

Supporting Information

for

Copper-catalyzed asymmetric methylation of fluoroalkylated pyruvates with dimethylzinc

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Experimental details and characterization data of new compounds with copies of ^1H , ^{13}C and ^{19}F NMR spectra

Table of Contents

General information	page S2
Experimental procedures	
Typical procedure I: synthesis of dialkyl oxalate	page S3–S4
Typical procedure II: synthesis of trifluoropyruvate derivatives	page S4–S6
Typical procedure III:	
Cu-catalyzed asymmetric methylation of fluoroalkylated pyruvate	page S7–S12
Typical procedure IV:	
Cu-catalyzed asymmetric methylation of trifluoropyruvate derivatives	page S13–S14
Determination of absolute configuration	page S14–S15
Synthesis of simple perfluoroalkylated ketone	page S15
Catalytic asymmetric methylation of perfluoroalkylated ketone	page S16–S17
References	page S17
NMR spectra	page S18–S40

General information:

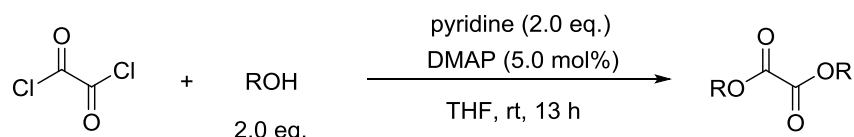
^1H , ^{13}C , and ^{19}F NMR spectra were measured on a Bruker AV300M (300 MHz) spectrometer. Chemical shifts of ^1H NMR were expressed in parts per million relative to the singlet ($\delta = 7.26$) for CHCl_3 as internal standard in CDCl_3 . Chemical shifts of ^{13}C NMR were expressed in parts per million relative to the central line of the triplet ($\delta = 77.0$) for CDCl_3 . Chemical shifts of ^{19}F NMR were expressed in parts per million relative to the singlet ($\delta = -63.24$) for BTF (benzotrifluoride) as an internal standard. Optical rotations were measured on JASCO P-1020. Mass spectra were measured on a JEOL JMS-T100CS (Accu-TOF) spectrometer. IR spectra were measured on a JASCO FT/IR-4200 spectrometer. High performance liquid chromatography (HPLC) was conducted on JASCO PU-980, LG-980-02, DG-980-50, MD-2010, and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by JASCO chrom NAV (Windows 7) as an automatic integrator. All experiments were carried out under argon atmosphere unless otherwise noted.

Copper(I) thiophene-2-carboxylate (CuTC), Me_2Zn (1 M in heptane solution), and *tert*-butyl methyl ether (dehydrate) were purchased from Aldrich. (*R*)-BTFM-Garphos was purchased from Strem Chemicals, Inc.

Substrates:

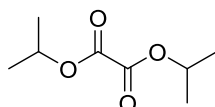
Ethyl trifluoropyruvate **1a** and was provided from Central Glass Co., Ltd. Methyl trifluoropyruvate **1b** was purchased from TCI. Ethyl difluoropyruvate **1g** [1], ethyl bromodifluoropyruvate **1h** [2], and ethyl perfluoroalkylpyruvates **1i–k** [3] were synthesized according to published procedure.

Typical procedure I: synthesis of dialkyl oxalate



To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added *N,N'*-dimethylaminopyridine (183 mg, 1.5 mmol), pyridine (4.84 mL, 60 mmol), ROH (60 mmol), and THF (200 mL). Oxalyl chloride (3.3 mL, 30 mmol) was added dropwise to the solution. After stirring at room temperature for 13 h, the reaction mixture was diluted with H₂O (100 mL) and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with saturated aq. NaHCO₃ (100 mL), water (100 mL), brine (100 mL), and dried over MgSO₄, and then filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the corresponding dialkyl oxalate.

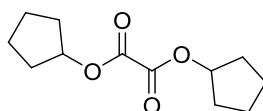
Diisopropyl oxalate [4]



The compound was purified by silica gel column chromatography (EtOAc/hexane 1:20) as a colorless liquid (76% yield). The product is known compound, the following data are identical to those given in corresponding literature [5].

¹H NMR (300 MHz, CDCl₃) δ 5.10 (sept, 2H, *J* = 6.3 Hz), 1.30 (d, 12H, *J* = 6.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 157.9, 71.3, 21.5.

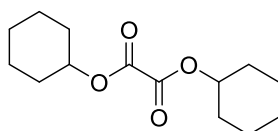
Dicyclopentyl oxalate



The compound was purified by silica-gel column chromatography (EtOAc/hexane 1:20) as a colorless liquid (91% yield).

¹H NMR (300 MHz, CDCl₃) δ 5.25-5.19 (m, 2H), 1.92-1.80 (m, 4H), 1.78-1.66 (m, 8H), 1.62-1.49 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 158.1, 80.1, 32.4, 23.6; HRMS (ESI-TOF) calcd for C₁₂H₁₈NaO₄ [M+Na]⁺: 249.1103, found: 249.1106; FT-IR (neat, cm⁻¹) 762, 852, 942, 1017, 1122, 1172, 1310, 1363, 1465, 1747, 1763, 2875, 2943, 2974.

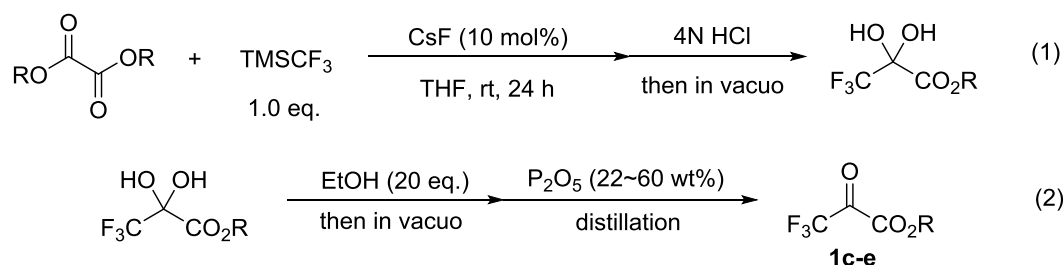
Dicyclohexyl oxalate



The compound was purified by silica-gel column chromatography (EtOAc/hexane 1:20) as white solid (92% yield).

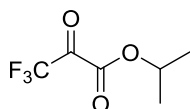
^1H NMR (300 MHz, CDCl_3) δ 4.94-4.85 (m, 2H), 1.93-1.88 (m, 4H), 1.81-1.74 (m, 4H), 1.60-1.48 (m, 6H), 1.44-1.20 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.9, 76.0, 31.3, 25.3, 23.7; HRMS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 277.1416, found: 277.1429; FT-IR (KBr, cm^{-1}) 758, 807, 920, 1007, 1037, 1089, 1146, 1179, 1247, 1262, 1314, 1360, 1442, 1739, 2060, 2104, 2153, 2228, 2251, 2293, 2495, 2654, 2864, 2951, 3473.

Typical procedure II: synthesis of trifluoropyruvate derivatives [6]



To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added dialkyl oxalate (10 mmol), cesium fluoride (151.9 mg, 1 mmol), TMSCF_3 (1.48 mL, 10 mmol), and THF (60 mL). After the reaction mixture was stirred for 24 h at room temperature, 4 N HCl (30 mL) was added and concentrated in vacuo to give the corresponding trifluoropyruvate hydrate (reaction 1). Then, a solution of trifluoropyruvate hydrate in ethanol was stirred at 70 °C for 4 h, and evaporated. The hemiacetal pyruvate was purified by distillation with P_2O_5 to provide the corresponding trifluoropyruvate (**1c,d**) (reaction 2).

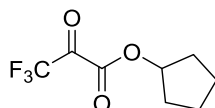
Isopropyl 3,3,3-trifluoro-2-oxopropanoate (**1c**)



The compound was purified by distillation with P_2O_5 (55 wt %, 263 Torr, 35 °C) as a colorless liquid (25% yield).

^1H NMR (300 MHz, CDCl_3) δ 5.23 (sept, 1H, $J = 6.3$ Hz), 1.36 (d, 6H, $J = 6.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 174.4 (q, $J_{\text{C-F}} = 38.3$ Hz), 156.3, 115.2 (q, $J_{\text{C-F}} = 288.4$ Hz), 73.2, 21.4; ^{19}F NMR (282 MHz, CDCl_3) δ -75.7 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_6\text{H}_7\text{F}_3\text{O}_3$ $[\text{M}]^-$: 184.0347, found: 184.0345; FT-IR (neat, cm^{-1}) 729, 810, 840, 904, 985, 1085, 1157, 1199, 1253, 1378, 1454, 1637, 1740, 2943, 2985, 3439.

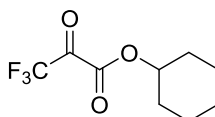
Cyclopentyl 3,3,3-trifluoro-2-oxopropanoate (1d)



The compound was purified by distillation with P₂O₅ (60 wt%, 229 Torr, 29 °C) as a colorless liquid (25% yield).

¹H NMR (300 MHz, Acetone-*d*₆) δ 5.44-5.38 (m, 1H), 2.01-1.92 (m, 2H), 1.86-1.77 (m, 2H), 1.77-1.60 (m, 4H); ¹³C NMR (75 MHz, Acetone-*d*₆) δ 174.0 (q, *J*_{C-F} = 36.4 Hz), 156.6, 116.3 (q, *J*_{C-F} = 288.2 Hz), 82.0, 33.0, 24.2; ¹⁹F NMR (282 MHz, Acetone-*d*₆) δ 75.7 (s, 3F); HRMS (APCI-TOF) calcd for C₈H₉F₃O₃ [M]⁻: 210.0538, found: 210.0530; FT-IR (neat, cm⁻¹) 728, 850, 950, 991, 1024, 1094, 1150, 1202, 1247, 1291, 1747, 1850, 2877, 2966, 3433.

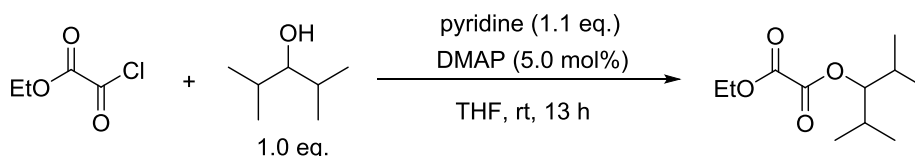
Cyclohexyl 3,3,3-trifluoro-2-oxopropanoate (1e)



The compound was purified by distillation with P₂O₅ (42 wt%, 41 Torr, 52~53 °C) (containing small amount of cyclohexene) as a colorless liquid (42% yield).

¹H NMR (300 MHz, CDCl₃) δ 5.09-5.01 (m, 1H), 1.98-1.88 (m, 3H), 1.82-1.75 (m, 2H), 1.69-1.50 (m, 3H), 1.49-1.28 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 174.6 (q, *J*_{C-F} = 38.5 Hz), 156.2, 115.2 (q, *J*_{C-F} = 288.4 Hz), 77.7, 31.1, 25.1, 23.4; ¹⁹F NMR (282 MHz, CDCl₃) δ 75.7 (s, 3F); HRMS (APCI-TOF) calcd for C₉H₁₁F₃O₃ [M]⁻: 224.0660, found: 224.0650; FT-IR (neat, cm⁻¹) 733, 828, 898, 1008, 1088, 1161, 1195, 1253, 1450, 1744, 1780, 2867, 2935, 3454.

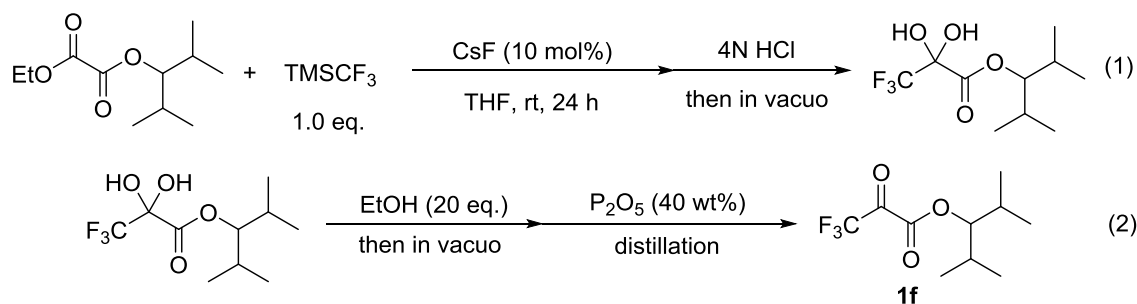
2,4-Dimethylpentan-3-yl ethyl oxalate



To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added *N,N'*-dimethylaminopyridine (366 mg, 3.0 mmol), pyridine (5.3 mL, 66 mmol), 2,4-dimethylpentan-3-ol (8.4 mL, 60 mmol), and THF (200 mL). Ethyl chloroglyoxylate (3.3 mL, 60 mmol) was added dropwise to the solution. After stirring at room temperature for 13 h, the reaction mixture was diluted with H₂O (100 mL) and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with saturated aq. NaHCO₃ (100 mL), water (100 mL), brine (100 mL), and dried over MgSO₄, filtered and concentrated under reduced pressure. Resulting crude product was purified by silica-gel column chromatography (hexane:EtOAc 20:1) to give 2,4-dimethylpentan-3-yl ethyl oxalate as a clear liquid (6.4 g, >99%).

^1H NMR (300 MHz, CDCl_3) δ 4.73 (t, 1H, $J = 6.2$ Hz), 4.34 (q, 2H, $J = 6.9$ Hz), 2.00 (m, 2H), 1.37 (t, 3H, $J = 7.0$ Hz), 0.92 (d, 6H, $J = 6.9$ Hz), 0.90 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 86.7, 63.0, 29.5, 19.5, 17.2, 14.1; HRMS (ESI-TOF) calcd for $\text{C}_{11}\text{H}_{20}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 239.1259, found: 239.1270; FT-IR (neat, cm^{-1}) 760, 859, 894, 935, 1011, 1099, 1130, 1187, 1306, 1370, 1389, 1458, 1748, 1767, 2882, 2935, 2970.

2,4-Dimethylpentan-3-yl 3,3,3-trifluoro-2-oxopropanoate (**1f**)



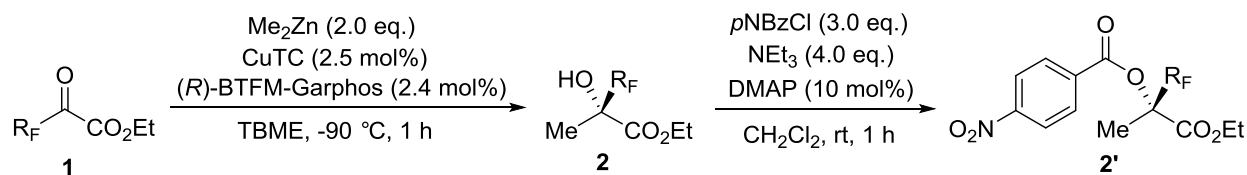
To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added 2,4-dimethylpentan-3-yl ethyl oxalate (2.16 g, 10 mmol), cesium fluoride (151.9 mg, 1 mmol), TMSCF_3 (1.48 mL, 10 mmol), and THF (60 mL). After the reaction mixture was stirred for 24 h at room temperature, 4 N HCl (60 mL) was added and extracted with Et_2O (3×50 mL). The combined organic layers were washed with brine (100 mL), and dried over Na_2SO_4 , filtered and concentrated under reduced pressure to afford the corresponding trifluoropyruvate hydrate as a yellow liquid (2.55 g, 99%) (reaction 1).

^1H NMR (300 MHz, CDCl_3) δ 4.76 (t, 1H, $J = 6.1$ Hz), 2.08-1.97 (m, 2H), 0.92 (d, 6H, $J = 6.9$ Hz), 0.91 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 174.0 (q, $J_{\text{C-F}} = 36.4$ Hz), 156.7, 116.3 (q, $J_{\text{C-F}} = 288.2$ Hz), 82.0, 33.0, 24.2; ^{19}F NMR (282 MHz, CDCl_3) δ 82.7 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_{10}\text{H}_{16}\text{F}_3\text{O}_4$ $[\text{M}-\text{H}]^-$: 243.0997, found: 243.0985; FT-IR (neat, cm^{-1}) 596, 657, 722, 878, 928, 985, 1085, 1165, 1191, 1253, 1366, 1386, 1466, 1366, 1386, 1466, 1740, 2878, 2943, 2974, 3454.

Then, a solution of trifluoropyruvate hydrate in ethanol was stirred at 70 °C for 4 h, and evaporated. The hemiacetal pyruvate was purified by distillation with P_2O_5 (40 wt%, 36 Torr, 52 °C) to provide the corresponding trifluoropyruvate (**1f**) as a colorless liquid (83% yield) (reaction 2).

^1H NMR (300 MHz, CDCl_3) δ 4.83 (t, 1H, $J = 6.1$ Hz), 2.12-1.97 (m, 2H), 0.93 (d, 6H, $J = 6.9$ Hz), 0.92 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 174.7 (q, $J_{\text{C-F}} = 38.9$ Hz), 157.0 (s), 115.0 (q, $J_{\text{C-F}} = 288.4$ Hz), 88.5, 29.3, 19.2, 16.8; ^{19}F NMR (282 MHz, CDCl_3) δ 75.8 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_{10}\text{H}_{15}\text{F}_3\text{O}_3$ $[\text{M}]^-$: 240.0973, found: 240.0973; FT-IR (neat, cm^{-1}) 720, 886, 931, 1010, 1089, 1172, 1191, 1254, 1304, 1371, 1393, 1469, 1743, 1777, 2879, 2943, 2977, 3459.

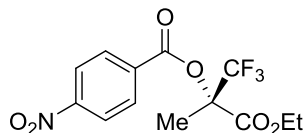
Typical procedure III: Cu-catalyzed asymmetric methylation of fluoroalkylated pyruvate



To a mixture of CuTC (1.0 mg, 0.005 mmol) and (R) -BTfM-Garphos (5.7 mg, 0.0048 mmol) was added CH_2Cl_2 (1.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (0.5 mL) under argon atmosphere. After the solution was cooled to -90°C , Me_2Zn (1.0 M in heptane, 0.4 mL, 0.4 mmol) followed by fluoroalkylated pyruvate **1** (0.2 mmol) in TBME (0.5 mL) were added in 30 min. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aq. NH_4Cl . The organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under controlled pressure (350 mmHg). The concentrated solution was used without purification for the next protection reaction. The yield of alcohol product **2** was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

To a solution of DMAP (2.4 mg, 0.02 mmol) and the crude alcohol in CH_2Cl_2 (2.0 mL) was added NEt_3 (56 μL , 0.4 mmol) at room temperature under argon atmosphere. After the reaction mixture was cooled to 0°C , *p*-nitrobenzoyl chloride (56 mg, 0.3 mmol) was added. Then the mixture was warmed to room temperature and stirred for 1 h. After 1 N HCl (5.0 mL) was added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layer was washed with saturated aq. NaHCO_3 , water, and brine, and then dried over anhydrous MgSO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give *p*-nitrobenzoylated alcohol **2'**. Enantiomeric excess was determined by chiral HPLC analysis.

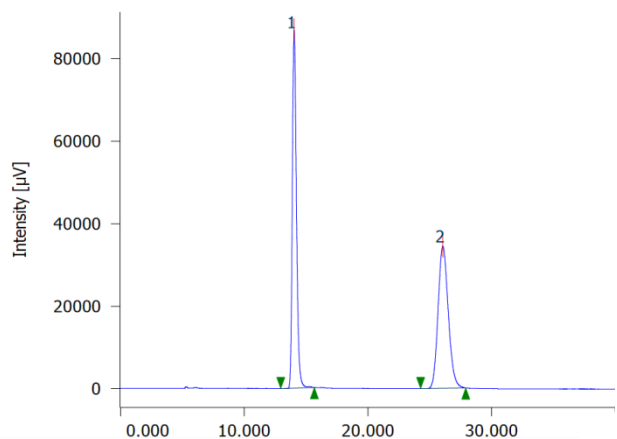
(*S*)-3-Ethoxy-1,1,1-trifluoro-2-methyl-3-oxopropan-2-yl 4-nitrobenzoate (**2a'**)



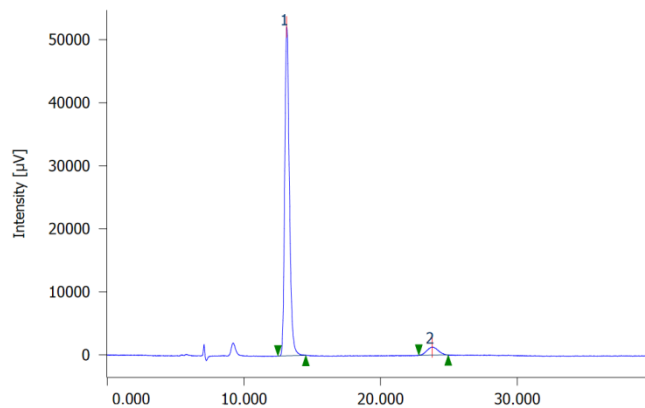
The yield of alcohol **2a** (86%) was determined by ^{19}F NMR analysis. *p*-Nitrobenzoylated alcohol **2a'** was purified by silica gel column chromatography (EtOAc/hexane 1:40) as a colorless liquid (53% yield for 2 steps, 89% ee).

^1H NMR (300 MHz, CDCl_3) δ 8.34–8.31 (m, 2H), 8.24–8.20 (m, 2H), 4.33 (q, 4H, $J = 6.9$ Hz), 1.97 (d, 3H, $J = 0.9$ Hz), 1.28 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 164.3, 162.3, 151.1, 134.0, 131.2, 123.7, 122.7 (q, $J_{\text{C-F}} = 282.9$ Hz), 80.7 (q, $J_{\text{C-F}} = 30.4$ Hz), 63.2, 16.6, 13.8; ^{19}F NMR (282 MHz, CDCl_3) δ -78.4 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}_6$ [M] $^-$: 335.0617, found: 335.0623; FT-IR (neat, cm^{-1}) 784, 813, 849, 876, 927, 1011, 1109, 1149, 1273, 1342, 1387, 1452,

1525, 1602, 1740, 1763, 2857, 2920, 2952, 2996, 3087, 3116; $[\alpha]_D^{22}$ -28.94 (*c* 0.20, CHCl₃), 89% *ee*; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) t_R of major isomer 13.1 min, t_R of minor isomer 23.8 min.

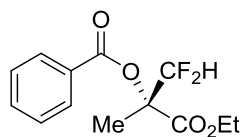


#	Time [min]	Area [μV-sec]	Area%	Height [μV]	Height%
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2	26.1	1970061	49.65	34456	28.42



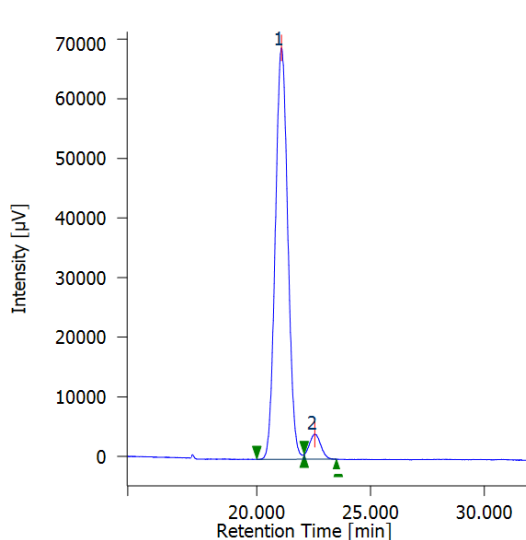
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1	13.1	1238061	94.32	52128	97.56
2	23.8	74616	5.68	1305	2.44

(*S*)-1-Ethoxy-3,3-difluoro-2-methyl-1-oxopropan-2-yl benzoate (**2g'**)

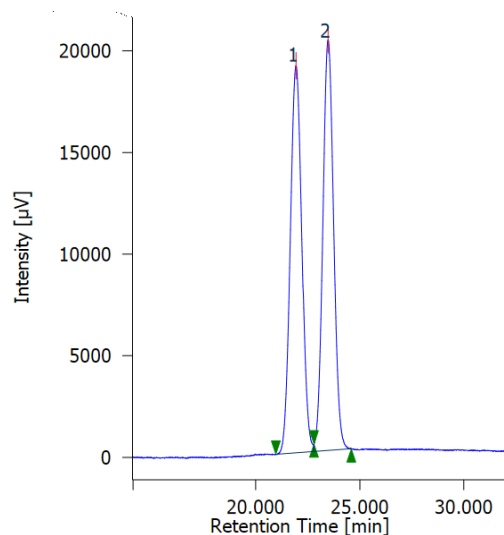


Reaction temperature was -78 °C. The yield of alcohol **2g** (89%) was determined by ¹⁹F NMR analysis. In the protection of alcohol, benzoyl chloride was used instead of *p*-nitrobenzoyl chloride. Benzoylated alcohol **2g'** was purified by silica gel column chromatography (EtOAc/hexane = 1/40) as a colorless liquid (41% yield for 2 steps, 89% *ee*).

¹H NMR (300 MHz, CDCl₃) δ 8.05 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.61 (tt, *J* = 6.7, 1.3 Hz, 1H), 7.44-7.49 (m, 2H), 6.30 (dd, *J*_{H-F} = 56.8, 54.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H) 1.77 (t, *J*_{H-F} = 1.6 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 164.8, 133.7, 130.0, 128.8, 128.5, 122.9 (dd, *J*_{C-F} = 250.0, 245.0 Hz), 79.7 (dd, *J*_{C-F} = 27.5, 21.9 Hz), 62.3, 14.6 (t, *J*_{C-F} = 3.2 Hz) 13.9; ¹⁹F NMR (282 MHz, CDCl₃) δ -128.40 (dd, *J* = 290.2 Hz, *J*_{F-H} = 54.7 Hz, 1F), -132.76 (dd, *J* = 289.90 Hz, *J*_{F-H} = 56.4 Hz, 1F); HRMS (APCI-TOF) calcd for C₁₃H₁₄F₂NaO₄ [M+Na]⁺: 295.0758, found: 295.0761; FT-IR (neat, cm⁻¹) 1026, 1093, 1114, 1216, 1279, 1388, 1452, 1602, 1730, 1747, 2938, 2985, 3021; $[\alpha]_D^{25}$ -7.47 (*c* 1.01, CHCl₃), 89% *ee*; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) t_R of major isomer 21.2 min, t_R of minor isomer 22.6 min.

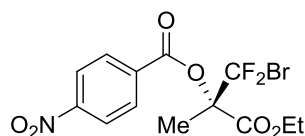


#	Time [min]	Area [µV-sec]	Area%	Height [µV]	Height%
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2	23.5	730490	50.02	20201	51.47



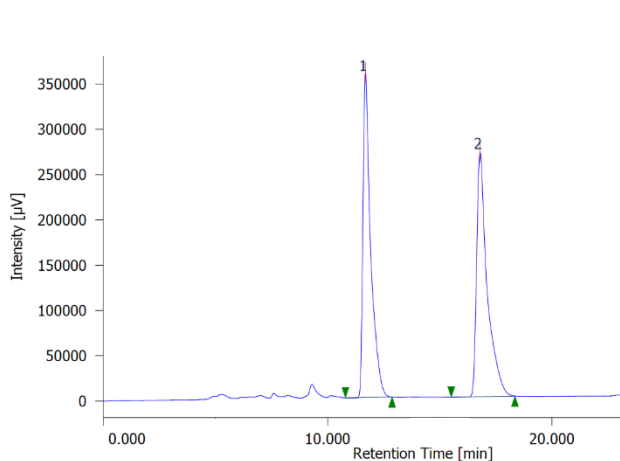
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1	21.2	2632083	94.60	69000	94.24
2	22.6	150116	5.40	4219	5.76

(S)-1-Bromo-3-ethoxy-1,1-difluoro-2-methyl-3-oxopropan-2-yl 4-nitrobenzoate (2h')

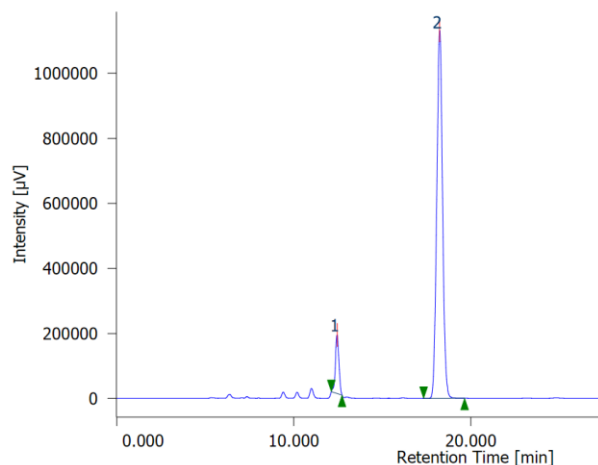


Reaction temperature was $-78\text{ }^{\circ}\text{C}$. The yield of alcohol **2h** (53%) was determined by ^{19}F NMR analysis. *p*-Nitrobenzoylated alcohol **2h'** was purified by silica gel column chromatography (EtOAc/hexane 1:50) as a white solid (32% yield for 2 steps, 82% ee).

^1H NMR (300 MHz, CDCl_3) δ 8.34-8.31 (m, 2H), 8.25-8.21 (m, 2H), 4.32 (q, 2H, $J = 7.2$ Hz), 2.02 (s, 3H), 1.29 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 164.3, 162.4, 151.2, 134.3, 131.3, 123.9, 121.0 (t, $J_{\text{C-F}} = 311.6$ Hz), 84.8 (dd, $J_{\text{C-F}} = 25.6, 23.4$ Hz), 63.4, 18.4, 14.0; ^{19}F NMR (282 MHz, CDCl_3) δ -56.9 (d, 1F, $J = 168.6$ Hz), -58.9 (d, 1F, $J = 165.3$ Hz); HRMS (APCI-TOF) calcd for $\text{C}_{13}\text{H}_{12}\text{BrF}_2\text{NO}_6$ $[\text{M}]^-$: 394.9816, found: 394.9835; FT-IR (KBr pellet, cm^{-1}) 716, 843, 876, 961, 1020, 1106, 1146, 1280, 1347, 1446, 1528, 1610, 1751, 2866, 2936, 2988; $[\alpha]_{\text{D}}^{22}$ -11.99 (*c* 1.55, CHCl_3), 82% ee; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, $20\text{ }^{\circ}\text{C}$ detection UV 254 nm) t_{R} of major isomer 18.2 min, t_{R} of minor isomer 12.5 min.

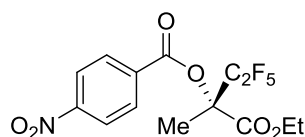


#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	11.7	8566119	49.44	358425	57.08
2	16.8	8760736	50.56	269527	42.92



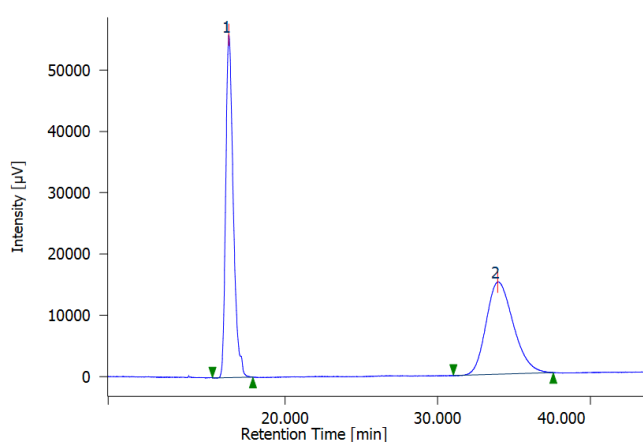
#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	12.5	2512608	8.83	180060	13.73
2	18.2	25954967	91.17	1131093	86.27

(S)-1-Ethoxy-3,3,4,4,4-pentafluoro-2-methyl-1-oxobutan-2-yl *p*-nitrobenzoate (2i'**)**

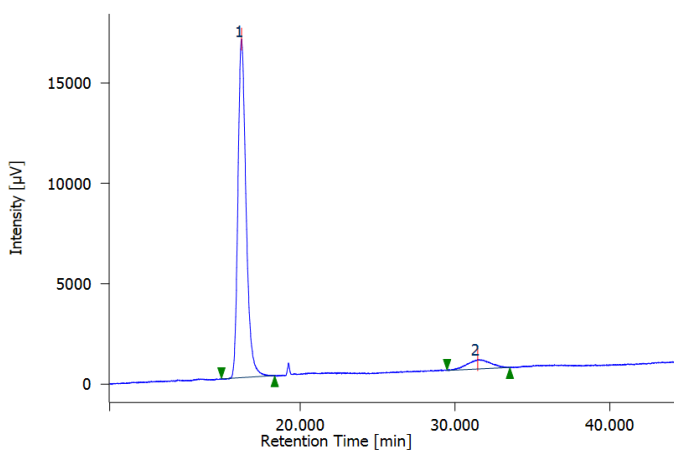


The yield of alcohol **2i** (87%) was determined by ^{19}F NMR analysis. *p*-Nitrobenzoylated alcohol **2i'** was purified by silica gel column chromatography (EtOAc/hexane 1:40) as a white solid (48% yield for 2 steps, 86% ee).

^1H NMR (300 MHz, CDCl_3) δ 8.30-8.35 (m, 2H) 8.16-8.21 (m, 2H), 4.27-4.37 (m, 2H), 2.04 (q, $J_{\text{H-F}} = 0.6$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.2 162.2, (d, $J_{\text{C-F}} = 2.0$ Hz) 151.0, 134.1, 131.0, 123.8, 118.6 (qt, $J_{\text{C-F}} = 286.1, 35.6$ Hz), 112.0 (tq, $J_{\text{C-F}} = 263.0, 36.8$ Hz), 81.3 (t, $J_{\text{C-F}} = 25.4$ Hz), 63.3, 16.6, 13.7; ^{19}F NMR (282 MHz, CDCl_3) δ -79.19 (s, 3F), -121.42 (d, $J = 280.9$ Hz, 1F), -122.98 (d, $J = 279.7$ Hz, 1F); HRMS (APCI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{F}_5\text{NO}_6$ [M] $^-$: 385.0585, found: 385.0582; FT-IR (KBr pellet, cm^{-1}) 1014, 1142, 1208, 1222, 1281, 1350, 1385, 1533, 1747, 2942, 2987, 3059; $[\alpha]_{\text{D}}^{25}$ -27.75 (c 1.02, CHCl_3), 86% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) t_{R} of major isomer 16.2 min, t_{R} of minor isomer 31.4 min.

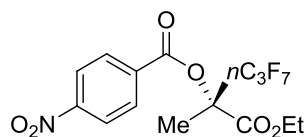


#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	16.3	1922723	50.80	55887	78.77
2	33.9	1862363	49.20	15067	21.23



#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	16.2	613879	92.76	16848	97.31
2	31.4	47932	7.24	466	2.69

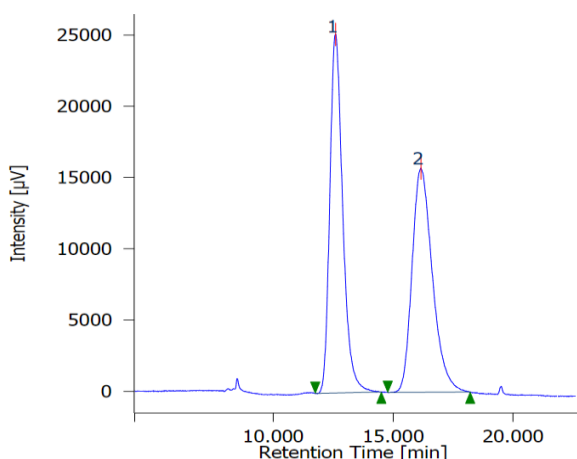
(S)-1-Ethoxy-3,3,4,4,5,5,5-heptafluoro-2-methyl-1-oxopentan-2-yl *p*-nitrobenzoate (2j')



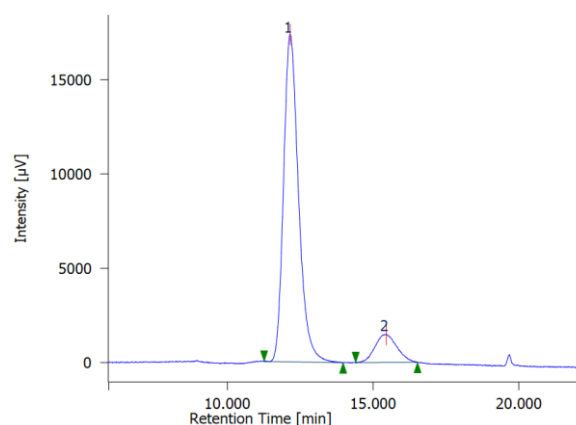
The yield of alcohol **2j** (98%) was determined by ^{19}F NMR analysis. *p*-Nitrobenzoylated alcohol **2j'** was purified by silica gel column chromatography (EtOAc/hexane 1:50) as a colorless oil (48% yield for 2 steps, 78% ee).

^1H NMR (300 MHz, CDCl_3) δ 8.31-8.35 (m, 2H) 8.16-8.21 (m, 2H), 4.29-4.36 (m, 2H), 2.07 (q, $J_{\text{H-F}} = 1.3$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.2 162.2, 151.0, 134.1, 131.0, 123.8, 117.6 (qt, $J_{\text{C-F}} = 286.9, 33.9$ Hz), 113.6 (tt, $J_{\text{C-F}} = 263.9, 30.9$ Hz), 122.9 (tq, $J_{\text{C-F}} = 266.9, 37.4$ Hz), 82.2 (t, $J_{\text{C-F}} = 25.7$ Hz), 63.4, 16.8, 13.7; ^{19}F NMR (282 MHz, CDCl_3) δ -80.6--80.70 (m, 3F), -117.75 (d, $J = 288.5$ Hz, 1F), -119.60 (d, $J = 288.2$ Hz, 1F), -123.882 (s, 2F).

HRMS (APCI-TOF) calcd for $\text{C}_{15}\text{H}_{12}\text{F}_7\text{NO}_6$ $[\text{M}]^-$: 435.0553, found: 435.0547; FT-IR (neat, cm^{-1}) 1090, 1140, 1200, 1233, 1349, 1387, 1534, 1609, 1744, 1761, 2942, 2988, 3059; $[\alpha]_{\text{D}}^{25}$ -22.60 (*c* 0.94, CHCl_3), 78% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) t_{R} of major isomer 12.2 min, t_{R} of minor isomer 15.5 min.

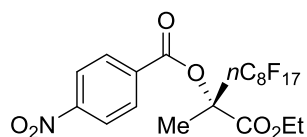


#	Time [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Area%	Height [μV]	Height%
1	12.7	942415	50.43	25143	61.52
2	16.2	926323	49.57	15729	38.48



#	Time [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Area%	Height [μV]	Height%
1	12.2	619959	88.86	17358	92.11
2	15.5	77697	11.14	1486	7.89

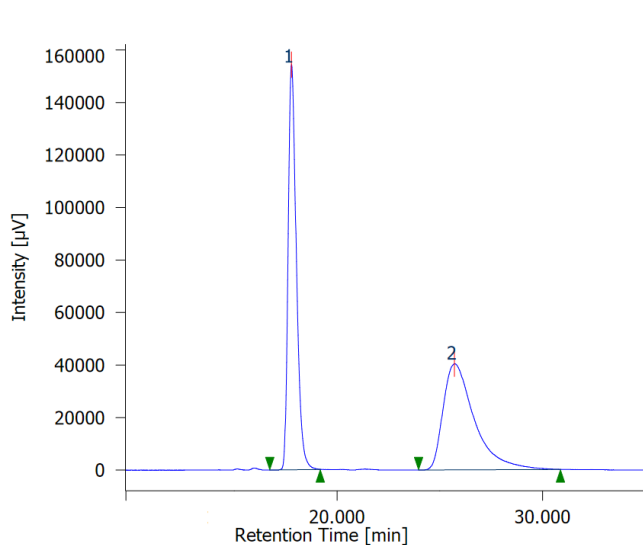
(S)-1-Ethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-methyl-1-oxodecan-2-yl *p*-nitrobenzoate (2k')



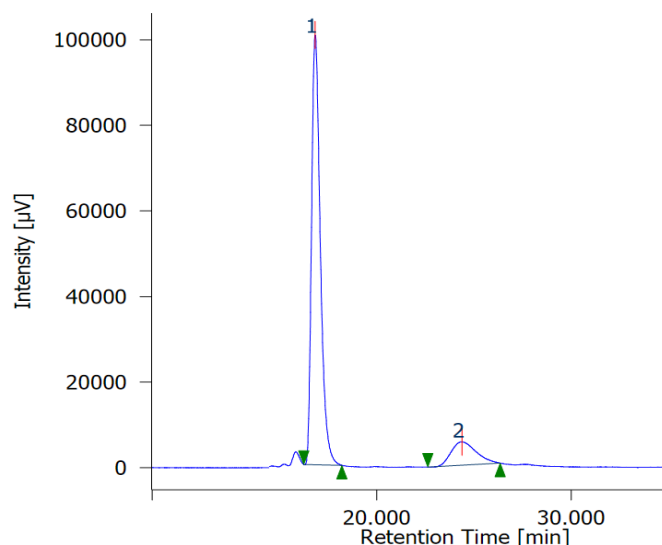
The yield of alcohol **2k** (92%) was determined by ^{19}F NMR analysis. *p*-Nitrobenzoylated alcohol **2k'** was purified by silica-gel column chromatography (EtOAc/hexane 1:50) as a white solid (85% yield

for 2 steps, 73% ee).

^1H NMR (300 MHz, CDCl_3) δ 8.36-8.31 (m, 2H), 8.20-8.16 (m, 2H), 4.36-4.29 (m, 2H), 2.08 (s, 3H), 1.28 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 164.3 162.4 151.2 134.3 131.2 123.9 118.4-104.7 (m) 117.3 (qt, $J_{\text{C-F}} = 288.4, 33.2$ Hz), 82.8 (t, $J_{\text{C-F}} = 25.4$ Hz), 63.5, 17.1, 13.8; ^{19}F NMR (282 MHz, CDCl_3) δ -80.6--80.8 (m, 3F), -116.4--126.0 (m, 14F); HRMS (APCI-TOF) calcd for $\text{C}_{20}\text{H}_{12}\text{F}_{17}\text{NO}_6$ $[\text{M}]^-$: 685.0393, found: 685.0362; FT-IR (KBr pellet cm^{-1}) 847, 969, 1009, 1142, 1214, 1246, 1297, 1472, 1530, 1613, 1732, 1757, 2339, 2360, 2860, 2922, 2997, 3112, 3454, 3493; $[\alpha]_{\text{D}}^{22}$ -11.93 (c 0.48, CHCl_3), 73% ee; HPLC (column, CHIRALPAK AD-3 and AD-H, Hexane/2-Propanol = 99.5/0.5, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) t_{R} of major isomer 16.8 min, t_{R} of minor isomer 24.4 min.

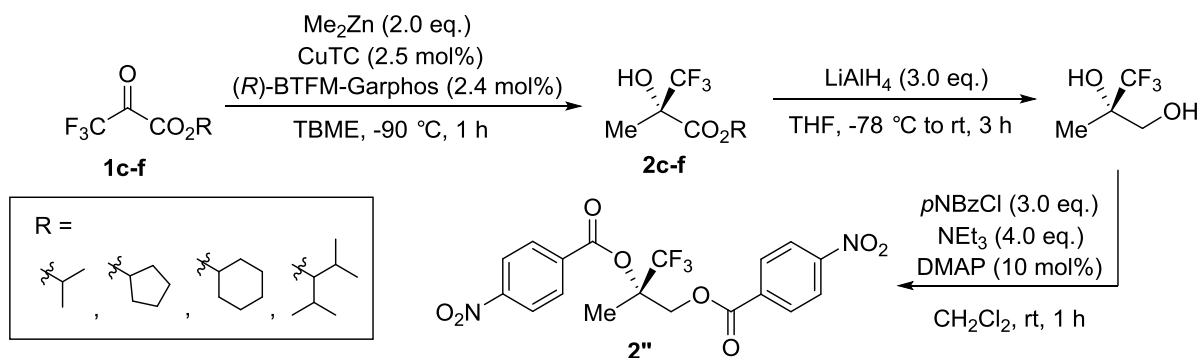


#	Time [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Area%	Height [μV]	Height%
1	17.8	4310404	50.22	154197	79.25
2	25.7	4271875	49.78	40381	20.75



#	Time [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Area%	Height [μV]	Height%
1	16.8	3133218	86.56	100378	94.81
2	24.4	486644	13.44	5495	5.19

Typical procedure IV: Cu-catalyzed asymmetric methylation of trifluoropyruvate derivatives



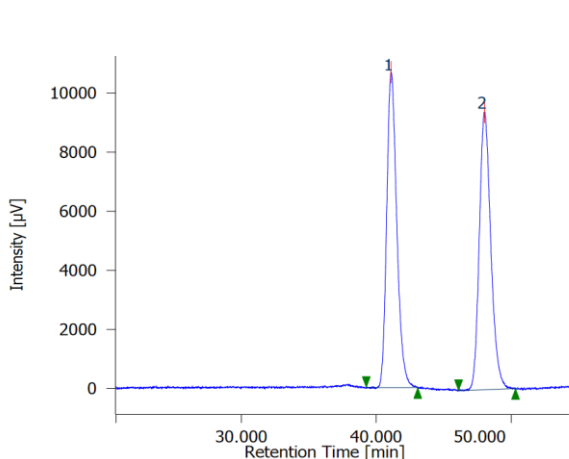
To a mixture of CuTC (1.0 mg, 0.005 mmol) and $(R)\text{-BTM-Garphos}$ (5.7 mg, 0.0048 mmol) was added CH_2Cl_2 (1.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (0.5 mL). After the solution was cooled to $-90\text{ }^\circ\text{C}$, Me_2Zn (1.0 M in heptane, 0.4 mL, 0.4 mmol), followed by trifluoropyruvate derivative **1** (0.2 mmol) in TBME (0.5 mL) were added in 30 min. The reaction mixture was stirred at the same temperature for 1 h. After the reaction mixture was quenched with saturated aq. NH_4Cl , the organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under controlled pressure (350 mmHg). The yields (**2c**: 59%, **2d**: 60%, **2e**: 64%, **2f**: 71%) were determined by ^{19}F NMR analysis using BTF as an internal standard. The concentrated solution was used without purification for the next reduction with LiAlH_4 .

To an oven-dried 30-mL two-neck round-bottomed flask equipped with magnetic stir bar was added LiAlH_4 (23 mg, 0.6 mmol) in THF (10 mL). After the solution was cooled to $-78\text{ }^\circ\text{C}$, the crude alcohol in THF (1 mL) was added dropwise. Then the mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was quenched with water (23 μL), 15% NaOH aq. (23 μL), and water (69 μL). After filtration, the solvent was evaporated under reduced pressure. The concentrated solution was used without purification for the next protection reaction.

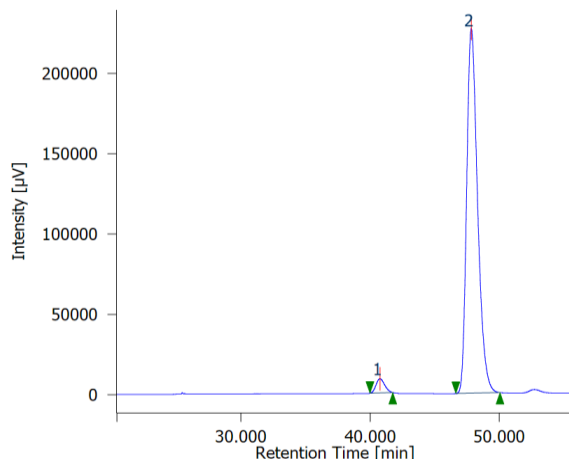
To a solution of DMAP (2.4 mg, 0.02 mmol) and the crude diol in CH_2Cl_2 (2.0 mL) was added NEt_3 (112 μL , 0.8 mmol) at room temperature. After the reaction mixture was cooled to $0\text{ }^\circ\text{C}$, p -nitrobenzoyl chloride (112 mg, 0.6 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h and 1 N HCl (5.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layers were washed with saturated aq. NaHCO_3 , water, brine, and dried over anhydrous MgSO_4 and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography ($\text{EtOAc}/\text{hexane}$ 1:20) to give the corresponding di- p -nitrobenzoylated product **2''** as a white solid (14% yield for 3 steps, 94% ee). Enantiomeric excess was determined by chiral HPLC analysis.

^1H NMR (300 MHz, CDCl_3) δ 8.31 (d, 2H, $J = 9.0$ Hz), 8.25 (d, 2H, $J = 8.7$ Hz), 8.18 (d, 2H, $J = 9.0$ Hz), 8.12 (d, 2H, $J = 8.7$ Hz), 5.25 (dd, 1H, $J = 12.6, 0.9$ Hz), 4.88 (d, 1H, $J = 12.9$ Hz), 1.95 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.7, 162.5, 151.2, 151.0, 134.8, 134.5, 131.1, 130.9, 124.1 (q, $J_{\text{C-F}} =$

282.5 Hz), 123.9, 123.8, 81.4 (q, $J_{C-F} = 29.1$ Hz), 63.0, 16.4 (q, $J_{C-F} = 1.3$ Hz); ^{19}F NMR (282 MHz, CDCl_3) δ 79.7 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_{18}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_8$ $[\text{M}]^-$: 442.0624, found: 442.0603; FT-IR (KBr pellet, cm^{-1}) 822, 1102, 1119, 1171, 1271, 1342, 1523, 1734, 1748, 2337, 2362, 2588, 2923, 2958, 3056, 3081, 3113; $[\alpha]_{\text{D}}^{23} +23.80$ (c 0.06, CHCl_3), 94% *ee*; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) t_{R} of major isomer 47.8 min, t_{R} of minor isomer 40.7 min.

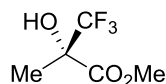


#	Time [min]	Area [µV-sec]	Area%	Height [µV]	Height%
1	41.1	553535	49.83	10673	53.20
2	48.0	557375	50.17	9389	46.80



#	Time [min]	Area [µV-sec]	Area%	Height [µV]	Height%
1	40.7	412890	3.01	8868	3.76
2	47.8	13310124	96.99	226983	96.24

Determination of the absolute configuration (Table 1, entry 17)



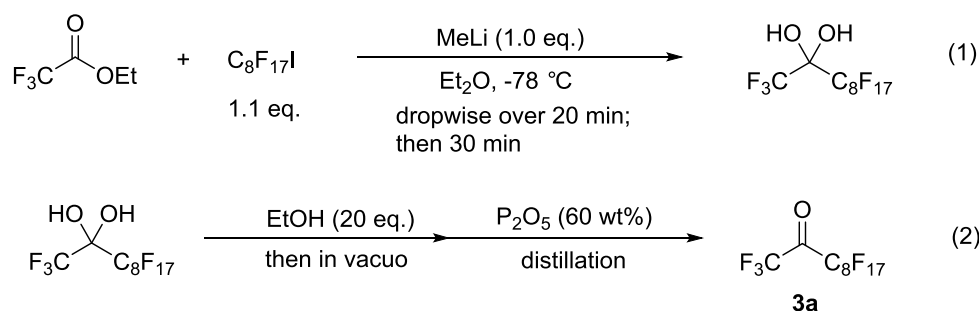
To a mixture of CuTC (9.5 mg, 0.05 mmol) and (*R*)-DTB-MeO-BIPHEP (55.7 mg, 0.054 mmol) was added CH_2Cl_2 (5.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (5.0 mL) under an argon atmosphere. After the solution was cooled to -78 °C, Me_2Zn (1.0 M in heptane, 4.0 mL, 4.0 mmol) followed by methyl trifluoropyruvate **1b** (244 μL , 2.0 mmol) in TBME (5.0 mL) were added. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aq. NH_4Cl . The organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under controlled pressure (350 mmHg), and the residue was purified by a distillation (70 kPa, 20 °C) to give **2b** in 8% yield. The product **2b** exhibited the same ^1H and ^{19}F NMR spectra as reported before [7]. ^1H NMR (300 MHz, CDCl_3) δ 1.59 (s, 3H), 3.77 (s, 1H), 3.91 (s, 3H); ^{19}F NMR (282 MHz, CDCl_3) δ -80.04 (s, 3F); $[\alpha]_{\text{D}}^{25} -2.12$ (c 2.20, CHCl_3).

The absolute configuration was determined to be *S* in comparison with the optical rotation of reported data [Ref 7: (*S*)-**2b** >95% *ee*, $[\alpha]_{\text{D}}^{20} = -14.4$ (c 3.65, CHCl_3)]. The absolute configurations of other alcohol products **2a** and **2c-k** were tentatively assigned by analogy to **2b**. Enantiomeric excess of

benzoylated alcohol **2b'** prepared by **Typical Procedure III** was determined by chiral HPLC analysis. Compound **2b'** was purified by silica-gel column chromatography (EtOAc/hexane 1:40) as a colorless oil (60% yield for 2 steps, 59% ee).

^1H NMR (300 MHz, CDCl_3) δ 1.94 (q, $J_{\text{H-F}} = 1.0$ Hz, 3H), 3.84 (s, 3H), 7.45-7.50 (m, 2H), 7.63 (tt, $J = 7.4, 1.9$ Hz, 1H), 8.03-8.07 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.7 (d, $J_{\text{C-F}} = 1.2$ Hz), 53.6, 79.8 (q, $J_{\text{C-F}} = 30.2$ Hz), 122.9 (q, $J_{\text{C-F}} = 282.8$ Hz), 128.6, 129.7, 130.1, 134.0, 164.2, 165.6; ^{19}F NMR (282 MHz, CDCl_3) δ -78.45 (s, 3F); HRMS (APCI-TOF) calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 299.0507, found: 299.0493; FT-IR (neat, cm^{-1}) 1069, 1110, 1137, 1188, 1216, 1271, 1289, 1304, 1384, 1452, 1602, 1734, 1759, 2928, 2958, 3022; $[\alpha]_{\text{D}}^{25} +21.07$ (c 0.80, CHCl_3).

Synthesis of simple perfluoroalkylated ketone (**3a**) [8]



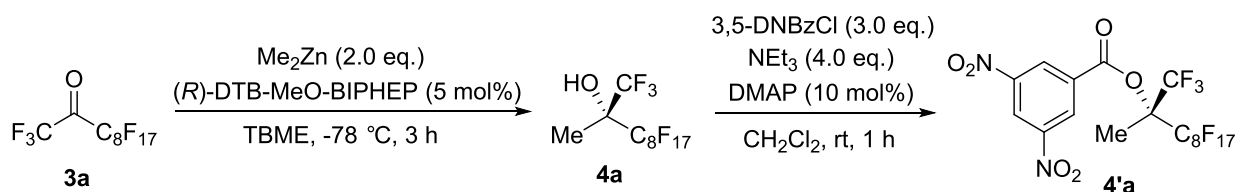
To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added ethyl trifluoroacetate (60 mmol), $\text{C}_8\text{F}_{17}\text{I}$ (66 mmol), and Et_2O (200 mL) under argon atmosphere. After the solution was cooled to -78°C , MeLi (60 mmol) was added dropwise in 20 min. After stirring at -78°C for 30 min, the reaction mixture was diluted with 1N HCl (100 mL) and extracted with Et_2O (3×50 mL). The combined organic extracts were washed with saturated aq. NaHCO_3 (100 mL), brine (100 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The hydrate product is known compound, the following data are identical to those given in corresponding literature [8] and used for next step without further purification. The yield was determined by ^{19}F NMR analysis using BTF as an internal standard (reaction 1).

Pink liquid (96% yield). ^{19}F NMR (282 MHz, CDCl_3) δ -81.2 (brs, 3F), -81.6 (brs, 3F) -120.4 (brs, 2F), -121.5--122.0 (m, 8F), -122.8 (brs, 2F), -126.2 (brs, 2F).

A solution of hydrate (10 mmol) in ethanol (200 mmol) was stirred at 70°C for 4 h, and evaporated under reduced pressure. The ethyl acetal was purified by distillation with P_2O_5 (760 Torr, 36°C) to provide the corresponding perfluoroalkylated ketone **3a**.

Colorless liquid (39% yield); ^{13}C NMR (75 MHz, Acetone- d_6) δ 176.0-173.5 (m), 114.3 (qt, $J_{\text{C-F}} = 287.9$ Hz), 114.3 (q, $J_{\text{C-F}} = 287.9$ Hz), 114.2-104.5 (m); ^{19}F NMR (282 MHz, Acetone- d_6) δ -75.2 (s, 3F), -81.8-81.9 (m, 3F), -118.9 (brs, 2F), -122.0--122.5 (m, 8F), -123.2 (brs, 2F), -126.9 (brs, 2F); HRMS (APCI-TOF) calcd for $\text{C}_{10}\text{F}_{20}\text{O}$ $[\text{M}]^-$: 515.9630, found: 515.9628; FT-IR (neat, cm^{-1}) 527, 558, 655, 724, 787, 818, 852, 910, 1004, 1062, 1146, 1208, 1793.

Catalytic asymmetric methylation of perfluoroalkylated ketone

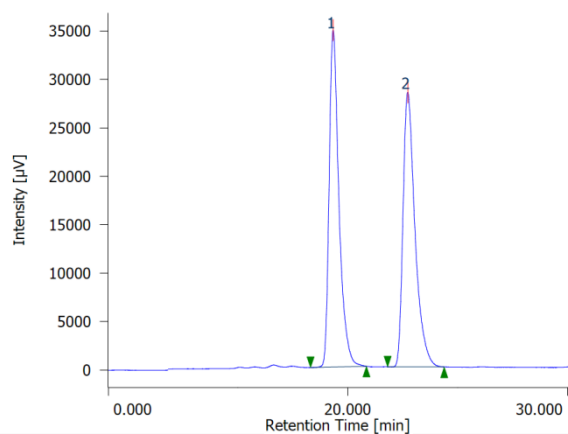


To a solution of (*R*)-DTB-MeO-BIPHEP (5.6 mg, 0.005 mmol) and **3a** (30 μ L, 0.1 mmol) in TBME (1.0 mL) was added Me₂Zn (1.0 M in heptane, 0.2 mL, 0.2 mmol) dropwise at -78 °C under argon atmosphere, and then the solution was stirred for 3 h. The reaction mixture was quenched with saturated aq. NH₄Cl. The organic layer was separated and the aqueous layer was extracted with Et₂O twice. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under controlled pressure (200 mmHg). The concentrated solution was used without purification for the next protection reaction. The yield of alcohol product **4a** (87%) was determined by ¹⁹F NMR analysis using benzotrifluoride (BTF) as an internal standard.

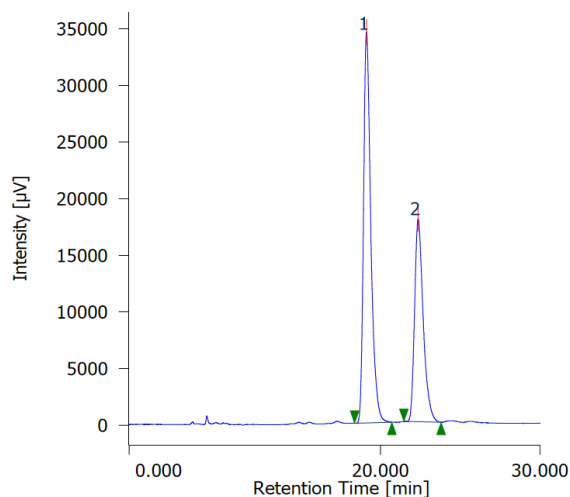
¹H NMR (300 MHz, CDCl₃) δ 2.90 (s, 1H), 1.67 (s, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -78.1 (s, 3F), -82.0--81.0 (m, 3F), -117.8--120.3 (m, 4F), -121.6--122.0 (m, 6F), -122.9 (s, 2F), -126.3 (brs, 2F).

To a solution of DMAP (1.2 mg, 0.01 mmol) and the crude product in CH₂Cl₂ (2.0 mL) was added NEt₃ (56 μ L, 0.4 mmol) at room temperature under argon atmosphere. After the reaction mixture was cooled to 0 °C, 3,5-dinitrobenzoyl chloride (69 mg, 0.3 mmol) was added. Then the mixture was warmed to room temperature and stirred for 1 h. After 1 N HCl (5.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et₂O twice. The combined organic layer was washed with saturated aq. NaHCO₃, water, brine, and dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (EtOAc/hexane 1:60) to give 3,5-dinitrobenzoylated alcohol **4'a** as a white solid (45% yield for 2 steps, 24% ee). Enantiomeric excess was determined by chiral HPLC analysis. The absolute configuration was not determined.

¹H NMR (300 MHz, CDCl₃) δ 9.30 (t, 1H, *J* = 2.1 Hz), 9.11 (d, 2H, *J* = 2.1 Hz), 2.28 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.6, 148.9, 132.3, 129.7, 123.4, 121.7 (q, *J*_{C-F} = 286.5 Hz), 120.5-104.3 (m), 117.1 (q, *J*_{C-F} = 286.8, 32.1 Hz), 84.9-83.9 (m); ¹⁹F NMR (282 MHz, CDCl₃) δ -73.5 (m, 3F), -80.8 (m, 3F), -116.4 (brs, 2F), -119.2 (brs, 2F), -121.4--121.9 (m, 6F), -122.7 (brs, 2F), -126.1 (brs, 2F); HRMS (ESI-TOF) calcd for C₁₃H₁₃F₃NaO₄ [M]⁻: 725.9907, found: 725.9934; FT-IR (KBr pellet, cm⁻¹) 653, 732, 928, 969, 1100, 1149, 1217, 1254, 1341, 1458, 1544, 1634, 1763, 2861, 2925, 2954, 3105; [α]_D²² -1.76 (*c* 0.61, CHCl₃), 24% ee; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 96/4, flow rate 0.8 mL/min, 20 °C detection UV 254 nm) *t*_R of major isomer 19.1 min, *t*_R of minor isomer 22.4 min.



#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	19.3	1077441	50.16	34774	55.11
2	22.7	1070546	49.84	28327	44.89

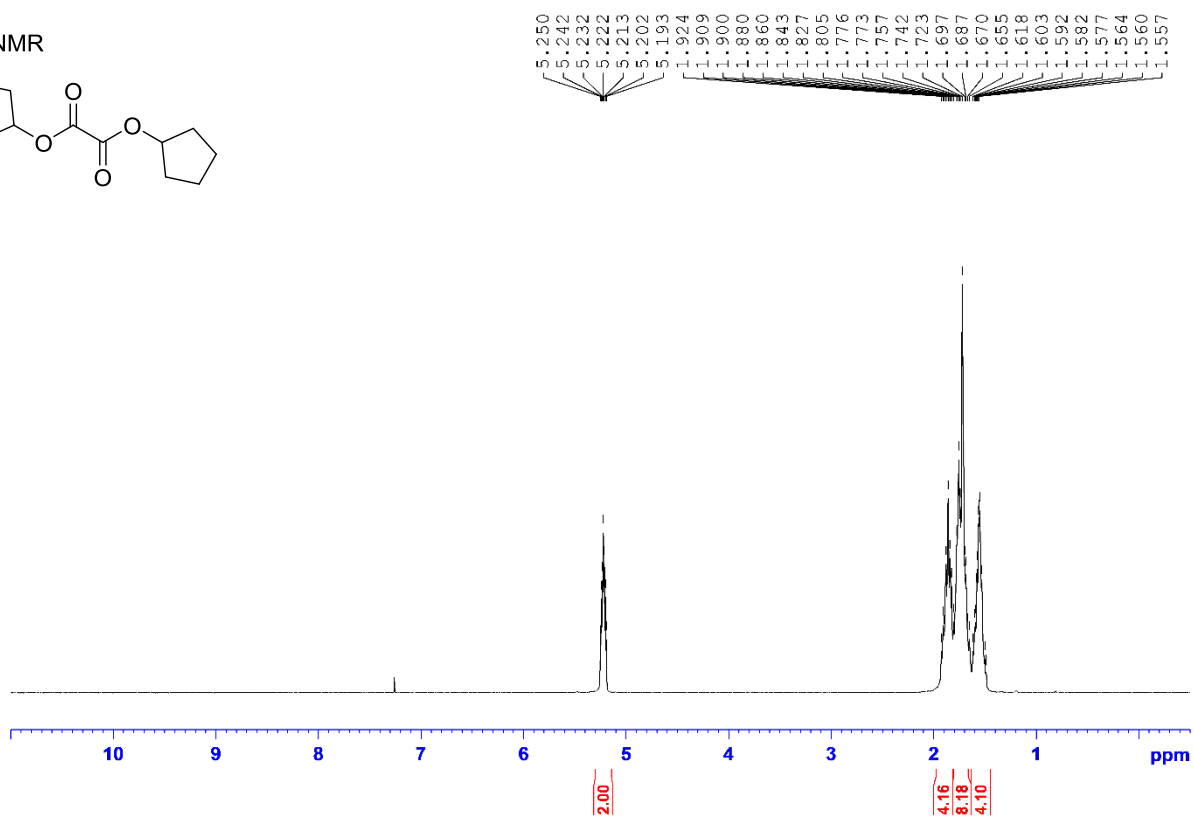
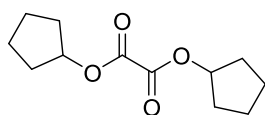


#	Time [min]	Area [µV·sec]	Area%	Height [µV]	Height%
1	19.1	1092999	61.99	34497	65.87
2	22.4	670234	38.01	17877	34.13

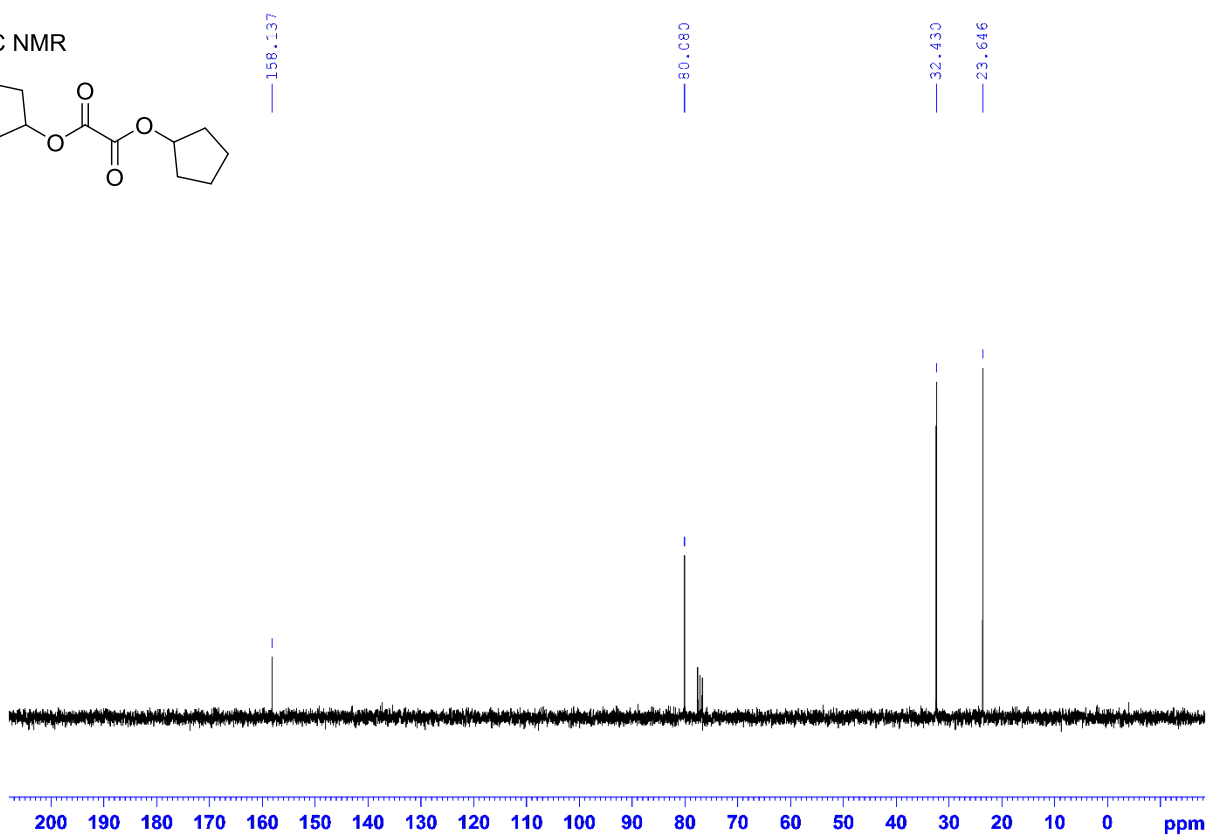
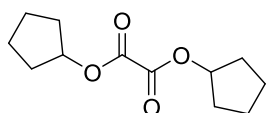
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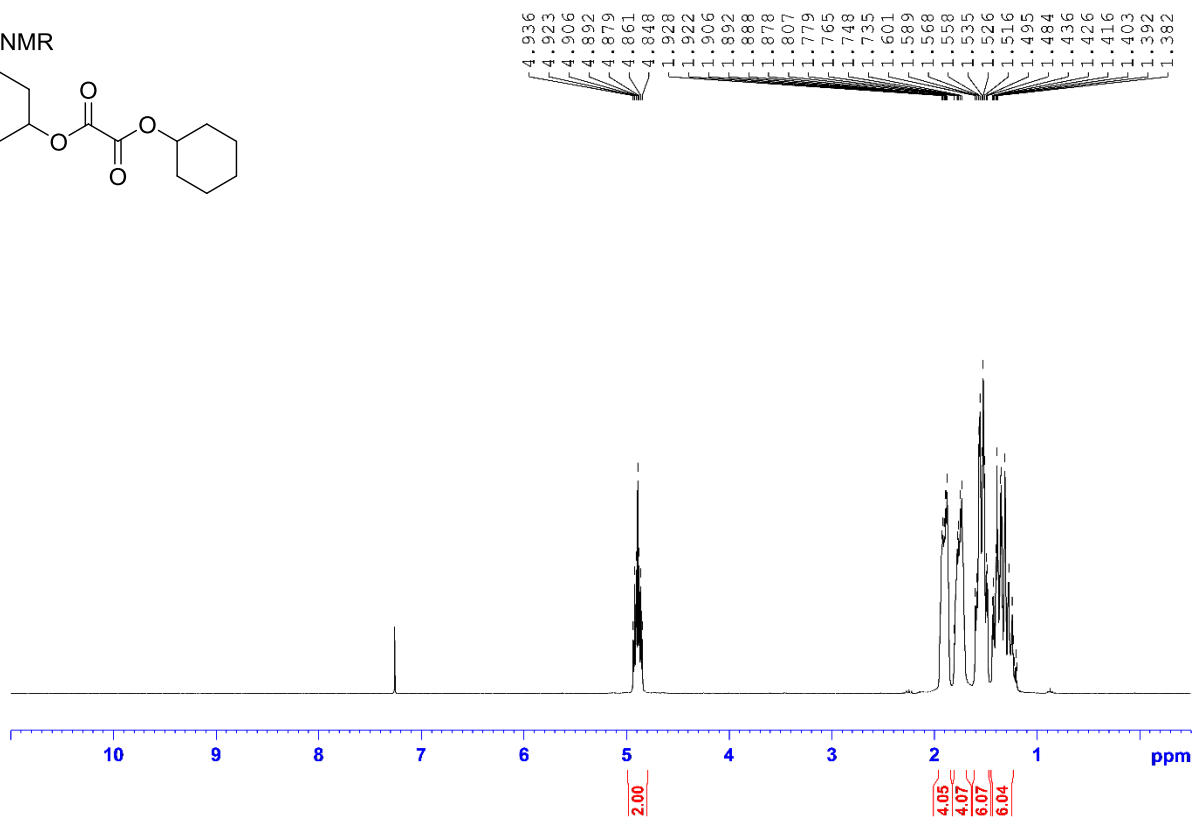
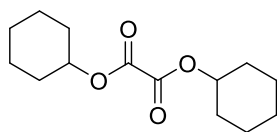
¹H NMR



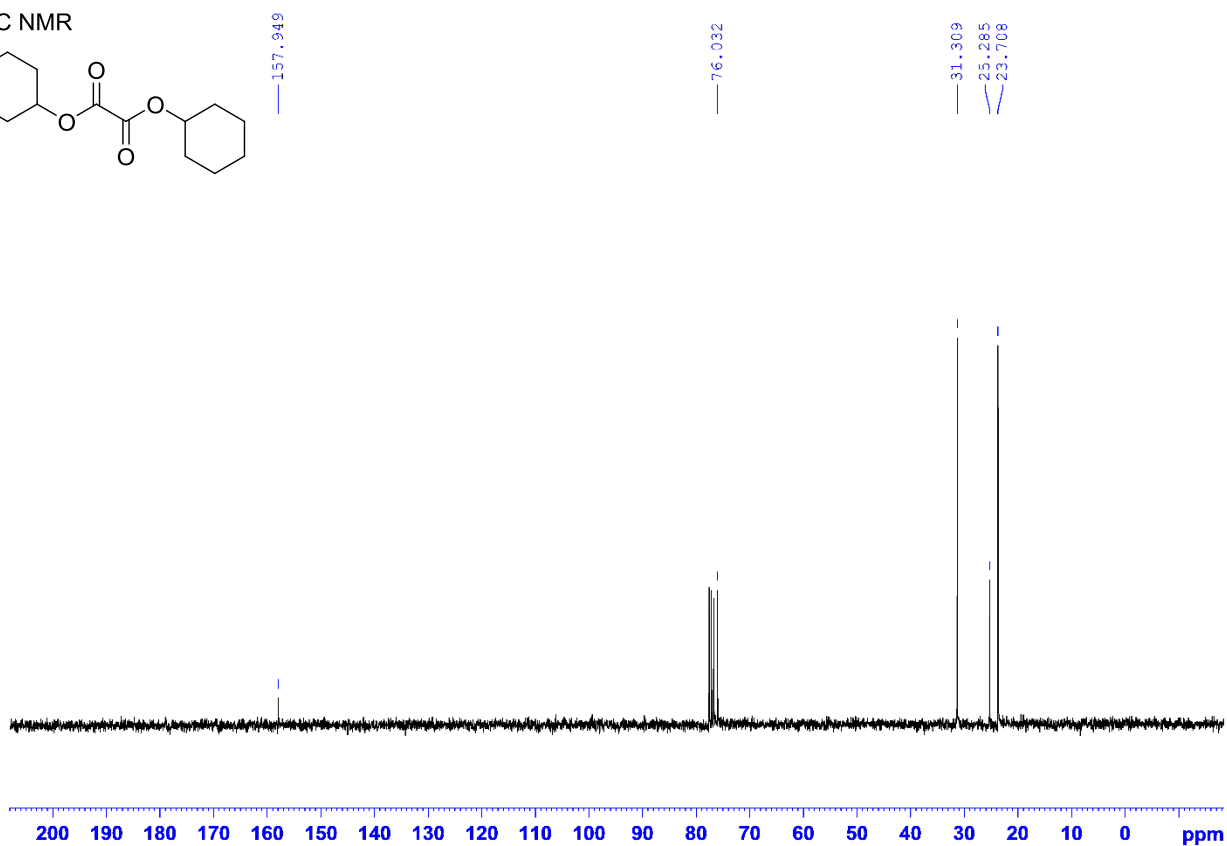
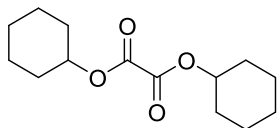
¹³C NMR



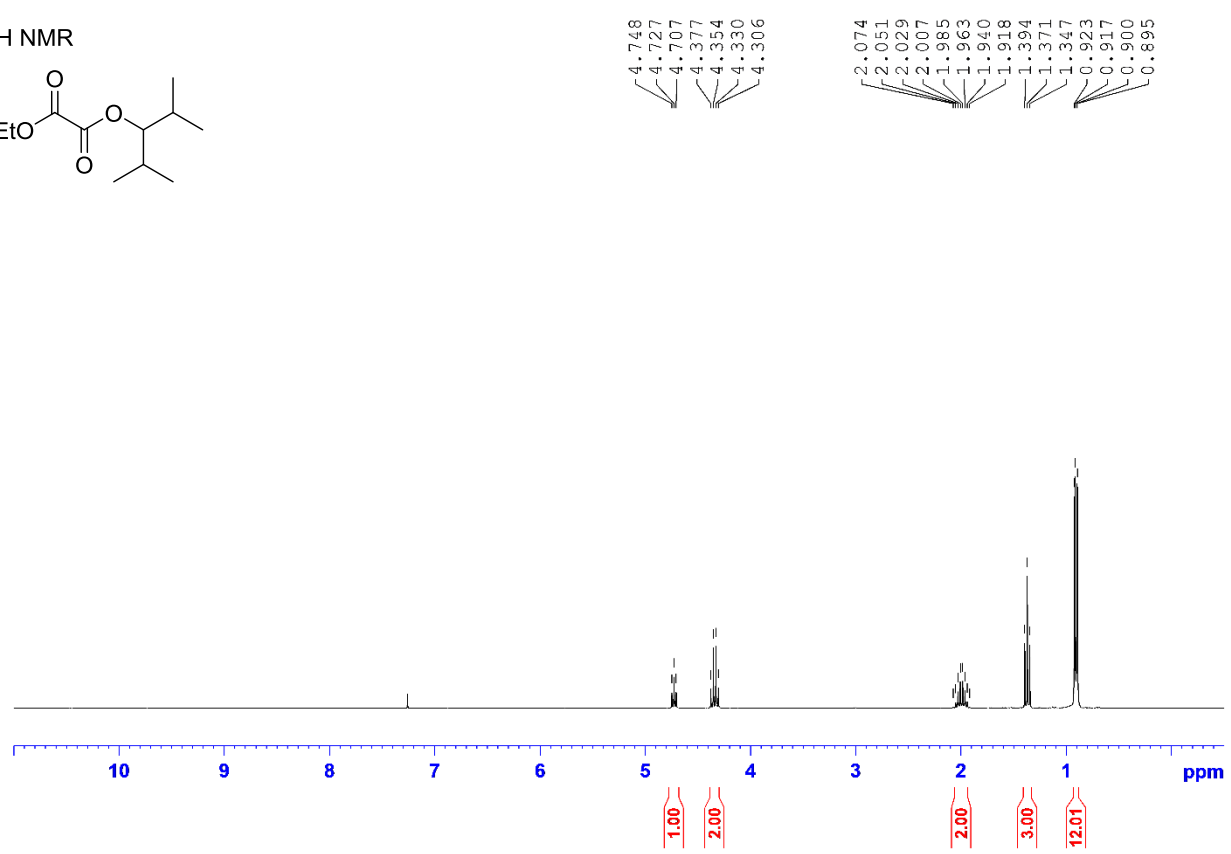
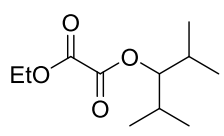
¹H NMR



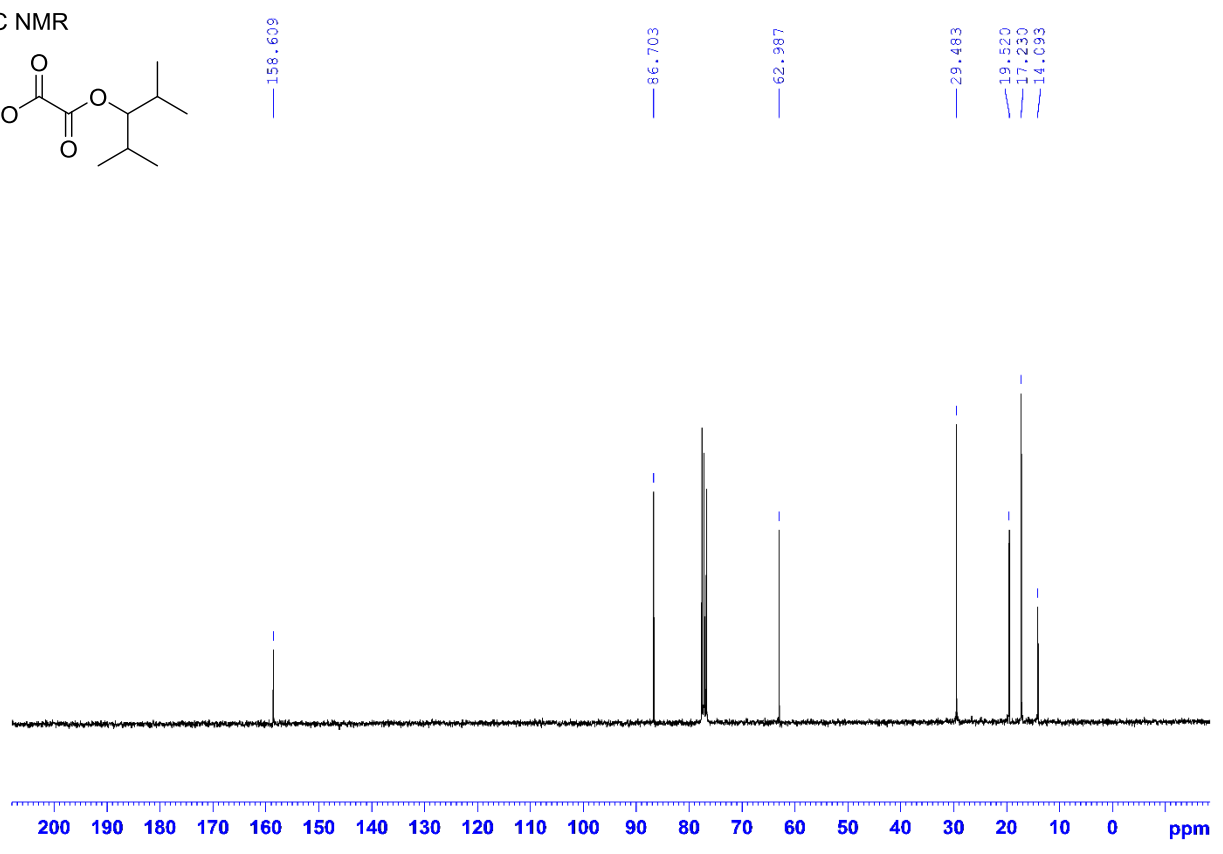
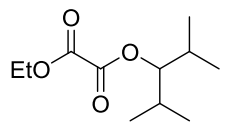
¹³C NMR



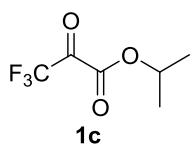
¹H NMR



¹³C NMR

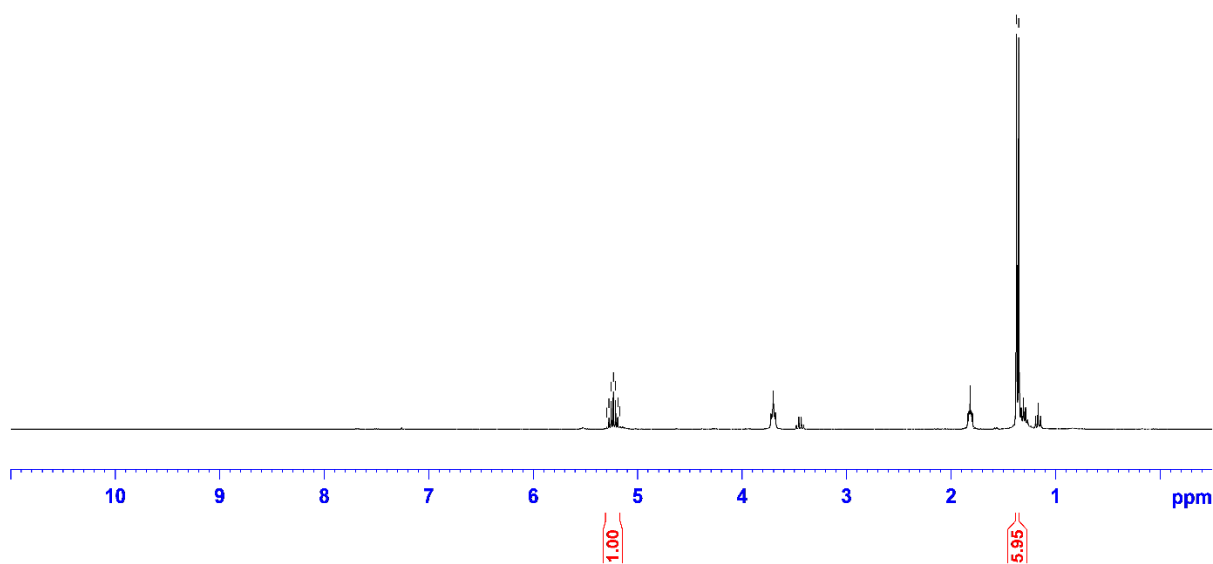


¹H NMR

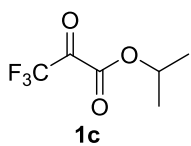


5.296
5.275
5.255
5.234
5.213
5.192
5.171

1.375
1.354



¹³C NMR



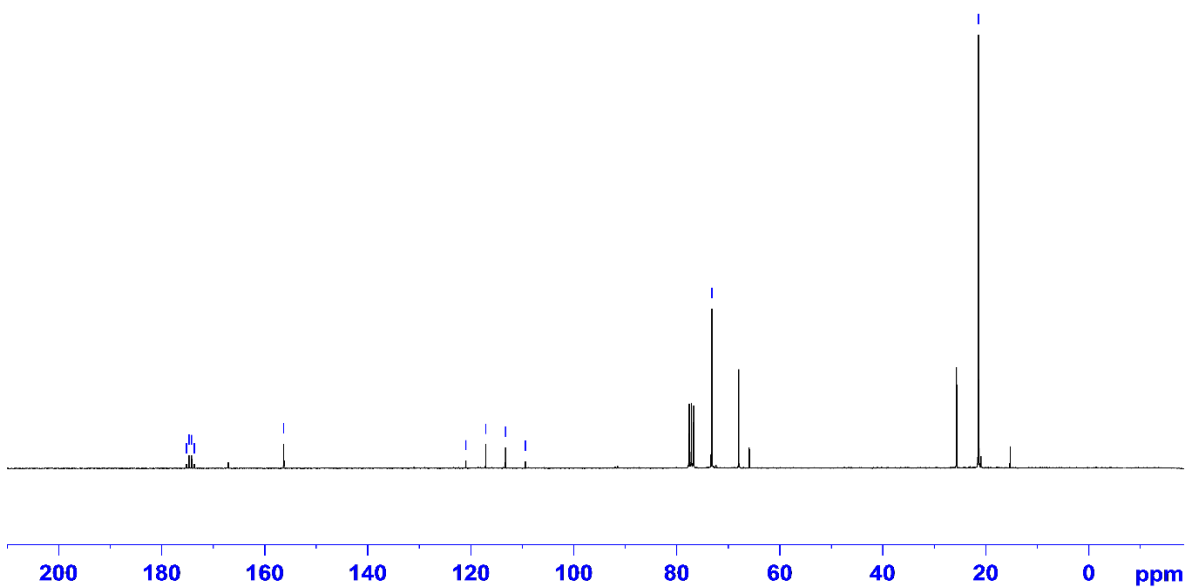
175.203
174.692
174.181
173.668

156.297

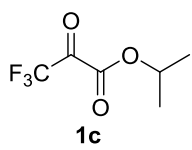
120.936
117.091
113.246
109.402

73.159

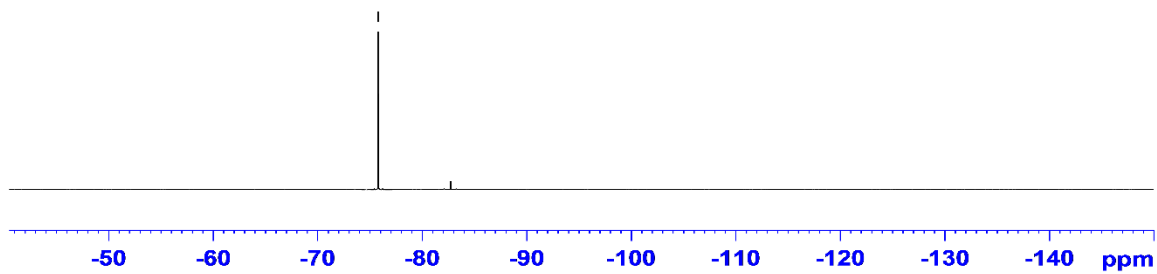
21.428



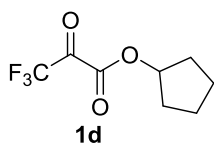
¹⁹F NMR



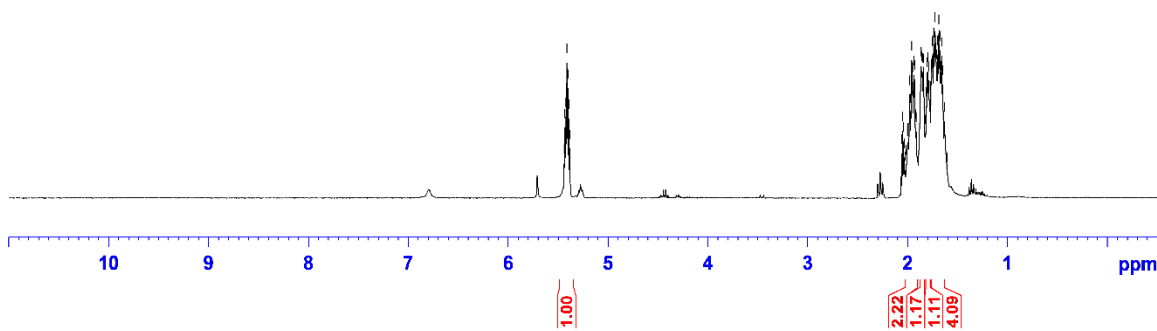
---75.781

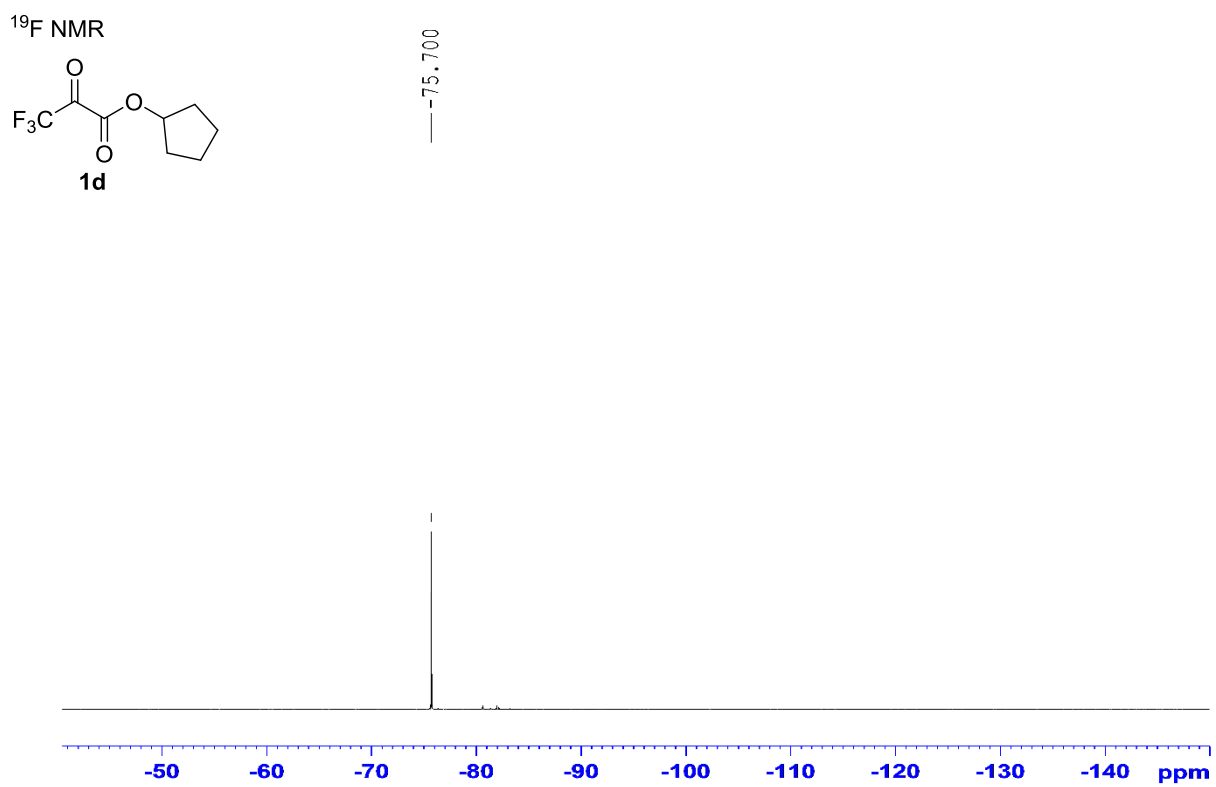
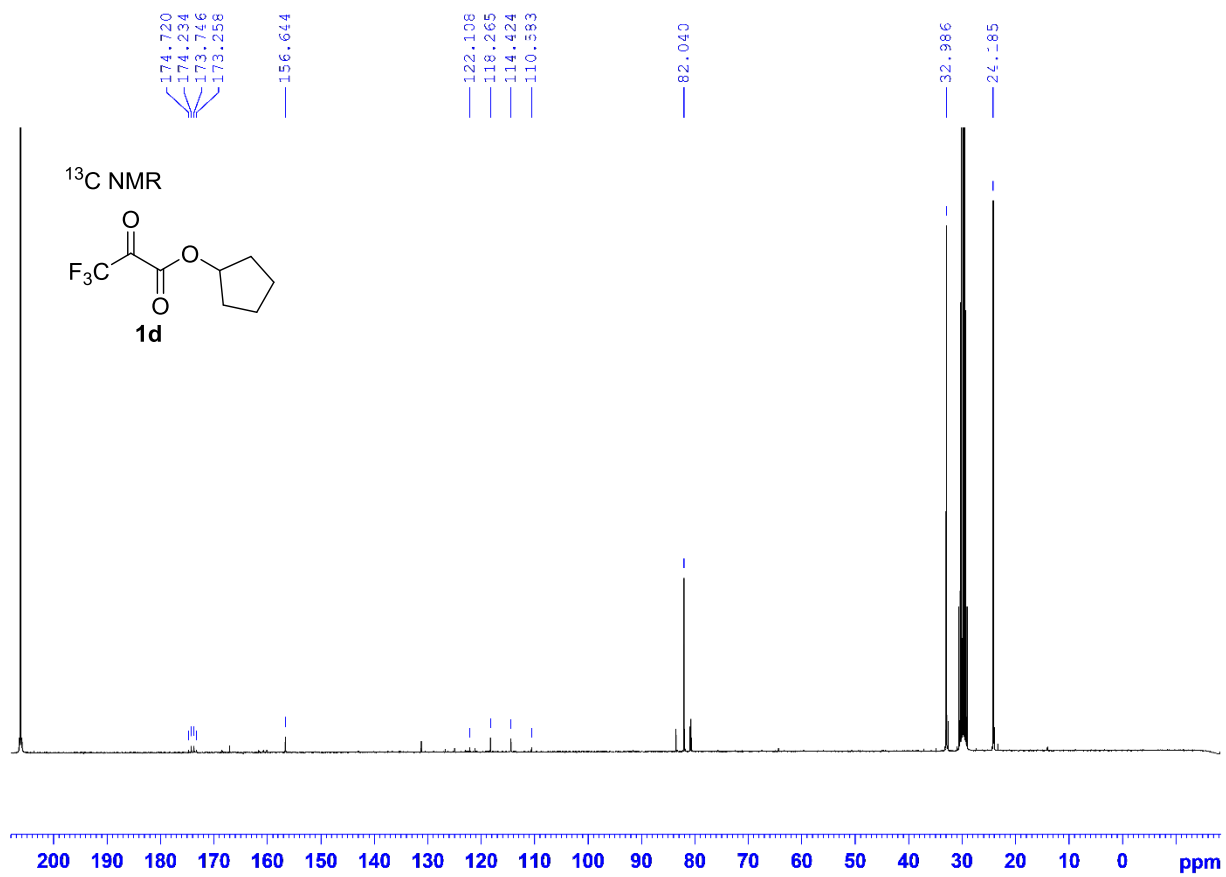


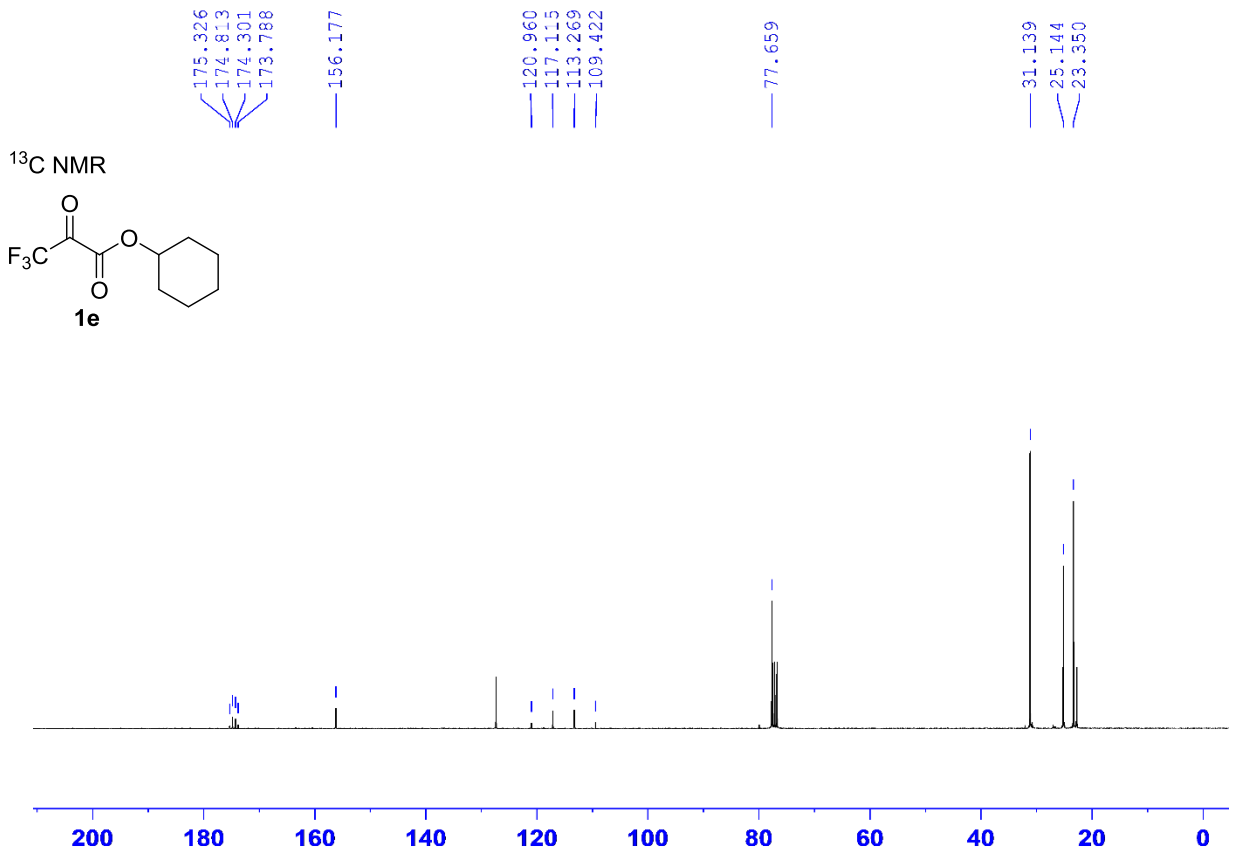
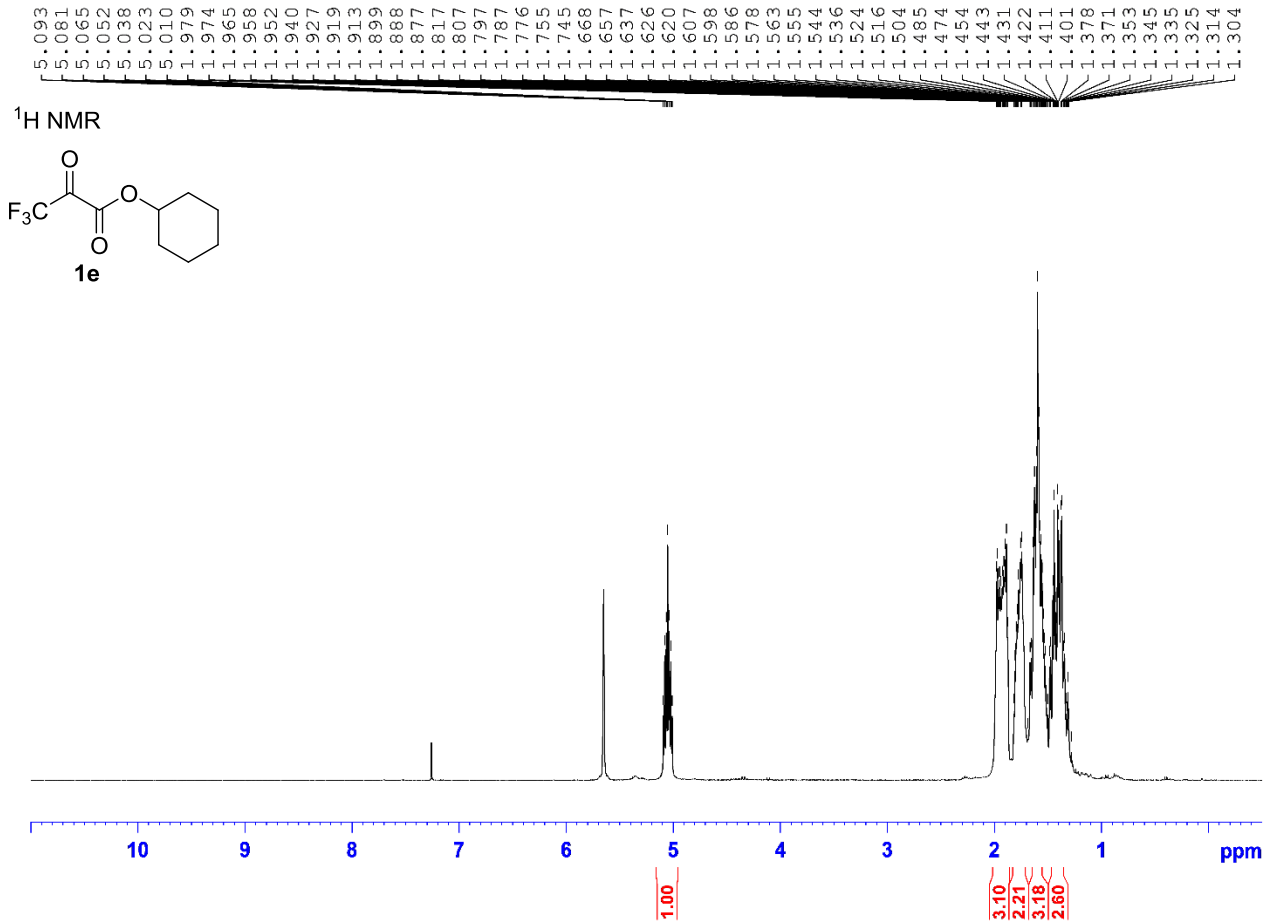
¹H NMR



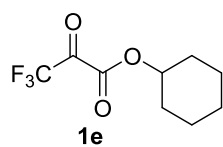
5.439
5.432
5.421
5.412
5.404
5.393
5.385
2.057
2.050
2.043
2.035
2.028
2.014
2.002
1.998
1.979
1.970
1.960
1.951
1.938
1.921
1.915
1.864
1.857
1.847
1.844
1.839
1.825
1.813
1.805
1.802
1.792
1.788
1.775
1.766
1.763
1.756



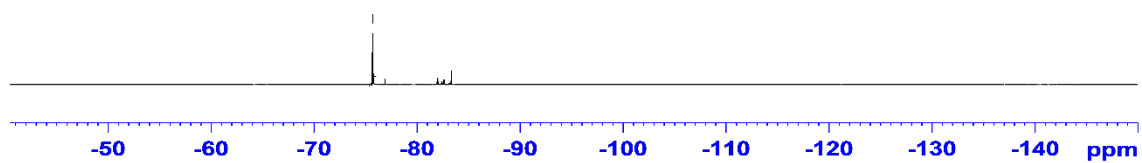




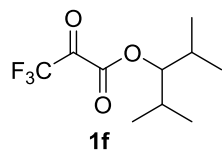
¹⁹F NMR



---75.682

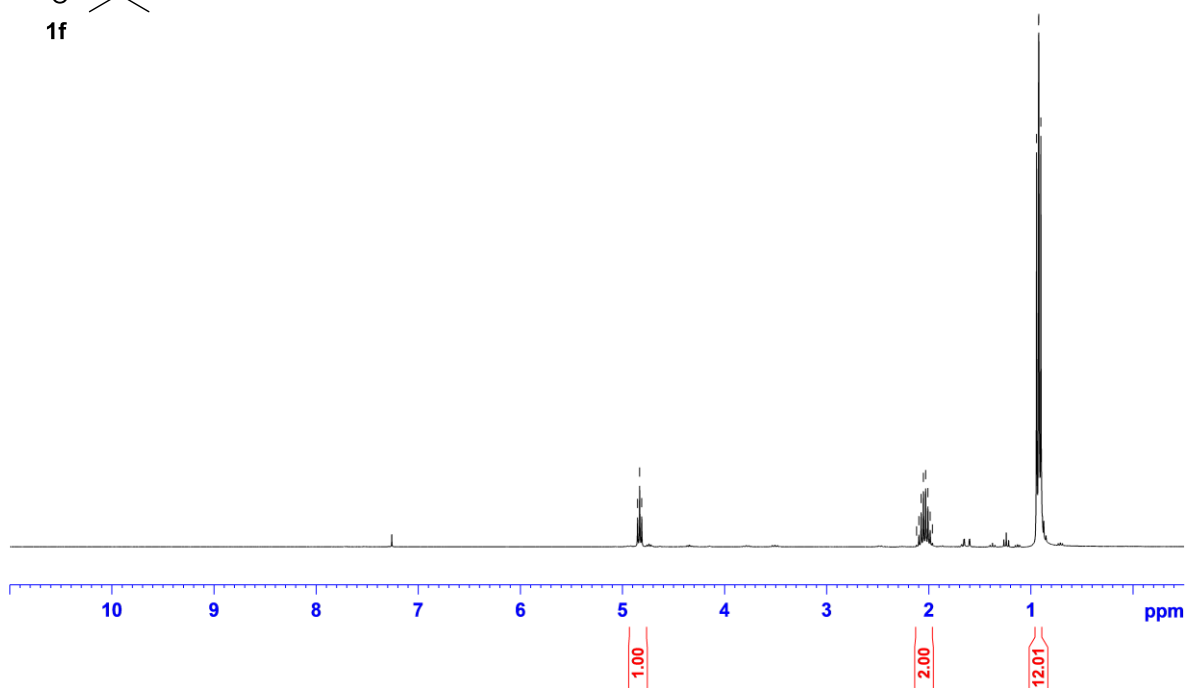


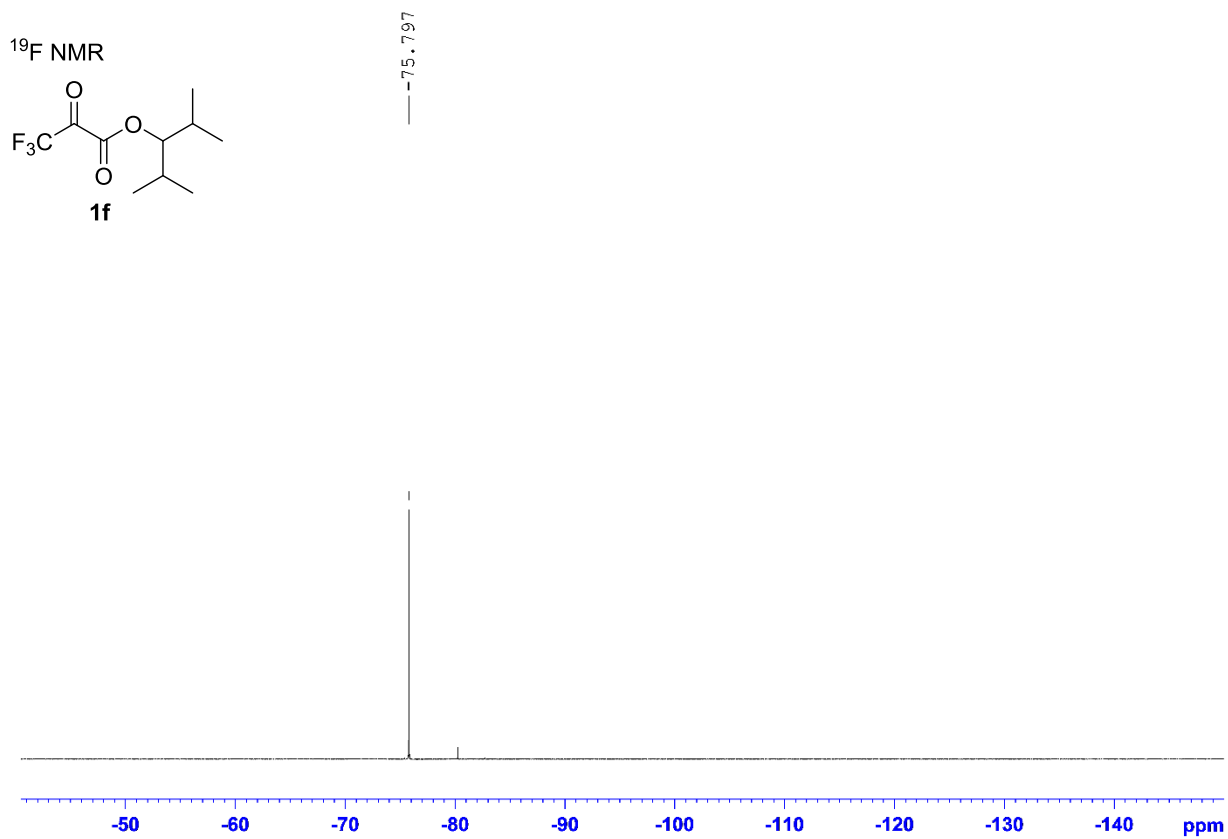
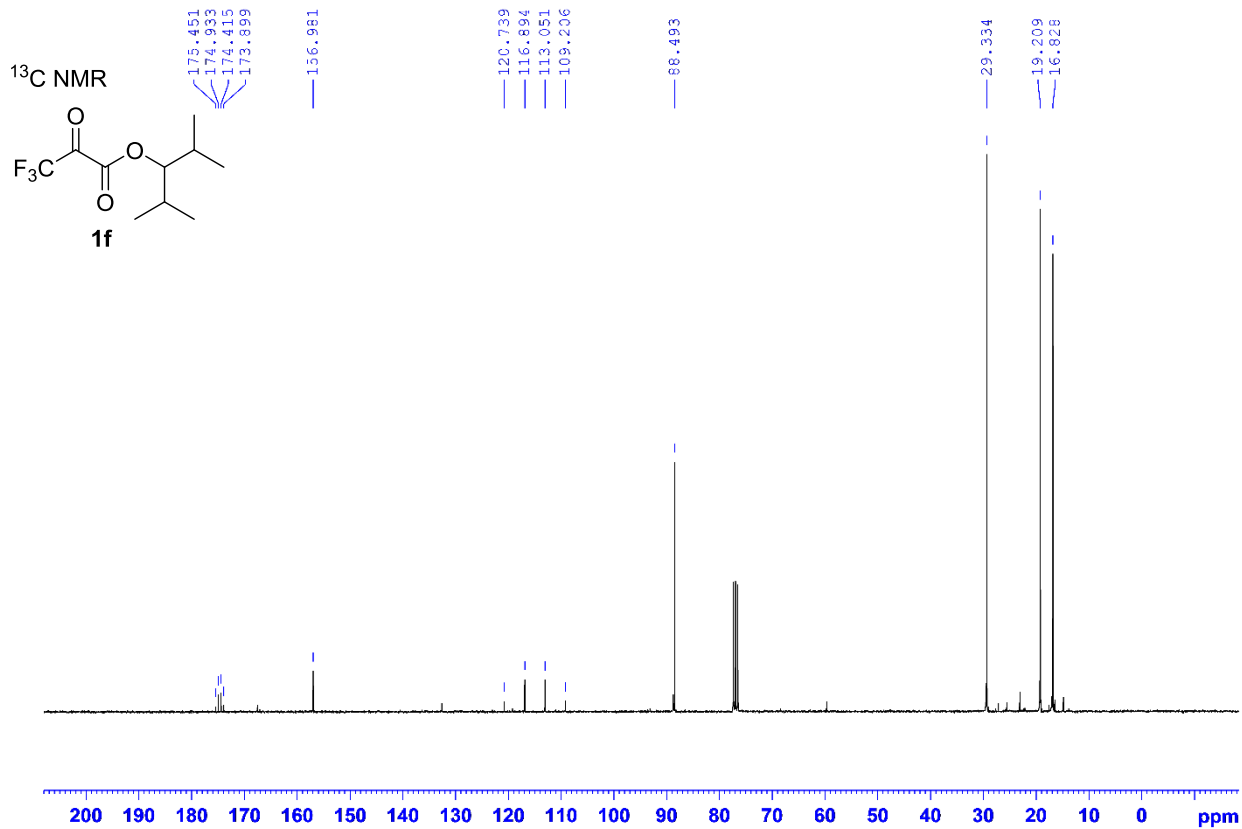
¹H NMR

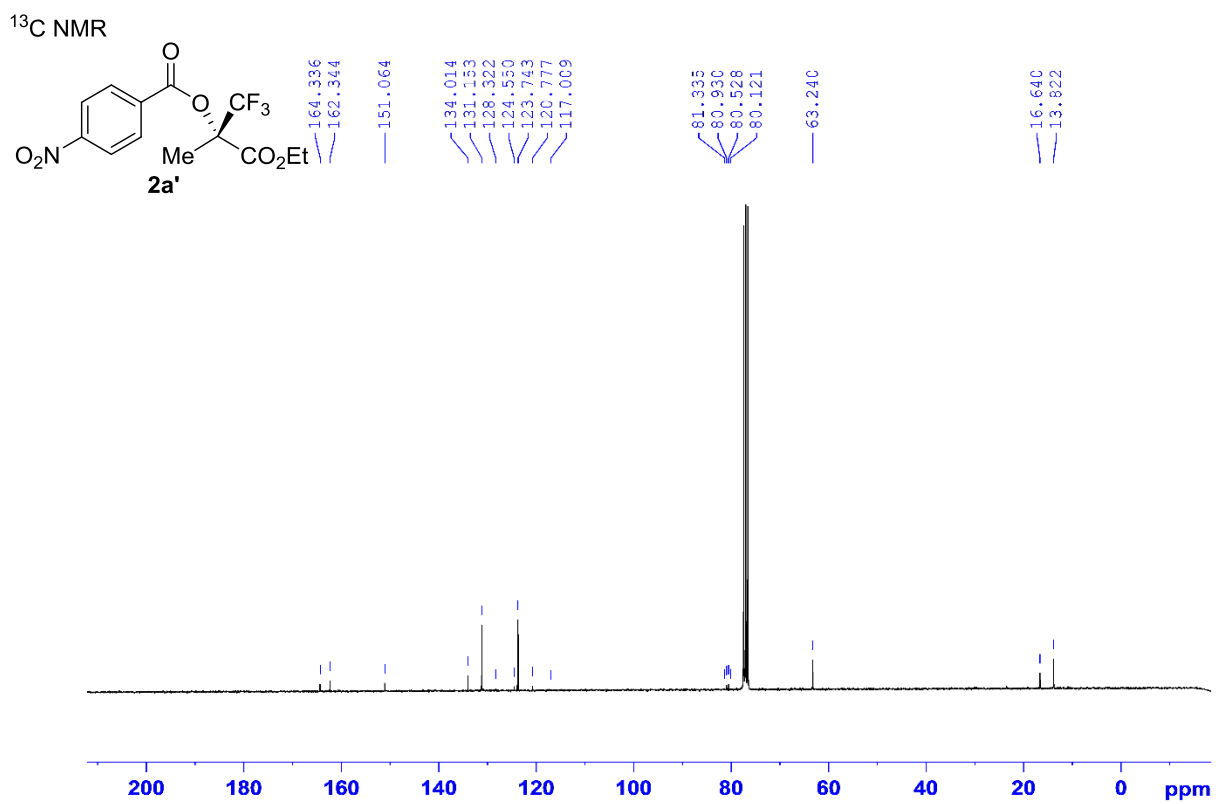
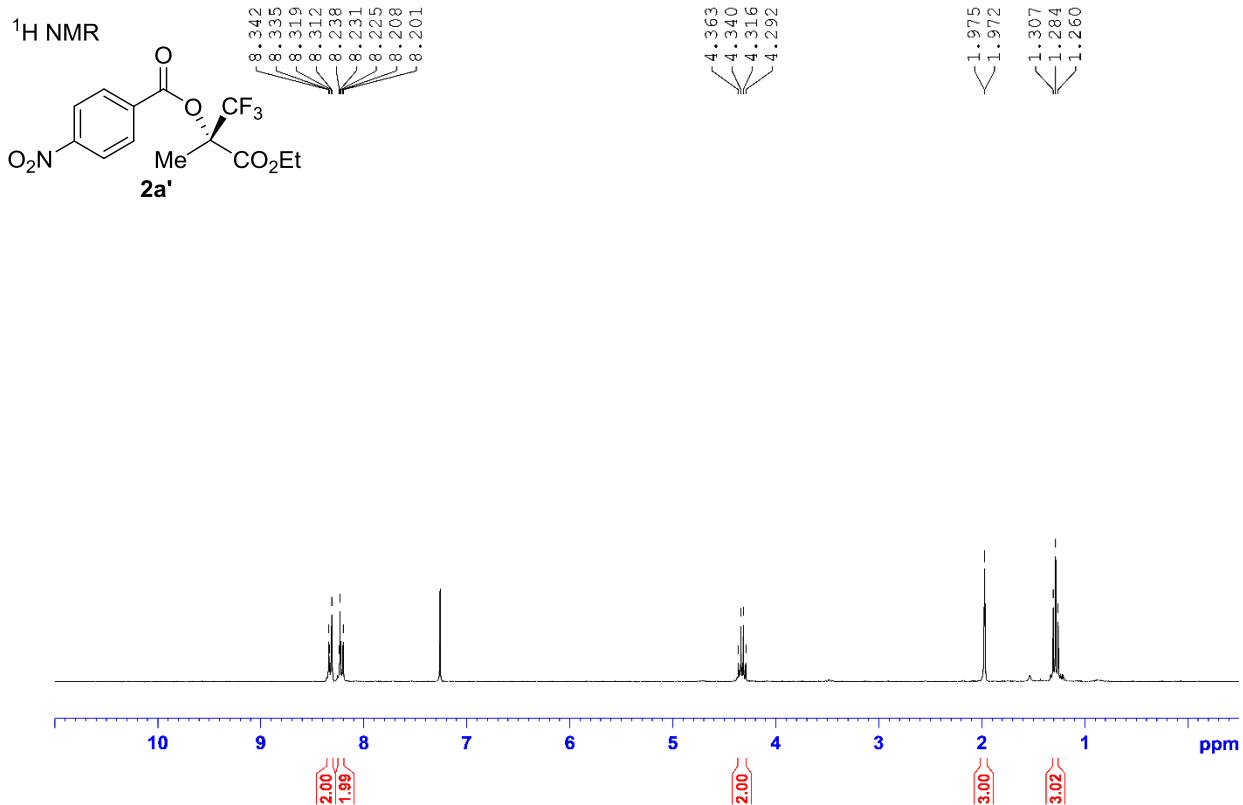


4.853
4.832
4.812

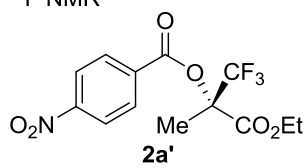
2.121
2.098
2.076
2.053
2.032
2.010
1.987
1.965
0.946
0.926
0.923
0.904



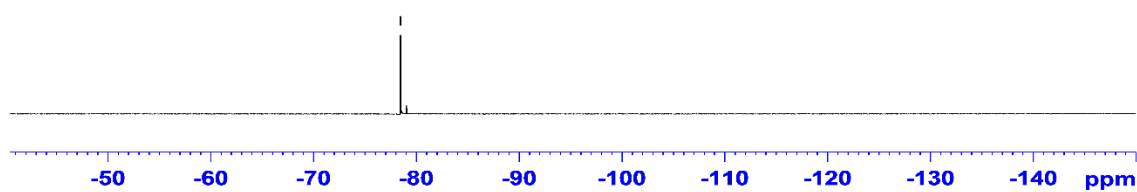




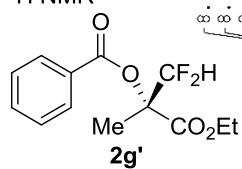
¹⁹F NMR



— -78.448



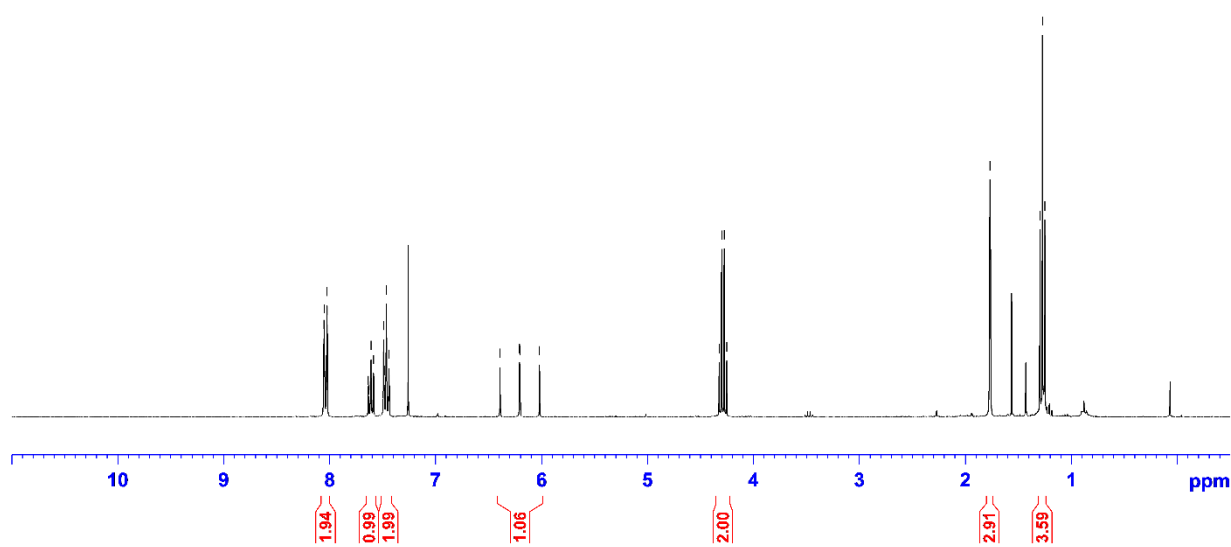
¹H NMR

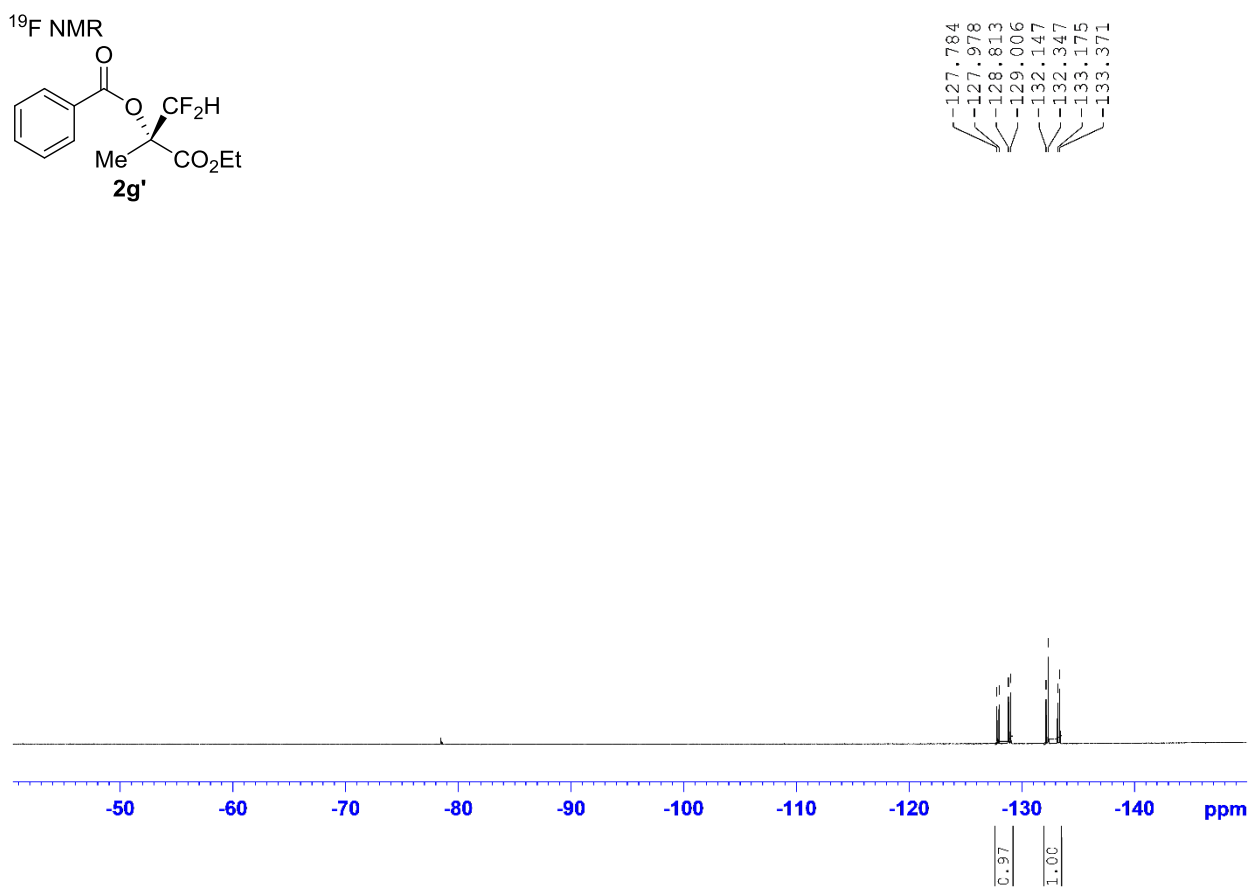
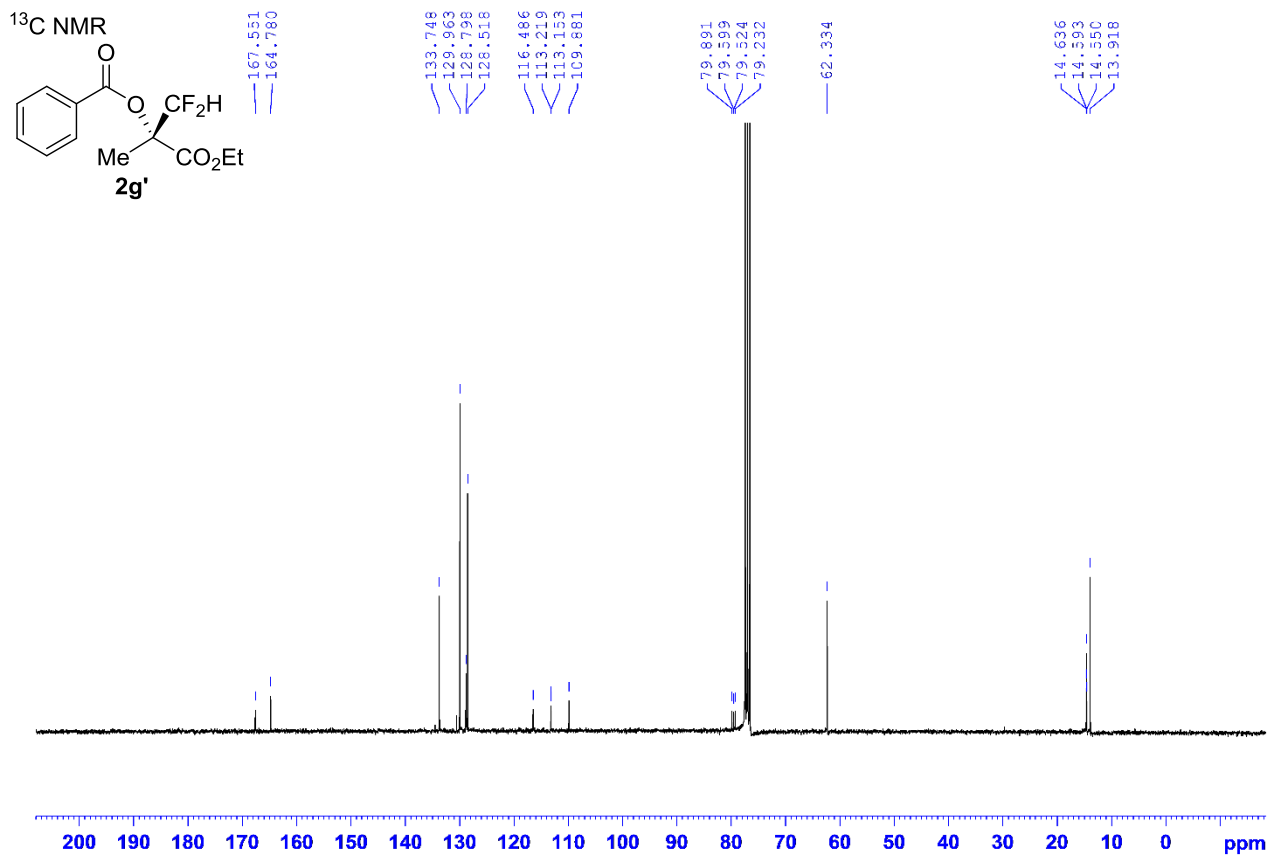


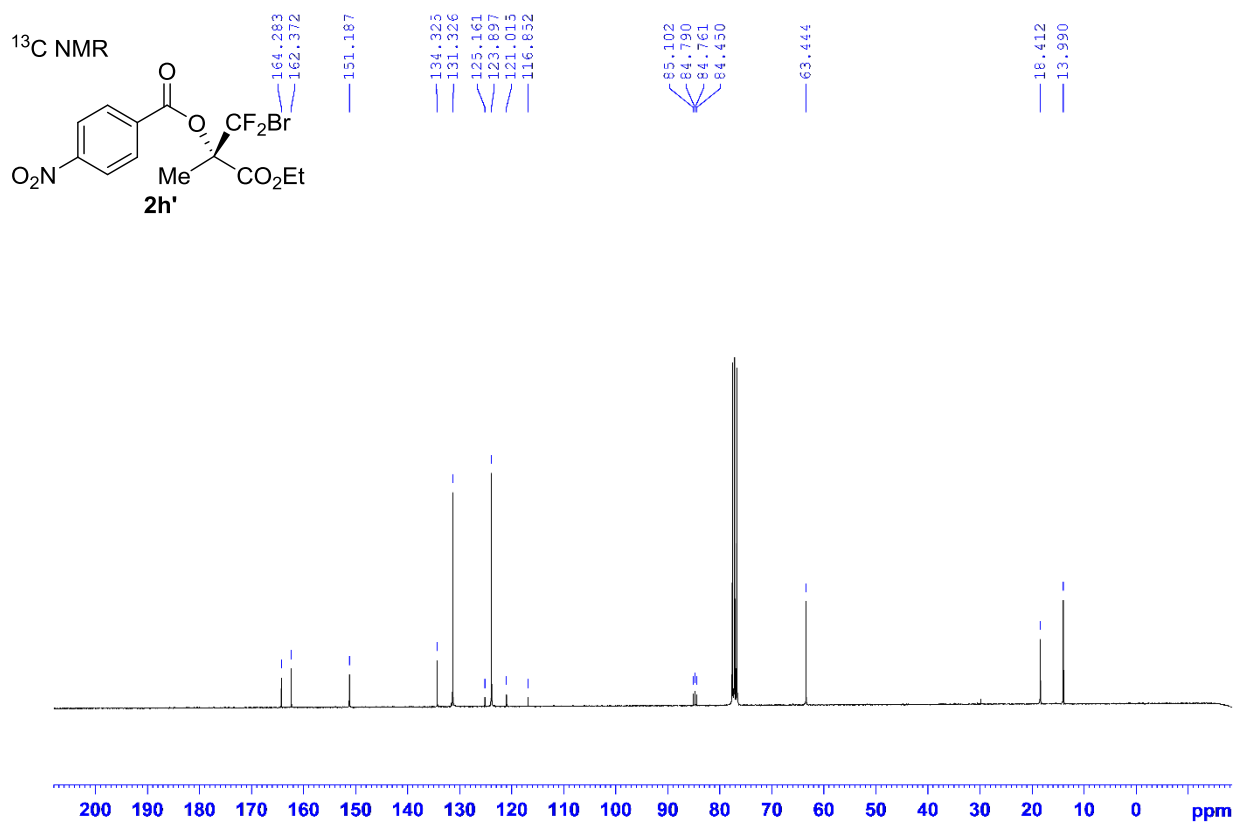
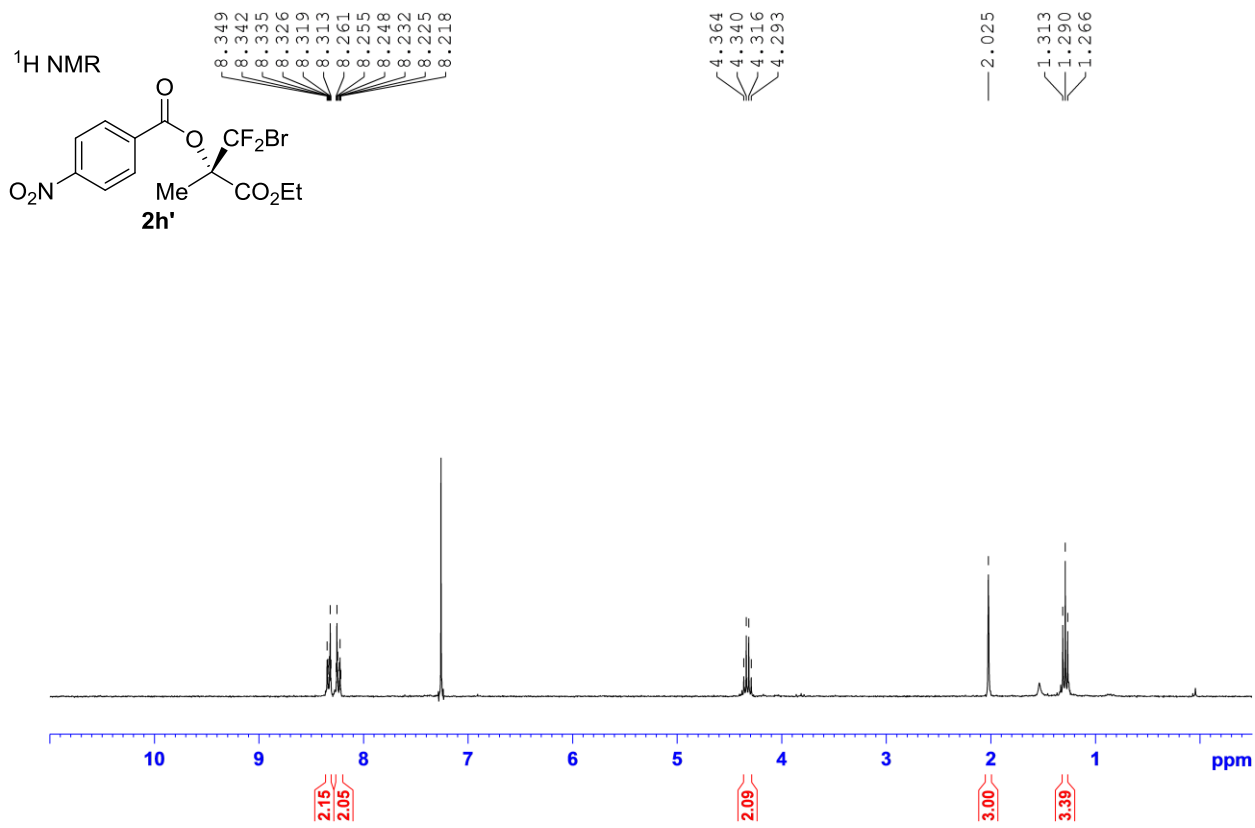
8.056
8.052
8.028
8.023
7.640
7.636
7.631
7.618
7.611
7.604
7.591
7.586
7.582
7.491
7.486
7.465
7.440
6.392
6.210
6.203
6.020

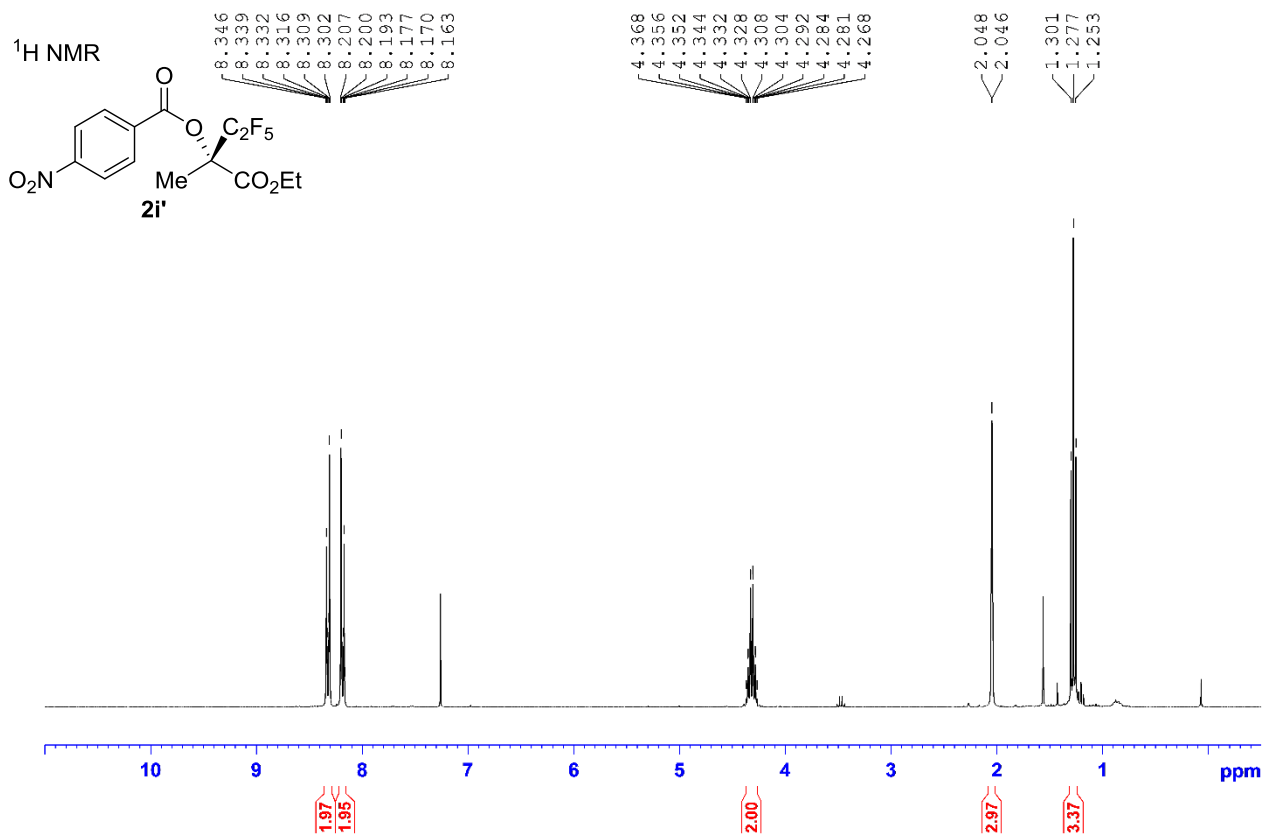
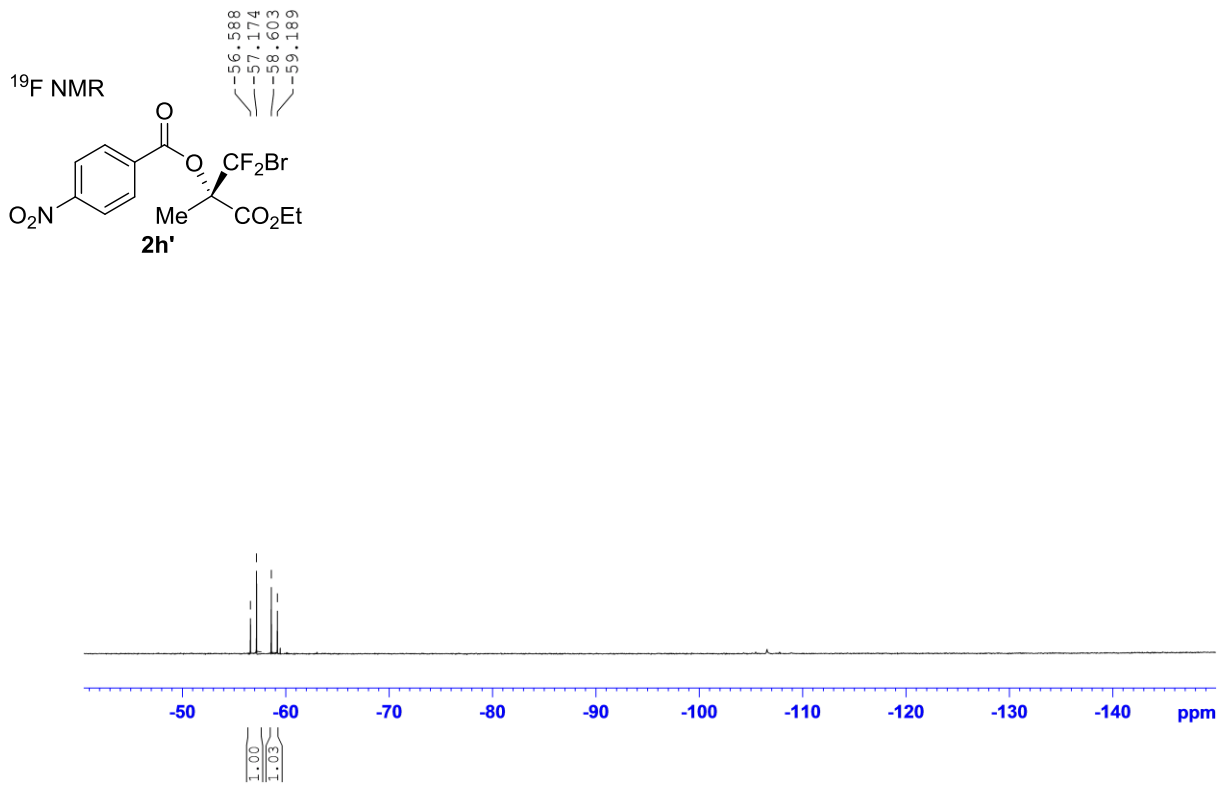
4.325
4.301
4.278
4.254

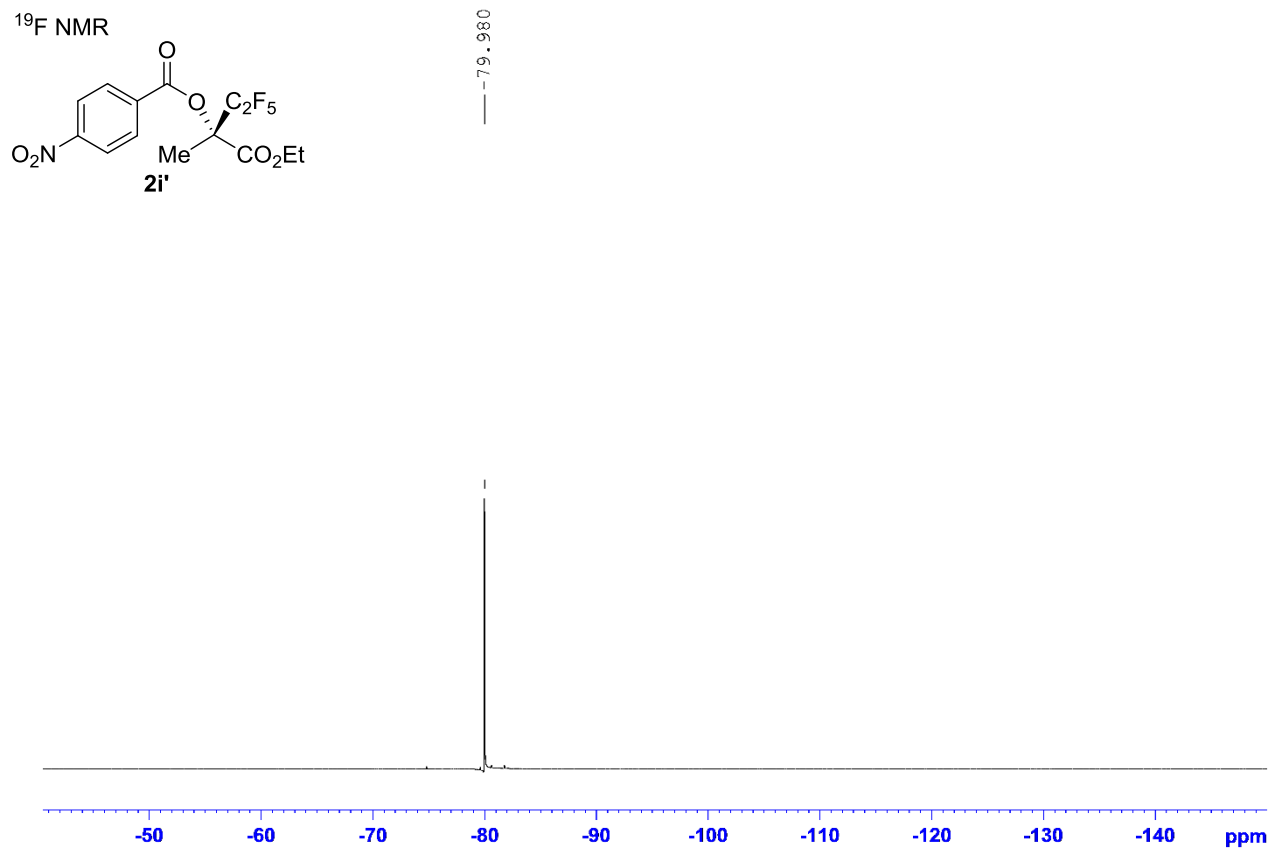
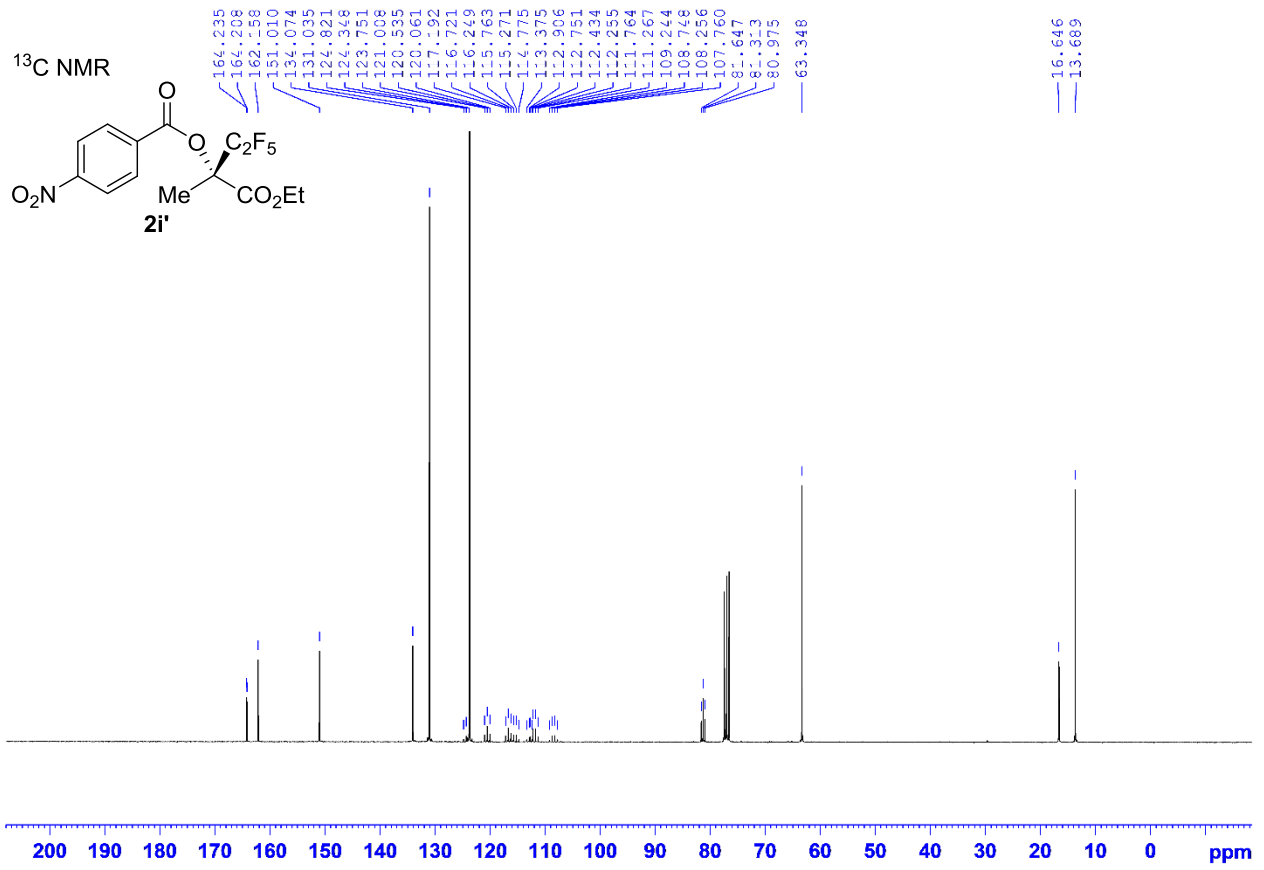
1.773
1.769
1.764
1.298
1.274
1.250

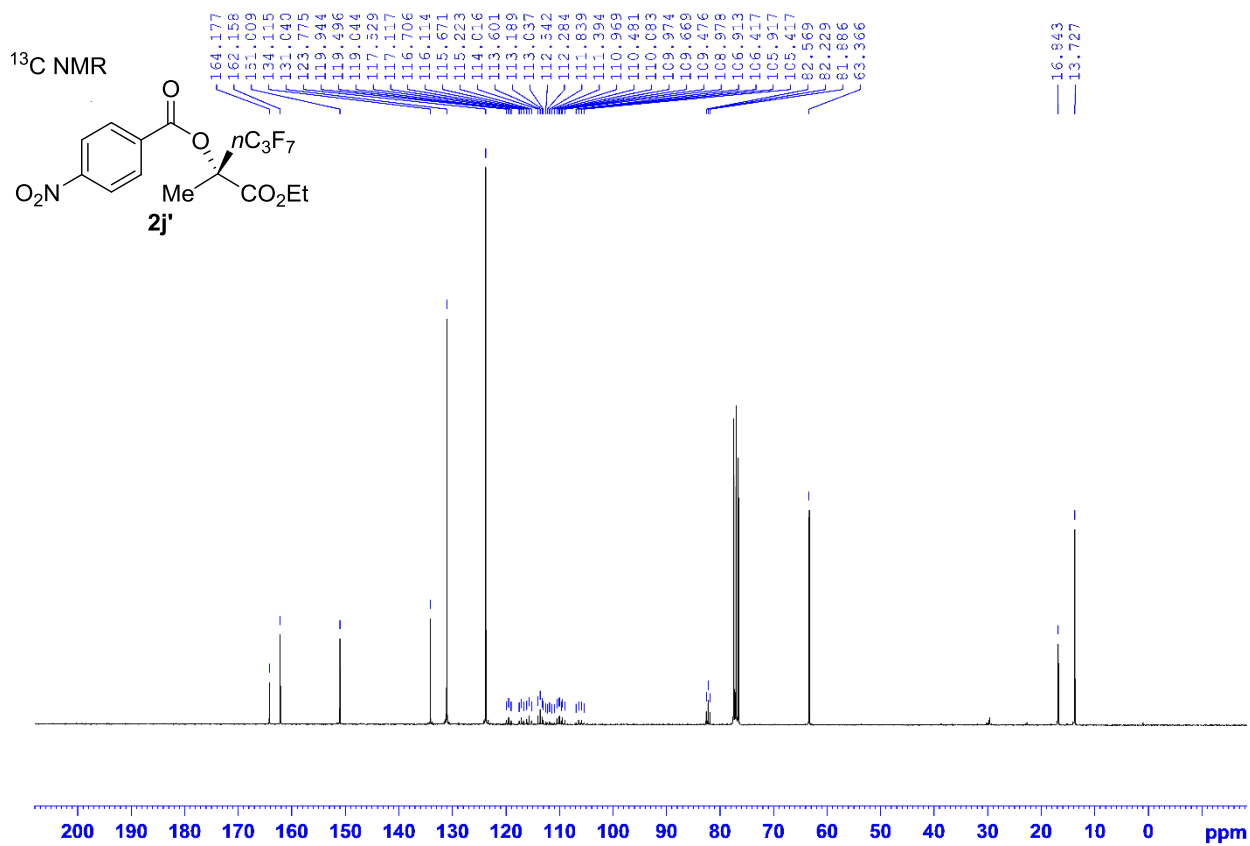
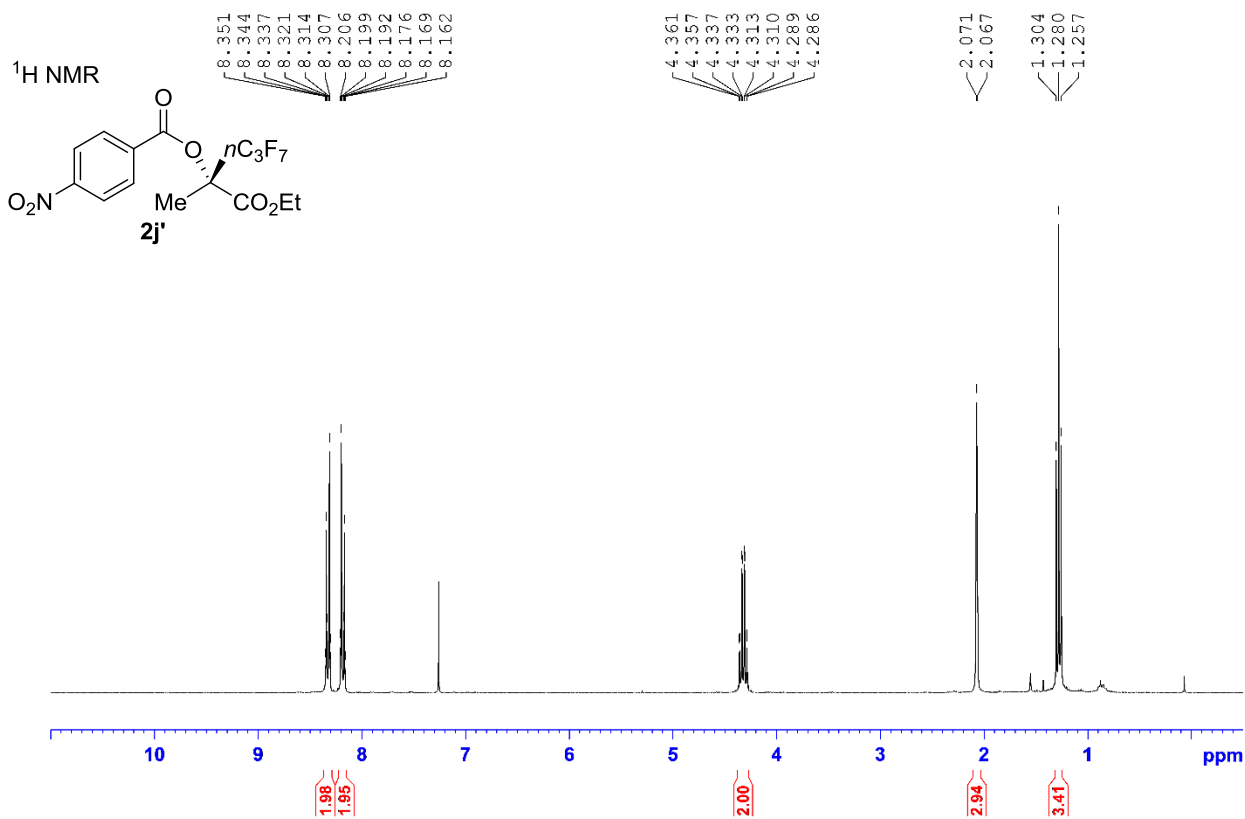




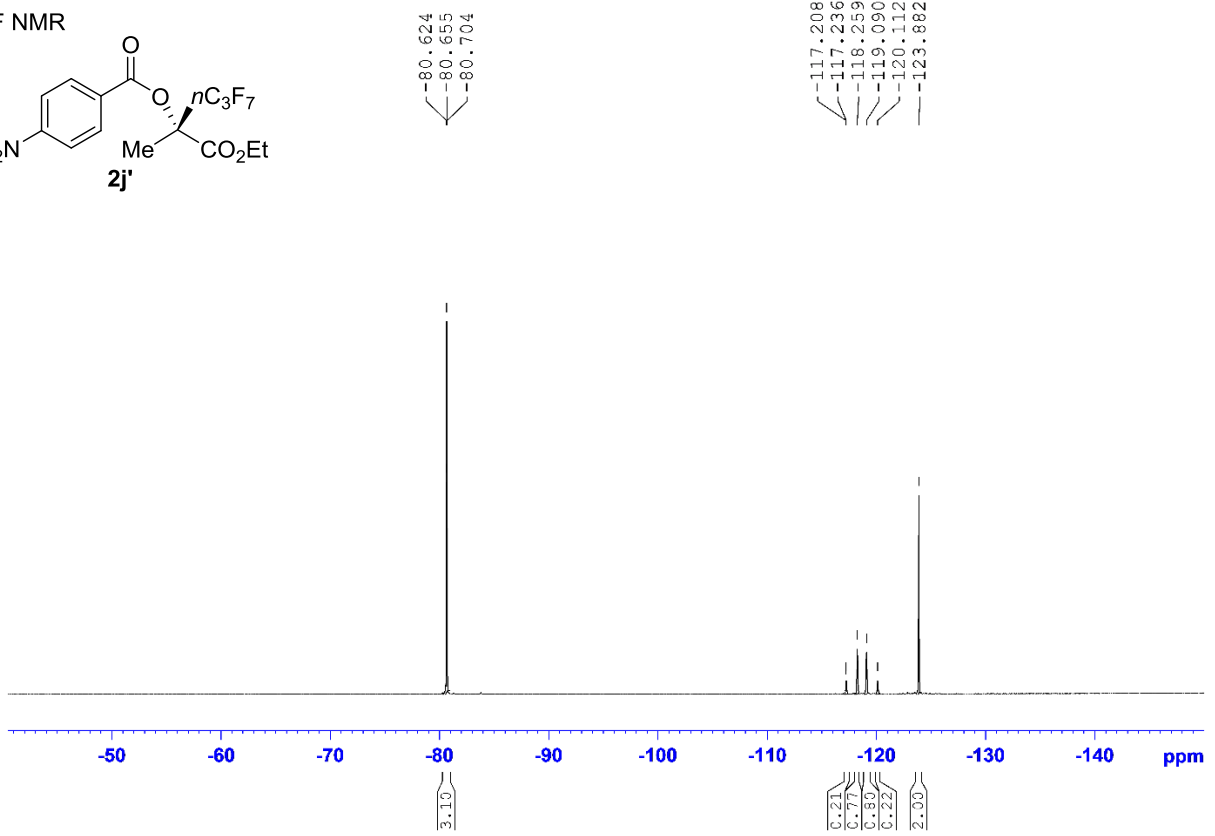
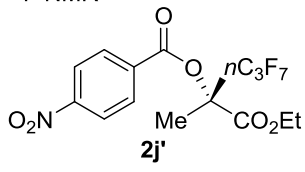




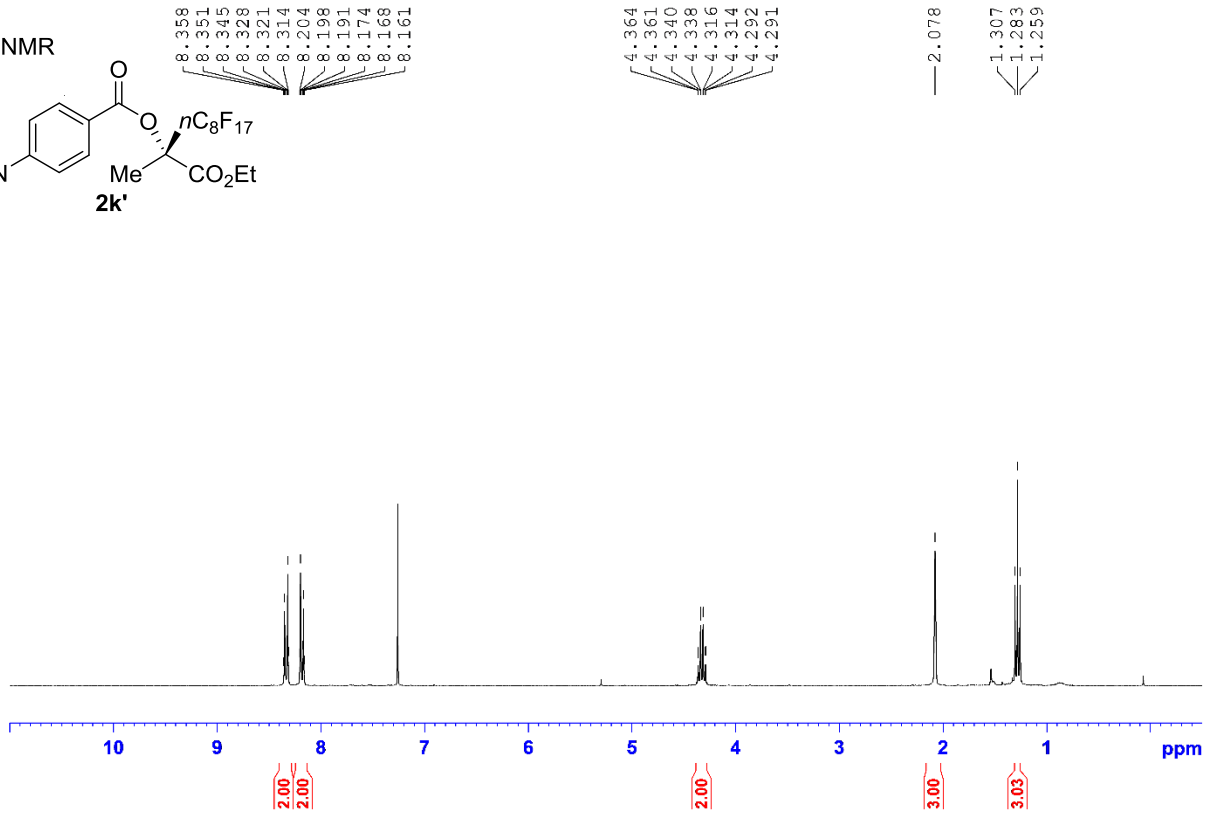
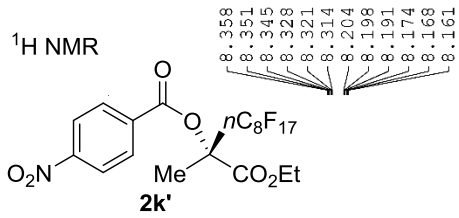


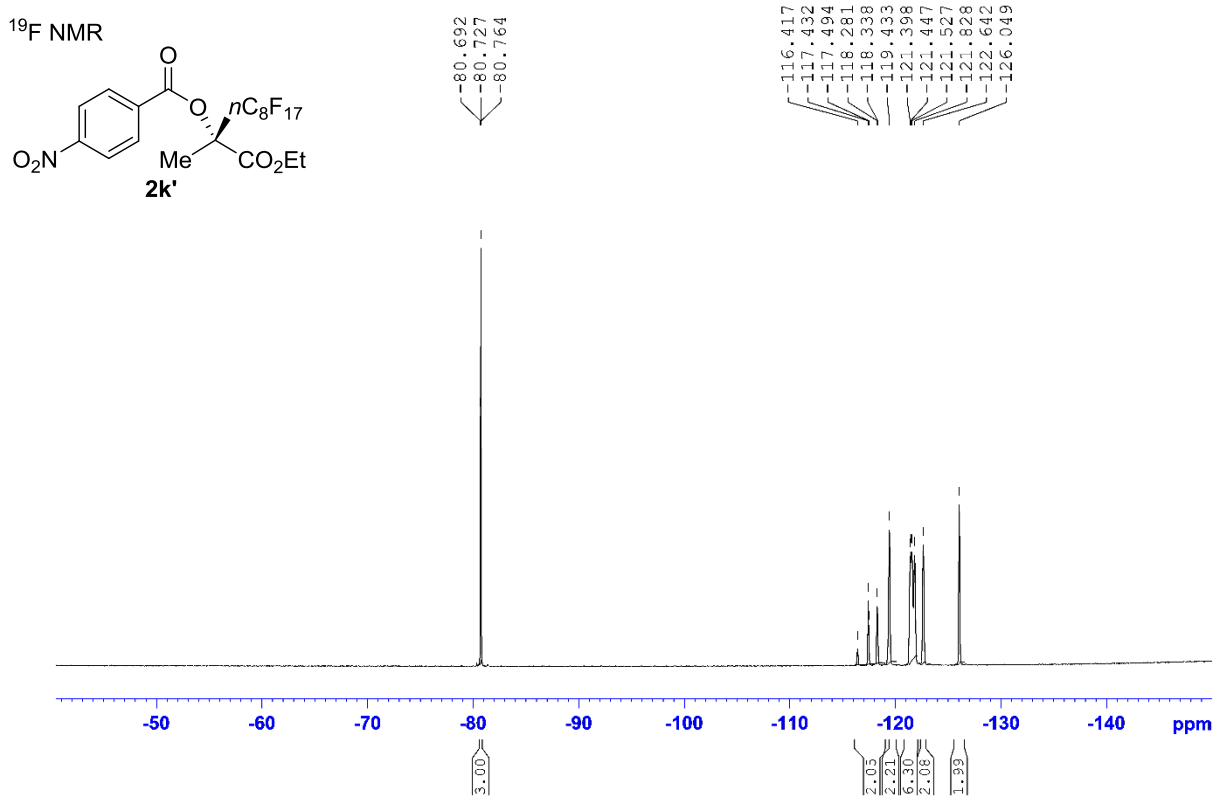
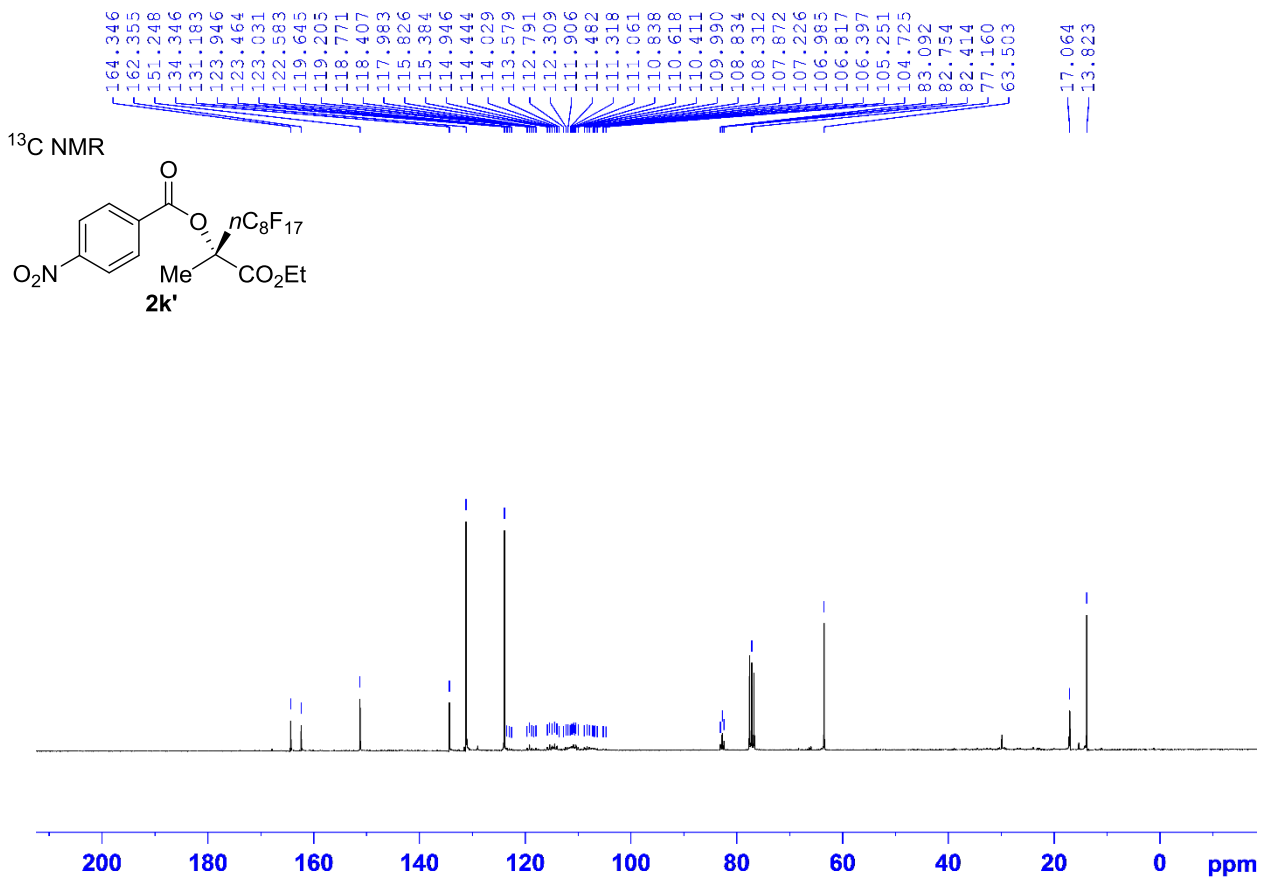


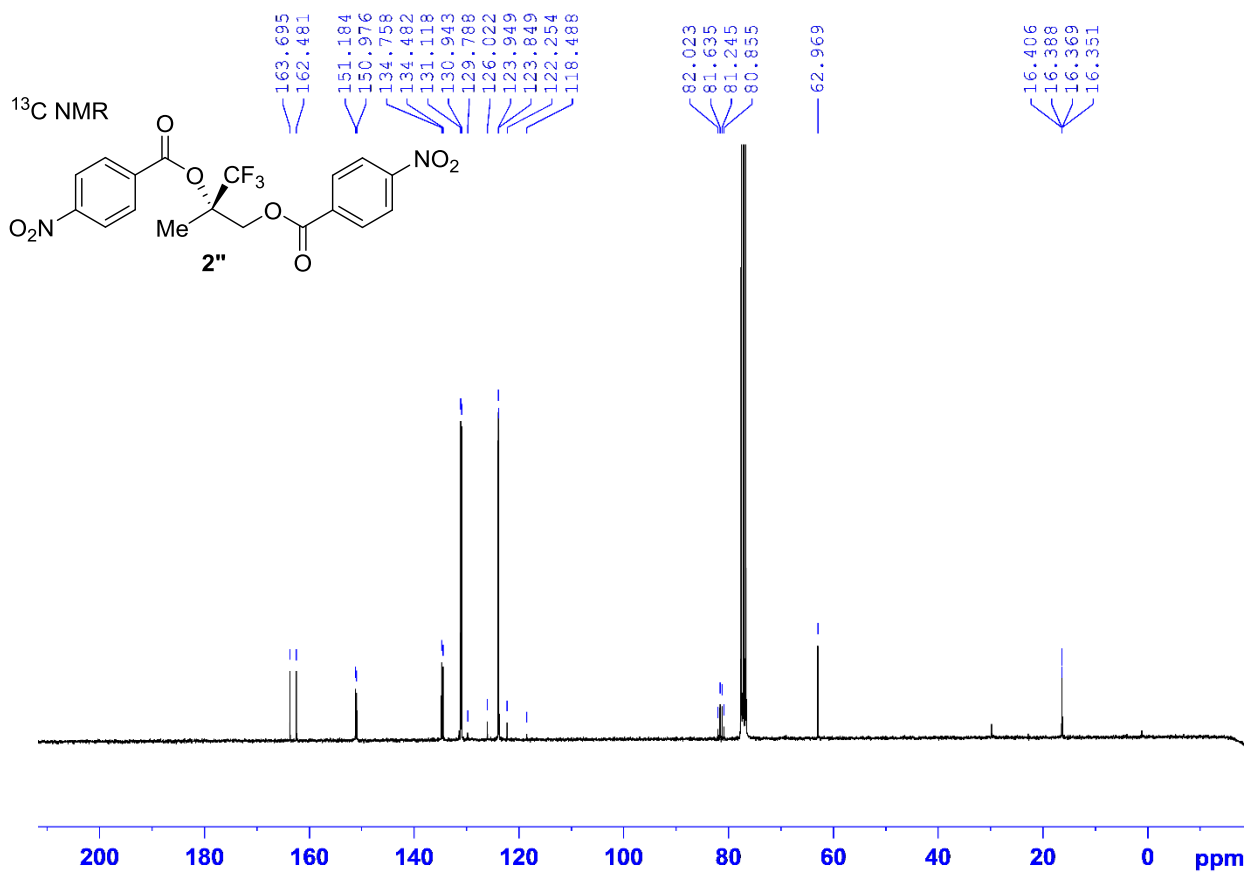
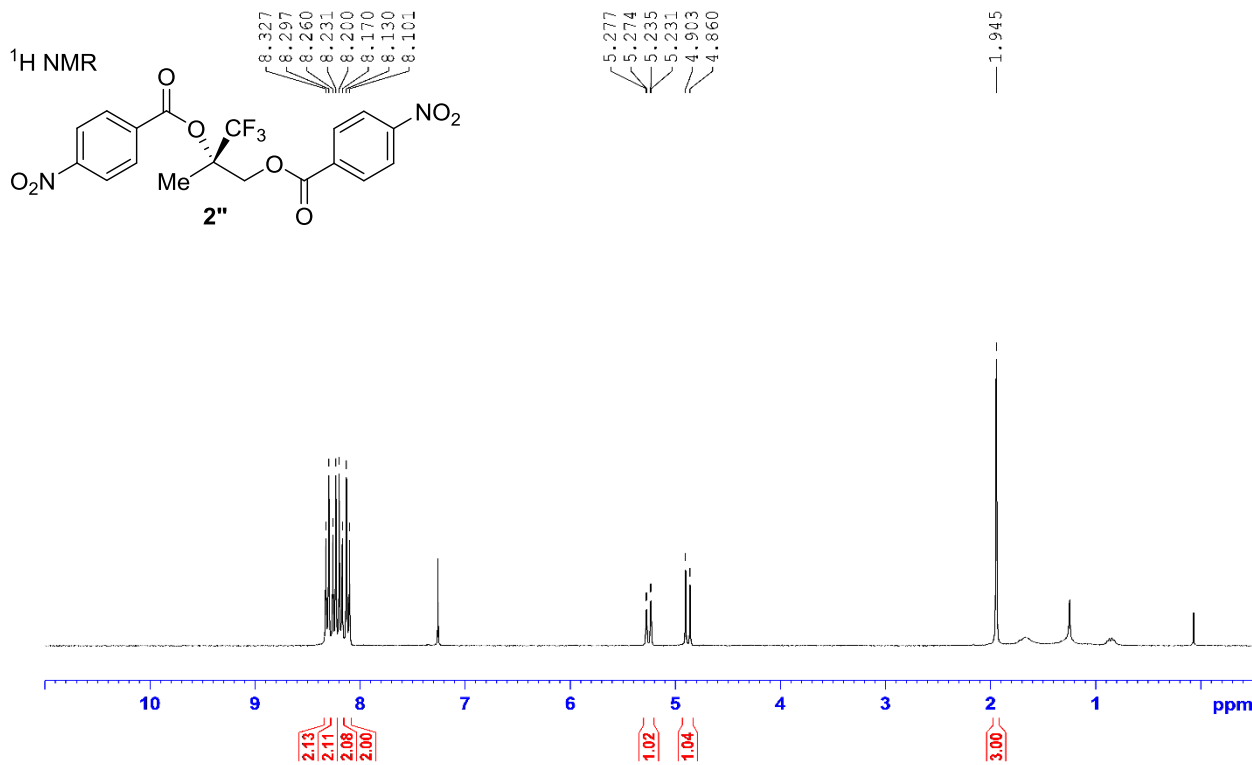
¹⁹F NMR

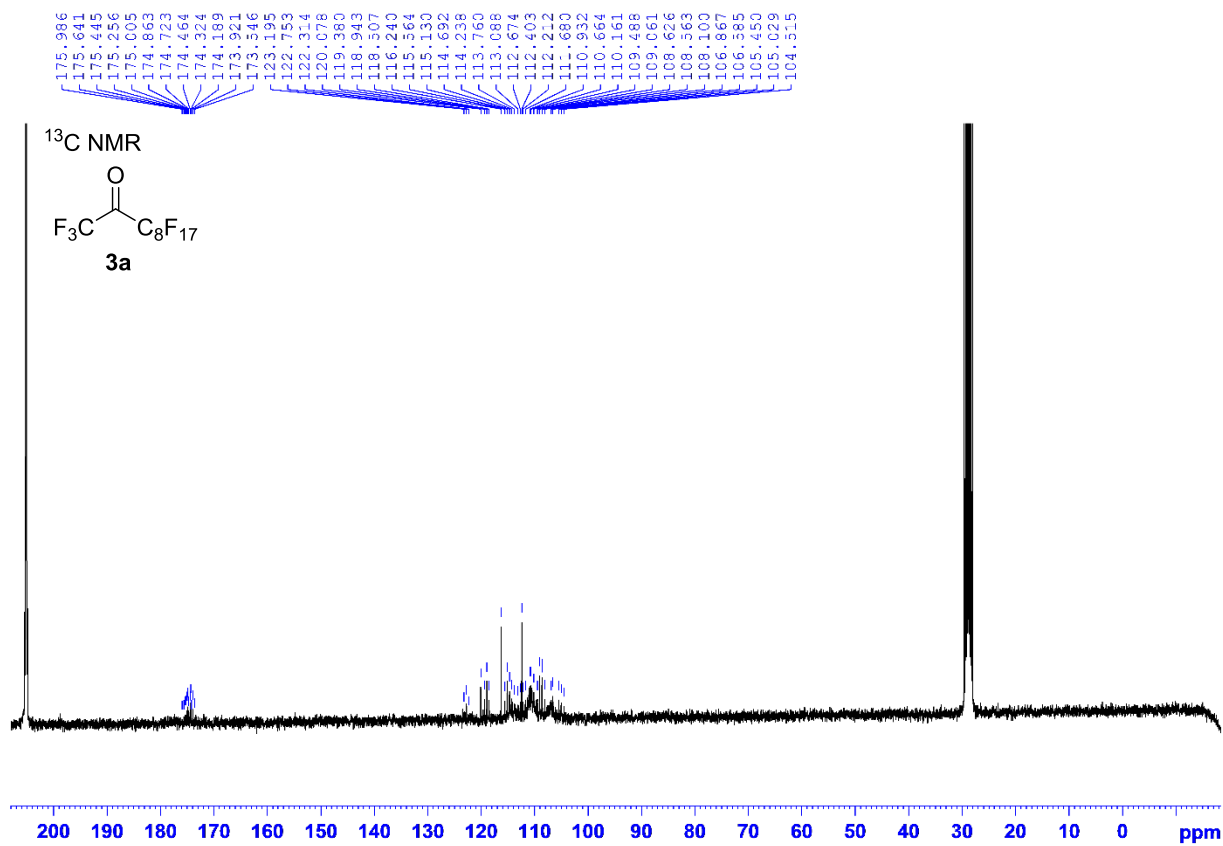
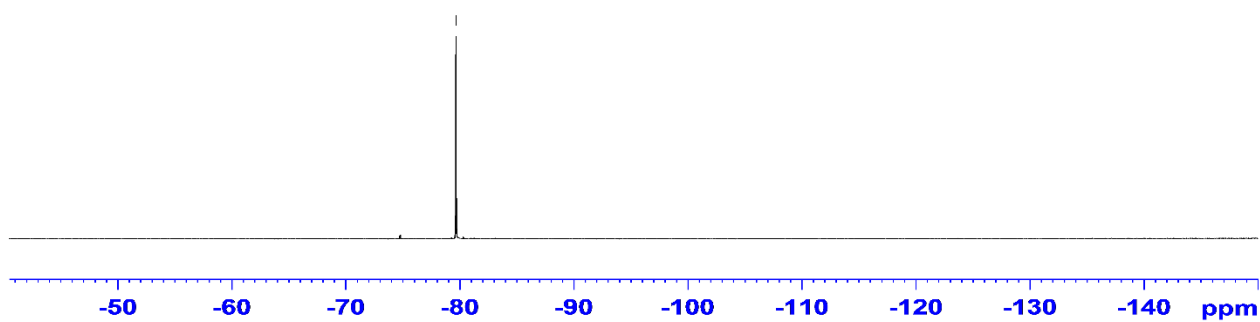
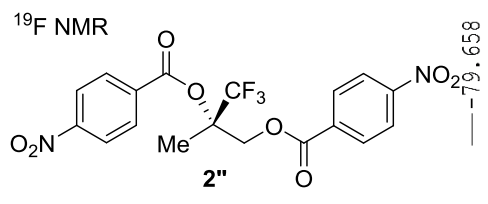


¹H NMR

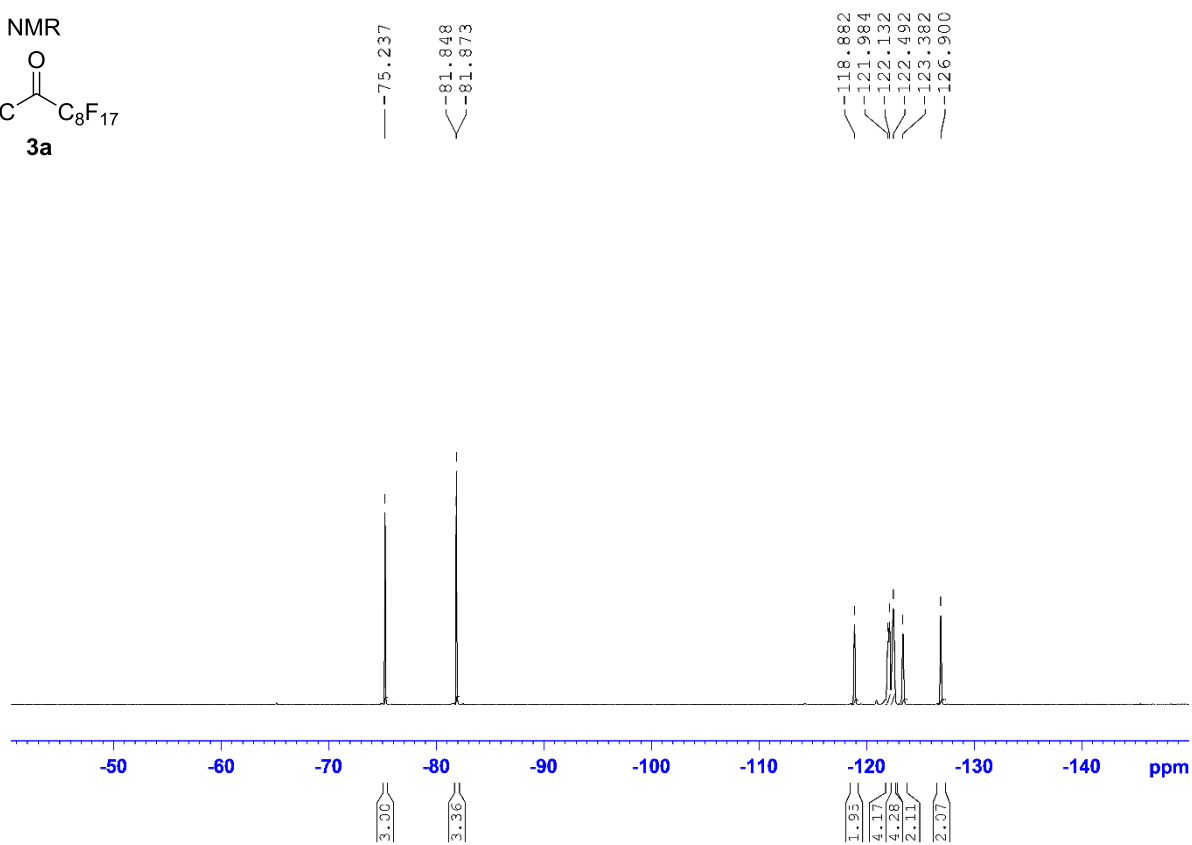
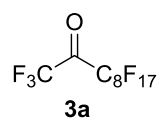




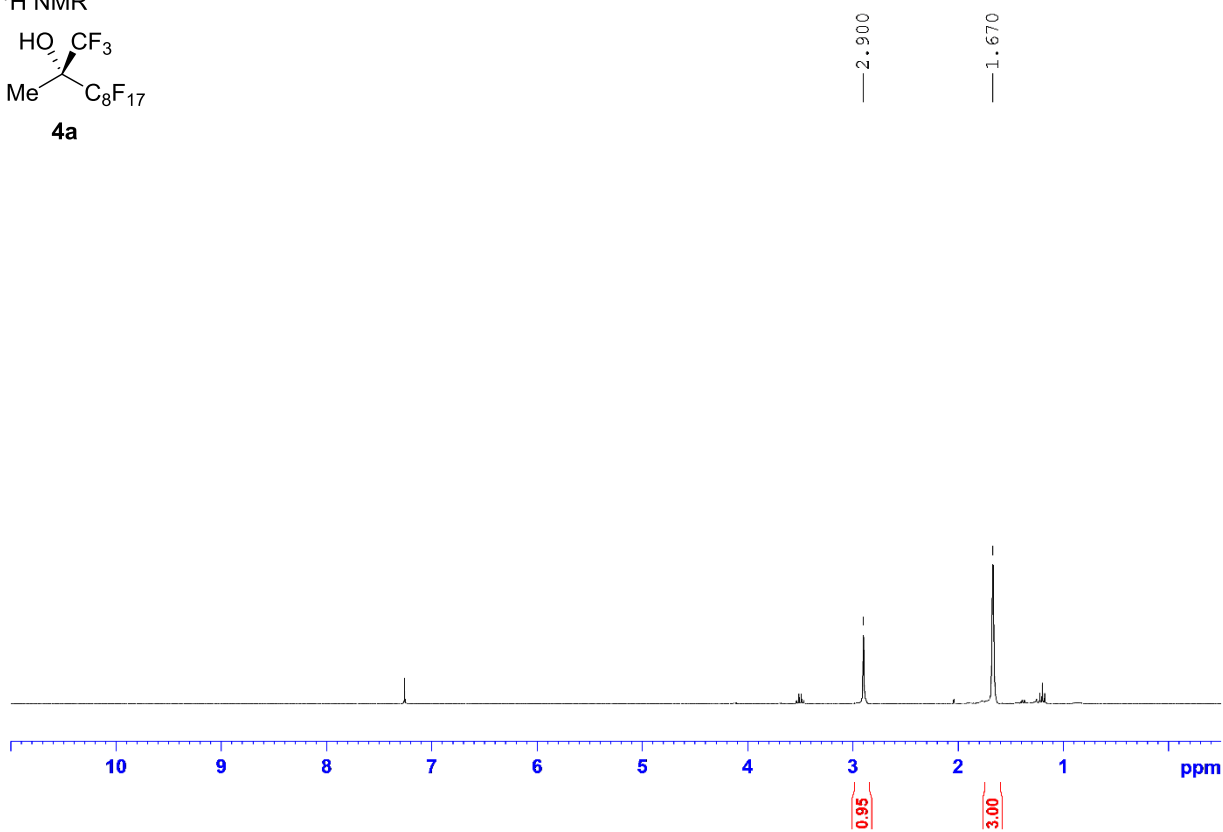
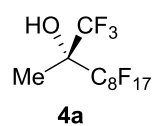




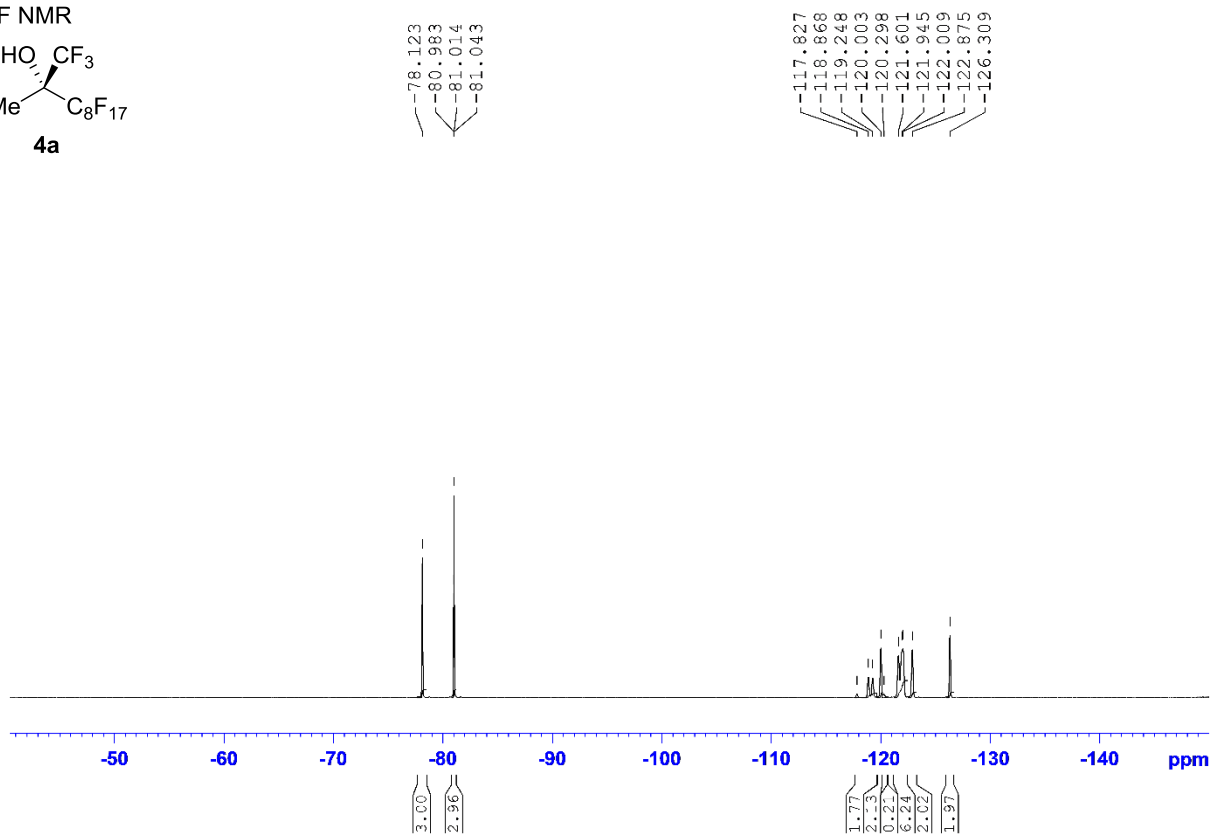
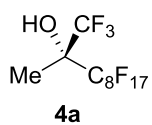
¹⁹F NMR



¹H NMR



¹⁹F NMR



¹H NMR

