Diastereoselective Mannich-Type Reaction of α-Fluorinated Carboxylate Esters: Synthesis of β-Amino Acids Containing α-Quaternary Fluorinated Carbon Centers

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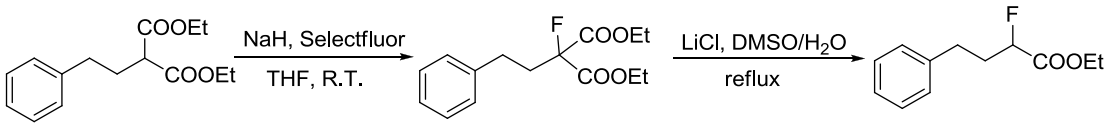
Contents

General Remarks

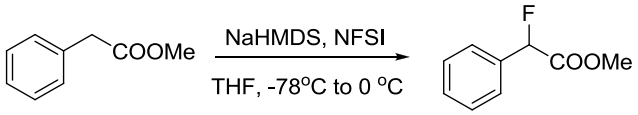
Unless otherwise mentioned, all commercial reagents and solvents were used directly as purchased. Compounds **1, 4**, **6** and **3j** were prepared according to literature methods.[1-4] THF was distilled from sodium/benzophenone. TMEDA was dried with 4Å molecular sieves. Flash chromatography was performed on silica gel with petroleum ether/ethyl acetate as the eluent. Melting points were uncorrected. Optical rotations were measured with a sodium lamp. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode. Chemical shifts (δ) are reported in parts per million and referenced to the residual solvent peak, and *J* values are given in *hertz* (Hz). HRMS data were obtained on an ESI-FTMS mass spectrometer.

Synthesis of α-fluorinated carboxylate esters

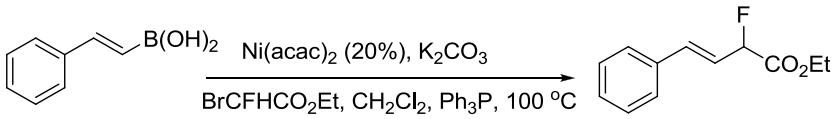
1) Typical synthetic route for the synthesis of α-alkylated fluoroacetate **1**[1]



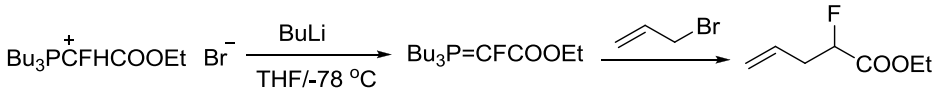
2) Typical synthetic route for the synthesis of α-phenylated fluoroacetate **4**[2]



3) Typical synthetic route for the synthesis of α-allenylated fluoroacetate **6**[3]



4) Typical synthetic route for the synthesis of ethyl 2-fluoropent-4-enoate **3j**[4]



[1] X. Jiang, S. Sakthivel, K. Kulbitski, G. Nisnevich, M. Gandelman. *J. Am. Chem. Soc*. **2014**, *136*, 9548–9551.

[2] W. Zhong, S. Hitchcock, V. F. Patel, M. Croghan, T. Dineen, S. Harried, D. Horne, T. Judd, M. Kaller, C. Kreiman, P. Lopez, H. Monenschein, T. Nguyen, M. Weiss, Q. Xue, B. Yang, WO2008147547 (A1).

[3] Y. Su, G. Feng, W. Yu, Q. Lan, X. Wang. *Angew. Chem., Int. Ed.* **2015**, *54*, 6003–6007.

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Typical Procedure for the Diastereoselective Addition of α-Alkylated Fluoroacetate 1 to N-*tert*-Butylsulfinyl Imines 2.

Under a N_2 atmosphere, LHMDS (0.6 mL, 1.0 mol/L in THF, 1.2 equiv) was added to a mixture of α-alkylated fluoroacetate **1** (0.6 mmol, 1.2 equiv), imine **2** (0.5 mmol, 1.0 equiv), TMEDA (0.15 mL), and THF (1.5 mL) at −70 ℃. The reaction mixtures were stirred at this temperature for 0.5 h. Then, 1N NH_4Cl/H_2O (2.0 mL) was added, and the quenched reaction mixture was extracted three times with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, and the volatile solvents were removed under vacuum. The crude product was purified by flash column chromatography on silica gel to give the desired product **3**.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido)(phenyl)methyl]-4-phenylbutyric Acid Ethyl Ester (3a). By following the general procedure, **3a** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (168 mg, 80%), m.p. 115.1−115.8 °C; $[\alpha]_D^{20}$ = −38.24 (*c* = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47−7.32 (m, 5H), 7.29−7.14 (m, 3H), 7.06 (d, *J* = 7.1 Hz, 2H), 4.66 (dd, *J* = 26.2, 10.5Hz, 1H), 4.38−4.18 (m, 2H), 4.08 (d, *J* = 10.5 Hz, 1H), 2.83–2.64(m, 1H), 2.58−2.39(m, 1H), 2.10 (dddd, *J* = 19.3, 14.4, 11.8, 5.4 Hz, 1H), 1.72 (dddd, *J* = 14.3, 11.8, 9.5, 4.9 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –179.4 (ddd, *J* = 35.5, 26.4, 8.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.9 (d, *J* = 26.2 Hz), 140.2, 137.0, 128.8, 128.6, 128.49 (d, *J* = 2.1 Hz), 128.43, 128.2, 126.2, 99.5 (d, J = 196.0 Hz), 65.3 (d, *J* = 19.0 Hz), 61.9, 56.6, 36.8 (d, *J* = 21.7 Hz), 29.3 (d, *J* = 3.3 Hz), 22.4, 14.2. IR (cm^{-1}): 2953, 1733, 1556, 1460, 1243, 1175, 1057, 829, 748. MS (ESI) *m/z*: 420.2 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{23}H_{31}FNO_3S^+$ $[M + H]^+$ 420.2003, found 420.2001.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido)(phenyl)methyl]-5-phenylpentanoic Acid Ethyl Ester (3b). By following the general procedure, **3b** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (160 mg, 74%), m.p. 119.9−120.5 °C; $[\alpha]_D^{20}$ = −37.05 (*c* = 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46−7.31 (m, 5H), 7.26

(dd, *J* = 12.9, 5.8 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 2 H), 4.61 (dd, *J* = 25.8, 10.6 Hz, 1H), 4.26 (dddd, *J* = 25.1, 10.7, 7.2, 3.6 Hz, 2H), 4.08 (d, *J* = 10.5 Hz, 1H), 2.49 (dtd, *J* = 14.3, 8.6, 4.6 Hz, 2H), 1.90–1.71 (m, 2H), 1.52–1.40 (m, 2H), 1.36–1.30 (m, 3H), 1.18 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −178.6 (t, *J* = 29.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.0 (d, *J* = 26.2 Hz), 141.3, 137.1, 128.7, 128.6, 128.5 (d, *J* = 2.0 H z), 128.3, 128.2, 125.9, 99.9 (d, *J* = 195.3 Hz), 65.3 (d, *J* = 19.4 Hz), 61.8, 56.5, 35.4, 34.7 (d, *J* = 21.8 Hz), 24.9 (d, *J* = 2.4 Hz), 22.4, 14.2. IR (cm^{-1}): 2956, 1740, 1541, 1507, 1459, 1253, 1038, 751, 729. MS (ESI) m/z: 434.2 [M + H] $^{+}$. HRMS (ESI) m/z: calcd for $C_{24}H_{33}FNO_3S^+$ [M + H]$^+$ 434.2160, fo und 434.2151.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido)(p-tolyl)methyl]-4-phenylb utyric Acid Ethyl Ester (3c). By following the general procedure, **3c** was isola ted by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/ 1) as a white solid (199 mg, 92%), m.p. 124.6–125.6 ℃; $[\alpha]_D^{20}$ = –40.44 (*c* = 0.69, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33–7.20 (m, 4H), 7.20–7.12 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 2H), 4.62 (dd, *J* = 26.5, 10.5 Hz, 1H), 4.33–4. 16 (m, 2H), 4.03 (d, *J* = 10.5 Hz, 1H), 2.73 (td, *J* = 13.3, 4.8 Hz, 1H), 2.57 –2.40 (m, 1H), 2.34 (s, 3H), 2.19–1.97 (m, 1H), 1.81–1.63 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –179.7 (br). ^{1} ^{3}C NMR (101 MHz, $CDCl_3$) δ = 170.0 (d, *J* = 26.3 Hz), 140.3, 138.4, 134.0, 129.5, 128.4, 128.35, 128.32, 126.2, 99.6 (d, *J* = 195.7 Hz), 65.2 (d, *J* = 18. 9 Hz), 61.9, 56.5, 36.7 (d, *J* = 21.8 Hz), 29.3 (d, *J* = 3.2 Hz), 22.4, 21.1, 14. 3. IR (cm^{-1}): 2952, 1756, 1556, 1467, 1245, 1176, 1057, 830, 749. MS (ESI) *m/z*: 434.2 [M + H]$^+$. HRMS (ESI) *m/z*: calcd for $C_{24}H_{33}FNO_3S^+$ [M + H]$^+$ 43 4.2160, found 434.2160.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido)(p-tolyl)methyl]-5-phenylp entanoic Acid Ethyl Ester (3d). By following the general procedure, **3d** was is olated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (177 mg, 79%), m.p. 117.2–118.1 ℃; $[\alpha]_D^{20}$ = –29.13 (*c*

= 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.26 (dd, *J* = 13.9, 6.5 Hz, 4H), 7.22–7.15 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 4.57 (dd, *J* = 26.2, 10.6 Hz, 1H), 4.26 (dddd, *J* = 25.1, 10.7, 7.2, 3.6 Hz, 2H), 4.03 (d, *J* = 10.6 Hz, 1H), 2.56 (dd, *J* = 12.5, 6.9 Hz, 1H), 2.49–2.40 (m, 1H), 2.37 (s, 3H), 1.87–1.72 (m, 2H), 1.53–1.41 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –178.8 (br). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.1 (d, J = 26.2 Hz), 141.4, 138.3, 134.1, 129.5 (d, *J* = 8.8 Hz), 128.4, 128.3, 128.3, 125.9, 100 (d, *J* = 195.1 Hz), 65.2 (d, *J* = 19.2 Hz), 61.8, 56.5, 35.4, 34.7 (d, *J* = 21.8 Hz), 24.9 (d, *J* = 2.6 Hz), 22.4, 21.2, 14.2. IR (cm^{-1}): 2955, 1732, 1472, 1456, 1326, 1150, 1104, 1068, 862. MS (ESI) *m/z*: 448.2 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{25}H_{35}FNO_3S^+$ $[M + H]^+$ 448.2316, found 448.2307.

(Rs,2R)-4-(1,3-Dioxan-2-yl)-2-fluoro-2-[(S)-(1,1-dimethylethylsulfinamido)(phenyl)methyl]-butyric Acid Ethyl Ester (3e). By following the general procedure, **3e** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (189 mg, 88%), m.p. 120.3–122.8 ℃; $[\alpha]_D^{20}$ = –32.90 (*c* = 0.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.76–6.98 (m, 5H), 4.62 (dd, *J* = 26.1, 10.6 Hz, 1H), 4.41–4.33 (m, 1H), 4.33–4.17 (m, 2H), 4.03 (dd, *J* = 17.4, 7.3 Hz, 3H), 3.66 (t, *J* = 11.9 Hz, 2H), 2.10–1.51 (m, 6H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –179.2 (d, *J* = 27.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.5 (d, *J* = 26.0 Hz), 136.9, 129.8 (d, *J* = 3.5 Hz), 128.8, 128.7, 128.5 (d, *J* = 2.0 Hz), 120.0, 99.5 (d, *J* = 196.8 Hz), 65.8, 65.2 (d, *J* = 18.8 Hz), 56.6, 39.7 (d, *J* = 21.4 Hz), 30.5, 22.4, 19.2, 13.6. IR (cm^{-1}): 2921, 1749, 1255, 1201, 1112, 1073, 1024, 994, 885. MS (ESI) *m/z*: 430.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{21}H_{33}FNO_5S^+$ $[M + H]^+$ 430.2058, found 430.2051.

(Rs,2R)-4-Benzyloxy-2-fluoro-2-[(S)-(3-trifluoromethylphenyl) (1,1-dimethylethyl sulfinamido) methyl]-butyric Acid Ethyl Ester (3f). By following the general procedure, **3f** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (197 mg, 76%), m.p. 80.9–81.2 ℃;

$[\alpha]_D^{20}$ = –9.88 (*c* = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.57 (dt, *J* = 18.8, 7.6 Hz, 4H), 7.38–7.23 (m, 5H), 4.71 (dd, *J* = 24.8, 10.8 Hz, 1H), 4.41 (s, 2H), 4.19(d, *J* = 10.4 Hz, 1H), 4.08 (dd, *J* = 13.8, 6.9 Hz, 2H), 3.63 –3.39 (m, 2H), 2.38–2.14 (m, 1H), 1.72–1.49 (m, 1H), 1.19 (d, *J* = 5.2Hz, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.3 – -64.3 (m), –179.3 (br). ^{13}C NM R (101 MHz, $CDCl_3$) δ = 169.4 (d, *J* = 25.9 Hz), 138.1, 137.7, 132.0, 131.0 (d, *J* = 32.6 Hz), 129.3, 128.3, 127.8, 127.7, 125.62, 125.58, 125.45, 97.2 (d, *J* = 195.8 Hz), 73.3, 65.0 (d, *J* = 19.4 Hz), 64.0 (d, *J* = 4.2 Hz), 62.0, 56.8, 35.4 (d, *J* = 21.5 Hz), 22.3, 13.9. IR (cm^{-1}): 2956, 1732, 1456, 1326, 1163, 1104, 1070, 863. MS (ESI) *m/z*: 518.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{25}H_{32}F_4NO_4S^+$ $[M + H]^+$ 518.1983, found 518.1971.

(Rs,2R)-4-Benzyloxy-2-[(S)-(4-bromophenyl)(1,1-dimethylethylsulfinamido)methyl]-2-fluoro-butyric Acid Ethyl Ester (3g). By following the general procedure, **3 g** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (200 mg, 76%), m.p. 71.1–71.2 ℃; $[\alpha]_D^{20}$ = –2. 92 (*c* = 0.47, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.4 Hz, 2H), 7.36–7.19 (m, 7H), 4.60 (dd, *J* = 25.6, 10.8 Hz, 1H), 4.39 (s, 2H), 4.0 7 (ddd, *J* = 12.0, 7.3, 5.1 Hz, 3H), 3.49 (ddd, *J* = 19.1, 9.6, 4.6 Hz, 2H), 2. 34–2.11 (m, 1H), 1.70–1.50 (m, 1H), 1.23–1.15 (m, 12H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –180.1 (t, *J* = 28.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169. 5 (d, *J* = 26.0 Hz), 137.8, 136.1, 131.9, 130.3 (d, *J* = 2.1 Hz), 128.3, 127.8, 127.7, 122.9, 97.2 (d, *J* = 195.4 Hz), 73.3, 65.0 (d, *J* = 19.1 Hz), 64.1 (d, *J* = 4.3 Hz), 61.9, 56.7, 35.4 (d, *J* = 21.5 Hz) , 22.3, 13.9. IR (cm^{-1}): 2924, 1720, 1460, 1274, 1230, 1130, 1108, 1047, 837. MS (ESI) *m/z*: 528.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{24}H_{32}BrFNO_4S^+$ $[M + H]^+$ 528.1214, found 528. 1206.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido) (p-tolyl)methyl]-hexanedioic Diethyl Ester (3h). By following the general procedure, **3h** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) as a pale yellow liquid (137 mg, 60%), $[\alpha]_D^{20}$ = –21.30 (*c* = 0.30, $CHCl_3$); ^1H

NMR (400 MHz, $CDCl_3$) δ = 7.20 (dd, *J* = 18.6, 8.0 Hz, 4H), 4.56 (dd, *J* = 26.4, 10.5 Hz, 1H), 4.37–4.18 (m, 2H), 4.15–4.04 (m, 2H), 3.99 (d, *J* = 10.5 Hz, 1H), 2.35 (s, 3H), 2.20 (t, *J* = 7.3 Hz, 2H), 1.80–1.67 (m, 2H), 1.57–1. 38 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -179.1 – -179.5 (m). ^{13}C NMR (101 M Hz, $CDCl_3$) δ = 173.2, 170.1 (d, *J* = 26.3 Hz), 138.4, 134.1, 129.5, 128.3 (d, *J* = 2.0 Hz), 100.9, 65.2 (d, *J* = 18.9 Hz), 61.8, 60.3, 56.5, 34.7 (d, *J* = 21. 8 Hz), 33.9, 24.6, 22.6 (d, *J* = 2.9 Hz), 22.4, 21.2, 14.2 (d, *J* = 3.1 Hz). IR (cm^{-1}): 2949, 2360, 1757, 1649, 1559, 1457, 1243, 1174, 833. MS (ESI) *m/z*: 458.2 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{23}H_{36}FNO_5S^+$ $[M + H]^+$ 458.237 1, found 458.2362.

(Rs,2R,4E)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido) (phenyl)methyl]-5-ph enylpentenoic Acid Ethyl Ester (3i). By following the general procedure, **3i** w as isolated by column chromatography on silica gel (petroleum ether/ethyl aceta te = 3/1) as a white solid (160 mg, 74%), m.p. 120.0–122.1 °C; $[\alpha]_D^{20}$ = –36. 23 (*c* = 0.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48–7.16 (m, 10H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.02 (ddd, *J* = 15.3, 8.7, 6.2 Hz, 1H), 4.69 (dd, *J* = 26.0, 10.4 Hz, 1H), 4.22 (tdd, *J* = 10.3, 7.1, 3.8 Hz, 2H), 4.06 (d, *J* = 1 0.2 Hz, 1H), 2.59 (ddd, *J* = 35.2, 14.5, 8.9 Hz, 1H), 2.40–2.23(m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -155.5 – -155.8 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.5 (d, *J* = 25.8 Hz), 136.8, 136.7, 134.9, 128.82, 128.76, 128.5, 127.6, 126.2, 120.94, 120.91, 99.6 (d, *J* = 197.2 Hz), 65.0 (d, *J* = 18.7 Hz), 61.9, 56.6, 39.0 (d, *J* = 21.5 Hz), 22.4, 14.3. IR (cm^{-1}): 2988, 1733, 1653, 1538, 1501, 1457, 1072, 977, 753. MS (ES I) *m/z*: 432.3 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{24}H_{31}FNO_3S^+$ $[M + H]^+$ 432.2003, found 432.1995.

(Rs,2R)-2-Fluoro-2-[(S)-(1,1-dimethylethylsulfinamido) (phenyl)methyl]-pentenoi c Acid Ethyl Ester (3j). By following the general procedure, **3j** was isolated b y column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (153 mg, 86%), m.p. 84.6–85.4 °C; $[\alpha]_D^{20}$ = –18.76 (*c* = 0.54,

$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50–7.31 (m, 5H), 5.68 (dddd, *J* = 16.1, 10.1, 8.6, 5.8 Hz, 1H), 5.09 (dd, *J* = 20.7, 13.6 Hz, 2H), 4.66 (dd, *J* = 26.1, 10.5 Hz, 1H), 4.26 (dddd, *J* = 17.9, 14.3, 9.0, 5.4 Hz, 2H), 4.09 (d, *J* = 10.4 Hz, 1H), 2.45 (ddd, *J* = 36.3, 14.6, 8.5 Hz, 1H), 2.18 (ddd, *J* = 14.8, 10.8, 5.7 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -156.0 – -156.2 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.4 (d, *J* = 26.0 Hz), 136.8, 129.7 (d, *J* = 3.3 Hz), 128.8, 128.7,128.5, 120.1, 99.4 (d, *J* = 196.8 Hz), 65.1 (d, *J* = 18.6 Hz), 61.9, 56.6, 39.7 (d, *J* = 21.5 Hz), 22.3, 14.2. IR (cm^{-1}): 2949, 1731, 1325, 1294, 1229, 1130, 1068, 937, 837. MS (ESI) *m/z*: 356.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{18}H_{27}FNO_3S^+$ $[M + H]^+$ 356.1690, found 356.1693.

(Rs,2R,3S)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2-(naphthalen-1-ylmethyl)-3-(p-tolyl) propionic Acid Ethyl Ester (3k). By following the general procedure, **3k** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (190 mg, 81%), m.p. 122.1–125.4 ^oC; $[\alpha]_D^{20}$ = 14.25 (*c* = 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83–7.70 (m, 3H), 7.58 (s, 1H), 7.49–7.42 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.27 (dd, *J* = 12.2, 4.3 Hz, 3H), 4.80 (dd, *J* = 25.9, 10.5 Hz, 1H), 4.03 (dt, *J* = 14.3, 8.9 Hz, 3H), 3.15 (dd, *J* = 39.1, 14.5 Hz, 1H), 2.89 (d, *J* = 13.3 Hz, 1H), 2.39 (s, 3H), 1.18 (s, 9H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -173.3 – -182.0 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.4 (d, *J* = 25.6 Hz), 138.6, 134.1, 133.2, 132.6, 131.4, 129.7, 128.8, 128.5, 128.0, 127.8, 127.6, 127.5, 126.0, 125.8, 100.3, 65.5 (d, *J* = 18.7Hz), 61.7, 56.5, 41.7, 22.4, 21.2, 13.9. IR (cm^{-1}): 3299, 2917, 1788, 1508, 1501, 1402, 1301, 1120, 1061. MS (ESI) *m/z*: 470.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{27}H_{33}FNO_3S^+$ $[M + H]^+$ 470.2160, found 470.2160.

(Rs,2R,3S)-2-Benzyl-2-fluoro-3-(1,1-dimethylethylsulfinamido)-3-(4-nitrophenyl)propionic Acid Ethyl Ester (3l). By following the general procedure, **3l** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (153 mg, 68%), m.p. 110.2–110.7 ^oC; $[\alpha]_D^{20}$ = 2.71 (*c* = 0.

75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.26 (dd, *J* = 8.3, 4.9 Hz, 3H), 7.18 –7.00 (m, 2H), 4.90 (dd, *J* = 23.7, 11.0 Hz, 1H), 4.29 (d, *J* = 10.9 Hz, 1H), 4.06 (d, *J* = 7.1 Hz, 2H), 3.07(dd, *J* = 38.6, 14.4Hz, 1H), 2.69 (t, *J* = 14.0 Hz, 1H), 1.19 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -175.6 – -176.5 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.8 (d, *J* = 25.0 Hz), 148.2, 144.1, 132.9, 129.9, 129.7 (d, *J* = 2.2 Hz), 128.4, 127.6, 124.0, 99.4 (d, *J* = 199.7 Hz), 64.7 (d, *J* = 19.7Hz), 62.1, 57.0, 41.5 (d, *J* = 20.8 Hz), 22.3, 13.9. IR (cm^{-1}): 2920, 1733, 1649, 1558, 1503, 1347, 1210, 1135, 1035. MS (ESI) *m/z*: 451.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{22}H_{28}FN_2O_5S^+$ $[M + H]^+$ 451.1697, found 451.1688.

(Rs,2R,3S)-2-Benzyl-2-fluoro-3-(furan-2-yl)-3-(1,1-dimethylethylsulfinamido)-propionic Acid Ethyl Ester (3m). By following the general procedure, **3m** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (164 mg, 83%), m.p. 147.7–148.1 ^oC; $[\alpha]_D^{20}$ = –11.00 (*c* = 0.54, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 0.9 Hz, 1H), 7.29–7.20 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.49 (d, *J* = 3.1 Hz, 1H), 6.41 (dd, *J* = 3.1, 1.8 Hz, 1H), 4.86 (dd, *J* = 24.2, 10.9 Hz, 1H), 4.08–3.95 (m, 3H), 3.06 (dd, *J* = 37.0, 14.5 Hz, 1H), 2.89 (t, *J* = 14.2 Hz, 1H), 1.16 (s, 9H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -174.7 – -175.2 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7 (d, *J* = 25.3 Hz), 149.9, 143.2, 133.5, 130.0, 128.3, 127.3, 110.7, 109.8, 99.17 (d, *J* = 199.8 Hz), 61.7, 59.4(d, *J* = 20.3 Hz), 56.7, 40.9 (d, *J* = 21.1 Hz), 22.4, 13.9. IR (cm^{-1}): 3335, 2958, 1765, 1515, 1475, 1431, 1366, 1249, 1062. MS (ESI) *m/z*: 396.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{20}H_{27}FNO_4S^+$ $[M + H]^+$ 396.1639, found 396.1637.

(Rs,2R)-2-Benzyl-2-fluoro-3-(1,1-dimethylethylsulfinamido)-3,3-diphenylpropionic Acid Ethyl Ester (3n). By following the general procedure, **3n** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (198 mg, 80%), m.p. 144.7–146.1 ^oC; $[\alpha]_D^{20}$ = –0.63 (*c* = 0.49, $CHCl_3$); ^1H

NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, J = 7.5 Hz, 2H), 7.49–7.43 (m, 2H), 7.38–7.29 (m, 8H), 7.21 (dd, J = 17.2, 7.2 Hz, 3H), 5.52 (s, 1H), 3.97–3.74 (m, 2H), 3.03–2.81 (m, 2H), 2.78–2.51 (m, 2H), 1.31 (d, J = 5.2 Hz, 9H), 0.99 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –164.2 (br). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.8, 140.5, 138.4, 130.9, 129.8 (d, J = 4.6 Hz), 128.5 (d, J = 11.2 Hz), 128.1 (d, J = 16.1Hz), 127.6 (d, J = 18.5Hz), 126.3, , 72.7, 72.5, 62.0, 57.3, 36.0, 29.7 (d, J = 6.6Hz), 23.2, 13.6. IR (cm^{-1}): 2914, 1705, 1448, 1369, 1305, 1229, 1076, 1008, 835. MS (ESI) *m/z*: 496.2 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{20}H_{27}FNO_4S^+$ $[M + H]^+$ 496.2316, found 496.2301.

Typical Procedure for the Diastereoselective Addition of α-Phenylated Fluoroacetate 4 to N-*tert*-Butylsulfinyl Imines 2.

Under a N_2 atmosphere, LHMDS (0.6 mL, 1.0 mol/L in THF, 1.2 equiv) was added to a mixture of α-phenylated fluoroacetate **4** (0.6 mmol, 1.2 equiv), imine **2** (0.5 mmol, 1.0 equiv), TMEDA (0.15 mL), and THF (1.5 mL) at −70 ℃. Reaction mixtures were stirred at this temperature for 0.5 h. Then, 1N TFA /THF (2 mL) was added, and the quenched reaction mixture was extracted three times with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and the volatile solvents were removed under vacuum. The crude product was purified by flash column chromatography on silica gel to give the corresponding product **5**.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2,3-diphenylpropionic Acid Methyl Ester (5a). By following the general procedure, **5a** was isolated by co lumn chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a w hite solid (144 mg, 76%), m.p . 160.0–160.2 ℃; $[\alpha]_D^{20}$ = –114.05 (c = 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J = 7.2 Hz, 2H), 7.48 (dq, J = 14.4, 7.2 Hz, 5H), 7.38 (d, J = 3.3 Hz, 3H), 5.31 (dd, J = 25.7, 1.8 Hz, 1H), 3.59 (d, J = 7.2 Hz, 4H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –178.6 (d, J = 26.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.5 (d, J = 25.6 Hz), 134.7, 134.2, 130.1 (d, J = 1.9 Hz), 129.6, 129.1 (d, J = 1.8 Hz), 128.9, 128.2, 125.4 (d, J = 10.3 Hz), 97.9 (d, J = 202.4 Hz), 62.6 (d, J = 19. 0 Hz), 55.8, 52.8, 22.3. IR (cm^{-1}): 2955, 1757, 1450, 1255, 1131, 1072, 1029,

811, 737. MS (ESI) *m/z*: 378.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{20}H_{25}FNO_3S^+$ $[M + H]^+$ 378.1534, found 378.1530.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2-phenyl-3-(p-tolyl)propionic Acid Methyl Ester (5b). By following the general procedure, **5b** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (141 mg, 72%), m.p. 166.0–166.3 ℃; $[\alpha]_D^{20}$ = –119.35 (*c* = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78–7.67 (m, 2H), 7.59–7.41 (m, 3H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.28 (dd, *J* = 25.8, 1.7 Hz, 1H), 3.58 (d, *J* = 25.3 Hz, 4H), 2.38 (s, 3H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –178.7 (d, *J* = 25.8 Hz). ^{13}C NMR (101MHz, $CDCl_3$) δ = 168.6, 138.7, 134.4, 131.5, 129.9, 129.5, 129.1 (d, *J* = 2.0 Hz), 129.0, 125.4 (d, *J* = 10.3 Hz), 97.7 (d, *J* = 202.4 Hz), 62.3 (d, *J* = 18.9 Hz), 55.7, 52.8, 22.3, 21.3. IR (cm^{-1}): 2954, 1754, 1450, 1365, 1257, 1134, 1066, 826, 795. MS (ESI) *m/z*: 392.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{21}H_{27}FNO_3S^+$ $[M + H]^+$ 392.1690, found 392.1682.

(Rs,2R,3R)-3-(4-Bromophenyl)-2-fluoro-3-(1,1-dimethylethylsulfinamido)-2-phenyl propionic acid methyl ester (5c). By following the general procedure, **5c** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (164 mg, 72%), m.p. 161.8–162.7 ℃; $[\alpha]_D^{20}$ = –103.42 (*c* = 0.49, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.1 Hz, 2H), 7.54–7.40 (m, 5H), 7.36 (d, *J* = 7.4 Hz, 2H), 5.28 (dd, *J* = 25.3, 1.1 Hz, 1H), 3.61(d, *J* = 14.3 Hz, 4H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –178.7 (d, *J* = 25.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.4 (d, *J* =25.4 Hz), 134.0 (t, *J* = 11.4 Hz), 133.8 (d, *J* = 4.9 Hz), 131.8 (d, *J* = 2.0 Hz), 131.5, 129.7, 129.2 (d, *J* = 1.9 Hz), 125.3 (d, *J* = 10.4 Hz), 123.2, 97.7 (d, *J* = 202.7 Hz), 61.9 (d, *J* = 19.3 Hz), 55.8, 53.0, 22.2. IR (cm^{-1}): 2953, 1743, 1487, 1433, 1364, 1272, 1073, 1011, 823. MS (ESI) *m/z*: 456.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{20}H_{24}BrFNO_3S^+$ $[M + H]^+$ 456.0639, found 456.0631.

(Rs,2R,3R)-2-(4-Chlorophenyl)-2-fluoro-3-(1,1-dimethylethylsulfinamido)-3-phenyl

propionic Acid Methyl Ester (5d). By following the general procedure, **5d** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (157 mg, 76%), m.p. 146.8–147.1 ℃; $[\alpha]_D^{20}$ = –77.74 (*c* = 0.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.41(dd, *J* = 27.5, 15.1 Hz, 7H), 5.24 (d, *J* = 25.2 Hz, 1H), 3.88 (s, 1H), 3.58 (d, *J* = 5.7Hz, 3H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –177.3 (d, *J* = 24.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.2 (d, *J* = 25.4 Hz), 135.8, 134.5, 132.6 (d, *J* = 23.4 Hz), 129.9, 129.2, 129.0, 128.3, ,127.0, 97.6, 62.6 (d, *J* = 19.3 Hz), 55.9, 53.0, 22.3. IR (cm^{-1}): 2959, 1758, 1739, 1646, 1558, 1540, 1270, 1071, 825. MS (ESI) *m/z*: 412.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{20}H_{24}ClFNO_3S^+$ $[M + H]^+$ 412.1144, found 412.1137.

(Rs,2R,3R)-2-(2-Chlorophenyl)-2-fluoro-3-(1,1-dimethylethylsulfinamido)-3-phenyl propionic Acid Methyl Ester (5e). By following the general procedure, **5e** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (195 mg, 95%), m.p. 166.3–167.2 ℃; $[\alpha]_D^{20}$ = –99.65 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 5.9, 3.6 Hz, 1H), 7.47–7.42 (m, 1H), 7.41–7.29 (m, 7H), 5.50 (dd, *J* = 21.4, 2.6 Hz, 1H), 4.19 (d, *J* = 2.1 Hz, 1H), 3.62 (s, 3H), 1.14 (s, 9H). ^{19}F NMR (376 M Hz, $CDCl_3$) δ = –162.1 (br). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.7 (d, *J* = 24.3Hz), 134.9, 132.6 (d, *J* = 10.6 Hz), 132.3, 131.4, 130.8, 130.3, 129.3 (d, *J* = 11.4 Hz), 128.8, 127.9 (d, *J* = 15.2 Hz), 127.0, 96.8 (d, *J* = 196.3 Hz), 61.3 (d, *J* = 22.5 Hz), 55.9, 53.0, 24.2. IR (cm^{-1}): 2956, 1767, 1656, 1558, 1 507, 1457, 1247, 1064, 759. MS (ESI) *m/z*: 412.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{20}H_{24}ClFNO_3S^+$ $[M + H]^+$ 412.1144 , found 412.1136.

(Rs,2R,3R)-2-(2-Chlorophenyl)-2-fluoro-3-((S)-1,1-dimethylethylsulfinamido)-3-(p-tolyl)propionic Acid Methyl Ester (5f). By following the general procedure, **5f** was isolated by column chromatography on silica gel (petroleum ether/ethyl ace tate = 3/1) as a white solid (204 mg, 96%), m.p. 162.6–162.7 ℃; $[\alpha]_D^{20}$ = –1 16.37 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 5.8, 3.7Hz, 1H), 7.45 (dd, *J* = 5.6, 3.7 Hz, 1H), 7.41–7.34 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.48 (dd, *J* = 21.6, 2.3 Hz, 1H), 4.1

3 (s, 1H), 3.62 (s, 3H), 2.37 (s, 3H), 1.14 (s, 9H). ^{19}F NMR (376 MHz, CDC l_3) δ = –162.5 (br). ^{13}C NMR (101 MHz, $CDCl_3$) δ =167.6 (d, J = 24.6 Hz), 138.6, 132.6, 131.7, 131.4, 130.7, 130.2, 129.4 (d, J = 11.5 Hz), 128.7, 127.0, 96.8 (d, J = 196.2 Hz), 60.9 (d, J = 22.4 Hz), 55.8, 53.0, 22.4, 21.3. IR (c m^{-1}): 2958, 1765, 1515, 1475, 1431, 1366, 1249, 1063, 830. MS (ESI) m/z: 4 26.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{21}H_{26}ClFNO_3S^+$ $[M + H]^+$ 426.13 00, found 426.1292.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2-(4-methoxyphenyl)-3-(p-to lyl)propionic Acid Methyl Ester (5g). By following the general procedure, **5g** was isolated by column chromatography on silica gel (petroleum ether/ethyl ace tate = 3/1) as a white solid (168 mg, 80%), m.p. 119.7–120.8 ℃; $[\alpha]_D^{20}$ = –9 4.30 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42–7.31 (m, 3H), 7.26 (dd, J = 15.5, 10.1 Hz, 3H), 7.15 (d, J = 7.7 Hz, 2H), 6.95 (d, J = 8.1 Hz, 1H), 5.25 (d, J = 25.9 Hz, 1H), 3.83 (d, J = 13.7 Hz, 3H), 3.57 (d, J = 8.1 Hz, 4H), 2.35 (s, 3H), 1.03 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -177.6 (d, J = 25.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.4 (d, J = 25.7 Hz), 160.1, 138.7, 135.7 (d, J = 23.1 Hz), 131.4, 130.1, 129.0, 115.4, 110.8 (d, J = 11.1 Hz), 97.8 (d, J = 202.4 Hz), 62.0 (d, J = 18.8 Hz), 60.4, 55.6 (d, J = 25.7 Hz), 52.9, 22.3, 21.3. IR (cm^{-1}): 2956, 1752, 1599, 1430, 1261, 1177, 1035, 1064, 889. MS (ESI) *m/z*: 444.1 $[M + Na]^+$. HRMS (ESI) *m/z*: ca lcd for $C_{22}H_{28}FNNaO_4S^+$ $[M + Na]^+$ 444.1612, found 444.1615.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-3-phenyl-2-(p-tolyl)propioni c Acid Ethyl Ester (5h). By following the general procedure, **5h** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) a s a white solid (167 mg, 82%), m.p. 140.4–140.6 ℃; $[\alpha]_D^{20}$ = –97.61 (*c* = 0.5 0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, J = 8.3 Hz, 2H), 7.55–7.44 (m, 2H), 7.40–7.29 (m, 5H), 5.28 (dd, J = 25.8, 1.4Hz, 1H), 4.03 (tdd, J = 10.7, 7.1, 3.6 Hz, 2H), 3.58 (s, 1H), 2.40 (s, 3H), 1.07 (t, J = 7.2 Hz, 3 H), 1.04 (d, J = 5.4Hz, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –178.7 (d, J = 26.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.0 (d, J = 25.6 Hz), 139.4,

134.8, 131.3 (d, *J* = 23.1 Hz) , 130.2, 129.7, 128.8, 128.1, 125.3 (d, *J* = 10. 1 Hz), 97.7 (d, *J* = 201.9 Hz), 62.5 (d, *J* = 18.7 Hz), 62.1, 55.7, 22.3, 21.2, 13.8. IR (cm^{-1}): 2956, 1750, 1515, 1467, 1368, 1257, 1105, 1072, 824, 721. MS (ESI) m/z: 406.2 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{22}H_{29}FNO_3S^+$ $[M + H]^+$ 406.1847, found 406.1840.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2,3-di-p-tolylpropionic Acid Ethyl Ester (5i). By following the general procedure, **5i** was isolated by colu mn chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a whi te solid (187 mg, 89%), m.p. 144.2–144.9 ℃; $[\alpha]_D^{20}$ = –113.76 (*c* = 0.50, CH Cl_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.26 (d, *J* = 25.9 Hz, 1H), 4.14–3.91 (m, 2H), 3.55 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –1 78.8 (d, *J* = 26.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.1 (d, *J* = 26.2 Hz), 139.4, 138.6, 131.6, 131.4 (d, *J* = 23.1 Hz), 130.1, 129.7, 129.5, 128.9, 1 25.3 (d, *J* = 10.1 Hz), 97.7 (d, *J* = 201.3 Hz), 62.1, 55.7, 22.3, 21.2, 13.8. I R (cm^{-1}): 2955, 1745, 1515, 1467, 1368, 1254, 1104, 1072, 824. MS (ESI) *m/ z*: $[M + H]^+$ 420.2. HRMS (ESI) *m/z*: calcd for $C_{23}H_{31}FNO_3S^+$ $[M + H]^+$ 420. 1995, found 420.2003.

(Rs,2R,3R)-2-Fluoro-3-(furan-2-yl)-3-(1,1-dimethylethylsulfinamido)-2-phenylprop ionic Acid Methyl Ester (5j). By following the general procedure, **5j** was isola ted by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/ 1) as a white solid (155 mg, 85%), m.p. 150.3–151.1 ℃; $[\alpha]_D^{20}$ = –80.96 (*c* = 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.6 (d, *J* = 7.7 Hz, 2H), 7.5 4–7.35 (m, 4H), 6.55–6.28 (m, 2H), 5.42 (dd, *J* = 25.8, 4.9 Hz, 1H), 3.68 (s, 3H), 3.53 (dd, *J* = 16.3, 11.7 Hz, 1H), 1.01 (s, 9H). ^{19}F NMR (376 MHz, C DCl_3) δ = –177.2 (d, *J* = 26.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.5 (d, *J* = 25.4 Hz) , 149.0, 143.0, 133.9 (d, *J* = 22.6 Hz), 129.5, 128.9, 125.2 (d, *J* = 10.3 Hz), 110.5 (d, *J* = 3.3 Hz), 97.5 (d, *J* = 200.8 Hz), 58.3, 58.1, 56.3, 53.1, 22.2. IR (cm^{-1}): 2958, 1756, 1451, 1259, 1133, 1074, 1033, 824, 7

43. MS (ESI) *m/z*: 368.1 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{18}H_{23}FNO_4S^+$ $[M + H]^+$ 368.1326, found 368.1319.

(Rs,2R,3R)-2-Fluoro-3-(1,1-dimethylethylsulfinamido)-2-phenylhexanoic Acid Methyl Ester (5k). By following the general procedure, **5k** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (155 mg, 85%), m.p. 81.2–82.2 ℃; $[\alpha]_D^{20}$ = –71.67 (*c* = 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60–7.29 (m, 5H), 4.20–4.04 (m, 1H), 3.78 (s, 3H), 3.28 (d, *J* = 6.5 Hz, 1H), 1.84–1.69 (m, 1H), 1.68–1.48 (m, 2H), 1.41 (dt, *J* = 16.9, 8.4 Hz, 1H), 1.03 (s, 9H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –177.0 (d, *J* = 26.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 135.3, 129.5, 128.7, 127.8, 124.6 (d, *J* = 10.3 Hz), 57.5, 56.3, 52.2, 34.2, 22.6 (d, *J* = 9.8 Hz), 18.8, 13.9. IR (cm^{-1}): 2956, 1740, 1653, 1641, 1558, 1457, 1263, 1034, 729. MS (ESI) *m/z*: 366.1 $[M + Na]^+$. HRMS (ESI) *m/z*: calcd for $C_{17}H_{26}FNNaO_3S^+$ $[M + Na]^+$ 366.1510, found 366.1510.

Typical Procedure for the Diastereoselective Addition of α-Allenylated Fluoroacetate 6 to N-*tert*-Butylsulfinyl Imines 2.

Under a N_2 atmosphere, LHMDS (0.6 mL, 1.0 mol/L in THF, 1.2 equiv) was added slowly to a mixture of α-allenylated fluoroacetate **6** (0.6 mmol, 1.2 equiv), imine **2** (0.5 mmol, 1.0 equiv), TMEDA (0.15 mL), and THF (1.5 mL) at −70 ℃. The reaction mixtures were stirred at this temperature for 0.5 h. Then, 1N TFA/THF (2.0 mL) was added, and the quenched reaction mixture was extracted three times with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, and the volatile solvents were removed under vacuum. The crude product was purified by flash column chromatography on silica gel to give the corresponding product 7.

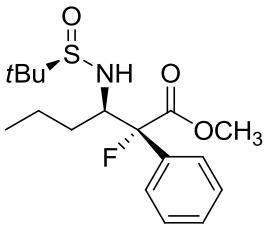
(Rs,2S,3R,3E)-2-Fluoro-2-[(1,1-dimethylethylsulfinamido)(phenyl)methyl]-4-phenylbutenoic Acid Ethyl Ester (7a). By following the general procedure, **7a** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (104 mg, 50%), m.p. 128.1–129.5 ℃; $[\alpha]_D^{20}$ = –194.63 (*c* = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.6 Hz, 2H), 7.42–7.28 (m, 8H), 6.95 (d, *J* = 16.1 Hz, 1H), 6.39 (dd, *J* = 20.4, 16.1 H

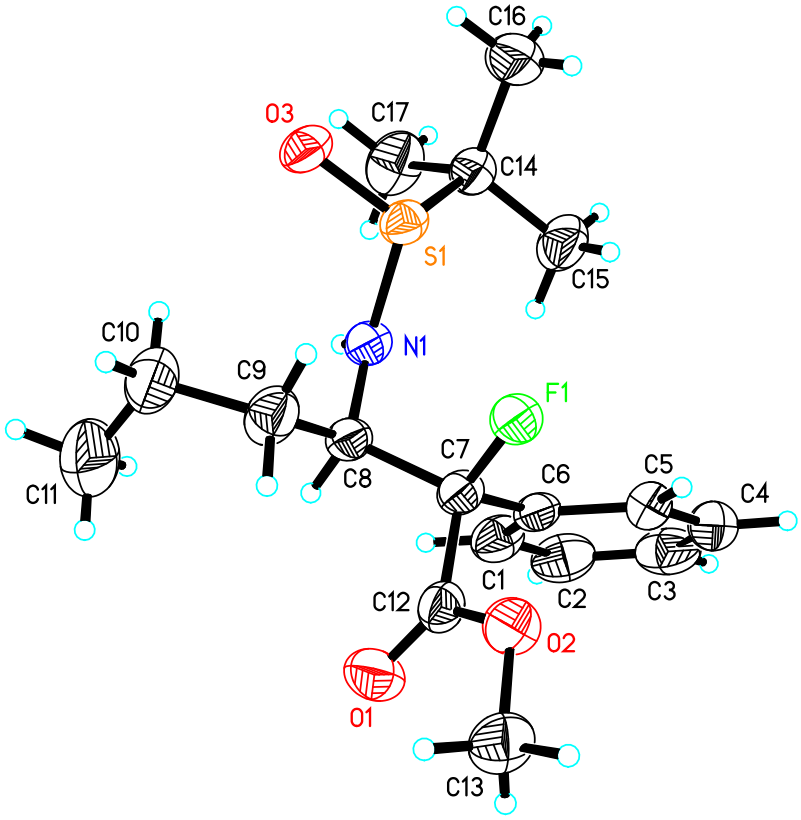
z, 1H), 4.93 (d, *J* = 23.0 Hz, 1H), 4.10 (dd, *J* = 13.6, 6.4 Hz, 3H), 1.22–1.09 (m, 12H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –177.8 (t, *J* = 21.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.6 (d, *J* = 25.4 Hz), 135.1, 135.0, 133.9, 133.8, 129.6, 128.8, 128.7, 128.2, 127.1, 123.1 (d, *J* = 19.0 Hz), 97.2 (d, *J* = 202.7 Hz), 62.3, 62.1, 56.0, 22.5, 13.9. IR (cm^{-1}): 2965, 1753, 1558, 1456, 1365, 1245, 1069, 978, 858. MS (ESI) *m/z*: 418.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{23}H_{29}FNO_3S^+$ $[M + H]^+$ 418.1847, found 418.1847.

(Rs,2S,3R,3E)-2-Fluoro-2-[(1,1-dimethylethylsulfinamido)(p-tolyl)methyl)-4-phenylbutenoic Acid Ethyl Ester (7b). By following the general procedure, **7b** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (155 mg, 72%), m.p. 135.1–136.3 ℃; $[\alpha]_D^{20}$ = –180.55 (*c* = 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.4 Hz, 2H), 7.40–7.25 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 16.1 Hz, 1H), 6.38 (dd, *J* = 20.5, 16.1 Hz, 1H), 4.89 (d, *J* = 22.8 Hz, 1H), 4.18–3.98 (m, 3H), 2.34 (s, 3H), 1.22–1.12 (m, 12H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = –177.7 (t, *J* = 20.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.6 (d, *J* = 25.4 Hz), 138.7, 135.1, 133.8, 133.7, 131.8, 129.4, 129.0, 128.8, 127.0, 123.2 (d, *J* = 19.0 Hz), 97.2 (d, *J* = 202.0 Hz), 62.2, 61.8 (d, *J* = 19.6 Hz), 55.9, 22.5, 21.2, 14.0. IR (cm^{-1}): 2949, 1758, 1469, 1364, 1246, 1151, 1098, 1035, 835. MS (ESI) *m/z*: 432.2 $[M + H]^+$. HRMS (ESI) *m/z*: calcd for $C_{24}H_{31}FNO_3S^+$ $[M + H]^+$ 432.2003, found 432.2002.

X-raycry stal structure of 5k

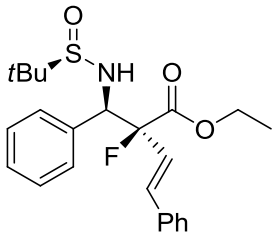
The thermal ellipsoids are drawn at a 30% probability level.

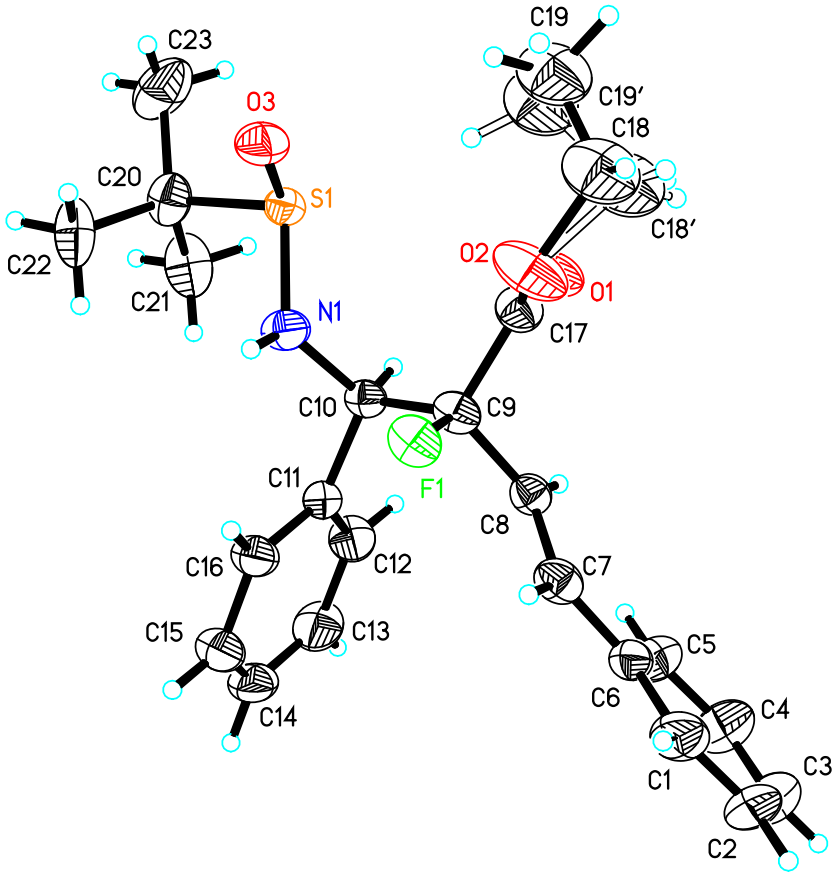




X-raycry stal structure of 7a

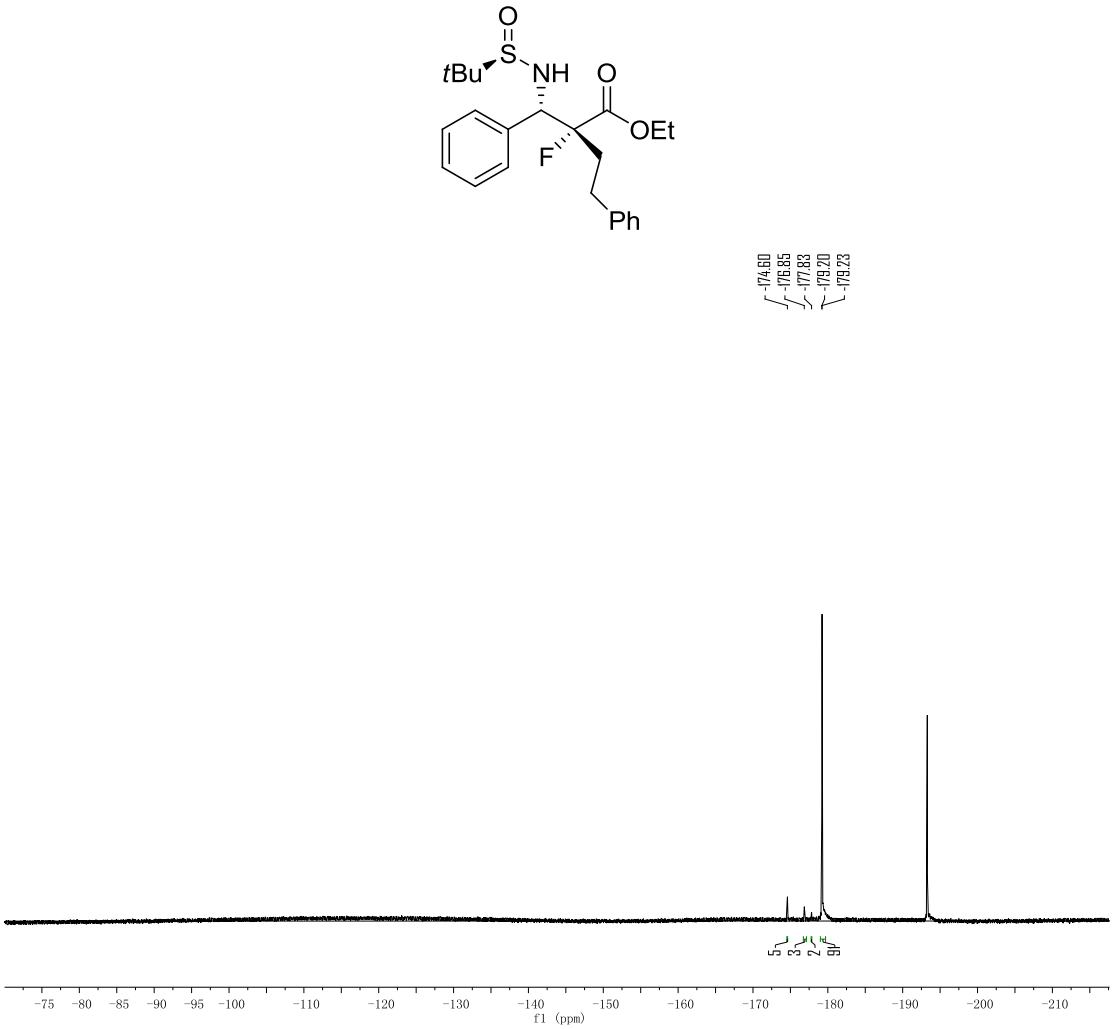
The thermal ellipsoids are drawn at a 30% probability level.





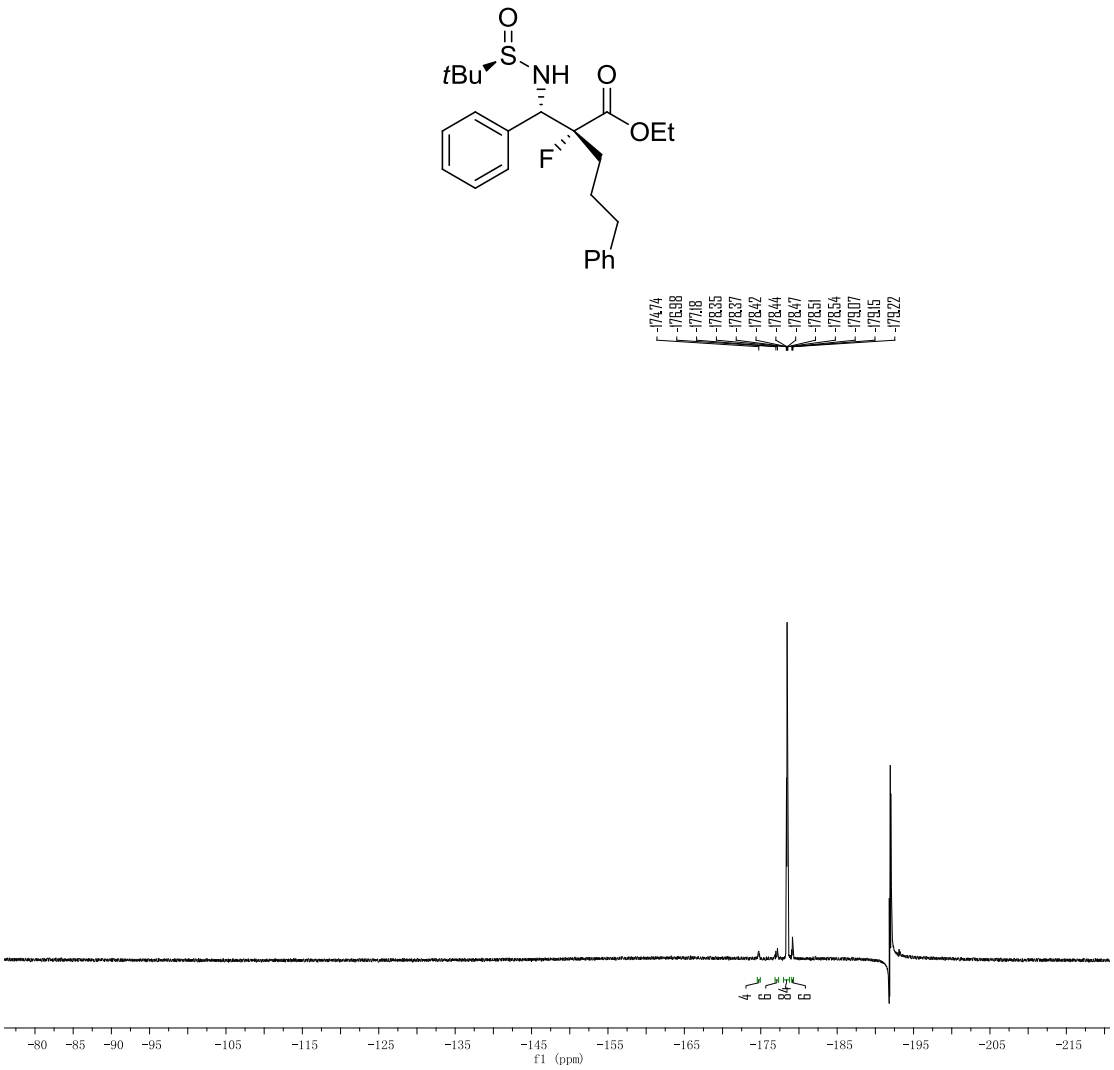
d.r. Determination by ^{19}F NMR on the Crude Products **3**, **5** and **7**.

Crude **3a**, d.r. = 91:2:2:5



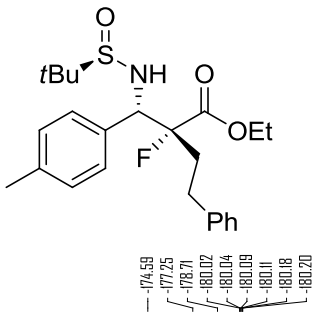
The stereoisomers are at δ −174.6 (br), δ −176.8 (br), δ −177.8 (br), and δ −179.2 (d, J = 10.0 Hz).

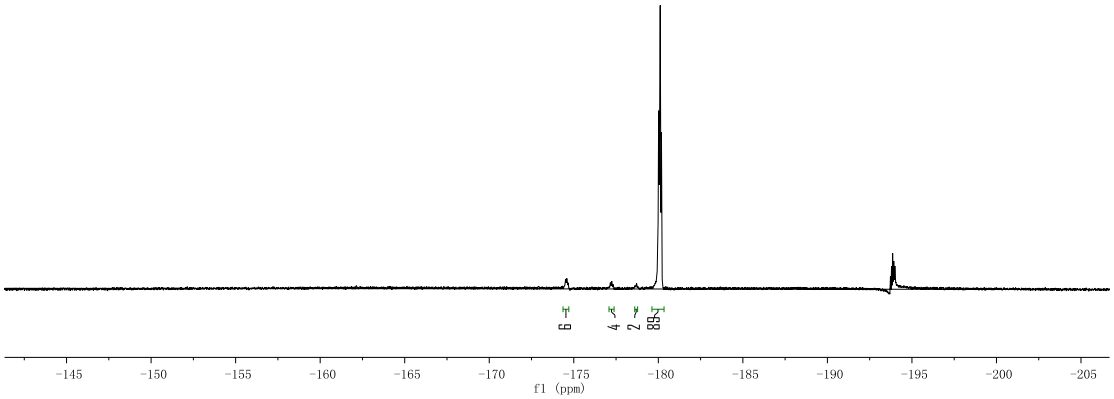
Crude **3b**, d.r. = 84:6:6:4



The stereoisomers are at δ −174.7 (s), δ −177.0 (d, *J* = 77.5 Hz), δ −178.4 (ddd, *J* = 35.4, 26.6, 8.6 Hz), and δ −179.1 (t, *J* = 27.0 Hz)

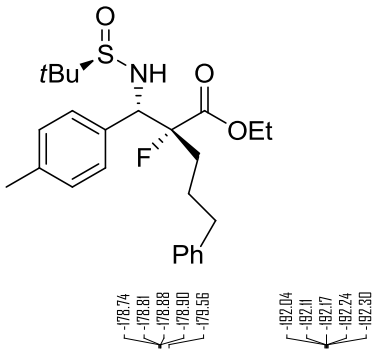
Crude **3c**, d.r. = 89:2:4:5

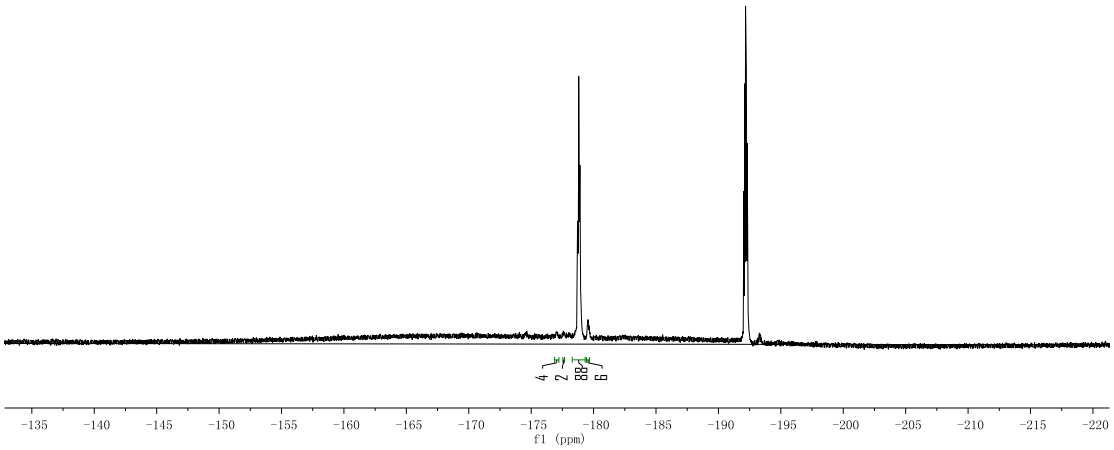




The stereoisomers are at δ −174.5 (br), δ −177.2 (br), δ −178.7 (br), and δ -179.6 – -180.3 (m).

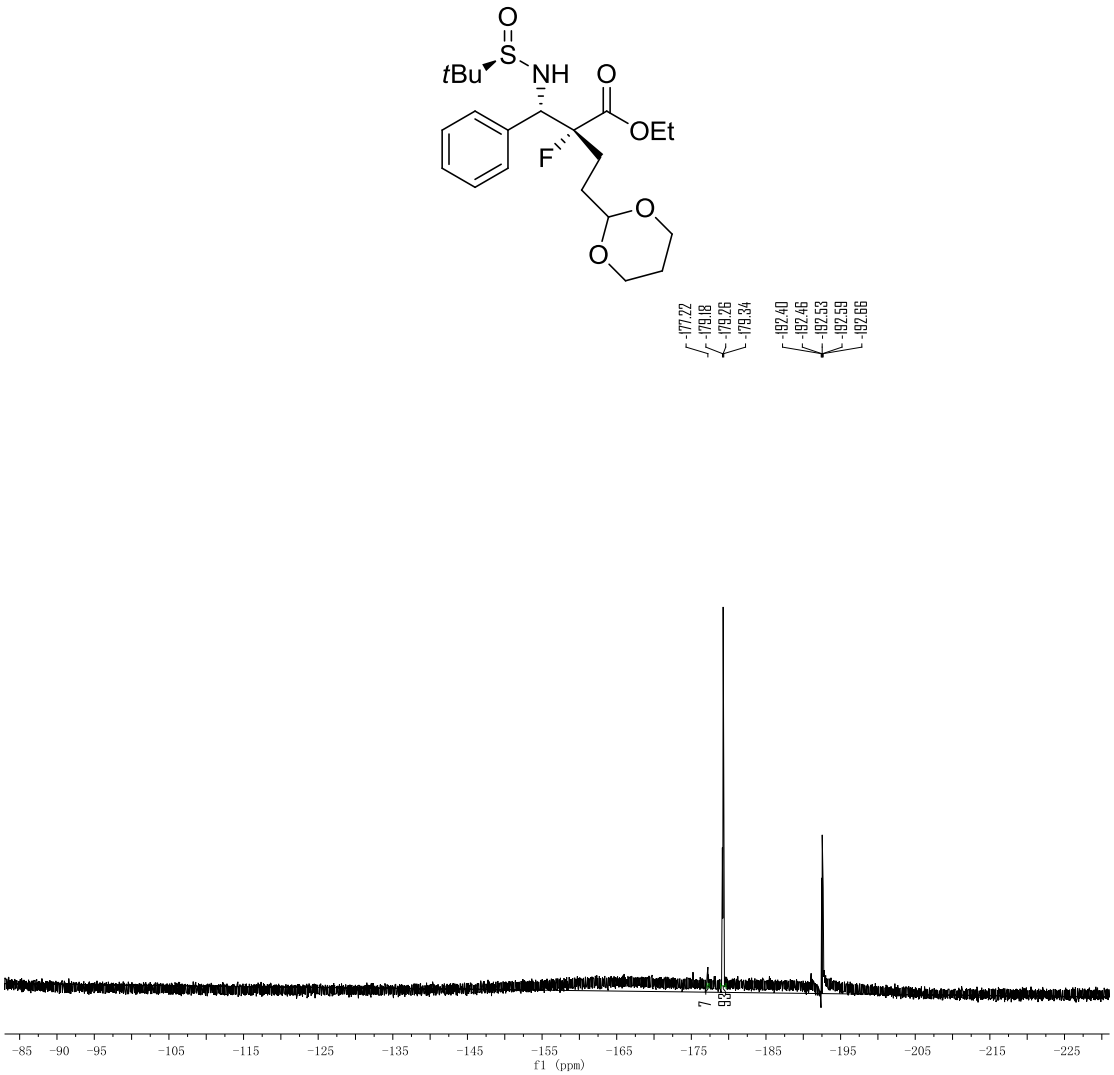
Crude **3d**, d.r. = 88:6:2:4





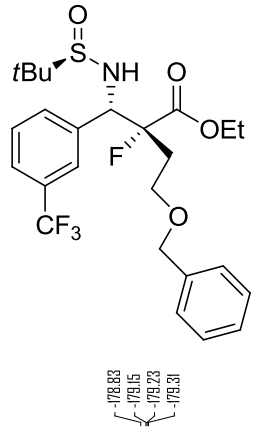
The stereoisomers are at δ -176.8− -177.1 (m), δ -177.3 − -177.7 (m), δ −178.8 (dd, *J* = 44.5, 17.4 Hz), and δ −179.5 (br).

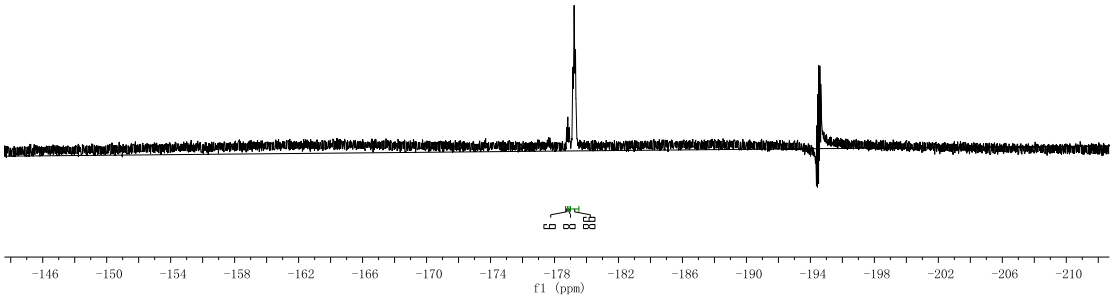
Crude **3e**, d.r. = 93:7



The stereoisomers are at δ −177.2 (s), δ −179.2 (t, J = 31.2 Hz).

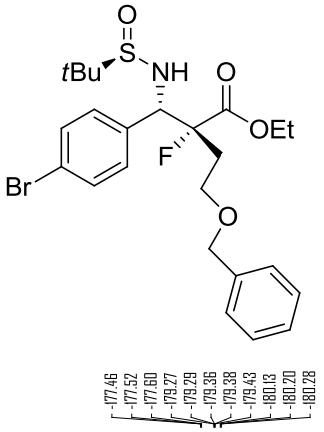
Crude **3f**, d.r. = 86:8:6

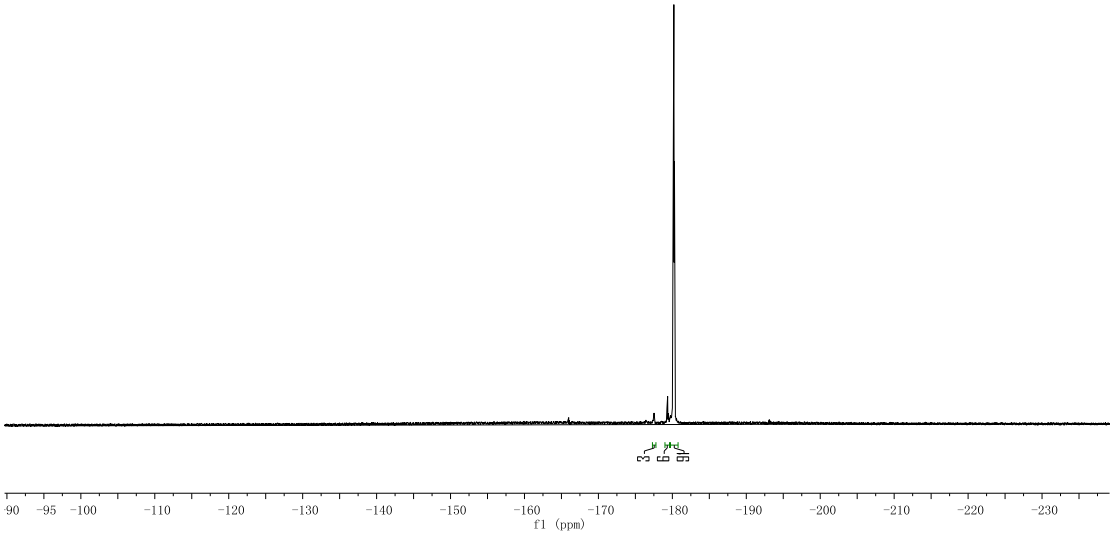




The stereoisomers are at δ −178.7 (br), δ -178.84− -178.9 (m), and δ -179.0− -179.5 (m).

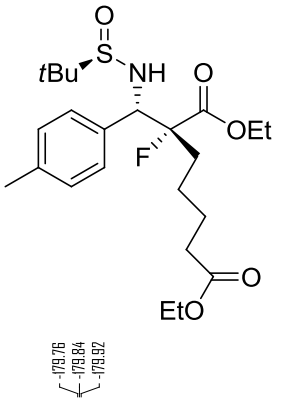
Crude **3g**, d.r. = 91:6:3

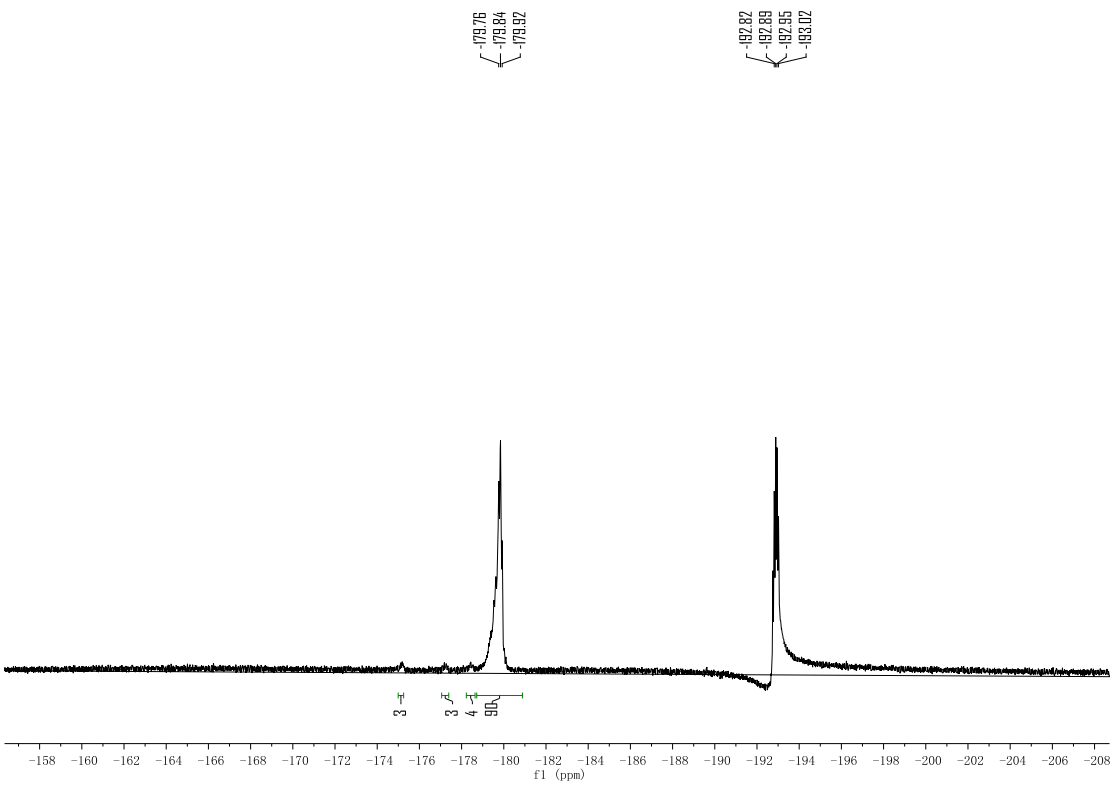




The stereoisomers are at δ -177.3 − -177.7 (m), δ -179.0 − -179.6 (m), and δ −180.2 (t, *J* = 28.8 Hz).

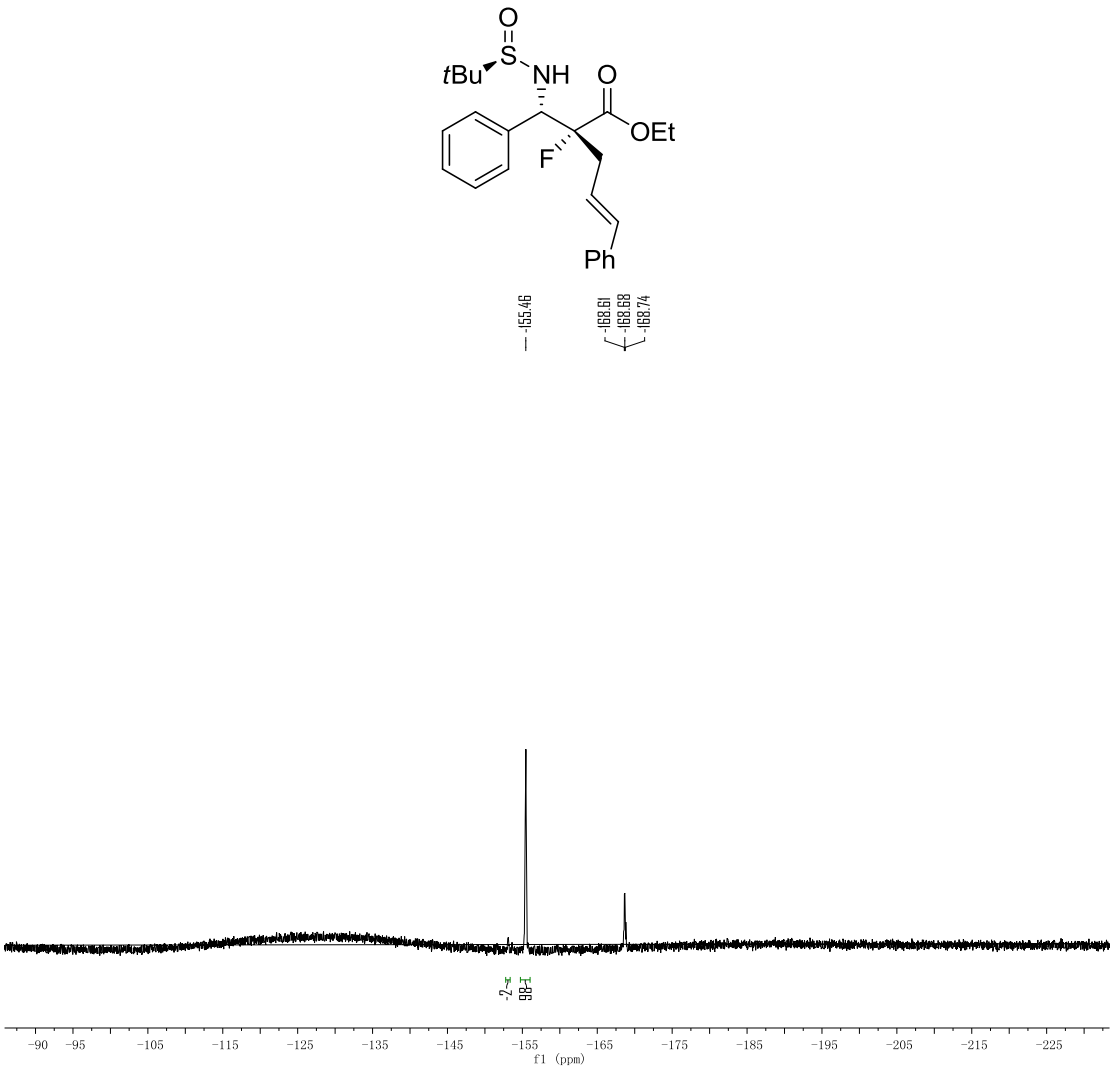
Crude **3h**, d.r. = 90:4:3:3





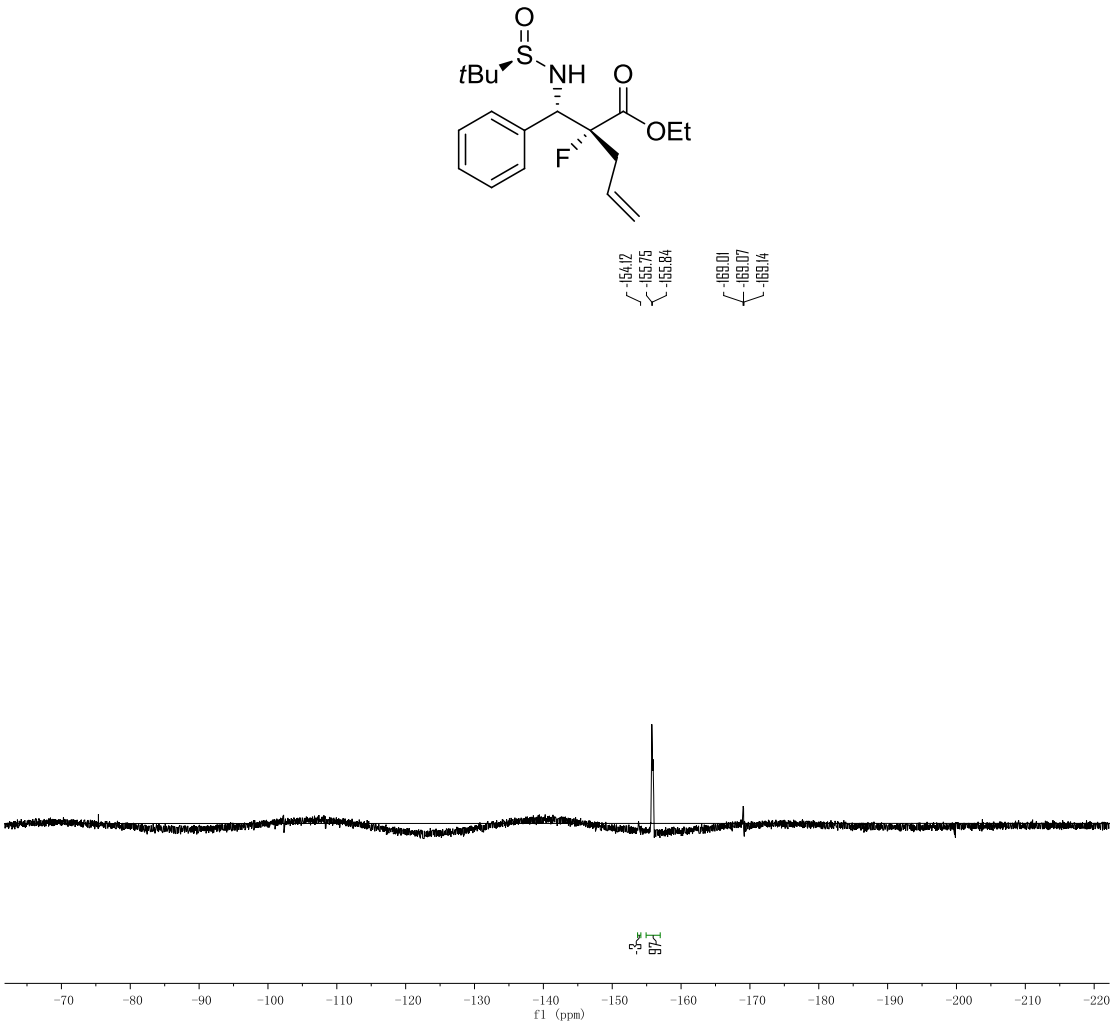
The stereoisomers are at δ -174.9 − -175.2 (m), δ -177.0 − -177.3 (m), δ -178.2 − -178.6 (m), and δ -178.7 − -180.8 (m).

Crude **3i**, d.r. = 98:2



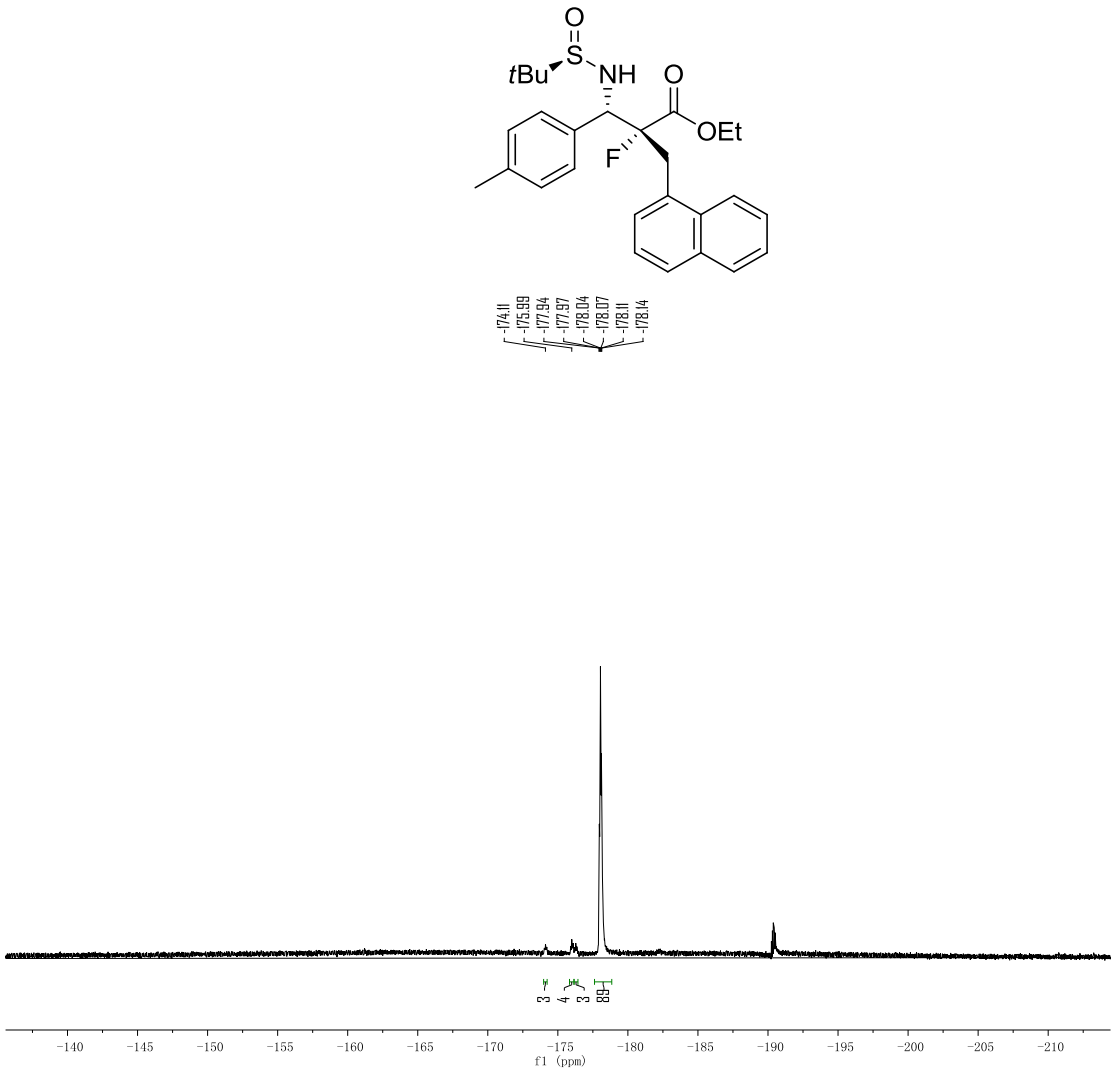
The stereoisomers are at δ -152.8 − -153.3 (m), δ −155.4 (br).

Crude **3j**, d.r. = 97:3



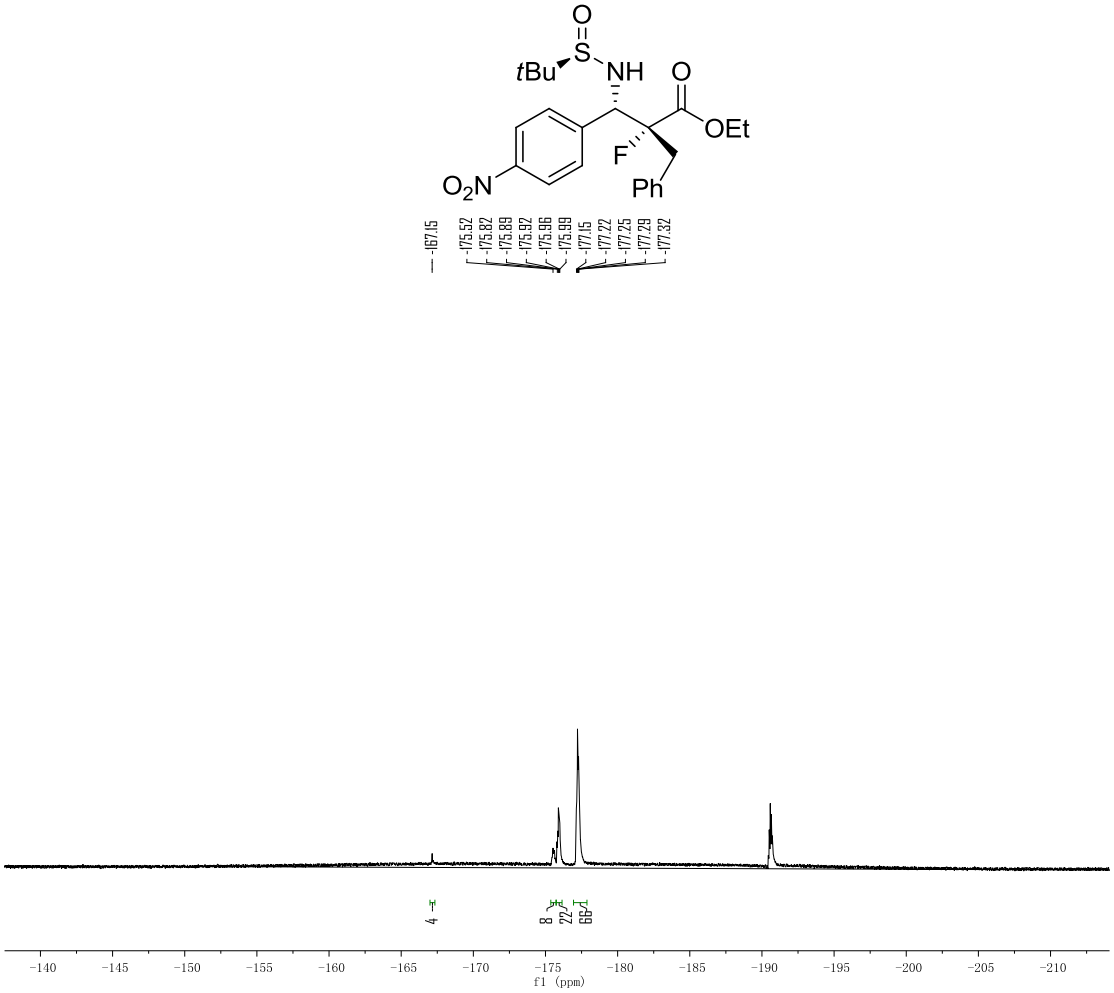
The stereoisomers are at δ −154.1 (br), δ −155.7 (d, *J* = 34.6 Hz).

Crude **3k**, d.r. = 89:3:5:3



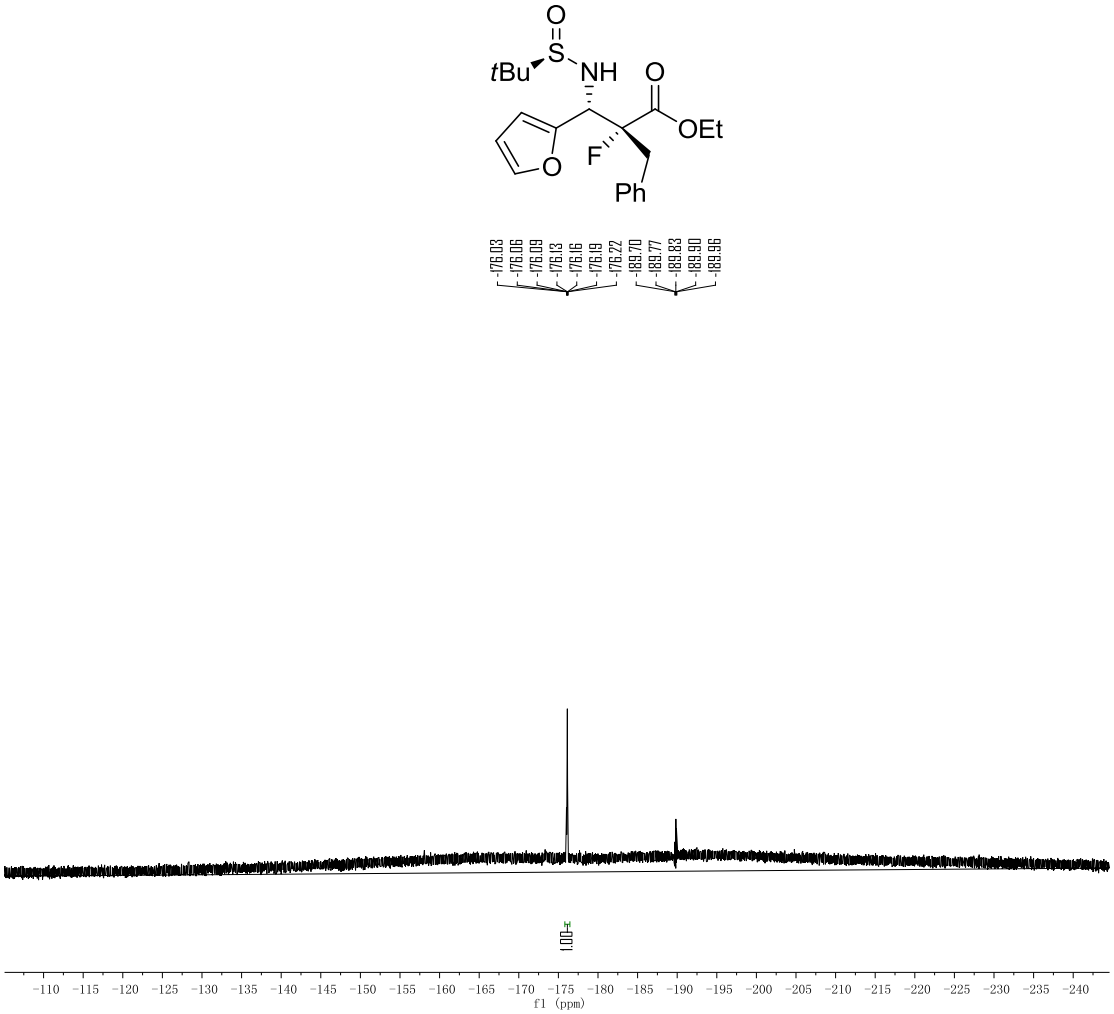
The stereoisomers are at δ −174.1 (br), δ −175.9 (br), δ -176.1 − -176.4 (m), δ -177.6 − -178.8 (m).

Crude **3l**, d.r. = 66:22:8:4



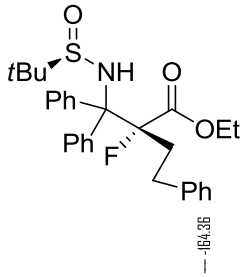
The stereoisomers are at δ −167.1 (br), δ −175.5 (br), δ -175.7 − -176.1 (br), δ -176.9 − -177.8 (m).

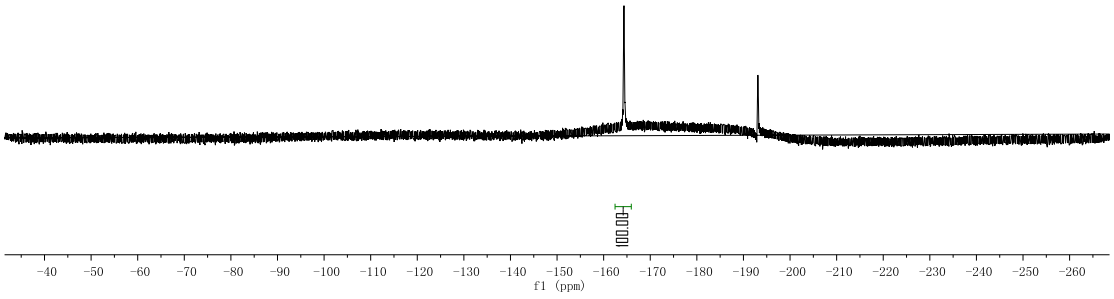
Crude **3m**, d.r. > 99:1



The stereoisomers are at δ -175.8 − -176.4 (m).

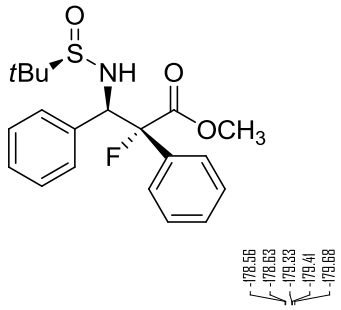
Crude **3n**, d.r. > 99:1

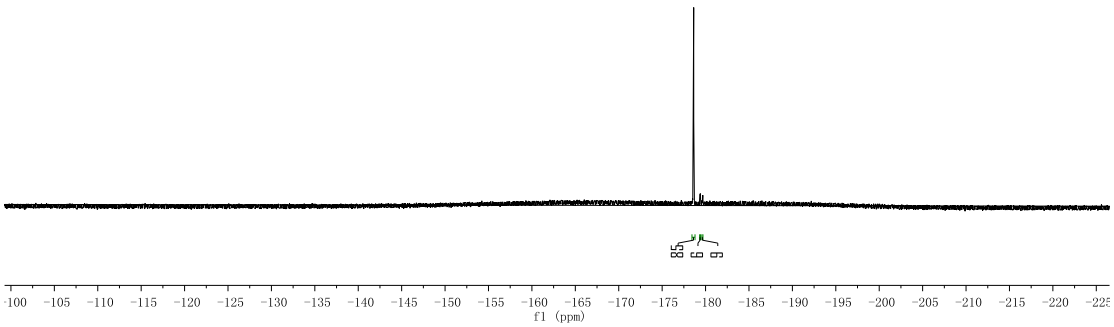




The stereoisomer is at δ −164.3 (br).

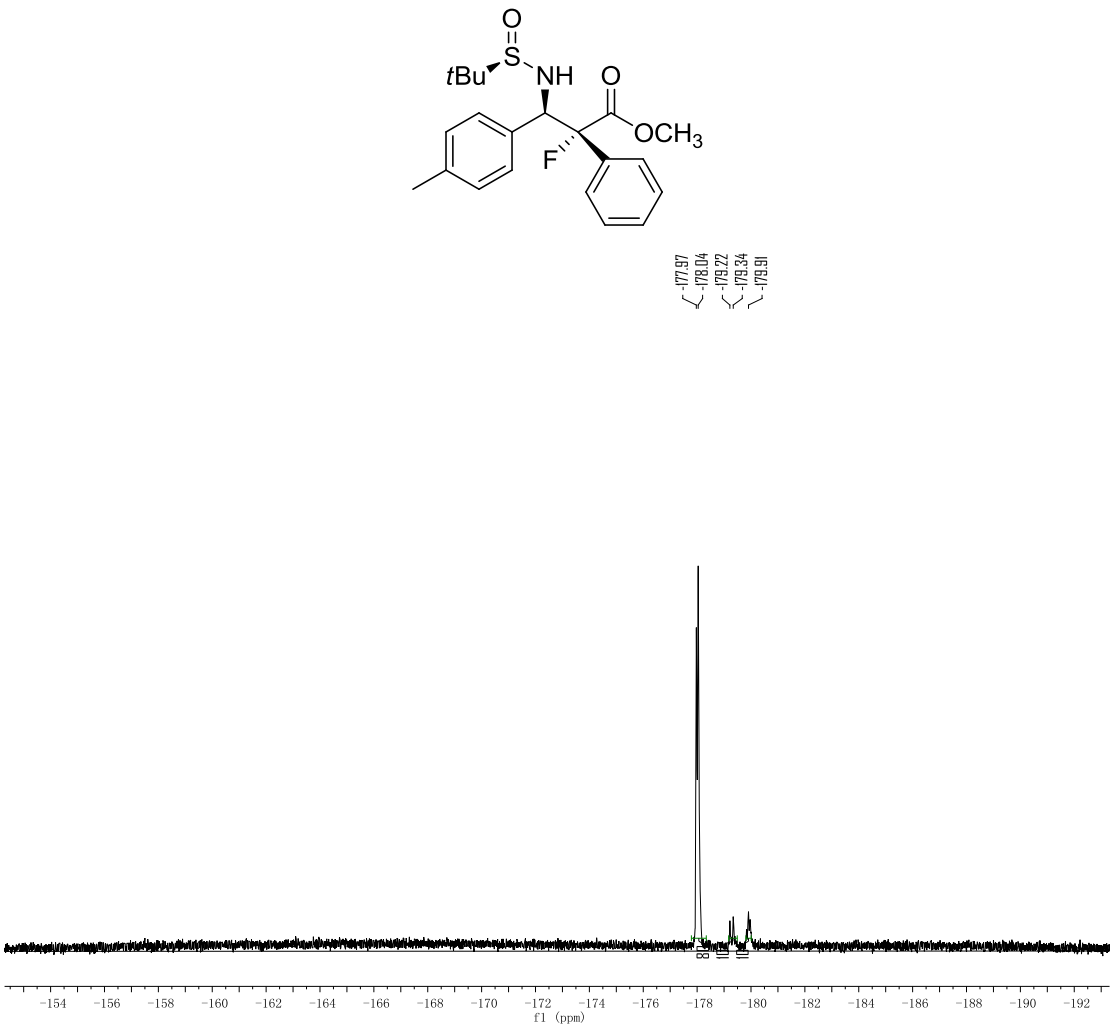
Crude **5a**, d.r. = 85:6:9





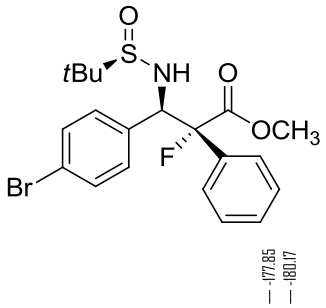
The stereoisomers are at δ −178.6 (d, *J* = 25.7 Hz), δ −179.3 (d, J = 26.7 Hz), δ −179.6 (br)

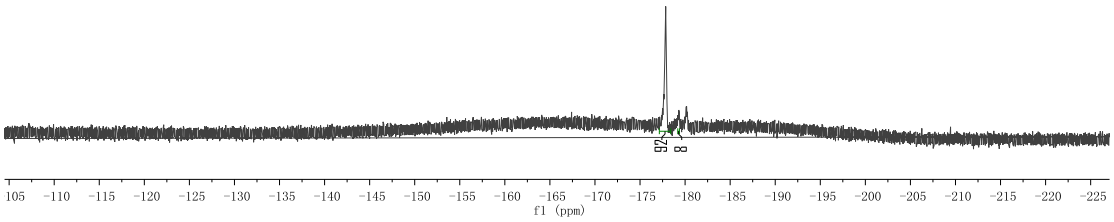
Crude **5b**, d.r. = 80:10:10



The stereoisomers are at δ −178.0 (d, J = 26.0 Hz), −179.2 (d, J = 47.0 Hz), −179.9 (br).

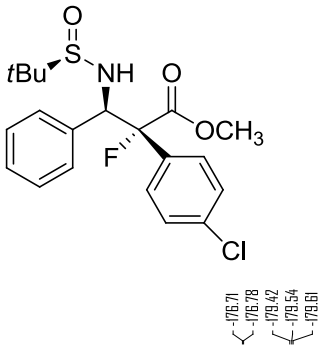
Crude **5c**, d.r. = 92:8

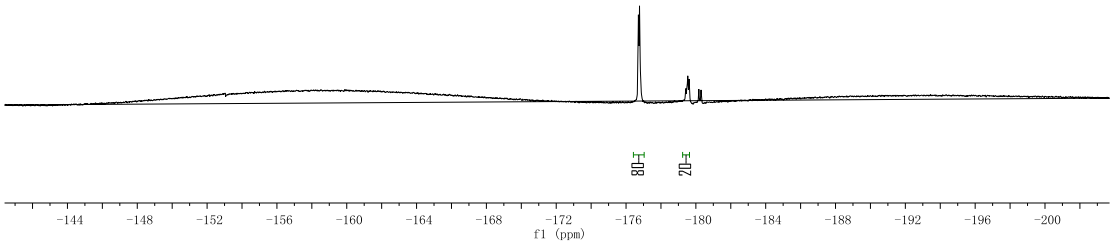




The stereoisomers are at δ −177.8 (br), −180.1 (br).

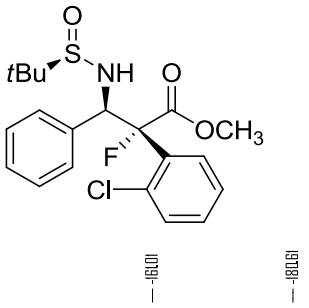
Crude **5d**, d.r. = 80:20

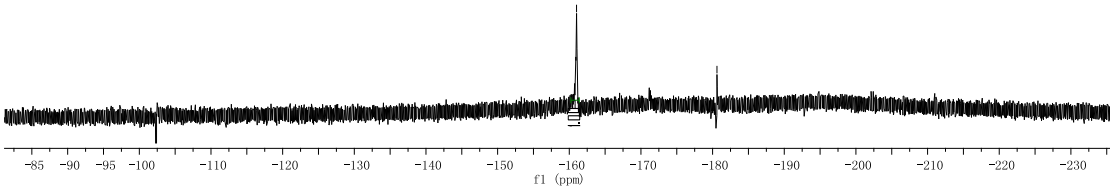




The stereoisomers are at δ −176.7 (d, *J* = 24.7 Hz), −179.5 (t, *J* = 35.8 Hz).

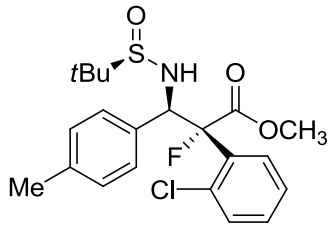
Crude **5e**, d.r. > 99:1

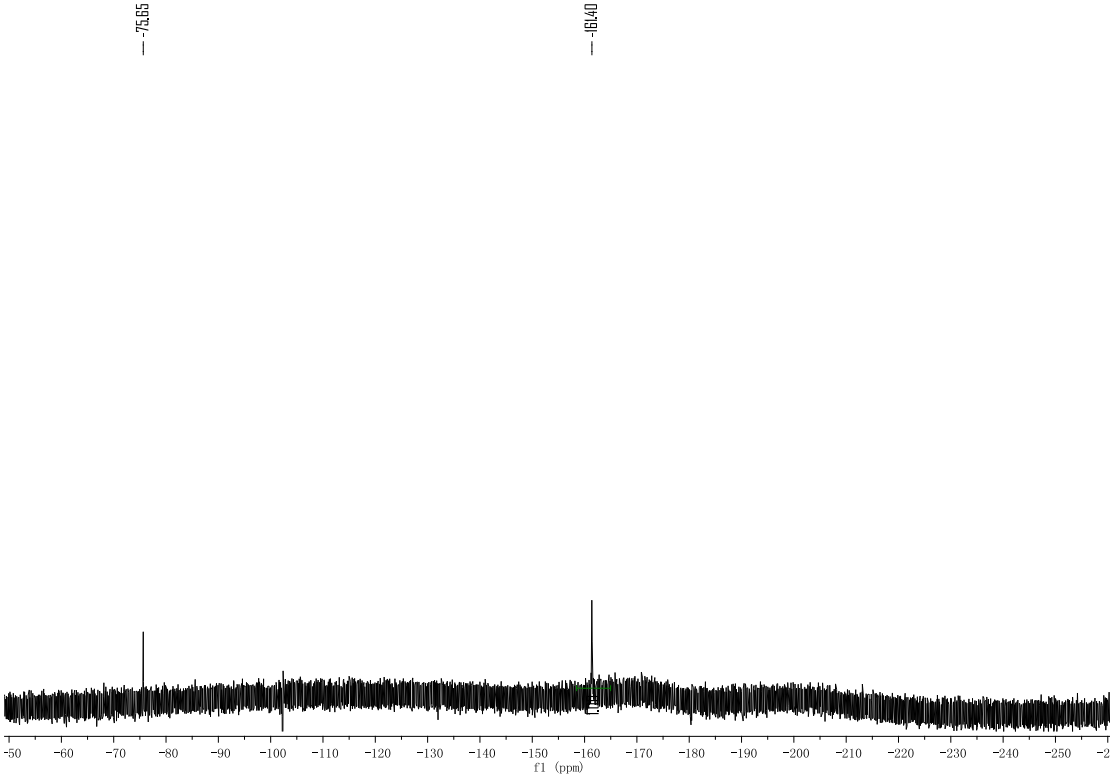




The stereoisomers are at δ −161.0 (br).

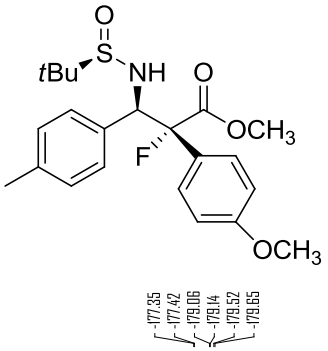
Crude **5f**, d.r. > 99:1

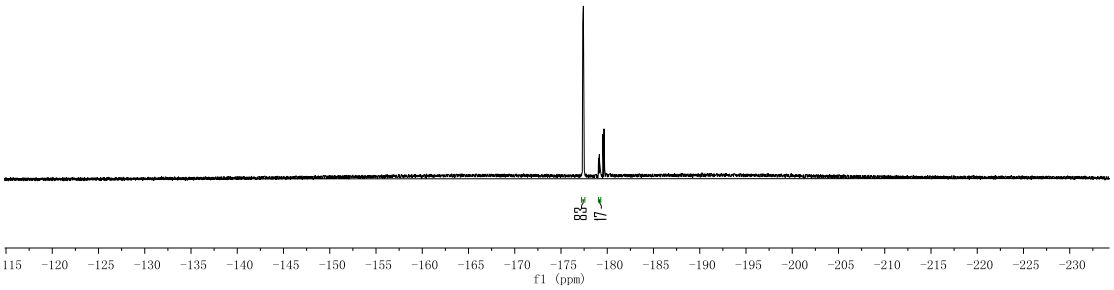




The stereoisomers are at δ −161.40 (s).

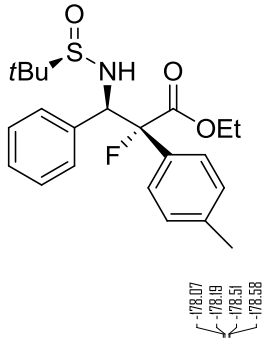
Crude **5g**, d.r. =83:17

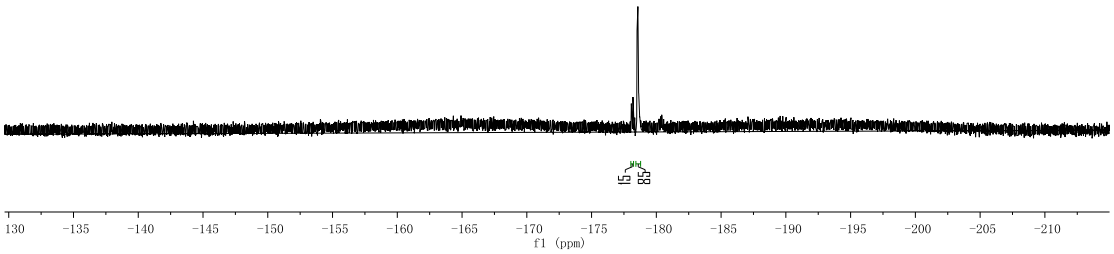




The stereoisomers are at δ −177.3 (d, *J* = 26.1 Hz), −179.1 (d, *J* = 30.0 Hz).

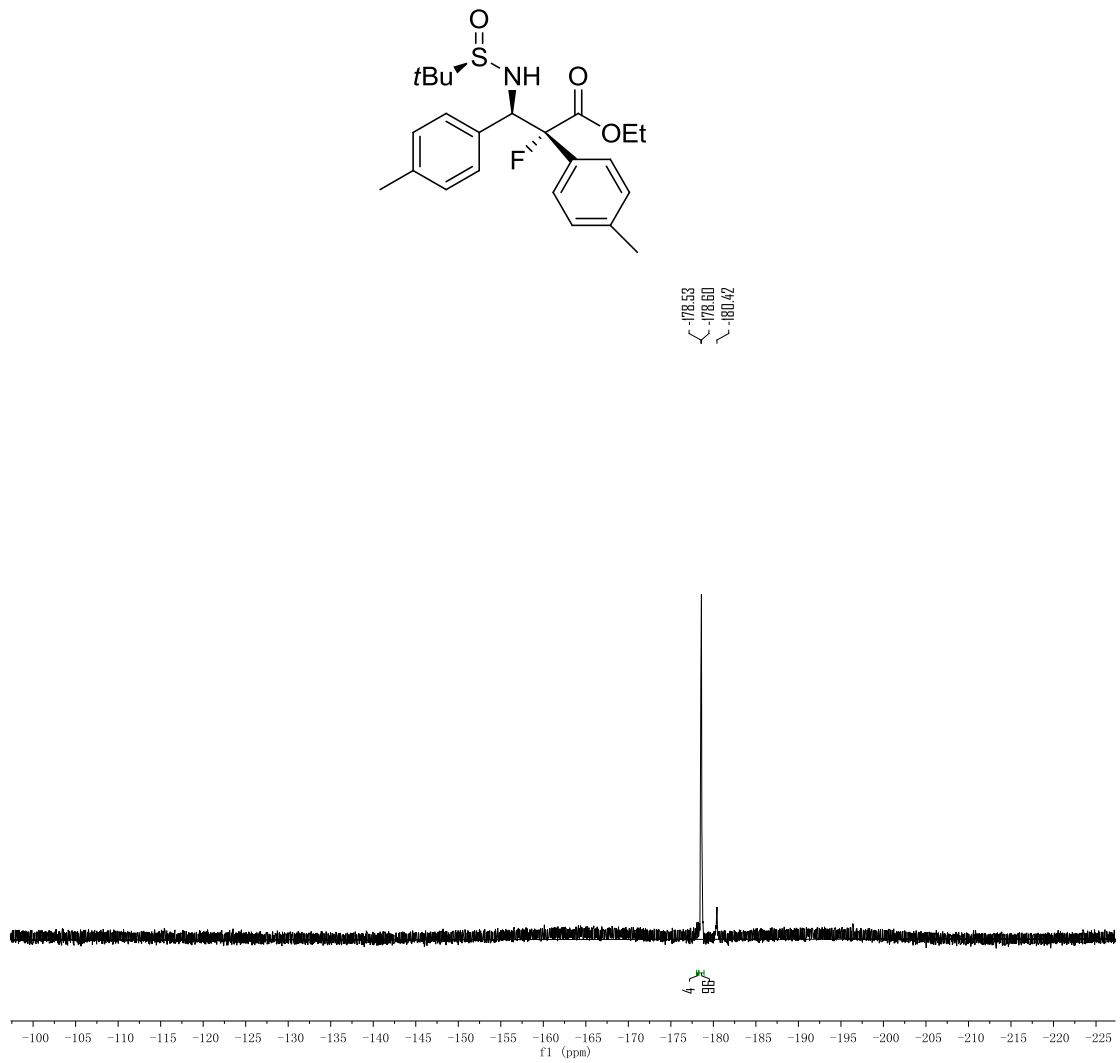
Crude **5h**, d.r. =85:15





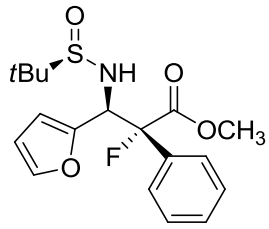
The stereoisomers are at δ −178.1 (d, *J* = 47.3 Hz), −178.5 (d, *J* = 25.3 Hz).

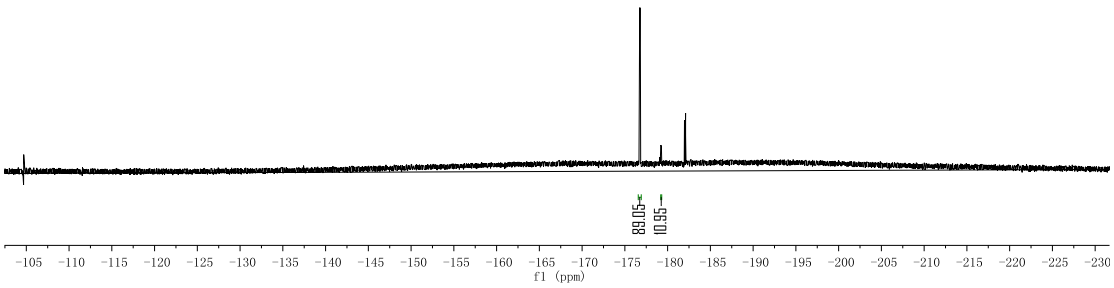
Crude **5i**, d.r. =96:4



The stereoisomers are at δ -178.01 − -178.24 (m), −178.56 (d, J = 25.8 Hz)

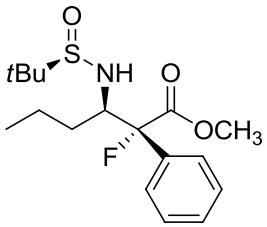
Crude **5j**, d.r. =89:11

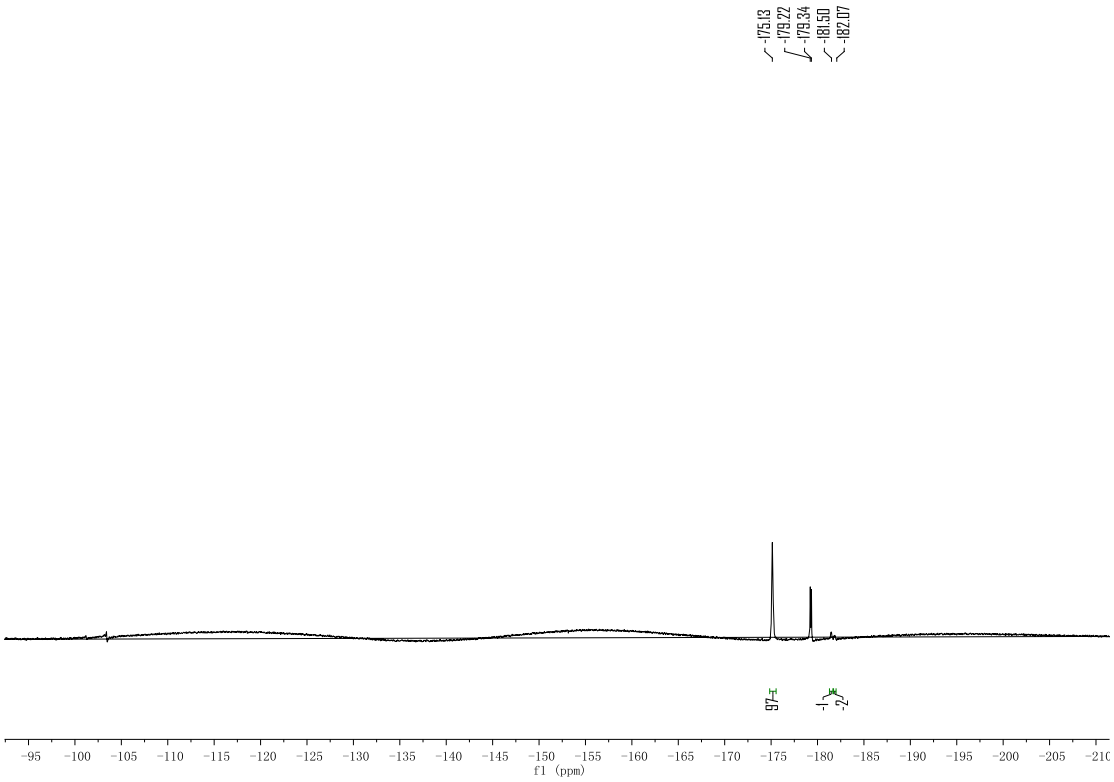




The stereoisomers are at δ −176.7 (d, *J* = 25.8 Hz), −179.2 (d, *J* = 27.7 Hz).

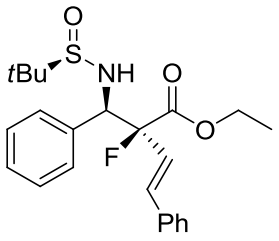
Crude **5k**, d.r. =97:1:2

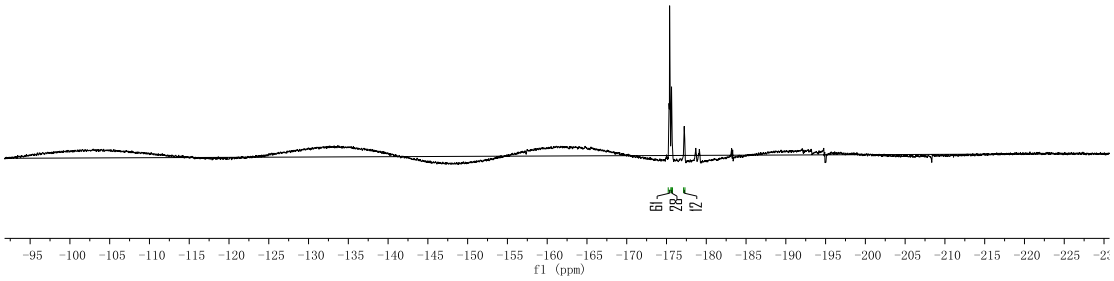




The stereoisomers are at δ −175.1 (br), −181.5 (br), -181.7 − -182.0 (m).

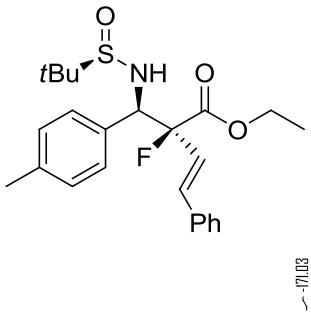
Crude **7a**, d.r. =60:28:12

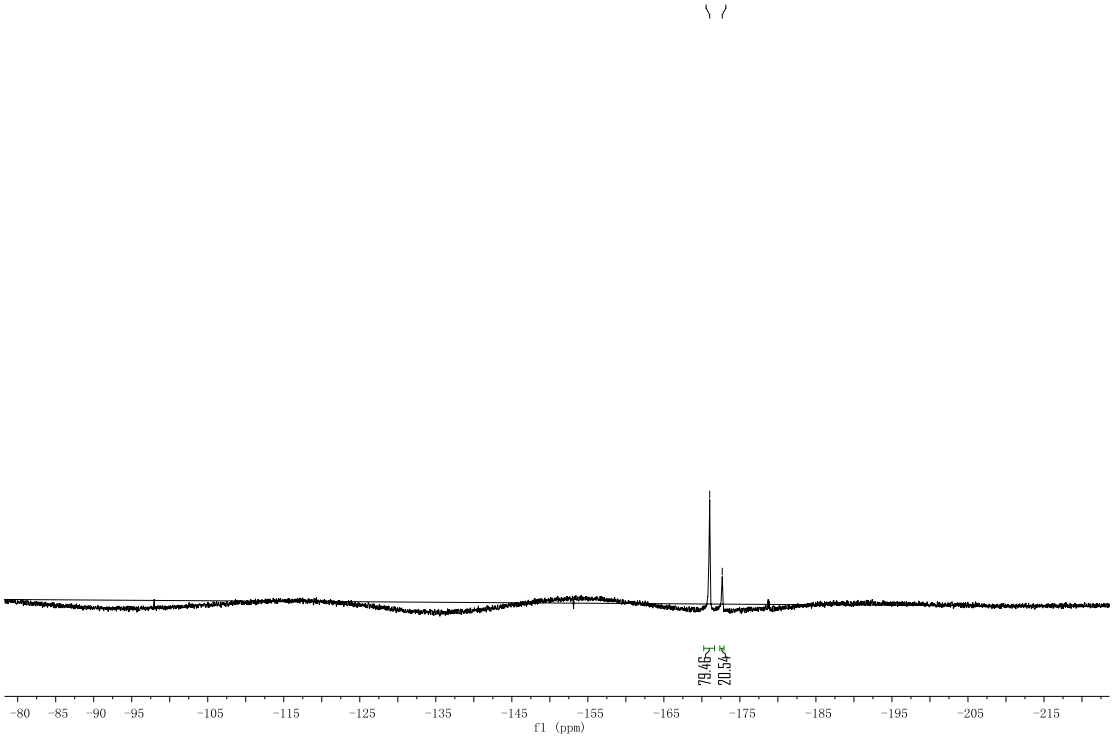




The stereoisomers are at δ −175.3 (t, J = 20.9 Hz), −175.6 (d, J = 19.5 Hz), −177.2 (t, J = 22.7 Hz).

Crude **7b**, d.r. =79:21

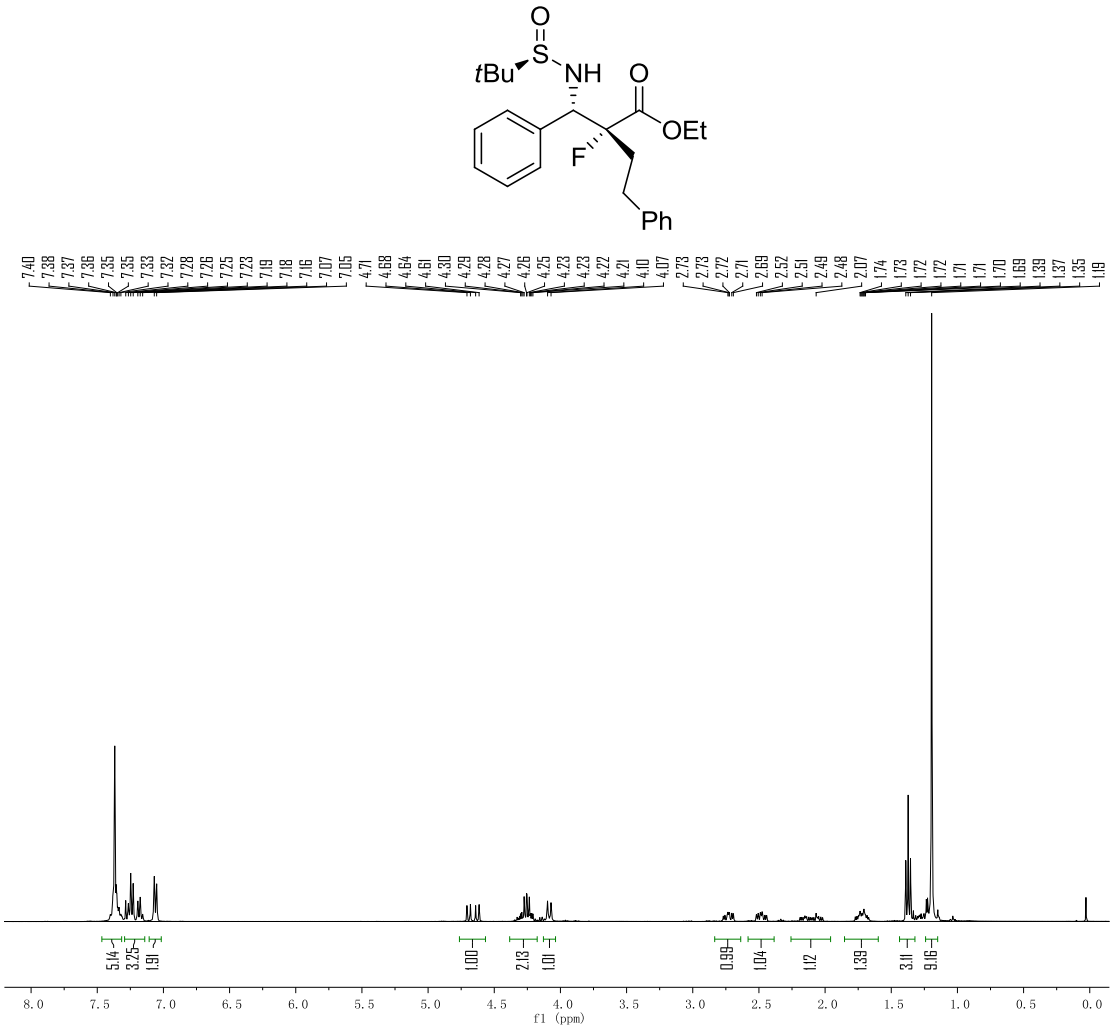




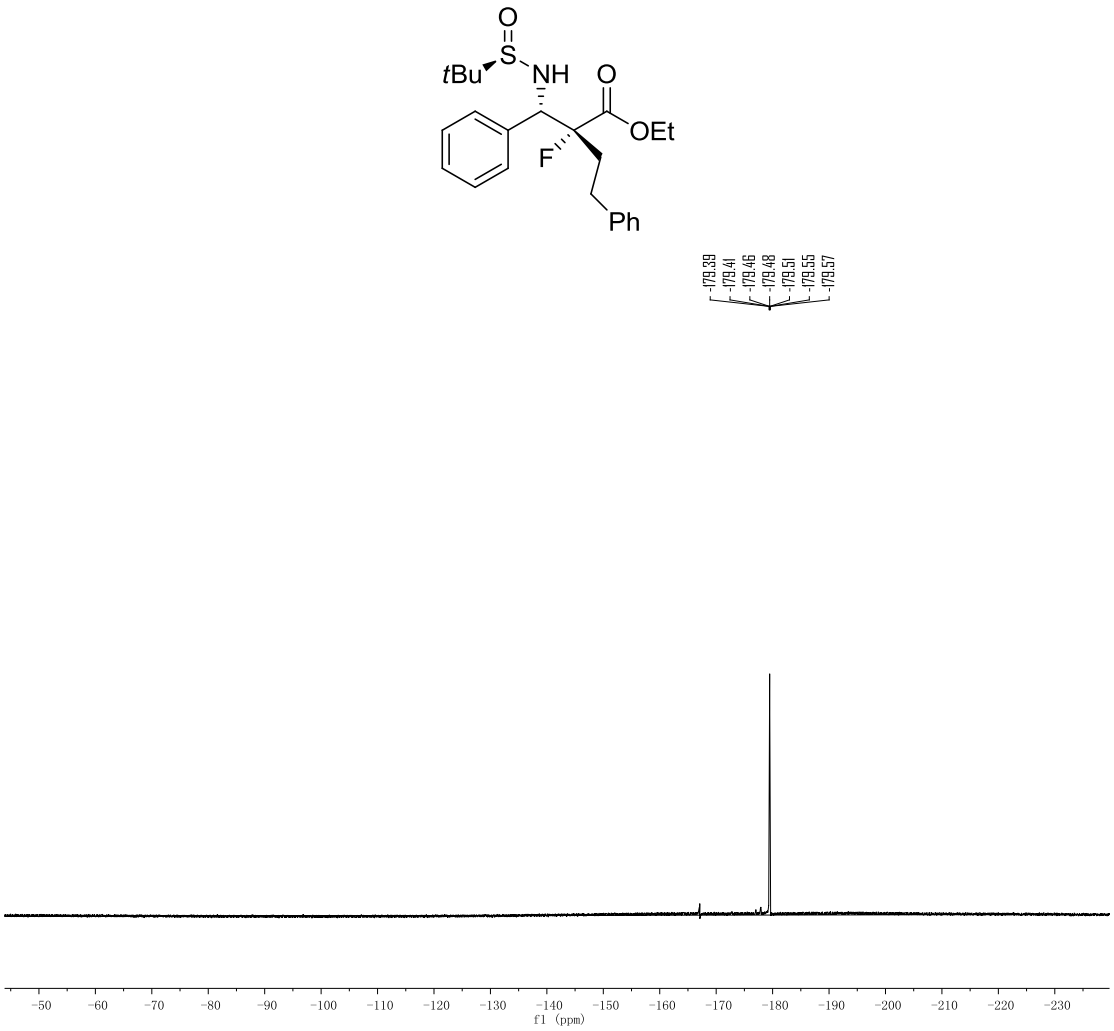
The stereoisomers are at δ −171.0 (br), −172.6 (br).

NMR Spectra for All New Compounds

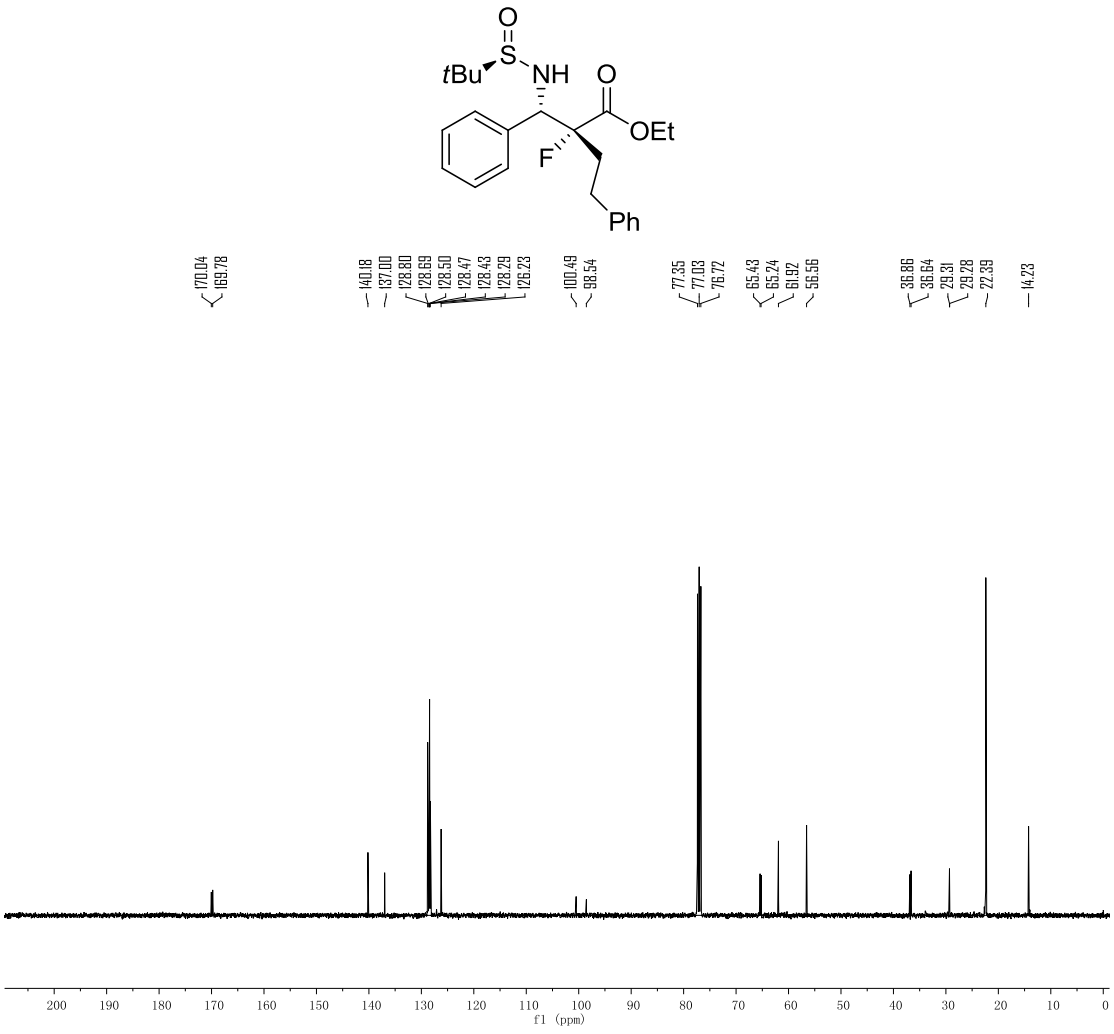
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



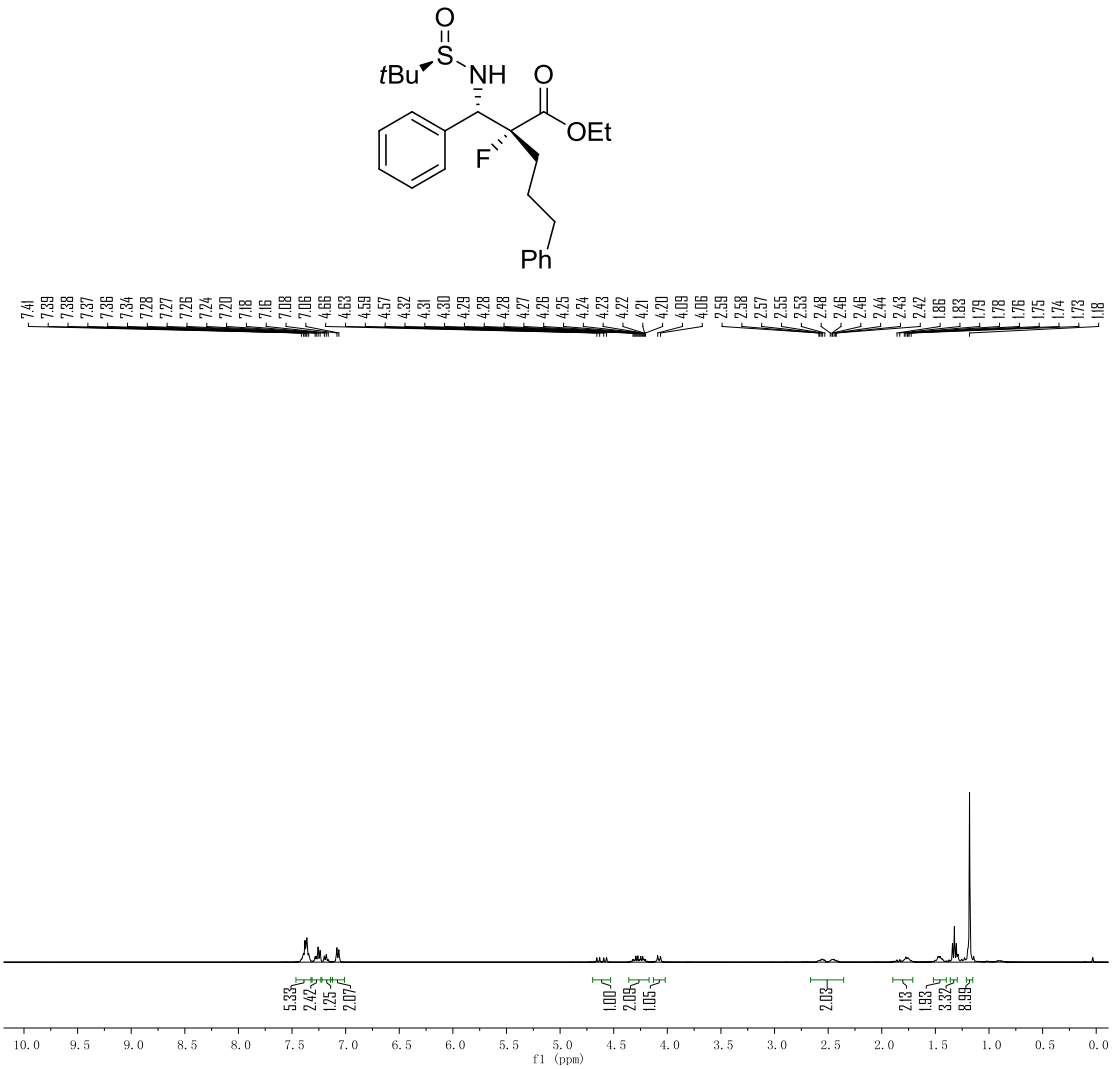
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3a**



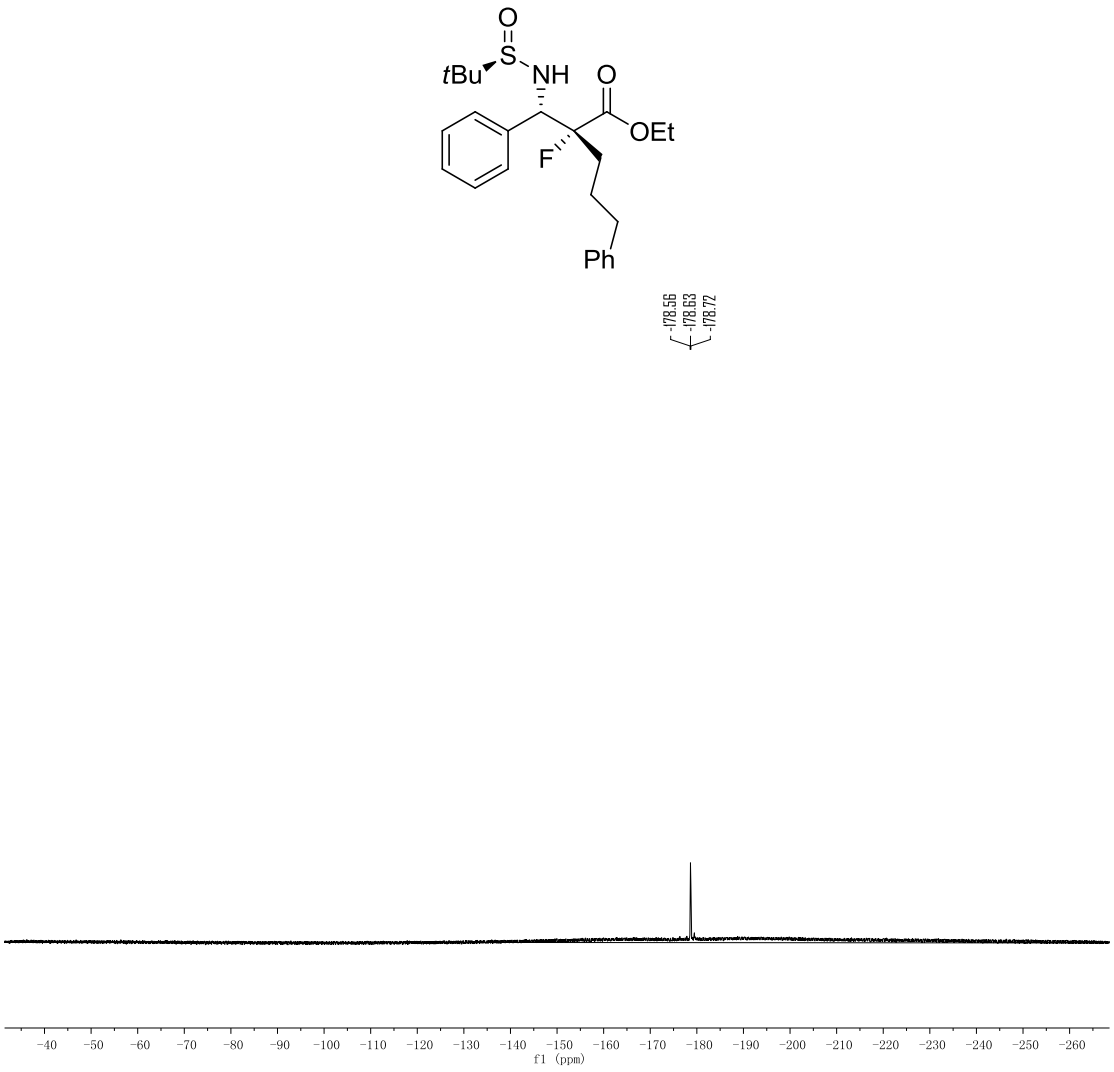
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**



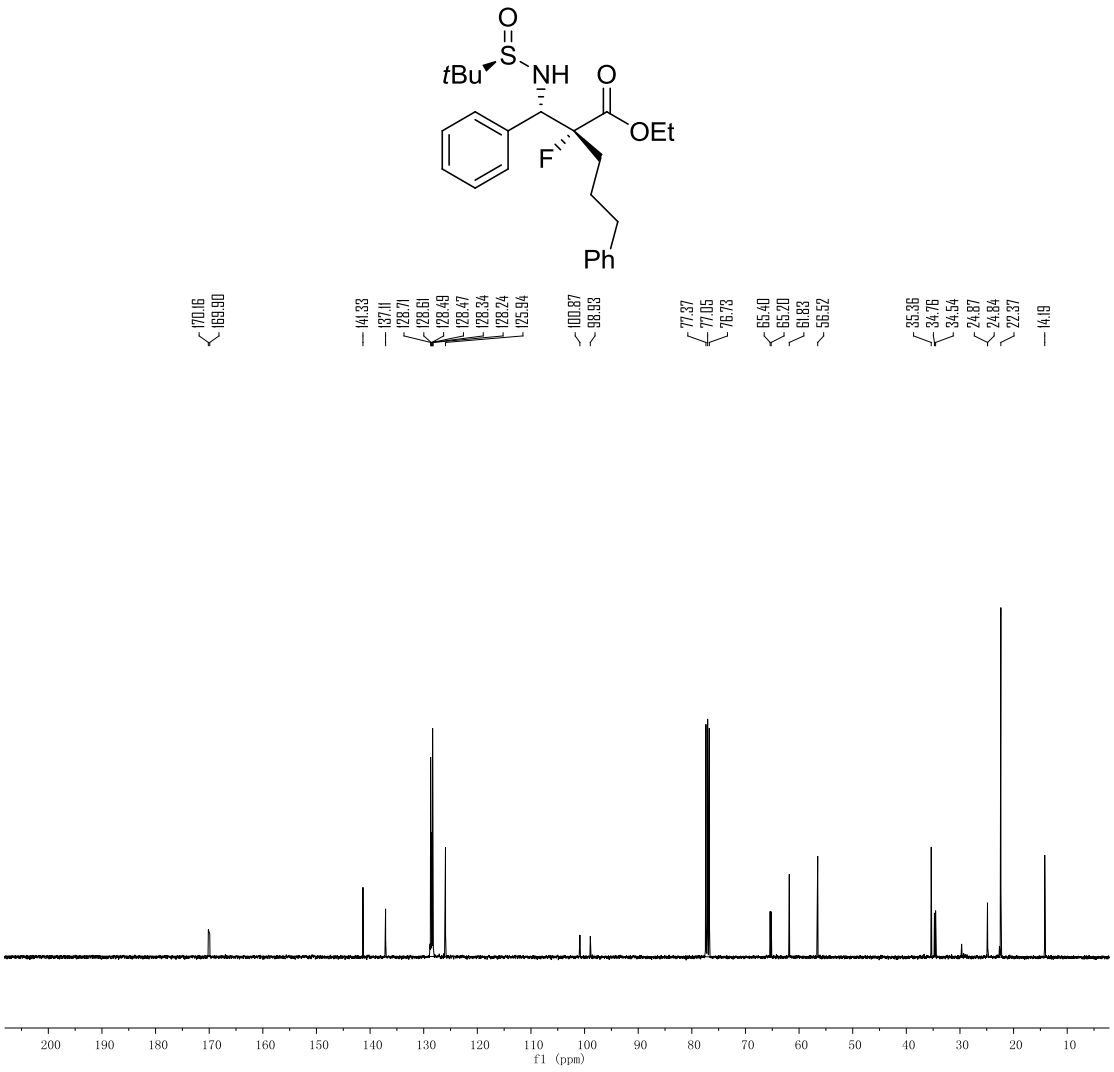
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



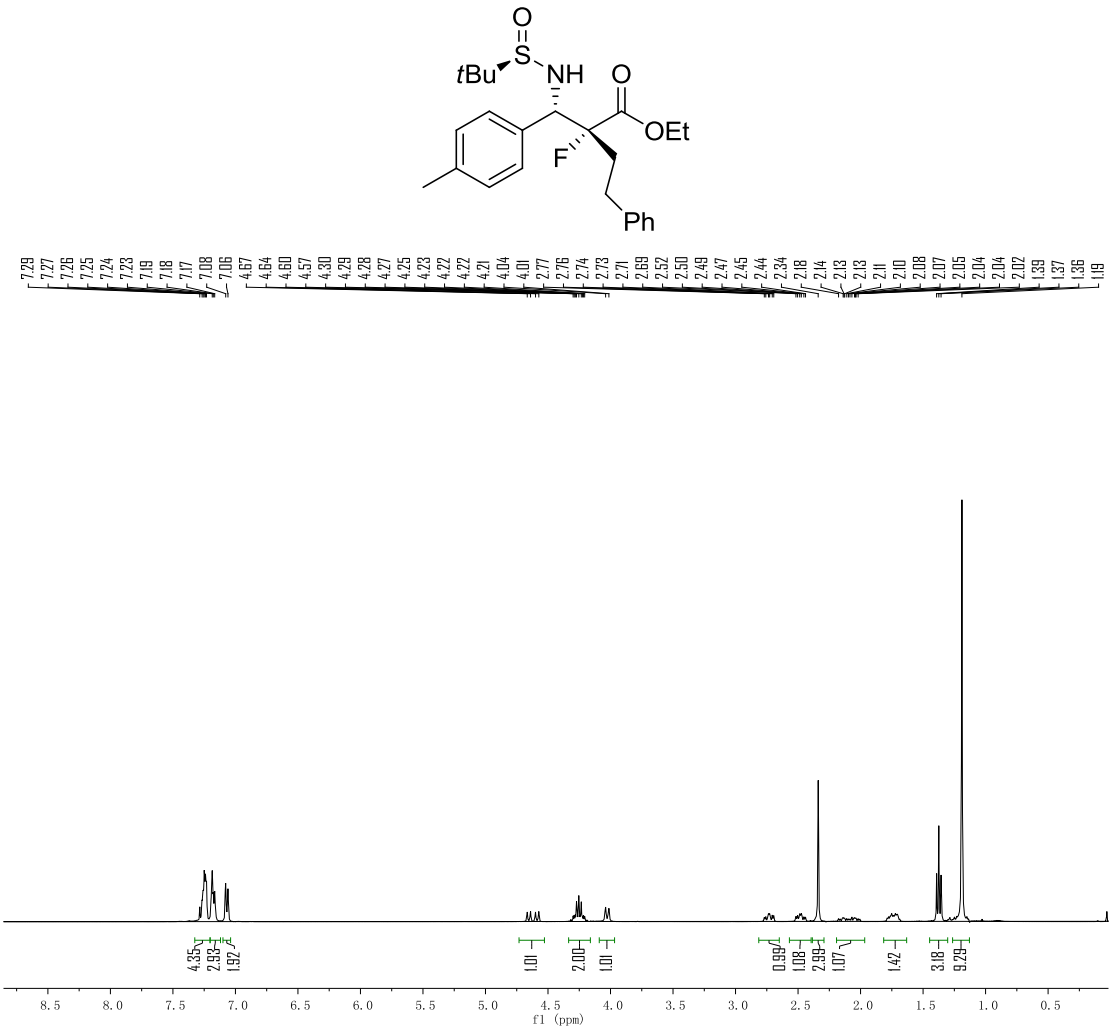
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3b**



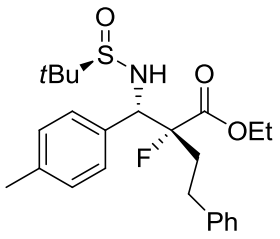
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**

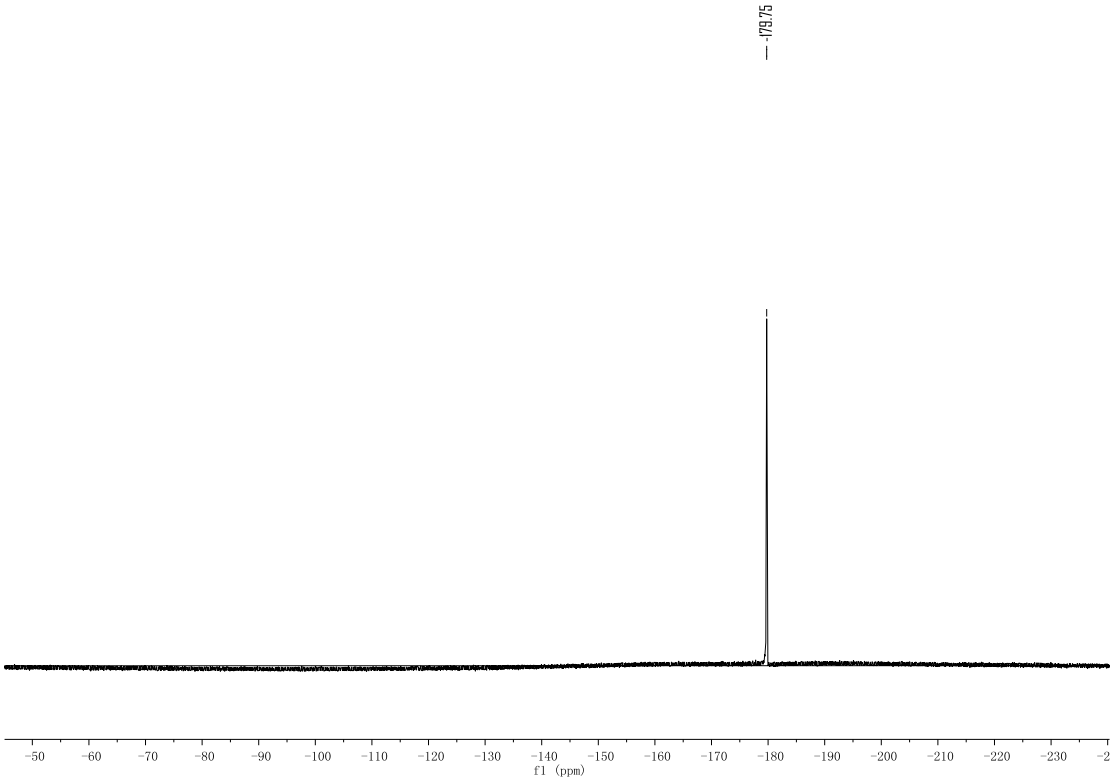


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



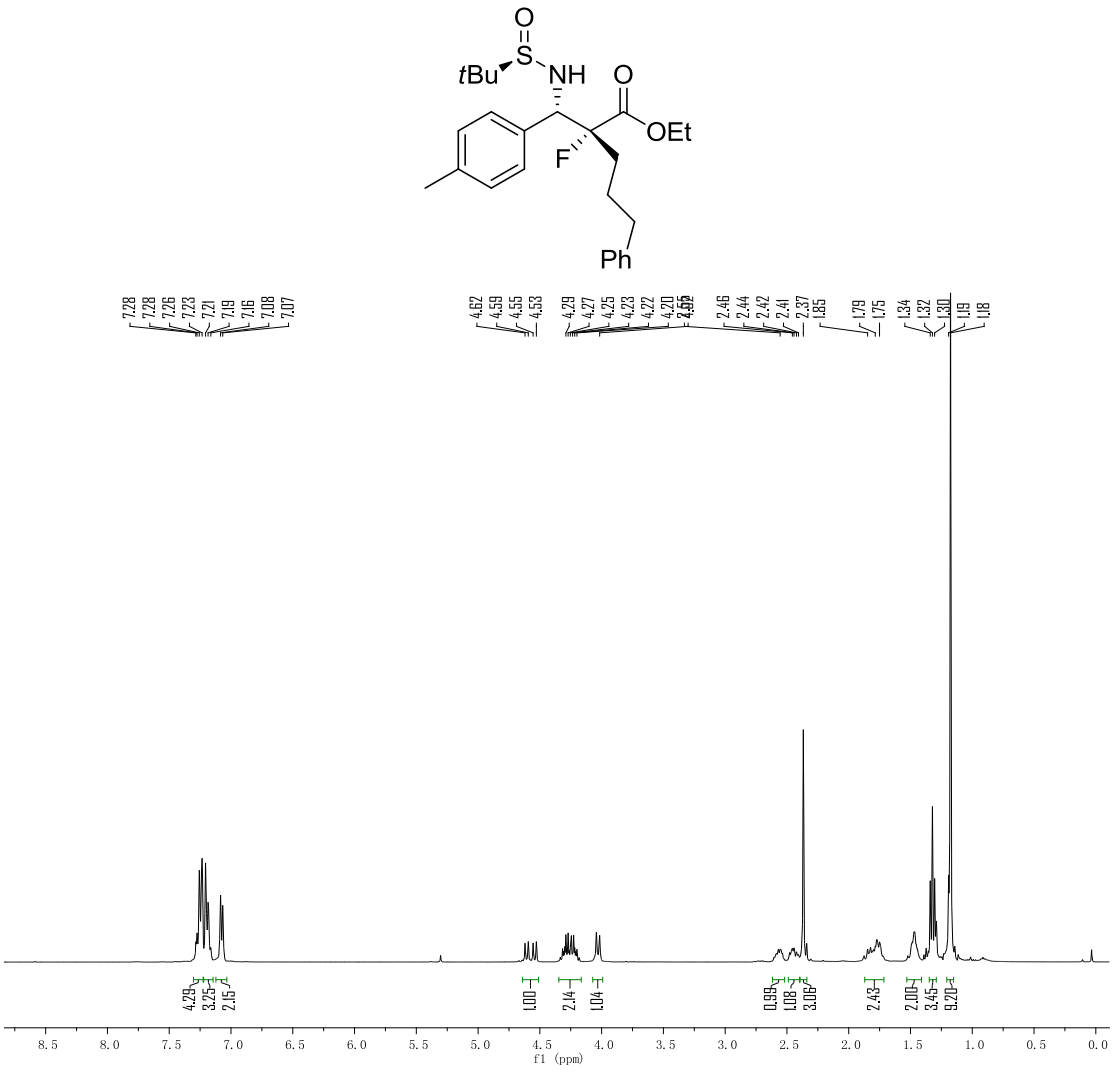
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3c**



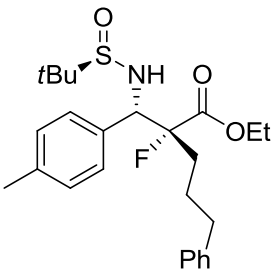


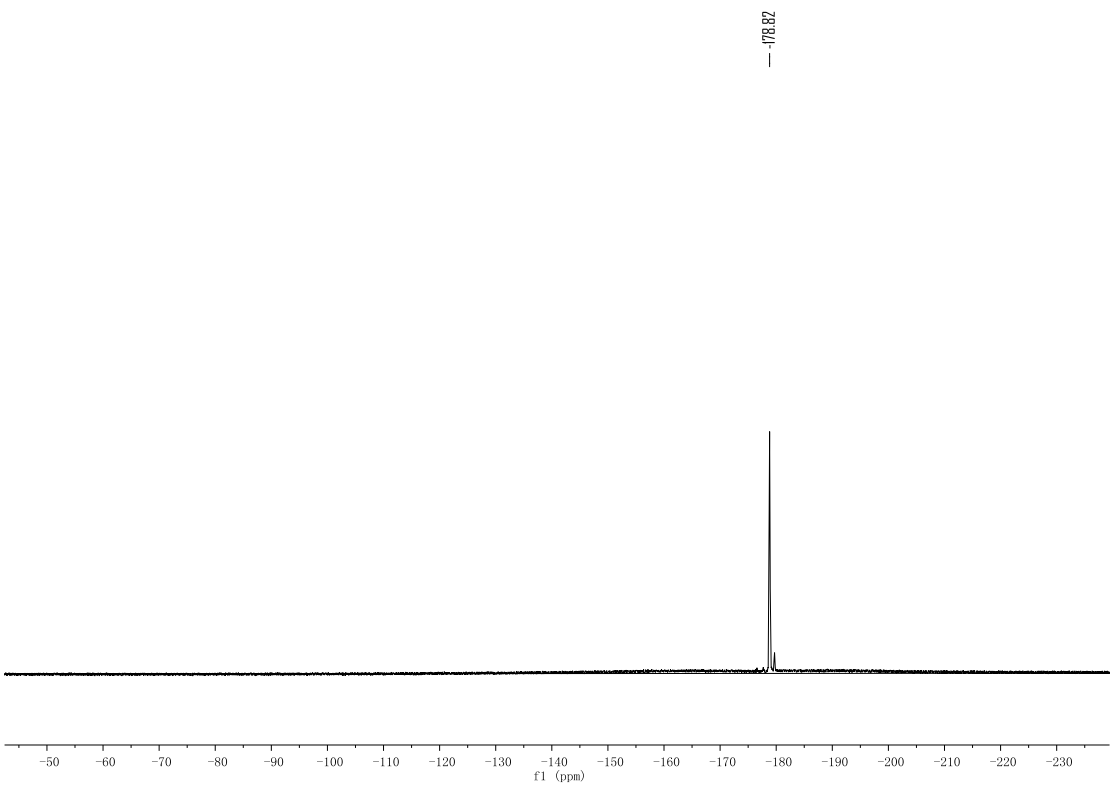
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3c**

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

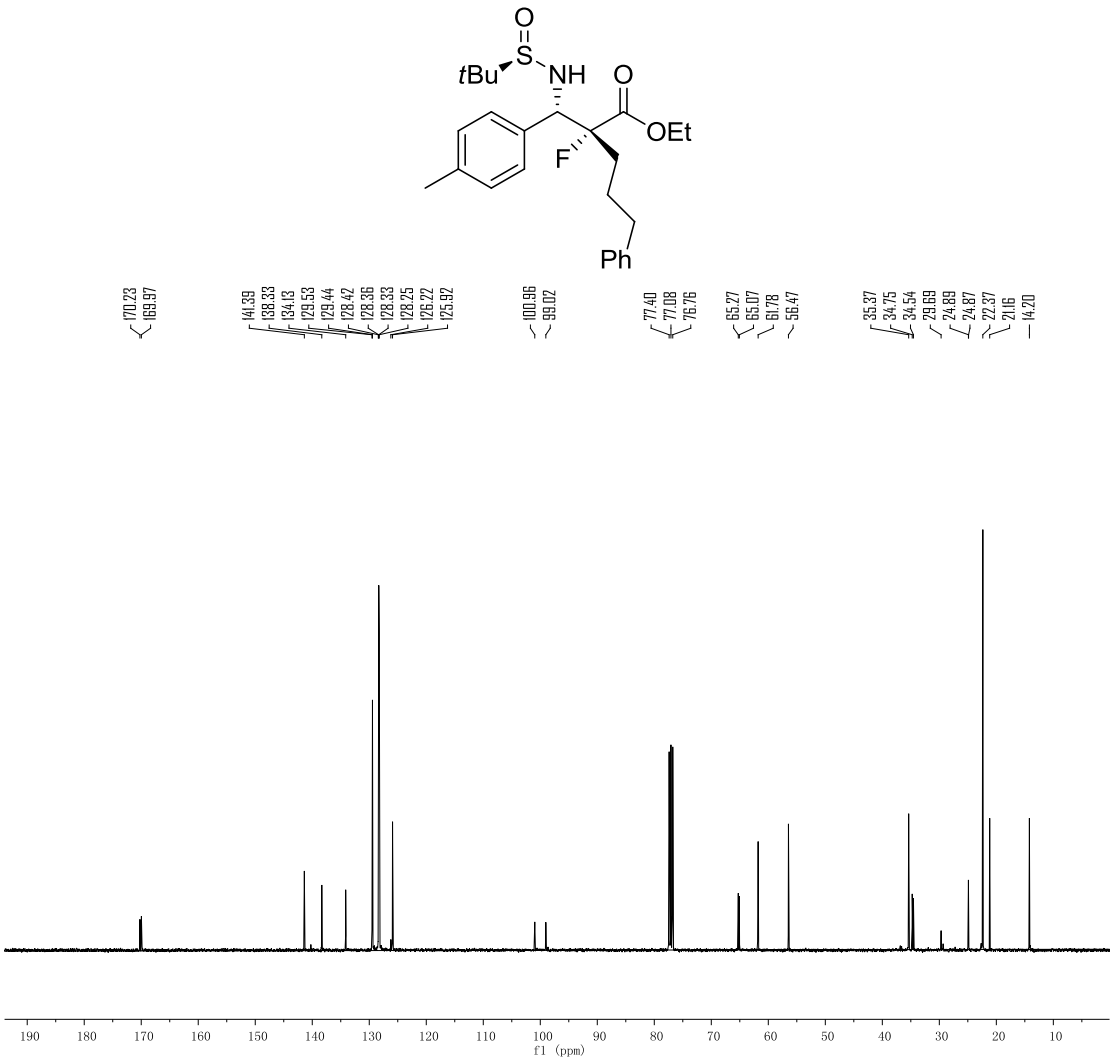


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3d**

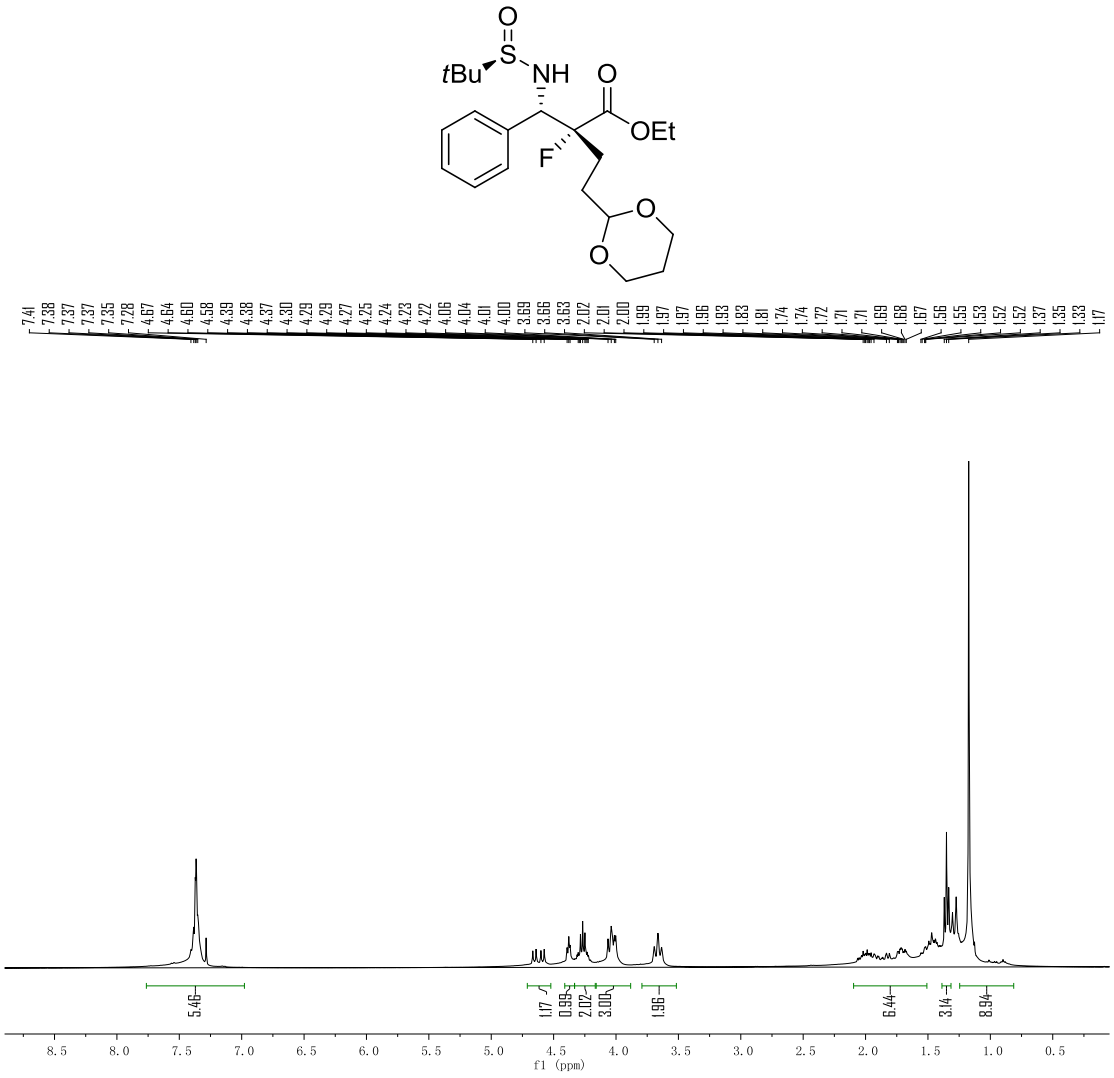




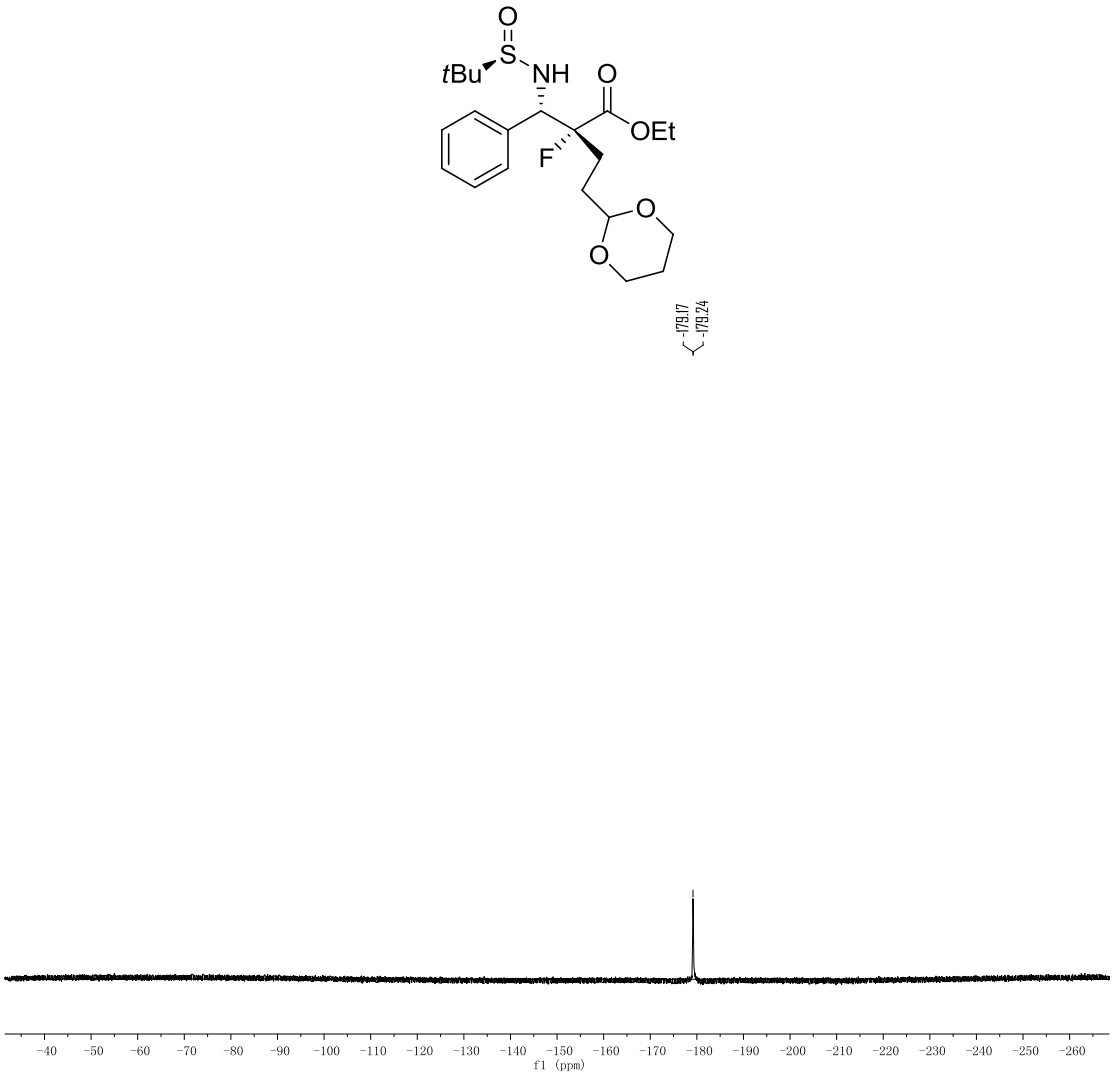
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3d**



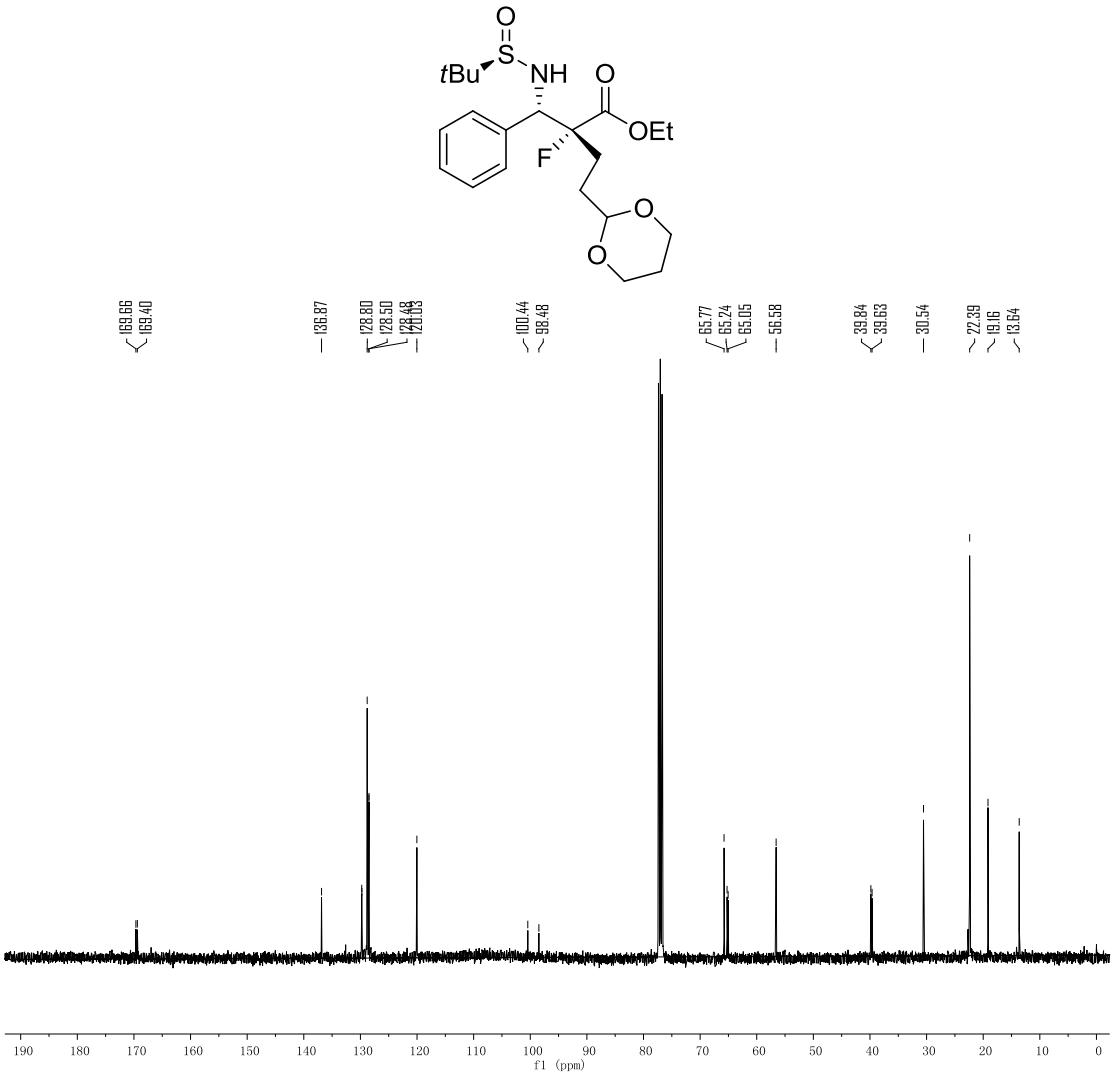
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



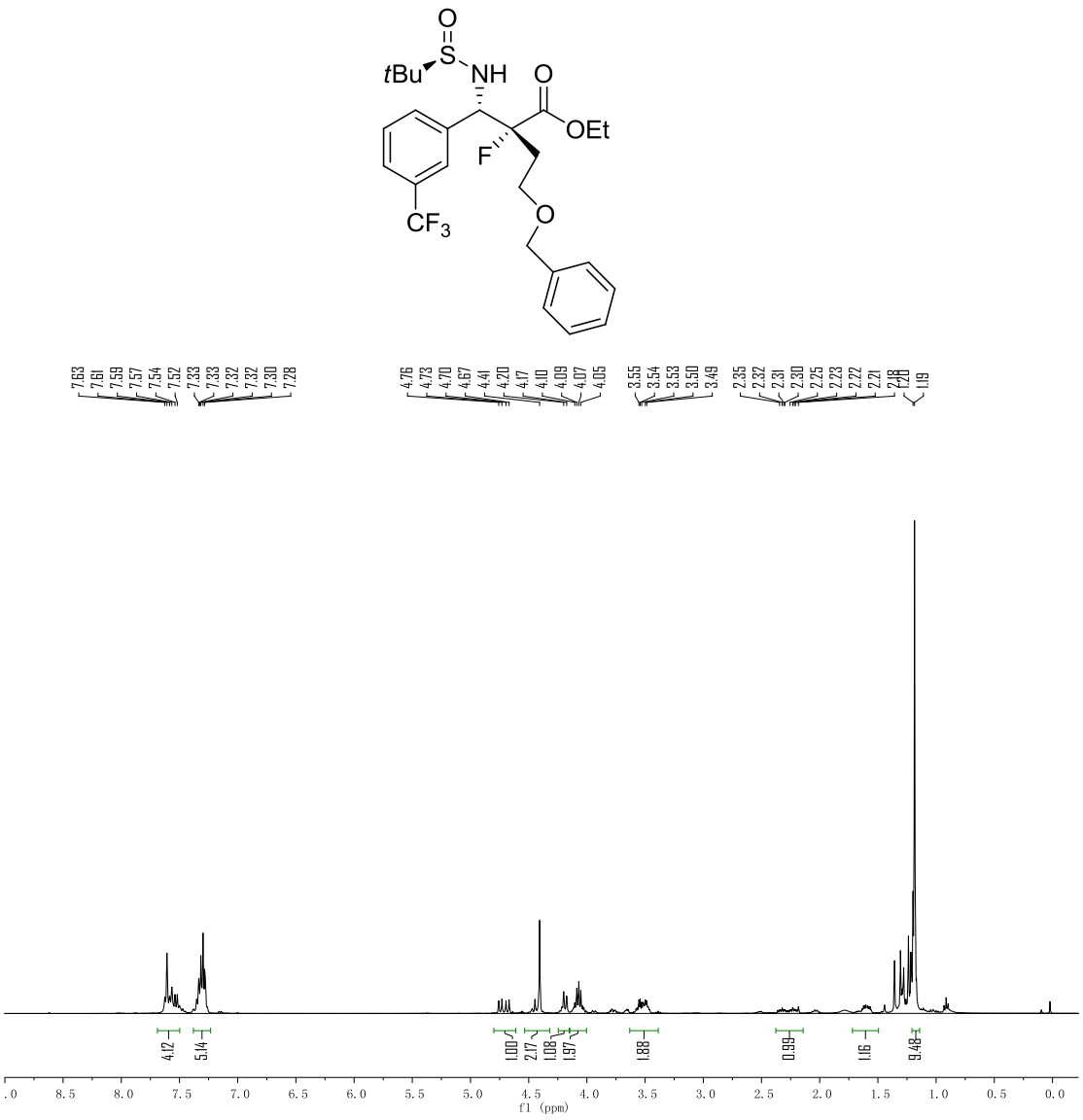
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3e**



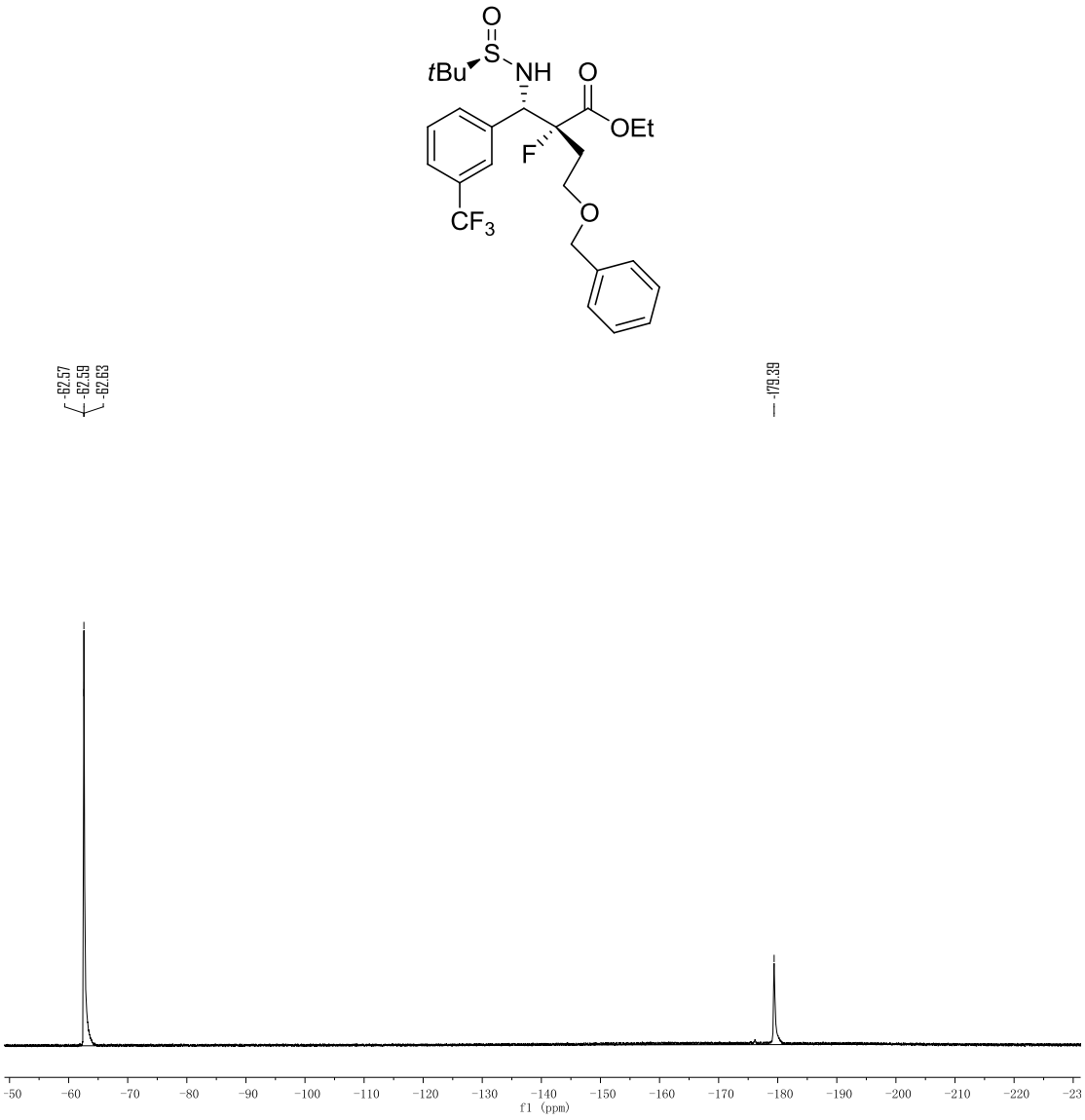
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3e**



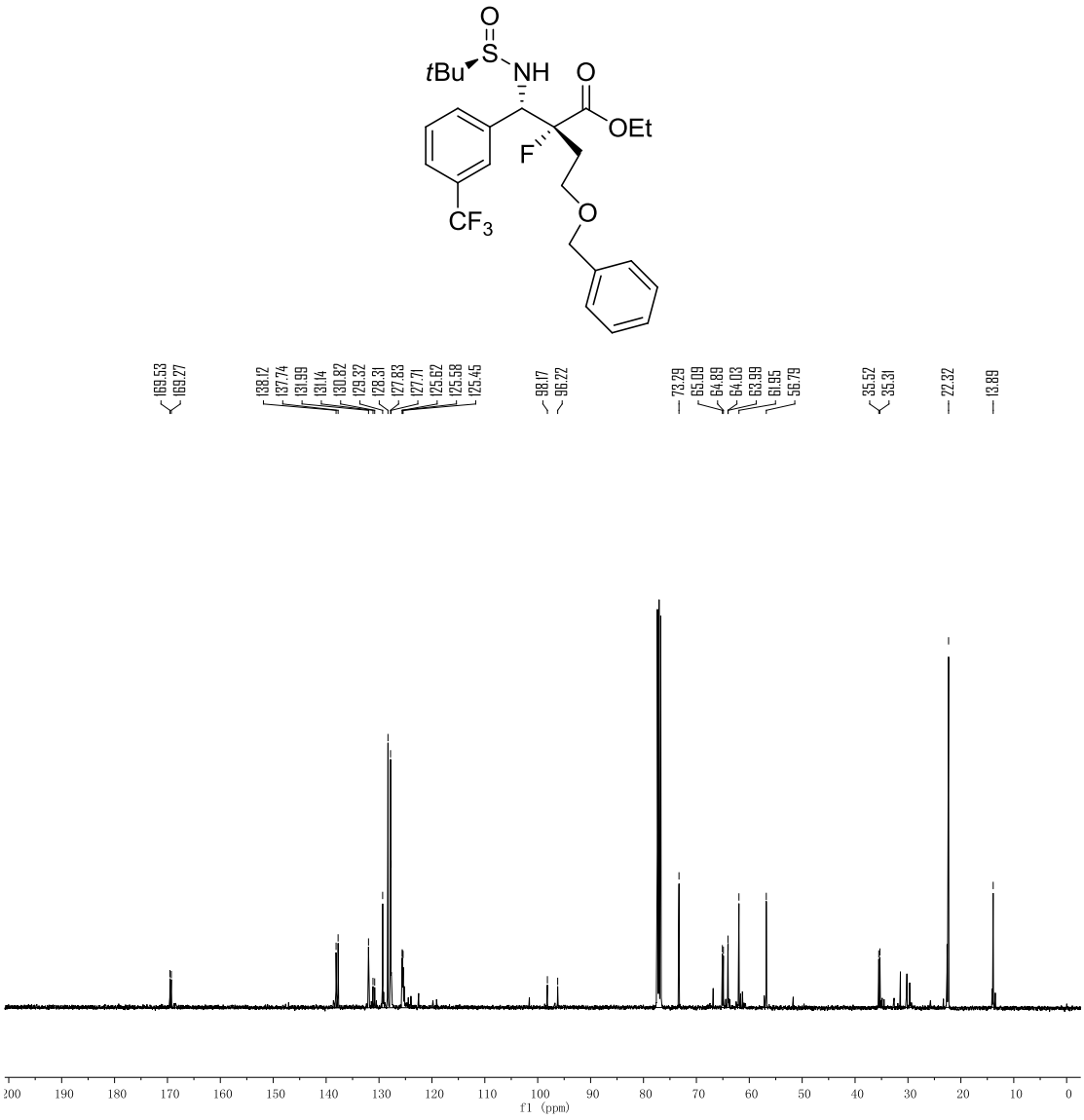
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



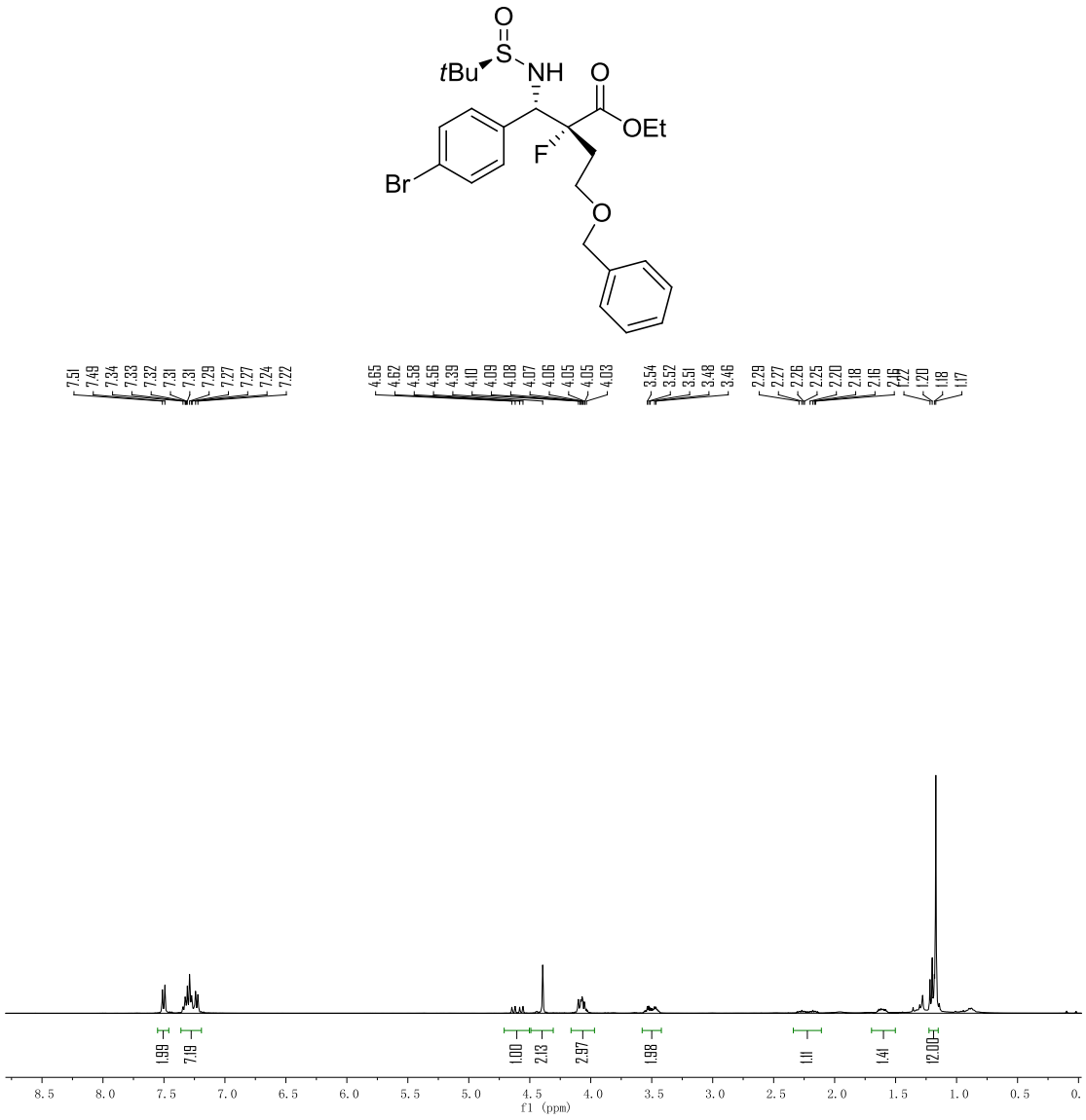
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3f**



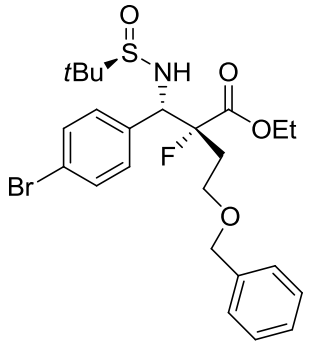
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3f**

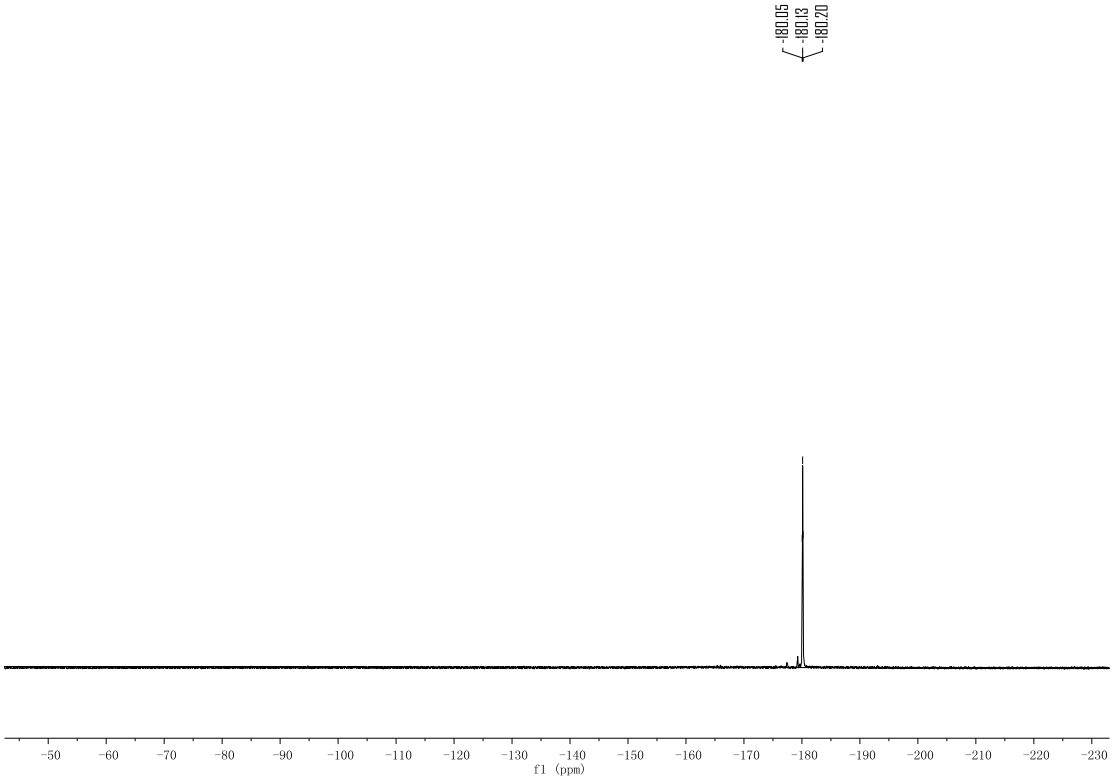


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**

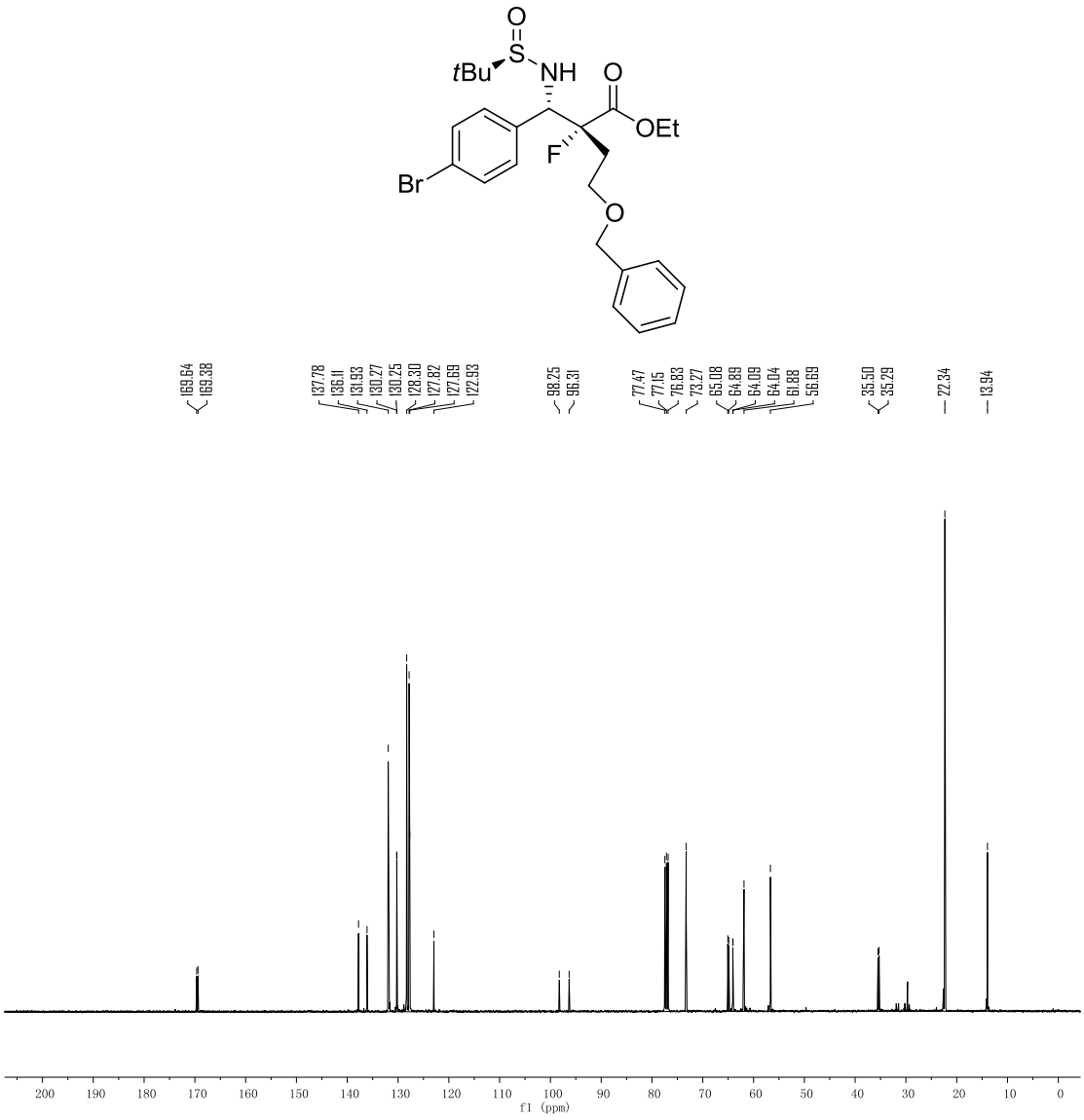


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3g**

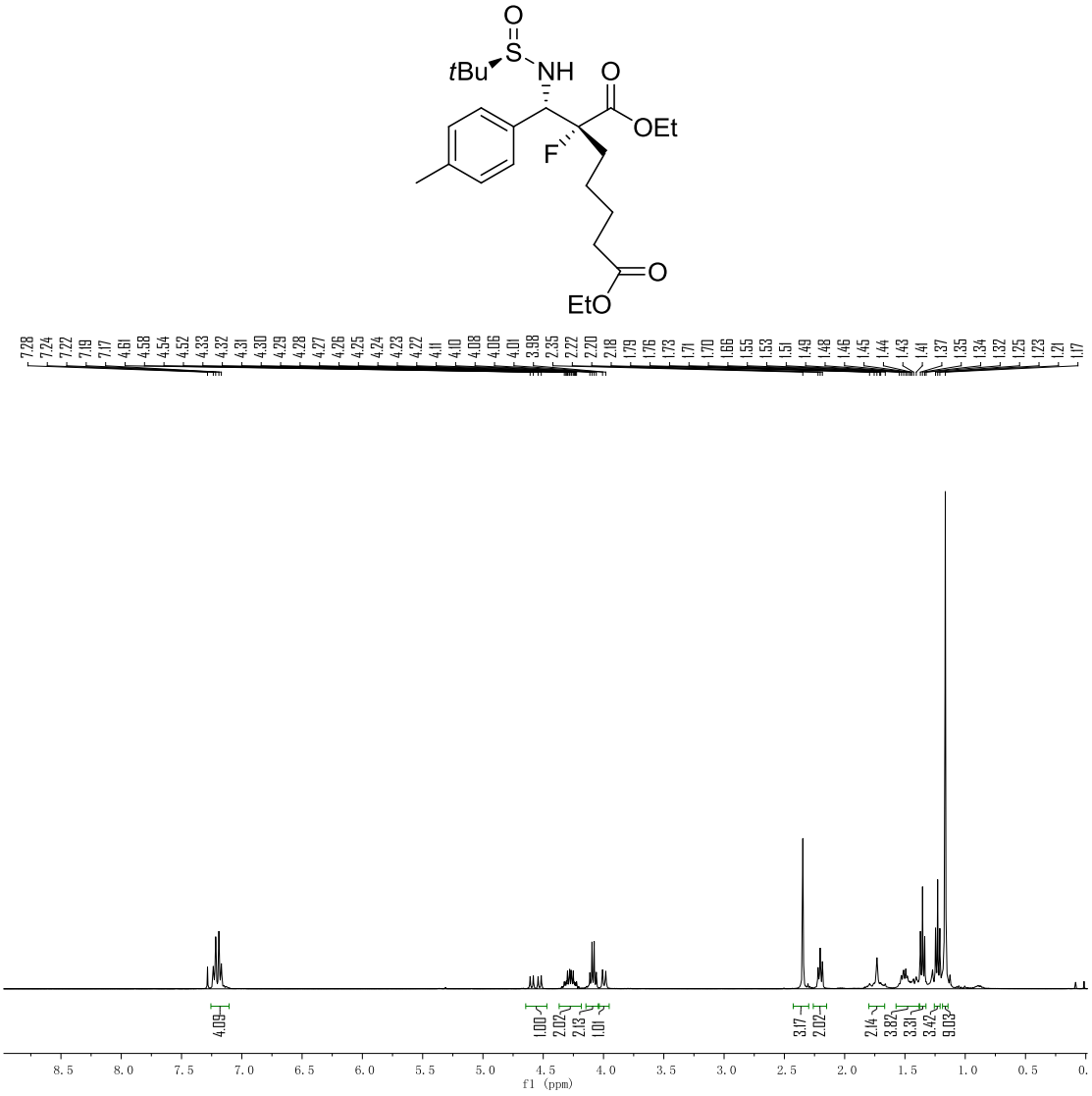




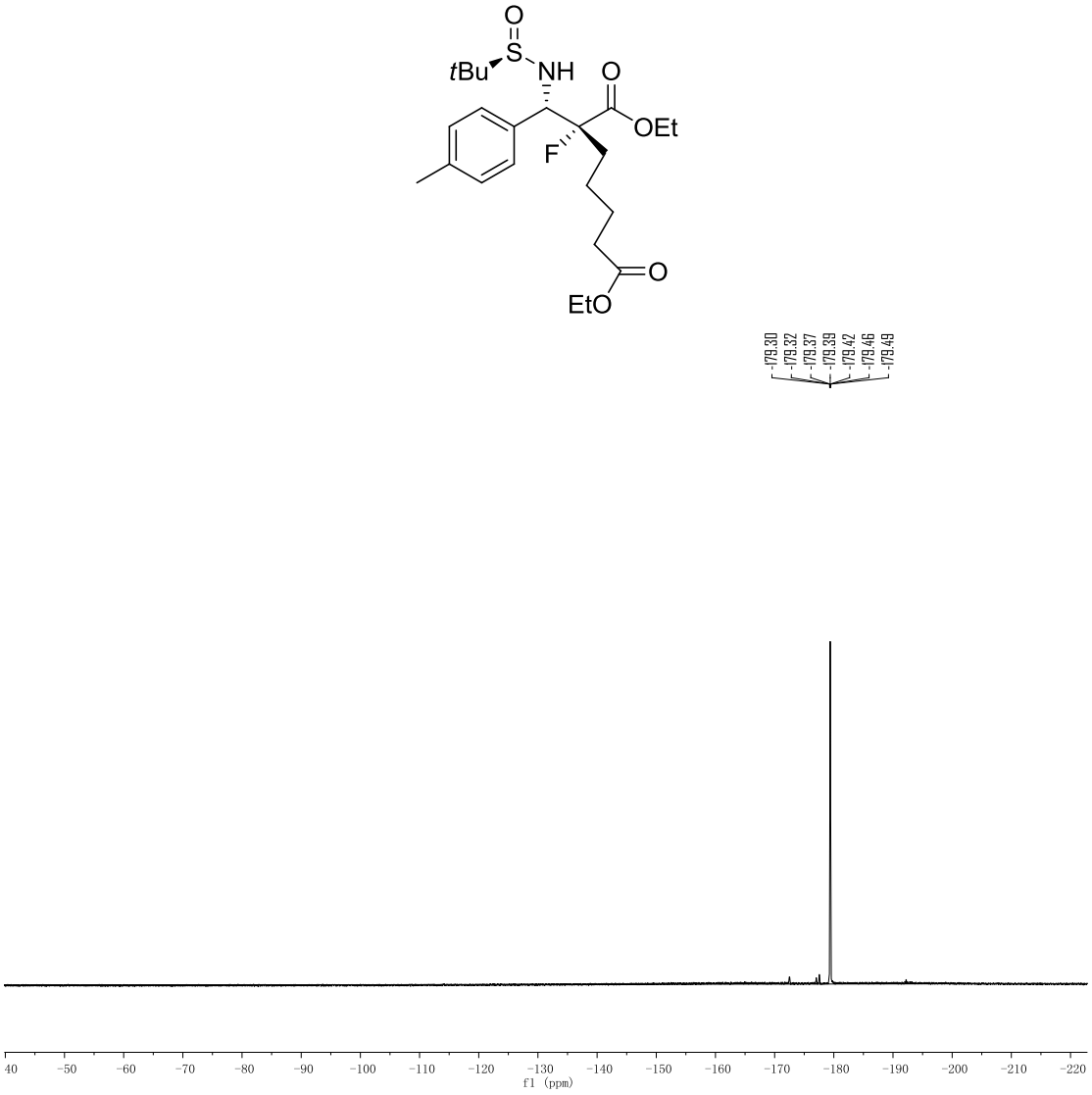
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3g**



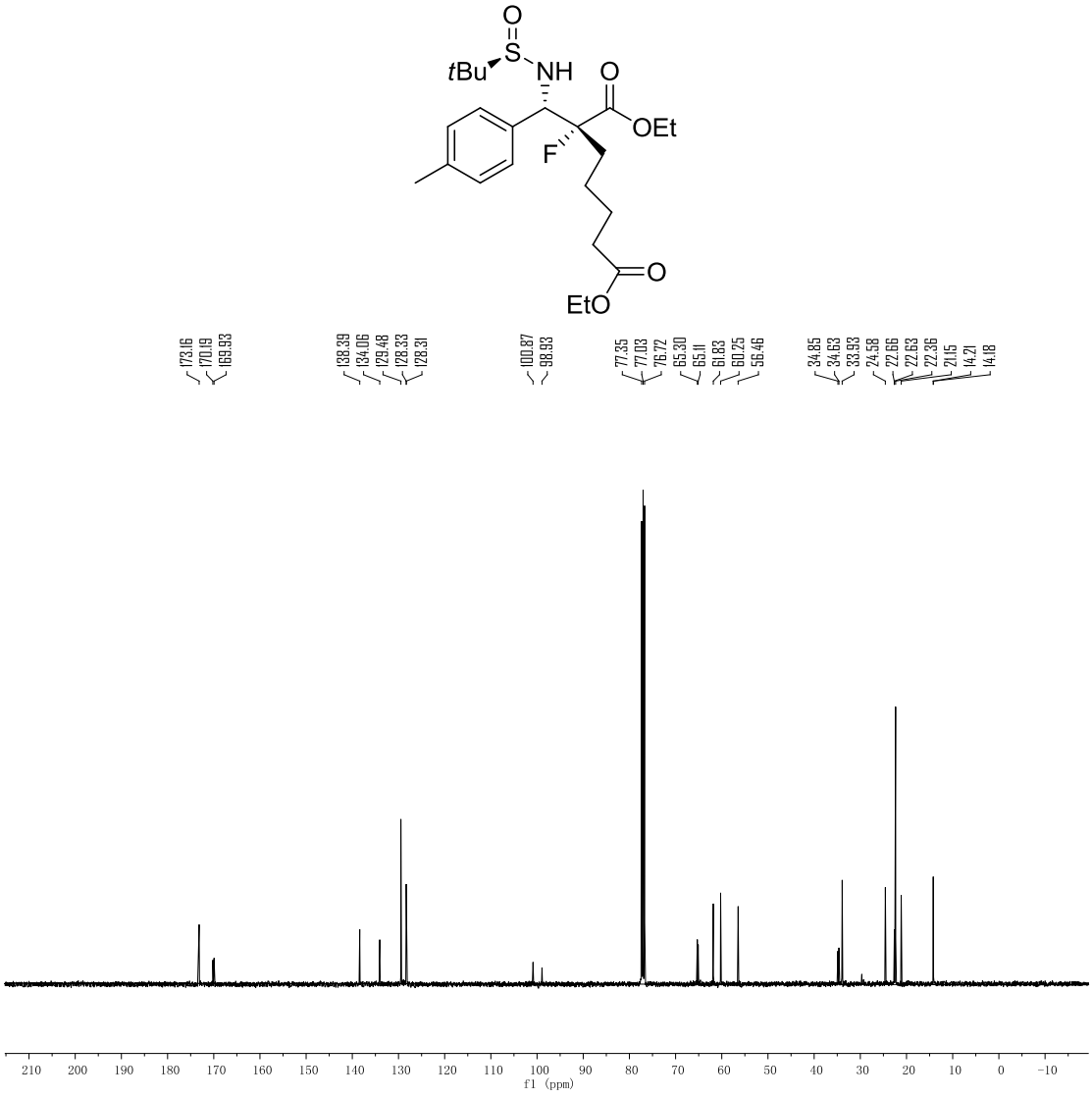
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



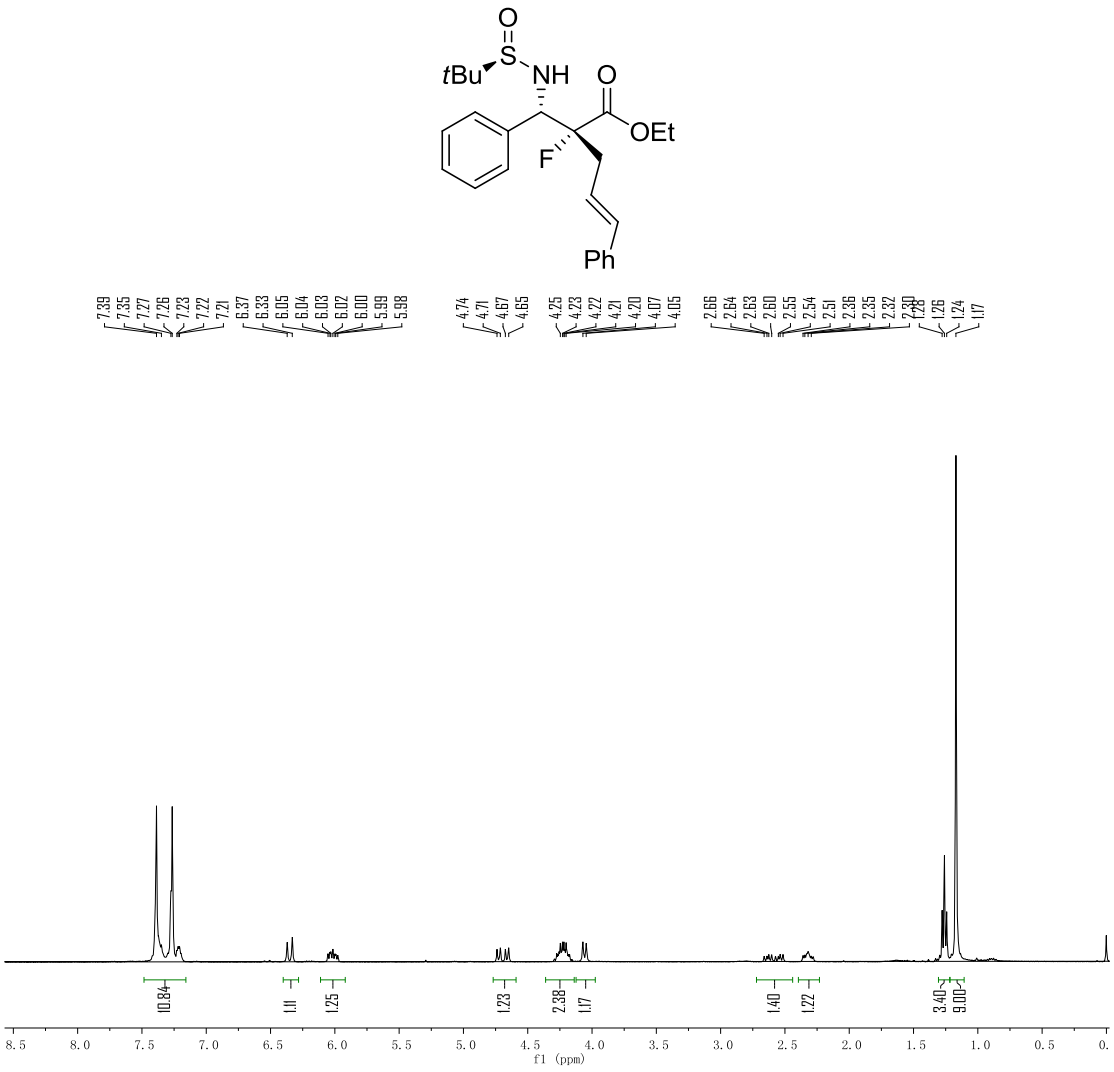
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3h**



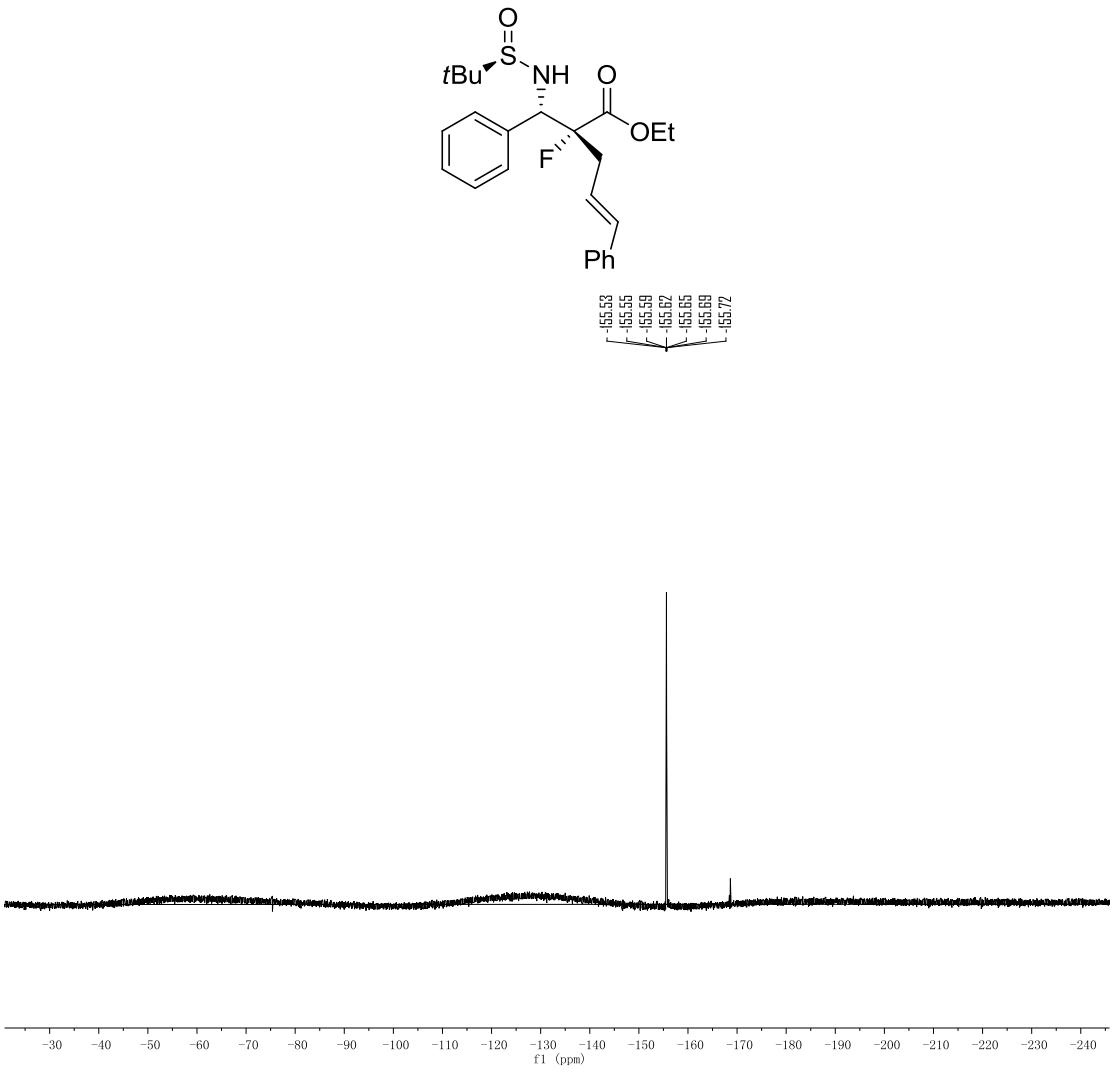
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3h**



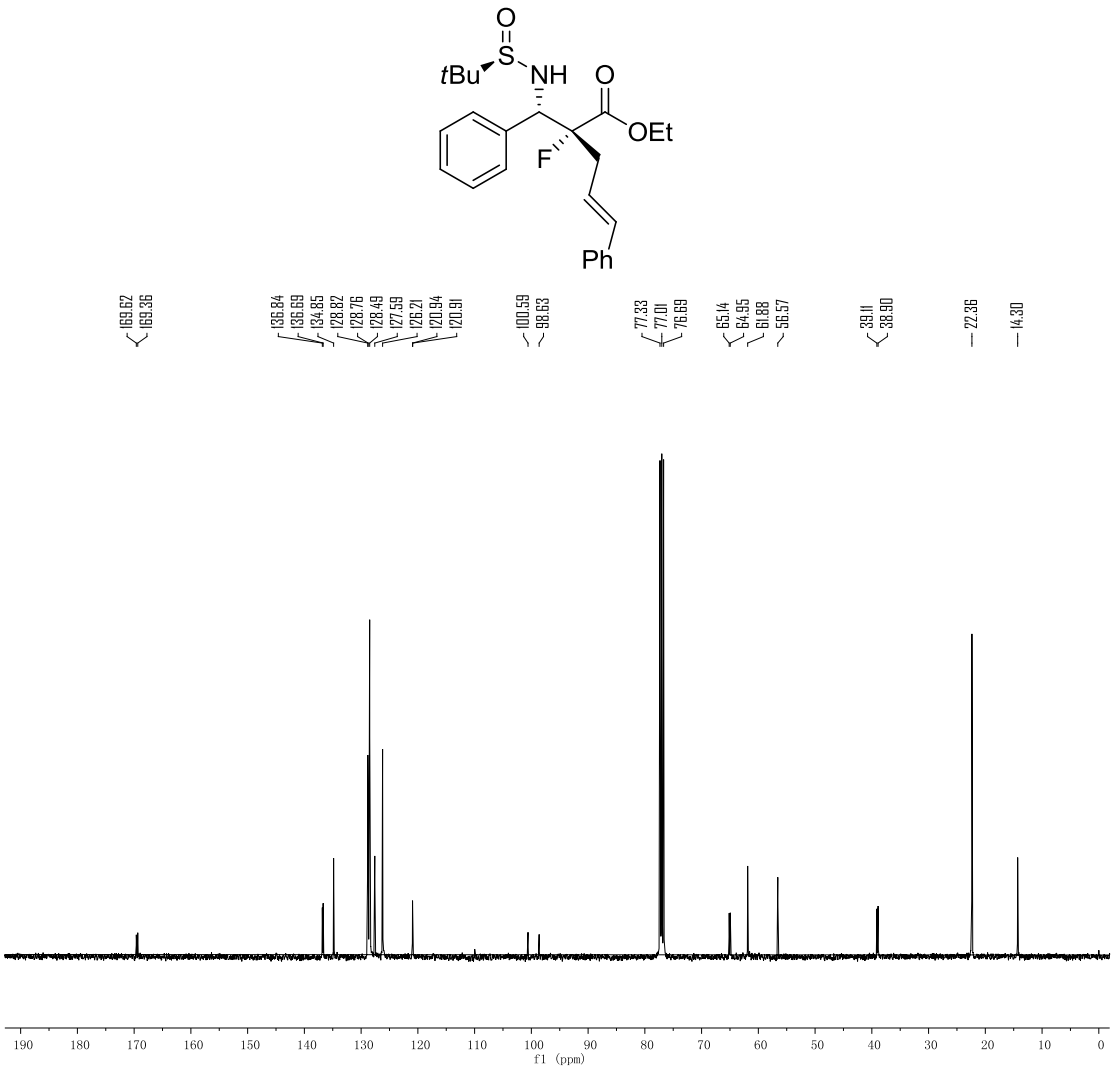
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**



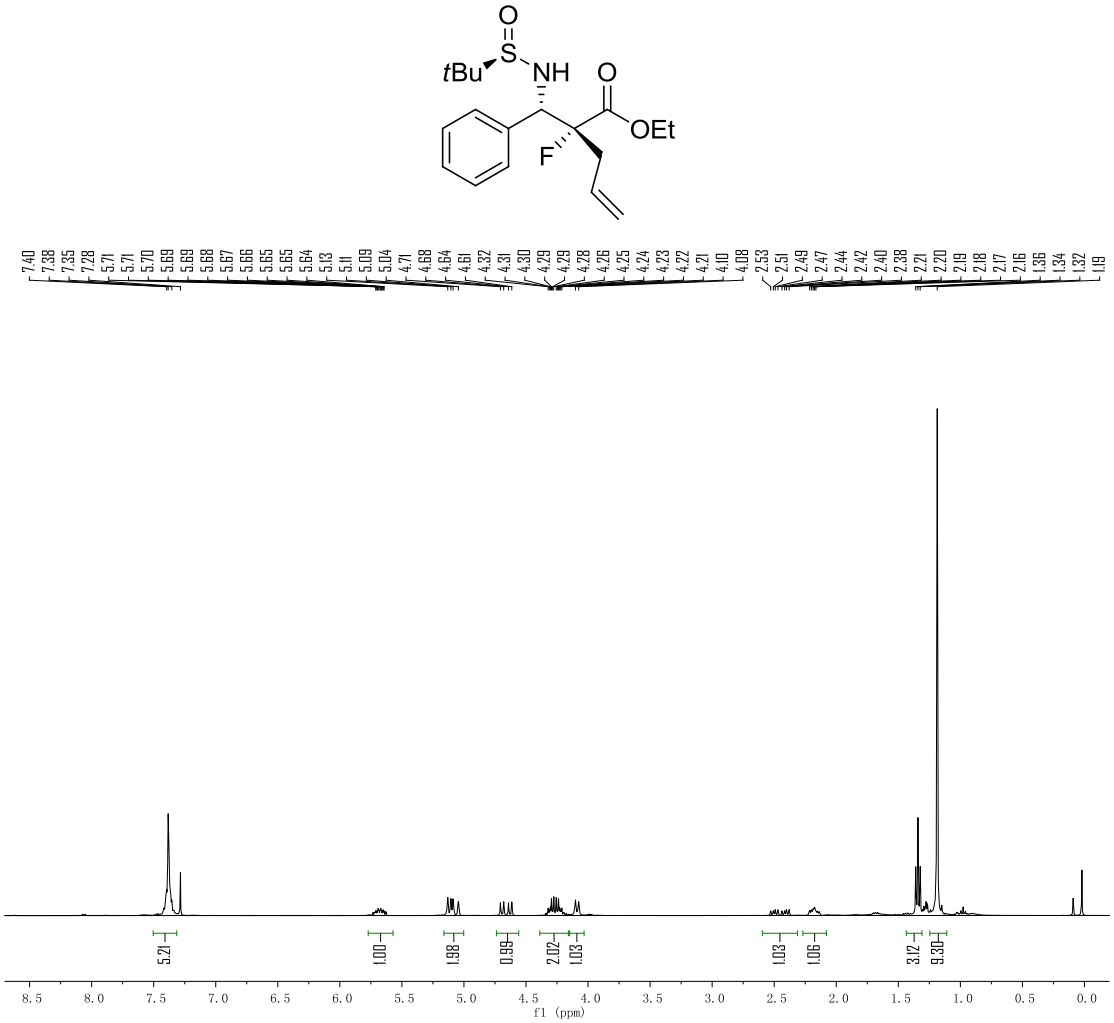
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3i**



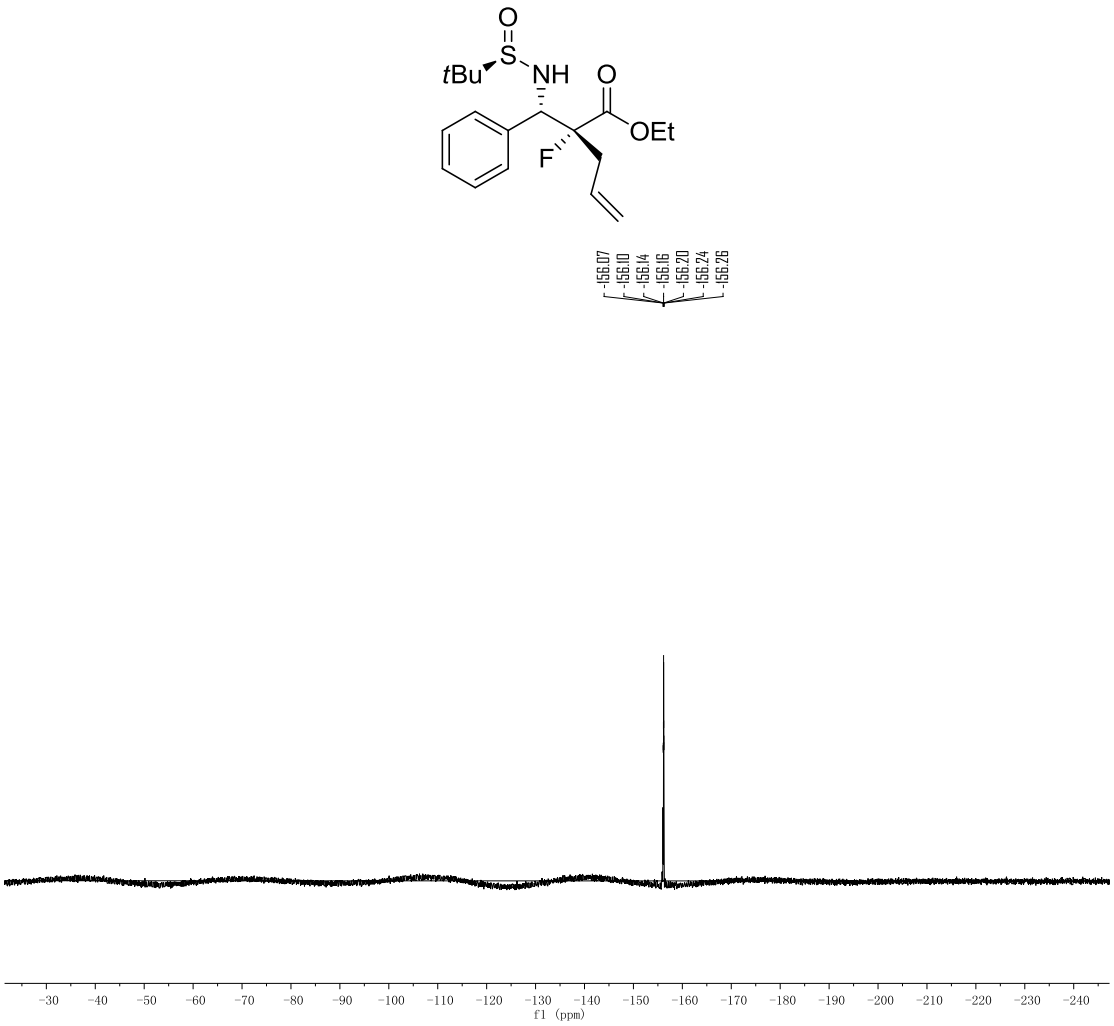
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3i**



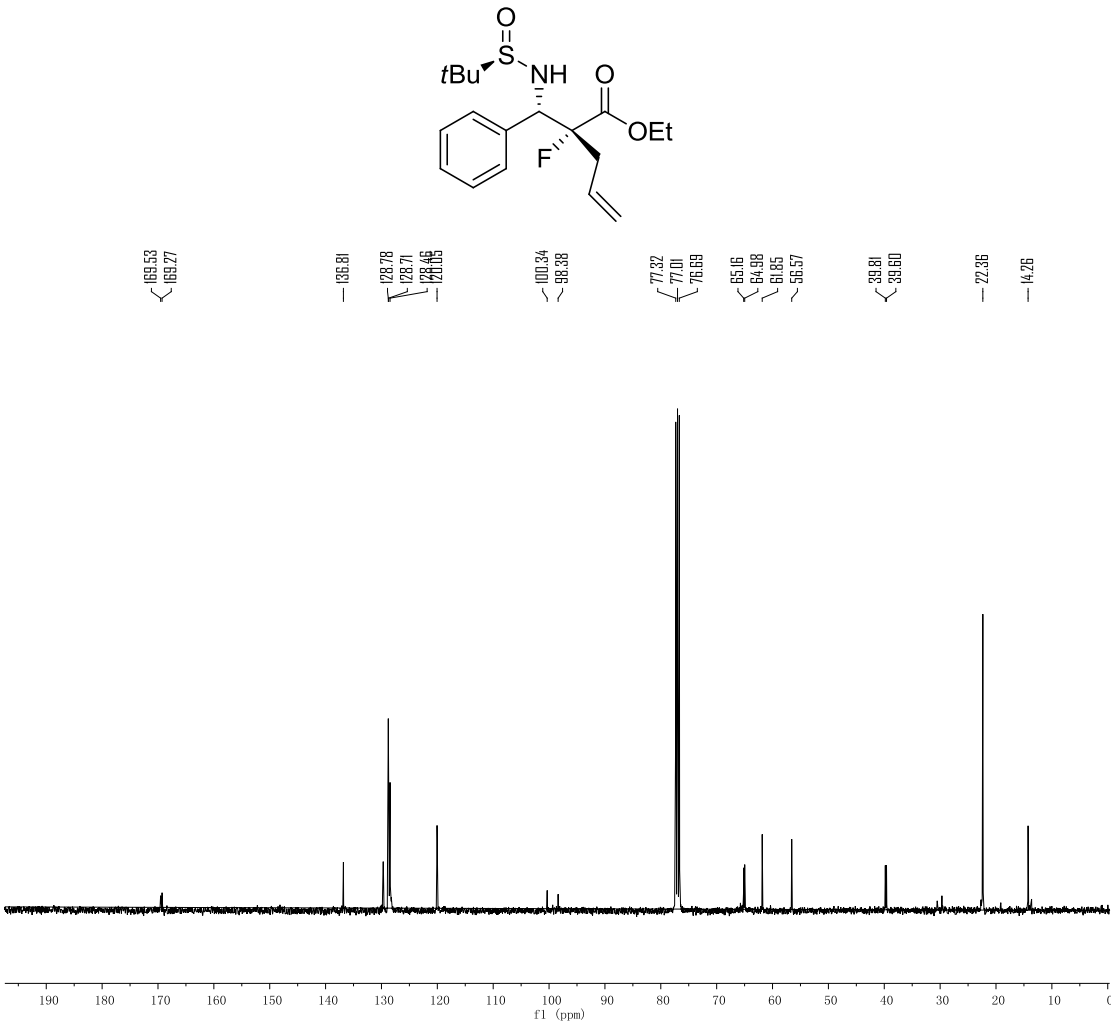
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**



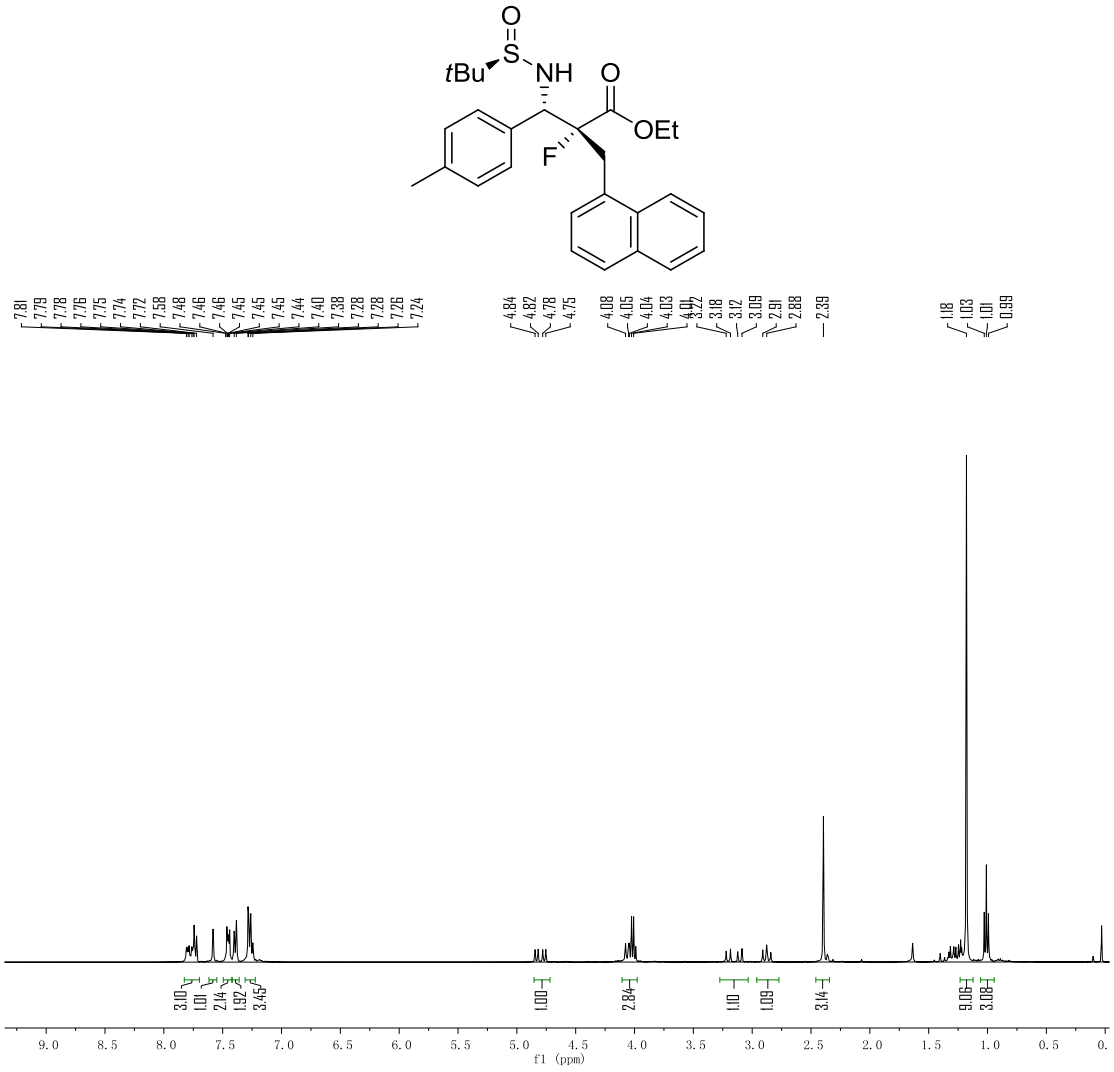
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3j**



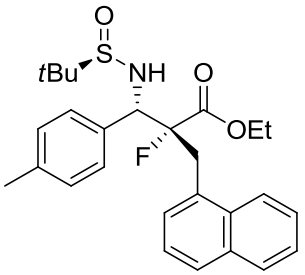
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3j**

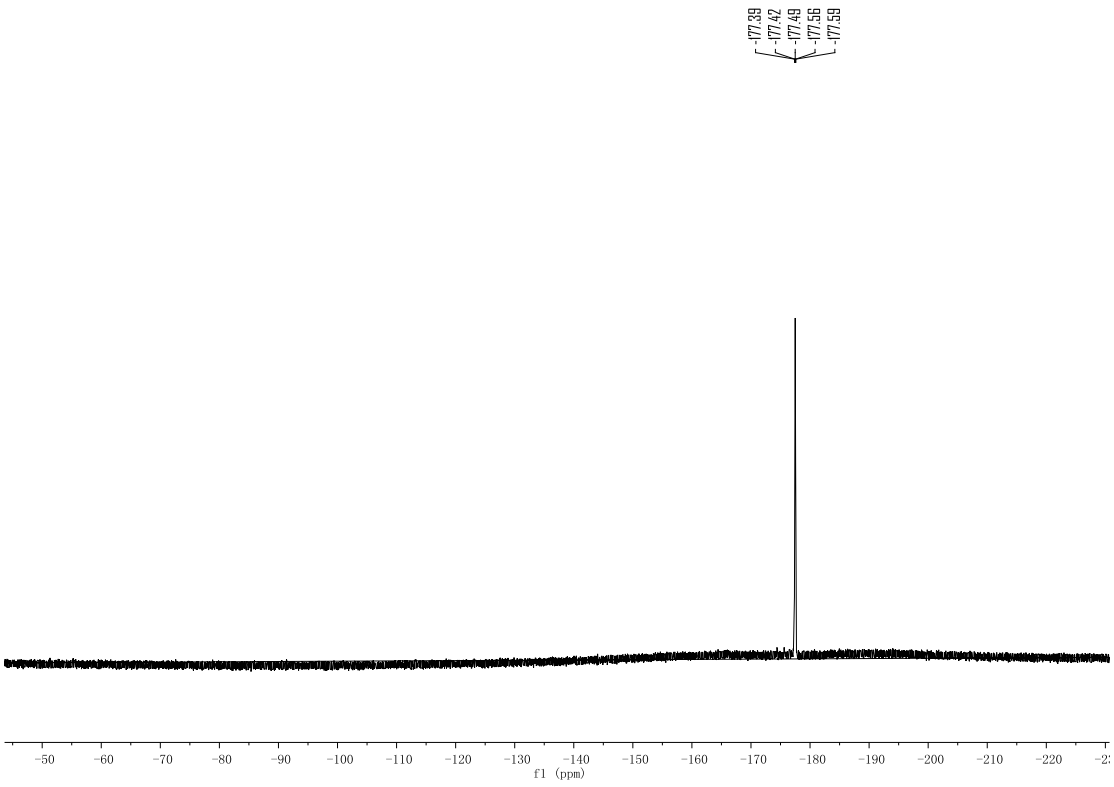


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**

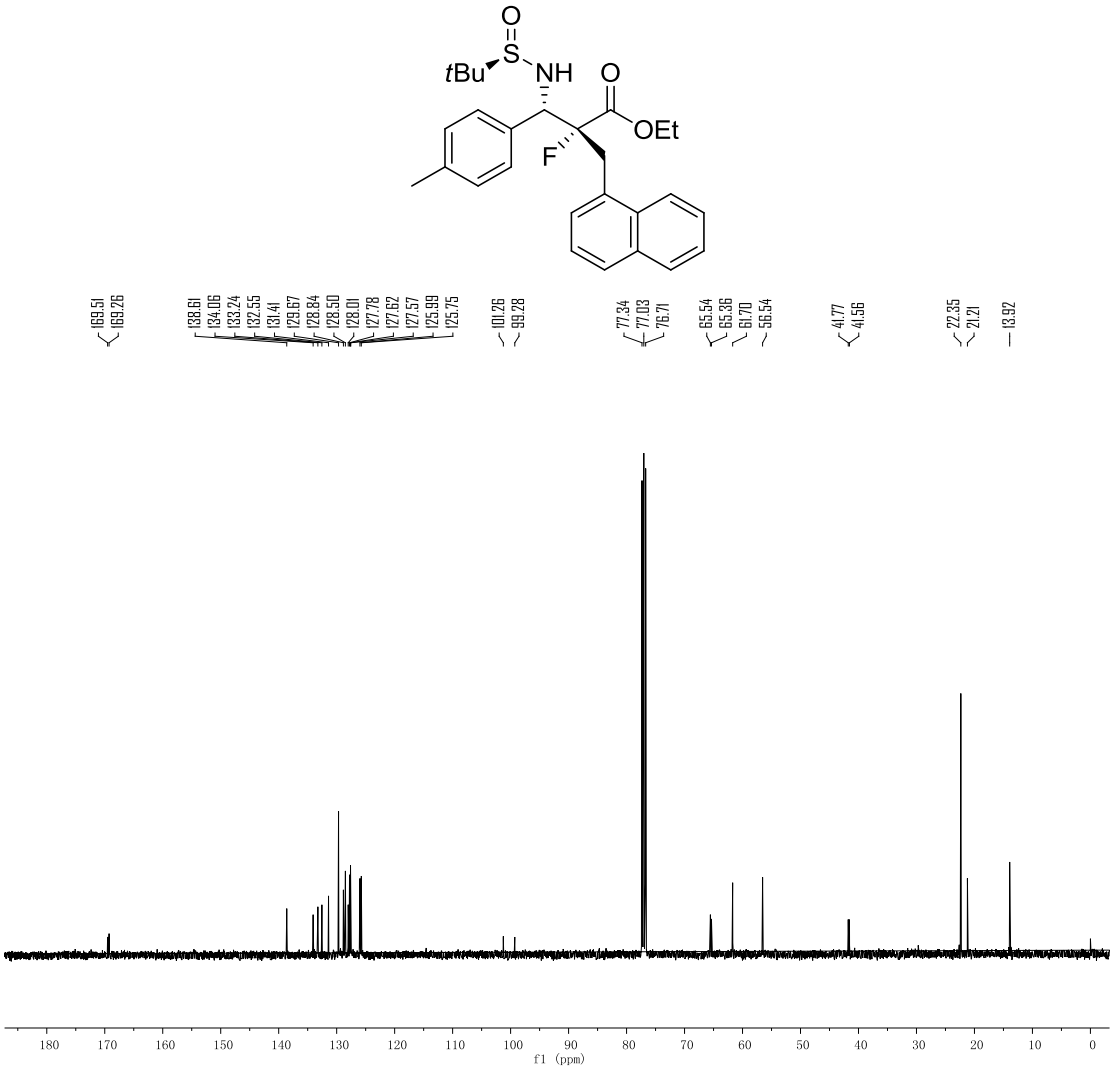


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3k**

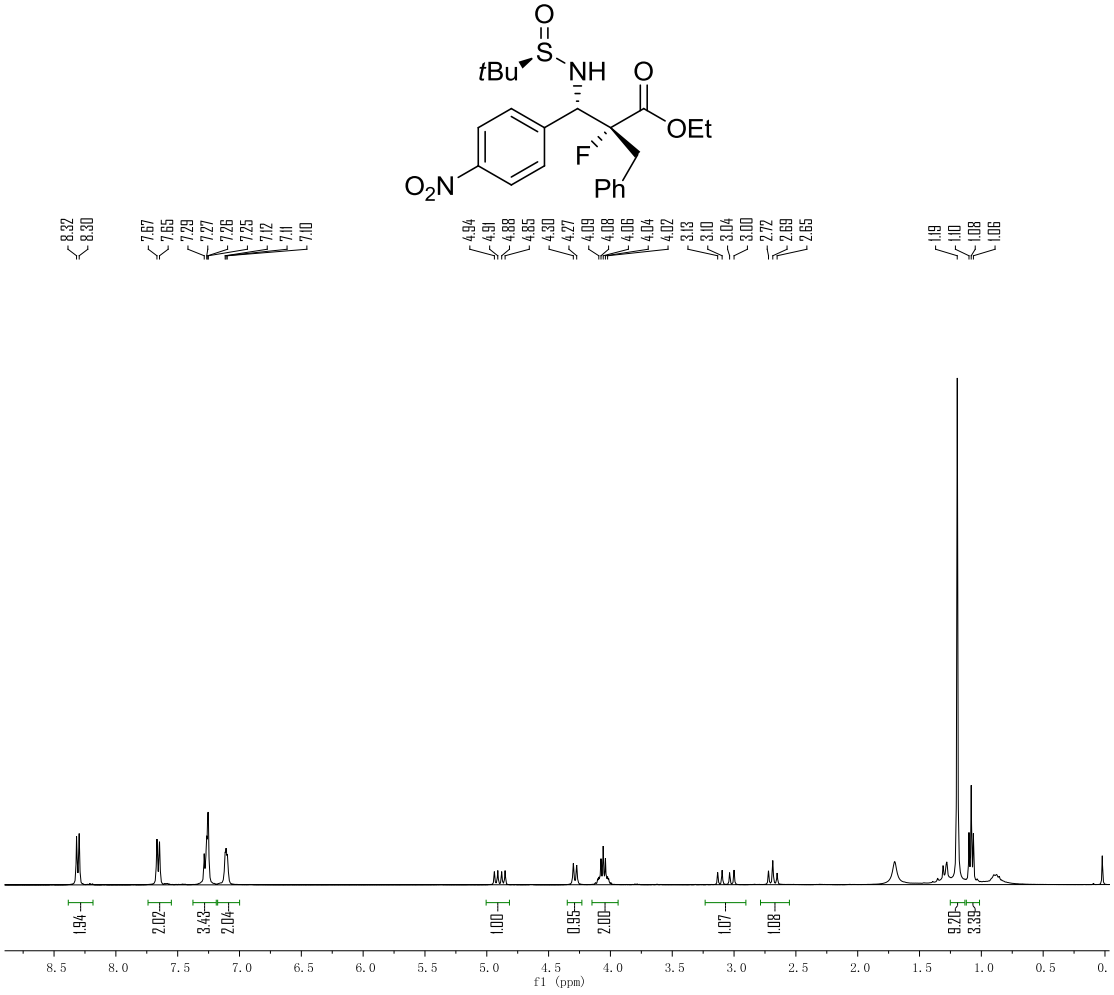




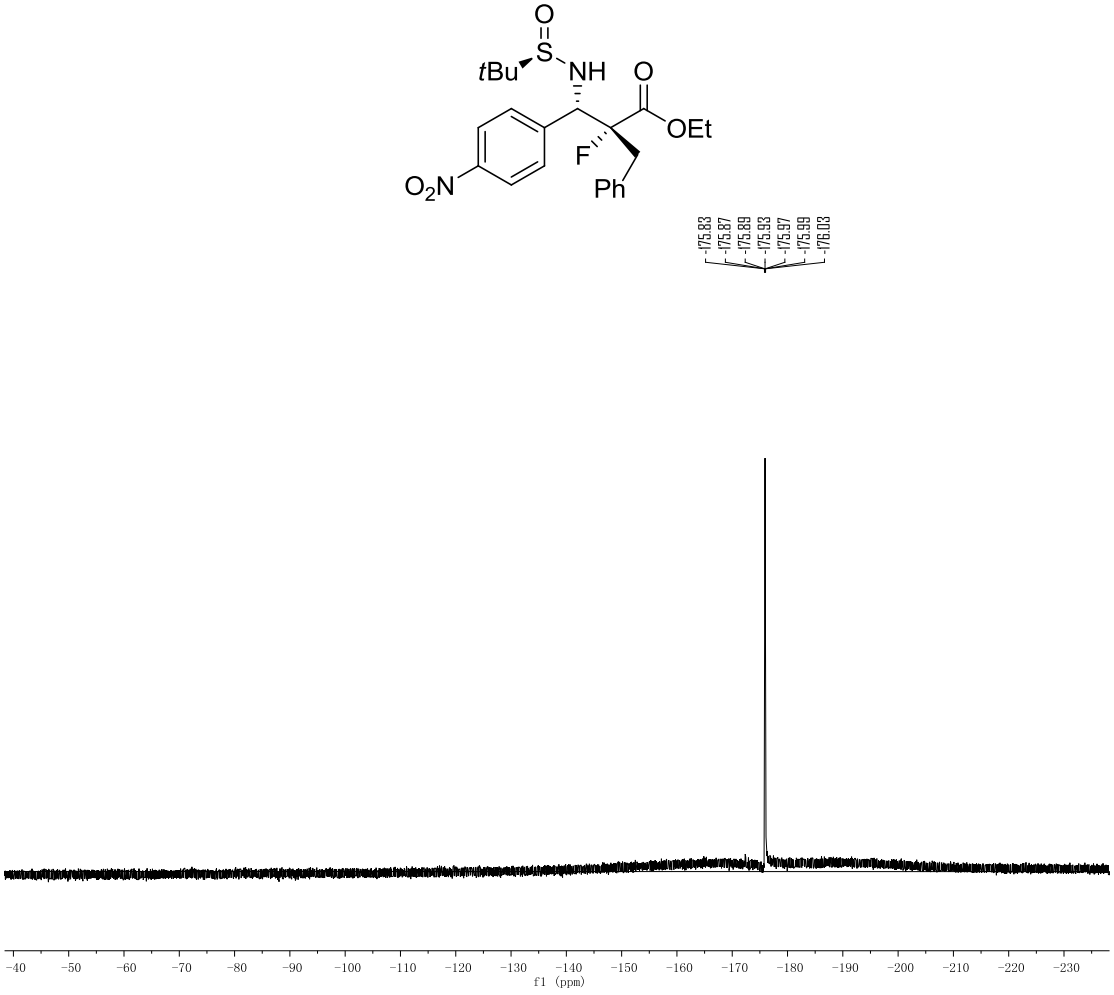
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3k**



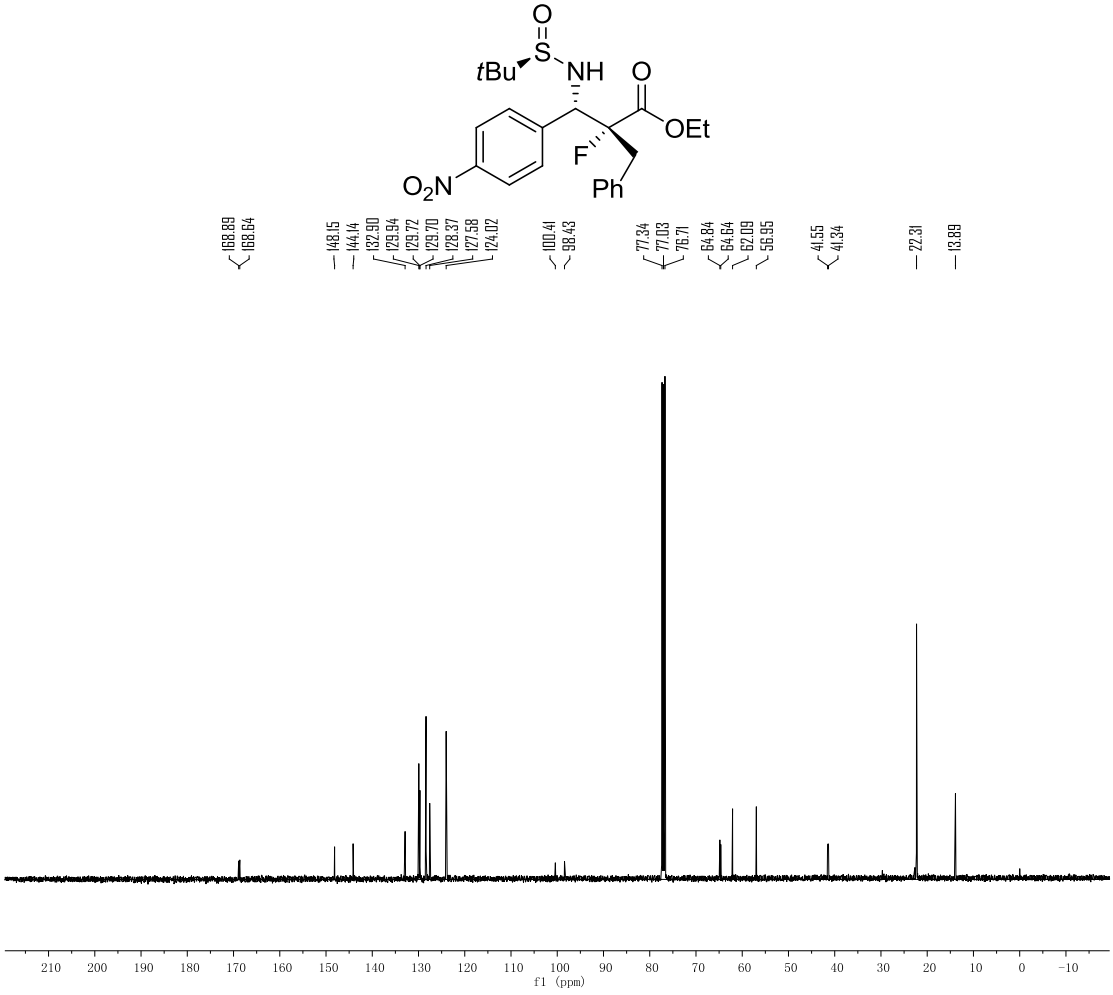
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



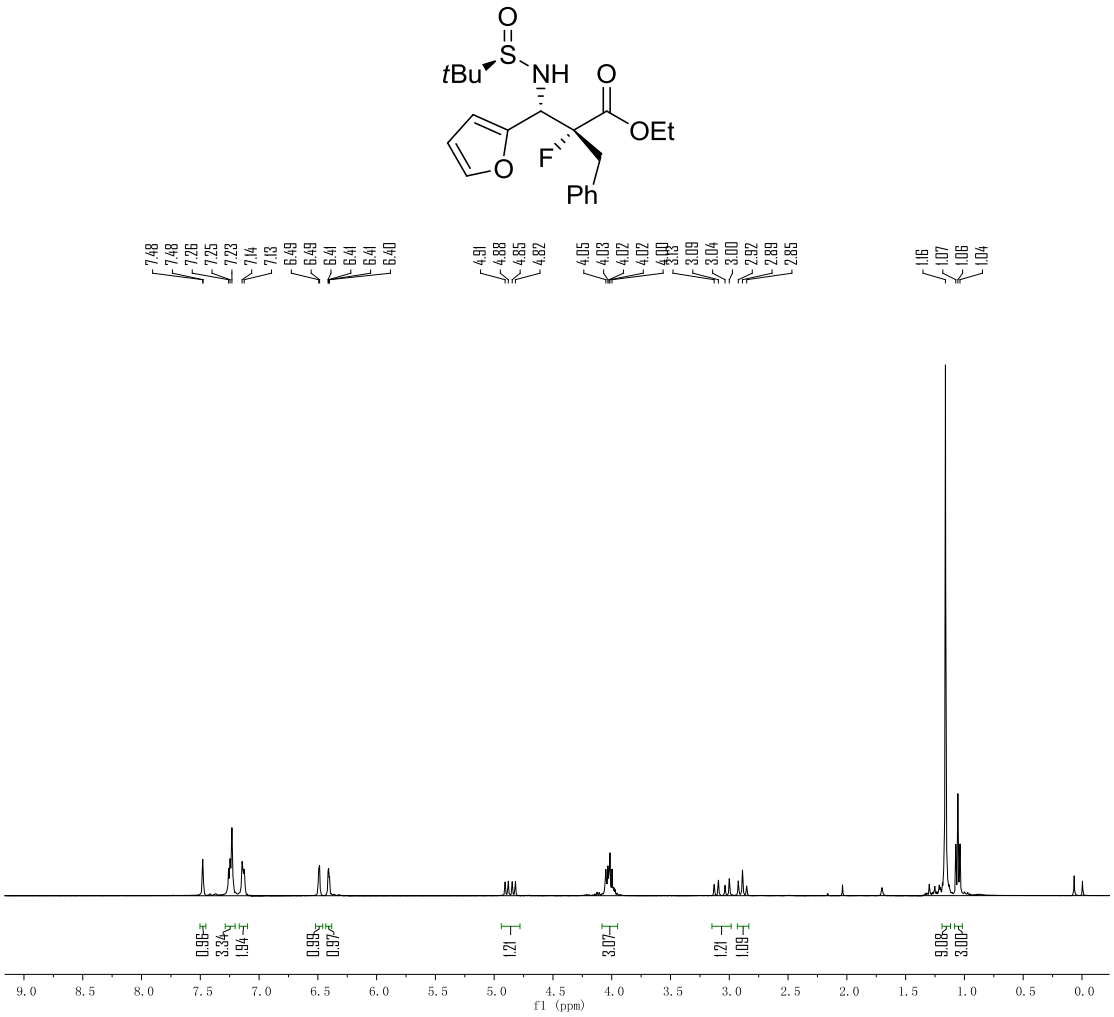
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3l**



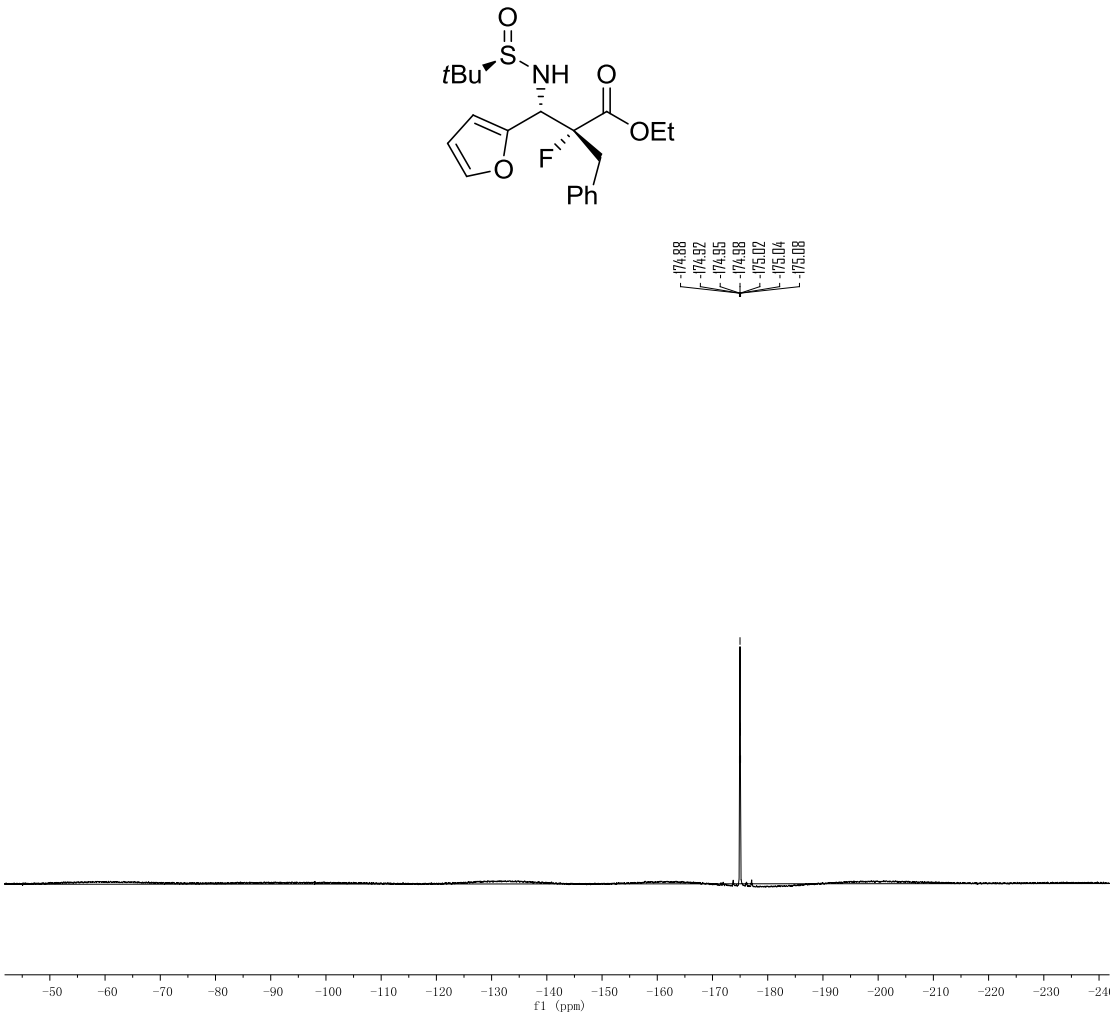
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3l**



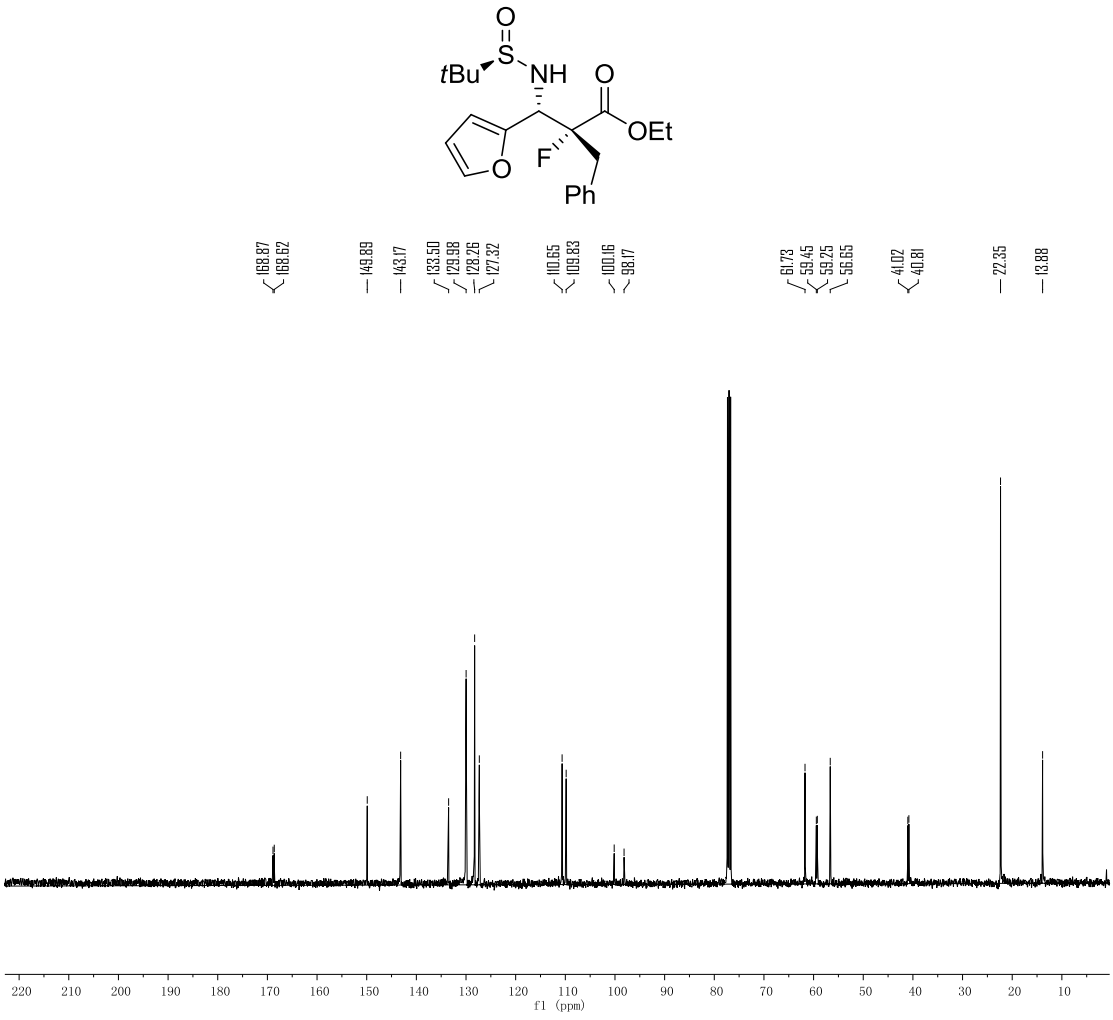
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



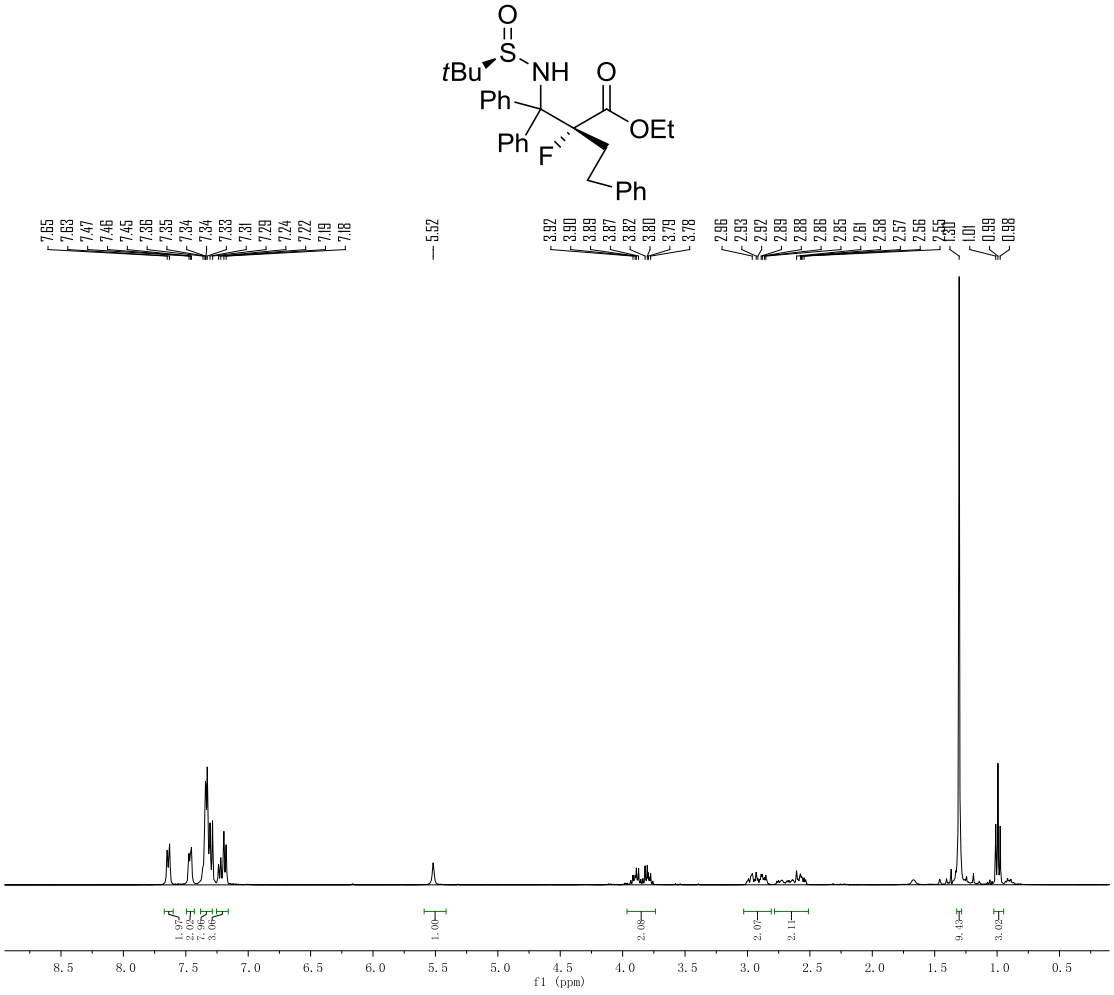
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3m**



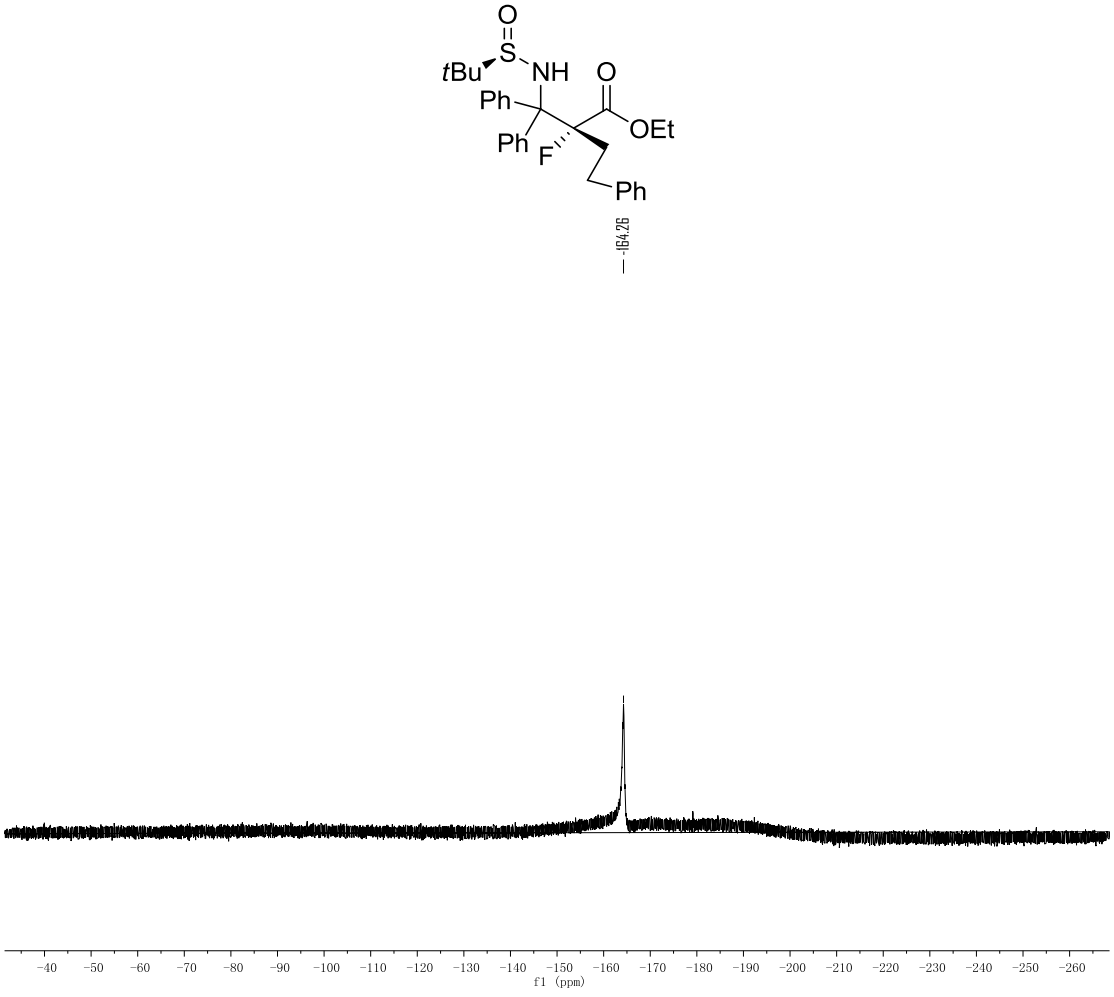
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3m**



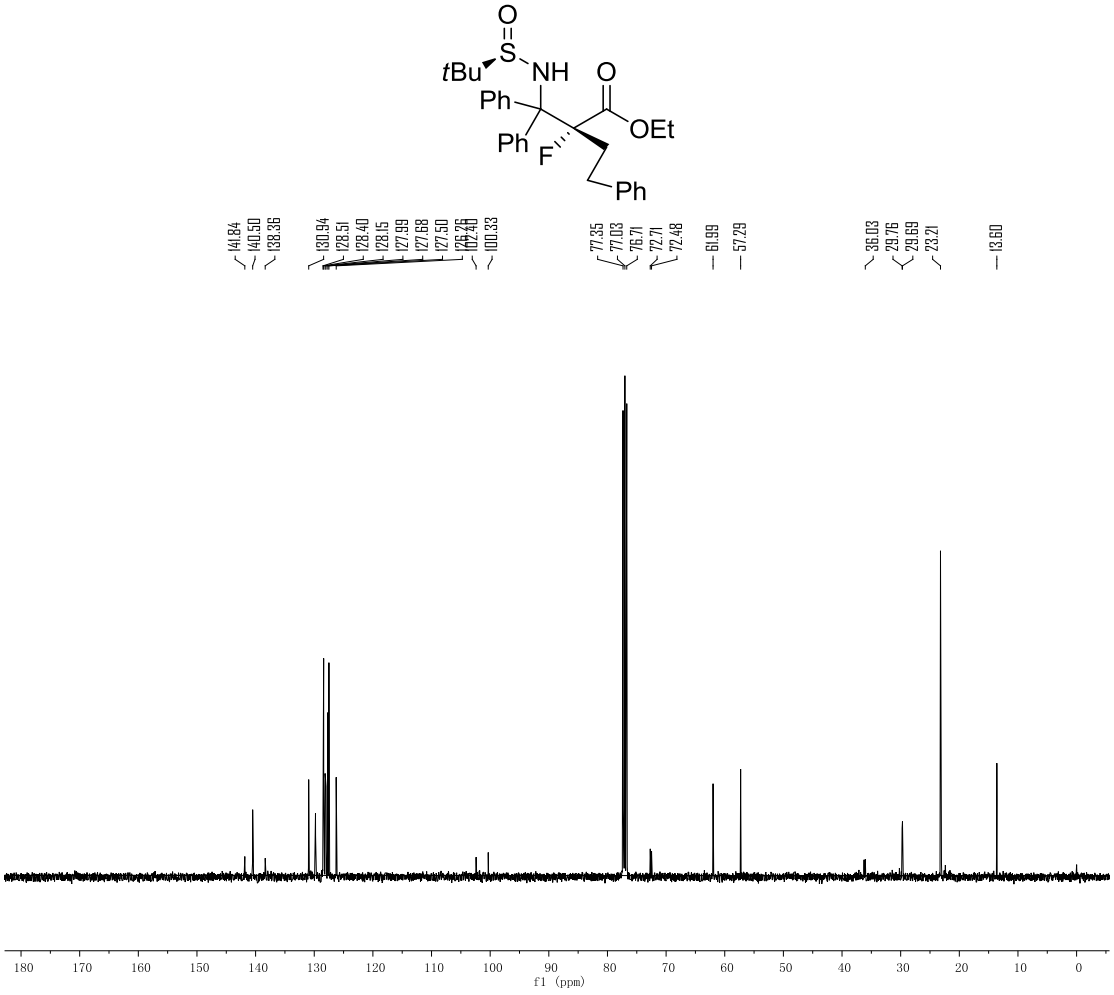
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**



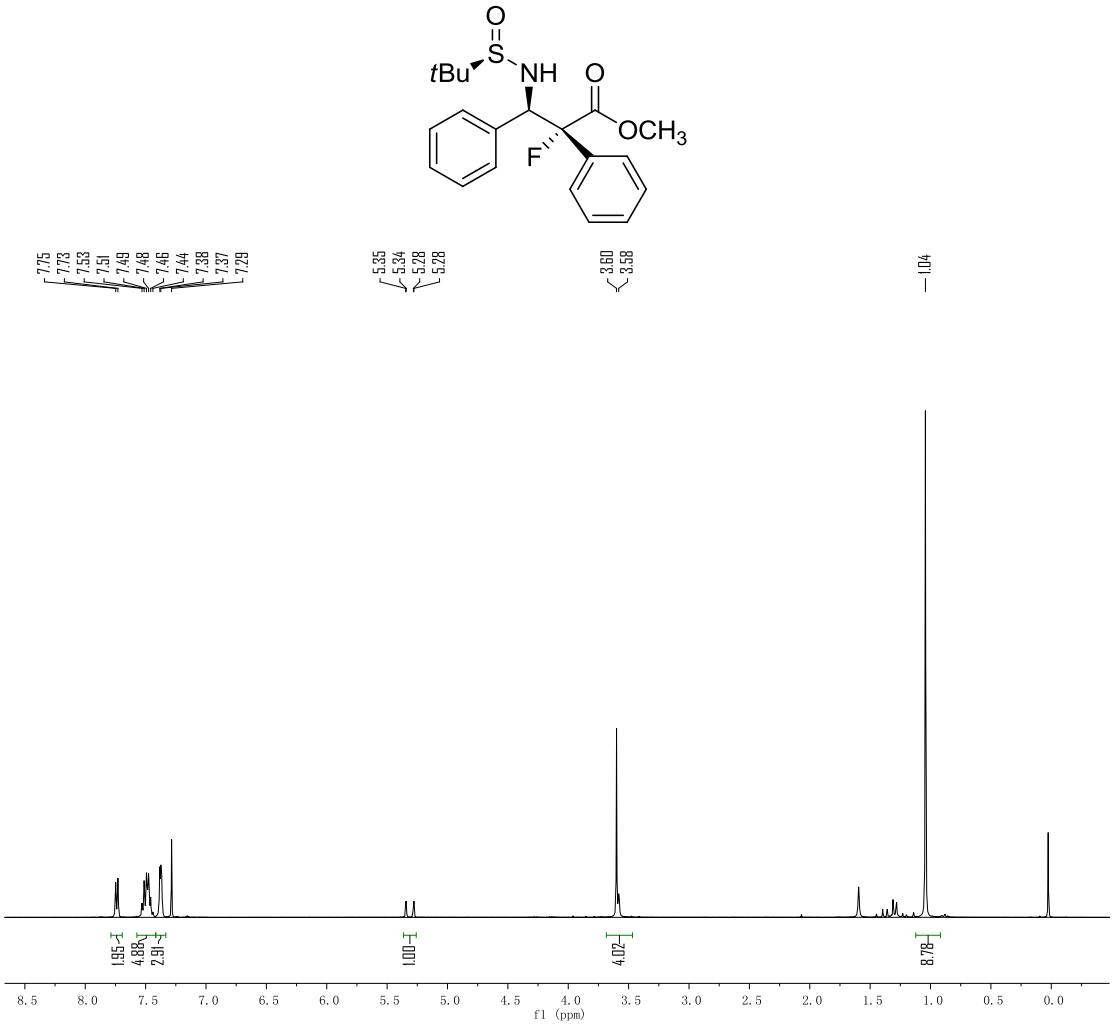
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3n**



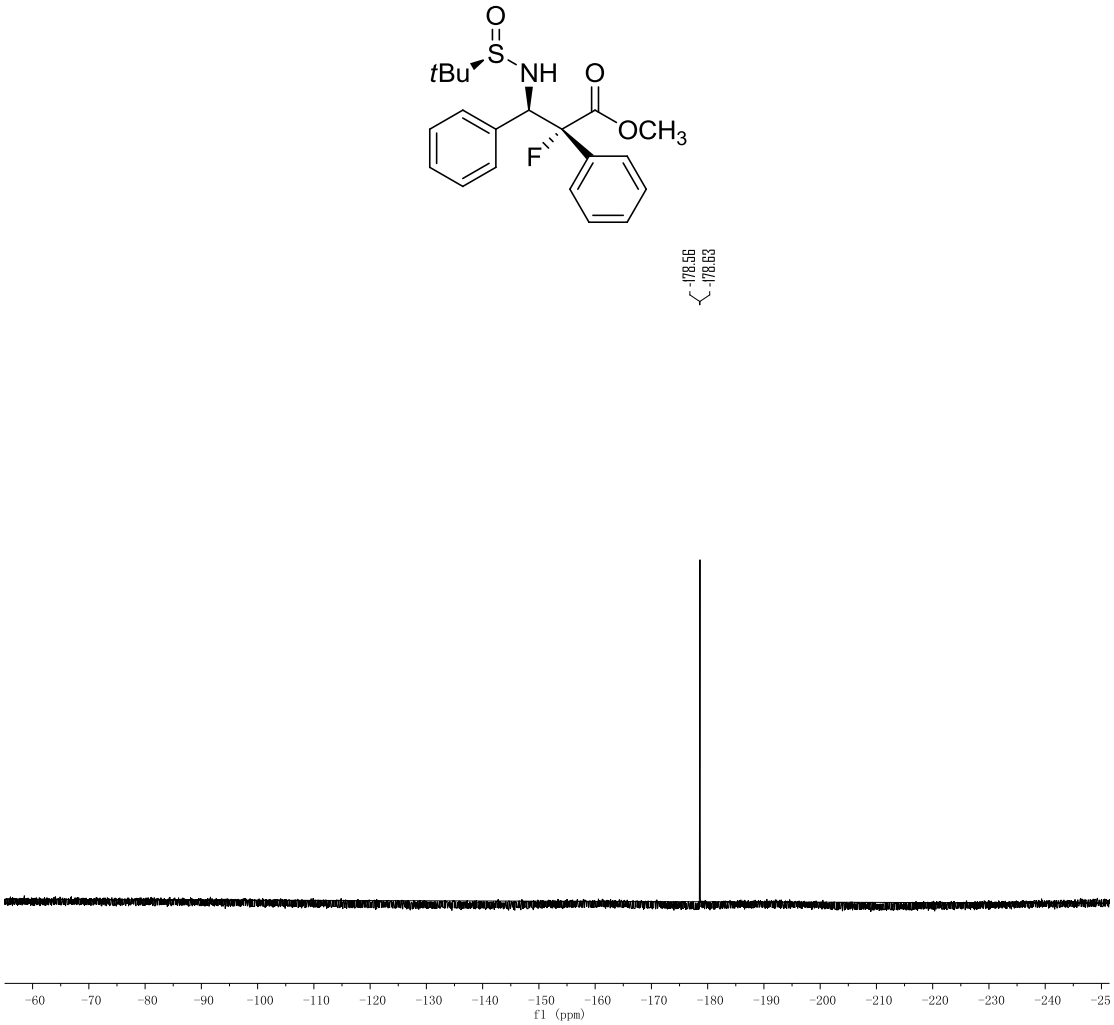
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3n**



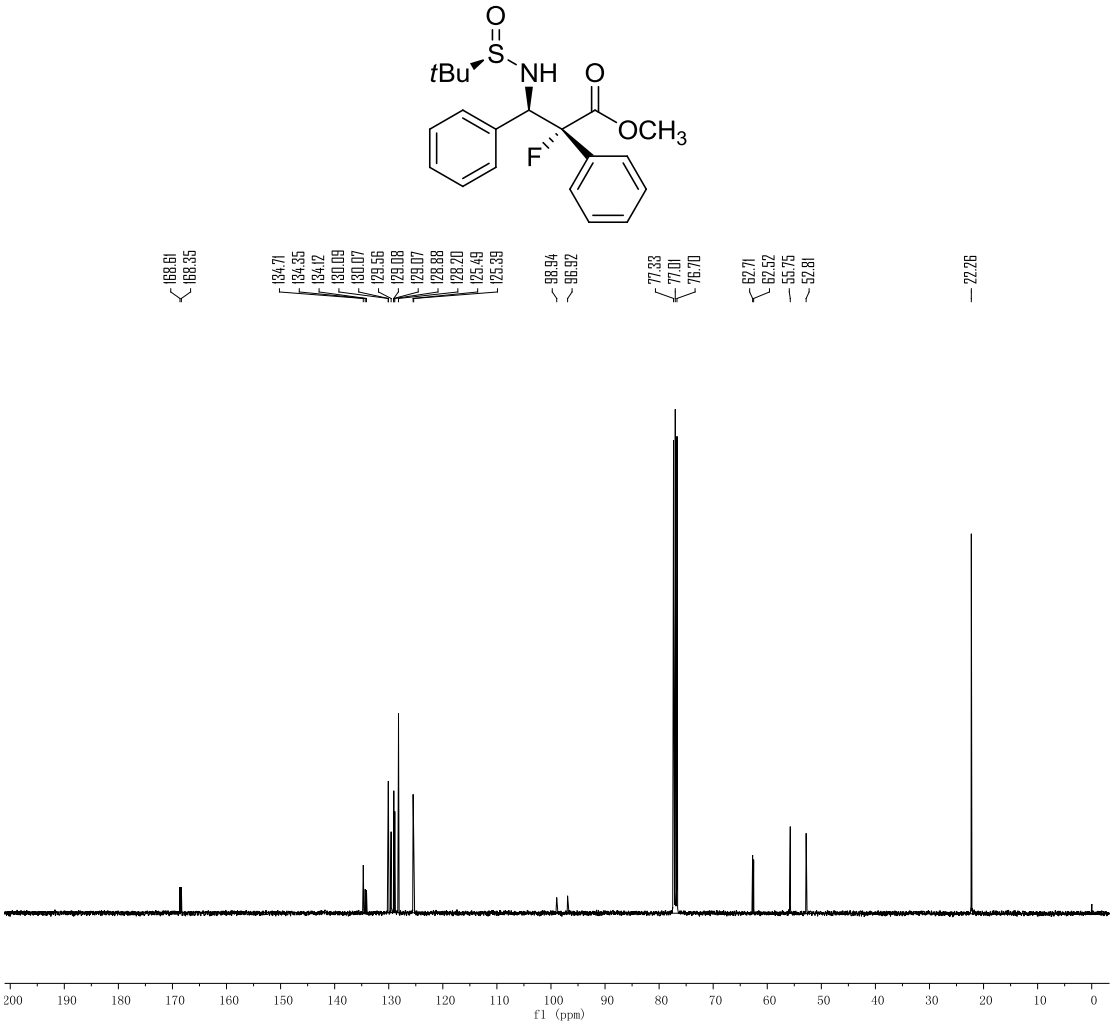
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**



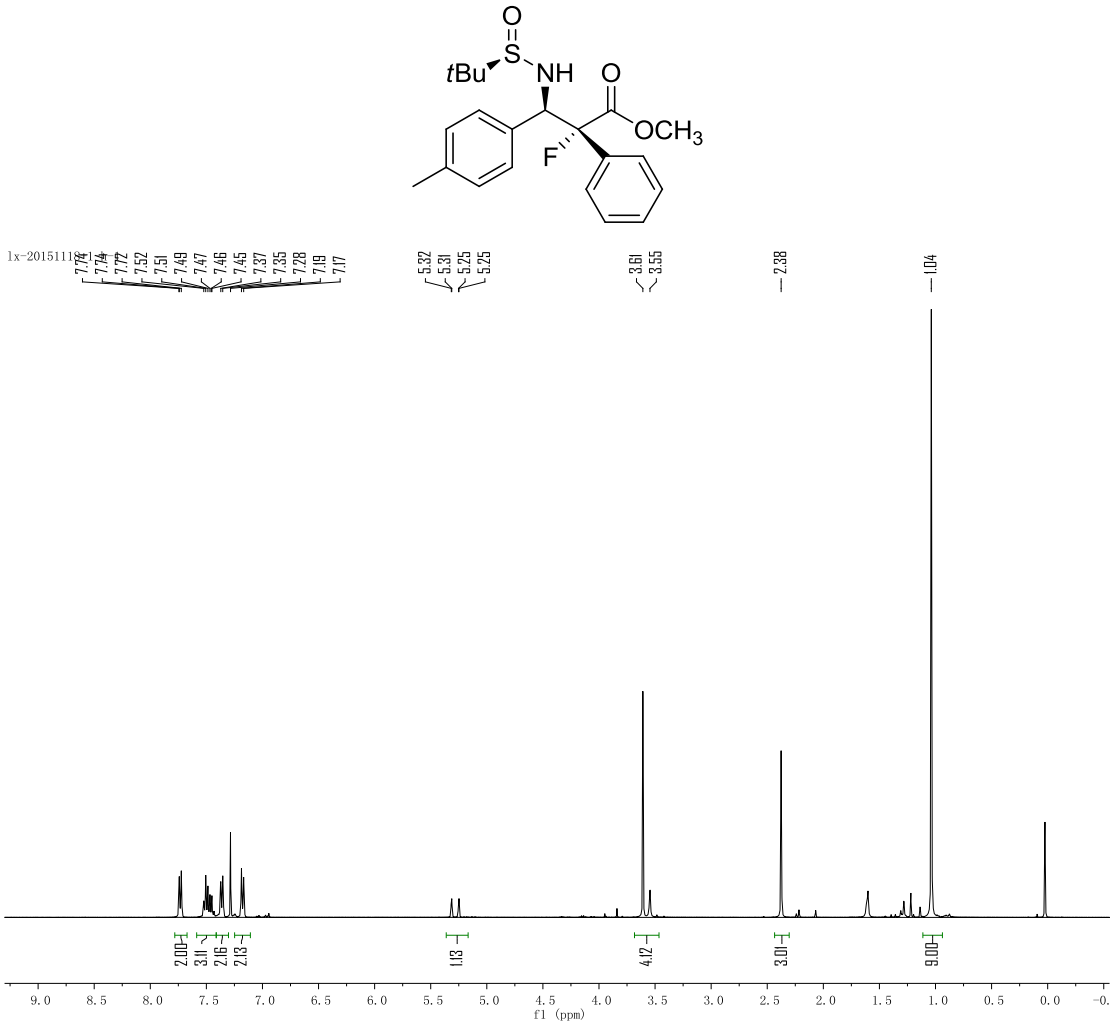
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5a**



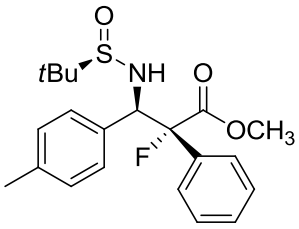
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5a**

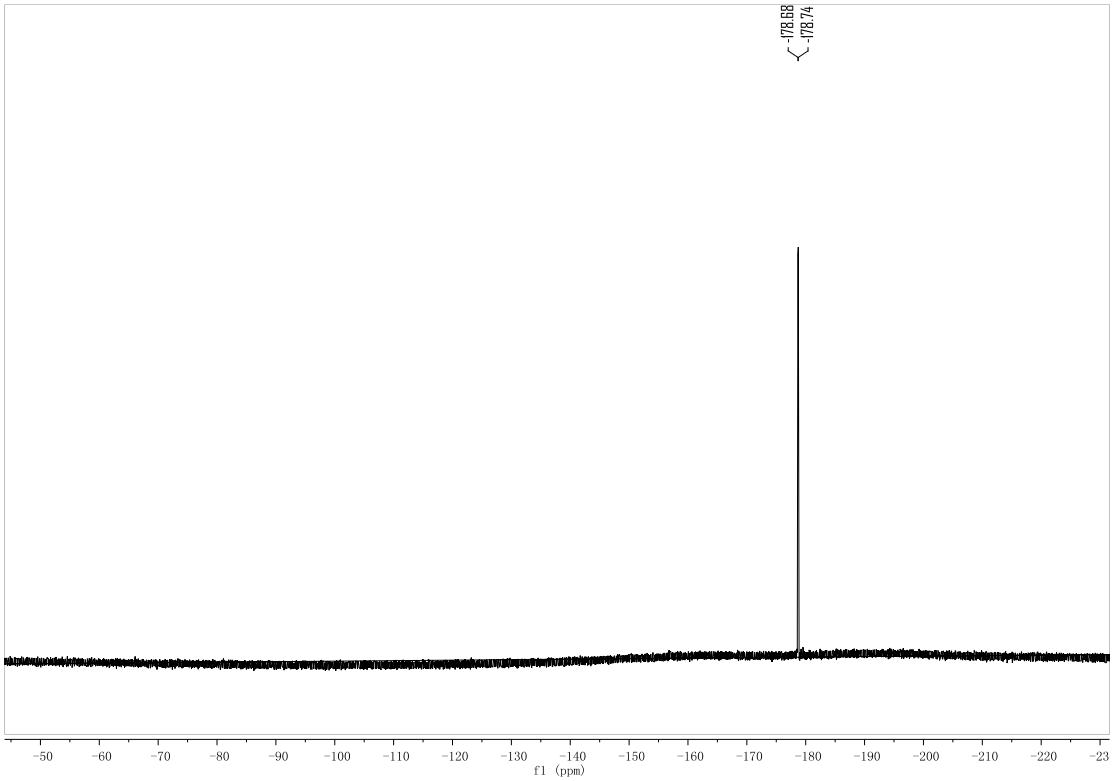


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

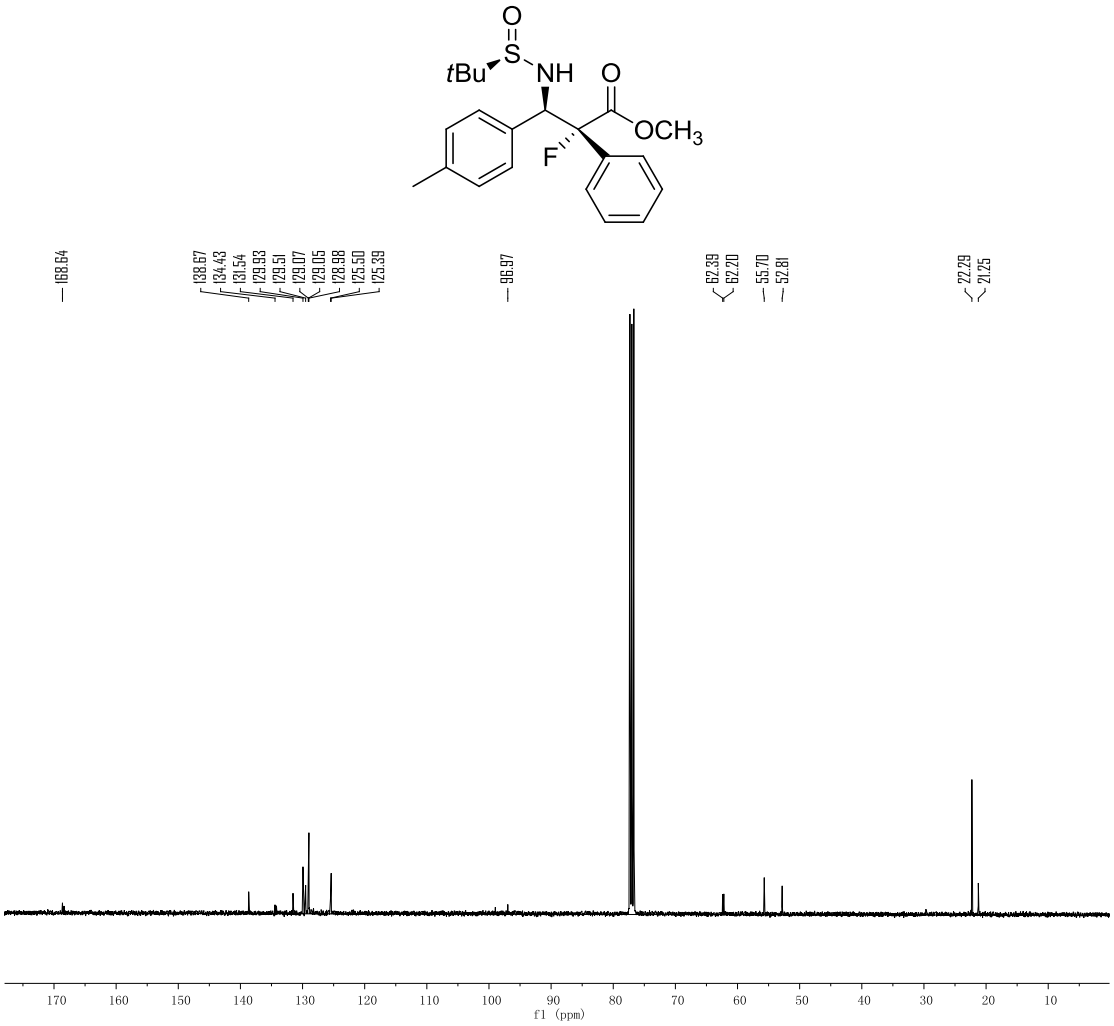


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5b**

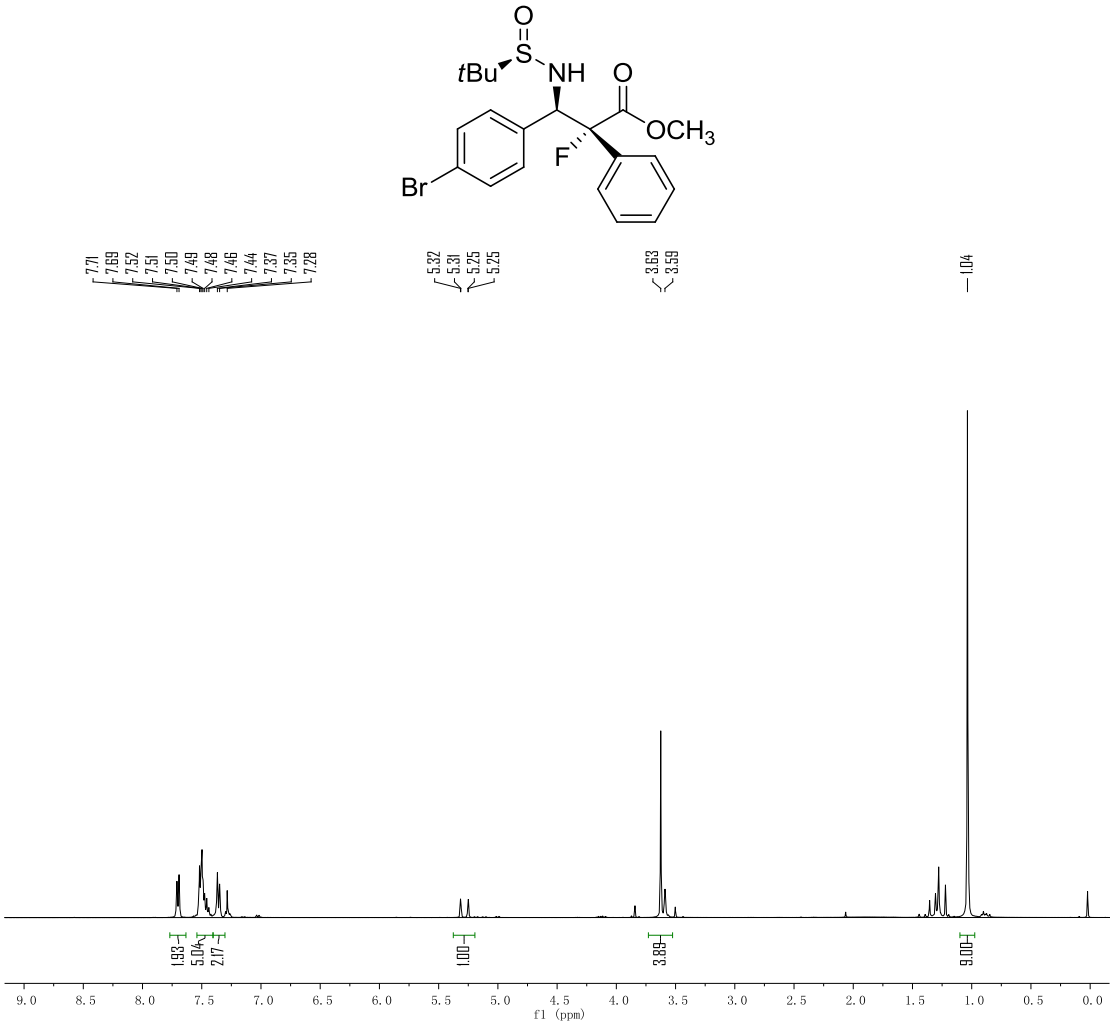




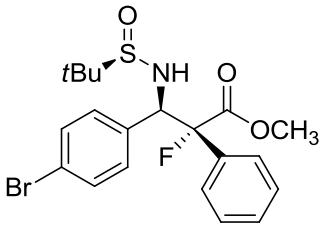
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5b**

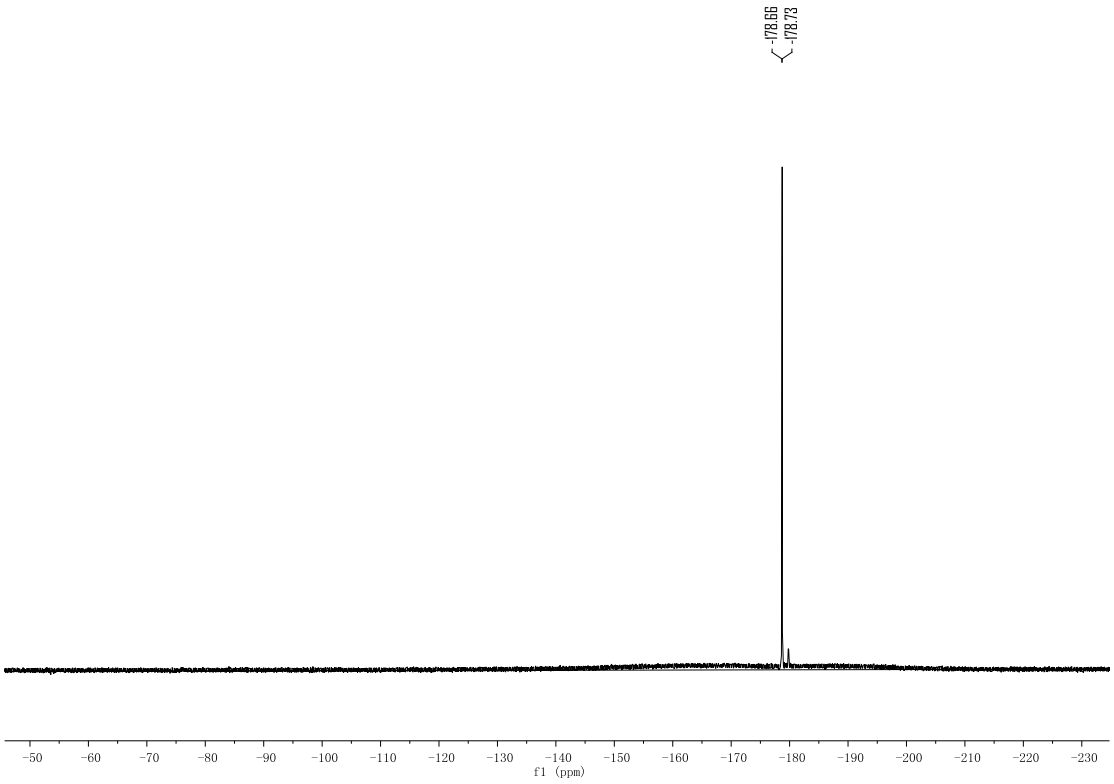


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5c**

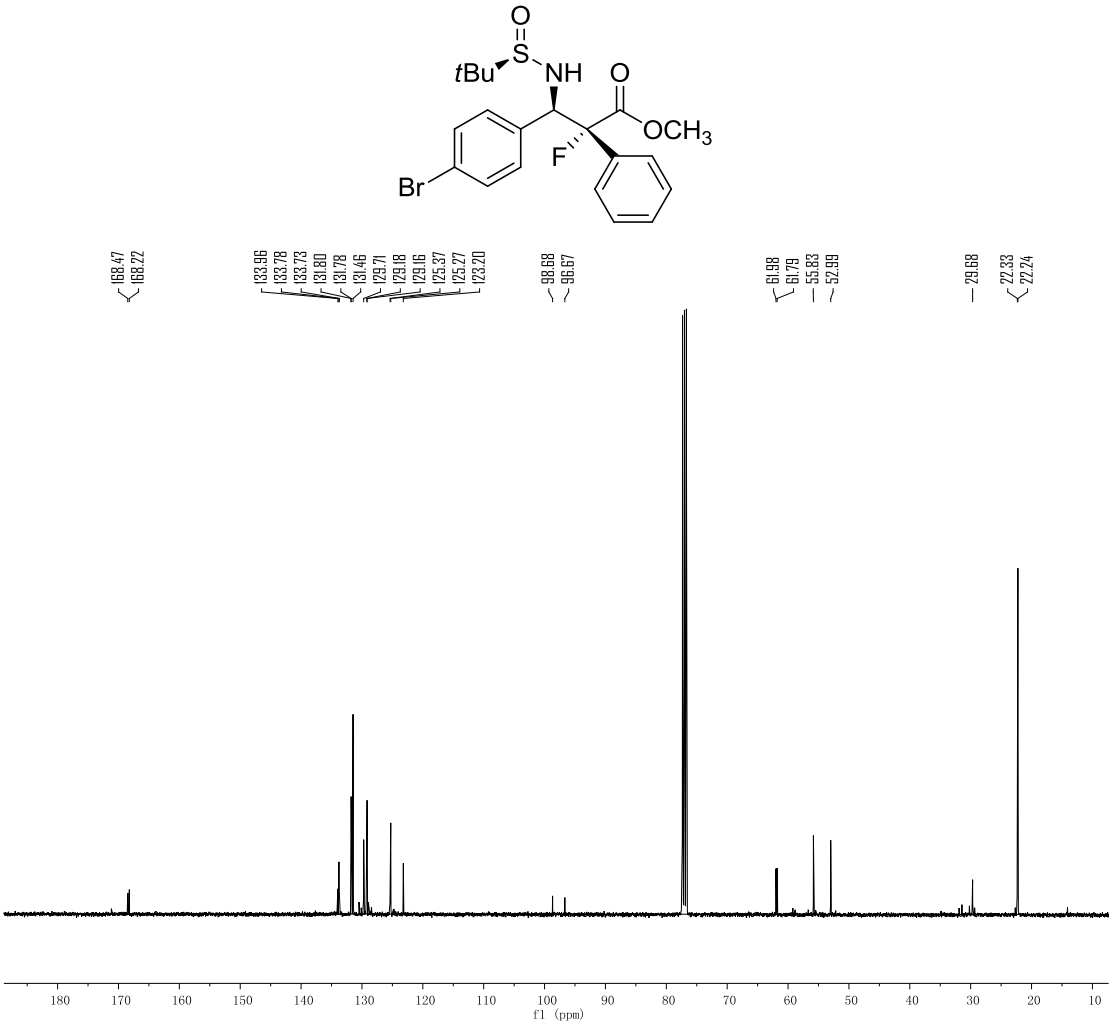


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5c**

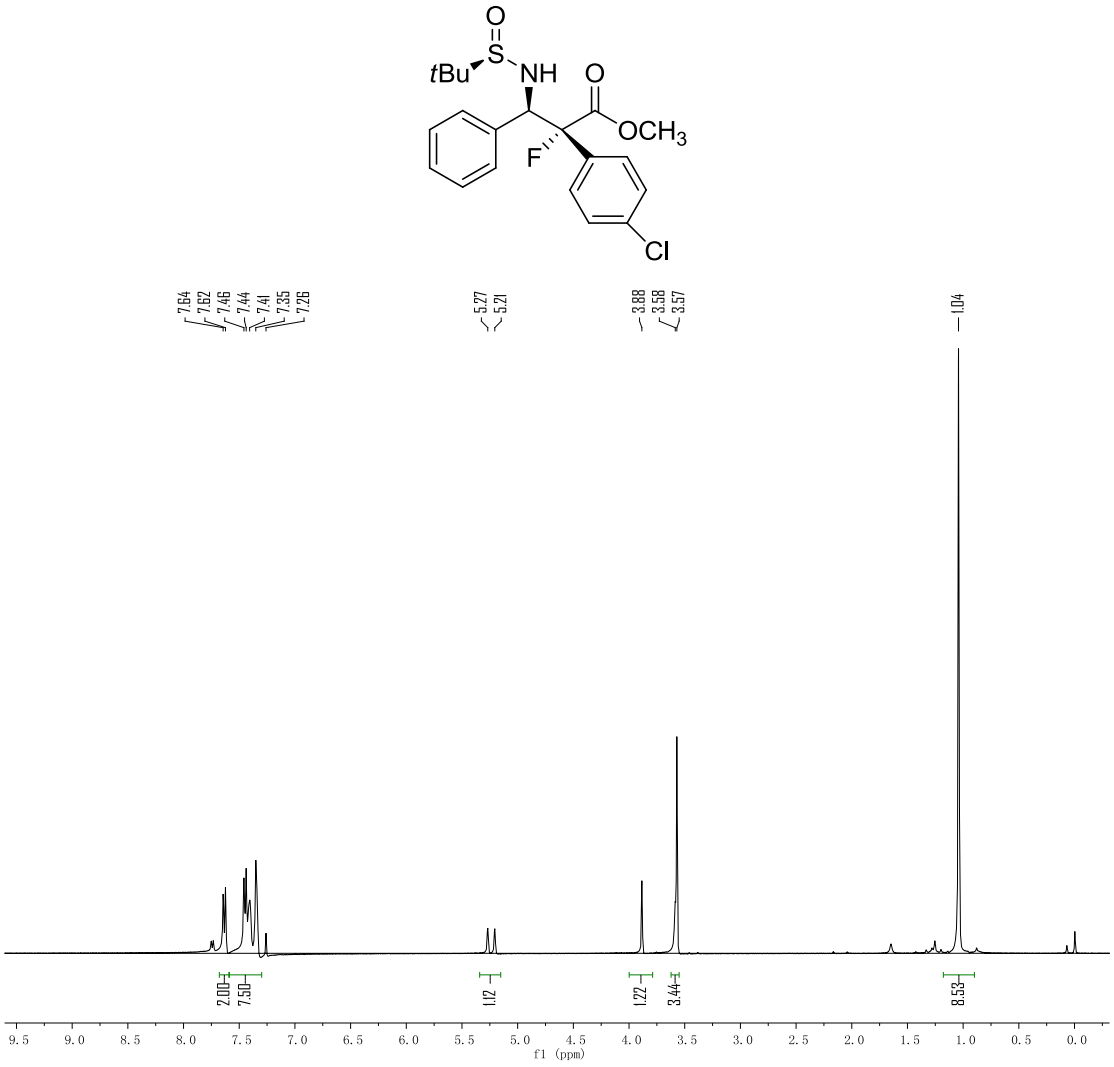




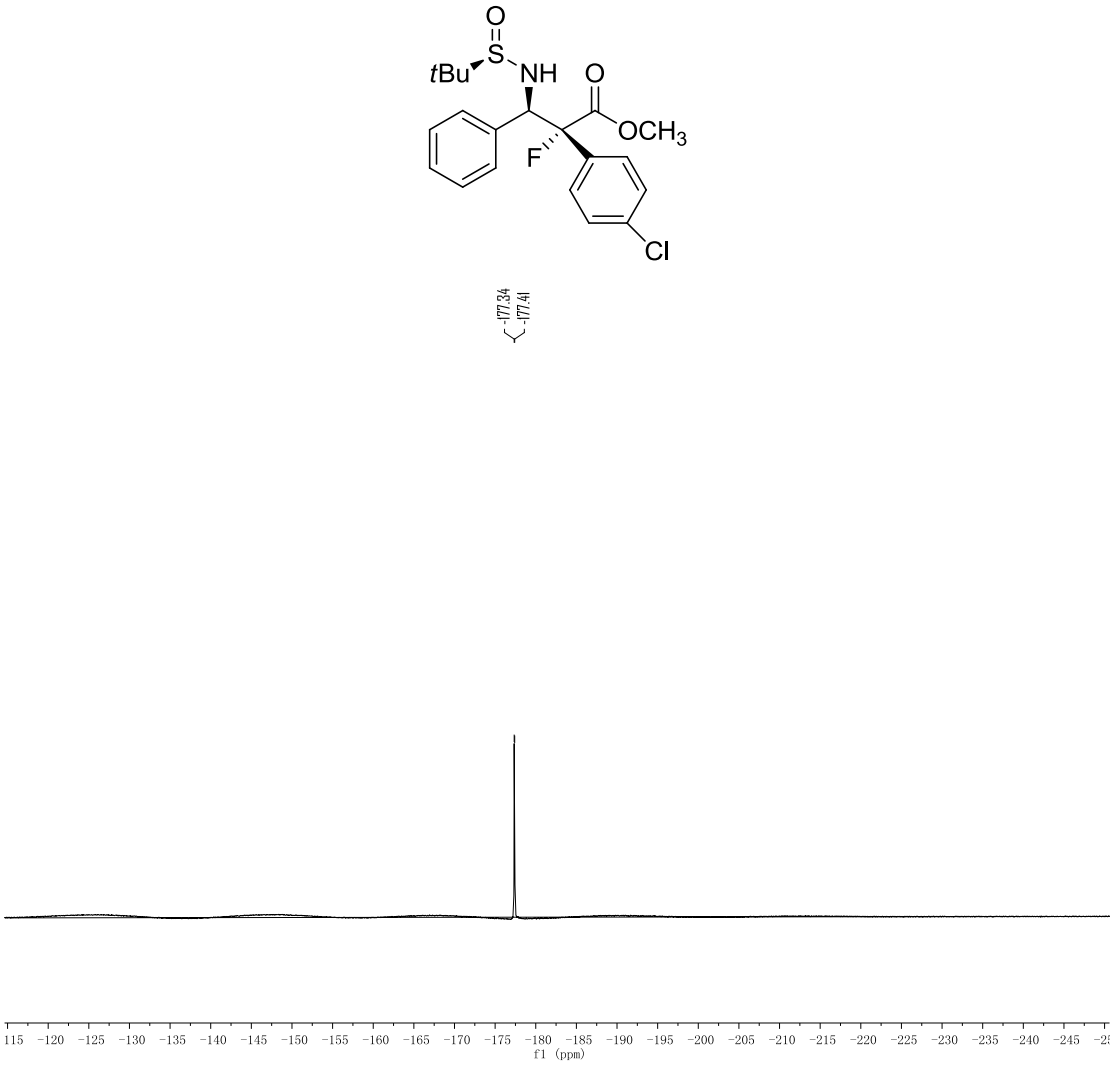
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5c**



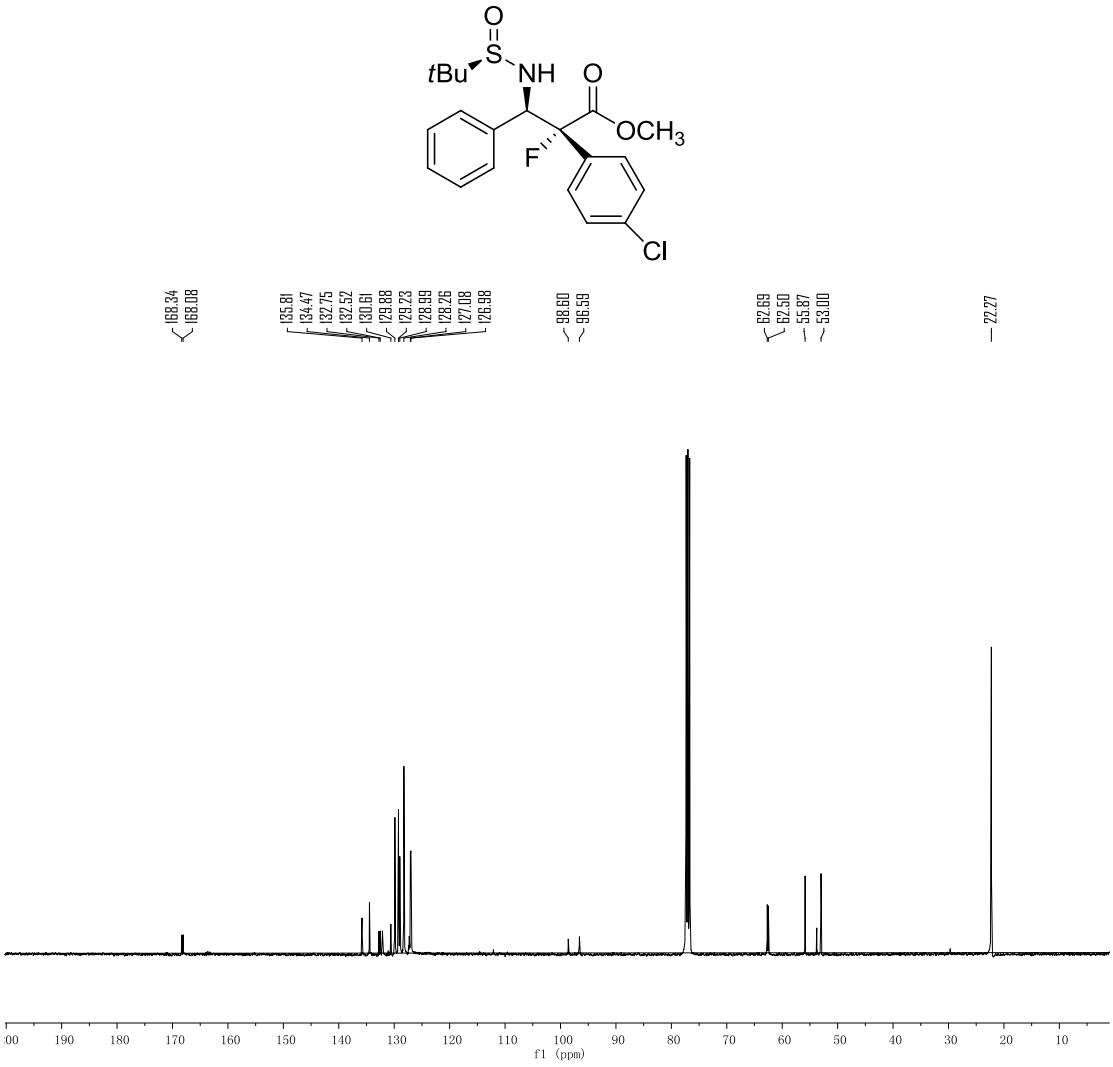
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**



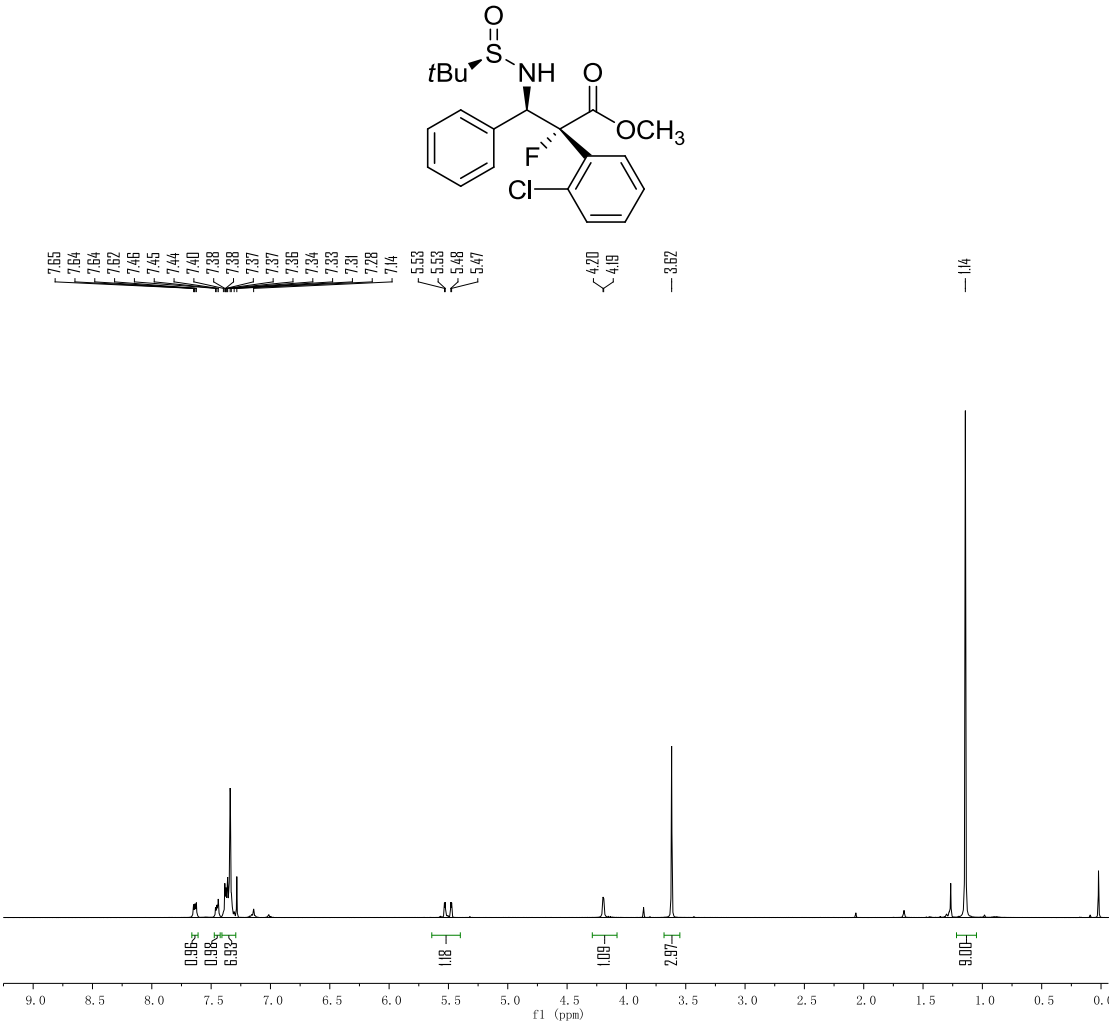
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5d**



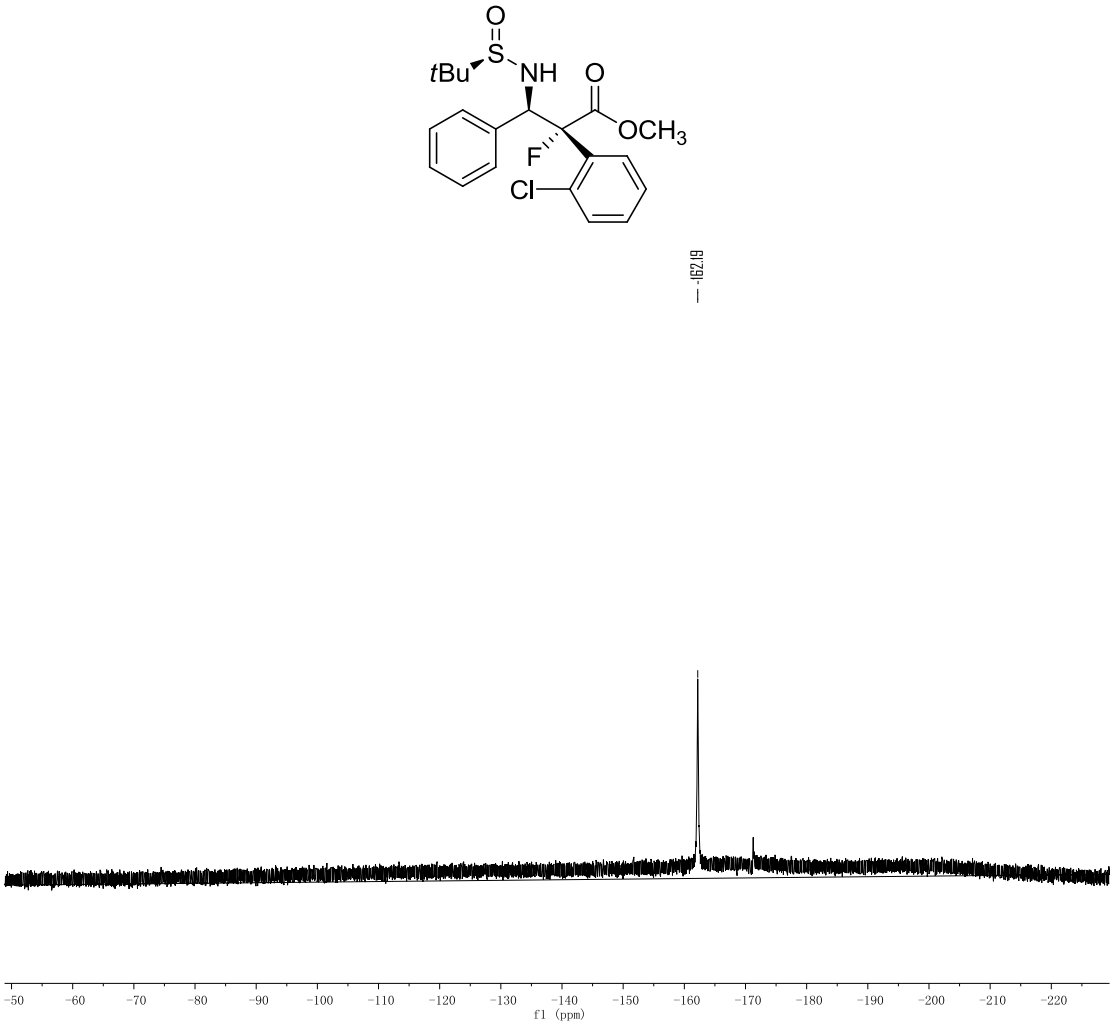
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5d**



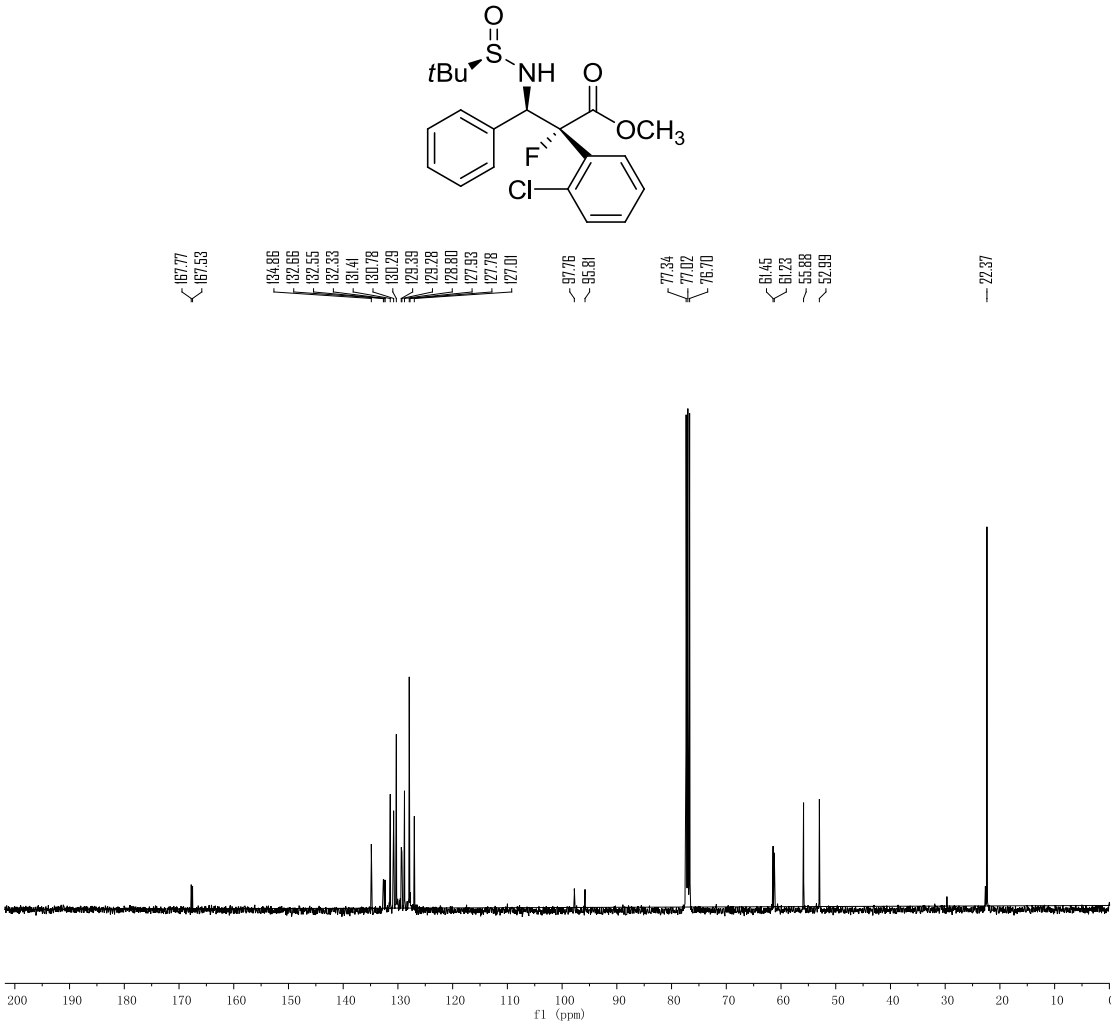
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**



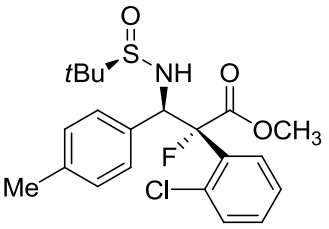
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5e**

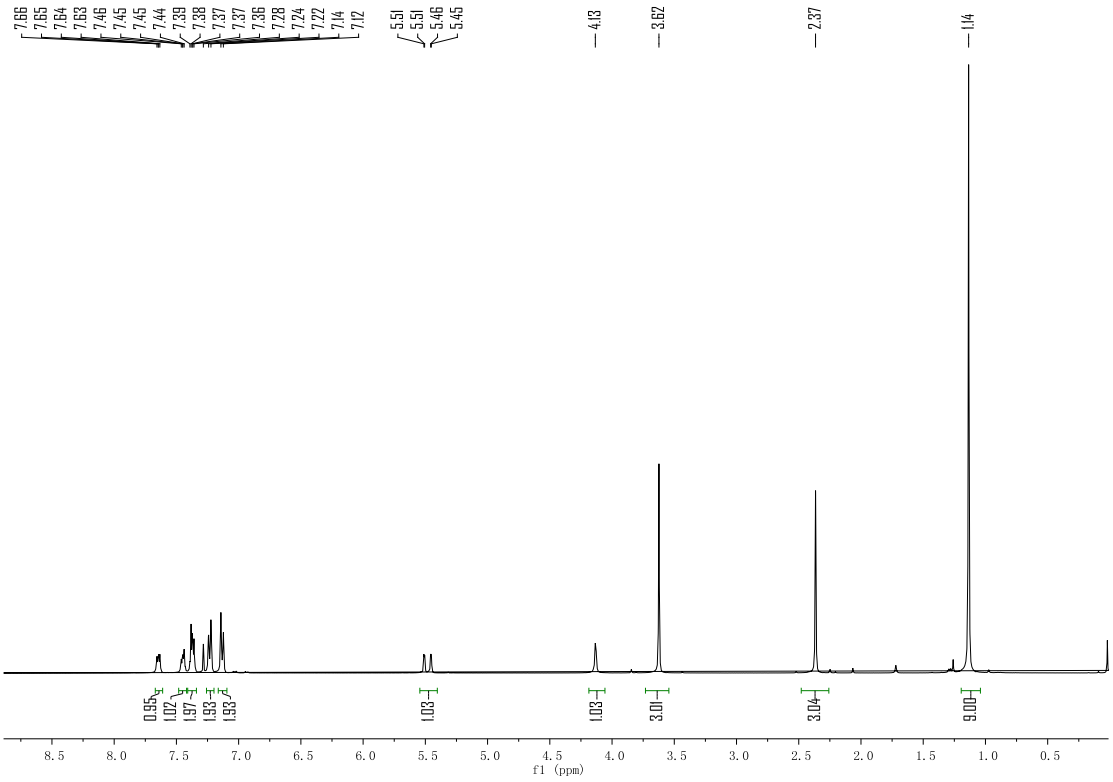


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5e**

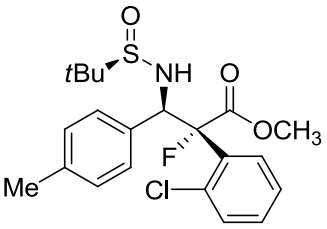


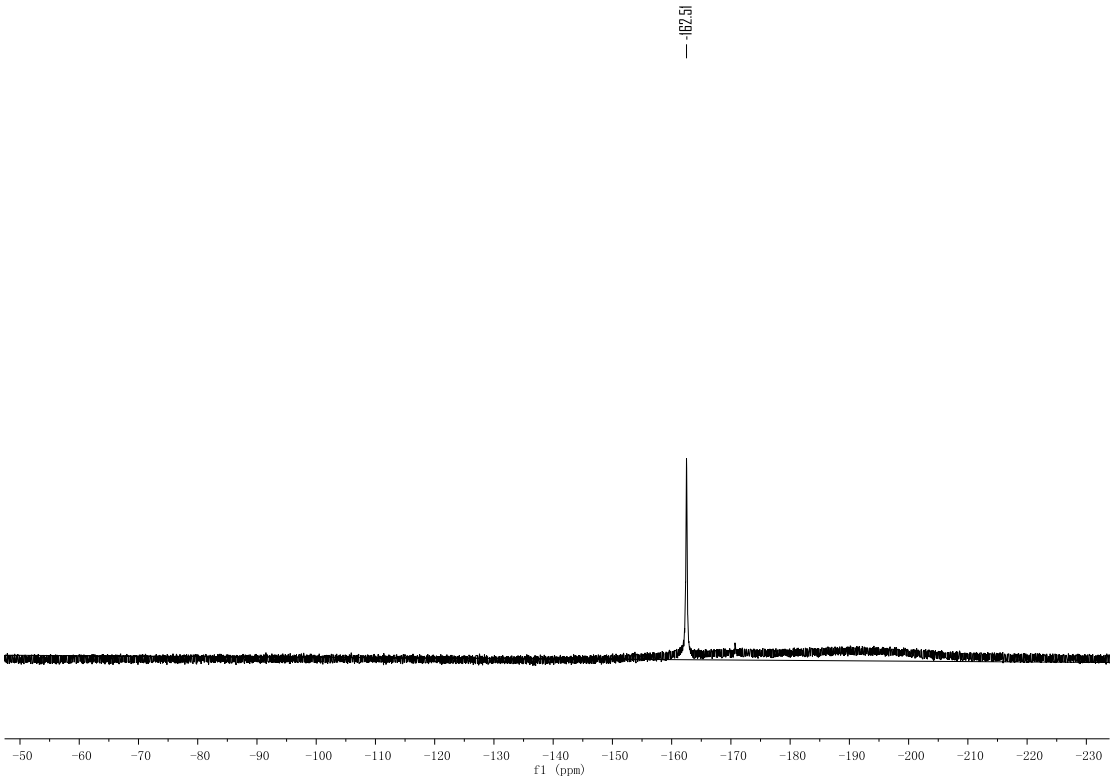
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5f**



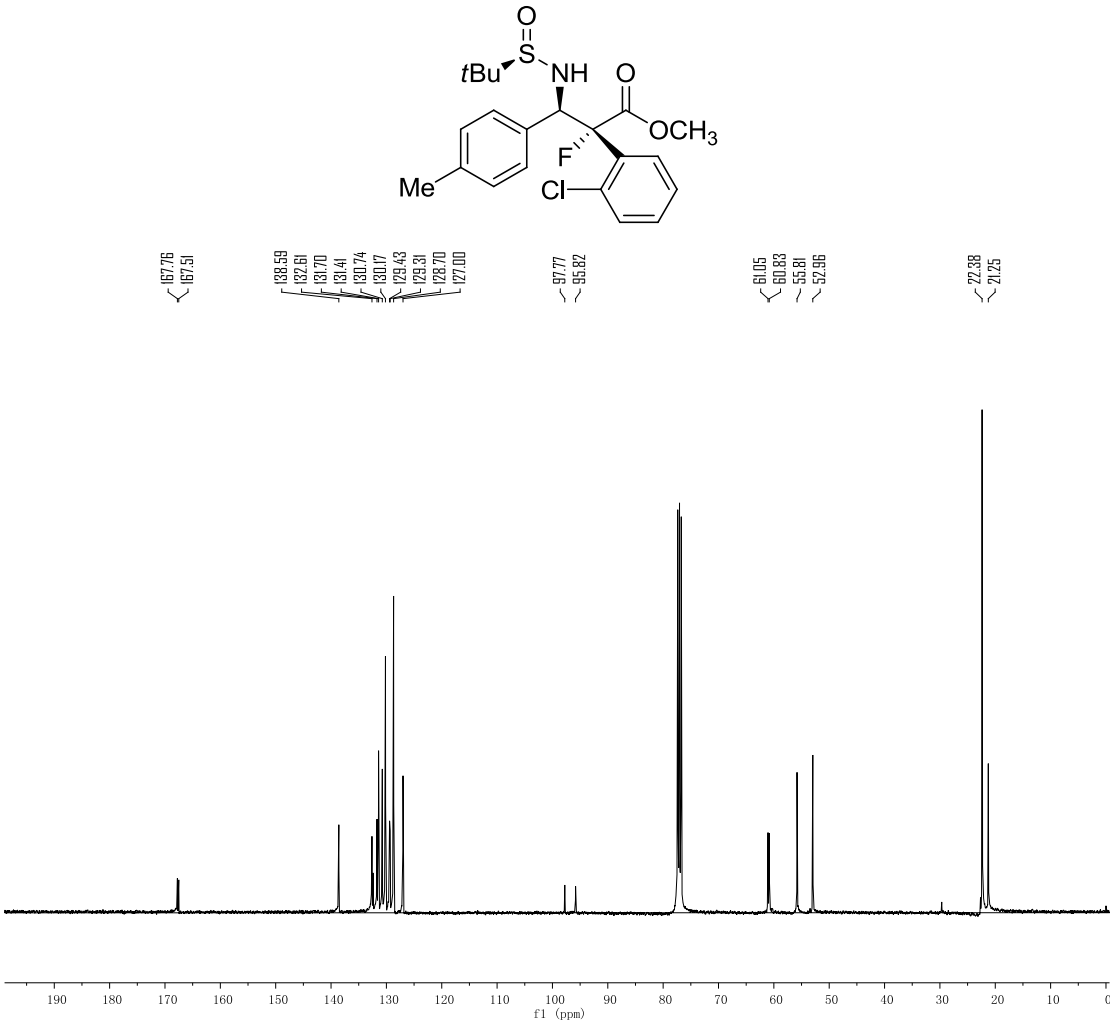


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5f**

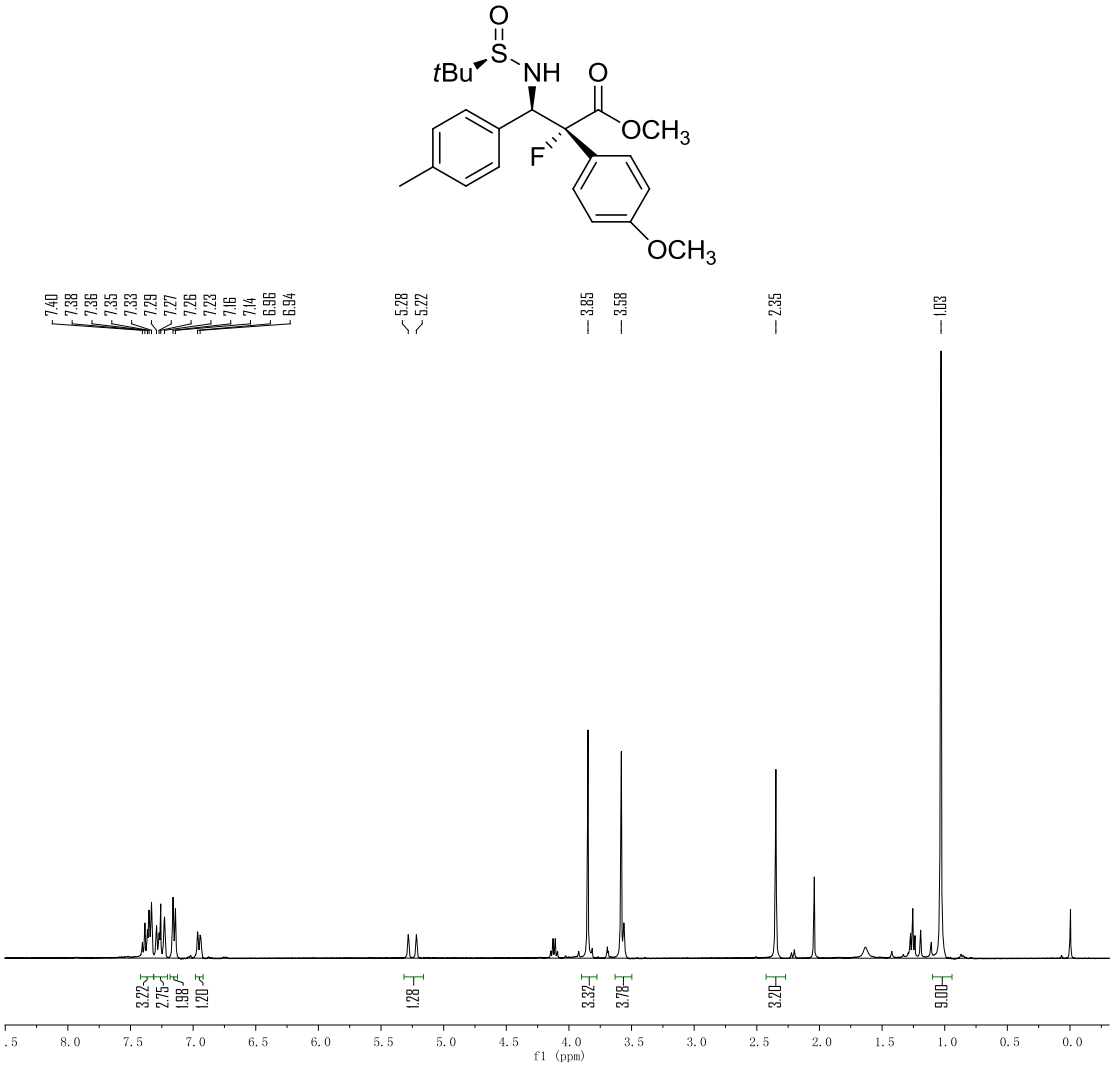




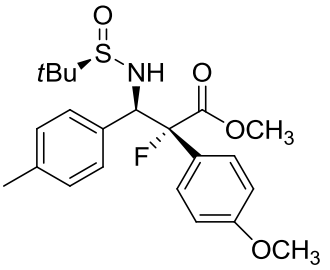
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5f**

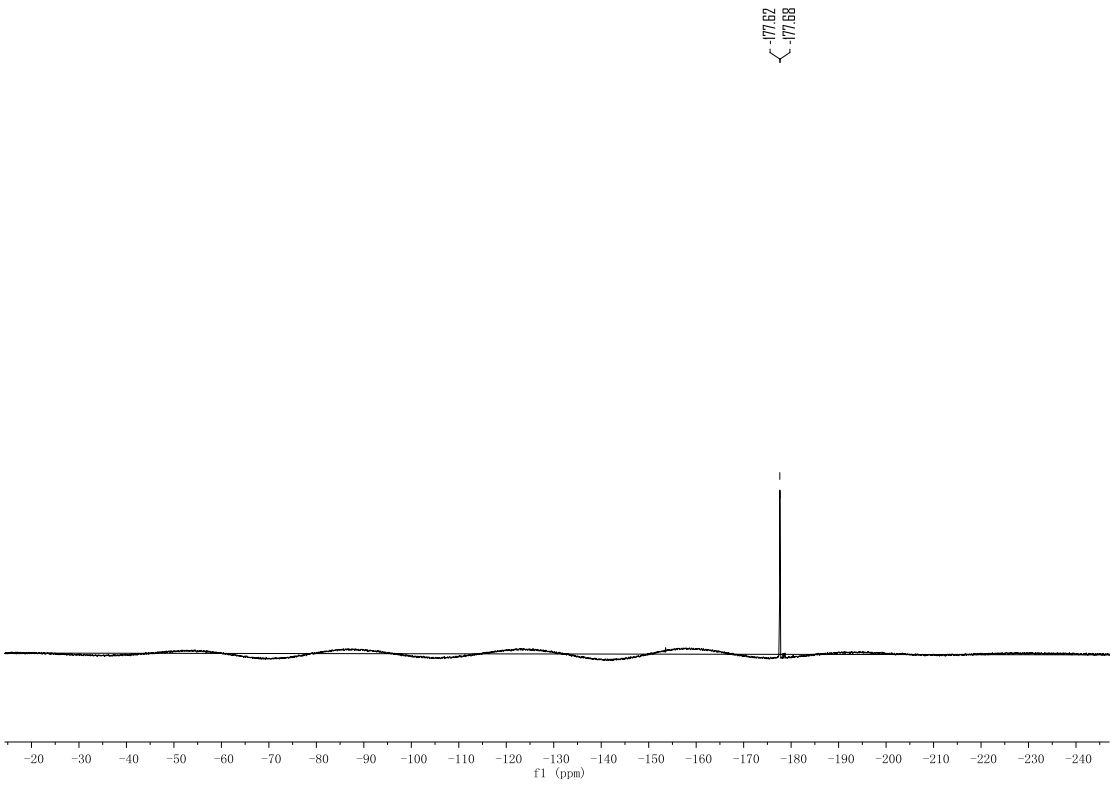


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5g**

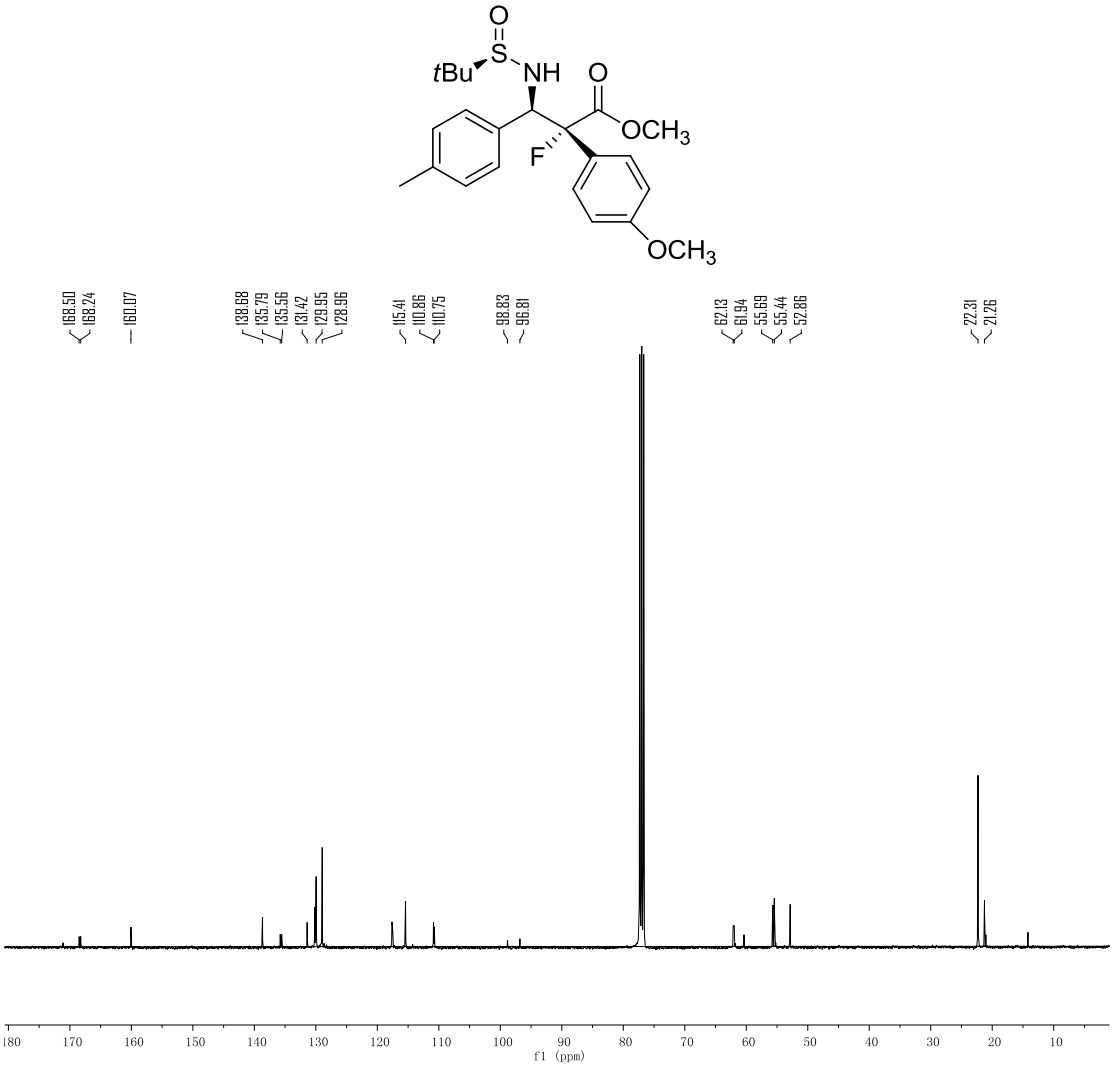


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5g**

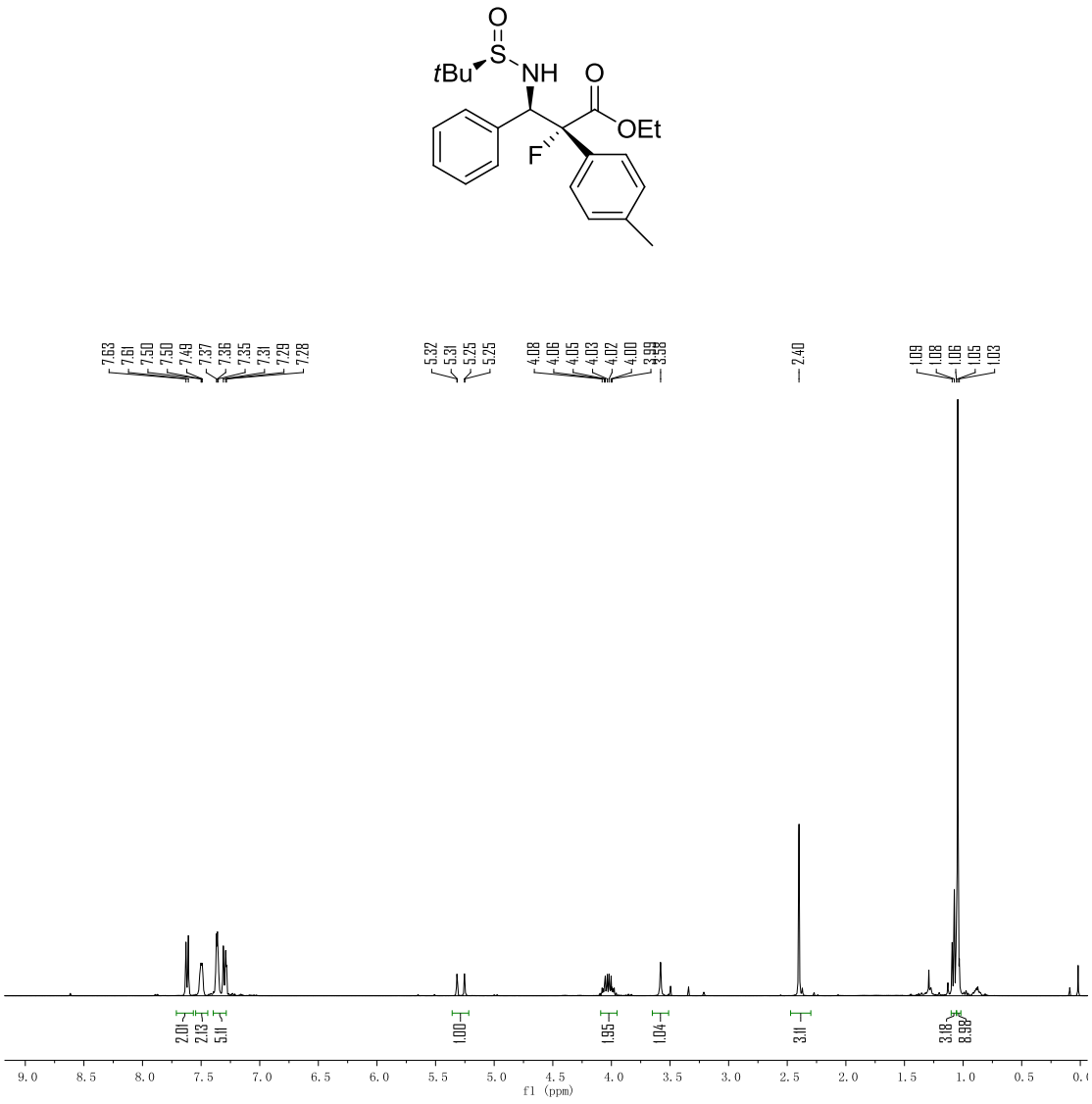




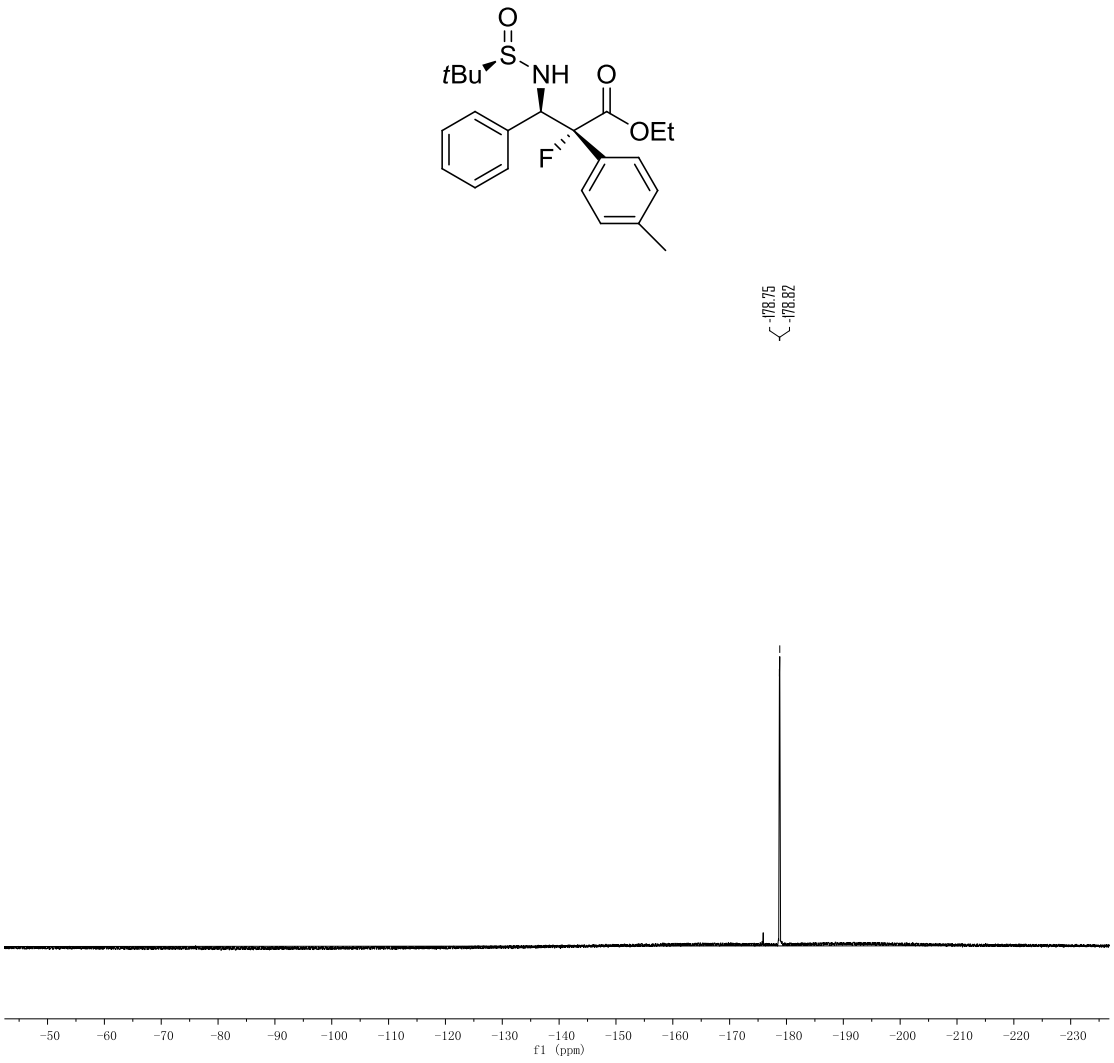
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5g**



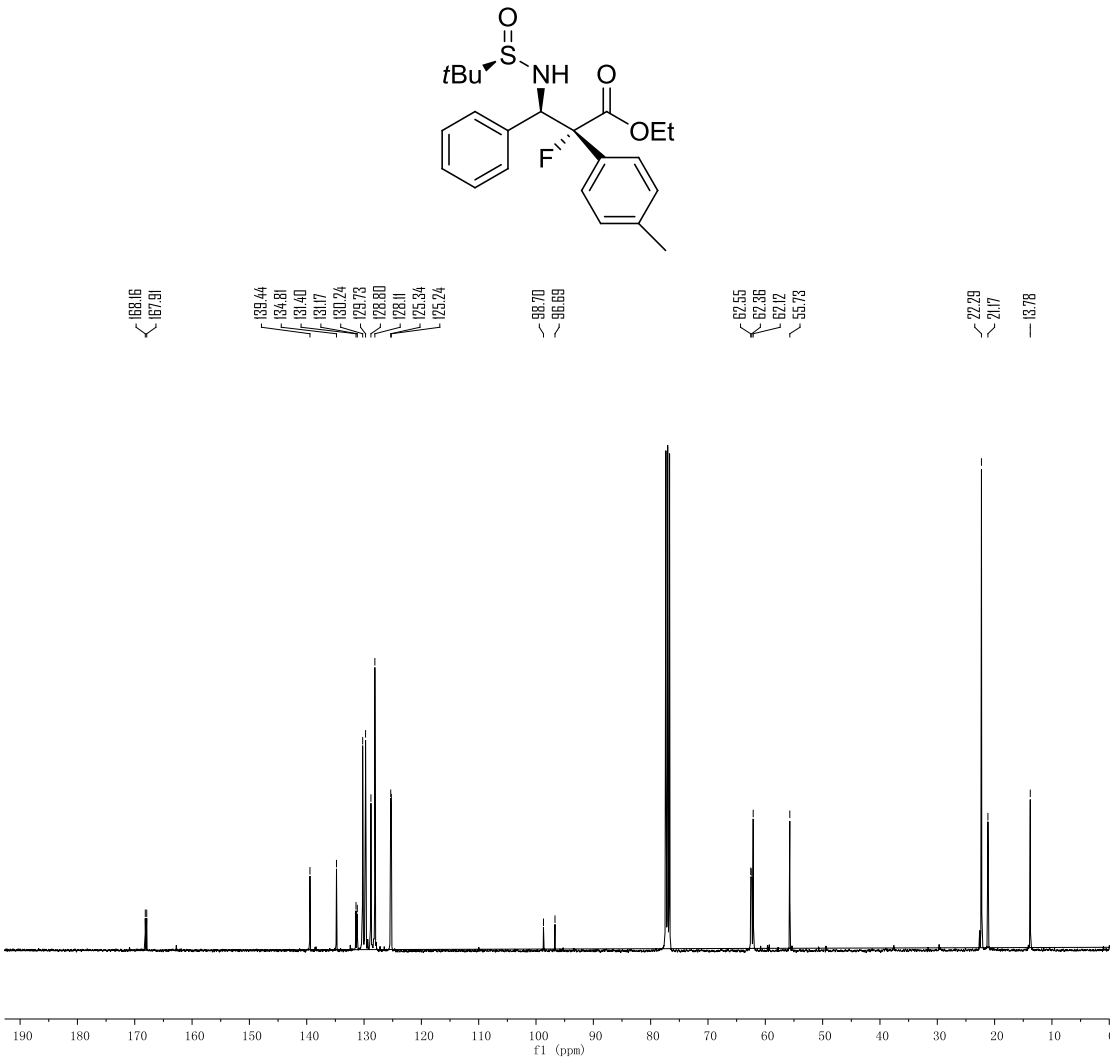
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5h**



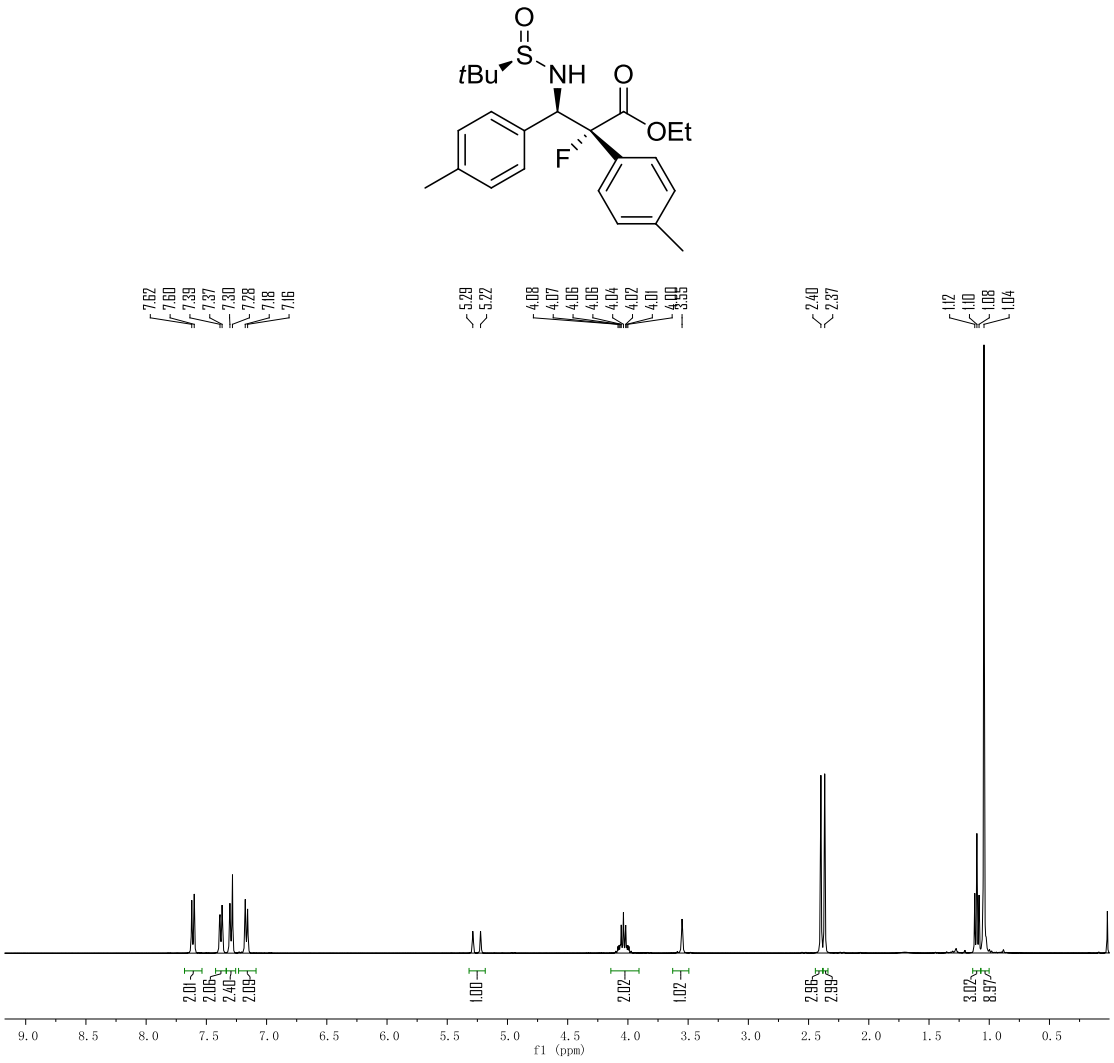
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5h**



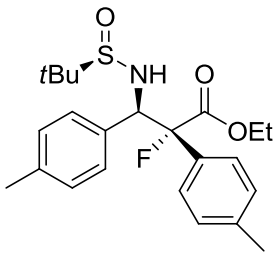
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5h**

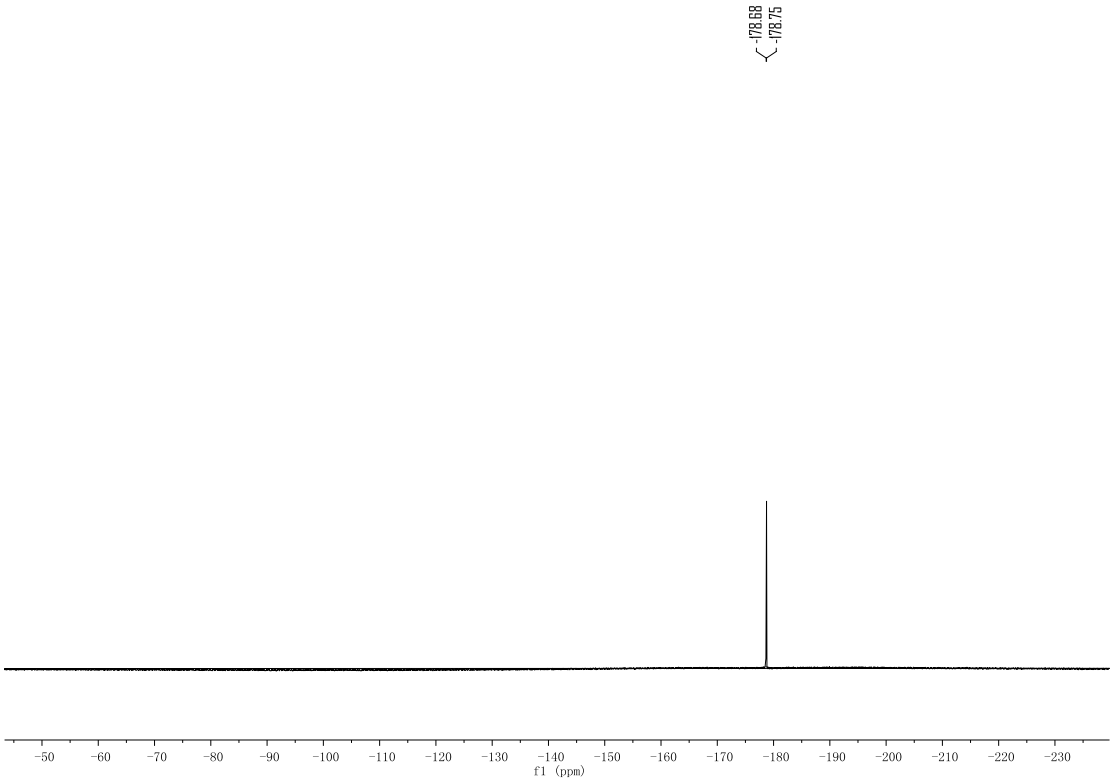


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5i**

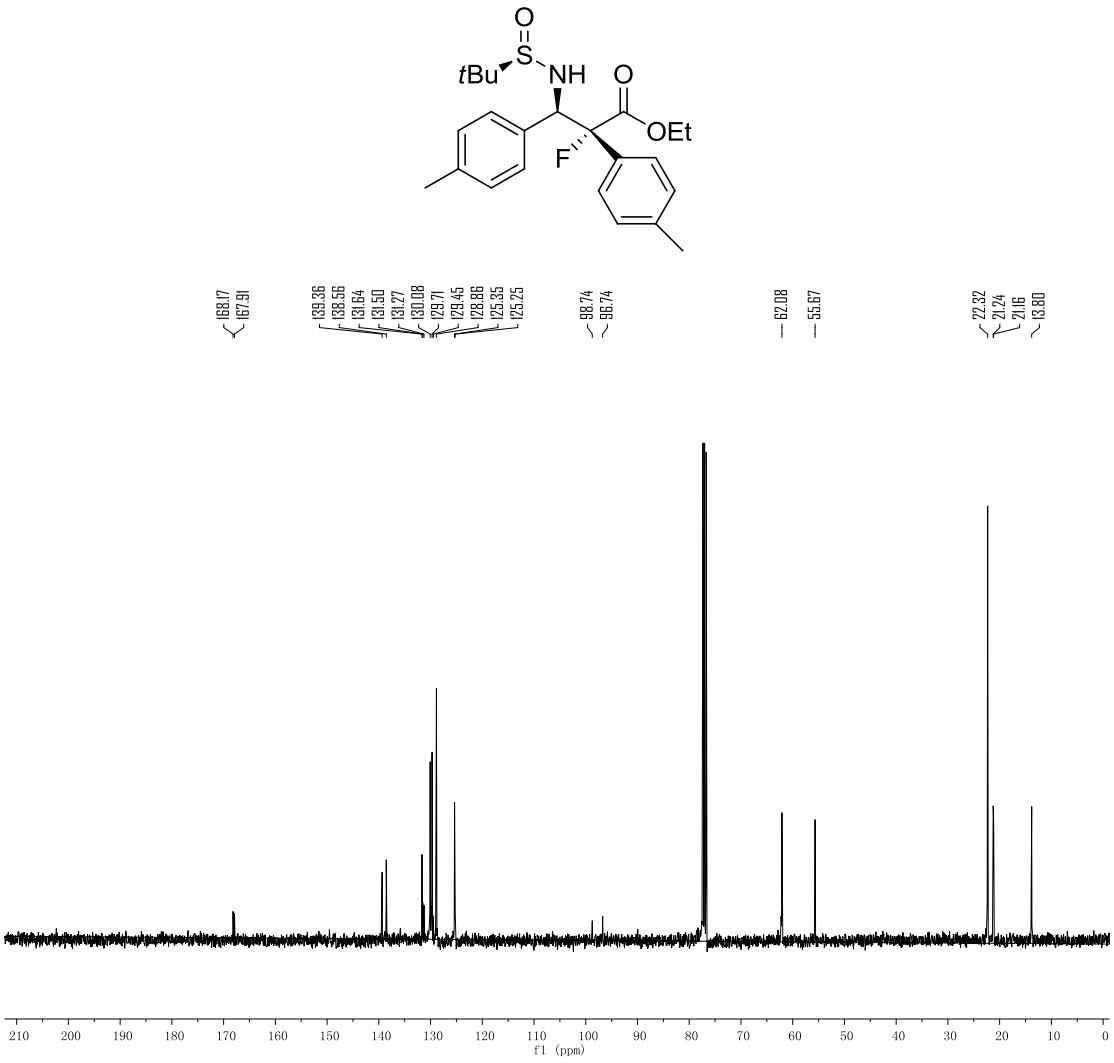


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5i**

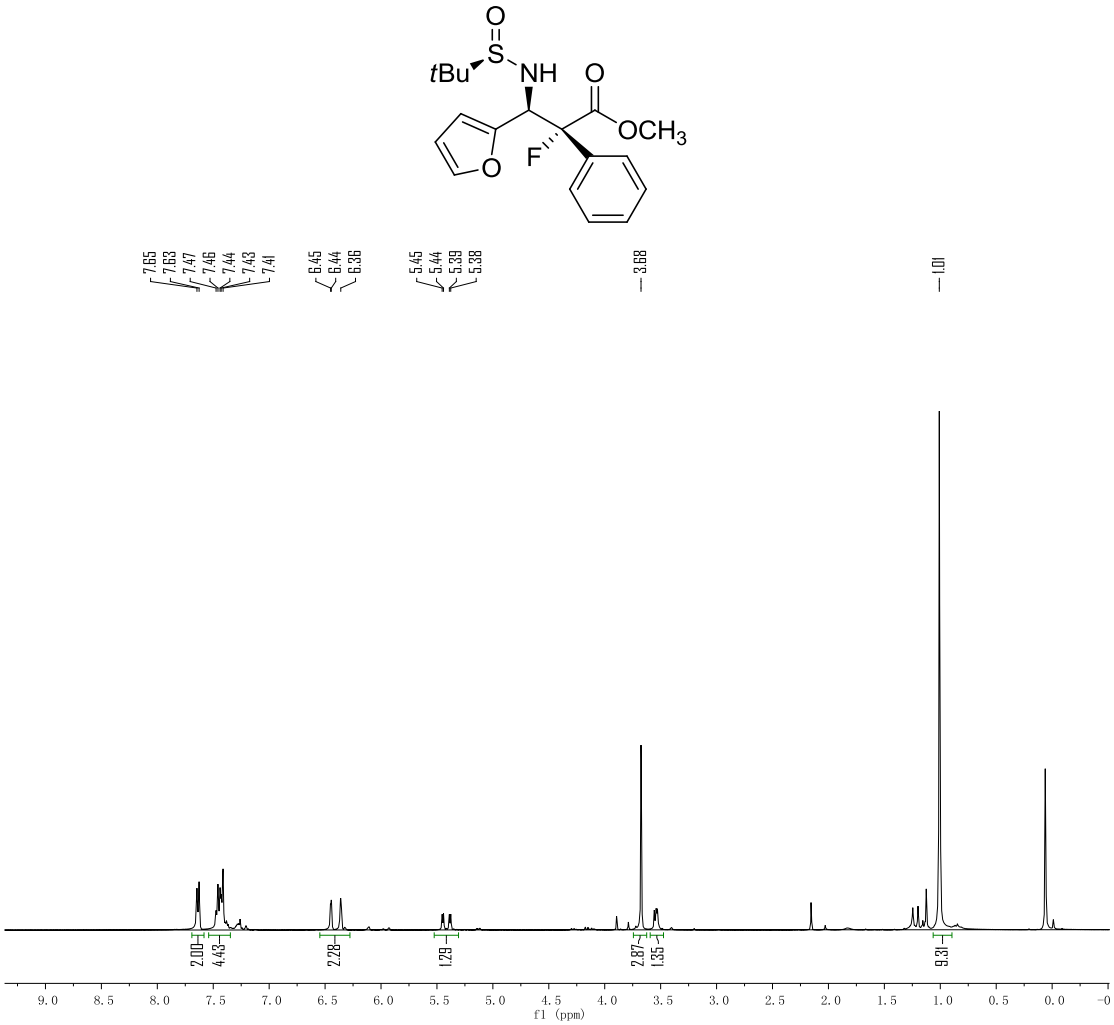




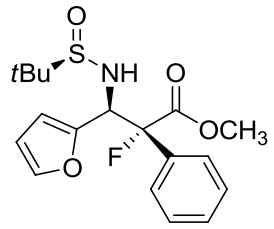
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5i**

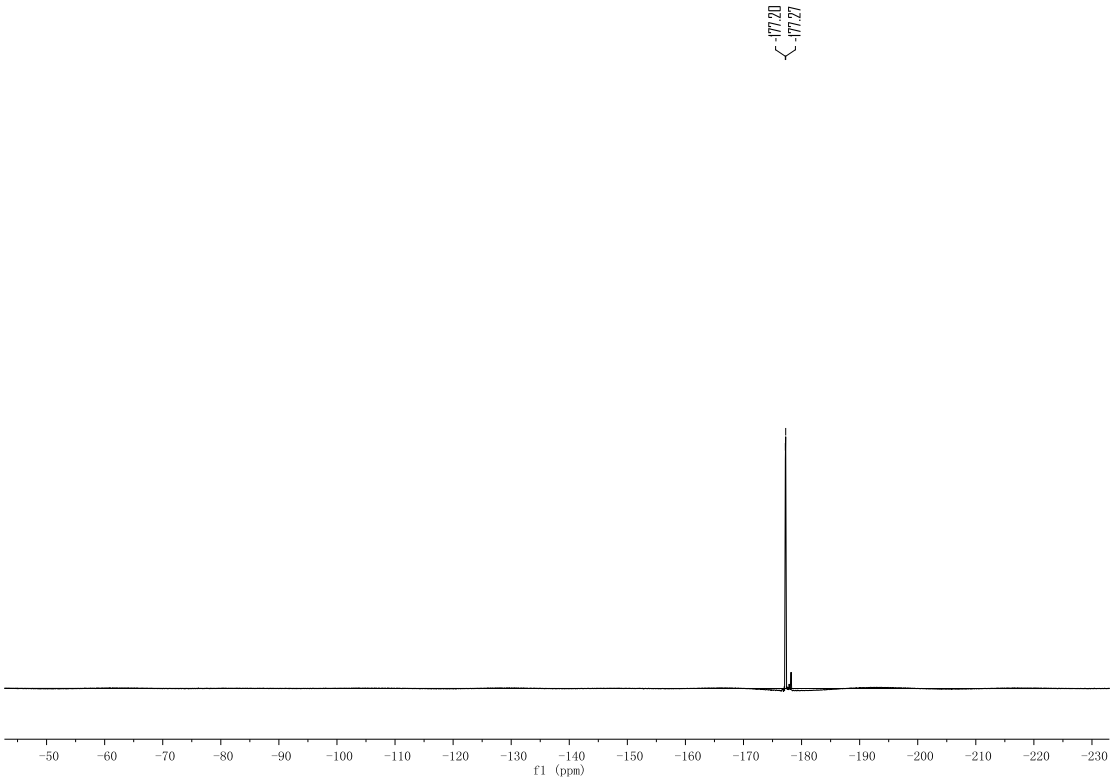


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5j**

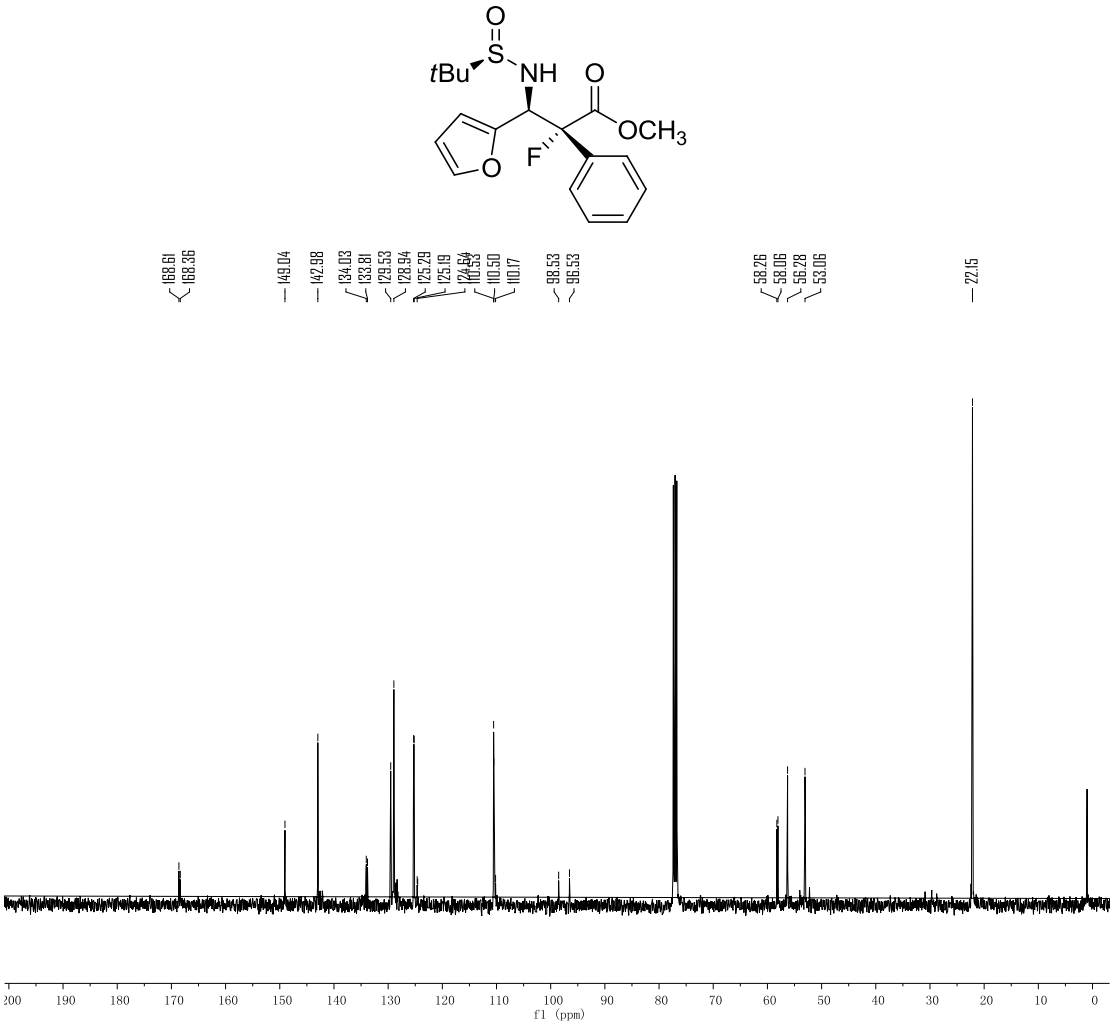


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5j**

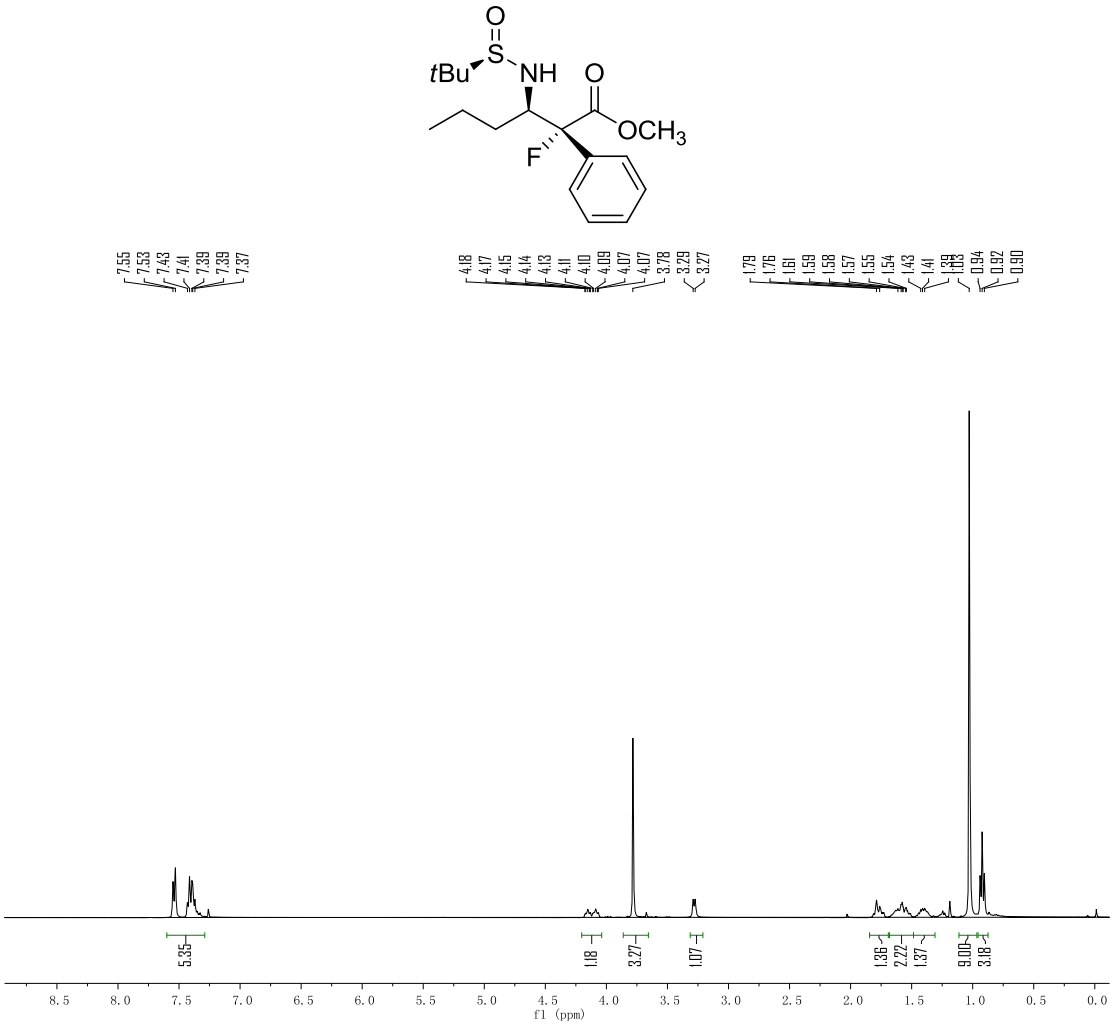




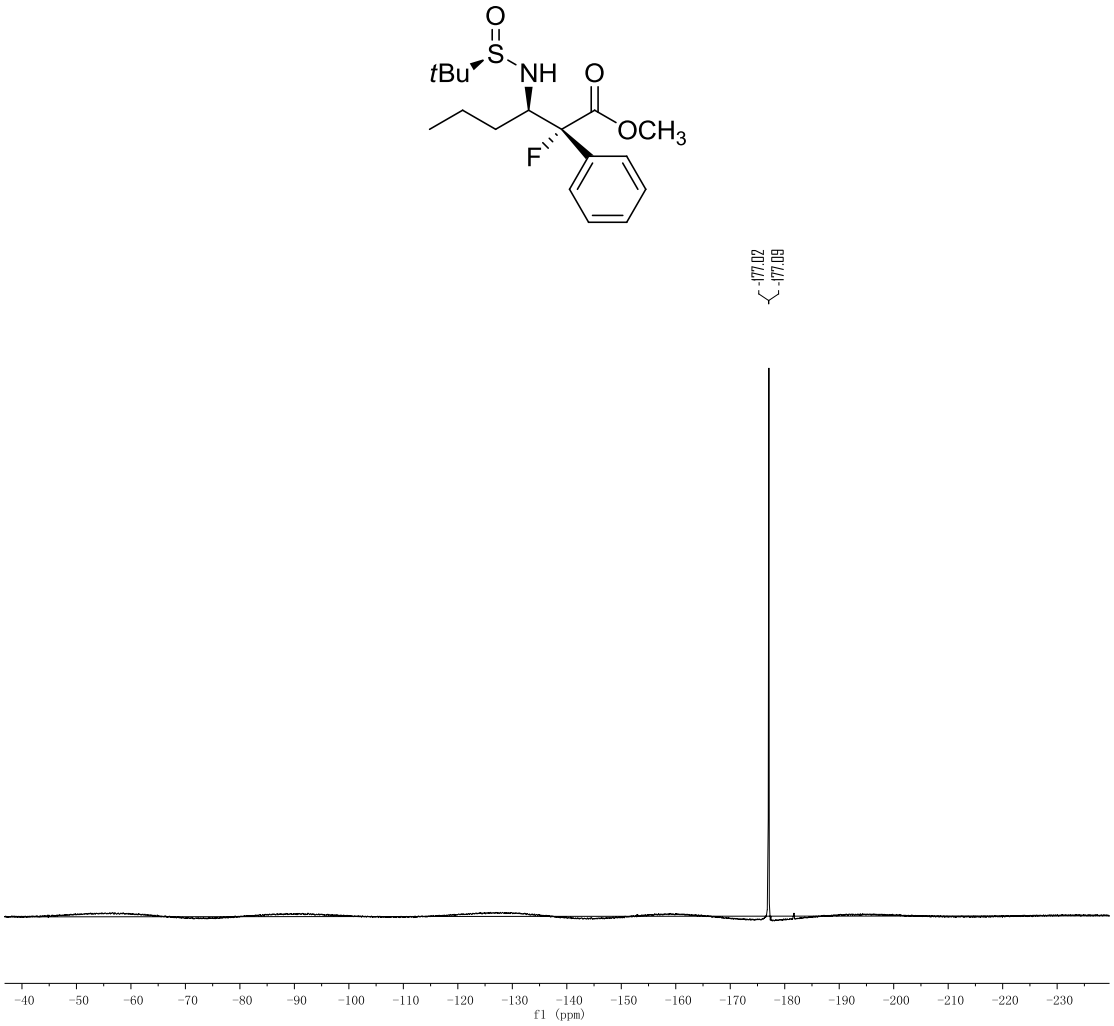
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5j**



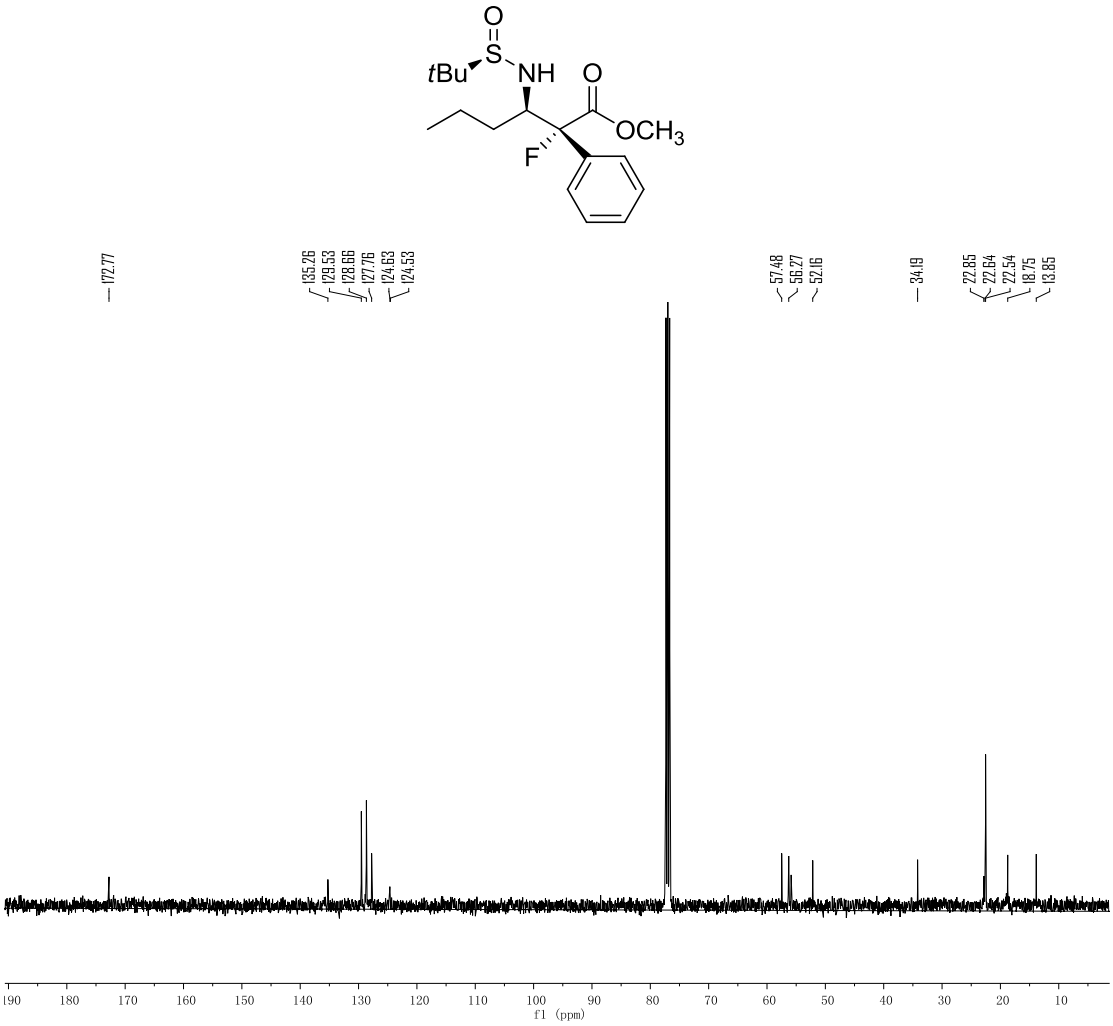
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5k**



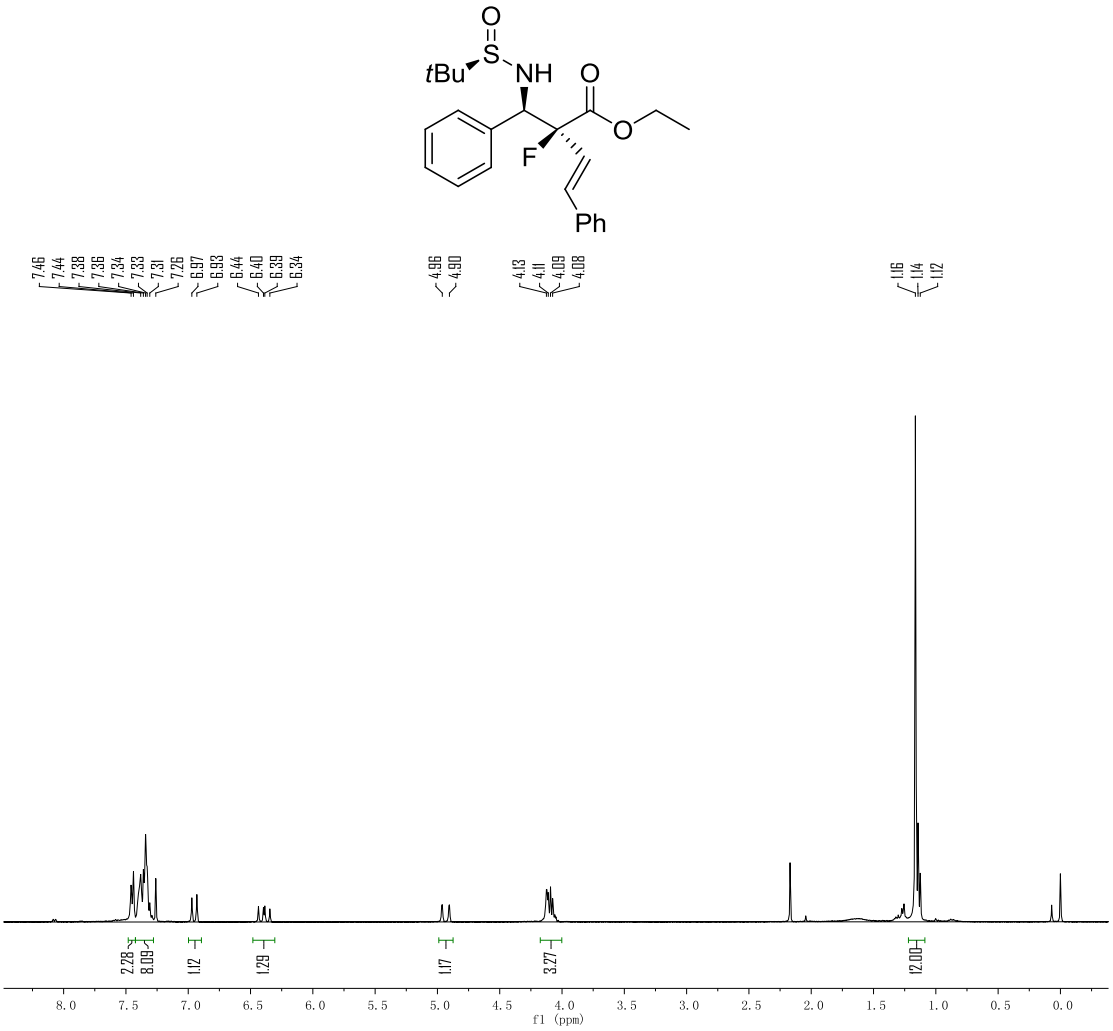
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5k**



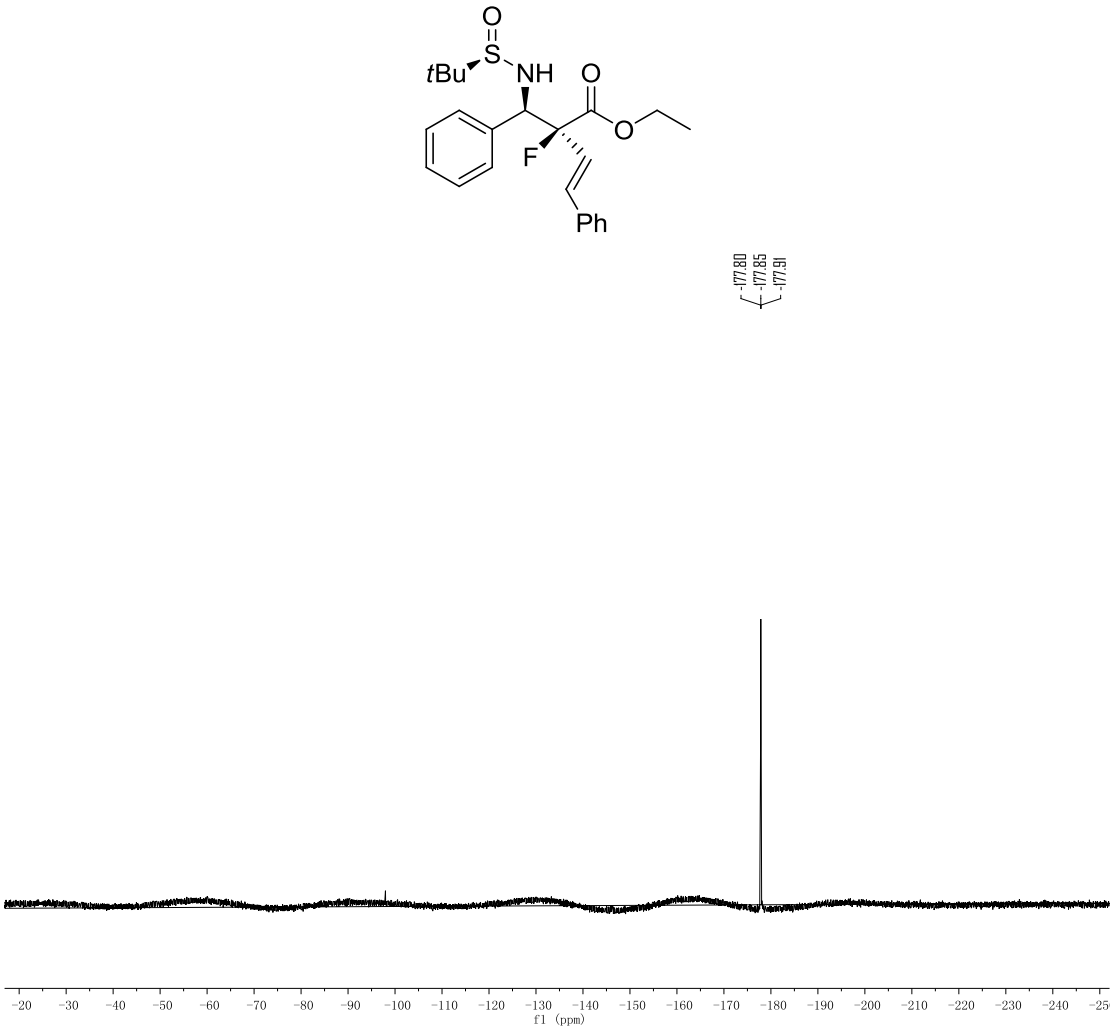
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5k**



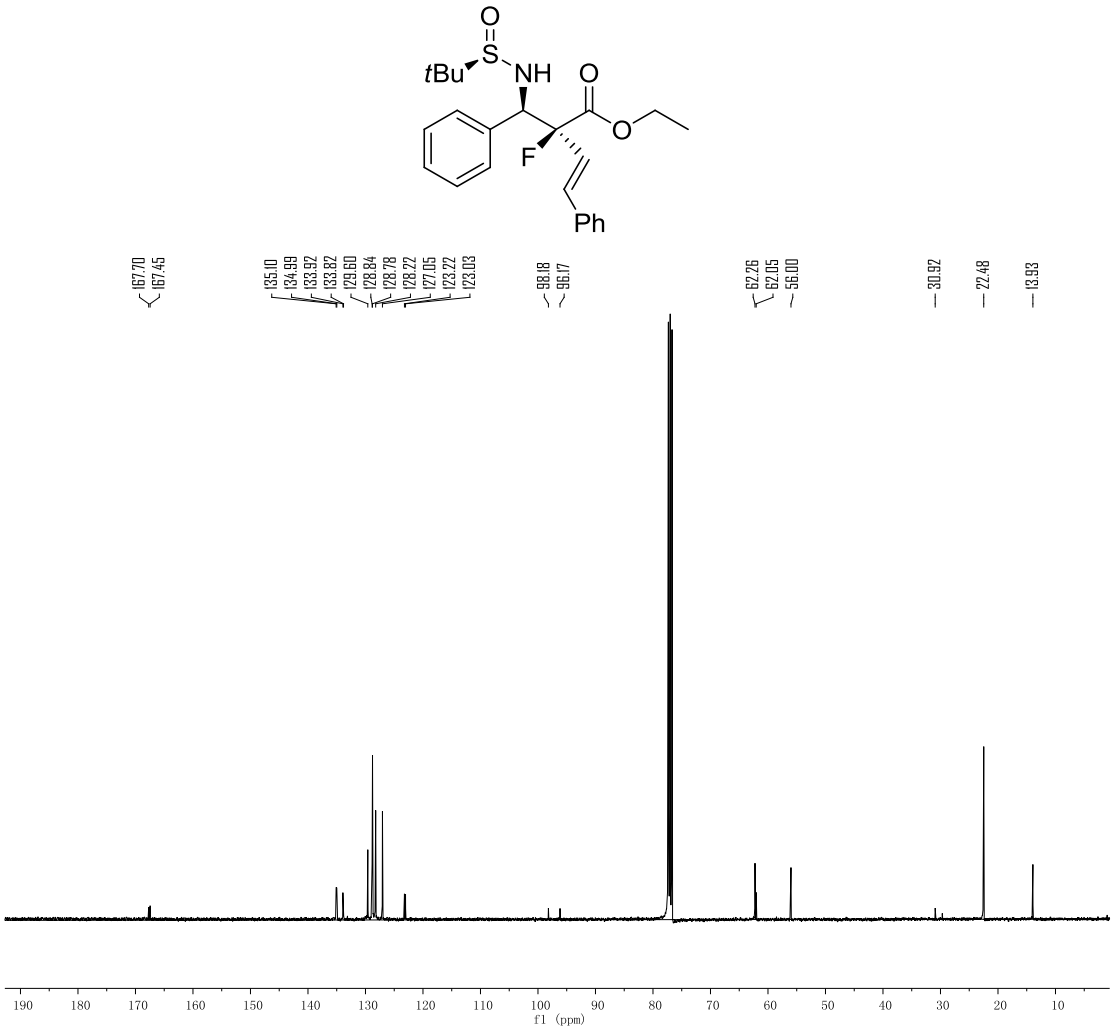
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7a**



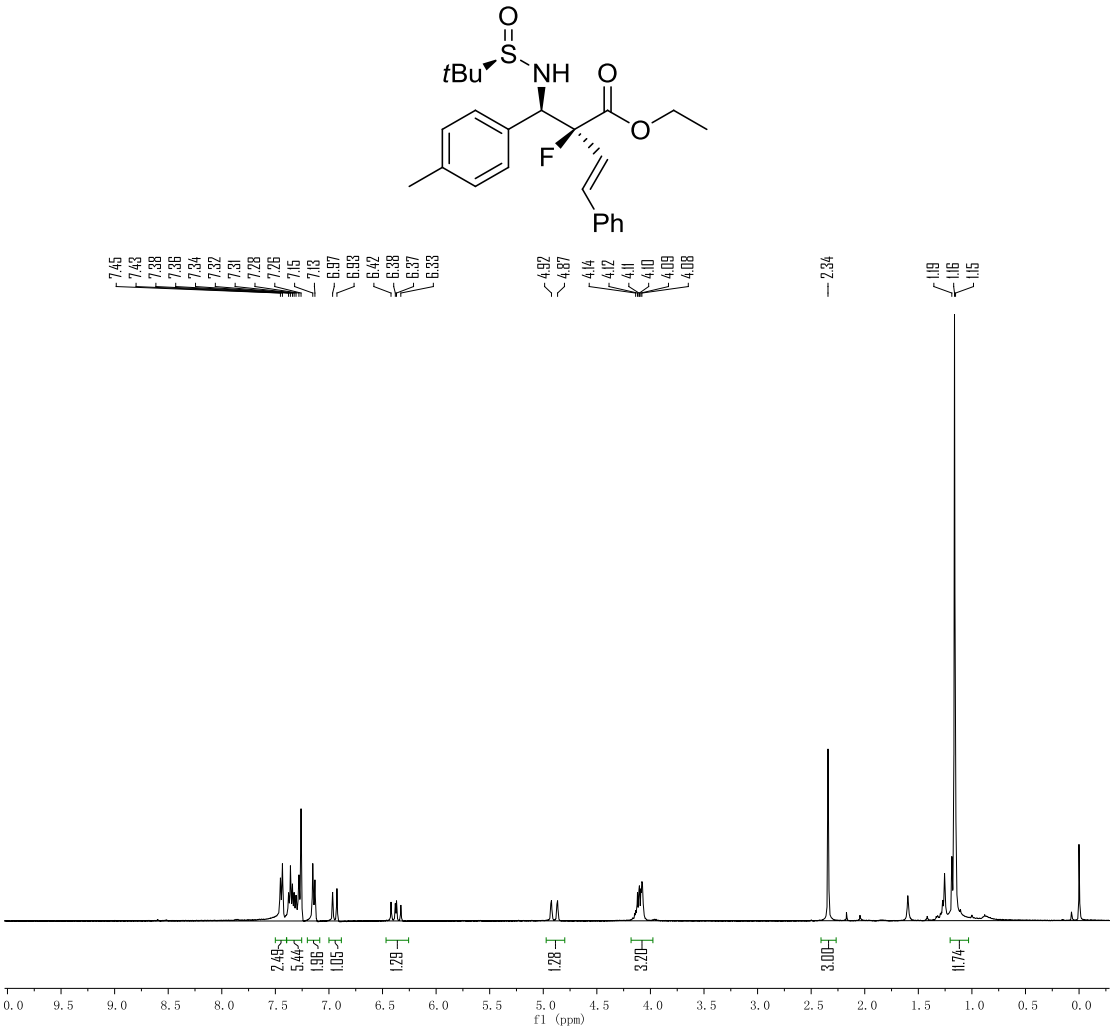
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7a**



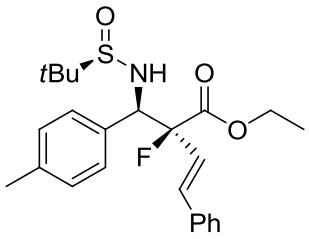
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7a**

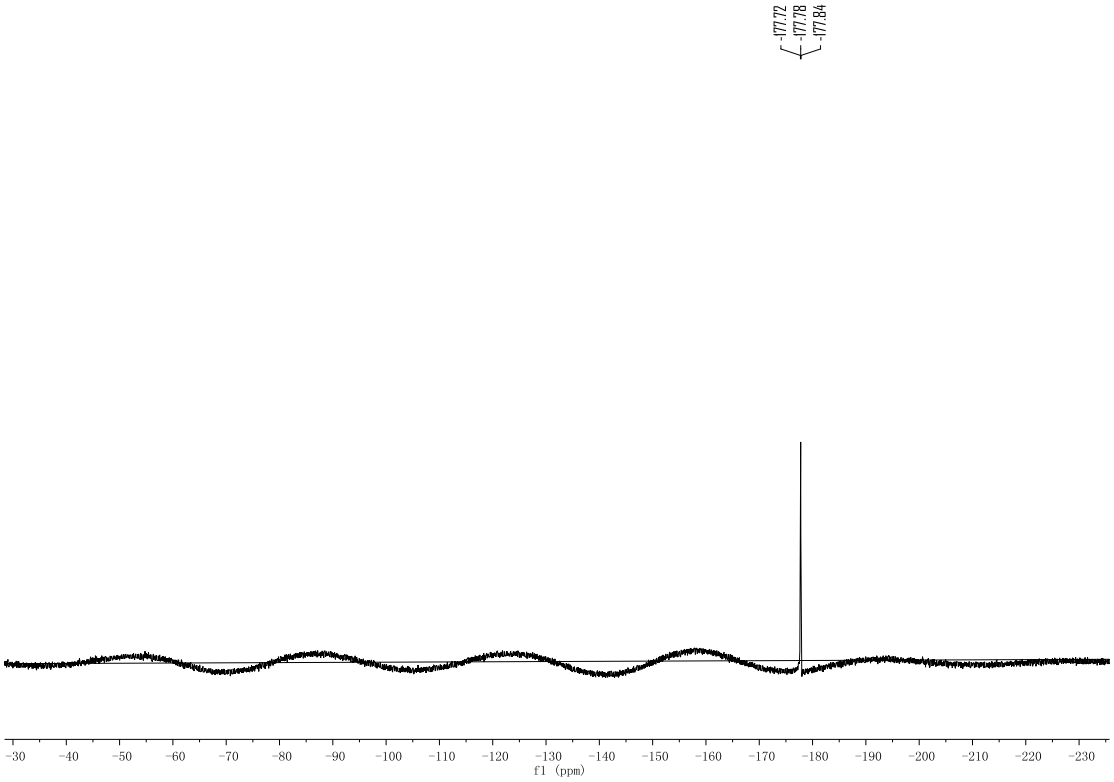


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7b**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7b**





^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7b**