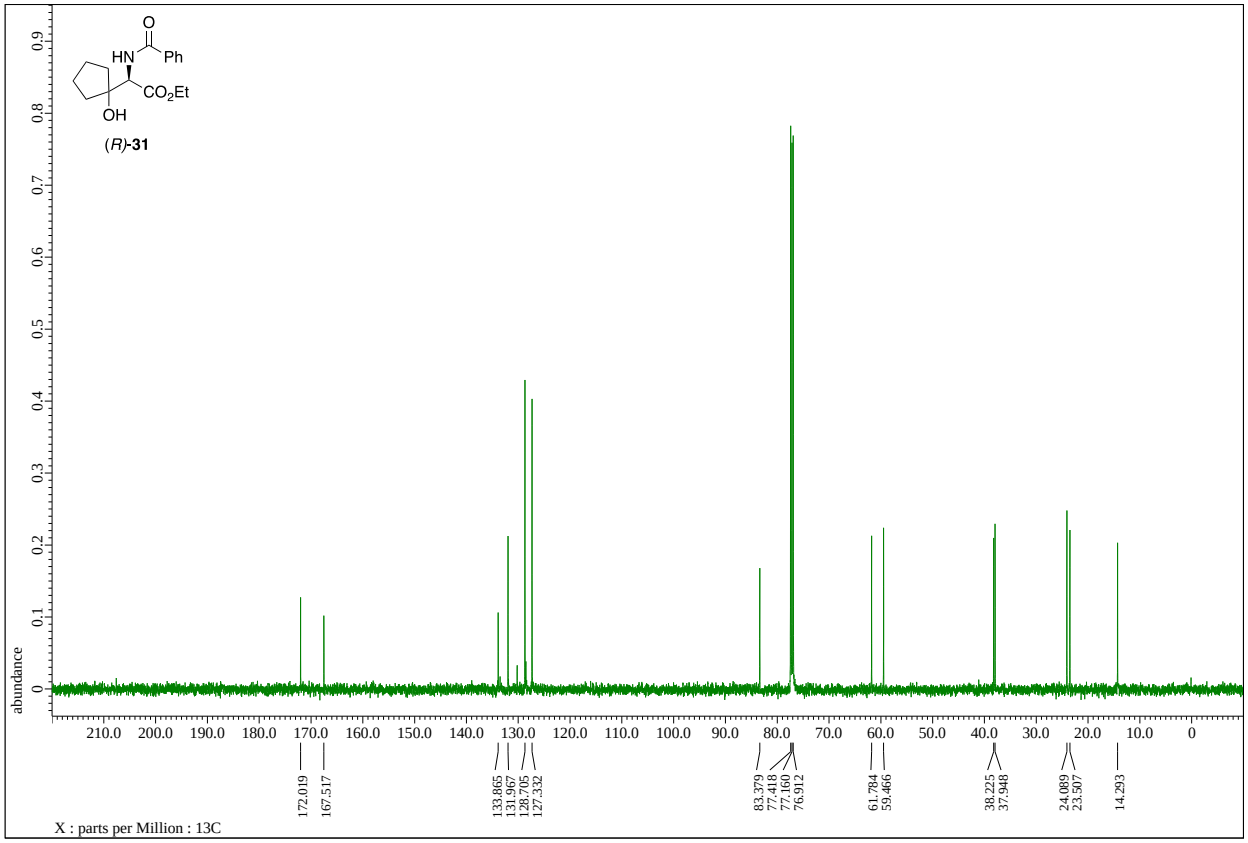
^{13}C-NMR spectra of (2*S*)-**21** (126 MHz, $CDCl_3$)



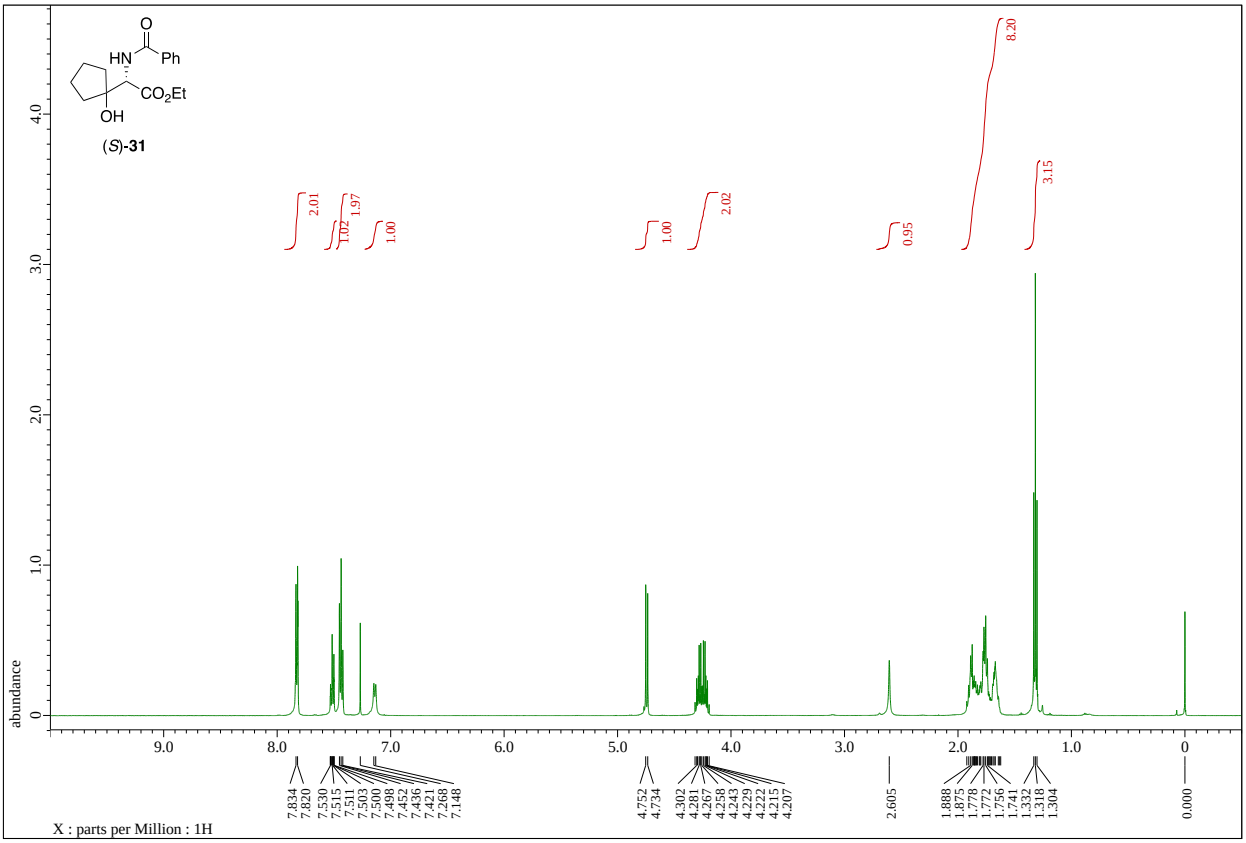
^{1}H-NMR spectra of (*R*)-**31** (500 MHz, $CDCl_3$)



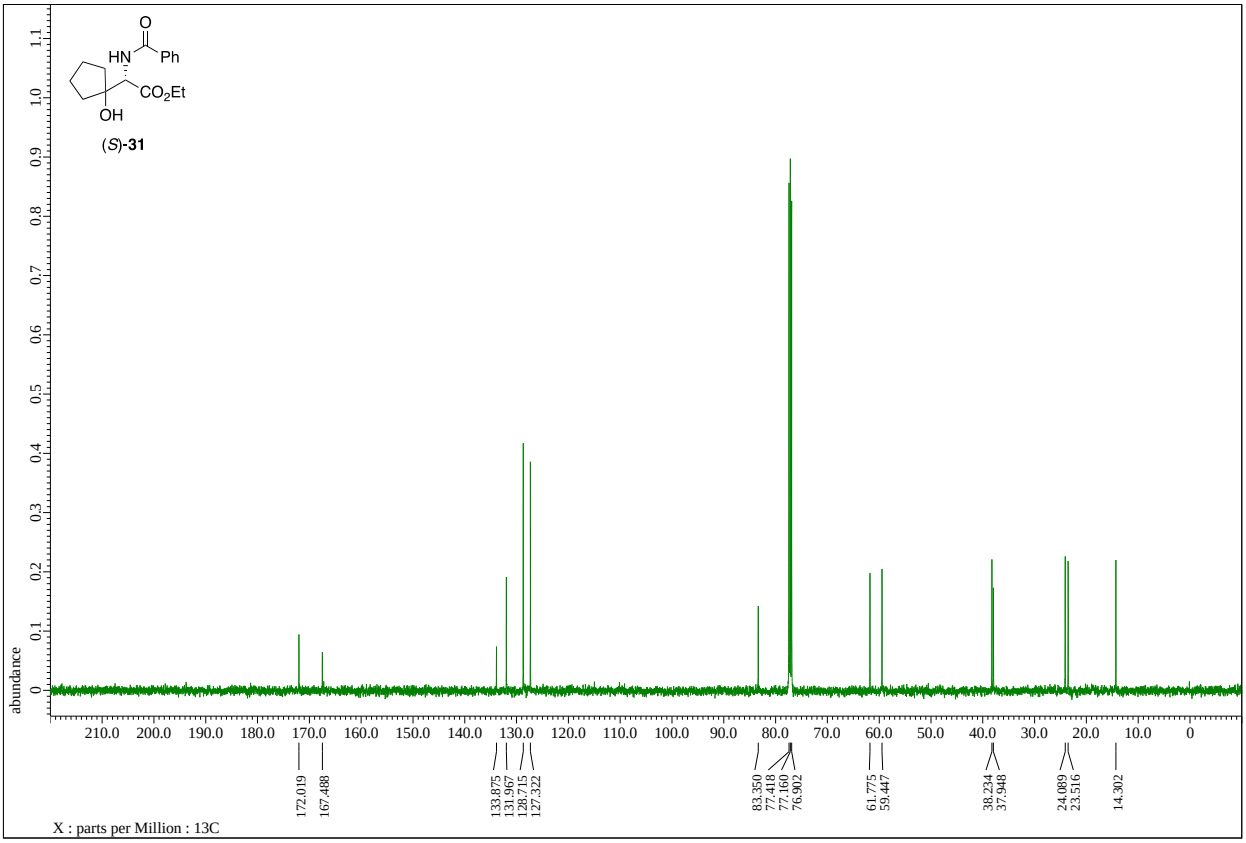
^{13}C-NMR spectra of (*R*)-**31** (126 MHz, $CDCl_3$)



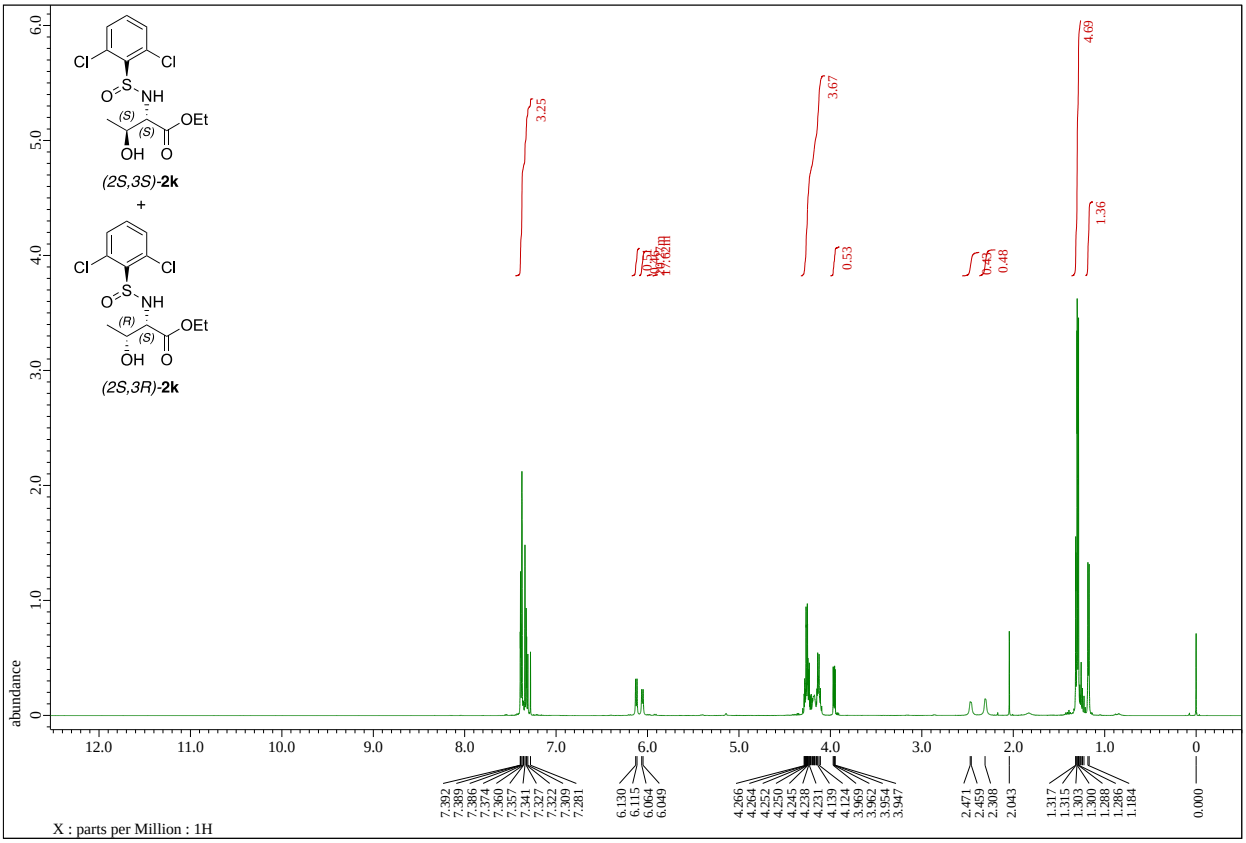
^{1}H-NMR spectra of (*S*)-**31** (500 MHz, $CDCl_3$)



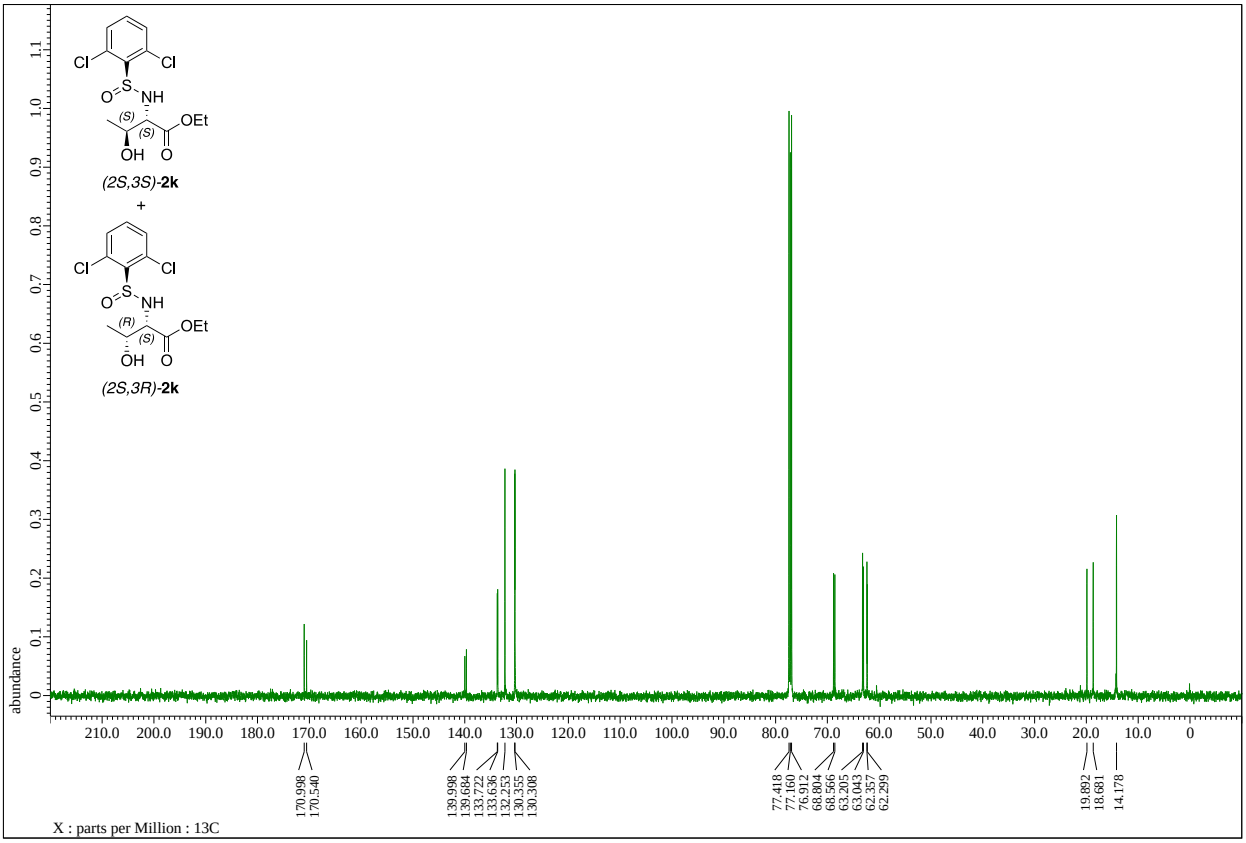
^{13}C-NMR spectra of (*S*)-**31** (126 MHz, $CDCl_3$)



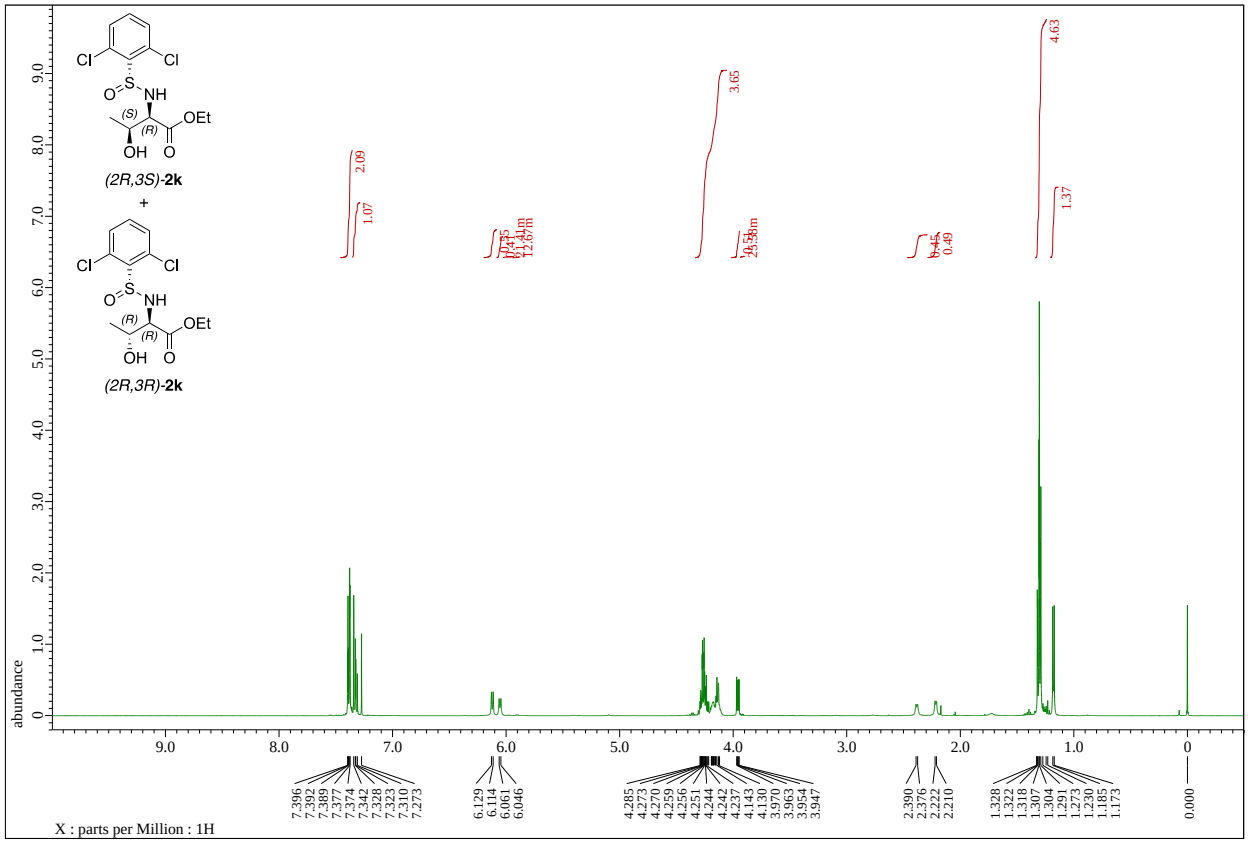
^{1}H-NMR spectra of (2*S*)-**2k** (500 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*S*,3*R*)-**2k** & (2*S*,3*S*)-**2k**)



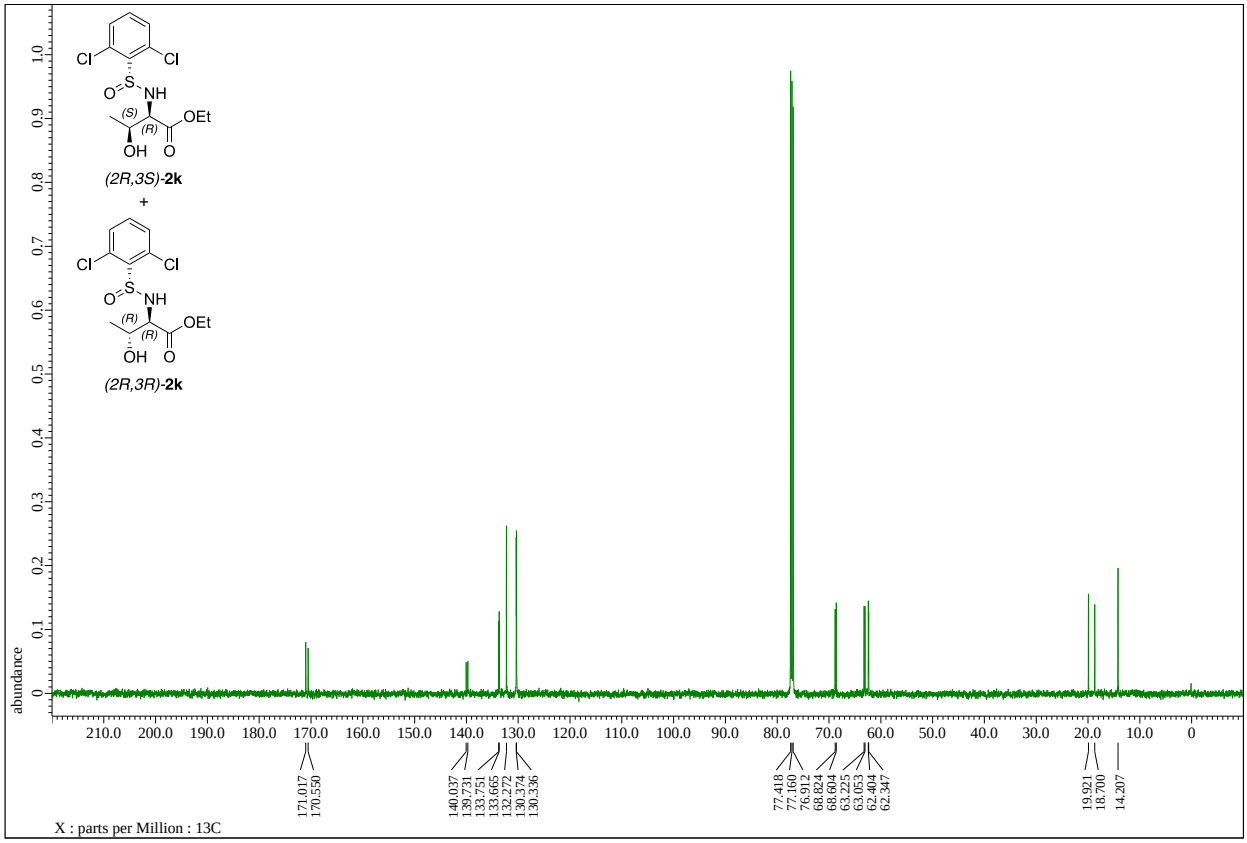
^{13}C-NMR spectra of (2*S*)-**2k** (126 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*S*,3*R*)-**2k** & (2*S*,3*S*)-**2k**)



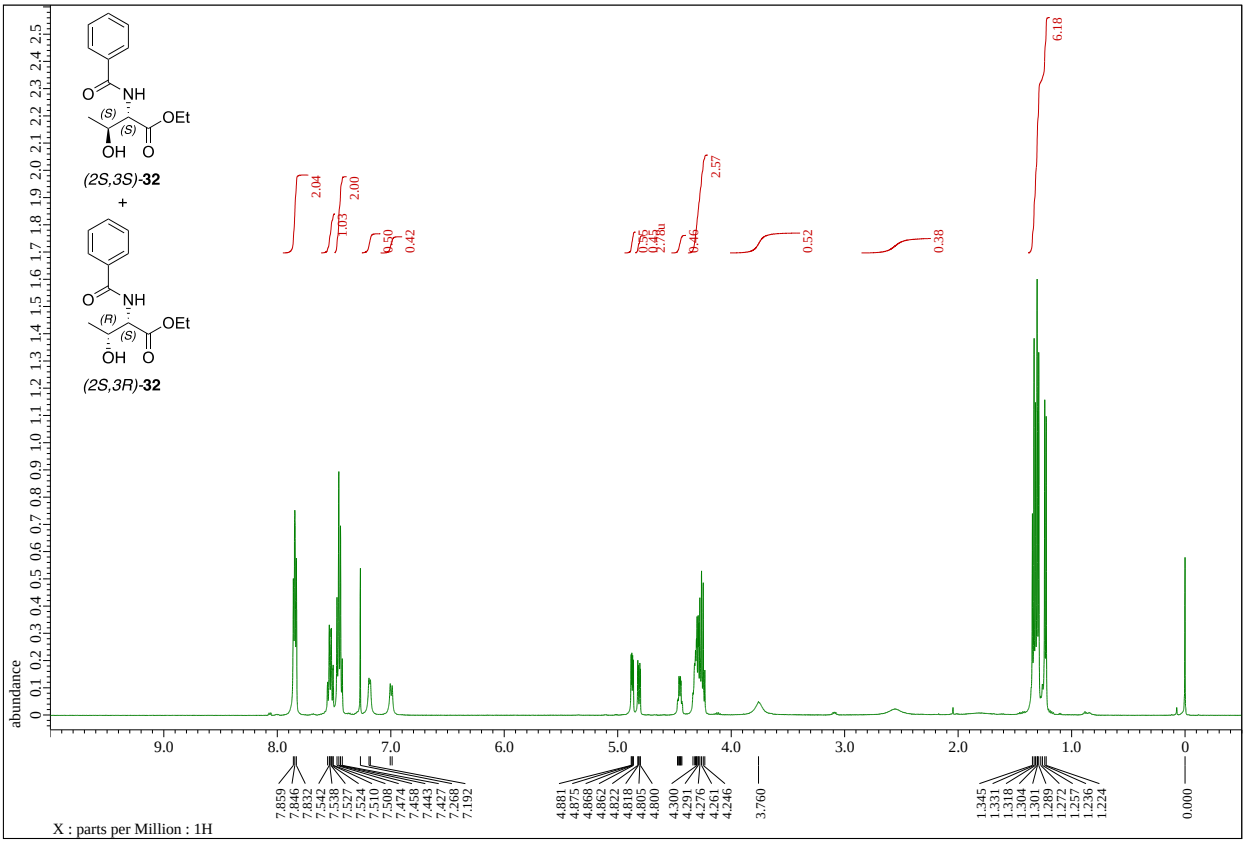
^{1}H-NMR spectra of (2*R*)-**2k** (500 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*R*,3*S*)-**2k** & (2*R*,3*R*)-**2k**)



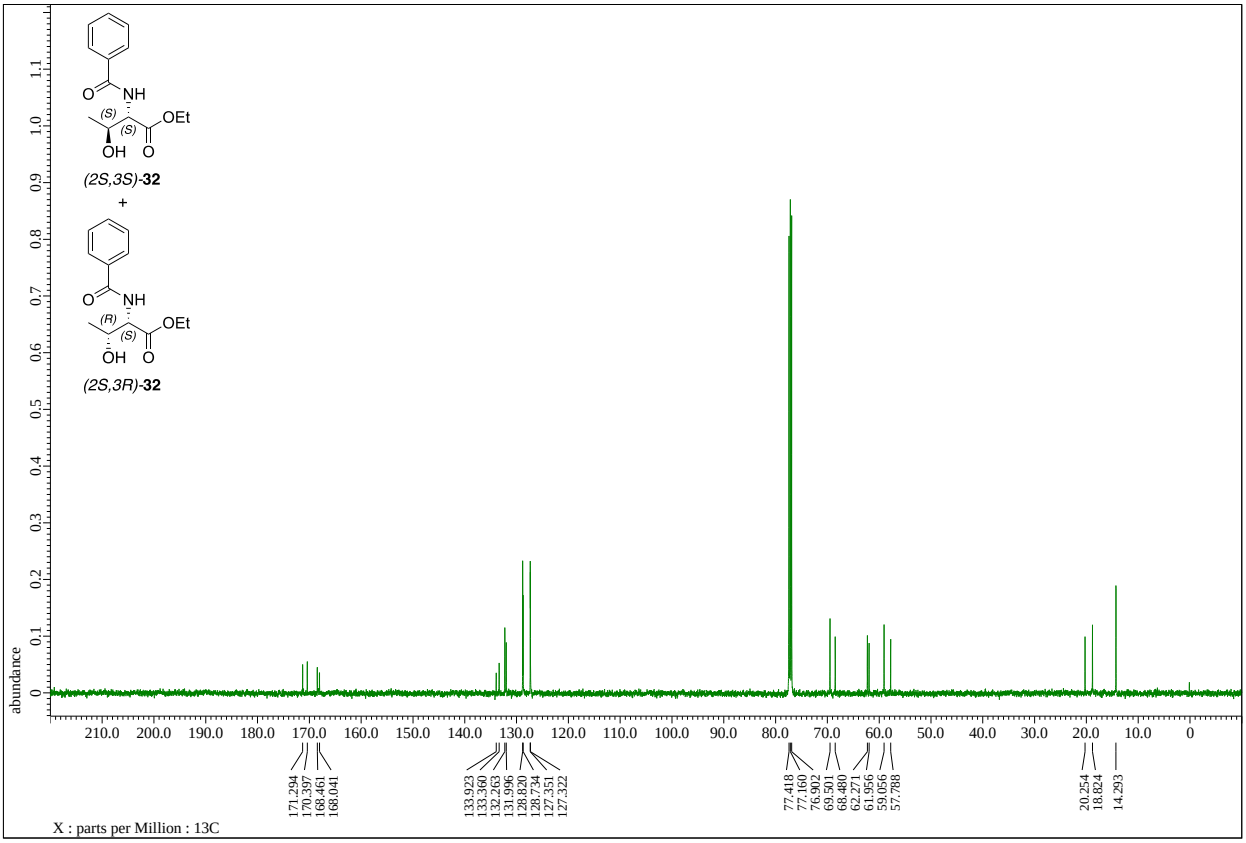
^{13}C-NMR spectra of (2*R*)-**2k** (126 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*R*,3*S*)-**2k** & (2*R*,3*R*)-**2k**)



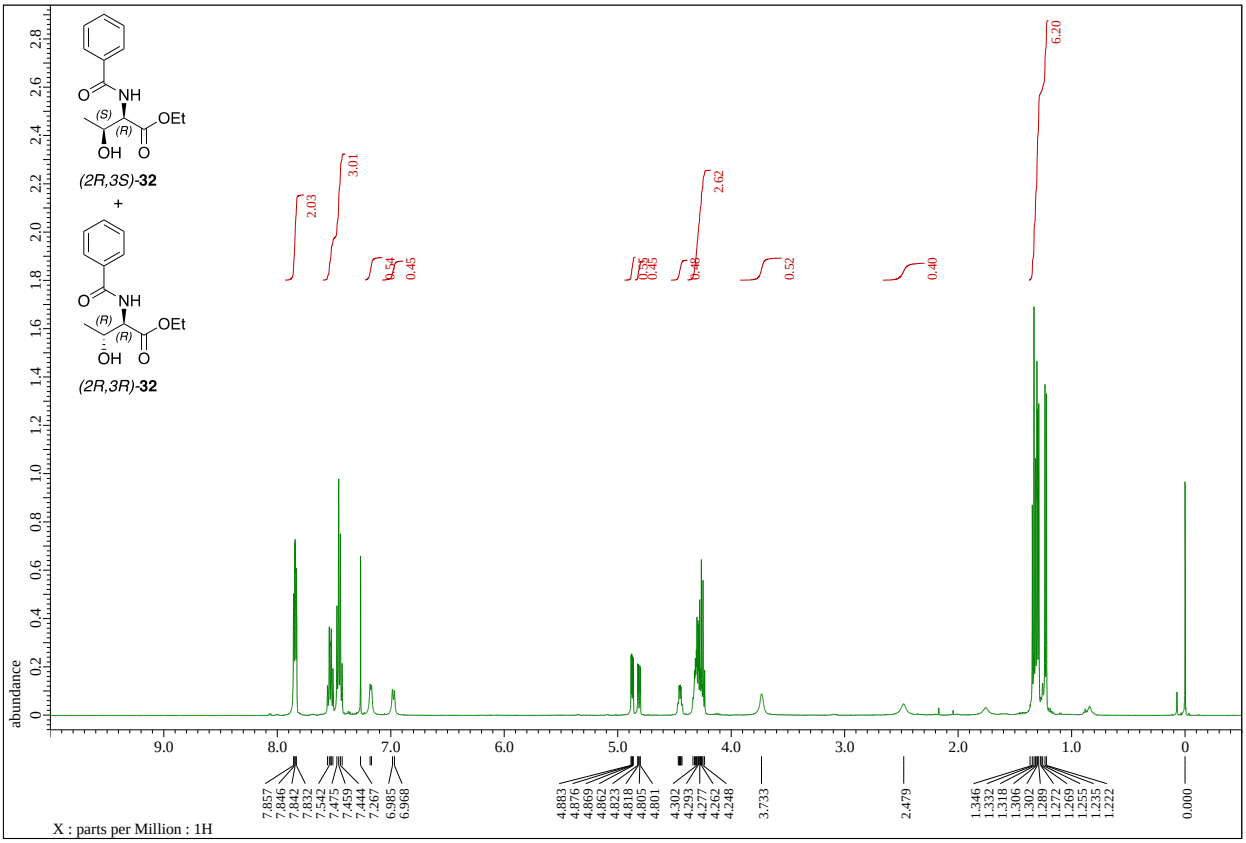
^{1}H-NMR spectra of (2*S*)-**32** (500 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*S*,3*R*)-**32** & (2*S*,3*S*)-**32**)



^{13}C-NMR spectra of (2*S*)-**32** (126 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*S*,3*R*)-**32** & (2*S*,3*S*)-**32**)



^{1}H-NMR spectra of (2*R*)-**32** (500 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*R*,3*S*)-**32** & (2*R*,3*R*)-**32**)



^{13}C-NMR spectra of (2*R*)-**32** (126 MHz, $CDCl_3$) (*syn*/*anti* isomers: (2*R*,3*S*)-**32** & (2*R*,3*R*)-**32**)