

Supporting Information

Nickel-Catalyzed Asymmetric Reductive Arylation of α -Chlorosulfones with Aryl Halides

Deli Sun, Guobin Ma, Xinluo Zhao, Chuanhu Lei* and Hegui Gong*

Center for Supramolecular Chemistry and Catalysis, College of Sciences, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China

Hegui_gong@shu.edu.cn

Table of Contents

| | | |
|------|---------------------------------------------------------------|------|
| I. | Experimental Section | S2 |
| | Part 1. General Information | S2 |
| | Part 2. Optimization experiments | S2 |
| | Part 3. Preparation of α -chlorosulfones | S4 |
| | Part 4. Cross-coupling reactions and product characterization | S13 |
| | Part 5. Control experiments and Limitations | S53 |
| II. | Reference | S57 |
| III. | HPLC Traces | S58 |
| IV. | NMR Data | S125 |

I. Experimental Section

Part 1. General Information

Commercial reagents were purchased from Adamas, Aldrich, Bide, Energy Chemical, TCI, Leyan and J&K chemical. Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 600 MHz spectrometer at STP. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ¹³C NMR spectra were recorded at 151 MHz. Data for ¹³C NMR spectra are reported in terms of chemical shift. NMR spectra are internally referenced to residual proton solvent signals (note: CDCl₃ referenced at 7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR; Acetone-*d*6 at 2.05 for ¹H NMR, 29.84 ppm for ¹³C NMR). Coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets). High-resolution mass spectra (HRMS) were obtained using Bruker APEXIII 7.0 TESLA FTMS or Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Optical rotations were taken on JASCO P1030. Enantiomeric excesses were determined by chiral HPLC using a Shimadzu instrument. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Optimization experiments

General procedure of optimization experiments: To a flame-dried tube with a stir bar vial was added the appropriate ligand (0.03 mmol, 20 mol %), reductant (0.45 mmol, 3.0 equiv), NiBr₂(dme) (0.015 mmol, 10 mol %), aryl bromide **2** (0.225 mmol, 1.5 equiv), and additive (0.15 mmol, 1.0 equiv). The vial was transferred into an N₂-filled glovebox and charged with the appropriate solvent (0.3 mL). The vial was sealed and removed from the glovebox. The mixture was stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min the mixture was cooled to 0 °C, then a solution of α -chlorosulfone **1** (0.15 mmol, 1.0 equiv) in DMF (0.3 mL) was added to the vial with a syringe over 1 min. The mixture was stirred vigorously at 0 °C for 48 h. The reaction mixture was loaded directly onto a silica gel to give the target molecule. The yield of target product was determined using 2,5-dimethylfuran as standard by ¹H NMR, and the enantioselectivity was determined by HPLC.

Table S1 Optimization of the reaction conditions ^{a,b}

1 + **2** → **3**

NiBr₂(dme) (10 mol %)
L (20 mol %)
Additive
Zn (300 mol %)
Solvent (0.6 mL), 0 °C

3

L1 n = 1

L2 n = 3

L3 R = Me

L4 R = H

L5 R = Ph

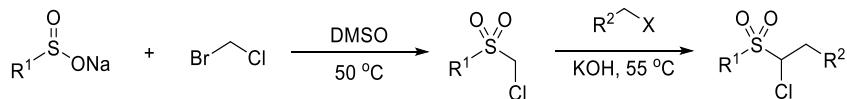
L6 R = i-Pr

| Entry | Ligand | Solvent | Ratio of 1/2 | Additive (equiv.) | Yield ^b % | e.e.% |
|-----------------|---------------------------------------|---------|--------------|------------------------------------|----------------------|-------|
| 1 | L1 | DMA | 1.5/1 | MgCl ₂ (2) | 37 | 78 |
| 2 | L1 | THF | 1.5/1 | MgCl ₂ (2) | 37 | 88 |
| 3 | L1 | NMP | 1.5/1 | MgCl ₂ (2) | 20 | 86 |
| 4 | L1 | DMF | 1.5/1 | MgCl ₂ (2) | 42 | 84 |
| 5 | L1 | DMF | 1/1 | MgCl ₂ (2) | 50 | 87 |
| 6 | L1 | DMF | 1/1.5 | MgCl ₂ (2) | 67 | 89 |
| 7 | L1 | THF | 1/1.5 | MgCl ₂ (2) | 38 | 90 |
| 8 | L1 | DMF | 1/2 | MgCl ₂ (2) | 64 | 89 |
| 9 | L1 | DMF | 1/1.5 | MgCl ₂ (1) | 73 | 91 |
| 10 | L1 | DMF | 1/1.5 | MgCl ₂ (0.5) | 41 | 91 |
| 11 | L1 | DMF | 1/1.5 | MgBr ₂ (1) | 63 | 55 |
| 12 ^c | L1 | DMF | 1/1.5 | TBAB (1) | trace | ND |
| 13 ^c | L1 | DMF | 1/1.5 | NaI (1) | trace | ND |
| 14 | L2 | DMF | 1/1.5 | MgCl ₂ (1) | 71 | 90 |
| 15 | L3 | DMF | 1/1.5 | MgCl ₂ (1) | 28 | 88 |
| 16 | L4 | DMF | 1/1.5 | MgCl ₂ (1) | 34 | 40 |
| 17 | L5 | DMF | 1/1.5 | MgCl ₂ (1) | 65 | 88 |
| 18 | L6 | DMF | 1/1.5 | MgCl ₂ (1) | 31 | 77 |
| 19 ^d | L1 | DMF | 1/1.5 | MgCl ₂ (1) | 74 | 88 |
| 20 ^e | L1 | DMF | 1/1.5 | MgCl ₂ (1) | 76 | 91 |
| 21 ^f | L1 | DMF | 1/1.5 | MgCl ₂ (1) | 73 | 91 |
| 22 ^g | (3 <i>R</i> , 8 <i>S</i>)- L1 | DMF | 1/1.5 | MgCl ₂ (1) | 75 | -92 |
| 23 | L1 | DMF | 1/1.5 | MgCl ₂ (1) TEMPO (1) | 5 | 90 |

[a] Reactions conducted under N₂ on 0.15 mmol scale for 48 h. [b] NMR yield using 2,5-dimethyl furan as the internal standard. [c] ND = no detection. [d] Mn instead of Zn. [e] 10 mol % preformed **L1**-NiBr₂ complex used. [f] 10 mol % preformed **L1**-NiCl₂ complex used. [g] 10 mol % preformed (3*R*, 8*S*)-**L1**-NiBr₂ complex used.

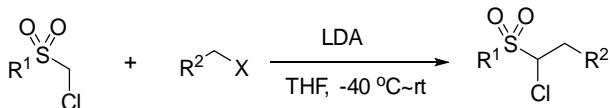
Part 3. Preparation of α -Chlorosulfones

General procedure for preparation of α -chlorosulfones (GP A).



The α -chlorosulfones were prepared according to the literature reported.^{1, 2} To a round-bottom flask with a stir bar was charged with the corresponding substituted sulfinate (1.0 equiv) and DMSO (0.1 M) followed by drop-wise addition of CH₂ClBr (1.2 equiv). The reaction mixture was warmed to 50 °C and stirred for 16 hours, then quenched with sat. NH₄Cl (aq). The aqueous phase was extracted with EtOAc. The organic phase were collected, dried over MgSO₄, concentrated under reduced pressure. The crude material was purified by flash column chromatograph on silica gel to give chloromethylsulfone. To a round-bottom flask with a stirring bar was charged with the resulting chloromethylsulfone (1.0 equiv) and an alkyl bromide (1.5 equiv) followed by addition of KOH (1.5 equiv). The mixture was stirred at 55 °C for 48 hours. Then quenched with sat. NH₄Cl (aq). The aqueous phase was extracted with EtOAc, the organic phase were collected, dried over MgSO₄, concentrated under reduced pressure, the crude material was purified by flash column chromatograph on silica gel to give α -chlorosulfone.

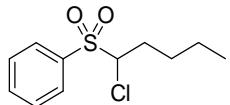
General procedure for preparation of α -chlorosulfones (GP B).



The α -chlorosulfones were prepared according to the literature reported.³ To a round-bottom flask with a stir bar was charged with according chloromethylsulfone (5 mmol, 1.0 equiv) and THF (50 mL, 0.1 M), the mixture was cooled to -40 °C, followed by drop-wise addition of LDA (6 mmol, 1.2 equiv). The reaction mixture was stirred at this temperature for 30 minutes, then a solution of an alkyl bromide (6 mmol, 1.2 equiv) in THF (6 mL) was added over 10 min. The reaction mixture was stirred at this temperature for 2 hours, and then it was allowed to warm to room temperature and stirred for 2 hours. The resulting reaction mixture was stirred at r.t. overnight, and then it was quenched with sat. NH₄Cl (aq), the aqueous phase was extracted with EtOAc. The organic phase were collected, dried over MgSO₄, concentrated under reduced pressure. The crude material was purified by flash column

chromatograph on silica to afford target material.

((1-Chloropentyl)sulfonyl)benzene (SM1)



SM1 was prepared by **GPA** as a white solid (630 mg, 51% yield).

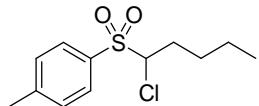
¹H NMR (600 MHz, CDCl₃) δ 8.01 – 7.93 (m, 2H), 7.74 – 7.69 (m, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 4.63 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.44 – 2.40 (m, 1H), 1.81 – 1.85 (m, 1H), 1.69 – 1.60 (m, 1H), 1.48 – 1.29 (m, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 135.4, 134.6, 130.2, 129.2, 75.1, 30.4, 28.1, 22.0, 13.9.

HRMS (ESI) calcd for: C₁₁H₁₉ClNO₂S [M+NH₄]⁺ m/z 264.0820, found 264.0817.

M.P. 39-41 °C.

1-((1-Chloropentyl)sulfonyl)-4-methylbenzene (SM2)



SM2 was prepared by **GPA** as a white solid (620 mg, 46% yield).

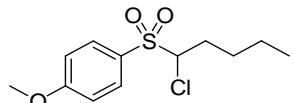
¹H NMR (600 MHz, CDCl₃) δ 7.89 – 7.79 (m, 2H), 7.42 – 7.35 (m, 2H), 4.61 (dd, *J* = 11.0, 2.8 Hz, 1H), 2.47 (s, 3H), 2.47 – 2.38 (m, 1H), 1.84 – 1.77 (m, 1H), 1.69 – 1.59 (m, 1H), 1.48 – 1.30 (m, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 145.8, 132.3, 130.2, 129.9, 75.3, 30.5, 28.2, 22.0, 21.9, 13.9.

HRMS (ESI) calcd for: C₁₂H₂₁ClNO₂S ([M+NH₄]⁺) m/z 278.0976, found 278.0979.

M.P. 41.8 - 43.5 °C.

1-((1-Chloropentyl)sulfonyl)-4-methoxybenzene (SM3)



SM3 was prepared by **GPA** as a white solid (595 mg, 43 % yield).

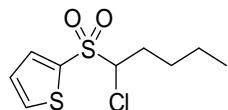
¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.80 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.22 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.70 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.44 – 2.41 (m, 1H), 1.87 – 1.81 (m, 1H), 1.69 – 1.60 (m, 1H), 1.52 – 1.31 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 137.0, 135.9, 135.3, 128.1, 76.1, 30.9, 28.2, 22.0, 13.9.

HRMS (ESI) calcd for: C₁₂H₁₆ClO₃S ([M-H]⁻) m/z 275.0514, found 275.0512.

M.P. 52.1 - 53.8 °C.

2-((1-Chloropentyl)sulfonyl)thiophene (SM4)



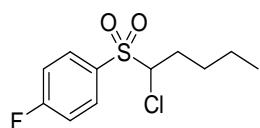
SM4 was prepared by **GPA** as a light-yellow oil (442 mg, 35 % yield).

¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.80 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.22 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.70 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.44 – 2.41 (m, 1H), 1.87 – 1.81 (m, 1H), 1.69 – 1.60 (m, 1H), 1.52 – 1.31 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 137.0, 135.9, 135.3, 128.1, 76.1, 30.9, 28.2, 22.0, 13.9.

HRMS (ESI) calcd for: C₉H₁₇ClNO₂S₂ ([M+NH₄]⁺) m/z 270.0384, found 270.0378.

1-((1-Chloropentyl)sulfonyl)-4-fluorobenzene (SM5)



SM5 was prepared by **GPA** as a colorless oil (450 mg, 34 % yield).

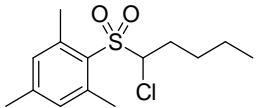
¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.96 (m, 2H), 7.30 – 7.26 (m, 2H), 4.61 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.47 – 2.39 (m, 1H), 1.88 – 1.77 (m, 1H), 1.70 – 1.60 (m, 1H), 1.48 – 1.32 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 166.5 (d, *J* = 257.7 Hz), 133.1 (d, *J* = 9.9 Hz), 131.3 (d, *J* = 3.2 Hz), 116.6 (d, *J* = 22.7 Hz), 75.2, 30.4, 28.1, 21.9, 13.8.

¹⁹F NMR (565 MHz, CDCl₃) δ -101.96.

HRMS (ESI) calcd for: C₁₁H₁₄ClFNaO₂S ([M+Na]⁺) m/z 287.0279, found 287.0272.

2-((1-Chloropentyl)sulfonyl)-1,3,5-trimethylbenzene (SM6)



SM6 was prepared by **GPA** as a white solid (420 mg, 29 % yield).

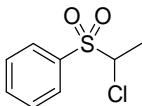
¹H NMR (600 MHz, CDCl₃) δ 6.99 (s, 2H), 4.71 (dd, *J* = 10.6, 3.0 Hz, 1H), 2.68 (s, 6H), 2.42 – 2.37 (m, 1H), 2.32 (s, 3H), 2.10 – 2.03 (m, 1H), 1.70 – 1.67 (m, 1H), 1.52 – 1.32 (m, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.2, 141.4, 132.5, 130.5, 75.0, 29.1, 28.2, 23.3, 22.1, 21.2, 13.9.

HRMS (ESI) calcd for: C₁₄H₂₁ClNaO₂S ([M+Na]⁺) m/z 311.0843, found 311.0841.

M.P. 119.8 – 121.5 °C.

((1-Chloroethyl)sulfonyl)benzene (SM7)



SM7 was prepared by **GPA** as a white solid (360 mg, 35 % yield).

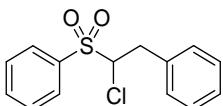
¹H NMR (600 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.75 – 7.70 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 2H), 4.80 (q, *J* = 6.8 Hz, 1H), 1.85 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 134.8, 134.73, 130.3, 129.3, 70.0, 18.3.

HRMS (ESI) calcd for: C₈H₉ClNaO₂S ([M+Na]⁺) m/z 226.9904, found 226.9905.

M.P. 50.8 - 52.3 °C.

(2-Chloro-2-(phenylsulfonyl)ethyl)benzene (SM8)



SM8 was prepared by **GPA** as a white solid (330 mg, 33 % yield).

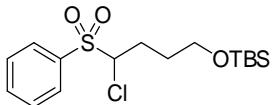
¹H NMR (600 MHz, CDCl₃) δ 8.04 – 7.98 (m, 2H), 7.75 – 7.71 (m, 1H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.33 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 4.79 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.88 (dd, *J* = 14.3, 2.5 Hz, 1H), 2.98 (dd, *J* = 14.3, 11.4 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 135.2, 134.8, 134.7, 130.2, 129.6, 129.3, 128.9, 127.8, 75.7, 37.0.

HRMS (ESI) calcd for: C₁₄H₁₃ClNaO₂S ([M+Na]⁺) m/z 303.0217, found 303.0211.

M.P. 45.3 – 46.9 °C.

***tert*-butyl(4-chloro-4-(phenylsulfonyl)butoxy)dimethylsilane (SM9)**



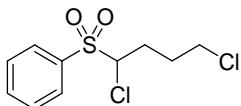
SM9 was prepared by **GPB** as a colorless oil (1.11 g, 61 % yield).

¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.91 (m, 2H), 7.74 – 7.68 (m, 1H), 7.62 – 7.56 (m, 2H), 4.79 (dd, J = 10.8, 2.9 Hz, 1H), 3.69 – 3.62 (m, 2H), 2.56 – 2.48 (m, 1H), 1.93 – 1.80 (m, 2H), 1.73–1.65 (m, 1H), 0.86 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H)..

¹³C NMR (151 MHz, CDCl₃) δ 135.4, 134.6, 130.2, 129.2, 75.1, 62.1, 28.9, 28.2, 26.0, 18.4, -5.3.

HRMS (ESI) calcd for: C₁₆H₂₇ClNaO₃SSi ([M+Na]⁺) m/z 385.1031, found 385.1032.

((1,4-Dichlorobutyl)sulfonyl)benzene (SM10)



SM10 was prepared by **GPA** as a white solid (388 mg, 29 % yield).

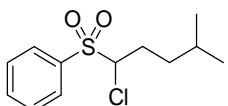
¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.93 (m, 2H), 7.76 – 7.71 (m, 1H), 7.64 – 7.58 (m, 2H), 4.69 (dd, J = 10.1, 3.3 Hz, 1H), 3.59 (t, J = 6.2 Hz, 2H), 2.64 – 2.59 (m, 1H), 2.20 – 2.12 (m, 1H), 2.07 – 1.93 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 135.1, 134.8, 130.2, 129.3, 74.1, 43.7, 28.9, 28.6.

HRMS (ESI) calcd for: C₁₀H₁₆Cl₂NO₂S ([M+NH₄]⁺) m/z 284.0273, found 284.0269.

M.P. 47.5 – 49.1 °C.

((1-Chloro-4-methylpentyl)sulfonyl)benzene (SM11)



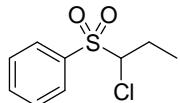
SM11 was prepared by **GPA** as a colorless oil (470 mg, 36 % yield).

¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.92 (m, 2H), 7.75 – 7.68 (m, 1H), 7.60 (t, J = 7.8 Hz, 2H), 4.60 (dd, J = 10.8, 2.8 Hz, 1H), 2.47 – 2.42 (m, 1H), 1.86 – 1.79 (m, 1H), 1.61 – 1.56 (m, 1H), 1.54 – 1.50 (m, 1H), 1.37 – 1.31 (m, 1H), 0.91 (dd, J = 12.4, 6.6 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 135.4, 134.6, 130.1, 129.2, 75.4, 35.0, 28.7, 27.7, 22.8, 22.2.

HRMS (ESI) calcd for: C₁₂H₂₁ClNO₂S ([M+NH₄]⁺) m/z 278.0976, found 278.0974.

((1-Chloropropyl)sulfonyl)benzene (SM12)



SM12 was prepared by **GPA** as a white solid (383 mg, 35 % yield).

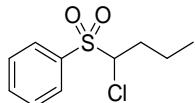
¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.76 – 7.69 (m, 1H), 7.64 – 7.56 (m, 2H), 4.58 (dd, J = 10.6, 3.0 Hz, 1H), 2.51 – 2.45 (m, 1H), 1.90 – 1.82 (m, 1H), 1.16 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 135.4, 134.6, 130.2, 129.2, 76.6 24.7, 10.8.

HRMS (ESI) calcd for: C₉H₁₅ClNO₂S ([M+NH₄]⁺) m/z 236.0507, found 236.0503.

M.P. 58.7 – 60.3 °C.

((1-Chlorobutyl)sulfonyl)benzene (SM13)



SM13 was prepared by **GPA** as a white solid (385 mg, 33 % yield).

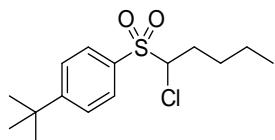
¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.92 (m, 2H), 7.74 – 7.68 (m, 1H), 7.59 (t, J = 7.9 Hz, 2H), 4.65 (dd, J = 11.0, 2.9 Hz, 1H), 2.39 – 2.34 (m, 1H), 1.85 – 1.79 (m, 1H), 1.74 – 1.66 (m, 1H), 1.51 – 1.44 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 135.3, 134.6, 130.2, 129.2, 74.8, 32.6, 19.4, 13.3.

HRMS (ESI) calcd for: C₁₀H₁₇ClNO₂S ([M+NH₄]⁺) m/z 250.0663, found 250.0660.

M.P. 41.3 – 42.8 °C.

1-(tert-Butyl)-4-((1-chloropentyl)sulfonyl)benzene (SM14)



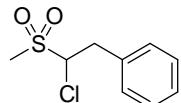
SM14 was prepared by **GPA** as a colorless oil (425 mg, 28 % yield).

¹H NMR (600 MHz, CDCl₃) δ 7.89 – 7.84 (m, 2H), 7.60 – 7.56 (m, 2H), 4.62 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.44 – 2.38 (m, 1H), 1.86 – 1.79 (m, 1H), 1.67 – 1.60 (m, 1H), 1.48 – 1.38 (m, 2H), 1.36 (s, 10H), 0.92 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.7, 132.3, 130.0, 126.2, 75.2, 35.5, 31.2, 30.5, 28.2, 22.0, 13.9.

HRMS (ESI) calcd for: C₁₅H₂₃ClNaO₂S ([M+Na]⁺) m/z 325.1000 , found 325.0999.

(2-Chloro-2-(methylsulfonyl)ethyl)benzene (SM15)



SM15 was prepared by **GPA** as a white solid (120 mg, 11 % yield).

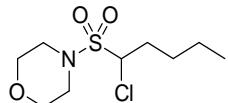
¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 7.29 (dd, *J* = 6.9, 1.7 Hz, 2H), 4.75 (dd, *J* = 11.0, 2.7 Hz, 1H), 3.81 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.12 – 3.04 (m, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 134.4, 129.7, 129.0, 127.9, 74.5, 37.6, 35.8.

HRMS (ESI) calcd for: C₉H₁₅ClNO₂S ([M+NH₄]⁺) m/z 236.0507, found 236.0501.

M.P. 71.5 – 73.2 °C.

4-((1-Chloropentyl)sulfonyl)morpholine (SM16)



SM16 was prepared by **GPB** as a white solid (350 mg, 68% yield).

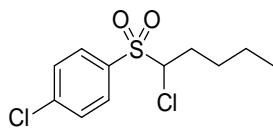
¹H NMR (600 MHz, CDCl₃) δ 4.68 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.79 – 3.69 (m, 4H), 3.54 – 3.42 (m, 4H), 2.32 – 2.28 (m, 1H), 1.99 – 1.94 (m, 1H), 1.69 – 1.61 (m, 1H), 1.49 – 1.31 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 73.2, 67.1, 47.2, 32.3, 28.1, 22.0, 13.9.

HRMS (ESI) calcd for: C₉H₁₈ClNNaO₃S ([M+Na]⁺) m/z 278.0588, found 278.0582.

M.P. 54.1 – 55.9 °C.

1-Chloro-4-((1-chloropentyl)sulfonyl)benzene (SM17)



SM17 was prepared by **GPA** as a white solid (338 mg, 24% yield).

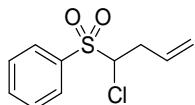
¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.85 (m, 2H), 7.61 – 7.53 (m, 2H), 4.62 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.45 – 2.39 (m, 1H), 1.85 – 1.78 (m, 1H), 1.68 – 1.60 (m, 1H), 1.48 – 1.32 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 141.6, 133.8, 131.6, 129.6, 75.1, 30.4, 28.1, 22.0, 13.9.

HRMS (ESI) calcd for: C₁₁H₁₈Cl₂NO₂S ([M+NH₄]⁺) m/z 298.0430, found 298.0422.

M.P. 33.9 – 35.8 °C.

((1-Chlorobut-3-en-1-yl)sulfonyl)benzene (**SM18**)



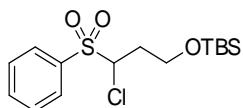
SM18 was prepared by **GPA** as a colorless oil (369 mg, 32% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.02 – 7.94 (m, 2H), 7.74 – 7.71 (m, 1H), 7.64 – 7.58 (m, 2H), 5.84 – 5.77 (m, 1H), 5.29 – 5.21 (m, 2H), 4.66 (dd, *J* = 10.5, 3.1 Hz, 1H), 3.21 – 3.16 (m, 1H), 2.62 – 2.56 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 135.2, 134.8, 130.9, 130.2, 129.2, 120.4, 73.9, 35.3.

HRMS (ESI) calcd for: C₁₀H₁₅ClNO₂S ([M+NH₄]⁺) m/z 248.0507, found 248.0499.

tert-Butyl(3-chloro-3-(phenylsulfonyl)propoxy)dimethylsilane (**SM19**)



SM19 was prepared by **GPA** as a colorless oil (1.15 g, 66% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.96 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.75 – 7.68 (m, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 4.94 (dd, *J* = 11.1, 2.6 Hz, 1H), 3.87 – 3.84 (m, 1H), 3.76 (td, *J* = 10.4, 3.4 Hz, 1H), 2.68 – 2.62 (m, 1H), 1.88 – 1.83 (m, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H)..

¹³C NMR (151 MHz, CDCl₃) δ 135.4, 134.6, 130.1, 129.2, 72.0, 58.2, 33.9, 26.0, 18.3, -5.3, -5.4.

HRMS (ESI) calcd for: C₁₅H₂₅ClNaO₃SSi ([M+Na]⁺) m/z 371.0874, found 371.0874.

3-Chloro-3-(phenylsulfonyl)propan-1-ol (SM20)

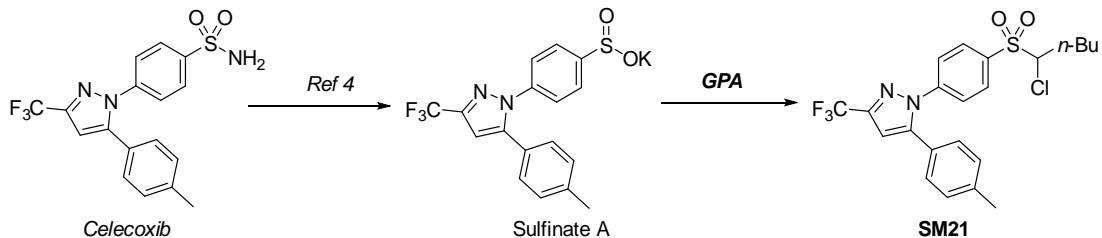
To a stirred solution of SM19 (698 mg, 2.0 mmol) in THF was added TBAF (1.0 M in THF) at rt, and then the mixture was stirred at rt overnight. Then the reaction was quenched with sat. NH₄Cl (aq), the aqueous phase was extracted with EtOAc. The organic phase were collected, dried over MgSO₄, concentrated under reduced pressure. The crude material was purified by flash column chromatograph on silica to give **SM20** as a colorless oil (380 mg, 81% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.63 – 7.57 (m, 2H), 5.00 (dt, *J* = 10.5, 2.1 Hz, 1H), 3.96 (dt, *J* = 10.1, 4.6 Hz, 1H), 3.81 (s, 1H), 2.71 – 2.65 (m, 1H), 2.03 – 1.98 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 135.2, 134.8, 130.1, 129.3, 71.8, 58.0, 33.6.

HRMS (ESI) calcd for: C₉H₁₁ClNaO₃S ([M+Na]⁺) m/z 257.0010, found 257.0007.

1-(4-((1-Chloropentyl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (SM21)



Sulfinate A was prepared from Celecoxib according to reported literature.⁴ **SM21** was prepared by **GPA** as a white solid (470 mg, 20% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.97 – 7.89 (m, 2H), 7.58 – 7.52 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.08 (m, 2H), 4.65 – 4.58 (m, 1H), 2.39 (s, 4H), 1.87 – 1.76 (m, 1H), 1.68 – 1.58 (m, 1H), 1.48 – 1.31 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).

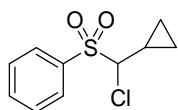
¹³C NMR (151 MHz, CDCl₃) δ 145.6, 144.5 (q, *J* = 38.7 Hz), 144.2, 140.1, 134.5, 131.3, 130.0, 128.9, 125.7, 125.4, 121.1 (q, *J* = 269.5 Hz), 106.7 (q, *J* = 1.51), 75.1, 30.4, 28.1, 22.0, 21.5, 13.8.

¹⁹F NMR (565 MHz, CDCl₃) δ -62.53.

HRMS (ESI) calcd for: C₂₂H₂₂ClF₃N₂NaO₂S ([M+Na]⁺) m/z 493.0935, found 493.0935.

M.P. 75.8 – 76.9 °C.

((Chloro(cyclopropyl)methyl)sulfonyl)benzene (69)



69 was prepared according to the reported literature (207 mg, 9% yield).⁵

¹H NMR (600 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.73 – 7.67 (m, 1H), 7.58 (t, *J* = 7.9 Hz, 2H), 4.24 (d, *J* = 8.7 Hz, 1H), 1.39 – 1.32 (m, 1H), 0.86 – 0.80 (m, 1H), 0.78 – 0.71 (m, 1H), 0.67 – 0.61 (m, 1H), 0.46–0.42 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 135.7, 134.6, 130.2, 129.1, 79.3, 12.8, 7.0, 4.3.

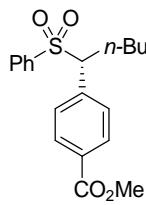
HRMS (ESI) calcd for: C₁₀H₁₁ClNaO₂S ([M+Na]⁺) m/z 253.0061, found 253.0063.

Part 4. Cross-coupling reactions and product characterization

General procedure for reductive enantioselective reductive cross-coupling reactions: To a flame-dried tube with a stir bar vial was added the appropriate reductant (0.45 mmol, 3.0 equiv), aryl halide (0.225 mmol, 1.5 equiv), MgCl₂ (0.15 mmol, 1.0 equiv), and **L1·NiBr₂** (0.015 mmol, 10 mol %).⁶ The vial was transferred into an N₂-filled glovebox and charged with the appropriate solvent (0.3 mL). The vial was sealed and removed from the glovebox. The mixture was stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min the mixture was cooled to 0 °C, then a solution of α-chlorosulfone (0.15 mmol, 1.0 equiv) in solvent (0.3 mL) was added to the vial by syringe over 1 min. The mixture was stirred vigorously at 0 °C for 48 h. The reaction mixture was loaded directly onto a silica gel to give the target molecular.

The absolute stereochemistry was assigned by comparing the optical rotation of compound **21** with the literature reported measurement.³ A *R*-configuration was determined for **21** accordingly, and was applied to all the products reported in this work.

Methyl (*R*)-4-(1-(phenylsulfonyl)pentyl)benzoate (**3**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **3** as an off-white solid (37.9 mg, 73% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 240 nm, *t_R* (minor) = 9.7 min,

t_R (major) = 12.5 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.92 – 7.86 (m, 2H), 7.56 – 7.49 (m, 3H), 7.41 – 7.34 (m, 2H), 7.19 – 7.14 (m, 2H), 4.08 (dd, J = 11.6, 3.6 Hz, 1H), 3.90 (s, 3H), 2.47 – 2.41 (m, 1H), 2.18 – 2.12 (m, 1H), 1.36 – 1.22 (m, 2H), 1.20 – 1.08 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

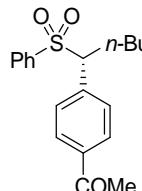
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.68, 137.81, 137.31, 133.77, 130.52, 129.98, 129.73, 129.08, 128.87, 71.54, 52.37, 28.97, 27.17, 22.35, 13.81.

HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_4\text{S}$ ($[\text{M}-\text{H}]^-$) m/z 345.1166, found 345.1160.

M.P. 75.2 – 76.9 °C.

$[\alpha]_D$ (25.0 °C, c = 1.00 in CHCl_3) = +87°.

(R)-1-(4-(1-(Phenylsulfonyl)pentyl)phenyl)ethan-1-one (4)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-(4-bromophenyl)ethan-1-one (44.8 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **4** as an off-white solid (27.3 mg, 55% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, *iPrOH*-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 12.9 min, t_R (major) = 16.8 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.85 – 7.79 (m, 2H), 7.57 – 7.49 (m, 3H), 7.41 – 7.35 (m, 2H), 7.23 – 7.17 (m, 2H), 4.09 (dd, J = 11.7, 3.6 Hz, 1H), 2.57 (s, 3H), 2.44 – 2.38 (m, 1H), 2.18 – 2.11 (m, 1H), 1.34 – 1.21 (m, 3H), 0.81 (t, J = 7.4 Hz, 3H).

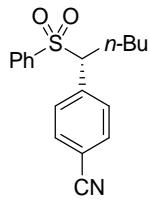
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 197.6, 137.9, 137.3, 137.3, 133.8, 130.2, 129.1, 128.9, 128.5, 71.5, 28.9, 27.2, 26.8, 22.3, 13.8.

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) m/z 331.1362, found 331.1372.

M.P. 94.8 – 96.3 °C.

$[\alpha]_D$ (25.0 °C, c = 0.45 in CHCl_3) = +81.333°.

(R)-4-(1-(Phenylsulfonyl)pentyl)benzonitrile (5)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromobenzonitrile (41 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **5** as an off-white solid (19.8 mg, 42% yield, 89% ee)

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 12.8 min, t_R (major) = 16.6 min.

¹H NMR (600 MHz, CDCl₃) δ 7.62 – 7.56 (m, 1H), 7.56 – 7.49 (m, 4H), 7.45 – 7.39 (m, 2H), 7.25 – 7.20 (m, 2H), 4.07 (dd, J = 11.6, 3.7 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.16 – 2.10 (m, 1H), 1.34 – 1.26 (m, 2H), 1.20 – 1.07 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H).

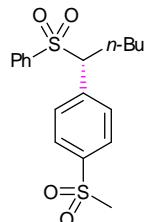
¹³C NMR (151 MHz, CDCl₃) δ 138.2, 137.1, 134.0, 132.3, 130.7, 129.1, 129.0, 118.4, 112.8, 71.4, 28.9, 27.2, 22.3, 13.8.

HRMS (ESI) calcd. for C₁₈H₁₉NNaO₂S ([M+Na]⁺) *m/z* 336.1028, found 336.1023.

M.P. 87.3 – 89 °C.

[*a*]D (25.0 °C, c = 0.50 in CHCl₃) = +91.6°.

(R)-1-(Methylsulfonyl)-4-(1-(phenylsulfonyl)pentyl)benzene (**6**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (0.15 mmol, 1.0 equiv) and 1-bromo-4-(methylsulfonyl)benzene (52.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **6** as an off-white solid (34.6 mg, 63% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 210 nm, t_R (minor) = 19.8 min, t_R (major) = 26.4 min.

¹H NMR (600 MHz, CDCl₃) δ 7.86 – 7.80 (m, 2H), 7.62 – 7.55 (m, 3H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 2H), 4.12 (dd, J = 11.6, 3.7 Hz, 1H), 3.05 (s, 3H), 2.39 – 2.33 (m, 1H), 2.7 – 2.11 (m, 1H), 1.33 – 1.21 (m, 2H), 1.17 – 1.07 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H).

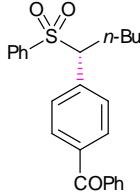
¹³C NMR (151 MHz, CDCl₃) δ 140.9, 139.0, 137.2, 134.1, 131.0, 129.1, 129.0, 127.6, 71.2, 44.6, 28.9, 27.5, 22.3, 13.8.

HRMS (ESI) calcd. for C₁₈H₂₁O₄S₂ ([M-H]⁻) *m/z* 365.0887, found 365.0894.

M.P. 54.2 – 56 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl₃) = +79.4°.

(R)-Phenyl(4-(1-(phenylsulfonyl)pentyl)phenyl)methanone (7)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and (4-bromophenyl)(phenyl)methanone (58.8 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **7** as an off-white solid (31.2 mg, 53% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 12.8 min, t_R (major) = 16.3 min.

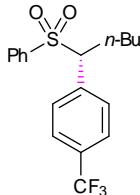
¹H NMR (600 MHz, CDCl₃) δ δ 7.79 – 7.74 (m, 2H), 7.71 – 7.65 (m, 2H), 7.63 – 7.55 (m, 4H), 7.49 (dd, J = 8.4, 7.1 Hz, 2H), 7.42 (dd, J = 8.4, 7.4 Hz, 2H), 7.23 (d, J = 1.7 Hz, 2H), 4.12 (dd, J = 11.6, 3.6 Hz, 1H), 2.46 – 2.41 (m, 1H), 2.22 – 2.15 (m, 1H), 1.38 – 1.27 (m, 2H), 1.20 (q, J = 8.2 Hz, 2H), 0.84 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 196.2, 137.8, 137.4, 137.4, 137.2, 133.8, 132.8, 130.2, 130.1, 129.9, 129.1, 128.9, 128.5, 71.6, 29.0, 27.3, 22.4, 13.8.

HRMS (ESI) calcd for C₂₄H₂₅O₃S ([M+H]⁺) *m/z* 393.1519, found 393.1521.

$[\alpha]_D$ (25.0 °C, c = 0.8 in CHCl₃) = +72.75°.

(R)-1-(1-(Phenylsulfonyl)pentyl)-4-(trifluoromethyl)benzene (8)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-bromo-4-(trifluoromethyl)benzene (50.6 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **8** as an off-white solid (33.2 mg, 62% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 220 nm, t_R (minor) = 6.0 min, t_R (major) = 7.3 min.

¹H NMR (600 MHz, CDCl₃) δ 7.59 – 7.52 (m, 3H), 7.50 (d, J = 8.1 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.08 (dd, J = 11.6, 3.6 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.18 – 2.11 (m, 1H), 1.37 –

1.22 (m, 2H), 1.21 – 1.09 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 137.2, 136.8, 133.9, 131.0 (q, J = 32.7 Hz), 130.4, 129.1, 128.9, 125.5 (q, J = 3.7 Hz), 123.95 (d, J = 272.2 Hz), 71.3, 28.9, 27.3, 22.3, 13.8.

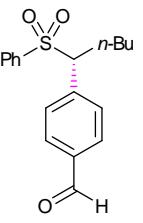
^{19}F NMR (565 MHz, CDCl_3) δ -62.75.

HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{F}_3\text{NO}_2\text{S}$ ($[\text{M}+\text{NH}_4]^+$) m/z 374.1396, found: 374.1398.

M.P. 113.1 – 114.9 °C.

$[\alpha]_D$ (25.0 °C, c = 0.72 in CHCl_3) = +77.778°.

(R)-4-(1-(Phenylsulfonyl)pentyl)benzaldehyde (9)

 This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromobenzaldehyde (41.6 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **9** as an off-white solid (19 mg, 40% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, $i\text{PrOH}$ -hexanes 20/80, 1.0 mL/min, 254 nm, t_R (minor) = 8.5 min, t_R (major) = 10.7 min.

^1H NMR (600 MHz, CDCl_3) δ 9.99 (s, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.40 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 4.12 (dd, J = 11.7, 3.6 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.21 – 2.14 (m, 1H), 1.36 – 1.26 (m, 2H), 1.22 – 1.09 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

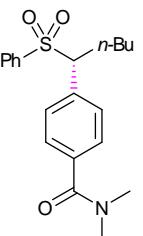
^{13}C NMR (151 MHz, CDCl_3) δ 191.77, 139.45, 137.24, 136.47, 133.89, 130.64, 129.76, 129.05, 128.95, 71.61, 28.96, 27.25, 22.34, 13.80.

HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{NaO}_3\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 339.1025, found 339.1025.

M.P. 74.3 – 76.1 °C.

$[\alpha]_D$ (25.0 °C, c = 0.50 in CHCl_3) = +73.8°.

(R)-N,N-Dimethyl-4-(1-(phenylsulfonyl)pentyl)benzamide (10)

 This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromo-N,N-dimethylbenzamide (51.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified

by flash column chromatograph to afford **10** as a light-yellow oil (22.1 mg, 41% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 240 nm, t_R (minor) = 11.0 min, t_R (major) = 13.9 min.

$^1\text{H NMR}$ (600 MHz, CDCl₃) δ 7.65 – 7.47 (m, 3H), 7.44 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 4.04 (dd, J = 11.7, 3.6 Hz, 1H), 3.01 (d, J = 97.7 Hz, 6H), 2.44 – 2.32 (m, 1H), 2.20 – 2.08 (m, 1H), 1.34 – 1.21 (m, 2H), 1.18 – 1.12 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl₃) δ 171.0, 137.5, 136.8, 134.1, 133.7, 130.0, 129.1, 128.8, 127.3, 71.5, 28.9, 27.2, 22.3, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₆NO₃S ([M+H]⁺) *m/z* 360.1628, found 360.1631.

[α]D (25.0 °C, c = 0.9 in CHCl₃) = +59.222°.

(R)-N-Methoxy-N-methyl-4-(1-(phenylsulfonyl)pentyl)benzamide (**11**)

This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromo-N-methoxy-N-methylbenzamide (54.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **11** as an off-white solid (40 mg, 71% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 254 nm, t_R (minor) = 9.3 min, t_R (major) = 11.7 min.

$^1\text{H NMR}$ (600 MHz, CDCl₃) δ 7.54–7.50 (m, 5H), 7.38 – 7.32 (m, 2H), 7.15 – 7.10 (m, 2H), 4.05 (dd, J = 11.6, 3.6 Hz, 1H), 3.51 (s, 3H), 3.33 (s, 3H), 2.44 – 2.38 (m, 1H), 2.19 – 2.09 (m, 1H), 1.37 – 1.21 (m, 2H), 1.20 – 1.09 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).

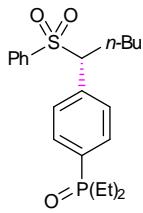
$^{13}\text{C NMR}$ (151 MHz, CDCl₃) δ 166.2, 137.4, 135.2, 134.4, 133.6, 129.6, 129.1, 128.8, 128.4, 71.4, 61.1, 28.9, 27.1, 22.3, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₆NO₄S ([M+H]⁺) *m/z* 376.1577, found: 376.1583.

M.P. 48.9 – 51.3 °C .

[α]D (25.0 °C, c = 0.36 in CHCl₃) = +105.833°.

Diethyl (R)-(4-(1-(phenylsulfonyl)pentyl)phenyl)phosphonate (**12**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and diethyl (4-bromophenyl)phosphonate (66 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **12** as a yellow oil (33.1 mg, 52% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 240 nm, t_R (minor) = 6.5 min, t_R (major) = 7.9 min.

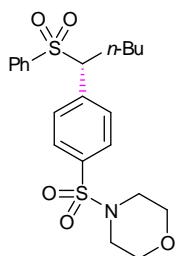
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.66 (dd, J = 13.0, 8.0 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.36 (t, J = 7.8 Hz, 2H), 7.20 (dd, J = 8.1, 3.7 Hz, 2H), 4.18 – 4.00 (m, 5H), 2.43 – 2.37 (m, 1H), 2.19 – 2.10 (m, 1H), 1.31 (td, J = 7.1, 2.0 Hz, 6H), 1.29 – 1.21 (m, 2H), 1.18 – 1.09 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 137.3, 137.21 (d, J = 3.3 Hz), 133.78, 131.90 (d, J = 10.4 Hz), 130.0 (d, J = 15.2 Hz), 129.1 (d, J = 188.75 Hz), 129.1, 128.8, 71.54, 62.38, 62.35, 28.94, 27.20, 22.33, 16.48, 16.44, 13.78.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_5\text{PS}$ ($[\text{M}+\text{H}]^+$) m/z 425.1546, found: 425.1554.

$[\alpha]_D$ (25.0 °C, c = 1.40 in CHCl_3) = +54.429°.

(*R*)-4-((4-(1-(Phenylsulfonyl)pentyl)phenyl)sulfonyl)morpholine (**13**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-((4-bromophenyl)sulfonyl)morpholine (68.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **13** as an off-white solid (46 mg, 70% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 19.6 min, t_R (major) = 31.5 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 (d, J = 7.9 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.52 – 7.47 (m, 2H), 7.43 – 7.37 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.11 (dd, J = 11.5, 3.7 Hz, 1H), 3.74 (t, J = 4.8 Hz, 4H), 2.95 – 2.89 (m, 4H), 2.47 – 2.42 (m, 1H), 2.19 – 2.13 (m, 1H), 1.34 – 1.24 (m, 2H), 1.21 – 1.09 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

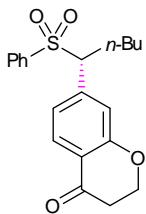
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 138.4, 137.2, 135.2, 133.9, 130.7, 129.0, 128.9, 128.0, 71.3, 66.1, 46.1, 29.0, 27.2, 22.3, 13.8.

HRMS (ESI) calcd. for $C_{21}H_{28}NO_5S_2$ ($[M+H]^+$) m/z 438.1403, found: 438.1411.

M.P. 127.8 – 129.4 °C.

$[\alpha]_D$ (25.0 °C, c = 1.00 in CHCl₃) = +76.515°.

(R)-7-(1-(Phenylsulfonyl)pentyl)chroman-4-one (14)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 7-bromochroman-4-one (51.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **14** as an off-white solid (30.1mg, 56% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 254 nm, t_R (minor) = 12.0 min, t_R (major) = 16.3 min.

¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, J = 8.1 Hz, 1H), 7.64 – 7.53 (m, 3H), 7.42 (t, J = 7.9 Hz, 2H), 6.80 (d, J = 1.7 Hz, 1H), 6.72 (dd, J = 8.1, 1.7 Hz, 1H), 4.57 – 4.44 (m, 2H), 4.00 (dd, J = 11.7, 3.6 Hz, 1H), 2.79 (dd, J = 7.1, 5.8 Hz, 2H), 2.38 – 2.32 (m, 1H), 2.15 – 2.04 (m, 1H), 1.35 – 1.23 (m, 13.7, 11.2, 6.8 Hz, 2H), 1.14 (p, J = 7.7 Hz, 2H), 0.81 (t, J = 7.3 Hz, 3H).

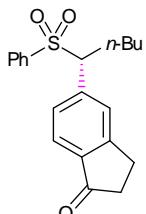
¹³C NMR (151 MHz, CDCl₃) δ 191.5, 161.7, 141.1, 137.3, 133.9, 129.1, 128.9, 127.3, 122.9, 121.4, 119.5, 71.5, 67.2, 37.8, 28.9, 27.4, 22.4, 13.8.

HRMS (ESI) calcd for $C_{20}H_{23}O_4S$ ($[M+H]^+$) m/z 359.1312, found 359.1319.

M.P. 96.4 – 97.8 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl₃) = +107.6°.

(R)-5-(1-(Phenylsulfonyl)pentyl)-2,3-dihydro-1*H*-inden-1-one (15)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromo-2,3-dihydro-1*H*-inden-1-one (47.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **15** as an off-white solid (33.4 mg, 65% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 251 nm, t_R (minor) = 19.5 min, t_R (major) = 26 min.

¹H NMR (600 MHz, CDCl₃) δ 7.61 – 7.52 (m, 4H), 7.44 – 7.37 (m, 2H), 7.32 (s, 1H), 7.06 – 6.99 (m, 1H), 4.11 (dd, *J* = 11.6, 3.7 Hz, 1H), 3.13 – 3.02 (m, 2H), 2.72 – 2.65 (m, 2H), 2.43 – 2.37 (m, 1H), 2.19–2.12 (m, 1H), 1.36 – 1.23 (m, 2H), 1.18– 1.12 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

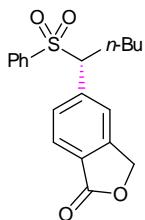
¹³C NMR (151 MHz, CDCl₃) δ 206.4, 155.3, 139.6, 137.5, 137.3, 133.8, 129.3, 129.1, 128.9, 128.3, 123.7, 71.8, 36.5, 29.0, 27.5, 25.8, 22.4, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₃O₃S ([M+H]⁺) *m/z* 343.1362, found: 343.1366.

M.P. 105.9 – 107.2 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +90.2°.

(R)-5-(1-(Phenylsulfonyl)pentyl)isobenzofuran-1(3H)-one (16)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromoisobenzofuran-1(3H)-one (47.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **16** as an off-white solid (26.9 mg, 52% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 240 nm, *t*_R (minor) = 16.0 min, *t*_R (major) = 19.6 min.

¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.46 – 7.34 (m, 2H), 7.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.27 (q, *J* = 15.3 Hz, 2H), 4.16 (dd, *J* = 11.6, 3.6 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.19 – 2.12 (m, 1H), 1.35 – 1.23 (m, 2H), 1.21 – 1.05 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

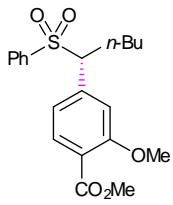
¹³C NMR (151 MHz, CDCl₃) δ 170.4, 146.9, 139.5, 137.2, 134.0, 131.1, 129.1, 129.0, 126.3, 125.8, 123.6, 71.6, 69.6, 29.0, 27.6, 22.3, 13.8.

HRMS (ESI) () calcd. for C₁₉H₂₀KO₄S ([M+K]⁺) *m/z* 383.0714, found 383.0718.

M.P. 101.5 – 102.9 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +96.8°.

Methyl (R)-2-methoxy-4-(1-(phenylsulfonyl)pentyl)benzoate (17)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromo-2-methoxybenzoate (55.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **17** as an off-white solid (23.7 mg, 42% yield, 83% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 14.0 min, t_R (major) = 16.6 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.64 (d, J = 8.3 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.42 – 7.37 (m, 2H), 6.68 (dt, J = 4.3, 2.2 Hz, 2H), 4.02 (dd, J = 11.6, 3.6 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 2.47 – 2.42 (m, 1H), 2.16 – 2.09 (m, 1H), 1.36 – 1.32 (m, 1H), 1.31 – 1.11 (m, 3H), 0.83 (t, J = 7.3 Hz, 3H).

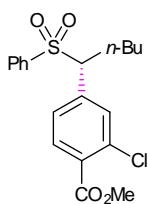
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.3, 159.1, 138.6, 137.4, 133.8, 131.8, 129.1, 128.9, 121.7, 120.3, 113.5, 71.7, 56.2, 52.3, 29.0, 27.1, 22.4, 13.8.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_5\text{S}$ ($[\text{M}+\text{H}]^+$) m/z 377.1417, found 377.1418.

M.P. 95.5 – 97.2 °C.

$[\alpha]_D$ (25.0 °C, c = 1.00 in CHCl_3) = + 61.7°.

Methyl (*R*)-2-chloro-4-(1-(phenylsulfonyl)pentyl)benzoate (**18**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromo-2-chlorobenzoate (56.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **18** as an off-white solid (17.7 mg, 31% yield, 81% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 210 nm, t_R (minor) = 10.1 min, t_R (major) = 14.8 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, J = 8.0 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.46 – 7.41 (m, 2H), 7.13 (d, J = 1.7 Hz, 1H), 7.10 (dd, J = 8.1, 1.8 Hz, 1H), 4.01 (dd, J = 11.6, 3.6 Hz, 1H), 3.92 (s, 3H), 2.43 – 2.38 (m, 1H), 2.12 – 2.04 (m, 1H), 1.36 – 1.23 (m, 2H), 1.19 – 1.09 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

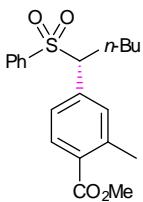
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 165.7, 138.0, 137.0, 134.1, 134.0, 132.4, 131.6, 130.2, 129.1, 129.1, 128.0, 71.0, 52.7, 28.9, 27.2, 22.3, 13.8.

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{22}\text{ClO}_4\text{S}$ ($[\text{M}+\text{H}]^+$) m/z 381.0922, found 381.0919.

M.P. 83.7 – 85.3 °C.

[*a*]D (25.0 °C, c = 0.50 in CHCl3) = +67°.

Methyl (*R*)-2-methyl-4-(1-(phenylsulfonyl)pentyl)benzoate (19)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromo-2-methylbenzoate (51.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **19** as an off-white solid (34.1 mg, 63% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 240 nm, tR (minor) = 8.2 min, tR (major) = 10.1 min.

1H NMR (600 MHz, CDCl3) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.42 – 7.37 (m, 2H), 6.98 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.94 – 6.90 (m, 1H), 4.01 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.87 (s, 3H), 2.48 (s, 3H), 2.48 – 2.36 (m, 1H), 2.19 – 2.08 (m, 1H), 1.34 – 1.23 (m, 2H), 1.18 – 1.10 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

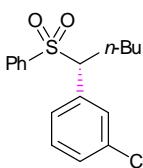
13C NMR (151 MHz, CDCl3) δ 167.7, 140.5, 137.3, 136.6, 133.7, 133.3, 130.8, 129.9, 129.2, 128.8, 127.1, 71.4, 52.1, 29.0, 27.1, 22.3, 21.7, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₄KO₄S ([M+K]⁺) m/z 399.1027, found: 399.1028.

M.P. 89.6 – 91.5 °C.

[*a*]D (25.0 °C, c = 0.68 in CHCl3) = +76.029°.

Methyl (*R*)-3-(1-(phenylsulfonyl)pentyl)benzoate (20)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 3-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **20** as an off-white solid (21.3 mg, 41% yield, 86% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 254 nm, tR (minor) = 10.4 min, tR (major) = 12.7 min.

1H NMR (600 MHz, CDCl3) δ 7.98 – 2.94 (m, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.41

– 7.31 (m, 4H), 4.08 (dd, J = 11.6, 3.6 Hz, 1H), 3.88 (s, 3H), 2.45 – 2.39 (m, 1H), 2.19 – 2.13 (m, 1H), 1.35 – 1.25 (m, 2H), 1.20 – 1.11 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl₃) δ) 167.4, 138.1, 134.0, 133.4, 132.3, 131.8, 130.7, 129.6, 129.0, 128.6, 128.3, 63.8, 52.2, 28.7, 27.6, 22.4, 13.8.

HRMS (ESI) calcd. for C₁₉H₂₆NO₄S ([M+NH₄]⁺) *m/z* 364.1577, found 364.1574.

M.P. 73.4 – 74.9 °C.

[*a*]_D (25.0 °C, c = 0.5 in CHCl₃) = +39°.

(*R*)-((1-Phenylpentyl)sulfonyl)benzene (**21**)³

This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and iodobenzene (35.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **21** as an off-white solid (45.9 mg, 80% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 5/95, 1.0 mL/min, 230 nm, *t_R* (minor) = 8.9 min, *t_R* (major) = 11.6 min.

^1H NMR (600 MHz, CDCl₃) δ 7.54–7.50 (m, , 3H), 7.36 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.08 (d, J = 7.4 Hz, 2H), 4.02 (dd, J = 11.7, 3.6 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.20 – 2.09 (m, 1H), 1.38 – 1.23 (m, 2H), 1.22 – 1.15 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

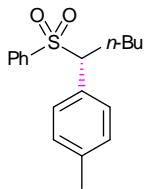
^{13}C NMR (151 MHz, CDCl₃) δ 137.6, 133.5, 132.5, 130.0, 129.1, 128.8, 128.7, 128.5, 71.8, 29.0, 27.1, 22.4, 13.8.

M.P. 76.9 – 78.6 °C.

[*a*]_D (25.0 °C, c = 1.00 in CHCl₃) = +71.7°.

Lit: [*a*] (25.0 °C, c = 1.08 in CHCl₃) = -78° (*S* enantiomer, 84% ee).³ Based on the literature precedent, we assign our product as the *R* enantiomer.

(*R*)-1-Methyl-4-(1-(phenylsulfonyl)pentyl)benzene (**22**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-iodo-4-methylbenzene (38.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **22** as an off-white solid (49.1 mg, 70% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 5/95, 1.0 mL/min, t_R (minor) = 8.2 min, t_R (major) = 10.0 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.57 – 7.49 (m, 3H), 7.37 (dd, J = 8.5, 7.1 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 7.00 – 6.94 (m, 2H), 3.98 (dd, J = 11.7, 3.6 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.31 (s, 3H), 2.16 – 2.05 (m, 1H), 1.36 – 1.22 (m, 2H), 1.21 – 1.10 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

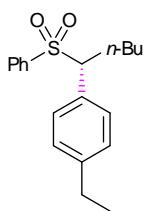
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 138.7, 137.67, 133.4, 129.8, 129.3, 129.3, 129.2, 128.7, 71.4, 29.0 27.1, 22.4, 21.3, 13.8.

HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_2\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 325.1233, found: 325.1240.

M.P. 80.5 – 81.8 °C.

$[\alpha]_D$ (25.0 °C, c = 0.52 in CHCl_3) = +78.654°.

(*R*)-1-Ethyl-4-(1-(phenylsulfonyl)pentyl)benzene (23)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-ethyl-4-iodobenzene (52.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **23** as an off-white solid (29 mg, 61% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 5/95, 1.0 mL/min, t_R (minor) = 7.3 min, t_R (major) = 8.5 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 – 7.47 (m, 3H), 7.39 – 7.33 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.01 – 6.95 (m, 2H), 3.99 (dd, J = 11.6, 3.6 Hz, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.40 – 2.35 (m, 1H), 2.15 – 2.09 (m, 1H), 1.35 – 1.26 (m, 2H), 1.23 – 1.13 (m, 5H), 0.82 (t, J = 7.3 Hz, 3H).

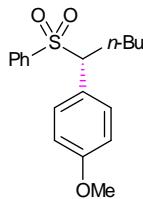
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 145.1, 137.7, 133.4, 129.9, 129.5, 129.2, 128.6, 128.1, 71.5, 29.0, 28.7, 27.1, 22.4, 15.6, 13.9.

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_2\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 339.1389, found: 339.1394.

M.P. 65.9 – 67.6 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl₃) = +71.4°.

(R)-1-Methoxy-4-(1-(phenylsulfonyl)pentyl)benzene (24)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-iodo-4-methoxybenzene (42.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **24** as an off-white solid (52.7 mg, 72% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 8.5 min, t_R (major) = 10.4 min.

¹H NMR (600 MHz, CDCl₃) δ 7.57 – 7.48 (m, 3H), 7.41 – 7.34 (m, 2H), 7.03 – 6.96 (m, 2H), 6.79 – 6.73 (m, 2H), 3.97 (dd, J = 11.7, 3.6 Hz, 1H), 3.78 (s, 3H), 2.41 – 2.35 (m, 1H), 2.14 – 2.03 (m, 1H), 1.37 – 1.23 (m, 2H), 1.19 – 1.13 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

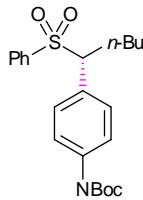
¹³C NMR (151 MHz, CDCl₃) δ 160.0, 137.7, 133.4, 131.1, 129.2, 128.7, 124.2, 114.0, 71.1, 55.4, 29.0, 27.1, 22.4, 13.9.

HRMS (ESI) calcd for C₁₈H₂₂NaO₃S ([M+Na]⁺) *m/z* 341.1182, found 341.1189.

M.P. 81.5 – 83.9 °C.

$[\alpha]_D$ (25.0 °C, c = 1.1 in CHCl₃) = +81.091°.

tert-Butyl (R)-(4-(1-(phenylsulfonyl)pentyl)phenyl)carbamate (25)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl (4-iodophenyl)carbamate (71.8 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **25** as an off-white solid (27.9 mg, 46% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 5/95, 1.0 mL/min, 254 nm, t_R (minor) = 21.8 min, t_R (major) = 23.4 min.

¹H NMR (600 MHz, CDCl₃) δ 7.56 – 7.49 (m, 3H), 7.38 (dd, J = 8.5, 7.1 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.01 – 6.96 (m, 2H), 6.53 (s, 1H), 3.97 (dd, J = 11.7, 3.5 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.14 – 2.01 (m, 1H), 1.50 (s, 9H), 1.35 – 1.21 (m, 3H), 1.19 – 1.10 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

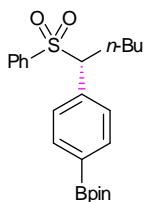
¹³C NMR (151 MHz, CDCl₃) δ 152.6, 138.9, 137.6, 133.5, 130.6, 129.2, 128.7, 126.6, 118.2, 80.9, 71.2, 29.0, 28.4, 27.1, 22.4, 13.9.

HRMS (ESI) calcd for C₂₂H₂₉NNaO₄S ([M+Na]⁺) *m/z* 426.1710, found 426.1712.

M.P. 154.4 – 155.8 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +74.8°.

(R)-4,4,5,5-Tetramethyl-2-(4-(phenylsulfonyl)pentyl)phenyl-1,3,2-dioxaborolane (26)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (74.2 mg, .225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **26** as an off-white solid (27.4 mg, 44% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 230 nm, *t_R* (minor) = 5.6 min, *t_R* (major) = 6.2 min.

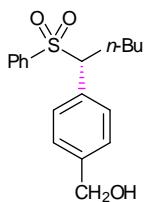
¹H NMR (600 MHz, CDCl₃) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.37 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 4.02 (dd, *J* = 11.7, 3.6 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.17 – 2.11 (m, 1H), 1.34 (s, 14H), 1.18 – 1.11 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 137.5, 135.6, 134.9, 133.6, 129.3, 129.2, 128.8, 84.1, 71.9, 29.0, 27.2, 25.0, 22.4, 13.8.

HRMS (ESI) calcd for C₂₃H₃₁BKO₄S ([M+K]⁺) *m/z* 453.1668, found 453.1676.

[*a*]D (25.0 °C, c = 0.4 in CHCl₃) = +60.5°.

(R)-(4-(Phenylsulfonyl)pentyl)phenylmethanol (27)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and (4-iodophenyl)methanol (52.7 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **27** as an off-white solid (30.1 mg, 63% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 240 nm, *t_R* (minor) = 7.5 min, *t_R* (major) = 11.5 min.

¹H NMR (600 MHz, CDCl₃) δ 7.59 – 7.48 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.66 (s, 2H), 4.02 (dd, *J* = 11.7, 3.5 Hz, 1H), 2.4 – 2.34 (m, 1H), 2.15 – 2.08 (m, 1H), 1.85 (s, 1H), 1.35 – 1.21 (m, 2H), 1.18 – 1.12 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

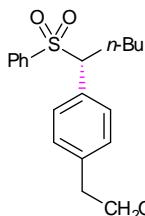
¹³C NMR (151 MHz, CDCl₃) δ 141.6, 137.5, 133.6, 131.7, 130.2, 129.1, 128.8, 127.0, 71.4, 64.9, 29.0, 27.2, 22.4, 13.8.

HRMS (ESI) calcd for C₁₈H₂₂KO₃S ([M+K]⁺) *m/z* 357.0921, found 357.0925.

M.P. 88 – 89.5 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +79.8°.

(R)-2-(4-(1-(Phenylsulfonyl)pentyl)phenyl)ethan-1-ol (28)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 2-(4-iodophenyl)ethan-1-ol (55.8 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **28** as an off-white solid (30.9mg, 62% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 240 nm, *t*_R (minor) = 7.4 min, *t*_R (major) = 9.5 min.

¹H NMR (600 MHz, CDCl₃) δ 7.56 – 7.49 (m, 3H), 7.40 – 7.35 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.00 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.39 – 2.32 (m, 1H), 2.15–2.10 (m, 1H), 1.35 – 1.26 (m, 3H), 1.19 – 1.14 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

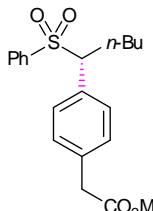
¹³C NMR (151 MHz, CDCl₃) δ 139.4, 137.6, 133.5, 130.5, 130.2, 129.2, 129.1, 128.7, 71.4, 63.6, 39.0, 29.0, 27.2, 22.4, 13.8.

HRMS (ESI) calcd. for C₁₉H₂₄NaO₃S ([M+Na]⁺) *m/z* 355.1338, found 355.1342.

M.P. 72.7 – 74.5 °C.

[*a*]D (25.0 °C, c = 1.00 in CHCl₃) = +70.4°.

Methyl (R)-2-(4-(1-(phenylsulfonyl)pentyl)phenyl)acetate (29)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 2-(4-iodophenyl)acetate (66.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **29** as an off-white solid (29.7 mg, 55% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 240 nm, t_R (minor) = 7.3 min, t_R (major) = 9.2 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 – 7.47 (m, 3H), 7.40 – 7.34 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.08 – 7.02 (m, 2H), 4.00 (dd, J = 11.6, 3.6 Hz, 1H), 3.70 (s, 3H), 3.59 (s, 2H), 2.41 – 2.35 (m, 1H), 2.15 – 2.08 (m, 1H), 1.35 – 1.23 (m, 2H), 1.20 – 1.13 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

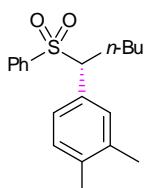
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.8, 137.5, 134.7, 133.5, 131.3, 130.2, 129.5, 129.2, 128.7, 71.4, 52.2, 40.9, 29.0, 27.2, 22.4, 13.8.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{24}\text{NaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 383.1288, found 383.1289.

M.P. 76.9 – 78.6 °C.

$[\alpha]_D$ (25.0 °C, c = 0.9 in CHCl_3) = +59.222°.

(*R*)-1,2-Dimethyl-4-(1-(phenylsulfonyl)pentyl)benzene (**30**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-iodo-1,2-dimethylbenzene (55.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **30** as an off-white solid (29 mg, 61% yield, 85% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 5/95, 1.0 mL/min, 254 nm, t_R (minor) = 7.6 min, t_R (major) = 8.8 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.57 – 7.50 (m, 3H), 7.42 – 7.35 (m, 2H), 6.98 (d, J = 7.7 Hz, 1H), 6.83 (d, J = 1.9 Hz, 1H), 6.79 (dd, J = 7.7, 2.0 Hz, 1H), 3.95 (dd, J = 11.7, 3.6 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 2.13 – 2.05 (m, 1H), 1.34 – 1.26 (m, 2H), 1.21 – 1.11 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 137.7, 137.3, 136.8, 133.4, 131.2, 129.7, 129.50, 129.3, 128.6, 127.3, 71.5, 29.0, 27.2, 22.4, 19.8, 19.6, 13.8.

HRMS (ESI) calcd. for C₁₉H₂₅O₂S ([M+NH₄]⁺) *m/z* 334.1835, found 334.1841..

M.P. 111.1 – 112.9 °C.

[*a*]D (25.0 °C, c = 0.6 in CHCl₃) = +65.167°.

(R)-1-Methoxy-3-(1-(phenylsulfonyl)pentyl)benzene (31)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-iodo-3-methoxybenzene (52.7 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **31** as an off-white solid (20.1 mg, 42% yield, 86% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 210 nm, *t*_R (minor) = 7.4 min, *t*_R (major) = 9.5 min.

¹H NMR (600 MHz, CDCl₃) δ 7.53 (dd, *J* = 7.7, 6.2 Hz, 3H), 7.38 (dd, *J* = 8.8, 6.9 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 2.1 Hz, 1H), 3.98 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.70 (s, 3H), 2.43 – 2.37 (m, 1H), 2.19 – 2.06 (m, 1H), 1.36 – 1.26 (m, 2H), 1.22 – 1.16 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

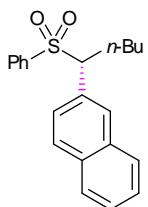
¹³C NMR (151 MHz, CDCl₃) δ 159.6, 137.6, 134.0, 133.5, 129.5, 129.2, 128.7, 122.4, 115.3, 114.5, 71.8, 55.4, 29.0, 27.2, 22.4, 13.9.

HRMS (ESI) calcd. for C₁₈H₂₂NaO₃S ([M+Na]⁺) *m/z* 341.1182, found 341.1188.

M.P. 97.2 – 98.8 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +91.8°.

(R)-2-(1-(Phenylsulfonyl)pentyl)naphthalene (32)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 2-iodonaphthalene (57.1 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **32** as an off-white solid (26.9 mg, 53% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 230 nm, *t*_R (minor) = 8.0 min, *t*_R (major) = 9.8 min.

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.78 (m, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.56 – 7.42 (m, 6H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.24 (s, 1H), 4.19 (dd, *J* = 11.7, 3.6 Hz, 1H), 2.51 –

2.46 (m, 1H), 2.32 – 2.21 (m, 1H), 1.38 – 1.25 (m, 2H), 1.22 - 1.15 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

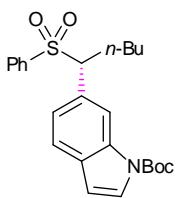
^{13}C NMR (151 MHz, CDCl_3) δ 137.5, 133.5, 133.3, 133.1, 130.0, 129.9, 129.2, 128.7, 128.3, 128.1, 127.8, 126.8, 126.7, 126.4, 71.9, 29.1, 27.2, 22.4, 13.9.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}_2\text{S}$ ($[\text{M}+\text{NH}_4]^+$) m/z 356.1679, found 356.1684.

M.P. 110.5 – 102.3 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl_3) = +79.6°.

***tert*-Butyl (R)-6-(1-(phenylsulfonyl)pentyl)-1*H*-indole-1-carboxylate (33)**



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl 6-iodo-1*H*-indole-1-carboxylate (77.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **33** as an off-white solid (40.4 mg, 63% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H, *iPrOH*-hexanes 10/90, 0.5 mL/min, 254 nm, t_R (minor) = 13.9 min, t_R (major) = 15.2 min.

^1H NMR (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.59 (s, 1H), 7.56 – 7.47 (m, 3H), 7.42 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 4.15 (dd, J = 11.7, 3.6 Hz, 1H), 2.46- 2.41 (m, 1H), 2.25 – 2.13 (m, 1H), 1.64 (s, 9H), 1.36 – 1.28 (m, 2H), 1.26 – 1.7 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

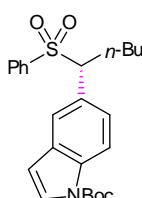
^{13}C NMR (151 MHz, CDCl_3) δ 149.6, 137.7, 135.1, 133.3, 131.0, 129.2, 128.6, 128.2, 126.9, 124.3, 120.9, 117.1, 107.1, 84.0, 72.3, 29.1, 28.3, 27.6, 22.4, 13.9.

HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{29}\text{NNaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 450.1710, found 450.1709.

M.P. 110.8 – 112.2 °C.

$[\alpha]_D$ (22.0 °C, c = 0.5 in CHCl_3) = +54.6°.

***tert*-Butyl (R)-5-(1-(phenylsulfonyl)pentyl)-1*H*-indole-1-carboxylate (34)**



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl 5-iodo-1*H*-indole-1-carboxylate (77.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture

was purified by flash column chromatograph to afford **34** as an off-white solid (34 mg, 53% yield, 82% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 6.7 min, t_R (major) = 7.9 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.99 (d, J = 8.6 Hz, 1H), 7.65 – 7.45 (m, 4H), 7.41 – 7.29 (m, 3H), 7.02 (d, J = 8.6 Hz, 1H), 6.47 (d, J = 3.7 Hz, 1H), 4.14 – 4.08 (m, 1H), 2.50 – 2.40 (m, 1H), 2.24 – 2.13 (m, 1H), 1.66 (s, 9H), 1.36 – 1.23 (m, 2H), 1.19 – 1.14 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).

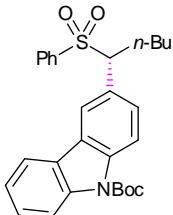
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.7, 137.7, 135.3, 133.4, 130.7, 129.2, 128.7, 126.7, 126.6, 126.0, 122.60, 115.2, 107.3, 84.1, 71.7, 29.0, 28.3, 27.5, 22.4, 13.9.

HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{29}\text{NNaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 450.1710, found 450.1710.

M.P. 69.1 – 70.8 °C.

$[\alpha]_D$ (22.0 °C, c = 0.3 in CHCl_3) = +130.333°.

***tert*-Butyl (*R*)-3-(1-(phenylsulfonyl)pentyl)-9*H*-carbazole-9-carboxylate (35)**



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl 3-iodo-9*H*-carbazole-9-carboxylate (88.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **35** as an off-white solid (36.5 mg, 51% yield, 85% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 7.1 min, t_R (major) = 8.0 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.28 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.71 (s, 1H), 7.59 – 7.52 (m, 2H), 7.49 (ddd, J = 13.8, 10.2, 7.3 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.17 (d, J = 8.6 Hz, 1H), 4.19 (dd, J = 11.9, 3.5 Hz, 1H), 2.53 – 2.48 (m, 1H), 2.30 – 2.20 (m, 1H), 1.75 (s, 9H), 1.38 – 1.26 (m, 2H), 1.23–1.17 (m, 2H), 0.81 (td, J = 7.3, 1.4 Hz, 3H).

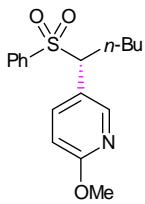
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 151.0, 138.9, 138.7, 137.6, 133.5, 129.2, 128.8, 128.7, 127.6, 127.1, 126.0, 125.3, 123.3, 121.0, 119.9, 116.4, 116.3, 84.4, 71.7, 29.1, 28.5, 27.5, 22.4, 13.9.

HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{31}\text{NNaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 500.1866, found 500.1868.

M.P. 104.4 – 106.1 °C.

$[\alpha]_D$ (22.0 °C, c = 0.5 in CHCl_3) = +1.2.6°.

(R)-2-Methoxy-5-(1-(phenylsulfonyl)pentyl)pyridine (36)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-iodo-2-methoxypyridine (52.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **36** as an off-white solid (19.2 mg, 41% yield, 87% ee; with Zn instead of Mn 21% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 8.3 min, t_R (major) = 10.2 min.

¹H NMR (600 MHz, CDCl₃) δ 7.65 (d, J = 2.5 Hz, 1H), 7.56 (dd, J = 8.1, 2.3 Hz, 3H), 7.49 (dd, J = 8.7, 2.5 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 6.69 (d, J = 8.6 Hz, 1H), 3.96 (dd, J = 11.8, 3.6 Hz, 1H), 3.88 (s, 3H), 2.41 – 2.36 (m, 1H), 2.12 – 2.00 (m, 1H), 1.34 – 1.22 (m, 2H), 1.18 – 1.13 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

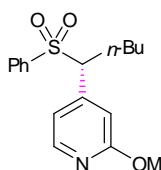
¹³C NMR (151 MHz, CDCl₃) δ 164.5, 148.6, 139.1, 137.3, 133.8, 129.1, 129.0, 121.1, 111.1, 68.5, 53.7, 28.9, 26.8, 22.3, 13.8.

HRMS (ESI) calcd. for C₁₇H₂₁NNaO₃S ([M+Na]⁺) *m/z* 342.1134, found 342.139.

M.P. 76.5 – 78.1 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = +59.8°.

(R)-2-Methoxy-4-(1-(phenylsulfonyl)pentyl)pyridine (37)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromo-2-methoxypyridine (42.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **37** as an off-white solid (22.1 mg, 46% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 230 nm, t_R (minor) = 7.3 min, t_R (major) = 10.9 min.

¹H NMR (600 MHz, CDCl₃) δ 8.05 – 8.01 (m, 1H), 7.63 – 7.55 (m, 3H), 7.47 – 7.39 (m, 2H), 6.66 (dd, J = 5.3, 1.5 Hz, 1H), 6.47 – 6.43 (m, 1H), 3.94 (dd, J = 11.6, 3.5 Hz, 1H), 3.88 (s, 3H), 2.39 – 2.33 (m, 1H), 2.11 – 2.04 (m, 1H), 1.37 – 1.20 (m, 2H), 1.17 – 1.12 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 164.5, 147.2, 144.5, 137.2, 134.0, 129.1, 129.0, 117.6, 112.2, 70.8,

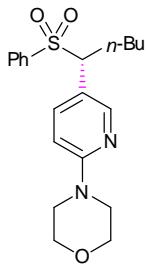
53.7, 28.9, 27.1, 22.4, 13.8.

HRMS (ESI) calcd. for C₁₇H₂₁NNaO₃S ([M+Na]⁺) *m/z* 342.1134, found 342.1139.

M.P. 64.3 – 65.9 °C.

[*a*]_D (22.0 °C, c = 0.5 in CHCl₃) = +74.8°.

(R)-4-(5-(1-(Phenylsulfonyl)pentyl)pyridin-2-yl)morpholine (38)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-(5-iodopyridin-2-yl)morpholine (66.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **38** as an off-white solid (21.4 mg, 38% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 254 nm, *t_R* (minor) = 11.4 min, *t_R* (major) = 13.7 min.

¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 2.5 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.43 (ddd, *J* = 8.5, 6.3, 1.9 Hz, 3H), 6.57 (d, *J* = 8.8 Hz, 1H), 3.92 (dd, *J* = 11.8, 3.6 Hz, 1H), 3.84 – 3.75 (m, 4H), 3.48 (dd, *J* = 5.9, 3.9 Hz, 4H), 2.36 – 2.30 (m, 1H), 2.07 – 2.00 (m, 1H), 1.35 – 1.23 (m, 2H), 1.17 – 1.12 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

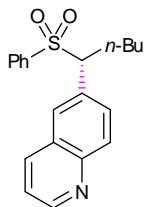
¹³C NMR (151 MHz, CDCl₃) δ 159.5, 149.6, 138.2, 137.5, 133.7, 129.1, 128.9, 117.2, 106.7, 68.6, 66.8, 45.5, 28.9, 26.8, 22.3, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₆N₂NaO₃S ([M+Na]⁺) *m/z* 397.1556, found 397.1556.

M.P. 145.1 – 146.3 °C.

[*a*]_D (22.0 °C, c = 0.5 in CHCl₃) = +106.8°.

(R)-6-(1-(Phenylsulfonyl)pentyl)quinoline (39)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 6-iodoquinoline (46.8 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **39** as an off-white solid (17.9 mg, 35% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 264 nm, *t_R* (minor) = 16.4 min, *t_R* (major) = 22.0 min.

¹H NMR (600 MHz, CDCl₃) δ 8.97 – 8.89 (m, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.48 (m, 4H), 7.45 – 7.38 (m, 2H), 7.33 (t, *J* = 8.1 Hz, 2H), 4.22 (dd, *J* = 11.7, 3.5 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.29 – 2.22 (m, 1H), 1.37 – 1.25 (m, 2H), 1.23 – 1.12 (m, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

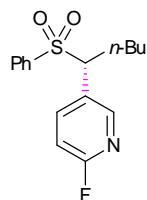
¹³C NMR (151 MHz, CDCl₃) δ 151.3, 148.2, 137.3, 136.3, 133.7, 131.1, 130.5, 129.8, 129.7, 129.1, 128.9, 128.0, 121.70, 71.6, 29.1, 27.4, 22.4, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₁NNaO₂S ([M+Na]⁺) *m/z* 362.1185, found 362.1190.

M.P. 39.9 – 41.5 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = +94°.

(R)-2-Fluoro-5-(1-(phenylsulfonyl)pentyl)pyridine (40)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromo-2-fluoropyridine (39.6 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **40** as an off-white solid (14.4 mg, 31% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 254 nm, *t*_R (minor) = 11.3 min, *t*_R (major) = 13.4 min.

¹H NMR (600 MHz, CDCl₃) δ 7.78–7.75 (m, 1H), 7.71 (s, 1H) 7.62 – 7.53 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 6.91 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.05 (dd, *J* = 11.9, 3.6 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.10 – 2.04 (m, 1H), 1.35 – 1.24 (m, 2H), 1.19 – 1.11 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.8 (d, *J* = 241.9 Hz), 149.2 (d, *J* = 15.1 Hz), 141.9 (d, *J* = 8.2 Hz), 136.9, 134.2, 129.2, 129.0, 126.6 (d, *J* = 4.7 Hz), 109.9 (d, *J* = 37.5 Hz), 68.1, 28.9, 27.0, 22.3, 13.8.

¹⁹F NMR (567 MHz, CDCl₃) δ -67.24.

HRMS (ESI) calcd. for C₁₆H₁₈FNNaO₂S ([M+Na]⁺) *m/z* 330.0935, found 330.0934.

M.P. 75.6 – 76.8 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = +50.8°.

(R)-2-Chloro-5-(1-(phenylsulfonyl)pentyl)pyridine (41)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromo-2-chloropyridine (43.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **41** as an off-white solid (18.6 mg, 38% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 12.1 min, t_R (major) = 13.5 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.88 (t, J = 2.0 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.45 (td, J = 8.0, 1.7 Hz, 2H), 7.30 (dd, J = 8.3, 1.6 Hz, 1H), 4.02 (ddd, J = 11.8, 3.9, 1.6 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.13 – 2.03 (m, 1H), 1.34 – 1.22 (m, 2H), 1.19 – 1.09 (m, 2H), 0.82 (td, J = 7.4, 1.7 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.1, 151.0, 139.4, 136.9, 134.2, 129.2, 129.0, 127.8, 124.5, 68.3, 28.9, 26.9, 22.3, 13.8.

HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{18}\text{ClNNaO}_2\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 346.0639, found 346.0638.

M.P. 108.9 – 110.5 °C.

$[\alpha]_D$ (22.0 °C, c = 0.5 in CHCl_3) = +35.8°.

(*R*)-2-Chloro-5-(1-(phenylsulfonyl)pentyl)-3-(trifluoromethyl)pyridine (**42**)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromo-2-chloro-3-(trifluoromethyl)pyridine (58.6 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **42** as an off-white solid (25.4 mg, 43% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 230 nm, t_R (minor) = 7.8 min, t_R (major) = 11.9 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.20 (t, J = 1.8 Hz, 1H), 7.76 (s, 1H), 7.65 (td, J = 7.4, 1.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.47 (m, 2H), 4.12 – 4.07 (m, 1H), 2.45 – 2.36 (m, 1H), 2.13 – 2.05 (m, 1H), 1.35 – 1.24 (m, 2H), 1.20 – 1.10 (m, 2H), 0.83 (td, J = 7.4, 1.5 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 153.2, 149.5, 137.40, 136.4, 134.6, 129.4, 129.1, 128.2, 125.4 (q, J = 33.5 Hz), 121.9 (q, J = 273.1 Hz), 68.1, 28.9, 27.0, 22.2, 13.7.

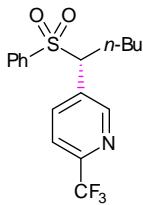
$^{19}\text{F NMR}$ (567 MHz, CDCl_3) δ -63.74.

HRMS (ESI) calcd. for C₁₇H₁₇ClF₃NNaO₂S ([M+Na]⁺) *m/z* 414.0513, found 414.0515.

M.P. 49.5 – 51.2 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = +52.2°.

(R)-5-(1-(Phenylsulfonyl)pentyl)-2-(trifluoromethyl)pyridine (43)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 5-bromo-2-(trifluoromethyl)pyridine (50.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **43** as an off-white solid (35.5 mg, 66% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 264 nm, *t*_R (minor) = 8.7 min, *t*_R (major) = 10.6 min.

¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, *J* = 2.1 Hz, 1H), 7.85 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.62 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 4.13 (dd, *J* = 11.6, 3.7 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.17 – 2.13 (m, 1H), 1.36 – 1.23 (m, 2H), 1.22 – 1.09 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 151.34, 148.53 (q, *J* = 35.3 Hz), 138.32, 136.80, 134.41, 132.24, 129.31, 128.98, 121.38 (d, *J* = 274.3 Hz), 120.42 (q, *J* = 2.3 Hz), 68.70, 28.90, 27.11, 22.30, 13.74.

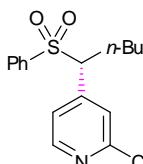
¹⁹F NMR (567 MHz, CDCl₃) δ -68.01.

HRMS (ESI) calcd. for C₁₇H₁₈F₃NNaO₂S ([M+Na]⁺) *m/z* 380.0903, found 380.0908.

M.P. 65.8 – 67.3 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = +65°.

(R)-4-(1-(Phenylsulfonyl)pentyl)-2-(trifluoromethyl)pyridine (44)



This compound was prepared according to the general procedure with Mn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 4-bromo-2-(trifluoromethyl)pyridine (50.9 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **44** as an off-white solid (27.4 mg, 51% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 220 nm, t_R (minor) = 7.9 min, t_R (major) = 11.5 min.

$^1\text{H NMR}$ (600 MHz, Acetone-*d*₆) δ 8.71 (d, J = 5.0 Hz, 1H), 7.73 (t, J = 7.4 Hz, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.57 (t, J = 7.7 Hz, 2H), 4.70 (dd, J = 11.2, 3.9 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.27 – 2.21 (m, 1H), 1.34 – 1.26 (m, 2H), 1.26 – 1.12 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, Acetone-*d*₆) δ 151.2, 148.5 (q, J = 34.7 Hz), 145.6, 138.2, 135.0, 130.0, 129.8, 128.7, 122.8 (m), 122.51 (q, J = 273.5 Hz), 69.9, 29.4, 27.7, 22.7, 13.9.

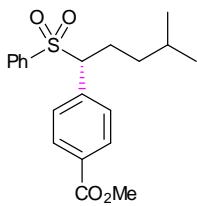
$^{19}\text{F NMR}$ (567 MHz, Acetone-*d*₆) δ -68.57.

HRMS (ESI) calcd. for C₁₇H₁₈F₃NNaO₂S ([M+Na]⁺) *m/z* 380.0903, found. 380.0905.

M.P. 85.6 – 87.1 °C.

[*a*]_D (22.0 °C, c = 0.5 in CHCl₃) = +45.4°.

Methyl (*R*)-4-(4-methyl-1-(phenylsulfonyl)pentyl)benzoate (**45**)



This compound was prepared according to the general procedure with Zn using ((1-chloro-4-methylpentyl)sulfonyl)benzene (39.1 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **45** as an off-white solid (47 mg, 88% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 8.1 min, t_R (major) = 9.4 min.

$^1\text{H NMR}$ (600 MHz, CDCl₃) δ 7.93 – 7.85 (m, 2H), 7.57 – 7.46 (m, 3H), 7.42 – 7.33 (m, 2H), 7.20 – 7.12 (m, 2H), 4.04 (dd, J = 11.7, 3.6 Hz, 1H), 3.90 (s, 3H), 2.49 – 2.43 (m, 1H), 2.18 – 2.11 (m, 1H), 1.56 – 1.47 (m, 1H), 1.13 – 1.07 (m, 1H), 1.00 – 0.91 (m, 1H), 0.82 (dd, J = 6.6, 4.2 Hz, 6H).

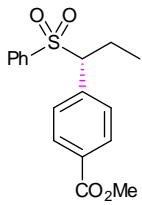
$^{13}\text{C NMR}$ (151 MHz, CDCl₃) δ 166.7, 137.8, 137.3, 133.8, 130.5, 130.0, 129.7, 129.1, 128.9, 71.8, 52.4, 35.9, 27.9, 25.4, 22.7, 22.1.

HRMS (ESI) calcd for C₂₀H₂₄NaO₄S ([M+Na]⁺) *m/z* 383.1288, found 383.1289.

M.P. 102.7 – 104.4 °C.

[*a*]_D (25.0 °C, c = 1.00 in CHCl₃) = +84°.

Methyl (*R*)-4-(1-(phenylsulfonyl)propyl)benzoate (**46**)



This compound was prepared according to the general procedure with Zn using ((1-chloropropyl)sulfonyl)benzene (32.8 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **46** as an off-white solid (37.9 mg, 73% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 210 nm, t_R (minor) = 13.5 min, t_R (major) = 16.6 min.

¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.53 (ddt, J = 14.7, 7.5, 1.3 Hz, 3H), 7.41 – 7.33 (m, 2H), 7.21 – 7.14 (m, 2H), 4.01 (dd, J = 11.5, 3.7 Hz, 1H), 3.90 (s, 3H), 2.53 – 2.46 (m, 1H), 2.20 – 2.12 (m, 1H), 0.85 (t, J = 7.4 Hz, 3H).

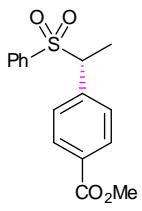
¹³C NMR (151 MHz, CDCl₃) δ 166.7, 137.4, 137.3, 133.8, 130.6, 130.0, 129.7, 129.1, 128.9, 73.0, 52.4, 21.2, 11.6.

HRMS (ESI) calcd. for C₁₇H₁₈NaO₄S ([M+Na]⁺) *m/z* 341.0818, found 341.0825.

M.P. 93.9 – 95.7 °C.

[*a*]_D (25.0 °C, c = 1.00 in CHCl₃) = +97°.

Methyl (*R*)-4-(1-(phenylsulfonyl)ethyl)benzoate (**47**)



This compound was prepared according to the general procedure with Zn using ((1-chloroethyl)sulfonyl)benzene (30.7 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **47** as an off-white solid (35.6 mg, 78% yield, 91% ee).

Chiral HPLC (CHIRALPAK AD-H, *i*PrOH-hexanes 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 43.5 min, t_R (major) = 46.0 min.

¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.87 (m, 2H), 7.63 – 7.50 (m, 3H), 7.46 – 7.39 (m, 2H), 7.24 – 7.14 (m, 2H), 4.29 (q, J = 7.1 Hz, 1H), 3.90 (s, 3H), 1.78 (d, J = 7.1 Hz, 3H).

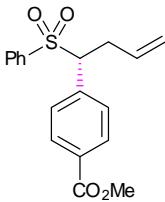
¹³C NMR (151 MHz, CDCl₃) δ 166.6, 139.0, 136.7, 133.9, 130.6, 129.7, 129.5, 129.3, 128.9, 66.0, 52.4, 14.1.

HRMS (ESI) calcd. for C₁₆H₂₀NO₄S ([M+NH₄]⁺) *m/z* 322.1108, found 322.1108.

M.P. 107.1 – 108.8 °C.

[*a*]_D (25.0 °C, c = 0.5 in CHCl₃) = +90.8°.

Methyl (*R*)-4-(1-(phenylsulfonyl)but-3-en-1-yl)benzoate (**48**)



This compound was prepared according to the general procedure with Zn using ((1-chlorobut-3-en-1-yl)sulfonyl)benzene (34.6 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **48** as an off-white solid (20.4 mg, 41% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 240 nm, t_R (minor) = 7.7 min, t_R (major) = 9.8 min.

¹H NMR (600 MHz, CDCl₃) δ 7.92 – 7.83 (m, 2H), 7.60 – 7.48 (m, 3H), 7.43 – 7.35 (m, 2H), 7.22 – 7.14 (m, 2H), 5.53 – 5.46 (m, 1H), 4.17 (dd, *J* = 11.5, 3.9 Hz, 1H), 3.90 (s, 3H), 3.26 – 3.17 (m, 1H), 2.94 – 2.89 (m, 1H).

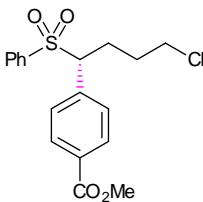
¹³C NMR (151 MHz, CDCl₃) δ 166.7, 137.1, 137.0, 134.0, 132.6, 130.6, 130.1, 129.7, 129.2, 129.0, 119.0, 70.9, 52.4, 32.0.

HRMS (ESI) calcd. for C₁₈H₁₉O₄S ([M+H]⁺) *m/z* 331.0999, found 331.1011.

M.P. 65.8 – 67.2 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +86.2°.

Methyl (*R*)-4-(4-chloro-1-(phenylsulfonyl)butyl)benzoate (**49**)



This compound was prepared according to the general procedure with Zn using ((1,4-dichlorobutyl)sulfonyl)benzene (40.1 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **49** as an off-white solid (28.7 mg, 52% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 21.6 min, t_R (major) = 23.3 min.

¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.89 (m, 2H), 7.59 – 7.55 (m, 1H), 7.54 – 7.50 (m, 2H), 7.42 – 7.37 (m, 2H), 7.21 – 7.17 (m, 2H), 4.13 (dd, *J* = 11.2, 4.1 Hz, 1H), 3.91 (s, 3H), 3.56 – 3.44 (m, 2H), 2.64 – 2.59 (m, 1H), 2.37 – 2.30 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.62 (m, 1H).

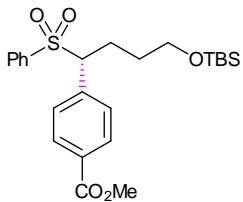
¹³C NMR (151 MHz, CDCl₃) δ 166.6, 137.2, 137.0, 134.0, 130.8, 129.9, 129.9, 129.1, 129.0, 70.8, 52.4, 44.0, 29.9, 25.3.

HRMS (ESI) calcd. for C₁₈H₂₀ClO₄S ([M+H]⁺) *m/z* 367.0765, found 367.0762.

M.P. 89.8 – 91.1 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = +102°.

Methyl (*R*)-4-((*tert*-butyldimethylsilyl)oxy)-1-(phenylsulfonyl)butylbenzoate (50)



This compound was prepared according to the general procedure with Zn using *tert*-butyl(4-chloro-4-(phenylsulfonyl)butoxy)dimethylsilane (54.5 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **50** as an off-white solid (56.3 mg, 81% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, *t*_R (minor) = 7.5 min, *t*_R (major) = 8.5 min.

¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.85 (m, 2H), 7.57 – 7.51 (m, 3H), 7.41 – 7.36 (m, 2H), 7.21 – 7.16 (m, 2H), 4.17 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.90 (s, 3H), 3.55 (td, *J* = 6.1, 1.8 Hz, 2H), 2.51 – 2.45 (m, 1H), 2.26 – 2.19 (m, 1H), 1.40 – 1.35 (m, 2H), 0.84 (s, 9H), -0.02 (d, *J* = 5.1 Hz, 6H).

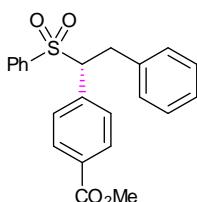
¹³C NMR (151 MHz, CDCl₃) δ 166.7, 137.6, 137.3, 133.8, 130.6, 130.1, 129.7, 129.1, 128.9, 71.2, 6, 62.3, 52.4, 29.7, 26.0, 24.5, 18.4, -5.3.

HRMS (ESI) calcd. for C₂₄H₃₄NaO₅SSi ([M+Na]⁺) *m/z* 485.1788, found 485.1788,.

M.P. 110.3 – 112.3 °C.

[*a*]D (25.0 °C, c = 0.90 in CHCl₃) = +53.111°.

Methyl (*R*)-4-(2-phenyl-1-(phenylsulfonyl)ethyl)benzoate (51)



This compound was prepared according to the general procedure with Zn using (2-chloro-2-(phenylsulfonyl)ethyl)benzene (42.1 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **51** as an off-white solid (47.4 mg, 83% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, *t*_R (minor) = 19.0 min, *t*_R (major) = 37.1 min.

¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.78 (m, 2H), 7.61 – 7.51 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.17

(d, $J = 7.9$ Hz, 2H), 7.14 – 7.05 (m, 3H), 6.98 – 6.89 (m, 2H), 4.34 (dd, $J = 11.8, 3.3$ Hz, 1H), 3.93 – 3.79 (m, 4H), 3.40 (dd, $J = 14.0, 11.8$ Hz, 1H).

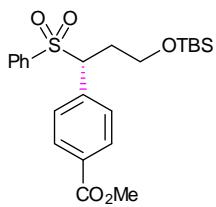
^{13}C NMR (151 MHz, CDCl₃) δ 166.6, 137.2, 137.1, 136.4, 133.9, 130.5, 130.2, 129.6, 129.1, 129.0, 129.0, 128.6, 127.0, 72.9, 52.3, 34.0.

HRMS (ESI) calcd. for C₂₂H₂₀NaO₄S ([M+Na]⁺) *m/z* 403.0975, found 403.0974.

M.P. 125.5 – 127.2 °C.

[*a*]D (25.0 °C, c = 0.55 in CHCl₃) = -4.364°.

Methyl (*R*)-4-(3-((*tert*-butyldimethylsilyl)oxy)-1-(phenylsulfonyl)propyl)benzoate (52)



This compound was prepared according to the general procedure with Zn using *tert*-butyl(3-chloro-3-(phenylsulfonyl)propoxy)dimethylsilane (52.3 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford

52 as an off-white solid (47.3 mg, 70% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 240 nm, *t*_R (minor) = 7.5 min, *t*_R (major) = 13.6 min.

^1H NMR (600 MHz, CDCl₃) δ 7.96 – 7.85 (m, 2H), 7.60 – 7.47 (m, 3H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 4.42 (dd, $J = 11.3, 3.6$ Hz, 1H), 3.91 (d, $J = 1.1$ Hz, 3H), 3.69 (dt, $J = 9.8, 4.5$ Hz, 1H), 3.27 (td, $J = 10.2, 4.0$ Hz, 1H), 2.67 – 2.62 (m, 1H), 2.28 – 2.20 (m, 1H), 0.80 (d, $J = 1.1$ Hz, 9H), -0.12 (d, $J = 31.1$ Hz, 6H).

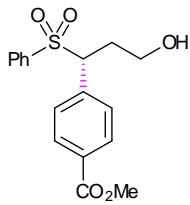
^{13}C NMR (151 MHz, CDCl₃) δ 166.7, 137.4, 137.3, 133.8, 130.5, 130.3, 129.7, 129.1, 129.0, 68.0, 59.1, 52.4, 30.8, 25.9, 18.2, -5.4, -5.5.

HRMS (ESI) calcd. for C₂₃H₃₂NaO₅SSi ([M+Na]⁺) *m/z* 471.1632, found 471.1635.

M.P. 130.2 – 131.9 °C.

[*a*]D (25.0 °C, c = 0.55 in CHCl₃) = +44.909°.

Methyl (*R*)-4-(3-hydroxy-1-(phenylsulfonyl)propyl)benzoate (53)



This compound was prepared according to the general procedure with Zn using 3-chloro-3-(phenylsulfonyl)propan-1-ol (35.2 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **53** as an off-white solid (23.2 mg, 46% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 240 nm, t_R (minor) = 12.2 min, t_R (major) = 17.1 min.

¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 8.0 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.43 – 7.34 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 4.45 (dd, J = 10.5, 4.4 Hz, 1H), 3.90 (s, 3H), 3.82 (d, J = 10.7 Hz, 1H), 3.43 – 3.38 (m, 1H), 2.76 – 2.70 (m, 1H), 2.36 – 2.31 (m, 1H).

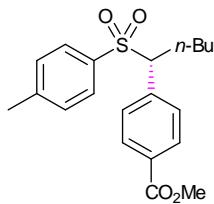
¹³C NMR (151 MHz, CDCl₃) δ 166.6, 137.5, 137.2, 133.9, 130.6, 130.1, 129.8, 129.1, 129.0, 67.9, 59.2, 52.4, 30.9.

HRMS (ESI) calcd. for C₁₇H₁₈NaO₅S ([M+Na]⁺) *m/z* 357.0767, found 357.0766.

M.P. 140.1 – 141.3 °C.

[*a*]D (25.0 °C, c = 0.7 in CHCl₃) = +96.286°.

Methyl (*R*)-4-(1-tosylpentyl)benzoate (**54**)



This compound was prepared according to the general procedure with Zn using 1-((1-chloropentyl)sulfonyl)-4-methylbenzene (39.1 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **54** as an off-white solid (35.8 mg, 66% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 9.5 min, t_R (major) = 11.9 min.

¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.41 – 7.36 (m, 2H), 7.21 – 7.13 (m, 4H), 4.05 (dd, J = 11.7, 3.6 Hz, 1H), 3.91 (s, 3H), 2.46 – 2.35 (m, 4H), 2.16 – 2.10 (m, 1H), 1.35 – 1.22 (m, 2H), 1.19 – 1.07 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

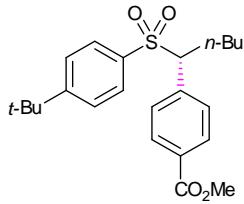
¹³C NMR (151 MHz, CDCl₃) δ 166.7, 144.8, 138.0, 134.4, 130.5, 130.0, 129.70, 129.50, 129.1, 71.5, 52.4, 29.0, 27.3, 22.4, 21.7, 13.8.

HRMS (ESI) calcd. for C₂₀H₂₄NaO₄S ([M+Na]⁺) *m/z* 383.1288, found 383.1290.

M.P. 87.2 – 88.9 °C.

[*a*]D (25.0 °C, c = 0.85 in CHCl3) = +113.059°.

Methyl (*R*)-4-(1-((4-(*tert*-butyl)phenyl)sulfonyl)pentyl)benzoate (55)



This compound was prepared according to the general procedure with Zn using 1-(*tert*-butyl)-4-((1-chloropentyl)sulfonyl)benzene (45.4 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv).

The crude mixture was purified by flash column chromatograph to afford **55** as an off-white solid (38.1 mg, 63% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 5/95, 1.0 mL/min, 240 nm, tR (minor) = 13.8 min, tR (major) = 14.5 min.

1H NMR (600 MHz, CDCl3) δ 7.94 – 7.84 (m, 2H), 7.46 – 7.40 (m, 2H), 7.41 – 7.35 (m, 2H), 7.22 – 7.15 (m, 2H), 4.06 (dd, *J* = 11.6, 3.7 Hz, 1H), 3.91 (s, 3H), 2.44 – 2.38 (m, 1H), 2.17 – 2.11 (m, 1H), 1.31 – 1.23 (m, 11H), 1.18 – 1.09 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

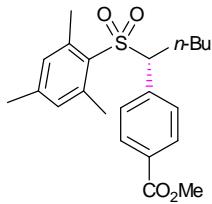
13C NMR (151 MHz, CDCl3) δ 166.8, 157.8, 138.0, 134.3, 130.5, 130.0, 129.7, 129.0, 125.9, 71.6, 52.4, 35.4, 31.2, 29.0, 27.3, 22.4, 13.9.

HRMS (ESI) calcd for C₂₃H₃₀NaO₄S ([M+Na]⁺) *m/z* 425.1757, found: 425.1759.

M.P. 99.6 – 101.2 °C.

[*a*]D (25.0 °C, c = 0.4 in CHCl3) = +144°.

Methyl (*R*)-4-(1-(mesitylsulfonyl)pentyl)benzoate (56)



This compound was prepared according to the general procedure with Zn using 2-((1-chloropentyl)sulfonyl)-1,3,5-trimethylbenzene (43.3 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **56** as an

off-white solid (29.8 mg, 51% yield, 95% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 10/90, 1.0 mL/min, 240 nm, tR (minor) = 6.5 min, tR (major) = 7.4 min.

1H NMR (600 MHz, CDCl3) δ 7.93 – 7.84 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 2H), 4.15 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.90 (s, 3H), 2.64 – 2.15 (m, 11H), 1.36 – 1.24 (m, 2H), 1.21 – 1.14 (m, 2H), 0.82

(t, $J = 7.3$ Hz, 3H).

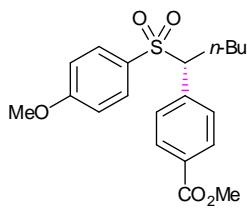
^{13}C NMR (151 MHz, CDCl_3) δ 166.8, 143.4, 140.6, 137.7, 132.1, 131.7, 130.4, 130.3, 129.6, 70.5, 52.3, 28.9, 26.1, 22.9, 22.4, 21.1, 13.8.

HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{28}\text{KO}_4\text{S}$ ($[\text{M}+\text{K}]^+$) m/z 427.1340, found 427.1332.

M.P. 101.2 – 102.7 °C.

$[\alpha]_D$ (25.0 °C, c = 1.10 in CHCl_3) = + 148.6°.

Methyl (R)-4-(1-((4-methoxyphenyl)sulfonyl)pentyl)benzoate (57)



This compound was prepared according to the general procedure with Zn using 1-((1-chloropentyl)sulfonyl)-4-methoxybenzene (41.5 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **57**

as a light-yellow oil (40.6 mg, 72% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, $i\text{PrOH}$ -hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 14.6 min, t_R (major) = 16.7 min.

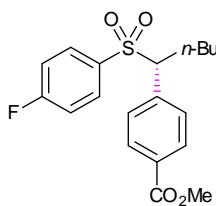
^1H NMR (600 MHz, CDCl_3) δ 7.93 – 7.87 (m, 2H), 7.44 – 7.38 (m, 2H), 7.21 – 7.15 (m, 2H), 6.85 – 6.79 (m, 2H), 4.04 (dd, $J = 11.7, 3.6$ Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.43 – 2.40 (m, 1H), 2.14 – 2.10 (m, 1H), 1.34 – 1.22 (m, 2H), 1.19 – 1.06 (m, 2H), 0.81 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 166.7, 163.8, 138.1, 131.2, 130.4, 130.0, 129.7, 128.8, 114.0, 71.7, 55.7, 52.3, 29.0, 27.3, 22.4, 13.8.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}_5\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 399.1237, found 399.1239.

$[\alpha]_D$ (25.0 °C, c = 0.8 in CHCl_3) = + 127.125°.

Methyl (R)-4-(1-((4-fluorophenyl)sulfonyl)pentyl)benzoate (58)



This compound was prepared according to the general procedure with Zn using 1-((1-chloropentyl)sulfonyl)-4-fluorobenzene (39.7 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **58** as an off-white solid (34.6 mg, 63% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, $i\text{PrOH}$ -hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 8.8 min,

t_R (major) = 15.6 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.95 – 7.88 (m, 2H), 7.54 – 7.47 (m, 2H), 7.21 – 7.15 (m, 2H), 7.09 – 7.01 (m, 2H), 4.06 (dd, J = 11.6, 3.7 Hz, 1H), 3.92 (s, 3H), 2.46 – 2.44 (m, 1H), 2.16 – 2.14 (m, 1H), 1.35 – 1.26 (m, 2H), 1.19 – 1.11 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.6, 165.9 (d, J = 256.7 Hz), 137.7, 133.4 (d, J = 3.0 Hz), 131.9 (d, J = 9.5 Hz), 130.7, 130, 129.9, 116.2 (d, J = 22.6 Hz), 71.7, 52.4, 29.0, 27.2, 22.4, 13.8.

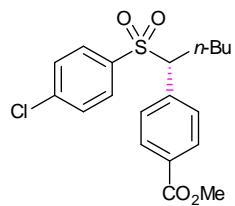
HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{21}\text{FNaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 387.1037, found 387.1036.

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -103.20.

M.P. 54.1 – 55.8 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl_3) = +68 °.

Methyl (R)-4-(1-((4-chlorophenyl)sulfonyl)pentyl)benzoate (59)



This compound was prepared according to the general procedure with Zn using 1-chloro-4-((1-chloropentyl)sulfonyl)benzene (42.2 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **59** as a yellow solid (28.6 mg, 50% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H, $i\text{PrOH}$ -hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 8.3 min, t_R (major) = 12.4 min.

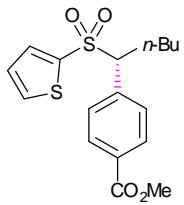
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.95 – 7.89 (m, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.21 – 7.16 (m, 2H), 4.06 (dd, J = 11.6, 3.6 Hz, 1H), 3.92 (s, 3H), 2.47 – 2.41 (m, 1H), 2.18 – 2.11 (m, 1H), 1.36 – 1.22 (m, 2H), 1.22 – 1.08 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.6, 140.6, 137.5, 135.8, 130.6, 130.8, 130.0, 129.9, 129.2, 71.6, 52.4, 29.0, 27.2, 22.4, 13.8.

HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{22}\text{ClO}_4\text{S}$ ($[\text{M}+\text{H}]^+$) m/z 381.0922, found 381.0925.

$[\alpha]_D$ (25.0 °C, c = 1.3 in CHCl_3) = +55.545 °.

Methyl (R)-4-(1-(thiophen-2-ylsulfonyl)pentyl)benzoate (60)



This compound was prepared according to the general procedure with Zn using 2-((1-chloropentyl)sulfonyl)thiophene (37.9 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **60** as an off-white solid (27.6 mg, 52% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 12.1 min, t_R (major) = 16.2 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.97 – 7.91 (m, 2H), 7.60 (dd, J = 4.9, 1.3 Hz, 1H), 7.26 – 7.24 (m, 3H), 6.99 (dd, J = 4.9, 3.8 Hz, 1H), 4.17 (dd, J = 11.5, 3.7 Hz, 1H), 3.92 (s, 3H), 2.52 – 2.45 (m, 1H), 2.23 – 2.16 (m, 1H), 1.38 – 1.27 (m, 2H), 1.23 – 1.12 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

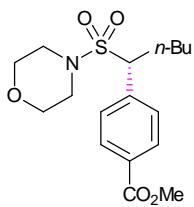
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.7, 138.1, 138.0, 135.2, 134.6, 130.7, 129.9, 129.9, 127.7, 72.8, 52.4, 29.1, 27.5, 22.4, 13.8.

HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{21}\text{O}_4\text{S}_2$ ([M+H] $^+$) m/z 353.0876, found 353.0873.

M.P. 81.2 – 83.1 °C.

$[\alpha]_D$ (25.0 °C, c = 0.5 in CHCl_3) = +98.6 °.

Methyl (*R*)-4-(1-(morpholinosulfonyl)pentyl)benzoate (**61**)



This compound was prepared according to the general procedure with Zn using 4-((1-chloropentyl)sulfonylmorpholine (38.4 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **61** as an off-white solid (21.4 mg, 40% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (major) = 10.4 min, t_R (minor) = 12.8 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.12 – 8.01 (m, 2H), 7.56 – 7.44 (m, 2H), 4.08 (dd, J = 11.4, 3.8 Hz, 1H), 3.93 (s, 3H), 3.56 – 3.52 (m, 2H), 3.48 – 3.44 (m, 2H), 3.07 – 3.03 (m, 2H), 2.78 (s, 2H), 2.37 – 2.32 (m, 1H), 2.19 – 2.09 (m, 1H), 1.38 – 1.22 (m, 2H), 1.21 – 1.04 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

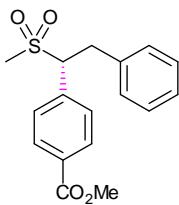
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.6, 138.7, 130.9, 130.2, 129.8, 68.3, 66.9, 52.5, 46.4, 29.8, 28.8, 22.3, 13.9.

HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{25}\text{NNaO}_5\text{S}$ ([M+Na] $^+$) m/z 378.1346, found 378.1348.

M.P. 81.8 – 83.5 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl3) = +34 °.

Methyl (*R*)-4-(1-(methylsulfonyl)-2-phenylethyl)benzoate (62)



This compound was prepared according to the general procedure with Zn using (2-chloro-2-(methylsulfonyl)ethyl)benzene (32.8 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **62** as an off-white solid (13.8 mg, 29% yield, 81% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 240 nm, tR (minor) = 18.1 min, tR (major) = 24.5 min.

1H NMR (600 MHz, CDCl3) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.09 (m, 3H), 7.05 – 6.91 (m, 2H), 4.30 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.91 (s, 3H), 3.80 (dd, *J* = 13.9, 3.6 Hz, 1H), 3.31 (dd, *J* = 13.9, 11.3 Hz, 1H), 2.64 (s, 3H).

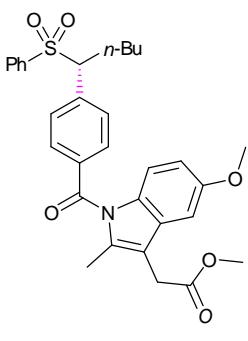
13C NMR (151 MHz, CDCl3) δ 166.5, 137.8, 136.2, 131.1, 130.3, 129.8, 129.1, 128.8, 127.1, 71.7, 52.5, 39.3, 33.8.

HRMS (ESI) calcd. for C17H18NaO4S ([M+Na]+) *m/z* 341.0818, found 341.0812.

M.P. 86.9 – 88.5 °C.

[*a*]D (25.0 °C, c = 0.32 in CHCl3) = -98.125°.

Methyl (*R*)-2-(5-methoxy-2-methyl-1-(4-(1-(phenylsulfonyl)pentyl)benzoyl)-1*H*-indol-3-yl)acetate (63)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and methyl 2-(1-(4-bromobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-acetate (93.7 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **63** as an off-white solid (42.8 mg, 52% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 210 nm, tR (minor) = 25.7 min, tR (major) = 35.5 min.

¹H NMR (600 MHz, CDCl₃) δ 7.66 – 7.52 (m, 5H), 7.47 – 7.40 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.13 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 3.67 (s, 2H), 2.52 – 2.47 (m, 1H), 2.32 (s, 3H), 2.21 – 2.15 (m, 1H), 1.39 – 1.27 (m, 2H), 1.22 – 1.15 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

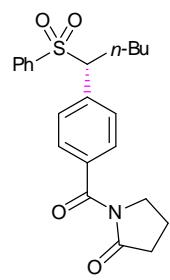
¹³C NMR (151 MHz, CDCl₃) δ 171.4, 168.9, 156.2, 137.9, 137.4, 136.0, 135.9, 133.9, 130.9, 130.8, 130.3, 129.8, 129.2, 128.9, 115.1, 112.7, 111.7, 101.3, 71.5, 55.9, 52.3, 30.3, 29.0, 27.2, 22.4, 13.9, 13.6.

HRMS (ESI) calcd. for C₃₁H₃₄NO₆S ([M+H]⁺) *m/z* 548.2101, found 548.2108.

M.P. 84.8 – 86.4 °C.

[*a*]D (25.0 °C, c = 0.58 in CHCl₃) = +129.828 °.

(R)-1-(4-(1-(Phenylsulfonyl)pentyl)benzoyl)pyrrolidin-2-one (**64**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 1-(4-bromobenzoyl)pyrrolidin-2-one (60.3 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **64** as an off-white solid (29.5 mg, 49% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 254 nm, *t*_R (minor) = 16.9 min, *t*_R (major) = 21.0 min.

¹H NMR (600 MHz, CDCl₃) δ 7.52 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.39–7.36 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.05 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.53 – 2.44 (m, 1H), 2.21 – 2.09 (m, 3H), 1.37 – 1.17 (m, 7H), 0.84 (t, *J* = 7.3 Hz, 3H).

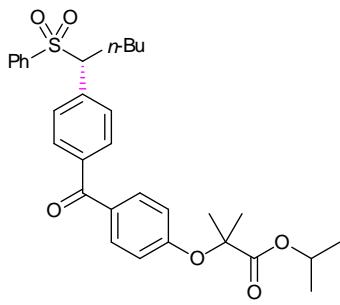
¹³C NMR (151 MHz, CDCl₃) δ 174.5, 170.19, 137.2, 136.5, 134.9, 133.6, 129.3, 129.23, 129.0, 128.9, 71.7, 46.5, 33.4, 29.0, 26.9, 22.4, 17.8, 13.8.

HRMS (ESI) calcd. for C₂₂H₂₆NO₄S ([M+H]⁺) *m/z* 400.1577, found 400.1580.

M.P. 140.1 – 141.6 °C.

[*a*]D (25.0 °C, c = 0.5 in CHCl₃) = + 84.6°.

Isopropyl (R)-2-methyl-2-(4-(1-(phenylsulfonyl)pentyl)benzoyl)phenoxy)propanoate (**65**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and isopropyl 2-(4-(4-bromobenzoyl)phenoxy)-2-methylpropanoate (91.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **65** as an off-white solid (55 mg, 68% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 20/80, 1.0 mL/min, 254 nm, t_R (minor) = 7.3 min, t_R (major) = 9.0 min.

¹H NMR (600 MHz, CDCl₃) δ 7.74 – 7.68 (m, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.58 – 7.53 (m, 3H), 7.43 – 7.36 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.90 – 6.81 (m, 2H), 5.08 (hept, J = 6.3 Hz, 1H), 4.11 (dd, J = 11.6, 3.6 Hz, 1H), 2.444 – 2.38 (m, 1H), 2.24 – 2.11 (m, 1H), 1.65 (s, 6H), 1.36 – 1.23 (m, 4H), 1.23 – 1.14 (m, 8H), 0.82 (t, J = 7.3 Hz, 3H).

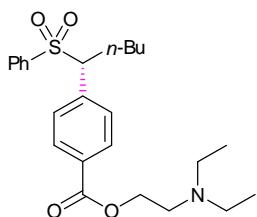
¹³C NMR (151 MHz, CDCl₃) δ 194.9, 173.2, 159.9, 137.4, 136.6, 133.8, 132.1, 130.3, 129.9, 129.1, 128.9, 117.3, 79.6, 71.5, 69.5, 29.0, 27.3, 25.5, 25.5, 22.4, 21.7, 13.8.

HRMS (ESI) calcd. for C₃₁H₃₇O₆S ([M+H]⁺) *m/z* 537.2305, found 537.2304.

M.P. 109.9 – 111.5 °C.

[*a*]D (25.0 °C, c = 0.9 in CHCl₃) = +87 °.

2-(Diethylamino)ethyl (*R*)-4-(1-(phenylsulfonyl)pentyl)benzoate (**66**)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and 2-(diethylamino)ethyl 4-bromobenzoate (67.5 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **66**

as a yellow oil (33.8 mg, 52% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H, *i*PrOH-hexanes 30/70, 1.0 mL/min, 240 nm, t_R (minor) = 4.7 min, t_R (major) = 5.4 min.

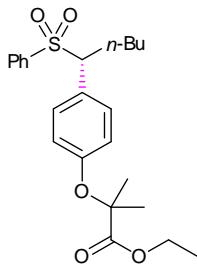
¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 8.3 Hz, 2H), 7.57 – 7.47 (m, 3H), 7.42 – 7.32 (m, 2H), 7.17 (d, J = 8.3 Hz, 2H), 4.37 (t, J = 6.2 Hz, 2H), 4.07 (dd, J = 11.6, 3.6 Hz, 1H), 2.83 (t, J = 6.2 Hz, 2H), 2.62 (q, J = 7.1 Hz, 4H), 2.47 – 2.41 (m, 1H), 2.18 – 2.12 (m, 1H), 1.38 – 1.22 (m, 2H), 1.06 (t, J = 7.1 Hz, 6H), 0.82 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 166.2, 137.8, 137.3, 133.8, 130.7, 130, 129.8, 129.1, 128.9, 71.6, 63.8, 51.2, 48.0, 29.0, 27.2, 22.4, 13.8, 12.2.

HRMS (ESI) calcd. for ([M+H]⁺) C₂₄H₃₄NO₄S *m/z* 432.2203, found 432.2210.

[*a*]D (25.0 °C, c = 0.9 in CHCl₃) = + 69°.

Ethyl (*R*)-2-methyl-2-(4-(1-(phenylsulfonyl)pentyl)phenoxy)propanoate (67)



This compound was prepared according to the general procedure with Zn using ((1-chloropentyl)sulfonyl)benzene (37 mg, 0.15 mmol, 1.0 equiv) and ethyl 2-(4-iodophenoxy)-2-methylpropanoate (75.2 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **67** as a yellow oil (27 mg, 43% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H, iPrOH-hexanes 20/80, 1.0 mL/min, 254 nm, *t_R* (minor) = 5.3 min, *t_R* (major) = 6.3 min.

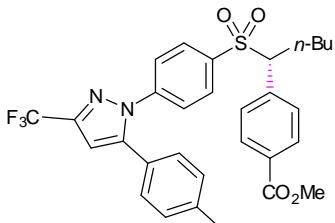
¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.45 (m, 3H), 7.37 – 7.32 (m, 2H), 7.00 – 6.86 (m, 2H), 6.74 – 6.60 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.95 (dd, *J* = 11.6, 3.6 Hz, 1H), 2.42 – 2.37 (m, 1H), 2.17 – 1.97 (m, 1H), 1.56 (d, *J* = 4.8 Hz, 6H), 1.33 – 1.26 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 (p, *J* = 7.6 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 174.1, 155.9, 137.6, 133.4, 130.8, 129.1, 128.6, 125.9, 119.0, 79.4, 71.1, 61.6, 29.0, 26.9, 25.5, 25.4, 22.4, 14.2, 13.9.

HRMS (ESI) calcd. for C₂₃H₃₀KO₅S ([M+K]⁺) *m/z* 457.1446, found 457.1440.

[*a*]D (25.0 °C, c = 0.9 in CHCl₃) = + 48.278°.

Methyl (*R*)-4-((1-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)pentyl)benzo-ate (68)



This compound was prepared according to the general procedure with Zn using 1-((4-((1-chloropentyl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (70.6 mg, 0.15 mmol, 1.0 equiv) and methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **68** as an off-white solid (53.1 mg, 62% yield, 92% ee).

Chiral HPLC (CHIRALPAK IB-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 8.0 min, t_R (major) = 8.6 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.91 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.17 (dd, J = 21.3, 7.9 Hz, 4H), 7.03 (d, J = 8.1 Hz, 2H), 6.71 (s, 1H), 4.09 (dd, J = 11.6, 3.6 Hz, 1H), 3.90 (s, 3H), 2.47 – 2.40 (m, 1H), 2.37 (s, 3H), 2.16 – 2.10 (m, 1H), 1.35 – 1.22 (m, 2H), 1.21 – 1.08 (m, 1H), 0.82 (t, J = 7.3 Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.5, 145.4, 144.3 (q, J = 38.6 Hz), 143.4, 140.0, 137.4, 136.6, 130.8, 130.3, 130.1, 130.0, 129.9, 129.8, 128.8, 125.7, 125.1, 121.1 (q, J = 269.3 Hz), 106.6 (d, J = 2.2 Hz), 71.6, 52.4, 28.9, 27.2, 22.3, 21.4, 13.8.

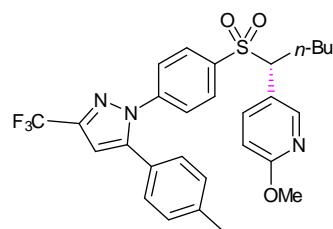
$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -62.47.

HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{29}\text{F}_3\text{N}_2\text{NaO}_4\text{S}$ ($[\text{M}+\text{Na}]^+$) m/z 593.1692, found 593.1699.

M.P. 135.2 – 136.9 °C.

$[\alpha]_D$ (22.0 °C, c = 0.5 in CHCl_3) = + 108.4°.

(*R*)-2-Methoxy-5-(1-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)pentyl)pyridine (69)



This compound was prepared according to the general procedure with Mn using 1-(4-((1-chloropentyl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (70.6 mg, 0.15 mmol, 1.0 equiv) and methyl 5-iodo-2-methoxypyridine (52.9 mg, 0.225 mmol, 1.5 equiv).

The crude mixture was purified by flash column chromatograph to afford **69** as an off-white solid (51.3 mg, 63% yield, 87% ee).

Chiral HPLC (CHIRALPAK IB-H, *i*PrOH-hexanes 10/90, 1.0 mL/min, 254 nm, t_R (minor) = 7.6 min, t_R (major) = 8.7 min.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.68 (d, J = 2.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.49 (dd, J = 8.7, 2.5 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.73 (s, 1H), 6.69 (d, J = 8.6 Hz, 1H), 3.98 (dd, J = 11.7, 3.6 Hz, 1H), 3.89 (s, 3H), 2.41 – 2.36 (m, 4H), 2.09 – 2.02 (m, 1H), 1.34 – 1.24 (m, 2H), 1.19 – 1.14 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 164.6, 148.7, 145.5, 144.35 (q, *J* = 38.6 Hz), 143.4, 140.0, 138.9, 136.7, 130.0, 129.9, 128.8, 125.7, 125.4, 121.1 (q, *J* = 269.2 Hz), 120.7, 111.3, 106.6, 68.6, 53.7, 28.9, 26.7, 22.3, 21.5, 13.8.

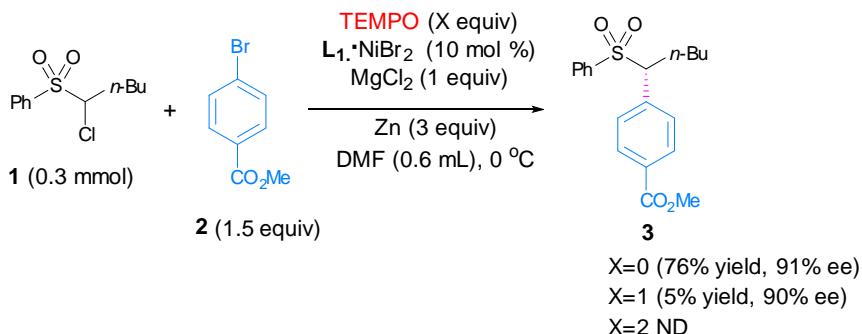
¹⁹F NMR (565 MHz, CDCl₃) δ -62.48.

M.P. 52.2 – 54.0 °C.

[*a*]D (22.0 °C, c = 0.5 in CHCl₃) = + 48.8°.

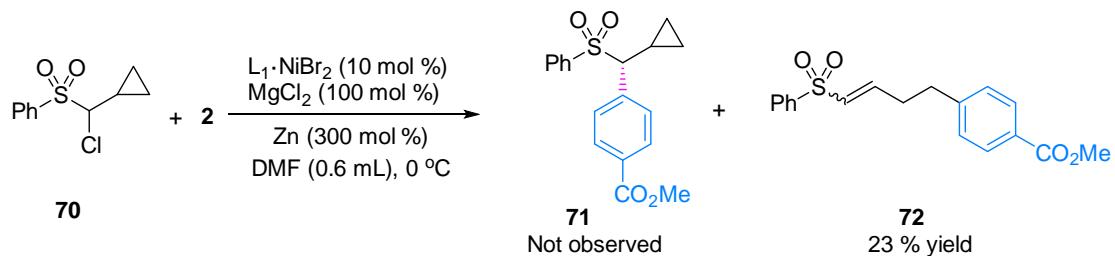
Part 5. Control Experiments and Limitations

Part 5.1 Reaction in presence of radical scavengers

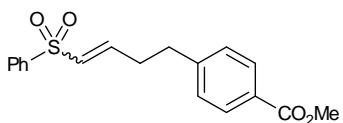


To a flame-dried tube with a stir bar vial was added the appropriate reductant Zn (29.5 mg, 0.45 mmol, 3.0 equiv), methyl 4-bromobenzoate (48.4 mg, 0.225 mmol, 1.5 equiv), MgCl₂ (0.15 mmol, 1.0 equiv), **L1·NiBr₂** (0.015 mmol, 10 mol %) and TEMPO (if needed, x equiv). The vial was transferred into an N₂-filled glovebox and charged with DMF (0.3 mL). The vial was sealed and removed from the glovebox. The mixture was stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min the mixture was cooled to 0 °C, then a solution of ((1-chloropentyl)sulfonyl)benzene (37mg, 0.15 mmol, 1.0 equiv) in DMF (0.3 mL) was added to the vial by syringe over 1 min. The mixture was stirred vigorously at 0 °C for 48 h. The reaction mixture was loaded directly onto a silica gel to give the target molecular and detected by ¹H NMR.

Part 5.2 Radical clock reaction



Methyl 4-(4-(phenylsulfonyl)but-3-en-1-yl)benzoate (72)



The reaction was proceeded according to the general procedure with Zn using ((chlorocyclopropyl)methyl)sulfonyl)benzene (34.6 mg, 0.15 mmol, 1.0 equiv) and ethyl 2-(4-iodophenoxy)-2-methylpropanoate (48.4 mg, 0.225 mmol, 1.5 equiv). The crude mixture was purified by flash column chromatograph to afford **72** as an off-white solid (11.5 mg, 23% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.83 – 7.75 (m, 2H), 7.64 – 7.58 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.20 – 7.15 (m, 2H), 6.97 (dt, J = 15.1, 6.9 Hz, 1H), 6.27 (dt, J = 15.1, 1.5 Hz, 1H), 3.91 (s, 3H), 2.84 (t, J = 7.6 Hz, 2H), 2.62 – 2.52 (m, 2H).

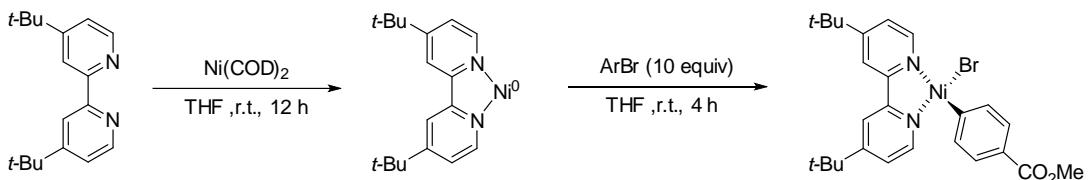
¹³C NMR (151 MHz, CDCl₃) δ 167.0, 145.4, 145.3, 140.6, 133.5, 131.7, 130.1, 129.4, 128.6, 128.5, 127.7, 52.2, 34.0, 32.8.

HRMS (ESI) calcd. for C₁₈H₁₈NaO₄S ([M+Na]⁺) *m/z* 353.0818, found 353.0819.

M.P. 90.6 – 92.1 °C.

Part 5.3 Stoichiometric reaction of Ar-Ni(II) (73) with 1

Part 5.3.1 Synthesis of Ar-Ni(L)Br (73)

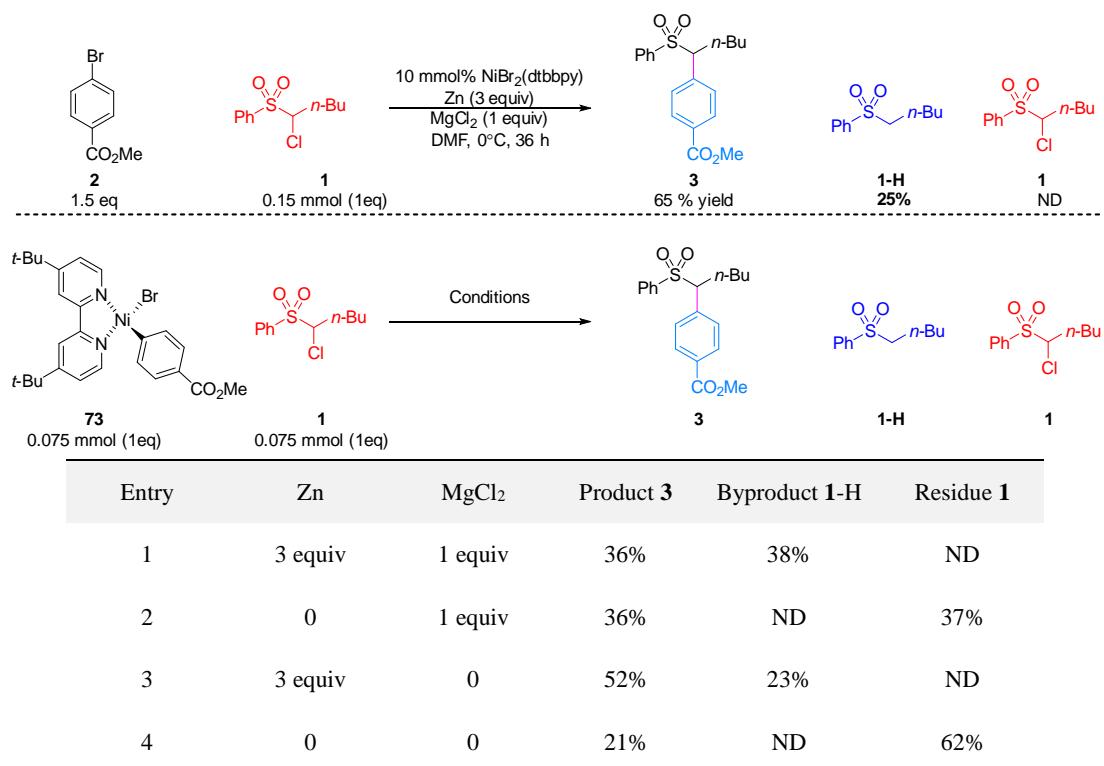


This compound was prepared according to the literature procedure.⁷ In a nitrogen filled glove box, a flame-dried round-bottomed flask was charged with Ni(COD)₂ (138 mg, 0.5 mmol, 1.0 equiv), dry THF (5 mL) and 4,4'-di-tert-butyl-2,2'-bipyridine (134 mg, 0.5 mmol, 1.0 equiv). After stirring at room temperature overnight, methyl 4-bromobenzoate (1.1 g, 5 mmol, 10 equiv) was added and stirred for additional 4 h. Dry pentane (30 mL) was added slowly to the deep red colored mixture and filtered. The resulting precipitate was washed with pentane (5 x 8 mL) and dried under vacum to afford Ni(II) complex **73** as a brown solid (160 mg, 59% yield). The product was used without further purification.

The complex was stored in a nitrogen filled glove box at -35 °C.

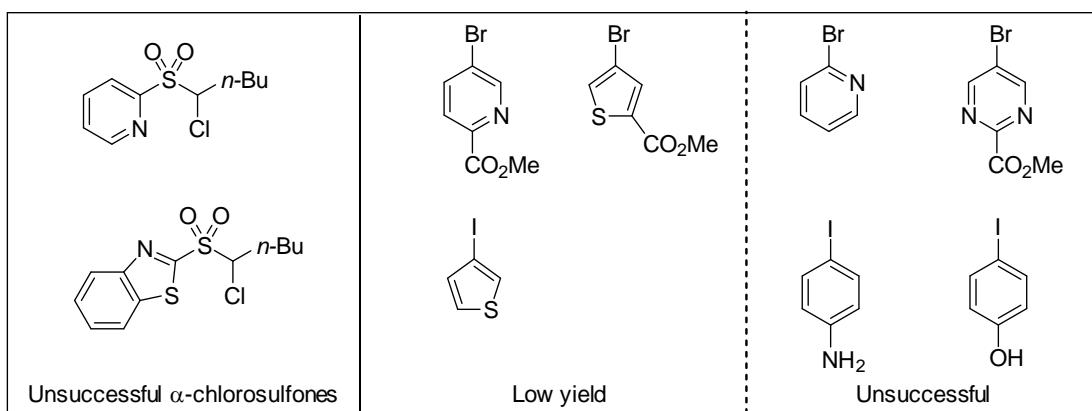
¹H NMR (600 MHz, Acetone-d₆) δ 9.23 (s, 1H), 8.44 (d, J = 15.1 Hz, 2H), 7.80 – 7.64 (m, 3H), 7.51 (d, J = 7.8 Hz, 2H), 7.41 (brs, 1H), 7.10 – 7.03 (m, 1H), 3.82 (s, 3H), 1.40 (m, 18H).

Part 5.3.2 Stoichiometric reaction of Ar-Ni(II) (73) with 1



The reaction was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added **Ar-Ni(L)Br** (**73**, 40.7 mg, 0.075 mmol), α -chlorosulfone **1** (18.5 mg, 0.075 mmol), **Zn** (if needed, 3 equiv) and **MgCl₂** (if needed, 1 equiv), followed by **DMF** (0.3 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 0 °C for 36 h. Then the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The mixture was extracted with **EtOAc** (3 x 15 mL), the combined organic phases were washed with water and brine, then dried over **MgSO₄** and concentrated. The reaction mixtures were analyzed by ¹H NMR with an internal standard.

Part 5.4 Limitations



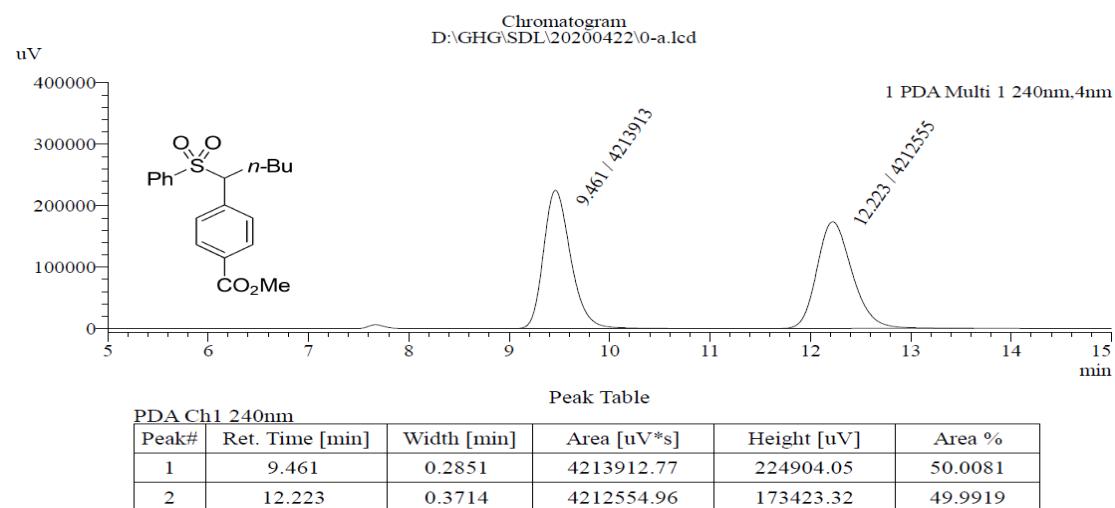
For the substances shown above, no noteworthy result was obtained under the standard reaction conditions.

II. Reference

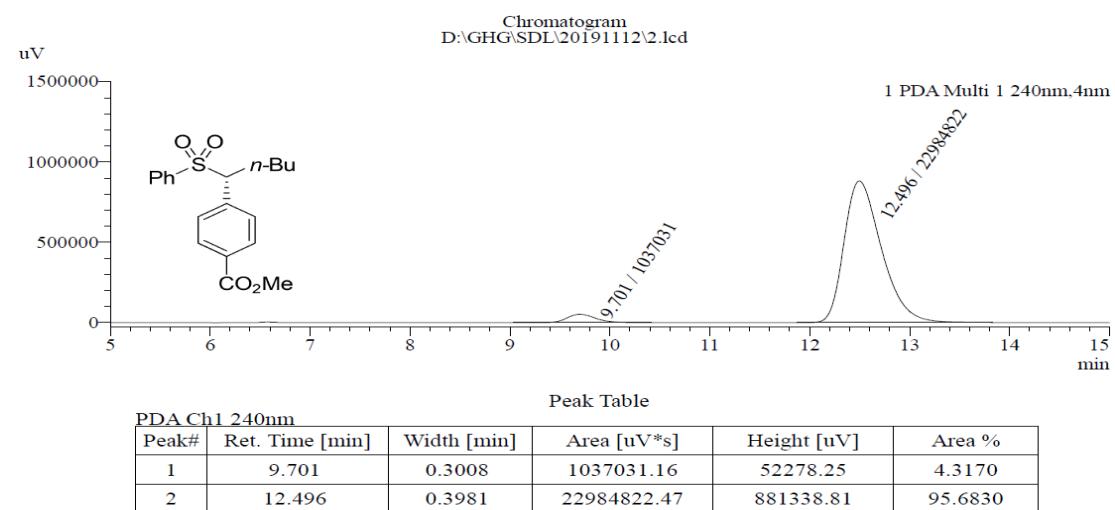
1. M. Makosza, J. Golinski, and J. Baran, *J. Org. Chem.* **1984**, *49*, 1488.
2. G. Bram, A. Loupy, M. C. Roux-Schmitt, J. Sansoulet, T. Strzalko, and J. Seyden-Penne, *Synthesis*, **1987**, *56*.
3. J. Choi, P. Martín-Gago and G. C. Fu, *J. Am. Chem. Soc.* **2014**, *136*, 12161.
4. P. S. Fier, and K. M. Maloney, *J. Am. Chem. Soc.* **2019**, *141*, 1441.
5. J.-M. Mattalia, M. Chanon, and C. J. M. Stirling, *J. Org. Chem.* **1996**, *61*, 1153.
6. N. Suzuki, J. L. Hofstra, K. E. Poremba, and S. E. Reisman, *Org. Lett.* **2017**, *19*, 2150.
7. L. Guo, F. Song, S. Zhu, H. Li and L Chu, *Nature Nat. Commun.* **2018**, *9*, 4543.

III. HPLC Traces

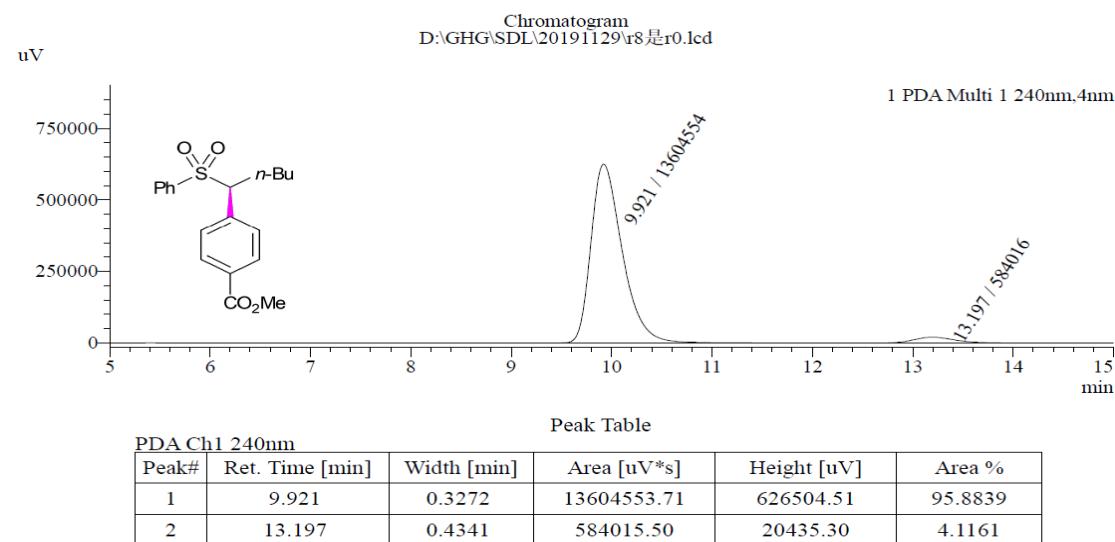
3: racemic



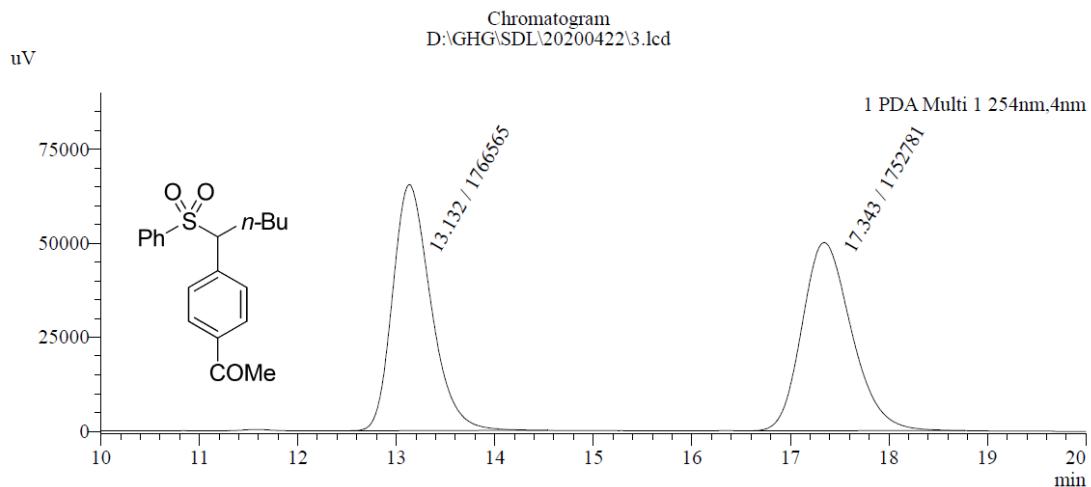
3: enantioenriched, 91% ee



3 S: enantioenriched, 92% ee



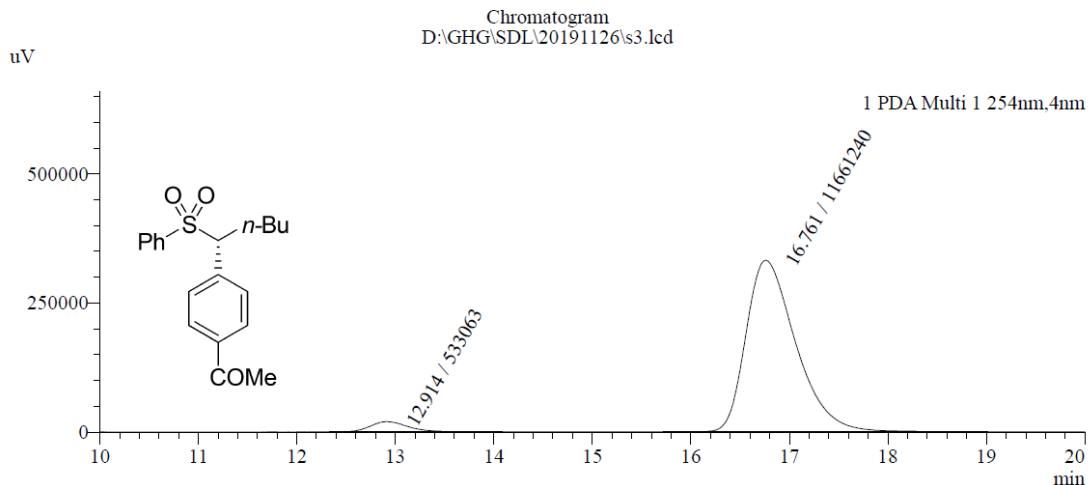
4: racemic



Peak Table

| PDA Ch1 254nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 13.132 | 0.4096 | 1766564.74 | 65458.87 | 50.1958 |
| 2 | 17.343 | 0.5369 | 1752781.36 | 50060.67 | 49.8042 |

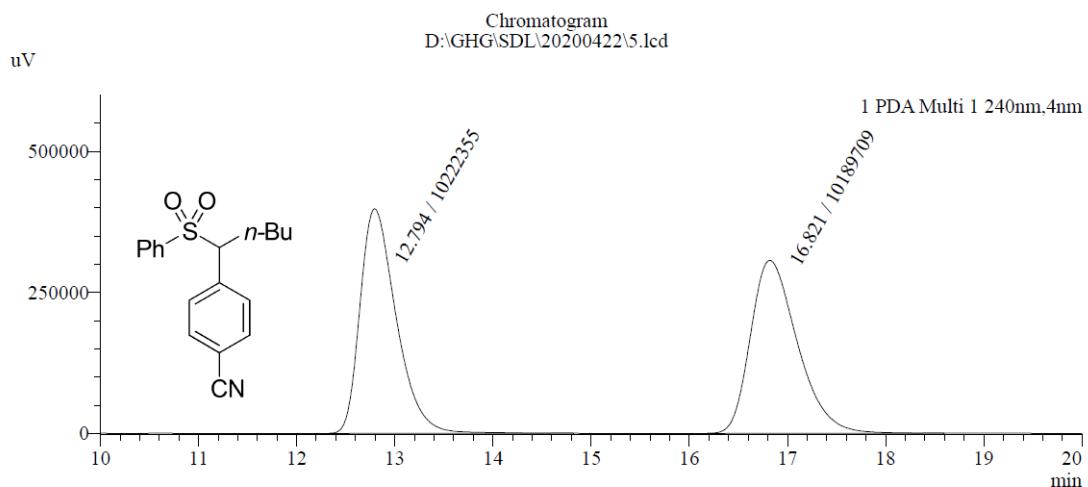
4: enantioenriched, 91% ee



Peak Table

| PDA Ch1 254nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 12.914 | 0.4051 | 533063.07 | 19867.41 | 4.3714 |
| 2 | 16.761 | 0.5341 | 11661239.78 | 332091.75 | 95.6286 |

5: racemic

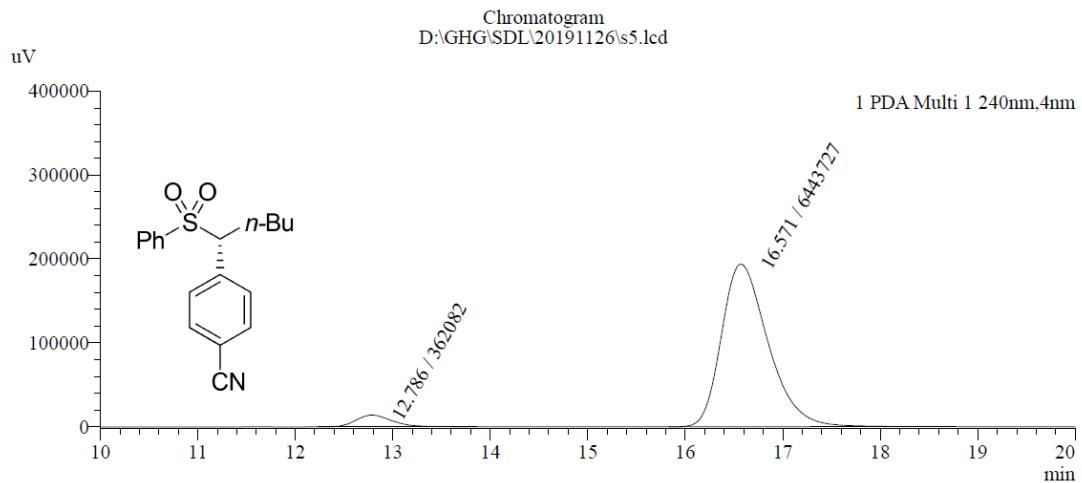


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 12.794 | 0.3895 | 10222354.51 | 397908.39 | 50.0800 |
| 2 | 16.821 | 0.5088 | 10189709.11 | 306472.60 | 49.9200 |

5: enantioenriched, 89% ee

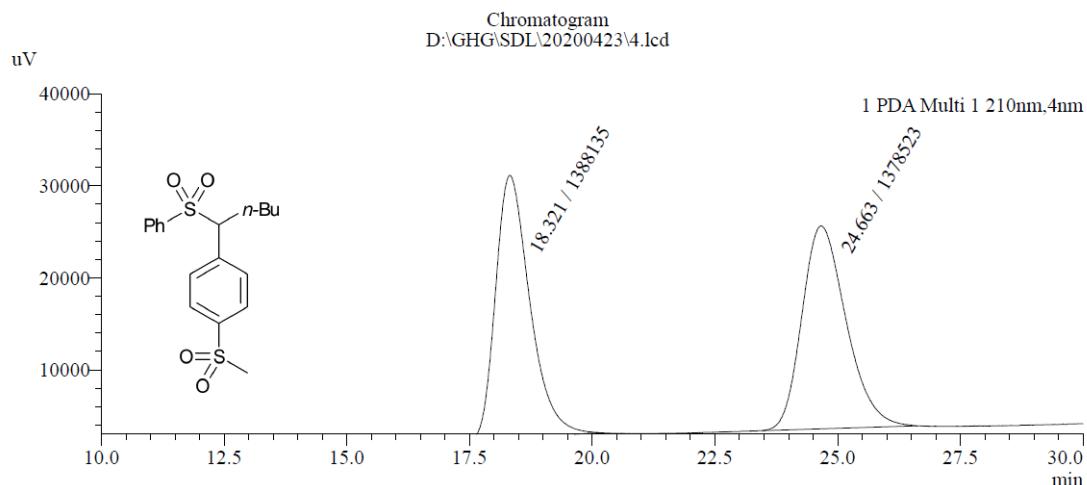


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 12.786 | 0.3917 | 362081.73 | 14020.26 | 5.3202 |
| 2 | 16.571 | 0.5057 | 6443726.75 | 193691.55 | 94.6798 |

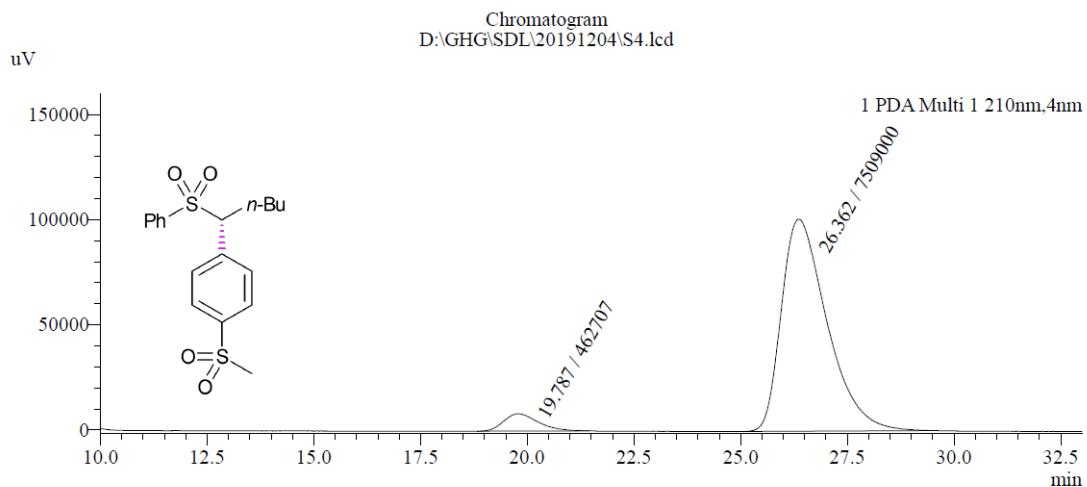
6: racemic



PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 18.321 | 0.7361 | 1388135.21 | 28565.29 | 50.1737 |
| 2 | 24.663 | 0.9627 | 1378523.48 | 22032.70 | 49.8263 |

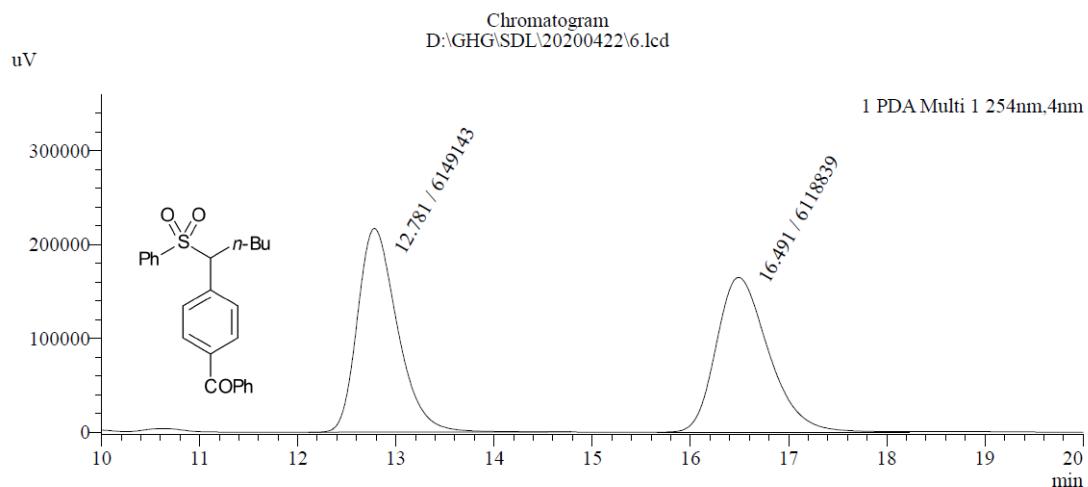
6: enantioenriched, 88% ee



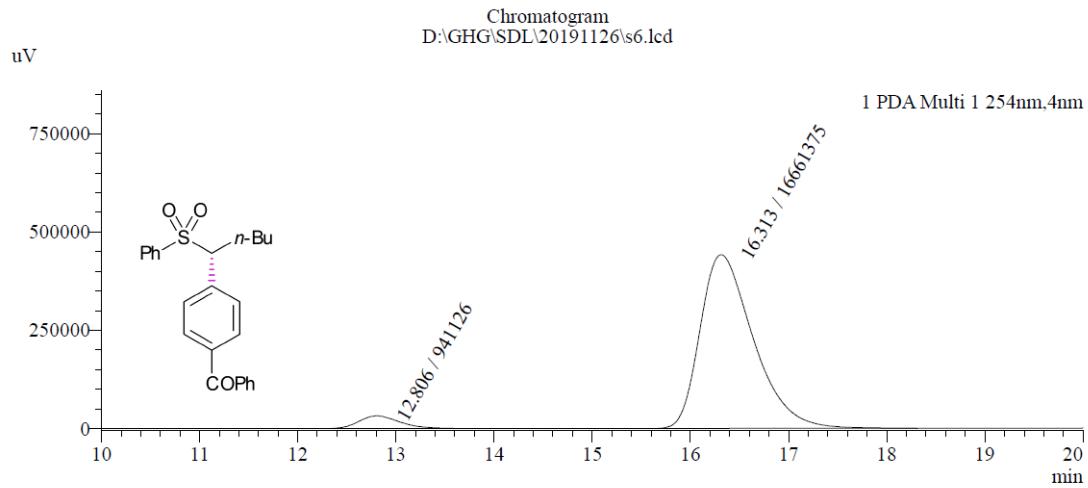
PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 19.787 | 0.8642 | 462707.41 | 8206.38 | 5.8044 |
| 2 | 26.362 | 1.1304 | 7508999.99 | 100925.66 | 94.1956 |

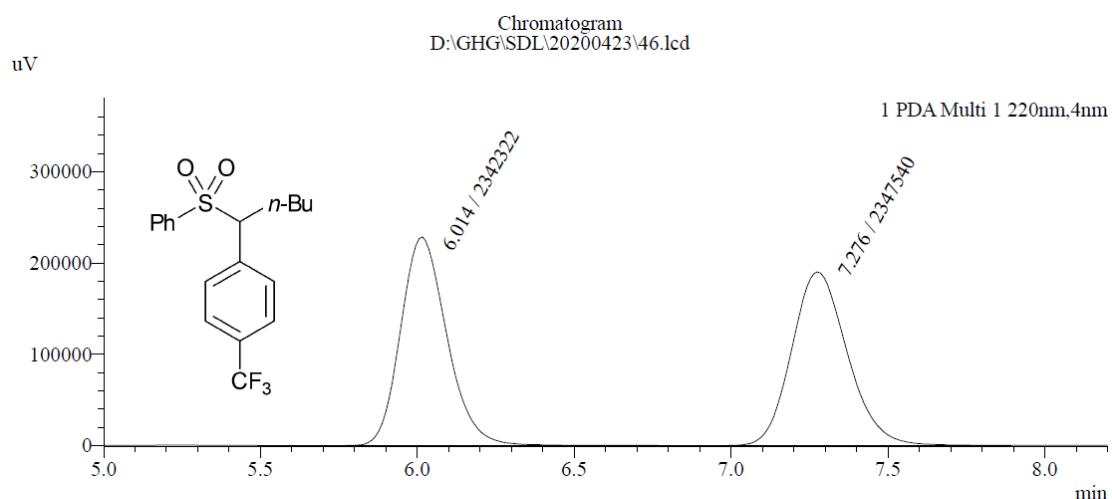
7: racemic



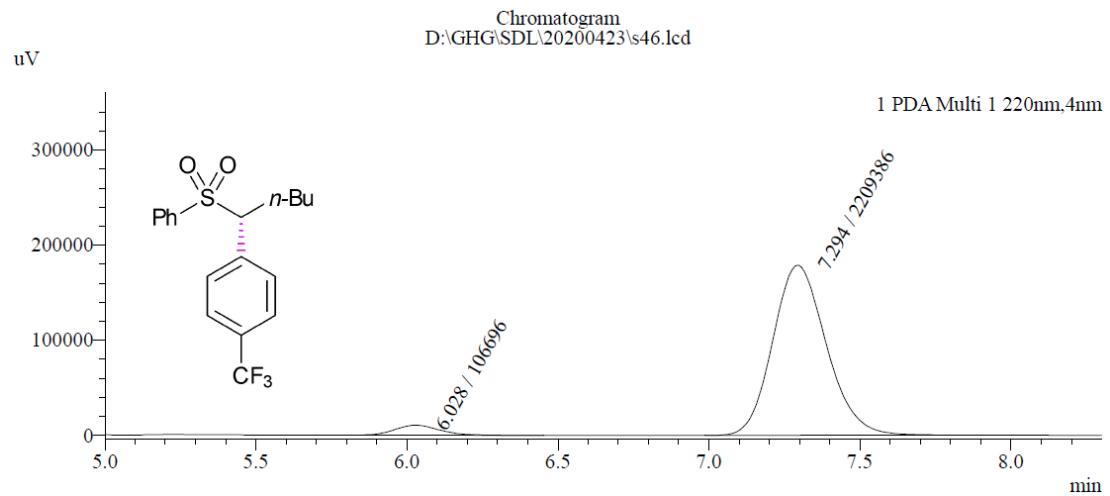
7: enantioenriched, 89% ee



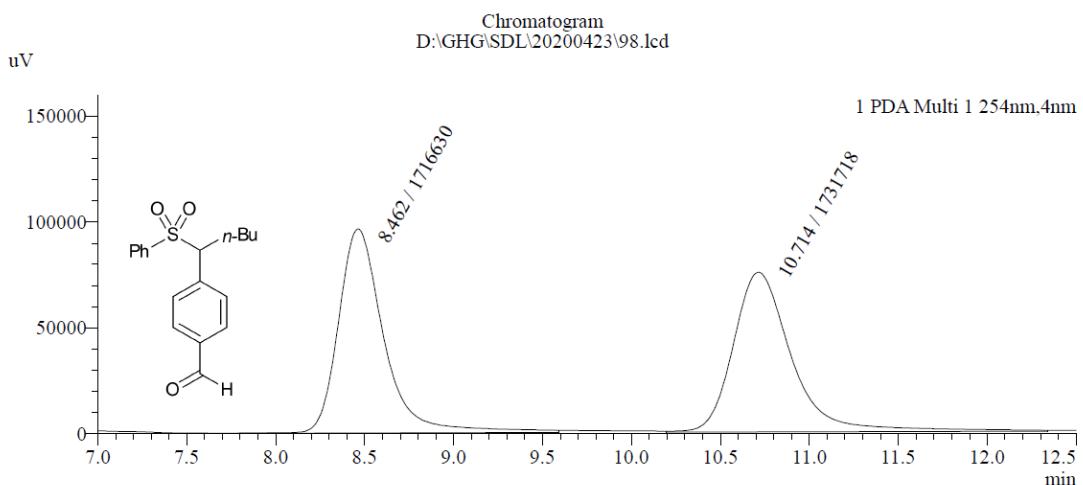
8: racemic



8: enantioenriched, 91% ee



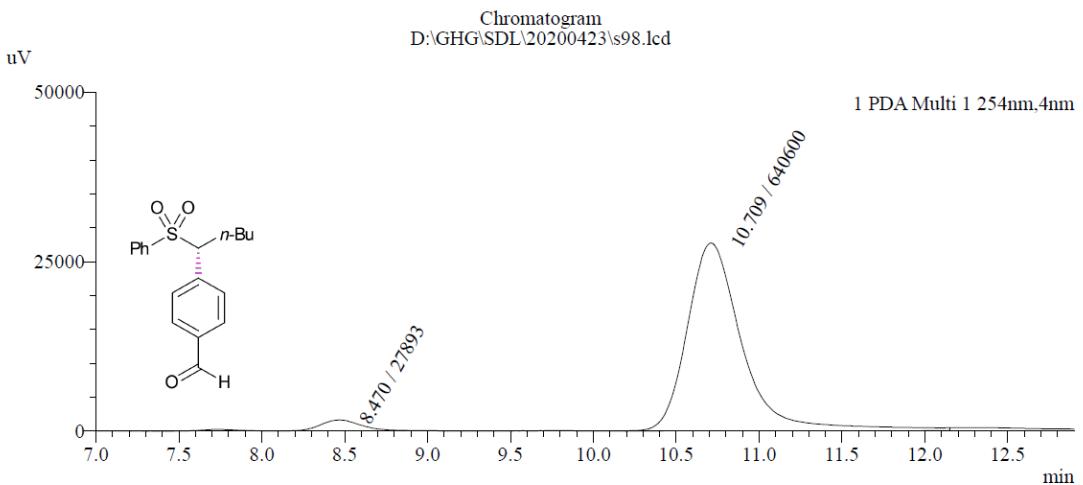
9: racemic



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.462 | 0.2546 | 1716629.87 | 96384.32 | 49.7812 |
| 2 | 10.714 | 0.3281 | 1731717.78 | 75427.95 | 50.2188 |

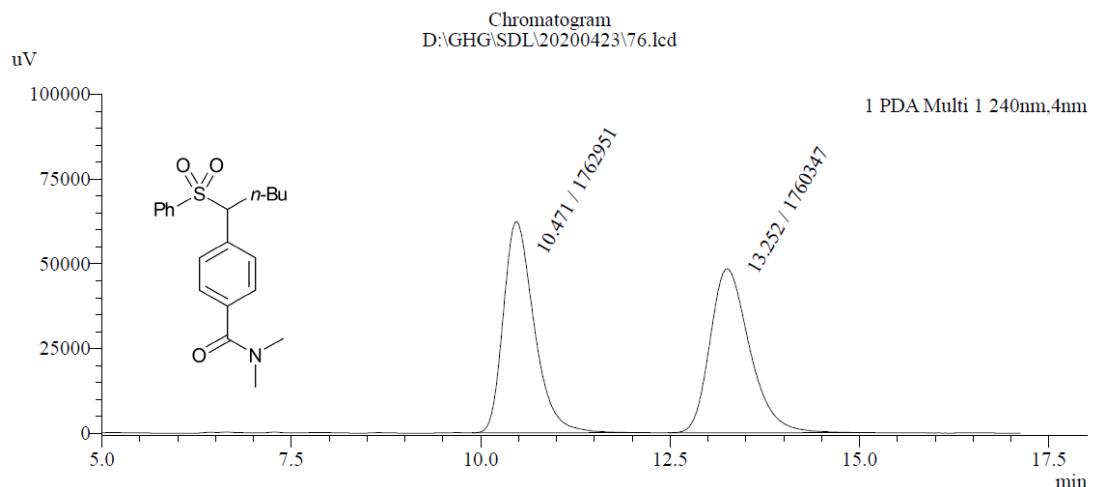
9: enantioenriched, 92% ee



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.470 | 0.2557 | 27892.68 | 1623.71 | 4.1725 |
| 2 | 10.709 | 0.3284 | 640599.51 | 27706.72 | 95.8275 |

10: racemic

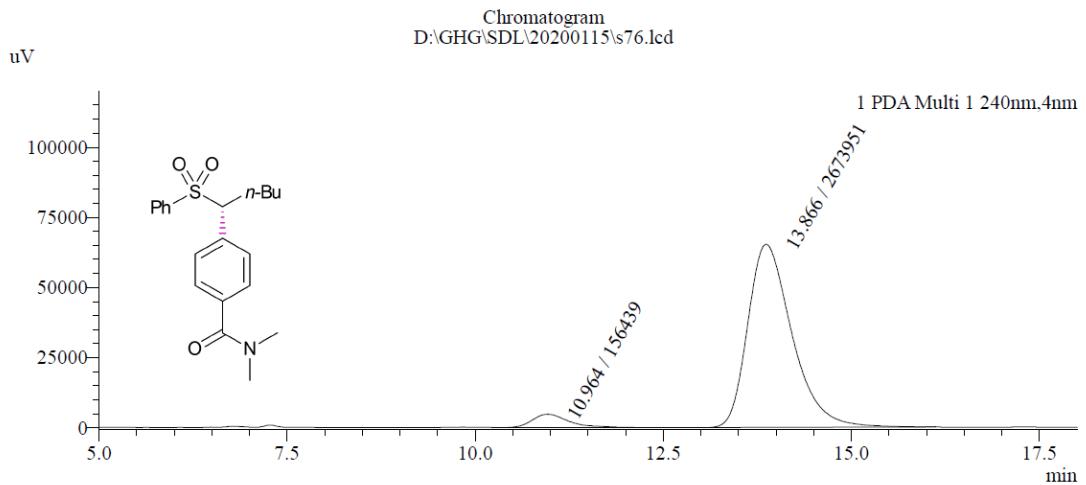


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 10.471 | 0.4256 | 1762950.55 | 62303.61 | 50.0370 |
| 2 | 13.252 | 0.5521 | 1760346.72 | 48340.66 | 49.9630 |

10: enantioenriched, 89% ee

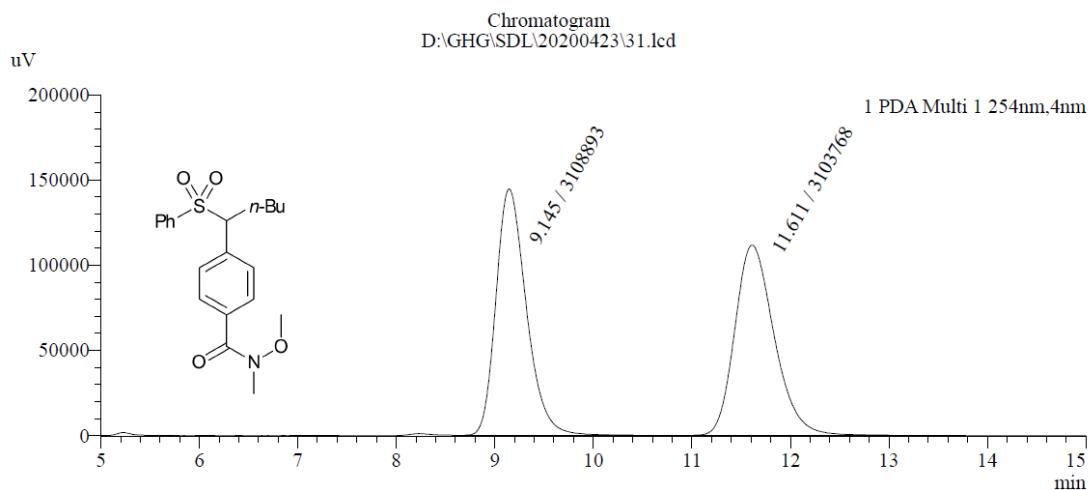


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 10.964 | 0.4910 | 156439.24 | 4721.02 | 5.5271 |
| 2 | 13.866 | 0.6162 | 2673950.71 | 65266.25 | 94.4729 |

11: racemic

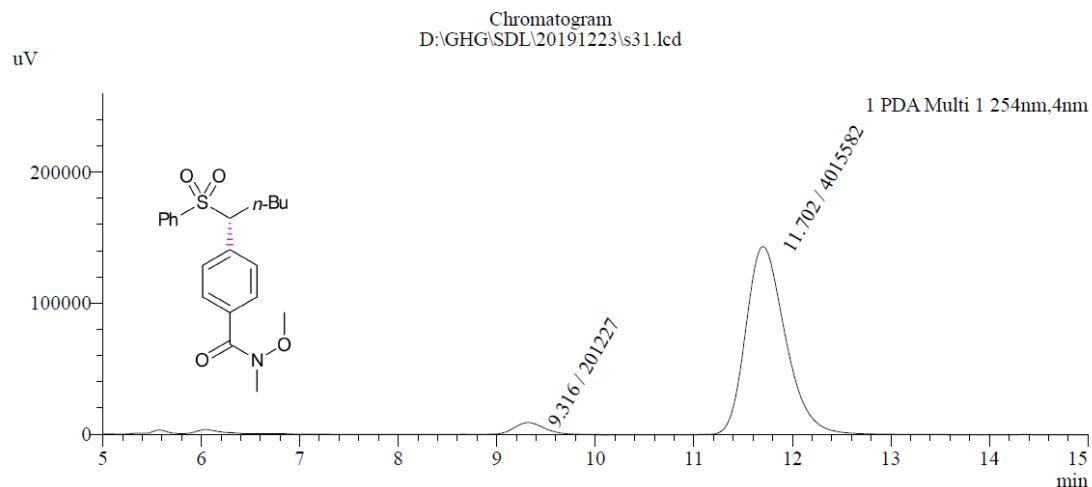


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 9.145 | 0.3261 | 3108892.73 | 144732.59 | 50.0412 |
| 2 | 11.611 | 0.4244 | 3103767.78 | 111630.50 | 49.9588 |

11: enantioenriched, 90% ee

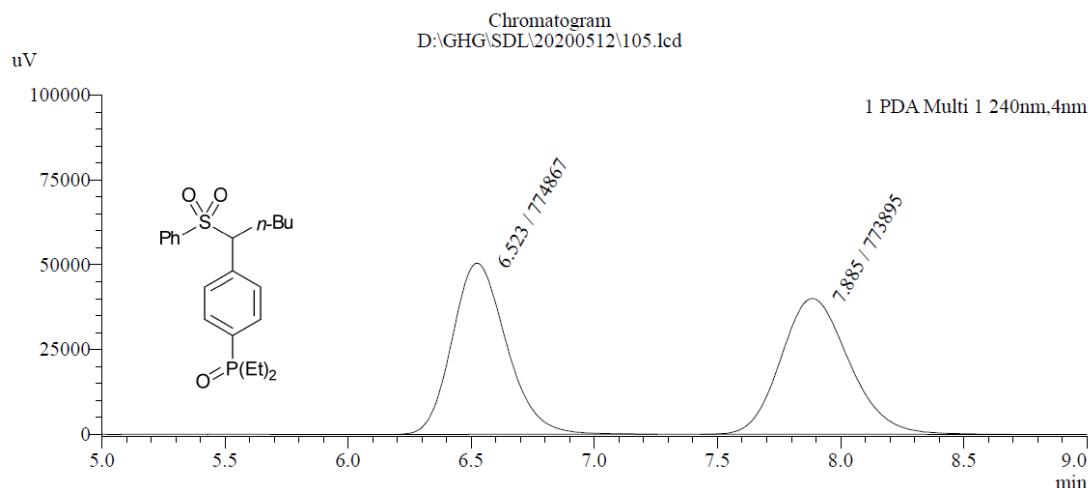


Peak Table

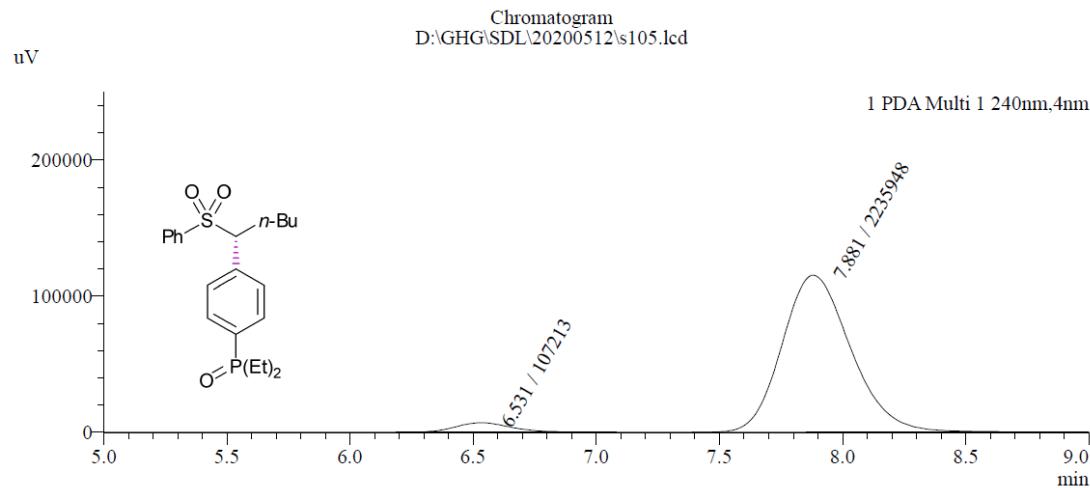
PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 9.316 | 0.3318 | 201226.97 | 9202.08 | 4.7720 |
| 2 | 11.702 | 0.4251 | 4015581.62 | 143635.80 | 95.2280 |

12: racemic



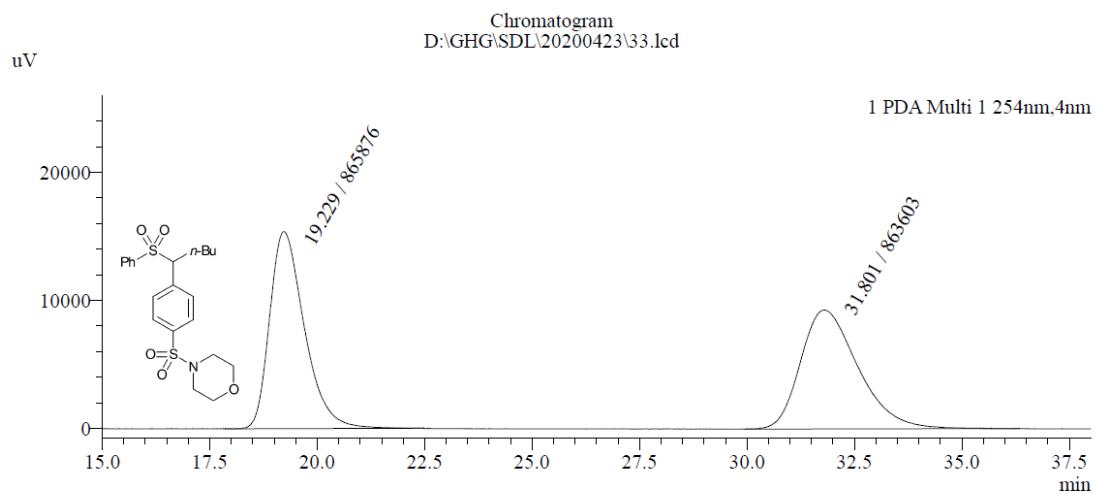
12: enantioenriched, 91% ee



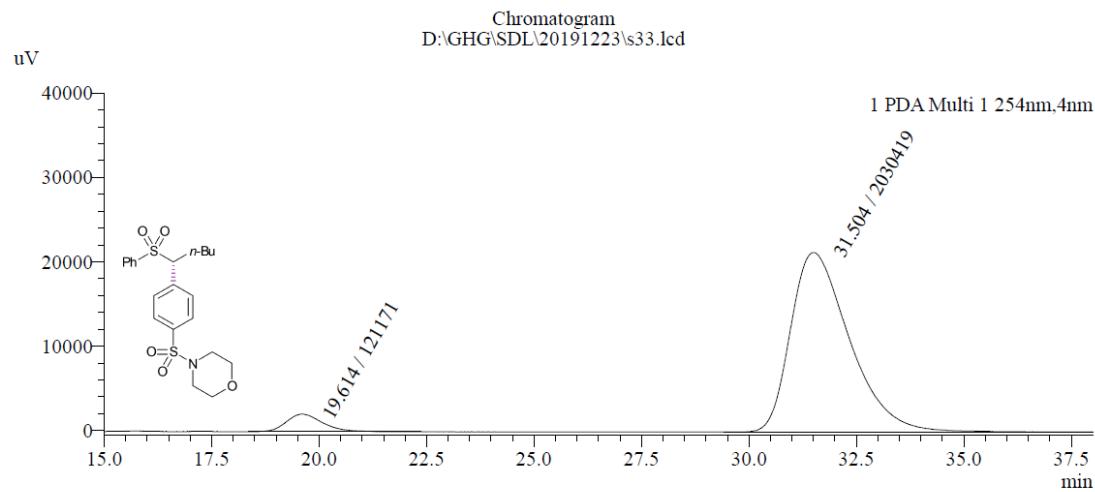
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 6.531 | 0.2377 | 107212.59 | 6905.84 | 4.5756 |
| 2 | 7.881 | 0.2982 | 2235948.12 | 115291.33 | 95.4244 |

13: racemic



13: enantioenriched, 89% ee

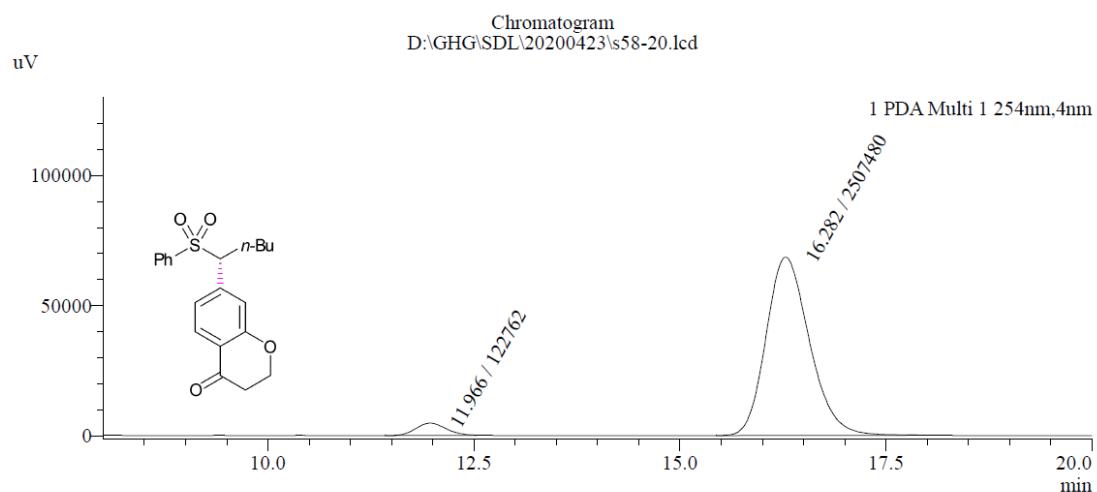


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 19.614 | 0.8882 | 121171.12 | 2072.81 | 5.6317 |
| 2 | 31.504 | 1.4514 | 2030419.01 | 21276.57 | 94.3683 |

14: racemic

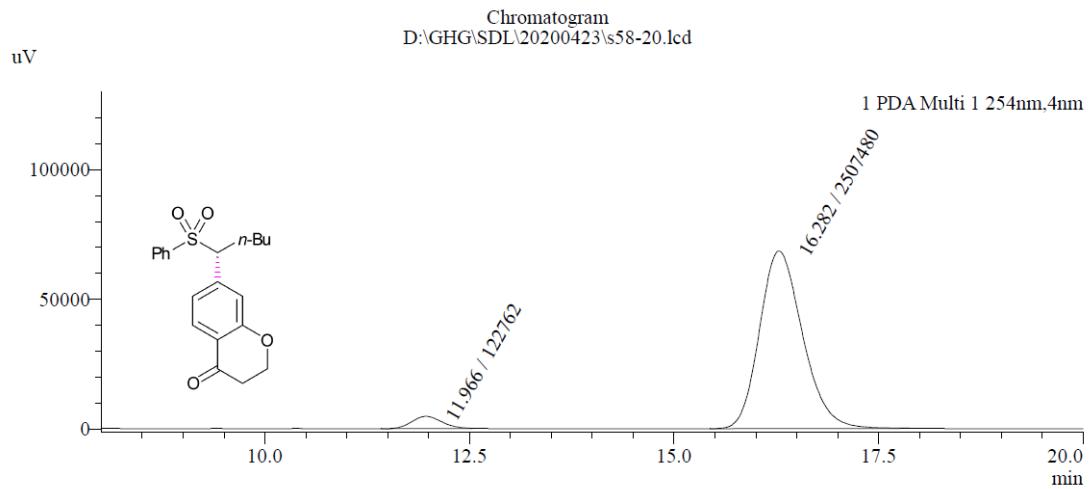


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.966 | 0.4018 | 122761.68 | 4742.24 | 4.6673 |
| 2 | 16.282 | 0.5608 | 2507480.50 | 68489.89 | 95.3327 |

14: enantioenriched, 91% ee

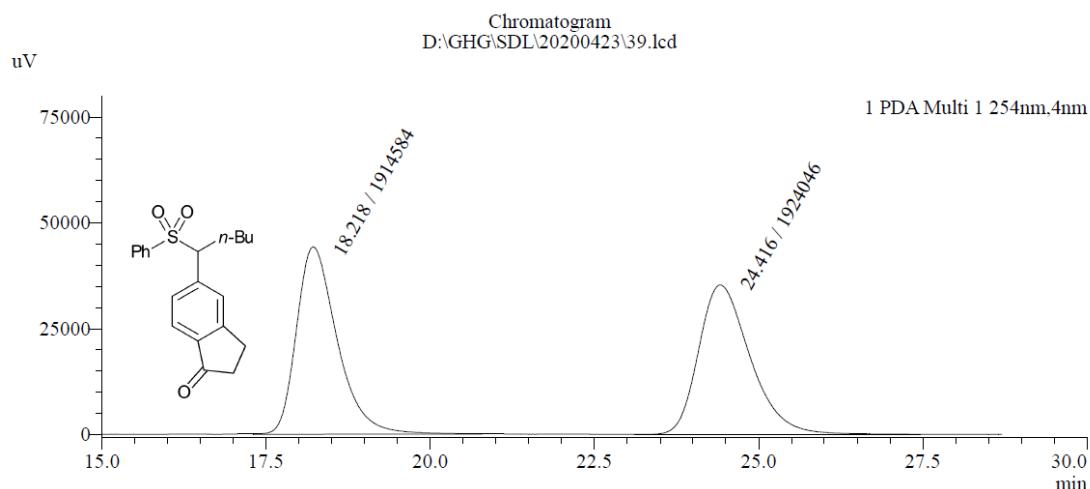


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.966 | 0.4018 | 122761.68 | 4742.24 | 4.6673 |
| 2 | 16.282 | 0.5608 | 2507480.50 | 68489.89 | 95.3327 |

15: racemic

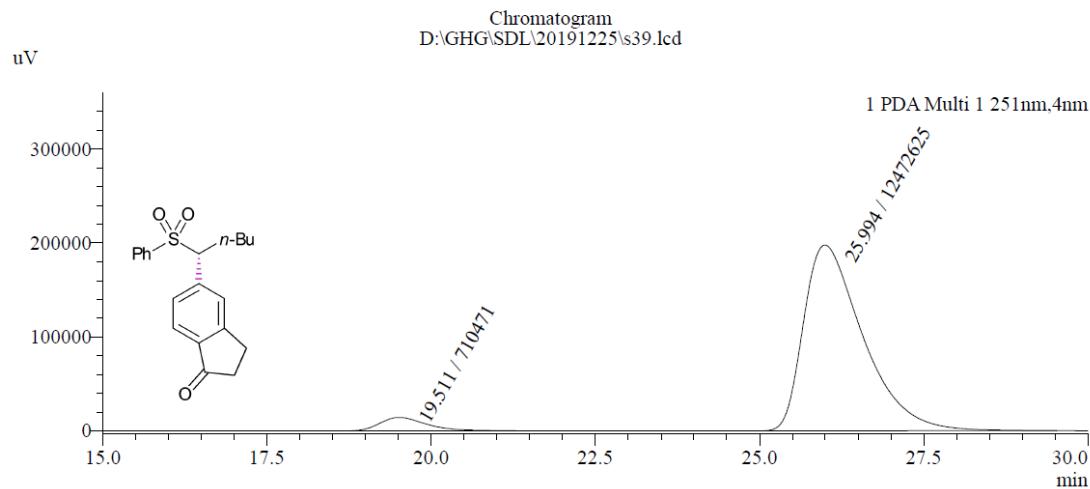


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 18.218 | 0.6451 | 1914584.07 | 44248.12 | 49.8768 |
| 2 | 24.416 | 0.8288 | 1924045.93 | 35294.15 | 50.1232 |

15: enantioenriched, 89% ee

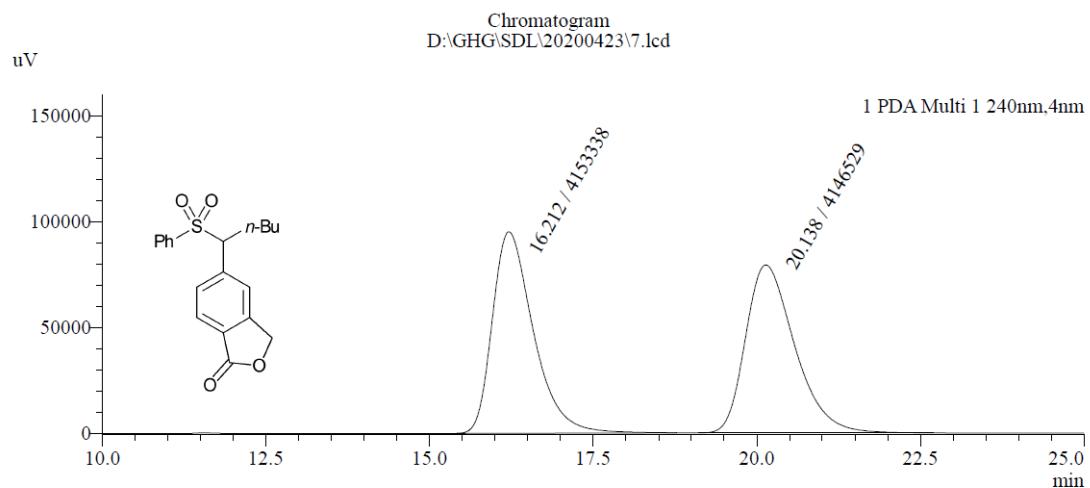


Peak Table

PDA Ch1 251nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 19.511 | 0.7415 | 710471.24 | 14300.07 | 5.3893 |
| 2 | 25.994 | 0.9510 | 12472624.77 | 197825.89 | 94.6107 |

16: racemic

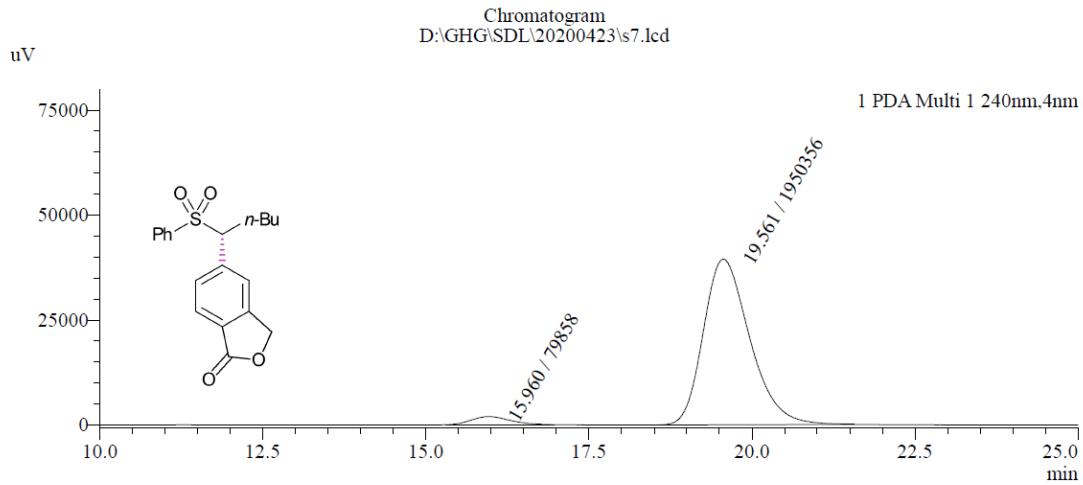


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 16.212 | 0.6545 | 4153338.44 | 95174.11 | 50.0410 |
| 2 | 20.138 | 0.7969 | 4146529.35 | 79313.62 | 49.9590 |

16: enantioenriched, 92% ee

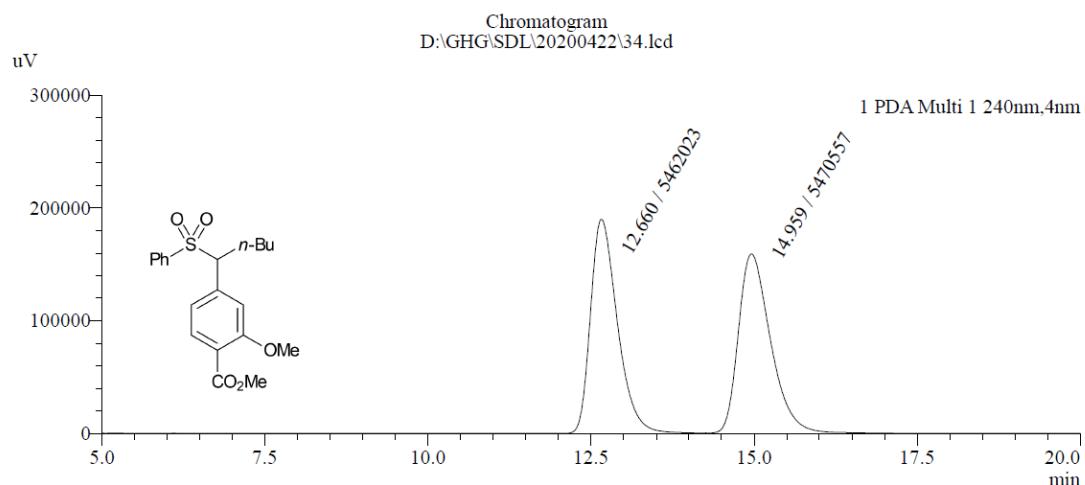


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 15.960 | 0.6442 | 79858.30 | 1935.24 | 3.9335 |
| 2 | 19.561 | 0.7555 | 1950355.79 | 39442.56 | 96.0665 |

17: racemic

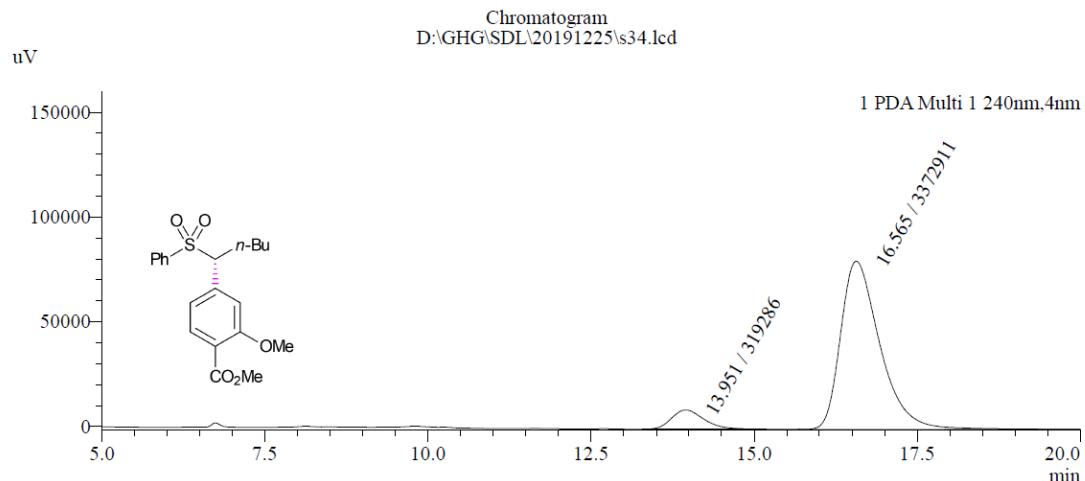


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 12.660 | 0.4353 | 5462022.98 | 190092.99 | 49.9610 |
| 2 | 14.959 | 0.5207 | 5470556.97 | 159214.57 | 50.0390 |

17: enantioenriched, 83% ee

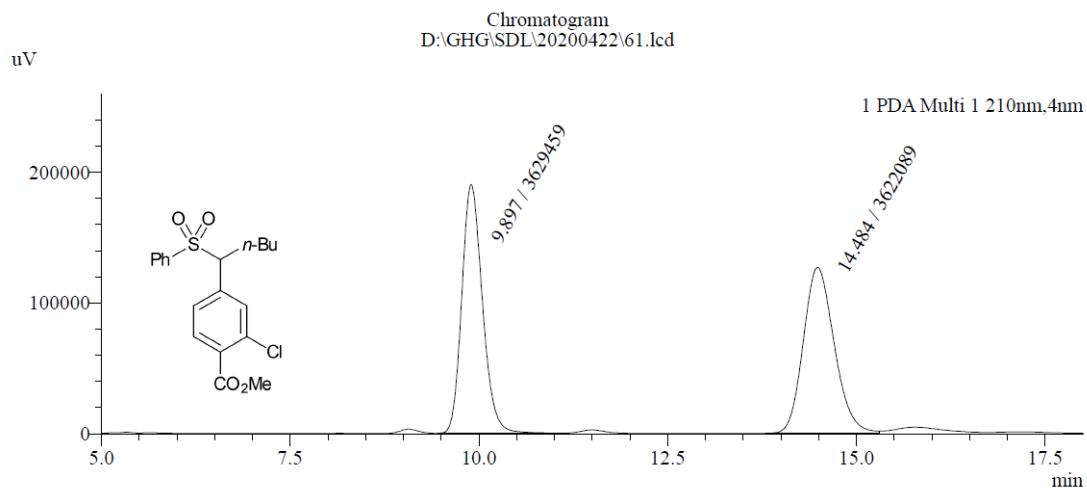


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 13.951 | 0.5274 | 319285.86 | 9212.33 | 8.6476 |
| 2 | 16.565 | 0.6275 | 3372911.04 | 80342.14 | 91.3524 |

18: racemic

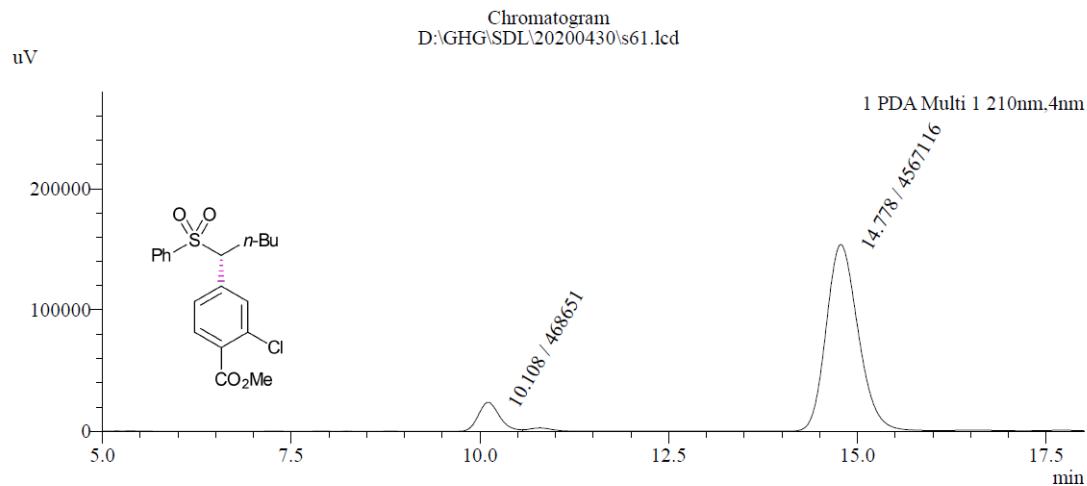


Peak Table

PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 9.897 | 0.2902 | 3629459.14 | 190416.93 | 50.0508 |
| 2 | 14.484 | 0.4384 | 3622088.98 | 126890.36 | 49.9492 |

18: enantioenriched, 81% ee

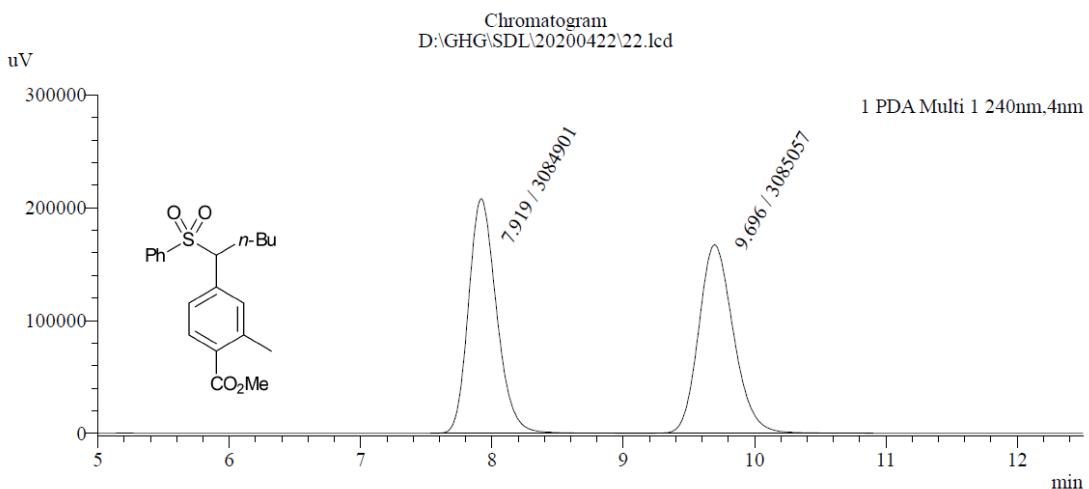


Peak Table

PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 10.108 | 0.2991 | 468651.05 | 23865.13 | 9.3064 |
| 2 | 14.778 | 0.4534 | 4567116.47 | 154022.44 | 90.6936 |

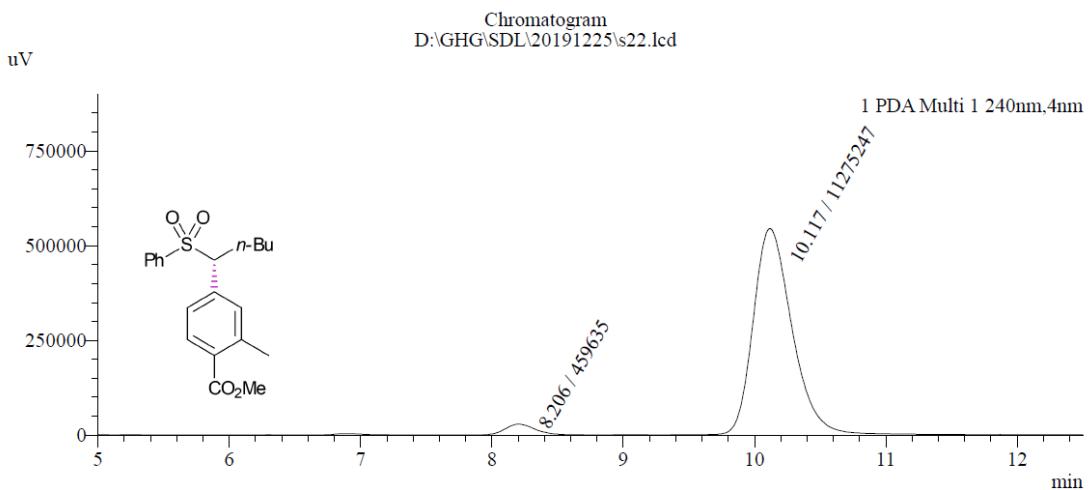
19: racemic



PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.919 | 0.2261 | 3084900.80 | 207930.37 | 49.9987 |
| 2 | 9.696 | 0.2822 | 3085057.05 | 167206.74 | 50.0013 |

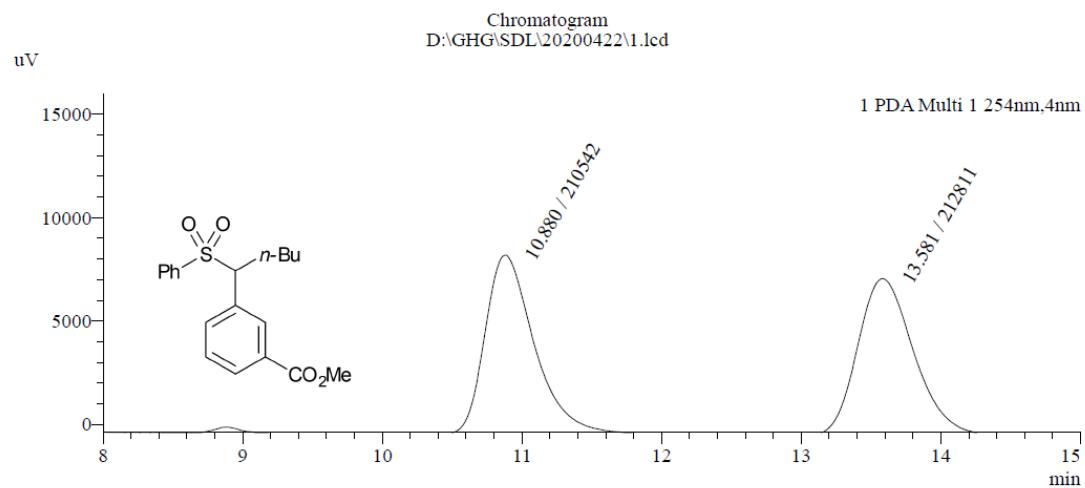
19: enantioenriched, 92% ee



PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.206 | 0.2454 | 459635.02 | 28466.14 | 3.9168 |
| 2 | 10.117 | 0.3111 | 11275247.06 | 545015.28 | 96.0832 |

20: racemic

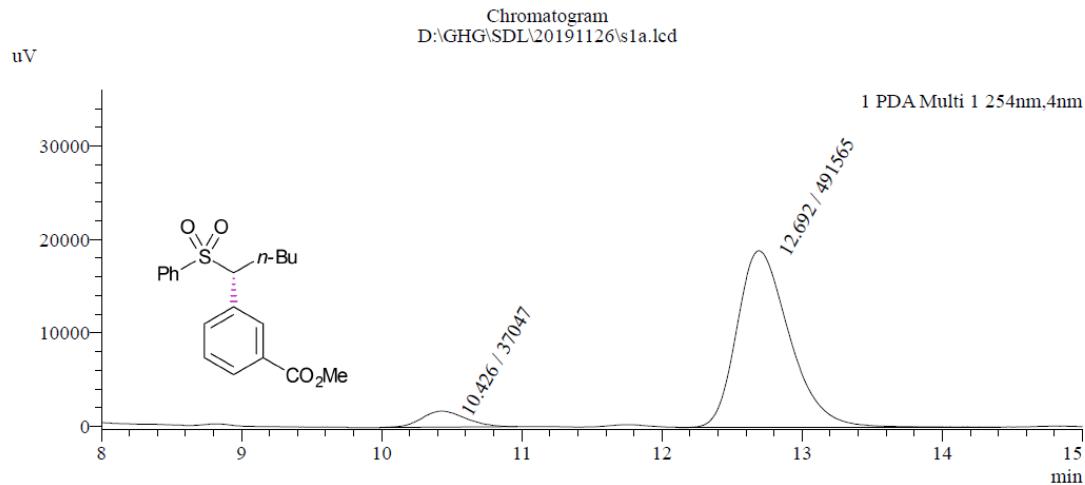


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 10.880 | 0.3658 | 210541.64 | 8640.28 | 49.7319 |
| 2 | 13.581 | 0.4322 | 212811.42 | 7596.24 | 50.2681 |

20: enantioenriched, 86% ee

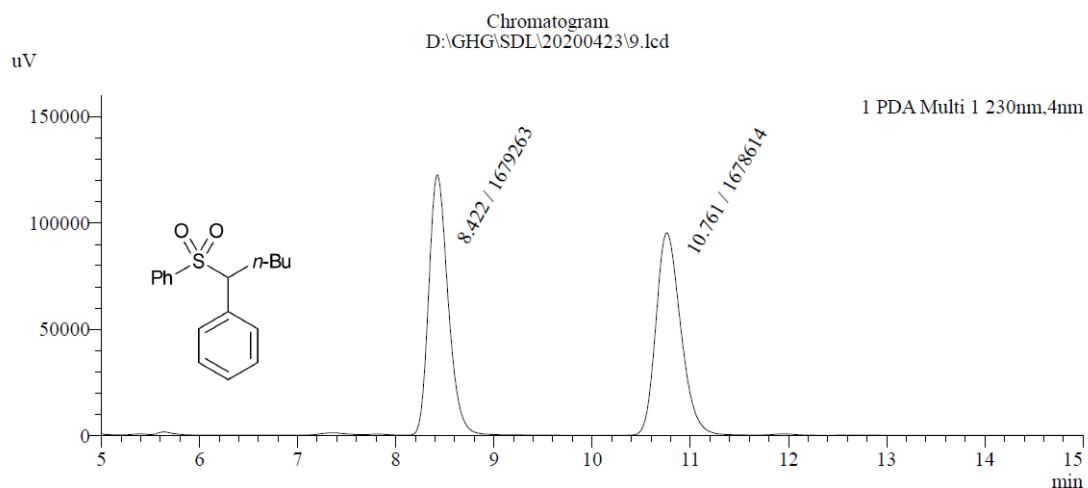


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 10.426 | 0.3388 | 37046.67 | 1703.26 | 7.0083 |
| 2 | 12.692 | 0.3968 | 491565.43 | 18882.42 | 92.9917 |

21: racemic

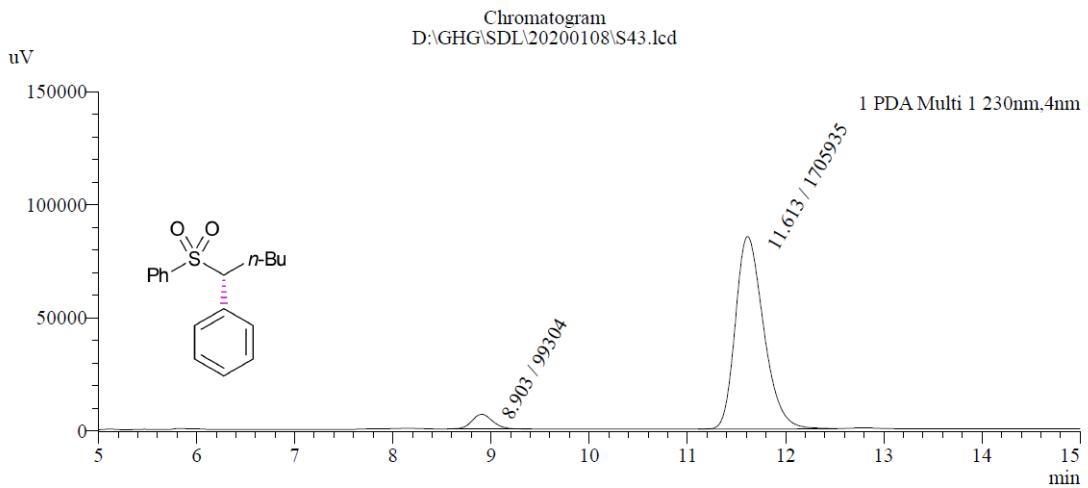


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.422 | 0.2092 | 1679262.51 | 122342.79 | 50.0097 |
| 2 | 10.761 | 0.2698 | 1678613.76 | 95304.71 | 49.9903 |

21: enantioenriched, 89% ee

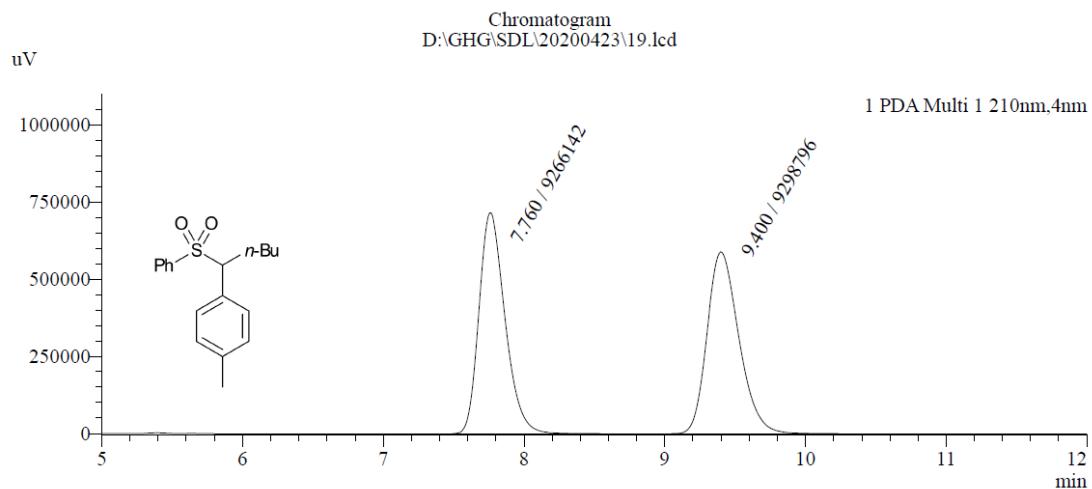


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.903 | 0.2268 | 99304.42 | 6576.21 | 5.5009 |
| 2 | 11.613 | 0.3057 | 1705935.38 | 85199.81 | 94.4991 |

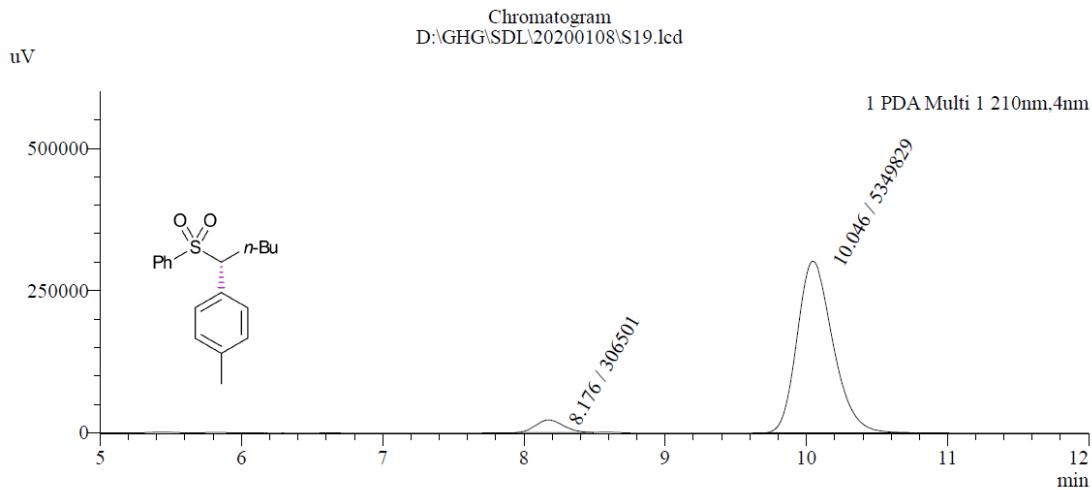
22: racemic



PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.760 | 0.1973 | 9266141.86 | 716510.86 | 49.9121 |
| 2 | 9.400 | 0.2413 | 9298796.21 | 589506.40 | 50.0879 |

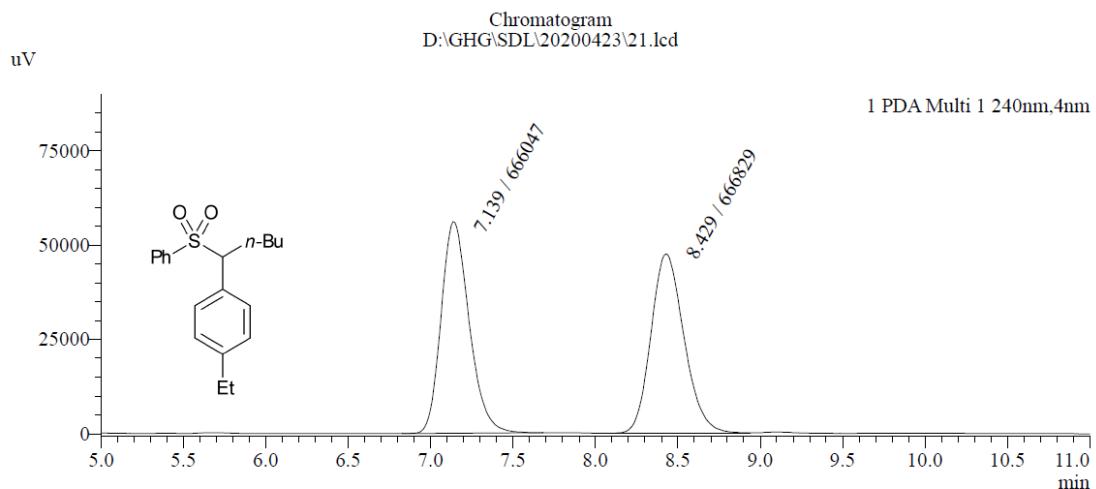
22: enantioenriched, 89% ee



PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.176 | 0.2158 | 306500.80 | 22312.94 | 5.4187 |
| 2 | 10.046 | 0.2703 | 5349829.25 | 302492.60 | 94.5813 |

23: racemic

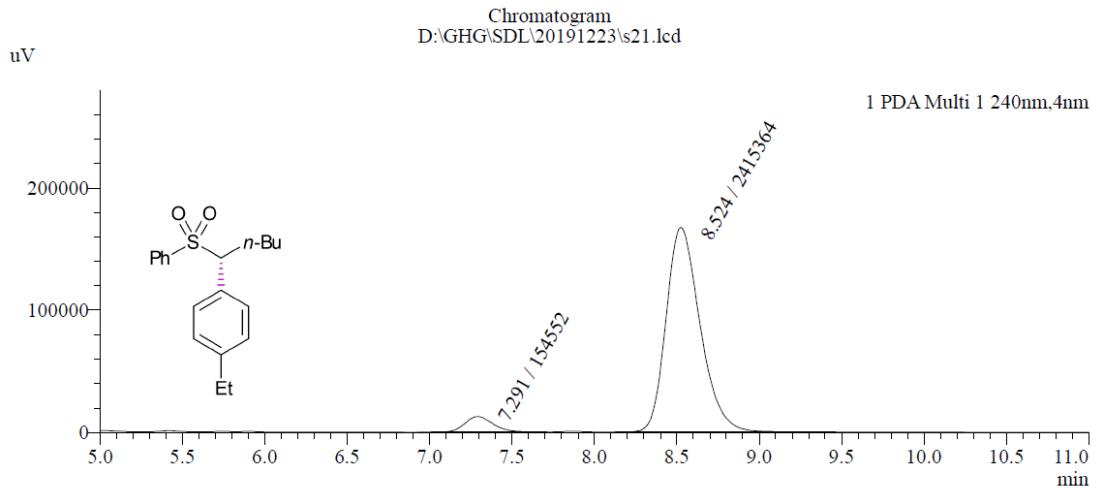


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.139 | 0.1814 | 666046.54 | 56080.25 | 49.9707 |
| 2 | 8.429 | 0.2151 | 666828.78 | 47562.66 | 50.0293 |

23: enantioenriched, 88% ee

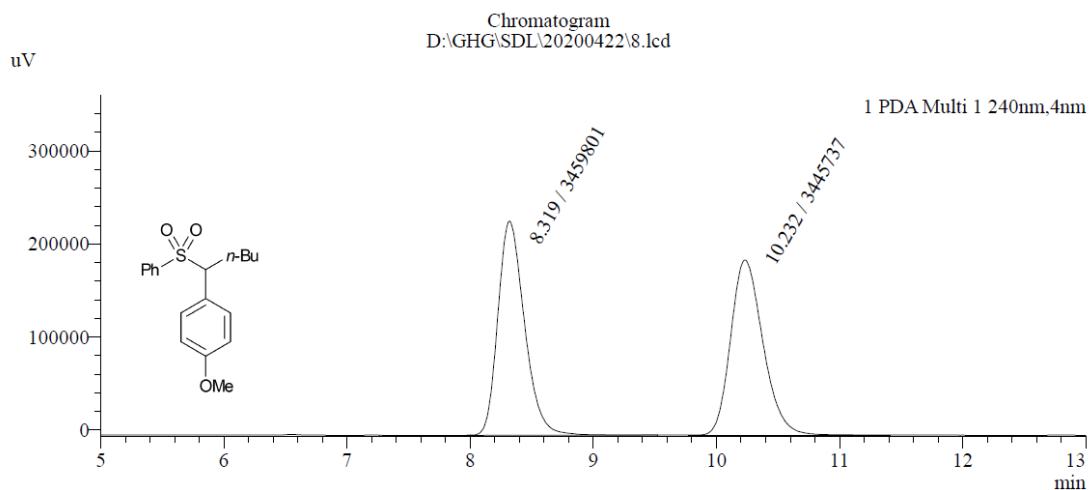


Peak Table

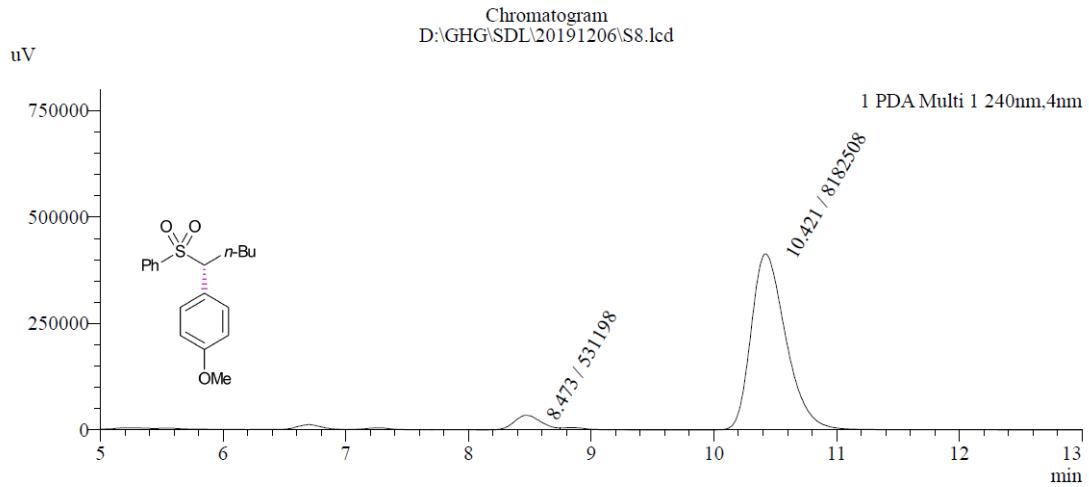
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.291 | 0.1832 | 154551.77 | 12718.56 | 6.0139 |
| 2 | 8.524 | 0.2192 | 2415364.06 | 167646.39 | 93.9861 |

24: racemic



24: enantioenriched, 88% ee

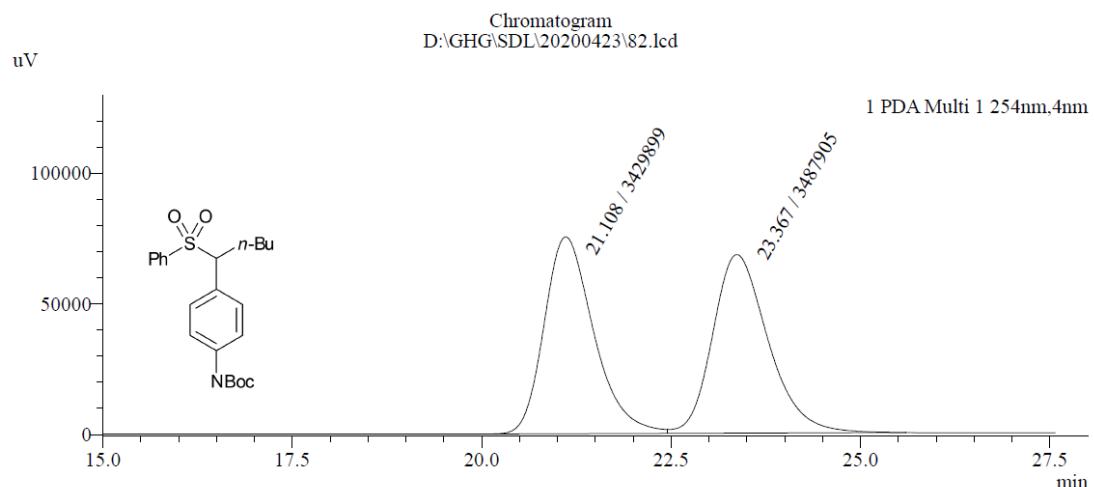


Peak Table

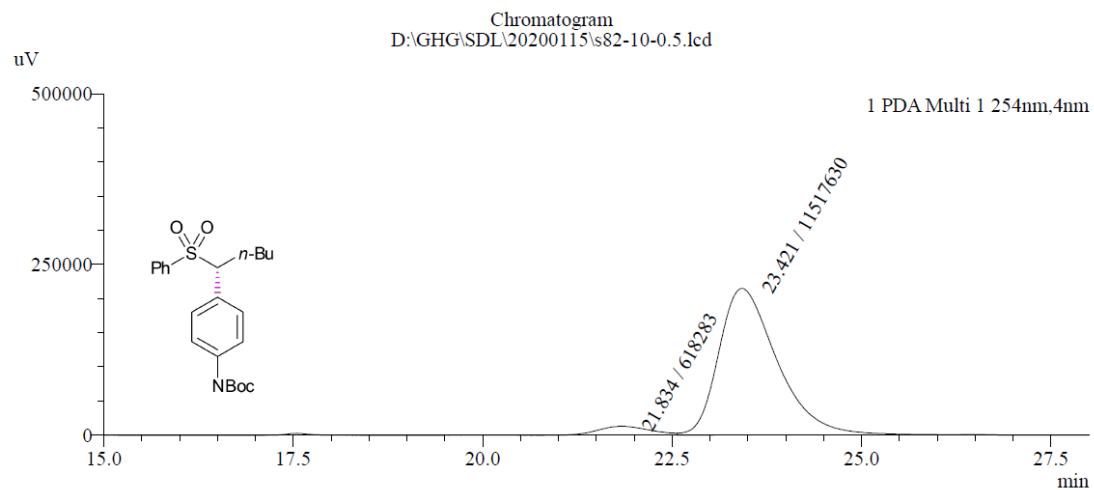
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.473 | 0.2382 | 531198.34 | 34501.39 | 6.0961 |
| 2 | 10.421 | 0.3009 | 8182507.63 | 414076.30 | 93.9039 |

25: racemic



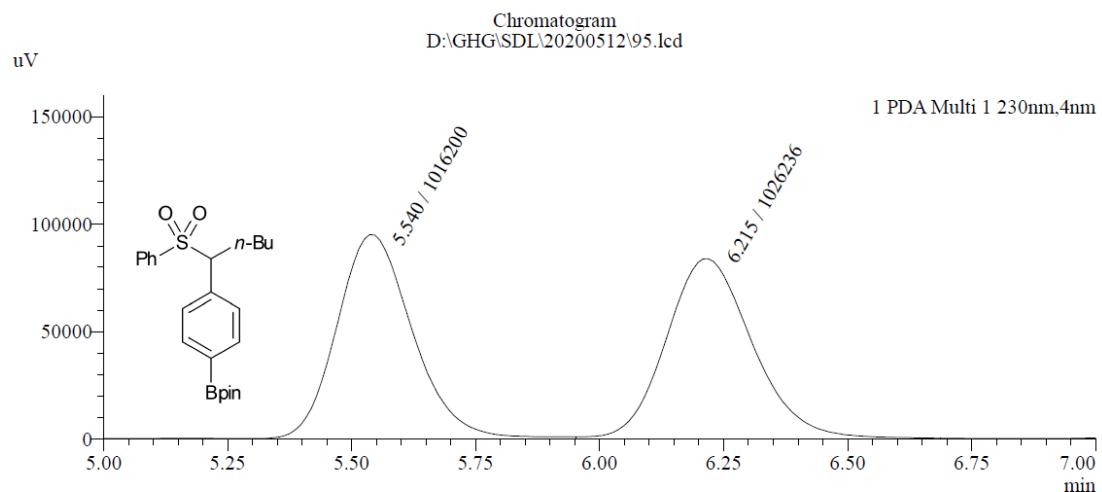
25: enantioenriched, 90% ee



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 21.834 | 0.7589 | 618282.55 | 12974.63 | 5.0947 |
| 2 | 23.421 | 0.8042 | 11517630.02 | 215133.32 | 94.9053 |

26: racemic

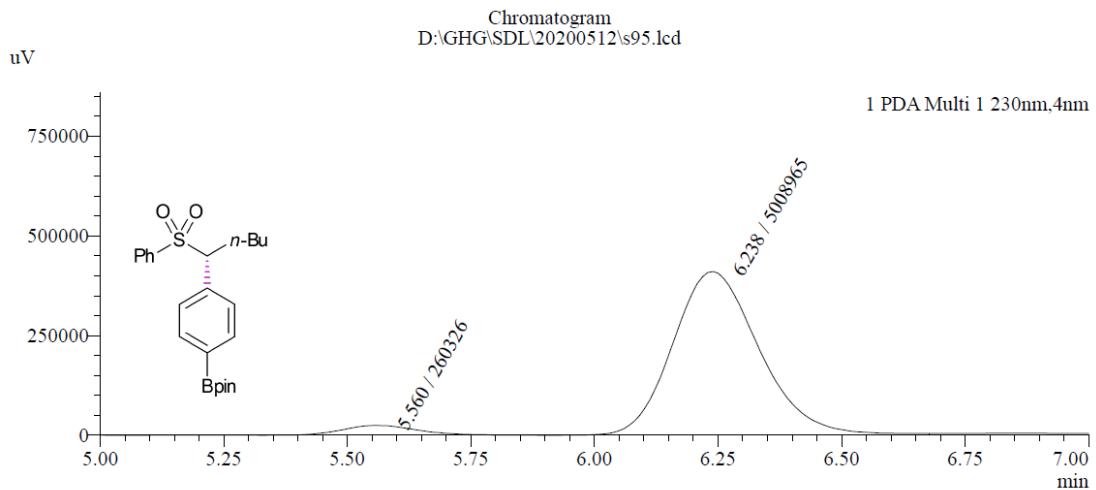


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 5.540 | 0.1619 | 1016199.91 | 95264.63 | 49.7543 |
| 2 | 6.215 | 0.1852 | 1026235.70 | 84052.86 | 50.2457 |

26: enantioenriched, 90% ee

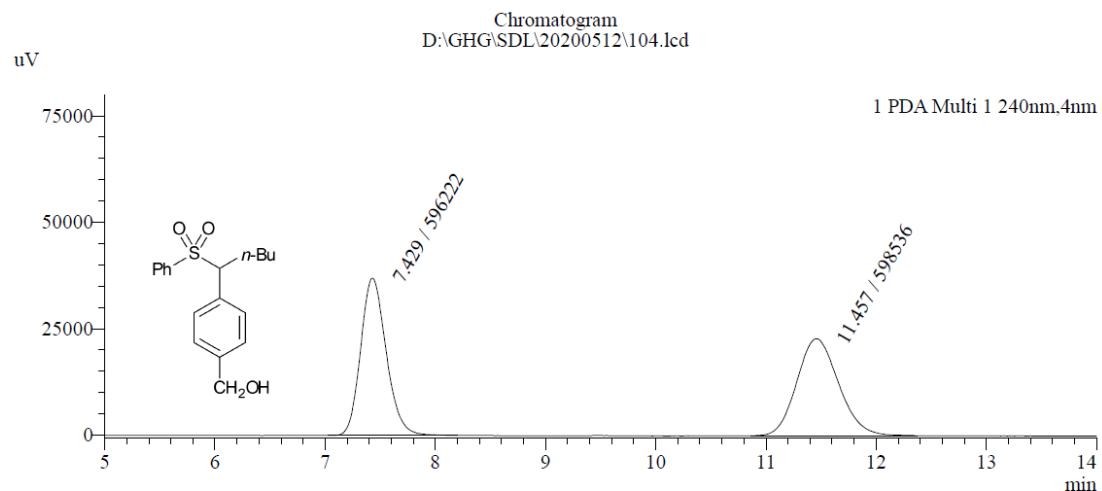


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 5.560 | 0.1623 | 260326.12 | 24573.02 | 4.9404 |
| 2 | 6.238 | 0.1861 | 5008965.09 | 410794.60 | 95.0596 |

27: racemic

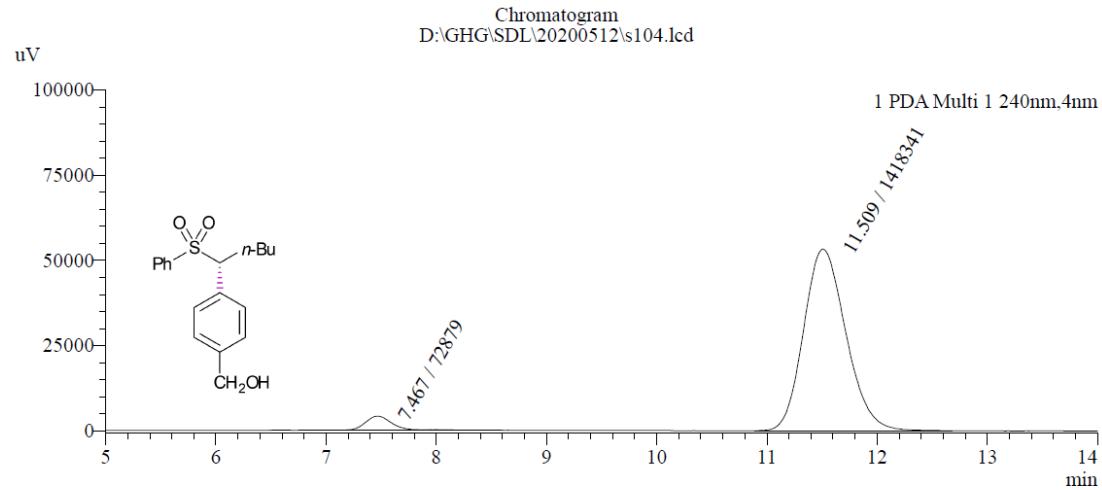


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.429 | 0.2470 | 596221.67 | 36966.05 | 49.9032 |
| 2 | 11.457 | 0.4065 | 598535.79 | 22788.76 | 50.0968 |

27: enantioenriched, 90% ee

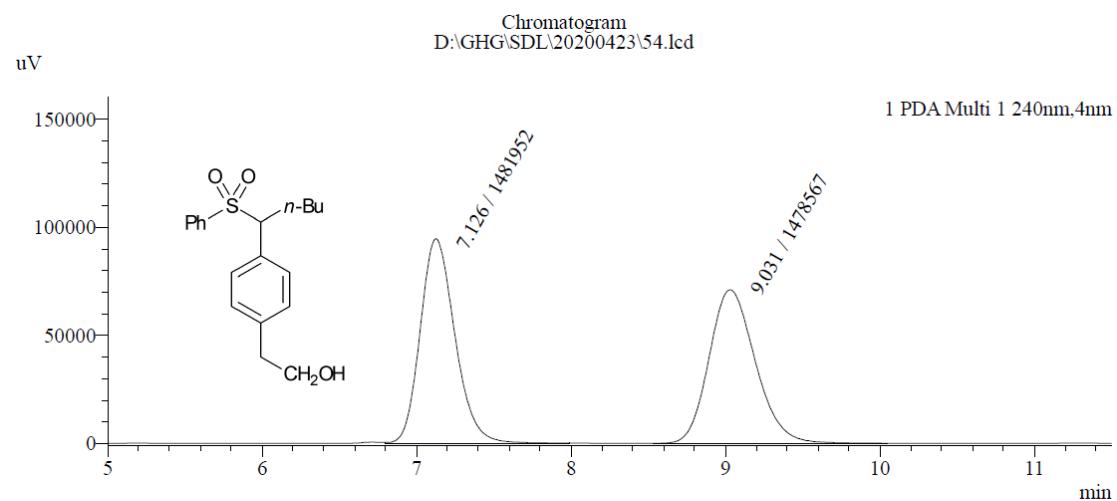


Peak Table

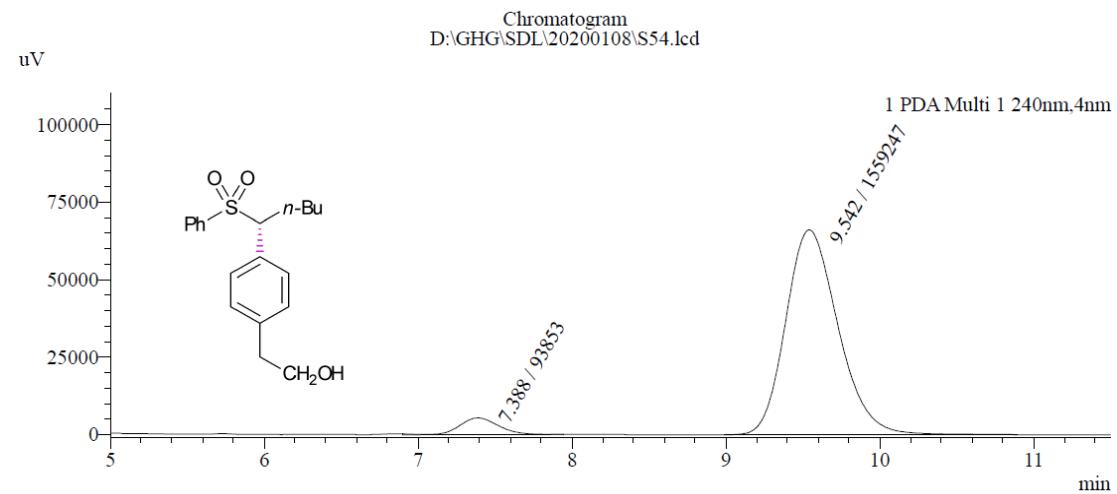
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.467 | 0.2518 | 72879.18 | 4161.31 | 4.8872 |
| 2 | 11.509 | 0.4116 | 1418341.00 | 53246.24 | 95.1128 |

28: racemic



28: enantioenriched, 89% ee

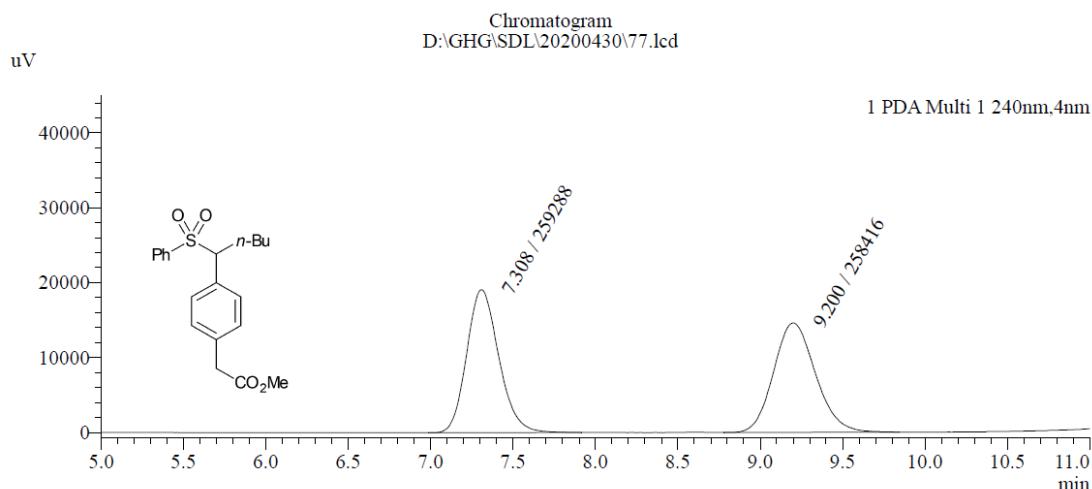


Peak Table

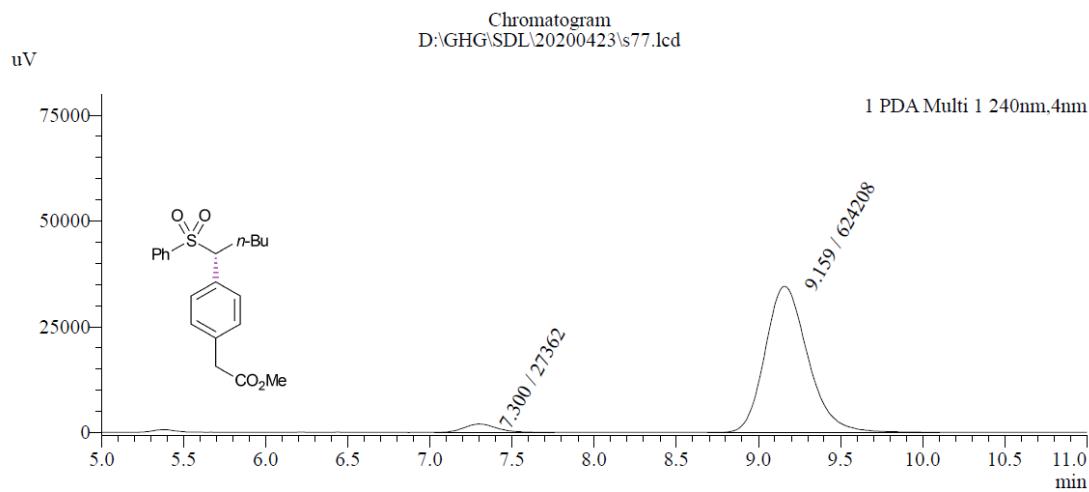
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.388 | 0.2660 | 93852.62 | 5379.75 | 5.6774 |
| 2 | 9.542 | 0.3619 | 1559246.59 | 66026.67 | 94.3226 |

29: racemic



29: enantioenriched, 92% ee

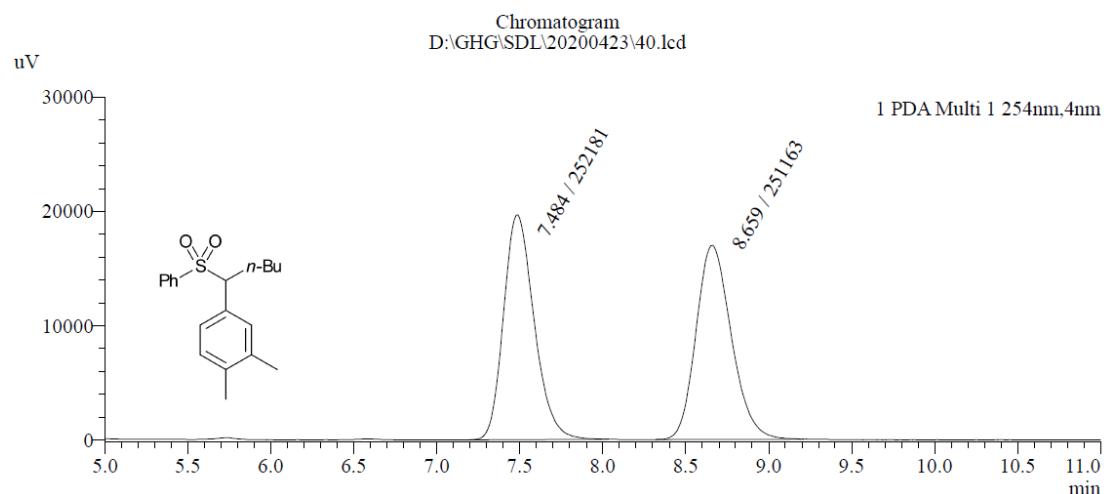


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.300 | 0.2105 | 27361.77 | 1982.11 | 4.1994 |
| 2 | 9.159 | 0.2742 | 624208.11 | 34537.19 | 95.8006 |

30: racemic

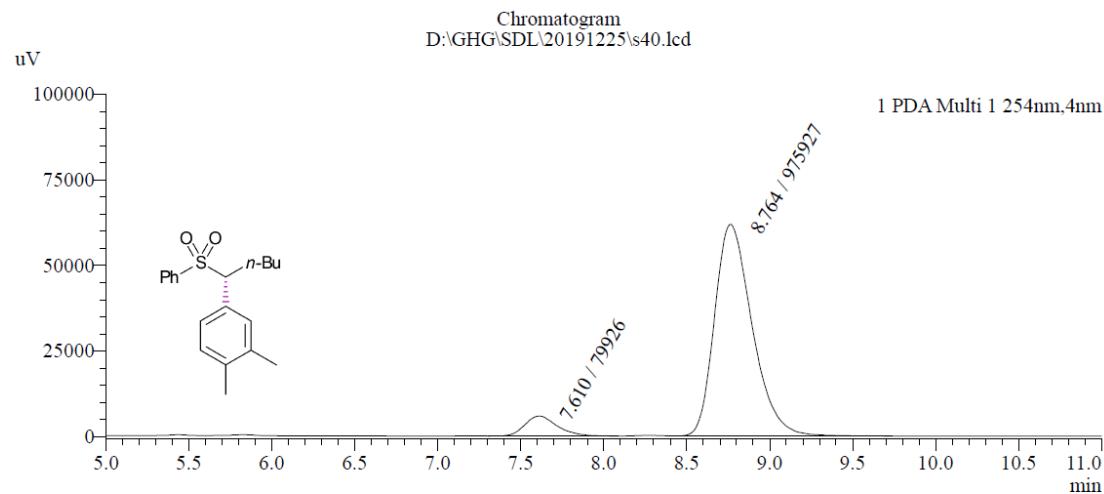


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.484 | 0.1962 | 252180.94 | 19668.72 | 50.1012 |
| 2 | 8.659 | 0.2276 | 251162.54 | 16975.70 | 49.8988 |

30: enantioenriched, 85% ee

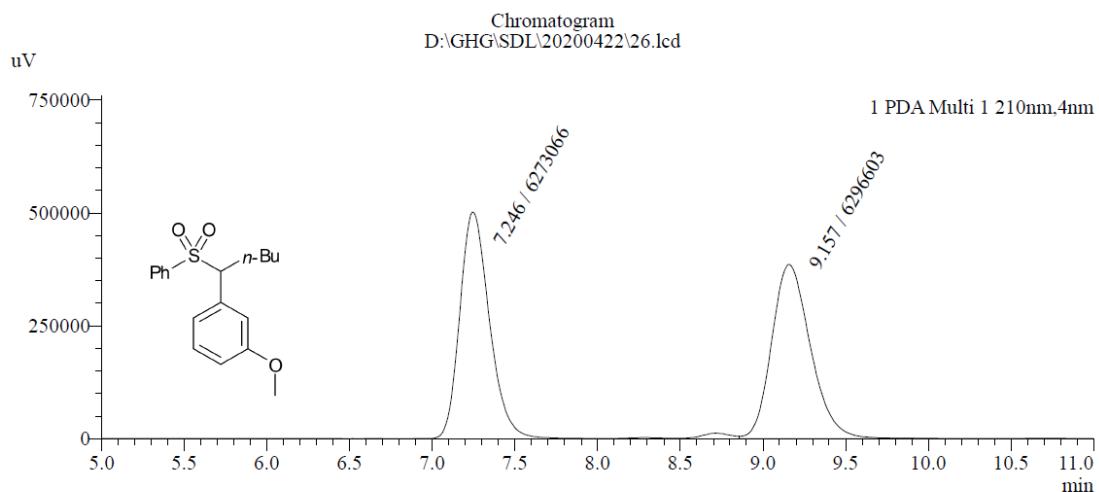


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.610 | 0.2050 | 79925.74 | 5846.36 | 7.5698 |
| 2 | 8.764 | 0.2407 | 975927.35 | 61785.87 | 92.4302 |

31: racemic

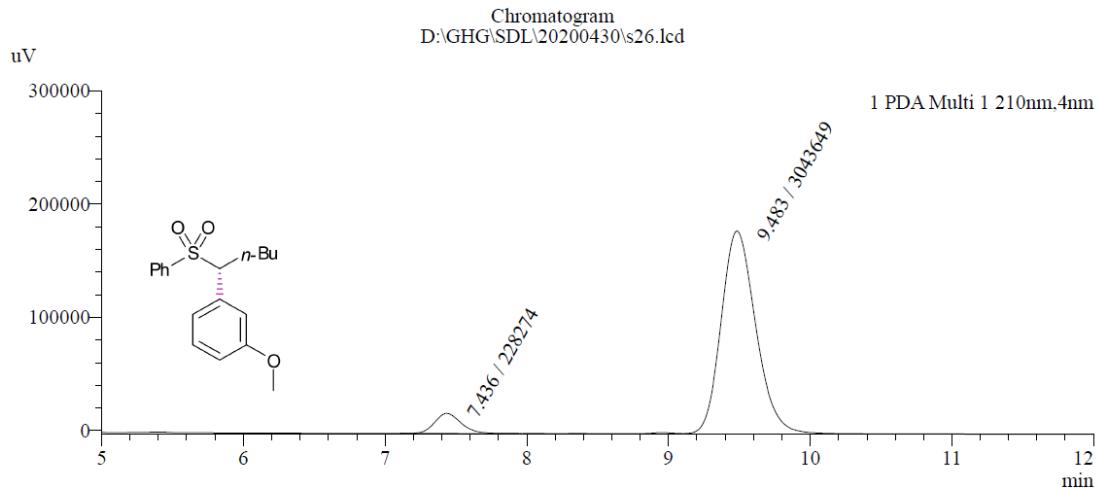


Peak Table

PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.246 | 0.1900 | 6273065.74 | 502465.21 | 49.9064 |
| 2 | 9.157 | 0.2494 | 6296602.82 | 385287.93 | 50.0936 |

31: enantioenriched, 86% ee

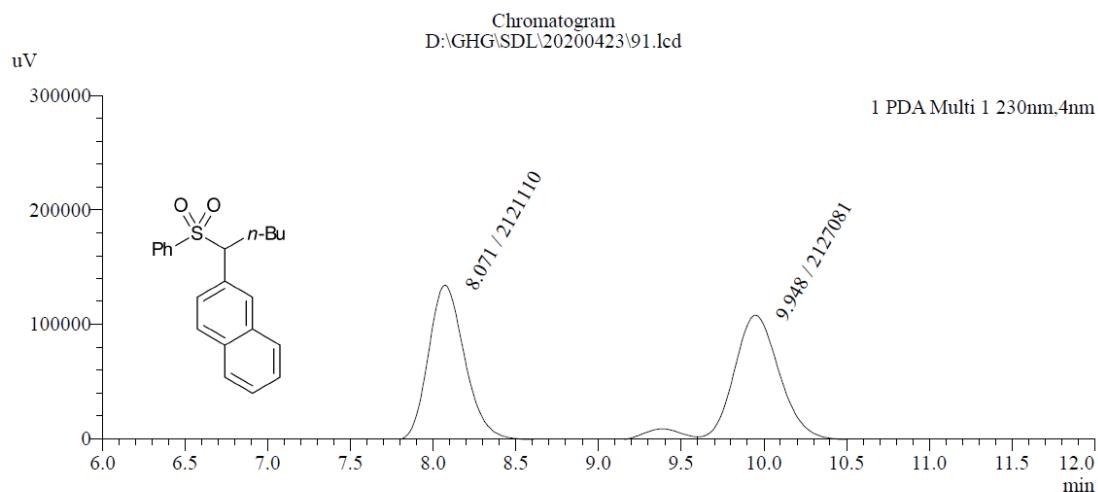


Peak Table

PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.436 | 0.1972 | 228274.47 | 17720.73 | 6.9768 |
| 2 | 9.483 | 0.2596 | 3043649.34 | 179135.73 | 93.0232 |

32: racemic

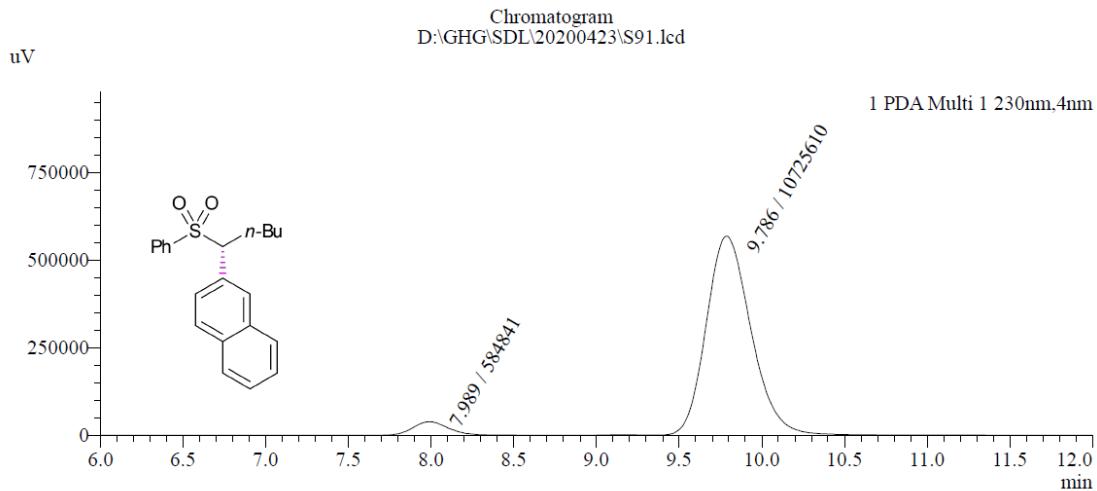


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.071 | 0.2356 | 212110.41 | 136120.55 | 49.9297 |
| 2 | 9.948 | 0.2937 | 2127080.57 | 109932.16 | 50.0703 |

32: enantioenriched, 90% ee

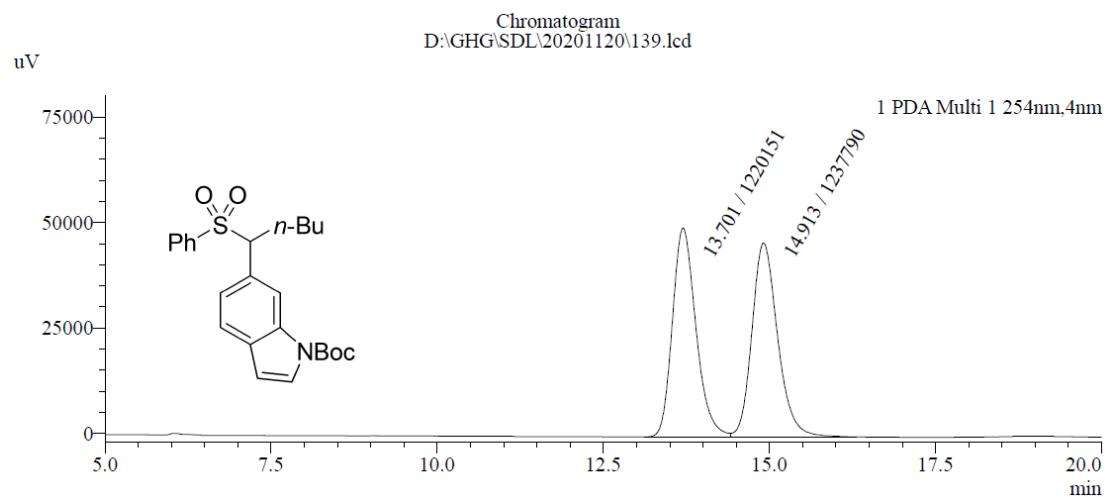


Peak Table

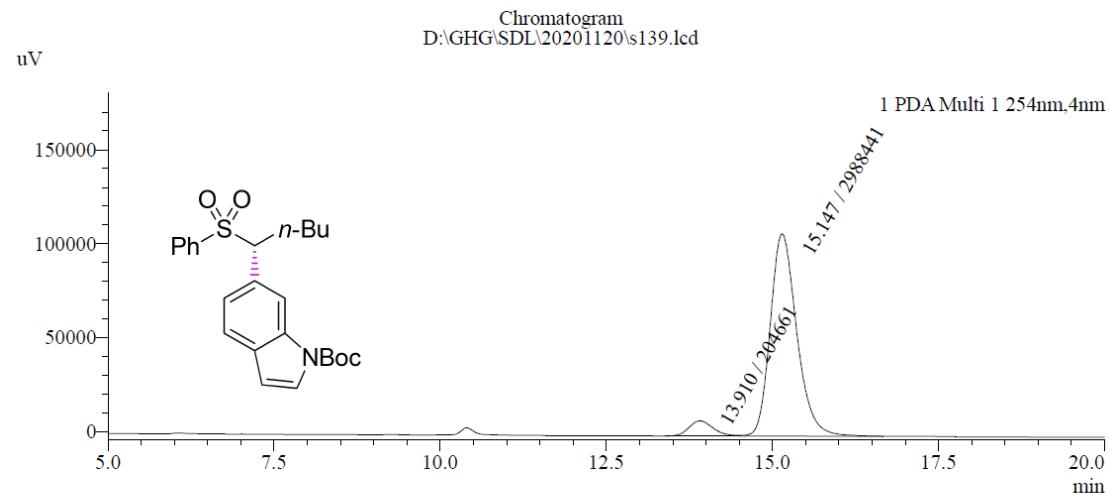
PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.989 | 0.2309 | 584841.13 | 38557.35 | 5.1708 |
| 2 | 9.786 | 0.2886 | 10725610.05 | 567833.47 | 94.8292 |

33: racemic



33: enantioenriched, 87% ee

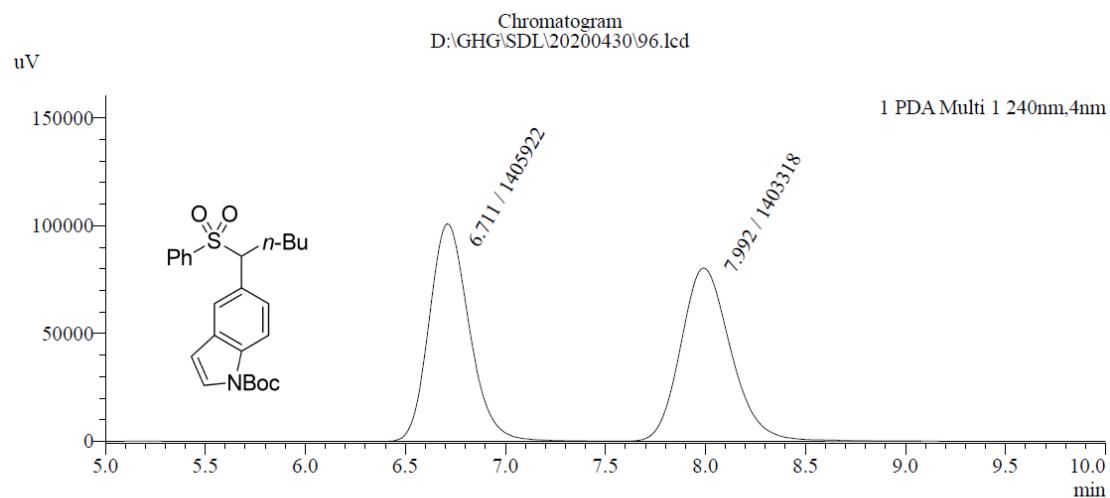


Peak Table

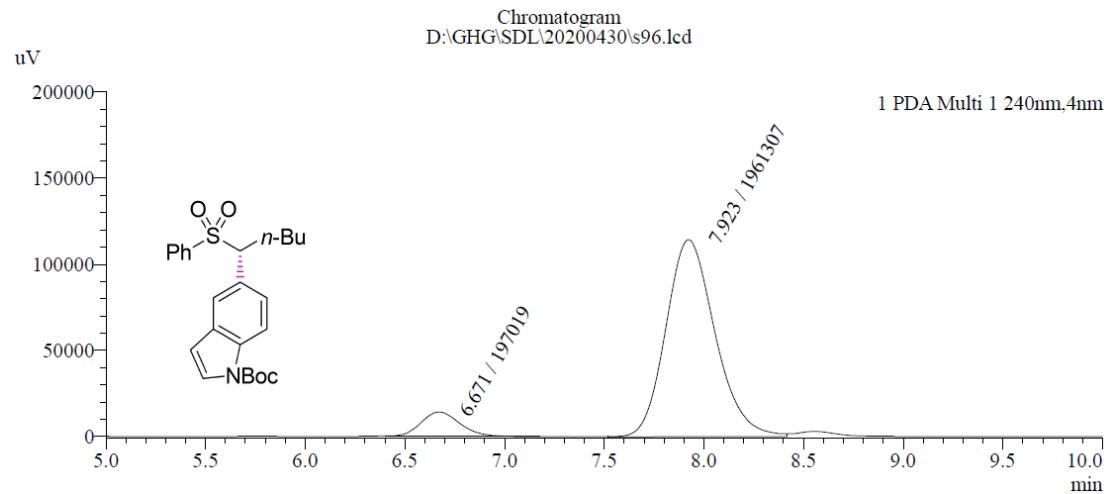
PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 13.910 | 0.3868 | 204660.57 | 8079.37 | 6.4095 |
| 2 | 15.147 | 0.4185 | 2988441.47 | 107671.33 | 93.5905 |

34: racemic



34: enantioenriched, 82% ee

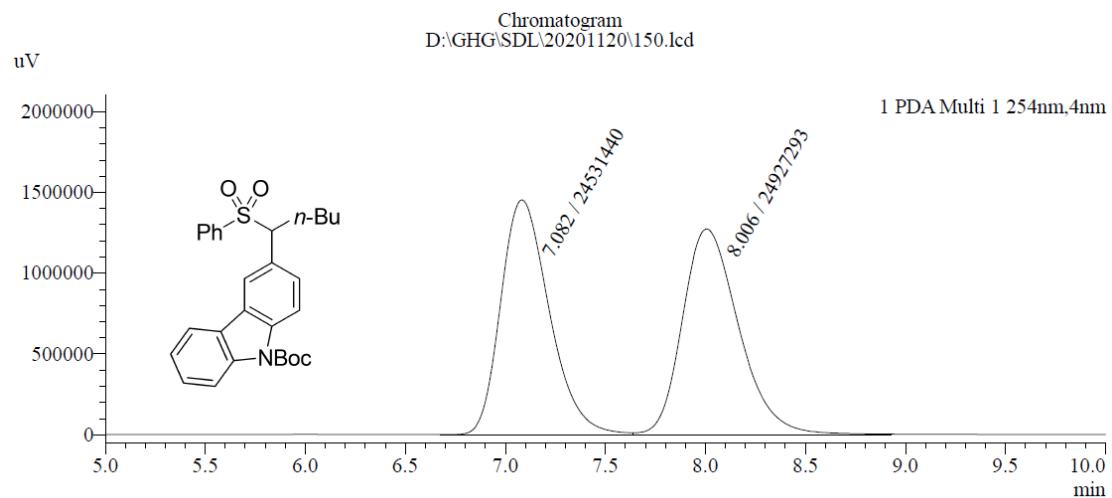


Peak Table

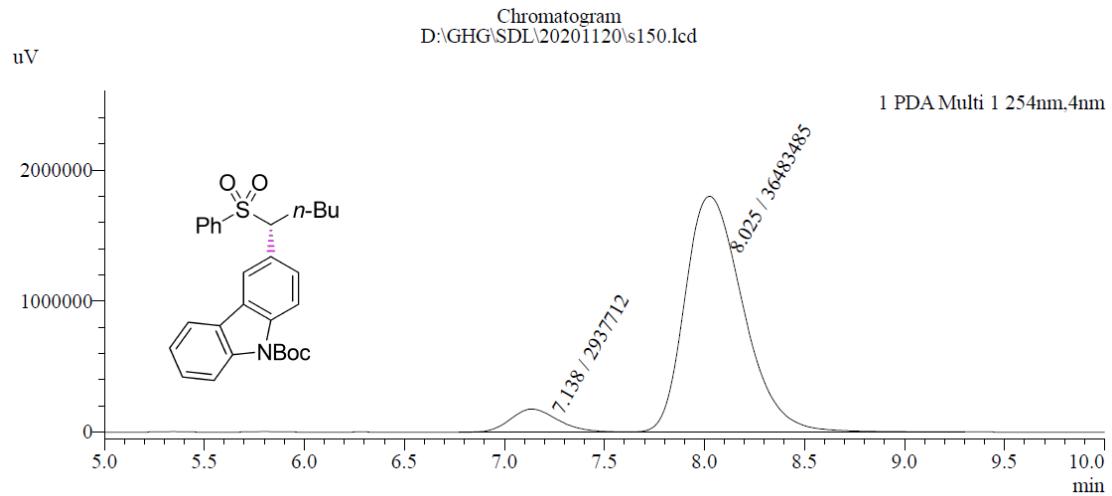
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 6.671 | 0.2105 | 197018.58 | 14270.15 | 9.1283 |
| 2 | 7.923 | 0.2617 | 1961307.26 | 114474.64 | 90.8717 |

35: racemic



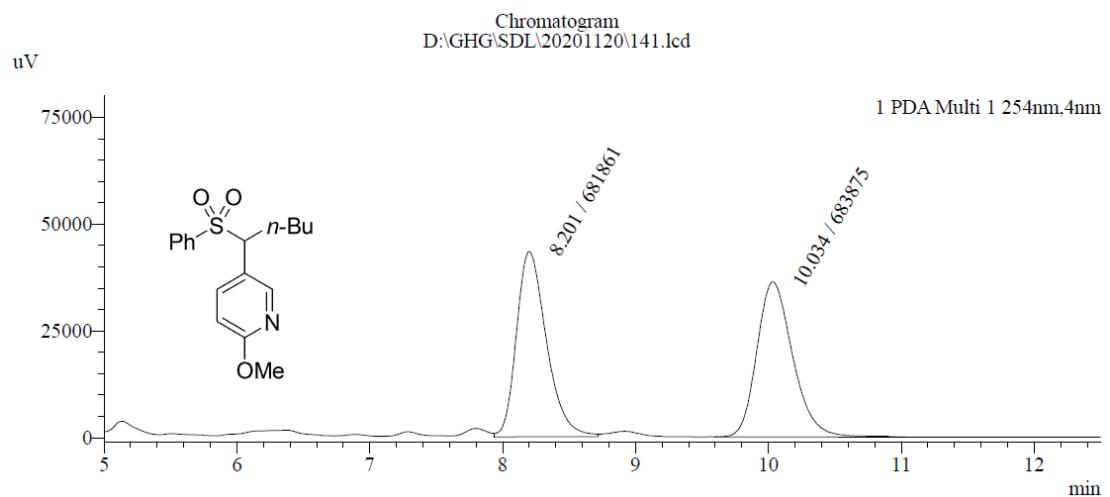
35: enantioenriched, 85% ee



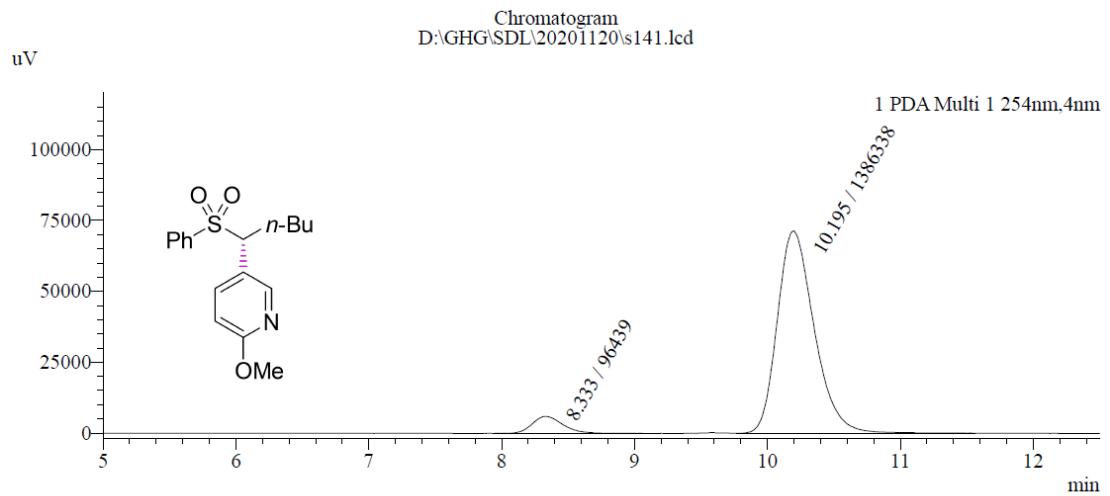
PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.138 | 0.2545 | 2937712.47 | 176556.48 | 7.4521 |
| 2 | 8.025 | 0.3114 | 36483485.22 | 1800515.21 | 92.5479 |

36: racemic



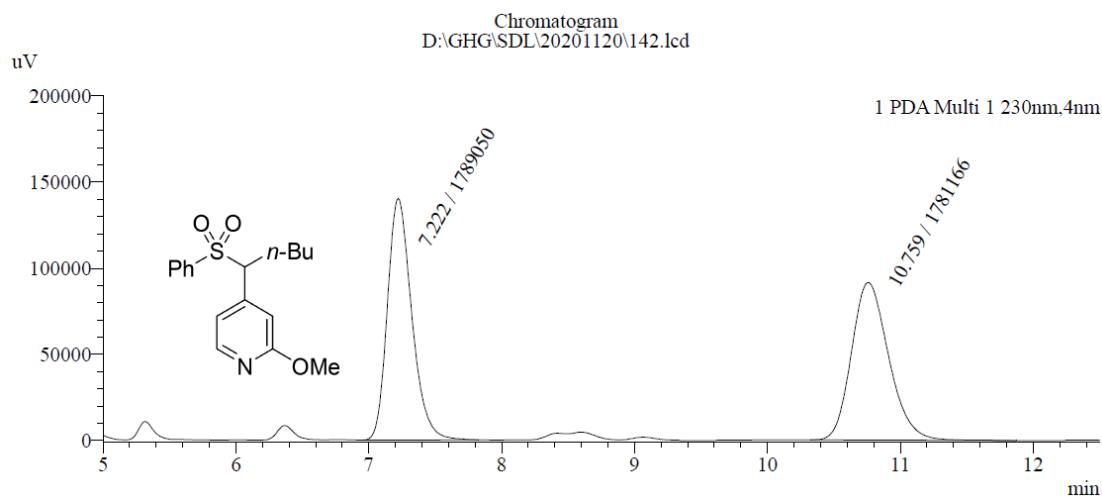
36: enantioenriched, 87% ee



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.333 | 0.2424 | 96438.50 | 6032.78 | 6.5039 |
| 2 | 10.195 | 0.2939 | 1386337.66 | 71408.47 | 93.4961 |

37: racemic

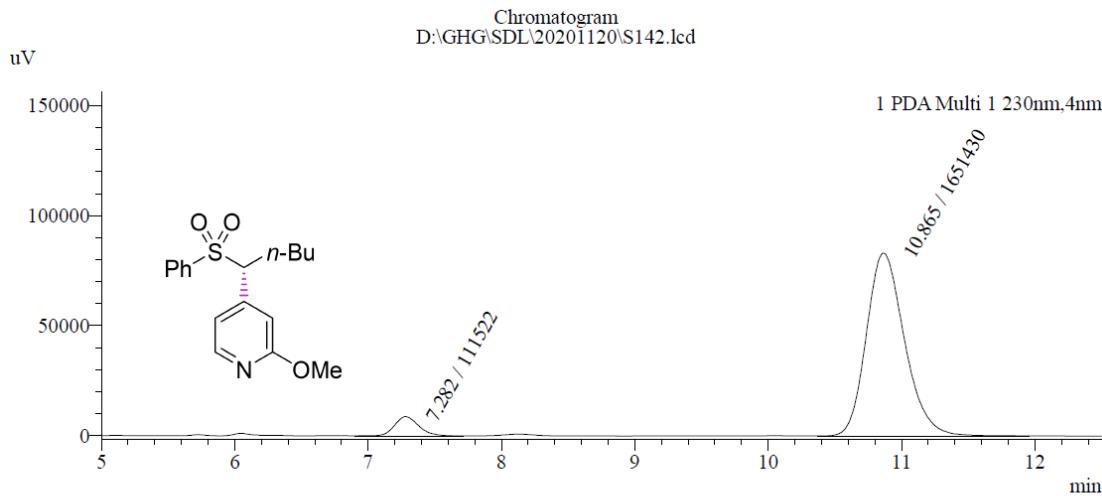


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.222 | 0.1937 | 1789049.69 | 140272.63 | 50.1104 |
| 2 | 10.759 | 0.2986 | 1781165.98 | 91504.39 | 49.8896 |

37: enantioenriched, 87% ee

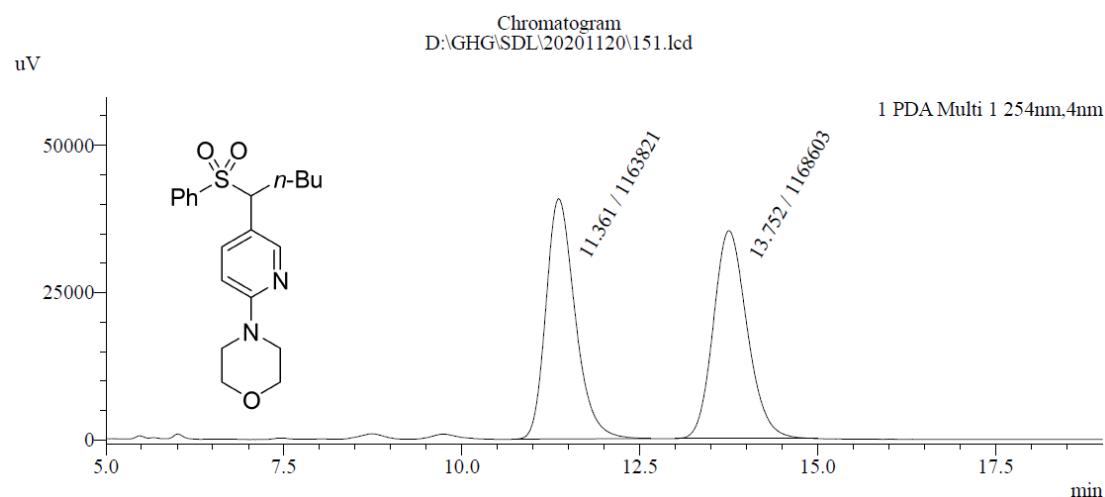


Peak Table

PDA Ch1 230nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.282 | 0.1918 | 111521.70 | 8748.11 | 6.3258 |
| 2 | 10.865 | 0.3032 | 1651430.42 | 83097.78 | 93.6742 |

38: racemic

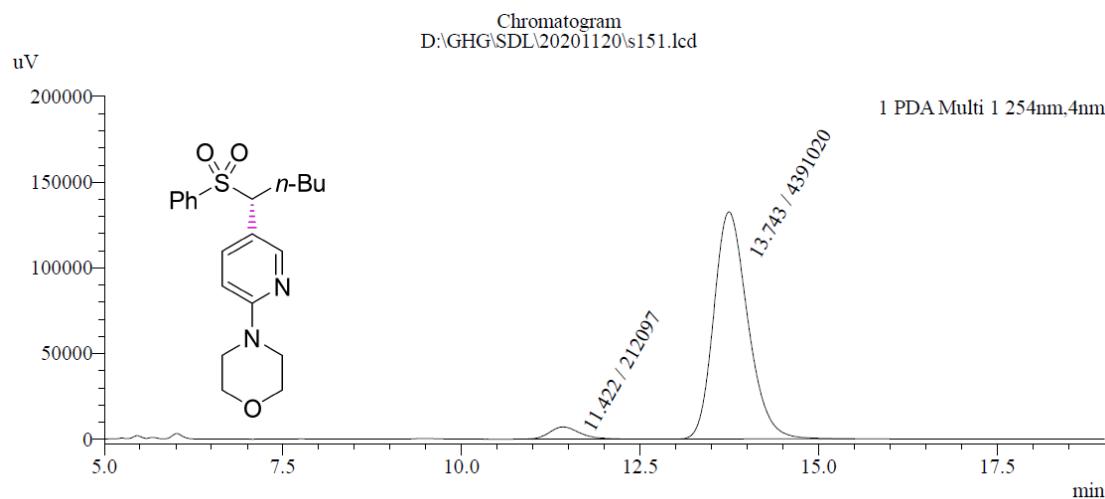


PDA Ch1 254nm

Peak Table

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.361 | 0.4321 | 1163820.60 | 40759.23 | 49.8975 |
| 2 | 13.752 | 0.5075 | 1168603.47 | 35281.06 | 50.1025 |

38: enantioenriched, 91% ee

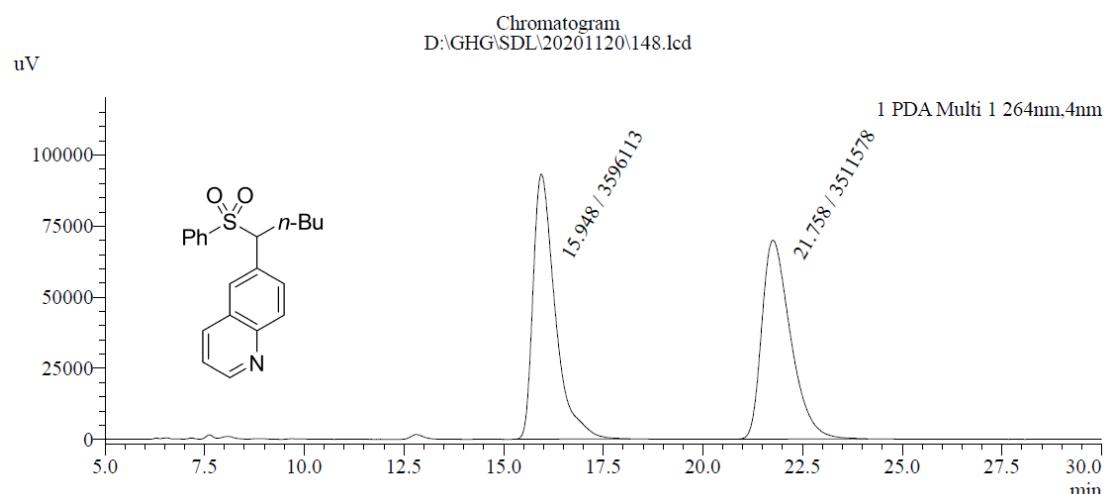


PDA Ch1 254nm

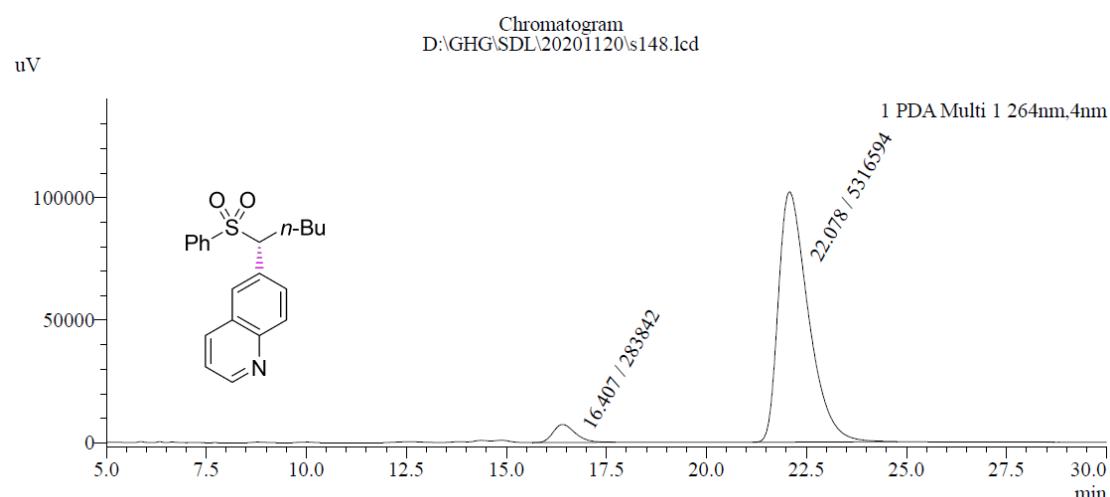
Peak Table

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.422 | 0.4445 | 212097.28 | 7145.65 | 4.6077 |
| 2 | 13.743 | 0.5063 | 4391020.38 | 132570.58 | 95.3923 |

39: racemic



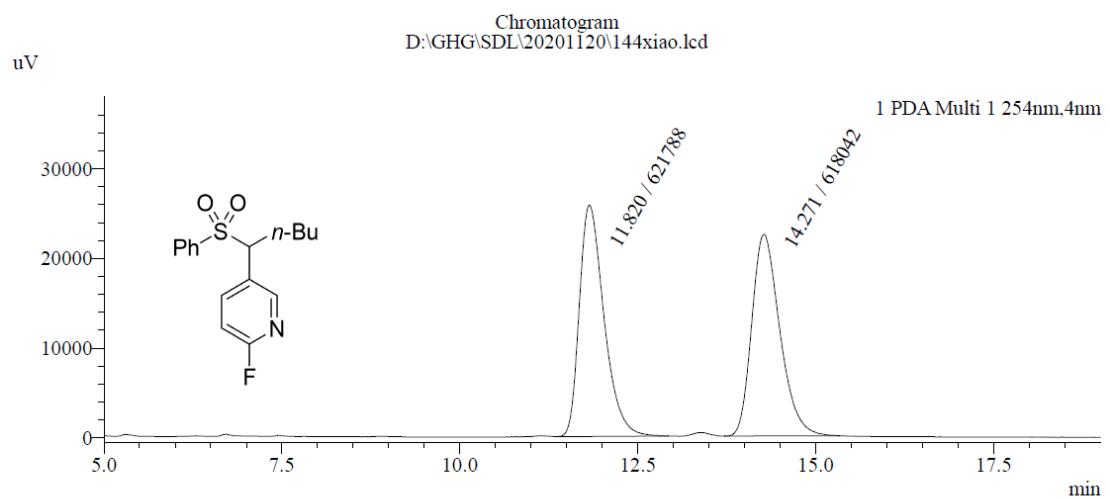
39: enantioenriched, 90% ee



PDA Ch1 264nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 16.407 | 0.5895 | 283842.06 | 7379.69 | 5.0682 |
| 2 | 22.078 | 0.7909 | 5316594.39 | 102008.76 | 94.9318 |

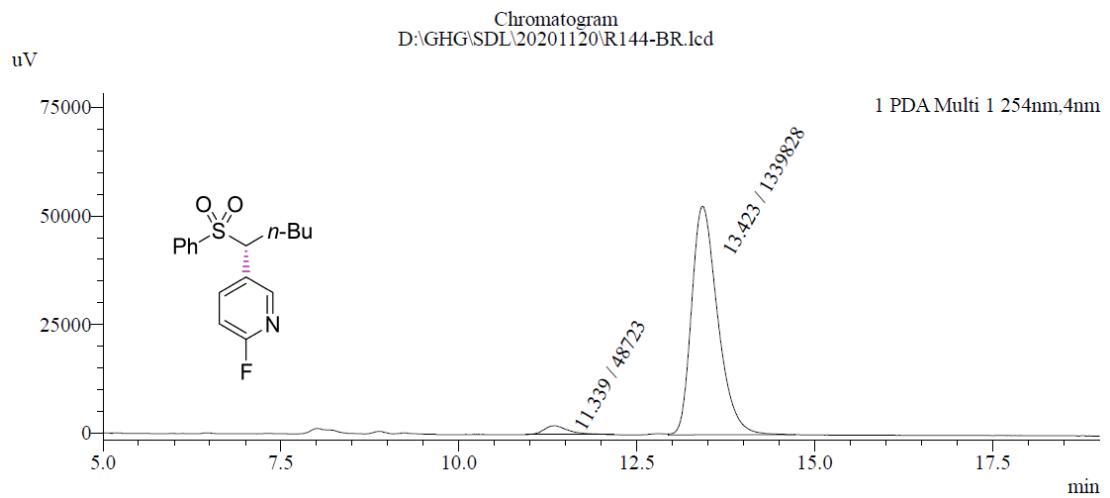
40: racemic



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.820 | 0.3655 | 621787.53 | 25804.83 | 50.1510 |
| 2 | 14.271 | 0.4186 | 618042.28 | 22512.56 | 49.8490 |

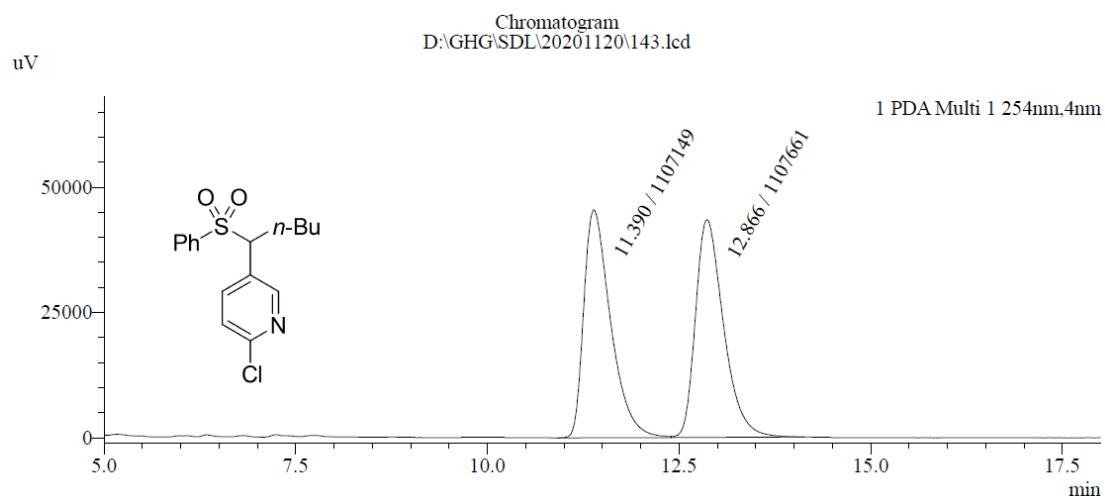
40: enantioenriched, 93% ee



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.339 | 0.3496 | 48723.19 | 2019.12 | 3.5089 |
| 2 | 13.423 | 0.3869 | 1339828.44 | 52560.57 | 96.4911 |

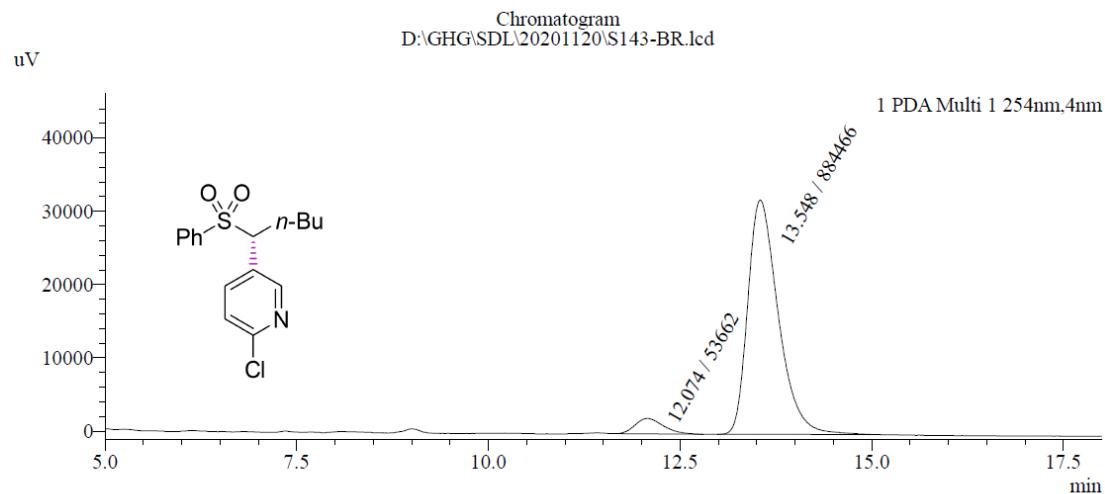
41: racemic



Peak Table

| PDA Ch1 254nm | Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|---------------|-------|-----------------|-------------|-------------|-------------|---------|
| | 1 | 11.390 | 0.3676 | 1107149.16 | 45450.31 | 49.9884 |
| | 2 | 12.866 | 0.3851 | 1107661.15 | 43447.23 | 50.0116 |

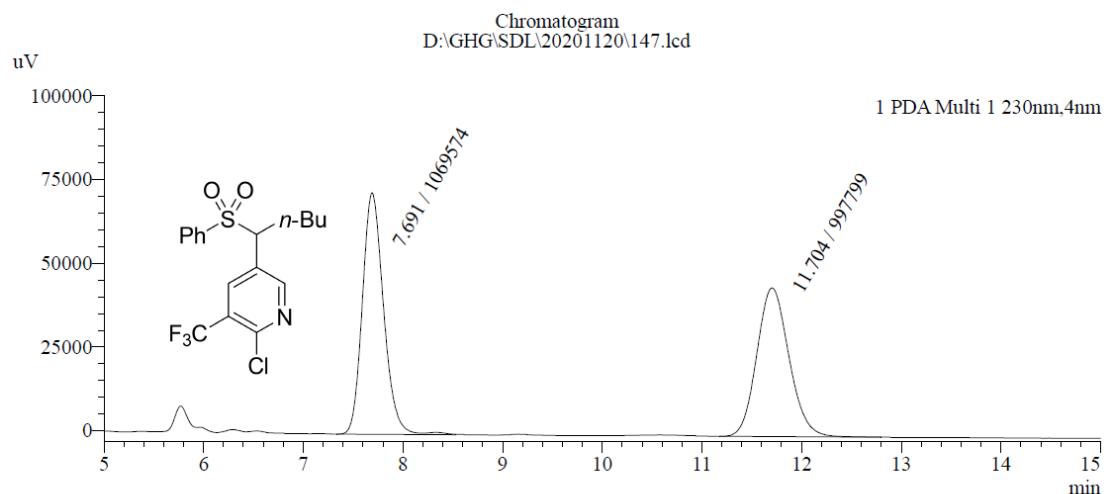
41: enantioenriched, 90% ee



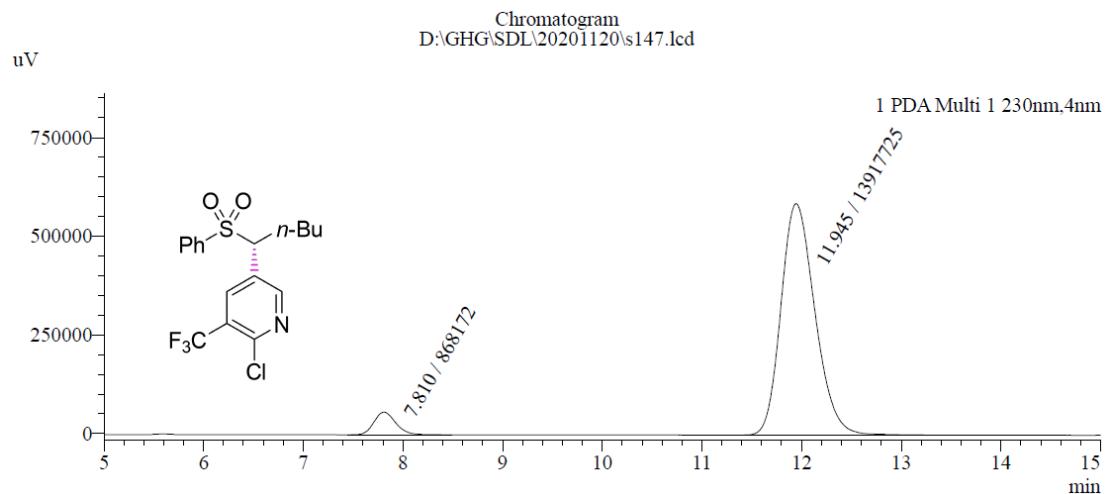
Peak Table

| PDA Ch1 254nm | Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|---------------|-------|-----------------|-------------|-------------|-------------|---------|
| | 1 | 12.074 | 0.3949 | 53662.08 | 2102.59 | 5.7201 |
| | 2 | 13.548 | 0.4170 | 884466.18 | 31954.88 | 94.2799 |

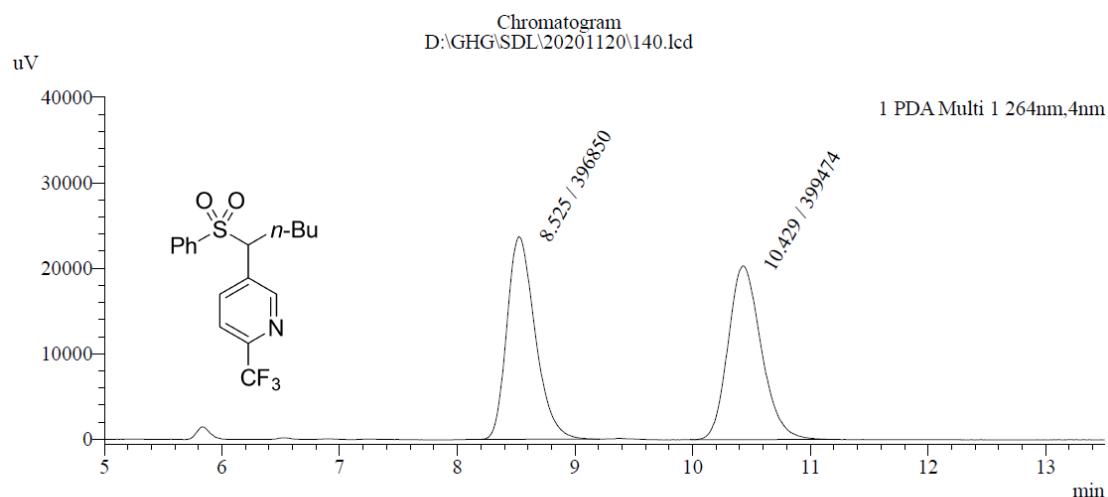
42: racemic



42: enantioenriched, 88% ee



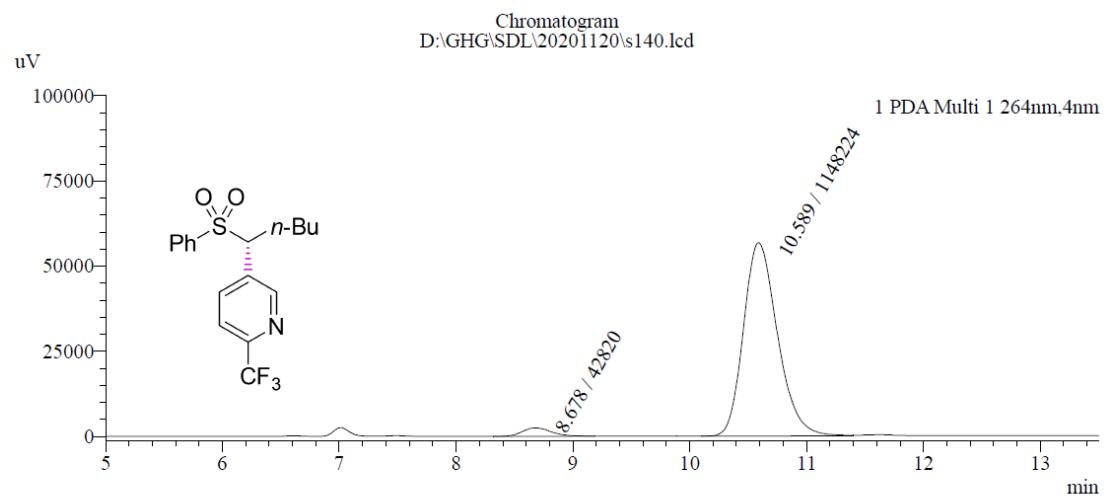
43: racemic



Peak Table

| PDA Ch1 264nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 8.525 | 0.2558 | 396850.27 | 23707.75 | 49.8353 |
| 2 | 10.429 | 0.3007 | 399474.12 | 20313.91 | 50.1647 |

43: enantioenriched, 93% ee

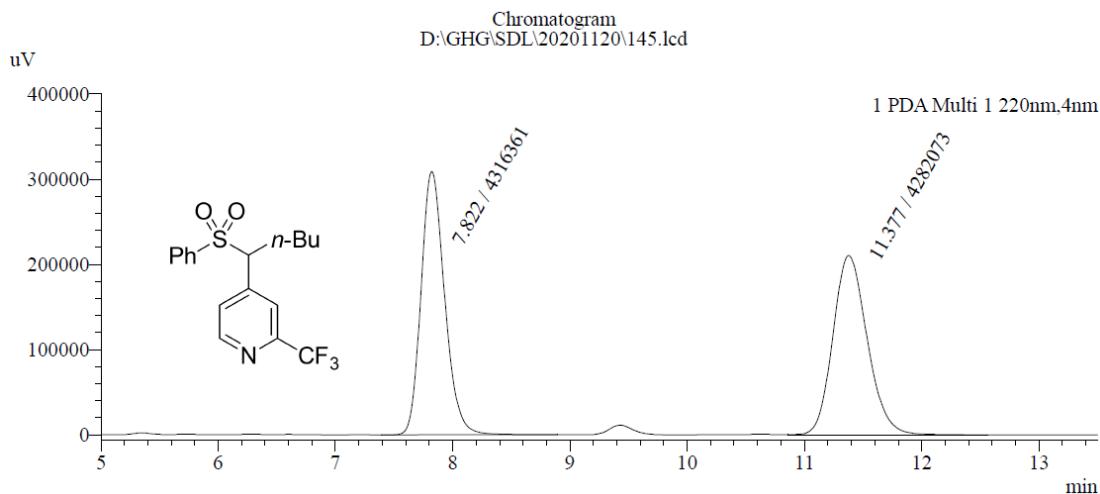


PPA-PPA-004

Peak Table

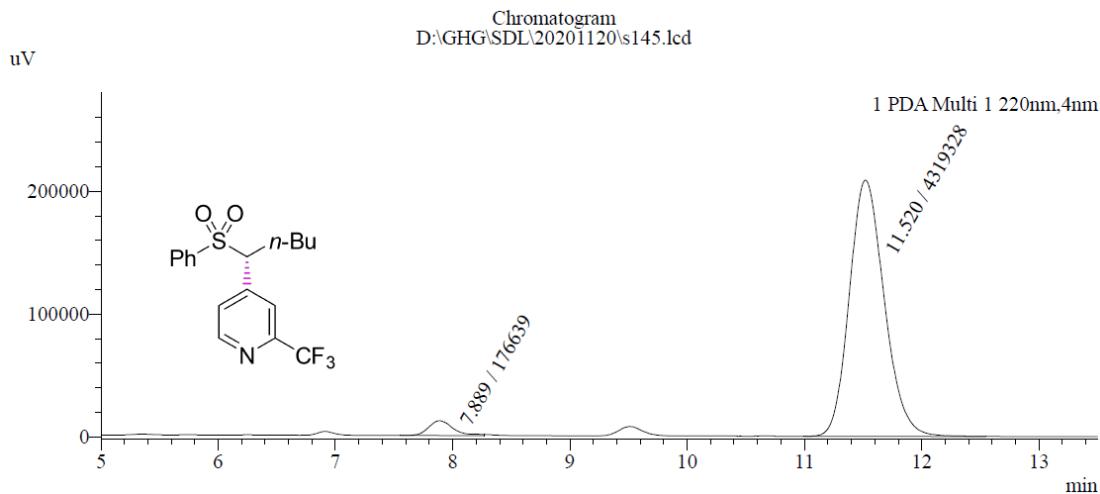
| PDA Ch1 264nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 8.678 | 0.2638 | 42819.99 | 2497.03 | 3.5952 |
| 2 | 10.589 | 0.3089 | 1148223.76 | 56765.33 | 96.4048 |

44: racemic



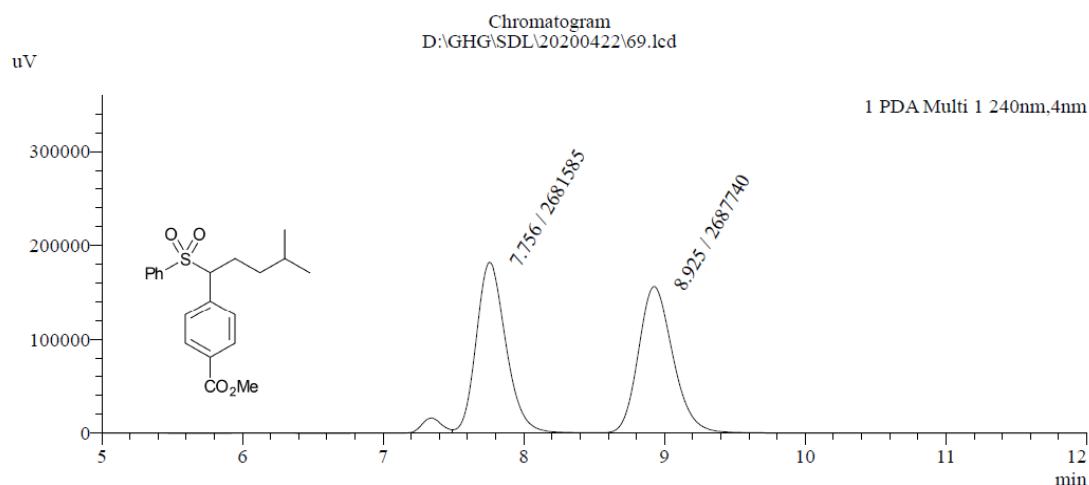
| PDA Ch1 220nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 7.822 | 0.2129 | 4316361.30 | 308962.21 | 50.1994 |
| 2 | 11.377 | 0.3120 | 4282073.40 | 210555.44 | 49.8006 |

44: enantioenriched, 92% ee

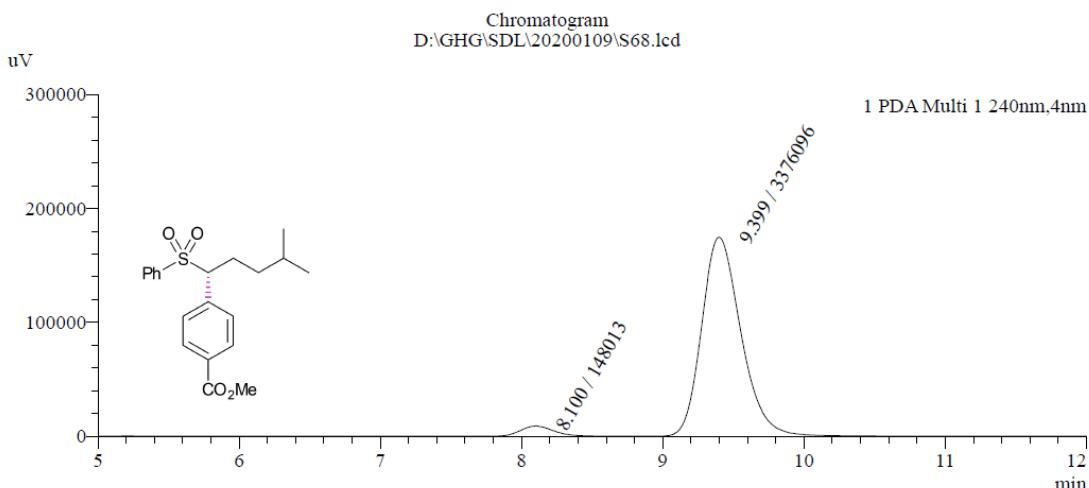


| PDA Ch1 220nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 7.889 | 0.2149 | 176638.55 | 12102.61 | 3.9288 |
| 2 | 11.520 | 0.3181 | 4319327.97 | 208682.77 | 96.0712 |

45: racemic



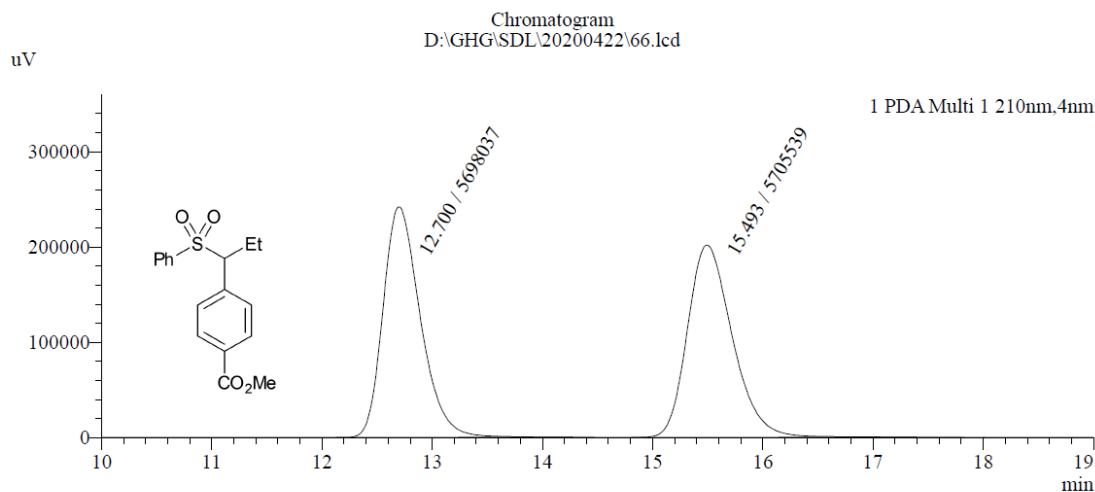
45: enantioenriched, 92% ee



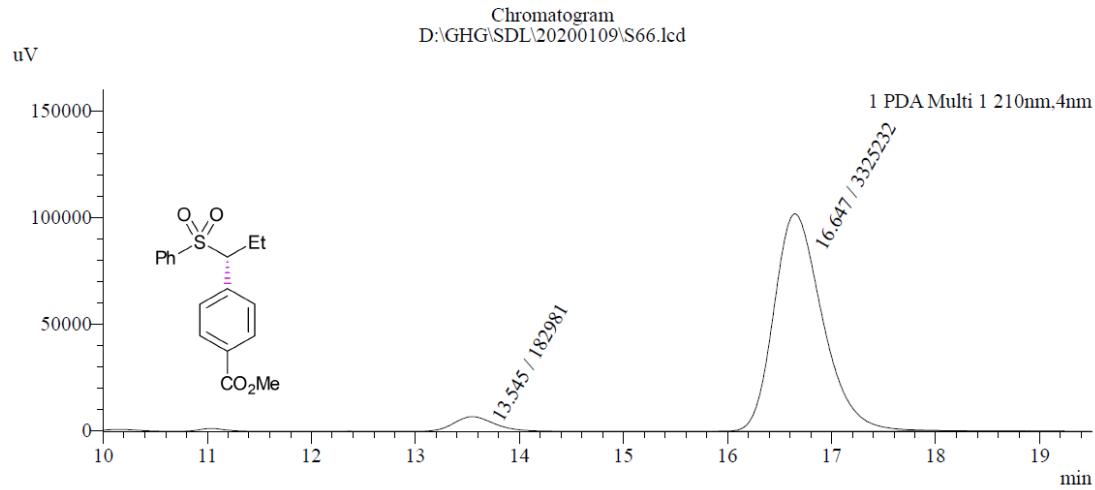
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.100 | 0.2516 | 148013.13 | 8980.86 | 4.2000 |
| 2 | 9.399 | 0.2937 | 3376095.54 | 174869.49 | 95.8000 |

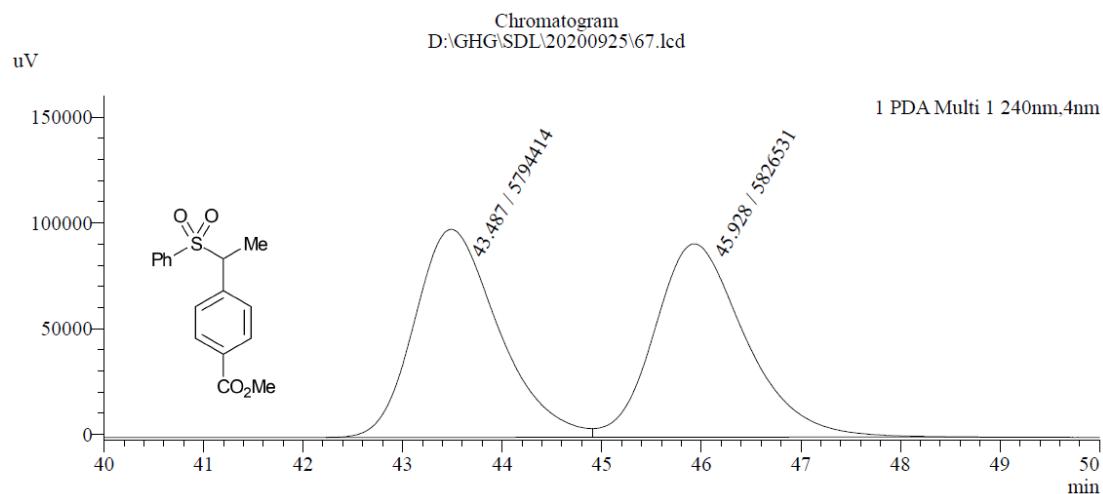
46: racemic



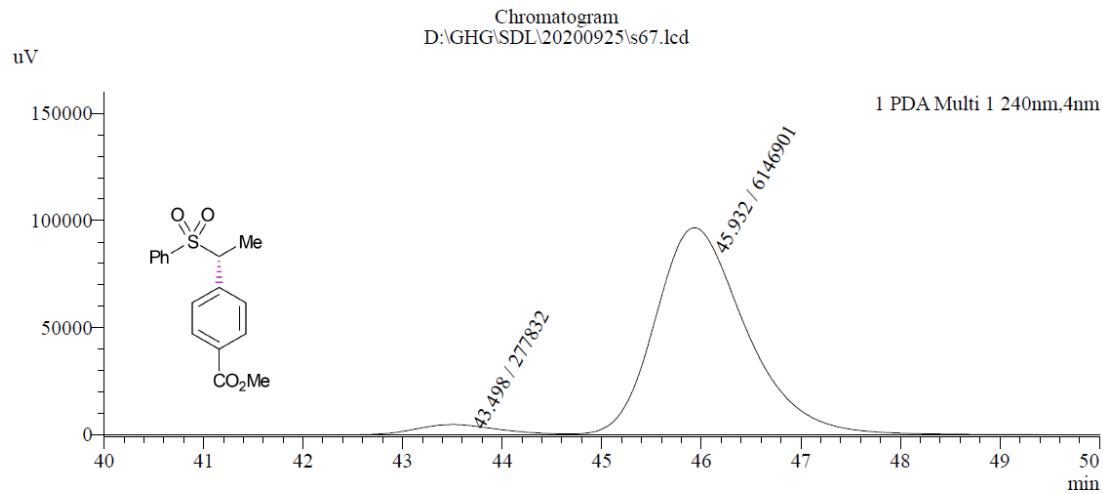
46: enantioenriched, 90% ee



47: racemic



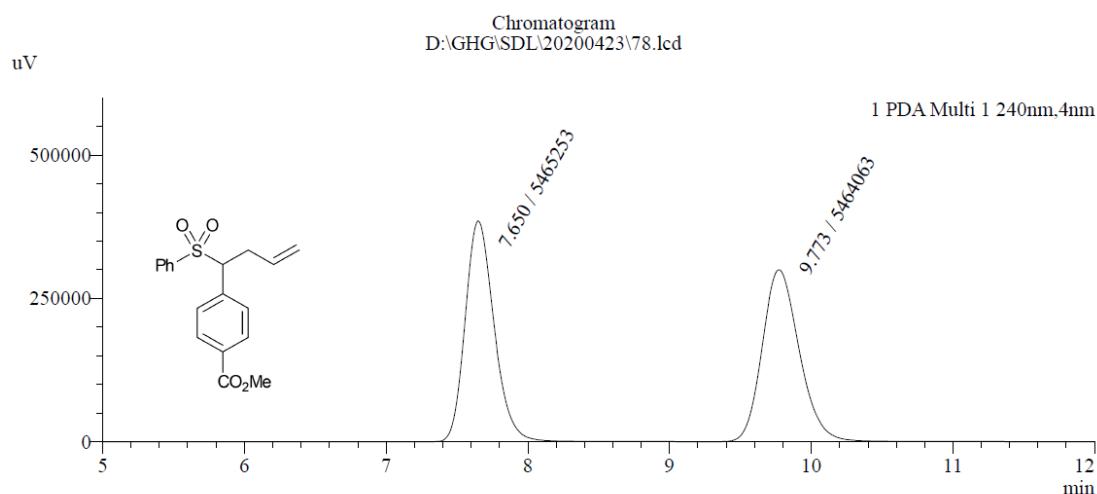
47: enantioenriched, 91% ee



PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 43.498 | 0.8921 | 277832.03 | 4796.24 | 4.3244 |
| 2 | 45.932 | 0.9557 | 6146901.17 | 96675.47 | 95.6756 |

48: racemic

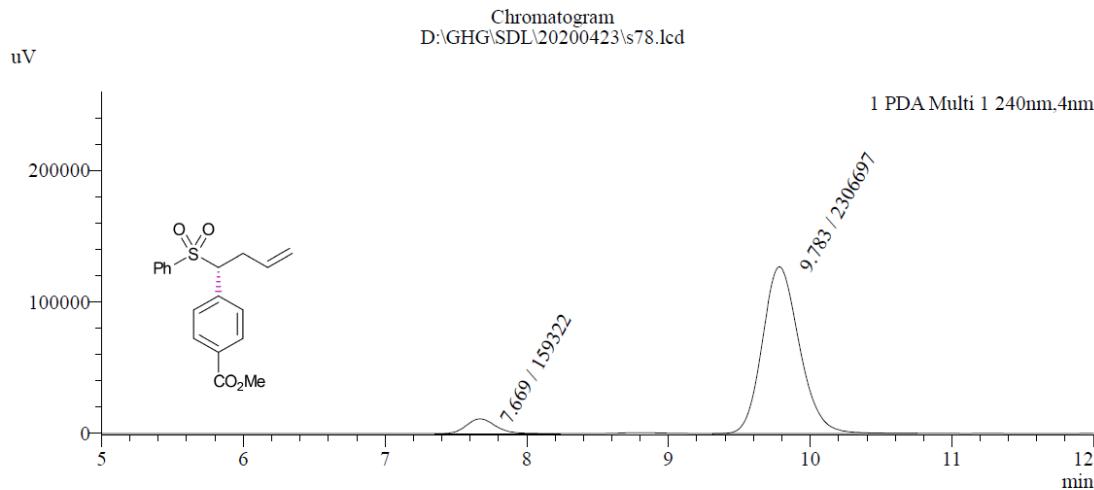


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.650 | 0.2160 | 5465253.34 | 385550.02 | 50.0054 |
| 2 | 9.773 | 0.2788 | 5464062.54 | 300081.37 | 49.9946 |

48: enantioenriched, 87% ee

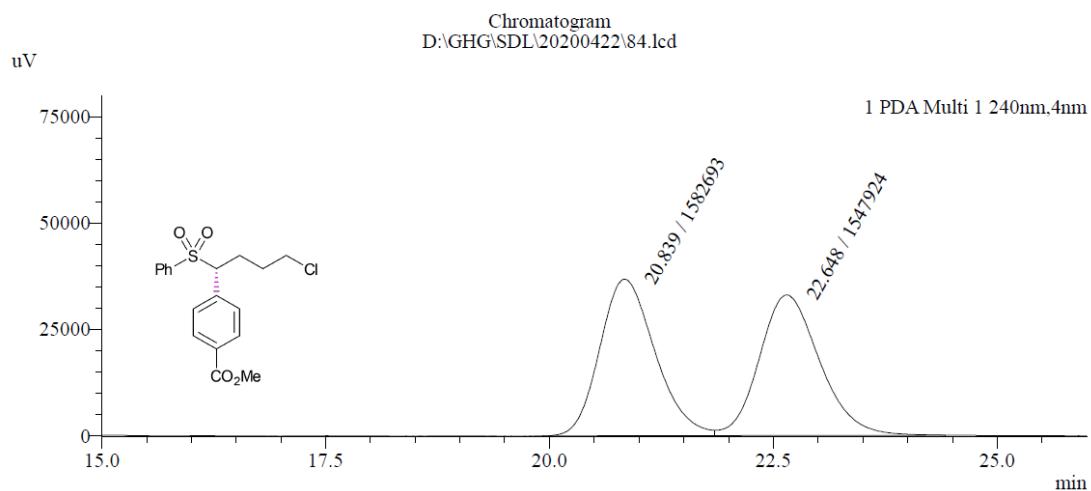


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.669 | 0.2167 | 159321.92 | 11255.74 | 6.4607 |
| 2 | 9.783 | 0.2782 | 2306696.60 | 126998.45 | 93.5393 |

49: racemic

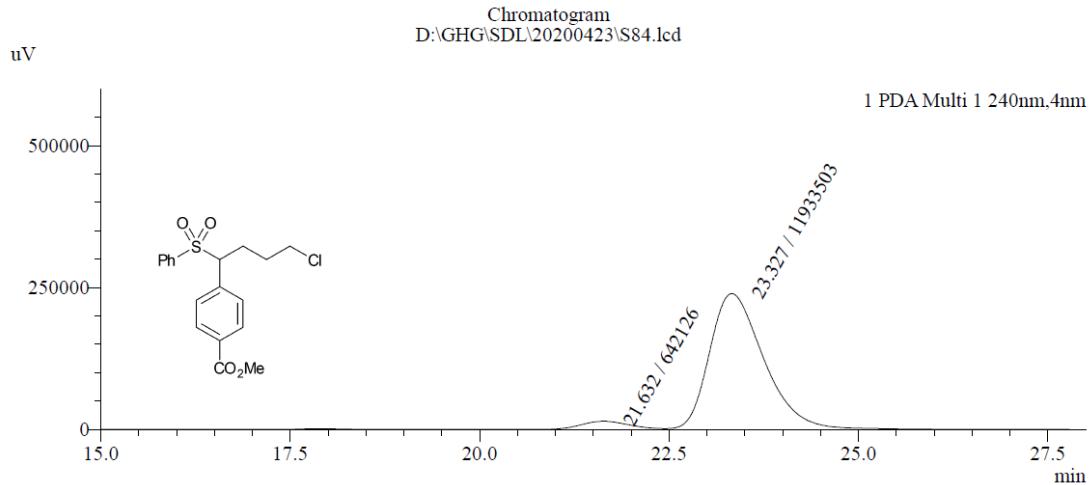


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 20.839 | 0.6624 | 1582693.29 | 36816.78 | 50.5553 |
| 2 | 22.648 | 0.7152 | 1547924.14 | 33034.01 | 49.4447 |

49: enantioenriched, 90% ee

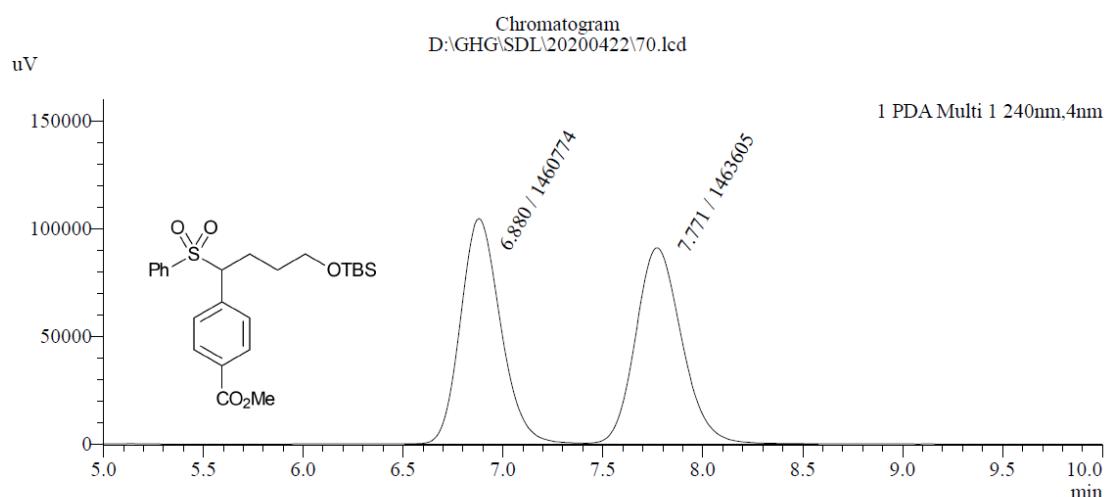


Peak Table

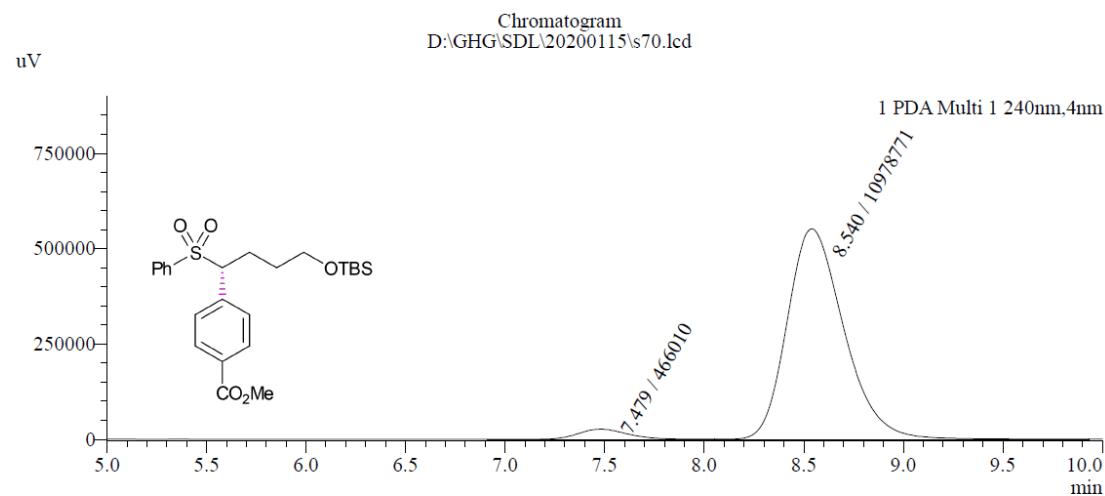
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 21.632 | 0.6973 | 642126.03 | 14391.48 | 5.1061 |
| 2 | 23.327 | 0.7585 | 11933503.43 | 239244.48 | 94.8939 |

50: racemic



50: enantioenriched, 92% ee

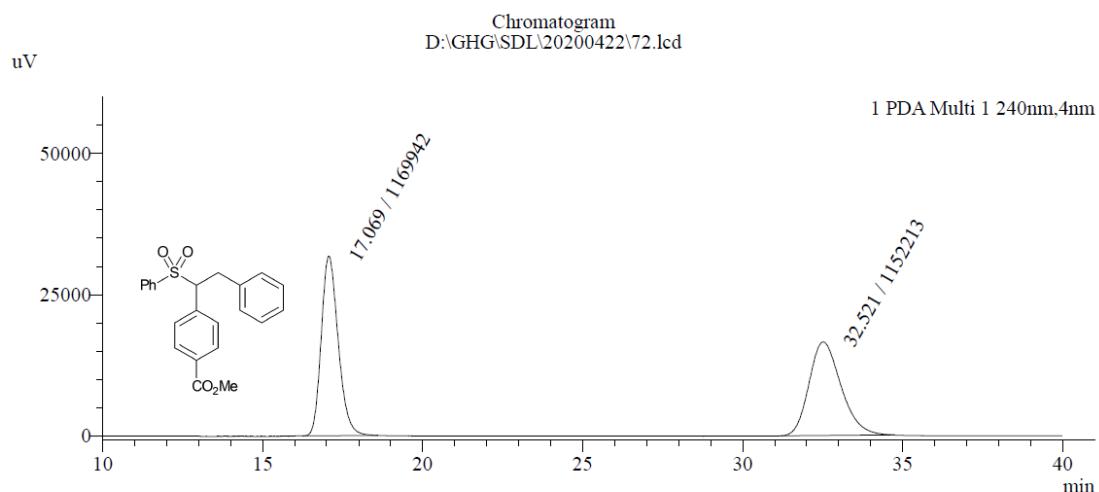


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.479 | 0.2644 | 466010.45 | 26764.75 | 4.0718 |
| 2 | 8.540 | 0.3027 | 10978770.96 | 552092.66 | 95.9282 |

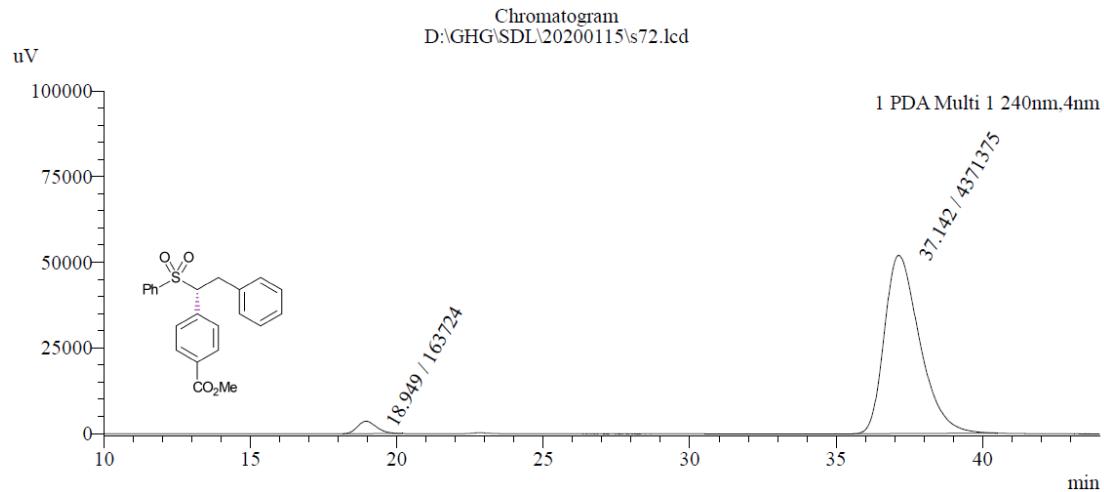
51: racemic



Peak Table

| PDA Ch1 240nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 17.069 | 0.5625 | 1169942.22 | 31784.07 | 50.3817 |
| 2 | 32.521 | 1.0667 | 1152213.42 | 16557.54 | 49.6183 |

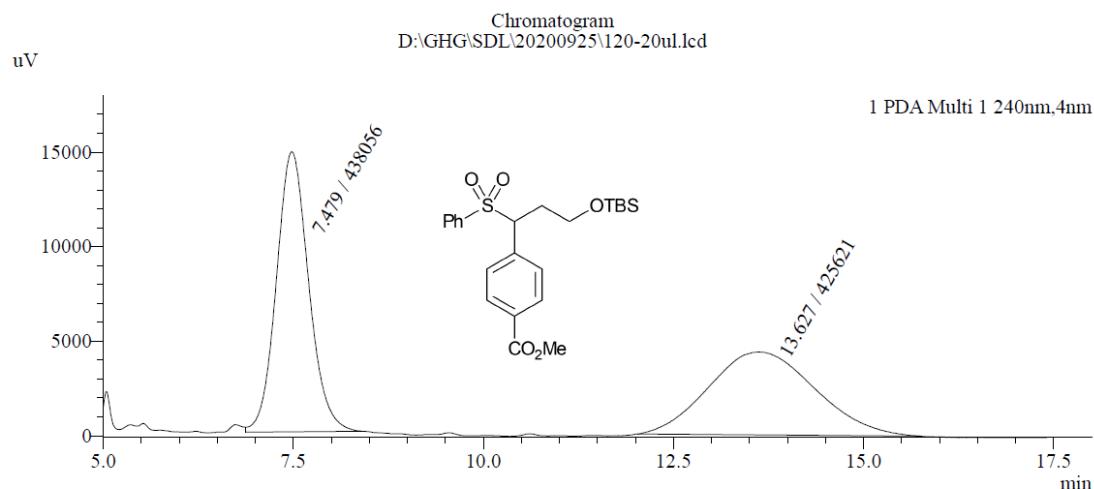
51: enantioenriched, 93% ee



Peak Table

| PDA Ch1 240nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 18.949 | 0.6952 | 163723.81 | 3635.39 | 3.6101 |
| 2 | 37.142 | 1.2769 | 4371375.02 | 52048.54 | 96.3899 |

52: racemic

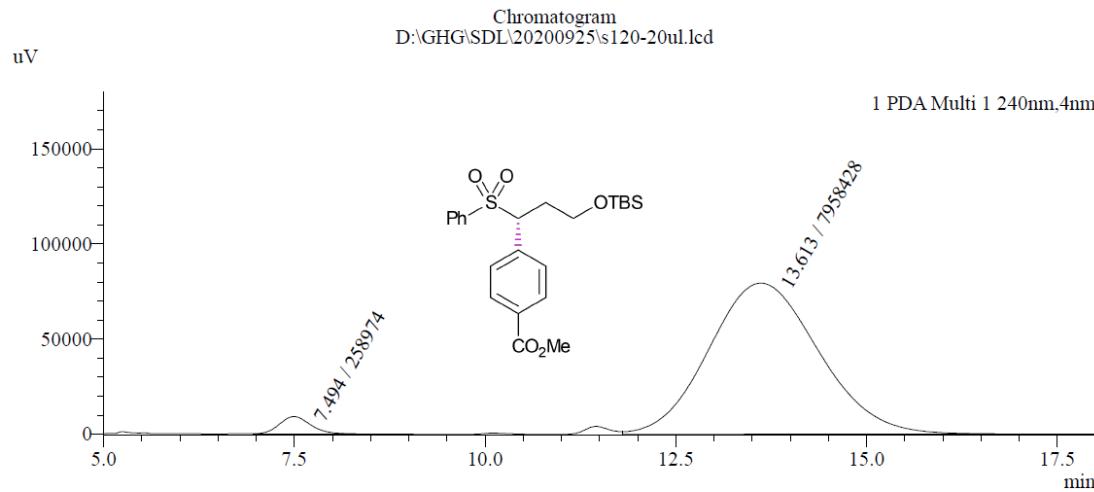


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.479 | 0.4490 | 438056.39 | 14811.28 | 50.7199 |
| 2 | 13.627 | 1.5411 | 425621.33 | 4380.76 | 49.2801 |

52: enantioenriched, 94% ee

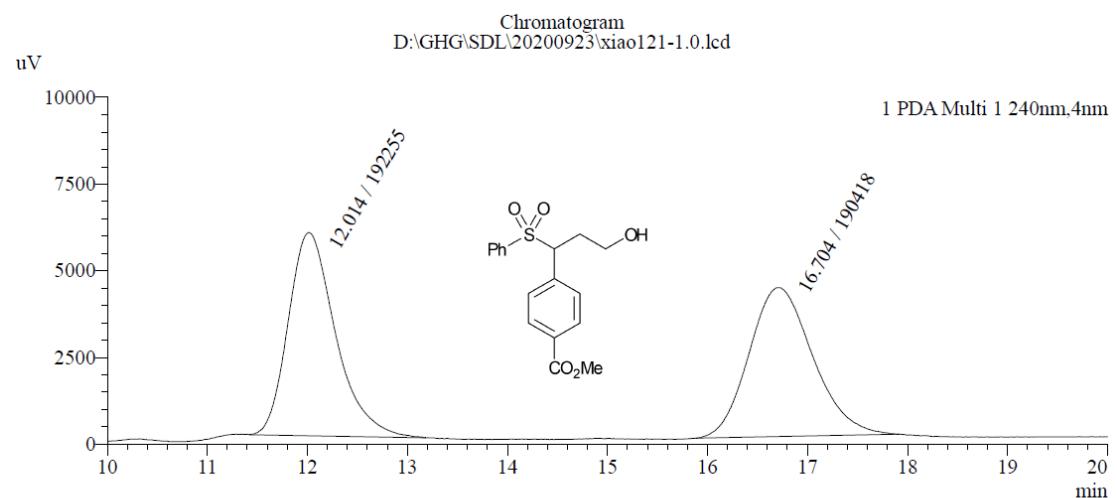


Peak Table

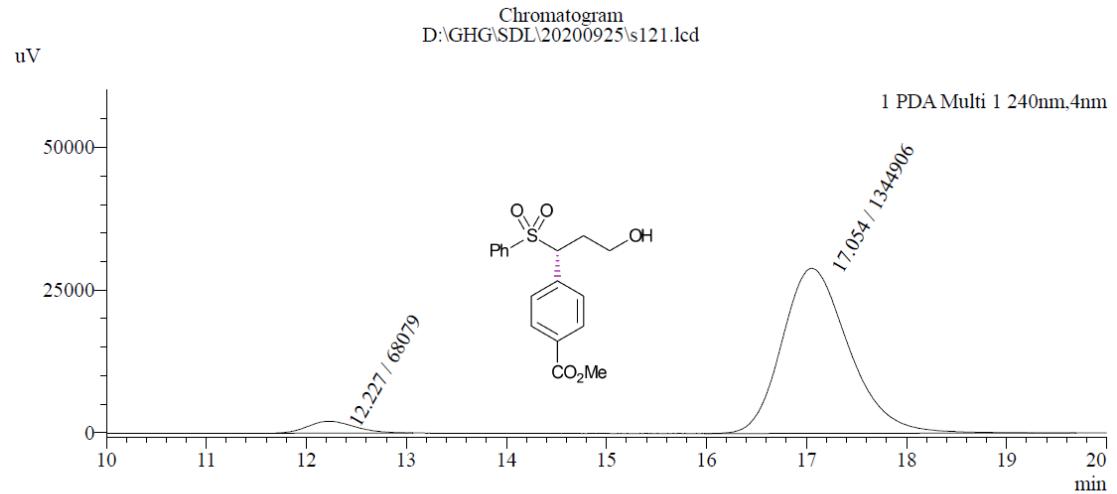
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.494 | 0.4344 | 258974.25 | 9130.56 | 3.1515 |
| 2 | 13.613 | 1.5636 | 7958427.79 | 79345.43 | 96.8485 |

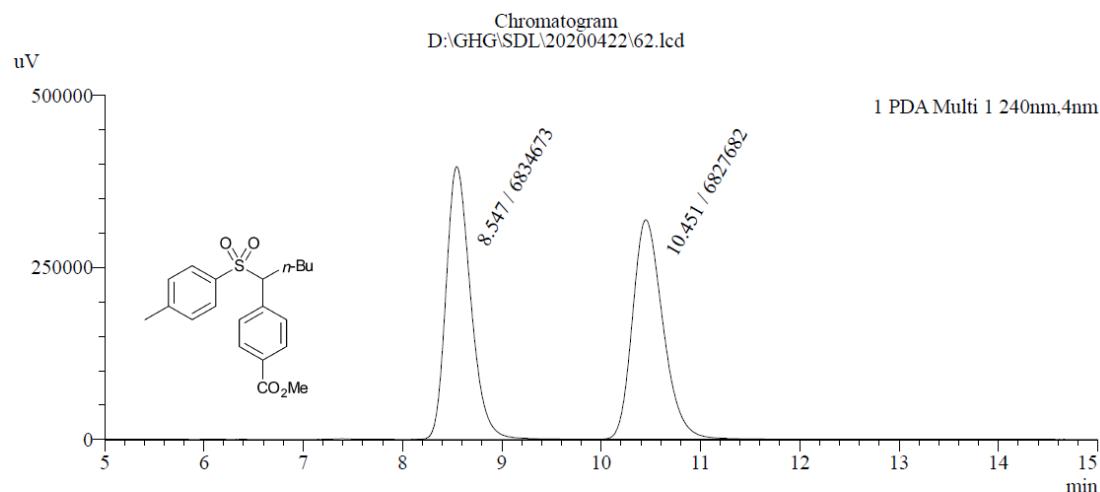
53: racemic



53: enantioenriched, 90% ee



54: racemic

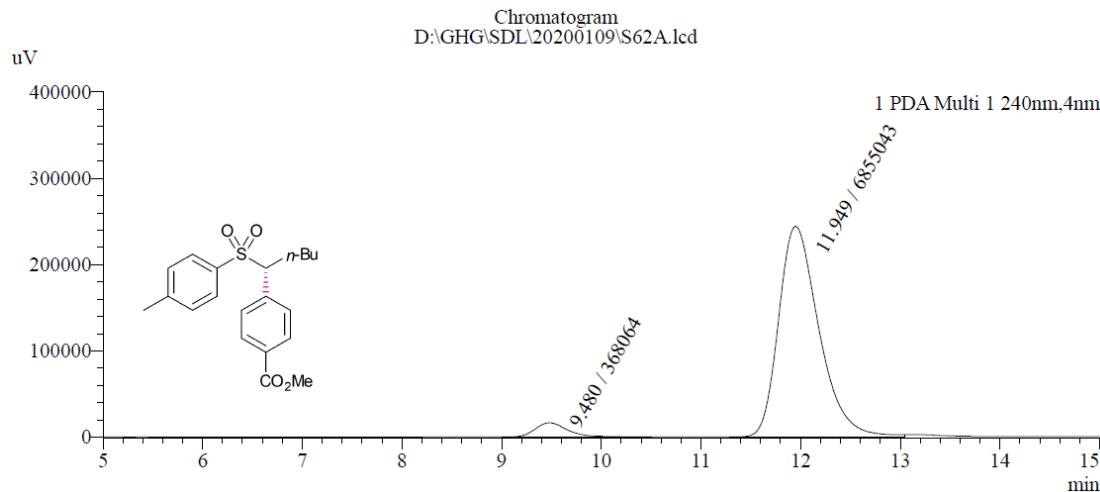


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.547 | 0.2614 | 6834672.93 | 396957.52 | 50.0256 |
| 2 | 10.451 | 0.3257 | 6827681.72 | 319481.89 | 49.9744 |

54: enantioenriched, 90% ee

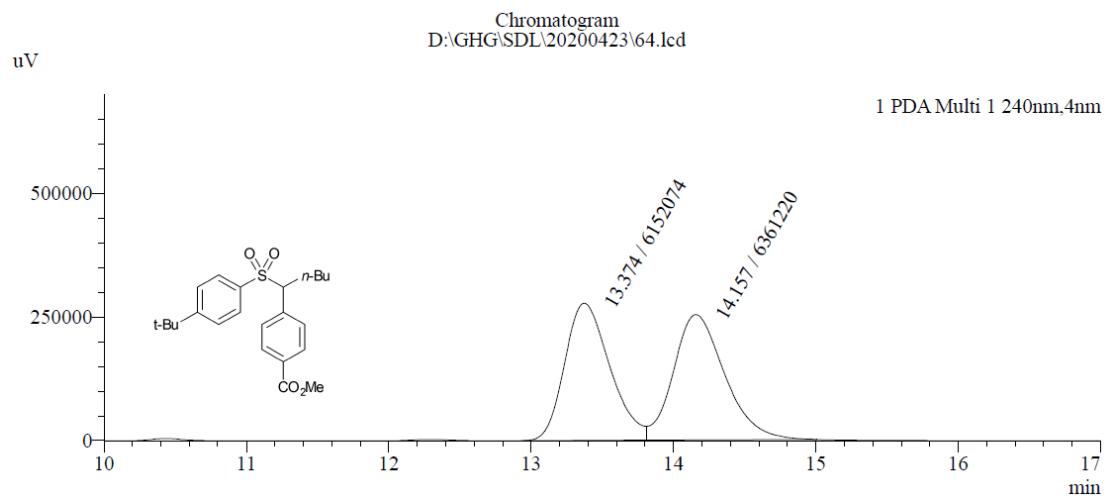


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 9.480 | 0.3367 | 368063.58 | 16355.52 | 5.0956 |
| 2 | 11.949 | 0.4247 | 6855043.31 | 244095.20 | 94.9044 |

55: racemic

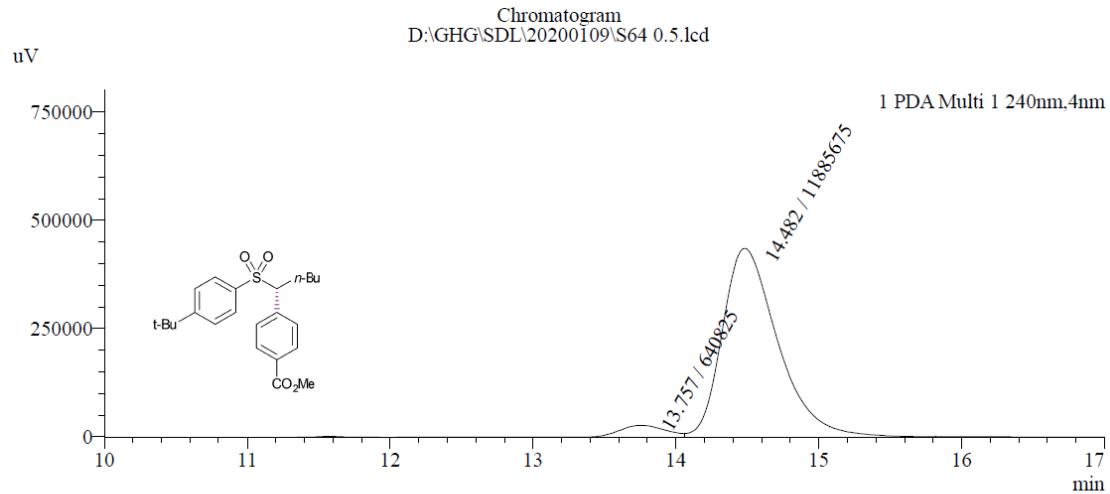


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 13.374 | 0.3421 | 6152073.62 | 278259.31 | 49.1643 |
| 2 | 14.157 | 0.3797 | 6361219.66 | 254204.09 | 50.8357 |

55: enantioenriched, 90% ee

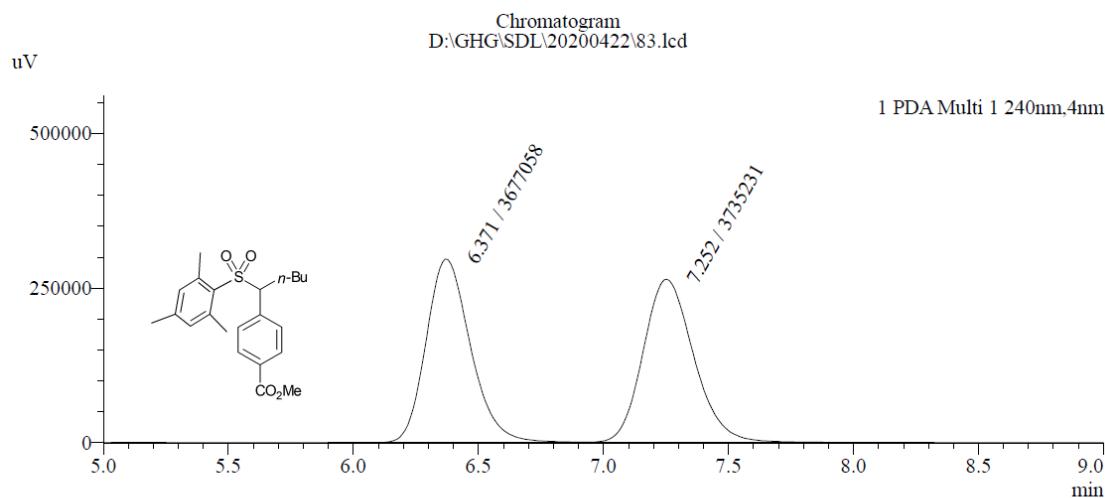


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 13.757 | 0.3709 | 640824.77 | 28100.94 | 5.1158 |
| 2 | 14.482 | 0.4060 | 11885675.30 | 436760.00 | 94.8842 |

56: racemic

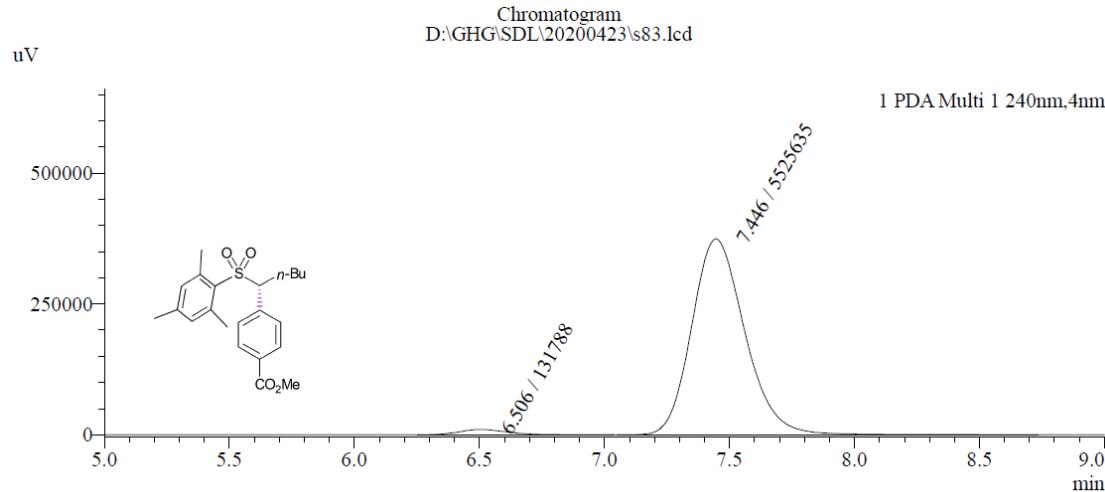


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 6.371 | 0.1884 | 3677058.10 | 296757.65 | 49.6076 |
| 2 | 7.252 | 0.2158 | 3735230.79 | 264232.87 | 50.3924 |

56: enantioenriched, 95% ee

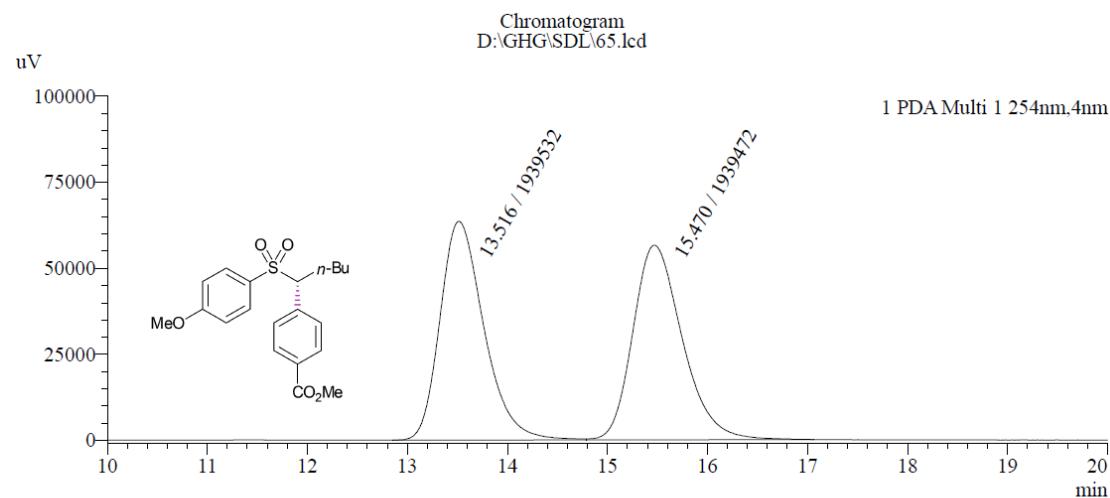


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 6.506 | 0.1989 | 131788.34 | 10067.90 | 2.3295 |
| 2 | 7.446 | 0.2250 | 5525635.22 | 374672.53 | 97.6705 |

57: racemic

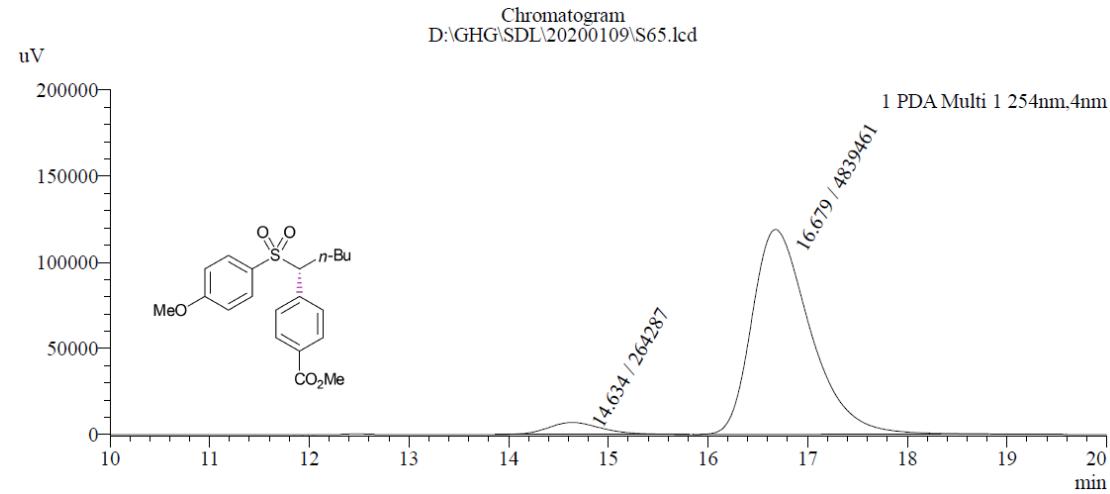


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 13.516 | 0.4619 | 1939531.86 | 63619.45 | 50.0008 |
| 2 | 15.470 | 0.5216 | 1939472.34 | 56551.24 | 49.9992 |

57: enantioenriched, 90% ee

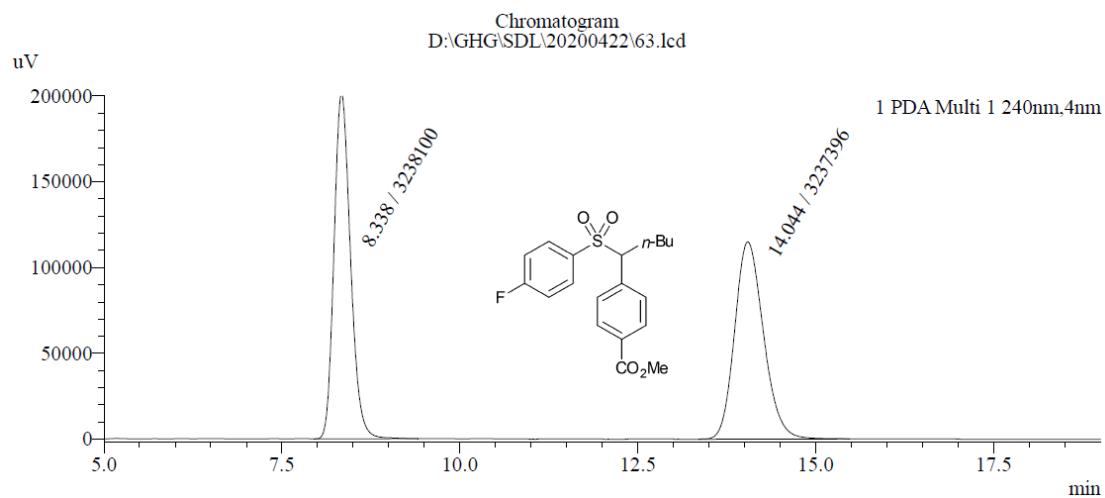


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 14.634 | 0.5713 | 264286.82 | 7012.01 | 5.1783 |
| 2 | 16.679 | 0.6141 | 4839460.79 | 118997.58 | 94.8217 |

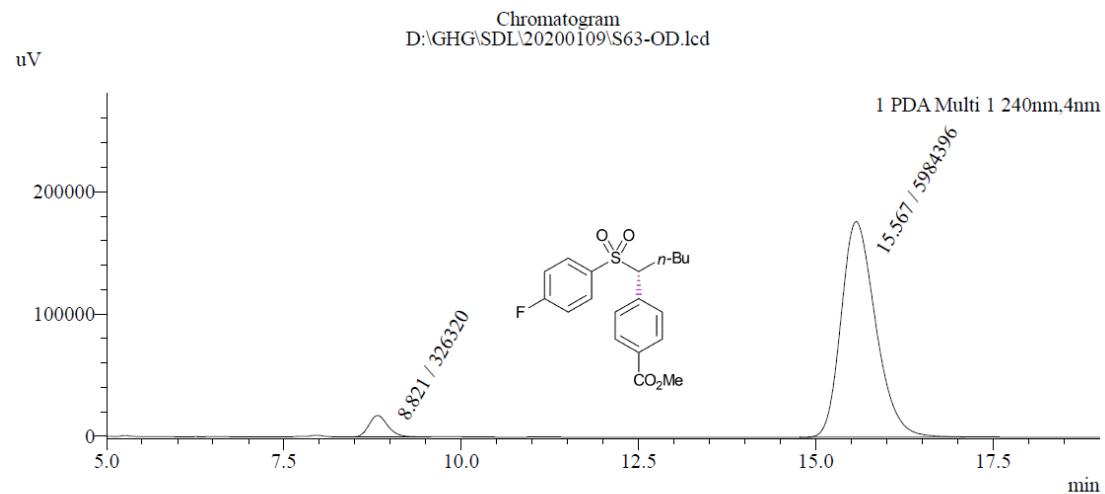
58: racemic



PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.338 | 0.2448 | 3238100.39 | 201596.87 | 50.0054 |
| 2 | 14.044 | 0.4327 | 3237395.73 | 114935.04 | 49.9946 |

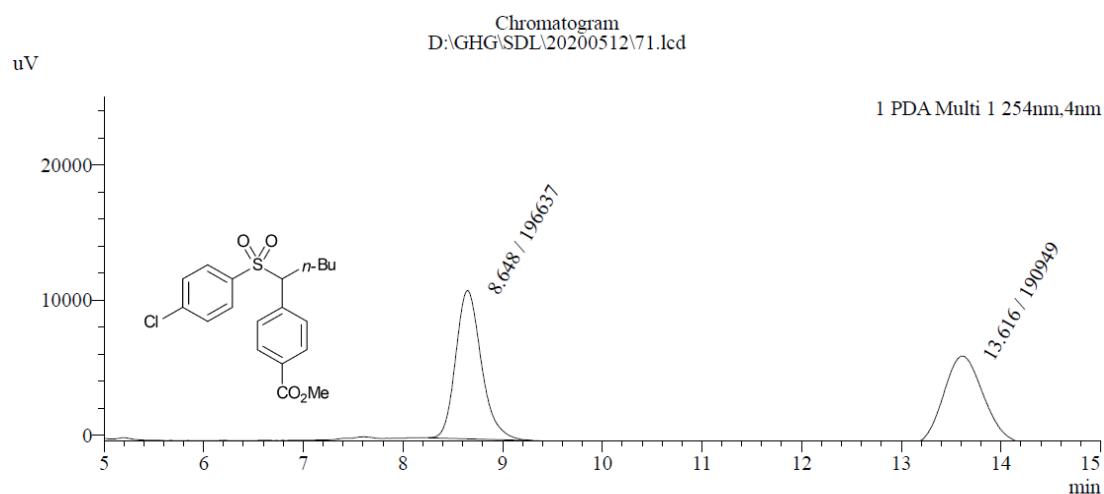
58: enantioenriched, 90% ee



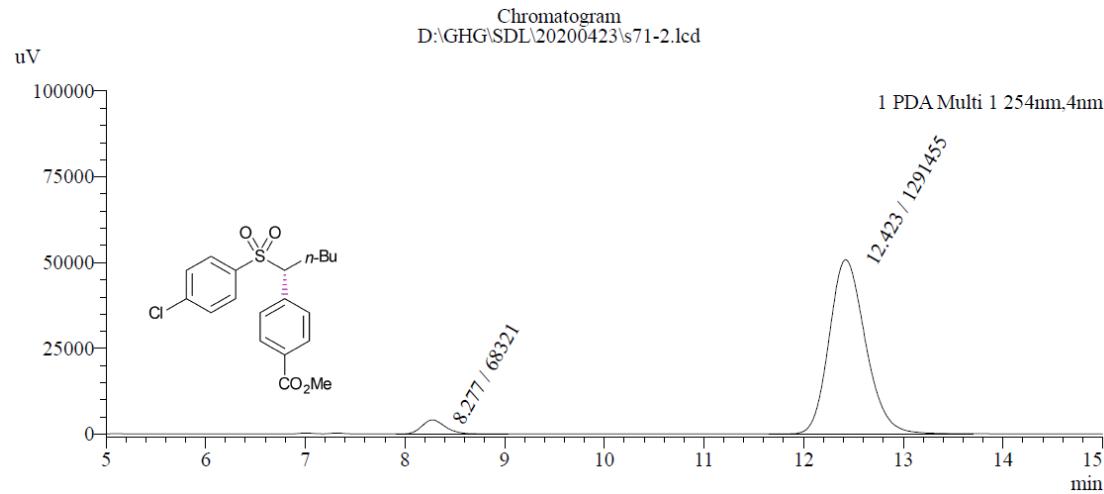
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.821 | 0.2831 | 326320.42 | 17593.36 | 5.1709 |
| 2 | 15.567 | 0.5196 | 5984396.42 | 176123.24 | 94.8291 |

59: racemic



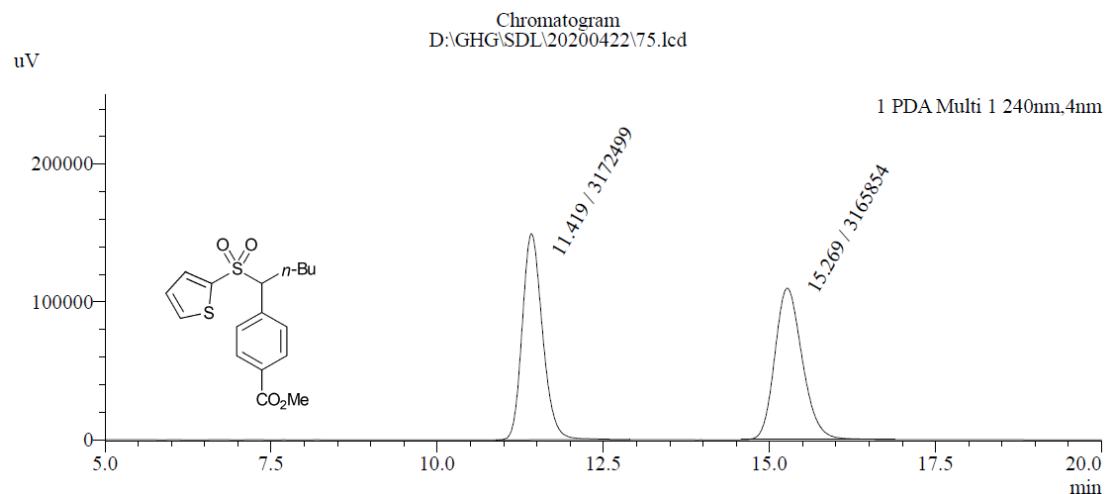
59: enantioenriched, 90% ee



PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 8.277 | 0.2505 | 68320.74 | 4123.51 | 5.0244 |
| 2 | 12.423 | 0.3880 | 1291455.48 | 50831.61 | 94.9756 |

60: racemic

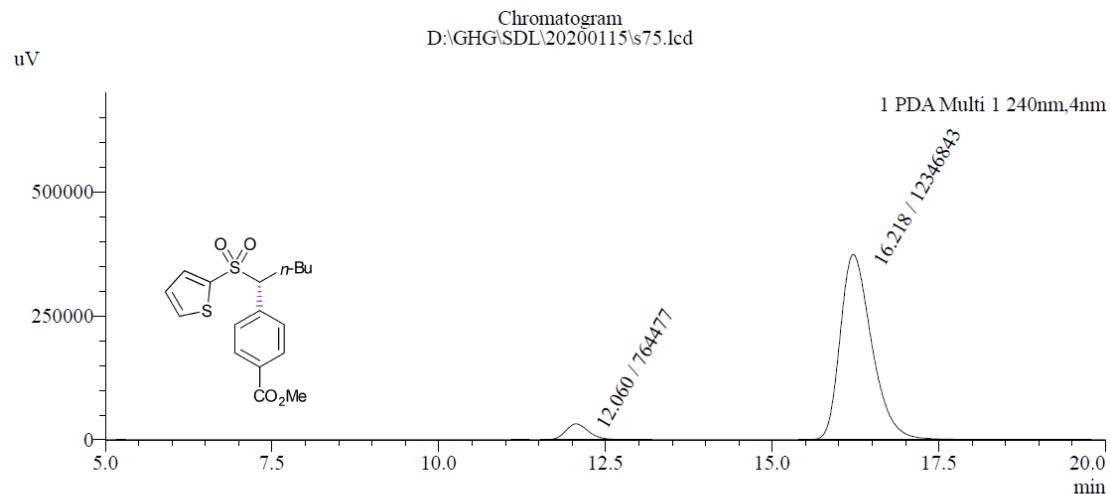


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 11.419 | 0.3233 | 3172498.90 | 149352.61 | 50.0524 |
| 2 | 15.269 | 0.4412 | 3165854.02 | 109792.26 | 49.9476 |

60: enantioenriched, 88% ee

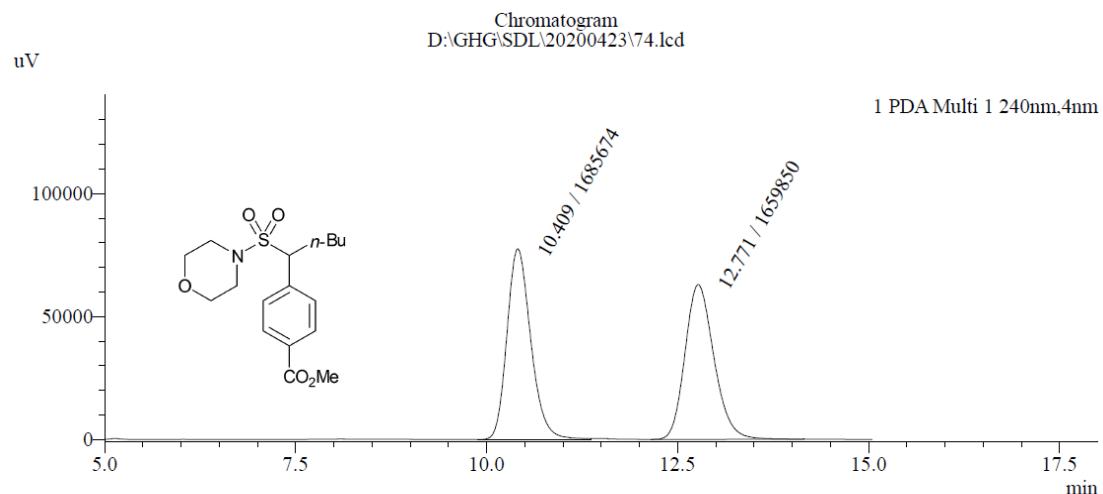


Peak Table

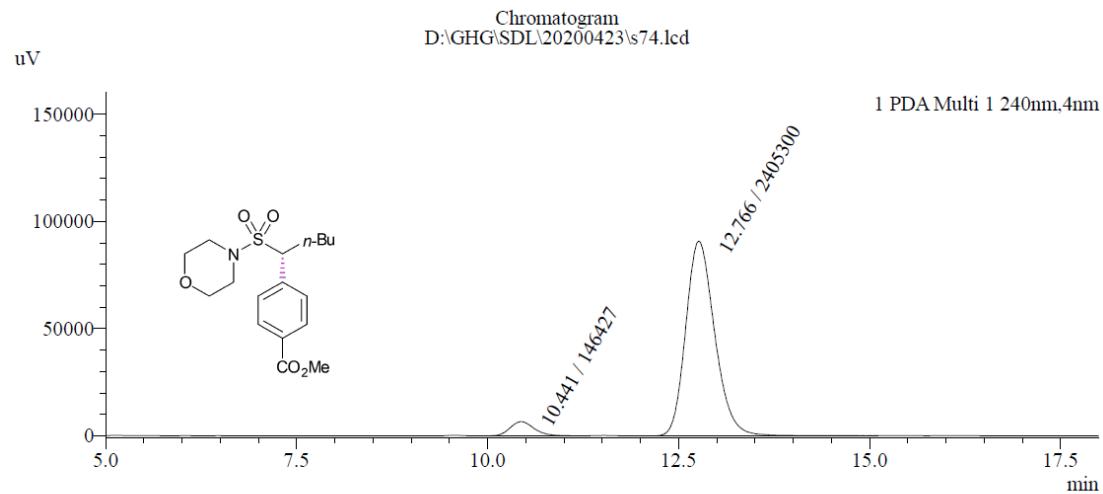
PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 12.060 | 0.3642 | 764476.82 | 31902.21 | 5.8307 |
| 2 | 16.218 | 0.5010 | 12346842.61 | 374157.70 | 94.1693 |

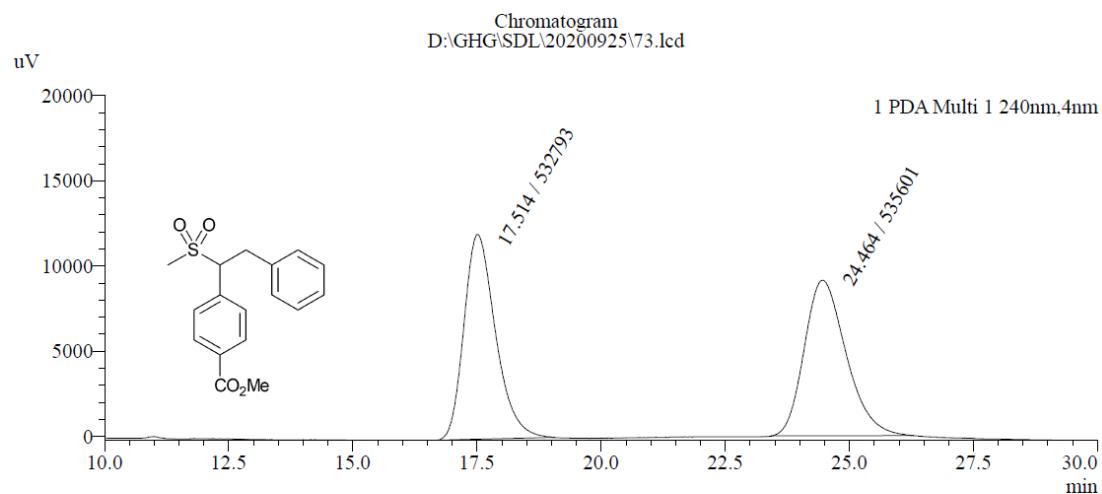
61: racemic



61: enantioenriched, 89% ee



62: racemic

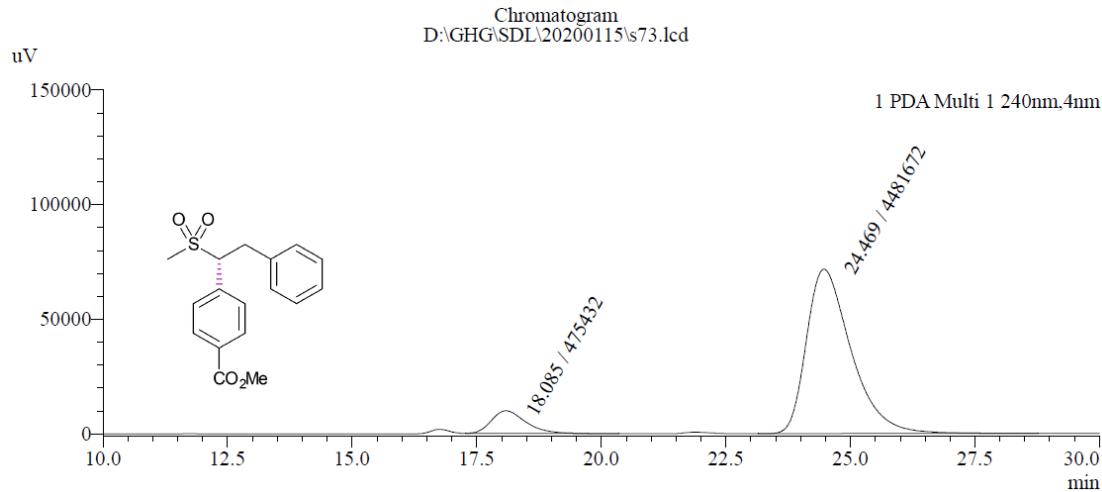


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 17.514 | 0.6721 | 532793.45 | 12033.77 | 49.8686 |
| 2 | 24.464 | 0.9004 | 535601.09 | 9128.58 | 50.1314 |

62: enantioenriched, 81% ee

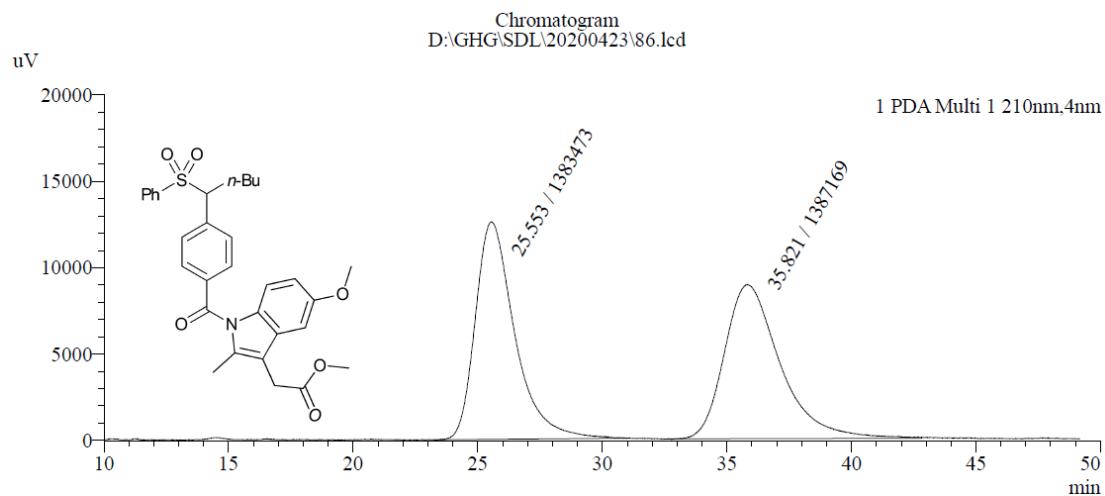


Peak Table

PDA Ch1 240nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 18.085 | 0.7271 | 475432.05 | 9883.46 | 9.5909 |
| 2 | 24.469 | 0.9370 | 4481671.53 | 71715.28 | 90.4091 |

63: racemic

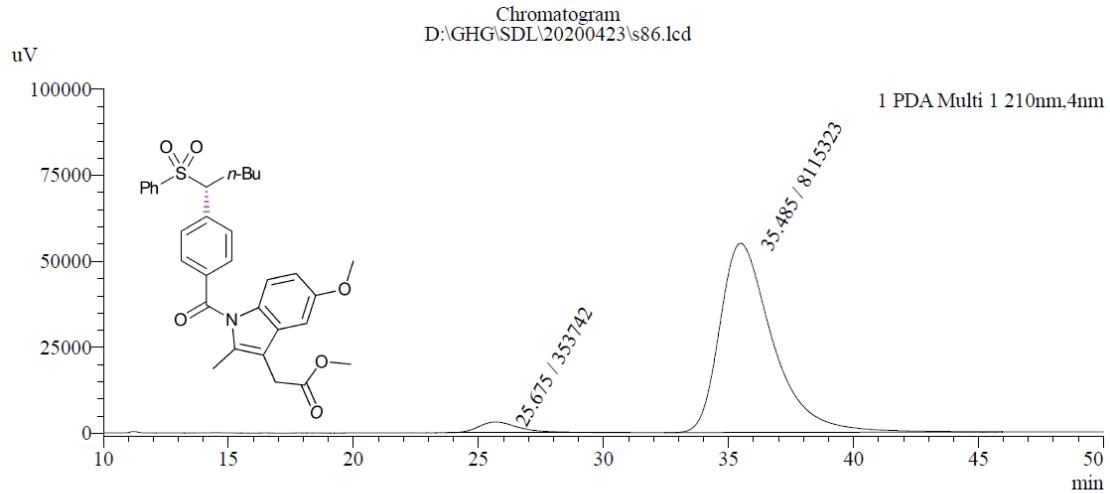


Peak Table

PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 25.553 | 1.6127 | 1383472.89 | 12587.36 | 49.9333 |
| 2 | 35.821 | 2.2835 | 1387168.78 | 8931.38 | 50.0667 |

63: enantioenriched, 92% ee

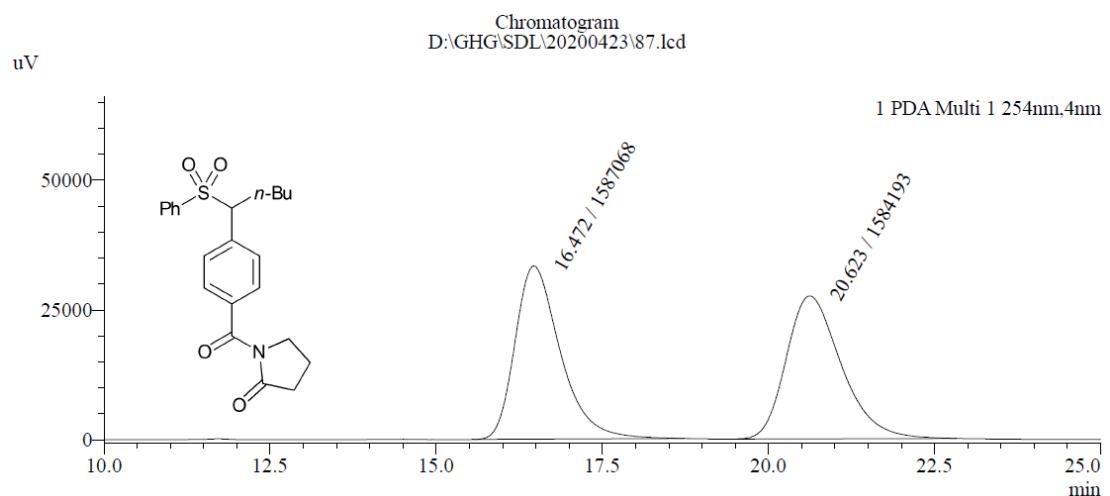


Peak Table

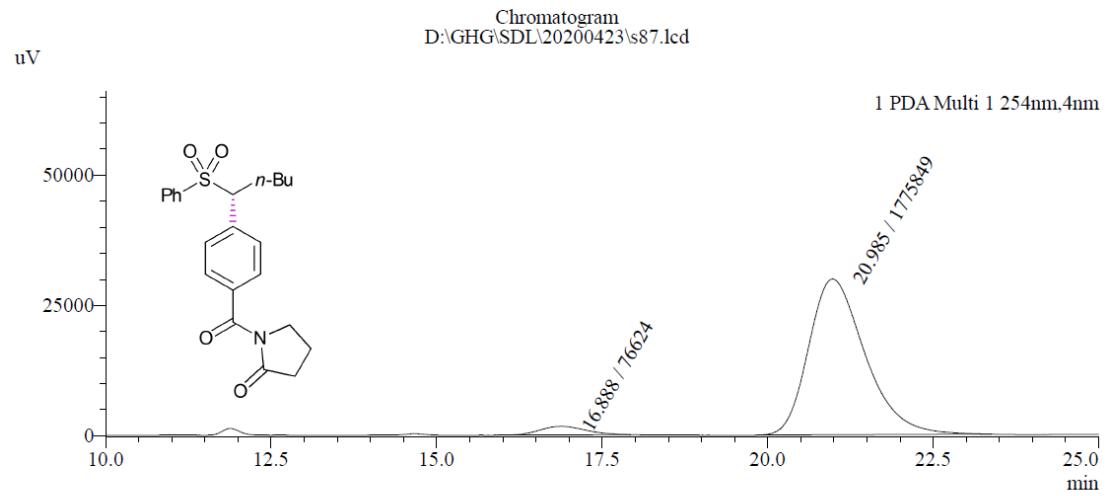
PDA Ch1 210nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 25.675 | 1.6540 | 353742.48 | 3136.57 | 4.1769 |
| 2 | 35.485 | 2.1587 | 8115322.87 | 55023.23 | 95.8231 |

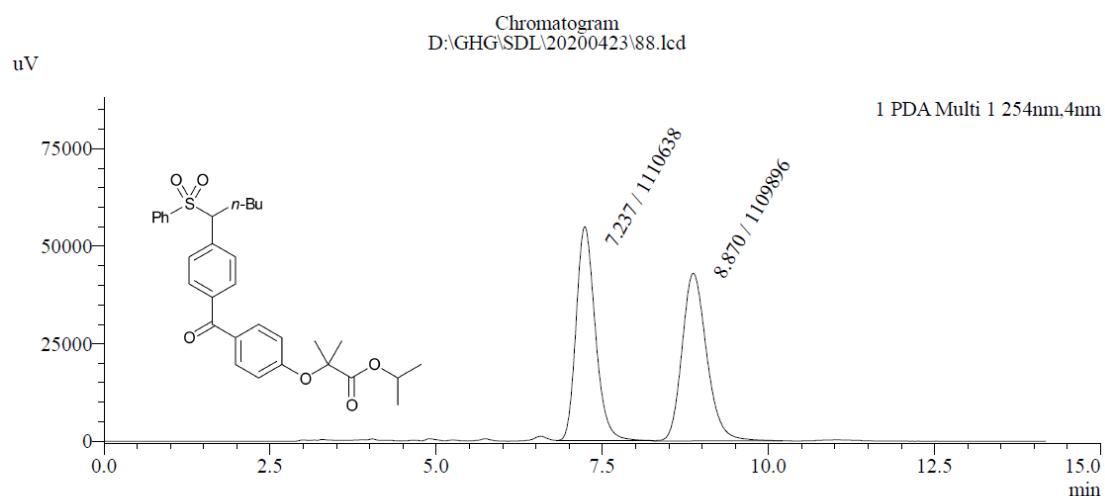
64: racemic



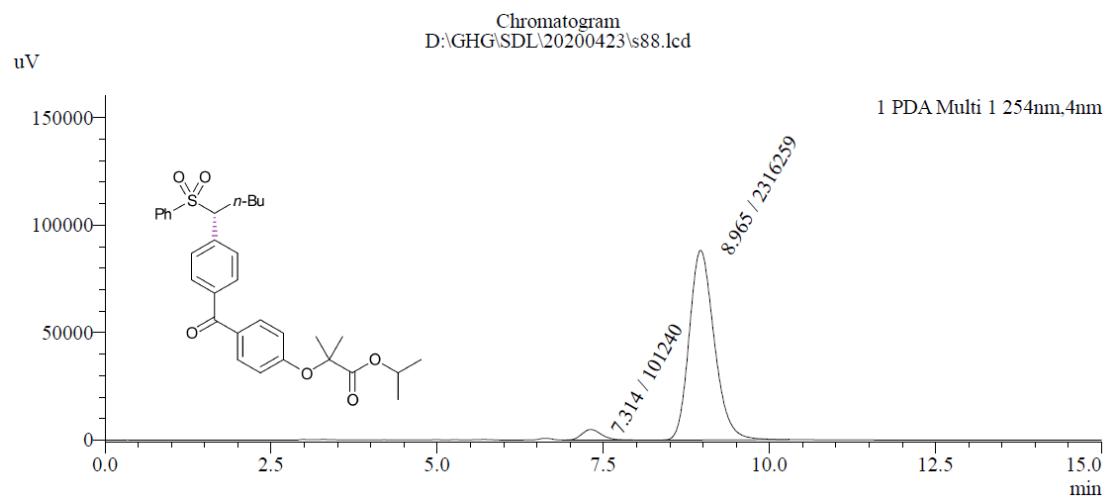
64: enantioenriched, 92% ee



65: racemic



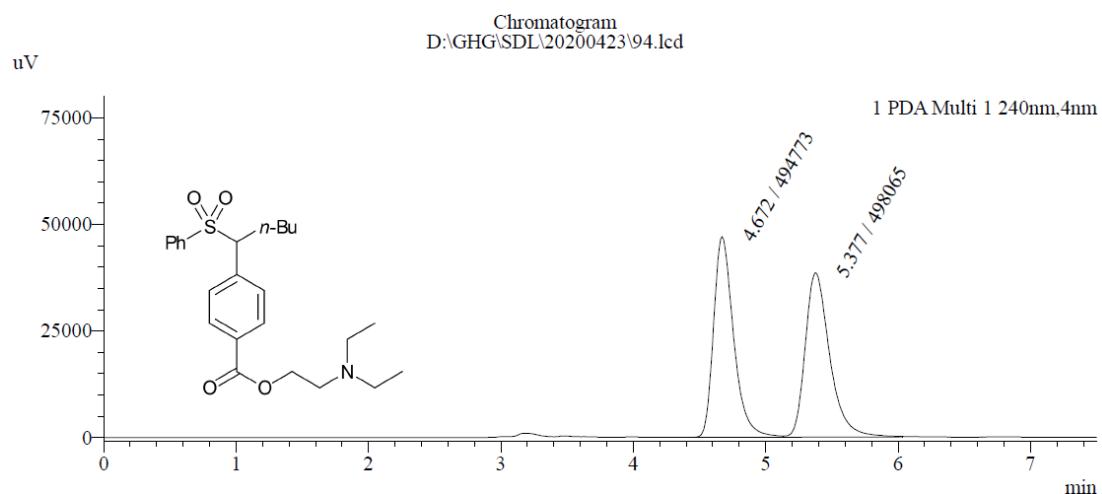
65: enantioenriched, 92% ee



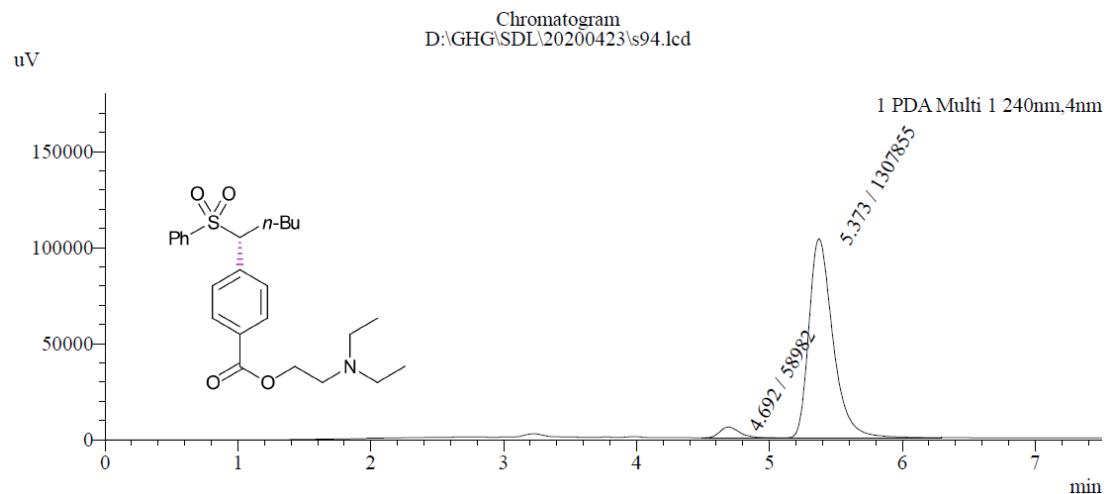
PDA Ch1 254nm

| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
|-------|-----------------|-------------|-------------|-------------|---------|
| 1 | 7.314 | 0.3160 | 101240.20 | 4927.83 | 4.1878 |
| 2 | 8.965 | 0.4002 | 2316258.58 | 88189.84 | 95.8122 |

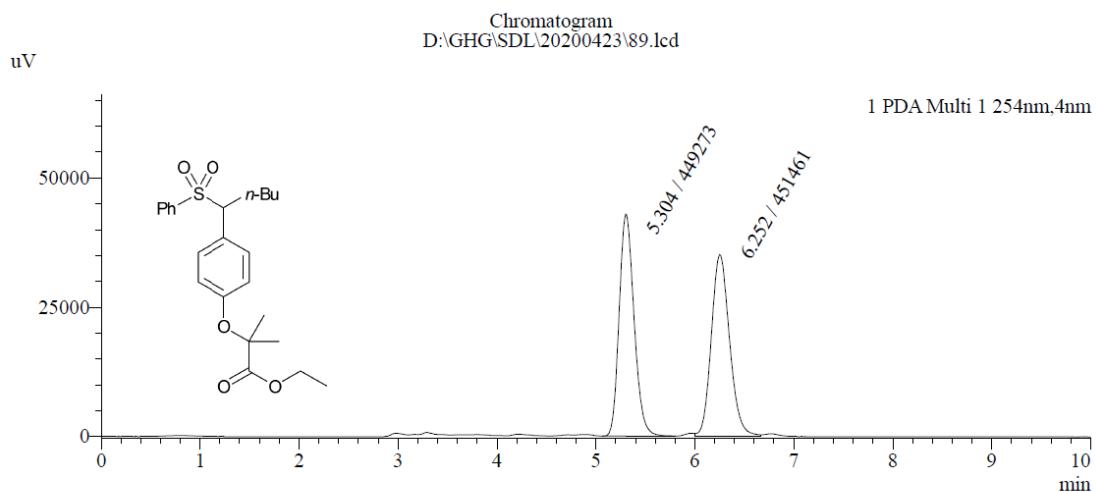
66: racemic



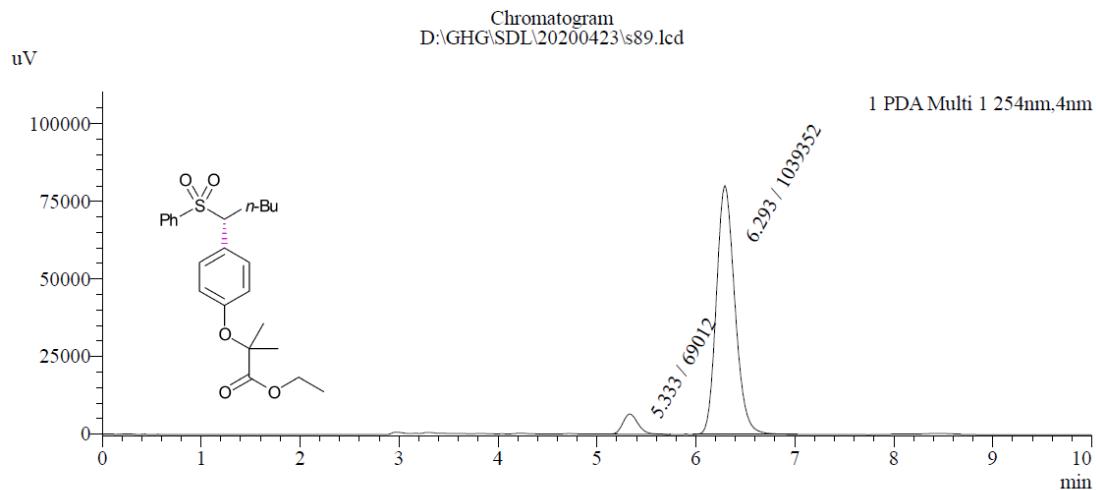
66: enantioenriched, 91% ee



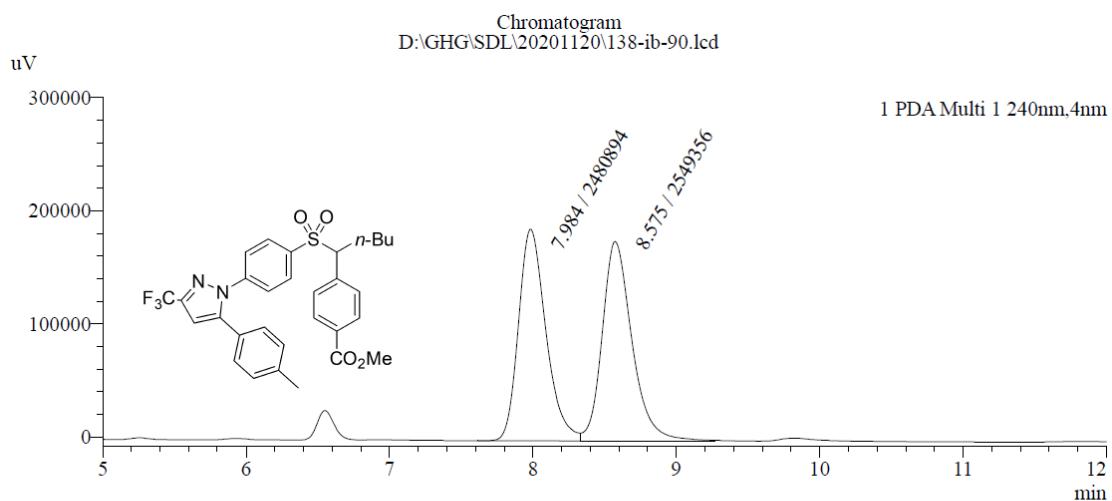
67: racemic



67: enantioenriched, 88% ee

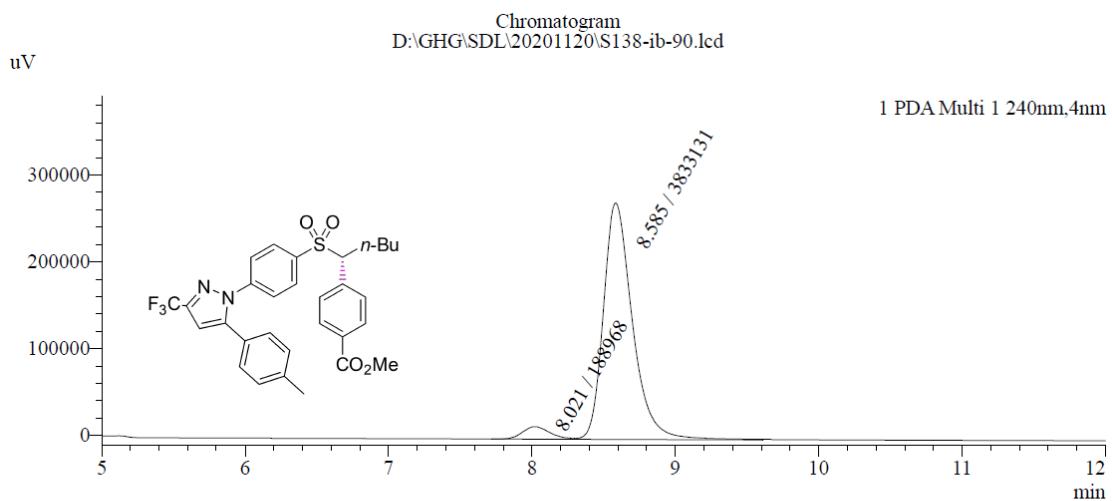


68: racemic



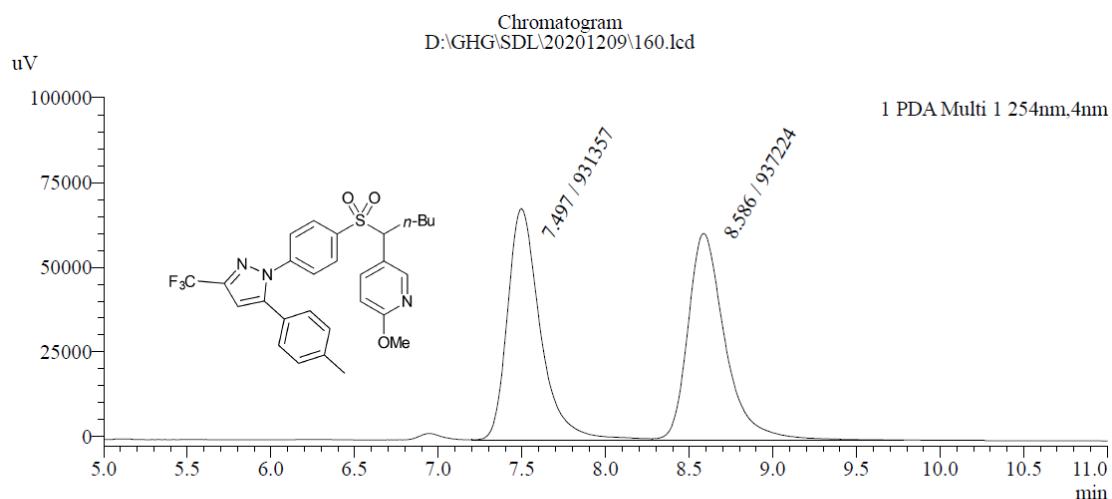
| PDA Ch1 240nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 7.984 | 0.2002 | 2480893.70 | 186877.17 | 49.3195 |
| 2 | 8.575 | 0.2139 | 2549356.03 | 176465.23 | 50.6805 |

68: enantioenriched, 91% ee

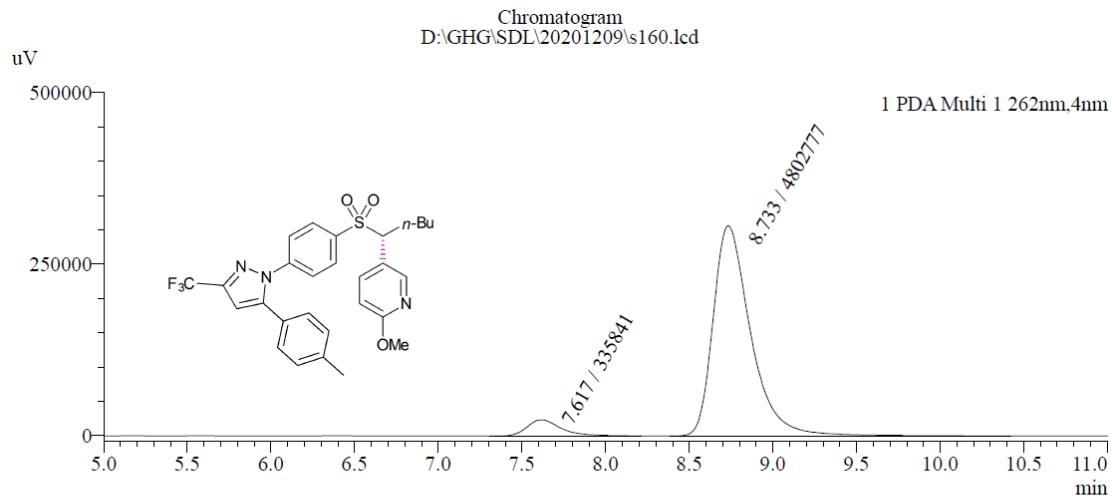


| PDA Ch1 240nm | | | | | |
|---------------|-----------------|-------------|-------------|-------------|---------|
| Peak# | Ret. Time [min] | Width [min] | Area [uV*s] | Height [uV] | Area % |
| 1 | 8.021 | 0.2014 | 188968.13 | 14335.84 | 4.6982 |
| 2 | 8.585 | 0.2084 | 3833130.82 | 272472.59 | 95.3018 |

69: racemic

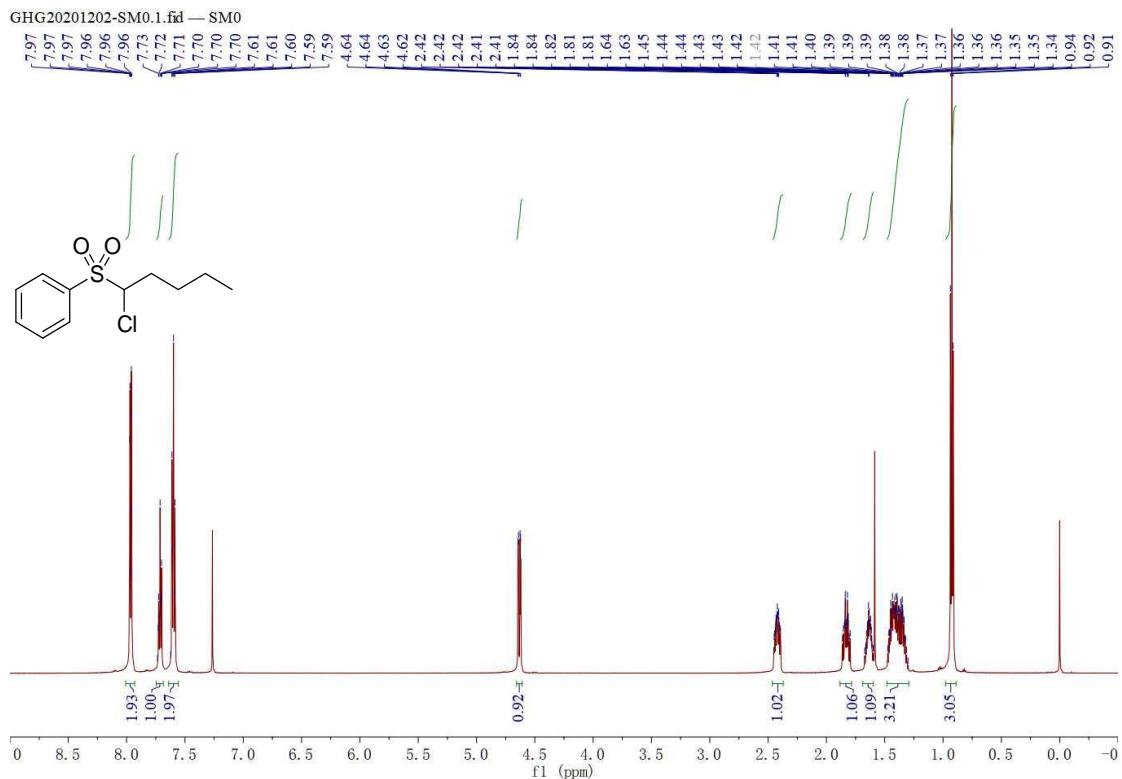


69: enantioenriched, 87% ee

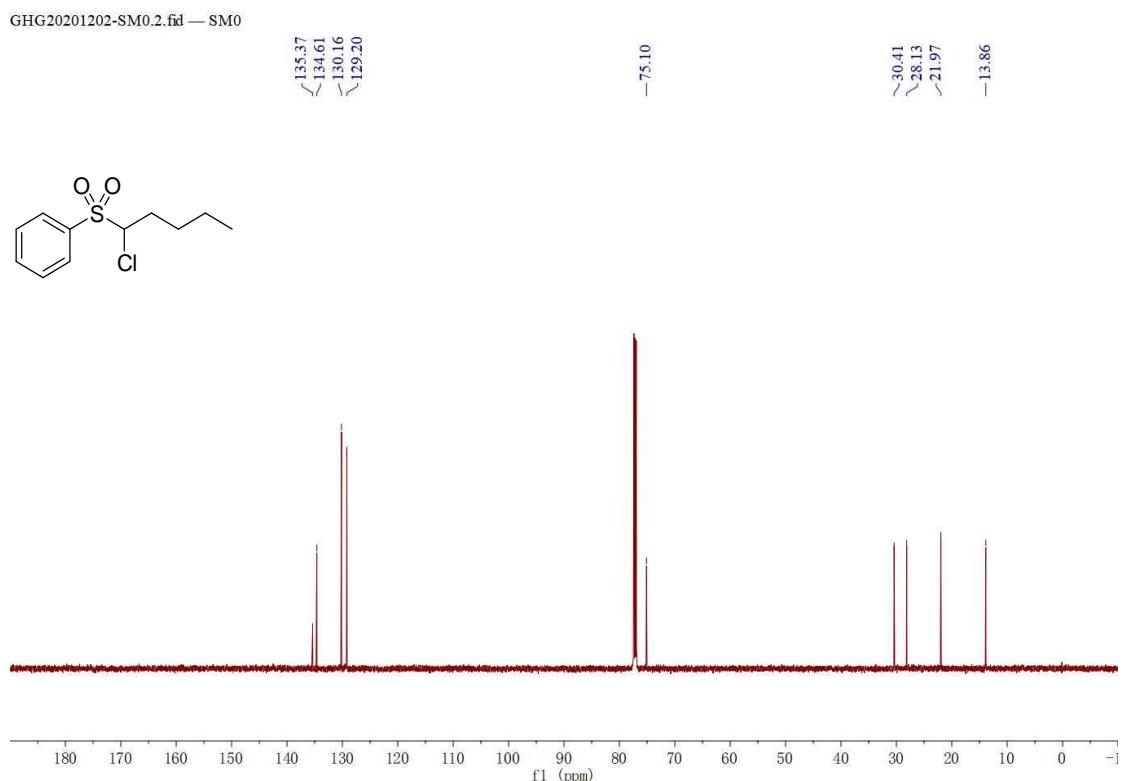


IV. NMR Data

SM1, ^1H -NMR (600 MHz, CDCl_3)

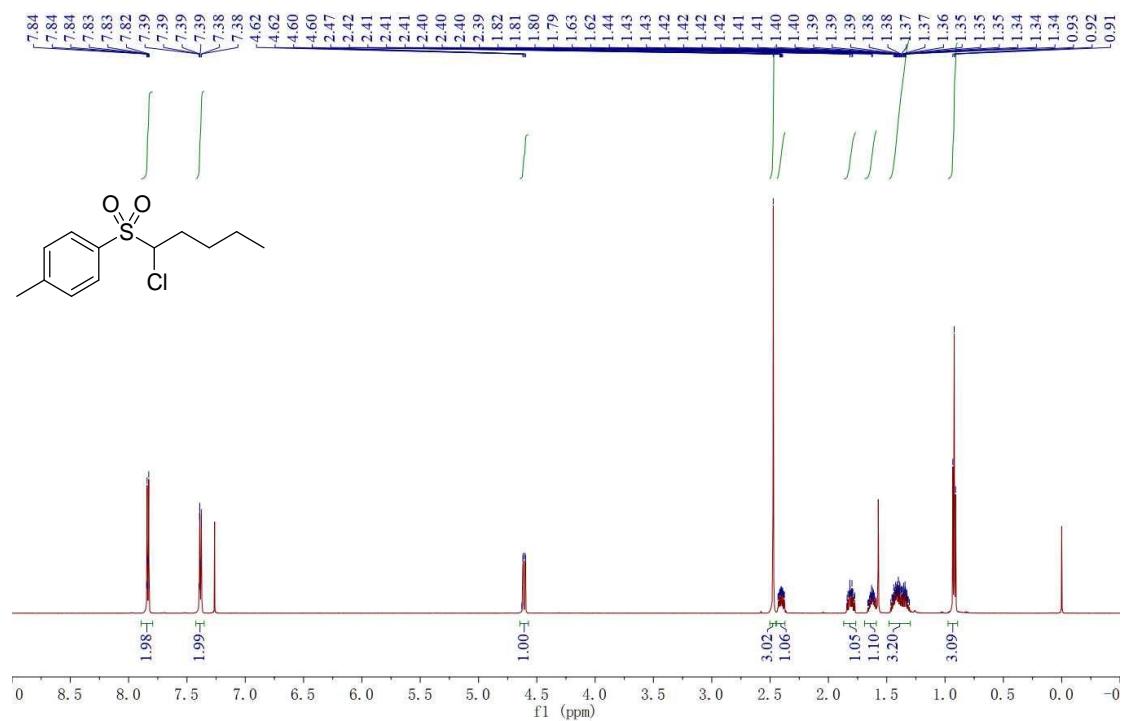


SM1, ^{13}C NMR (151 MHz, CDCl_3)



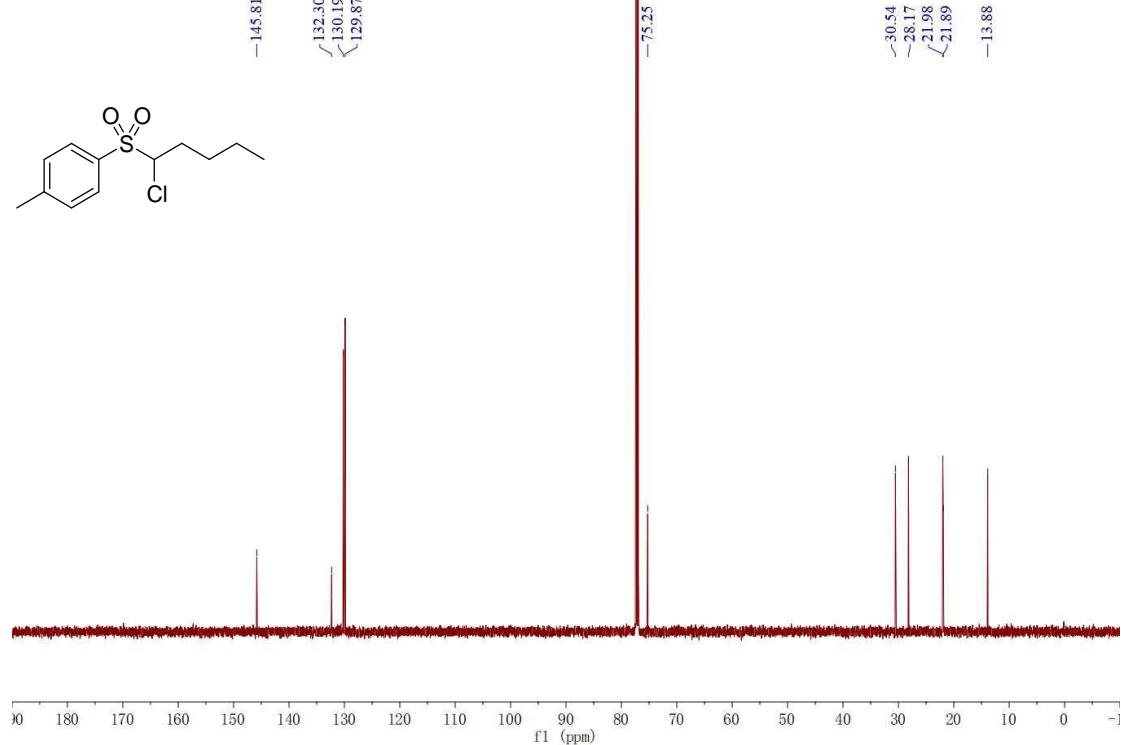
SM2, ^1H -NMR (600 MHz, CDCl_3)

GHG20200325.1.fid —



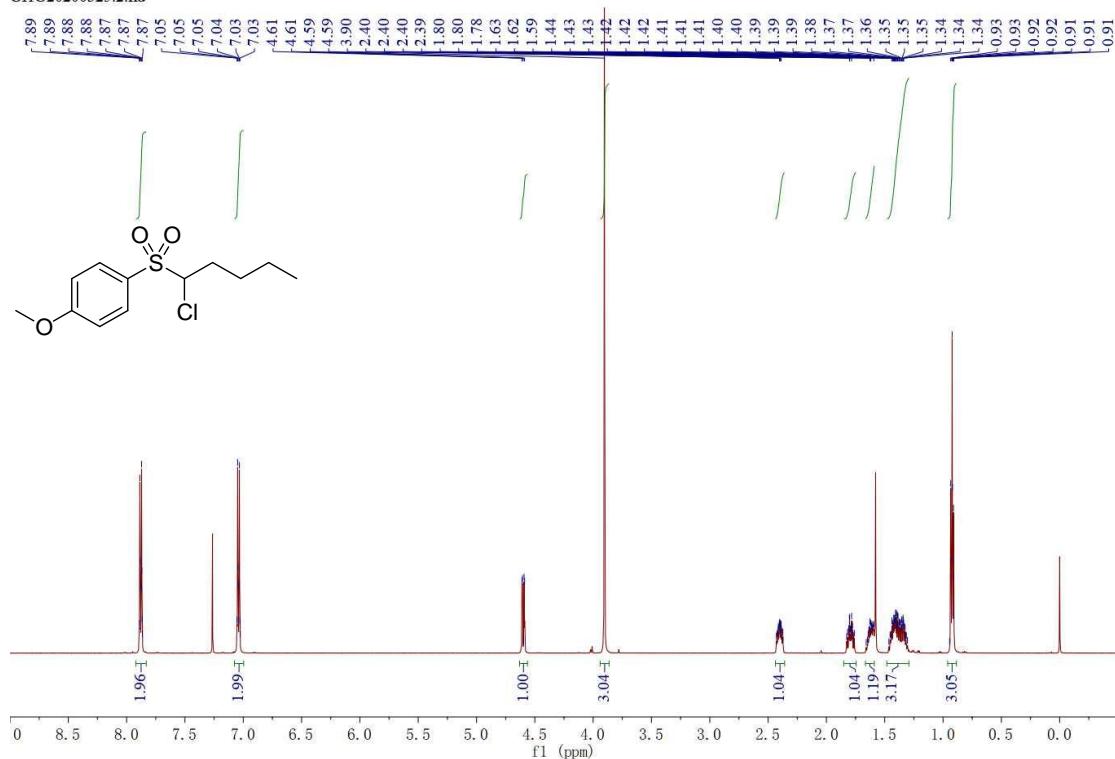
SM2, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.1.fid —



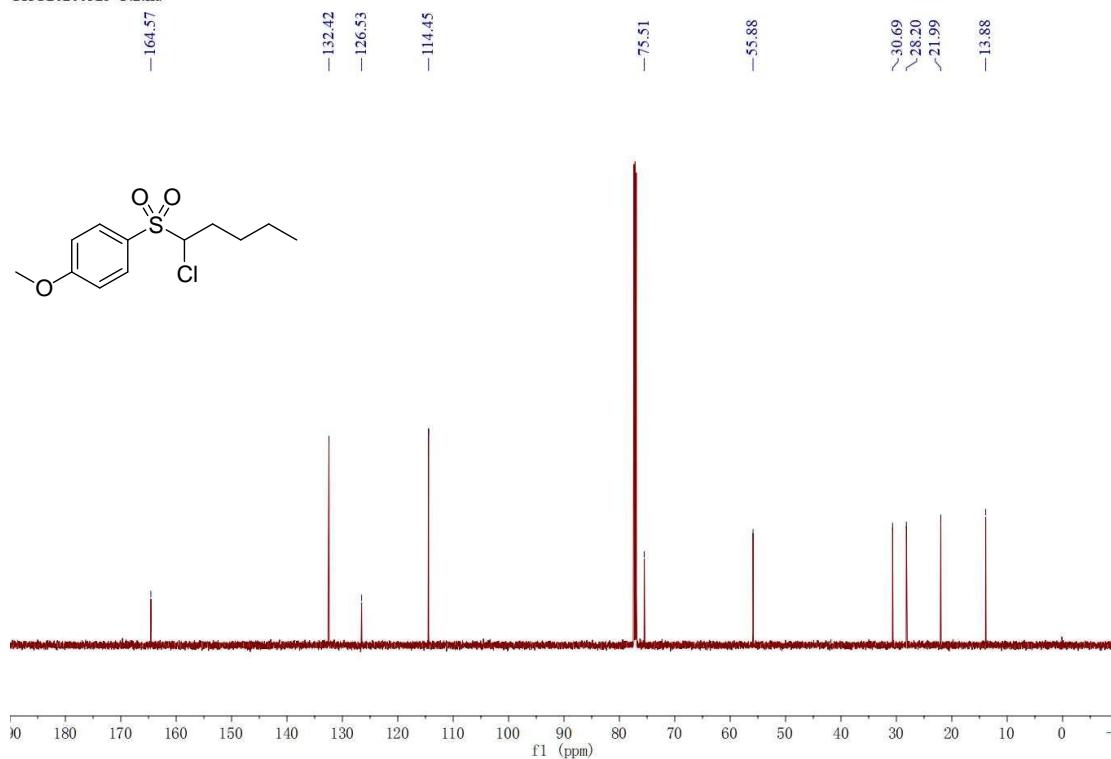
SM3, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200325.2.fid —

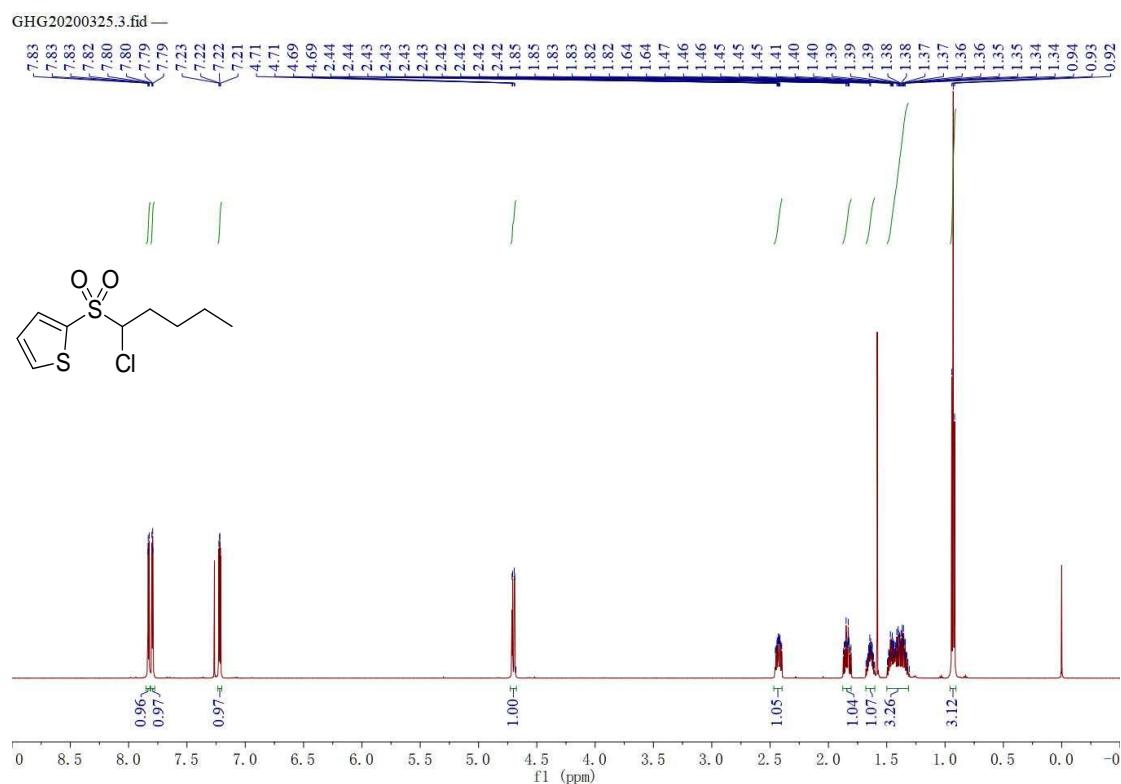


SM3, ^{13}C NMR (151 MHz, CDCl_3)

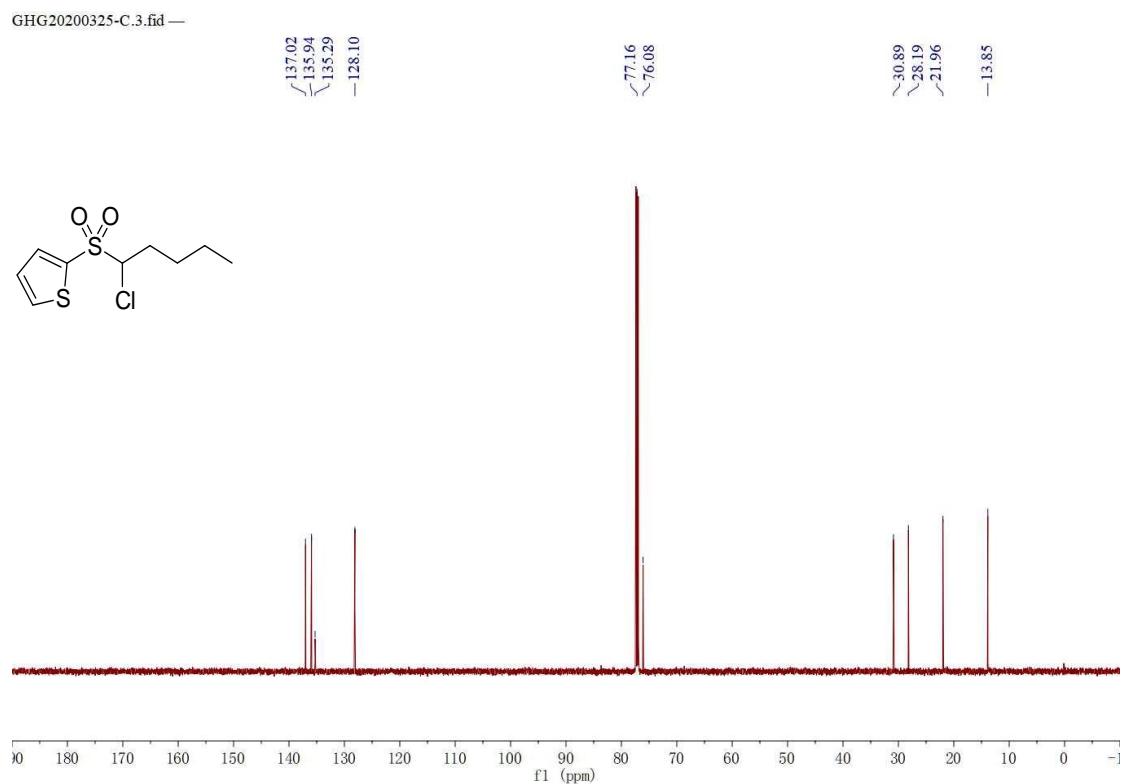
GHG20200325-C.2.fid —



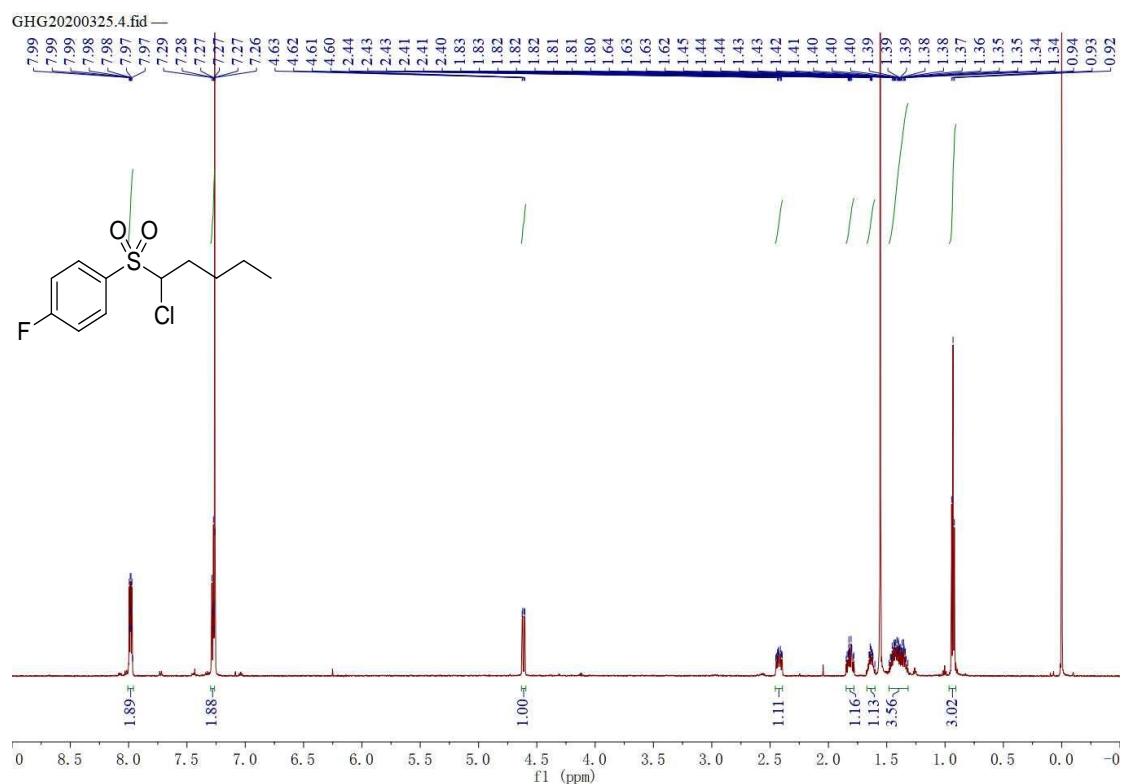
SM4, ^1H -NMR (600 MHz, CDCl_3)



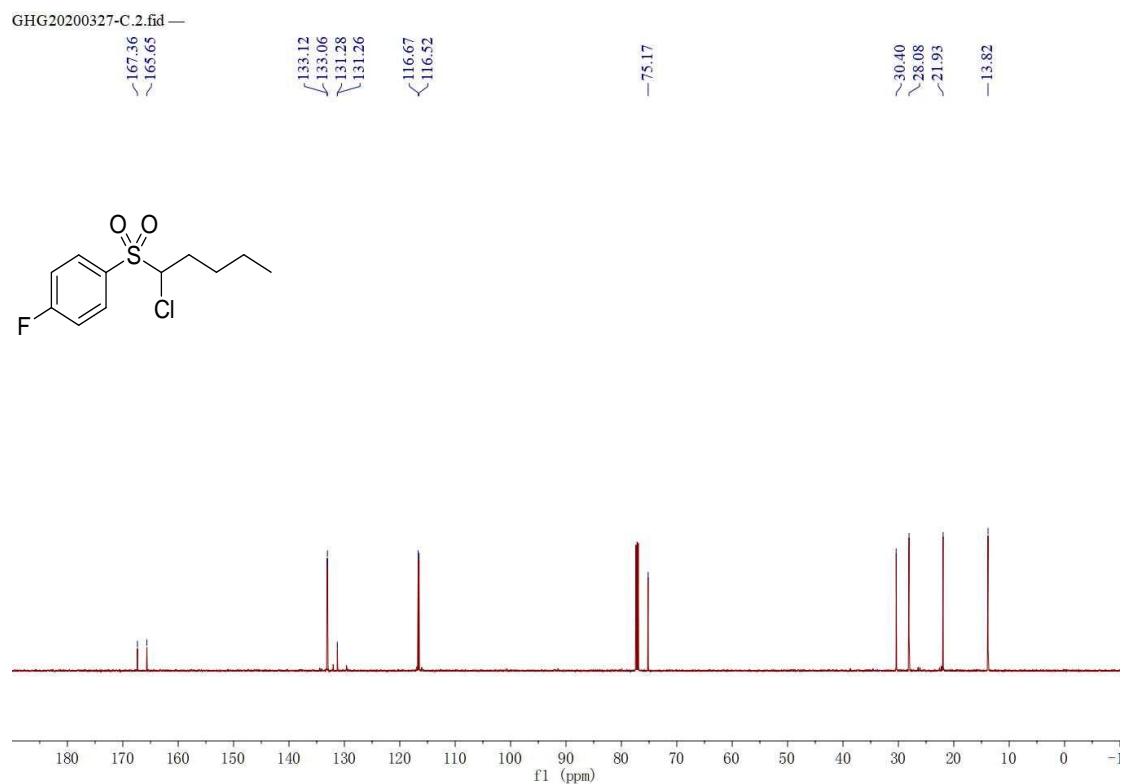
SM4, ^{13}C NMR (151 MHz, CDCl_3)



SM5, ^1H -NMR (600 MHz, CDCl_3)

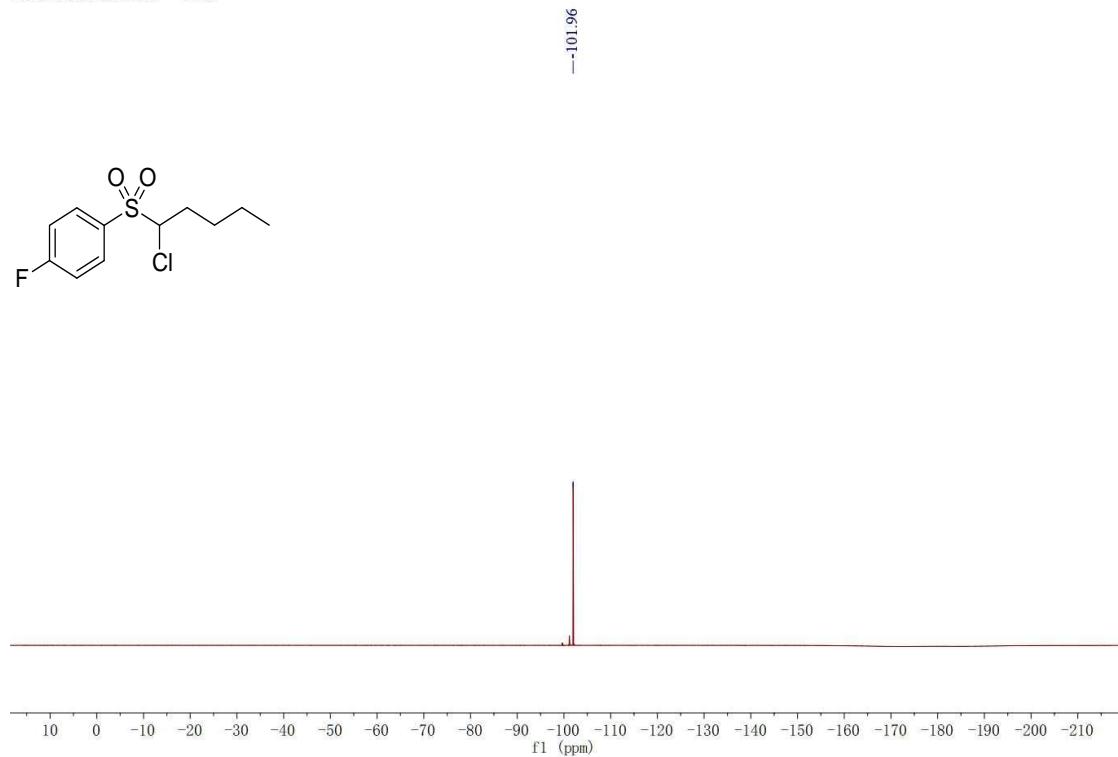
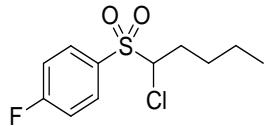


SM5, ^{13}C NMR (151 MHz, CDCl_3)



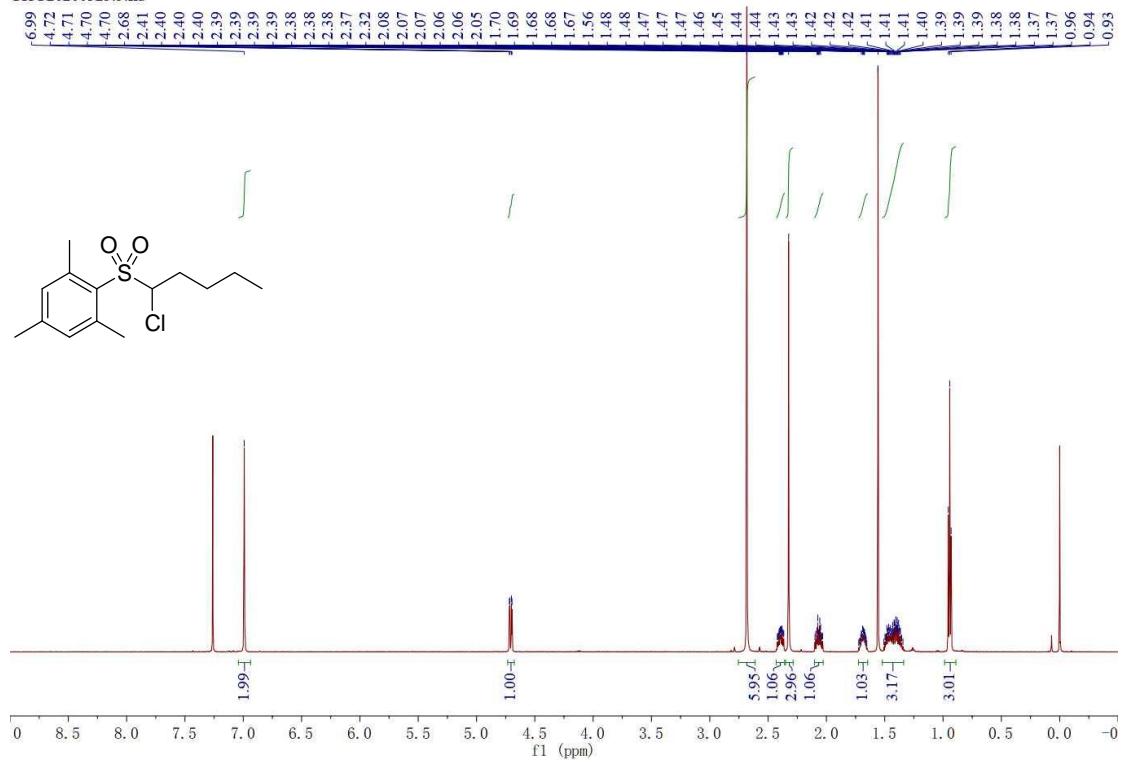
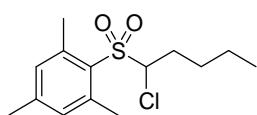
SM5, ^{19}F NMR (565 MHz, CDCl_3)

GHG20200416-F.1.fid — SM5

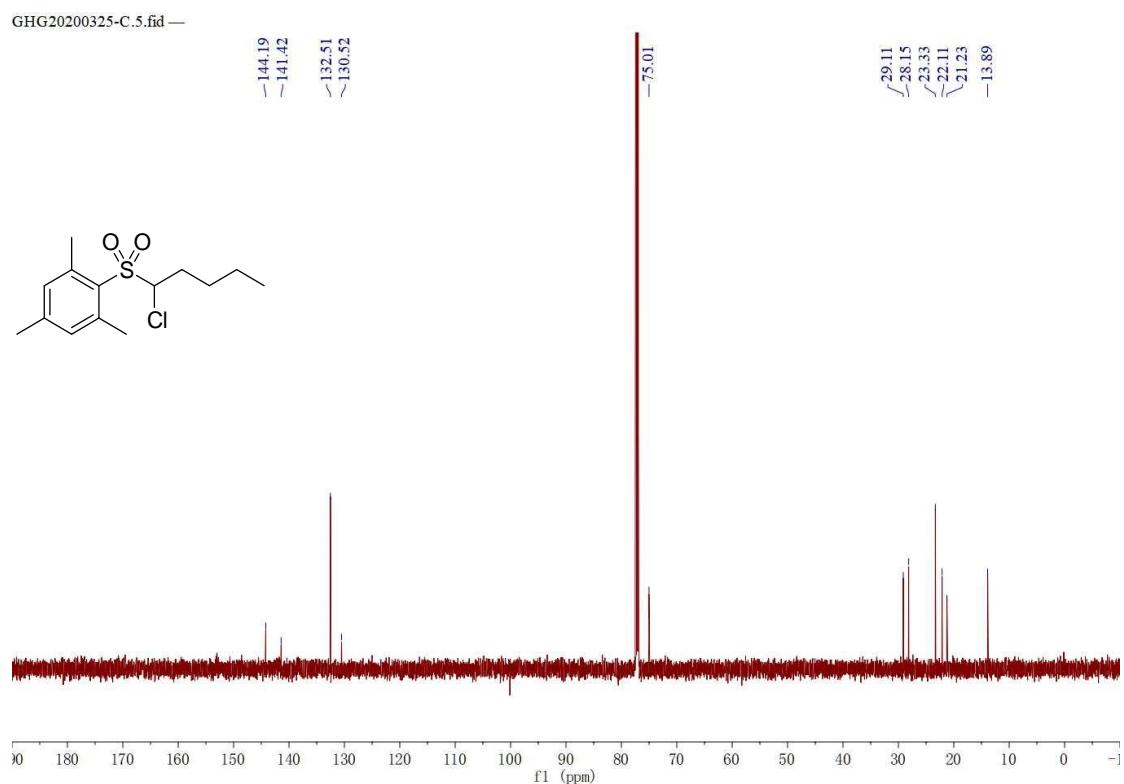


SM6, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

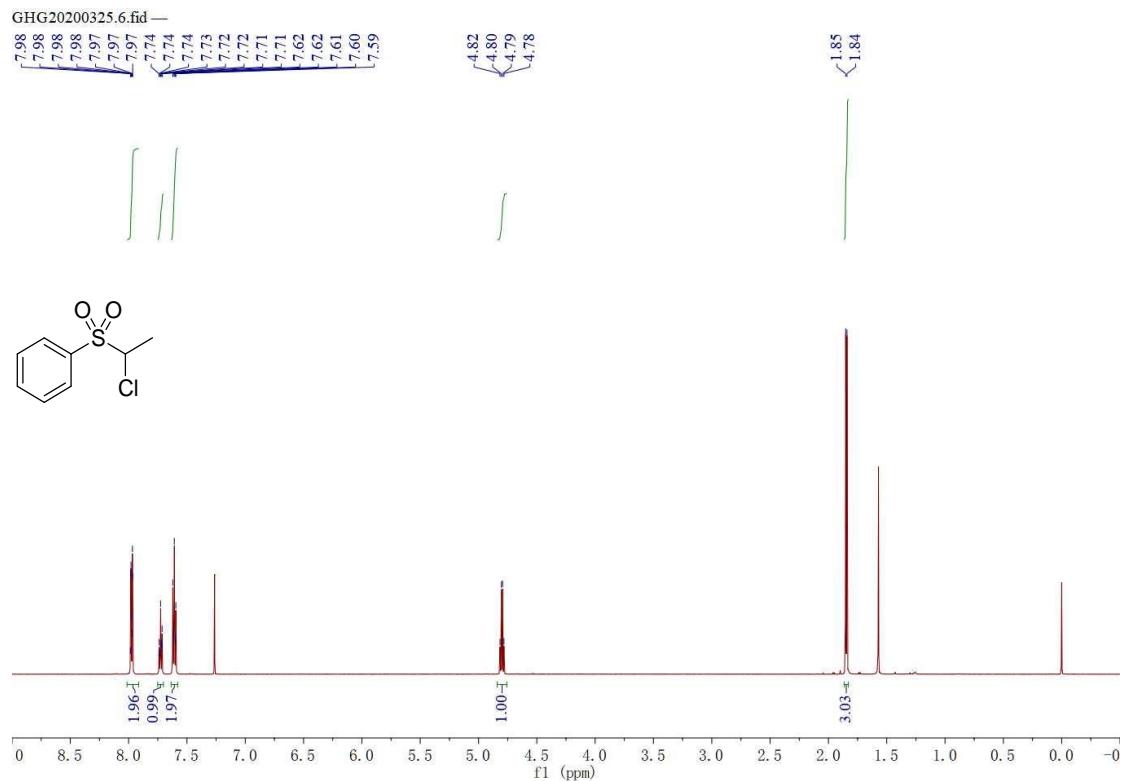
GHG20200325.5.fid —



SM6, ^{13}C NMR (151 MHz, CDCl_3)

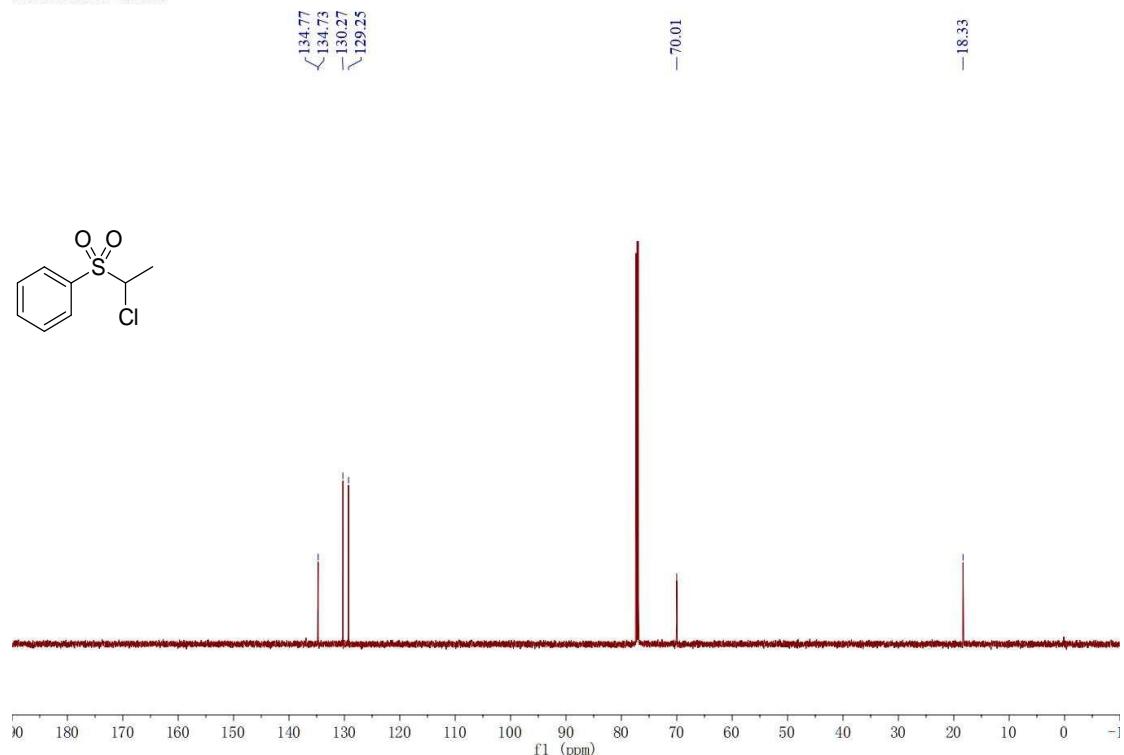


SM7, ^1H -NMR (600 MHz, CDCl_3)



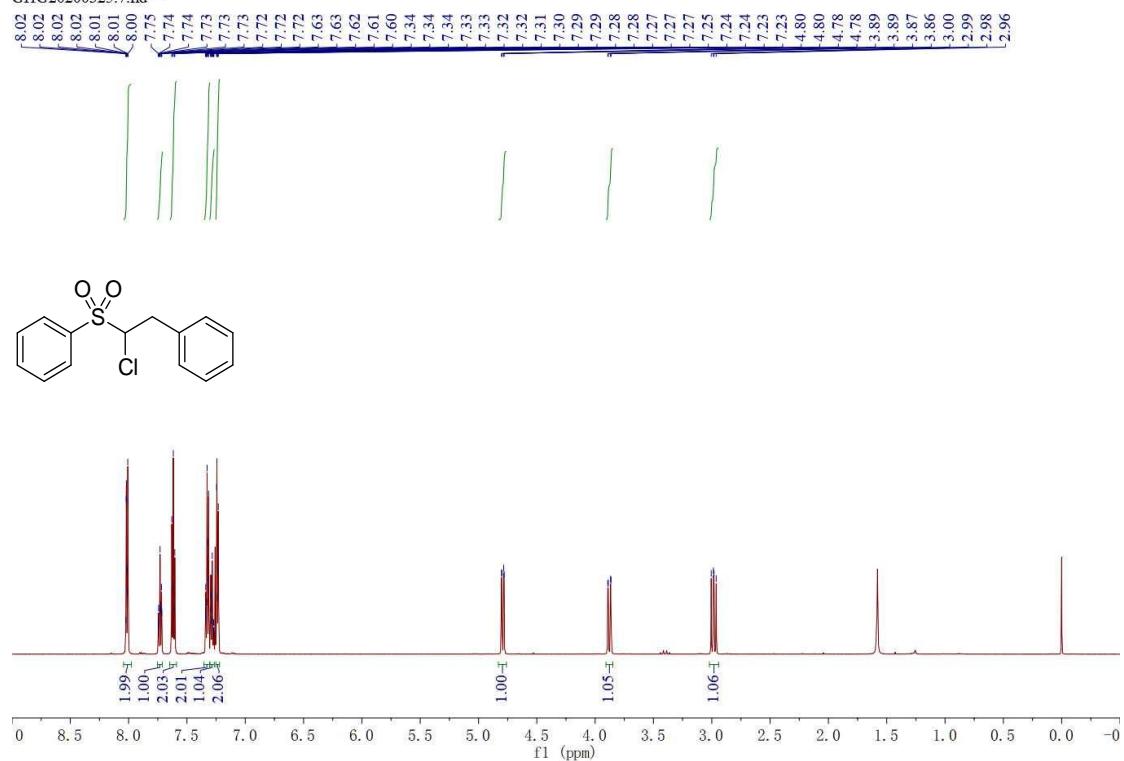
SM7, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.6.fid —



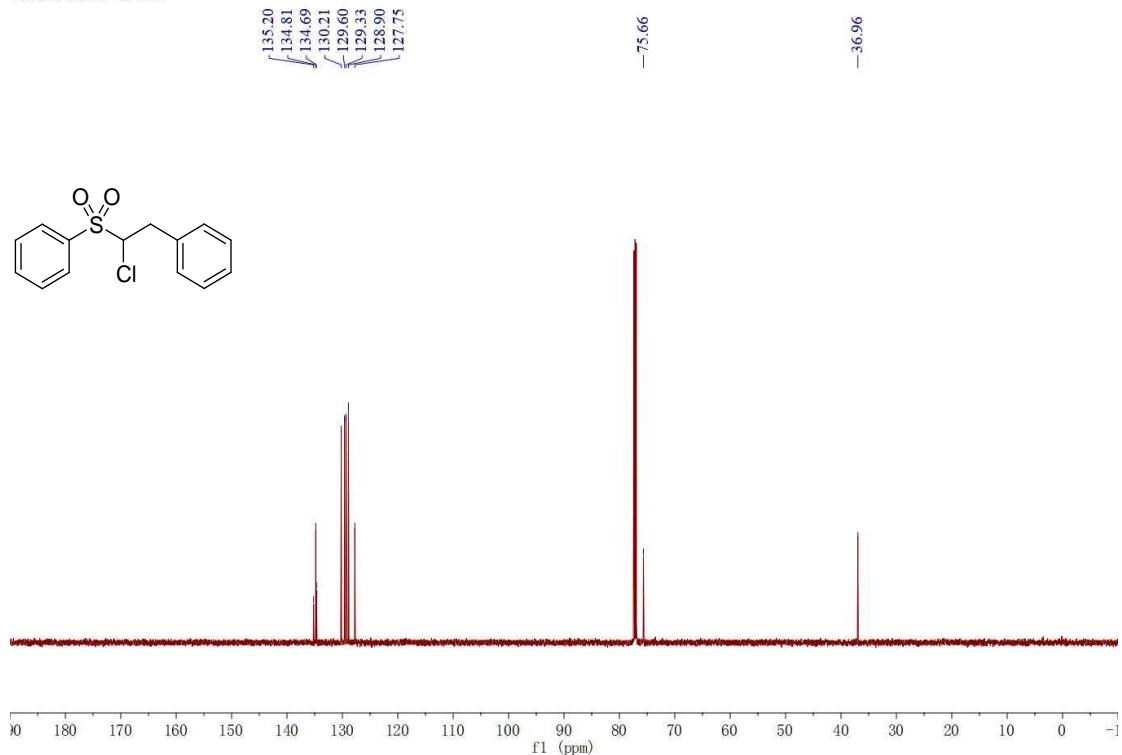
SM8, ^1H -NMR (600 MHz, CDCl_3)

GHG20200325.7.fid —



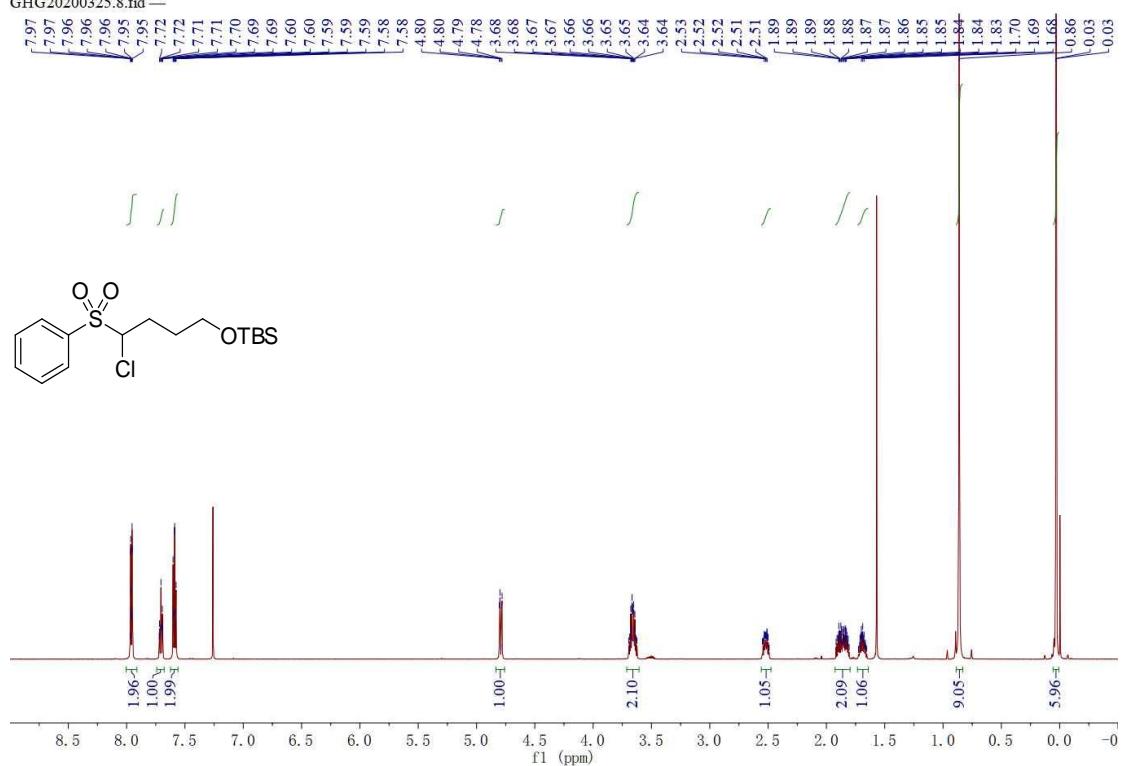
SM8, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.7.fid —



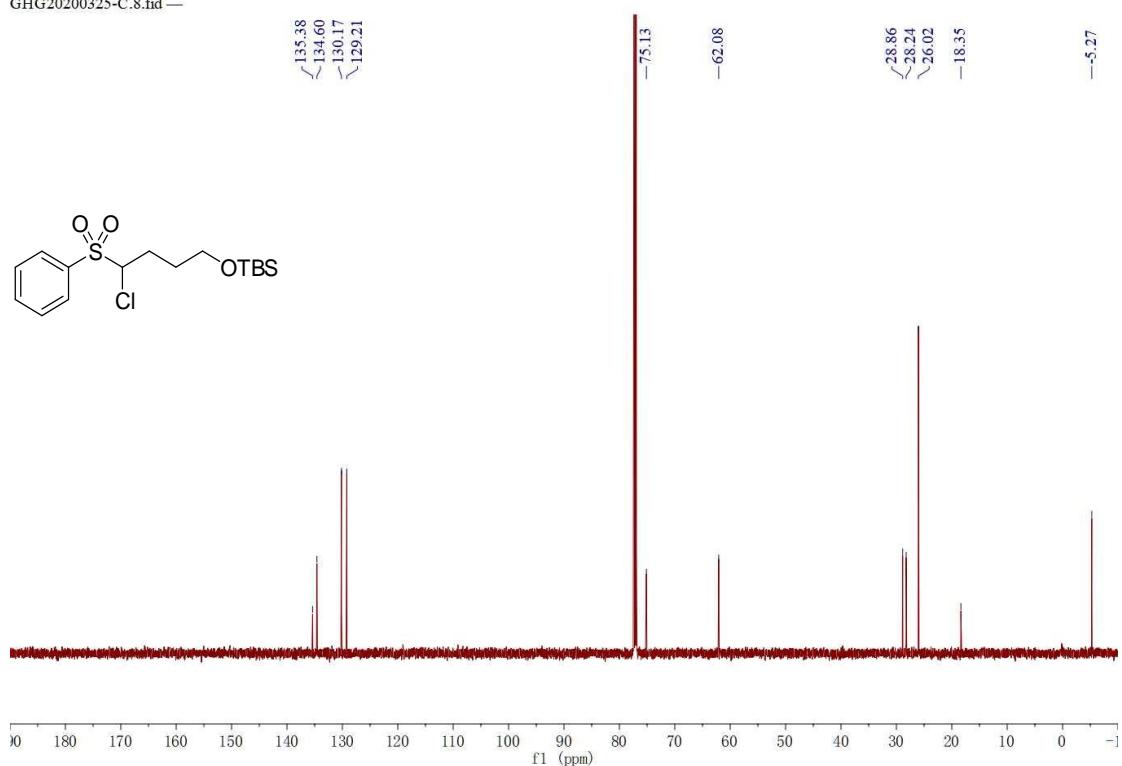
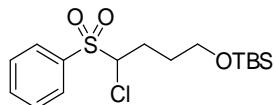
SM9, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHC20200325 8 fid —



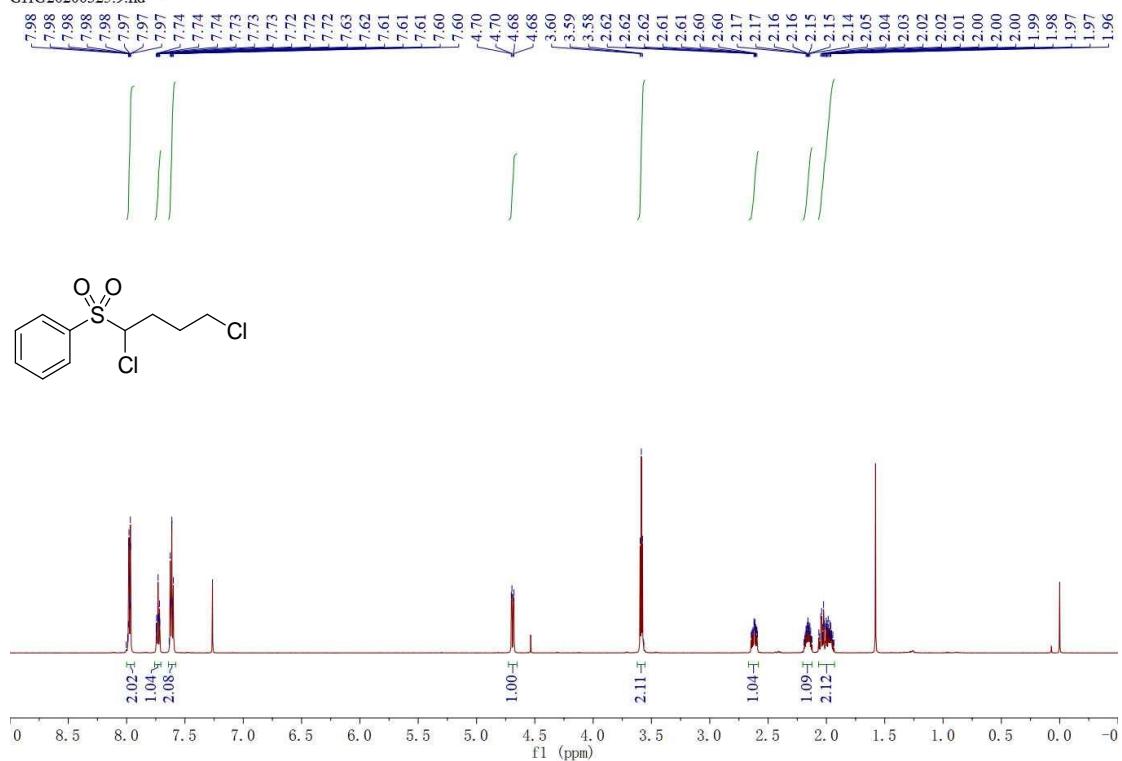
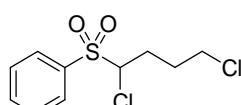
SM9, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.8.fid —



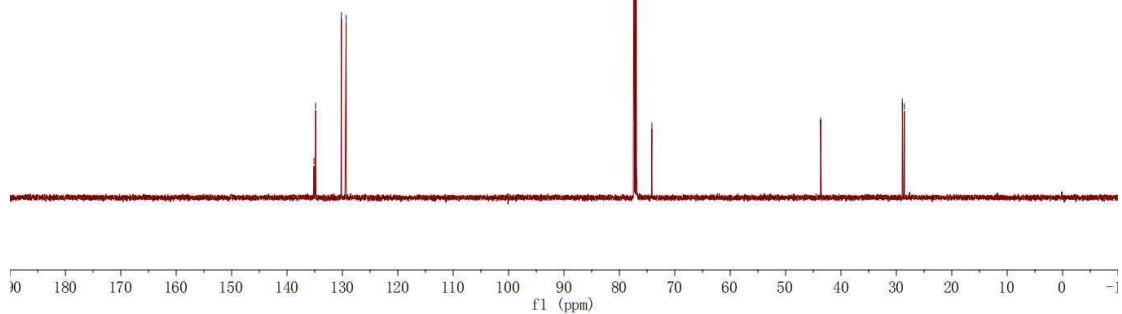
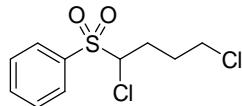
SM10, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200325.9.fid —



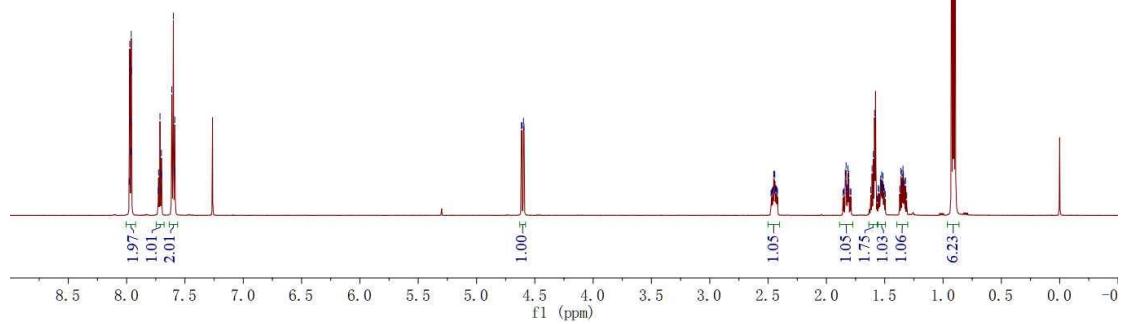
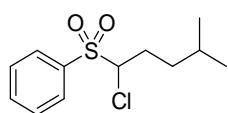
SM10, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.9.fid —



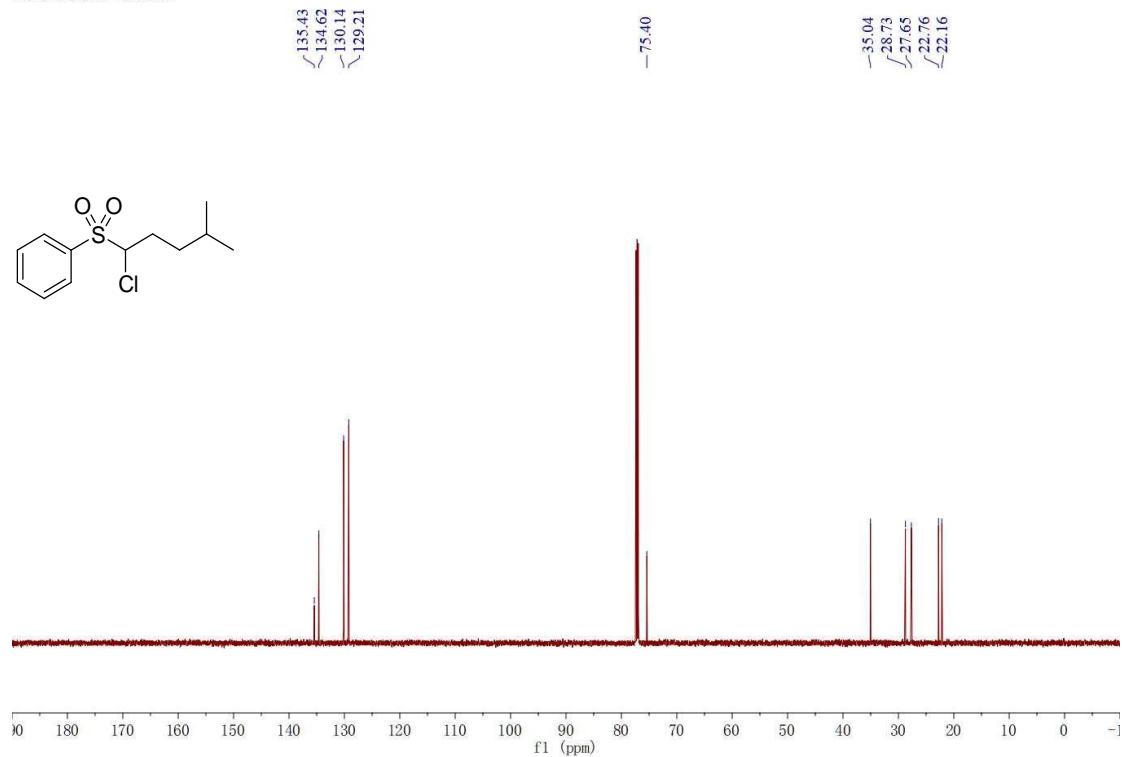
SM11, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200325.11.fid —



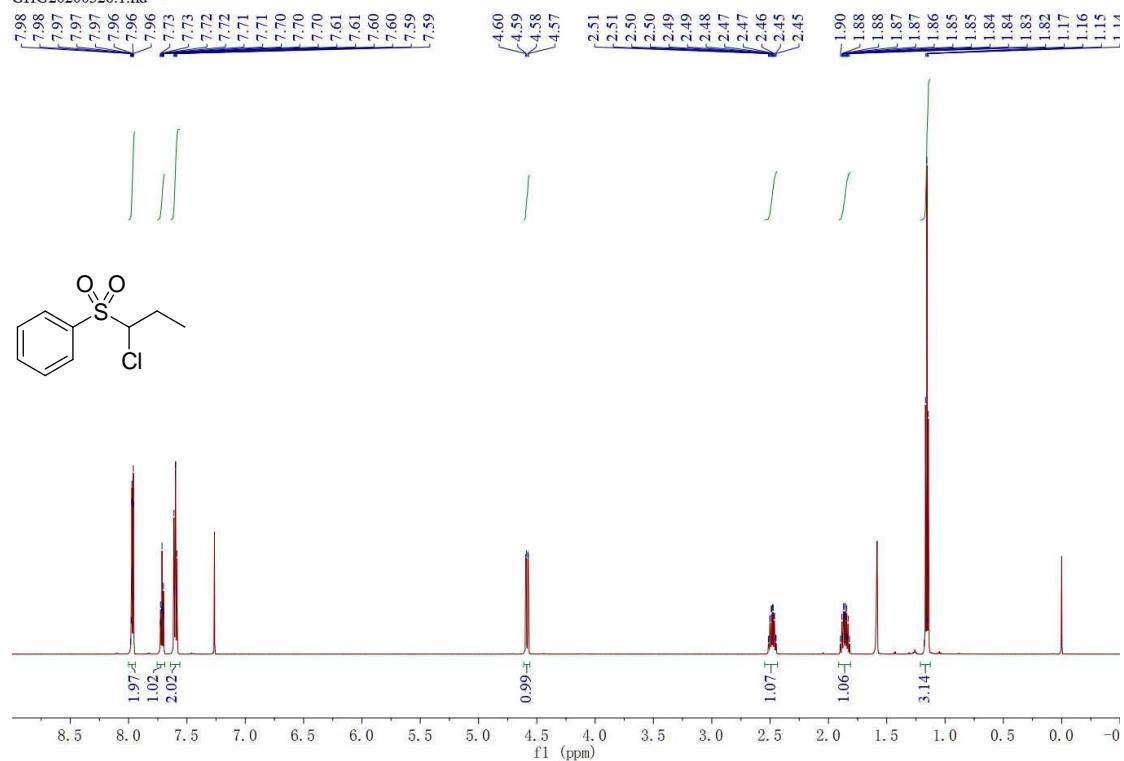
SM11, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200325-C.11.fid —



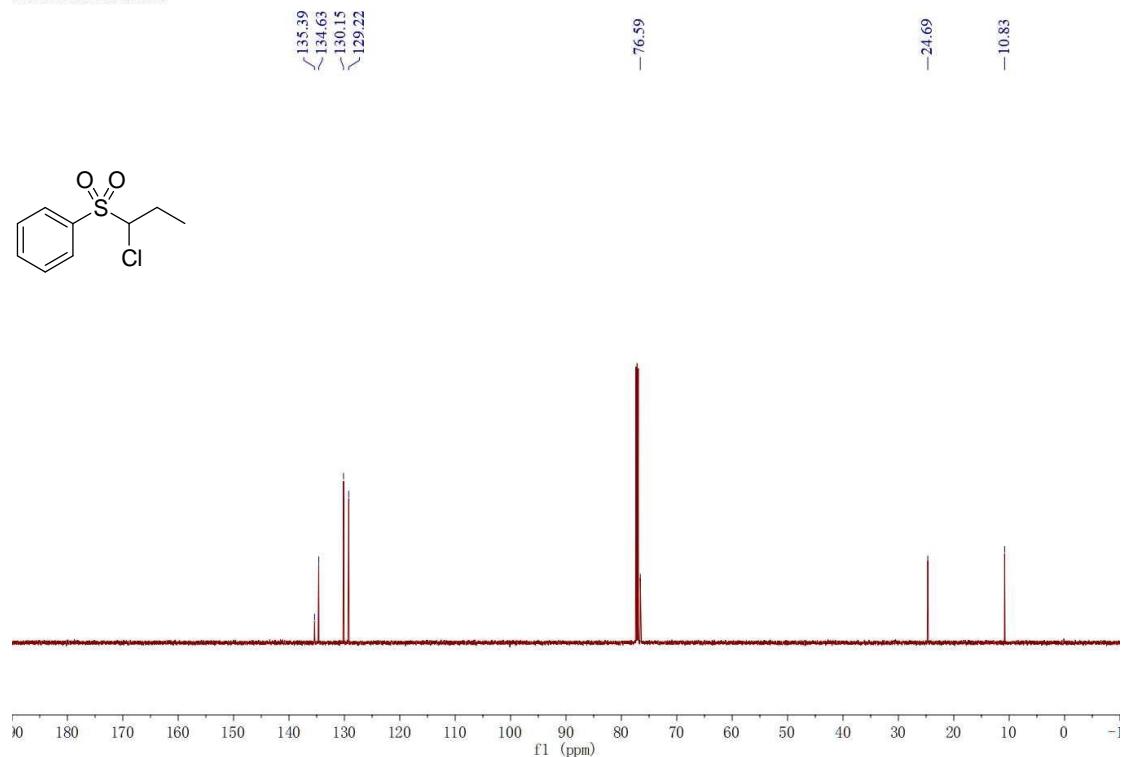
SM12, ^1H -NMR (600 MHZ, CDCl_3)

GHG20200326.1.fid —



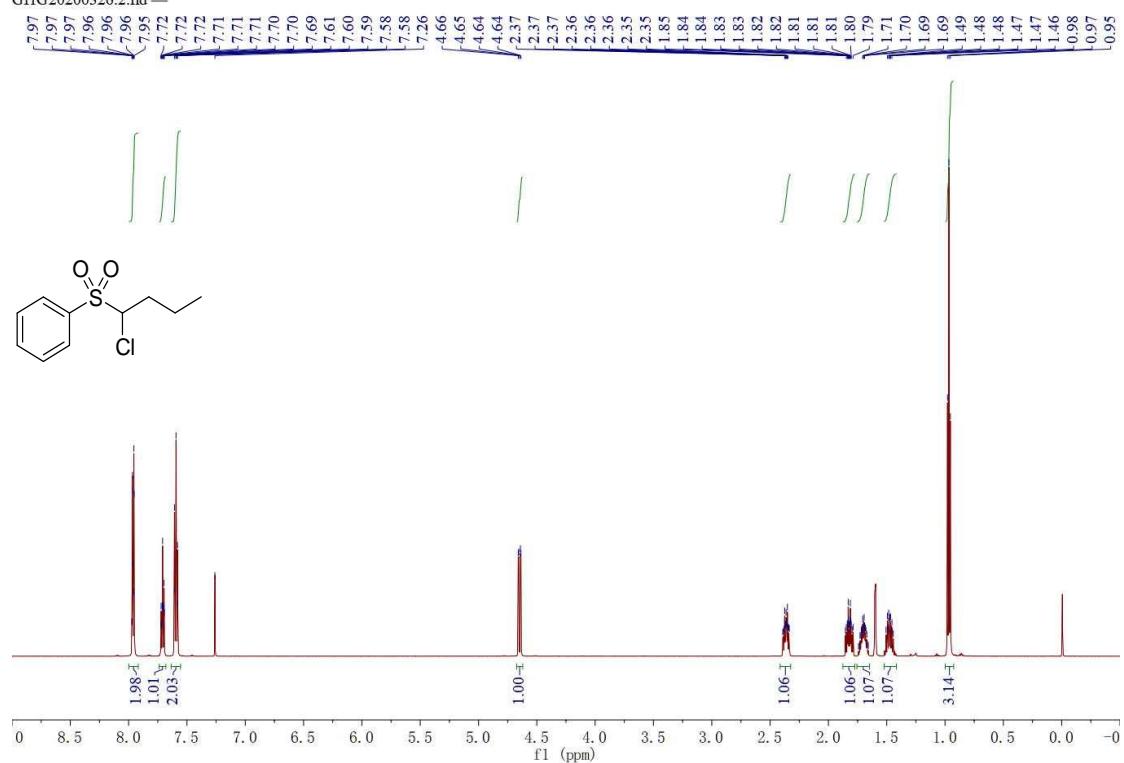
SM12, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200326-C.1.fid —



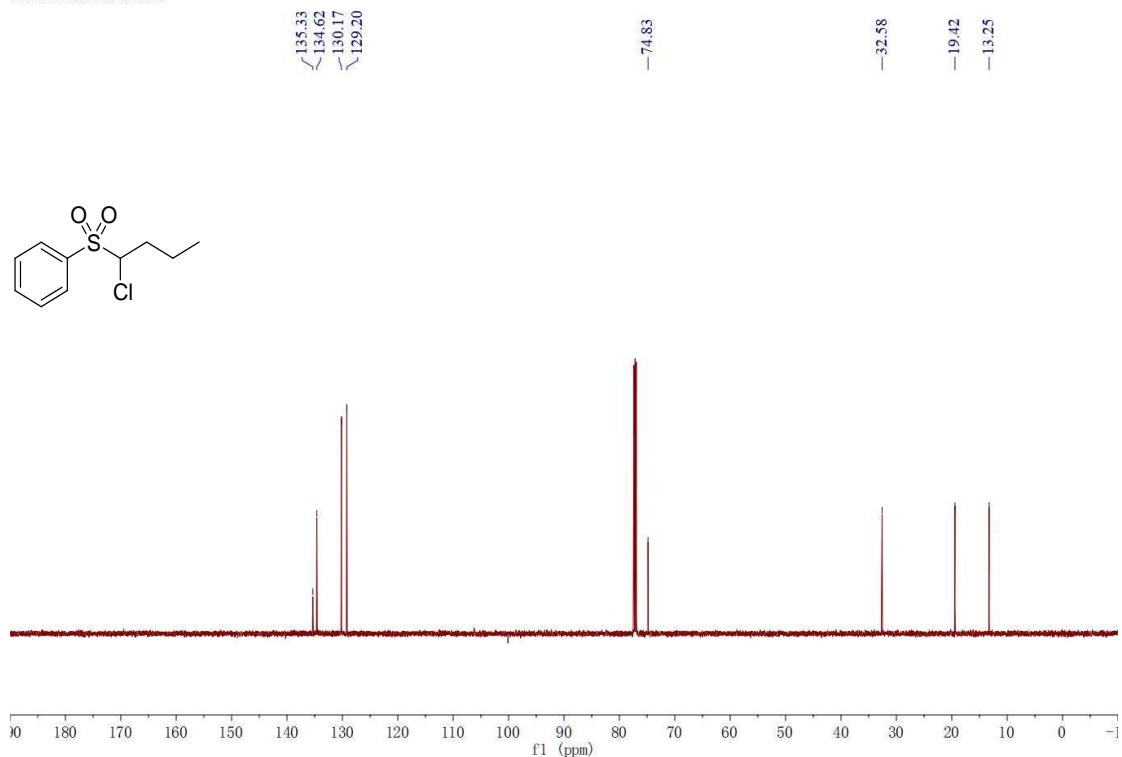
SM13, ^1H -NMR (600 MHZ, CDCl_3)

GHG20200326.2.fid —



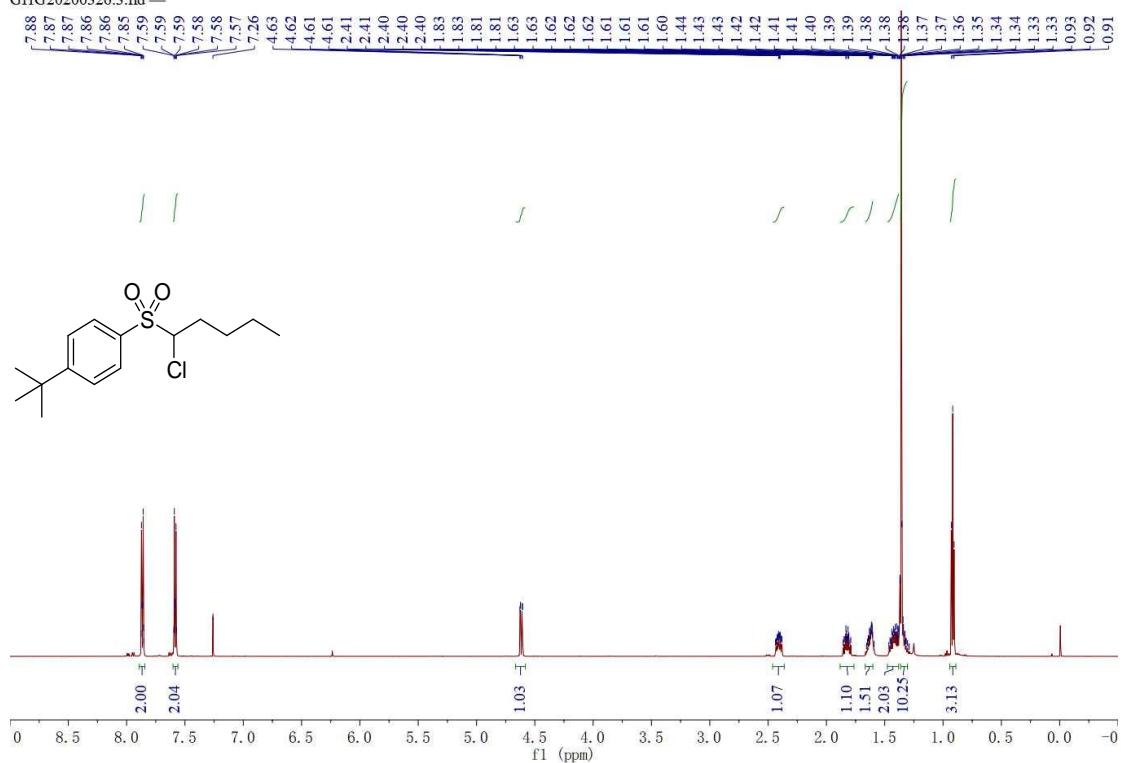
SM13, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200326-C.2.fid —

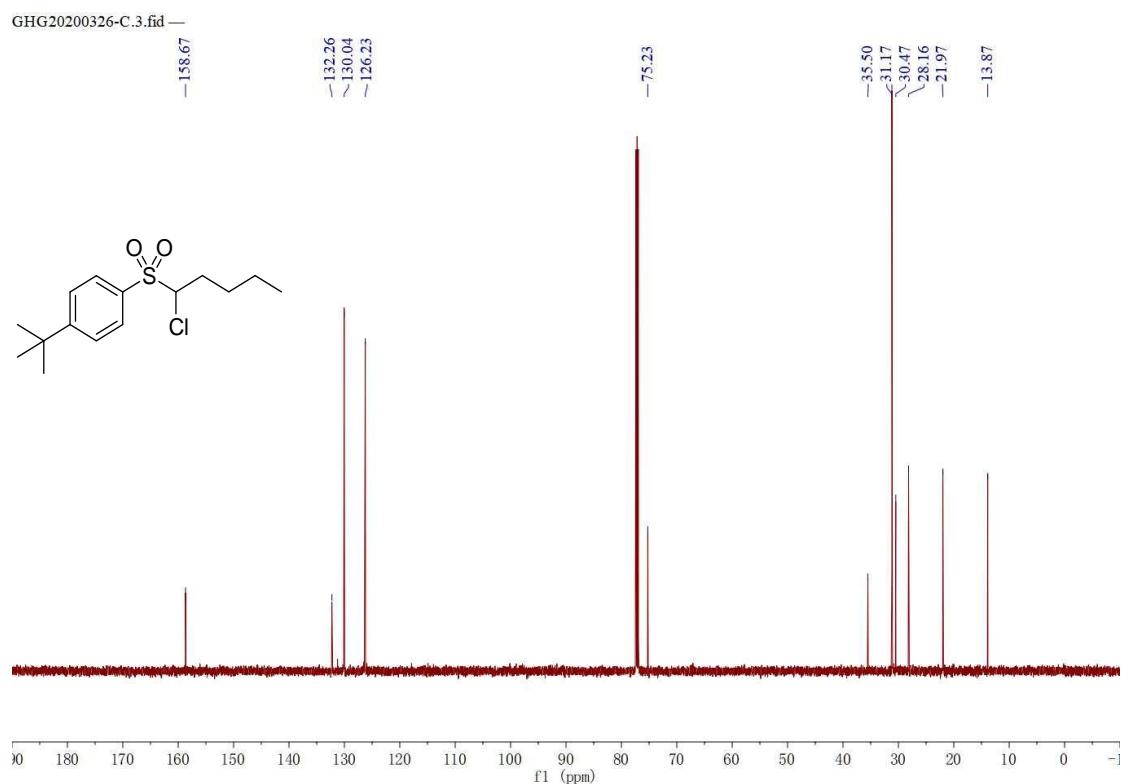


SM14, ^1H -NMR (600 MHZ, CDCl_3)

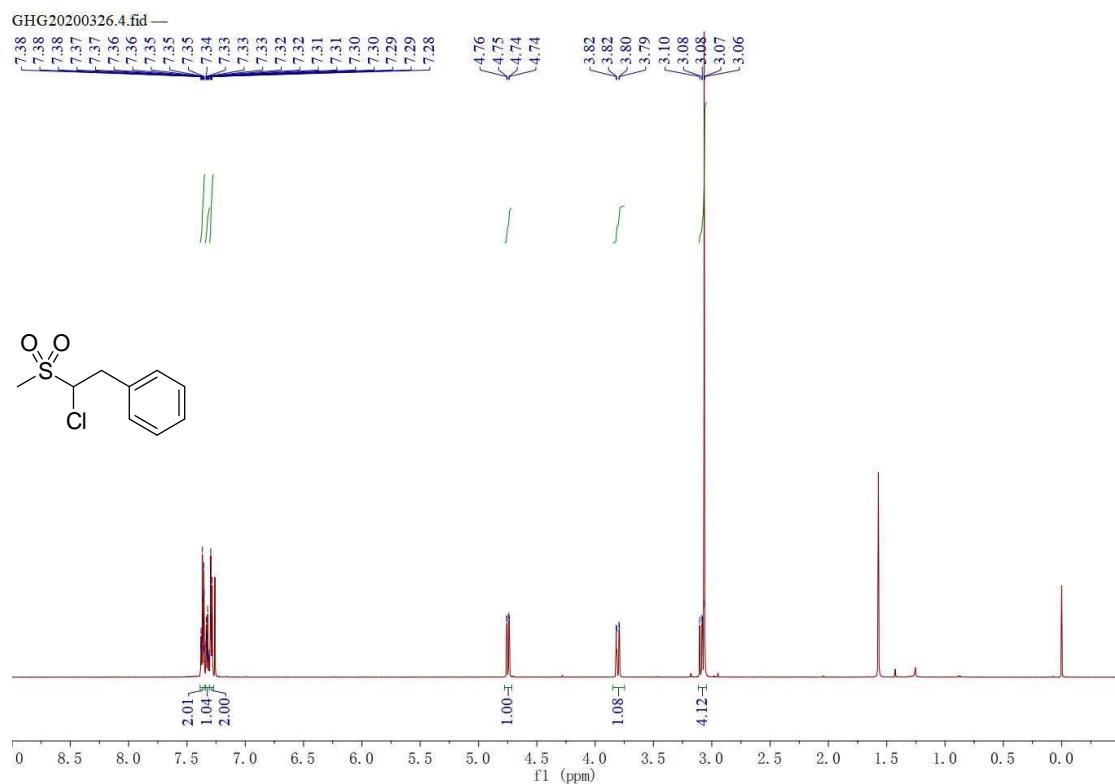
GHG20200326.3.fid —



SM14, ^{13}C NMR (151 MHz, CDCl_3)

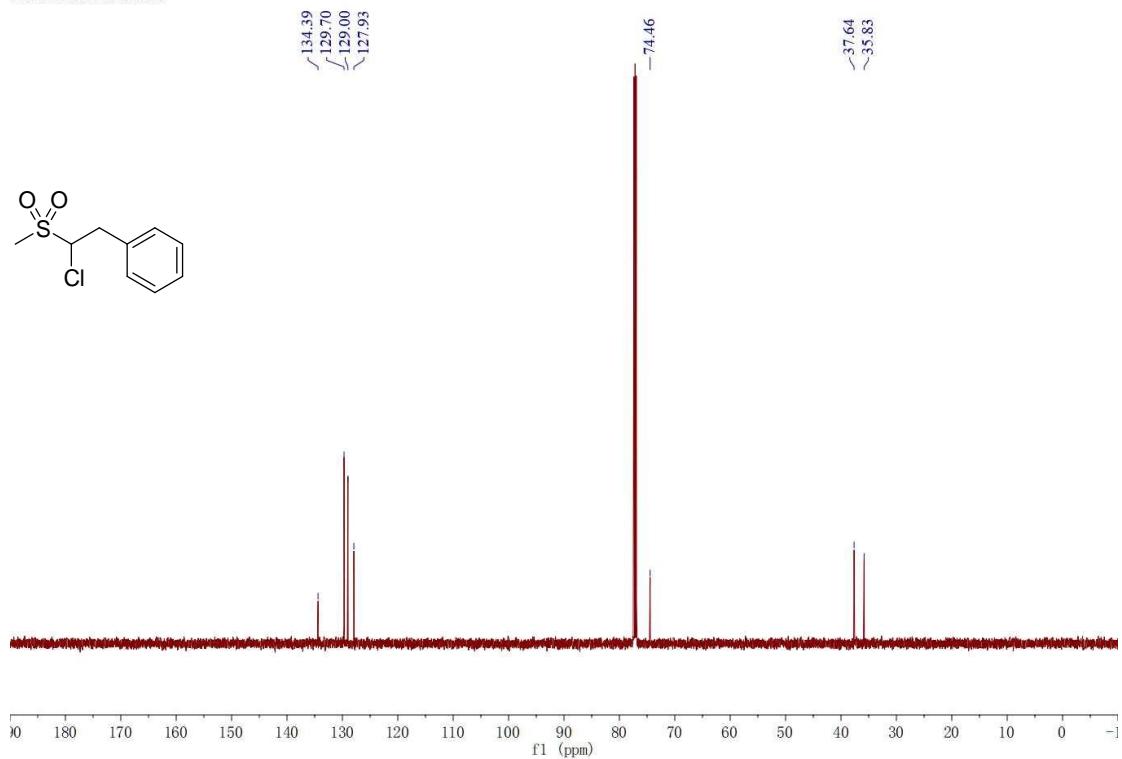
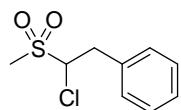


SM15, -NMR (600 MHZ, CDCl_3)



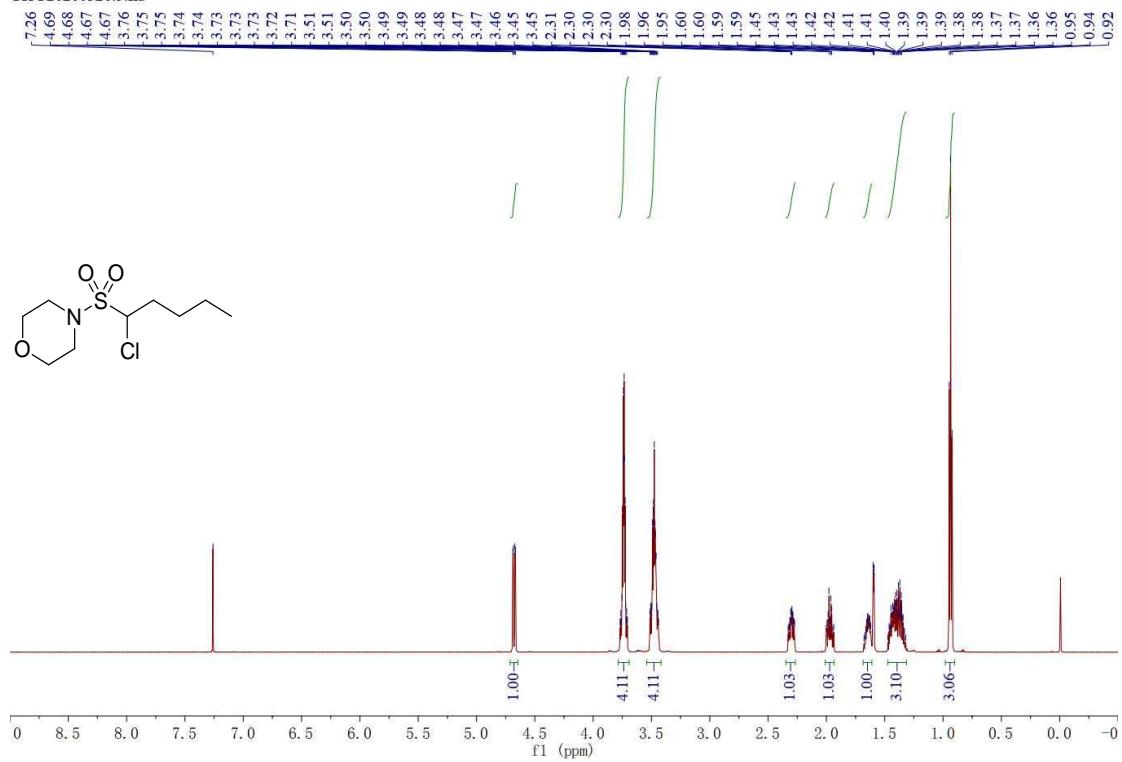
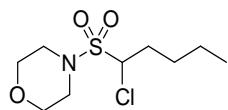
SM15, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200326-C.4.fid —



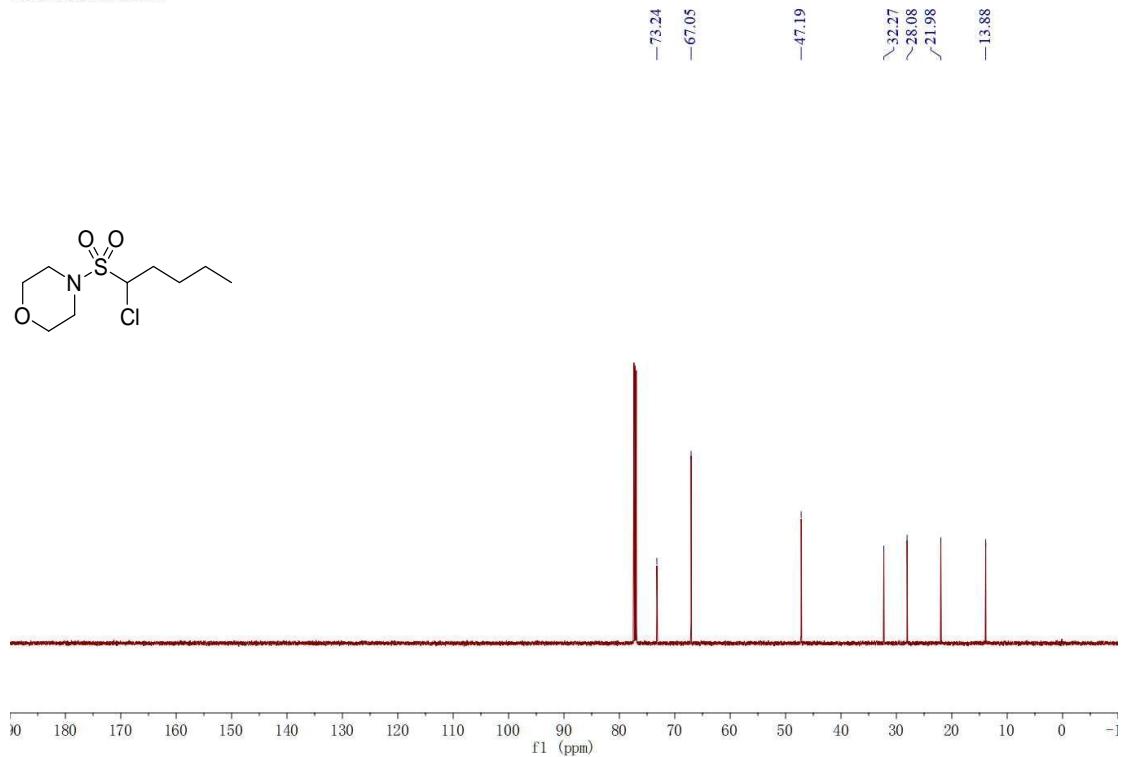
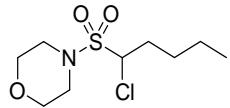
SM16, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200326.5.fid —



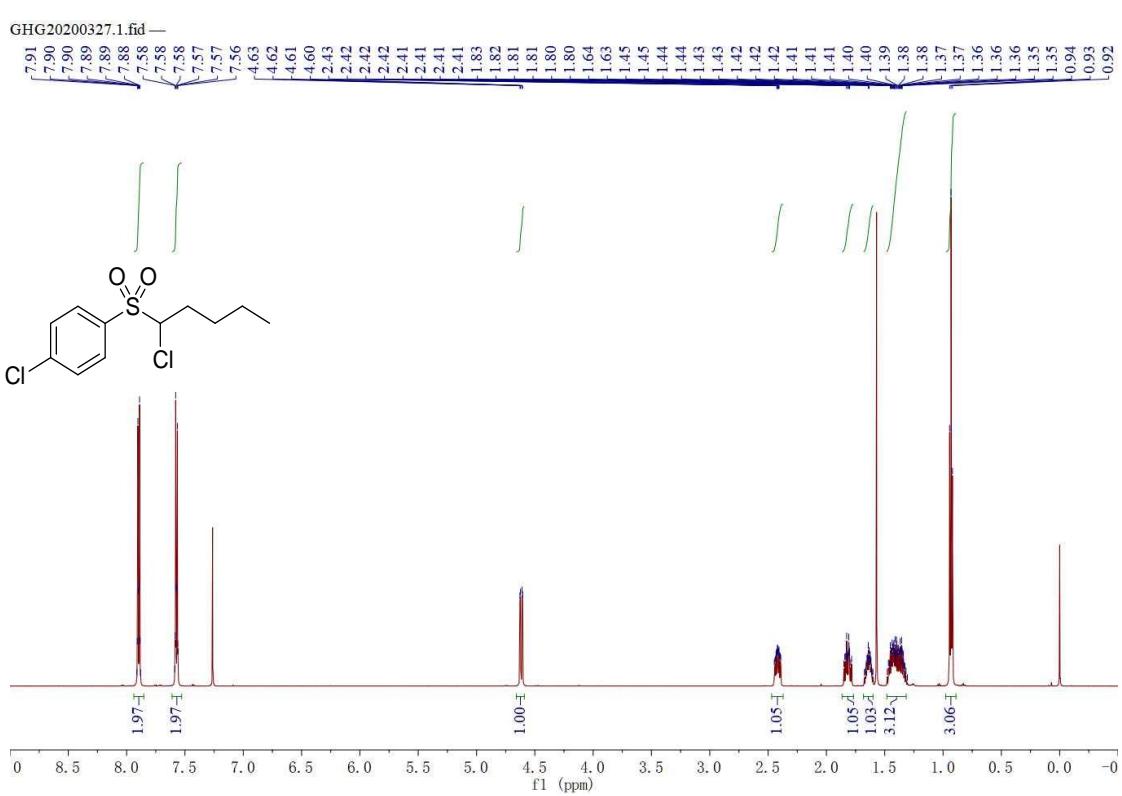
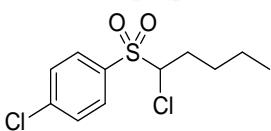
SM16, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200326-C.5.fid —



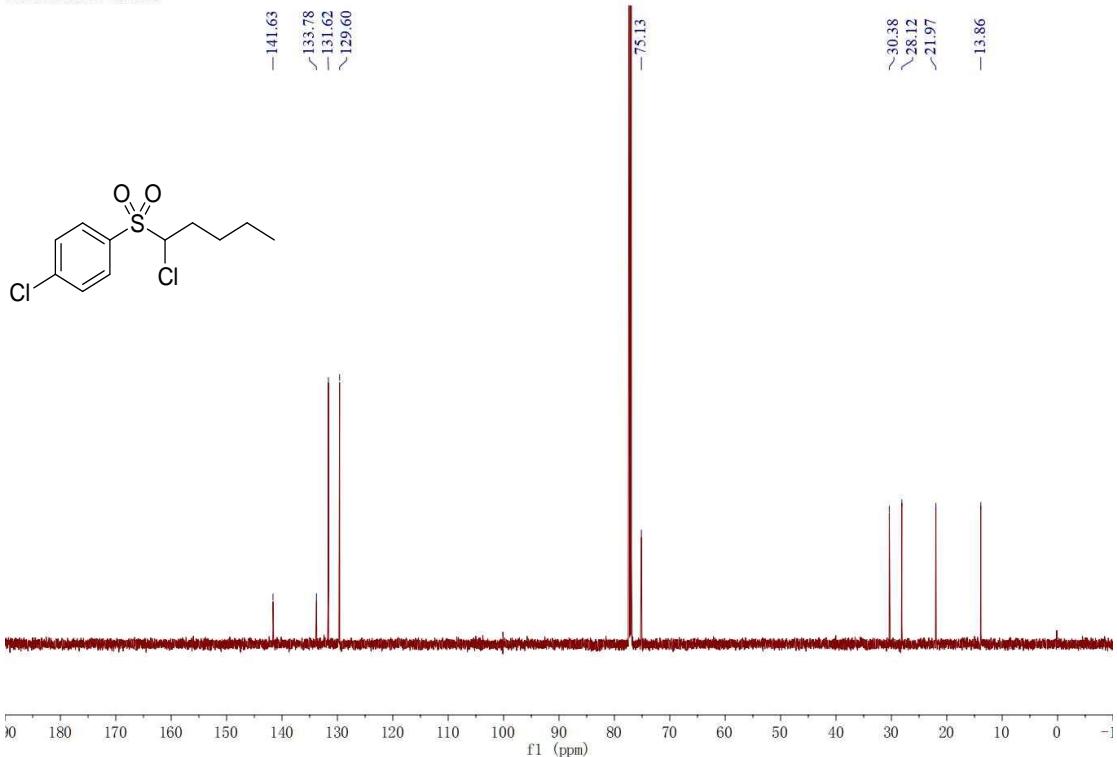
SM17, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200327.1.fid —



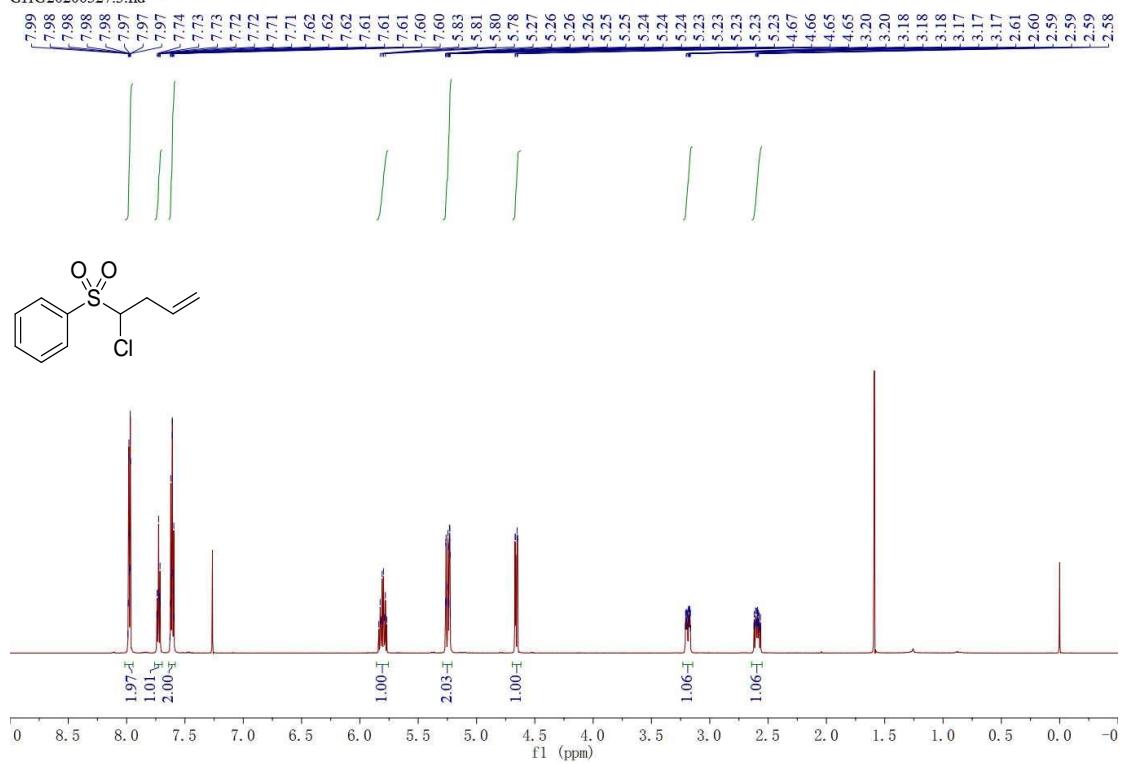
SM17, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200327-C.1.fid —



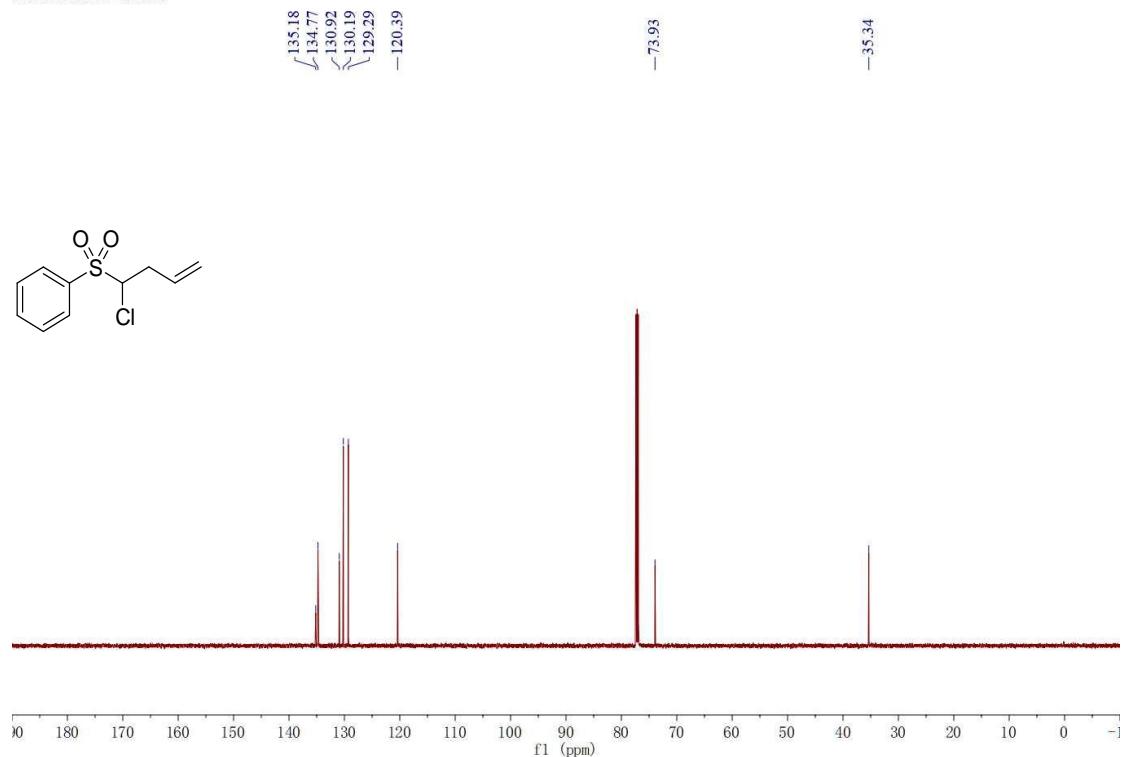
SM18, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200327.3.fid —



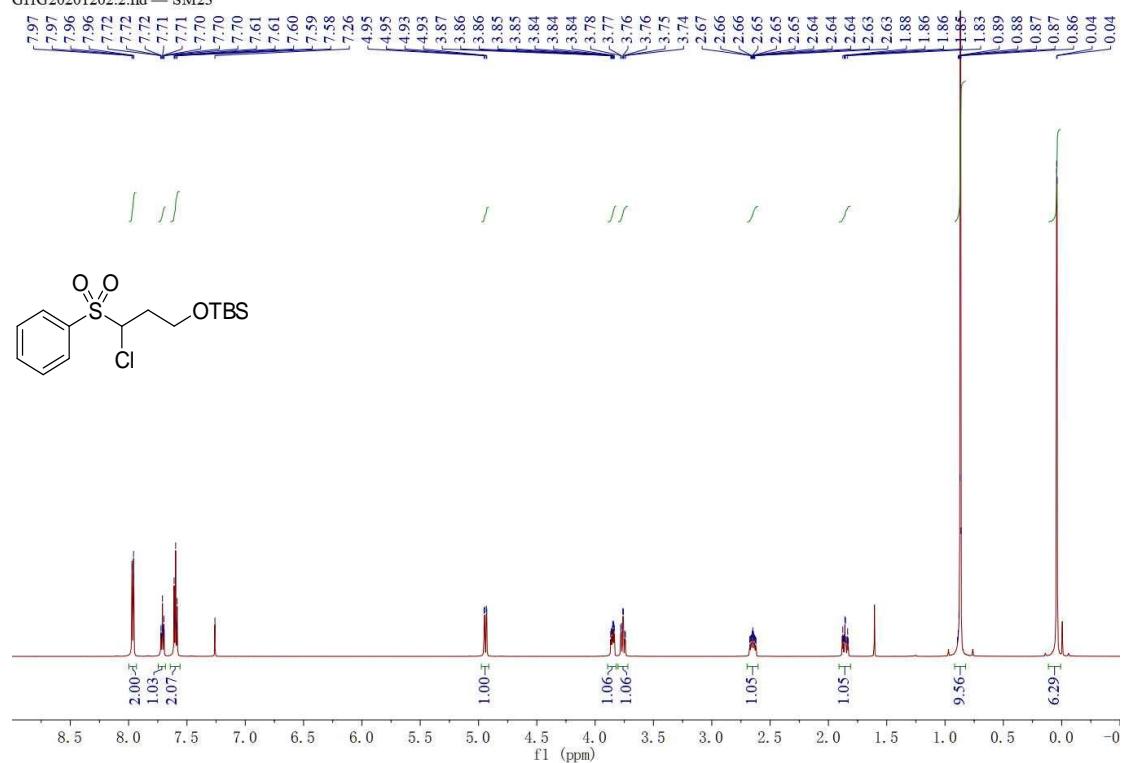
SM18, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200327-C.3.fid —



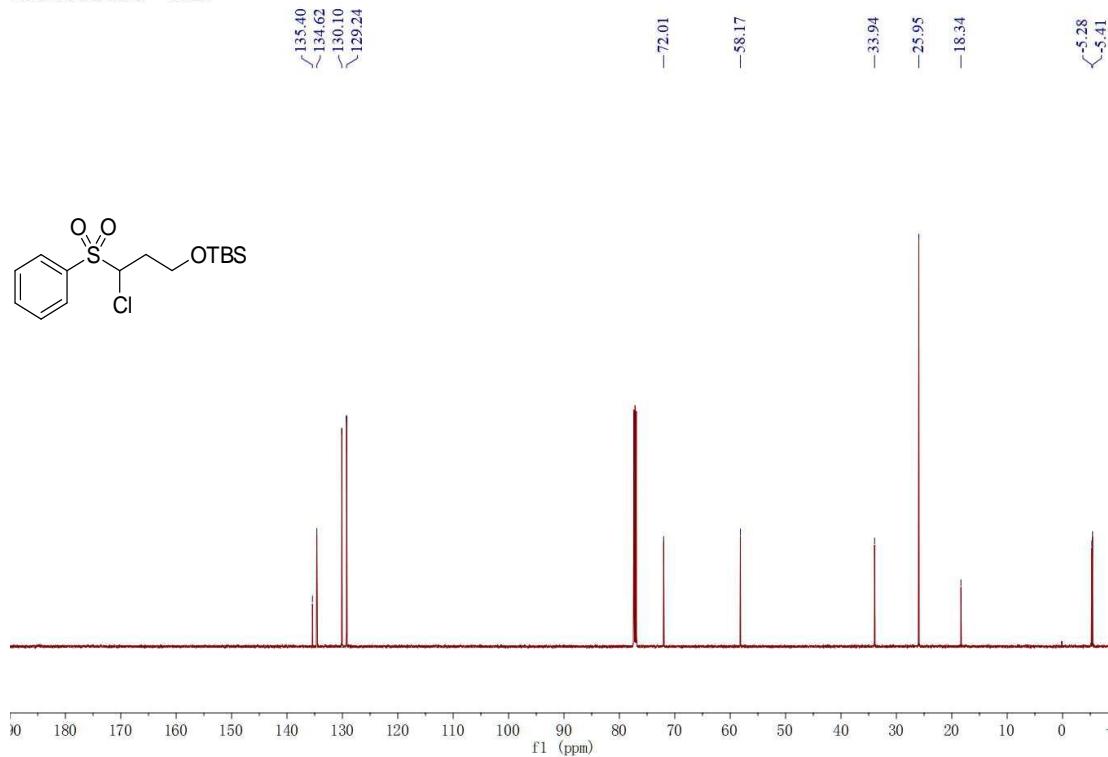
SM19, ^1H -NMR (600 MHZ, CDCl_3)

GHG20201202.2.fid — SM23



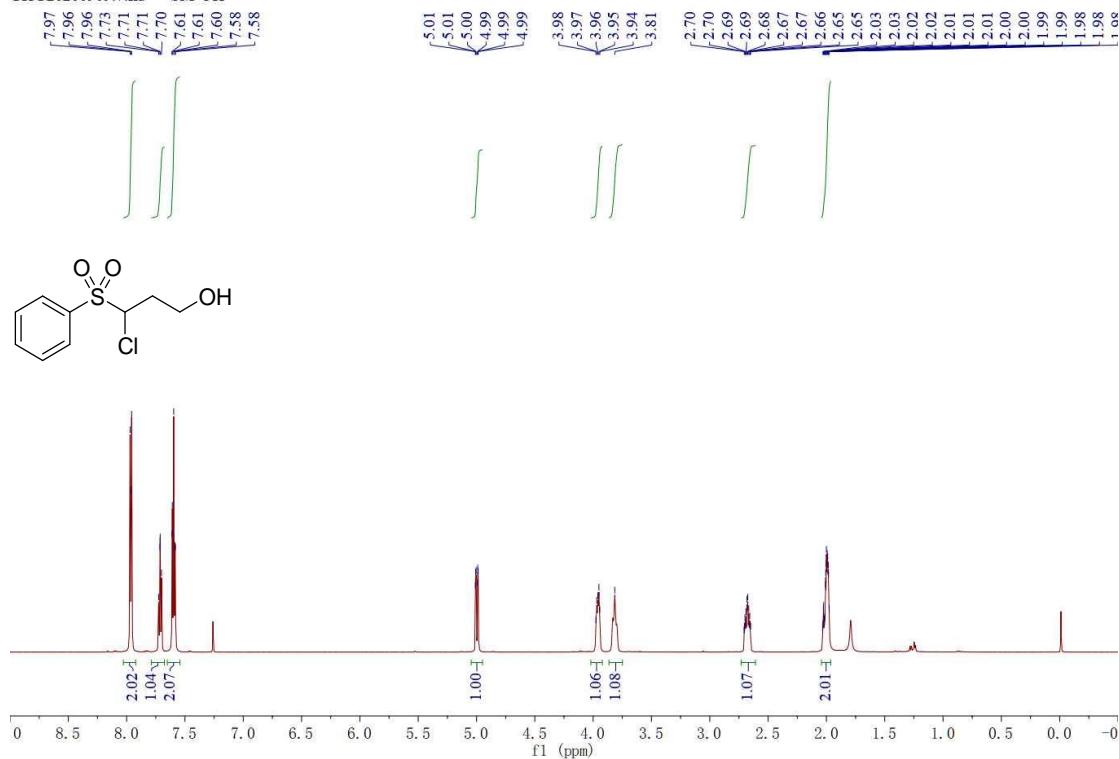
SM19, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201202.6.fid — SM23



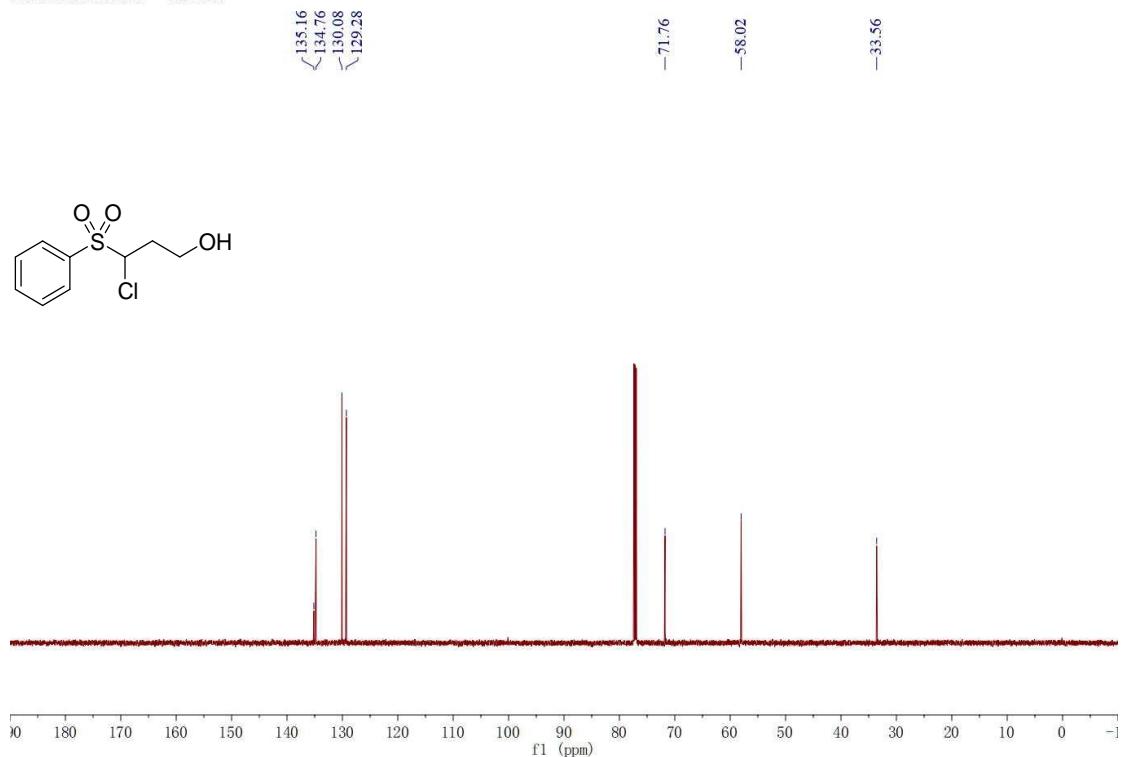
SM20, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200909.7.fid — SM-OH



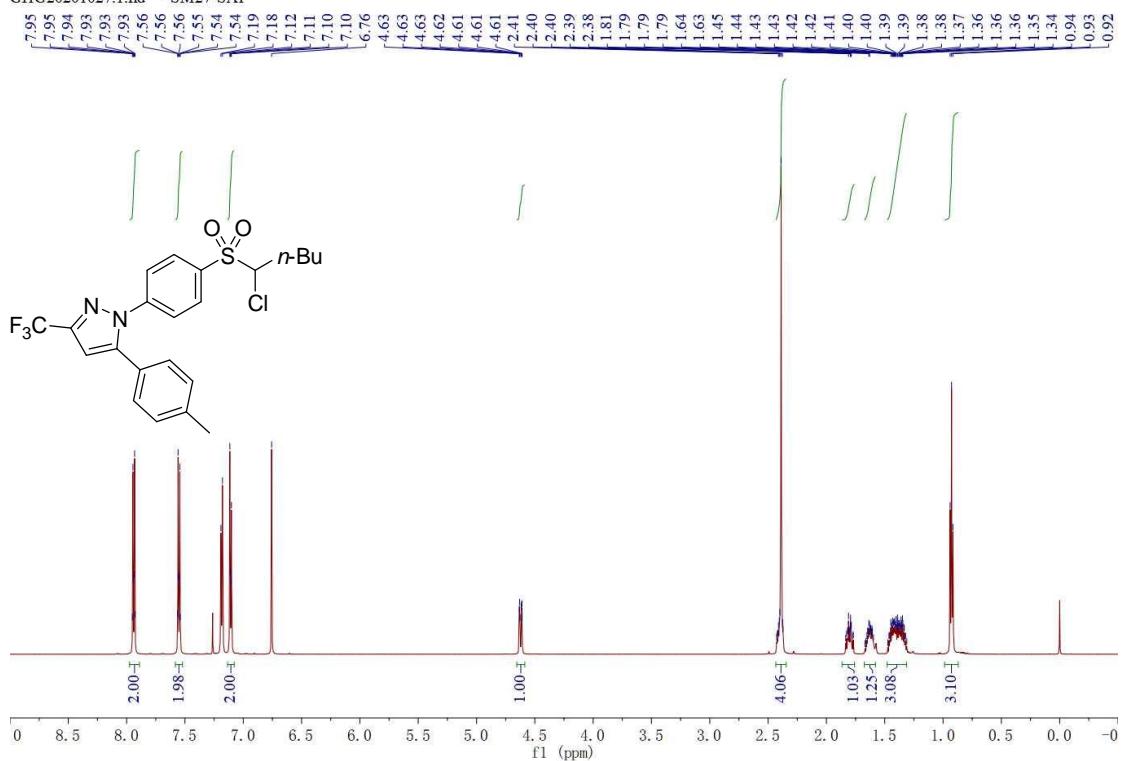
SM20, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200909.8.fid — SM-OH



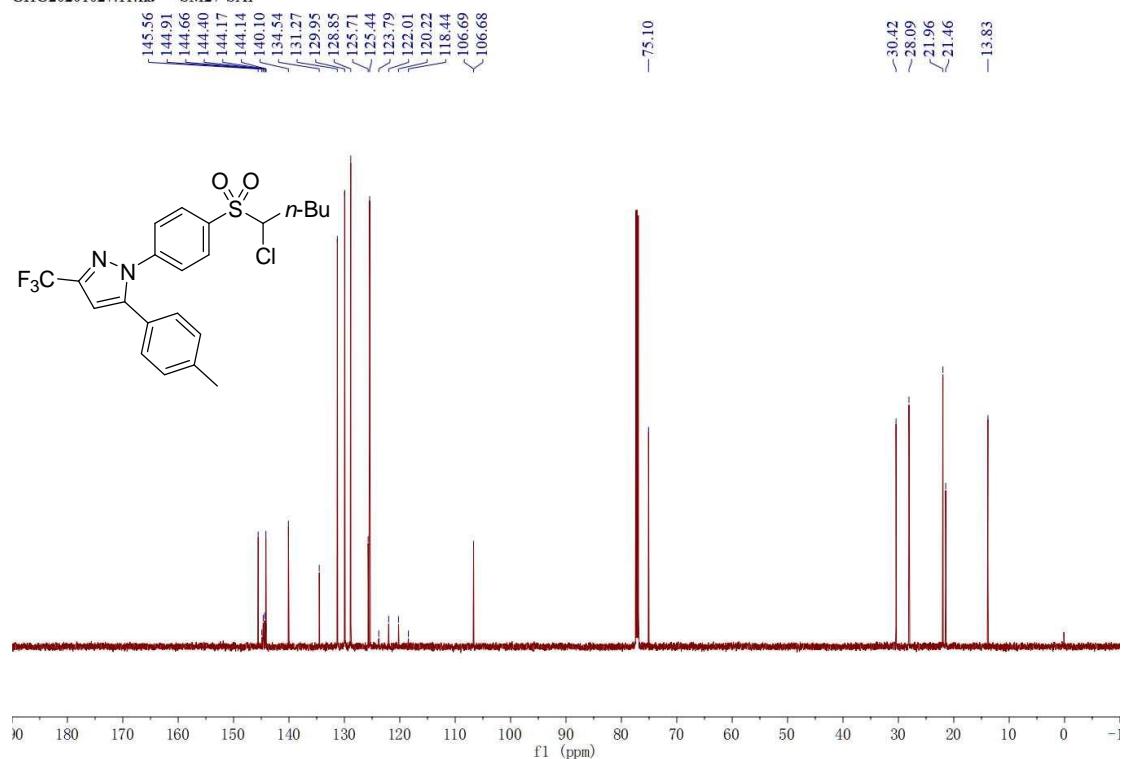
SM21, ^1H -NMR (600 MHZ, CDCl_3)

GHG20201027.1.fid — SM27-SAI



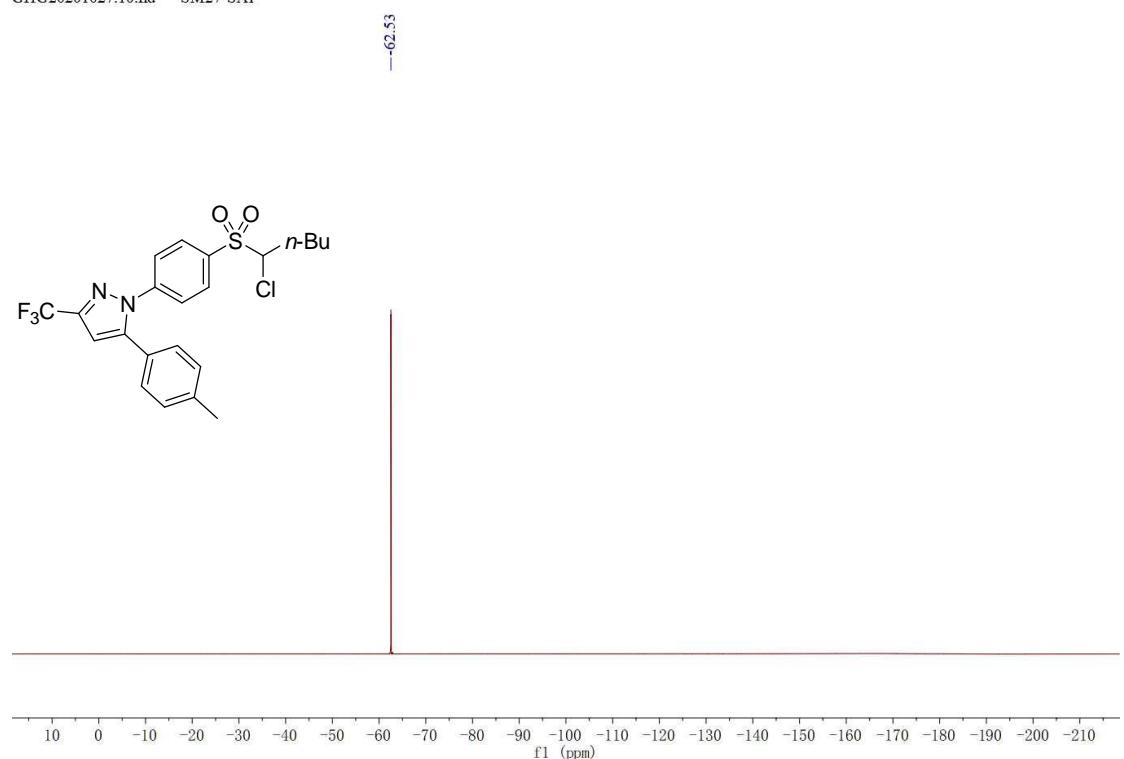
SM21, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201027.11.fid — SM27-SAI



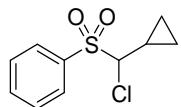
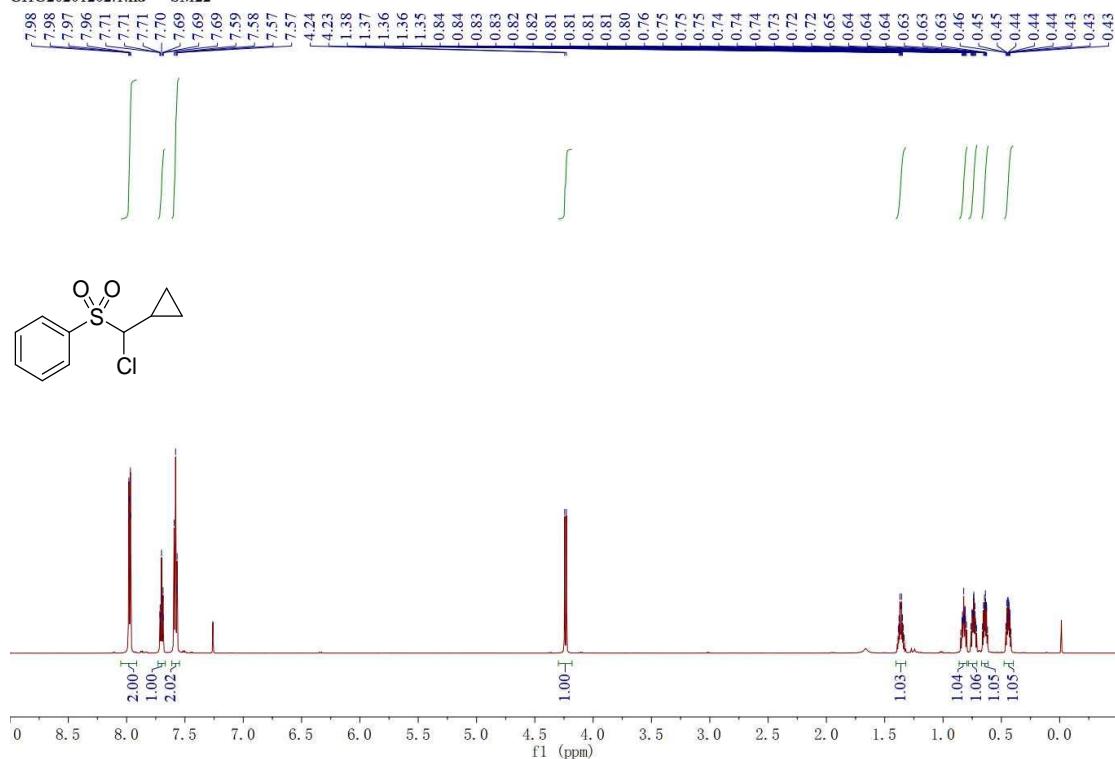
SM21, ^{19}F NMR (565 MHz, CDCl_3)

GHG20201027.10.fid — SM27-SAI



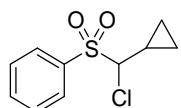
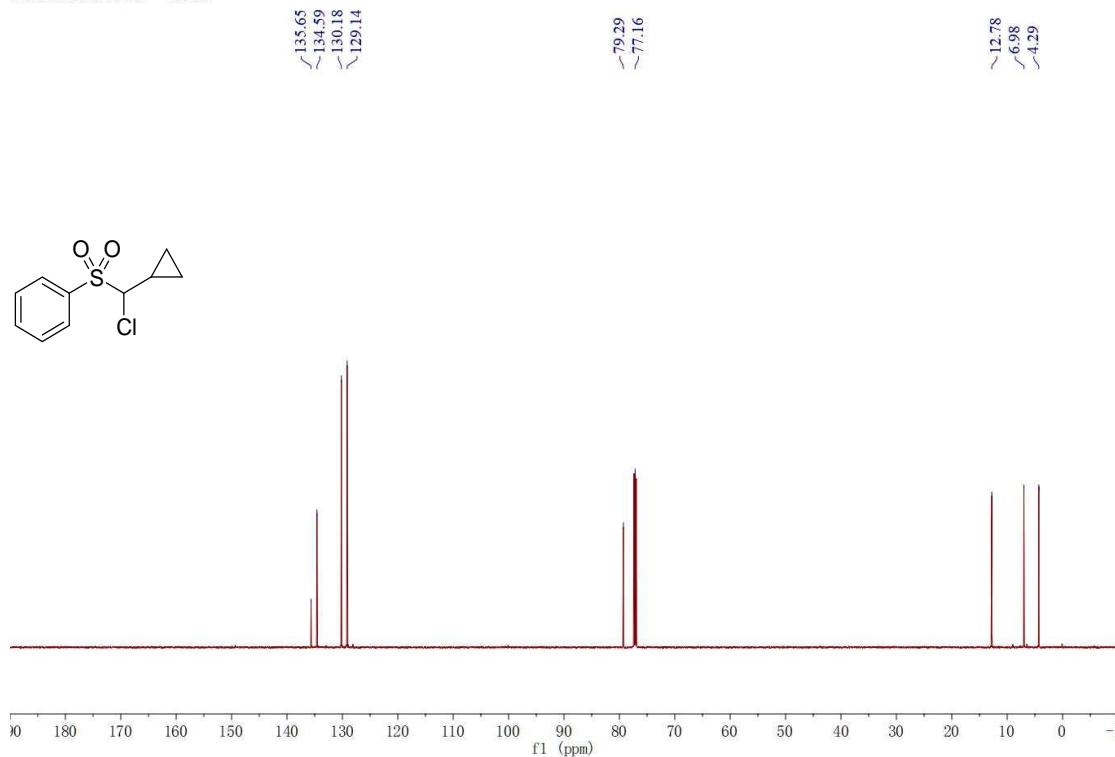
70, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20201202.1.fid — SM22

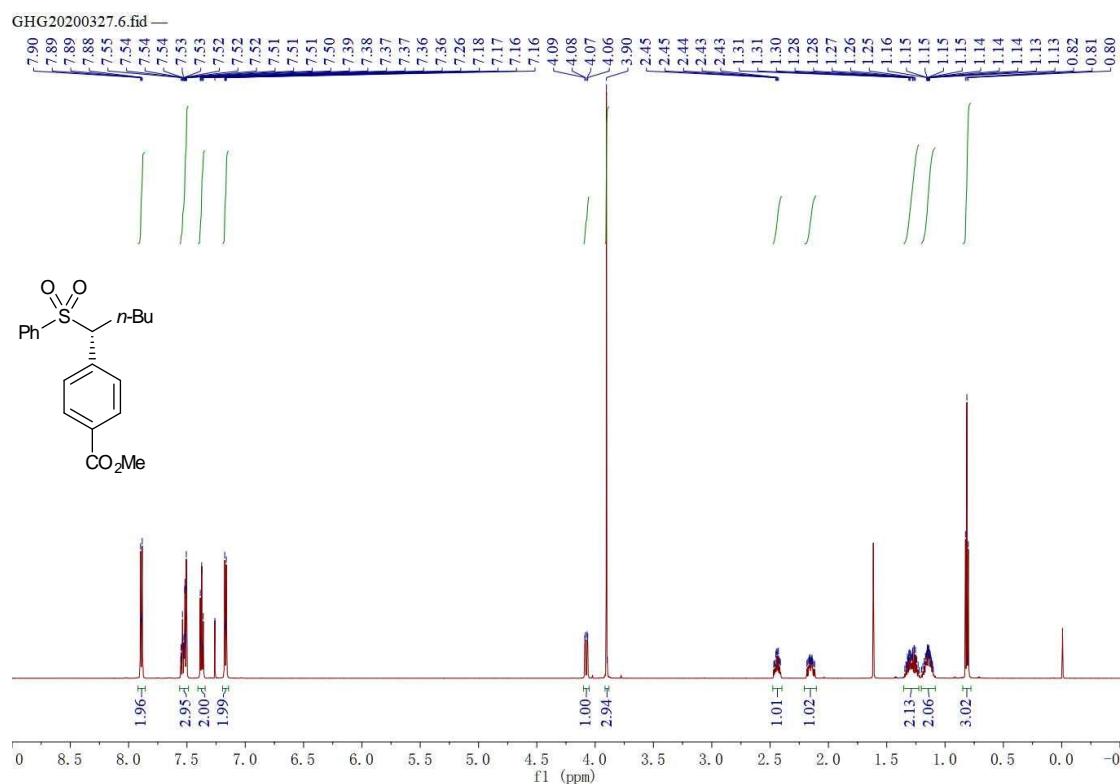


70, ^{13}C NMR (151 MHz, CDCl_3)

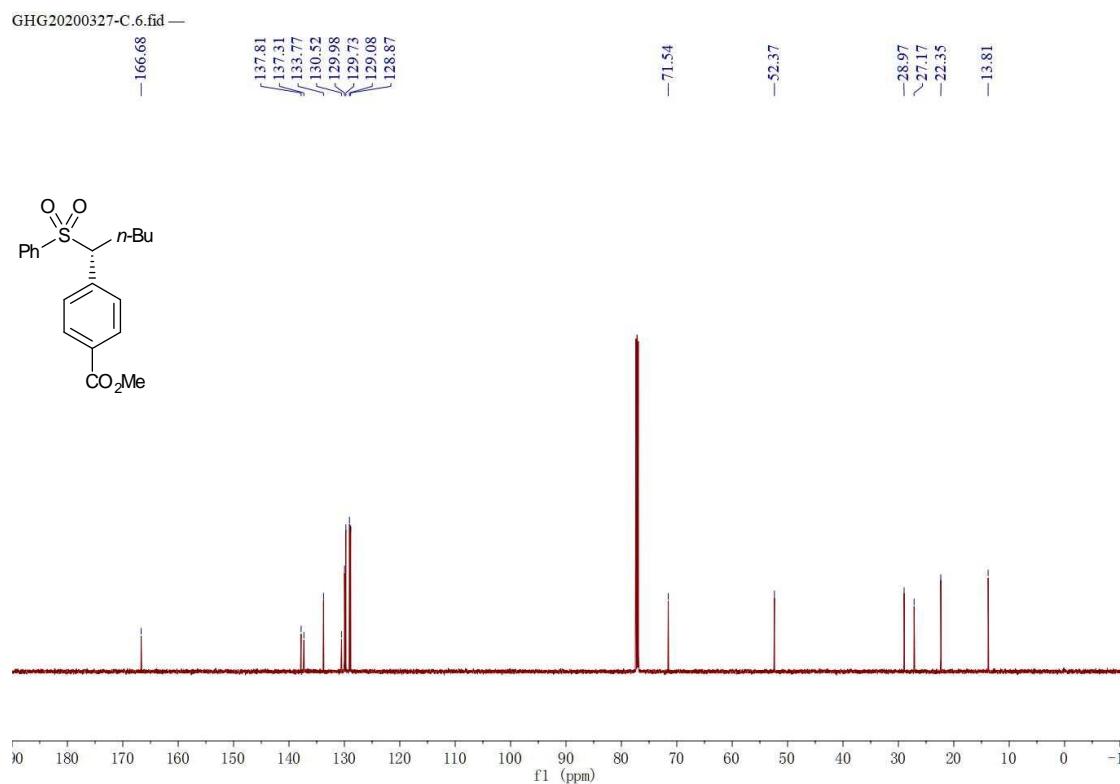
GHG20201202.5.fid — SM22



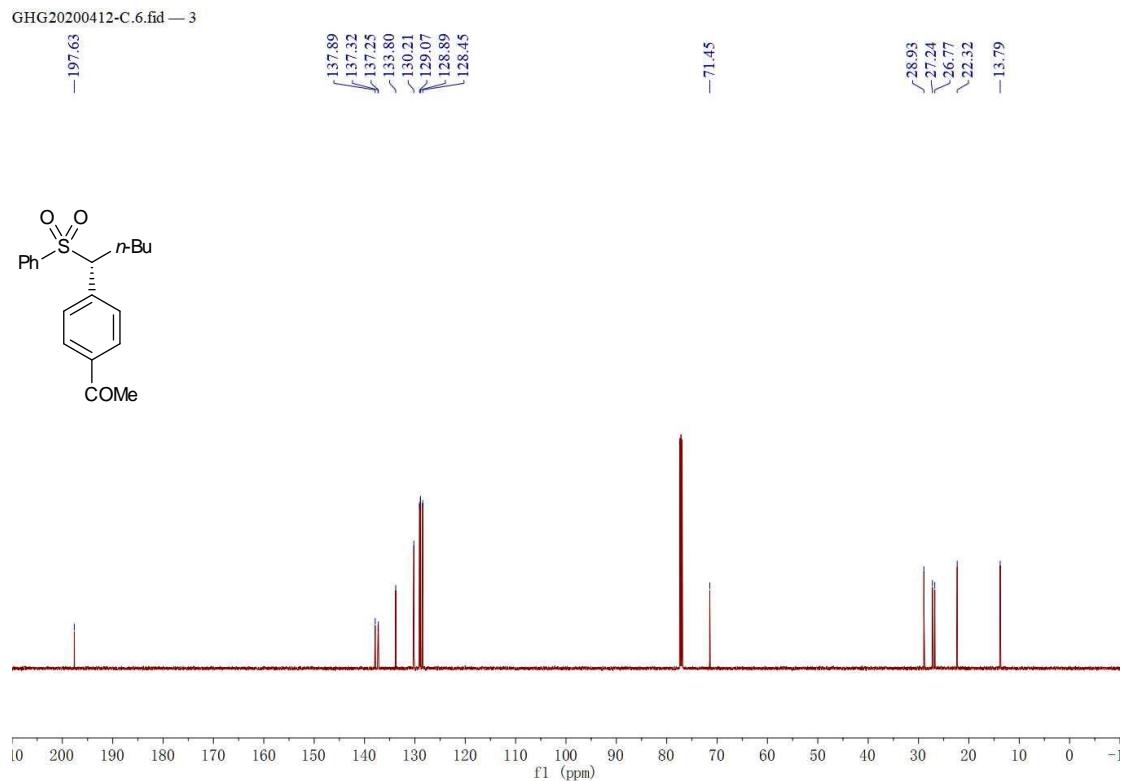
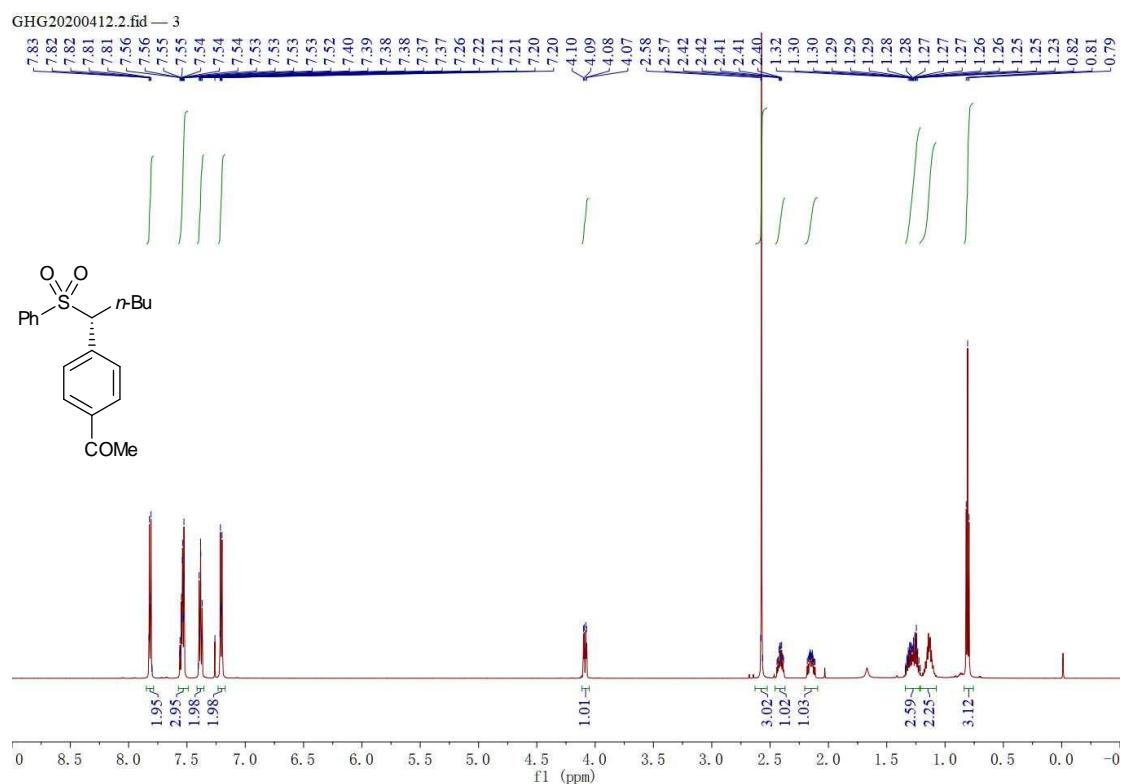
3, ^1H -NMR (600 MHz, CDCl_3)



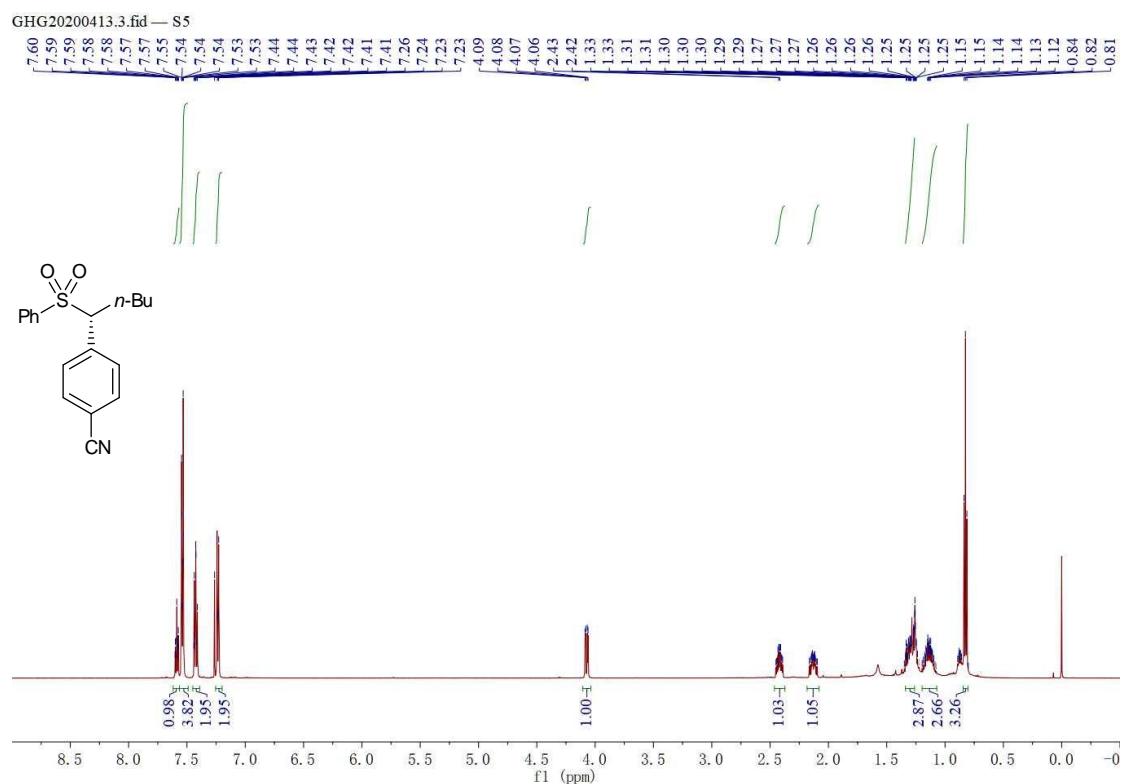
3, ^{13}C NMR (151 MHz, CDCl_3)



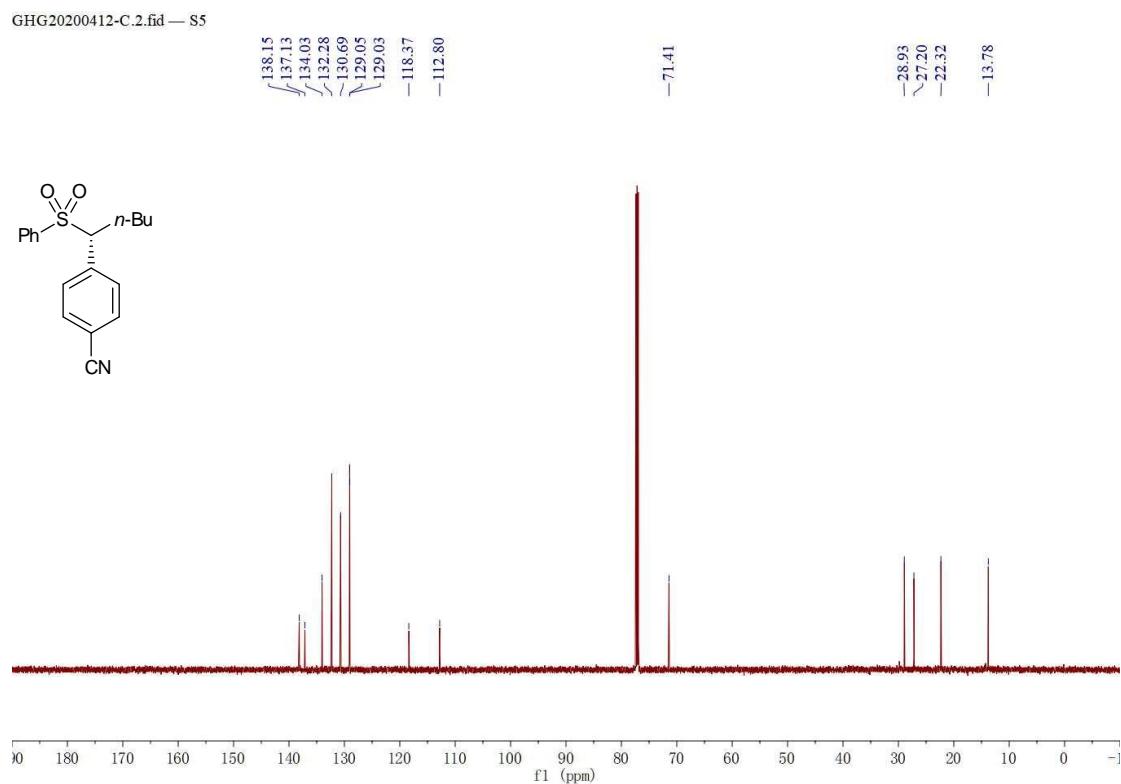
4, ^1H -NMR (600 MHz, CDCl_3)



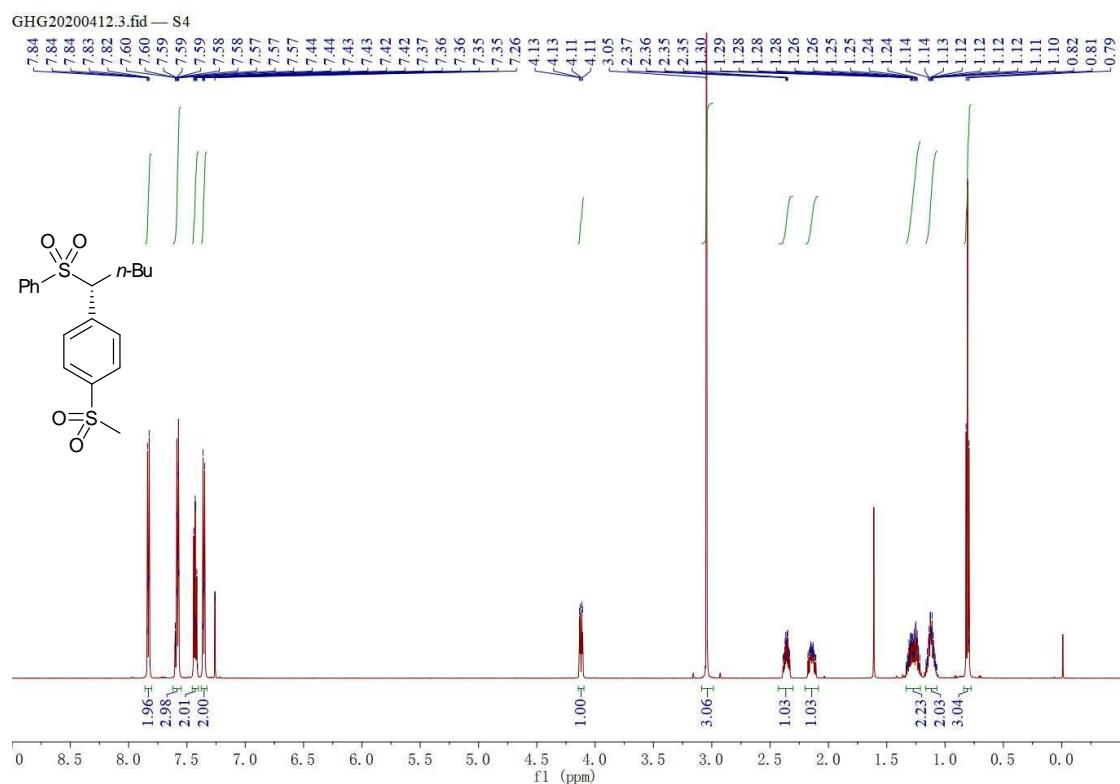
5, ^1H -NMR (600 MHz, CDCl_3)



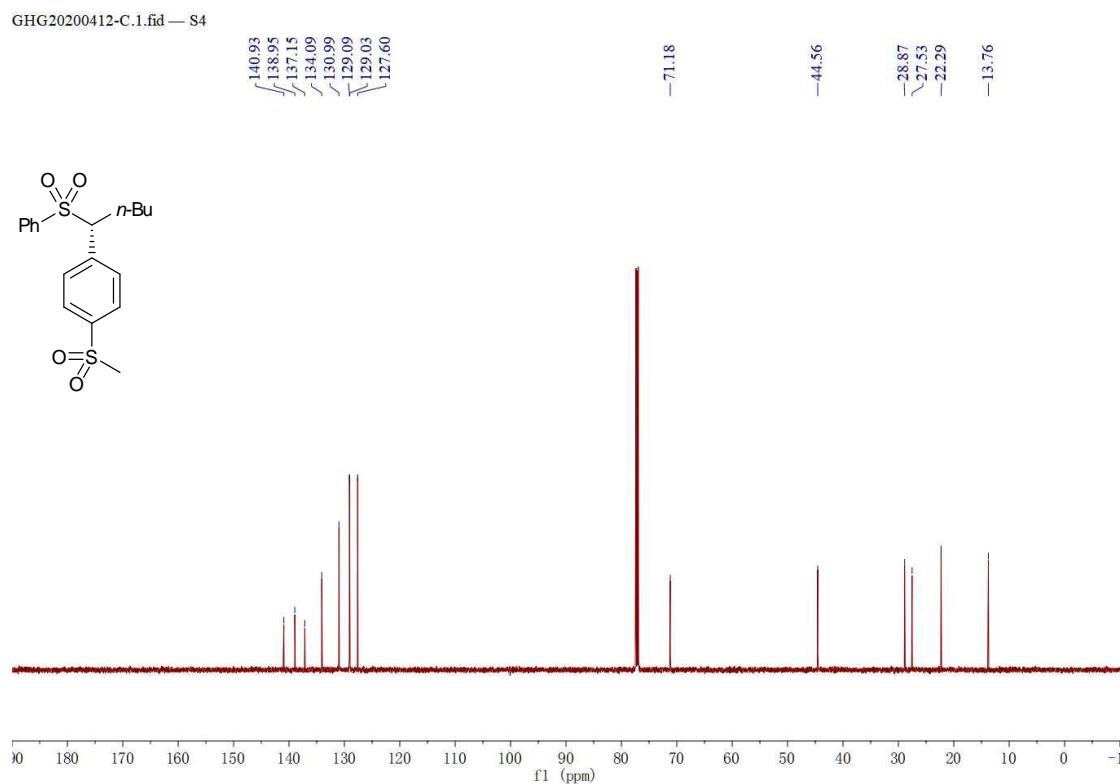
5, ^{13}C NMR (151 MHz, CDCl_3)



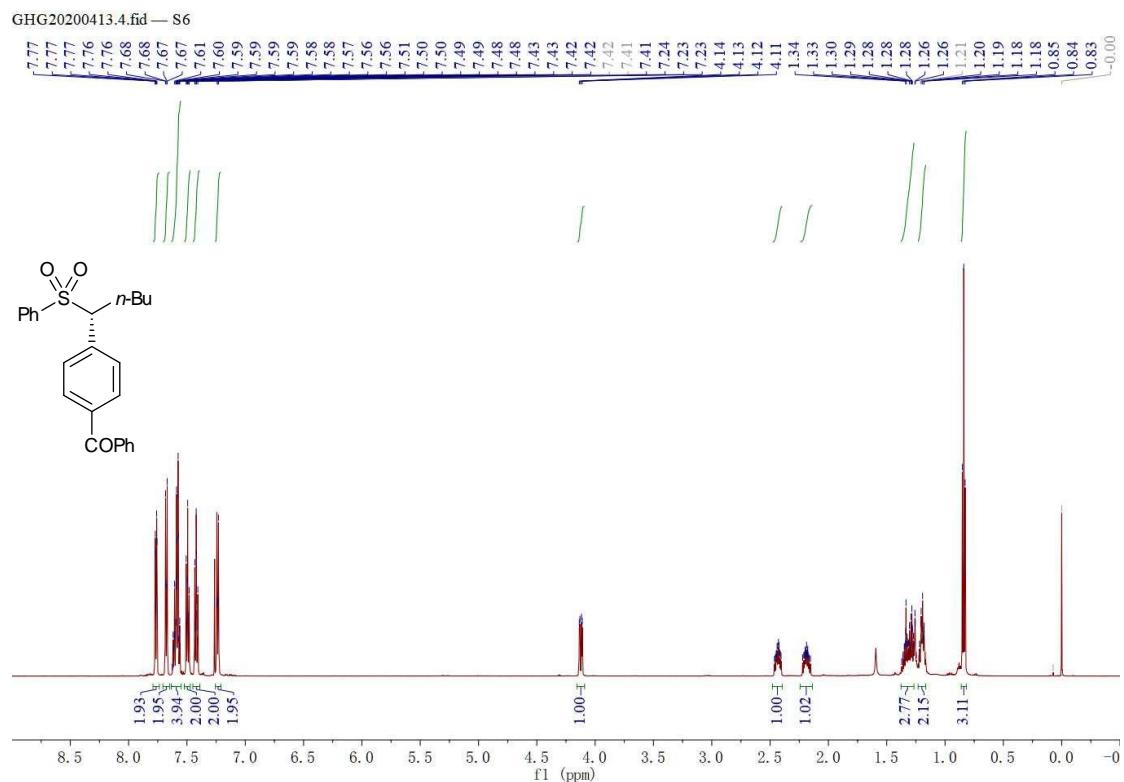
6, ^1H -NMR (600 MHz, CDCl_3)



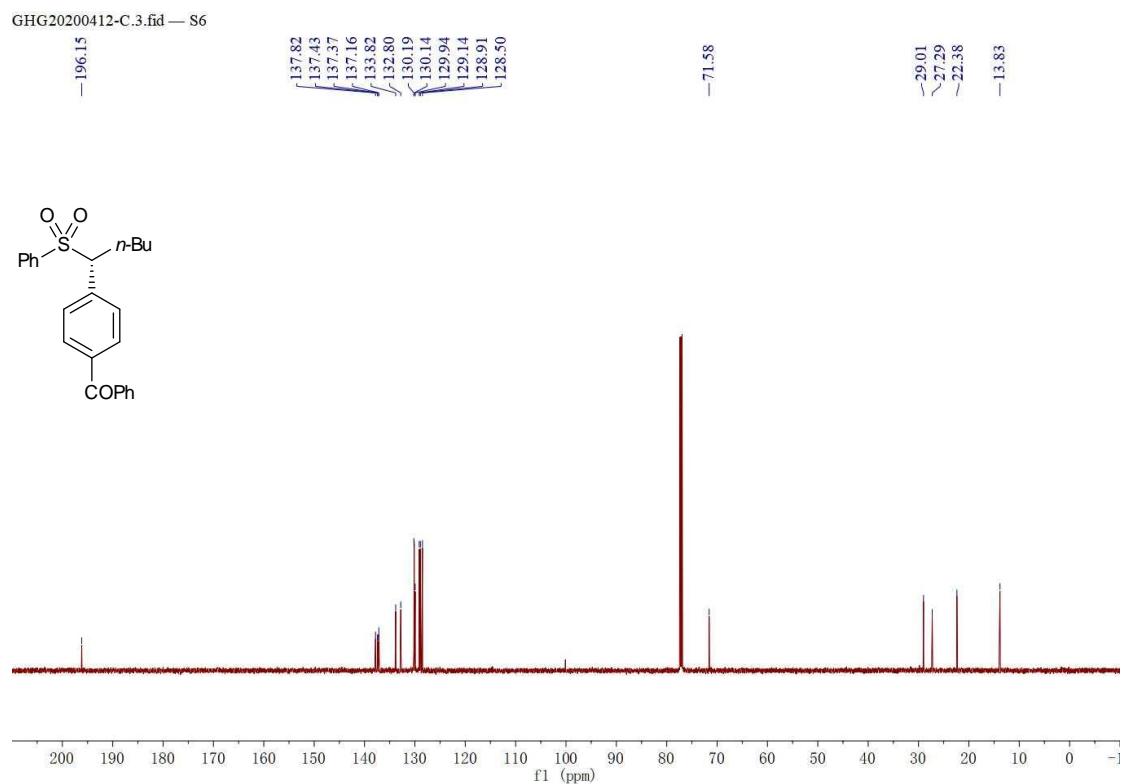
6, ^{13}C NMR (151 MHz, CDCl_3)



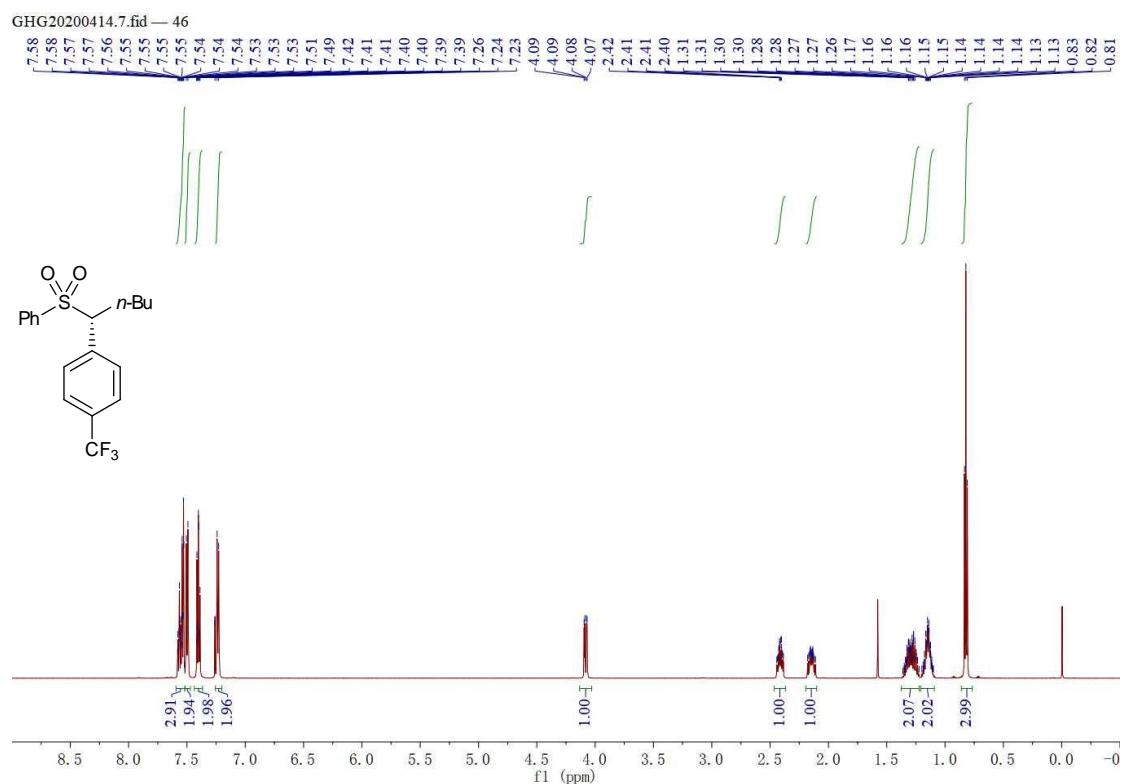
7, ^1H -NMR (600 MHz, CDCl_3)



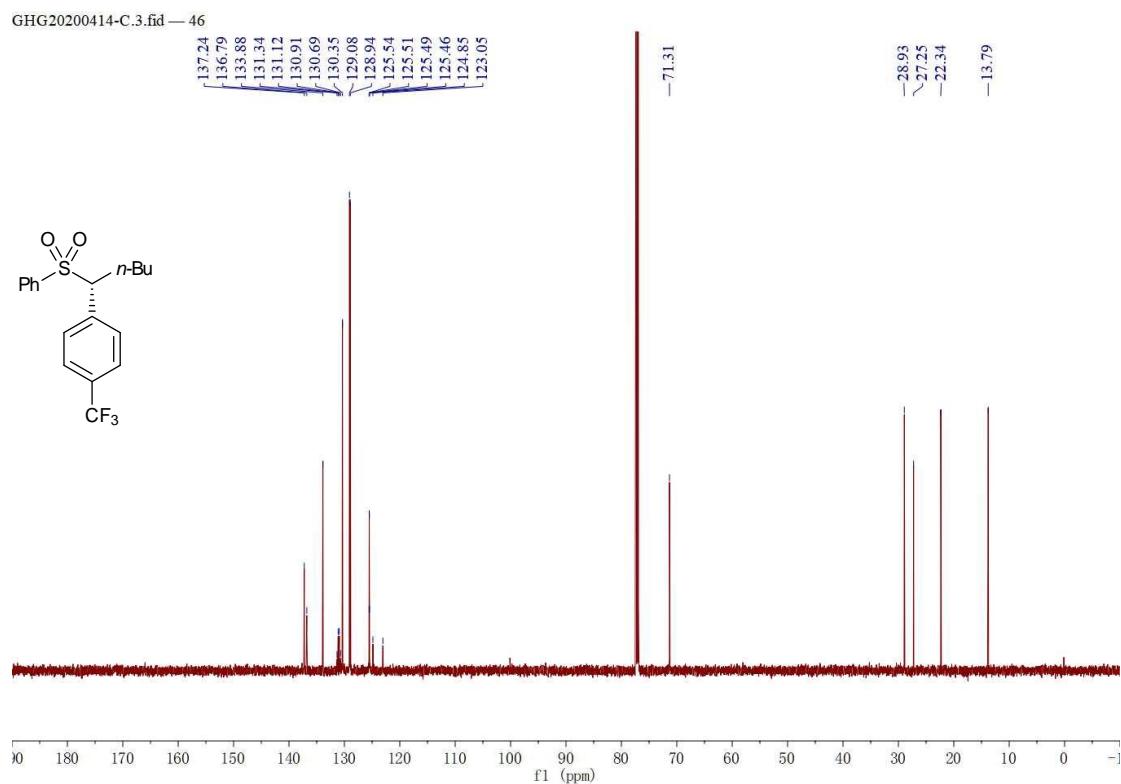
7, ^{13}C NMR (151 MHz, CDCl_3)



8, ^1H -NMR (600 MHz, CDCl_3)

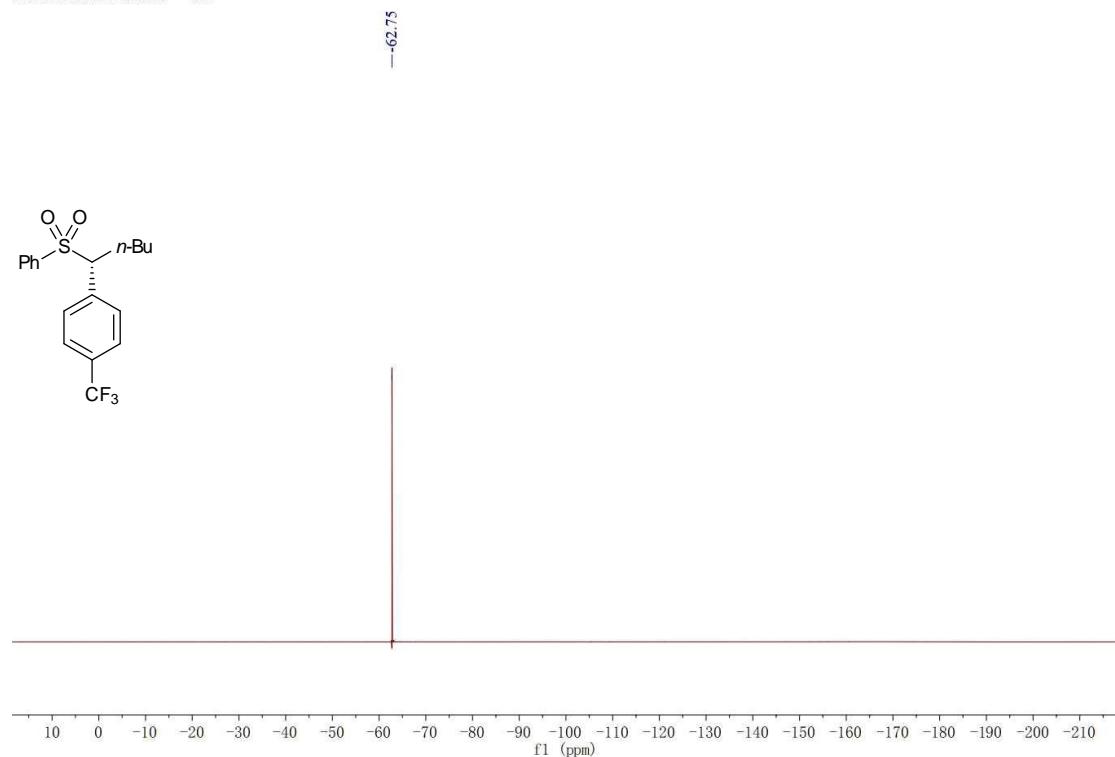


8, ^{13}C NMR (151 MHz, CDCl_3)



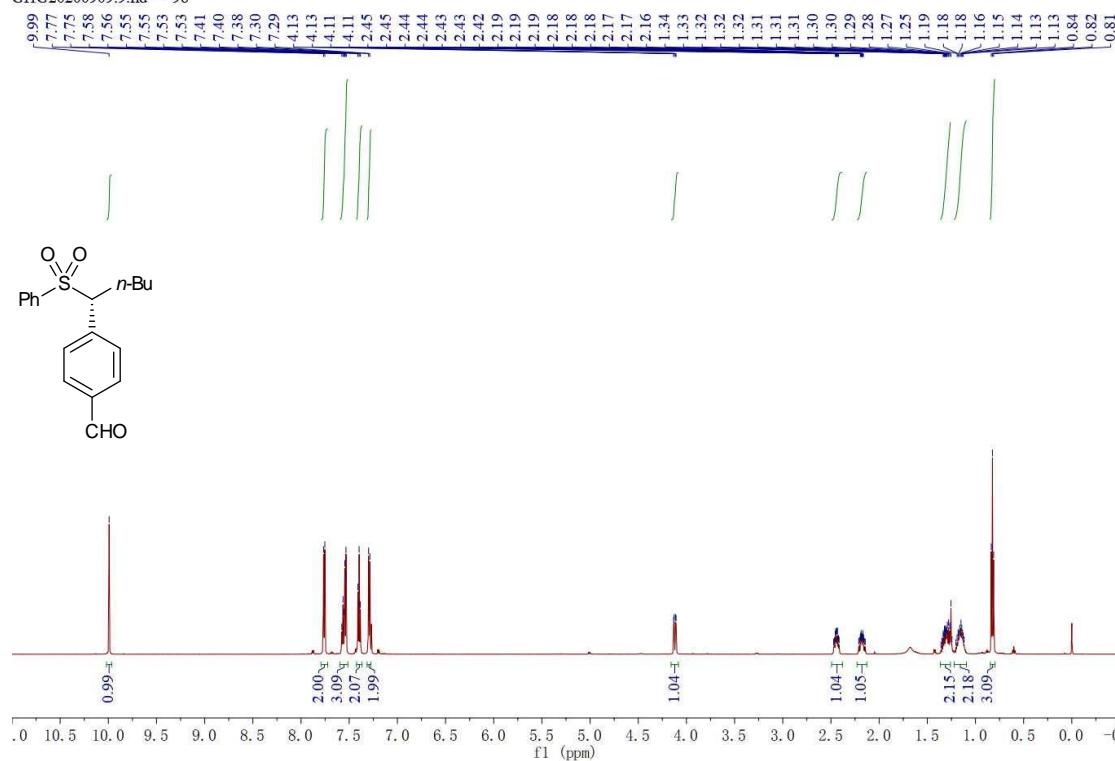
8, ^{19}F NMR (567 MHz, CDCl_3)

GHG20200414-C.4.fid — 46F



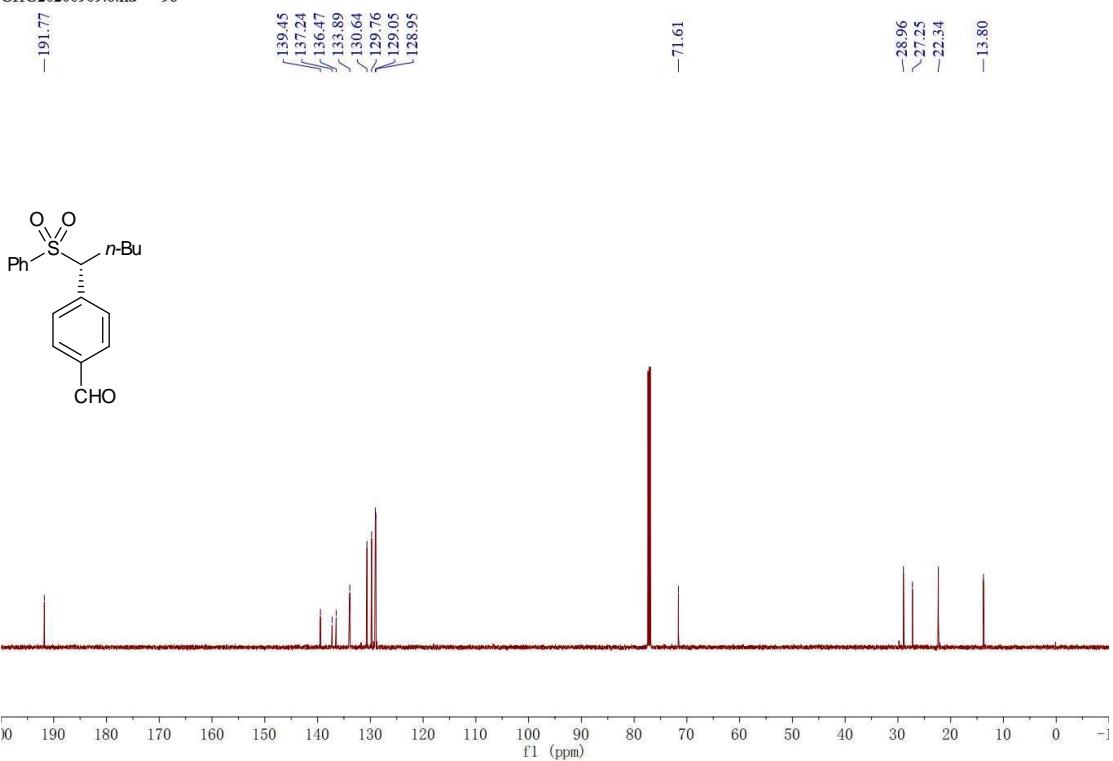
9, ^1H -NMR (600 MHZ, CDCl_3)

GHG20200909.9.fid — 98



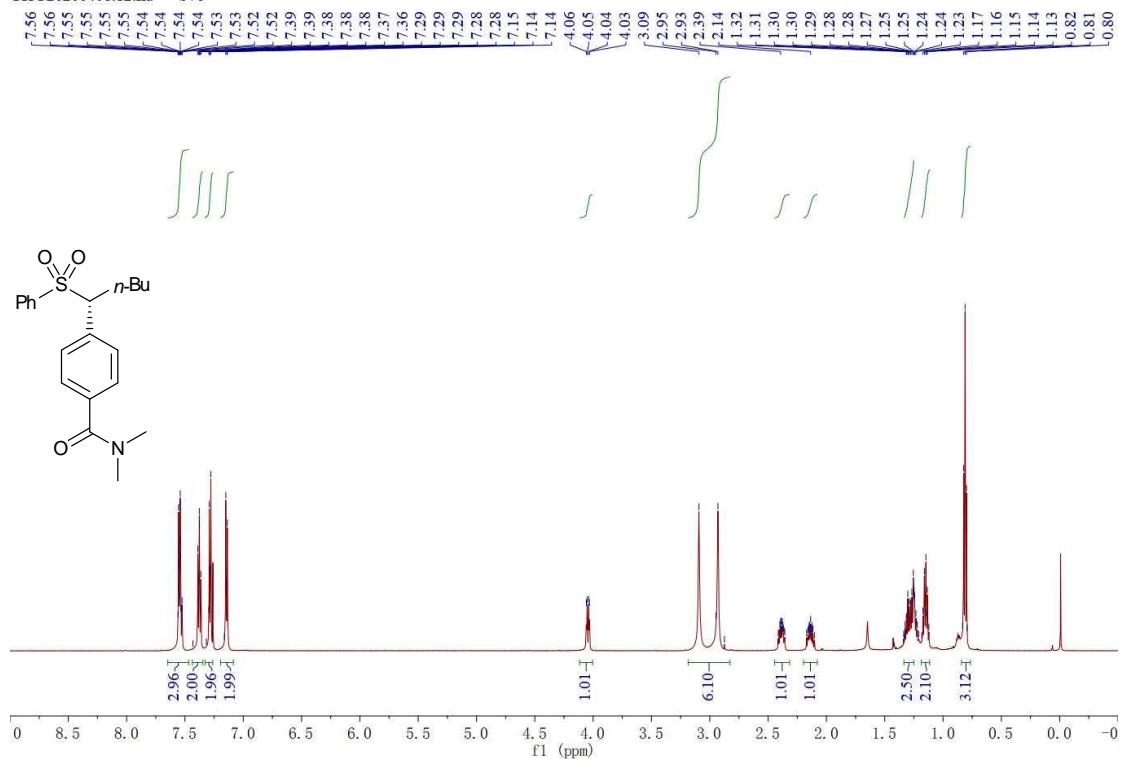
9, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200909.6.fid — 98



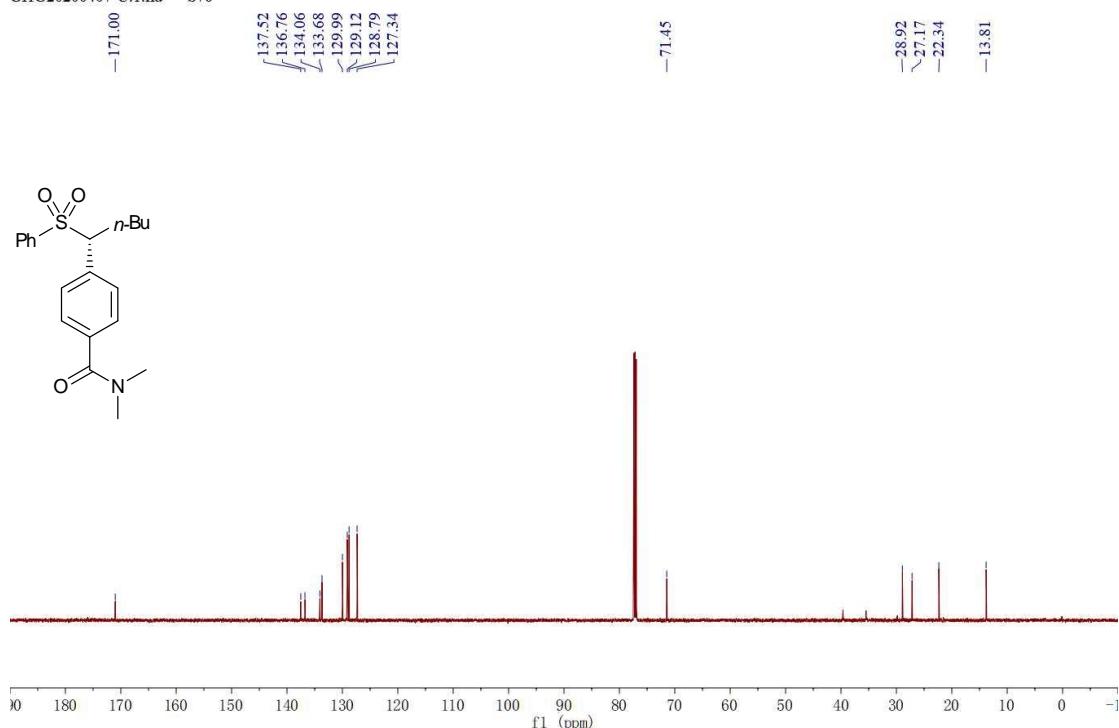
10, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200408.12.fid — S76



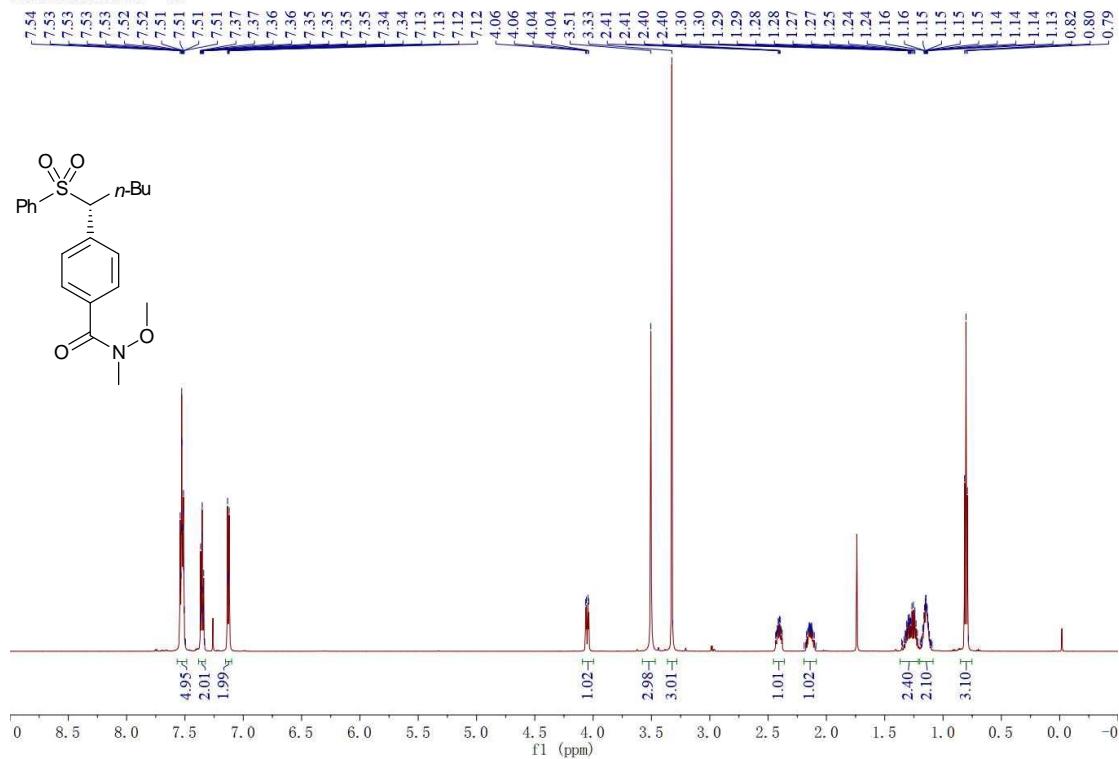
10, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200407-C.1.fid — S76



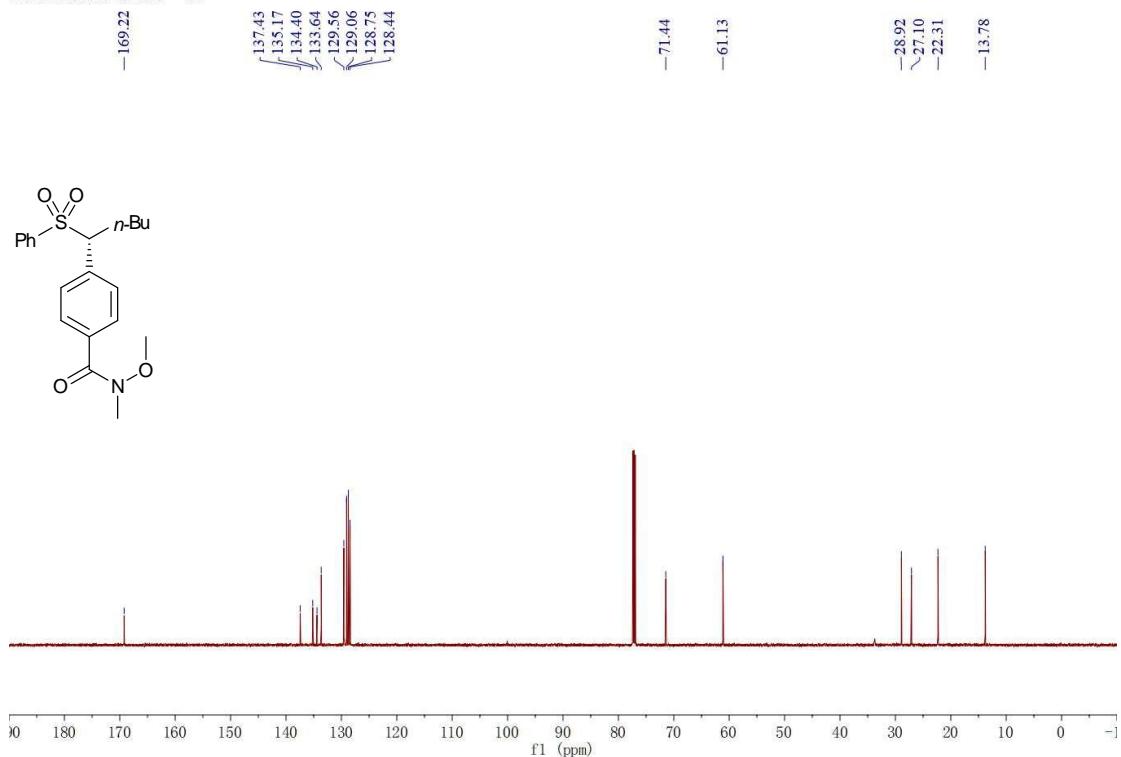
11, ^1H -NMR (600 MHz, CDCl_3)

GHG20200409.5.fid — 31



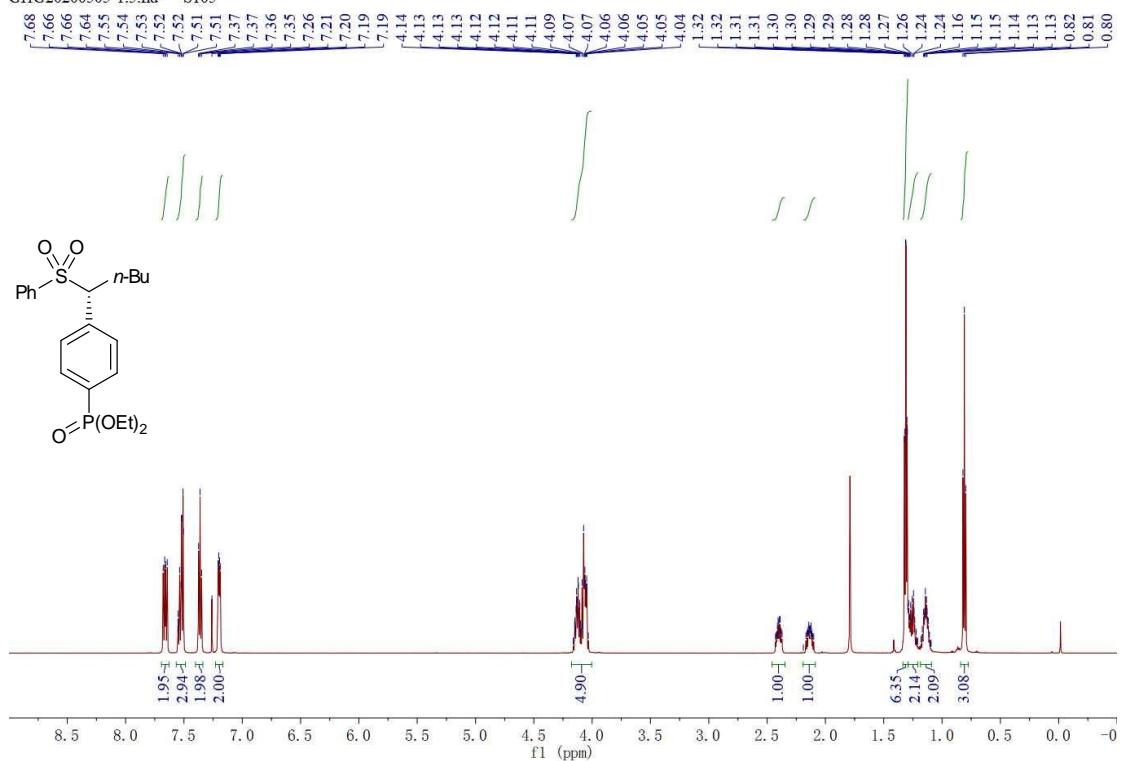
11, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200409-C.6.fid — 31



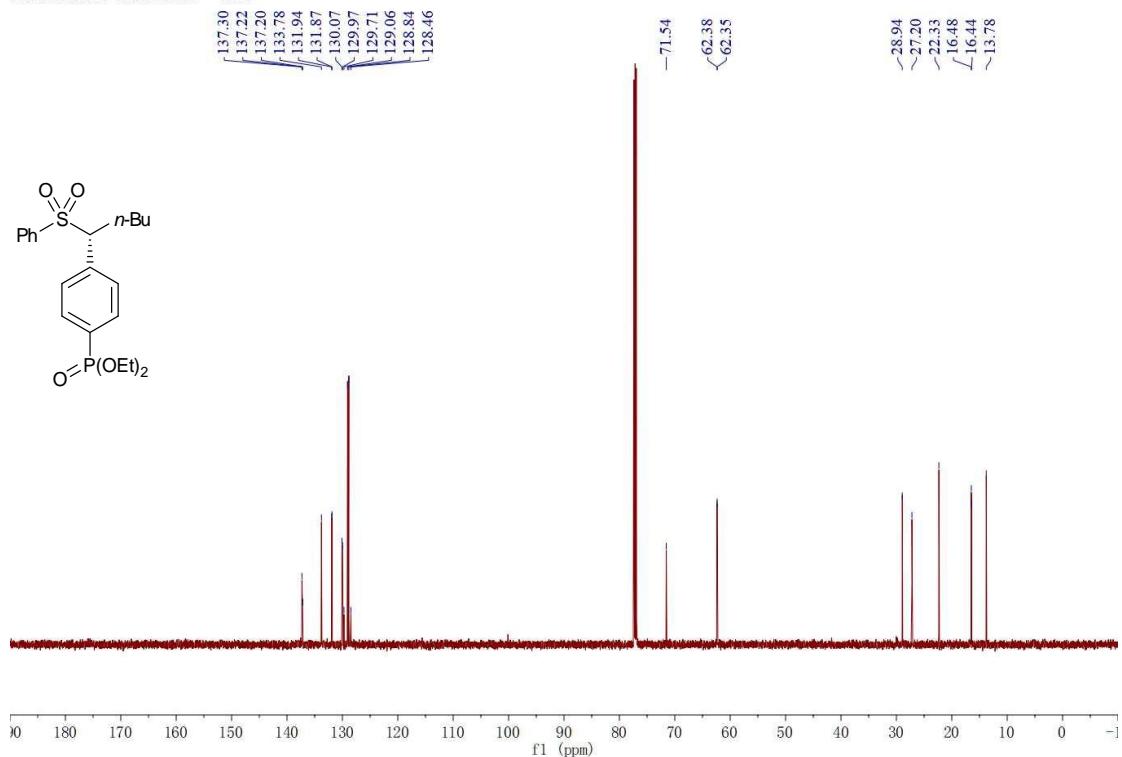
12, ^1H -NMR (600 MHz, CDCl_3)

GHG20200505-1.5.fid — S105



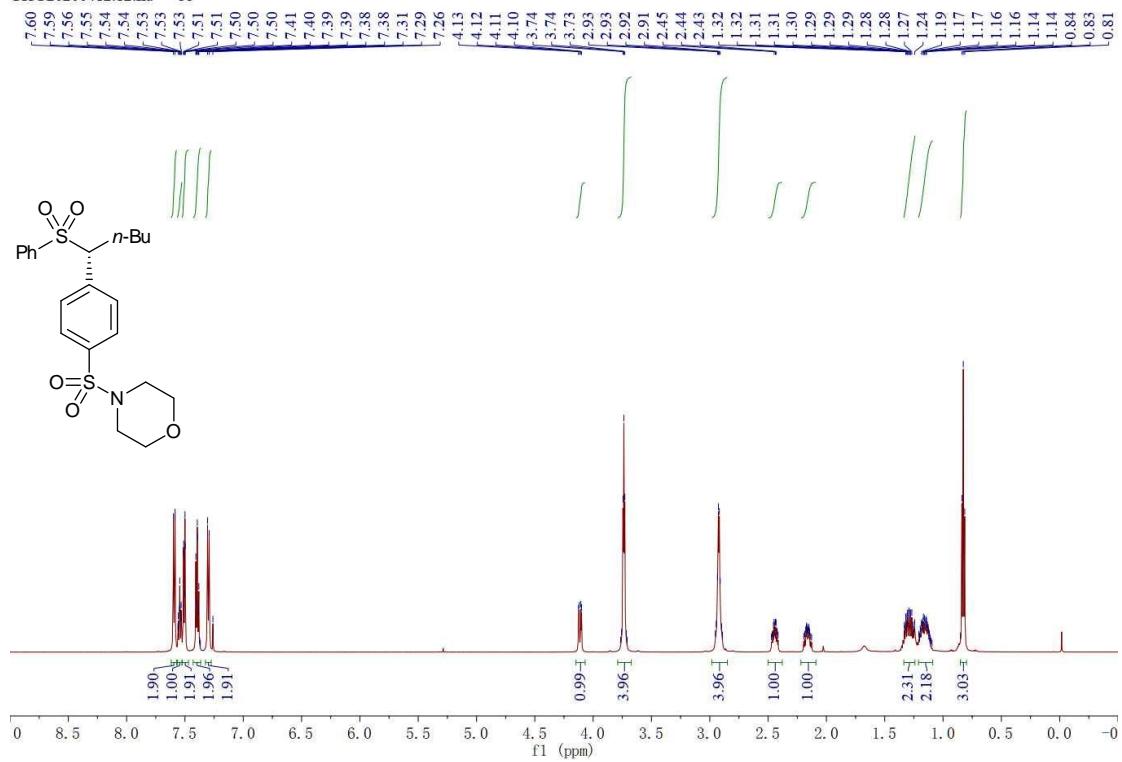
12, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200505-S105C.8.fid — S105



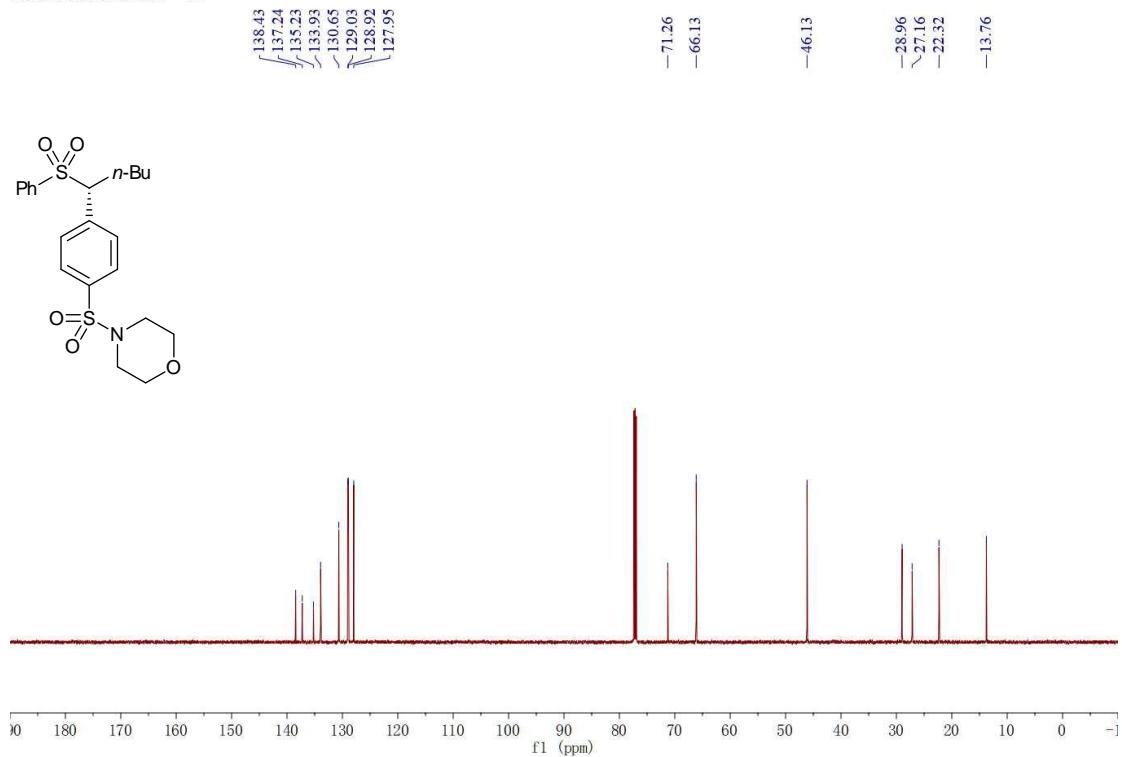
13, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200412.12.fid — 33



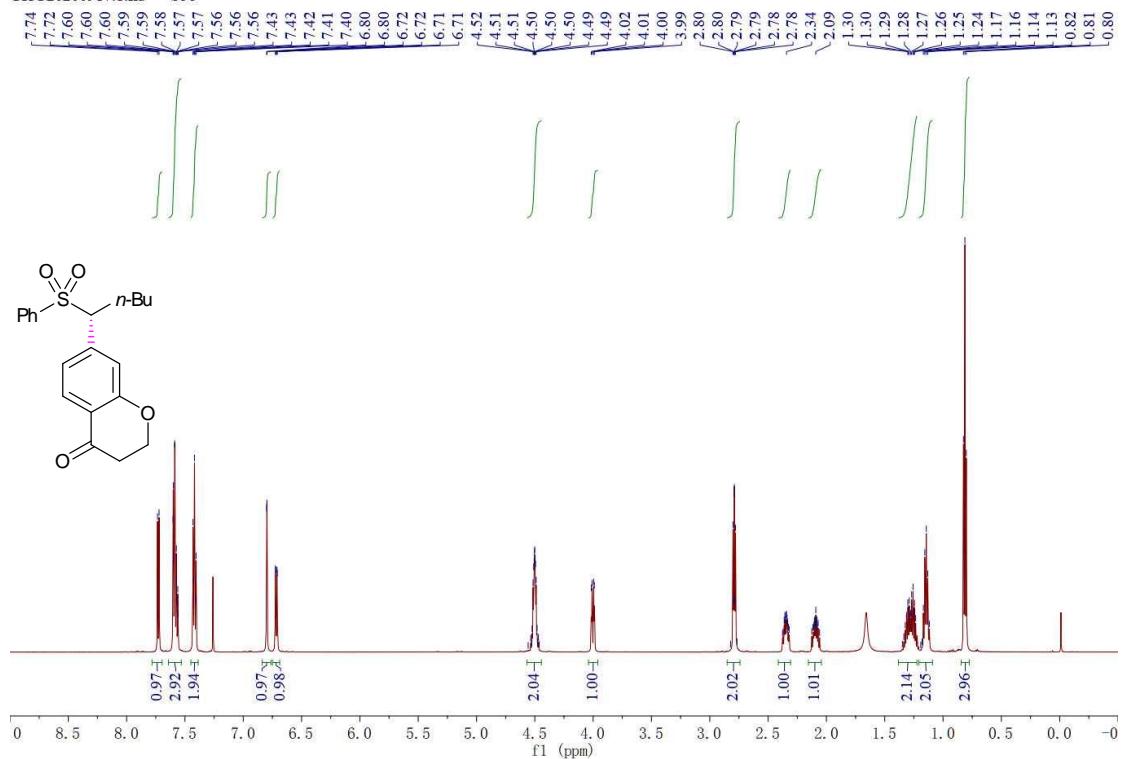
13, ¹³C NMR (151 MHz, CDCl₃)

GHG20200412-C.9.fid — 33

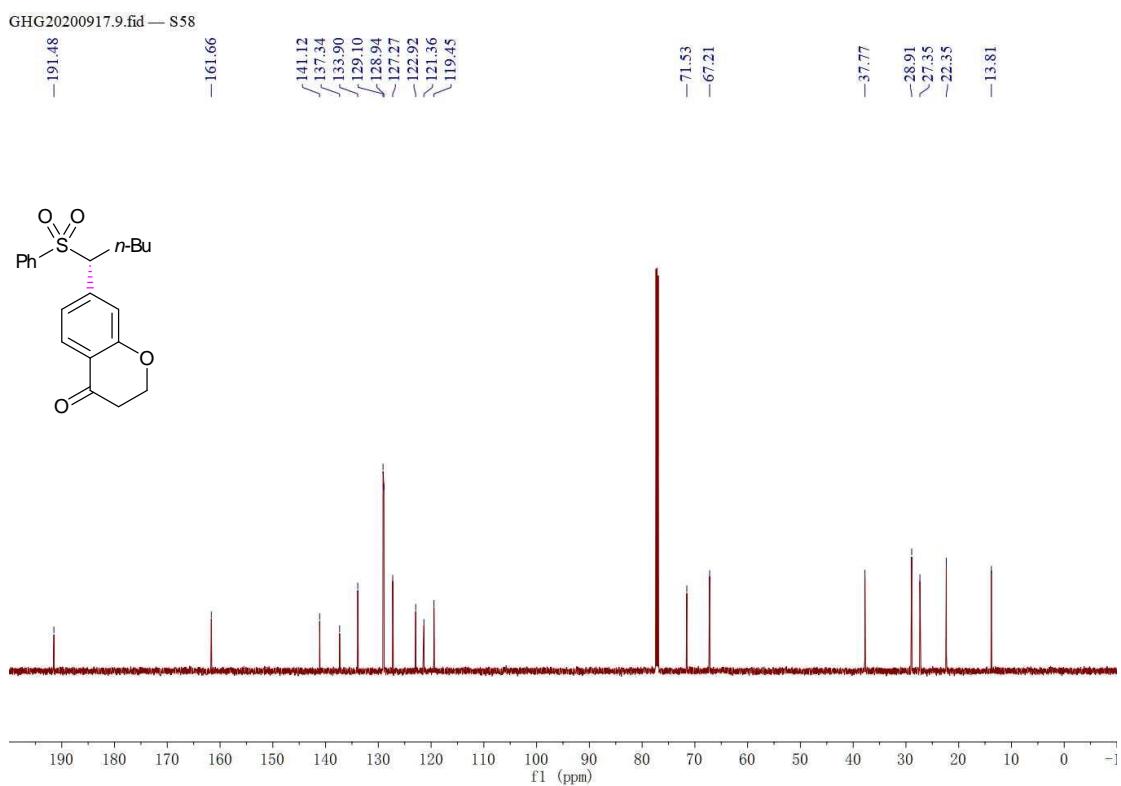


14, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

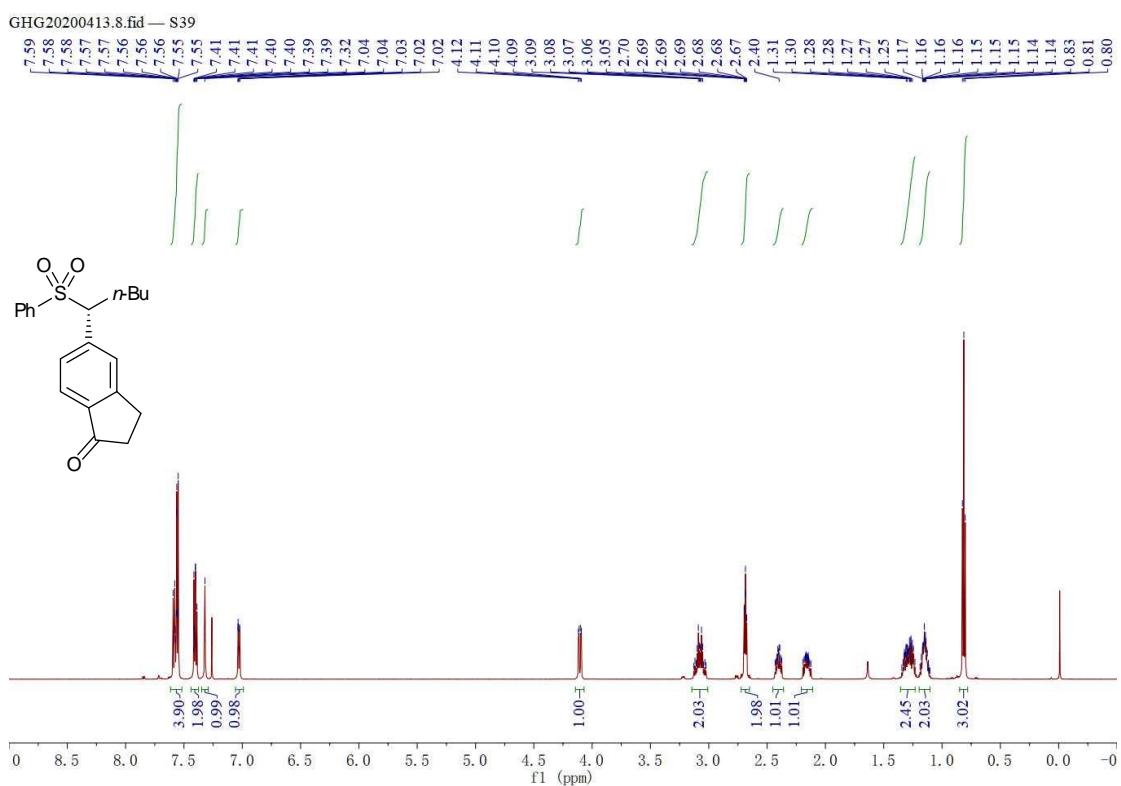
GHG20200917.1.fid — S58



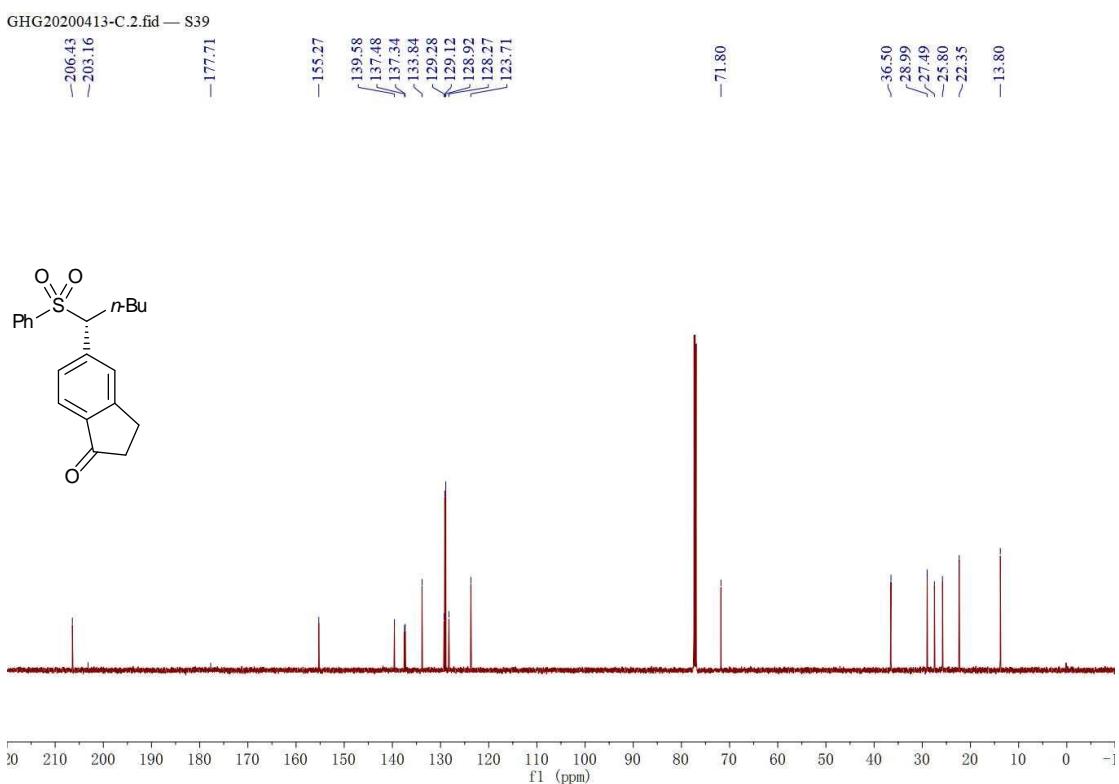
14, ^{13}C NMR (151 MHz, CDCl_3)



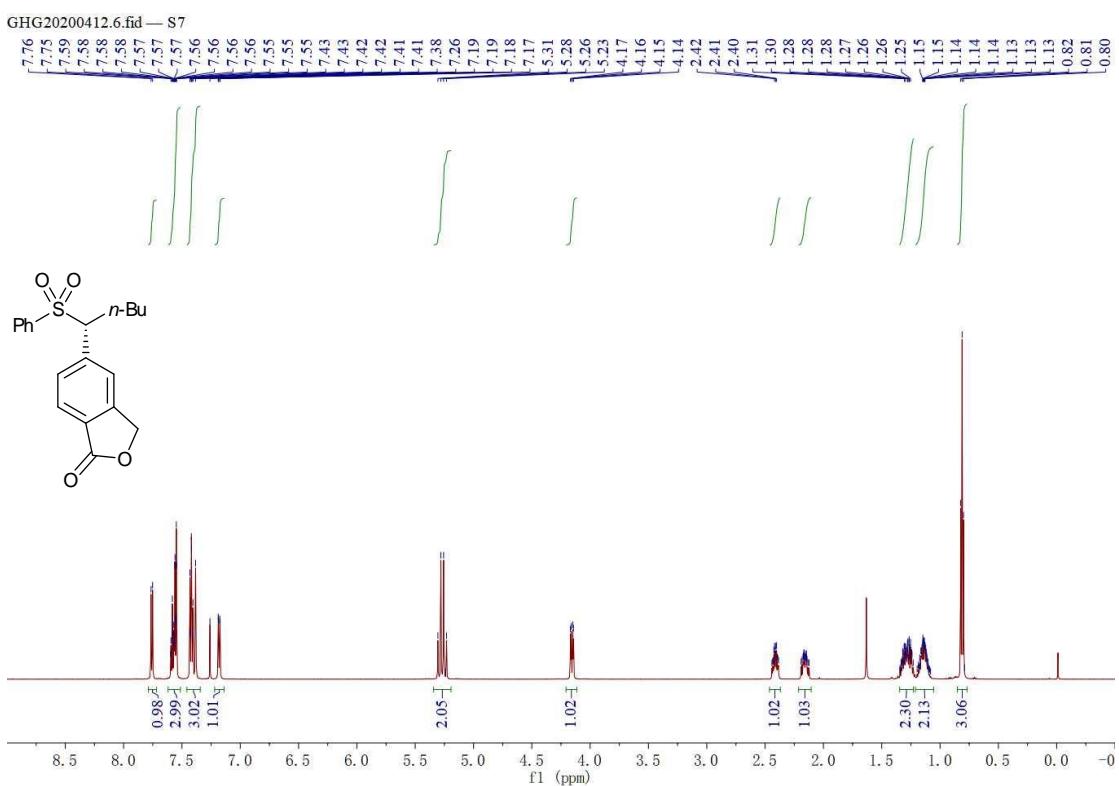
15, ^1H -NMR (600 MHz, CDCl_3)



15, ^{13}C NMR (151 MHz, CDCl_3)

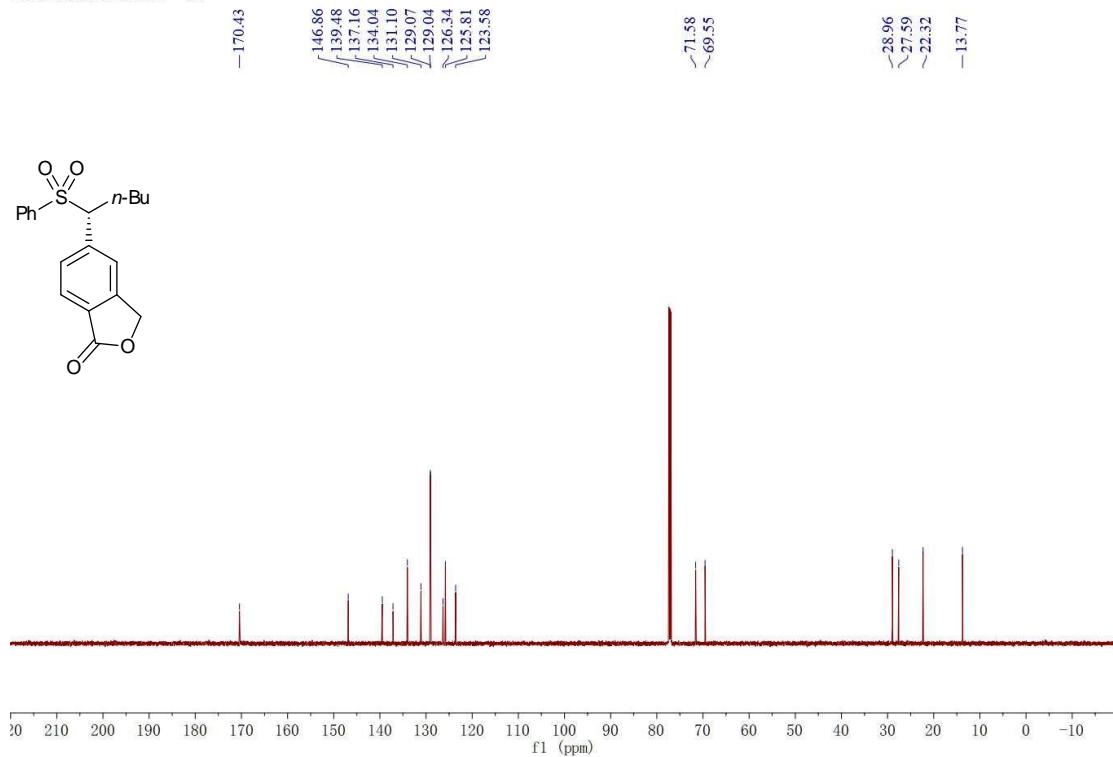


16, ^1H -NMR (600 MHz, CDCl_3)



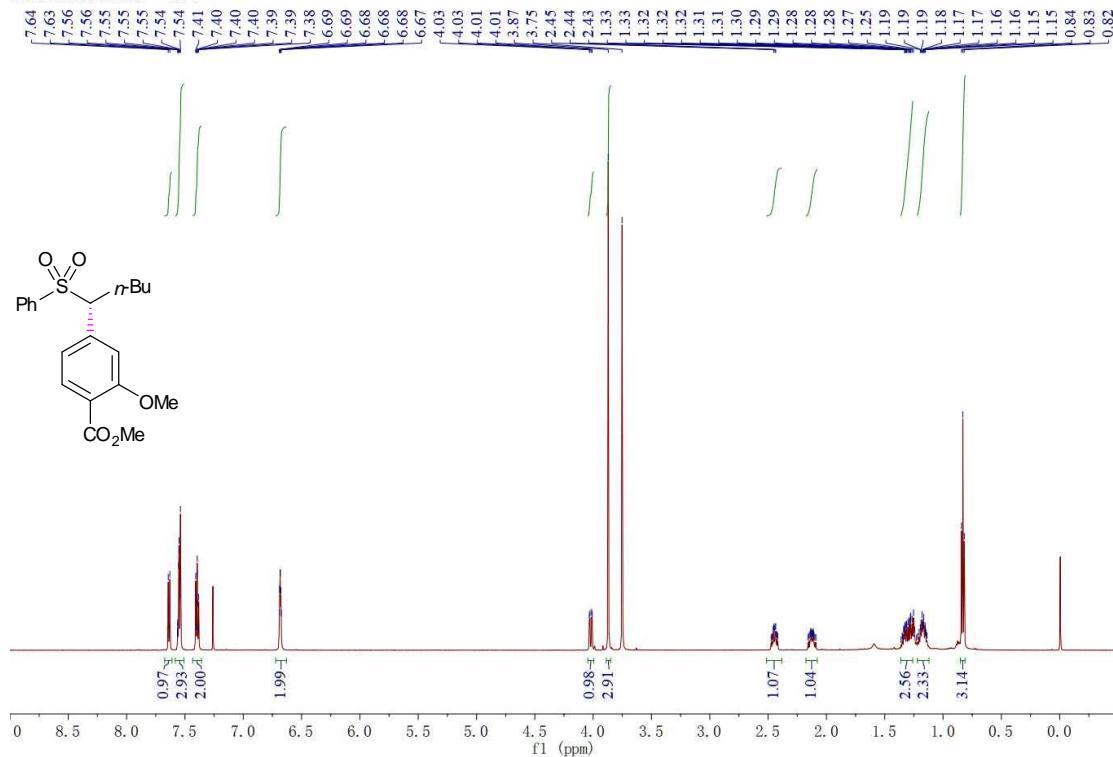
16, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200412-C.4.fid — S7

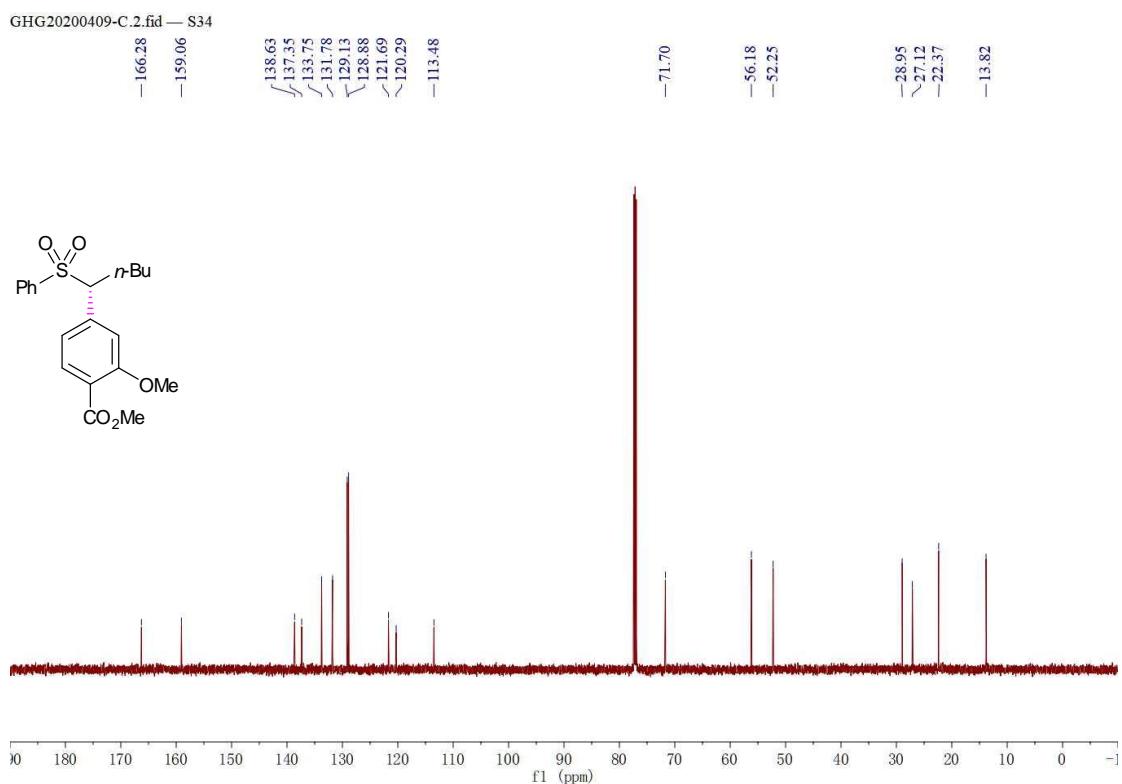


17, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

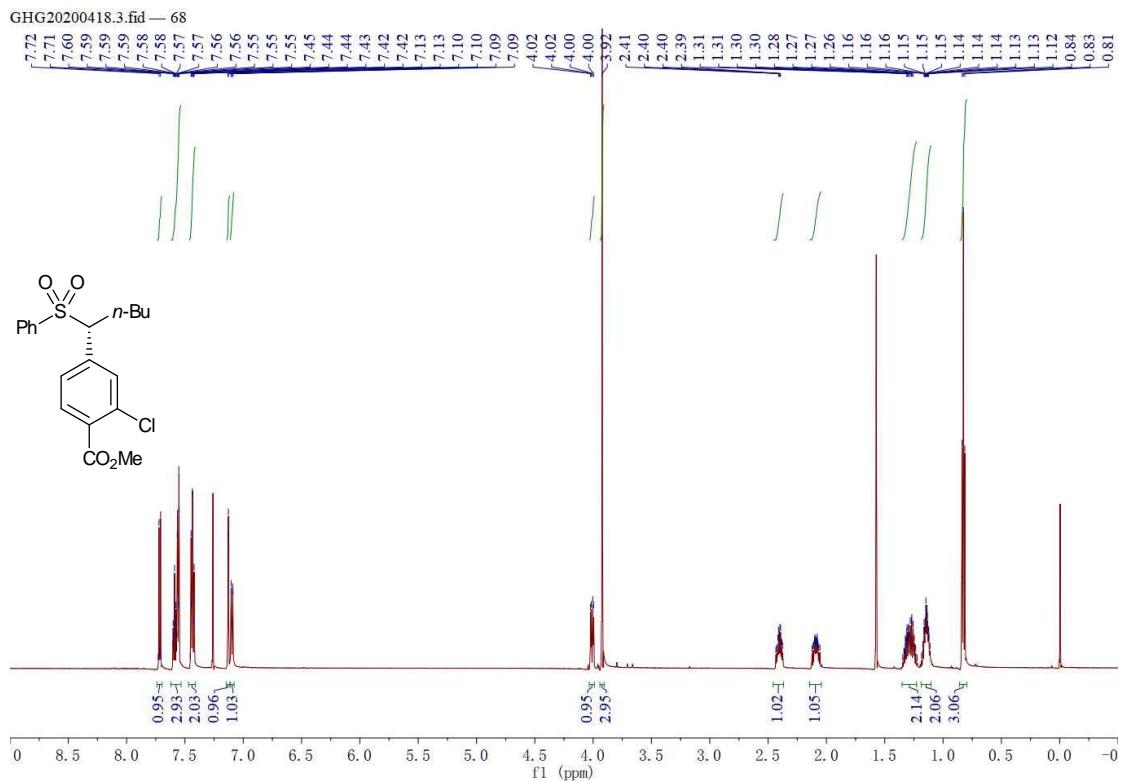
GHG20200413.7.fid — S34



17, ^{13}C NMR (151 MHz, CDCl_3)

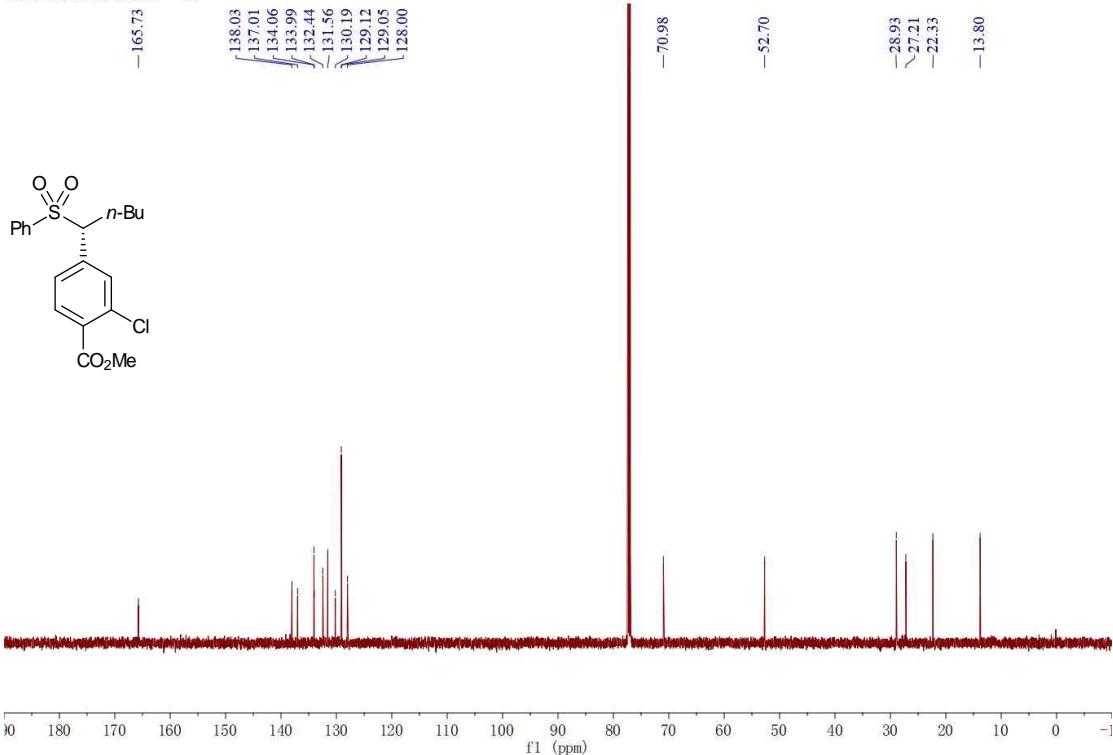


18, ^1H -NMR (600 MHz, CDCl_3)



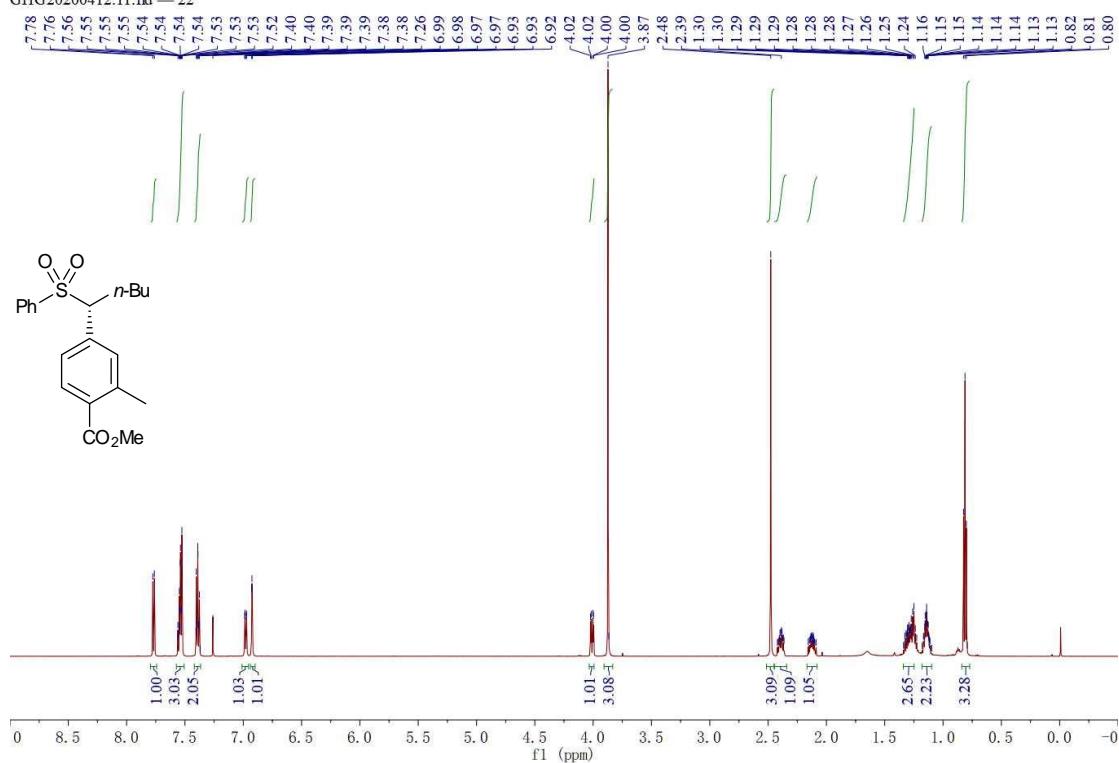
18, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200418-C.2.fid — 68



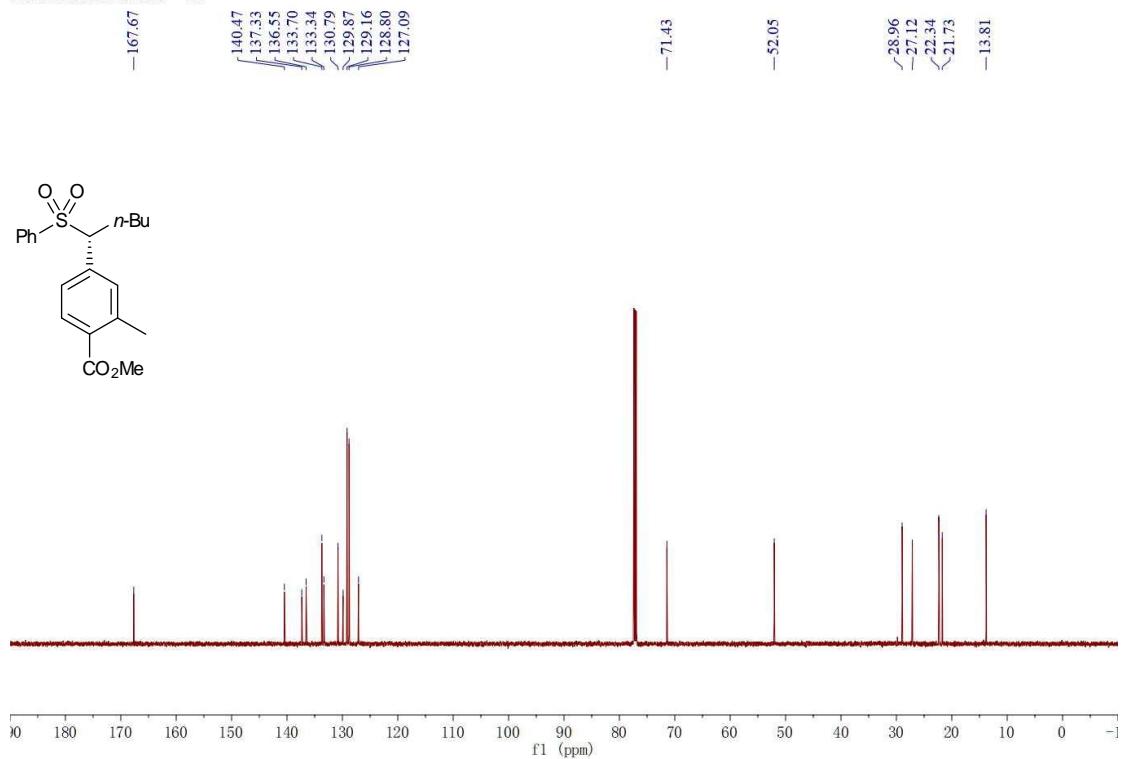
19, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200412.11.fid - 22



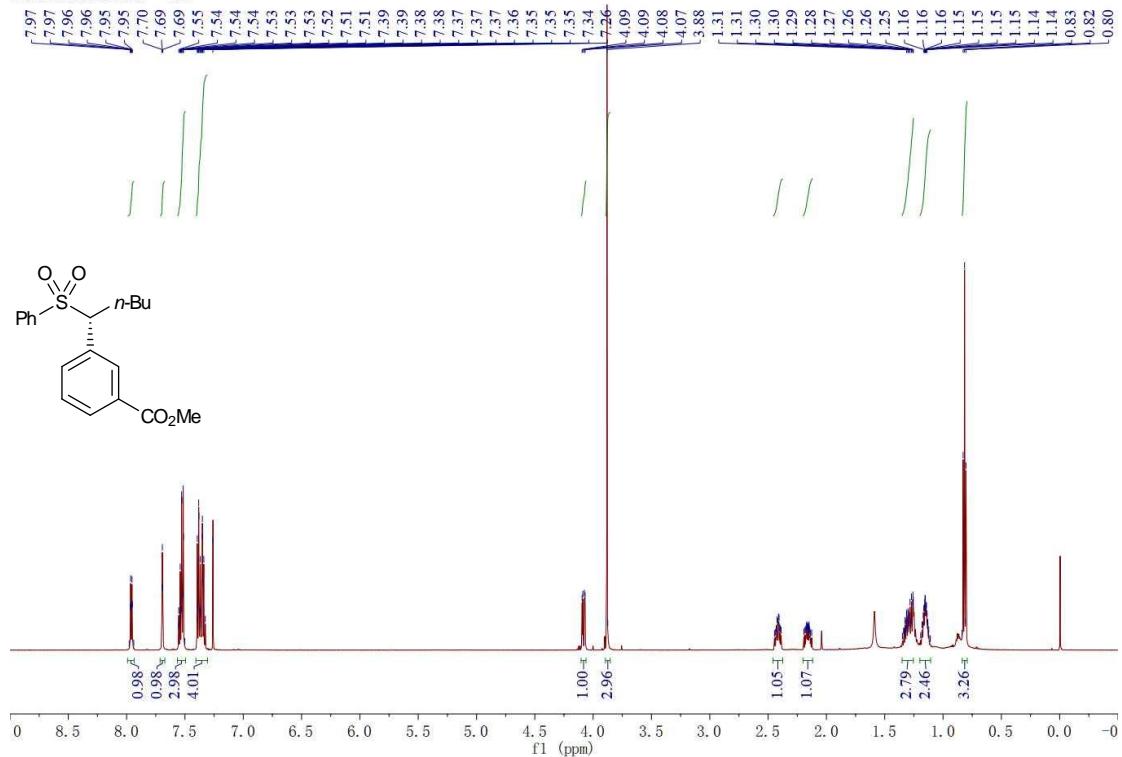
19, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200412-C.8.fid — 22



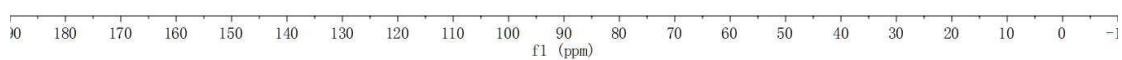
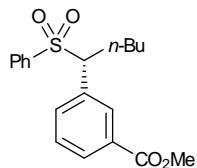
20, ^1H -NMR (600 MHz, CDCl_3)

GHG20200412.1.fid — S1



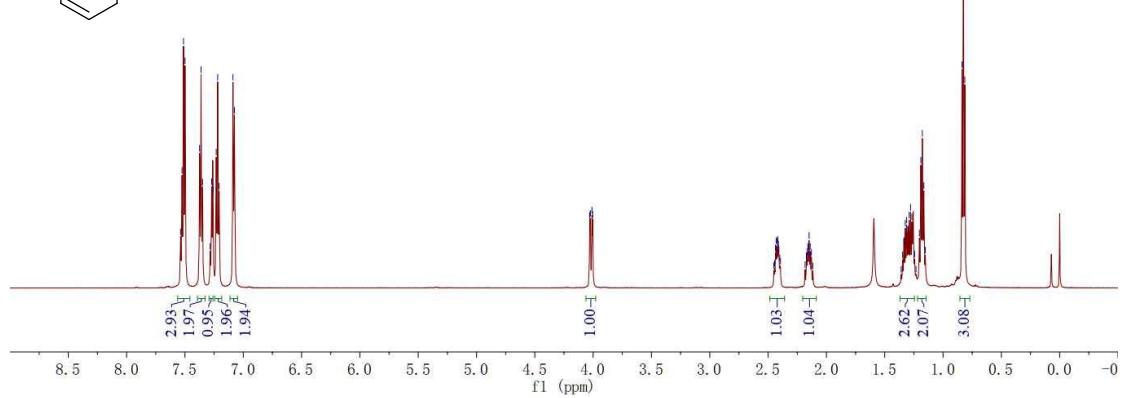
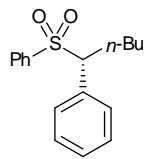
20, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200414-C.1.fid — 2



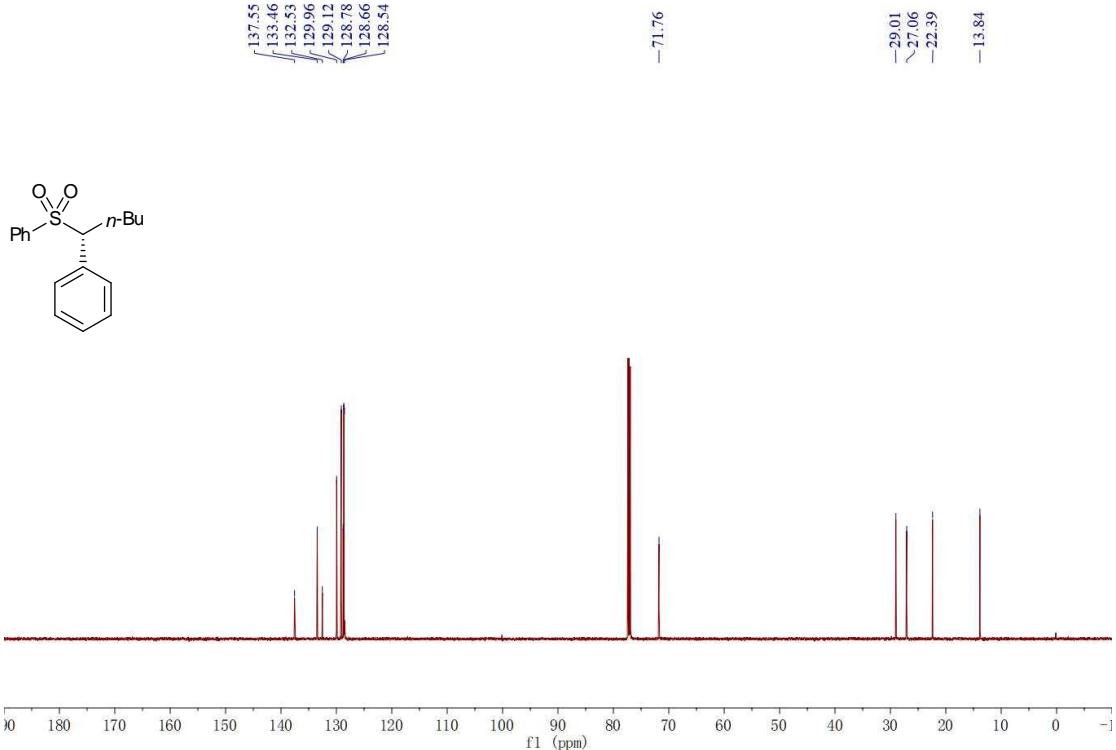
21, ^1H -NMR (600 MHz, CDCl_3)

GHG20191008.1.fid —



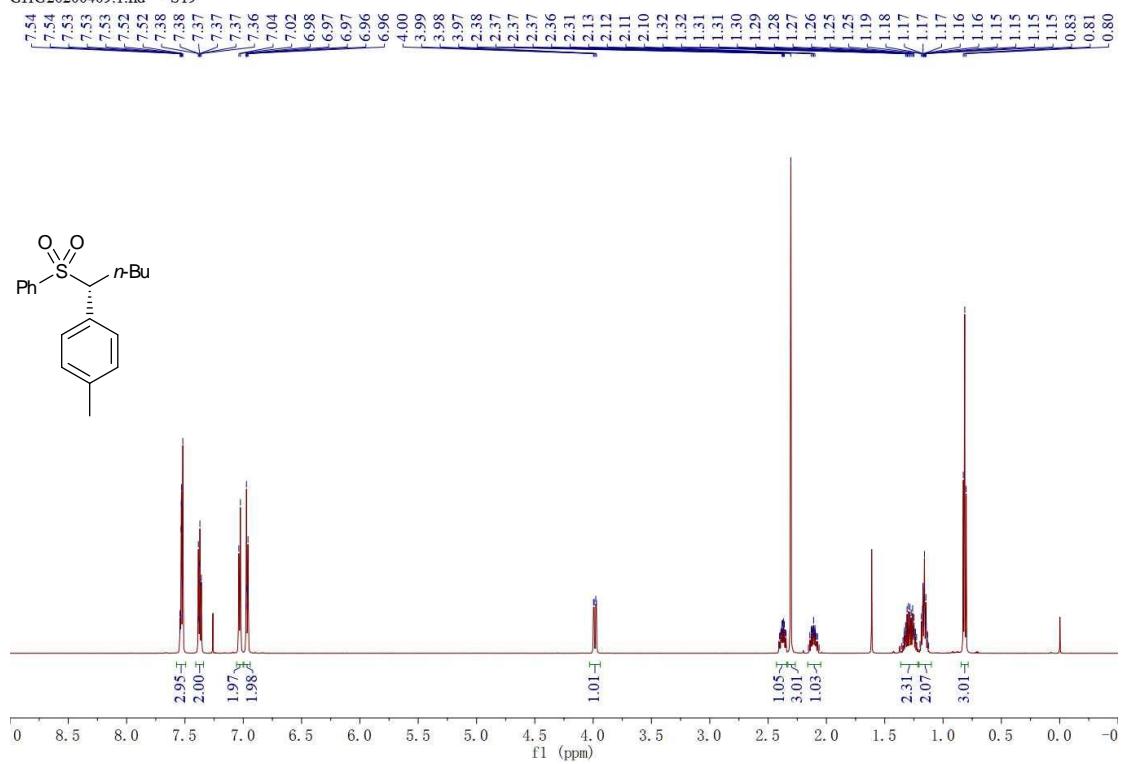
21, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201202.4.fid — 9



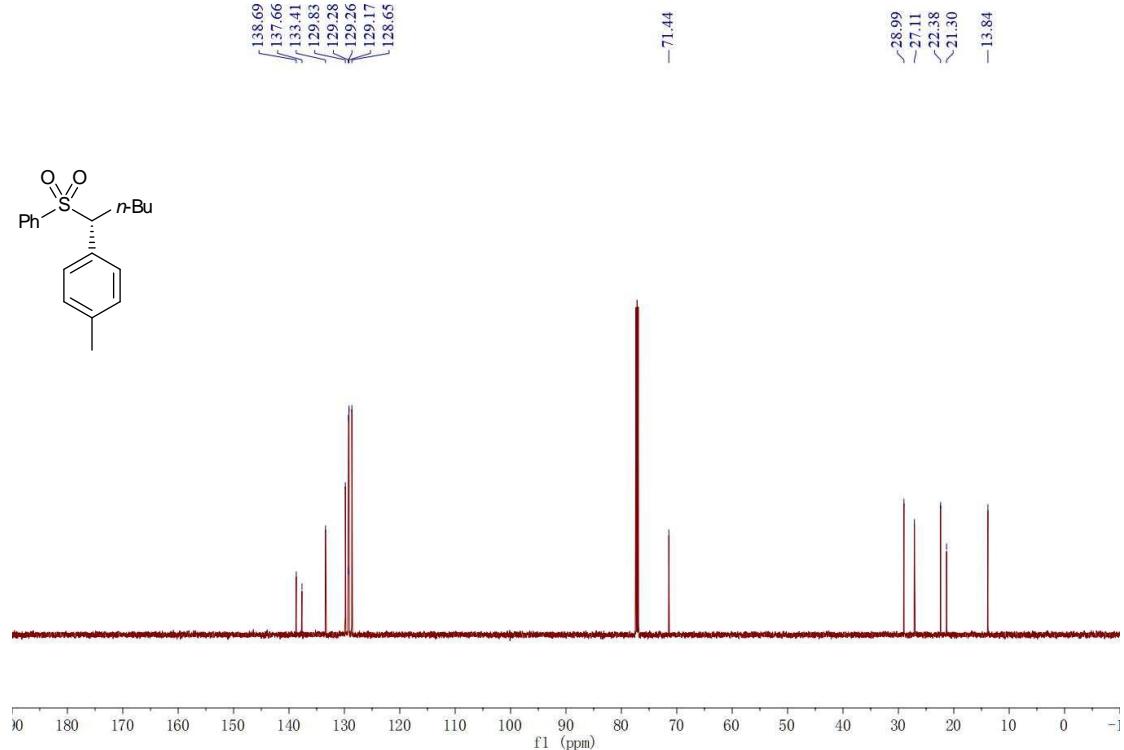
22, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200409.1.fid — S19



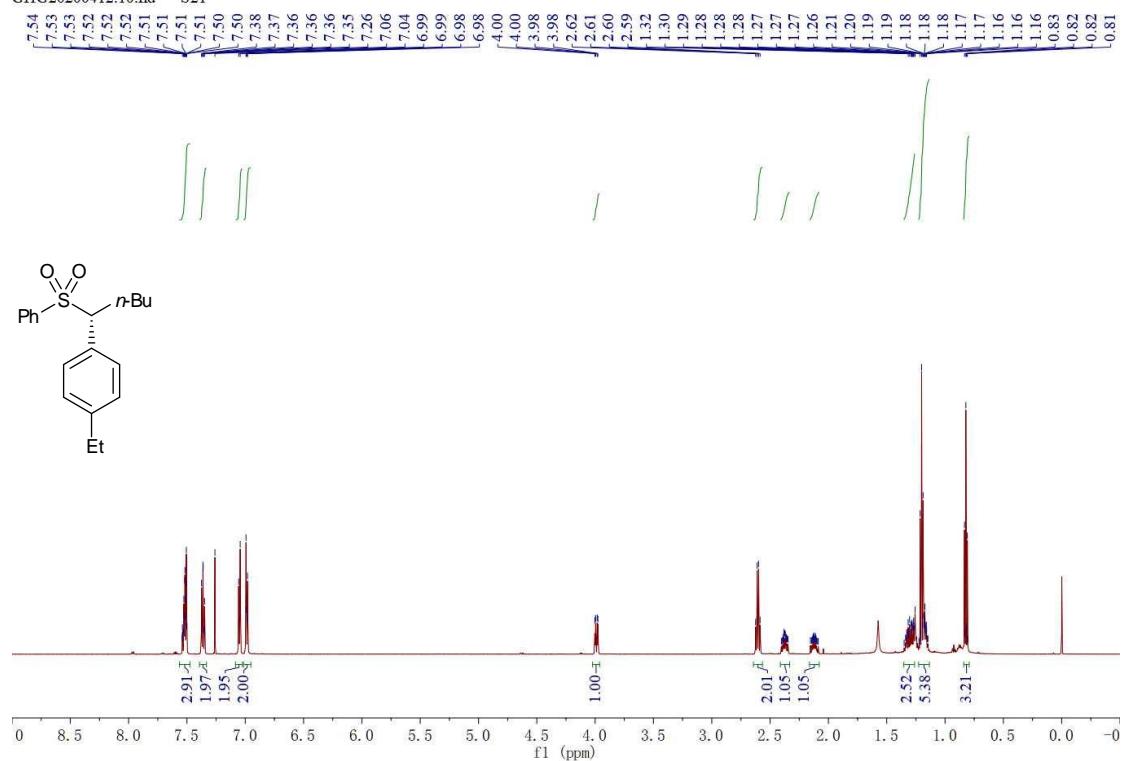
22, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200409-C.1.fid — S19



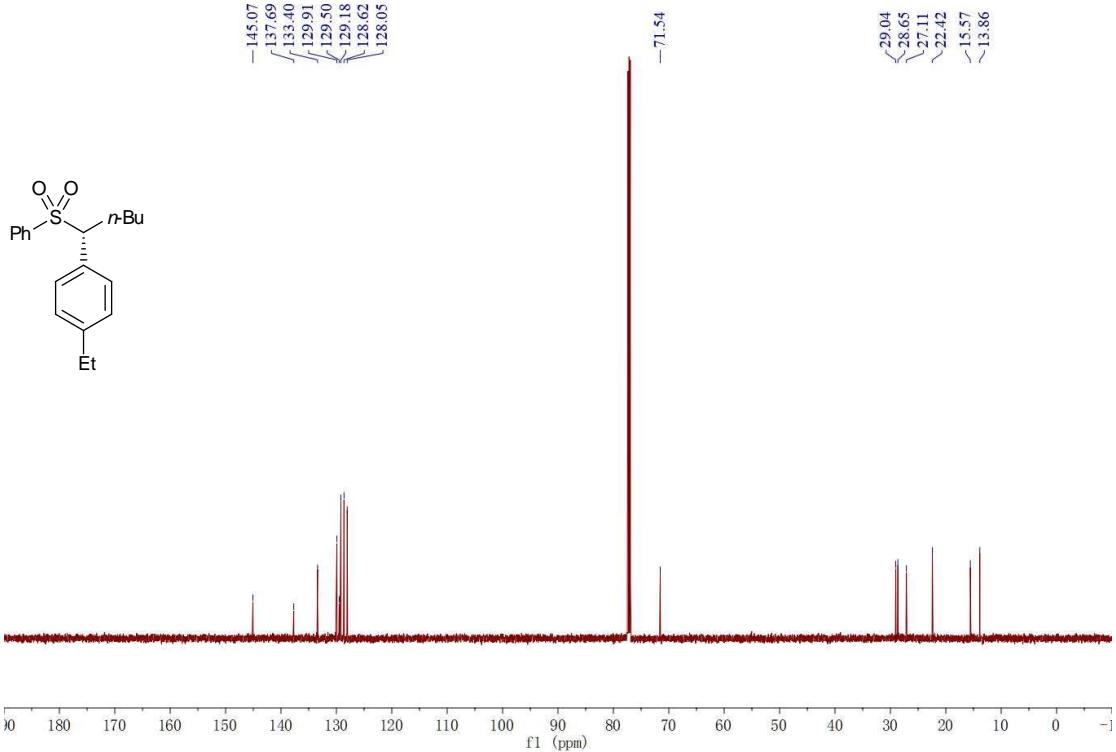
23, ^1H -NMR (600 MHz, CDCl_3)

GHG20200412.10.fid — S21



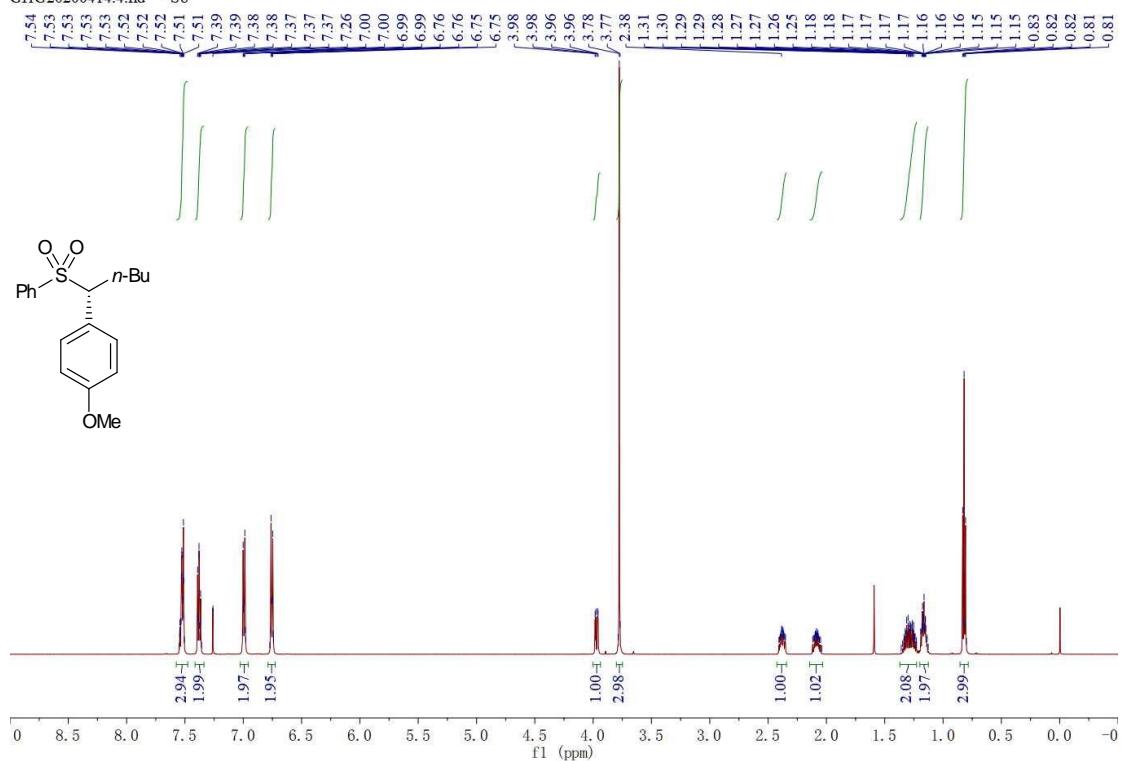
23, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200412-C.5.fid — S21



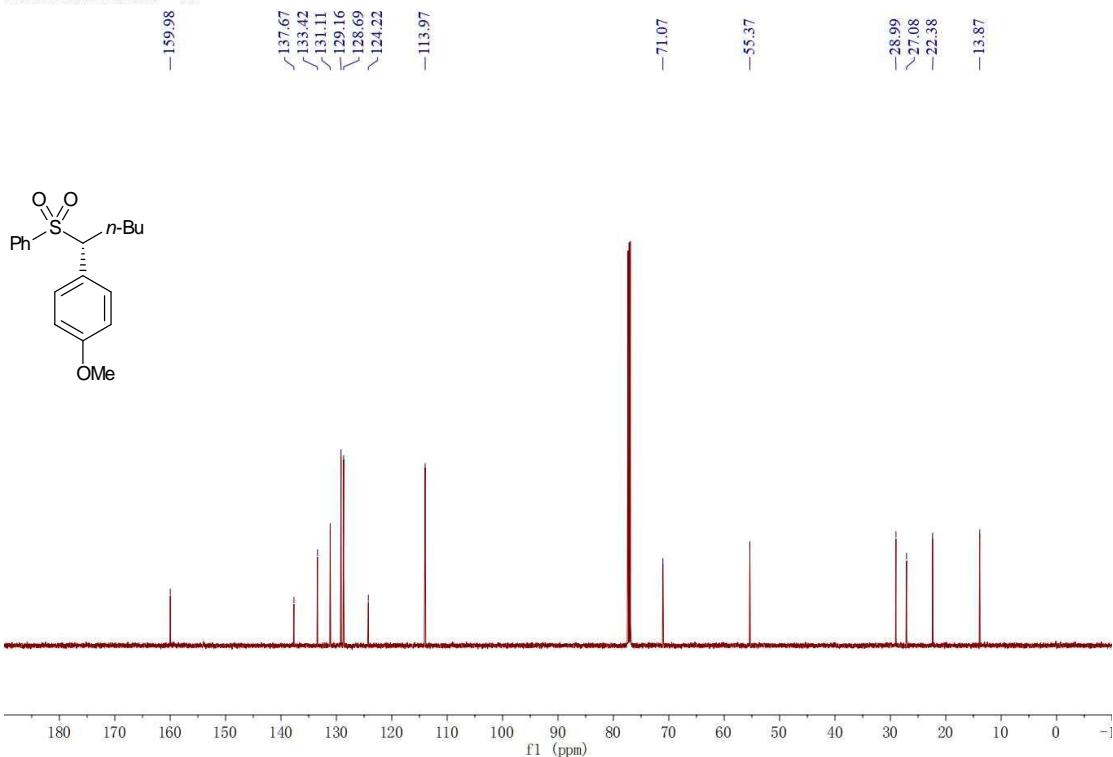
24, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200414.4.fid — S8



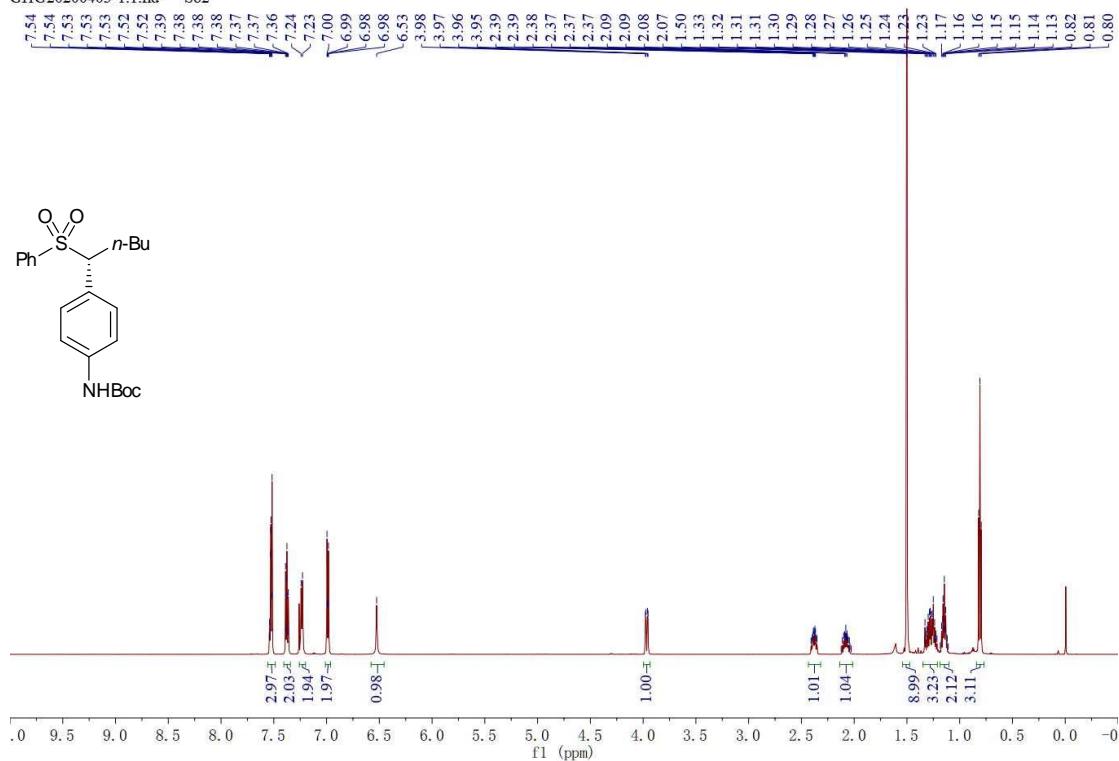
24, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200414-C.2.fid — S8



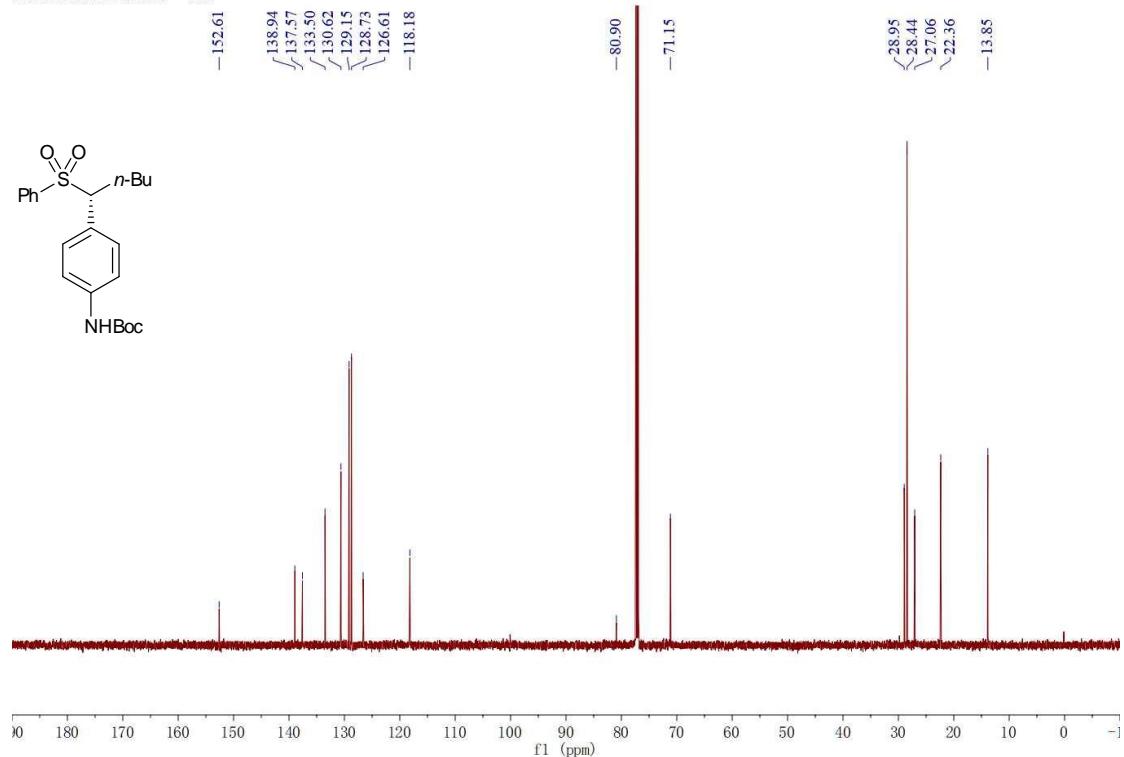
25, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200403-1.1.fid — S82

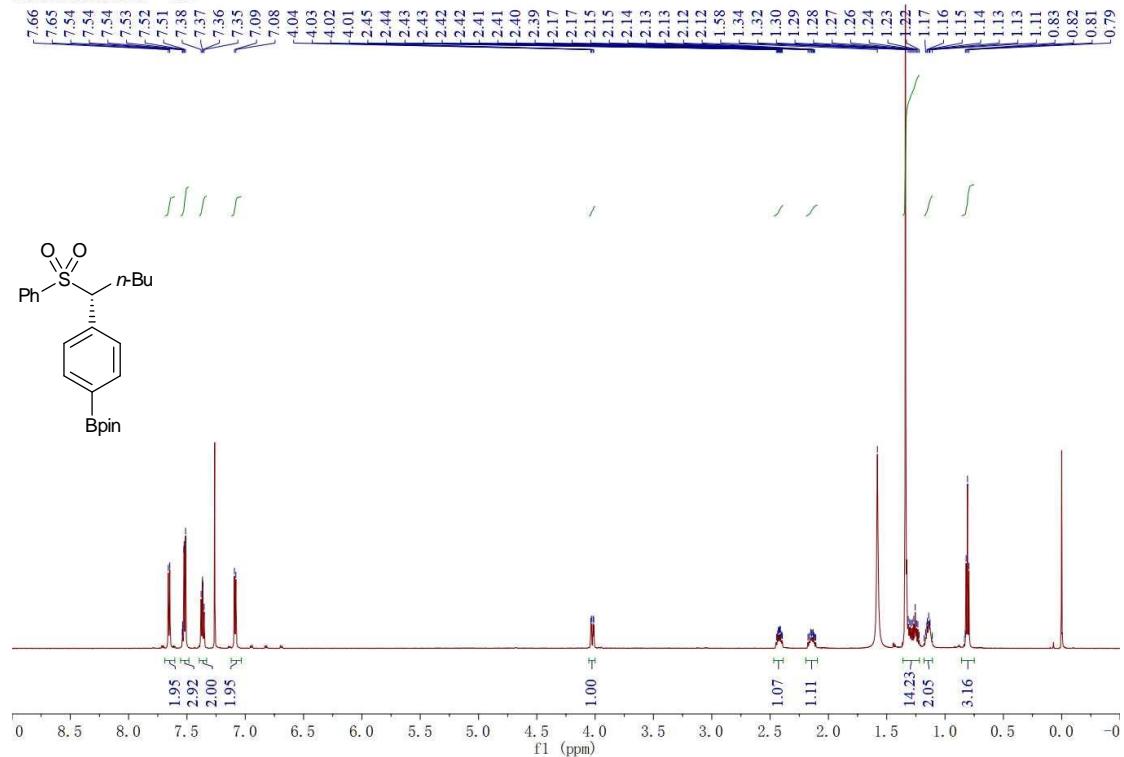


25, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200403-C.1.fid — S82

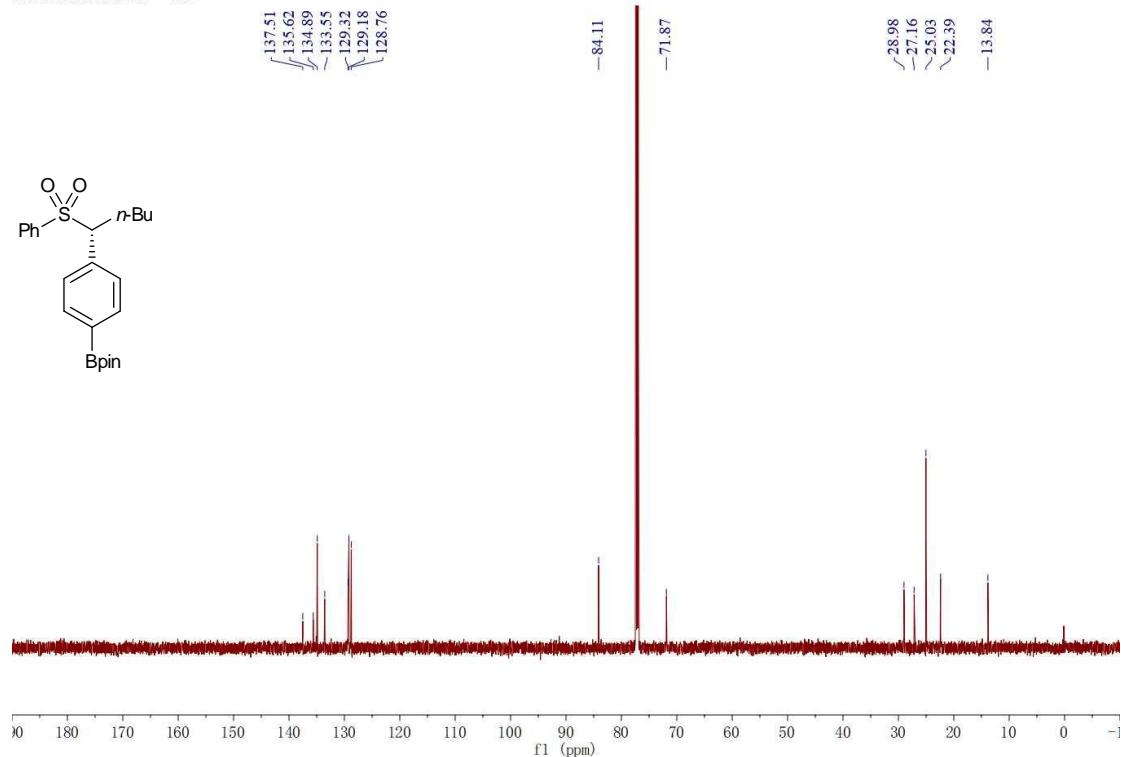


GHG20200508.2.fid — S95



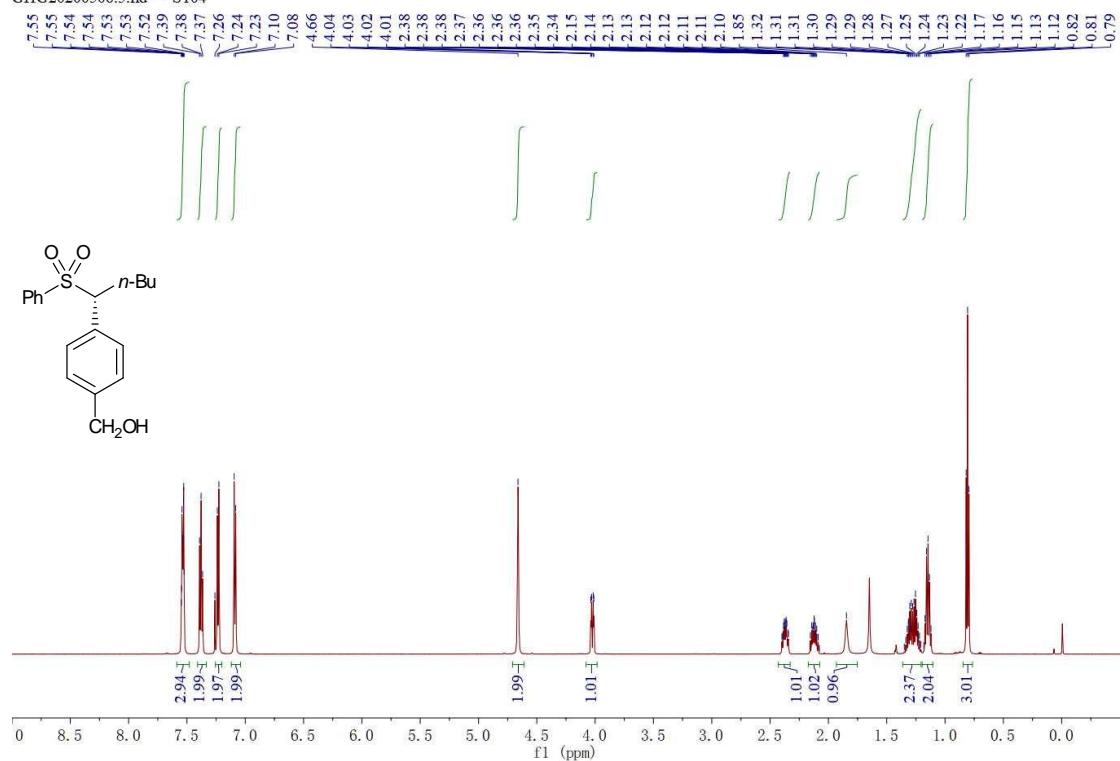
26, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200508.5.fid — S95



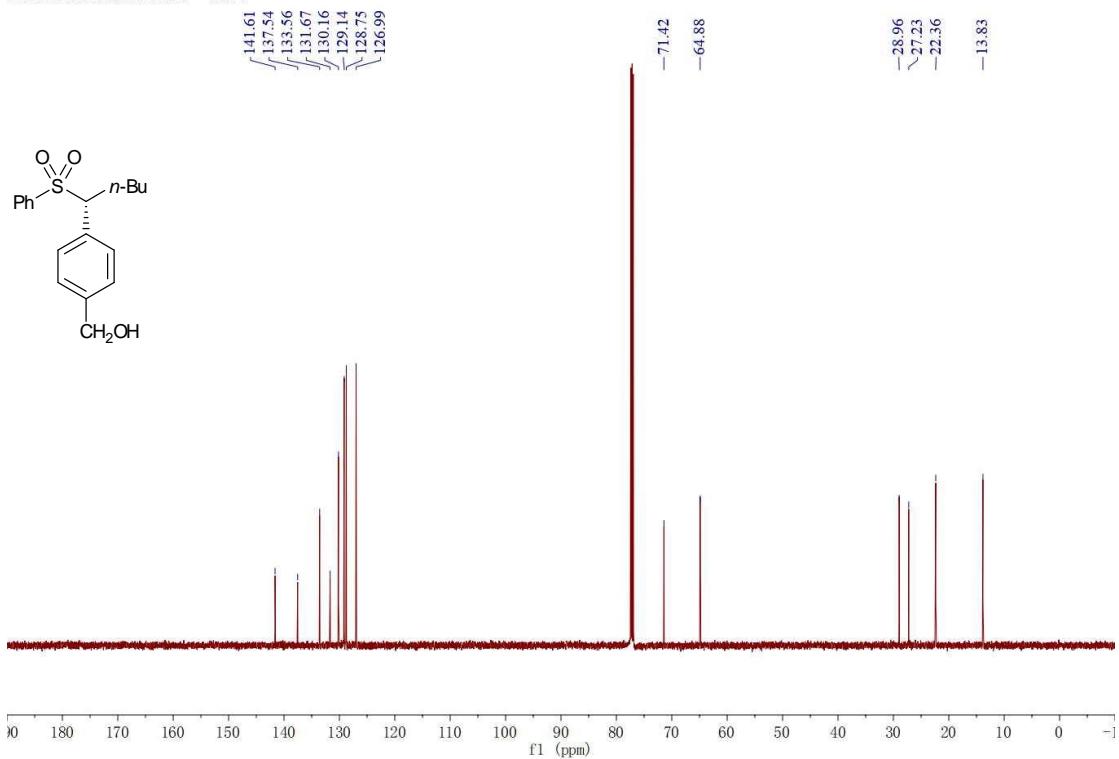
27, ^1H -NMR (600 MHz, CDCl_3)

GHG20200506.5.fid — S104



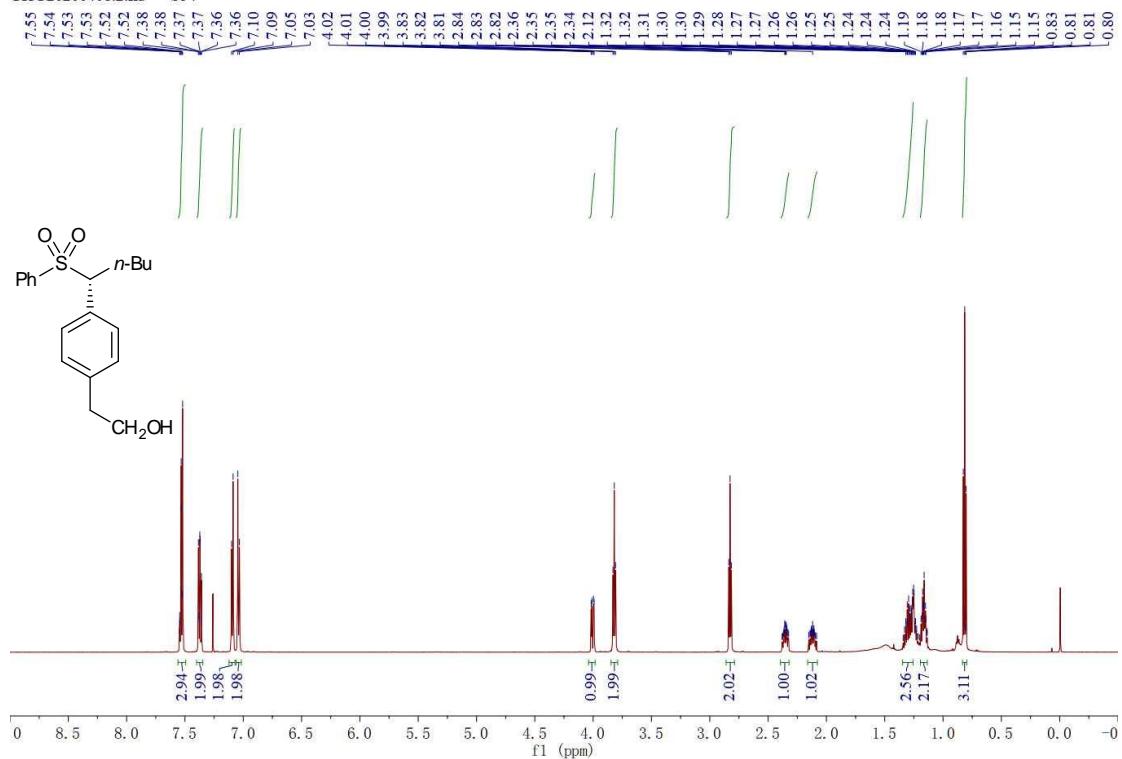
27, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200506-s104c.1.fid — S104



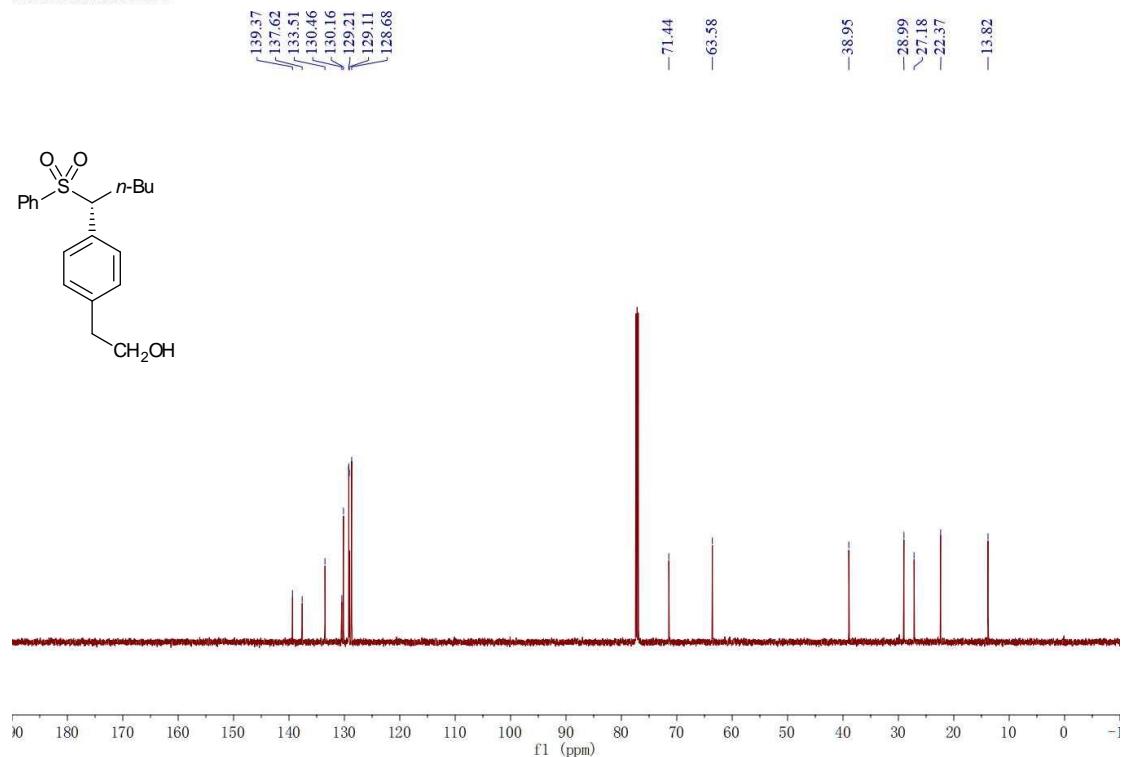
28, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200408.2.fid — S54



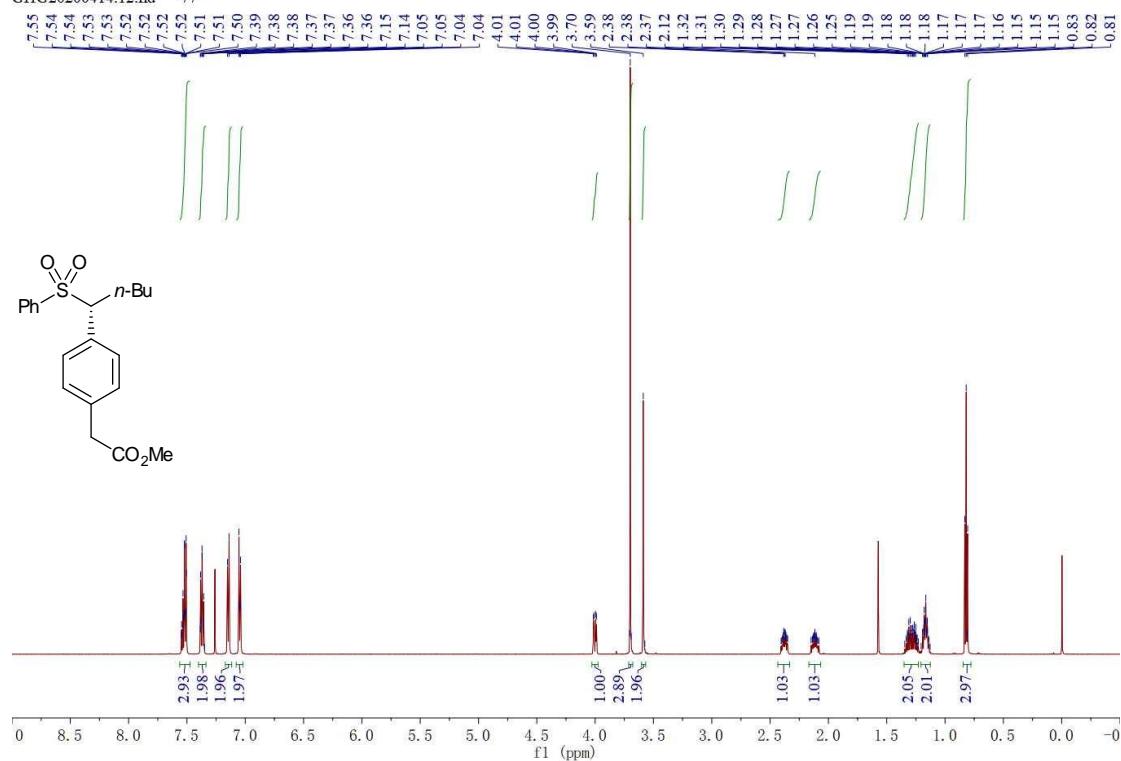
28, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200406-54.3.fid —

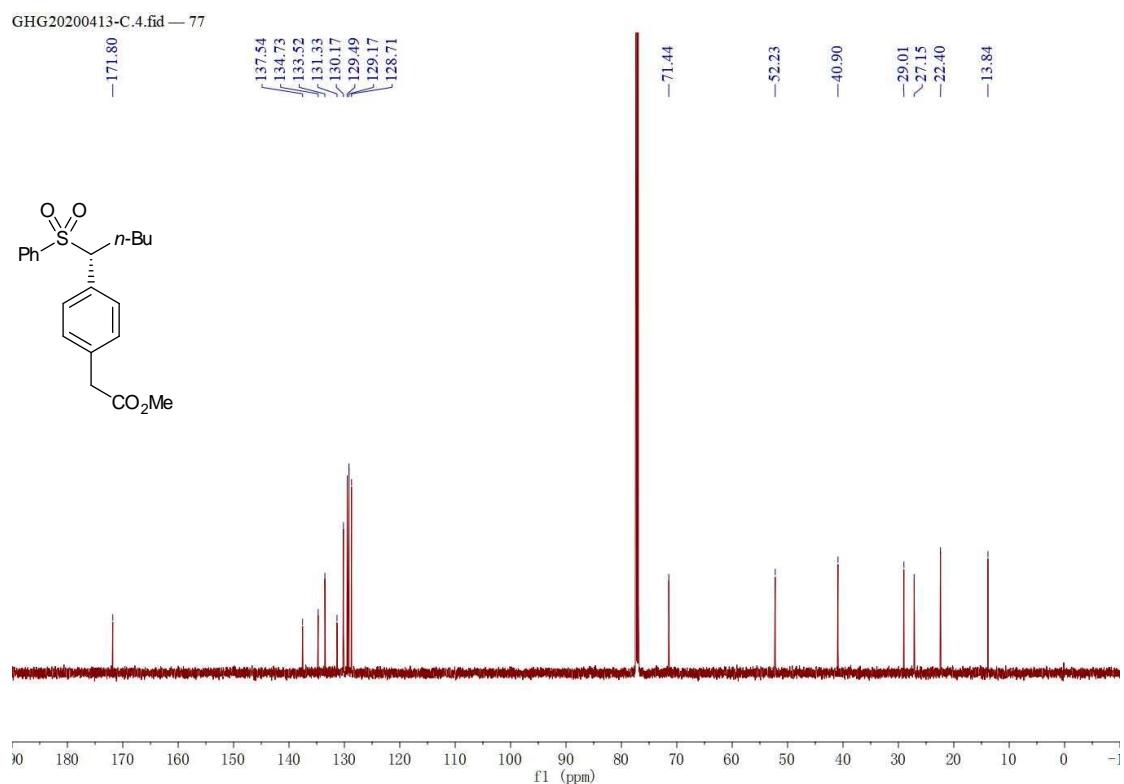


29, ^1H -NMR (600 MHz, CDCl_3)

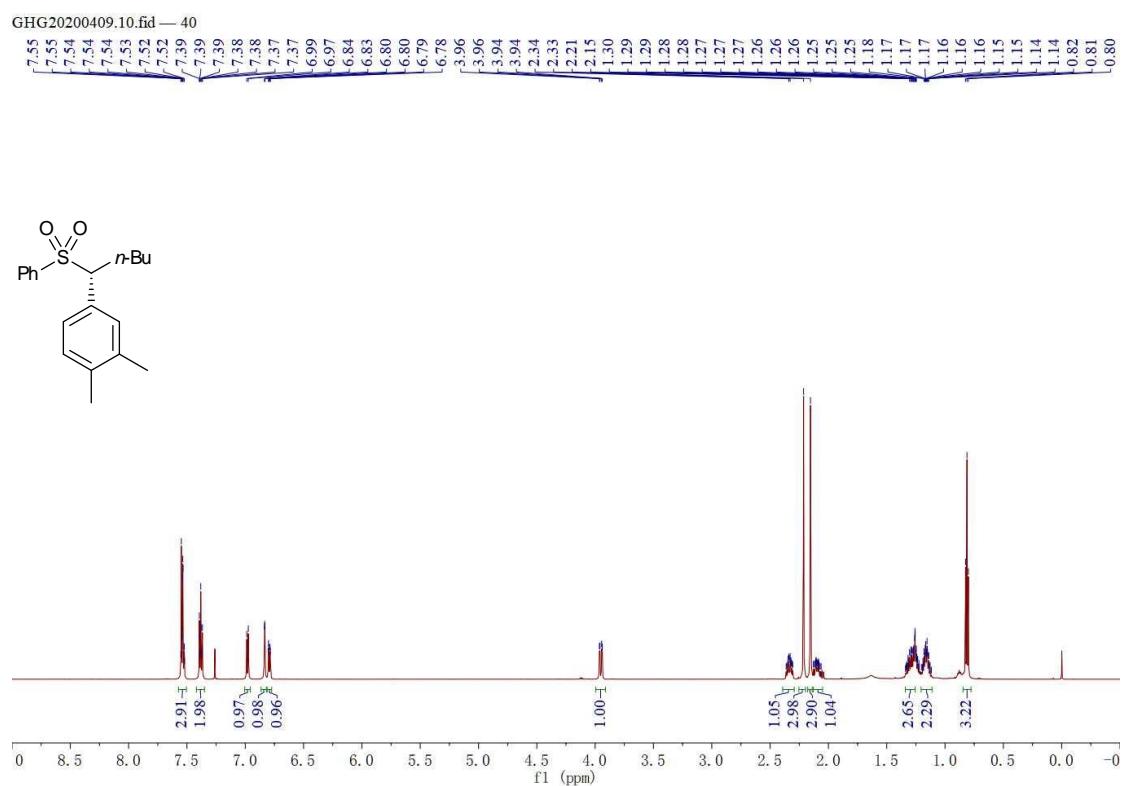
GHG20200414.12.fid — 77



29, ^{13}C NMR (151 MHz, CDCl_3)

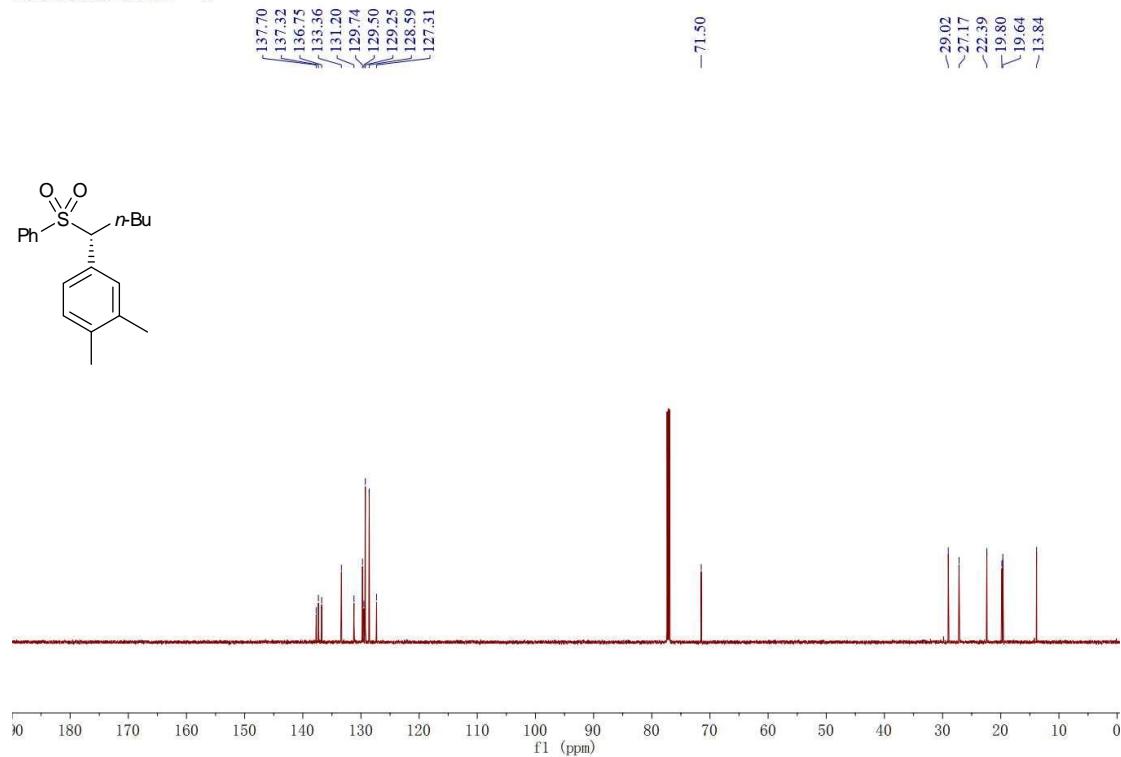


30, ^1H -NMR (600 MHz, CDCl_3)



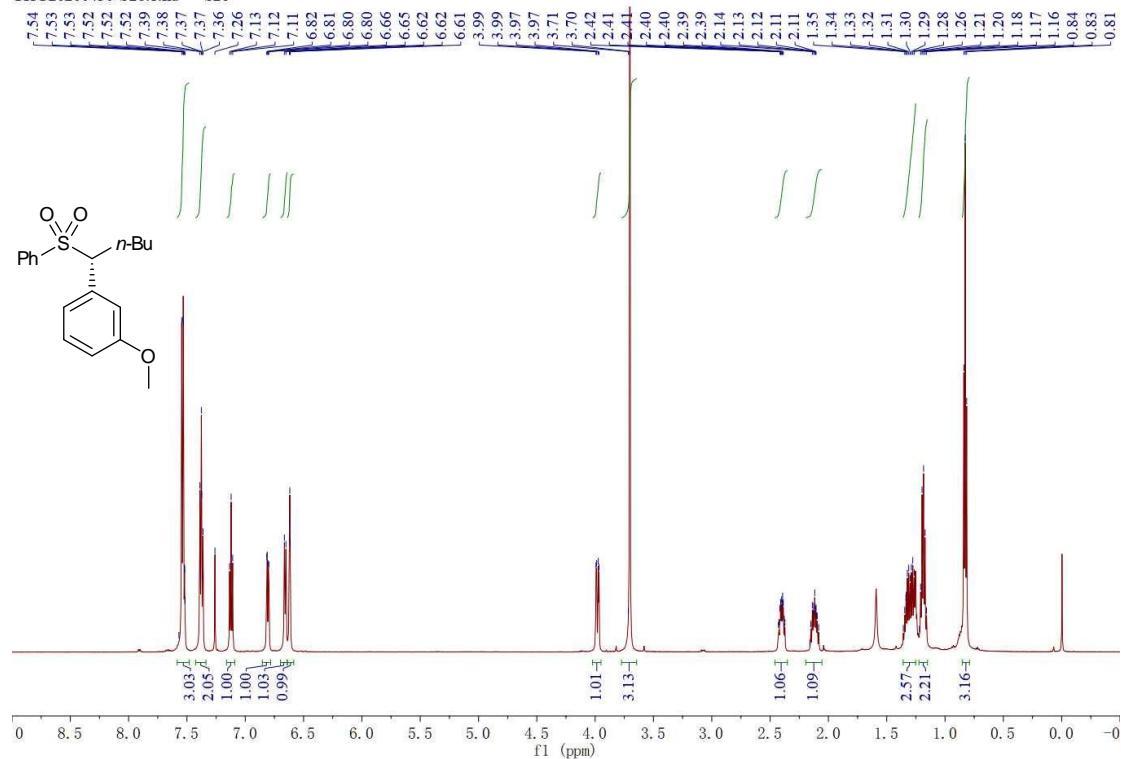
30, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200409-C.12.fid — 40

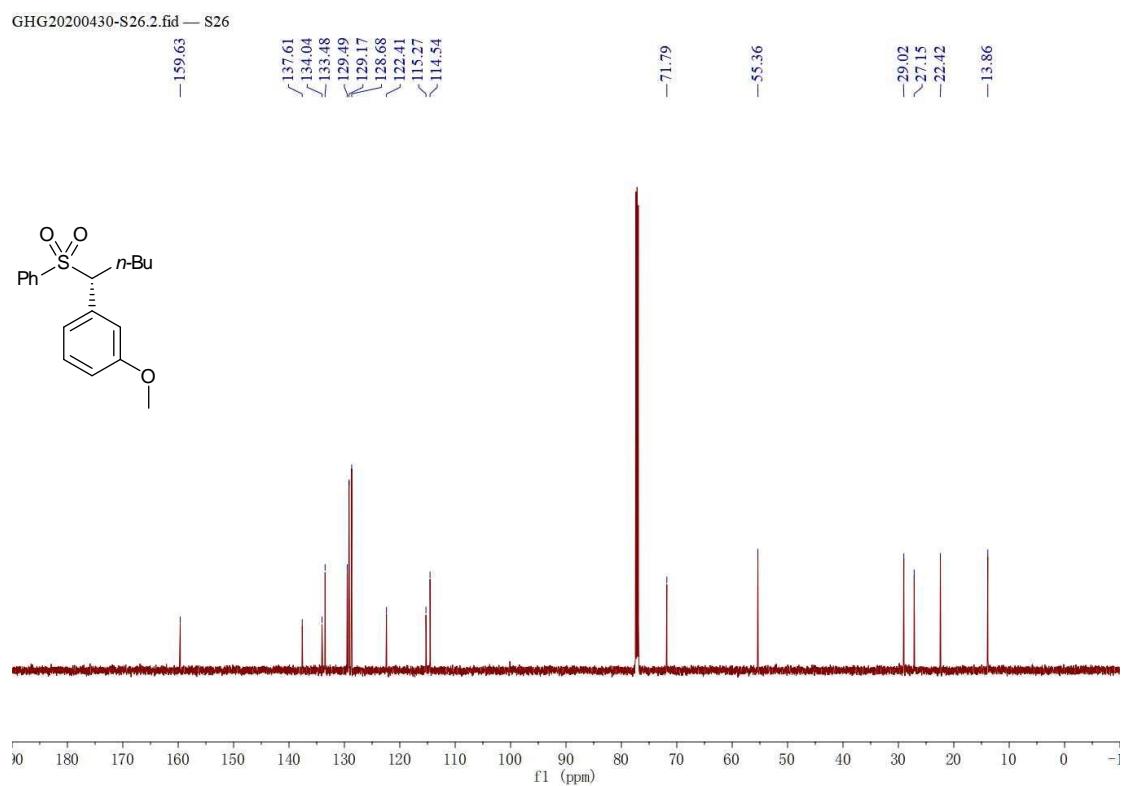


31, ^1H -NMR (600 MHz, CDCl_3)

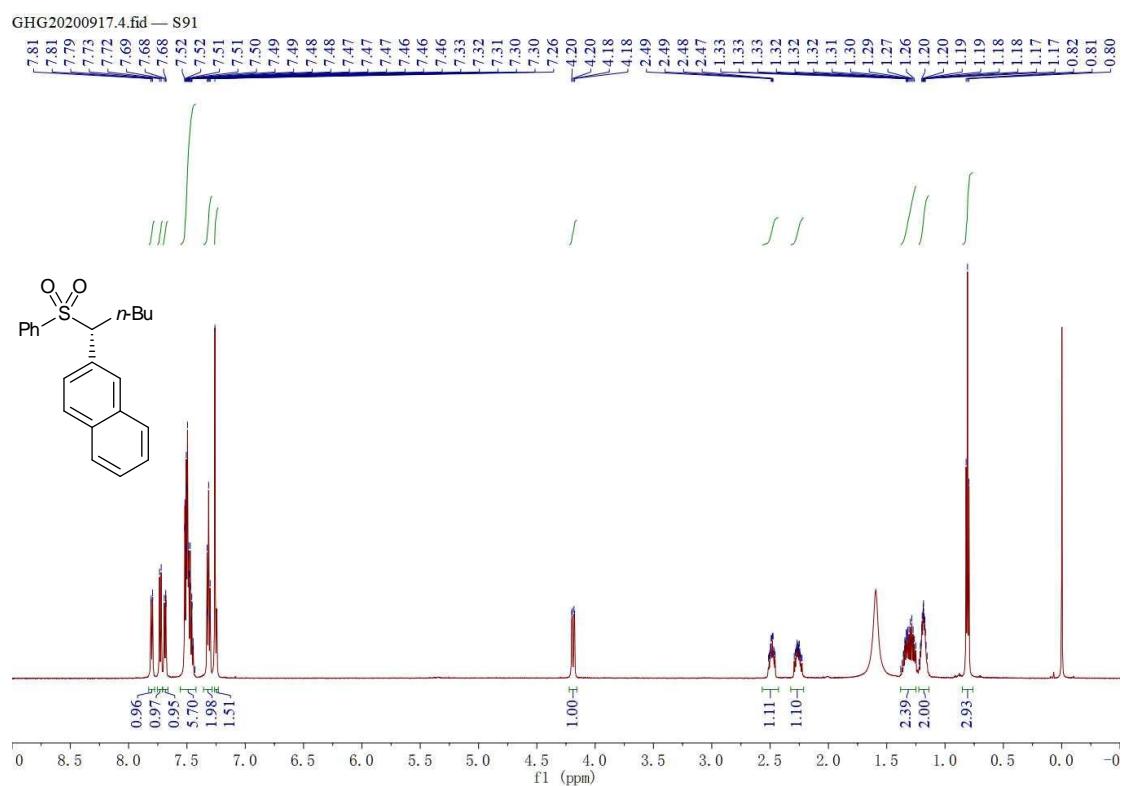
GHG20200430-S26.1.fid — S26



31, ^{13}C NMR (151 MHz, CDCl_3)

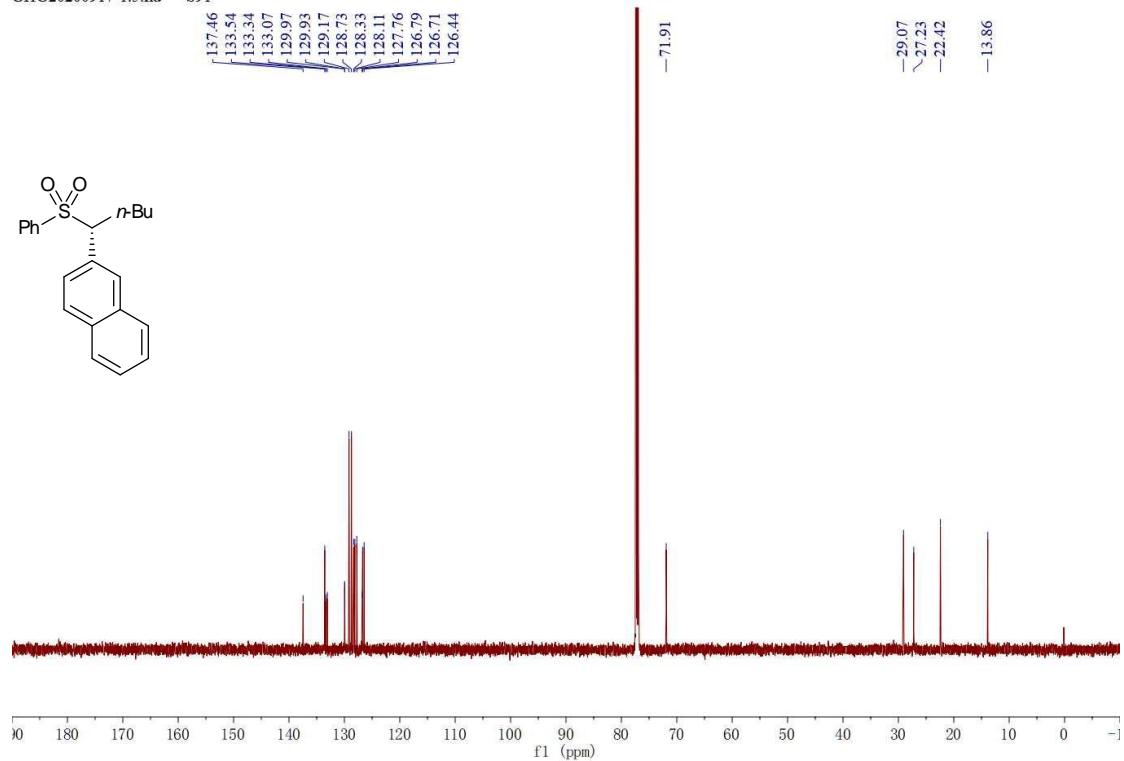


32, ^1H -NMR (600 MHz, CDCl_3)



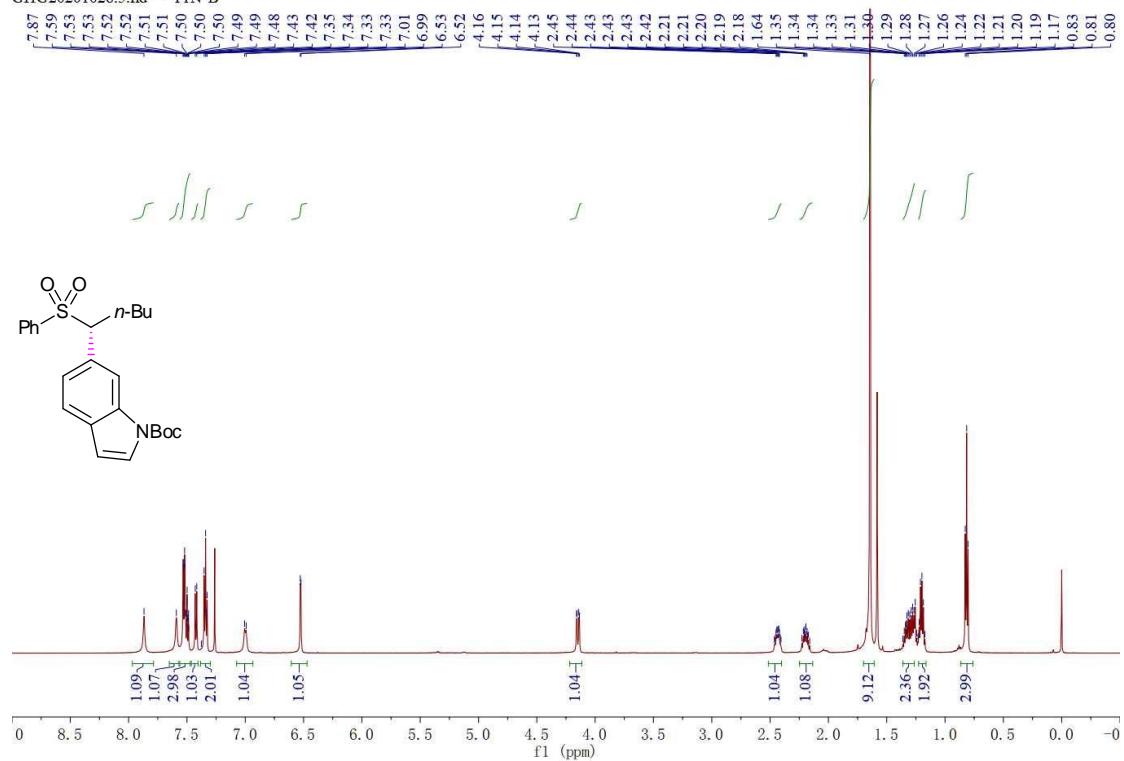
32, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200917-1.5.fid — S91

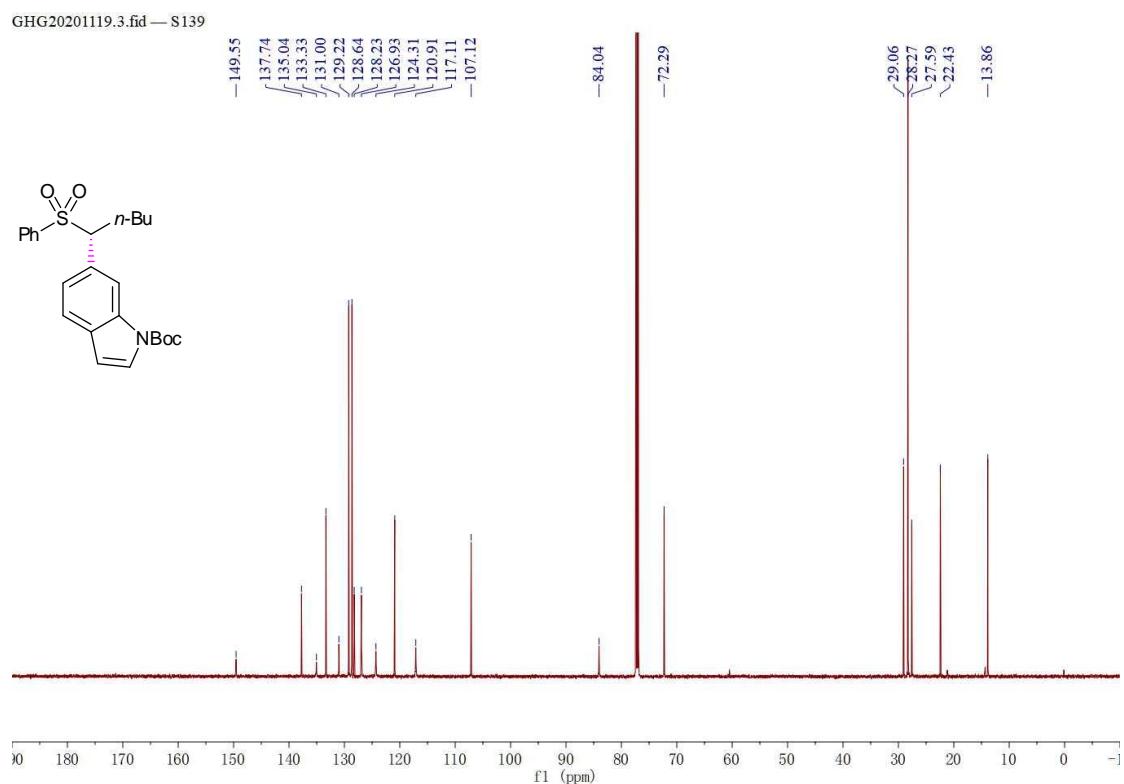


33, ^1H -NMR (600 MHz, CDCl_3)

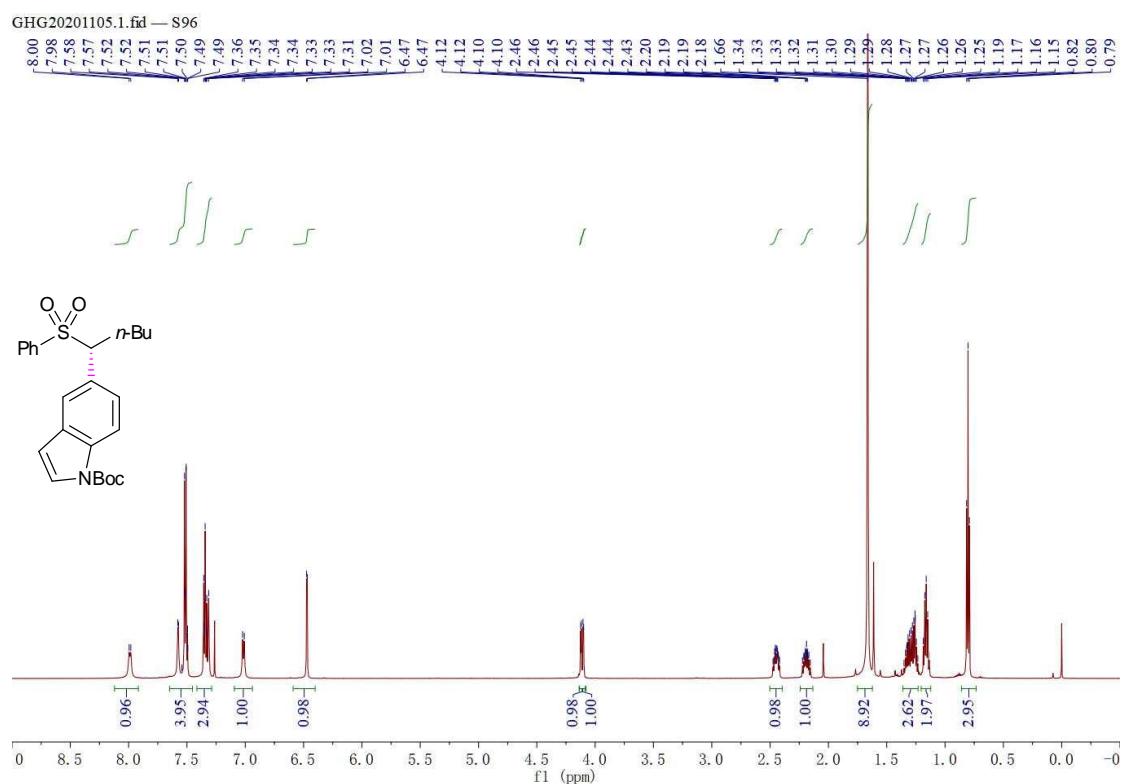
GHG20201028.5.fid — YIN-B



33, ^{13}C NMR (151 MHz, CDCl_3)

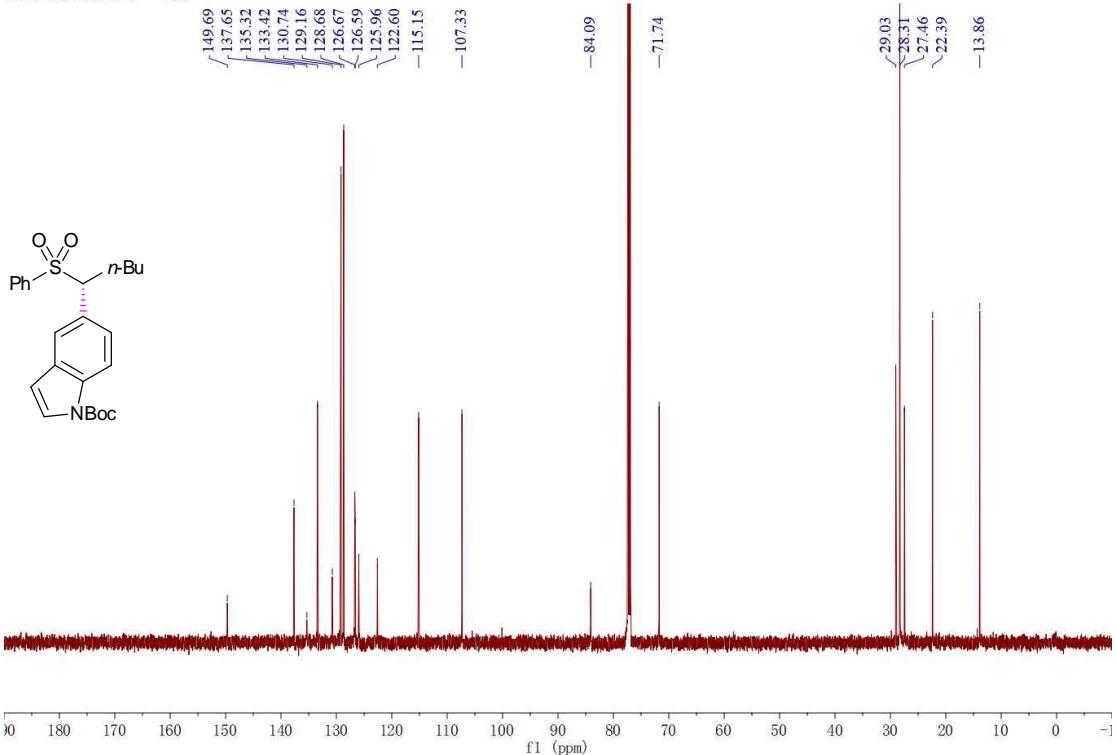


34, ^1H -NMR (600 MHz, CDCl_3)



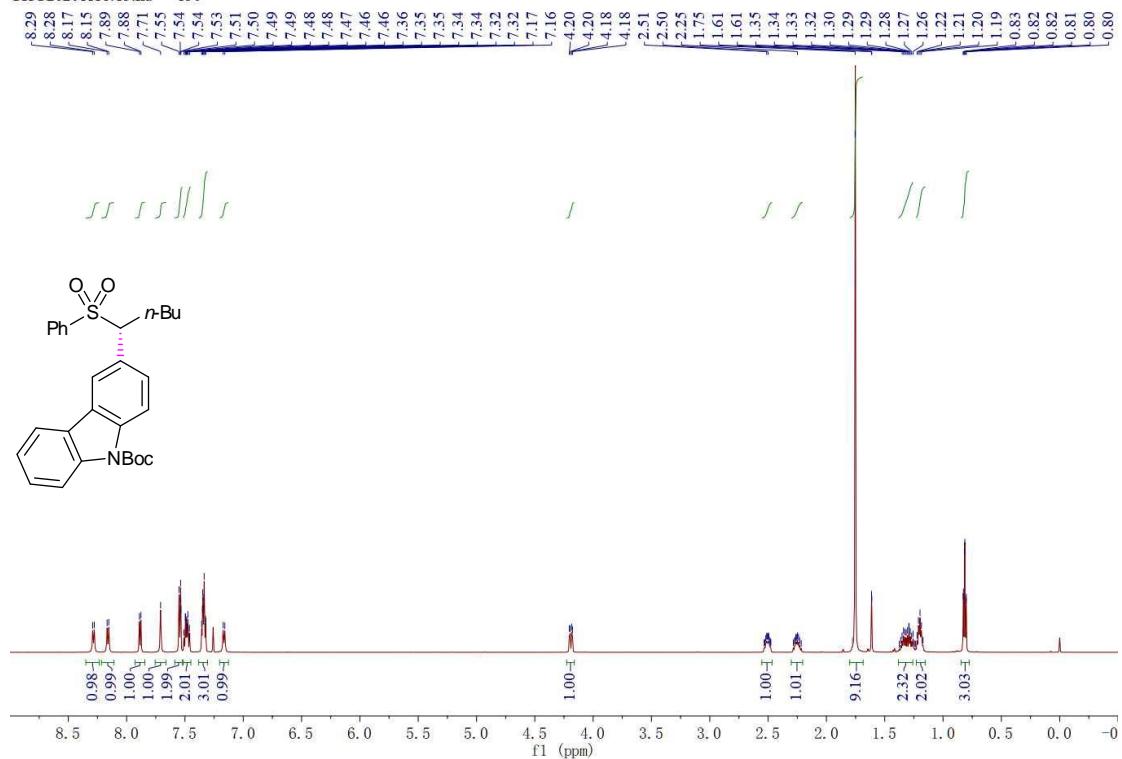
34, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201105.6.fid — S96

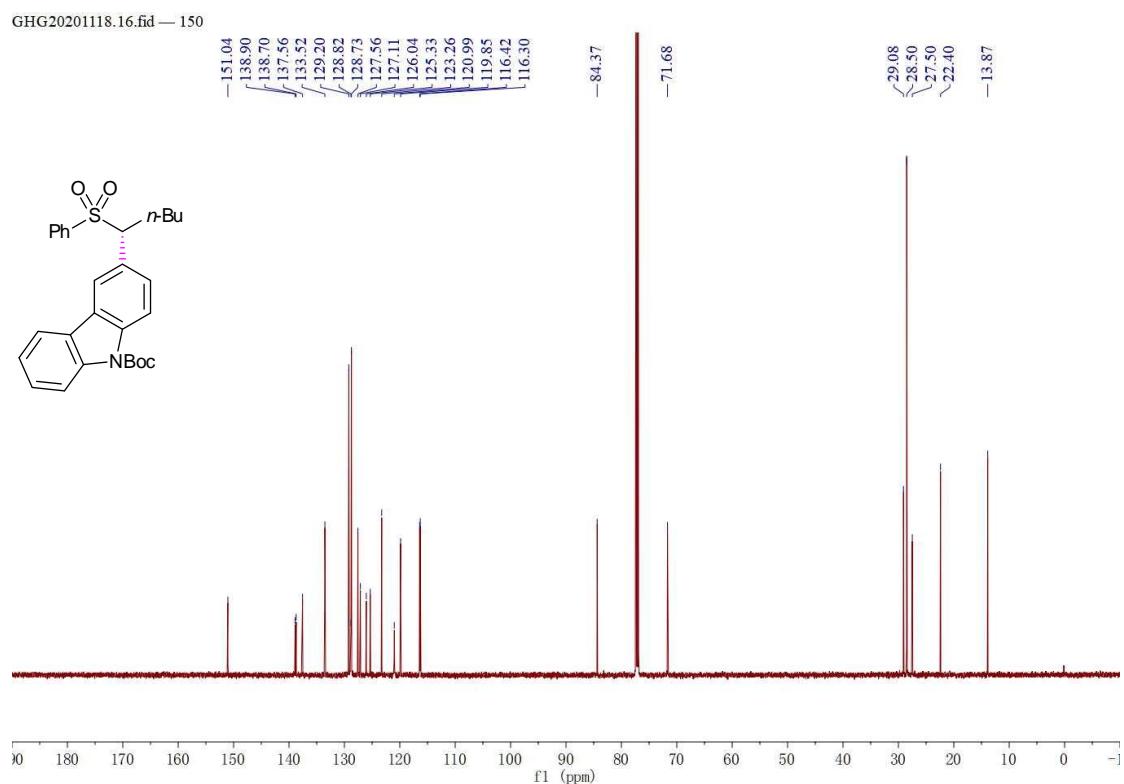


35, ^1H -NMR (600 MHz, CDCl_3)

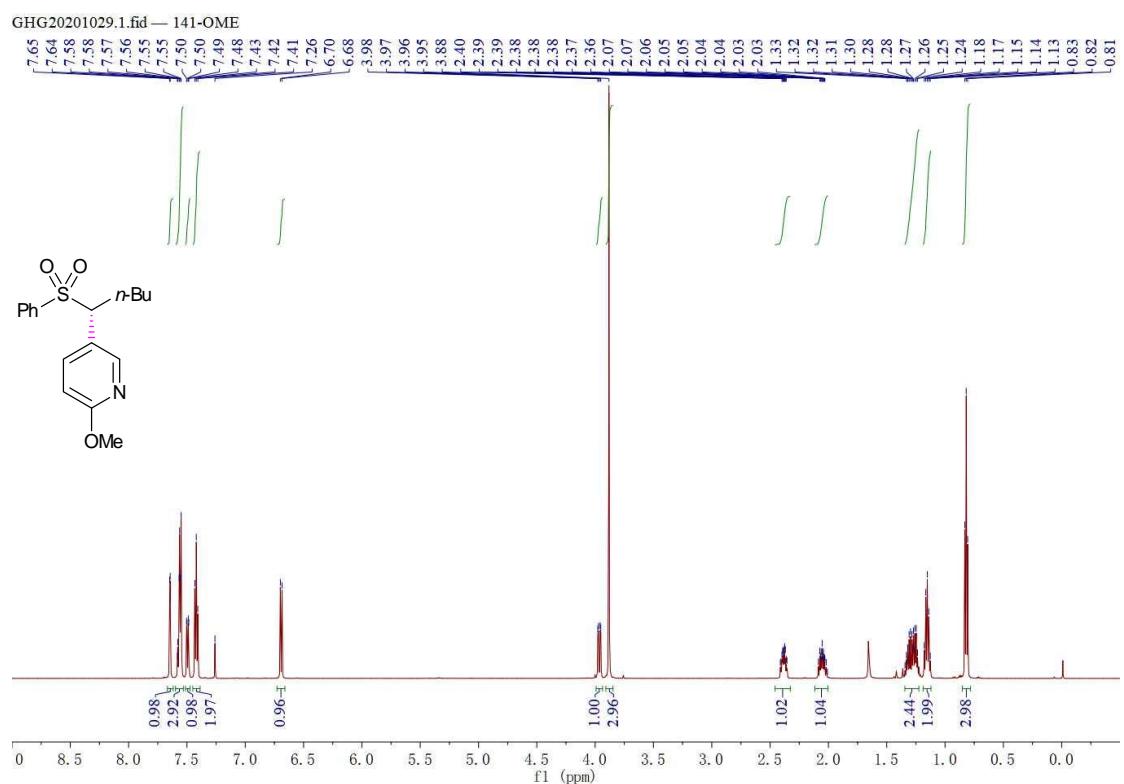
GHG20201118.15.fid — 150



35, ^{13}C NMR (151 MHz, CDCl_3)

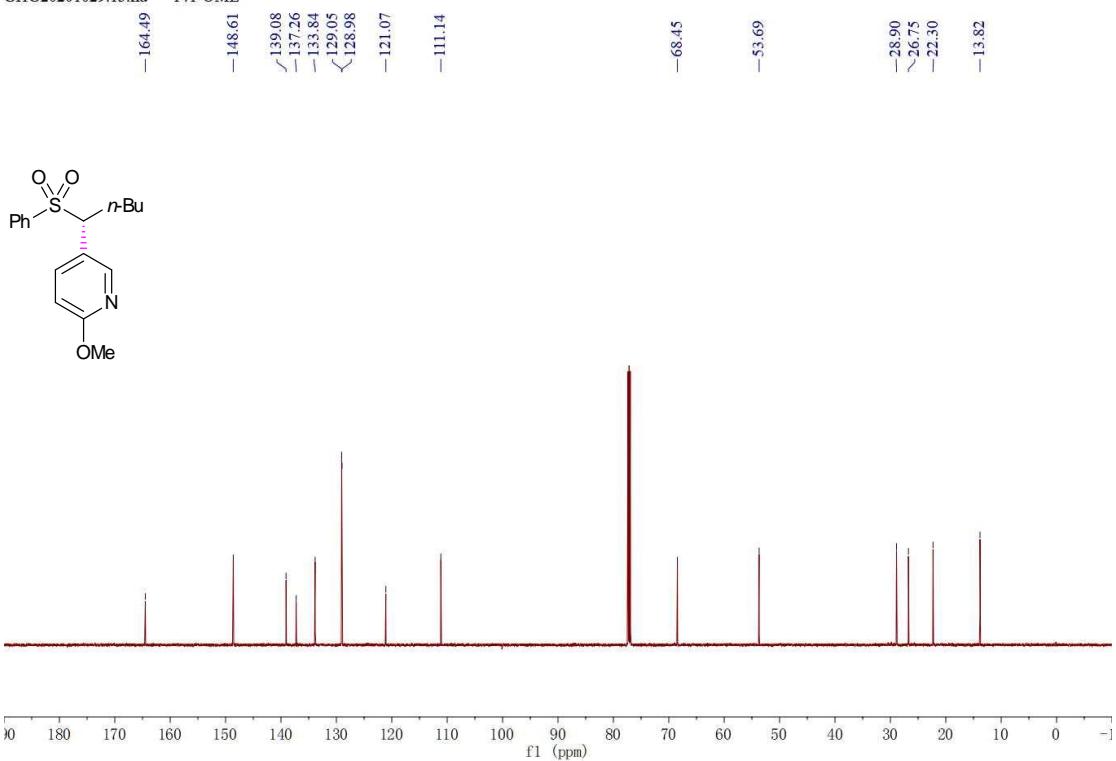


36, ^1H -NMR (600 MHz, CDCl_3)



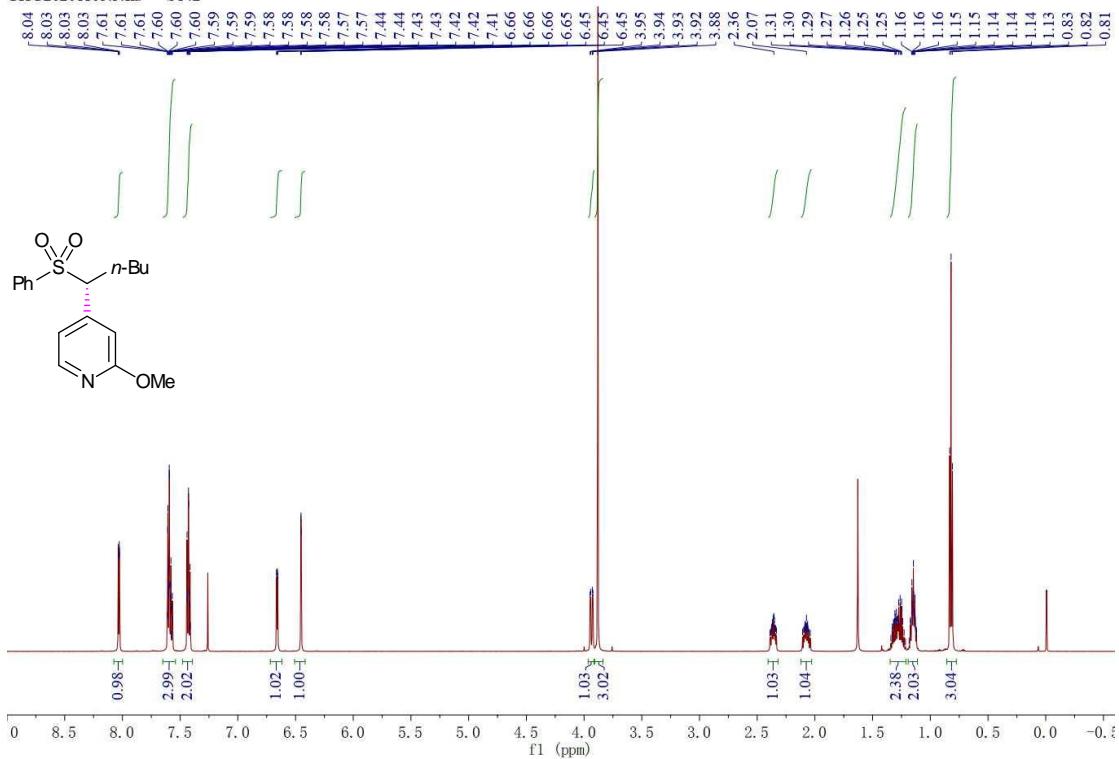
36, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201029.13.fid — 141-OME

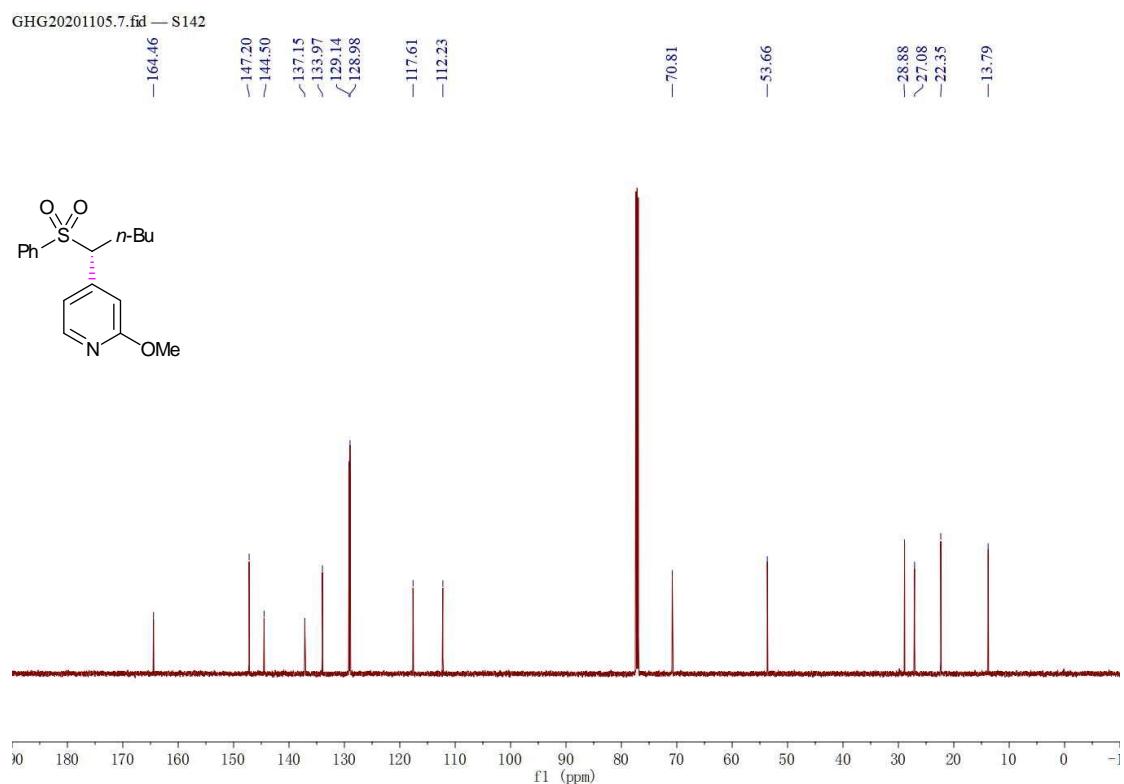


37, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

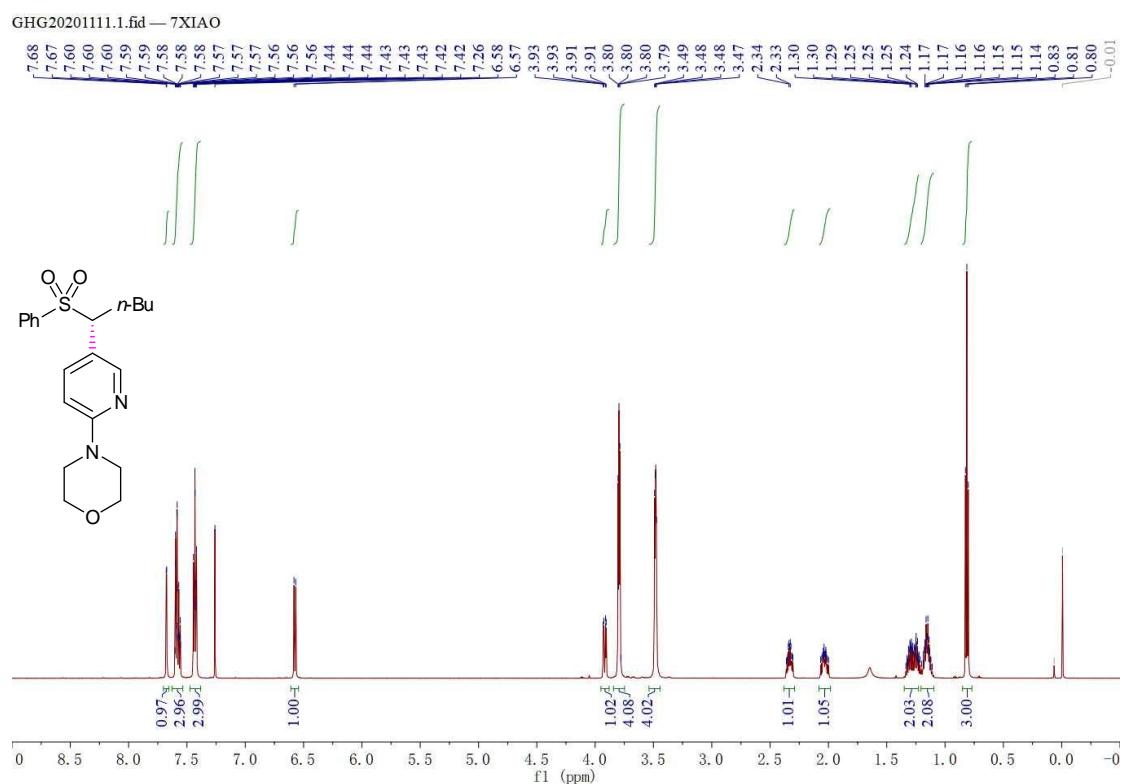
GHG20201105.3.fid — S142



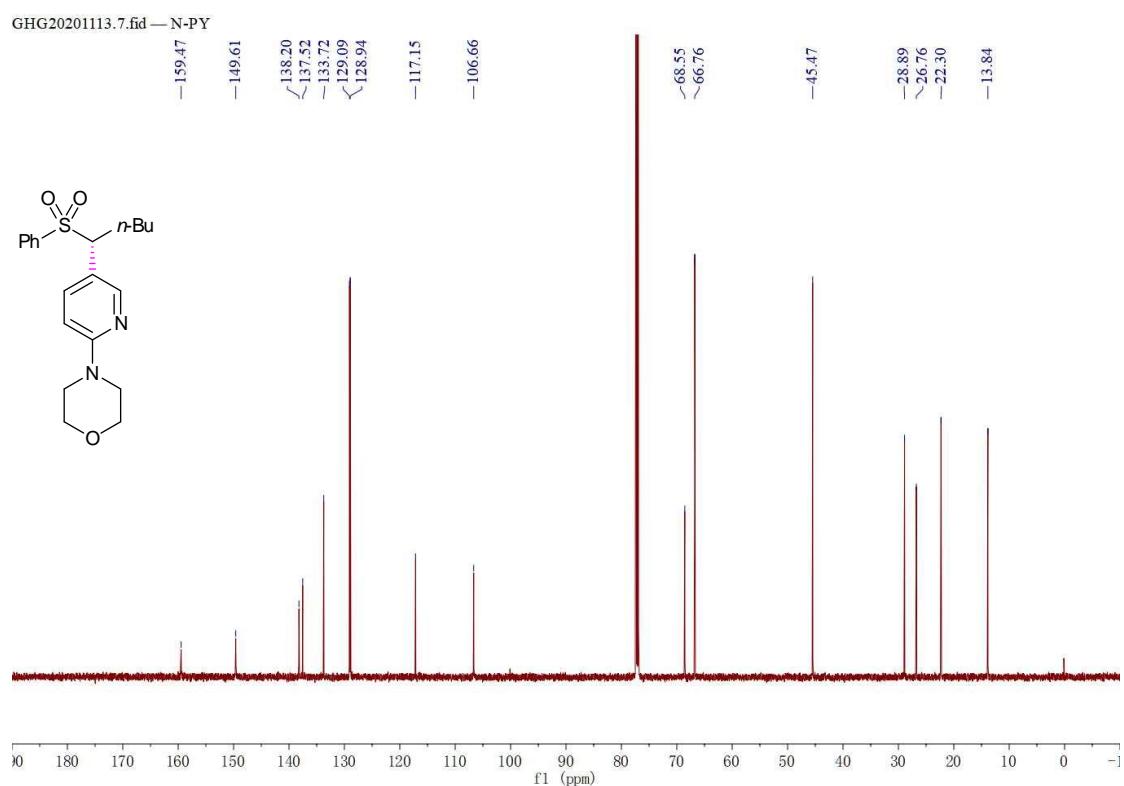
37, ^{13}C NMR (151 MHz, CDCl_3)



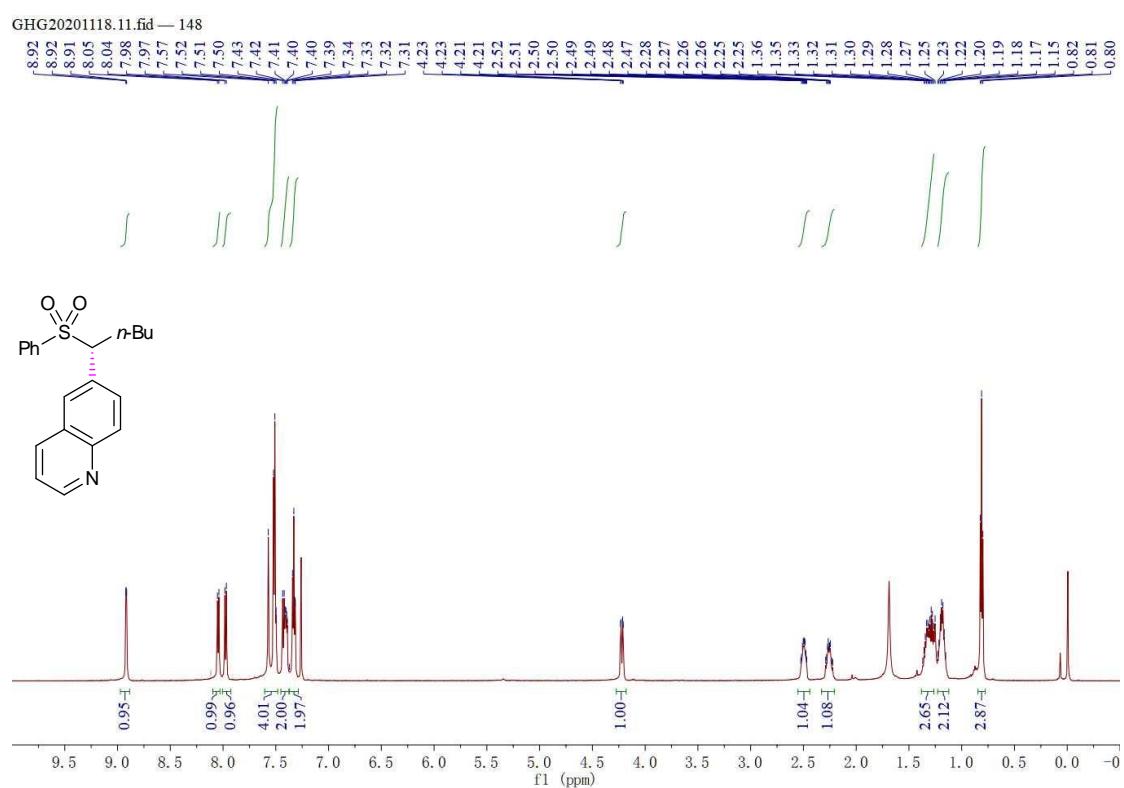
38, ^1H -NMR (600 MHz, CDCl_3)



38, ^{13}C NMR (151 MHz, CDCl_3)

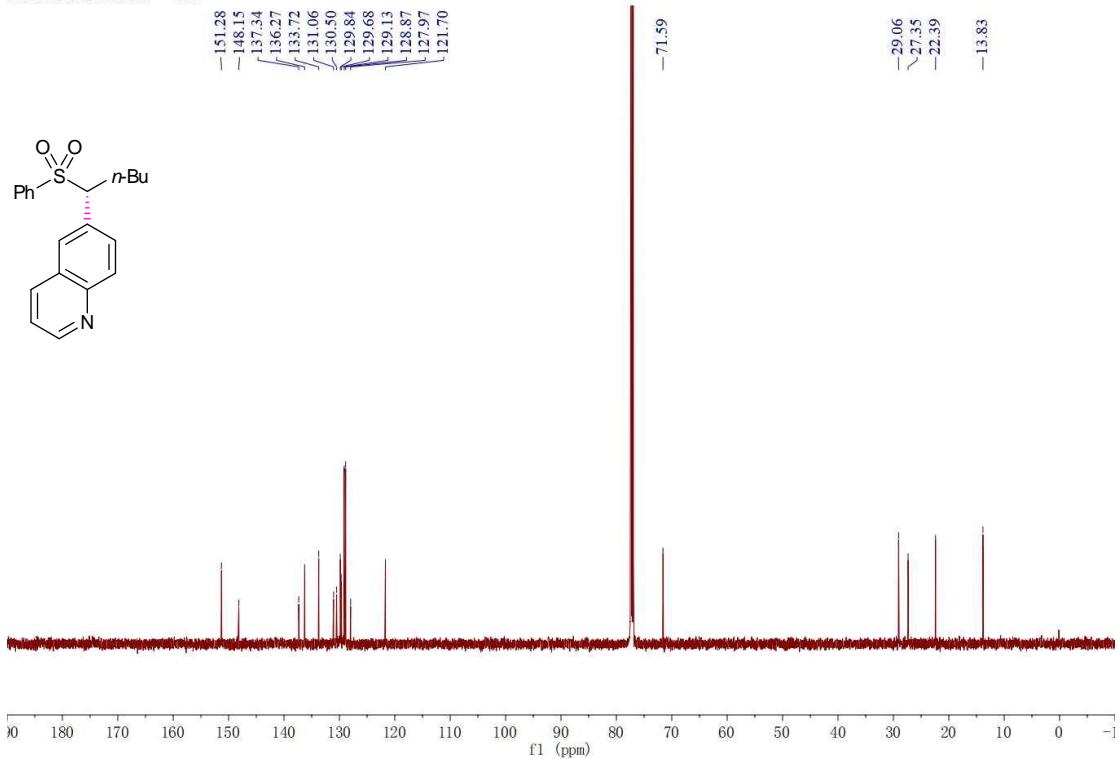
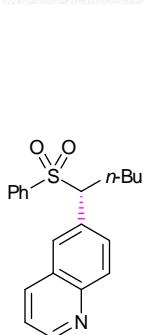


39, ^1H -NMR (600 MHz, CDCl_3)



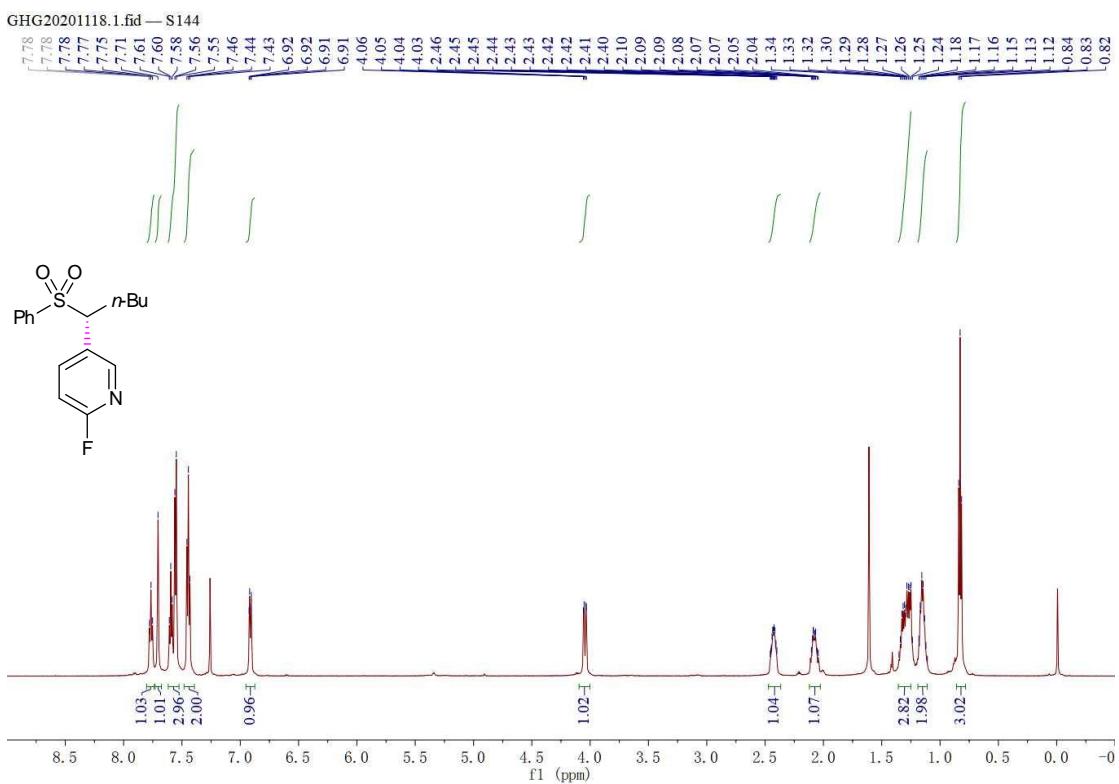
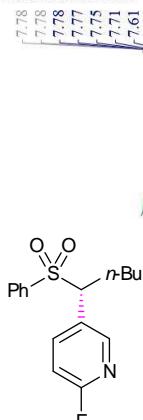
39, ^{13}C NMR (151 MHz, CDCl_3)

GHG20201118.12.fid — 148

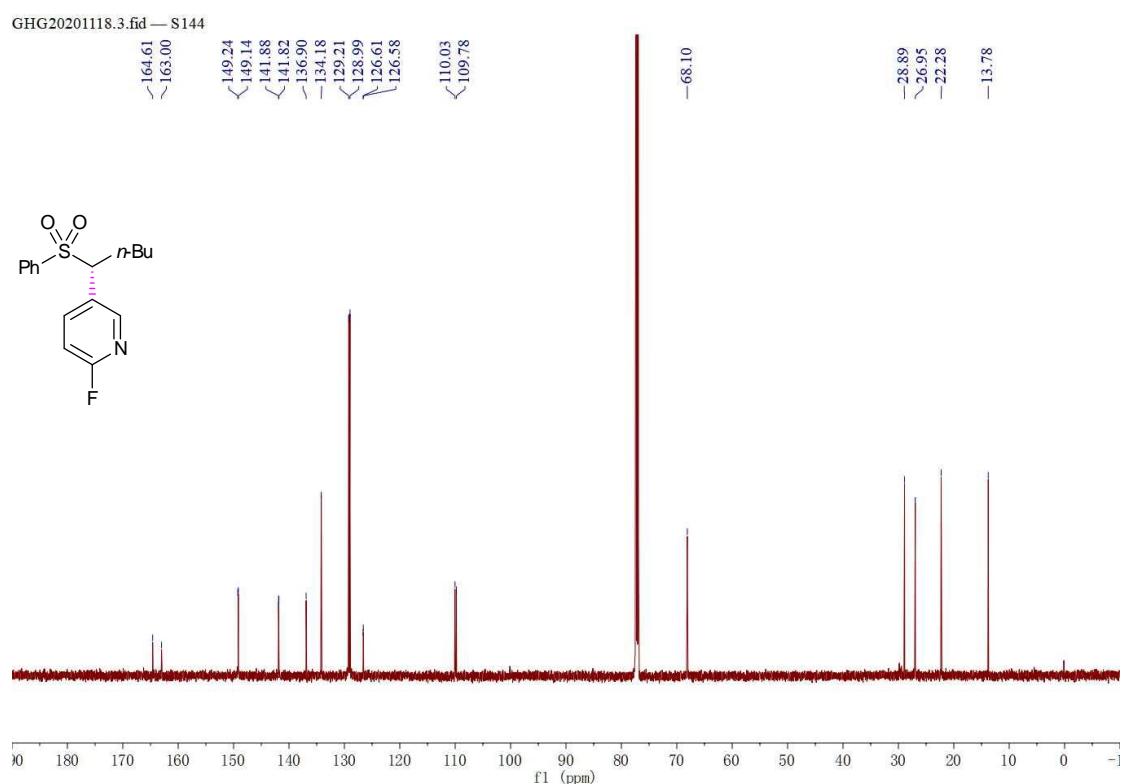


40, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

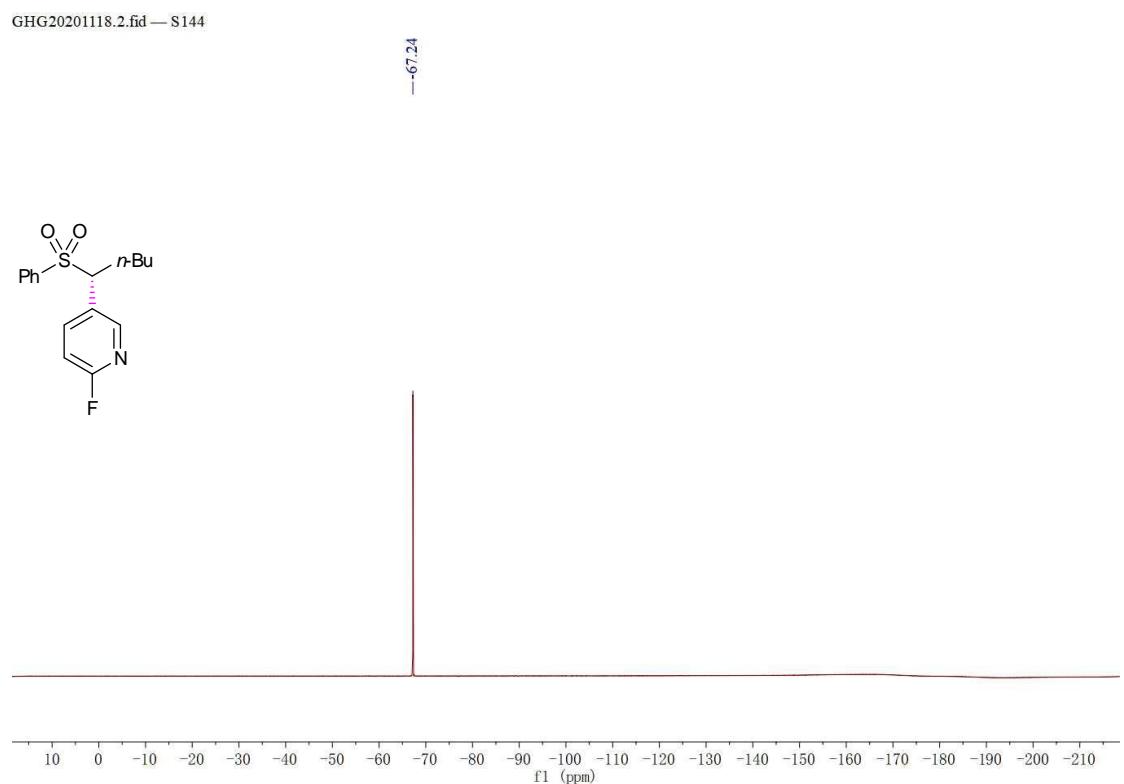
GHG20201118.1.fid — S144



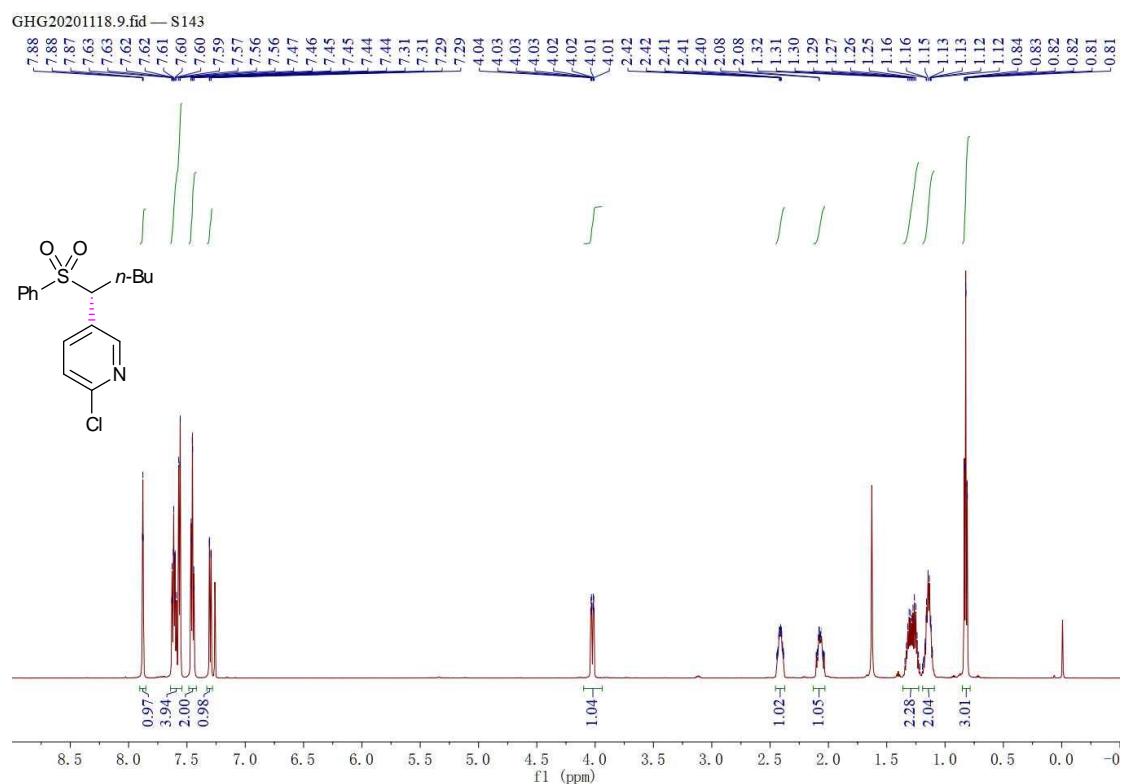
40, ^{13}C NMR (151 MHz, CDCl_3)



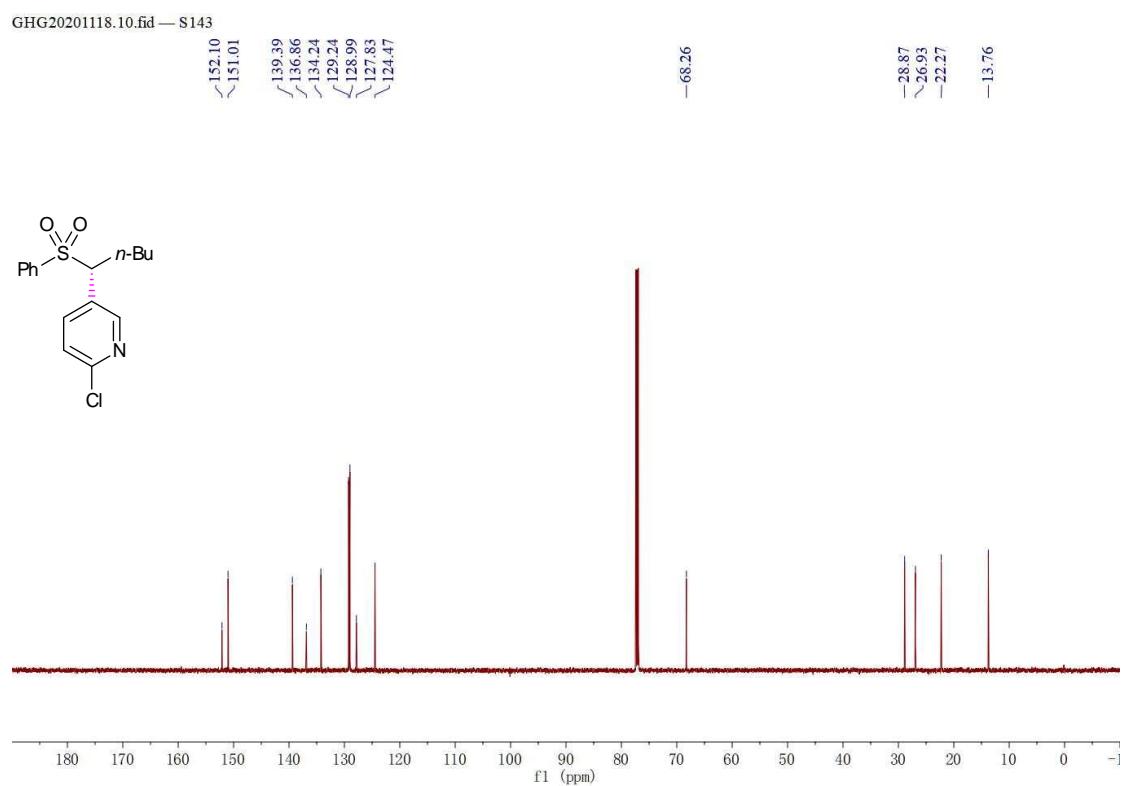
40, ^{19}F NMR (567 MHz, CDCl_3)



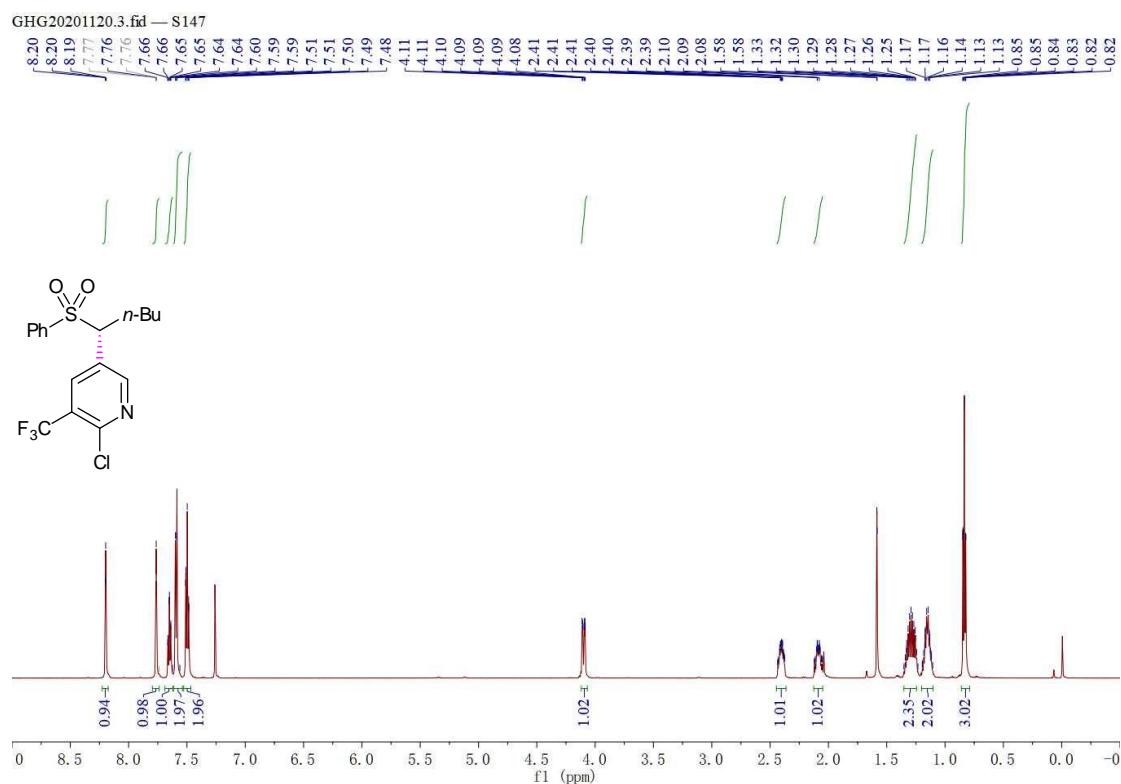
41, ^1H -NMR (600 MHz, CDCl_3)



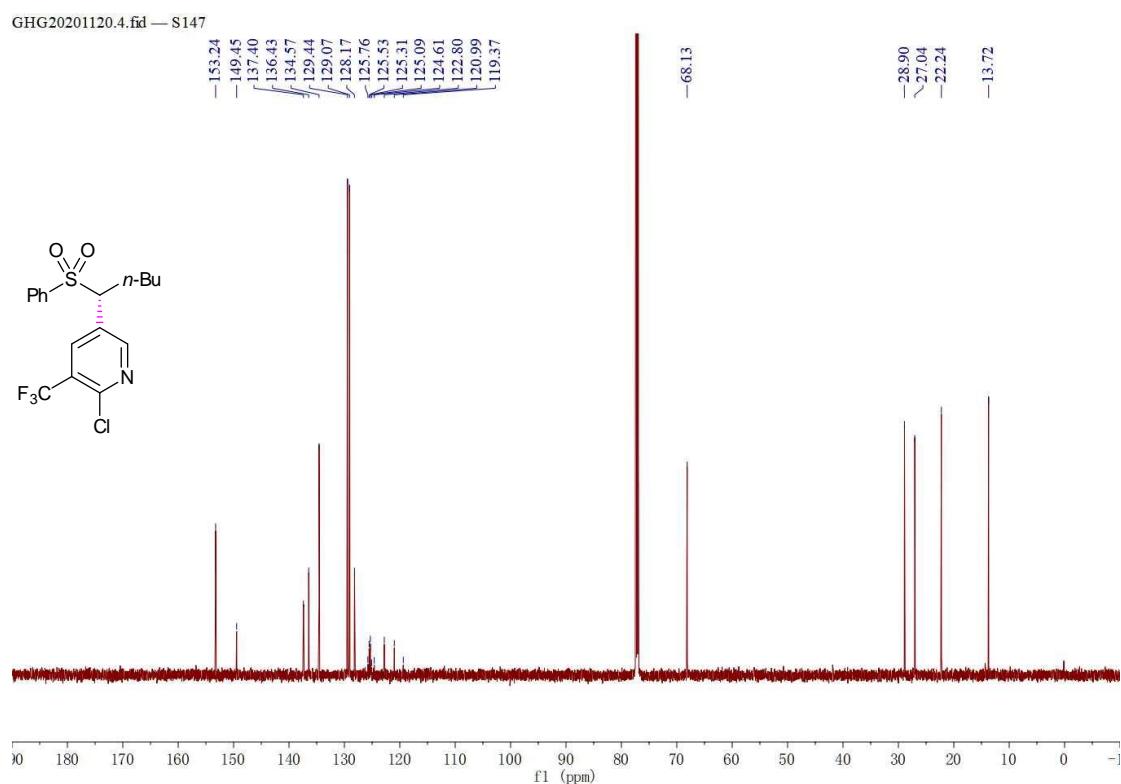
41, ^{13}C NMR (151 MHz, CDCl_3)



42, ^1H -NMR (600 MHz, CDCl_3)

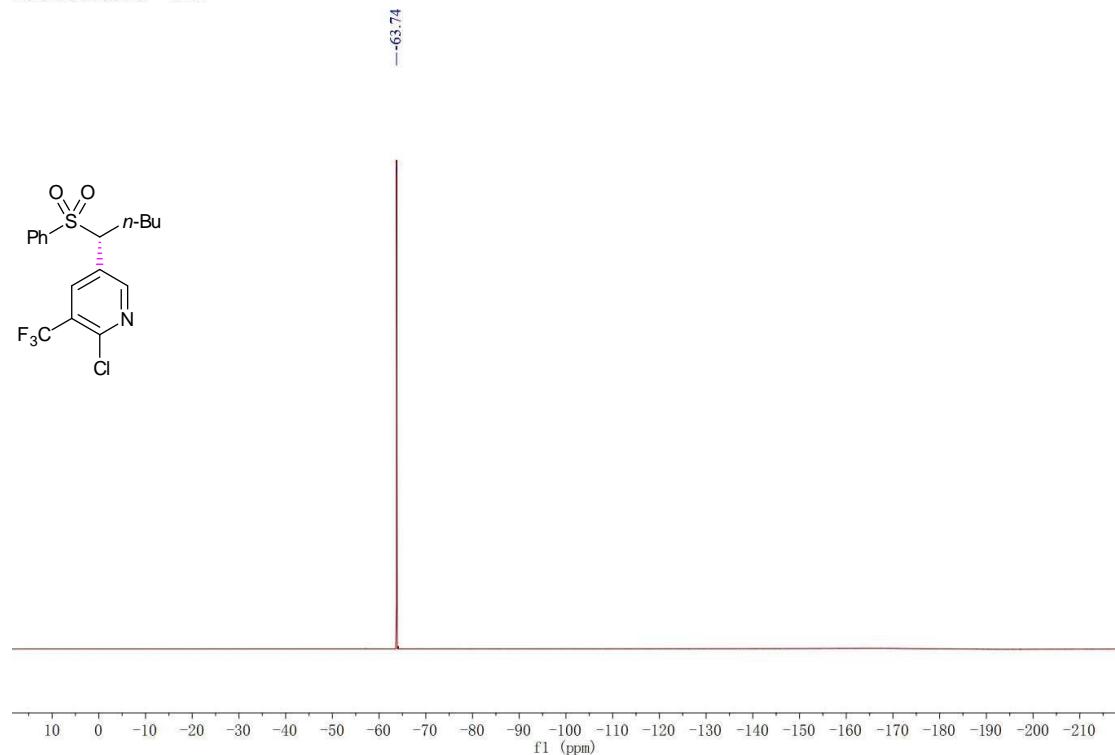


42, ^{13}C NMR (151 MHz, CDCl_3)



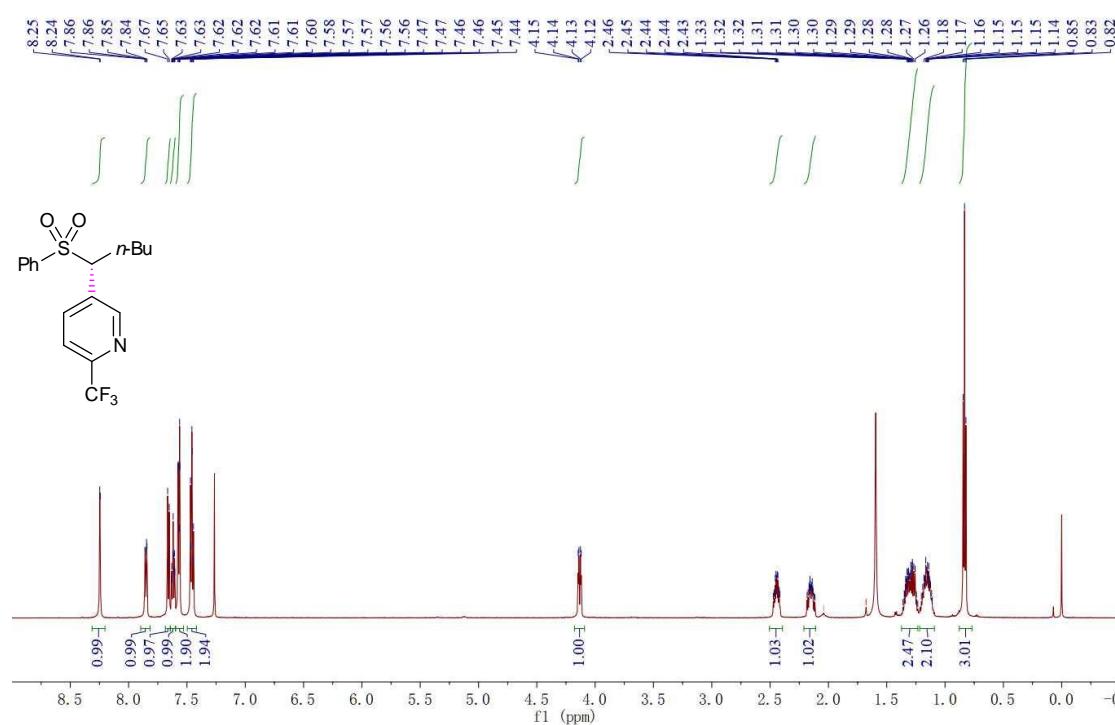
42, ^{19}F NMR (567 MHz, CDCl_3)

GHG20201220.2.fid — S147

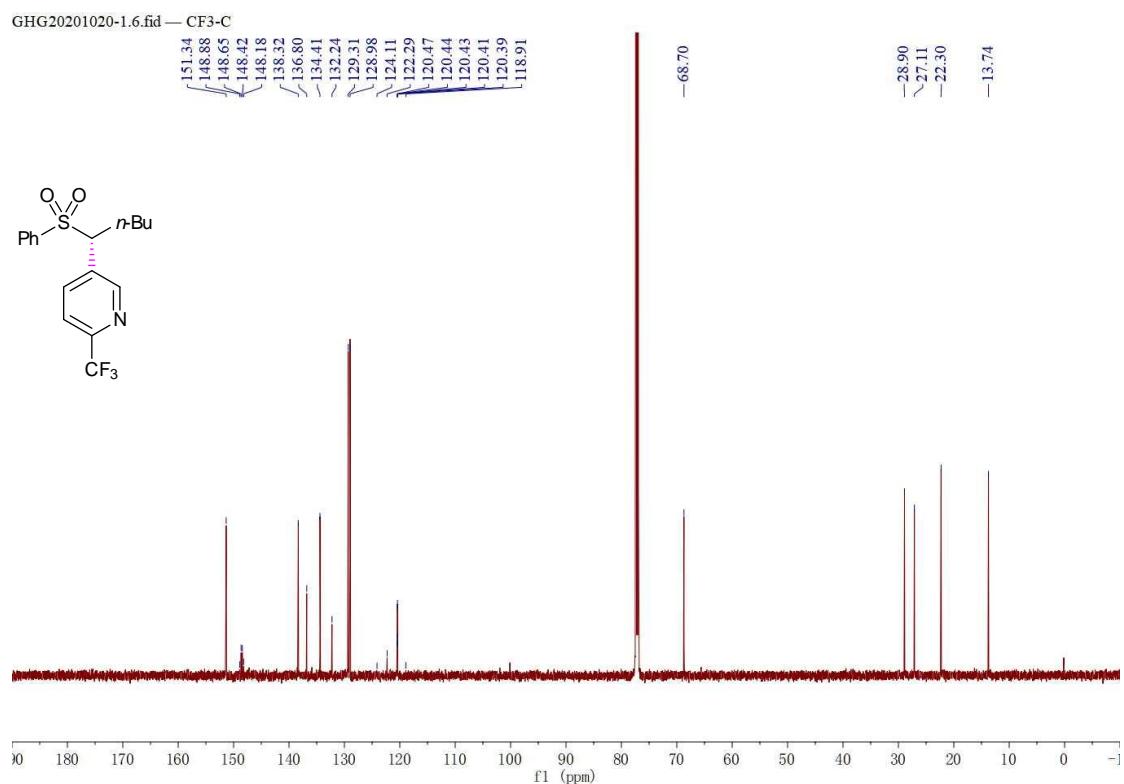


43, ^1H -NMR (600 MHz, CDCl_3)

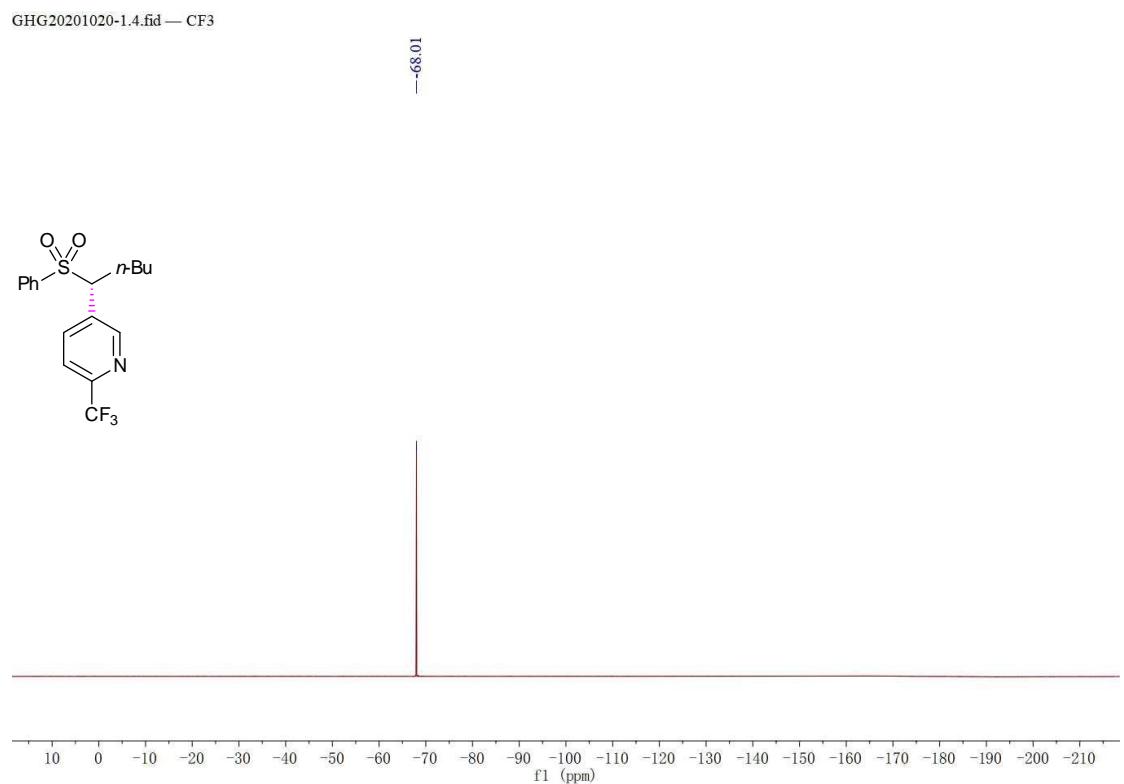
GHG20201020-1.2.fid — CF3



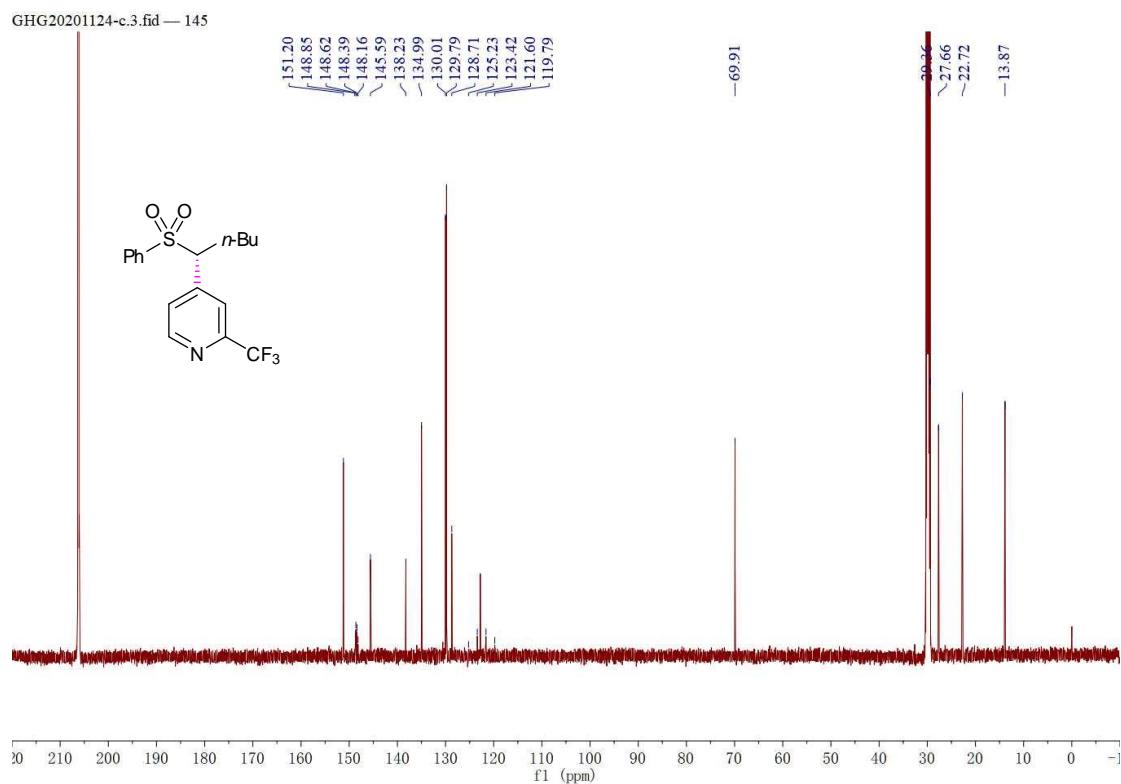
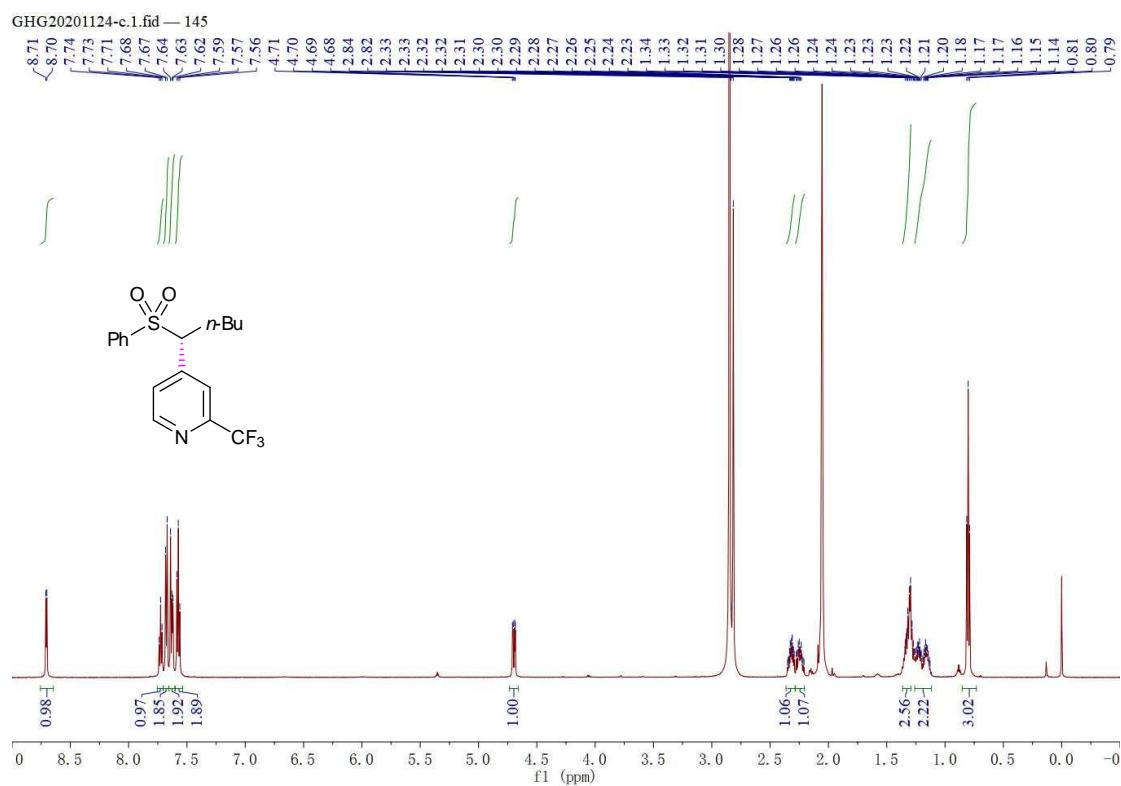
43, ^{13}C NMR (151 MHz, CDCl_3)



43, ^{19}F NMR (567 MHz, CDCl_3)

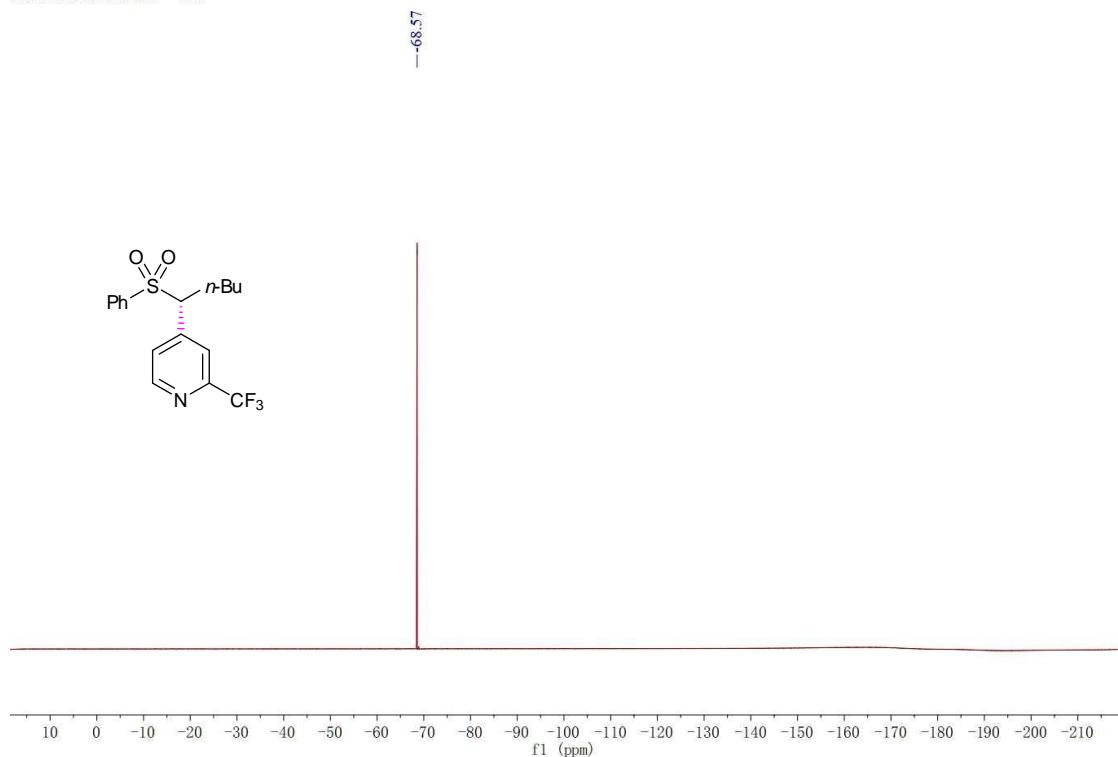
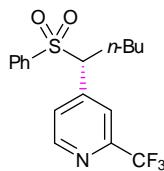


44, ^1H -NMR (600 MHz, Acetone- d_6)



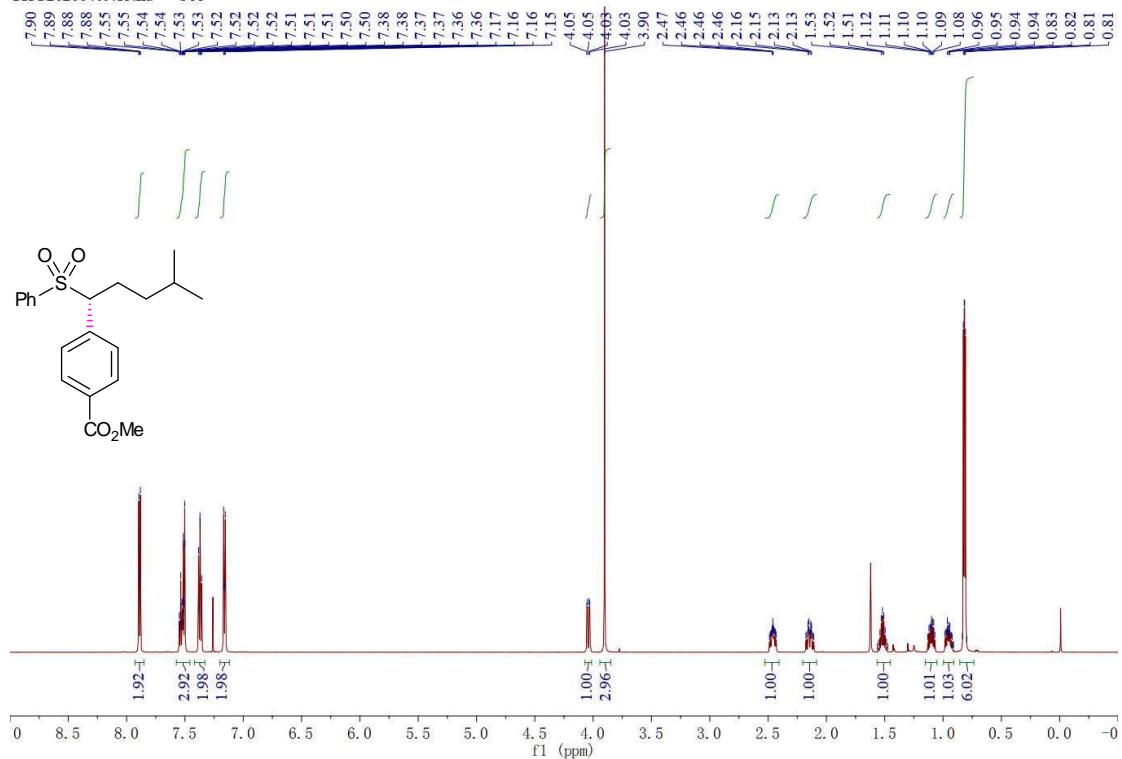
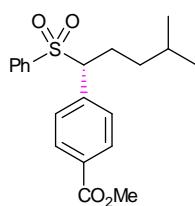
44, ^{19}F NMR (567 MHz, Acetone- d_6)

GHG20201124-c.2.fid — 145



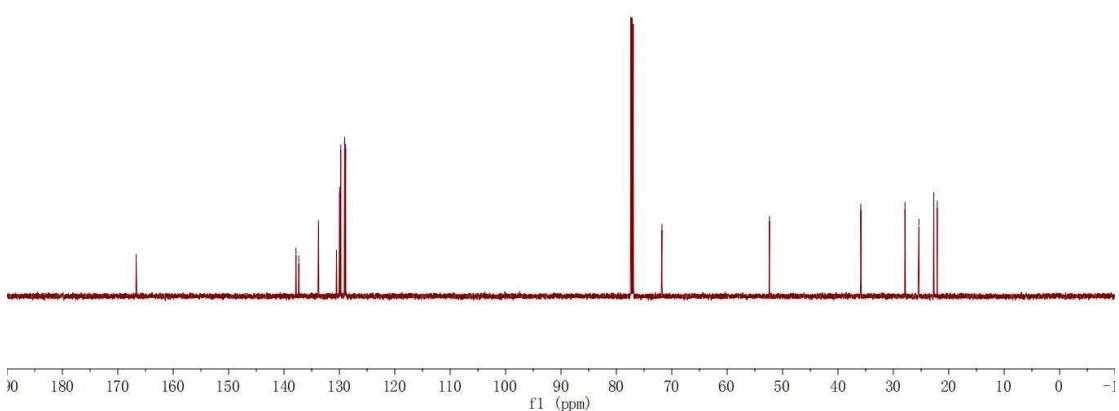
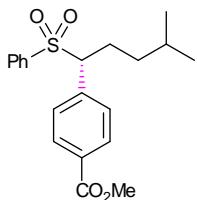
45, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200409.15.fid — S68



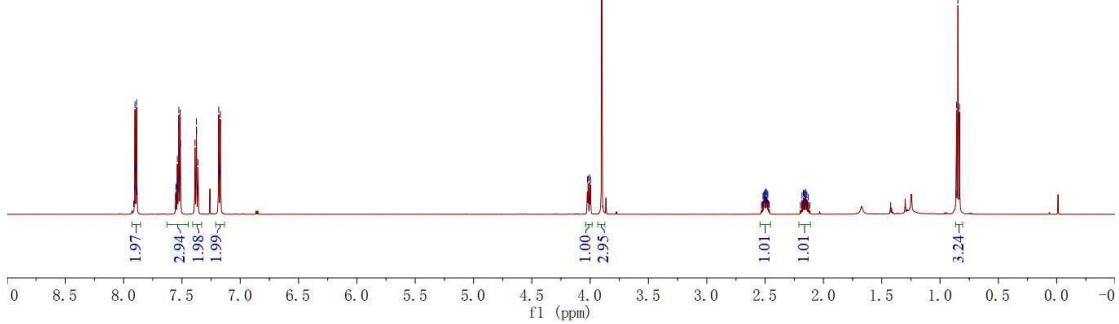
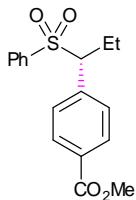
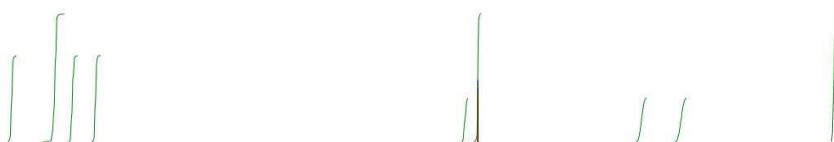
45, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200409-C.3.fid — S68

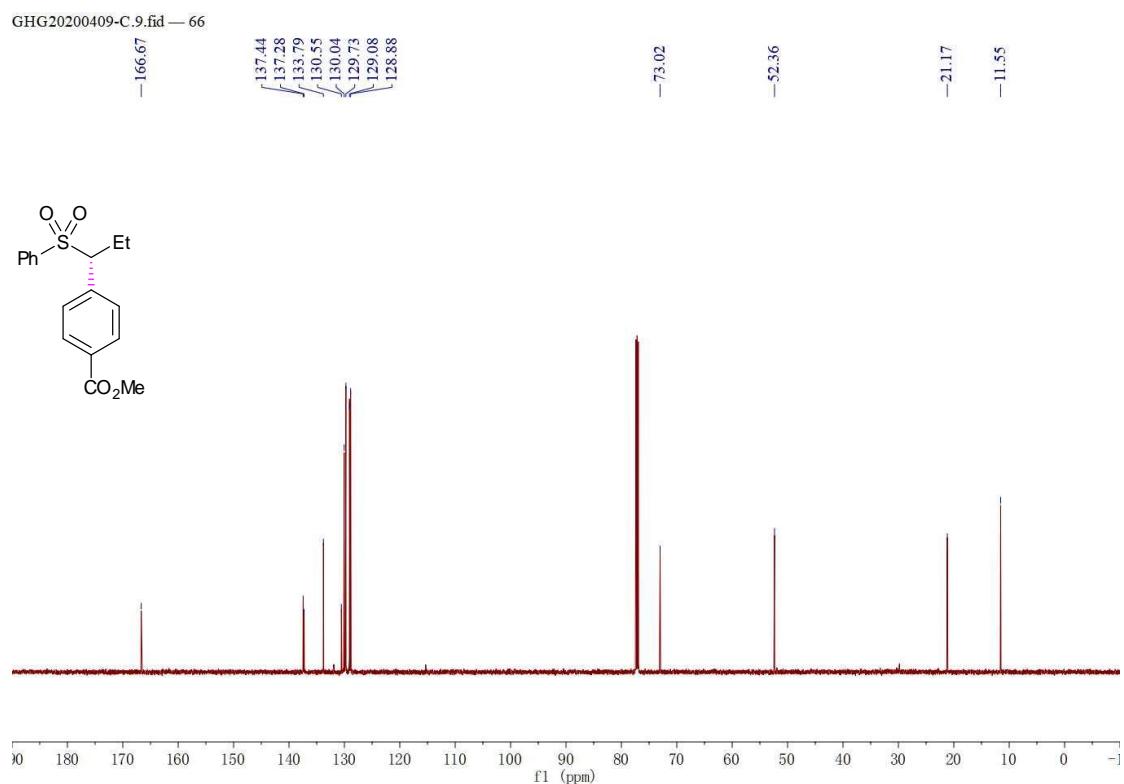


46, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

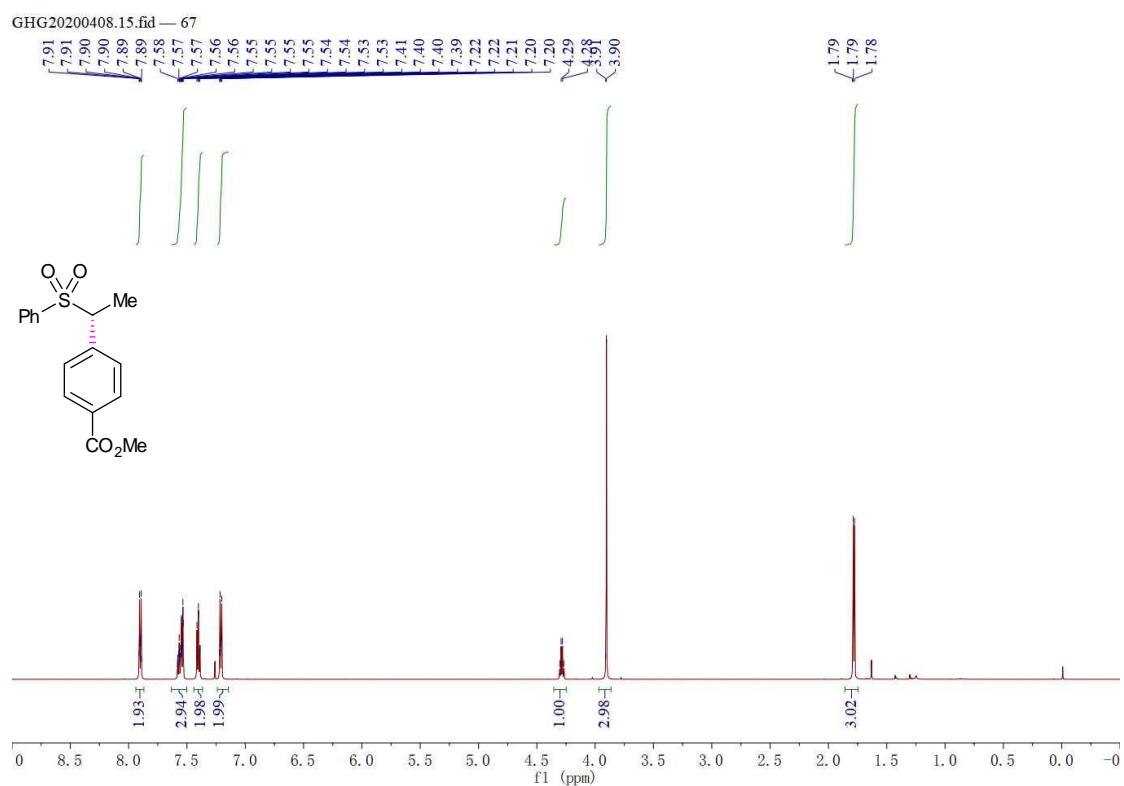
GHG20200409.14.fid — 66



46, ^{13}C NMR (151 MHz, CDCl_3)

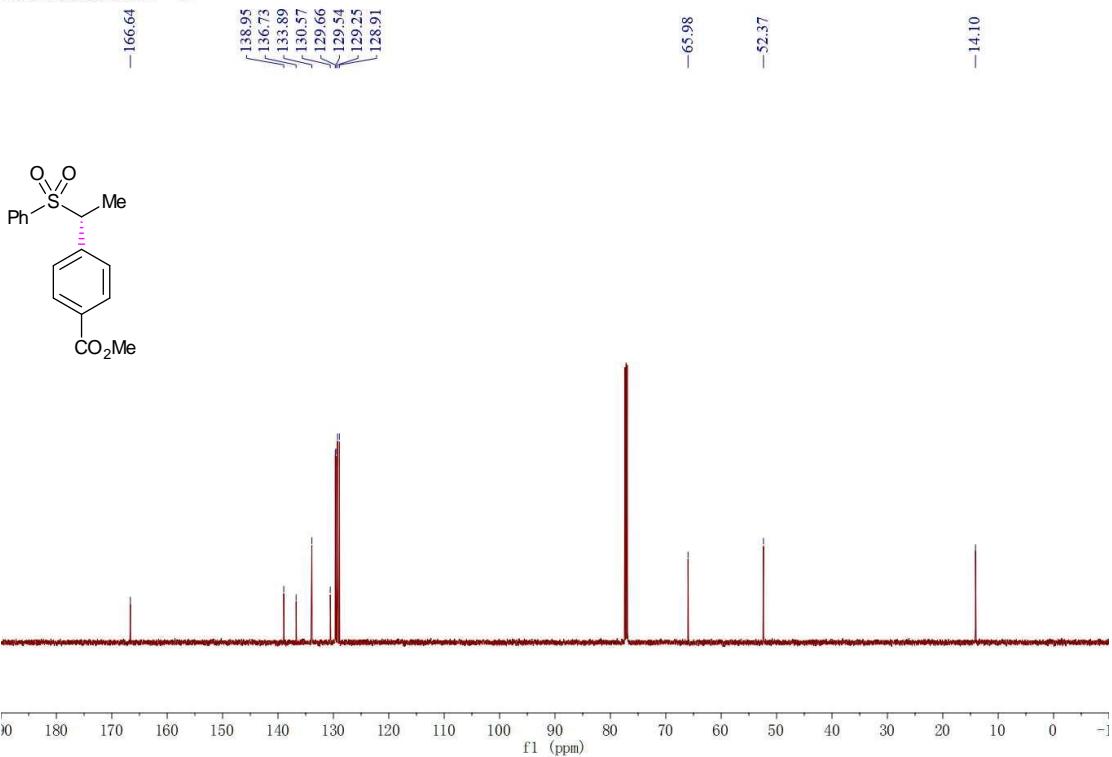


47, ^1H -NMR (600 MHz, CDCl_3)



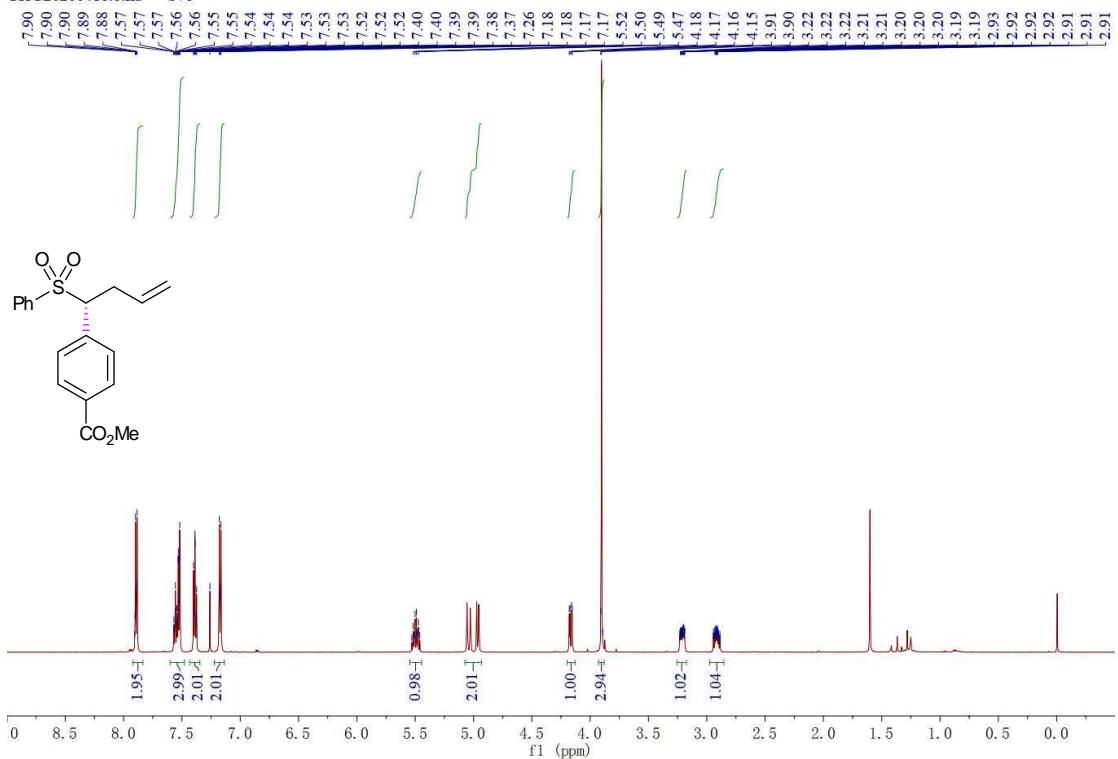
47, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200408-C.3.fid — 67



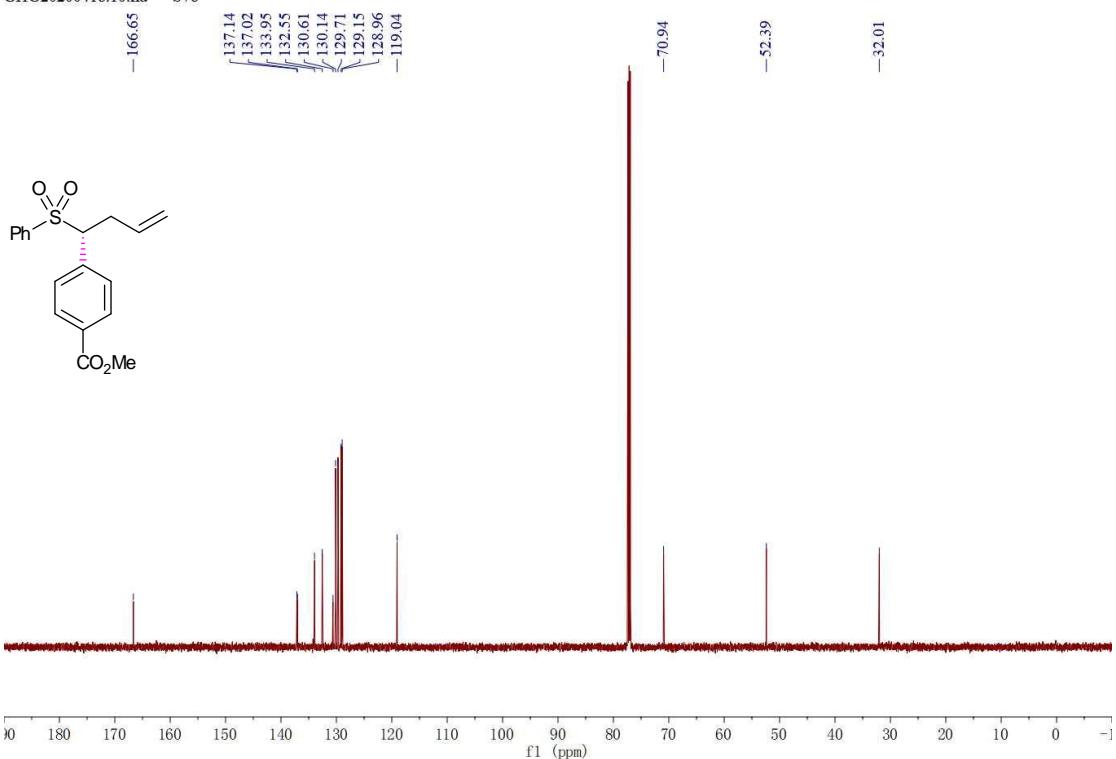
48, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200418.6.fid — S78



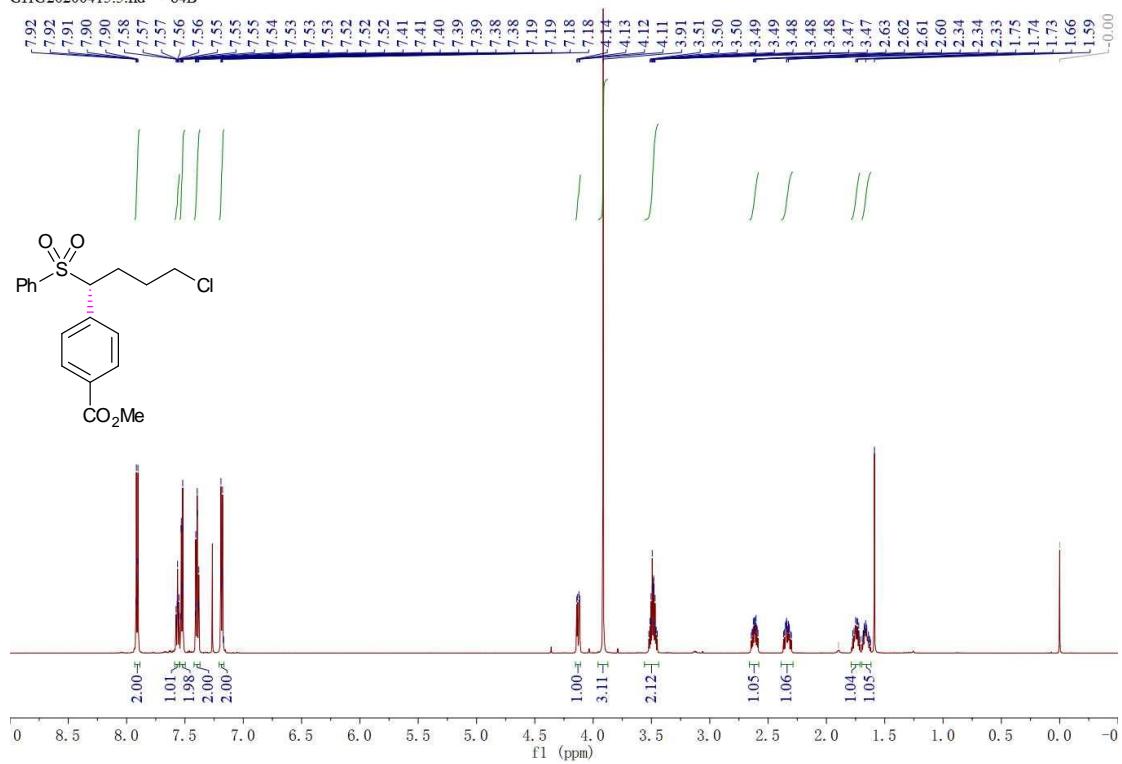
48, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200418.10.fid — S78



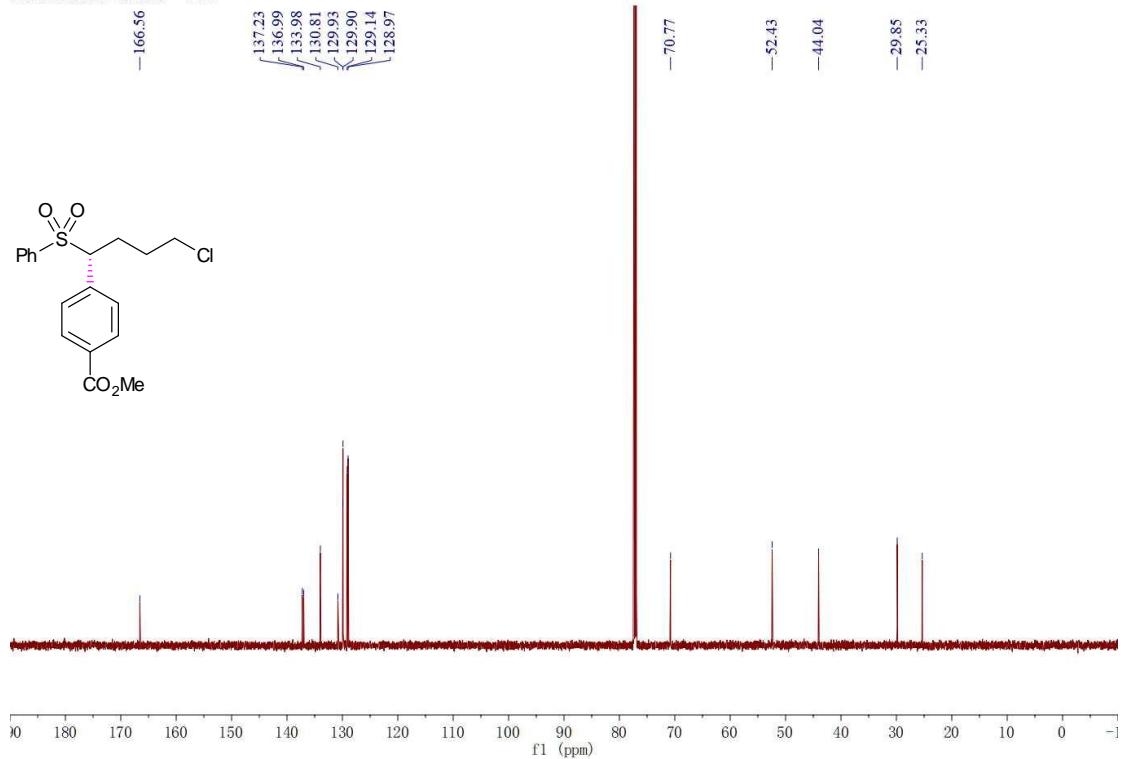
49, ^1H -NMR (600 MHz, CDCl_3)

GHG20200415.5.fid — 84B



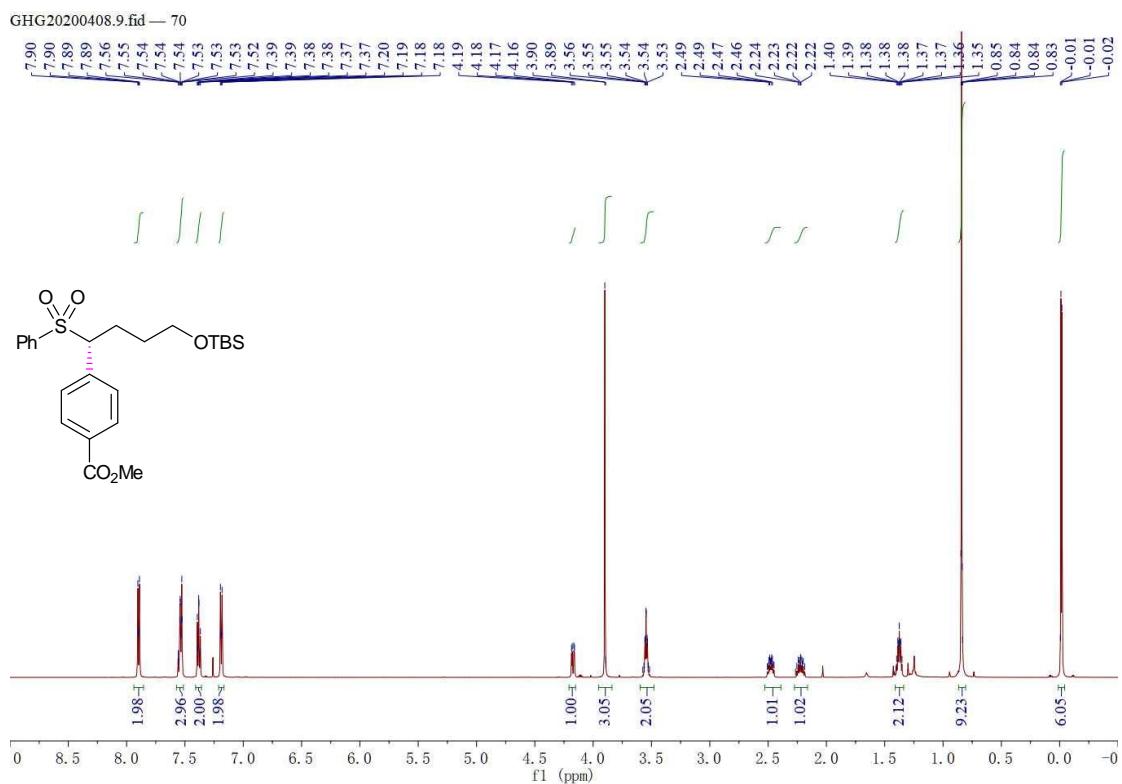
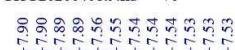
49, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200415-C.1.fid — 84B

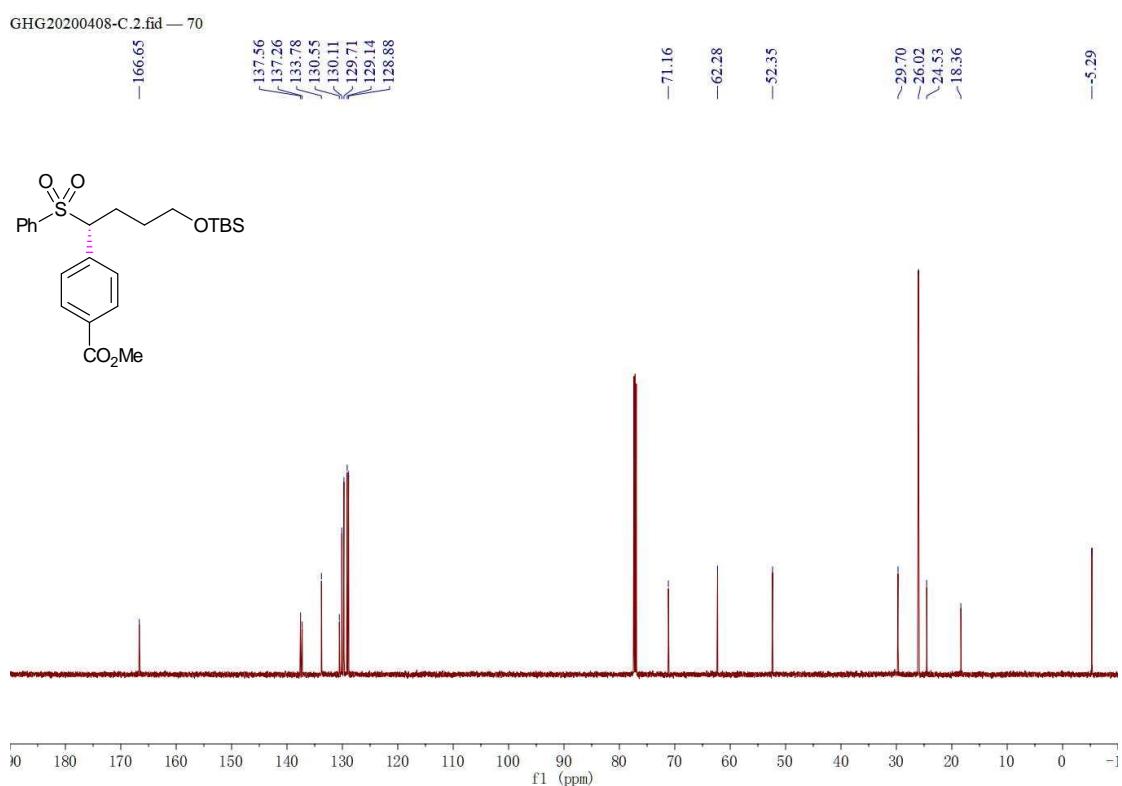


50, ^1H -NMR (600 MHz, CDCl_3)

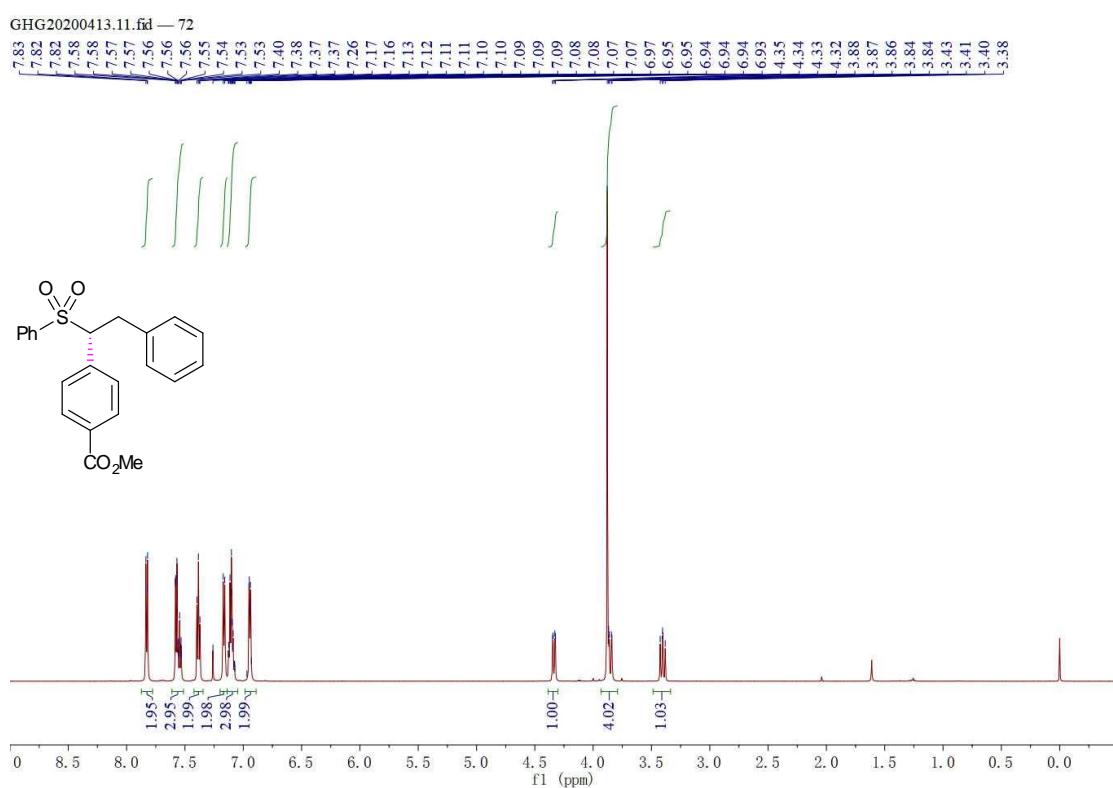
GHG20200408.9.fid — 70



50, ^{13}C NMR (151 MHz, CDCl_3)

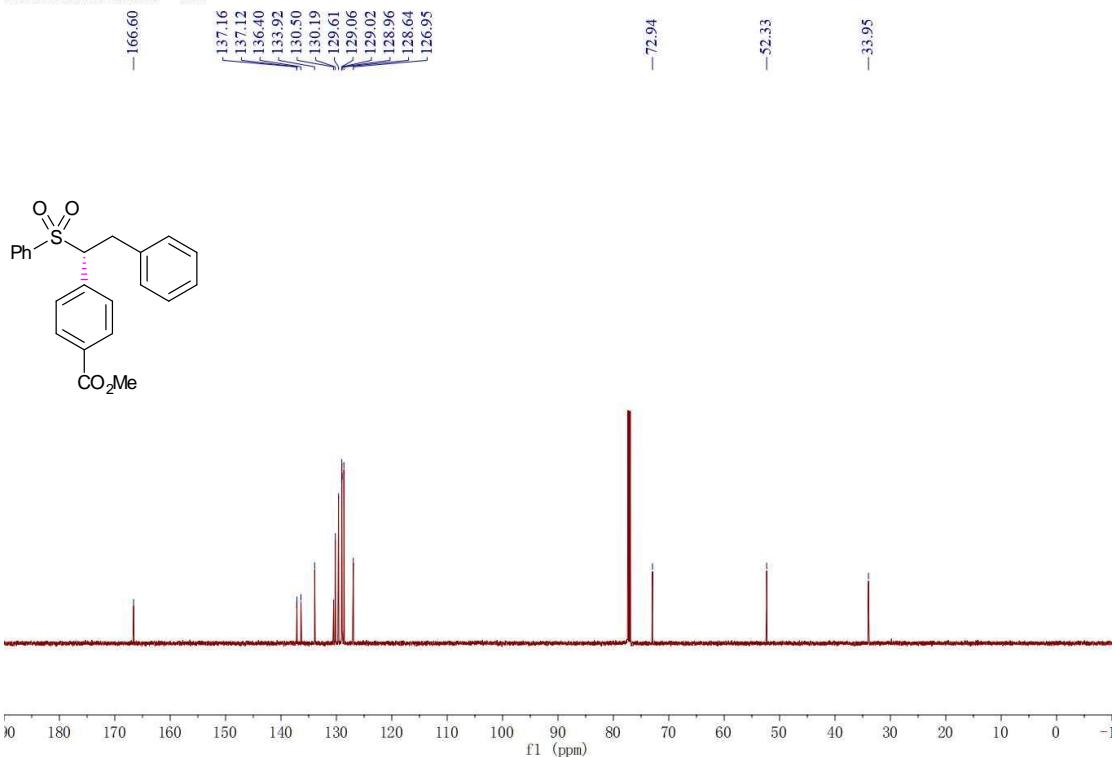


51, ^1H -NMR (600 MHz, CDCl_3)



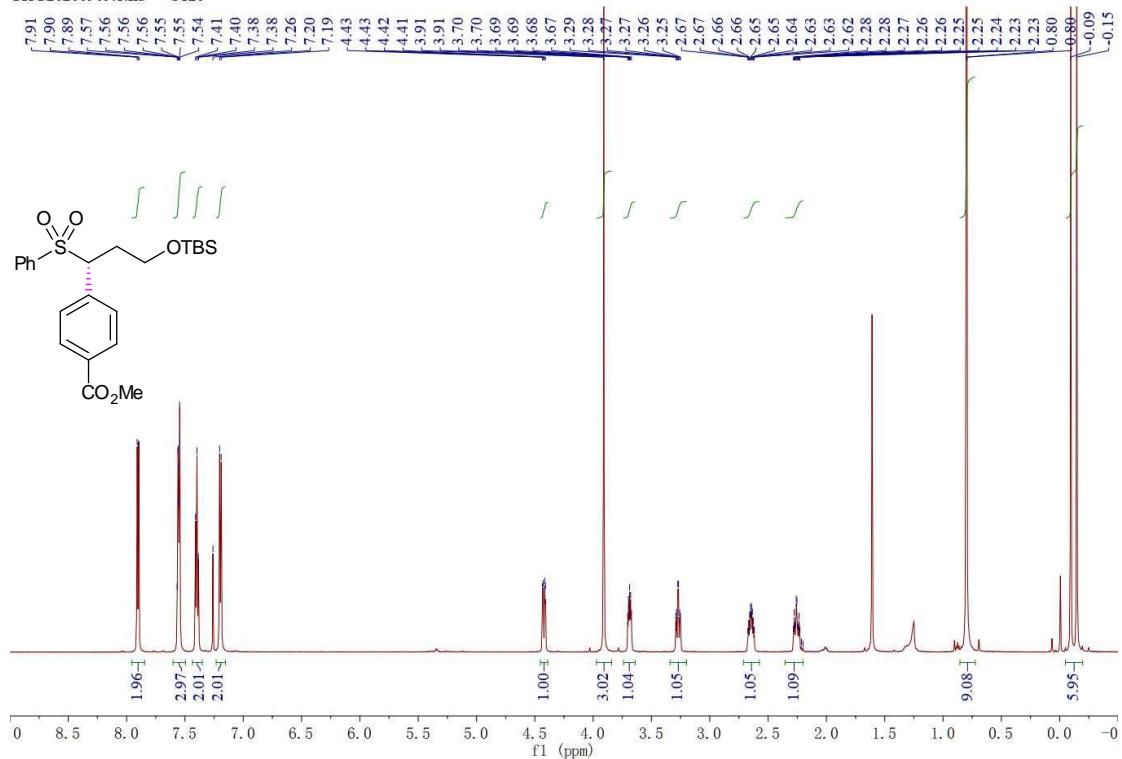
51, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200409-C.4.fid — S72

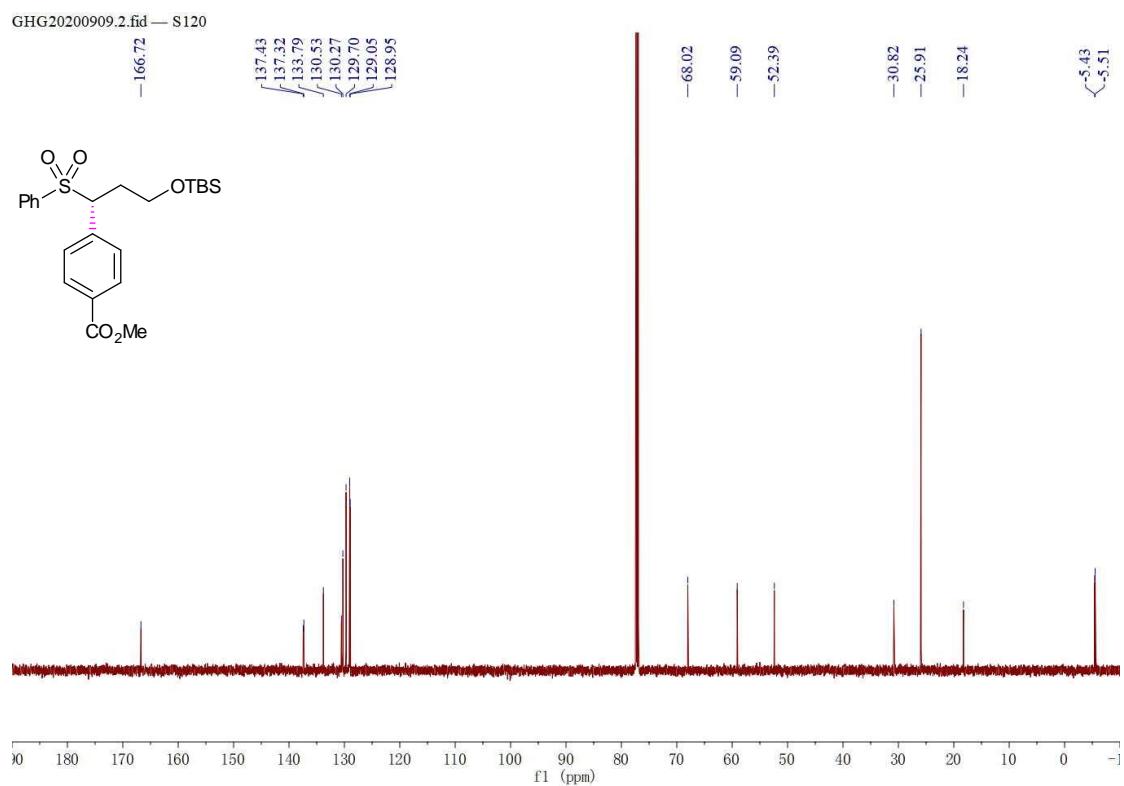


52, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

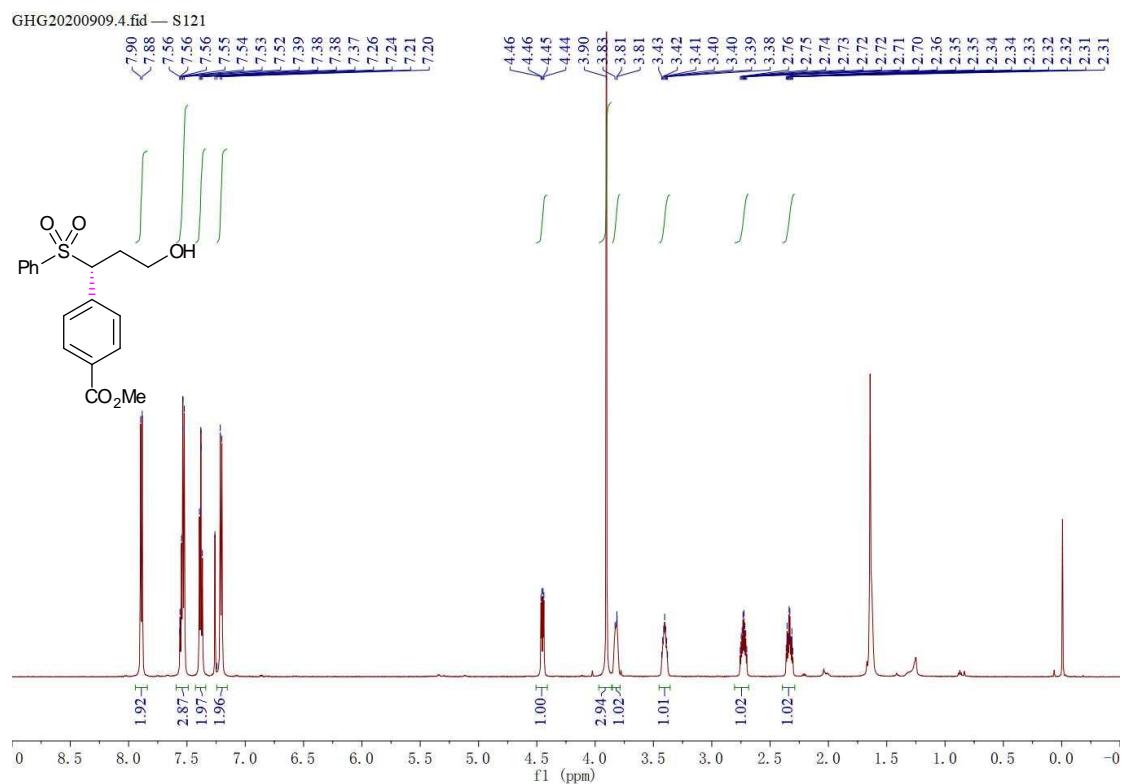
GHG20200909.1.fid — S120



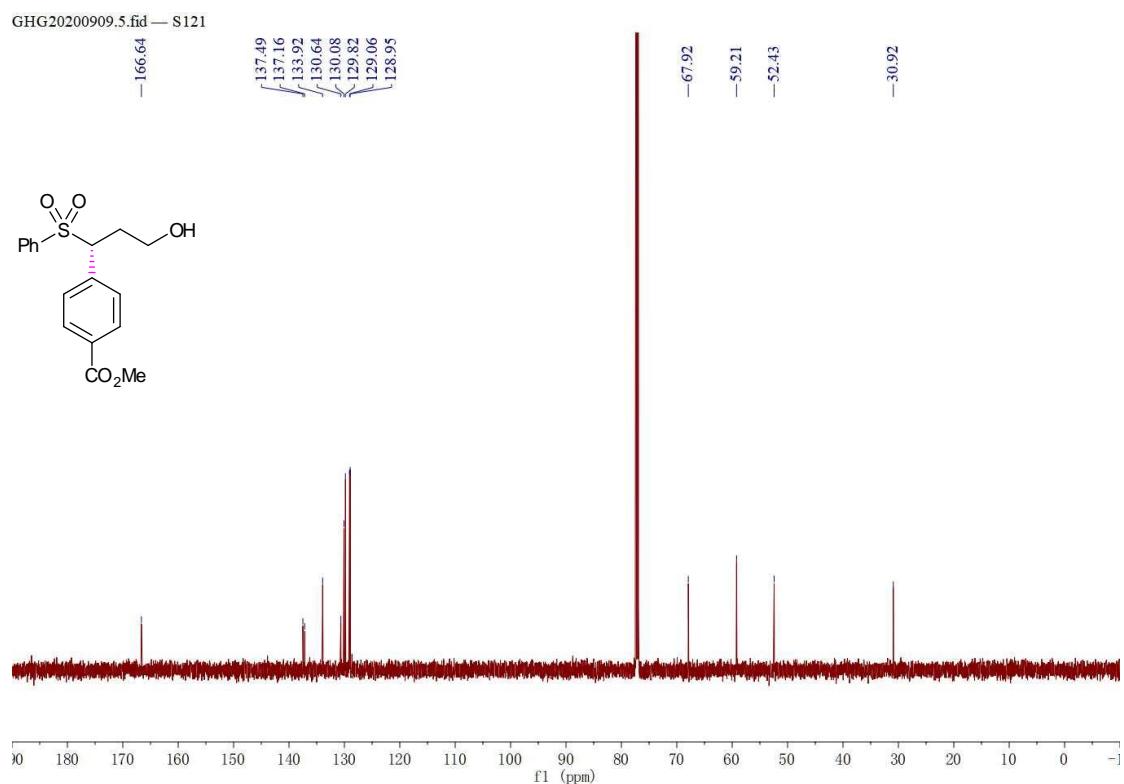
52, ^{13}C NMR (151 MHz, CDCl_3)



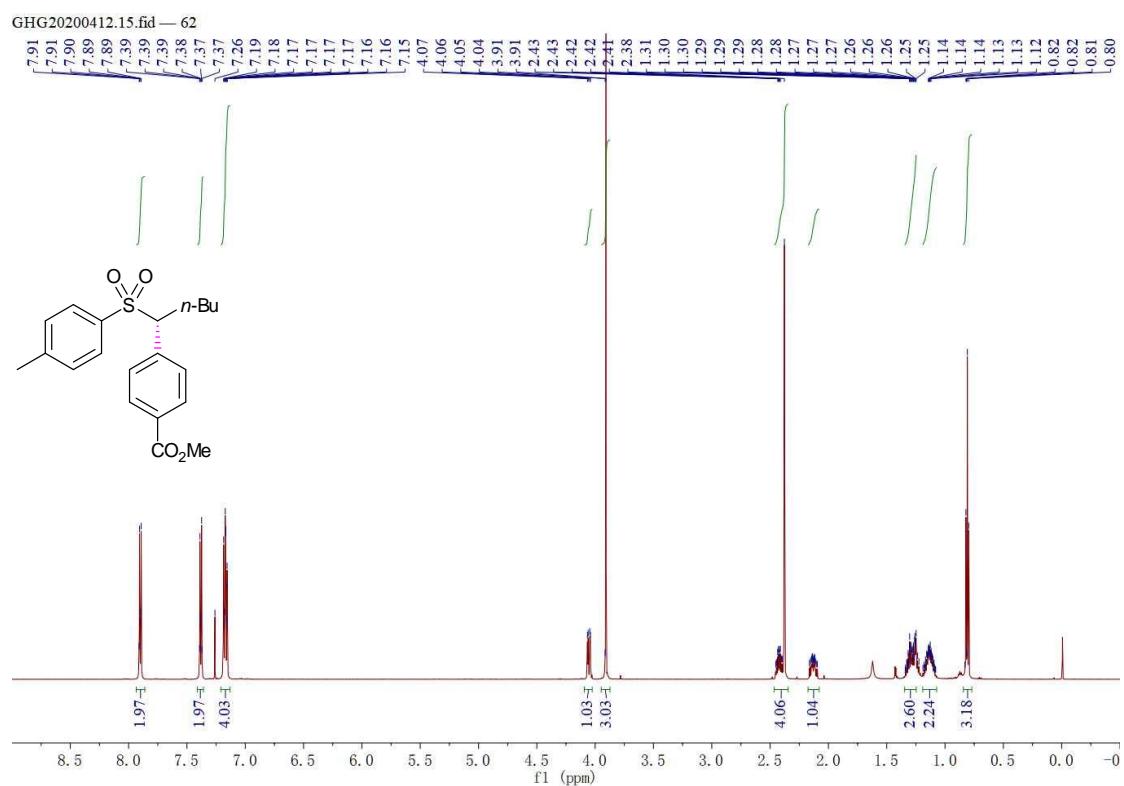
53, ^1H -NMR (600 MHz, CDCl_3)



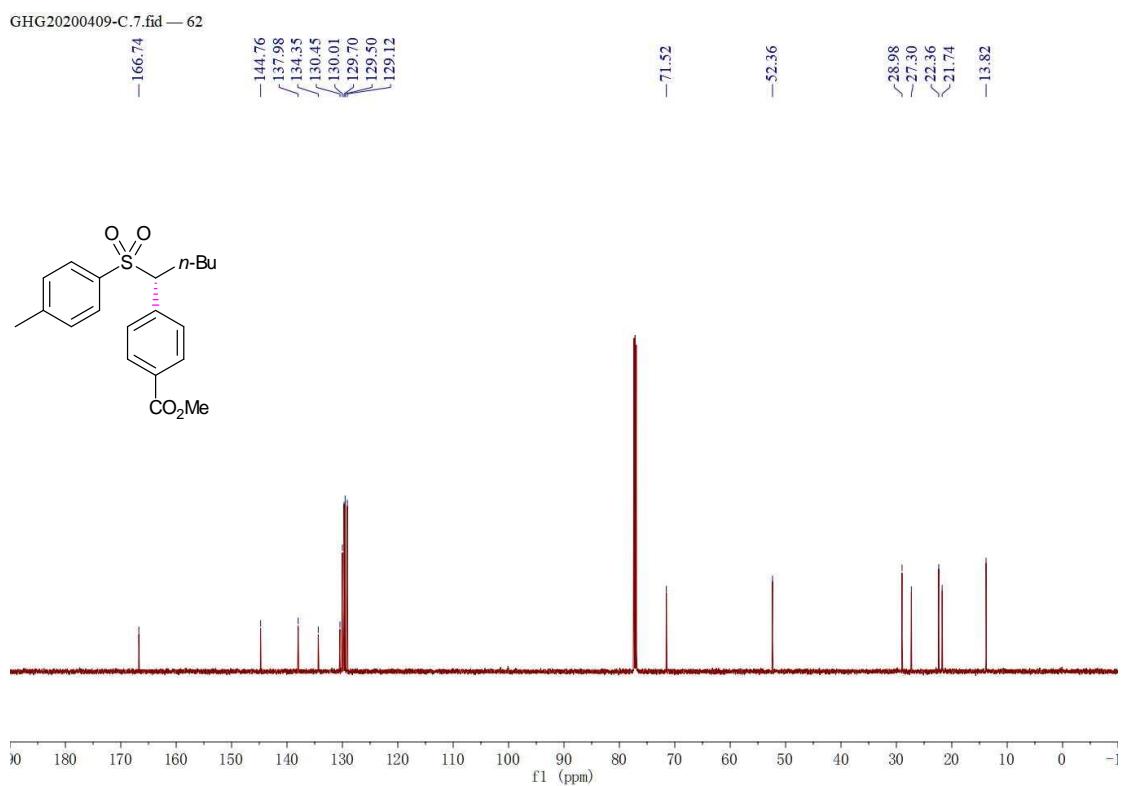
53, ^{13}C NMR (151 MHz, CDCl_3)



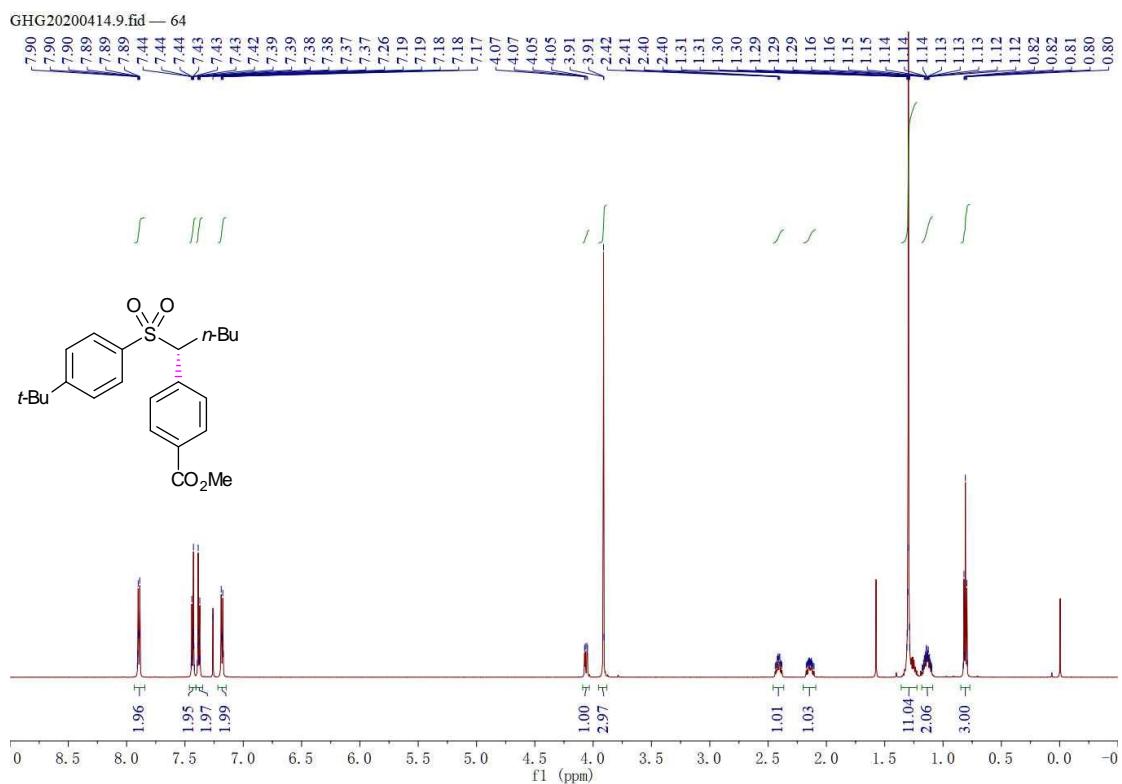
54, ^1H -NMR (600 MHz, CDCl_3)



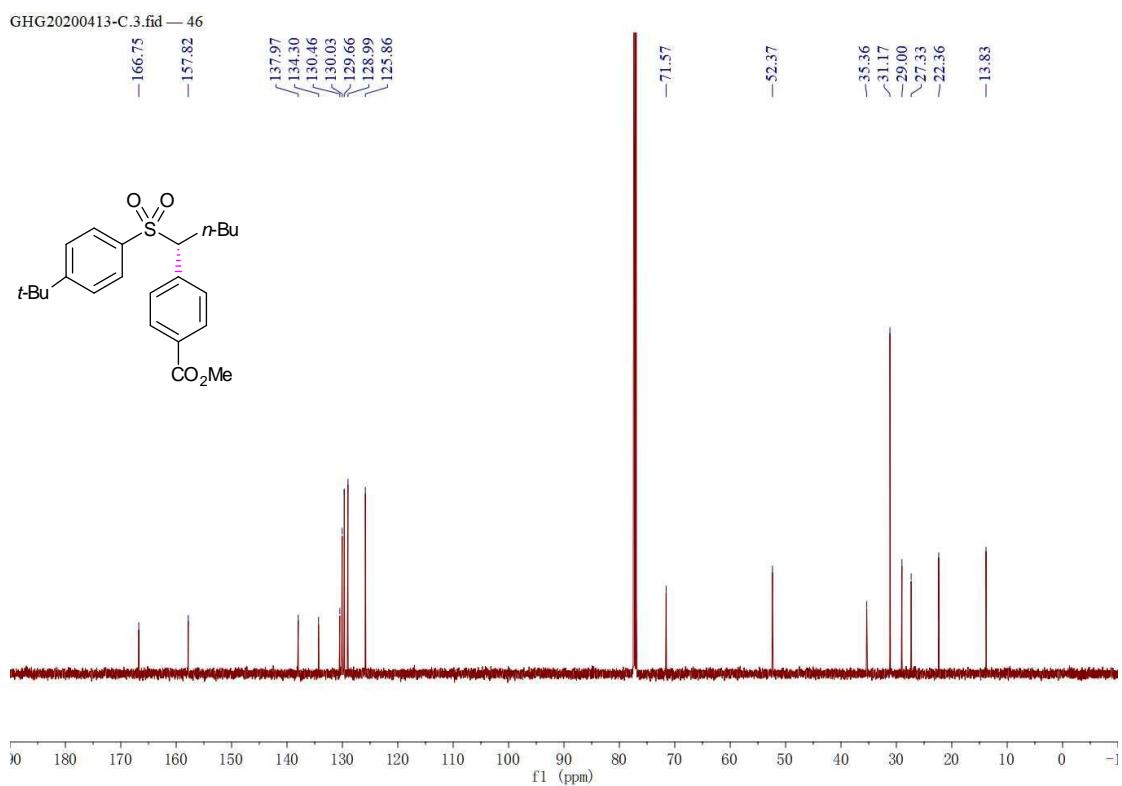
54, ^{13}C NMR (151 MHz, CDCl_3)



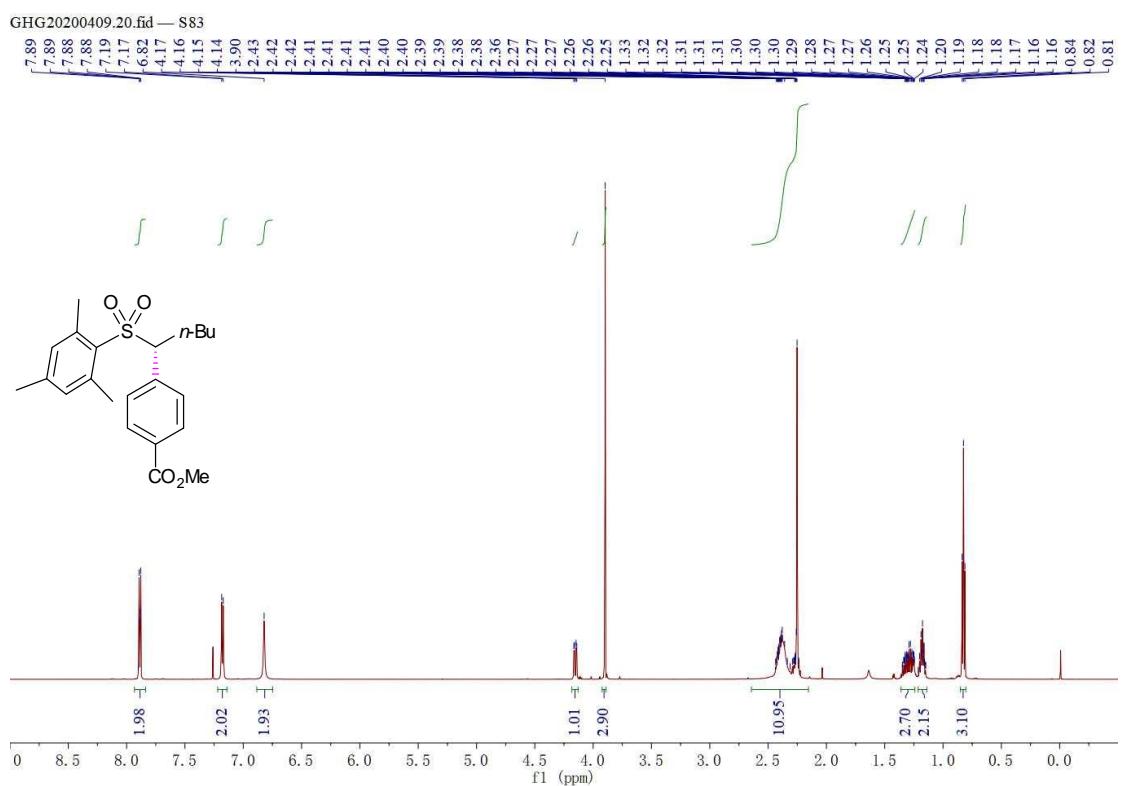
55, ^1H -NMR (600 MHz, CDCl_3)



55, ^{13}C NMR (151 MHz, CDCl_3)

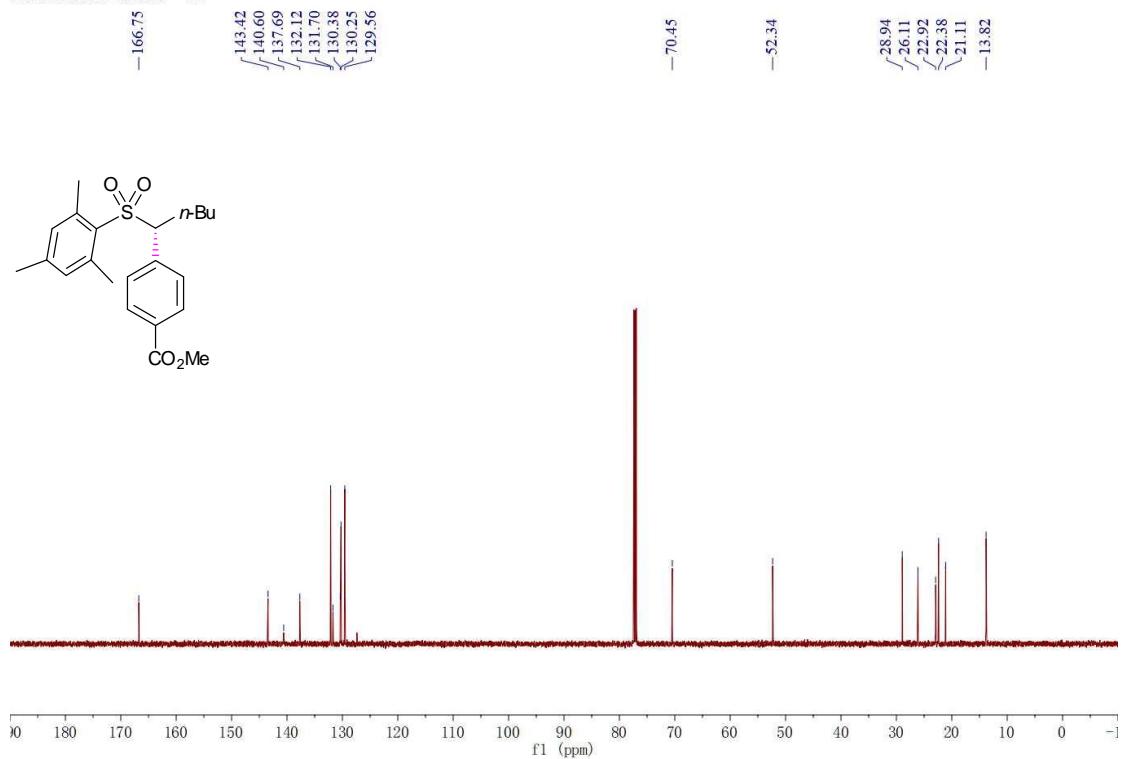


56, $^1\text{H-NMR}$ (600 MHz, CDCl_3)



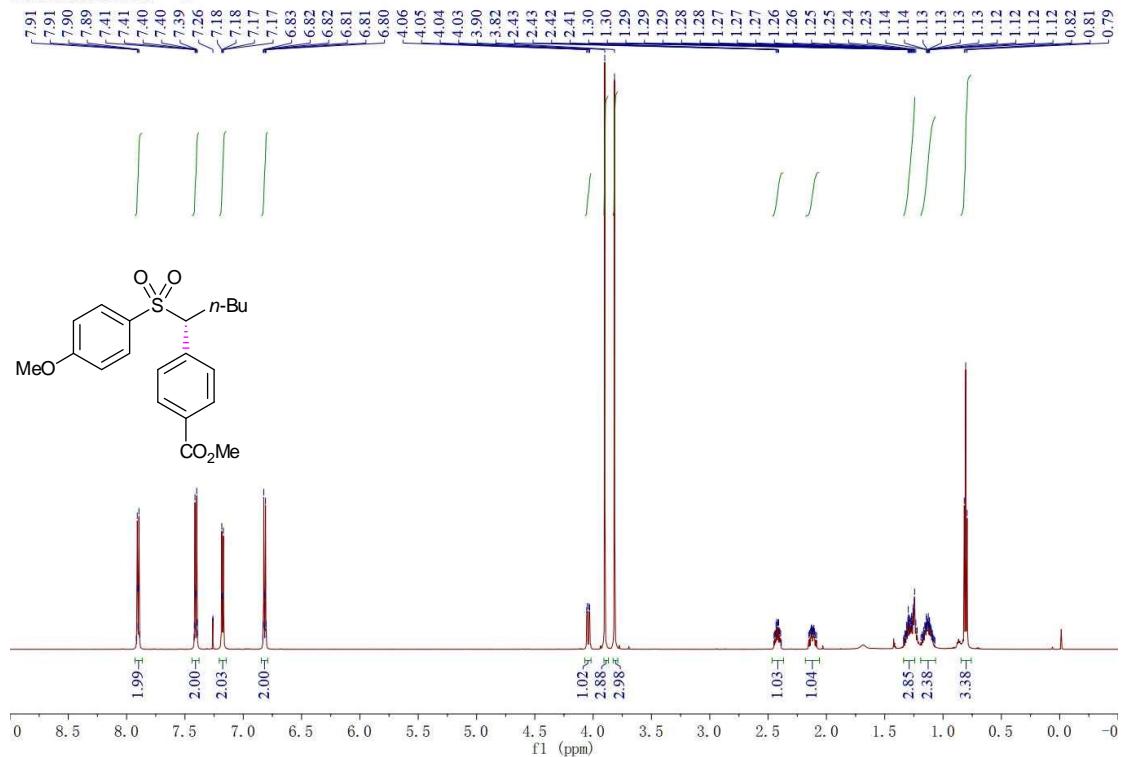
56, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200407-C.2.fid — 83



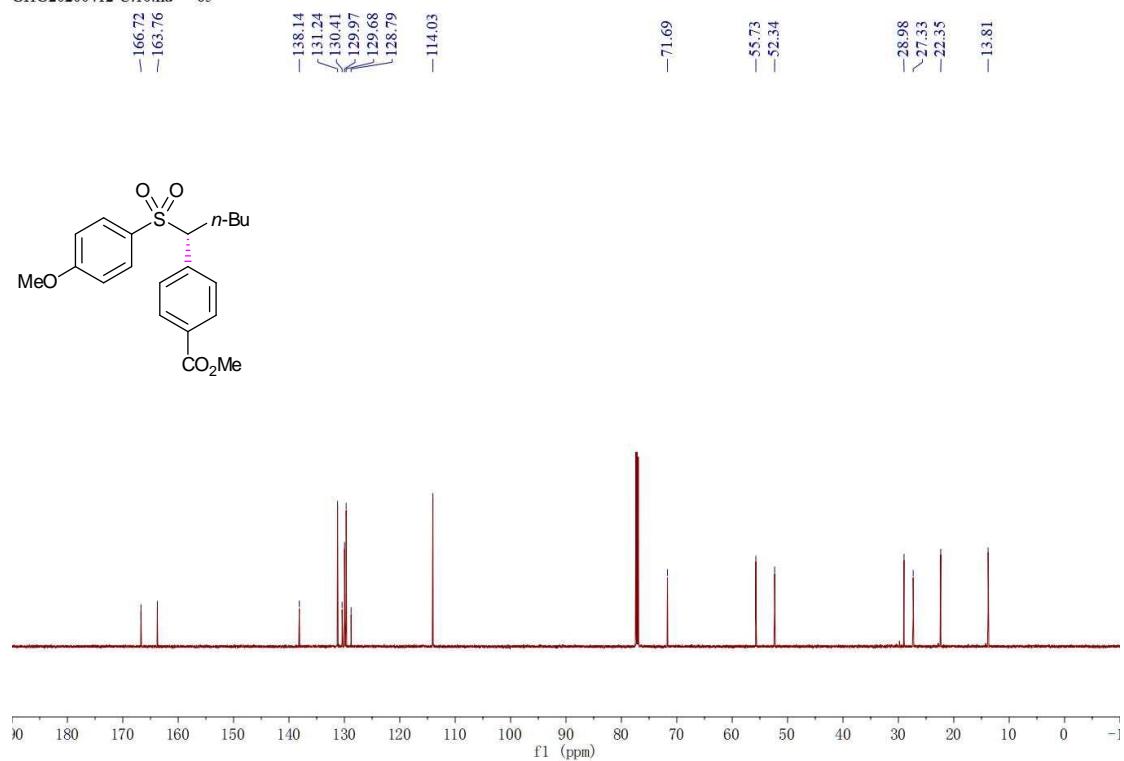
57, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200412.17.fid — 65



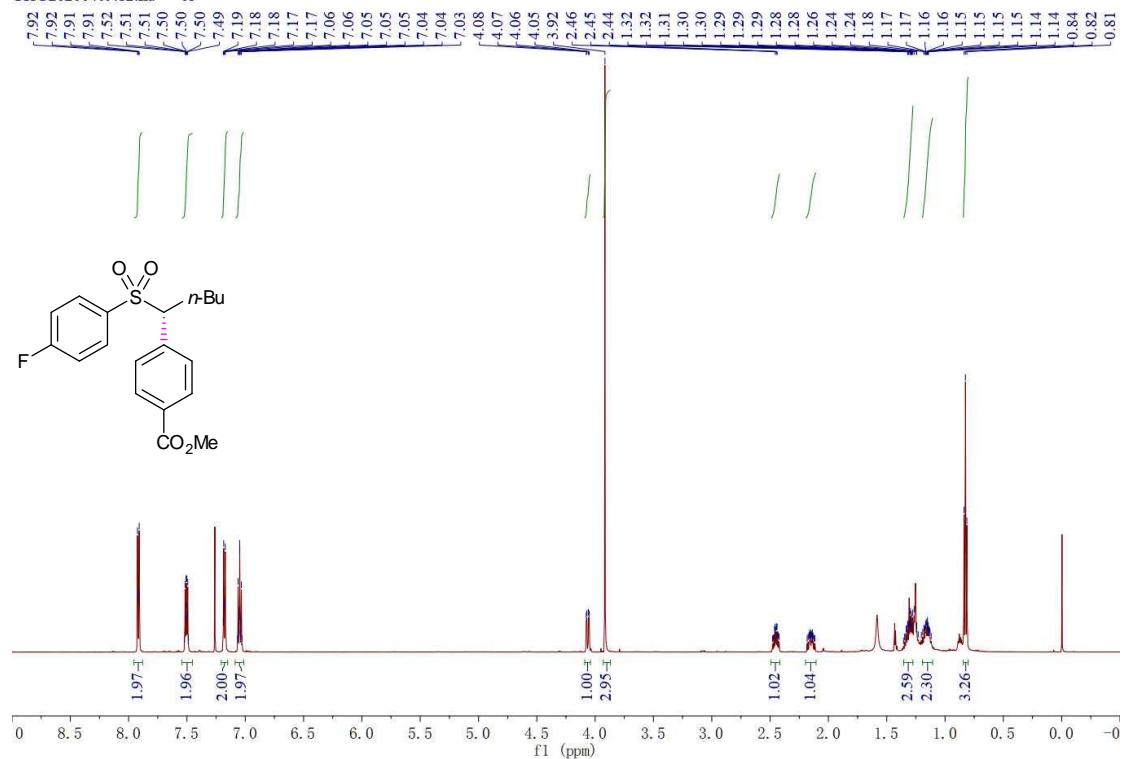
57, ^{13}C NMR (151 MHz, CDCl_3)

GHG20200412-C.10.fid — 65

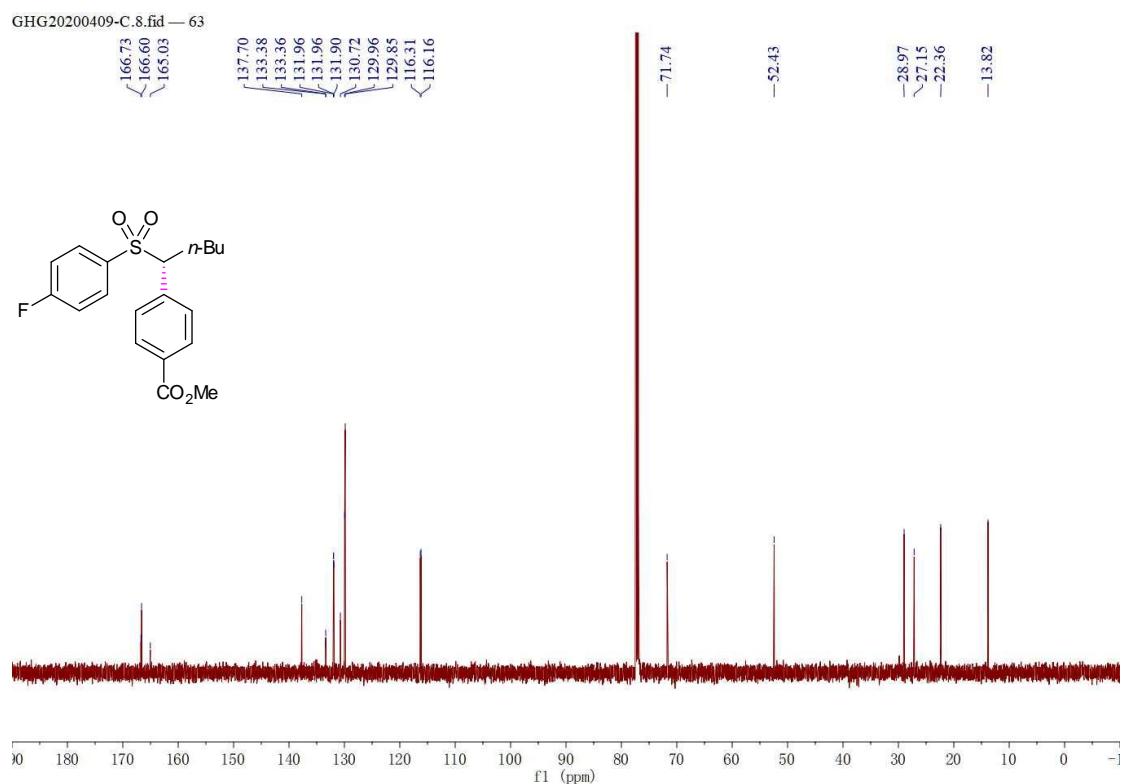


58, ^1H -NMR (600 MHz, CDCl_3)

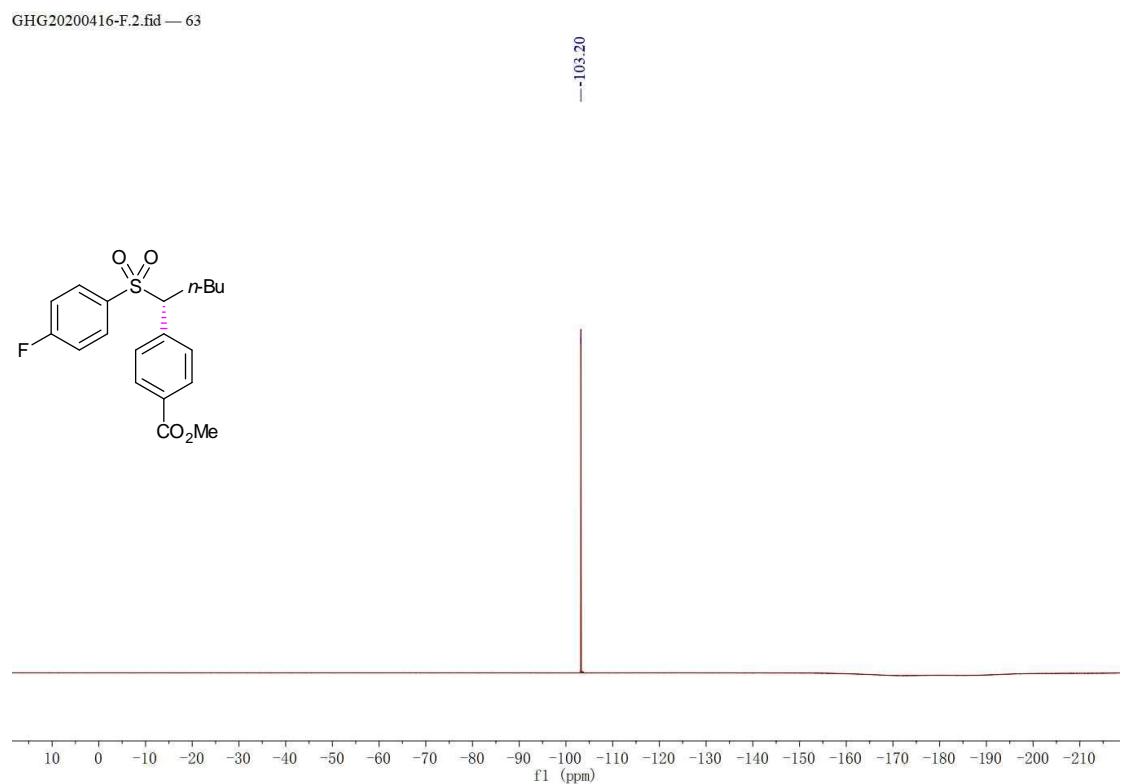
GHG20200409.12.fid — 63



58, ^{13}C NMR (151 MHz, CDCl_3)

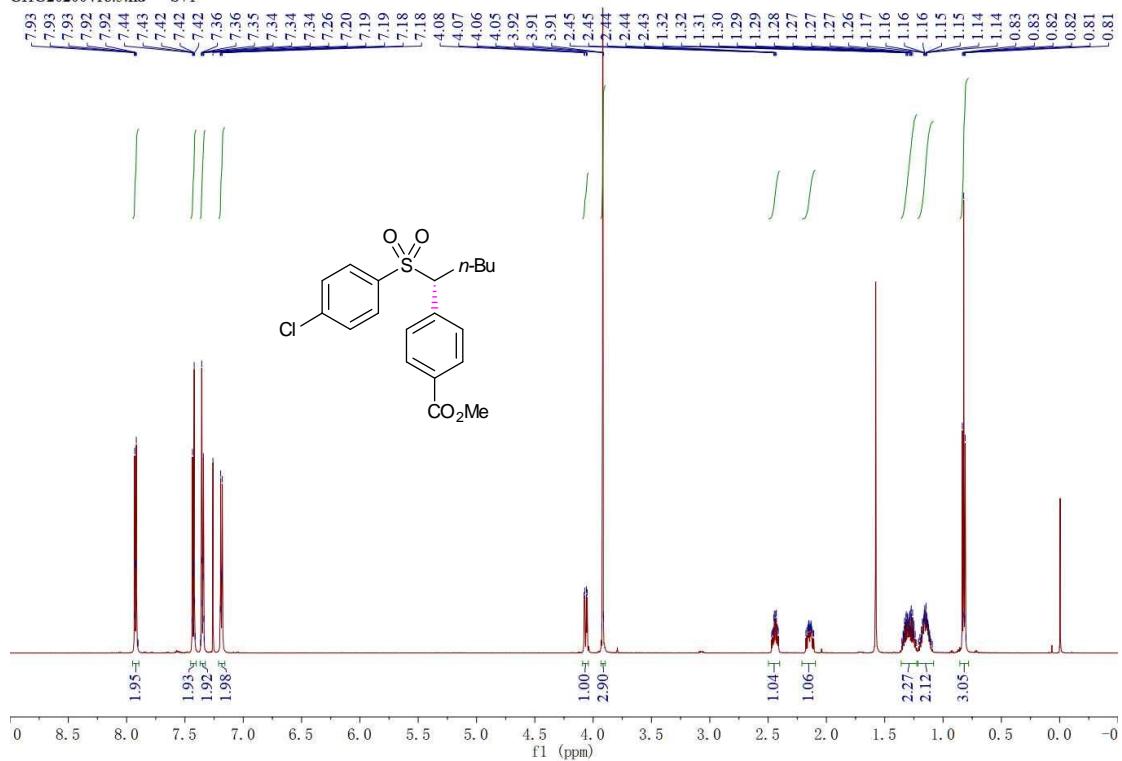


58, ^{19}F NMR (565 MHz, CDCl_3)



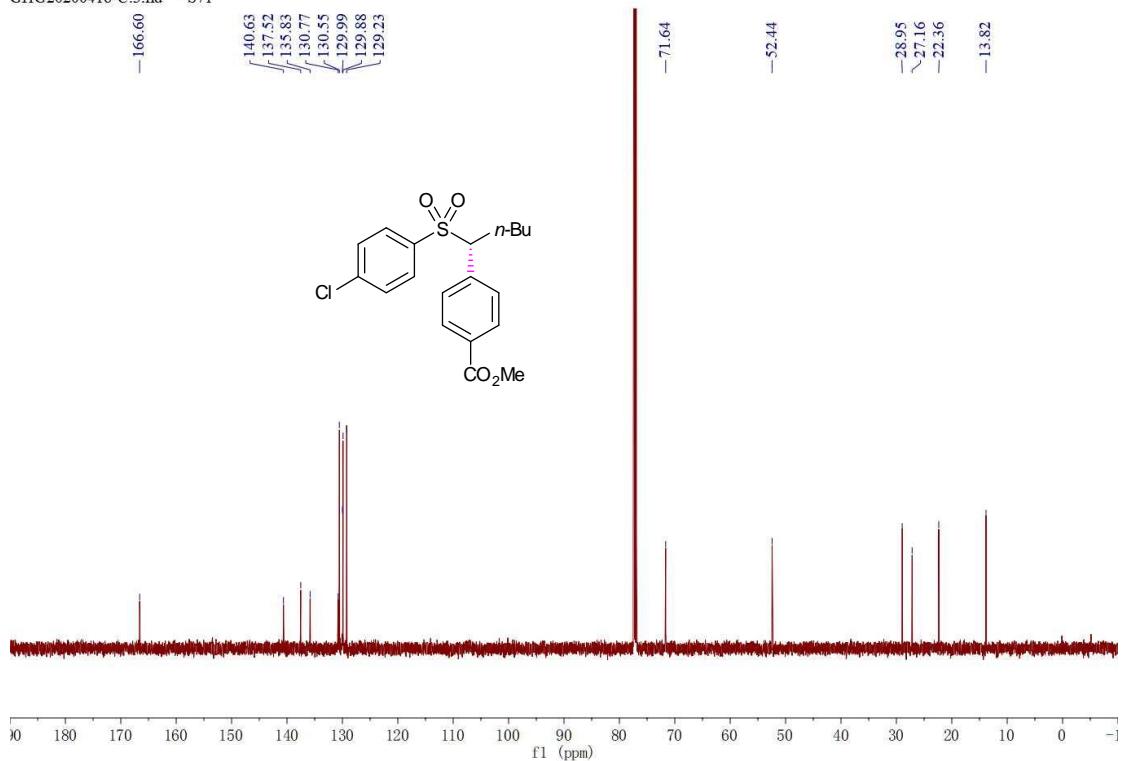
59, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

GHG20200418.5.fid — S71

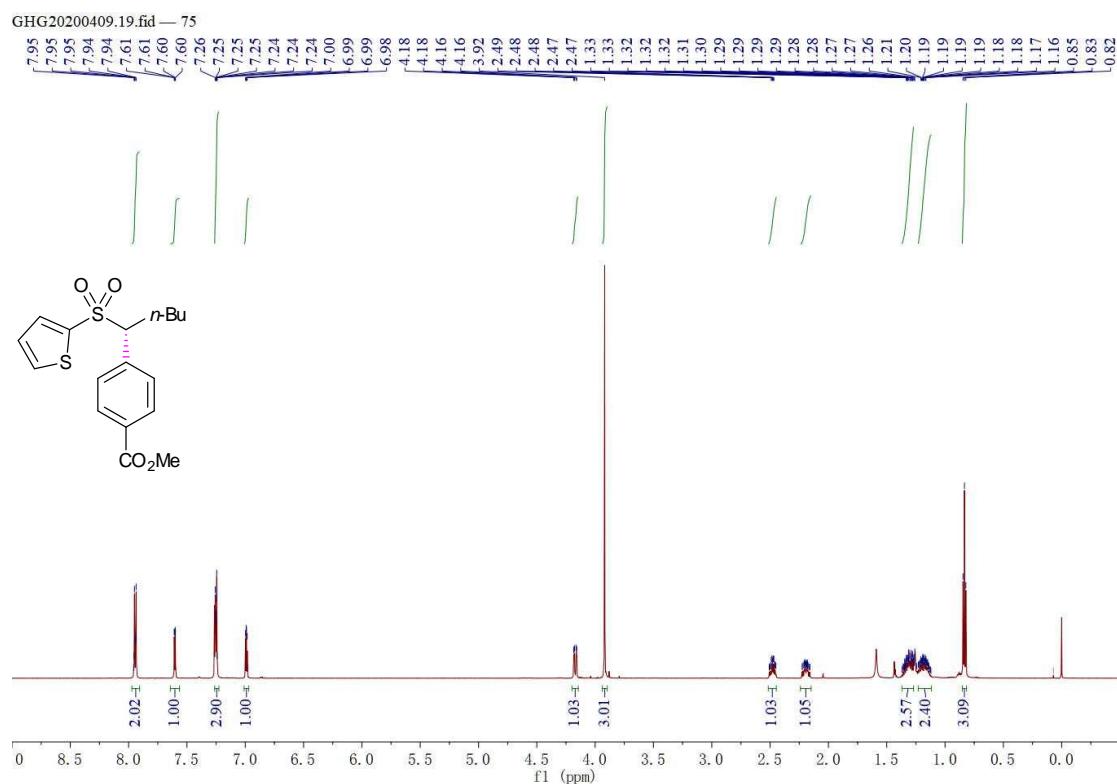


59, ^{13}C NMR (151 MHz, CDCl_3)

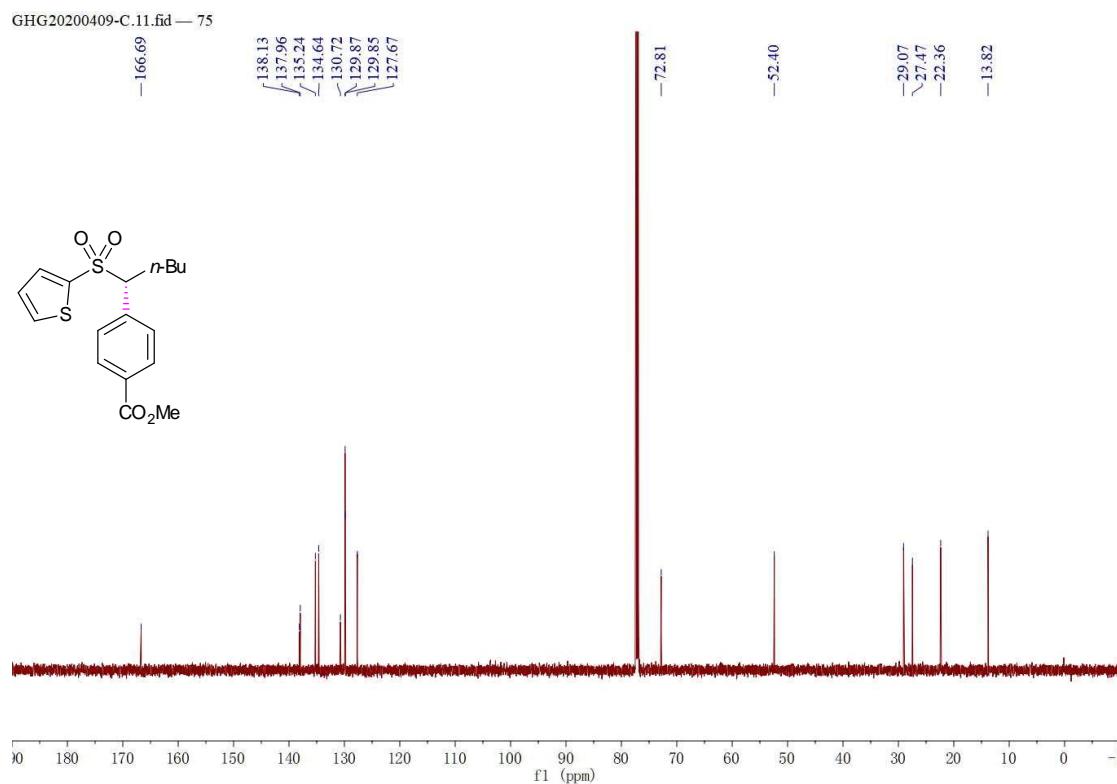
GHG20200418-C.3.fid — S71



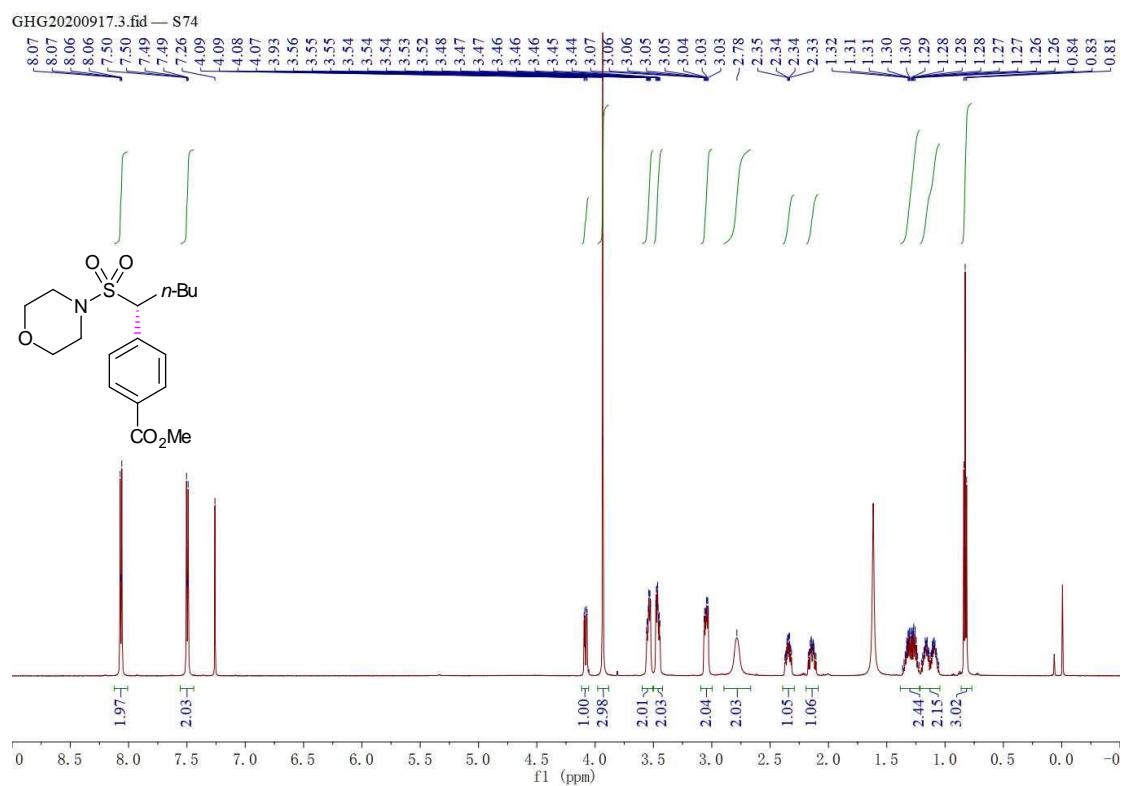
60, ^1H -NMR (600 MHz, CDCl_3)



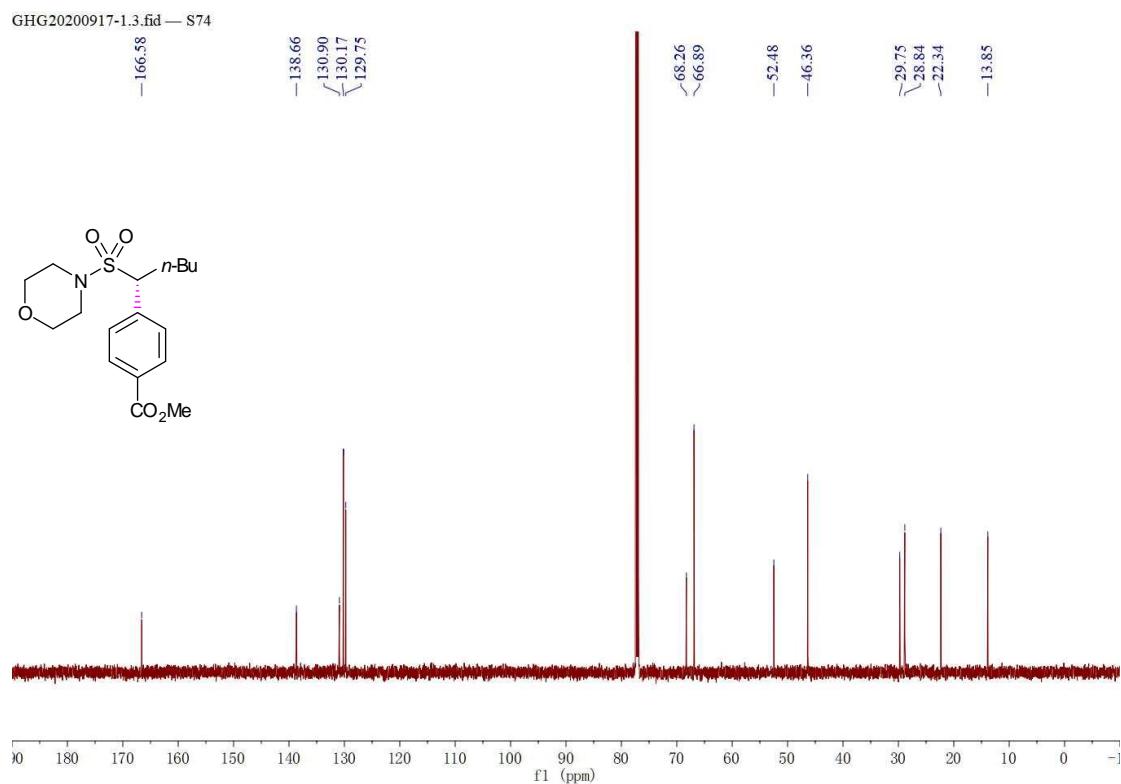
60, ^{13}C NMR (151 MHz, CDCl_3)



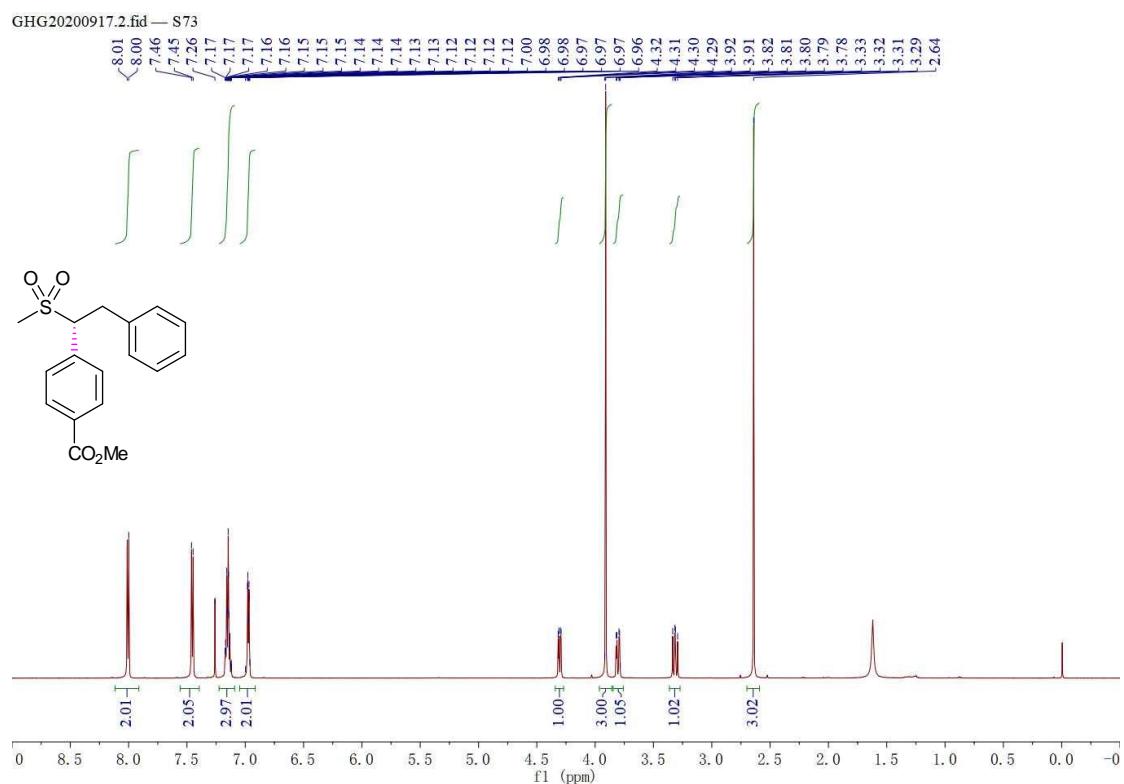
61, ^1H -NMR (600 MHz, CDCl_3)



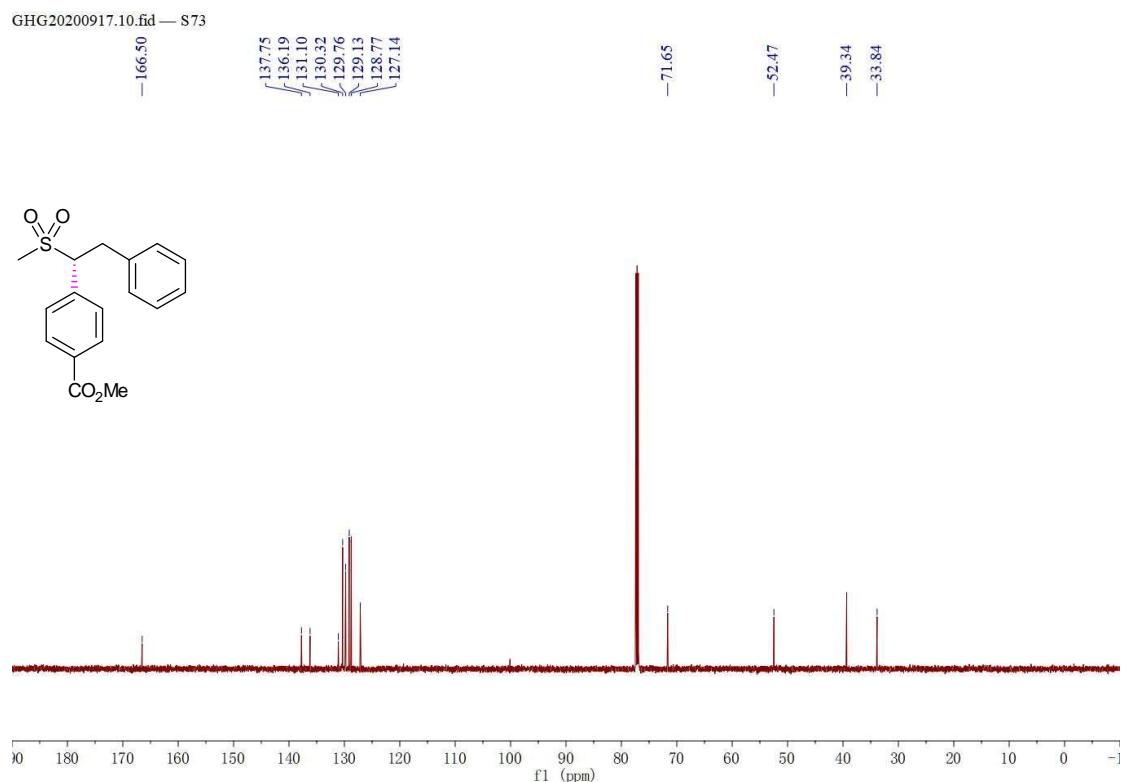
61, ^{13}C NMR (151 MHz, CDCl_3)



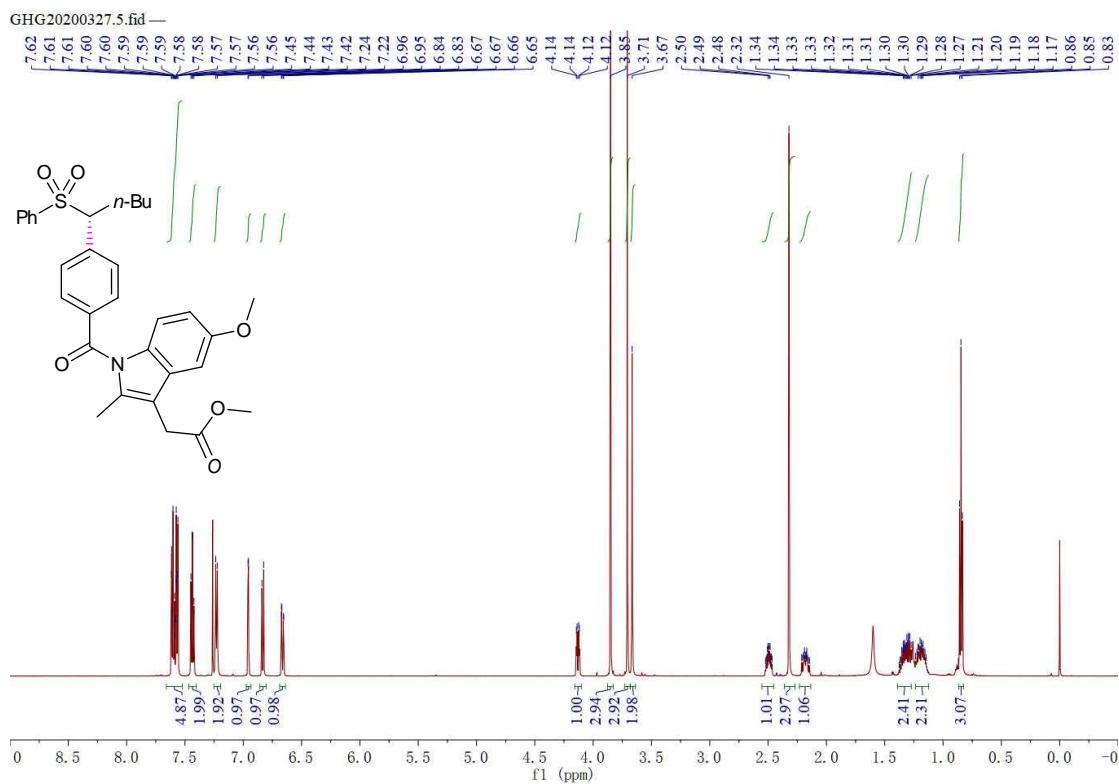
62, ^1H -NMR (600 MHz, CDCl_3)



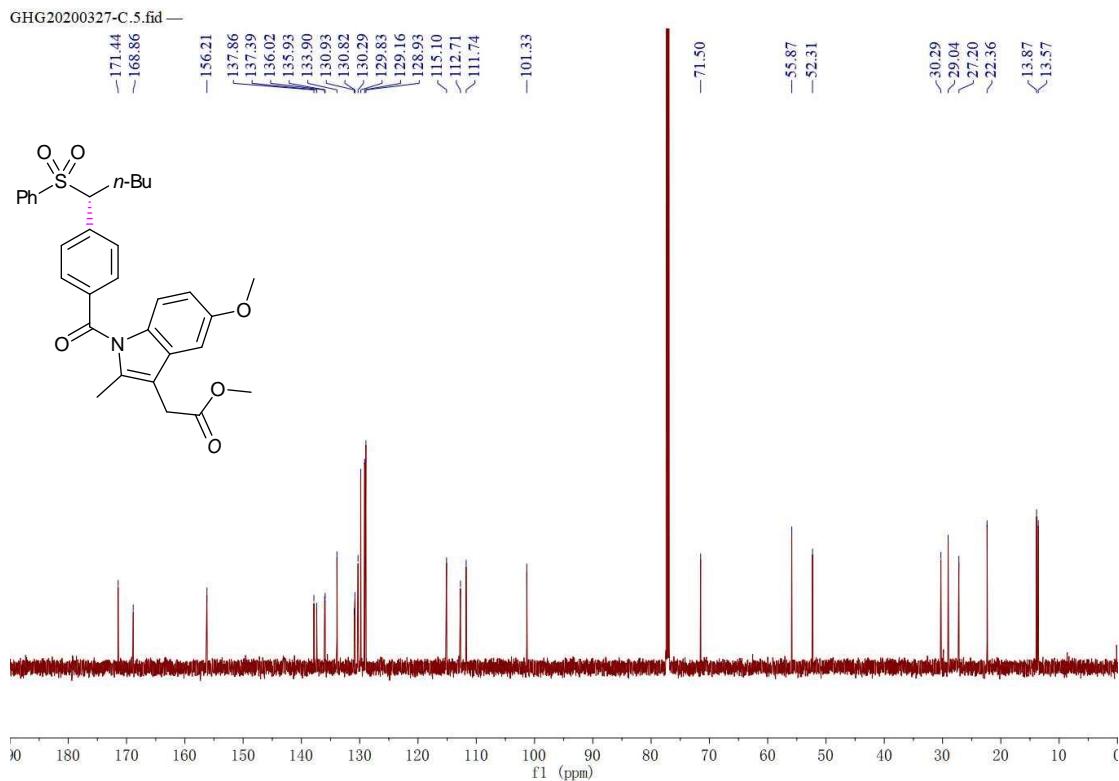
62, ^{13}C NMR (151 MHz, CDCl_3)



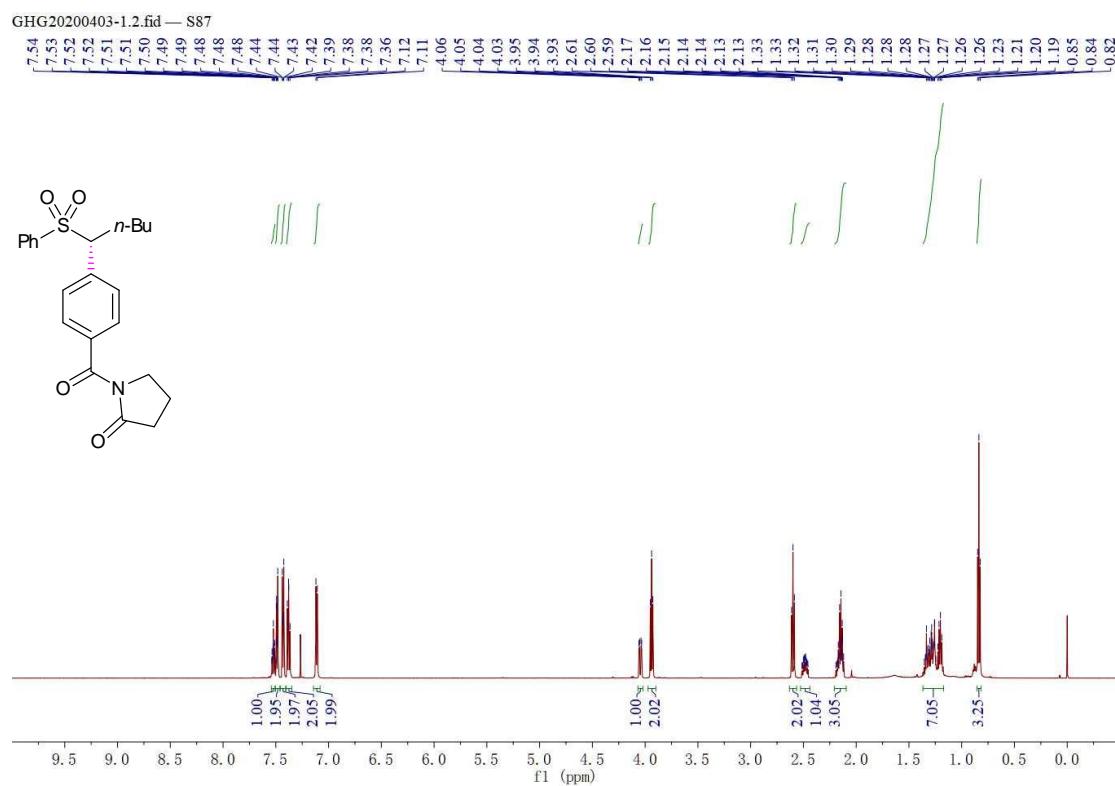
63, $^1\text{H-NMR}$ (600 MHz, CDCl_3)



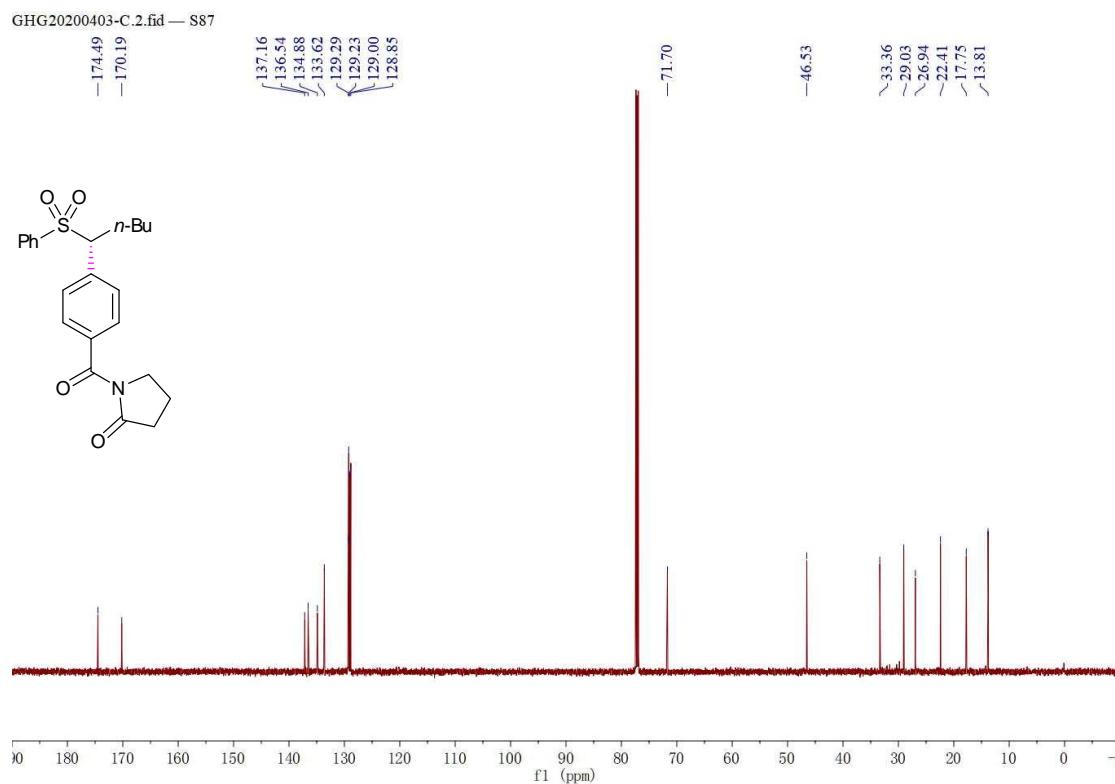
63, ^{13}C NMR (151 MHz, CDCl_3)



64, ^1H -NMR (600 MHz, CDCl_3)

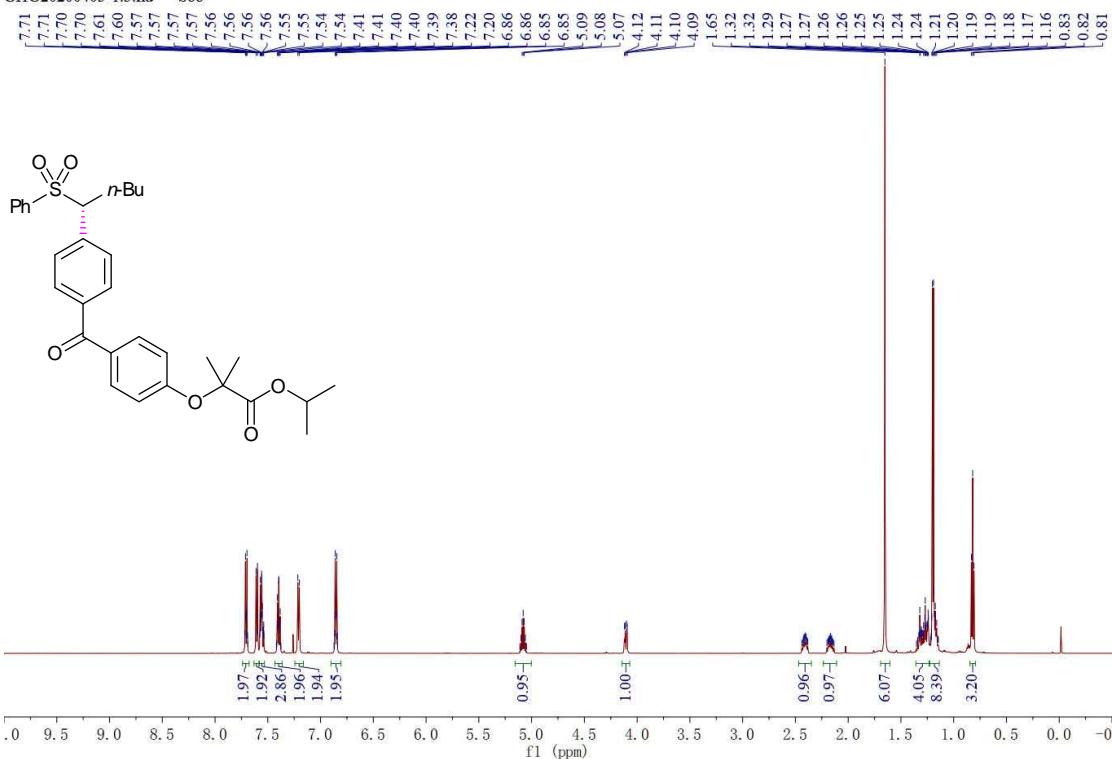


64, ^{13}C NMR (151 MHz, CDCl_3)



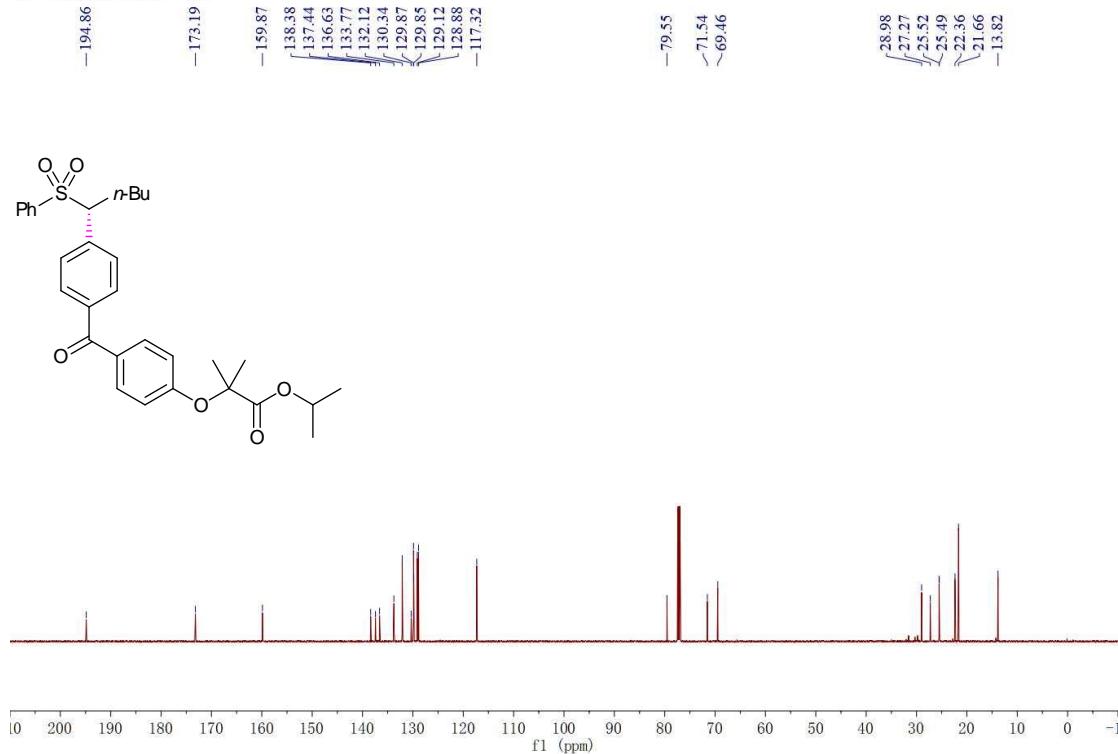
65, ^1H -NMR (600 MHz, CDCl_3)

GHG20200403-1.3.fid — S88

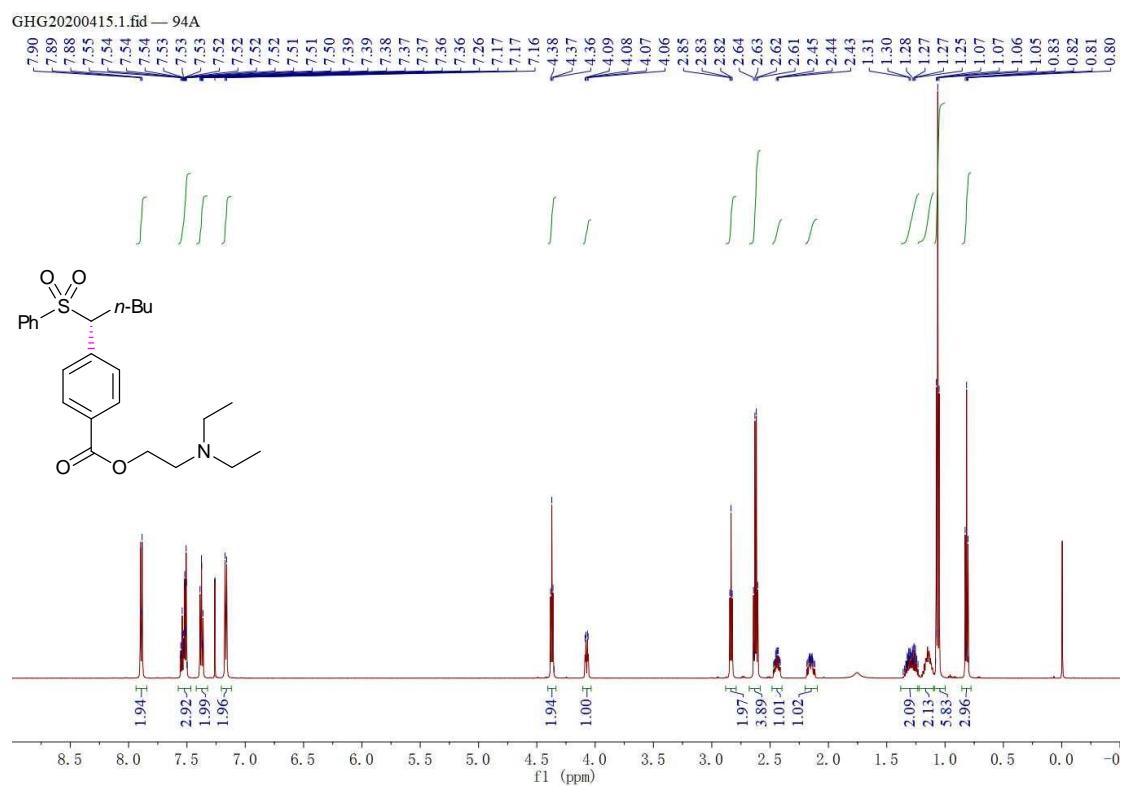


65, ^{13}C NMR (151 MHz, CDCl_3)

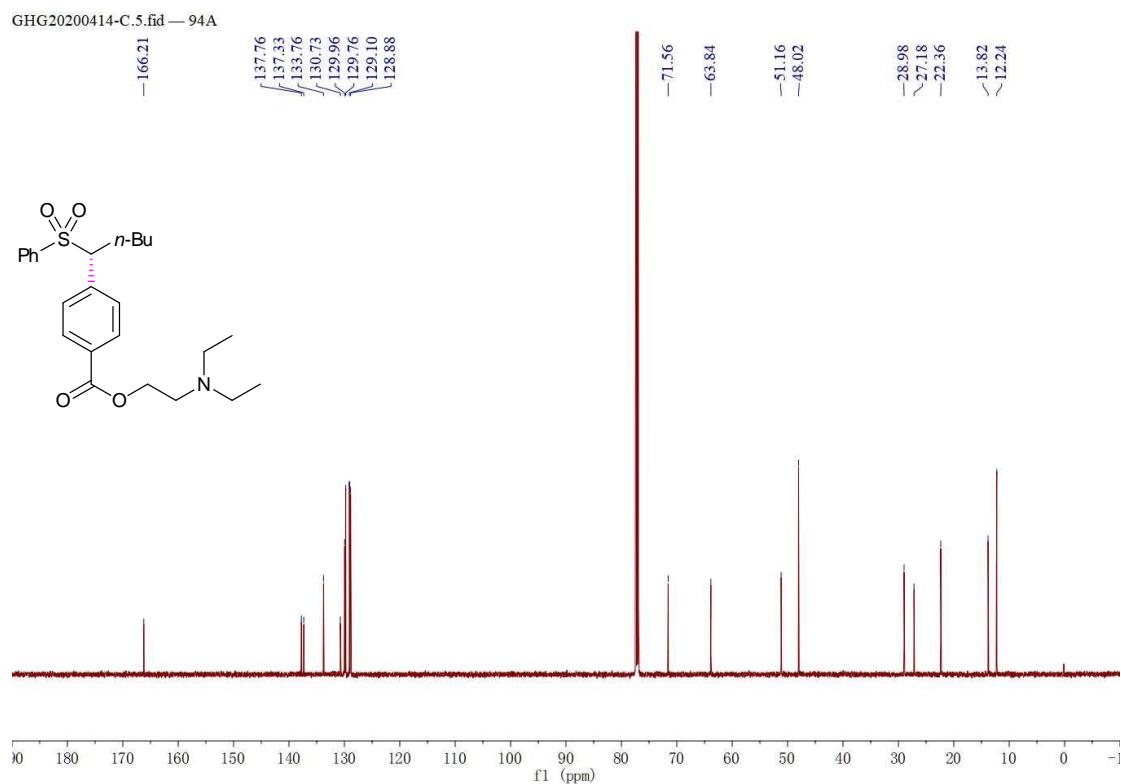
GHG20200403-C.3.fid — S88



66, ^1H -NMR (600 MHz, CDCl_3)

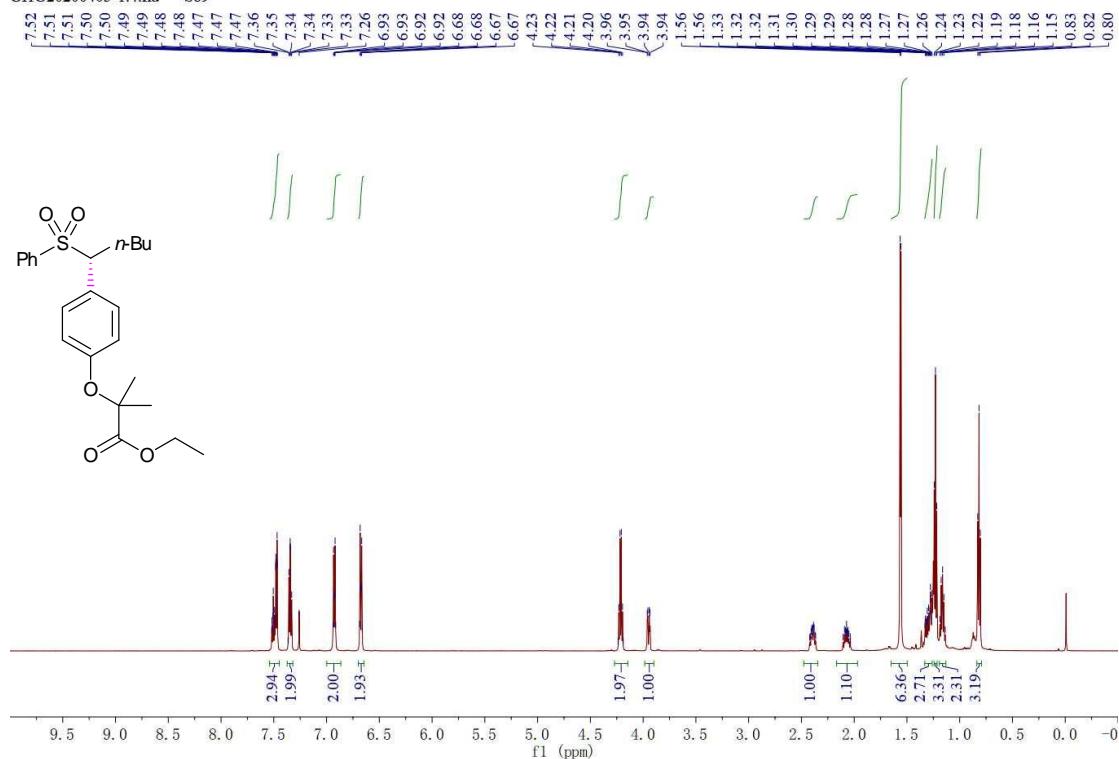


66, ^{13}C NMR (151 MHz, CDCl_3)



67, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

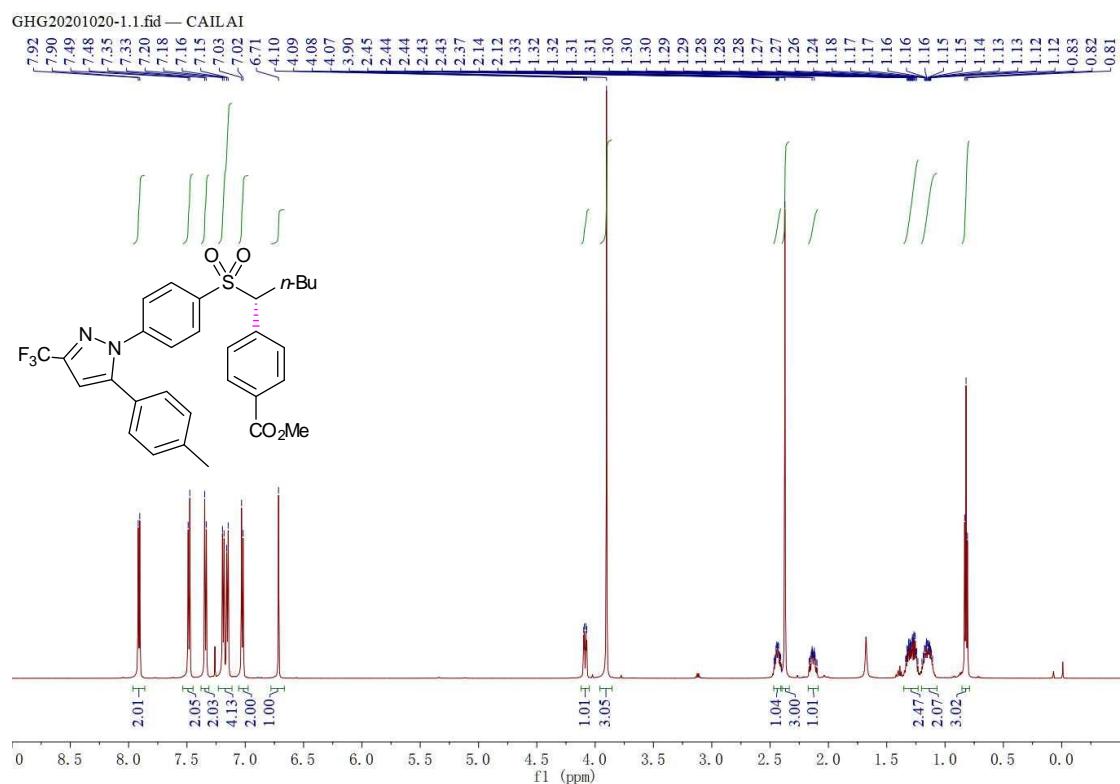
GHG20200403-1.4.fid — S89



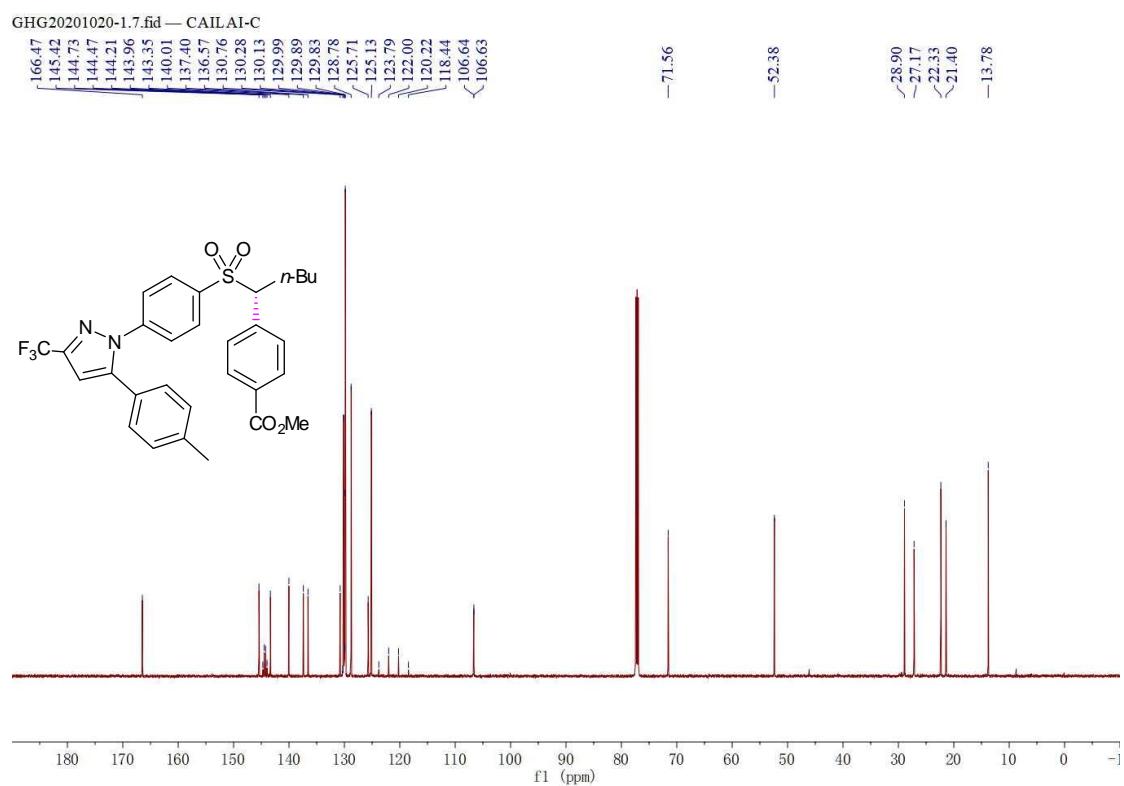
67, ^{13}C NMR (151 MHz, CDCl_3)

δ (ppm): 137.61, 133.38, 130.76, 129.13, 128.63, 125.88, 119.04, 79.35, 71.10, 61.59, 29.00, 26.94, 25.50, 25.37, 22.37, 14.22, 13.85.

68, ^1H -NMR (600 MHz, CDCl_3)

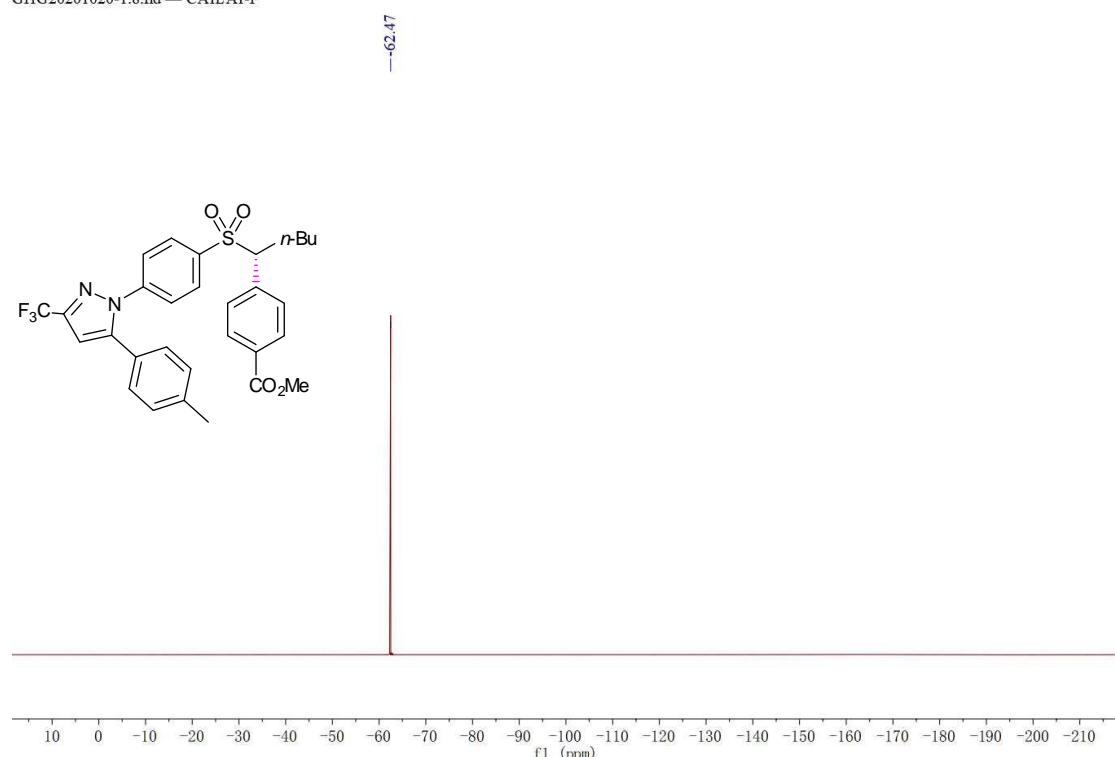


68, ^{13}C NMR (151 MHz, CDCl_3)



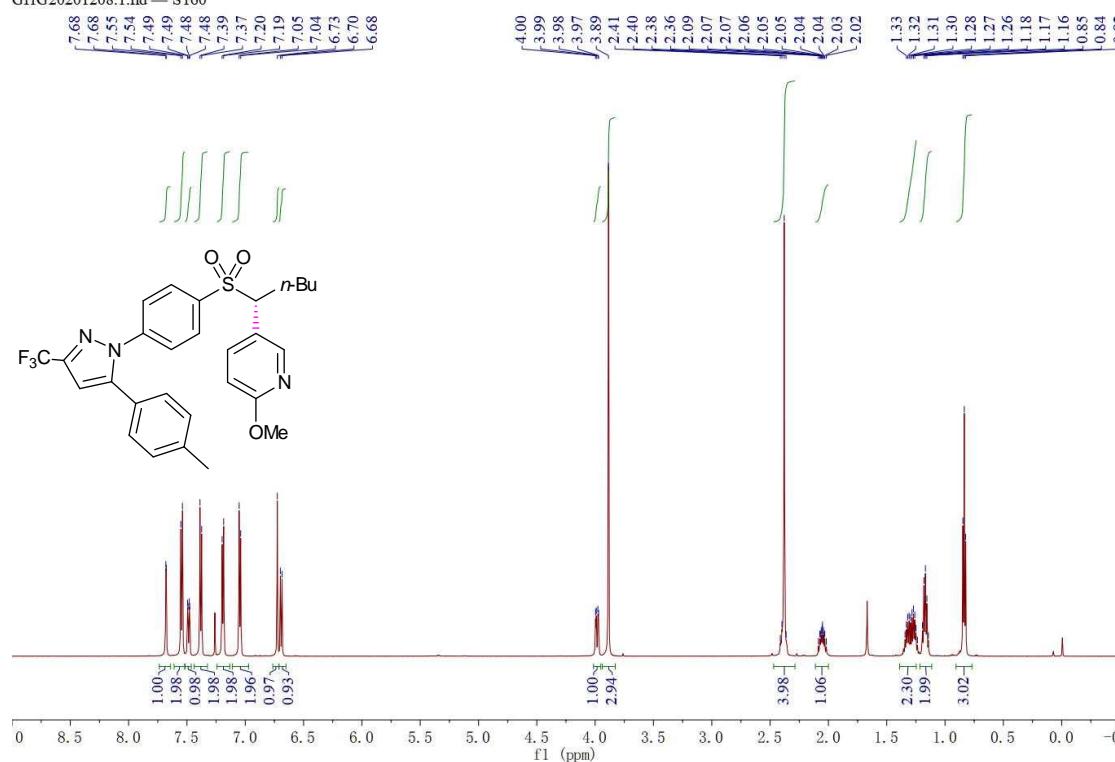
68, ^{19}F NMR (565 MHz, CDCl_3)

GHG20201020-1.8.fid — CAILAI-F

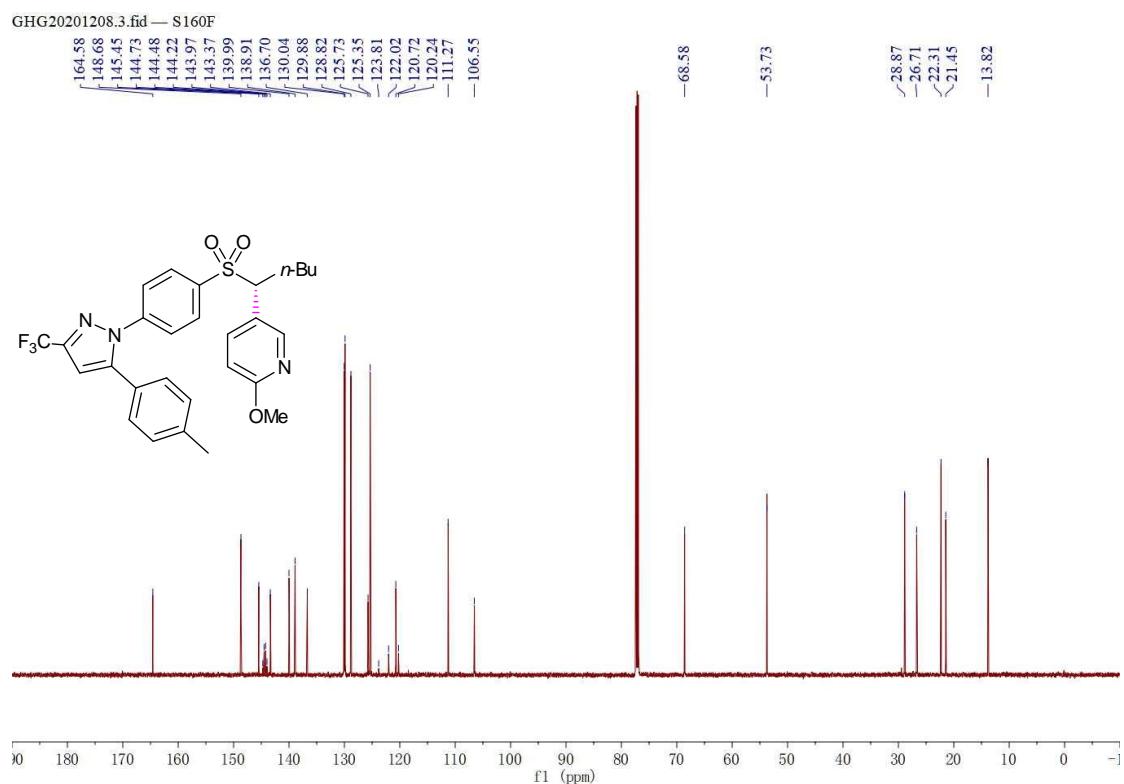


69, $^1\text{H-NMR}$ (600 MHz, CDCl_3)

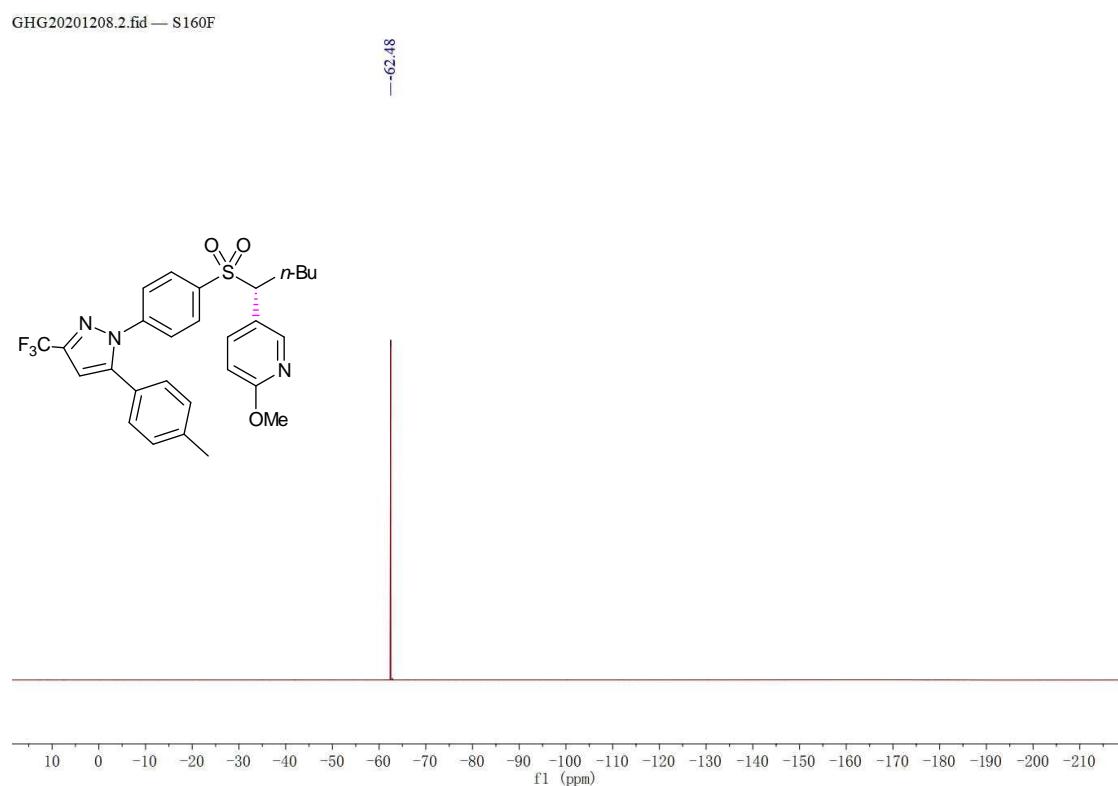
GHG20201208.1.fid — S160



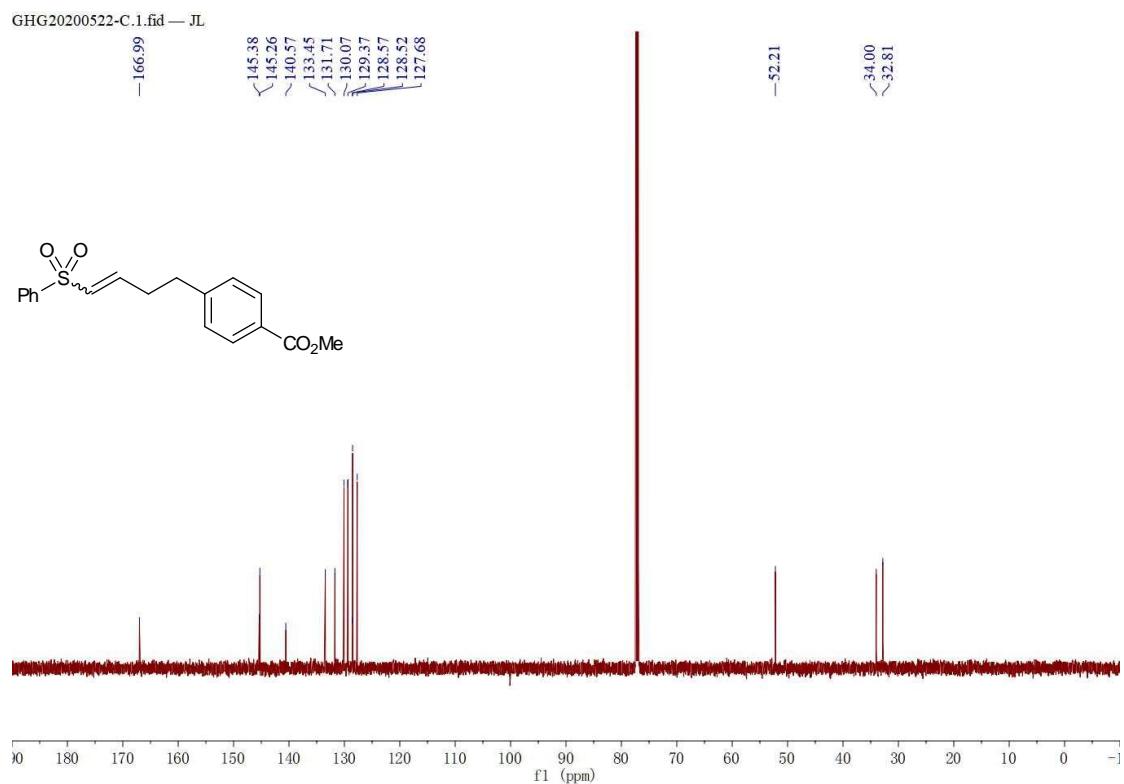
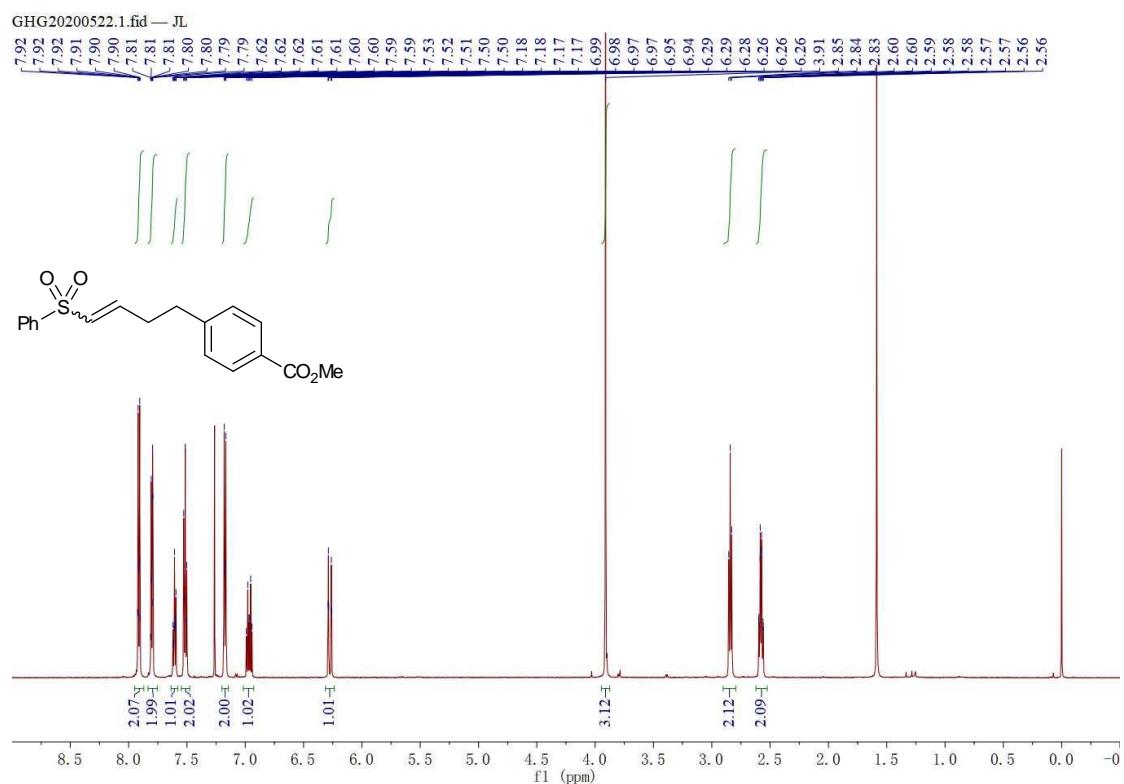
69, ^{13}C NMR (151 MHz, CDCl_3)



69, ^{19}F NMR (565 MHz, CDCl_3)



72, ^1H -NMR (600 MHz, CDCl_3)



73, $^1\text{H-NMR}$ (600 MHZ, Acetone- d_6)

