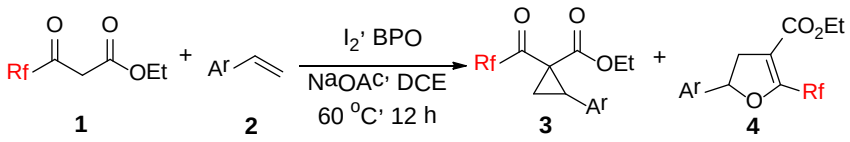
Electronic supplementary information

General Information:

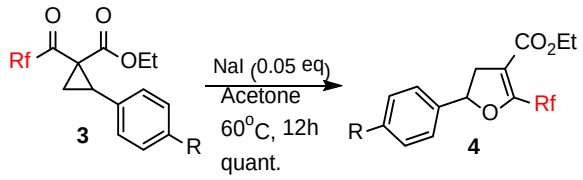
Unless otherwise noted, all commercial reagents and solvents were used as received from commercial sources without further purification. Silica gel plates (GF254) were used for TLC monitoring and silica gel (300 - 400 mesh) was used for flash column chromatography. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz for ^{1}H; 101 MHz for ^{13}C; 376 MHz for ^{19}F), ^{1}HNMR and ^{13}CNMR chemical shifts were determined relative to internal standard TMS at δ 0.0 as an external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer. High-resolution mass spectra were obtained using a Thermo Fisher Scientific LTQ FT Ultra in positive direct analysis in real time (DART) ionization method.

General Procedure



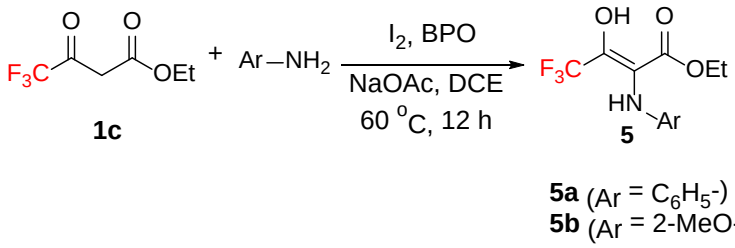
General Procedure for the Cyclopropanation:

In a Schlenk tube equipped with a stirring bar, NaOAc (41.0 mg, 0.50 mmol), I_2 (12.7 mg, 0.05 mmol) were added under N_2 atmosphere. 1,2-Dichloroethane (DCE, 2.0 mL) was injected into the tube. After the dissolution of I_2, ethyl 4,4,4-trifluoroacetoacetate or ethyl 4,4-difluoro-3-oxobutyrate **1** (0.50 mmol), alkene **2** (1.0 mmol) and benzoyl peroxide (BPO, 121.0 mg, 0.50 mmol) were added into the Schlenk tube under N_2 atmosphere. The reaction was then stirred at 60℃ for 12 h. After completion, the reaction was quenched with saturated $Na_2S_2O_3$ solution. Then the reaction mixture was extracted with ethyl ether (3 x 10 mL). The organic layers were combined and wash with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1 or petroleum ether : dichloromethane = 15:1).



General Procedure for the Dihydrofuran Transformation:

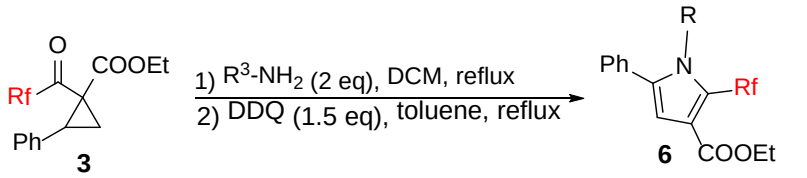
To a solution of cyclopropane product **3** (0.5 mmol) in acetone (2 mL) was added NaI (0.025 mmol). The mixture was stirred at 60°C for 12h. After removal of solvent, dihydrofuran product **4** was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1).



5a (Ar = C_6H_5-)
5b (Ar = 2-MeO-C_6H_5-)

General Procedure of Ethyl Trifluoroacetoacetate and Aromatic amine:

In a Schlenk tube equipped with a stirring bar, NaOAc (41.0 mg, 0.50 mmol), I_2 (12.7 mg, 0.05 mmol) were added under N_2 atmosphere. 1,2-Dichloroethane (DCE, 2.0 mL) was injected into the tube. After the dissolution of I_2, Ethyl Trifluoroacetoacetate **1c** (0.50 mmol), aromatic amine (1.0 mmol) and benzoyl peroxide (BPO, 121.0 mg, 0.50 mmol) were added into the Schlenk tube under N_2 atmosphere. The reaction was then stirred at 60℃ for 12 h. After completion, the reaction was quenched with saturated $Na_2S_2O_3$ solution. Then the reaction mixture was extracted with ethyl ether (3 x 10 mL). The organic layers were combined and wash with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. The pure product was obtained by flash column chromatography on silica gel (petroleum ether : dichloromethane = 30:1).



6a Rf = CF_2H, R^3=Bn 40%
6b Rf = CF_3, R^3=Ph 95%
6c Rf = CF_2H, R^3=Ph 80%

General Procedure for the Pyrrole Transformation:

To a solution of cyclopropane product **3** (0.5 mmol) in DCE (2 mL) was added aniline or benzylamine (1.0 mmol). The mixture was stirred at 60 or 80 °C for 8h. After removal of solvent, dihydropyrrole was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1). The dihydropyrrole was mixed with DDQ (1.5 eq) in toluene, and refluxed overnight. Pyrrole product **6** was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1).

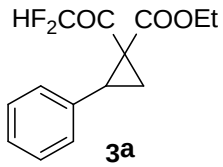
Synthesis of Ethyl 4,4-Difluoro-2-iodo-3-oxobutanoate and Ethyl 4,4-Difluoro-3-hydroxy-2-iodobut-2-enoate (1a):

Finely powdered CuO (80 mg, 1.0 mmol) and I_2 (254 mg, 1.0 mmol) were added to a well-stirred solution of the ethyl trifluoroacetoacetate (184 mg, 1.0 mmol) in anhydrous EtOH (10 mL). The mixture was then heated at 70°C for 12 h. After cooling, the mixture was filtered and the solvent was removed under reduced pressure (Note: the mixture could not be treated with $Na_2S_2O_3$ because it reacted with iodinated product). The product **1a** was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1).

Synthesis of Ethyl 2-Iodo-3-oxobutanoate and Ethyl 3-Hydroxy-2-iodobut-2-enoate (1e):

To the DMSO solution of 1,3-keto ester (1.0 mmol), *N*-iodosuccinimide (1.05 mmol) was added, and the resultant mixture was stirred for 1h at room temperature. After completion of the reaction as indicated by thin layer chromatography (TLC), the reaction mixture was washed with NH_4Cl solution. The product was extracted with ethyl acetate, dried over Na_2SO_4, and purified by column chromatography (petroleum ether : ethyl acetate = 40:1).

Detail Descriptions for Products



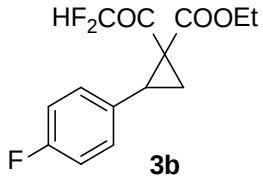
3a

Ethyl 1-(2,2-difluoroacetyl)-2-phenylcyclopropanecarboxylate (3a)

E isomer: yellow liquid (73.8 mg, 55%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 5H), 6.45 (t, *J* = 53.5 Hz, 1H), 3.82 – 3.70 (m, 2H), 3.33 (t, *J* = 9.0 Hz, 1H), 2.36 (dd, *J* = 9.0, 4.8 Hz, 1H), 1.83 (dd, *J* = 9.0, 4.8 Hz, 1H), 0.8 – 0.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.83 (t, J_{CF} = 23 Hz), 166.73, 133.65, 129.27, 128.24, 127.86, 125.62, 109.38 (t, J_{CF} = 249 Hz), 61.56, 41.09, 37.23, 22.72, 13.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.43 (d, *J* = 296.4 Hz, 1F), -129.49 (d, *J* = 296.4 Hz, 1F). IR (KBr, cm^{-1}): 2986, 1720 ,1606, 1453, 1377, 1319, 1253, 1214, 1174, 1077, 897, 753, 702, 526.

Z isomer: yellow liquid (36.2 mg, 27%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.16 (m, 2H), 5.79 (t, *J* = 53.2 Hz 1H), 4.37 – 4.23 (m, 2H), 3.54 (t, *J* = 8.4 Hz, 1H), 2.44 (dd, *J* = 8.4, 5.1 Hz, 1H), 1.82 (dd, *J* = 8.4, 5.1 Hz, 1H), 1.32 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.34 (t, J_{CF} = 25 Hz), 169.15, 132.36, 128.87, 128.42, 127.95, 109.12 (t, J_{CF} = 250 Hz), 62.15, 41.25, 36.82, 18.21, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.21 (s), -129.30 (s). IR (KBr, cm^{-1}): 2923, 1723, 1607, 1496, 1456, 1378, 1274, 1168, 1096, 1057, 1023, 974, 916, 842, 762, 703, 581, 537.

HRMS (EI) for $C_{14}H_{14}F_2O_3$ $[M]^+$: calcd, 268.0911; found 268.0913.



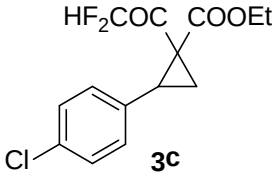
3b

Ethyl 1-(2,2-difluoroacetyl)-2-(4-fluorophenyl)cyclopropanecarboxylate (3b)

E isomer: yellow liquid (60.1 mg, 42%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.03 – 6.95 (m, 2H), 6.49 (t, *J* = 53.5 Hz, 1H), 3.97 – 3.78 (m, 2H), 3.40 – 3.32 (m, 1H), 2.43 – 2.36 (m, 1H), 1.95 – 1.87 (m, 1H), 0.97 – 0.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.68 (t, J_{CF} = 25 Hz), 166.54, 162.40 (d, J_{CF} = 246 Hz), 130.91 (d, J_{CCF} = 8 Hz), 129.44, 115.20 (d, J_{CCF} = 23 Hz), 109.37 (t, J_{CF} = 250 Hz), 61.67, 40.99, 36.09, 22.71, 13.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.95 (s, 1F), -127.42 (d, *J* = 296.6 Hz, 1F), -129.32 (d, *J* = 296.6 Hz, 1F). IR (KBr, cm^{-1}): 2923, 1720, 1602, 1511, 1451, 1376, 1318, 1270, 1171, 1081, 903, 843, 753, 703.

Z isomer: yellow liquid (34.3 mg, 24%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.12 (m, 2H), 7.00 – 6.94 (m, 2H), 5.92 (t, *J* = 53.7 Hz, 1H), 4.37 – 4.23 (m, 2H), 3.54 – 3.50 (m, 1H), 2.42 – 2.36 (m, 1H), 1.84 – 1.81 (m, 1H), 1.36 – 1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.12 (t, J_{CF} = 25 Hz), 169.01, 162.40 (d, J_{CF} = 246 Hz), 130.64 (d, J_{CCF} = 8 Hz), 128.11, 115.38 (d, J_{CCF} = 21 Hz), 109.15 (t, J_{CF} = 250 Hz), 62.21, 41.17, 36.38, 18.52, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.86 (s, 1F), -129.44 (s, 2F). IR (KBr, cm^{-1}): 2922, 1721, 1603, 1512, 1450, 1376, 1311, 1273, 1231, 1166, 1092, 839, 753, 549.

HRMS (EI) for $C_{14}H_{13}F_3O_3$ $[M]^+$: calcd, 286.0817; found 286.0813.



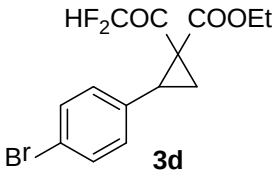
3c

Ethyl 2-(4-chlorophenyl)-1-(2,2-difluoroacetyl)cyclopropanecarboxylate (3c)

E isomer: yellow liquid (108.9 mg, 72%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 6.48 (t, *J* = 53.5 Hz, 1H), 3.98 – 3.82 (m, 2H), 3.35 (t, *J* = 8.8 Hz, 1H), 2.38 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.90 (dd, *J* = 8.8, 5.2 Hz, 1H), 0.96 – 0.91 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.59 (t, J_{CF} = 25 Hz), 166.43, 133.84, 132.20, 130.58, 128.43, 109.38 (t, J_{CF} = 249 Hz), 77.22, 61.76, 53.40, 40.95, 35.86, 22.51, 13.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.41 (d, *J* = 296.7 Hz, 1F), -129.20 (d, *J* = 296.7 Hz, 1F). IR (KBr, cm^{-1}): 2923, 1720, 1492, 1446, 1375, 1267, 1212, 1172, 1085, 1040, 899, 836, 753, 520.

Z isomer: yellow liquid (42.4 mg, 28%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 5.92 (t, *J* = 53.7 Hz, 1H), 4.39 – 4.20 (m, 2H), 3.50 (t, *J* = 8.8 Hz, 1H), 2.40 (dd, *J* = 8.8, 5.0 Hz, 1H), 1.83 (dd, *J* = 8.8, 5.0 Hz, 1H), 1.34 – 1.31 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.05 (t, J_{CF} = 25 Hz), 168.92, 133.96, 130.92, 130.26, 128.62, 109.12 (t, J_{CF} = 250 Hz), 62.27, 41.20, 36.27, 18.41, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.35 (s). IR (KBr, cm^{-1}): 2922, 1723, 1495, 1454, 1377, 1273, 1168, 1091, 1019, 972, 830, 753, 538.

HRMS (EI) for $C_{14}H_{13}ClF_2O_3$ $[M]^+$: calcd, 302.0521; found 302.0514.



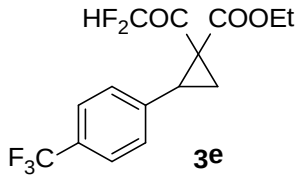
3d

Ethyl 2-(4-bromophenyl)-1-(2,2-difluoroacetyl)cyclopropanecarboxylate (3d)

E isomer: yellow liquid (78.1 mg, 45%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.48 (t, *J* = 53.5 Hz, 1H), 3.95 – 3.85 (m, 2H), 3.33 (t, *J* = 8.9 Hz, 1H), 2.37 (dd, *J* = 8.9, 4.9 Hz, 1H), 1.90 (dd, *J* = 8.9, 4.9 Hz, 1H), 0.96 – 0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.60 (t, J_{CF} = 25 Hz), 166.41, 132.74, 131.39, 130.91, 121.95, 109.41 (t, J_{CF} = 247 Hz), 61.78, 40.89, 35.85, 22.44, 13.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.40 (d, *J* = 296.8 Hz, 1F), -129.17 (d, *J* = 296.8 Hz, 1F). IR (KBr, cm^{-1}): 2986, 1721, 1452, 1376, 1317, 1269, 1172, 1075, 837, 753.

Z isomer: yellow liquid (62.5 mg, 36%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 5.92 (t, *J* = 53.6 Hz, 1H), 4.42 – 4.18 (m, 2H), 3.60 – 3.44 (m, 1H), 2.47 – 2.29 (m, 1H), 1.87 – 1.77 (m, 1H), 1.34 –1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.01(t, J_{CF} = 25 Hz), 168.89, 131.57, 131.49, 130.59, 122.11, 109.13 (t, J_{CF} = 250 Hz), 99.99, 77.35, 77.03, 76.71, 62.28, 41.16, 36.30, 18.36, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.32 (s). IR (KBr, cm^{-1}): 2985, 1721, 1591, 1489, 1375, 1311, 1271, 1207, 1168, 1015, 972, 824, 752, 527.

HRMS (EI) for $C_{14}H_{13}BrF_2O_3$ $[M]^+$: calcd, 346.0016; found 346.0011.

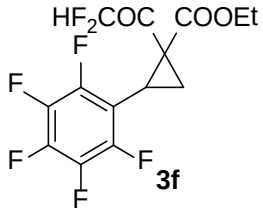


Ethyl 1-(2,2-difluoroacetyl)-2-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (3e)

E isomer: yellow liquid (36.9 mg, 22%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.51 (t, *J* = 52.6 Hz, 1H), 3.97 – 3.83 (m, 2H), 3.44 (t, *J* = 8.9 Hz, 1H), 2.45 (dd, *J* = 8.9, 5.0 Hz, 1H), 1.96 (dd, *J* = 8.9, 5.0 Hz, 1H), 0.93 – 0.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.52 (t, J_{CF} = 25 Hz), 193.28, 166.32, 137.85, 130.30, 129.98, 129.66, 125.24, 125.20, 125.16, 125.13, 122.60, 109.44 (t, J_{CF} = 247 Hz), 61.83, 40.78, 35.38, 22.28, 13.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69 (s, 3F), -127.44 (d, *J* = 297.0 Hz, 1F), -129.04 (d, *J* = 297.0 Hz, 1F). IR (KBr, cm^{-1}): 1722, 1624, 1560, 1476, 1426, 1364, 1324, 1174, 1032, 847, 798, 728, 574.

Z isomer: yellow liquid (33.6 mg, 20%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.93 (t, *J* = 53.7 Hz, 1H), 4.42 – 4.21 (m, 2H), 3.56 (t, *J* = 8.8 Hz, 1H), 2.46 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.87 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.36 – 1.31 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.92 (t, J_{CF} = 25 Hz), 167.74, 135.60, 129.63, 129.57, 129.30, 128.98, 128.33, 127.87, 127.52, 124.40, 124.36, 124.32, 124.29, 123.09 (t, J_{CF} = 270 Hz),, 118.87, 108.09 (t, J_{CF} = 250 Hz), 61.40, 40.23, 35.14, 17.37, 12.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72 (s, 3F), -129.38 (s, 1F), -129.41 (s, 1F). IR (KBr, cm^{-1}): 2925, 1725, 1449, 1377, 1325, 1274, 1168, 1123, 1018, 974, 915, 842, 711, 601.

HRMS (EI) for $C_{15}H_{13}F_5O_3$ $[M]^+$: calcd, 336.0785; found 336.0778.



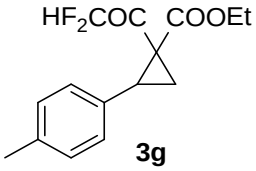
Ethyl 1-(2,2-difluoroacetyl)-2-(pentafluorophenyl)cyclopropanecarboxylate (3f)

E isomer: yellow liquid (17.9 mg, 10%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (t, *J* = 53.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 9.1 Hz, 1H), 2.36 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.06 (dd, *J* = 9.1, 5.3 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.08 (t, J_{CF} = 25 Hz), 166.53, 134.35, 130.38, 128.81, 128.49, 126.54, 109.27 (t, J_{CF} = 249 Hz), 108.85, 62.34, 37.83, 23.16, 23.02, 13.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.81 (s, 2F), -140.93 (d, *J* = 15.7 Hz, 2F), -153.88 (t, *J* = 21.0 Hz, 1F), -162.16 (dt, *J* = 22.3, 8.2 Hz, 2F). IR (KBr, cm^{-1}): 3478, 2923, 1729, 1645, 1559, 1499, 1364, 1317, 1013, 960, 798, 764, 575.

Z isomer: yellow liquid (17.9 mg, 10%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (t, *J* = 53.4 Hz, 1H), 4.33 – 4.21 (m, 2H), 3.13 (t, *J* = 9.0 Hz, 1H), 2.43 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.05 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.31 – 1.26 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.90 (t, J_{CF} = 25 Hz), 168.17, 146.22 (d, J_{CF} = 248 Hz), 137.49 (d, J_{CF} = 255 Hz), 128.50, 108.85 (t, J_{CF} = 249 Hz), 107.81, 62.67, 37.85, 26.41, 22.28, 13.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.30 – -128.39 (m, 2F), -140.49 – -140.94 (m, 2F), -153.43 (tt, *J* = 20.8, 1.9 Hz, 1F), -161.83 –

-162.10 (m, 2F). IR (KBr, cm^{-1}): 2923, 2856, 1727, 1653, 1502, 1380, 1297, 1142, 1099, 978, 913, 730, 506.

HRMS (EI) for $C_{14}H_8F_7O_3$ $[M]^+$: calcd, 358.0440; found 358.0443.

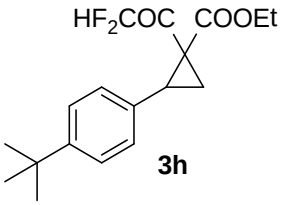


3g

Ethyl 1-(2,2-difluoroacetyl)-2-(*p*-tolyl)cyclopropanecarboxylate (3g)

E isomer: yellow liquid (42.3 mg, 30%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.12 (m, 4H), 6.51 (t, *J* = 53.7 Hz, 1H), 3.96 – 3.76 (m, 2H), 3.40 – 3.35 (m, 1H), 2.45 – 2.40 (m, 1H), 2.31 (s, 3H), 1.97 – 1.86 (m, 1H), 0.95 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.84 (t, J_{CF} = 25 Hz), 166.73, 137.64, 130.49, 129.11, 128.91, 109.38(t, J_{CF} = 249 Hz), 61.53, 41.23, 37.34, 22.85, 21.09, 13.55. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.32 (d, *J* = 296.6 Hz, 1F), -129.49 (d, *J* = 296.5 Hz, 1F). IR (KBr, cm^{-1}): 2924, 1721, 1454, 1377, 1317, 1268, 1171, 1084, 753, 704.

HRMS (EI) for $C_{15}H_{16}F_2O_3$ $[M]^+$: calcd, 282.1068; found 282.1062.



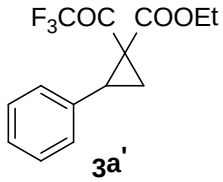
3h

Ethyl 2-(4-(*tert*-butyl)phenyl)-1-(2,2-difluoroacetyl)cyclopropanecarboxylate (3h)

E isomer: yellow liquid (79.5 mg, 49%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.54 (t, *J* = 54.6, 1H), 3.90 – 3.75 (m, 2H), 3.38 (t, *J* = 8.9 Hz, 1H), 2.43 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.92 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.28 (s, 9H), 0.80 – 0.76 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.84 (t, J_{CF} = 25 Hz), 166.86, 151.00, 130.55, 128.95, 125.12, 109.37 (t, J_{CF} = 246 Hz), 61.44, 41.20, 37.46, 34.52, 31.25, 22.90, 13.37. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.40 (d, *J* = 296.4 Hz, 1F), -129.68 (d, *J* = 296.4 Hz, 1F). IR (KBr, cm^{-1}): 2962, 1720, 1515, 1466, 1374, 1320, 1256, 1172, 1076, 1040, 869, 842, 731, 570.

Z isomer: yellow liquid (35.7 mg, 22%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 5.75 (t, *J* = 54.4, 1H), 4.40 – 4.17 (m, 2H), 3.49 (t, *J* = 8.8 Hz, 1H), 2.41 (dd, *J* = 8.8, 5.1 Hz, 1H), 1.80 (dd, *J* = 8.81, 5.1 Hz, 1H), 1.34 – 1.29(m, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.49 (t, J_{CF} = 25 Hz), 169.23, 150.96, 129.22, 128.52, 125.73, 125.34, 109.13 (t, J_{CF} = 250 Hz), 62.09, 41.24, 36.55, 34.49, 31.28, 31.22, 18.27, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.64 (d, *J* = 294.2 Hz), -129.74 (d, *J* = 294.2 Hz). IR (KBr, cm^{-1}): 2963, 1724, 1515, 1466, 1373, 1167, 1096, 974, 919, 836, 719, 570.

HRMS (EI) for $C_{18}H_{22}F_2O_3$ $[M]^+$: calcd, 324.1537; found 324.1536.



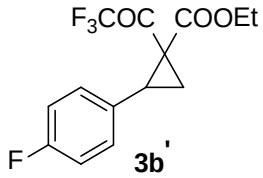
3a'

Ethyl 2-phenyl-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3a')

E isomer: clear liquid (84.4 mg, 59%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.23 (m, 5H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.40 (m, 1H), 2.46 – 2.40 (m, 1H), 1.83 – 1.77 (m, 1H), 0.96 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 186.97 (d, J_{CF} = 36 Hz), 165.12, 133.01, 129.13, 128.27, 128.13, 127.93, 115.63(d, J_{CF} = 289 Hz), 61.99, 40.70, 33.78, 21.99, 13.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.62 (s, 3F). IR (KBr, cm^{-1}): 2928, 1733, 1452, 1377, 1319, 1184, 1015, 857, 700.

Z isomer: clear liquid (17.2 mg, 12%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.10 (m, 5H), 4.43 – 4.17 (m, 2H), 3.53 (t, *J* = 8.6 Hz, 1H), 2.42 (dd, *J* = 8.6, 5.6 Hz, 1H), 1.83 (dd, *J* = 8.6, 5.6 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.82 (d, J_{CF} = 36 Hz), 168.28, 131.60, 128.54, 128.49, 128.16, 114.84 (d, J_{CF} = 290 Hz), 62.49, 41.15, 35.98, 17.65, 13.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.29 (s, 3F). IR (KBr, cm^{-1}): 1732, 1560, 1479, 1365, 1279, 1202, 1020, 969, 798, 733, 699, 576.

HRMS (EI) for $C_{14}H_{13}F_3O_3$ $[M]^+$: calcd, 286.0817; found 286.0820.



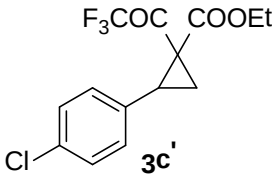
3b'

Ethyl 2-(4-fluorophenyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3b')

E isomer: clear liquid (24.3 mg, 16%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.01 – 3.88 (m, 2H), 3.40 (t, *J* = 9.0 Hz, 1H), 2.38 (dd, *J* = 9.0, 5.2 Hz, 1H), 1.81 (dd, *J* = 9.0, 5.2 Hz, 1H), 1.03 – 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.82 (d, J_{CF} = 36 Hz), 165.02, 162.43 (d, J_{CF} = 246 Hz), 130.79 (d, J_{CCF} = 8 Hz), 128.78, 117.03, 115.25 (d, J_{CCCF} = 22 Hz), 114.13, 62.11, 40.57, 32.81, 21.99, 13.57. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.65 (s, 3F), -113.88 (s, 1F). IR (KBr, cm^{-1}): 2923, 1733, 1605, 1514, 1447, 1375, 1318, 1193, 1012, 842, 737, 548.

Z isomer: clear liquid (18.3 mg, 12%), analytical TLC, petroleum ether : ethyl acetate = 20 : 1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.3 Hz, 2H), 6.90 (t, *J* = 8.3 Hz, 2H), 4.35 – 4.10 (m, 2H), 3.46 – 3.40 (t, *J* = 8.7 Hz, 1H), 2.36 – 2.26 (m, 1H), 1.80 – 1.72 (m, 1H), 1.28 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.73(d, J_{CF} = 36 Hz), 185.18, 168.13, 162.56 (d, J_{CF} = 246 Hz), 130.21(d, J_{CCF} = 8 Hz), 127.42, 127.39, 116.26, 115.59(d, J_{CCCF} = 22 Hz), 113.39, 62.57, 41.09, 35.23, 17.84, 13.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.25 (s, 3F), -113.49 (s, 1F). IR (KBr, cm^{-1}): 2926, 1732, 1606, 1514, 1450, 1376, 1281, 1176, 1101, 1020, 839, 712.

HRMS (EI) for $C_{14}H_{12}F_4O_3$ $[M]^+$: calcd, 304.0723; found 304.0722.

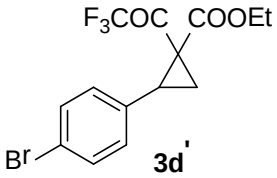


Ethyl 2-(4-chlorophenyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3c')

E isomer: clear liquid (59.3 mg, 37%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.95 – 3.81 (m, 2H), 3.31 (t, *J* = 8.9 Hz, 1H), 2.29 (dd, *J* = 8.9, 5.6 Hz, 1H), 1.72 (dd, *J* = 8.9, 5.6 Hz, 1H), 0.98 -0.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.74 (d, J_{CF} = 36 Hz), 164.94, 133.93, 131.56, 130.46, 128.49, 115.57 (d, J_{CF} = 289.6 Hz), 62.20, 40.55, 32.64, 21.74, 13.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.64 (s, 3F). IR (KBr, cm^{-1}): 3401, 2923, 1733, 1494, 1447, 1377, 1321, 1189, 1095, 1014, 837, 710, 527.

Z isomer: clear liquid (25.6 mg, 16%), analytical TLC, petroleum ether: ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.42 – 4.19 (m, 2H), 3.49 (t, *J* = 8.7 Hz, 1H), 2.37 (dd, *J* = 8.7, 5.5 Hz, 1H), 1.84 (dd, *J* = 8.7, 5.5 Hz, 1H), 1.33 – 1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.62 (d, J_{CF} = 36 Hz), 168.02, 134.23, 130.25, 129.80, 129.46, 128.78, 114.82 (d, J_{CF} = 289 Hz), 62.63, 41.10, 35.15, 17.74, 13.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.19 (s, 3F). IR (KBr, cm^{-1}): 2924, 1733, 1495, 1736, 1277, 1180, 1095, 1020 ,969, 833, 749, 706.

HRMS (EI) for $C_{14}H_{12}ClF_3O_3$ $[M]^+$: calcd, 320.0427; found 320.0421.

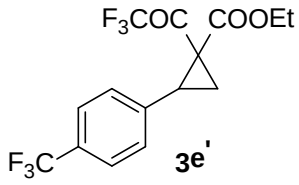


Ethyl 2-(4-bromophenyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3d')

E isomer: yellow liquid (74.8 mg, 41%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 4.06 – 3.91 (m, 2H), 3.36 (t, *J* = 9.0 Hz, 1H), 2.37 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.80 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.06 – 0.99 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.74 (d, J_{CF} = 36 Hz), 164.94, 132.08, 131.45, 131.25, 130.93, 130.79, 122.06, 115.6 (d, J_{CF} = 290 Hz), 62.24, 61.88, 40.50, 32.68, 21.70, 13.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.62 (s, 3F). IR (KBr, cm^{-1}): 3364, 2988, 1732, 1689, 1488, 1445, 1377, 1329, 1185, 1053, 1011, 835, 707, 522.

Z isomer: yellow liquid (31.0 mg, 17%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.41 –4.19 (m, 2H), 3.47 (t, *J* = 8.4 Hz, 1H), 2.37 (dd, *J* = 8.4, 5.5 Hz, 1H), 1.84 (dd, *J* = 8.4, 5.5 Hz, 1H), 1.34 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.97 (d, J_{CF} = 37 Hz), 185.42, 168.01, 131.75, 130.78, 130.11, 129.81, 128.86, 122.35, 114.82 (d, J_{CF} = 290 Hz), 62.64, 41.05, 35.18, 17.70, 13.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.16 (s, 3F). IR (KBr, cm^{-1}): 2923, 1733, 1454, 1375, 1286, 1242, 1174, 1018, 787, 726.

HRMS (EI) for $C_{14}H_{12}BrF_3O_3$ $[M]^+$: calcd, 363.9922; found 363.9924.

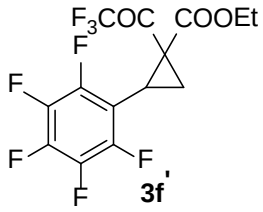


Ethyl 1-(2,2,2-trifluoroacetyl)-2-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (3e')

E isomer: yellow liquid (24.8 mg, 14%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.06 – 3.87 (m, 2H), 3.45 (t, *J* = 9.0 Hz, 1H), 2.42 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.84 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.03- 0.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.60 (d, J_{CF} = 36 Hz), 164.82, 137.15, 130.36, 130.04, 129.63, 129.53, 125.25, 125.21, 122.59, 115.54 (d, J_{CF} = 290 Hz), 62.31, 40.49, 32.35, 21.44, 13.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.71 (s, 3F), -73.63 (s, 3F). IR (KBr, cm^{-1}): 3467, 2923, 1735, 1450, 1376, 1326, 1171, 1126, 1069, 1015, 848, 704.

Z isomer: yellow liquid (26.6 mg, 15%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.43 – 4.13 (m, 2H), 3.55 (t, *J* = 8.8 Hz, 1H), 2.43 (dd, *J* = 8.8, 5.6 Hz, 1H), 1.89 (dd, *J* = 8.8, 5.6 Hz, 1H), 1.35 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.20 (d, J_{CF} = 36 Hz), 167.85, 135.93, 128.86, 125.55, 125.51, 62.78, 41.18, 34.94, 17.68, 13.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80 (s, 3F), -75.25 (s ,3F). IR (KBr, cm^{-1}): 2922, 1735, 1622, 1454, 1378, 1327, 1279, 1173, 1127, 1069, 1019, 970, 844, 705.

HRMS (EI) for $C_{15}H_{12}F_6O_3$ $[M]^+$: calcd, 354.0691; found 354.0685.

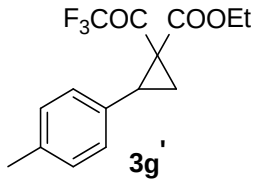


Ethyl 2-(pentafluorophenyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3f')

E isomer: yellow liquid (54.5 mg, 29%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 9.0 Hz, 1H), 2.31 (dd, *J* = 9.0, 5.6 Hz, 1H), 2.03 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.24 – 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.14 (d, J_{CF} = 36 Hz), 165.61, 115.38 (d, J_{CF} = 290 Hz), 108.18, 99.99, 62.79, 37.35, 21.05, 20.77, 13.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (s, 3F), -140.91 (d, *J* = 15.2 Hz, 2F), -153.64 (d, *J* = 20.8 Hz, 1F), -161.25 – -162.58 (m, 2F). IR (KBr, cm^{-1}): 3487, 1737, 1651, 1559, 1500, 1429, 1364, 1321, 1199, 1016, 961, 798, 716, 573.

Z isomer: yellow liquid (54.5 mg, 29%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 – 4.17 (m, 2H), 3.15 (t, *J* = 8.9 Hz, 1H), 2.46 (dd, *J* = 8.9, 5.6 Hz, 1H), 1.98 (dd, *J* = 8.9, 5.6 Hz, 1H), 1.31– 1.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.27 (d, J_{CF} = 37 Hz), 167.32, 115.07 (d, J_{CF} = 290 Hz), 109.41, 107.61, 63.06, 37.61, 24.76, 20.32, 13.71. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.30 (t, *J* = 3.7 Hz, 3F), -140.84 (d, *J* = 20.0 Hz, 2F), -152.88 (t, *J* = 20.9 Hz, 1F), -161.53 (dt, *J* = 20.9, 10.5 Hz, 2F). IR (KBr, cm^{-1}): 2925, 1737, 1658, 1501, 1452, 1382, 1284, 1187 ,1097, 1012, 969, 847, 802, 713.

HRMS (EI) for $C_{14}H_8F_8O_3$ $[M]^+$: calcd, 376.0346; found 376.0344.



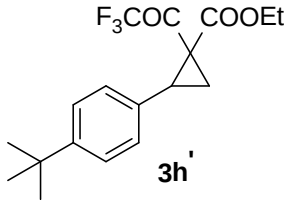
3g'

Ethyl 2-(*p*-tolyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3g')

E isomer: yellow liquid (54.0 mg, 36%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 3.93 – 3.80 (m, 2H), 3.33 (t, *J* = 8.8 Hz, 1H), 2.33 (dd, *J* = 8.8, 5.0 Hz, 1H), 2.24 (s, 3H), 1.71 (dd, *J* = 8.8, 5.0 Hz, 1H), 0.96 – 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.98 (d, J_{CF} = 36 Hz), 165.19, 137.69, 129.90, 128.99, 128.97, 115.64 (d, J_{CF} = 290 Hz), 61.95, 40.71, 33.81, 22.14, 21.10, 13.55. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.61 (s, 3F). IR (KBr, cm^{-1}): 2926, 1733, 1518, 1448, 1377, 1318, 1185, 1017, 825, 713, 549.

Z isomer: yellow liquid (27.0 mg, 18%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 4.34 – 4.11 (m, 2H), 3.43 (t, *J* = 8.7 Hz, 1H), 2.34 (dd, *J* = 8.7, 5.7 Hz, 1H), 2.22 (s, 3H), 1.74 (dd, *J* = 8.7, 5.7 Hz, 1H), 1.27 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.87 (d, J_{CF} = 37 Hz), 168.36, 137.98, 133.22, 129.84, 129.41, 129.23, 128.48, 128.44, 128.39, 126.30, 114.86 (d, J_{CF} = 290 Hz), 62.41, 36.02, 21.05, 17.79, 13.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.22 (s, 3F). IR (KBr, cm^{-1}): 2920, 1730, 1520, 1380, 1180, 820, 550.

HRMS (EI) for $C_{15}H_{15}F_3O_3$ $[M]^+$: calcd, 300.0973; found 300.0969.

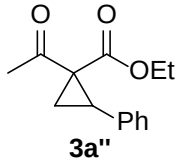


3h'

Ethyl 2-(4-(*tert*-butyl)phenyl)-1-(2,2,2-trifluoroacetyl)cyclopropanecarboxylate (3h')

E isomer: clear liquid (71.8 mg, 42%), analytical TLC, petroleum ether : ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 3.42 (t, *J* = 8.4 Hz, 1H), 2.42 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.80 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.28 (s, 9H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.99 (d, J_{CF} = 35 Hz), 165.21, 151.01, 129.87, 128.96, 128.78, 125.17, 125.00, 115.64 (d, J_{CF} = 289 Hz), 61.88, 40.89, 34.52, 33.98, 31.24, 22.26, 13.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.63 (s, 3F). IR (KBr, cm^{-1}): 3337, 2964, 1733, 1515, 1461, 1376, 1322, 1187, 1016, 841, 710, 568.

HRMS (EI) for $C_{18}H_{21}F_3O_3$ $[M]^+$: calcd, 342.1443; found 342.1438.



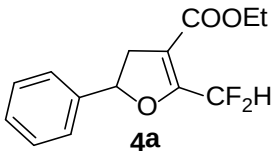
3a''

Ethyl 1-acetyl-2-phenylcyclopropane-1-carboxylate (3a'')

E/Z mixture (E/Z = 2.8/1): clear liquid, analytical TLC, petroleum ether : ethyl acetate = 30:1, R_f = 0.5.

E isomer：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.07 (m, 5H), 3.93 – 3.69 (m, 2H), 3.28(m , 1H), 2.45 (s, 1H), 2.23 (dd, *J* = 8.1, 4.6 Hz, 1H), 1.72 (dd, *J* = 8.1, 4.6 Hz, 1H), 0.85 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.31, 168.18, 134.90, 128.89, 128.36, 128.07, 127.34, 61.07, 44.56, 35.33, 29.55, 21.42, 13.61.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.05 (m, 5H), 4.40 – 4.13 (m, 2H), 3.28 – 3.22 (m, 1H), 2.29 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.94 (s, 1H), 1.68 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.01, 170.47, 133.85, 128.89, 128.36, 128.07, 127.34, 61.61, 44.39, 34.40, 30.22, 17.75, 14.12.



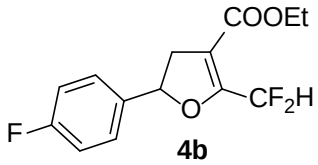
4a

Ethyl 2-(difluoromethyl)-5-phenyl-4,5-dihydrofuran-3-carboxylate (4a)

Colorless liquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 5H), 7.13 (t, *J* = 50.9 Hz, 1H), 5.85 – 5.73 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.38 (m, 1H), 3.06 – 2.95 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.59, 157.16 (d, J_{CF} = 22 Hz), 140.40, 128.83, 128.51, 125.45, 108.99, 106.83 (t, J_{CF} = 236 Hz), 84.40, 60.77, 38.04, 14.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.77 (d, *J* = 328.6 Hz, 1F), -125.85 (d, *J* = 328.6 Hz, 1F). IR (KBr, cm^{-1}): 3676, 2981, 1706, 1669, 1454, 1369, 1313, 1139, 1096, 1041, 918, 845, 743, 698. IR (KBr, cm^{-1}): 2926, 2360, 1707, 1457, 1320, 1233, 1045, 925, 594.

HRMS (EI) for $C_{14}H_{14}F_2O_3$ $[M]^+$: calcd, 268.0911; found 268.0910.



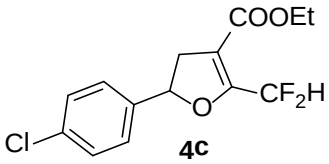
4b

Ethyl 2-(difluoromethyl)-5-(4-fluorophenyl)-4,5-dihydrofuran-3-carboxylate (4b)

Colorless liquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.12 (t, *J* = 52.6 Hz, 1H), 7.10 – 7.07 (m, 2H), 5.86 – 5.74 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.56 – 3.33 (m, 1H), 3.09 – 2.93 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.73 (d, J_{CF} = 51 Hz), 161.52, 157.10 (t, J_{CF} = 22 Hz), 136.16 (d, J_{CCF} = 6 Hz), 127.39 (d, J_{CCF} = 8 Hz), 115.90, 115.68, 108.99 (t, J_{CCF} = 7 Hz), 106.75 (t, J_{CF} = 236 Hz), 83.79, 60.84, 38.05, 14.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.26 (s, 1F), -124.78 (d, *J* = 329.0 Hz, 1F), -125.91 (d, *J* = 329.0 Hz, 1F). IR (KBr, cm^{-1}): 3482, 2924, 1706, 1667, 1559, 1510, 1479, 1427, 1365, 1232, 1141, 1044, 972, 836, 798, 763, 583 IR (KBr, cm^{-1}): 2926, 2358, 1708, 1606, 1511, 1382, 1232, 1045, 826, 593.

HRMS (EI) for $C_{14}H_{13}F_3O_3$ $[M]^+$: calcd, 286.0817; found 286.0821.



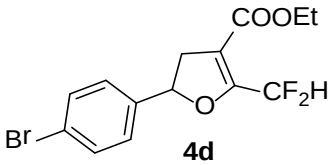
4c

Ethyl 5-(4-chlorophenyl)-2-(difluoromethyl)-4,5-dihydrofuran-3-carboxylate (4c)

Colorless liquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 712 (t , *J* = 52.8 Hz, 1H), 5.80 – 5.73 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.40 (m, 1H), 3.05 – 2.87 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 157.09, 138.89, 134.39, 129.04, 126.84, 106.73 (t, J_{CF} = 236 Hz), 83.56, 60.86, 38.03, 14.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.77 (d, *J* = 329.2 Hz, 1F), -125.91 (d, *J* = 329.3 Hz, 1F). IR (KBr, cm^{-1}): 2927, 2357, 1708, 1491, 1457, 1319, 1233, 1138, 1045, 751.

MS (EI) for $C_{14}H_{13}ClF_2O_3$ $[M]^+$: calcd, 302.05; found 302.26.



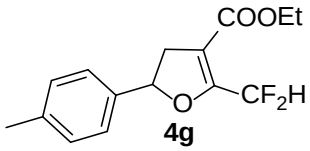
4d

Ethyl 5-(4-bromophenyl)-2-(difluoromethyl)-4,5-dihydrofuran-3-carboxylate (4d)

Colorless liquid, yield > 99%; analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 52.8 Hz, 1H), 5.80 – 5.70 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.51. – 3.39 (m, 1H), 3.03 – 2.90 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 157.07, 139.43, 131.99, 128.95, 127.13, 122.48, 109.10, 106.74 (t, J_{CF} = 236 Hz), 83.56, 60.87, 37.99, 14.20. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.75 (d, *J* = 329.2 Hz, 1F), -125.90 (d, *J* = 329.1 Hz, 1F). IR (KBr, cm^{-1}): 2980, 2358, 1707, 1485, 1381, 1233, 1137, 977, 763.

MS (EI) for $C_{14}H_{13}BrF_2O_3$ $[M]^+$: calcd, 346.00; found 346.10.



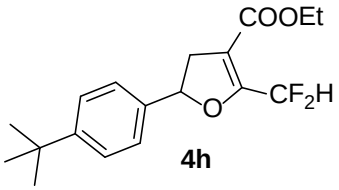
4g

Ethyl 2-(difluoromethyl)-5-(*p*-tolyl)-4,5-dihydrofuran-3-carboxylate (4g)

Yellow liquid (42.3 mg, 30%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 52.9 Hz, 1H), 5.80 – 5.73 (m, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.47 – 3.35 (m, 1H), 3.07 – 2.95 (m, 1H), 2.35 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.66, 157.29 (t, J_{CF} = 22 Hz), 138.42, 137.35, 129.47, 125.55, 108.96 (t, J_{CCF} = 6 Hz), 106.84 (t, J_{CF} = 236 Hz), 84.53, 60.73, 37.91, 21.15, 14.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.79 (d, *J* = 328.6 Hz, 1F), -125.84 (d, *J* = 328.5 Hz, 1F). IR (KBr, cm^{-1}): 2926, 1705, 1667, 1477, 1375, 1316, 1233, 1138, 1044, 967, 922, 820, 762, 585.

HRMS (EI) for $C_{15}H_{16}F_2O_3$ $[M]^+$: calcd, 282.1068; found 282.1062.



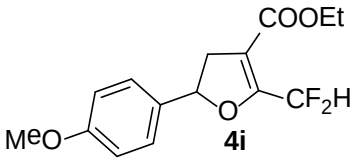
4h

Ethyl 5-(4-(*tert*-butyl)phenyl)-2-(difluoromethyl)-4,5-dihydrofuran-3-carboxylate (4h)

Colorless liquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 52.9 Hz, 1H), 5.85 – 5.70 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.35 (m, 1H), 3.10 – 2.97 (m, 1H), 1.38 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.67, 151.67, 137.30, 125.74, 125.38, 106.85 (t, J_{CF} = 236 Hz), 84.44, 60.71, 37.81, 34.62, 31.28, 14.23. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.78 (d, *J* = 328.5 Hz, 1F), -125.84 (d, *J* = 328.7 Hz, 1F). IR (KBr, cm^{-1}): 2963, 2361, 1707, 1667, 1463, 1379, 1233, 1046, 837.

MS (EI) for $C_{18}H_{22}F_2O_3$ $[M]^+$: calcd, 324.15; found 324.20.



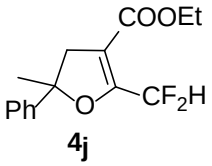
4i

Ethyl 2-(difluoromethyl)-5-(4-methoxyphenyl)-4,5-dihydrofuran-3-carboxylate (4i)

Yellow liquid (37.3 mg, 25%); analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 52.9 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 5.77 – 5.70 (m, 1H), 4.23 (q, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 3.45 – 3.34 (m, 1H), 3.07 – 2.96 (m, 1H), 1.30 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.67, 159.89, 157.23 (t, J_{CF} = 22 Hz), 132.28, 127.18, 114.21, 108.95(t, J_{CCF} = 7 Hz), 106.83 (t, J_{CF} = 236 Hz), 84.56, 60.72, 55.32, 37.77, 14.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.79 (d, *J* = 328.5 Hz, 1F), -125.84 (d, *J* = 328.4 Hz, 1F). IR (KBr, cm^{-1}): 2921, 1703, 1665, 1513, 1456, 1377, 1305, 1232, 1173, 1101, 915, 830 ,728, 559.

HRMS (EI) for $C_{15}H_{16}F_2O_4$ $[M]^+$: calcd, 298.1017; found 298.1014.



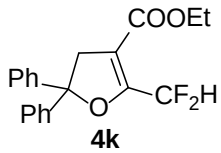
4j

Ethyl 2-(difluoromethyl)-5-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (4j)

Yellow liquid (43.8 mg, 31%); analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.32 – 7.26 (m, 1H), 7.05 (t, *J* = 53.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.26 – 3.11 (m, 2H), 1.762 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.75, 156.28 (t, J_{CF} = 22 Hz), 145.33, 128.59, 128.19, 127.57, 126.96, 124.05, 108.48 (t, J_{CCF} = 6 Hz), 106.91 (t, J_{CF} = 236 Hz), 90.81, 60.66, 44.31, 29.36, 14.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.32 (s, 2F). IR (KBr, cm^{-1}): 2975, 1707, 1668, 1448, 1375, 1310, 1242, 1133, 1041, 918, 764, 699, 560.

HRMS (EI) for $C_{15}H_{16}F_2O_3$ $[M]^+$: calcd, 282.1068; found 282.1060.



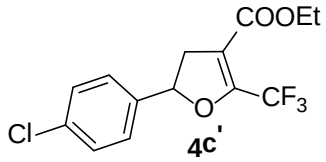
4k

Ethyl 2-(difluoromethyl)-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (4k)

Yellow liquid (80.9 mg, 47%); analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 4H), 7.26 (t, *J* = 7.5 Hz, 4H), 7.31 – 7.25 (m, 2H), 7.07 (t, *J* = 52.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.73 – 3.66 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.46, 156.04 (t, J_{CF} = 21 Hz), 144.08, 132.41, 130.07, 128.53, 128.29, 127.90, 125.51, 108.94 (t, J_{CCF} = 7 Hz), 106.90 (t, J_{CF} = 236 Hz), 93.52, 60.81, 44.16, 14.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.05 (s, 2F). IR (KBr, cm^{-1}): 2922, 1707, 1670, 1449, 1377, 1311, 1236, 1142, 1049, 954, 851, 750, 698, 612.

HRMS (EI) for $C_{20}H_{18}F_2O_3$ $[M]^+$: calcd, 344.1224; found 344.1218.



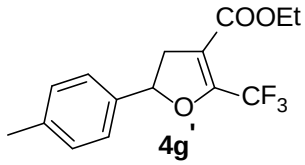
4c'

Ethyl 5-(4-chlorophenyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4c')

Colorless liquidliquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 5.78 – 5.71 (m, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.57 – 3.48 (m, 1H), 3.20 – 2.97 (m, 1H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.20, 138.12, 134.69, 129.12, 127.00, 108.94, 83.45, 61.08, 39.19, 13.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.82 (s, 3F). IR (KBr, cm^{-1}): 2929, 2359, 1720, 1665, 1490, 1456, 1376, 1244, 1160, 829.

MS (EI) for $C_{14}H_{12}ClF_3O_3$ $[M]^+$: calcd, 320.04; found 320.05.



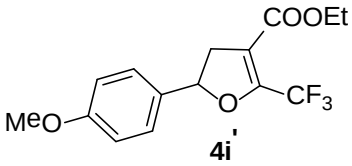
4g'

Ethyl 5-(*p*-tolyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4g')

Colorless liquidliquid, yield > 99%; analytical TLC, *n*-hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 5.76 – 5.69 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.49 - 3.47 (mz, 1H), 3.15 – 3.11 (m, 1H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz,3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.44, 138.76, 136.60, 129.55, 125.82, 125.74, 125.57, 116.85, 108.84, 84.41, 60.94, 39.06, 31.26, 21.16, 13.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.82 (s, 3F). IR (KBr, cm^{-1}): 2968, 2358, 1721, 1663, 1515, 1376, 1244, 1114, 907, 754.

MS (EI) for $C_{15}H_{15}F_3O_3$ $[M]^+$: calcd, 300.10; found 300.14.



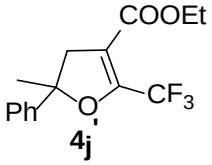
4i'

Ethyl 5-(4-methoxyphenyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4i')

Yellow liquid (31.6 mg, 20%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 2H), 5.77 – 5.68 (m, 1H), 4.24 (q, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 3.55 – 3.38 (m, 1H), 3.23 – 3.08 (m, 1H), 1.30 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.47, 160.09, 150.81 (d, J_{CF} = 39 Hz), 131.48, 127.40, 118.18 (d, J_{CF} = 271 Hz), 114.28, 108.80, 84.45, 60.94, 55.34, 38.90, 13.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.83 (s, 3F). IR (KBr, cm^{-1}): 3857, 3747, 3621, 3312, 2918, 2848, 1721, 1662, 1516, 1460, 1376, 1303, 1245, 1163, 1112, 1028, 830, 727.

HRMS (EI) for $C_{15}H_{15}F_3O_4$ $[M]^+$: calcd, 316.0922; found 316.0927.



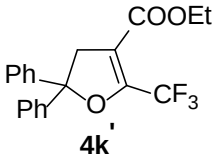
4j'

Ethyl 5-methyl-5-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4j')

Yellow liquid (24.0 mg, 16%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.17 (m, 2H), 1.76 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.52, 149.85 (d, J_{CF} = 40 Hz), 144.76, 128.66, 127.76, 124.01, 118.23 (d, J_{CF} = 271 Hz), 108.27, 90.61, 60.89, 45.33, 29.32, 13.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.95 (s, 3F). IR (KBr, cm^{-1}): 2982, 1720, 1663, 1448, 1371, 1323, 1248, 1181, 1057, 1026, 989, 913, 837, 766, 731, 700, 558.

HRMS (EI) for $C_{15}H_{15}F_3O_3$ $[M]^+$: calcd, 300.0973; found 300.0974.



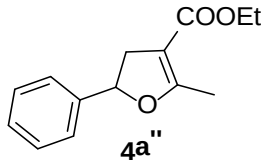
4k'

Ethyl 5,5-diphenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4k')

Yellow liquid (52.5 mg, 29%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 10H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.80 (d, *J* = 2.2 Hz, 2H), 1.29 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.24, 149.61(d, J_{CF} = 40 Hz), 143.62, 128.61, 128.06, 126.16, 125.42, 117.61 (d, J_{CF} = 293 Hz), 108.78, 93.28, 61.02, 45.22, 29.70, 13.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.70 (s, 3F). IR (KBr, cm^{-1}): 2923, 1719, 1666, 1450, 1370, 1322, 1248, 1172, 1043, 913, 835, 750, 699, 619.

HRMS (EI) for $C_{14}H_9F_7O_3$ $[M]^+$: calcd, 358.0440; found 358.0443.

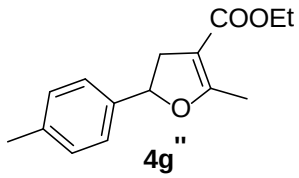


4a''

Ethyl 2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (4a'')

Yellow liquid (36.0 mg, 31%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 5.65 – 5.53 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.37 – 3.27 (m, 1H), 2.96 – 2.86 (m, 1H), 2.28 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 166.05, 141.60, 128.67, 128.12, 125.67, 101.76, 83.11, 59.52, 38.02, 14.45, 14.09.

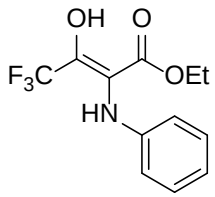


4g''

Ethyl 2-methyl-5-(*p*-tolyl)-4,5-dihydrofuran-3-carboxylate (4g'')

Yellow liquid (65.0 mg, 53%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.59 – 5.48 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.35 – 3.24 (m, 1H), 2.95 – 2.85 (m, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.65, 166.07, 138.58, 137.93, 129.33, 125.76, 101.76, 83.16, 59.47, 37.90, 21.14, 14.47, 14.11.

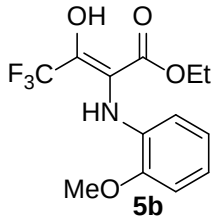


5a

Ethyl 4,4,4-trifluoro-3-hydroxy-2-(phenylamino)but-2-enoate (5a)

Yellow liquid (19.3 mg, 28%); analytical TLC, *n*-Hexane : dichloromethane = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 5.34 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.68, 147.16 (q, J_{CF} = 31.6 Hz), 138.37, 138.13, 129.28, 128.95, 126.63, 126.01, 125.99, 125.71, 120.24 (q, J_{CF} = 278.8 Hz), 118.53, 88.55 (q, J_{CF} = 5.4 Hz), 60.13, 14.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.33.

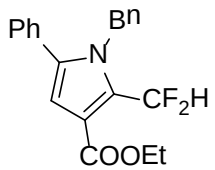


5b

Ethyl 4,4,4-trifluoro-3-hydroxy-2-((2-methoxyphenyl)amino)but-2-enoate (5b)

Yellow liquid (23.6 mg, 31%); analytical TLC, *n*-Hexane : dichloromethane = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.21 (t, *J* = 7.3 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 2H), 5.38 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47, 153.79, 147.19 (q, J_{CF} = 31.5 Hz), 127.52, 127.23, 126.22, 126.20, 126.17, 126.14, 120.33, 120.27 (q, J_{CF} = 278.4 Hz),117.31, 110.93, 88.96 (q, J_{CF} = 5.4 Hz), 60.02, 55.72, 14.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.42.



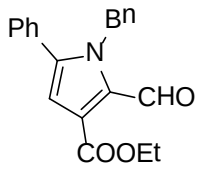
6a

Ethyl 1-benzyl-2-(difluoromethyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (6a)

Yellow liquid (70.0 mg, 40%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.6.

Unstable with the silica, easily turned to **6a'**, mixed with **6a'**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 53.0 Hz, 1H), 7.15 – 7.30 (m, 8H), 6.82 – 6.79 (m, 2H), 5.38 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.06, 138.14, 137.87, 137.78, 131.26, 129.58, 128.70, 128.44, 128.38, 128.34, 127.13, 125.79, 117.22, 111.15, 109.34 (t, J_{CF} = 231.3 Hz), 60.43, 49.74, 14.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.42 (s, 2F). IR (KBr, cm^{-1}): 3741, 2925, 2360,1709, 1525, 1463, 1248, 1199, 1022, 855.

MS (EI) for $C_{21}H_{19}F_2NO_2$ $[M]^+$: calcd, 355.14; found 355.22.



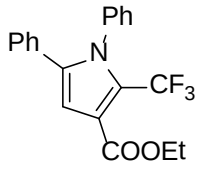
6a'

Ethyl 1-benzyl-2-formyl-5-phenyl-1*H*-pyrrole-3-carboxylate (6a')

Yellow liquid (83.0 mg, 50%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.40 – 7.15 (m, 8H), 6.87 – 6.83 (m 2H), 6.81 (s, 1H), 5.65 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.49, 163.64, 142.12, 137.87, 131.66, 130.45, 129.49, 129.11, 128.70, 128.55, 127.23, 125.93, 125.39, 113.49, 60.85, 49.95, 14.35. IR (KBr, cm^{-1}): 3853, 3740, 2923, 2358, 1709, 1659, 1549, 1459, 1381, 1247, 1189, 1033, 767, 695.

MS (EI) for $C_{21}H_{19}NO_3$ $[M]^+$: calcd, 333.14; found 333.23.



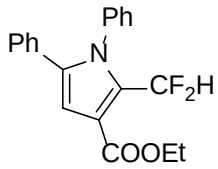
6b

Ethyl 1,5-diphenyl-2-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate (6b)

Yellow liquid (143.0 mg, 80%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.21 – 7.19 (m, 5H), 7.07 – 7.00 (m, 2H), 6.79 (s, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.60, 138.03, 137.54, 130.83, 129.11, 129.03, 128.87, 128.36, 128.13, 127.84, 111.56, 60.96, 14.15. ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.98 (s, 3F). IR (KBr, cm^{-1}): 3066, 2983, 2928, 2359, 1727, 1588, 1463, 1386, 1233, 1170, 1034, 768.

MS (EI) for $C_{20}H_{16}NF_3O_2$ $[M]^+$: calcd, 359.11; found 359.23.



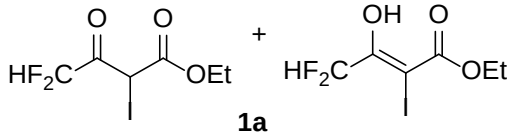
6c

Ethyl 2-(difluoromethyl)-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (6c)

Yellow liquid (162.0 mg, 95%); analytical TLC, *n*-Hexane : ethyl acetate = 20:1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (q, *J* = 52.9 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 7.12 – 7.07 (m, 2H), 6.84 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.04, 138.01, 137.80, 131.06, 129.77, 128.87, 128.79, 128.67, 128.12, 127.61, 117.69, 110.56(t, J_{CF} = 5.4 Hz), 108.87 (t, J_{CF} = 232.3 Hz), 60.54, 14.37. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.32 (s, 2F). IR (KBr, cm^{-1}): 3741, 3066, 2978, 2927, 2360, 1711, 1570, 1489, 1226, 1099, 1037, 766, 697.

MS (EI) for $C_{20}H_{17}NF_2O_2$ $[M]^+$: calcd, 341.12; found 341.19.

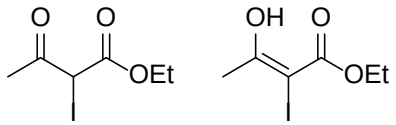


1a

Ethyl 4,4-difluoro-3-oxobutanoate and Ethyl 4,4-difluoro-3-hydroxy-2-iodobut-2-enoate (1a)

Yellow liquid; analytical TLC, *n*-Hexane : ethyl acetate =4:1, R_f = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) 6.14 (t, *J* = 53.2 Hz, 1H), 5.94 (t, *J* = 53.2 Hz, 1H), 5.47 (s, 1H), 5.05 (br, 1H), 4.57 (s, 1H), 4.30 (dd, *J* = 7.1 Hz, 4H), 13.2 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.46, 171.59, 165.31, 115.09, 112.62, 110.26, 110.14, 107.74, 105.22, 99.99, 92.67, 63.78, 63.06, 29.68, 19.02, 18.90, 13.72, 13.52. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.40 (s), -123.86 (d, *J* = 313.8 Hz), -125.93 (d, *J* = 313.9 Hz), -132.96 (d, *J* = 286.4 Hz), -138.48 (d, *J* = 286.4 Hz).



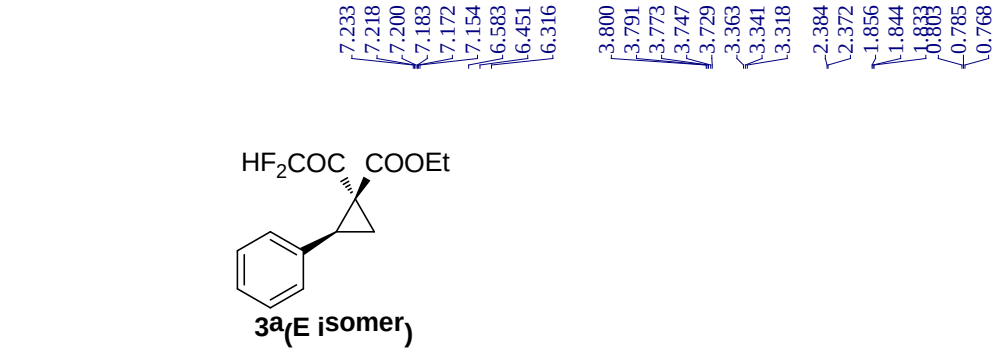
1e

Ethyl 2-iodo-3-oxobutanoate and ethyl 3-hydroxy-2-iodobut-2-enoate (1e)

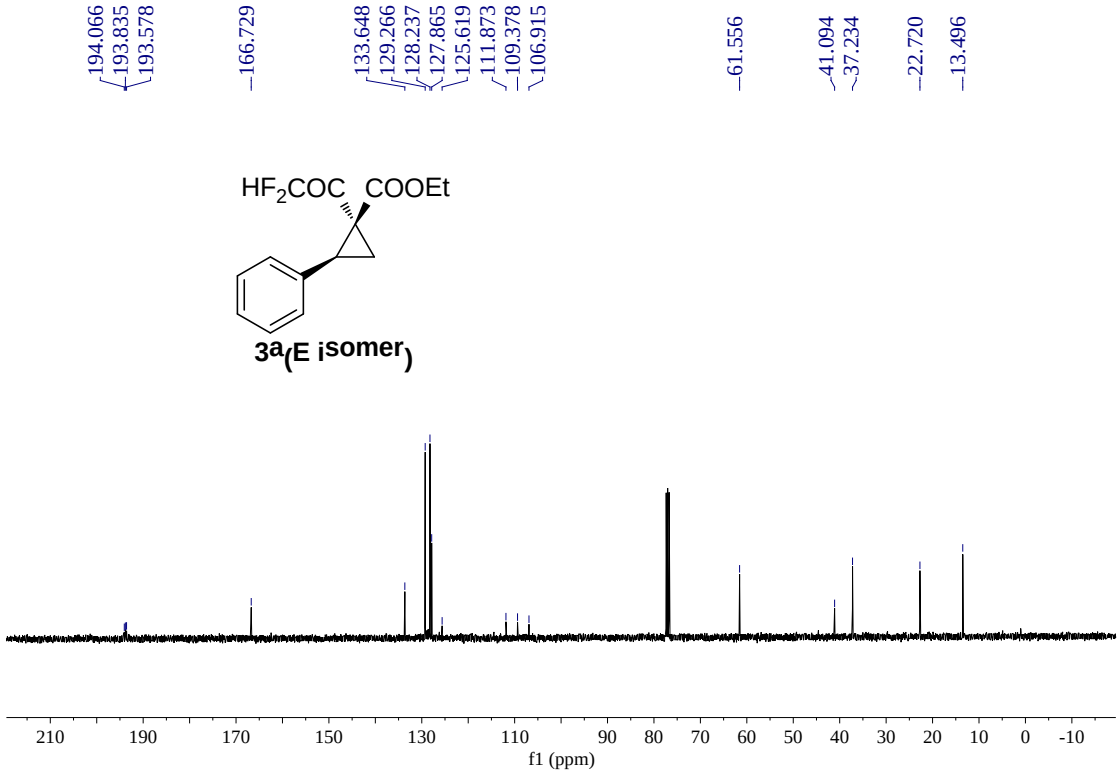
Mixture, yellow liquid, analytical TLC, petroleum ether : ethyl acetate = 20:1, Rf = 0.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.25, 192.25, 166.65, 165.83, 64.72, 63.05, 26.19, 25.65, 21.25, 13.83, 13.56, 5.40.

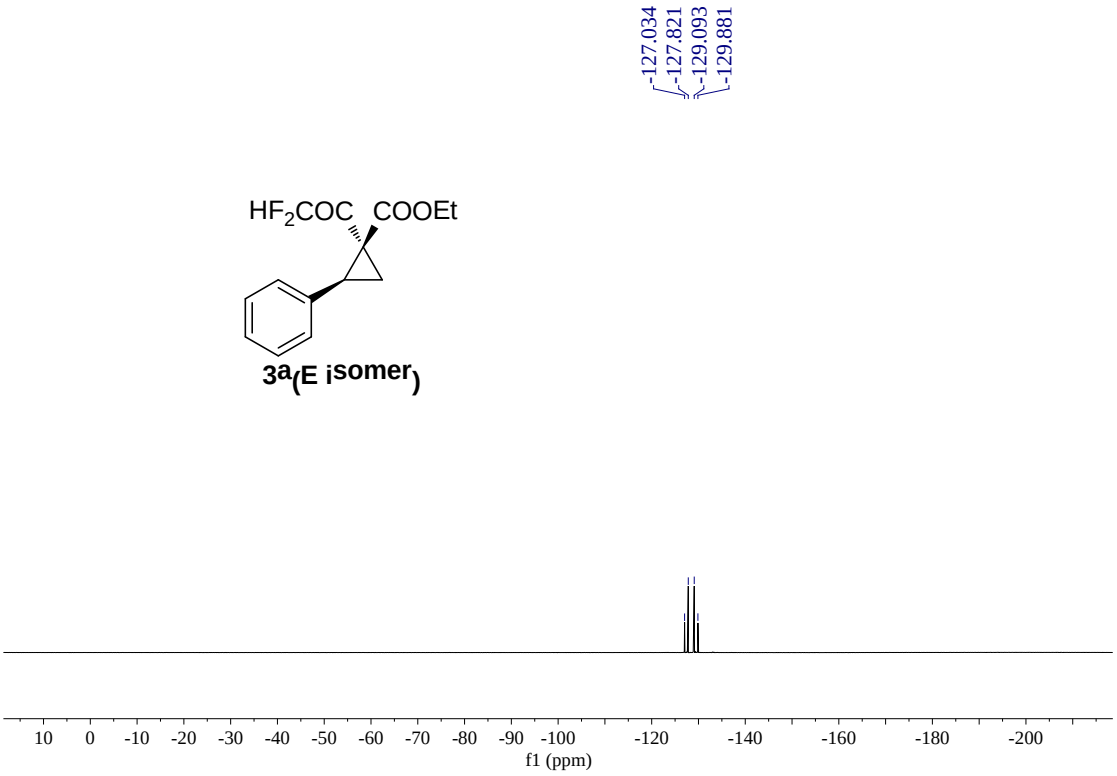
NMR Spectra for Products



^{1}H NMR of *E*-3a in $CDCl_3$

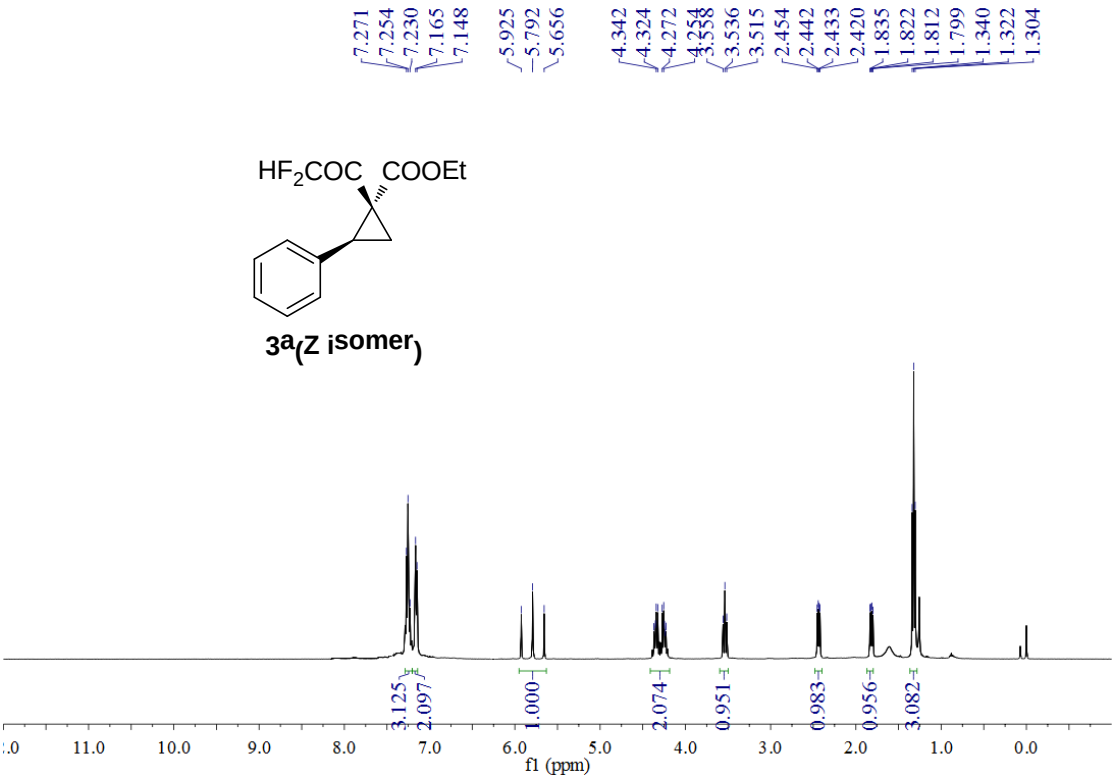


^{13}C NMR of *E*-3a in $CDCl_3$



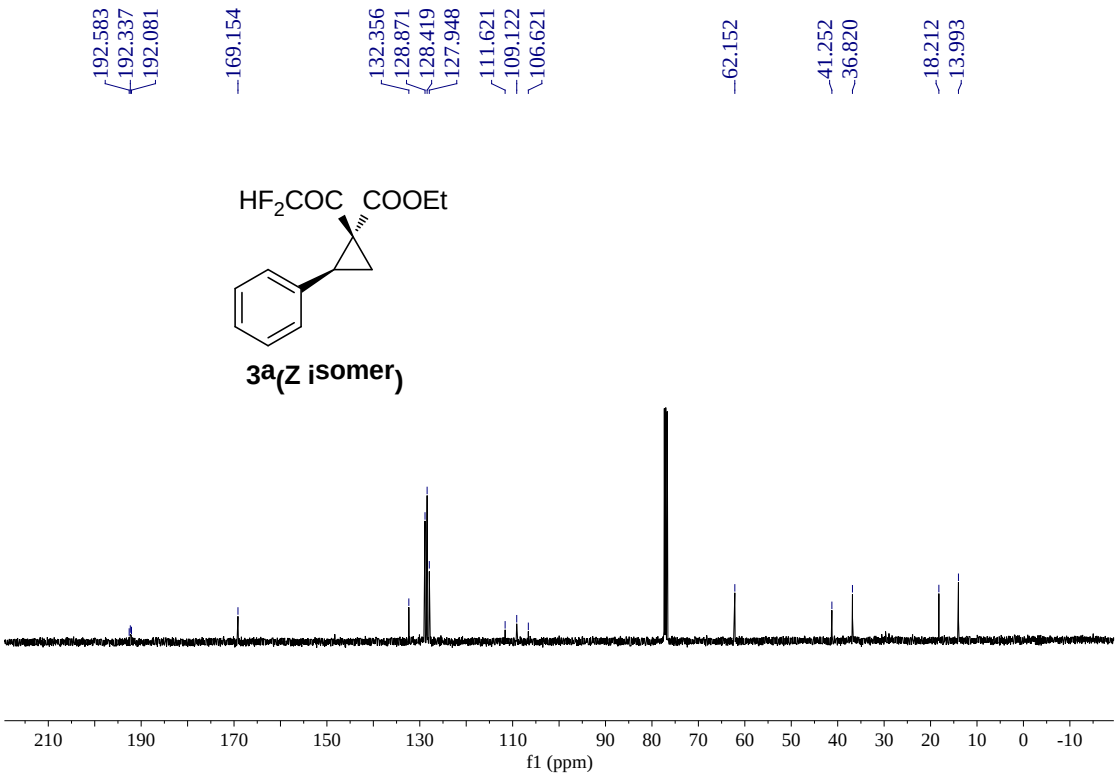
3a(E isomer)

^{19}F NMR of *E*-3a in $CDCl_3$

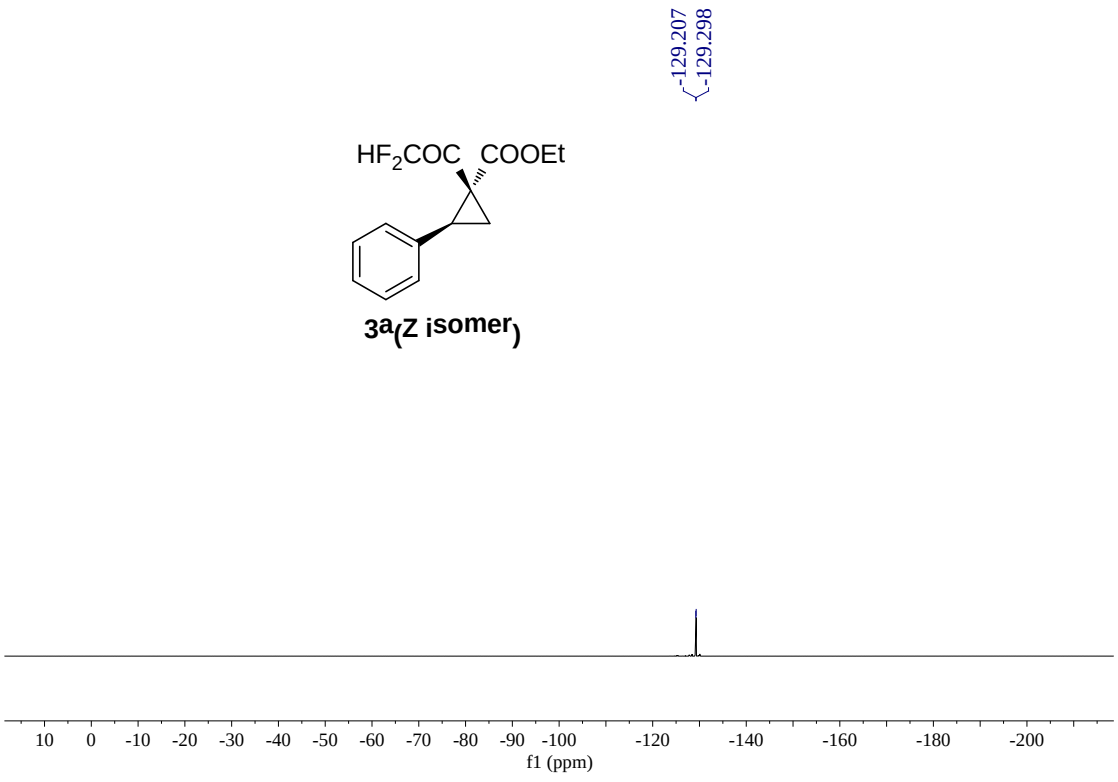


3a(Z isomer)

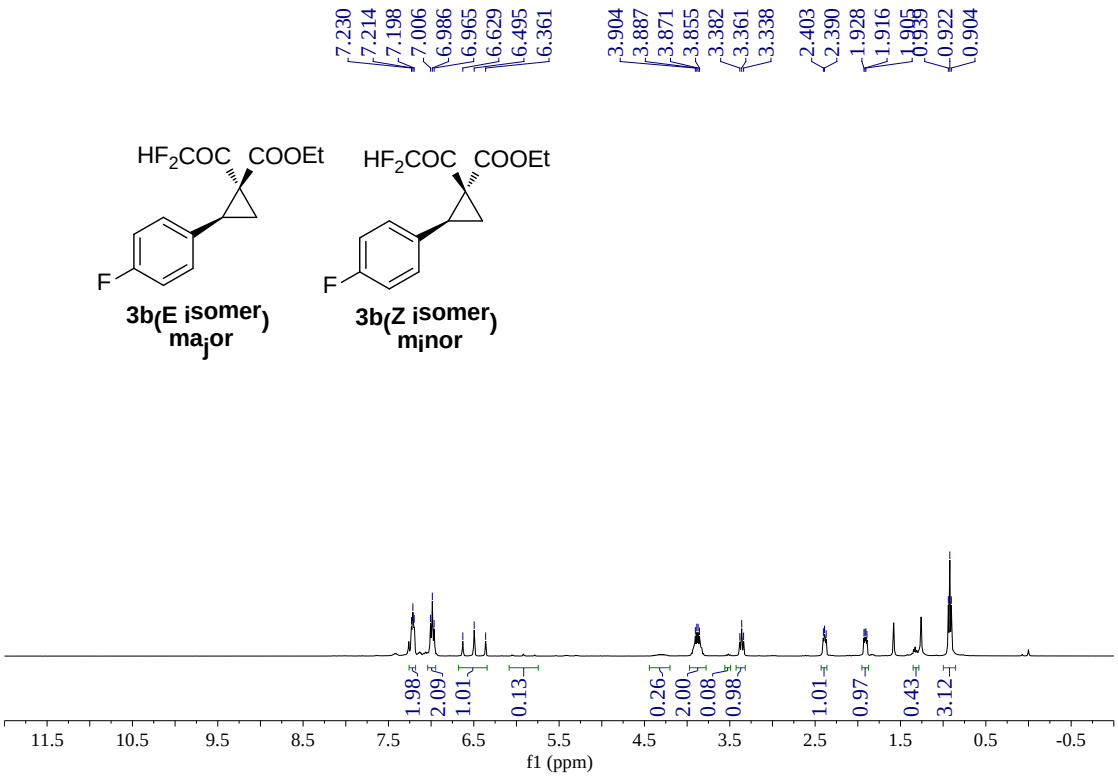
^{1}H NMR of *Z*-3a in $CDCl_3$



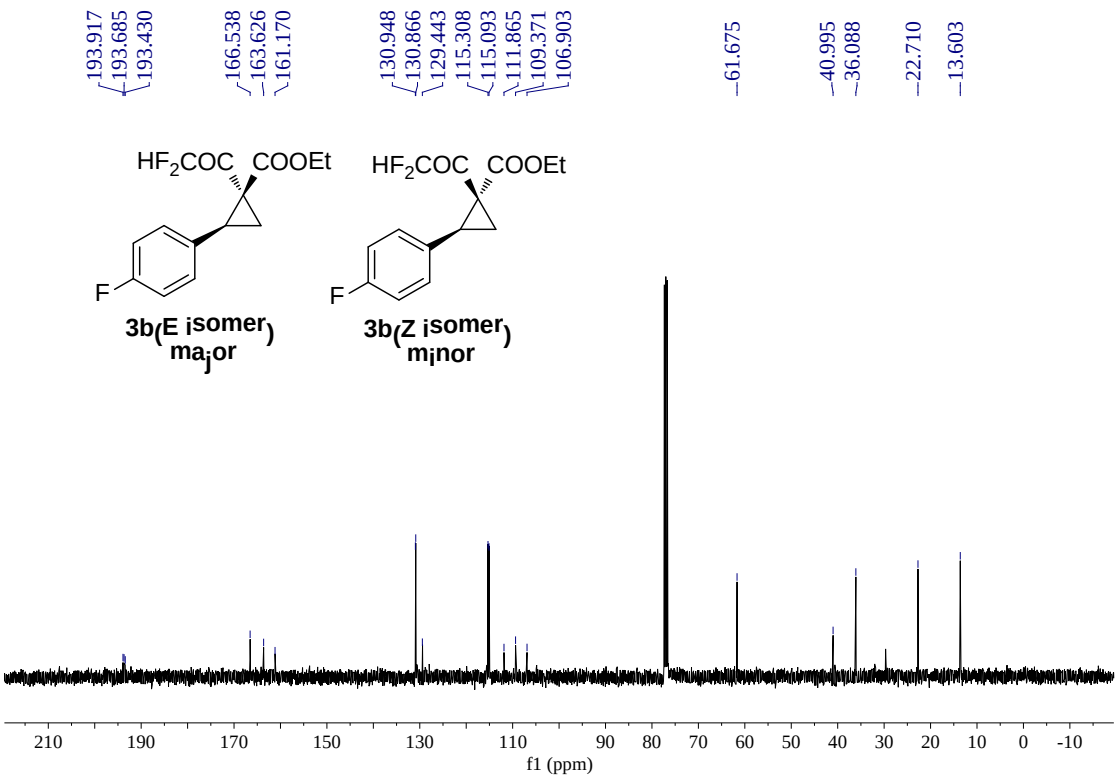
^{13}C NMR of *Z*-3a in $CDCl_3$



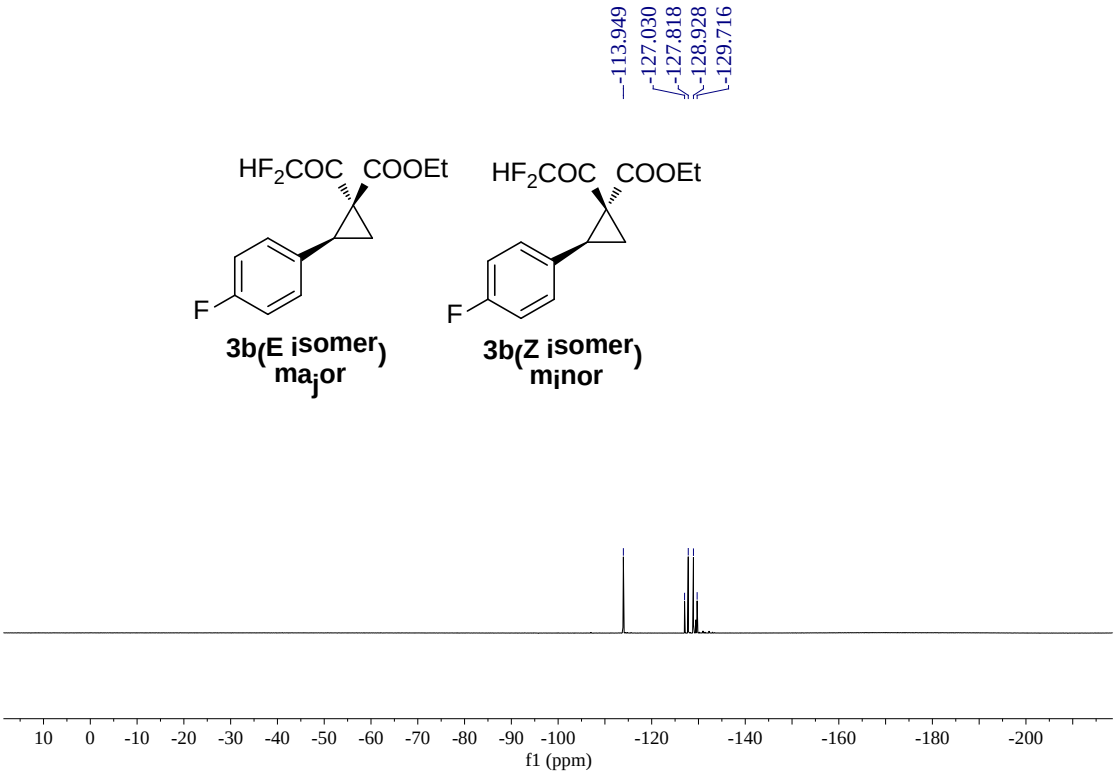
^{19}F NMR of *Z*-3a in $CDCl_3$



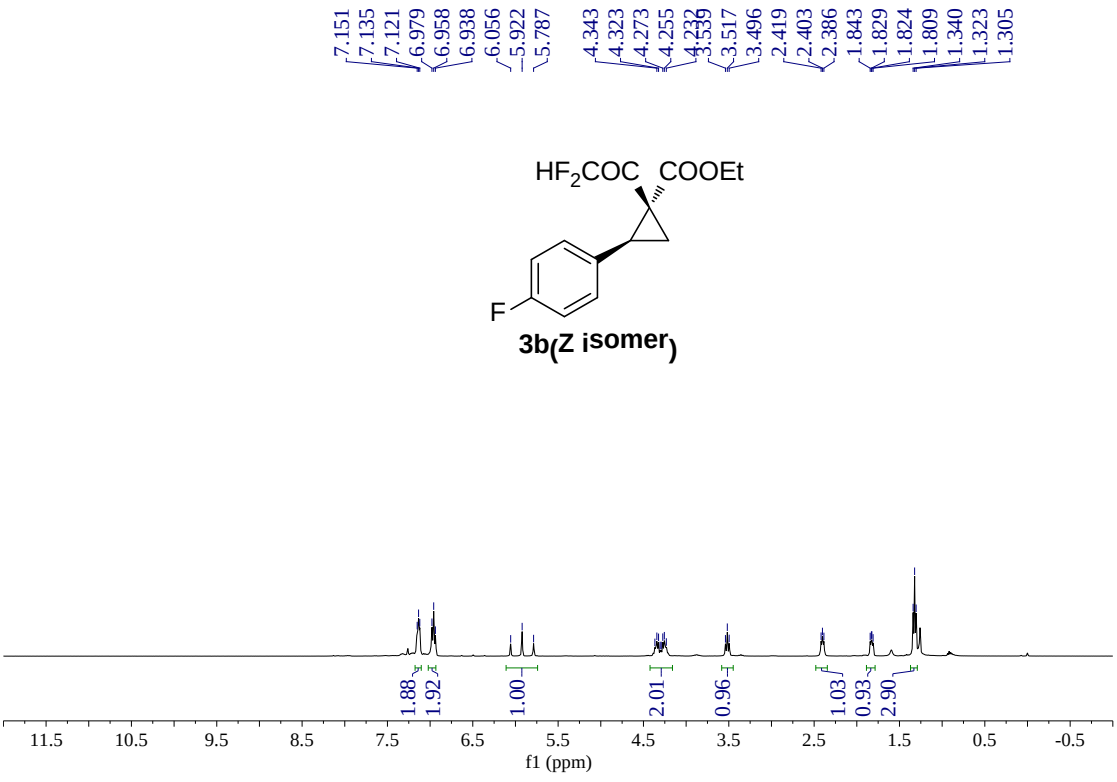
^{1}H NMR of 3b(*E*+*Z*) in $CDCl_3$



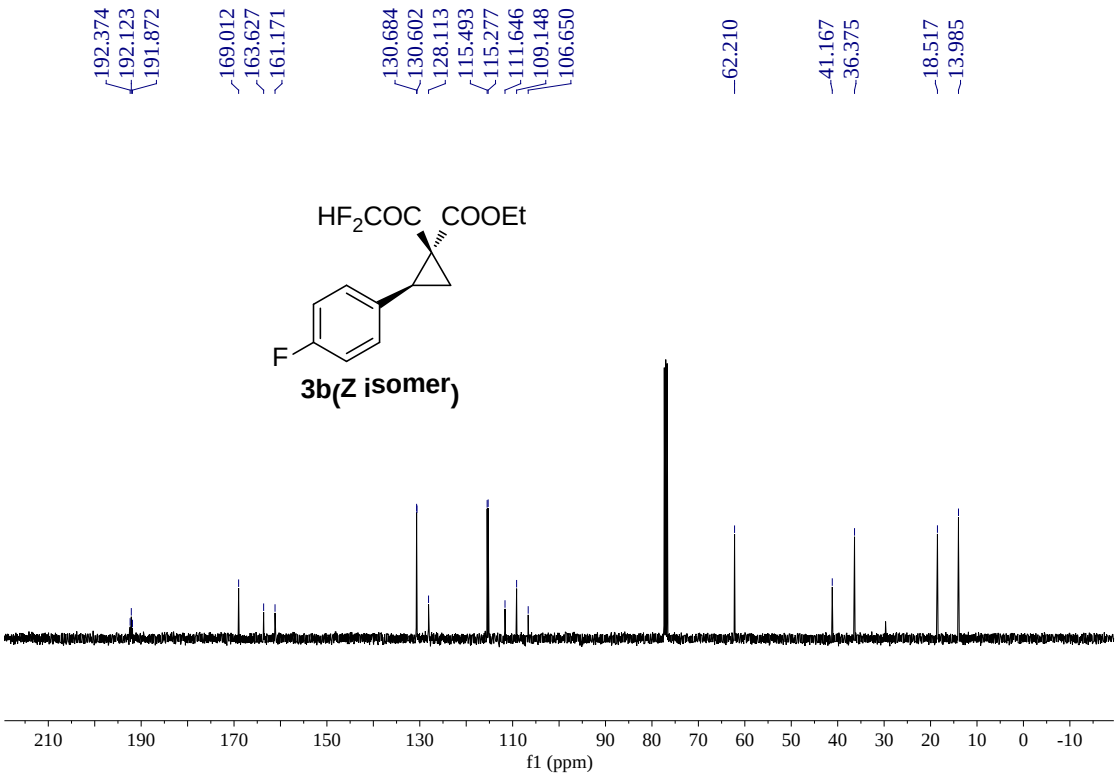
^{13}C NMR of 3b(*E*+*Z*) in $CDCl_3$



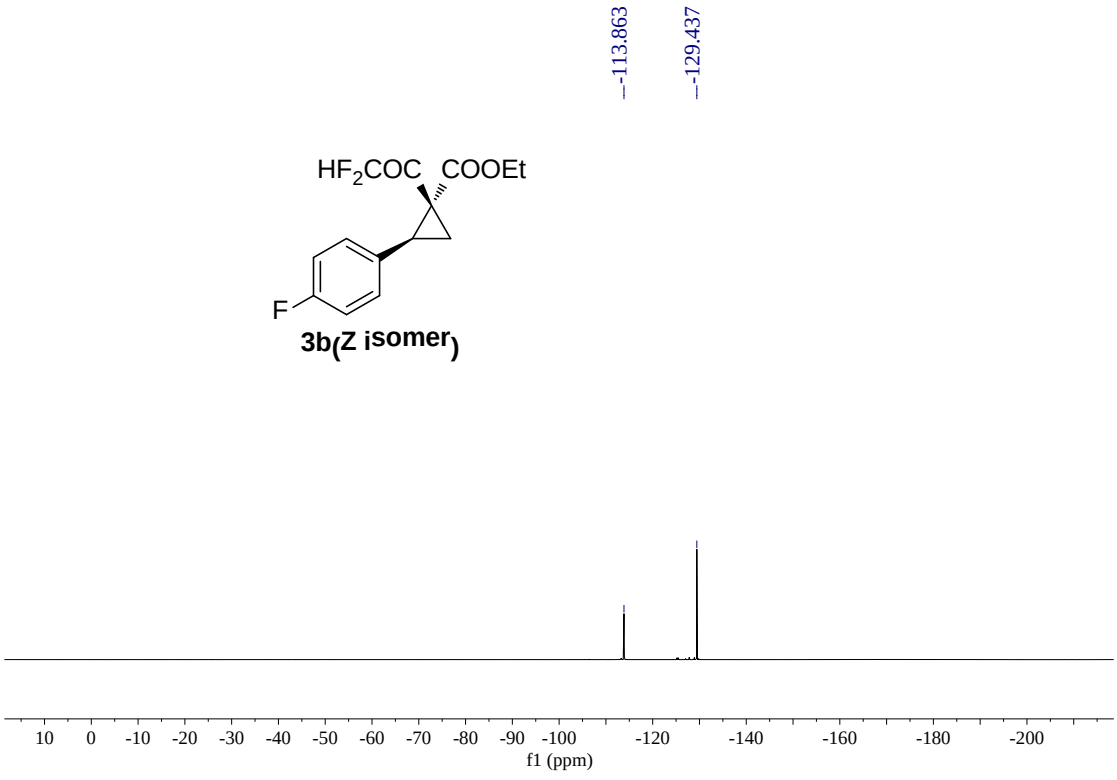
^{19}F NMR of 3b(*E*+*Z*) in $CDCl_3$



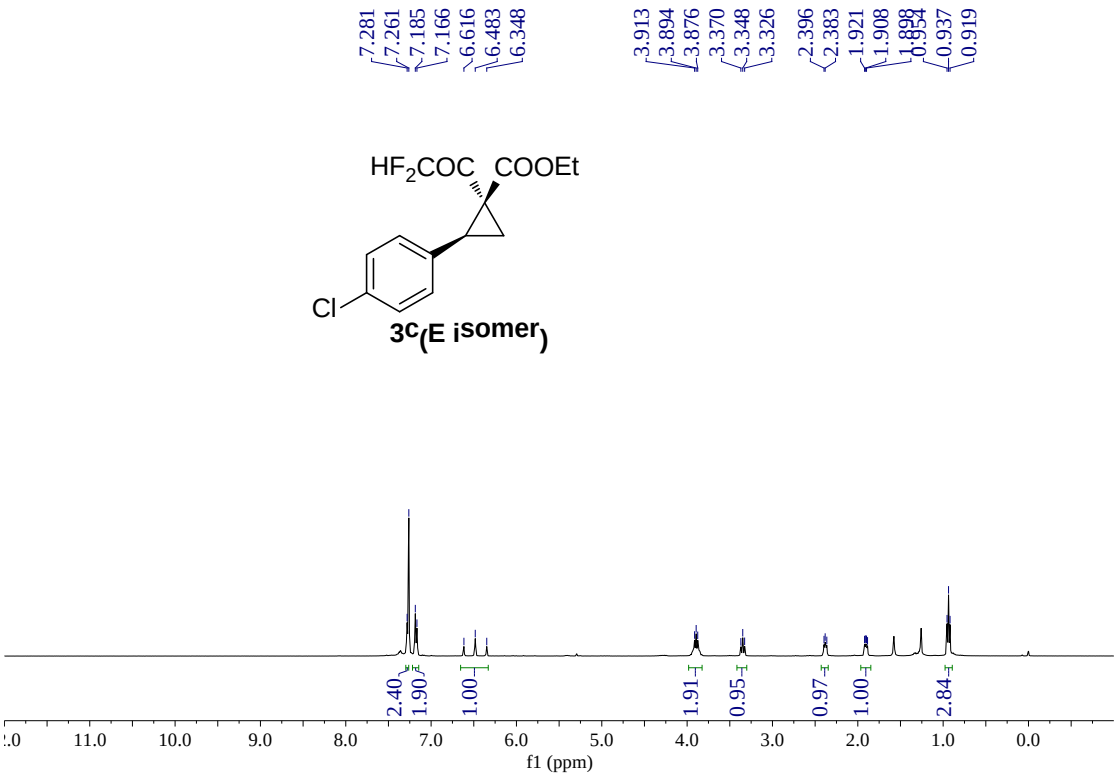
^{1}H NMR of *Z*-3b in $CDCl_3$



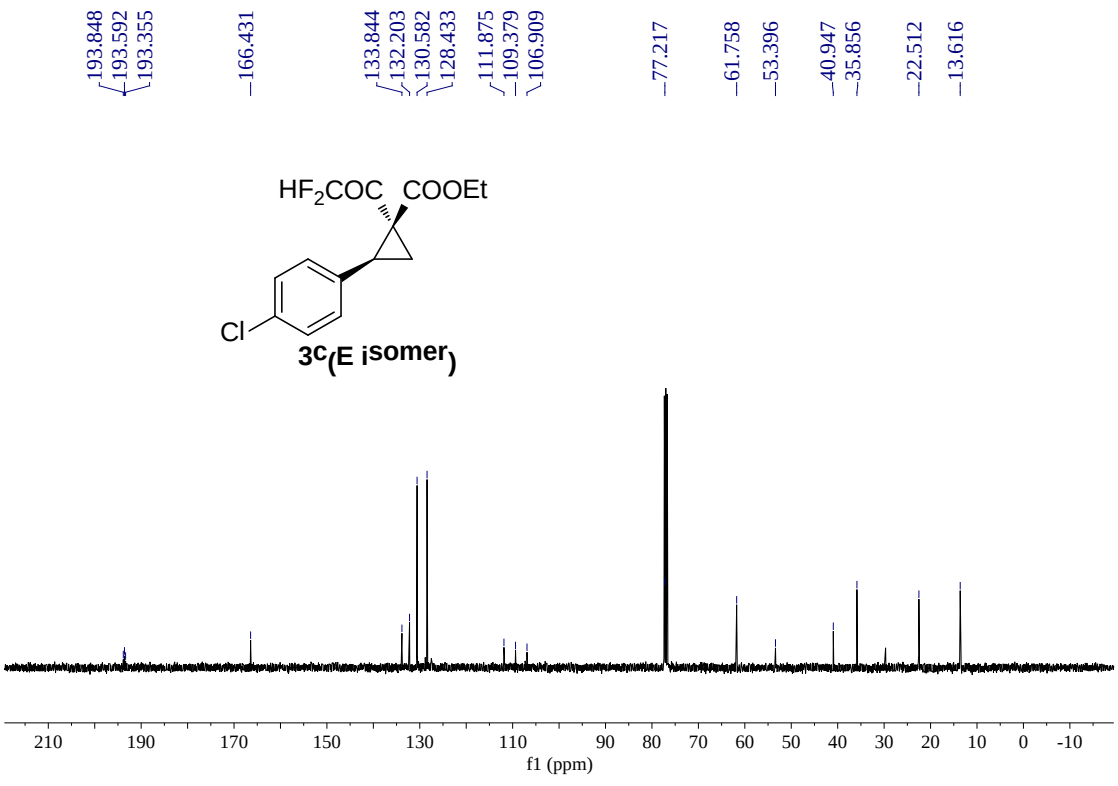
^{13}C NMR of *Z*-3b in $CDCl_3$



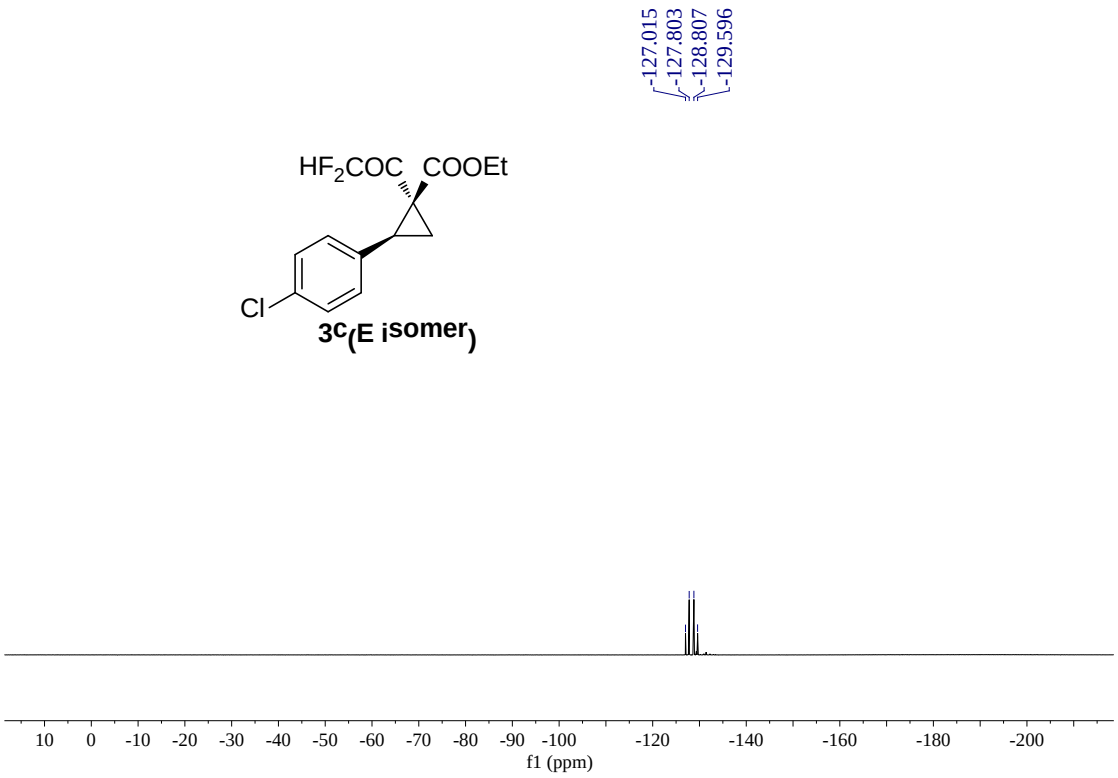
^{19}F NMR of *Z*-3b in $CDCl_3$



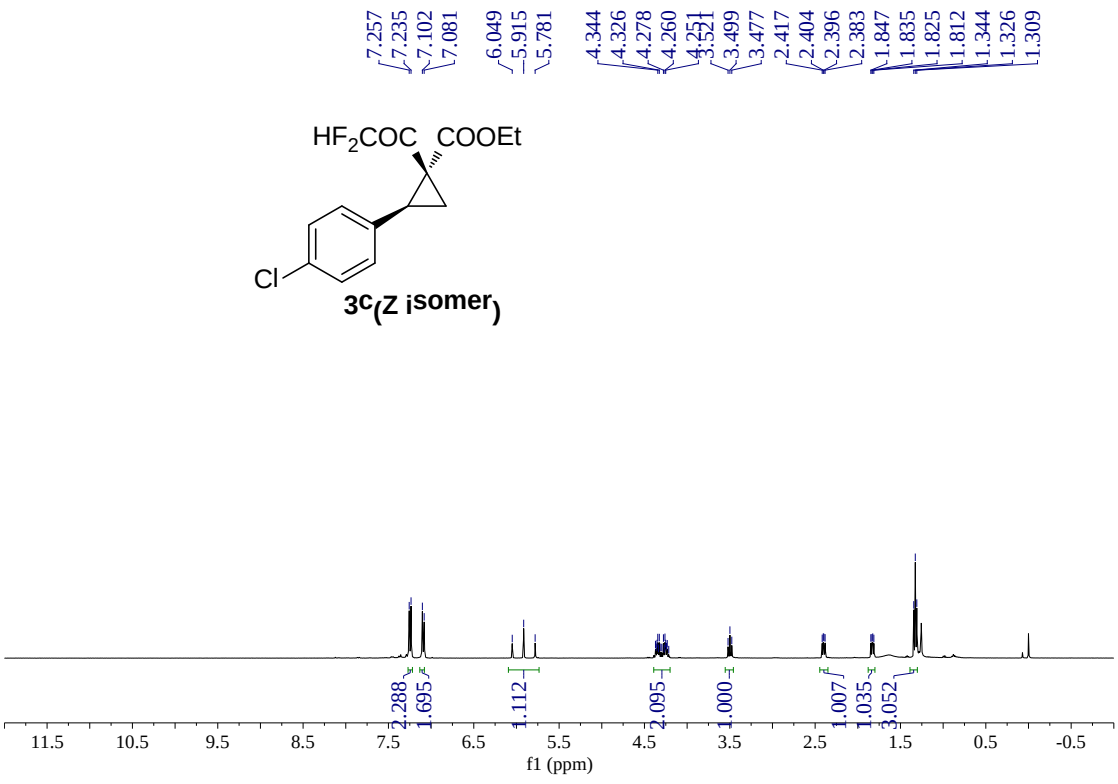
^{1}H NMR of *E*-3c in $CDCl_3$



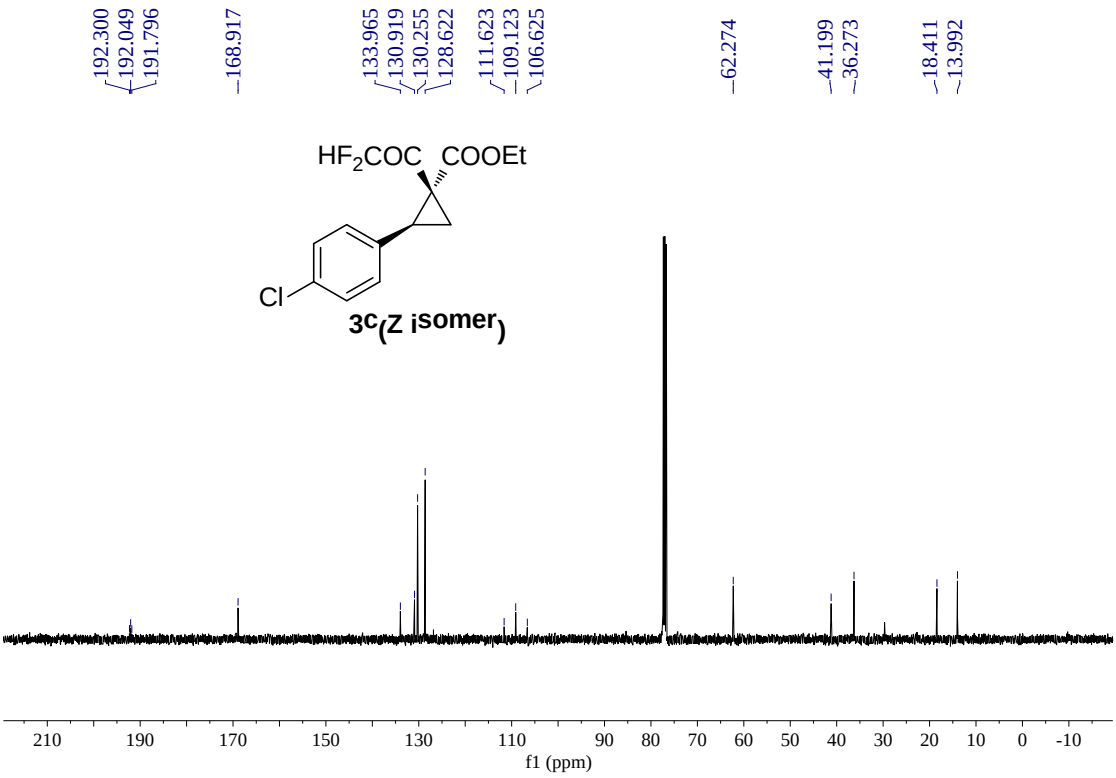
^{13}C NMR of *E*-3c in $CDCl_3$



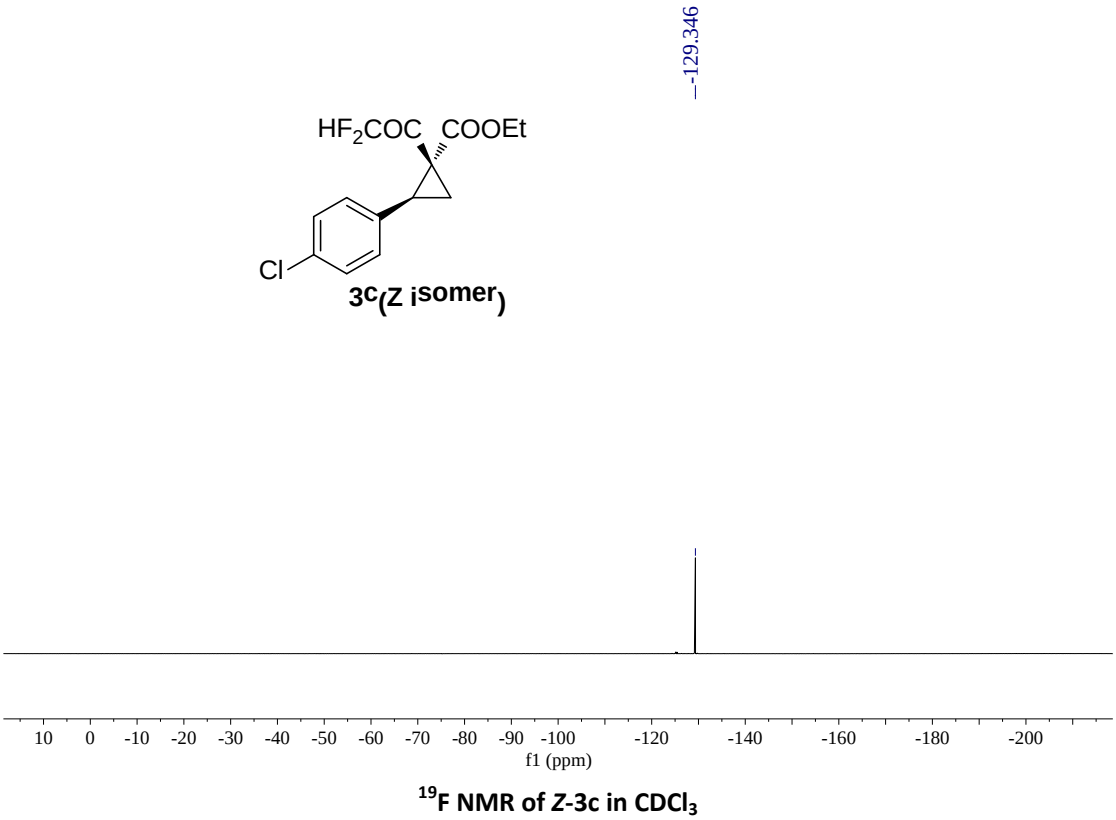
^{19}F NMR of *E*-3c in $CDCl_3$



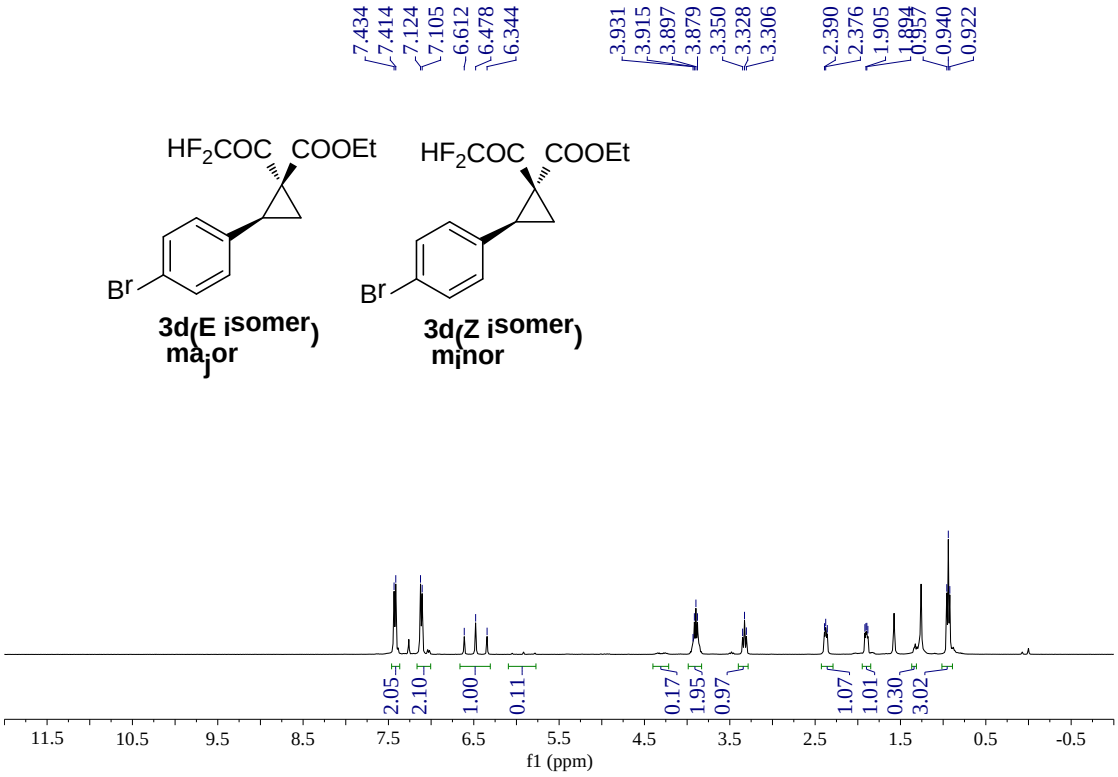
^{1}H NMR of *Z*-3c in $CDCl_3$



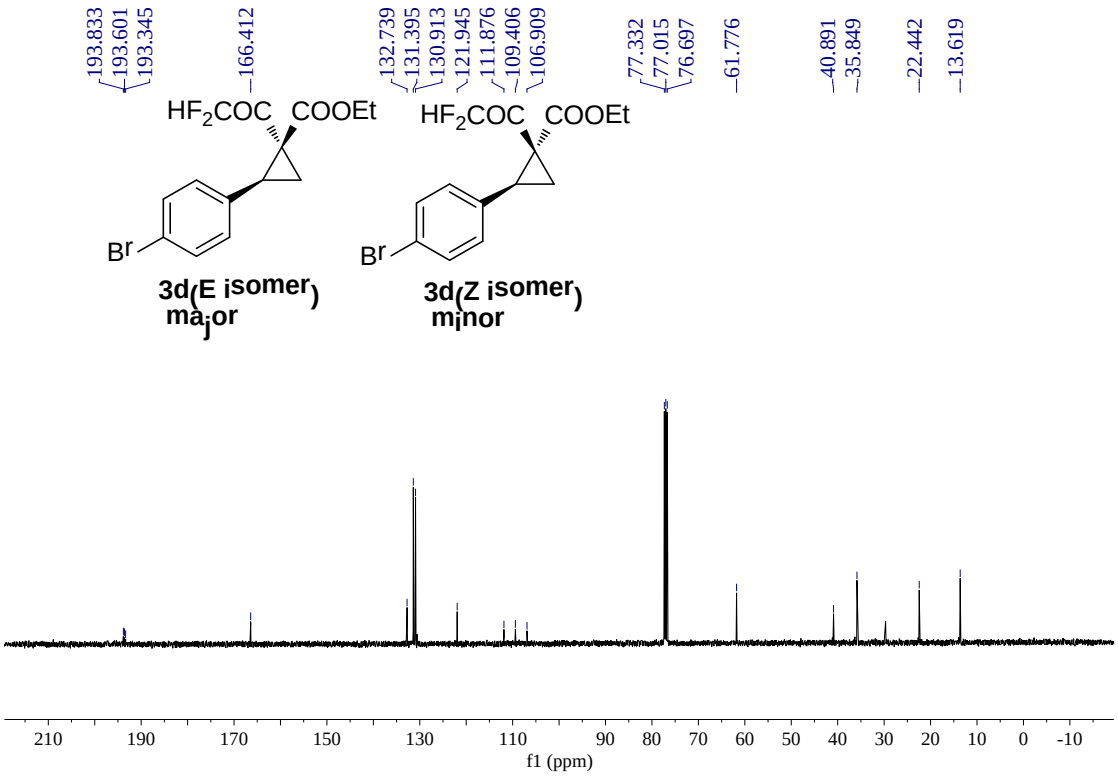
^{13}C NMR of *Z*-3c in $CDCl_3$



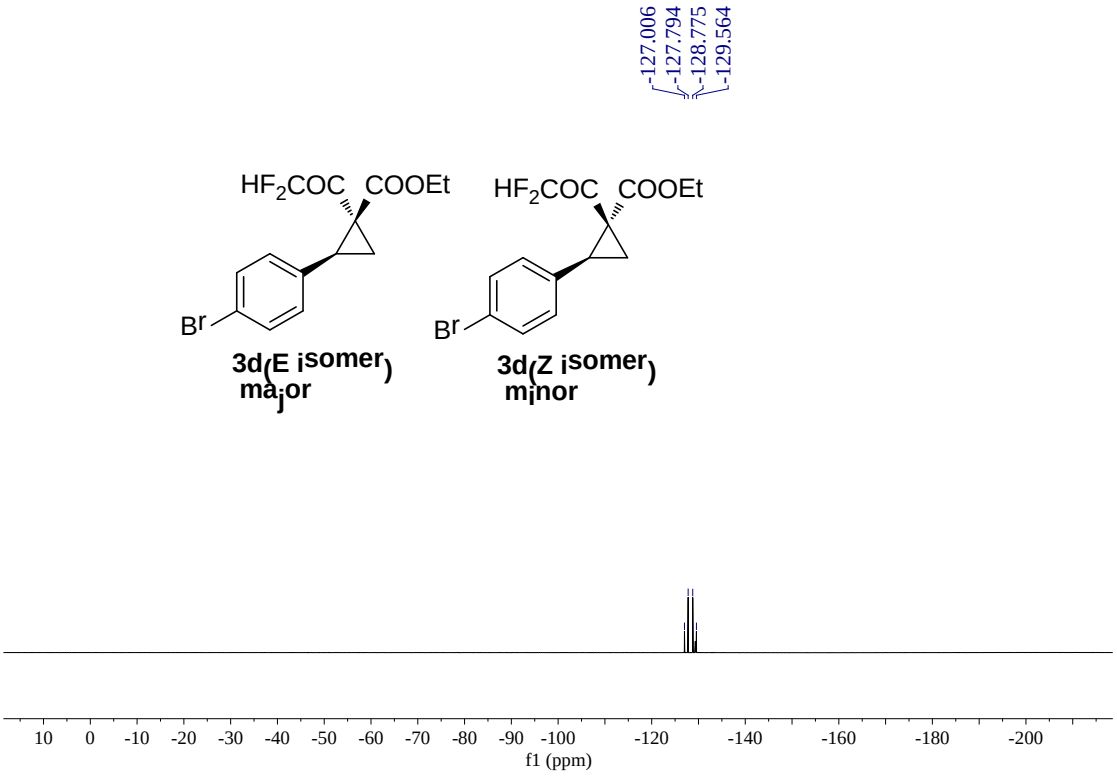
^{19}F NMR of *Z*-3c in $CDCl_3$



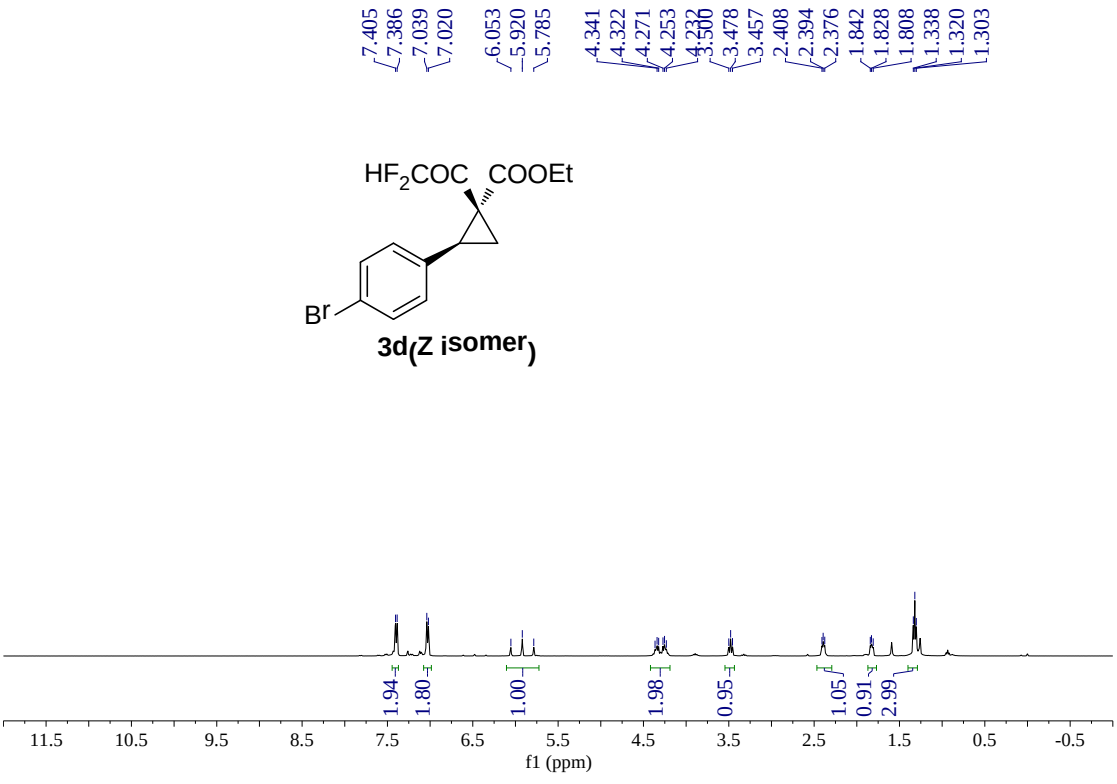
^{1}H NMR of 3d(*E*+*Z*) in $CDCl_3$



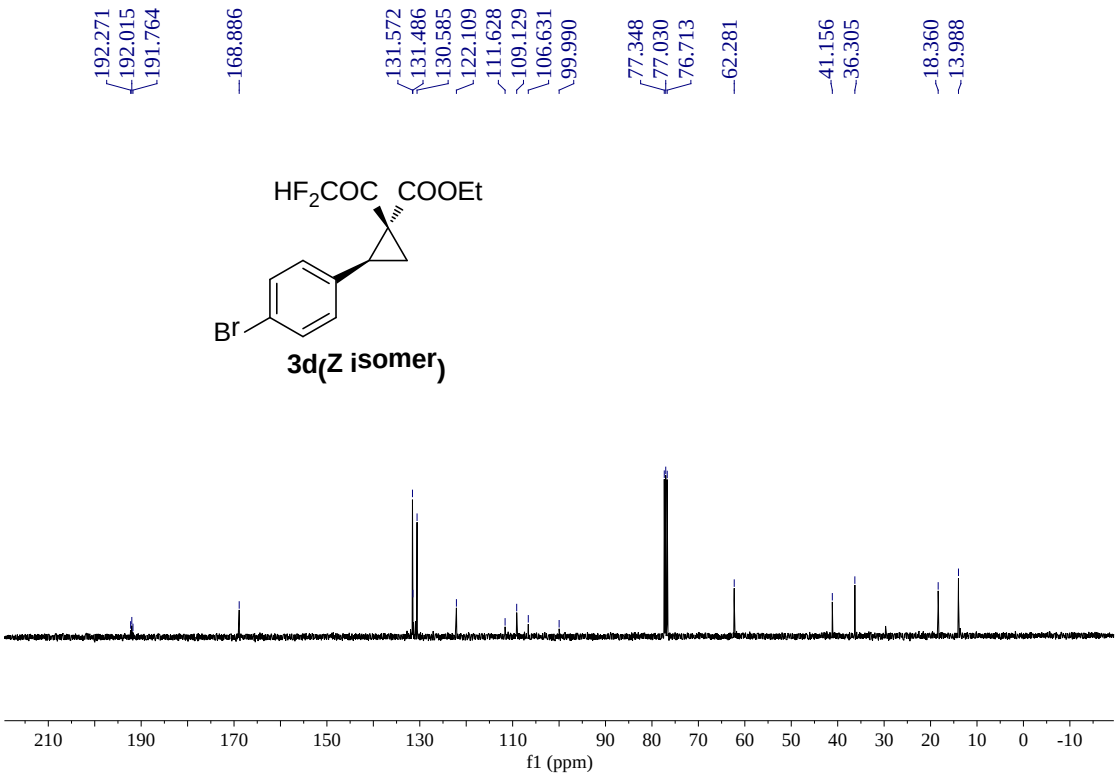
^{13}C NMR of 3d(*E*+*Z*) in $CDCl_3$



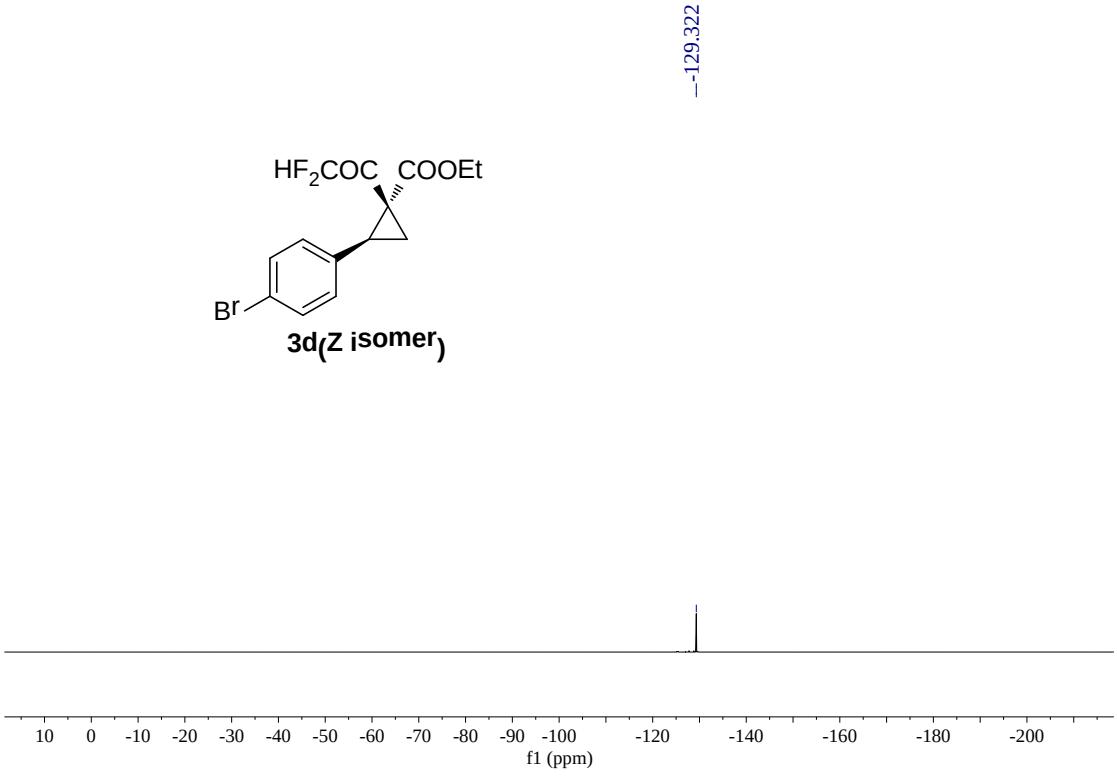
^{19}F NMR of 3d(*E*+*Z*) in $CDCl_3$



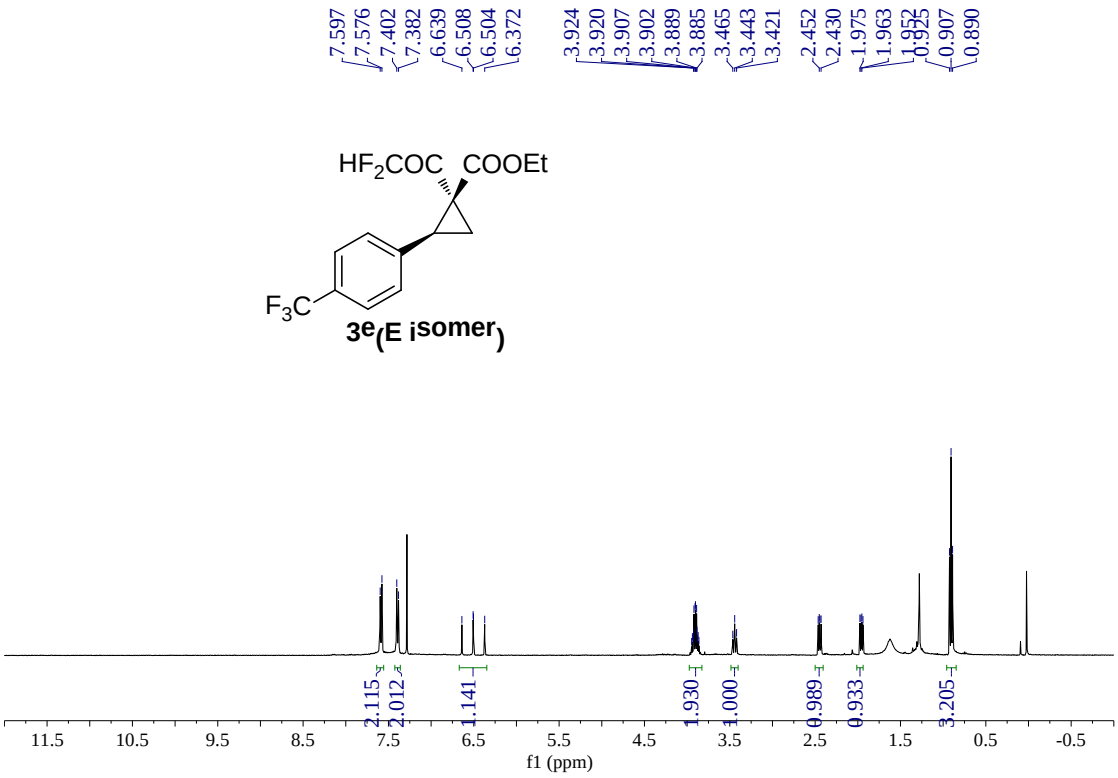
^{1}H NMR of *Z*-3d in $CDCl_3$



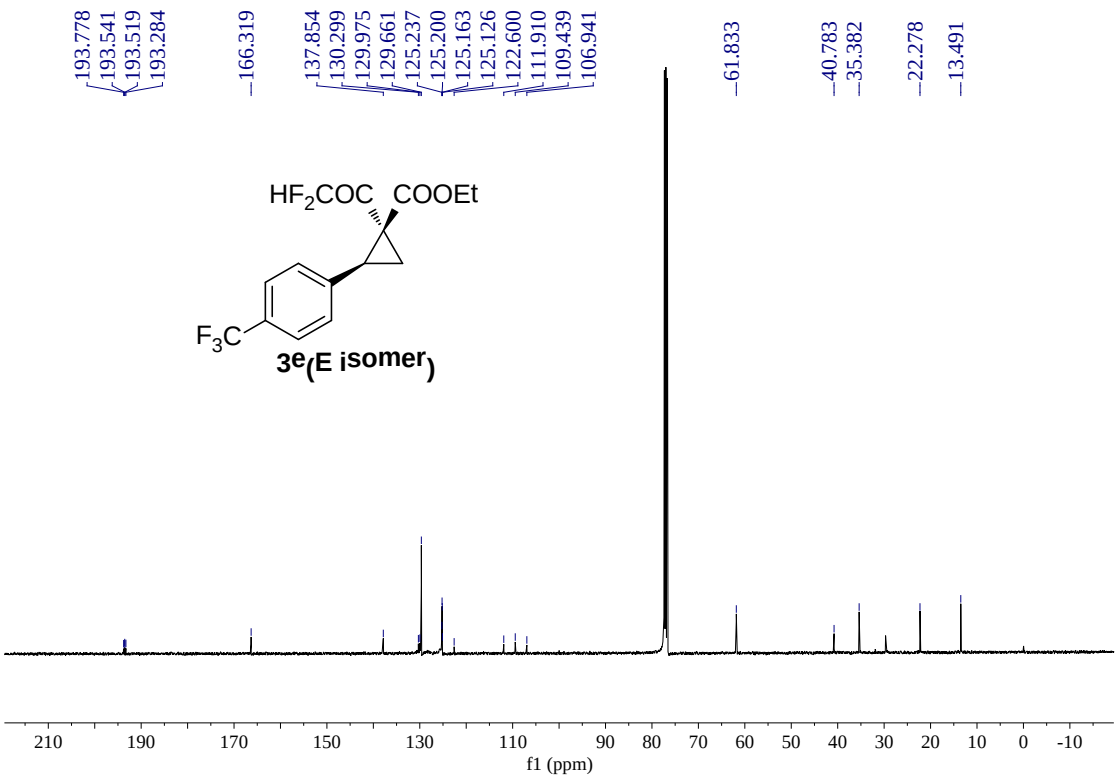
^{13}C NMR of *Z*-3d in $CDCl_3$



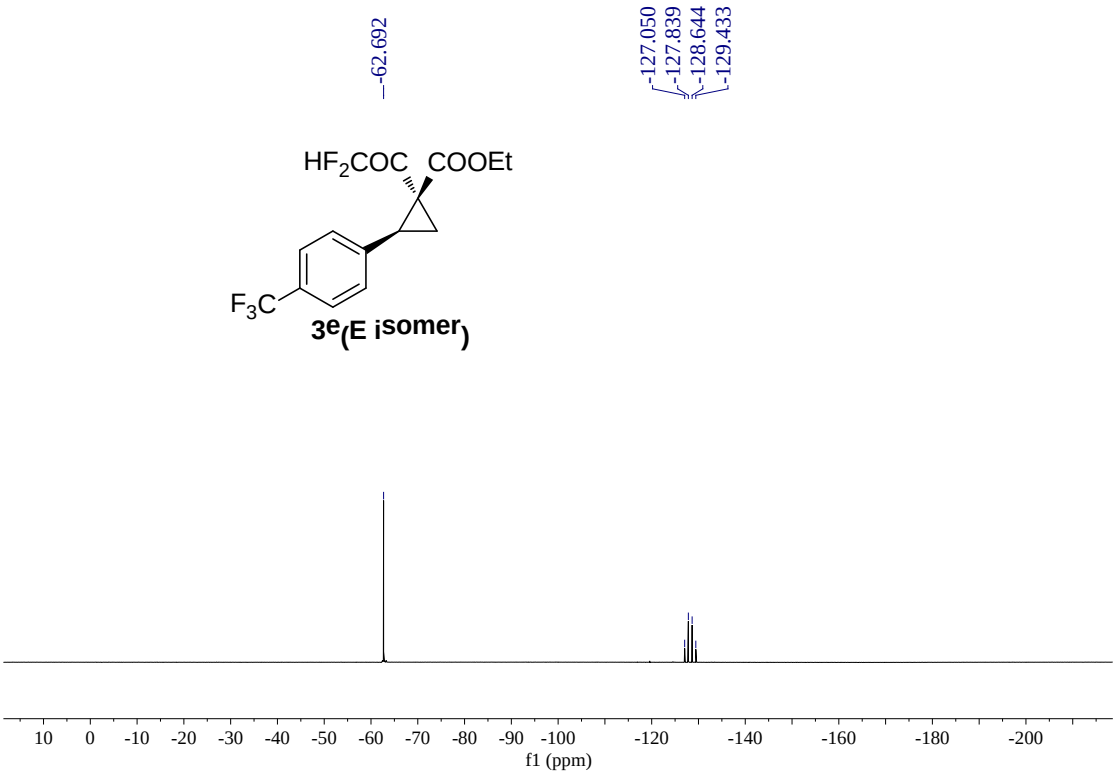
^{19}F NMR of *Z*-3d in $CDCl_3$



^{1}H NMR of *E*-3e in $CDCl_3$

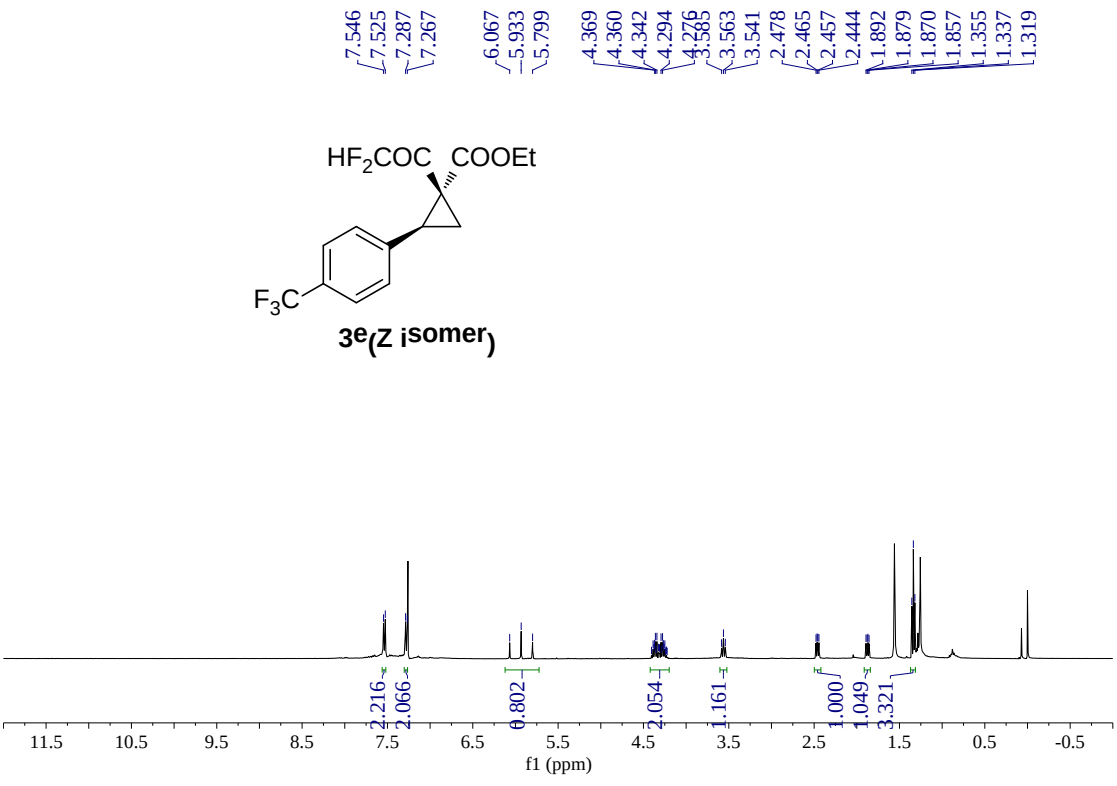


^{13}C NMR of *E*-3e in $CDCl_3$



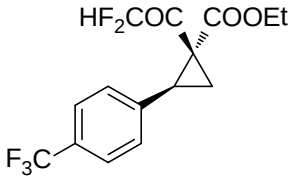
3e(E isomer)

^{19}F NMR of *E*-3e in $CDCl_3$

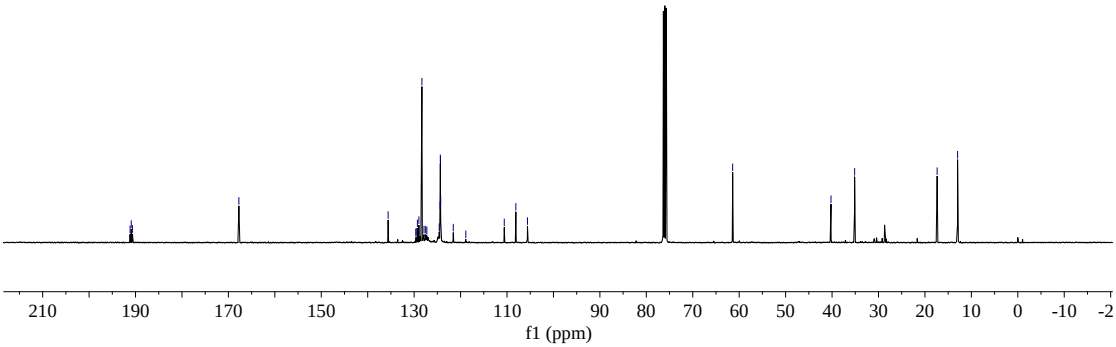


3e(Z isomer)

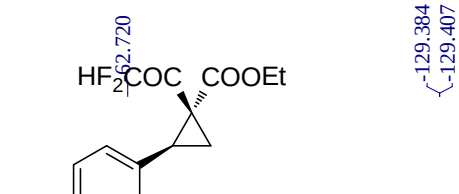
^{1}H NMR of *Z*-3e in $CDCl_3$



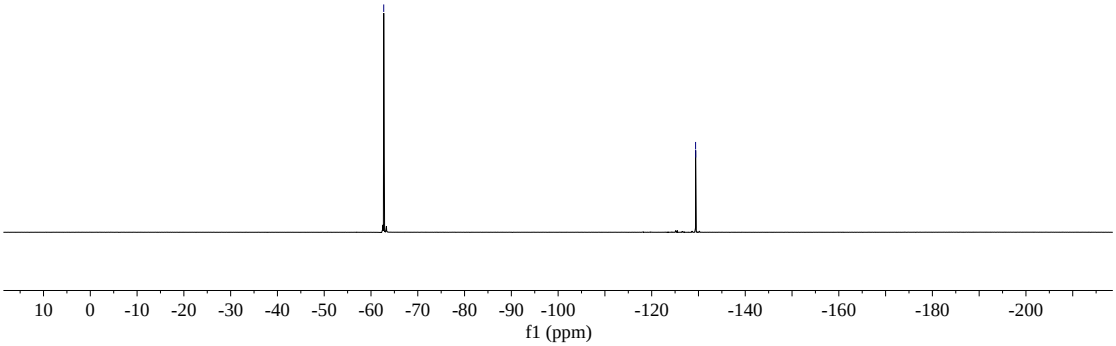
3e(Z isomer)



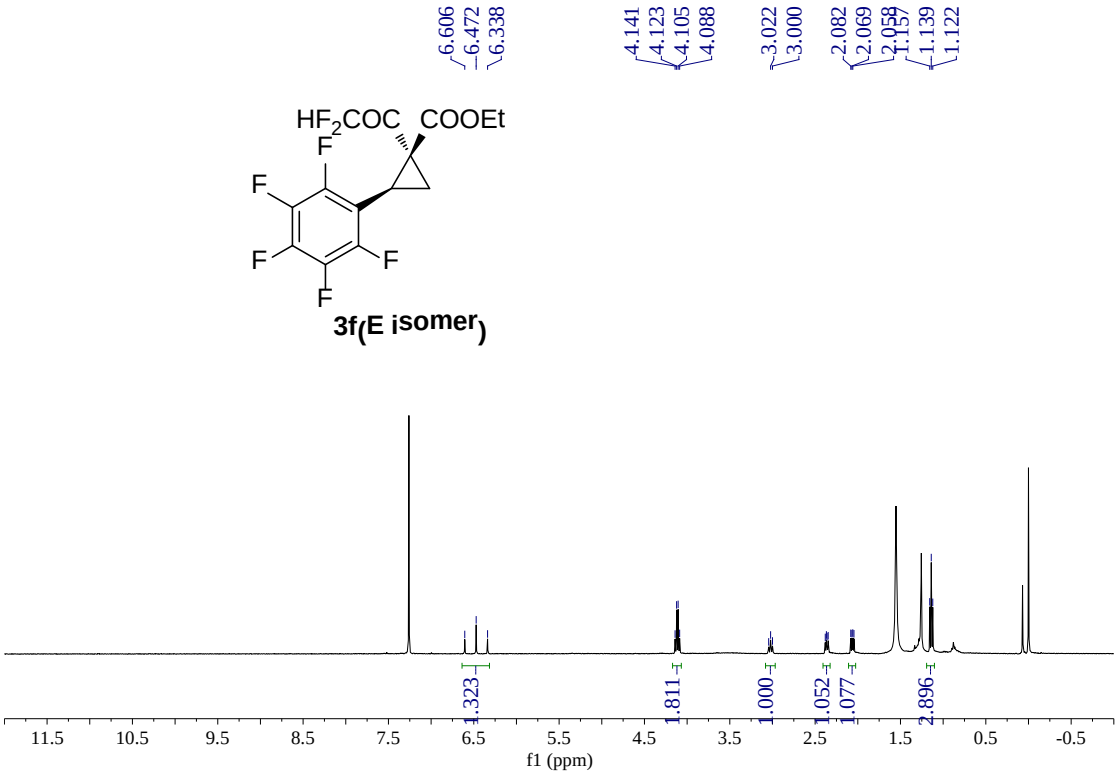
^{13}C NMR of *Z*-3e in $CDCl_3$



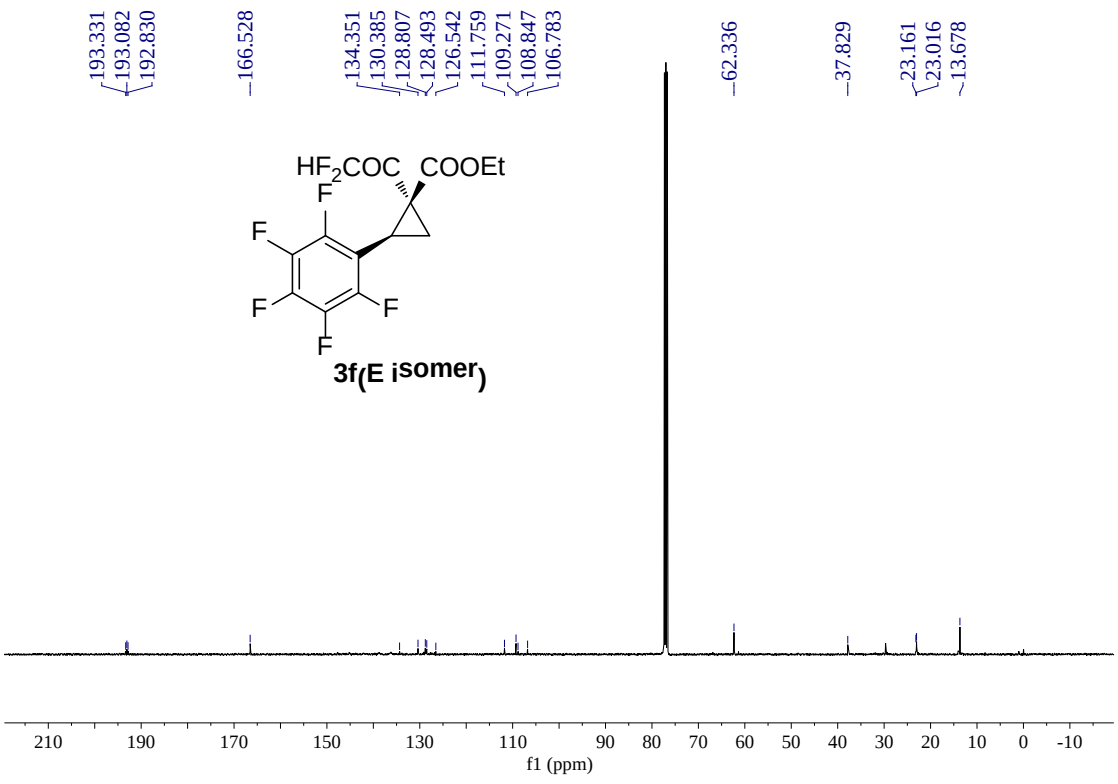
3e(Z isomer)



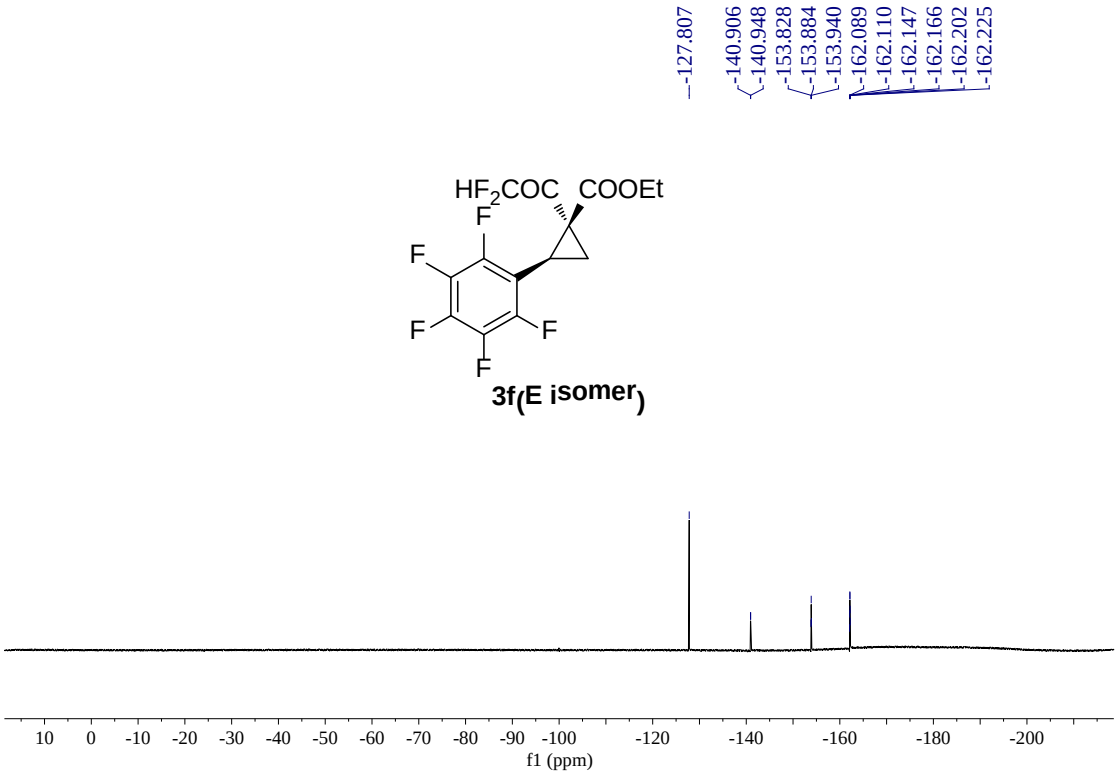
^{19}F NMR of *Z*-3e in $CDCl_3$



^{1}H NMR of *E*-3f in $CDCl_3$

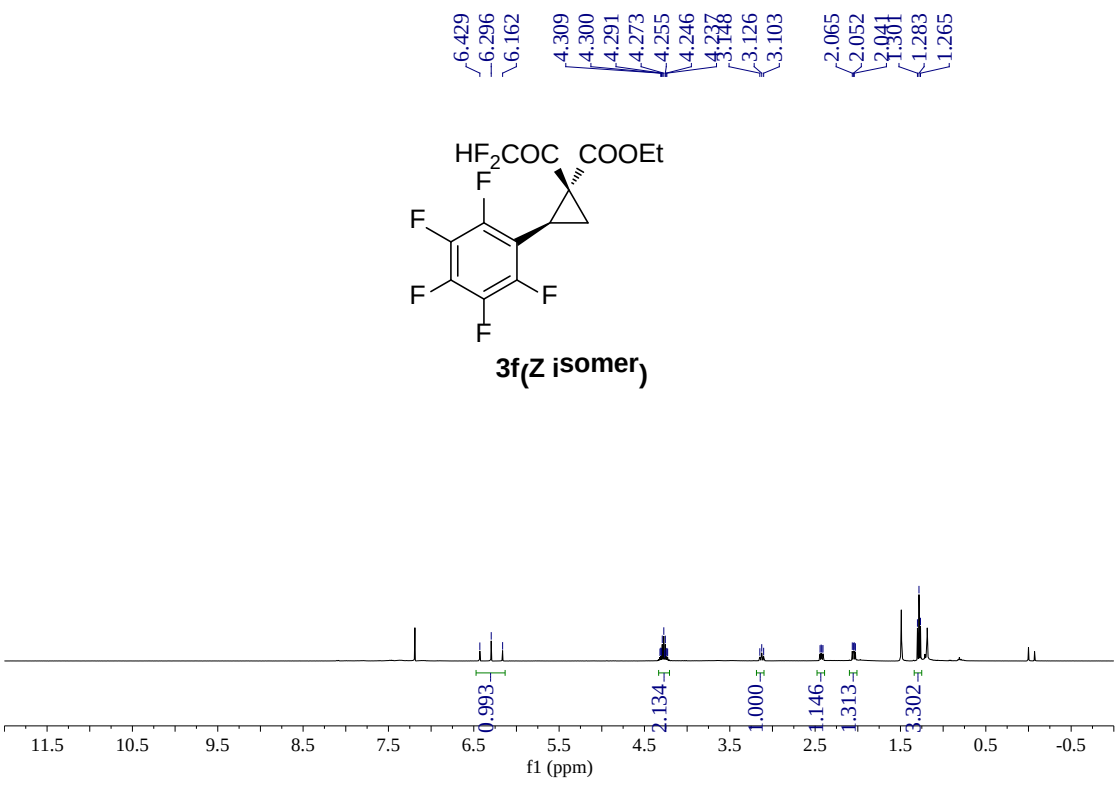


^{13}C NMR of *E*-3f in $CDCl_3$



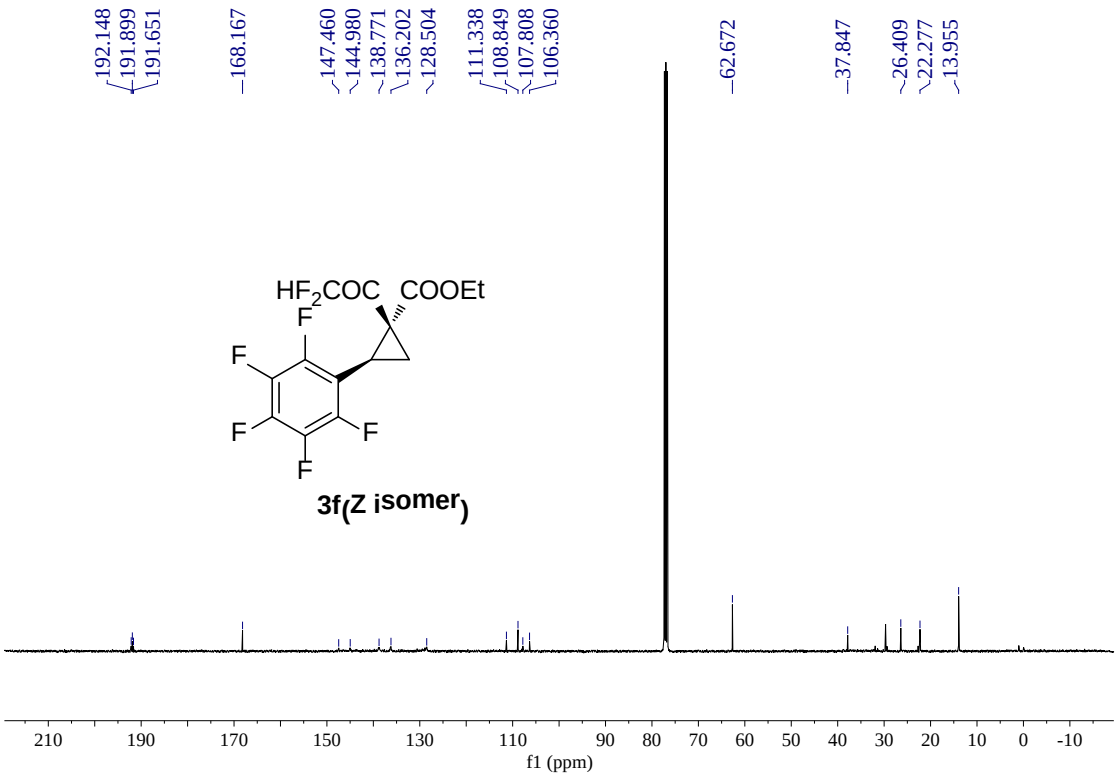
3f(E isomer)

^{19}F NMR of *E*-3f in $CDCl_3$



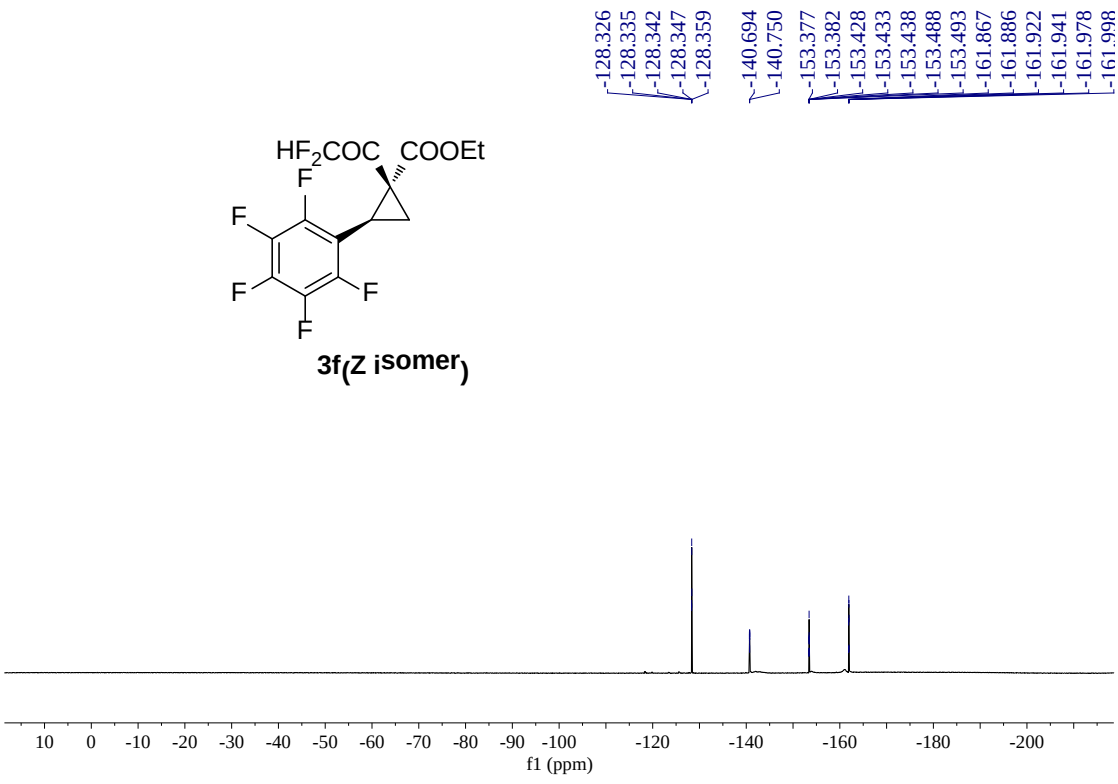
3f(Z isomer)

^{1}H NMR of *Z*-3f in $CDCl_3$



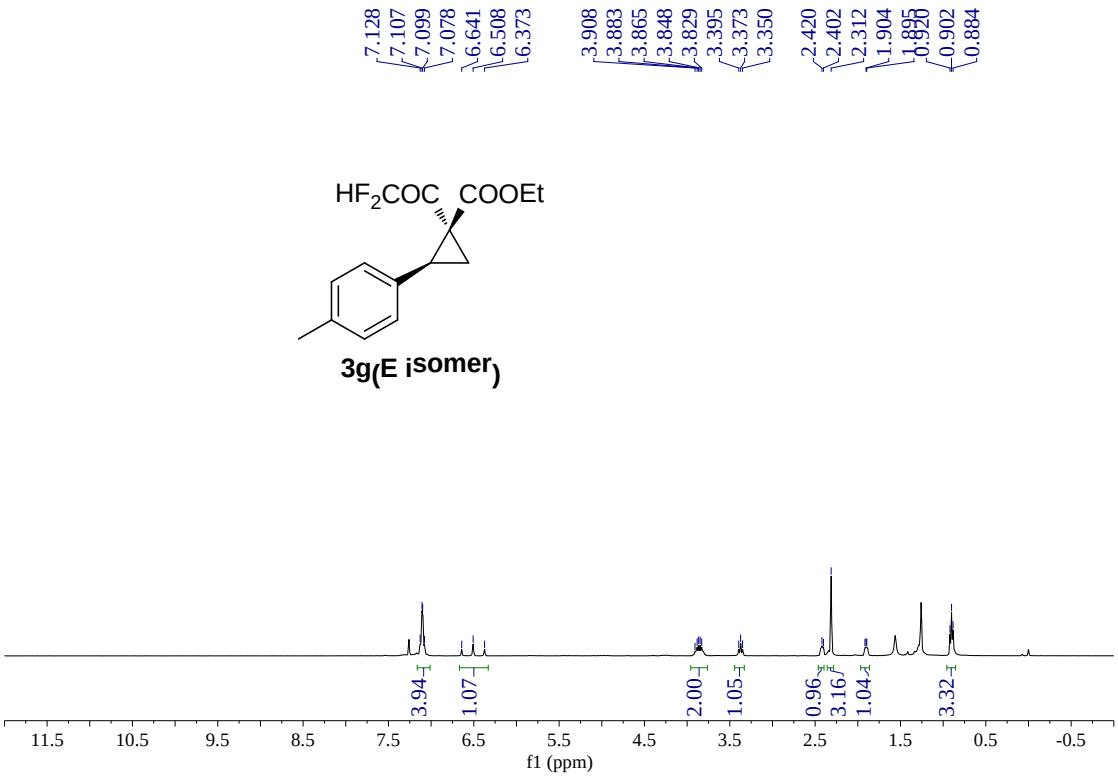
3f(Z isomer)

^{13}C NMR of *Z*-3f in $CDCl_3$



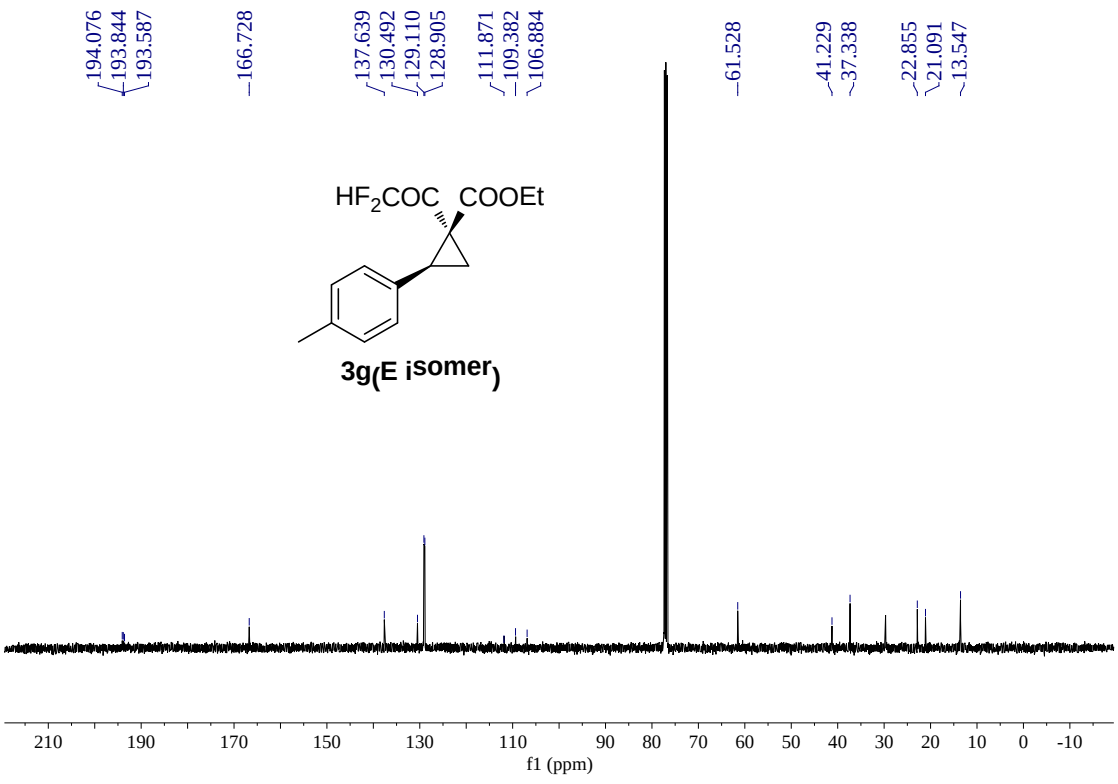
3f(Z isomer)

^{19}F NMR of *Z*-3f in $CDCl_3$



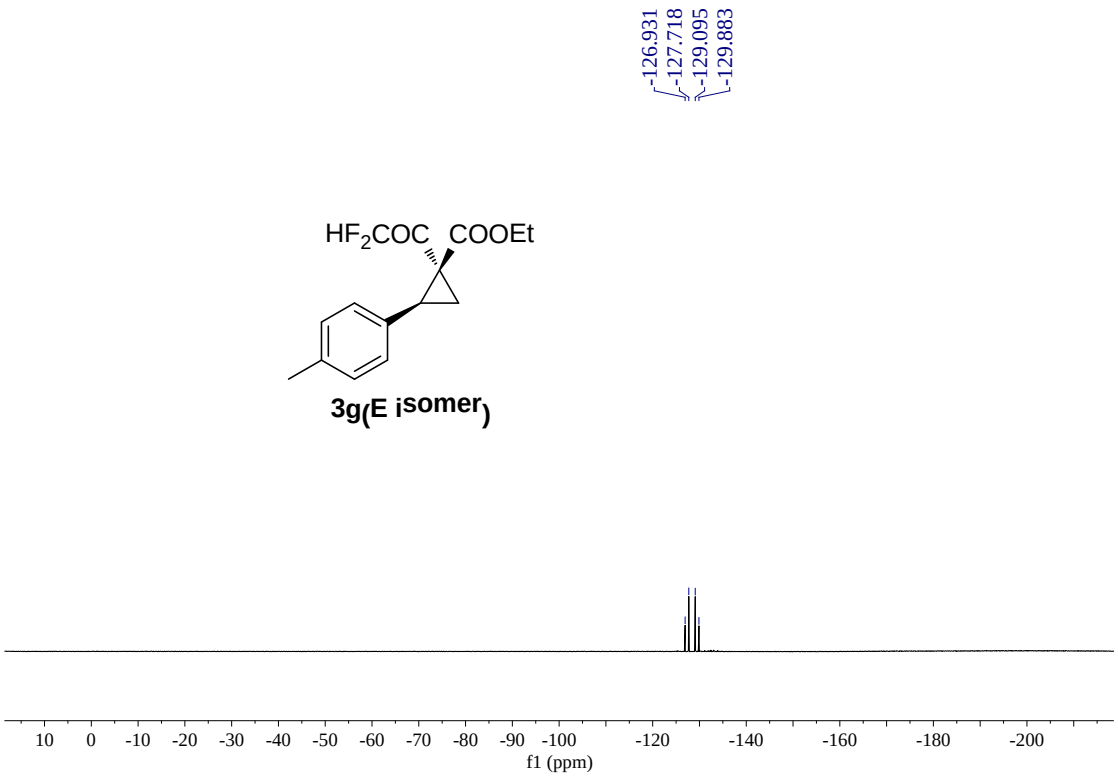
3g(E isomer)

^{1}H NMR of *E*-3g in $CDCl_3$

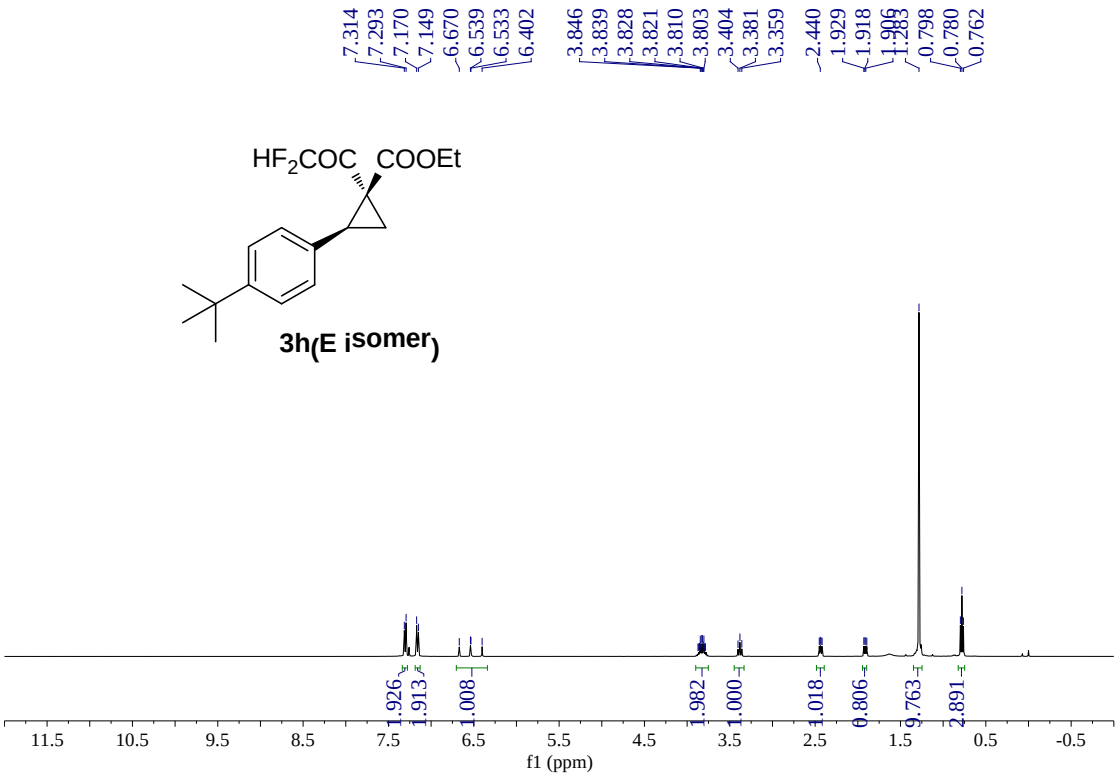


3g(E isomer)

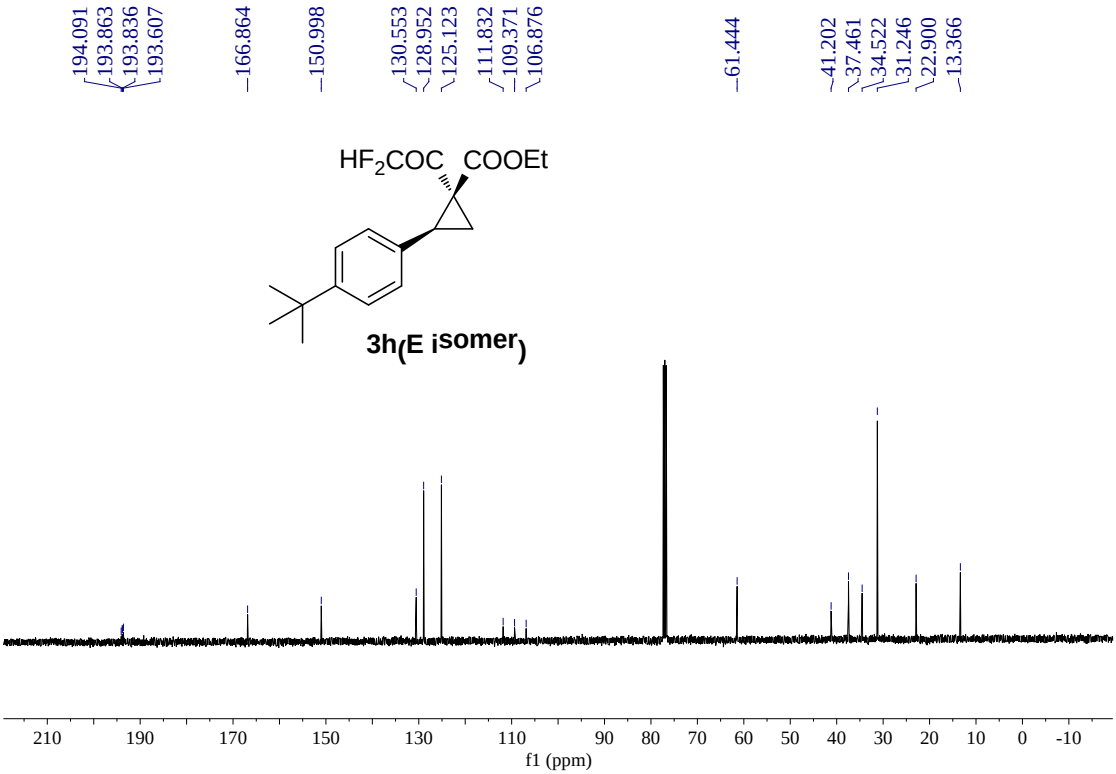
^{13}C NMR of *E*-3g in $CDCl_3$



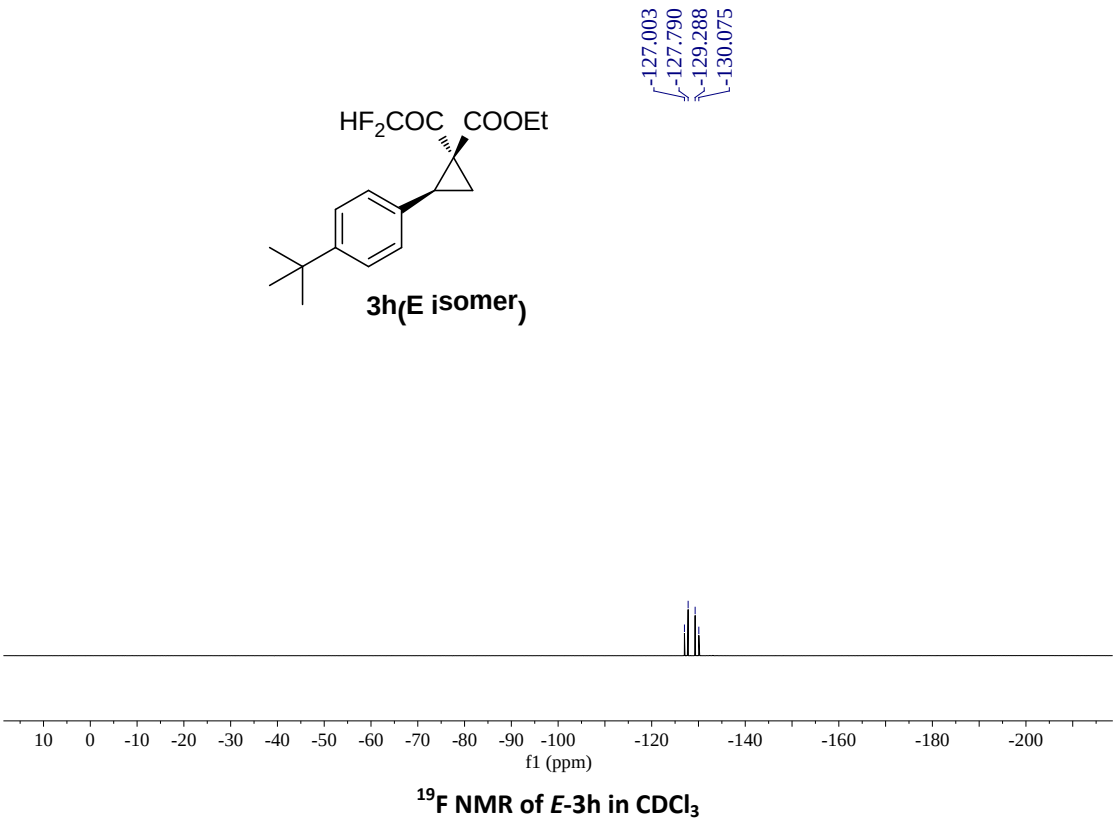
^{19}F NMR of *E*-3g in $CDCl_3$



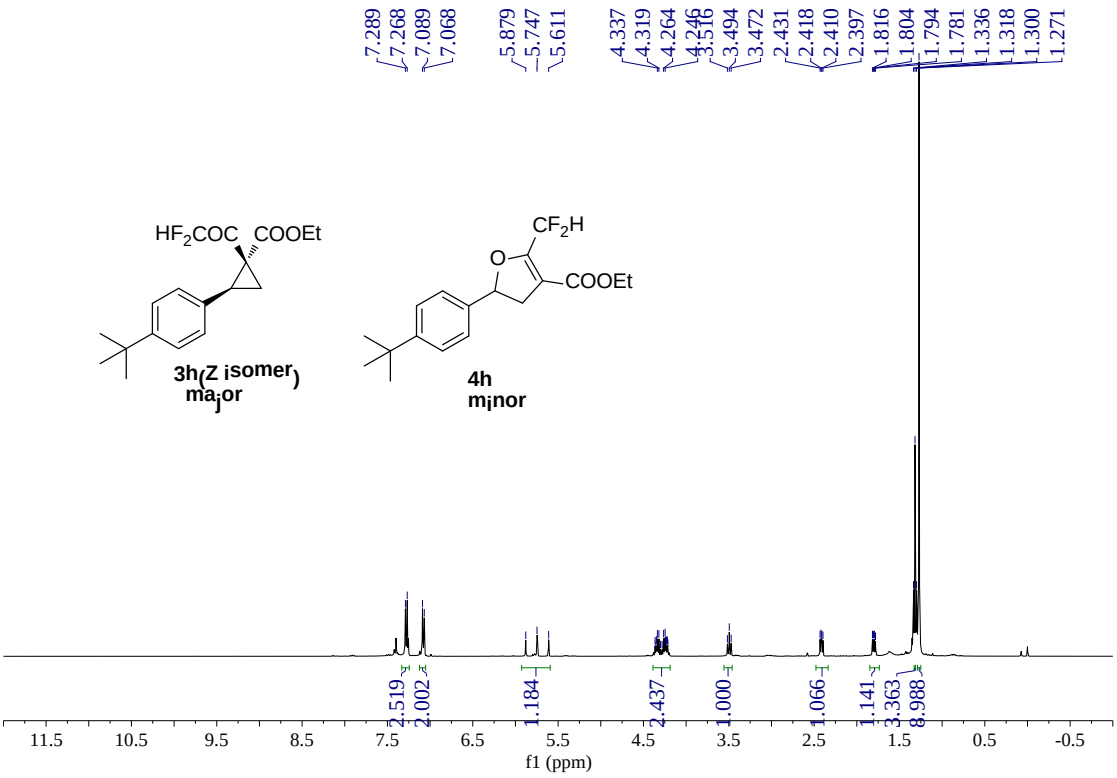
^{1}H NMR of *E*-3h in $CDCl_3$



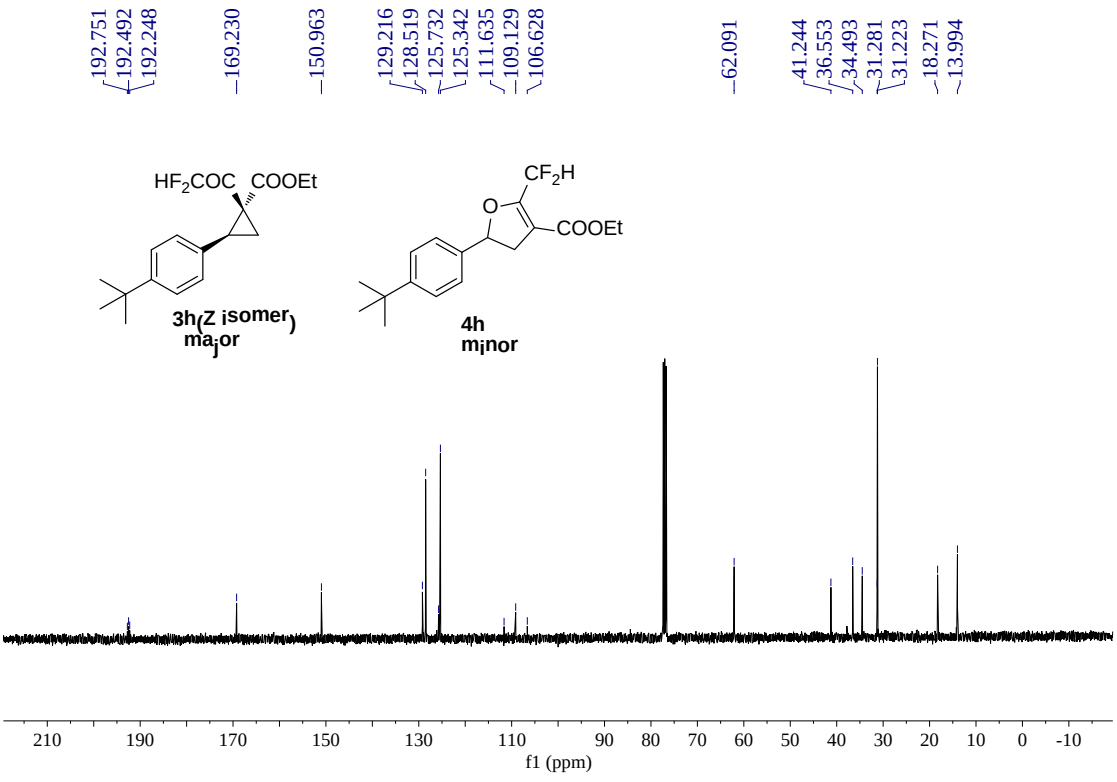
^{13}C NMR of *E*-3h in $CDCl_3$



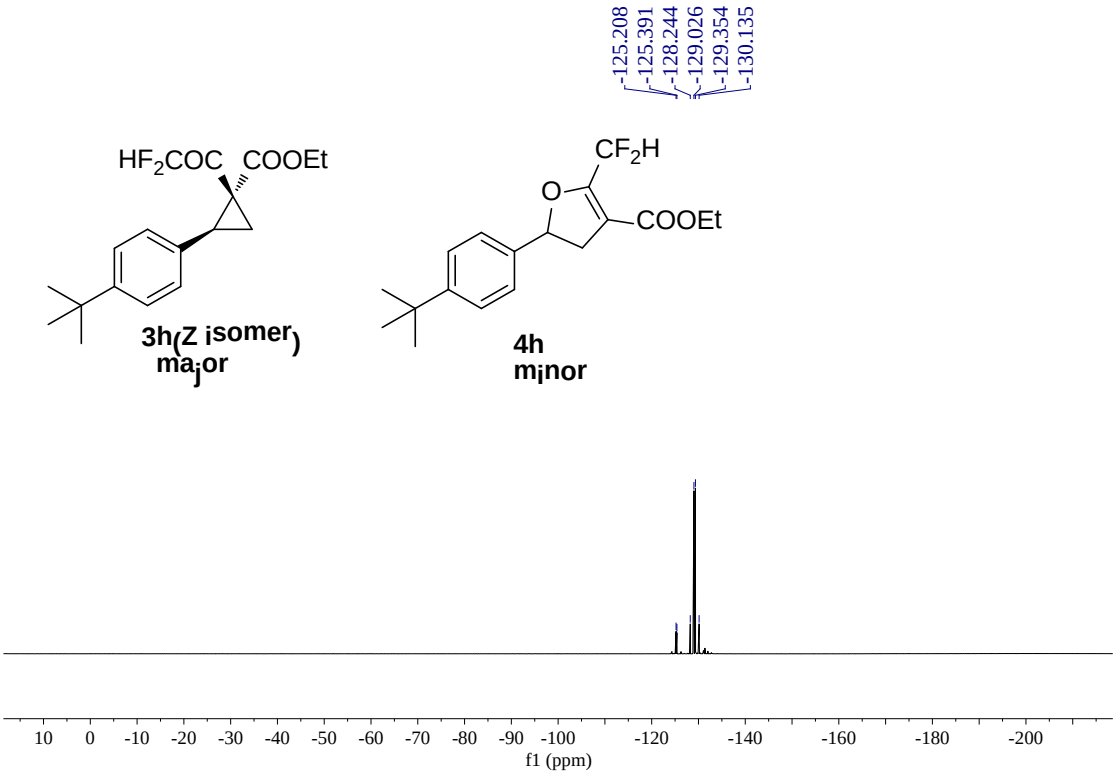
^{19}F NMR of *E*-3h in $CDCl_3$



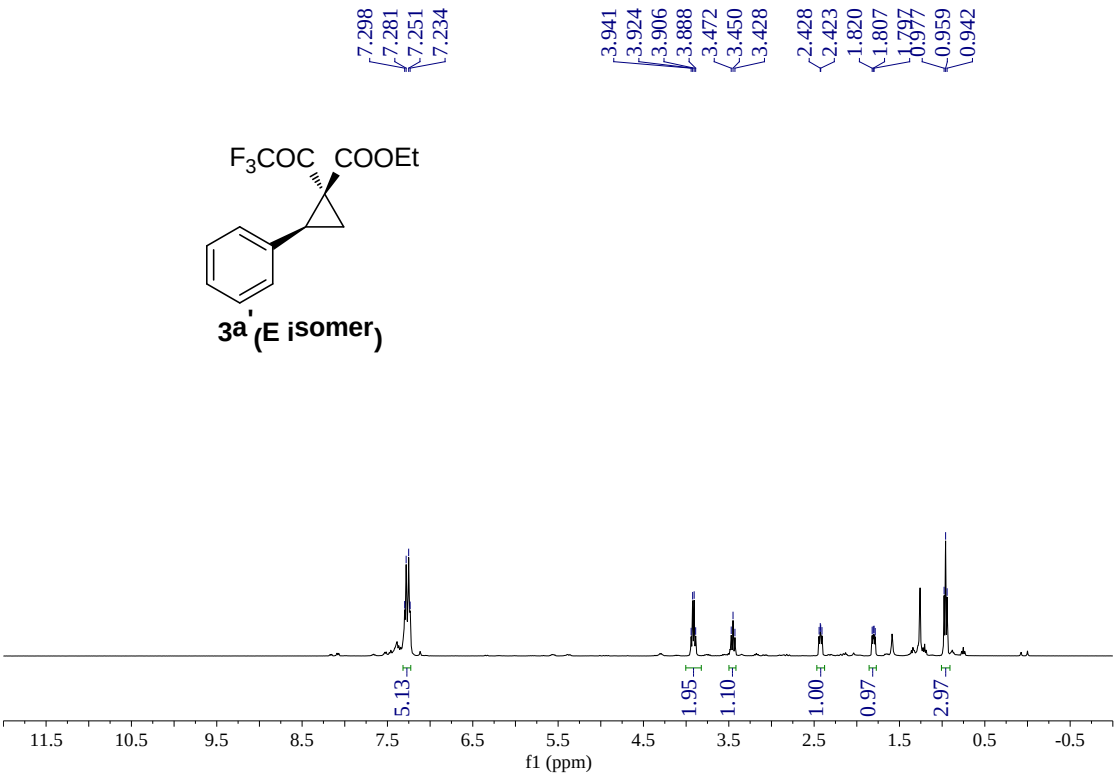
^{1}H NMR of *Z*-3h+4h in $CDCl_3$



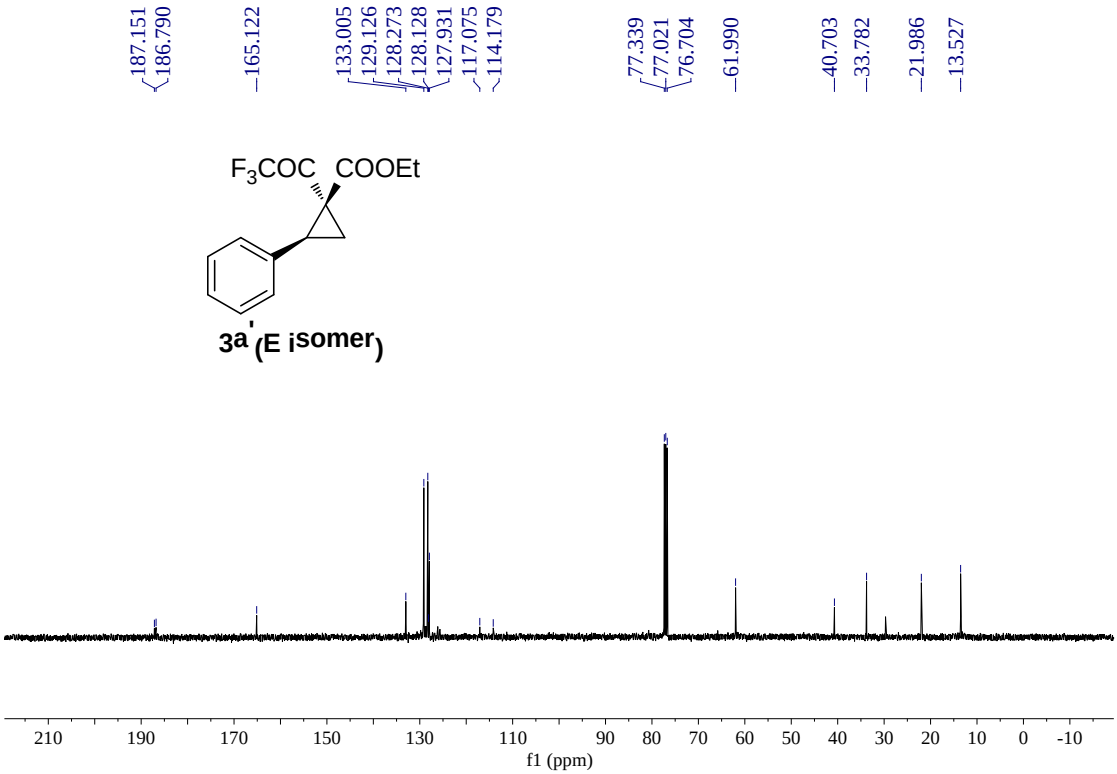
^{13}C NMR of *Z*-3h+4h in $CDCl_3$



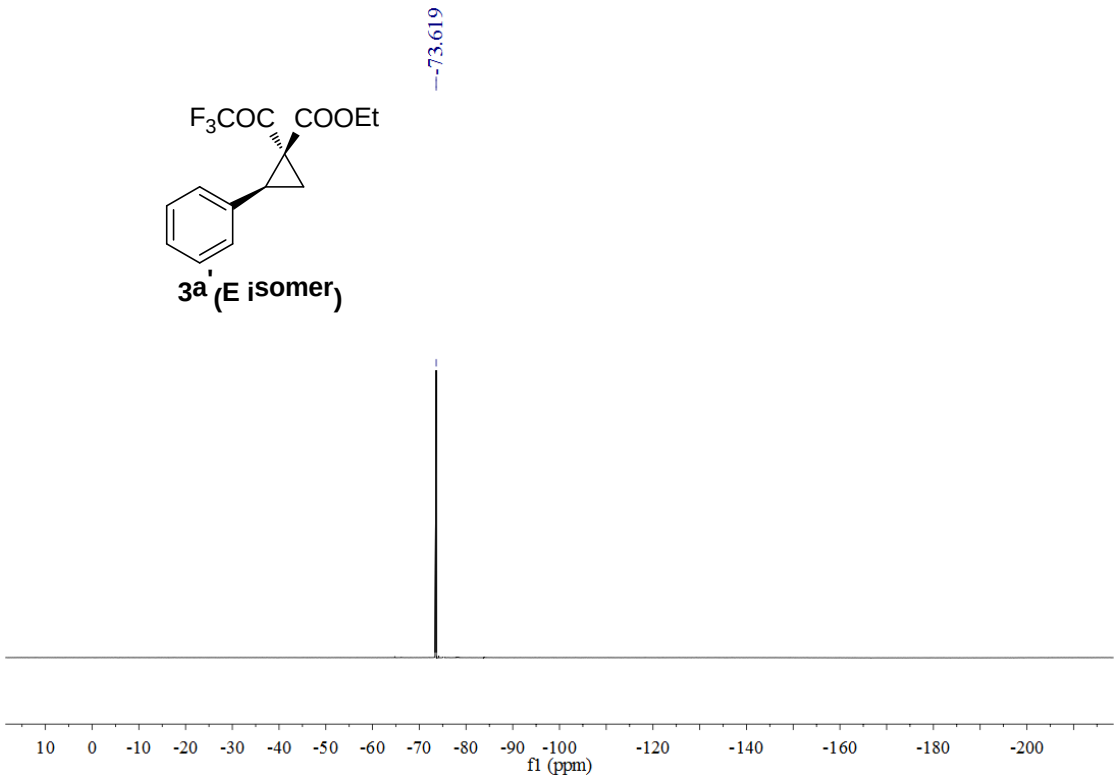
^{19}F NMR of *Z*-3h+4h in $CDCl_3$



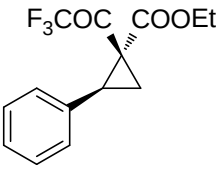
^{1}H NMR of *E*-3a' in $CDCl_3$



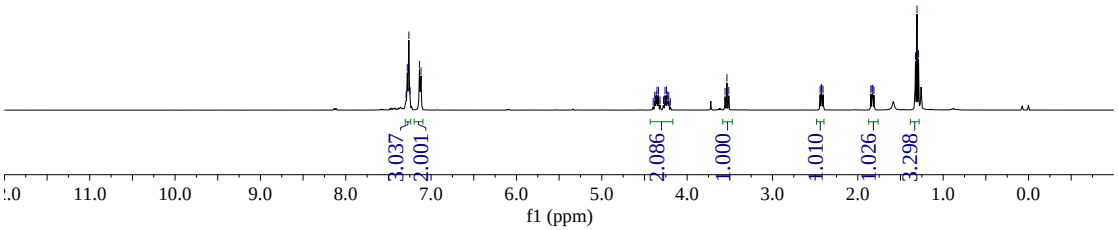
^{13}C NMR of *E*-3a' in $CDCl_3$



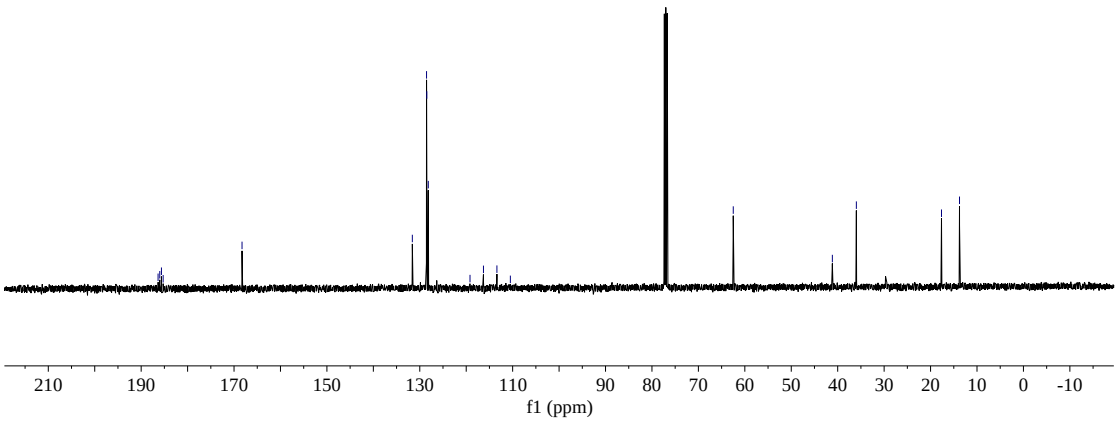
^{19}F NMR of *E*-3a' in $CDCl_3$



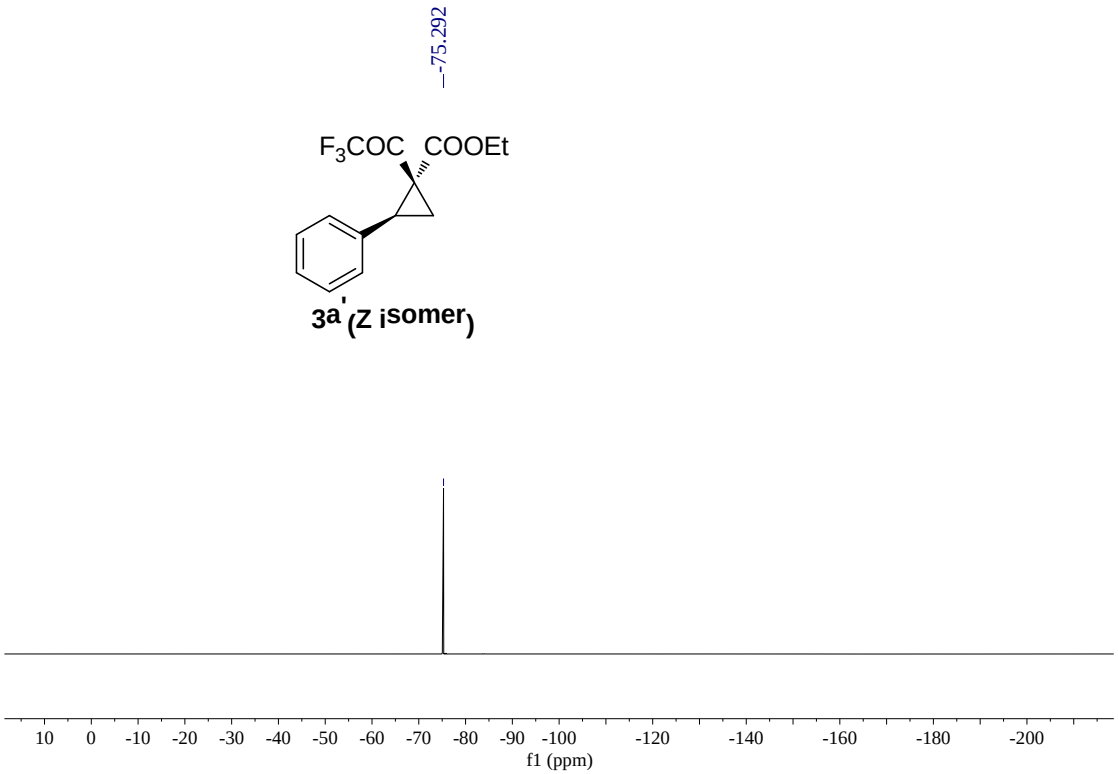
3a'(Z isomer)



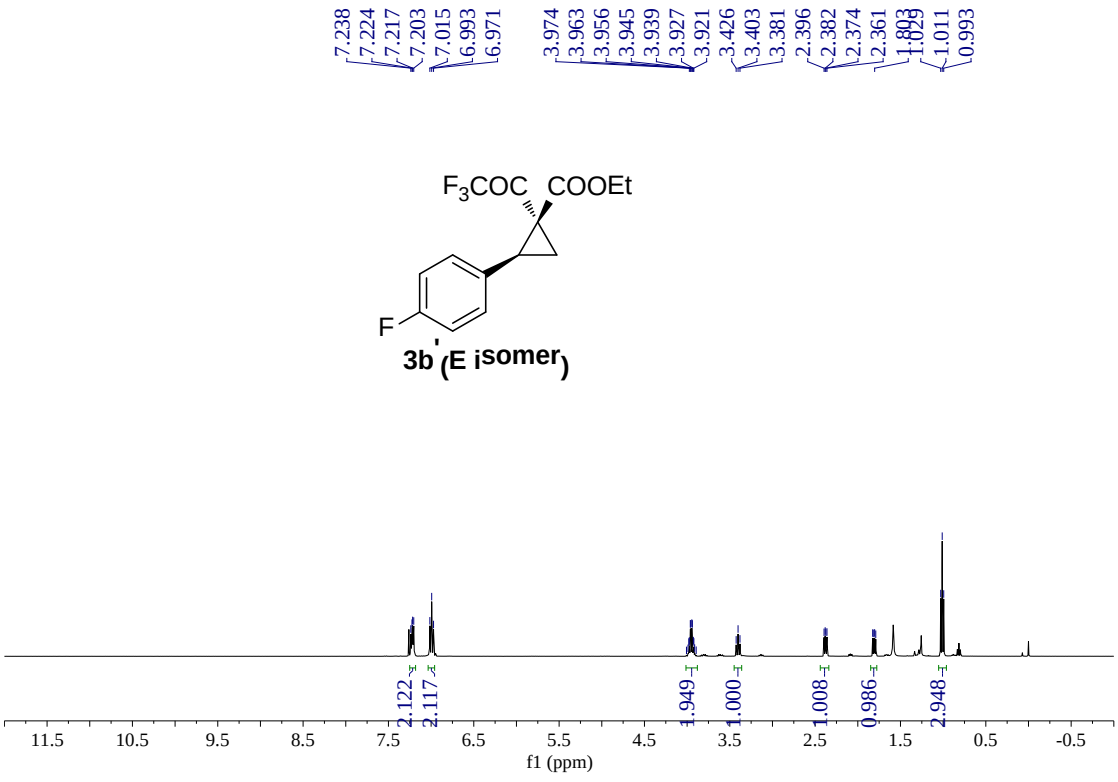
^{1}H NMR of *Z*-3a' in $CDCl_3$



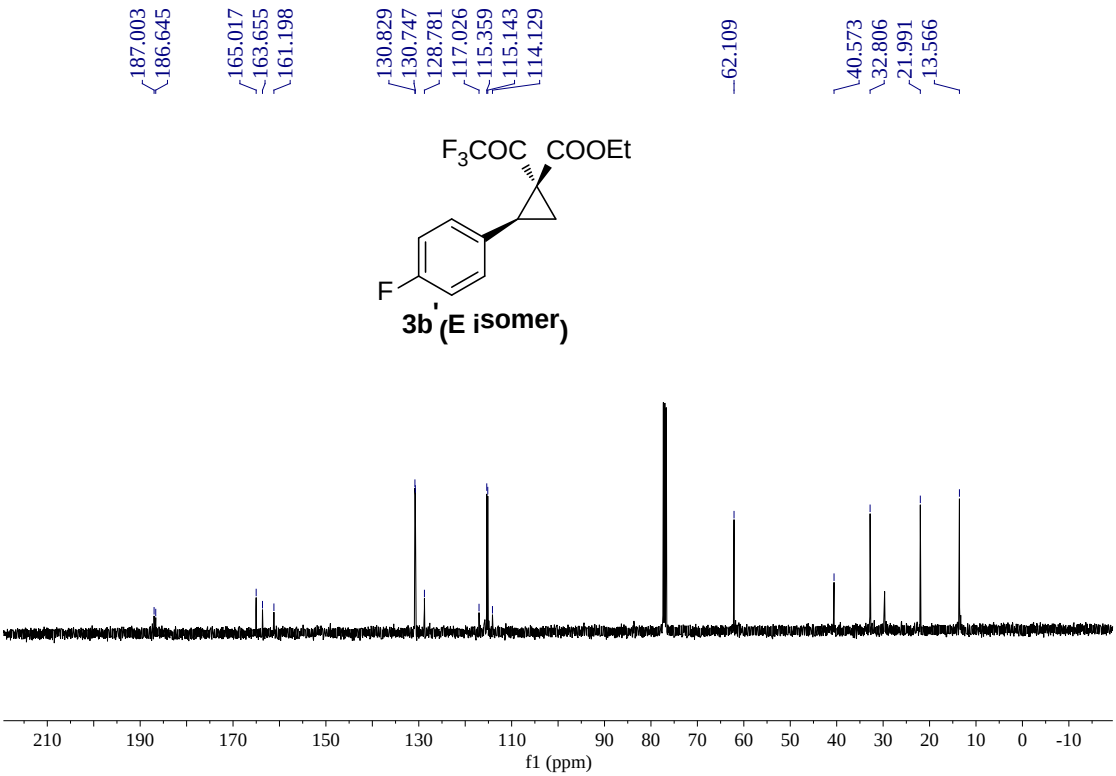
^{13}C NMR of *Z*-3a' in $CDCl_3$



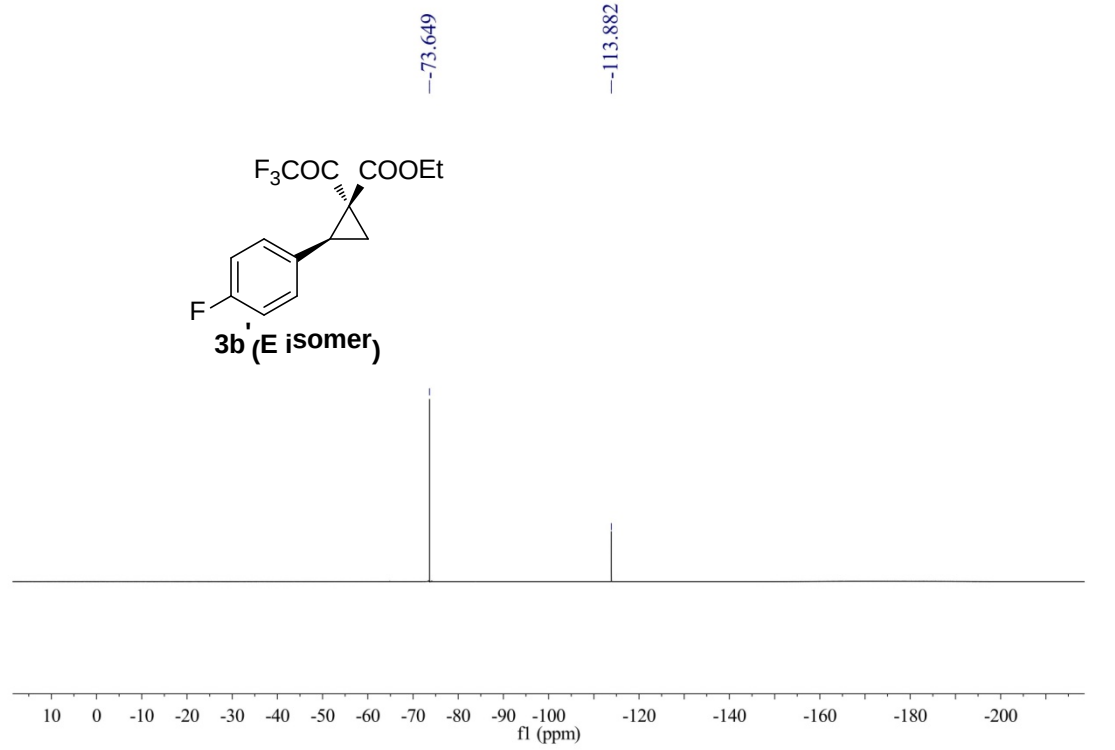
^{19}F NMR of *Z*-3a' in $CDCl_3$



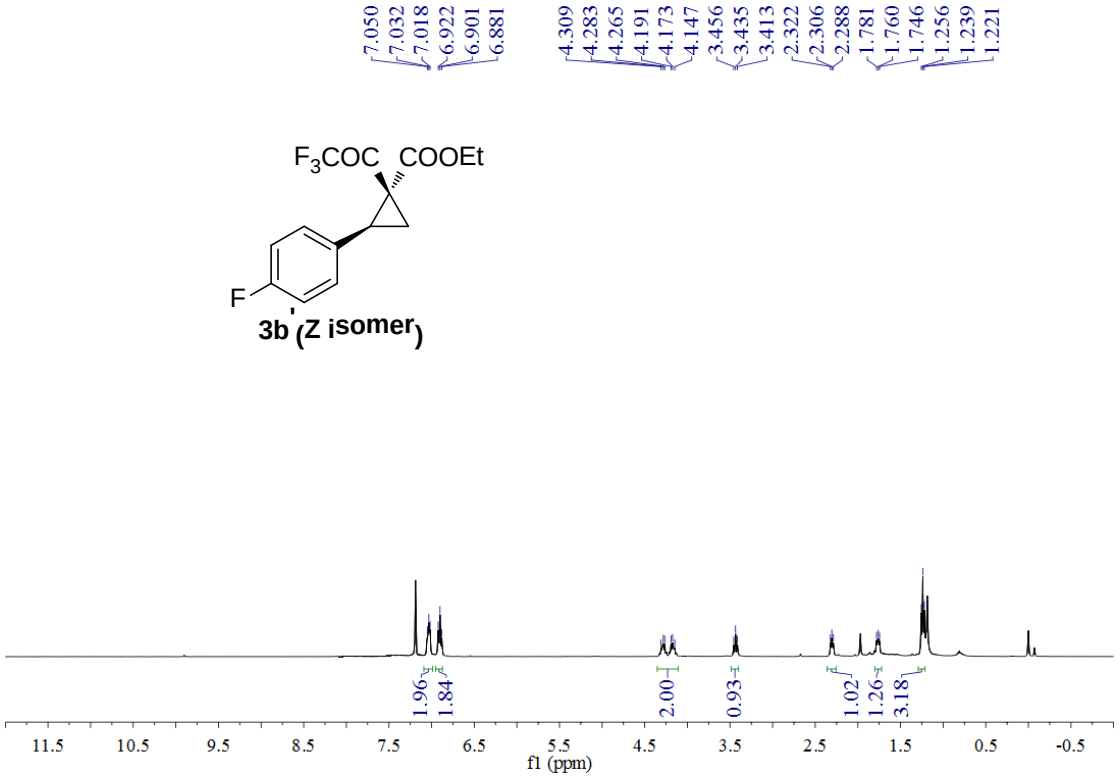
^{1}H NMR of *E*-3b' in $CDCl_3$



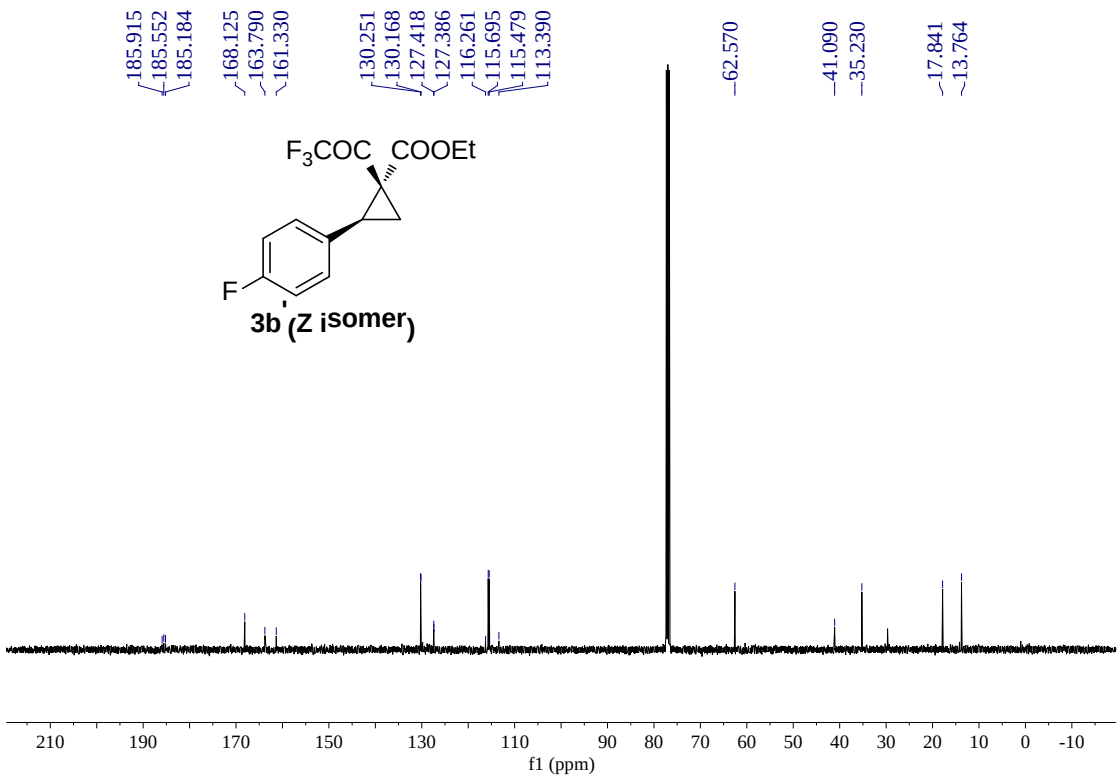
^{13}C NMR of *E*-3b' in $CDCl_3$



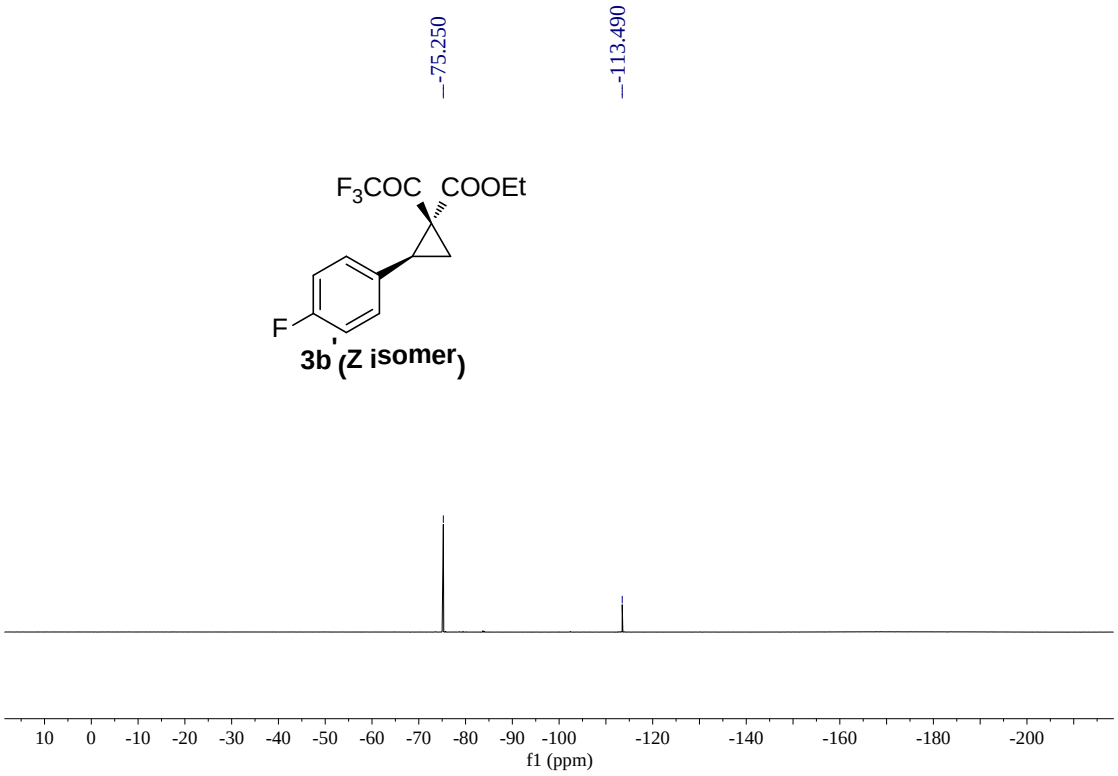
^{19}F NMR of *E*-3b' in $CDCl_3$



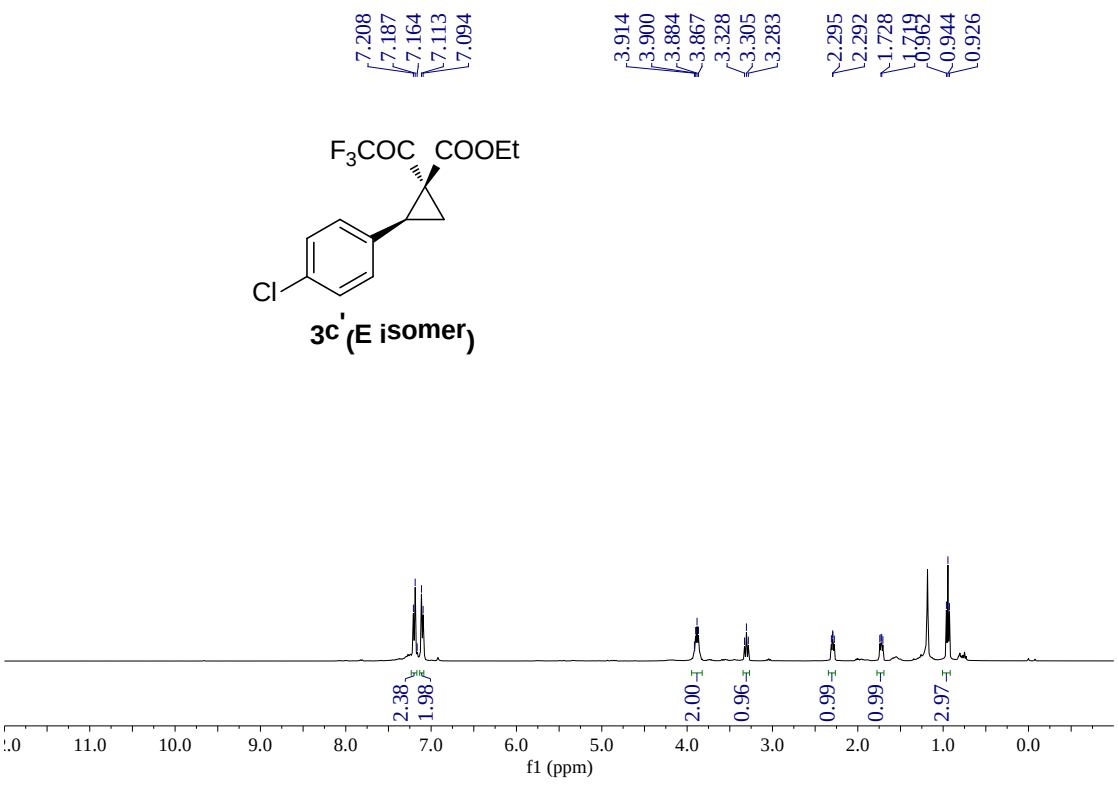
^{1}H NMR of *Z*-3b' in $CDCl_3$



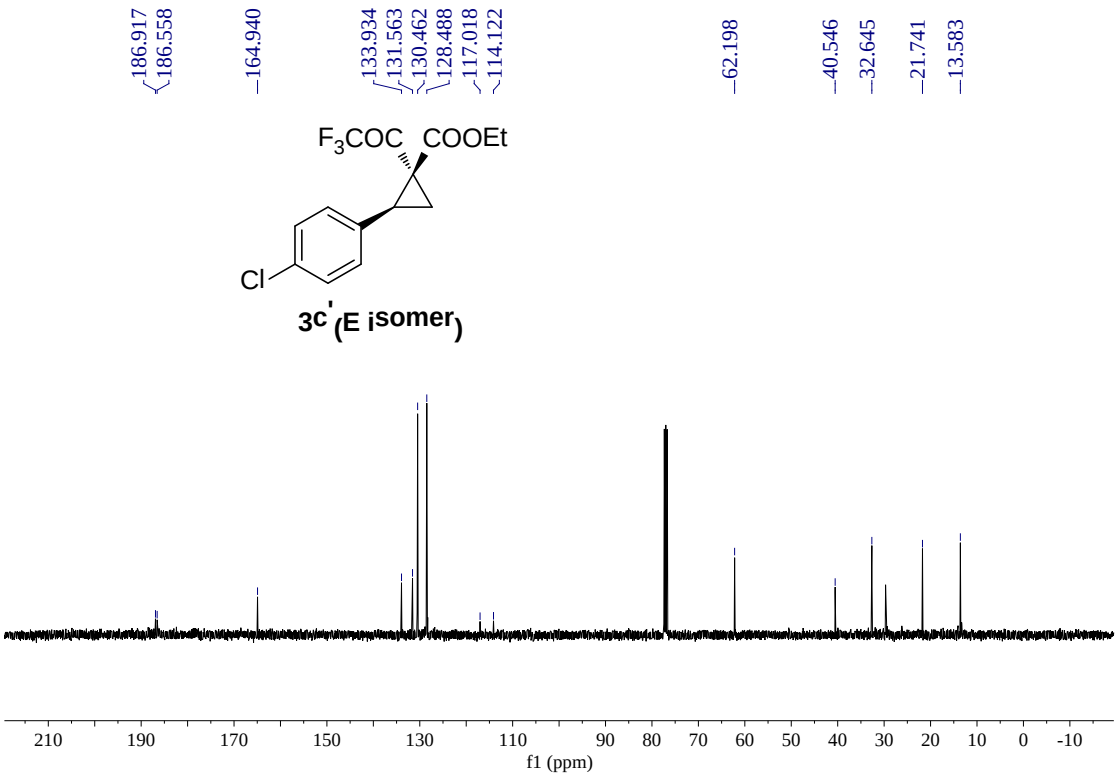
^{13}C NMR of *Z*-3b' in $CDCl_3$



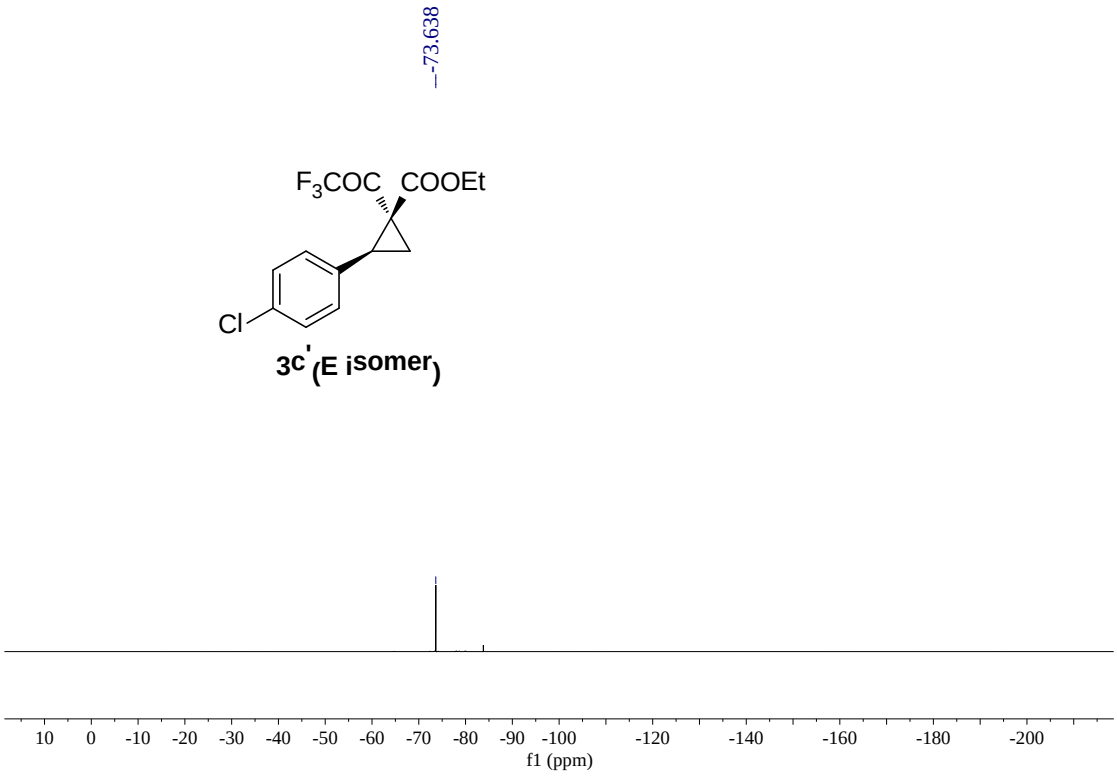
^{19}F NMR of *Z*-3b' in $CDCl_3$



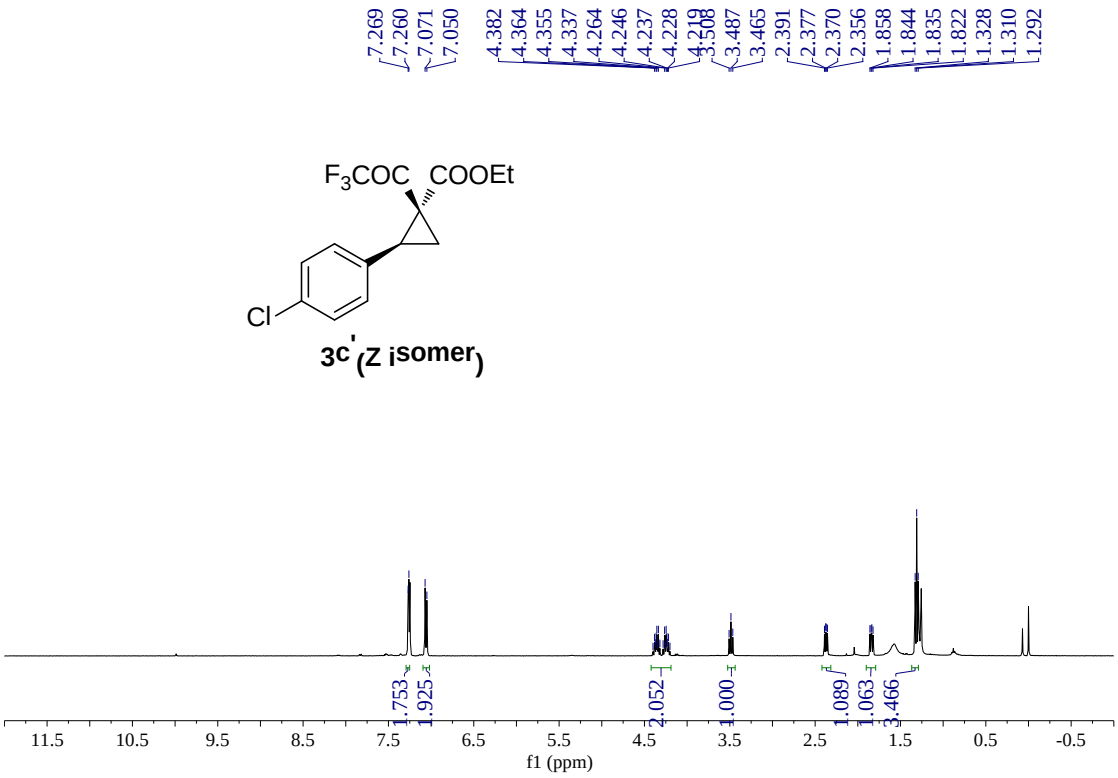
^{1}H NMR of *E*-3c' in $CDCl_3$



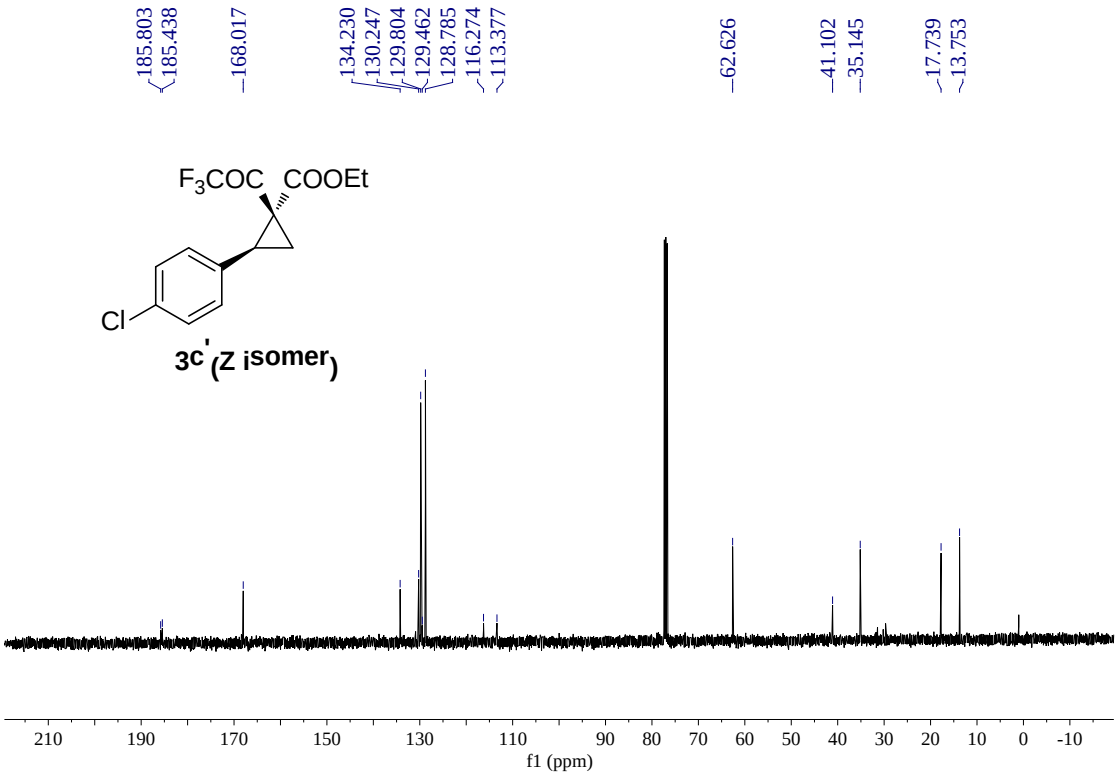
^{13}C NMR of *E*-3c' in $CDCl_3$



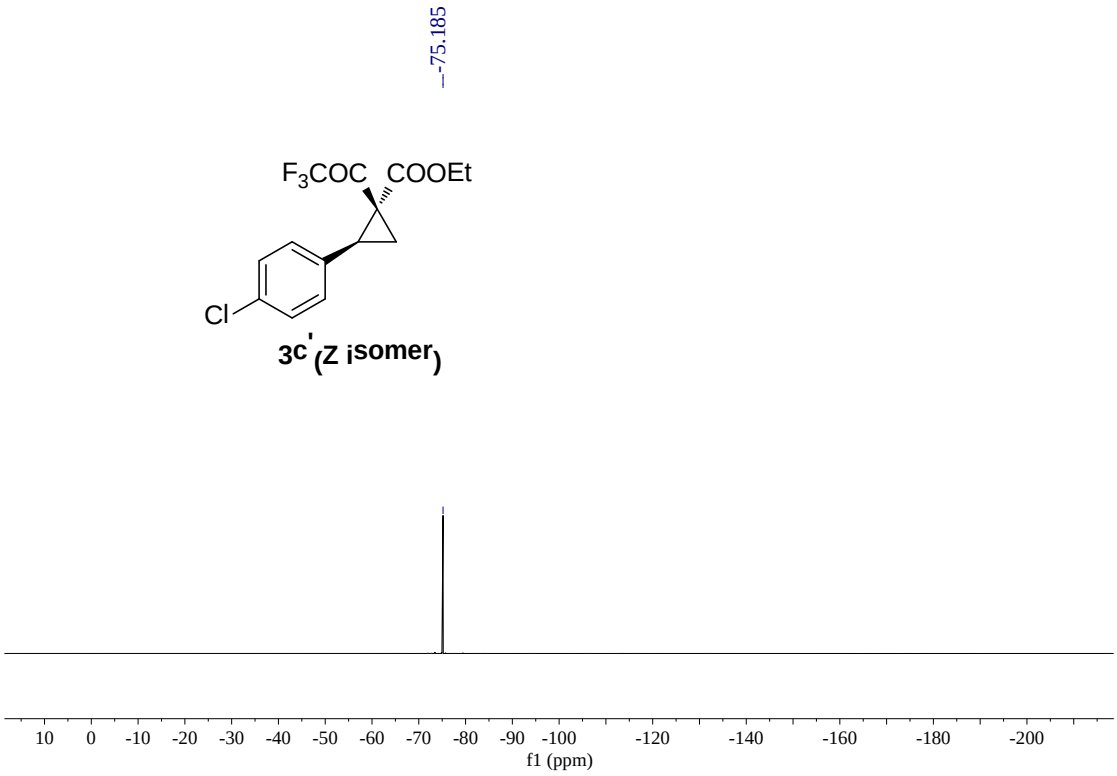
^{19}F NMR of *E*-3c' in $CDCl_3$



^{1}H NMR of *Z*-3c' in $CDCl_3$

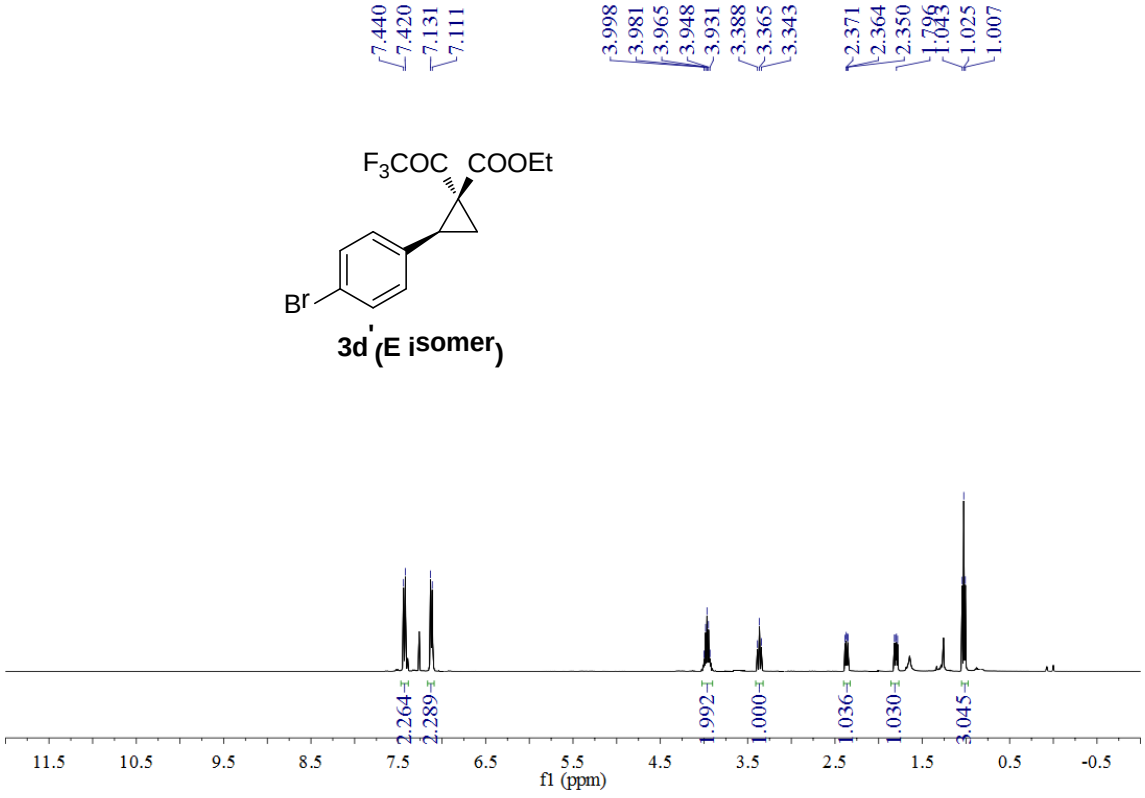


^{13}C NMR of *Z*-3c' in $CDCl_3$



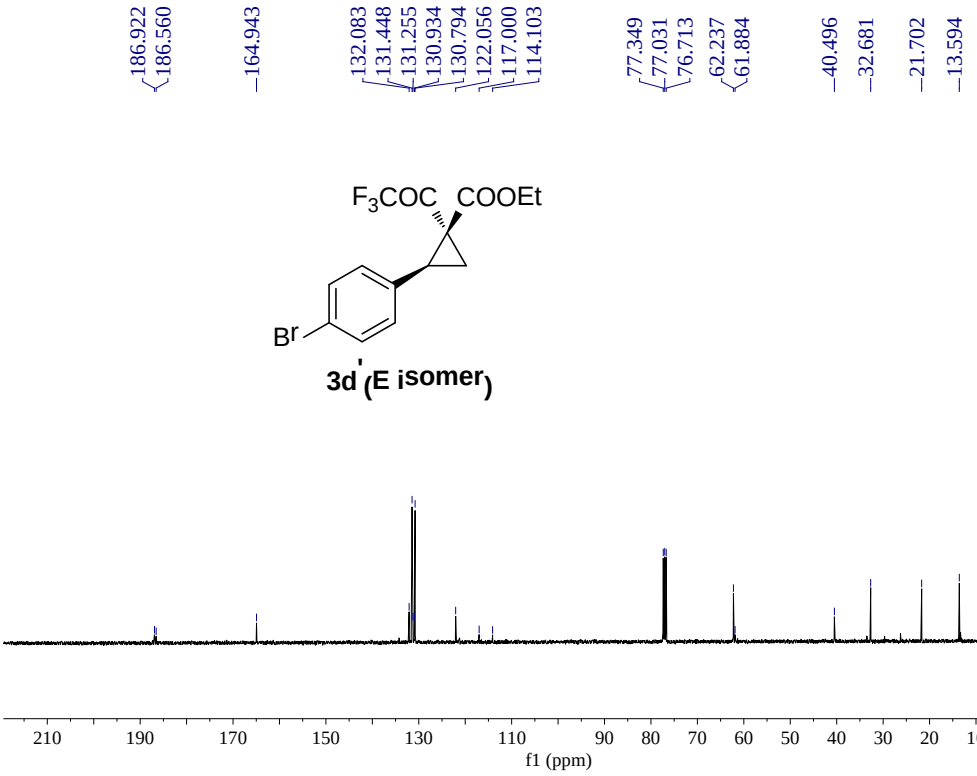
3c'(Z isomer)

^{19}F NMR of *Z*-3c' in $CDCl_3$



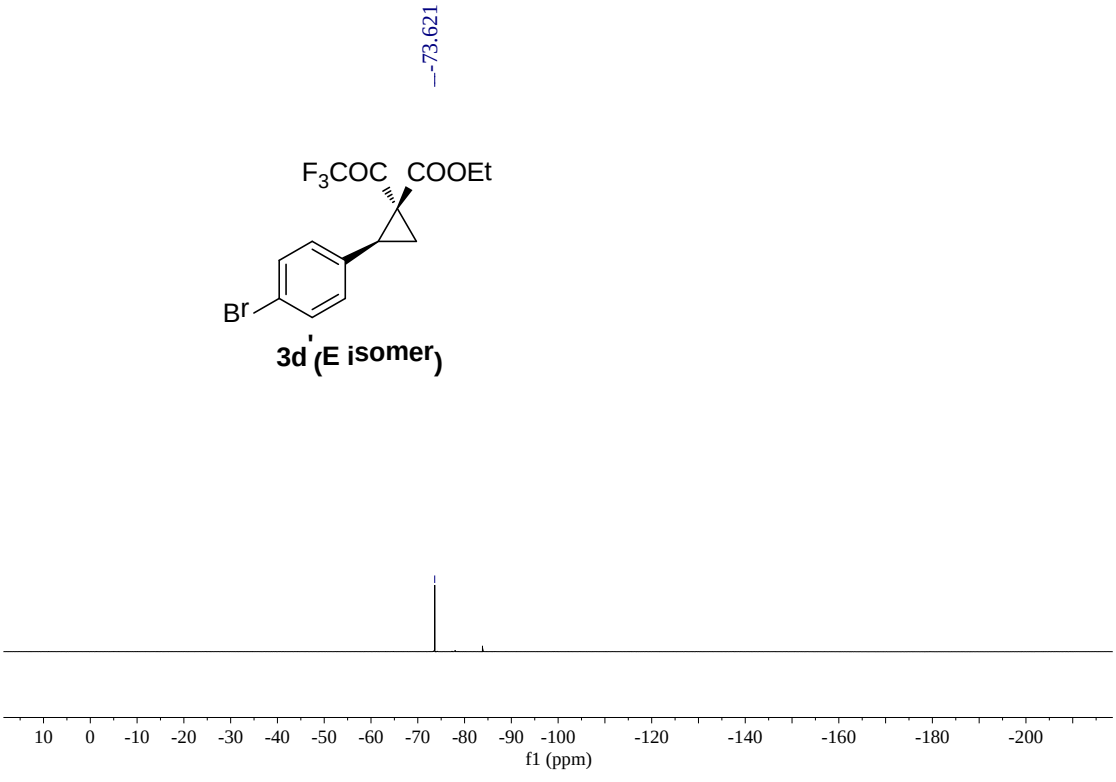
3d'(E isomer)

^{1}H NMR of *E*-3d' in $CDCl_3$



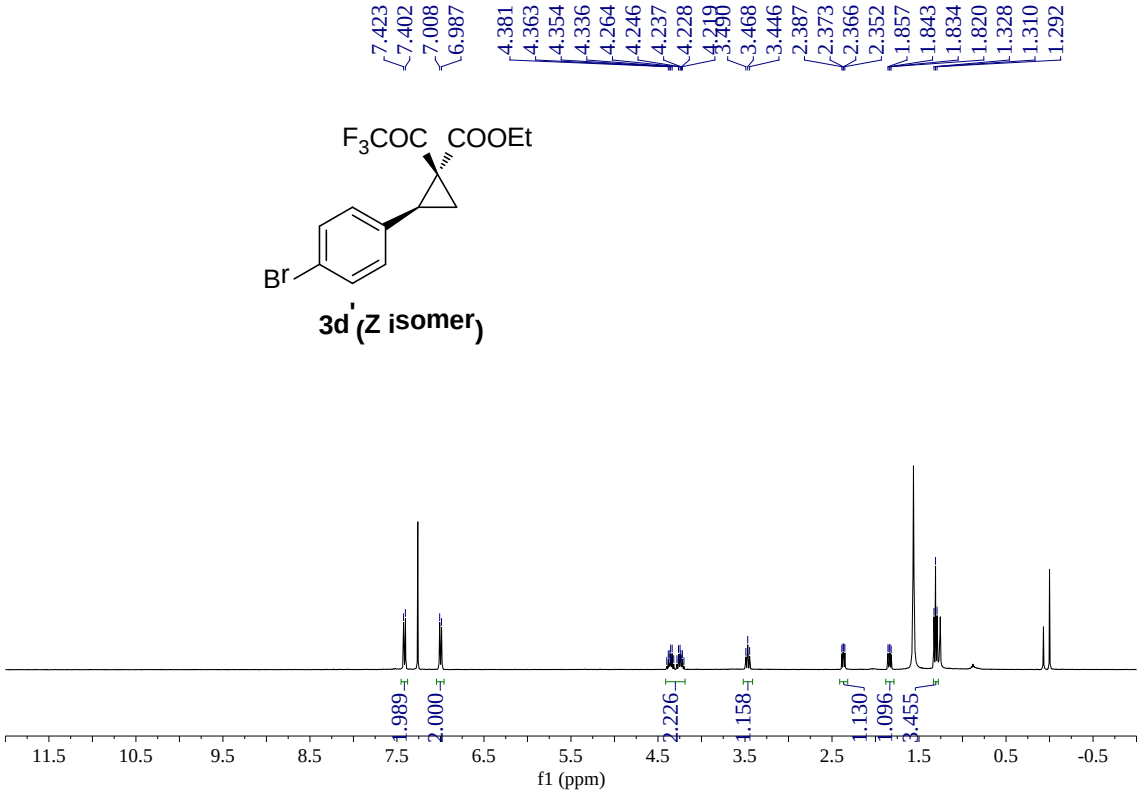
3d'(E isomer)

^{13}C NMR of *E*-3d' in $CDCl_3$



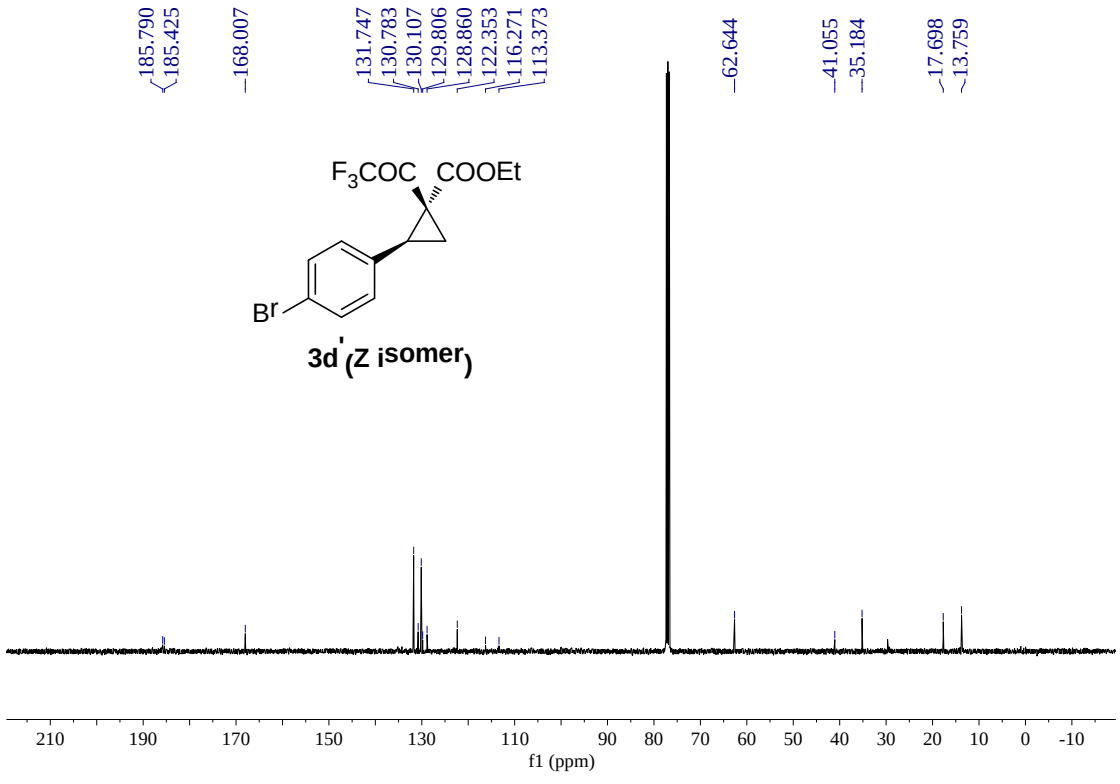
3d'(E isomer)

^{19}F NMR of *E*-3d' in $CDCl_3$



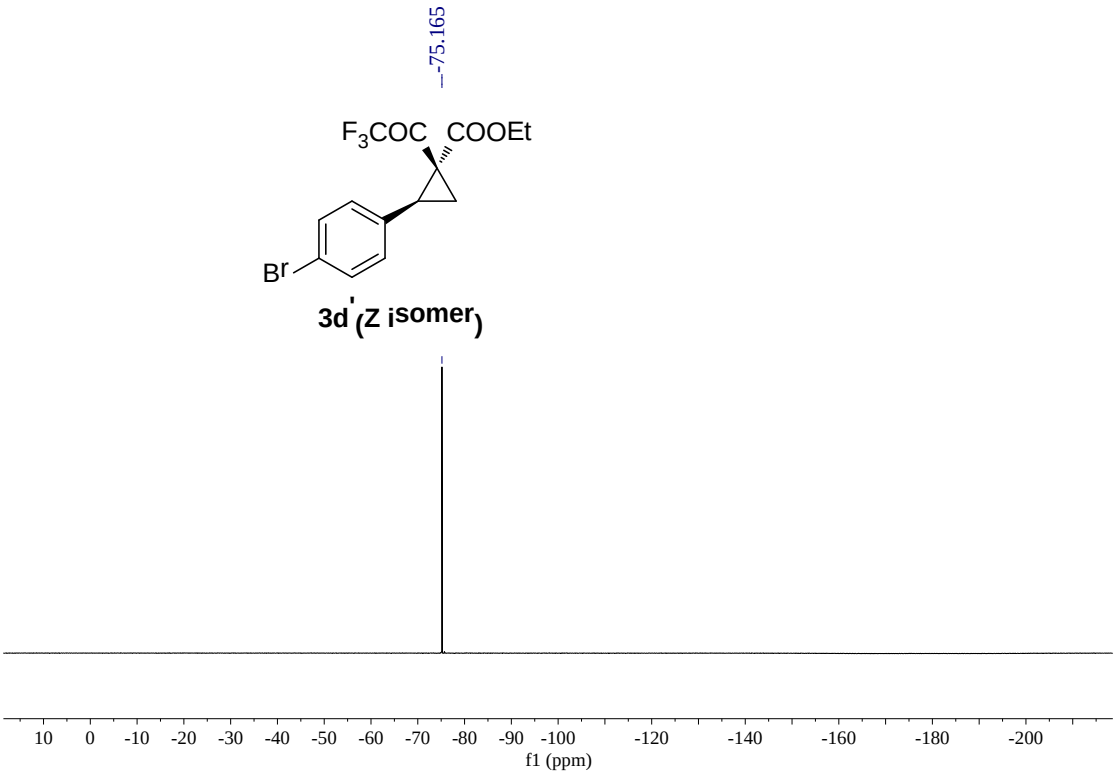
3d'(Z isomer)

^{1}H NMR of *Z*-3d' in $CDCl_3$



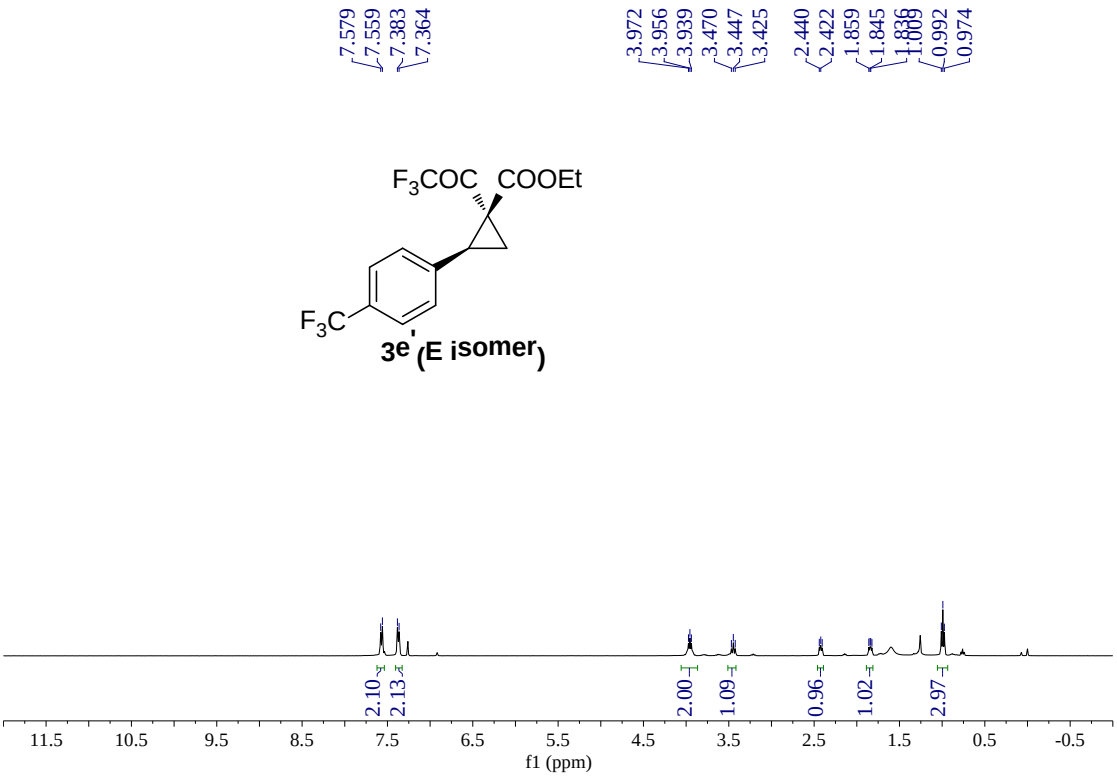
3d'(Z isomer)

^{13}C NMR of *Z*-3d' in $CDCl_3$



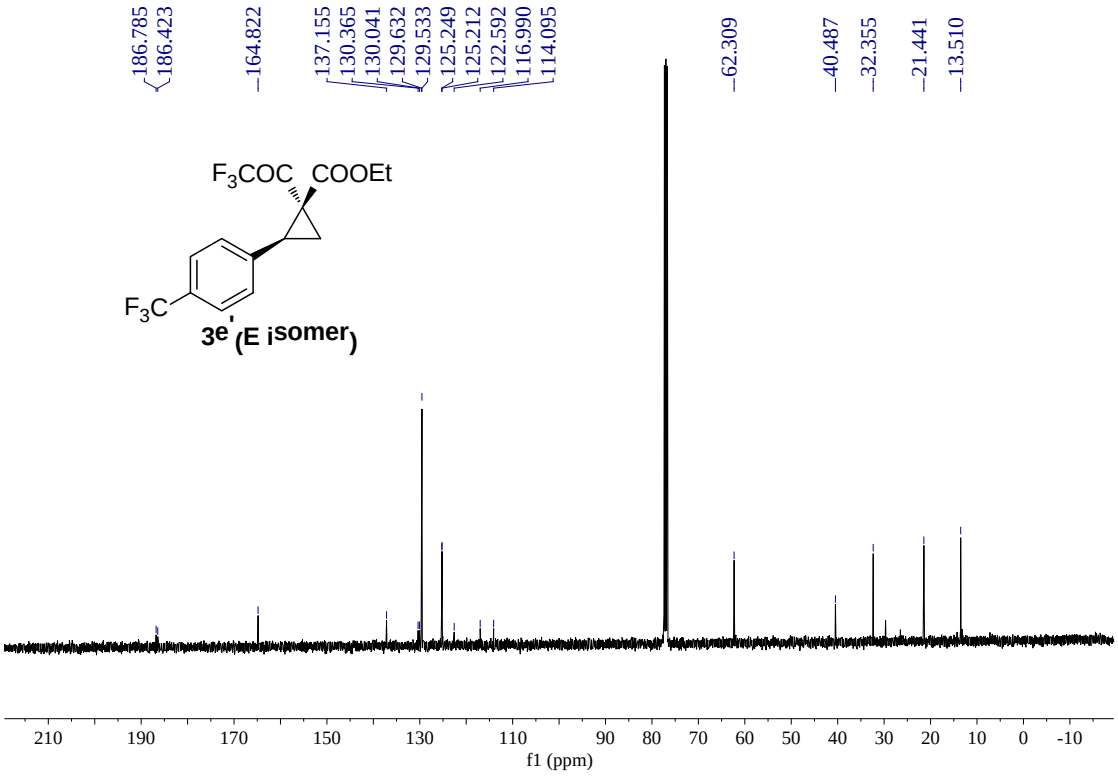
3d' (Z isomer)

^{19}F NMR of *Z*-3d' in $CDCl_3$

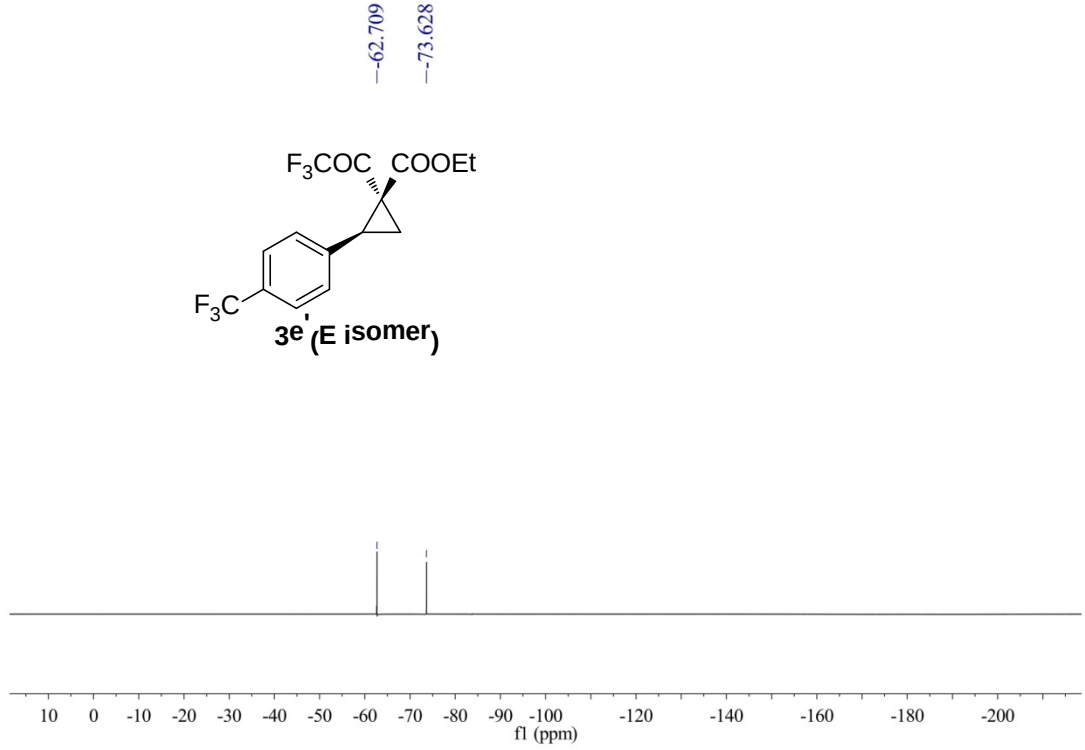


3e' (E isomer)

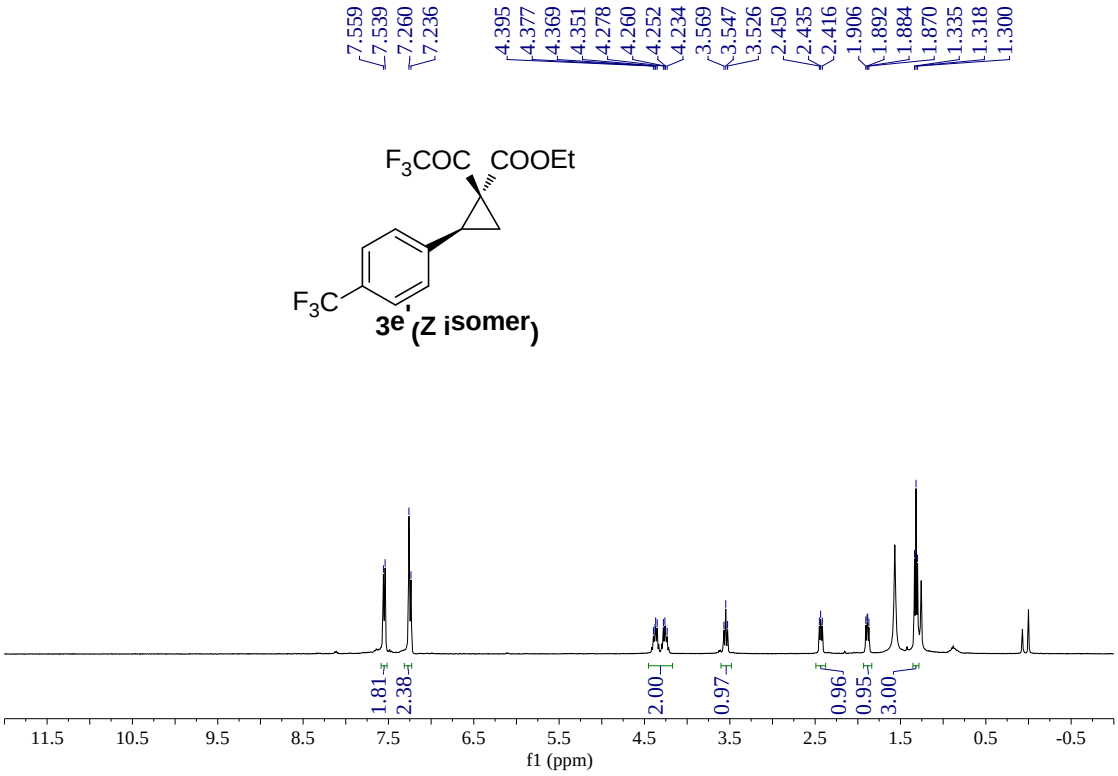
^{1}H NMR of *E*-3e' in $CDCl_3$



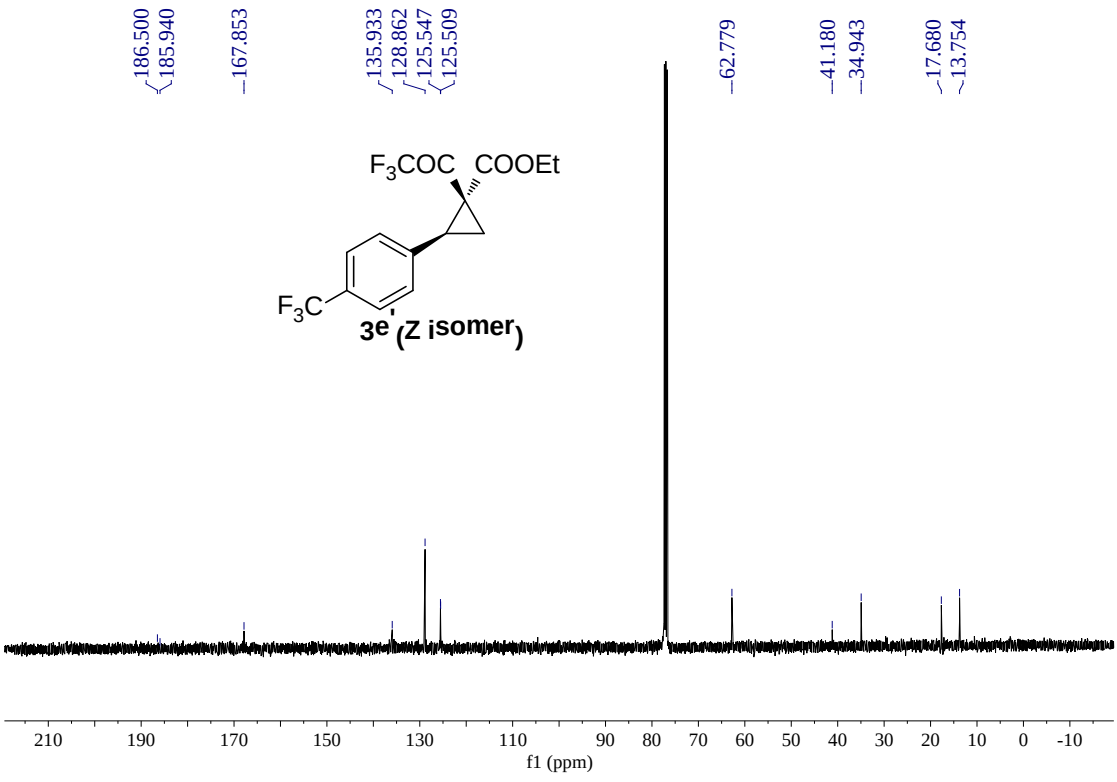
^{13}C NMR of *E*-3e' in $CDCl_3$



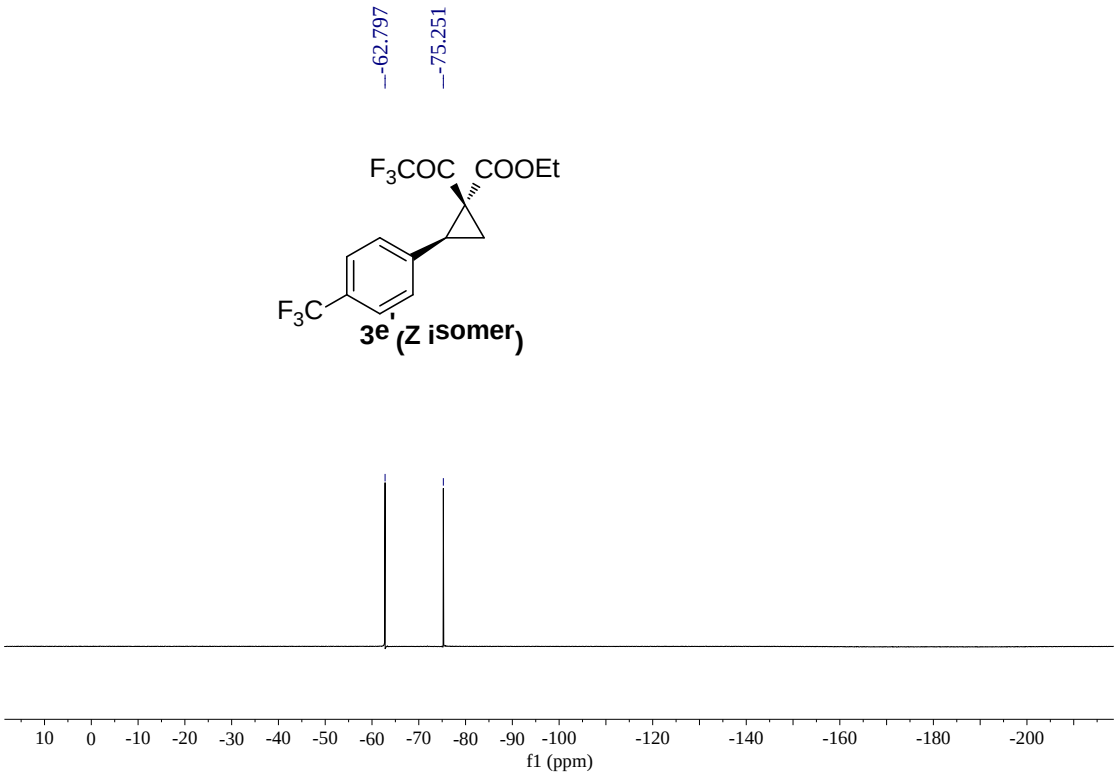
^{19}F NMR of *E*-3e' in $CDCl_3$



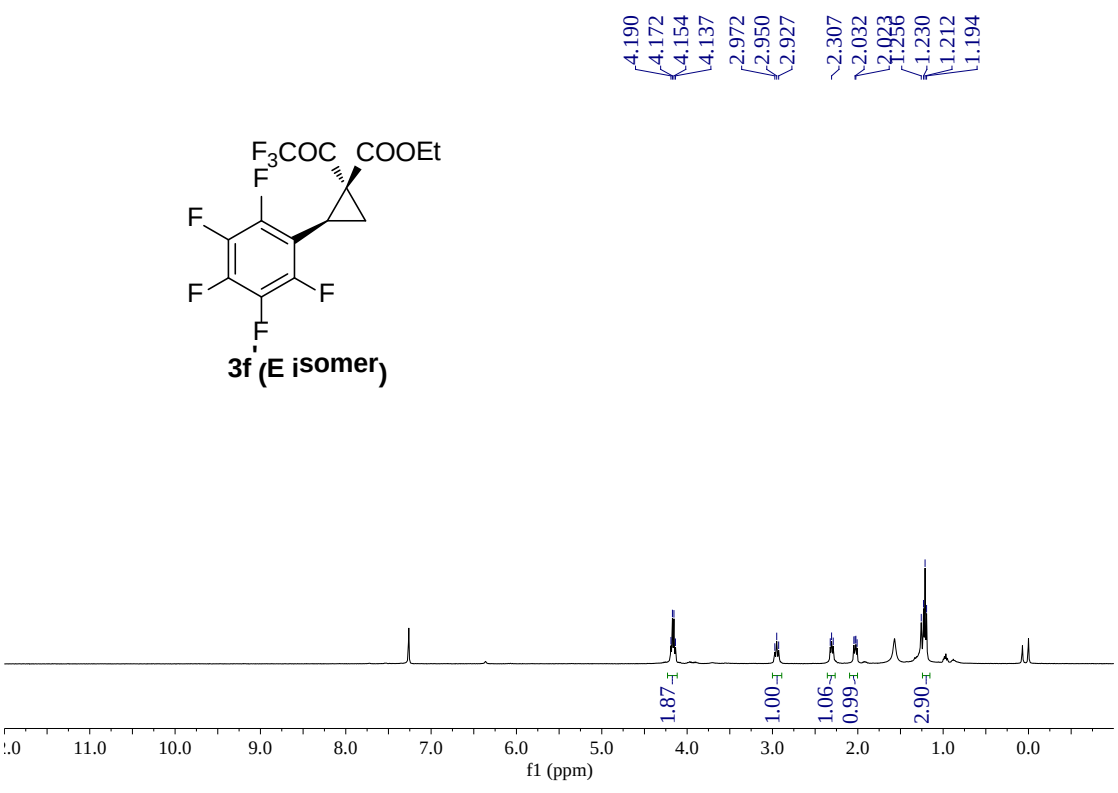
^{1}H NMR of *Z*-3e' in $CDCl_3$



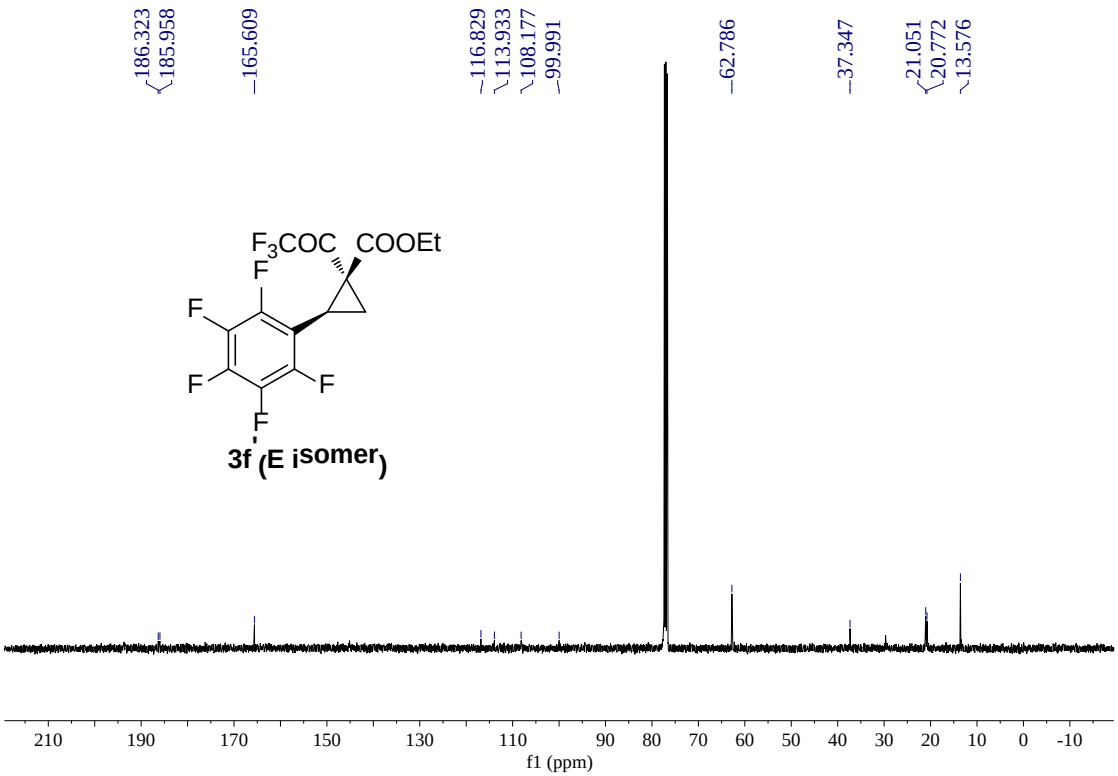
^{13}C NMR of *Z*-3e' in $CDCl_3$



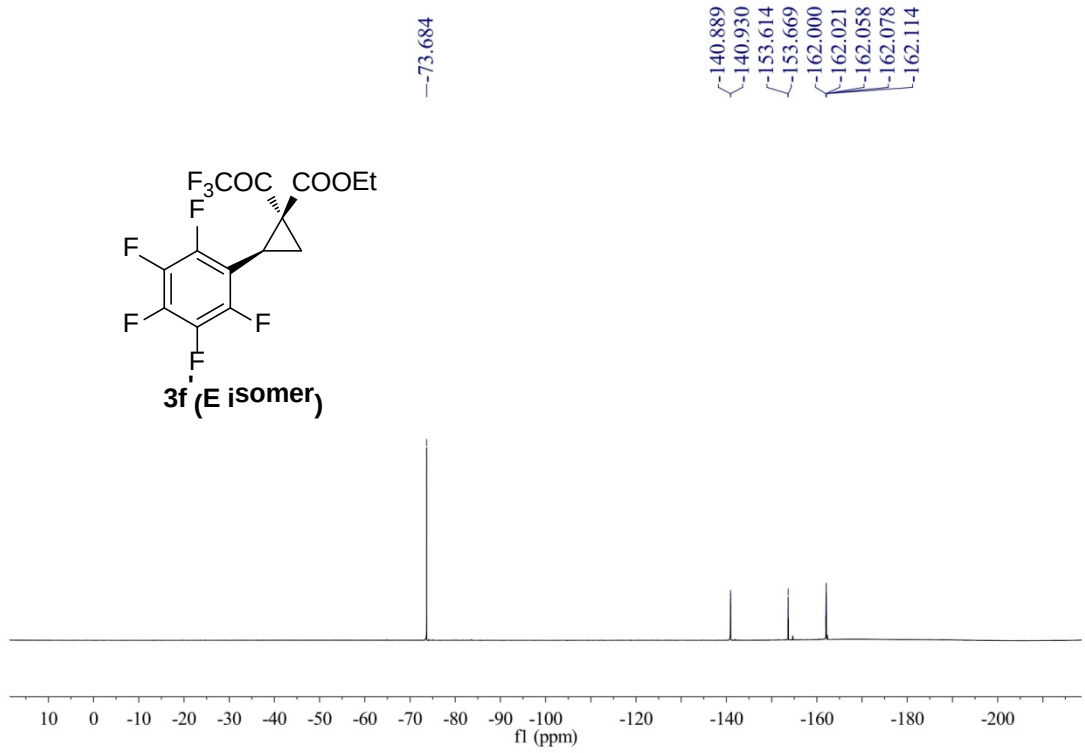
^{19}F NMR of *Z*-3e' in $CDCl_3$



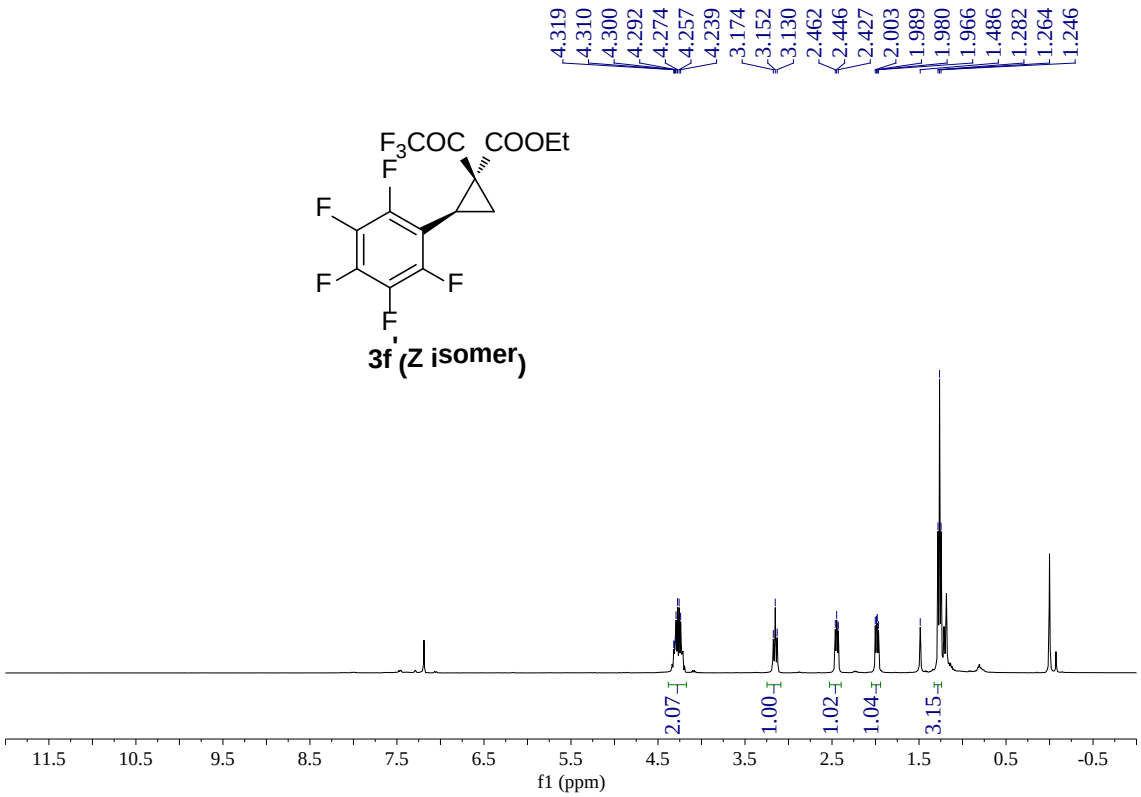
^{1}H NMR of *E*-3f' in $CDCl_3$



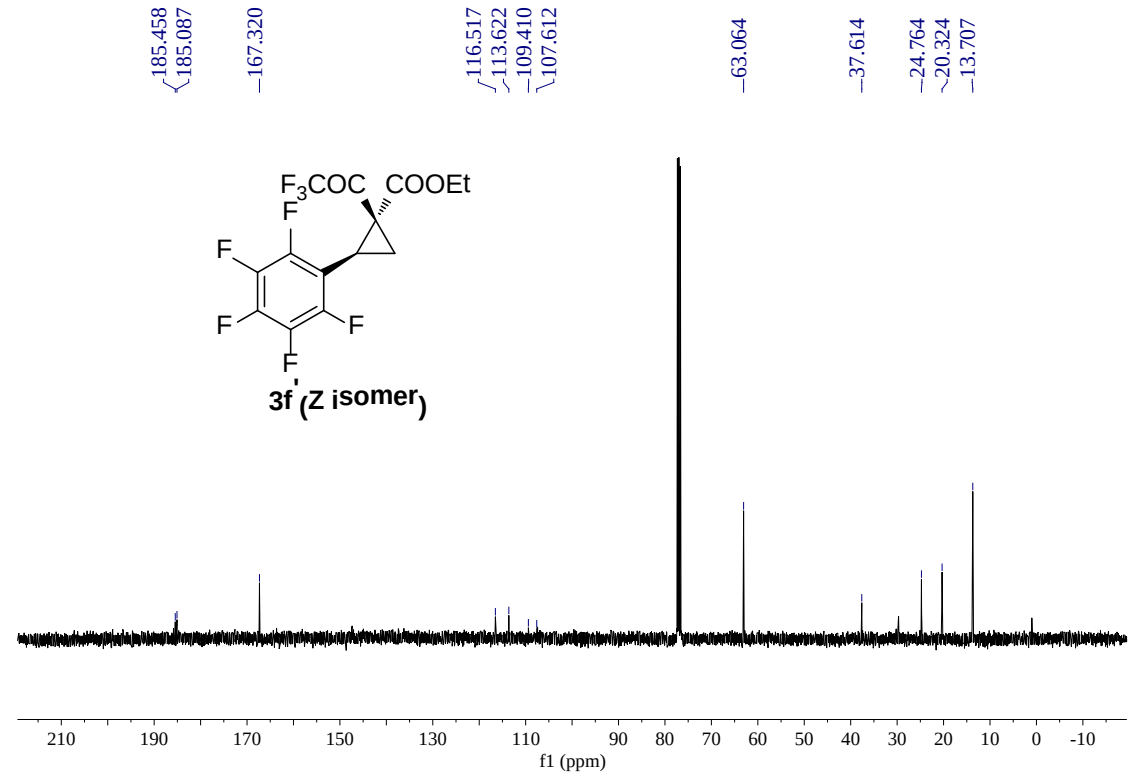
^{13}C NMR of *E*-3f' in $CDCl_3$



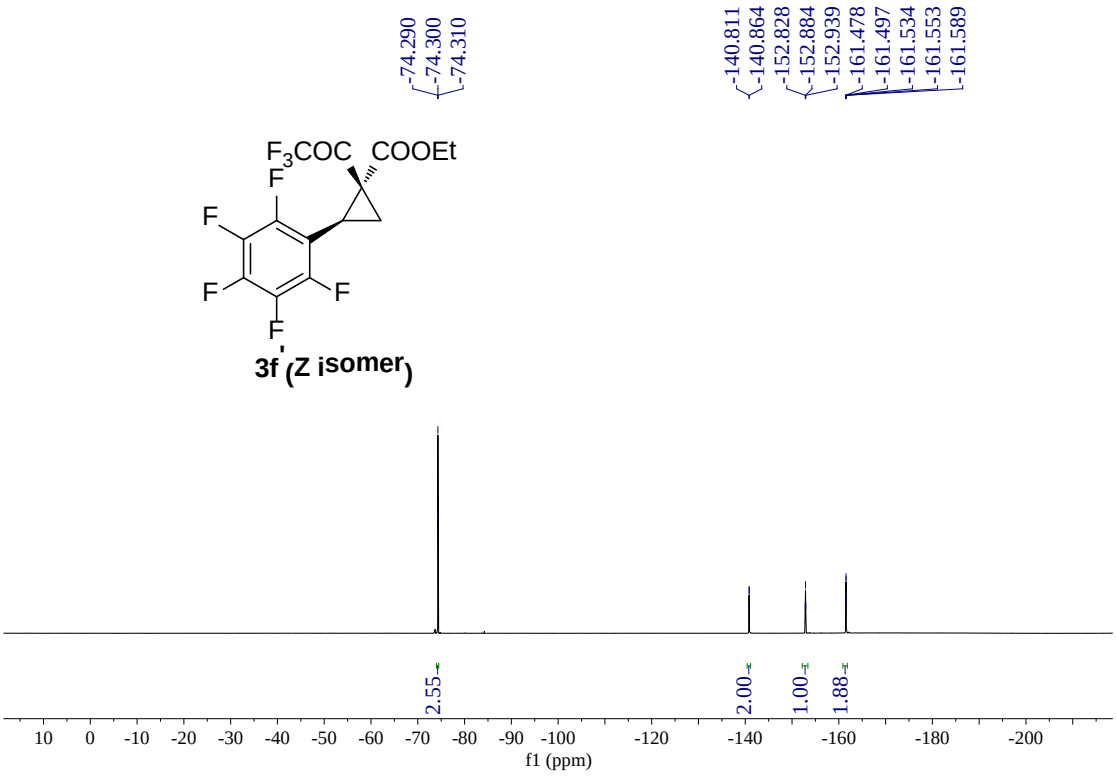
^{19}F NMR of *E*-3f' in $CDCl_3$



^{1}H NMR of *Z*-3f' in $CDCl_3$

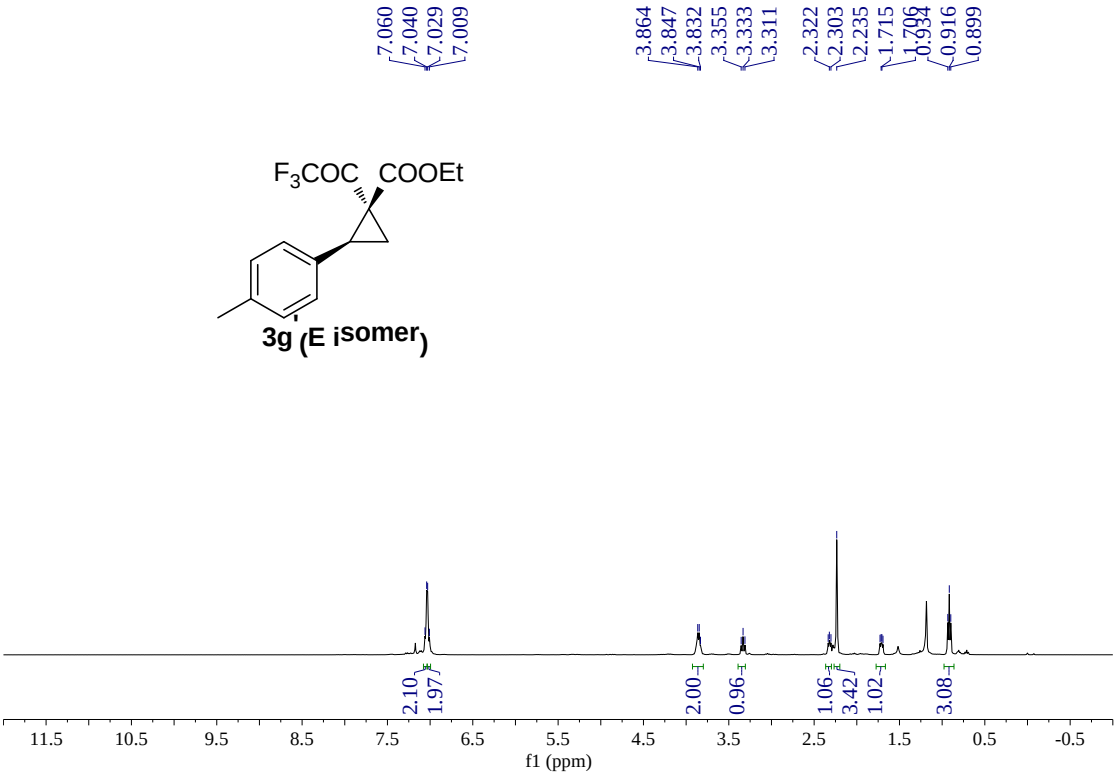


^{13}C NMR of *Z*-3f' in $CDCl_3$



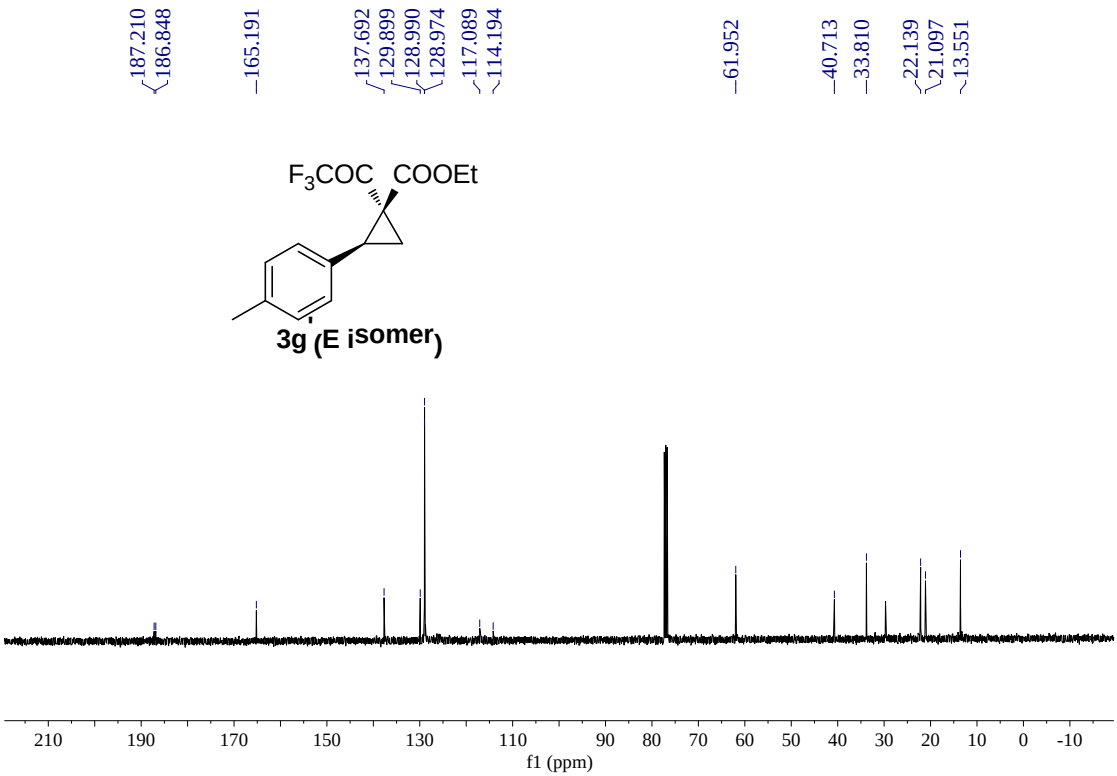
3f' (Z isomer)

^{19}F NMR of *Z*-3f' in $CDCl_3$

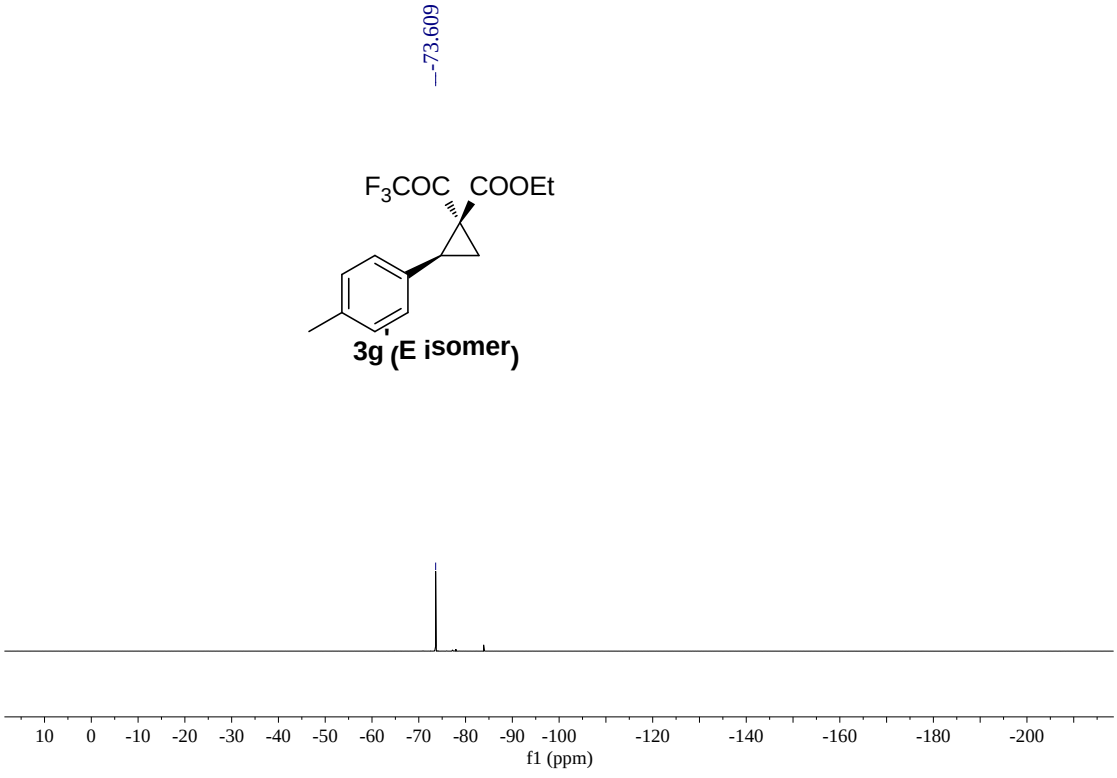


3g (E isomer)

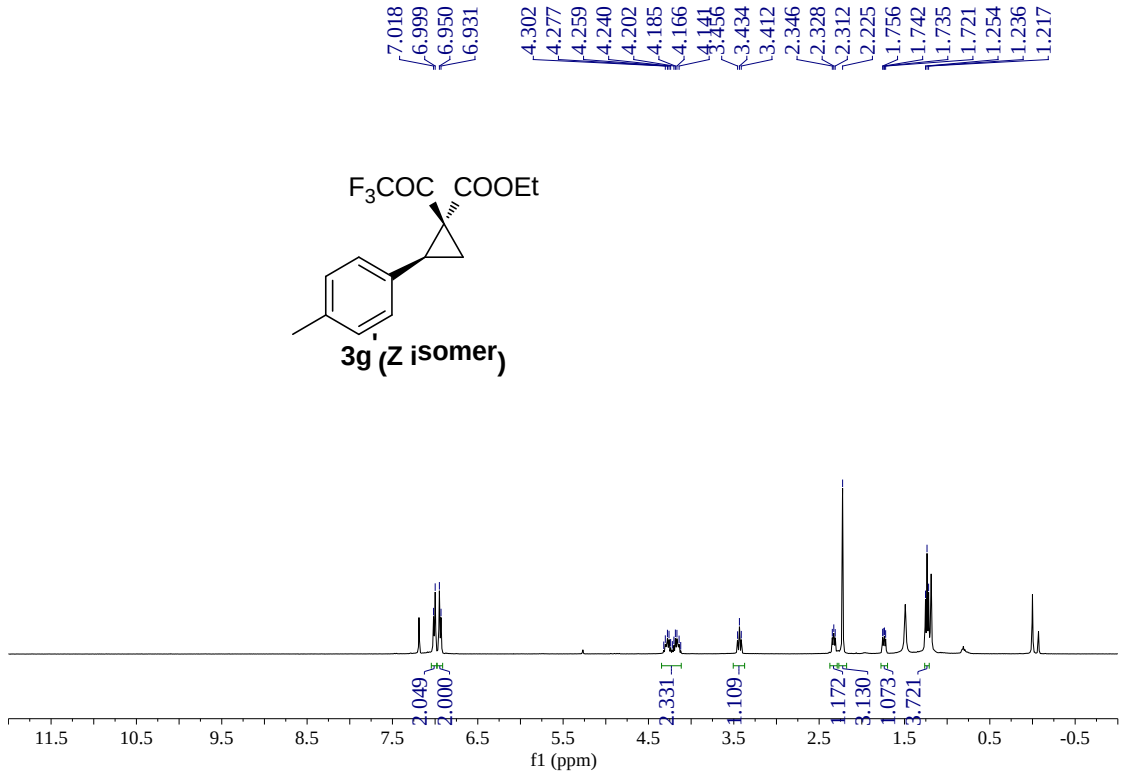
^{1}H NMR of *E*-3g' in $CDCl_3$



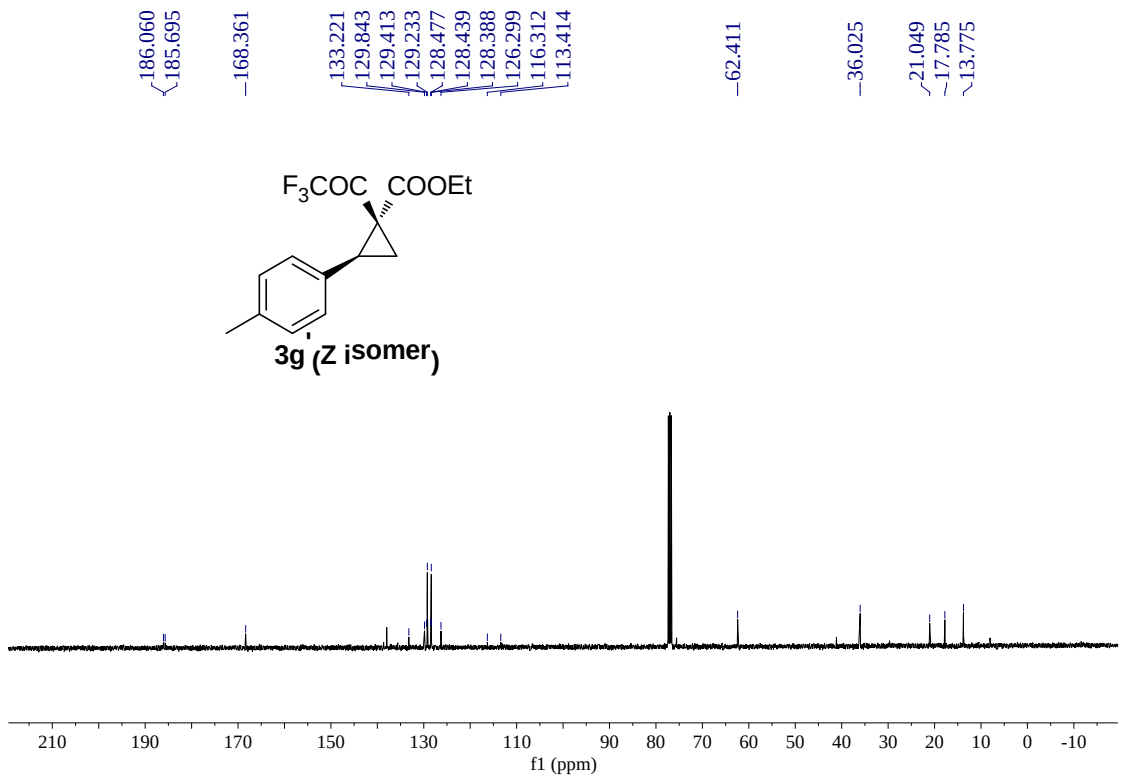
^{13}C NMR of *E*-3g' in $CDCl_3$



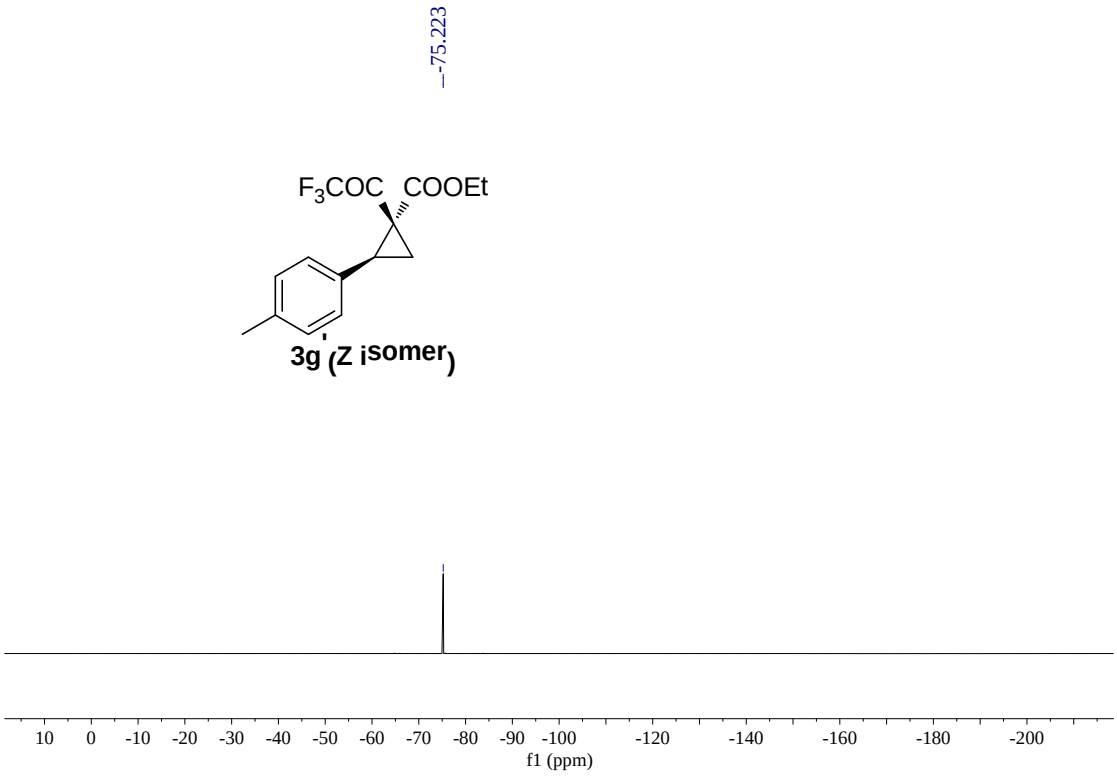
^{19}F NMR of *E*-3g' in $CDCl_3$



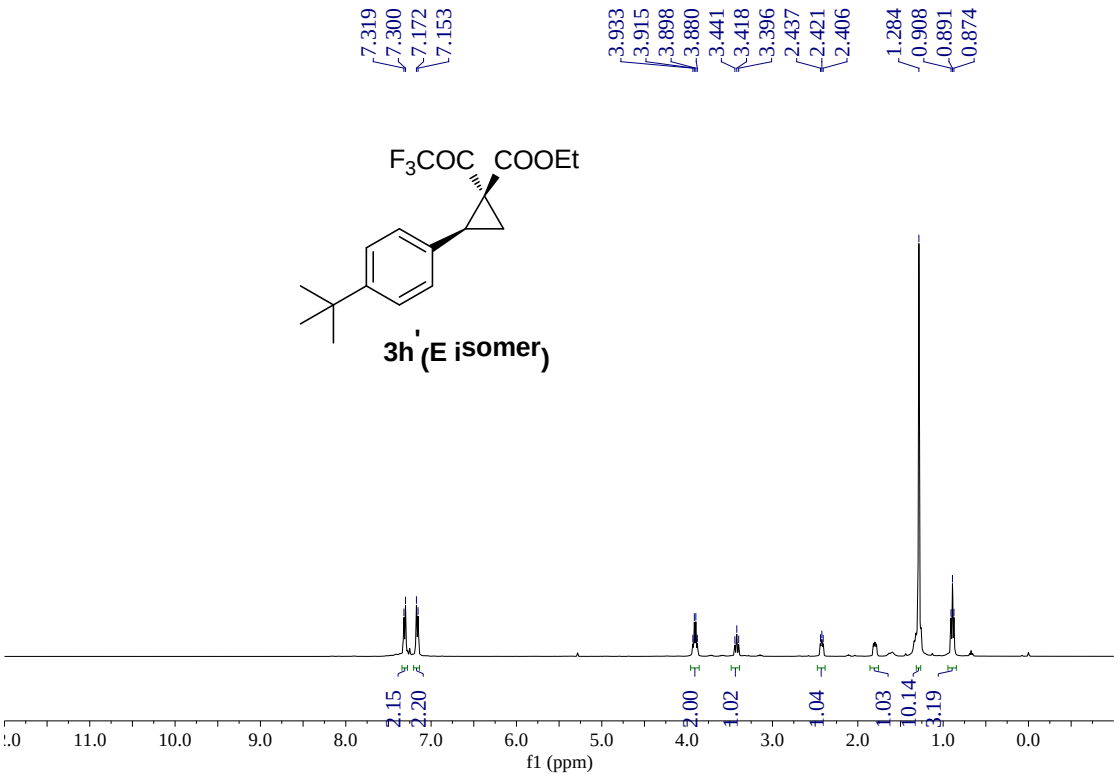
^{1}H NMR of *Z*-3g' in $CDCl_3$



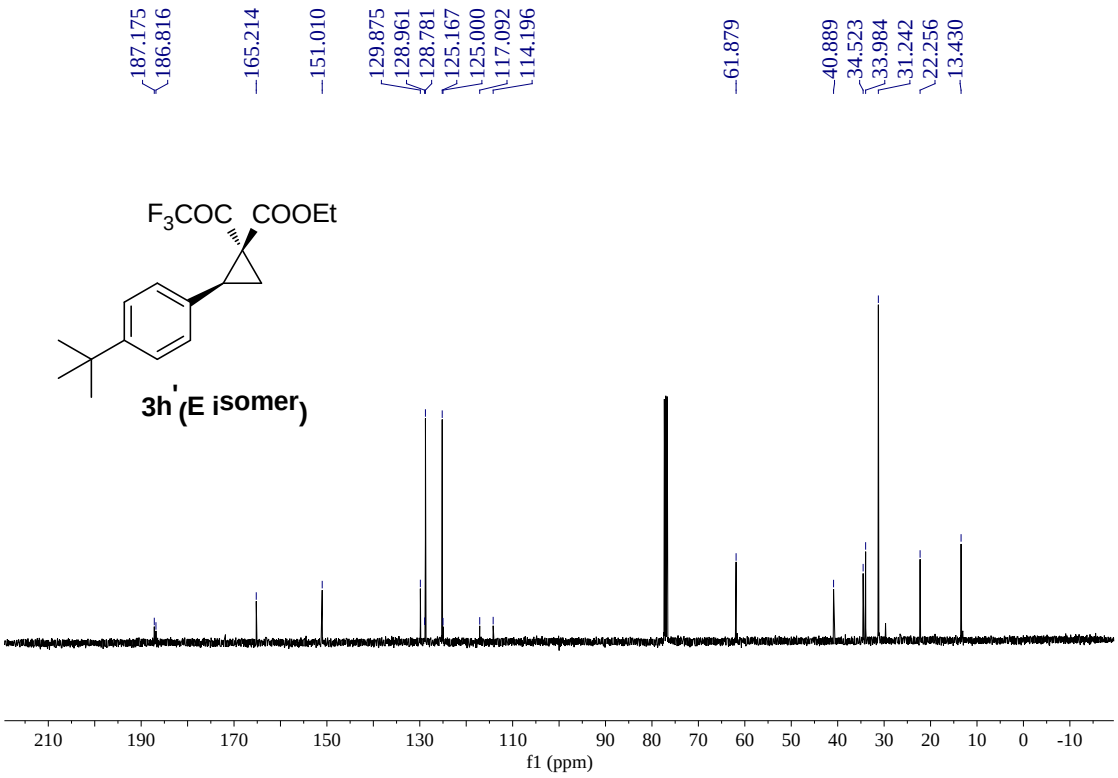
^{13}C NMR of *Z*-3g' in $CDCl_3$



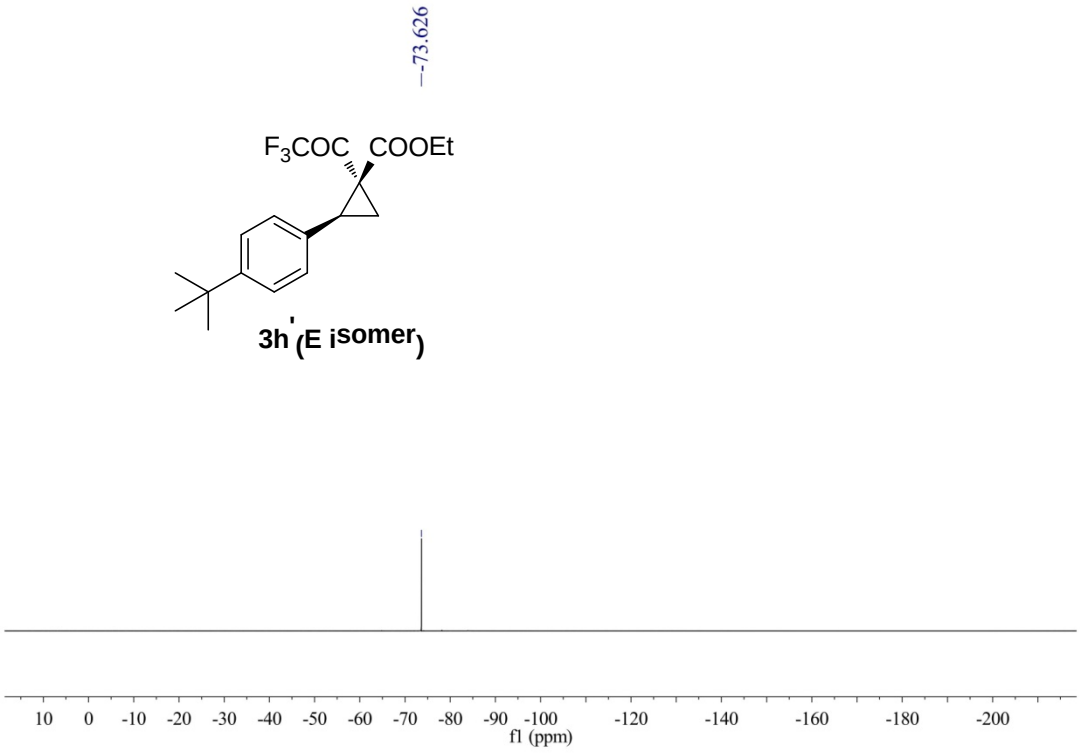
^{19}F NMR of *Z*-3g' in $CDCl_3$



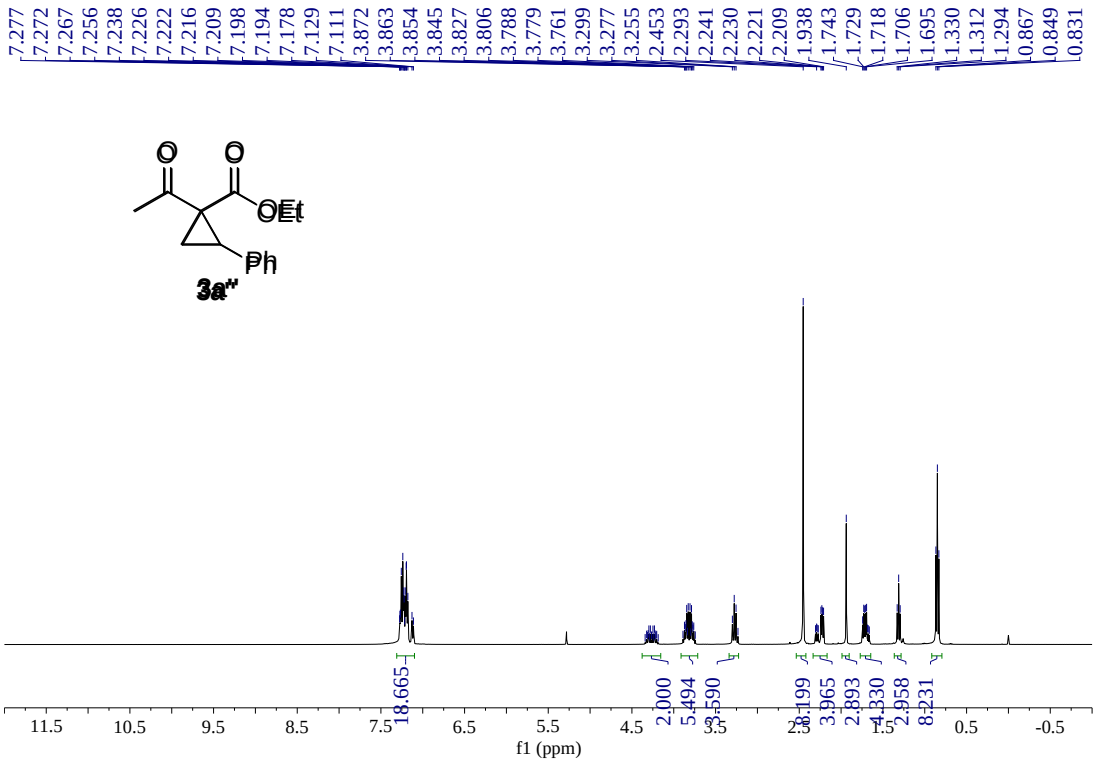
^{1}H NMR of *E*-3h' in $CDCl_3$



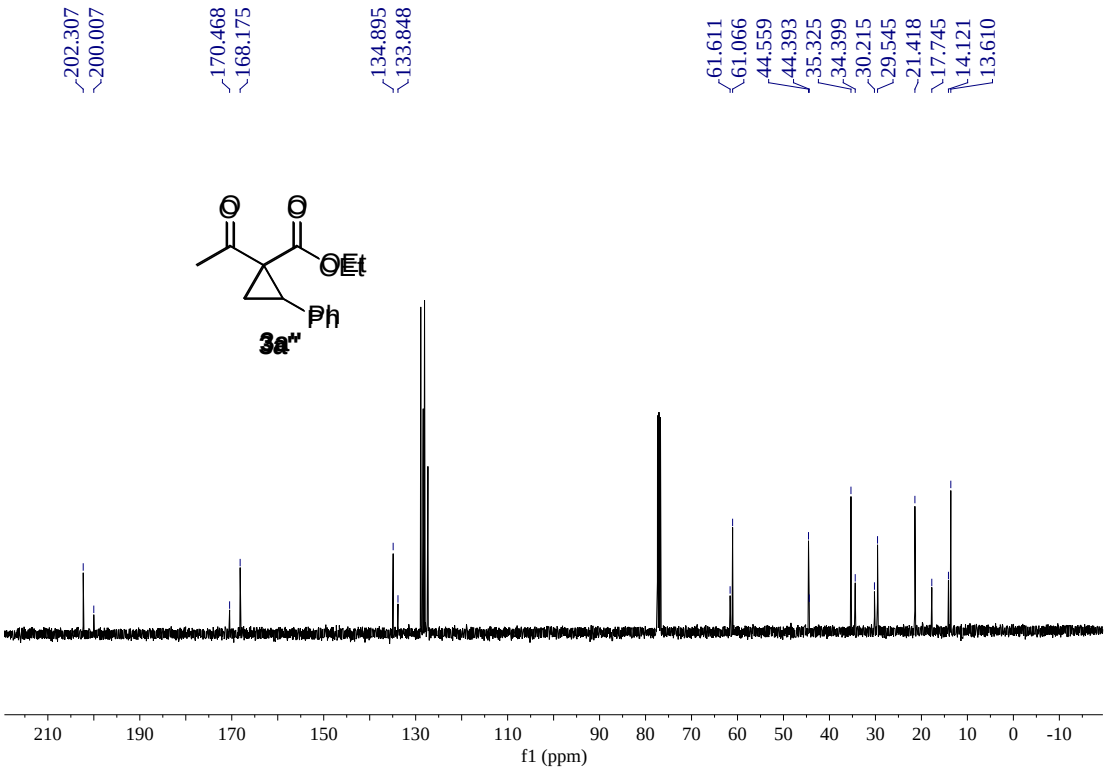
^{13}C NMR of *E*-3h' in $CDCl_3$



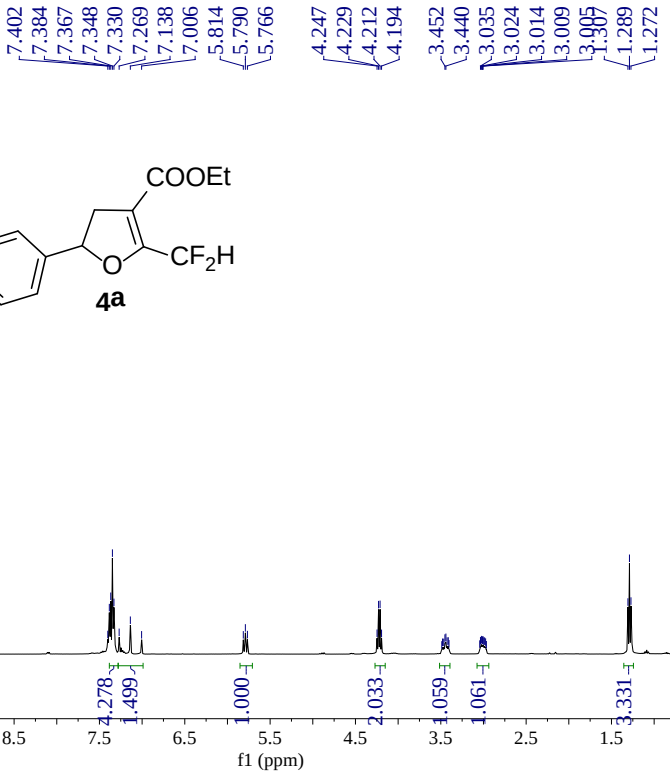
^{19}F NMR of *E*-3h' in $CDCl_3$



^{1}H NMR of 3a'' in $CDCl_3$



^{13}C NMR of 3a'' in $CDCl_3$



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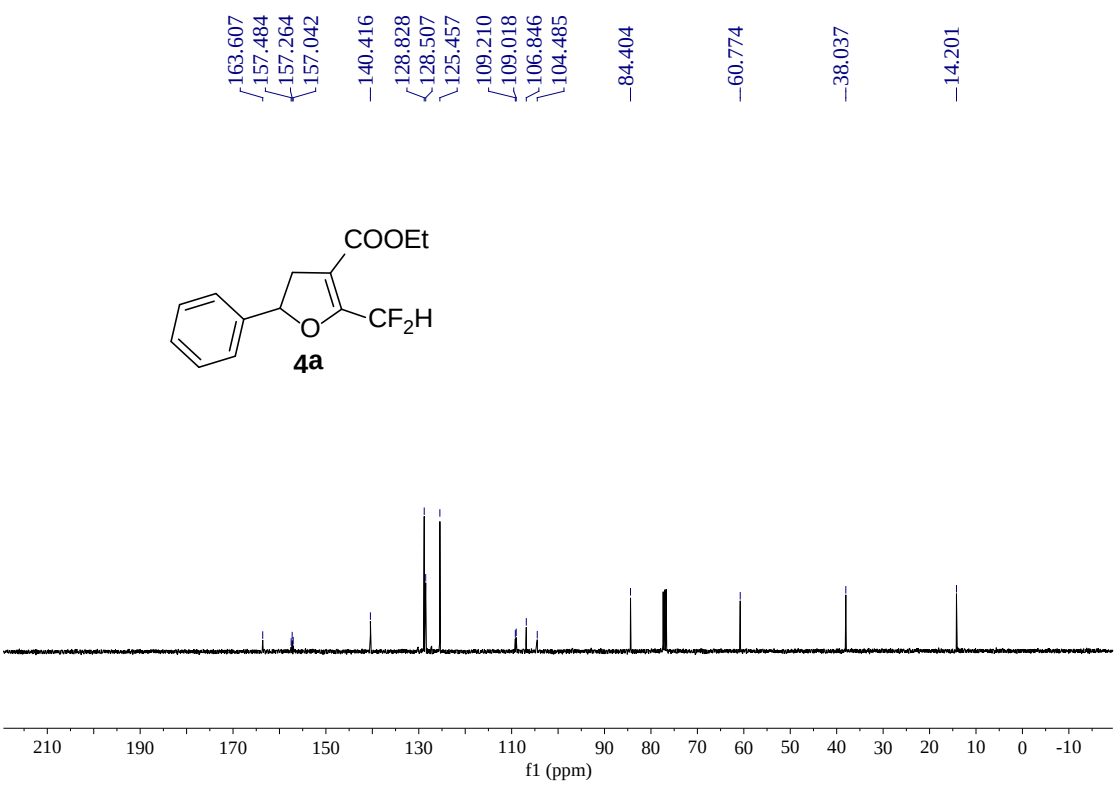
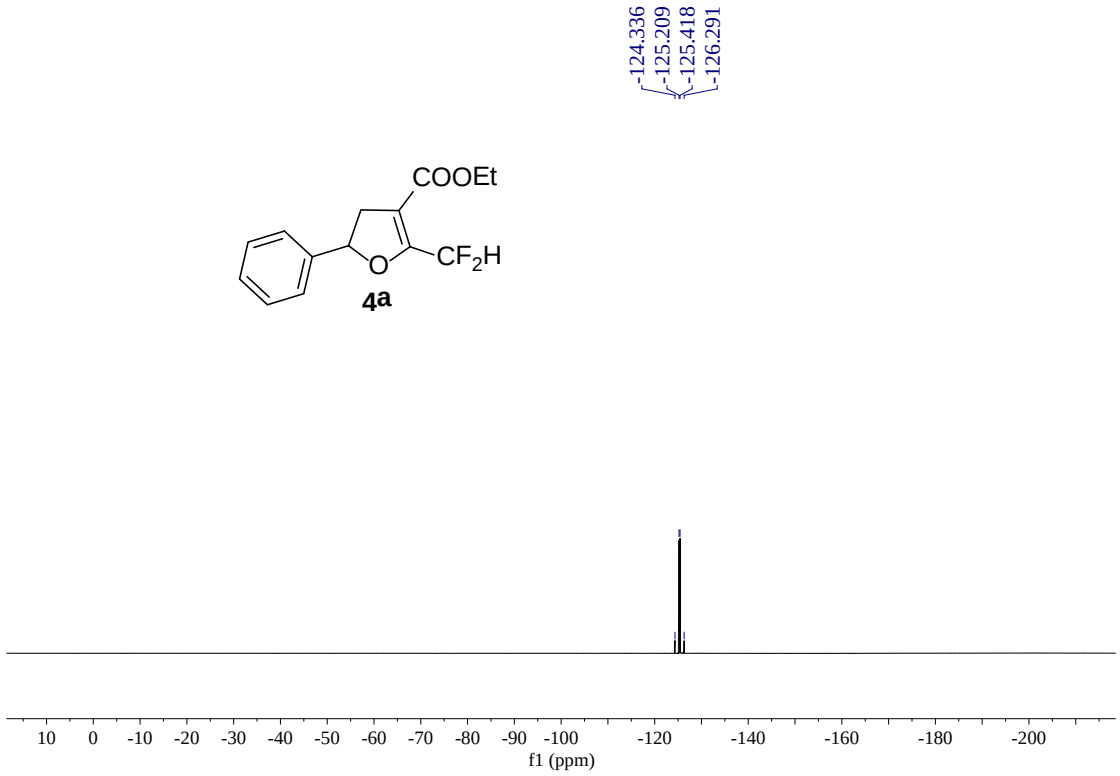
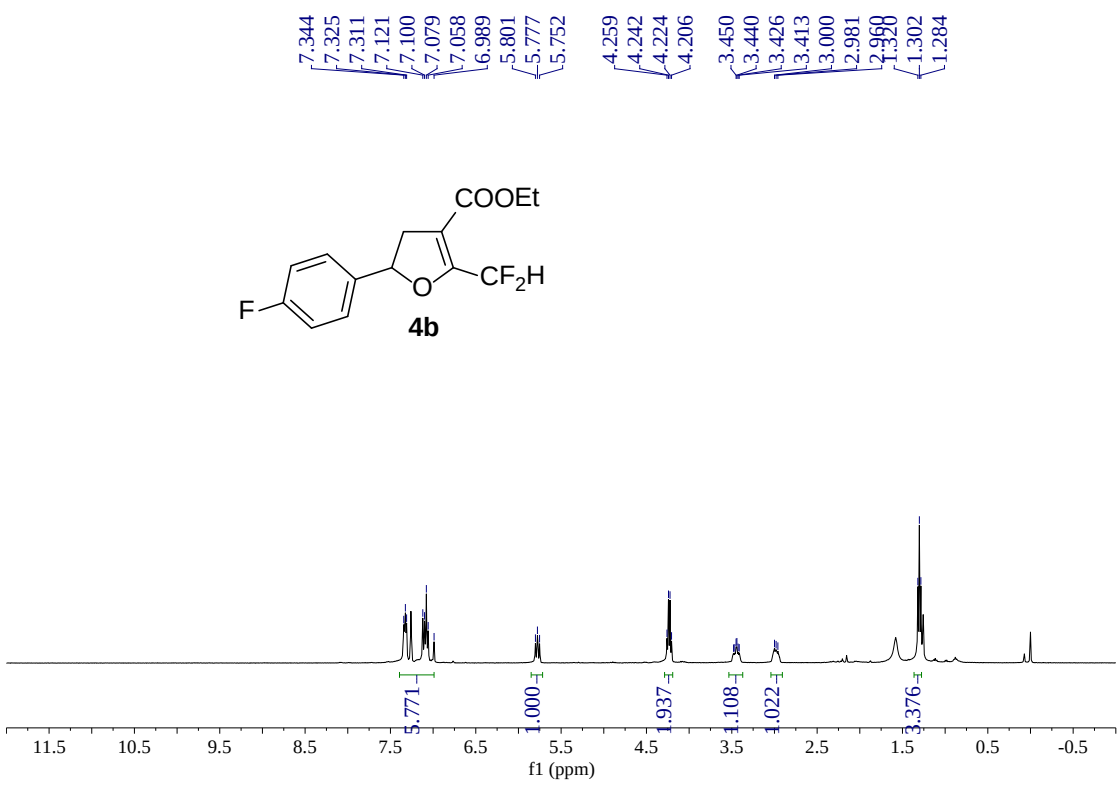


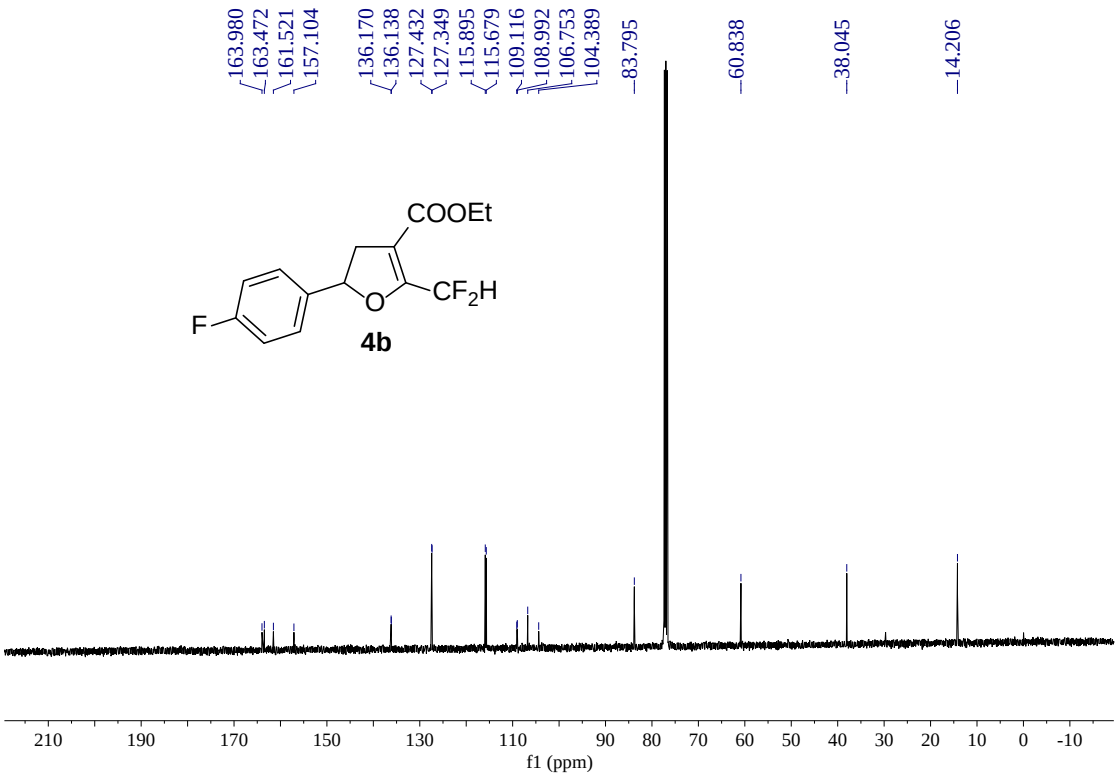
^{13}C NMR of 4a in $CDCl_3$



^{19}F NMR of 4a in $CDCl_3$



^{1}H NMR of 4b in $CDCl_3$



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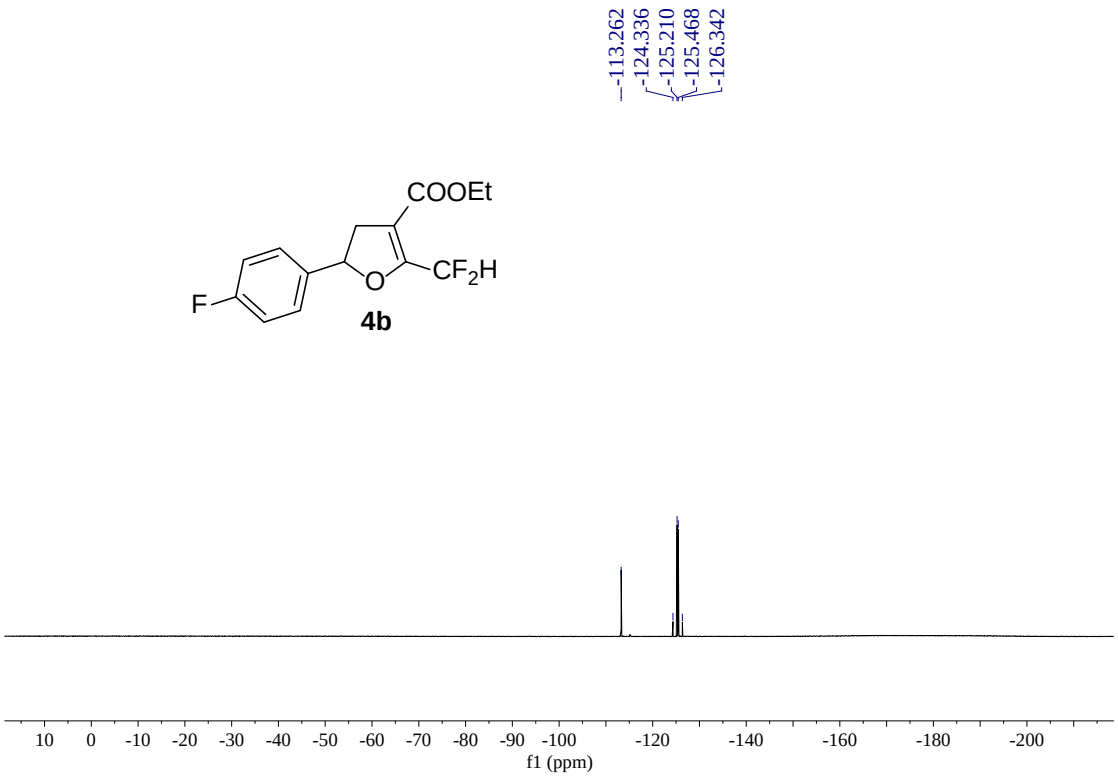
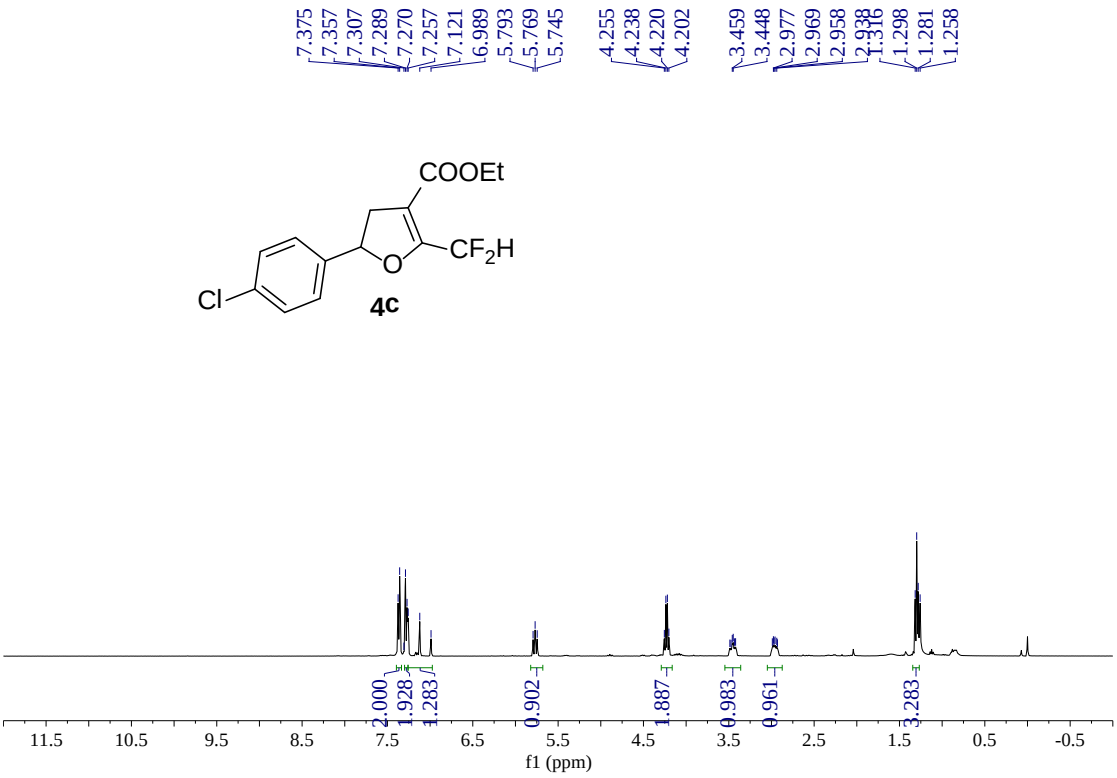
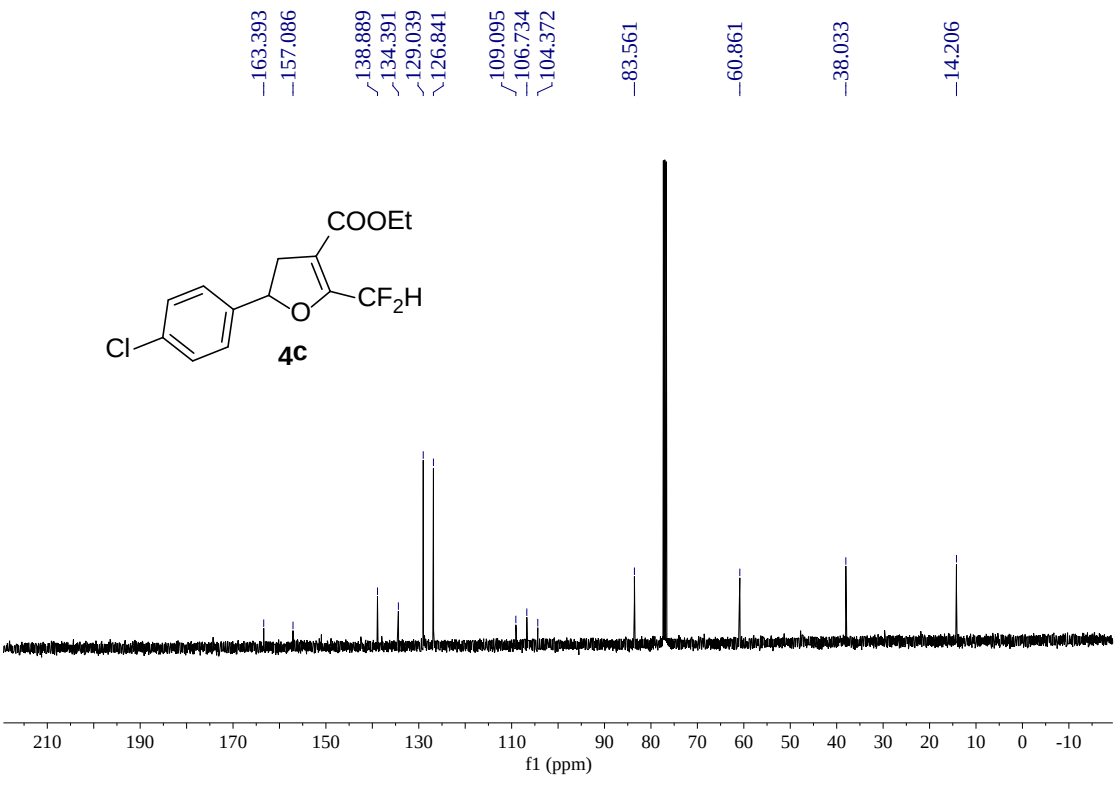


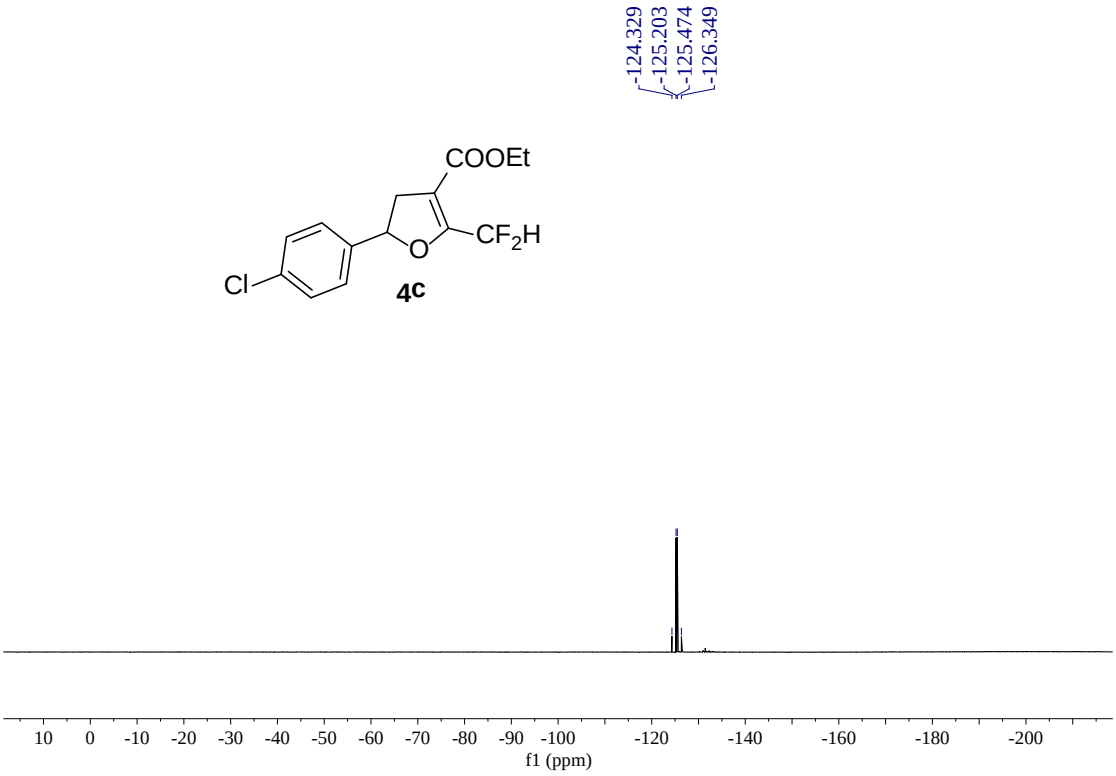
^{19}F NMR of 4b in $CDCl_3$



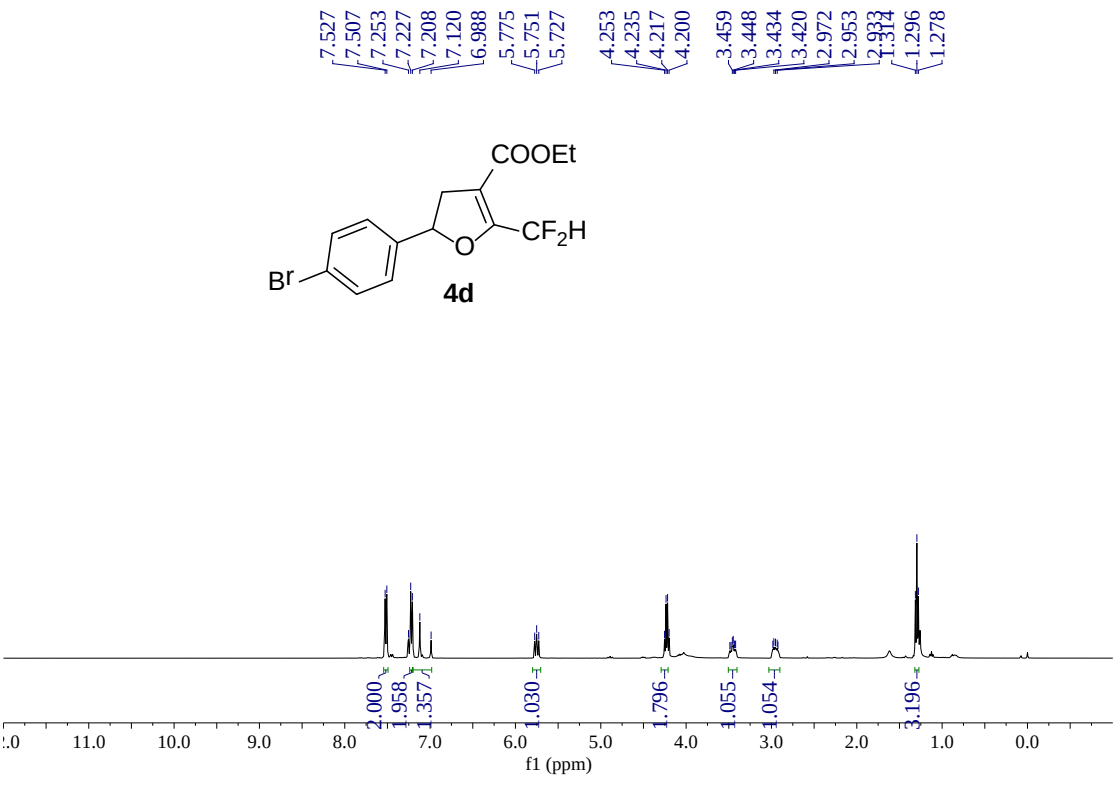
^{1}H NMR of 4c in $CDCl_3$



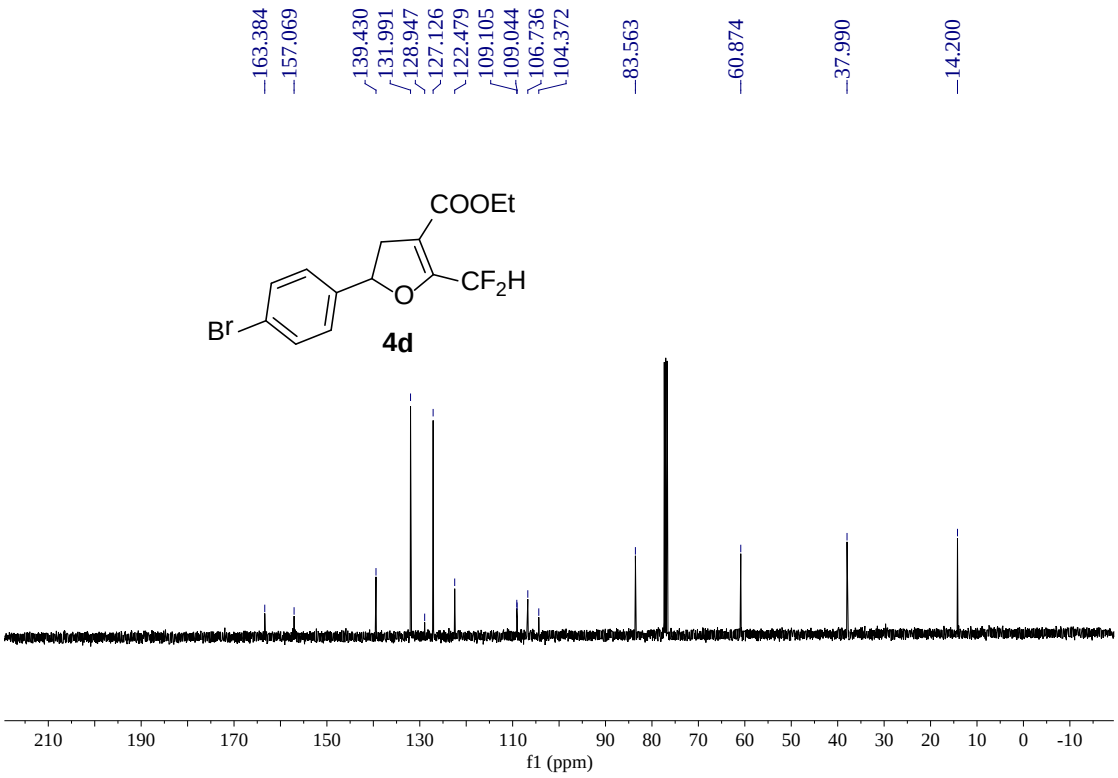
^{13}C NMR of 4c in $CDCl_3$



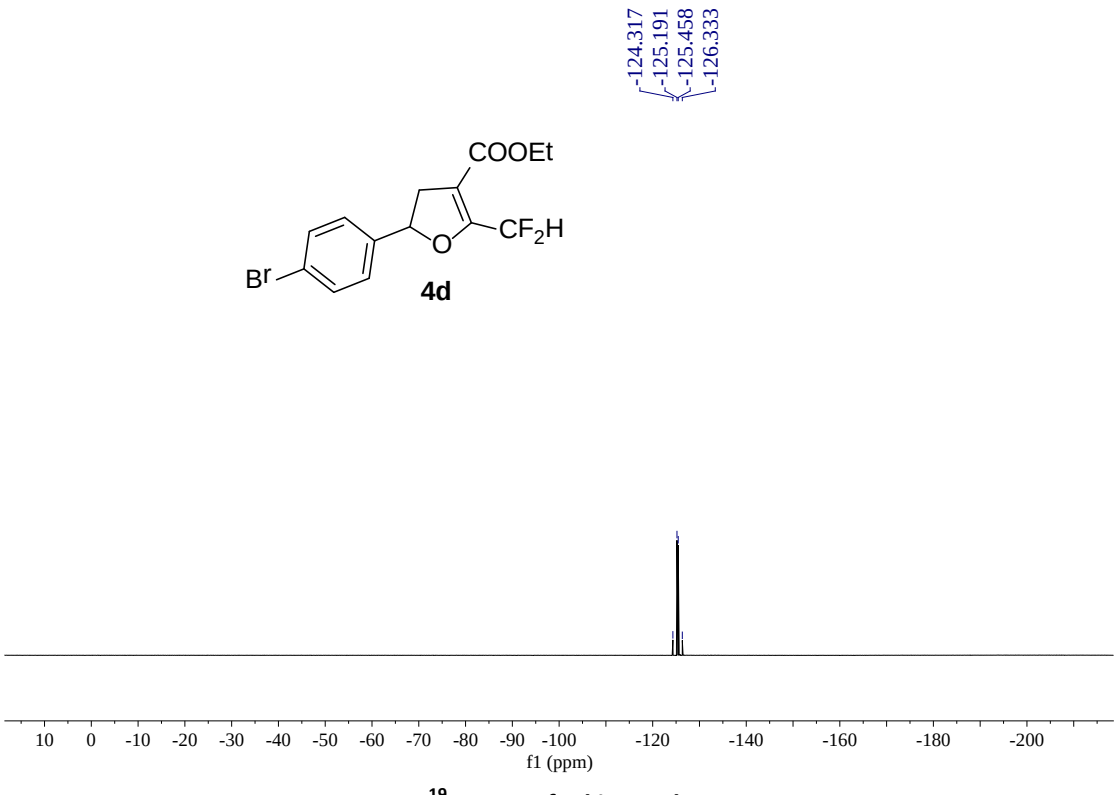
^{19}F NMR of 4c in $CDCl_3$



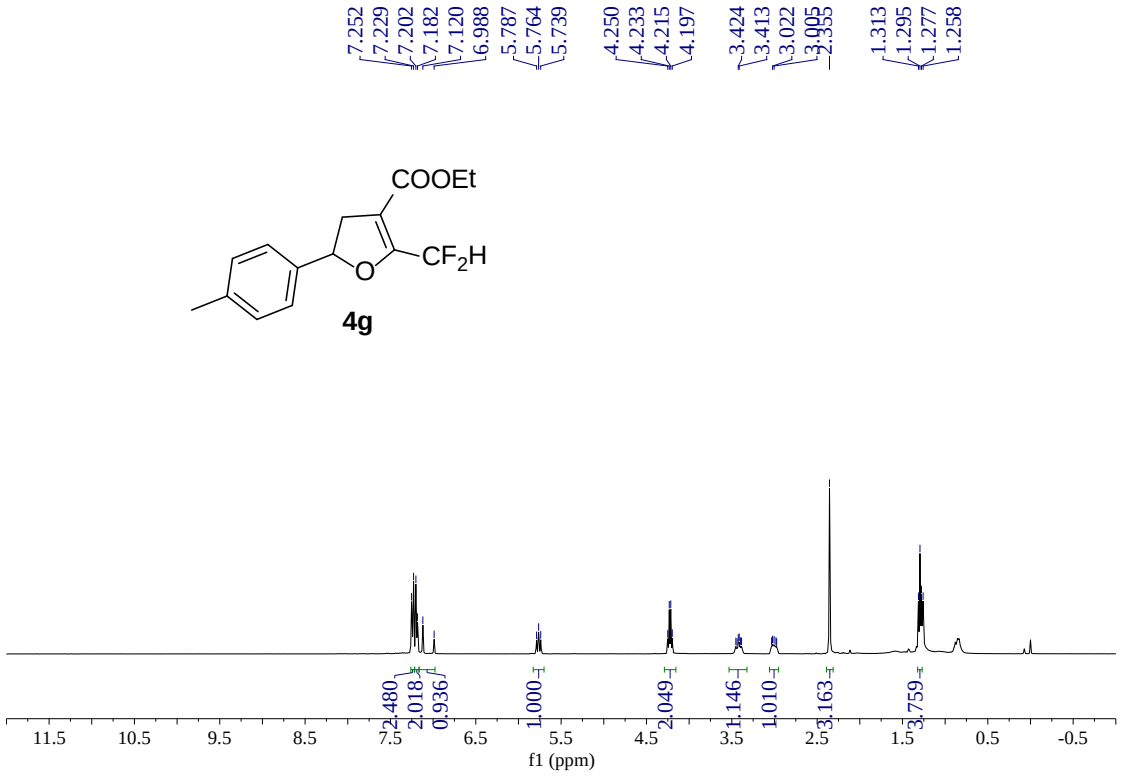
^{1}H NMR of 4d in $CDCl_3$



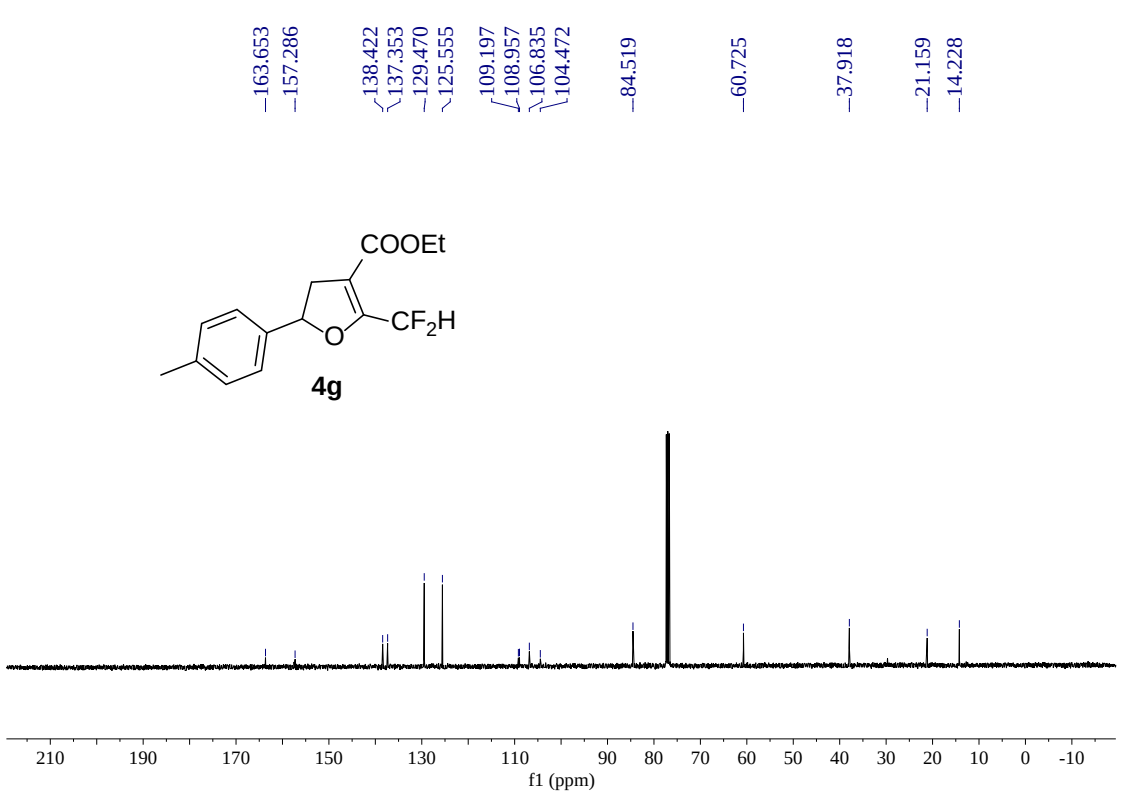
^{13}C NMR of 4d in $CDCl_3$



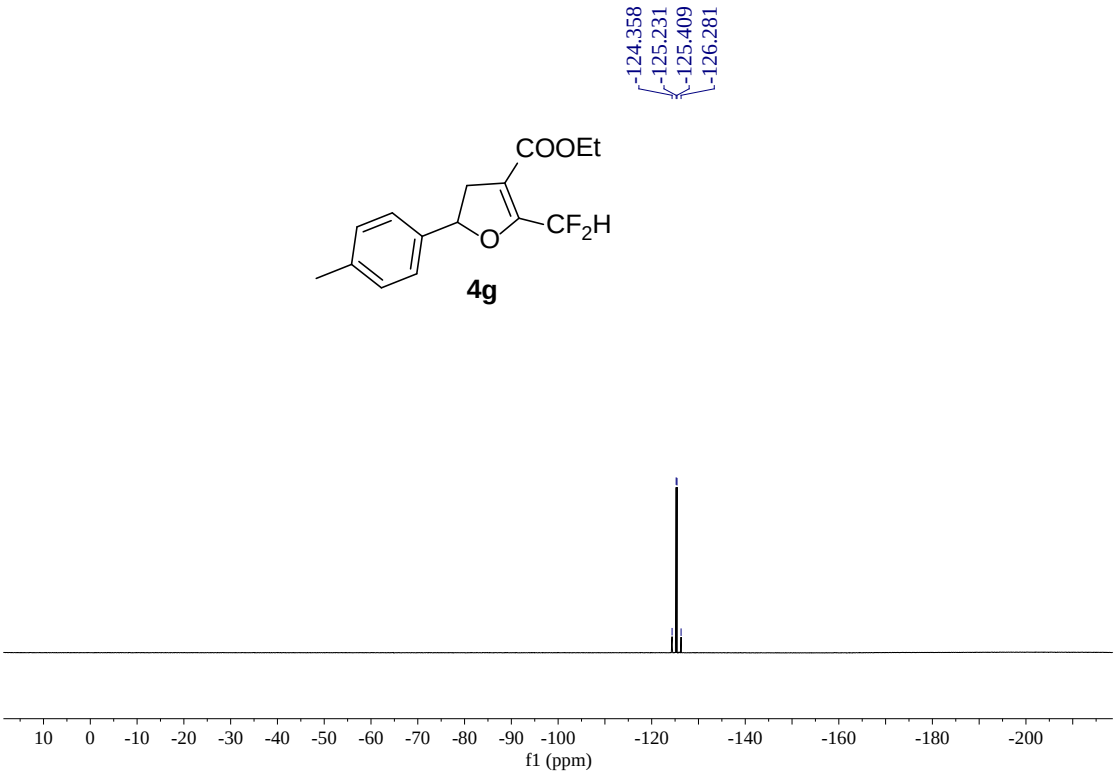
^{19}F NMR of 4d in $CDCl_3$



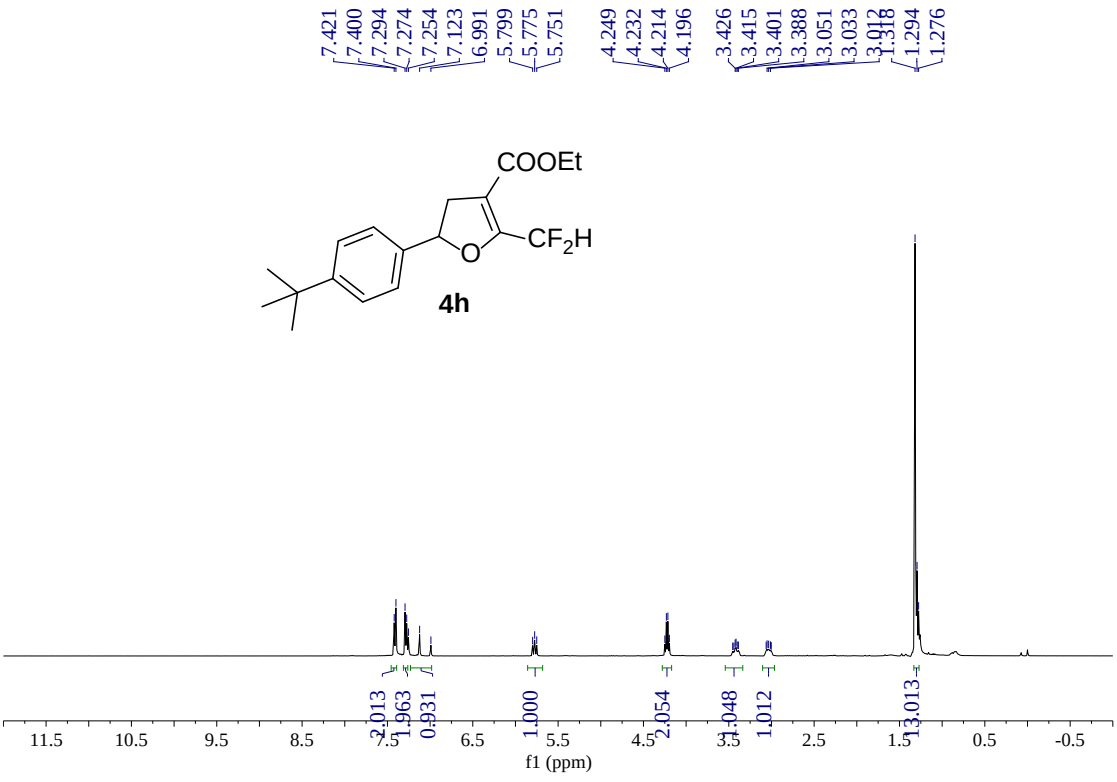
^{1}H NMR of 4g in $CDCl_3$



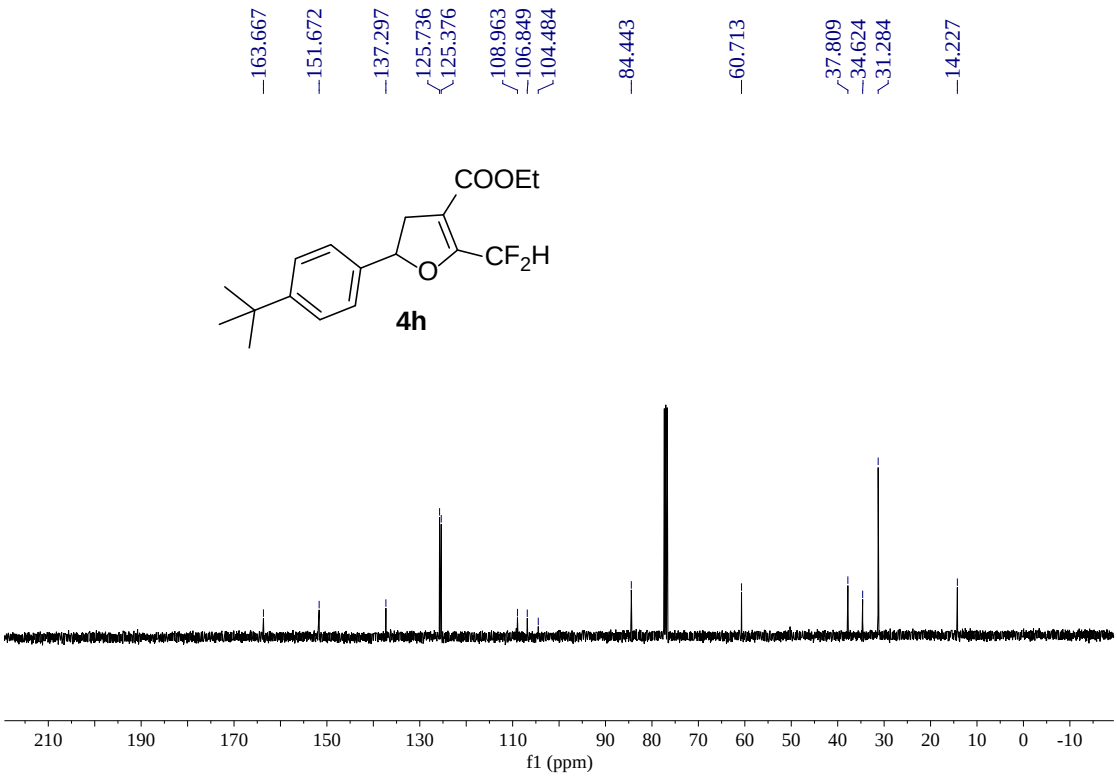
^{13}C NMR of 4g in $CDCl_3$



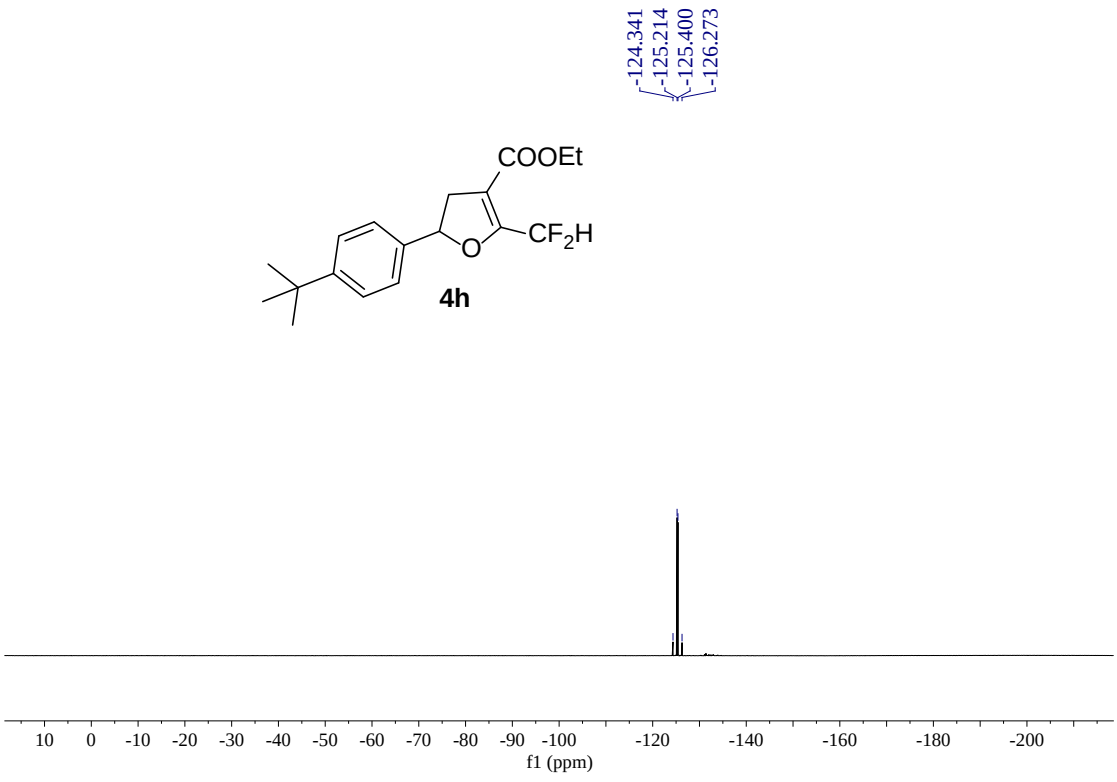
^{19}F NMR of 4g in $CDCl_3$



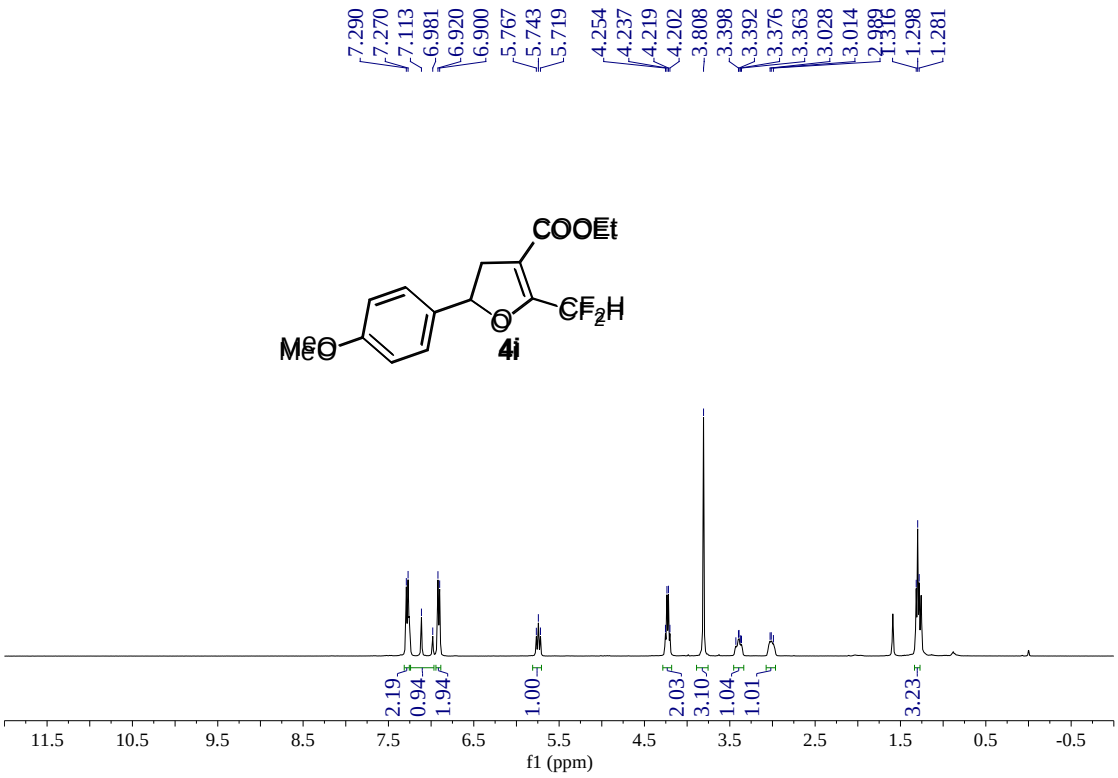
^{1}H NMR of 4h in $CDCl_3$



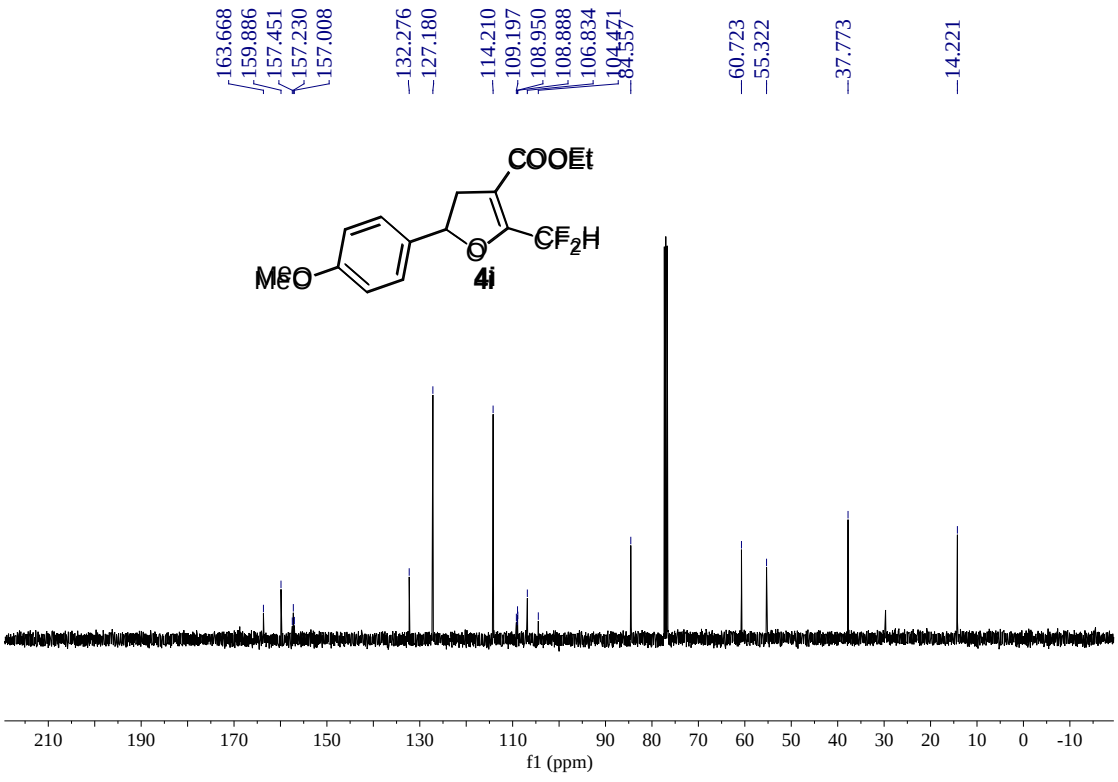
^{13}C NMR of 4h in $CDCl_3$



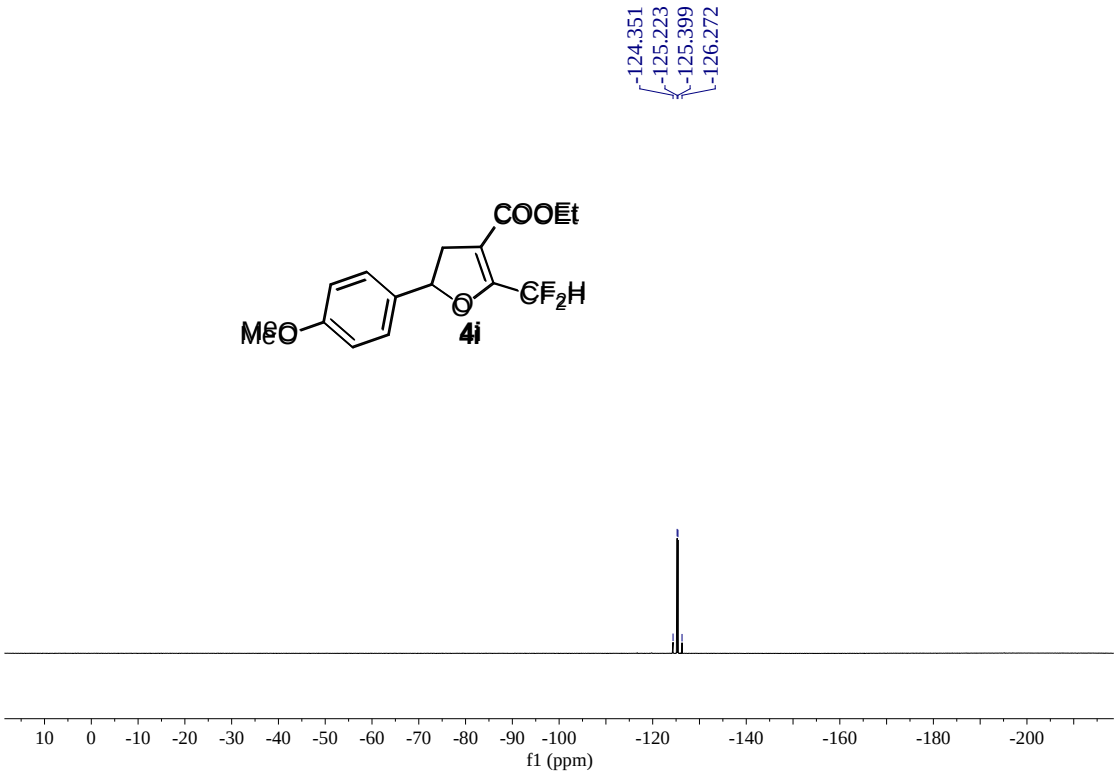
^{19}F NMR of 4h in $CDCl_3$



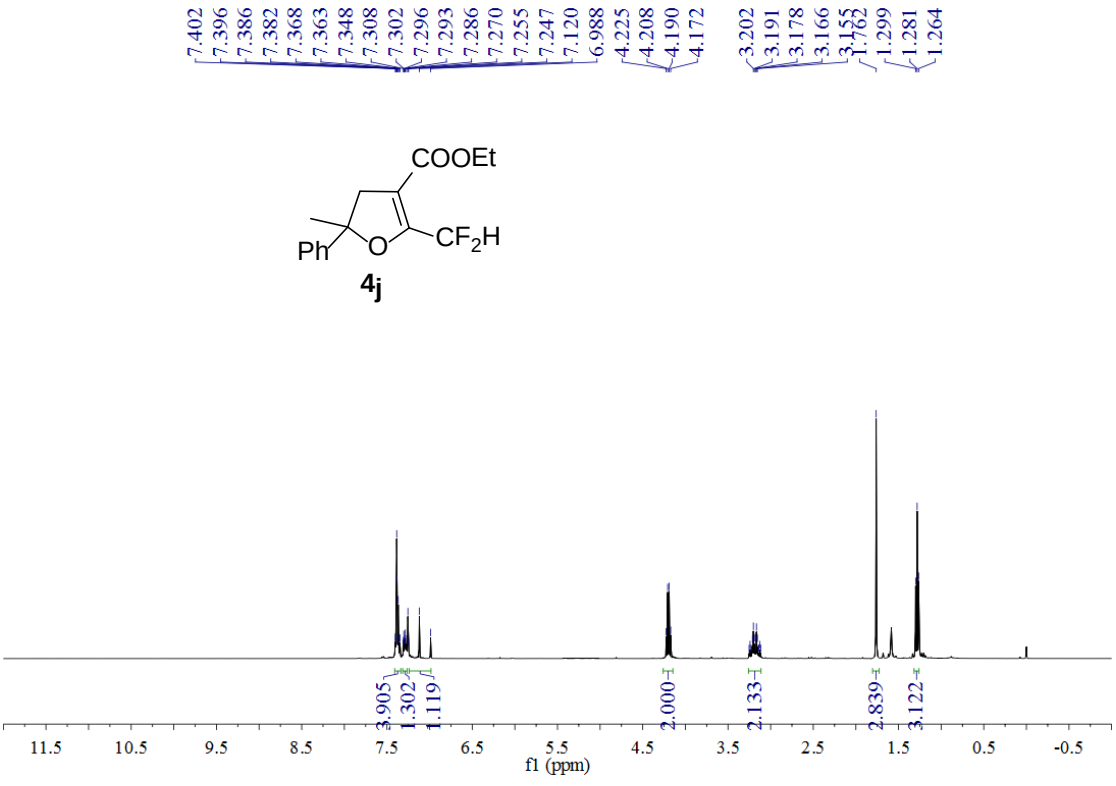
^{1}H NMR of 4i in $CDCl_3$



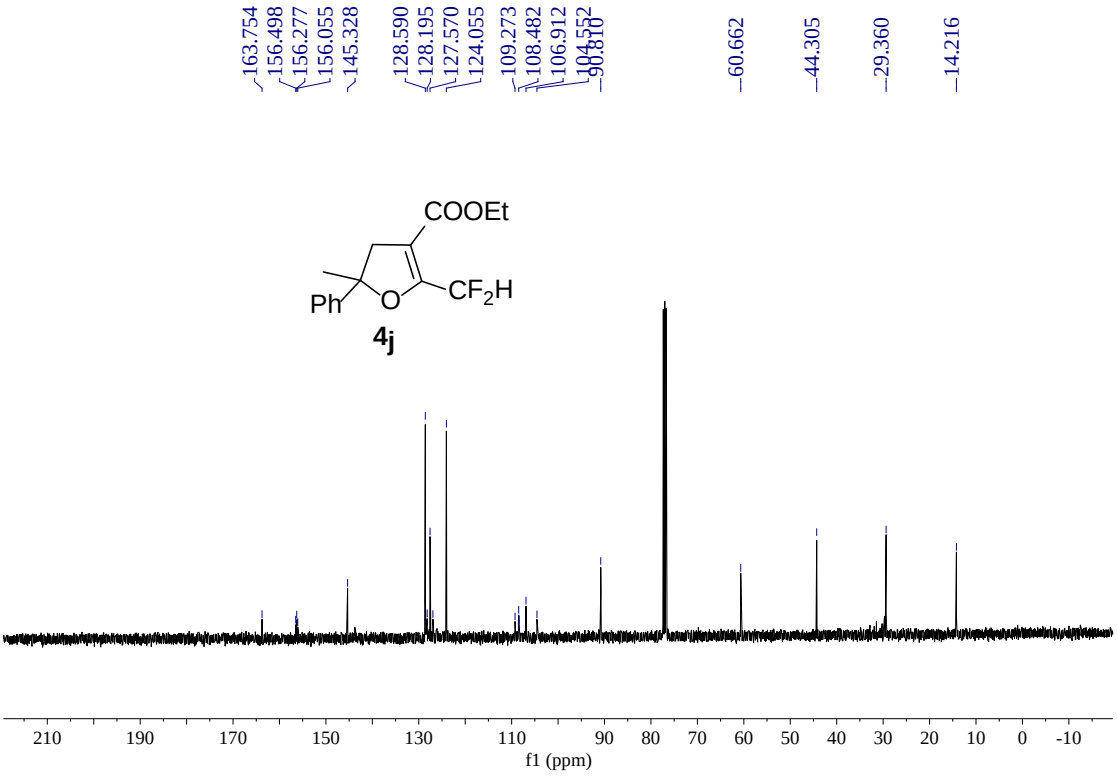
^{13}C NMR of 4i in $CDCl_3$



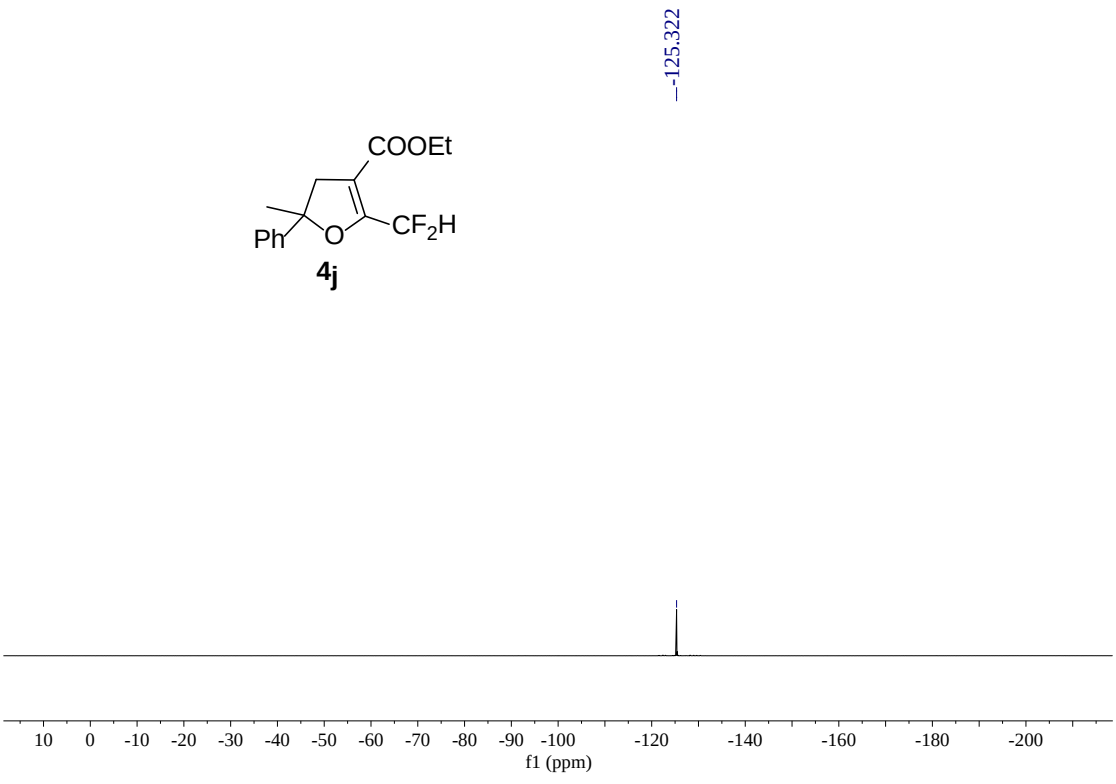
^{19}F NMR of 4i in $CDCl_3$



^{1}H NMR of 4j in $CDCl_3$



^{13}C NMR of 4j in $CDCl_3$



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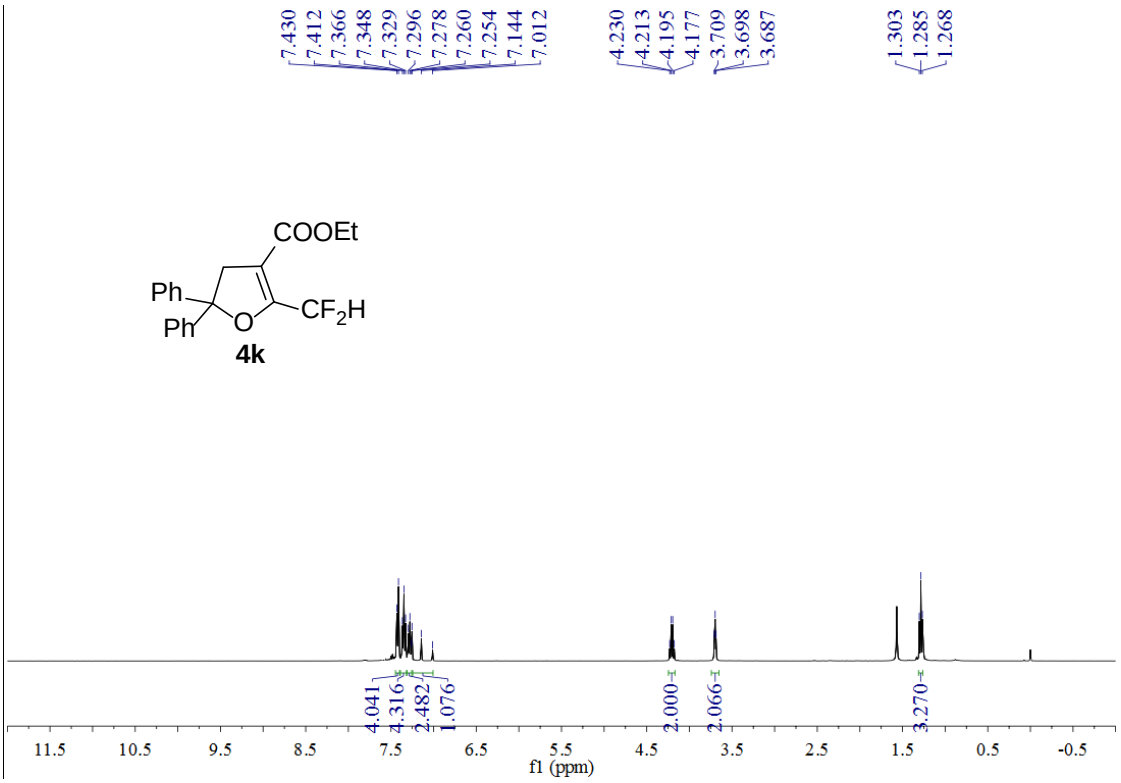
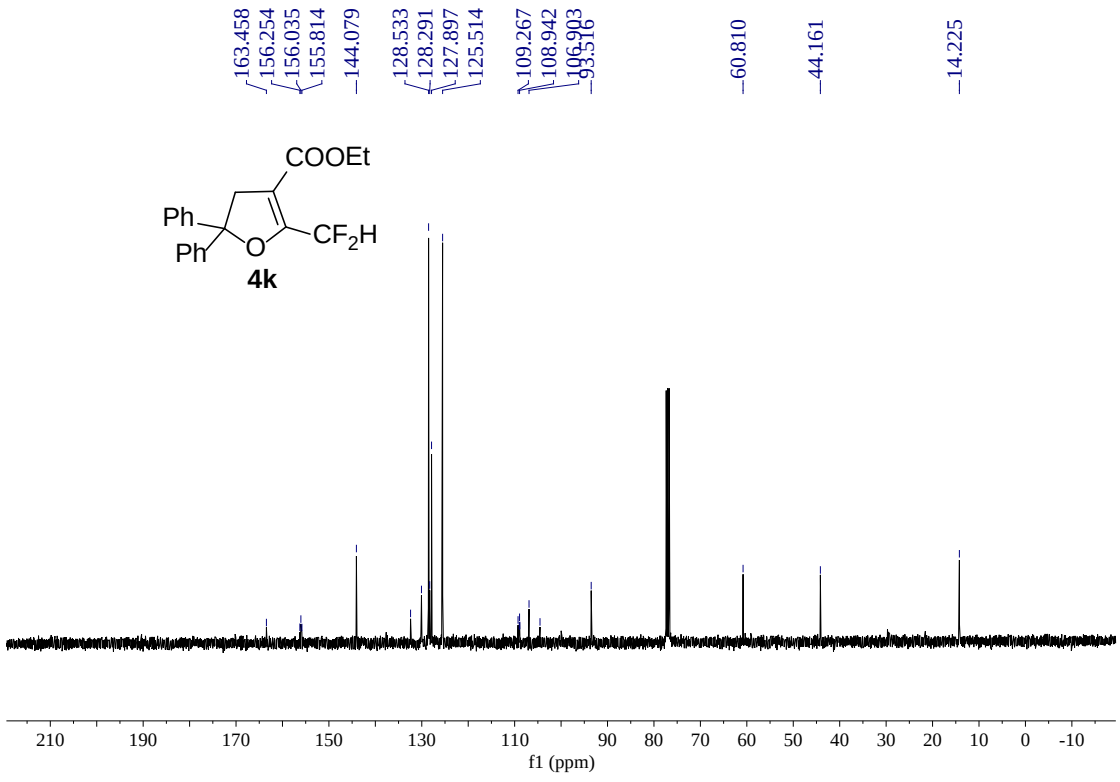


^{1}H NMR of 4k in $CDCl_3$



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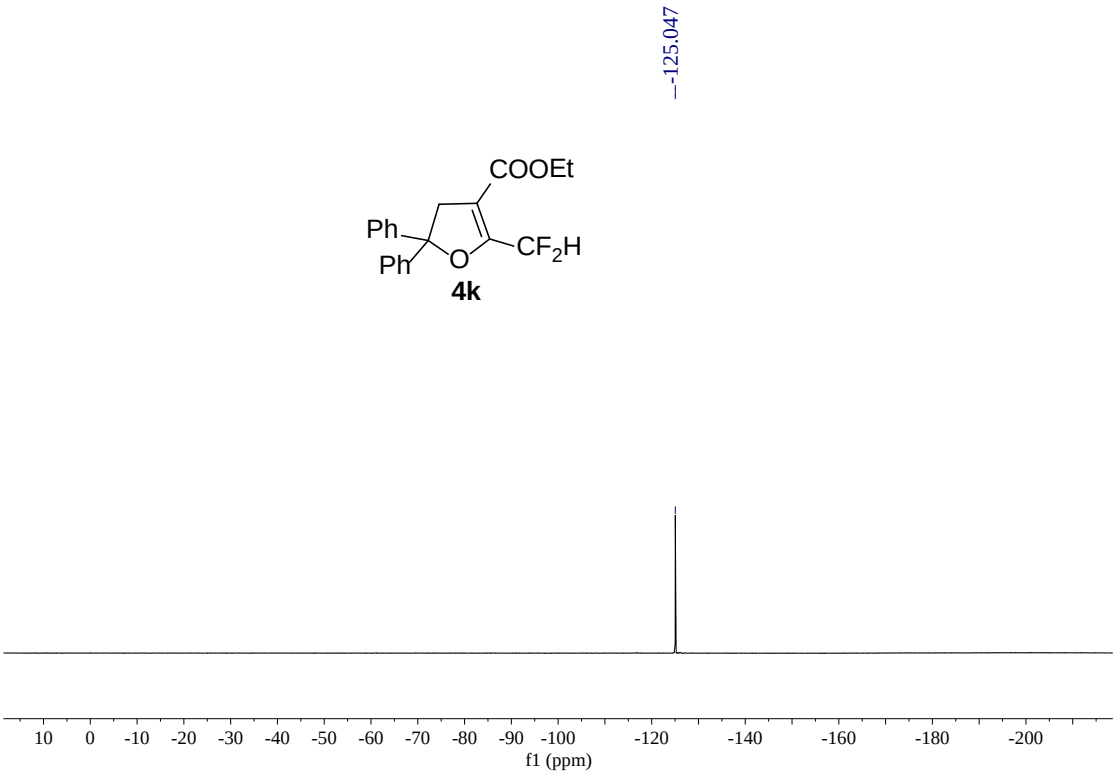
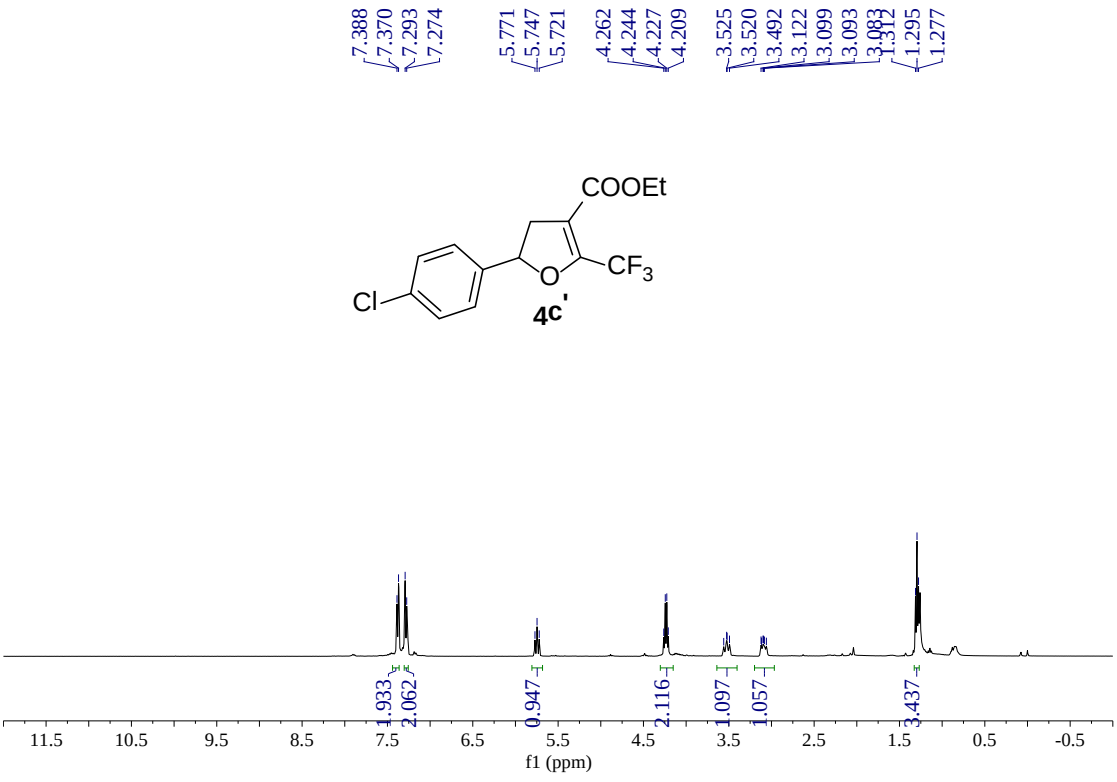


^{19}F NMR of 4k in $CDCl_3$



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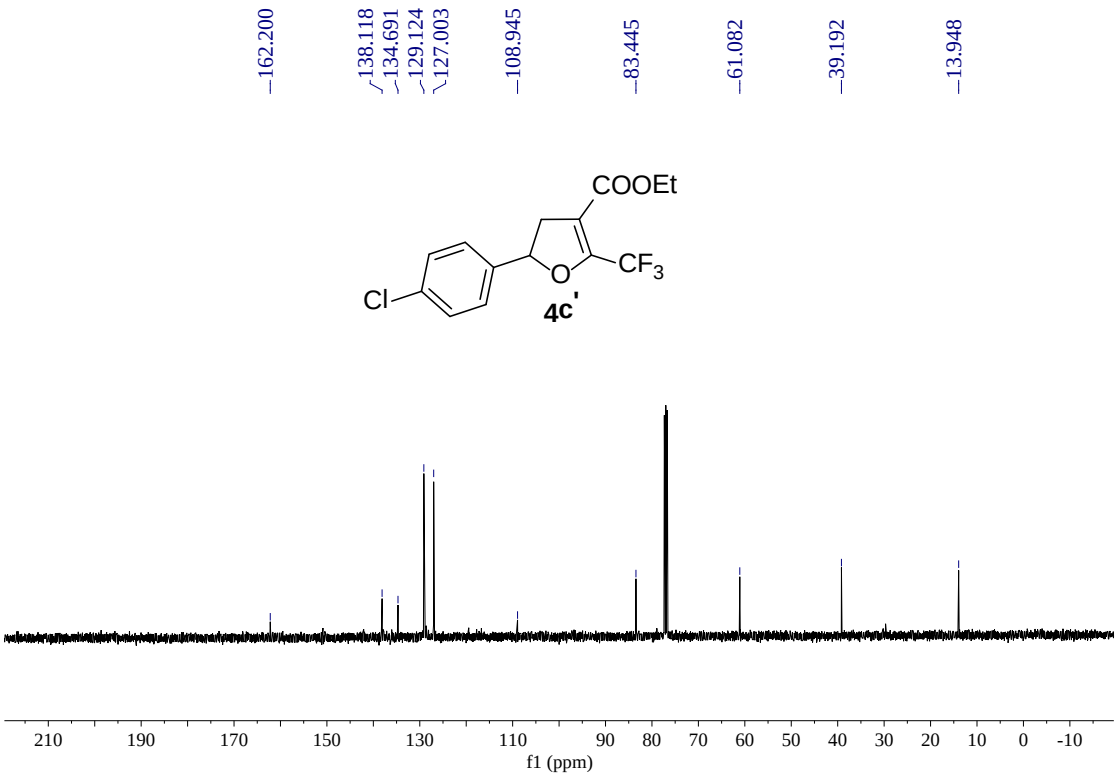
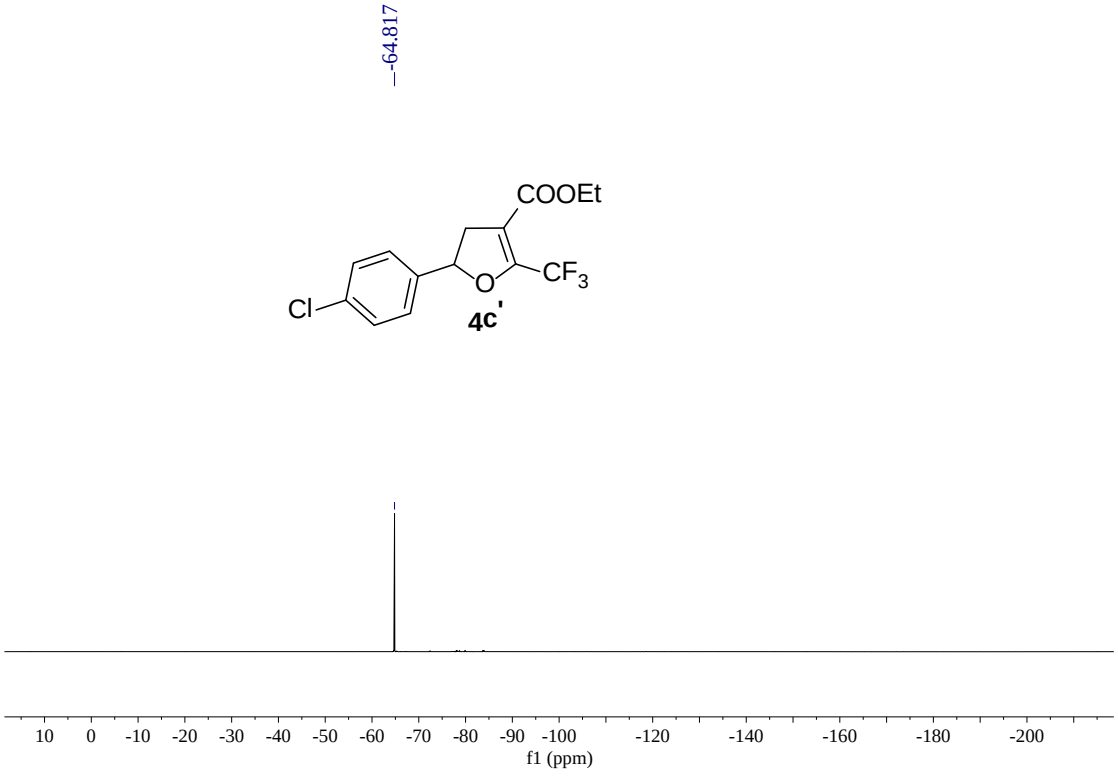
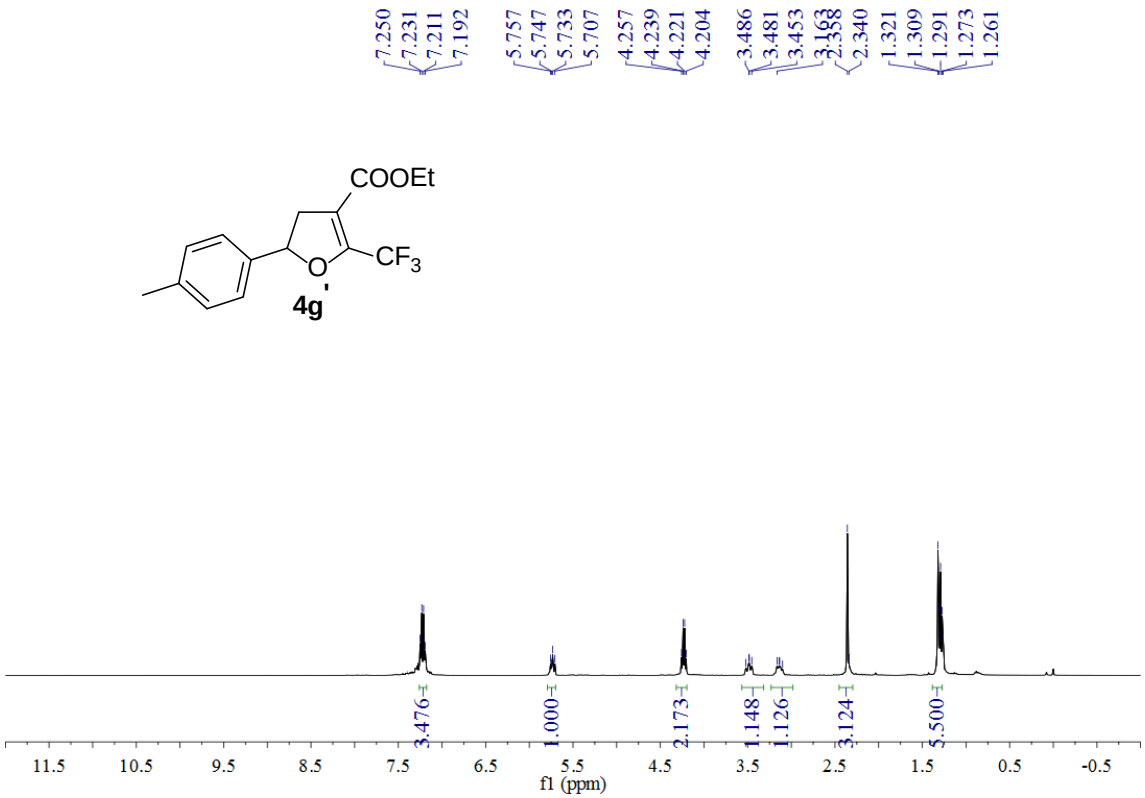


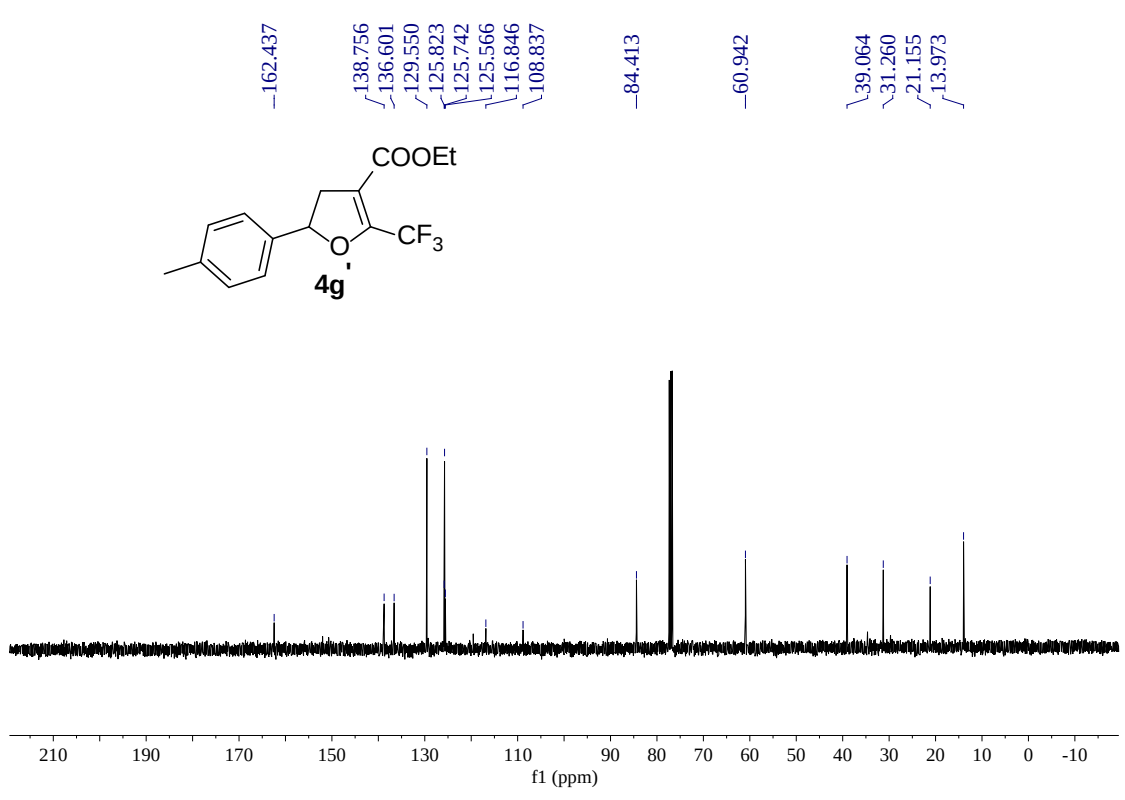
^{13}C NMR of 4c' in $CDCl_3$



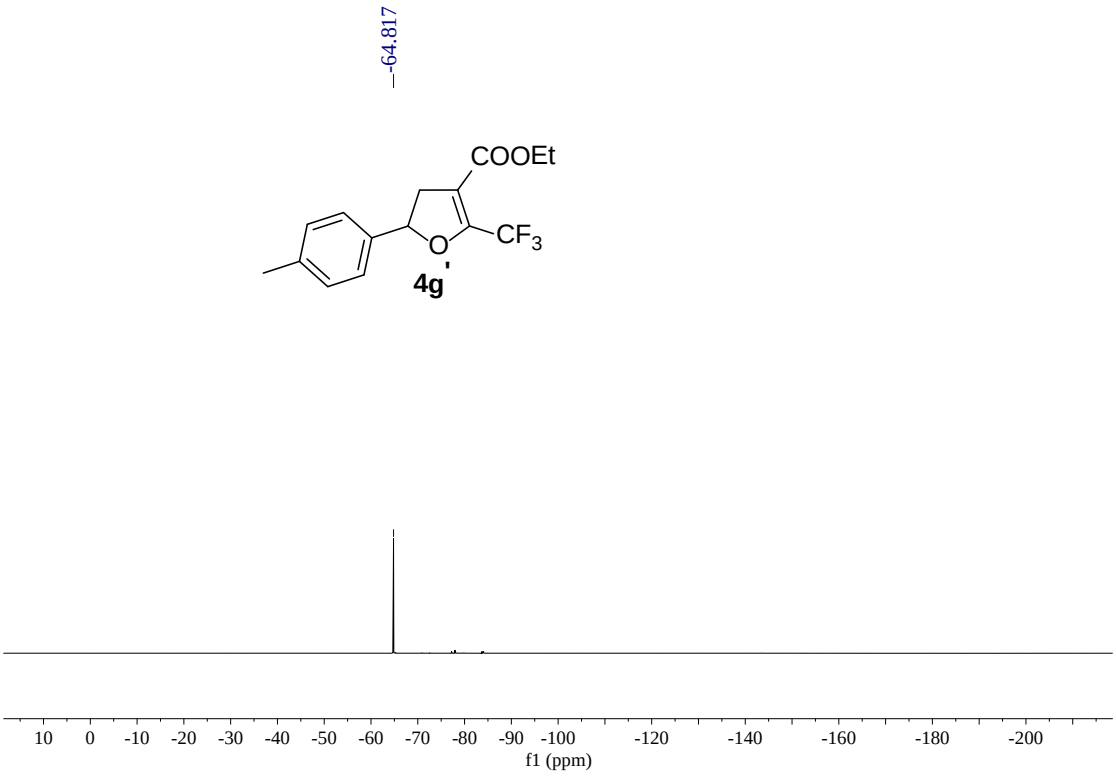
^{19}F NMR of 4c' in $CDCl_3$



^{1}H NMR of 4g' in $CDCl_3$



^{13}C NMR of 4g' in $CDCl_3$



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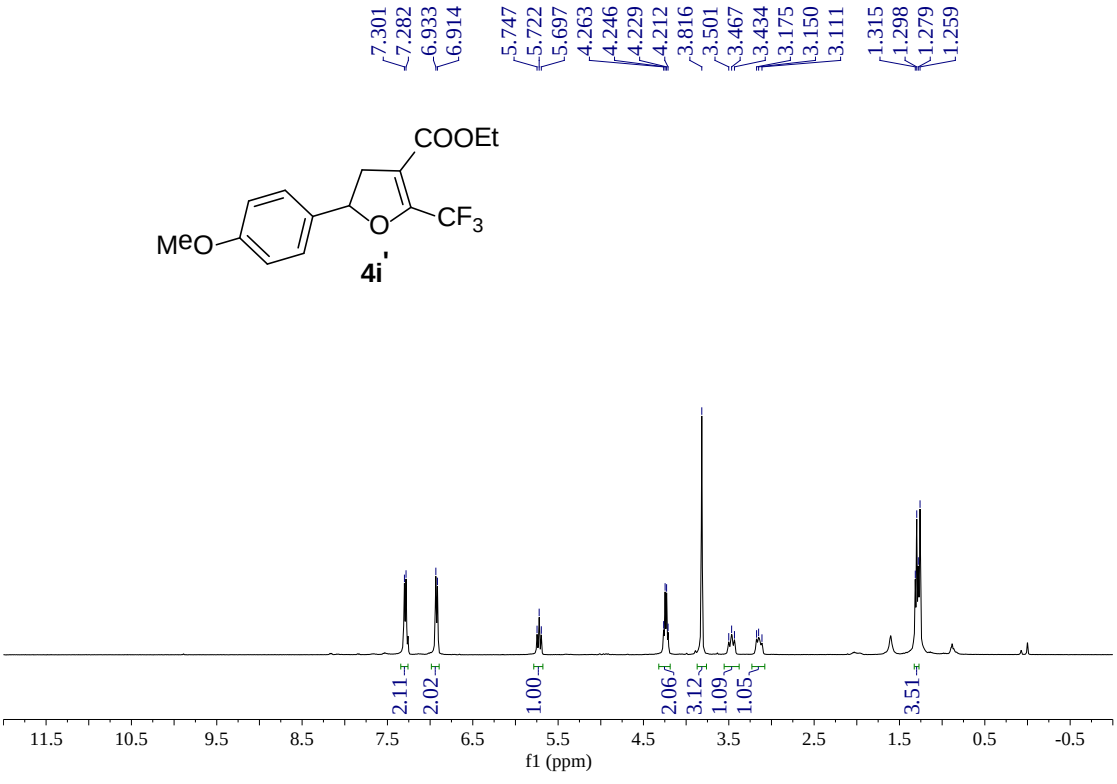

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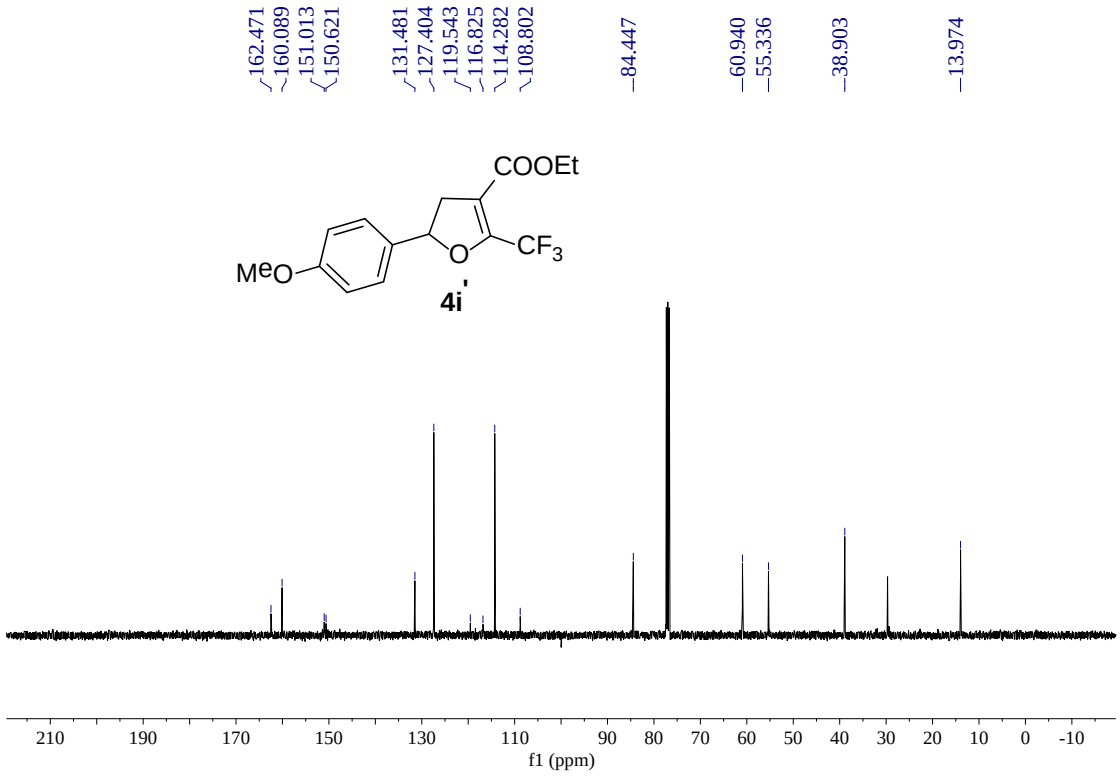
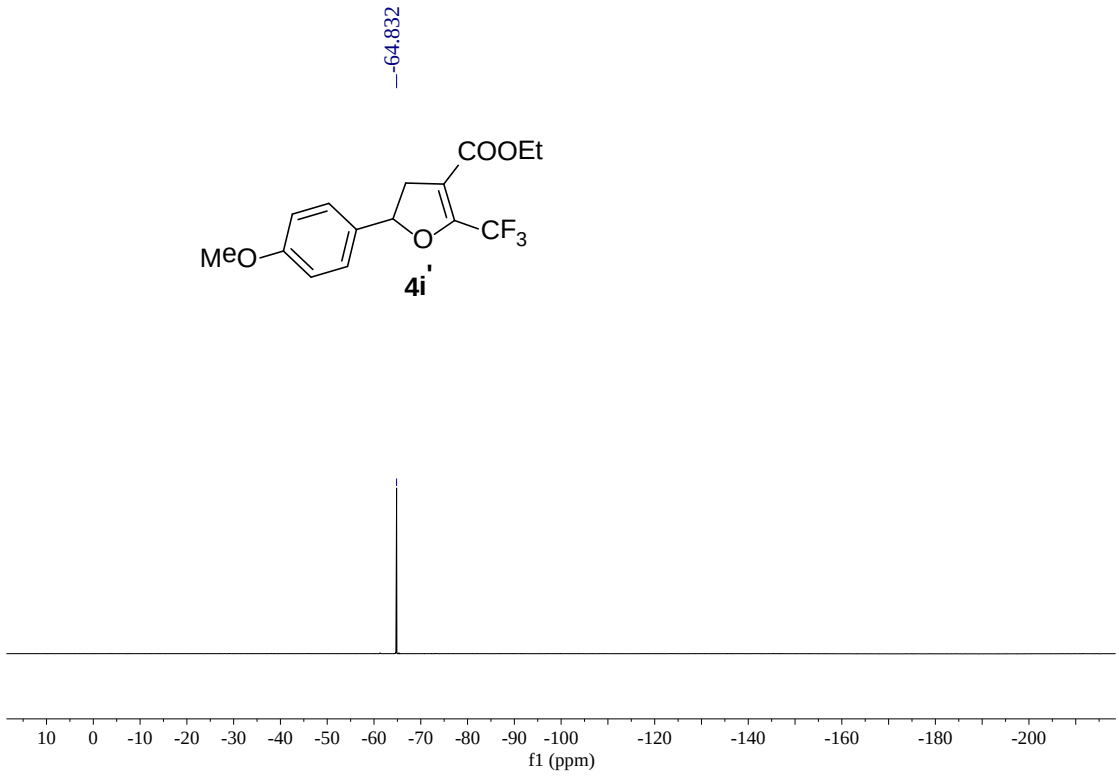
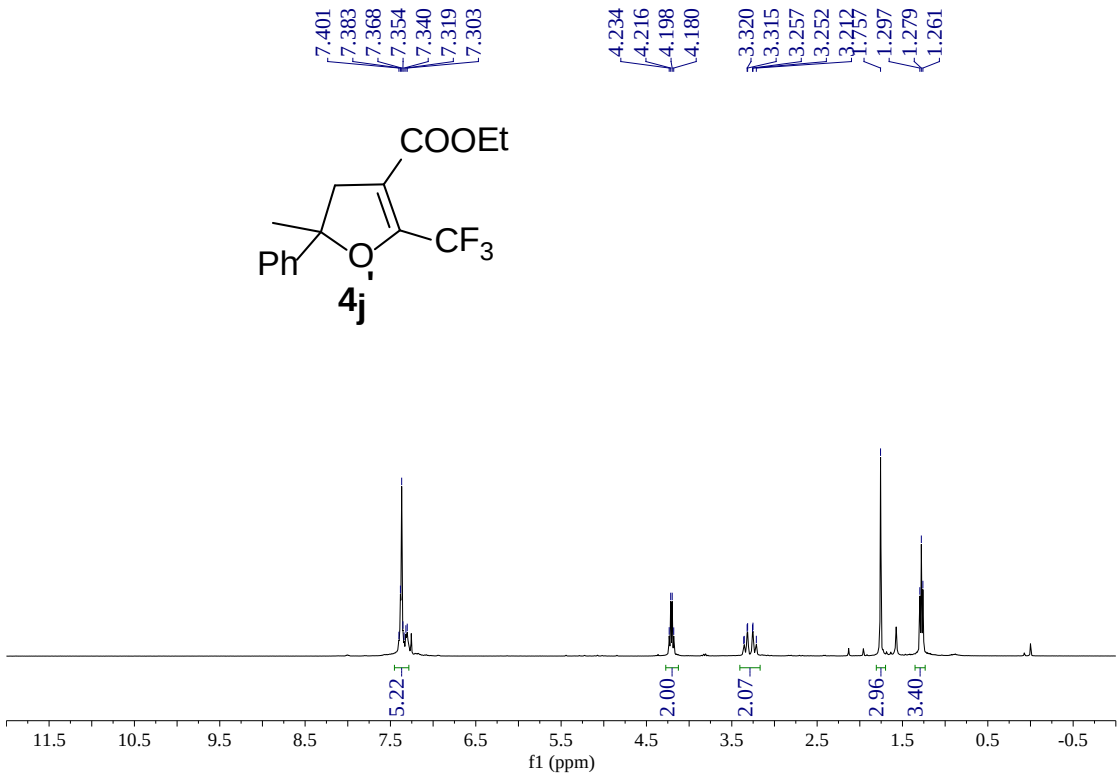


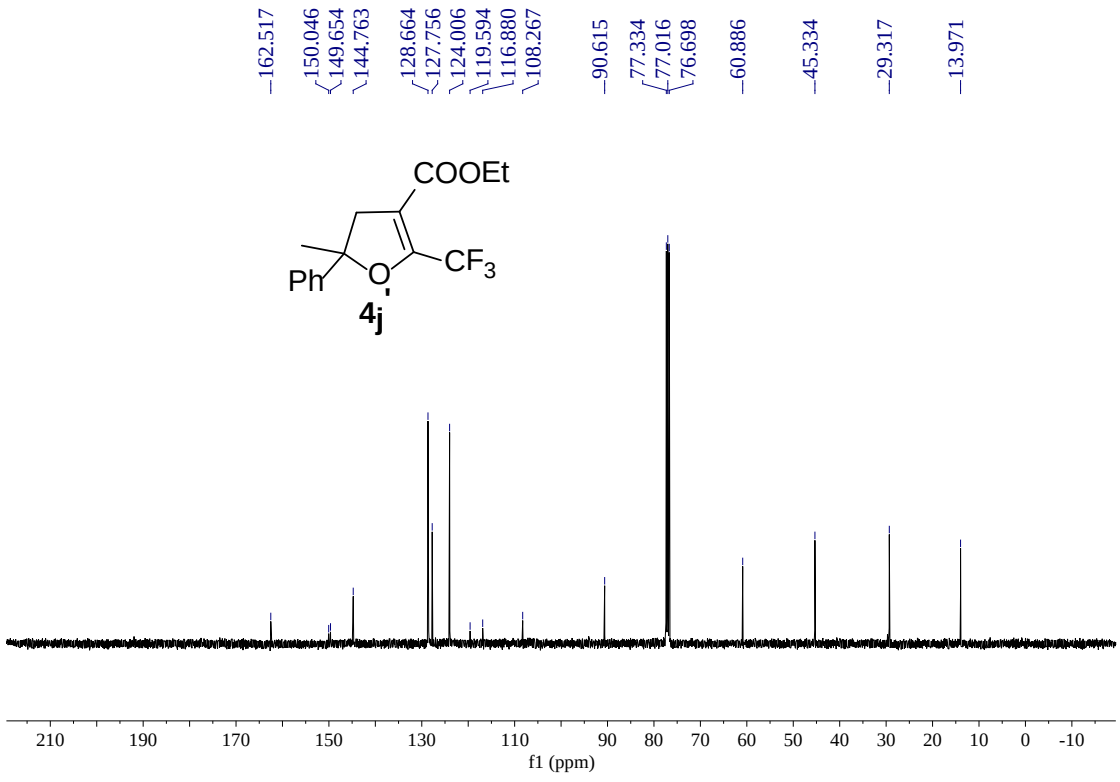
^{13}C NMR of 4i' in $CDCl_3$



^{19}F NMR of 4i' in $CDCl_3$



^{1}H NMR of 4j' in $CDCl_3$



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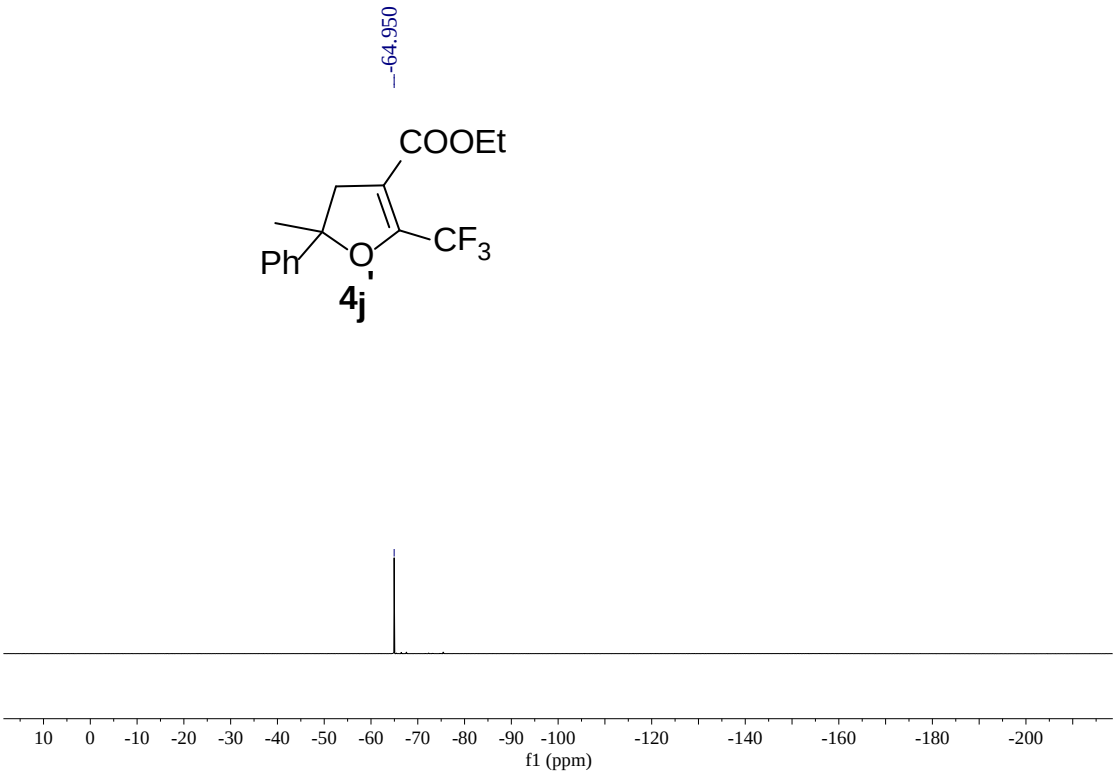
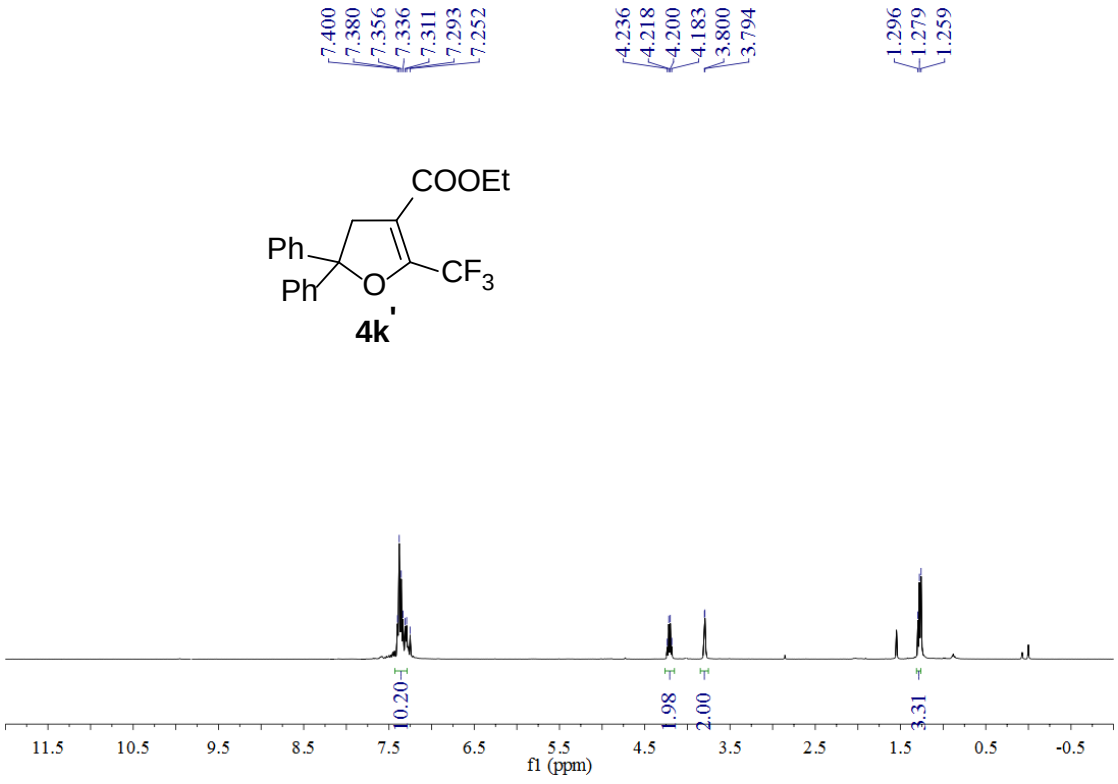
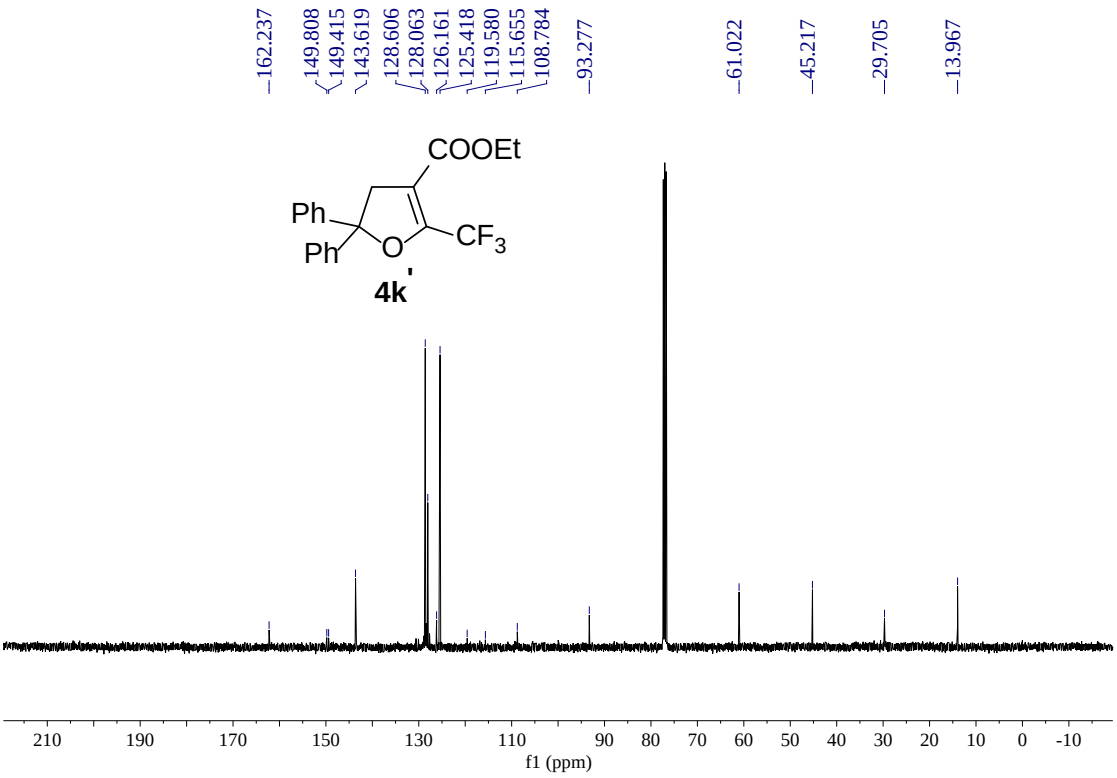


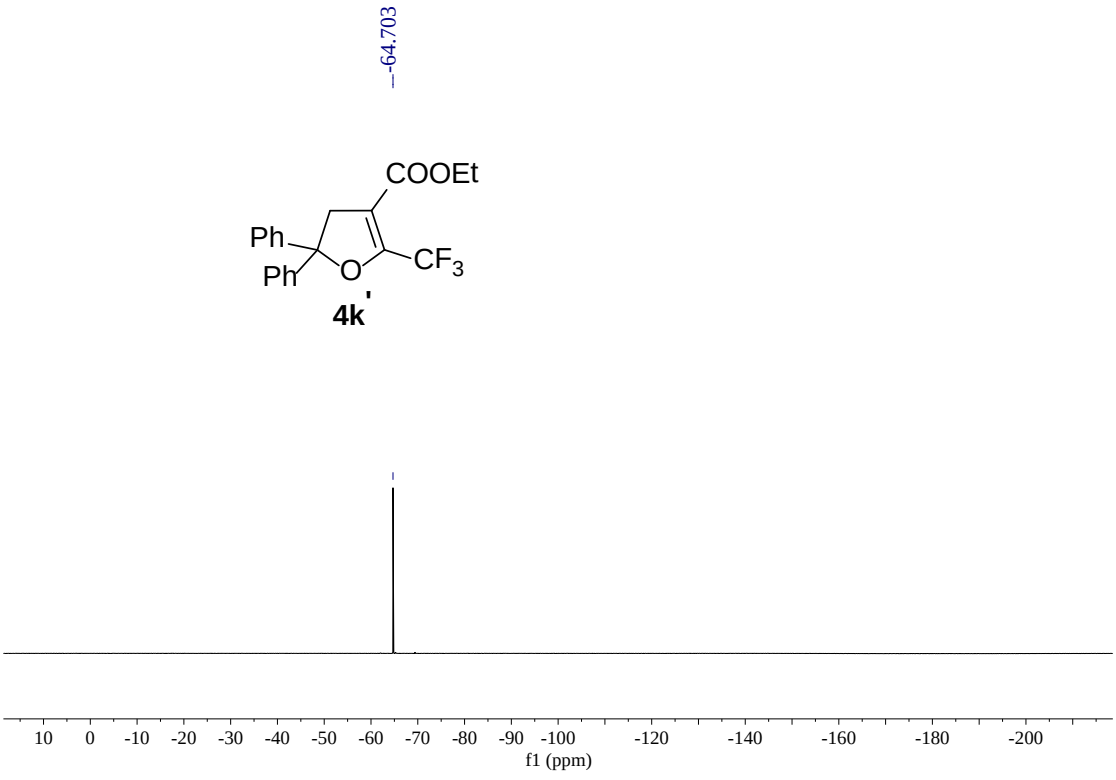
^{19}F NMR of 4j' in $CDCl_3$



^{1}H NMR of 4k' in $CDCl_3$



^{13}C NMR of 4k' in $CDCl_3$



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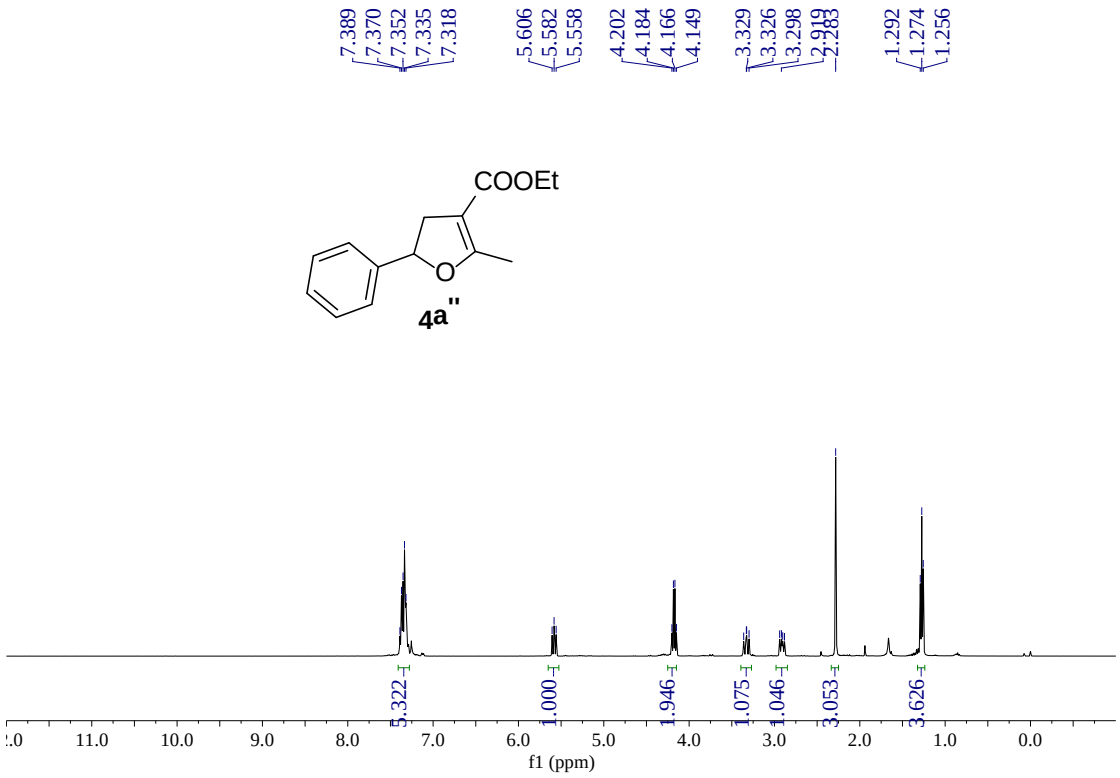

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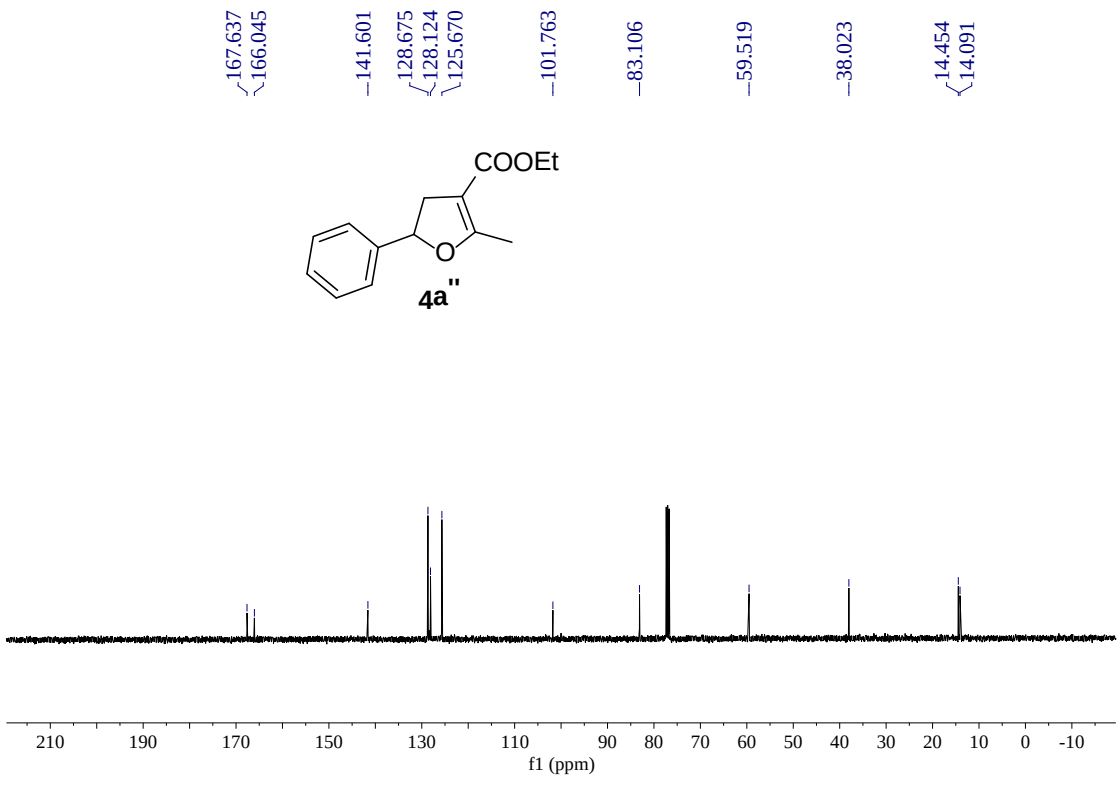
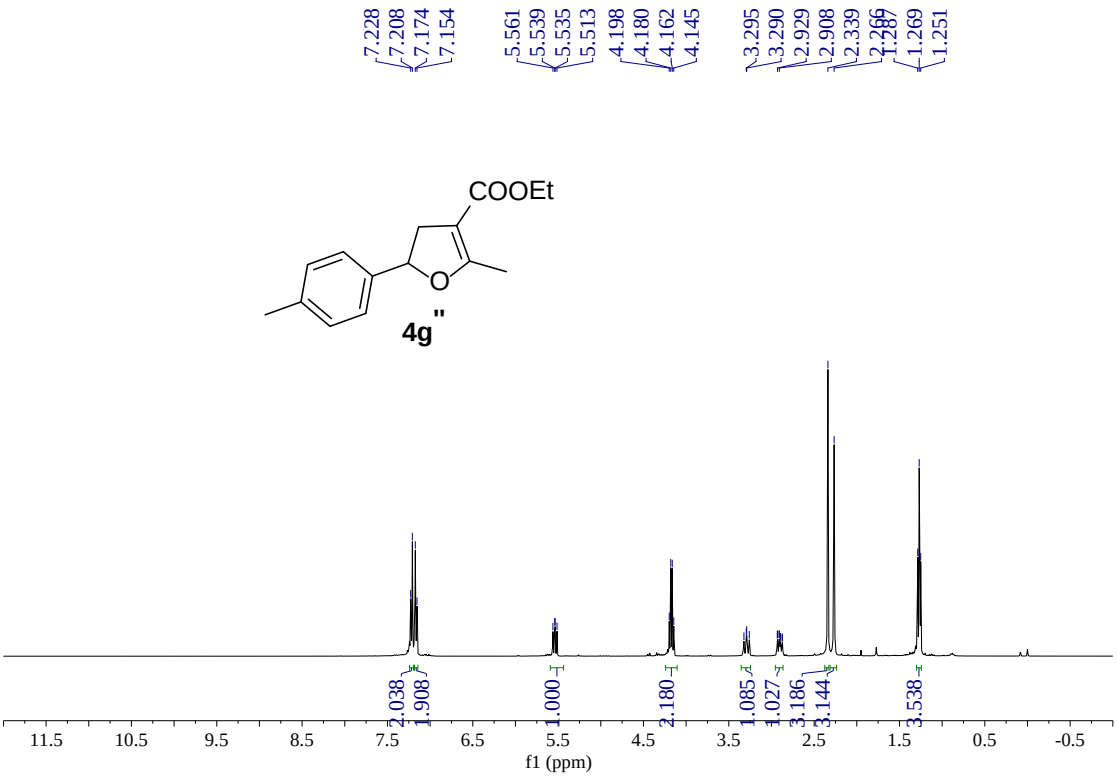


^{13}C NMR of 4a'' in $CDCl_3$



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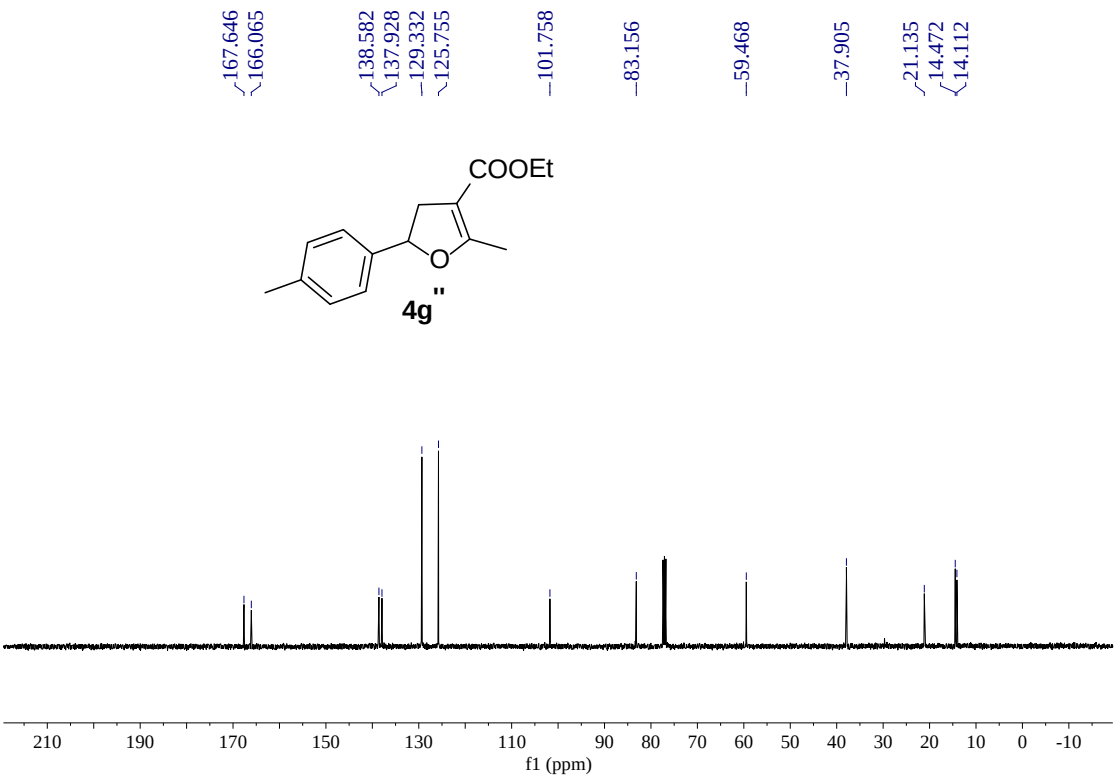
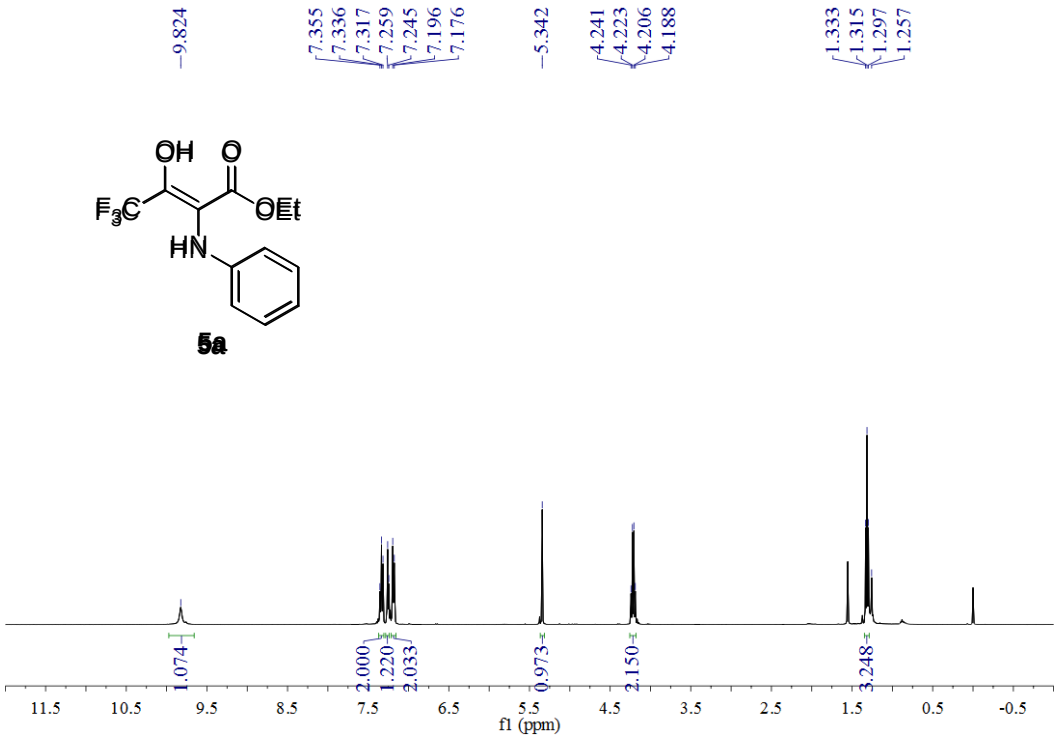
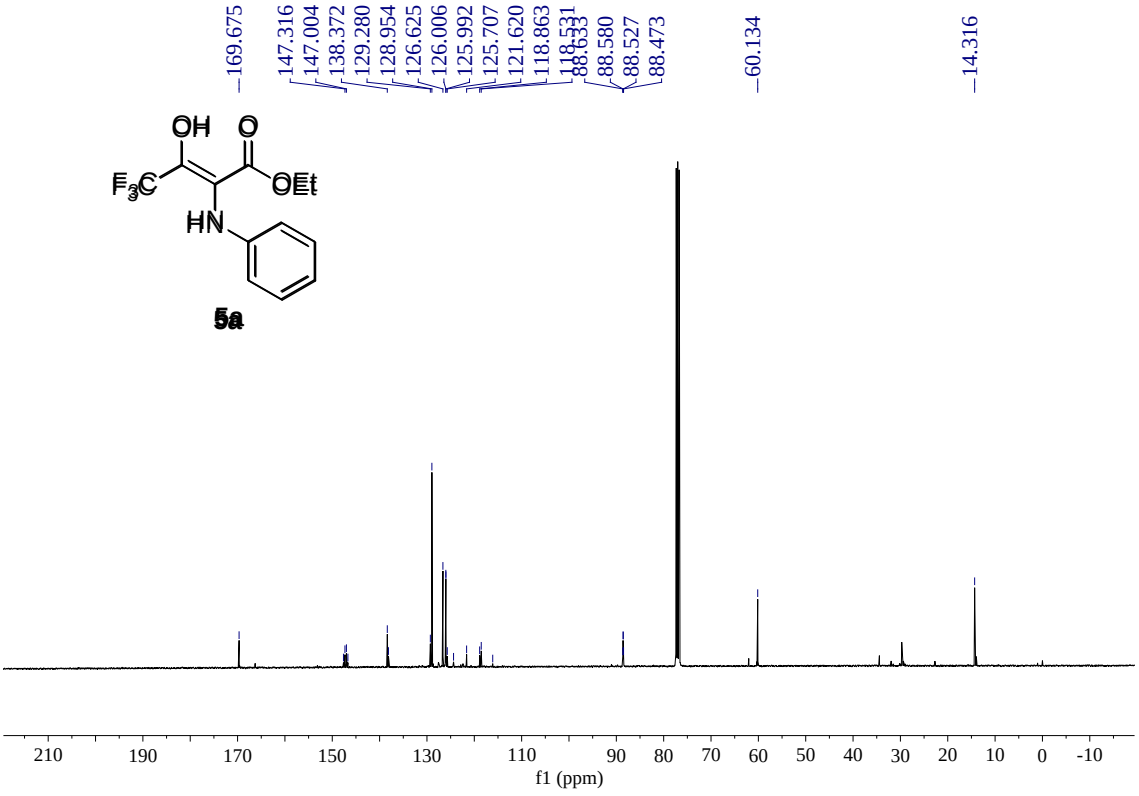


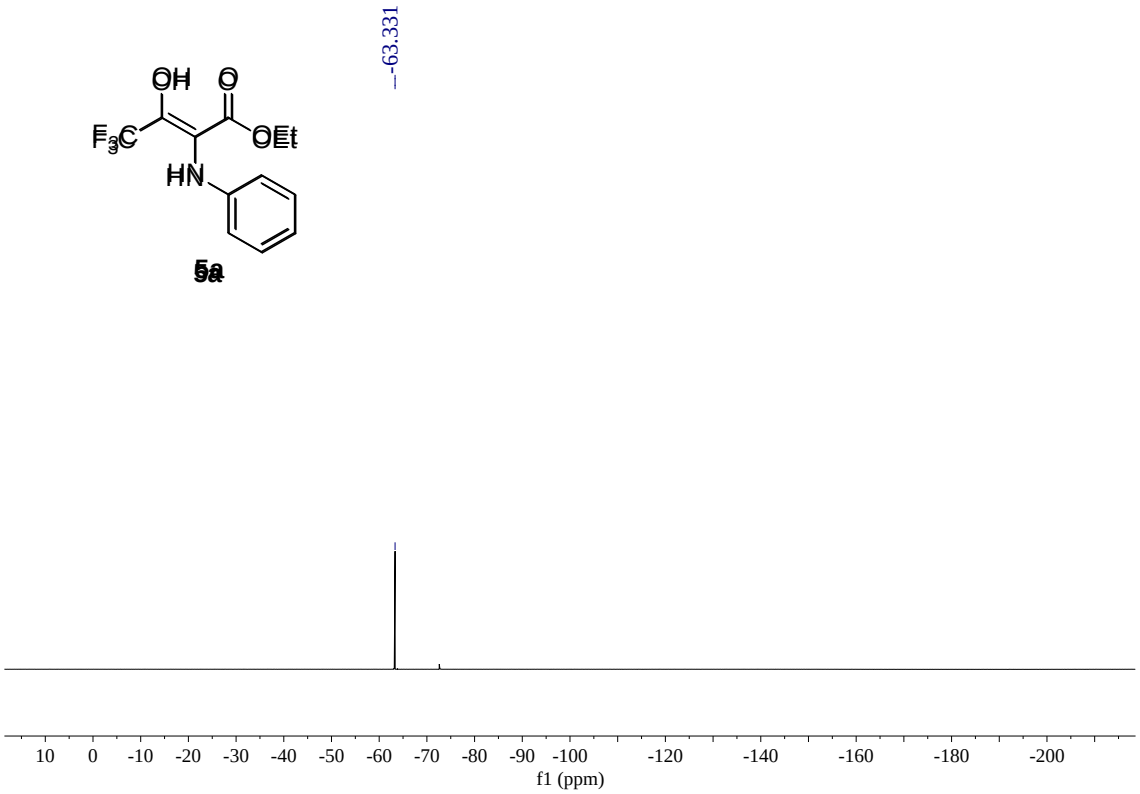
^{13}C NMR of 4g'' in $CDCl_3$



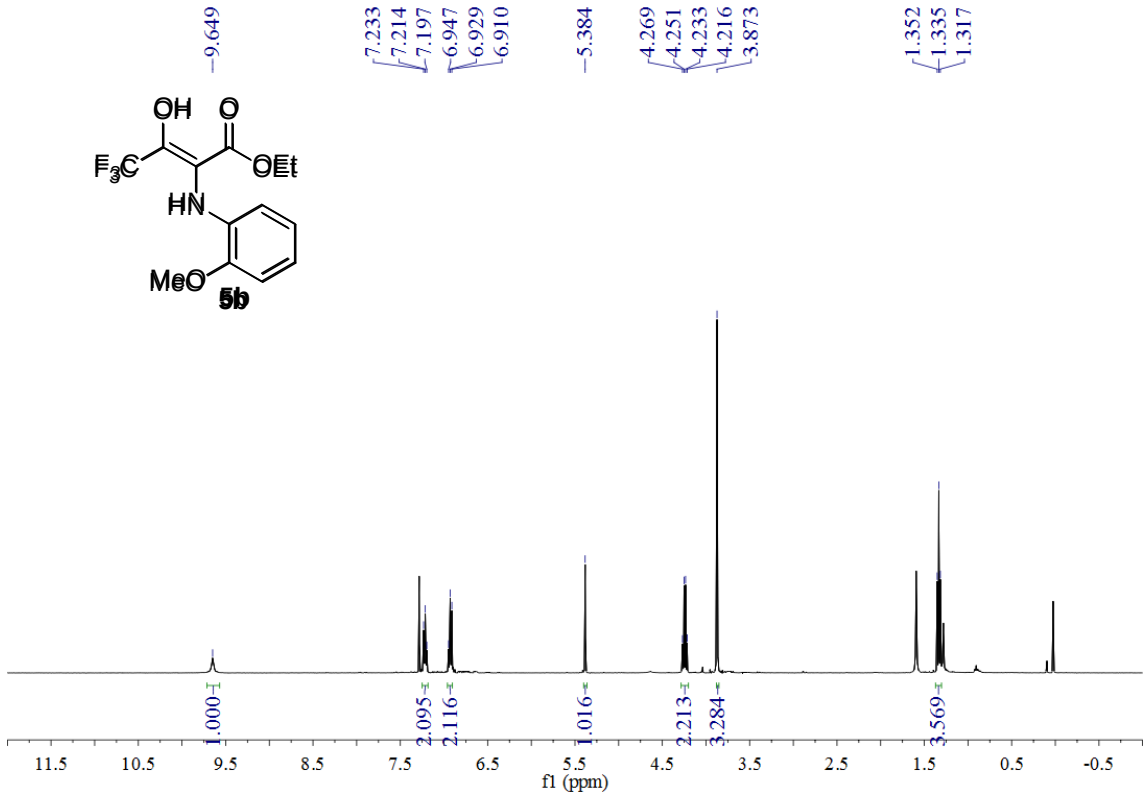
^{1}H NMR of 5a in $CDCl_3$



^{13}C NMR of 5a in $CDCl_3$



^{19}F NMR of 5a in $CDCl_3$



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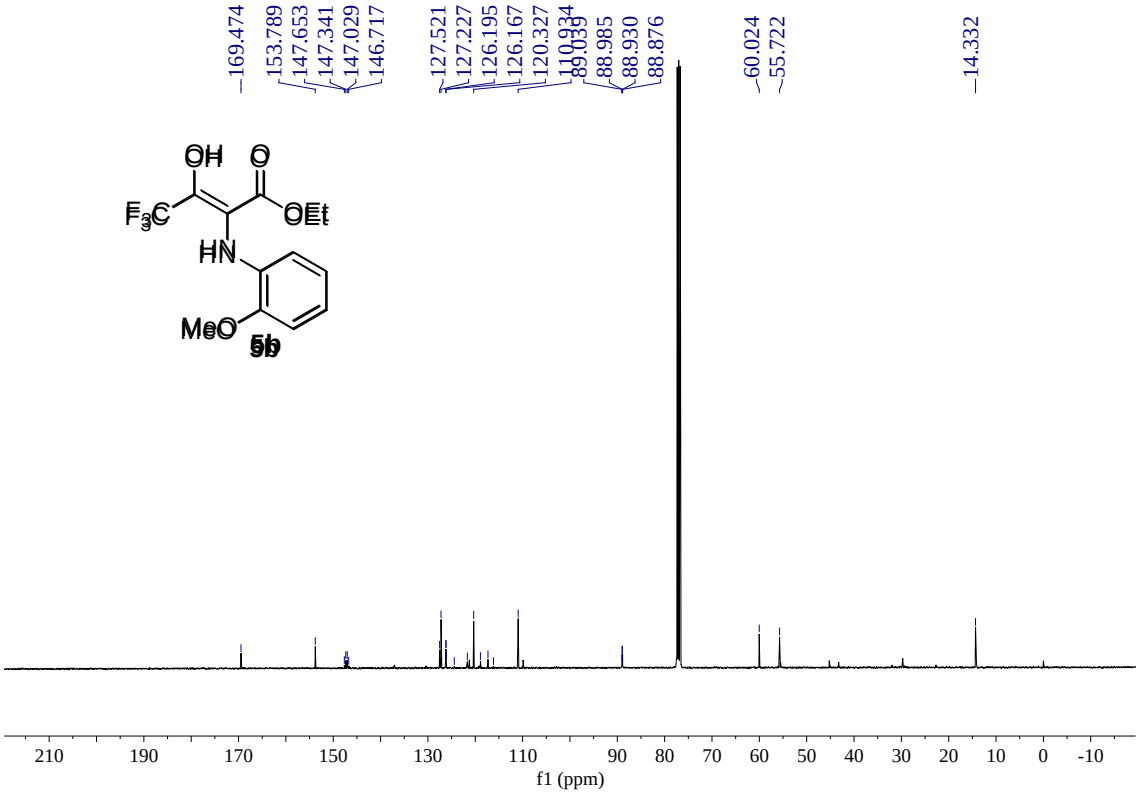

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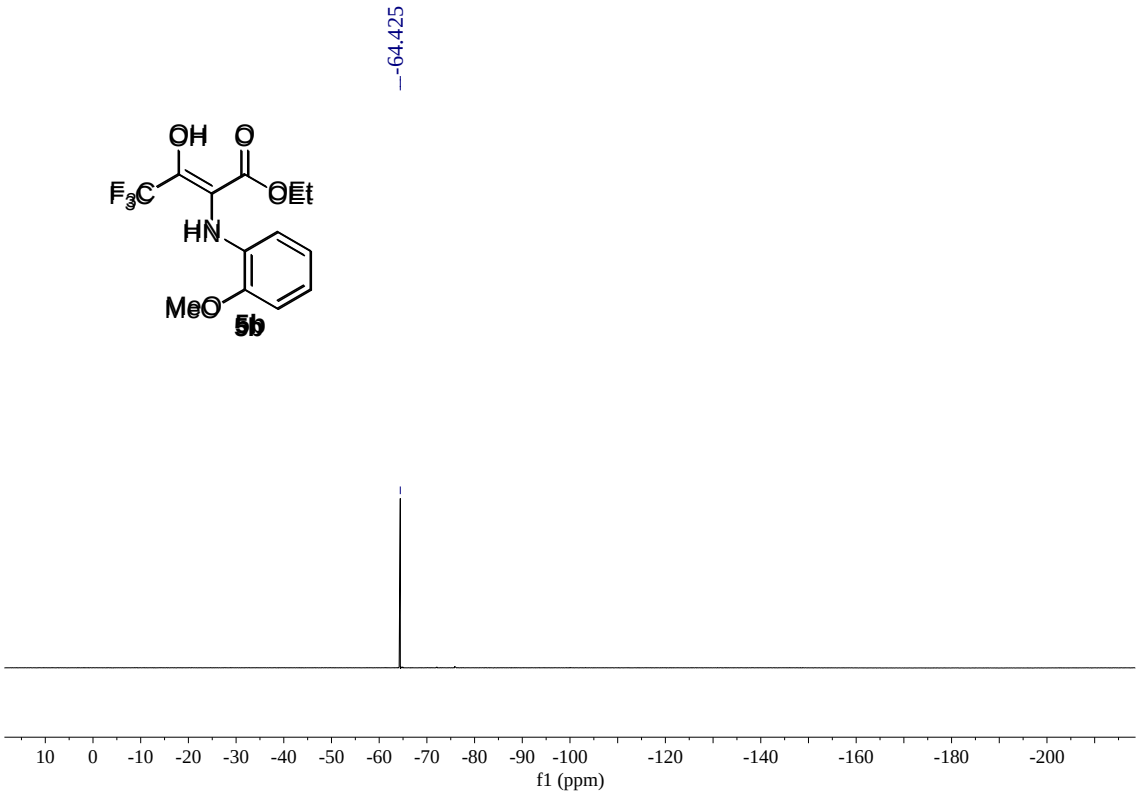
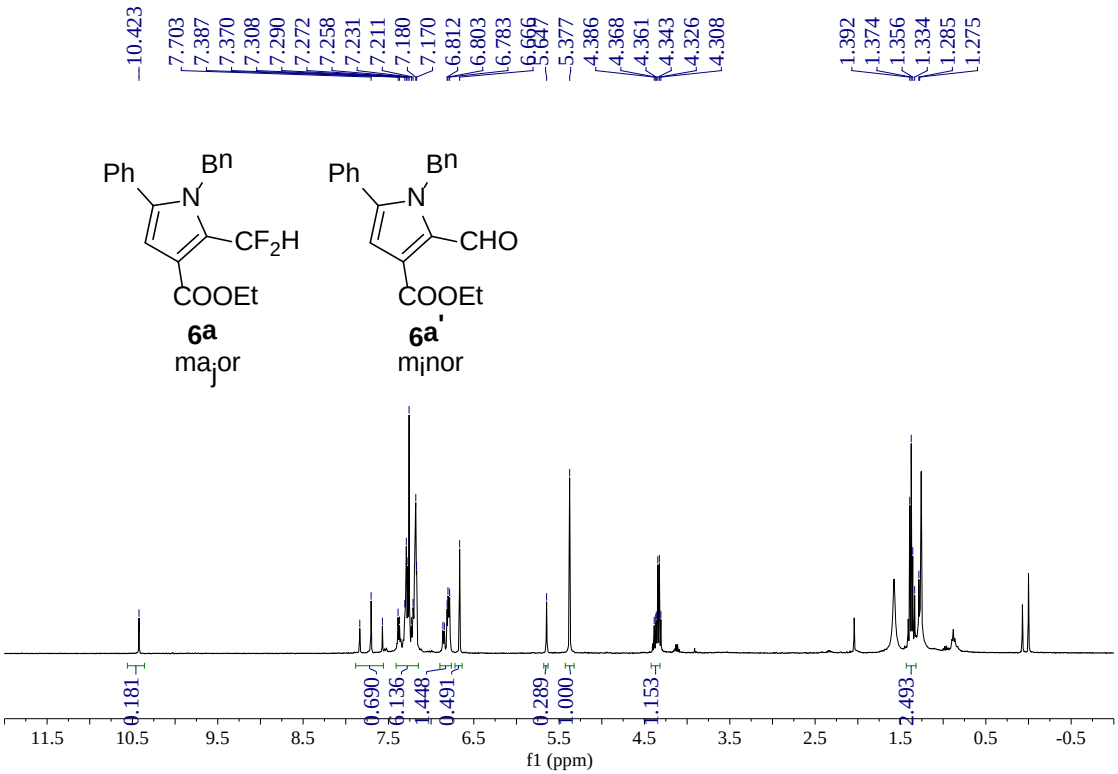
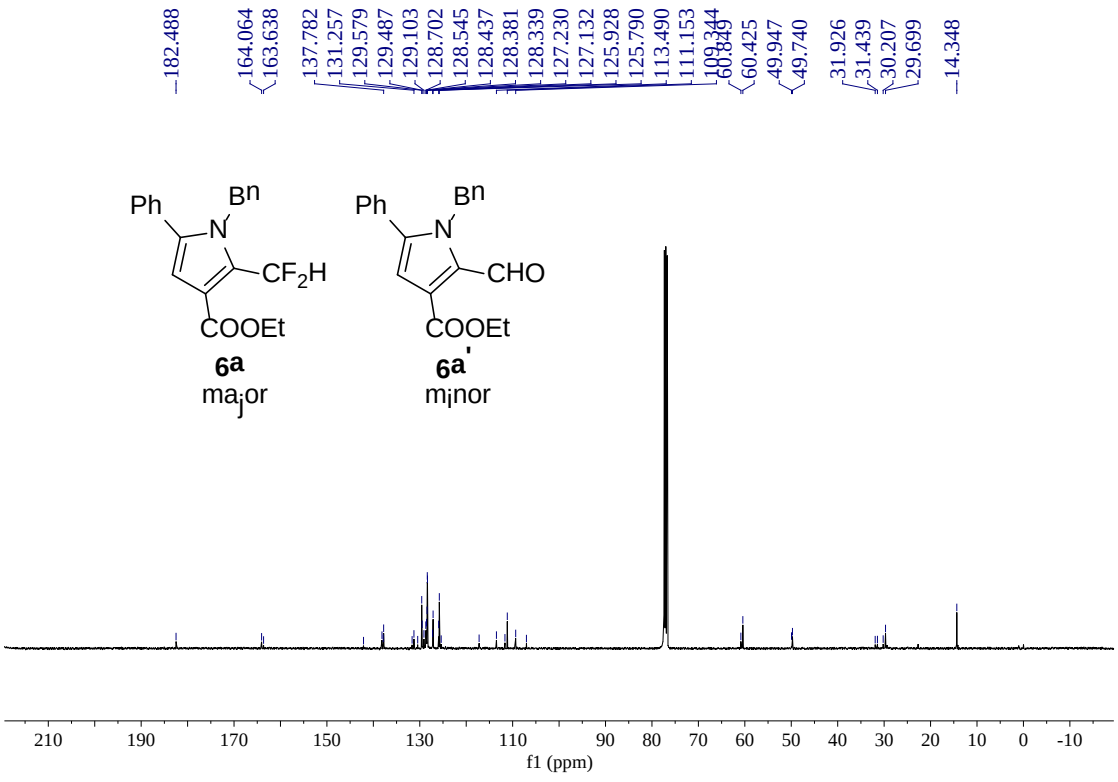


^{19}F NMR of 6a in $CDCl_3$



^{1}H NMR of 6a+6a' in $CDCl_3$



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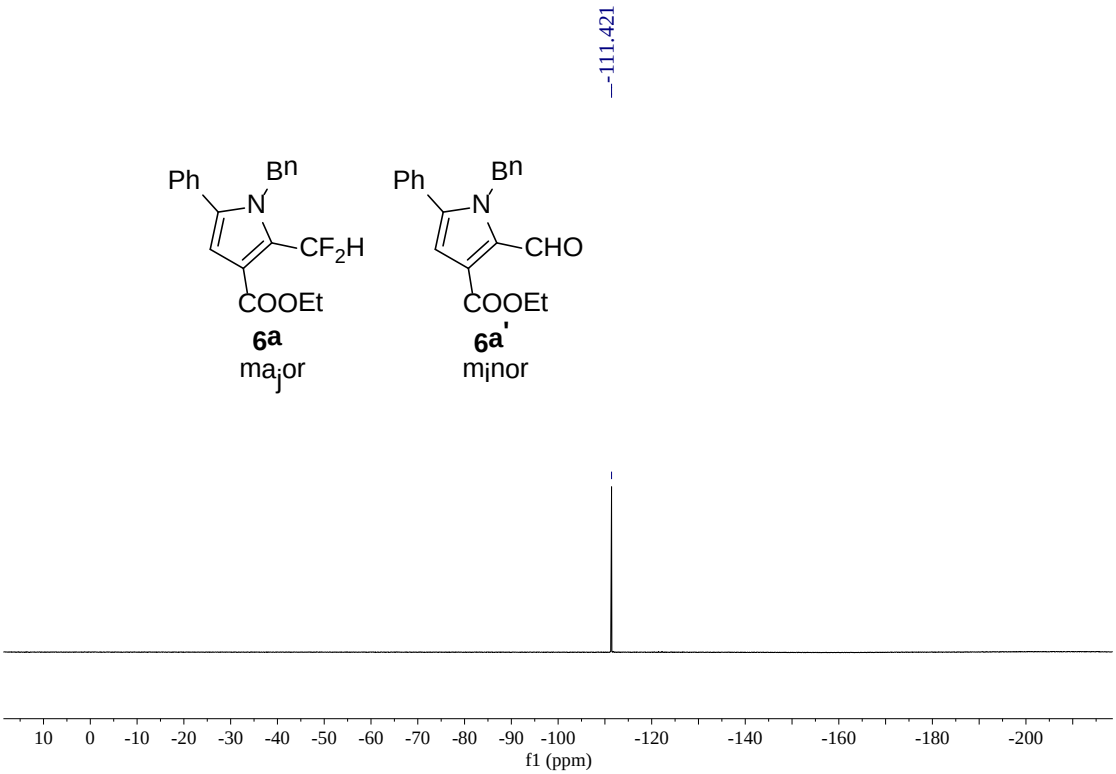

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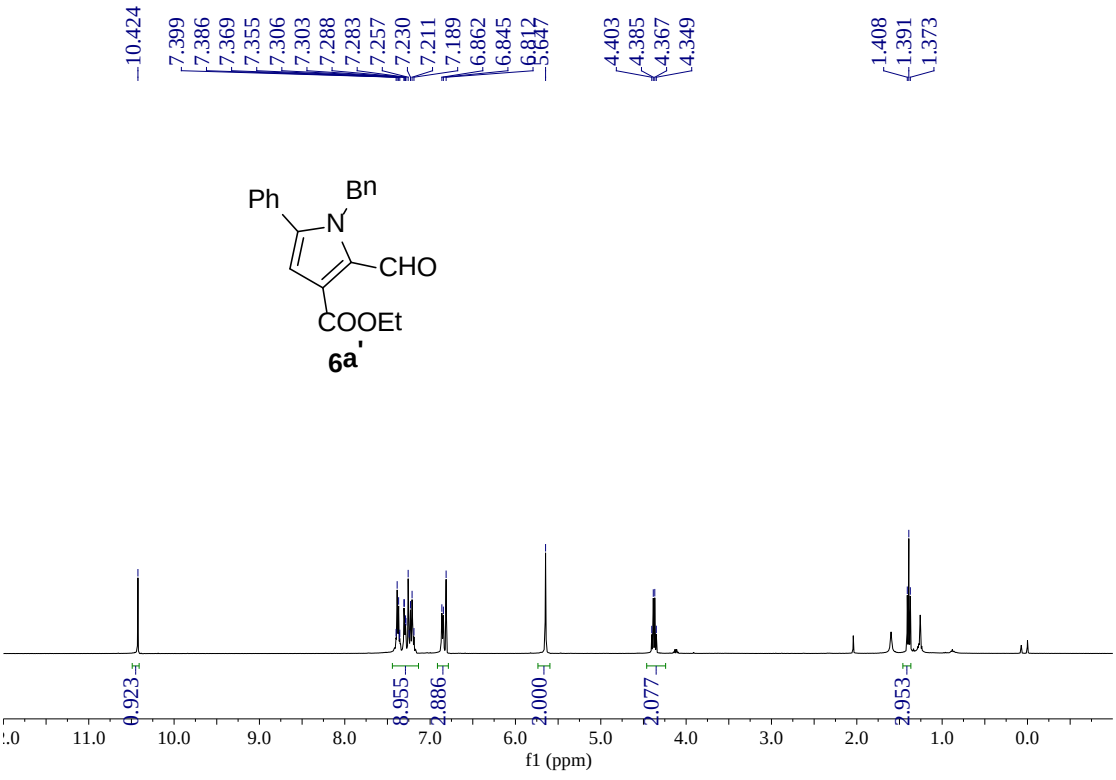

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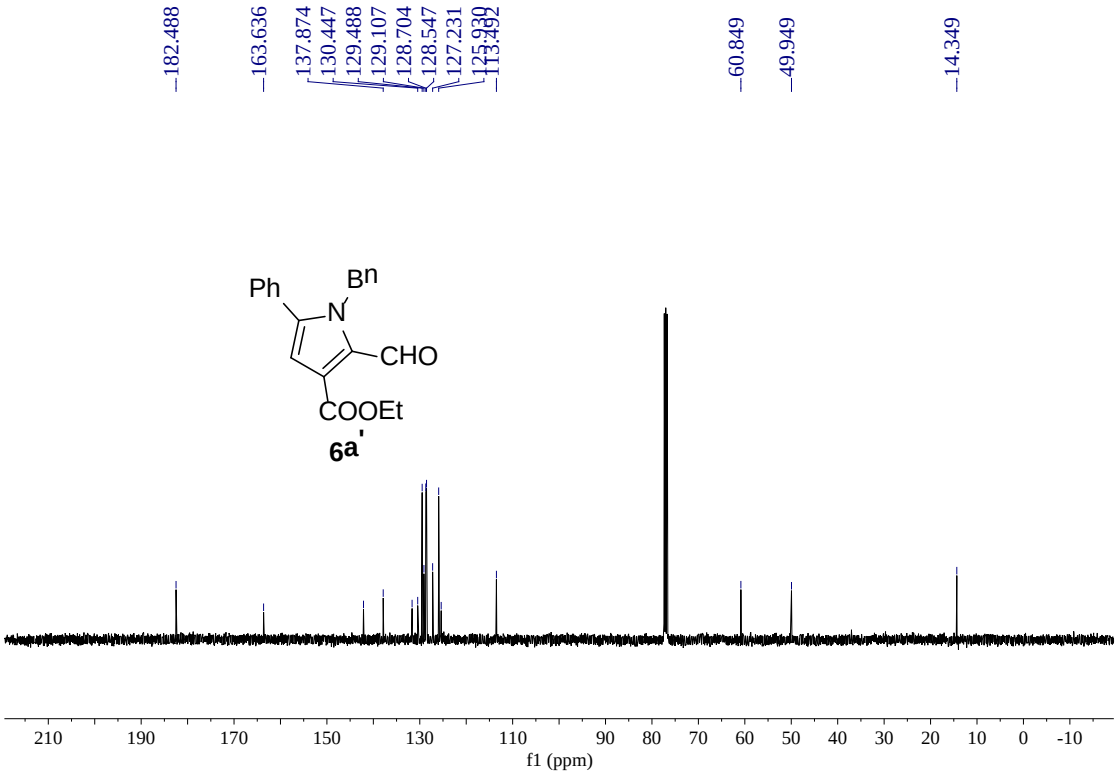
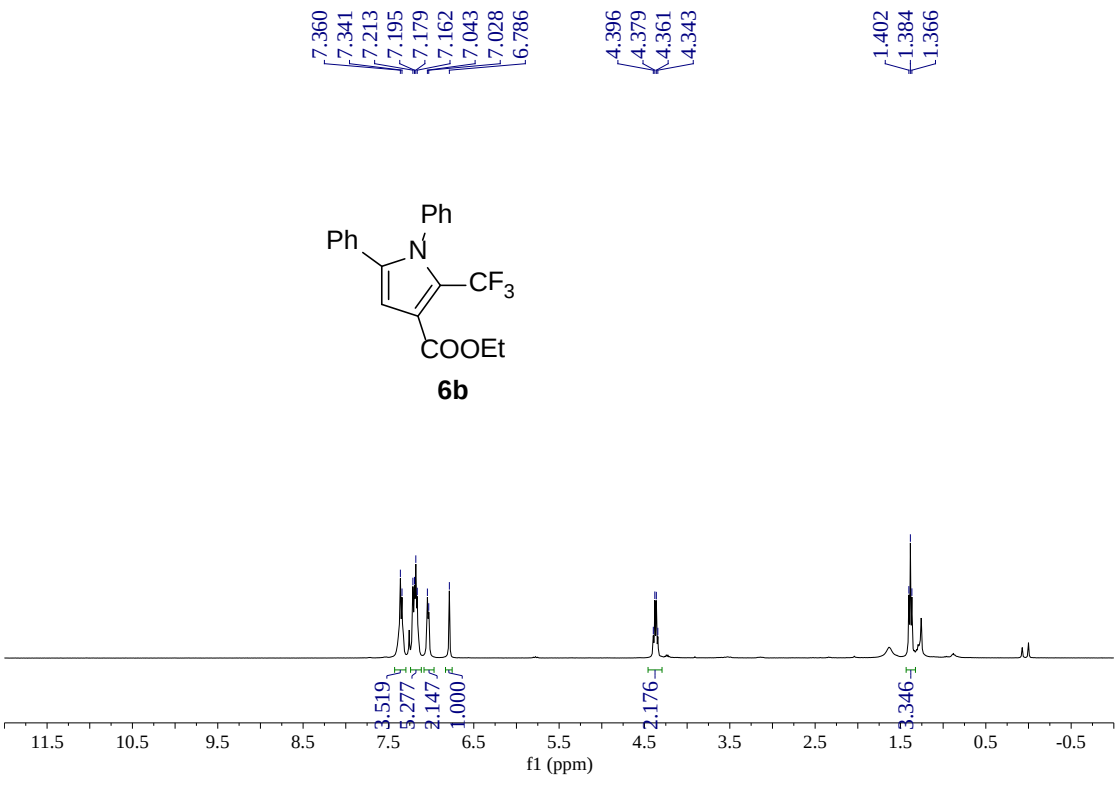
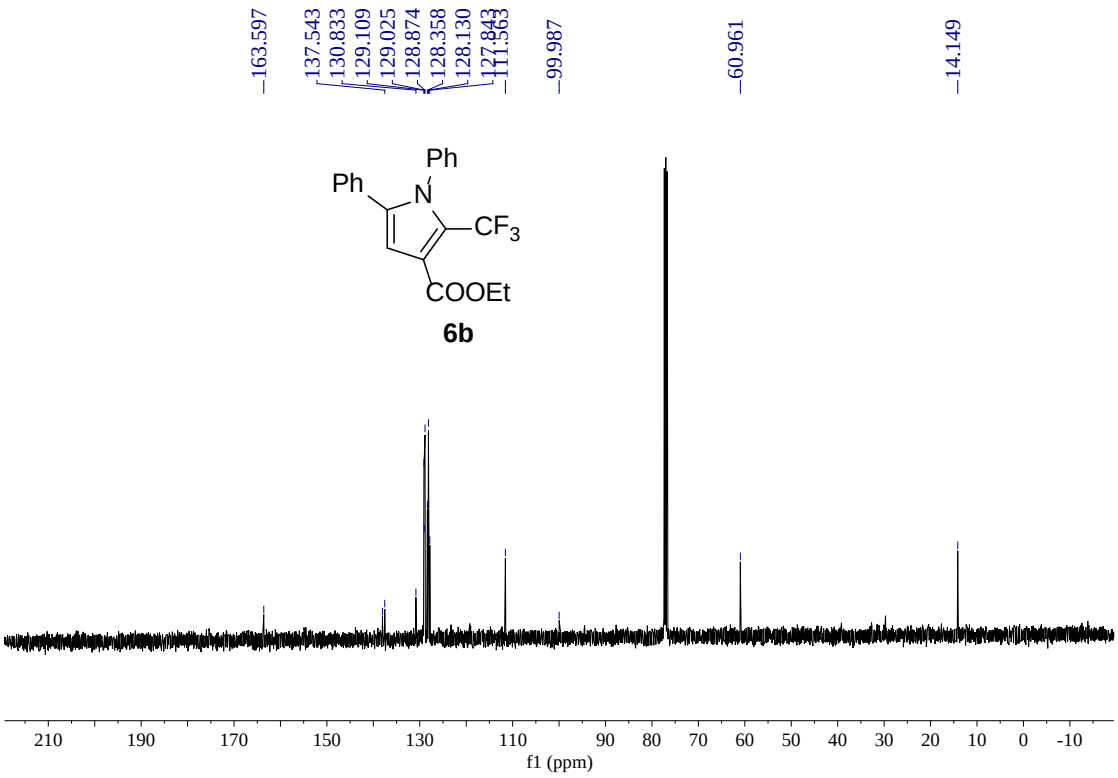


^{13}C NMR of 6a' in $CDCl_3$



^{1}H NMR of 6b in $CDCl_3$



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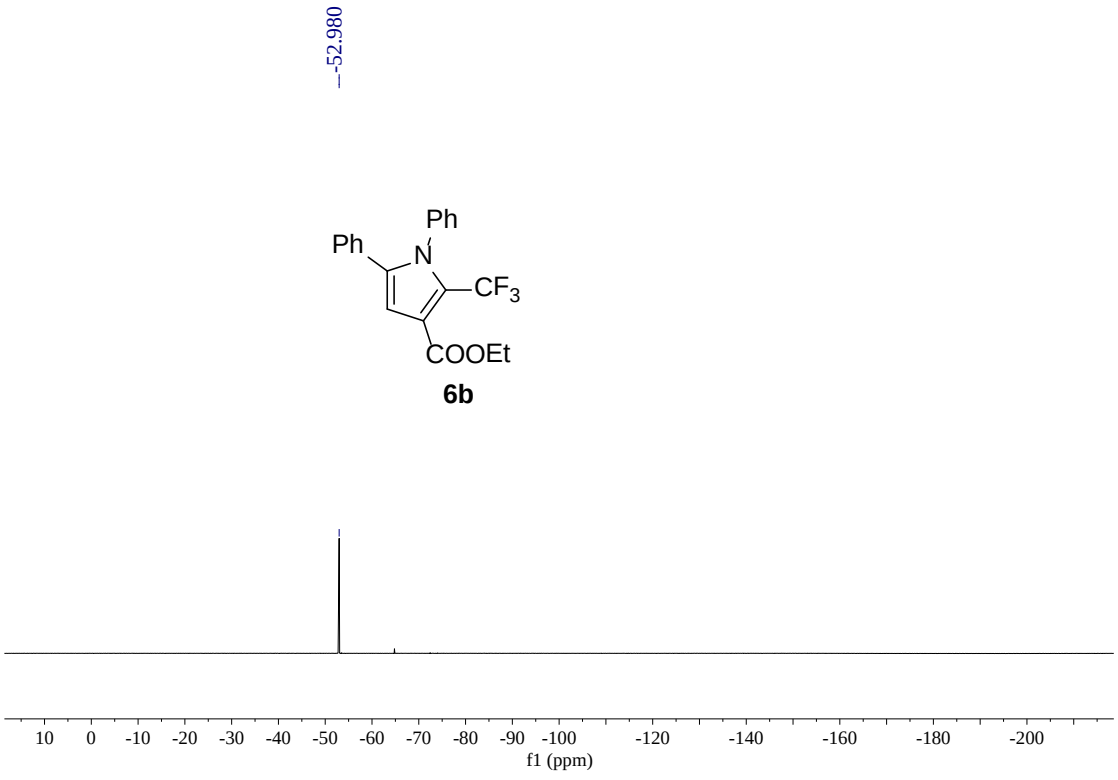

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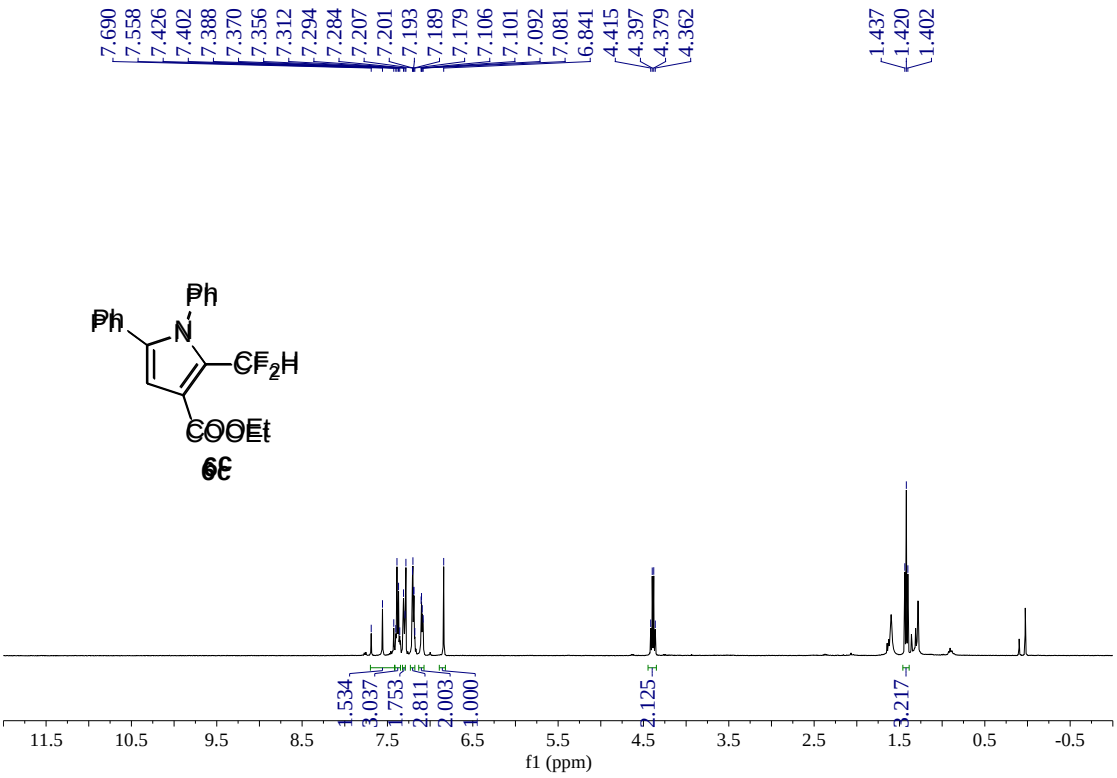

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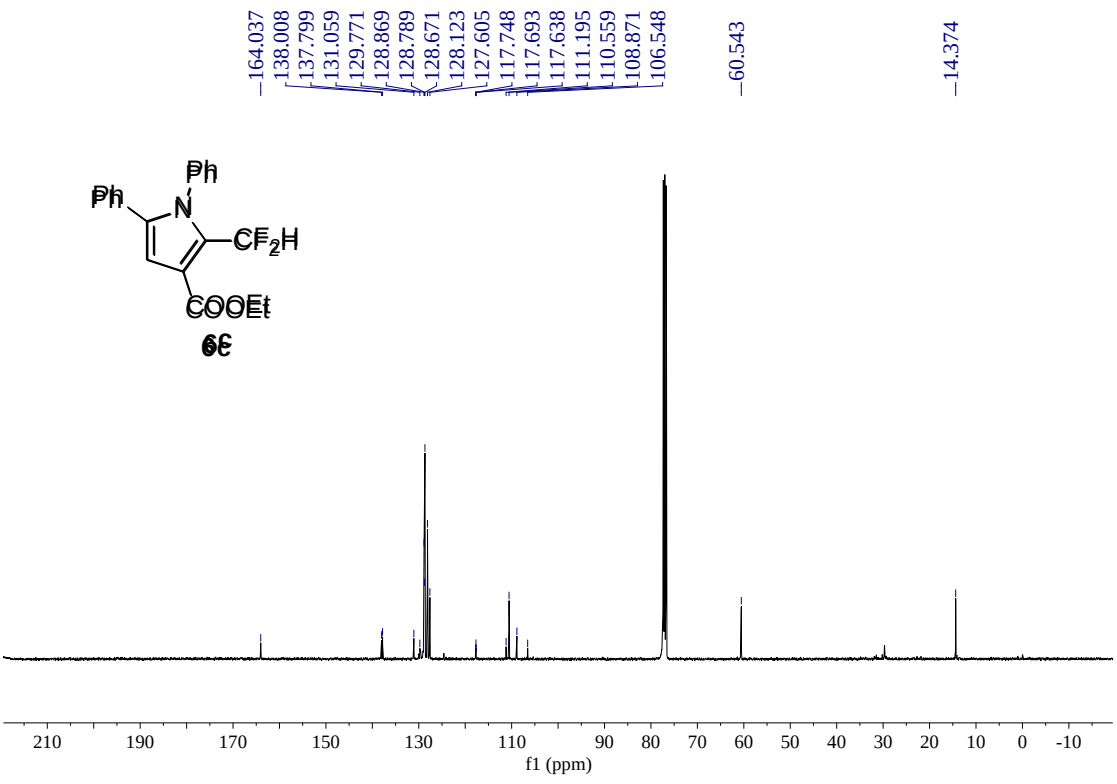
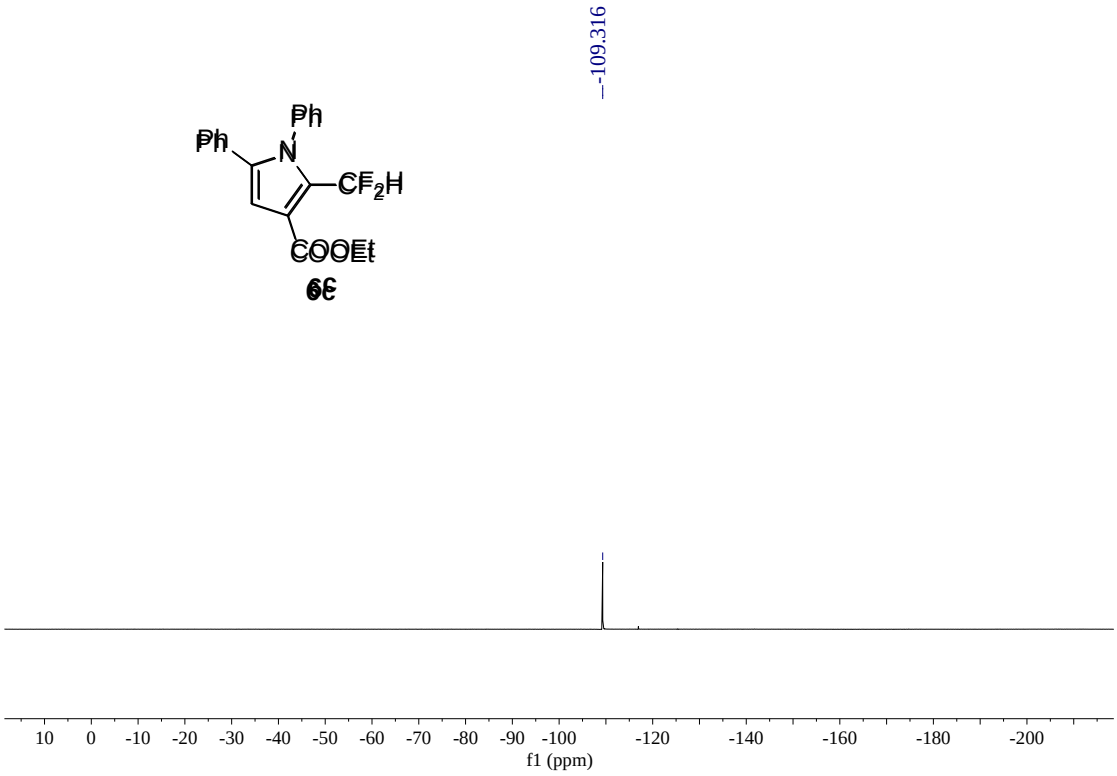


^{13}C NMR of 6c in $CDCl_3$



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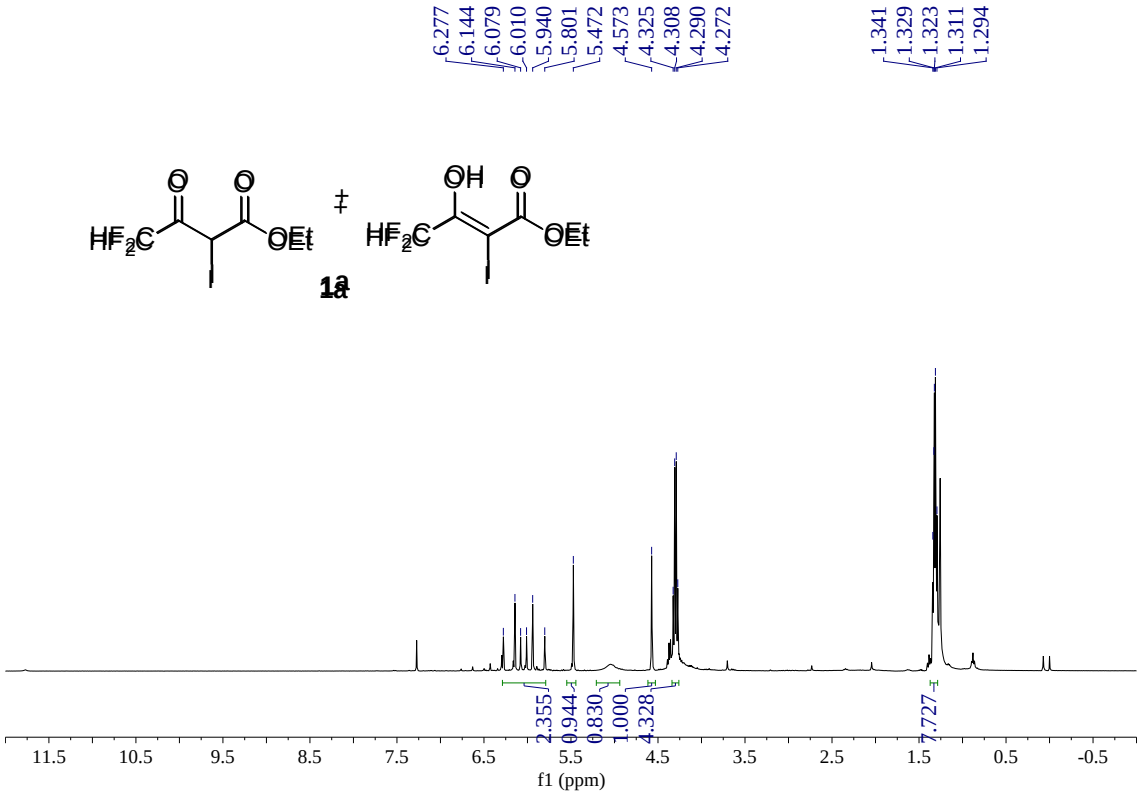
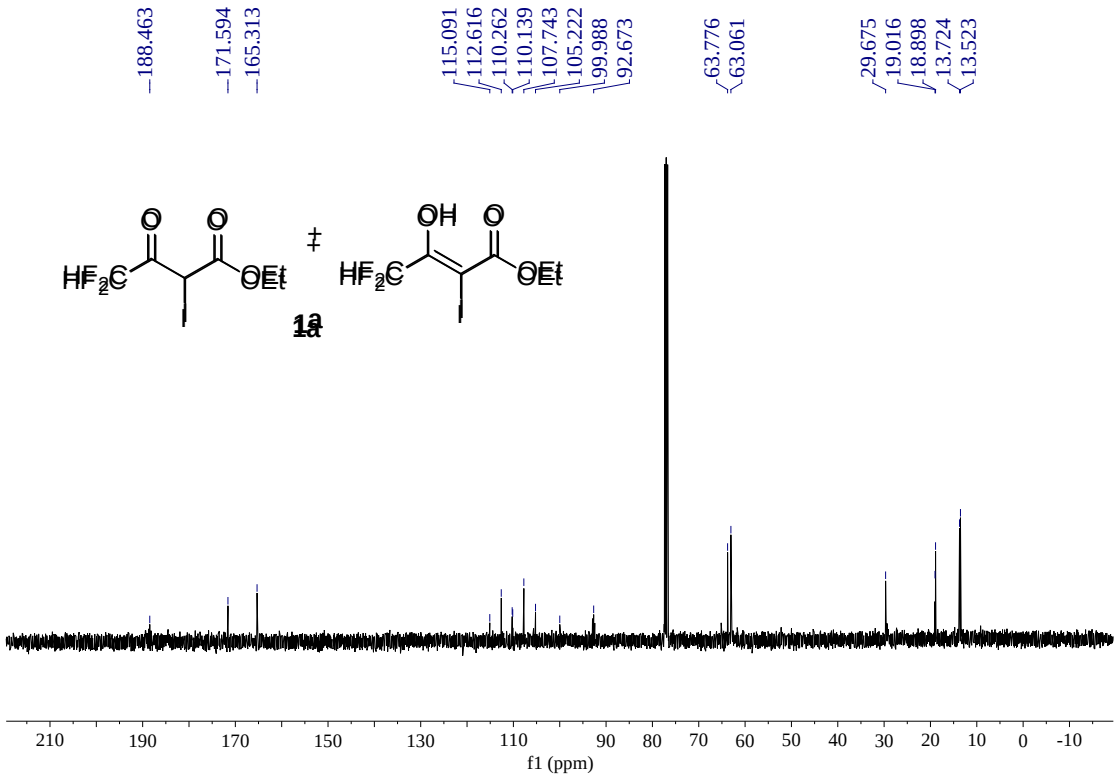


^{1}H NMR of 1a in $CDCl_3$



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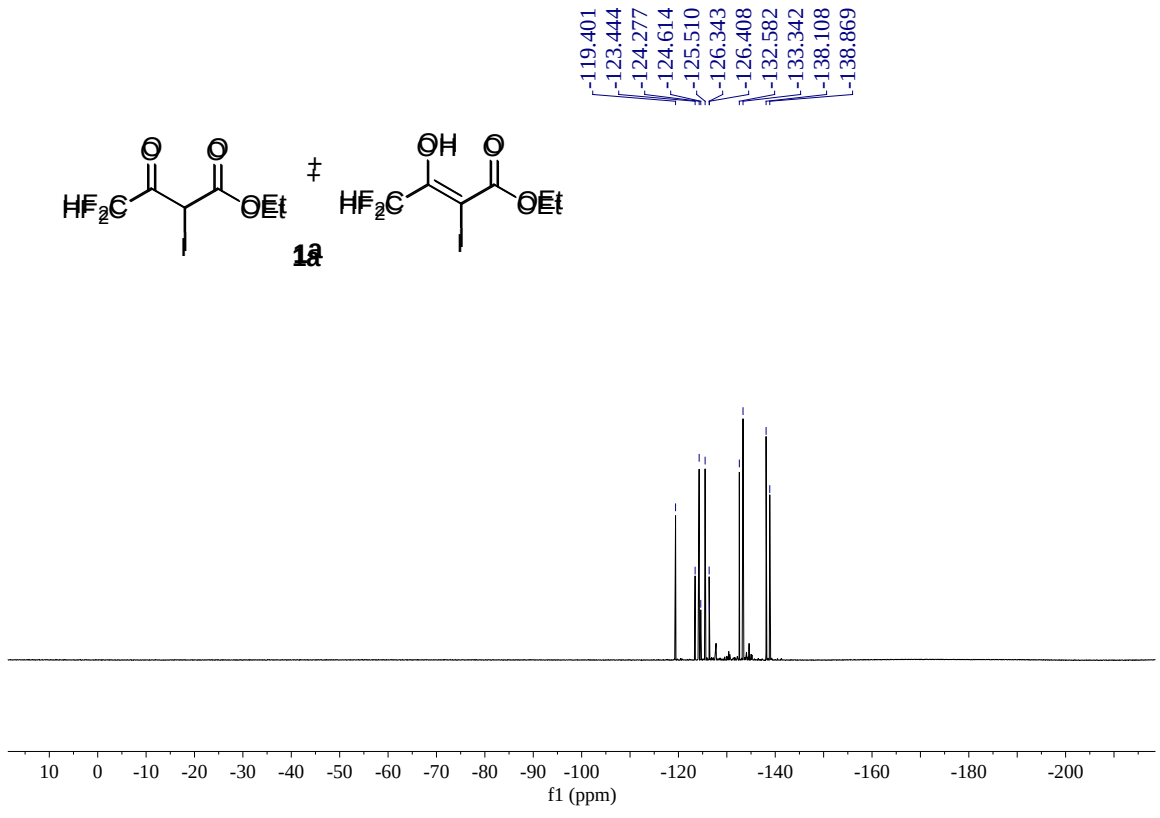
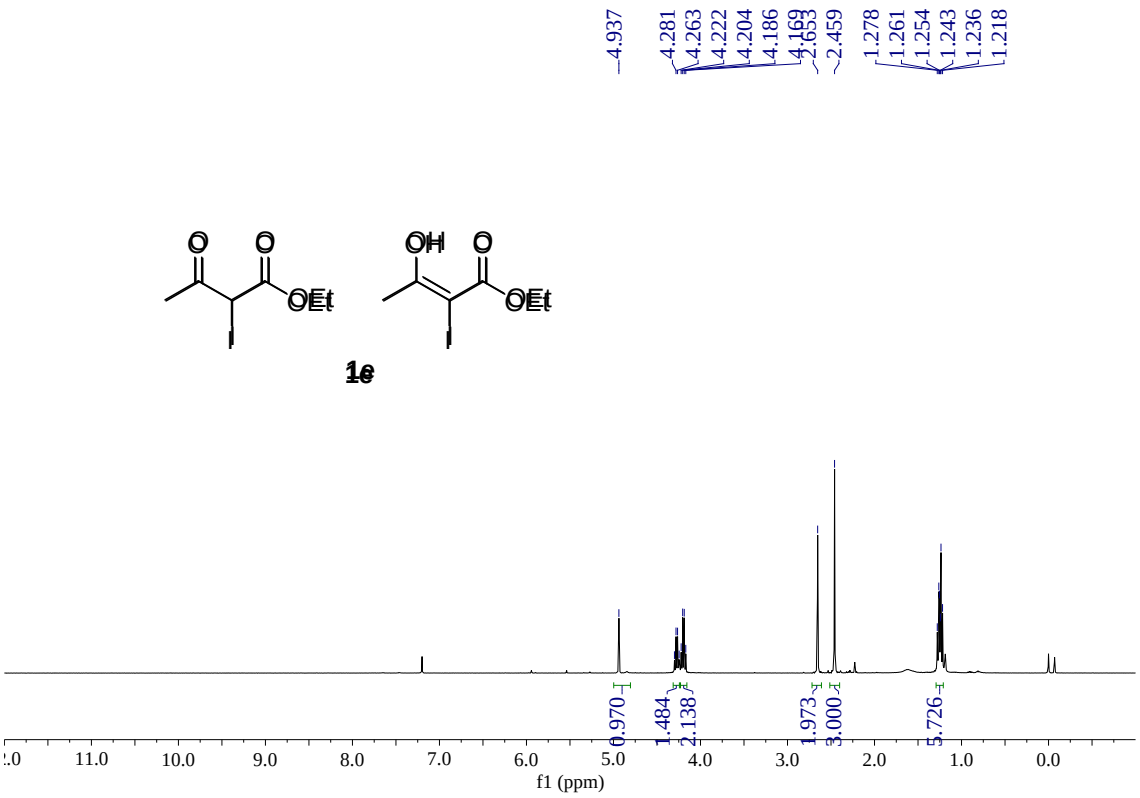
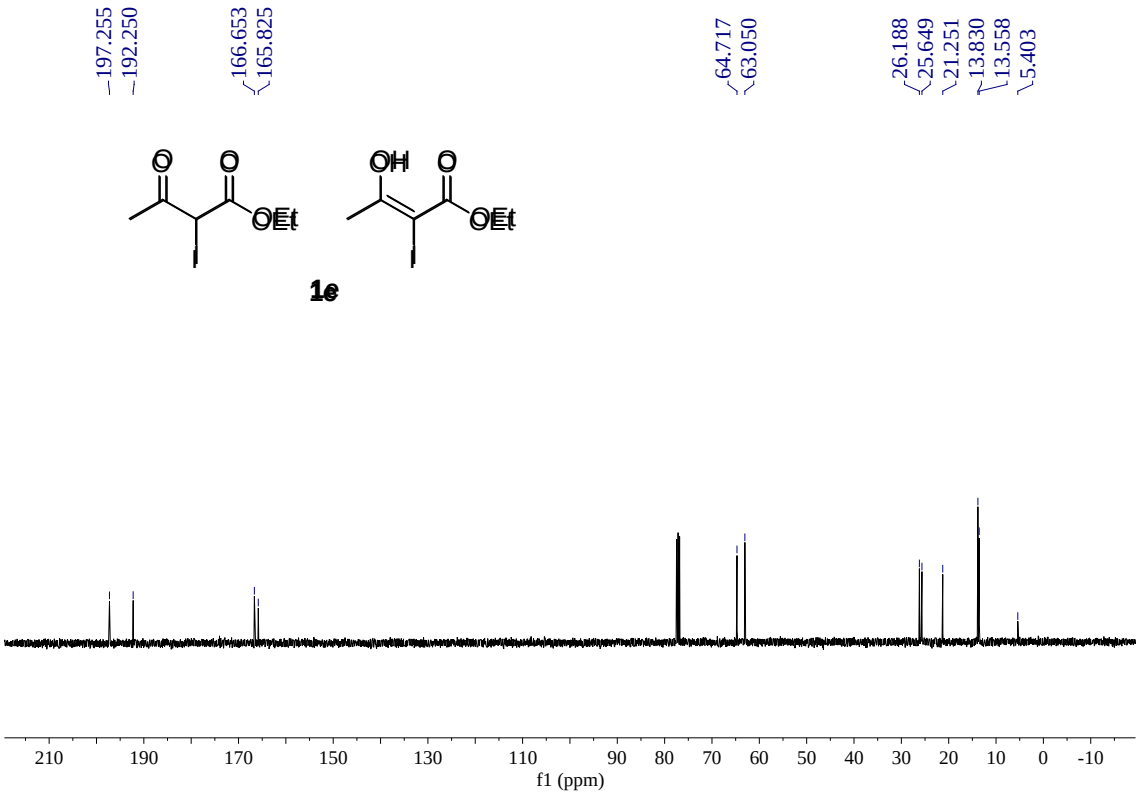


^{19}F NMR of 1a in $CDCl_3$



1e

^{1}H NMR of 1e in $CDCl_3$



1e