Supporting Information

Nickel^{II}-catalyzed asymmetric photoenolization/Mannich reaction of (2-alkylphenyl) ketones

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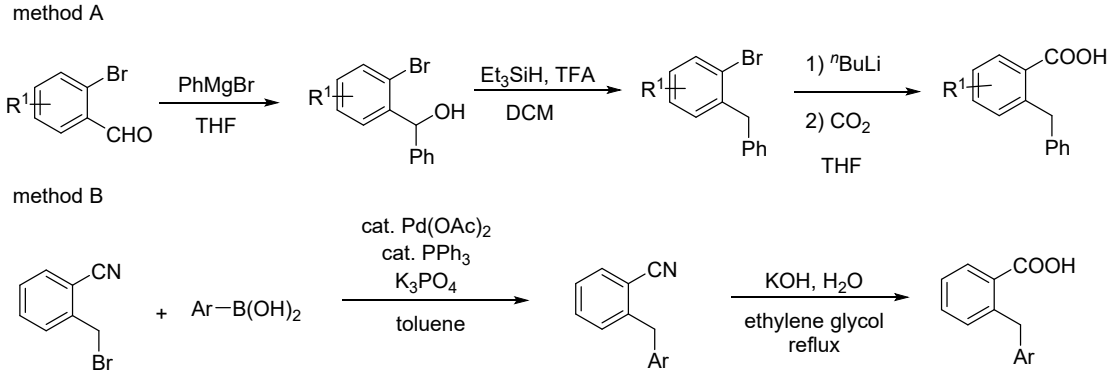
1 General information

^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiple, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz or 150 MHz with complete proton decoupling. ^{19}F NMR spectra were collected on commercial instruments (376 MHz or 565 MHz) with complete proton decoupling. Melting points (Mp) were determined using OptiMelt automated melting point system. Enantiomeric excesses (ee) were determined by chiral HPLC analysis by using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C, and UPC[2] at 35 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ (c: g/100 mL, in solvent). High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode and methanol were used to dissolve the sample. IR spectra were recorded on Pierkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm^{-1}. Solvents were dried and distilled prior to use according to the standard methods. Unless noted, other commercially available reagents were used without further purification. The chiral *N*,*N*′-dioxide ligands were synthesized by the same procedure in the literature[1].

2 Synthesis of the substrates

2.1 General procedure A for the synthesis of the substrates B15-B19 and B23-B41

2.1-1 Methods for the synthesis of α-aryl-*o*-toluic acids



The α-phenyl-*o*-toluic acid used for synthesizing the substrates **B15-B19** was commercially available, and the starting α-aryl-*o*-toluic acids used for synthesizing the substrates **B23**-**B27** were prepared by method **A** according to the literature[2] and the α-aryl-*o*-toluic acids used for synthesizing substrates **B28**-**B41** were prepared by method **B** according to the literature[3].

Method **A**: The commercially available substituted *o*-bromo-benzaldehyde was dissolved in dry THF (2.0 M) under an Ar atmosphere. Phenylmagnesium bromide solution (1.5 equiv., 1.0 M in THF) was slowly added under vigorous stirring. The resultant mixture was stirred at rt until the

reaction was completed as monitored by TLC. Then, a saturated aqueous solution of NH_4Cl was added to the reaction mixture slowly, and extracted with EtOAc (3 times). The combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography to give the corresponding alcohol as colorless oil.

CF_3CO_2H (2.0 equiv.) was added dropwise to the alcohol (1.0 equiv.) solution in DCM (0.3 M) reaction mixture at 0 °C under Ar atmosphere. After stirred for 10 min, Et_3SiH (4.0 equiv.) was added dropwise, and the resulting mixture was stirred overnight at rt. The solvent was removed in vacuum, and the residue was purified by flash column chromatography to give the substituted diarylmethane as colorless oil.

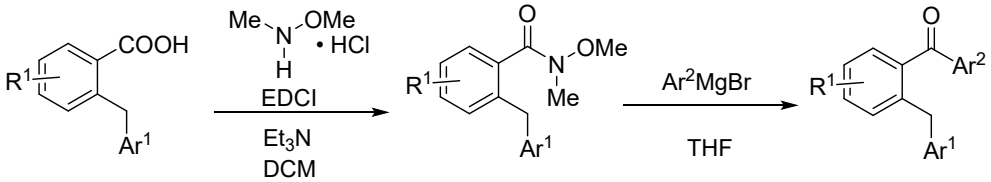
To a solution of the substituted diarylmethane (1.0 equiv.) in THF (0.5 M) was added ^{n}BuLi (1.05 equiv.) dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 h. Then anhydrous CO_2 was bubbled through the mixture for 30 min. The mixture was allowed to warm to rt for 30 min. The reaction was quenched with H_2O, basified with aqueous NaOH until p*H* value is about 12~14, and washed with Et_2O. The resulting aqueous phase was acidified with aqueous HCl until p*H* value is about 1~2, and extracted twice with EtOAc. The combined organic layers were washed with water and brine, then dried over Na_2SO_4 and evaporated under reduced pressure to give the crude carboxylic acid , which were used in the next step without further purification.

Method **B**: A flask was charged with $Pd(OAc)_2$ (0.01 equiv.), PPh_3 (0.02 equiv.), arylboric acid (1.5 equiv.), K_3PO_4 (4.0 equiv.). The flask was evacuated and back filled with argon, and then the 2-(bromomethyl)benzonitrile (1.0 equiv.) in toluene (0.3 M) were added. The reaction mixture was stirred at 80 °C for 9 h. When all the starting material has been consumed, the reaction mixture was quenched with water. The organic materials were extracted with Et_2O. The combined organic extracts were washed with water, and 1N NaOH solution and then with brine and dried over anhydrous $MgSO_4$. The solvents were removed in vacuo and the resulting crude material was subjected to flash column chromatography to afford 2-benzylbenzonitrile.

2-Benzylbenzonitrile was added to KOH (8.0 equiv.) in ethylene glycol (0.5 M) and water (1.0 mL/6.0 mmol). The solution was heated at reflux for 3 h, allowed to cool to room temperature, and made acidic to p*H* 2 with 5% HCl. The suspension was extracted with $CHCl_3$ (3 × 50 mL), and the extracts were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude carboxylic acid, which were used in the next step without further purification.

2.1-2 General procedure for the synthesis of the substrates

(1) The substrates **B15**-**B19** and **B23**-**B41** were synthesized according to reference work[4].

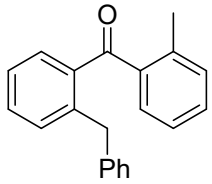


To an oven-dried flask equipped with a stirrer bar was added 2-benzylbenzoic acid (1.0 equiv.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (1.5 equiv.) and *N*, *O*-dimethylhydroxylamine hydrochloride (1.5 equiv.). The flask was capped with a rubber septum, evacuated and refilled with argon three times. Dry dichloroethane (0.4 M) and triethylamine (1.5 equiv.) were added by syringe. After being stirred at room temperature for 6 h, water was added to

the reaction mixture, and the aqueous layer was extracted with dichloroethane (3 times), washed with water, saturated aq. NaCl and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure. The crude amide was used for the next reaction without further purification.

To an oven-dried flask equipped with a stirrer bar was capped with a rubber septum, evacuated and refilled with argon three times. The solution of amide in dry THF (2.0 M) was added by syringe and cooled to -78 °C. The 1.0 M THF solution of Grignard reagent (1.1 equiv.) was added dropwise by syringe. After being stirred at room temperature for 5 h, a saturated aqueous solution of NH_4Cl was added to the reaction mixture, and the aqueous layer was extracted with ethyl acetate (3 times), washed with water, brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography to give (2-benzylphenyl)(phenyl)methanone.

(2-benzylphenyl)(o-tolyl)methanone (B15)



B15

81% yield, colourless oil.

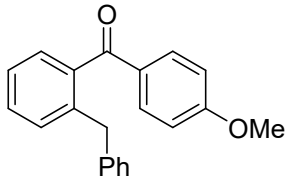
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 1H), 7.35 – 7.33 (m, 1H), 7.28 – 7.25 (m, 2H), 7.23 – 7.19 (m, 4H), 7.17 – 7.16 (m, 1H), 7.14 – 7.07 (m, 4H), 4.20 (s, 2H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 200.6, 140.8, 140.6, 139.3, 138.5, 138.4, 131.3, 131.2, 131.0, 130.6, 130.3, 129.2, 128.3, 126.0, 125.8, 125.2, 38.9, 20.6.

ESI-HRMS: calcd for $C_{21}H_{18}ONa^+$ ($[M + Na]^+$) = 309.1250, found 309.1247.

IR (neat): 1661, 1598, 1450, 1299, 1254, 926, 735, 699, 641 cm^{-1}.

(2-benzylphenyl)(4-methoxyphenyl)methanone (B16)



B16

80% yield, white solid: mp: 70-73 °C.

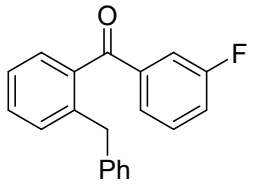
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.42 – 7.33 (m, 1H), 7.30 – 7.22 (m, 3H), 7.20 – 7.13 (m, 2H), 7.13 – 7.04 (m, 3H), 6.92 – 6.75 (m, 2H), 4.02 (s, 2H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 163.6, 140.4, 139.6, 139.2, 132.5, 130.6, 130.5, 129.9, 129.1, 128.2, 128.1, 125.9, 125.5, 113.5, 55.5, 38.7.

ESI-HRMS: calcd for $C_{21}H_{18}O_2Na^+$ ($[M + Na]^+$) = 325.1199, found 325.1198.

IR (neat): 1655, 1597, 1257, 1150, 1028, 932, 748, 699 cm^{-1}.

(2-benzylphenyl)(3-fluorophenyl)methanone (B17)



B17

86% yield, colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 3H), 7.34 – 7.22 (m, 4H), 7.21 – 7.10 (m, 3H), 7.10 – 7.01 (m, 3H), 4.06 (s, 2H).

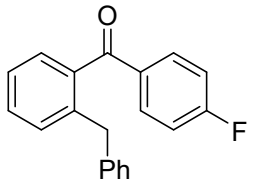
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.0, 162.4 (d, *J* = 248.9 Hz), 140.2, 140.2, 139.6 (d, *J* = 6.1 Hz), 138.1, 130.9, 130.5, 129.8 (d, *J* = 7.8 Hz), 129.1, 128.5, 128.2, 126.0,125.9 (d, *J* = 2.9 Hz), 125.6, 120.0 (d, *J* = 21.7 Hz), 116.4 (d, *J* = 22.2 Hz), 38.75.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -111.87.

ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ($[M + Na]^+$) = 313.0999, found 313.0996.

IR (neat): 1665, 1586, 1481, 1439, 1267, 1210, 849, 739, 698, 642 cm^{-1}.

(2-benzylphenyl)(4-fluorophenyl)methanone (B18)



B18

87% yield, white solid: mp: 52-55 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 2H), 7.48 – 7.35 (m, 1H), 7.30 – 7.24 (m, 3H), 7.17 – 7.13 (m, 2H), 7.11 – 6.99 (m, 5H), 4.05 (s, 2H).

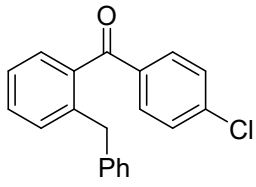
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.76, 166.5 (d, *J* = 256.0 Hz), 140.9 (d, *J* = 27.0 Hz), 139.3, 134.7 (d, *J* = 2.9 Hz), 133.5 (d, *J* = 9.5 Hz), 131.7, 131.1, 129.9, 129.1, 129.0, 126.8, 126.4, 116.3, 116.1, 39.6.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -104.83.

ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ($[M + Na]^+$) = 313.0999, found 313.0996.

IR (neat): 1663, 1595, 1449, 1268, 1231, 1149, 931, 853, 746, 698 cm^{-1}.

(2-benzylphenyl)(4-chlorophenyl)methanone (B19)



B19

72% yield, white solid: mp: 74-77 ℃.

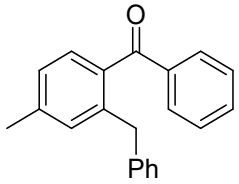
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 7.18 – 7.11 (m, 2H), 7.11 – 7.00 (m, 3H), 4.06 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.2, 140.2, 140.1, 139.5, 138.3, 135.9, 131.4, 130.9, 130.5, 129.1, 128.6, 128.5, 128.3, 126.0, 125.7, 38.8.

ESI-HRMS: calcd for $C_{20}H_{15}{}^{35}ClONa^+$ ([M + Na]$^+$) = 329.0704, found 329.0701, $C_{20}H_{15}{}^{37}ClONa^+$ ([M + Na]$^+$) = 331.0674, found 331.0666.

IR (neat): 1663, 1585, 1488, 1399, 1265, 1090, 928, 848, 743, 699, 660 cm^{-1}.

(2-benzyl-4-methylphenyl)(phenyl)methanone (B23)



B23

28% yield, colourless oil.

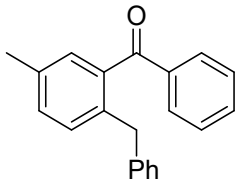
^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 2H), 7.54 – 7.47 (m, 1H), 7.39 – 7.35 (m, 2H), 7.22 – 7.13 (m, 3H), 7.13 – 7.02 (m, 5H), 4.07 (s, 2H), 2.34 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.5, 140.7, 140.6, 140.4, 138.0, 135.8, 132.8, 131.6, 130.1, 129.2, 129.1, 128.2, 128.2, 126.2, 125.9, 38.7, 21.4.

ESI-HRMS: calcd for $C_{21}H_{18}ONa^+$ ([M + Na]$^+$) = 309.1250, found 309.1248.

IR (neat): 1659, 1601, 1448, 1271, 1166, 950, 826, 720, 698, 601 cm^{-1}.

(2-benzyl-5-methylphenyl)(phenyl)methanone (B24)



B24

22% yield, colourless oil.

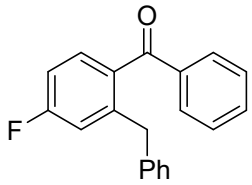
^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.56 – 7.48 (m, 1H), 7.40 – 7.36 (m, 2H), 7.22 – 7.19 (m, 1H), 7.17 – 7.12 (m, 3H), 7.11 – 7.02 (m, 4H), 4.00 (s, 2H), 2.31 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.7, 140.7, 138.7, 137.7, 136.9, 135.2, 133.0, 131.0, 130.7, 130.1, 129.0, 129.0, 128.2, 128.2, 125.9, 38.4, 20.8.

ESI-HRMS: calcd for $C_{21}H_{18}ONa^+$ ([M + Na]$^+$) = 309.1250, found 309.1246.

IR (neat): 1662, 1596, 1493, 1449, 1314, 1287, 1212, 1176, 966, 852, 728, 697, 652 cm^{-1}.

(2-benzyl-4-fluorophenyl)(phenyl)methanone (B25)

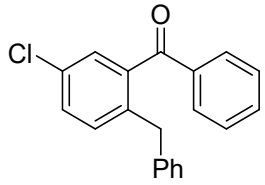


B25

31% yield, colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 2H), 7.58 – 7.54 (m, 1H), 7.44 – 7.40 (m, 2H), 7.33 – 7.29 (m, 1H), 7.25 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 6.98 – 6.89 (m, 2H), 4.08 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 163.6 (d, *J* = 251.9 Hz), 143.8 (d, *J* = 7.8 Hz), 139.6, 137.7, 134.6 (d, *J* = 7.8 Hz), 133.2, 131.1 (d, *J* = 8.9 Hz), 130.1, 129.2, 128.4, 128.4, 126.3, 117.7 (d, *J* = 21.8 Hz), 112.6 (d, *J* = 21.7 Hz), 38.7.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -109.22.
ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ([M + Na]$^+$) = 313.0999, found 313.0995.
IR (neat): 1662, 1582, 1492, 1449, 1314, 1265, 1233, 1150, 968, 831, 722, 699 cm^{-1}.

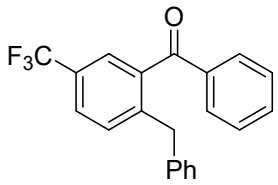
(2-benzyl-5-chlorophenyl)(phenyl)methanone (B26)



B26

31% yield, colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.58 – 7.49 (m, 1H), 7.44 – 7.34 (m, 2H), 7.30 – 7.20 (m, 3H), 7.19 – 7.15 (m, 2H), 7.13 – 7.03 (m, 3H), 4.03 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 142.4, 139.4, 137.3, 137.0, 136.2, 133.3, 130.7, 130.0, 129.1, 128.4, 128.3, 126.3, 125.8, 38.5.
ESI-HRMS: calcd for $C_{20}H_{15}{}^{35}ClONa^+$ ([M + Na]$^+$) = 329.0704, found 329.0702. $C_{20}H_{15}{}^{37}ClONa^+$ ([M + Na]$^+$) = 331.0674, found 331.0665.
IR (neat): 1663, 1590, 1449, 1313, 1279, 1151, 929, 828, 739, 697 cm^{-1}.

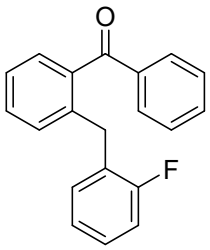
(2-benzyl-5-chlorophenyl)(phenyl)methanone (B27)



B27

38% yield, colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.60 – 7.50 (m, 3H), 7.42 – 7.38 (m, 3H), 7.20 – 7.12 (m, 2H), 7.12 – 7.00 (m, 3H), 4.07 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 142.3, 140.9, 139.1, 136.7, 133.7, 131.9 (q, *J* = 32.4 Hz), 130.0, 129.1, 128.5, 128.4, 127.4 (q, *J* = 3.8 Hz), 126.4, 123.7 (q, *J* = 273.6 Hz), 122.7 (q, *J* = 3.8 Hz), 38.8.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -62.74.
ESI-HRMS: calcd for $C_{21}H_{15}F_3ONa^+$ ([M + Na]$^+$) = 363.0967, found 363.0962.
IR (neat): 1668, 1597, 1329, 1270, 1164, 1124, 1073, 936, 839, 704, 660 cm^{-1}.

(2-(2-fluorobenzyl)phenyl)(phenyl)methanone (B28)



B28

49% yield, colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.60 – 7.51 (m, 1H), 7.46 – 7.36 (m, 3H), 7.35 – 7.20 (m, 3H), 7.14 – 7.02 (m, 2H), 7.00 – 6.86 (m, 2H), 4.10 (s, 2H).

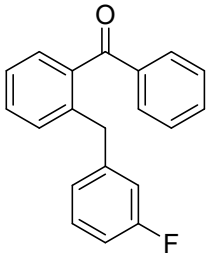
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 161.0 (d, J = 245.7 Hz), 138.8 (d, J = 20.9 Hz), 137.7, 133.2, 131.5, 131.4, 130.6, 130.5, 130.2, 128.7, 128.4, 128.0 (d, J = 8.0 Hz), 127.5 (d, J = 15.9 Hz), 125.7, 124.0 (d, J = 3.5 Hz), 115.2 (d, J = 21.9 Hz).31.9, 31.9.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -117.16.

ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ([M + Na]$^+$) = 313.0999, found 313.0994.

IR (neat): 1663, 1596, 1489, 1450, 1268, 1231, 935, 759, 705, 640 cm^{-1}.

(2-(3-fluorobenzyl)phenyl)(phenyl)methanone (B29)



B29

38% yield, colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 2H), 7.60 – 7.49 (m, 1H), 7.47 – 7.36 (m, 3H), 7.34 – 7.24 (m, 3H), 7.16 – 7.05 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.82 – 6.71 (m, 2H), 4.06 (s, 2H).

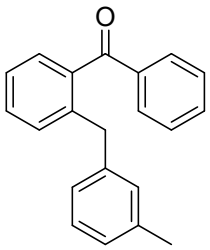
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ198.3, 162.7 (d, J = 245.0 Hz), 143.0 (d, J = 7.2 Hz), 139.3, 138.7, 137.5, 133.2, 130.9, 130.4, 130.1, 129.6 (d, J = 8.1 Hz), 128.8, 128.3, 125.8, 124.8 (d, J = 2.9 Hz), 115.9 (d, J = 21.1 Hz), 112.9 (d, J = 21.1 Hz), 38.5.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -113.60.

ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ([M + Na]$^+$) = 313.0999, found 313.0993.

IR (neat): 1662, 1591, 1485, 1447, 1314, 1267, 1136, 932, 765, 707, 641 cm^{-1}.

(2-(3-methylbenzyl)phenyl)(phenyl)methanone (B30)



B30

40% yield, colourless oil.

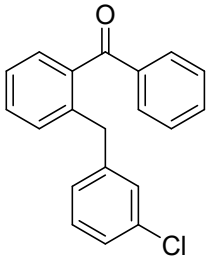
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.57 – 7.49 (m, 1H), 7.43 – 7.35 (m, 3H), 7.31 – 7.22 (m, 3H), 7.07 – 7.03 (m, 1H), 6.93 – 6.82 (m, 3H), 4.02 (s, 2H), 2.18 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.6, 140.3, 140.1, 138.7, 137.8, 137.6, 133.1, 130.7, 130.2, 130.1, 129.9, 128.4, 128.2, 128.1, 126.7, 126.2, 125.5, 38.7, 21.2.

ESI-HRMS: calcd for $C_{21}H_{18}ONa^+$ ([M + Na]$^+$) = 309.1250, found 309.1246.

IR (neat): 1663, 1598, 1447, 1313, 1268, 924, 762, 708, 641 cm^{-1}.

(2-(3-chlorobenzyl)phenyl)(phenyl)methanone (B31)



B31

73% yield, colourless oil.

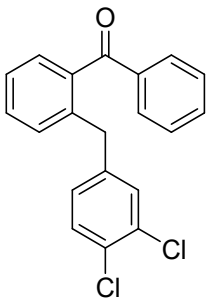
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.56 – 7.52 (m, 1H), 7.46 – 7.36 (m, 3H), 7.35 – 7.25 (m, 3H), 7.09 – 7.03 (m, 3H), 6.98 – 6.95 (m, 1H), 4.04 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 142.4, 139.2, 138.7, 137.4, 134.0, 133.2, 130.9, 130.4, 130.1, 129.4, 129.1, 128.8, 128.3, 127.3, 126.2, 125.8, 38.5.

ESI-HRMS: calcd for $C_{20}H_{15}{}^{35}ClONa^+$ ([M + Na]$^+$) = 329.0704, found 329.0700. $C_{20}H_{15}{}^{37}ClONa^+$ ([M + Na]$^+$) = 331.0674, found 331.0666.

IR (neat): 1661, 1596, 1475, 1445, 1313, 1269, 937, 919, 765, 706, 641 cm^{-1}.

(2-(3,4-dichlorobenzyl)phenyl)(phenyl)methanone (B32)



B32

71% yield, colourless oil.

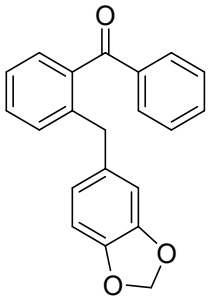
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.60 – 7.52 (m, 1H), 7.48 – 7.36 (m, 3H), 7.34 – 7.26 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.02 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 140.7, 138.8, 138.6, 137.3, 133.3, 132.1, 131.0, 130.9, 130.5, 130.1, 130.1, 129.9, 128.9, 128.6, 128.3, 126.0, 38.0.

ESI-HRMS: calcd for $C_{20}H_{14}{}^{35}Cl_2ONa^+$ ([M + Na]$^+$) = 363.0314, found 363.0310, $C_{20}H_{14}{}^{35,37}Cl_2ONa^+$ ([M + Na]$^+$) = 365.0284, found 365.0279, $C_{20}H_{14}{}^{37}Cl_2ONa^+$ ([M + Na]$^+$) = 367.0255, found 367.0240.

IR (neat): 1661, 1596, 1469, 1314, 1269, 1030, 918, 763, 707, 639 cm^{-1}.

(2-(benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)(phenyl)methanone (B33)



B33

21% yield, colourless oil.

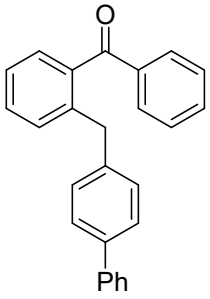
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.51 – 7.43 (m, 1H), 7.35 – 7.31 (m, 3H), 7.22 – 7.17 (m, 3H), 6.55 – 6.39 (m, 3H), 5.75 (s, 2H), 3.89 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 147.4, 145.7, 140.2, 138.7, 137.5, 134.2, 133.1, 130.6, 130.2, 130.1, 128.5, 128.3, 125.6, 122.2, 109.7, 107.9, 100.7, 38.5.

ESI-HRMS: calcd for $C_{21}H_{16}O_3Na^+$ ([M + Na]$^+$) = 339.0992, found 339.0989.

IR (neat): 1662, 1486, 1444, 1269, 1244, 1039, 928, 766, 707, 641 cm^{-1}.

(2-([1,1'-biphenyl]-4-ylmethyl)phenyl)(phenyl)methanone (B34)



B34

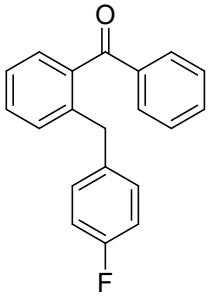
60% yield, white solid; mp: 92-94 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.55 – 7.45 (m, 3H), 7.45 – 7.34 (m, 7H), 7.34 – 7.24 (m, 4H), 7.15 – 7.13 (m, 2H), 4.10 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 140.9, 140.0, 139.5, 138.9, 138.8, 137.6, 133.1, 130.8, 130.3, 130.1, 129.5, 128.6, 128.6, 128.3, 127.0, 126.9, 125.6, 38.5.

ESI-HRMS: calcd for $C_{26}H_{20}ONa^+$ ([M + Na]$^+$) = 371.1406, found 371.1404.
IR (neat): 1662, 1597, 1486, 1447, 1314, 1269, 936, 760, 700, 641 cm^{-1}.

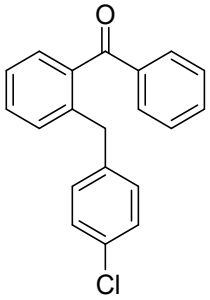
(2-(4-fluorobenzyl)phenyl)(phenyl)methanone (B35)



B35

60% yield, colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.35 (m, 3H), 7.33 – 7.23 (m, 3H), 7.05 – 7.00 (m, 2H), 6.89 – 6.77 (m, 2H), 4.03 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ161.2 (d, *J* = 244.1 Hz), 139.9, 138.6, 137.5, 136.1 (d, *J* = 3.5 Hz), 133.2, 130.7, 130.5 (d, *J* = 7.8 Hz), 130.3, 130.1, 128.7, 128.3, 125.7, 114.95 (d, *J* = 21.0 Hz), 38.0.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -117.29.
ESI-HRMS: calcd for $C_{20}H_{15}FONa^+$ ([M + Na]$^+$) = 313.0999, found 313.0995.
IR (neat): 1662, 1599, 1508, 1446, 1269, 1222, 1156, 934, 766, 705, 640 cm^{-1}.

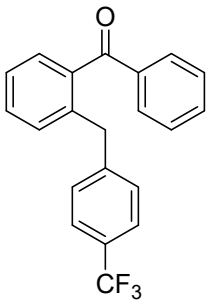
(2-(4-chlorobenzyl)phenyl)(phenyl)methanone (B36)



B36

66% yield, colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.59 – 7.52 (m, 1H), 7.43 – 7.38 (m, 3H), 7.33 – 7.23 (m, 3H), 7.15 – 7.09 (m, 2H), 7.02 – 6.99 (m, 2H), 4.03 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 139.6, 138.9, 138.6, 137.5, 133.2, 131.8, 130.8, 130.4, 130.4, 130.1, 128.8, 128.3, 125.8, 38.2.
ESI-HRMS: calcd for $C_{20}H_{15}{}^{35}ClONa^+$ ([M + Na]$^+$) = 329.0704, found 329.0700, $C_{20}H_{15}{}^{37}ClONa^+$ ([M + Na]$^+$) = 331.0674, found 331.0665.
IR (neat): 1662, 1489, 1446, 1314, 1269, 1092, 935, 760, 706, 639 cm^{-1}.

phenyl(2-(4-(trifluoromethyl)benzyl)phenyl)methanone (B37)



B37

31% yield, colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.36 (m, 5H), 7.36 – 7.27 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.14 (s, 2H).

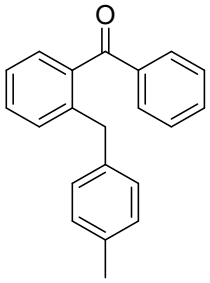
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 144.6, 139.0, 138.7, 137.4, 133.3, 130.9, 130.5, 130.1, 129.4, 128.9, 128.3, 128.3 (q, *J* = 32.2 Hz), 126.0, 125.1 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.9 Hz), 38.7.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -62.40.

ESI-HRMS: calcd for $C_{21}H_{15}F_3ONa^+$ ([M + Na]$^+$) = 363.0967, found 363.0959.

IR (neat): 1662, 1323, 1268, 1160, 1115, 1066, 936, 765, 735, 706 cm^{-1}.

(2-(4-methylbenzyl)phenyl)(phenyl)methanone (B38)



B38

63% yield, colourless oil.

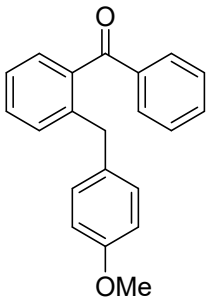
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.56 – 7.49 (m, 1H), 7.43 – 7.34 (m, 3H), 7.31 – 7.20 (m, 3H), 6.96 (s, 4H), 4.01 (s, 2H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 140.3, 138.7, 137.6, 137.3, 135.4, 133.0, 130.6, 130.2, 130.1, 129.0, 128.9, 128.5, 128.2, 125.4, 38.3, 20.9.

ESI-HRMS: calcd for $C_{21}H_{18}ONa^+$ ([M + Na]$^+$) = 309.1250, found 309.1247.

IR (neat): 1662, 1597, 1513, 1446, 1313, 1267, 936, 791, 765, 704, 640 cm^{-1}.

(2-(4-methoxybenzyl)phenyl)(phenyl)methanone (B39)



39

65% yield, colourless oil.

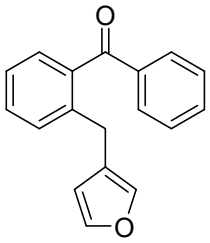
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.55 – 7.51 (m, 1H), 7.44 – 7.33 (m, 3H), 7.32 – 7.21 (m, 3H), 7.03 – 6.93 (m, 2H), 6.73 – 6.66 (m, 2H), 3.99 (s, 2H), 3.70 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.6, 157.8, 140.5, 138.7, 137.6, 133.0, 132.5, 130.6, 130.2, 130.1, 130.1, 128.4, 128.2, 125.5, 113.6, 55.1, 37.9.

ESI-HRMS: calcd for $C_{21}H_{18}O_2Na^+$ ([M + Na]$^+$) = 325.1199, found 325.1195.

IR (neat): 1662, 1598, 1510, 1446, 1246, 1178, 1035, 933, 766, 705, 640 cm^{-1}.

(2-(furan-3-ylmethyl)phenyl)(phenyl)methanone (B40)



B40

36% yield, colourless oil.

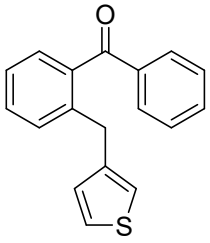
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.57 – 7.55 (m, 1H), 7.46 – 7.37 (m, 3H), 7.35 – 7.33 (m, 1H), 7.32 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 7.08 (s, 1H), 6.16 (s, 1H), 3.85 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 142.7, 139.8, 139.5, 138.4, 137.6, 133.1, 130.3, 130.3, 130.1, 128.7, 128.3, 125.6, 123.6, 111.1, 28.4.

ESI-HRMS: calcd for $C_{18}H_{14}O_2Na^+$ ([M + Na]$^+$) = 285.0886, found 285.0882.

IR (neat): 1661, 1596, 1446, 1313,1267, 1153, 1022, 934, 873, 764,705, 640 cm^{-1}.

phenyl(2-(thiophen-3-ylmethyl)phenyl)methanone (B41)



B41

58% yield, white solid; mp 47-50 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.58 – 7.49 (m, 1H), 7.44 – 7.36 (m, 3H), 7.34 – 7.23 (m, 3H), 7.12 – 7.10 (m, 1H), 6.88 – 6.72 (m, 2H), 4.05 (s, 2H).

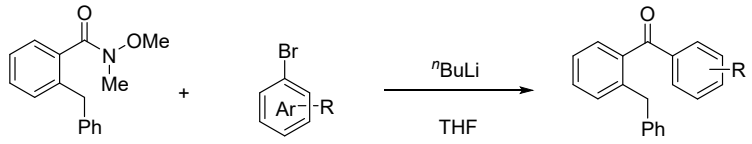
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 140.6, 139.7, 138.5, 137.5, 133.1, 130.5, 130.3, 130.0, 128.6, 128.4, 128.2, 125.6, 125.4, 121.8, 33.6.

ESI-HRMS: calcd for $C_{18}H_{14}OSNa^+$ ([M + Na]$^+$) = 301.0658, found 301.0659.

IR (neat): 1660, 1596, 1445, 1313, 1266, 1152, 932, 759, 705, 639 cm^{-1}.

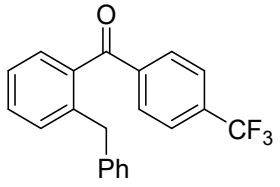
(2) General procedure for the synthesis of the substrates B20–B22

The substrates **B20–B22** were prepared as shown below according to the known literature[5].



To an oven-dried microwave vial charged with arylbromide (2.0 equiv.) under a N_2 atmosphere was added THF (0.33 M). The solution was cooled to –78 °C and ^{n}BuLi (2.0 equiv.) was added dropwise. The resulting mixture was stirred at –78 °C for 30 mins, then **S1** (1.0 equiv.) in THF (0.5 M) was added dropwise. The reaction mixture was stirred for 30 mins or until full consumption of **S1** (as judged by TLC) and was then quenched with a saturated aqueous solution of NH_4Cl. Water was added, and the aqueous phase was extracted with Et_2O (3 times). The combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. Purification by column chromatography (petroleum ether / ethyl acetate mobile phase) afforded the desired aryl ketone.

(2-benzylphenyl)(4-(trifluoromethyl)phenyl)methanone (B20)



B20

69% yield, white solid: mp: 50 -54 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.64 – 7.62 (m, 2H), 7.49 – 7.41 (m, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.24 (m, 2H), 7.16 – 7.13 (m, 2H), 7.10 – 7.02 (m, 3H), 4.10 (s, 2H).

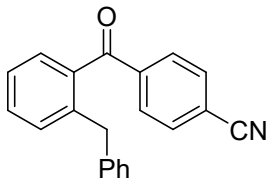
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 140.6, 140.5, 140.2, 137.9, 134.1 (q, J = 32.8 Hz), 131.2, 130.9, 130.2, 129.1, 128.8, 128.3, 126.1, 125.8, 125.2 (q, J = 3.6 Hz), 123.6 (q, J = 273.6 Hz), 38.89.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -63.04.

ESI-HRMS: calcd for $C_{21}H_{15}F_3ONa^+$ ([M + Na]$^+$) = 363.0967, found 363.0962.

IR (neat): 1670, 1409, 1324, 1266, 1169, 1128, 1065, 932, 859, 739, 700, 653 cm^{-1}.

4-(2-benzylbenzoyl)benzonitrile (B21)



B21

40% yield, white solid: mp: 101 – 105 ℃.

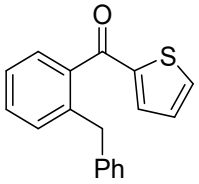
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.68 – 7.61 (m, 2H), 7.49 – 7.45 (m, 1H), 7.37 – 7.35 (m, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.16 – 7.10 (m, 2H), 7.09 – 6.99 (m, 3H), 4.09 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.9, 140.7, 140.7, 140.1, 137.4, 132.0, 131.3, 131.0, 130.2, 129.1, 128.7, 128.3, 126.1, 125.8, 118.0, 116.0, 38.9.

ESI-HRMS: calcd for $C_{21}H_{15}NONa^+$ ([M + Na]$^+$) = 320.1046, found 320.1043.

IR (neat): 2231, 1668, 1291, 1266, 930, 857, 747, 698 cm^{-1}.

(2-benzylphenyl)(thiophen-2-yl)methanone (B22)



B22

65% yield, yellow oil.

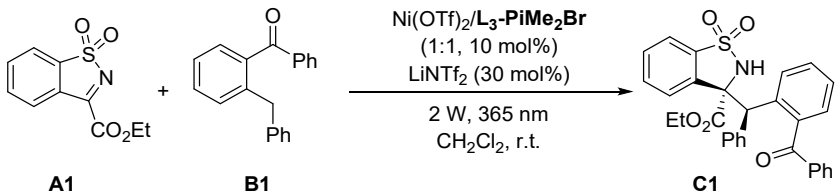
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.66 (m, 1H), 7.45 – 7.36 (m, 2H), 7.32 – 7.23 (m, 3H), 7.20 – 7.13 (m, 2H), 7.11 – 7.07 (d, *J* = 7.5 Hz, 3H), 7.05 – 6.99 (m, 1H), 4.10 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.3, 144.9, 140.3, 139.7, 138.5, 135.6, 134.9, 130.8, 130.4, 129.2, 128.2, 128.1, 128.0, 125.9, 125.5, 38.6.

ESI-HRMS: calcd for $C_{18}H_{14}OSNa^+$ ([M + Na]$^+$) = 301.0658, found 301.0655.

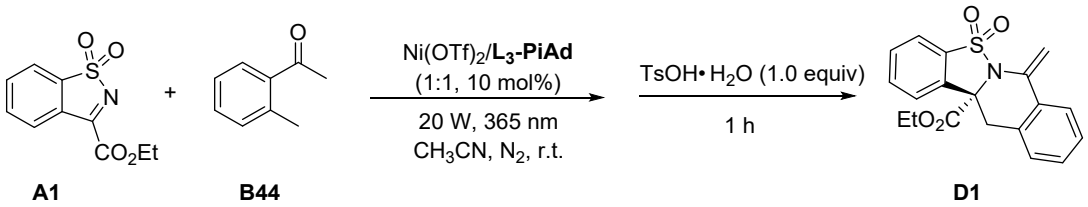
IR (neat): 1639, 1514, 1410, 1293, 1048, 851, 728, 699, 647 cm^{-1}.

3 General procedures for the catalytic asymmetric reaction



Procedure for the synthesis of the adduct C: To a dry quartz tube under nitrogen atmosphere was added **L_3-PiMe$_2$Br** (10 mol%), $Ni(OTf)_2$ (10 mol%), $LiNTf_2$ (30 mol%), *N*-sulfonyl cyclic ketimine **A** (0.1 mmol), ketone substrate **B** (0.2 mmol) in CH_2Cl_2 (2.5 mL), and the mixture was stirred at 35 ℃ for 30 minutes. Then the resulting mixture was degassed for 10 mins and stirred under UV LED (2 W, λ_{max} = 365 nm) irradiation at room temperature. After the *N*-sulfonyl cyclic

ketimine was fully consumed (detected by TLC), the residue was purified by column chromatography (petroleum ether:ethyl acetate: = 3:1) on silica gel to afford the product **C**.



Procedure for the synthesis of the adduct D: To a dry quartz tube under nitrogen atmosphere was added **L_3-PiAd** (10 mol%), $Ni(OTf)_2$ (10 mol%), *N*-sulfonyl cyclic ketimine **A** (0.1 mmol), **B** (0.2 mmol) and CH_3CN (1.0 mL), and the mixture was stirred at 35 ℃ for 30 minutes. Then the resulting mixture was degassed for 10 mins and stirred under UV LED (20 W, λ_{max} = 365 nm) irradiation at room temperature. After the *N*-sulfonyl cyclic ketimine was fully consumed (detected by TLC), $TsOH{\cdot}H_2O$ (1.0 equiv.) was added. After the conversion is completed, the solvent was removed in vacuo, and the residue was purified by column chromatography (petroleum ether:ethyl acetate: = 4:1) on silica gel to afford the product **D**.

The corresponding racemic products were obtained by using racemic *N*,*N*'-dioxide (±)-**L_3-PiAd** as the ligand under the respective catalytic reaction conditions.

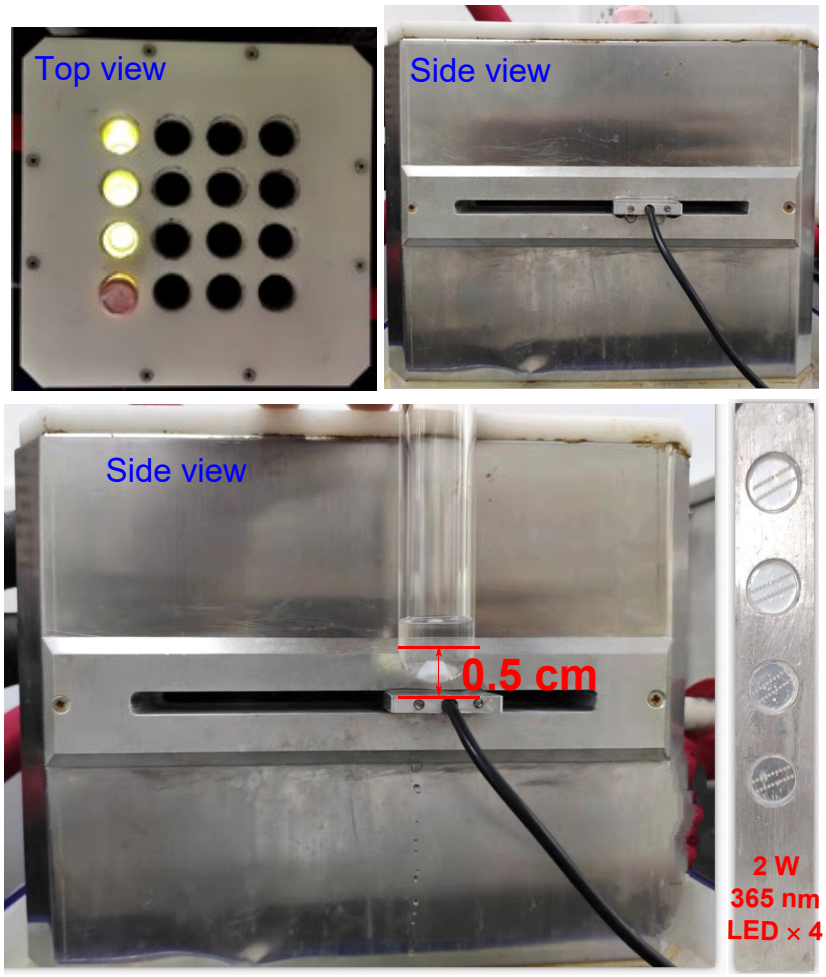
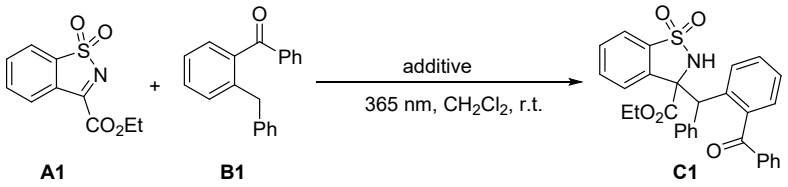


Figure S1. Photochemical setup with UV LED

Note: The distance between UV LED and reaction mixture is about 0.5 cm.

3.1 Optimization of the reaction conditions

Table 1. The background reaction

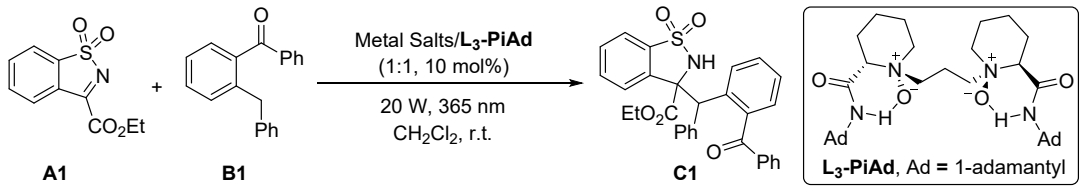


A1 **B1** **C1**

Entry[a]	Additive	conditions	Yield (%)[b]	dr[c]
1	-	20 W, 2.5 h	43	28:72
2	30 mol% $LiNTf_2$	20W, 2.5 h	67	56:44
3	-	20 W, 20 min	19	38:62
4	30 mol% $LiNTf_2$	20 W, 20 min	41	71:29
5[d]	-	2 W, 30 min	13	70:30
6[d]	-	2 W, 2 h	32	68:32
7[d]	-	2 W, 8 h	67	69:31
8[d]	30 mol% $LiNTf_2$	2 W, 8 h	56	78:22
9[d]	10 mol% $Ni(OTf)_2$	2 W, 8 h	25	58:42
10[d]	30 mol% $LiNTf_2$ + 10 mol% $Ni(OTf)_2$	2 W, 8 h	50	61:39

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), additive in CH_2Cl_2 (1.5 mL) under N_2 protection and irradiation (λ_{max} = 365 nm) at room temperature for a certain time. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]2.5 mL CH_2Cl_2 and 0.2 mmol **B1** was used.

Table 2. Screening of metal salts



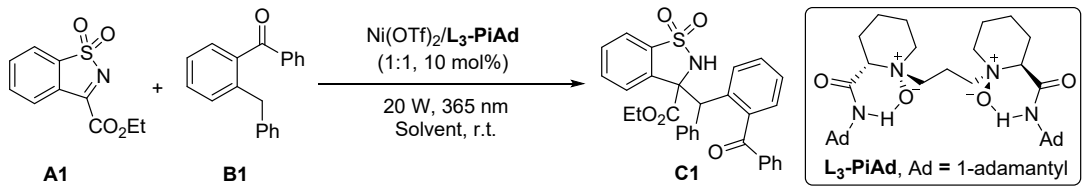
A1 **B1** **C1**

Entry[a]	Metal Salts	Yield (%)[b]	dr[c]	ee (%)[d]
1	$Sc(OTf)_3$	67	54:46	0
2	$Mg(OTf)_2$	76	64:36	4/9
3	$Ni(OTf)_2$	68	58:42	57/52
4	$Cu(OTf)_2$	75	33:67	-4/3
5	$Zn(OTf)_2$	67	53:47	5/5
6	$Ba(OTf)_2$	59	17/83	7/0

7	$Co(OTf)_2$	69	49/51	19/16
8	AgOTf	58	40/60	0
9	$Al(OTf)_3$	67	47:53	0
10	$In(OTf)_3$	72	48:52	0
11	$Y(OTf)_3$	70	37:63	7/0
12	$La(OTf)_3$	64	40:60	0
13	$Fe(OTf)_3$	75	62:38	17/15

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), metal salt (10 mol%), **L_3-PiAd** (10 mol%) in CH_2Cl_2 (1.5 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2.5 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC[2] on a chiral stationary phase.

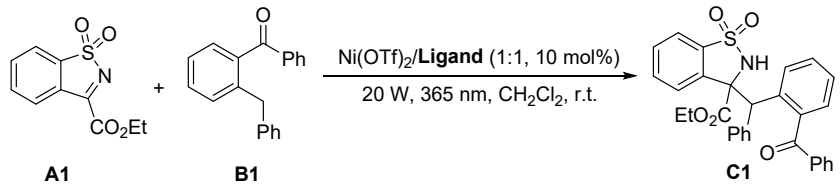
Table 3. Screening of solvents

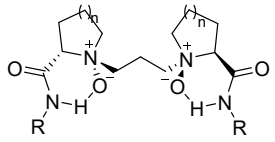


Entry[a]	Solvent	Yield (%)[b]	dr[c]	ee (%)[d]
1	CH_2Cl_2	68	58:42	57/52
2	THF	81	10:90	11/8
3	Toluene	66	39:61	0/5
4	MeOH	75	24:76	-9/7
5	Et_2O	35	14:86	0
6	Acetone	81	10:90	17
7	EtOAc	92	14:86	0/14
8	CH_3CN	87	23:77	5/12

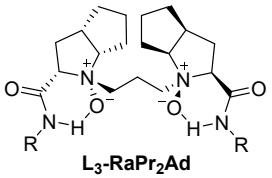
[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiAd** (10 mol%) in solvent (1.5 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2.5 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC[2] on a chiral stationary phase.

Table 4. Screening of chiral *N,N′*-dioxide ligands

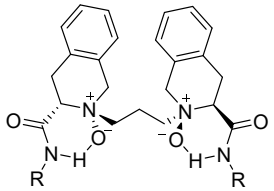




L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-PiAd: R = 1-adamantyl, n = 2
L_3-PiCPh$_2$: R = CHPh$_2$, n = 2
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2



L_3-RaPr$_2$Ad
R= 2,6-^{i}Pr$_2$-4-(1-adamantyl)-C$_6$H$_2$

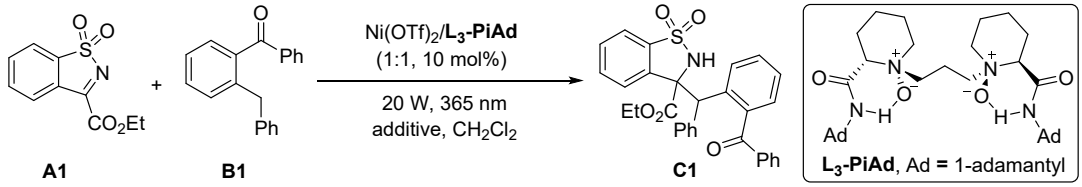


L_3-TQsEPh: R = (*S*)-1-phenylethyl
L_3-TQAd: R = 1-adamantyl

Entry[a]	Ligand	Yield (%)[b]	dr[c]	ee (%)[d]
1	**L_3-PiAd**	68	58:42	57/52
2	**L_3-PiPr$_2$**	85	64:36	8/14
3	**L_3-RaPr$_2$Ad**	86	54:46	0/18
4	**L_3-TQ*s*EPh**	60	47:53	6/8
5	**L_3-PrPr$_2$**	75	58:42	-4/5
6[e]	**L_3-PiCPh$_2$**	74	53:47	22/23

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), Ni(OTf)$_2$ (10 mol%), **Ligand** (10 mol%) in CH_2Cl_2 (1.5 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2.5 h. [b]Yield of the isolated product. [c]The dr values were determined by ^{1}H NMR analysis. [d]The ee values were determined by UPC^2 on a chiral stationary phase. [e]CH_2ClCH_2Cl as the solvent and Ni(BF$_4$)$_2$·6H$_2$O instead of Ni(OTf)$_2$.

Table 5. Screening of additives with different metal salts and temperature

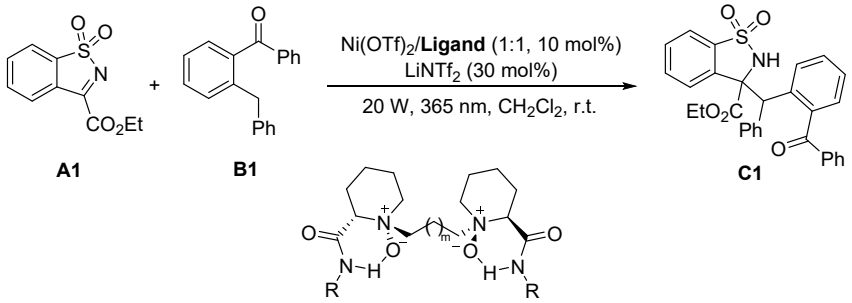


Entry[a]	Metal Salts	Additive (x mol%)	T (°C)	Yield (%)[b]	dr[c]	ee (%)[d]
1	Ni(OTf)$_2$	None	rt	68	58:42	57/52
2	Ni(OTf)$_2$	NaBAr$^F_4$ (10 mol%)	rt	74	74:26	81/52
3	Ni(OTf)$_2$	NaBAr$^F_4$ (20 mol%)	rt	67	65:35	73/50
4	Ni(OTf)$_2$	NaBAr$^F_4$ (30 mol%)	rt	53	66:34	56/35
5	Ni(OTf)$_2$	LiNTf$_2$ (10 mol%)	rt	77	66:34	81/70
6	Ni(OTf)$_2$	LiNTf$_2$ (20 mol%)	rt	90	65:35	88/84
7	Ni(OTf)$_2$	LiNTf$_2$ (30 mol%)	rt	94	74:26	89/85

8	$Ni(OTf)_2$	$LiNTf_2$ (40 mol%)	rt	89	65:35	89/86
9	$Ni(OTf)_2$	$LiNTf_2$ (50 mol%)	rt	80	69:31	87/82
10	$Ni(OTf)_2$	$LiNTf_2$ (100 mol%)	rt	89	64:36	86/84
11	$Ni(OTf)_2$	LiCl (30 mol%)	rt	77	64:36	47/54
12	$Ni(OTf)_2$	$LiBF_4$ (30 mol%)	rt	76	60:40	54/57
13	$Ni(OTf)_2$	LiOTf (30 mol%)	rt	74	58:42	46/67
14	$Ni(OTf)_2$	$NaNTf_2$ (30 mol%)	rt	71	68:32	77/40
15	$Ni(OTf)_2$	$LiNTf_2$ (30 mol%)	0	86	71:29	86/80
16	$Ni(OTf)_2$	$LiNTf_2$ (30 mol%)	-20	63	53:47	63/76
17	$Ni(NTf_2)_2$	None	rt	80	73:27	76/52
18	$NiCl_2$+$AgNTf_2$	None	rt	64	51:49	5/-13
19	$Ni(NTf_2)_2$	$LiNTf_2$ (20 mol%)	rt	90	58:42	84/78
20	$Ni(ClO_4)_2{\cdot}6H_2O$	None	rt	73	65:35	0
21	$Ni(ClO_4)_2{\cdot}6H_2O$	$LiNTf_2$ (30 mol%)	rt	66	73:27	77/39
22	$Ni(BF_4)_2{\cdot}6H_2O$	None	rt	80	63:37	36/4
23	$Ni(BF_4)_2{\cdot}6H_2O$	$LiNTf_2$ (30 mol%)	rt	72	72:28	78/37

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiAd** (10 mol%), additive in CH_2Cl_2 (1.5 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2.5 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC[2] on a chiral stationary phase.

Table 6. Rescreening of chiral *N,N′*-dioxide ligands



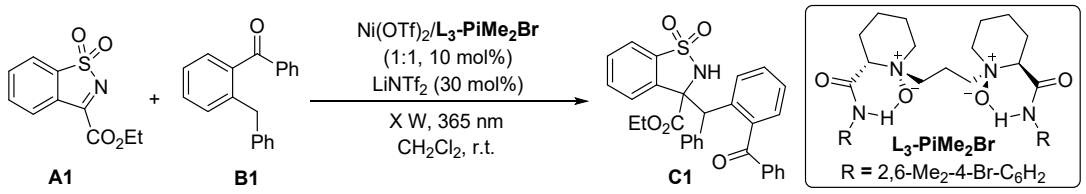
L_2-PiAd: R = 1-adamantyl, m = 0
L_3-PiAd: R = 1-adamantyl, m = 1
L_3-PiAd^2: R = 2-adamantyl, m = 1
L_4-PiAd: R = 1-adamantyl, m = 2
L_3-PiMe$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 1
L_3-PiMe$_2$Br: R = 2,4-Me$_2$-4-BrC$_6$H$_2$, m = 1
L_3-PiMe$_3$: R = 2,4,6-Me$_3$C$_6$H$_2$, m = 1
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, m = 1
L_3-PiEt$_2$Me: R = 2,4-Et$_2$-4-MeC$_6$H$_2$, m = 1
***ent*-L_3-PiEt$_2$Br**: R = 2,4-Et$_2$-4-BrC$_6$H$_2$, m = 1
L_3-PiEt$_3$: R = 2,4,6-Et$_3$C$_6$H$_2$, m = 1
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 1
L_3-PiPr$_3$: R = 2,6-^{i}Pr$_2$C$_6$H$_2$, m = 1
L_3-PiPr$_2$Ad: R = 2,6-^{i}Pr$_2$-4-(1-adamantyl)-C$_6$H$_2$, m = 1

Entry[a]	**Ligand**	Yield (%)[b]	dr[c]	ee (%)[d]
1	**L_3-TQAd**	77	63:37	47/38
2	**L_4-PiAd**	78	62:38	10/10

3	**L_3-PiAd**	94	74:26	89/85
4	**L_2-PiAd**	82	70:30	80/66
5	**L_3-PiAd^2**	85	64:36	91/89
6	**L_3-PiMe$_2$**	72	76:24	49/19
7	**L_3-PiMe$_3$**	89	63:37	83/74
8	**L_3-PiMe$_2$Br**	91	72:28	92/84
9	**L_3-PiEt$_2$**	84	71:29	65/52
10	**L_3-PiEt$_2$Me**	81	70:30	69/56
11	***ent*-L_3-PiEt$_2$Br**	80	74:26	-69/-31
12	**L_3-PiEt$_3$**	74	59:41	37/27
13	**L_3-PiPr$_3$**	73	53:47	4/4
14	**L_3-PiPr$_2$Ad**	72	57:43	2/4

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(OTf)_2$ (10 mol%), **Ligand** (10 mol%), $LiNTf_2$ (30 mol%) in CH_2Cl_2 (1.5 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2.5 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC^2 on a chiral stationary phase.

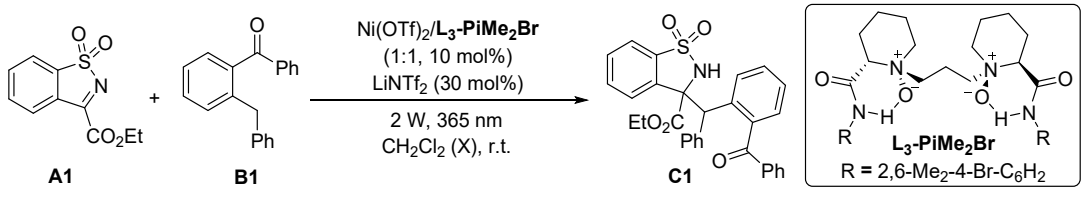
Table 7. Screening of illumination intensity



Entry[a]	Intensity (W)	Time (h)	Yield (%)[b]	dr[c]	ee (%)[d]
1	20	2.5	91	72:28	92/84
2	5	5	89	85:15	93/76
3	2	8	79	90:10	93/65

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiMe$_2$Br** (10 mol%), $LiNTf_2$ (30 mol%) in CH_2Cl_2 (1.5 mL) under N_2 protection and X W LED (λ_{max} = 365 nm) irradiation at room temperature for a certain time. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC^2 on a chiral stationary phase.

Table 8. Screening of reaction concentration

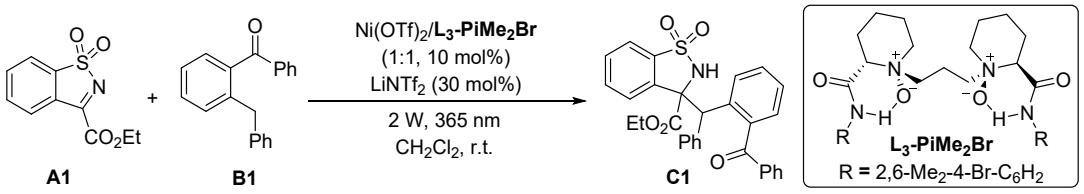


Entry[a]	X (mL)	Yield (%)[b]	dr[c]	ee (%)[d]

1	1.5	79	90:10	93/65
2	2.5	90	91:9	93/64
3	3.5	90	90:10	92/61

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiMe$_2$Br** (10 mol%), $LiNTf_2$ (30 mol%) and CH_2Cl_2 under N_2 protection and 2 W LED (λ_{max} = 365 nm) irradiation at room temperature for 8 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC^2 on a chiral stationary phase.

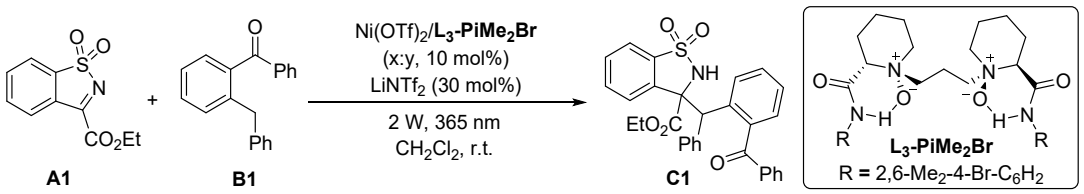
Table 9. Screening of the ratio of the substrates



Entry[a]	Ratio (**A1**:**B1**)	Yield (%)[b]	dr[c]	ee (%)[d]
1	1:1.5	90	91:9	93/64
2	1:2	96	92:8	93/65
3[e]	1:2	82	91:9	93/63
4	1:3	98	91:9	93/64

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (x mmol), $Ni(OTf)_2$ (10 mol%), **L_3- PiMe$_2$Br** (10 mol%), $LiNTf_2$ (30 mol%) in CH_2Cl_2 (2.5 mL) under N_2 protection and 2 W LED (λ_{max} = 365 nm) irradiation at room temperature for 8 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H NMR analysis. [d]The ee values were determined by UPC^2 on a chiral stationary phase. [e]The reaction time was 6 h.

Table 10. Screen of the ratio of metal salt and ligand

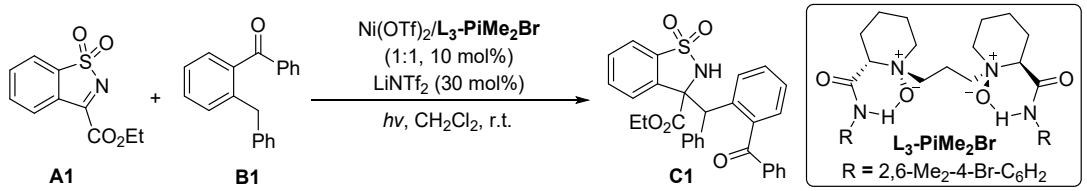


Entry[a]	x:y	Yield (%)[b]	dr[c]	ee (%)[d]
1	1.1:1	70	89:11	90/40
2	1:1	96	92:8	93/65
3[e]	1:1	91	92:8	91/65
4	1:1.1	95	92:8	93/66
5	1:1.2	96	92:8	93/66

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.2 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiMe$_2$Br** (10 mol%), $LiNTf_2$ (30 mol%) in CH_2Cl_2 (2.5 mL) under N_2 protection and 2 W LED (λ_{max} = 365 nm) irradiation at room temperature for 8 h. [b]Yield of the isolated product. [c]The dr values were determined by ^1H

NMR analysis. [d]The ee values were determined by UPC[2] on a chiral stationary phase. [e] $Ni(OTf)_2$/**L_3-PiMe$_2$Br** (5 mol%).

Table 11. Screen of the light sources

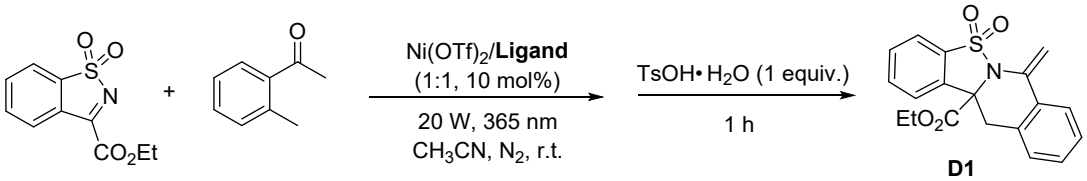


A1 **B1** **C1**

Entry[a]	Light source	Yield (%)[b]	dr[c]	ee (%)[d]
1[e]	2 W 365 nm (0.5 h)	10	80:20	78/11
2[e]	2 W 365 nm (2 h)	26	81:19	77/14
3[e]	2 W 365 nm	84	80:20	77/13
4	2 W 365 nm	96	92:8	93/65
5	2 W 385 nm	92	58:42	91/72
6	2W 400 nm	48	90:10	91/54
7[f]	2W 400 nm	87	90:10	91/52
8[g]	20 W 400 nm	73	88:12	91/65
9[h]	20 W 420 nm	11	92:8	92/63
10[h]	20 W 440 nm	0	-	-

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.2 mmol), $Ni(OTf)_2$ (10 mol%), **L_3-PiMe$_2$Br** (10 mol%), $LiNTf_2$ (30 mol%) in CH_2Cl_2 (2.5 mL) under N_2 protection and irradiation at room temperature for 8 h. [b]Yield of the isolated product. [c]The dr values were determined by ^{1}H NMR analysis. [d]The ee values were determined by UPC[2] on a chiral stationary phase. [e]Without $LiNTf_2$. [f]16 h. [g]3 h. [h]12 h.

Table 12. Screen of the conditions of produce for the synthesis of the adduct **D**



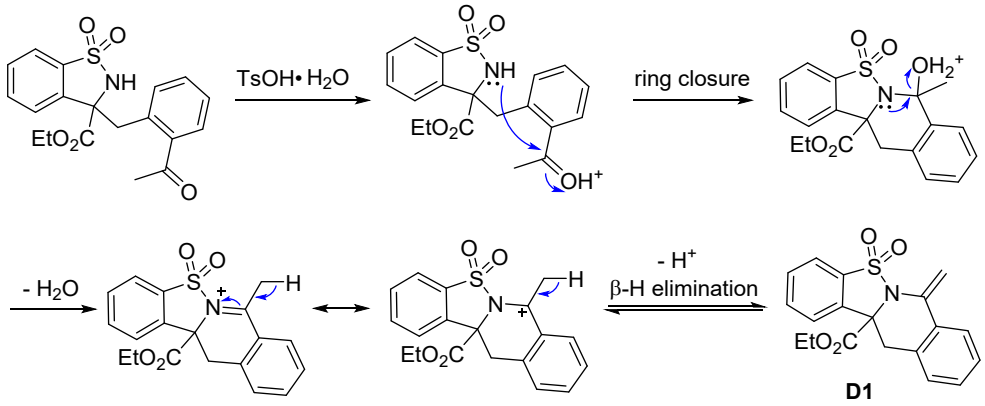
A1 **B44** **D1**

Entry[a]	Ligand	Additive	Yield (%)[b]	ee (%)[c]
1[d]	**L_3-PiMe$_2$Br**	30 mol% $LiNTf_2$	37	54
2	**L_3-PiMe$_2$Br**	-	70	60
3	**L_3-PiAd**	30 mol% $LiNTf_2$	49	89
4	**L_3-PiAd**	-	60	90
5[e]	**L_3-PiAd**	-	59	90

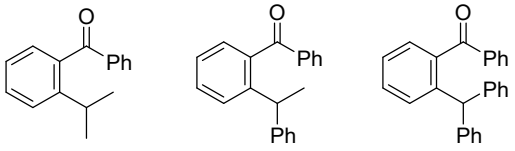
6[f]	**L_3-PiAd**	-	56	89
7[g]	**L_3-PiAd**	-	56	89

[a]Unless otherwise noted, the reactions were carried out with **A1** (0.1 mmol), **B1** (0.2 mmol), $Ni(OTf)_2$ (10 mol%), **Ligand** (10 mol%) and CH_3CN (1.0 mL) under N_2 protection and 20 W LED (λ_{max} = 365 nm) irradiation at room temperature for 2 h. [b]Yield of the isolated product. [c]The ee values were determined by UPC[2] on a chiral stationary phase. [d]2.5 mL CH_2Cl_2 as the solvent. [e]2 W 365 nm, 24 h. [f]0.15 mmol **B44**. [g]0.3 mmol **B44**.

3.2 The possible mechanism of ring-closure reaction

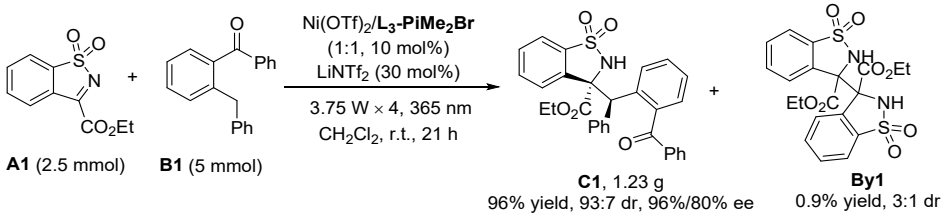


3.3 Limitations of the asymmetric PEM reaction



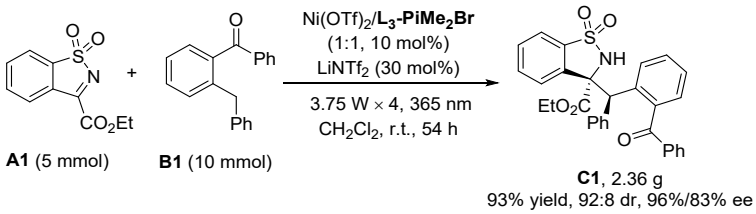
4 Gram-scale synthesis and further transformations

4.1 Procedure for the gram-scale synthesis



2.5 mmol scale synthesis: A dry round-bottom quartz flask was charged with **L_3-PiMe$_2$Br** (173.0 mg, 10 mol%), $Ni(OTf)_2$ (89.2 mg, 10 mol%) under N_2 atmosphere. Then CH_2Cl_2 (62.5 mL) was added and the mixture was stirred at 35 ℃ for 48 hours. The mixture was evaporated under reduced pressure, then $LiNTf_2$ (216.8 mg), **A1** (597.5 mg), **B1** (1360.0 mg), 62.5 mL CH_2Cl_2 were added under N_2 protection. The mixture was degassed for 10 mins and stirred under 3.75 W UV LED × 4 (λ_{max} = 365 nm) irradiation at room temperature. After **A1** was fully consumed (21 h), the residue was purified by column chromatography on silica gel to afford the product **C1** as white solid (1.23 g, 96% yield, 93:7 dr, 96%/80% ee). The absolute configuration of **C1** (CCDC:

2081680) was determined to be (*S*,*R*) by X-ray crystal analysis. The self-coupling product (**By1**) of the imine was obtained (52.1 mg, 3:1 dr).



5 mmol scale synthesis: A dry round-bottom quartz flask was charged with **L3-PiMe$_2$Br** (346.0 mg, 10 mol%), Ni(OTf)2 (178.4 mg, 10 mol%) under N_2 atmosphere. Then CH_2Cl_2 (100 mL) was added and the mixture was stirred at 35 ℃ for 48 hours. The mixture was evaporated under reduced pressure, then $LiNTf_2$ (433.6 mg), **A1** (1195.0 mg), **B1** (2720.0 mg), 100 mL CH_2Cl_2 were added under N_2 protection. The mixture was degassed for 10 mins and stirred under 3.75 W UV LED × 4 (λ_{max} = 365 nm) irradiation at room temperature. After **A1** was fully consumed (54 h), the residue was purified by column chromatography on silica gel to afford the product **C1** as white solid (2.36 g, 93% yield, 92:8 dr, 96%/83% ee).

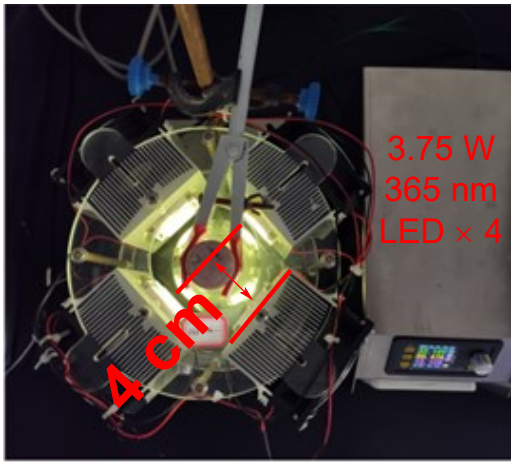
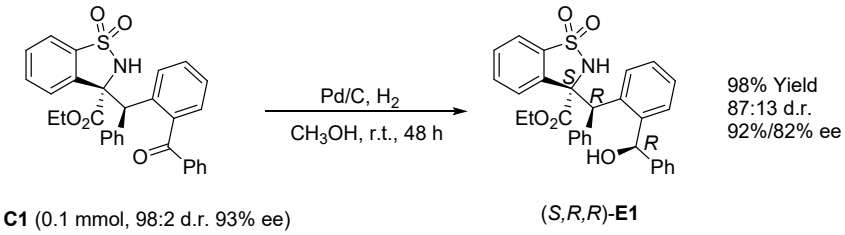


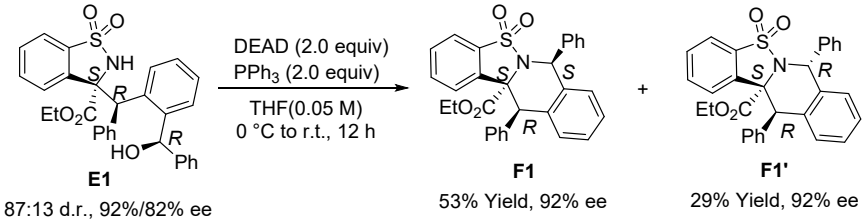
Figure S2. Gram-scale photochemical setup

Notes: Compared with the 0.1 mmol scale synthesis using a test tube, the gram-scale synthesis was performed in a big round-bottom flask, which requires four UV LEDs to achieve full illumination of the reaction mixture (3.75 W UV LED ×4). Moreover, The distance between UV LED and the center of reaction mixture is about 4.0 cm rather than 0.5 cm in the 0.1 mmol scale synthesis.

4.2 Transformation of the product C1



To a stirred solution of **C1** (51.1 mg, 0.1 mmol, 98:2 dr, 93% ee) in MeOH (2 mL) at r.t. was added Pd/C (5% w/w Pd on carbon) (23 mg), the reaction mixture was stirred at room temperature under H_2 atmosphere for 48 h. Then, the mixture was filtered and the filtrate was concentrated under reduced pressure to give the crude product and was subsequently purified by flash column chromatography (petroleum ether : ethyl acetate: = 2:1) to afford **E1** (50.2 mg) in 98% yield with 87:13 dr and 92%/82% ee. The absolute configuration of **E1** (CCDC: 2130299) was determined to be (*S*,*R*,*R*) by X-ray crystal analysis.



E1
87:13 d.r., 92%/82% ee

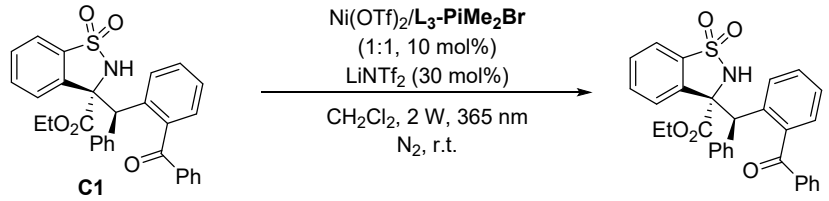
F1
53% Yield, 92% ee

F1'
29% Yield, 92% ee

To a solution of PPh_3 (43.4 mg, 0.166 mmol) and **E1** (42.5 mg, 0.083 mmol, 87:13 dr, 92%/82% ee) in THF (2 mL), diethyl azodiformate (DEAD) (28.9 mg) was added dropwise at 0 °C. After being stirred at room temperature overnight, the mixture was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:ethyl acetate: = 4:1) to give 21.5 mg **F1** in 53% yield with 92% ee and 11.8 mg **F1′** in 29% yield with 92% ee. The absolute configuration of **F1′** (CCDC: 2171982) was determined to be (*S*,*R*,*R*) by X-ray crystal analysis. The absolute configuration of **F1** was determined by NOE analysis based on the configuration of **E1** and **F1′**.

5 Control experiments

5.1 Illumination experiments of the product C1 in different conditions



C1
93:7 dr, 96%/80% ee

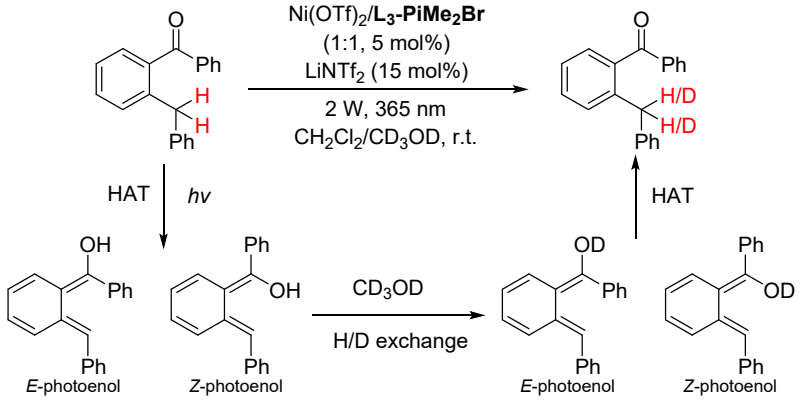
Entry	variation from the standard conditions	Yield (%)	dr	ee (%)
1	-	89	91:9	96/87
2	no $LiNTf_2$	92	79:21	96/91
3	no $LiNTf_2$, 192 h	54	13:87	83/95
4	no $Ni(OTf)_2$/**L_3-PiMe$_2$Br**	83	92:8	96/82
5	no $LiNTf_2$ and **L_3-PiMe$_2$Br**	91	87:13	96/88
6	no $LiNTf_2$ and $Ni(OTf)_2$/**L_3-PiMe$_2$Br**	92	82:18	96/91
7	20 W for 45 h	54	12:88	80/95
8	no $LiNTf_2$, 20 W for 20 h	51	10:90	76/95

9	no $LiNTf_2$ and $Ni(OTf)_2$/**L_3-PiMe$_2$Br**, 20 W for 20 h	52	11:89	78/95
10	2 w 385 nm	74	37:63	95/93
11	20 w 385 nm	37	6:94	-/96
12	2 w 400 nm	98	90:10	96/87

Standard conditions: To a dry quartz tube under nitrogen atmosphere was added **L_3-PiMe$_2$Br** (10 mol%), $Ni(OTf)_2$ (10 mol%), $LiNTf_2$ (30 mol%) and **C1** (0.1 mmol, 93:7 dr, 96%/80% ee) in CH_2Cl_2 (2.5 mL), and the mixture was stirred at 35 ℃ for 30 minutes. Then the resulting mixture was degassed for 10 mins and stirred under UV LED (2 W, λ_{max} = 365 nm) irradiation at room temperature for 10 h. The yield and dr values were determined by ^{1}H NMR analysis of the crude products, 1,1,2,2-Tetrachlorethan (1.0 equiv.) as the internal standard. The ee values were determined by UPC[2] on a chiral stationary phase.

We have screened other solvents (such as THF, CH_3CN, Toluene and Acetone) to reverse the diastereoselectivity, but no better result was obtained. C1 were mainly decomposed into the corresponding retro-aza-vinylogous Michael product.

5.2 Deuteration of substrate B1



Entry	variation from the standard conditions	Recovered SM (%)	Deuteration (%)
1	without light	100	0
2	-	94	27

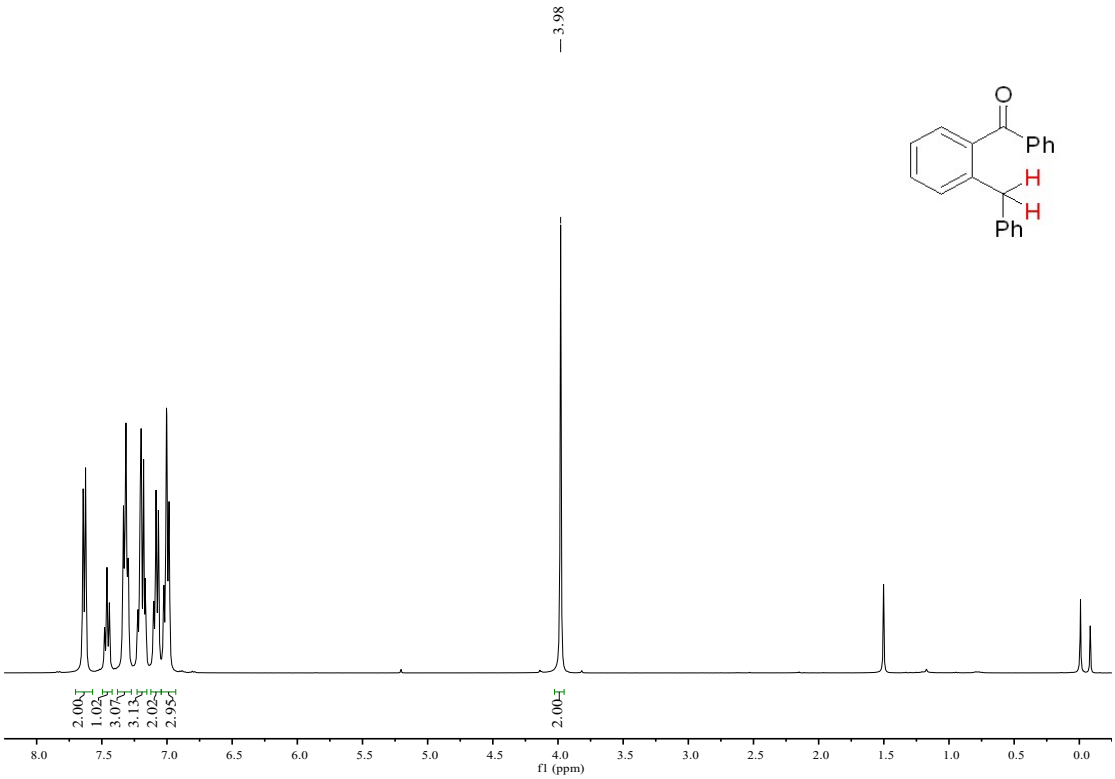


Figure S3. Proton spectrum of **B1** without irradiation in CH_2Cl_2/CD_3OD

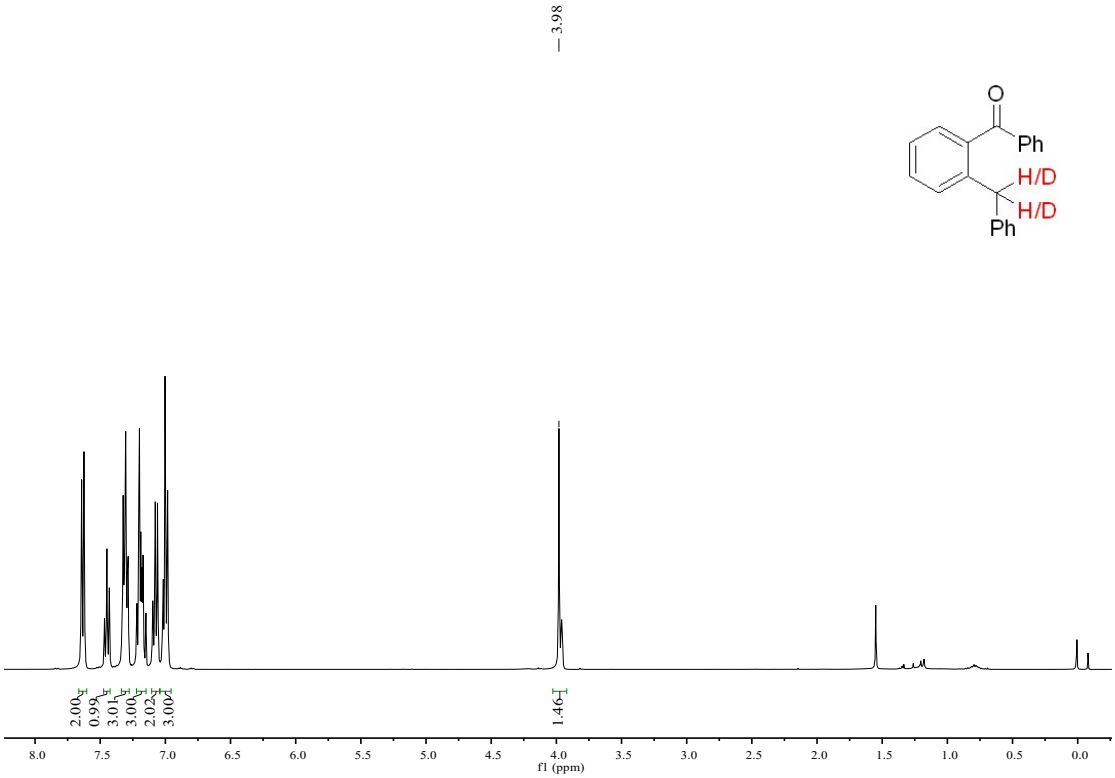


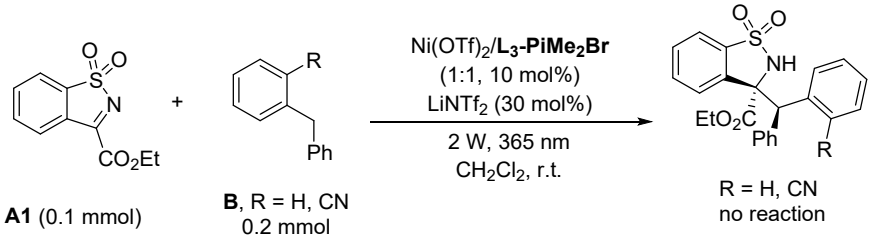
Figure S4. Proton spectrum of **B1** after irradiation in CH_2Cl_2/CD_3OD

Standard conditions: To a dry quartz tube under nitrogen atmosphere was added **L_3-PiMe$_2$Br** (5 mol%), $Ni(OTf)_2$ (5 mol%), $LiNTf_2$ (15 mol%), **B1** (0.2 mmol) in CH_2Cl_2/CD_3OD (2.4 mL/0.1 mL), and the mixture was stirred at 35 ℃ for 30 minutes. Then the resulting mixture was degassed for 10 mins and stirred under UV LED (2 W, λ_{max} = 365 nm) irradiation at room temperature for 8

h. Then the solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel to afford the deuterium **B1.**

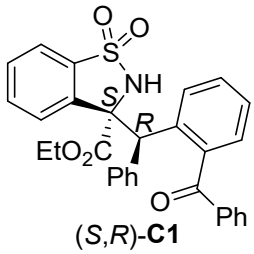
The deuteration of substrate **B1** strongyl indicated a intramolecular HAT process.

5.3 Investigating the process of intermolecular hydrogen atom transfer



To a dry quartz tube under nitrogen atmosphere was added **L_3-PiMe$_2$Br** (10 mol%), Ni(OTf)$_2$ (10 mol%), LiNTf$_2$ (30 mol%), *N*-sulfonyl cyclic ketimine **A1** (0.1 mmol), **B** (0.2 mmol) in CH_2Cl_2 (2.5 mL), and the mixture was stirred at 35 ℃ for 30 minutes. Then the resulting mixture was degassed for 10 mins and stirred under UV LED (2 W, λ_{max} = 365 nm) irradiation at room temperature for 8 h. No reaction occurred when replacing benzoyl group with cyan or hydrogen atom.

6 X-ray crystal structure



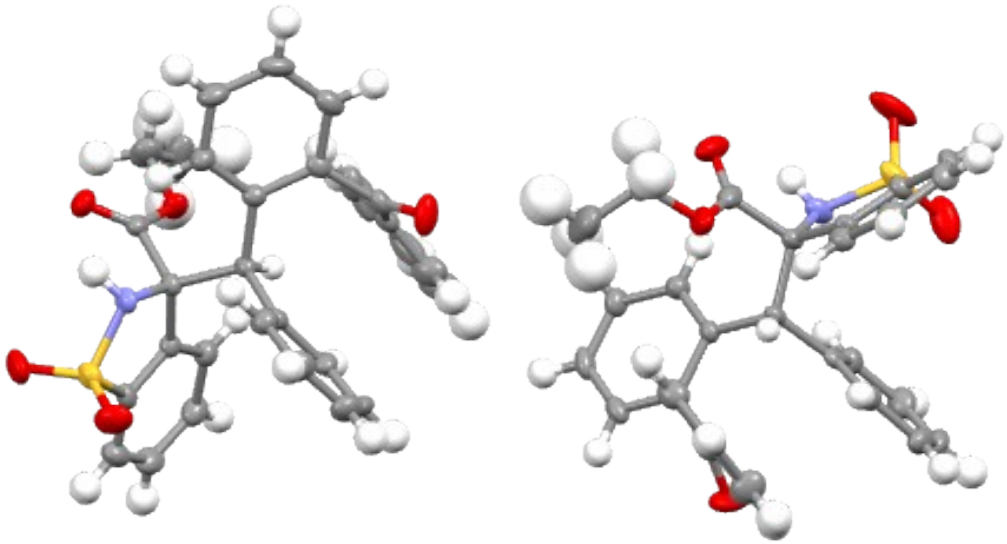
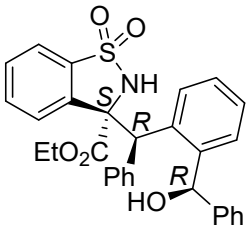


Figure S5. X-ray Crystal Structure of the product **C1**

The crystal of product **C1** was obtained in the solvents of anhydrous methanol and *n*-hexane. CCDC: 2081680 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.



(*S*,*R*,*R*)-**E1**

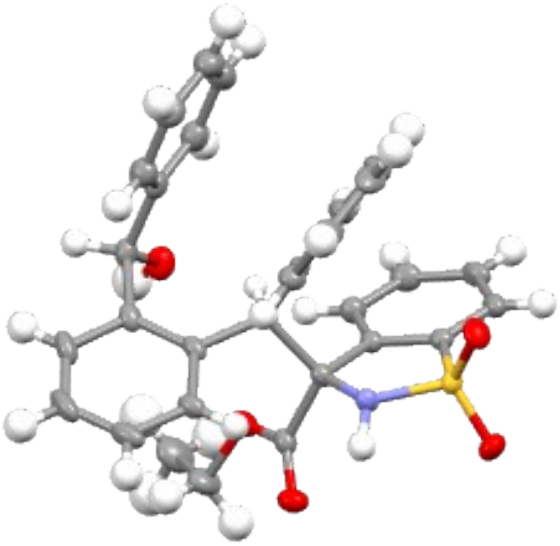
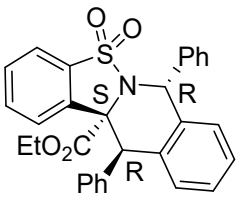


Figure S6. X-ray Crystal Structure of the product **E1**

The crystal of the product **E1** was obtained in the solvents of anhydrous CH_2Cl_2 and *n*-hexane. CCDC: 2130299 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.



(*S*,*R*,*R*)-**F1'**

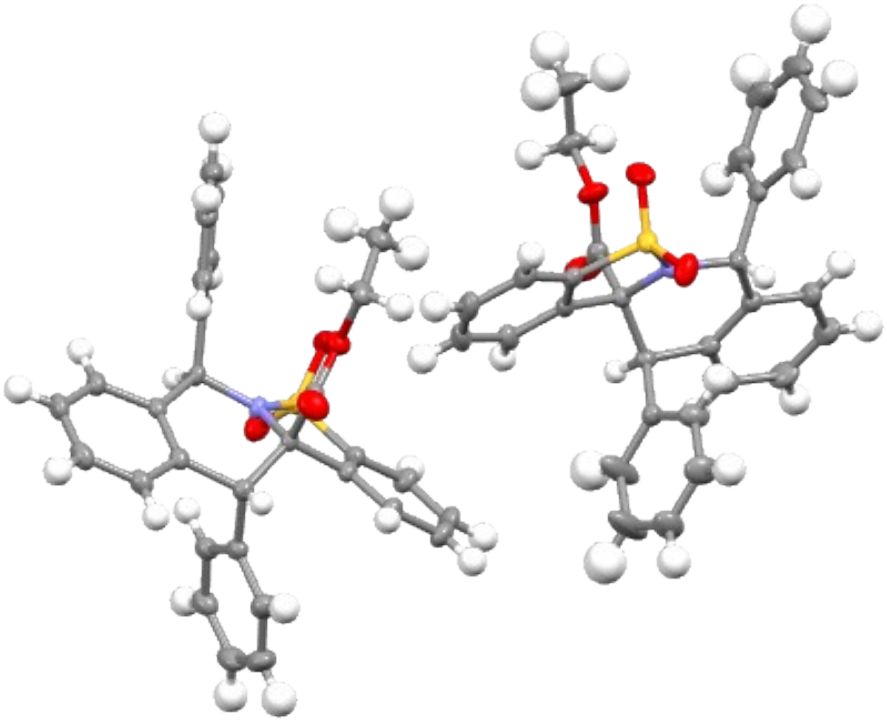


Figure S7. X-ray Crystal Structure of the product **F1'**

The crystal of the product **F1'** was obtained in the solvents of anhydrous CH_2Cl_2 and petroleum ether. CCDC: 2171982 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.

Crystallographic Data for C60 H50 N2 O10 S2, C30 H27 N O5 S and C60 H50 N2 O8 S2.

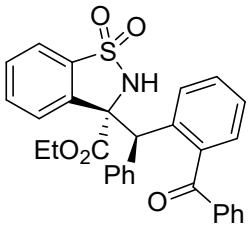
Formula	C60 H50 N2 O10 S2	C30 H27 N O5 S	C60 H50 N2 O8 S2
Formula mass (amu)	1023.14	513.58	991.14
Space group	P 21	P 21 21 21	P 21 21 21
a (Å)	12.1285 (12)	9.4559 (3)	9.6145 (2)
b (Å)	14.0298 (14)	16.0249 (5)	18.9746 (4)
c (Å)	15.1633 (17)	16.2168 (5)	26.9615 (6)
α (deg)	90	90	90
β (deg)	104.928 (4)	90	90
γ (deg)	90	90	90
V (Å^3)	2493.1 (5)	2457.33 (13)	4918.62 (18)
Z	2	4	4
λ (Å)	0.71073	1.54178	1.54178
T (K)	173 K	173 K	175 K
ρ_{calcd} (g cm^{-3})	1.363	1.388	1.338
μ (mm^{-1})	0.172	1.526	1.476
Transmission factors	0.915-0.998	0.785-1.000	0.592-0.970
θ_{max} (deg)	27.567	80.535	80.527
No. of unique data, including $F_o^2 < 0$	10901	4900	10276
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	7797	4740	9982
No. of variables	677	343	651
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0620	0.0355	0.0319
$R_w(F_o^2)$ [b]	0.1180	0.0906	0.0812
Goodness of fit	1.086	1.089	1.039

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7 The analytical and spectral characterization data for the products

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C1)



C1

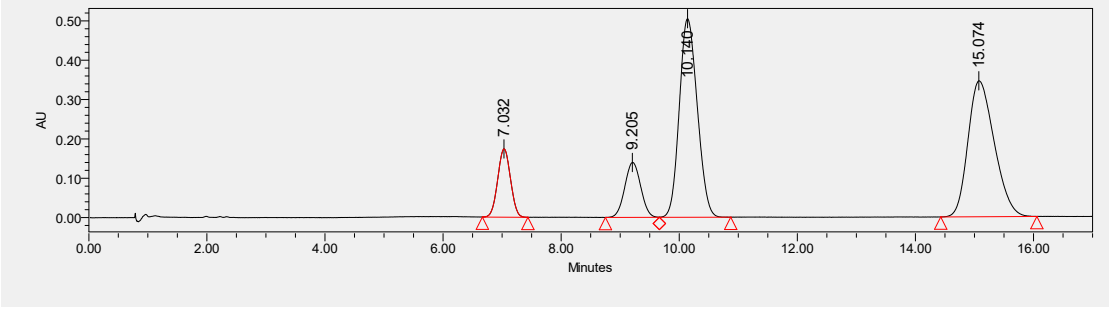
White solid; mp: 65-69 °C; 96% yield, 92:8 dr (determined by ^{1}H NMR), 93%/65% ee. $[\alpha]_{589}^{20}$ = -146.3 (c = 0.70, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.04 min, t_{R2} = 9.17 min, t_{R3} = 10.16 min, t_{R4} = 14.78 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.60 (m, 1H), 7.58 – 7.56 (m, 1H), 7.54 -7.52 (m, 3H), 7.49 – 7.45 (m, 2H), 7.36 – 7.33 (m, 1H), 7.30 – 7.26 (m, 3H), 6.96-6.90 (m, 5H), 6.08 (s, 1H), 5.53 (s, 1H), 4.10 – 4.07 (m, 1H), 3.92 – 3.89 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H).

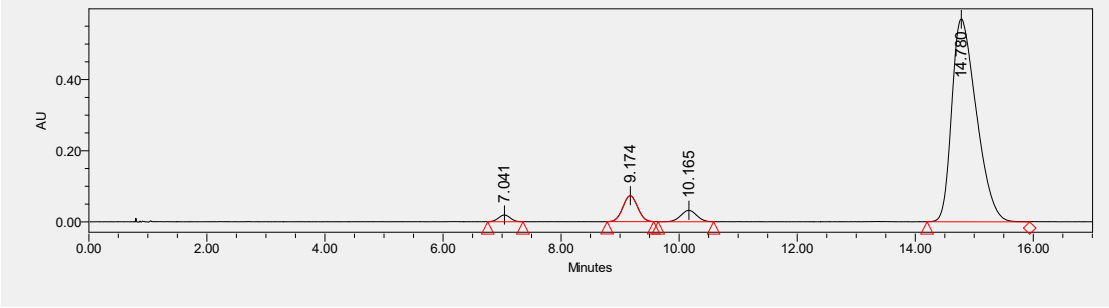
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.8, 139.2, 138.0, 137.5, 136.7, 135.9, 135.0, 133.2, 133.2, 130.5, 130.2, 130.1, 129.2, 128.8, 128.2, 127.6, 127.1, 126.6, 125.9, 121.4, 72.9, 64.0, 52.7, 13.4.

ESI-HRMS: calcd for $C_{30}H_{25}NO_5SNa^+$ ([M + Na]$^+$) = 534.1346, found 534.1346.

IR (neat): 3265, 1735, 1661, 1450, 1312, 1242, 1170, 930, 710 cm^{-1}

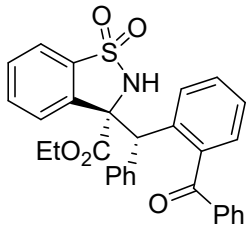


	Retention Time	Area	% Area
1	7.032	2612008	9.82
2	9.205	2620568	9.85
3	10.140	10684355	40.15
4	15.074	10691445	40.18



	Retention Time	Area	% Area
1	7.041	267515	1.44
2	9.174	1222596	6.58
3	10.165	604869	3.26
4	14.780	16479055	88.72

ethyl (*S*)-3-((*S*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C1-(II))



C1-(II)

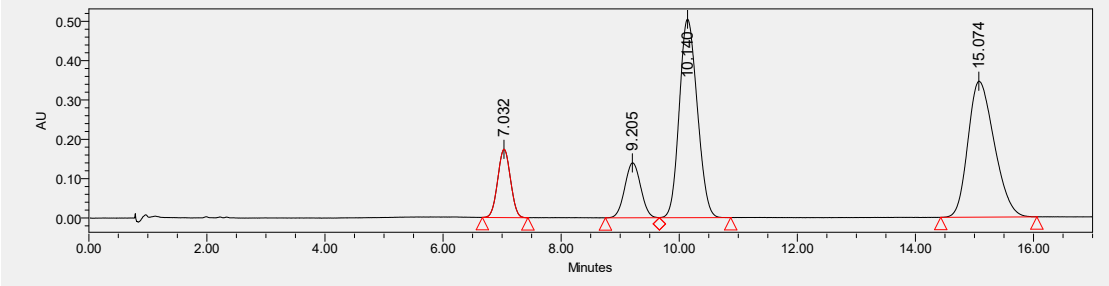
White solid; mp: 67-71 ℃; 51% yield, 10:90 dr (determined by ^{1}H NMR), 76%/95% ee. $[\alpha]_{589}^{28.4}$ = -55.6 (c = 0.53, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.84 min, t_{R2} = 8.92 min, t_{R3} = 9.81 min, t_{R4} = 14.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.41 - 7.39 (m, 1H), 7.34 – 7.36 (m, 2H), 7.30 – 7.26 (m, 3H), 7.25 – 7.23 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 7.05 – 7.03 (m, 1H), 5.98 (s, 1H), 5.91 (s, 1H), 4.09 – 3.98 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

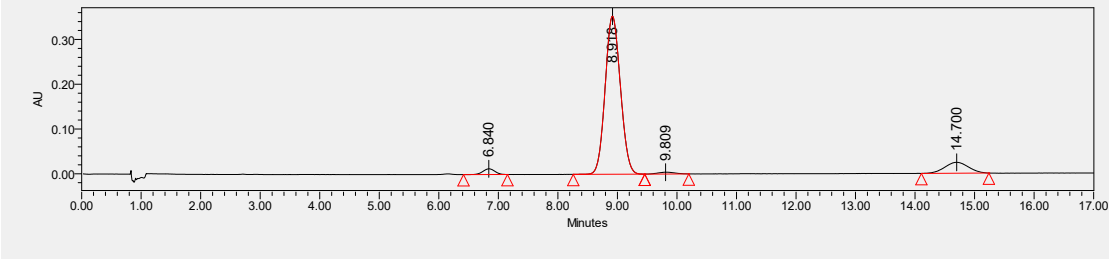
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.6, 169.8, 139.1, 138.4, 137.5, 136.5, 135.5, 134.8, 133.4, 133.0, 131.5, 130.7, 130.4, 129.1, 129.0, 128.6, 128.1, 127.4, 126.3, 126.0, 121.0, 73.1, 63.8, 50.2, 13.6.

ESI-HRMS: calcd for $C_{30}H_{25}NO_5SNa^+$ ([M + Na]$^+$) = 534.1346, found 534.1346.

IR (neat): 3266, 1736, 1657, 1450, 1312, 1242, 1171, 930, 708 cm^{-1}

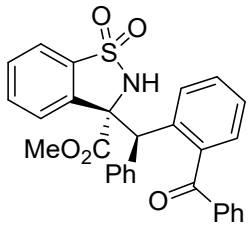


	Retention Time	Area	% Area
1	7.032	2612008	9.82
2	9.205	2620568	9.85
3	10.140	10684355	40.15
4	15.074	10691445	40.18



	Retention Time	Area	% Area
1	6.840	175822	2.45
2	8.918	6247513	87.14
3	9.809	78298	1.09
4	14.700	667674	9.31

methyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C2)



C2

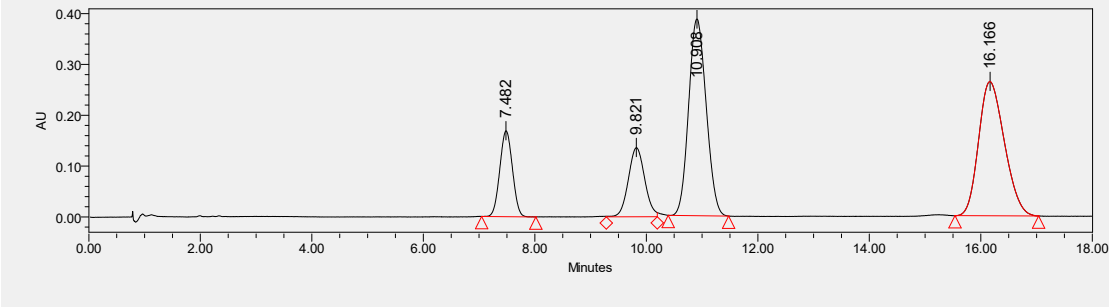
White solid; mp: 96-100 ℃ ; 98% yield, 87:13 dr (determined by ^{1}H NMR), 86%/53% ee. $[\alpha]_{589}^{18}$ = -95.2 (c = 1.00, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.42 min, t_{R2} = 9.72 min, t_{R3} = 10.84 min, t_{R4} = 15.95 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.50 (m, 6H), 7.45 – 7.43 (m, 1H), 7.36 – 7.30 (m, 4H), 7.03 – 7.01 (m, 2H), 6.97 – 6.94 (m, 3H), 6.00 (s, 1H), 5.50 (s, 1H), 3.51 (s, 3H).

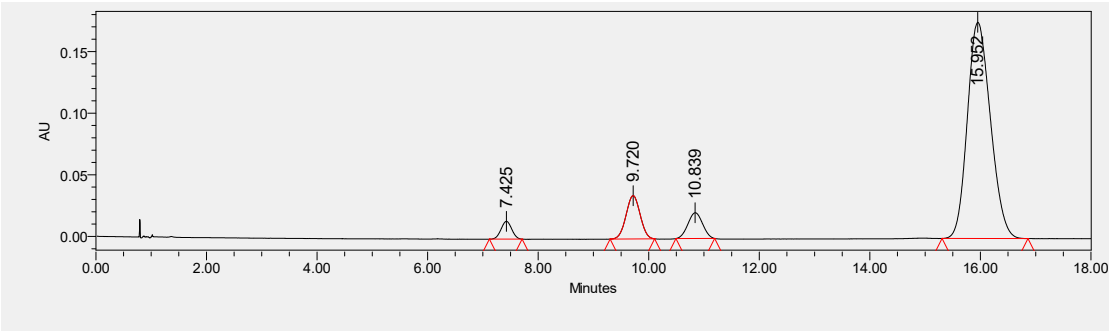
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.2, 170.3, 139.1, 137.8, 137.5, 136.2, 136.1, 134.9, 133.3, 130.6, 130.5, 130.2, 130.1, 129.4, 129.2, 128.3, 127.7, 127.2, 126.8, 126.0, 121.3, 73.0, 54.25, 52.5.

ESI-HRMS: calcd for $C_{29}H_{23}NO_5SNa^+$ ($[M + Na]^+$) = 520.1189, found 520.1188.

IR (neat): 3268, 1740, 1660, 1450, 1312, 1251, 1170, 930, 756, 710 cm^{-1}.

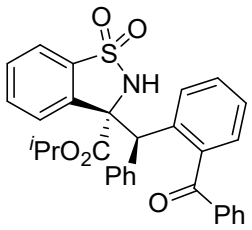


	Retention Time	Area	% Area
1	7.482	2657467	11.89
2	9.821	2757237	12.34
3	10.908	8465324	37.88
4	16.166	8469475	37.90



	Retention Time	Area	% Area
1	7.425	195002	3.10
2	9.720	621720	9.88
3	10.839	384207	6.10
4	15.952	5094341	80.92

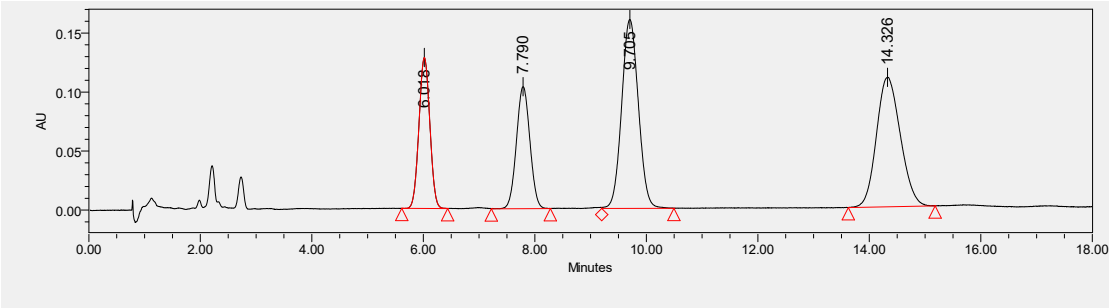
isopropyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C3)



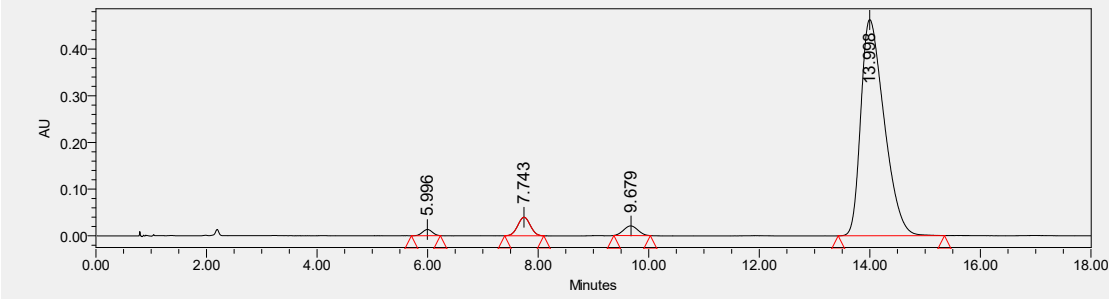
C3

White solid; mp: 67-70 °C; 99% yield, 94:6 dr (determined by ^{1}H NMR), 95%/57% ee. $[\alpha]_{589}^{20}$ = -196.6 (c = 0.93, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.00 min, t_{R2} = 7.74 min, t_{R3} = 9.68 min, t_{R4} = 14.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.59 – 7.46 (m, 3H), 7.32 – 7.40 (m, 4H), 7.25 – 7.23 (m, 1H), 7.18 – 7.14 (m, 2H), 6.93 – 6.90 (m, 1H), 6.85 – 6.81 (m, 2H), 6.70 – 6.68 (m, 2H), 6.19 (s, 1H), 5.48 (s, 1H), 4.91 – 4.82 (m, 1H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.7, 169.3, 139.7, 138.3, 137.5, 137.4, 135.3, 135.1, 133.3, 133.0, 130.5, 130.4, 130.2, 129.8, 128.8, 128.0, 127.8, 127.4, 127.0, 126.5, 125.5, 121.4, 72.9, 72.6, 53.4, 21.3, 20.3.
ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ($[M + Na]^+$) = 548.1502, found 548.1504.
IR (neat): 3259, 1728, 1662, 1313, 1255, 1174, 1103, 930, 736, 710 cm^{-1}.

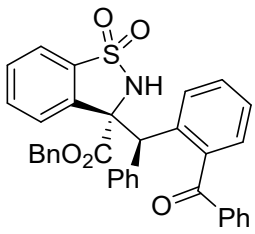


	Retention Time	Area	% Area
1	6.018	1735142	17.23
2	7.790	1740139	17.28
3	9.705	3328688	33.05
4	14.326	3267830	32.45



	Retention Time	Area	% Area
1	5.996	165611	1.12
2	7.743	625298	4.24
3	9.679	368443	2.50
4	13.998	13588018	92.14

benzyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C4)



C4

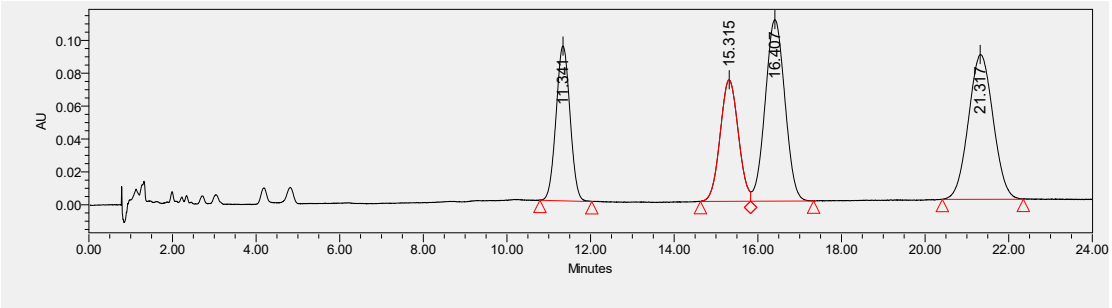
White solid; mp: 103-107 °C; 99% yield, 88:12 dr (determined by ^{1}H NMR), 88%/56% ee. $[\alpha]_{589}^{19}$ = -115.2 (c = 1.01, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 11.17 min, t_{R2} = 15.06 min, t_{R3} = 16.17 min, t_{R4} = 20.82 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.48 (m, 6H), 7.44 – 7.40 (m, 1H), 7.33 – 7.22 (m, 7H), 7.06 – 7.04 (m, 2H), 6.96 – 6.91 (m, 5H), 6.02 (s, 1H), 5.64 (s, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H).

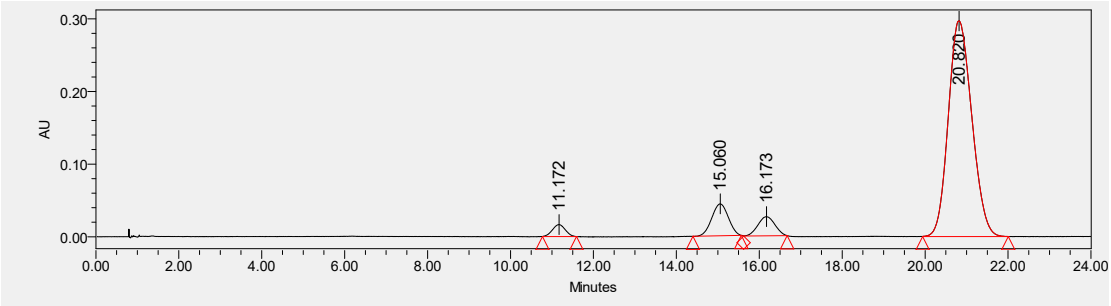
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 169.8, 139.0, 138.1, 137.5, 136.4, 136.1, 134.8, 133.9, 133.2, 133.1, 130.6, 130.5, 130.2, 130.1, 129.6, 128.8, 128.5, 128.5, 128.5, 128.3, 128.2, 127.7, 127.1, 126.6, 126.0, 121.3, 72.8, 69.3, 52.3.

ESI-HRMS: calcd for $C_{35}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 596.1502, found 596.1502.

IR (neat): 3269, 1738, 1660, 1451, 1311, 1224, 1170, 930, 736, 707 cm^{-1}.



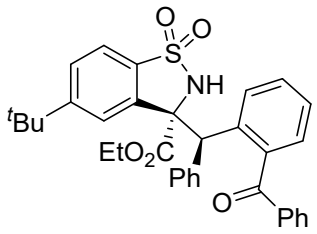
	Retention Time	Area	% Area
1	11.341	2187119	18.80
2	15.315	2226458	19.14
3	16.407	3615293	31.07
4	21.317	3605715	30.99



	Retention	Area	% Area

	Time		
1	11.172	353464	2.52
2	15.060	1220283	8.69
3	16.173	753474	5.37
4	20.820	11710319	83.42

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-5-(tert-butyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C5)



C5

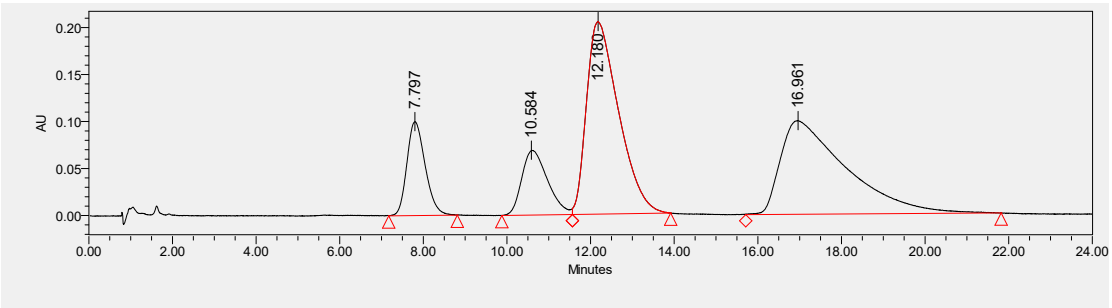
White solid; mp: 157-160 °C; 93% yield, 90:10 dr (determined by ^{1}H NMR), 91%/56% ee. $[\alpha]_{589}^{17}$ = -125.4 (c = 0.98, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 88/12, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.64 min, t_{R2} = 10.47 min, t_{R3} = 12.22 min, t_{R4} = 16.65 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.71 (s, 1H), 7.60 – 7.55 (m, 3H), 7.51 – 7.49 (m, 1H), 7.44 (s, 2H), 7.35 – 7.29 (m, 4H), 6.95 – 6.89 (m, 5H), 5.97 (s, 1H), 5.45 (s, 1H), 4.09 – 4.07 (m, 1H), 3.80 – 3.62 (m, 1H), 1.30 (s, 9H), 1.03 (t, *J* = 7.2 Hz, 3H).

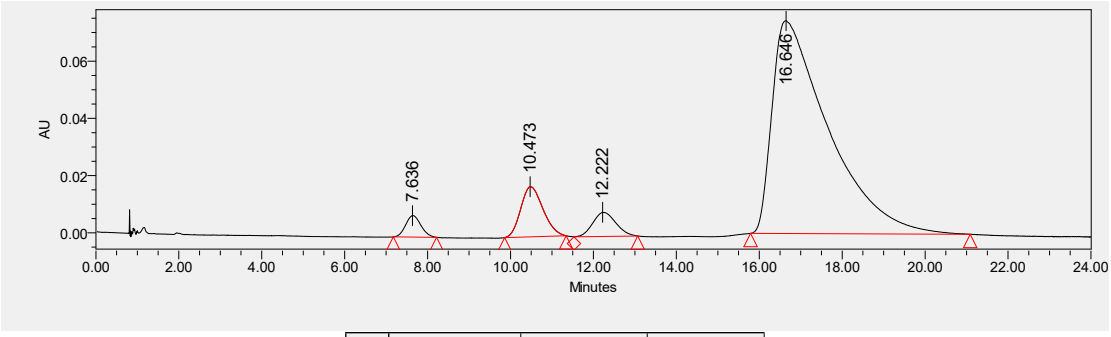
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.9, 157.3, 139.3, 137.8, 137.6, 136.4, 136.3, 133.2, 132.2, 130.6, 130.0, 130.0, 129.3, 128.3, 127.6, 127.6, 127.0, 126.8, 123.0, 120.9, 72.9, 63.7, 52.6, 35.3, 31.0, 13.5.

ESI-HRMS: calcd for $C_{34}H_{33}NO_5SNa^+$ ([M + Na]$^+$) = 590.1972, found 590.1973.

IR (neat): 3269, 2964, 1735, 1662, 1597, 1312, 1242, 1199, 1152, 1107, 1031, 930, 712 cm^{-1}.

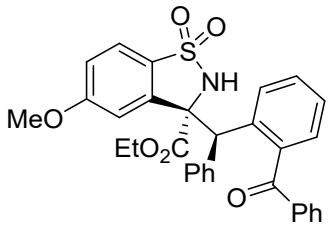


	Retention Time	Area	% Area
1	7.797	3034119	10.94
2	10.584	2957079	10.67
3	12.180	10899662	39.31
4	16.961	10833305	39.08



	Retention Time	Area	% Area
1	7.636	192194	2.35
2	10.473	651532	7.97
3	12.222	325424	3.98
4	16.646	7009679	85.71

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl-5-methoxy-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C6)



C6

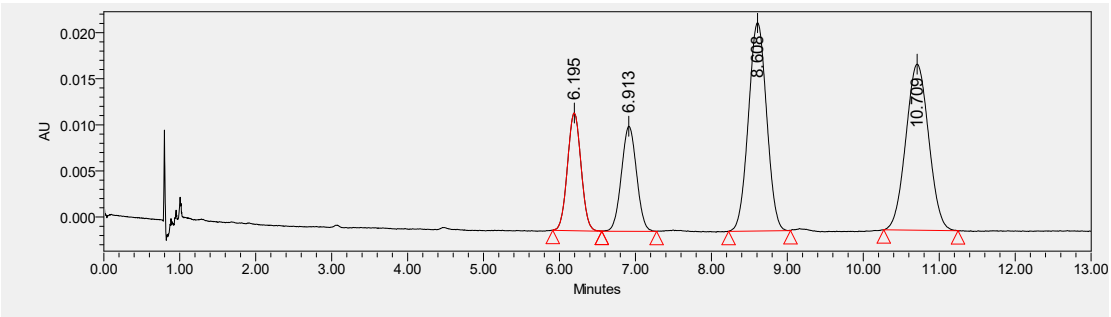
White solid; mp: 90-93 °C; 80% yield, 84:16 dr (determined by ^{1}H NMR), 93%/60% ee. $[\alpha]_{589}^{18}$ = -157.5 (c = 0.87, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.18 min, t_{R2} = 6.89 min, t_{R3} = 8.60 min, t_{R4} = 10.61 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.53 (m, 3H), 7.49 – 7.46 (m, 1H), 7.43 -7.42 (m, 1H), 7.34 – 7.32 (m, 1H), 7.29 – 7.27 (m, 3H), 7.22 – 7.22 (m, 1H), 6.98 – 6.93 (m, 6H), 6.03 (s, 1H), 5.46 (s, 1H), 4.09 – 4.06 (m, 1H), 3.89 – 3.84 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H).

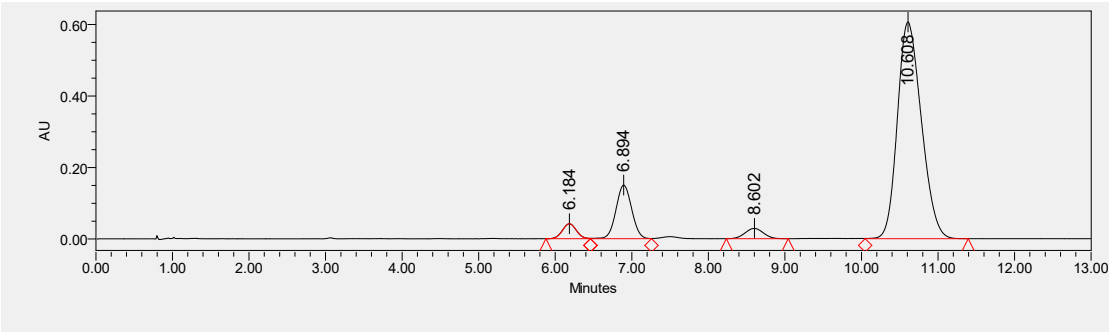
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.7, 163.5, 139.3, 139.2, 138.0, 137.6, 136.1, 133.2, 130.5, 130.1, 130.0, 129.3, 128.9, 128.2, 127.7, 127.1, 126.7, 122.7, 127.3, 117.0, 110.0, 72.5, 63.9, 55.9, 52.6, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_6SNa^+$ ([M + Na]$^+$) = 564.1451, found 564.1451.

IR (neat):3267, 1735, 1661, 1596, 1287, 1250, 1186, 930, 711 cm^{-1}.

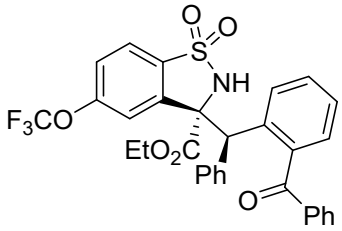


	Retention Time	Area	% Area
1	6.195	158799	14.85
2	6.913	157687	14.75
3	8.608	376283	35.20
4	10.709	376316	35.20



	Retention Time	Area	% Area
1	6.184	535179	3.28
2	6.894	2141928	13.11
3	8.602	484950	2.97
4	10.608	13169840	80.64

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-5-(trifluoromethoxy)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C7)



C7

White solid; mp: 73-76 °C; 87% yield, 80:20 dr (determined by ^{1}H NMR), 75%/60% ee. $[\alpha]_{589}^{19}$ = -147.0 (c = 0.93, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.28 min, t_{R2} = 6.14 min, t_{R3} = 7.01 min, t_{R4} = 10.21 min.

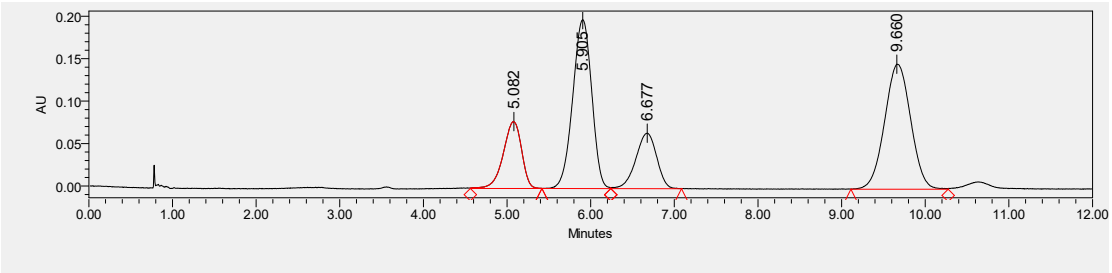
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.53 (m, 5H), 7.50 – 7.46 (m, 1H), 7.36 – 7.27 (m, 5H), 7.02 – 6.89 (m, 5H), 6.10 (s, 1H), 5.43 (s, 1H), 4.12 – 4.07 (m, 1H), 3.91 – 3.83 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 169.1, 152.4 (q, *J* = 1.9), 139.2, 137.5, 137.3, 135.6, 133.3, 130.6, 130.3, 130.1, 130.0, 129.4, 128.93, 129.0,128.9, 128.3, 127.9, 127.4, 126.9, 123.4, 123.3, 118.30, 72.5, 64.4, 52.6, 13.3.

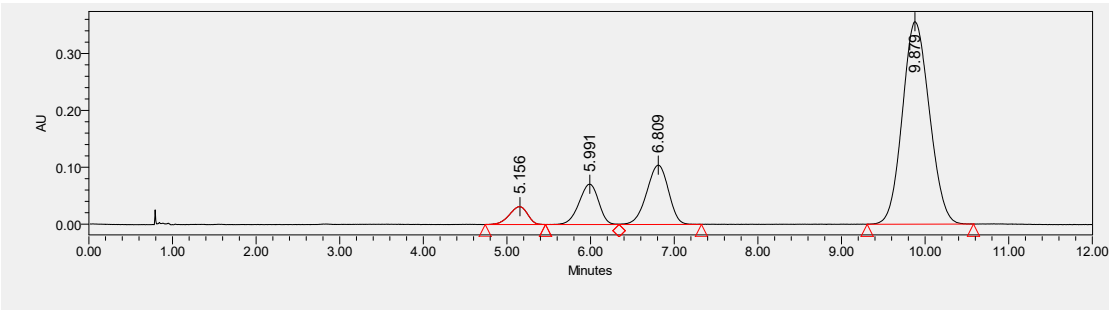
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -57.89.

ESI-HRMS: calcd for $C_{31}H_{24}F_3NO_5SNa^+$ ($[M + Na]^+$) = 618.1169, found 618.1168.

IR (neat): 3265, 1739, 1661, 1255, 1213, 1180, 736, 709 cm^{-1}.

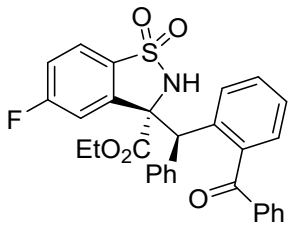


	Retention Time	Area	% Area
1	5.082	1204017	13.89
2	5.905	3136417	36.18
3	6.677	1138982	13.14
4	9.660	3190330	36.80



	Retention Time	Area	% Area
1	5.156	477406	4.14
2	5.991	1154894	10.02
3	6.809	1889407	16.39
4	9.879	8003806	69.44

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-5-fluoro-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C8)



C8

White solid; mp: 96-99 °C; 87% yield, 85:15 dr (determined by ^{1}H NMR), 87%/57% ee. $[\alpha]_{589}^{20}$ = -129.7 (c = 0.86, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.04 min, t_{R2} = 5.55 min, t_{R3} = 6.03 min, t_{R4} = 7.47 min.

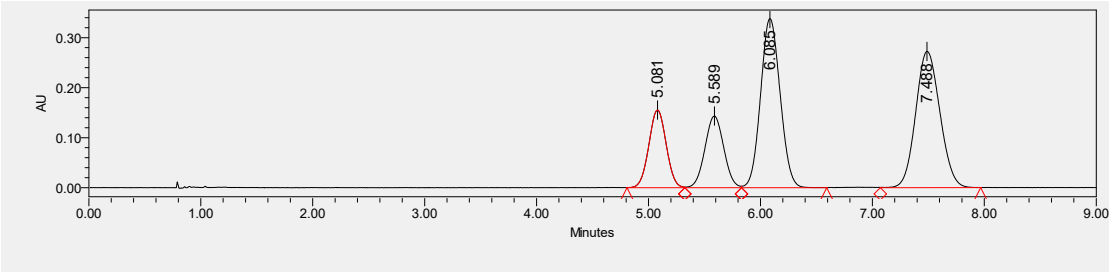
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.48 (m, 6H), 7.36 – 7.32 (m, 1H), 7.31 – 7.26 (m, 3H), 7.18 – 7.13 (m, 1H), 7.00 – 6.91 (m, 5H), 6.11 (s, 1H), 5.46 (s, 1H), 4.12 – 4.07 (m, 1H), 3.97 – 3.89 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 169.3, 165.4 (d, *J* = 256.5 Hz), 139.9 (d, *J* = 9.4 Hz), 139.2, 137.7, 137.4, 135.7, 133.3, 131.1 (d, *J* = 2.6 Hz), 130.6, 130.2, 130.1, 129.3, 128.7, 128.2, 127.8, 127.3, 126.8, 123.6 (d, *J* = 10.0 Hz), 118.7 (d, *J* = 24.3 Hz), 112.9 (d, *J* = 24.9 Hz), 72.5, 72.4, 64.3, 52.7, 13.4.

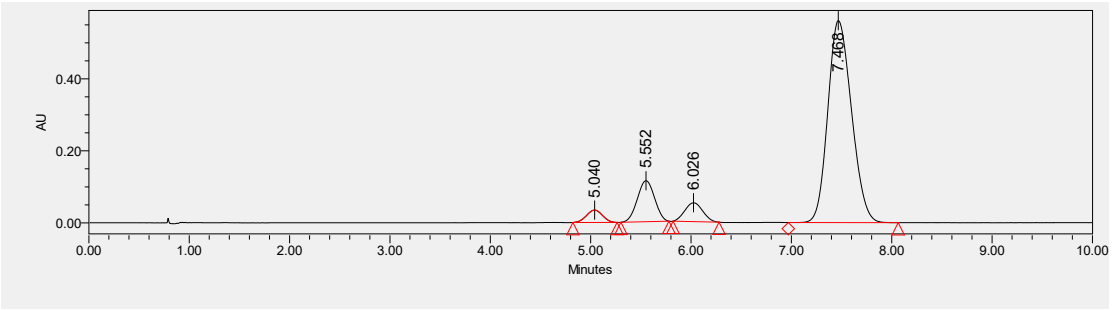
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -103.13.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1251.

IR (neat): 3263, 1737, 1661, 1594, 1314, 1239, 1179, 929, 711 cm^{-1}.

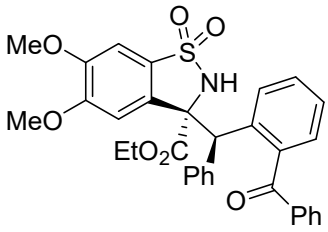


	Retention Time	Area	% Area
1	5.081	1672297	14.49
2	5.589	1675533	14.52
3	6.085	4102600	35.54
4	7.488	4092791	35.46



	Retention Time	Area	% Area
1	5.040	375461	3.23
2	5.552	1350713	11.62
3	6.026	683715	5.88
4	7.468	9216315	79.27

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-5,6-dimethoxy-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C9)



C9

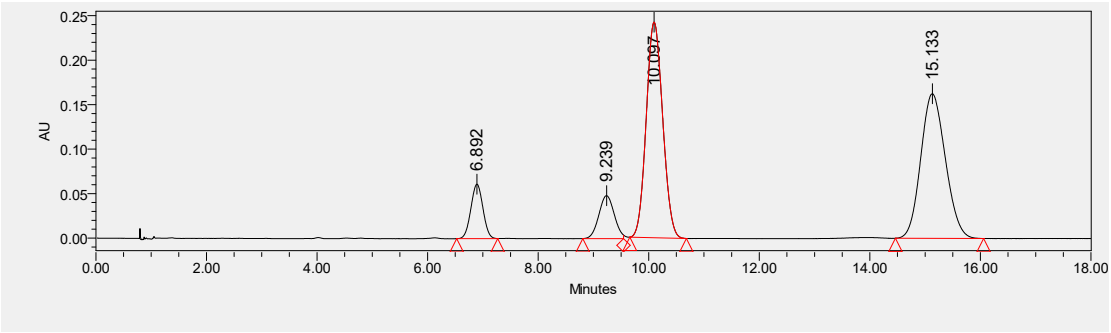
White solid; mp: 107-110 °C; 93% yield, 85:15 dr (determined by 1H NMR), 94%/60% ee. $[\alpha]_{589}^{19}$ = -153.8 (c = 1.00, in CH2Cl2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.98 min, t_{R2} = 9.36 min, t_{R3} = 10.25 min, t_{R4} = 15.26 min.

^{1}H NMR (600 MHz, CDCl3) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.49 – 7.47 (m, 1H), 7.35 – 7.32 (m, 1H), 7.30 – 7.25 (m, 4H), 7.09 (s, 1H), 6.99 – 6.95 (m, 4H), 6.90 (s, 1H), 5.99 (s, 1H), 5.45 (s, 1H), 4.09 – 4.06 (m, 1H), 3.93 (s, 3H), 3.84 – 3.83 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H).

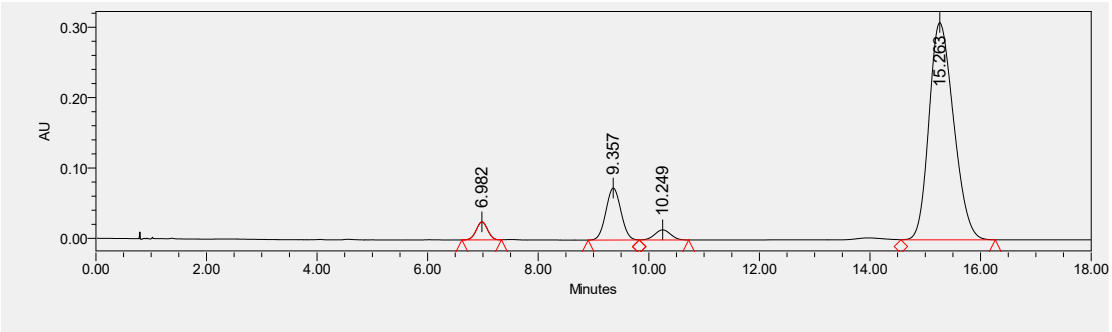
^{13}C{^{1}H} NMR (151 MHz, CDCl3) δ 198.4, 169.9, 153.4, 151.2, 139.2, 137.9, 137.7, 136.2, 133.1, 130.6, 130.0, 130.0, 129.7, 129.4, 129.0, 128.2, 127.7, 127.1, 127.1, 126.7, 106.4, 101.9, 72.3, 63.7, 56.4, 56.2, 52.3, 13.5.

ESI-HRMS: calcd for $C_{32}H_{29}NO_7SNa^+$ ([M + Na]$^+$) = 594.1557, found 594.1562.

IR (neat): 3270, 1734, 1661, 1594, 1501, 1283, 1243, 1151, 931, 859, 712 cm^{-1}.



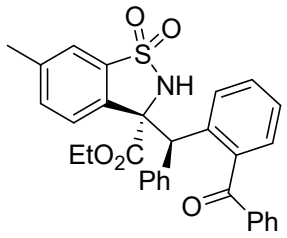
	Retention Time	Area	% Area
1	6.892	927045	7.80
2	9.239	931071	7.83
3	10.097	5001908	42.08
4	15.133	5025533	42.28



	Retention	Area	% Area

	Time		
1	6.982	366137	3.16
2	9.357	1393047	12.02
3	10.249	289432	2.50
4	15.263	9540983	82.32

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-6-methyl-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C10)



C10

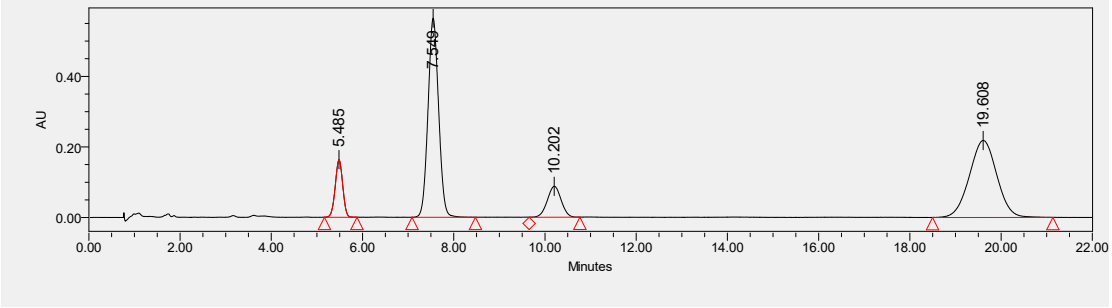
White solid; mp: 89-93 °C; 91% yield, 90:10 dr (determined by ^{1}H NMR), 94%/63% ee. $[\alpha]_{589}^{19}$ = -141.0 (c = 0.90, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.38 min, t_{R2} = 7.38 min, t_{R3} = 9.89 min, t_{R4} = 18.72 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.53 – 7.51 (m, 2H), 7.48 – 7.45 (m, 1H), 7.40 – 7.39 (m, 1H), 7.34 – 7.32 (m, 2H), 7.28 – 7.25 (m, 3H), 6.96 – 6.90 (m, 5H), 6.06 (s, 1H), 5.48 (s, 1H), 4.07 – 4.04 (m, 1H), 3.89 – 3.86 (m, 1H), 2.35 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).

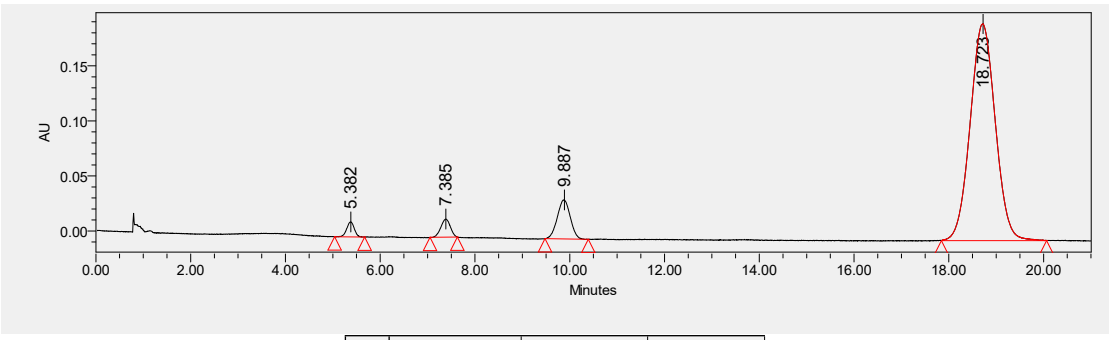
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 170.0, 141.3, 139.2, 138.1, 137.5, 136.1, 135.0, 134.4, 133.9, 133.2, 130.9, 130.2, 130.1, 129.2, 128.8, 128.1, 127.6, 127.0, 126.6, 125.5, 121.3, 72.7, 63.9, 52.6, 21.1, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1503.

IR (neat): 3266, 1734, 1661, 1449, 1312, 1245, 1162, 930, 712 cm^{-1}.

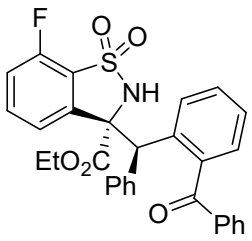


	Retention Time	Area	% Area
1	5.485	1859034	8.48
2	7.549	9099349	41.49
3	10.202	1851983	8.44
4	19.608	9121467	41.59



	Retention Time	Area	% Area
1	5.382	153286	1.85
2	7.385	227896	2.75
3	9.887	673131	8.11
4	18.723	7240677	87.29

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-7-fluoro-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C11)



C11

White solid; mp: 91-95 °C; 91% yield, 85:15 dr (determined by ^{1}H NMR), 85%/59% ee. $[\alpha]_{589}^{17}$ = -127.5 (c = 0.90, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.21 min, t_{R2} = 9.90 min, t_{R3} = 12.21 min, t_{R4} = 18.93 min.

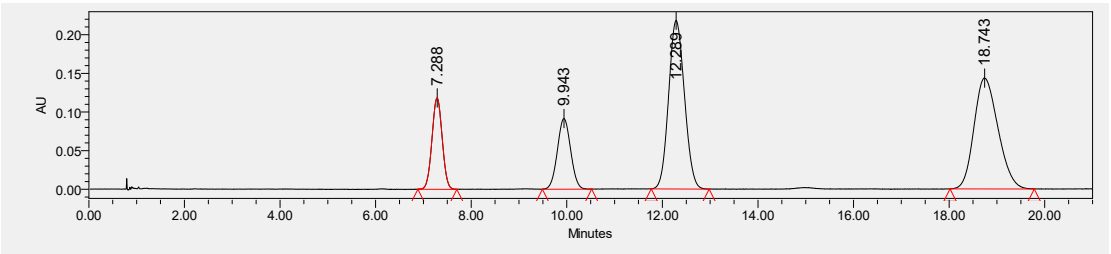
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.62 – 7.54 (m, 2H), 7.52 – 7.47 (m, 3H), 7.34 – 7.32 (m, 1H), 7.29 – 7.25 (m, 3H), 7.11 – 7.08 (m, 1H), 7.01 – 6.88 (m, 5H), 6.19 (s, 1H), 5.52 (s, 1H), 4.11 – 4.06 (m, 1H), 3.94 – 3.90 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 196.4, 156.0 (d, *J* = 262.6 Hz), 140.0, 139.2, 137.8, 137.4, 135.6, 135.6, 133.2, 130.5, 130.2, 130.0, 129.3, 128.6, 128.2, 127.8, 127.3, 126.7, 123.3 (d, *J* = 19.8 Hz) 121.5 (d, *J* = 4.1 Hz), 117.2 (d, *J* = 18.3 Hz), 73.03, 64.25, 52.72, 13.35.

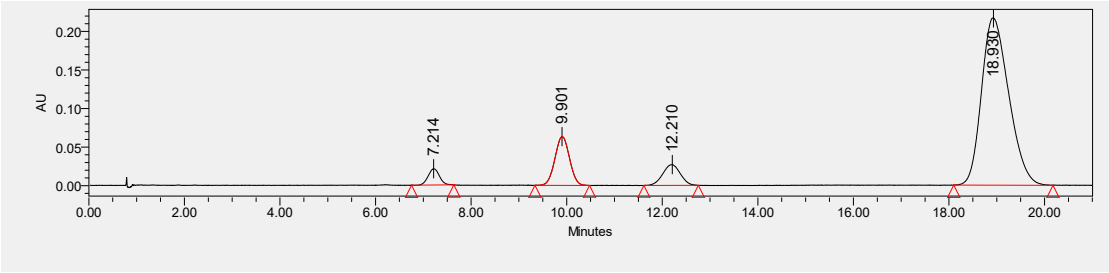
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -114.55.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1251.

IR (neat): 3258, 1736, 1661, 1596, 1472, 1320, 1262, 1226, 1179, 1113, 1020, 928, 760, 708 cm^{-1}.

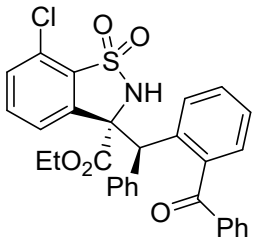


	Retention Time	Area	% Area
1	7.288	1761337	12.99
2	9.943	1764755	13.02
3	12.289	5016990	37.01
4	18.743	5011288	36.97



	Retention Time	Area	% Area
1	7.214	336764	3.07
2	9.901	1331008	12.15
3	12.210	694387	6.34
4	18.930	8597076	78.45

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-7-chloro-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C12)



C12

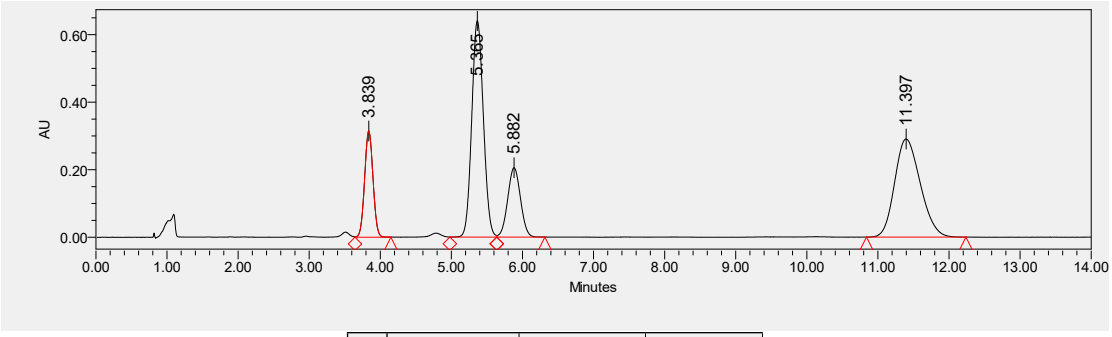
White solid; mp: 85-89 °C; 87% yield, 90:10 dr (determined by ^{1}H NMR), 86%/58% ee. $[\alpha]_{589}^{16}$ = -105.7 (c = 0.76, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 70/30, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 3.84 min, t_{R2} = 5.38 min, t_{R3} = 5.88 min, t_{R4} = 11.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.46 (m, 5H), 7.39 – 7.32 (m, 2H), 7.30 – 7.26 (m, 3H), 7.00 – 6.92 (m, 5H), 6.17 (s, 1H), 5.54 (s, 1H), 4.09 – 4.02 (m, 1H), 3.94 – 3.83 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

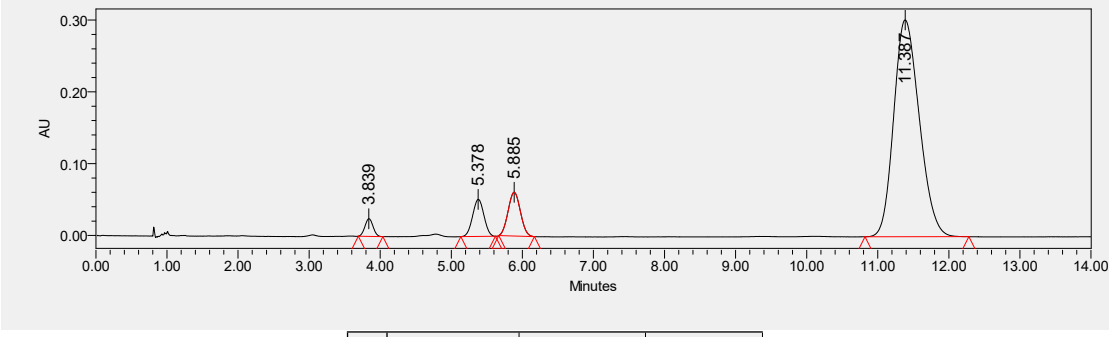
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 169.4, 139.3, 139.1, 137.8, 137.4, 135.6, 134.2, 133.2, 133.0, 131.2, 130.6, 130.1, 130.1, 129.3, 128.9, 128.7, 128.2, 127.8, 127.4, 126.7, 124.2, 72.0, 64.2, 52.4, 13.3.

ESI-HRMS: calcd for $C_{30}H_{24}{}^{35}ClNO_5SNa^+$ ([M + Na]$^+$) = 568.0956, found 568.0957. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 570.0926, found 570.0933

IR (neat): 3258, 1735, 1661, 1593, 1452, 1318, 1257, 1224, 1173, 1114, 931, 755, 710 cm^{-1}.

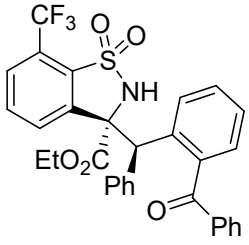


	Retention Time	Area	% Area
1	3.839	2566952	13.04
2	5.365	7277565	36.97
3	5.882	2567332	13.04
4	11.397	7273094	36.95



	Retention Time	Area	% Area
1	3.839	195462	2.16
2	5.378	573108	6.33
3	5.885	733366	8.10
4	11.387	7548704	83.41

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-7-(trifluoromethyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C13)



C13

White solid; mp: 86-89 ℃; 92% yield, 81:19 dr (determined by ^{1}H NMR), 67%/57% ee. $[\alpha]_{589}^{19}$ = -89.1 (c = 0.94, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 3.87 min, t_{R2} = 5.59 min, t_{R3} = 6.26 min, t_{R4} = 12.85 min.

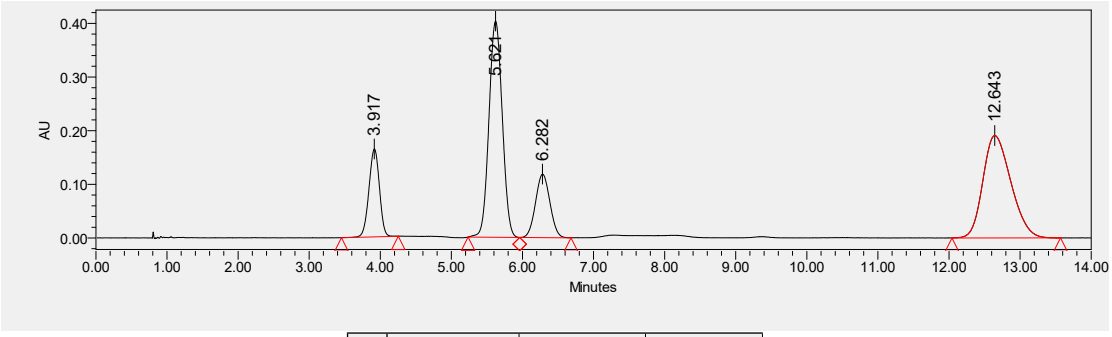
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.57 – 7.48 (m, 4H), 7.37 – 7.27 (m, 6H), 6.96 – 6.93 (m, 4H), 5.60 (s, 1H), 4.11 – 4.03 (m, 1H), 3.95 – 3.87 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 169.3, 139.0, 137.7, 137.4, 135.6, 133.4, 133.3, 130.6, 130.1, 130.1, 129.9, 129.4, 128.9, 128.8, 128.7, 128.4 (q, *J* = 4.4), 128.2, 127.9, 127.4, 126.8, 122.0 (q, *J* = 275.4 Hz) 72.3, 64.3, 52.5, 13.3.

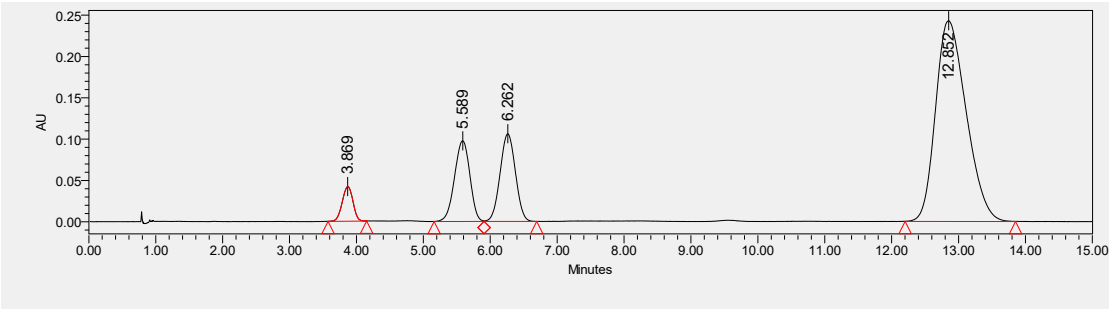
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -59.59.

ESI-HRMS: calcd for $C_{31}H_{24}F_3NO_5SNa^+$ ([M + Na]$^+$) = 602.1219, found 602.1221.

IR (neat): 3255, 1736, 1660, 1447, 1386, 1322, 1261, 1229, 1177, 1141, 931, 709 cm^{-1}.

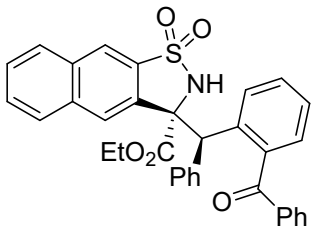


	Retention Time	Area	% Area
1	3.917	1666550	12.11
2	5.621	5220030	37.93
3	6.282	1658900	12.05
4	12.643	5216429	37.90



	Retention Time	Area	% Area
1	3.869	465781	4.08
2	5.589	1556850	13.62
3	6.262	1689377	14.78
4	12.852	7717333	67.52

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(phenyl)methyl)-2,3-dihydronaphtho[2,3-*d*]isothiazole-3-carboxylate 1,1-dioxide (C14)



C14

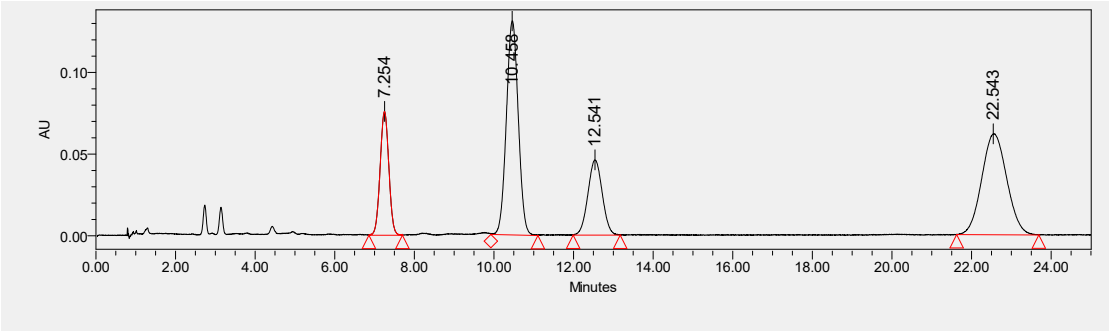
White solid; mp: 103-108 °C; 77% yield, 87:13 dr (determined by ^{1}H NMR), 80%/37% ee. $[\alpha]_{589}^{18}$ = -114.1 (c = 0.80, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.25 min, t_{R2} = 10.46 min, t_{R3} = 12.55 min, t_{R4} = 22.42 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.61 – 7.54 (m, 5H), 7.49 – 7.46 (m, 1H), 7.36 – 7.34 (m, 1H), 7.31 – 7.27 (m, 3H), 7.01 – 7.00 (m, 2H), 6.89 – 6.85 (m, 3H), 6.24 (s, 1H), 5.67 (s, 1H), 4.10 – 4.05 (m, 1H), 3.92 – 3.87 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

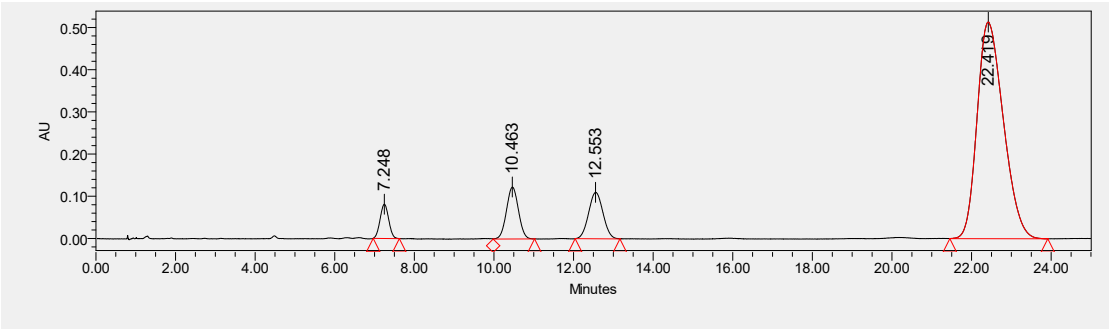
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.4, 169.8, 139.2, 138.1, 137.5, 136.0, 135.6, 134.2, 133.6, 133.2, 130.7, 130.6, 130.1, 130.1, 129.3, 129.1, 129.0, 128.3, 128.2, 128.2, 127.7, 127.1, 126.7, 124.9, 123.2, 121.3, 72.8, 64.0, 51.9, 13.4.

ESI-HRMS: calcd for $C_{34}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 584.1502, found 584.1501.

IR (neat): 3264, 1735, 1661, 1131, 1249, 1165, 1017, 931, 758, 707 cm^{-1}.

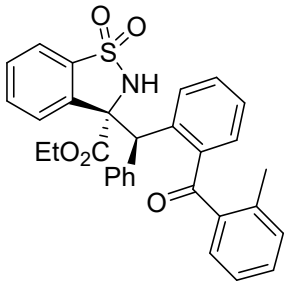


	Retention Time	Area	% Area
1	7.254	1150834	14.89
2	10.458	2721434	35.20
3	12.541	1151069	14.89
4	22.543	2707847	35.03



	Retention Time	Area	% Area
1	7.248	1216996	4.05
2	10.463	2561834	8.53
3	12.553	2760507	9.19
4	22.419	23498890	78.23

ethyl (*S*)-3-((*R*)-(2-(2-methylbenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole -3-carboxylate 1,1-dioxide (C15)



C15

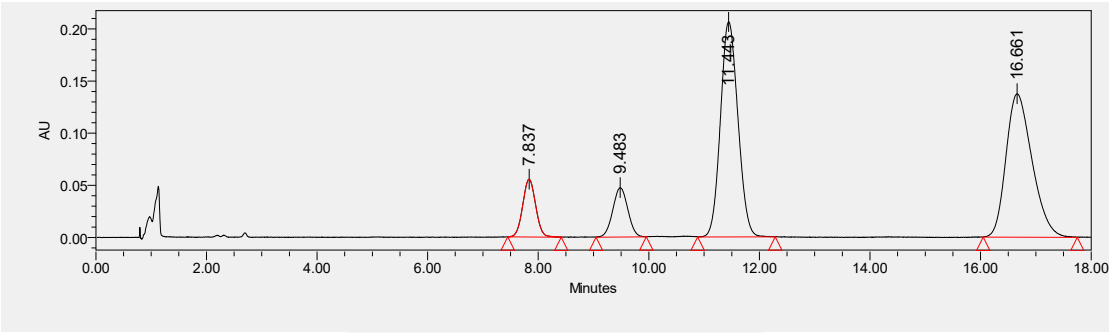
White solid; mp: 143-147 ℃; 81% yield, 90:10 dr (determined by ^{1}H NMR), 63%/61% ee. $[\alpha]_{589}^{18}$ = -112.4 (c = 0.82, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.78 min, t_{R2} = 9.39 min, t_{R3} = 11.38 min, t_{R4} = 16.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.58 – 7.53 (m, 2H), 7.51 – 7.46 (m, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.19 (m, 2H), 6.99 - 6.97 (m, 1H), 6.95 – 6.89 (m, 3H), 6.88 – 6.80 (m, 3H), 6.10 (s, 1H), 5.82 (s, 1H), 4.15 – 4.09 (m, 1H), 4.06 – 4.00 (m, 1H), 2.37 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.6, 169.9, 140.1, 138.5, 138.3, 137.0, 135.6, 135.1, 133.3, 131.5, 131.4, 131.0, 130.5, 130.5, 130.3, 128.6, 127.6, 127.1, 126.9, 125.8, 125.2, 121.4, 73.1, 64.0, 52.5, 20.6, 13.4.

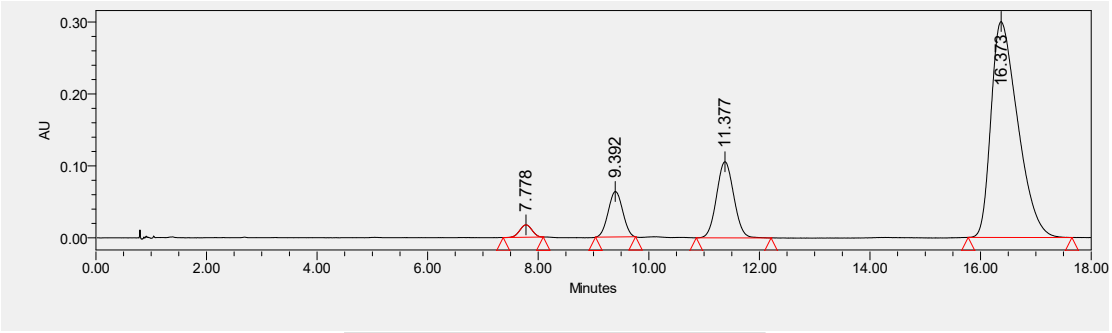
ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1501.

IR (neat): 3264, 1734, 1661, 1452, 1303, 1245, 1170, 1033, 927, 735, 703 cm^{-1}.



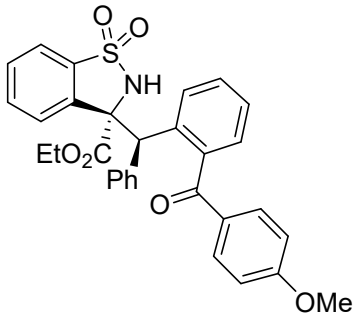
	Retention Time	Area	% Area
1	7.837	900927	8.32
2	9.483	894149	8.26

3	11.443	4535293	41.87
4	16.661	4500254	41.55



	Retention Time	Area	% Area
1	7.778	264411	1.92
2	9.392	1150341	8.35
3	11.377	2295971	16.67
4	16.373	10061296	73.06

ethyl (*S*)-3-((*R*)-(2-(4-methoxybenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C16)



C16

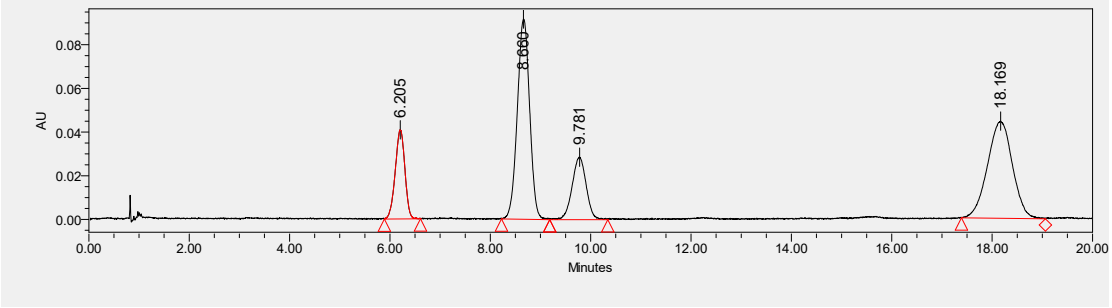
White solid; mp: 96-100 °C; 78% yield, 84:16 dr (determined by ^{1}H NMR), 78%/42% ee. $[\alpha]_{589}^{18}$ = -94.3 (c = 0.46, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.97 min, t_{R2} = 8.45 min, t_{R3} = 9.51 min, t_{R4} = 17.93 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.56 – 7.51 (m, 2H), 7.48 – 7.44 (m, 3H), 7.34 – 7.31 (m, 1H), 7.27 – 7.25 (m, 1H), 6.96 – 6.92 (,, 1H), 6.90 – 6.89 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 5.43 (s, 1H), 4.08 – 4.04 (m, 1H), 3.92 – 3.87 (m, 1H), 3.78 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

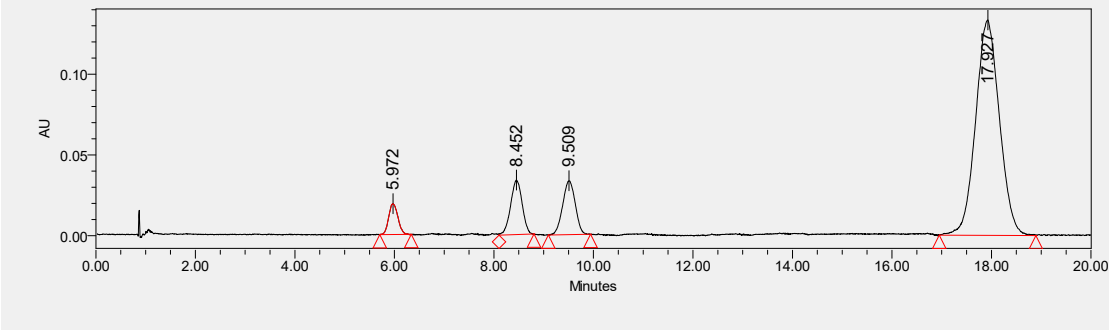
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 196.9, 169.8, 163.6, 139.8, 137.5, 136.8, 136.0, 135.0, 133.2, 132.4, 130.5, 130.2, 130.1, 129.1, 128.8, 128.7, 127.6, 127.0, 126.7, 125.9, 121.4, 113.3, 73.0, 64.0, 55.4, 53.0, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_6SNa^+$ ([M + Na]$^+$) = 564.1451, found 564.1453.

IR (neat): 3263, 1734, 1653, 1597, 1311, 1256, 1173, 1027, 931, 850, 756, 701 cm^{-1}.

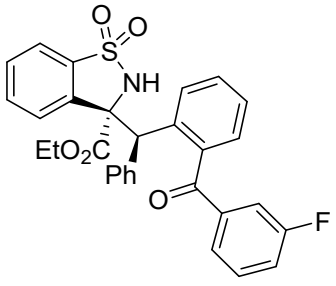


	Retention Time	Area	% Area
1	6.205	547064	13.06
2	8.660	1545773	36.90
3	9.781	559677	13.36
4	18.169	1536347	36.68



	Retention Time	Area	% Area
1	5.972	246129	4.24
2	8.452	543208	9.37
3	9.509	583908	10.07
4	17.927	4426389	76.32

ethyl (*S*)-3-((*R*)-(2-(3-fluorobenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C17)



C17

Colorless oil; 99% yield, 79:21 dr (determined by ^{1}H NMR), 93%/61% ee. $[\alpha]_{589}^{18}$ = -132.6 (c = 1.02, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 85/15,

flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 4.93 min, t_{R2} = 6.62 min, t_{R3} = 7.31 min, t_{R4} = 10.45 min.

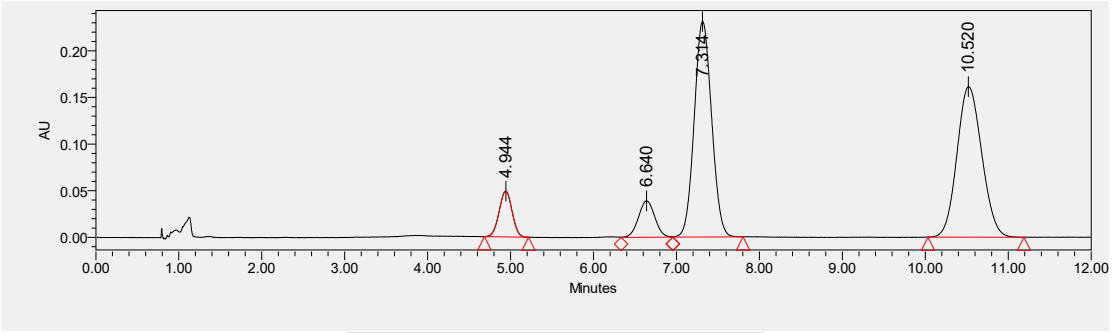
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.59 – 7.56 (m, 1H), 7.53 – 7.52 (m, 1H), 7.48 – 7.46 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.29 – 7.23 (m, 3H), 7.20 – 7.17 (m, 2H), 7.16 – 7.13 (m, 1H), 6.97 – 6.93 (m, 1H), 6.92 – 6.84 (m, 4H), 6.10 (s, 1H), 5.46 (s, 1H), 4.13 – 4.07 (m, 1H), 3.99 – 3.94 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.0, 169.8, 162.3 (d, *J* = 248.5 Hz), 139.5 (d, *J* = 6.2 Hz), 138.8, 138.2, 136.7, 135.6, 135.1, 133.3, 130.7, 130.6, 130.3, 129.8 (d, *J* = 7.6 Hz), 129.0, 128.6, 127.6, 127.2, 126.8, 126.0 (d, *J* = 2.7 Hz), 125.7, 121.4, 120.2 (d, *J* = 21.4 Hz), 116.3 (d, *J* = 22.6 Hz), 72.87, 64.02, 53.04, 13.40.

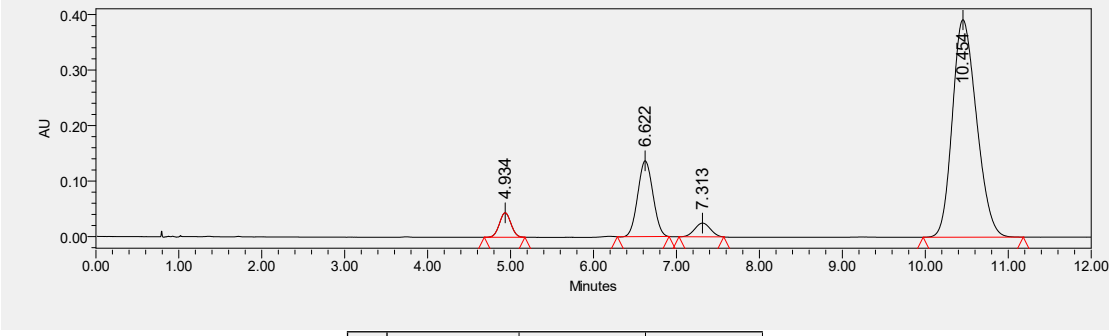
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -111.93.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1249.

IR (neat): 3265, 1735, 1665, 1587, 1447, 1373, 1297, 1241, 1170,1135, 1033, 892, 754, 703 cm^{-1}.

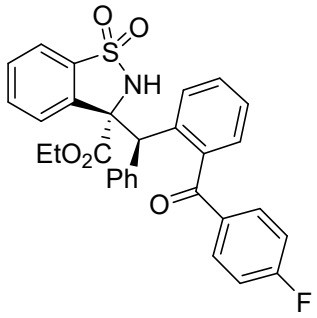


	Retention Time	Area	% Area
1	4.944	533922	6.85
2	6.640	533272	6.84
3	7.314	3367233	43.21
4	10.520	3358180	43.09



	Retention Time	Area	% Area
1	4.934	426447	4.10
2	6.622	1733259	16.67
3	7.313	326319	3.14
4	10.454	7913600	76.10

ethyl (*S*)-3-((*R*)-(2-(4-fluorobenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C18)



C18

White solid; mp: 70-73 °C; 90% yield, 89:11 dr (determined by ^{1}H NMR), 93%/67% ee. $[\alpha]_{589}^{18}$ = -140.5 (c = 0.43, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 4.86 min, t_{R2} = 6.24 min, t_{R3} = 7.45 min, t_{R4} = 10.12 min.

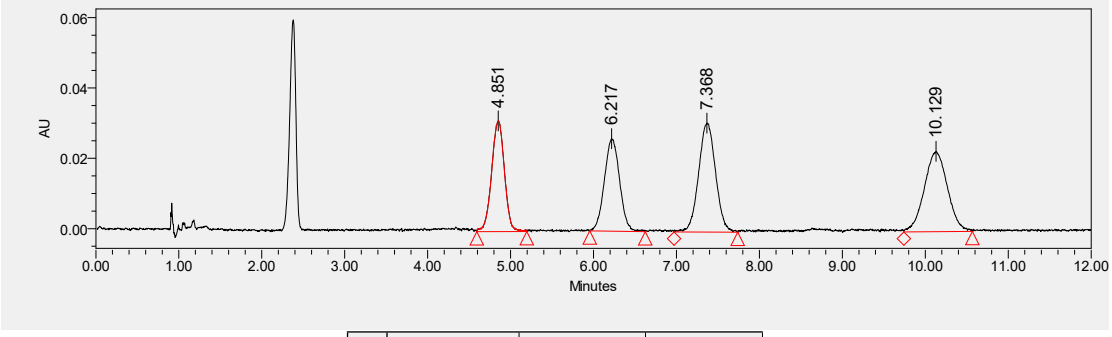
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.58 – 7.55 (m, 1H), 7.53 – 7.52 (m, 1H), 7.49 – 7.46 (m, 3H), 7.36 – 7.33 (m, 1H), 7.25 – 7.24 (m, 1H), 6.96 – 6.94 (m, 1H), 6.90 – 6.87 (m, 4H), 6.85 – 6.83 (m, 2H), 6.11 (s, 1H), 5.42 (s, 1H), 4.12 – 4.06 (m, 1H), 3.98 – 3.93 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 196.8, 169.8, 165.7 (d, *J* = 255.6 Hz), 139.2, 137.9, 136.8, 135.6, 135.0, 133.7 (d, *J* = 2.7 Hz), 133.3, 132.6(d, *J* = 9.7 Hz), 130.6, 130.5, 130.3, 128.7, 128.6, 127.6, 127.2, 126.8, 125.7, 121.4, 115.3 (d, *J* = 21.9 Hz), 72.9, 64.0, 53.1, 13.4.

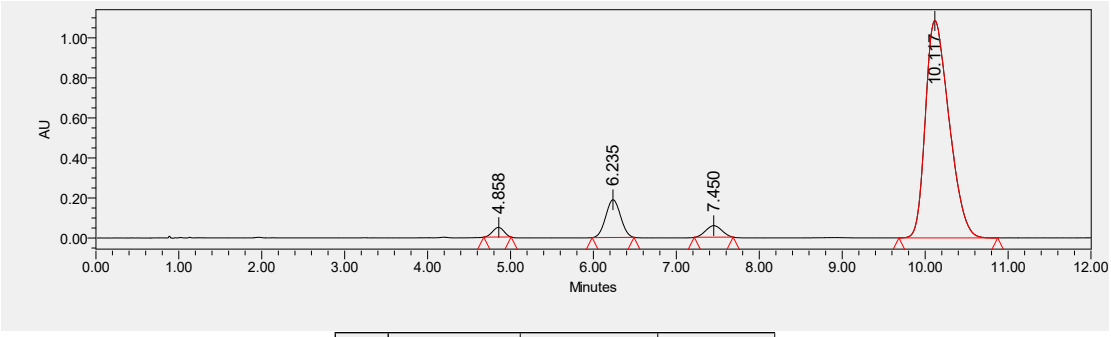
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.41.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1249.

IR (neat): 3264, 1734, 1662, 1596, 1308, 1237, 1169, 931, 855, 756, 702 cm^{-1}.

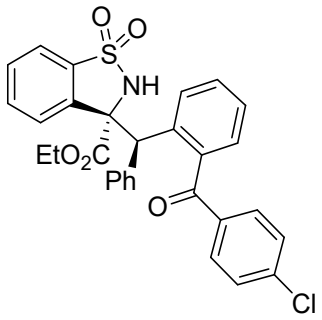


	Retention Time	Area	% Area
1	4.851	338405	21.73
2	6.217	336281	21.60
3	7.368	441273	28.34
4	10.129	441024	28.33



	Retention Time	Area	% Area
1	4.858	459570	1.83
2	6.235	2337475	9.32
3	7.450	777029	3.10
4	10.117	21515912	85.75

ethyl (*S*)-3-((*R*)-(2-(4-chlorobenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C19)



C19

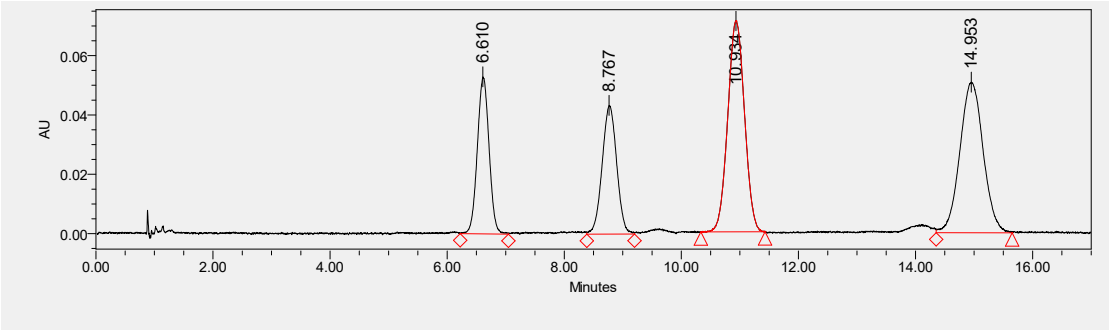
White solid; mp: 77-81 °C; 92% yield, 84:16 dr (determined by ^{1}H NMR), 95%/75% ee. $[\alpha]_{589}^{17}$ = -139.5 (c = 0.91, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.67 min, t_{R2} = 8.74 min, t_{R3} = 10.93 min, t_{R4} = 14.77 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.56 (m, 1H), 7.53 – 5.52 (m, 1H), 7.48 – 7.46 (m, 1H), 7.40 – 7.38 (m, 2H), 7.36 – 7.34 (m, 1H), 7.25 – 7.24 (m, 1H), 7.19 – 7.18 (m, 2H), 6.97 – 6.95 (m, 1H), 6.91 – 6.88 (m, 2H), 6.84 – 6.82 (m, 2H), 6.10 (s, 1H), 5.42 (s, 1H), 4.12 – 4.06 (m, 1H), 3.99 – 3.93 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H).

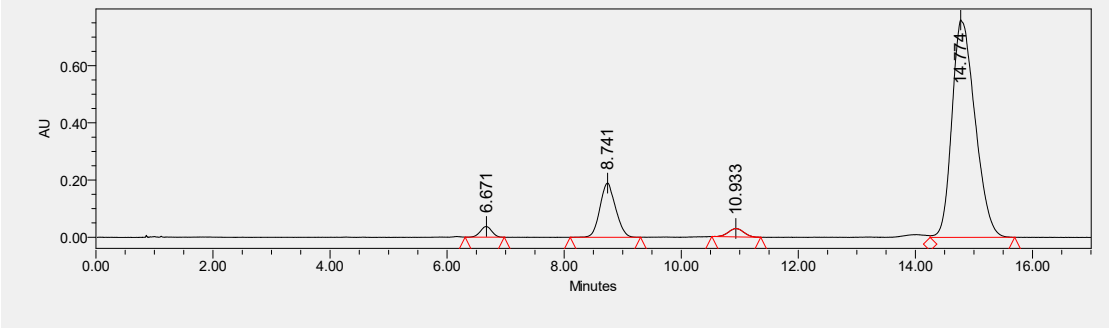
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.3, 169.9, 139.8, 139.1, 138.1, 136.8, 135.8, 135.6, 135.1, 133.4, 131.3, 130.7, 130.7, 130.3, 128.9, 128.7, 128.5, 127.7, 127.3, 126.7, 125.8, 121.5, 72.9, 64.1, 53.2, 13.5

ESI-HRMS: calcd for $C_{30}H_{24}{}^{35}ClNO_5SNa^+$ ([M + Na]$^+$) = 568.0956, found 568.0958. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 570.0926, found 570.0933

IR (neat): 3264, 1735, 1662, 1586, 1309, 1242, 1171, 1091, 929, 754, 705 cm^{-1}.

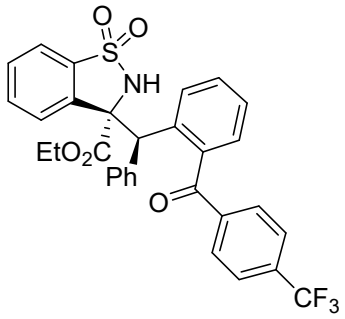


	Retention Time	Area	% Area
1	6.610	738665	17.16
2	8.767	746213	17.34
3	10.934	1412977	32.83
4	14.953	1405550	32.66



	Retention Time	Area	% Area
1	6.671	508972	2.01
2	8.741	3511775	13.84
3	10.933	533469	2.10
4	14.774	20819904	82.05

ethyl (*S*)-3-((*R*)-phenyl(2-(4-(trifluoromethyl)benzoyl)phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C20)



C20

White solid; mp: 63-67 ℃; 85% yield, 74:26 dr (determined by ^{1}H NMR), 92%/52% ee. $[\alpha]_{589}^{19}$ = -131.6 (c = 1.08, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH =

85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 2.67 min, t_{R2} = 3.45 min, t_{R3} = 4.36 min, t_{R4} = 5.43 min.

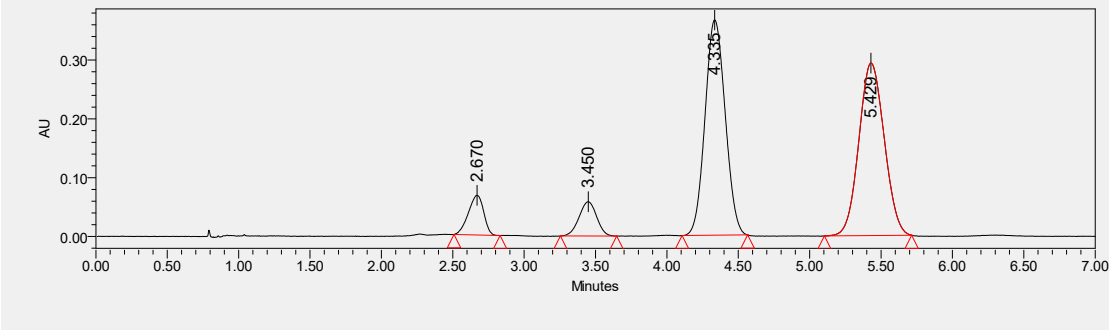
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.52 (m, 3H), 7.47 – 7.46 (m, 2H), 7.39 – 7.36 (m, 1H), 7.27 – 7.25 (m, 2H), 6.97 – 6.93 (m, 1H), 6.89 – 6.85 (m, 2H), 6.79 – 6.77 (m, 2H), 6.11 (s, 1H), 5.41 (s, 1H), 4.15 – 4.07 (m, 1H), 4.04 – 3.98 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.5, 169.8, 140.2, 138.7, 138.2, 136.7, 135.4, 135.1, 134.3 (q, *J* = 32.9 Hz), 133.3, 131.0, 130.6, 130.3, 130.1, 129.0, 128.6, 128.6, 127.6, 127.3, 126.9, 125.6, 125.1 (q, J = 3.7 Hz), 121.5, 72.8, 64.1, 53.3, 13.4.

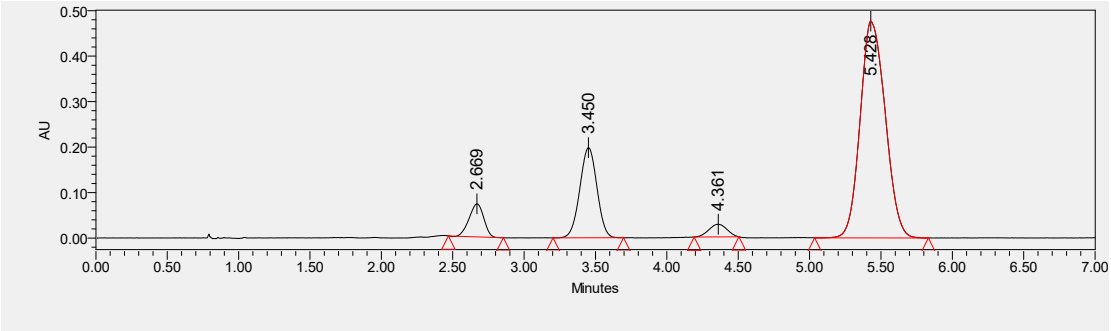
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -63.21.

ESI-HRMS: calcd for $C_{31}H_{24}F_3NO_5SNa^+$ ([M + Na]$^+$) = 602.1219, found 602.1221.

IR (neat): 3265, 1735, 1670, 1324, 1242, 1170, 1132, 1066, 931, 858, 757, 707 cm^{-1}.

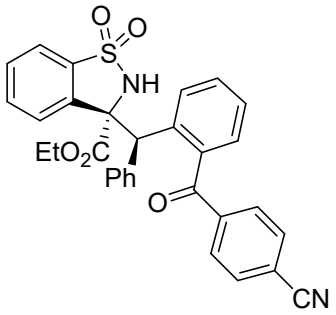


	Retention Time	Area	% Area
1	2.670	504680	6.14
2	3.450	498355	6.06
3	4.335	3597551	43.74
4	5.429	3624281	44.06



	Retention Time	Area	% Area
1	2.669	519492	6.29
2	3.450	1639819	19.85
3	4.360	272554	3.30
4	5.428	5827274	70.56

ethyl (*S*)-3-((*R*)-(2-(4-cyanobenzoyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C21)



C21

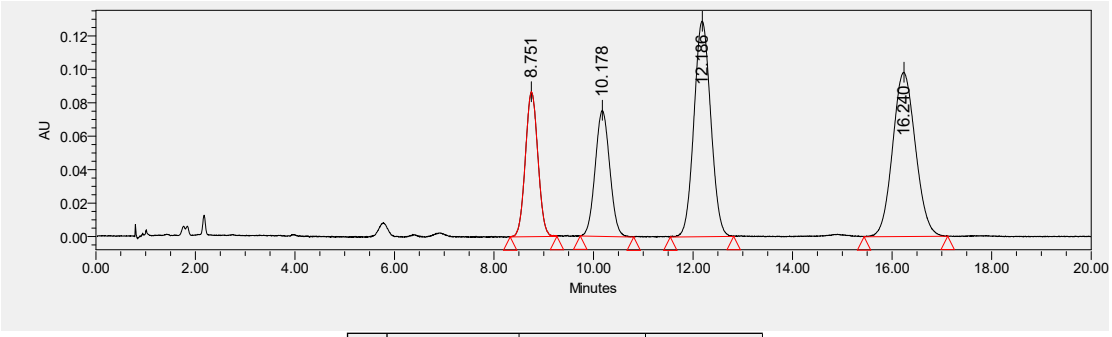
White solid; mp: 105-107 °C; 65% yield, 87:13 dr (determined by ^{1}H NMR), 41%/45% ee. $[\alpha]_{589}^{18}$ = -33.6 (c = 0.68, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 8.70 min, t_{R2} = 10.09 min, t_{R3} = 10.93 min, t_{R4} = 14.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.49 (s, 1H), 7.46 – 7.42 (m, 3H), 7.40 – 7.38 (m, 2H), 7.29 – 7.27 (d, *J* = 4.4 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.19 – 7.12 (m, 2H), 6.98 – 6.96 (m, 1H), 5.99 (s, 1H), 5.93 (s, 1H), 4.08 – 4.00 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H)..

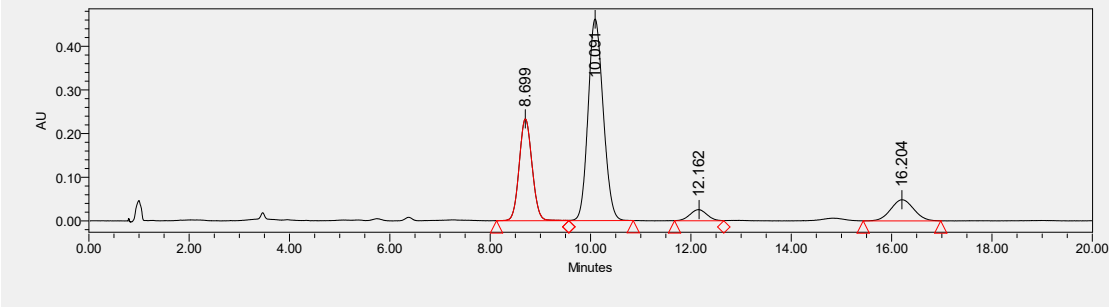
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.0, 169.6, 140.6, 138.7, 137.1, 136.8, 135.6, 135.0, 133.3, 131.8, 131.4, 130.5, 130.5, 129.0, 128.8, 128.7, 127.6, 126.3, 126.2, 121.2, 117.8, 116.1, 72.9, 63.9, 50.0, 13.6.

ESI-HRMS: calcd for $C_{31}H_{24}N_2O_5SNa^+$ ([M + Na]$^+$) = 559.1298, found 559.1300.

IR (neat): 3262, 1737, 1665, 1311, 1242, 1170, 930, 857, 755, 706 cm^{-1}.

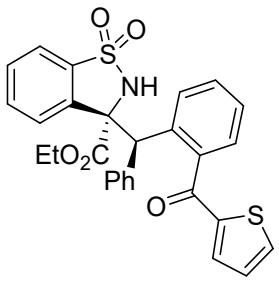


	Retention Time	Area	% Area
1	8.751	1513637	16.47
2	10.178	1529577	16.64
3	12.186	3022902	32.89
4	16.240	3123597	33.99



	Retention Time	Area	% Area
1	8.699	4058874	25.78
2	10.091	9619301	61.09
3	12.162	570239	3.62
4	16.204	1498139	9.51

ethyl (*S*)-3-((*R*)-phenyl(2-(thiophene-2-carbonyl)phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C22)



C22

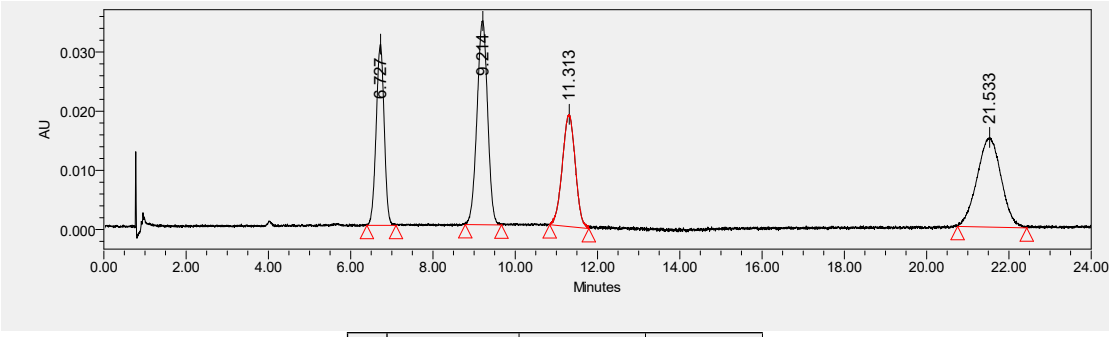
White solid; mp: 95-98 °C; 42% yield, 75:25 dr (determined by ^{1}H NMR), 73%/12% ee. $[\alpha]_{589}^{18}$ = -110.8 (c = 0.23, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.78 min, t_{R2} = 9.29 min, t_{R3} = 11.36min, t_{R4} = 21.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.56 – 7.52 (m, 2H), 7.50 – 7.47 (m, 1H), 7.45 – 7.42 (m, 1H), 7.38 – 7.34 (m, 1H), 7.24 – 7.20 (m, 1 H), 7.02 – 7.00 (m, 1H), 6.95 – 6.92 (m, 3H), 6.87 – 6.85 (m, 1H), 6.08 (s, 1H), 5.55 (s, 1H), 4.08 – 4.03 (m, 1H), 3.87 – 3.79 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

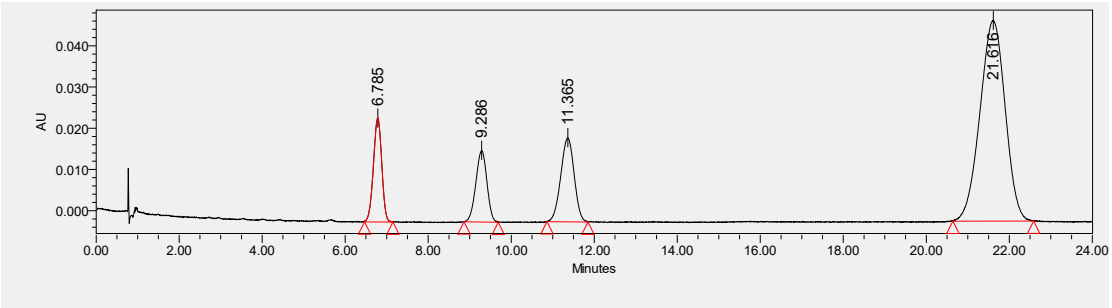
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.1, 169.9, 144.7, 139.0, 137.8, 136.7, 136.2, 135.0, 133.3, 130.7, 130.6, 130.2, 129.0, 128.9, 128.8, 128.6, 128.0, 127.7, 127.2, 126.8, 126.0, 121.4, 73.0, 64.0, 52.7, 13.4.

ESI-HRMS: calcd for $C_{28}H_{23}NO_5S_2Na^+$ ($[M + Na]^+$) = 540.0910, found 540.0908.

IR (neat): 3266, 1735, 1637, 1411, 1298, 1239, 1170, 1035, 853, 753, 728 cm^{-1}.

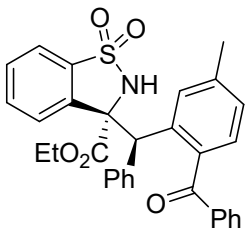


	Retention Time	Area	% Area
1	6.727	414066	20.09
2	9.214	618356	30.00
3	11.313	414835	20.13
4	21.533	613852	29.78



	Retention Time	Area	% Area
1	6.785	361423	10.88
2	9.286	335219	10.09
3	11.365	466392	14.04
4	21.616	2158189	64.98

ethyl (*S*)-3-((*R*)-(2-benzoyl-5-methylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C23)



C23

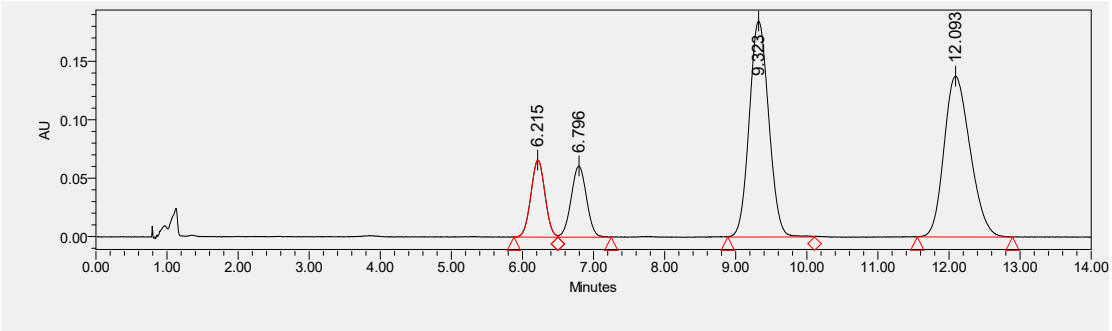
White solid; mp: 94-96 ℃; 86% yield, 88:12 dr (determined by ^{1}H NMR), 77%/37% ee. $[\alpha]_{589}^{18}$ = -113.4 (c = 0.77, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.22 min, t_{R2} = 6.79 min, t_{R3} = 9.33 min, t_{R4} = 11.98 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.56 – 7.53 (m, 3H), 7.49 – 7.44 (m, 2H), 7.31 – 7.28 (m, 2H), 7.21 – 7.19 (m, 1H), 7.13 -7.12 (m, 1H), 7.02 – 7.01 (m, 2H), 6.97 – 6.92 (m, 3H), 6.08 (s, 1H), 5.62 (s, 1H), 4.10 – 4.04 (m, 1H), 3.89 – 3.83 (m, 1H), 2.49 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

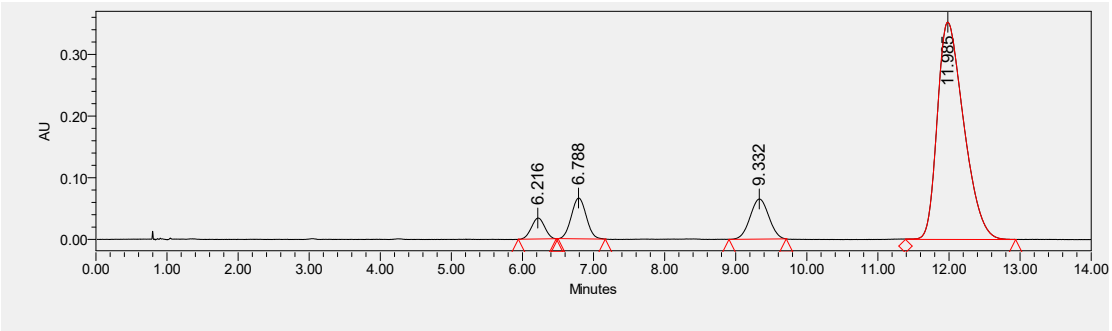
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.9, 141.07, 138.4, 138.0, 136.7, 136.2, 136.2, 135.0, 133.2, 133.0, 130.5, 130.2, 130.1, 129.9, 129.6, 128.1, 127.7, 127.2, 127.1, 126.0, 121.3, 73.0, 63.9, 52.1, 21.9, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1502.

IR (neat): 3263, 1735, 1658, 1450, 1310, 1241, 1171, 1035, 907, 711 cm^{-1}.

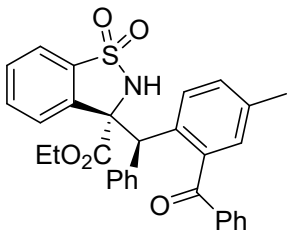


	Retention Time	Area	% Area
1	6.215	906273	10.25
2	6.796	913093	10.33
3	9.323	3517090	39.78
4	12.093	3504915	39.64



	Retention Time	Area	% Area
1	6.216	443198	3.79
2	6.788	963123	8.24
3	9.332	1190455	10.18
4	11.985	9093158	77.79

ethyl (*S*)-3-((*R*)-(2-benzoyl-4-methylphenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C24)



C24

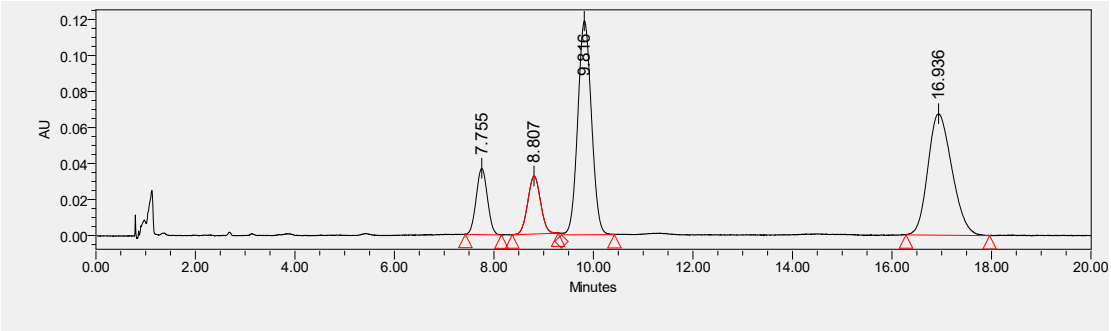
White solid; mp: 210-214 °C; 98% yield, 87:13 dr (determined by ^{1}H NMR), 91%/68% ee. $[\alpha]_{589}^{19}$ = -136.6 (c = 0.87, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.73 min, t_{R2} = 8.78 min, t_{R3} = 9.81 min, t_{R4} = 16.69 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.50 (m, 3H), 7.48 – 7.43 (m, 2H), 7.37 – 7.35 (m, 1H), 7.29 – 7.26 (m, 2H), 7.10 – 7.07 (m, 1H), 6.96 – 6.87 (m, 5H), 6.06 (s, 1H), 5.43 (s, 1H), 4.11 – 4.06 (m, 1H), 3.92 – 3.86 (m, 1H), 2.33 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

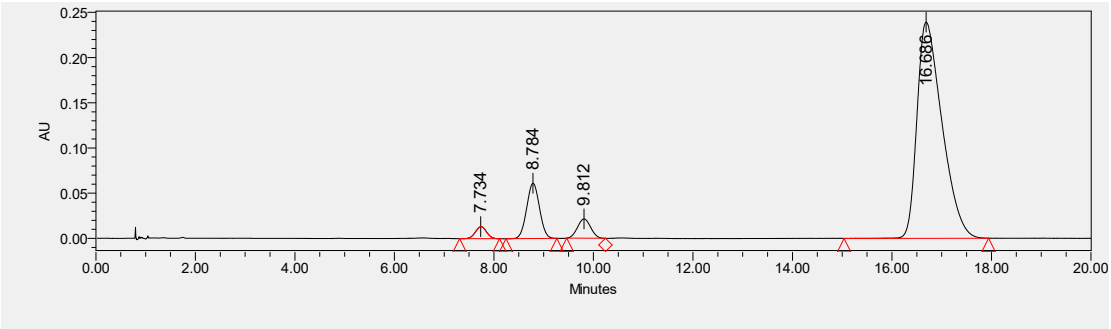
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.5, 169.9, 139.2, 137.6, 136.7, 136.5, 136.2, 135.0, 134.9, 133.2, 133.1, 131.2, 130.4, 130.1, 130.1, 129.6, 128.8, 128.1, 127.6, 127.0, 125.9, 121.3, 73.0, 64.0, 52.5, 20.9, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1501.

IR (neat): 3264, 1734, 1661, 1450, 1312, 1240, 1172, 1034, 857, 716 cm^{-1}.

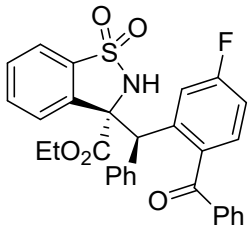


	Retention Time	Area	% Area
1	7.755	574970	10.13
2	8.807	573838	10.11
3	9.816	2263673	39.89
4	16.936	2262097	39.86



	Retention Time	Area	% Area
1	7.734	208221	2.07
2	8.784	1092445	10.88
3	9.812	391689	3.90
4	16.686	8352276	83.15

ethyl (*S*)-3-((*R*)-(2-benzoyl-5-fluorophenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C25)



C25

White solid; mp: 93-97 °C; 88% yield, 88:12 dr (determined by ^{1}H NMR), 93%/68% ee. $[\alpha]_{589}^{18}$ = -129.3 (c = 0.92, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.45 min, t_{R2} = 6.83 min, t_{R3} = 7.71 min, t_{R4} = 15.56 min.

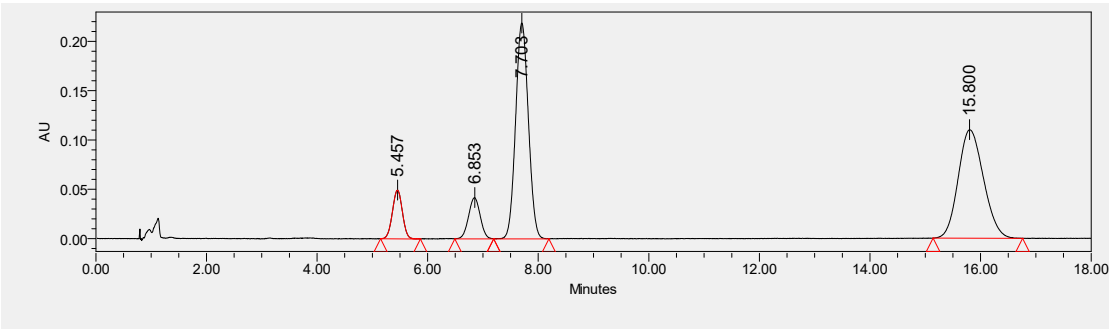
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.54 – 7.52 (m, 3H), 7.52 – 7.49 (m, 1H), 7.47 – 7.44 (m, 1H), 7.32 – 7.29 (m, 3H), 7.04 – 6.93 (m, 6H), 6.08 (s, 1H), 5.61 (s, 1H), 4.13 – 4.08 (m, 1H), 3.93 – 3.87 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.2, 169.6, 163.5 (d, *J* = 252.6 Hz), 141.5 (d, *J* = 7.7 Hz), 137.6, 136.3, 135.5, 135.1 (d, *J* = 3.0 Hz), 135.0, 133.3, 133.3, 131.7 (d, *J* = 8.9 Hz), 130.6, 130.1, 130.0, 128.3, 127.8, 127.4, 125.8, 121.4, 116.6 (d, *J* = 23.1 Hz), 113.7 (d, *J* = 21.6 Hz), 72.8, 64.2, 52.1, 13.4.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -106.77.

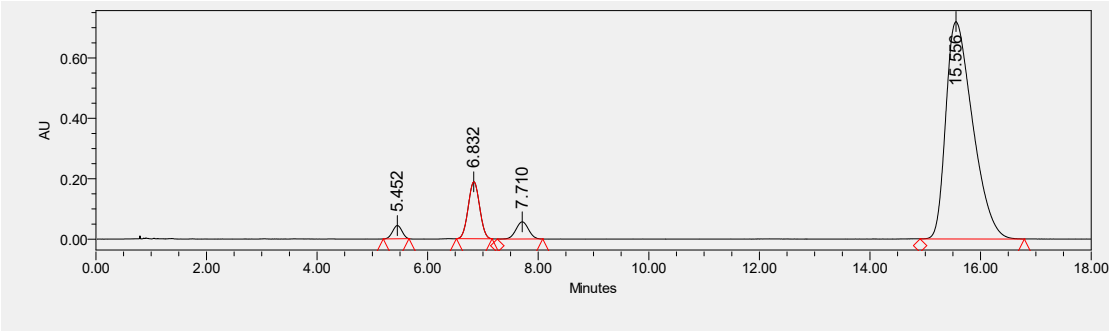
ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1250.

IR (neat): 3259, 1735, 1661, 1585, 1313, 1244, 1171, 1034, 857, 712 cm^{-1}.



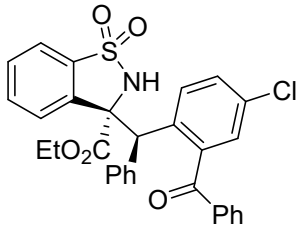
	Retention Time	Area	% Area
1	5.457	621094	7.53
2	6.853	614469	7.45
3	7.703	3511787	42.59

4	15.800	3498150	42.42



	Retention Time	Area	% Area
1	5.452	516499	1.82
2	6.832	2705940	9.55
3	7.710	895637	3.16
4	15.556	24221754	85.47

ethyl (*S*)-3-((*R*)-(2-benzoyl-4-chlorophenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C26)



C26

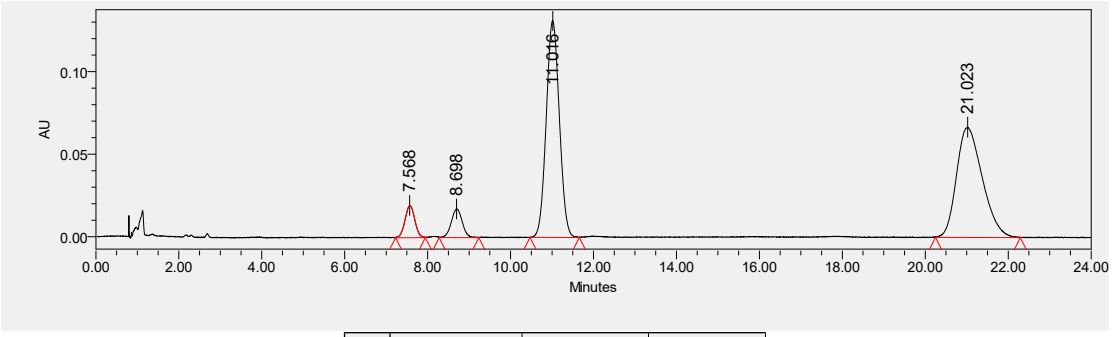
White solid; mp: 134-138 °C; 99% yield, 94:6 dr (determined by ^{1}H NMR), 95%/56% ee. $[\alpha]_{589}^{19}$ = -175.1 (c = 1.02, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.55 min, t_{R2} = 8.68 min, t_{R3} =10.99 min, t_{R4} = 20.42 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.53 – 7.48 (m, 4H), 7.47 – 7.44 (m, 1H), 7.33 – 7.28 (m, 3H), 7.24 – 7.23 (m, 1H), 6.98 – 6.92 (m, 5H), 6.12 (s, 1H), 5.51 (s, 1H), 4.15 – 4.10 (m, 1H), 3.95 – 3.90 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

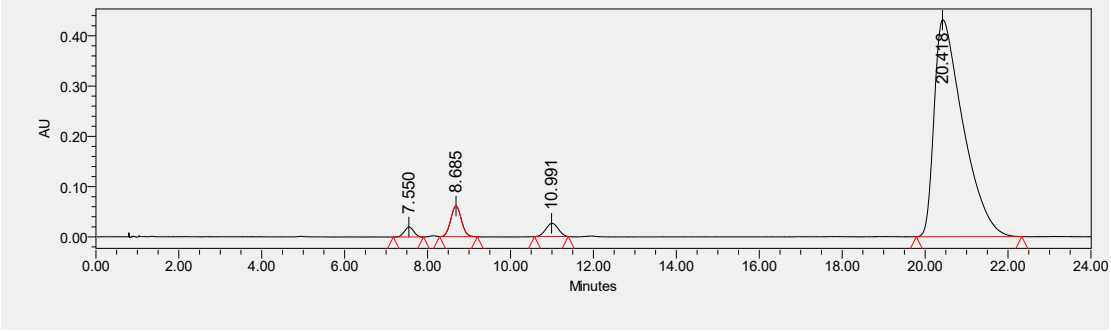
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.2, 169.6, 140.3, 137.5, 137.2, 136.7, 136.4, 135.2, 135.0, 133.4, 133.3, 130.6, 130.6, 130.2, 130.0, 129.1, 128.3, 127.8, 127.4, 126.9, 125.8, 121.4, 72.7, 64.2, 52.3, 13.4.

ESI-HRMS: calcd for $C_{30}H_{24}{}^{35}ClNO_5SNa^+$ ([M + Na]$^+$) = 568.0956, found 568.0956. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 570.0926, found 570.0932.

IR (neat): 3254, 1734, 1662, 1588, 1450, 1312, 1241, 1170, 931, 757, 711 cm^{-1}.

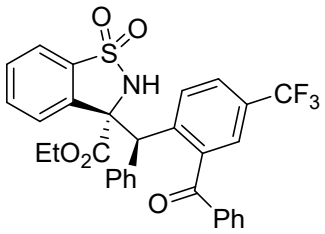


	Retention Time	Area	% Area
1	7.568	319437	4.99
2	8.698	319120	4.98
3	11.016	2884336	45.04
4	21.023	2881324	44.99



	Retention Time	Area	% Area
1	7.550	309328	1.35
2	8.685	1092140	4.78
3	10.991	550653	2.41
4	20.418	20880917	91.45

ethyl (*S*)-3-((*R*)-(2-benzoyl-4-(trifluoromethyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C27)



C27

White solid; mp: 70-74 ℃; 94% yield, 89:11 dr (determined by ^{1}H NMR), 88%/26% ee. $[\alpha]_{589}^{17}$ = -140.2 (c = 1.02, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm), retention time: t_{R1} = 4.13 min, t_{R2} = 4.58 min, t_{R3} = 6.10 min, t_{R4} = 7.98 min.

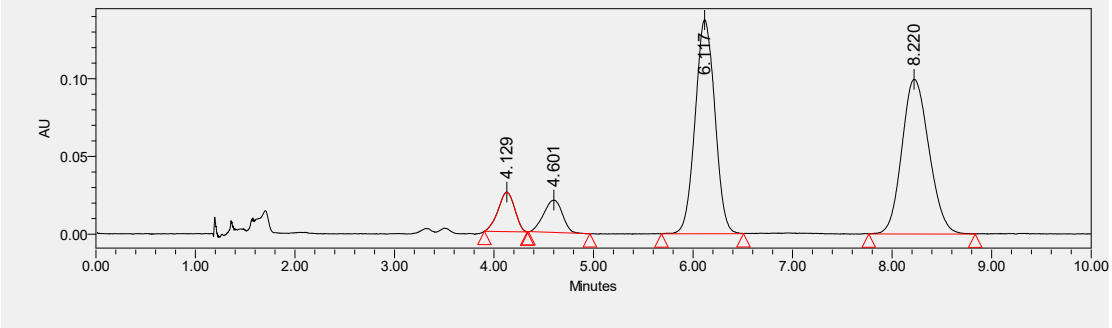
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.53 – 7.51 (m, 1H), 7.49 – 7.44 (m, 4H), 7.40 – 7.39 (m, 1H), 7.26 – 7.22 (m, 2H), 6.96 – 6.94 (m, 1H), 6.90 – 6.87 (m, 2H), 6.79 – 6.78 (m, 2H), 6.18 (s, 1H), 5.40 (s, 1H), 4.16 – 4.11 (m, 1H), 4.03 – 3.98 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.1, 169.5, 143.0, 139.0, 136.5, 135.1, 134.6, 133.7, 133.4, 132.1 (q, *J* = 32.6 Hz), 130.7, 130.3, 130.0, 129.0, 128.3, 127.8, 127.5, 125.6, 125.1 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 3.5 Hz), 123.5 (q, *J* = 272.9 Hz), 121.5, 72.7, 64.3, 53.3, 13.4.

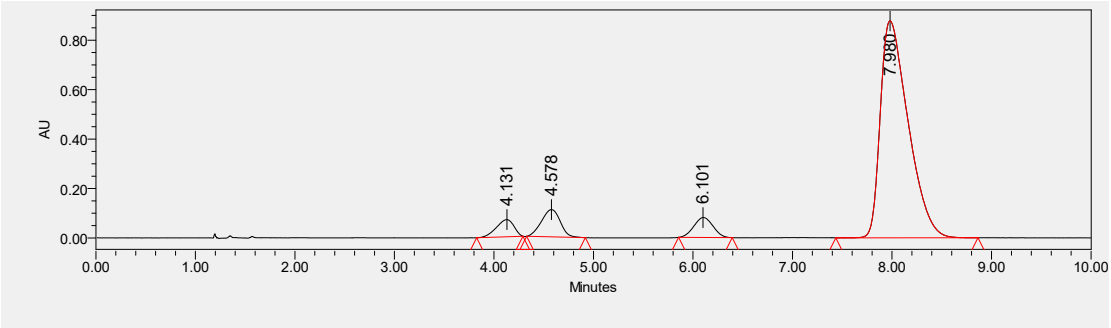
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -62.77.

ESI-HRMS: calcd for $C_{31}H_{24}F_3NO_5SNa^+$ ([M + Na]$^+$) = 602.1219, found 602.1219.

IR (neat): 3257, 1735, 1666, 1329, 1242, 1170, 1130, 1073, 936, 852, 711 cm^{-1}.

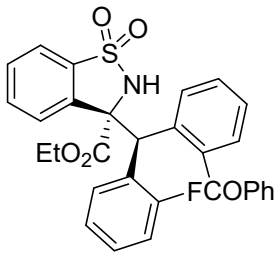


	Retention Time	Area	% Area
1	4.129	293211	6.74
2	4.601	272220	6.26
3	6.117	1896545	43.62
4	8.220	1885812	43.37



	Retention Time	Area	% Area
1	4.131	853006	4.18
2	4.578	1456168	7.13
3	6.101	1082516	5.30
4	7.980	17031873	83.39

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(2-fluorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C28)



C28

White solid; mp: 73-77 °C; 82% yield, 41:59 dr (determined by ^{1}H NMR), 65%/55% ee. $[\alpha]_{589}^{20}$ = -48.2 (c = 0.83, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.65 min, t_{R2} = 9.52 min, t_{R3} = 13.02 min, t_{R4} = 26.40 min.

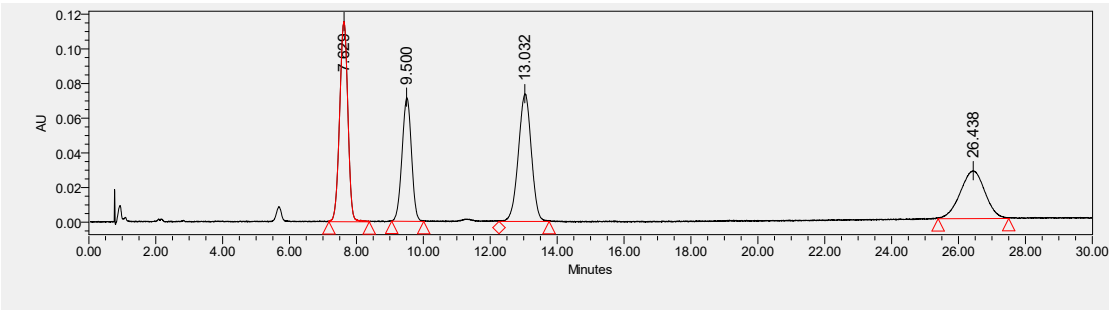
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.71 – 7.67 (m, 1H), 7.50 – 7.42 (m, 4H), 7.39 – 7.34 (m, 3H), 7.29 – 7.27 (m, 2H), 7.14 – 7.11 (m, 2H), 7.07 – 7.05 (m, 1H), 6.95 – 6.92 (m, 1H), 6.86 – 6.81 (m, 1H), 6.18 (s, 1H), 5.94 (s, 1H), 4.11 – 4.05 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 169.6, 160.0 (d, *J* = 248.5 Hz), 139.0, 137.1, 136.9, 135.5, 135.1, 134.8, 133.2, 133.0, 131.1, 130.7, 130.4, 130.2, 129.3 (d, *J* = 8.7 Hz), 128.6, 128.0, 127.1, 126.4, 124.2 (d, *J* = 3.5 Hz), 120.9, 115.4 (d, *J* = 23.4 Hz), 72.3, 63.9, 44.6, 13.5.

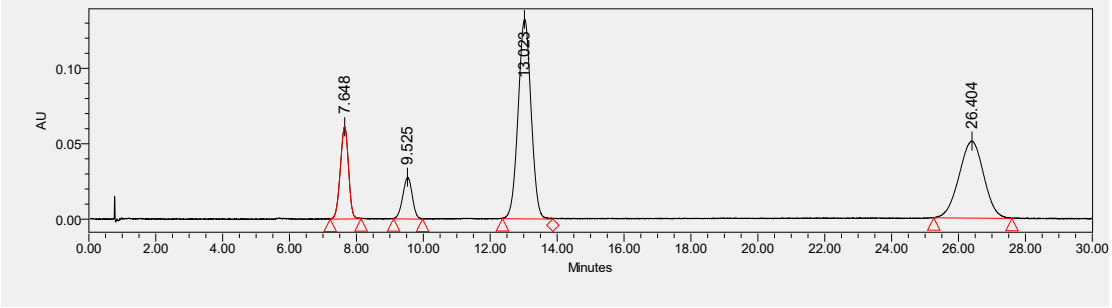
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -115.16.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1251.

IR (neat): 3263, 1736, 1663, 1451, 1313, 1243, 1172, 1027, 931, 758, 708 cm^{-1}.

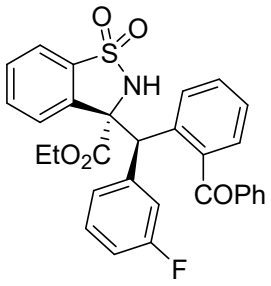


	Retention Time	Area	% Area
1	7.629	1967874	29.08
2	9.500	1396717	20.64
3	13.032	1984669	29.33
4	26.438	1416767	20.94



	Retention Time	Area	% Area
1	7.648	1040985	13.40
2	9.525	547192	7.04
3	13.023	3552502	45.72
4	26.404	2629178	33.84

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(3-fluorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C29)



C29

White solid; mp: 76-79 °C; 98% yield, 80:20 dr (determined by ^{1}H NMR), 91%/73% ee. $[\alpha]_{589}^{19}$ = -133.9 (c = 0.90, in CH_2Cl_2), dissolved in MeOH for **HPLC** (Chiralcel **IF**, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm), retention time: t_{R1} = 20.28 min, t_{R2} = 28.42 min, t_{R3} = 30.58 min, t_{R4} = 42.60 min.

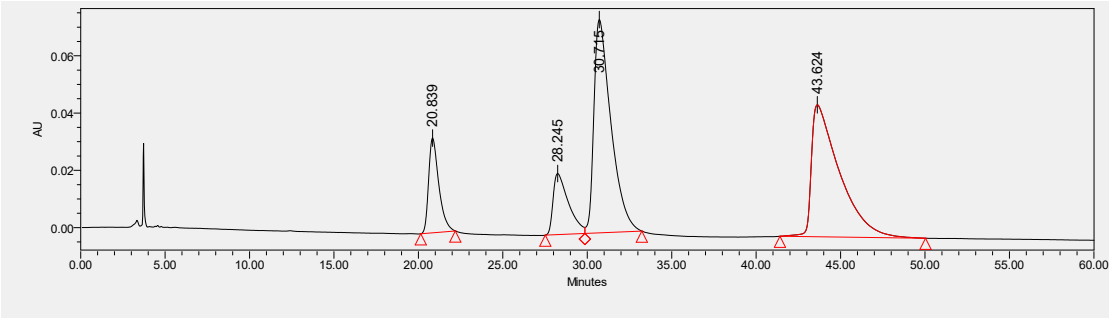
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.58 – 7.52 (m, 4H), 7.50 – 7.46 (m, 2H), 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 4H), 6.87 – 6.82 (m, 1H), 6.68 – 6.66 (m, 2H), 6.10 (s, 1H), 5.49 (s, 1H), 4.10 – 4.05 (m, 1H), 3.94 – 3.86 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 169.6, 162.0 (d, *J* = 246.0), 139.2, 138.3 (d, *J* = 7.5), 137.5, 137.4, 136.5, 135.1, 133.4, 133.3, 130.7, 130.7, 130.0, 129.3, 128.9 (d, *J* =8.4), 128.6, 128.2, 126.9, 125.8 (d, *J* = 2.7), 125.6, 121.5, 117.4 (d, *J* = 25.8), 114.1 (d, *J* = 21.0), 72.7, 64.2, 52.4, 13.3.

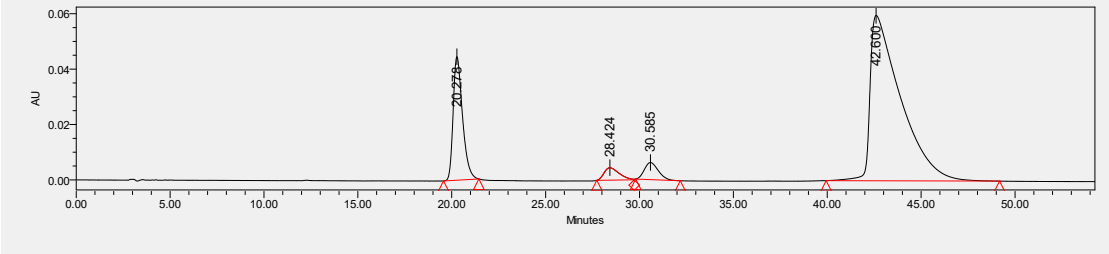
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -113.49.

ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ([M + Na]$^+$) = 552.1251, found 552.1259.

IR (neat): 3262, 1736, 1660, 1590, 1449, 1313, 1244, 1172, 929, 759, 711 cm^{-1}.

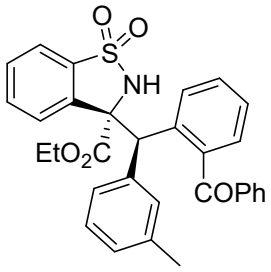


	Retention Time	Area	% Area
1	20.839	1388118	10.43
2	28.245	1350024	10.15
3	30.715	5249188	39.46
4	43.624	5315591	39.96



	Retention Time	Area	% Area
1	20.278	1548116	17.47
2	28.424	249344	2.81
3	30.585	318770	3.60
4	42.600	6746702	76.12

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(m-tolyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C30)



C30

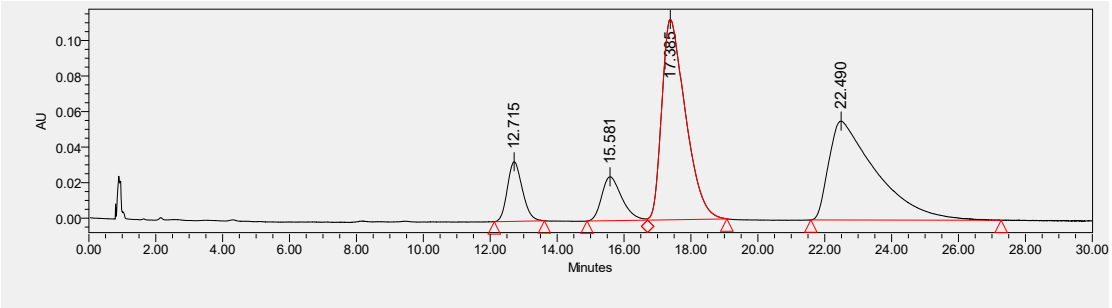
White solid; mp: 67-70 °C; 92% yield, 91:9 dr (determined by ^{1}H NMR), 91%/56% ee. $[\alpha]_{589}^{18}$ = -123.9 (c = 0.92, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 12.66 min, t_{R2} = 15.51 min, t_{R3} = 17.69 min, t_{R4} = 22.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.52 (m, 5H), 7.50 – 7.42 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.28 (m, 3H), 6.81 – 6.80 (m, 2H), 6.75 – 6.73 (m, 1H), 6.69 (s, 1H), 6.04 (s, 1H), 5.45 (s, 1H), 4.11 – 4.03 (m, 1H), 3.92 – 3.84 (m, 1H), 1.99 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

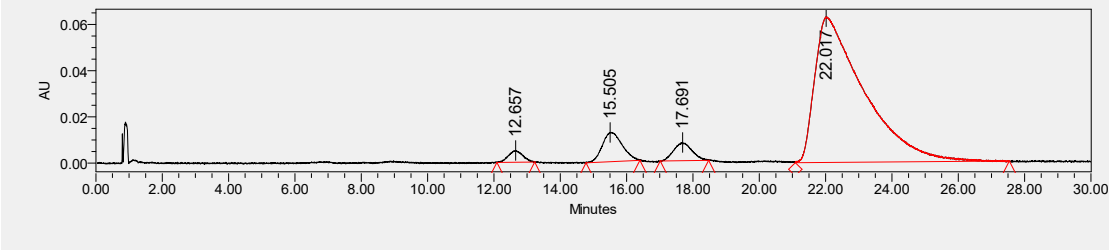
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 169.8, 139.2, 138.0, 137.5, 137.1, 136.7, 135.8, 135.0, 133.1, 133.1, 131.0, 130.5, 130.4, 130.1, 129.1, 128.9, 128.1, 127.8, 127.5, 127.2, 126.6, 125.9, 121.3, 72.9, 64.0, 52.5, 21.1, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1501.

IR (neat): 3266, 1735, 1661, 1312, 1243, 1172, 930, 761, 711 cm^{-1}.

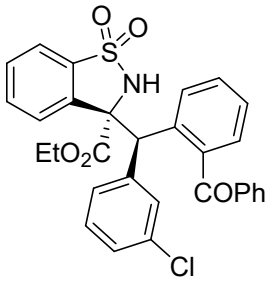


	Retention Time	Area	% Area
1	12.715	1041907	7.95
2	15.581	1029053	7.85
3	17.385	5529396	42.20
4	22.490	5502292	41.99



	Retention Time	Area	% Area
1	12.657	150542	2.02
2	15.505	529289	7.11
3	17.691	301123	4.05
4	22.017	6463286	86.82

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(3-chlorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C31)



C31

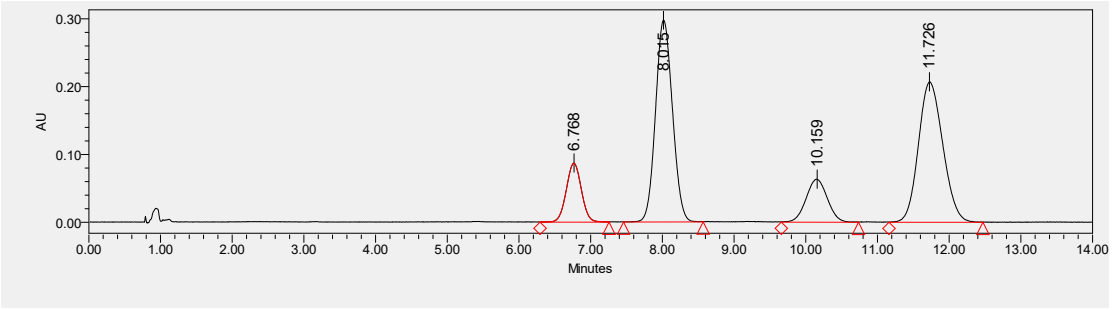
White solid; mp: 75-79 °C; 95% yield, 81:19 dr (determined by ^{1}H NMR), 88%/56% ee. $[\alpha]_{589}^{18}$ = -130.8 (c = 0.93, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.76 min, t_{R2} = 8.03 min, t_{R3} = 10.13 min, t_{R4} = 11.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.58 – 7.51 (m, 4H), 7.51 – 7.46 (m, 2H), 7.39 – 7.35 (m, 1H), 7.33 – 7.27 (m, 4H), 6.93 – 6.91 (m, 1H), 6.85 (s, 2H), 6.11 (s, 1H), 5.43 (s, 1H), 4.11 – 4.04 (m, 1H), 3.94 – 3.86 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

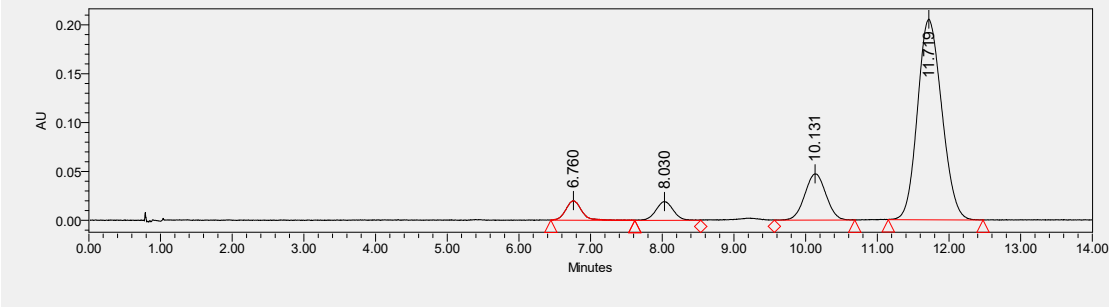
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 169.5, 139.2, 137.8, 137.4, 137.3, 136.3, 135.1, 133.4, 133.4, 133.4, 130.7, 130.7, 130.5, 130.0, 129.3, 128.8, 128.6, 128.2, 127.3, 127.0, 125.6, 121.5, 72.7, 64.2, 52.4, 13.4.

ESI-HRMS: calcd for $C_{30}H_{24}{}^{35}ClNO_5SNa^+$ ([M + Na]$^+$) = 568.0956, found 568.0961. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 570.0926, found 570.0937.

IR (neat): 3261, 1736, 1660, 1313, 1245, 1171, 1031, 931, 762, 712 cm^{-1}.

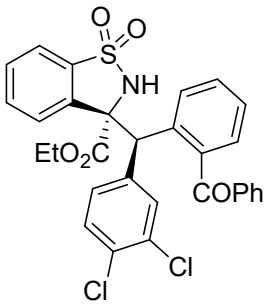


	Retention Time	Area	% Area
1	6.768	1273720	10.31
2	8.015	4883826	39.53
3	10.159	1307420	10.58
4	11.726	4890926	39.58



	Retention Time	Area	% Area
1	6.760	264015	4.16
2	8.030	309405	4.87
3	10.131	951005	14.97
4	11.719	4827109	76.00

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(3,4-dichlorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C32)



C32

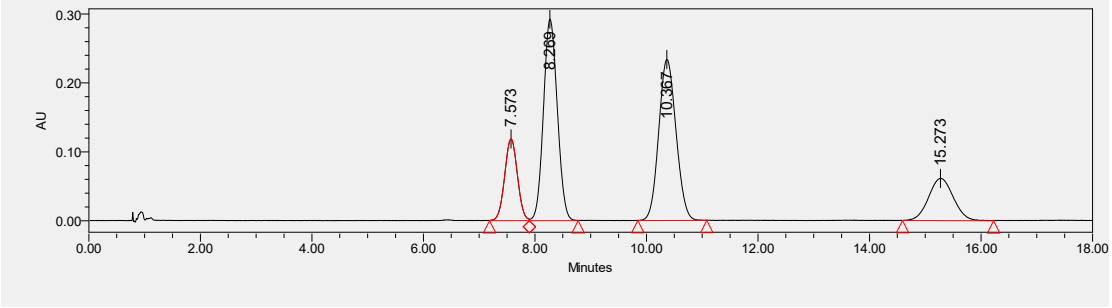
White solid; mp: 81-84 °C; 96% yield, 78:22 dr (determined by ^{1}H NMR), 85%/47% ee. $[\alpha]_{589}^{18}$ = -104.1 (c = 1.11, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.54 min, t_{R2} = 8.24 min, t_{R3} = 10.31 min, t_{R4} = 15.22 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.50 (m, 6H), 7.38 – 7.30 (m, 5H), 6.98 – 6.96 (m, 2H), 6.88 – 6.85 (m, 1H), 6.11 (s, 1H), 5.43 (s, 1H), 4.11 – 4.05 (m, 1H), 3.92 – 3.84 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H).

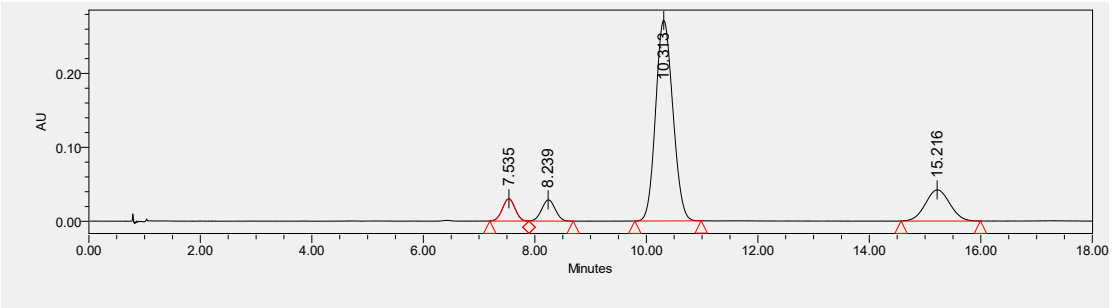
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.0, 169.4, 139.1, 137.3, 137.2, 136.3, 136.1, 135.1, 133.6, 133.5, 132.3, 131.6, 131.4, 130.9, 130.8, 130.0, 129.5, 129.5, 129.4, 128.5, 128.3, 127.1, 125.5, 121.7, 72.5, 64.3, 51.8, 13.3

ESI-HRMS: calcd for $C_{30}H_{23}{}^{35}Cl_2NO_5SNa^+$ ([M + Na]$^+$) = 602.0566, found 602.0571. $C_{30}H_{23}{}^{35}Cl^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 604.0537, found 604.0540. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 606.0507, found 606.0515.

IR (neat): 3261, 1737, 1661, 1470, 1314, 1246, 1172, 1031, 931, 765, 712 cm^{-1}.

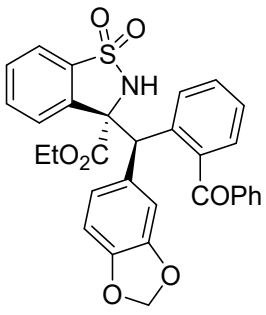


	Retention Time	Area	% Area
1	7.573	1815236	13.32
2	8.269	5003270	36.70
3	10.367	4991470	36.61
4	15.274	1822836	13.37



	Retention Time	Area	% Area
1	7.535	467029	5.81
2	8.239	462636	5.75
3	10.313	5821847	72.41
4	15.216	1289087	16.03

ethyl (*S*)-3-((*R*)-benzo[d][1,3]dioxol-5-yl(2-benzoylphenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C33)



C33

White solid; mp: 96-99 °C; 64% yield, 92:8 dr (determined by ^{1}H NMR), 91%/39% ee. $[\alpha]_{589}^{19}$= -118.2 (c = 0.66, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH =

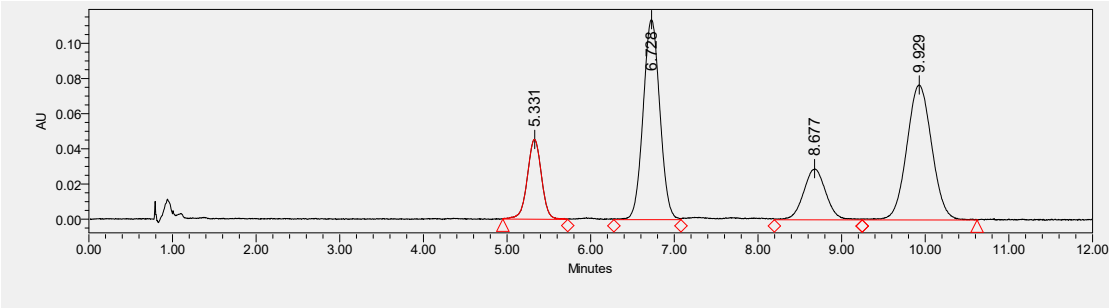
80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.31 min, t_{R2} = 6.71 min, t_{R3} = 8.64 min, t_{R4} = 9.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.58 – 7.52 (m, 4H), 7.51 – 7.46 (m, 2H), 7.35 – 7.27 (m, 4H), 6.53 (d, *J* = 1.6 Hz, 1H), 6.28 – 6.22 (m, 2H), 6.08 (s, 1H), 5.73 (s, 2H), 5.43 (s, 1H), 4.11 – 4.03 (m, 1H), 3.95 – 3.87 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

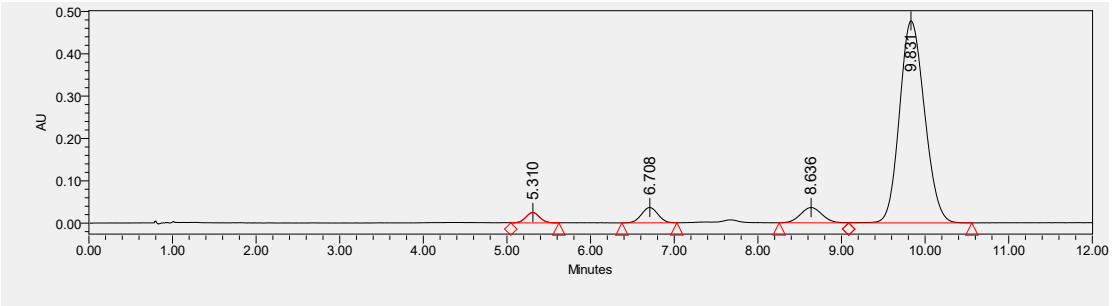
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 169.9, 147.1, 146.5, 139.2, 138.4, 137.5, 136.9, 135.2, 133.4, 133.2, 130.6, 130.6, 130.1, 129.6, 129.2, 128.4, 128.2, 126.7, 125.8, 124.1, 121.5, 110.9, 107.3, 100.8, 73.0, 64.1, 52.4, 13.4.

ESI-HRMS: calcd for $C_{31}H_{25}NO_7SNa^+$ ([M + Na]$^+$) = 578.1244, found 578.1246.

IR (neat): 3262, 1735, 1661, 1487, 1446, 1313, 1246, 1172, 1038, 929, 760, 709 cm^{-1}.

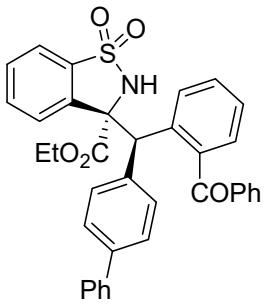


	Retention Time	Area	% Area
1	5.331	534962	12.60
2	6.728	1577544	37.15
3	8.677	538188	12.67
4	9.929	1595821	37.58



	Retention Time	Area	% Area
1	5.310	266915	2.37
2	6.708	465138	4.14
3	8.636	612004	5.44
4	9.831	9899508	88.05

ethyl (*S*)-3-((*R*)-[1,1'-biphenyl]-4-yl(2-benzoylphenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C34)



C34

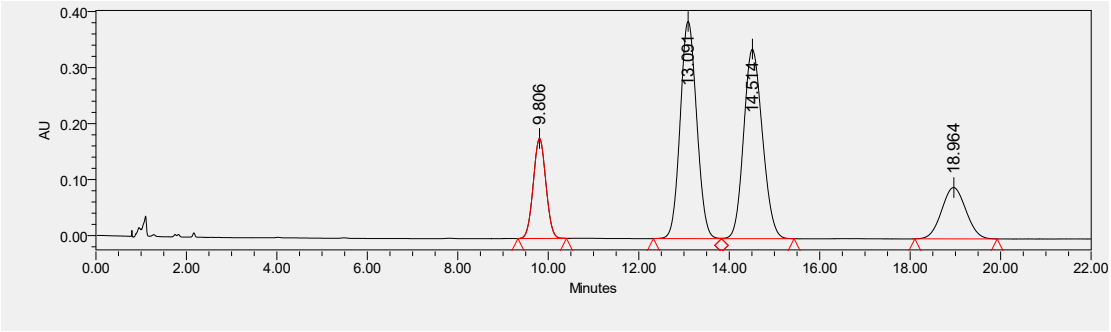
White solid; mp: 103-107 °C; 78% yield, 87:13 dr (determined by ^{1}H NMR), 88%/35% ee. $[\alpha]_{589}^{17}$ = -68.6 (c = 0.91, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 9.87 min, t_{R2} = 13.20 min, t_{R3} = 14.62 min, t_{R4} = 19.26 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.55 (m, 5H), 7.50 – 7.46 (m, 2H), 7.39 – 7.37 (m, 2H), 7.35 – 7.27 (m, 7H), 7.16 – 7.15 (m, 2H), 7.07 – 7.06 (m, 2H), 6.10 (s, 1H), 5.59 (s, 1H), 4.10 – 4.05 (m, 1H), 3.91 – 3.85 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

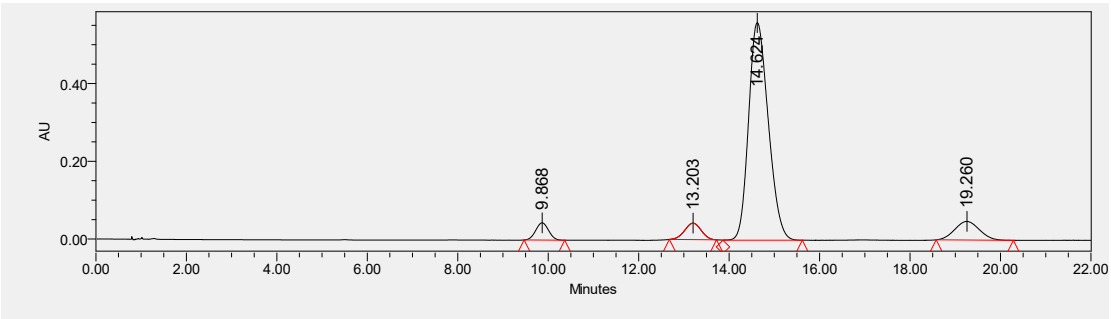
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.8, 140.4, 139.6, 139.1, 138.0, 137.5, 136.5, 135.2, 135.0, 133.3, 133.2, 130.6, 130.6, 130.5, 130.1, 129.3, 128.9, 128.5, 128.2, 127.0, 126.8, 126.7, 126.3, 125.9, 121.5, 72.9, 64.0, 52.2, 13.4.

ESI-HRMS: calcd for $C_{36}H_{29}NO_5SNa^+$ ([M + Na]$^+$) = 610.1659, found 610.1664.

IR (neat): 3267, 1736, 1661, 1449, 1314, 1244, 1171, 930, 761, 703 cm^{-1}.

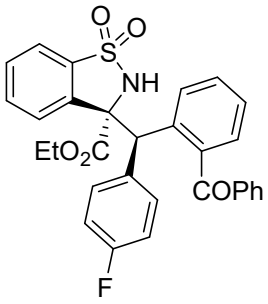


	Retention Time	Area	% Area
1	9.806	3454104	13.06
2	13.091	9823452	37.13
3	14.514	9755795	36.87
4	18.964	3423436	12.94



	Retention Time	Area	% Area
1	9.868	878640	4.25
2	13.203	1083226	5.23
3	14.624	16924538	81.78
4	19.260	1807835	8.74

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(4-fluorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C35)



C35

White solid; mp: 71-75 ℃; 94% yield, 79:21 dr (determined by ^{1}H NMR), 88%/51% ee. $[\alpha]_{589}^{17}$ = -125.7 (c = 0.92, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 12.61 min, t_{R2} = 15.16 min, t_{R3} = 17.40 min, t_{R4} = 19.88 min.

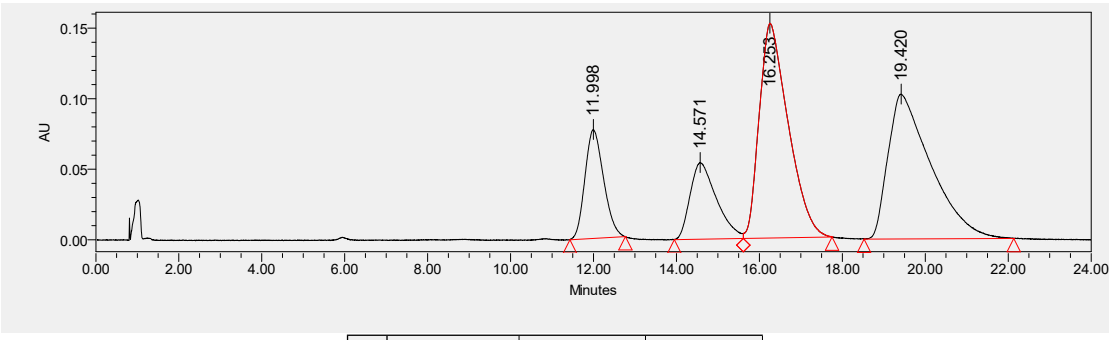
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.58 – 7.54 (m, 2H), 7.52 – 7.47 (m, 4H), 7.36 – 7.34 (m, 1H), 7.30 – 7.27 (m, 3H), 6.90 – 6.88 (m, 2H), 6.60 – 6.57 (m, 2H), 6.13 (s, 1H), 5.50 (s, 1H), 4.11 – 4.04 (m, 1H), 3.93 – 3.88 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.7, 161.8 (d, *J* = 246.6), 139.1, 138.0, 137.4, 136.6, 135.0, 133.4, 133.3, 131.9 (d, *J* = 8.5), 130.8, 130.6, 130.6, 130.0, 129.3, 128.4, 128.2, 126.7, 125.7, 121.5, 114.5 (d, *J* = 21.4), 72.9, 64.1, 52.0, 13.4.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -115.04.

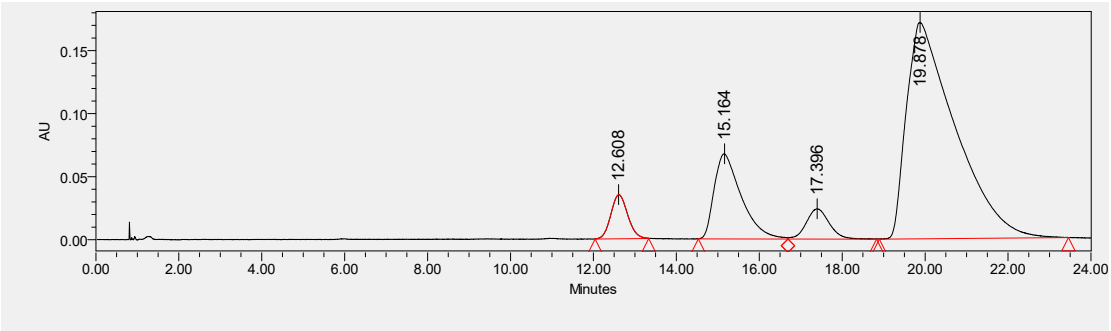
ESI-HRMS: calcd for $C_{30}H_{24}FNO_5SNa^+$ ($[M + Na]^+$) = 552.1251, found 552.1252.

IR (neat): 3264, 1736, 1661, 1508, 1313, 1234, 1170, 1031, 930, 762, 707 cm^{-1}.



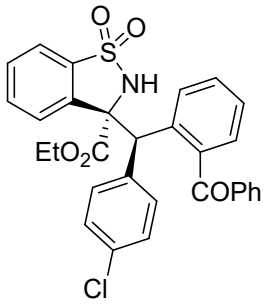
	Retention Time	Area	% Area
1	11.998	2413326	12.36

2	14.571	2401714	12.30
3	16.253	7371012	37.74
4	19.420	7346331	37.61



	Retention Time	Area	% Area
1	12.608	983922	5.18
2	15.164	3054698	16.08
3	17.396	925970	4.88
4	19.878	14027036	73.86

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(4-chlorophenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C36)



C36

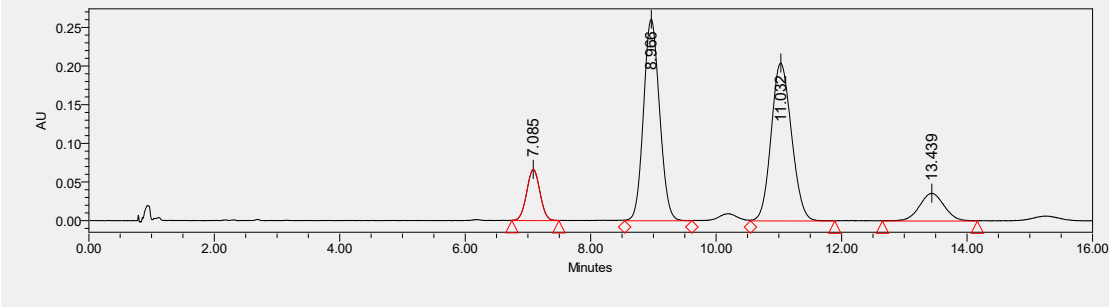
White solid; mp: 75-78 °C; 96% yield, 90:10 dr (determined by ^{1}H NMR), 94%/60% ee. $[\alpha]_{589}^{19}$ = -122.1 (c = 1.06, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 7.11 min, t_{R2} = 9.00 min, t_{R3} = 10.99 min, t_{R4} = 13.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.46 (m, 7H), 7.37 – 7.29 (m, 4H), 6.92 – 6.86 (m, 4H), 6.10 (s, 1H), 5.51 (s, 1H), 4.11 – 4.03 (m, 1H), 3.91 – 3.83 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H).

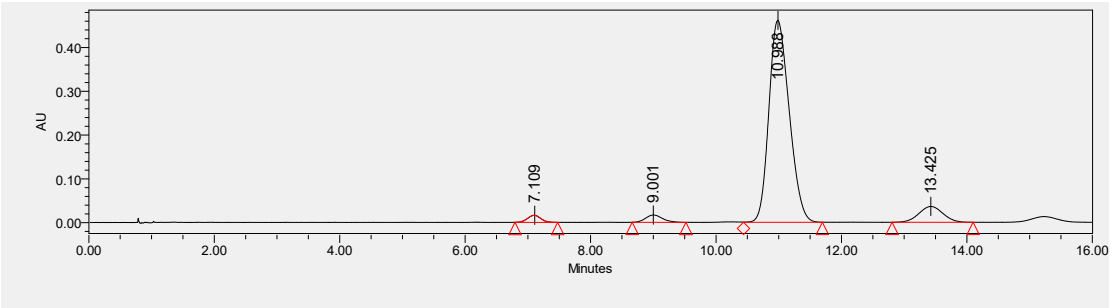
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1, 169.6, 139.0, 137.8, 137.4, 136.4, 135.0, 134.6, 133.4, 133.3, 133.1, 131.5, 130.7, 130.1, 129.4, 128.6, 128.3, 127.8, 126.8, 125.7, 121.5, 72.7, 64.1, 51.9, 13.3.

ESI-HRMS: calcd for $C_{30}H_{24}{}^{35}ClNO_5SNa^+$ ([M + Na]$^+$) = 568.0956, found 568.0958. $C_{30}H_{24}{}^{37}ClNO_5SNa^+$ ([M + Na]$^+$) = 570.0926, found 570.0935.

IR (neat): 3262, 1735, 1661, 1586, 1490, 1373, 1313, 1242, 1171, 1017, 930, 853, 759, 709 cm^{-1}.

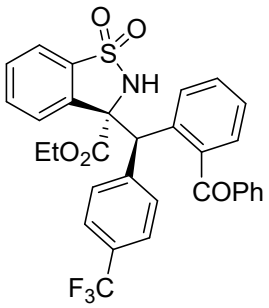


	Retention Time	Area	% Area
1	7.085	996155	8.84
2	8.966	4658761	41.35
3	11.032	4646336	41.24
4	13.439	964259	8.56



	Retention Time	Area	% Area
1	7.109	238893	2.00
2	9.001	318489	2.67
3	10.988	10385857	87.16
4	13.425	972067	8.16

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(4-(trifluoromethyl)phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C37)



C37

White solid; mp:78-80 ℃; 91% yield, 78:22 dr (determined by ^{1}H NMR), 87%/35% ee. $[\alpha]_{589}^{18}$ = -109.1 (c = 1.06, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **ID-3**, CO_2/MeOH =

95/5, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 13.02 min, t_{R2} = 14.99 min, t_{R3} = 18.51 min, t_{R4} = 20.26 min.

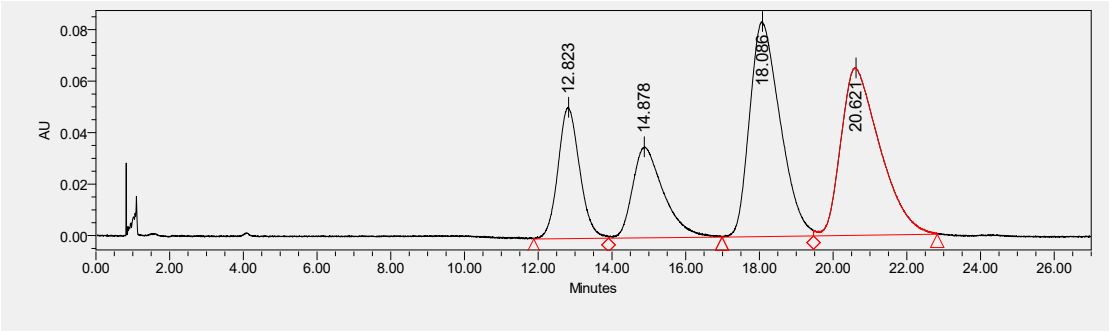
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.59 – 7.55 (m, 2H), 7.52 – 7.47 (m, 4H), 7.38 – 7.35 (m, 1H), 7.31 – 7.28 (m, 3H), 7.16 – 7.15 (m, 2H), 7.12 – 7.11 (m, 2H), 6.14 (s, 1H), 5.59 (s, 1H), 4.10 – 4.05 (m, 1H), 3.91 – 3.85 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.1, 169.5, 140.1, 139.1, 137.4, 137.3, 136.2, 135.0, 133.5, 133.4, 130.8, 130.8, 130.6, 130.4, 130.0, 129.4, 128.7, 128.2, 127.0, 125.6, 124.5 (q, *J* = 3.3 Hz), 123.9 (q, *J* = 272.0 Hz), 121.64, 72.55, 64.24, 52.26, 13.34.

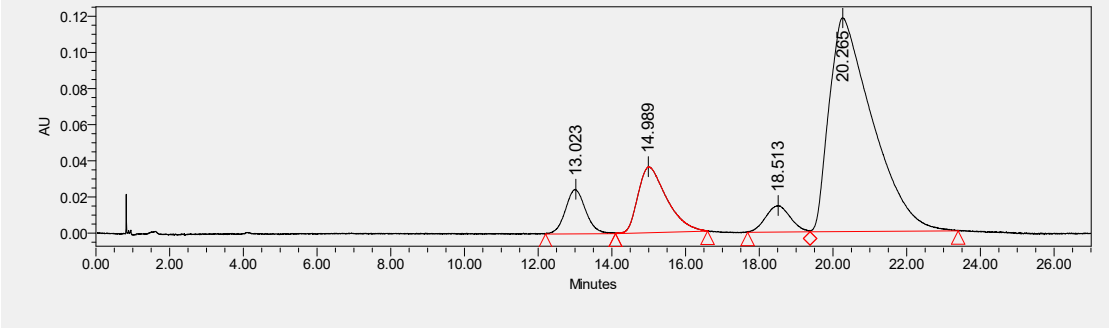
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -62.67.

ESI-HRMS: calcd for $C_{31}H_{24}F_3NO_5SNa^+$ ([M + Na]$^+$) = 602.1219, found 602.1221.

IR (neat):3261, 1736, 1660, 1450, 1323, 1240, 1166, 1119, 1069, 1020, 930, 856, 760, 736, 709 cm^{-1}.

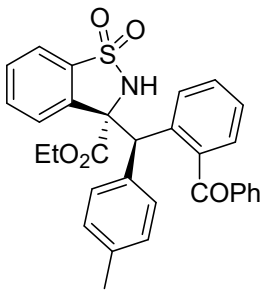


	Retention Time	Area	% Area
1	12.823	2083478	15.21
2	14.878	2059265	15.03
3	18.086	4790062	34.96
4	20.621	4768519	34.80



	Retention Time	Area	% Area
1	13.023	939959	7.10
2	14.989	1966348	14.86
3	18.513	679171	5.13
4	20.265	9647374	72.90

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(p-tolyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C38)



C38

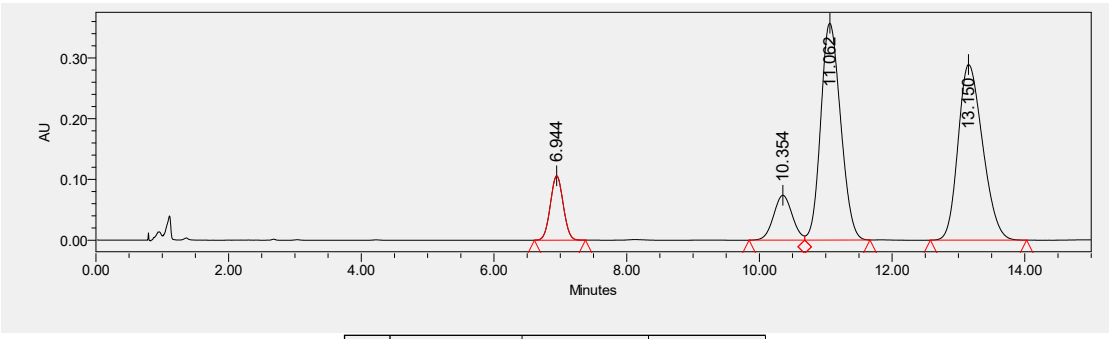
White solid; mp: 72-76 °C; 96% yield, 89:11 dr (determined by ^{1}H NMR), 89%/41% ee. $[\alpha]_{589}^{18}$ = -118.5 (c = 0.84, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.96 min, t_{R2} = 10.42 min, t_{R3} = 11.16 min, t_{R4} = 13.19 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.56 – 7.53 (m, 4H), 7.50 – 7.48 (m, 1H), 7.46 – 7.44 (m, 1H), 7.33 – 7.27 (m, 4H), 6.86 – 6.85 (m, 2H), 6.72 – 6.71 (m, 2H), 6.05 (s, 1H), 5.51 (s, 1H), 4.09 – 4.05 (m, 1H), 3.89 – 3.84 (m, 7.2 Hz, 1H), 2.07 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

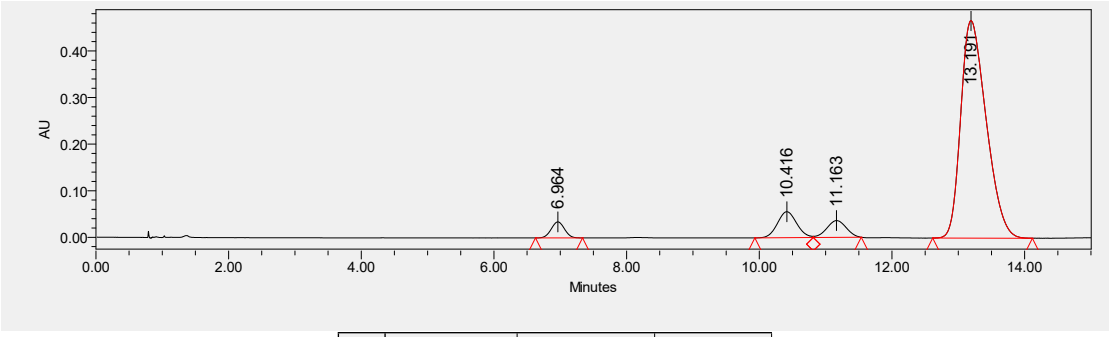
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.3, 169.9, 139.0, 138.4, 137.5, 136.7, 136.6, 134.9, 133.2, 133.1, 133.0, 130.5, 130.4, 130.1, 130.0, 129.3, 128.9, 128.4, 128.1, 126.5, 125.9, 121.3, 72.9, 63.9, 52.2, 20.9, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 548.1502, found 548.1501.

IR (neat): 3266, 1734, 1661, 1449, 1373, 1312, 1242, 1170, 1029, 930, 759, 707 cm^{-1}.

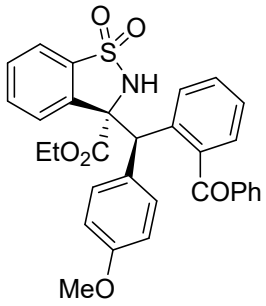


	Retention Time	Area	% Area
1	6.944	1427526	8.05
2	10.354	1442432	8.13
3	11.062	7434791	41.92
4	13.150	7429503	41.89



	Retention Time	Area	% Area
1	6.964	477260	3.23
2	10.416	1128193	7.63
3	11.163	733814	4.96
4	13.191	12446837	84.18

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(4-methoxyphenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole -3-carboxylate 1,1-dioxide (C39)



C39

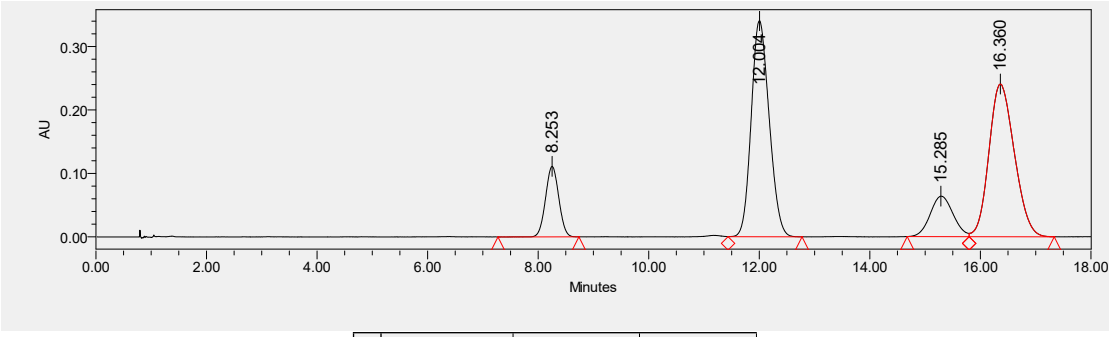
White solid; mp: 66-69 °C; 67% yield, 92:8 dr (determined by ^{1}H NMR), 84%/31% ee. $[\alpha]_{589}^{19}$= -102.6 (c = 0.72, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 8.32 min, t_{R2} = 12.16 min, t_{R3} = 15.57 min, t_{R4} = 16.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.52 (m, 4H), 7.50 – 7.44 (m, 2H), 7.32 – 7.27 (m, 4H), 6.87 – 6.84 (m, 2H), 6.45 – 6.42 (m, 2H), 6.05 (s, 1H), 5.47 (s, 1H), 4.11 – 4.03 (m, 1H), 3.92 – 3.84 (m, 1H), 3.58 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).

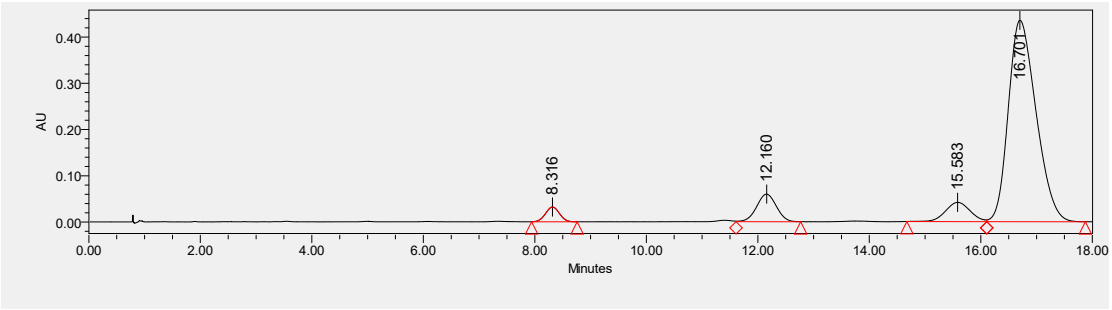
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 169.9, 158.4, 139.0, 138.5, 137.5, 136.8, 135.0, 133.2, 133.2, 131.3, 130.5, 130.4, 130.1, 129.2, 128.6, 128.2, 128.1, 126.5, 125.8, 121.4, 113.0, 73.1, 64.0, 54.9, 51.9, 13.4.

ESI-HRMS: calcd for $C_{31}H_{27}NO_6SNa^+$ ([M + Na]$^+$) = 564.1451, found 564.1453.

IR (neat): 3265, 1734, 1661, 1511, 1310, 1245, 1174, 1032, 930, 762, 707 cm^{-1}.

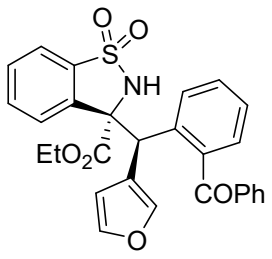


	Retention Time	Area	% Area
1	8.253	1849748	9.71
2	12.004	7679931	40.31
3	15.285	1841125	9.66
4	16.360	7679122	40.31



	Retention Time	Area	% Area
1	8.316	432035	2.74
2	12.160	1182864	7.51
3	15.570	830703	5.27
4	16.700	13303452	84.47

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(furan-3-yl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C40)



C40

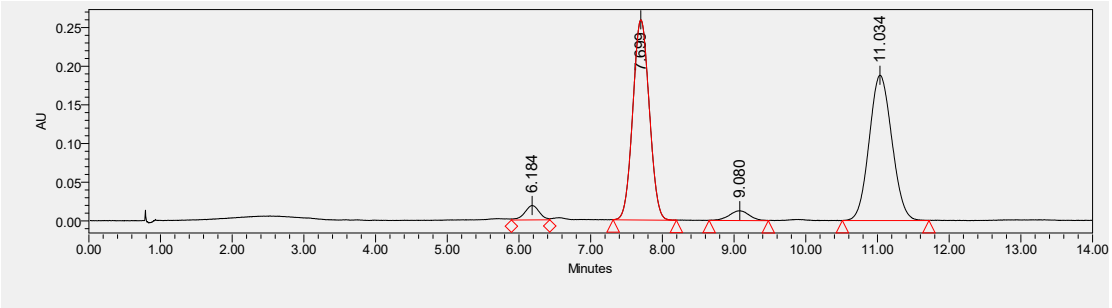
White solid; mp: 83-87 °C; 64% yield, 96:4 dr (determined by ^{1}H NMR), 90% ee. $[\alpha]_{589}^{18}$ = -89.1 (c = 0.68, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.20 min, t_{R2} = 7.73 min, t_{R3} = 9.12 min, t_{R4} = 11.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.68 (m, 3H), 7.65 – 7.51 (m, 5H), 7.44 – 7.36 (m, 4H), 7.05 (s, 1H), 6.97 (s, 1H), 5.99 (s, 1H), 5.93 (s, 1H), 5.39 (s, 1H), 4.10 – 4.02 (m, 1H), 3.83 – 3.75 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 3H).

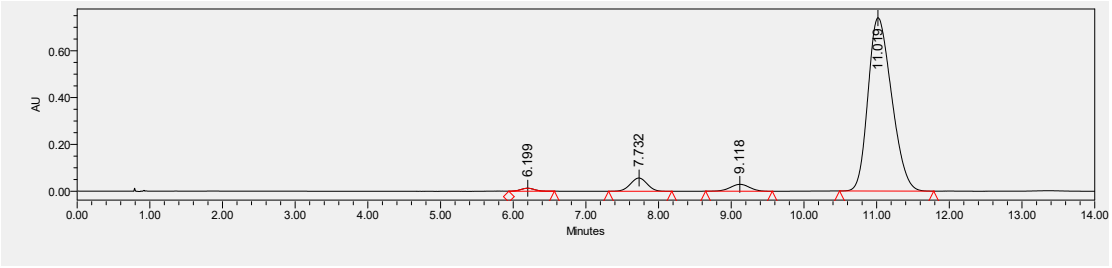
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.9, 169.3, 142.2, 141.6, 138.5, 137.8, 137.6, 136.3, 135.1, 133.4, 133.4, 131.0, 130.6, 130.1, 129.7, 129.5, 128.4, 127.1, 125.6, 121.5, 121.1, 110.9, 72.7, 64.0, 44.8, 13.4.

ESI-HRMS: calcd for $C_{28}H_{23}NO_6SNa^+$ ([M + Na]$^+$) = 524.1138, found 524.1140.

IR (neat): 3269, 1736, 1659, 1310, 1245, 1170, 1025, 930, 708 cm^{-1}.

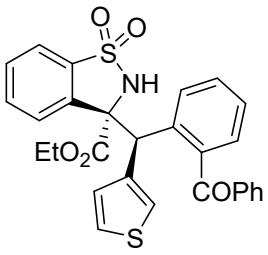


	Retention Time	Area	% Area
1	6.184	234804	2.69
2	7.699	4123947	47.19
3	9.080	245824	2.81
4	11.034	4134628	47.31



	Retention Time	Area	% Area
1	6.199	155152	0.85
2	7.732	894422	4.90
3	9.118	542933	2.97
4	11.019	16677084	91.28

ethyl (*S*)-3-((*R*)-(2-benzoylphenyl)(thiophen-3-yl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C41)



C41

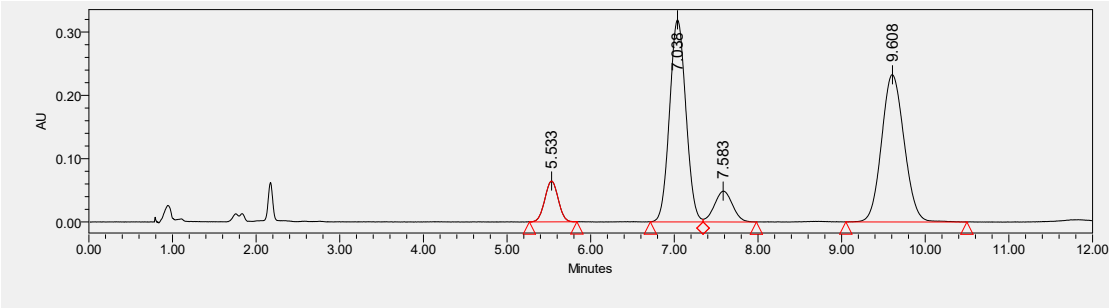
White solid; mp: 65-69 °C; 92% yield, 92:8 dr (determined by ^{1}H NMR), 88%/49% ee. $[\alpha]_{589}^{18}$ = -89.2 (c = 0.86, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.52 min, t_{R2} = 7.02 min, t_{R3} = 7.55 min, t_{R4} = 9.52 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.58 (m, 4H), 7.57 – 7.55 (m, 1H), 7.54 – 7.51 (m, 1H), 7.49 – 7.47 (m, 1H), 7.37 – 7.32 (m, 4H), 6.90 – 6.88 (m, 1H), 6.83 – 6.83 (m, 1H), 6.58 – 6.57 (m, 1H), 5.99 (s, 1H), 5.61 (s, 1H), 4.08 – 4.03 (m, 1H), 3.84 – 3.79 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H).

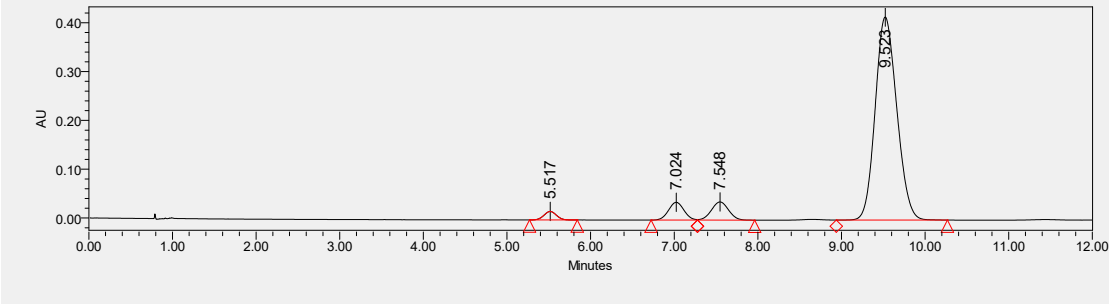
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.1, 169.5, 138.8, 137.7, 137.6, 136.7, 136.6, 134.9, 133.4, 133.3, 130.8, 130.6, 130.0, 129.4, 129.2, 128.5, 128.3, 126.9, 125.6, 124.7, 124.5, 121.4, 72.8, 64.0, 48.6, 13.3.

ESI-HRMS: calcd for $C_{28}H_{23}NO_5S_2Na^+$ ([M + Na]$^+$) = 540.0910, found 540.0911.

IR (neat): 3268, 1735, 1659, 1311, 1246, 1170, 929, 764, 712 cm^{-1}.

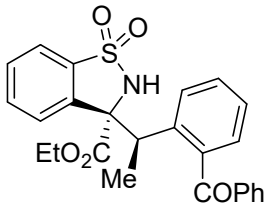


	Retention Time	Area	% Area
1	5.533	662031	7.03
2	7.038	4043880	42.96
3	7.583	671406	7.13
4	9.608	4035582	42.87



	Retention Time	Area	% Area
1	5.517	180474	2.09
2	7.024	467527	5.41
3	7.548	530482	6.14
4	9.523	7455852	86.35

ethyl (*S*)-3-((*R*)-1-(2-benzoylphenyl)ethyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (C42)



C42

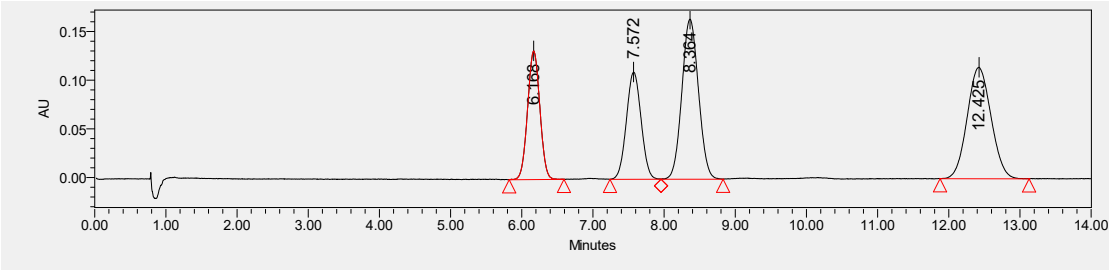
White solid; mp: 67-70 °C; 87% yield, 48:52 dr (determined by ^{1}H NMR), 93%/83% ee. $[\alpha]_{589}^{24}$ = -29.5 (c = 0.78, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IA-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 6.20 min, t_{R2} = 7.58 min, t_{R3} = 8.40 min, t_{R4} = 12.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.81 (m, 2H), 7.76 – 7.56 (m, 3H), 7.51 – 7.34 (m, 6H), 7.24 – 7.11 (m, 1H), 7.07 – 7.01 (m, 1H), 5.87 (s, 1H), 4.64 – 4.58 (m, 1H), 4.35 – 4.23 (m, 2H), 1.40 – 1.39 (d, *J* = 7.2 Hz, 3H), 1.31 – 1.27 (t, *J* = 7.2 Hz, 3H).

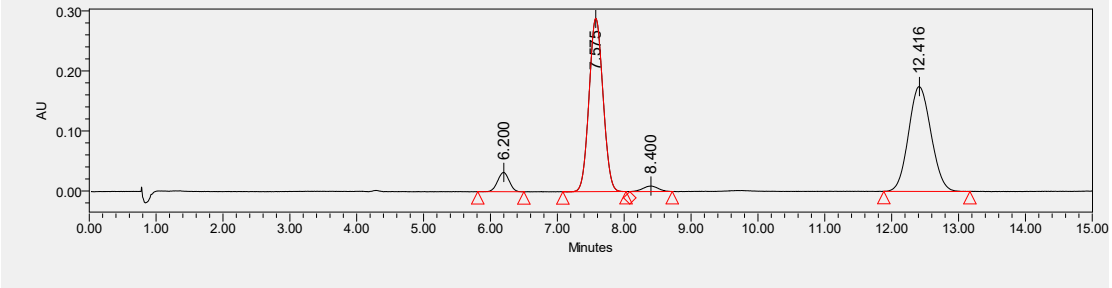
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 170.4, 139.8, 138.0, 137.9, 135.3, 135.3, 133.4, 133.1, 130.8, 130.6, 130.0, 129.5, 129.1, 128.5, 126.9, 126.1, 121.4, 73.0, 63.8, 42.5, 18.5, 13.9.

ESI-HRMS: calcd for $C_{25}H_{23}NO_5SNa^+$ ($[M + Na]^+$) = 472.1189, found 472.1185.

IR (neat): 3278, 1735, 1659, 1450, 1310, 1246, 1173, 1135, 1021, 762, 709 cm^{-1}.

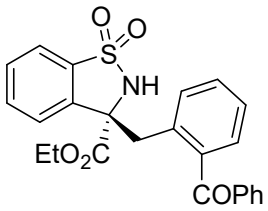


	Retention Time	Area	% Area
1	6.168	1581308	18.63
2	7.572	1580365	18.62
3	8.364	2664330	31.40
4	12.425	2659856	31.34

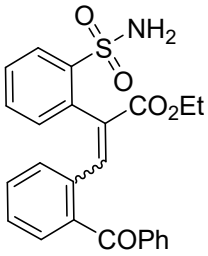


	Retention Time	Area	% Area
1	6.200	386781	4.39
2	7.575	4187878	47.56
3	8.400	147403	1.67
4	12.416	4083013	46.37

ethyl (*S*)-3-(2-benzoylbenzyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C43) and ethyl 3-(2-benzoylphenyl)-2-(2-sulfamoylphenyl)acrylate (C43-(II))



C43



C43-(II)

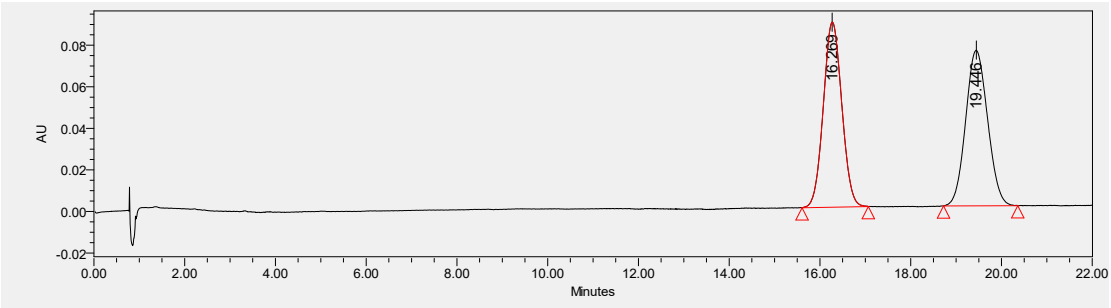
C43 White solid; mp: 66-70 °C; 54% yield, 61% ee. $[\alpha]_{589}^{24}$ = -42.5 (c = 0.47, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IA-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 16.10 min, t_{R2} = 19.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H), 7.67 – 7.55 (m, 3H), 7.54 – 7.48 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.14 – 7.08 (m, 1H), 6.75 (s, 1H), 4.19 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.06 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.89 (d, *J* = 14.0 Hz, 1H), 3.56 (d, *J* = 14.0 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).

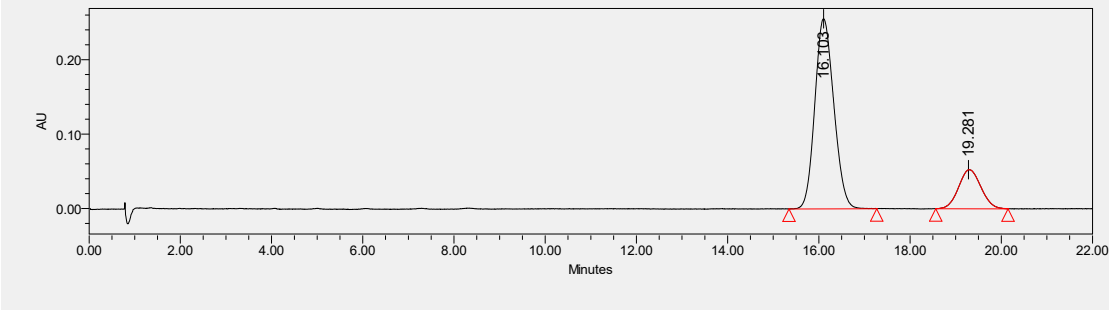
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.5, 170.0, 138.7, 137.4, 137.3, 135.5, 133.6, 133.4, 133.2, 132.3, 130.8, 130.6, 130.5, 130.4, 128.3, 126.7, 125.4, 121.3, 69.2, 63.3, 40.6, 13.8.

ESI-HRMS: calcd for $C_{24}H_{21}NO_5SNa^+$ ([M + Na]$^+$) = 458.1033, found 458.1028.

IR (neat): 3274, 1734, 1657, 1450, 1299, 1250, 1169, 764, 708 cm^{-1}.



	Retention Time	Area	% Area
1	16.269	2515418	50.06
2	19.446	2509825	49.94



	Retention Time	Area	% Area
1	16.103	7393418	80.53
2	19.281	1788050	19.47

The retro-vinylogous Michael product **C43-(II)** was obtained in 18% yield and 1:1 *Z*/*E*, which could also be found in other substrates.

Analytic data of the less polar isomer:

White solid; mp: 57-61 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.99 (m, 1H), 7.81 – 7.72 (m, 2H), 7.61 – 7.54 (m, 3H), 7.54 – 7.49 (m, 2H), 7.49 – 7.39 (m, 4H), 7.26 (m, 1H), 7.17 (s, 1H), 5.71 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.7, 166.5, 141.4, 140.7, 137.7, 137.4, 136.7, 136.0, 133.2, 133.1, 132.5, 132.3, 131.3, 130.6, 130.3, 129.8, 128.7, 128.4, 127.7, 127.5, 61.0, 13.5.

ESI-HRMS: calcd for $C_{24}H_{21}NO_5SNa^+$ ([M + Na]$^+$) = 458.1033, found 458.1026.

IR (neat): 3354, 3264, 1709, 1652, 1343, 1272, 1216, 1166, 1027, 933, 766, 705 cm^{-1}.

Analytic data of the more polar isomer:

White solid; mp: 161-164 ℃

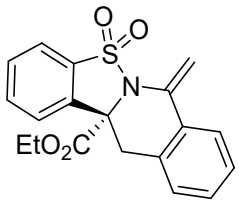
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 1H), 7.98 (s, 1H), 7.86 – 7.79 (m, 2H), 7.64 (m, 1H), 7.51 (m, 2H), 7.42 (m, 2H), 7.36 (m, 1H), 7.25 – 7.19 (m, 2H), 7.19 – 7.12 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.42 (s, 2H), 4.35 – 4.15 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 167.6, 141.6, 139.9, 138.2, 137.2, 135.5, 134.1, 133.4, 133.0, 132.4, 130.9, 130.9, 130.4, 129.7, 129.0, 128.5, 128.3, 127.6, 61.8, 14.0.

ESI-HRMS: calcd for $C_{24}H_{21}NO_5SNa^+$ ([M + Na]$^+$) = 458.1033, found 458.1025.

IR (neat): 3261, 1693, 1654, 1342, 1250, 1164, 1032, 934, 764, 706 cm^{-1}.

ethyl (*S*)-7-methylene-7,12-dihydro-12a*H*-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (D1)



D1

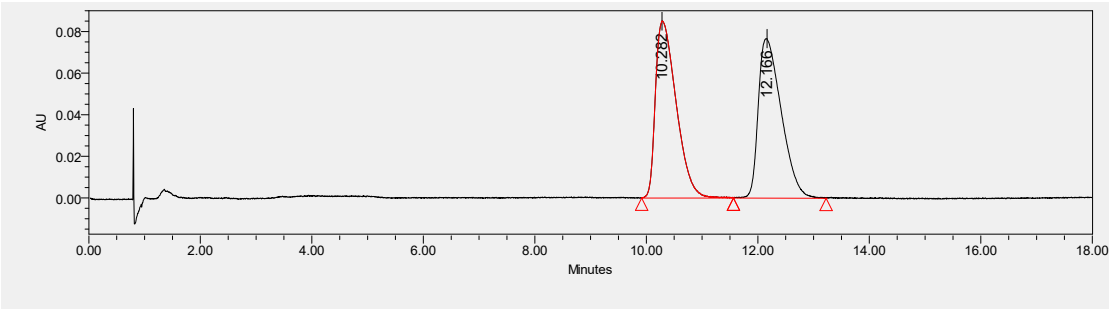
Colorless oil; 60% yield, 90% ee. $[\alpha]_{589}^{18}$ = -195.5 (c = 0.43, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IA-3**, CO_2/MeOH = 96/4, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 10.57 min, t_{R2} = 11.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.69 – 7.65 (m, 1H), 7.32 – 7.27 (m, 2H), 7.20 – 7.18 (m, 1H), 5.62 (d, *J* = 2.8 Hz, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 4.11 – 4.03 (m, 1H), 4.01 – 3.95 (m, 1H), 3.86 (d, *J* = 15.2 Hz, 1H), 3.17 (d, *J* = 15.2 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

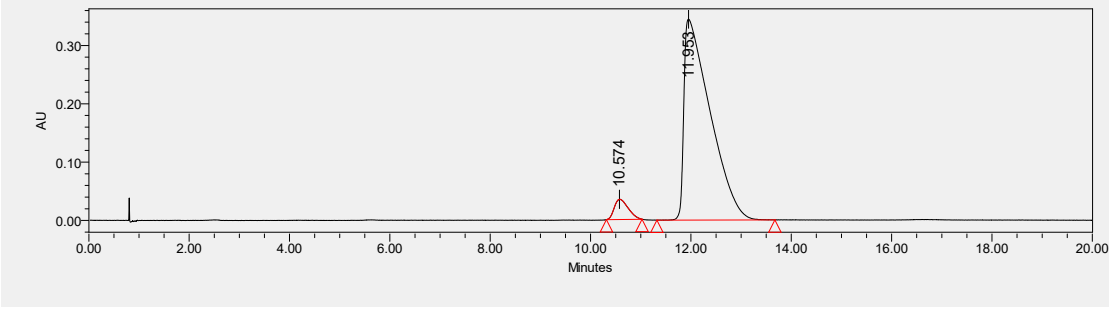
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.9, 134.6, 134.2, 134.0, 133.7, 130.7, 129.8, 129.6, 129.0, 128.9, 127.8, 124.4, 123.8, 121.8, 94.6, 66.8, 62.7, 40.1, 13.7.

ESI-HRMS: calcd for $C_{19}H_{17}NO_4SNa^+$ ([M + Na]$^+$) = 378.0770, found 378.0769.

IR (neat): 1742, 1619, 1455, 1312, 1179, 1048, 772 cm^{-1}.

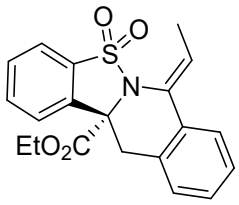


	Retention Time	Area	% Area
1	10.282	2193745	50.05
2	12.166	2189278	49.95



	Retention Time	Area	% Area
1	10.574	665815	5.06
2	11.953	12496830	94.94

ethyl (*S,Z*)-7-ethylidene-7,12-dihydro-12a*H*-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (D2)



D2

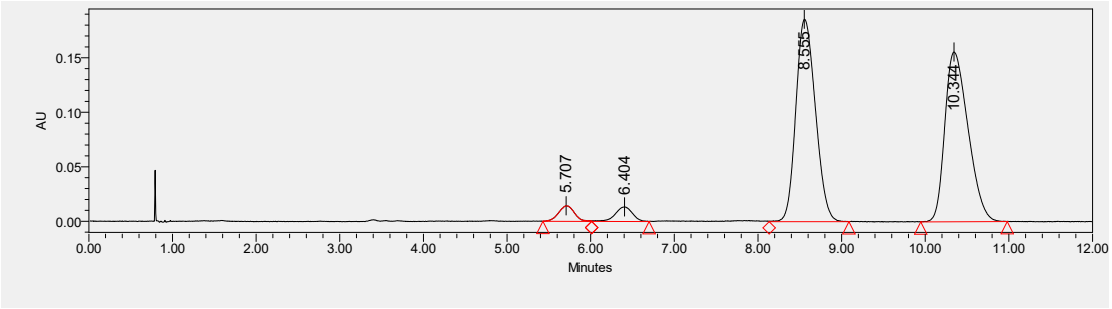
White solid; mp: 196-198 °C; 56% yield, 94:6 (*Z:E*) (determined by ^{1}H NMR), 90% ee. $[\alpha]_{589}^{16}$ = -239.9 (c = 0.41, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OD-3**, CO_2/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 5.72 min, t_{R2} = 6.43 min, t_{R3} = 8.53 min, t_{R4} = 10.49 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.62 – 7.57 (m, 2H), 7.23 – 7.14 (m, 2H), 7.06 – 7.04 (m, 1H), 6.65 – 6.60 (m, 1H), 4.25 – 4.08 (m, 2H), 3.74 (d, *J* = 16.4 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 2.20 (d, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

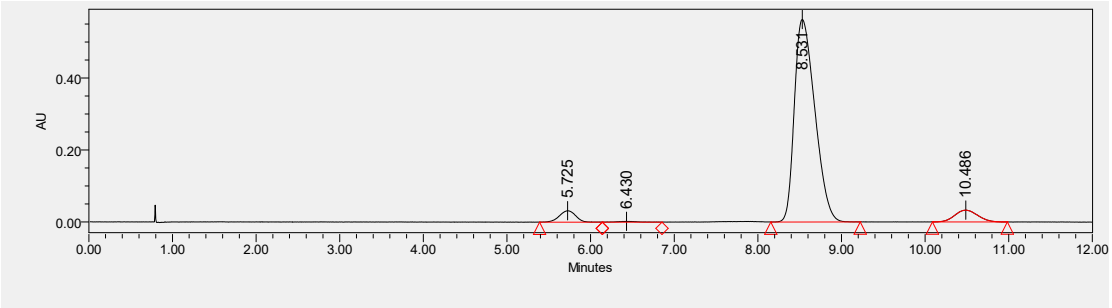
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.3, 137.8, 134.0, 133.3, 131.7, 130.1, 129.6, 128.6, 128.5, 127.8, 127.3, 126.4, 123.5, 123.1, 121.9, 67.0, 62.7, 37.4, 15.0, 13.8.

ESI-HRMS: calcd for $C_{20}H_{19}NO_4SNa^+$ ([M + Na]$^+$) = 392.0927, found 392.0924.

IR (neat):1734, 1453, 1311, 1251, 1225, 1175, 1054, 762 cm^{-1}.

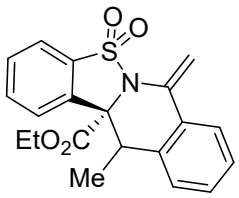


	Retention Time	Area	% Area
1	5.707	186736	2.92
2	6.404	192237	3.00
3	8.555	3017429	47.16
4	10.344	3002008	46.92



	Retention Time	Area	% Area
1	5.725	428227	4.03
2	6.430	38446	0.36
3	8.531	9590668	90.17
4	10.486	578885	5.44

ethyl (12*R*,12*aS*)-12-methyl-7-methylene-7,12-dihydro-12a*H*-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (D3)



D3

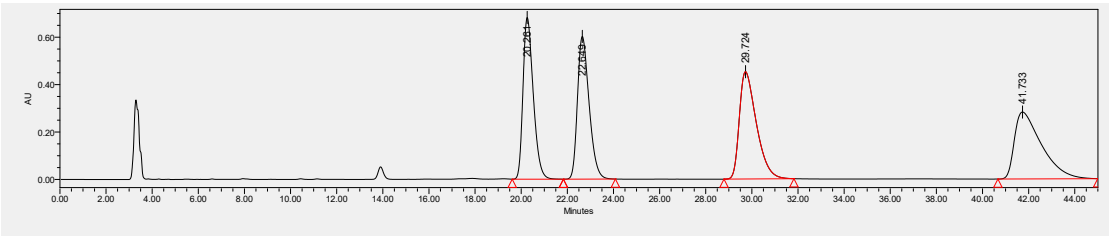
White solid; mp: 109-111 ℃; 86% yield, 54:46 dr (determined by ^{1}H NMR), 90%/90% ee. $[\alpha]_{589}^{18}$ = -171.6 (c = 0.63, in CH_2Cl_2), dissolved in MeOH for **HPLC** (Chiralcel **ID**, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm), retention time: t_{R1} = 20.23 min, t_{R2} = 22.78 min, t_{R3} = 30.09 min, t_{R4} = 41.98 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.61 (m, 5H), 7.36 – 7.18 (m, 5H), 5.66 – 5.39 (m, 1H), 4.07 – 3.34 (m, 3H), 1.74 – 0.83 (m, 6H)

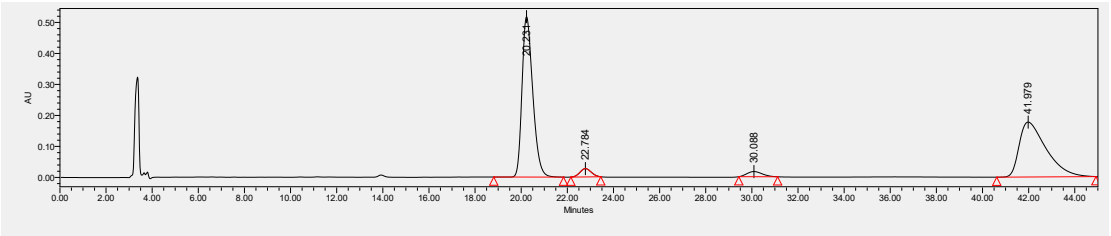
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.5, 136.3, 134.8, 134.3, 132.8, 130.9, 130.7, 129.2, 128.9, 127.8, 127.5, 124.8, 124.0, 121.8, 92.5, 71.0, 62.6, 42.5, 16.9, 13.6.

ESI-HRMS: calcd for $C_{20}H_{19}NO_4SNa^+$ ([M + Na]$^+$) = 392.0927, found 392.0924.

IR (neat):1741, 1619, 1455, 1312, 1239, 1178, 1025, 770 cm^{-1}.

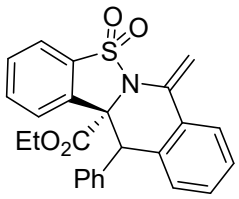


	Retention Time	Area	% Area
1	20.261	21110341	23.88
2	22.649	21128901	23.90
3	29.724	23167610	26.21
4	41.733	22989702	26.01



	Retention Time	Area	% Area
1	20.231	16778632	51.17
2	22.784	913286	2.79
3	30.088	773799	2.36
4	41.979	14325211	43.69

ethyl (12*R*,12*aS*)-7-methylene-12-phenyl-7,12-dihydro-12a*H*-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (D4)



D4

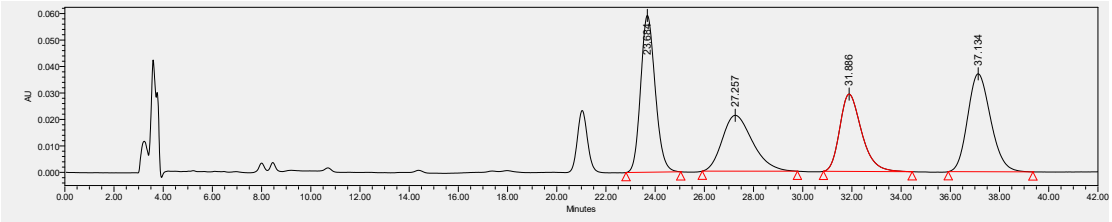
White solid; mp: 108-110 ℃; 72% yield, 67:33 dr (determined by ^{1}H NMR), 92%/89% ee. $[\alpha]_{589}^{17}$ = -290.2 (c = 0.62, in CH_2Cl_2), dissolved in MeOH for **HPLC** (Chiralcel **ID**, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm), retention time: t_{R1} = 23.57 min, t_{R2} = 27.29 min, t_{R3} = 31.68 min, t_{R4} = 37.22 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.64 – 7.58 (m, 2H), 7.47 – 7.43 (m, 1H), 7.39 – 7.36 (m, 1H), 7.33 – 7.30 (m, 1H), 7.27 – 7.25 (m, 1H), 7.20 – 7.17 (m, 1H), 7.04 – 6.99 (m, 3H), 6.97 – 6.95 (m, 1H), 5.62 (d, *J* = 2.8, 1H), 5.57 – 5.56 (d, *J* = 2.8, 1H) 5.19 (s, 1H), 4.08 – 3.93 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.5, 136.4, 134.7, 134.3, 133.6, 132.9, 132.1, 130.4, 129.9, 129.7, 129.3, 128.3, 128.0, 127.9, 127.5, 124.8, 124.4, 121.2, 92.7, 71.1, 62.9, 52.7, 13.6.

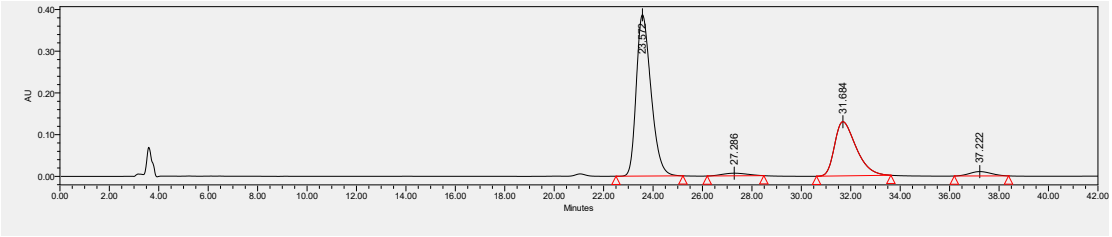
ESI-HRMS: calcd for $C_{25}H_{21}NO_4SNa^+$ ([M + Na]$^+$) = 454.1084, found 454.1082.

IR (neat):1736, 1618, 1452, 1313, 1225, 1179, 1028, 767, 705 cm^{-1}.



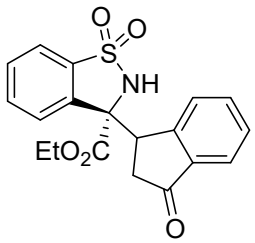
	Retention Time	Area	% Area
1	23.684	2434373	28.84

2	27.257	1799476	21.32
3	31.886	1804924	21.38
4	37.134	2402041	28.46



	Retention Time	Area	% Area
1	23.572	16018634	64.15
2	27.286	449746	1.80
3	31.684	7866494	31.50
4	37.222	634705	2.54

ethyl (*S*)-3-((*R*)-3-oxo-2,3-dihydro-1*H*-inden-1-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C44)



C44

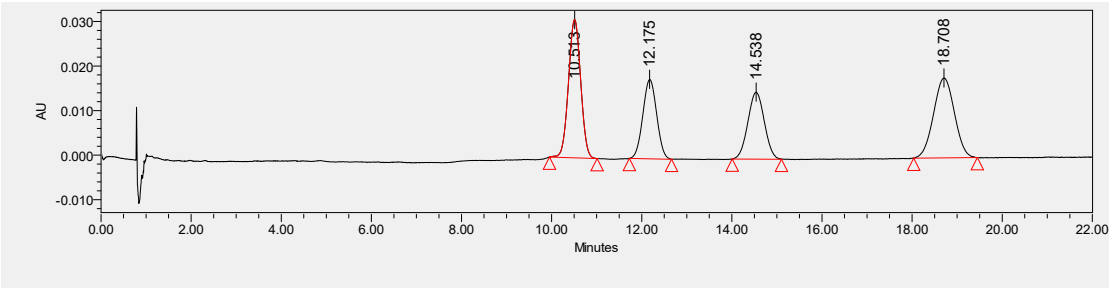
White solid; mp: 171-175 °C; 47% yield, 58:42 dr (determined by ^{1}H NMR), 34%/37% ee. $[\alpha]_{589}^{19}$ = -25.0 (c = 0.33, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **IC-3**, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 10.58 min, t_{R2} = 12.26 min, t_{R3} = 14.64, t_{R4} = 18.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.80 (m, 2H), 7.72 – 7.67 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 - 7.47 (m, 1H), 7.28 – 7.27 (m, 1H), 4.45 (dd, *J* = 7.2, 2.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H) , 2.44 (dd, *J* = 18.8, 7.6 Hz, 1H), 2.20 (dd, *J* = 18.8, 3.2 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H).

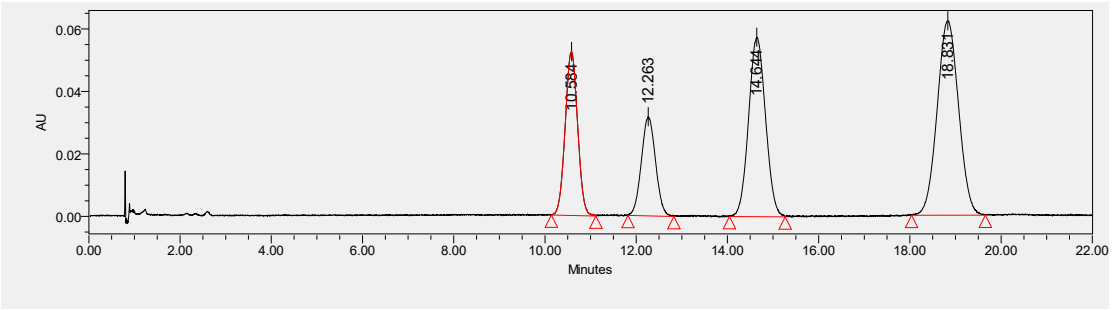
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.6, 169.9, 150.6, 138.5, 136.4, 135.4, 134.7, 134.0, 131.2, 129.2, 125.3, 124.9, 124.4, 122.0, 71.3, 64.0, 46.1, 38.6, 14.1.

ESI-HRMS: calcd for $C_{19}H_{17}NO_5SNa^+$ ([M + Na]$^+$) = 394.0720, found 394.0720.

IR (neat): 3272, 1712, 1467, 1305, 1245, 1166, 935, 762, 735

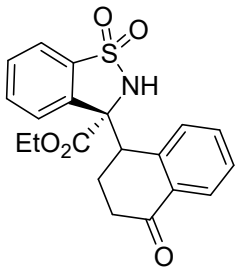


	Retention Time	Area	% Area
1	10.513	582464	30.35
2	12.175	379422	19.77
3	14.538	380921	19.85
4	18.708	576355	30.03



	Retention Time	Area	% Area
1	10.584	1204525	19.59
2	12.263	782839	12.73
3	14.644	1691535	27.51
4	18.831	2470016	40.17

ethyl (*S*)-3-((*R*)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (C45)



C45

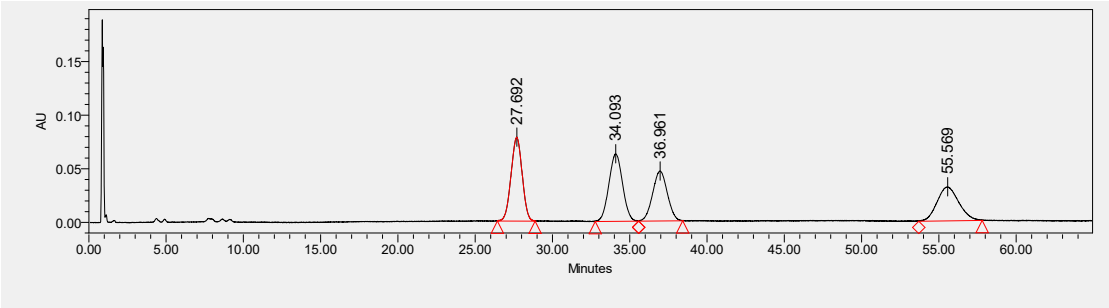
White solid; mp: 173-176 °C; 61% yield, 57:43 dr (determined by ^{1}H NMR), 75%/80% ee. $[\alpha]_{589}^{19}$ = -67.7 (c = 0.37, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: t_{R1} = 27.86 min, t_{R2} = 34.04 min, t_{R3} = 36.95, t_{R4} = 56.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 -8.11 (m, 1H), 7.86 – 7.82 (m, 2H), 7.79 – 7.76 (s, 1H), 7.52 – 7.44 (m, 2H), 7.35 – 7.27 (m, 1H), 7.20 – 7.10 (m, 1H), 4.29 – 4.21 (qd, *J* = 7.2, 4.6 Hz, 2H), 4.07 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.40 – 2.33 (m, 1H), 2.17 – 2.08 (m, 1H), 1.92 – 1.85 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).

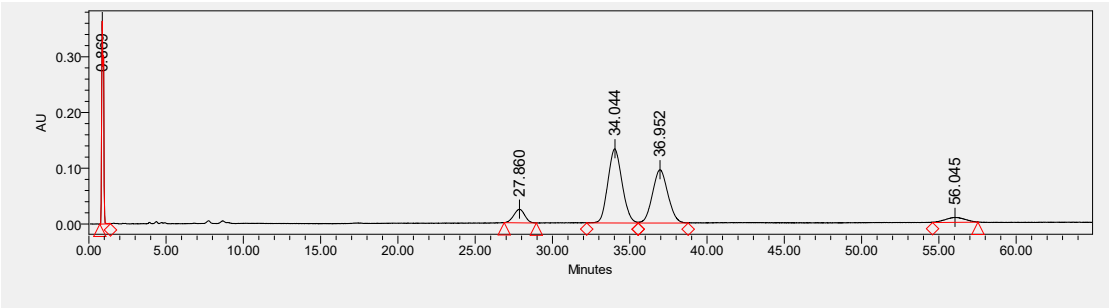
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.1, 169.8, 139.8, 136.8, 135.0, 134.4, 133.9, 132.1, 131.1, 128.6, 128.1, 128.0, 125.7, 122.0, 73.1, 63.8, 46.2, 33.3, 22.8, 13.9.

ESI-HRMS: calcd for $C_{20}H_{19}NO_5SNa^+$ ([M + Na]$^+$) = 408.0876, found 408.0873.

IR (neat): 3270, 1733, 1680, 1305, 1241, 1169, 1025, 761, 734 cm^{-1}.

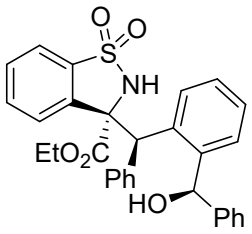


	Retention Time	Area	% Area
1	27.692	3918661	28.05
2	34.093	3875316	27.74
3	36.961	3084670	22.08
4	55.569	3091939	22.13



	Retention Time	Area	% Area
1	27.860	1209867	7.27
2	34.044	8289239	49.79
3	36.952	6430891	38.63
4	56.045	718375	4.31

ethyl (*S*)-3-((*R*)-(2-((*R*)-hydroxy(phenyl)methyl)phenyl)(phenyl)methyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (E1)



E1

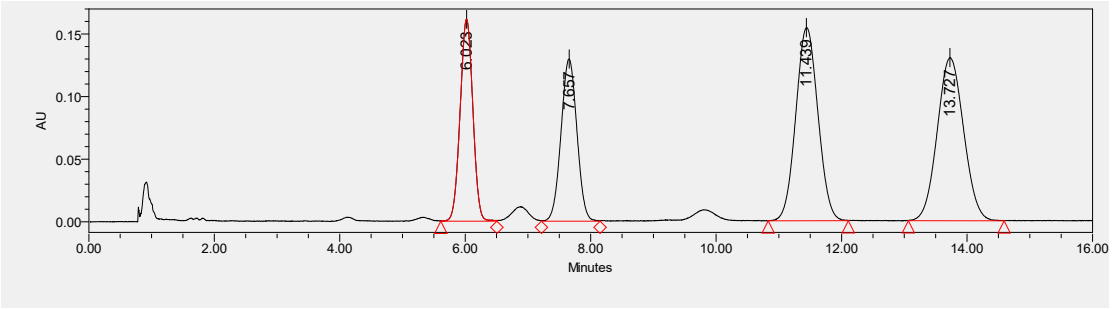
White solid; mp: 234-239 °C; 98% yield, 87:13 dr (determined by ^{1}H NMR), 92%/82% ee. $[\alpha]_{589}^{19}$ = -159.8 (c = 0.87, in THF), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 211 nm), retention time: t_{R1} = 5.95 min, t_{R2} = 7.59 min, t_{R3} = 11.40, t_{R4} = 13.60 min.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.69 (s, 1H), 7.82 – 7.75 (m, 2H), 7.73 (d, J = 7.8 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.55 – 7.53 (m, 2H), 7.45 – 7.42 (m, 3H), 7.39 – 7.36 (m, 1H), 7.33 – 7.28 (m, 2H), 7.07 – 7.01 (m, 3H), 6.77 – 7.66 (m, 2H), 5.63 (d, J = 4.2 Hz, 1H), 5.48 (d, J = 4.8 Hz, 1H), 5.03 (s, 1H), 3.66 – 3.60 (m, 1H), 3.51 – 3.45 (m, 1H), 0.44 (t, J = 7.2 Hz, 3H).

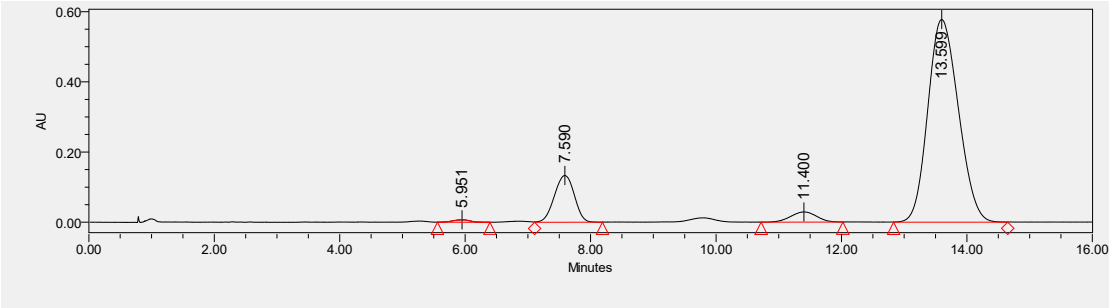
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 169.2, 143.7, 142.4, 137.3, 136.3, 136.0, 134.8, 133.3, 130.9, 130.5, 128.5, 128.3, 127.7, 127.4, 126.9, 126.9, 126.8, 126.8, 126.6, 124.9, 121.0, 72.0, 71.0, 61.9, 53.6, 12.9.

ESI-HRMS: calcd for $C_{30}H_{27}NO_5SNa^+$ ([M + Na]$^+$) = 536.1502, found 536.1502.

IR (neat): 3263, 1733, 1452, 1312, 1244, 1201, 1171, 1035, 762, 703 cm^{-1}.

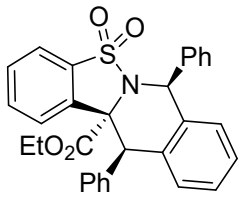


	Retention Time	Area	% Area
1	6.023	2274030	18.73
2	7.657	2274961	18.73
3	11.439	3785273	31.17
4	13.727	3809252	31.37



	Retention Time	Area	% Area
1	5.951	136339	0.58
2	7.590	2945601	12.53
3	11.400	827040	3.52
4	13.599	19598006	83.37

ethyl (7*S*,12*R*,12*S*)-7,12-diphenyl-7,12-dihydro-12aH-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (F1)



F1

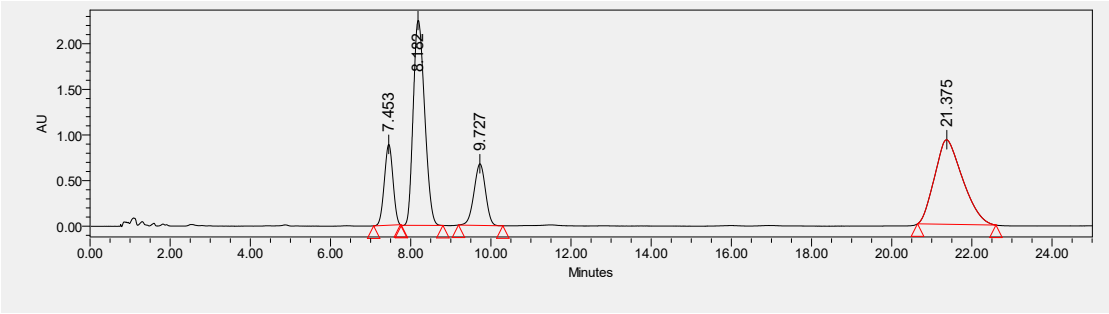
White solid; mp: 210-214 °C; 53% yield, 92% ee. $[\alpha]_{589}^{15}$ = -144.2 (c = 0.45, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 211 nm), retention time: t_{R1} = 8.23 min, t_{R2} = 21.83 min.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.60 (m, 4H), 7.52 – 7.48 (m, 3H), 7.45 – 7.42 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.11 (m, 3H), 7.07 – 7.04 (m, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.07 (s, 1H), 5.50 (s, 1H), 4.16 – 3.99 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

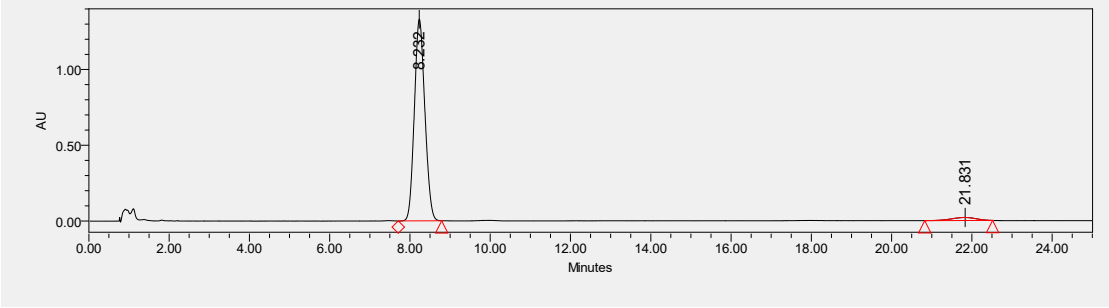
^{13}C{^{1}H} NMR (101 MHz, DMSO- d_6) δ 168.6, 139.4, 138.4, 135.7, 135.6, 135.0, 133.1, 132.8, 131.4, 130.8, 130.2, 129.6, 128.8, 128.3, 128.1, 128.1, 127.6, 127.3, 127.2, 125.0, 121.0, 72.2, 62.6, 59.4, 48.7, 13.7.

ESI-HRMS: calcd for $C_{30}H_{25}NO_4SNa^+$ ([M + Na]$^+$) = 518.1397, found 518.1387.

IR (neat): 1736, 1452, 1311, 1230, 1178, 748, 726, 699 cm^{-1}.

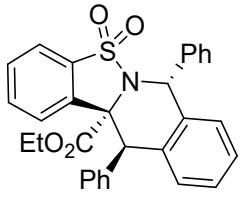


	Retention Time	Area	% Area
1	7.453	13177325	11.35
2	8.182	44607275	38.41
3	9.727	13425060	11.56
4	21.375	44911829	38.68



	Retention Time	Area	% Area
1	8.232	24192776	96.57
2	21.831	859747	3.43

ethyl (7*R*,12*R*,12*S*)-7,12-diphenyl-7,12-dihydro-12aH-benzo[4,5]isothiazolo[2,3-*b*]isoquinoline-12a-carboxylate 5,5-dioxide (F1′)



F1'

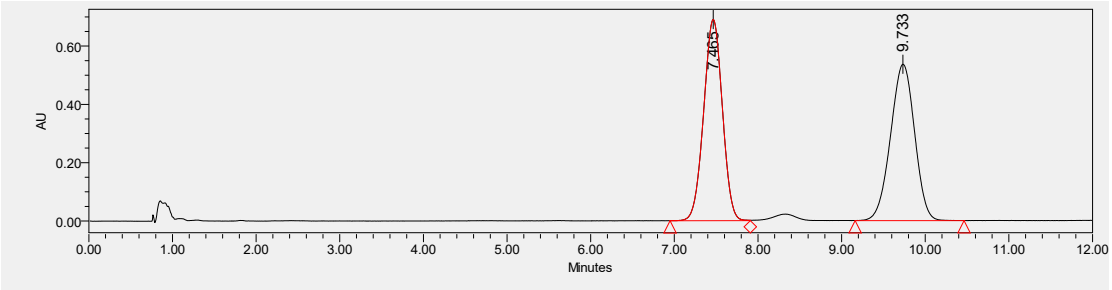
White solid; mp: 93-96 °C; 29% yield, 92% ee. $[\alpha]_{589}^{16}$ = -241.9 (c = 0.22, in CH_2Cl_2), dissolved in MeOH for **UPC²** (Daicel Chiralcel **OX-3**, CO_2/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 211 nm), retention time: t_{R1} =7.44 min, t_{R2} = 9.73 min.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.52 – 7.46 (m, 3H), 7.43 – 7.34 (m, 4H), 7.28 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 7.02 – 6.94 (m, 5H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.36 (s, 1H), 5.55 (s, 1H), 3.96 – 3.88 (m, 1H), 3.83 – 3.75 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO- d_6) δ 170.1, 140.7, 138.4, 135.6, 134.5, 133.7, 133.5, 133.1, 130.6, 130.0, 129.7, 129.4, 128.2, 128.2, 128.1, 128.0, 127.9, 127.4, 126.9, 124.9, 120.8, 69.9, 62.3, 56.6, 50.4, 13.3.

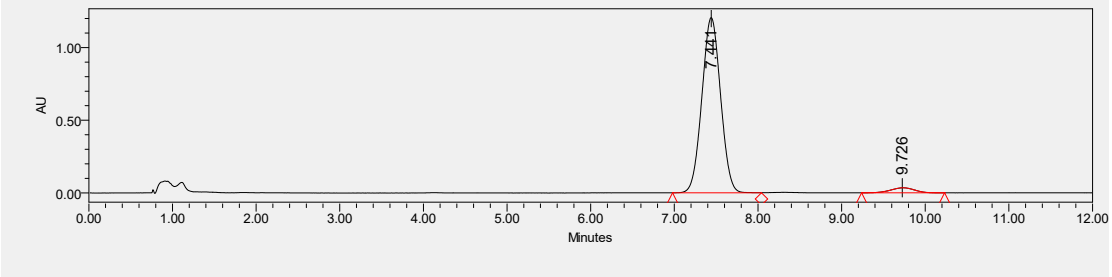
ESI-HRMS: calcd for $C_{30}H_{25}NO_4SNa^+$ ([M + Na]$^+$) = 518.1397, found 518.1391.

IR (neat): 1731, 1452, 1303, 1240, 1179, 965, 753, 704 cm^{-1}.



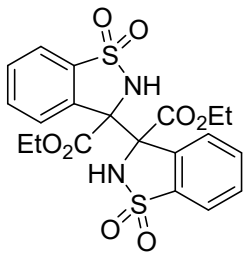
	Retention	Area	% Area

	Time		
1	7.465	10714867	49.97
2	9.733	10728934	50.03



	Retention Time	Area	% Area
1	7.441	18695456	96.44
2	9.726	690378	3.56

diethyl [3,3'-bibenzo[*d*]isothiazole]-3,3'(2H,2'H)-dicarboxylate 1,1,1',1'-tetraoxide (By1)



By1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (m, 2H), 7.66 (m, 2H), 7.62 – 7.57 (m, 2H), 7.50 (m, 2H), 6.17 (s, 2H), 4.32 – 4.22 (m, 4H), 1.26 (t, J = 7.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.8, 136.4, 132.7, 131.7, 131.6, 127.3, 121.5, 73.7, 64.4, 13.7.

8 References

1 (a) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie and X. M. Feng, *Angew. Chem. Int. Ed.*, 2008, **47**, 1308-1311; (b) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu and X. M. Feng, *Org. Lett.*, 2009, **11**, 1401-1404.

2 D.-M. Yan, Q.-Q. Zhao, L. Rao, J.-R. Chen and W.-J. Xiao, *Chem. Eur. J.*, 2018, **24**, 16895-16901.

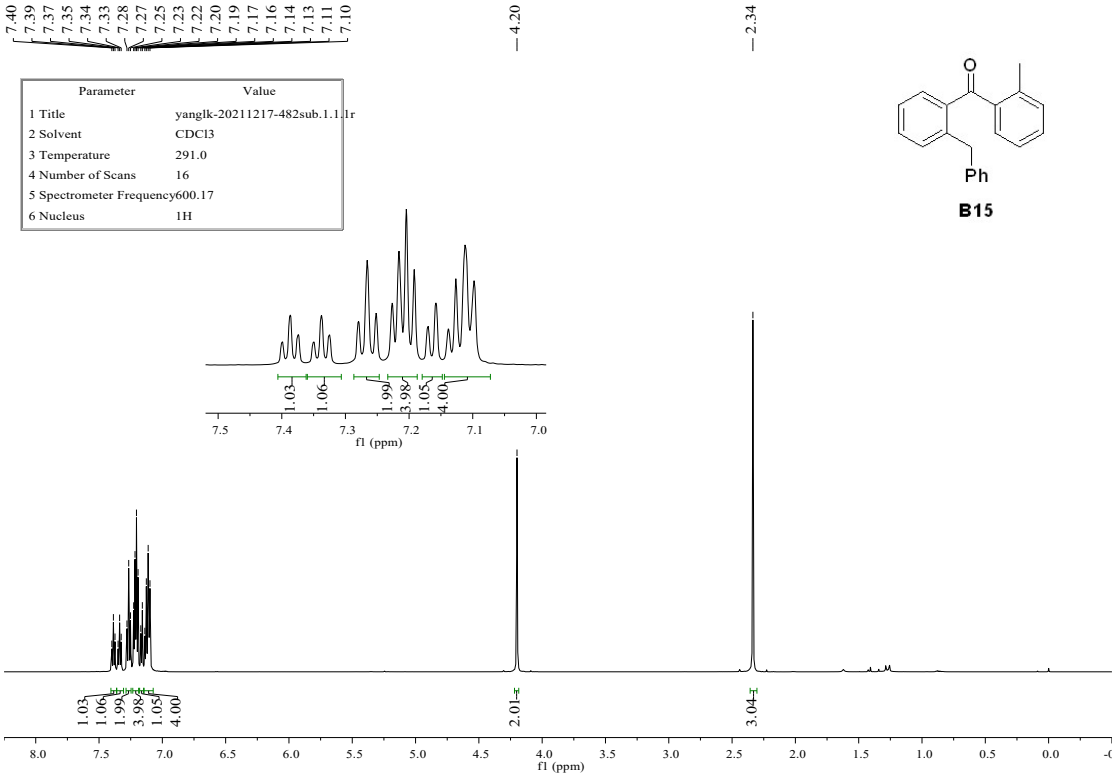
3 L. Zhang, G. Y. Ang and S. Chiba, *Org. Lett.*, 2011, **13**, 1622-1625.

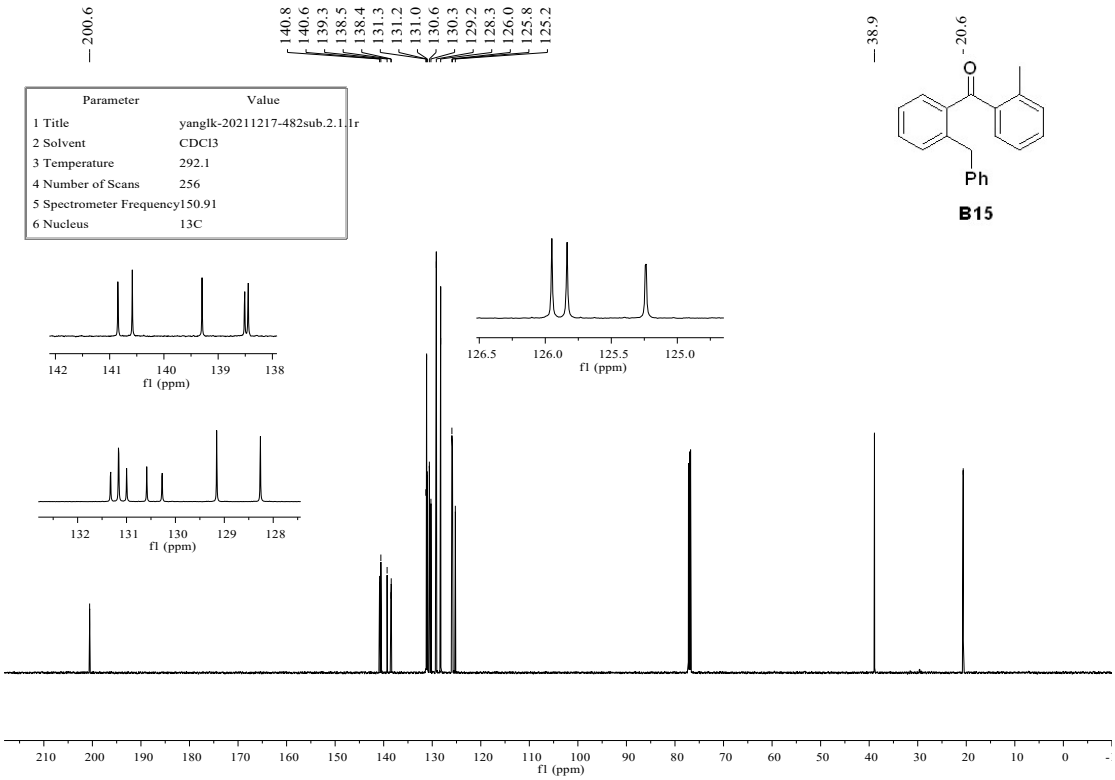
4 Y. Masuda, N. Ishida and M. Murakami, *J. Am. Chem. Soc.*, 2015, **137**, 14063-14066.

5 J. Jurczyk, M. C. Lux, D. Adpressa, S. F. Kim, Y.-h. Lam, C. S. Yeung and R. Sarpong, *Science*, 2021, **373**, 1004-1012.

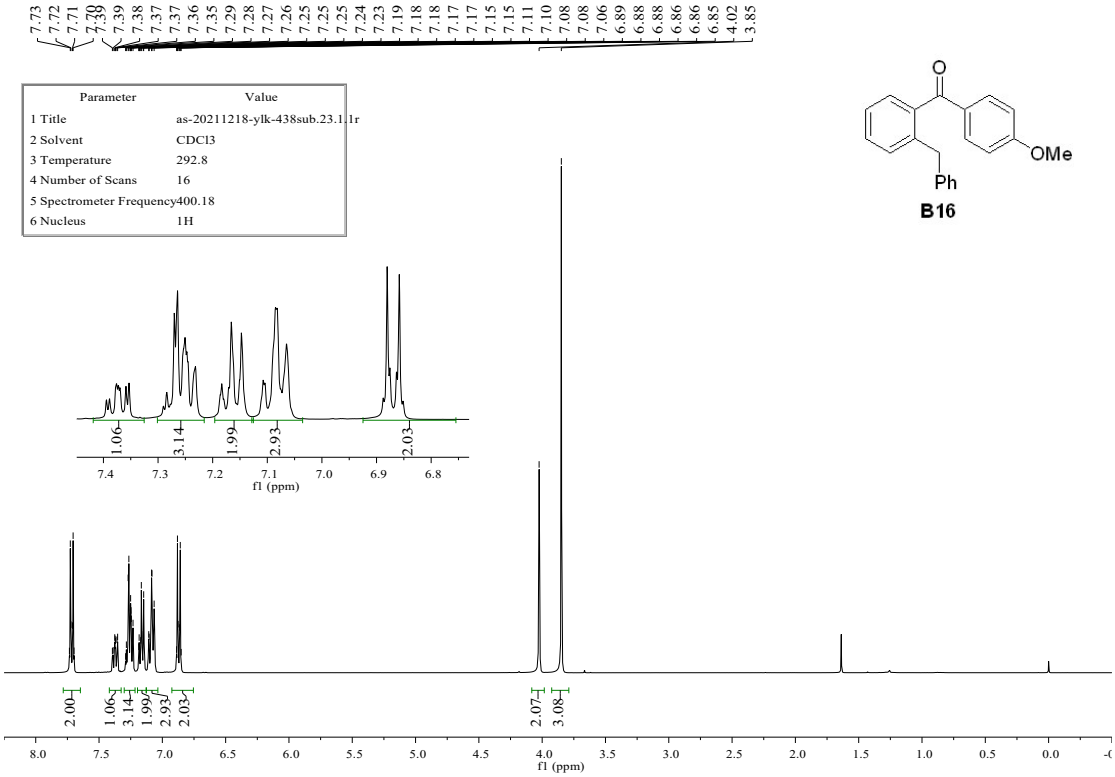
9 Copies of the NMR spectra for new compounds

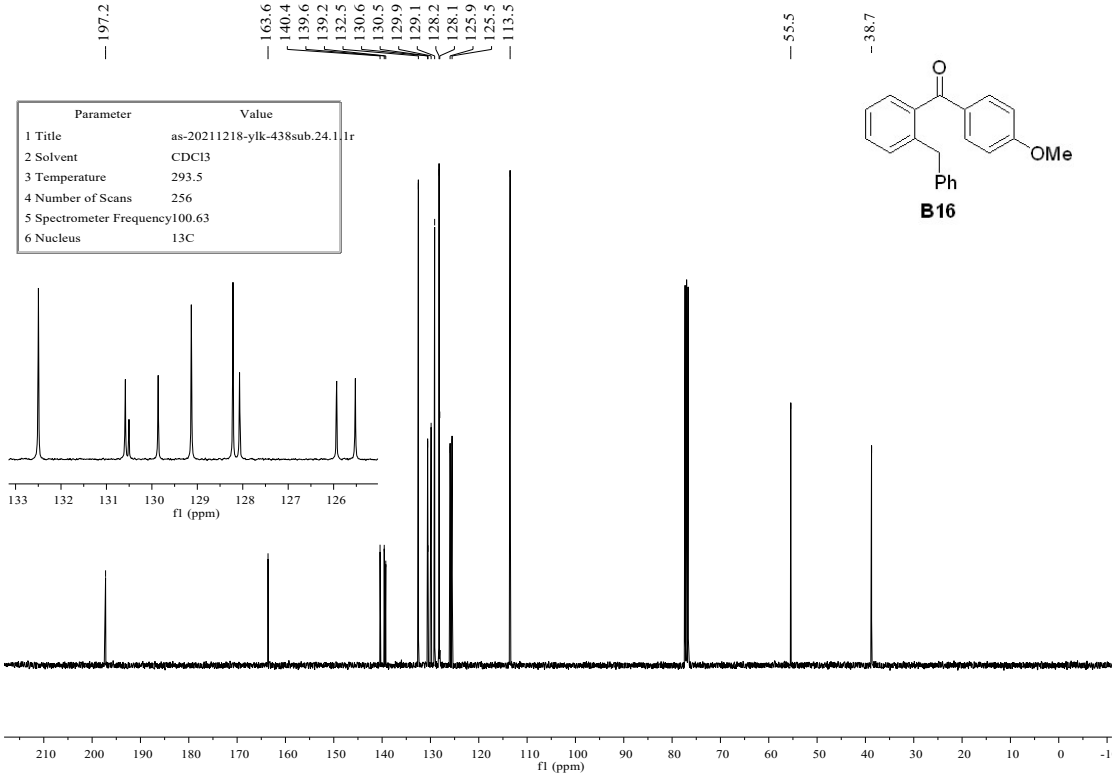
B15



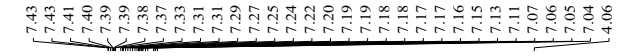


B16

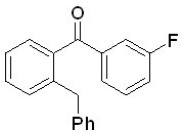

7.73 7.72 7.71 7.40 7.39 7.38 7.37 7.37 7.36 7.35 7.29 7.28 7.27 7.26 7.25 7.25 7.24 7.23 7.19 7.18 7.18 7.17 7.17 7.15 7.15 7.11 7.10 7.08 7.08 7.06 6.89 6.88 6.88 6.86 6.86 6.85 4.02 3.85
Parameter Value
1 Title as-20211218-ylk-438sub.23.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
OMe
Ph
B16
1.06 3.14 1.99 2.93 2.03
f1 (ppm)
2.00 1.06 3.14 1.99 2.93 2.03 2.07 3.08
f1 (ppm)


197.2
163.6 140.4 139.6 139.2 132.5 130.6 130.5 129.9 129.1 128.2 128.1 125.9 125.5 113.5
55.5
38.7
Parameter Value
1 Title as-20211218-ylk-438sub.24.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
OMe
Ph
B16
f1 (ppm)
f1 (ppm)

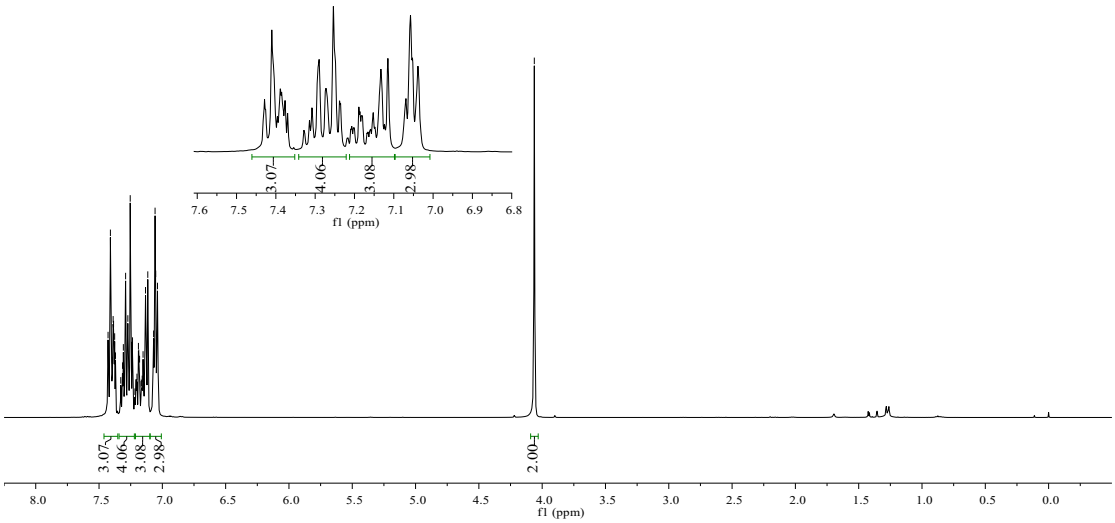
B17

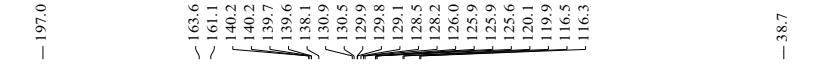


Parameter	Value
1 Title	as-20211218-ylk-458sub.1.1.1r
2 Solvent	CDCl3
3 Temperature	292.5
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

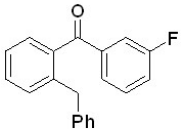


B17

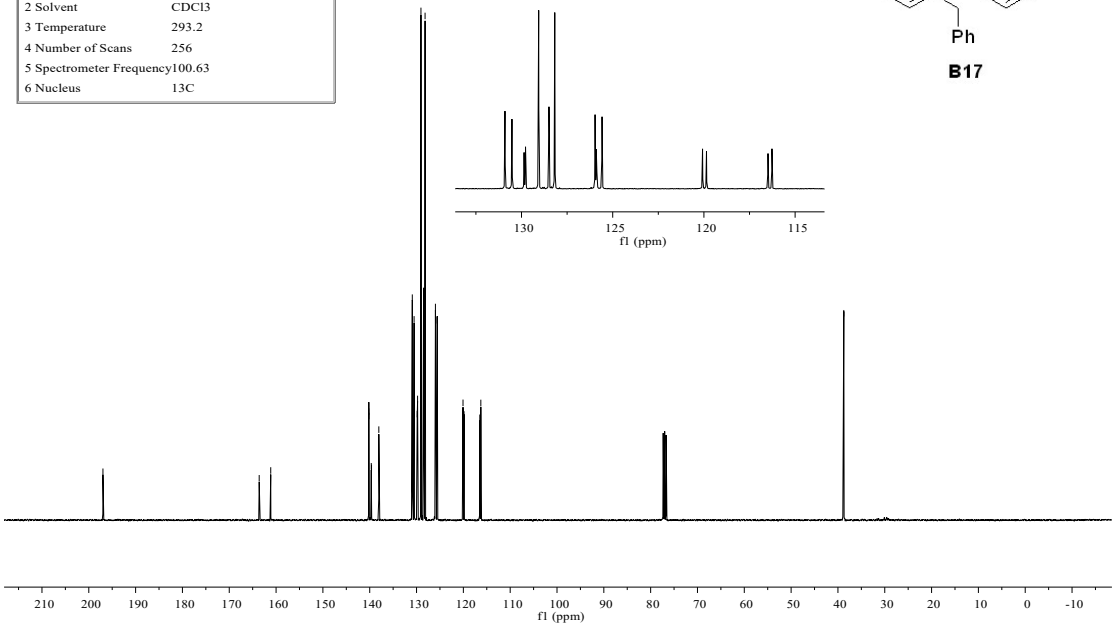




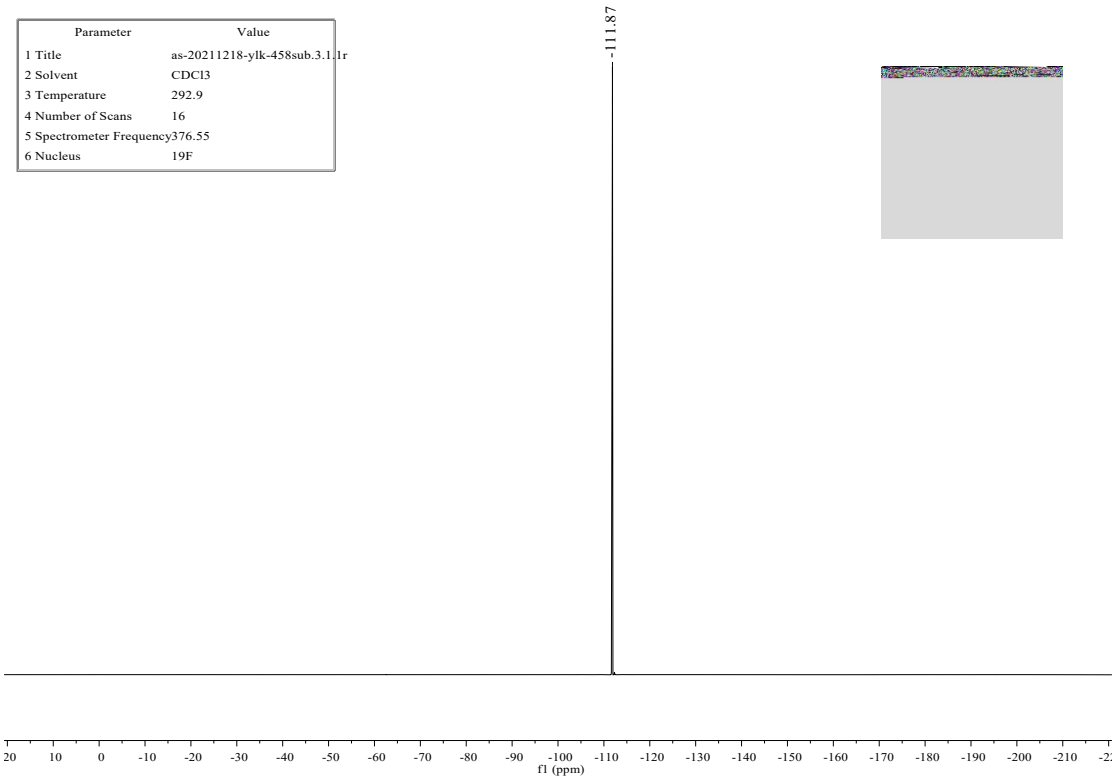
Parameter	Value
1 Title	as-20211218-ylk-458sub.2.1.1r
2 Solvent	CDCl3
3 Temperature	293.2
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C



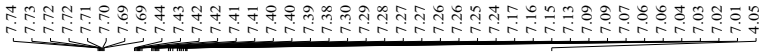
B17



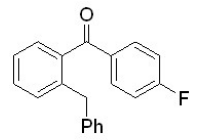
Parameter	Value
1 Title	as-20211218-ylk-458sub.3.1.1r
2 Solvent	CDCl3
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



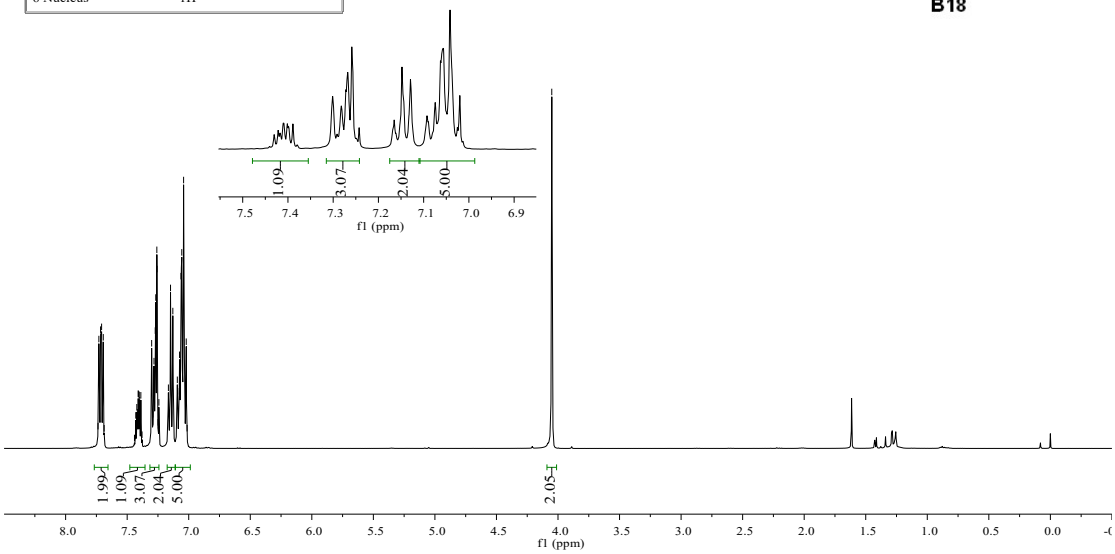
B18

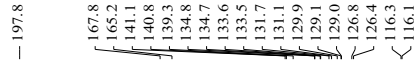


Parameter	Value
1 Title	as-20211218-ylk-436sub.7.1.1r
2 Solvent	CDCl3
3 Temperature	292.8
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H



B18





Parameter	Value
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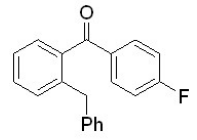
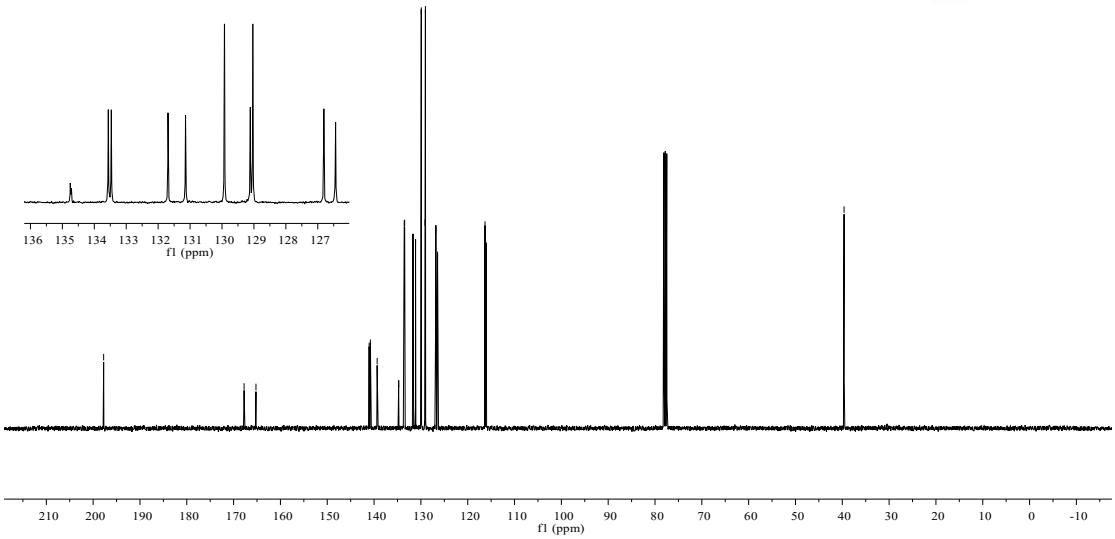
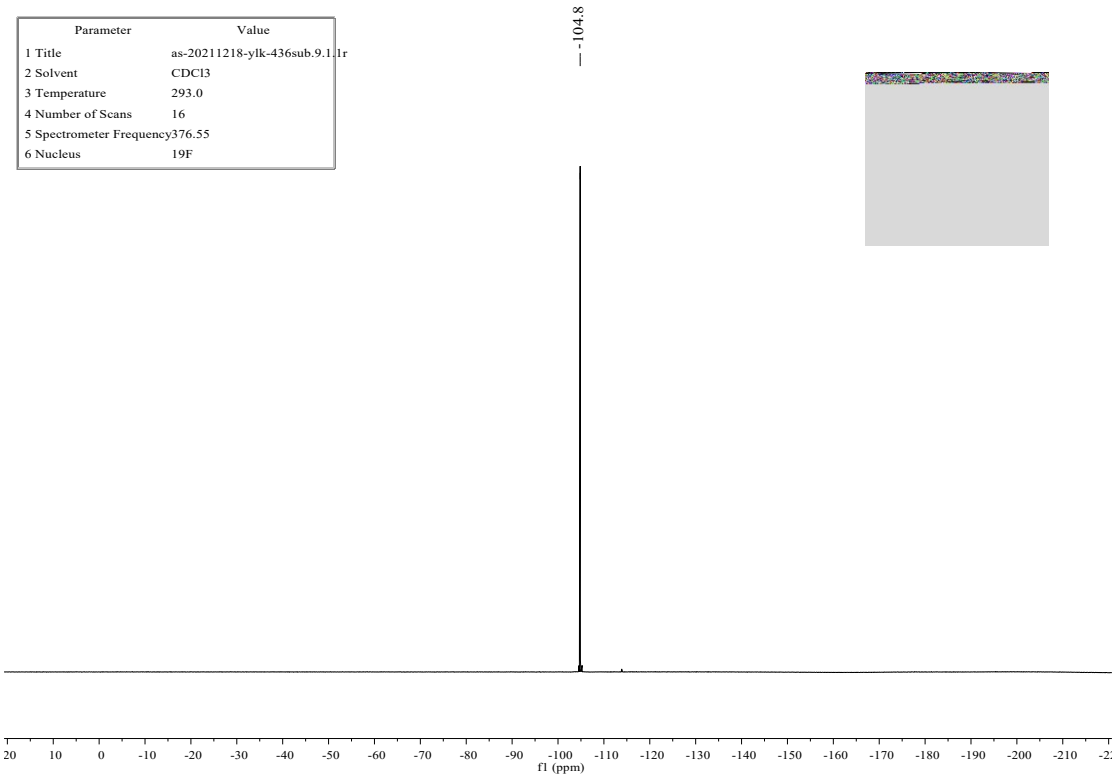
2 Solvent	CDCl3
3 Temperature	293.4
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C



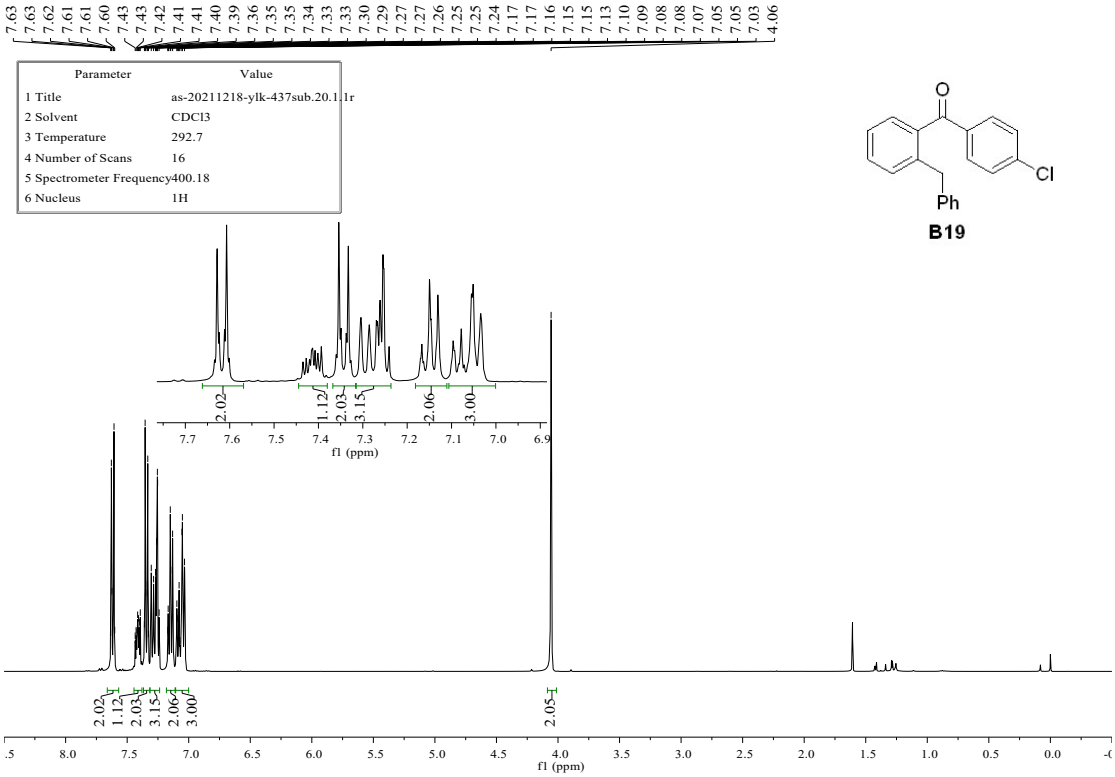
B18

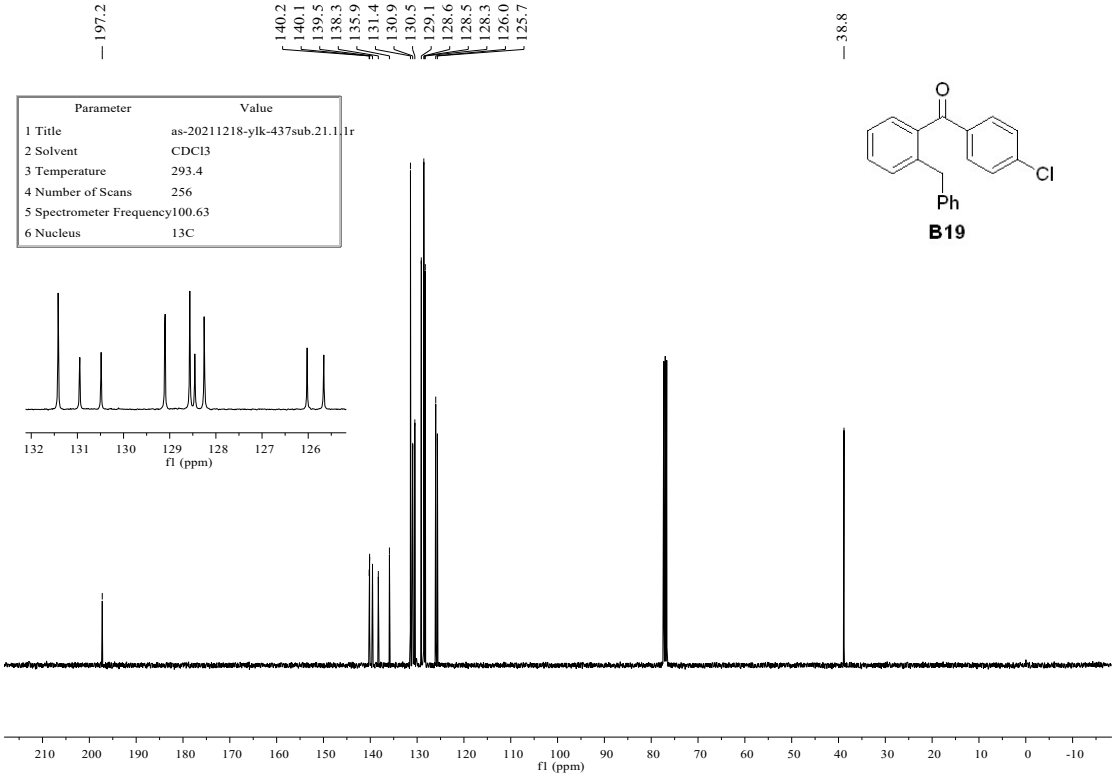


Parameter	Value
1 Title	as-20211218-ylk-436sub.9.1.1r
2 Solvent	CDCl3
3 Temperature	293.0
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

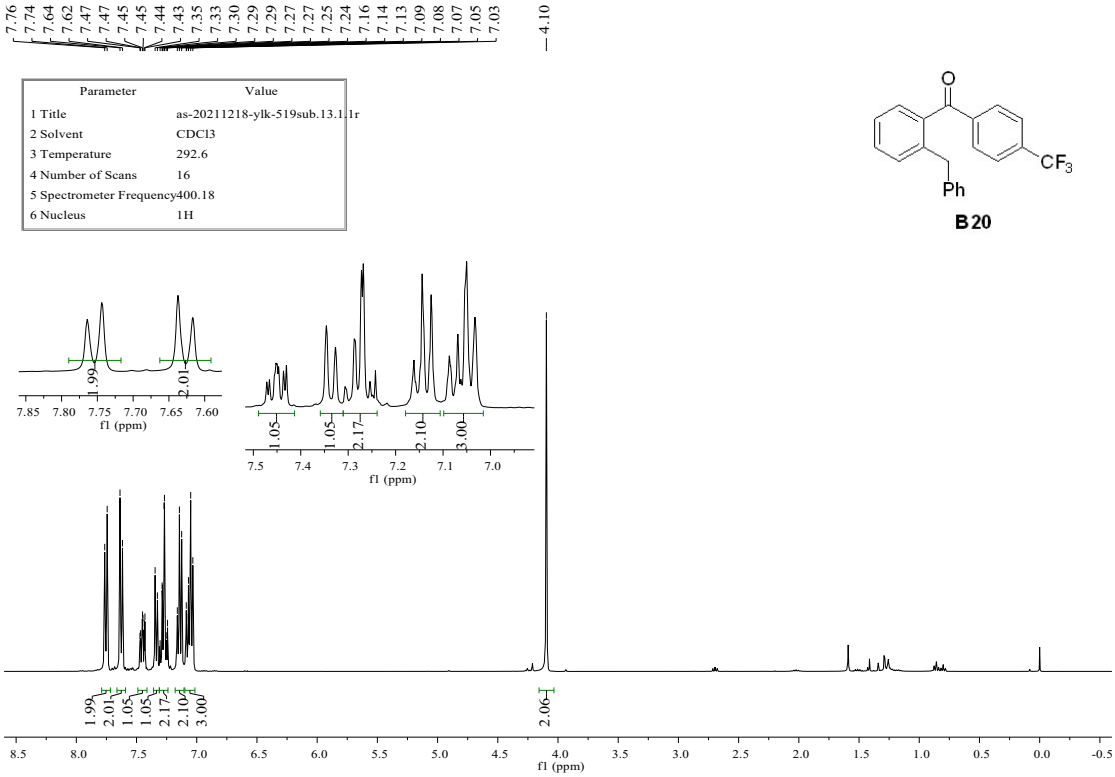


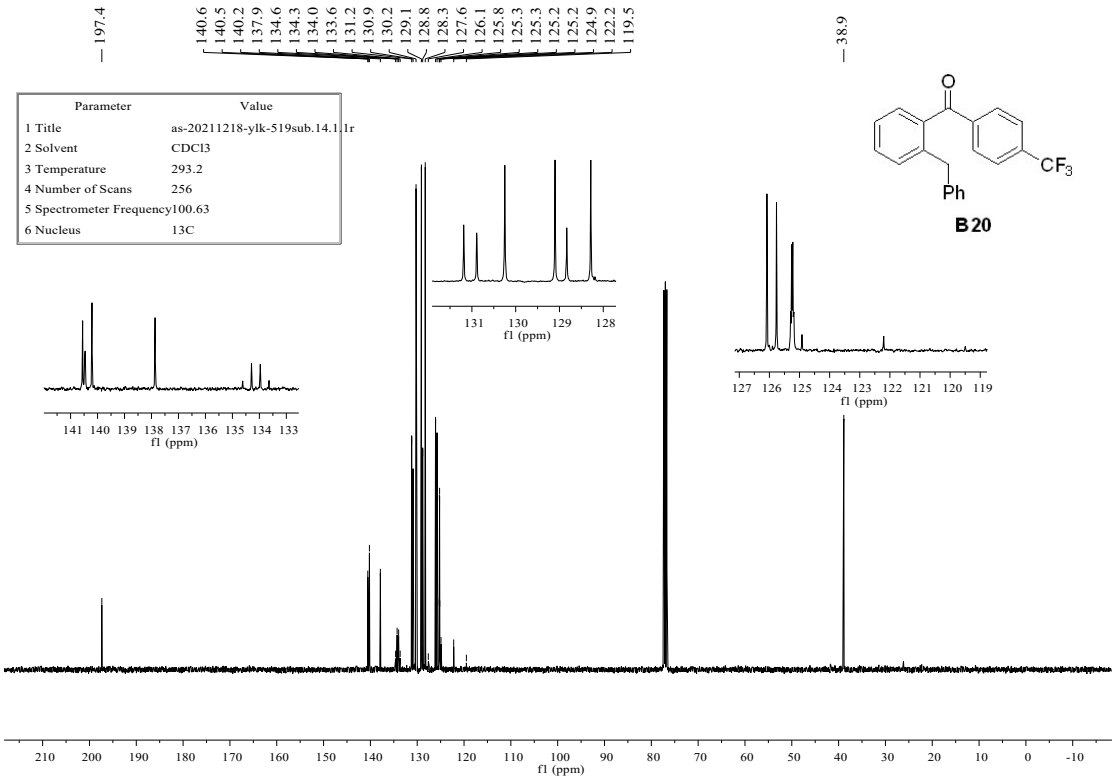
B19

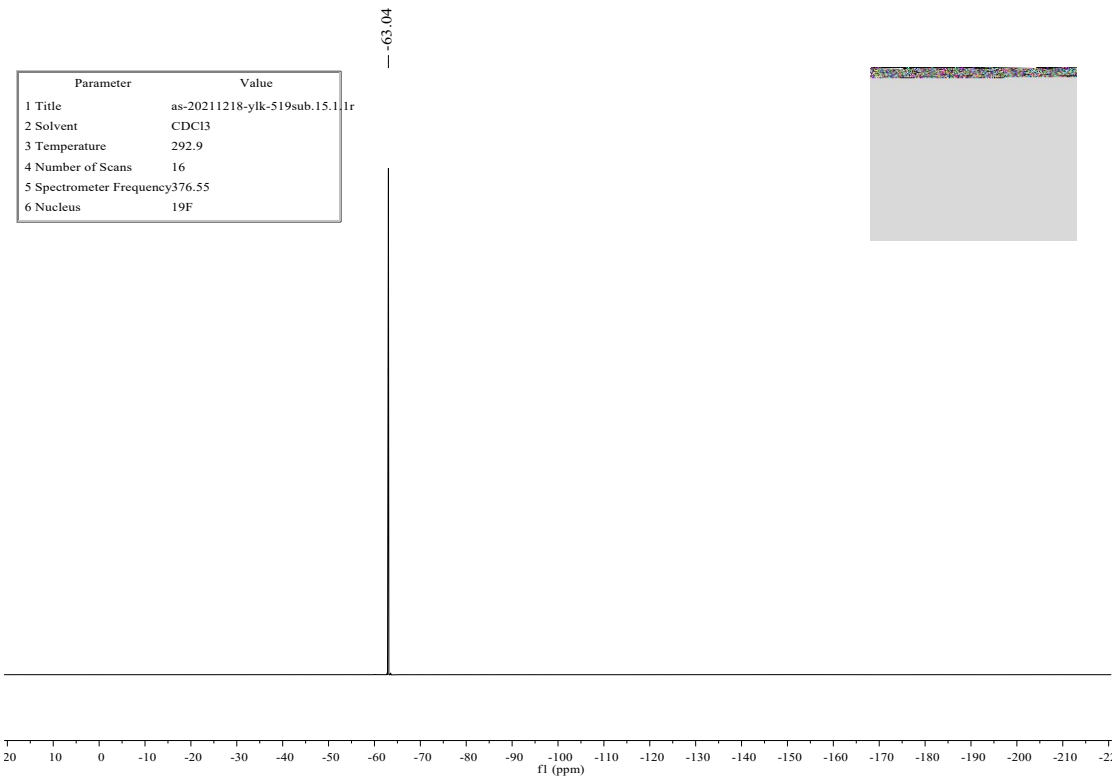

Parameter Value
1 Title as-20211218-ylk-437sub.20.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Cl
Ph
B19
f1 (ppm)


Parameter Value
1 Title as-20211218-ylk-437sub.21.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
Cl
Ph
B19
f1 (ppm)

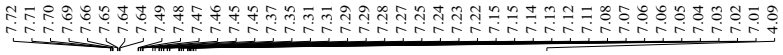
B20


7.76 7.74 7.64 7.62 7.47 7.47 7.45 7.45 7.44 7.43 7.35 7.33 7.30 7.29 7.29 7.27 7.27 7.25 7.24 7.16 7.14 7.13 7.09 7.08 7.07 7.05 7.03
4.10
Parameter Value
1 Title as-20211218-ylk-519sub.13.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
CF3
Ph
B20
1.99 2.01
1.05 1.05 2.17 2.10 3.00
f1 (ppm)
1.99 2.01 1.05 1.05 2.17 2.10 3.00 2.06
f1 (ppm)

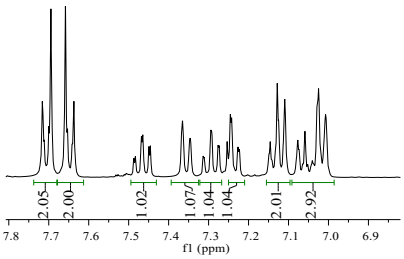

197.4
140.6 140.5 140.2 137.9 134.6 134.3 134.0 133.6 131.2 130.9 130.2 129.1 128.8 128.3 127.6 126.1 125.8 125.3 125.3 125.2 125.2 124.9 122.2 119.5
38.9
Parameter Value
1 Title as-20211218-ylk-519sub.14.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
CF3
Ph
B20
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)

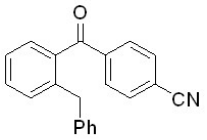

-63.04
Parameter Value
1 Title as-20211218-ylk-519sub.15.1.1r
2 Solvent CDCl3
3 Temperature 292.9
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

B21

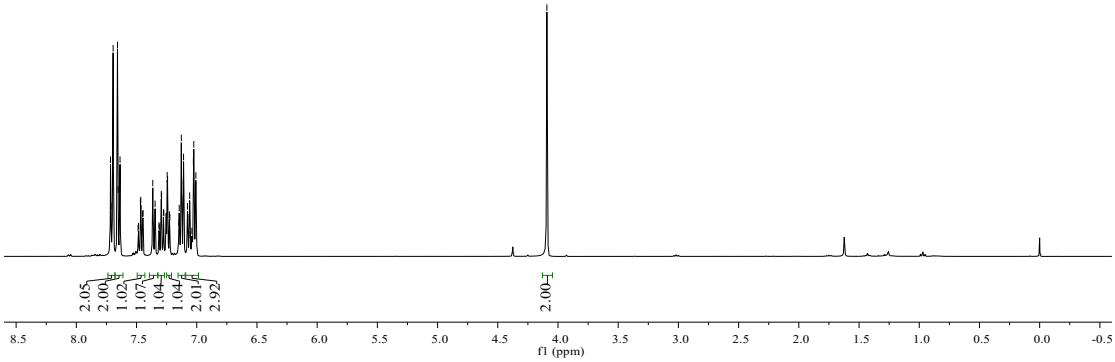


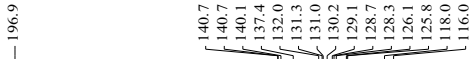
Parameter	Value
1 Title	as-20211218-ylk-540sub.27.1.1r
2 Solvent	CDCl3
3 Temperature	292.6
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H



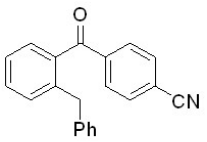


B21

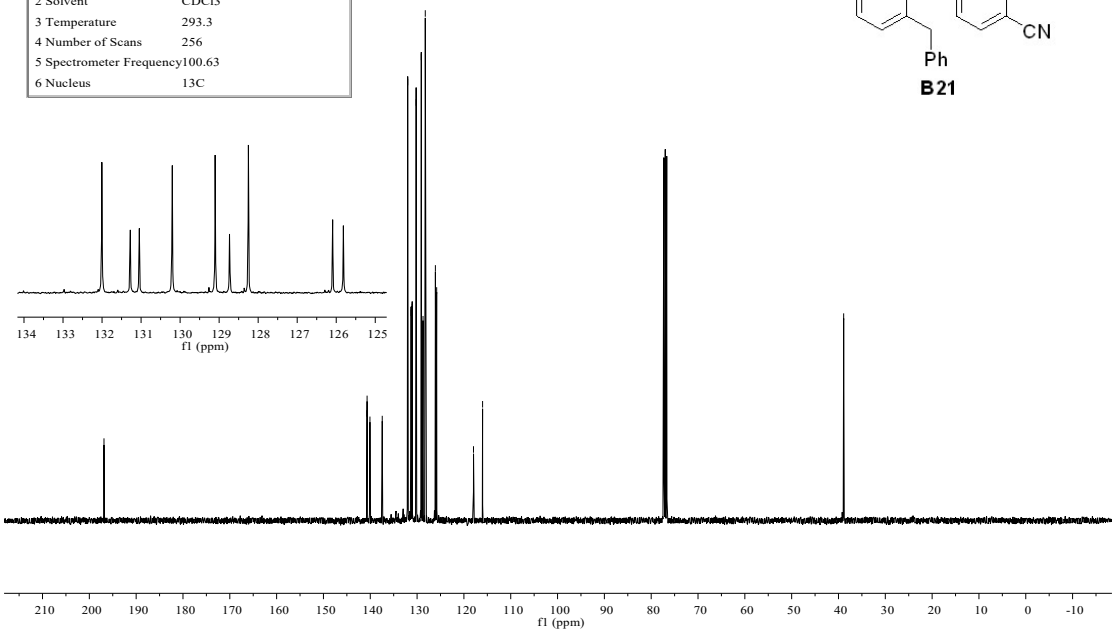




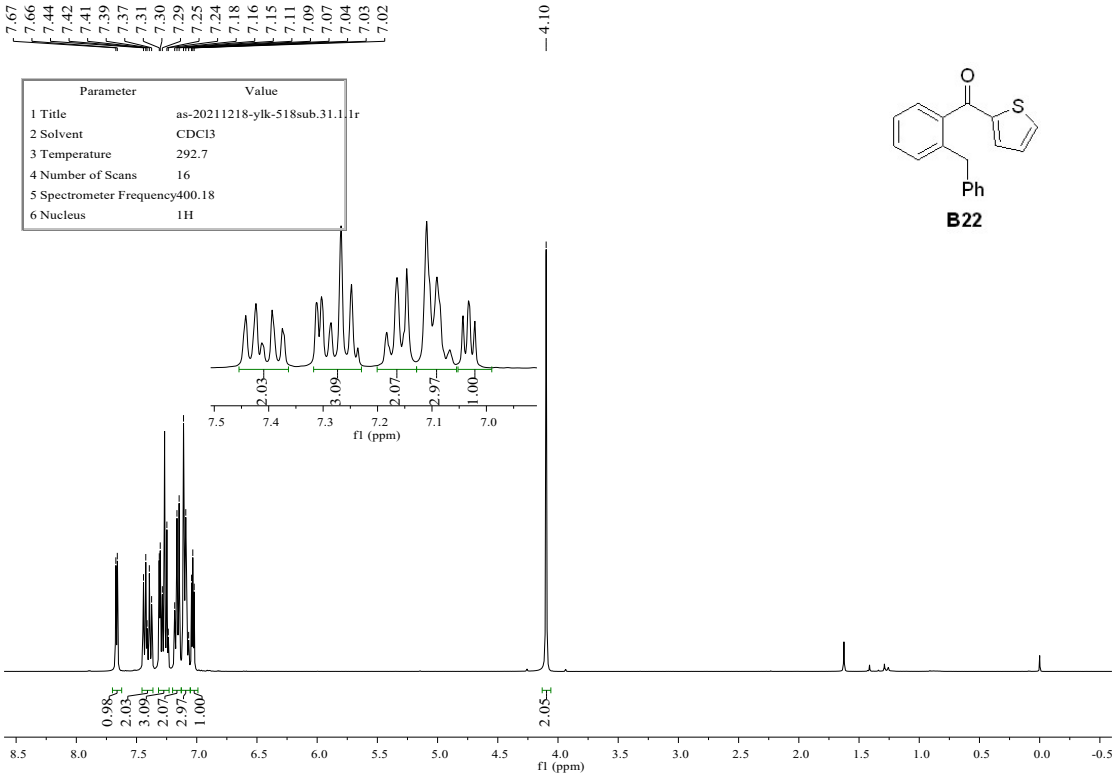
Parameter	Value
1 Title	as-20211218-ylk-540sub.28.1.1r
2 Solvent	CDCl3
3 Temperature	293.3
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

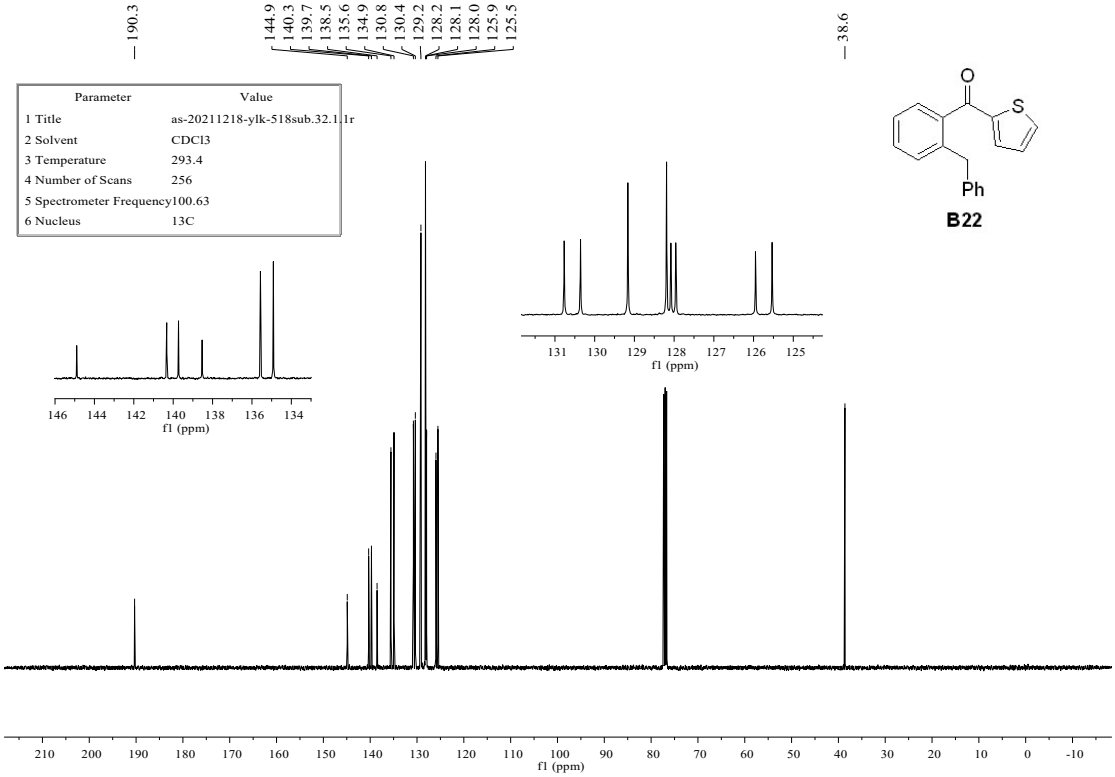


B21

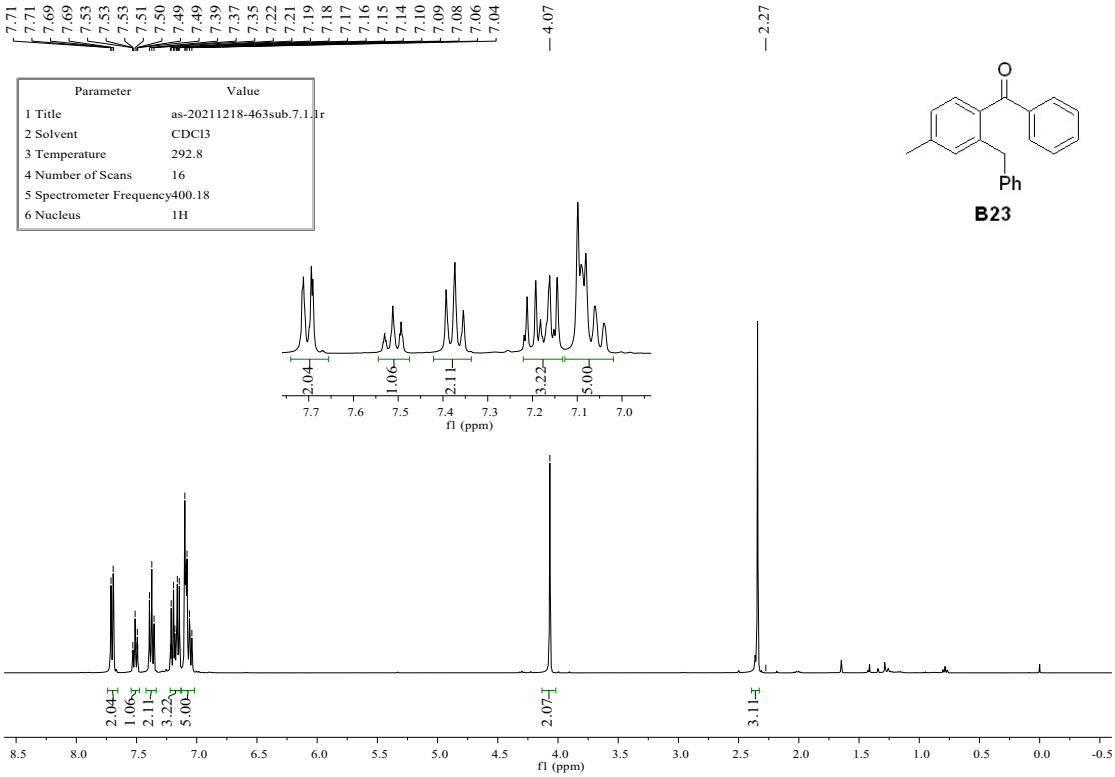


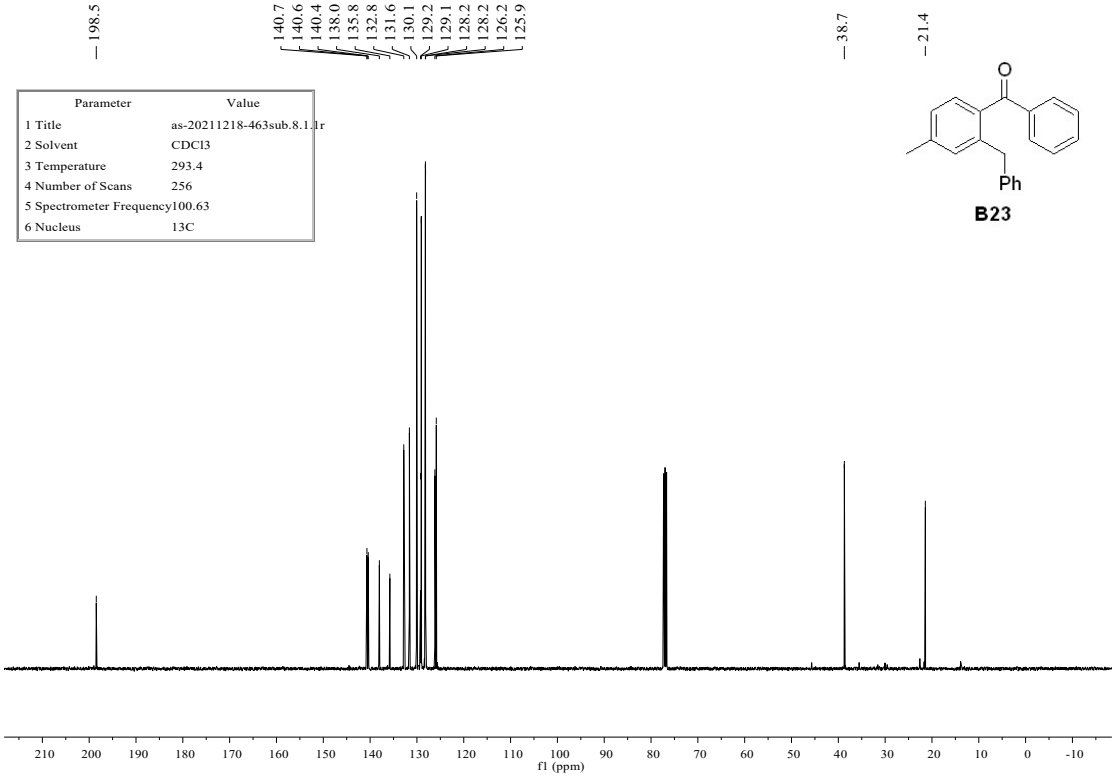
B22


7.67 7.66 7.44 7.42 7.41 7.39 7.37 7.31 7.30 7.29 7.25 7.24 7.18 7.16 7.15 7.11 7.09 7.07 7.04 7.03 7.02
4.10
Parameter Value
1 Title as-20211218-ylk-518sub.31.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
S
Ph
B22
2.03 3.09 2.07 2.97 1.00
f1 (ppm)
0.98 2.03 3.09 2.07 2.97 1.00 2.05
f1 (ppm)

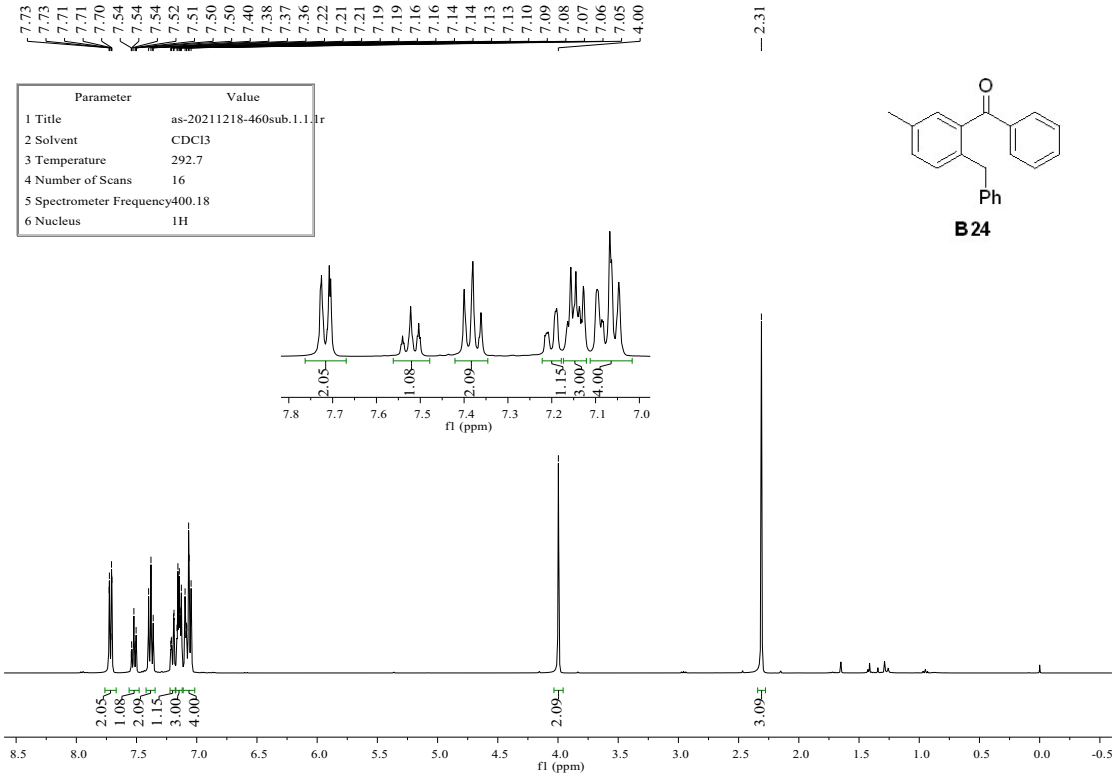

190.3
144.9 140.3 139.7 138.5 135.6 134.9 130.8 130.4 129.2 128.2 128.1 128.0 125.9 125.5
38.6
Parameter Value
1 Title as-20211218-ylk-518sub.32.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
S
Ph
B22
f1 (ppm)
f1 (ppm)
f1 (ppm)

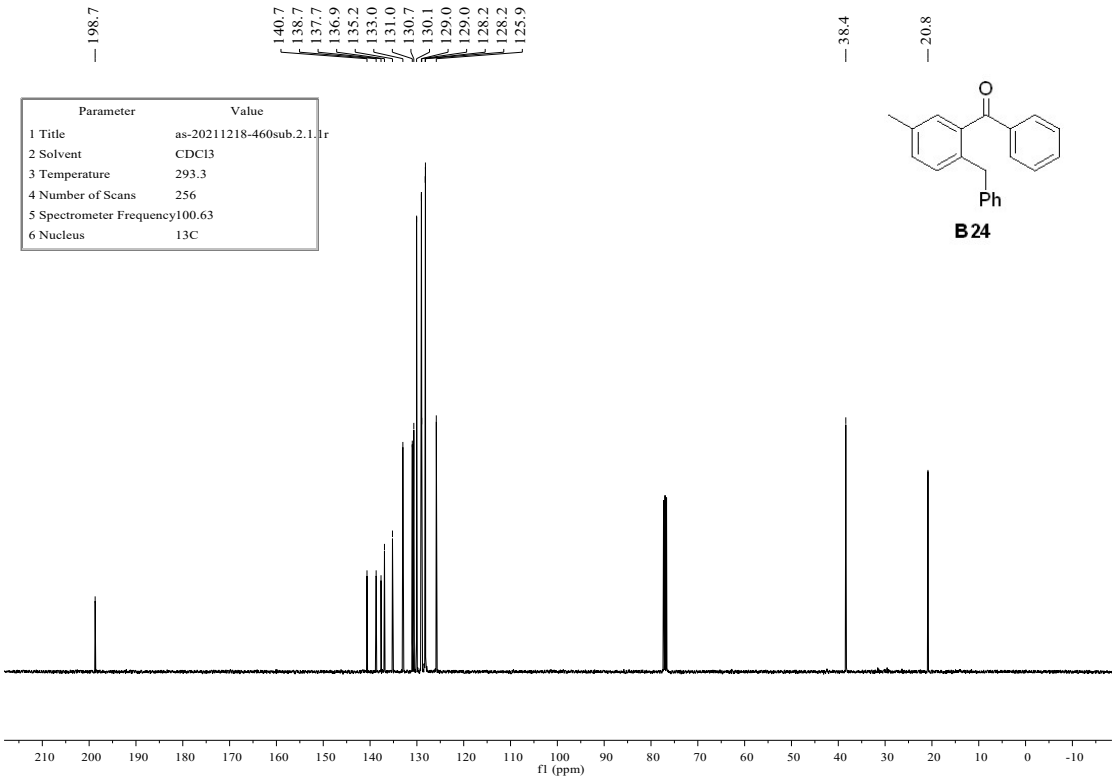
B23


7.71 7.71 7.69 7.69 7.53 7.53 7.51 7.50 7.49 7.49 7.39 7.37 7.35 7.22 7.21 7.19 7.18 7.17 7.16 7.15 7.14 7.10 7.09 7.08 7.06 7.04
4.07
2.27
Parameter Value
1 Title as-20211218-463sub.7.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
Ph
B23
2.04 1.06 2.11 3.22 5.00
f1 (ppm)
2.04 1.06 2.11 3.22 5.00 2.07 3.11
f1 (ppm)

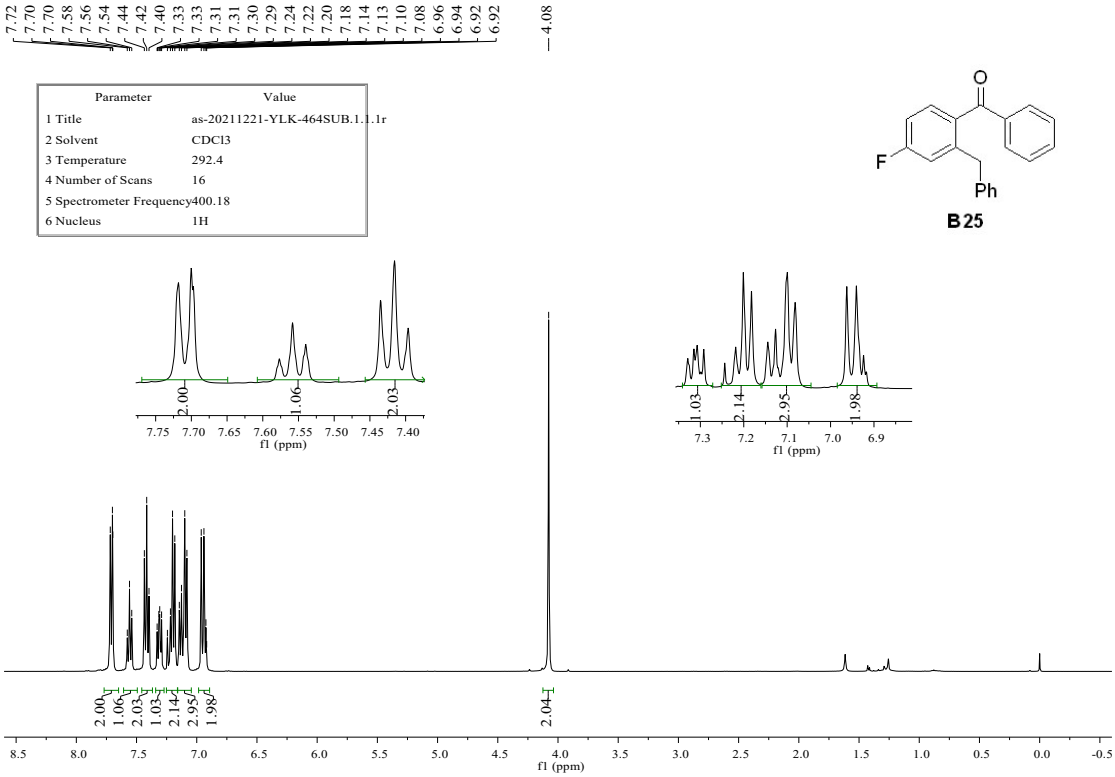

198.5
140.7 140.6 140.4 138.0 135.8 132.8 131.6 130.1 129.2 129.1 128.2 128.2 126.2 125.9
38.7
21.4
Parameter Value
1 Title as-20211218-463sub.8.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
Ph
B23
f1 (ppm)

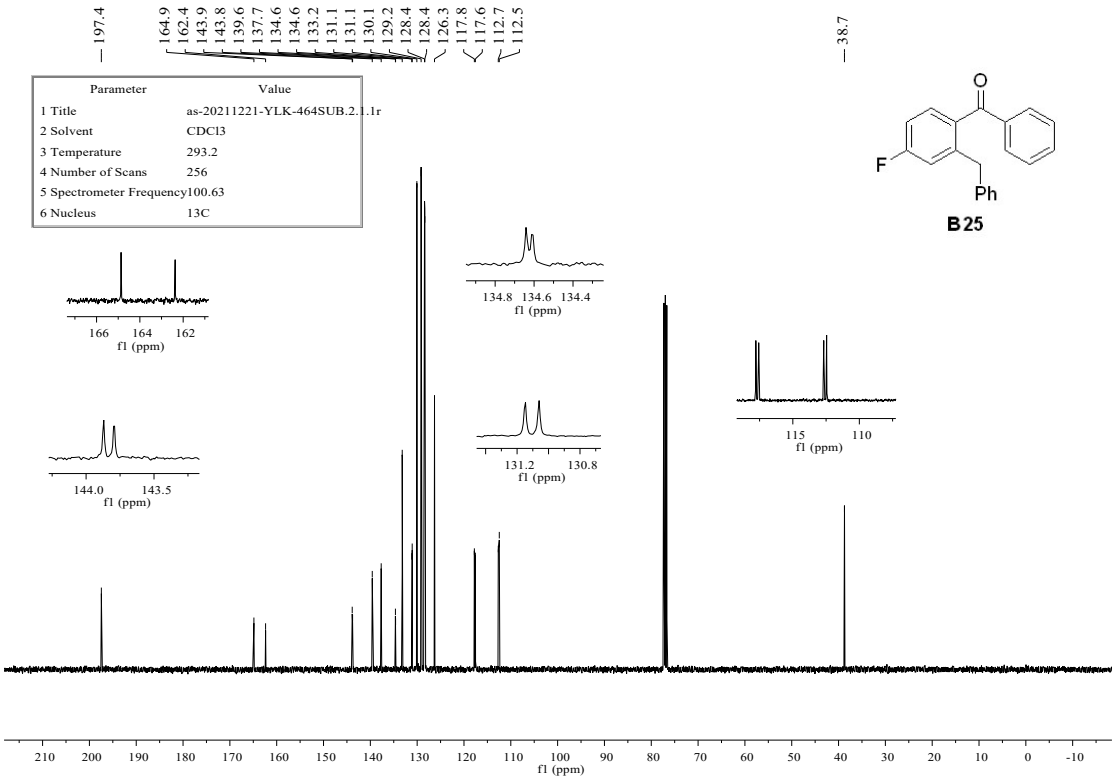
B24


7.73 7.73 7.71 7.71 7.70 7.54 7.54 7.54 7.52 7.51 7.50 7.50 7.40 7.38 7.37 7.36 7.22 7.21 7.21 7.19 7.19 7.16 7.16 7.14 7.14 7.13 7.13 7.10 7.09 7.08 7.07 7.06 7.05 4.00
2.31
Parameter Value
1 Title as-20211218-460sub.1.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
Ph
B24
2.05 1.08 2.09 1.15 3.00 4.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.05 1.08 2.09 1.15 3.00 4.00 2.09 3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

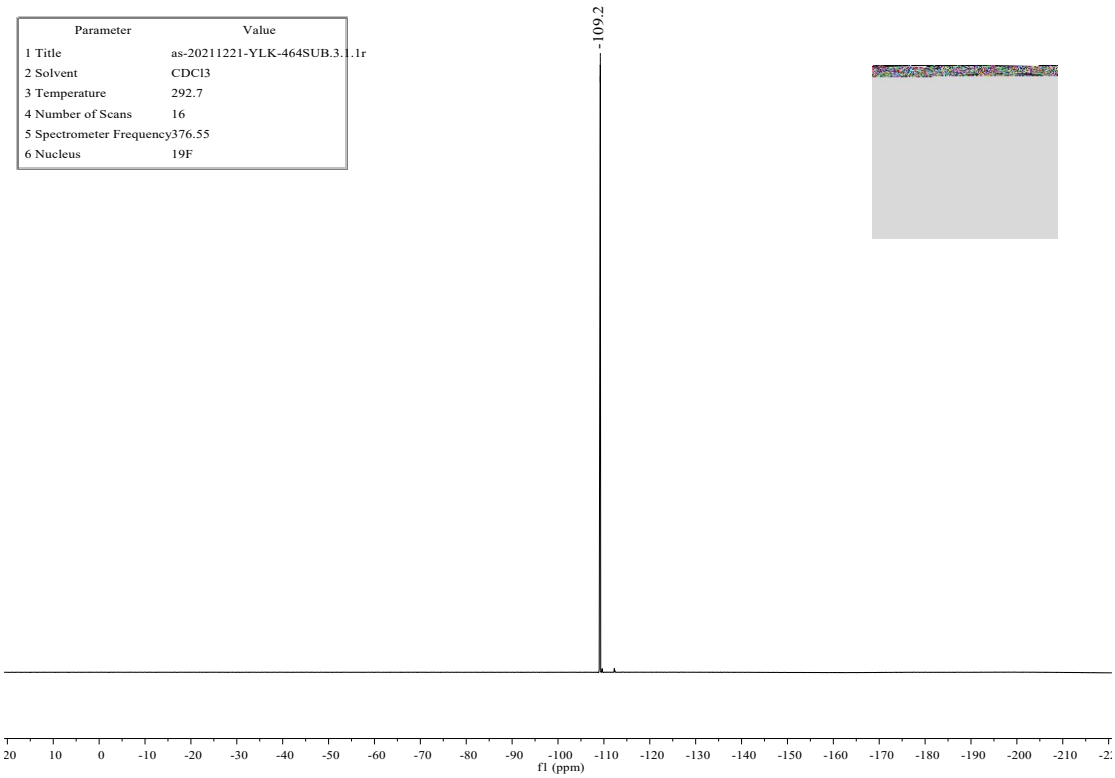

198.7
140.7 138.7 137.7 136.9 135.2 133.0 131.0 130.7 130.1 129.0 129.0 128.2 128.2 125.9
38.4
20.8
Parameter Value
1 Title as-20211218-460sub.2.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
Ph
B24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

B25

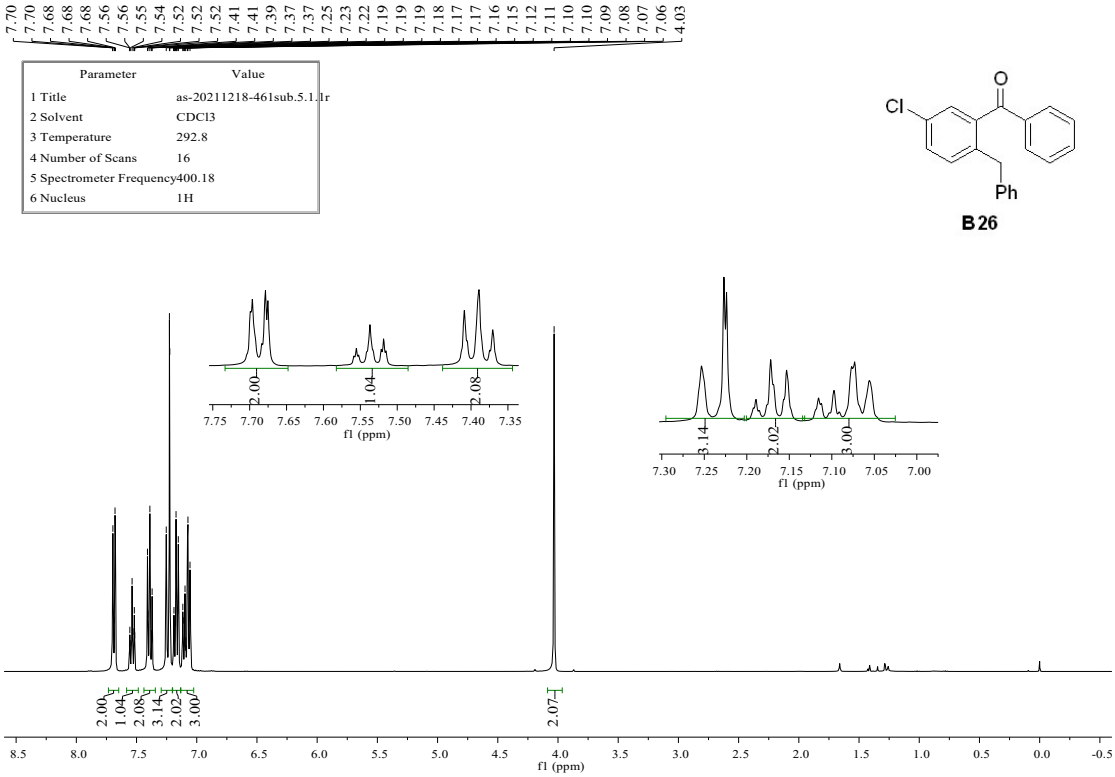

7.72 7.70 7.70 7.58 7.56 7.54 7.44 7.42 7.40 7.33 7.33 7.31 7.31 7.30 7.29 7.24 7.22 7.20 7.18 7.14 7.13 7.10 7.08 6.96 6.94 6.92 6.92
4.08
Parameter Value
1 Title as-20211221-YLK-464SUB.1.1.1r
2 Solvent CDCl3
3 Temperature 292.4
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
F
Ph
B25
2.00 1.06 2.03
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
f1 (ppm)
1.03 2.14 2.95 1.98
7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.00 1.06 2.03 1.03 2.14 2.95 1.98
2.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

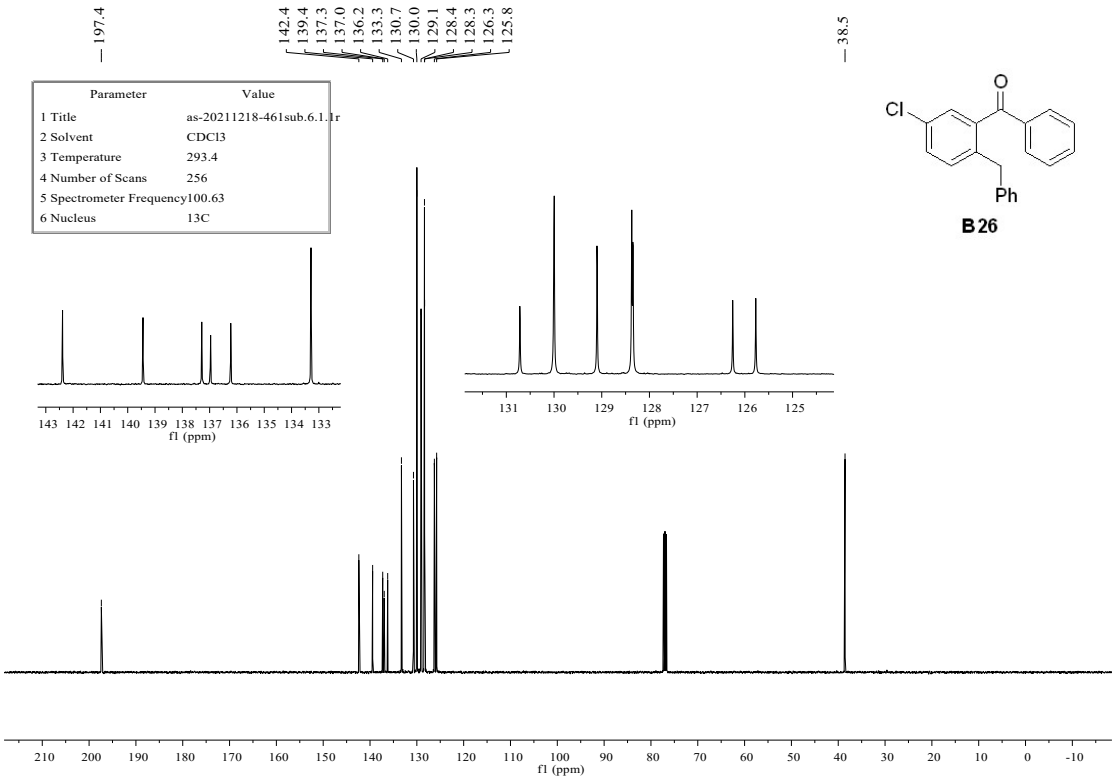

197.4
164.9 162.4 143.9 143.8 139.6 137.7 134.6 134.6 133.2 131.1 131.1 130.1 129.2 128.4 128.4 126.3 117.8 117.6 112.7 112.5
38.7
Parameter Value
1 Title as-20211221-YLK-464SUB.2.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
F
Ph
B25
166 164 162
f1 (ppm)
144.0 143.5
f1 (ppm)
134.8 134.6 134.4
f1 (ppm)
131.2 130.8
f1 (ppm)
115 110
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Title	as-20211221-YLK-464SUB.3.1.1r
2 Solvent	CDCl3
3 Temperature	292.7
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

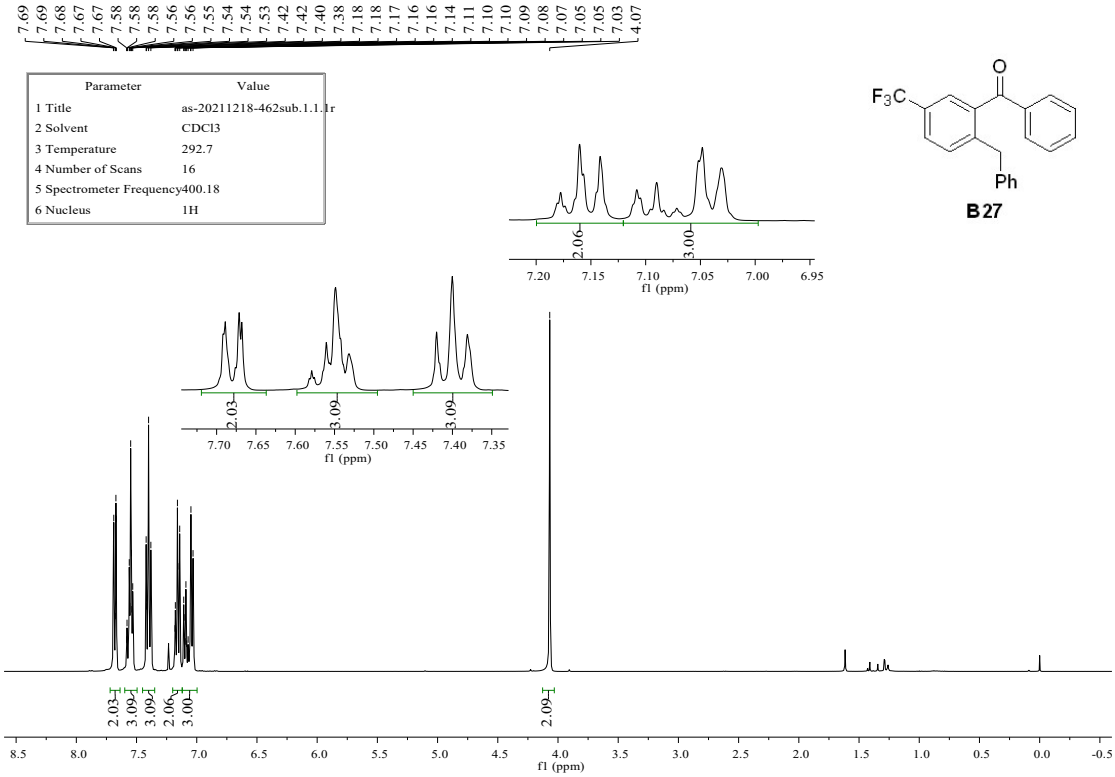


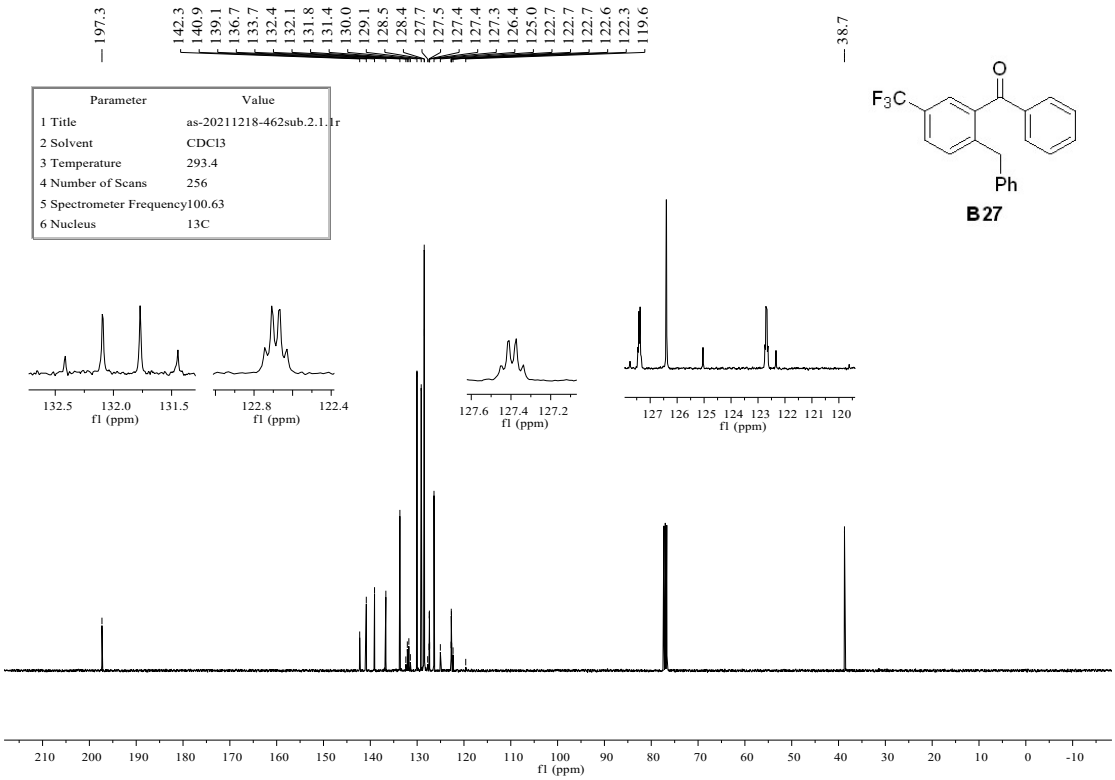
B26


7.70 7.70 7.68 7.68 7.68 7.56 7.56 7.55 7.54 7.52 7.52 7.52 7.41 7.41 7.39 7.37 7.37 7.25 7.23 7.22 7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.12 7.11 7.10 7.10 7.09 7.08 7.07 7.06 4.03
Parameter Value
1 Title as-20211218-461sub.5.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Cl
O
Ph
B26
2.00 1.04 2.08
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
3.14 2.02 3.00
7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
2.00 1.04 2.08 3.14 2.02 3.00
2.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

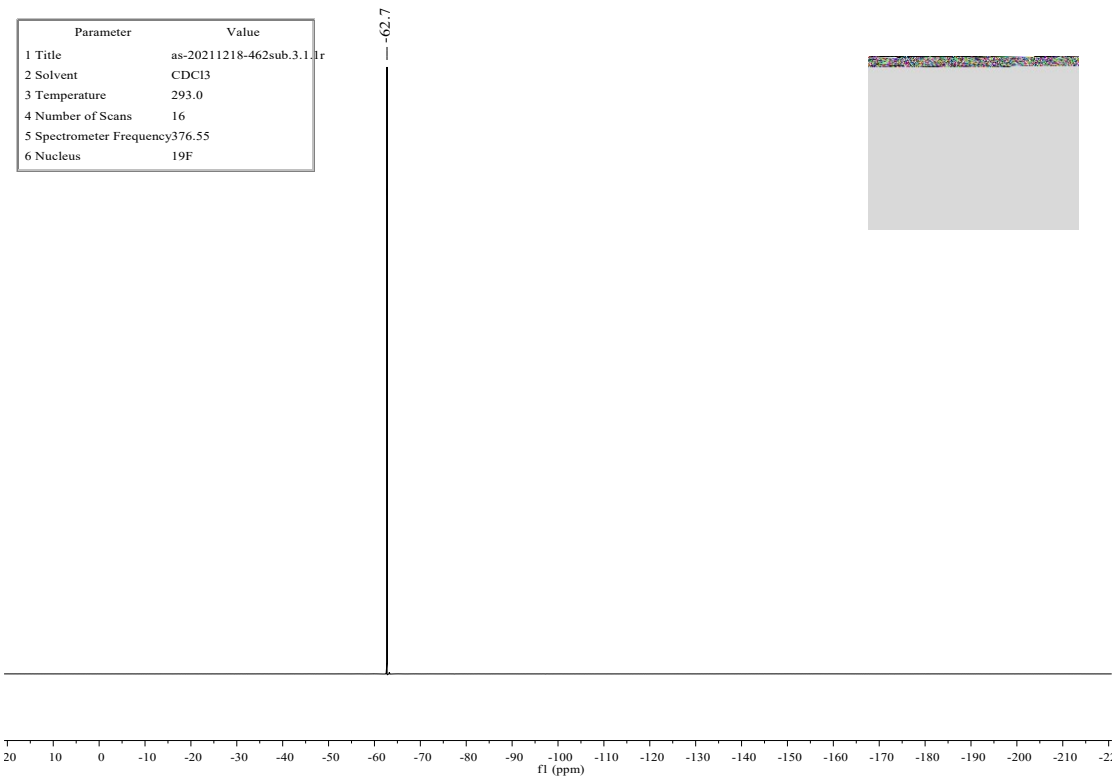

197.4
142.4 139.4 137.3 137.0 136.2 133.3 130.7 130.0 129.1 128.4 128.3 126.3 125.8
38.5
Parameter Value
1 Title as-20211218-461sub.6.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
Cl
O
Ph
B26
143 142 141 140 139 138 137 136 135 134 133
f1 (ppm)
131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

B27

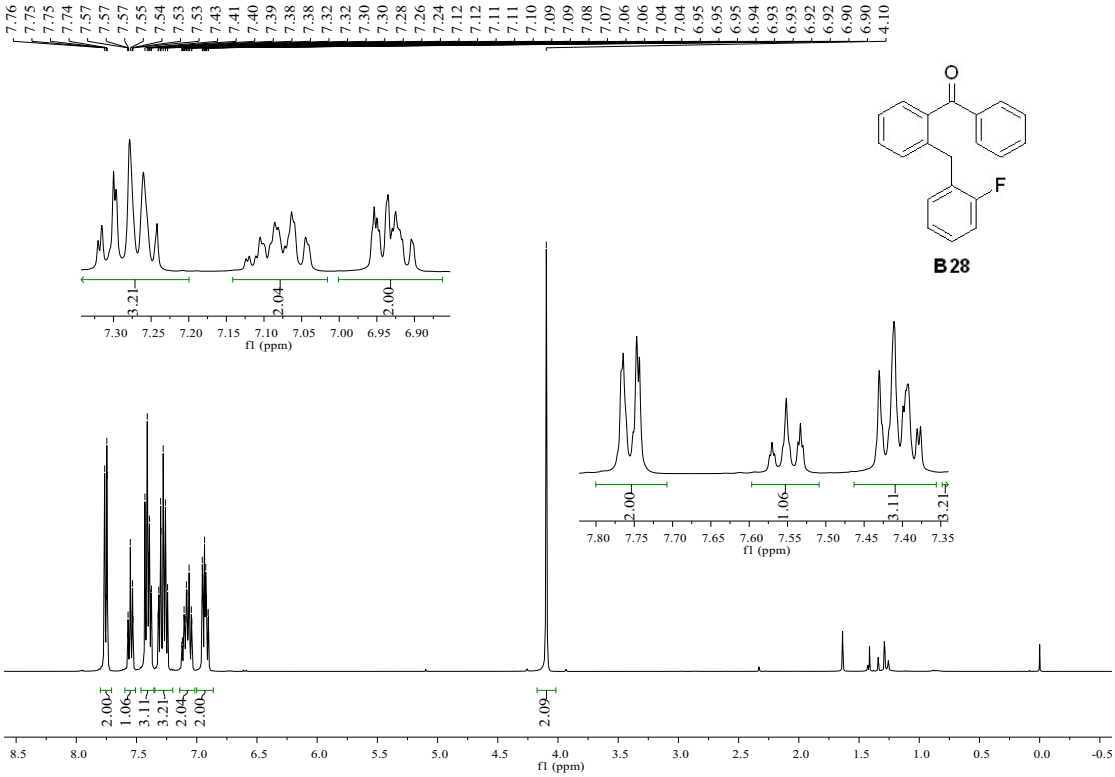

7.69 7.69 7.68 7.67 7.67 7.58 7.58 7.58 7.56 7.56 7.55 7.54 7.54 7.53 7.42 7.42 7.40 7.38 7.18 7.18 7.17 7.16 7.16 7.14 7.11 7.10 7.10 7.09 7.08 7.07 7.05 7.05 7.03 4.07
Parameter Value
1 Title as-20211218-462sub.1.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
F3C
O
Ph
B27
2.06
3.00
f1 (ppm)
2.03
3.09
3.09
f1 (ppm)
2.03
3.09
2.06
3.00
2.09
f1 (ppm)

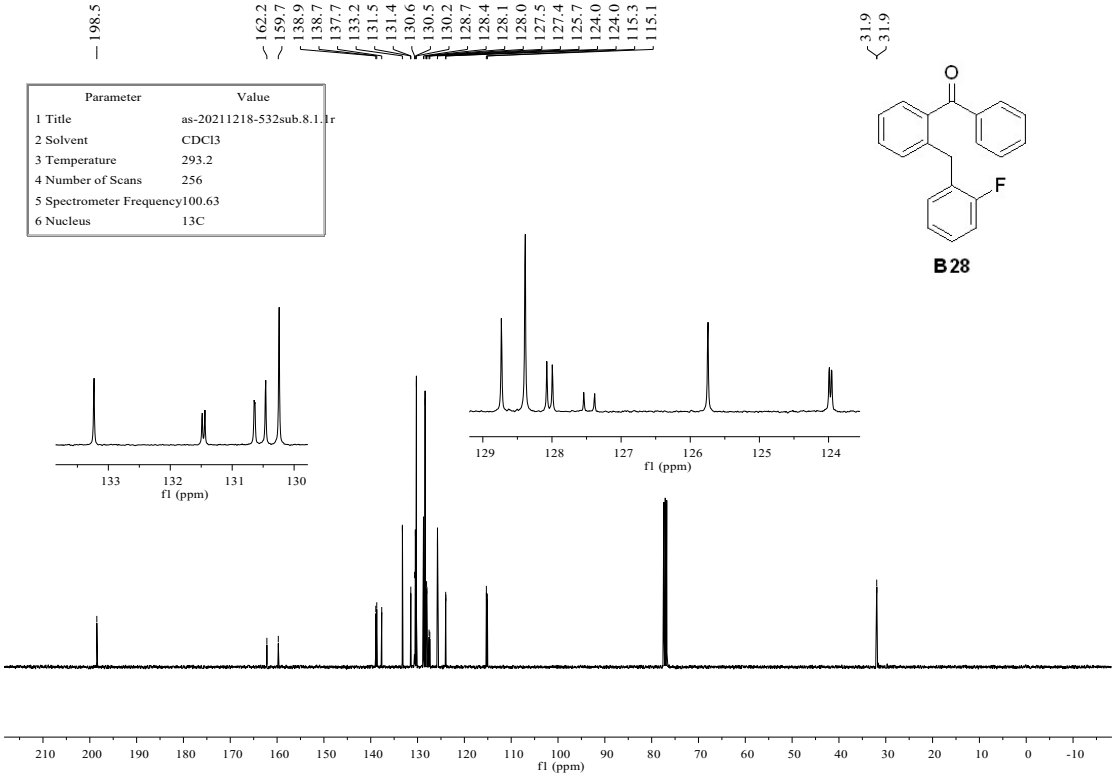

197.3
142.3 140.9 139.1 136.7 133.7 132.4 132.1 131.8 131.4 130.0 129.1 128.5 128.4 127.7 127.5 127.4 127.4 127.3 126.4 125.0 122.7 122.7 122.7 122.6 122.3 119.6
38.7
Parameter Value
1 Title as-20211218-462sub.2.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
F3C
O
Ph
B27
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	as-20211218-462sub.3.1.1r
2 Solvent	CDCl3
3 Temperature	293.0
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

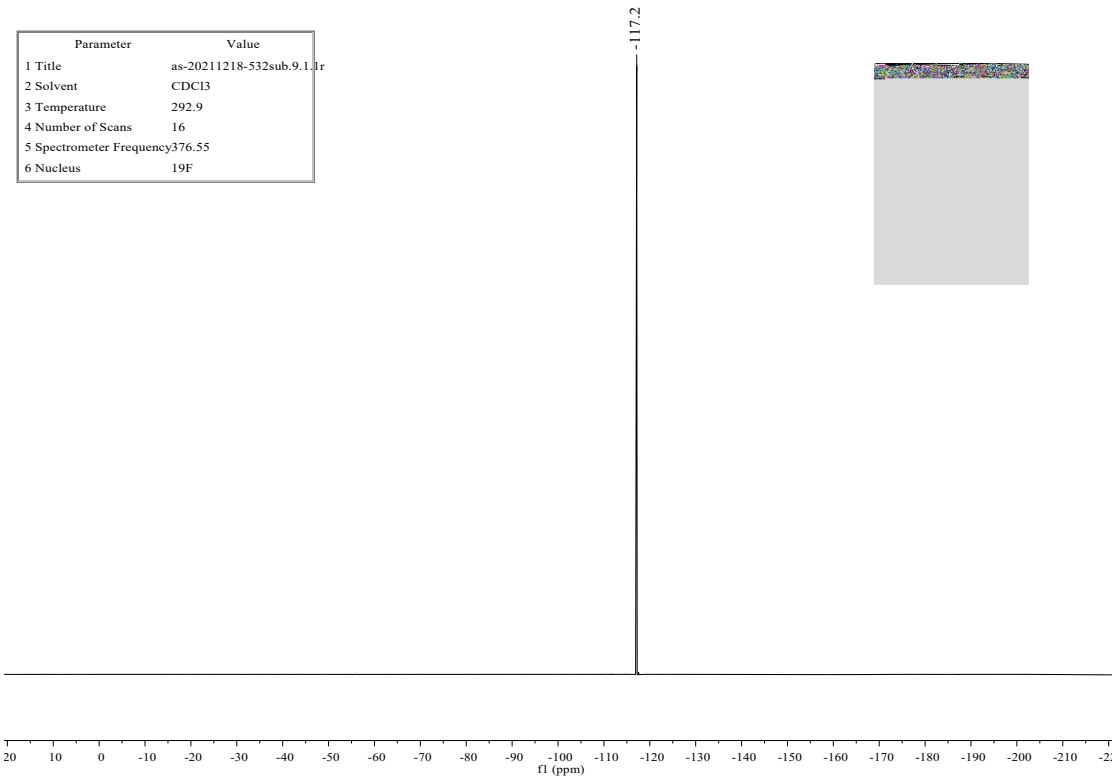


B28

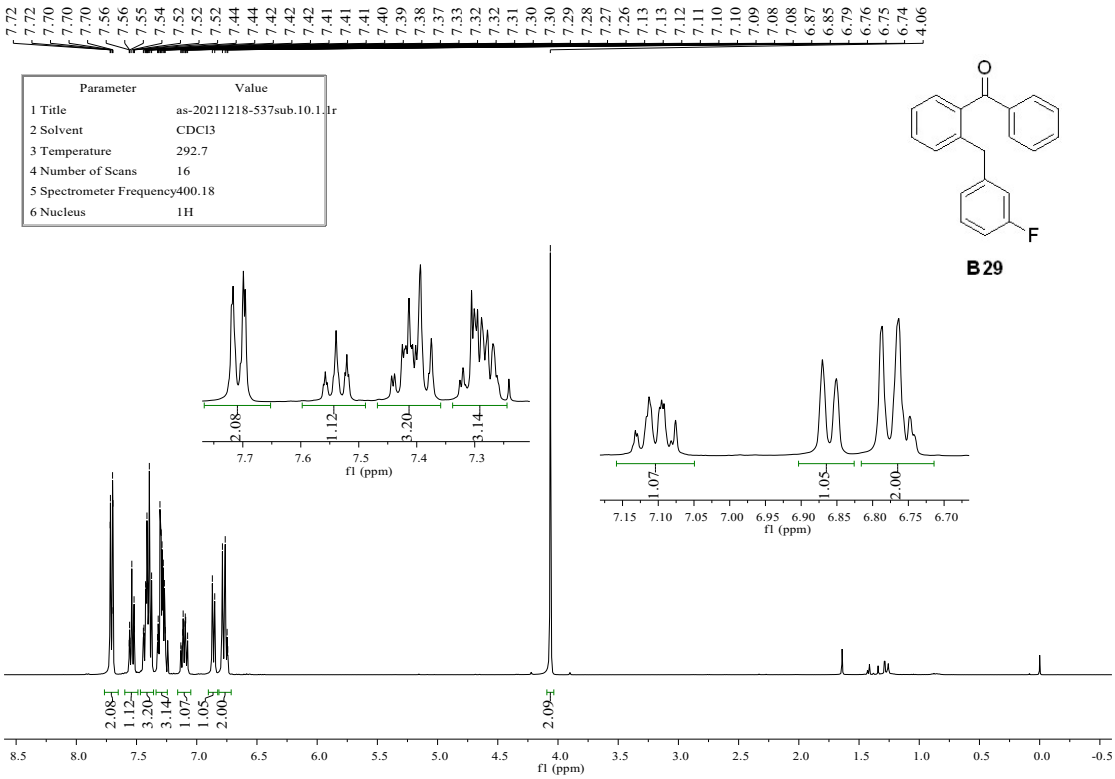

7.76 7.75 7.75 7.74 7.57 7.57 7.57 7.55 7.54 7.53 7.53 7.43 7.41 7.40 7.39 7.38 7.38 7.32 7.32 7.30 7.30 7.28 7.26 7.24 7.12 7.12 7.11 7.11 7.10 7.09 7.09 7.08 7.07 7.06 7.06 7.04 7.04 6.95 6.95 6.94 6.93 6.93 6.92 6.92 6.90 6.90 4.10
O
F
B28
3.21 2.04 2.00
7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)
2.00 1.06 3.11 3.21
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
2.00 1.06 3.11 3.21 2.04 2.00 2.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

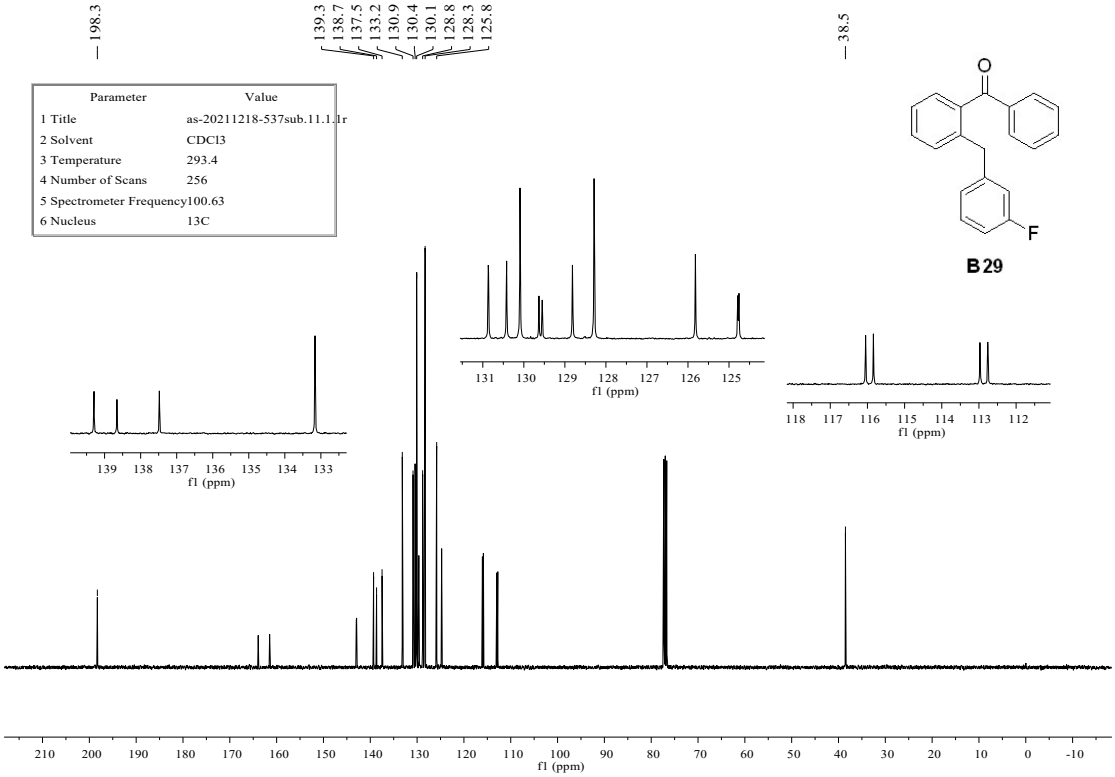

198.5
162.2 159.7 138.9 138.7 137.7 133.2 131.5 131.4 130.6 130.5 130.2 128.7 128.4 128.1 128.0 127.5 127.4 125.7 124.0 124.0 115.3 115.1
31.9 31.9
Parameter Value
1 Title as-20211218-532sub.8.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
F
B28
133 132 131 130
f1 (ppm)
129 128 127 126 125 124
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Title	as-20211218-532sub.9.1.1r
2 Solvent	CDCl3
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

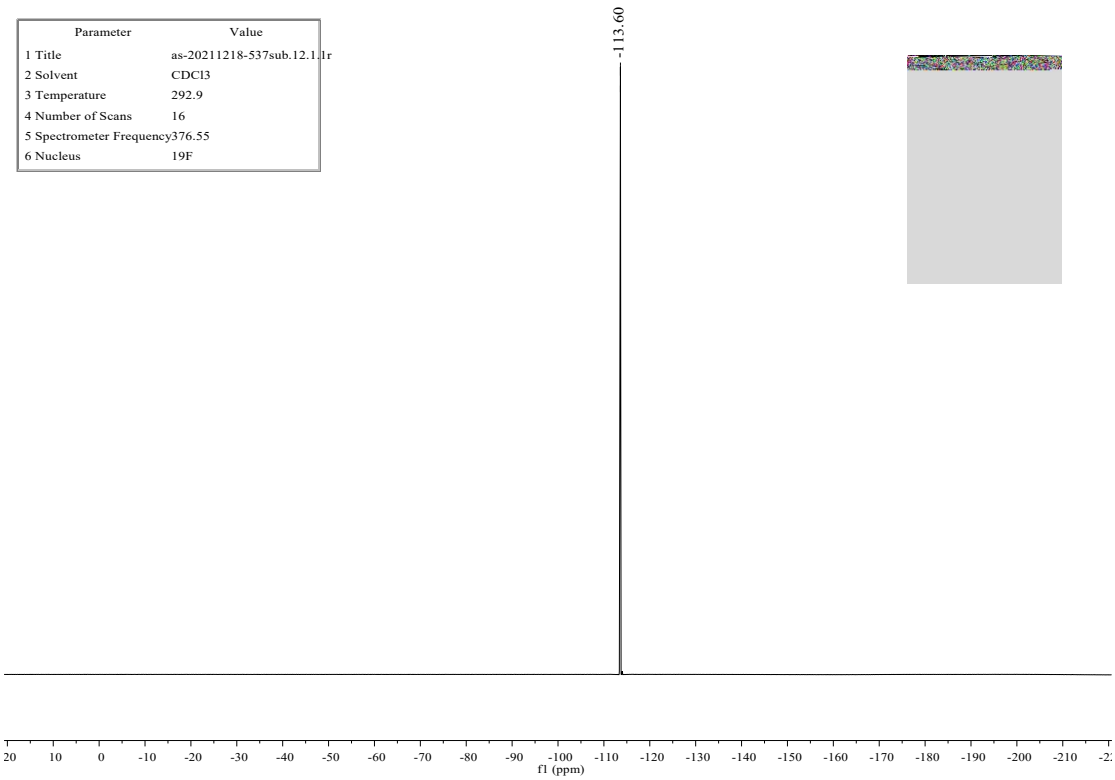


B29

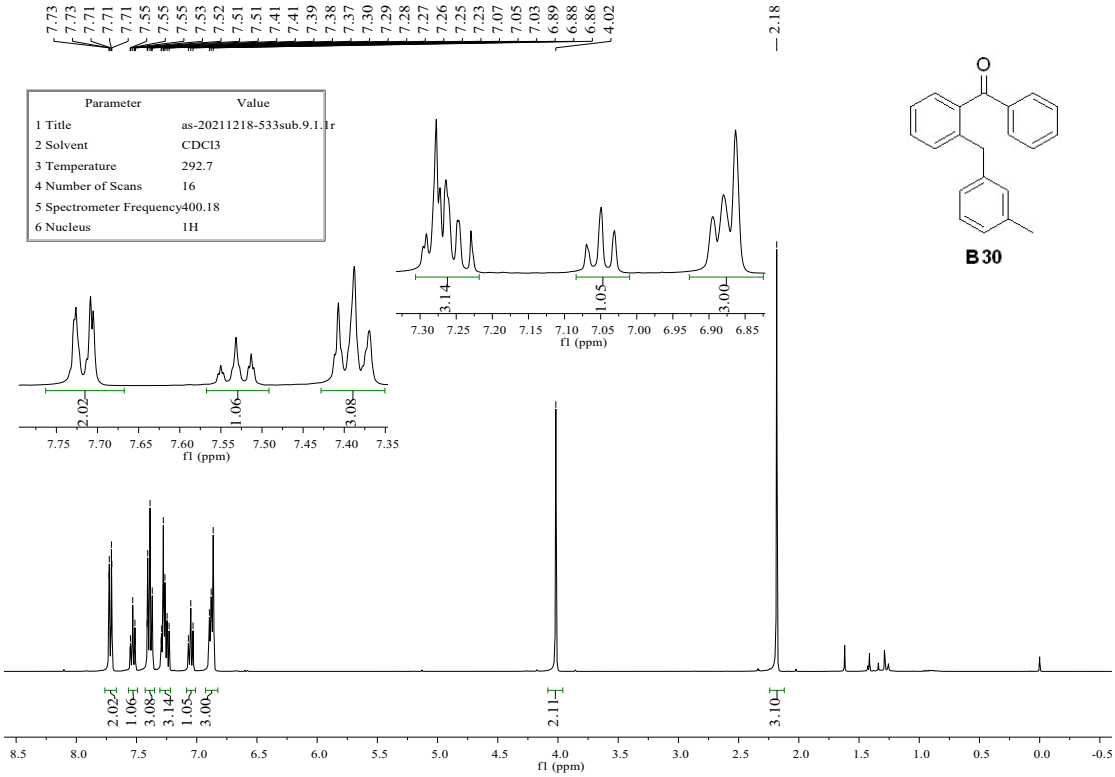

7.72 7.72 7.70 7.70 7.70 7.56 7.56 7.55 7.54 7.52 7.52 7.52 7.44 7.44 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.38 7.37 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.26 7.13 7.13 7.12 7.11 7.10 7.10 7.09 7.08 7.08 6.87 6.85 6.79 6.76 6.75 6.74 4.06
Parameter Value
1 Title as-20211218-537sub.10.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
F
B29
2.08 1.12 3.20 3.14
7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.07 1.05 2.00
7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (ppm)
2.08 1.12 3.20 3.14 1.07 1.05 2.00 2.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

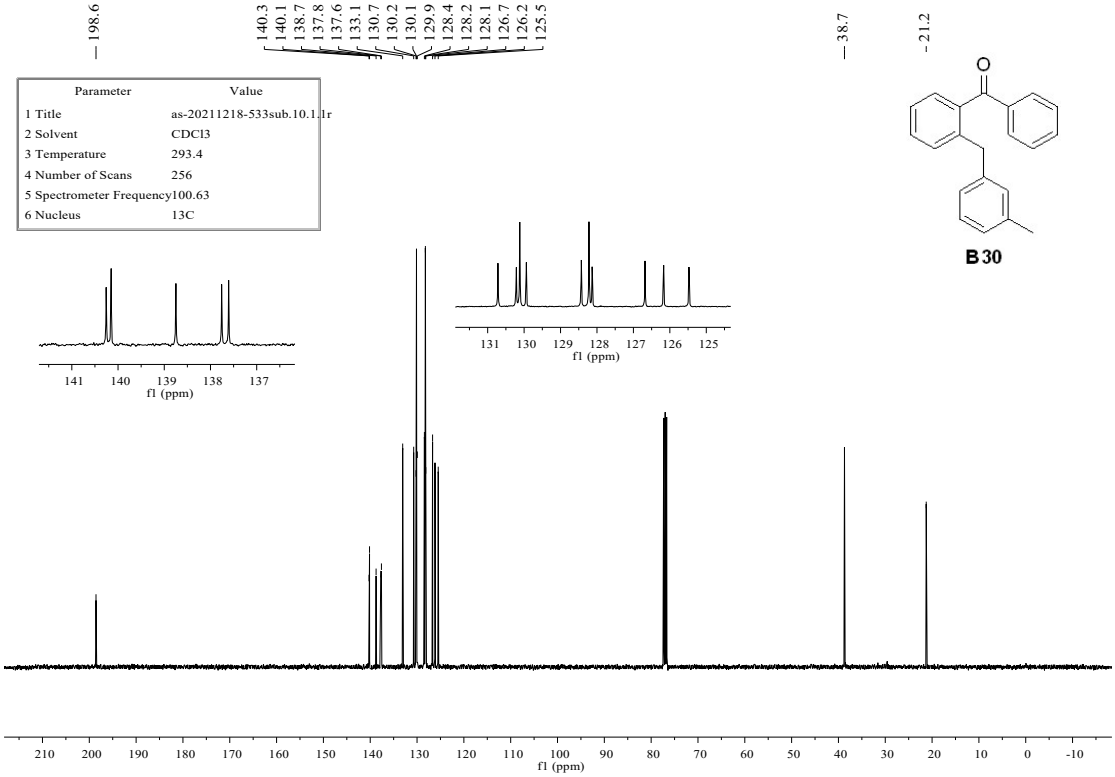

198.3
139.3 138.7 137.5 133.2 130.9 130.4 130.1 128.8 128.3 125.8
38.5
Parameter Value
1 Title as-20211218-537sub.11.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
F
B29
139 138 137 136 135 134 133
f1 (ppm)
131 130 129 128 127 126 125
f1 (ppm)
118 117 116 115 114 113 112
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Title	as-20211218-537sub.12.1.1r
2 Solvent	CDCl3
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

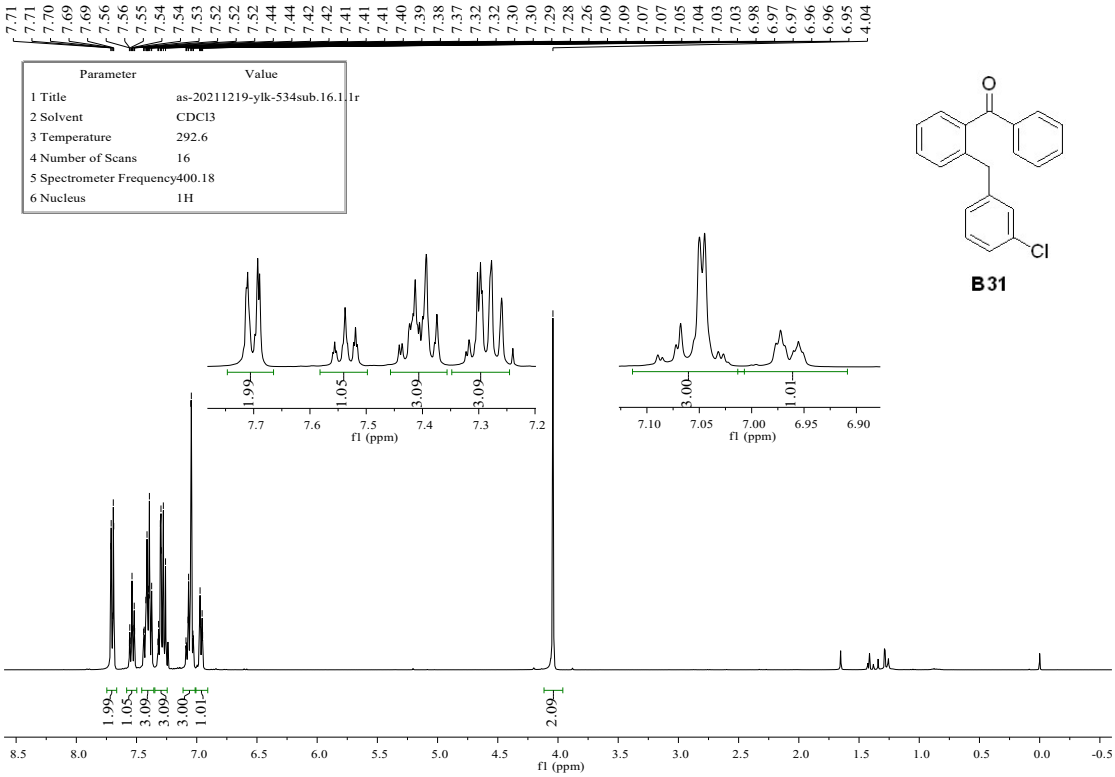


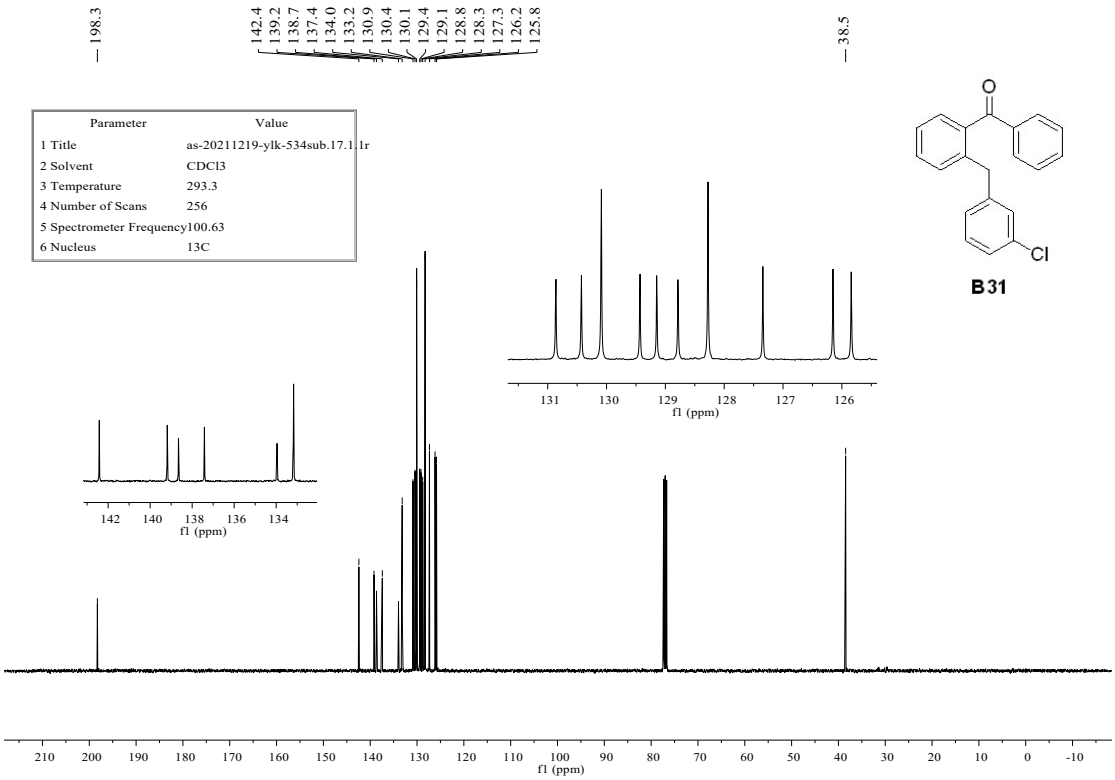
B30


7.73 7.73 7.71 7.71 7.71 7.55 7.55 7.55 7.53 7.52 7.51 7.51 7.41 7.41 7.39 7.38 7.37 7.30 7.29 7.28 7.27 7.26 7.25 7.23 7.07 7.05 7.03 6.89 6.88 6.86 4.02
2.18
Parameter Value
1 Title as-20211218-533sub.9.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
B30
f1 (ppm)
2.02 1.06 3.08 3.14 1.05 3.00 2.11 3.10

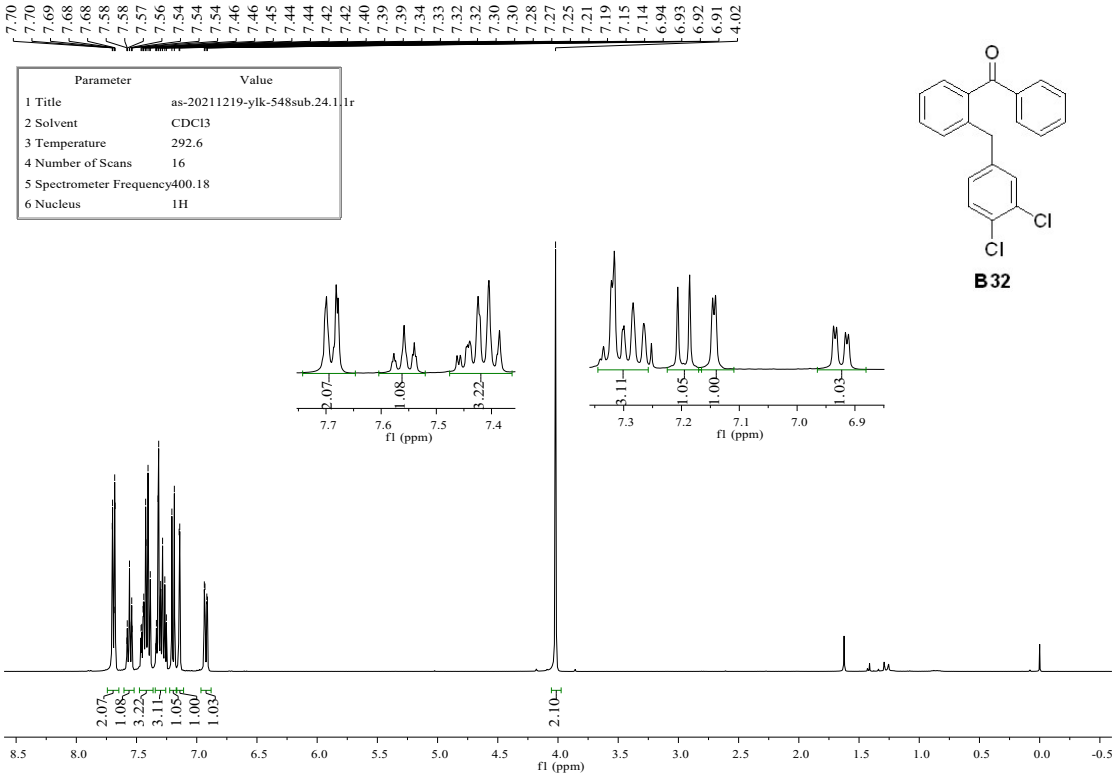

198.6
140.3 140.1 138.7 137.8 137.6 133.1 130.7 130.2 130.1 129.9 128.4 128.2 128.1 126.7 126.2 125.5
38.7
21.2
Parameter Value
1 Title as-20211218-533sub.10.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
B30
f1 (ppm)

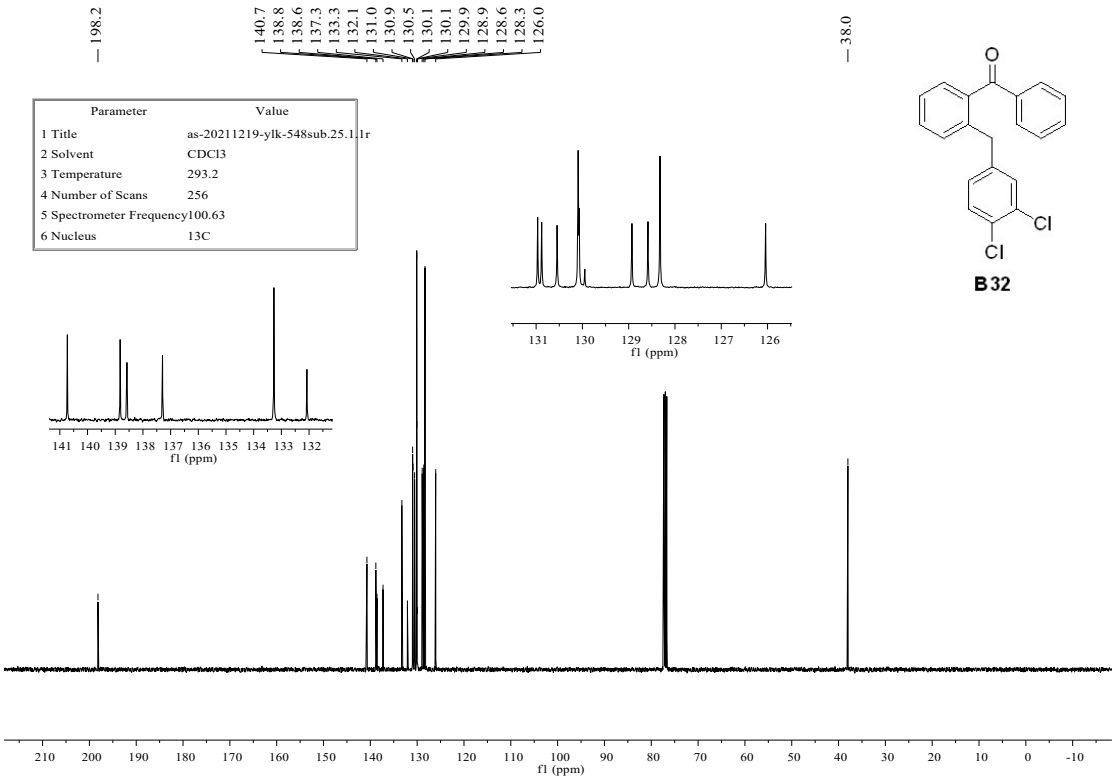
B31


Parameter Value
1 Title as-20211219-ylk-534sub.16.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
B31
f1 (ppm)

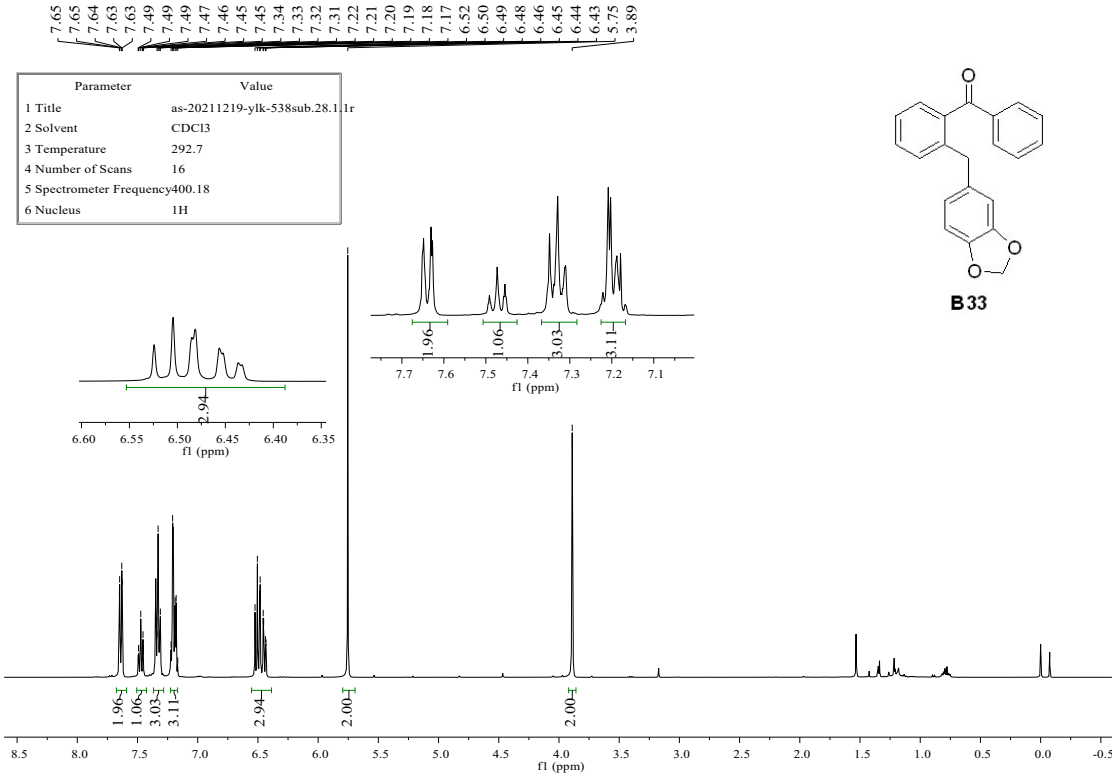

Parameter Value
1 Title as-20211219-ylk-534sub.17.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
B31
f1 (ppm)

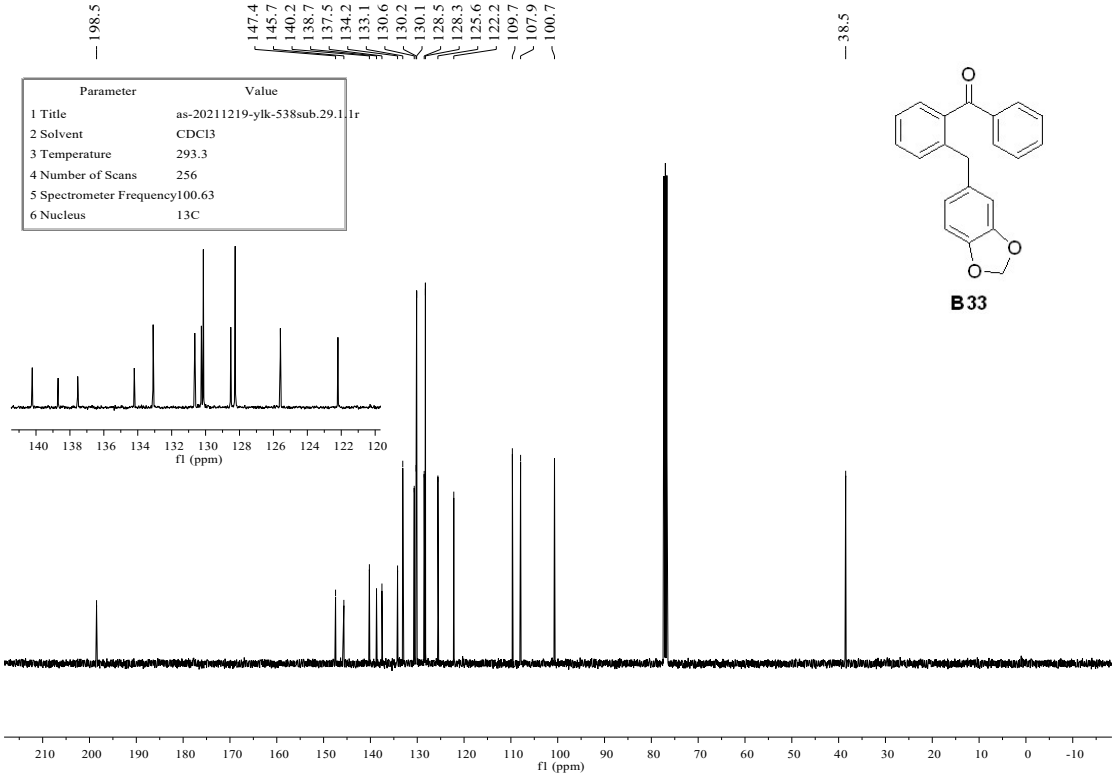
B32


7.70 7.70 7.69 7.68 7.68 7.58 7.58 7.57 7.56 7.54 7.54 7.54 7.46 7.46 7.45 7.44 7.44 7.42 7.42 7.40 7.39 7.39 7.34 7.33 7.32 7.32 7.30 7.30 7.28 7.27 7.25 7.21 7.19 7.15 7.14 6.94 6.93 6.92 6.91 4.02
Parameter Value
1 Title as-20211219-ylk-548sub.24.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
Cl
Cl
B32
2.07 1.08 3.22
7.7 7.6 7.5 7.4
f1 (ppm)
3.11 1.05 1.00 1.03
7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.07 1.08 3.22 3.11 1.05 1.00 1.03 2.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

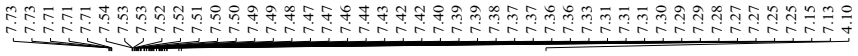

198.2
140.7 138.8 138.6 137.3 133.3 132.1 131.0 130.9 130.5 130.1 130.1 129.9 128.9 128.6 128.3 126.0
38.0
Parameter Value
1 Title as-20211219-ylk-548sub.25.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
Cl
Cl
B32
131 130 129 128 127 126
f1 (ppm)
141 140 139 138 137 136 135 134 133 132
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

B33

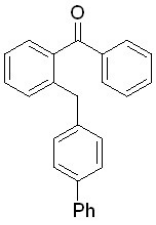

7.65 7.65 7.64 7.63 7.63 7.49 7.49 7.49 7.47 7.46 7.45 7.45 7.34 7.33 7.32 7.31 7.22 7.21 7.20 7.19 7.18 7.17 6.52 6.50 6.49 6.48 6.46 6.45 6.44 6.43 5.75 3.89
Parameter Value
1 Title as-20211219-ylk-538sub.28.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
B33
1.96 1.06 3.03 3.11
2.94
2.00 2.00
f1 (ppm)


198.5
147.4 145.7 140.2 138.7 137.5 134.2 133.1 130.6 130.2 130.1 128.5 128.3 125.6 122.2 109.7 107.9 100.7
38.5
Parameter Value
1 Title as-20211219-ylk-538sub.29.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
B33
f1 (ppm)

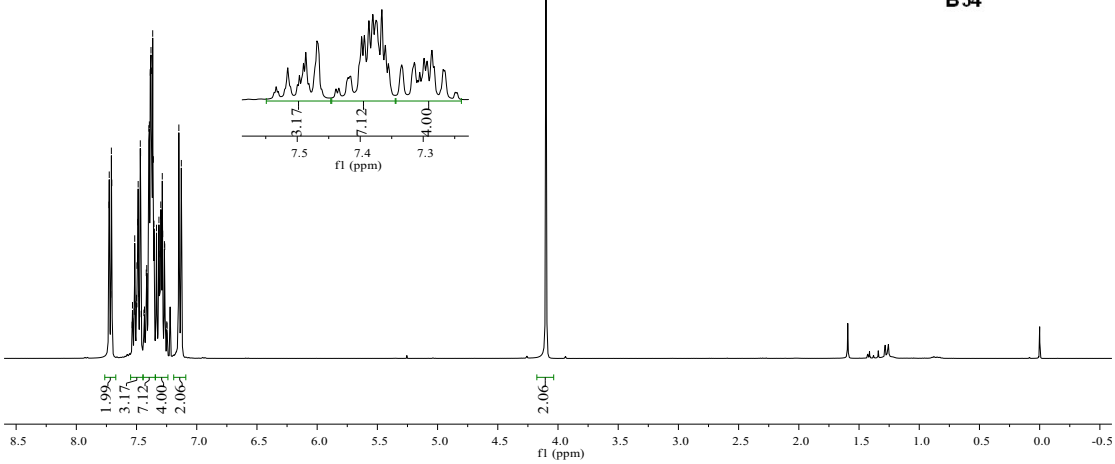
B34

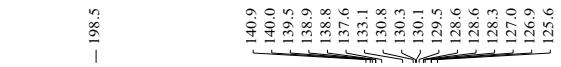


Parameter	Value
1 Title	as-20211219-ylk-500sub.22.1.1r
2 Solvent	CDCl3
3 Temperature	292.6
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

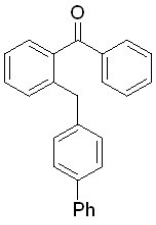


B34

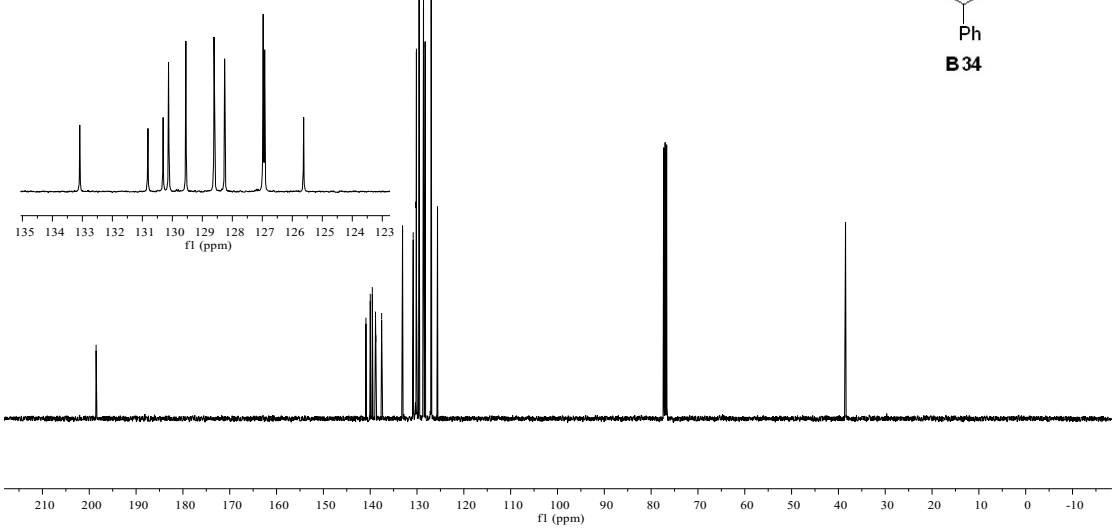




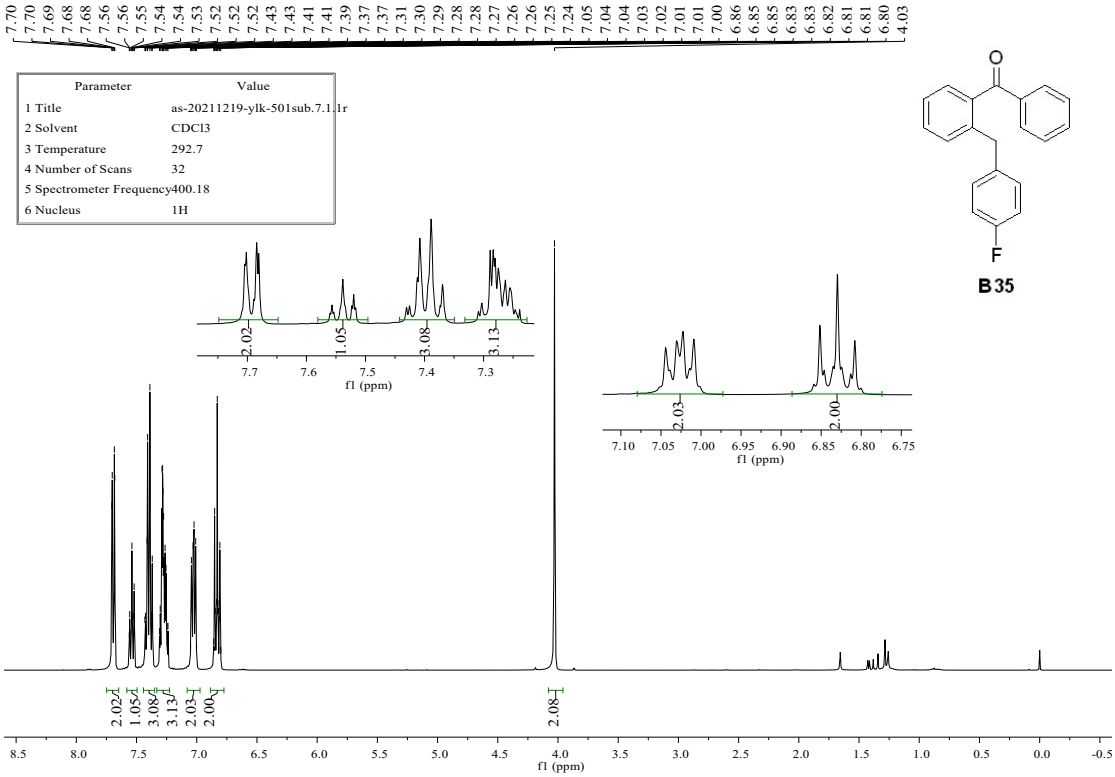
Parameter	Value
1 Title	as-20211219-ylk-500sub.23.1.1r
2 Solvent	CDCl3
3 Temperature	293.3
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

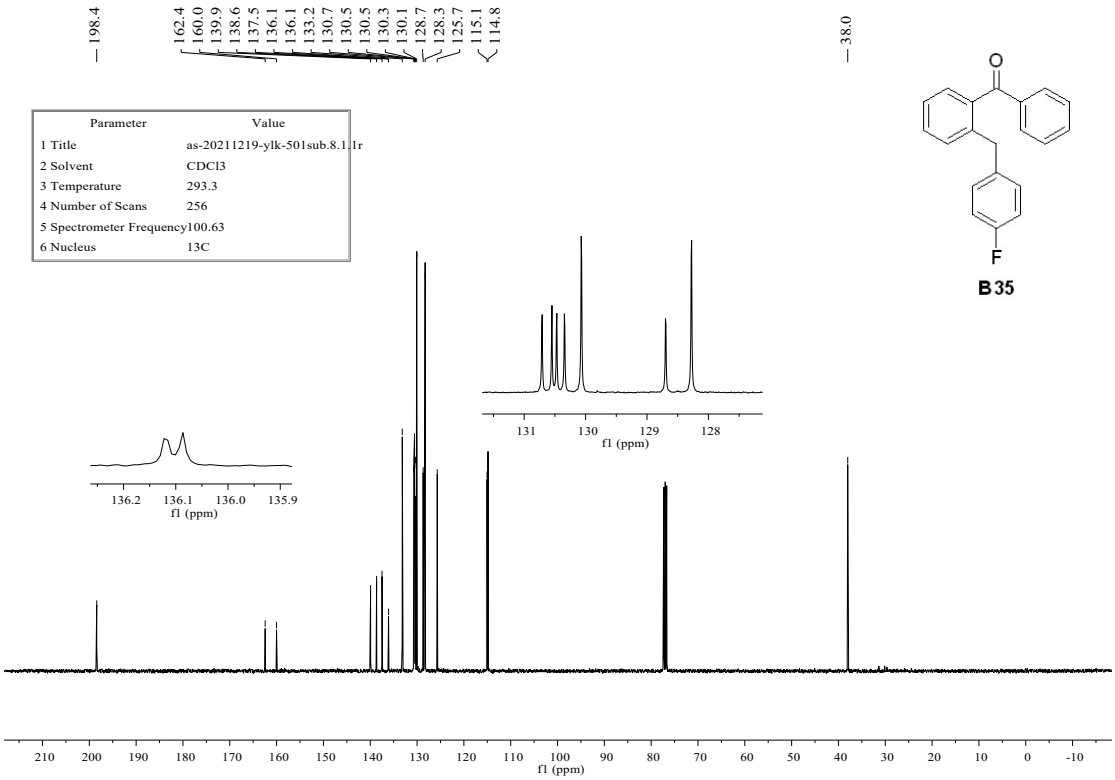


B34

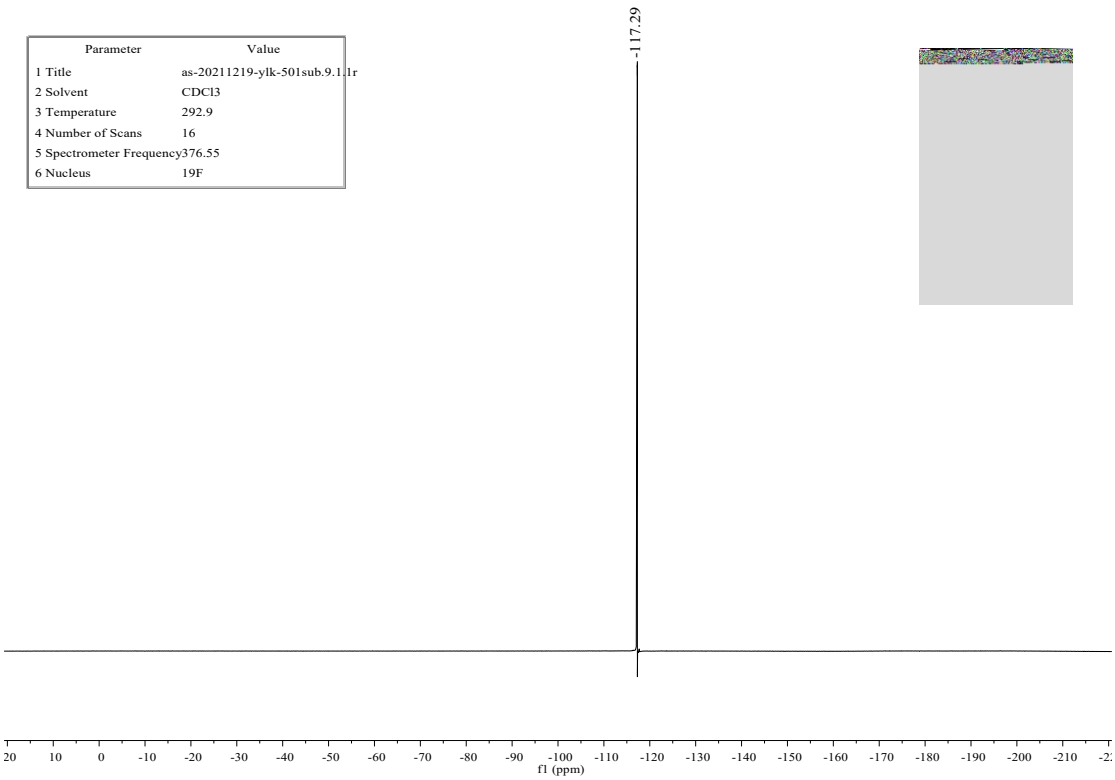


B35

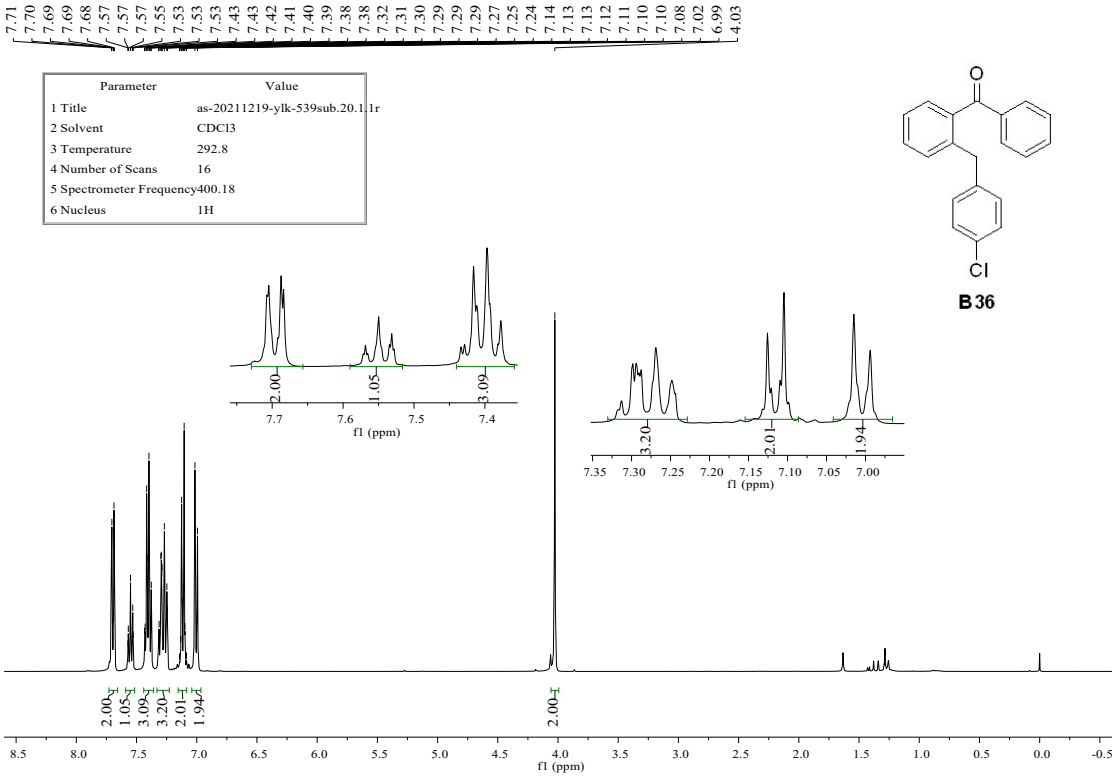

7.70 7.70 7.69 7.68 7.68 7.56 7.56 7.55 7.54 7.54 7.53 7.52 7.52 7.52 7.43 7.43 7.41 7.41 7.39 7.37 7.37 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.05 7.04 7.04 7.03 7.02 7.01 7.01 7.00 6.86 6.85 6.85 6.83 6.83 6.82 6.81 6.81 6.80 4.03
Parameter Value
1 Title as-20211219-ylk-501sub.7.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
F
B35
2.02 1.05 3.08 3.13
f1 (ppm)
2.03 2.00
f1 (ppm)
2.02 1.05 3.08 3.13 2.03 2.00 2.08
f1 (ppm)

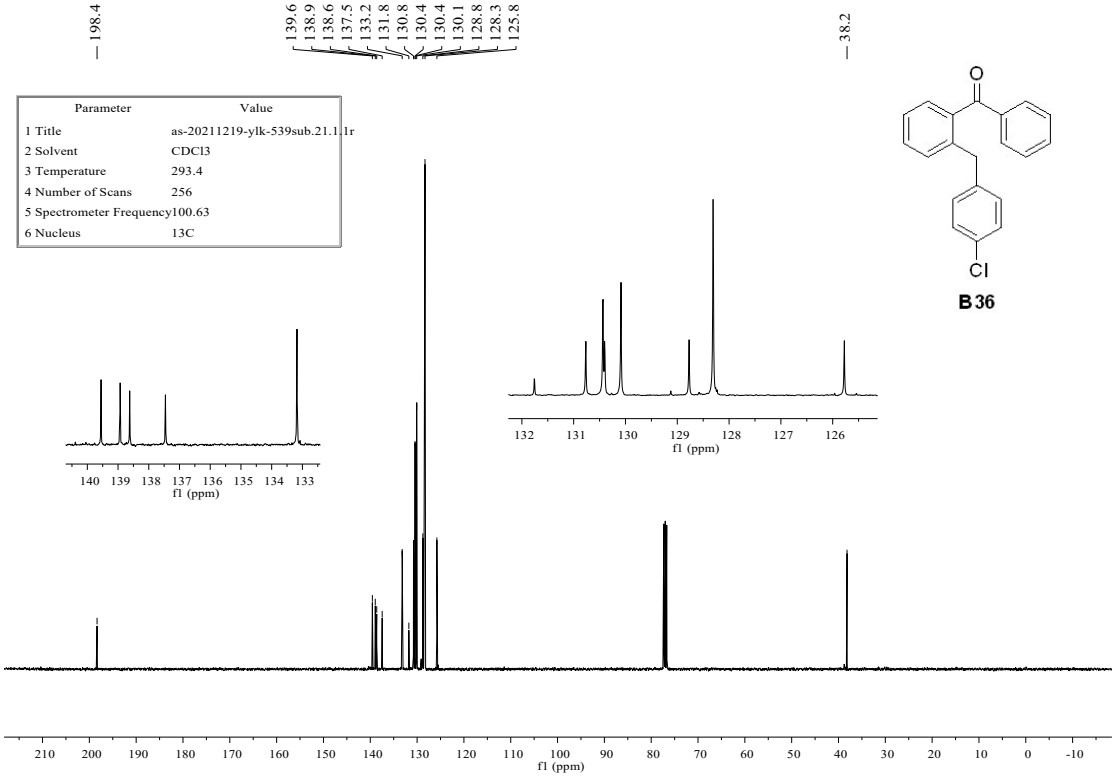

198.4
162.4 160.0 139.9 138.6 137.5 136.1 136.1 133.2 130.7 130.5 130.5 130.3 130.1 128.7 128.3 125.7 115.1 114.8
38.0
Parameter Value
1 Title as-20211219-ylk-501sub.8.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
F
B35
136.2 136.1 136.0 135.9
f1 (ppm)
131 130 129 128
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	as-20211219-ylk-501sub.9.11r
2 Solvent	CDCl3
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

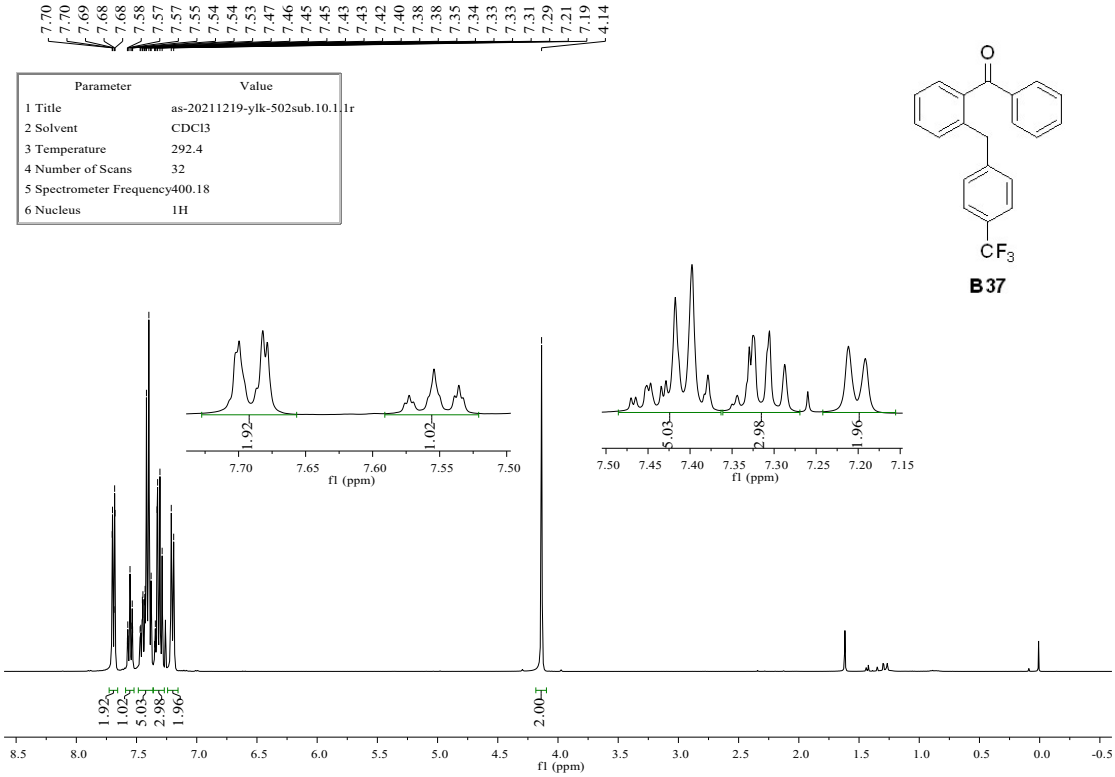


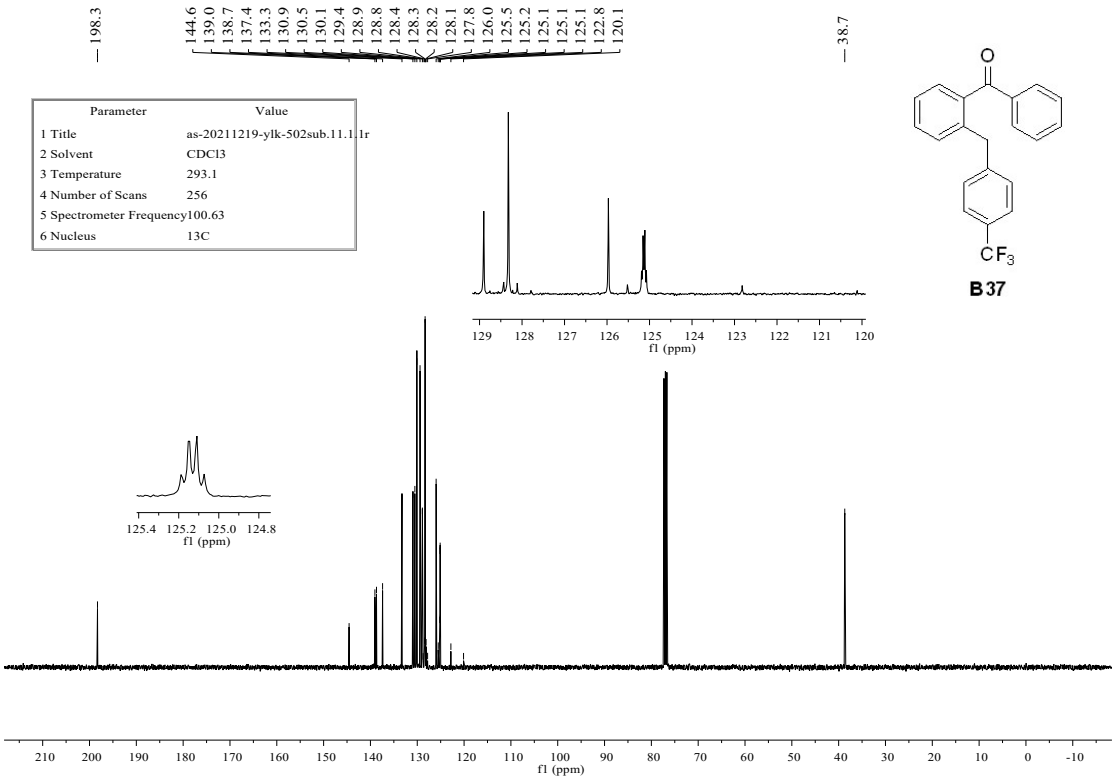
B36


7.71 7.70 7.69 7.69 7.68 7.57 7.57 7.57 7.55 7.53 7.53 7.53 7.43 7.43 7.42 7.41 7.40 7.39 7.38 7.38 7.32 7.31 7.30 7.29 7.29 7.29 7.27 7.25 7.24 7.14 7.13 7.13 7.12 7.11 7.10 7.10 7.08 7.02 6.99 4.03
Parameter Value
1 Title as-20211219-ylk-539sub.20.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
Cl
B36
2.00 1.05 3.09
7.7 7.6 7.5 7.4
f1 (ppm)
3.20 2.01 1.94
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
2.00 1.05 3.09 3.20 2.01 1.94 2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

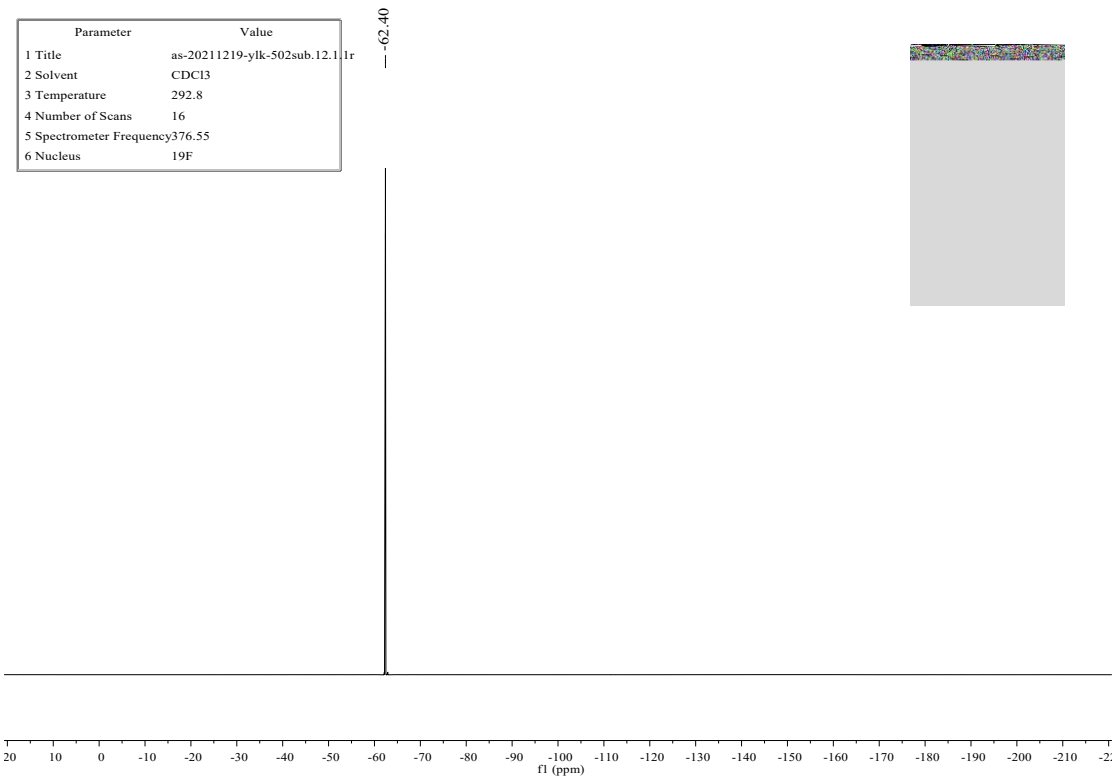

198.4
139.6 138.9 138.6 137.5 133.2 131.8 130.8 130.4 130.4 130.1 128.8 128.3 125.8
38.2
Parameter Value
1 Title as-20211219-ylk-539sub.21.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
Cl
B36
140 139 138 137 136 135 134 133
f1 (ppm)
132 131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

B37

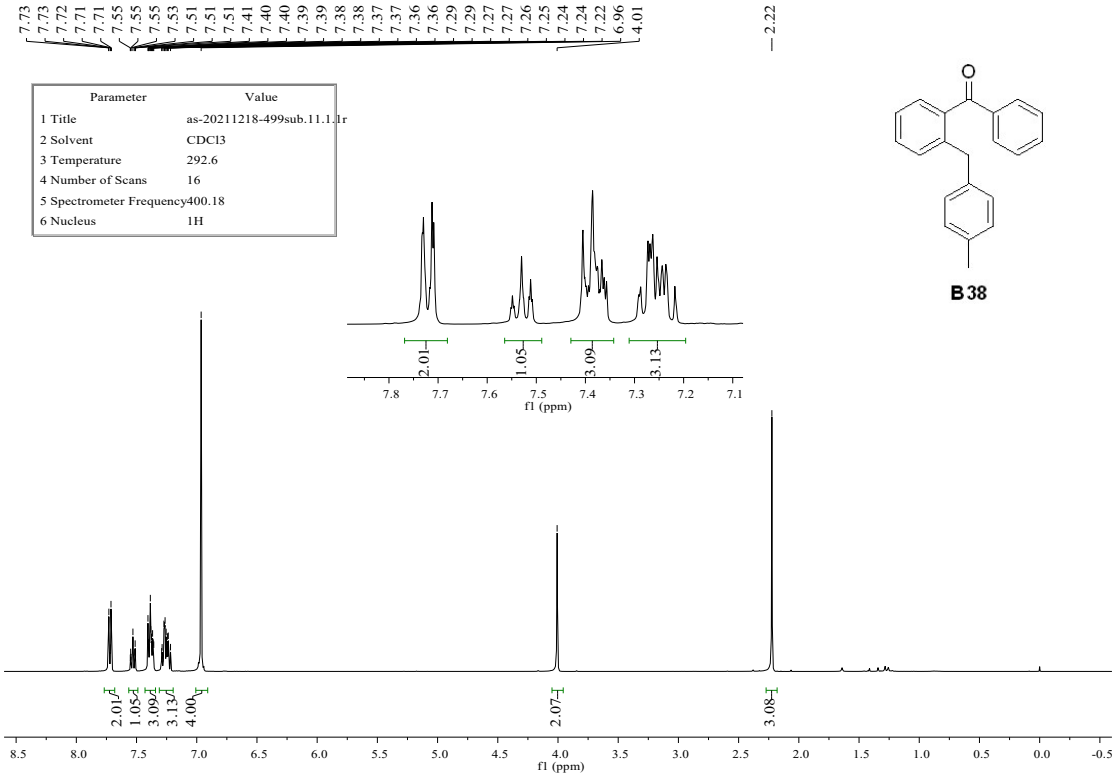

7.70 7.70 7.69 7.68 7.68 7.58 7.57 7.57 7.55 7.54 7.54 7.53 7.47 7.46 7.45 7.45 7.43 7.43 7.42 7.40 7.38 7.38 7.35 7.34 7.33 7.33 7.31 7.29 7.21 7.19 4.14
Parameter Value
1 Title as-20211219-ylk-502sub.10.1.1r
2 Solvent CDCl3
3 Temperature 292.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
CF3
B37
1.92 1.02 5.03 2.98 1.96 2.00
f1 (ppm)

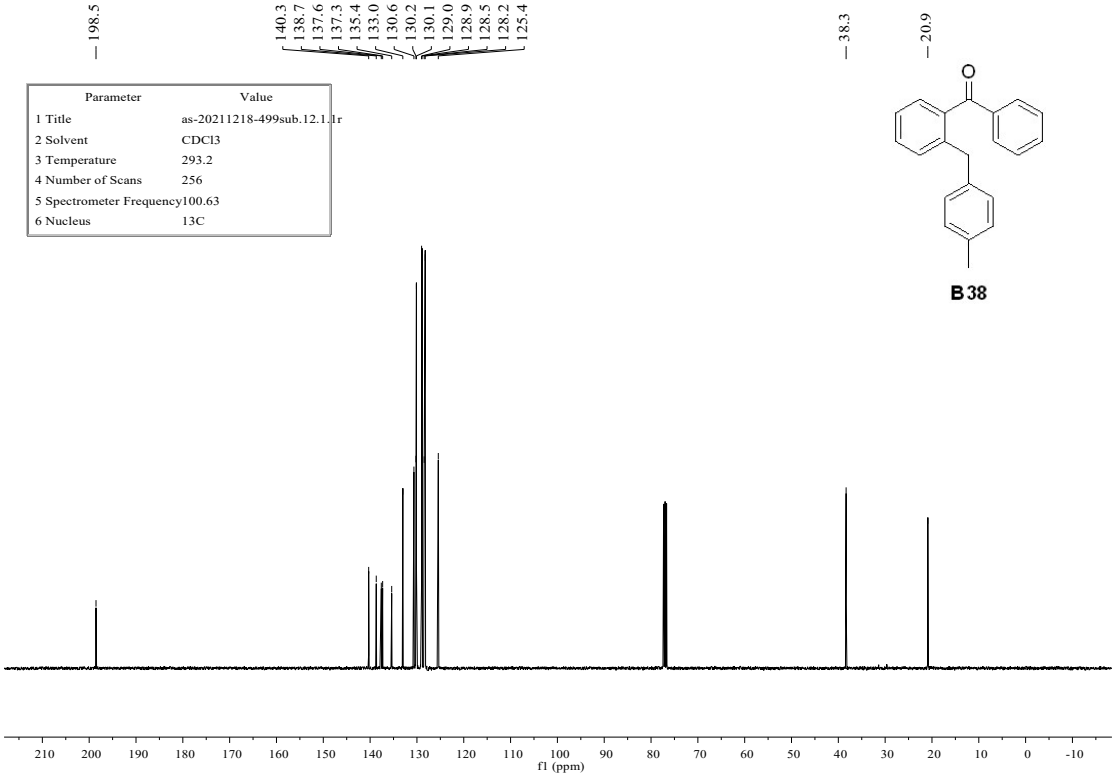

198.3
144.6 139.0 138.7 137.4 133.3 130.9 130.5 130.1 129.4 128.9 128.8 128.4 128.3 128.2 128.1 127.8 126.0 125.5 125.2 125.1 125.1 125.1 122.8 120.1
38.7
Parameter Value
1 Title as-20211219-ylk-502sub.11.1.1r
2 Solvent CDCl3
3 Temperature 293.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
CF3
B37
f1 (ppm)

Parameter	Value
1 Title	as-20211219-ylk-502sub.12.1.1r
2 Solvent	CDCl3
3 Temperature	292.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

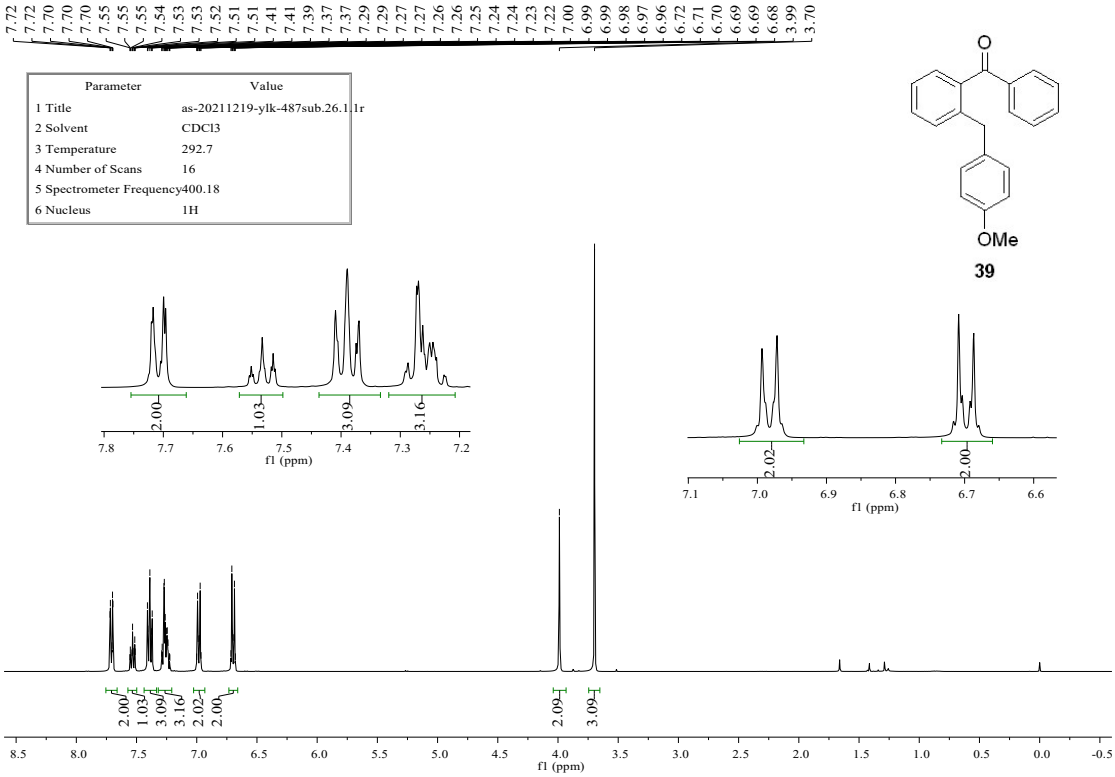


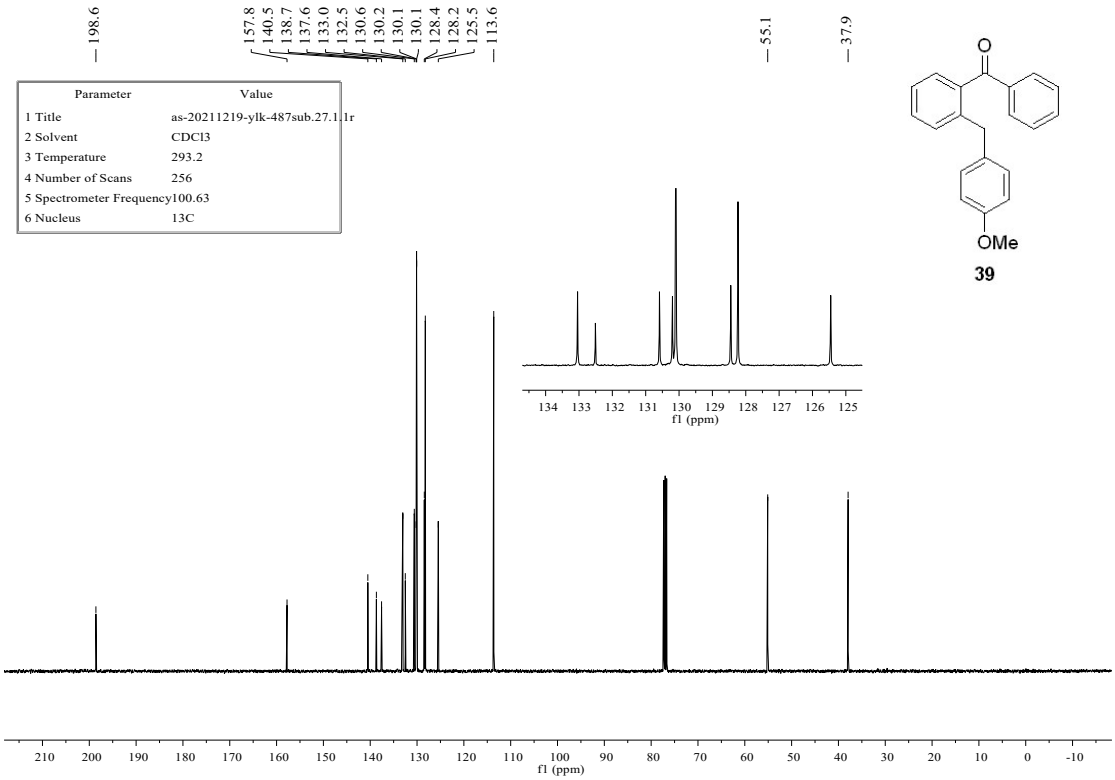
B38


7.73 7.73 7.72 7.71 7.71 7.55 7.55 7.55 7.53 7.51 7.51 7.51 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.29 7.29 7.27 7.27 7.26 7.25 7.24 7.24 7.22 6.96 4.01
2.22
Parameter Value
1 Title as-20211218-499sub.11.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
2.01 1.05 3.09 3.13
f1 (ppm)
B38
2.01 1.05 3.09 3.13 4.00 2.07 3.08
f1 (ppm)

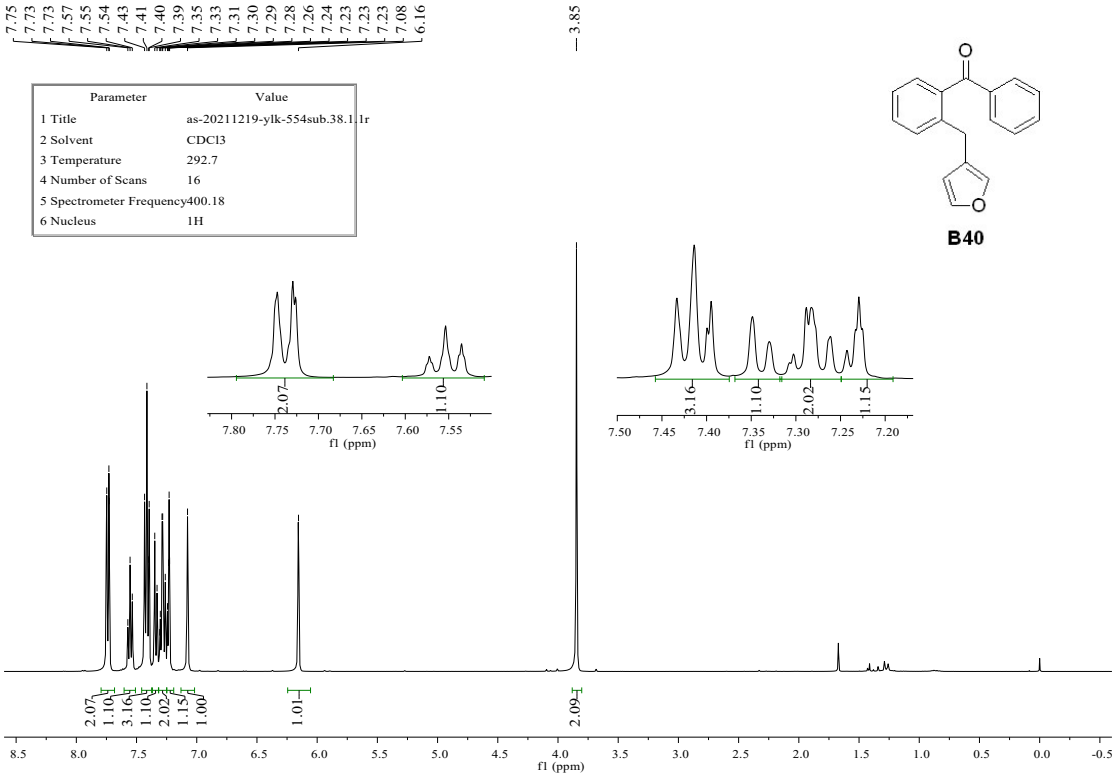

198.5
140.3 138.7 137.6 137.3 135.4 133.0 130.6 130.2 130.1 129.0 128.9 128.5 128.2 125.4
38.3
20.9
Parameter Value
1 Title as-20211218-499sub.12.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
B38
f1 (ppm)

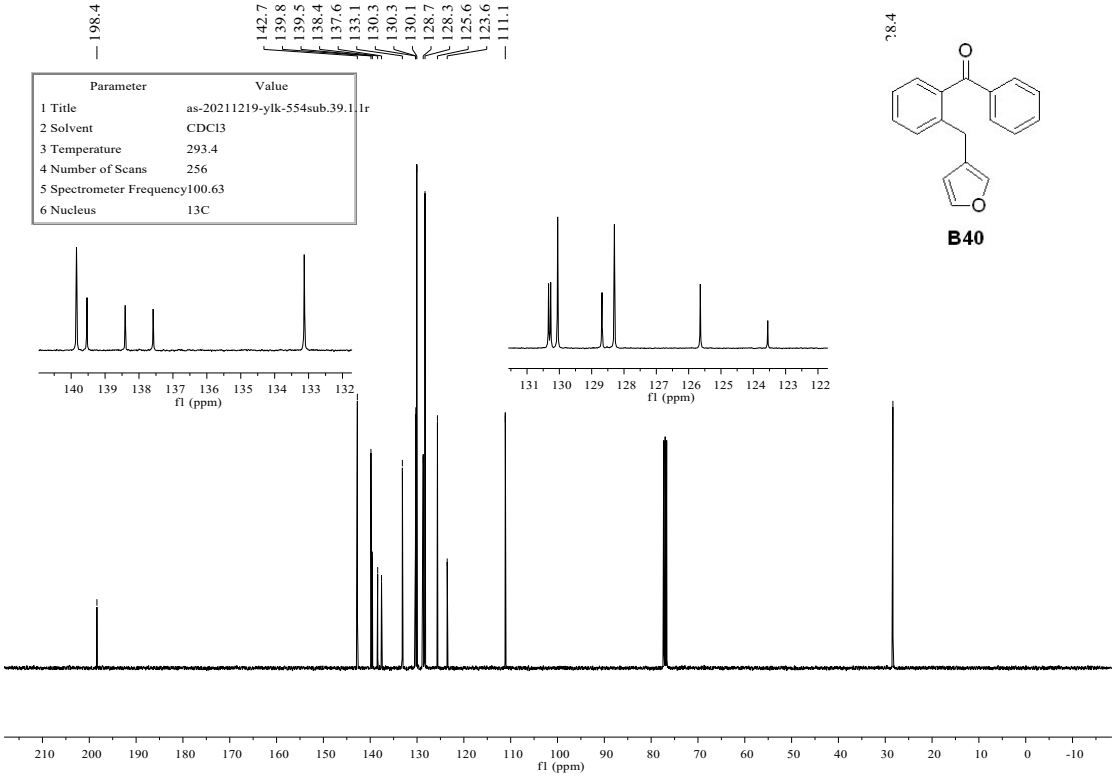
B39


7.72 7.72 7.70 7.70 7.70 7.55 7.55 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.41 7.41 7.39 7.37 7.37 7.29 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.00 6.99 6.99 6.98 6.97 6.96 6.72 6.71 6.70 6.69 6.69 6.68 3.99 3.70
Parameter Value
1 Title as-20211219-ylk-487sub.26.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
OMe
39
2.00 1.03 3.09 3.16
f1 (ppm)
2.02 2.00
f1 (ppm)
2.00 1.03 3.09 3.16 2.02 2.00 2.09 3.09
f1 (ppm)

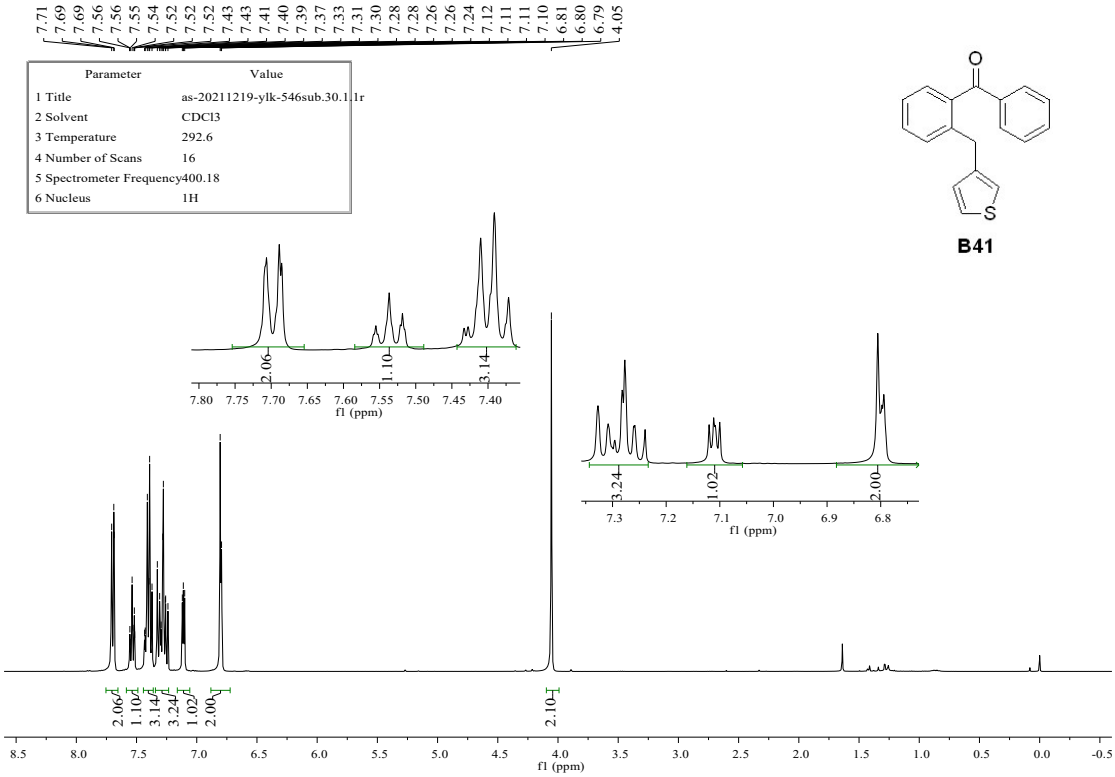

198.6
157.8 140.5 138.7 137.6 133.0 132.5 130.6 130.2 130.1 130.1 128.4 128.2 125.5 113.6
55.1
37.9
Parameter Value
1 Title as-20211219-ylk-487sub.27.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
OMe
39
f1 (ppm)
f1 (ppm)

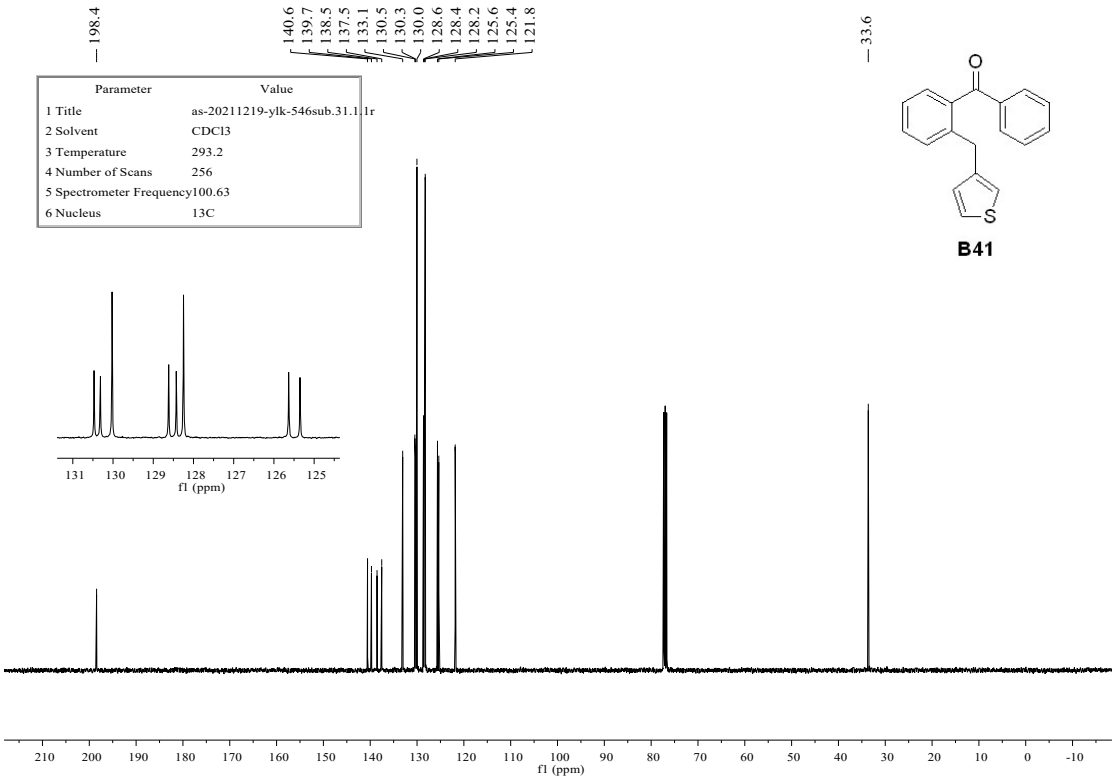
B40


7.75 7.73 7.73 7.57 7.55 7.54 7.43 7.41 7.40 7.39 7.35 7.33 7.31 7.30 7.29 7.28 7.26 7.24 7.23 7.23 7.23 7.08 6.16
3.85
Parameter Value
1 Title as-20211219-ylk-554sub.38.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
B40
2.07 1.10 3.16 1.10 2.02 1.15 1.00 1.01 2.09
f1 (ppm)

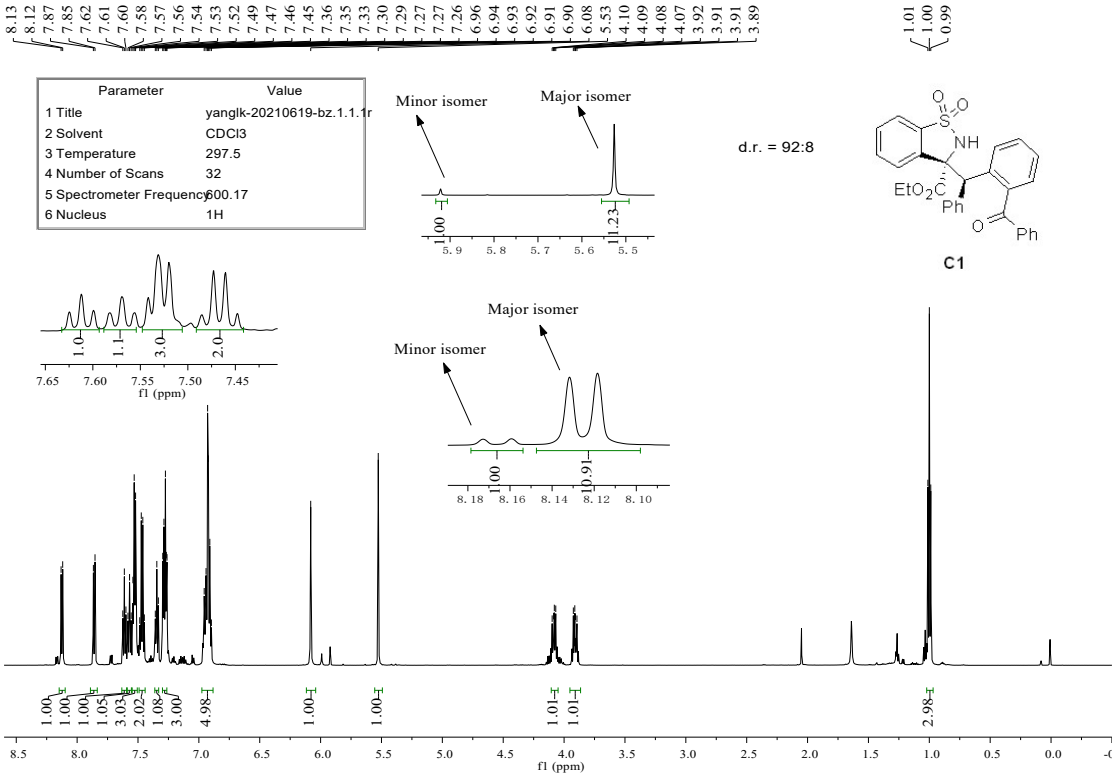

198.4
142.7 139.8 139.5 138.4 137.6 133.1 130.3 130.3 130.1 128.7 128.3 125.6 123.6 111.1
Parameter Value
1 Title as-20211219-ylk-554sub.39.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
B40
f1 (ppm)

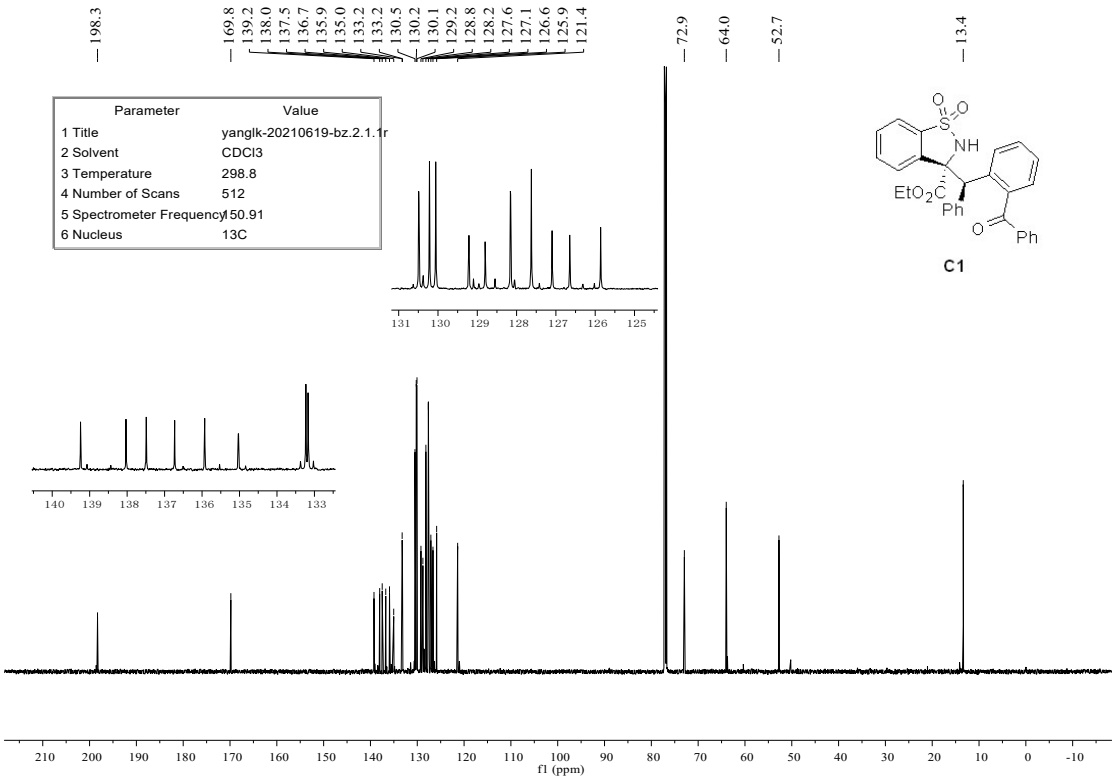
B41


7.71 7.69 7.69 7.56 7.56 7.55 7.54 7.52 7.52 7.52 7.43 7.43 7.41 7.40 7.39 7.37 7.33 7.31 7.30 7.28 7.28 7.26 7.26 7.24 7.12 7.11 7.11 7.10 6.81 6.80 6.79 4.05
Parameter Value
1 Title as-20211219-ylk-546sub.30.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
S
B41
2.06 1.10 3.14
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
f1 (ppm)
3.24 1.02 2.00
7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
2.06 1.10 3.14 3.24 1.02 2.00 2.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

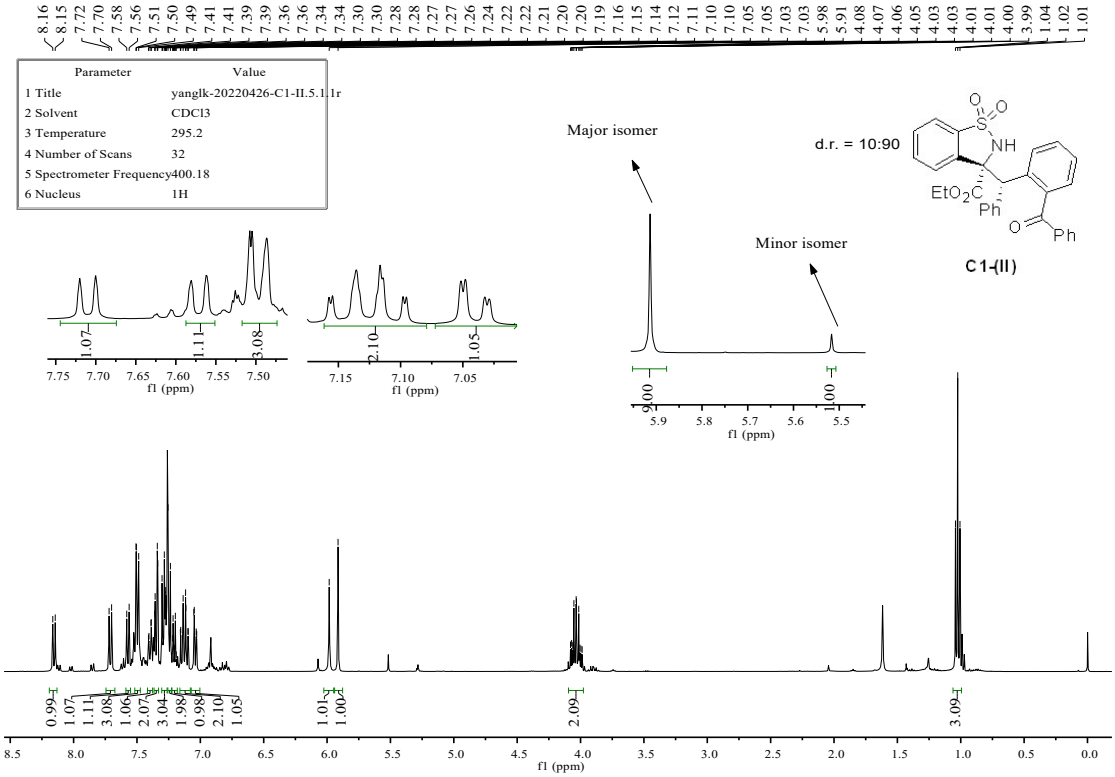

198.4
140.6 139.7 138.5 137.5 133.1 130.5 130.3 130.0 128.6 128.4 128.2 125.6 125.4 121.8
33.6
Parameter Value
1 Title as-20211219-ylk-546sub.31.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
S
B41
131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

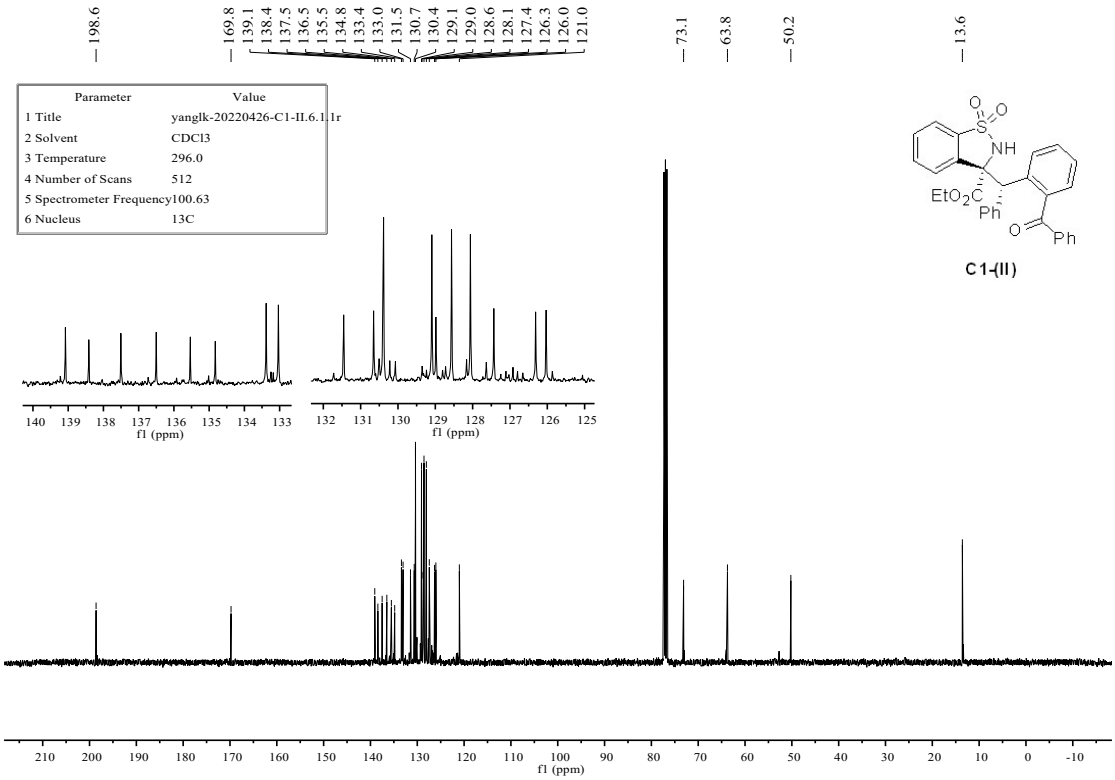
C1


Parameter Value
1 Title yanglk-20210619-bz.1.1.1r
2 Solvent CDCl3
3 Temperature 297.5
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
Minor isomer
Major isomer
d.r. = 92:8
C1
f1 (ppm)

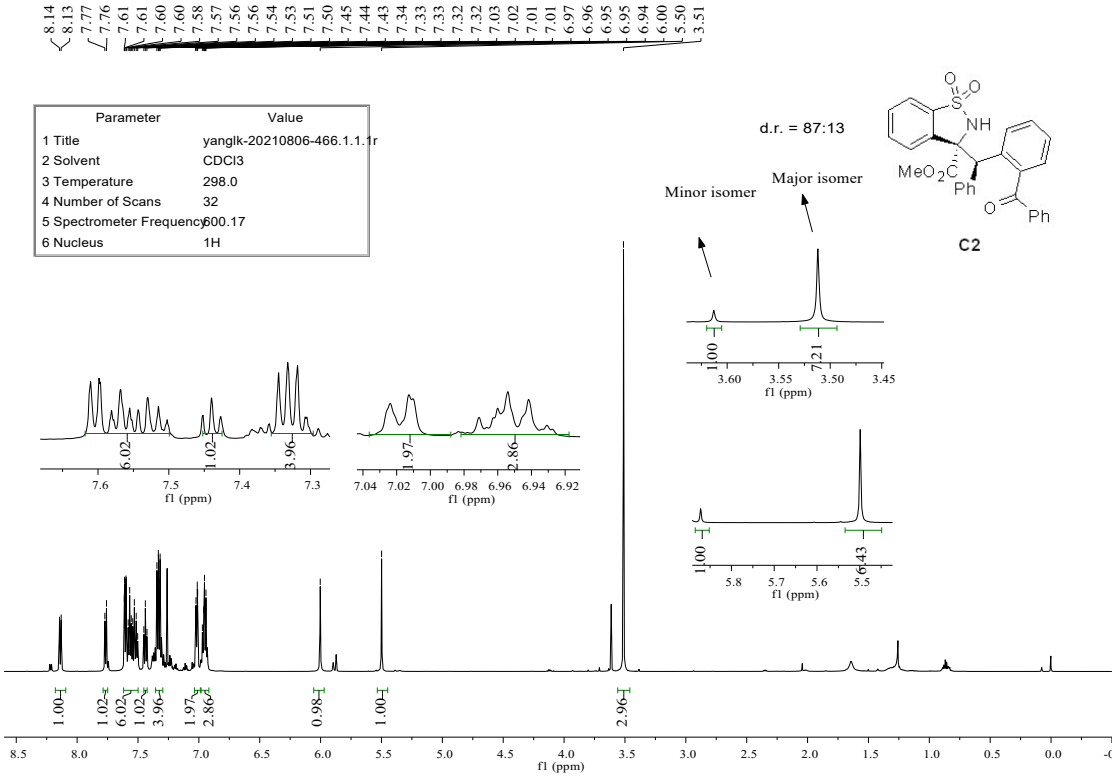

Parameter Value
1 Title yanglk-20210619-bz.2.1.1r
2 Solvent CDCl3
3 Temperature 298.8
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C1
f1 (ppm)

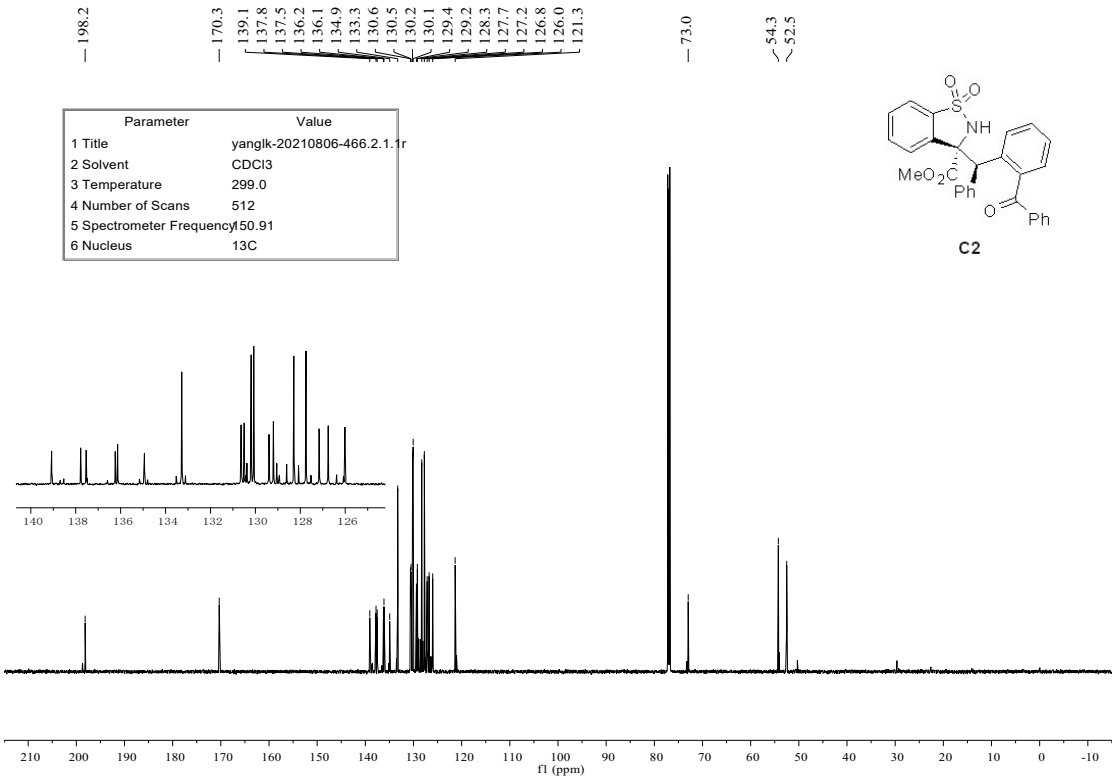
C1-(II)


Parameter Value
1 Title yanglk-20220426-C1-II.5.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
d.r. = 10:90
C1-(II)
f1 (ppm)

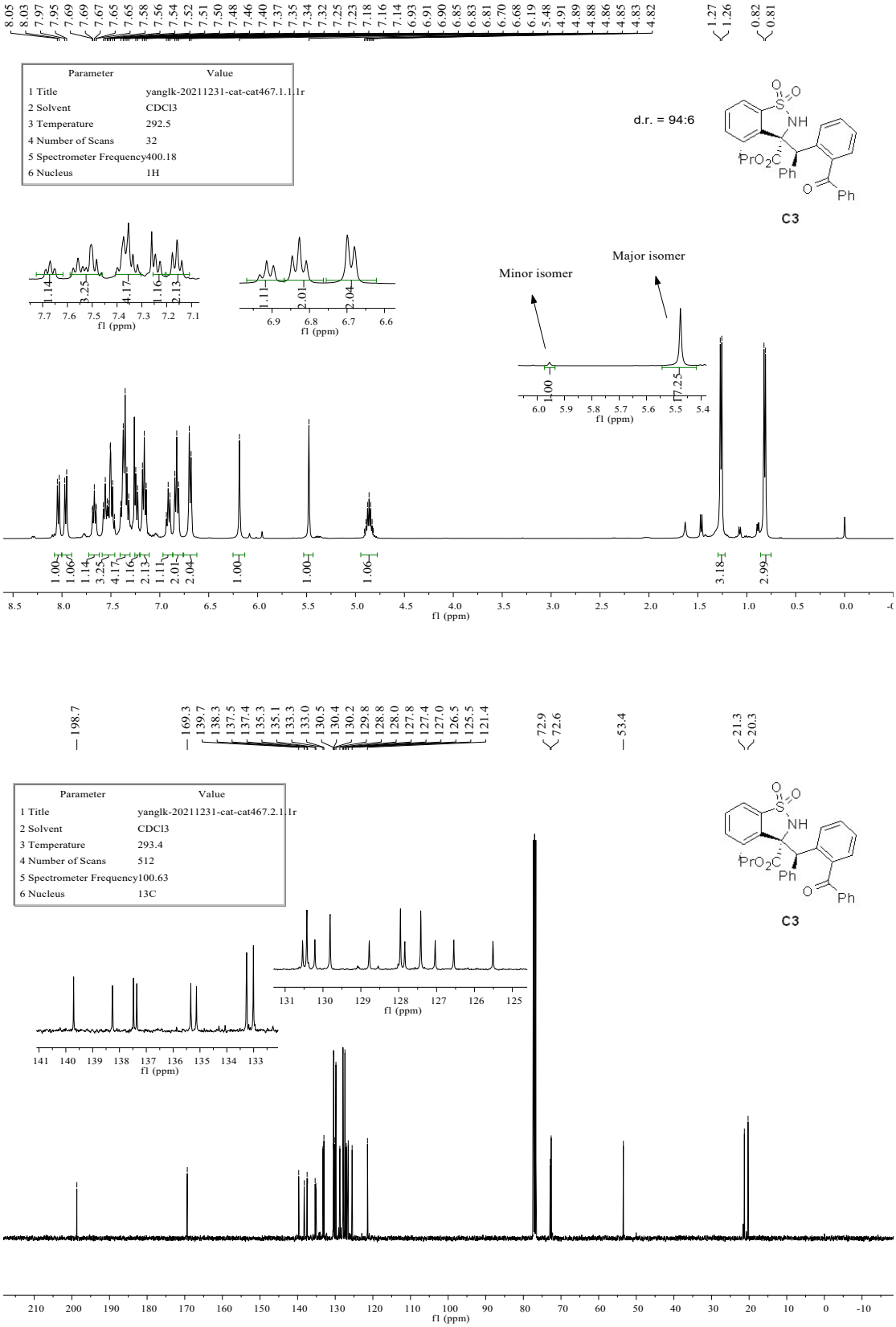

Parameter Value
1 Title yanglk-20220426-C1-II.6.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C1-(II)
f1 (ppm)

C2


8.14 8.13 7.77 7.76 7.61 7.61 7.60 7.60 7.58 7.57 7.56 7.56 7.54 7.53 7.51 7.50 7.45 7.44 7.43 7.34 7.33 7.33 7.32 7.32 7.03 7.02 7.01 7.01 6.97 6.96 6.95 6.95 6.94 6.00 5.50 3.51
Parameter Value
1 Title yanglk-20210806-466.1.1.1r
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 87:13
Minor isomer
Major isomer
C2
f1 (ppm)

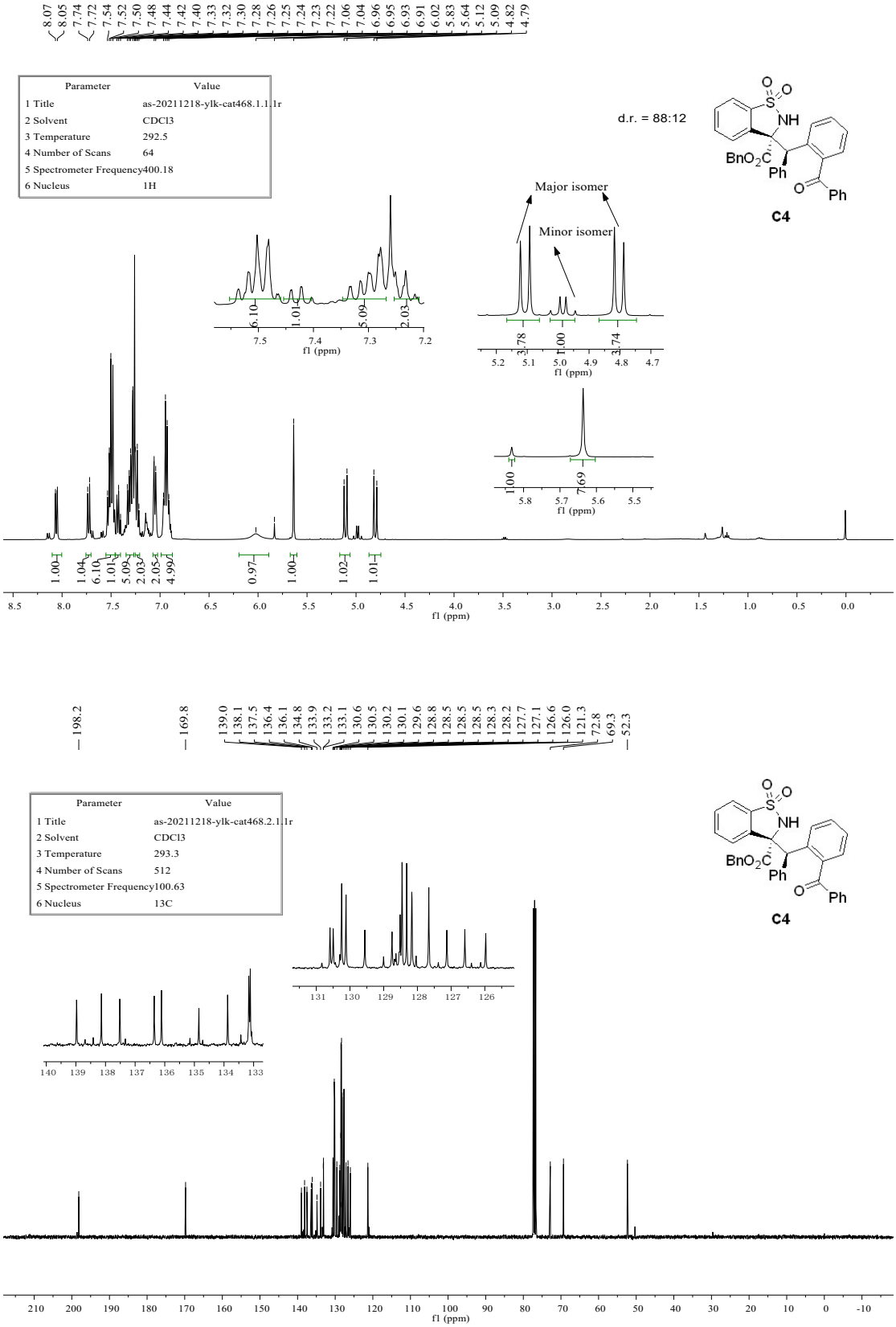

198.2 170.3 139.1 137.8 137.5 136.2 136.1 134.9 133.3 130.6 130.5 130.2 130.1 129.4 129.2 128.3 127.7 127.2 126.8 126.0 121.3 73.0 54.3 52.5
Parameter Value
1 Title yanglk-20210806-466.2.1.1r
2 Solvent CDCl3
3 Temperature 299.0
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C2
f1 (ppm)

C3


8.05 8.03 7.97 7.95 7.69 7.69 7.67 7.65 7.65 7.58 7.56 7.54 7.52 7.51 7.50 7.48 7.46 7.40 7.37 7.35 7.34 7.32 7.25 7.23 7.18 7.16 7.14 6.93 6.91 6.90 6.85 6.83 6.81 6.70 6.68 6.19 5.48 4.91 4.89 4.88 4.86 4.85 4.83 4.82
1.27 1.26 0.82 0.81
Parameter Value
1 Title yanglk-20211231-cat-cat467.1.1.1r
2 Solvent CDCl3
3 Temperature 292.5
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 94:6
C3
Major isomer
Minor isomer
1.00 1.06 1.14 3.25 4.17 1.16 2.13 1.11 2.01 2.04 1.00 1.00 1.06 3.18 2.99
f1 (ppm)

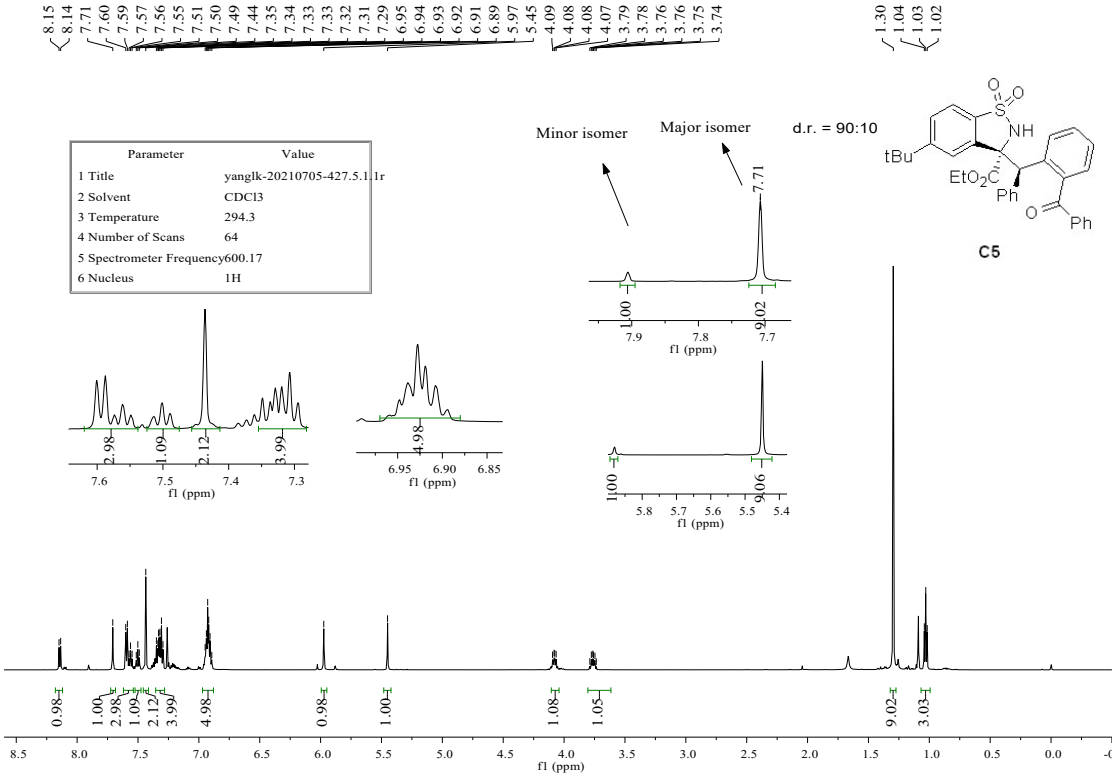
198.7
169.3 139.7 138.3 137.5 137.4 135.3 135.1 133.3 133.0 130.5 130.4 130.2 129.8 128.8 128.0 127.8 127.4 127.0 126.5 125.5 121.4
72.9 72.6
53.4
21.3 20.3
Parameter Value
1 Title yanglk-20211231-cat-cat467.2.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C3
f1 (ppm)

C4

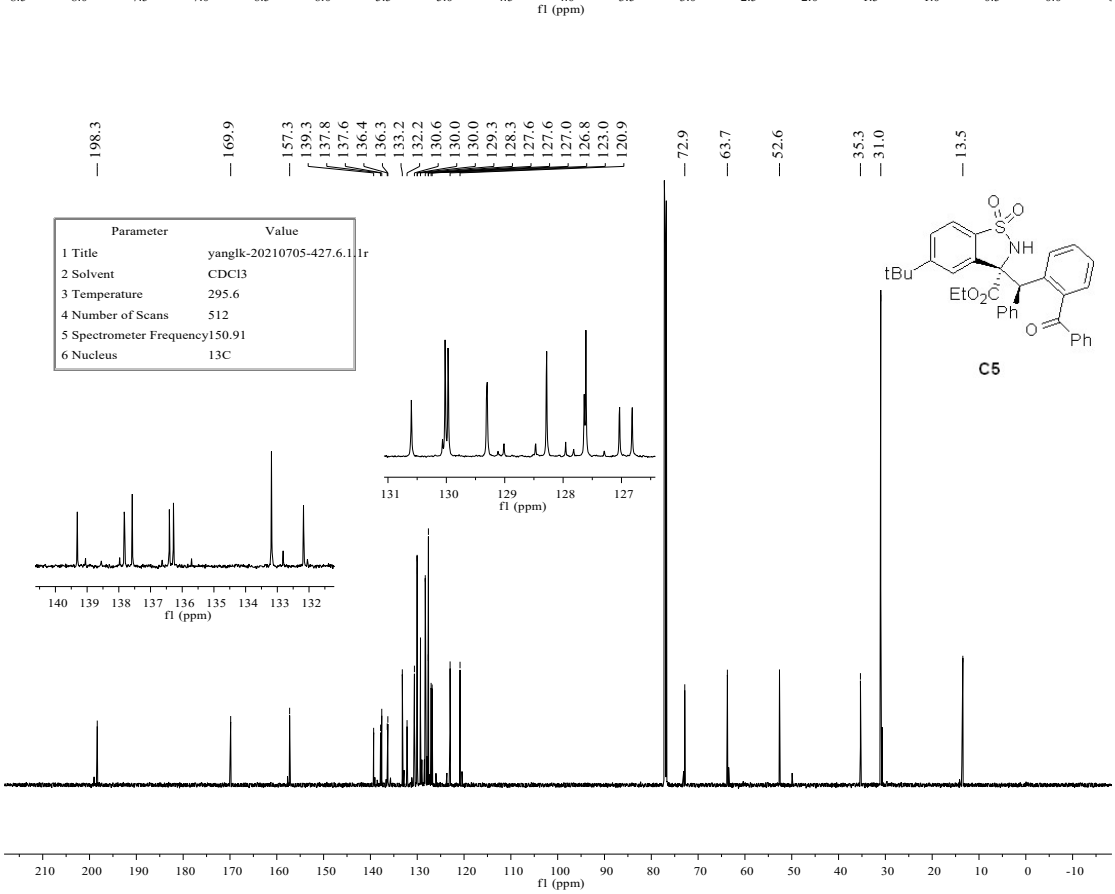

Parameter Value
1 Title as-20211218-ylk-cat468.1.1.1r
2 Solvent CDCl3
3 Temperature 292.5
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 88:12
Major isomer
Minor isomer
C4
f1 (ppm)

Parameter Value
1 Title as-20211218-ylk-cat468.2.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C4
f1 (ppm)

C5

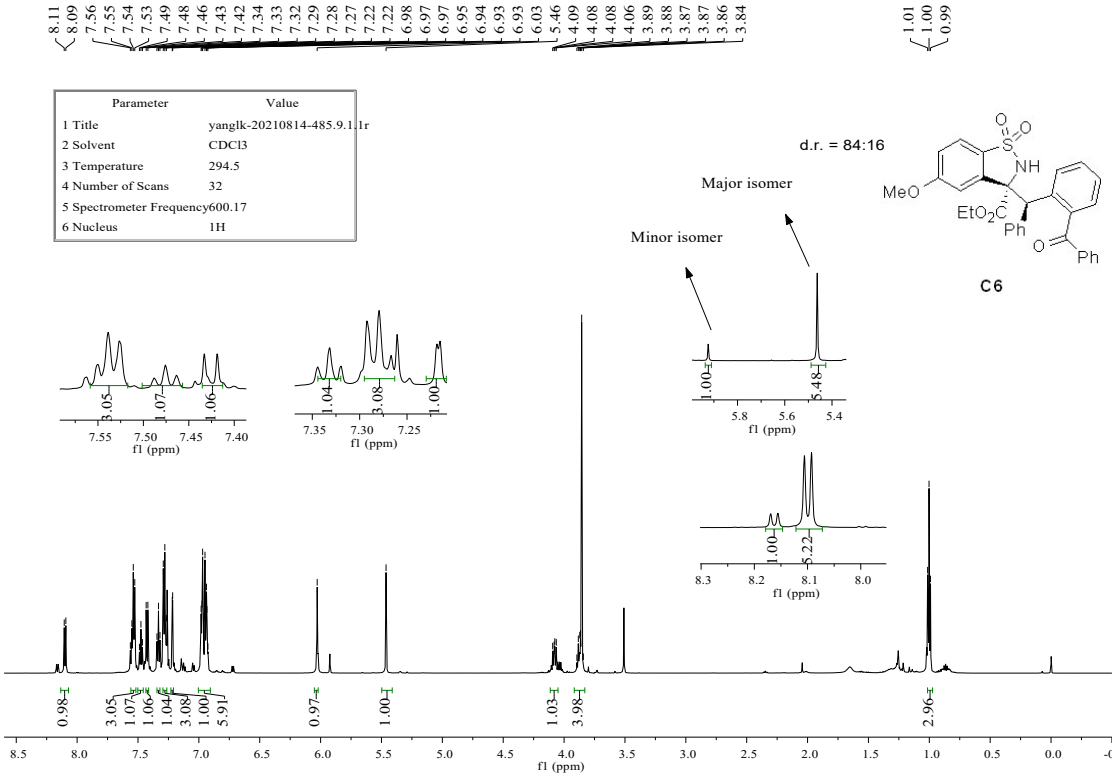


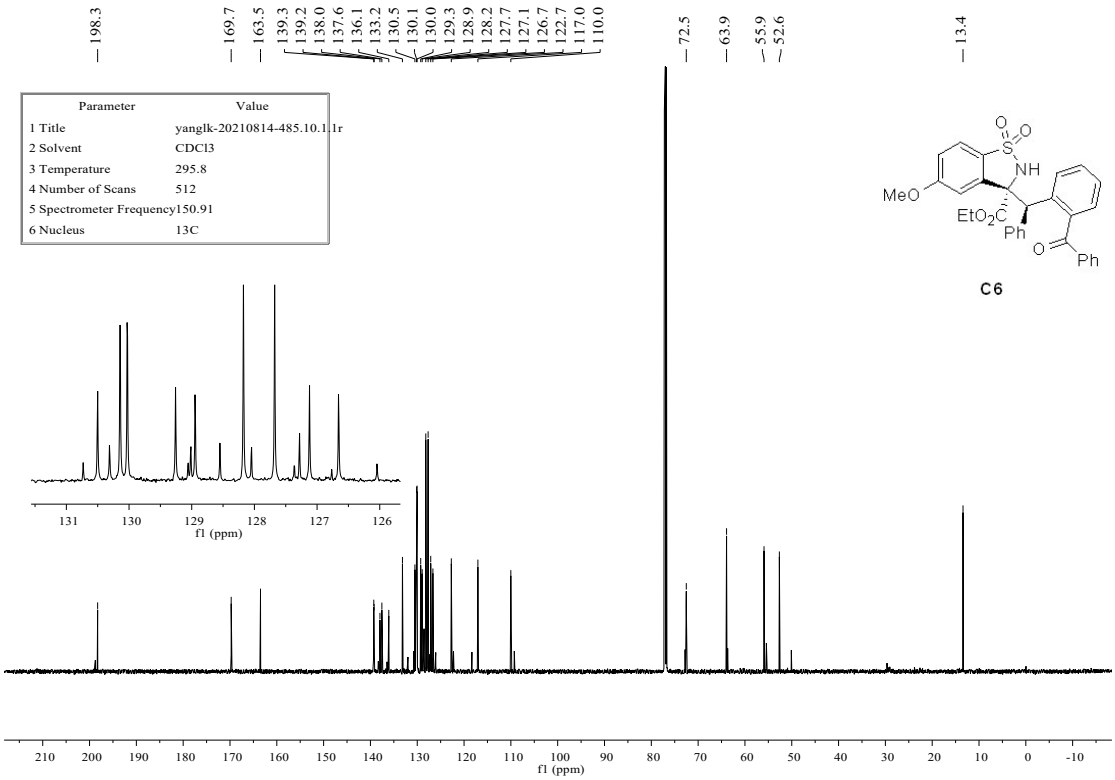
Parameter	Value
1 Title	yanglk-20210705-427.5.1.1r
2 Solvent	CDCl3
3 Temperature	294.3
4 Number of Scans	64
5 Spectrometer Frequency	600.17
6 Nucleus	1H



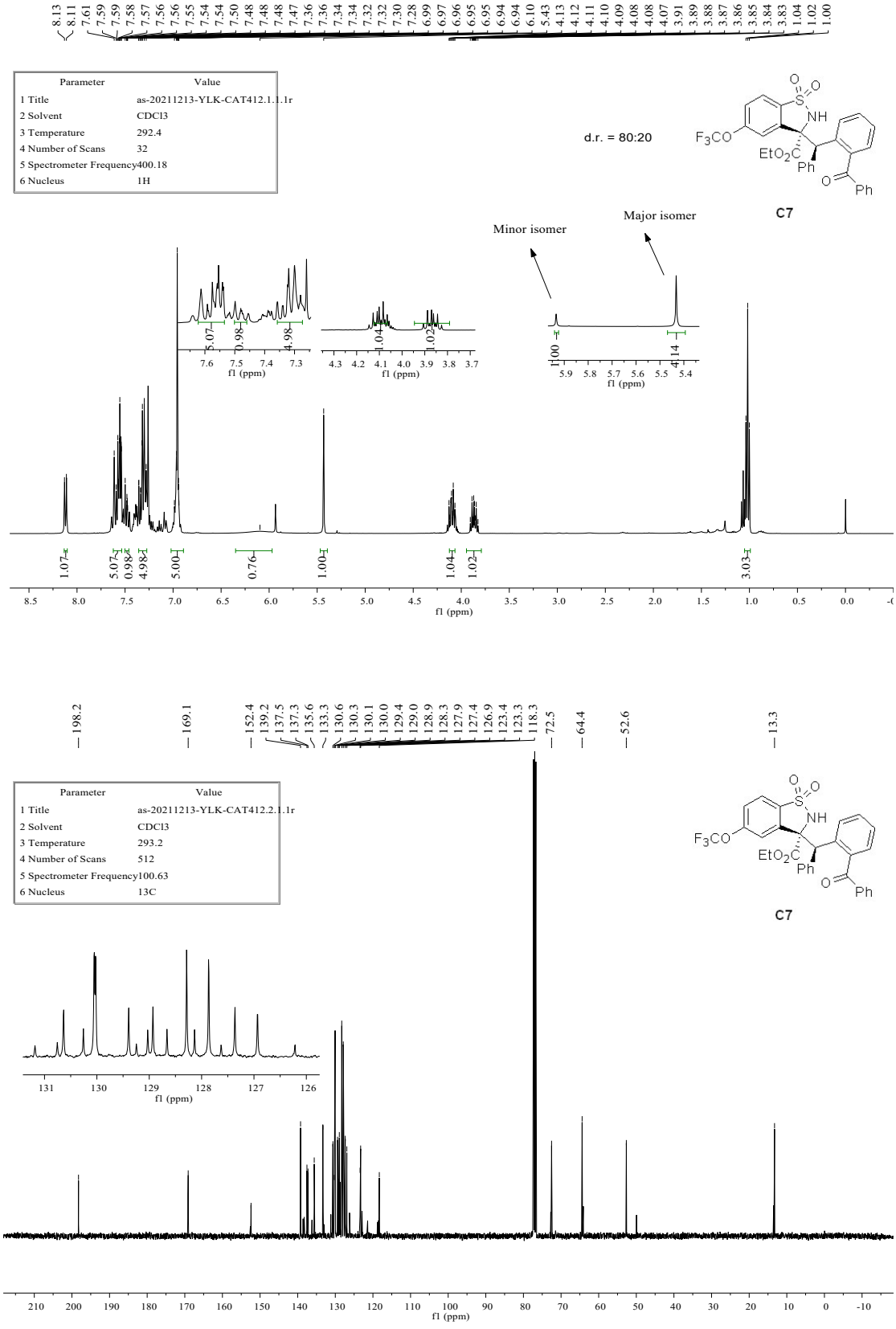
Parameter	Value
1 Title	yanglk-20210705-427.6.1.1r
2 Solvent	CDCl3
3 Temperature	295.6
4 Number of Scans	512
5 Spectrometer Frequency	150.91
6 Nucleus	13C

C6


8.11 8.09 7.56 7.55 7.54 7.53 7.49 7.48 7.46 7.43 7.42 7.34 7.33 7.32 7.29 7.28 7.27 7.22 7.22 6.98 6.97 6.97 6.95 6.94 6.93 6.93 6.03 5.46 4.09 4.08 4.08 4.06 3.89 3.88 3.87 3.87 3.86 3.84
1.01 1.00 0.99
Parameter Value
1 Title yanglk-20210814-485.9.1.1r
2 Solvent CDCl3
3 Temperature 294.5
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 84:16
Major isomer
Minor isomer
MeO
EtO2C
Ph
NH
C6
f1 (ppm)
0.98 3.05 1.07 1.06 1.04 3.08 1.00 5.91 0.97 1.00 1.03 3.98 2.96


198.3 169.7 163.5 139.3 139.2 138.0 137.6 136.1 133.2 130.5 130.1 130.0 129.3 128.9 128.2 127.7 127.1 126.7 122.7 117.0 110.0 72.5 63.9 55.9 52.6 13.4
Parameter Value
1 Title yanglk-20210814-485.10.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
MeO
EtO2C
Ph
NH
C6
f1 (ppm)

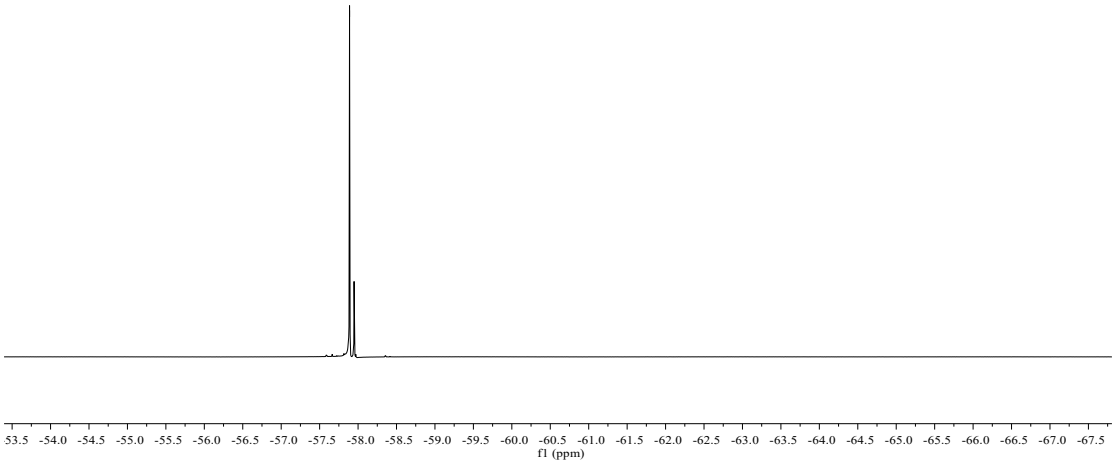
C7


Parameter Value
1 Title as-20211213-YLK-CAT412.1.1.1r
2 Solvent CDCl3
3 Temperature 292.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 80:20
C7
Minor isomer
Major isomer
f1 (ppm)
Parameter Value
1 Title as-20211213-YLK-CAT412.2.1.1r
2 Solvent CDCl3
3 Temperature 293.2
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C7
f1 (ppm)

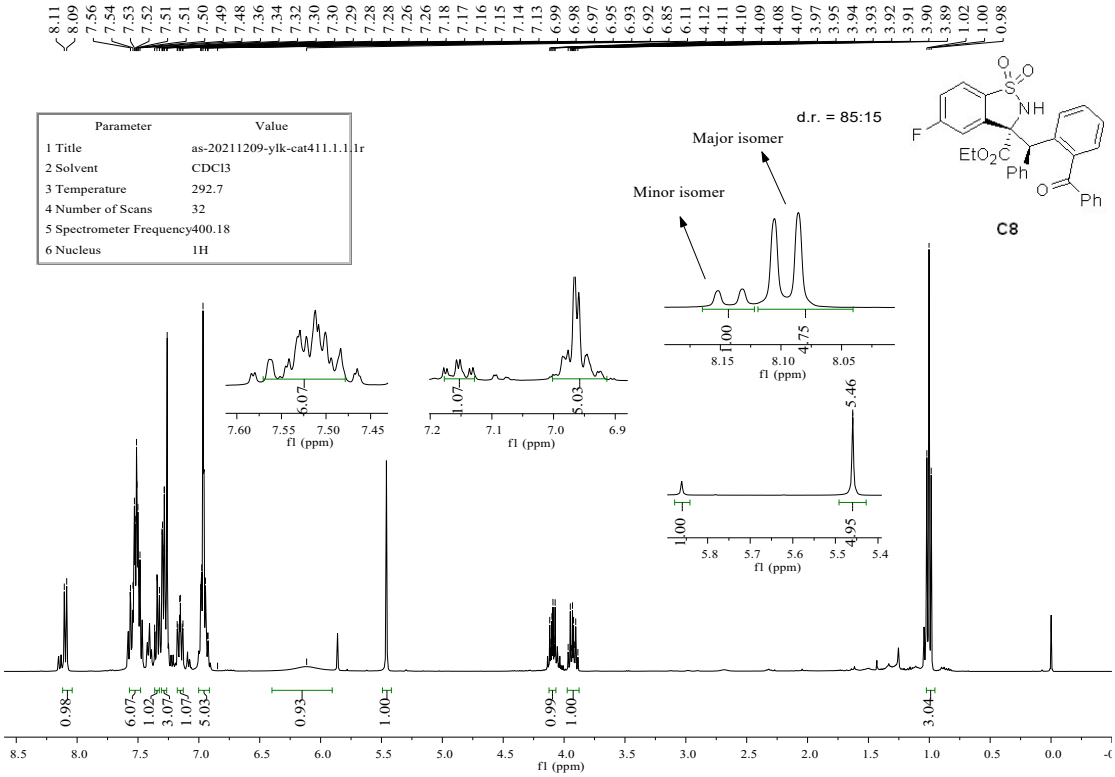
^{19}F NMR (377 MHz, CDCl$_3$) δ -57.89.

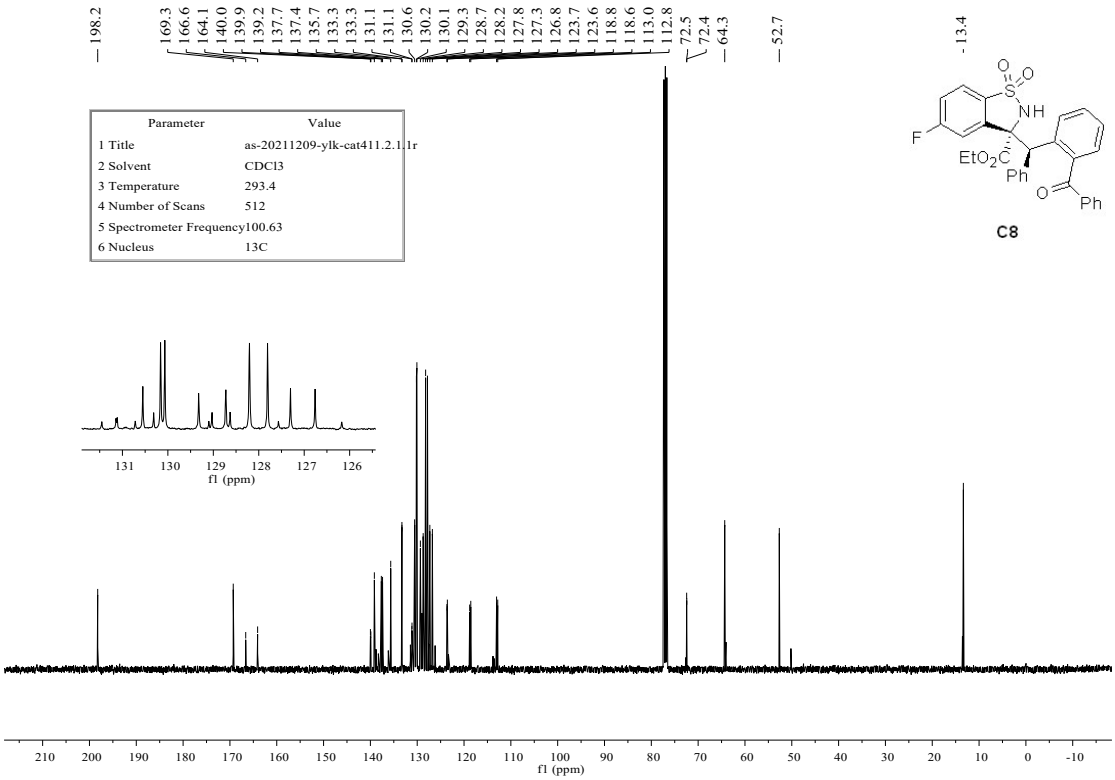
-57.89

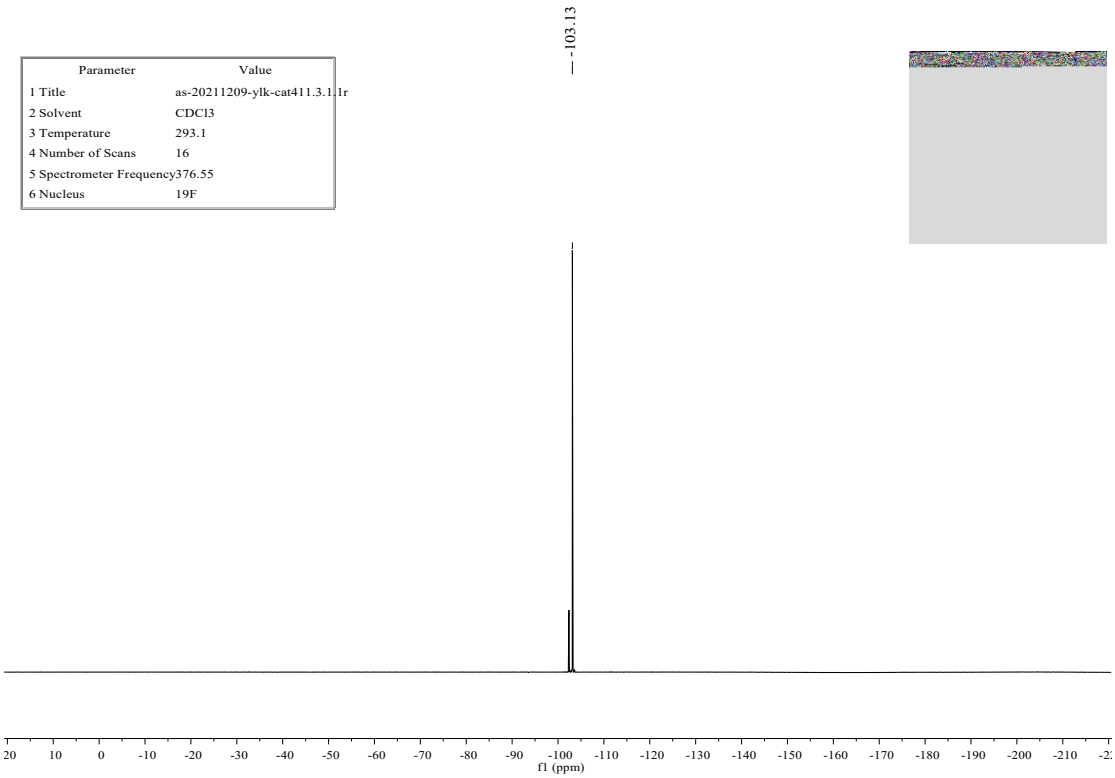
Parameter	Value
1 Title	as-20211213-YLK-CAT412.3.1.1r
2 Solvent	CDCl3
3 Temperature	292.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



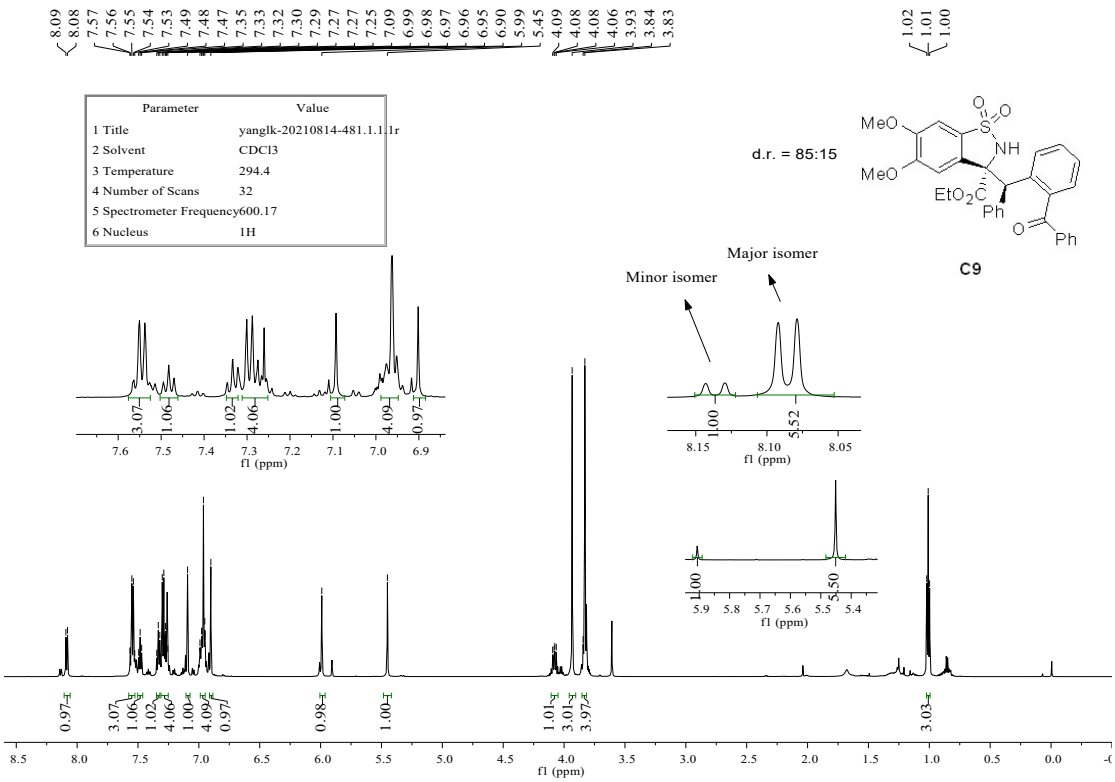
C8

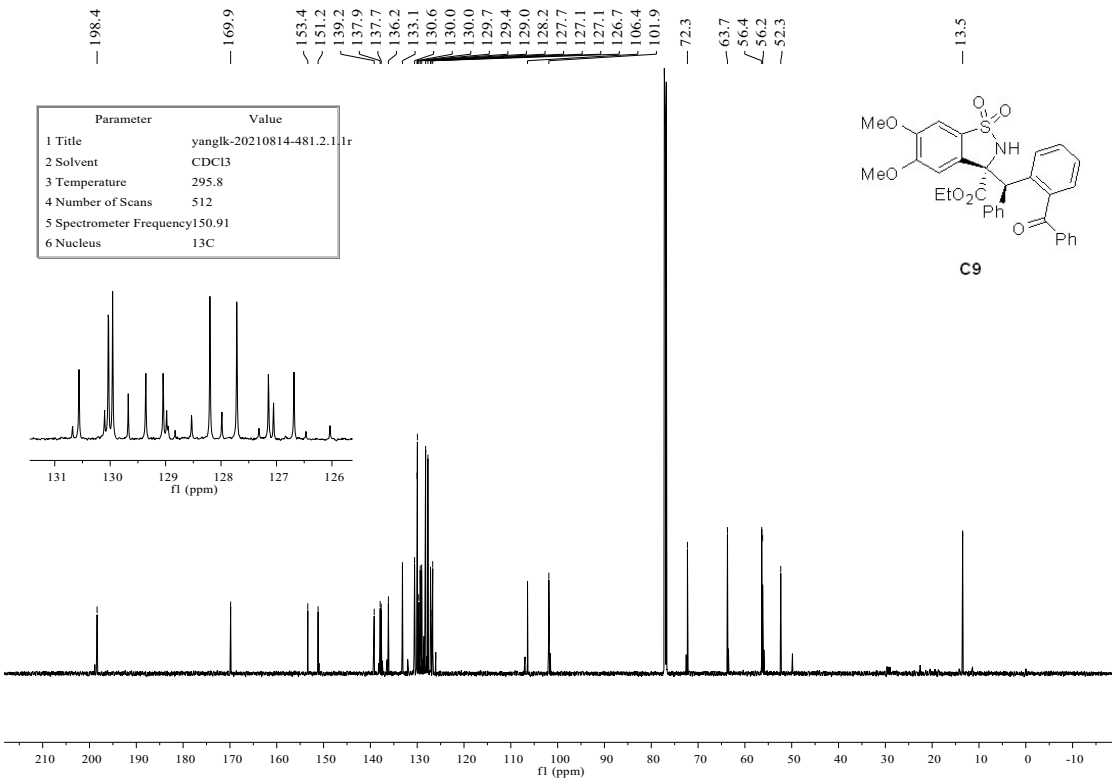

Parameter Value
1 Title as-20211209-ylk-cat411.1.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 85:15
Major isomer
Minor isomer
C8
f1 (ppm)


Parameter Value
1 Title as-20211209-ylk-cat411.2.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C8
f1 (ppm)

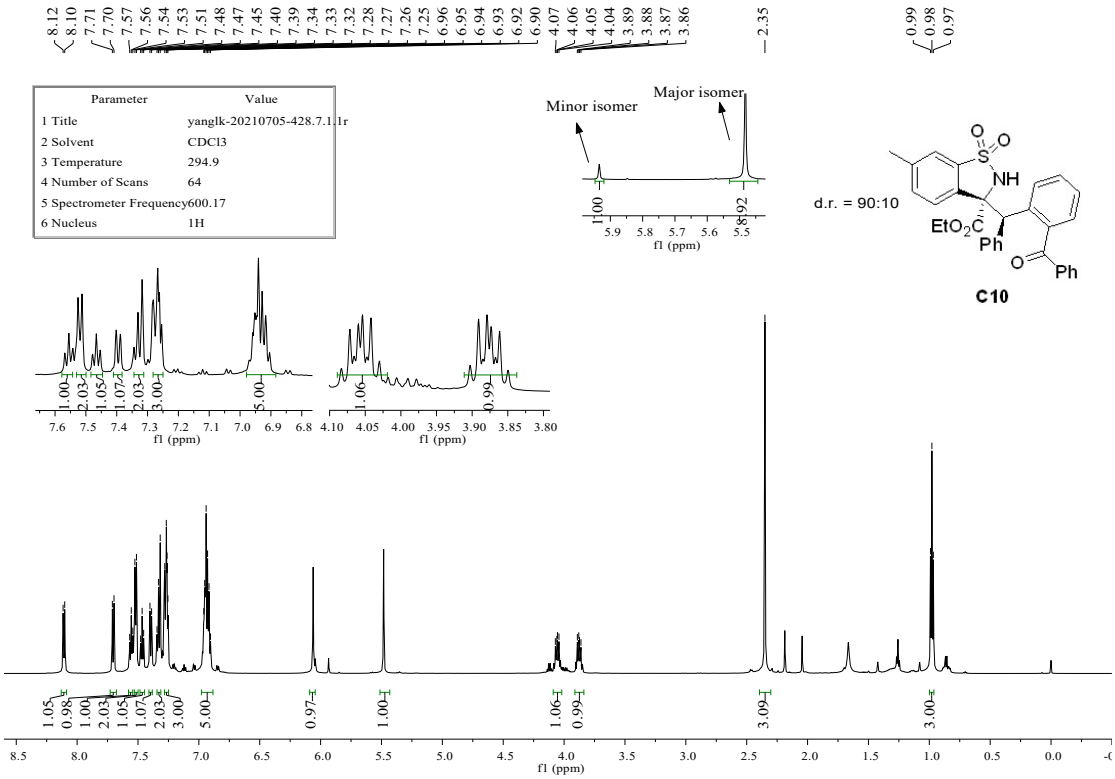

Parameter Value
1 Title as-20211209-ylk-cat411.3.1.1r
2 Solvent CDCl3
3 Temperature 293.1
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-103.13
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

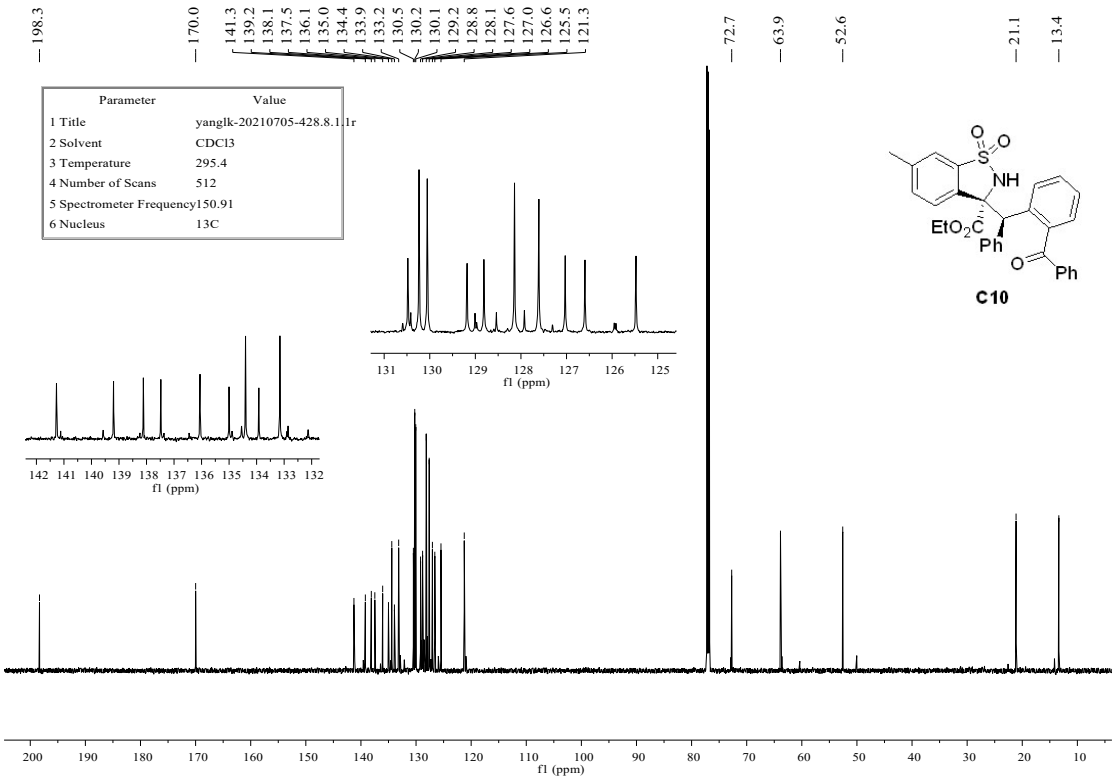
C9


Parameter Value
1 Title yanglk-20210814-481.1.1.1r
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 85:15
Major isomer
Minor isomer
C9
f1 (ppm)

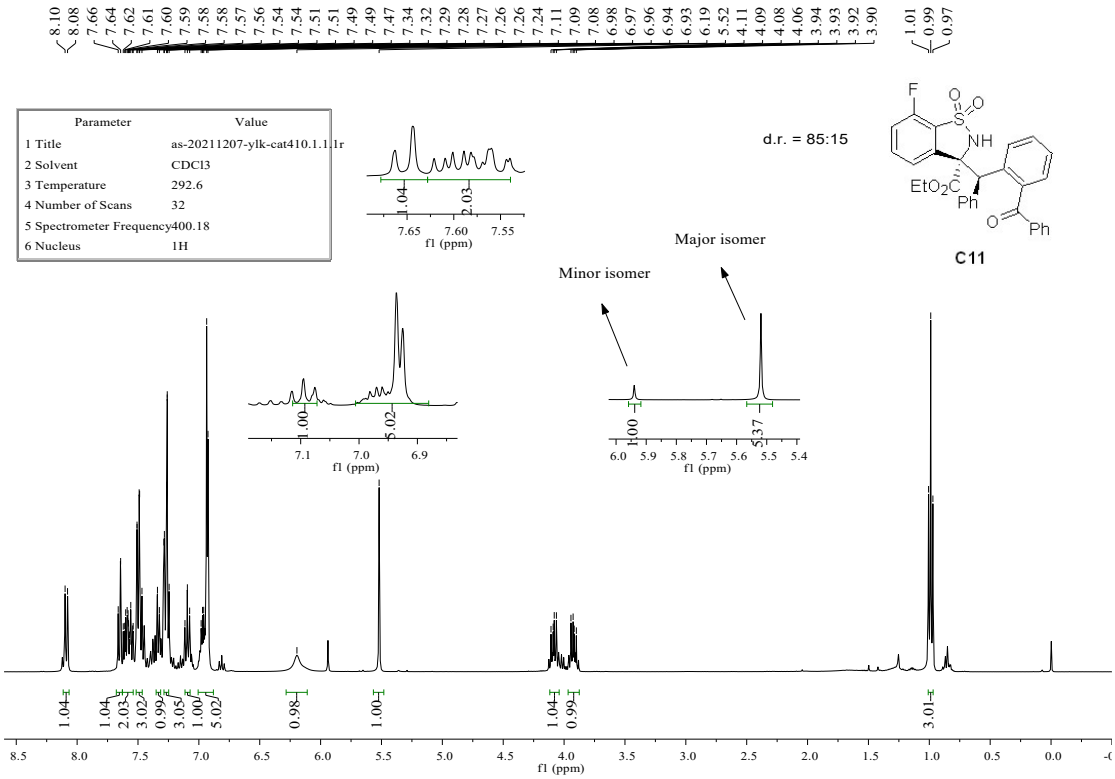

Parameter Value
1 Title yanglk-20210814-481.2.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C9
f1 (ppm)

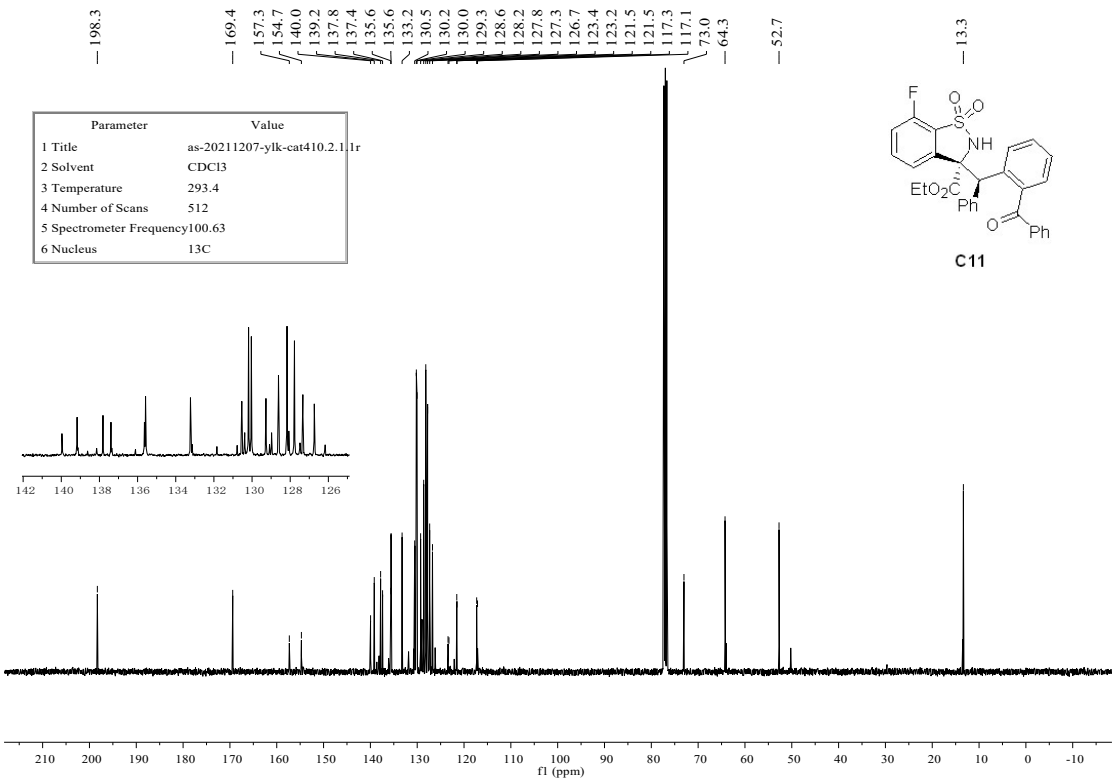
C10

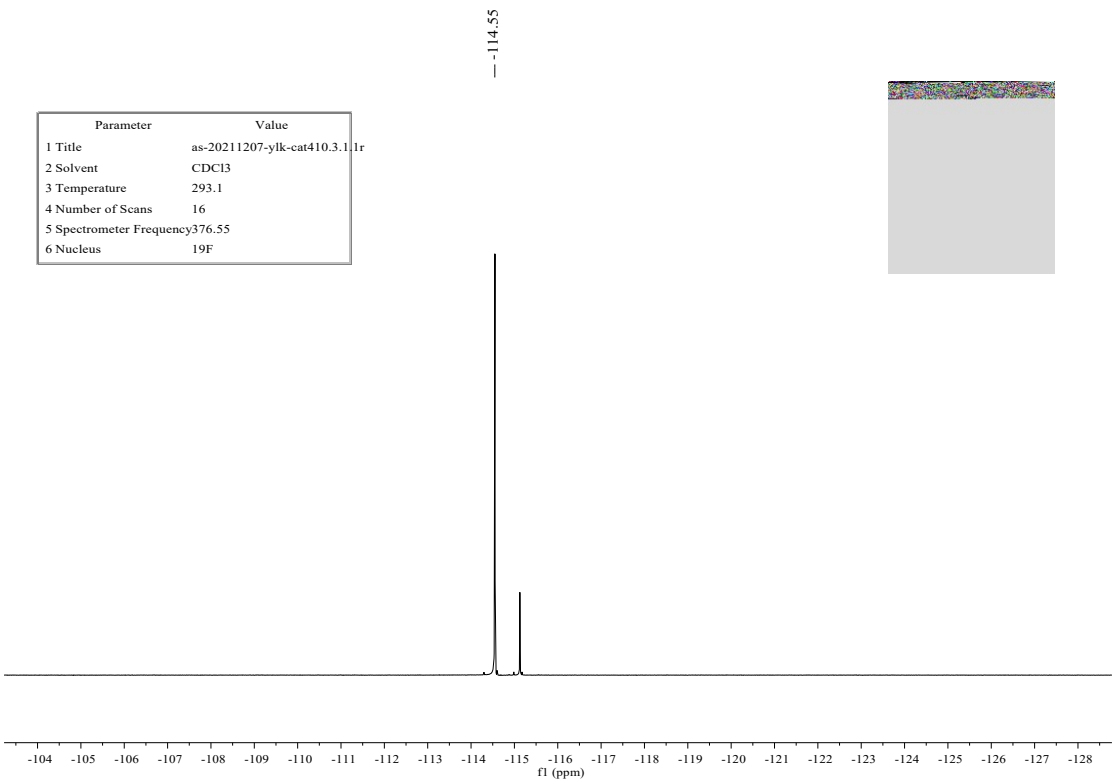

Parameter Value
1 Title yanglk-20210705-428.7.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 64
5 Spectrometer Frequency 600.17
6 Nucleus 1H
Minor isomer
Major isomer
d.r. = 90:10
C10
f1 (ppm)


Parameter Value
1 Title yanglk-20210705-428.8.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C10
f1 (ppm)

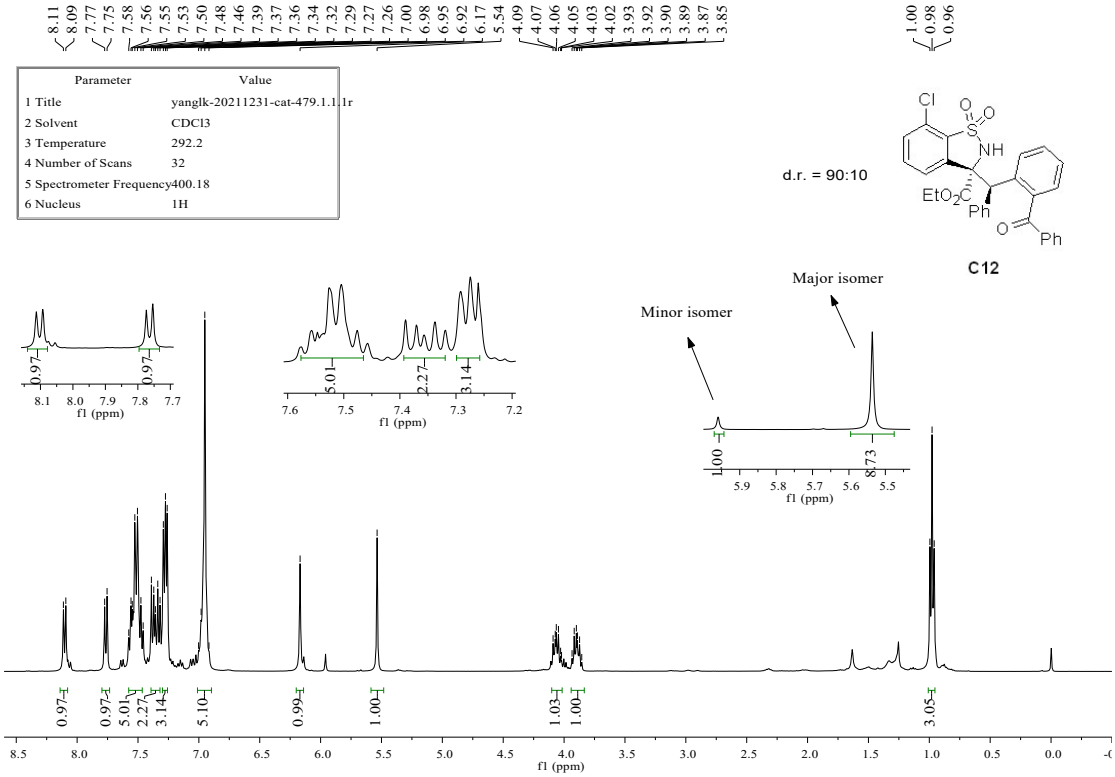
C11

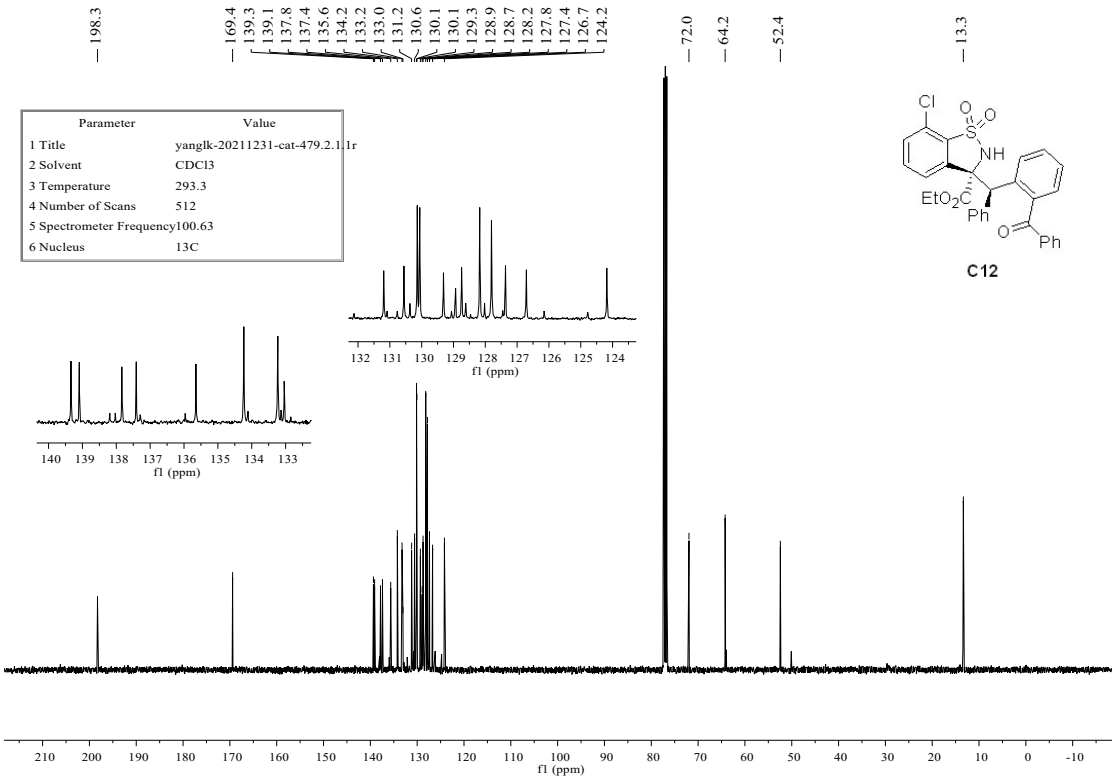

8.10 8.08 7.66 7.64 7.62 7.61 7.60 7.59 7.58 7.58 7.57 7.56 7.54 7.54 7.51 7.51 7.49 7.49 7.47 7.34 7.32 7.29 7.28 7.27 7.26 7.26 7.24 7.11 7.09 7.08 6.98 6.97 6.96 6.94 6.93 6.19 5.52 4.11 4.09 4.08 4.06 3.94 3.93 3.92 3.90 1.01 0.99 0.97
Parameter Value
1 Title as-20211207-ylk-cat410.1.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 85:15
Major isomer
Minor isomer
C11
f1 (ppm)
1.04 1.04 2.03 3.02 0.99 3.05 1.00 5.02 0.98 1.00 1.04 0.99 3.01


198.3 169.4 157.3 154.7 140.0 139.2 137.8 137.4 135.6 135.6 133.2 130.5 130.2 130.0 129.3 128.6 128.2 127.8 127.3 126.7 123.4 123.2 121.5 121.5 117.3 117.1 73.0 64.3 52.7 13.3
Parameter Value
1 Title as-20211207-ylk-cat410.2.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C11
f1 (ppm)

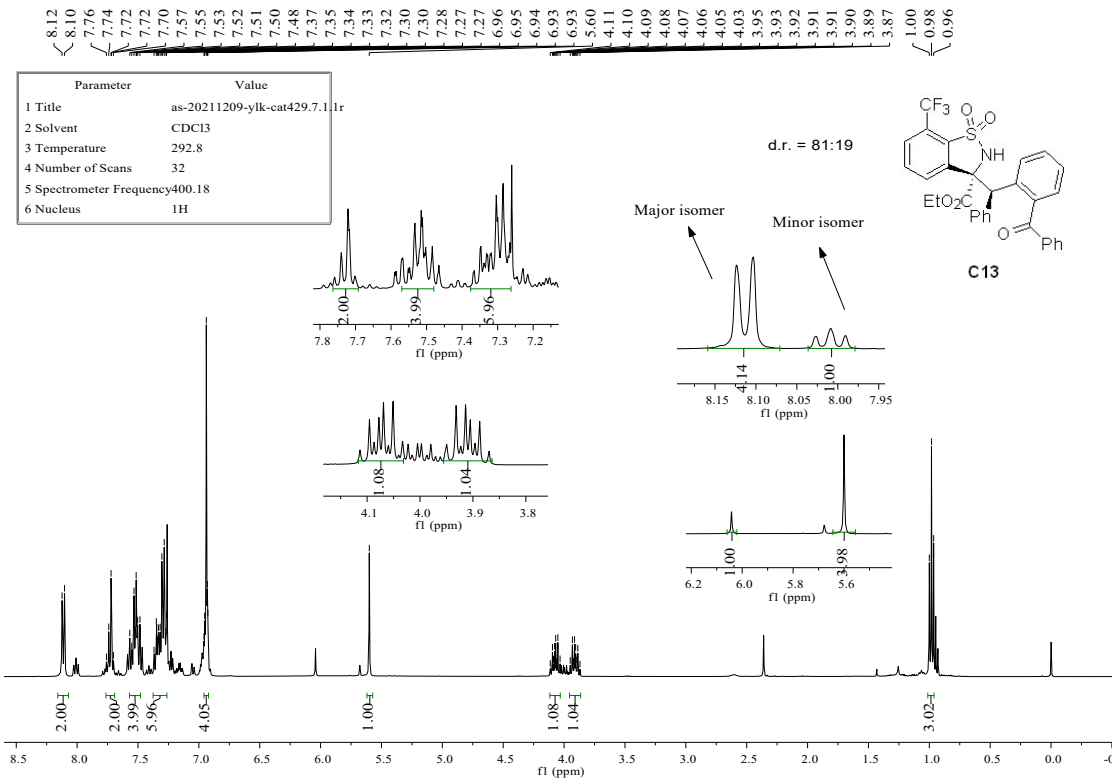

-114.55
Parameter Value
1 Title as-20211207-ylk-cat410.3.11r
2 Solvent CDCl3
3 Temperature 293.1
4 Number of Scans 16
5 Spectrometer Frequency376.55
6 Nucleus 19F
-104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128
f1 (ppm)

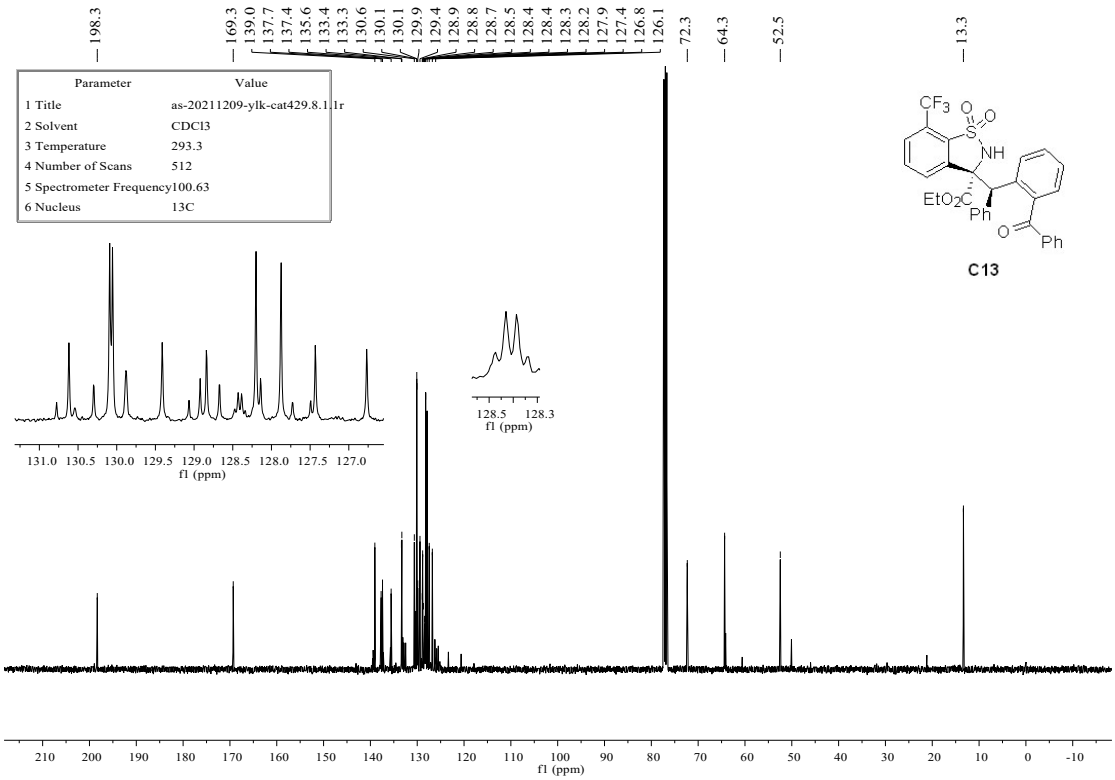
C12


Parameter Value
1 Title yanglk-20211231-cat-479.1.1.1r
2 Solvent CDCl3
3 Temperature 292.2
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 90:10
C12
Major isomer
Minor isomer
f1 (ppm)


Parameter Value
1 Title yanglk-20211231-cat-479.2.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C12
f1 (ppm)

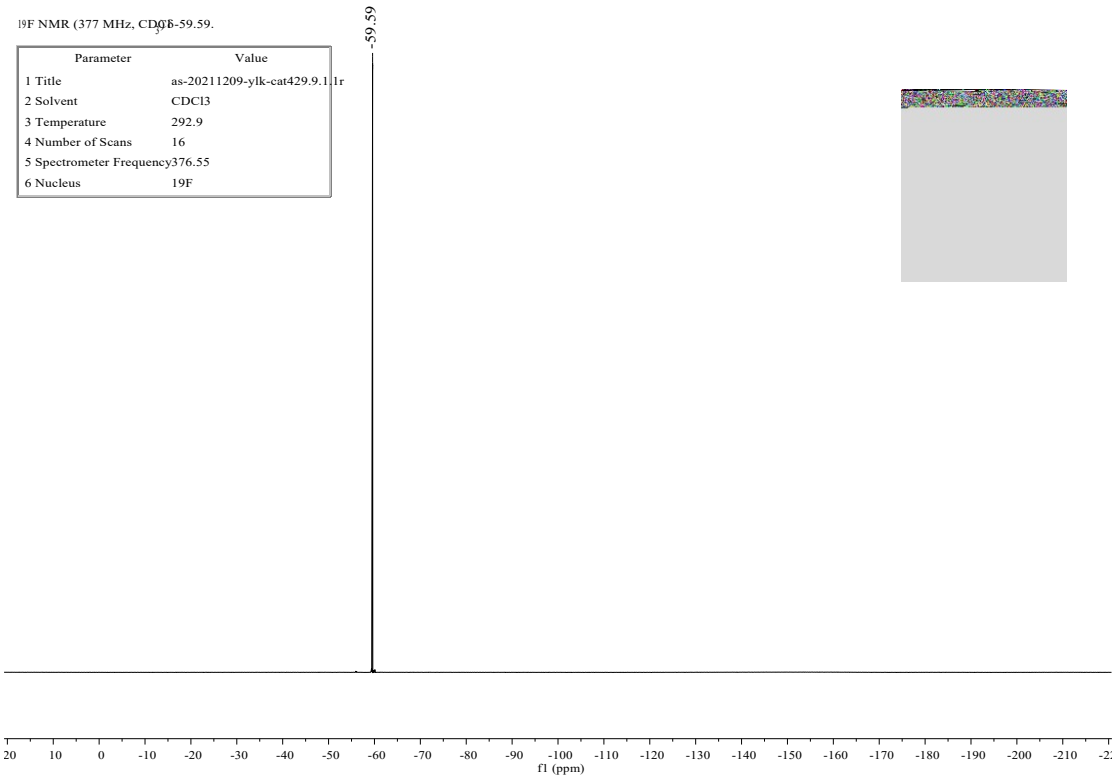
C13


Parameter Value
1 Title as-20211209-ylk-cat429.7.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 81:19
Major isomer
Minor isomer
C13
f1 (ppm)

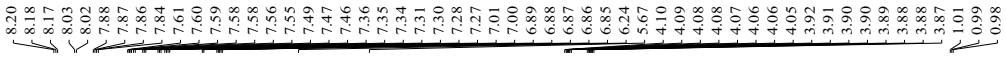

Parameter Value
1 Title as-20211209-ylk-cat429.8.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C13
f1 (ppm)

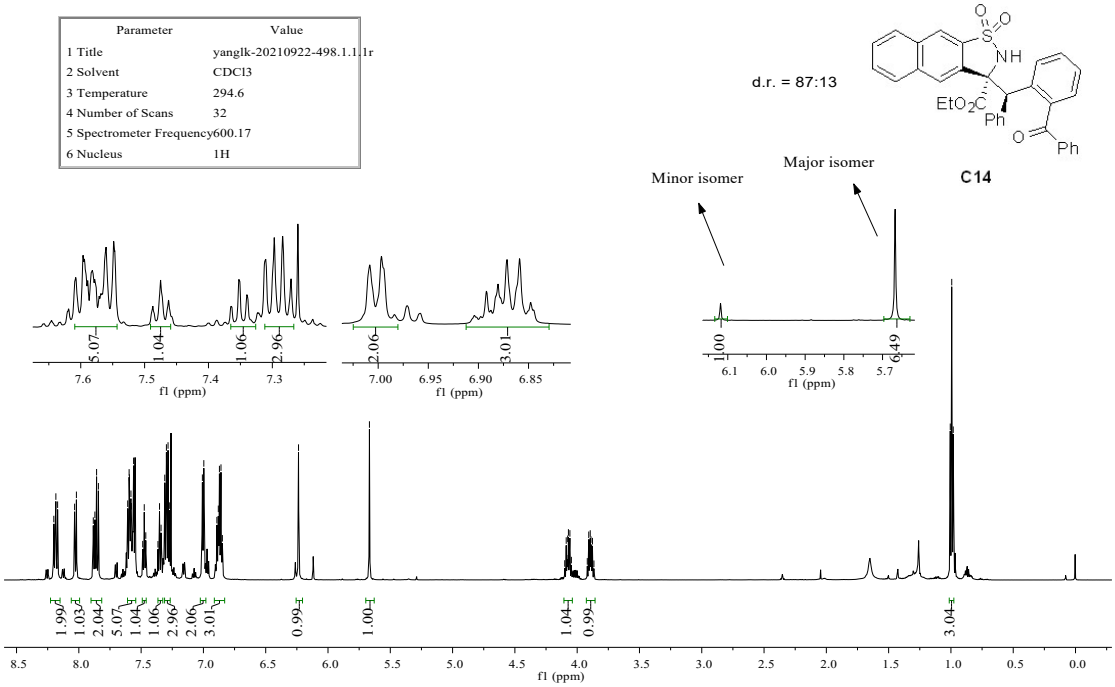
19F NMR (377 MHz, CDCl3) δ -59.59.

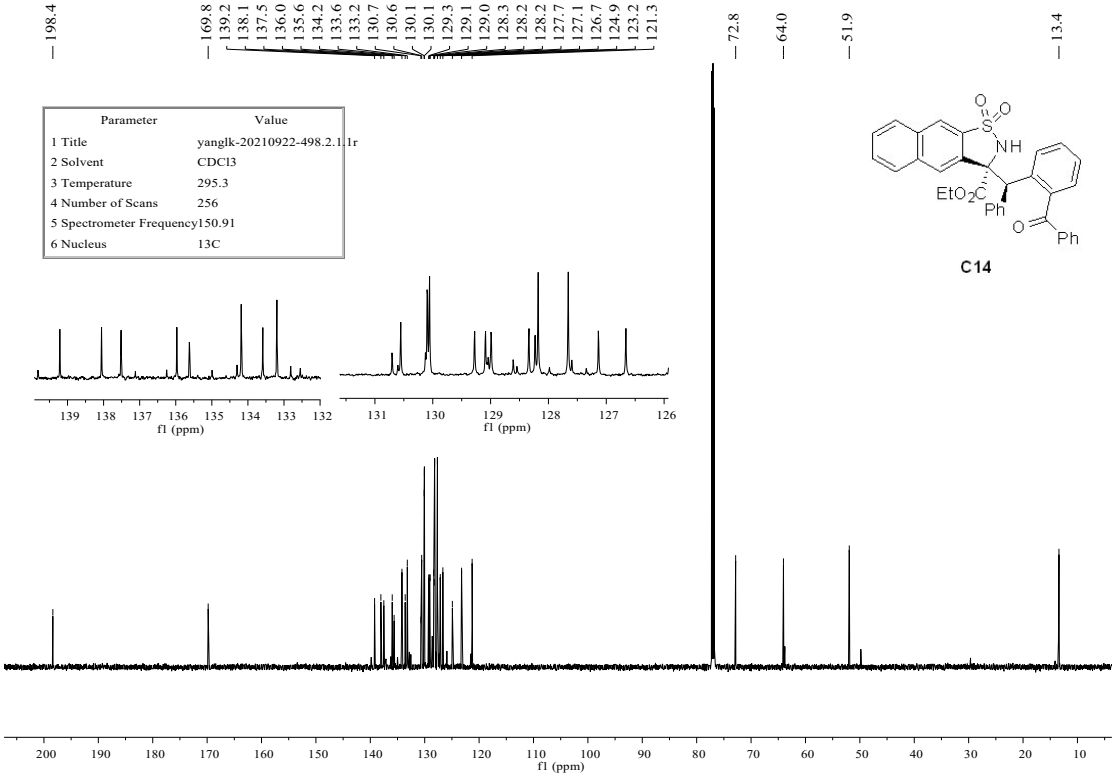
Parameter	Value
1 Title	as-20211209-ylk-cat429.9.1.1r
2 Solvent	CDCl3
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



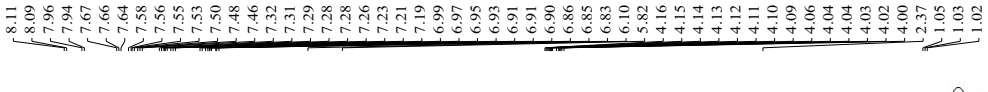
C14

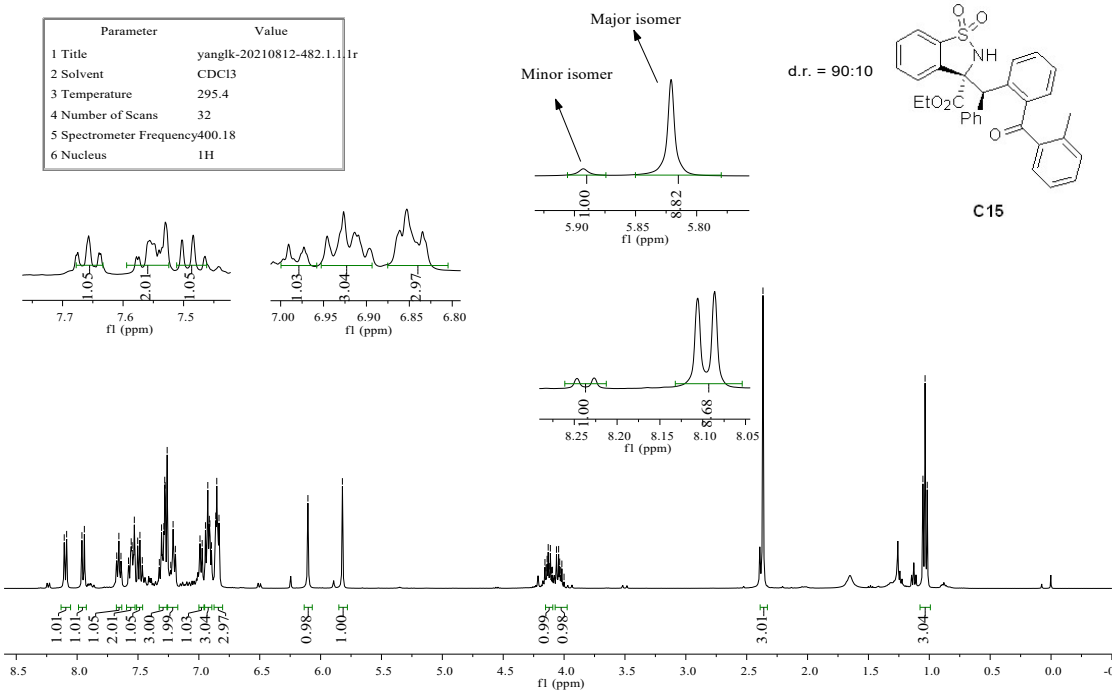

8.20 8.18 8.17 8.03 8.02 7.88 7.87 7.86 7.84 7.61 7.60 7.59 7.58 7.58 7.56 7.55 7.49 7.47 7.46 7.36 7.35 7.34 7.31 7.30 7.28 7.27 7.01 7.00 6.89 6.88 6.87 6.86 6.85 6.24 5.67 4.10 4.09 4.08 4.08 4.07 4.06 4.06 4.05 3.92 3.91 3.90 3.90 3.89 3.88 3.88 3.87 1.01 0.99 0.98

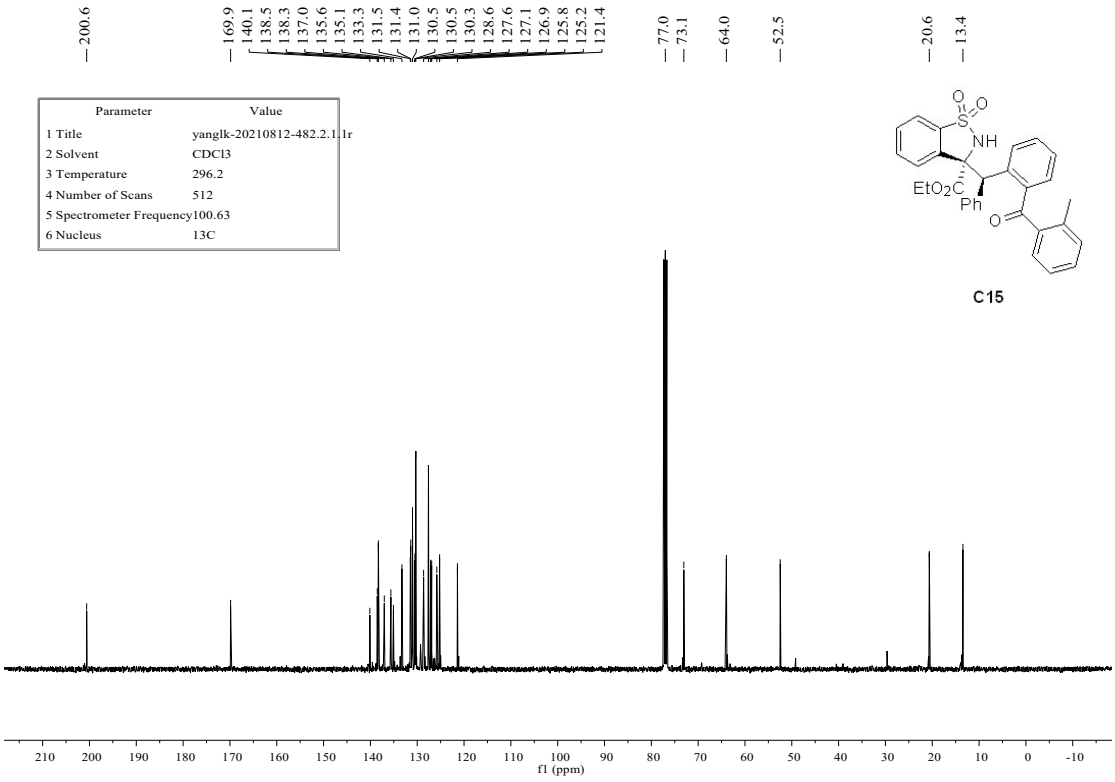

Parameter Value
1 Title yanglk-20210922-498.1.1.1r
2 Solvent CDCl3
3 Temperature 294.6
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 87:13
Minor isomer
Major isomer
C14
f1 (ppm)


198.4 169.8 139.2 138.1 137.5 136.0 135.6 134.2 133.6 133.2 130.7 130.6 130.1 130.1 129.3 129.1 129.0 128.3 128.2 128.2 127.7 127.1 126.7 124.9 123.2 121.3 72.8 64.0 51.9 13.4
Parameter Value
1 Title yanglk-20210922-498.2.1.1r
2 Solvent CDCl3
3 Temperature 295.3
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C14
f1 (ppm)

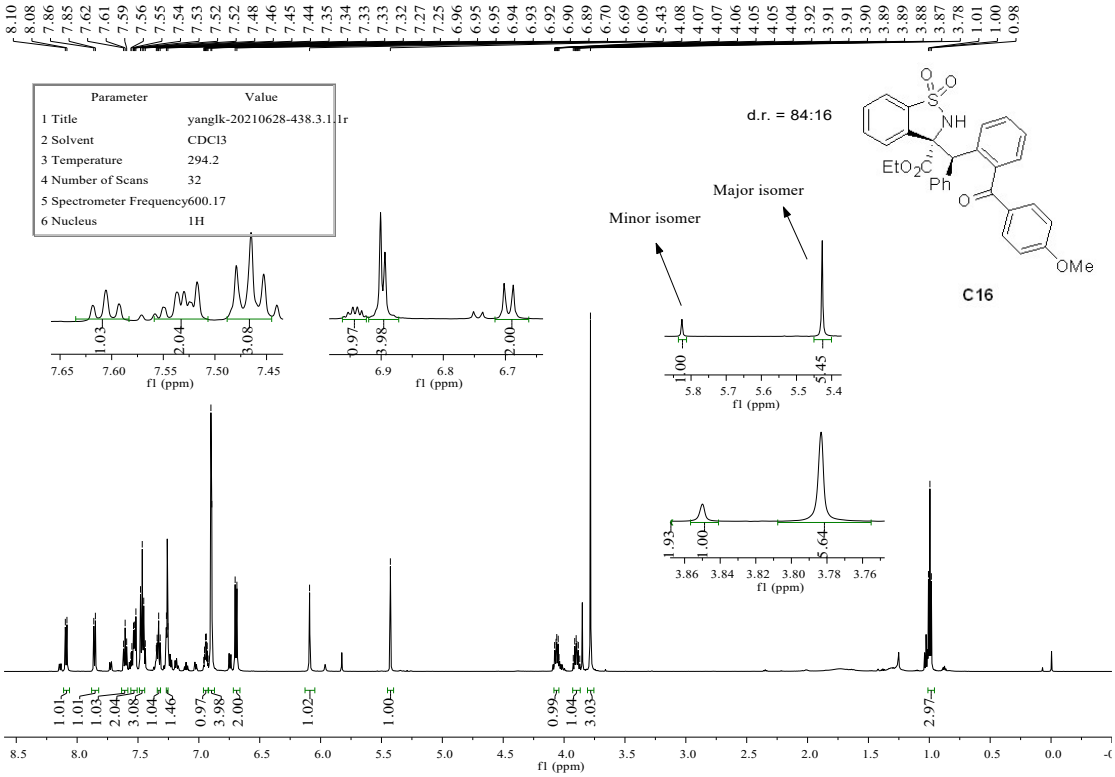
C15

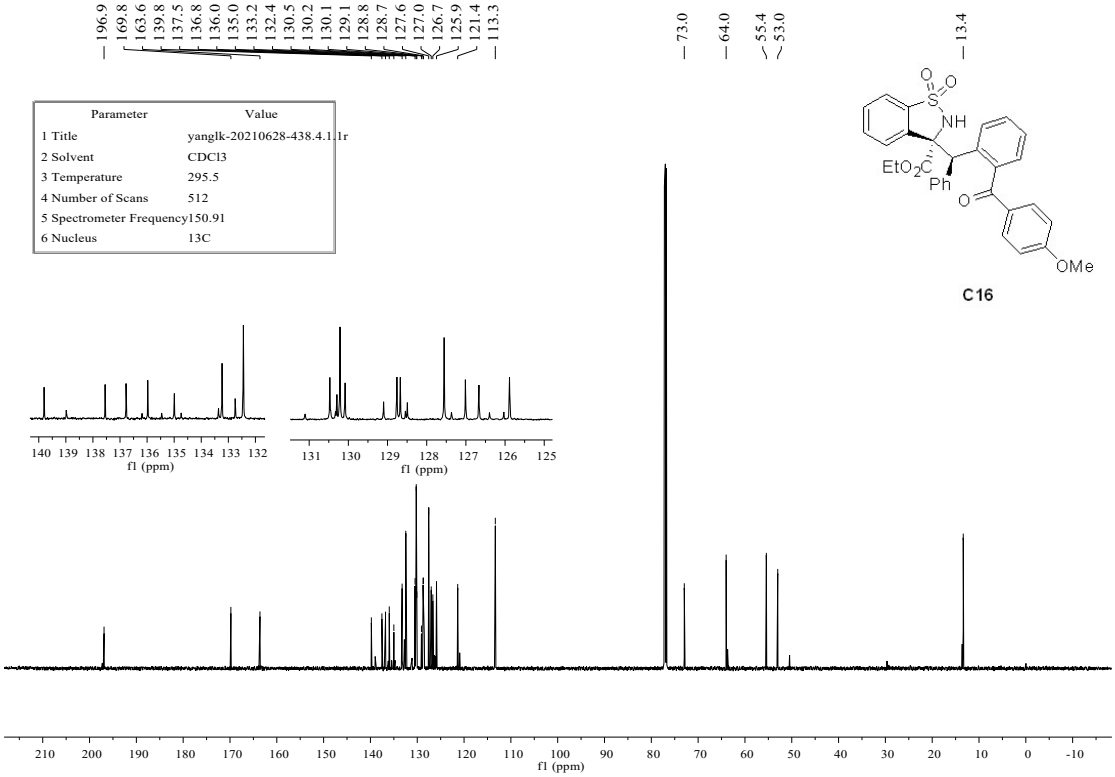



Parameter Value
1 Title yanglk-20210812-482.1.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
d.r. = 90:10
C15
f1 (ppm)

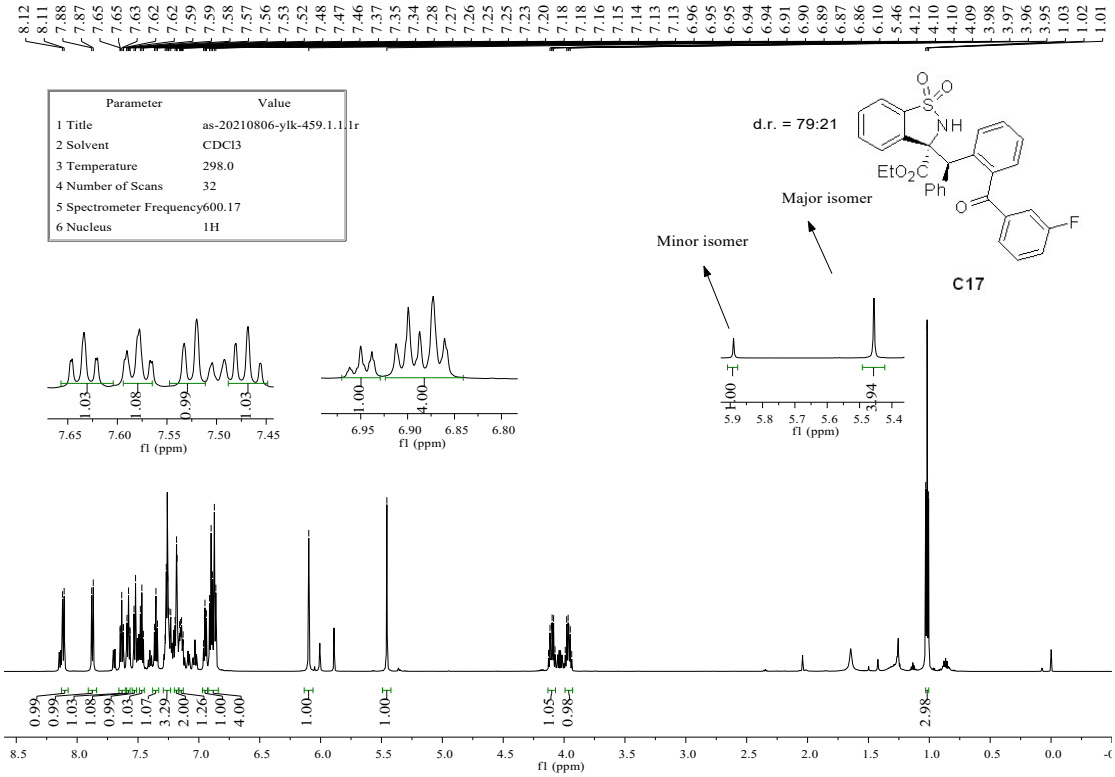

Parameter Value
1 Title yanglk-20210812-482.2.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C15
f1 (ppm)

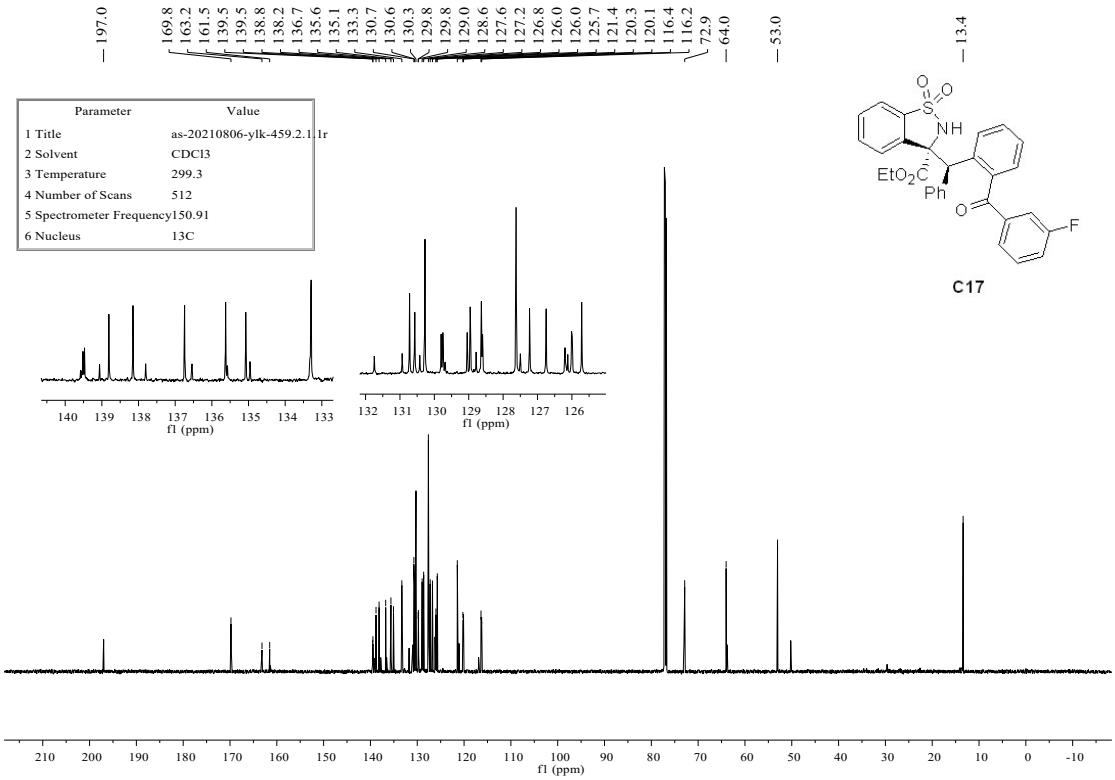
C16


Parameter Value
1 Title yanglk-20210628-438.3.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 84:16
Major isomer
Minor isomer
C16
f1 (ppm)


Parameter Value
1 Title yanglk-20210628-438.4.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C16
f1 (ppm)

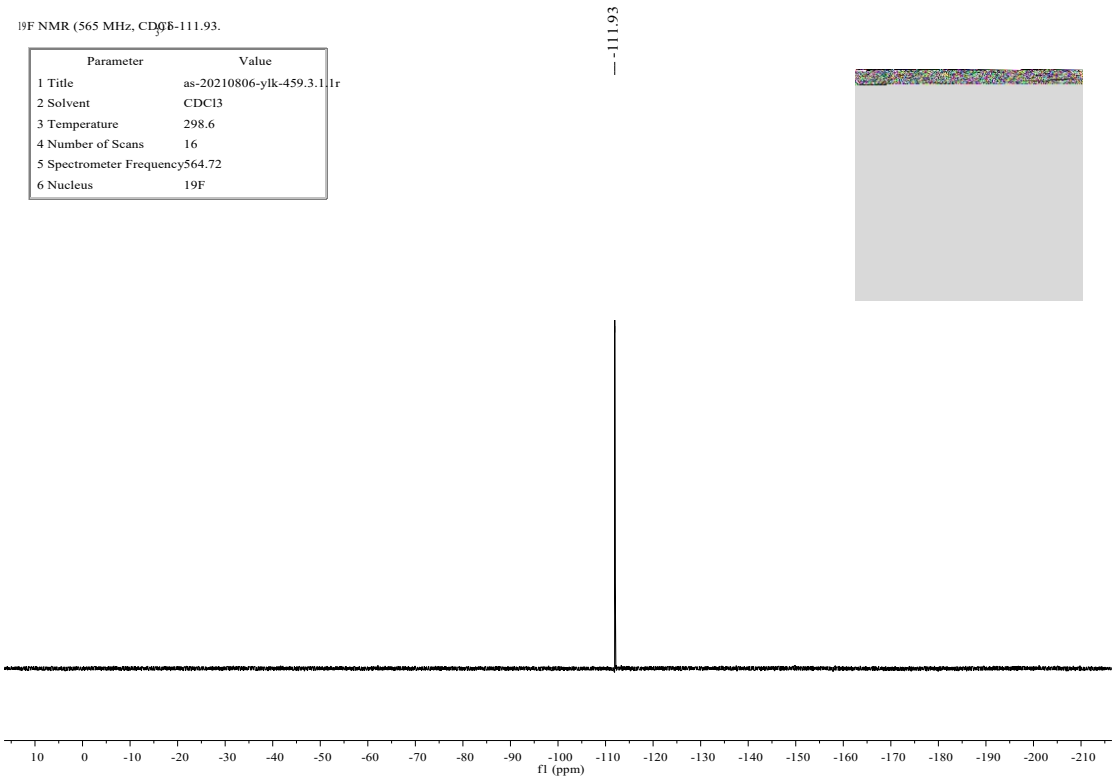
C17


Parameter Value
1 Title as-20210806-ylk-459.1.1.1r
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 79:21
Major isomer
Minor isomer
C17
f1 (ppm)

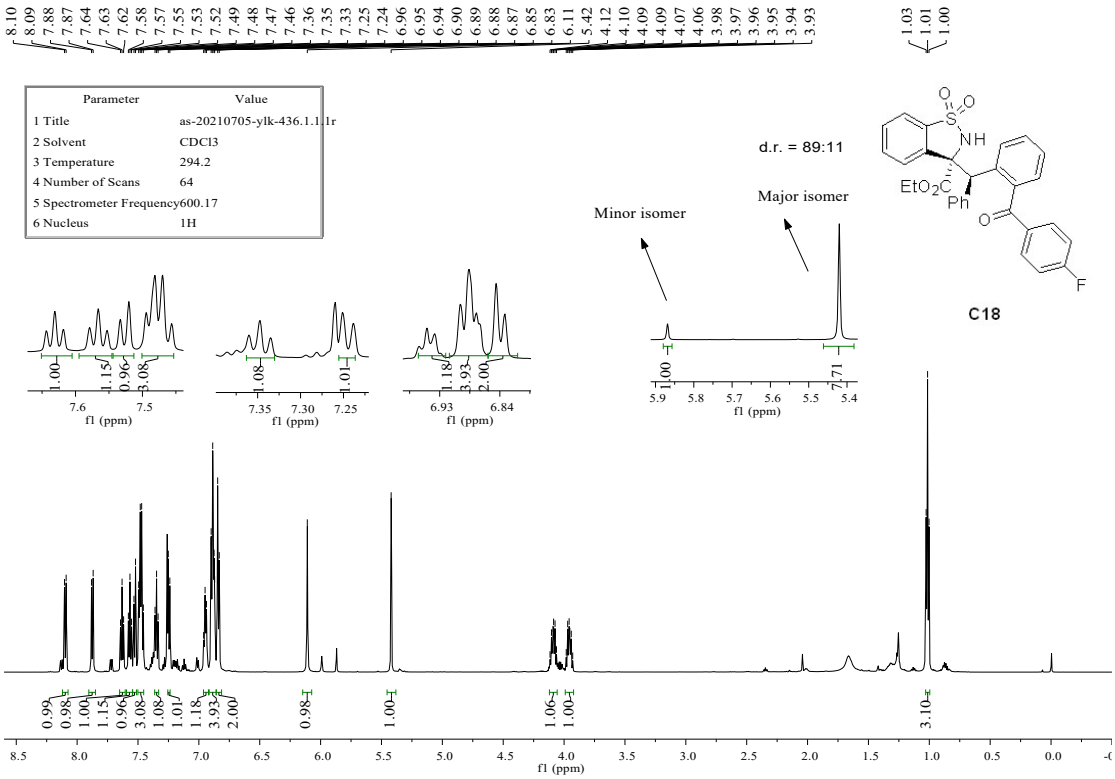

Parameter Value
1 Title as-20210806-ylk-459.2.1.1r
2 Solvent CDCl3
3 Temperature 299.3
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C17
f1 (ppm)

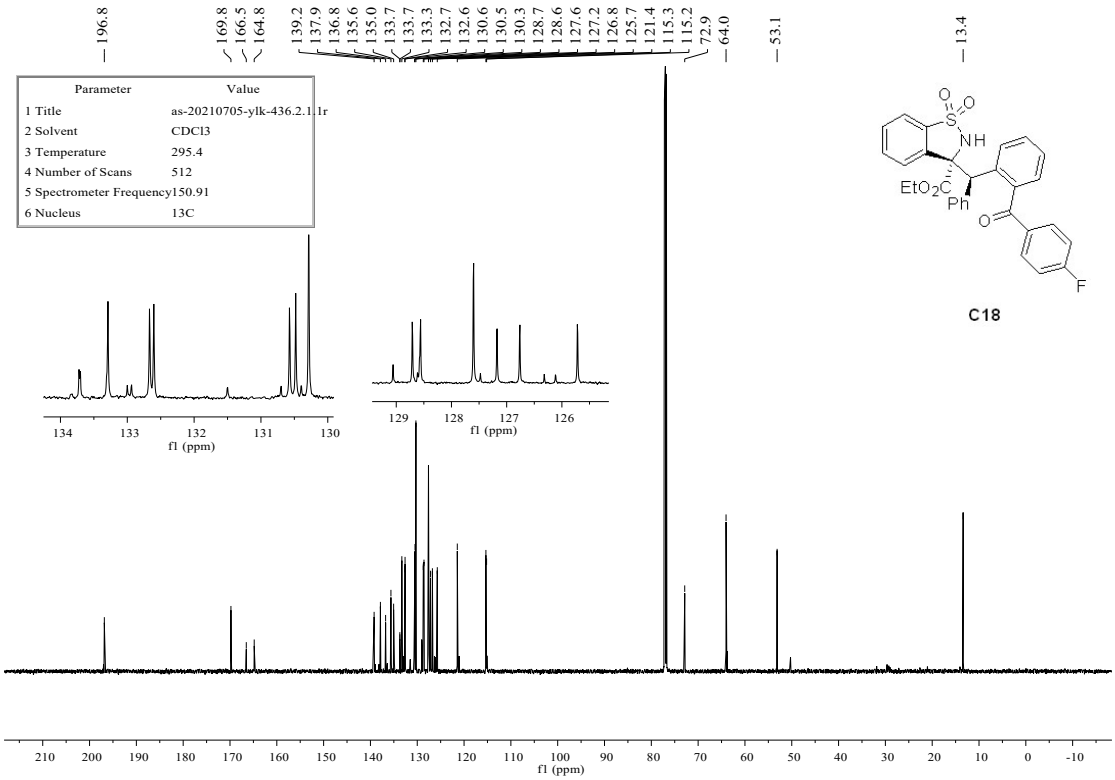
^{19}F NMR (565 MHz, CDCl$_3$) δ -111.93.

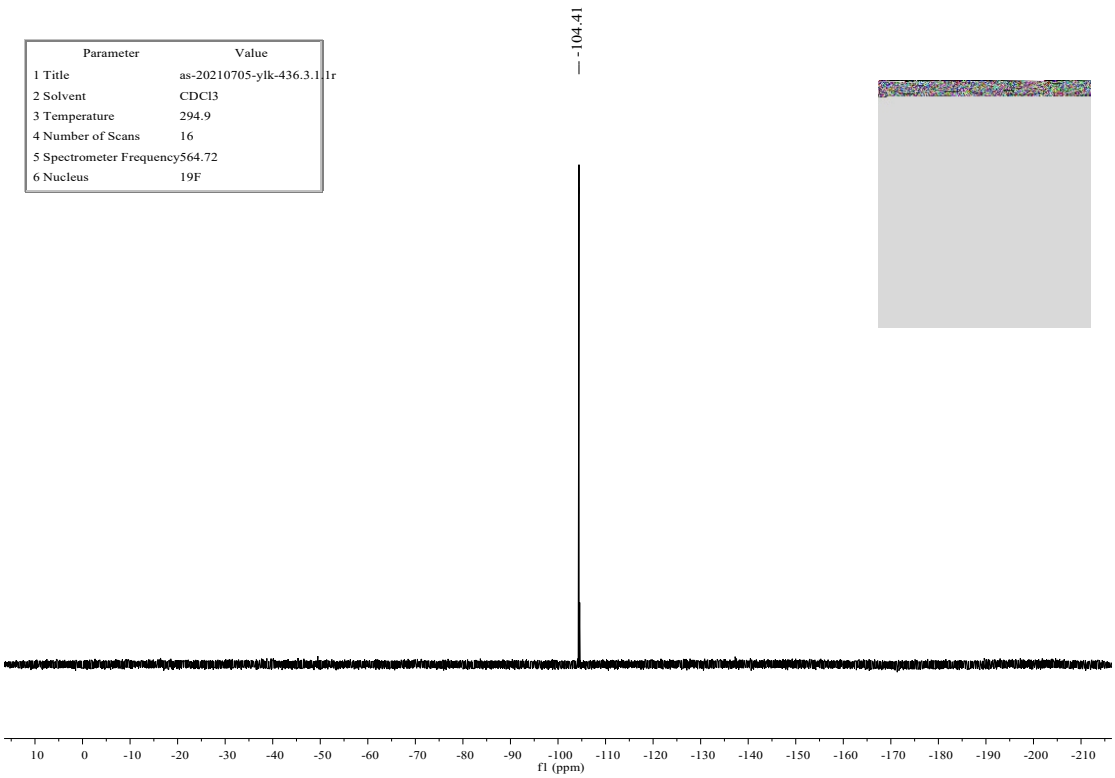
Parameter	Value
1 Title	as-20210806-ylk-459.3.1.1r
2 Solvent	CDCl3
3 Temperature	298.6
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F



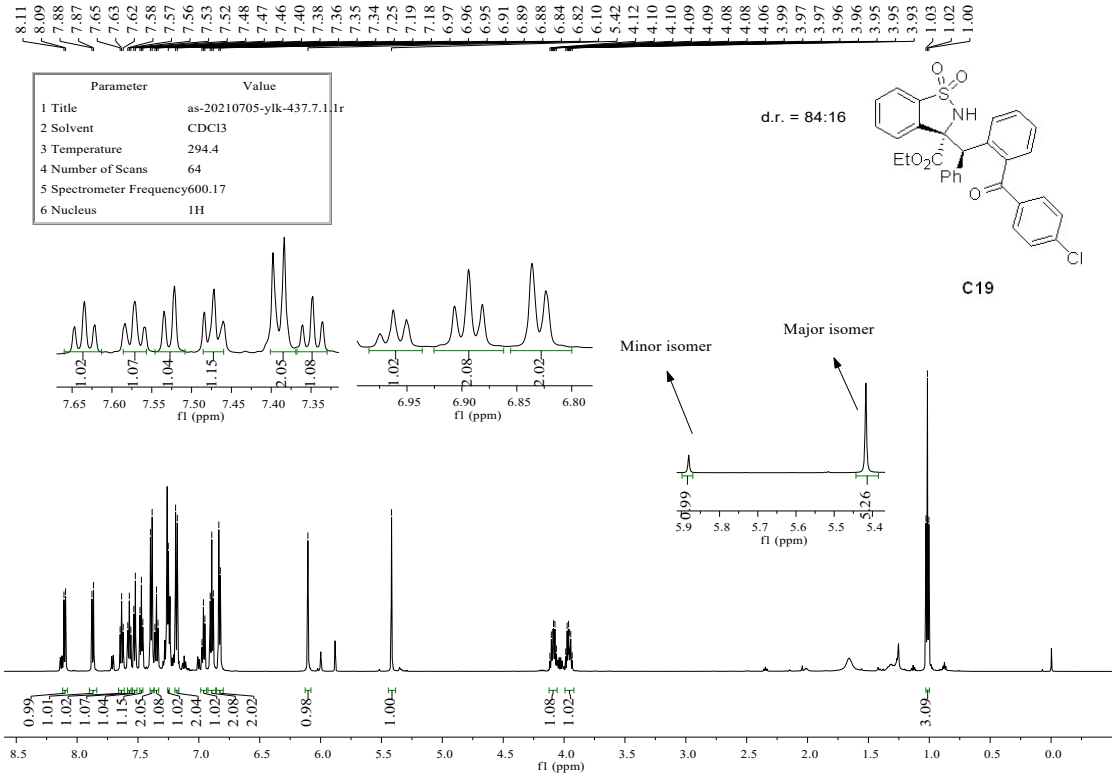
C18

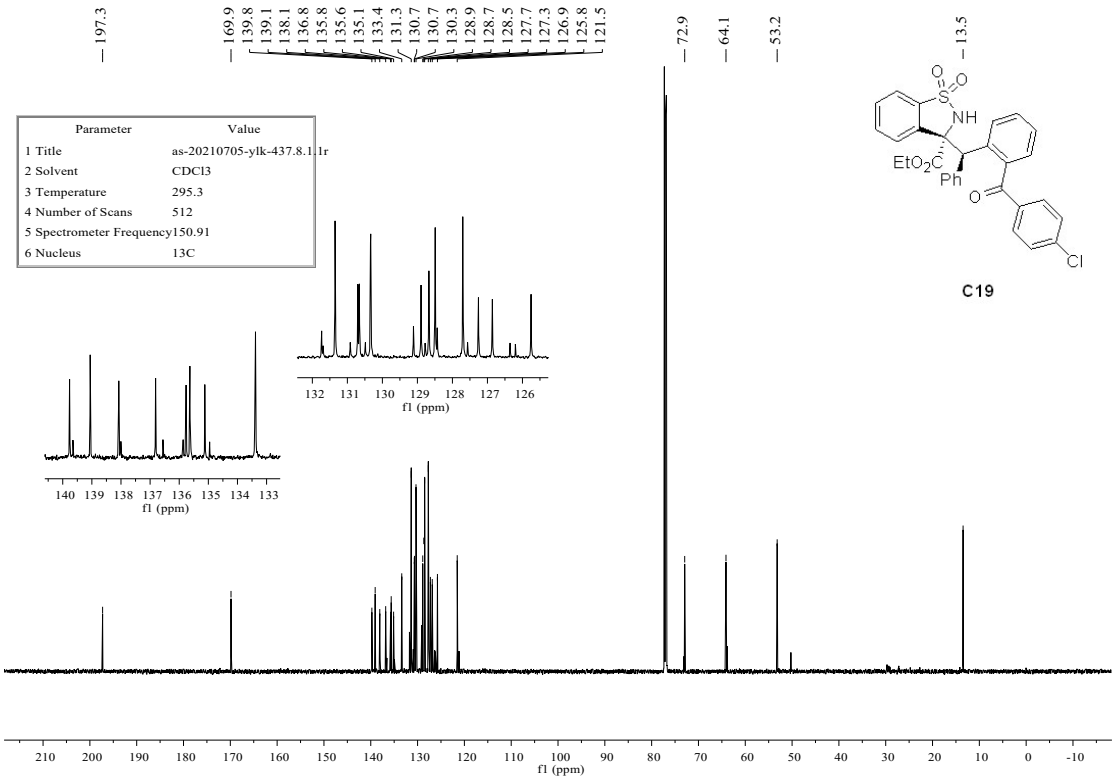

Parameter Value
1 Title as-20210705-ylk-436.1.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 64
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 89:11
Minor isomer
Major isomer
C18
f1 (ppm)


Parameter Value
1 Title as-20210705-ylk-436.2.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C18
f1 (ppm)

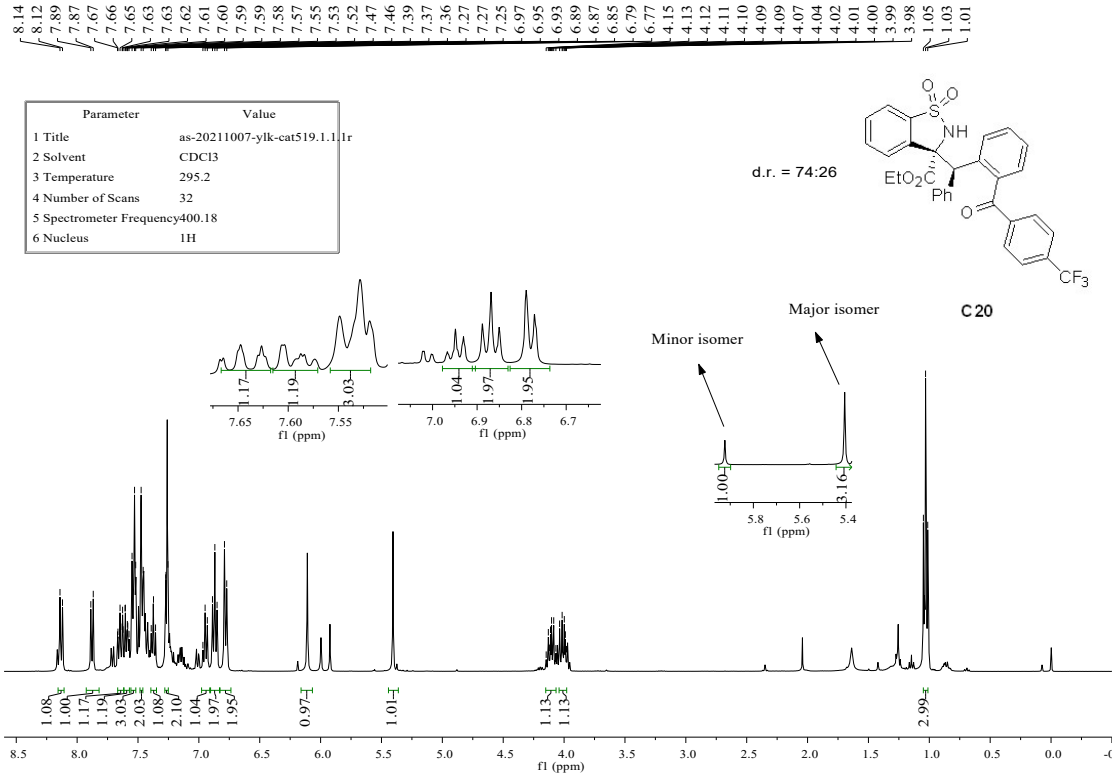

Parameter Value
1 Title as-20210705-ylk-436.3.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-104.41
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

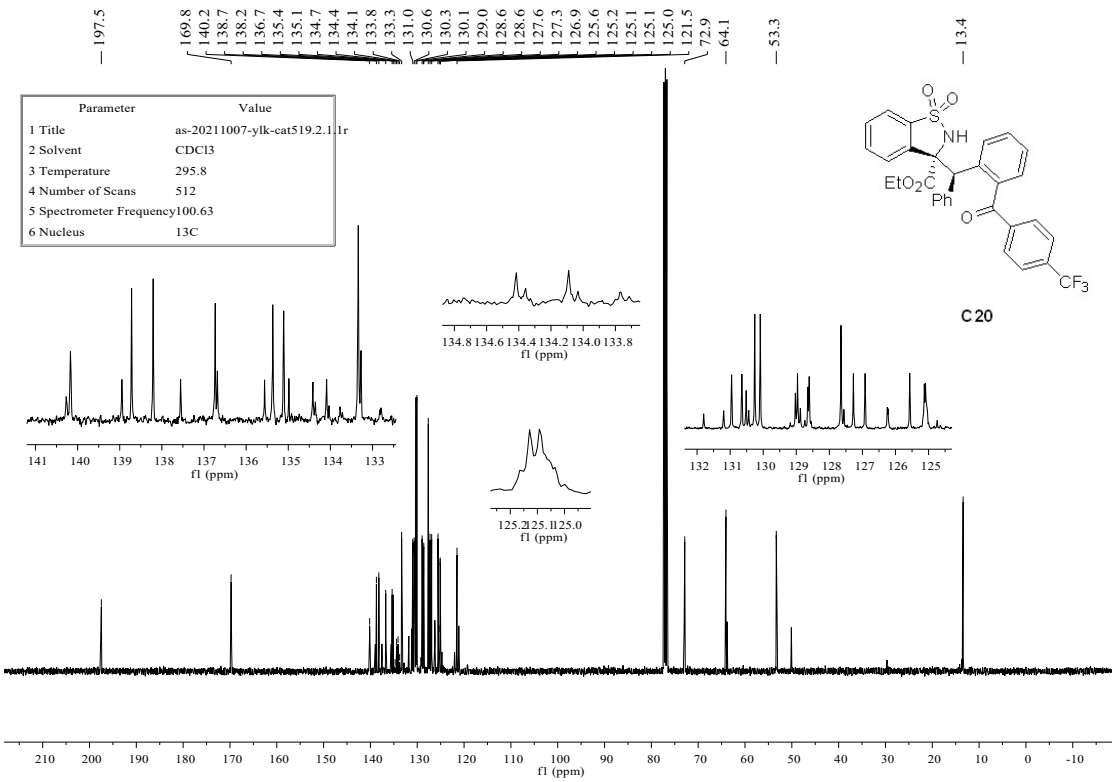
C19


Parameter Value
1 Title as-20210705-ylk-437.7.1.1r
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 64
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 84:16
C19
Minor isomer
Major isomer
f1 (ppm)

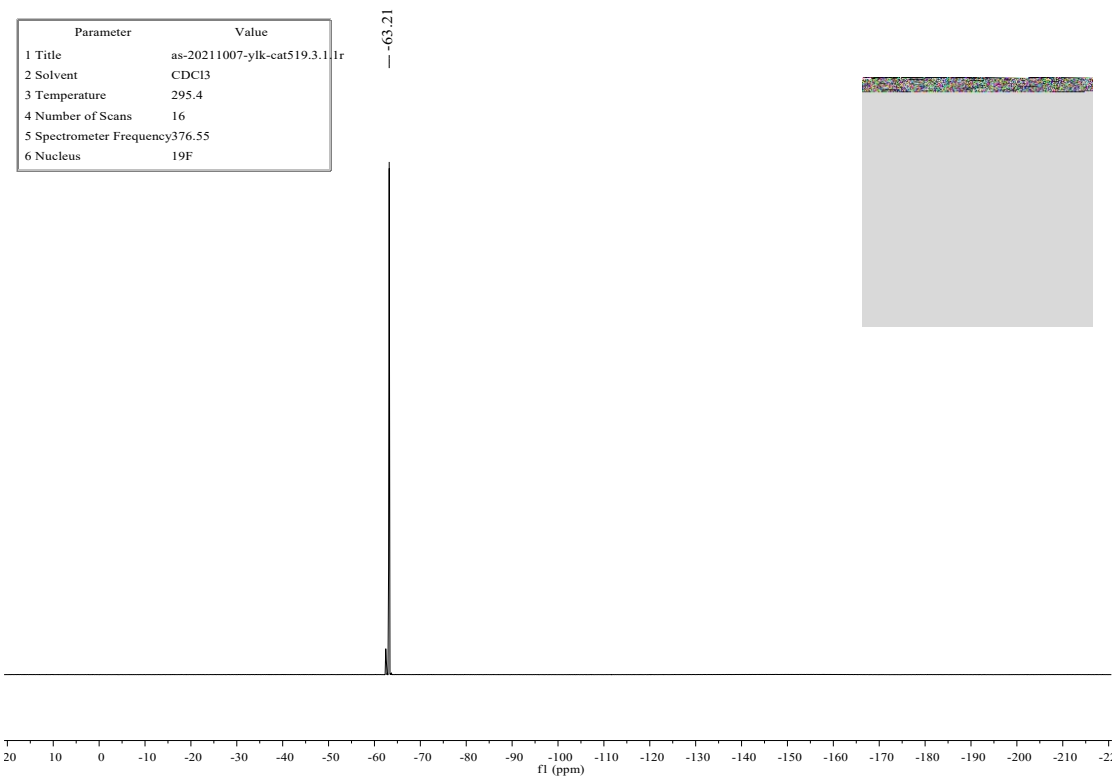

Parameter Value
1 Title as-20210705-ylk-437.8.1.1r
2 Solvent CDCl3
3 Temperature 295.3
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C19
f1 (ppm)

C20

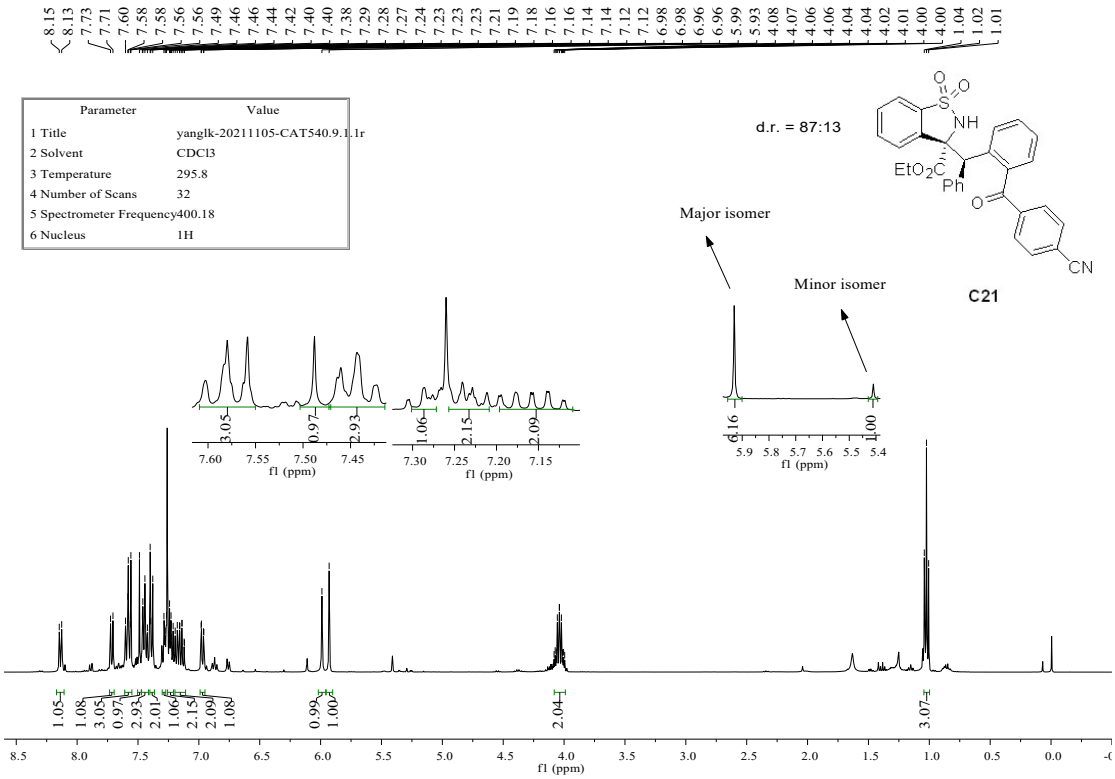

Parameter Value
1 Title as-20211007-ylk-cat519.1.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 74:26
Major isomer
Minor isomer
C20
f1 (ppm)

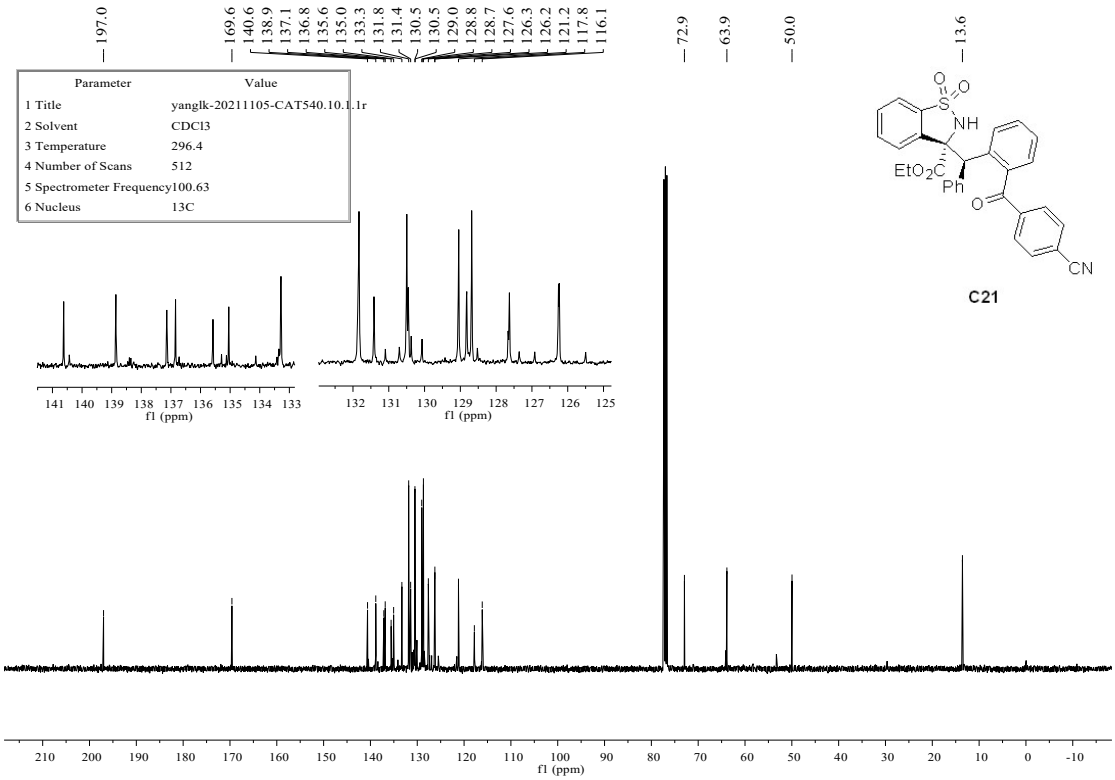

Parameter Value
1 Title as-20211007-ylk-cat519.2.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C20
f1 (ppm)

Parameter	Value
1 Title	as-20211007-ylk-cat519.3.1.1r
2 Solvent	CDCl3
3 Temperature	295.4
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

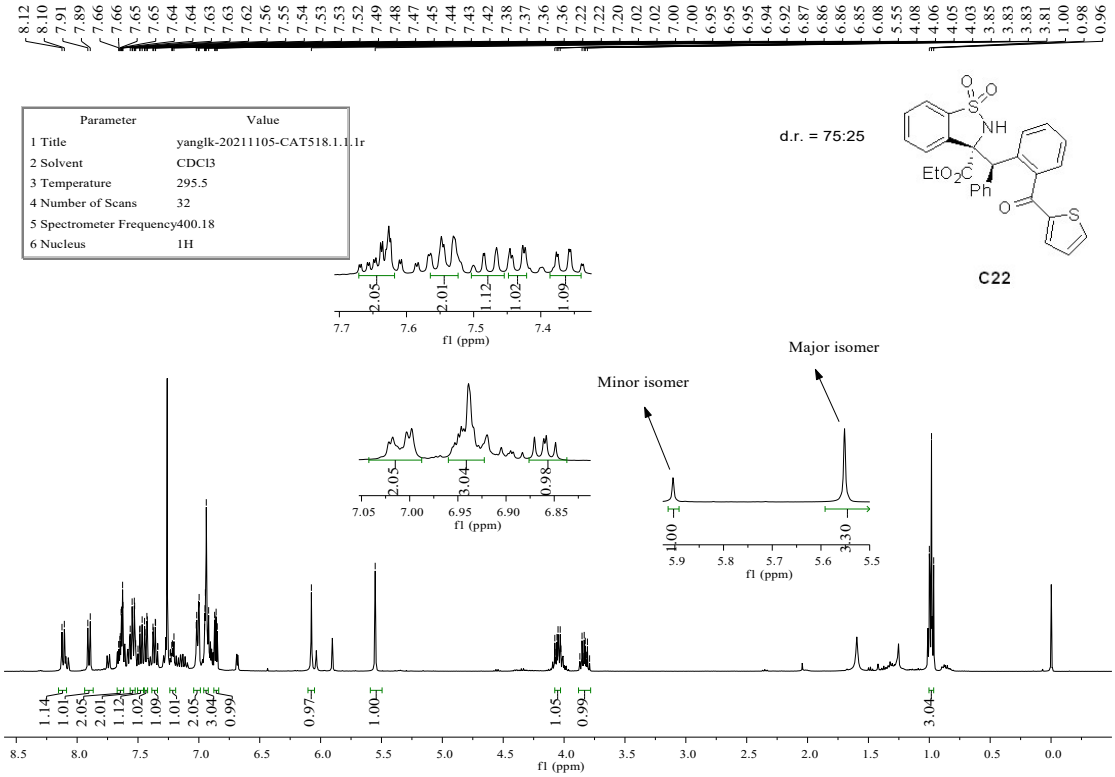


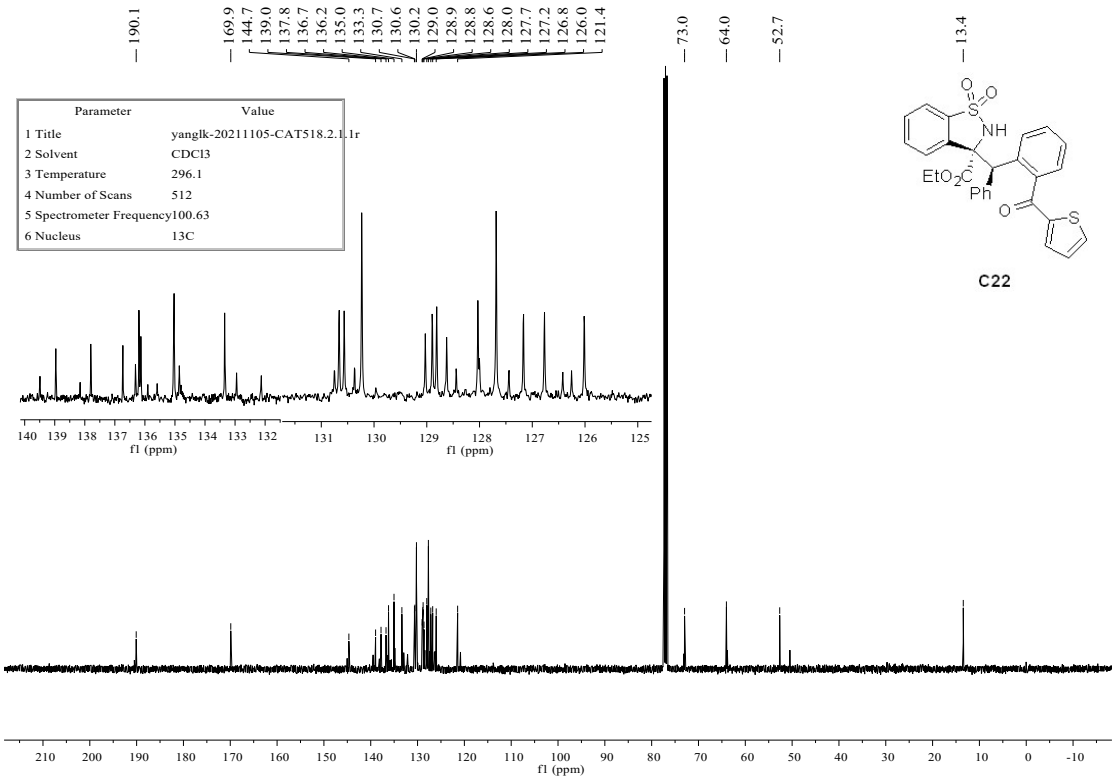
C21


Parameter Value
1 Title yanglk-20211105-CAT540.9.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 87:13
Major isomer
Minor isomer
C21
f1 (ppm)

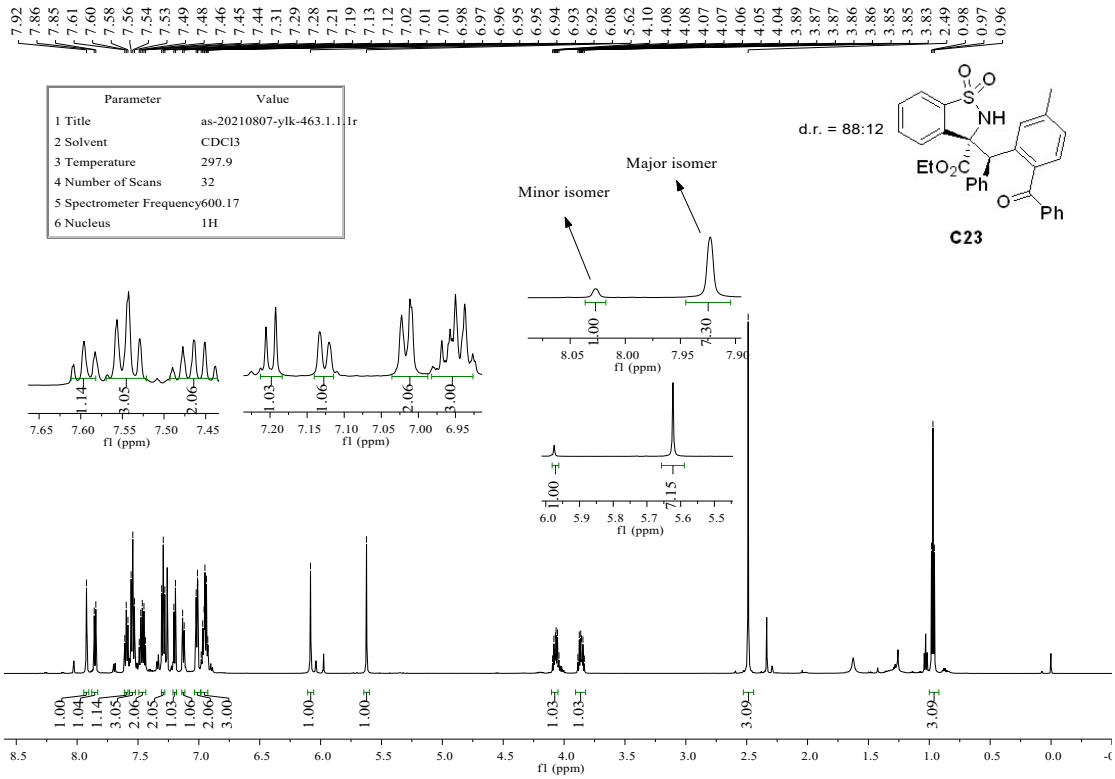

Parameter Value
1 Title yanglk-20211105-CAT540.10.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C21
f1 (ppm)

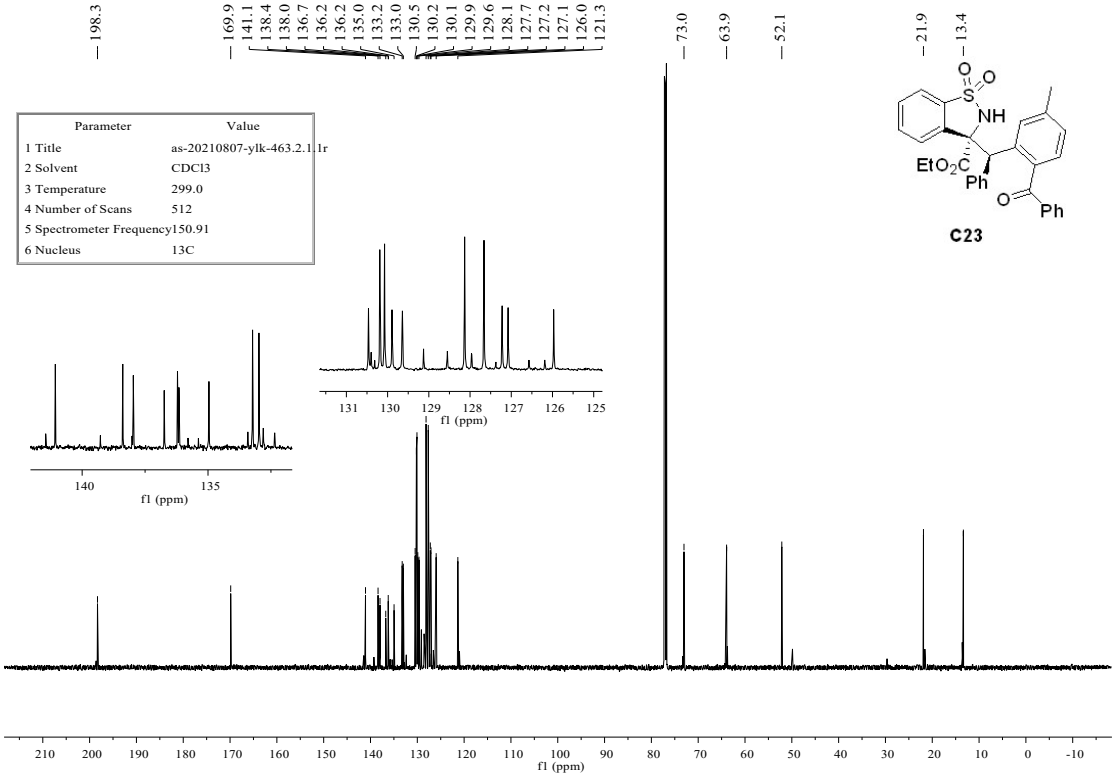
C22


Parameter Value
1 Title yanglk-20211105-CAT518.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 75:25
C22
Major isomer
Minor isomer
f1 (ppm)

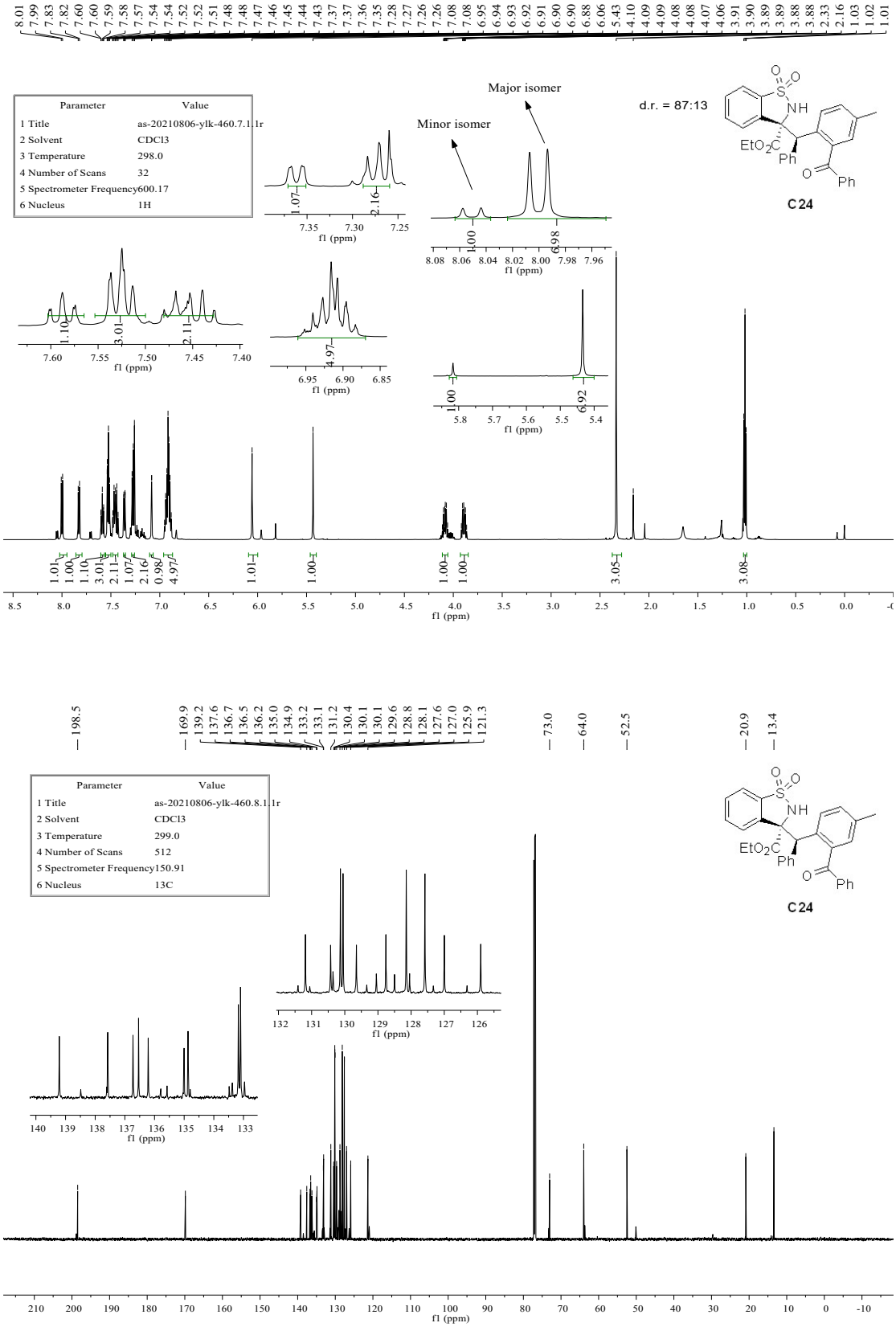

Parameter Value
1 Title yanglk-20211105-CAT518.2.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C22
f1 (ppm)

C23

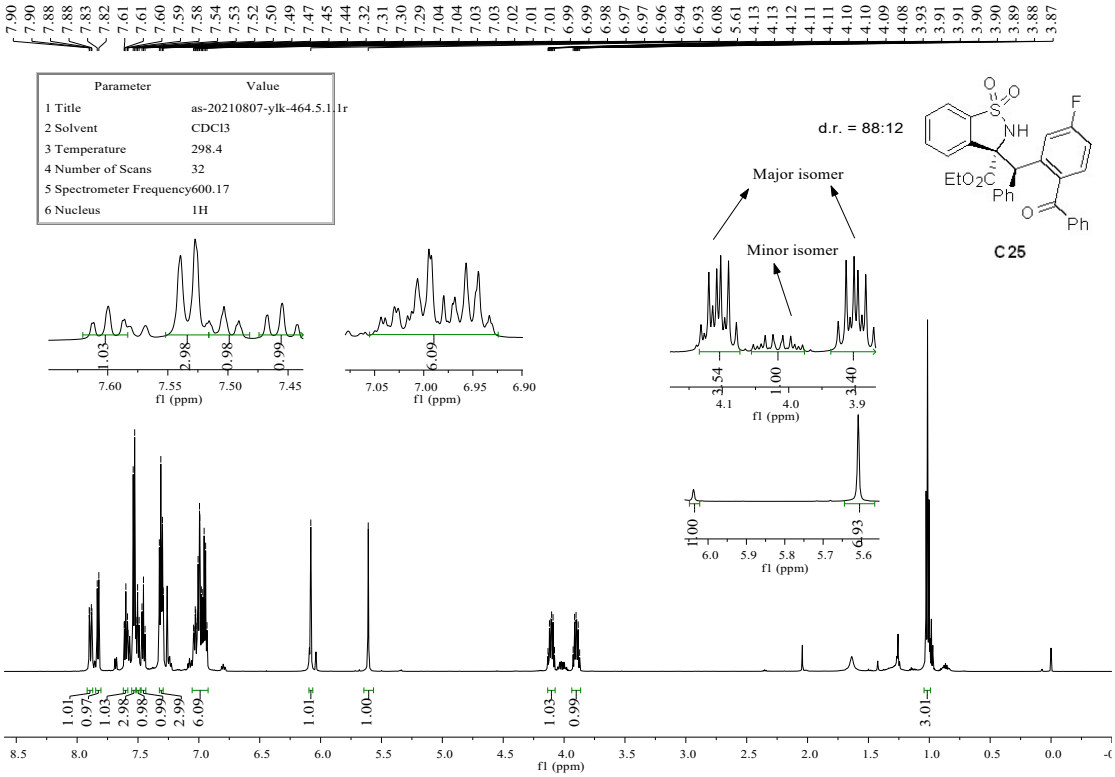

Parameter Value
1 Title as-20210807-ylk-463.1.1.1r
2 Solvent CDCl3
3 Temperature 297.9
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 88:12
Major isomer
Minor isomer
C23
f1 (ppm)

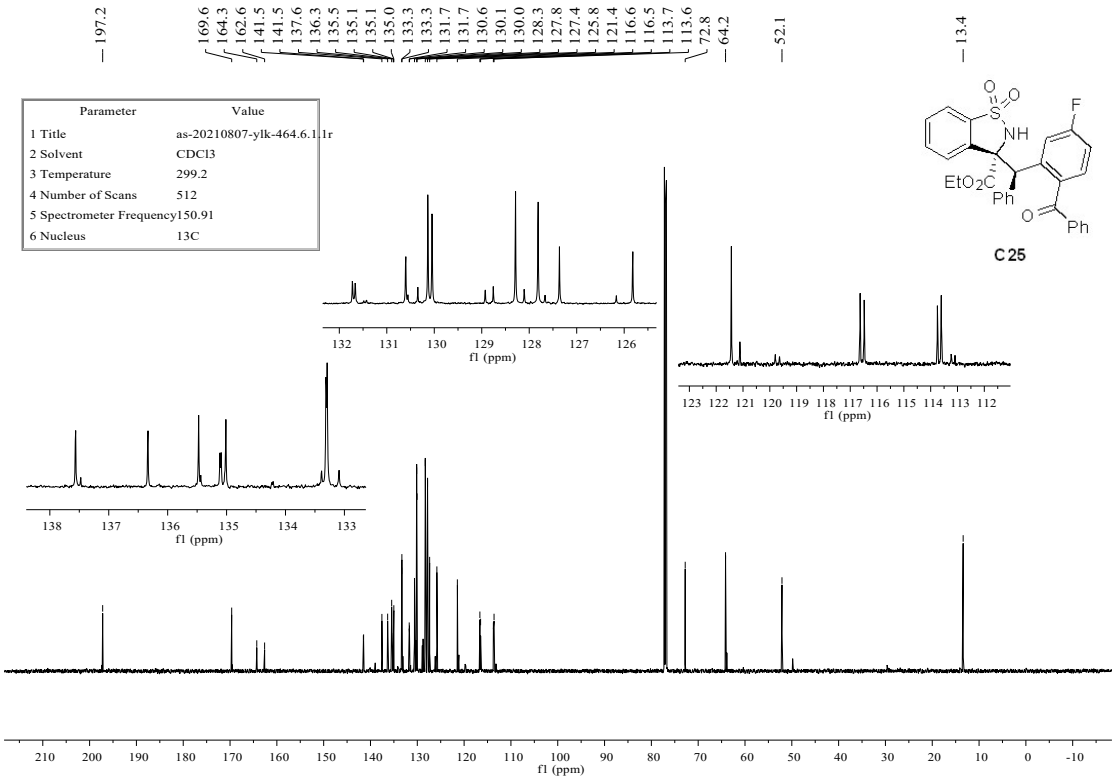

Parameter Value
1 Title as-20210807-ylk-463.2.1.1r
2 Solvent CDCl3
3 Temperature 299.0
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C23
f1 (ppm)

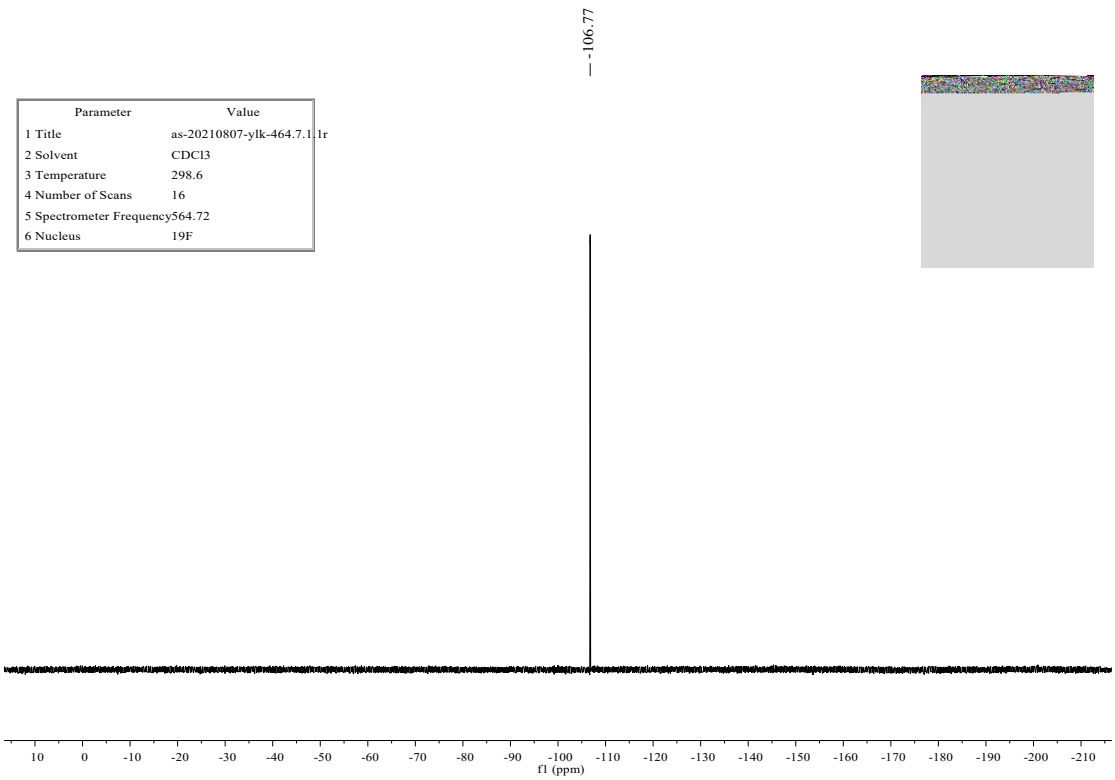
C24



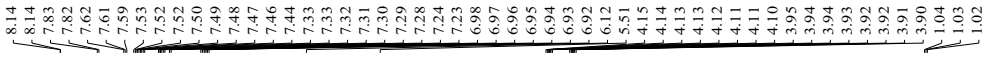
C25

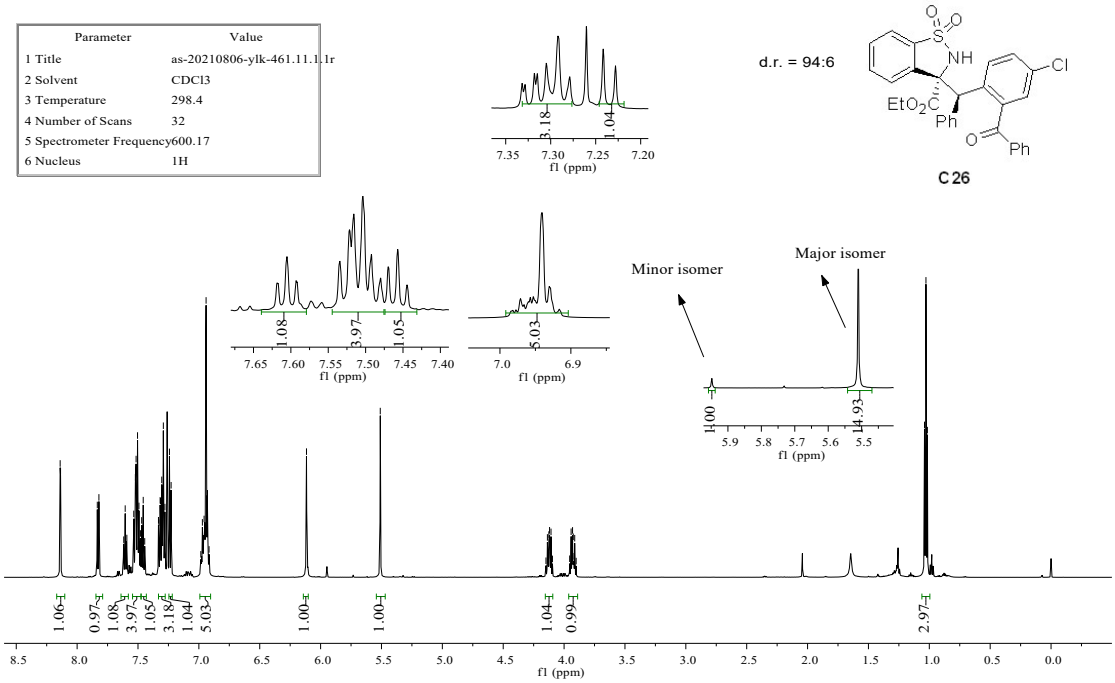

Parameter Value
1 Title as-20210807-ylk-464.5.1.1r
2 Solvent CDCl3
3 Temperature 298.4
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 88:12
Major isomer
Minor isomer
C25
f1 (ppm)

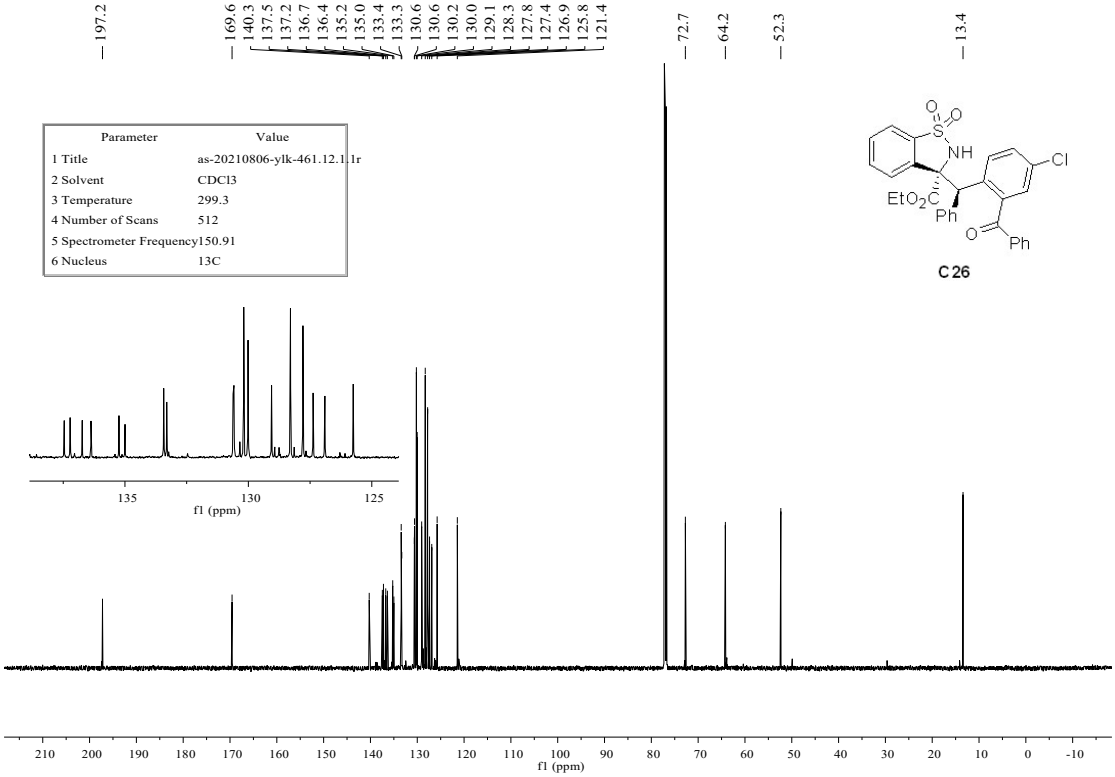

Parameter Value
1 Title as-20210807-ylk-464.6.1.1r
2 Solvent CDCl3
3 Temperature 299.2
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C25
f1 (ppm)


— -106.77
Parameter Value
1 Title as-20210807-ylk-464.7.1.1r
2 Solvent CDCl3
3 Temperature 298.6
4 Number of Scans 16
5 Spectrometer Frequency564.72
6 Nucleus 19F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

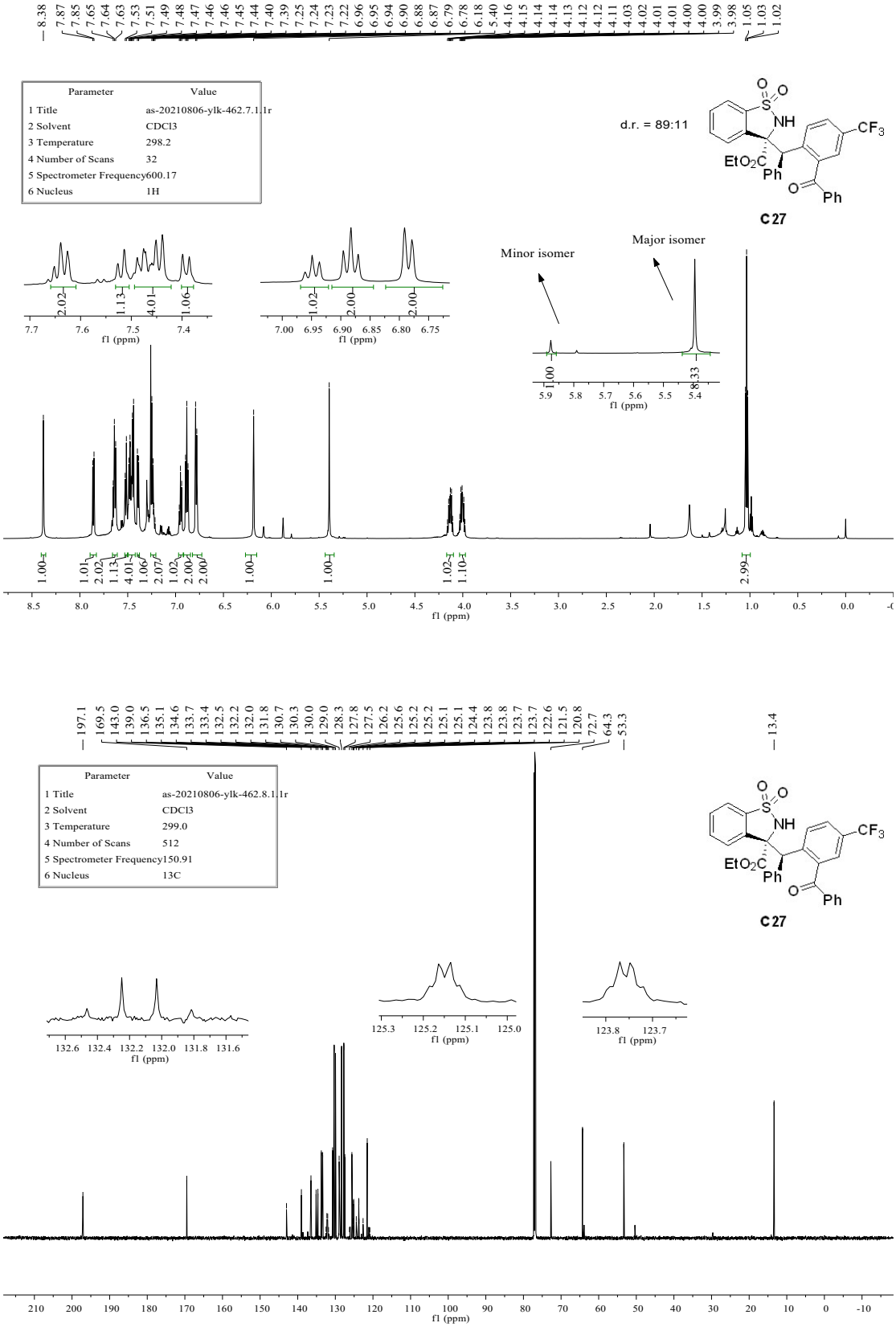
C26

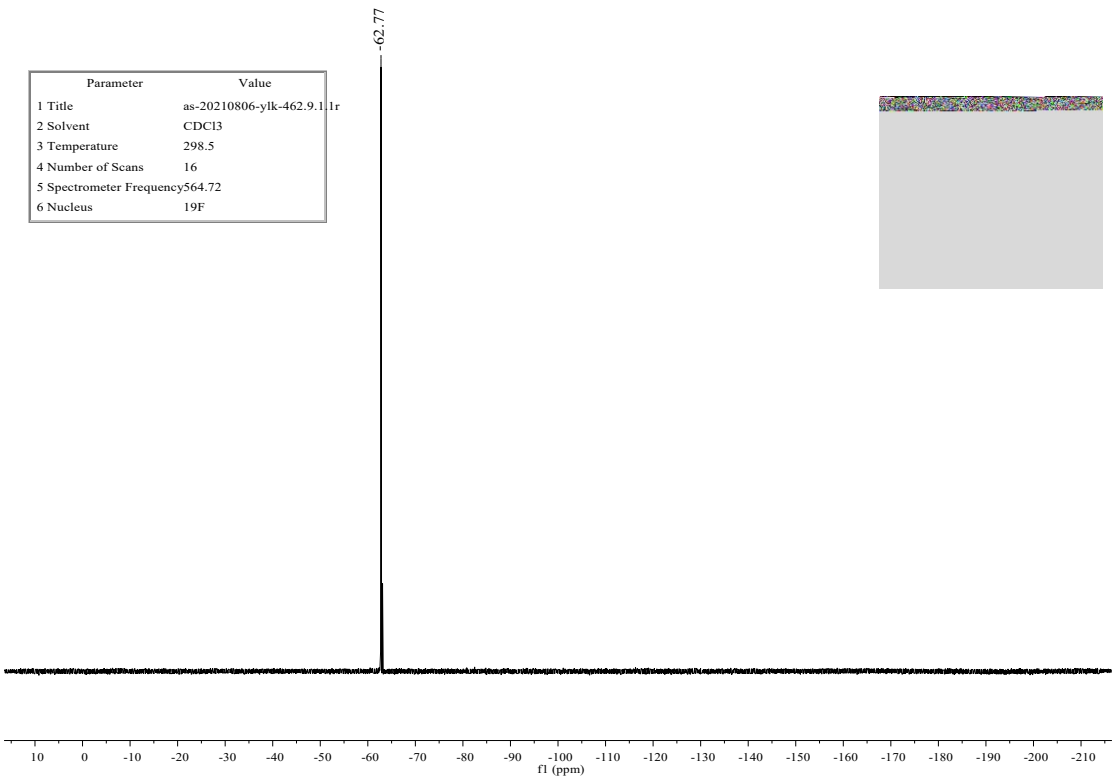

8.14 8.14 7.83 7.82 7.62 7.61 7.59 7.53 7.52 7.52 7.50 7.49 7.48 7.47 7.46 7.44 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.24 7.23 6.98 6.97 6.96 6.95 6.94 6.93 6.92 6.12 5.51 4.15 4.14 4.13 4.13 4.12 4.11 4.11 4.10 3.95 3.94 3.94 3.93 3.92 3.92 3.91 3.90 1.04 1.03 1.02


Parameter Value
1 Title as-20210806-ylk-461.11.1.1r
2 Solvent CDCl3
3 Temperature 298.4
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 94:6
C26
Minor isomer
Major isomer
f1 (ppm)

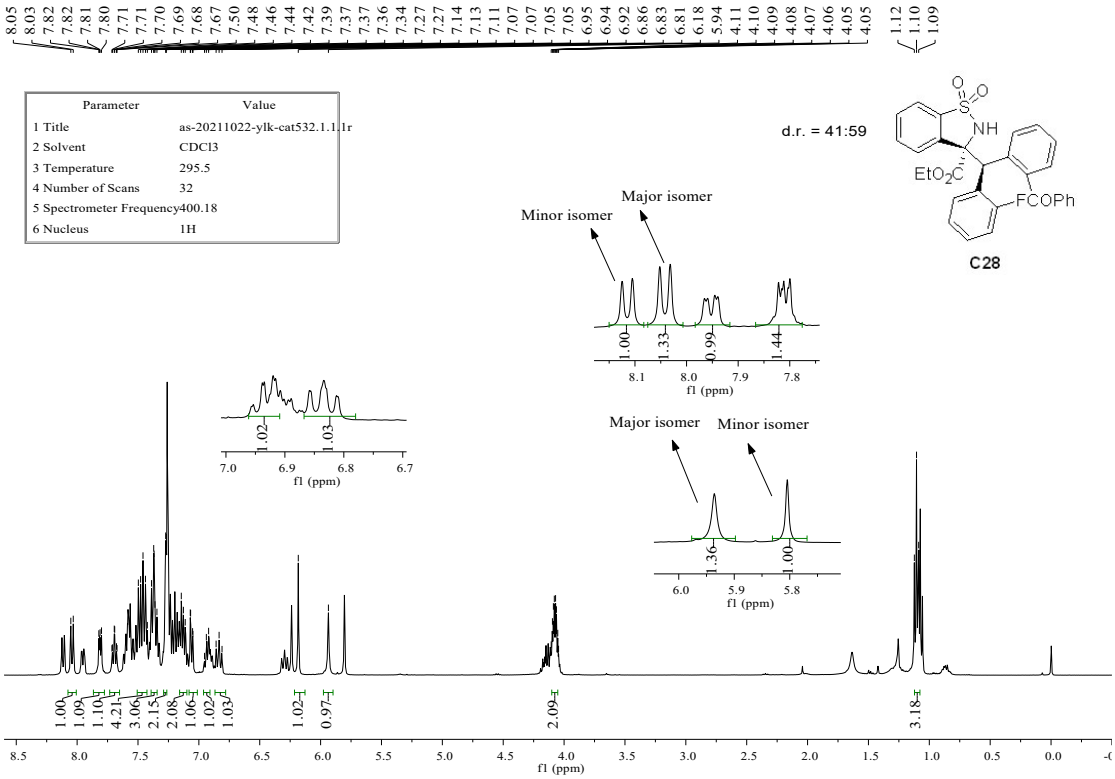

Parameter Value
1 Title as-20210806-ylk-461.12.1.1r
2 Solvent CDCl3
3 Temperature 299.3
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C26
f1 (ppm)

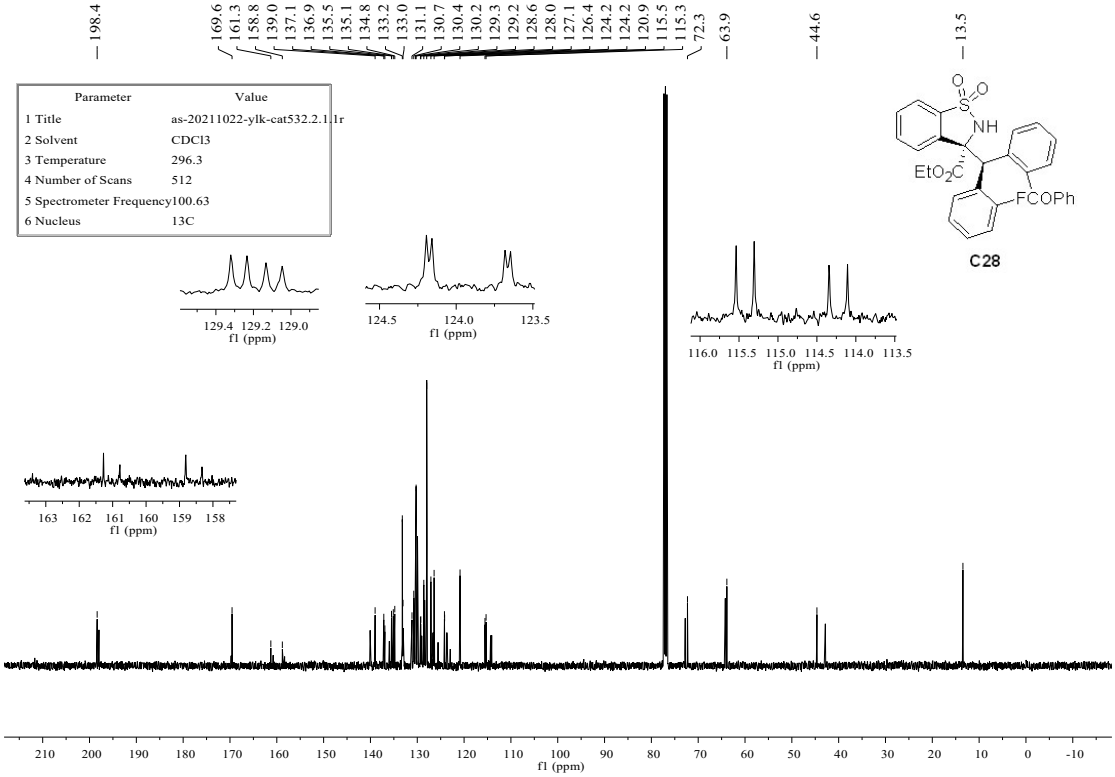
C27


Parameter Value
1 Title as-20210806-ylk-462.7.1.1r
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 89:11
C27
Minor isomer
Major isomer
f1 (ppm)
Parameter Value
1 Title as-20210806-ylk-462.8.1.1r
2 Solvent CDCl3
3 Temperature 299.0
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C27
f1 (ppm)


-62.77
Parameter Value
1 Title as-20210806-ylk-462.9.1.1r
2 Solvent CDCl3
3 Temperature 298.5
4 Number of Scans 16
5 Spectrometer Frequency564.72
6 Nucleus 19F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

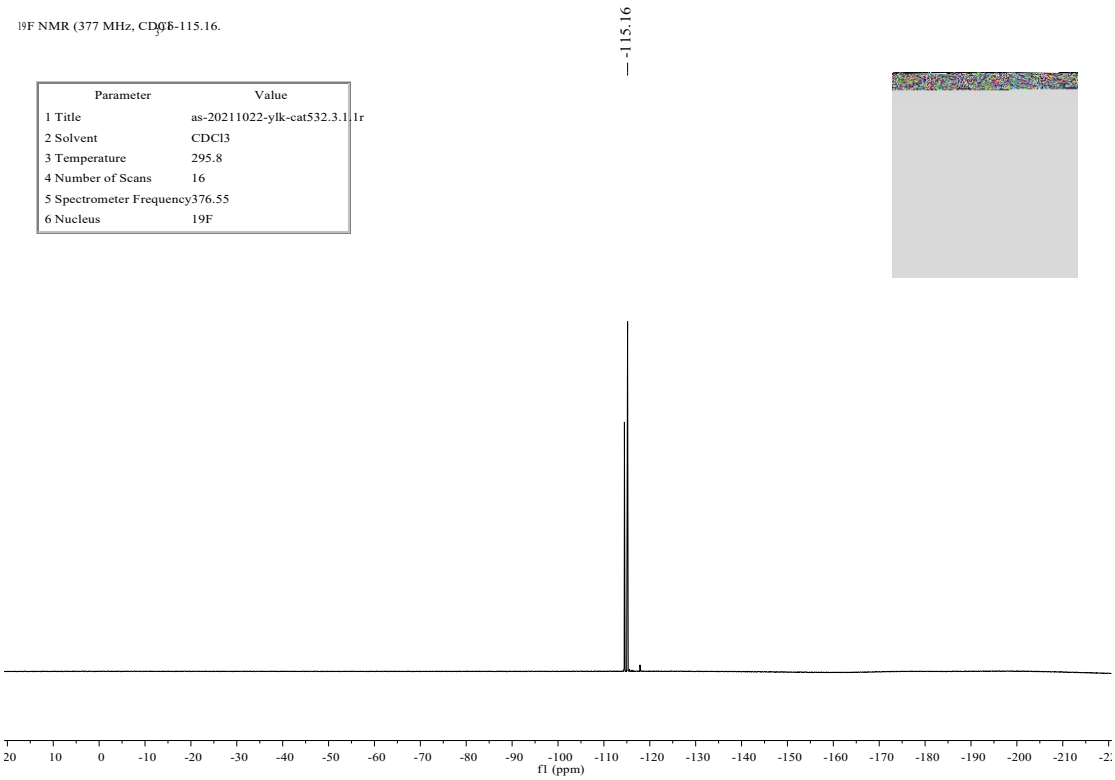
C28


8.05 8.03 7.82 7.82 7.81 7.80 7.71 7.71 7.70 7.69 7.68 7.67 7.50 7.48 7.46 7.44 7.42 7.39 7.37 7.37 7.36 7.34 7.27 7.27 7.14 7.13 7.11 7.07 7.07 7.05 7.05 6.95 6.94 6.92 6.86 6.83 6.81 6.18 5.94 4.11 4.10 4.09 4.08 4.07 4.06 4.05 4.05 1.12 1.10 1.09
Parameter Value
1 Title as-20211022-ylk-cat532.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 41:59
Major isomer
Minor isomer
C28
1.00 1.33 0.99 1.44
f1 (ppm)
1.02 1.03
Major isomer Minor isomer
1.36 1.00
1.00 1.09 1.10 4.21 3.06 2.15 2.08 1.06 1.02 1.03 1.02 0.97 2.09 3.18
f1 (ppm)

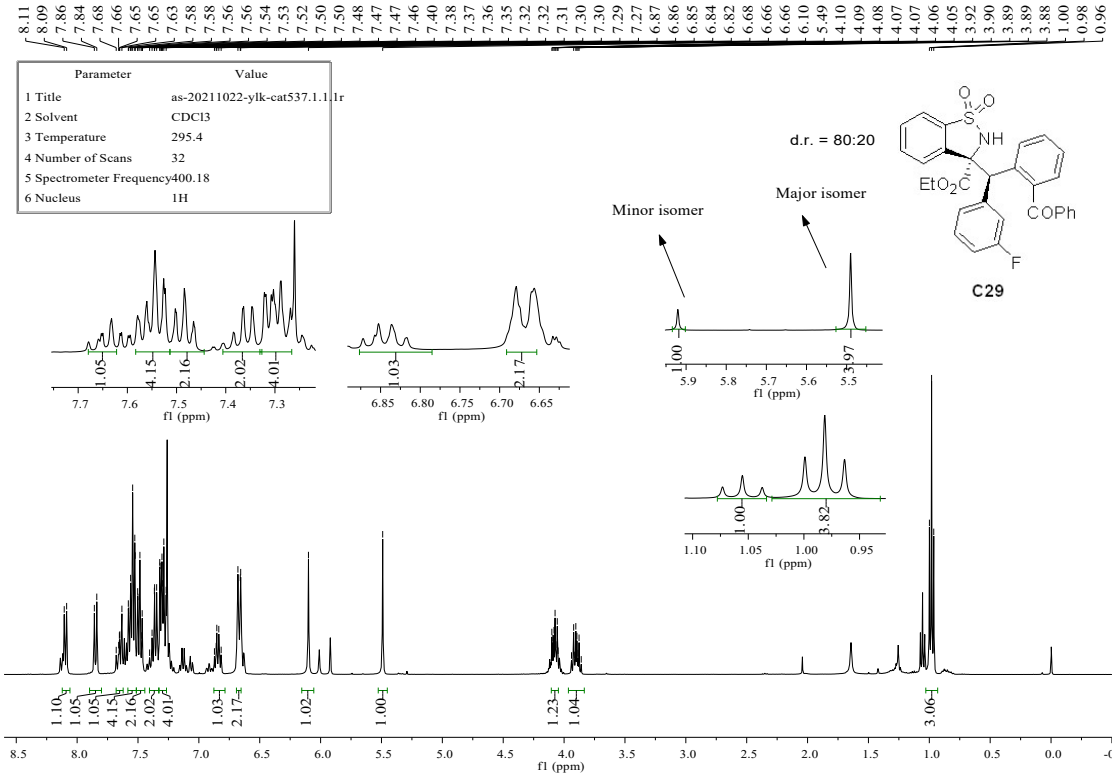

198.4 169.6 161.3 158.8 139.0 137.1 136.9 135.5 135.1 134.8 133.2 133.0 131.1 130.7 130.4 130.2 129.3 129.2 128.6 128.0 127.1 126.4 124.2 124.2 120.9 115.5 115.3 72.3 63.9 44.6 13.5
Parameter Value
1 Title as-20211022-ylk-cat532.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C28
129.4 129.2 129.0 f1 (ppm)
124.5 124.0 123.5 f1 (ppm)
116.0 115.5 115.0 114.5 114.0 113.5 f1 (ppm)
163 162 161 160 159 158 f1 (ppm)
f1 (ppm)

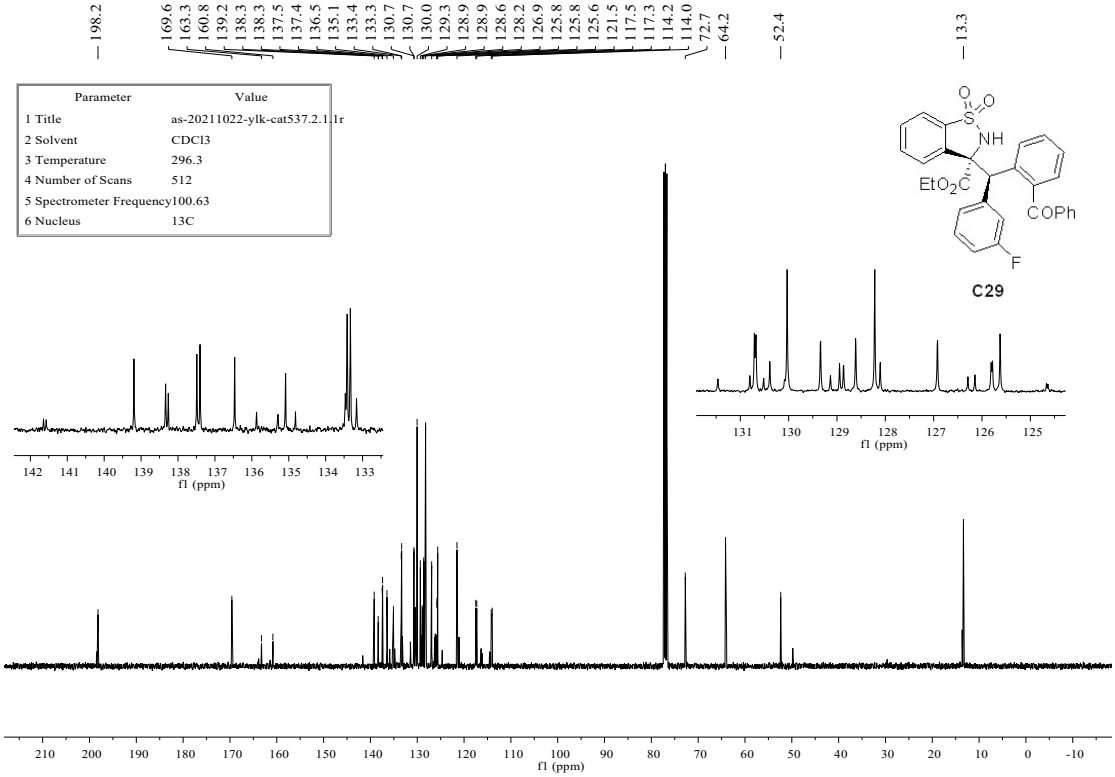
^{19}F NMR (377 MHz, CDCl$_3$) δ -115.16.

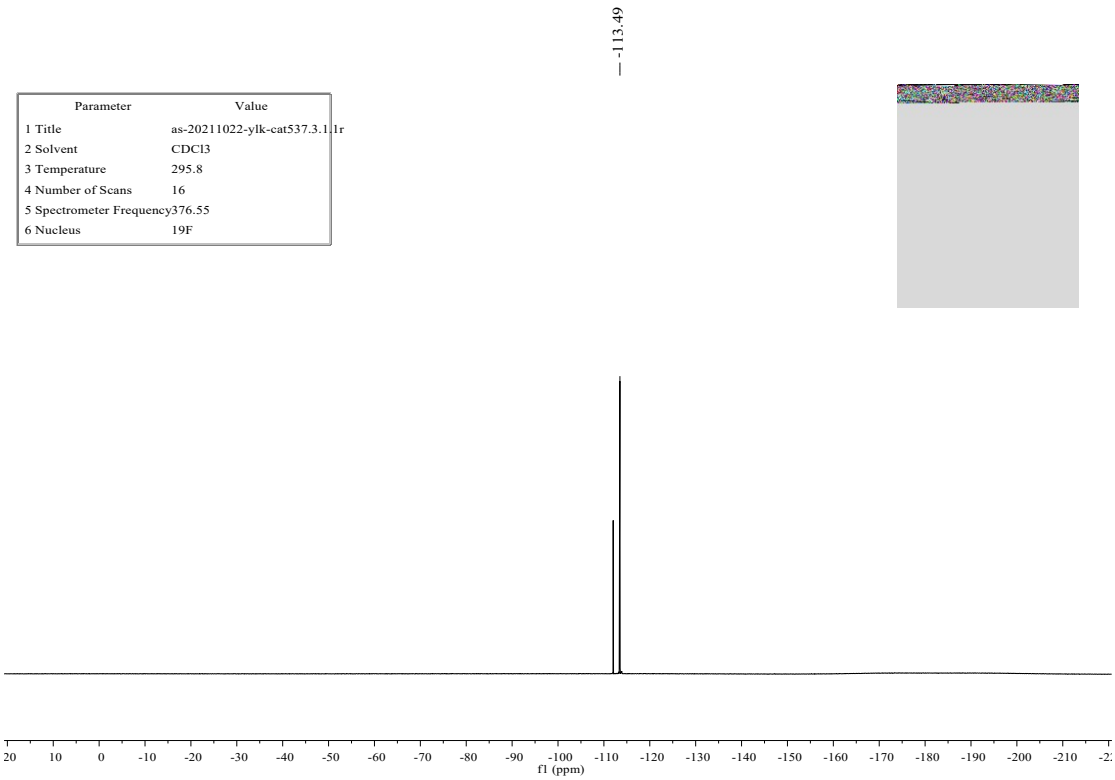
Parameter	Value
1 Title	as-20211022-ylk-cat532.3.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



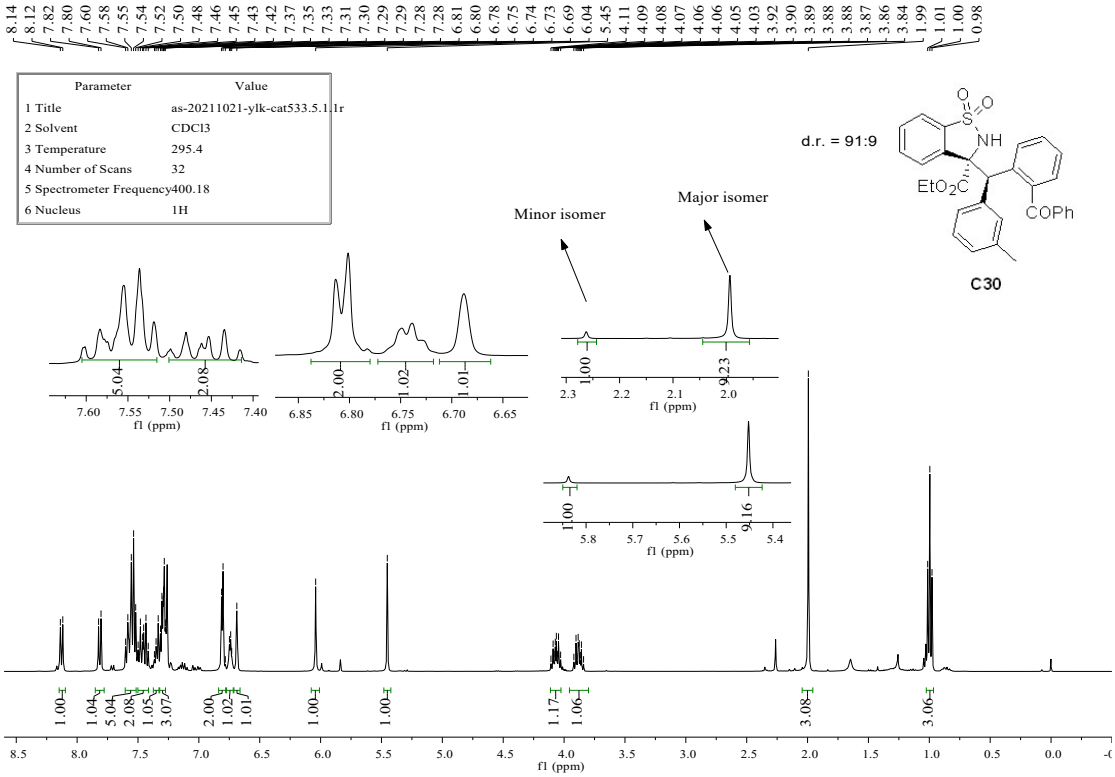
C29

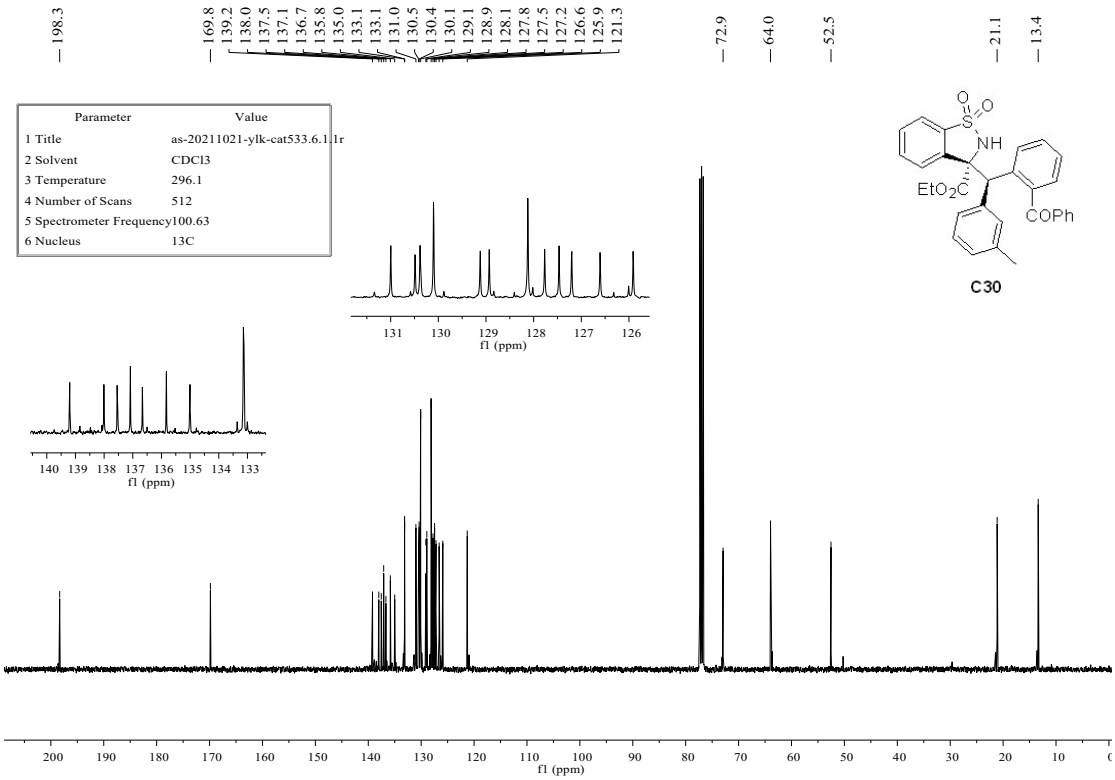

Parameter Value
1 Title as-20211022-ylk-cat537.1.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 80:20
Minor isomer
Major isomer
C29
f1 (ppm)


Parameter Value
1 Title as-20211022-ylk-cat537.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C29
f1 (ppm)

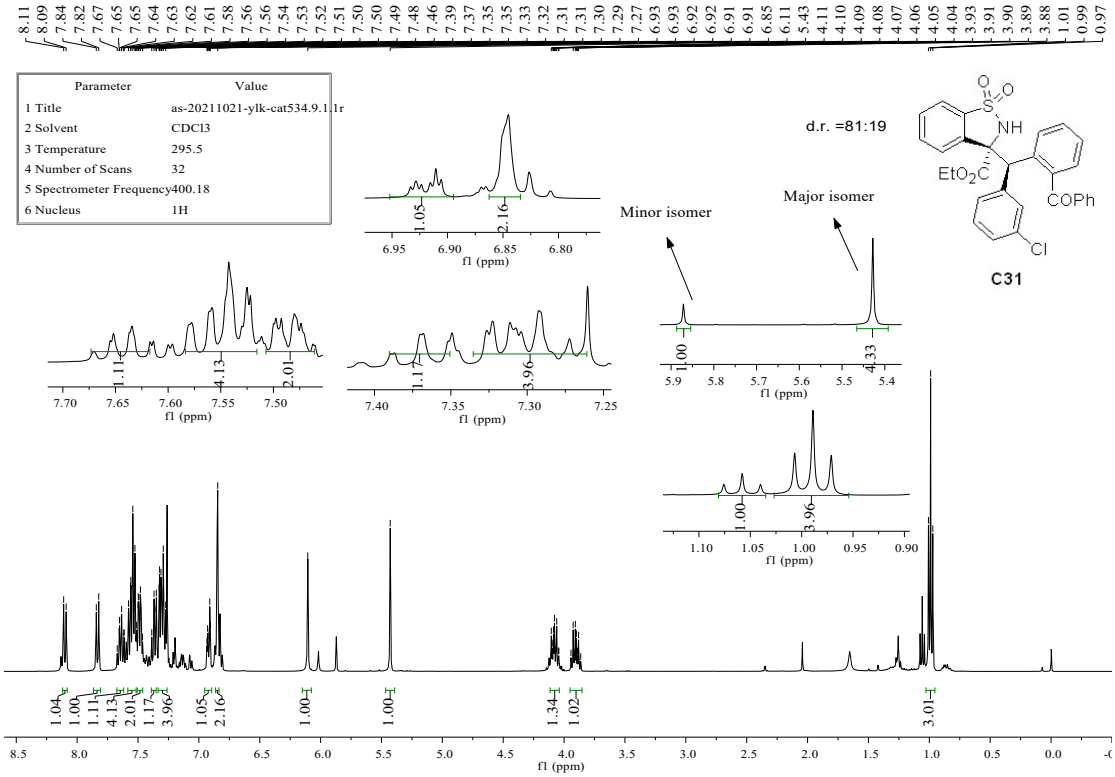

-113.49
Parameter Value
1 Title as-20211022-ylk-cat537.3.11r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

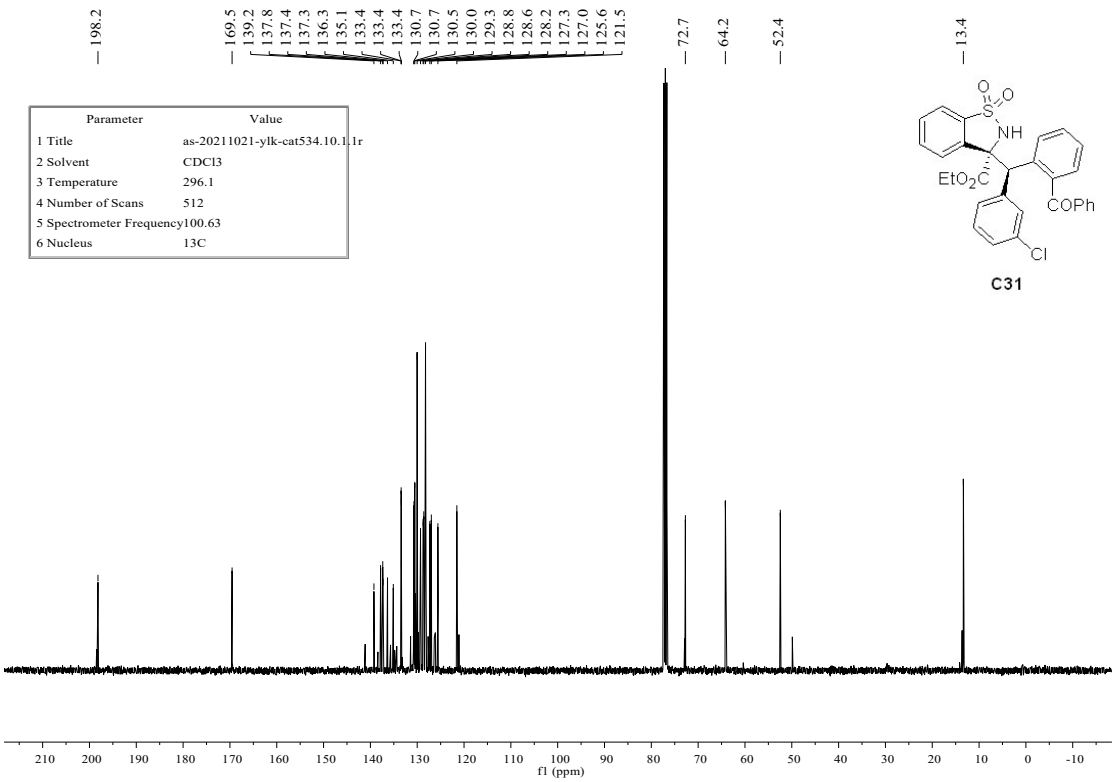
C30


Parameter Value
1 Title as-20211021-ylk-cat533.5.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 91:9
Minor isomer
Major isomer
C30
f1 (ppm)

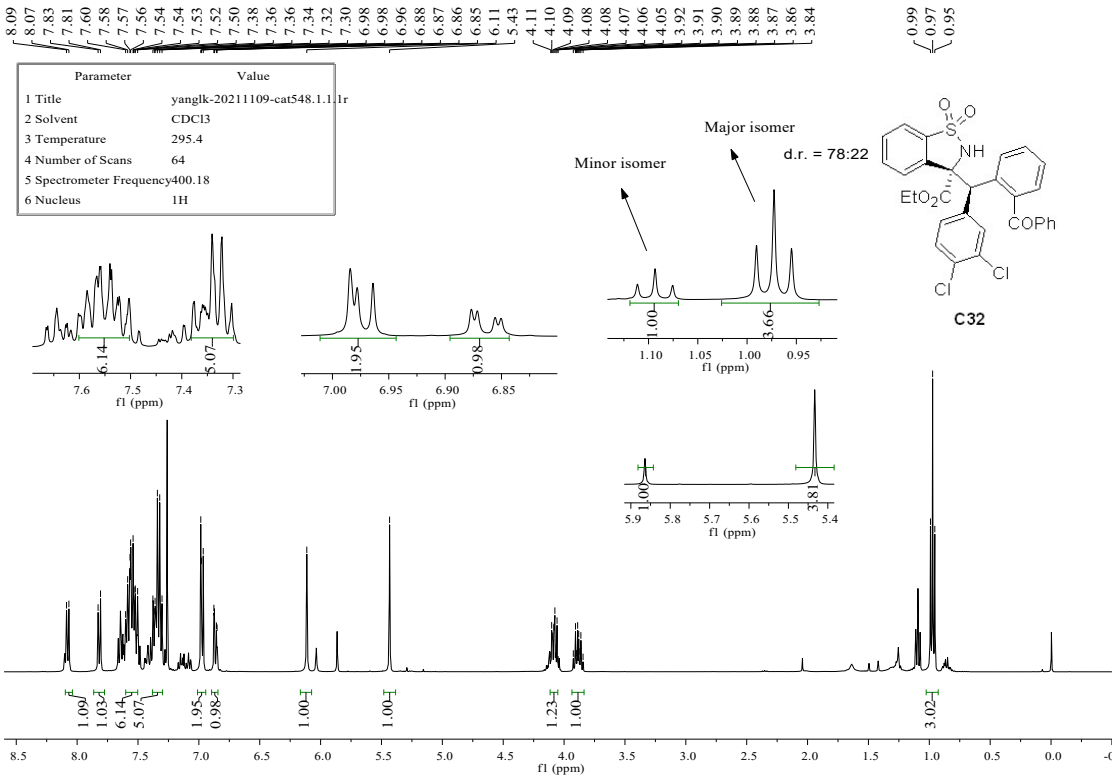

Parameter Value
1 Title as-20211021-ylk-cat533.6.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C30
f1 (ppm)

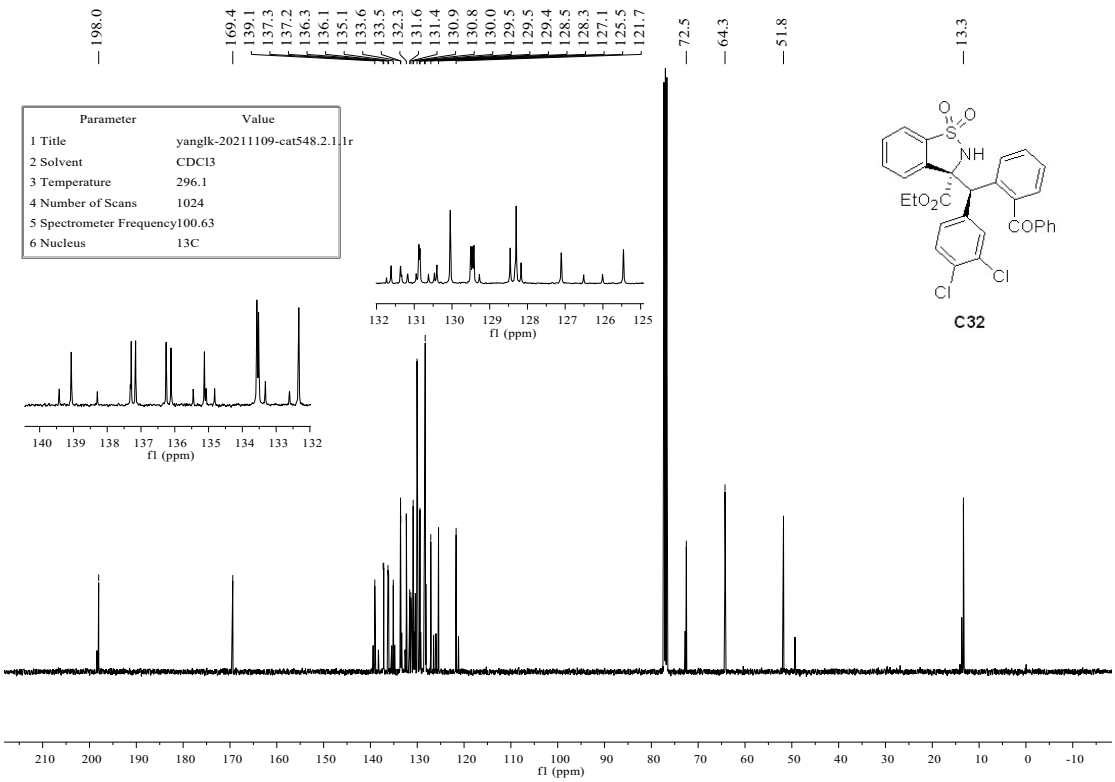
C31


Parameter Value
1 Title as-20211021-ylk-cat534.9.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. =81:19
Minor isomer
Major isomer
C31
f1 (ppm)

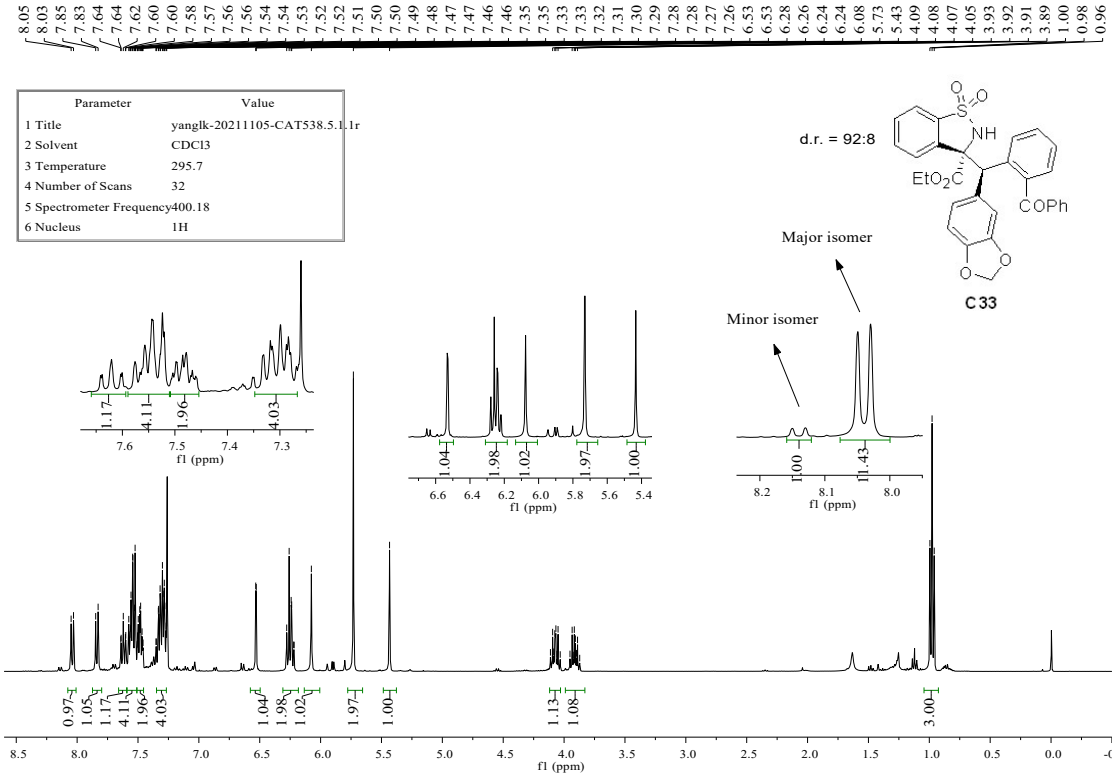

Parameter Value
1 Title as-20211021-ylk-cat534.10.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C31
f1 (ppm)

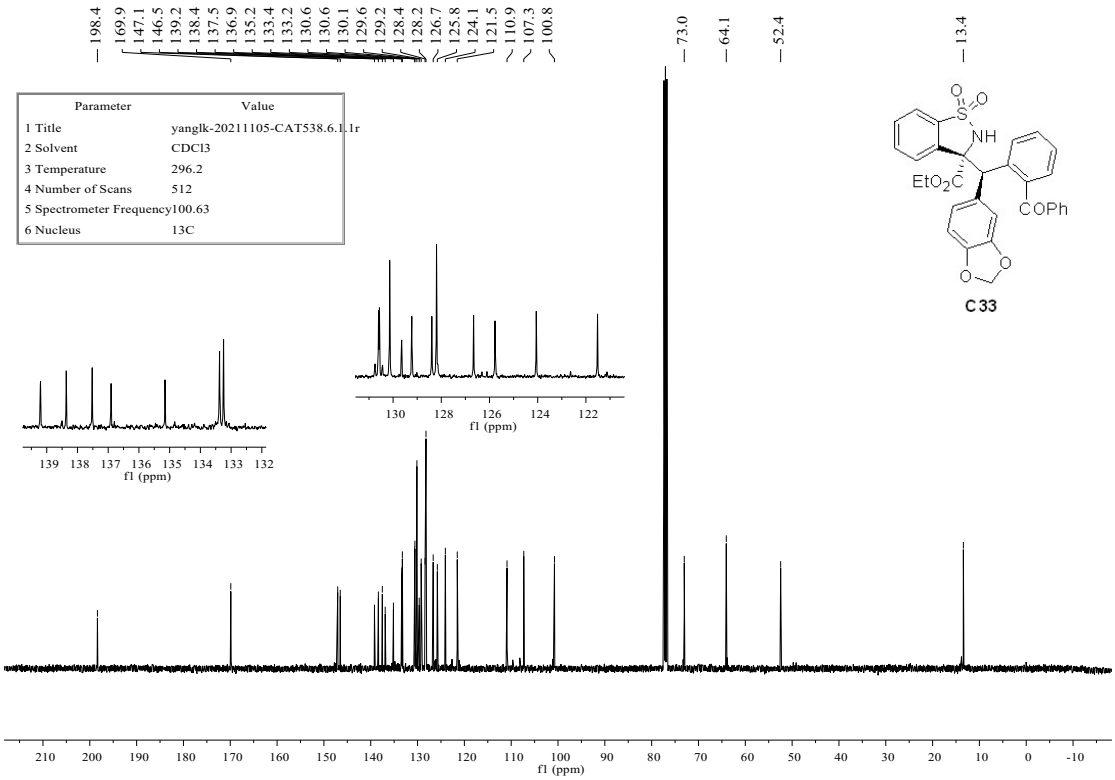
C32


Parameter Value
1 Title yanglk-20211109-cat548.1.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Major isomer
Minor isomer
d.r. = 78:22
C32
f1 (ppm)

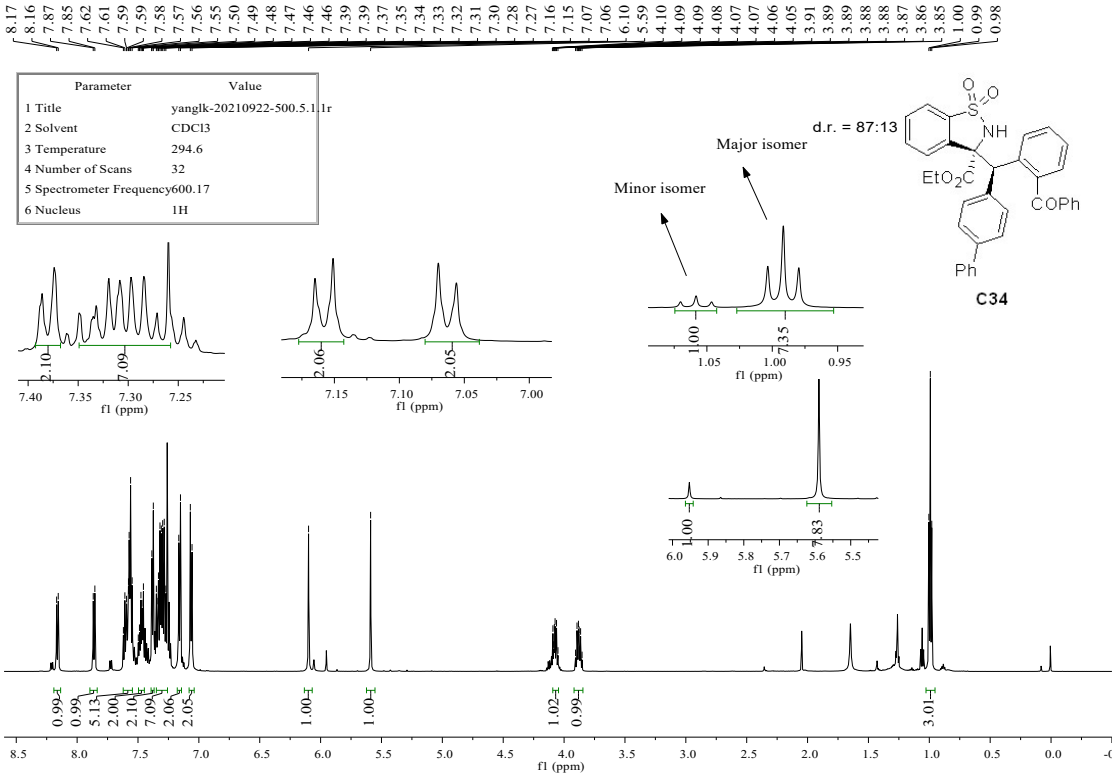

Parameter Value
1 Title yanglk-20211109-cat548.2.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 1024
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C32
f1 (ppm)

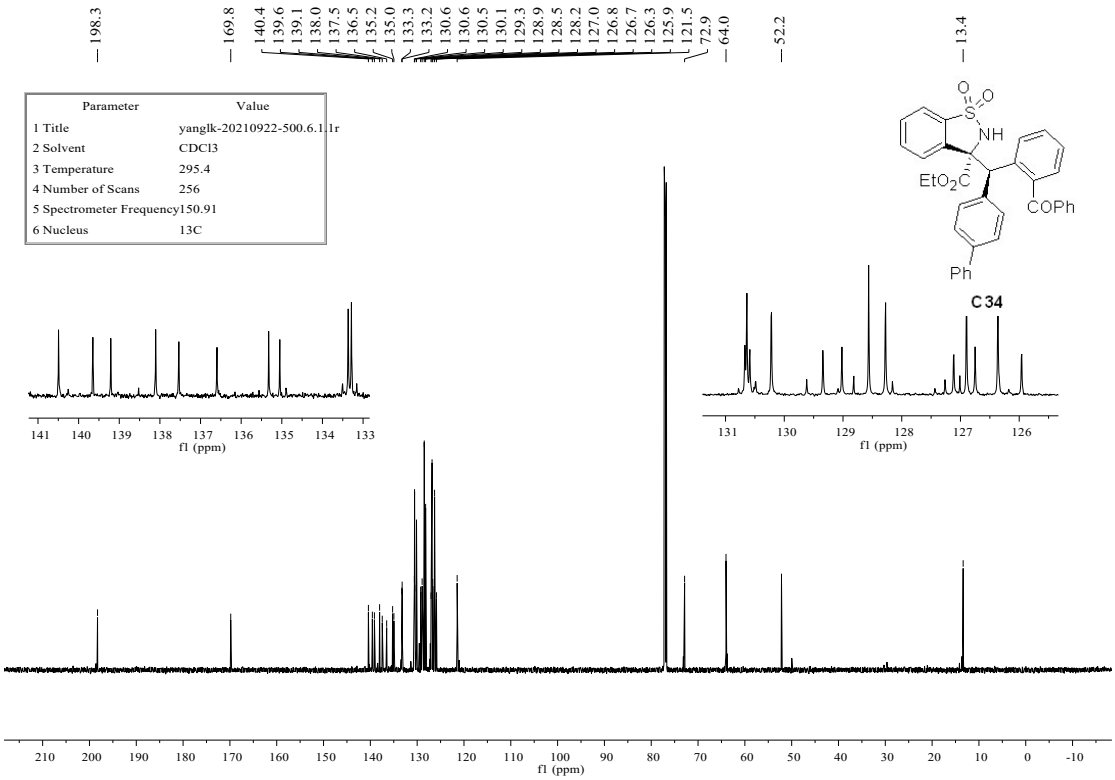
C33


Parameter Value
1 Title yanglk-20211105-CAT538.5.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 92:8
Major isomer
Minor isomer
C33
f1 (ppm)

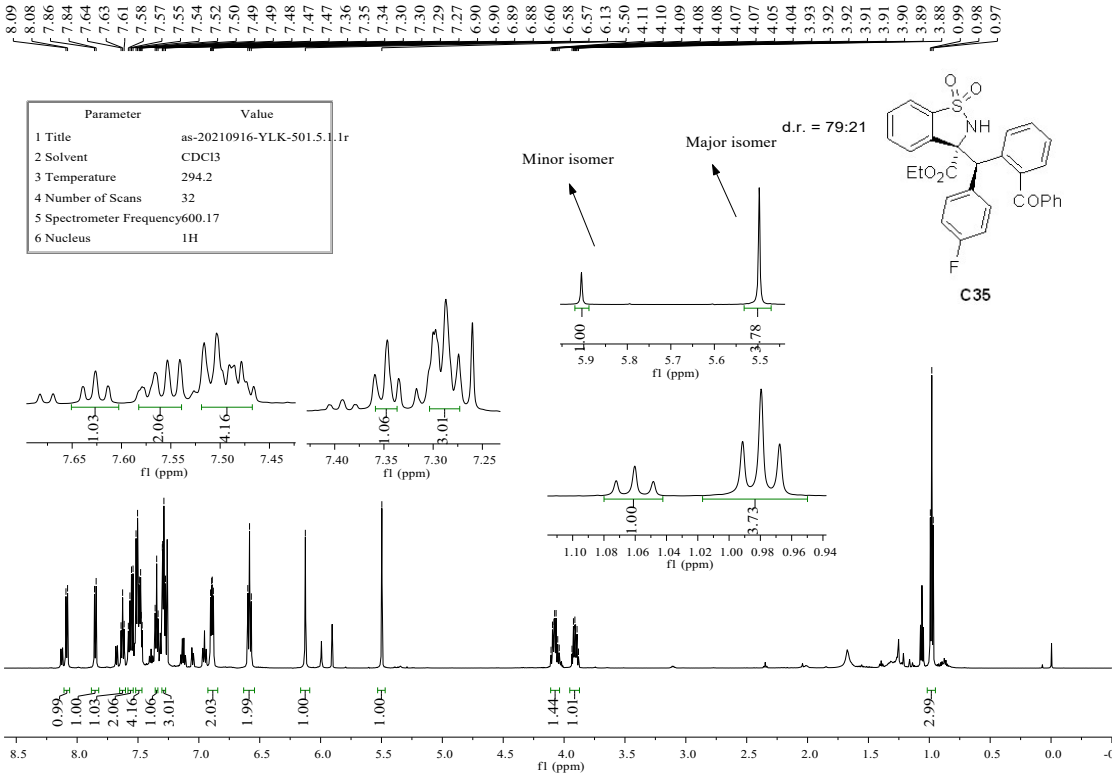

Parameter Value
1 Title yanglk-20211105-CAT538.6.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C33
f1 (ppm)

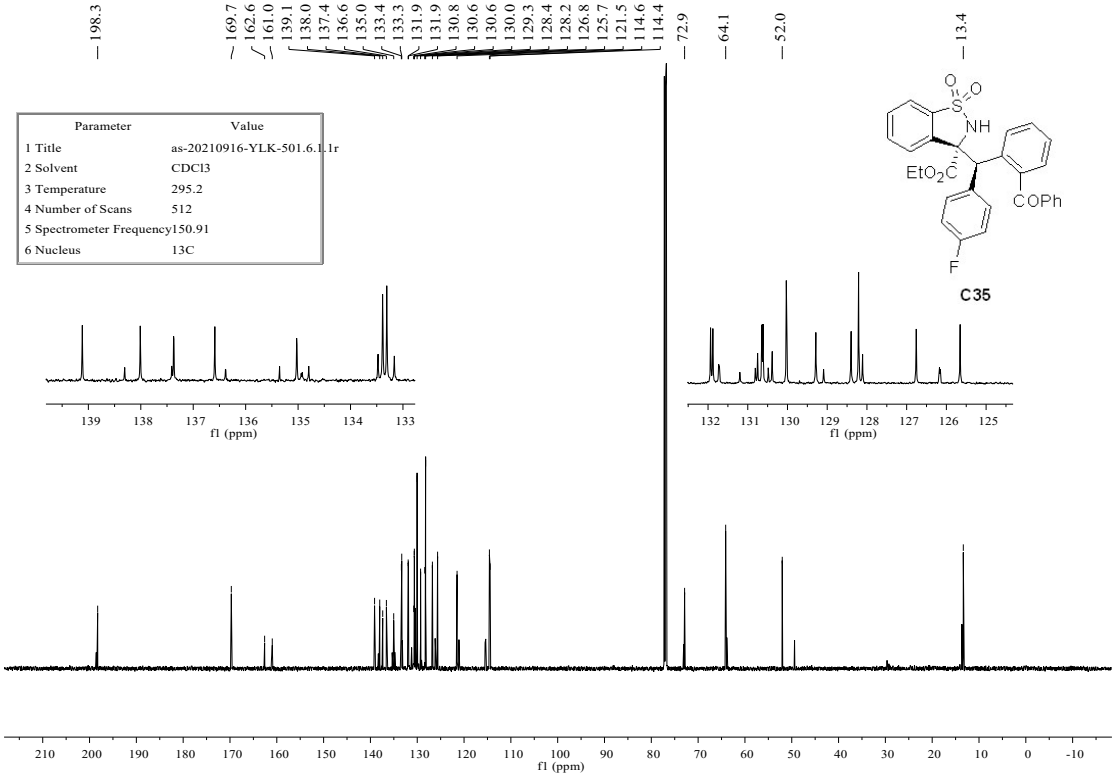
C34

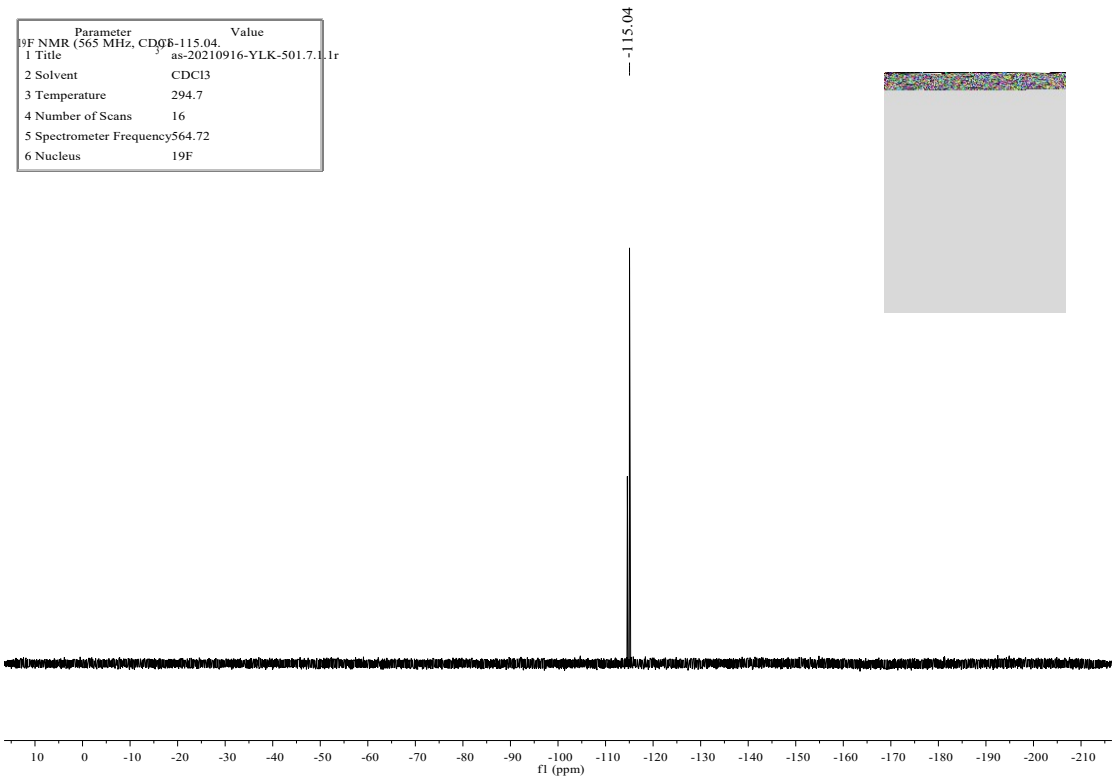

Parameter Value
1 Title yanglk-20210922-500.5.1.1r
2 Solvent CDCl3
3 Temperature 294.6
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 87:13
Major isomer
Minor isomer
C34
f1 (ppm)


Parameter Value
1 Title yanglk-20210922-500.6.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C34
f1 (ppm)

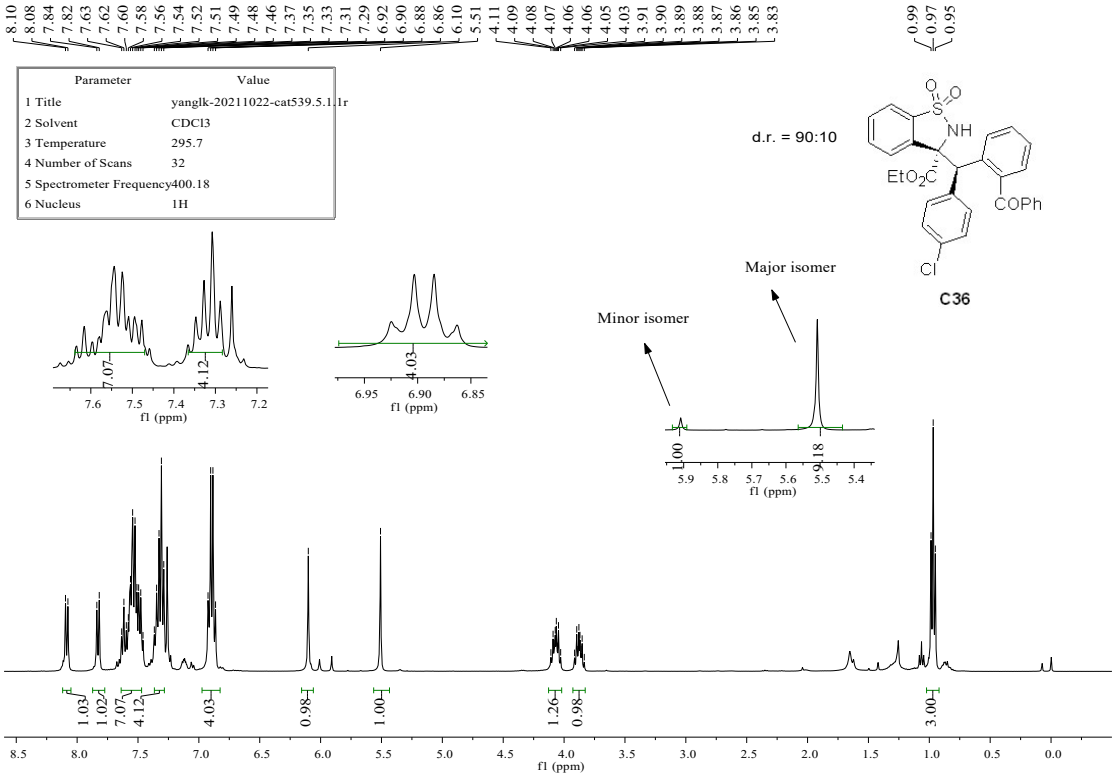
C35

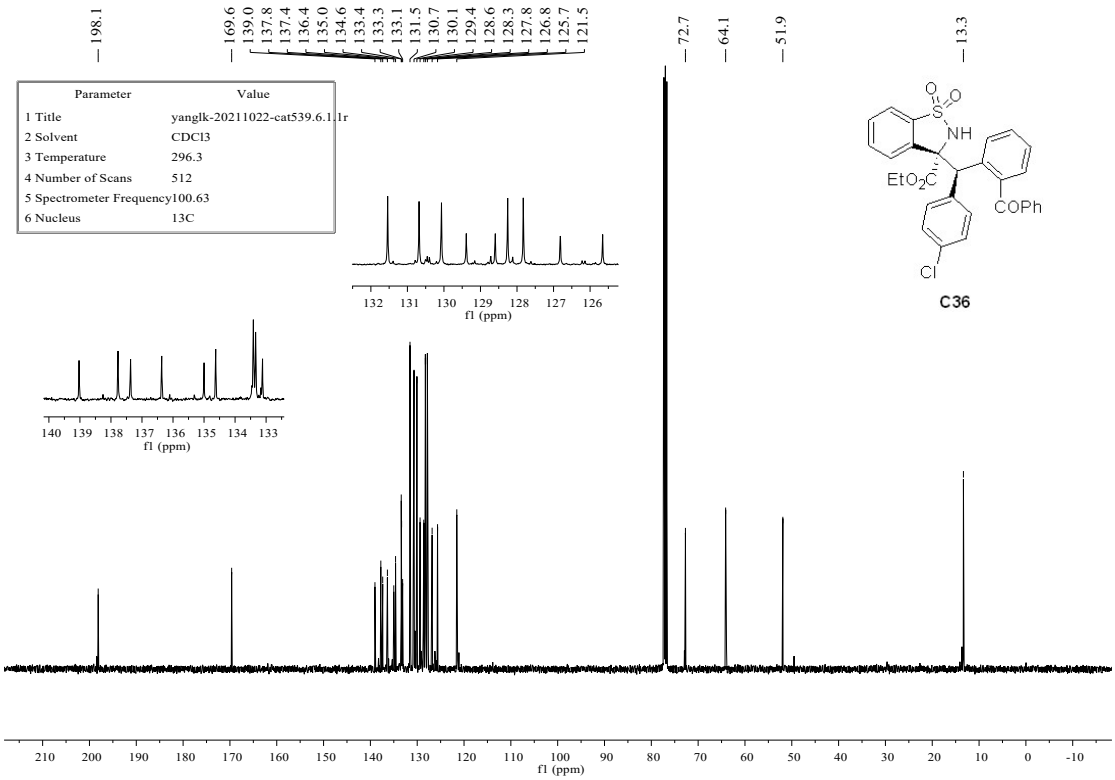

Parameter Value
1 Title as-20210916-YLK-501.5.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 79:21
Minor isomer
Major isomer
C35
f1 (ppm)


Parameter Value
1 Title as-20210916-YLK-501.6.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C35
f1 (ppm)

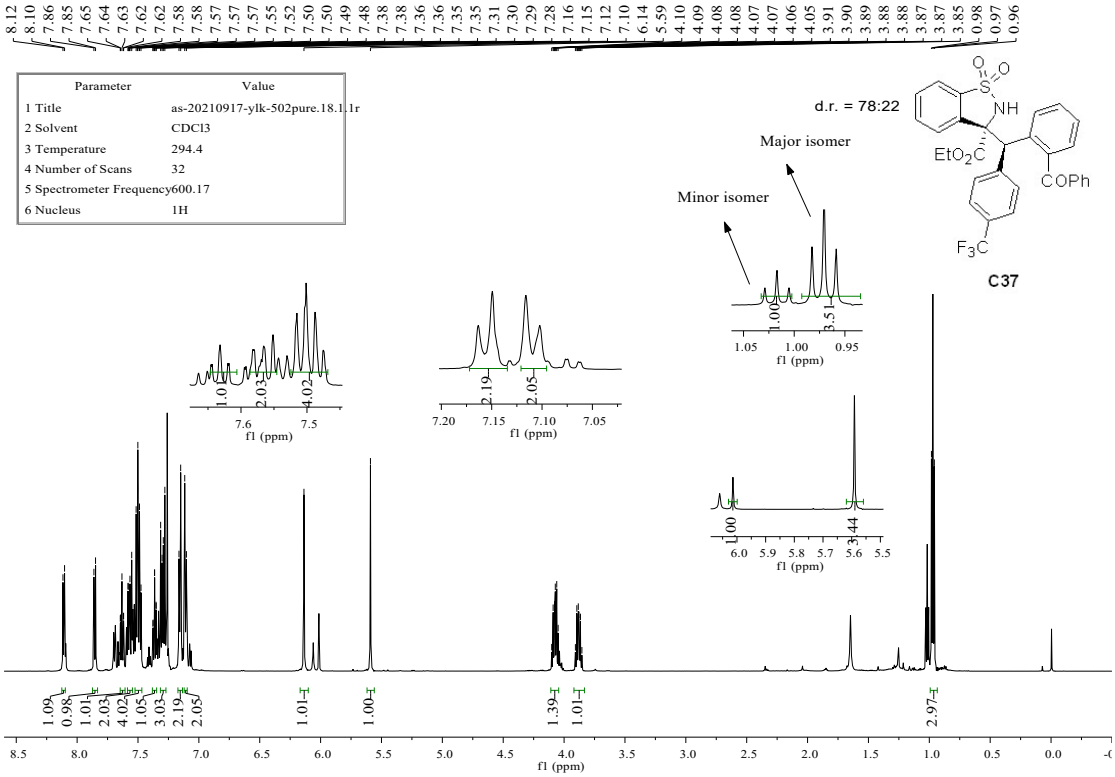

19F NMR (565 MHz, CDCl3)
Parameter Value
1 Title as-20210916-YLK-501.7.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-115.04
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

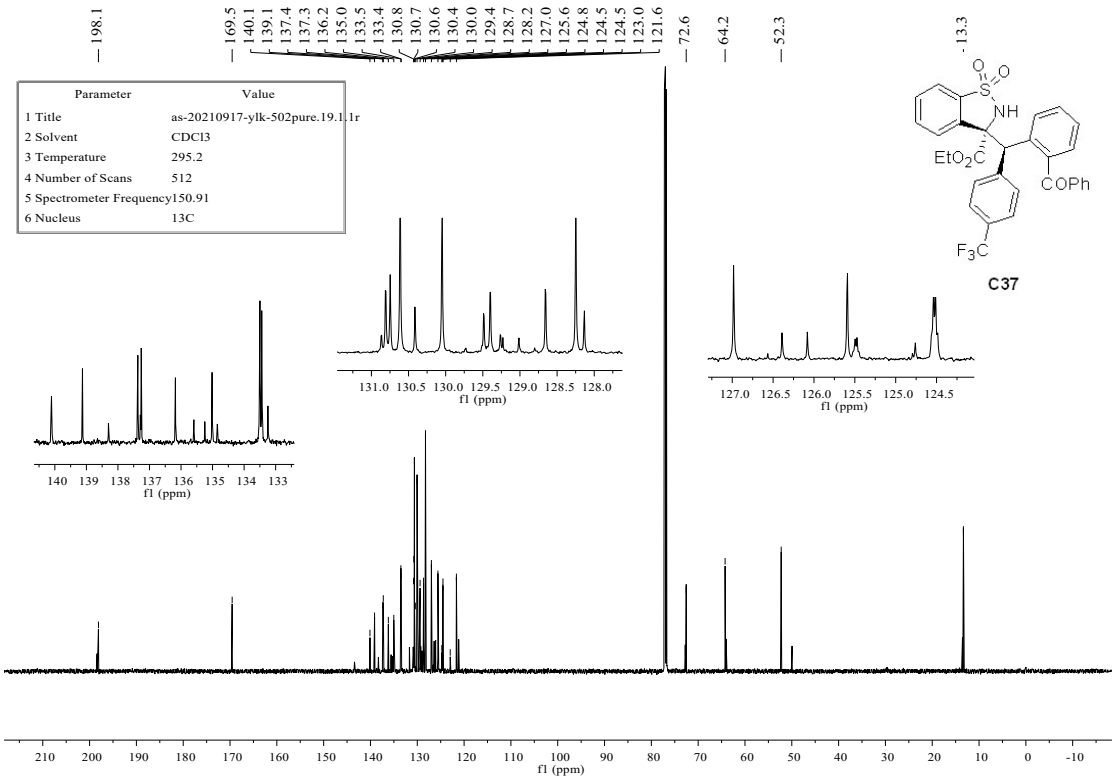
C36

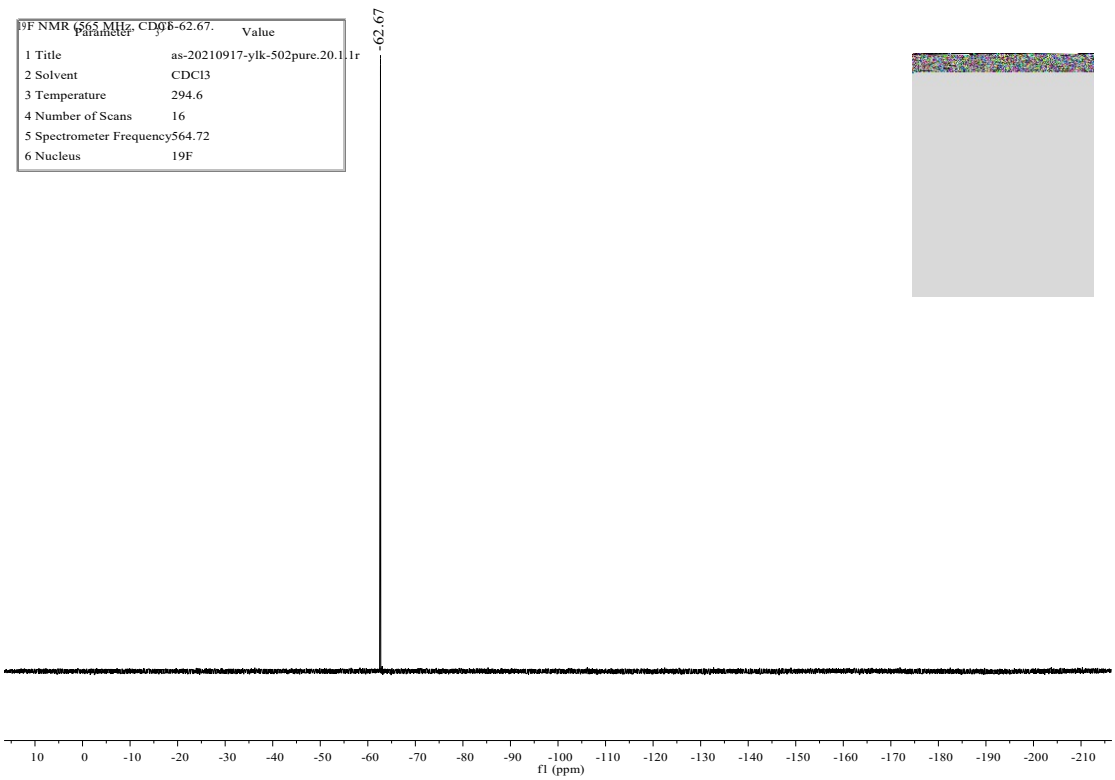

Parameter Value
1 Title yanglk-20211022-cat539.5.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 90:10
Major isomer
Minor isomer
C36
f1 (ppm)


Parameter Value
1 Title yanglk-20211022-cat539.6.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C36
f1 (ppm)

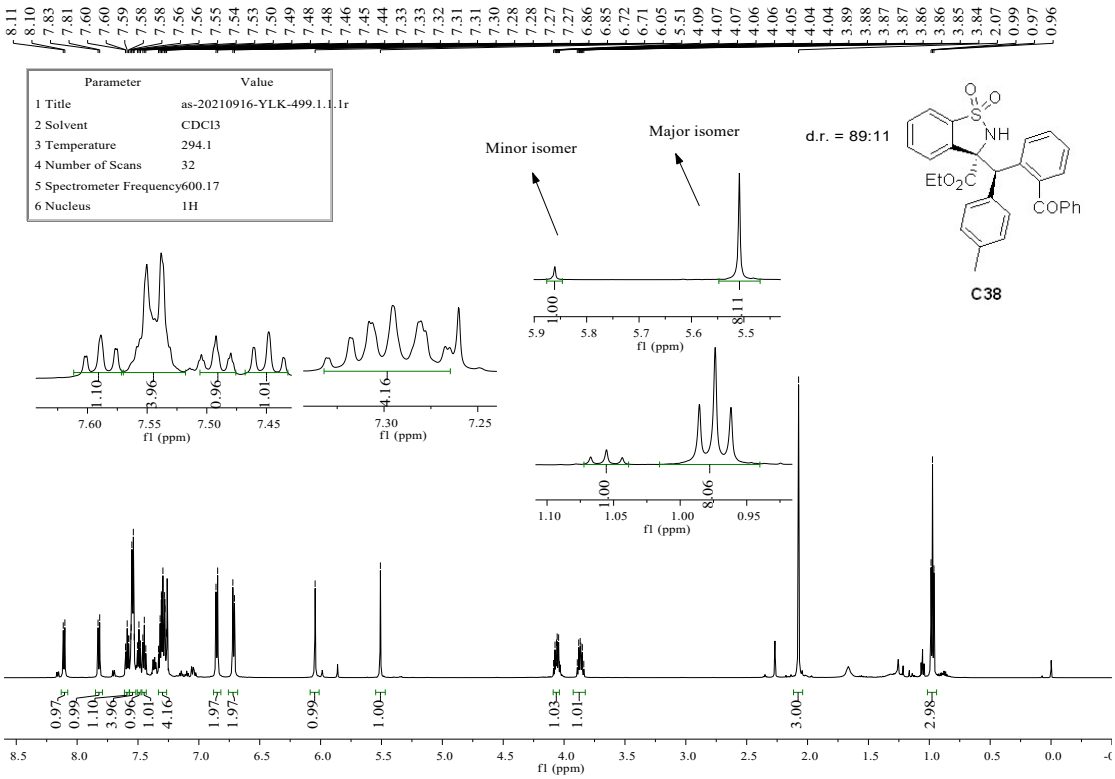
C37

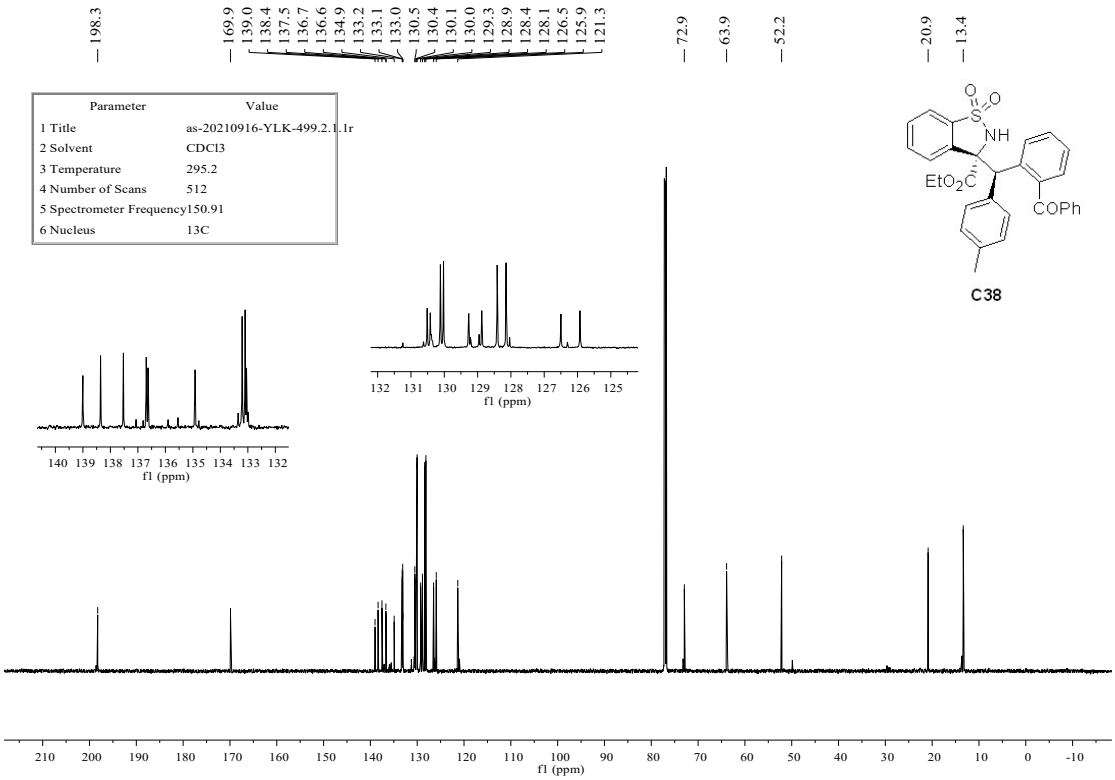

Parameter Value
1 Title as-20210917-ylk-502pure.18.1.1r
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 78:22
Major isomer
Minor isomer
C37
f1 (ppm)


Parameter Value
1 Title as-20210917-ylk-502pure.19.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C37
f1 (ppm)

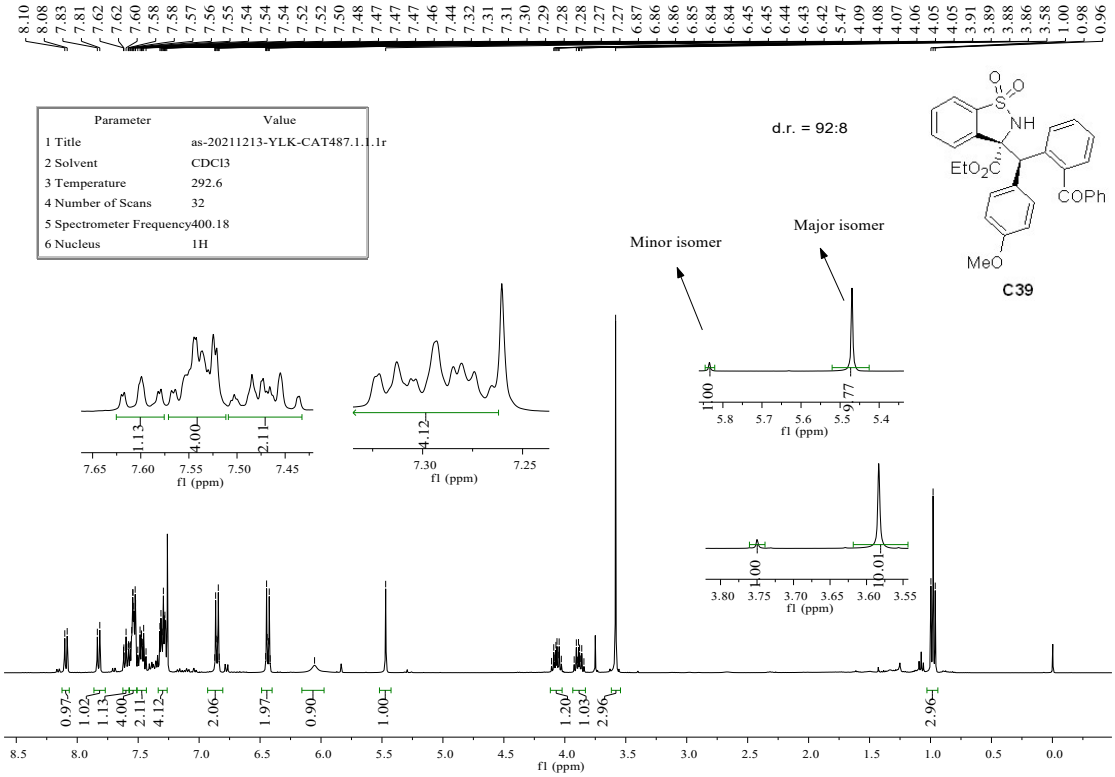

19F NMR (565 MHz, CDCl3) δ -62.67.
Parameter Value
1 Title as-20210917-ylk-502pure.20.1.1r
2 Solvent CDCl3
3 Temperature 294.6
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-62.67
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

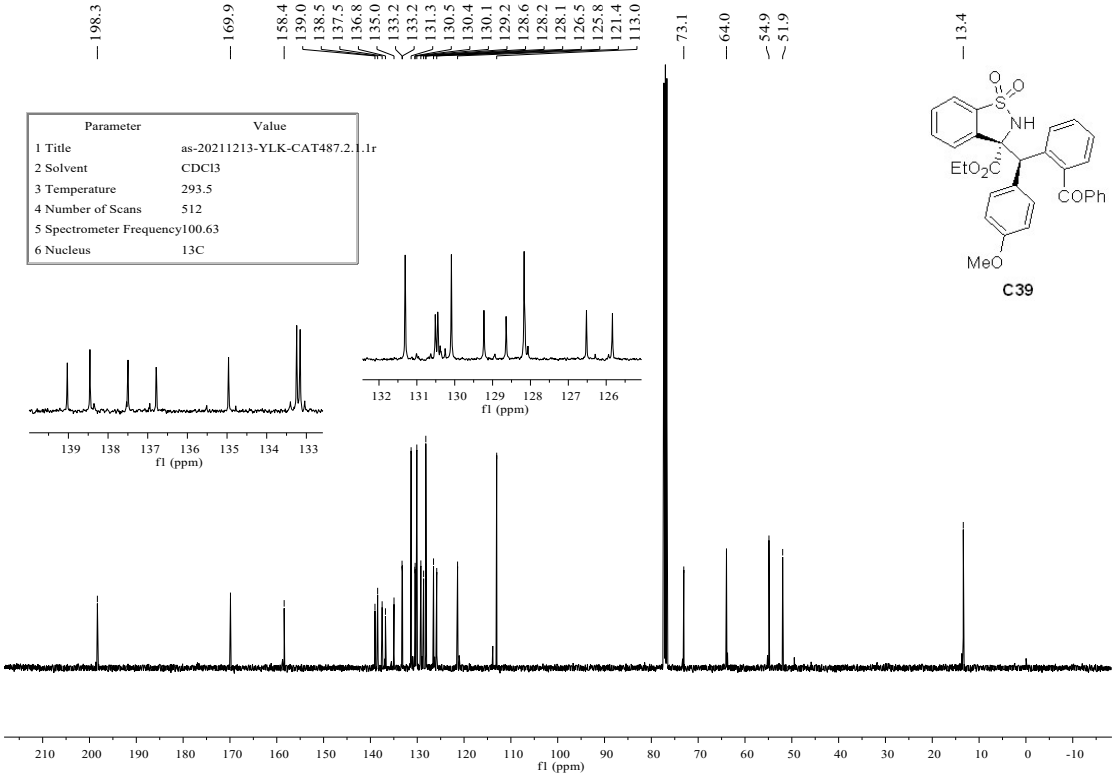
C38


Parameter Value
1 Title as-20210916-YLK-499.1.1.1r
2 Solvent CDCl3
3 Temperature 294.1
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
Minor isomer
Major isomer
d.r. = 89:11
C38
f1 (ppm)

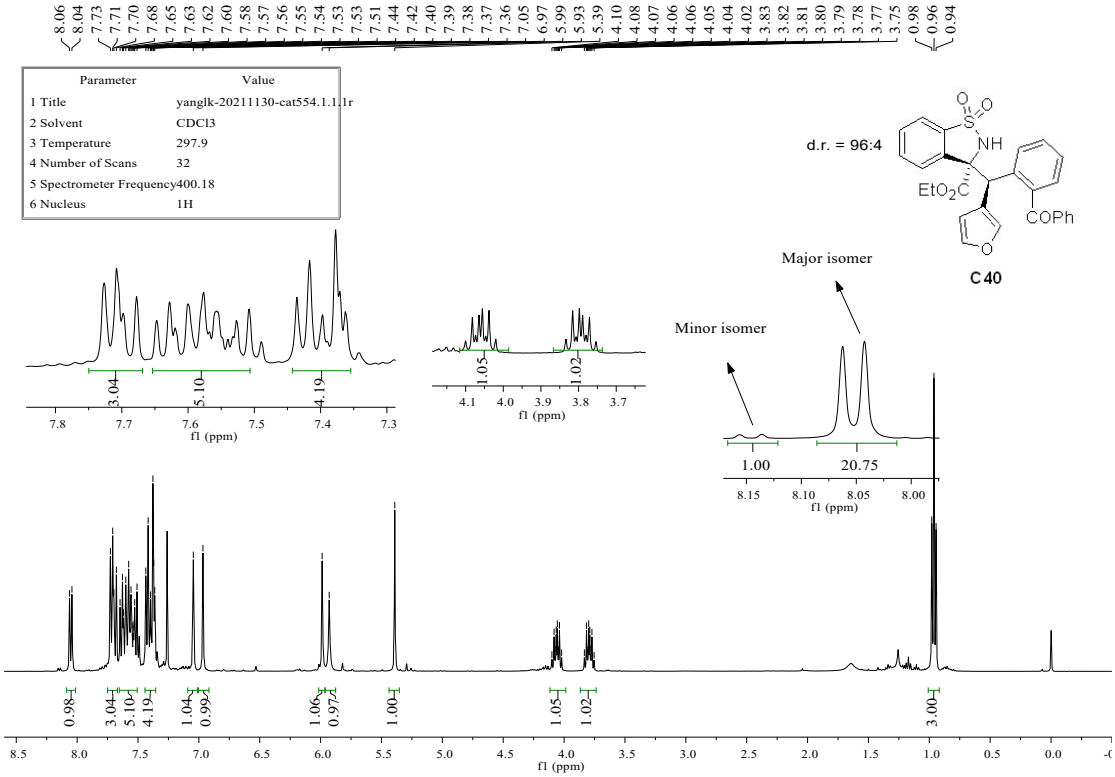

Parameter Value
1 Title as-20210916-YLK-499.2.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C38
f1 (ppm)

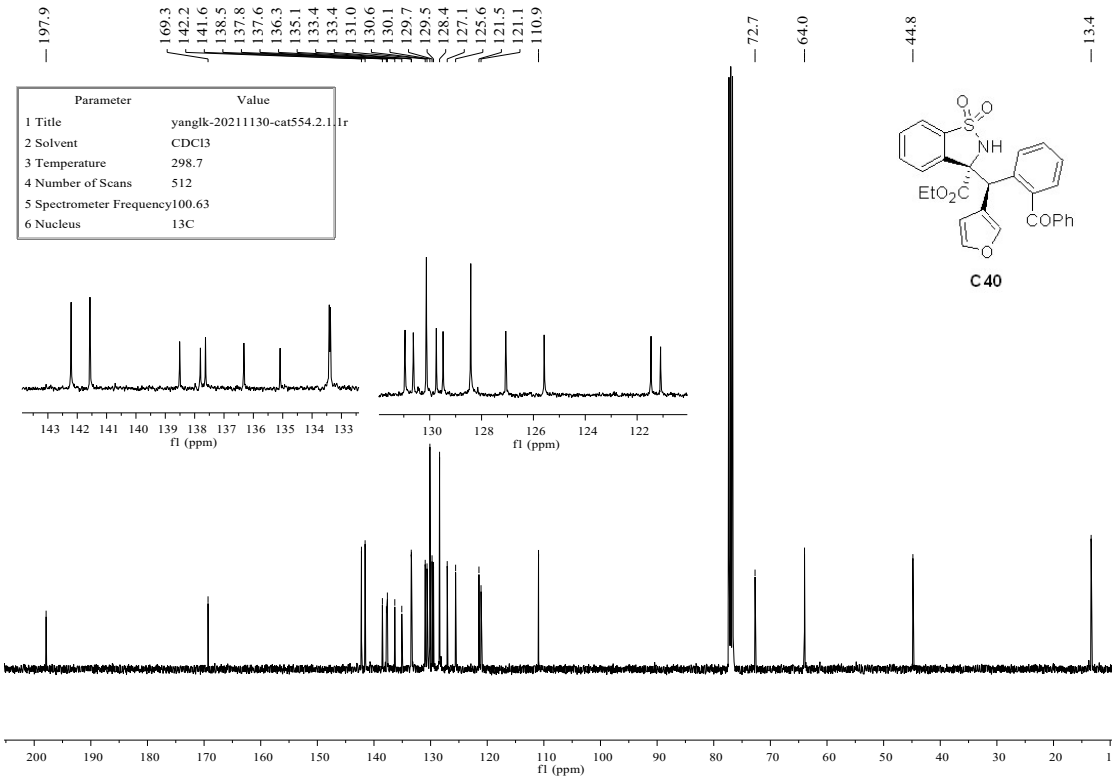
C39


Parameter Value
1 Title as-20211213-YLK-CAT487.1.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 92:8
Minor isomer
Major isomer
C39
f1 (ppm)

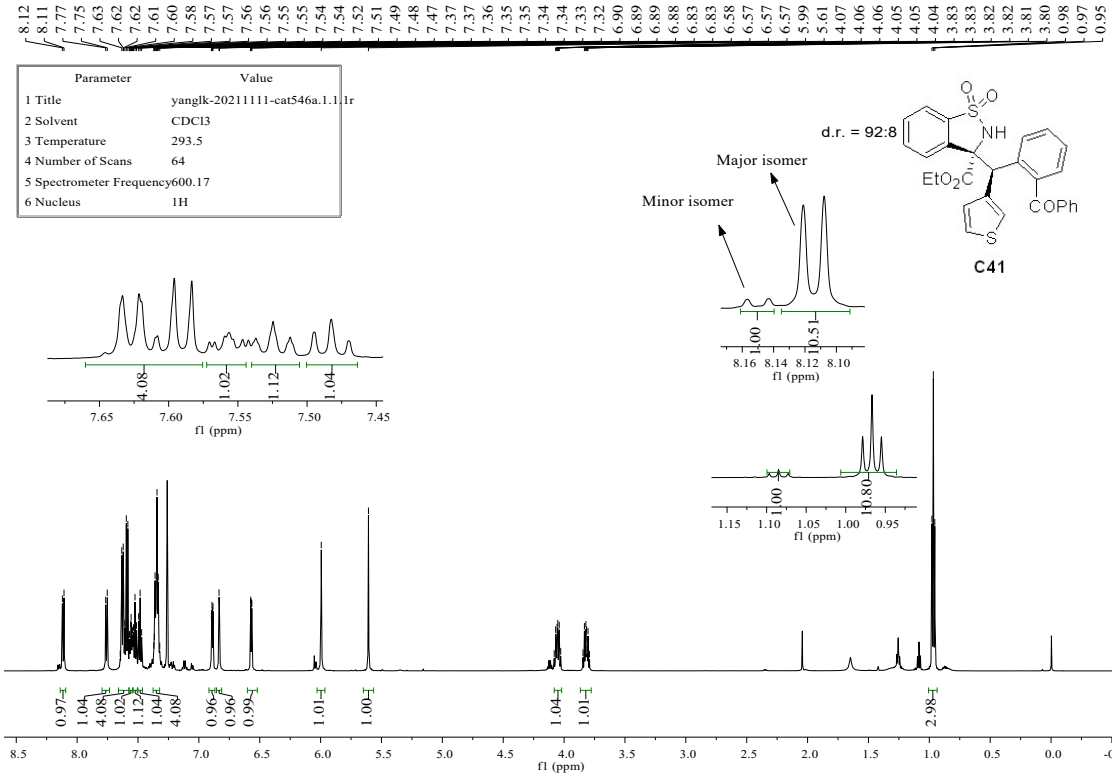

Parameter Value
1 Title as-20211213-YLK-CAT487.2.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C39
f1 (ppm)

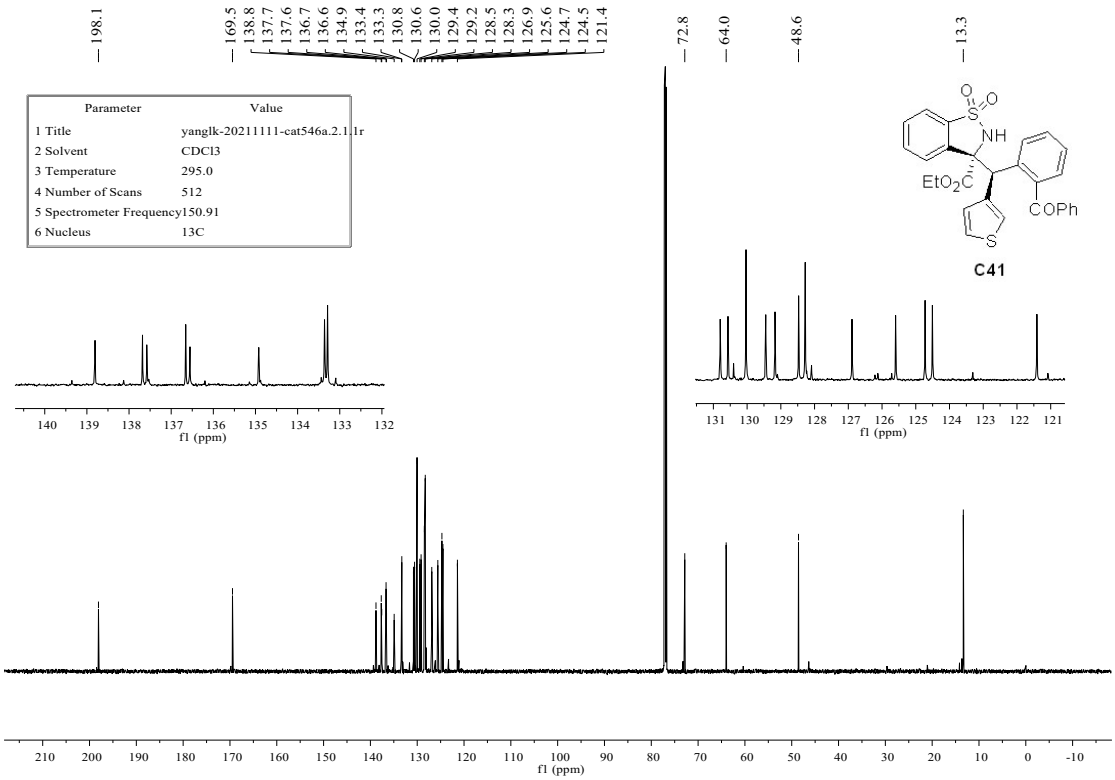
C40


Parameter Value
1 Title yanglk-20211130-cat554.1.1.1r
2 Solvent CDCl3
3 Temperature 297.9
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 96:4
Major isomer
Minor isomer
C40
f1 (ppm)


Parameter Value
1 Title yanglk-20211130-cat554.2.1.1r
2 Solvent CDCl3
3 Temperature 298.7
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C40
f1 (ppm)

C41

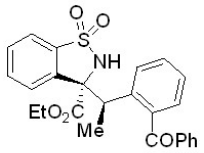

Parameter Value
1 Title yanglk-20211111-cat546a.1.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 64
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 92:8
Major isomer
Minor isomer
C41
f1 (ppm)


Parameter Value
1 Title yanglk-20211111-cat546a.2.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
C41
f1 (ppm)

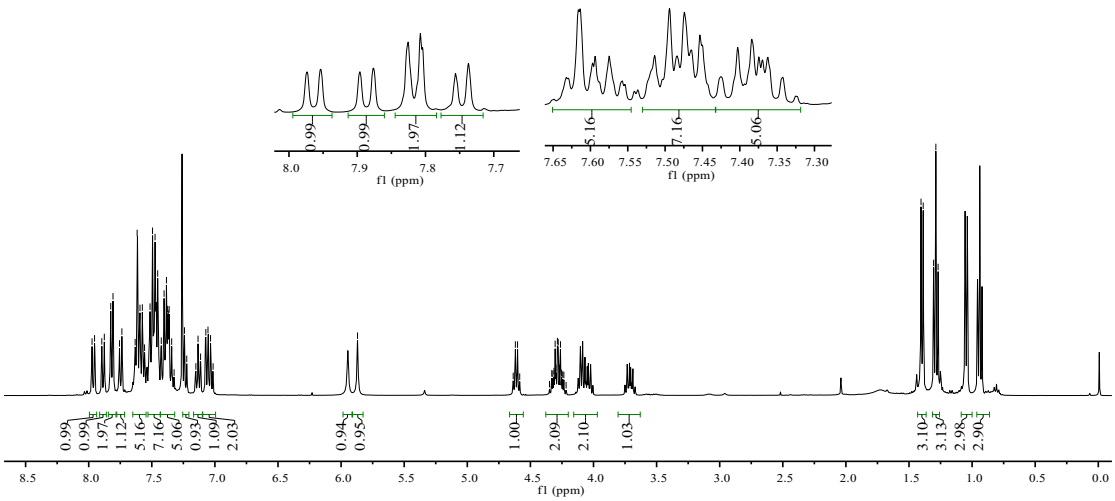
C42

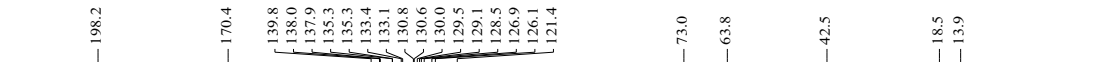
Parameter	Value
1 Title	yanglk-20220320-bs-cat54.7.1.1r
2 Solvent	CDCl3
3 Temperature	293.0
4 Number of Scans	32
5 Spectrometer Frequency	400.18
6 Nucleus	1H

d.r. = 48:52

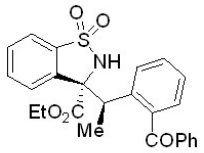


C42

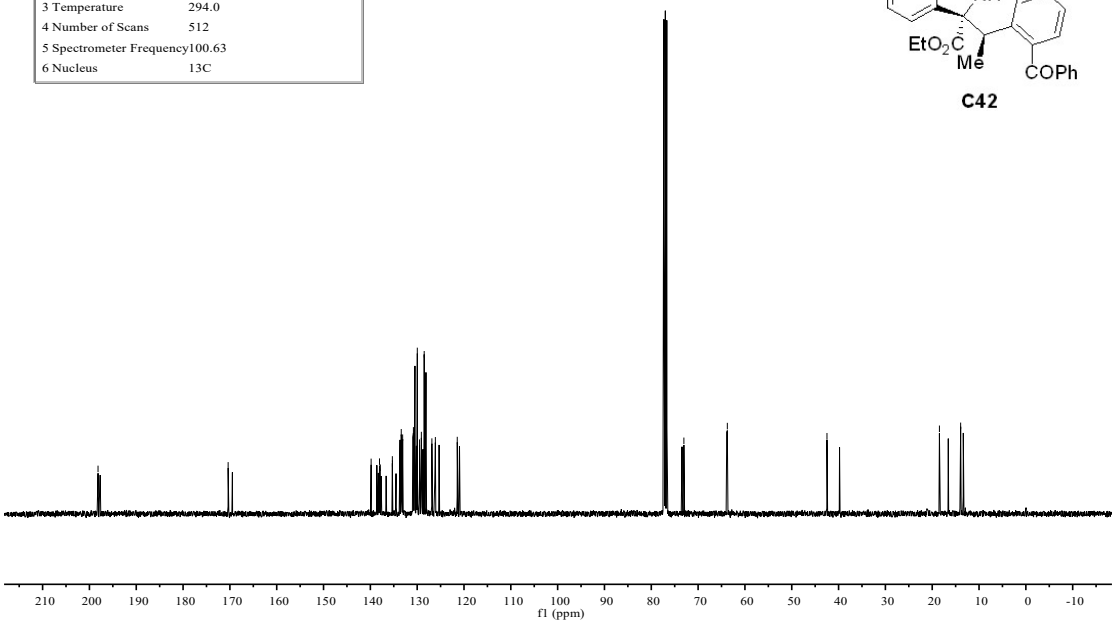




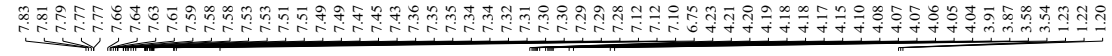
Parameter	Value
1 Title	yanglk-20220320-bs-cat54.6.1.1r
2 Solvent	CDCl3
3 Temperature	294.0
4 Number of Scans	512
5 Spectrometer Frequency	100.63
6 Nucleus	13C



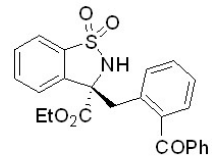
C42



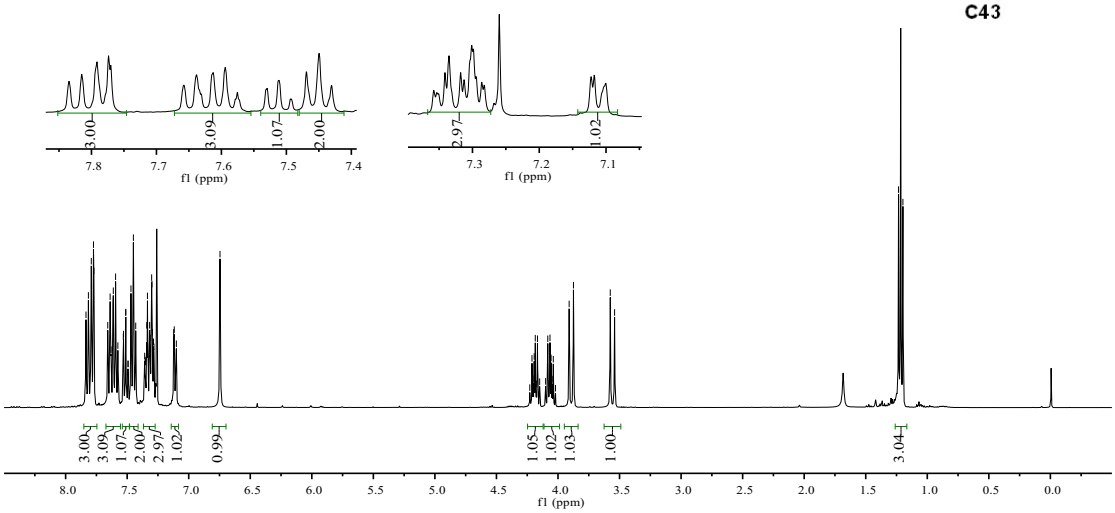
C43

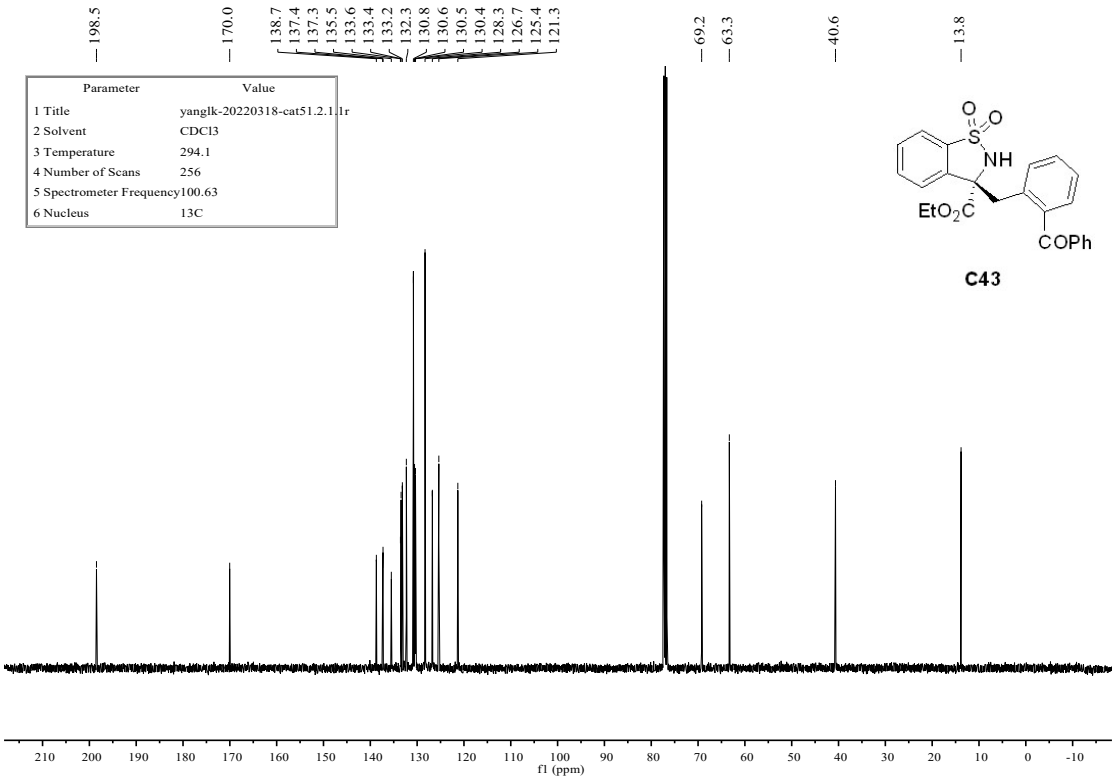


Parameter	Value
1 Title	yanglk-20220318-cat51.1.1.1r
2 Solvent	CDCl3
3 Temperature	293.3
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H



C43

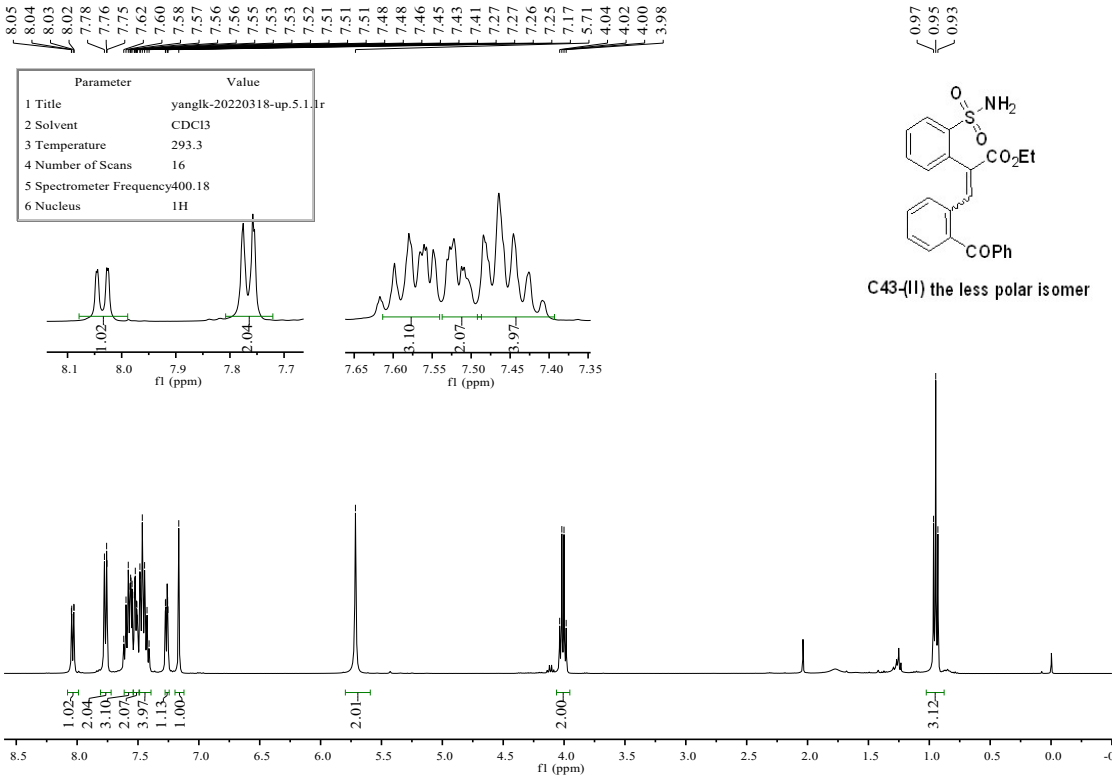


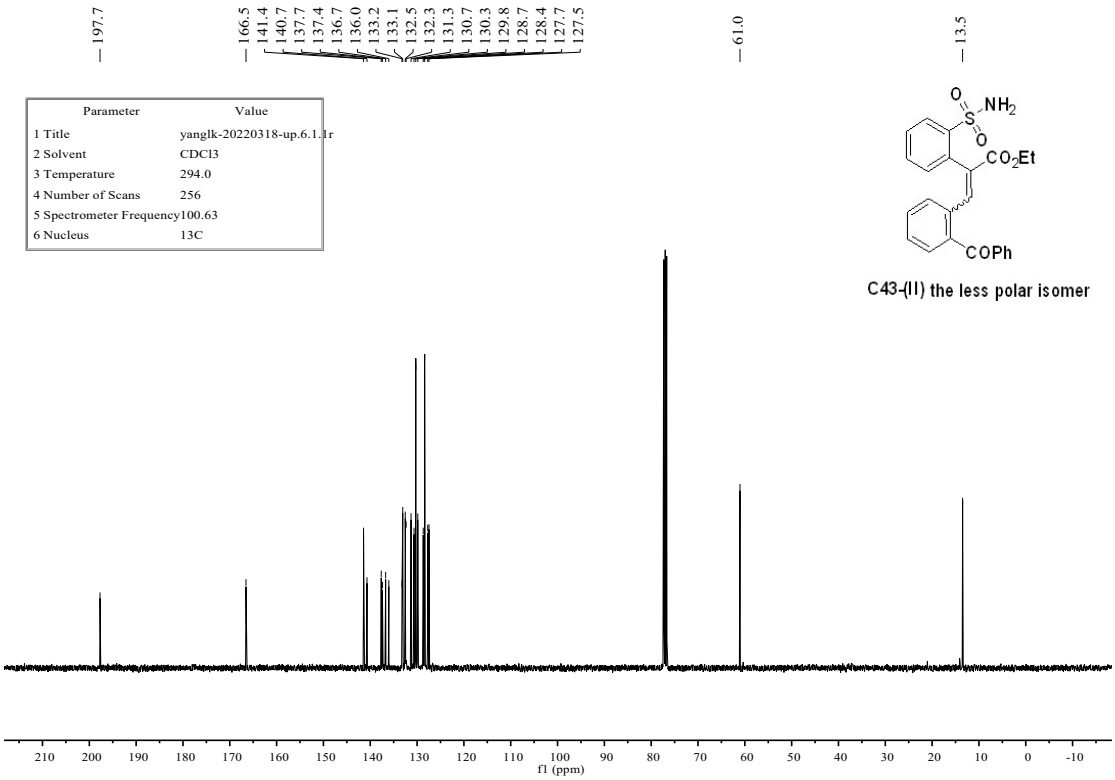


Parameter	Value
1 Title	yanglk-20220318-cat51.2.1.1r
2 Solvent	CDCl3
3 Temperature	294.1
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

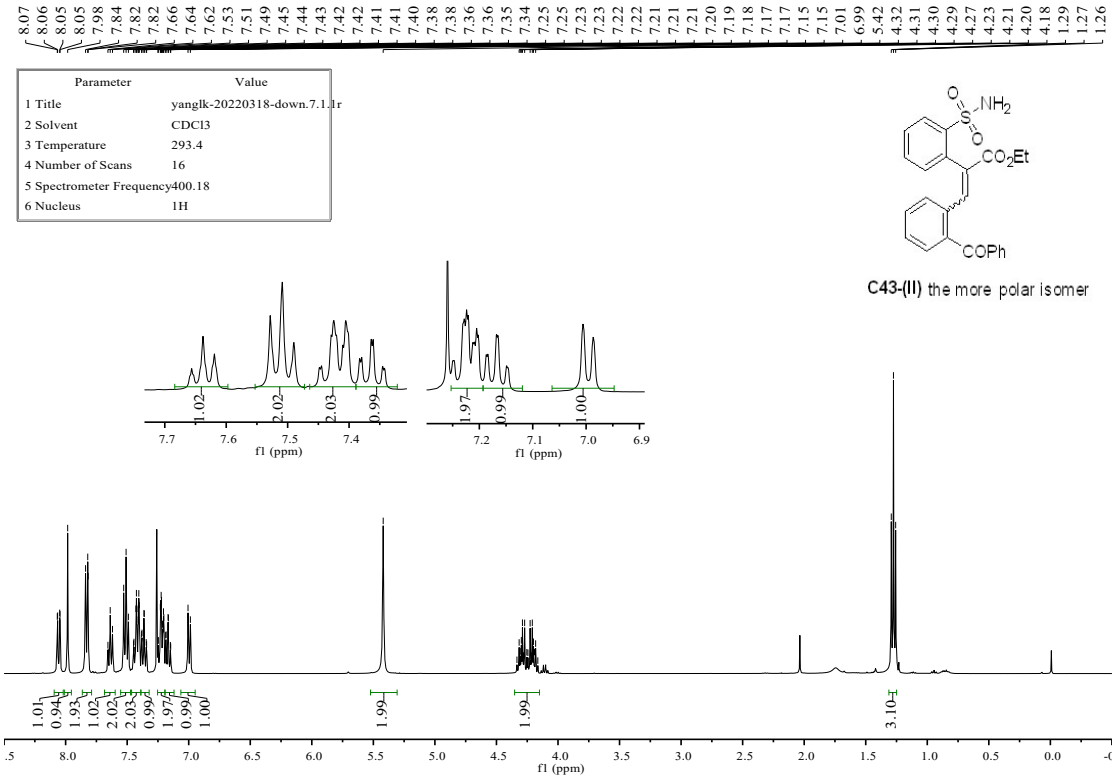
C43

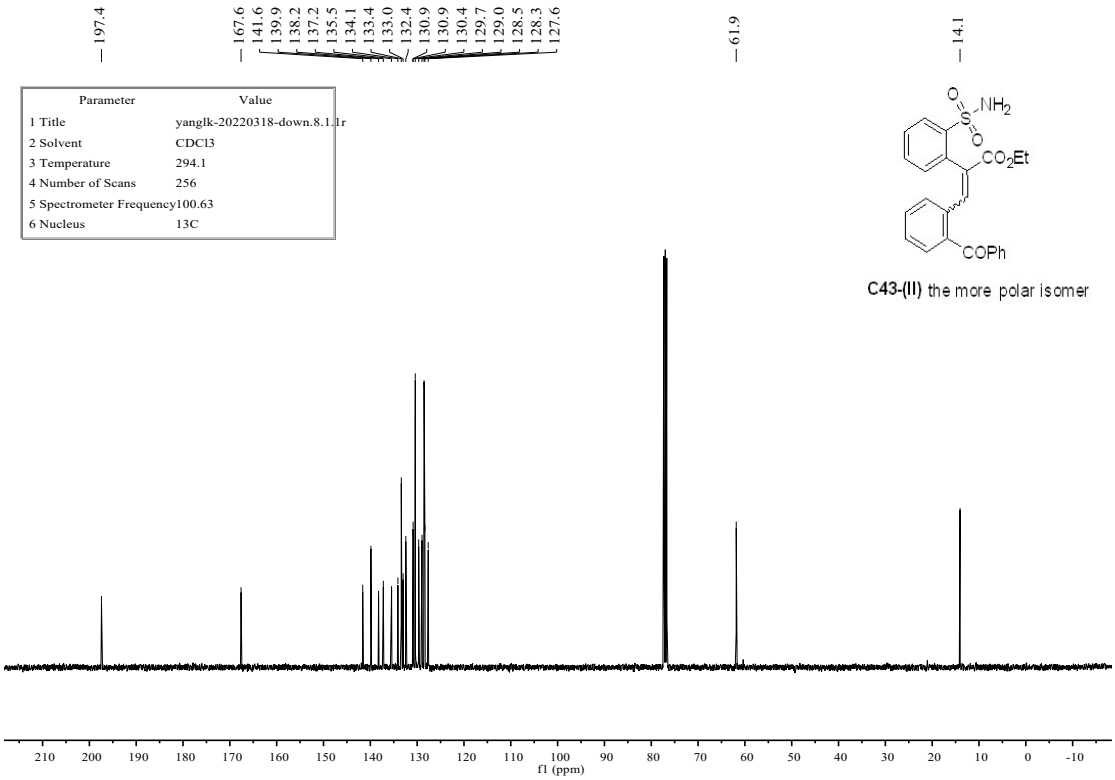
C43-(II) the less polar isomer



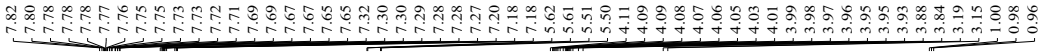


C43-(II) the more polar isomer

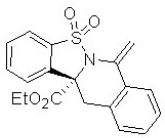




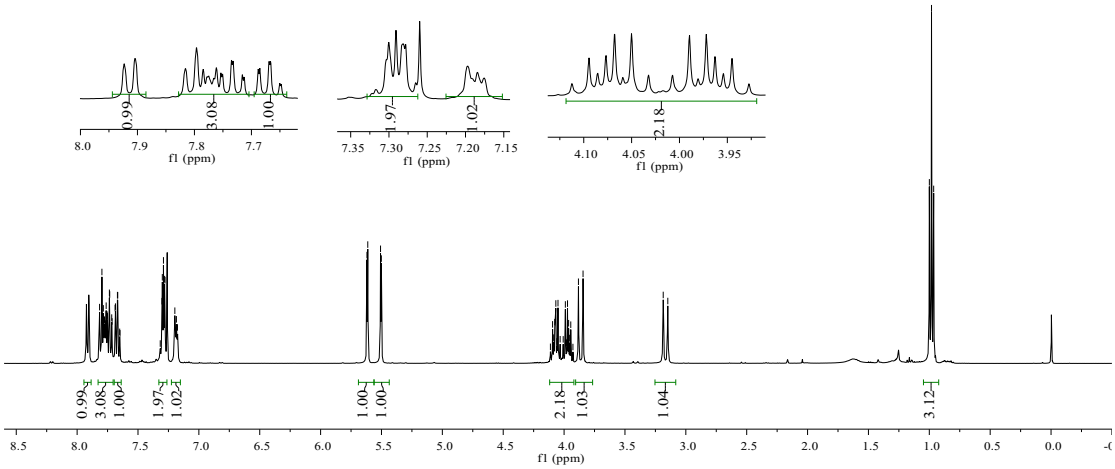
D1

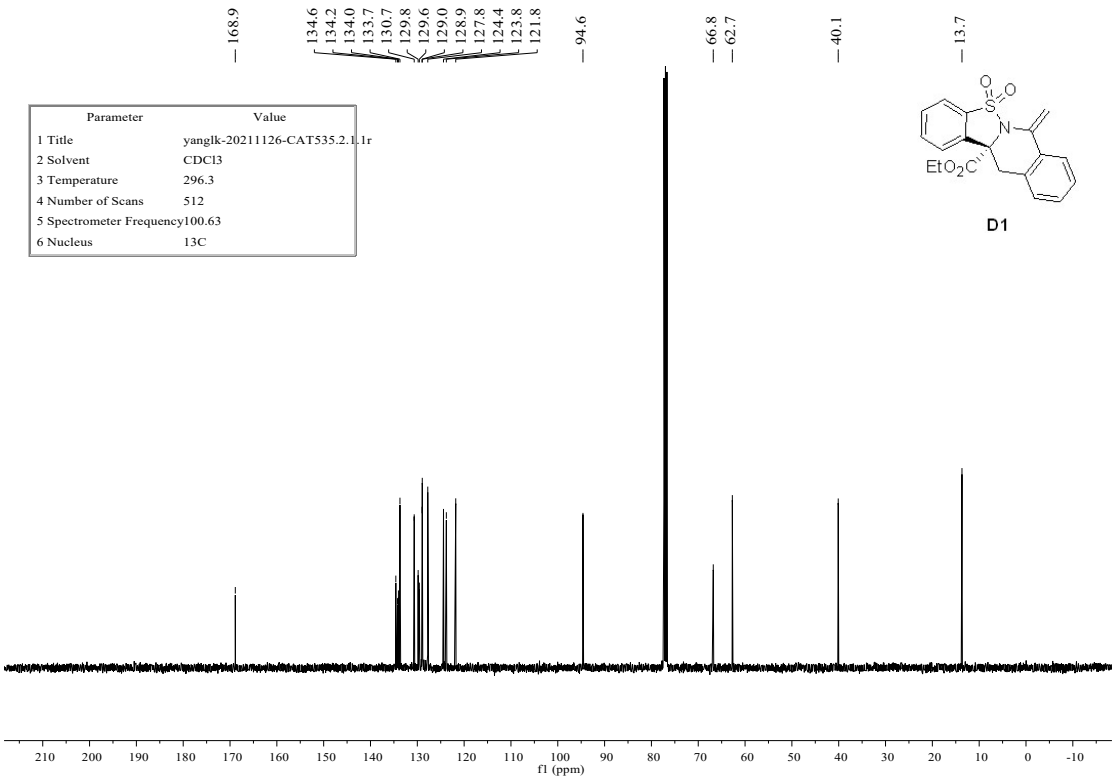


Parameter	Value
1 Title	yanglk-20211126-CAT535.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.5
4 Number of Scans	32
5 Spectrometer Frequency	400.18
6 Nucleus	1H



D1

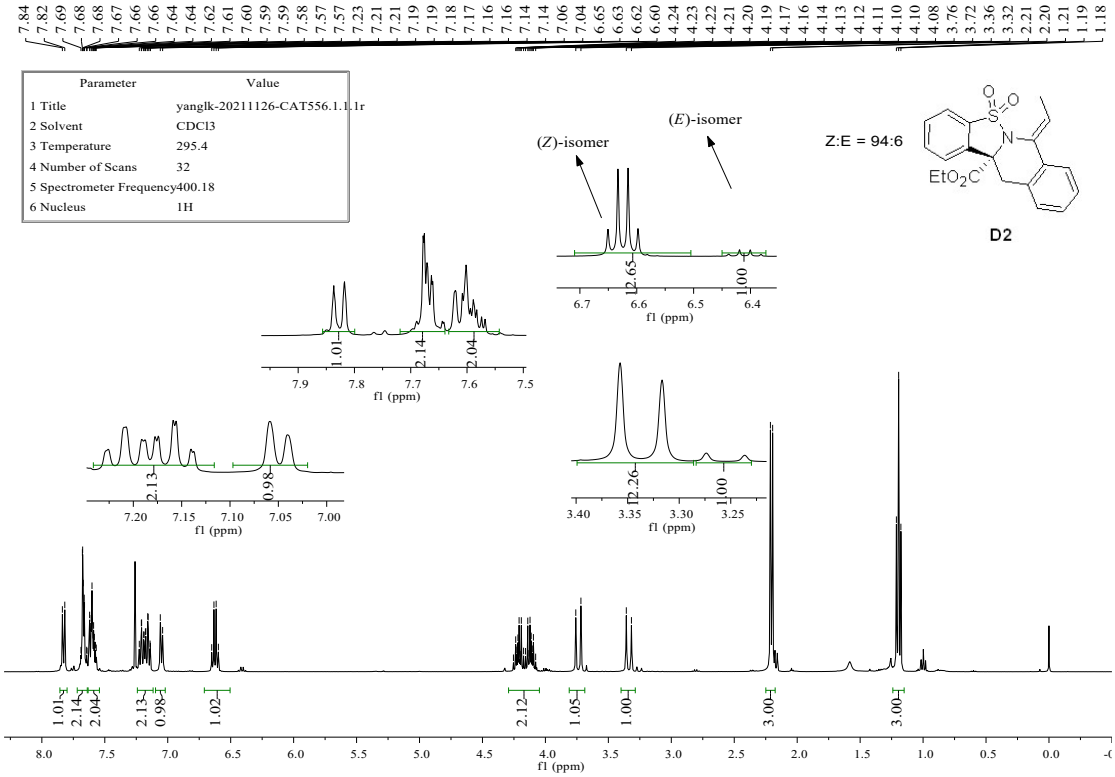


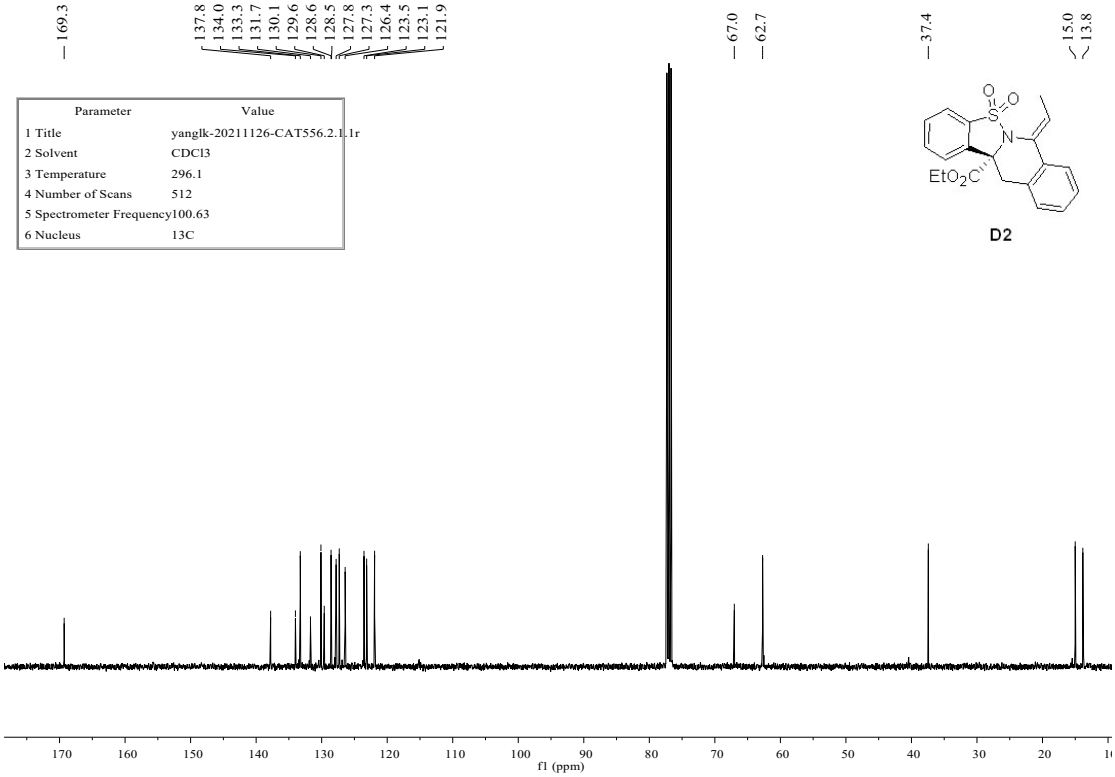


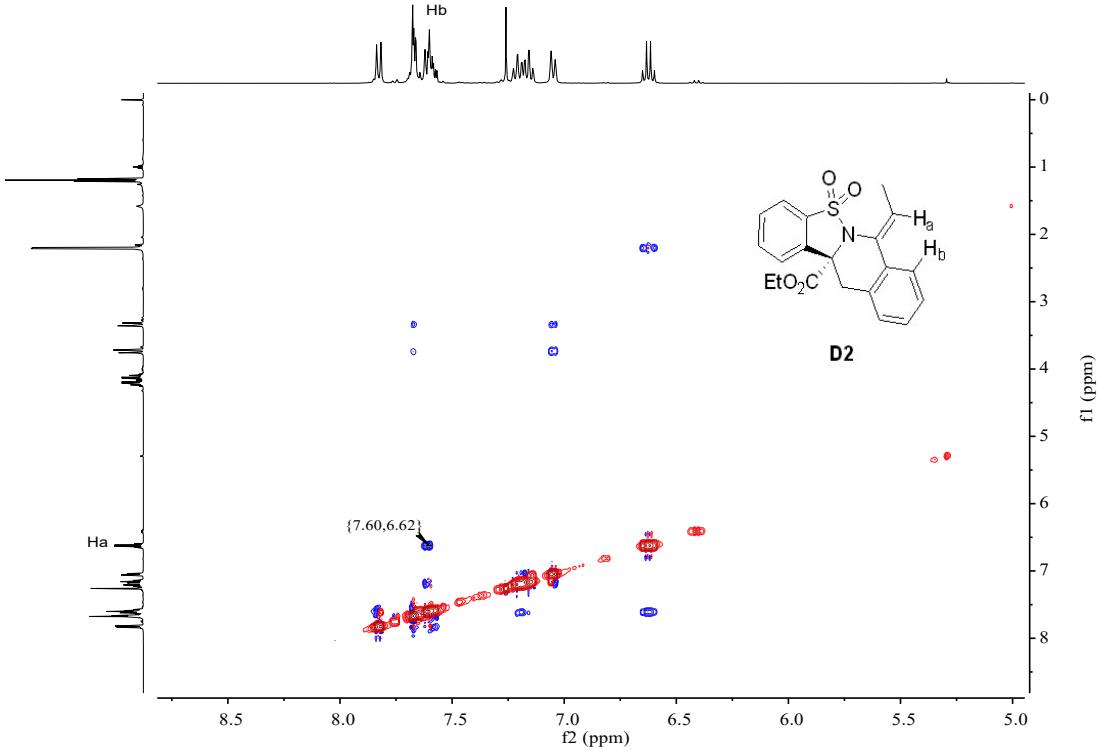
Parameter	Value
1 Title	yanglk-20211126-CAT535.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	512
5 Spectrometer Frequency	100.63
6 Nucleus	13C

D1

D2

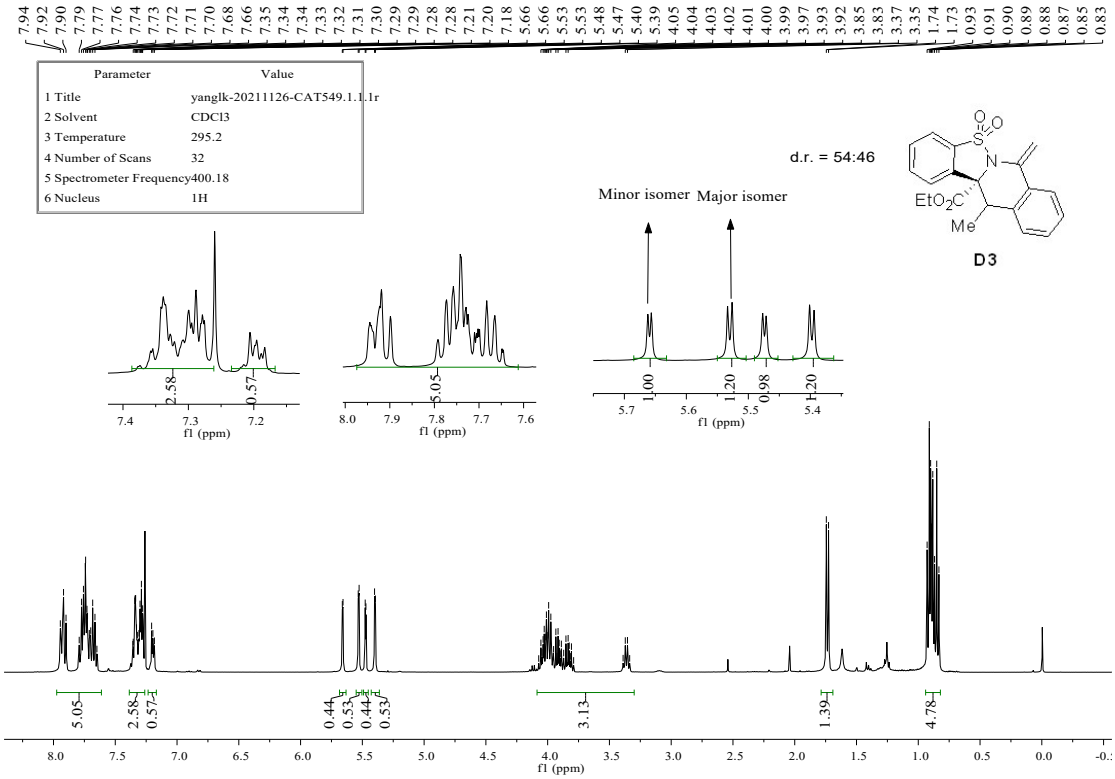

Parameter Value
1 Title yanglk-20211126-CAT556.1.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
(Z)-isomer
(E)-isomer
Z:E = 94:6
D2
f1 (ppm)

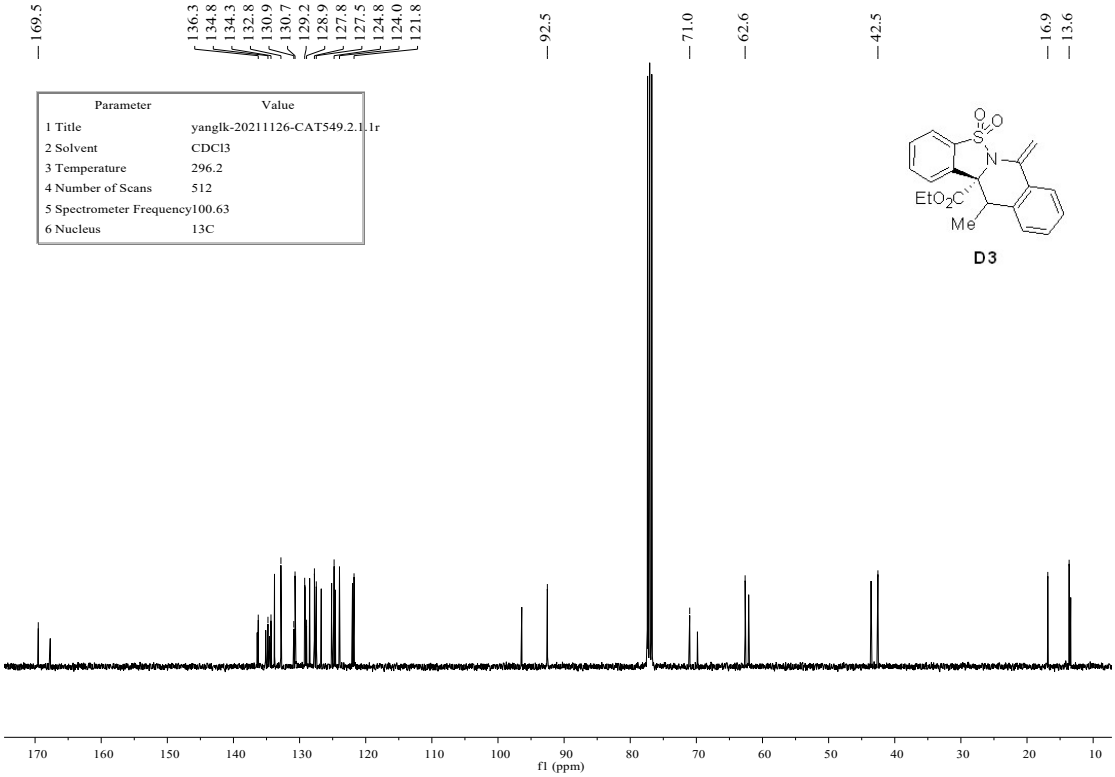

Parameter Value
1 Title yanglk-20211126-CAT556.2.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
D2
f1 (ppm)



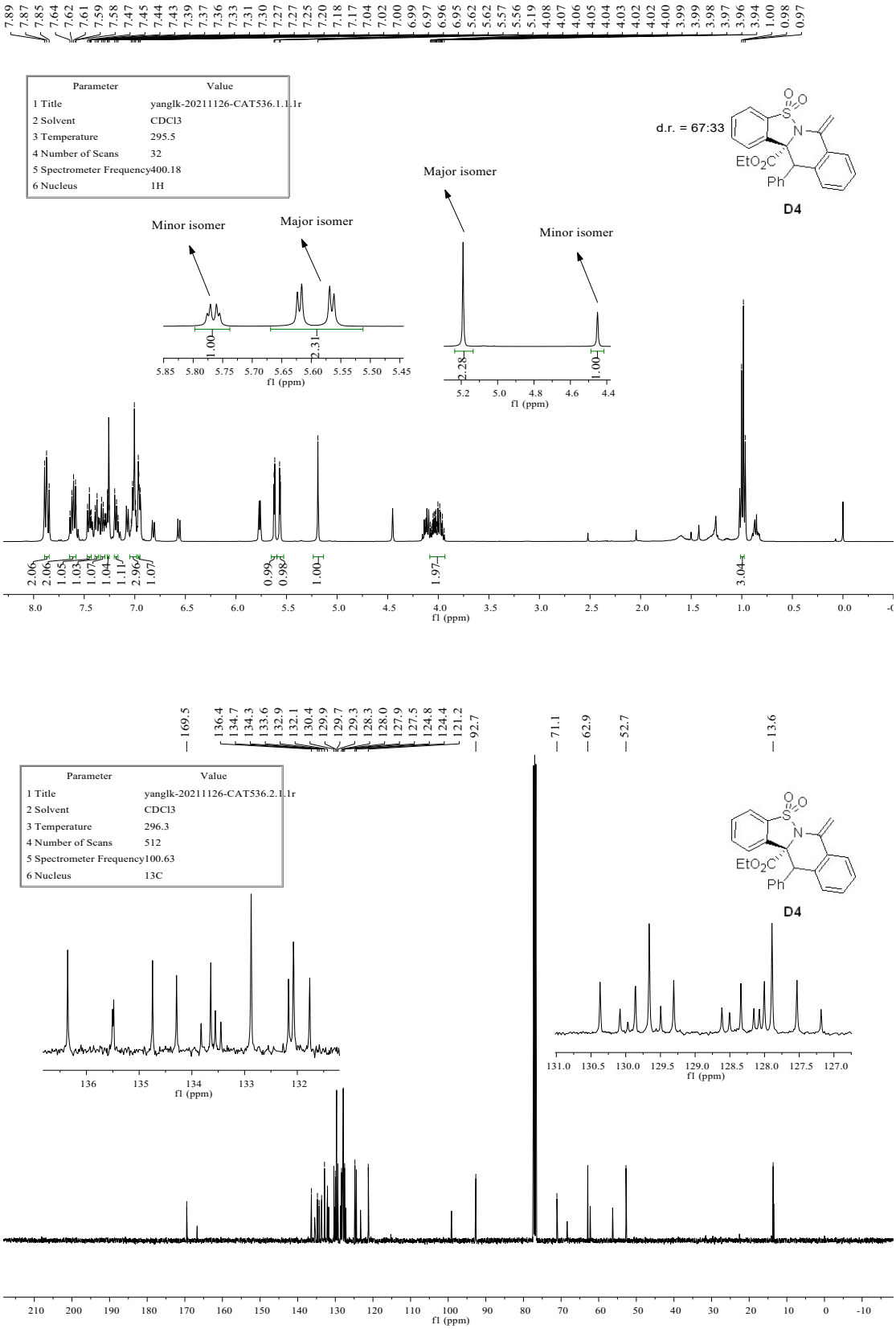
^{1}H NMR - NOESY (400 MHz, CDCl3) – (**D2**)

D3

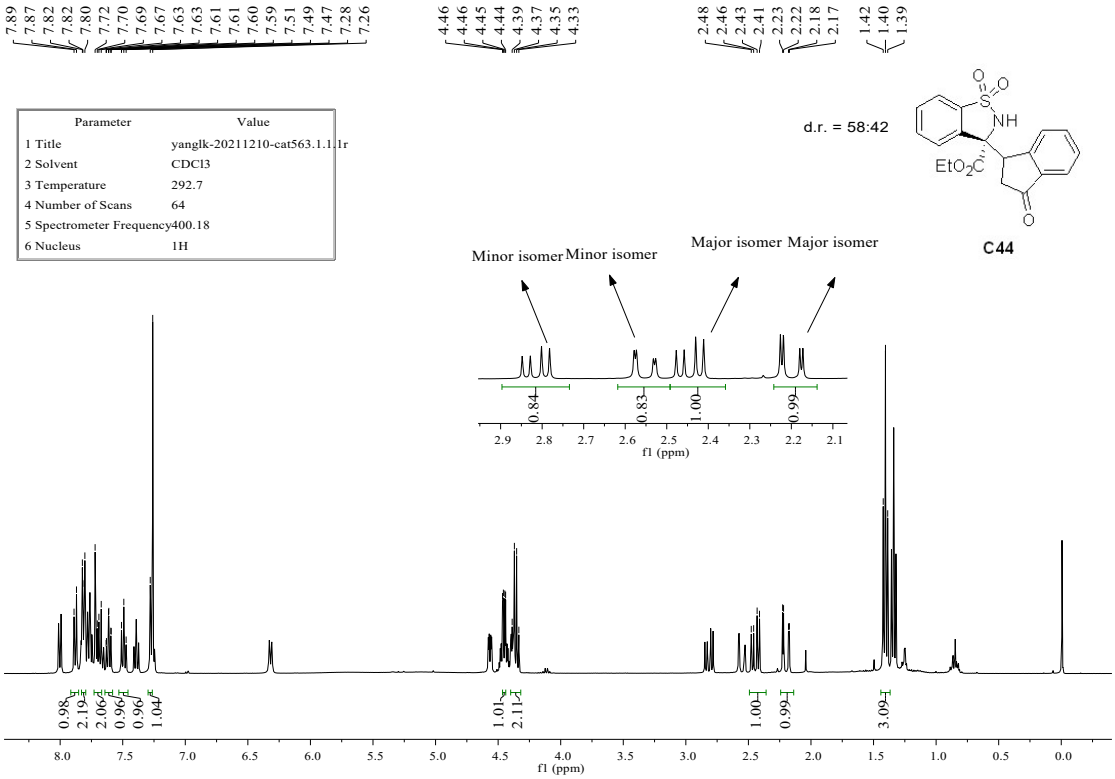

Parameter Value
1 Title yanglk-20211126-CAT549.1.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 54:46
Minor isomer
Major isomer
D3
f1 (ppm)

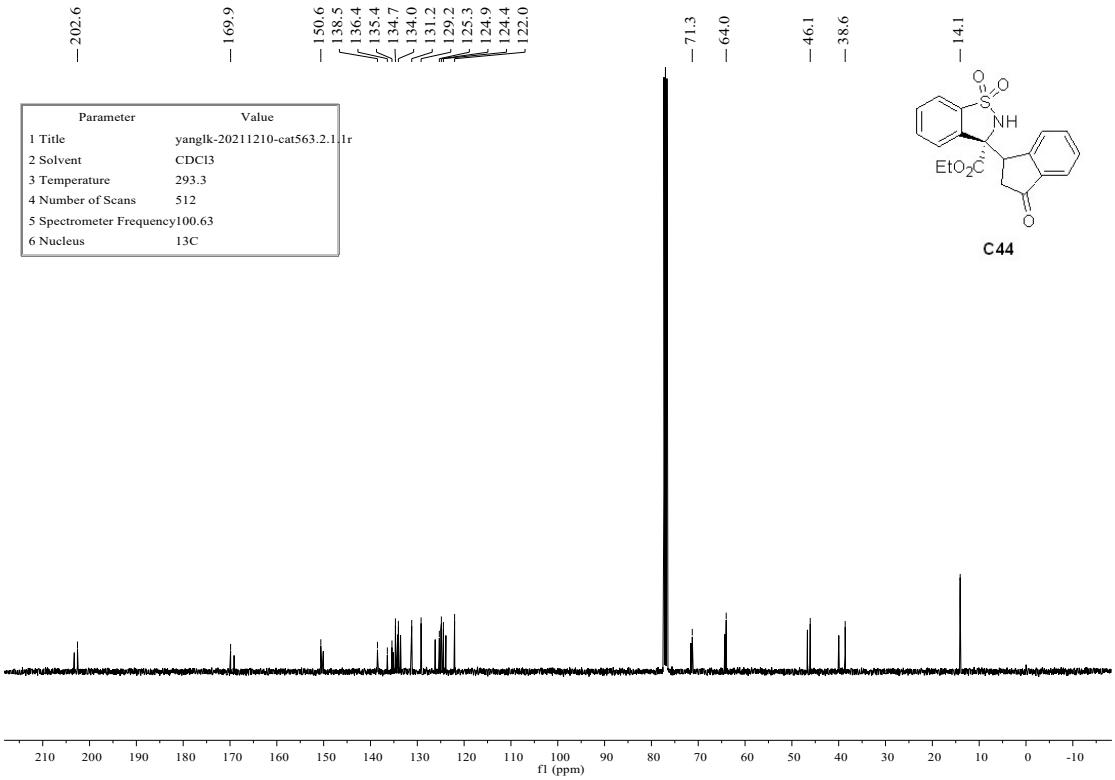

Parameter Value
1 Title yanglk-20211126-CAT549.2.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
D3
f1 (ppm)

D4

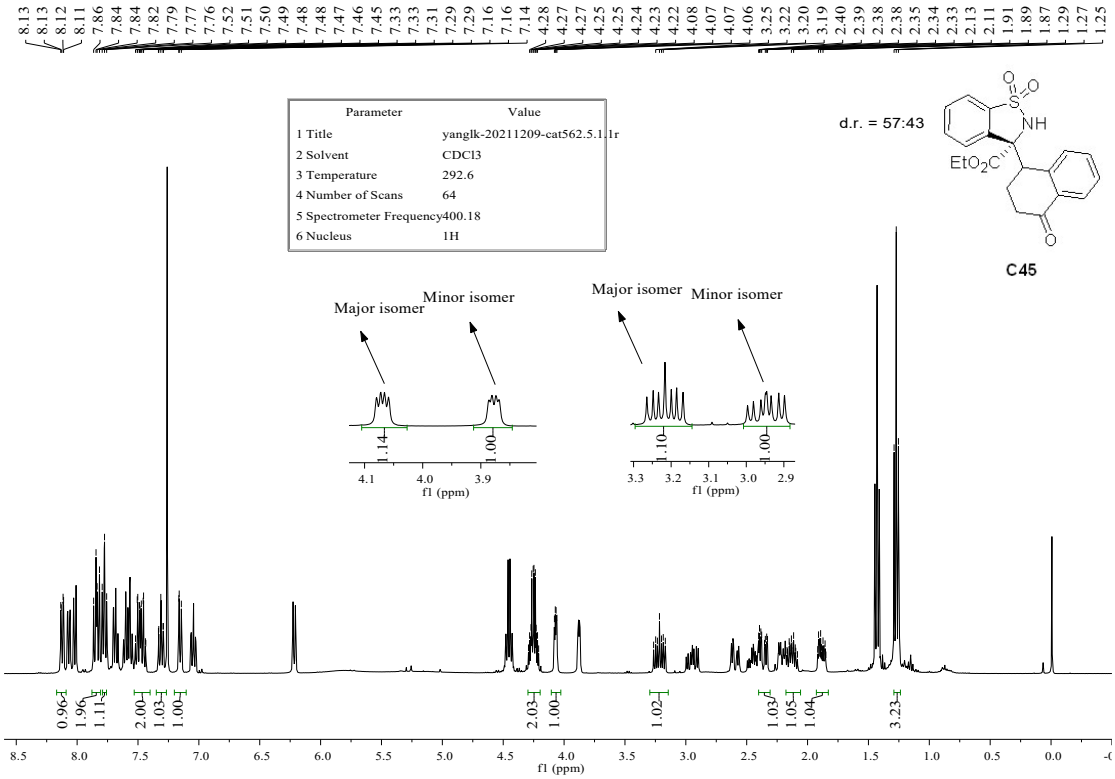

Parameter Value
1 Title yanglk-20211126-CAT536.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 32
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 67:33
D4
Major isomer
Minor isomer
Minor isomer
Major isomer
f1 (ppm)
Parameter Value
1 Title yanglk-20211126-CAT536.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
D4
f1 (ppm)

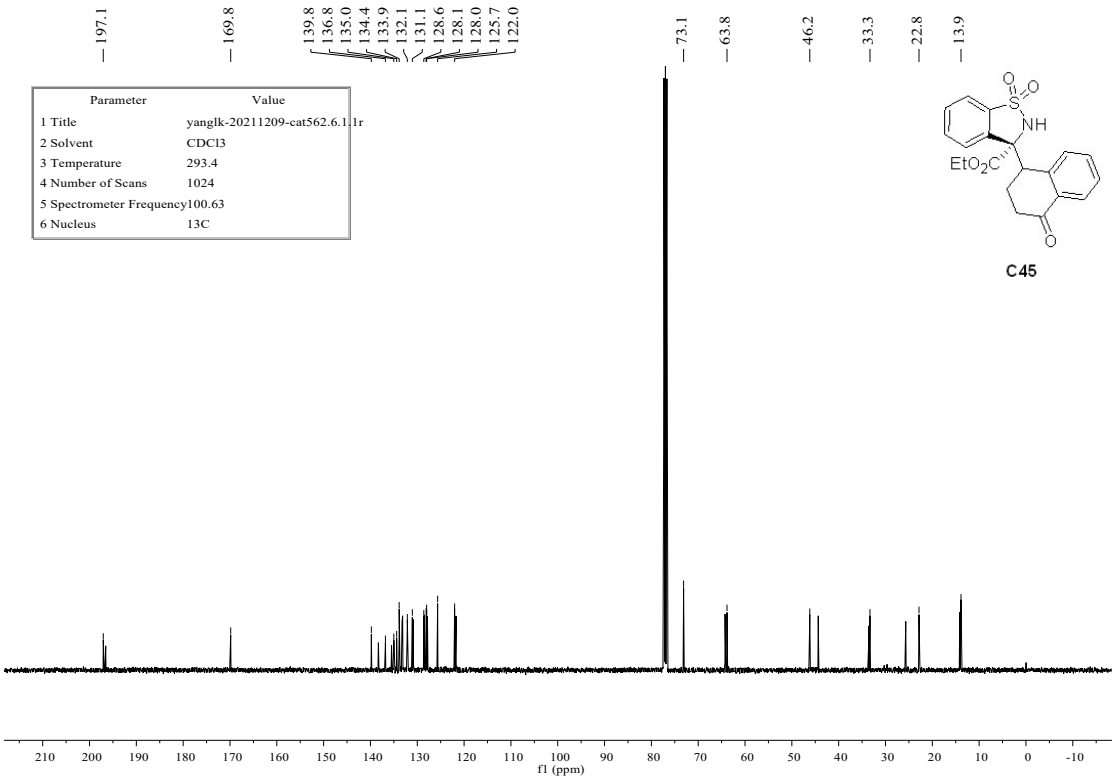
C44


7.89 7.87 7.82 7.82 7.80 7.72 7.70 7.69 7.67 7.63 7.63 7.61 7.61 7.60 7.59 7.51 7.49 7.47 7.28 7.26
4.46 4.46 4.45 4.44 4.39 4.37 4.35 4.33
2.48 2.46 2.43 2.41 2.23 2.22 2.18 2.17
1.42 1.40 1.39
Parameter Value
1 Title yanglk-20211210-cat563.1.1.1r
2 Solvent CDCl3
3 Temperature 292.7
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 58:42
C44
Minor isomer Minor isomer Major isomer Major isomer
0.84 0.83 1.00 0.99
f1 (ppm)
0.98 2.19 2.06 0.96 0.96 1.04
1.01 2.11 1.00 0.99 3.09
f1 (ppm)

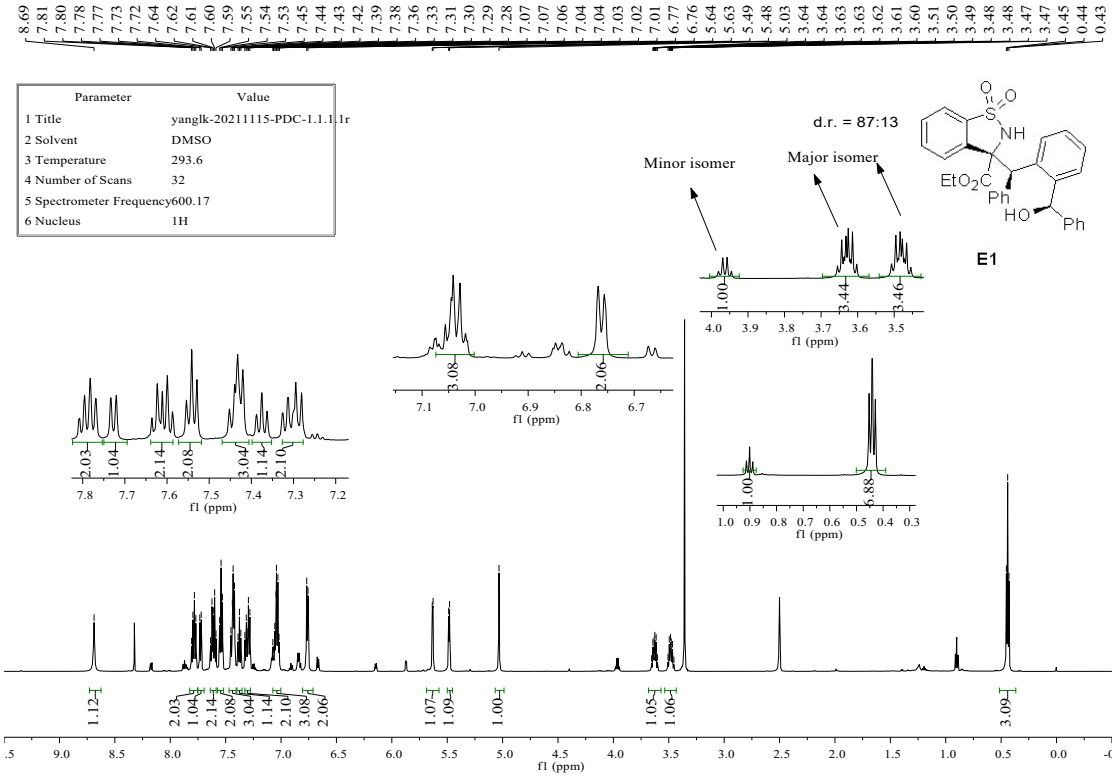

202.6 169.9 150.6 138.5 136.4 135.4 134.7 134.0 131.2 129.2 125.3 124.9 124.4 122.0
71.3 64.0 46.1 38.6 14.1
Parameter Value
1 Title yanglk-20211210-cat563.2.1.1r
2 Solvent CDCl3
3 Temperature 293.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C44
f1 (ppm)

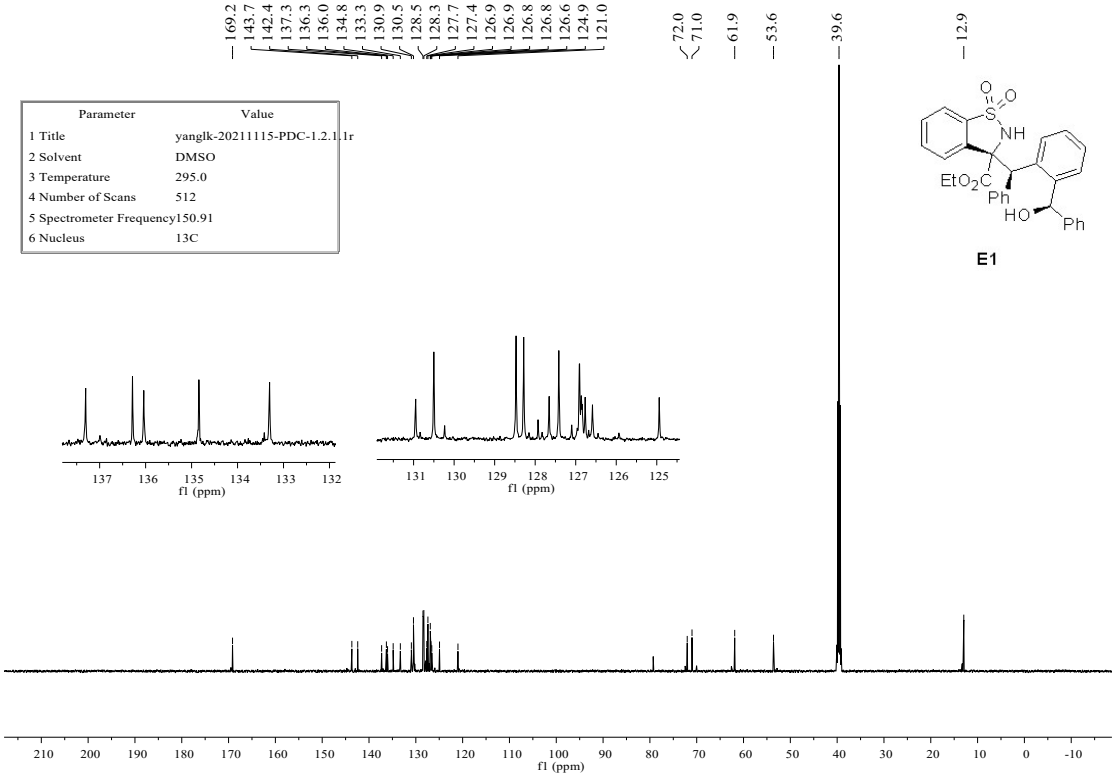
C45


8.13 8.13 8.12 8.11 7.86 7.84 7.84 7.82 7.79 7.77 7.76 7.52 7.51 7.50 7.49 7.48 7.48 7.47 7.46 7.45 7.33 7.33 7.31 7.29 7.29 7.16 7.16 7.14 4.28 4.27 4.27 4.25 4.25 4.24 4.23 4.22 4.08 4.07 4.07 4.06 3.25 3.22 3.20 3.19 2.40 2.39 2.38 2.38 2.35 2.34 2.33 2.13 2.11 1.91 1.89 1.87 1.29 1.27 1.25
Parameter Value
1 Title yanglk-20211209-cat562.5.1.1r
2 Solvent CDCl3
3 Temperature 292.6
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 57:43
C45
Major isomer
Minor isomer
Major isomer
Minor isomer
1.14
1.00
1.10
1.00
f1 (ppm)
0.96 1.96 1.11 2.00 1.03 1.00 2.03 1.00 1.02 1.03 1.05 1.04 3.23
f1 (ppm)

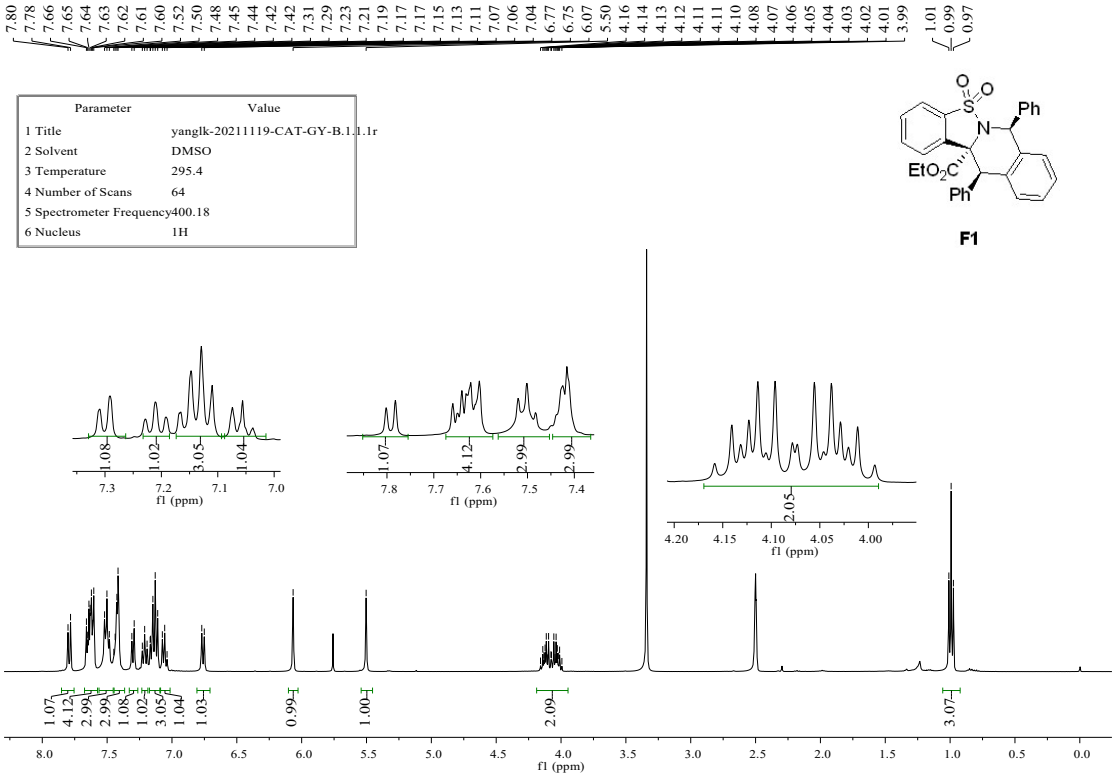

197.1 169.8 139.8 136.8 135.0 134.4 133.9 132.1 131.1 128.6 128.1 128.0 125.7 122.0 73.1 63.8 46.2 33.3 22.8 13.9
Parameter Value
1 Title yanglk-20211209-cat562.6.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 1024
5 Spectrometer Frequency 100.63
6 Nucleus 13C
C45
f1 (ppm)

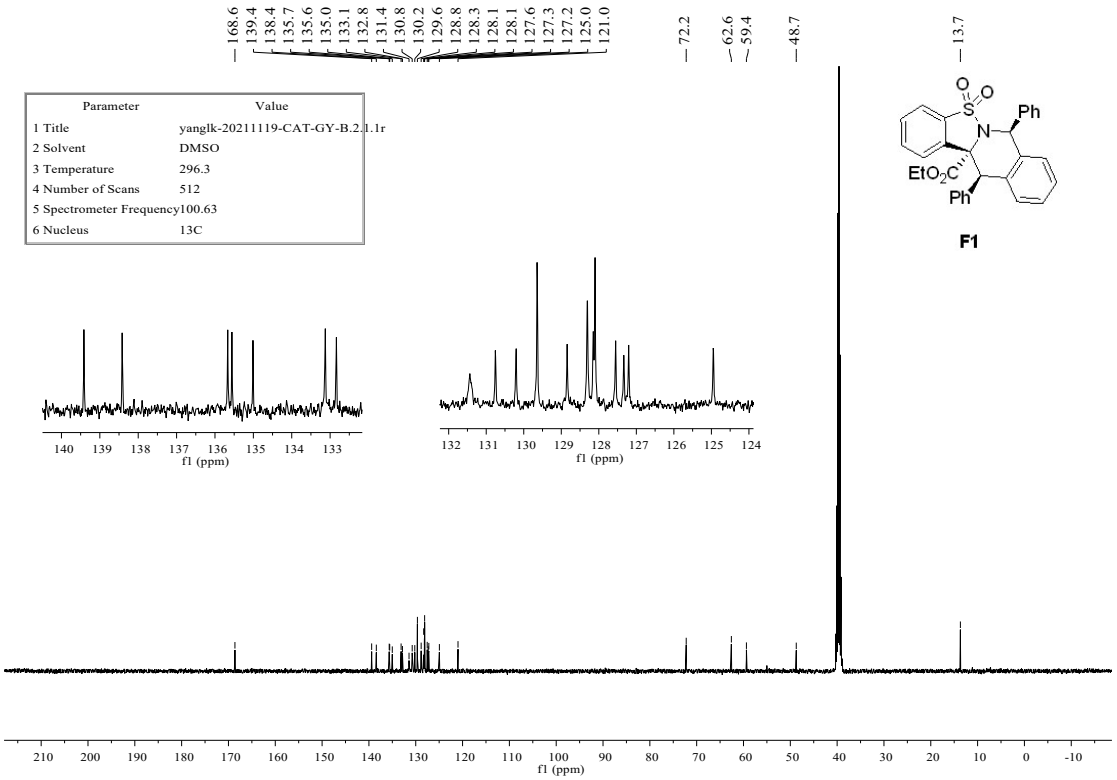
E1

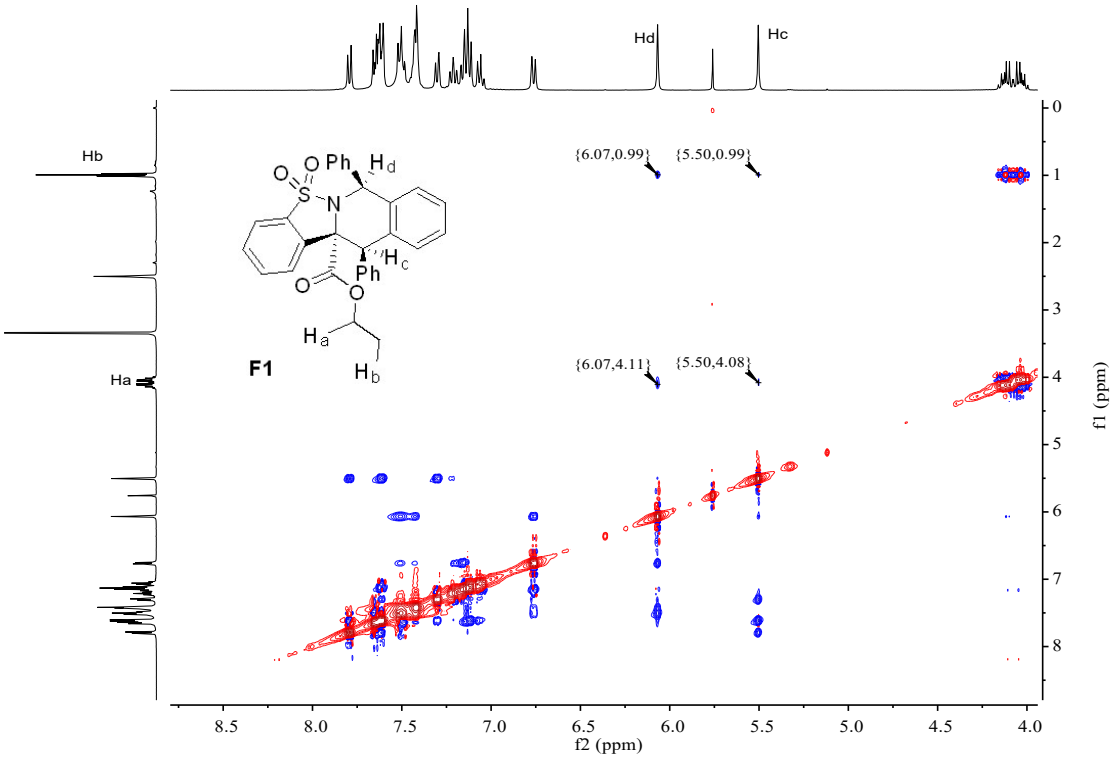

Parameter Value
1 Title yanglk-20211115-PDC-1.1.1.1r
2 Solvent DMSO
3 Temperature 293.6
4 Number of Scans 32
5 Spectrometer Frequency 600.17
6 Nucleus 1H
d.r. = 87:13
Minor isomer
Major isomer
E1
f1 (ppm)


Parameter Value
1 Title yanglk-20211115-PDC-1.2.1.1r
2 Solvent DMSO
3 Temperature 295.0
4 Number of Scans 512
5 Spectrometer Frequency 150.91
6 Nucleus 13C
E1
f1 (ppm)

F1

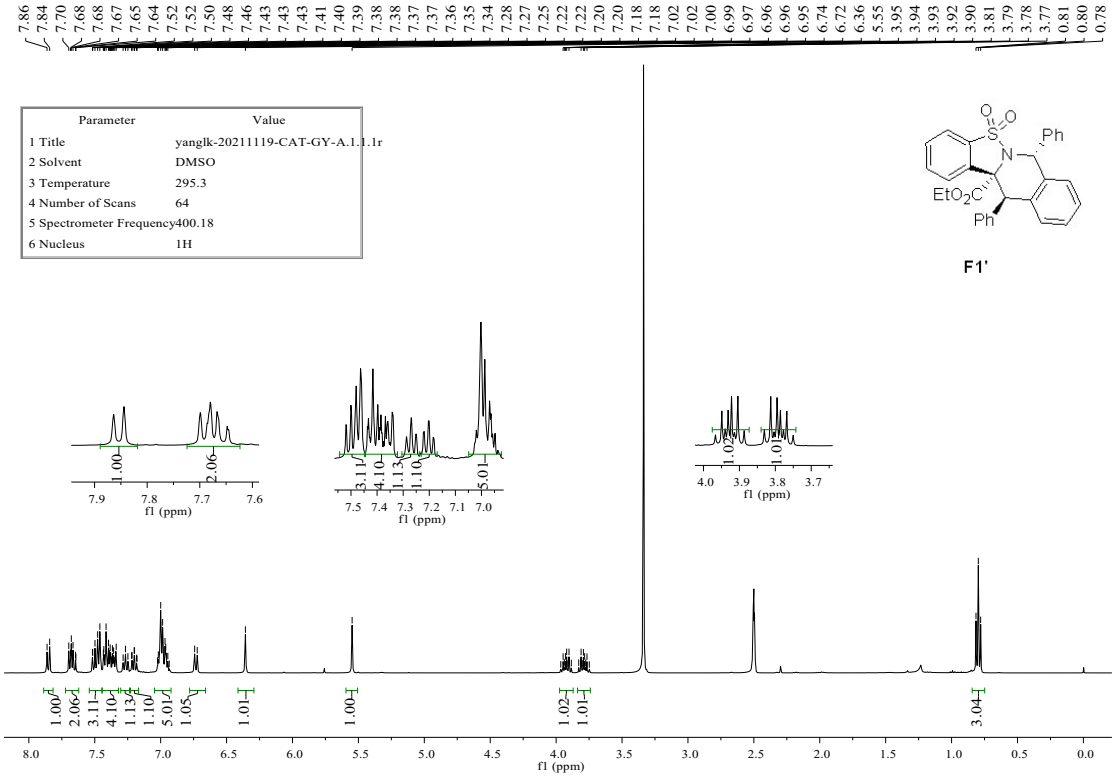

Parameter Value
1 Title yanglk-20211119-CAT-GY-B.1.1.1r
2 Solvent DMSO
3 Temperature 295.4
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
F1
f1 (ppm)

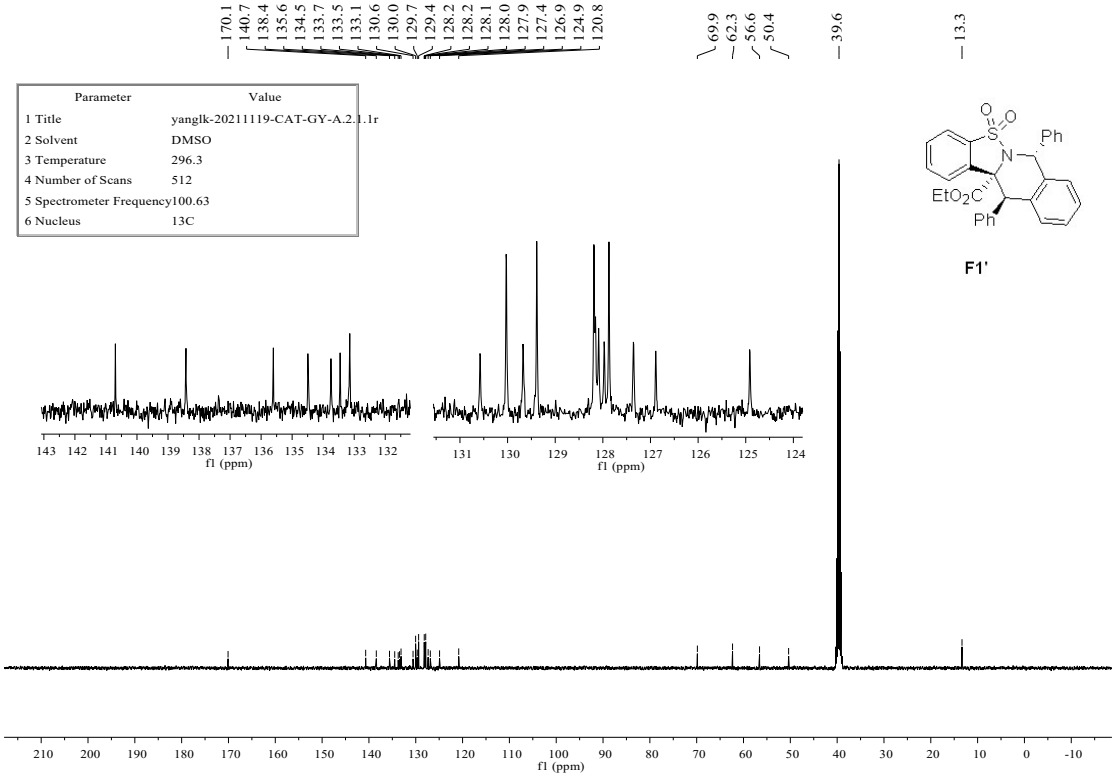

Parameter Value
1 Title yanglk-20211119-CAT-GY-B.2.1.1r
2 Solvent DMSO
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
F1
f1 (ppm)

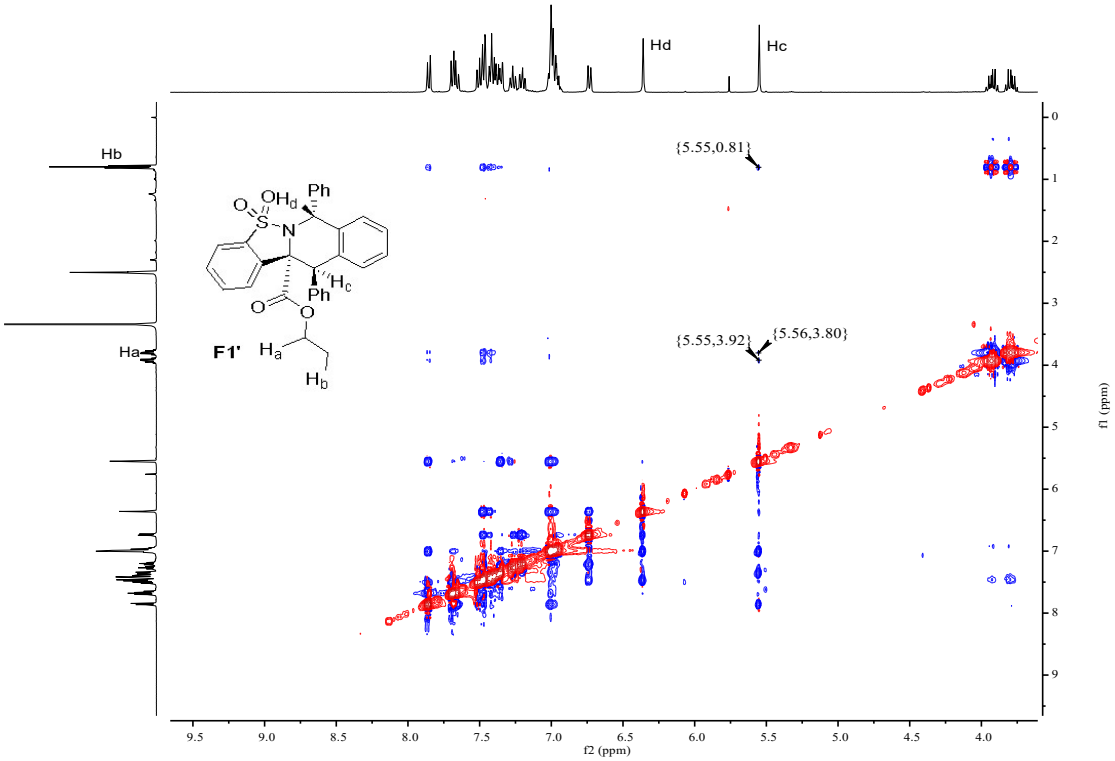


^{1}H NMR - NOESY (400 MHz, DMSO-d_6) – (**F1**)

F1′

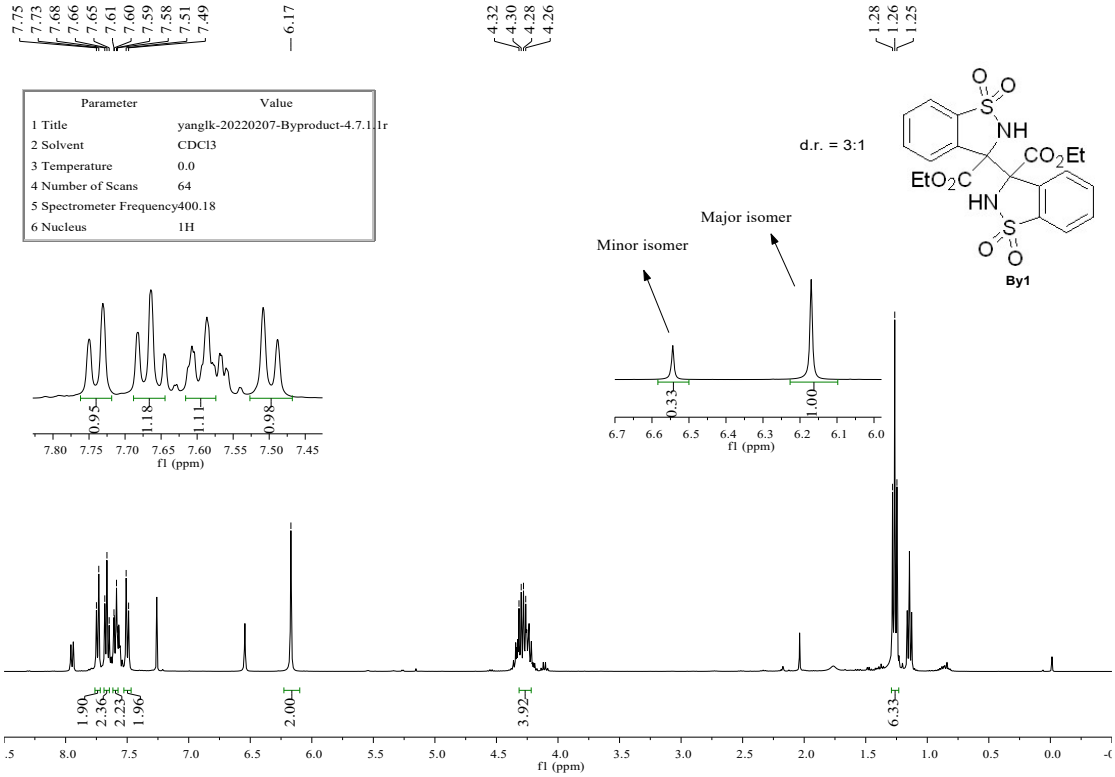

Parameter Value
1 Title yanglk-20211119-CAT-GY-A.1.1.1r
2 Solvent DMSO
3 Temperature 295.3
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
F1'
f1 (ppm)

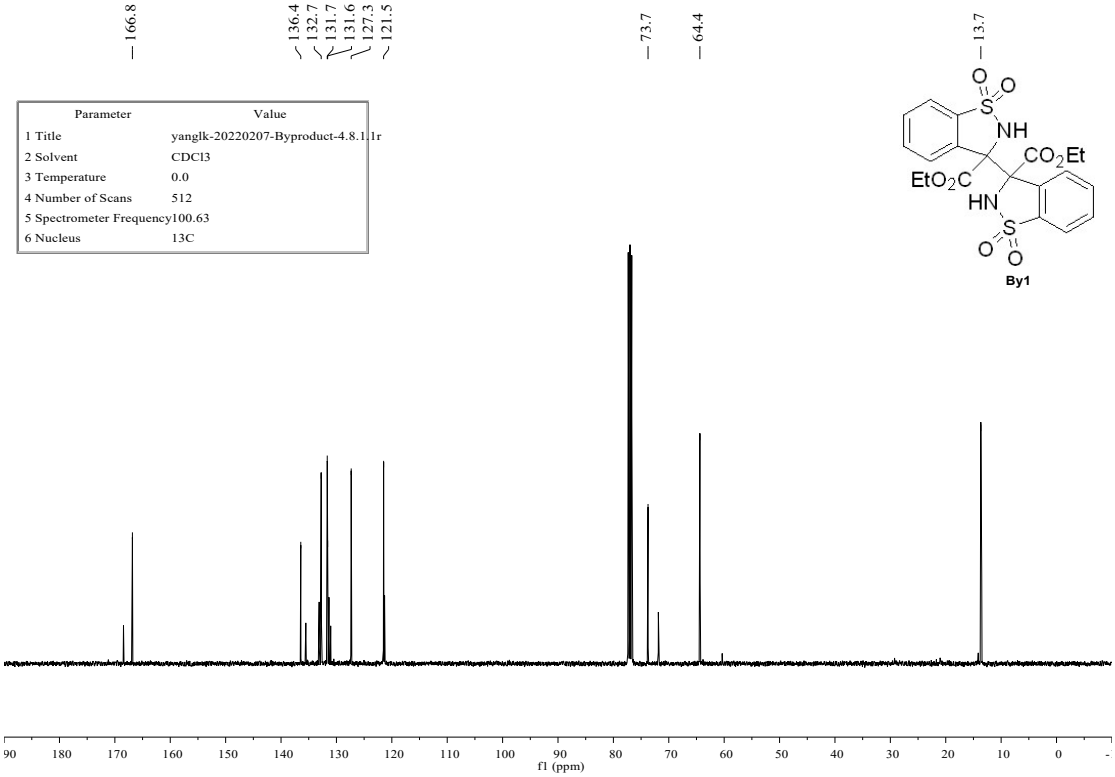

Parameter Value
1 Title yanglk-20211119-CAT-GY-A.2.1.1r
2 Solvent DMSO
3 Temperature 296.3
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
F1'
f1 (ppm)



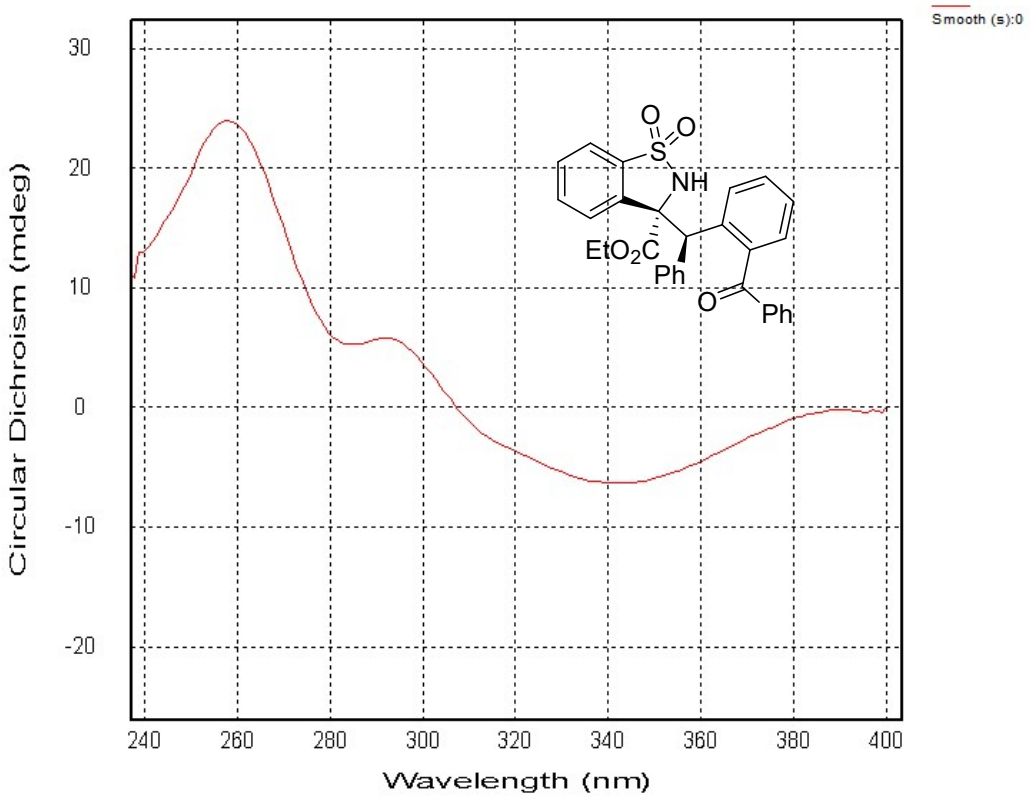
^{1}H NMR - NOESY (400 MHz, DMSO-d_6) – (**F1′**)

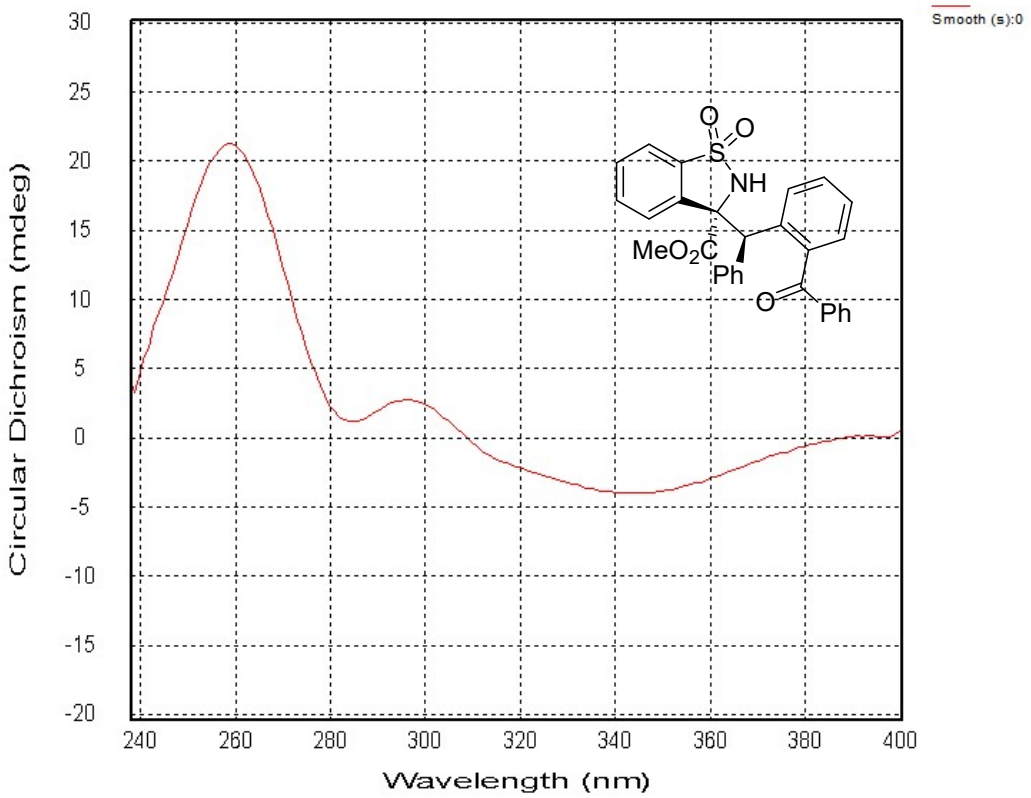
By1

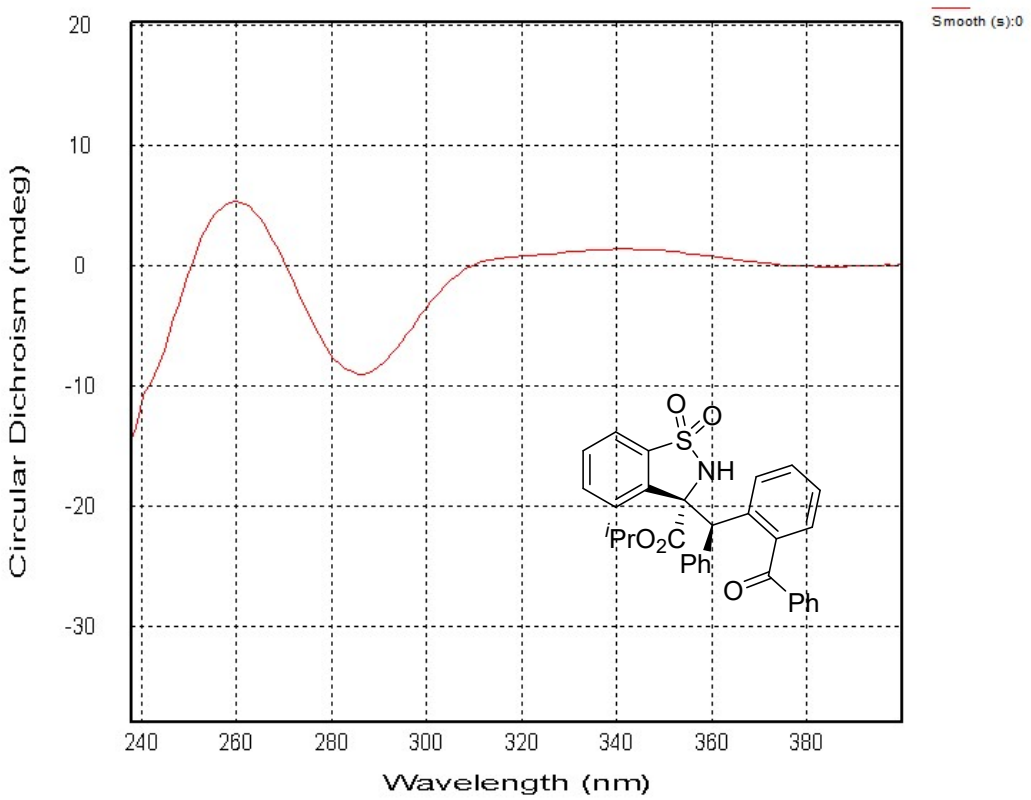

7.75 7.73 7.68 7.66 7.65 7.61 7.60 7.59 7.58 7.51 7.49
6.17
4.32 4.30 4.28 4.26
1.28 1.26 1.25
Parameter Value
1 Title yanglk-20220207-Byproduct-4.7.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 64
5 Spectrometer Frequency 400.18
6 Nucleus 1H
d.r. = 3:1
Major isomer
Minor isomer
By1
0.95 1.18 1.11 0.98
0.33 1.00
1.90 2.36 2.23 1.96
2.00
3.92
6.33
f1 (ppm)


166.8
136.4 132.7 131.7 131.6 127.3 121.5
73.7
64.4
13.7
Parameter Value
1 Title yanglk-20220207-Byproduct-4.8.1.1r
2 Solvent CDCl3
3 Temperature 0.0
4 Number of Scans 512
5 Spectrometer Frequency 100.63
6 Nucleus 13C
By1
f1 (ppm)

10 CD spectra of the products



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Wavelength (nm)
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S
NH
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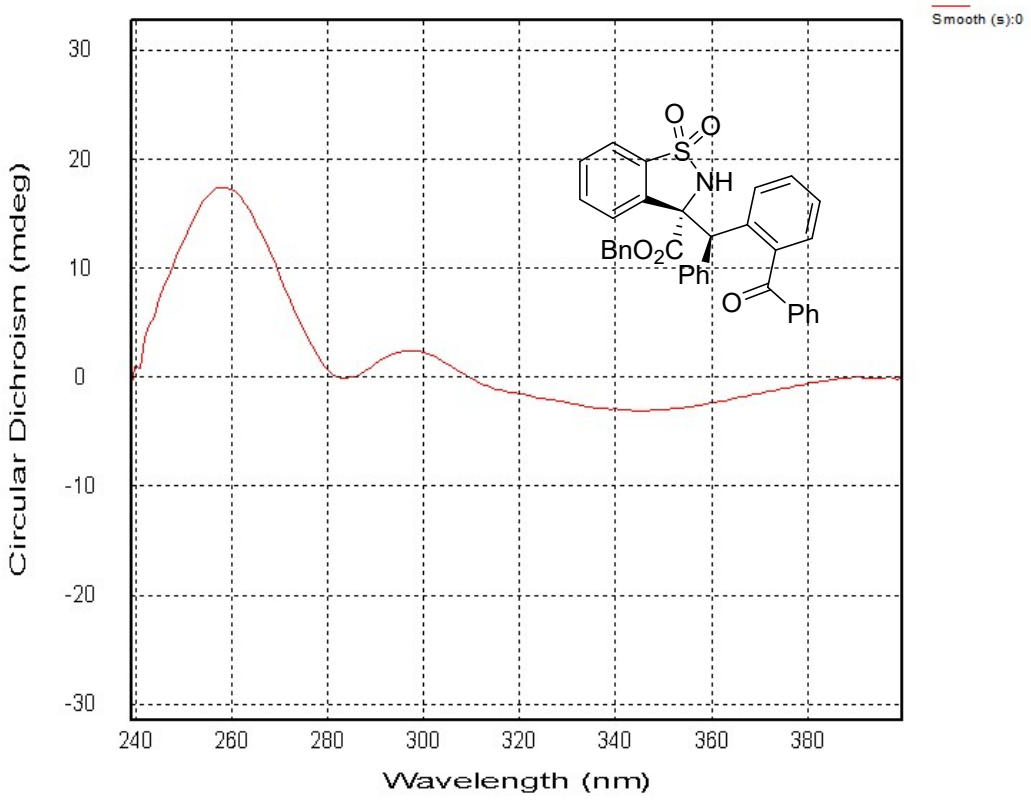
Ph
O
Ph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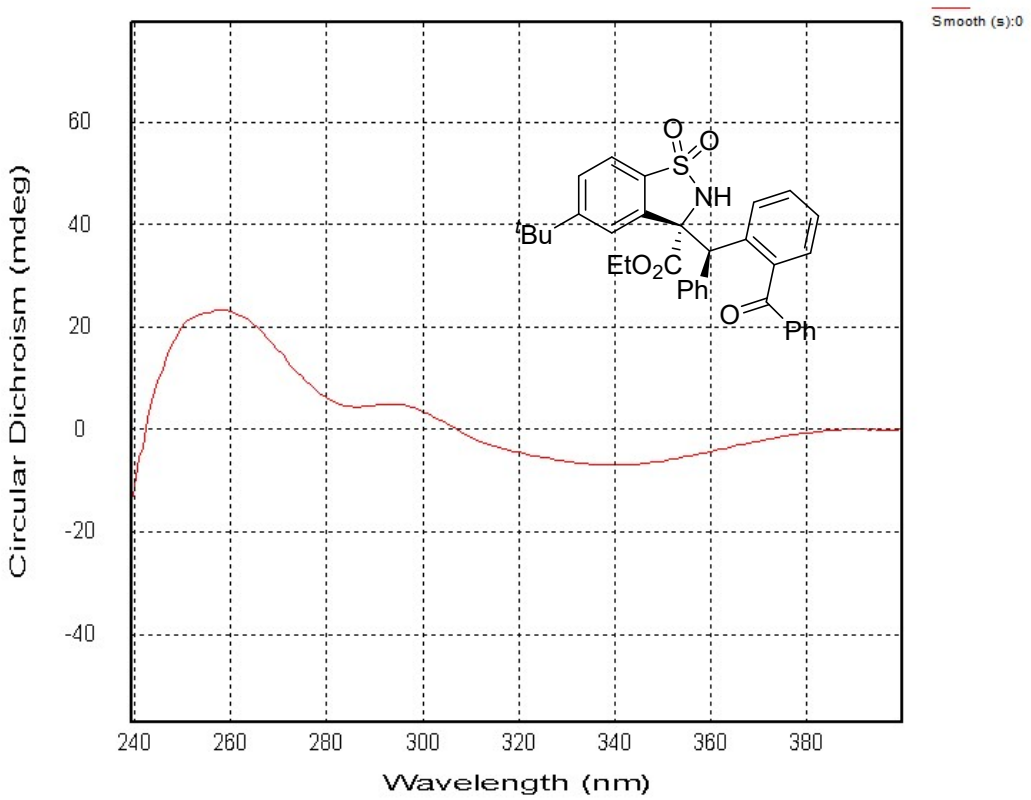
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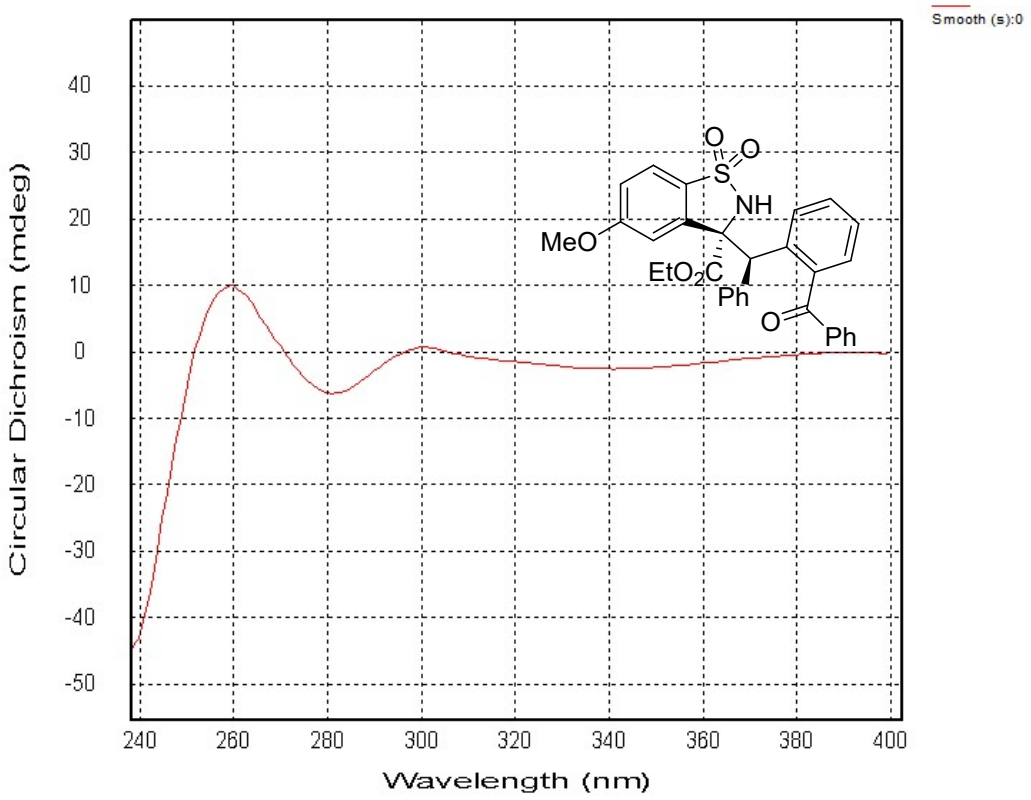
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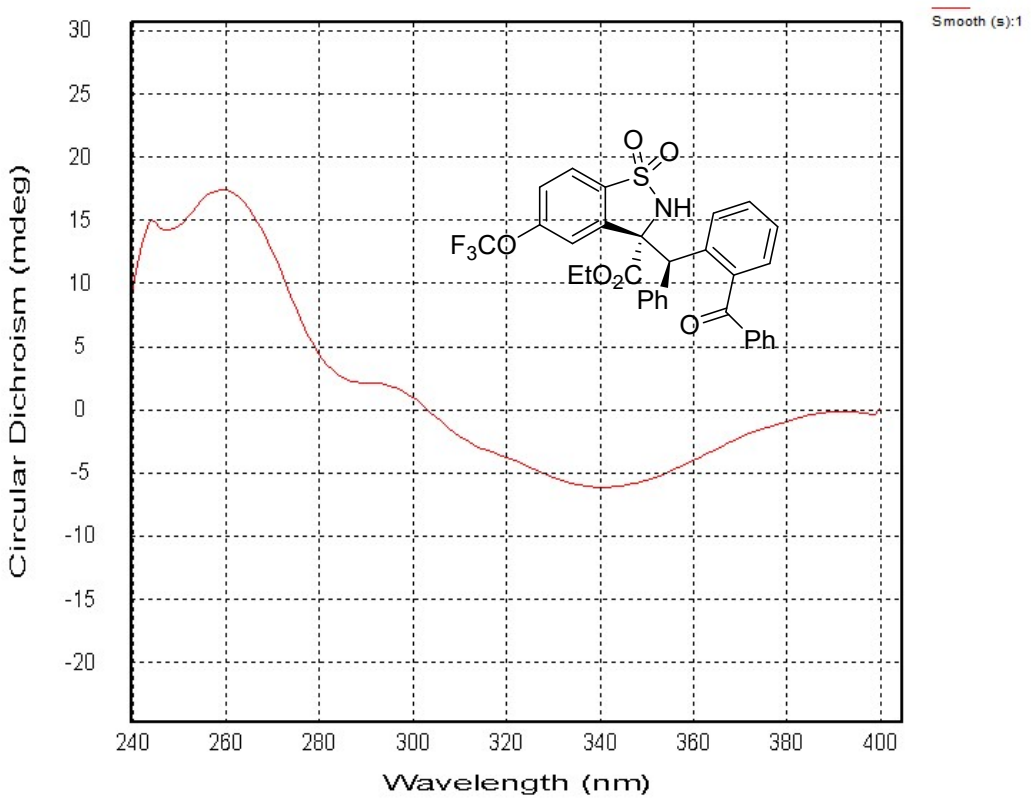
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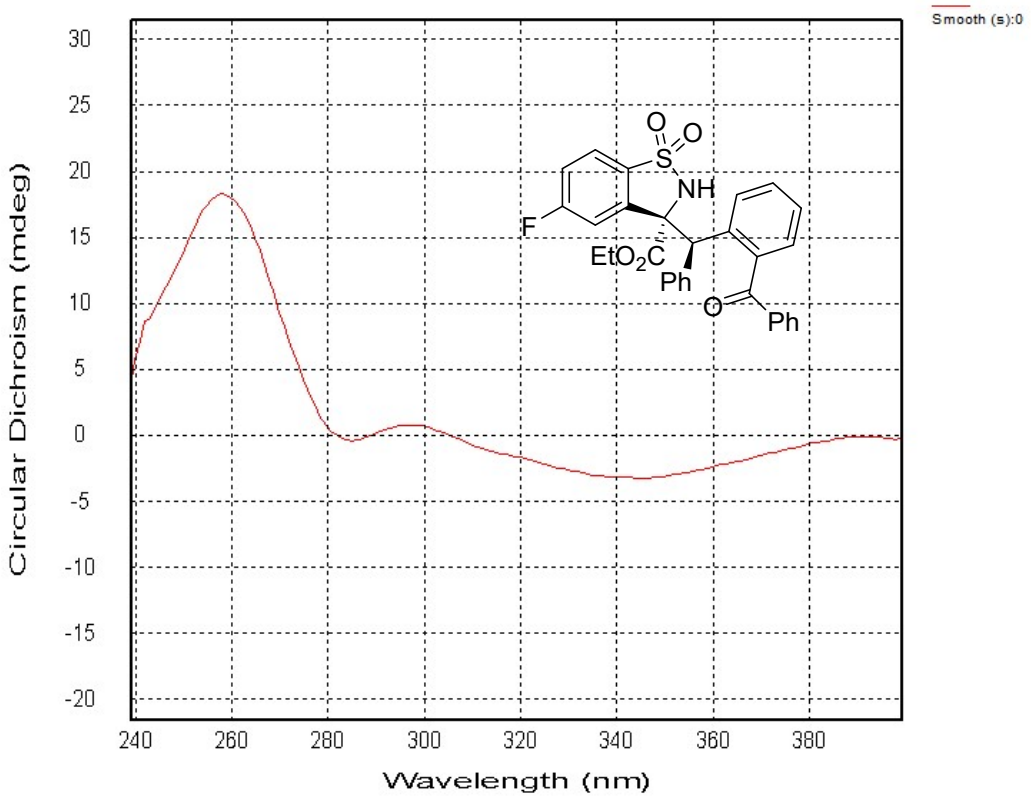
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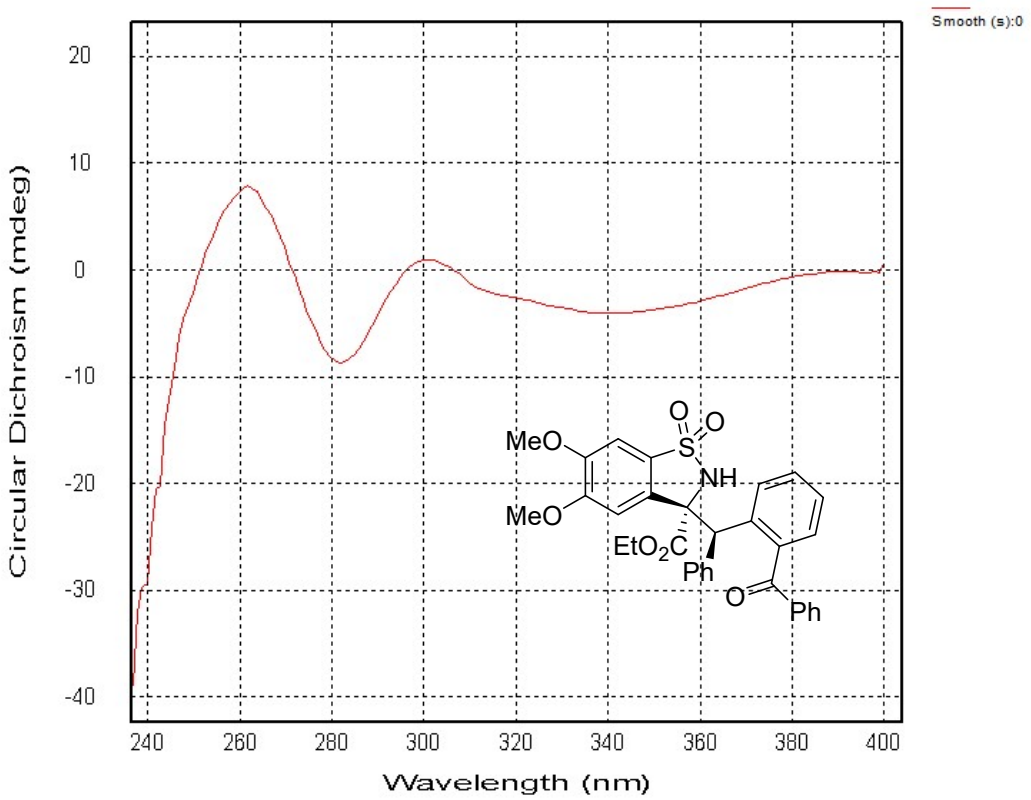
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MeO
O
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S
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Ph
O
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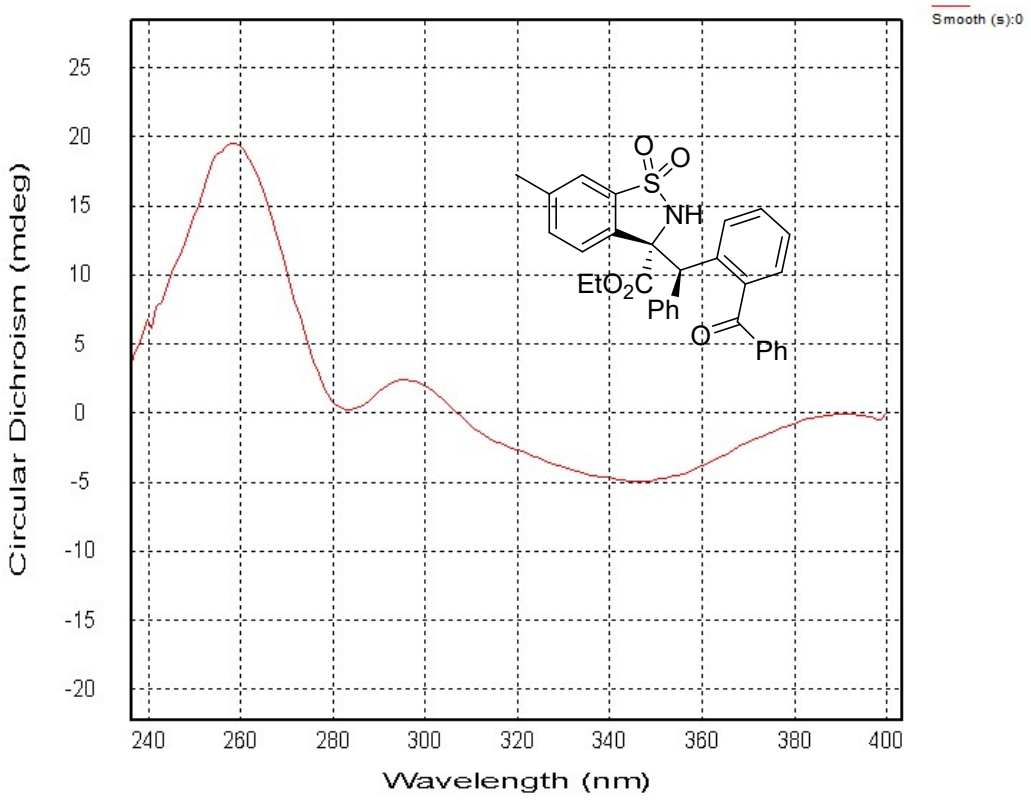
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S
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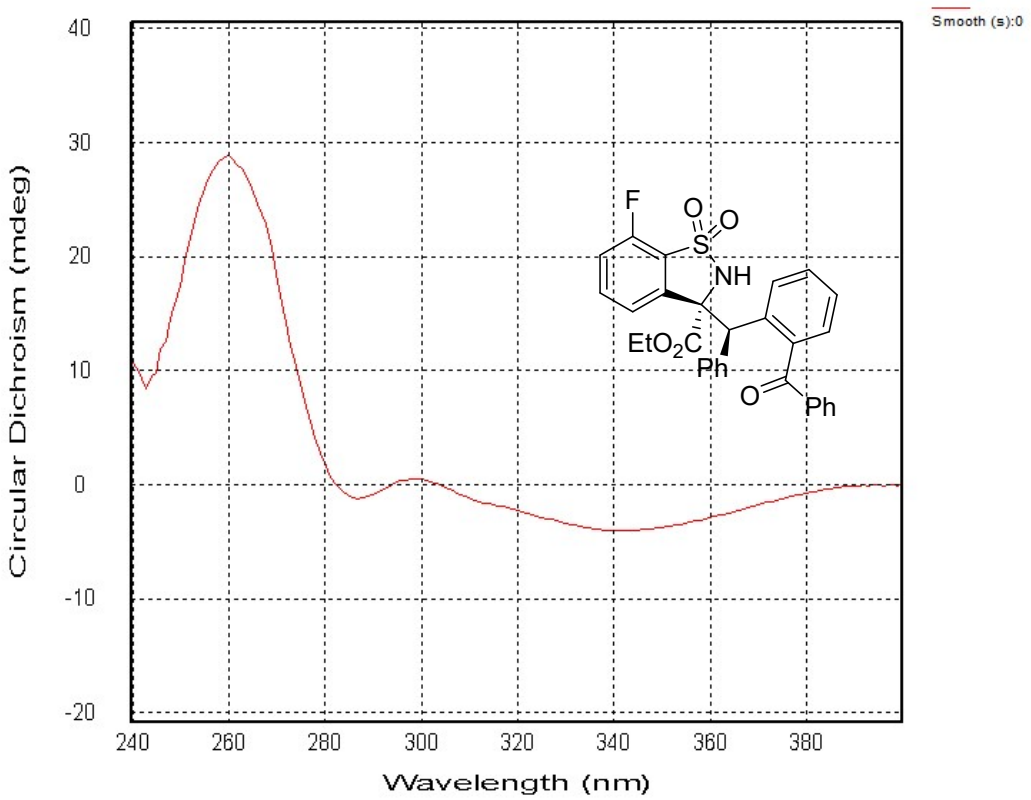
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Wavelength (nm)
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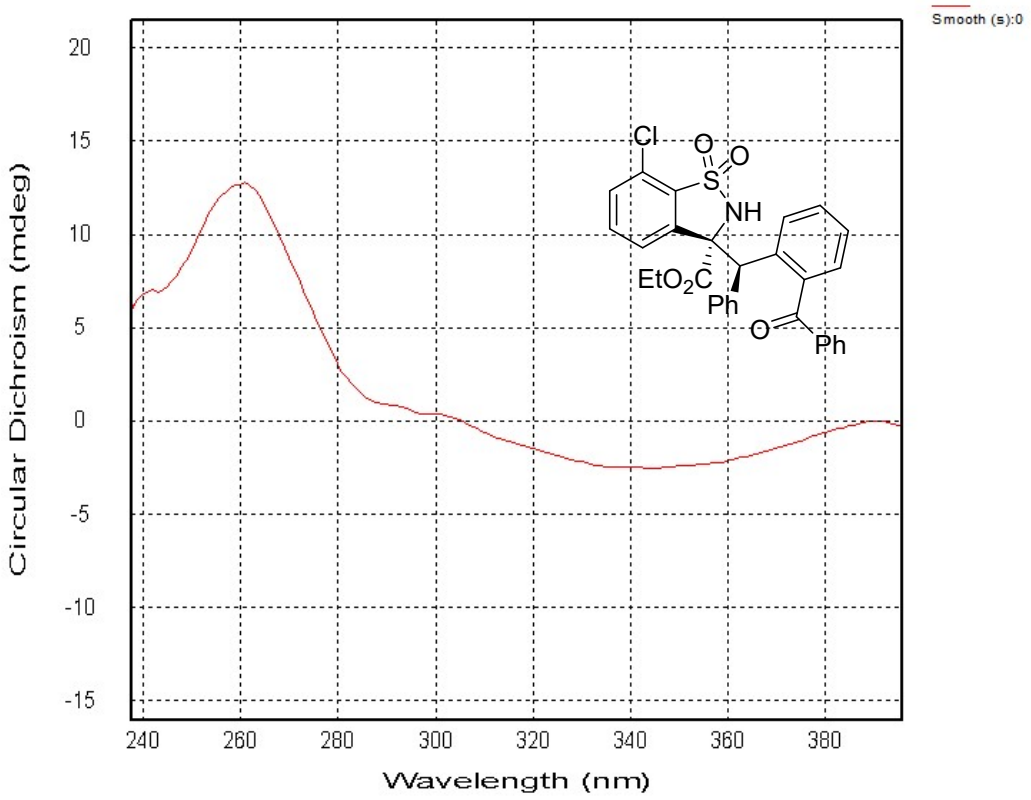
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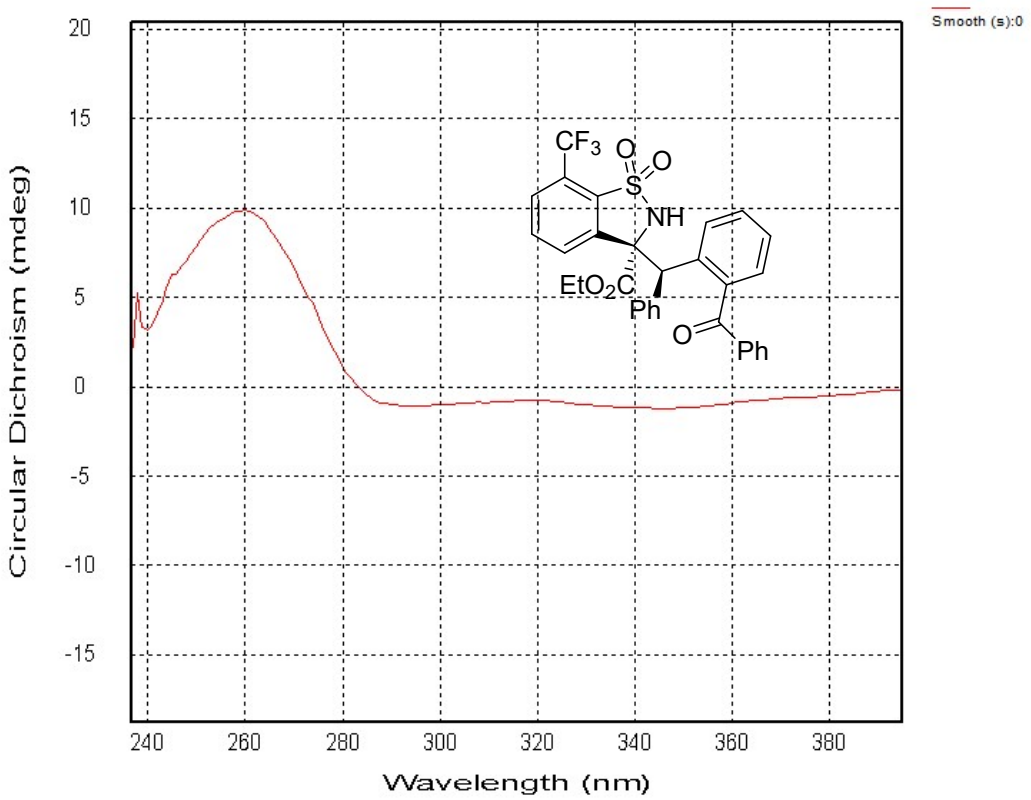
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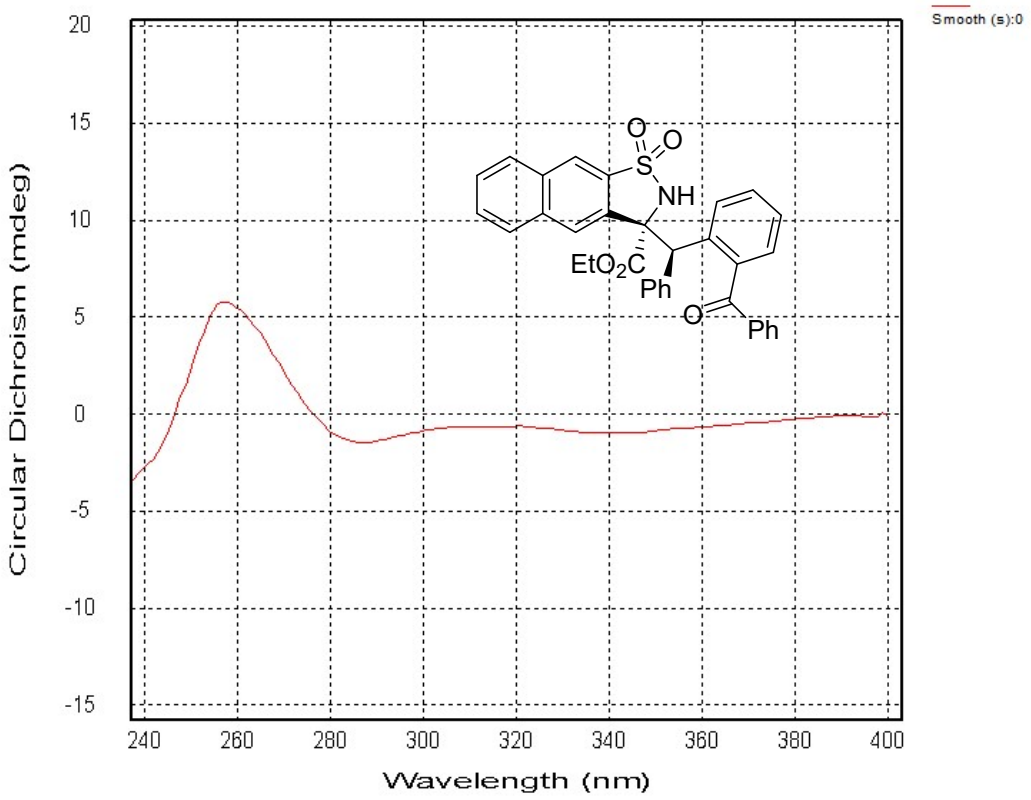
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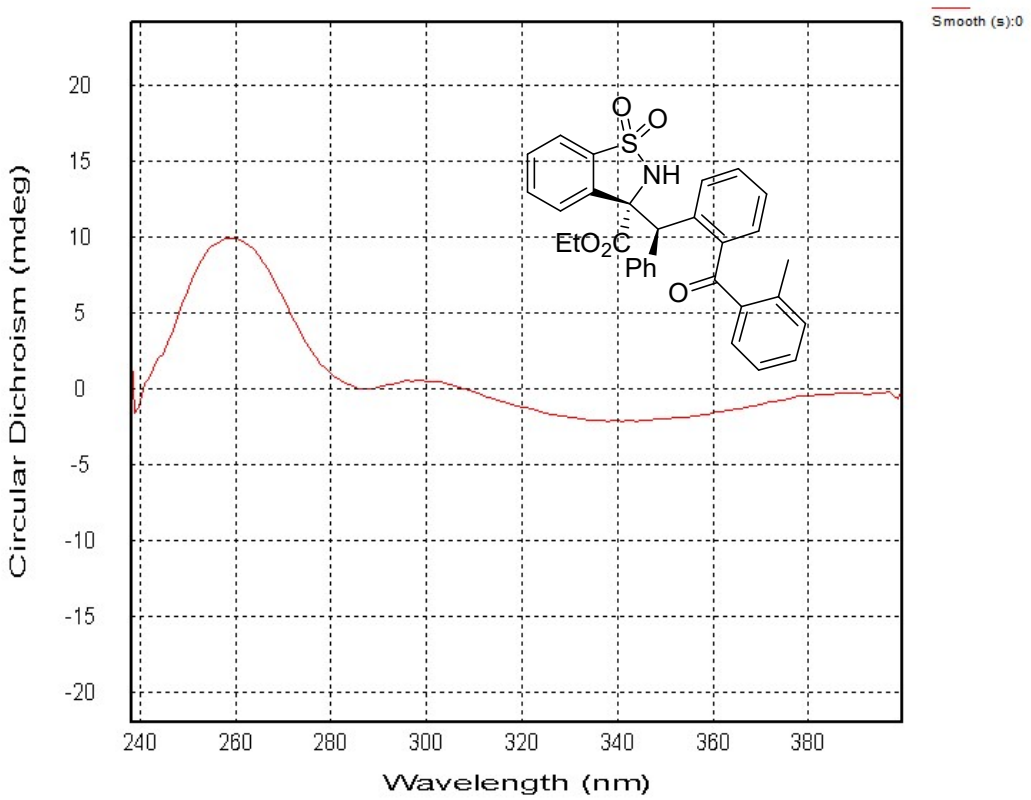
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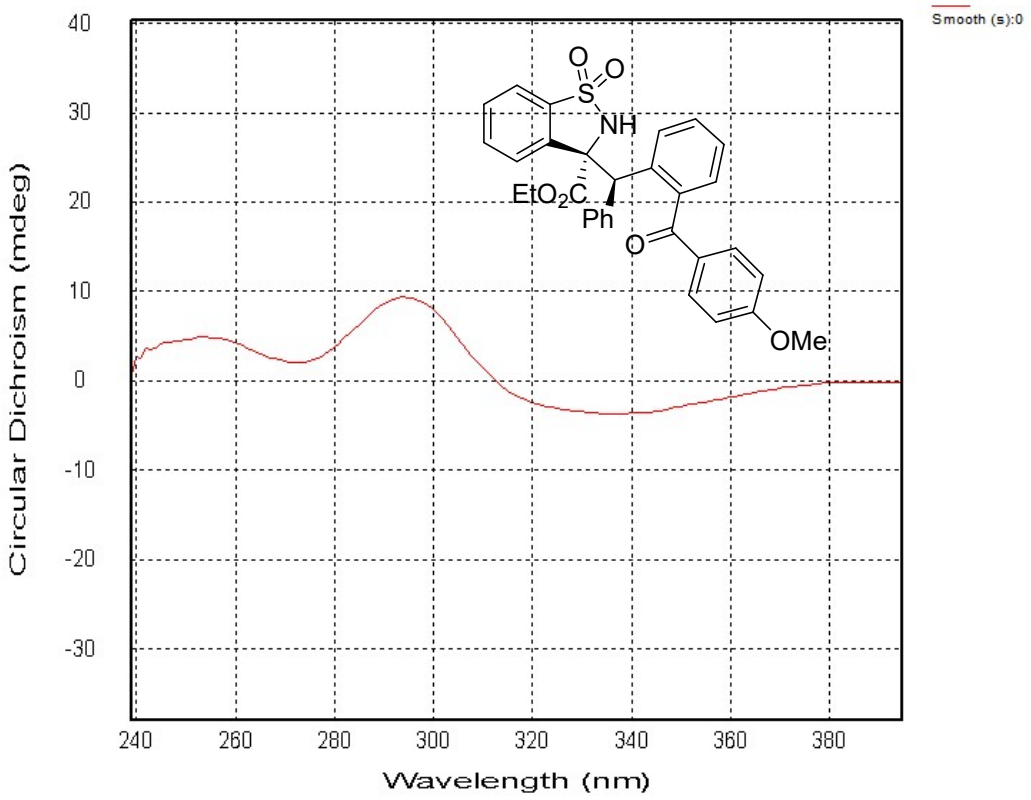
EtO2C
Ph
O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Ph
O
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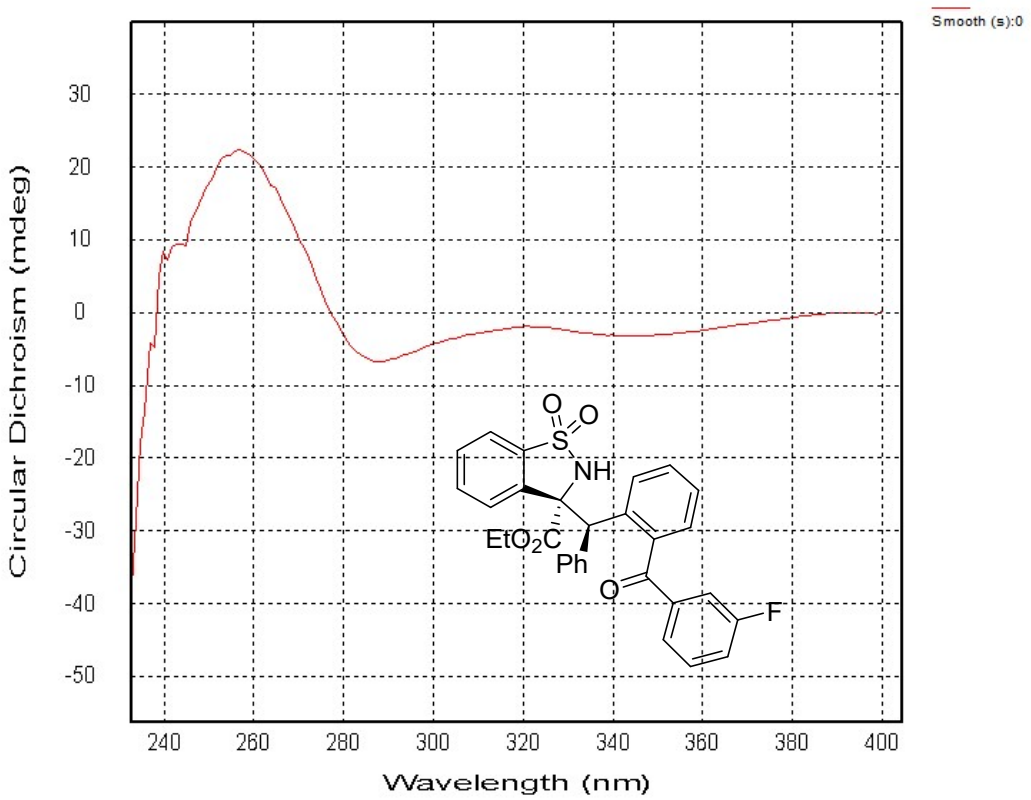
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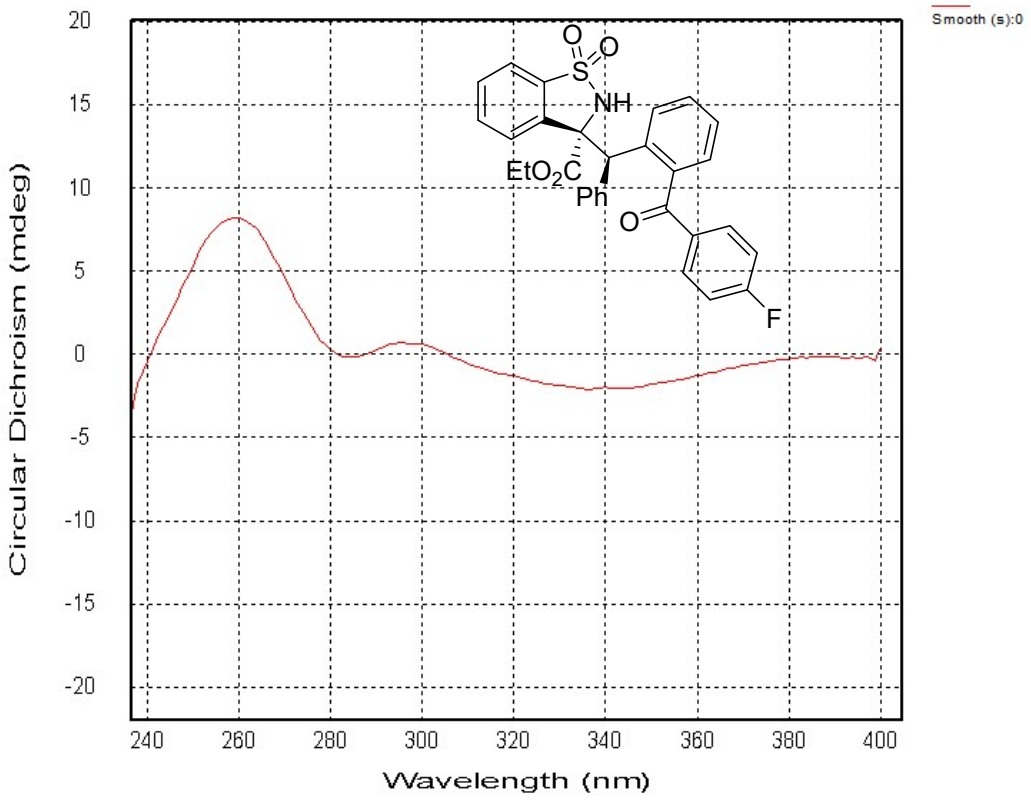
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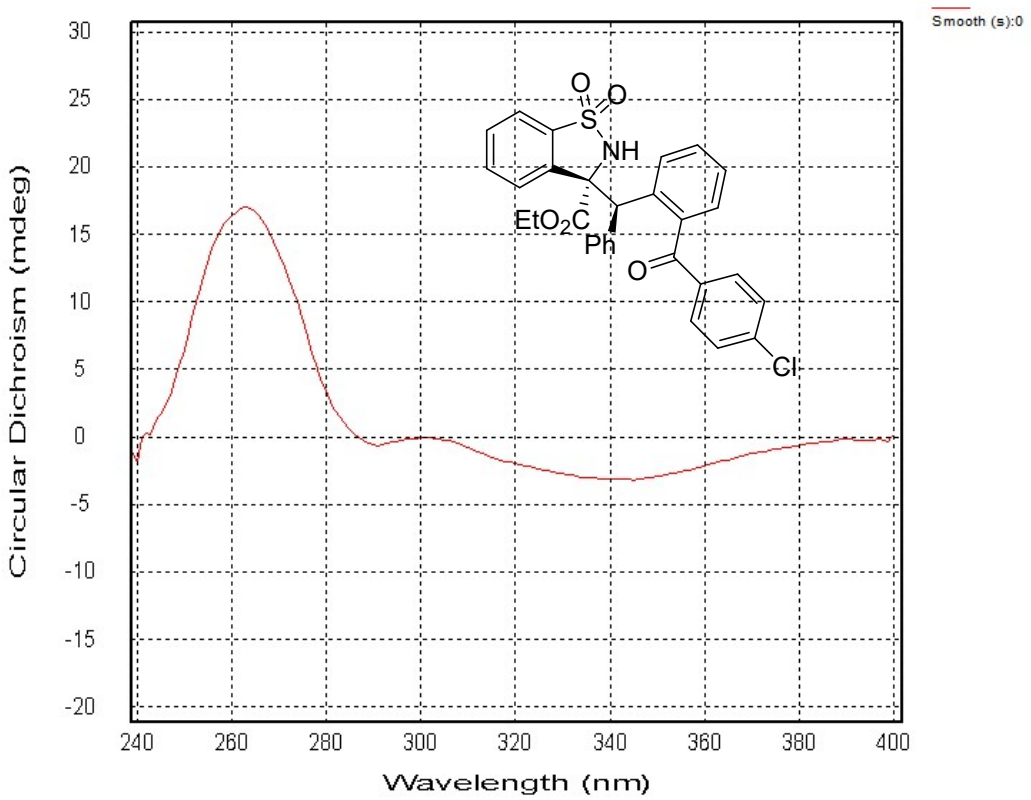
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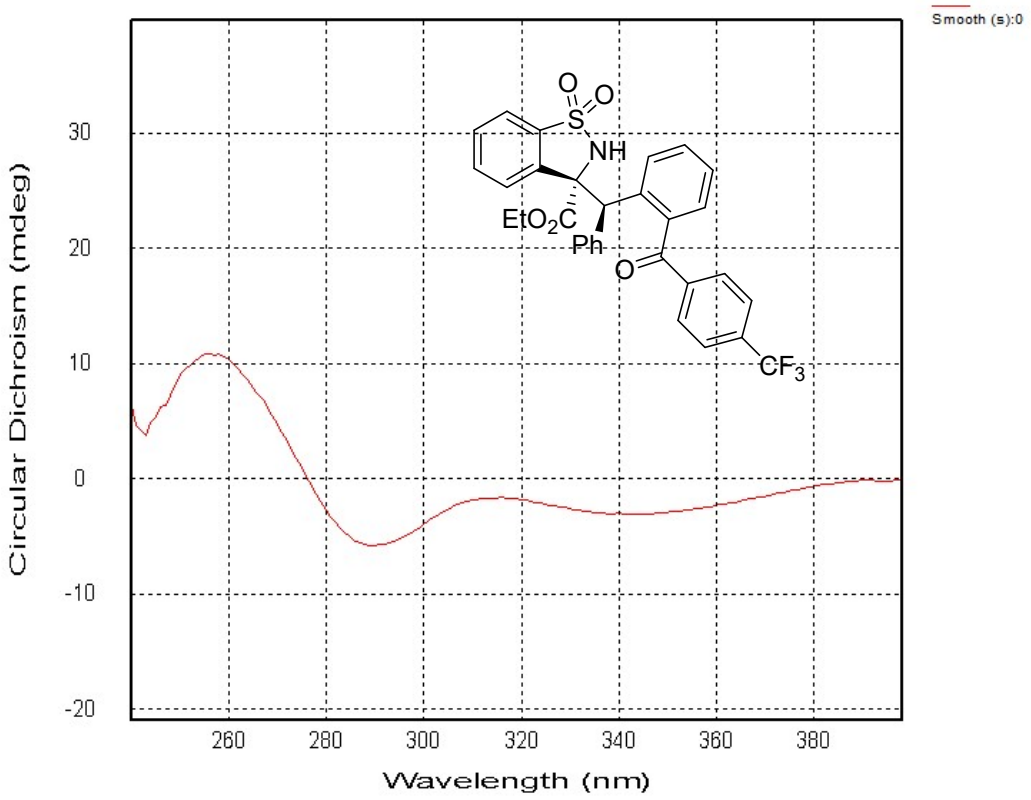
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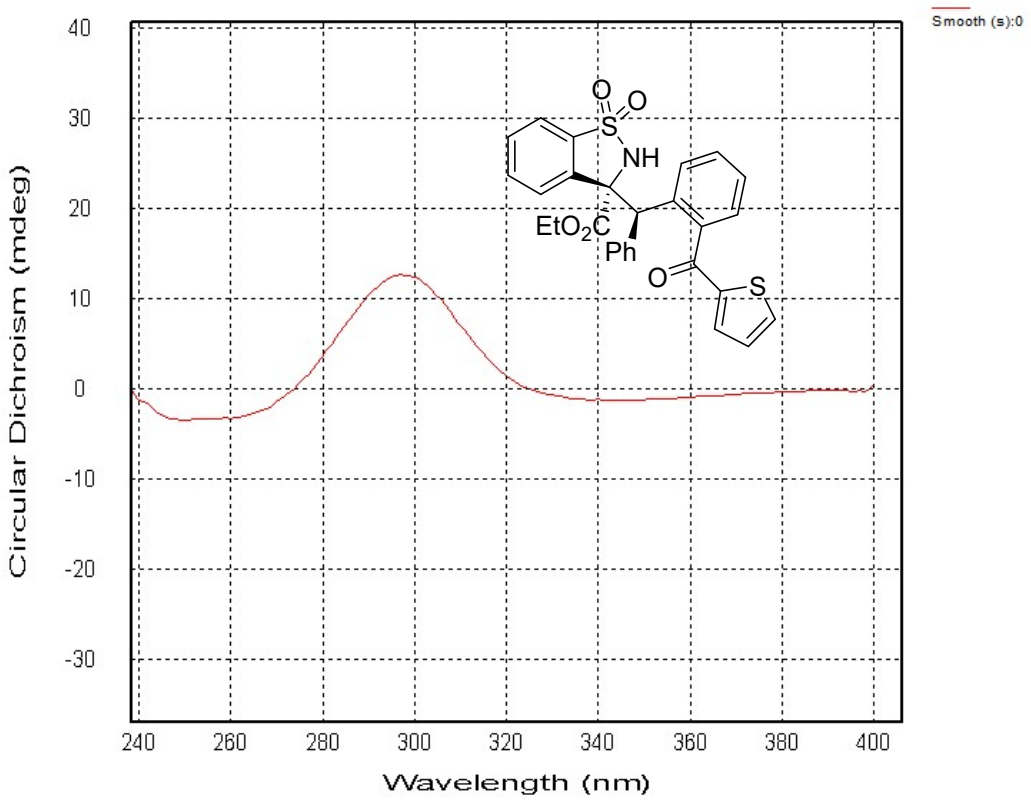
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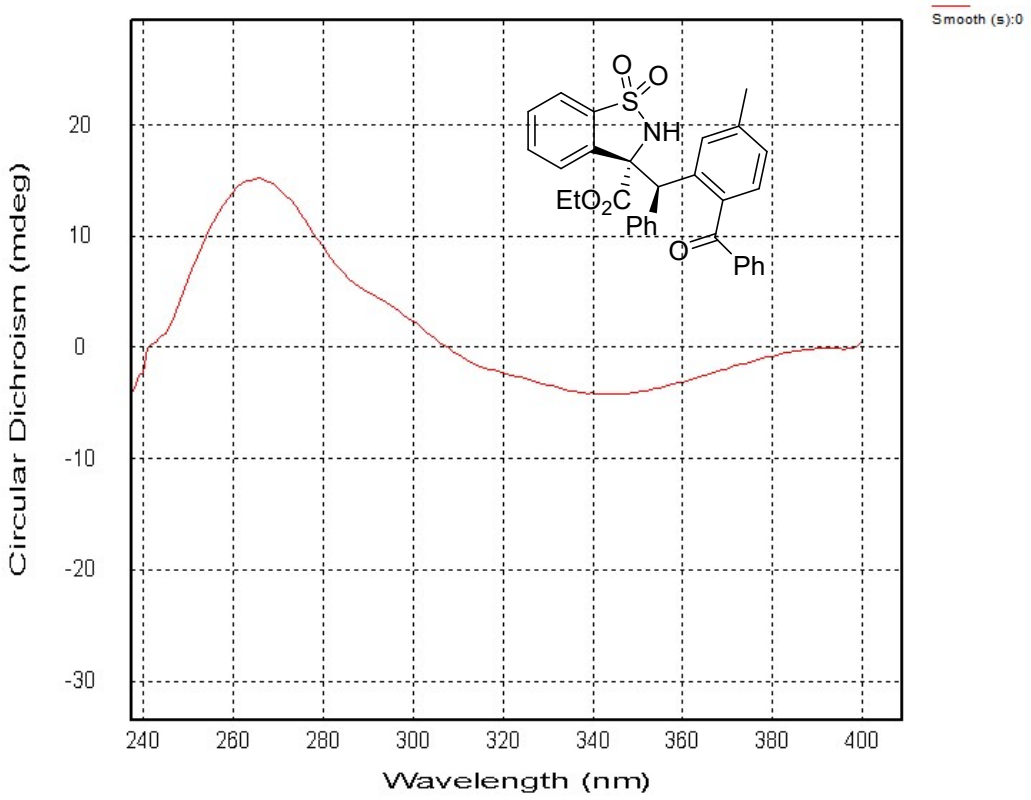
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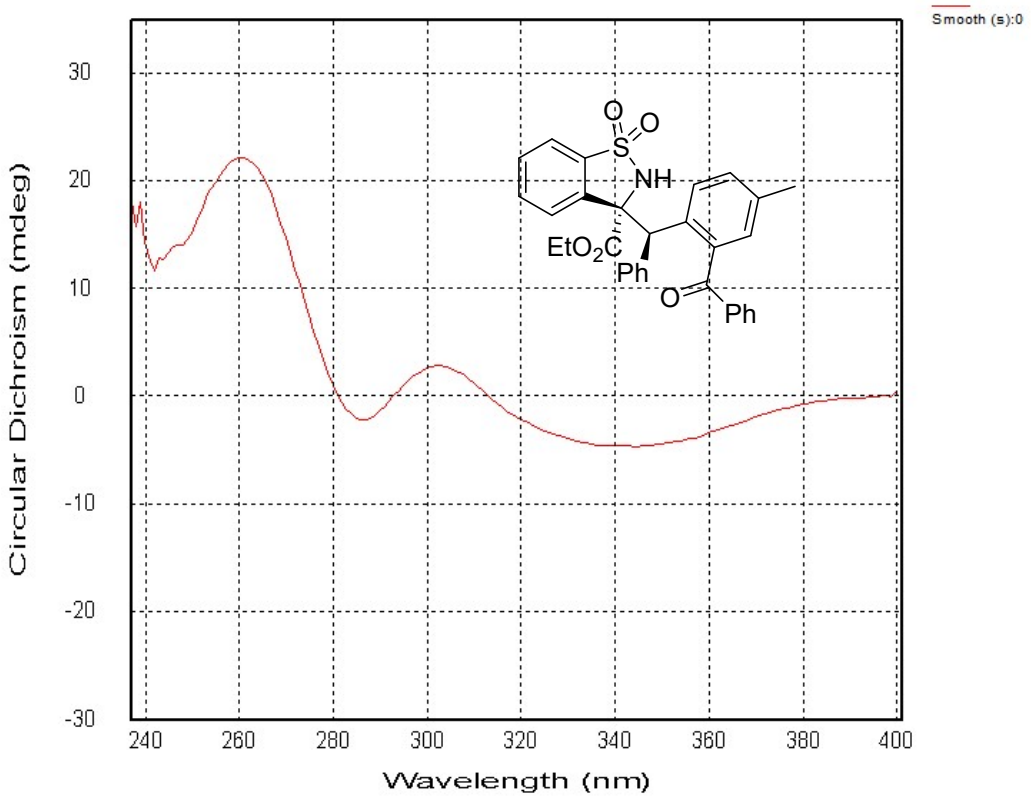
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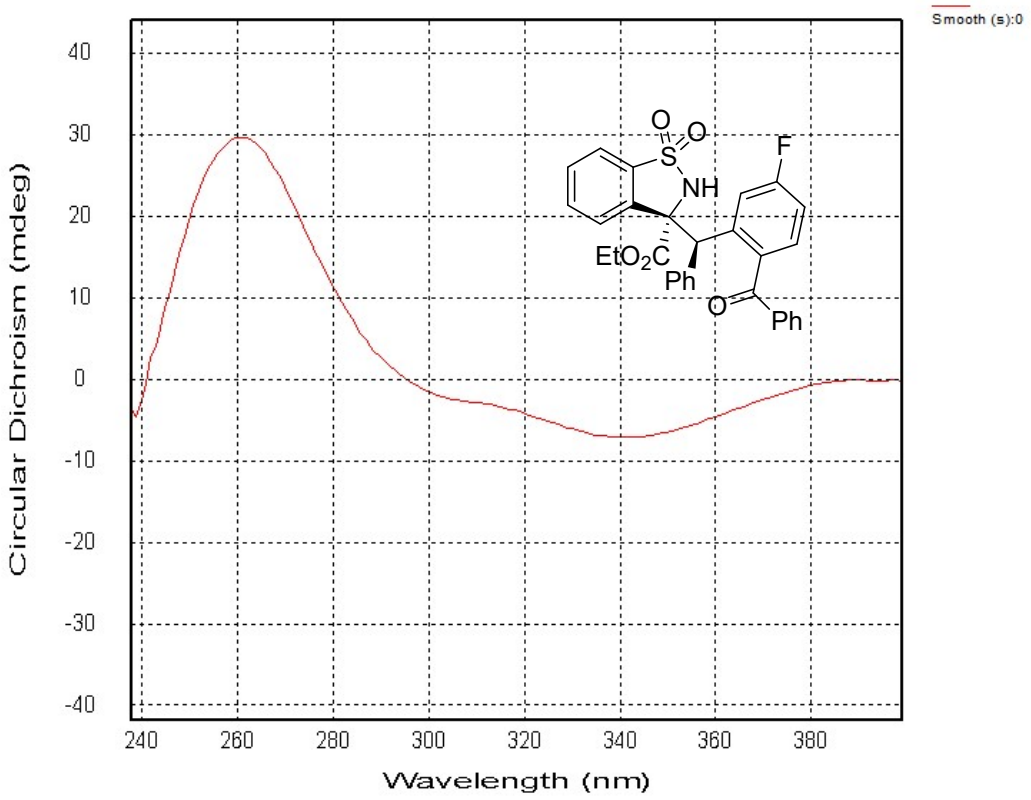
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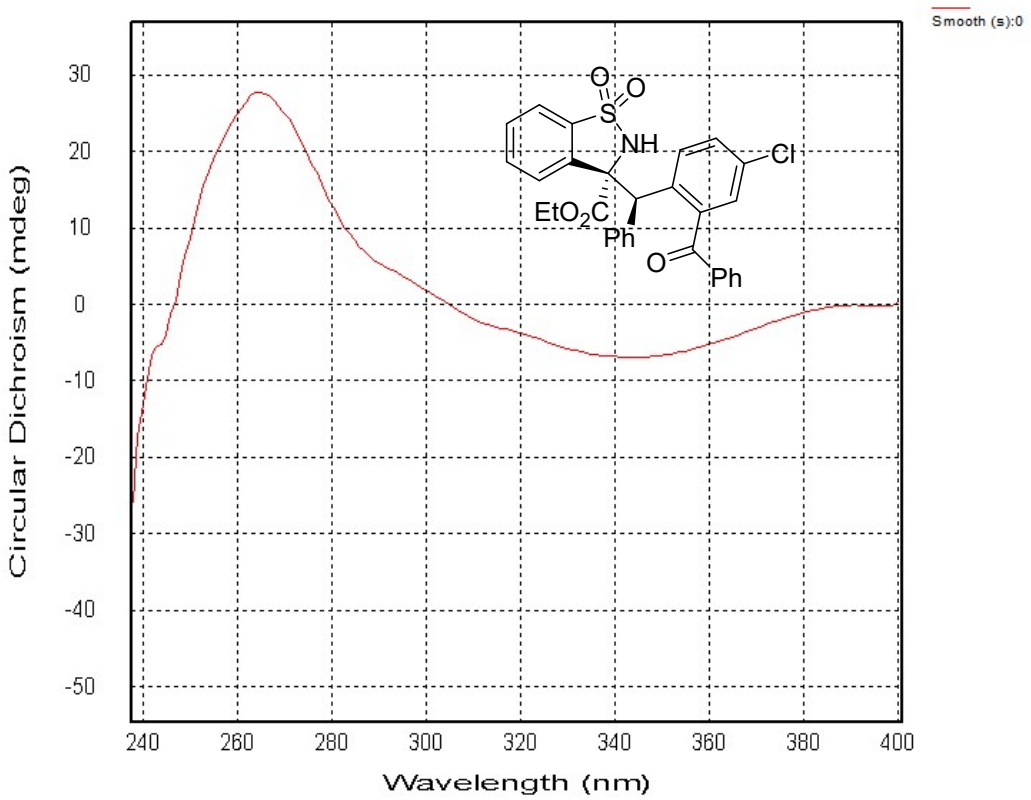
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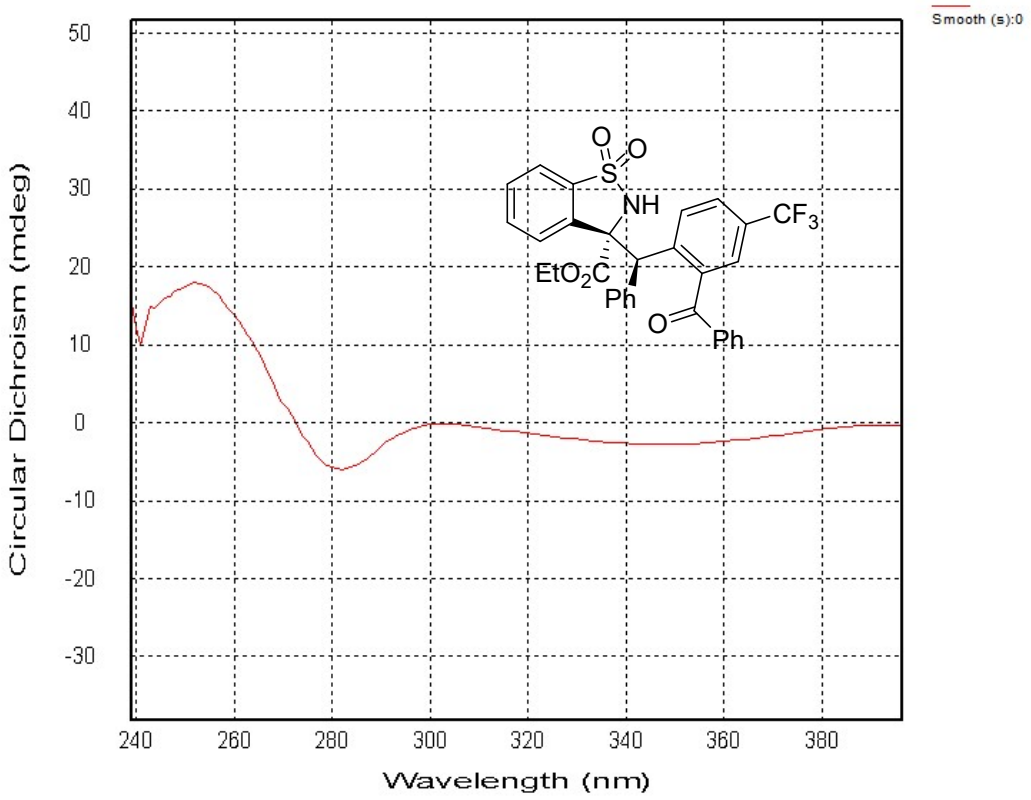
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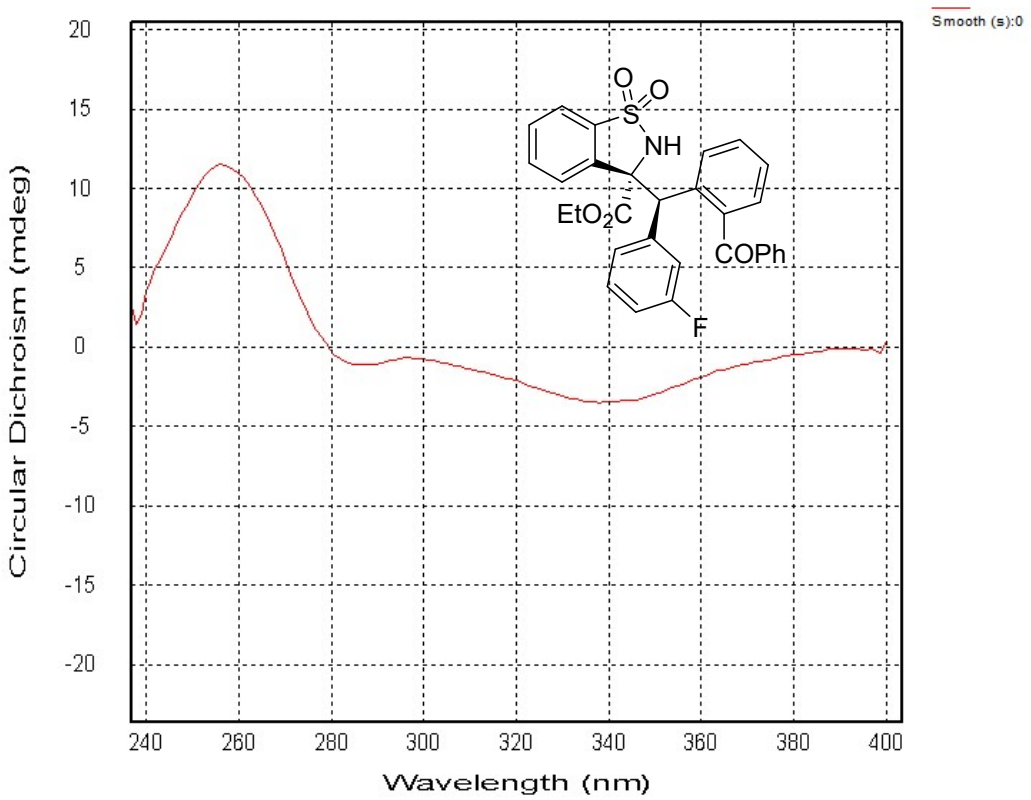
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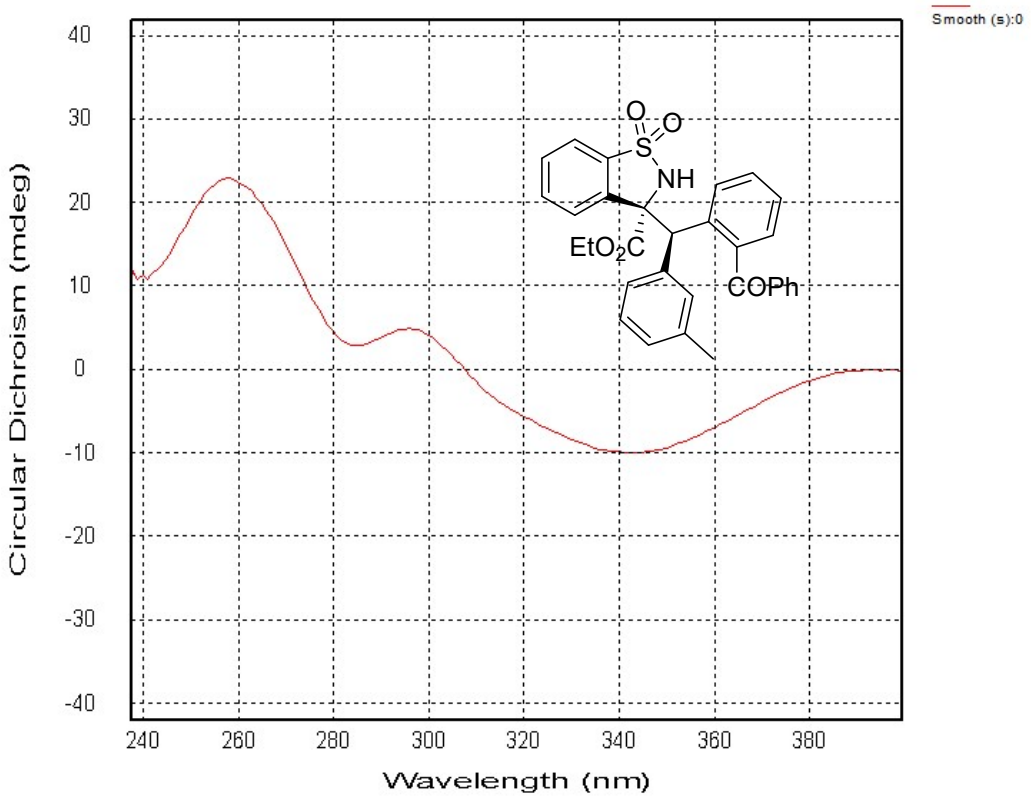
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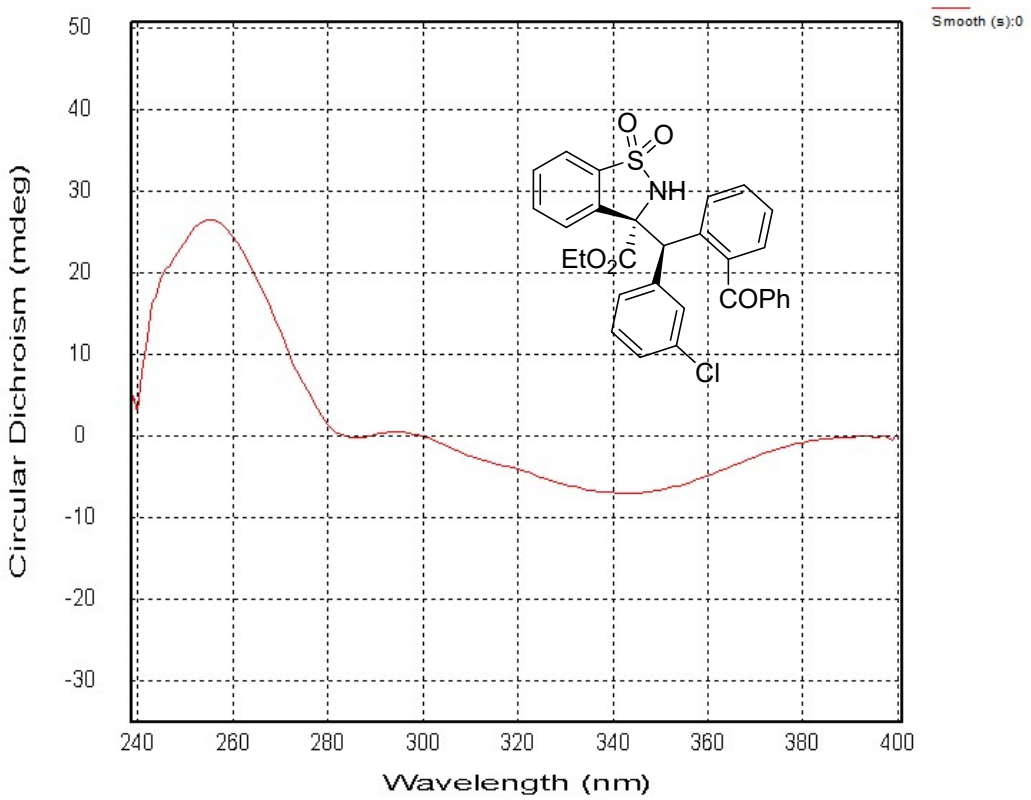
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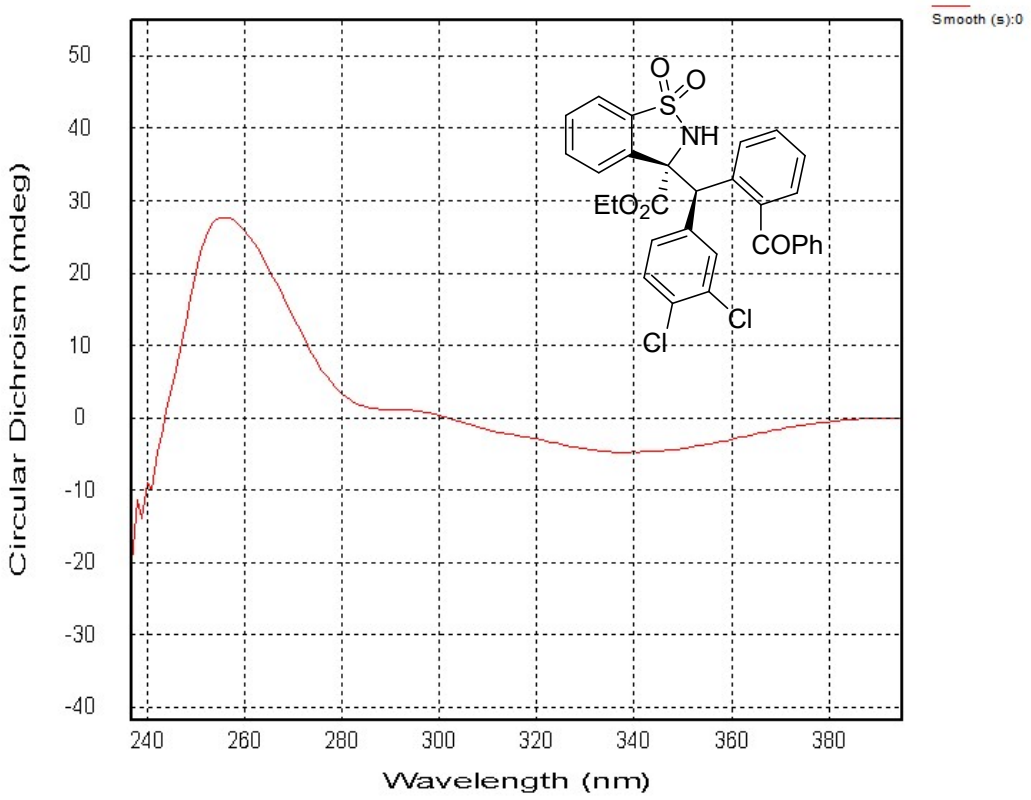
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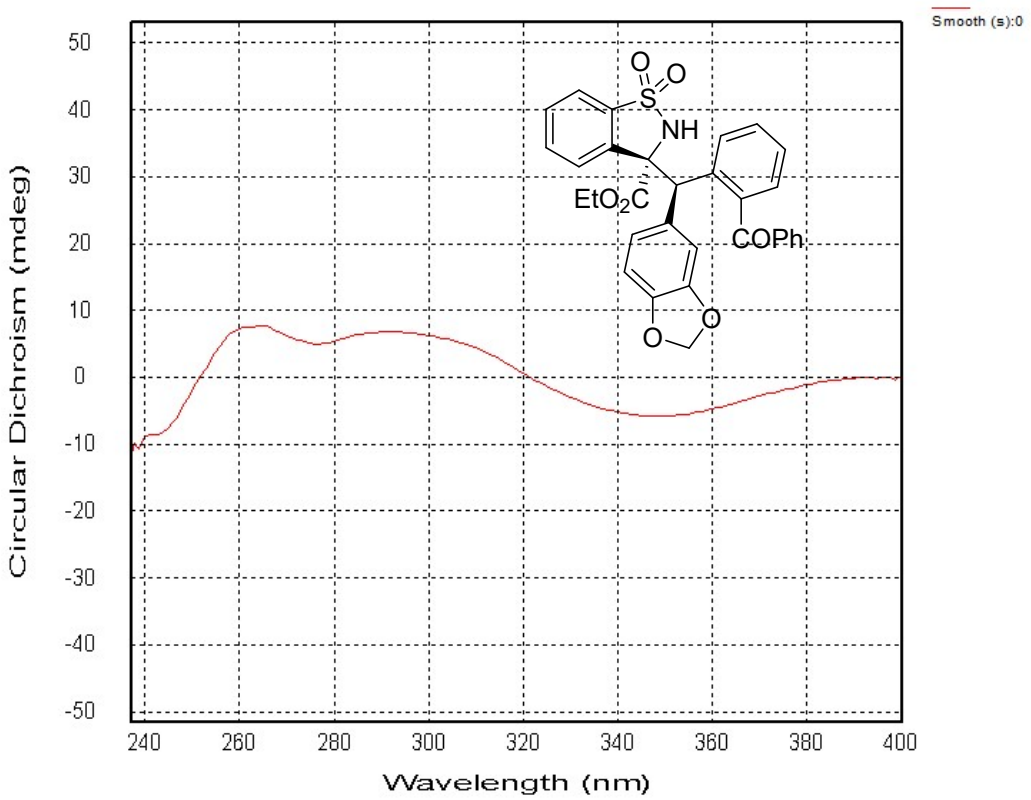
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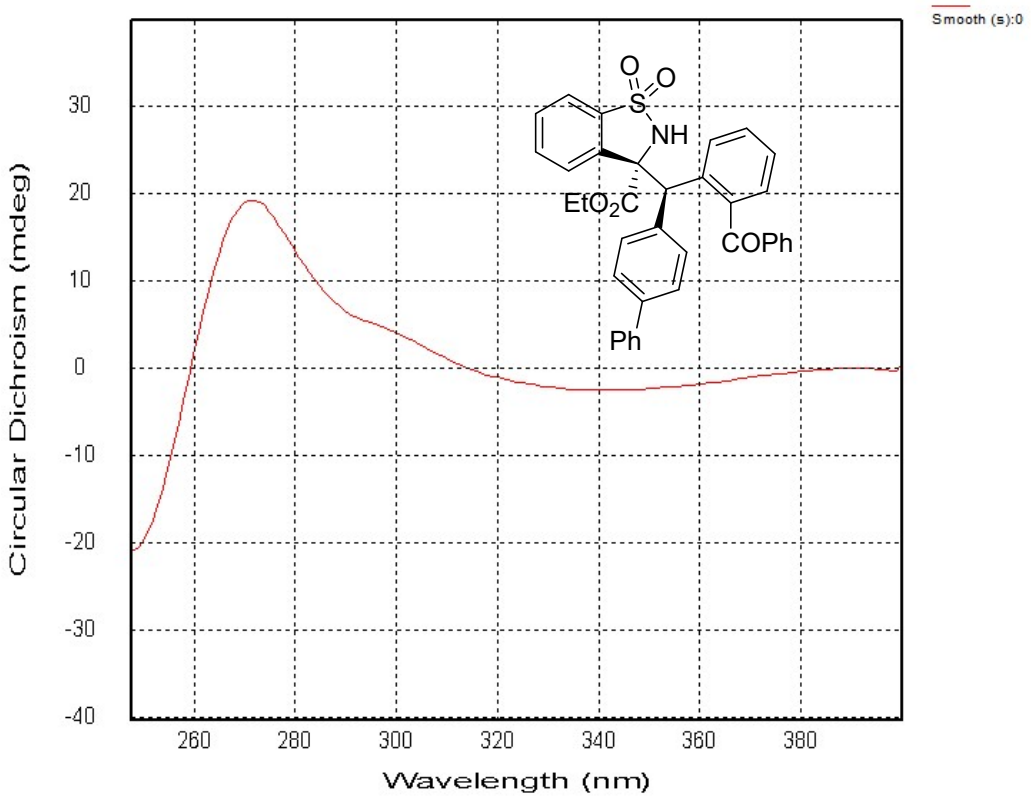
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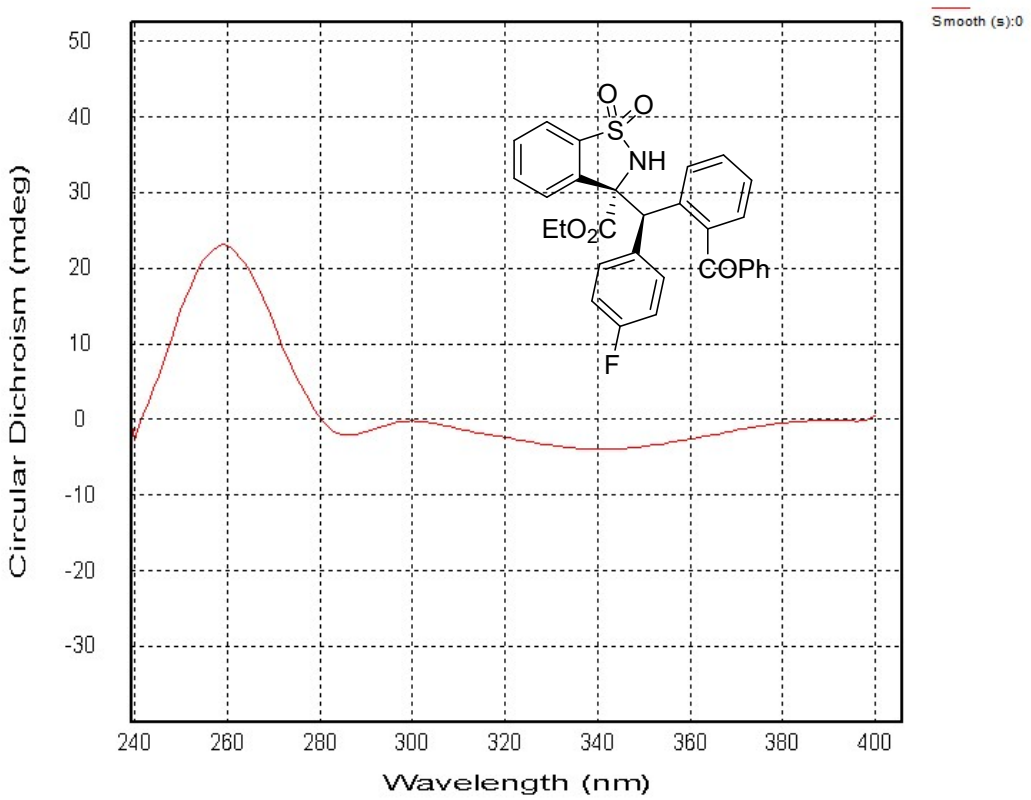
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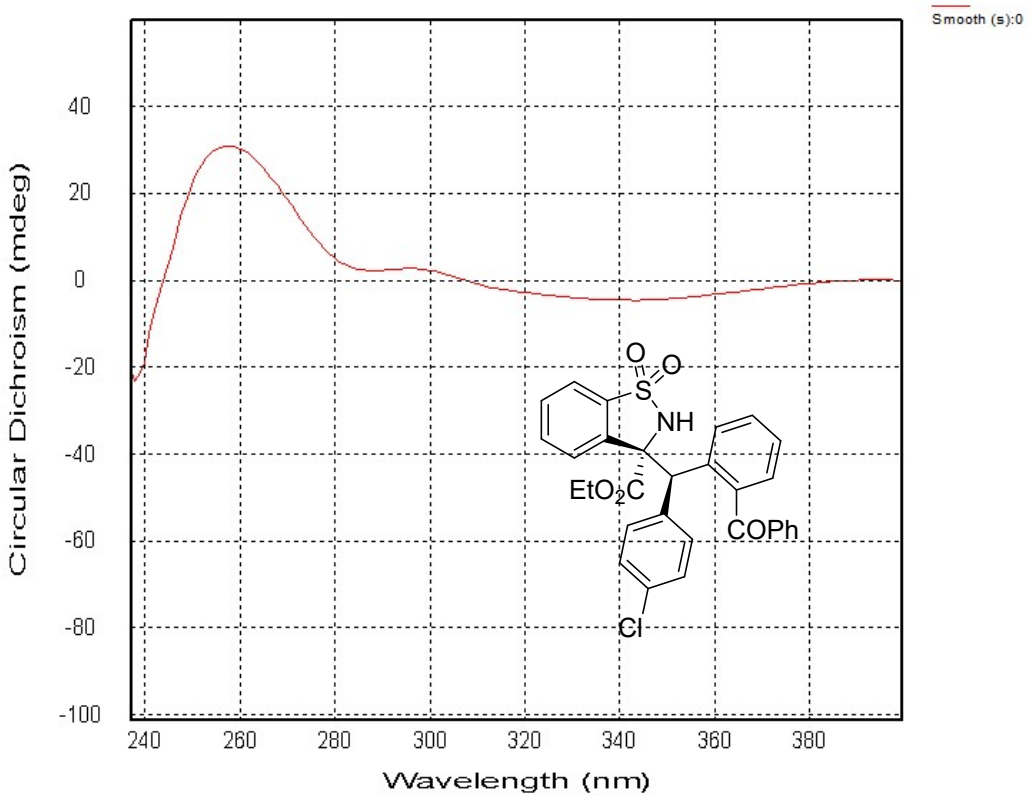
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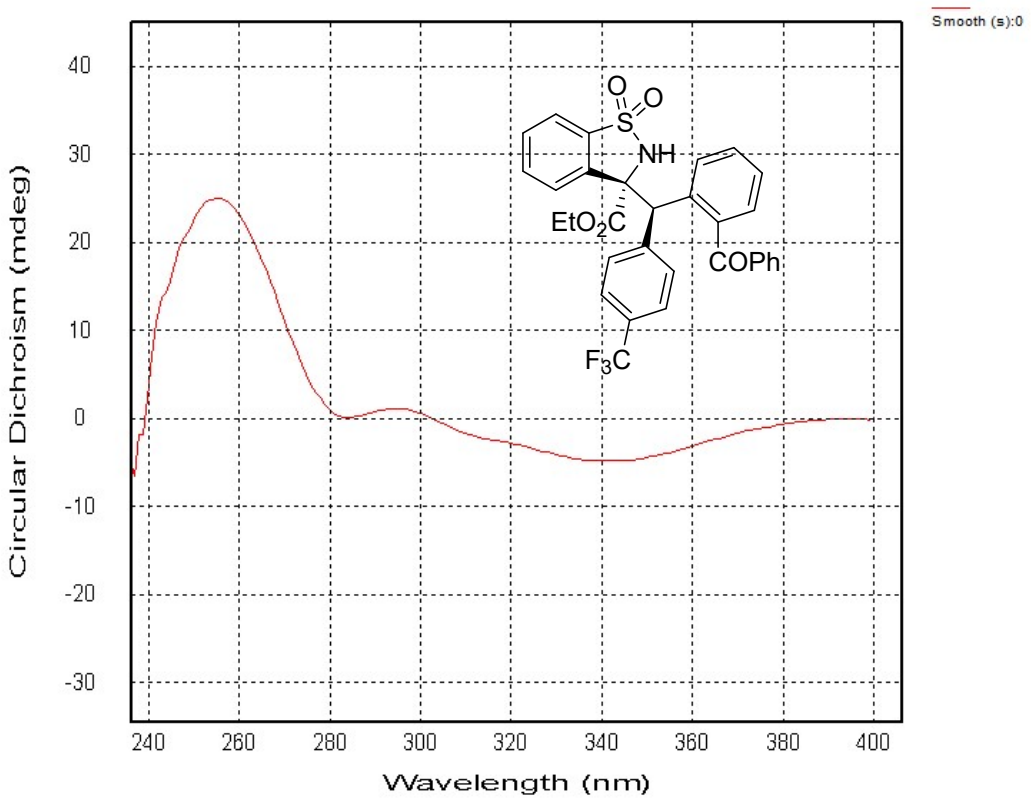
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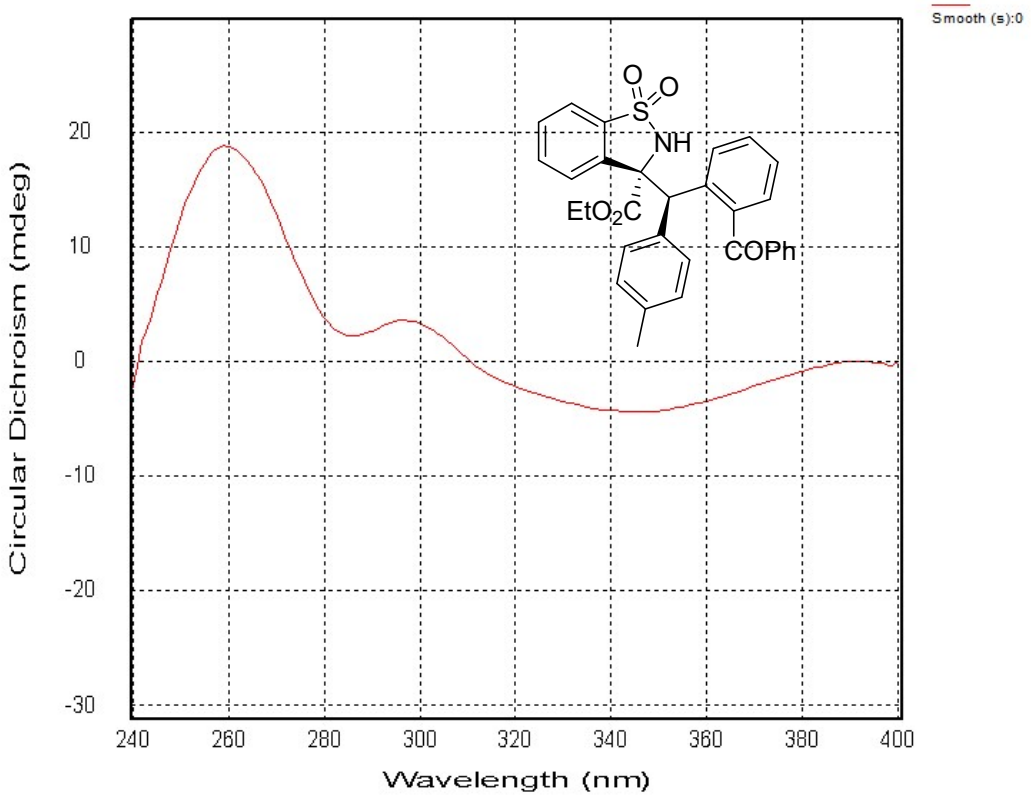
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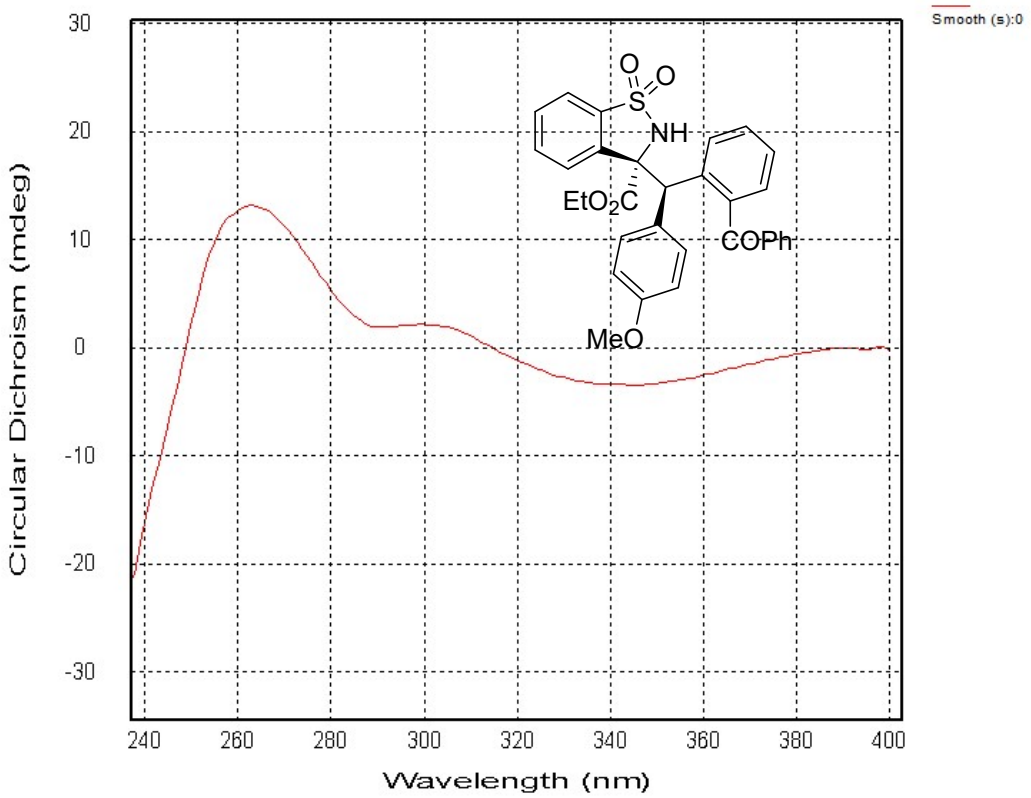
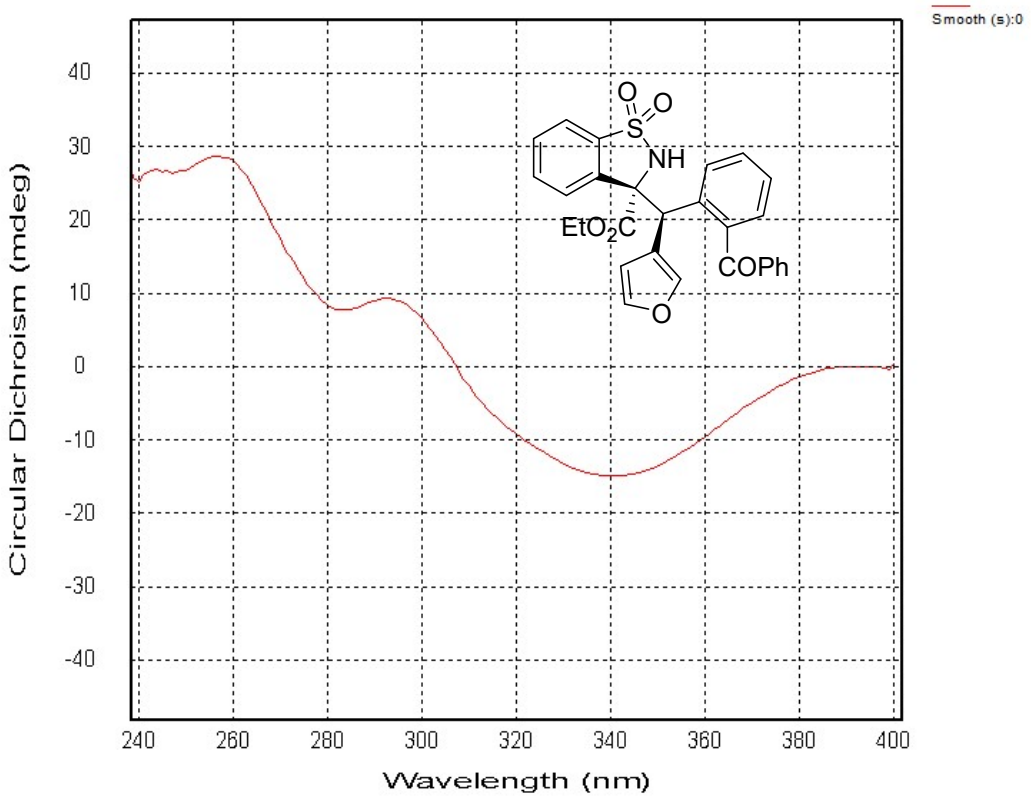
400
Wavelength (nm)
O
O
S
NH
EtO2C
COPh


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
240
260
280
300
320
340
360
380
400
Wavelength (nm)
O
O
S
NH
EtO2C
COPh
MeO


Smooth (s):0
Circular Dichroism (mdeg)
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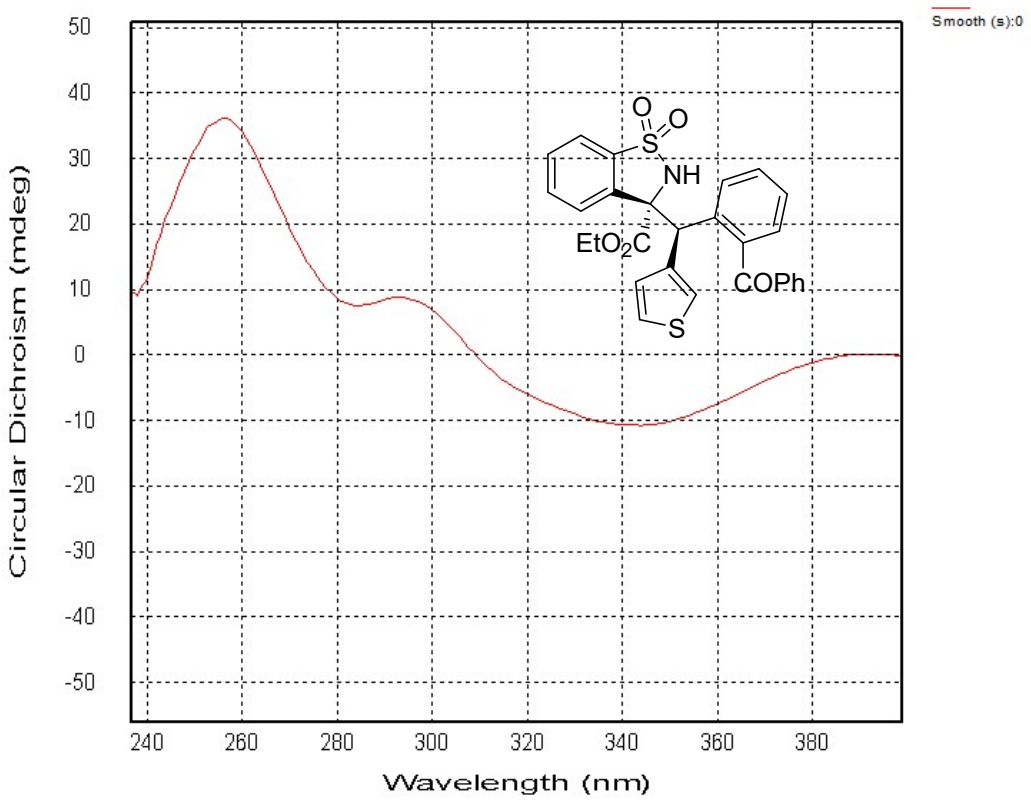
30
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
360
380
400
Wavelength (nm)
O
O
S
NH
EtO2C
COPh
O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Circular Dichroism (mdeg)
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30
20
10
0
-10
-20
-30
-40
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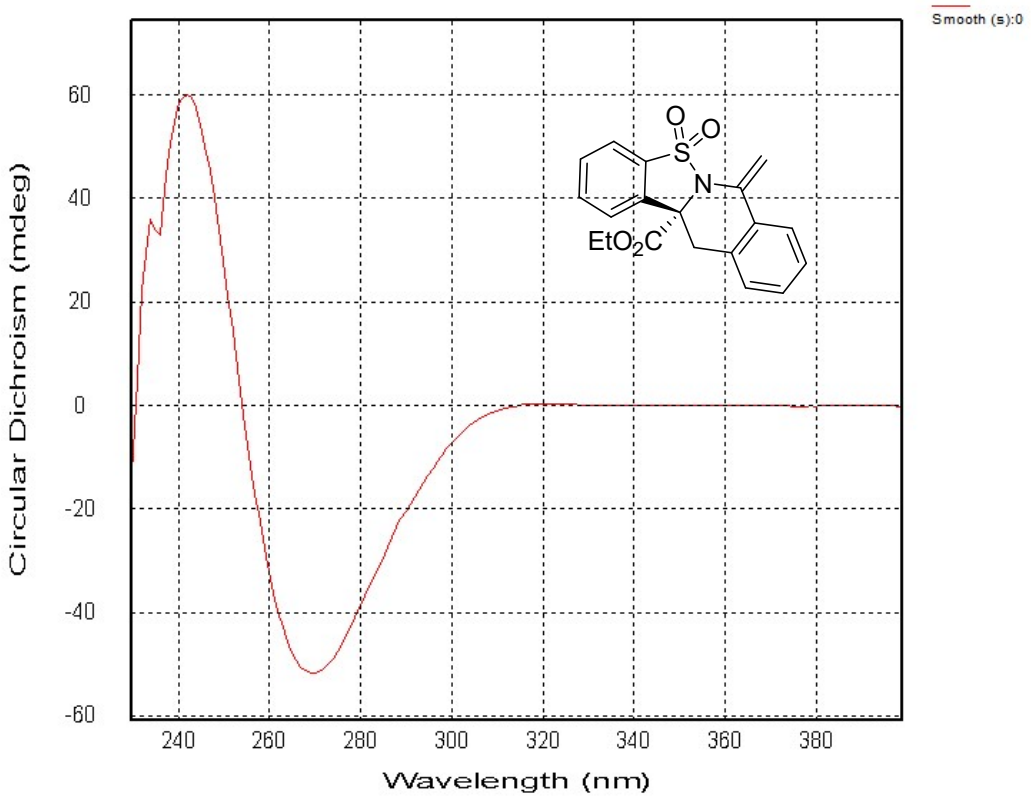
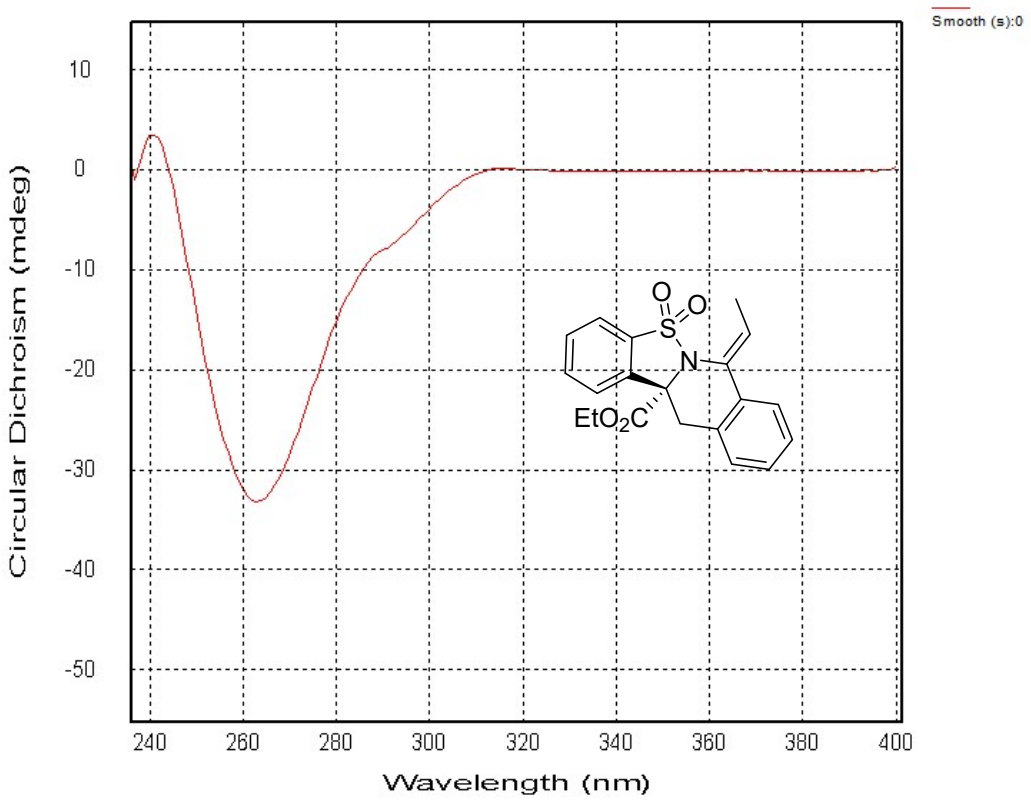
240
260
280
300
320
340
360
380
Wavelength (nm)
O
O
S
NH
EtO2C
COPh
S


Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
240
260
280
300
320
340
360
380
Wavelength (nm)
O
O
S
N
EtO2C


Smooth (s):0
Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
240
260
280
300
320
340
360
380
400
Wavelength (nm)
O
O
S
N
EtO2C