Supporting Information

Asymmetric synthesis of (3*S*,1'*S*)-3-(1-amino-2,2,2-trifluoroethyl)-1-(alkyl)-indolin-2-one derivatives by additions of (*S*)-*N*-*t*-butylsulfinyl-3,3,3-trifluoroacetaldimine to 1-(alkyl)-indolin-2-ones

Ping Qian, Chen Xie, Lingmin Wu, Haibo Mei, Vadim A. Soloshonok, Jianlin Han,* and Yi Pan*

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1. General information

Oxoindoles were synthesized according to literature[1,2]. Sulfinylimine **1** was synthesized due to literature[3]. Other reagents were obtained from commercial suppliers and used without further purification. The reactions were conducted in a closed system in an atmosphere of N_2 and were monitored by TLC. Solvents were dried and distilled prior to use. Flash chromatography was performed using silica gel 60 (300–400 mesh). Thin layer chromatography was carried out on silica gel 60 F-254 TLC plates of 20 cm × 20 cm. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE400M spectrometer. Melting points were uncorrected. Values of optical rotation were measured on a Rudolph Automatic Polarimeter A21101. Infrared spectra were obtained on a Bruker Vector 22 in KBr pellets. HRMS were conducted on an Agilent 6540Q-TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive or negative ion mode.

Reference

1 B. M. Trost, J. Xie and J. D. Sieber, *J. Am. Chem. Soc.*, **2011**, 133, 20611-20622.

2 X. H. Xu, X. Wang, G. Liu, E. Tokunaga and N. Shibata, *Org. Lett.*, **2012**, 14, 2544-2547.

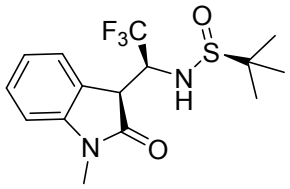
3 V. L. Truong and J. Y. Pfeiffer, *Tetrahedron Lett.*, **2009**, 50, 1633-1635.

2. Typical procedure for asymmetric addition of sulfinylimine

Into an oven-dried reaction vial flushed with N_2 was taken oxoindole **4** (0.6 mmol) and anhydrous DCM (3.0 mL). The reaction vial was cooled to −78 °C and LDA (2 M in Hexene, 0.36 mL) was added dropwise with stirring. After 1 hour at −78 °C, sulfinyl-imine **1** (0.5 mmol) dissolved in anhydrous DCM (2 mL) was pre-cooled to −78 °C, and then added dropwise to the reaction mixture. Stirring was continued at −78 °C for 5 h, and then the reaction was quenched with saturated NH_4Cl (3.0 mL), followed by H_2O (3.0 mL) and the mixture was brought to room temperature. The

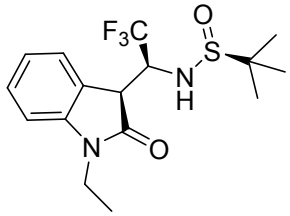
organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with water (1 × 30 mL) and brine solution (1 × 30 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude mixture was charged onto silica gel and purified by flash chromatography to furnish the corresponding product.

3. Characterization data of compounds 5a-5e, 7a-7l



(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-1-methyl-2-oxoindolin-3-yl)ethyl)propane-2-sulfinamide (5a)

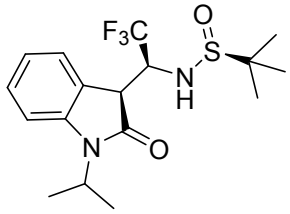
White solid (153.3 mg, 88%), mp 159-163 °C, $[\alpha]_D^{25}$ = -50.9 (*c* = 1.05, $CHCl_3$). (major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 2H), 7.12 (t, *J* = 6.9 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 4.69-4.49 (m, 1H), 3.86 (s, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 3.19 (s, 3H), 0.97 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.71. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 145.2, 129.7, 125.7, 124.8 (q, J_{FC} = 283.4 Hz), 123.1, 121.8, 108.6, 59.0 (q, $^2J_{FC}$ = 31.3 Hz), 57.1, 46.4, 26.4, 22.1. IR (cm^{-1}): *v* 3242, 3066, 2969, 2928, 1704, 1614, 1498, 1472, 1430, 1382, 1340, 1244, 1170, 1115, 1082, 769, 658, 541. HRMS (ESI):[M+Na$^+$] calcd for $C_{15}H_{19}F_3N_2O_2SNa$: 371.1017, found: 371.1019.



(S)-N-((S)-1-((S)-1-ethyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (5b)

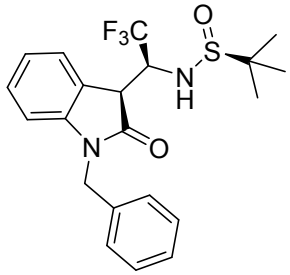
Yellow oil (168.5 mg, 93%), $[\alpha]_D^{25}$ = -22.7 (*c* = 3.16, $CHCl_3$). (major isomer) ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.57 (dqd, *J* = 10.5, 8.1, 2.3 Hz, 1H), 3.85 (s,1H), 3.80 (m, 1H), 3.69 (m, 1H), 3.58 (d, *J* = 10.9 Hz, 1H), 1.27 (t, *J* = 7.2Hz, 3H), 0.99 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 144.3, 129.6, 124.9 (q, J_{FC} = 283.6 Hz), 125.7, 122.9, 122.0, 108.7, 58.7 (q, $^2J_{FC}$ = 31.2 Hz), 57.2, 46.3, 35.1, 22.1, 12.5. IR (cm^{-1}): *v* 3234, 3052, 2975, 2932, 2872, 1696, 1611, 1491, 1466, 1373, 1341, 1269, 1

251, 1171, 1137, 1114, 1076, 998, 896, 817, 770, 760, 658, 601, 488, 447. HRMS (ESI): [M+Na$^+$] calcd for $C_{16}H_{21}F_3N_2O_2SNa$: 385.1174, found: 385.1173.



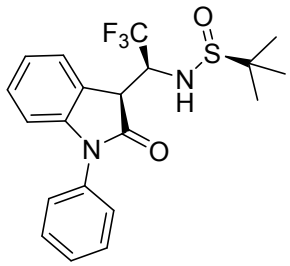
(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-1-isopropyl-2-oxoindolin-3-yl)ethyl)propane-2-sulfinamide (5c)

Yellow oil (148.7 mg, 79%), $[\alpha]_D^{25}$ = -14.7 (*c* = 1.65, $CHCl_3$). (major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 2H), 7.10-6.99 (m, 2H), 4.64-4.52 (m, 2H), 3.84-3.76 (m, 2H), 1.47 (t, *J* = 6.5 Hz, 6H), 1.02 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.44. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 143.7 ,129.2, 125.5, 125.0 (q, J_{FC} = 283.8 Hz), 122.5, 122.4, 110.3, 58.3 (q, $^2J_{FC}$ =30.9 Hz), 57.2, 46.3, 44.3, 22.2, 19.3, 19.1. IR (cm^{-1}): *v* 3230, 3058, 2976, 2925, 2872, 2853, 1712, 1705, 1650, 1610, 1486, 1468, 1401, 1361, 1322, 1259,1233, 1204, 1170, 1120, 1089, 894, 751, 657, 442. HRMS (ESI): [M+Na$^+$] calcd for $C_{17}H_{23}F_3N_2O_2SNa$: 399.1330, found: 399.1331.



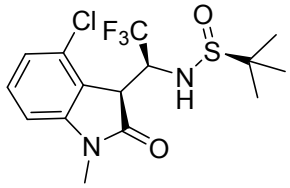
(S)-N-((S)-1-((S)-1-benzyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (5d)

Yellow oil (199.5 mg, 94%), $[\alpha]_D^{25}$ = -40.4 (*c* = 4.00, $CHCl_3$). (major isomer) ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 7H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.83(d, *J* = 7.0 Hz, 1H), 5.08 (d, *J* = 15.5 Hz, 1H), 4.65 (d, *J* = 15.5 Hz,1H), 4.68-4.59 (m, 1H), 3.96 (s, 1H), 3.75 (d, *J*= 10.8 Hz,1H), 0.97 (s,9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.49. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 144.3, 135.1, 129.5, 128.9, 127.9, 127.6, 125.5, 124.9 (q, J_{FC} = 283.6 Hz), 124.7, 124.1, 123.1, 121.9, 109.6, 58.5 (q, $^2J_{FC}$ = 31.1 Hz), 57.2, 46.4, 44.2, 22.1. IR (cm^{-1}): *v* 3471, 3230, 3062, 2959, 2925, 2854, 1713, 1613, 1489, 1468, 1456, 1438, 1366, 1270, 1252, 1199, 1170, 1122, 1082, 1017, 923, 910, 893, 820, 752, 735, 698, 663, 638, 550, 443. HRMS (ESI): [M+Na$^+$] calcd for $C_{21}H_{23}F_3N_2O_2SNa$: 447.1330, found: 447.1330.



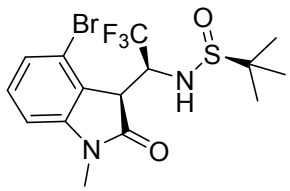
(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-2-oxo-1-phenylindolin-3-yl)ethyl)propane-2-sulfinamide (5e)

Yellow oil (201.0 mg, 95%), $[\alpha]_D^{25}$ = -82.1 (*c* = 1.02, $CHCl_3$). (major isomer) ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.55-7.35 (m, 6H), 7.32-7.25 (m, 1H), 7.16-7.13 (m, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 4.71-4.62 (m, 1H), 4.05 (s, 1H), 3.80 (d, *J* = 10.9 Hz, 1H), 1.04 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.37. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 145.0, 133.8, 129.8, 129.5, 128.4, 126.4, 126.2, 125.7, 124.9 (q, J_{FC} = 283.6 Hz), 124.6, 124.3, 123.6, 121.8, 110.1, 58.7 (q, $^2J_{FC}$ = 31.1 Hz), 57.2, 46.7, 22.3. IR (cm^{-1}): *v* 3230, 3062, 2959, 2926, 2868, 1724, 1670, 1612, 1594, 1503, 1483, 1466, 1420, 1373, 1330, 1254, 1226, 1201, 1173, 1121, 1095,1029, 1002, 752, 696, 663, 608, 489, 445. HRMS (ESI): [M+Na$^+$] calcd for $C_{20}H_{21}F_3N_2O_2SNa$: 433.1174, found: 433.1173.



(S)-N-((S)-1-((S)-4-chloro-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (7a)

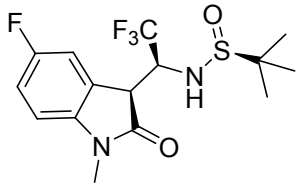
Yellow oil (185.7 mg, 97%), $[\alpha]_D^{25}$ = +28.0 (*c* = 2.91, $CHCl_3$). (major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 5.09-4.95 (m, 1H), 3.86 (s, 1H), 3.13 (s, 3H), 1.22 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.85. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 145.0, 131.1, 130.4, 124.6 (q, J_{FC} = 283.4 Hz) 123.6, 121.4, 107.2, 57.4, 54.4 (q, $^2J_{FC}$ = 29.8 Hz), 45.8, 26.5, 22.3.IR (cm^{-1}): *v* 3264, 3062, 2958, 2924, 2870, 2854, 1712, 1705, 1611, 1592, 1463, 1422, 1365, 1343, 1295, 1273, 1249, 1194, 1168, 1124, 1112, 1092, 1018, 933, 906, 772, 669, 568, 506, 461. HRMS (ESI): [M+Na$^+$] calcd for $C_{15}H_{18}{}^{35}ClF_3N_2O_2SNa$: 405.0627, found: 405.0625.



(S)-N-((S)-1-((S)-4-bromo-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-met

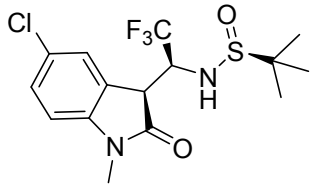
hylpropane-2-sulfinamide (7b)

Yellow oil (194.4 mg, 91%), $[\alpha]_D^{25}$ = +27.0 (*c* = 1.45, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.21 (m, 2H), 6.84-6.82 (m, 1H), 6.11 (d, *J* = 10.48 Hz, 1H), 5.23 (m, 1H), 3.91 (d, *J* = 4.7 Hz, 1H), 3.21 (s, 3H), 1.3 2 (s, 9H). ^{19}FNMR (376 MHz, $CDCl_3$) δ -70.83. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 145.1, 130.6, 126.6, 124.6 (q, J_{FC} = 284.5 Hz) 123.6, 119.5, 107.7, 5 7.5, 54.0 (q, $^2J_{FC}$ = 29.9 Hz), 47.0, 26.5, 22.4. IR (cm^{-1}): *v* 3261, 3060, 2959, 2928, 2870, 1708, 1608, 1583, 1459, 1423, 1364, 1344, 1275, 1247, 1193, 116 8, 1124, 1103, 928, 769, 667, 562, 500. HRMS (ESI): [M+Na^+] calcd for $C_{15}H_{18}{}^{79}BrF_3N_2O_2SNa$:449.0122, found: 449.0121.



(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-5-fluoro-1-methyl-2-oxoindolin-3-yl)eth yl)propane-2-sulfinamide (7c)

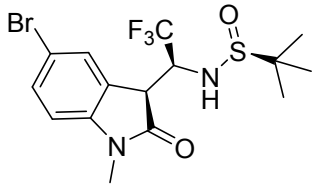
White solid (170.3 mg, 93%), mp 158-162 °C, $[\alpha]_D^{25}$ = -43.5 (*c* = 1.09, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ = 7.15-7.08 (m, 2H), 6.82 (d d,*J* = 8.5, 4.2 Hz, 1H), 4.59 (dqd, *J* = 10.5, 8.1, 2.3 Hz, 1H), 3.85 (s, 1H), 3.5 5 (d, *J* = 10.8 Hz, 1H), 3.18 (s, 3H), 1.00 (s, 9H). ^{19}F NMR (376 MHz, CD Cl_3) δ -71.59, -119.21. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 159.2 (q, *J* = 2 42.0 Hz), 141.2 (d, *J* = 20 Hz), 124.7 (q, J_{FC} = 283.2 Hz), 123.5 (d, *J* = 8.5 Hz), 116.0 (d, *J* = 23.4 Hz), 114.0 (dq, *J* = 25.6 Hz, 2 Hz) , 109.0 (d, *J* = 8.2 Hz), 58.8 (q, $^2J_{FC}$ = 31.3 Hz), 57.2, 46.8, 26.6, 22.1. IR (cm^{-1}): *v* 3264, 2 967, 2924, 2873, 1711, 1625, 1479, 1472, 1458, 1428, 1372, 1339, 1282, 1244,1 201, 1176, 1150, 1120, 1083, 998, 939, 924, 864, 829, 790, 758, 706, 682, 66 6, 559. HRMS (ESI): [M+Na^+] calcd for $C_{15}H_{18}F_4N_2O_2SNa$: 389.0923, found: 3 89.0923.



(S)-N-((S)-1-((S)-5-chloro-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-met hylpropane-2-sulfinamide (7d)

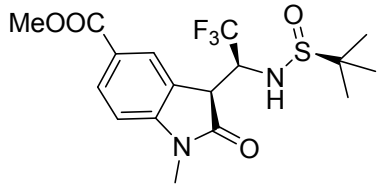
White solid (176.1 mg, 92%), mp 179-184 °C, $[\alpha]_D^{25}$ = +18.6 (*c* = 0.44, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 6.83 (d, *J* =8.2 Hz, 1H), 4.58 (dqd, *J* = 10.5, 8.1, 2.3 Hz, 1H), 3.85 (d, *J* = 1.0 Hz, 1H),3.60 (d, *J* = 10.8 Hz, 1H), 3.18 (s, 3H), 1.00 (s, 9H). ^{19}F NMR (376 M Hz, $CDCl_3$) δ -71.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 143.7, 129.6, 128.5 , 126.2 (q, *J* = 3.3 Hz), 124.7 (q, J_{FC} = 283.2 Hz), 123.5, 109.4, 58.8 (q, $^2J_{FC}$

=31.3 Hz), 57.2, 46.5, 26.6, 22.1. IR (cm^{-1}): *v* 3262, 2984, 2960, 2924, 2870, 1709, 1491, 1468, 1428, 1370, 1335, 1275, 1245, 1172, 1120, 1085, 938, 865, 832, 785, 662, 644, 550. HRMS (ESI): [M+Na^+] calcd for $C_{15}H_{18}{}^{35}ClF_3N_2O_2SN$ a:405.0627, found: 405.0626.



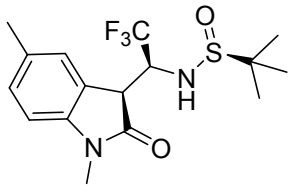
(S)-N-((S)-1-((S)-5-bromo-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (7e)

White solid (194.3 mg, 91%), mp 187-192 °C, $[\alpha]_D^{25}$ = +39.0 (*c* = 1.01, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 4.62-4.53 (m, 1H), 3.86 (s, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.18 (s, 3H), 1.00 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.54. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 144.2, 132.6, 128.9 (q, *J* = 3.4 Hz), 124.7 (q, J_{FC} = 283.4 Hz), 123.9, 115.8, 109.9, 58.8 (q, $^2J_{FC}$ = 31.3 Hz), 57.2, 46.4, 26.6, 2 2.1. IR (cm^{-1}): *v* 3277, 3249, 2961, 2923, 2870, 1708, 1669, 1610, 1488, 1468,1 424, 1369, 1334, 1275, 1242, 1203, 1173, 1120, 1085, 938, 901, 883, 826, 78 2, 752, 661, 635, 538, 443. HRMS (ESI): [M+Na^+] calcd for $C_{15}H_{18}{}^{79}BrF_3N_2O_2$ SNa: 449.0122, found: 449.0120.



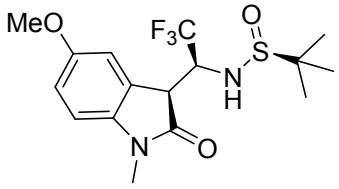
(S)-methyl 3-((S)-1-((S)-1,1-dimethylethylsulfinamido)-2,2,2-trifluoroethyl)-1-methyl-2-oxoindoline-5-carboxylate (7f)

White solid (182.7 mg, 90%), mp 183-188 °C, $[\alpha]_D^{25}$ = +32.5 (*c* = 0.86, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 8. 04 (s, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.73-4.49 (m, 1H), 3.92 (s, 3H), 3.90 (s, 1H), 3.66 (d, *J* = 10.8 Hz, 1H), 3.23 (s, 3H), 0.99 (s, 9H). ^{19}F NMR (376 M Hz, $CDCl_3$) δ -71.59. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 166.4, 149.0, 132.3 , 126.8, 125.2, 124.7 (q, J_{FC} = 283.4 Hz), 122.0, 108.2, 58.8 (q, $^2J_{FC}$ = 31.3H z), 57.2, 52.3, 46.3, 26.7, 22.1. IR (cm^{-1}): *v* 3259, 2953, 2925, 1713, 1616, 14 99, 1454, 1428, 1369, 1357, 1288, 1245, 1175, 1136, 1121, 1079, 975, 722,66 3, 549. HRMS (ESI): [M+Na^+] calcd for $C_{17}H_{21}F_3N_2O_4SNa$: 429.1072, found:42 9.1071.



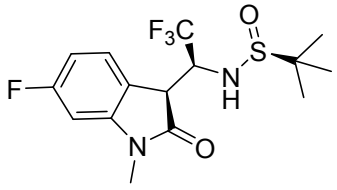
(S)-N-((S)-1-((S)-1,5-dimethyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (7g)

Light yellow solid (177.4 mg, 98%), mp 148-150 °C, $[\alpha]_D^{25}$ = -11.4 (*c* = 1.02, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 6.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.55 (dqd, *J* = 10.4, 8.1, 2.2 Hz, 1H), 3.81 (s,1H), 3.43 (d, *J* = 11.1 Hz, 1H), 3.17 (s, 3H), 2.35 (s, 3H), 0.98 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.79. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 142.8, 132.8, 129.9, 126.5, 124.8 (q, J_{FC} = 283.5 Hz), 121.7, 108.3, 59.0 (q, $^2J_{FC}$ = 31.3Hz), 57.2, 46.4, 26.5, 22.1, 21.2. IR (cm^{-1}): *v* 3257, 2987, 2922, 2852,1706, 1621, 1604, 1500, 1467, 1371, 1337, 1287, 1246, 1199, 1170, 1118, 1085,938, 835, 825, 664, 553. HRMS (ESI): [M+Na^+] calcd for $C_{16}H_{21}F_3N_2O_2SNa$: 385.1174, found: 385.1173.



(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-5-methoxy-1-methyl-2-oxoindolin-3-yl)ethyl)propane-2-sulfinamide (7h)

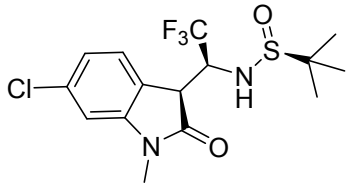
White solid (176.4 mg, 93%), mp 174-179 °C, $[\alpha]_D^{25}$ = -1.35 (*c* = 1.04, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.91 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.65-4.49 (m, 1H), 3.81 (s, 1H), 3.80 (s, 3H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.16 (s, 3H), 0.99 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 156.2, 138.6, 124.9 (q, J_{FC} = 283.5 Hz), 123.0, 113.8, 113.2, 108.9, 59.0 (q, $^2J_{FC}$ = 31.3Hz), 57.2, 55.8, 46.8, 26.5,22.1. IR (cm^{-1}): *v* 3474, 3253, 2971, 2933, 2873, 2847, 1703, 1601, 1498, 1459, 1440, 1428, 1371, 1292, 1247, 1206, 1171, 1158, 1119, 1078, 1029, 939, 865, 819, 789, 757, 675, 667, 592, 566, 545. HRMS(ESI): [M+Na^+] calcd for $C_{16}H_{21}F_3N_2O_3SNa$: 401.1123, found: 401.1122.



(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-6-fluoro-1-methyl-2-oxoindolin-3-yl)ethyl)propane-2-sulfinamide (7i)

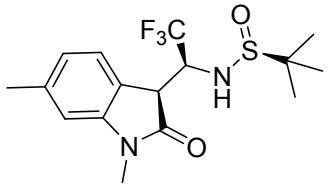
White solid (164.7 mg, 90%), mp 153-158 °C, $[\alpha]_D^{25}$ = -50.5 (*c* = 1.12, $CHCl_3$).

(major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 1H), 6.80 (td, J = 9. 2, 2.3 Hz, 1H), 6.64 (dd, J = 8.6, 2.3 Hz, 1H), 4.56 (dqd, J = 10.4, 8.1, 2.2 Hz, 1H), 3.83 (s, 1H), 3.47 (d, J = 11.0, 1H), 3.18 (s, 3H), 0.99 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.75, -109.80. ^{13}C NMR (101 MHz, $CDCl_3$) δ 1 74.4, 163.8 (d, J = 247.9 Hz), 146.9 (d, J = 11.4 Hz), 127.0, 124.8 (q, J_{FC} = 283.4 Hz), 117.1 (d, J = 3.2 Hz), 109.3 (d, J = 22.3 Hz), 97.5 (d, J = 3.2 H z), 59.0 (q, $^{2}J_{FC}$ = 31.2 Hz), 57.2, 46.0, 26.6, 22.1. IR (cm^{-1}): v 3250, 2983, 2927, 2870, 1715, 1621, 1505, 1468, 1384, 1337, 1283, 1249, 1209, 1173, 113 8, 1114, 1081, 1062, 966, 836, 761, 658, 580, 548. HRMS (ESI): [M+Na$^+$] cal -cd for $C_{15}H_{18}F_4N_2O_2SNa$: 389.0923, found: 389.0923.



(S)-N-((S)-1-((S)-6-chloro-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-met hylpropane-2-sulfinamide (7j)

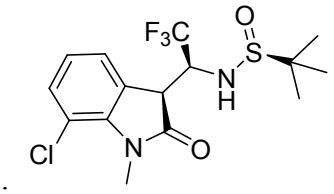
White solid (186.2 mg, 97%), mp 176-179 ^{o}C, $[\alpha]_D^{25}$ = -45.6 (c = 1.02, $CHCl_3$). (major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 1H), 7.1 0(dd, J = 8.0, 1.8 Hz, 1H), 6.89 (d, J = 1.8 Hz, 1H), 4.57 (dqd, J = 10.5, 8. 1,2.3 Hz, 1H), 3.83 (s, 1H), 3.52 (d, J = 10.9 Hz, 1H), 3.18 (s, 3H), 1.00 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.59. ^{13}C NMR (101 MHz, $CDCl_3$) δ 1 74.0, 146.4, 135.6, 126.6, 124.7 (q, J_{FC} =283.4 Hz), 122.9, 120.5, 109.4, 58.9 (q, $^{2}J_{FC}$ = 31.3 Hz), 57.2, 46.1, 26.6, 22.1. IR (cm^{-1}): v 3407, 3248, 2969, 29 35, 2871, 1712, 1613, 1498, 1471, 1435, 1377, 1341, 1270, 1242, 1205, 1190, 1162, 1137, 1112, 1079, 947, 804, 653, 523. HRMS (ESI): [M+Na$^+$] calcd for $C_{15}H_{18}{}^{35}ClF_3N_2O_2SNa$: 405.0627, found: 405.0625.



(S)-N-((S)-1-((S)-1,6-dimethyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpr opane-2-sulfinamide (7k)

Light yellow solid (164.8 mg, 91%), mp 153-157 ^{o}C, $[\alpha]_D^{25}$ = -50.5 (c = 1.07, $CHCl_3$). (major isomer) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6, 1H), 6.70 (s, 1H), 4.54 (dqd, J = 10.4, 8.1, 2.1 Hz, 1 H),3.80 (s, 1H), 3.44 (d, J = 11.1 Hz, 1H), 3.17 (s, 3H), 2.40 (d, J = 6.8 Hz, 3H), 0.99 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.89. ^{13}C NMR (101 MH z,$CDCl_3$) δ 174.4, 145.3, 140.1, 125.4 (q, J = 3.4 Hz), 124.9 (q, J_{FC} =283.4 Hz), 123.7, 118.6, 109.5, 59.1 (q, $^{2}J_{FC}$ = 31.3 Hz), 57.1, 46.2, 26.4, 22.1, 21.8. IR (cm^{-1}): v 3246, 3062, 2925, 2870, 1709, 1621, 1459, 1384, 1340, 1247, 11

72, 1116, 1083, 993, 812, 658, 571. HRMS (ESI): [M+Na$^+$] calcd for $C_{16}H_{21}F_3N_2O_2SNa$: 385.1174, found: 385.1172



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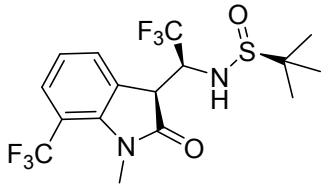
(S)-N-((S)-1-((S)-7-chloro-1-methyl-2-oxoindolin-3-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (7l)

White solid (170.3 mg, 89%), mp 140-144 ^oC, $[\alpha]_D^{25}$ = -82.1 (*c* = 1.02, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 19.2, 7.6 Hz, 2 H), 7.03 (t, *J* = 7.7 Hz, 1H), 4.62-4.54 (m, 1H), 3.86 (s, 1H), 3.60 (s, 1H), 3.57 (s, 3H), 1.03 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.30. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 141.0, 132.0, 124.7 (q, J_{FC} = 283.4 Hz), 124.7 (s), 124.0 (q, *J* = 3.4 Hz), 123.8, 116.1, 59.0 (q, $^2J_{FC}$ = 31.3 Hz), 57.3, 46.3, 30.1, 22.1. IR (cm^{-1}): *v* 3264, 2983, 2904, 1705, 1608, 1583, 1465, 1370, 1342, 1248, 1193, 1135, 1080, 1053, 1004, 940, 798, 732, 666, 528. HRMS (ESI): [M+Na$^+$] calcd for $C_{15}H_{18}{}^{35}ClF_3N_2O_2SNa$: 405.0627, found: 405.0627.

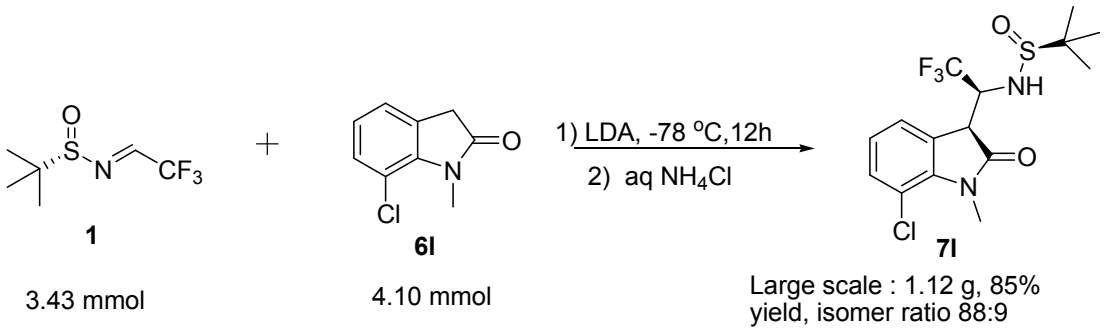


(S)-2-methyl-N-((S)-2,2,2-trifluoro-1-((S)-1-methyl-2-oxo-7-(trifluoromethyl)indolin-3-yl)ethyl)propane-2-sulfinamide (7m)

Light yellow solid (174.8 mg, 84%), mp 169-173 ^oC, $[\alpha]_D^{25}$ = -43.7 (*c* = 0.64, $CHCl_3$). (major isomer) ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 4.61 (dqd, *J* = 10.5, 8.1, 2.3 Hz, 1H), 3.88 (s, 1H), 3.55 (s, 1H), 3.41 (dd, *J* = 4.5, 2.2 Hz, 3H), 1.00 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.20, -71.17. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 143.0, 128.9 (d, *J* = 2.9 Hz), 127.5 (q, *J* = 8.1 Hz), 124.6 (q, J_{FC} = 283.4 Hz), 124.5, 122.4, 123.28 (q, *J* = 271.5 Hz), 113.1 (q, *J* = 33.2 Hz), 59.2 (q, *J* = 31.5 Hz), 57.3, 45.1, 29.2 (q, *J* = 6.6 Hz), 22.0. IR(cm^{-1}): *v* 3267, 2967, 2924, 2854, 1713, 1600, 1600, 1488, 1459, 1419, 1391, 1357, 1341, 1318, 1263, 1180, 1111, 1084, 1054, 1004, 946, 811, 787, 749, 663, 600, 502. HRMS (ESI): [M+Na$^+$] calcd for $C_{16}H_{18}F_6N_2O_2SNa$: 439.0891, found: 439.0891.

4. Reaction of large scale application study

Into an oven-dried round-bottom flask flushed with N_2 were taken compound **6l** (745 mg, 4.10 mmol) and anhydrous DCM (20.0 mL). The reaction flask was cooled to -78 ^oC and LDA (2 M in Hexene, 4.11 mL) was added dropwise with stirring. After 3 h at -78 ^oC, sulfinylimine **1** (690 mg, 3.43 mmol) dissolved in anhydrous DCM (10.0 mL) was added dropwise. Stirring was continued at -78 ^oC for 12 h, then the reaction was quenched with saturated NH_4Cl (10.0 mL), followed by H_2O (10.0 mL) and the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography (hexane/EtOAc, 2:1).



5. X-ray crystallography for 5a

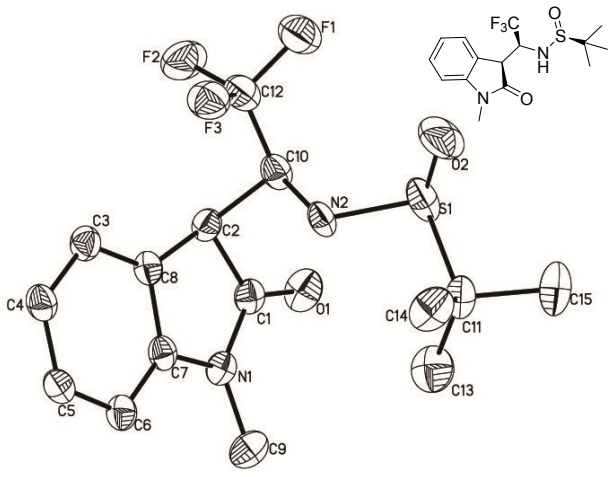
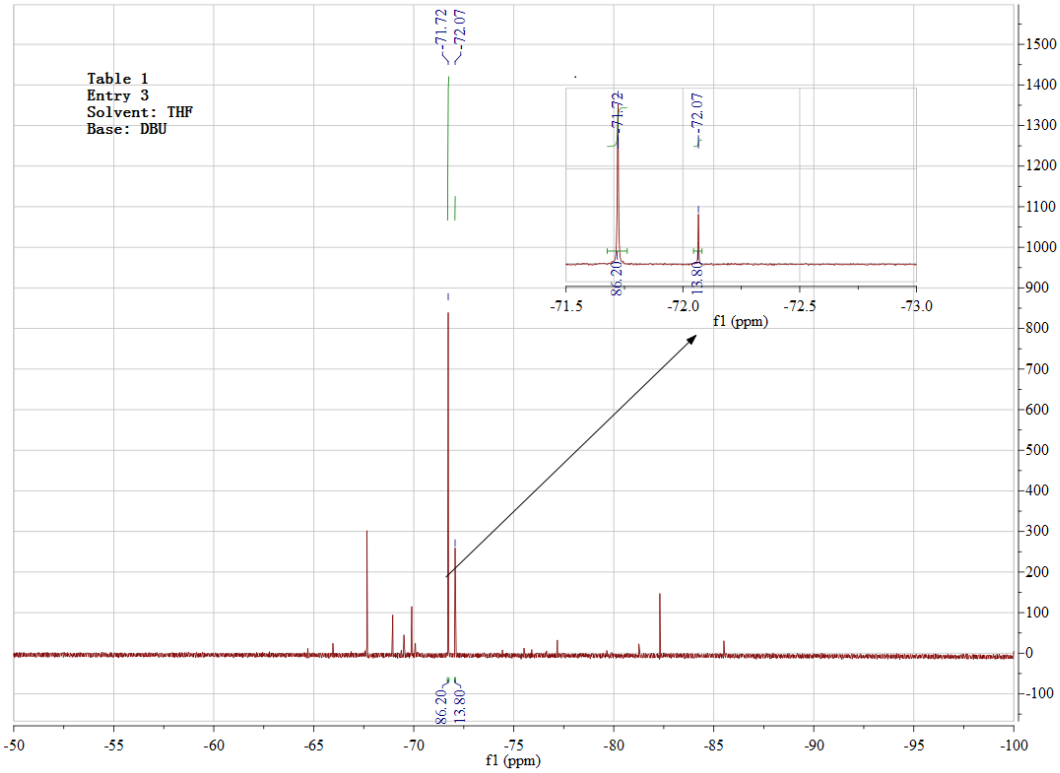


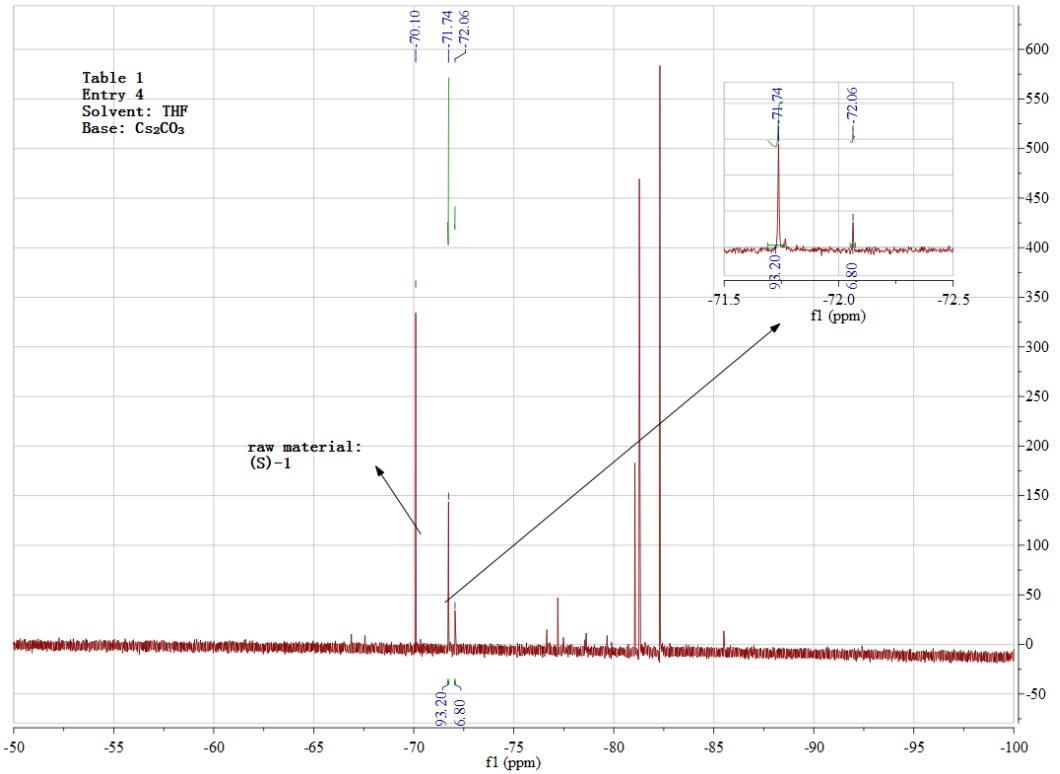
Figure 2 ORTEP diagram showing compound **5a** (ccdc number 1007432).

6. ^{19}F-NMR spectra of crude reaction mixture for optimization of the reaction conditions (Table 1, 2)

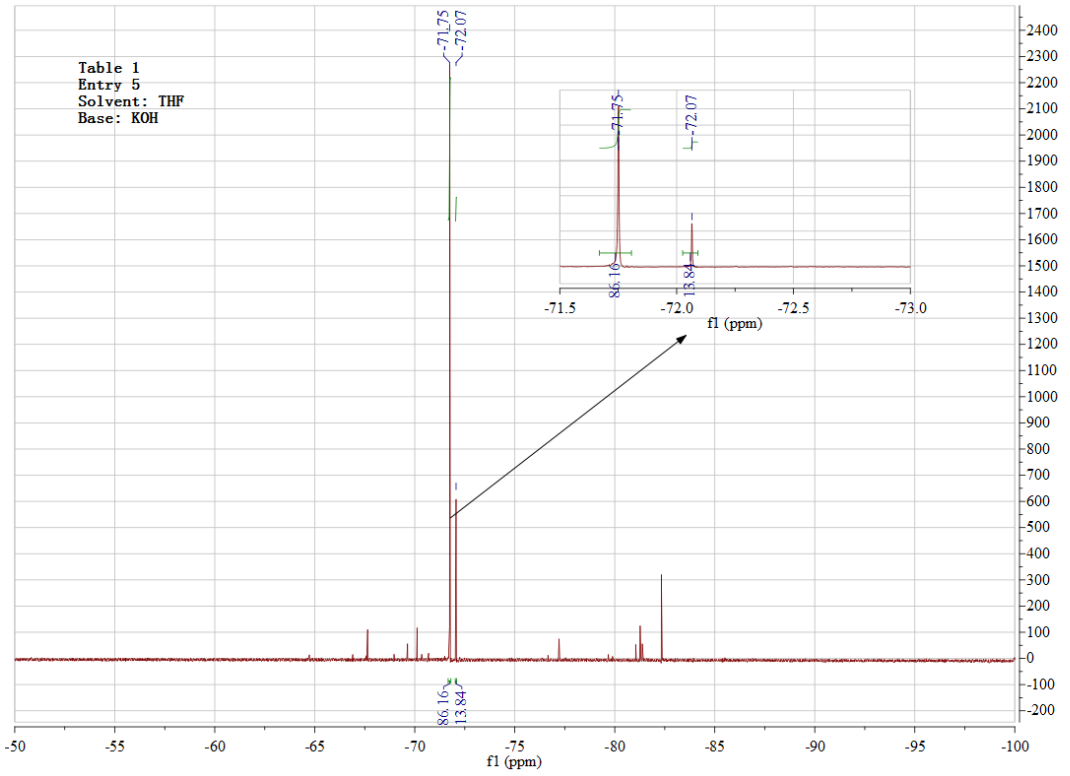
^{19}F-NMR spectra of crude reaction mixture for Entry 3 of Table 1



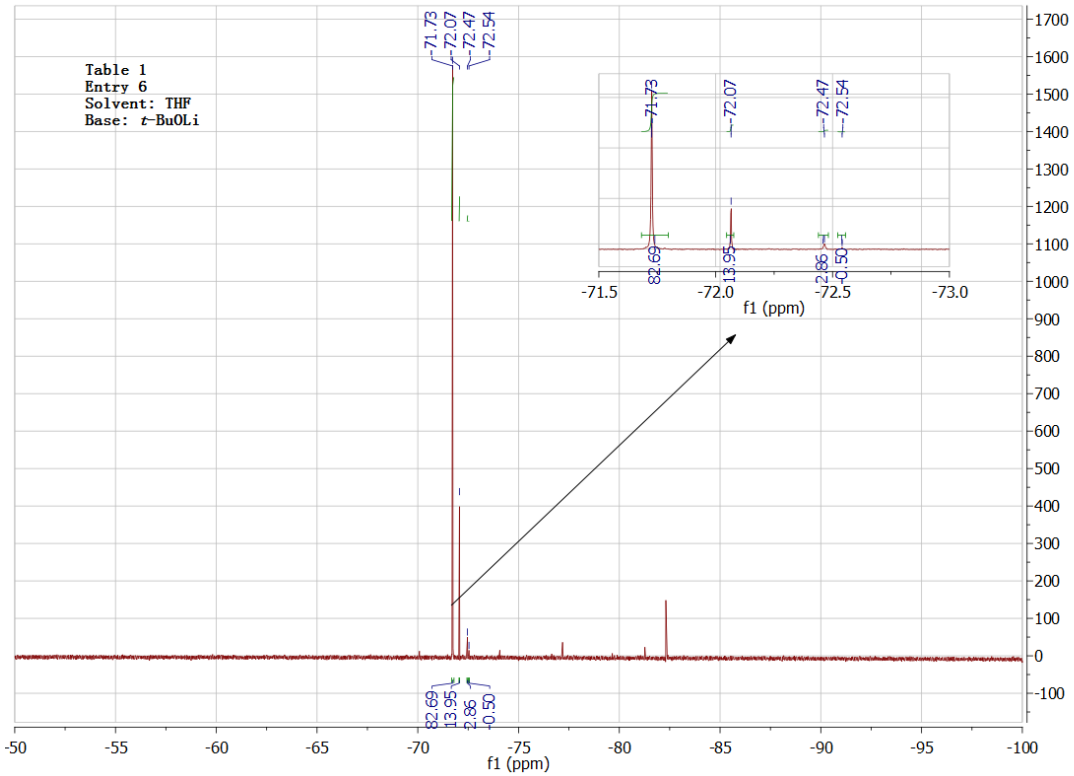
^{19}F-NMR spectra of crude reaction mixture for Entry 4 of Table 1



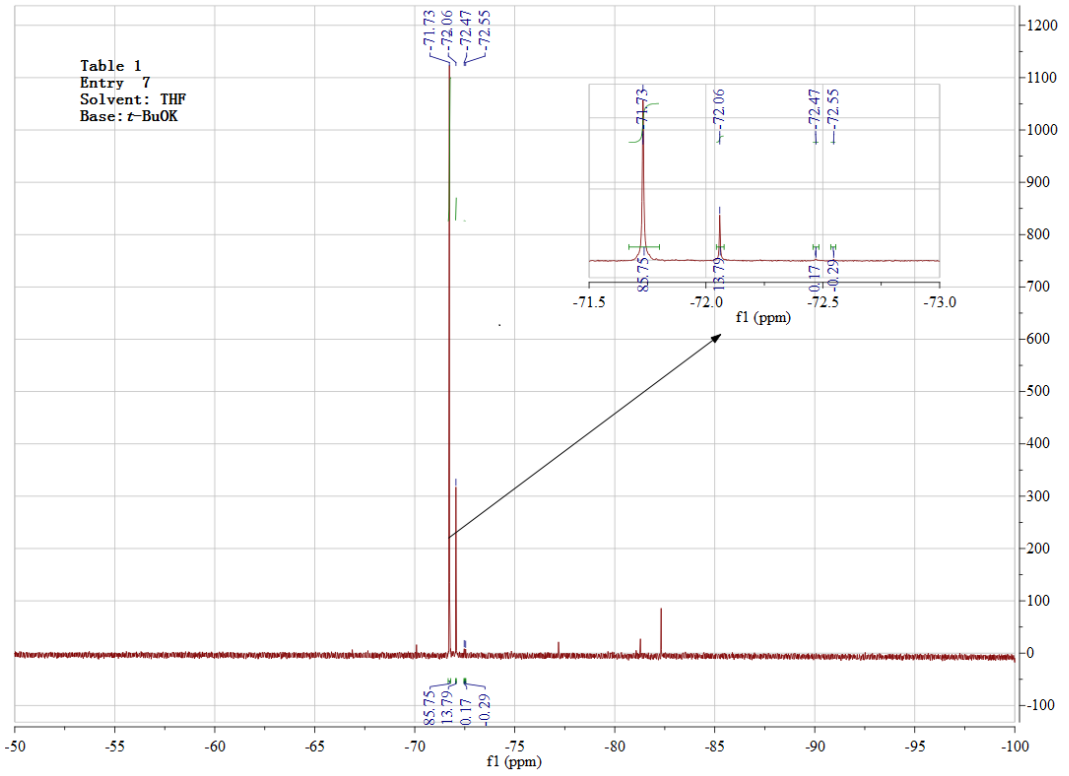
^{19}F-NMR spectra of crude reaction mixture for Entry 5 of Table 1



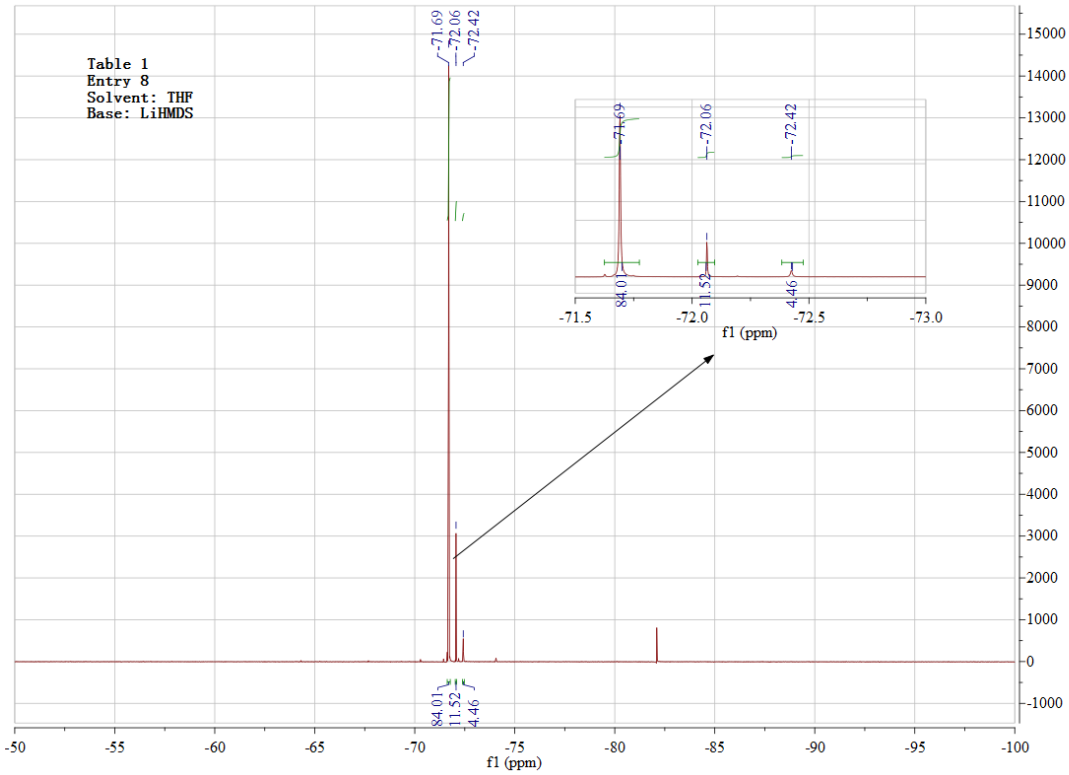
^{19}F-NMR spectra of crude reaction mixture for Entry 6 of Table 1



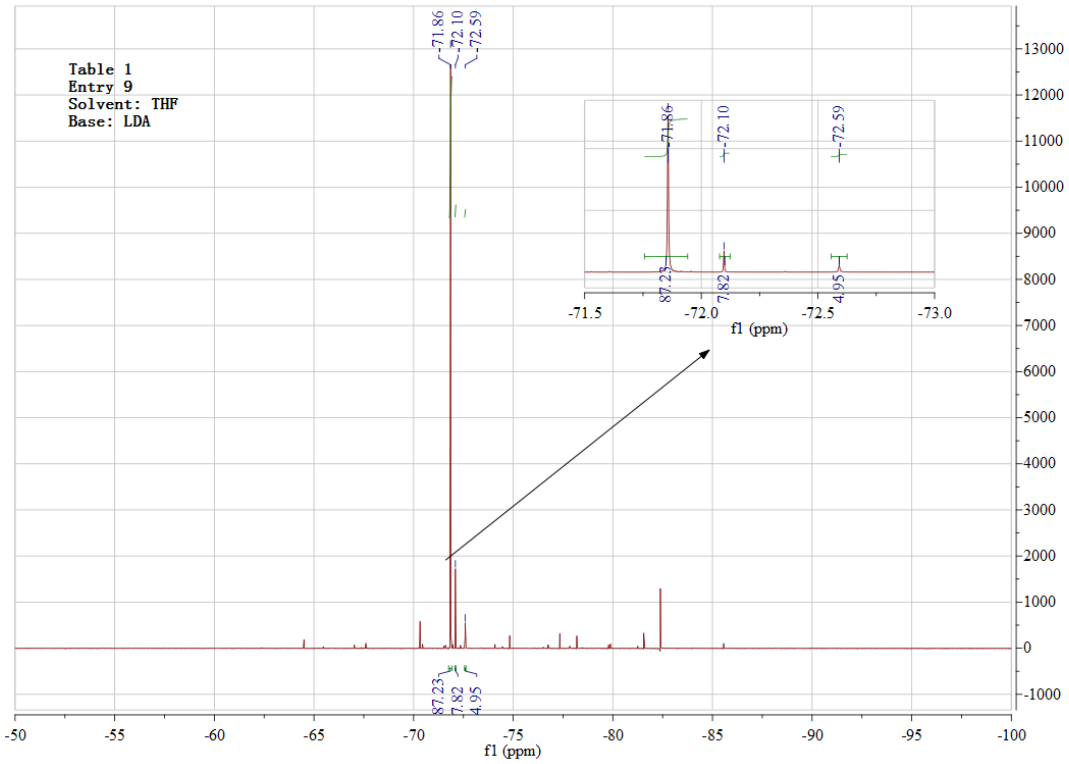
^{19}F-NMR spectra of crude reaction mixture for Entry 7 of Table 1



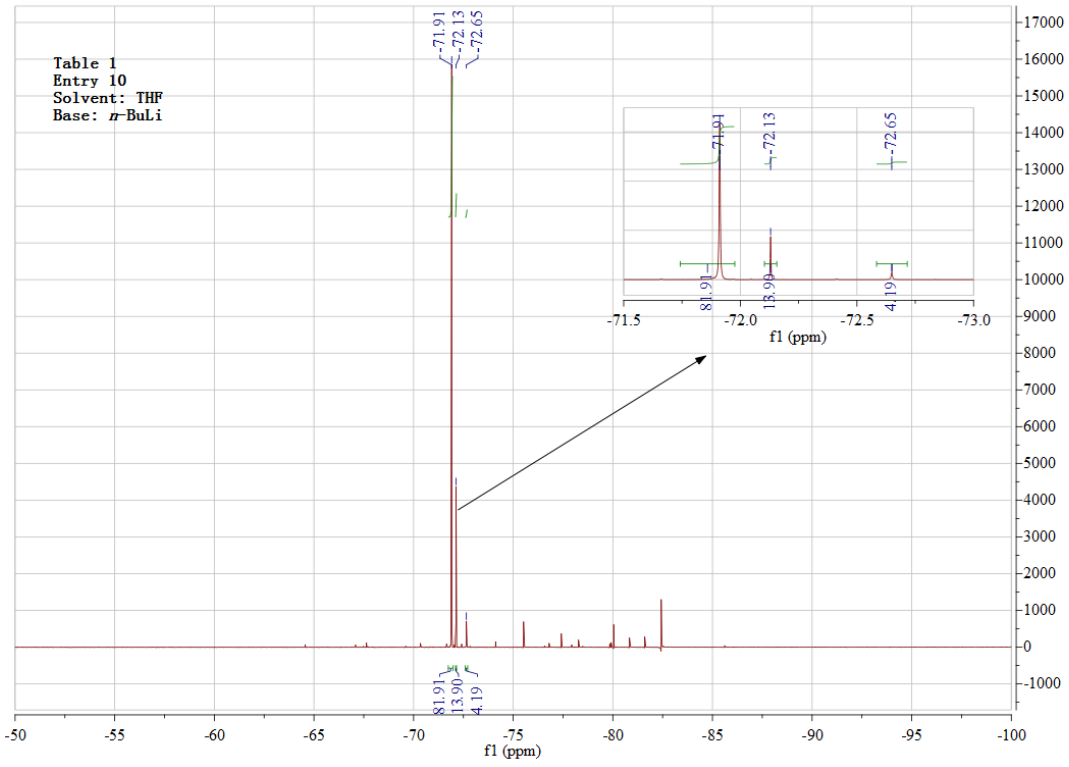
^{19}F-NMR spectra of crude reaction mixture for Entry 8 of Table 1



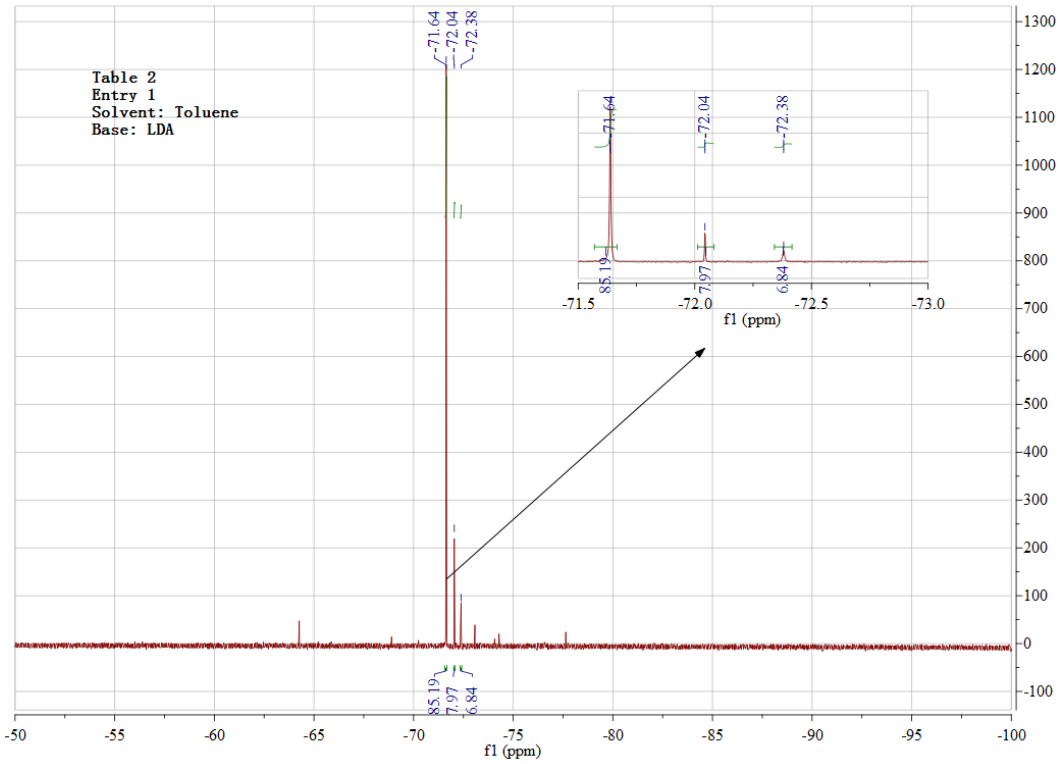
^{19}F-NMR spectra of crude reaction mixture for Entry 9 of Table 1



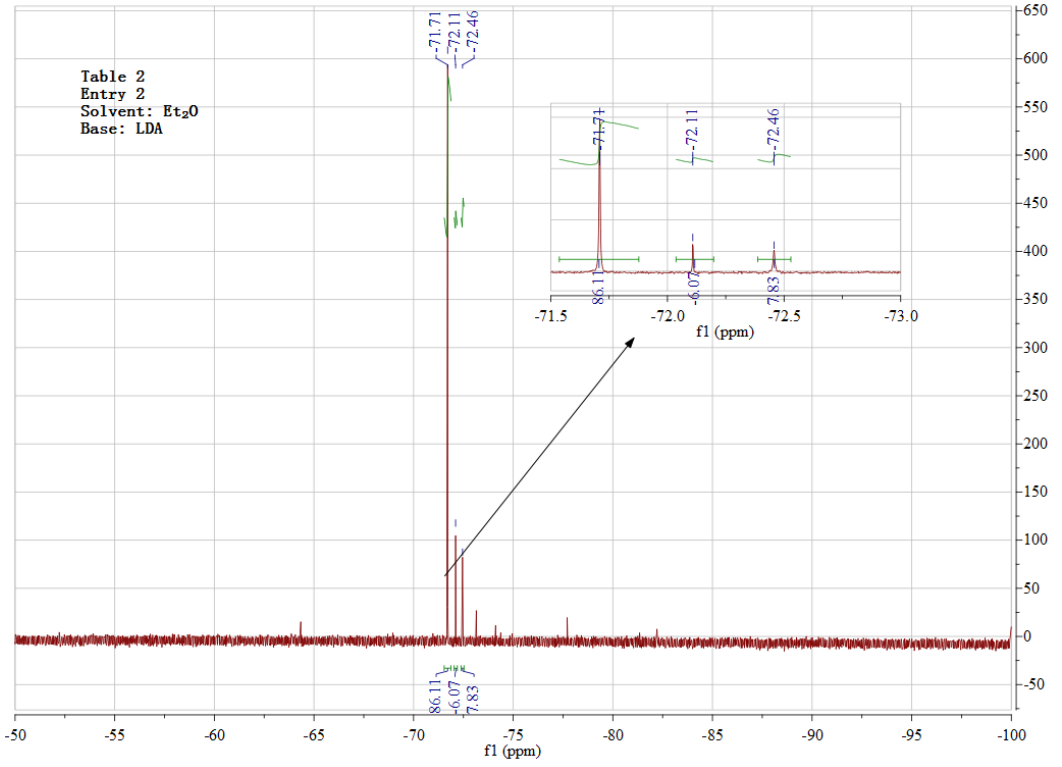
^{19}F-NMR spectra of crude reaction mixture for Entry 10 of Table 1



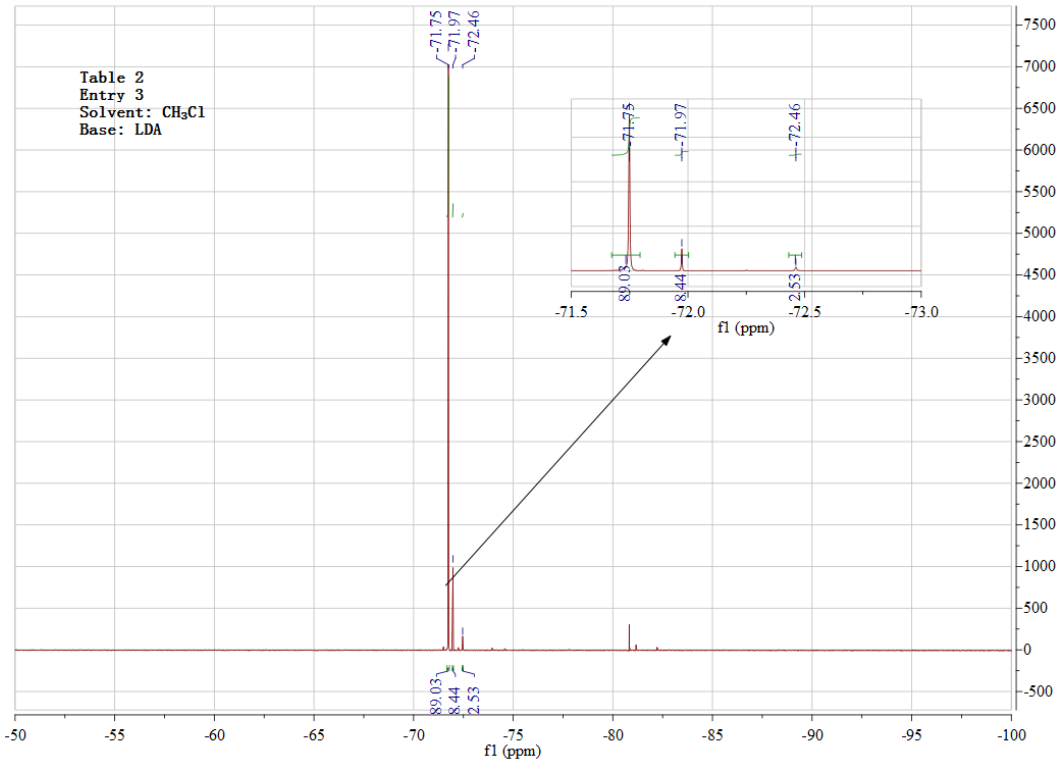
^{19}F-NMR spectra of crude reaction mixture for Entry 1 of Table 2



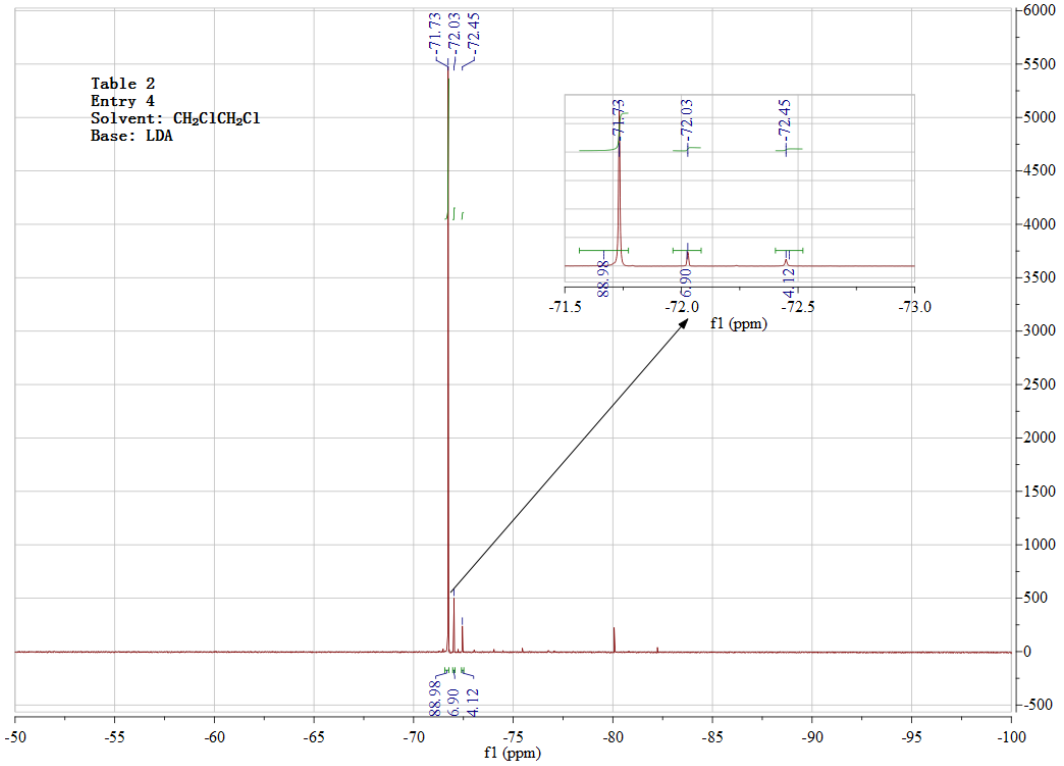
^{19}F-NMR spectra of crude reaction mixture for Entry 2 of Table 2



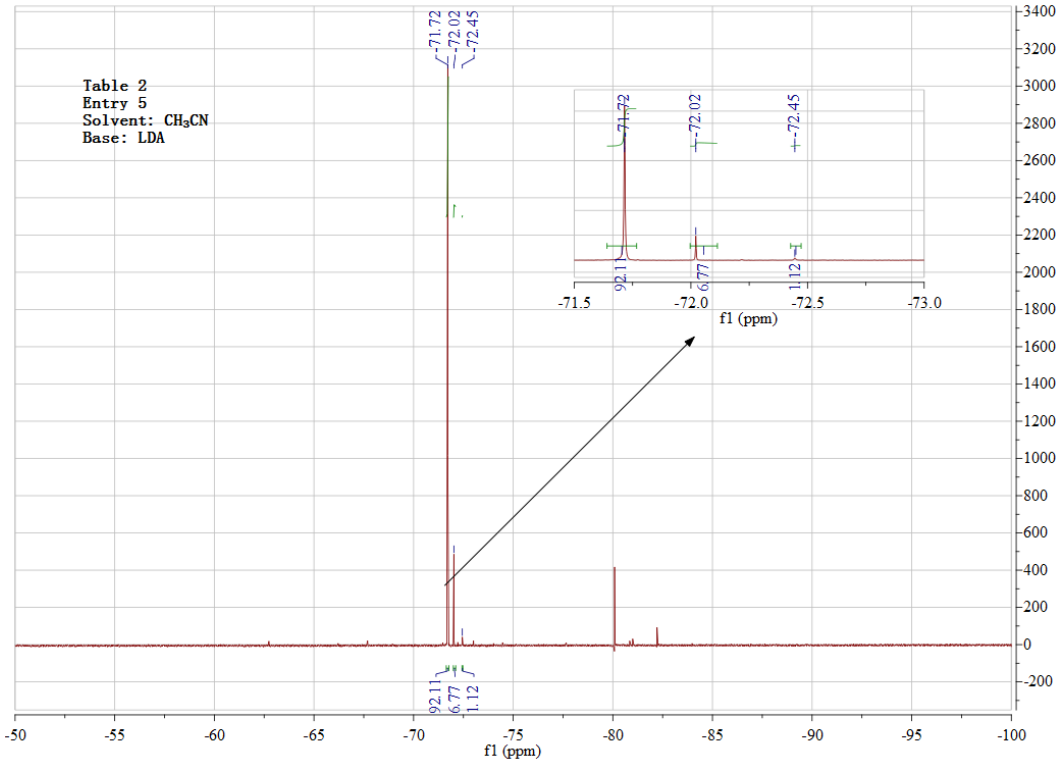
^{19}F-NMR spectra of crude reaction mixture for Entry 3 of Table 2



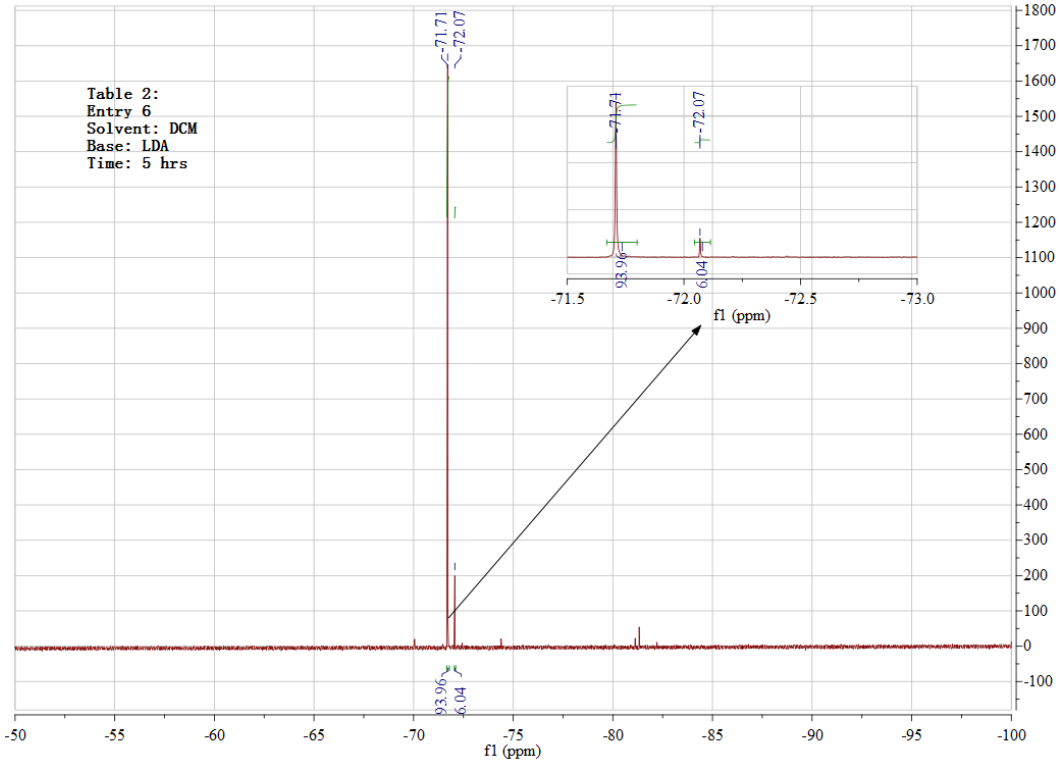
^{19}F-NMR spectra of crude reaction mixture for Entry 4 of Table 2



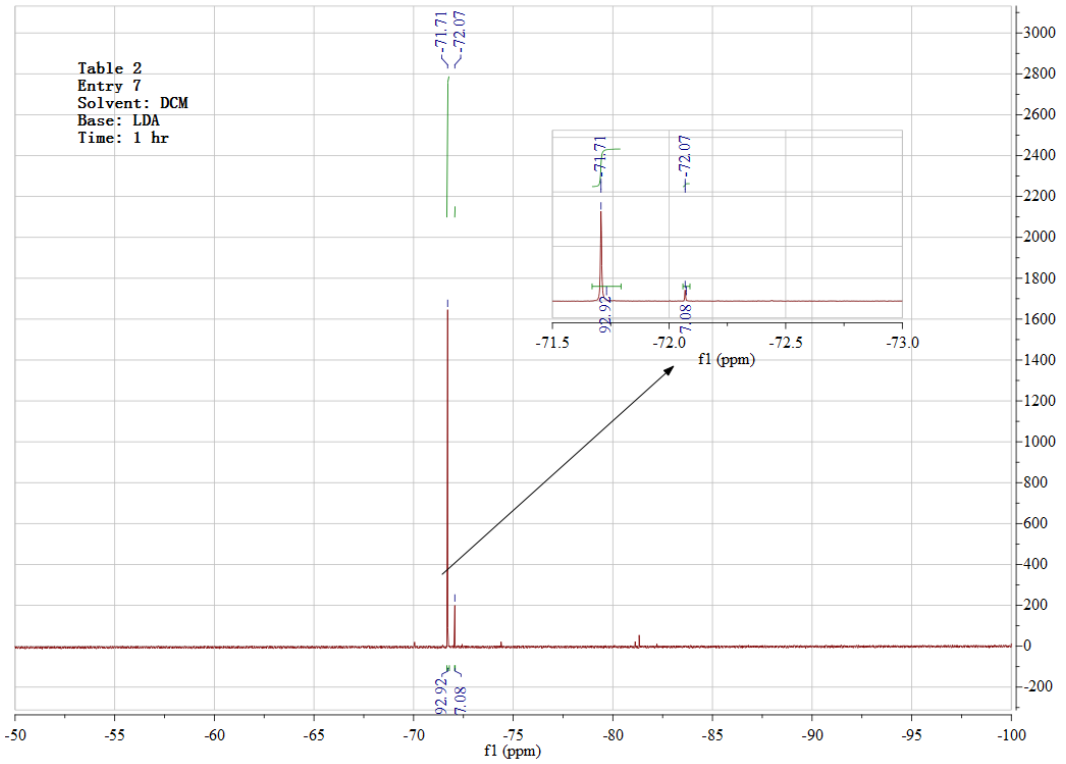
^{19}F-NMR spectra of crude reaction mixture for Entry 5 of Table 2



^{19}F-NMR spectra of crude reaction mixture for Entry 6 of Table 2

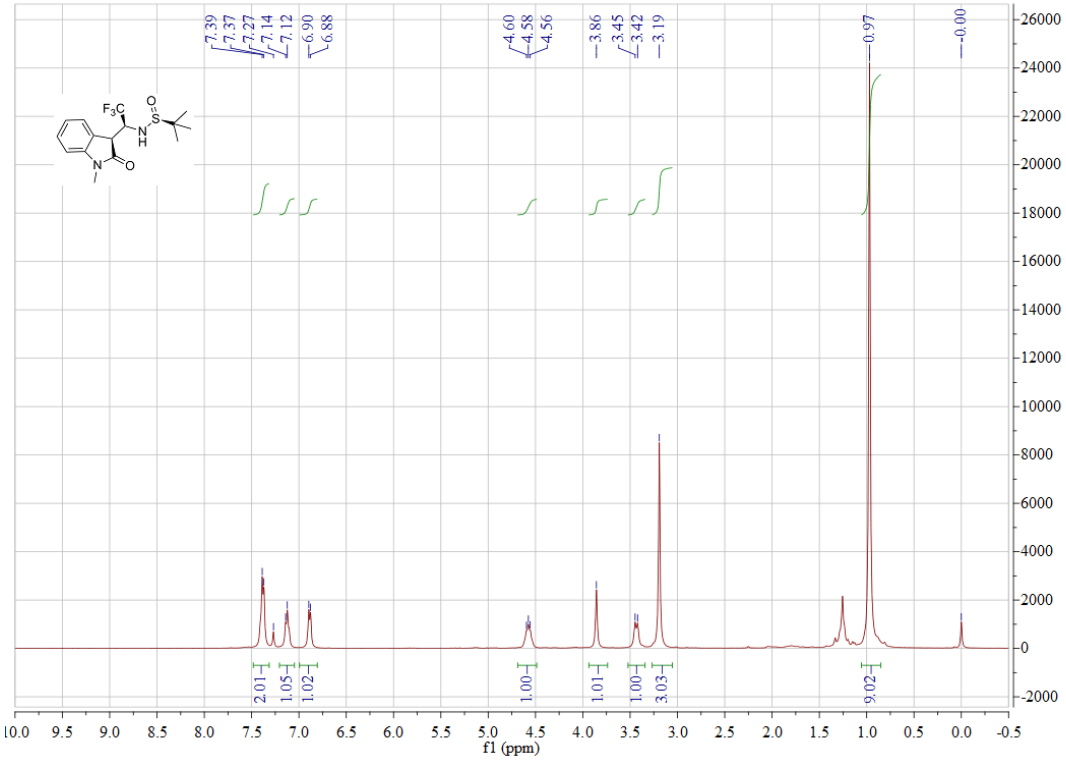


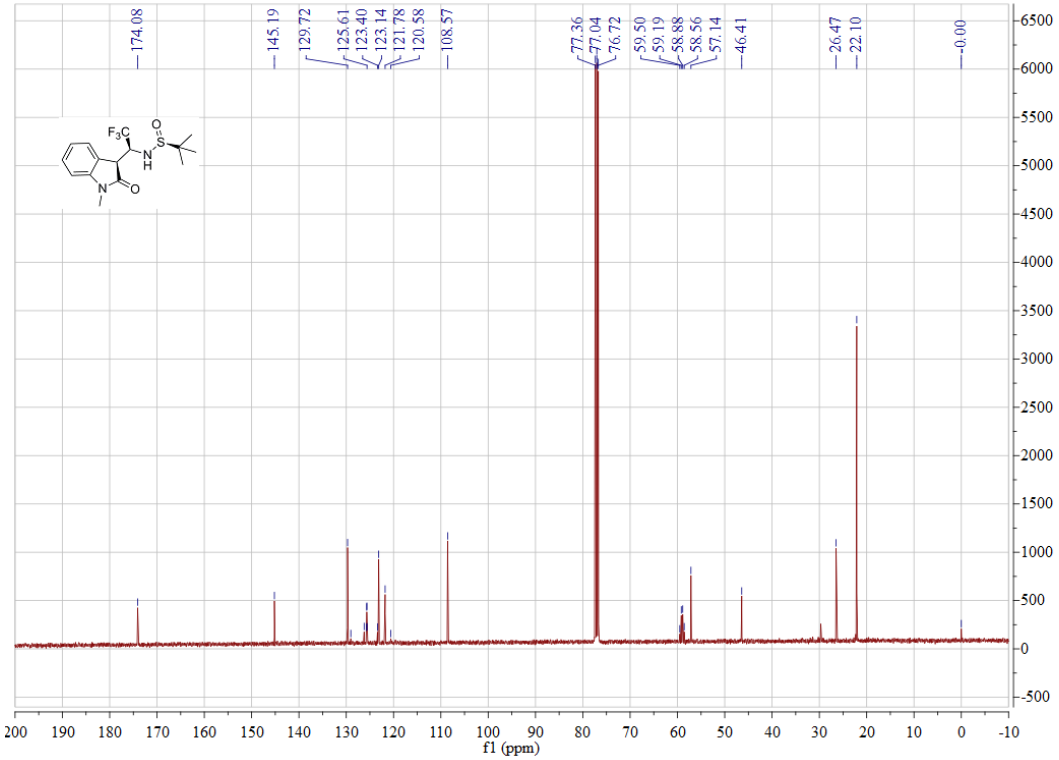
^{19}F-NMR spectra of crude reaction mixture for Entry 7 of Table 2



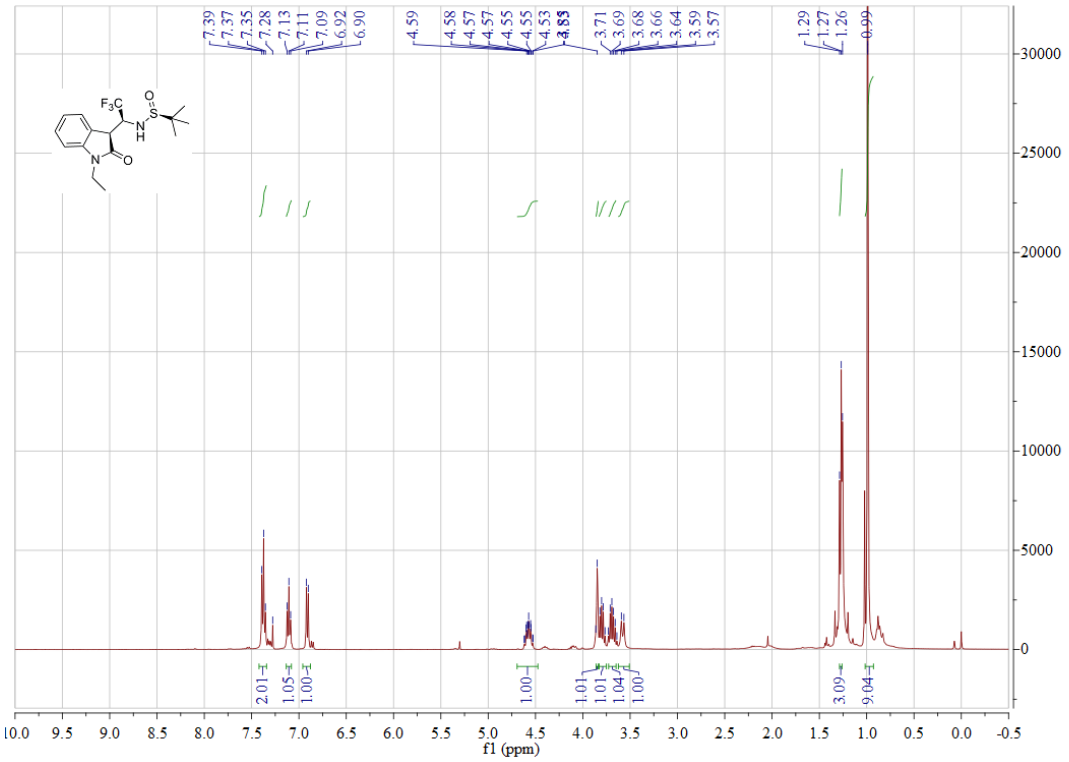
7. ^{1}H and ^{13}C NMR spectra for compounds 5 and 7

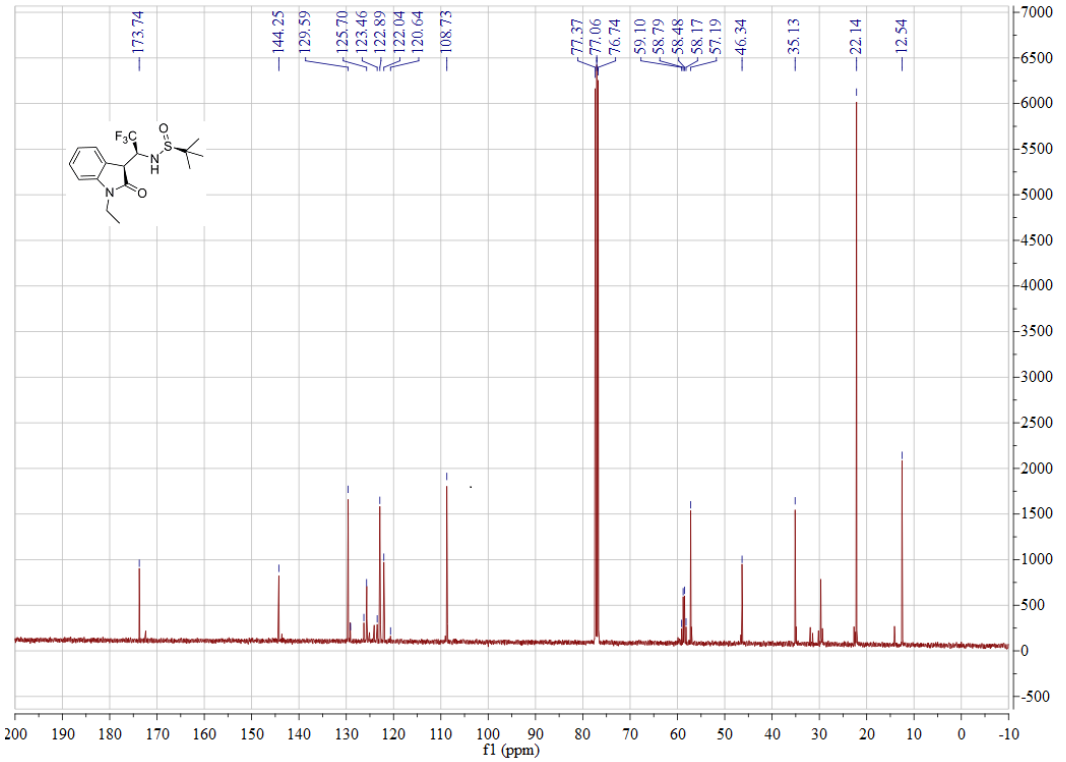
^{1}H NMR and ^{13}C NMR spectrum of **5a**



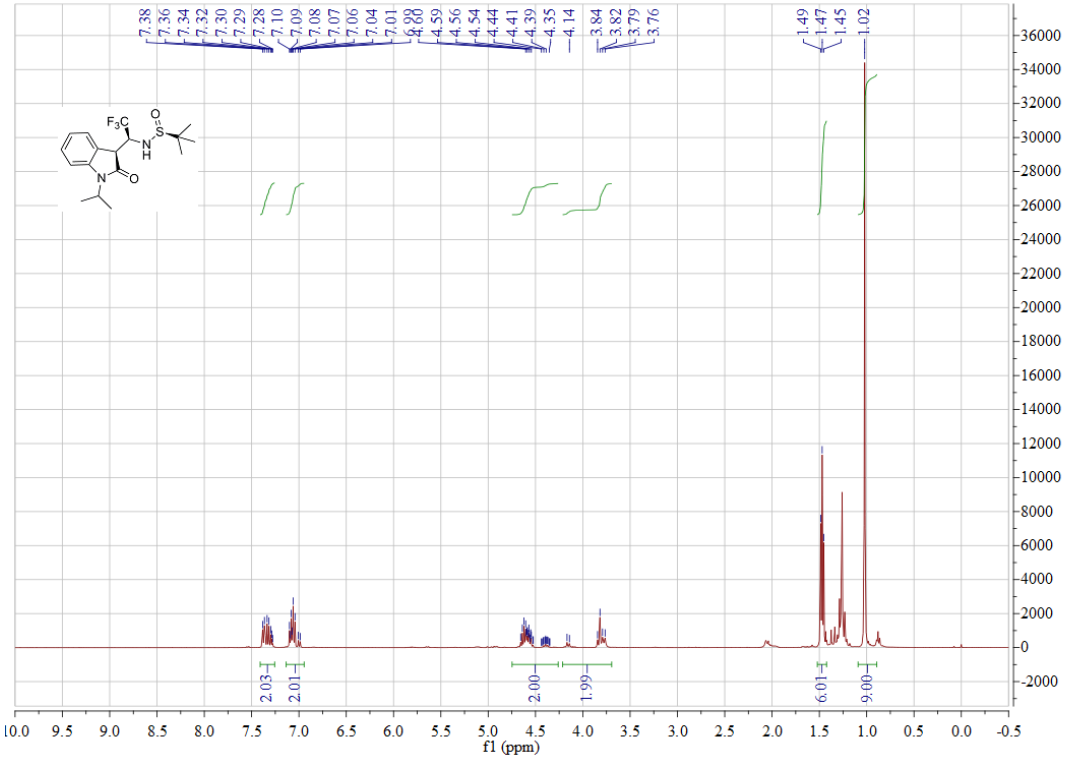


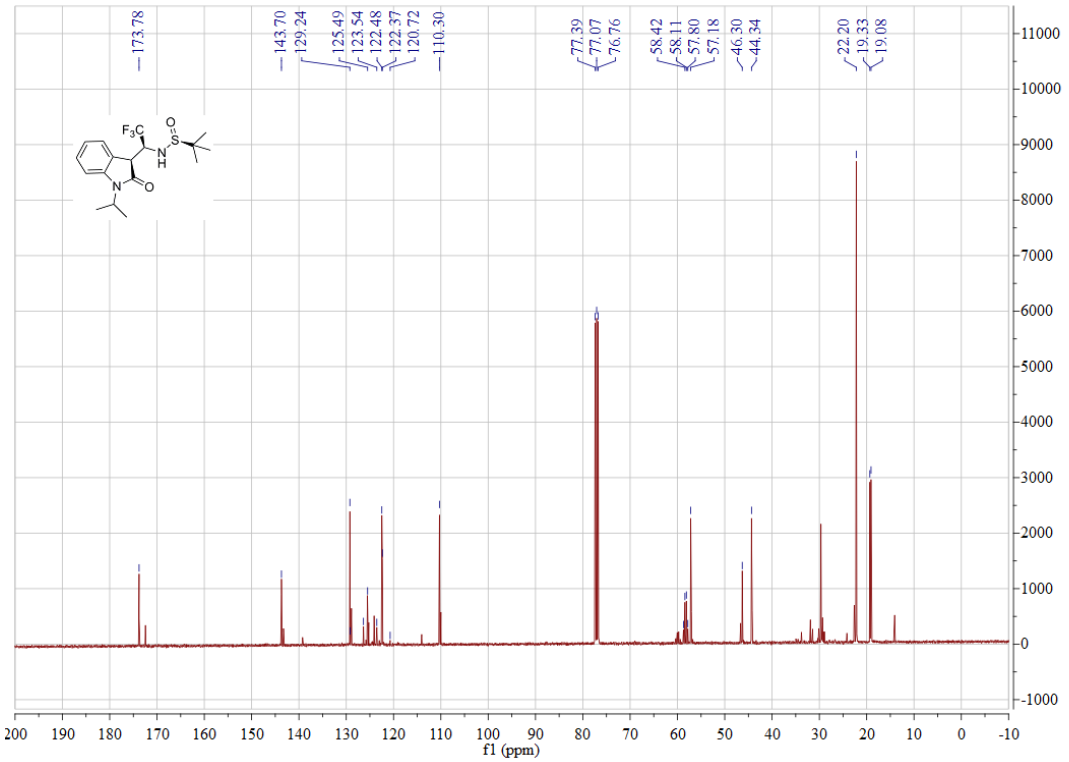
^{1}H NMR and ^{13}C NMR spectrum of **5b**



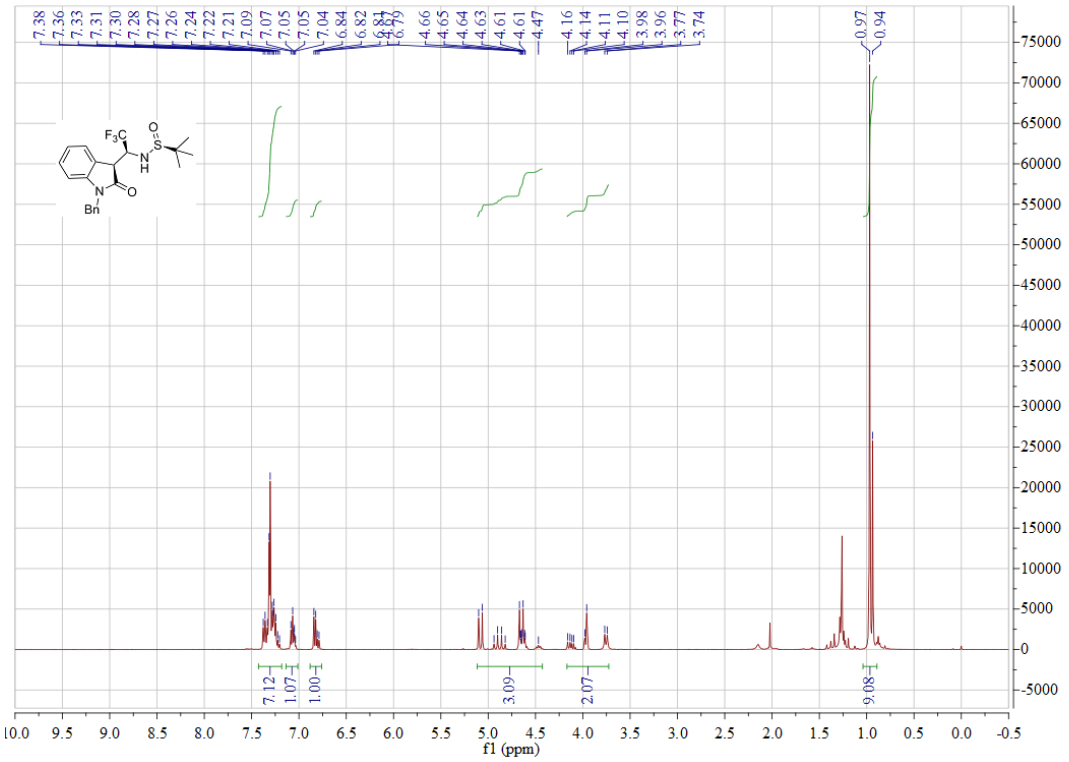


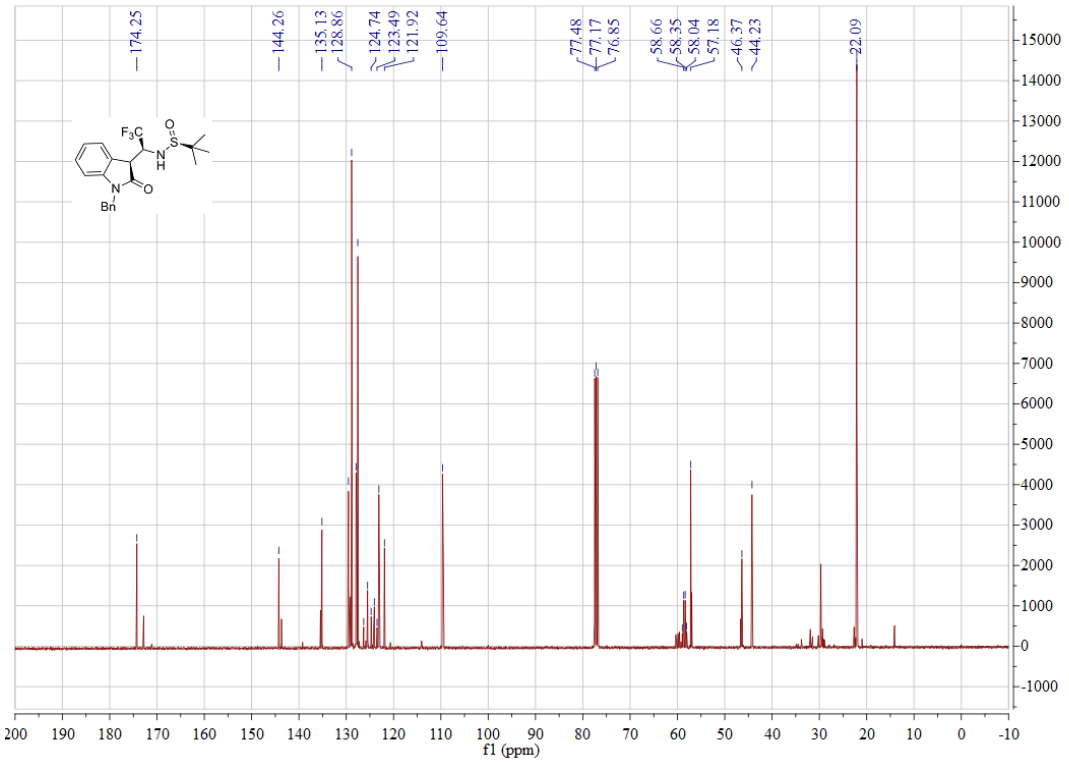
^{1}H NMR and ^{13}C NMR spectrum of **5c**



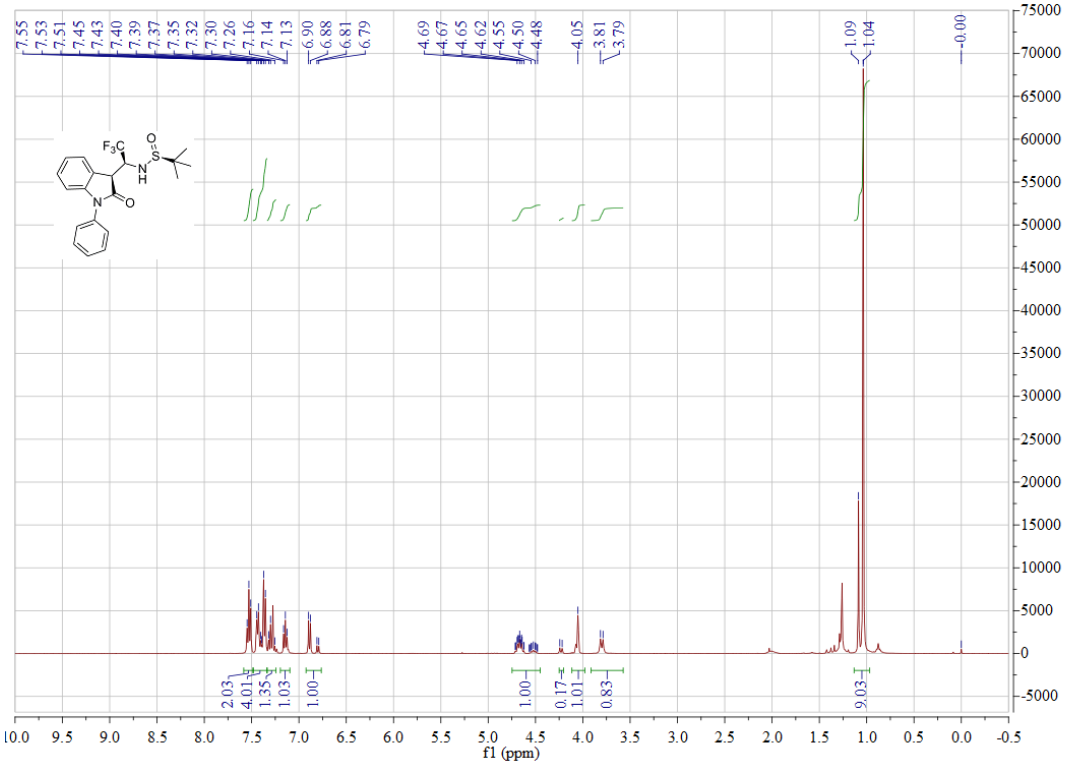


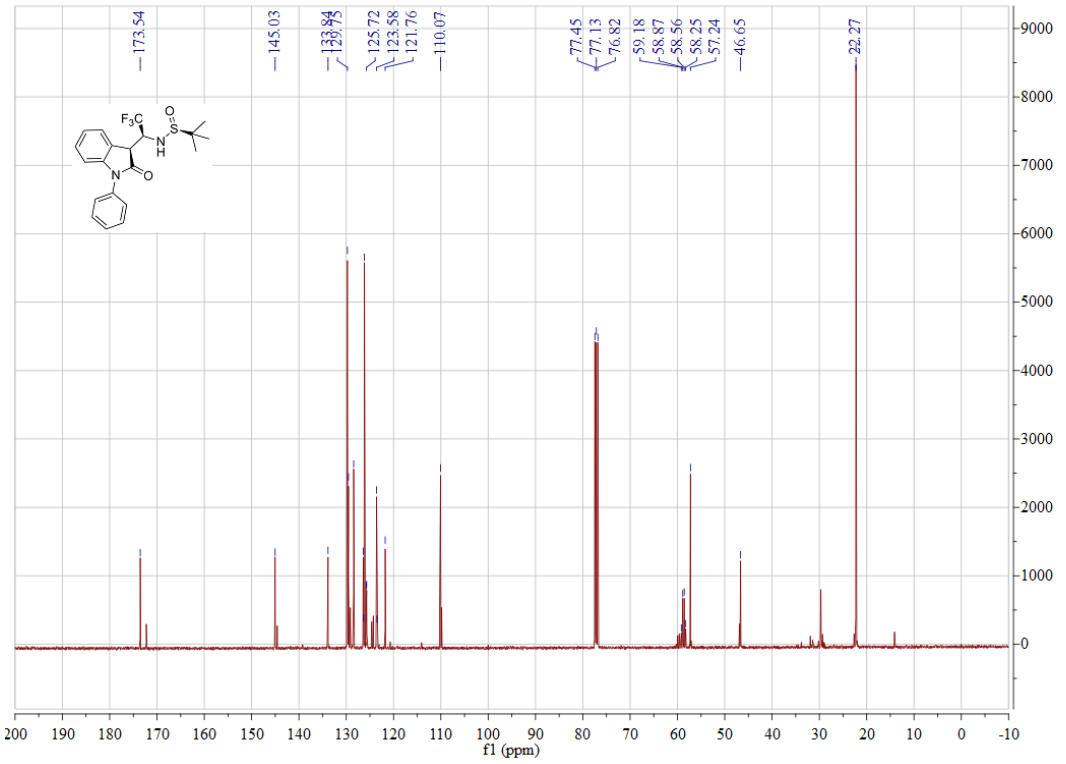
^{1}H NMR and ^{13}C NMR spectrum of **5d**



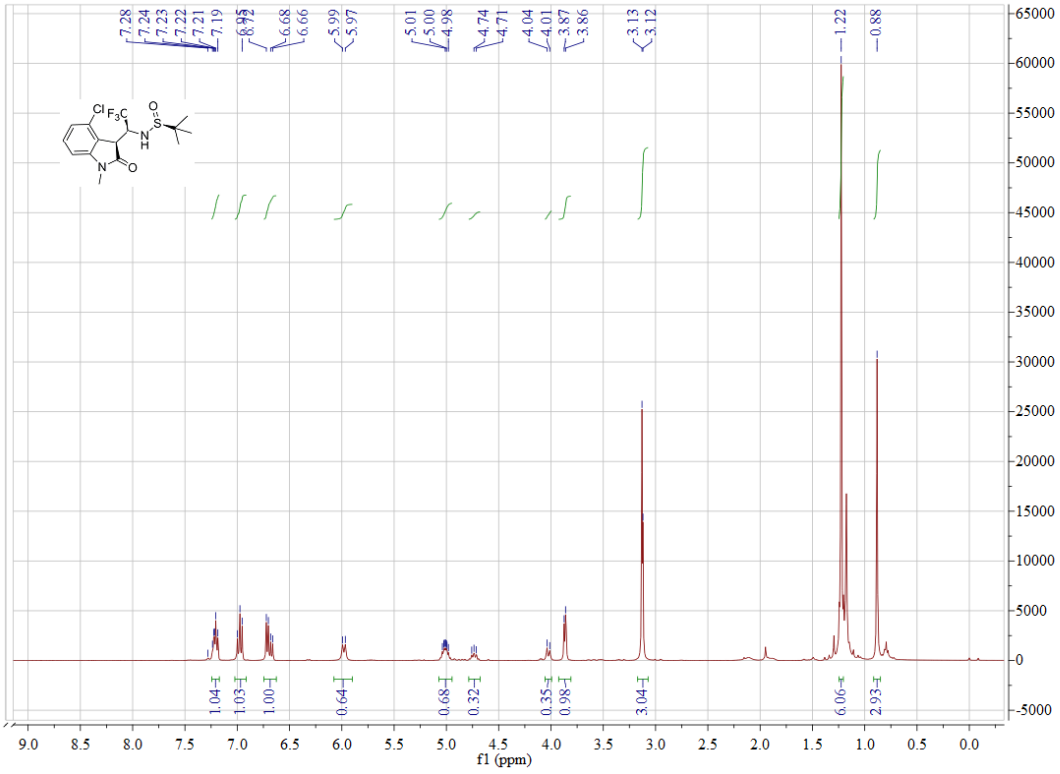


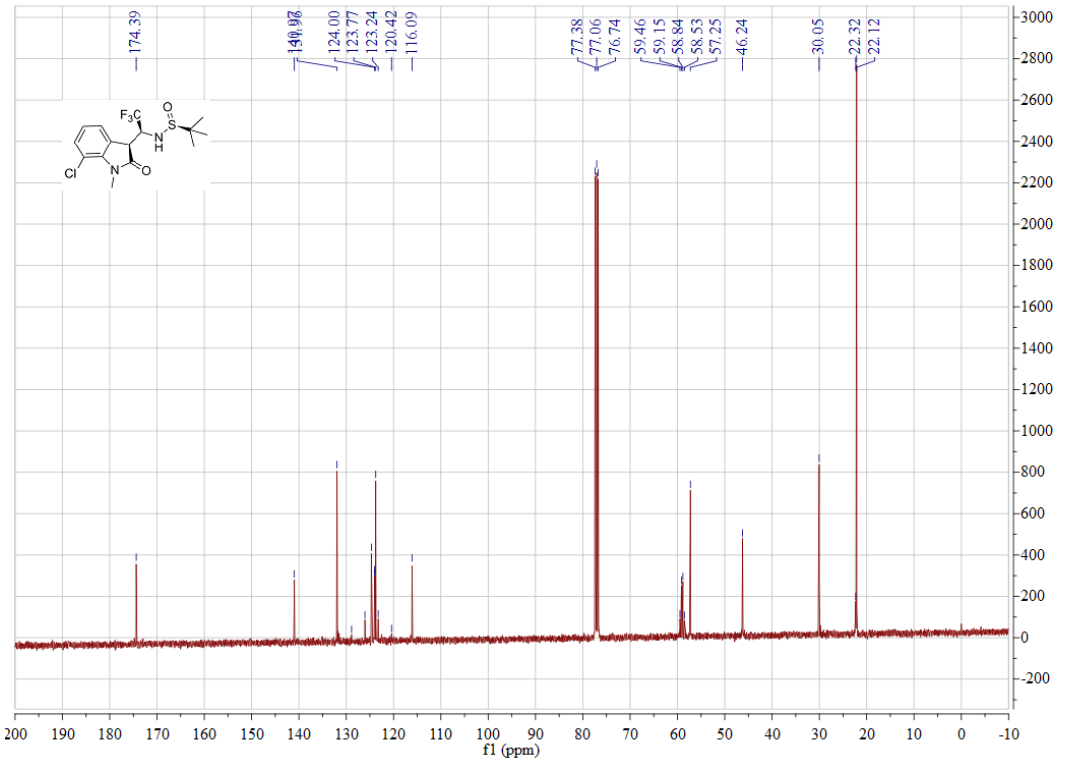
^{1}H NMR and ^{13}C NMR spectrum of **5e**

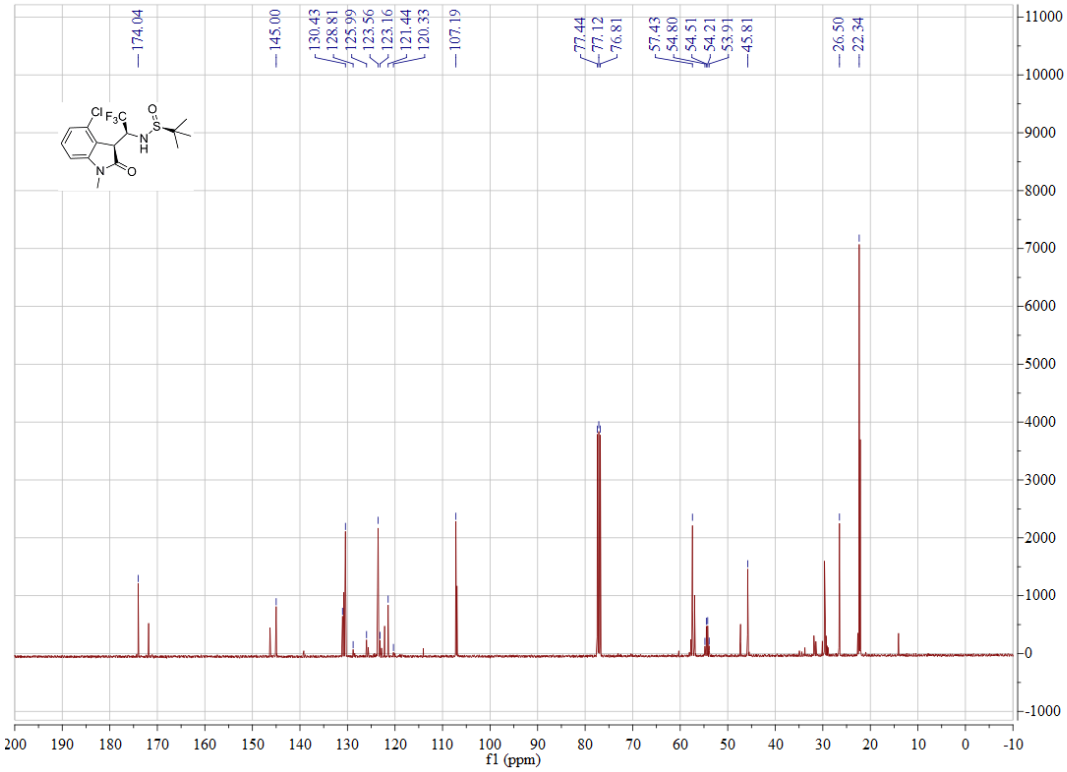




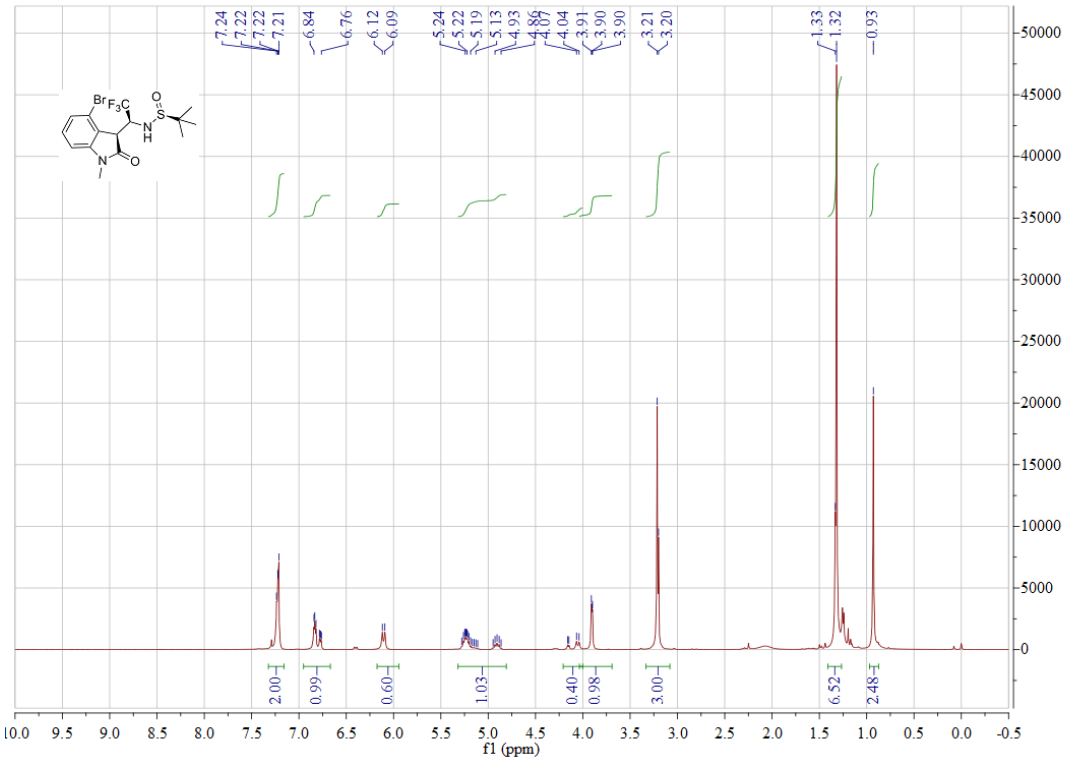
^{1}H NMR and ^{13}C NMR spectrum of **7a**

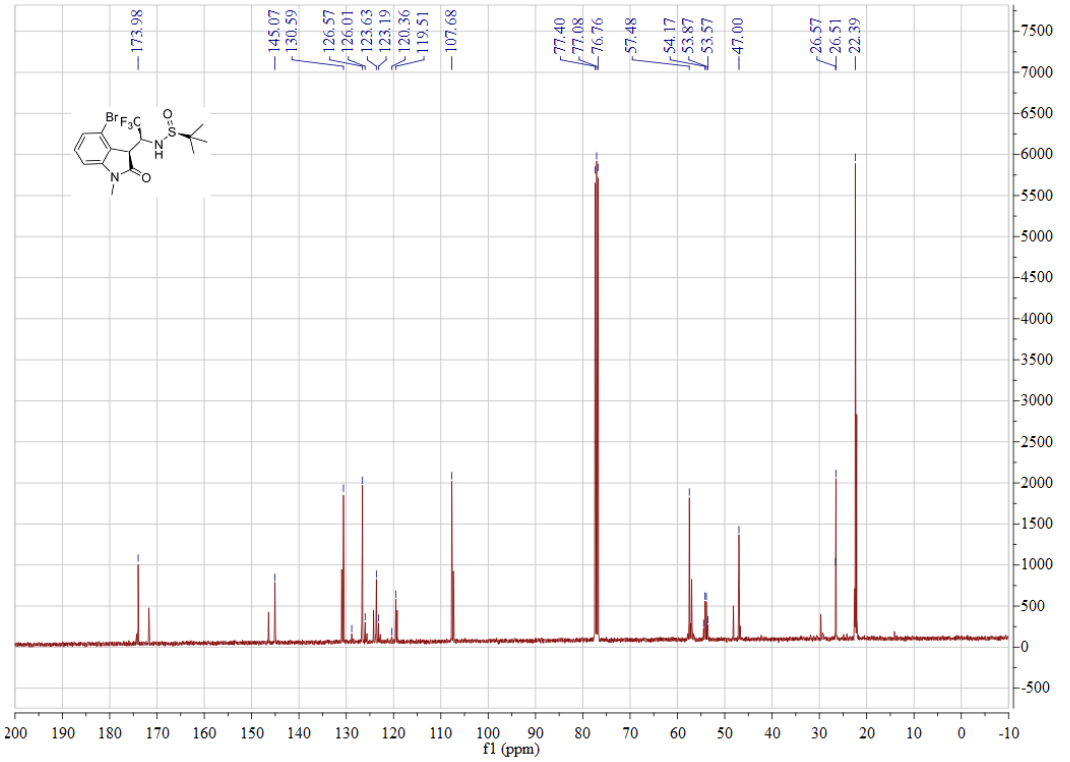



174.39
140.97
140.92
124.00
123.77
123.24
120.42
116.09
77.38
77.06
76.74
59.46
59.15
58.84
58.53
57.25
46.24
30.05
22.32
22.12
f1 (ppm)

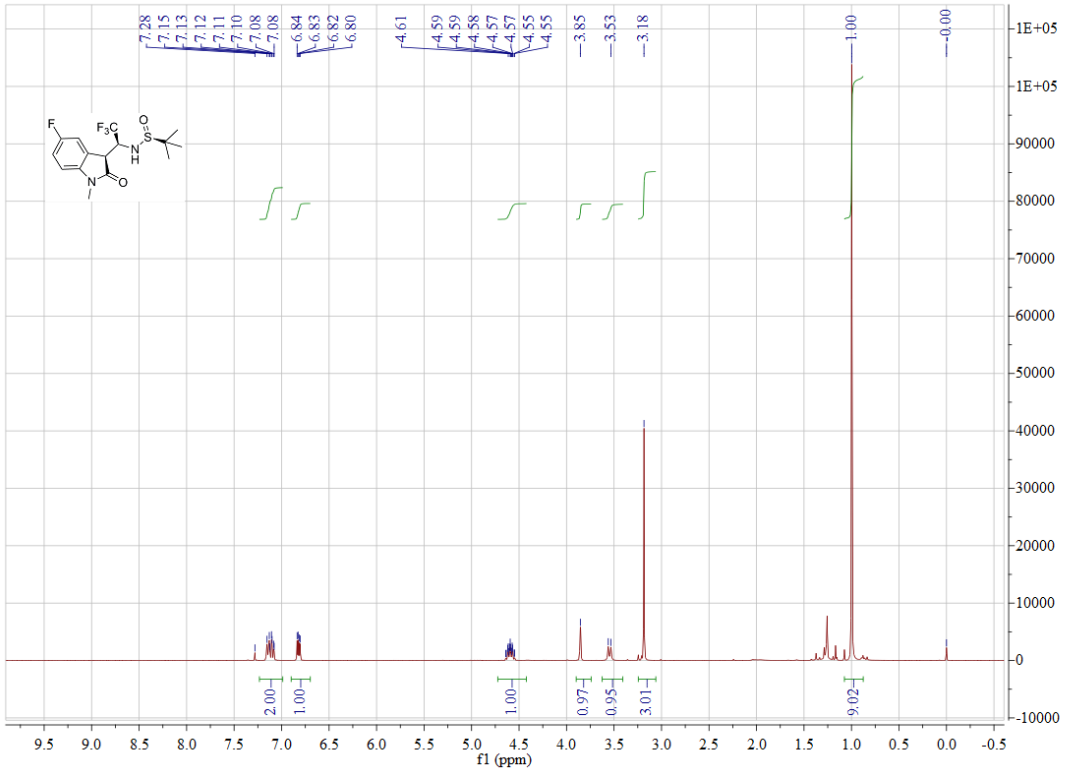

174.04
145.00
130.43
128.81
125.99
123.56
123.16
121.44
120.33
107.19
77.44
77.12
76.81
57.43
54.80
54.51
54.21
53.91
45.81
26.50
22.34
f1 (ppm)

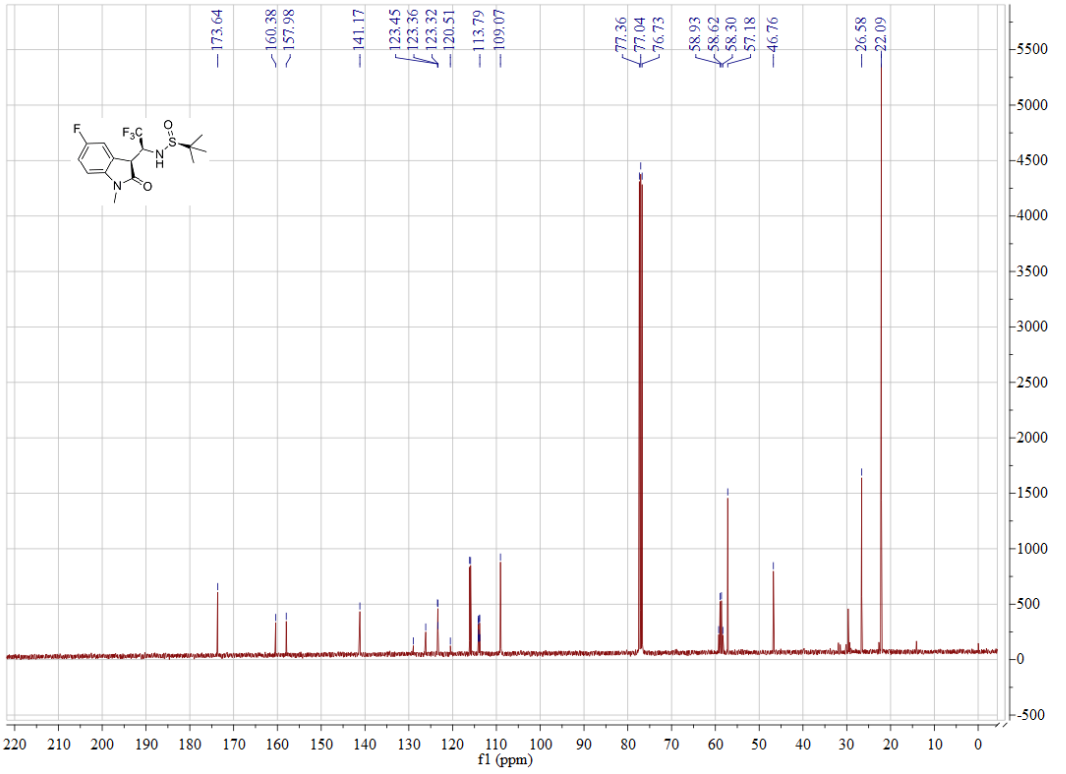
^{1}H NMR and ^{13}C NMR spectrum of **7b**



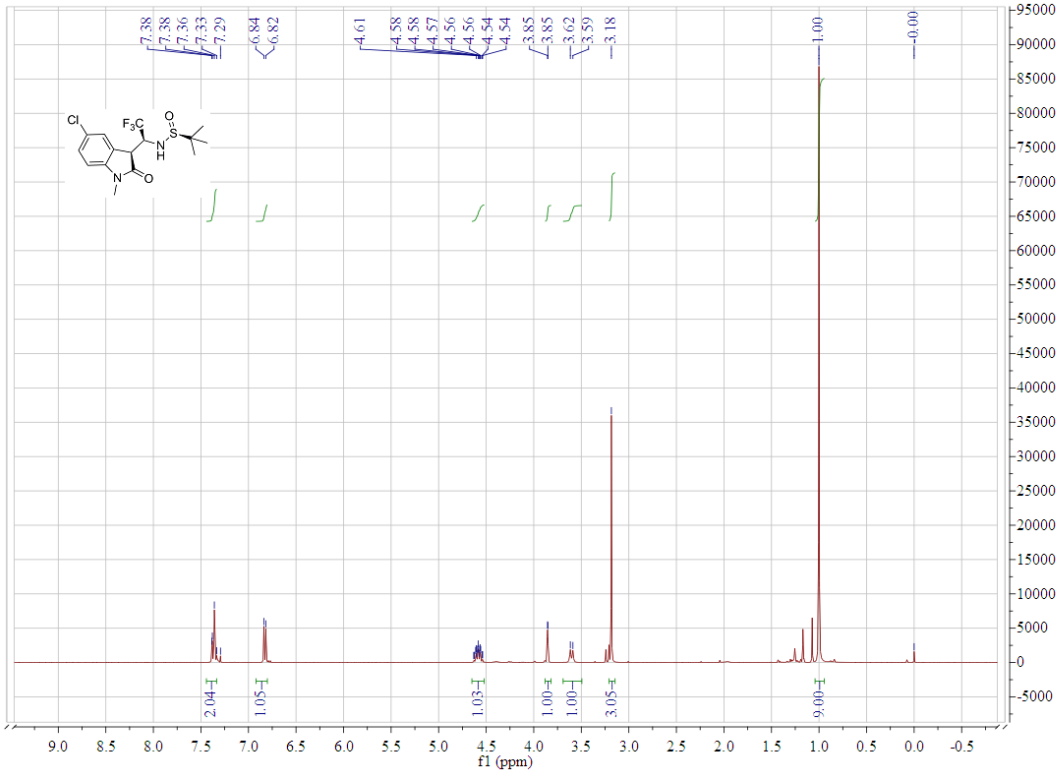


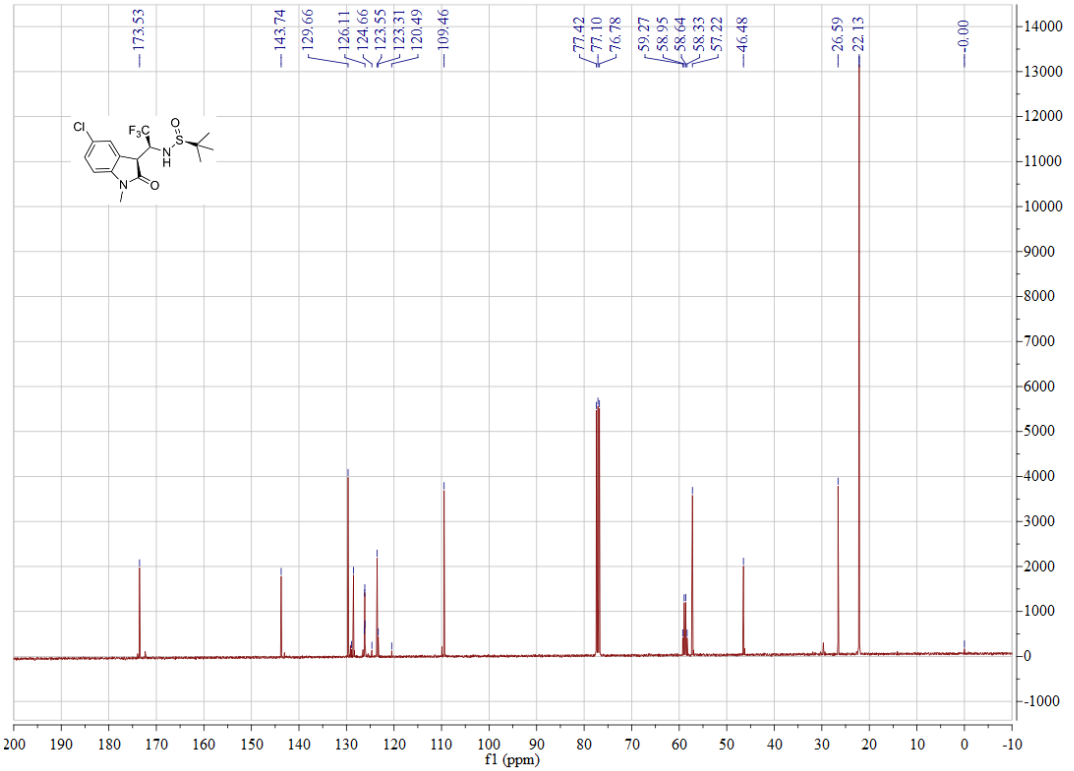
^{1}H NMR and ^{13}C NMR spectrum of **7c**



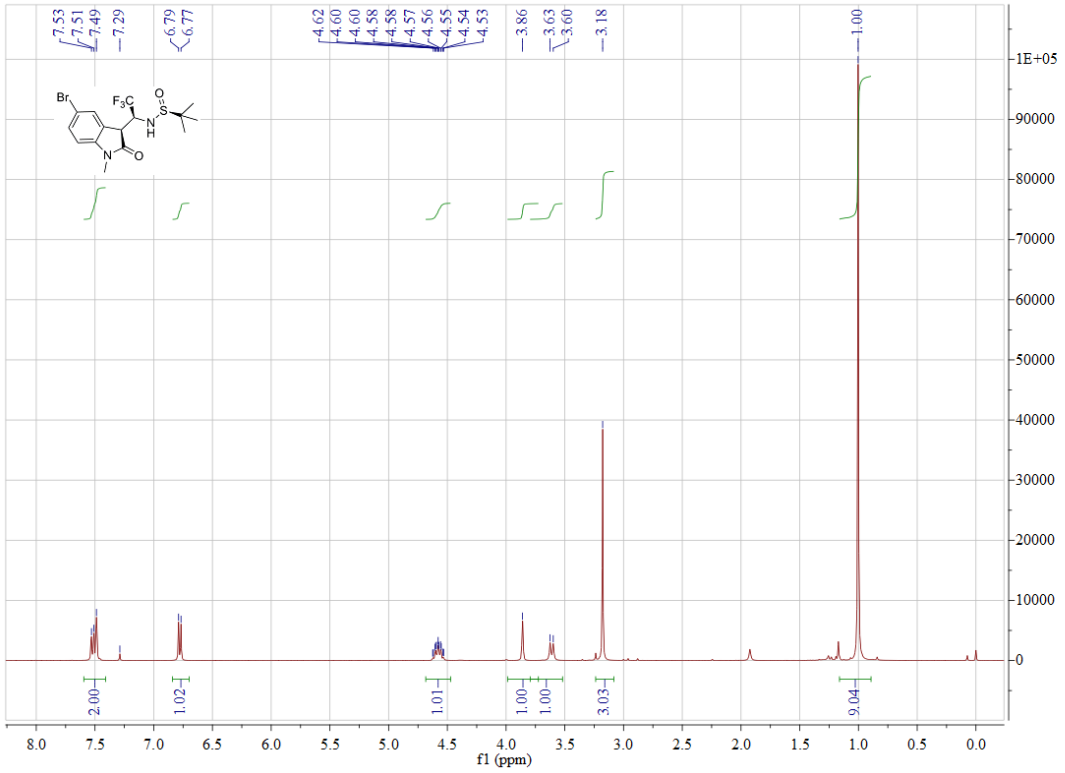


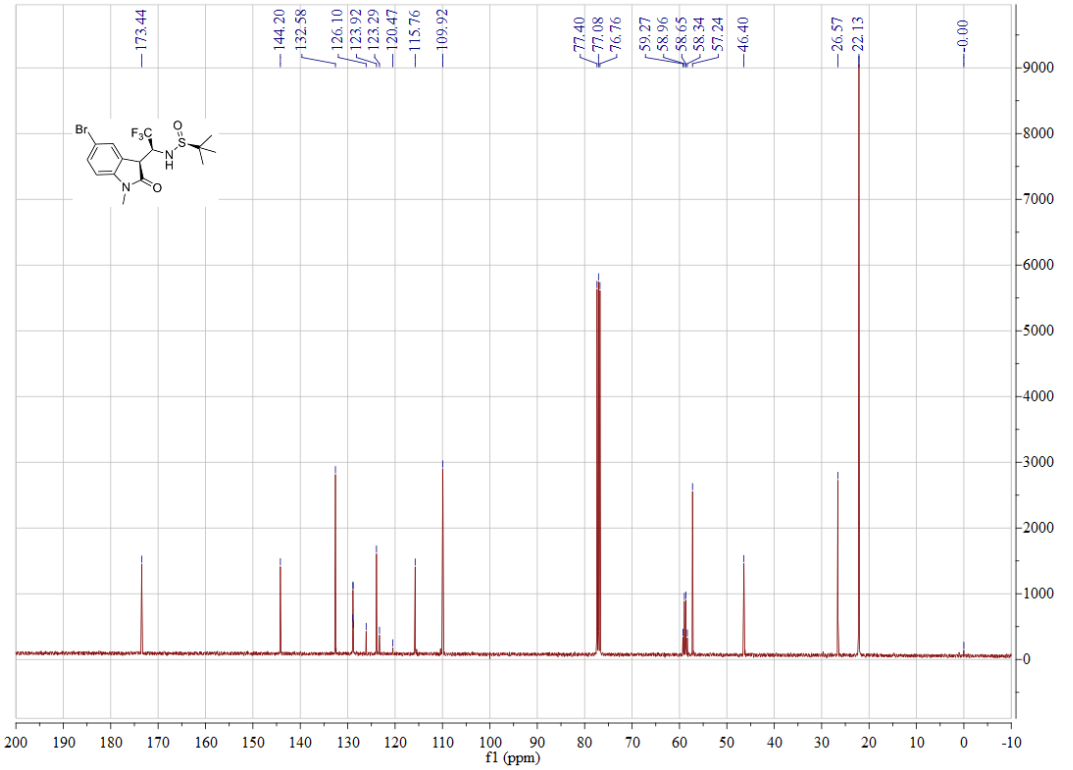
^{1}H NMR and ^{13}C NMR spectrum of **7d**



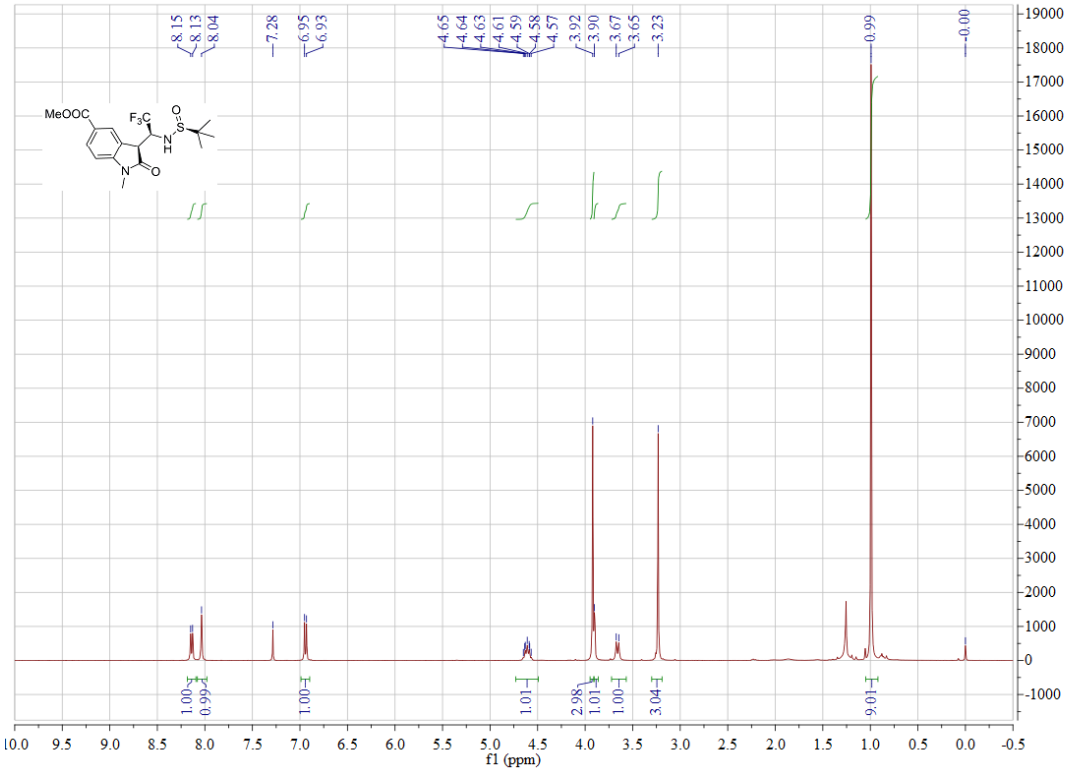


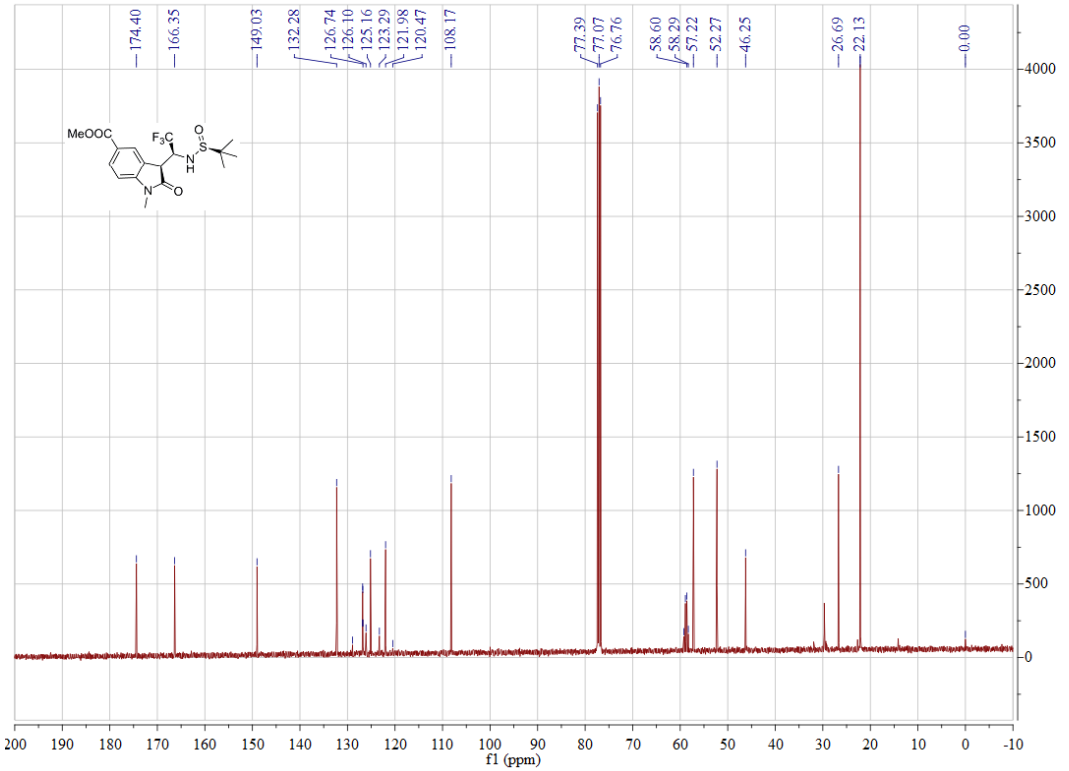
^{1}H NMR and ^{13}C NMR spectrum of **7e**



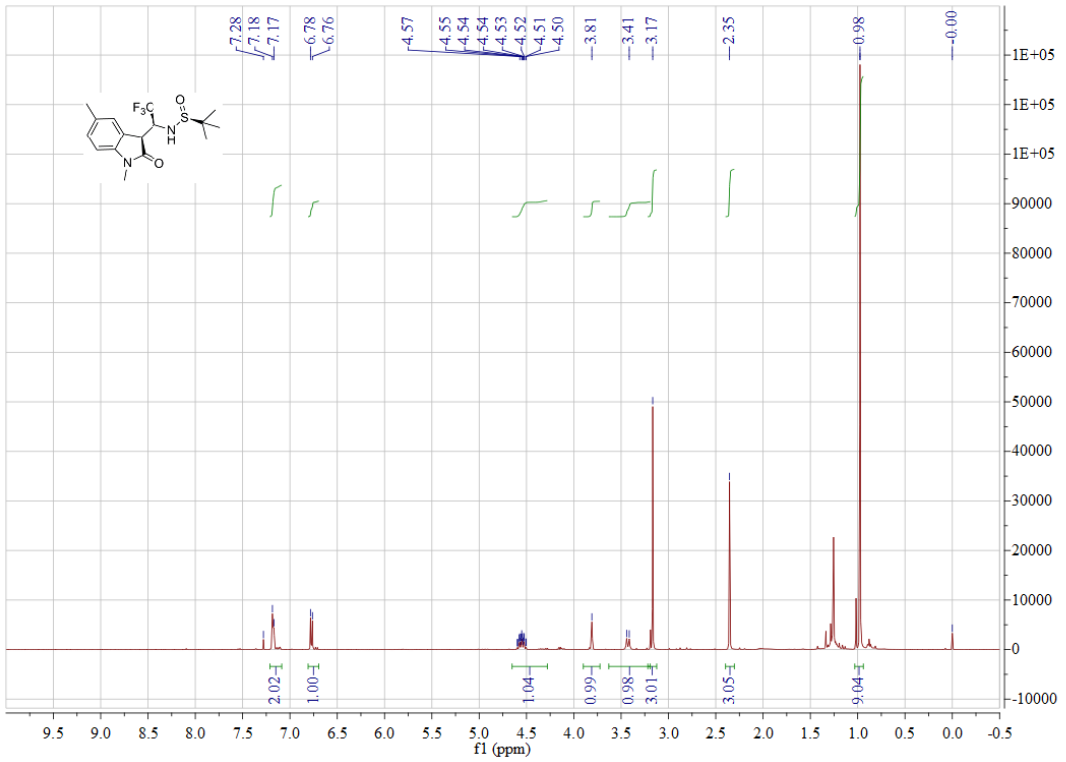


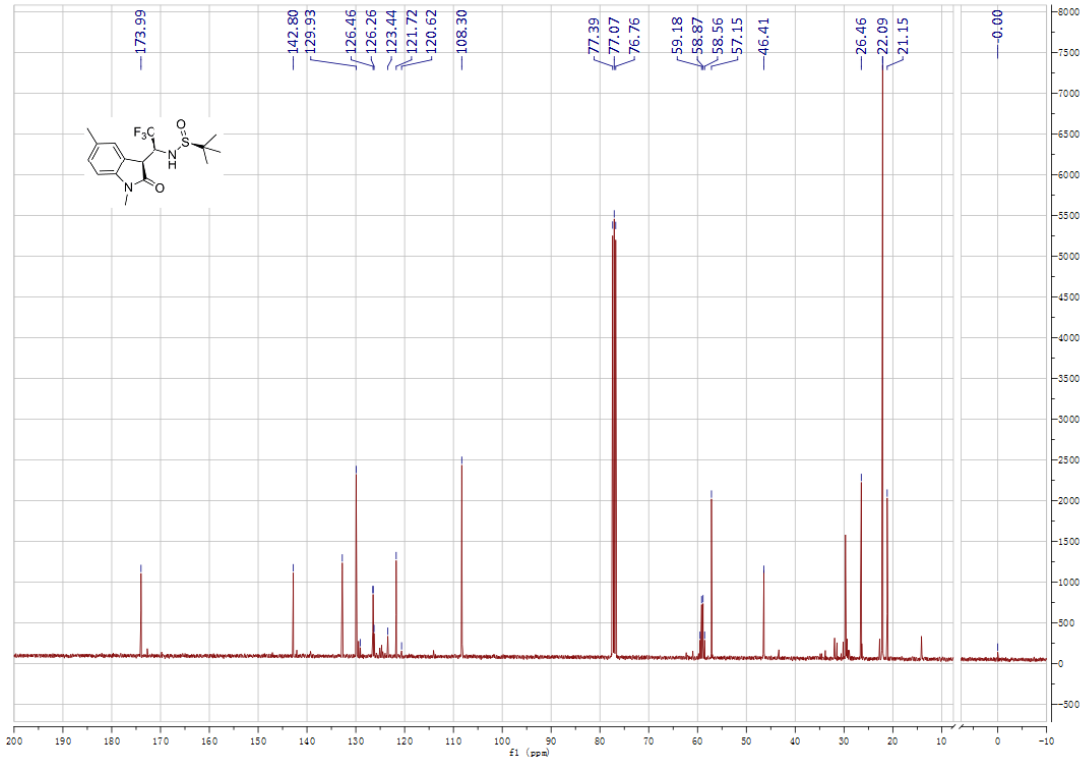
^{1}H NMR and ^{13}C NMR spectrum of **7f**



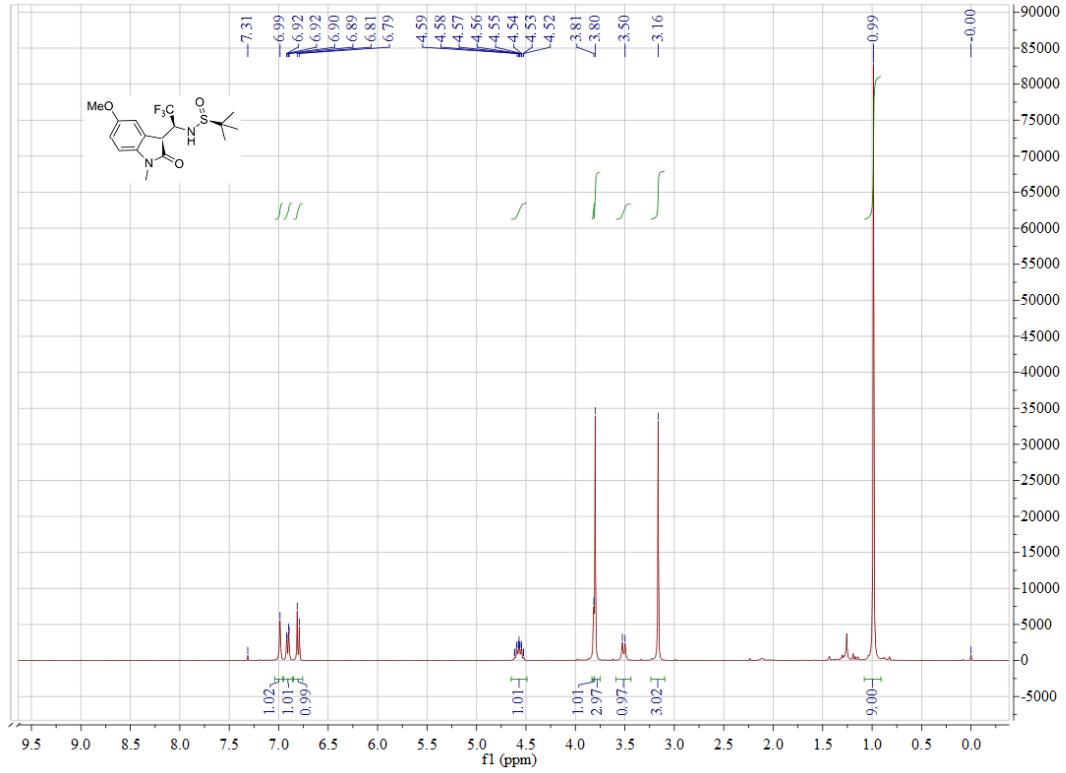


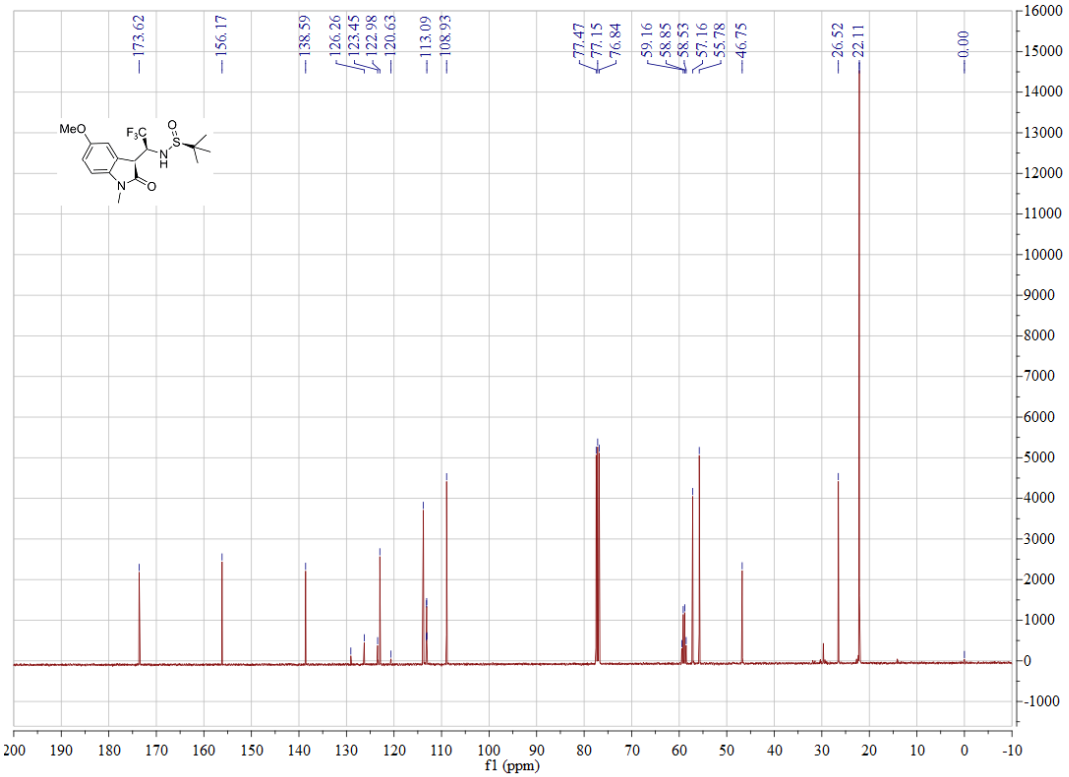
^{1}H NMR and ^{13}C NMR spectrum of **7g**



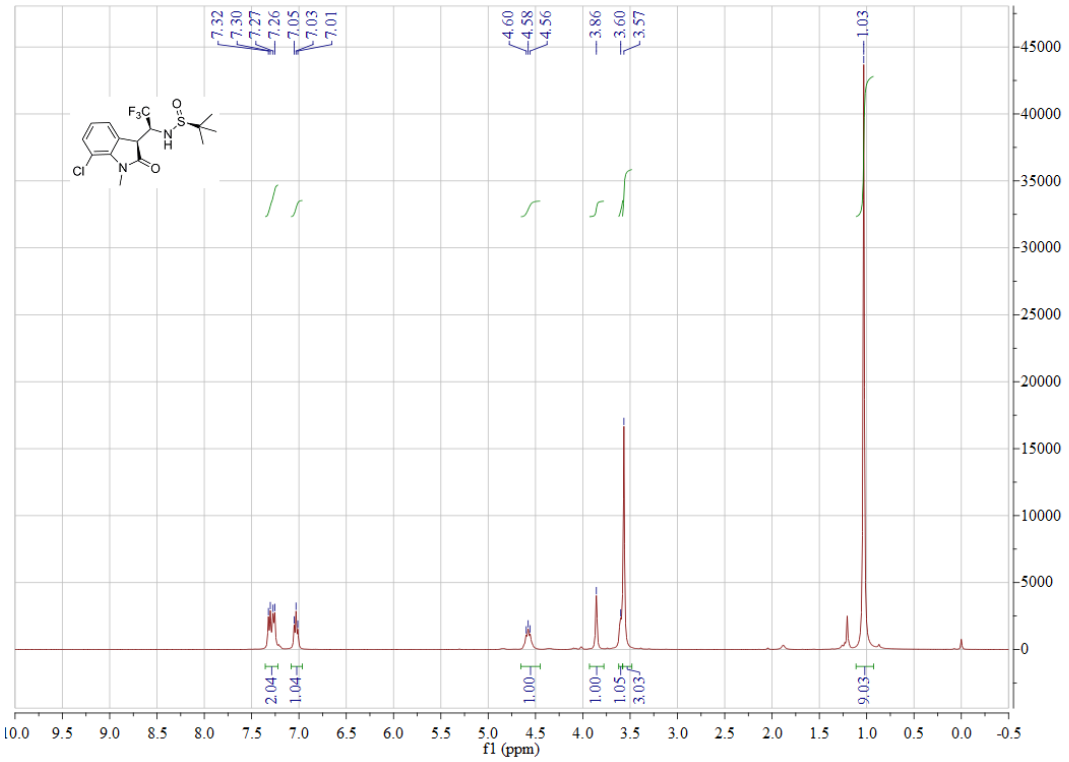


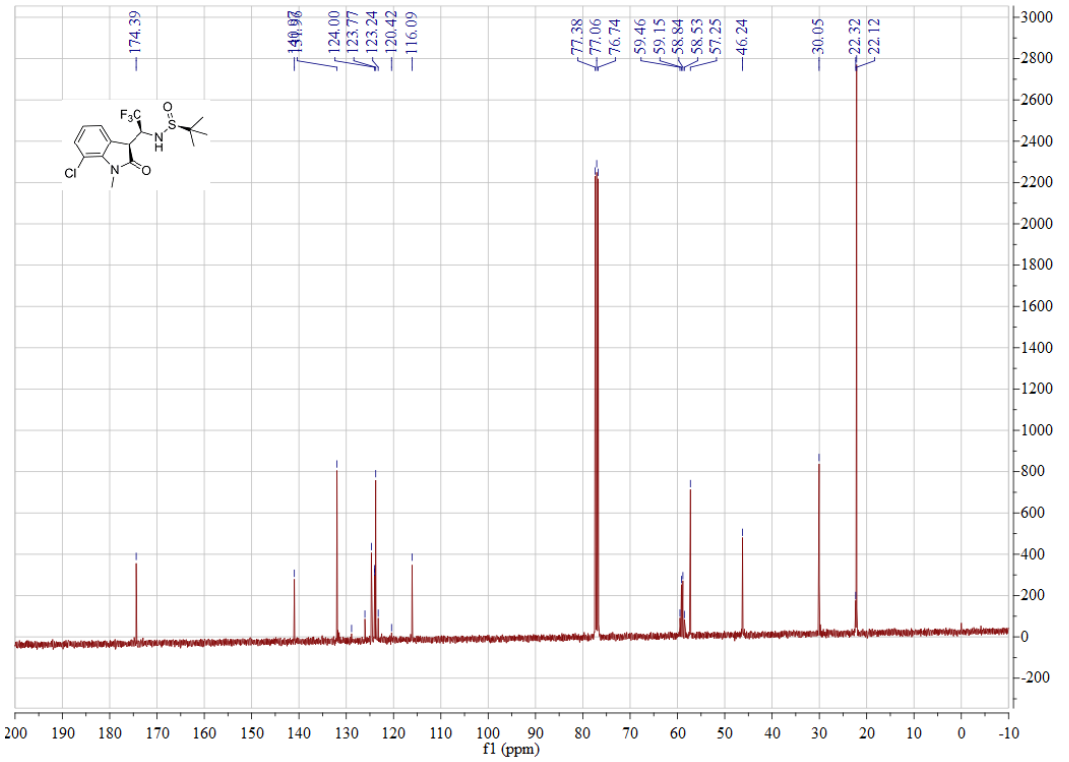
^{1}H NMR and ^{13}C NMR spectrum of **7h**





^{1}H NMR and ^{13}C NMR spectrum of **7l**





^{1}H NMR and ^{13}C NMR spectrum of **7m**