Supporting Information

Photoredox-catalyzed selective deuterodefluorination of *α, α*-difluoroarylacetic esters and amides

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Table of Contents

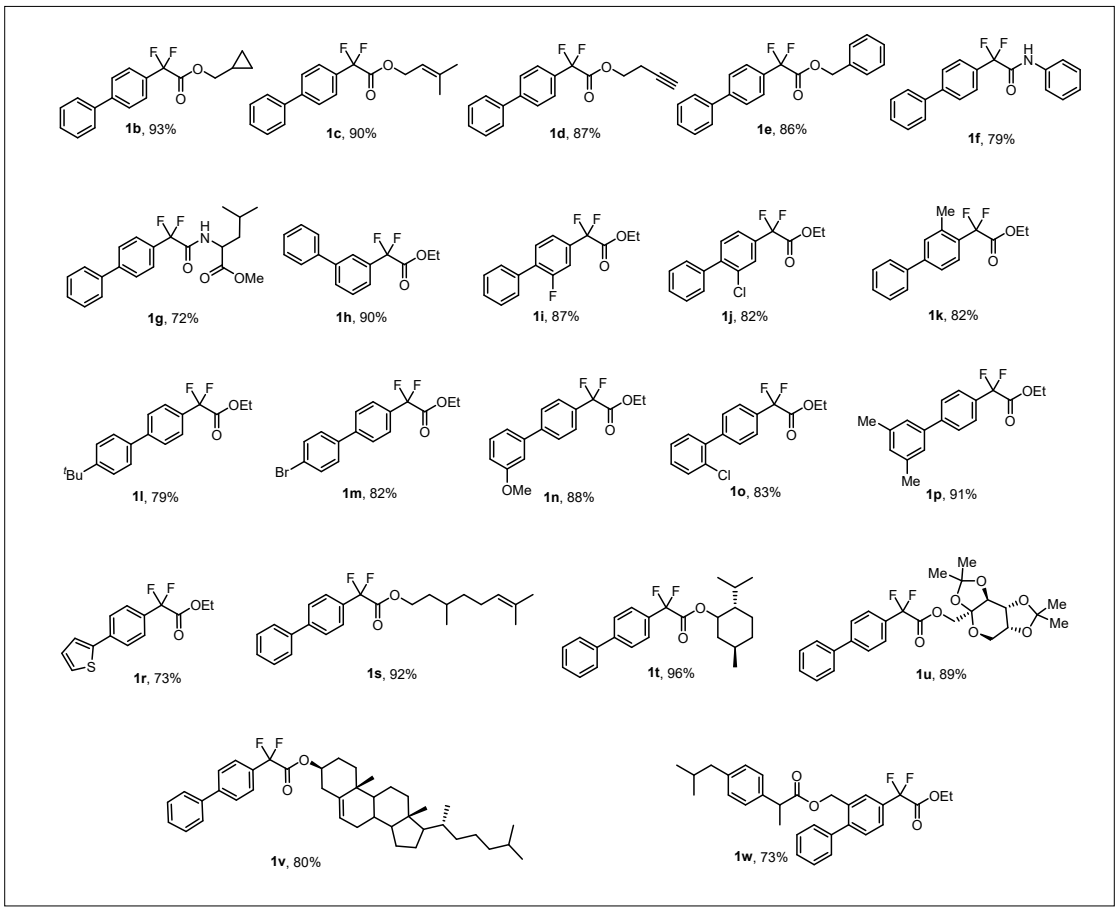
1. General Information

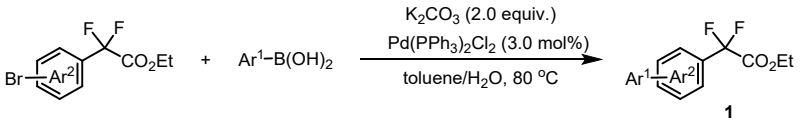
All reactions were conducted in 10 mL oven-dried sealed tube under N_2 atmosphere. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (100 MHz for ^{13}C NMR) spectrometer at ambient temperature. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.16; $CFCl_3$ as an external standard and low field is positive). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplets), dd (doublet of doublets) and m (multiplet). FT-IR spectra were recorded on a Bruker V 70 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a WATERS I-Class VION IMS Q-Tof. Melting points were measured using open glass capillaries in a SGW® X-4A apparatus. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60F-254. Compounds were visualized by exposure to UV-light or by dipping the plates in $KMnO_4$ stain followed by heating.

2. Starting Materials

The ethyl-2-(4-biphenylyl)-2,2-difluoro-acetate **1a** and bromoaryl difluoroacetic acid ethyl ester were prepared according to the literature.[1]

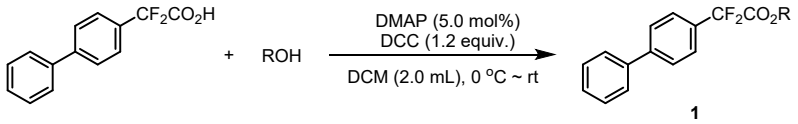
2.1 Synthesis of 1b-1v



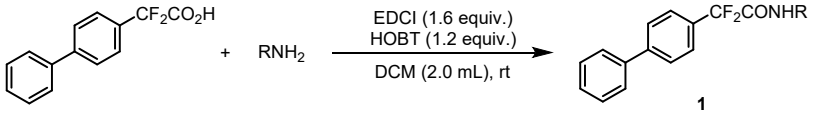


To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with arylboronic acid (2.4 mmol), K_2CO_3 (2.0 equiv.) and $Pd(PPh_3)Cl_2$ (3.0 mol%) were added. The vessel was evacuated and filled with nitrogen (three times). A solution of bromoaryl difluoroacetic acid ethyl ester (2.0 mmol) in toluene (2.0 mL) and H_2O (1.0 mL), was added via syringe. The tube was put into a heating jacket and stirred at 80 °C overnight. The reaction mixture was cooled to room temperature. The aqueous layer was extracted with ethyl acetate, the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was

purified by column chromatography on silica gel (PE/EtOAc = 30:1) to give the desired coupling products **1b-1l**.[1, 2]

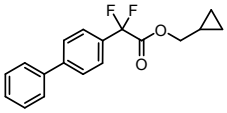


A solution of aryl difluorocarboxylic acid (2.0 mmol), corresponding alcohol (2.4 mmol), and DMAP (5.0 mol%) in DCM (2.0 mL) at 0 °C was added DCC (2.4 mmol) in one portion. A precipitate began to form almost immediately. The reaction was stirred at 0 °C for 10 min and then warmed to room temperature. After completion as detected by TLC, the reaction was then diluted with pentane (10 mL) and filtered through a short plug of silica. The aqueous layer was extracted with ethyl acetate, the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 30:1 to 10:1) to afford aryl difluorinated esters **1m-1p**, **1s-1v**.[2]



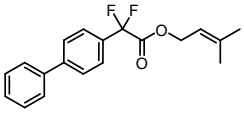
A 50 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with aryl difluorocarboxylic acid (2.0 mmol), EDCI (1.6 equiv.), HOBt (1.5 equiv.), and corresponding amine (2.4 mmol) were dissolved in 10 mL DCM under N_2, then Et_3N (4.0 mmol) was added. The reaction mixture stirred overnight. Subsequently, water was added to the Schlenk-tube. The resulting mixture was extracted with DCM (three times), and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) to afford aryl difluorinated amides **1q and 1r**.[2]

2.2 Characterization data of 1



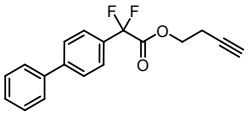
Cyclopropylmethyl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1b)

Colorless oil (93%, 561.9 mg); m.p.: 51-52 °C; R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 4H), 7.63 – 7.61 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.34 (m, 1H), 4.12 (d, *J* = 7.4 Hz, 2H), 1.25 – 1.15 (m, 1H), 0.63 – 0.58 (m, 2H), 0.35 – 0.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (t, *J* = 35.1Hz), 144.1, 140.10, 131.9 (t, *J* = 25.6 Hz), 129.2, 128.2, 127.6, 127.5, 126.2 (t, *J* = 6.0 Hz), 113.8 (t, *J* = 250.6 Hz), 72.1, 9.7, 3.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.45 (s); HRMS (ESI) calcd for $C_{18}H_{16}F_2O_2Li$ $[M+Li]^+$ 285.1273, found 285.1269.



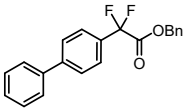
3-Methylbut-2-en-1-yl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1c)

Colorless oil (90%, 568.9 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 5.37 (t, *J* = 7.2 Hz, 1H), 4.76 (d, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (t, *J* = 35.0 Hz), 144.0, 141.4, 140.1, 131.8 (t, *J* = 25.6 Hz), 129.1, 128.1, 127.5, 127.4, 126.1 (t, *J* = 5.9 Hz), 117.1, 113.7 (t, *J* = 250.7 Hz), 64.0, 25.9, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.32 (s); HRMS (ESI) calcd for $C_{19}H_{18}F_2O_2Na$ $[M+Na]^+$ 339.1167, found 339.1155.



But-3-yn-1-yl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1d)

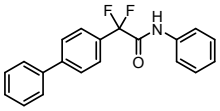
Colorless oil (87%, 522.2 mg); R_f = 0.5 (PE/EtOAc = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 4H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 4.36 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 1.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (t, *J* = 36.5 Hz), 144.2, 140.0, 131.4 (t, *J* = 25.6 Hz), 129.0, 128.1, 127.5, 127.3, 126.1 (t, *J* = 5.9 Hz), 113.5 (t, *J* = 250.6 Hz), 78.8, 70.6, 64.4, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.67 (s); HRMS (ESI) calcd for $C_{18}H_{18}F_2O_2N$ $[M+NH_4]^+$ 318.1300, found 318.1302.



Benzyl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1e)

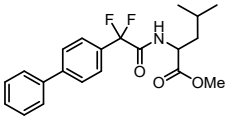
Colorless oil (86%, 581.5 mg); m.p.: 62-63 °C; R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 5H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.46 (m, 3H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.34 (m, 5H), 5.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (t, *J* = 35.5 Hz), 144.1, 140.0, 134.3, 131.49 (t, *J* = 25.5 Hz), 129.0, 128.82, 128.76, 128.3, 128.1, 127.5 , 127.3, 126.1 (t, *J* = 6.0 Hz), 113.6 (t, *J* = 250.7 Hz), 68.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.57 (s); HRMS (ESI) calcd for $C_{21}H_{16}F_2O_2$ $[M]^+$

338.1113, found 338.1105.



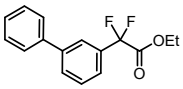
2-([1,1'-Biphenyl]-4-yl)-2,2-difluoro-*N*-phenylacetamide (1f)

White solid (79%, 510.5 mg); m.p.: 160-161 °C; R_f = 0.5 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 5.2 Hz, 2H), 7.61 (m, 4H), 7.49 – 7.45 (m, 2H), 7.41 – 7.36 (m, 3H), 7.22 – 7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (t, *J* = 29.9 Hz), 144.2, 140.1, 136.2, 131.5 (t, *J* = 26.0 Hz), 129.4, 129.1, 128.2, 127.6, 127.4, 126.3 (t, *J* = 6.0 Hz), 125.8, 120.3, 115.0 (t, *J* = 252.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.11 (s); HRMS (ESI) calcd for $C_{20}H_{16}F_2ON$ $[M+H]^+$ 324.1195, found 324.1206.



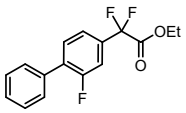
Methyl (2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetyl)leucinate (1g)

White solid (72%, 540.3 mg); m.p.: 92-93 °C; R_f = 0.5 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 6.95 (d, *J* = 6.4 Hz, 1H), 4.71 – 4.68 (m, 1H), 3.76 (s, 3H), 1.79 – 1.65 (m, 3H), 0.96 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 164.0 (t, *J* = 31.4 Hz), 144.0, 140.1, 131.7 (t, *J* = 25.3 Hz), 129.0, 128.1, 127.5, 127.4, 126.1 (t, *J* = 5.9 Hz), 115.0 (t, *J* = 251.5 Hz), 52.7, 51.1, 41.6, 25.0, 22.8, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.14 (d, *J* = 255.7 Hz), -102.97 (d, *J* = 255.3 Hz); HRMS (ESI) calcd for $C_{21}H_{24}F_2O_3N$ $[M+H]^+$ 376.1719, found 376.1726.



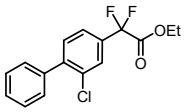
Ethyl 2-([1,1'-biphenyl]-3-yl)-2,2-difluoroacetate (1h)

Colorless oil (90%, 497.0 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 3H), 7.56 – 7.38 (m, 4H), 4.33 (q, *J* = 6.8 Hz, 2H), 1.33 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.40 (t, *J* = 35.1 Hz), 142.0, 140.1, 133.5 (t, *J* = 25.3 Hz), 129.9, 129.3, 129.1, 128.0, 127.3, 124.4 (t, *J* = 6.0 Hz), 113.5 (t, *J* = 250.5 Hz), 63.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.72 (s); HRMS (ESI) calcd for $C_{16}H_{14}F_2O_2$ $[M]^+$ 276.0956, found 276.0943.



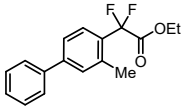
Ethyl 2,2-difluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)acetate (1i)

Colorless oil (87%, 511.7 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 3H), 7.49 – 7.43 (m, 5H), 4.35 (q, *J* = 6.8 Hz, 2H), 1.35 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (t, *J* = 34.9 Hz), 159.6 (d, *J* = 248.4 Hz), 134.7, 133.8 (dt, *J* = 26.3, 7.9 Hz), 132.1 (d, *J* = 13.4 Hz), 131.4 (d, *J* = 3.7 Hz), 130.7 (d, *J* = 8.0 Hz), 129.1 (d, *J* = 2.8 Hz), 128.7, 128.5, 121.6 (t, *J* = 5.8 Hz), 118.3 (d, *J* = 21.4 Hz), 114.0 (dt, *J* = 26.1, 6.4 Hz), 112.7 (t, *J* = 251.2 Hz), 63.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.64 (s), -115.97 (t, *J* = 9.0 Hz); HRMS (ESI) calcd for $C_{16}H_{13}F_3O_2$ $[M]^+$ 294.0862, found 294.0860.



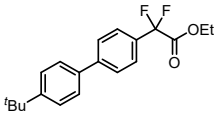
Ethyl 2-(2-chloro-[1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1j)

Colorless oil (82%, 508.6 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.46 (s, 6H), 4.37 (q, *J* = 6.8 Hz, 2H), 1.37 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (t, *J* = 34.7 Hz), 143.4, 138.4, 133.3, 133.2 (t, *J* = 34.2 Hz), 131.8, 129.4, 128.3, 127.3 (t, *J* = 6.2 Hz), 124.1 (t, *J* = 5.8 Hz), 112.7 (t, *J* = 251.5 Hz), 63.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.72 (s); HRMS (ESI) calcd for $C_{16}H_{13}ClF_2O_2$ $[M]^+$ 310.0567, found 310.0581.



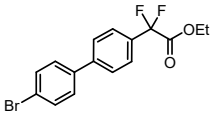
Ethyl 2,2-difluoro-2-(3-methyl-[1,1'-biphenyl]-4-yl)acetate (1k)

Colorless oil (82%, 475.8 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 3H), 7.52 – 7.39 (m, 5H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (t, *J* = 35.0 Hz), 143.7, 140.1, 137.0 (t, *J* = 2.9 Hz), 130.7, 130.1 (t, *J* = 23.3 Hz), 129.0, 128.0, 127.3, 126.85 (t, *J* = 8.4 Hz), 124.7, 114.5 (t, *J* = 250.7 Hz), 63.3, 20.0, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.97 (s); HRMS (ESI) calcd for $C_{17}H_{17}F_2O_2$ $[M+H]^+$ 291.1191, found 291.1195.



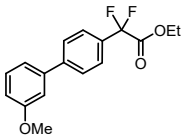
Ethyl 2-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1l)

White solid (79%, 524.8 mg); m.p.: 62-63 °C; R_f = 0.5 (PE/EtOAc = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 4.36 (q, *J* = 6.8 Hz, 2H), 1.41 (s, 9H), 1.37 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (t, *J* = 35.2 Hz), 151.3, 143.9, 137.1, 131.4 (t, *J* = 25.5 Hz), 127.3, 127.0, 126.0 (t, *J* = 6.1 Hz), 113.7 (t, *J* = 250.4 Hz), 63.3, 34.7, 31.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.45 (s); HRMS (ESI) calcd for $C_{20}H_{22}F_2O_2Na$ $[M+Na]^+$ 355.1480, found 355.1484.



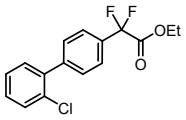
Ethyl 2-(4'-bromo-[1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1m)

Colorless oil (82%, 580.9 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.64 – 7.57 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (t, *J* = 35.1 Hz), 142.8, 138.9, 132.2, 128.9, 127.3, 126.2 (t, *J* = 6.0 Hz), 122.5, 113.5 (t, *J* = 250.7 Hz), 63.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.65 (s); HRMS (ESI) calcd for $C_{16}H_{13}BrF_2O_2Li$ $[M+Li]^+$ 361.0222, found 361.021.



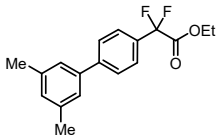
Ethyl 2,2-difluoro-2-(3'-methoxy-[1,1'-biphenyl]-4-yl)acetate (1n)

Colorless oil (88%, 538.8 mg); R_f = 0.5 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.41 – 7.37 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.34 (q, *J* = 6.8 Hz, 2H), 3.88 (s, 3H), 1.34 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (t, *J* = 35.2 Hz), 160.2, 143.9, 141.6, 131.9 (t, *J* = 25.5 Hz), 130.1, 127.5, 126.1 (t, *J* = 6.0 Hz), 119.8, 113.6, 113.5, 113.2 (t, *J* = 250.7 Hz), 63.3, 55.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.57 (s); HRMS (ESI) calcd for $C_{17}H_{16}F_2O_3Na$ $[M+NH_4]^+$ 329.0960, found 329.0961.



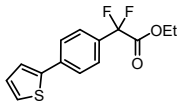
Ethyl 2-(3'-chloro-[1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1o)

Colorless oil (83%, 514.7 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 5.6 Hz, 1H), 7.33 (s, 3H), 4.34 (q, *J* = 6.8 Hz, 2H), 1.34 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.32 (t, *J* = 35.1 Hz), 142.3, 139.4, 132.5, 132.1 (t, *J* = 25.6 Hz), 131.4, 130.2, 129.9, 129.3, 127.1, 125.4 (t, *J* = 5.9 Hz), 113.5 (t, *J* = 250.6 Hz), 63.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.51 (s); HRMS (ESI) calcd for $C_{16}H_{13}ClF_2O_2$ $[M]^+$ 310.0567, found 310.0553.



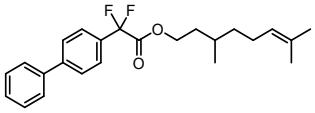
Ethyl 2-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1p)

Colorless oil (91%, 553.5 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 4H), 7.29 – 7.26 (m, 2H), 7.09 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 6H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (t, *J* = 35.2 Hz), 144.3, 140.1, 138.6, 131.5 (t, *J* = 25.6 Hz), 129.8, 127.5, 126.0 (t, *J* = 5.9 Hz), 125.3, 113.6 (t, *J* = 250.1 Hz), 63.3, 21.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.52 (s); HRMS (ESI) calcd for $C_{18}H_{18}F_2O_2Li$ $[M+Li]^+$ 311.142, found 311.1417.



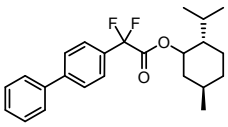
Ethyl 2,2-difluoro-2-(4-(thiophen-2-yl)phenyl)acetate (1r)

Colorless oil (73%, 411.8 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.11 (s, 1H), 4.31 (q, *J* = 6.8 Hz, 2H), 1.32 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (t, *J* = 35.2 Hz), 143.0, 137.2, 131.7, 128.4, 126.3 (t, *J* = 6.1 Hz), 126.1, 126.1, 124.4, 113.5 (t, *J* = 250.6 Hz), 63.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.86 (s); HRMS (ESI) calcd for $C_{14}H_{13}F_2O_2S$ $[M+H]^+$ 283.0599, found 283.0616.



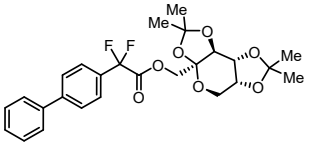
3,7-Dimethyloct-6-en-1-yl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1s)

Colorless oil (92%, 710.6 mg); R_f = 0.5 (PE/EtOAc = 50:1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 4H), 7.60 – 7.59 (m, 2H), 7.48 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 5.06 (s, 1H), 4.31 (s, 2H), 1.95 – 1.92 (m, 4H), 1.75 – 1.67 (m, 3H), 1.58 – 1.50 (m, 2H), 1.32 – 1.27 (m, 1H), 1.17 (s, 1H), 0.89 – 0.88 (m, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (t, *J* = 35.0 Hz), 144.2, 140.2, 131.9 (t, *J* = 25.7 Hz), 129.2, 128.3, 127.6, 127.5, 126.2 (t, *J* = 5.9 Hz), 124.6, 113.7 (t, *J* = 250.6 Hz), 65.9, 37.1, 35.3, 29.6, 25.9, 25.6, 19.5, 17.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.83 (s); HRMS (ESI) calcd for $C_{24}H_{28}F_2O_2Na$ $[M+Na]^+$ 409.1950, found 409.1951.



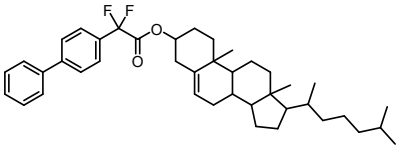
2-Isopropyl-5-methylcyclohexyl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1t)

White solid (96%, 741.5 mg, d.r. = 1:1); m.p.: 99-100 °C; R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.41 – 7.37 (m, 1H), 4.79 (t, *J* = 10.8 Hz, 1H), 4.68 (t, *J* = 10.8 Hz, 1H), 2.04 (s, 1H), 1.98 (d, *J* = 7.6 Hz, 1H), 1.89 – 1.85 (m, 1H), 1.69 (s, 1H), 1.66 (s, 1H), 1.48 – 1.42 (m, 1H), 1.40 – 1.31 (m, 1H), 1.06 – 1.02 (m, 1H), 0.91 (s, 3H), 0.89 (s, 3H), 0.81 – 0.76 (m, 1H), 0.64 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 163.9 (t, *J* = 35.1 Hz), 143.9, 140.1, 131.9 (t, *J* = 25.5 Hz), 129.0, 128.1, 127.34, 127.32, 126.0 (t, *J* = 5.9 Hz), 113.6 (t, *J* = 251.1 Hz), 77.8, 74.3, 47.1, 47.0, 41.0, 40.2, 34.3, 34.1, 31.5, 26.4, 26.1, 23.6, 23.4, 22.1, 22.0, 21.4, 20.8, 20.6, 16.5, 16.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.16 (d, *J* = 250.4 Hz), -105.07 (d, *J* = 250.4 Hz); HRMS (ESI) calcd for $C_{24}H_{28}F_2O_2Na$ $[M+NH_4]^+$ 409.1950, found 409.1949.



((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1u)

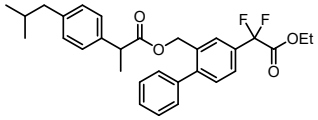
Colorless oil (89%, 872.6 mg, d.r. = 1:1); R_f = 0.5 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.44 – 7.40 (m, 1H), 4.66 (d, *J* = 7.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.37 (s, 1H), 4.28 – 4.22 (m, 2H), 3.98 – 3.78 (m, 2H), 1.55 (s, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (t, *J* = 35.8 Hz), 144.2, 139.9, 131.3 (t, *J* = 25.4 Hz), 129.0, 128.1, 127.5, 127.3, 126.1 (t, *J* = 5.9 Hz), 113.5 (t, *J* = 250.9 Hz), 109.3, 109.3, 100.9, 70.8, 70.2, 67.0, 66.4, 61.5, 26.6, 26.0, 25.0, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.14 (d, *J* = 253.8 Hz), -102.94 (d, *J* = 253.8 Hz); HRMS (ESI) calcd for $C_{26}H_{32}F_2O_7N$ $[M+NH_4]^+$ 508.2141, found 508.2163.



10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1v)

White solid (80%, 986.2 mg, d.r. = 1:1); m.p.: 108-109 °C; R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 5.41 (s, 1H), 4.83 – 4.76 (m, 2H), 2.47 – 2.40 (m, 2H), 2.06 – 1.89 (m, 6H), 1.75 – 1.46 (m, 9H), 1.39 – 1.29 (m, 5H), 1.18 – 1.09 (m, 8H), 1.05 (d, *J* = 15.8 Hz, 5H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 6H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (t, *J* = 34.9 Hz), 143.9, 140.0, 138.9, 131.9 (t, *J* = 25.6 Hz), 129.0, 128.1, 127.4, 127.3, 126.1 (t, *J* = 5.8 Hz), 123.5,

113.6 (t, J = 250.6 Hz), 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 37.7, 36.9, 36.6, 36.3, 35.9, 32.0, 31.9, 28.4, 28.1, 27.5, 24.4, 24.0, 23.0, 22.7, 21.1, 19.4, 18.8, 12.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.52 (s); HRMS (ESI) calcd for $C_{41}H_{58}F_2O_2N$ $[M+NH_4]^+$ 634.4421, found 634.4430.

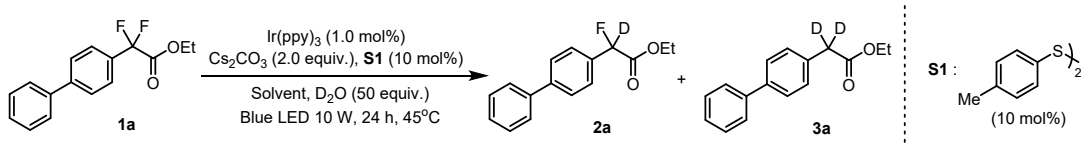


(4-(2-ethoxy-1,1-difluoro-2-oxoethyl)-[1,1'-biphenyl]-2-yl)methyl-2-(4-isobutylphenyl)propanoate (1w)

Colorless oil (73%, 721.5 mg); R_f = 0.5 (PE/EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.40 – 7.35 (m, 3H), 7.22 (d, J = 7.2 Hz, 4H), 7.14 (d, J = 7.6 Hz, 2H), 5.04 (dd, J = 36.8, 12.8 Hz, 2H), 4.37 (q, J = 6.8 Hz, 2H), 3.76 (q, J = 6.8 Hz, 1H), 2.49 (d, J = 6.8 Hz, 2H), 1.92 – 1.85 (m, 1H), 1.52 (d, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 2H), 0.93 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 164.3 (t, J = 34.8 Hz), 145.0, 140.8, 139.2, 137.5, 134.1, 132.2 (t, J = 25.4 Hz), 130.6, 129.5, 129.0, 128.9, 128.5, 128.0, 127.3, 126.4 (t, J = 6.1 Hz), 125.4 (t, J = 6.3 Hz), 113.3 (t, J = 250.6 Hz), 64.4, 63.4, 45.22, 45.18, 30.3, 22.5, 18.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.47 (s), -103.51 (s); HRMS (ESI) calcd for $C_{30}H_{36}F_2O_4N$ $[M+NH_4]^+$ 512.2607, found 512.2584.

3. Optimization of Reaction Conditions

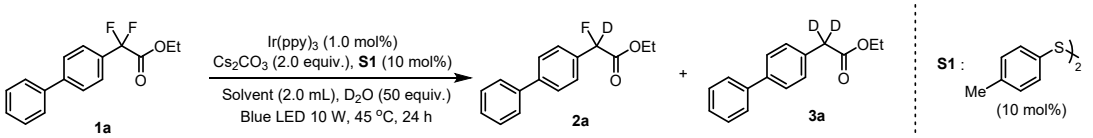
3.1 General Procedures for the Ethyl 2-(4-Biphenylyl)-2,2-difluoroacetate 1a with D_2O



A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with ethyl 2-(4-biphenylyl)-2,2-difluoroacetate **1a** (0.20 mmol), photocatalyst, base and additive. Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (50 equiv.) in solvent (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for a specified time. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone = 30:1 to 5:1) furnishes the desired product **2a**/**3a** as oil.

3.2 Optimization of the Reaction 1a, D_2O[a]

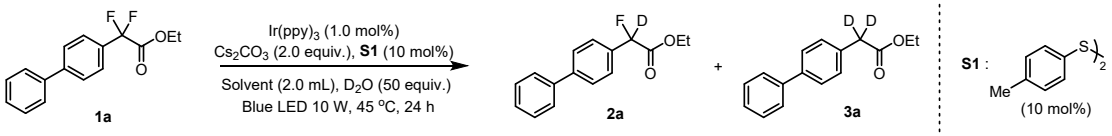
Solvent



Entry	Solvent	Yield of **2a** (%)	Yield of **3a** (%)
1	DMSO	trace	trace
2	DMF	31 (97% D)	4
3	DMAc	trace	trace
4	NMP	58 (97% D)	6
5	THF	trace	trace
6	1,4-diaxone	trace	trace
7	EtOAc	trace	trace
8	MTBE	trace	trace
9	$MeNO_2$	trace	trace
10	toluene	trace	trace

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), Solvent (2.0 mL), D_2O (50 equiv.), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

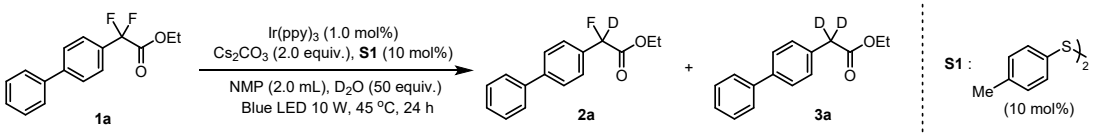
Time



Entry	Time (h)	Yield of **2a** (%)	Yield of **3a** (%)
1[b]	8	12 (97% D)	trace
2[b]	16	20 (97% D)	2
3[b]	24	31 (97% D)	4
4[b]	32	31 (97% D)	4
5[c]	8	9 (97% D)	trace
6[c]	16	47 (97% D)	5
7[c]	24	58 (97% D)	6
8[c]	32	59 (97% D)	6

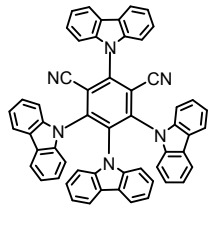
[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (50 equiv.), Blue LED 10 W, 45 °C, x h, Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]DMF was used as solvent (2.0 mL), [c]NMP was used as solvent (2.0 mL).

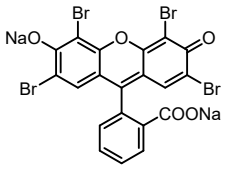
Photocatalyst

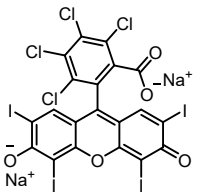


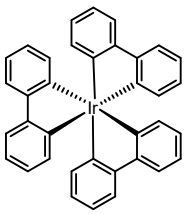
Entry	PC	Yield of **2a** (%)	Yield of **3a** (%)
1	$Ir(ppy)_3$	58 (97% D)	6
2	4CzIPN	21 (97% D)	trace
3	Rhodamine B	0	0
4	EosinY	0	0
5	Rose Bengale	0	0
6	Methlyene Blue	0	0

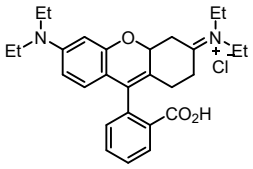
[a]Reaction conditions：**1a** (0.2 mmol), PC (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (50 equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

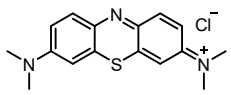




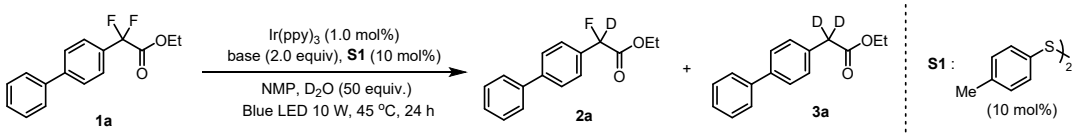








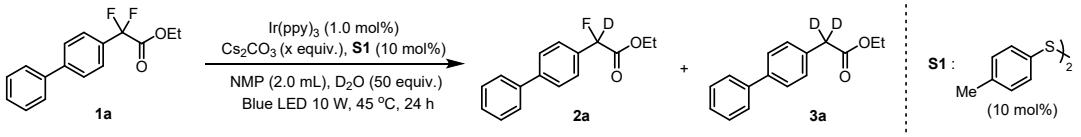
Base



Entry	Base	Yield of **2a** (%)	Yield of **3a** (%)
1	Li_2CO_3	21 (97% D)	trace
2	Na_2CO_3	19 (97% D)	trace
3	K_2CO_3	25 (97% D)	3
4	Cs_2CO_3	58 (97% D)	6
5	NaOAc	trace	trace
6	KOAc	trace	trace
7	Et_3N	0	trace
8	DBU	trace	0
9[b]	Cs_2CO_3	3	86 (98% D)
10[b,c]	Cs_2CO_3	2	86 (98% D)

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Base (2.0 equiv.), **S1** (10 mol%), D_2O (50 equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]extra Et_3N (3.0 equiv.) was used. [c]DMF (2.0 mL) was used as solvent.

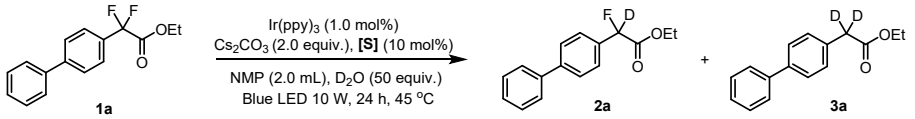
Equiv. of Cs_2CO_3



Entry	Cs_2CO_3 (x equiv.)	Yield of **2a** (%)	Yield of **3a** (%)
1	/	0	0
2	0.5	12 (97% D)	trace
3	1	42 (97% D)	3
4	2	58 (97% D)	6
5	3	59 (97% D)	6

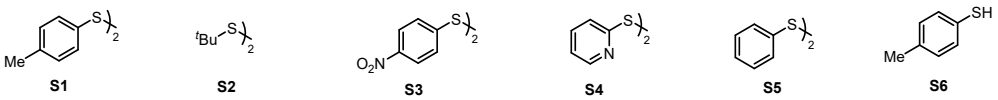
[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (x equiv.), **S1** (10 mol%), D_2O (50 equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

D-transfer mediator

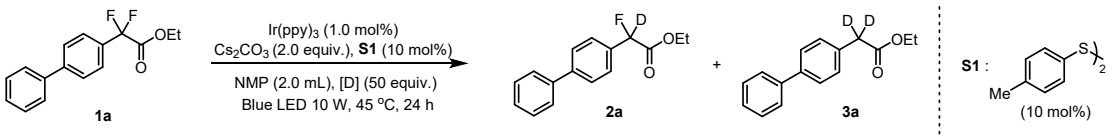


Entry	**[S]**	Yield of **2a** (%)	Yield of **3a** (%)
1	/	0	0
2	**S1**	58 (97% D)	6
3	**S2**	0	trace
4	**S3**	trace	trace
5	**S4**	trace	trace
6	**S5**	50 (97% D)	5
7	**S6**	32 (90% D)	3
8[b]	**S1**	52 (97% D)	5
9[c]	**S1**	58 (97% D)	6

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **[S]** (10 mol%), D_2O (50 equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]5 mol% of **S1** was used. [c]15 mol% of **S1** was used.



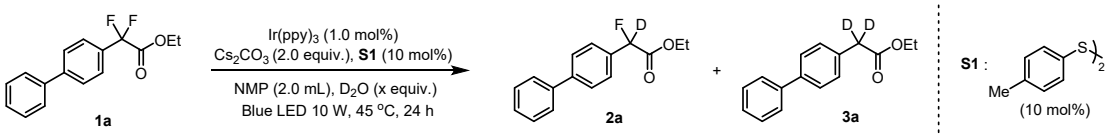
D-Source



Entry	**[D]**	Yield of **2a** (%)	Yield of **3a** (%)
1	D_2O	58 (97% D)	6
2	MeOD	9	trace
3	acetone-d_6	7	trace
4	CD_3CN	trace	trace
5	DMSO-d_6	trace	trace

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), [D] (50 equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

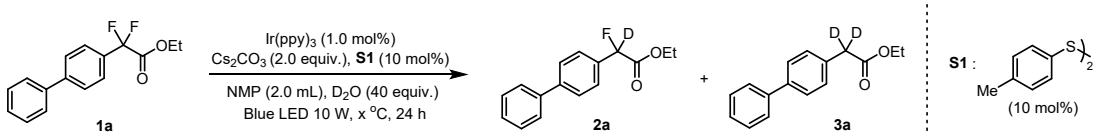
Equiv. of D_2O



Entry	D_2O (x equiv.)	Yield of **2a** (%)	Yield of **3a** (%)
1	20	32 (86% D)	3
2	40	63 (97% D)	6
3	50	58 (97% D)	6
4	80	43 (97% D)	4
5	120	39 (97% D)	3

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (x equiv.), NMP (2.0 mL), Blue LED 10 W, 45 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

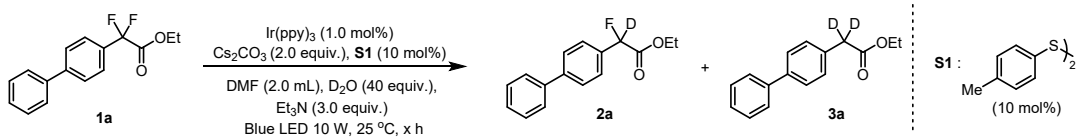
Temperature



Entry	x °C	Yield of **2a** (%)	Yield of **2a** (%)
1	45	63 (97% D)	6
2	35	69 (97% D)	5
3	25	78 (97% D)	3

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (40 equiv.), NMP (2.0 mL), Blue LED 10 W, x °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis.

Time



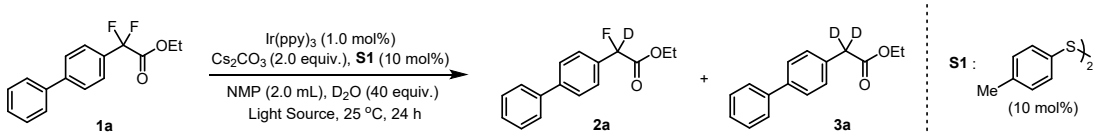
Entry	Time	Yield of **2a** (%)	Yield of **3a** (%)
1	1	16 (97% D)	29 (98% D)
2	4	31 (97% D)	47 (98% D)
3	8	32 (97% D)	55 (98% D)
4	12	2	86 (98% D)
5	16	2	86 (98% D)
6	20	2	86 (98% D)
7	24	2	86 (98% D)
8[b]	12	2	81 (98% D)
9[c]	12	3	86 (98% D)

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (40 equiv.), DMF (2.0 mL), Et_3N (3.0 equiv.), Blue LED 10 W, 25 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]2.0 equiv. of Et_3N was used, [c]4.0 equiv. of Et_3N

was used.

Light Source

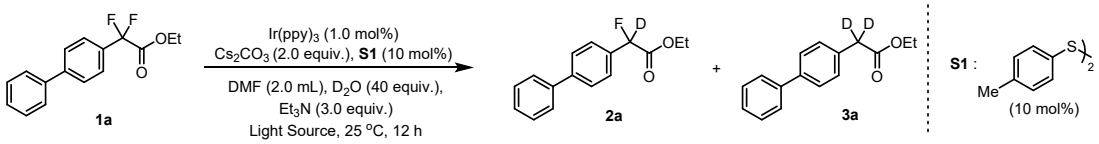
Monodeuterodefluorination



Entry	Light Source	Yield of **2a** (%)	Yield of **3a** (%)
1	Blue LED (5 W)	69 (97% D)	2
2	Blue LED (10 W)	78 (97% D)	3
3	Blue LED (15 W)	78 (97% D)	5
4	CFL (15 W)	0[b]	0

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (40 equiv.), NMP (2.0 mL), Light Source, 25 °C, 24 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]92% of **1a** was recovered.

Dideuterodefluorination

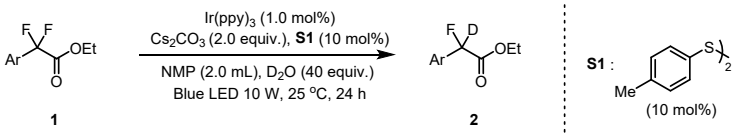


Entry	Light Source	Yield of **2a** (%)	Yield of **3a** (%)
1	Blue LED (5 W)	2	81 (98% D)
2	Blue LED (10 W)	2	86 (98% D)
3	Blue LED (15 W)	4	85 (98% D)
4	CFL (15 W)	0	0[b]

[a]Reaction conditions：**1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%), D_2O (40 equiv.), Et_3N (2.0 equiv.), NMP (2.0 mL), Light Source, 25 °C, 12 h. Yields of isolated products and the deuterated incorporations were determined by ^1H NMR analysis. [b]90% of **1a** was recovered.

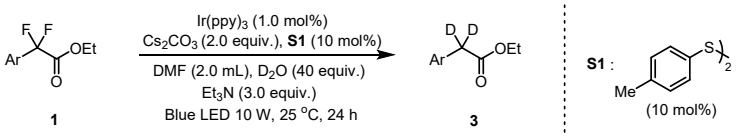
4. Representative Procedure for the Deutodeflurination of 1 with D_2O

4.1 Monodeuterodefluorination reaction



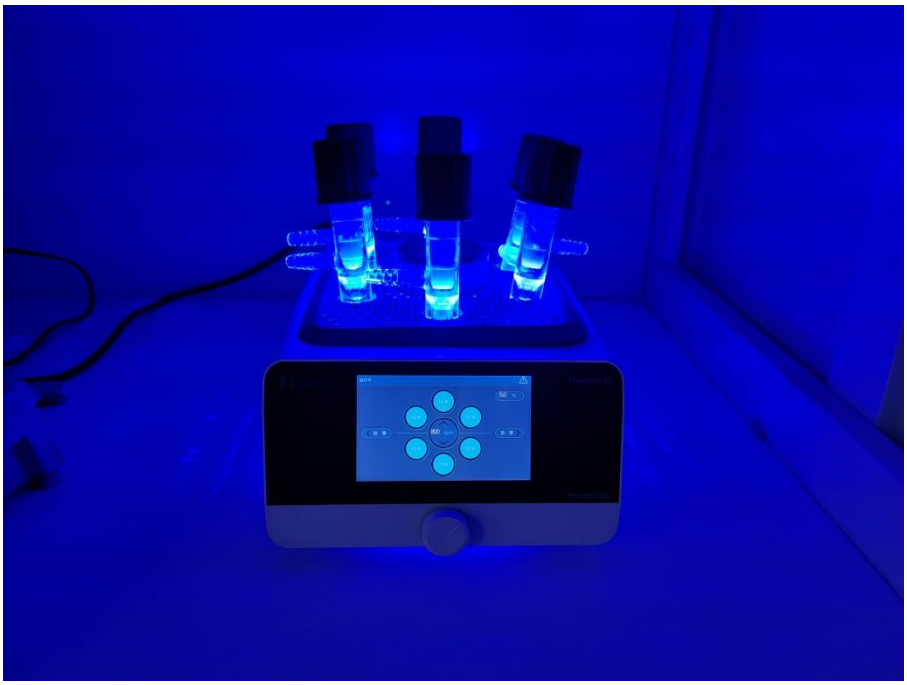
A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with ethyl *α,α*-difluoroaryl acetate derivatives **1** (0.20 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%). Then, the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in NMP (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone: 30:1 to 20:1) furnishes the desired products **2**.

4.2 Dideuterodefluorination reaction



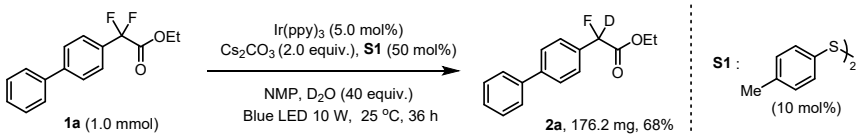
A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with ethyl α,α-difluoroaryl acetate derivatives **1** (0.20 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), Et_3N (3.0 equiv.), **S1** (10 mol%). Then, the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in DMF (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone: 30:1 to 20:1) furnishes the desired products **3**.

The Visible-Light Photoredox Catalysis Experimental Setup (photographed by author Li-Na Guo)

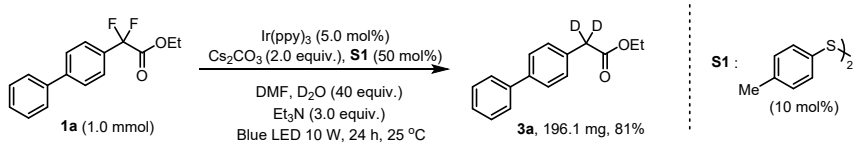


4.3 Applied Research

*Large Scale Synthesis of **2a** and **3a***

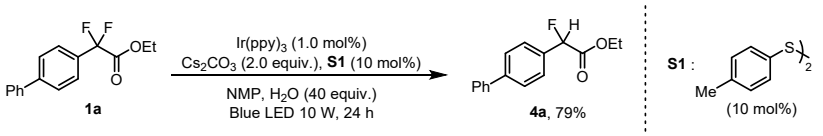


A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 2-(4-Biphenylyl)-2,2-difluoroacetate **1a** (1.0 mmol), $Ir(ppy)_3$ (5.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (50 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in NMP (10 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 36 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone = 30:1) furnishes the desired product **2a**.

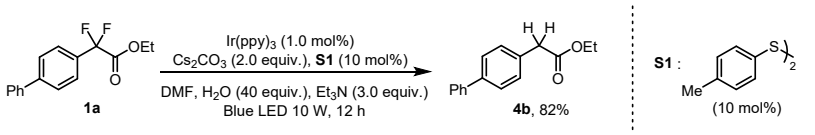


A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 2-(4-Biphenylyl)-2,2-difluoroacetate **1a** (1.0 mmol), $Ir(ppy)_3$ (5.0 mol%), Cs_2CO_3 (2.0 equiv.), Et_3N (3.0 equiv.) **S1** (50 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in DMF (10 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone = 30:1) furnishes the desired product **3a**.

*Selective hydrodefluorination of **1a***

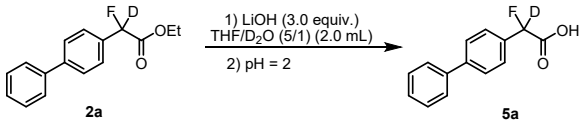


A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 2-(4-Biphenylyl)-2,2-difluoroacetate **1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of H_2O (40 equiv.) in NMP (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone = 30:1) furnishes the desired product **4a**.



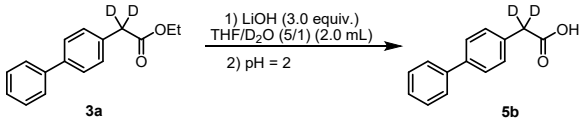
A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 2-(4-Biphenylyl)-2,2-difluoroacetate **1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), Et_3N (3.0 equiv.) **S1** (10 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in DMF (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone = 30:1) furnishes the desired product **4b**.

*Hydrolysis of **2a** and **3a***



2a **5a**

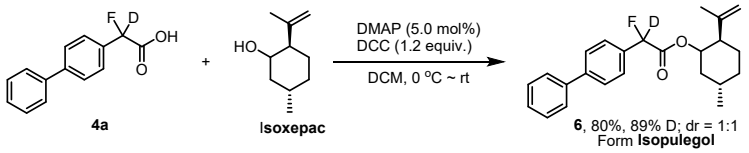
In a 50 mL round bottom flask, **2a** (0.2 mmol, 1.0 equiv.) was added to a mixture of THF/D_2O (5/1, 2.0 mL) and LiOH (3.0 equiv.) and stirred for 10 h at room temperature. The reaction was then poured into 1 M HCl aq. to acidify to pH = 2, and the aqueous phase was extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to afford product **5a**.



3a **5b**

In a 50 mL round bottom flask, **3a** (0.2 mmol, 1.0 equiv.) was added to a mixture of THF/D_2O (5/1, 2.0 mL) and LiOH (3.0 equiv.) and stirred for 10 h at room temperature. The reaction was then poured into 1 M HCl aq. to acidify to pH = 2, and the aqueous phase was extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to afford product **5b**.

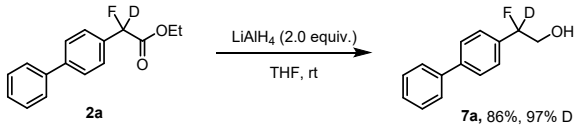
*Esterification of **5a***



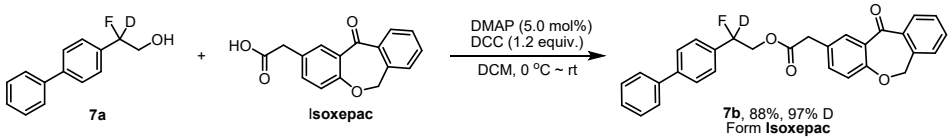
4a **Isoxepac** **6**, 80%, 89% D; dr = 1:1
Form **Isopulegol**

To a solution of **4a** (0.1 mmol), Isoxepac (0.12 mmol), and DMAP (5.0 mol%) in DCM (1.0 mL) at 0 °C was added DCC (0.24 mmol) in one portion. A precipitate began to form almost immediately. The reaction was stirred at 0 °C for 10 min and then warmed to room temperature. After completion as detected by TLC, the reaction was then diluted with pentane (5.0 mL) and filtered through a short plug of silica. The aqueous layer was extracted with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to afford product **6**.

*Reduction and further esterification of **2a***



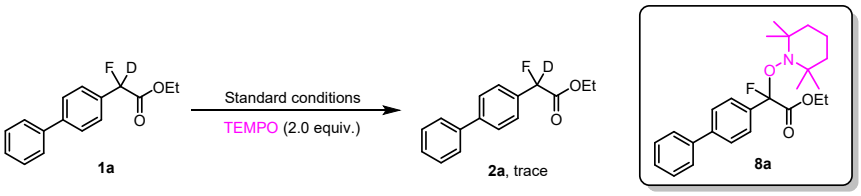
To a solution of **2a** (0.2 mmol, 1.0 equiv.) in THF (2.0 mL) was added lithium aluminium tetrahydride (0.42 mmol, 2.1 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 8 h. After completion as detected by TLC, the reaction was quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to afford product **7a**.



To a solution of **4a** (0.1 mmol), Isoxepac (0.12 mmol), and DMAP (5.0 mol%) in DCM (1.0 mL) at 0 °C was added DCC (0.24 mmol) in one portion. A precipitate began to form almost immediately. The reaction was stirred at 0 °C for 10 min and then warmed to room temperature. After completion as detected by TLC, the reaction was then diluted with pentane (5.0 mL) and filtered through a short plug of silica. The aqueous layer was extracted with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to afford product **7b**.

5. Mechanism Studies

5.1 Radical Inhibiting Experiments



A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with **1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), **S1** (10 mol%) and TEMPO (0.4 mmol, 2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in NMP (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h.

After that, it was found that a trace amount of **2a** was observed, along with the TEMPO adduct **8a** was detected by LC-HRMS (HRMS (ESI) calcd for $C_{25}H_{32}FNO_3Na$ $[M+Na]^+$ 436.2258, found 436.2274). This result indicates that a radical intermediate might be involved in this transformation. The results are shown in Figure S1.

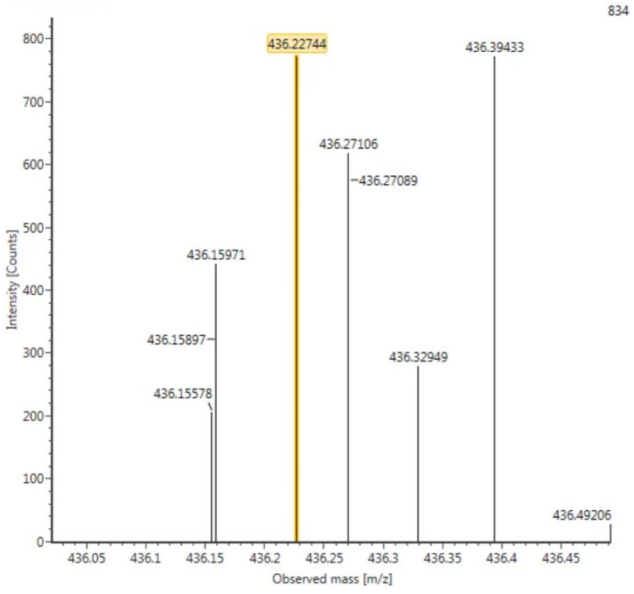
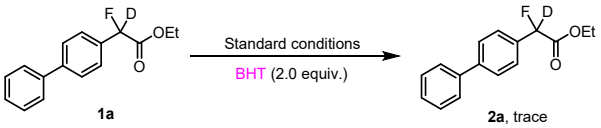


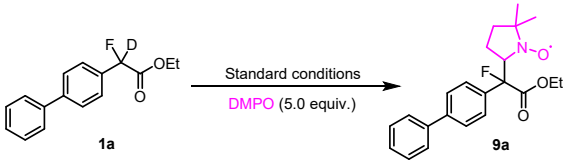
Figure S1. LC-HRMS Spectra of **7a**



1a **2a**, trace

Similarly, when 2.0 equiv. of BHT was subjected into the reaction of **1a** with D_2O under the standard conditions, only a trace amount of **2a** was observed. This result also indicates that a radical pathway might be involved in this transformation.

5.2 EPR Experiment



A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 2-(4-Biphenylyl)-2,2-difluoroacetate **1a** (0.2 mmol), $Ir(ppy)_3$ (1.0 mol%), Cs_2CO_3 (2.0 equiv.), S1 (10 mol%) and DMPO (5.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of D_2O (40 equiv.) in NMP (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h.

When 5.0 equiv. of DMPO was subjected into the reaction of **1a** with D_2O under the standard conditions. It was found that only a trace amount of **2a** was observed, along with the DMPO adduct **9a** was detected by EPR and LC-HRMS (HRMS (ESI) calcd for $C_{25}H_{32}FNO_3Na$ $[M]^+$ 370.1813, found 370.1816). This result indicates that a radical intermediate might be involved in this transformation. The results are shown in Figure S2 and Figure S3.

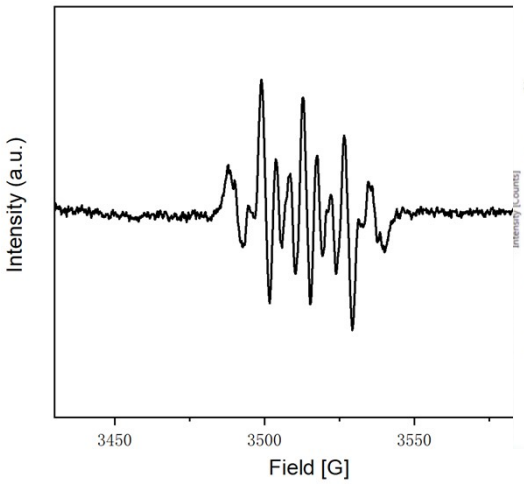


Figure S2. EPR Spectra of **8a**

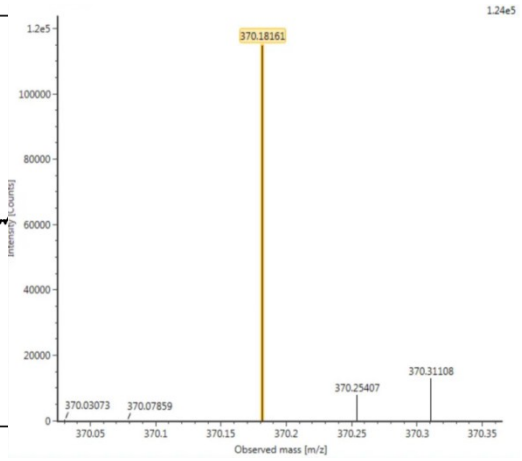
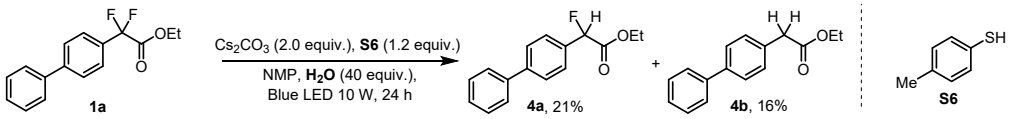


Figure S3. LC-HRMS Spectra of **8a**

5.3 Transformation of 1a to 4a/5a without $Ir(ppy)_3$



A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with **1a** (0.2 mmol), Cs_2CO_3 (2.0 equiv.), **S6** (1.2 equiv.). Then the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of H_2O (40 equiv.) in NMP (2.0 mL) was added by a syringe. The reaction mixture was stirred under the irradiation of a 10 W Blue LED (λ = 460−470 nm; distance app. 1.0 cm from the bulb) for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/acetone: 30:1) furnishes the desired products **4a** and **4b**.

5.4 Stern-Volmer Fluorescence Quenching Experiments

To a solution of $Ir(ppy)_3$ in anhydrous, N_2-saturated NMP (5×10^{-4} mol/L) in a quartz cuvette, different amounts of **S1** was added, and the resulting changes in fluorescence intensity (concentration of **S1**: 5×10^{-5} mol/L, 10×10^{-5} mol/L, 15×10^{-5} mol/L, 20×10^{-5} mol/L, 25×10^{-5} mol/L) were collected. The emission intensity at 536 nm was collected with excited wavelength of 460 nm. The results are shown in Figure S4.

a) b)

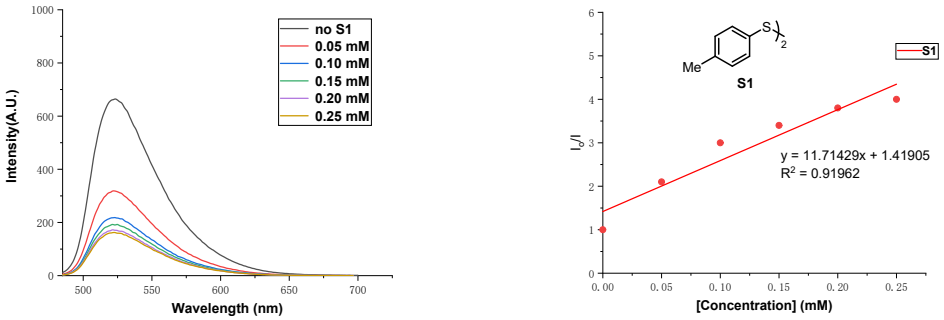


Figure S4. (a) The fluorescence emission spectra of $Ir(ppy)_3$ with different concentration of **1a** added. (b) The Stern–Volmer emission quenching studies of **1a**. I_0 is the inherent fluorescence intensity of $Ir(ppy)_3$. I is the fluorescence intensity of $Ir(ppy)_3$ in the presence of **1a**.

To a solution of **S6** anion (freshly prepared in situ by the deprotonation of **S6** with NaOH) in anhydrous, N_2-saturated NMP (5×10^{-4} mol/L) in a quartz cuvette, different amounts of **1a** was added, and the resulting changes in fluorescence intensity (concentration of **1a** anion: 5×10^{-5} mol/L, 10×10^{-5} mol/L, 15×10^{-5} mol/L, 20×10^{-5} mol/L, 25×10^{-5} mol/L) were collected. The emission intensity at 536 nm was collected with excited wavelength of 460 nm. The results are shown in Figure S5.

a) b)

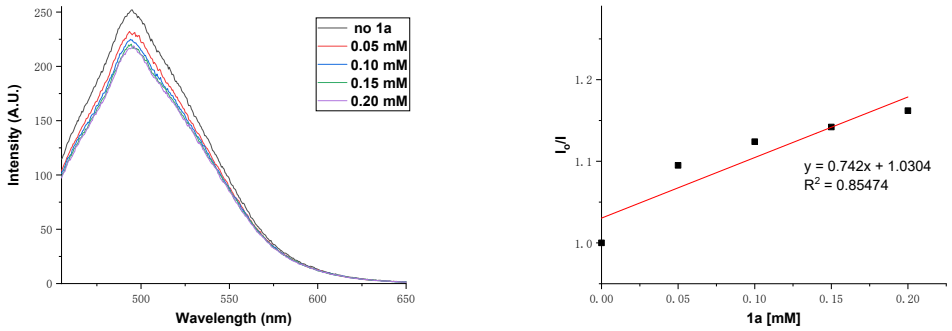


Figure S5. (a) The fluorescence emission spectra of **S6** anion with different concentration of **1a** added. (b) The Stern–Volmer emission quenching studies of **1a**. I_0 is the inherent fluorescence intensity of **S6** anion. I is the fluorescence intensity of **S6** anion in the presence of **1a**.

5.5 Light On-Off Experiments

To further examine the impact of light, we conducted the reaction of **1a** with D_2O under alternating periods of irradiation and darkness. The results are shown in Figure S6.

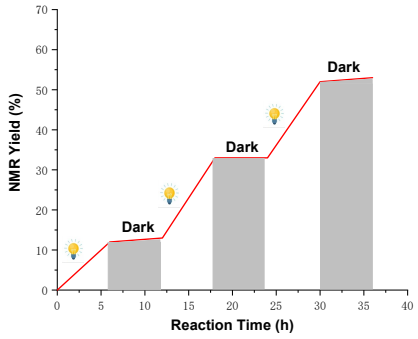


Figure S6. Yield of **2a** with or without light irridiation

The results of light on-off experiments indicated that the reaction proceeded only

under the irradiation of light. Suggesting the reaction that proceeded via a catalytic process rather than a radical chain process.

5.6 Cyclic Voltammetry and UV/vis Absorption Experiments

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line at room temperature. A cyclic voltammograms in **1a** or **2a** by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The scan rate was 50 mV/s, ranging from 0 V to -4.0 V *n*Bu4NBF4 (0.1 M) was used as the electrolyte, MeCN or DMF as the solvent.

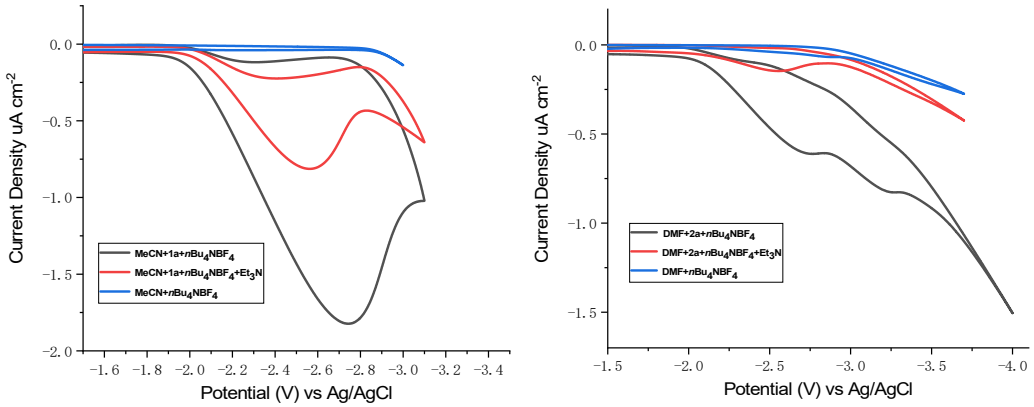


Figure S7 Cyclic Voltammetry Experiments

The results of Cyclic voltammetry experiments indicated that the role of Et_3N in the reaction, adding Et_3N change the reduction potential of **1a** from $E_{red\ p/2}$ = -2.28 V vs. SCE to $E_{red\ p/2}$ = -2.22 V vs. SCE. Furthermore, Changing the reduction potential of **2a** from $E_{red\ p/2}$ = -2.21 V vs. SCE to $E_{red\ p/2}$ = -2.17 V vs. SCE. The addition of Et_3N to the reaction substantially changed the CV profile of the **1a** or **2a** and made them easier to be reduced. The results are shown in Figure S7.

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line at room temperature. A cyclic voltammograms in **S6** anion (generated in situ by the deprotonation of the **S6** with 1.2 equiv. NaOH) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The scan rate was 50 mV/s, ranging from 0 V to -4.0 V nBu$_4$NPF$_6$ (0.1M) was used as the electrolyte, dry MeCN as the solvent. The results are shown in Figure S8 and Figure S9.

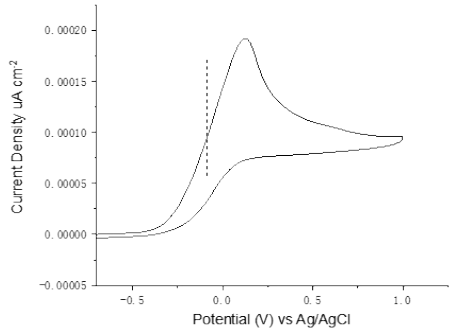


Figure S8. Cyclic Voltammetry Experiments

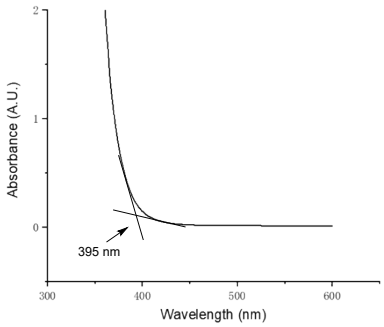
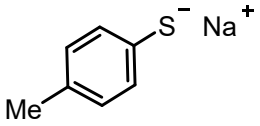


Figure S9. UV/vis absorption spectra of **S6** anion



$E_{p/2}$(**S6**$^{\bullet}$/**S6**$^{-}$) = -0.16 V vs. SCE

The results of Cyclic voltammetry experiments indicated that $E_{p/2}$(**S6**$^{\bullet}$/**S6**$^{-}$) = -0.16 V vs SCE. With this data in hand, we calculated the redox potential of the excited **S6** anion employing the following equation: [4]

$$E_{p/2}(\mathbf{S6}^{\bullet}/\mathbf{S6}^{*-}) = E_{p/2}(\mathbf{S6}^{\bullet}/\mathbf{S6}^{-}) - E_{0\text{-}0}(\mathbf{S6}^{*-}/\mathbf{S6}^{-})$$

$E_{p/2}$(**S6**$^{\bullet}$/**S6**$^{-}$) = -0.16 V vs SCE, In the absence of vibrational structures, $E_{0\text{-}0}$ can be roughly estimated from the absorption.[5] This corresponds to 395 nm, which translates into an $E_{0\text{-}0}$(**S6**$^{*-}$/**S6**$^{-}$) of 3.17 eV for the **S6** anion.

$E_{p/2}$(**S6**$^{\bullet}$/**S6**$^{*-}$) = $E_{p/2}$(**S6**$^{\bullet}$/**S6**$^{-}$) – $E_{0\text{-}0}$(**S6**$^{*-}$/**S6**$^{-}$) = -0.16 – 3.17 = -3.33 V vs SCE.

5.7 Proportions of 2a and 3a under Conditions A and B

In order to further investigate the proportion and conversion of products **2a** and **3a** under different conditions, we obtained the yields of products **1a** and **2a** at different reaction times. The results are shown in Figure S10.

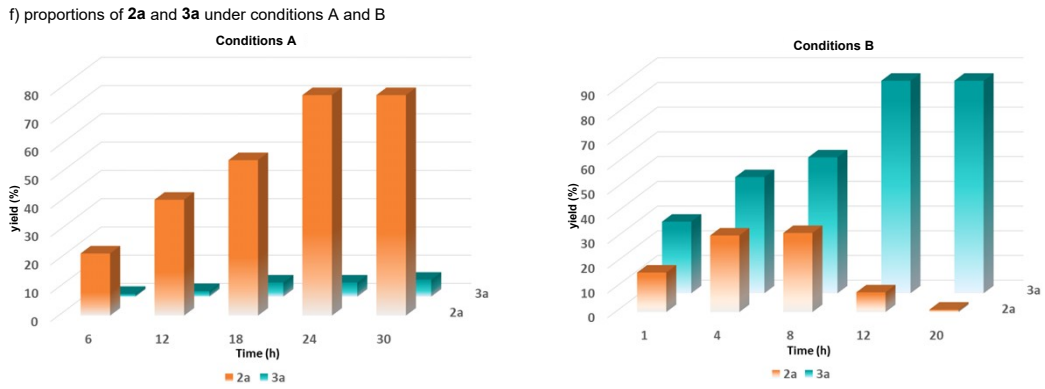


Figure S10. Proportions of **2a** and **3a** under Conditions A and B

The competitive formations of **2a** and **3a** were detected under reaction conditions A and B, respectively (Figure S4). Under condition A, the yield of **2a** gradually increased with time, while the yield of **3a** remained below than 10% all the time. Under condition B, the yield of **3a** gradually increased with time. Here, the yield of **2a** can reach up to 31% and then it is converted to **3a** with time.

5.8 Proposed mechanism (dideuterodefluorination)

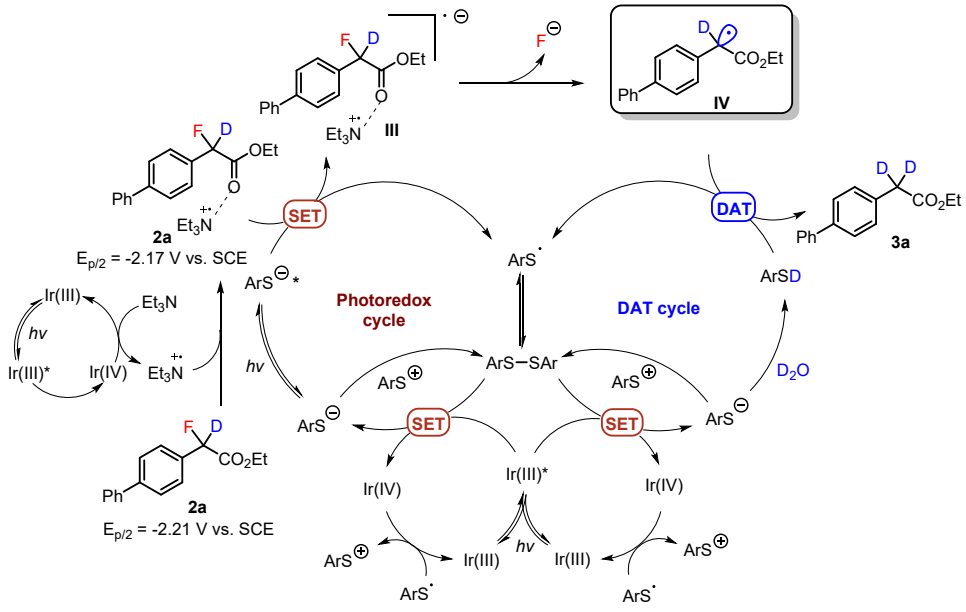
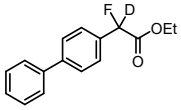


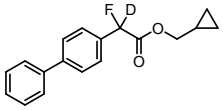
Figure S11. Proposed mechanism (dideuterodefluorination)

6 Characterization of Products



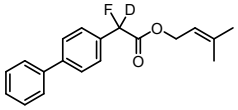
Propyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2a)

Colorless oil (78%, 40.4 mg, 97% D); R_f = 0.5 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 6H), 7.38 – 7.34 (m, 2H), 7.30 – 7.27 (m, 1H), 4.26 – 4.11 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.6 Hz), 142.7 (d, *J* = 2.2 Hz), 140.4, 133.2 (d, *J* = 20.5 Hz), 129.0, 127.9, 127.6, 127.3, 127.2, 89.0 (dt, *J* = 183.1, 23.3 Hz), 62.0, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.36 – -180.04 (m); HRMS (ESI) calcd for $C_{16}H_{14}FDO_2K$ $[M+K]^+$ 298.0750, found 298.0763.



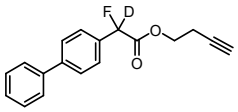
Cyclopropylmethyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2b)

Colorless oil (72%, 41.1 mg, 96% D); R_f = 0.5 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 6H), 7.47 – 7.44 (m, 2H), 7.39 – 7.36 (m, 1H), 4.12 – 3.99 (m, 2H), 1.18 – 1.12 (m, 1H), 0.59 – 0.54 (m, 2H), 0.30 – 0.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (d, *J* = 27.4 Hz), 142.7 (d, *J* = 2.2 Hz), 140.4, 133.3 (d, *J* = 20.6 Hz), 129.0, 127.9, 127.6, 127.4, 127.3, 89.0 (dt, *J* = 183.8, 23.9 Hz), 70.8, 9.8, 3.51, 3.46; ^{19}F NMR (376 MHz, $CDCl_3$) δ -177.47 – -181.66 (m); HRMS (ESI) calcd for $C_{18}H_{20}FDNO_2$ $[M+NH_4]^+$ 303.1614, found 303.1608.



3-Methylbut-2-en-1-yl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2c)

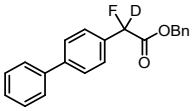
Colorless oil (63%, 37.7 mg, 96% D); R_f = 0.5 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 6H), 7.46 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 5.34 – 5.30 (m, 1H), 4.76 – 4.59 (m, 2H), 1.73 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.5 Hz), 142.7 (d, *J* = 2.2 Hz), 140.6, 140.5, 133.3 (d, *J* = 20.4 Hz), 129.0, 127.9, 127.6, 127.4, 127.3, 117.8, 89.0 (dt, *J* = 183.8, 22.8 Hz), 62.8, 25.9, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.01 – -179.68 (m); HRMS (ESI) calcd for $C_{19}H_{18}FDO_2Na$ $[M+Na]^+$ 322.1324, found 322.1334.



But-3-yn-1-yl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2d)

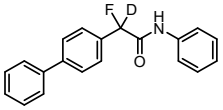
Colorless oil (65%, 36.8 mg, 97% D); R_f = 0.5 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 6H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.28 (m, 1H), 4.39 – 4.07 (m, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 1.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 (d, *J* = 28.0 Hz), 142.8 (d, *J* = 2.2 Hz), 140.4, 132.9 (d, *J* = 20.5 Hz), 129.0, 127.9, 127.7, 127.4, 127.3, 89.2 (dt, *J* = 183.2, 18.2 Hz), 79.4, 70.4, 63.4, 19.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ -179.76 – -180.43 (m); HRMS (ESI) calcd for $C_{18}H_{14}FDO_2K$ $[M+K]^+$ 322.0750, found 322.0737.



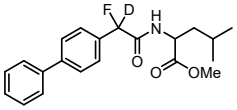
Benzyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2e)

Colorless oil (58%, 37.2 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 6H), 7.49 – 7.45 (m, 2H), 7.41 – 7.31 (m, 6H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.29 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.51 (d, *J* = 27.9 Hz), 142.76 (d, *J* = 2.1 Hz), 140.4, 135.0, 133.0 (d, *J* = 20.5 Hz), 129.0, 128.73, 128.66, 128.3, 127.9, 127.6, 127.4, 127.3, 89.0 (dt, *J* = 184.0, 24.2 Hz), 67.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.39 – -180.06 (m); HRMS (ESI) calcd for $C_{21}H_{16}FO_2D$ $[M]^+$ 321.1270, found 321.1279.



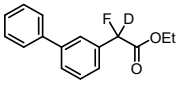
2-([1,1'-Biphenyl]-4-yl)-2-fluoro-N-phenylacetamide-2-d (2f)

White solid (43%, 26.3 mg, 97% D); m.p.: 151-152 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.66 – 7.58 (m, 8H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 3H), 7.20 – 7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (d, *J* = 20.7 Hz), 142.8 (d, *J* = 2.4 Hz), 140.5, 136.8, 133.4 (d, *J* = 19.1 Hz), 129.3, 129.0, 127.8, 127.7, 127.33, 127.28, 125.3, 120.2, 91.5 (dt, *J* = 188.2, 23.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.65 – -178.33 (m); HRMS (ESI) calcd for $C_{20}H_{15}FDNONa$ $[M+Na]^+$ 329.1171, found 329.1170.



Methyl (2-([1,1'-biphenyl]-4-yl)-2-fluoroacetyl)leucinate (2g)

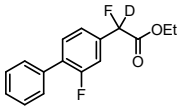
White solid (51%, 36.5 mg, 92% D); m.p.: 65-66 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 5H), 7.52 – 7.43 (m, 3H), 7.39 – 7.35 (m, 1H), 4.74 – 4.68 (m, 1H), 3.78 (s, 1.5H), 3.74 (s, 1.5H), 1.75 – 1.62 (m), 1.00 (d, *J* = 2.8 Hz, 1.5H), 0.99 (d, *J* = 2.8 Hz, 1.5H), 0.94 (d, *J* = 6.0 Hz, 1.5H), 0.92 (d, *J* = 6.1 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.96, 172.94, 168.52 (d, *J* = 22.2 Hz), 168.46 (d, *J* = 22.3 Hz), 142.65 (d, *J* = 12.2 Hz), 142.63 (d, *J* = 11.9 Hz), 140.53, 140.48, 133.60 (d, *J* = 19.1 Hz), 133.50 (d, *J* = 19.1 Hz), 128.95 (s), 127.76 (s), 127.70 (s), 127.63 (s), 127.30 (s), 127.19 (s), 91.41 (dt, *J* = 191.5, 21.6 Hz), 52.62 (s), 52.58 (s), 41.64 (s), 41.55 (s), 25.02 (s), 22.97 (s), 22.86 (s), 22.04 (s), 21.92 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -175.32 – -176.00 (m), -177.71 – -178.39 (m); HRMS (ESI) calcd for $C_{21}H_{23}FDNO_3Na$ $[M+Na]^+$ 381.1695, found 381.1698.



Ethyl 2-([1,1'-biphenyl]-3-yl)-2-fluoroacetate-d (2h)

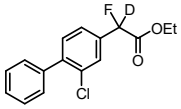
Colorless oil (70%, 36.3 mg, 99% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.65 – 7.59 (m, 3H), 7.51 – 7.44 (m, 4H), 7.40 – 7.35 (m,

1H), 4.35 – 4.19 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (d, *J* = 27.5 Hz), 142.0, 140.4, 134.8 (d, *J* = 20.8 Hz), 129.3, 129.0, 128.5 (d, *J* = 1.4 Hz), 127.8, 127.3, 125.5 (t, *J* = 5.7 Hz), 88.9 (dt, *J* = 184.6, 22.7 Hz), 62.0, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.92 – -180.60 (m); HRMS (ESI) calcd for $C_{16}H_{14}FDO_2K$ $[M+K]^+$ 298.0750, found 298.0746.



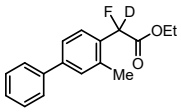
Ethyl 2-fluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)acetate-d (2i)

Colorless oil (49%, 27.2 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.51 – 7.44 (m, 3H), 7.41 – 7.37 (m, 1H), 7.34 – 7.28 (m, 2H), 4.36 – 4.22 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (d, *J* = 26.9 Hz), 161.0, 158.5, 135.3 (dd, *J* = 21.0, 7.8 Hz), 135.1, 131.3 (d, *J* = 3.8 Hz), 130.5 (dd, *J* = 13.4, 1.8 Hz), 129.1 (d, *J* = 2.8 Hz), 128.7, 128.2, 122.5 (dd, *J* = 6.1, 3.5 Hz), 114.5 (dd, *J* = 24.7, 6.7 Hz), 88.4 (dt, *J* = 184.7, 25.0 Hz), 62.3, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.23 – -117.06 (t, *J* = 9.8 Hz), -181.41 – -182.30 (m); HRMS (ESI) calcd for $C_{16}H_{13}F_2DO_2Na$ $[M+Na]^+$ 300.0917, found 300.0923.



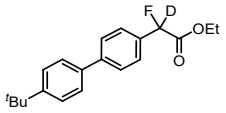
Ethyl 2-(2-chloro-[1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2j)

Colorless oil (58%, 34.0 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.44 – 7.38 (m, 7H), 4.37 – 4.22 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1 (d, *J* = 27.0 Hz), 141.9 (d, *J* = 1.9 Hz), 138.7, 134.8 (d, *J* = 21.0 Hz), 133.1, 131.8, 129.5, 128.3, 128.2 (d, *J* = 6.7 Hz), 128.1, 125.0 (d, *J* = 6.1 Hz), 88.2 (dt, *J* = 185.4, 23.0 Hz), 62.4, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -181.52 – -182.17 (m); HRMS (ESI) calcd for $C_{16}H_{17}FClDO_2N$ $[M+NH_4]^+$ 311.1067, found 311.1077.



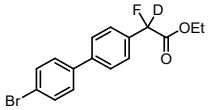
Ethyl 2-fluoro-2-(2-methyl-[1,1'-biphenyl]-4-yl)acetate-d (2k)

Colorless oil (51%, 27.9 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.42 (m, 5H), 7.37 (d, *J* = 7.2 Hz, 1H), 4.37 – 4.18 (m, 2H), 2.51 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 (d, *J* = 28.0 Hz), 142.6 (d, *J* = 2.7 Hz), 140.5, 137.1 (d, *J* = 3.7 Hz), 131.8 (d, *J* = 19.2 Hz), 129.8, 128.9, 128.0 (d, *J* = 6.5 Hz), 127.8, 127.3, 88.8 (dt, *J* = 185.2, 25.3 Hz), 62.0, 19.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.64 – -179.93 (m); HRMS (ESI) calcd for $C_{17}H_{16}FDO_2K$ $[M+K]^+$ 312.0906, found 312.0907.



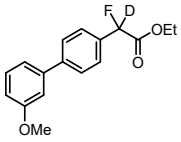
Ethyl 2-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2l)

Colorless oil (68%, 42.9 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.52 (m, 4H), 7.48 (d, *J* = 7.2 Hz, 2H), 4.35 – 4.20 (m, 2H), 1.37 (s, 9H), 1.29 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.6 Hz), 151.0, 142.6, 137.5, 132.9 (d, *J* = 20.2 Hz), 127.5, 127.3 (d, *J* = 5.8 Hz), 126.9, 126.0, 87.2 (dt, *J* = 184.6, 22.5 Hz), 62.0, 34.7, 31.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.02 – -179.70 (m); HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}FDO_2$ 316.1818; Found: 316.1820. HRMS (ESI) calcd for $C_{20}H_{23}FDO_2$ $[M+H]^+$ 316.1818, found 316.1820.



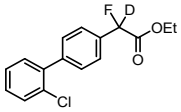
Ethyl 2-(4'-bromo-[1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2m)

Colorless oil (52%, 35.1 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 6H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.35 – 4.2 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (d, *J* = 27.3 Hz), 141.4 (d, *J* = 2.0 Hz), 139.3, 133.7 (d, *J* = 20.3 Hz), 132.1, 128.9, 127.42, 127.37, 127.3, 122.2, 88.9 (dt, *J* = 182.6, 24.0 Hz), 62.1, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.95 – -180.62 (m); HRMS (ESI) calcd for $C_{16}H_{13}BrFDO_2K$ $[M+K]^+$ 375.9856, found 375.9854.



Ethyl 2-fluoro-2-(3'-methoxy-[1,1'-biphenyl]-4-yl)acetate-d (2n)

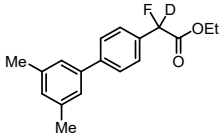
Colorless oil (77%, 44.5 mg, 97% D); R_f = 0.5 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 6.92 (dd, *J* = 8.0 Hz, 1H), 4.33 – 4.22 (m, 2H), 3.87 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.3 Hz), 160.1, 142.6, 141.9, 133.4 (d, *J* = 20.3 Hz), 130.0, 127.7, 127.2 (d, *J* = 5.8 Hz), 119.8, 113.2 (d, *J* = 14.2 Hz), 89.0 (dt, *J* = 185.4, 23.0 Hz), 62.1, 55.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.50 – -180.17 (m); HRMS (ESI) calcd for $C_{17}H_{16}FDO_3K$ $[M+K]^+$ 328.0856, found 328.0848.



Ethyl 2-(2'-chloro-[1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2o)

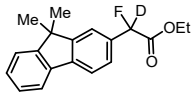
Colorless oil (51%, 29.9 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 5H), 7.33 – 7.29 (m, 3H), 4.36 – 4.21 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.62 (d, *J* = 27.4 Hz), 140.8 (d, *J* = 2.2 Hz), 139.8, 133.6 (d, *J* = 20.6 Hz), 132.6, 131.4, 130.2, 130.0, 129.0, 127.1, 126.5

(d, J = 6.z Hz), 88.9 (dt, J = 184.8, 22.5 Hz), 62.1, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.18 – -180.84 (m); HRMS (ESI) calcd for $C_{16}H_{17}ClFDO_2$ $[M+NH_4]^+$ 311.1067, found 311.1059.



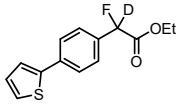
Ethyl 2-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2p)

Colorless oil (67%, 38.5 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.20 (s, 2H), 7.02 (s, 1H), 4.35 – 4.2 (m, 2H), 2.39 (s, 6H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, J = 27.7 Hz), 143.0 (d, J = 4.4 Hz), 140.5, 138.5, 133.0 (d, J = 20.6 Hz), 129.5, 127.7, 127.2 (d, J = 5.9 Hz), 125.2, 89.4 (dt, J = 184.3, 24.1 Hz), 62.0, 21.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.15 – -179.83 (m); HRMS (ESI) calcd for $C_{18}H_{18}FDO_2Na$ $[M+Na]^+$ 310.1324, found 310.1313.



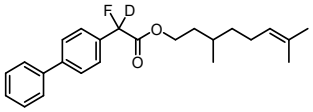
Ethyl 2-(9,9-dimethyl-9H-fluoren-2-yl)-2-fluoroacetate-d (2q)

Colorless oil (58%, 34.7 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 6.4 Hz, 2H), 7.55 (s, 1H), 7.45 – 7.44 (m, 2H), 7.37 – 7.35 (m, 2H), 4.35 – 4.21 (m, 2H), 1.50 (s, 6H), 1.28 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (d, J = 27.9 Hz), 154.2 (d, J = 23.7 Hz), 140.9 (d, J = 2.2 Hz), 138.4, 133.1 (d, J = 20.2 Hz), 128.0, 127.2, 126.0 (d, J = 5.9 Hz), 122.8, 121.2 (d, J = 5.8 Hz), 120.4 (d, J = 15.3 Hz), 89.5 (dt, J = 182.6, 24.0 Hz), 61.9, 47.1, 27.2, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -177.13 – -177.80 (m); HRMS (ESI) calcd for $C_{19}H_{18}FDO_2Na$ $[M+Na]^+$ 322.1324, found 322.1317.



Ethyl 2-fluoro-2-(4-(thiophen-2-yl)phenyl)acetate-d (2r)

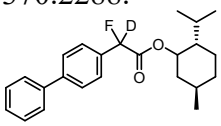
Colorless oil (56%, 29.7 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.10 – 7.09 (m, 1H), 4.33 – 4.19 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (d, J = 27.6 Hz), 143.5, 135.8 (d, J = 2.3 Hz), 133.3 (d, J = 20.3 Hz), 128.3, 127.4 (d, J = 5.9 Hz), 126.3, 125.6, 123.9, 88.9 (dt, J = 184.2, 4.6 Hz), 62.1, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.74 – -180.42 (m); HRMS (ESI) calcd for $C_{14}H_{13}FDO_2S$ $[M+H]^+$ 266.0756, found 266.0749.



3,7-Dimethyloct-6-en-1-yl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2s)

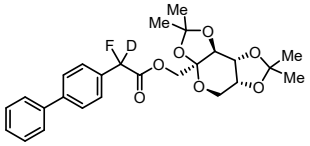
Colorless oil (49%, 36.2 mg, 96% D, dr = 1:1); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 6H), 7.45 (t, J = 7.2 Hz, 2H), 7.39 – 7.36

(m, 1H), 5.05 (t, *J* = 7.2 Hz, 1H), 4.26 – 4.23 (m, 2H), 1.95 – 1.89 (m, 2H), 1.69 – 1.65 (m, 4H), 1.59 – 1.57 (m, 3H), 1.46 – 1.42 (m, 2H), 1.29 – 1.28 (m, 1H), 1.16 – 1.14 (m, 1H), 0.87 (t, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (d, *J* = 27.5 Hz), 142.7 (d, *J* = 1.9 Hz), 140.4, 133.3 (d, *J* = 20.6 Hz), 131.6, 129.0, 127.9, 127.6, 127.27, 127.26 (d, *J* = 1.4 Hz), 127.2, 124.6, 89.0 (dt, *J* = 184.8, 16.7 Hz), 64.5, 37.0, 35.4, 29.5, 29.5, 25.8, 25.5, 19.5, 19.4, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.62 – -180.42 (m); HRMS (ESI) calcd for $C_{24}H_{29}FDO_2$ $[M+H]^+$ 370.2287, found 370.2288.



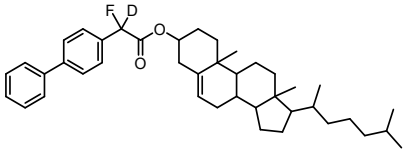
2-Isopropyl-5-methylcyclohexyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2t)

Colorless oil (61%, 45.0 mg, 99% D, dr = 1:1); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 6H), 7.48 – 7.45 (m, 2H), 7.40 – 7.36 (m, 1H), 4.86 – 4.74 (m, 1H), 2.07 – 1.88 (m, 1H), 1.692 – 1.61 (m, 2H), 1.48 – 1.28 (m, 3H), 1.11 – 0.97 (m, 2H), 0.92 – 0.84 (m, 5.5H), 0.78 (d, *J* = 5.6 Hz, 1.5H), 0.69 (d, *J* = 5.6 Hz, 1.5H), 0.53 (d, *J* = 5.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45 (d, *J* = 8.6 Hz), 168.2 (d, *J* = 7.9 Hz), 142.7 (d, *J* = 2.1 Hz), 142.5 (d, *J* = 2.2 Hz), 140.5, 140.4, 129.0, 127.8, 127.53, 127.50, 127.4 (d, *J* = 5.5 Hz), 127.3, 127.2 (d, *J* = 6.0 Hz), 89.02 (dt, *J* = 183.3, 24.6 Hz), 88.99 (dt, *J* = 182.8, 23.5 Hz), 76.2, 47.1, 47.0, 40.8, 40.4, 34.22, 34.19, 31.52, 31.47, 26.3, 25.8, 23.5, 23.3, 22.1, 22.0, 20.8, 20.7, 16.3, 16.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.34 – -179.81 (m); HRMS (ESI) calcd for $C_{24}H_{29}FDO$ $[M+H]^+$ 370.2287, found 370.2289.



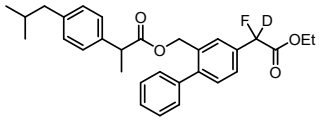
((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2u)

Colorless oil (52%, 49.2 mg, 96% D, dr = 1:1); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 6H), 7.47 – 7.44 (m, *J* = 7.2 Hz, 2H), 7.40 – 7.36 (m, 1H), 4.63 – 4.6 (m, 1H), 4.52 – 4.48 (m, 1H), 4.33 – 4.14 (m, 3H), 3.92 – 3.52 (m, 3H), 1.52 (s, 3H), 1.49 – 1.47 (m, 3H), 1.34 – 1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (d, *J* = 4.5 Hz), 142.9, 140.4, 132.8 (d, *J* = 20.0 Hz), 129.0, 127.9, 127.74, 127.72, 127.67, 127.6 (d, *J* = 5.6 Hz), 127.3, 109.4, 109.3, 109.19, 109.15, 101.3, 101.2, 89.7 (dt, *J* = 183.4, 23.3Hz), 70.90, 70.87, 70.4, 70.11, 70.10, 66.0, 65.9, 61.5, 42.7, 34.1, 26.6, 26.0, 25.2, 25.0, 24.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -177.76 – -178.70 (m); HRMS (ESI) calcd for $C_{26}H_{29}FDO_7$ $[M+H]^+$ 474.203, found 474.2045.



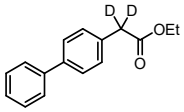
10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (2v)

White solid (50%, 59.9 mg, 99% D, dr = 1:1); m.p.: 95-96 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 6H), 7.47 – 7.44 (m, 2H), 7.39 – 7.35 (m, 1H), 5.39 (s, 0.5H), 5.35 (s, 0.5H), 4.77 – 4.75 (m, 1H), 2.40 – 2.27 (m, 2H), 2.03 – 1.79 (m, 6H), 1.59 – 1.47 (m, 8H), 1.35 – 1.25 (m, 5H), 1.12 – 1.06 (m, 6H), 1.02 – 0.98 (s, 5H), 0.93 – 0.86 (m, 8H), 0.70 – 0.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1 (d, *J* = 27.2 Hz), 142.6 (d, *J* = 2.1 Hz), 140.4, 139.2 (d, *J* = 5.7 Hz), 133.4 (d, *J* = 20.3 Hz), 129.0, 127.8, 127.6, 127.3, 127.2, 123.3 (d, *J* = 5.0 Hz), 87.2 (dt, *J* = 183.4, 21.8 Hz) 75.9, 56.8, 56.2, 50.1, 42.4, 39.8, 39.7, 38.0, 37.8, 37.0, 36.9, 36.7, 36.3, 35.9, 32.01, 31.95, 28.4, 28.2, 27.8, 27.6, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.95 – -179.61 (m); HRMS (ESI) calcd for $C_{41}H_{54}FDO_2K$ $[M+K]^+$ 638.3880, found 638.3862.



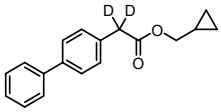
(4-(2-Ethoxy-1-fluoro-2-oxoethyl-1-d)-[1,1'-biphenyl]-2-yl)methyl-2-(4-isobutylphenyl)propanoate (2w)

Colorless oil (52%, 49.6 mg, 99% D, dr = 1:1); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.2 Hz, 2H), 7.33 – 7.32 (m, 4H), 7.21 – 7.19 (m, 4H), 7.12 (d, *J* = 6.8 Hz, 2H), 5.04 (d, *J* = 12.4 Hz, 1H), 4.98 (d, *J* = 12.4 Hz, 1H),4.35 – 4.24 (m, 2H), 3.73 (q, *J* = 7.6 Hz, 1H), 2.47 (d, *J* = 5.6 Hz, 2H), 1.89 – 1.83 (m, 1H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.31 (t, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 174.3, 168.5 (d, *J* = 27.2 Hz), 143.6 (d, *J* = 5.6 Hz), 143.58 (d, *J* = 5.6 Hz), 140.8, 139.6, 137.6, 134.1, 133.7, 133.5, 130.7, 129.5, 129.1, 128.4, 127.7, 127.4, 126.4 (d, *J* = 5.6 Hz), 126.2 (d, *J* = 5.7 Hz), 88.8 (dt, *J* = 181.9, 23.2 Hz), 64.4, 62.1, 45.22, 45.16, 30.3, 22.5, 18.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.44 – -180.55 (m); HRMS (ESI) calcd for $C_{30}H_{32}FDO_4K$ $[M+K]^+$ 516.2057, found 516.2062.



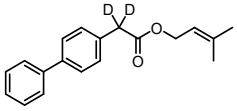
Ethyl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3a)

Colorless oil (86%, 41.6 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 4H), 7.49 – 7.46 (m, 2H), 7.42 – 7.36 (m, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 140.9, 140.1, 133.2, 129.7, 128.8, 127.4, 127.3, 127.1, 61.0, 41.9 – 40.2 (m), 14.3; HRMS (ESI) calcd for $C_{16}H_{18}D_2O_2N$ $[M+NH_4]^+$ 260.1614, found 260.1605.



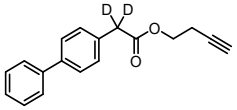
Cyclopropylmethyl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3b)

Colorless oil (80%, 42.9 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.47 – 7.34 (m, 5H), 3.98 (d, *J* = 7.2 Hz, 2H), 1.20 – 1.13 (m, 1H), 0.59 (d, *J* = 6.8 Hz, 2H), 0.31 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 140.9, 140.1, 133.3, 129.8, 128.9, 127.41, 127.36, 127.2, 69.8, 42.2 – 40.0 (m), 9.9, 3.4; HRMS (ESI) calcd for $C_{18}H_{16}D_2O_2K$ $[M+K]^+$ 307.1064, found 307.1054.



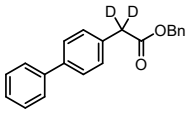
3-methylbut-2-en-1-yl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3c)

Colorless oil (73%, 41.2 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.46 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 5.36 (t, *J* = 6.8 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 2H), 1.77 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 141.0, 140.2, 139.4, 133.2, 129.8, 128.9, 127.44, 127.38, 127.2, 118.6, 62.0, 41.04 – 40.66 (m), 25.9, 18.2; HRMS (ESI) calcd for $C_{19}H_{18}D_2O_2K$ $[M+K]^+$ 321.1220, found 321.1216.



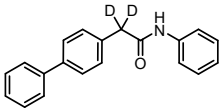
But-3-yn-1-yl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3d)

White solid (69%, 36.7 mg, 98% D); m.p.: 64-65 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 4H), 7.46 – 7.43 (m, 2H), 7.39 – 7.34 (m, 3H), 4.24 (t, *J* = 6.2 Hz, 2H), 2.55 (t, *J* = 6.0 Hz, 2H), 1.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.9, 140.3, 132.9, 129.8, 128.9, 127.5, 127.4, 127.2, 62.7, 40.9 – 39.9 (m), 19.1; HRMS (ESI) calcd for $C_{18}H_{14}D_2O_2$ $[M]^+$ 266.1270, found 266.1261.



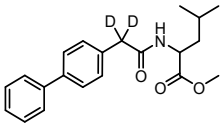
Benzyl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3e)

White solid (75%, 45.6 mg, 96% D); m.p.: 72-73 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 8H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.9, 140.3, 136.0, 133.0, 129.8, 128.9, 128.7, 128.4, 128.3, 127.5, 127.4, 127.2, 66.8, 41.2 – 40.1 (m); HRMS (ESI) calcd for $C_{21}H_{20}D_2O_2N$ $[M+NH_4]^+$ 322.1771, found 322.1789.



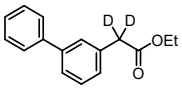
2-([1,1'-biphenyl]-4-yl)-*N*-phenylacetamide-2,2-d_2 (3f)

White solid (75%, 43.4 mg, 96% D); m.p.: 133-134 °C; R_f = 0.5 (PE/acetone = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.48 – 7.37 (m, 6H), 7.31 – 7.29 (m, 2H), 7.11 – 7.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 140.8, 140.6, 137.7, 133.4, 130.1, 129.1, 129.0, 128.1, 127.7, 127.2, 124.7, 120.0, 42.8 – 42.1 (m); HRMS (ESI) calcd for $C_{20}H_{15}D_2ON$ $[M]^+$ 289.1430, found 289.1425.



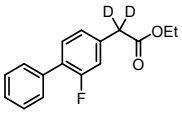
Methyl (2-([1,1'-biphenyl]-4-yl)acetyl)leucinate-d_2 (3g)

White solid (73%, 49.8 mg, 95% D); m.p.: 67-68 °C; R_f = 0.5 (petroleum ether/acetone = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 4H), 7.46 – 7.43 (m, 2H), 7.36 – 7.35 (m, 3H), 5.87 (d, *J* = 6.8 Hz, 1H), 4.67 – 4.63 (m, 1H), 3.71 (s, 3H), 1.63 – 1.47 (m, 3H), 0.91 – 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 170.8, 140.7, 140.4, 133.6, 129.9, 128.9, 127.8, 127.5, 127.2, 52.4, 50.9, 43.2 – 42.2 (m), 41.6, 25.0, 22.9, 22.1; HRMS (ESI) calcd for $C_{18}H_{18}F_2O_2N$ $[M+Na]^+$ 364.1852, found 364.1860.



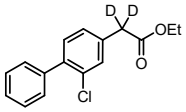
Ethyl 2-([1,1'-biphenyl]-3-yl)acetate-d_2 (3h)

Colorless oil (81%, 39.2 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.8 Hz, 2H), 7.56 – 7.32 (m, 2H), 7.48 – 7.36 (m, 4H), 7.32 – 7.31 (m, 1H), 4.20 (q, *J* = 6.8 Hz, 2H), 1.30 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 141.7, 141.1, 134.7, 129.2, 128.9, 128.3, 127.5, 127.4, 126.1, 61.1, 41.6 – 40.5 (m), 14.4; HRMS (ESI) calcd for $C_{16}H_{14}D_2O_2Na$ $[M+Na]^+$ 265.1168, found 265.1156.



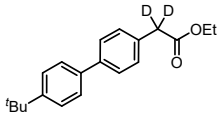
Ethyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)acetate-d_2 (3i)

Colorless oil (71%, 36.9 mg, 96% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.15 – 7.12 (m, 2H), 4.20 (q, *J* = 6.8 Hz, 2H), 1.30 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 160.9, 158.5, 135.6, 135.4 (d, *J* = 8.1 Hz), 130.9 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 2.8 Hz), 128.5, 127.9 (d, *J* = 13.4 Hz), 127.8, 125.4 (d, *J* = 2.9 Hz), 117.1 (d, *J* = 23.6 Hz), 61.2, 40.8 – 4.1 (m), 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.93 (t, *J* = 9.8 Hz). HRMS (ESI) calcd for $C_{16}H_{14}FD_2O_2$ $[M+H]^+$ 261.1254, found 261.1255.



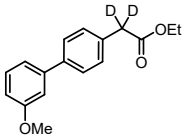
Ethyl 2-(2-chloro-[1,1'-biphenyl]-4-yl)acetate-d_2 (3j)

Colorless oil (65%, 35.9 mg, 96% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 6H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.4, 139.2, 134.8, 132.6, 131.6, 130.8, 129.6, 128.2, 127.9, 127.7, 61.3, 40.6 – 40.0 (m), 14.3; HRMS (ESI) calcd for $C_{16}H_{13}ClD_2O_2Na$ $[M+Na]^+$ 299.0778, found 299.0769.



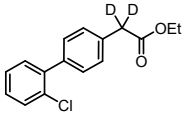
Ethyl 2-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)acetate-d_2 (3k)

Colorless oil (79%, 47.1 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 4H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 2H), 4.21 (q, *J* = 6.8 Hz, 2H), 1.40 (s, 9H), 1.31 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 150.4, 134.0, 138.0, 132.9, 129.7, 127.3, 126.8, 125.8, 61.0, 41.3 – 40.1 (m), 34.6, 31.5, 14.3; HRMS (ESI) calcd for $C_{20}H_{22}D_2O_2Li$ $[M+Li]^+$ 305.2056, found 305.2070.



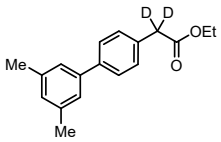
Ethyl 2-(3'-methoxy-[1,1'-biphenyl]-4-yl)acetate-d_2 (3l)

Colorless oil (83%, 45.2 mg, 96% D); R_f = 0.4 (PE/acetone = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.28 (d, *J* = 6.0 Hz, 3H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.03 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 1.19 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 160.1, 142.5, 140.0, 133.4, 129.9, 129.7, 127.5, 119.7, 112.9, 112.8, 61.0, 55.4, 41.1 – 40.1 (m), 14.3; HRMS (ESI) calcd for $C_{17}H_{16}D_2O_3$ $[M]^+$ 272.1376, found 272.1375.



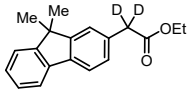
Ethyl 2-(2'-chloro-[1,1'-biphenyl]-4-yl)acetate-d_2 (3m)

Colorless oil (66%, 36.4 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.42 – 7.29 (m, 5H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 140.2, 138.2, 133.5, 132.5, 131.4, 130.0, 129.7, 129.0, 128.8, 128.6, 127.4, 127.1, 126.9, 61.0, 41.2 – 40.2 (m), 14.3; HRMS (ESI) calcd for $C_{16}H_{17}ClD_2O_2N$ $[M+NH_4]^+$ 294.1224, found 294.1234.



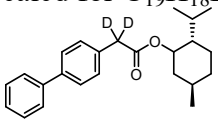
Ethyl 2-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)acetate-d_2 (3n)

Colorless oil (78%, 42.1 mg, 97% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.0 Hz, 2H), 7.40 (d, *J* = 6.4 Hz, 2H), 7.25 (s, 2H), 7.04 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 6H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 140.9, 140.3, 138.3, 133.0, 129.6, 129.0, 127.4, 125.1, 61.0, 41.1 – 40.1 (m), 21.5, 14.3; HRMS (ESI) calcd for $C_{18}H_{18}D_2O_2Li$ $[M+Li]^+$ 277.1743, found 277.1744.



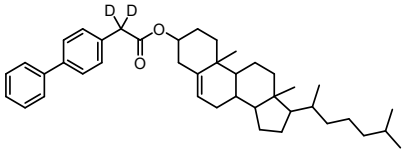
Ethyl 2-(9,9-dimethyl-9H-fluoren-2-yl)acetate-d_2 (3o)

Colorless oil (68%, 38.4 mg, 98% D); R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.47 (d, *J* = 6.4 Hz, 1H), 7.4 (m, 1H), 7.37 – 7.30 (m, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.53 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 154.1, 153.8, 139.0, 138.3, 133.2, 128.1, 127.3, 127.1, 123.7, 122.6, 120.1, 120.0, 60.9, 46.9, 41.4 – 40.8 (m), 27.2, 14.3; HRMS (ESI) calcd for $C_{19}H_{18}D_2O_2Li$ $[M+Li]^+$ 289.1743, found 289.1757.



2-Isopropyl-5-methylcyclohexyl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3p)

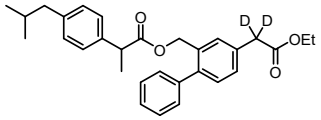
Colorless oil (66%, 46.5 mg, 97% D, dr = 1:1); R_f = 0.5 (PE/acetone = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 3H), 4.76 – 4.70 (m, 2H), 2.07 (s, 1H), 2.03 (d, *J* = 12.0 Hz, 1H), 1.94 – 1.87 (m, 1H), 1.81 – 1.77 (m, 1H), 1.69 (s, 1H), 1.51 (s, 1H), 1.40 (t, *J* = 10.8 Hz, 1H), 1.08 – 1.00 (m, 1H), 0.93 (d, *J* = 6.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 1H), 0.73 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.8, 141.0, 140.0, 133.5, 129.7, 128.9, 127.4, 127.2, 74.9, 47.2, 40.9, 41.1 – 40.8 (m), 34.4, 31.5, 26.3, 23.5, 22.2, 20.9, 16.4; HRMS (ESI) calcd for $C_{24}H_{28}D_2O_2Na$ $[M+Na]^+$ 375.2264, found 375.2257.



10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-([1,1'-biphenyl]-4-yl)acetate-d_2 (3q)

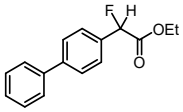
White solid (50%, 58.2 mg, 96% D); m.p.: 98-99 °C; R_f = 0.4 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.42 – 7.36 (m, 3H), 5.42 (s, 1H), 4.74 – 4.67 (m, 1H), 2.39 (d, *J* = 7.2 Hz, 2H), 2.08 – 1.90 (m,

6H), 1.71 – 1.49 (m, 8H), 1.40 – 1.30 (m, 5H), 1.18 – 1.14 (m, 6H), 1.09 – 1.04 (m, 5H), 0.98 – 0.92 (m, 8H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 140.9, 140.0, 139.7, 133.4, 129.7, 128.9, 127.4, 127.3, 127.2, 122.8, 74.6, 56.8, 56.2, 50.1, 42.4, 41.2 – 40.6 (m), 39.8, 39.6, 38.2, 37.1, 36.7, 36.3, 35.9, 32.01, 31.96, 28.4, 28.1, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0; HRMS (ESI) calcd for $C_{41}H_{54}D_2O_2$ $[M]^+$ 582.4400, found 582.4415.



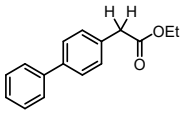
(4-(2-Ethoxy-2-oxoethyl-1,1-d2)-[1,1'-biphenyl]-2-yl)methyl-2-(4-isobutylphenyl)propanoate (3r)

Colorless oil (67%, 61.7 mg, 96% D); R_f = 0.3 (PE/acetone = 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 4H), 7.28 – 7.22 (m, 6H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.02 (q, *J* = 12.4 Hz, 2H), 4.22 (q, *J* = 6.0 Hz, 2H), 3.75 (q, *J* = 6.0 Hz, 1H), 2.50 (d, *J* = 6.4 Hz, 2H), 1.97 – 1.82 (m, 1H), 1.51 (d, *J* = 6.0 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 171.6, 141.2, 140.7, 140.1, 137.7, 133.5, 133.4, 130.5, 130.4, 129.5, 129.2, 129.1, 128.3, 127.4, 127.4, 64.7, 61.1, 45.2, 45.2, 41.1 – 40.2 (m), 30.3, 22.5, 18.5, 14.3; HRMS (ESI) calcd for $C_{30}H_{32}D_2O_4Na$ $[M+Na]^+$ 483.2475, found 483.2489.



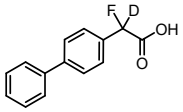
Ethyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate (4a)[1]

Colorless oil (79%, 40.8 mg); R_f = 0.5 (PE/acetone = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 6H), 7.48 – 7.37 (m, 2H), 7.40 – 7.33 (m, 1H), 5.84 (d, *J* = 47.6 Hz, 1H), 4.36 – 4.21 (m, 2H), 1.30 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.4 Hz), 142.7 (d, *J* = 2.2 Hz), 140.4, 133.3 (d, *J* = 20.5 Hz), 129.0, 127.8, 127.6, 127.3, 127.2, 90.3, 88.4, 62.0, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.38 (d, *J* = 47.8 Hz). Characterization data consistent with reported data[1].



Ethyl 2-([1,1'-biphenyl]-4-yl)acetate (4b)[3b]

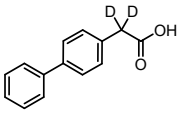
Colorless oil (82%, 39.4 mg); R_f = 0.5 (PE/acetone = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 3H), 4.19 (q, *J* = 6.8 Hz, 2H), 3.67 (s, 2H), 1.29 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 140.9, 140.1, 133.2, 129.7, 128.8, 127.4, 127.3, 127.1, 61.0, 41.1, 14.3. Characterization data consistent with reported data[3b].



2-([1,1'-biphenyl]-4-yl)-2-fluoroacetic-2-d acid (5a)

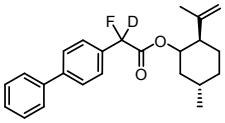
White solid (80%, 33.7 mg, 89% D); m.p.: 131-132 °C; R_f = 0.5 (PE/acetone = 4:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 – 7.67 (m, 4H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.50

– 7.46 (m, 1H), 7.41 – 7.37 (m, 1H); ^{19}F NMR (376 MHz, DMSO) δ -175.62 – -176.28 (m); ^{13}C NMR (100 MHz, DMSO) δ 169.8 (d, *J* = 27.0 Hz), 141.3 (d, *J* = 2.3 Hz), 139.5, 134.1 (d, *J* = 19.9 Hz), 129.0, 127.9, 127.6 (d, *J* = 5.4 Hz), 127.1, 126.8, 88.17 (dt, *J* = 177.1, 20.6 Hz); HRMS (ESI) calcd for $C_{14}H_{10}FDO_2K$ $[M+K]^+$ 270.0437, found 270.0425.



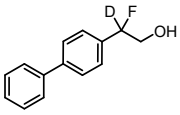
2-([1,1'-Biphenyl]-4-yl)acetic-2,2-d$_2$ acid (5b)

White solid (82%, 35.1 mg, 90% D); R_f = 0.5 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, DMSO) δ 12.31 (s, 1H), 7.58 – 7.52 (m, 4H), 7.39 – 7.36 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 173.1, 140.4, 139.0, 134.7, 130.4, 129.4, 127.8, 127.0. Characterization data consistent with reported data[3a].



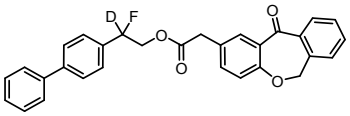
(2R,5S)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl-2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate-d (6)

Colorless oil (80%, 29.4 mg, 89% D); R_f = 0.5 (PE/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.52 – 7.44 (m, 4H), 7.39 – 7.36 (m, 1H), 4.94 – 4.85 (m, 1H), 4.74 (d, *J* = 7.2 Hz, 1H), 4.42 (d, *J* = 26.4 Hz, 1H), 2.18 – 2.02 (m, 1H), 1.93 – 1.91 (m, 1H), 1.75 – 1.68 (m, 1H), 1.65 (s, 3H), 1.58 – 1.57 (m, 1H), 1.40 (s, 3H), 1.37– 1.30 (m, 1H), 1.09 – 1.01 (m, 1H), 0.94– 1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (d, *J* = 27.4 Hz), 168.0 (d, *J* = 26.8 Hz), 145.7, 145.1, 142.40, 142.38, 140.5, 140.4, 133.4 (d, *J* = 20.2 Hz), 133.3 (d, *J* = 20.1 Hz), 128.9, 127.7, 127.7, 127.4, 127.3, 127.32, 127.25, 112.3, 112.1, 88.99 (dt, *J* = 154.8, 22.4 Hz), 88.98 (dt, *J* = 155.9, 21.7 Hz), 75.4, 75.3, 50.6, 50.5, 40.3, 39.9, 34.9, 34.0, 33.9, 31.39, 31.36, 30.5, 30.3, 25.5, 24.7, 22.0, 21.9, 19.4, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.48 – -179.93 (m); HRMS (ESI) calcd for $C_{24}H_{26}FDO_2K$ $[M+K]^+$ 406.1689, found 406.1698.



2-([1,1'-Biphenyl]-4-yl)-2-fluoroethan-2-d-1-ol (7a)

White solid (86%, 37.3 mg, 92% D); m.p.: 97-98 °C; R_f = 0.5 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.49 – 7.41 (m, 5H), 4.05 – 3.85 (m, 2H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.88 (d, *J* = 1.3 Hz), 140.6, 135.5, 135.3, 129.0, 127.7, 127.4, 127.2, 126.4, 126.3, 94.37 (dt, *J* = 170.0, 23.5 Hz), 66.47 (d, *J* = 24.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -186.17 – -187.00 (m); HRMS (ESI) calcd for $C_{14}H_{12}FDONa$ $[M+Na]^+$ 240.0905, found 240.0910.



2-([1,1'-Biphenyl]-4-yl)-2-fluoroethyl-2-d-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (7b)

Colorless oil (88%, 41.1 mg, 92% D); R_f = 0.5 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.54 (m, 5H), 7.49 – 7.35 (m, 8H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.17 (s, 2H), 4.51 – 4.37 (m, 2H), 3.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 171.3, 160.7, 142.1, 140.5 (d, *J* = 5.6 Hz), 136.5, 135.7, 134.7 (d, *J* = 19.8 Hz), 132.9, 132.7, 129.6, 129.4, 129.0, 127.9, 127.7, 127.5, 127.3, 126.4 126.4, 125.3, 121.3, 91.1 (dt, *J* = 175.9, 23.2 Hz), 73.7, 67.3, 67.0, 40.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -183.90 – -184.73 (m); HRMS (ESI) calcd for $C_{30}H_{22}FDO_4Li$ $[M+Li]^+$ 474.1798, found 474.1778.

7. References

1. S. Mizuta, I. S. R. Stenhagen, M. O'Duill, J. Wolstenhulme, A. K. Kirjavainen, S. J. Forsback, M. Tredwell, G. Sandford, P. R. Moore, M. Huiban, S. K. Luthra, J. Passchier, O. Solin and V. Gouverneur, *Org. Lett*. **2013**, 15, 2648-2651.
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3. (*a*) M. Peng, H. Li, Z. Qin, J. Li, Y. Sun, X. Zhang, L. Jiang, D. Hainam and J. An, *Adv. Synth. Catal.* **2022**, 364, 2184-2186; (*b*) Y. Lan, D.-G. Yu, *Chem. Sci*. **2018**, 9, 4873-4878.
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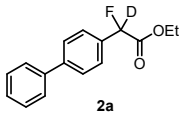
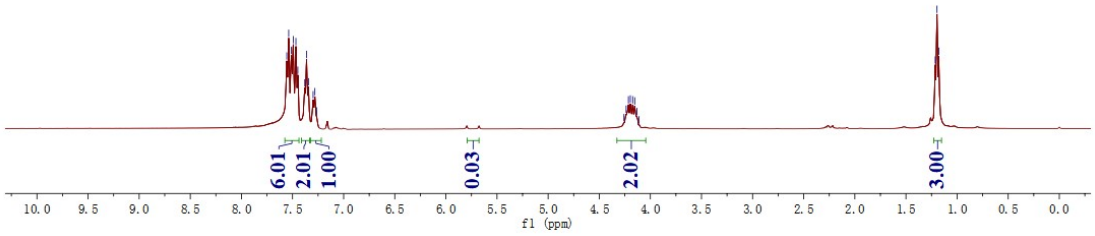
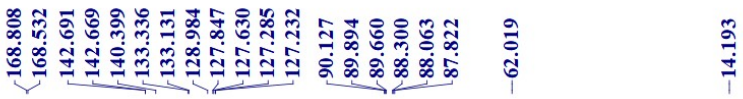
8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Products 2, 3 - 7 and Materials 1

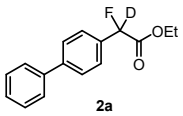
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2a (Chloroform-d)



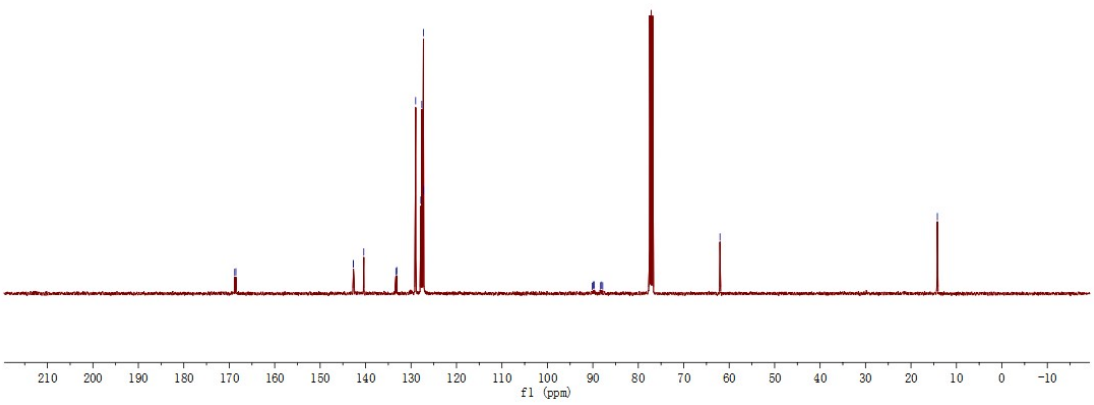
2a

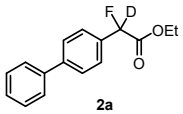






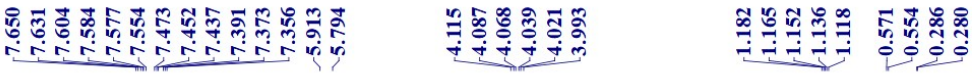
2a

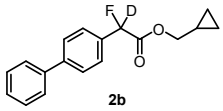




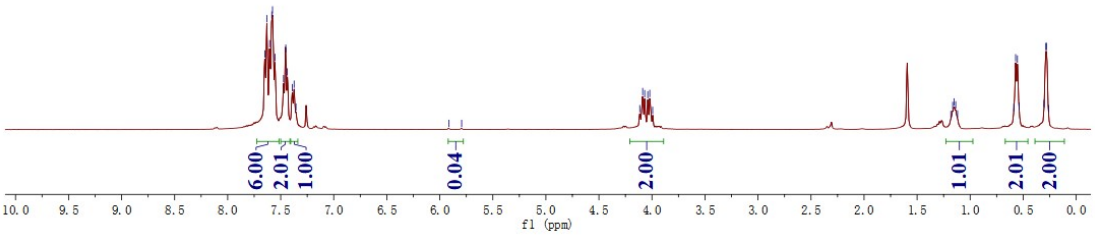
2a

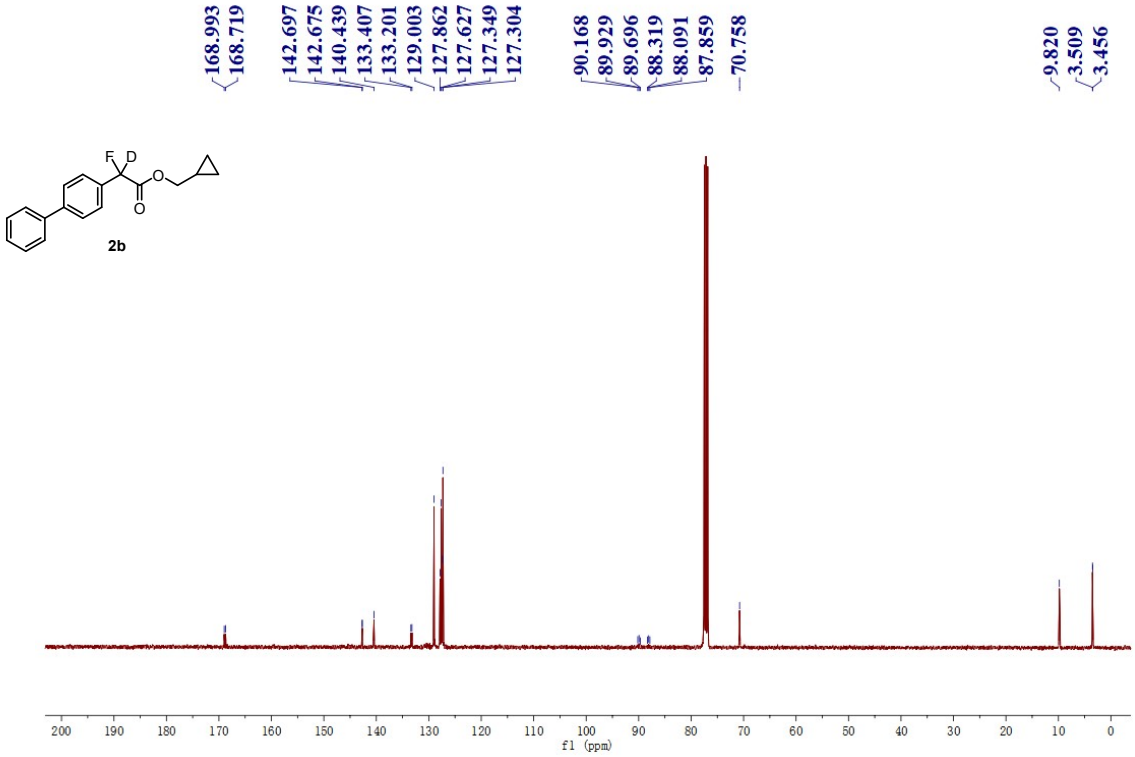
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2b (Chloroform-d)





2b

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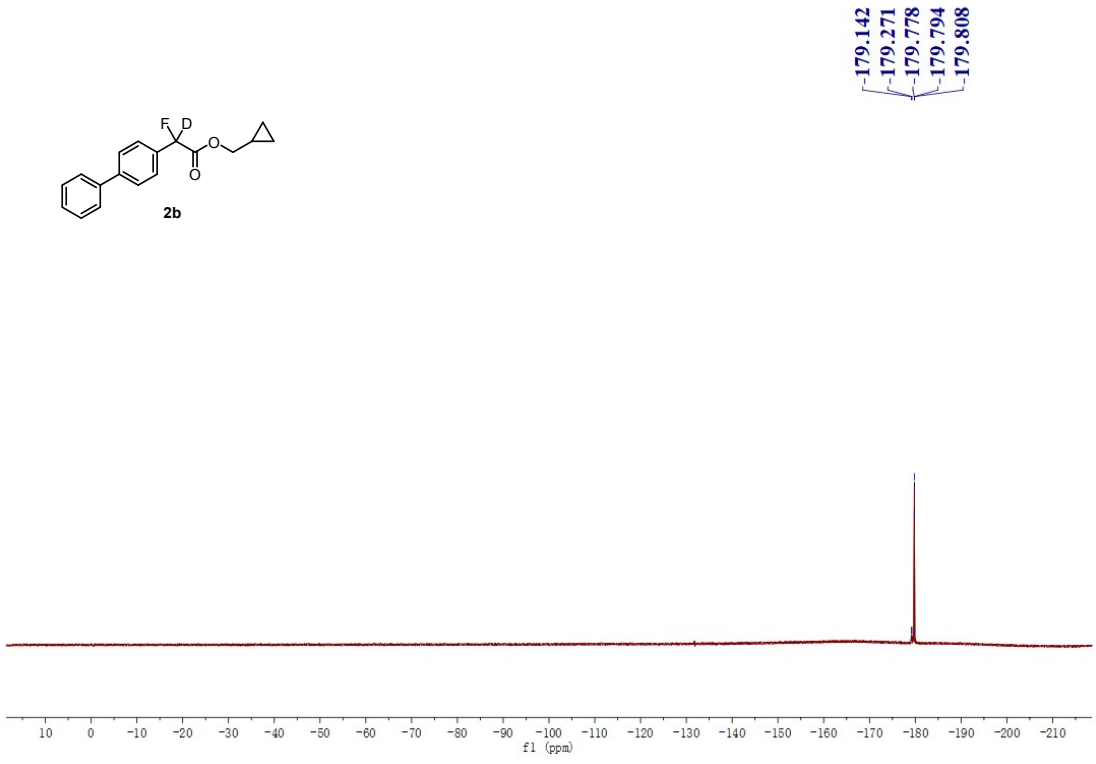
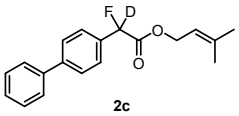
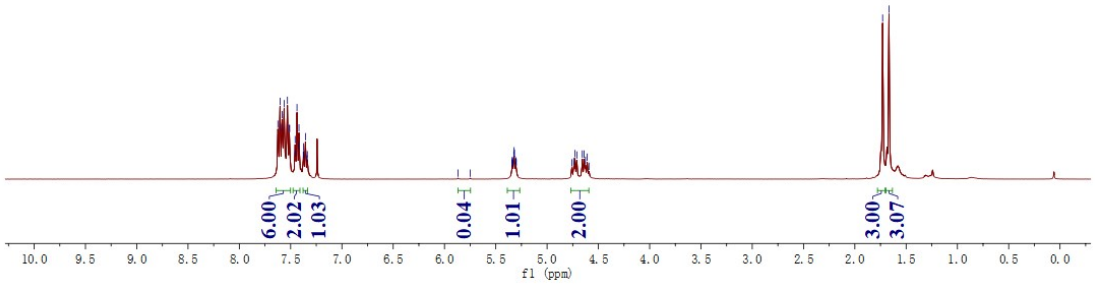
142.675
140.439
133.407
133.201
129.003
127.862
127.627
127.349
127.304
90.168
89.929
89.696
88.319
88.091
87.859
70.758
9.820
3.509
3.456
F
D
O
O
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

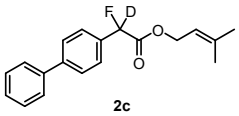

-179.142
-179.271
-179.778
-179.794
-179.808
F
D
O
O
2b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2c (Chloroform-d)

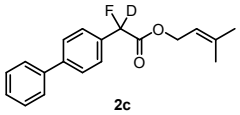


2c

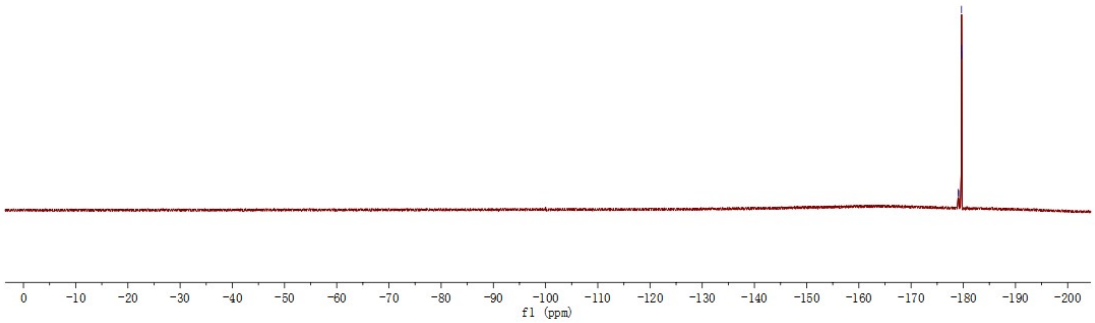




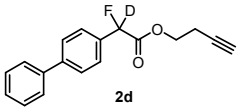
2c



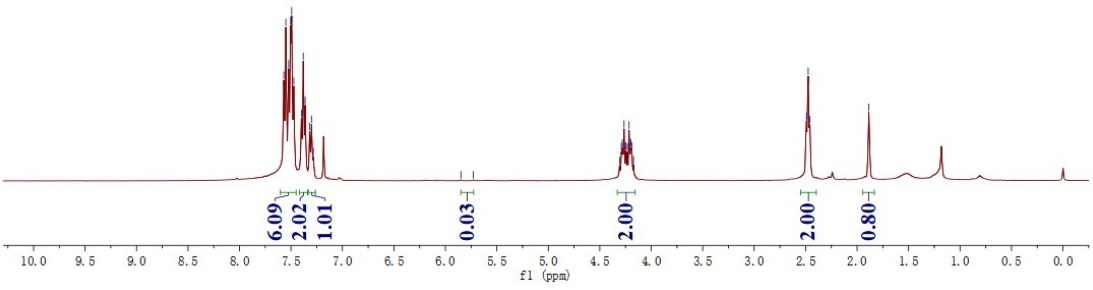
2c

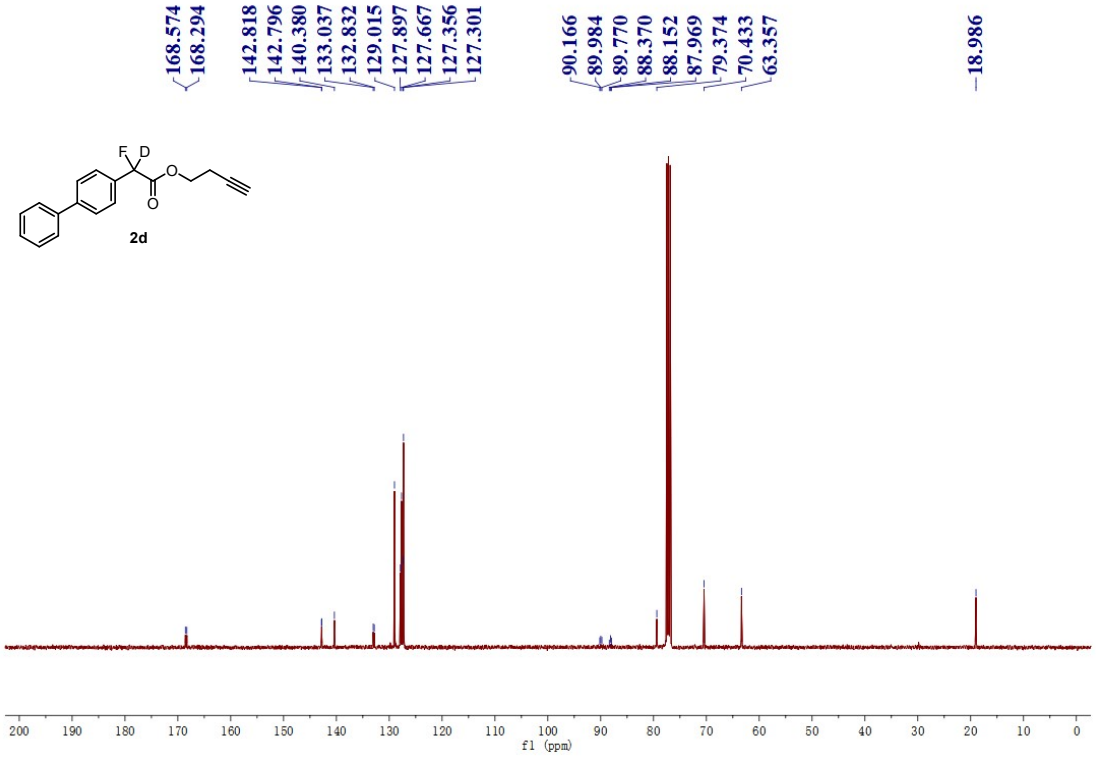


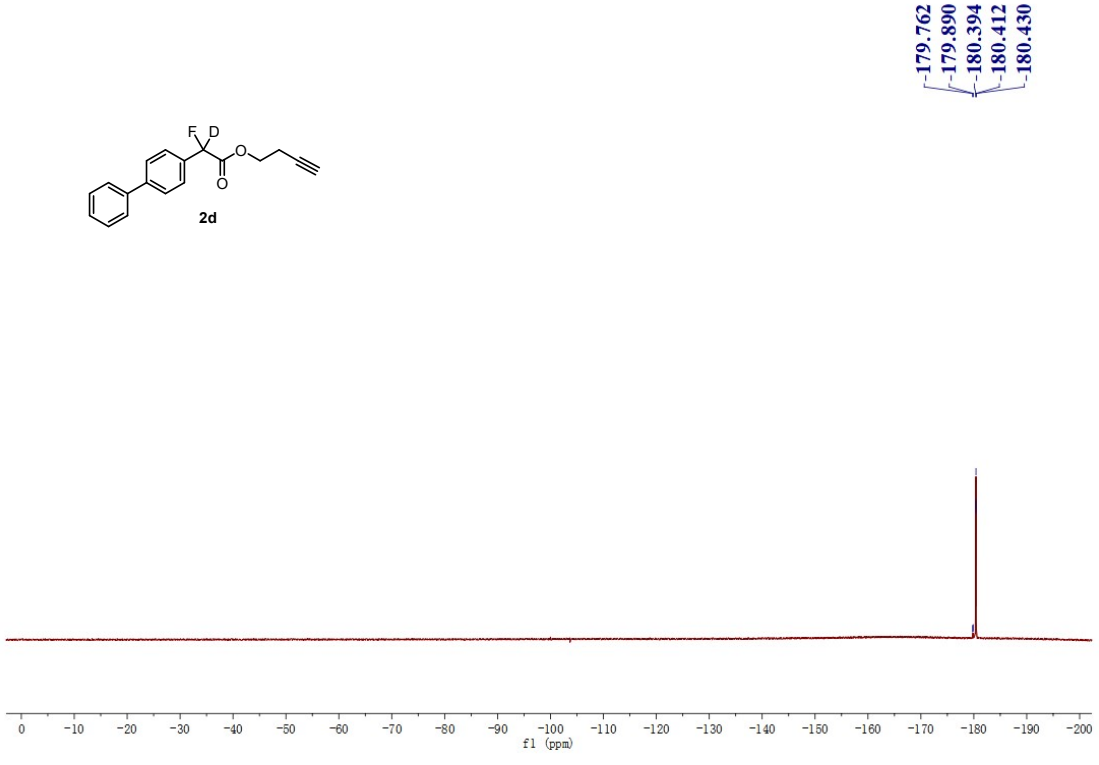
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2d (Chloroform-d)



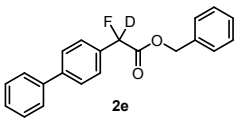
2d

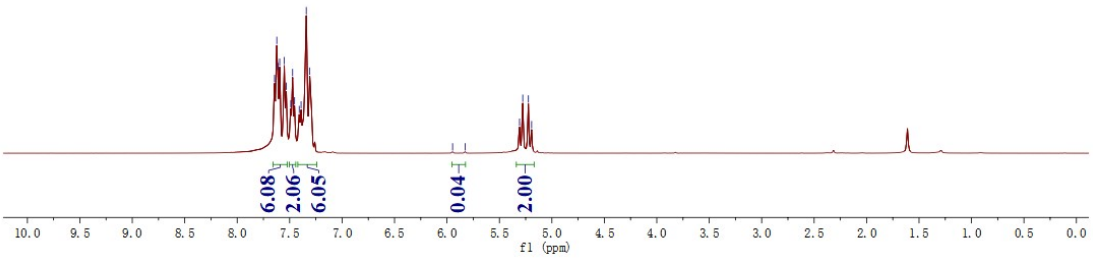


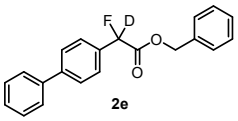

168.574
168.294
142.818
142.796
140.380
133.037
132.832
129.015
127.897
127.667
127.356
127.301
90.166
89.984
89.770
88.370
88.152
87.969
79.374
70.433
63.357
18.986
F
D
O
O
2d
f1 (ppm)

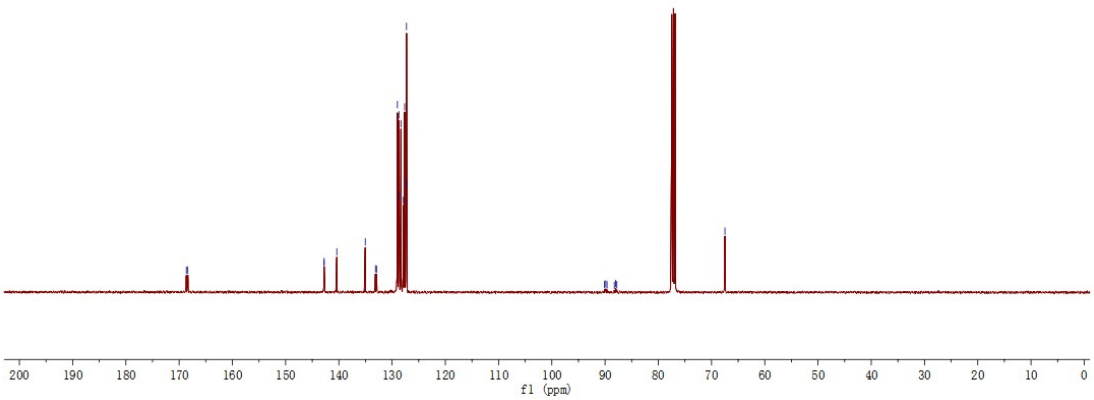

179.762
179.890
180.394
180.412
180.430
F
D
O
O
2d
f1 (ppm)

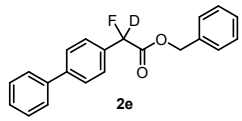
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2e (Chloroform-d)



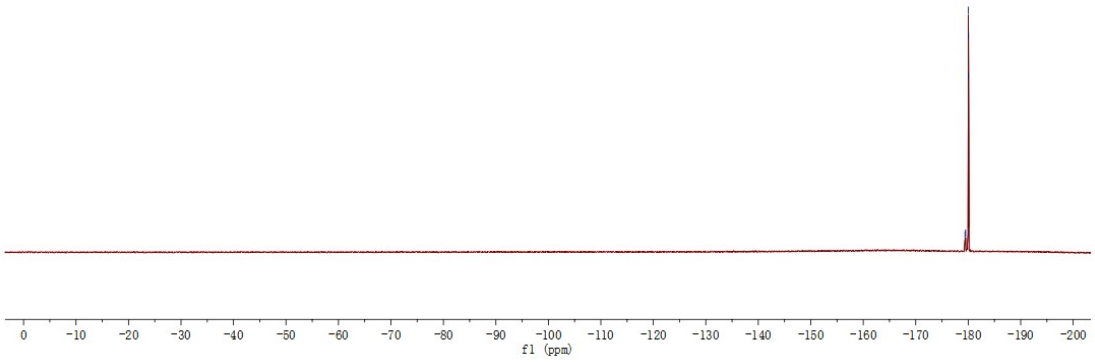




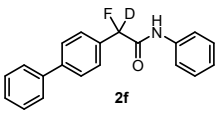




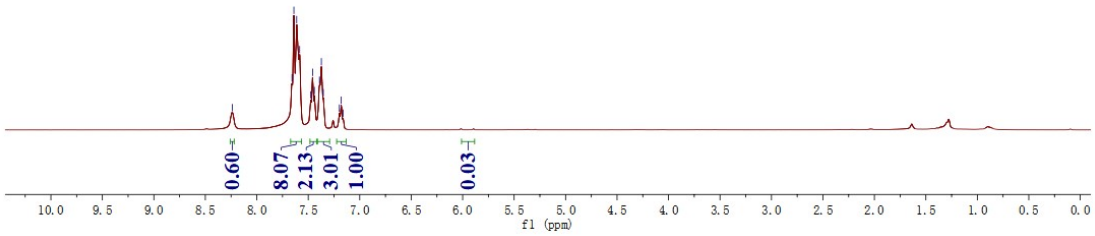
2e

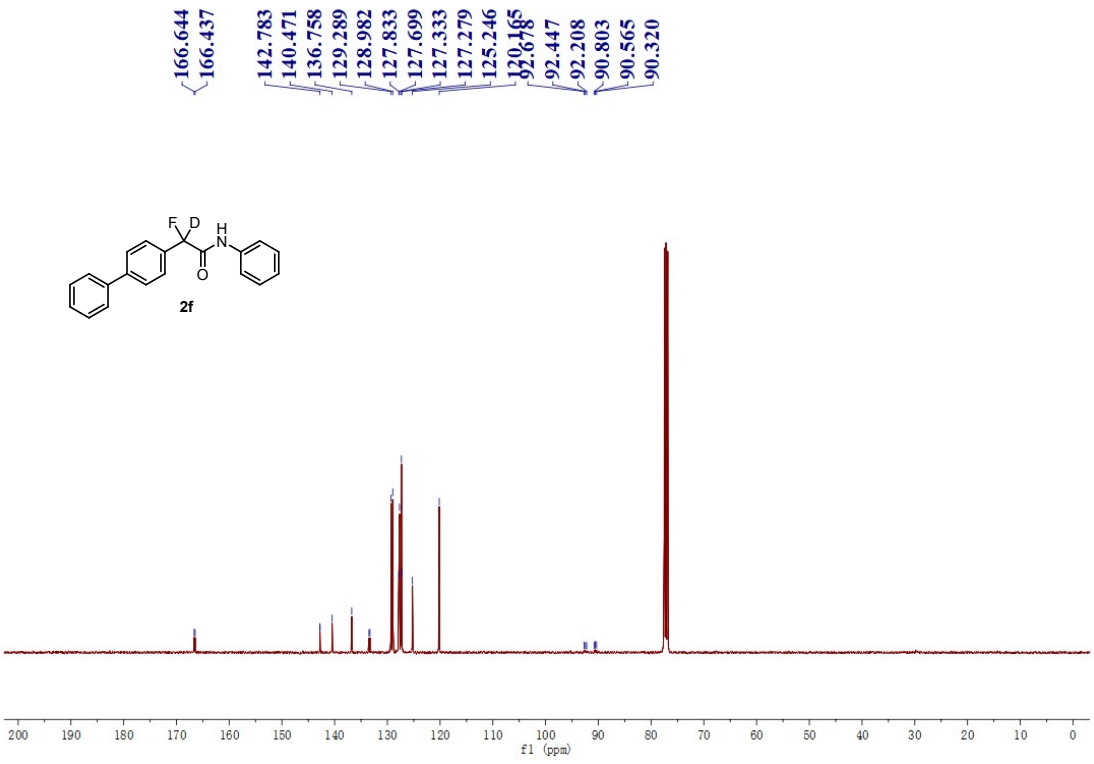


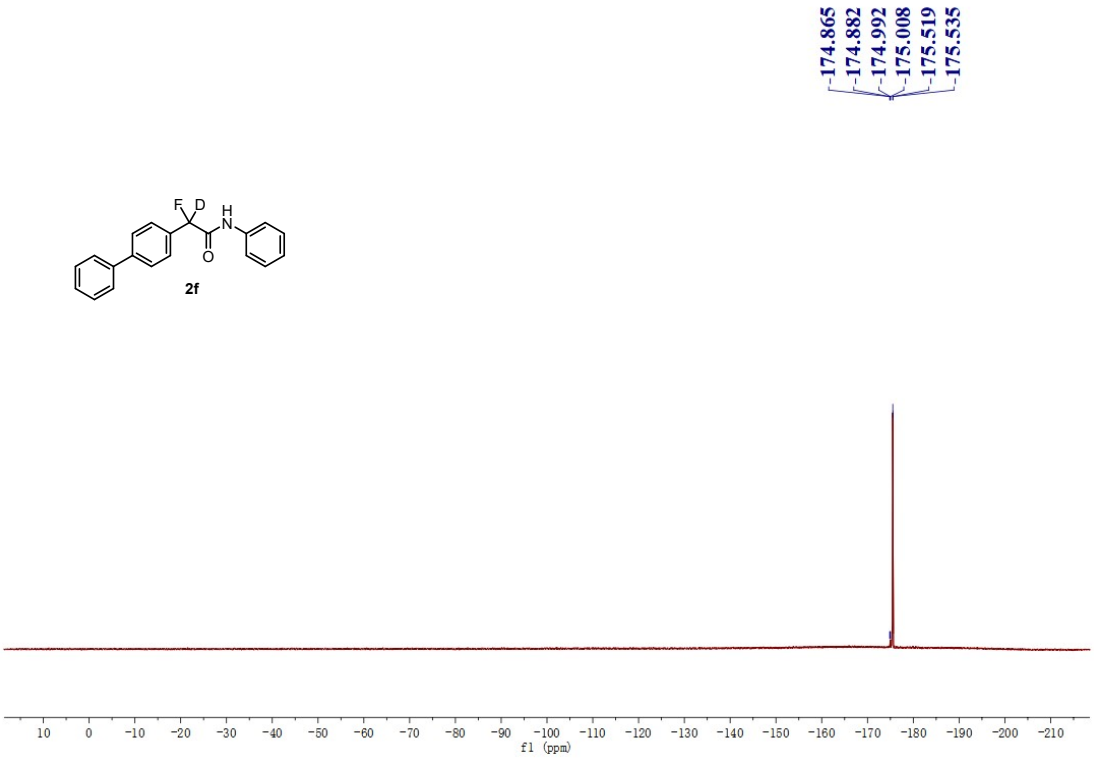
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2f (Chloroform-d)



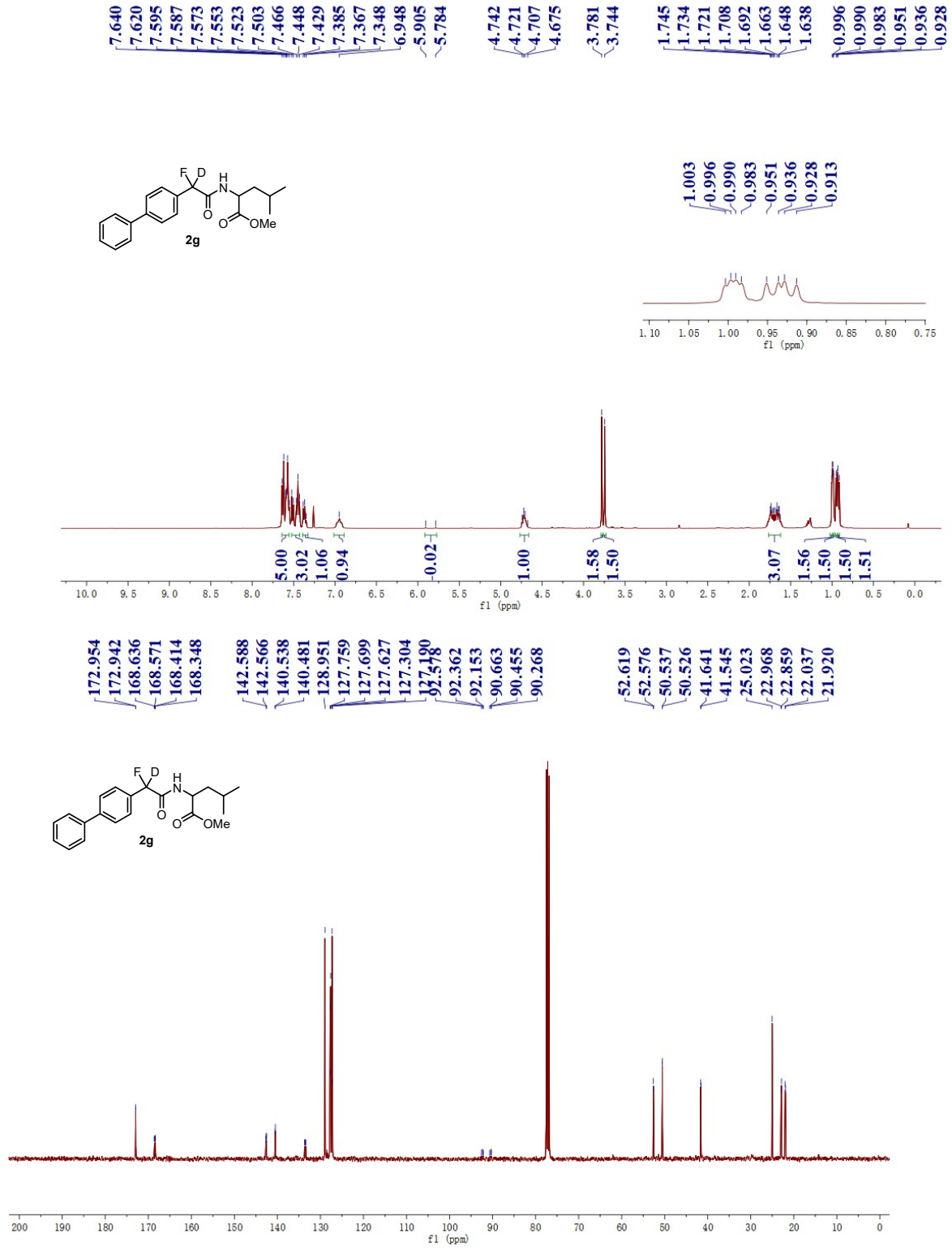
2f

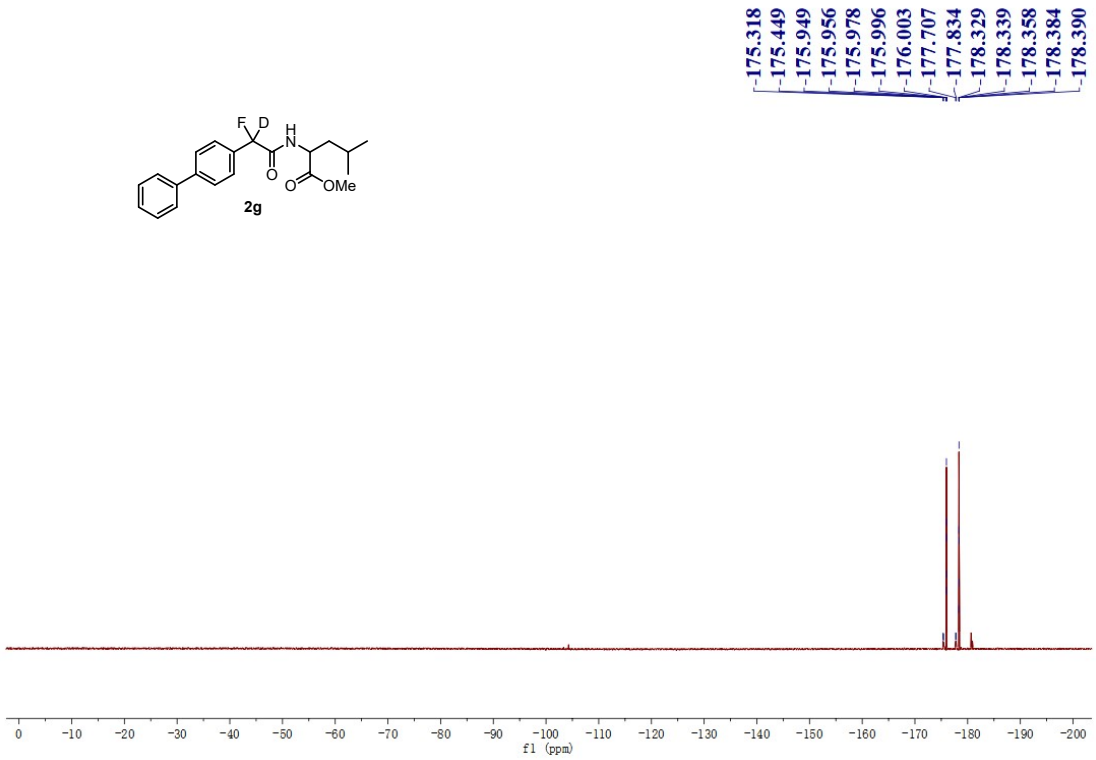



166.644
166.437
142.783
140.471
136.758
129.289
128.982
127.833
127.699
127.333
127.279
125.246
120.165
92.678
92.447
92.208
90.803
90.565
90.320
F
D
H
N
O
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

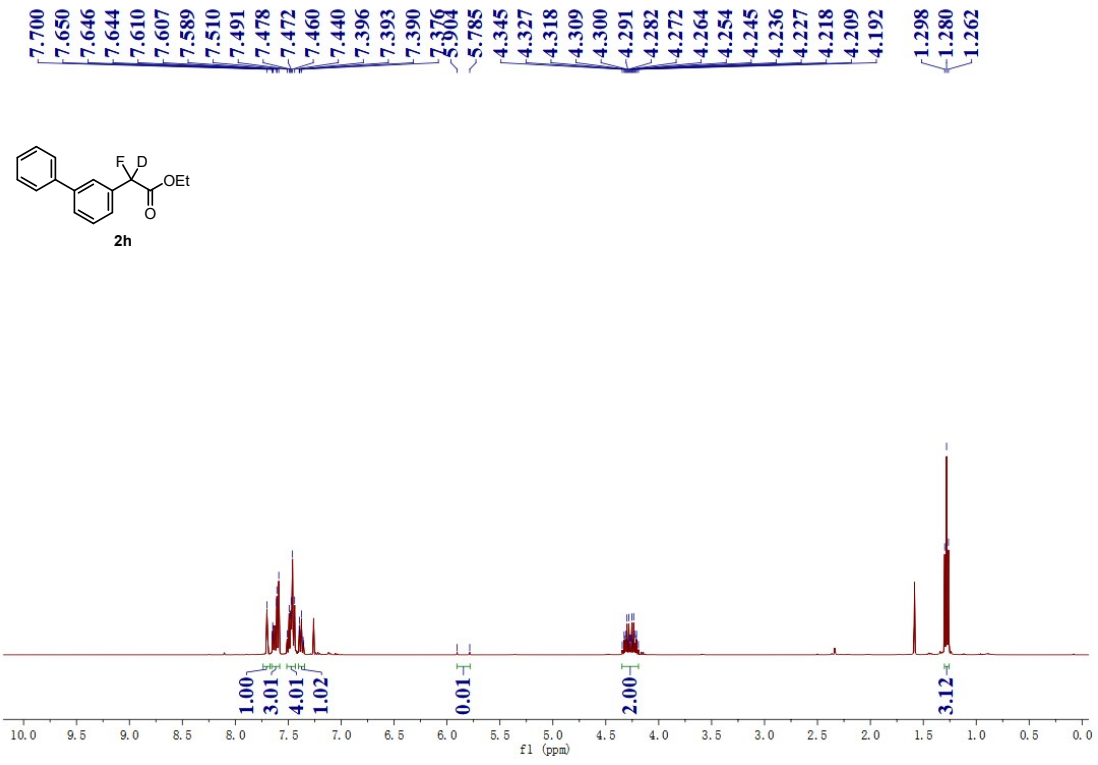

-174.865
-174.882
-174.992
-175.008
-175.519
-175.535
F
D
H
N
O
2f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

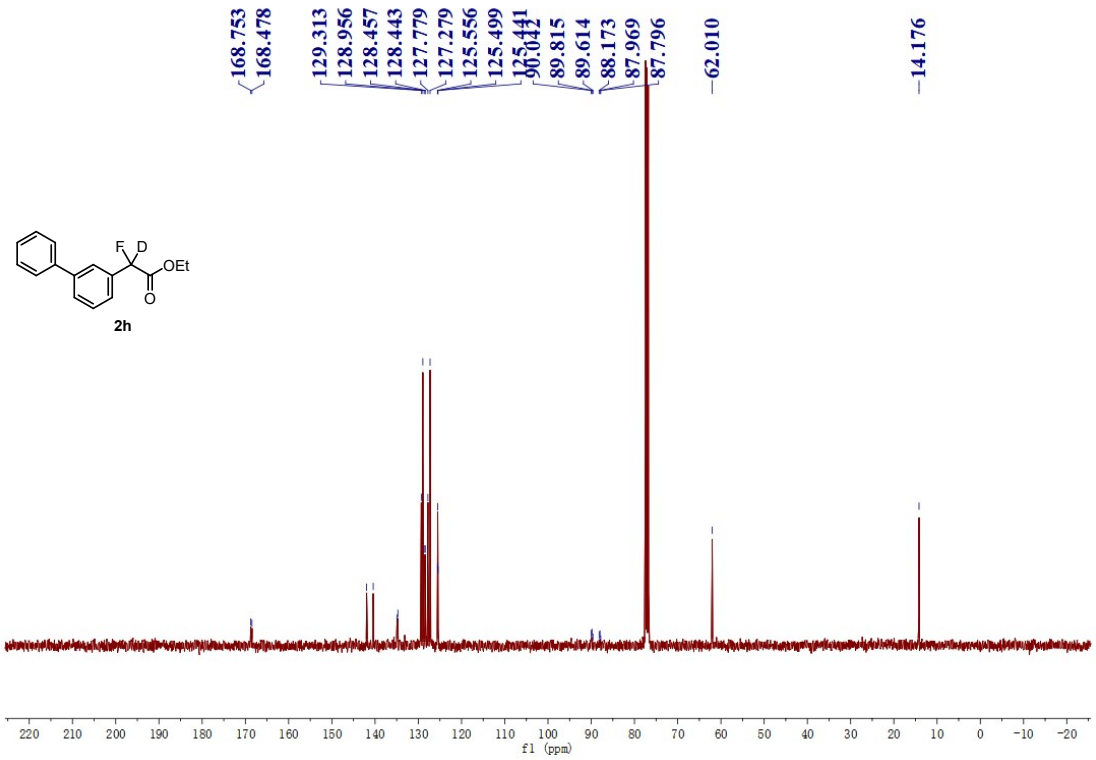
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2g (Chloroform-d)

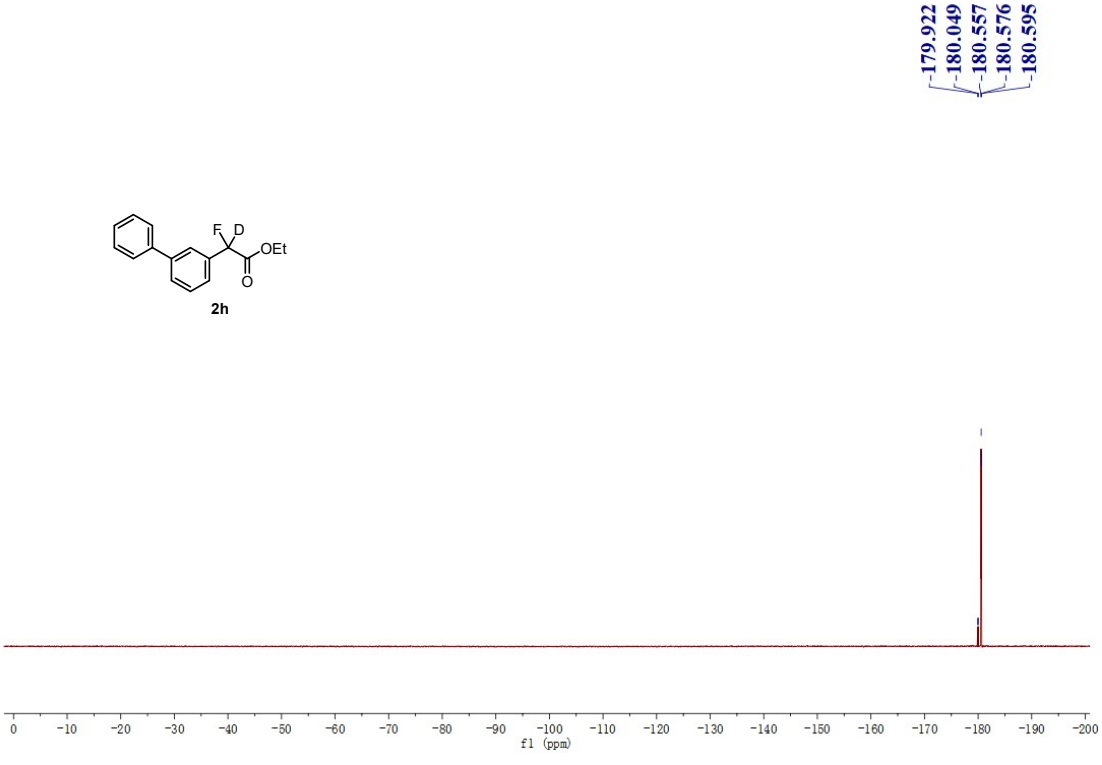




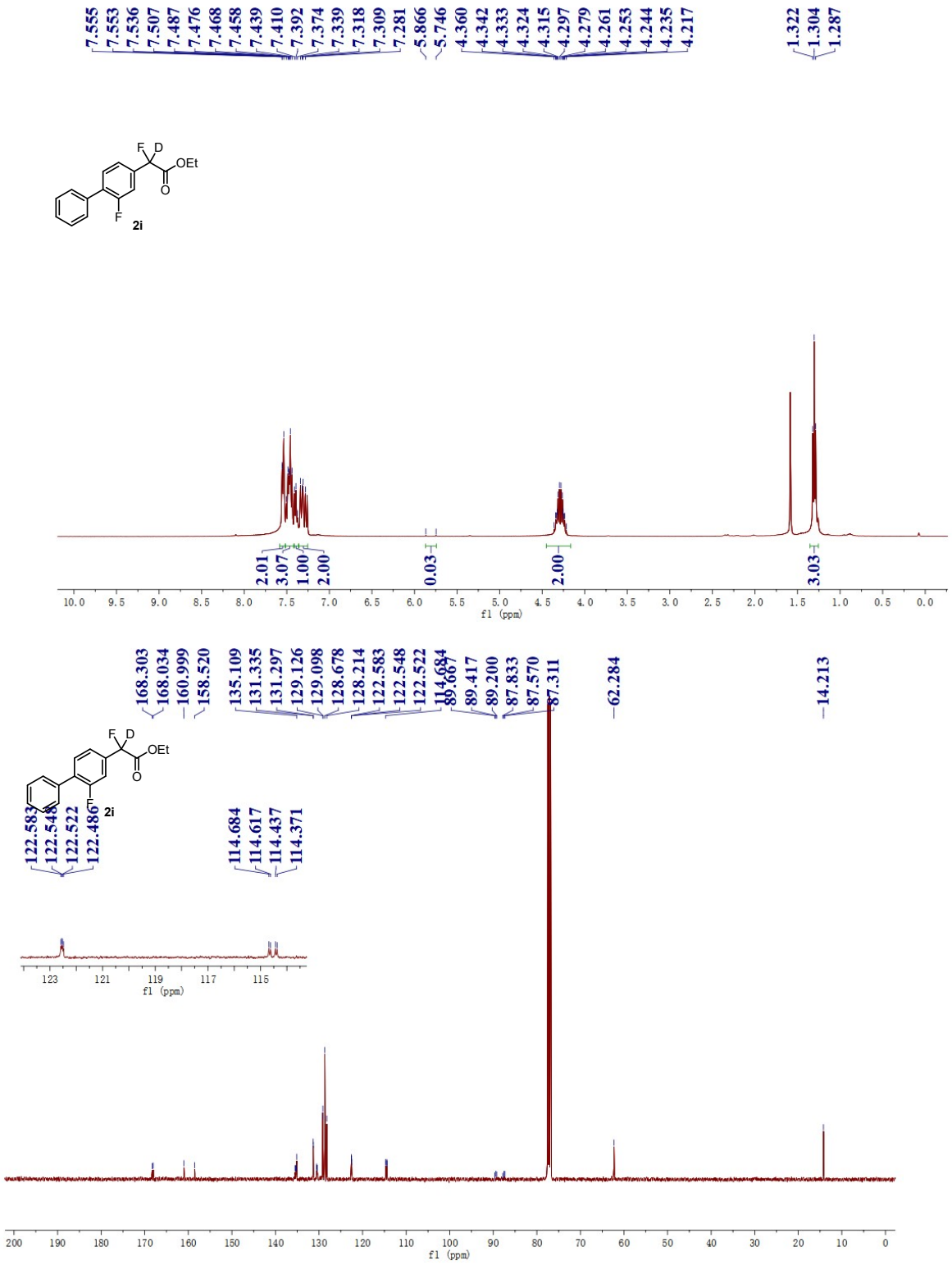
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2h (Chloroform-d)

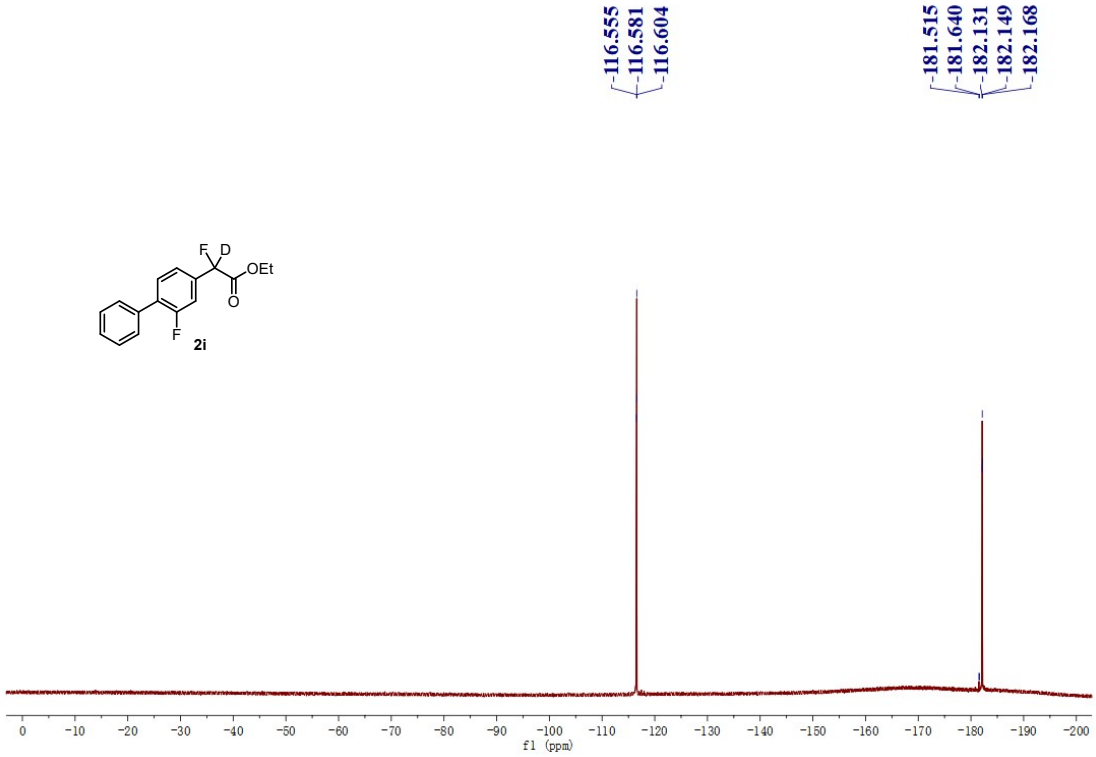



168.753
168.478
129.313
128.956
128.457
128.443
127.779
127.279
125.556
125.499
125.441
90.042
89.815
89.614
88.173
87.969
87.796
62.010
14.176
F
D
OEt
O
2h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

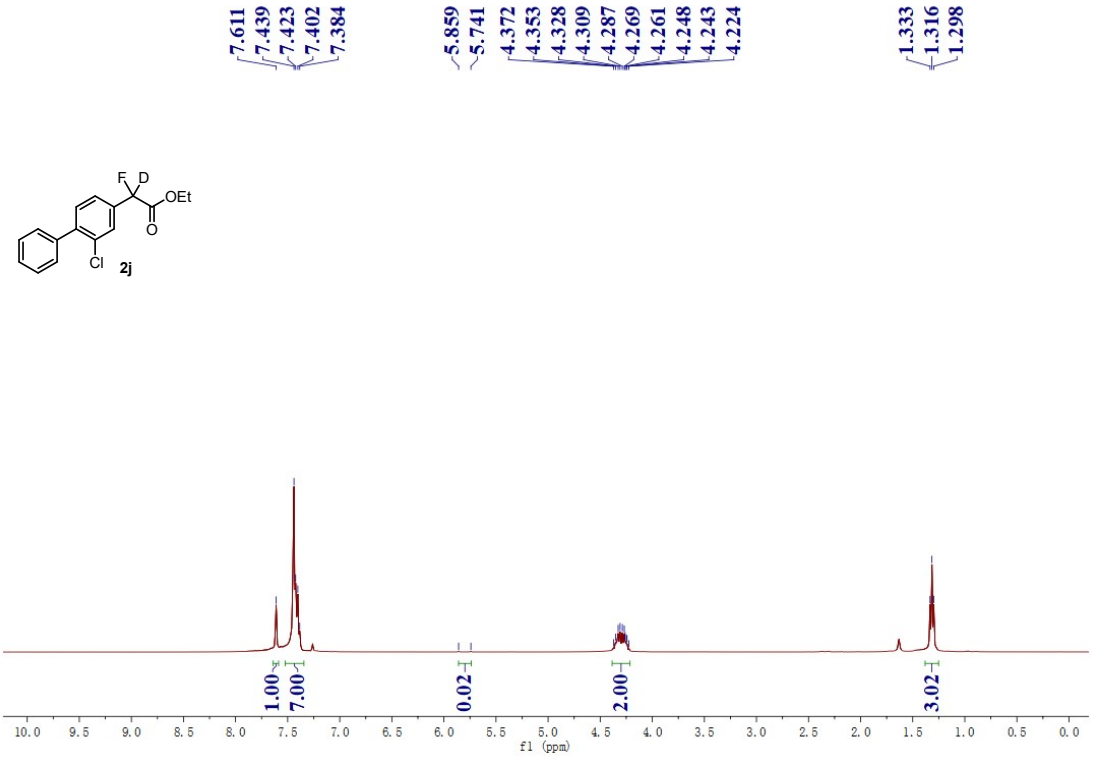

179.922
180.049
180.557
180.576
180.595
F
D
OEt
O
2h
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

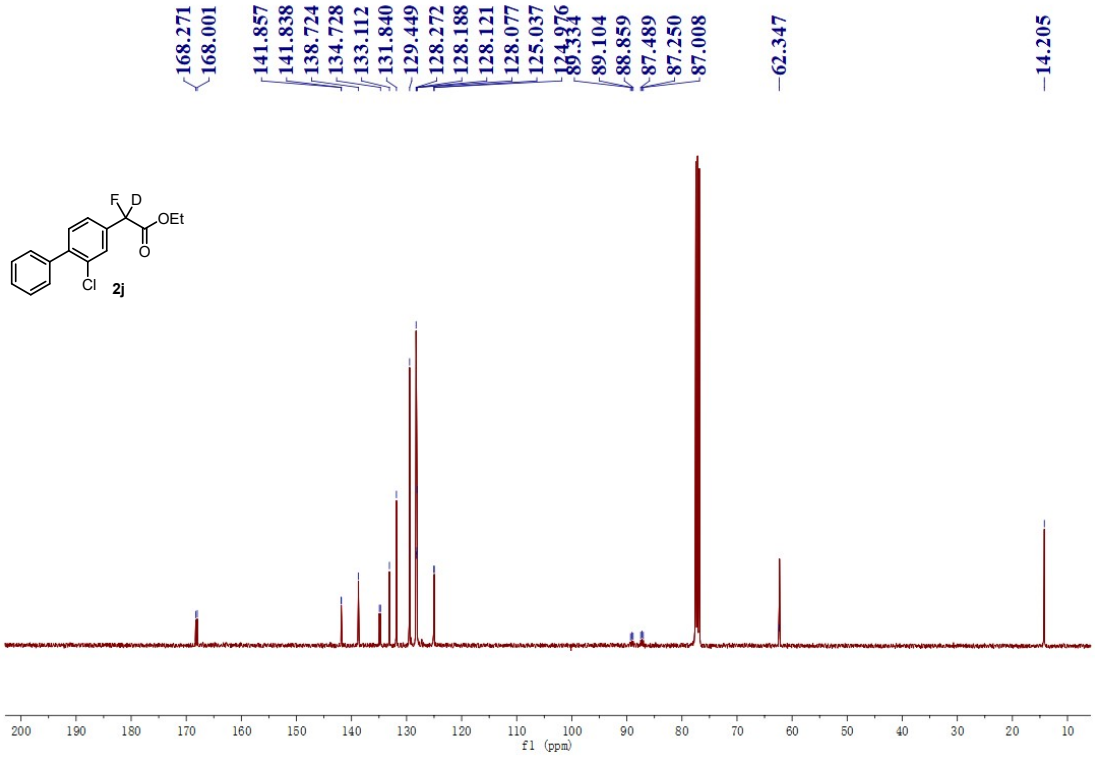
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2i (Chloroform-d)

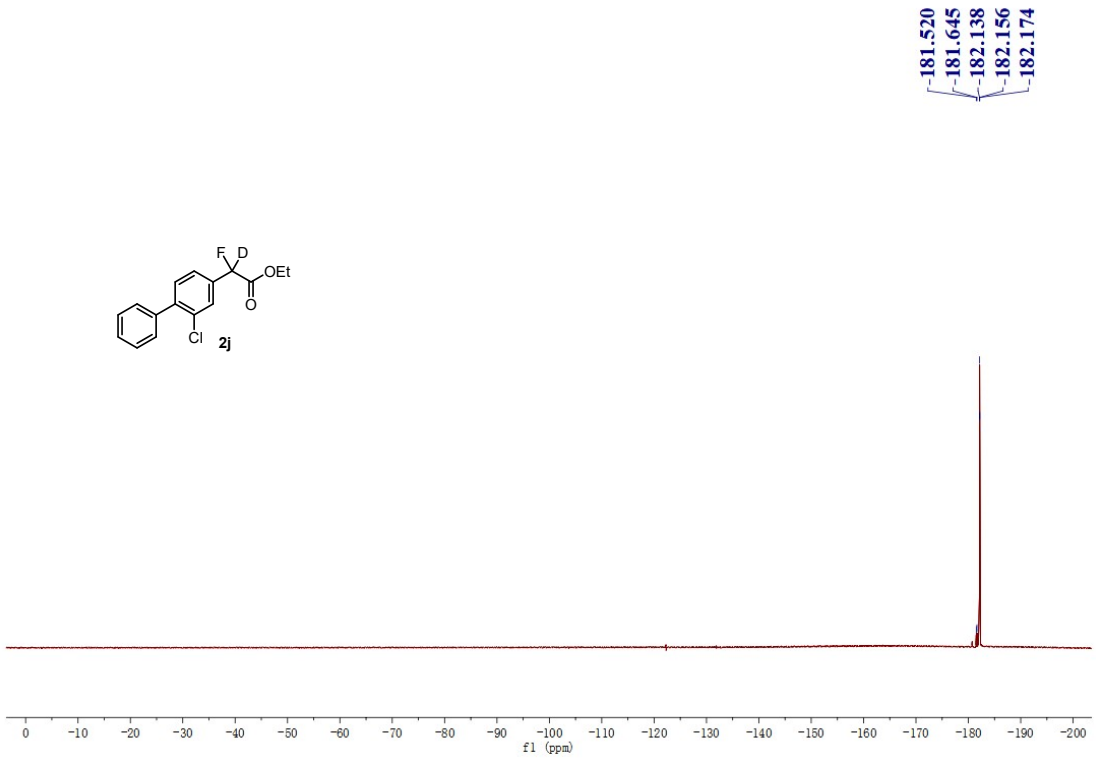




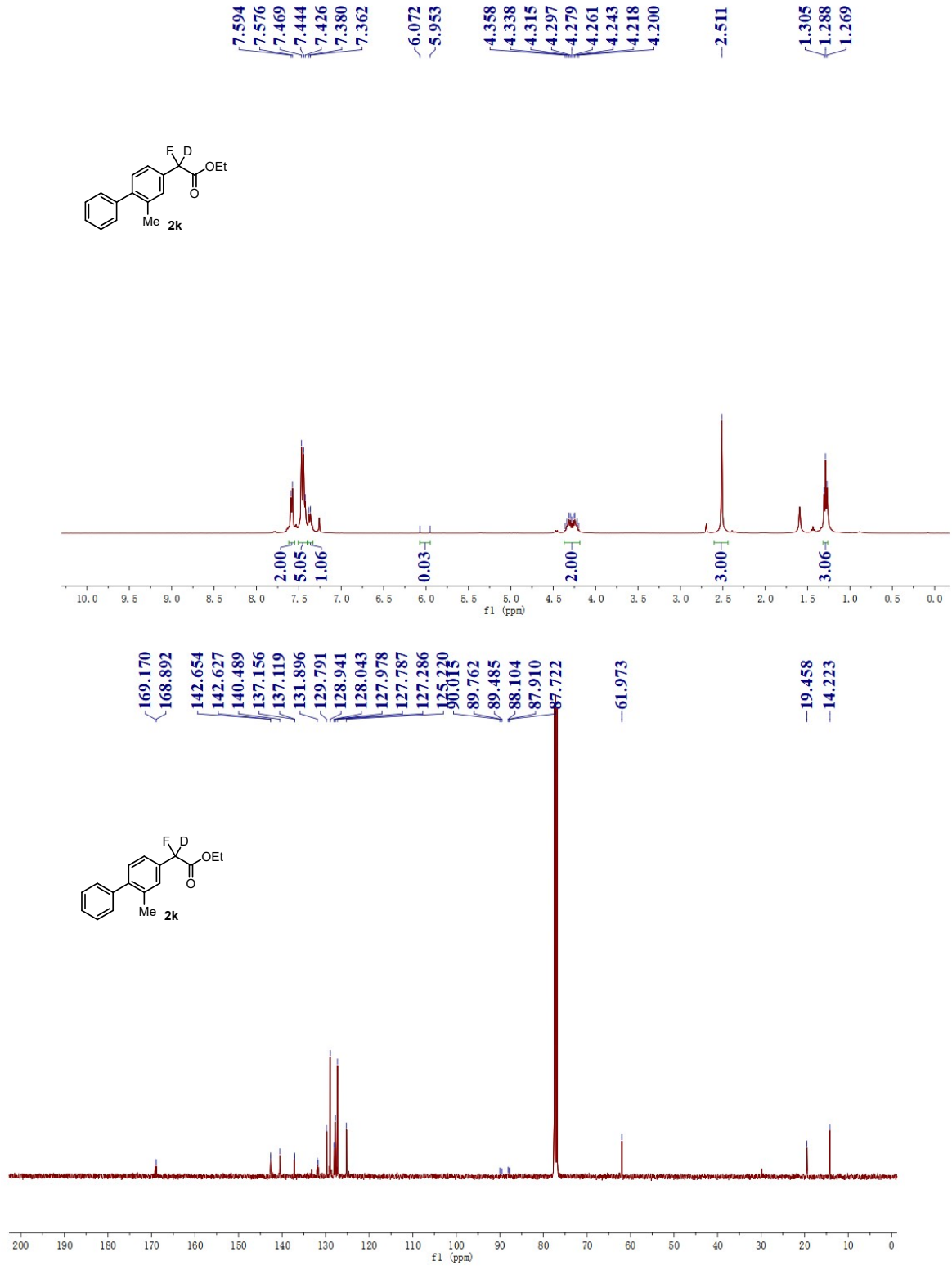
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2j (Chloroform-d)

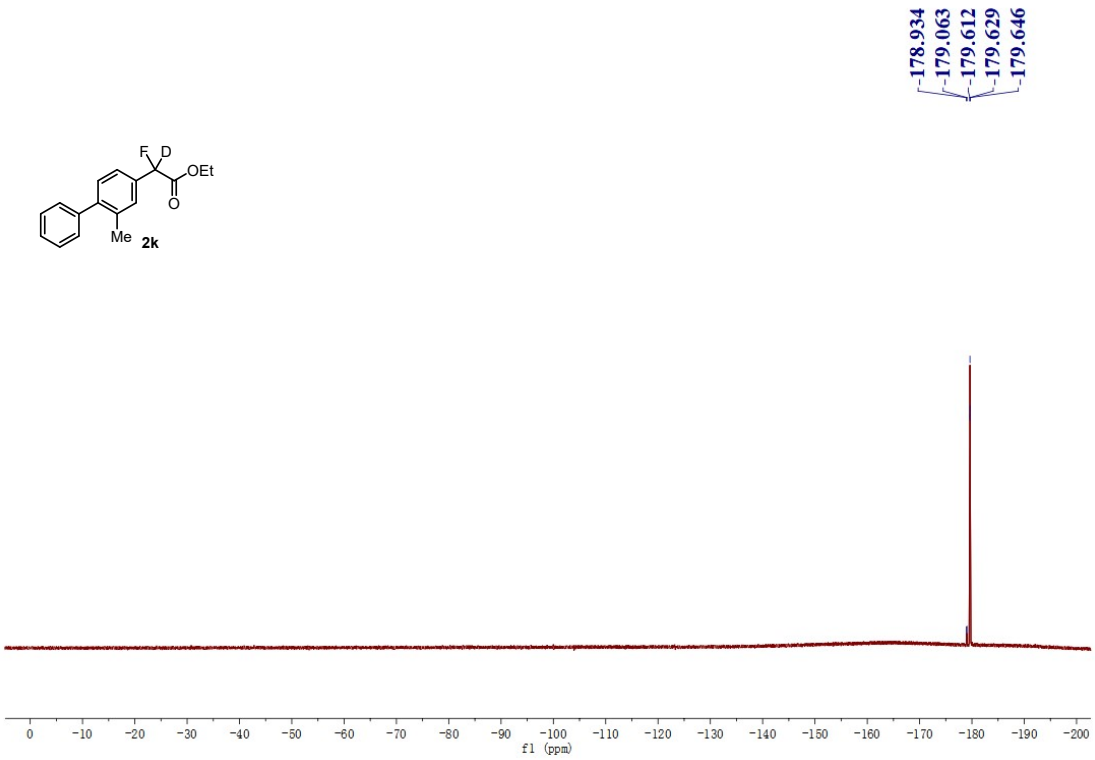



168.271
168.001
141.857
141.838
138.724
134.728
133.112
131.840
129.449
128.272
128.188
128.121
128.077
125.037
124.976
89.334
89.104
88.859
87.489
87.250
87.008
62.347
14.205
F
D
OEt
O
Cl
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

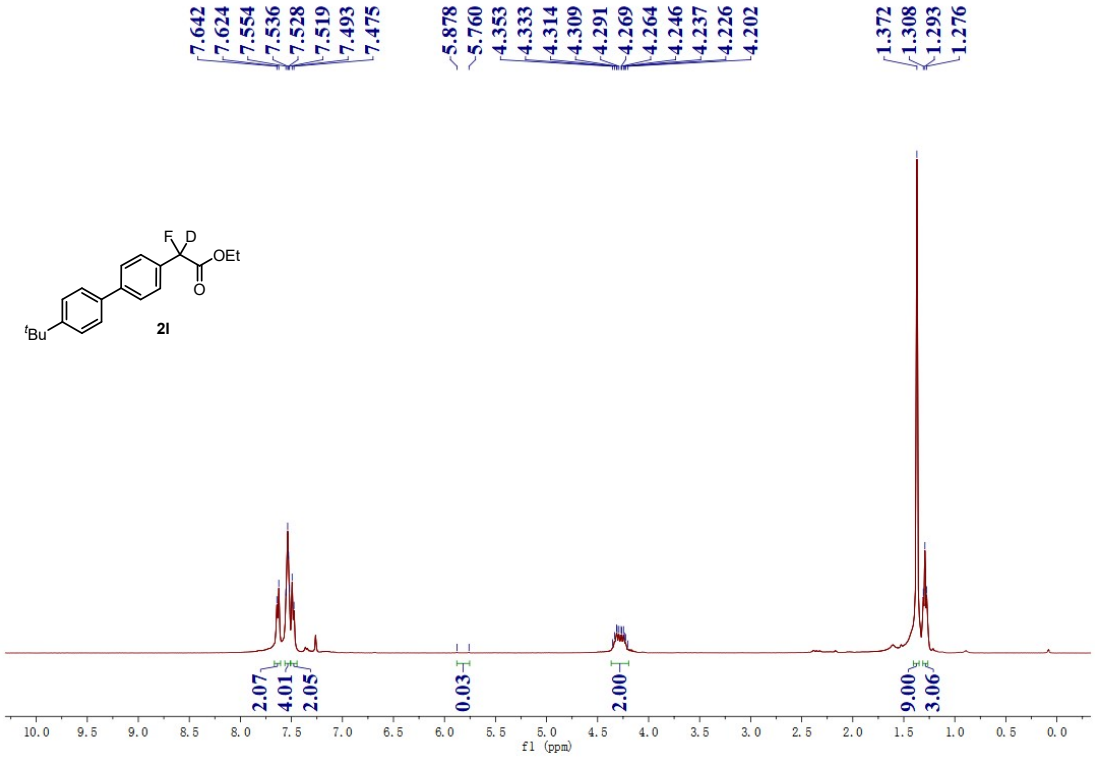

181.520
181.645
182.138
182.156
182.174
F
D
OEt
O
Cl
2j
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

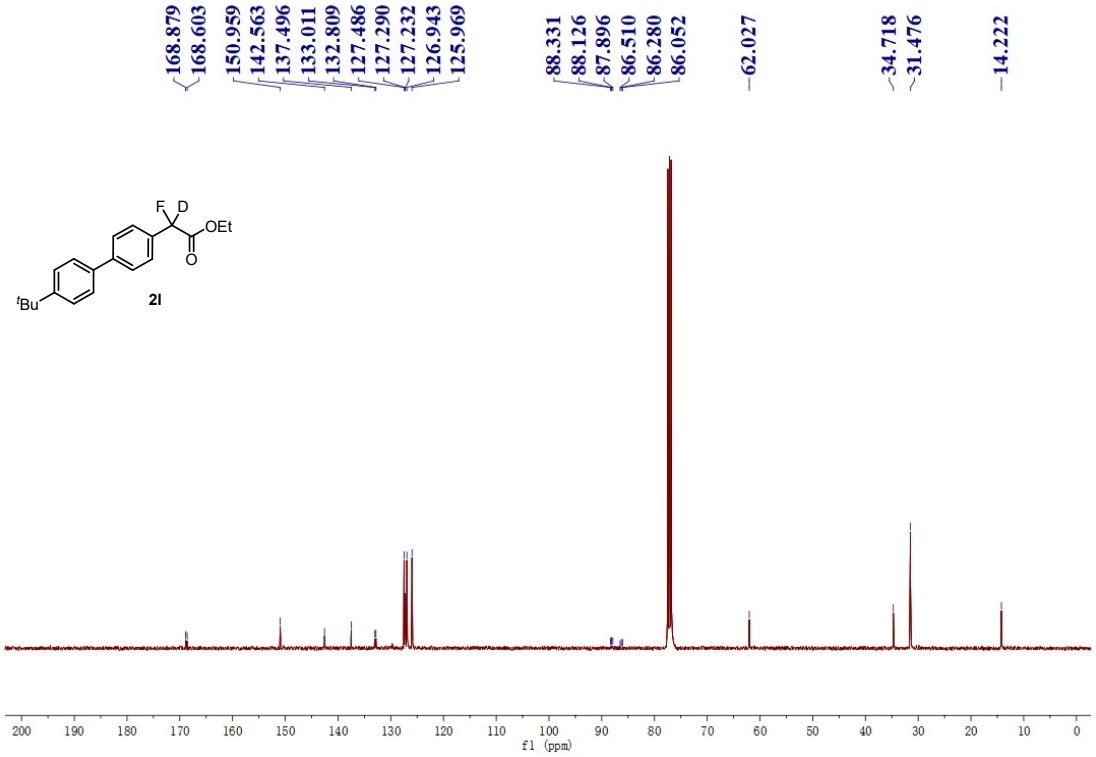
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2k (Chloroform-d)

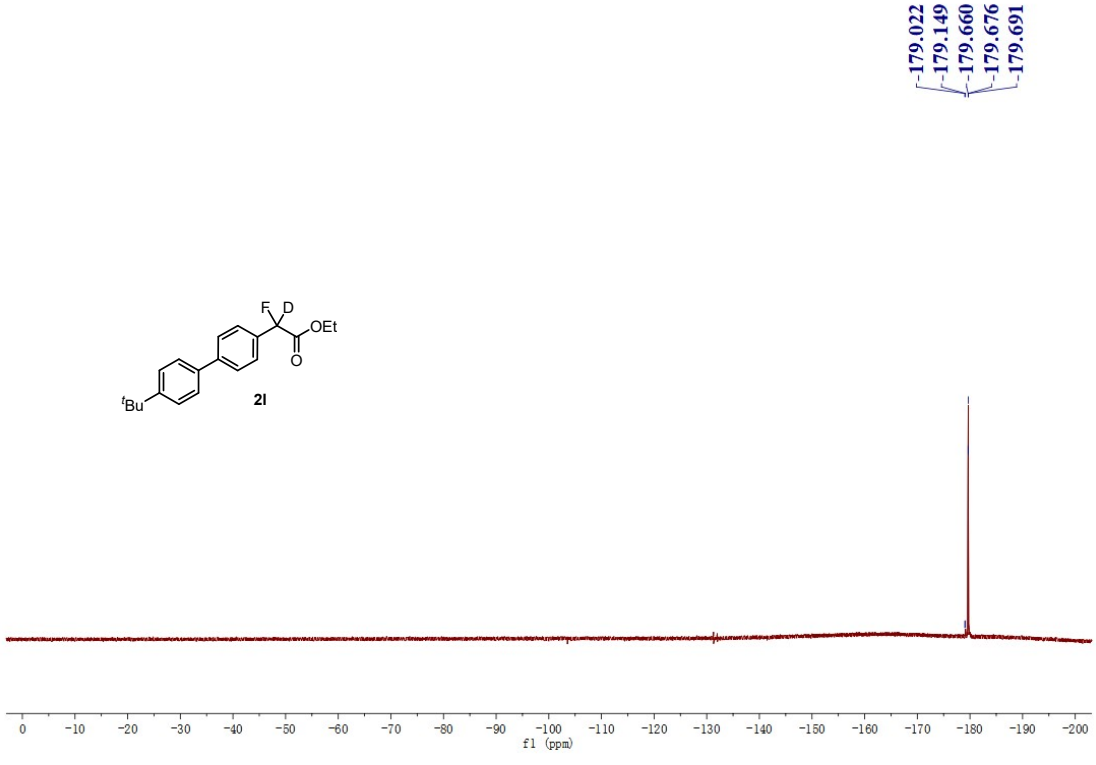




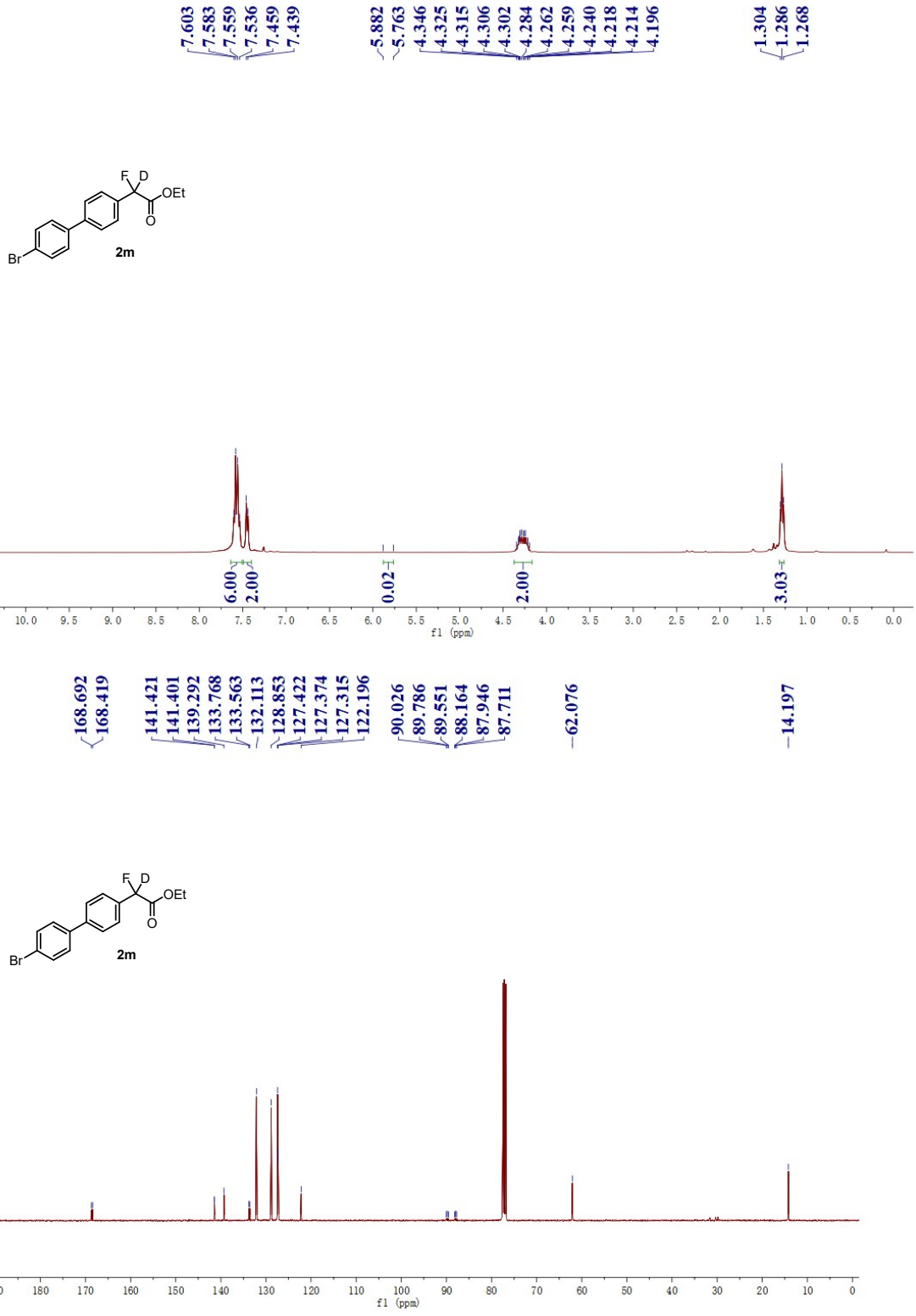
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2l (Chloroform-d)

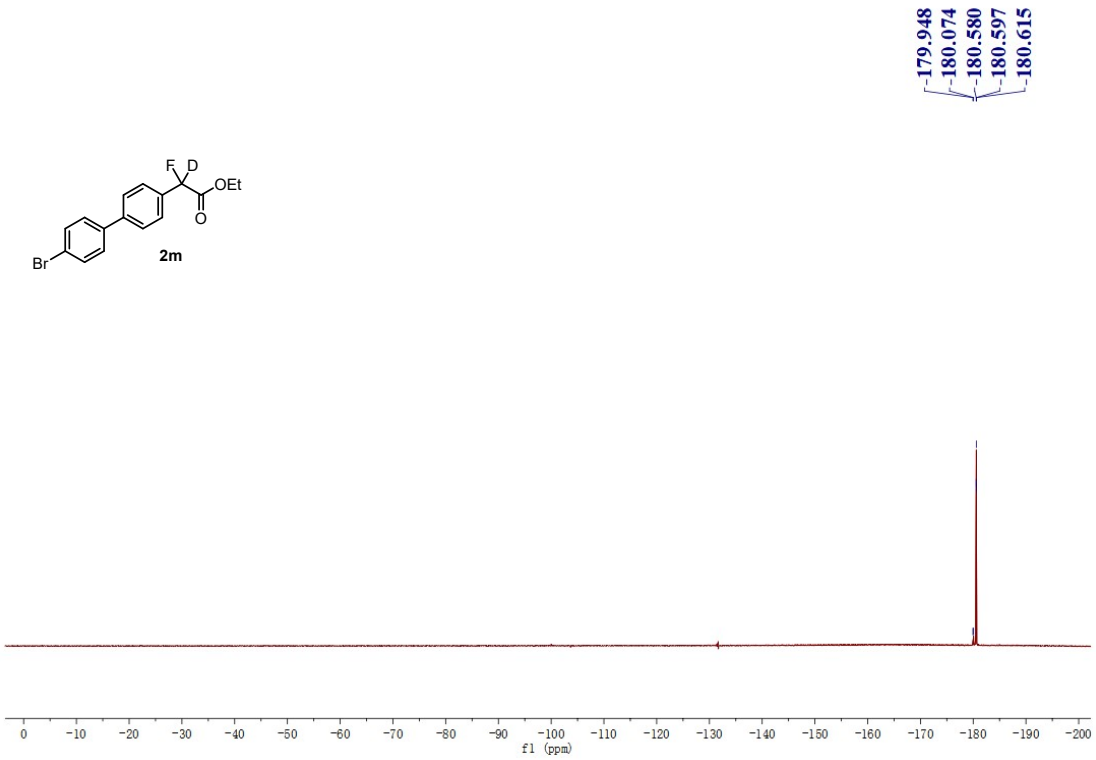



168.879
168.603
150.959
142.563
137.496
133.011
132.809
127.486
127.290
127.232
126.943
125.969
88.331
88.126
87.896
86.510
86.280
86.052
62.027
34.718
31.476
14.222
F
D
OEt
O
tBu
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

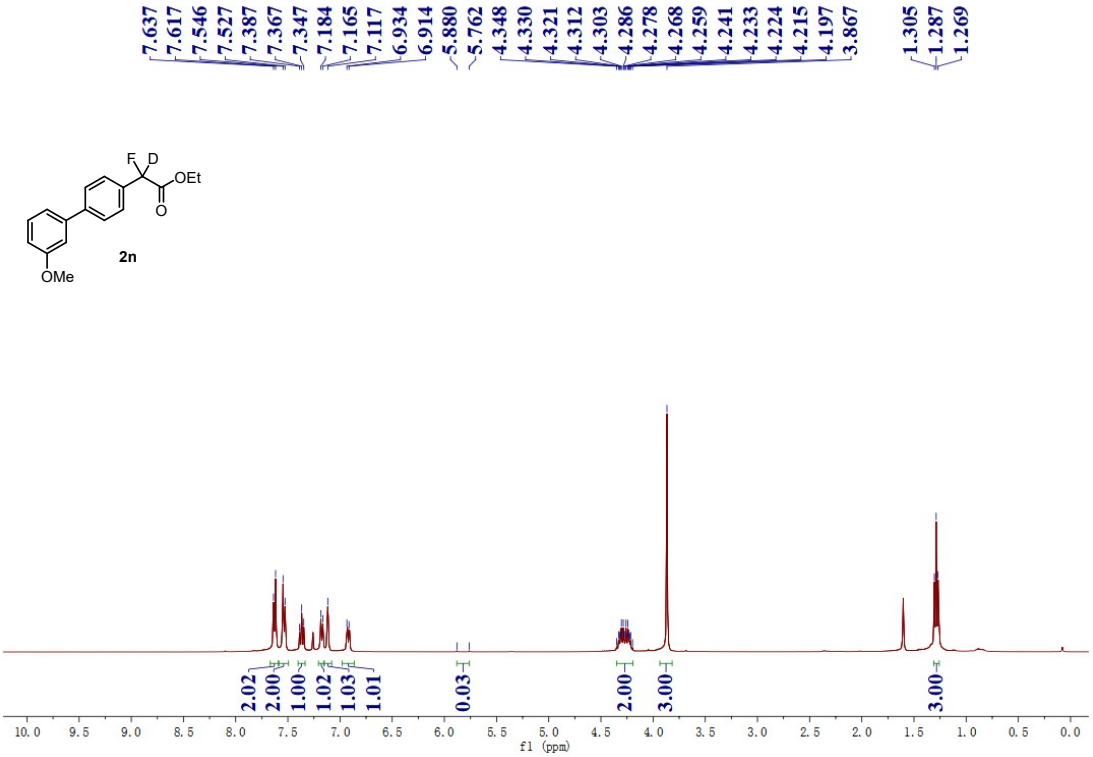

179.022
179.149
179.660
179.676
179.691
F
D
OEt
O
tBu
2l
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

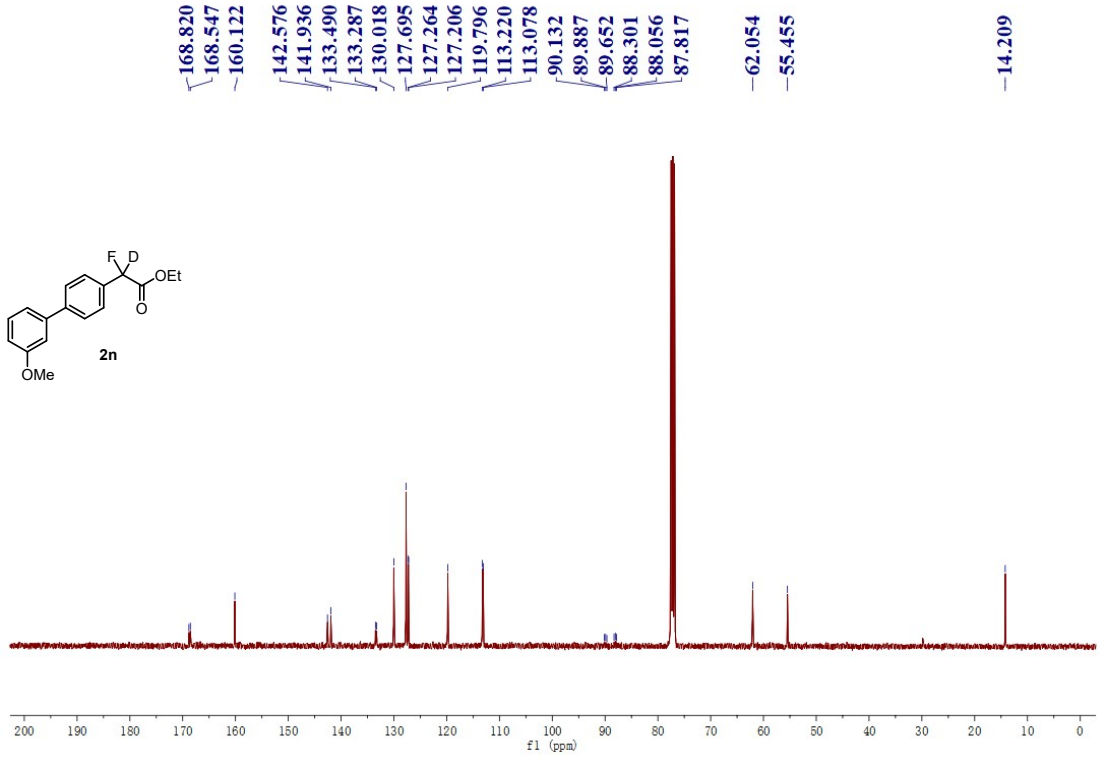
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2m (Chloroform-d)

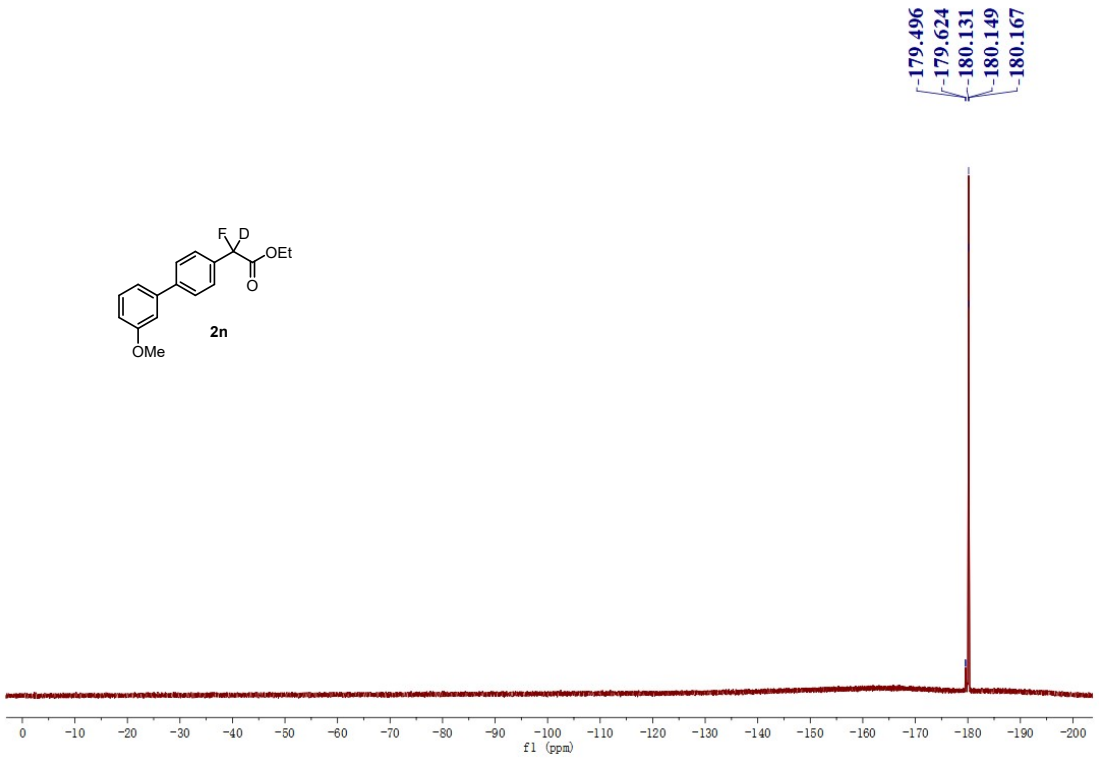




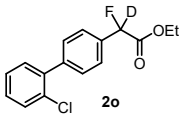
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2n (Chloroform-d)

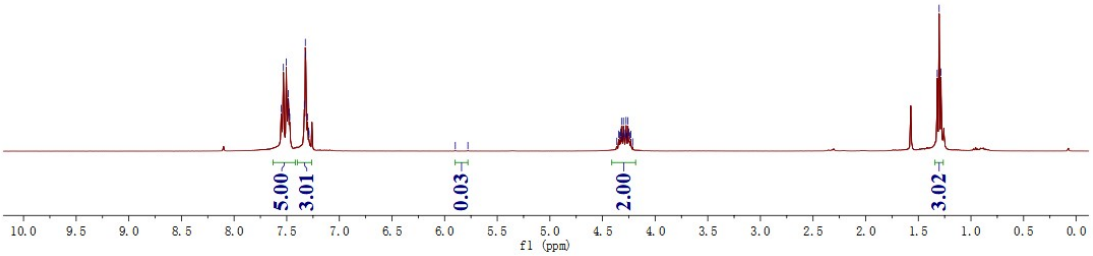


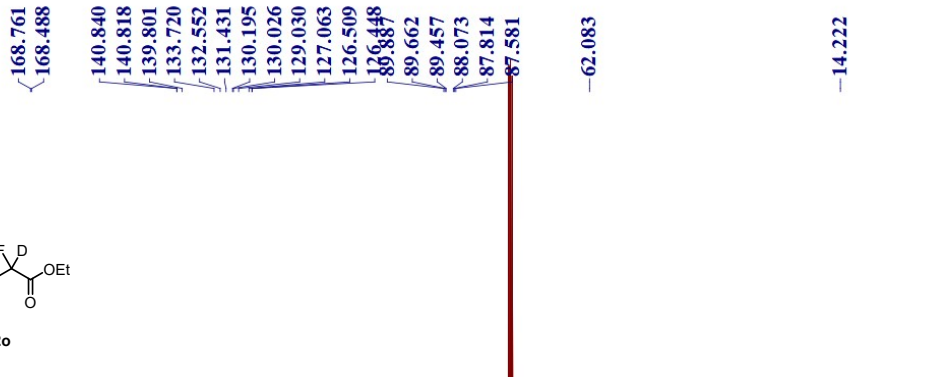

168.820
168.547
160.122
142.576
141.936
133.490
133.287
130.018
127.695
127.264
127.206
119.796
113.220
113.078
90.132
89.887
89.652
88.301
88.056
87.817
62.054
55.455
14.209
F
D
OEt
O
OMe
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

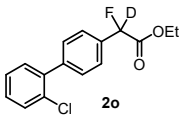

179.496
179.624
180.131
180.149
180.167
F
D
OEt
O
OMe
2n
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

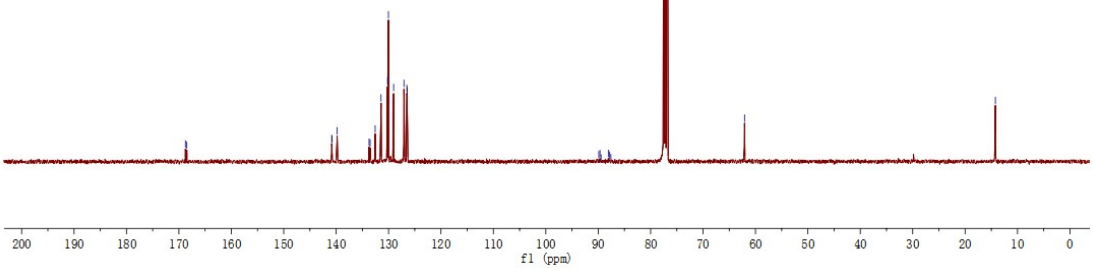
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2o (Chloroform-d)

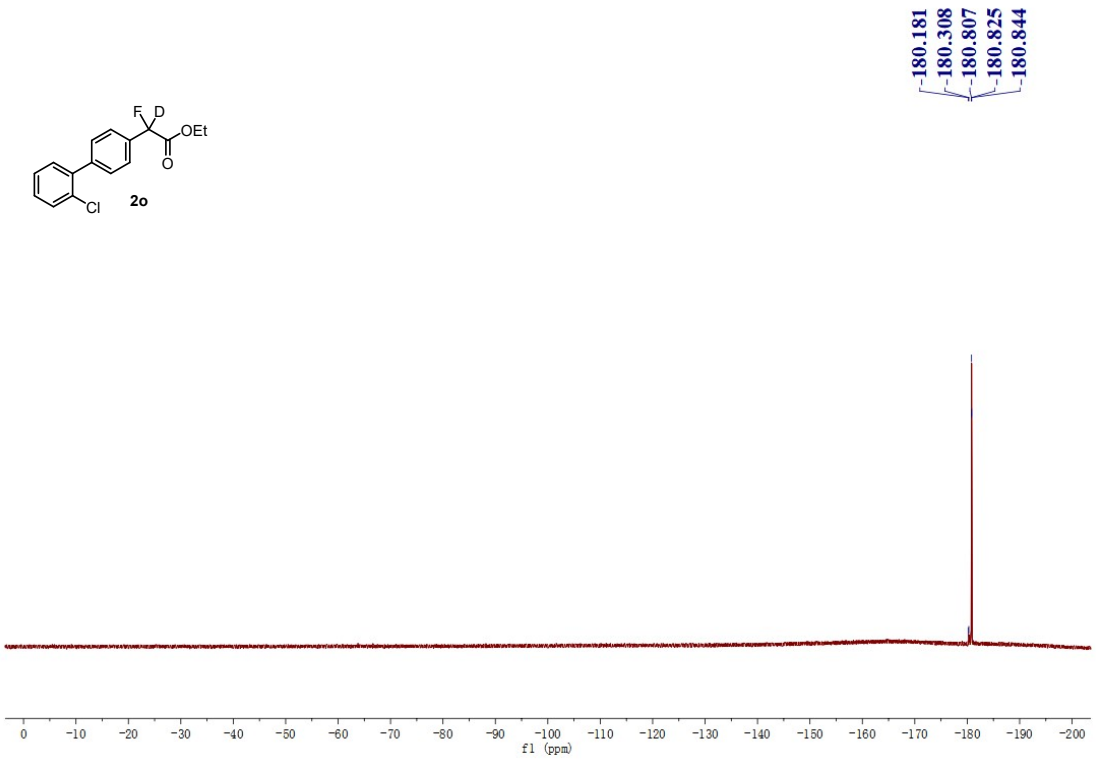




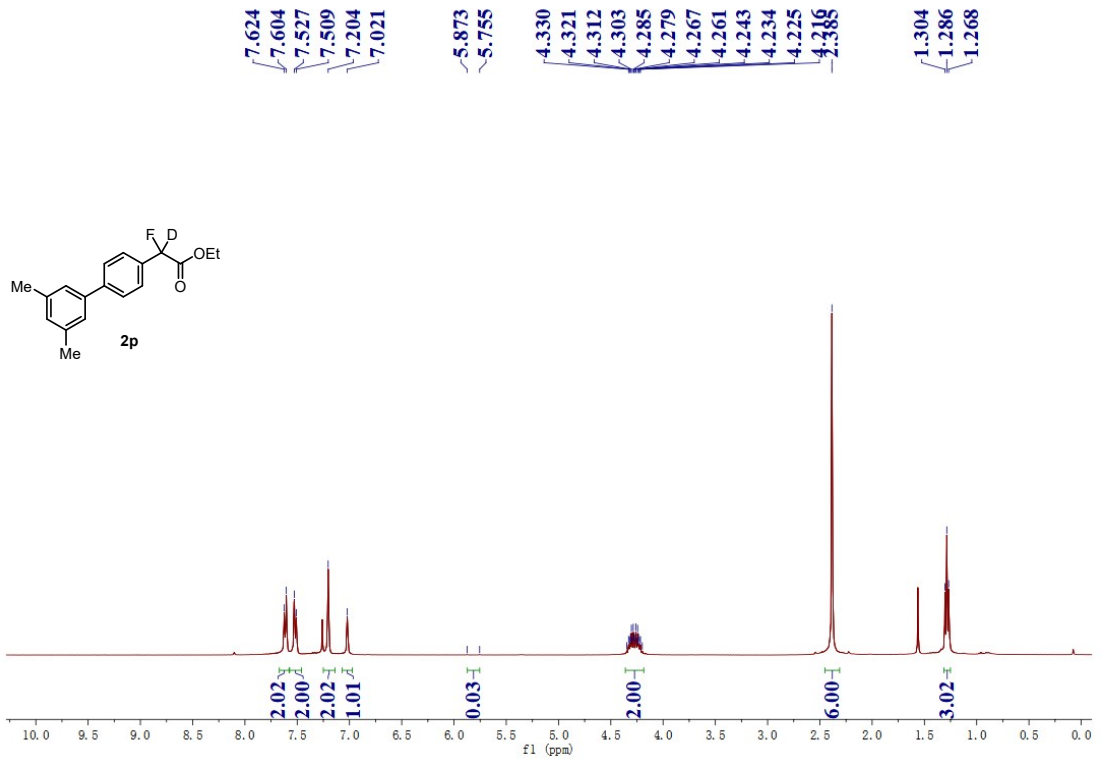


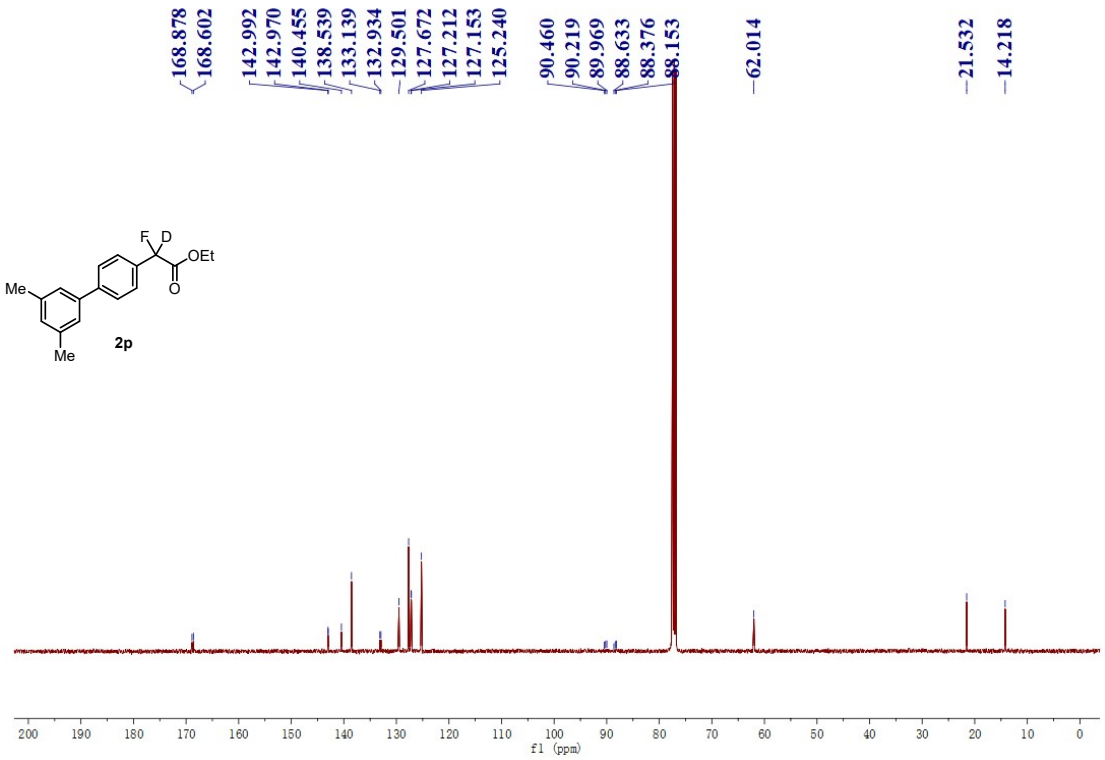


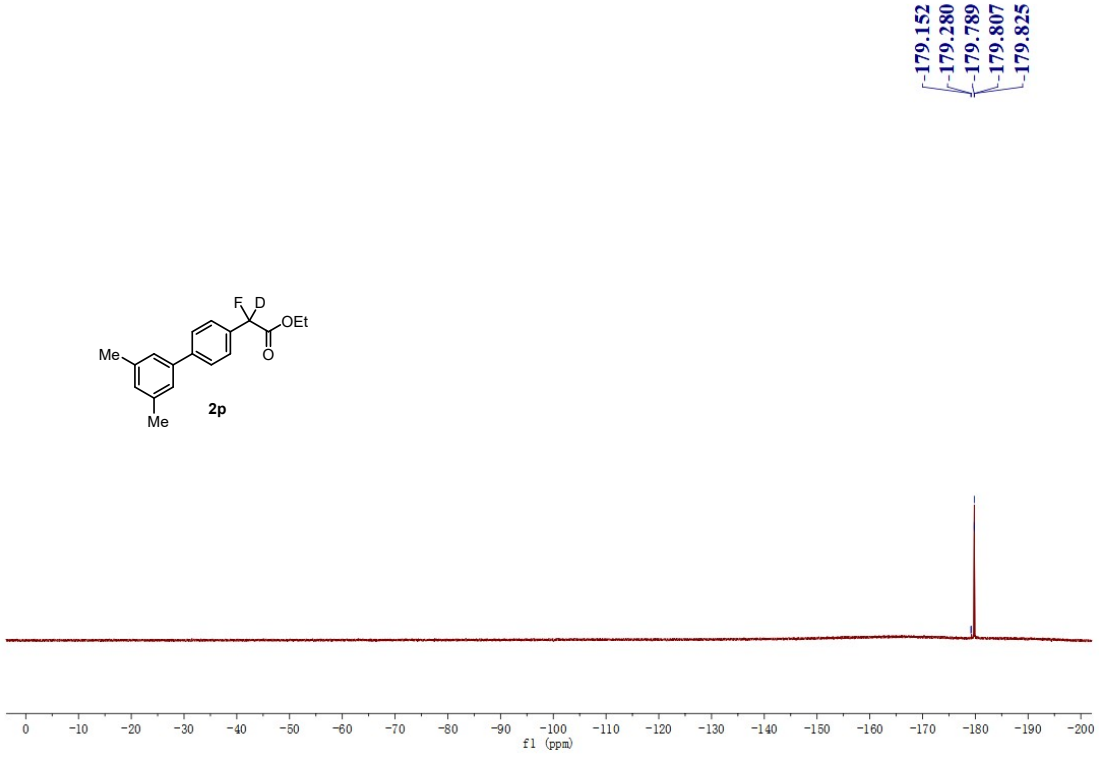




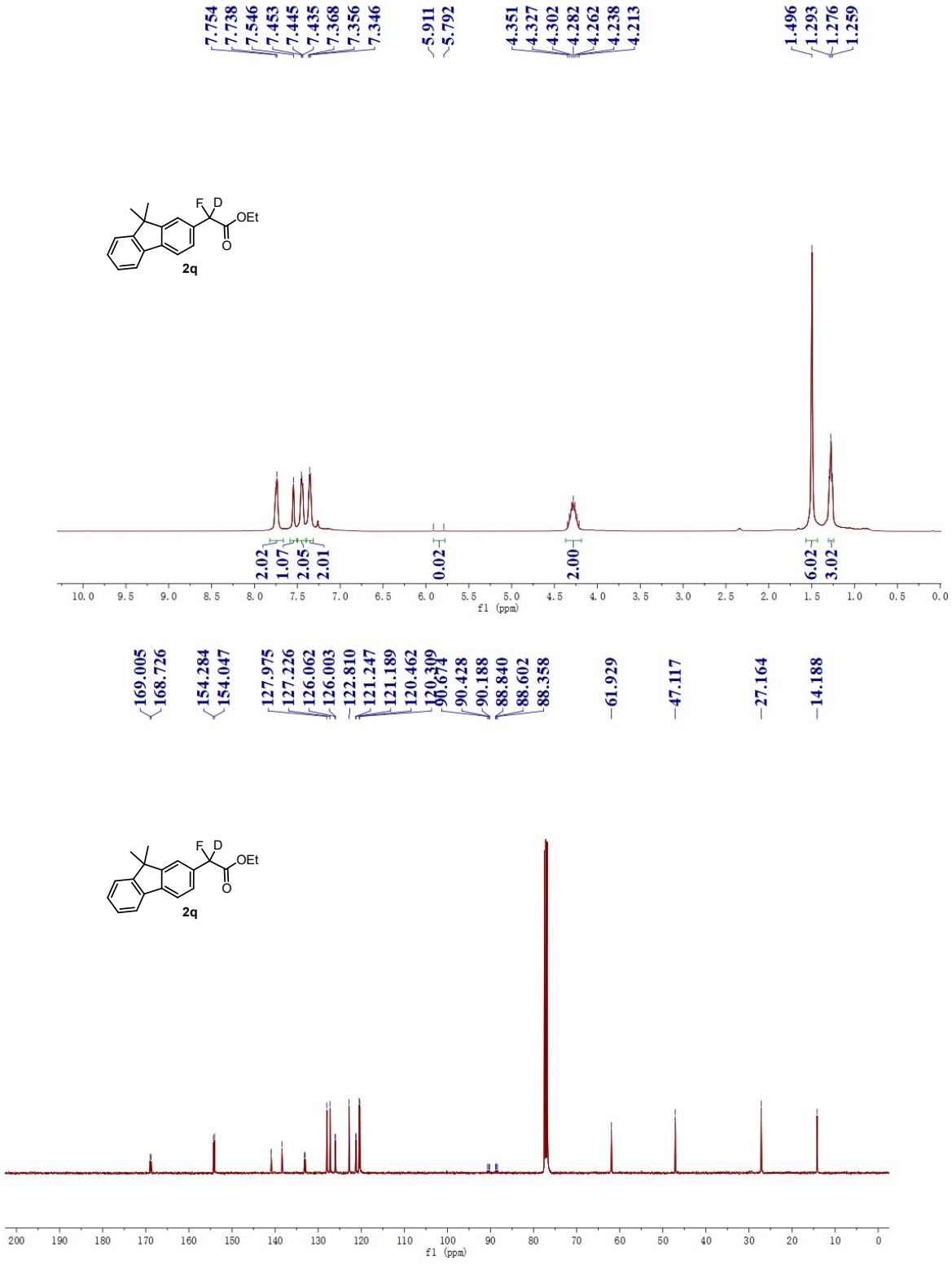
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2p (Chloroform-d)

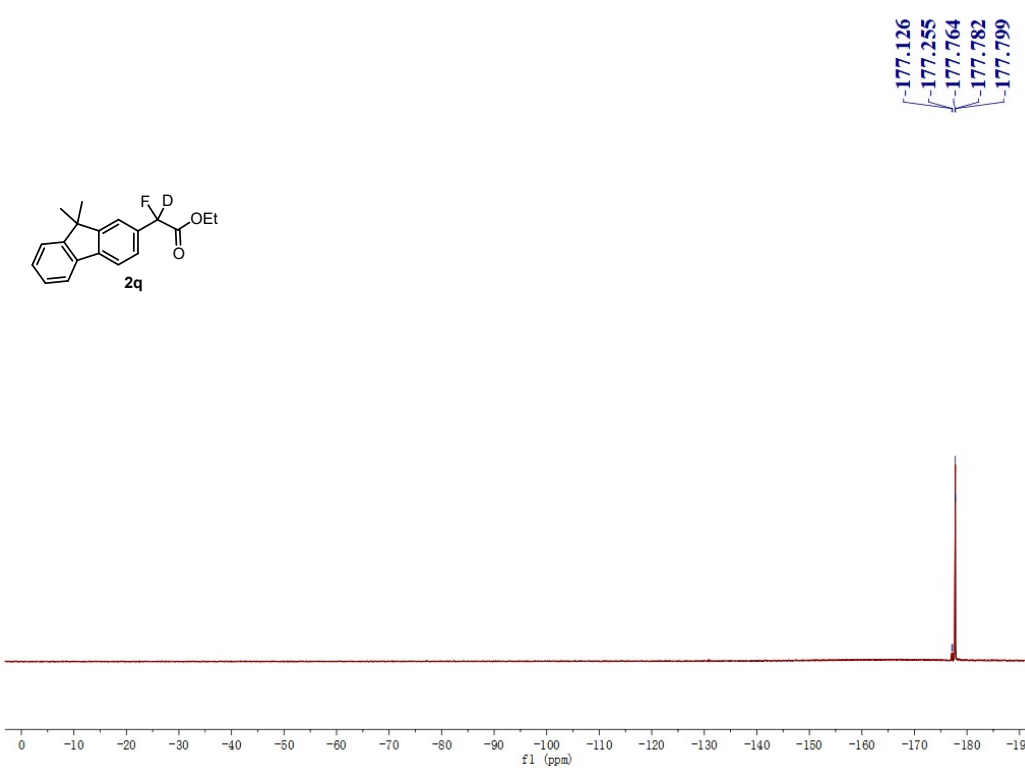



168.878
168.602
142.992
142.970
140.455
138.539
133.139
132.934
129.501
127.672
127.212
127.153
125.240
90.460
90.219
89.969
88.633
88.376
88.153
62.014
21.532
14.218
F
D
OEt
O
Me
Me
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

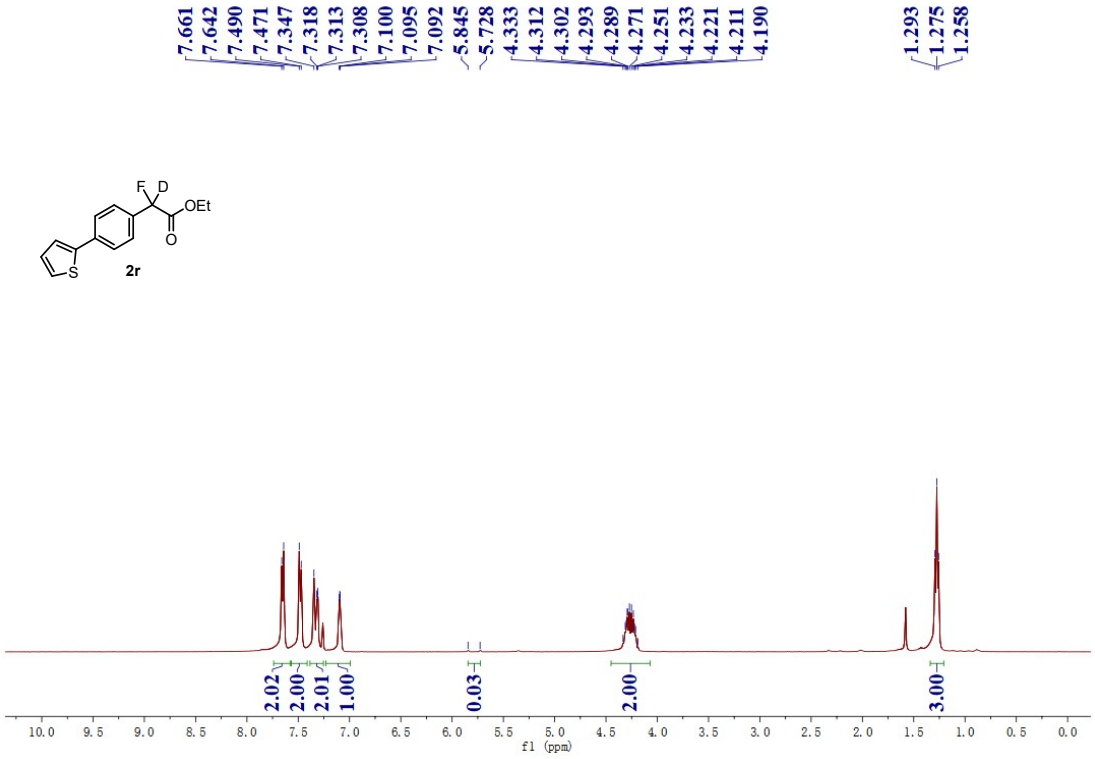

179.152
179.280
179.789
179.807
179.825
F
D
OEt
O
Me
Me
2p
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

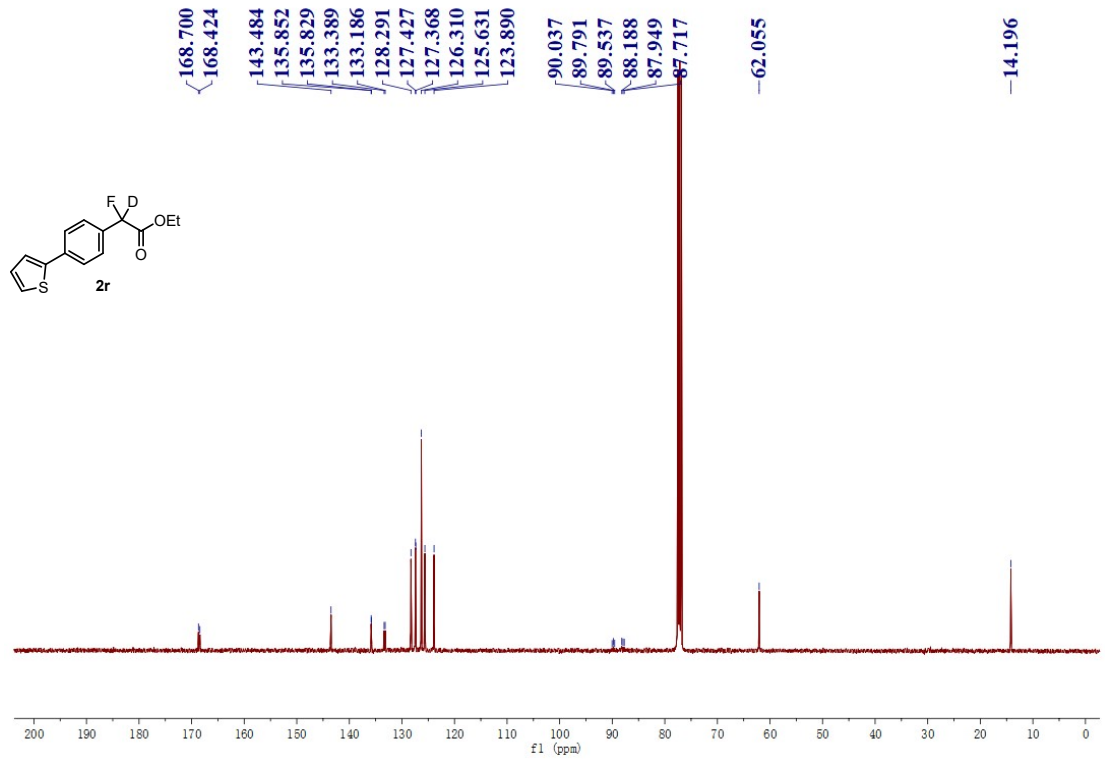
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2q (Chloroform-d)

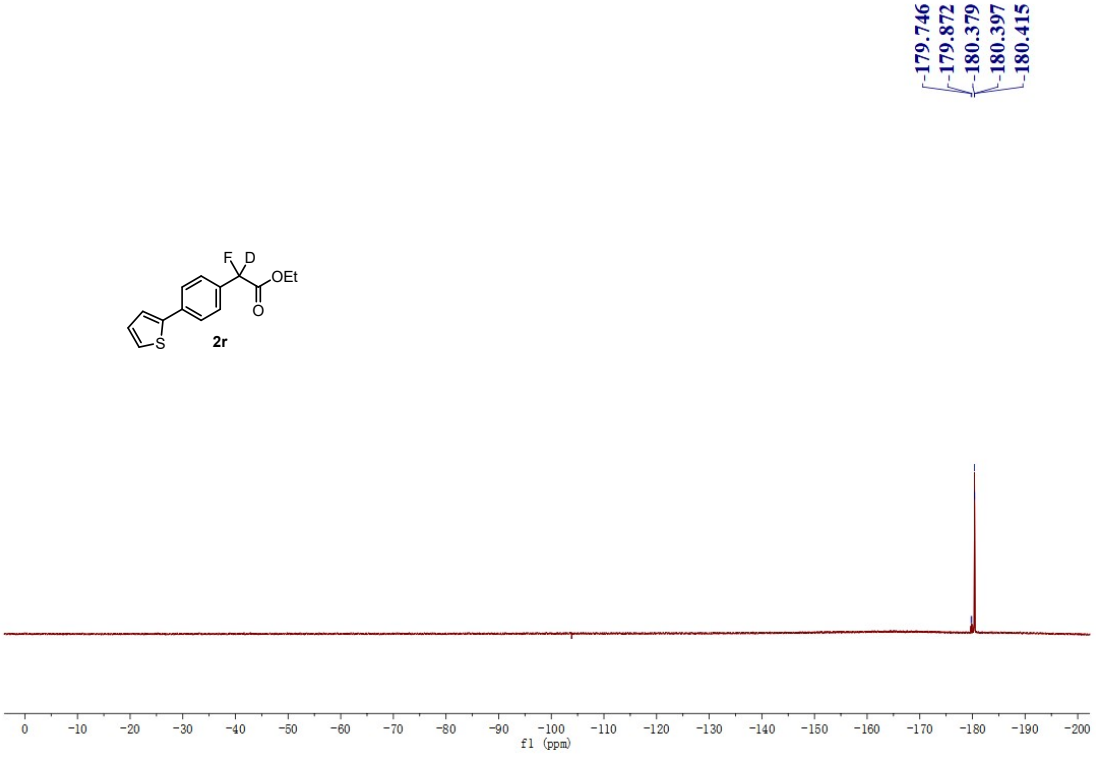




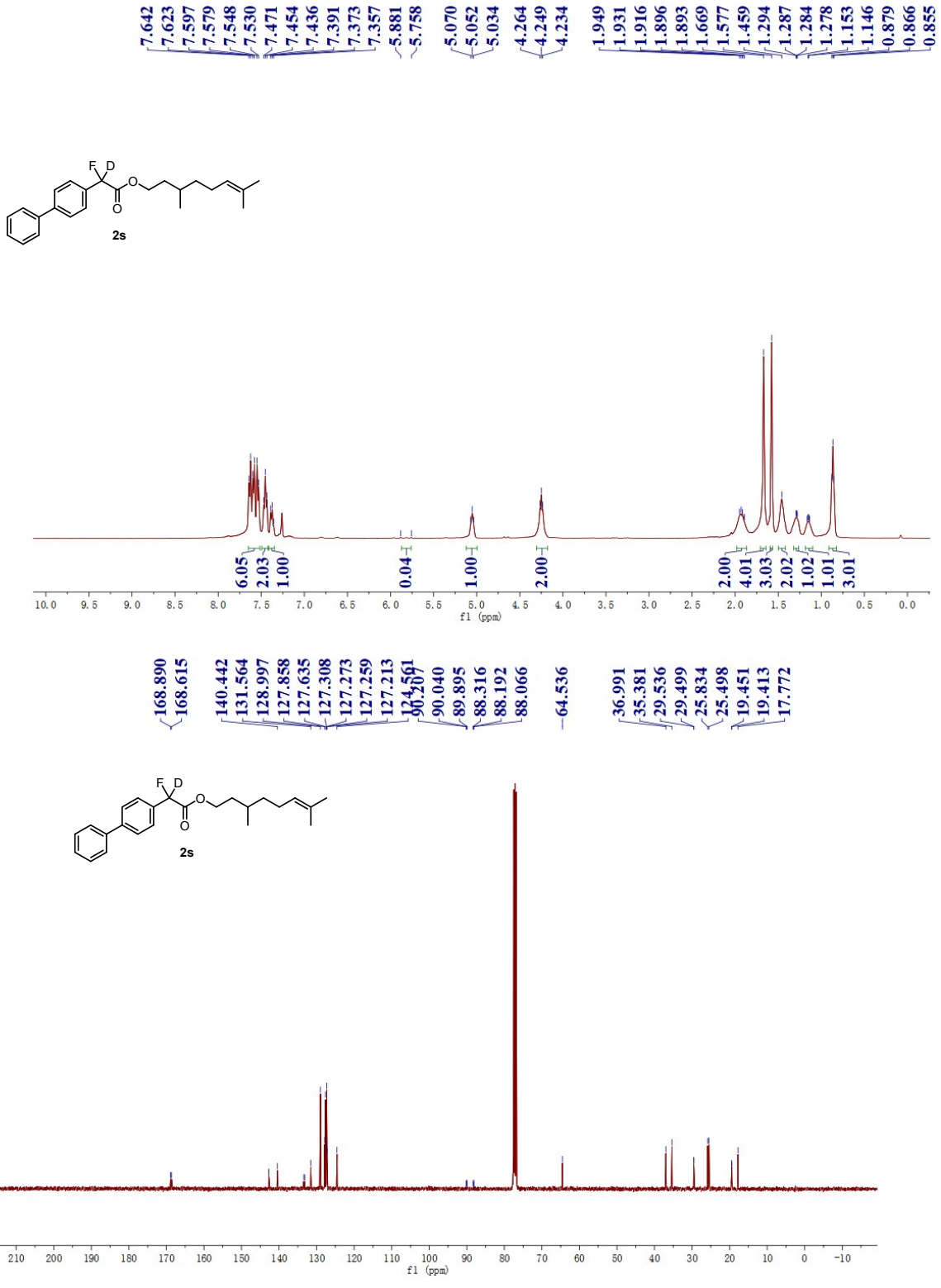
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2r (Chloroform-d)



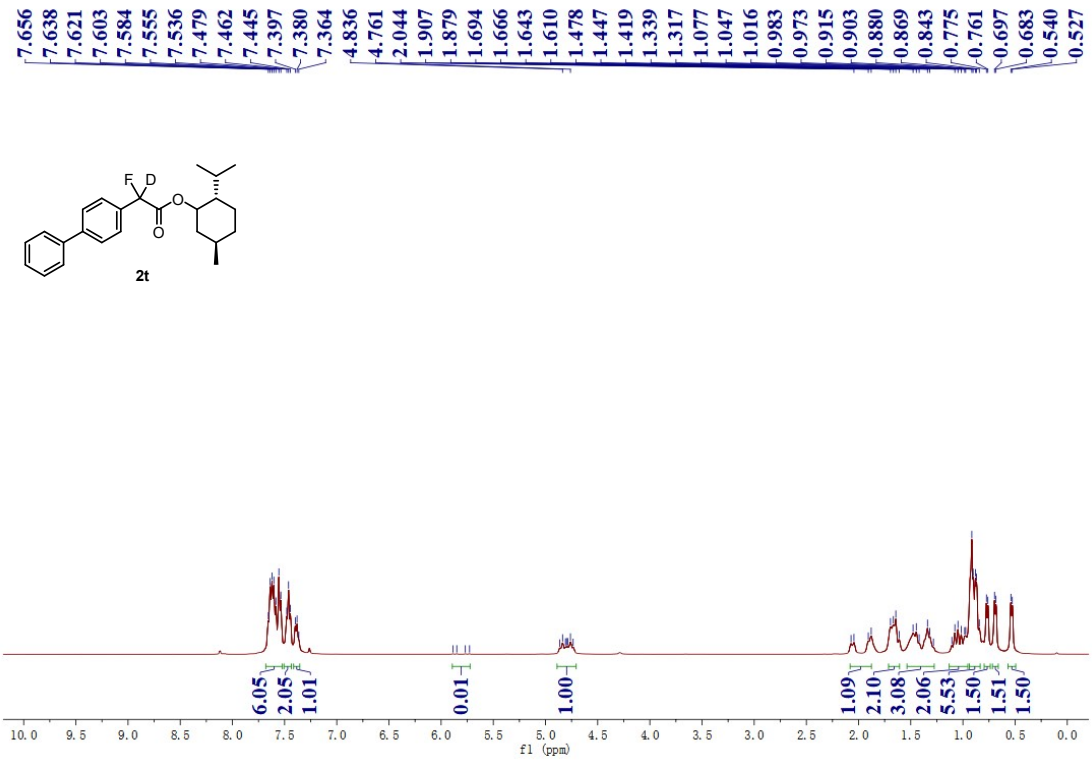

168.700
168.424
143.484
135.852
135.829
133.389
133.186
128.291
127.427
127.368
126.310
125.631
123.890
90.037
89.791
89.537
88.188
87.949
87.717
62.055
14.196
F
D
OEt
O
S
2r
f1 (ppm)

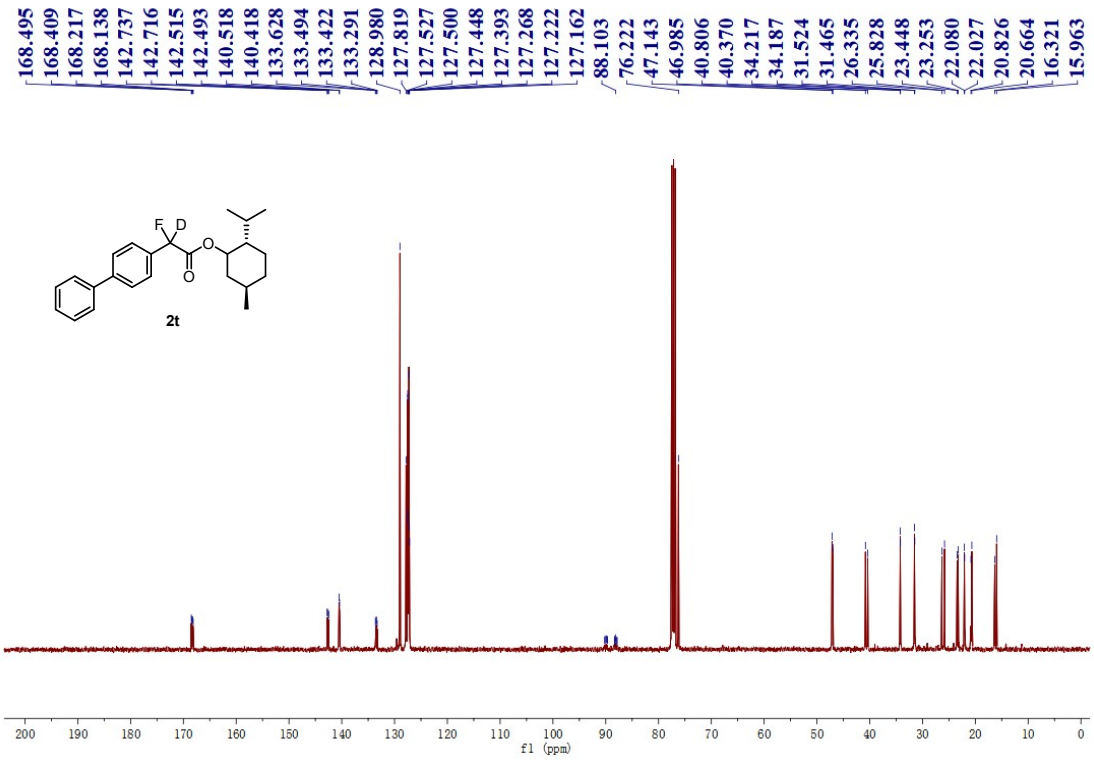

179.746
179.872
180.379
180.397
180.415
F
D
OEt
O
S
2r
f1 (ppm)

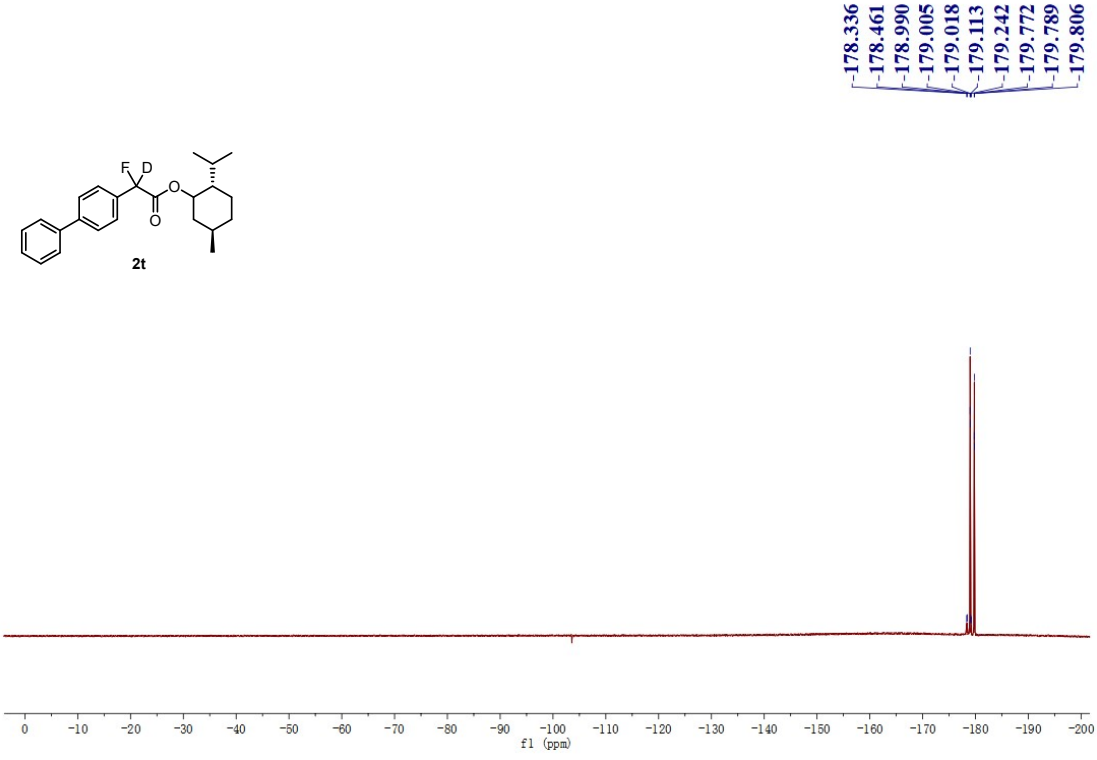
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2s (Chloroform-d)



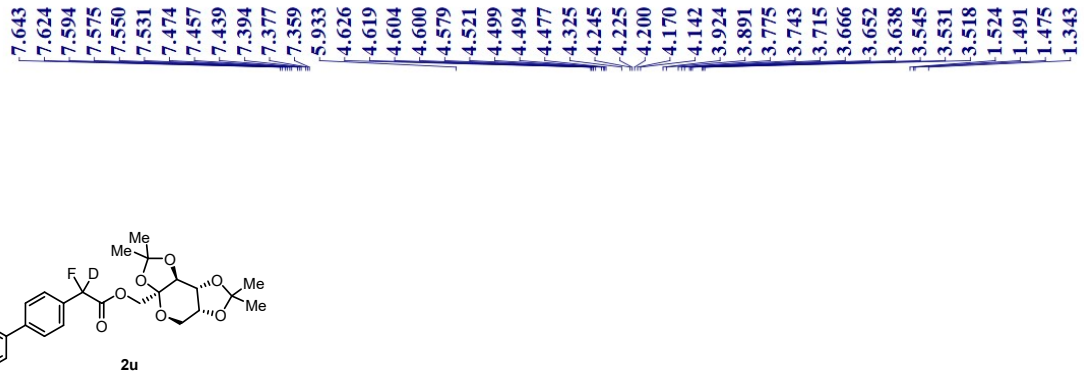
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2t (Chloroform-d)



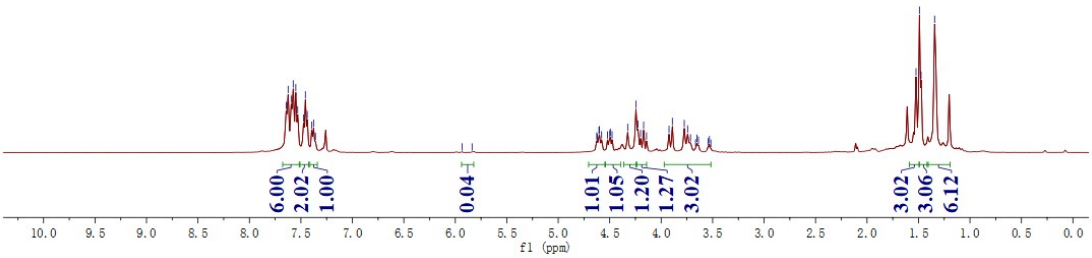

168.495
168.409
168.217
168.138
142.737
142.716
142.515
142.493
140.518
140.418
133.628
133.494
133.422
133.291
128.980
127.819
127.527
127.500
127.448
127.393
127.268
127.222
127.162
88.103
76.222
47.143
46.985
40.806
40.370
34.217
34.187
31.524
31.465
26.335
25.828
23.448
23.253
22.080
22.027
20.826
20.664
16.321
15.963
F
D
O
O
2t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

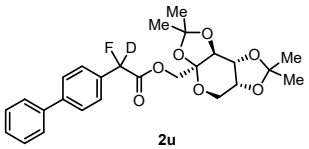

178.336
178.461
178.990
179.005
179.018
179.113
179.242
179.772
179.789
179.806
F
D
O
O
2t
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2u (Chloroform-d)

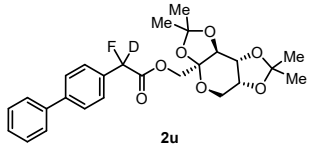


2u

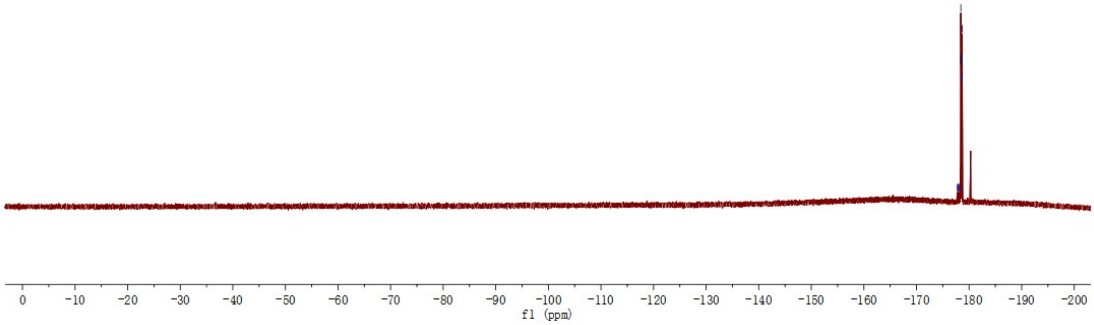




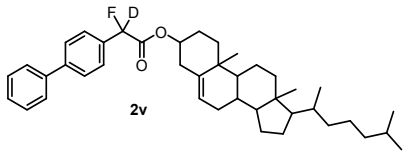
2u



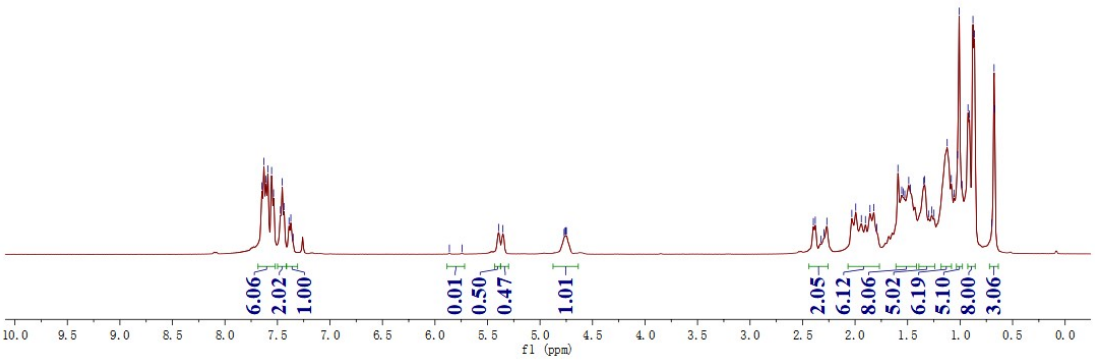
2u

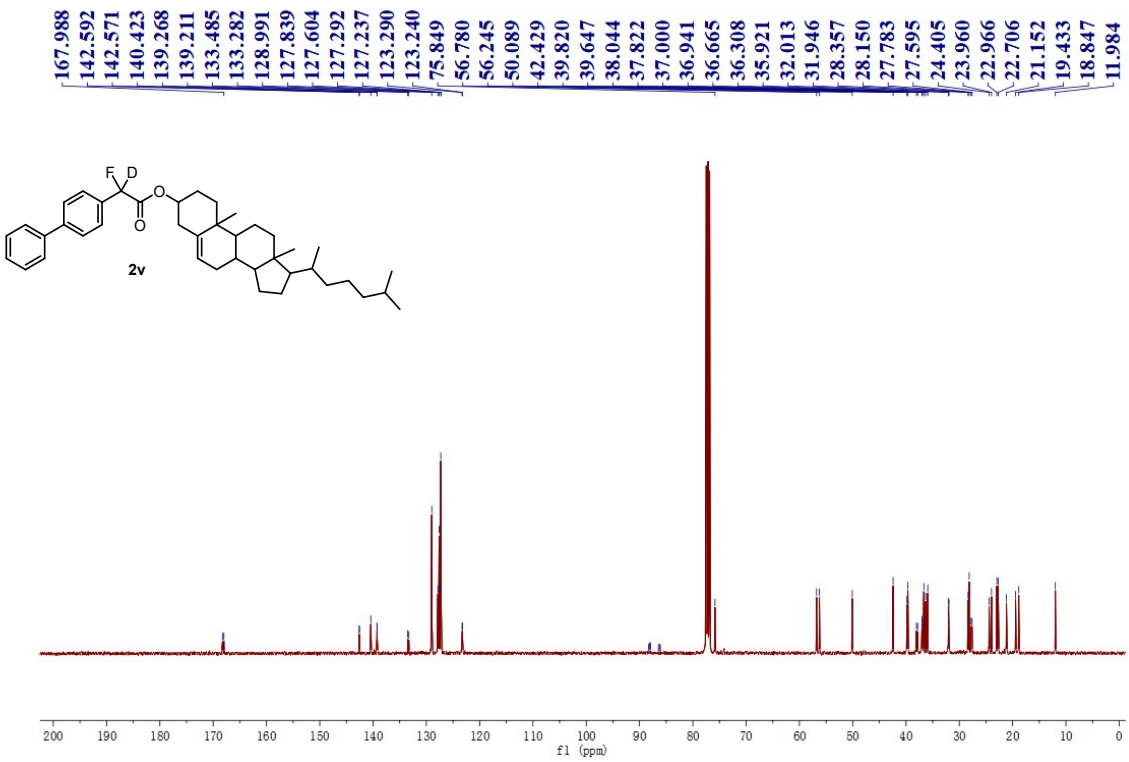


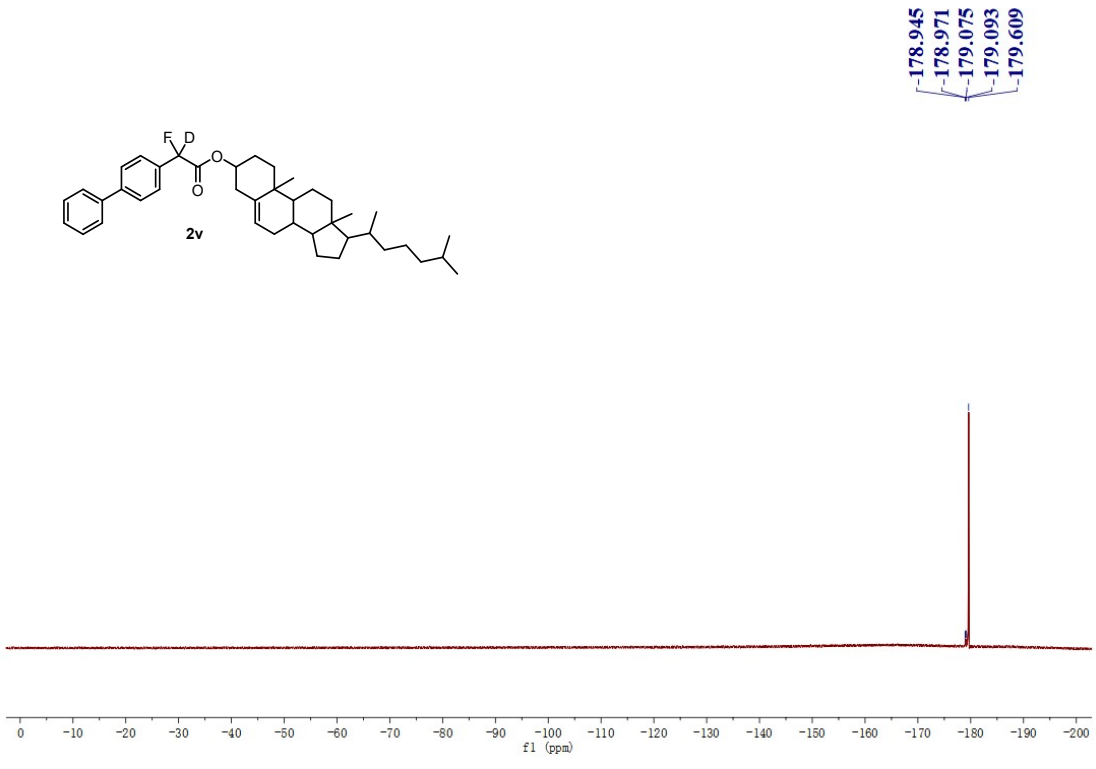
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2v (Chloroform-d)



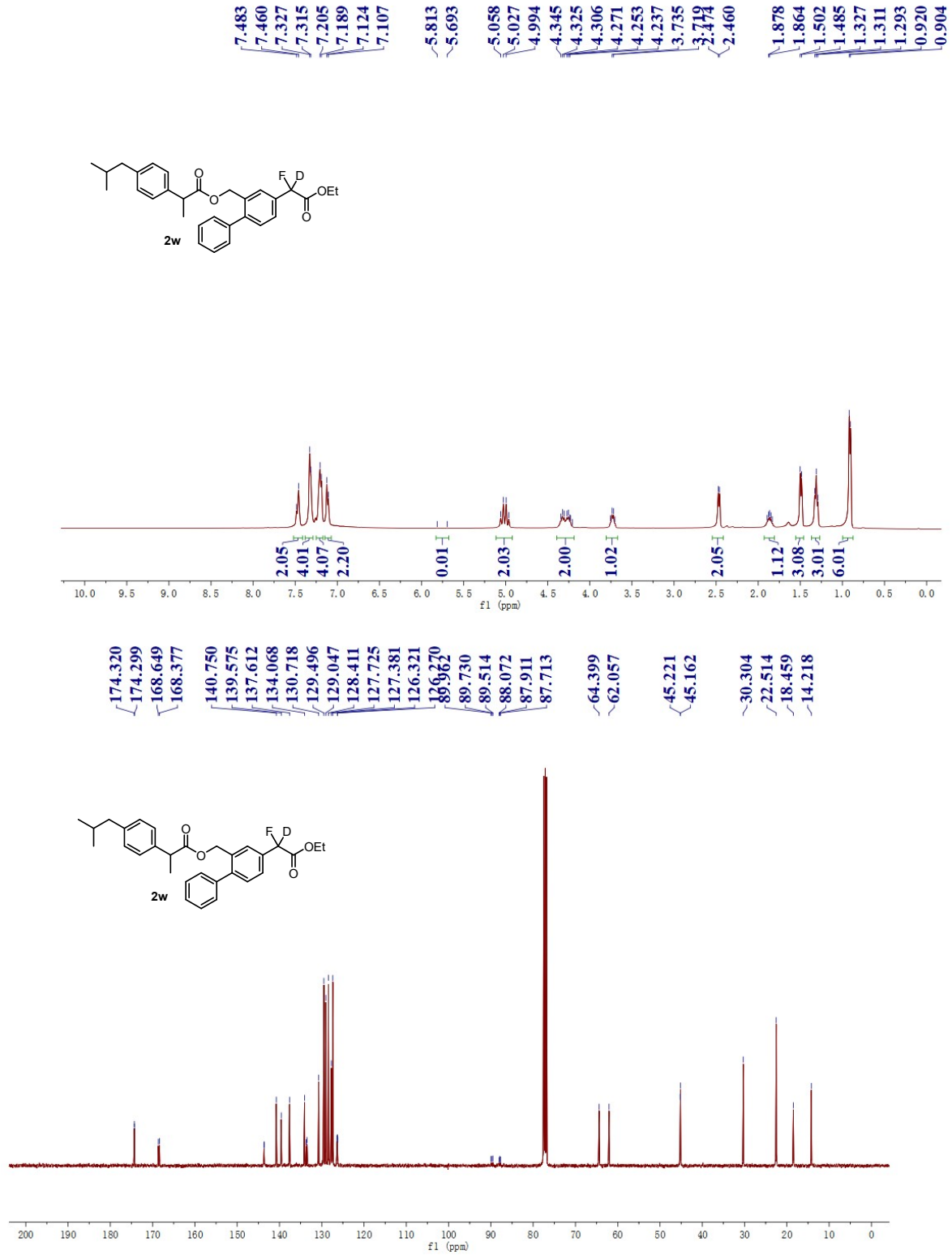
2v

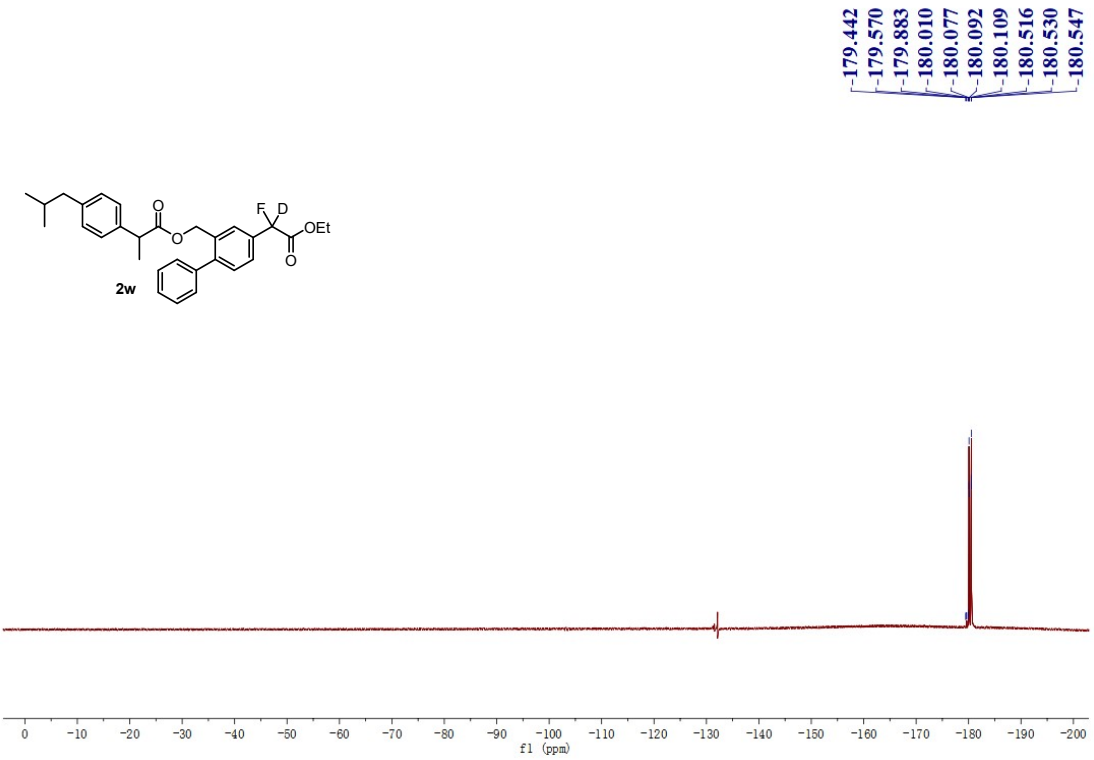



167.988
142.592
142.571
140.423
139.268
139.211
133.485
133.282
128.991
127.839
127.604
127.292
127.237
123.290
123.240
75.849
56.780
56.245
50.089
42.429
39.820
39.647
38.044
37.822
37.000
36.941
36.665
36.308
35.921
32.013
31.946
28.357
28.150
27.783
27.595
24.405
23.960
22.966
22.706
21.152
19.433
18.847
11.984
F
D
O
O
2v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

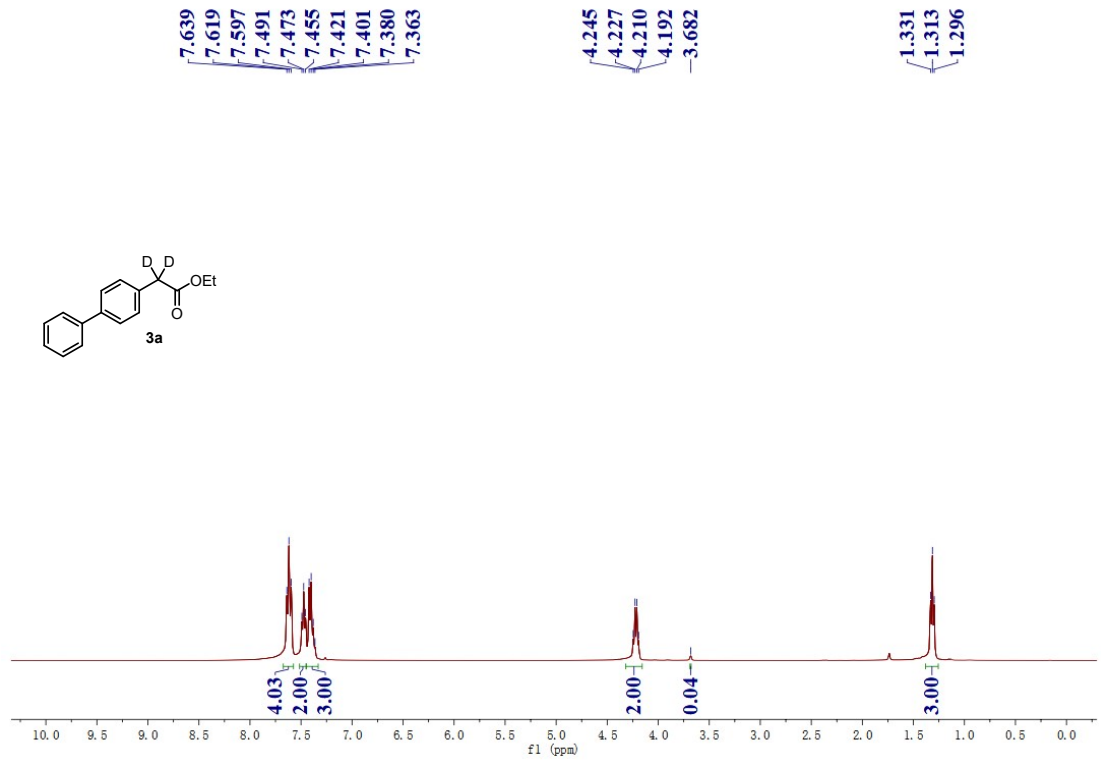

178.945
178.971
179.075
179.093
179.609
F
D
O
O
2v
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

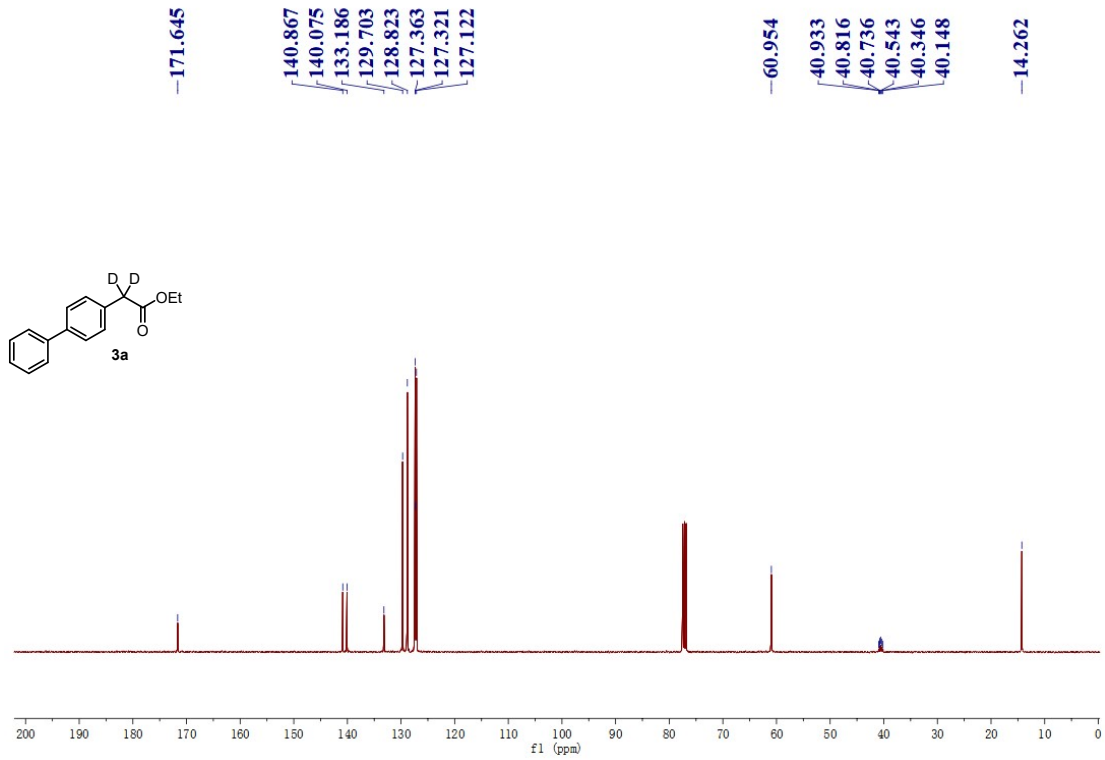
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 2w (Chloroform-d)



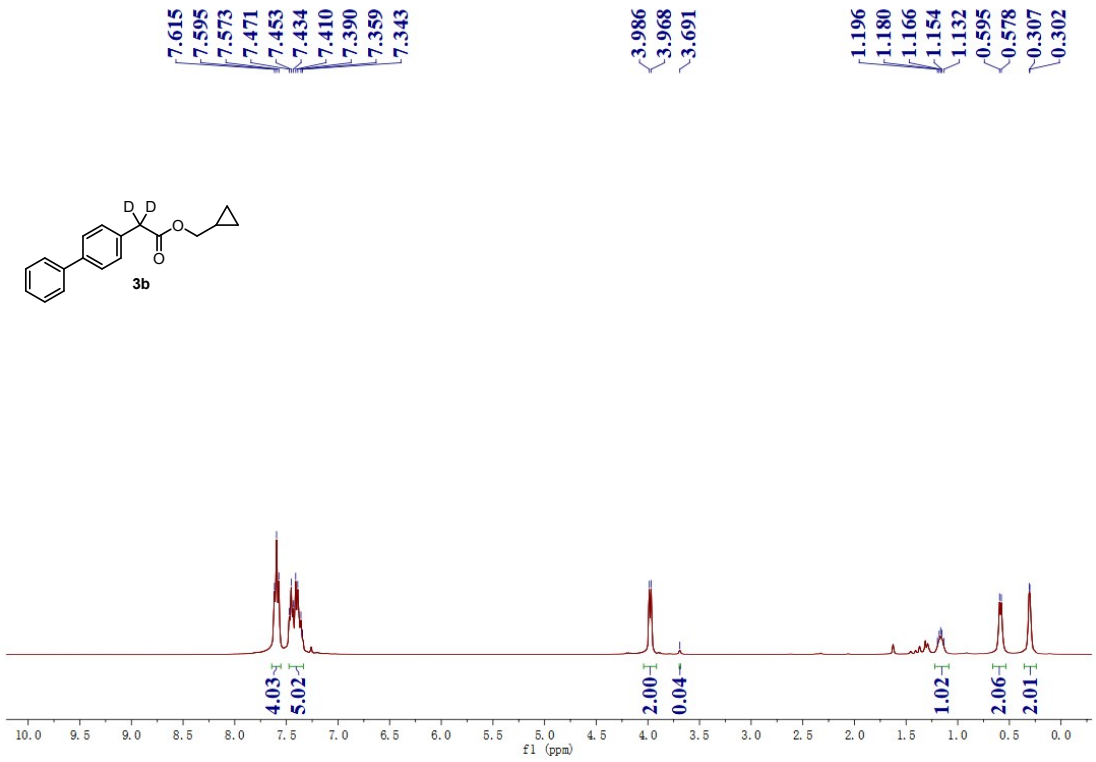


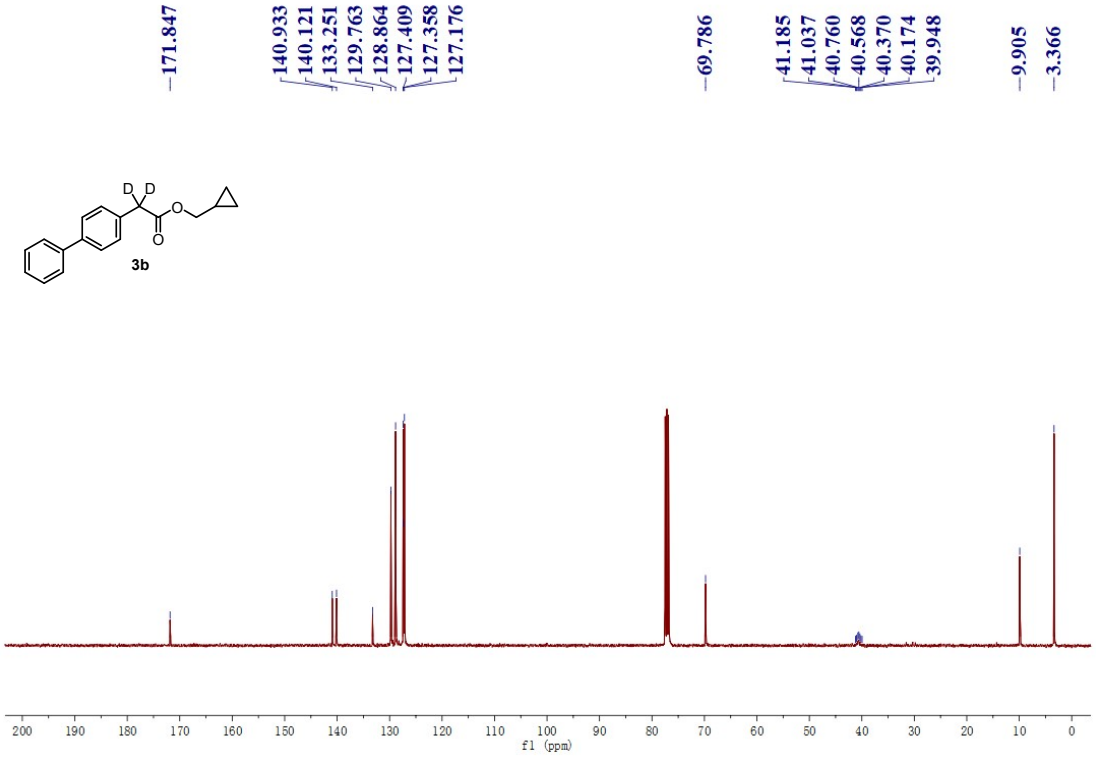
^{1}H and ^{13}C NMR spectra for compound 3a (Chloroform-d)



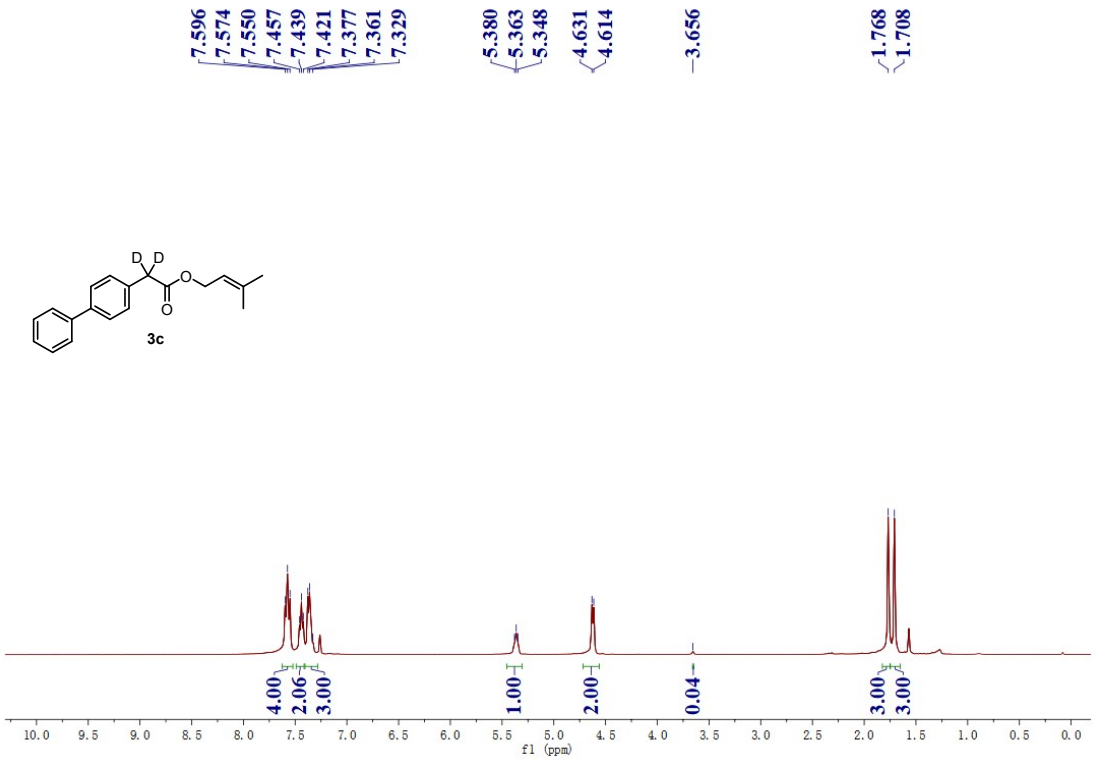


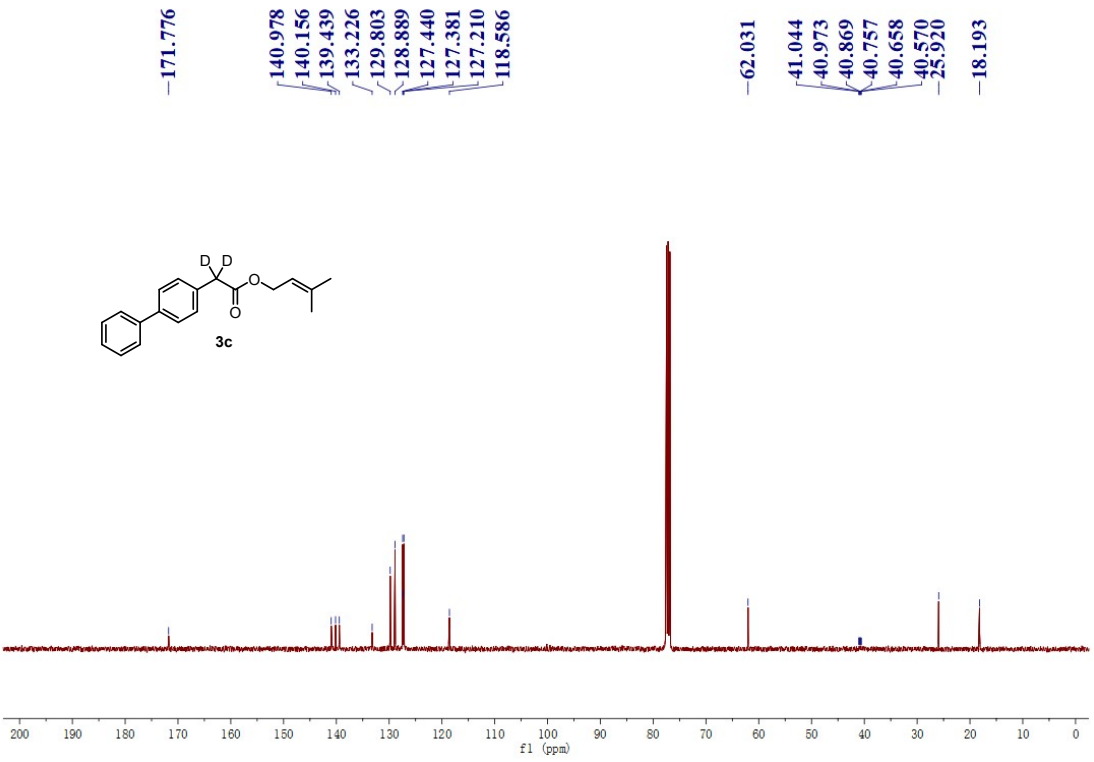
^{1}H and ^{13}C NMR spectra for compound 3b (Chloroform-d)



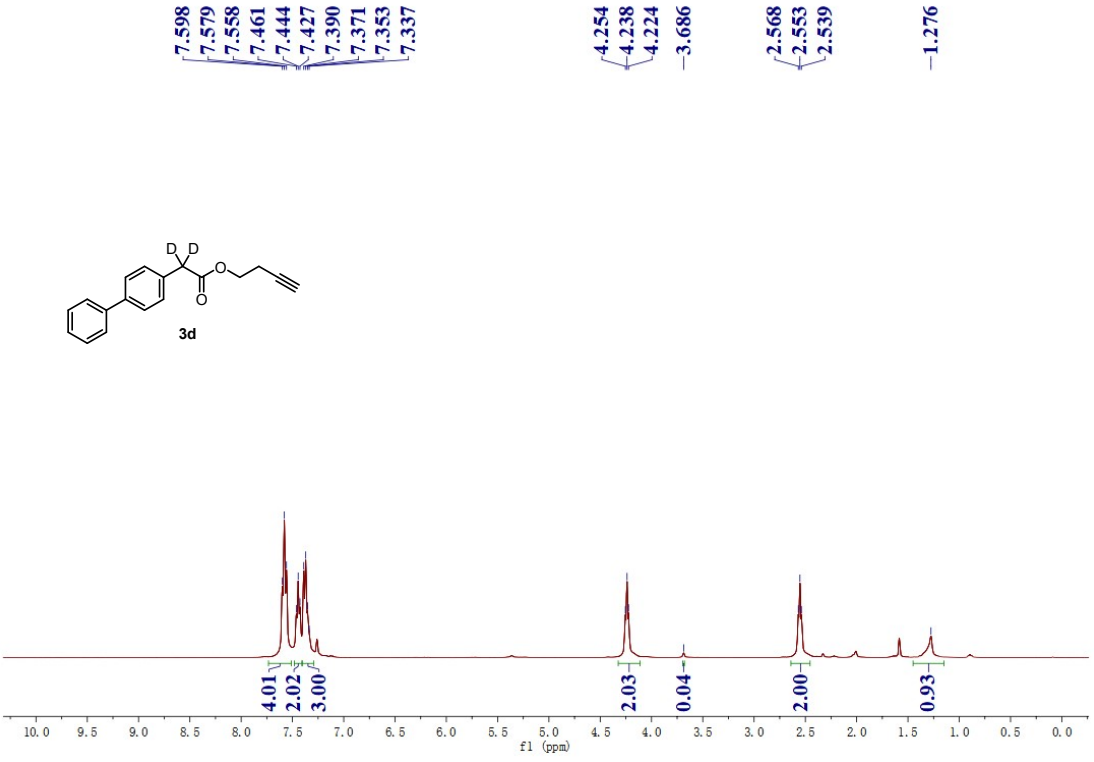


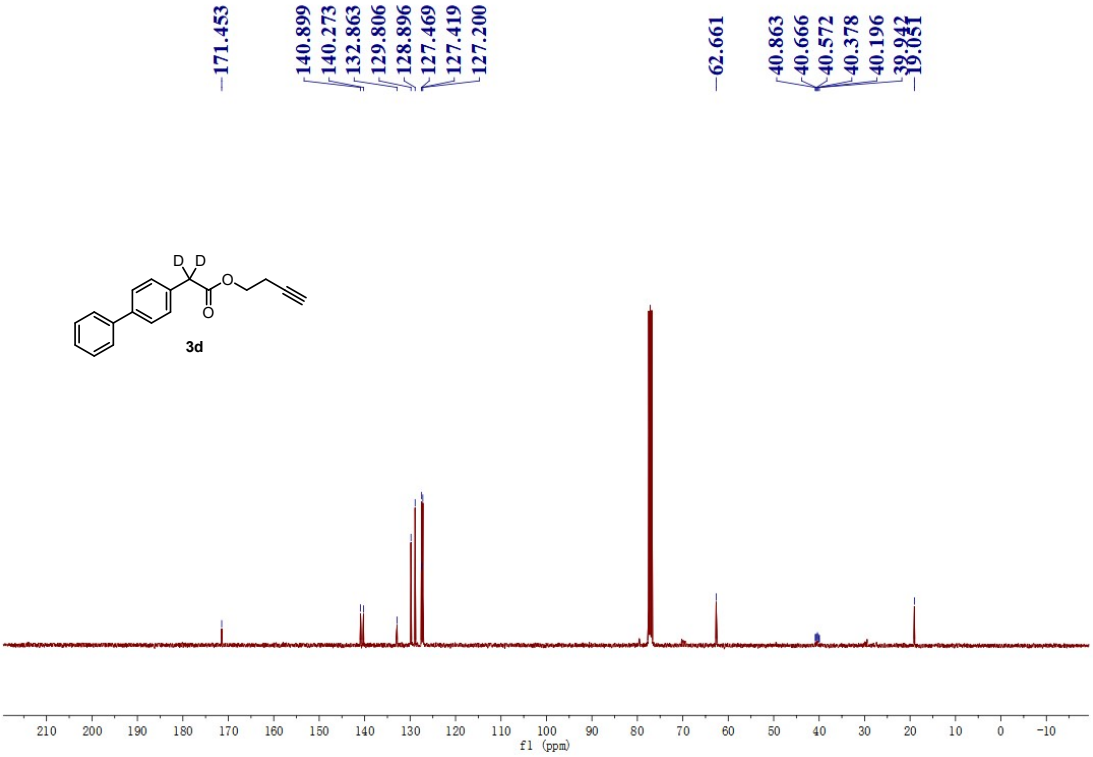
^{1}H and ^{13}C NMR spectra for compound 3c (Chloroform-d)



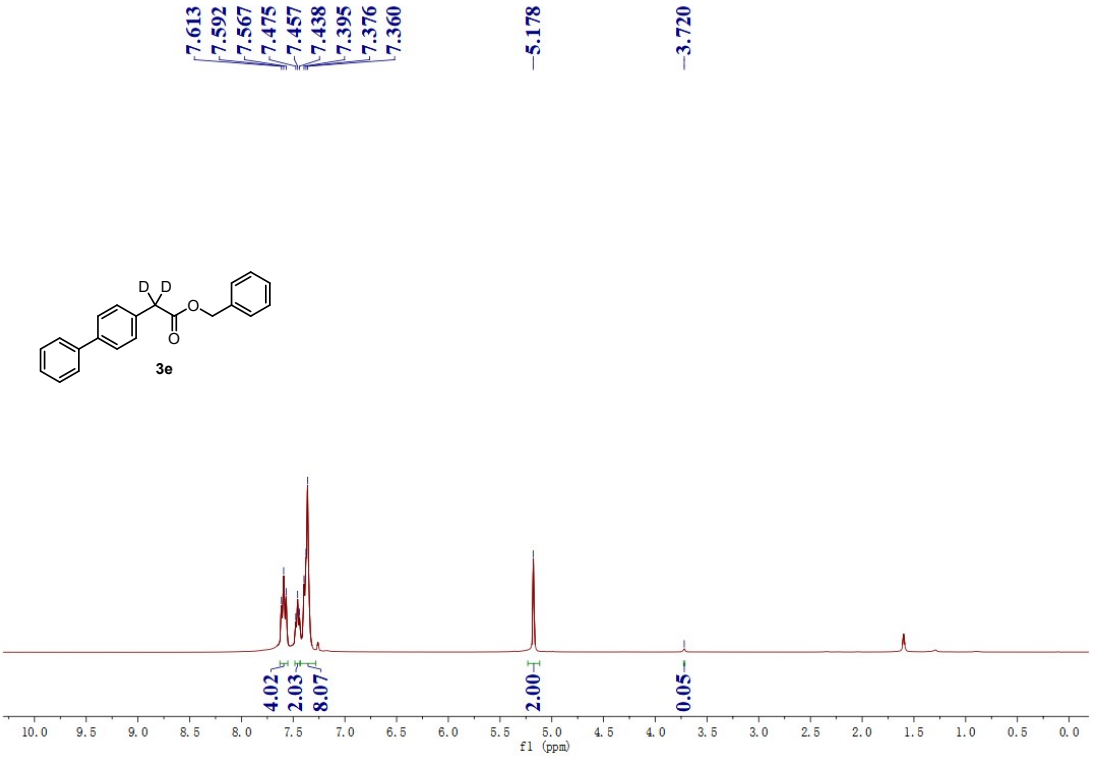


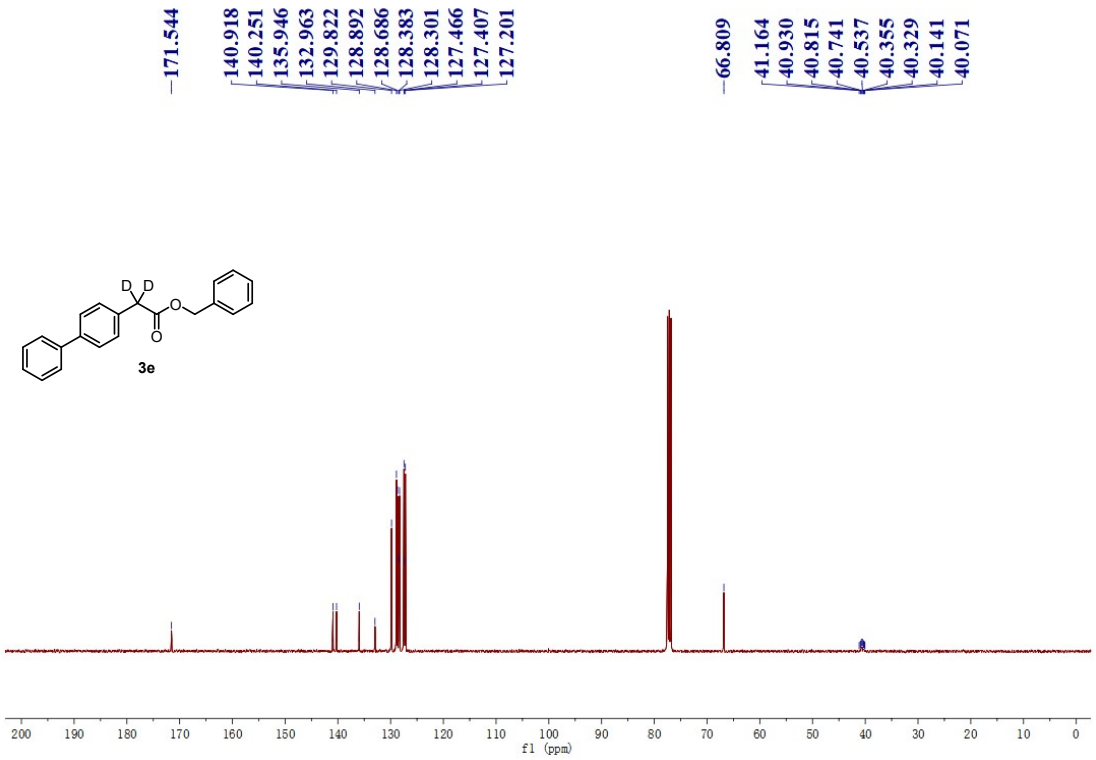
^{1}H and ^{13}C NMR spectra for compound 3d (Chloroform-d)



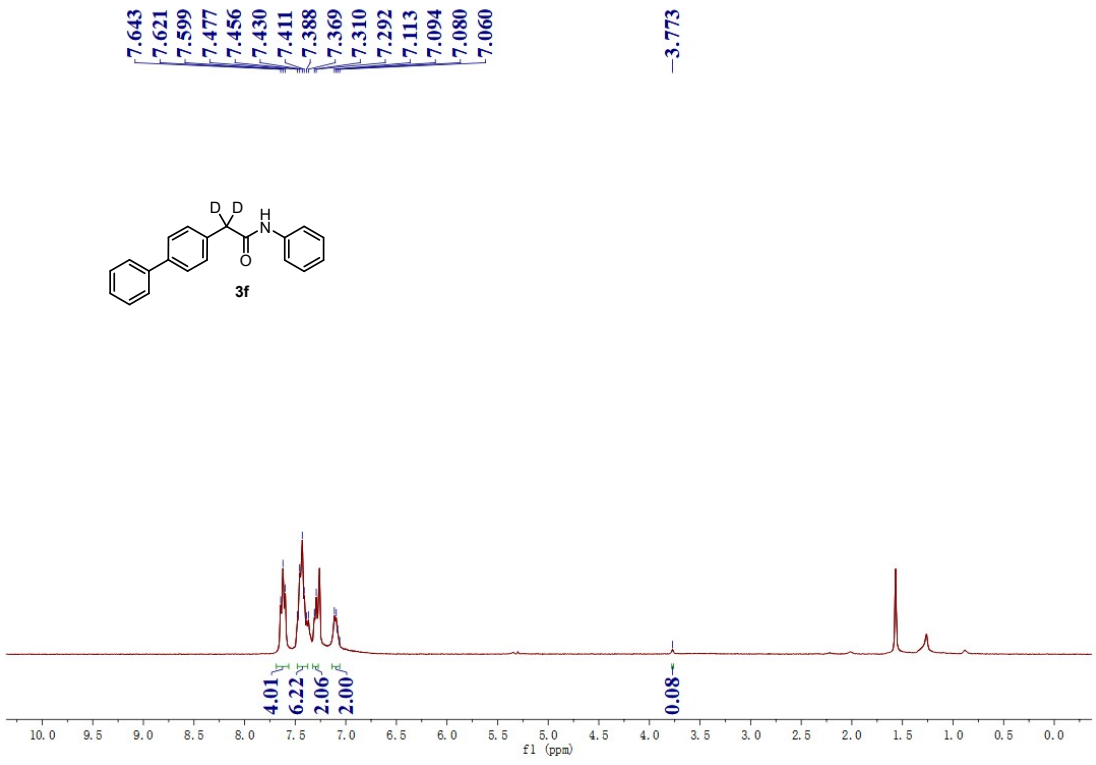


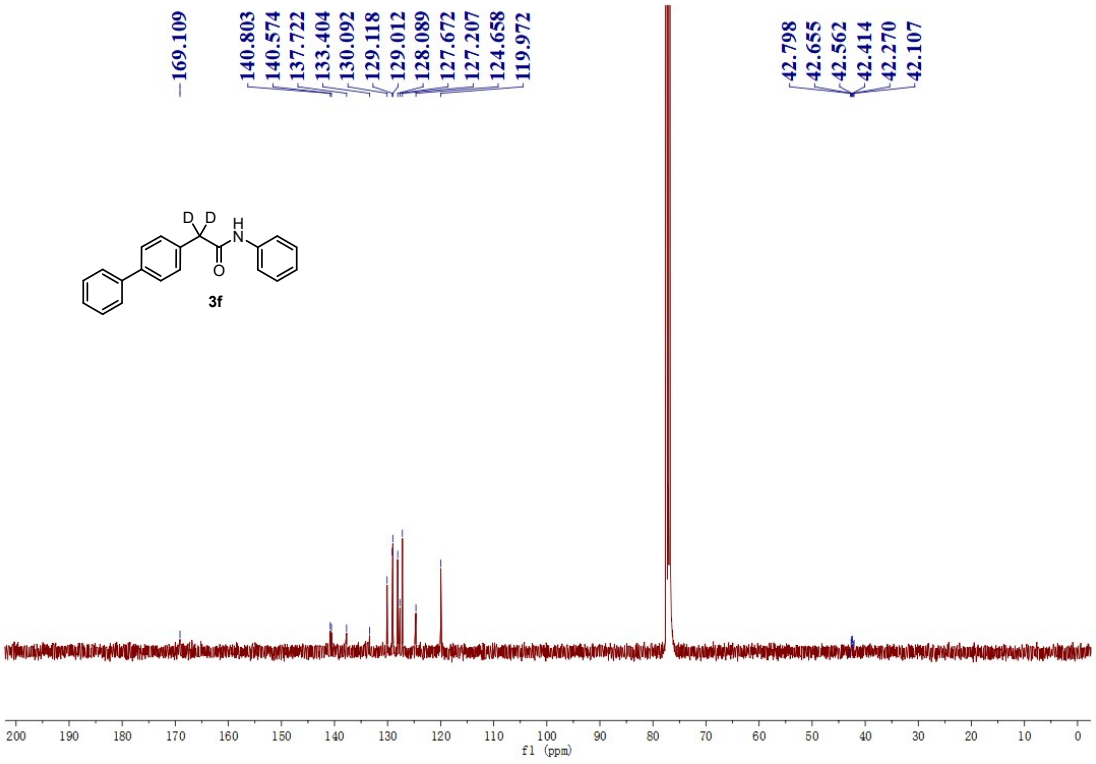
^{1}H and ^{13}C NMR spectra for compound 3e (Chloroform-d)



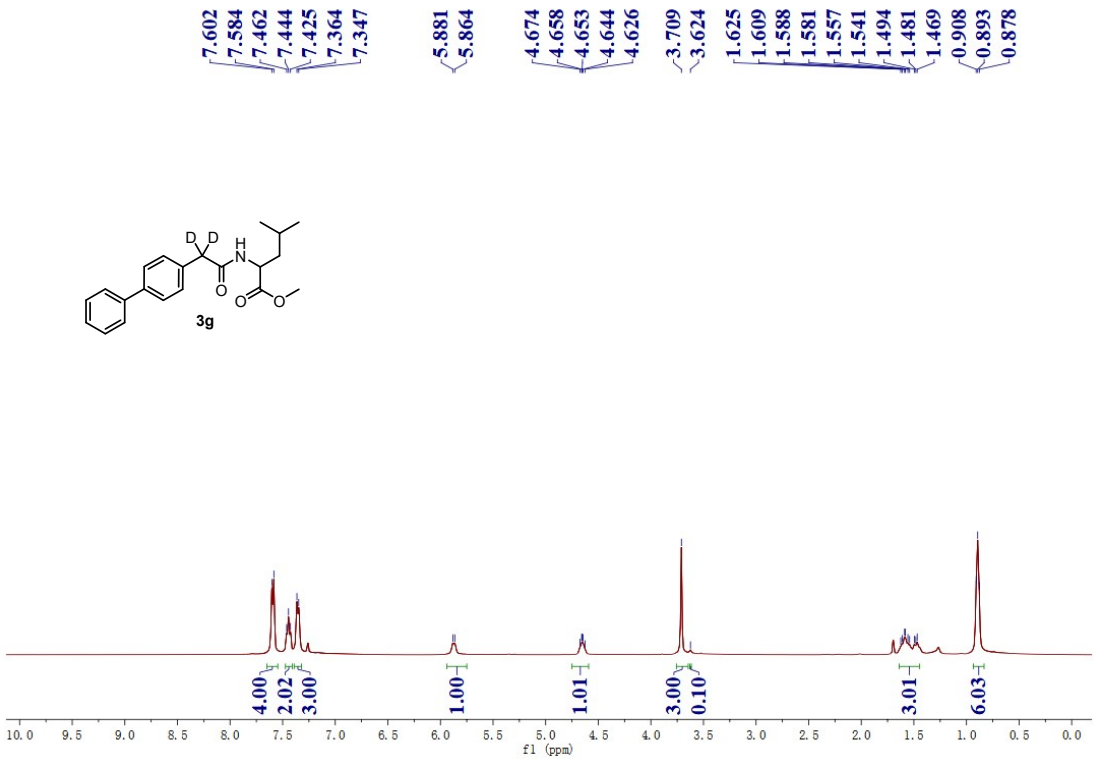


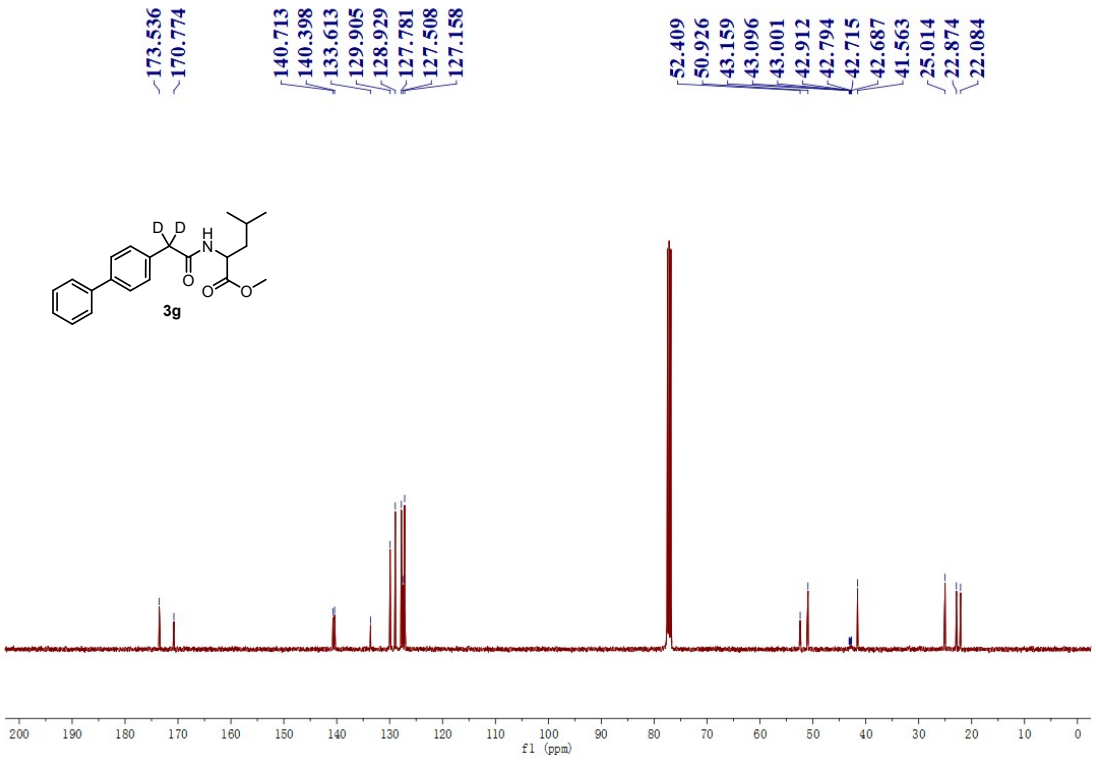
^{1}H and ^{13}C NMR spectra for compound 3f (Chloroform-d)



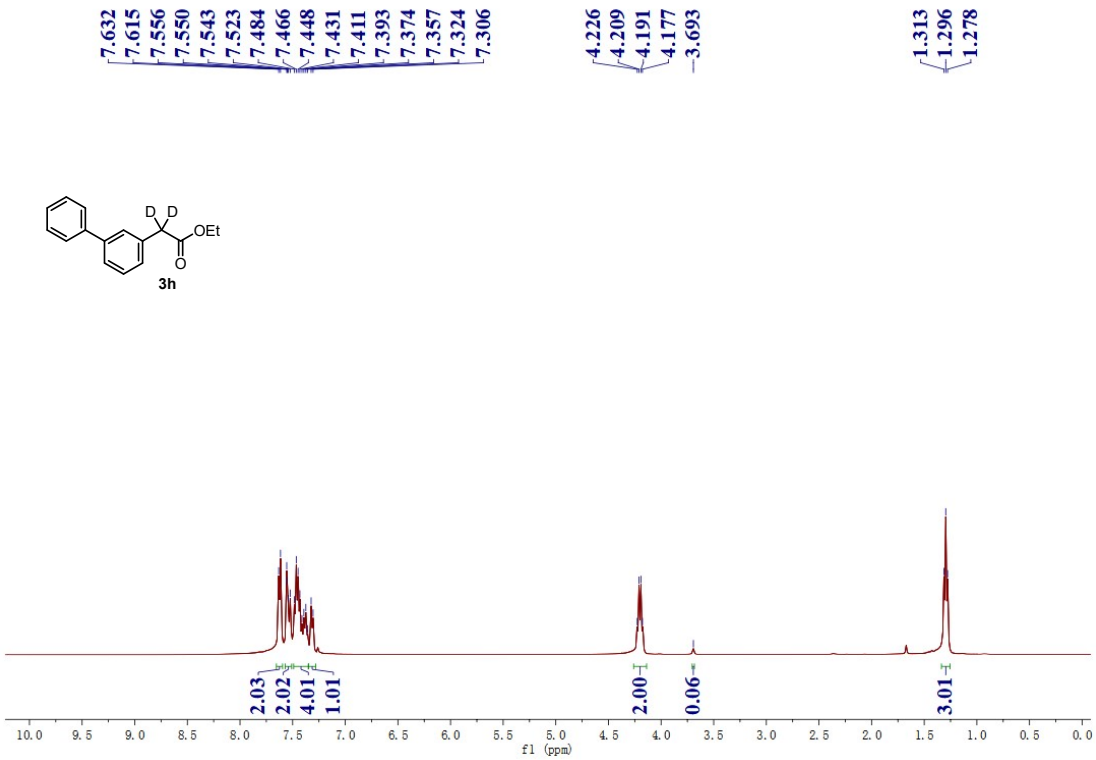


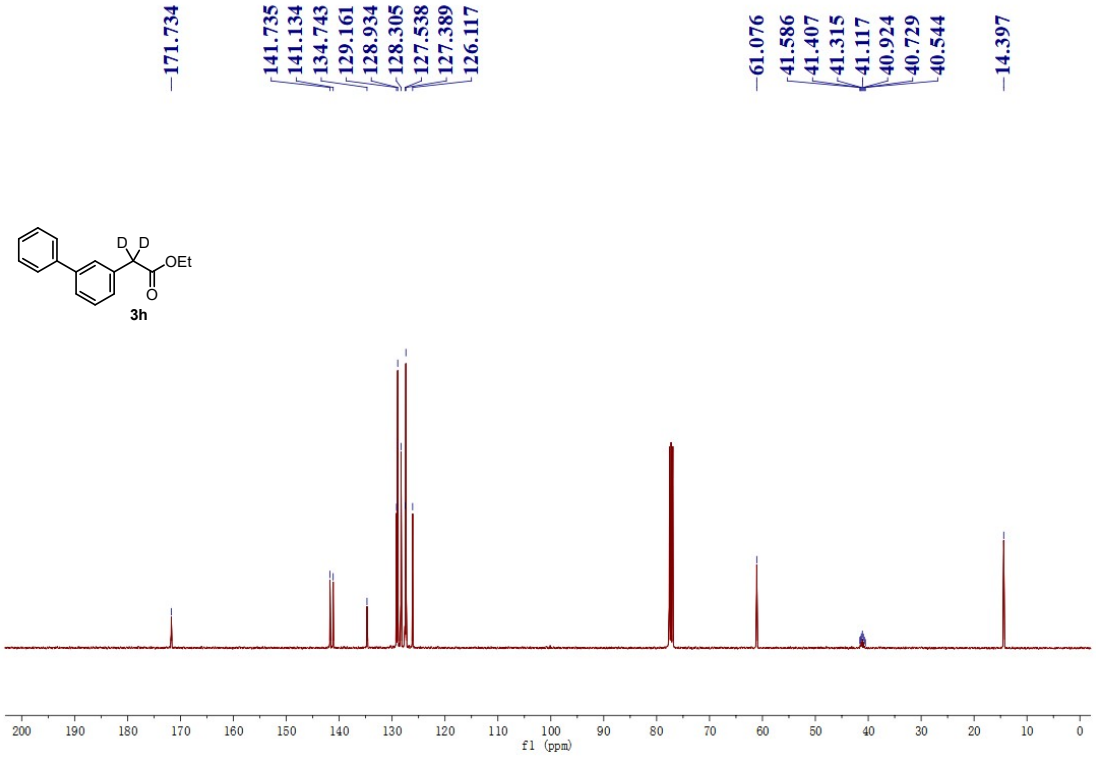
^{1}H and ^{13}C NMR spectra for compound 3g (Chloroform-d)



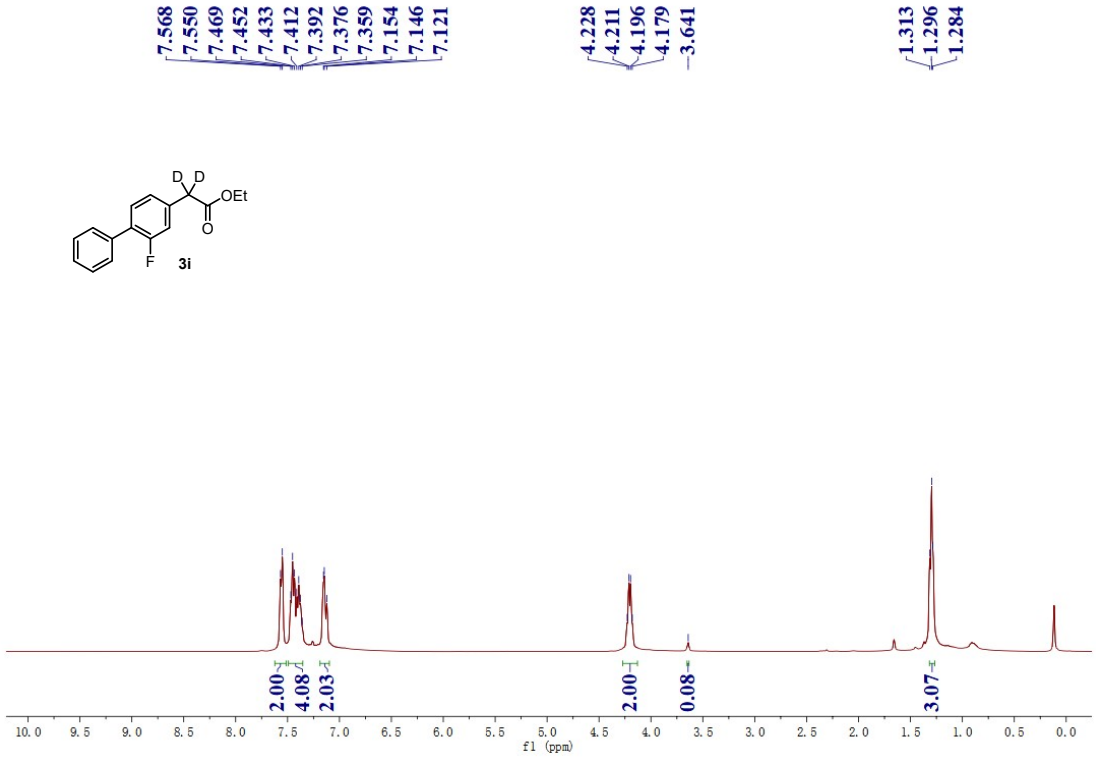


^{1}H and ^{13}C NMR spectra for compound 3h (Chloroform-d)

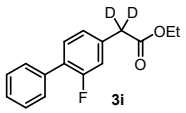




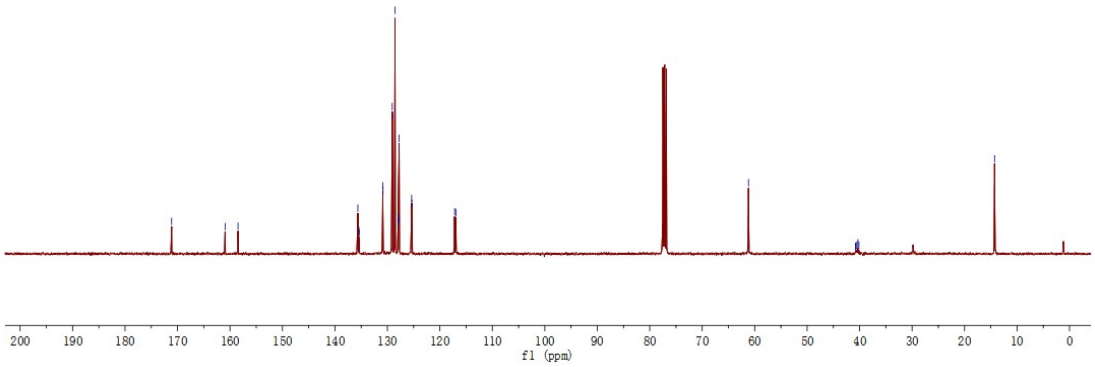
^{1}H, ^{13}C and ^{19}F NMR spectra for compound 3i (Chloroform-d)



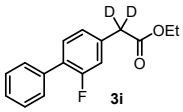
171.126
160.934
158.467
135.632
135.450
135.369
130.874
130.835
129.078
129.050
128.541
127.971
127.837
127.756
125.376
125.348
117.187
116.953
61.177
40.793
40.698
40.513
40.326
40.128
14.277



3i

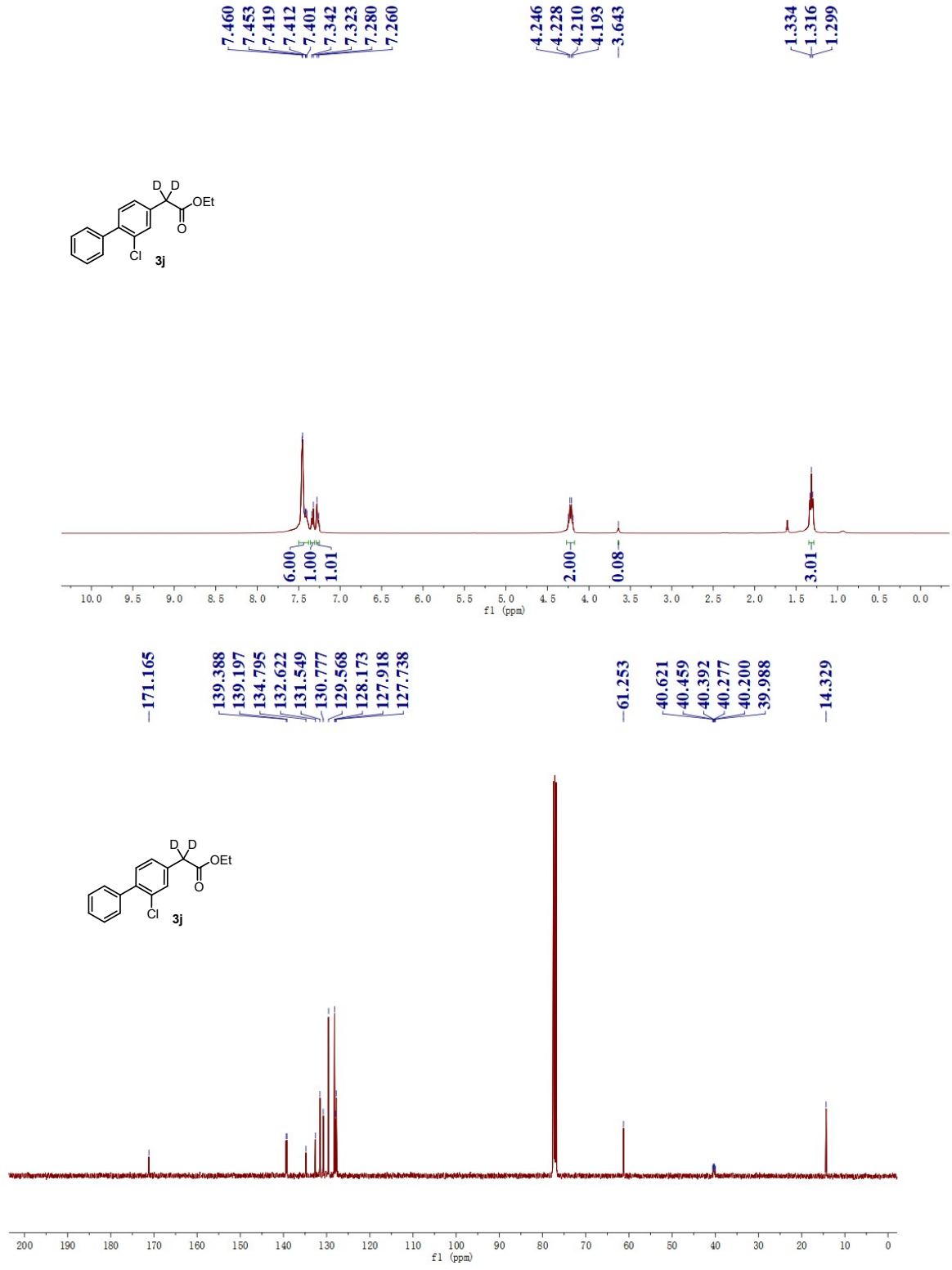


117.906
117.932
117.957

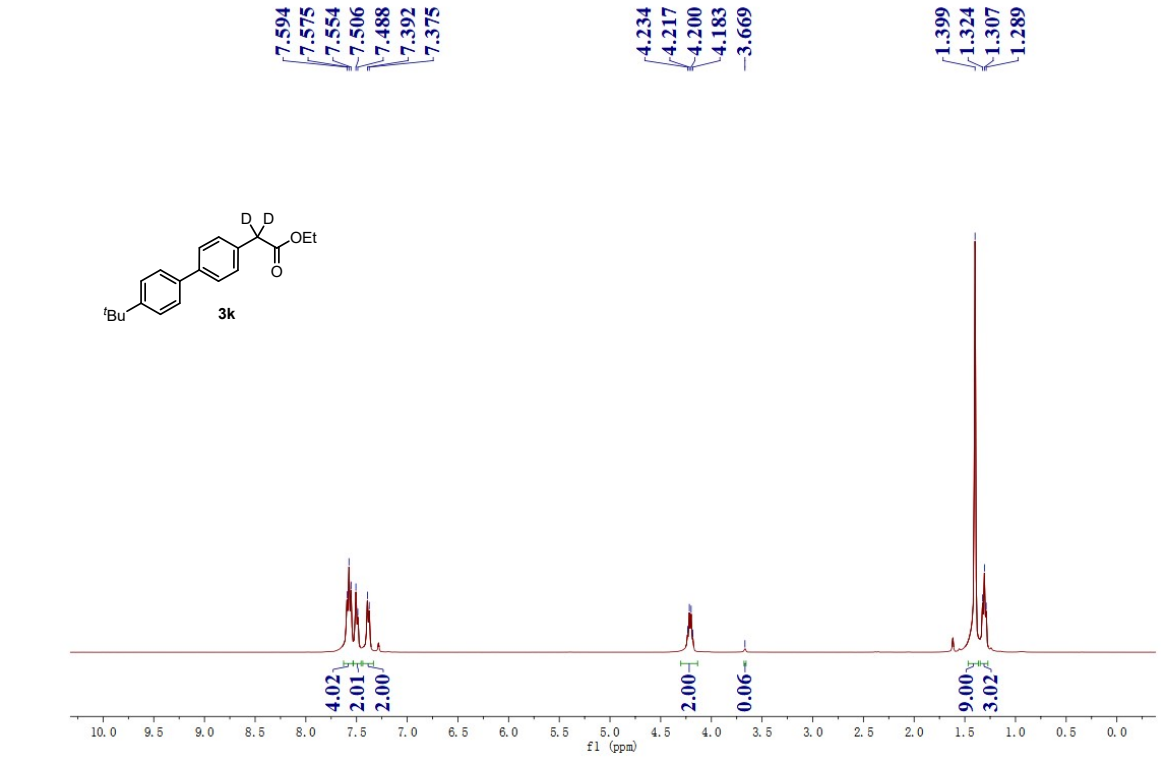


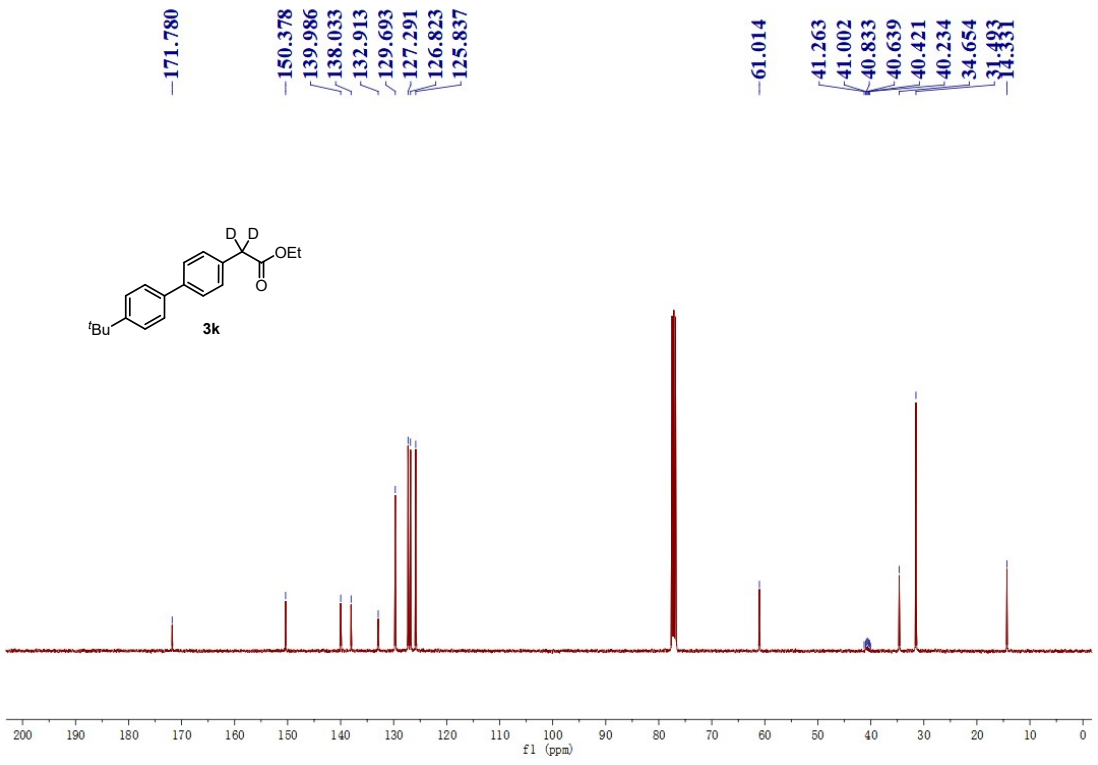
3i

^{1}H and ^{13}C NMR spectra for compound 3j (Chloroform-d)

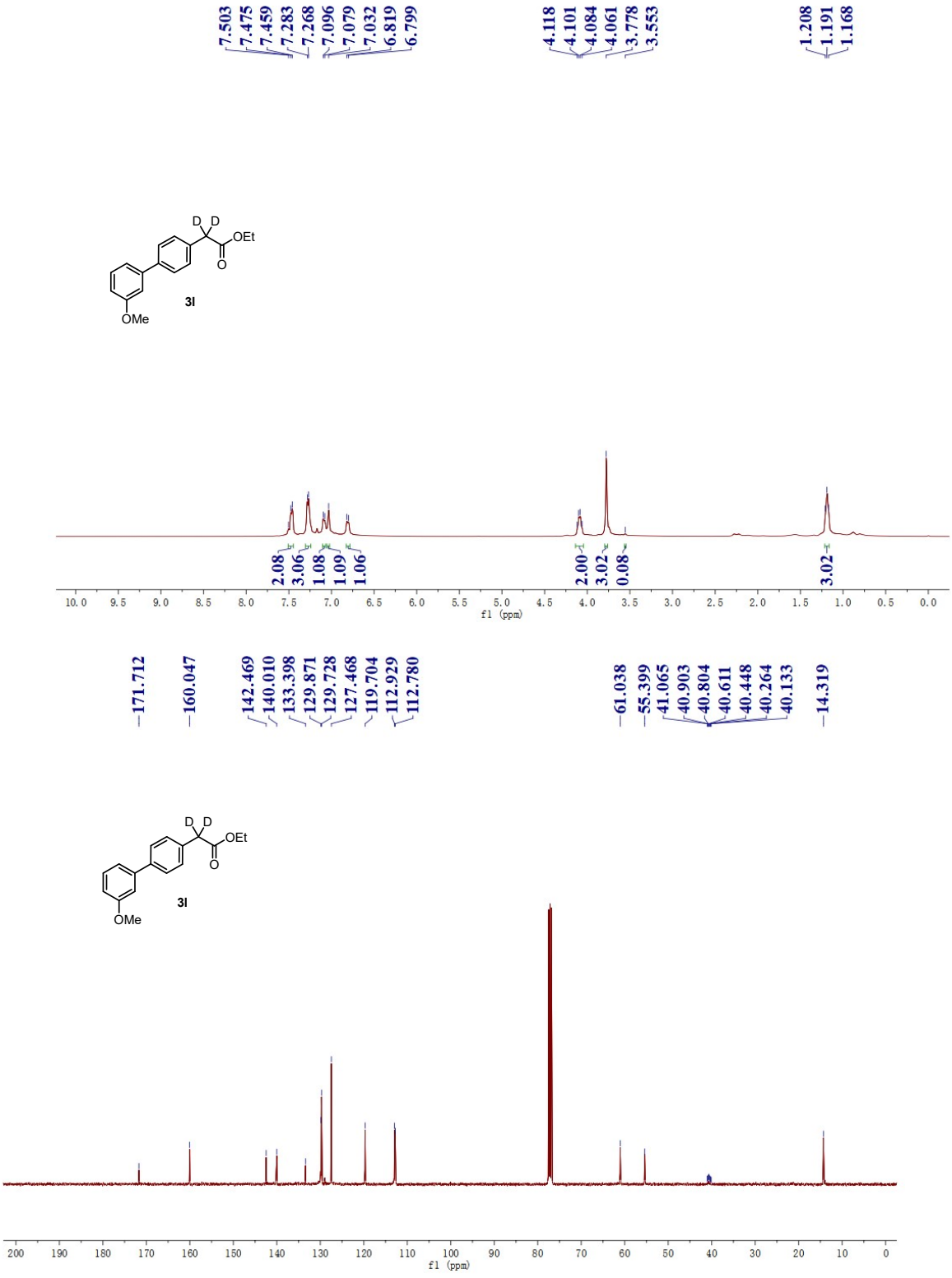


^{1}H and ^{13}C NMR spectra for compound 3k (Chloroform-d)

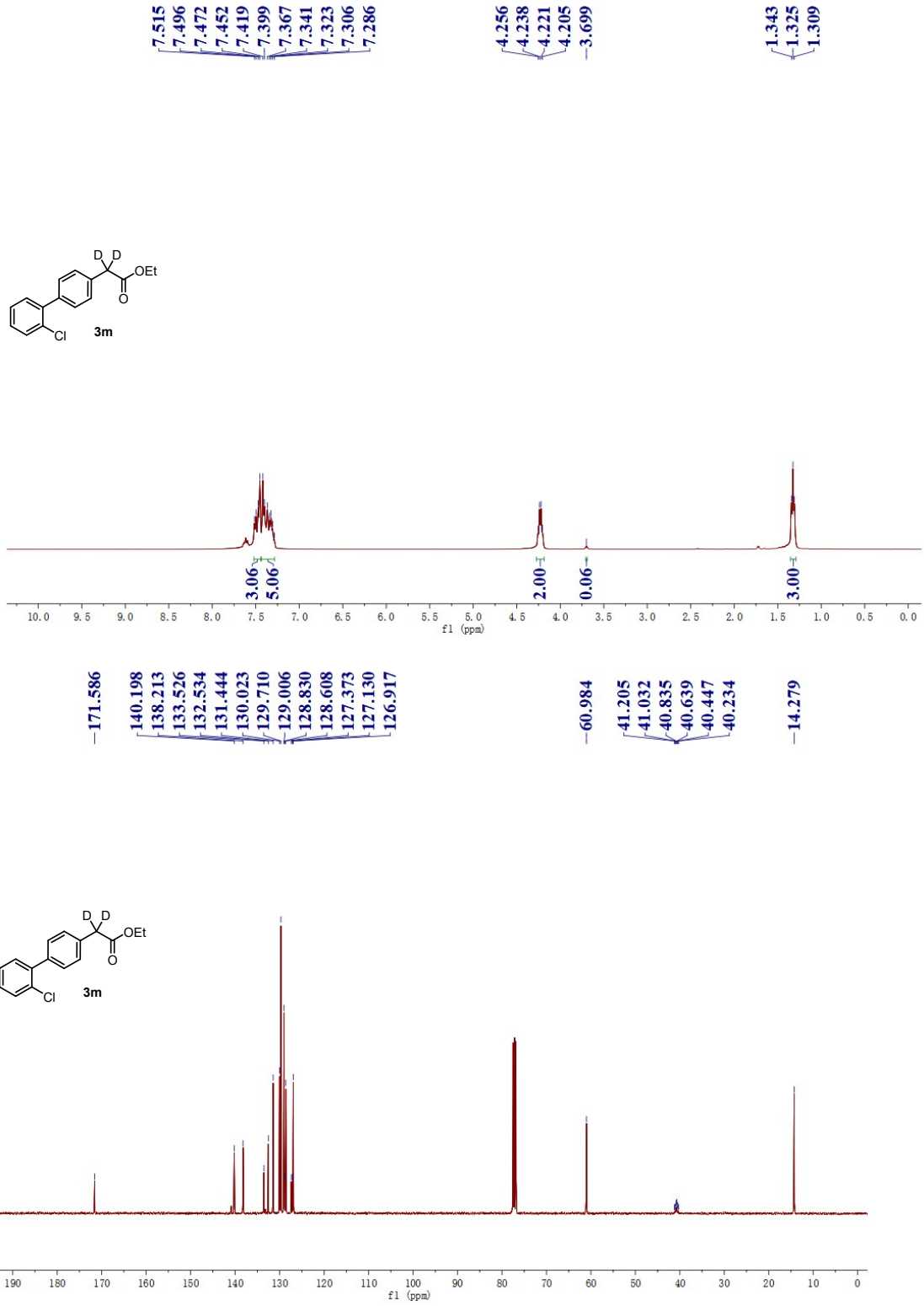




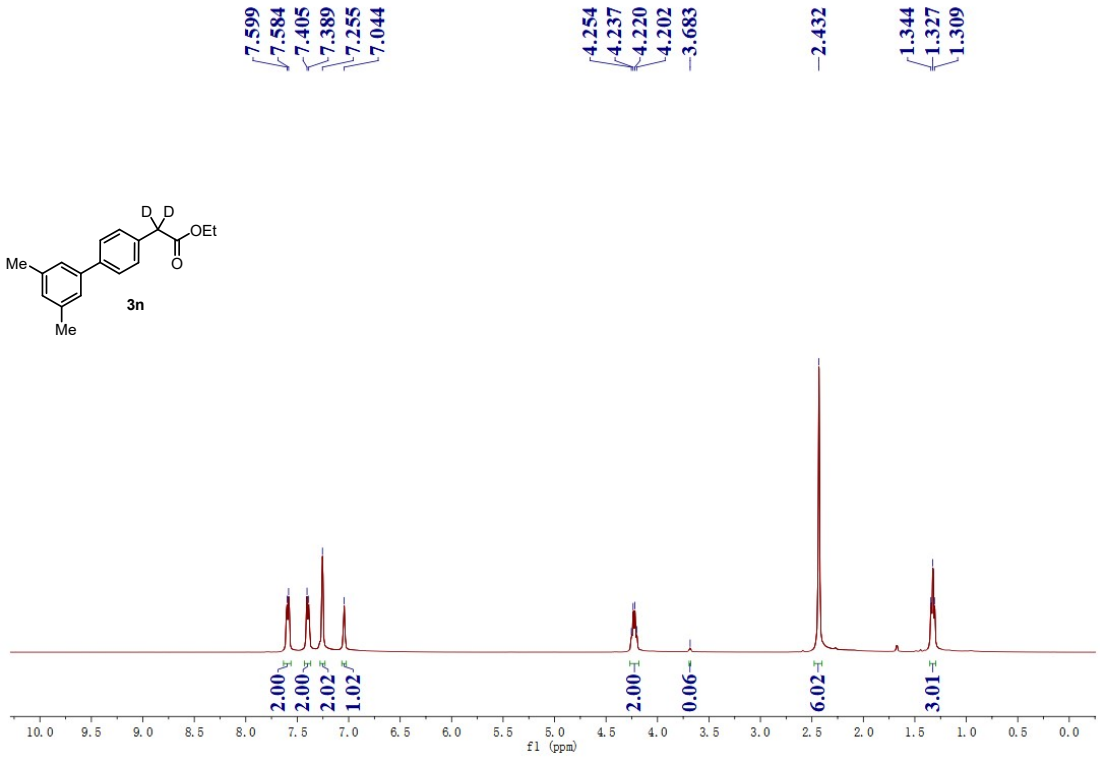
^{1}H and ^{13}C NMR spectra for compound 3l (Chloroform-d)

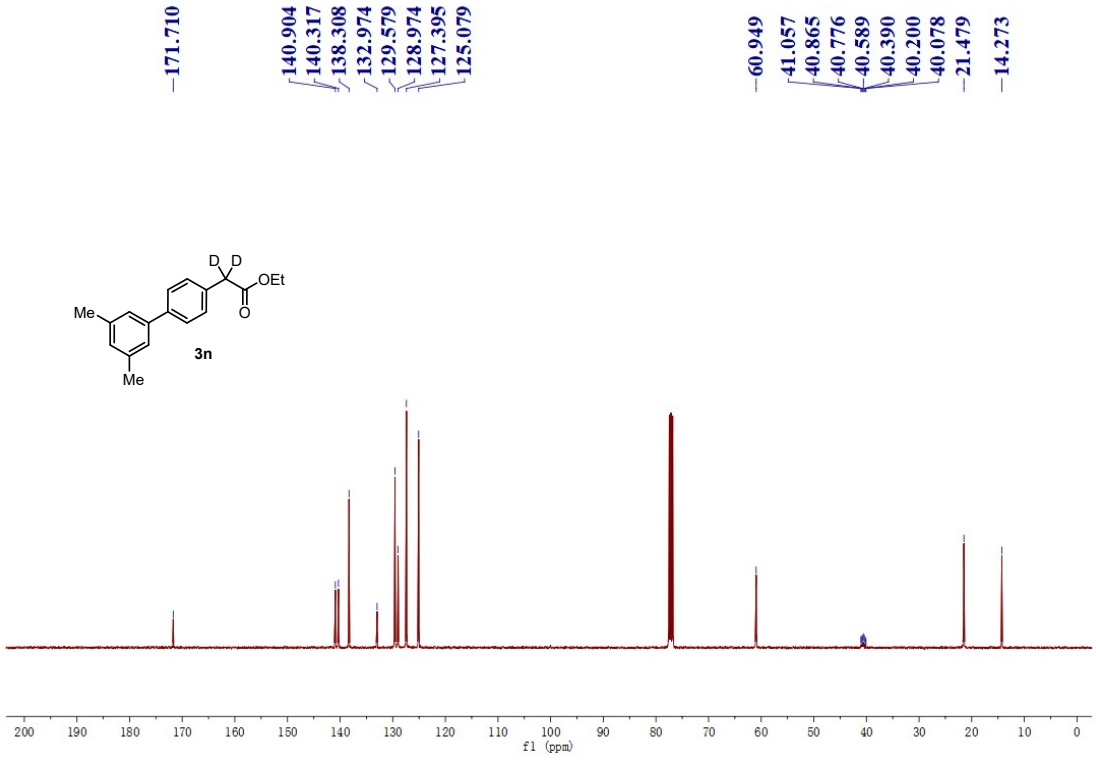


^{1}H and ^{13}C NMR spectra for compound 3m (Chloroform-d)

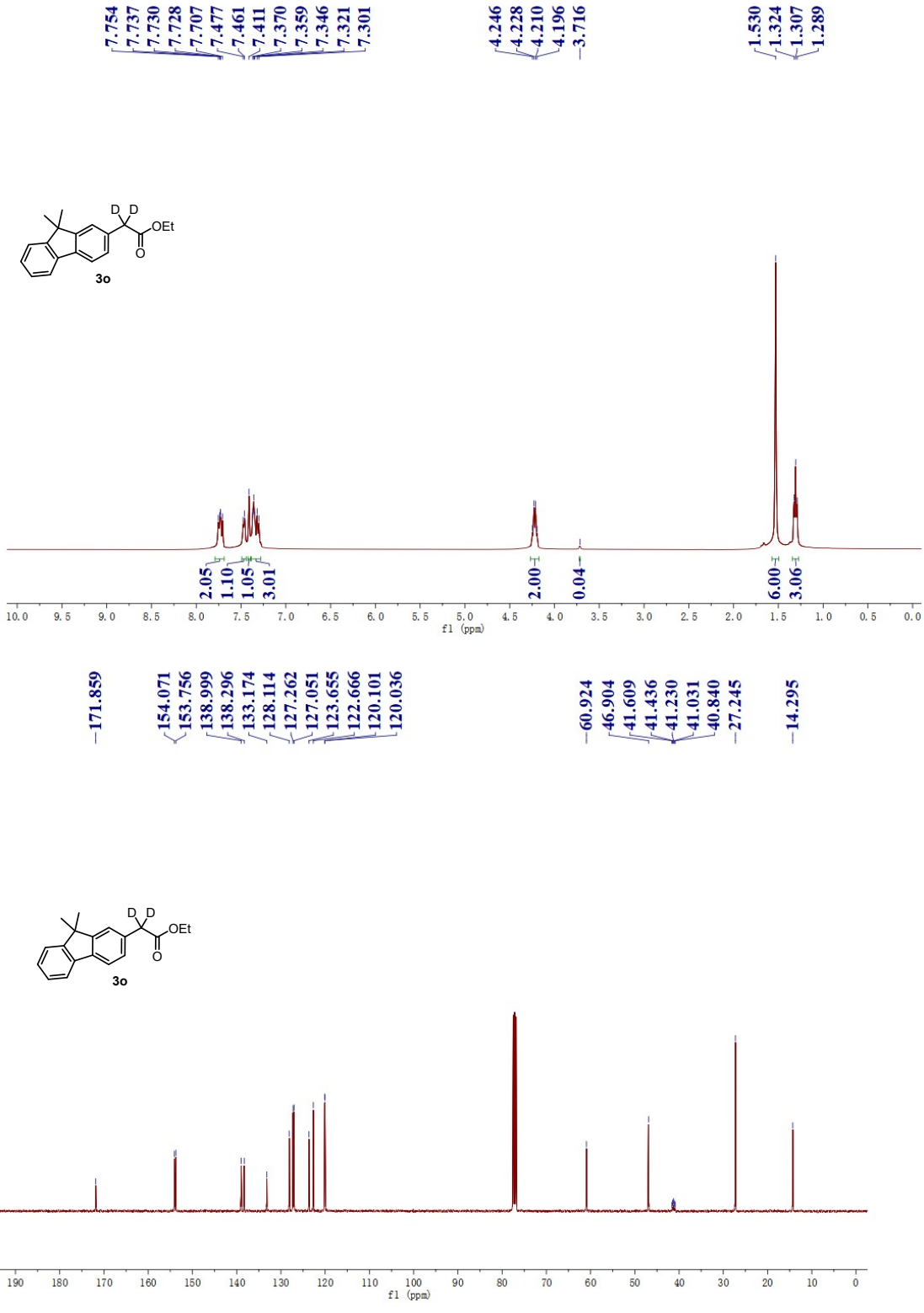


^{1}H and ^{13}C NMR spectra for compound 3n (Chloroform-d)

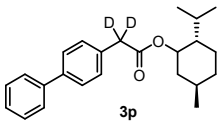


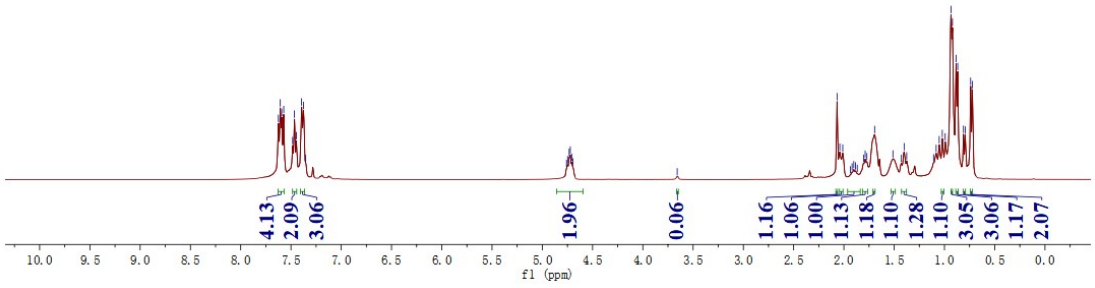


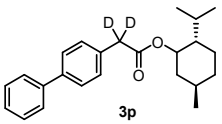
^{1}H and ^{13}C NMR spectra for compound 3o (Chloroform-d)

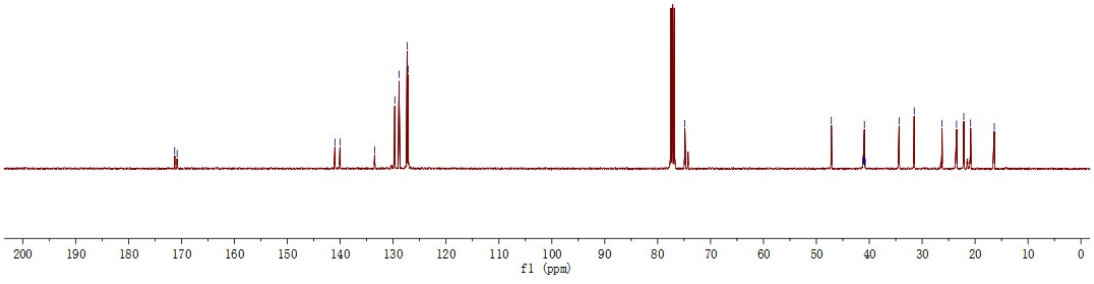


^{1}H and ^{13}C NMR spectra for compound 3p (Chloroform-d)

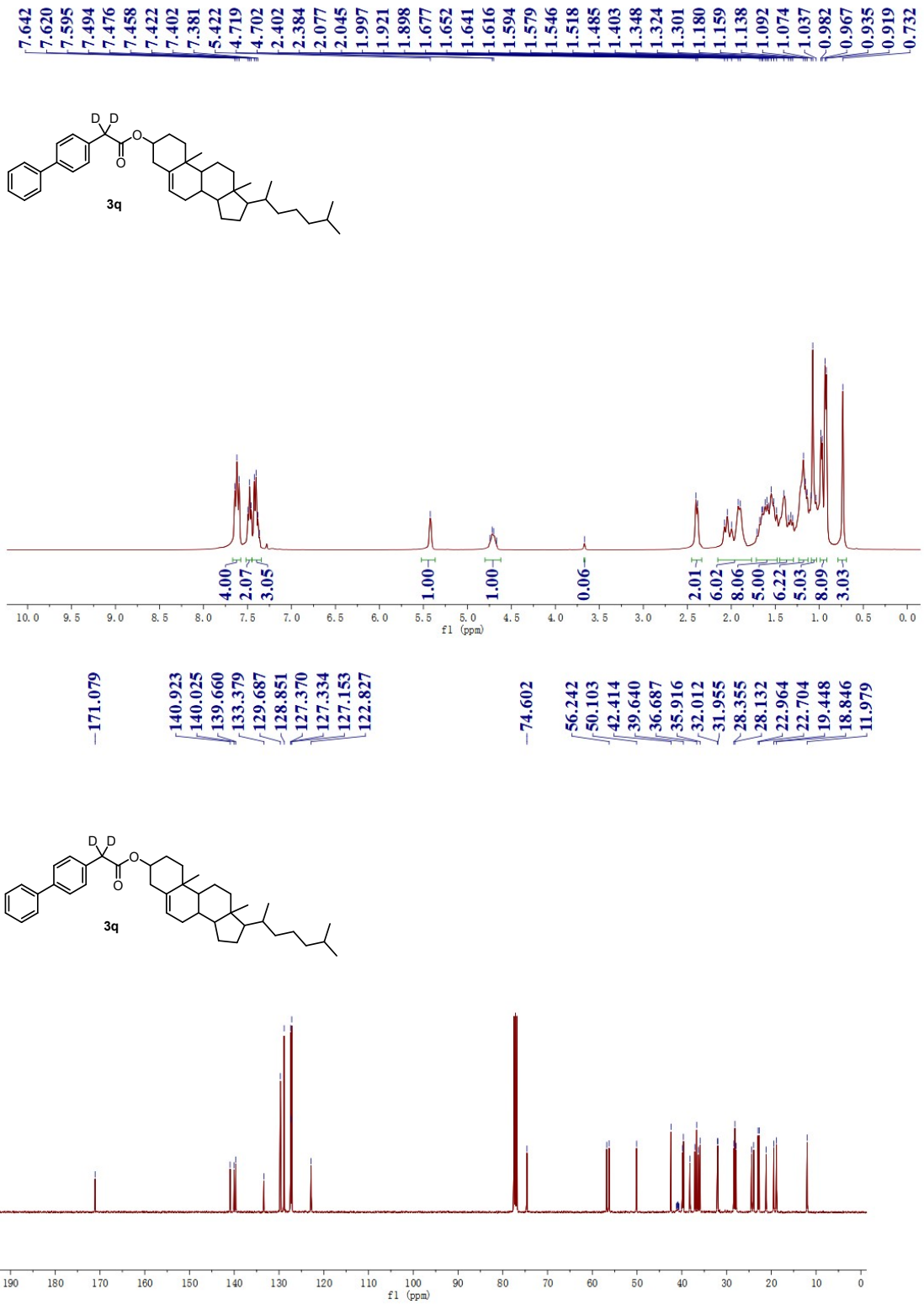




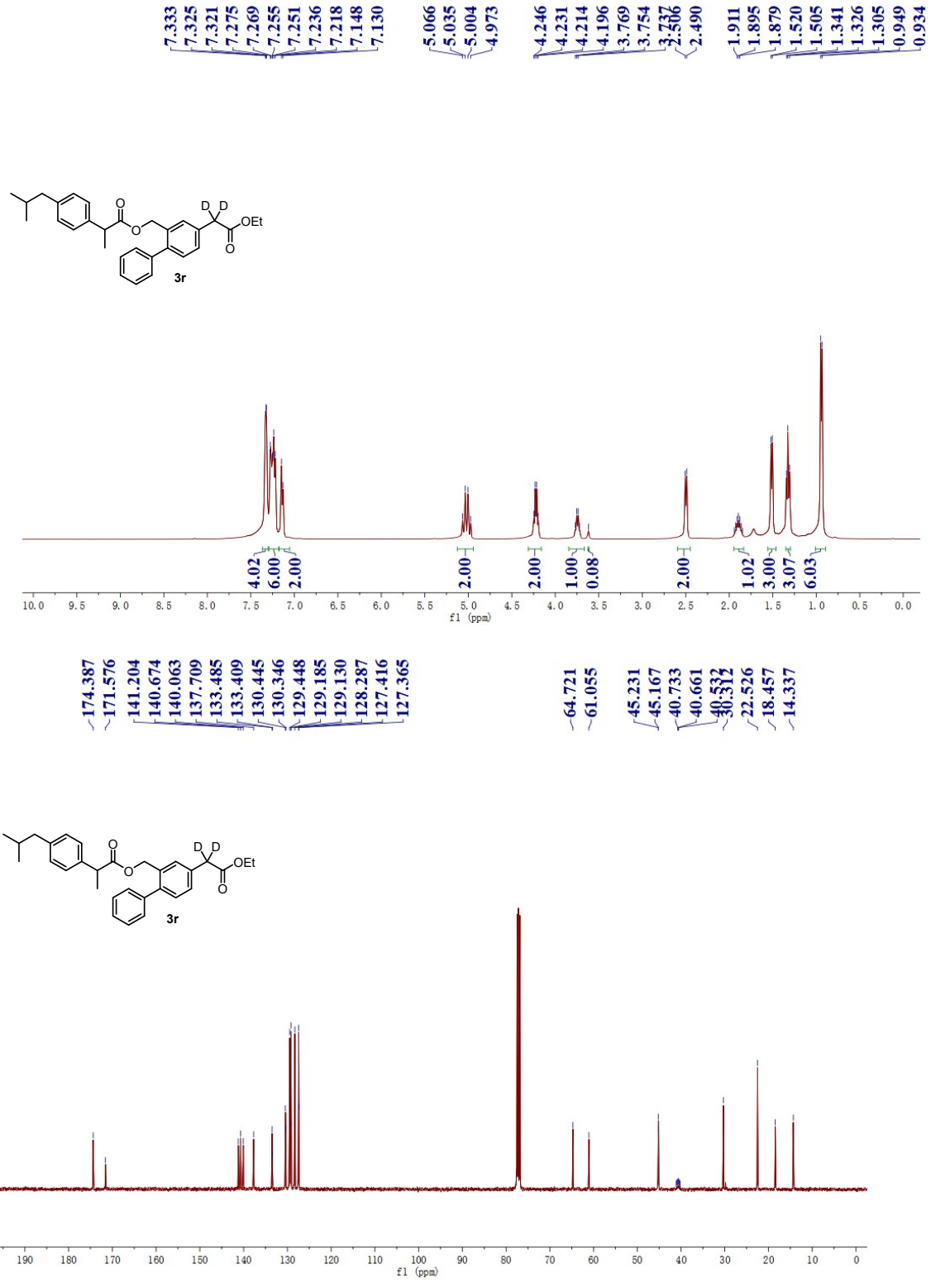




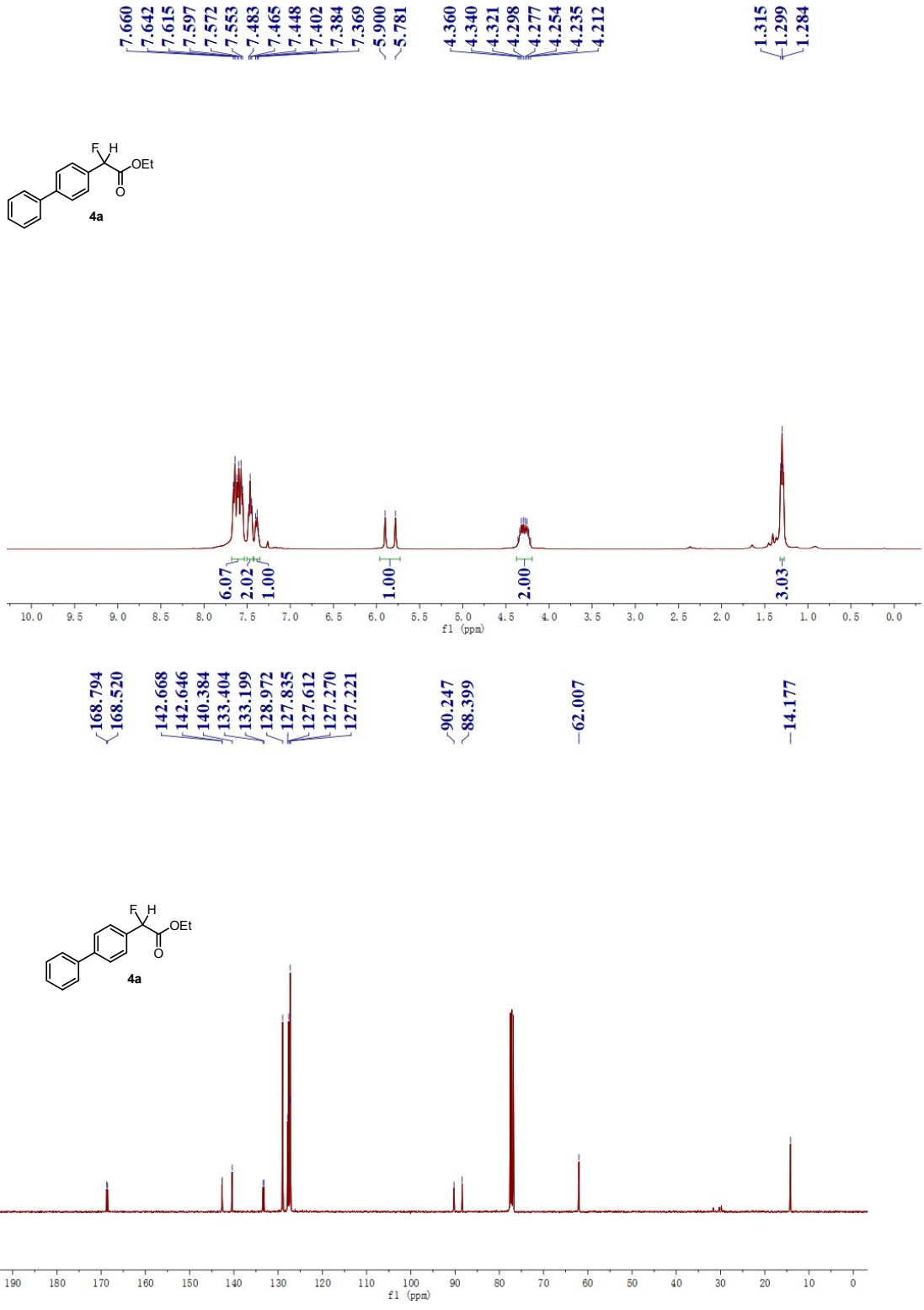
^{1}H and ^{13}C NMR spectra for compound 3q (Chloroform-d)

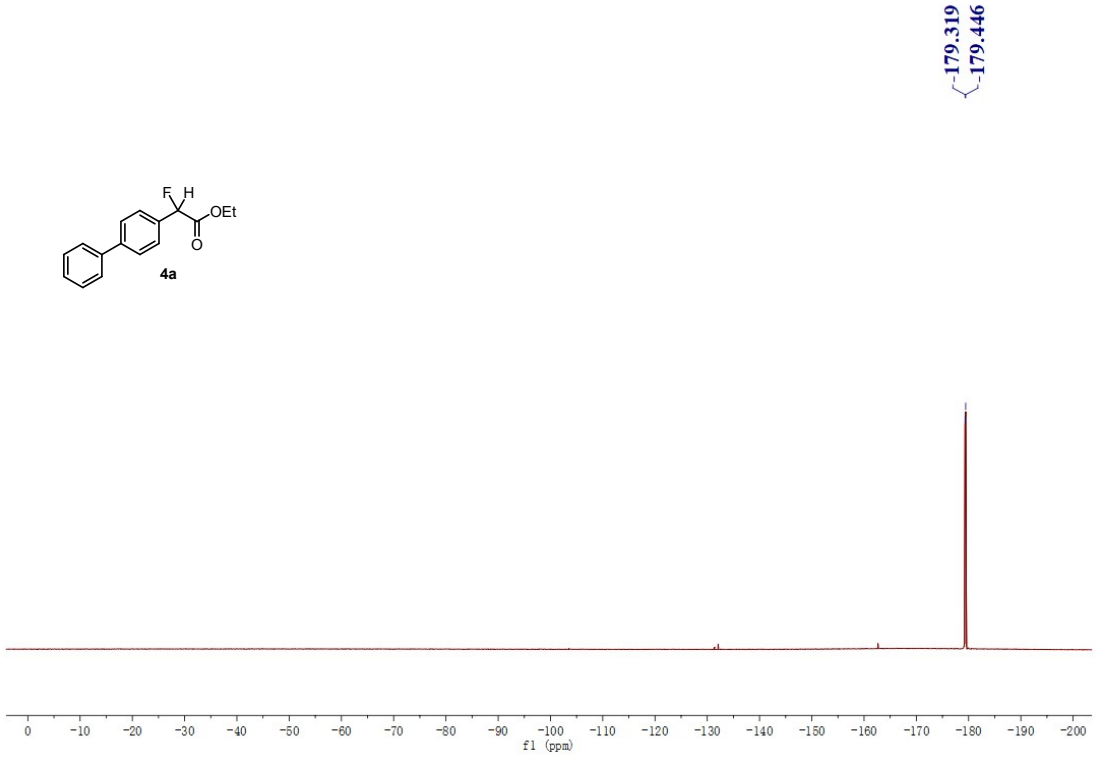


^{1}H and ^{13}C NMR spectra for compound 3r (Chloroform-d)

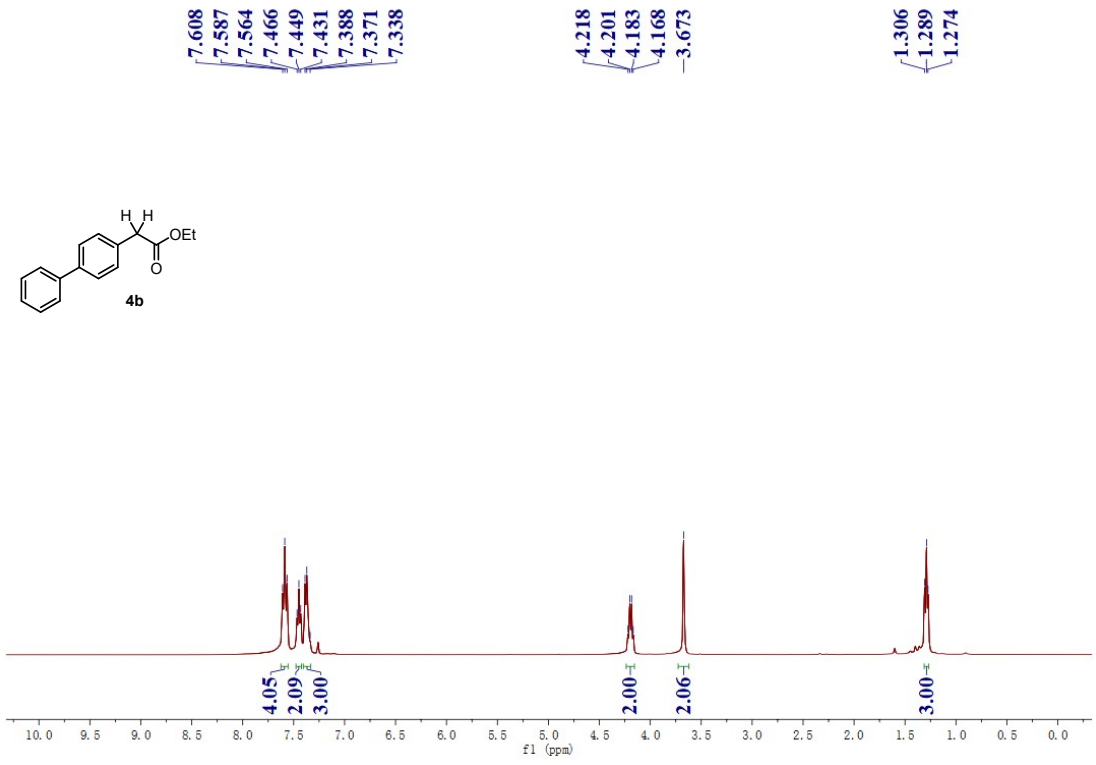


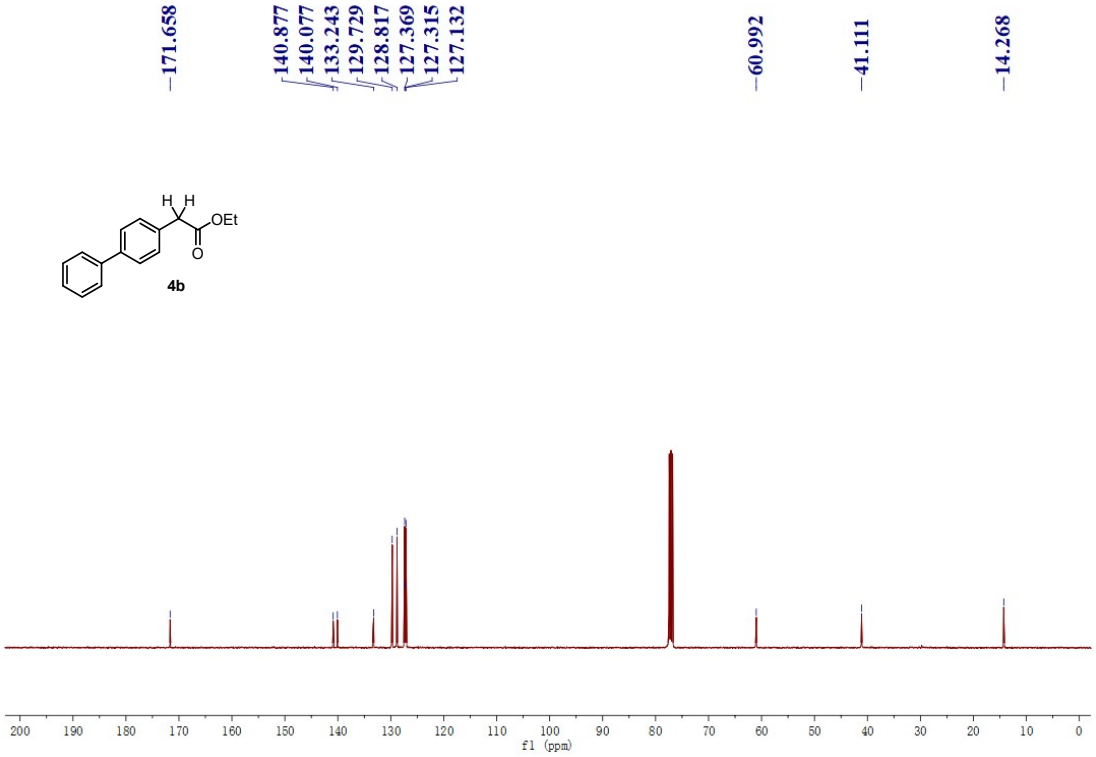
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 4a (Chloroform-d)



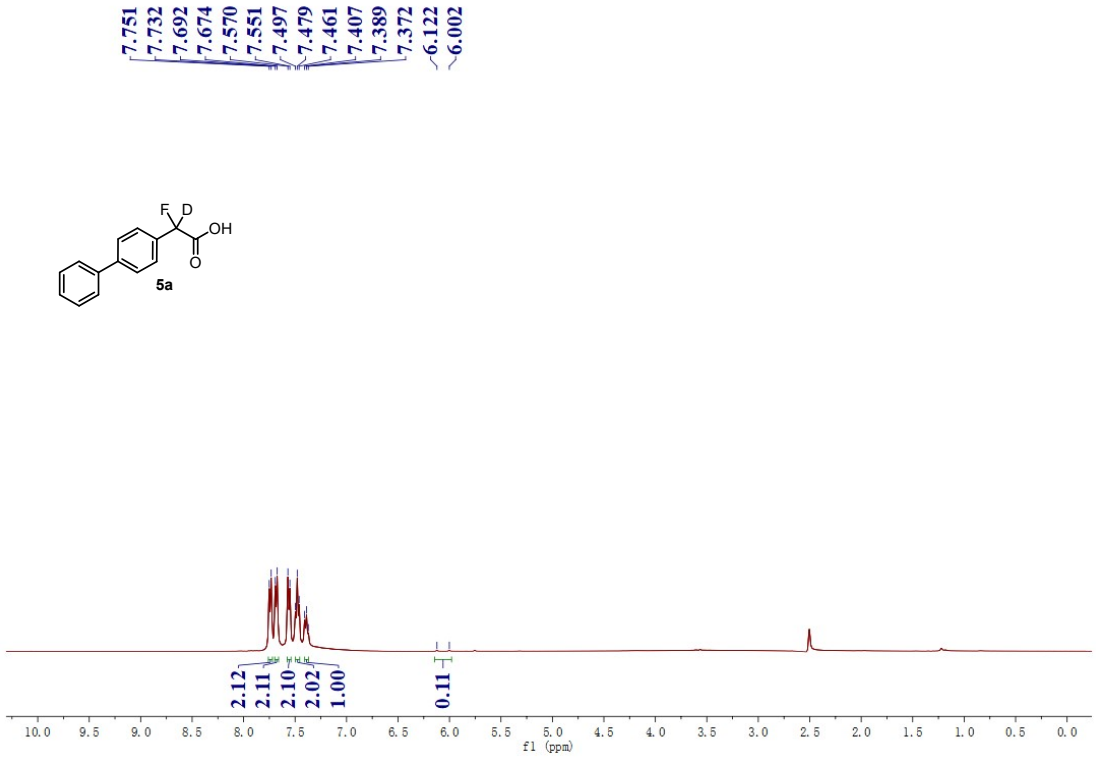


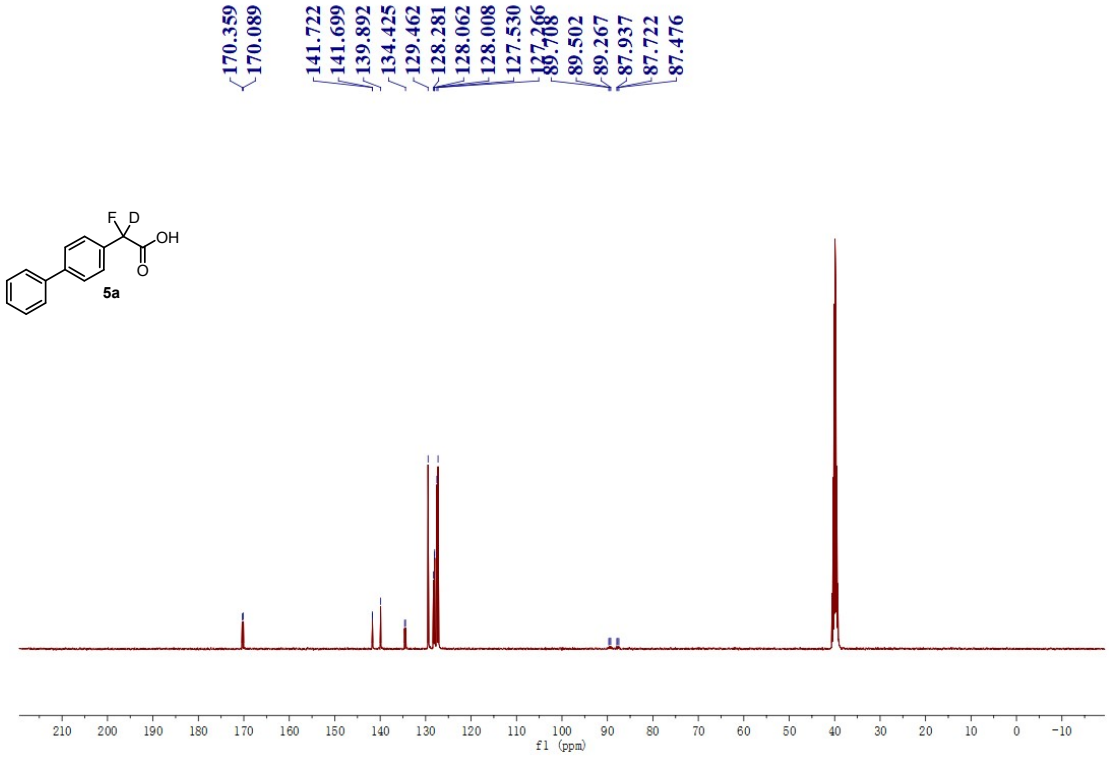
^{1}H and ^{13}C NMR spectra for compound 4b (Chloroform-d)

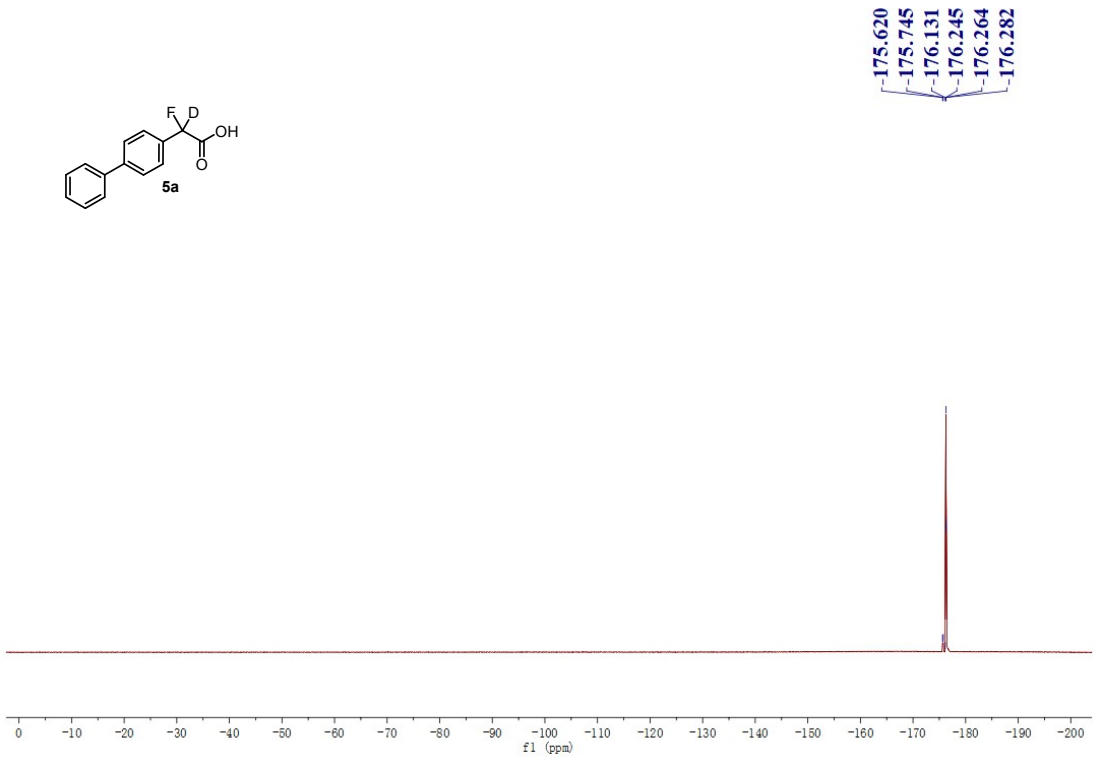




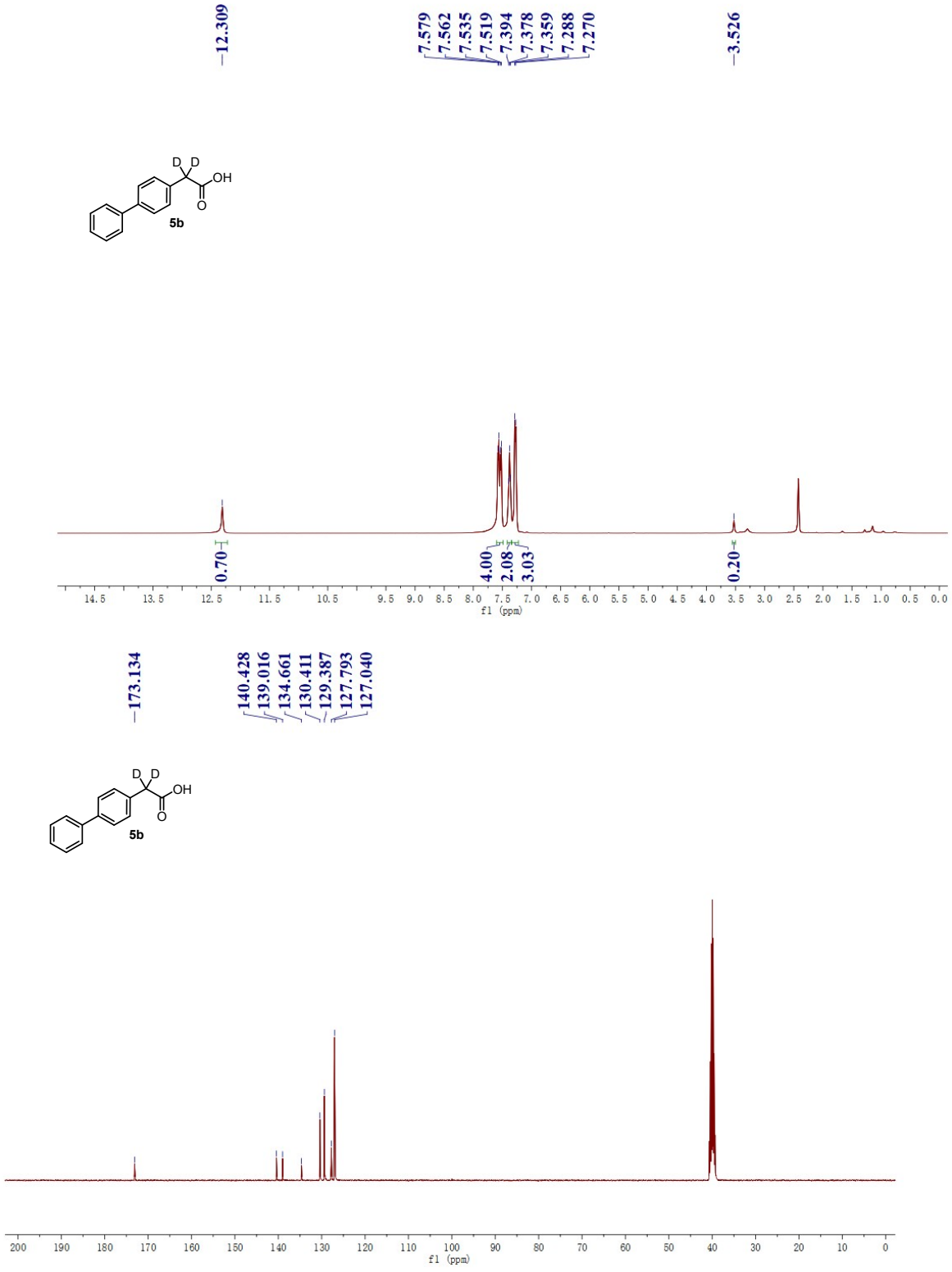
^{1}H, ^{13}C and ^{19}F NMR NMR spectra for compound 5a (DMSO-d$_6$)



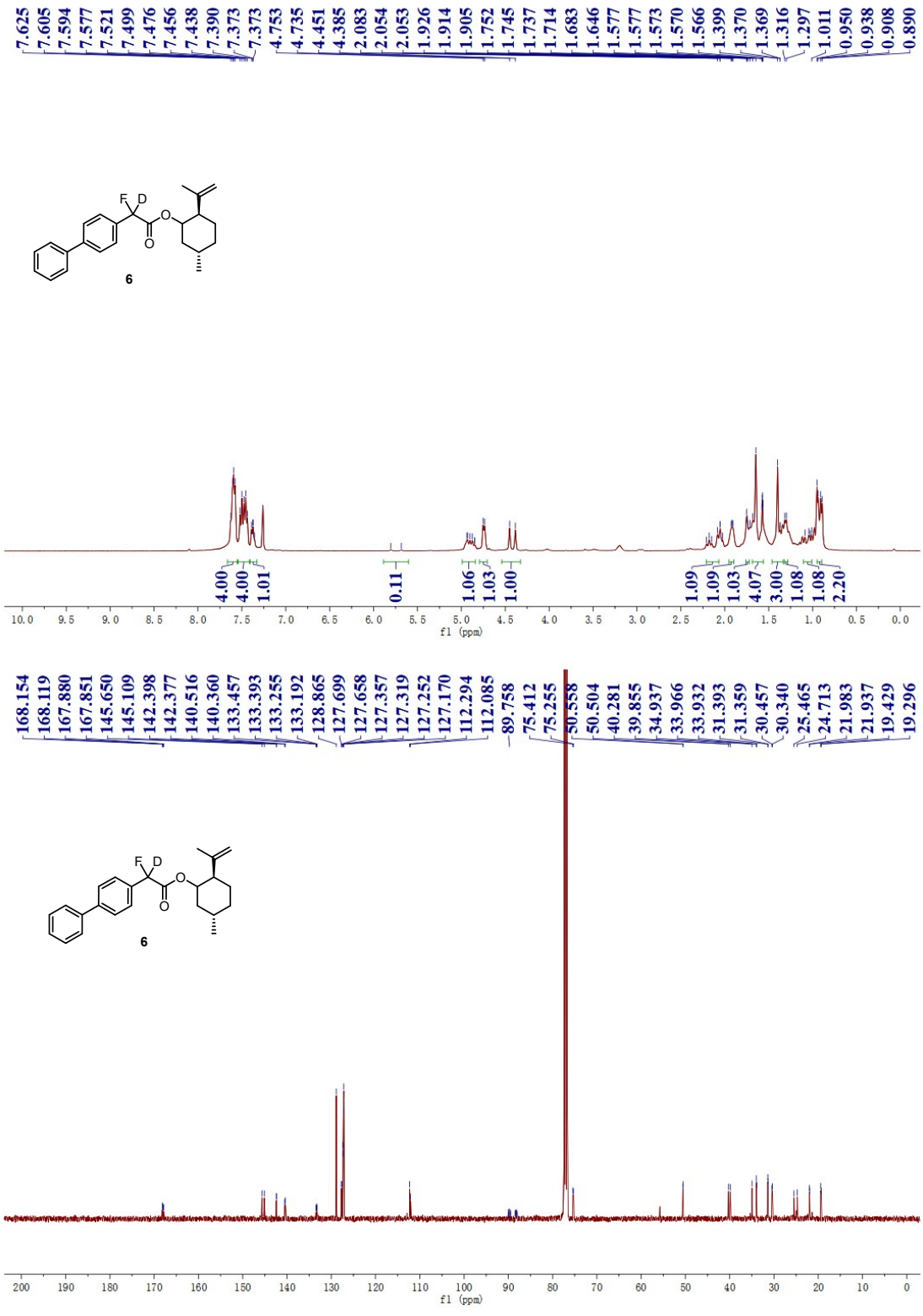

170.359
170.089
141.722
141.699
139.892
134.425
129.462
128.281
128.062
128.008
127.530
127.266
89.708
89.502
89.267
87.937
87.722
87.476
F
D
OH
O
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

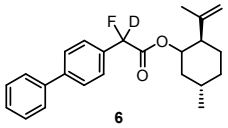

175.620
175.745
176.131
176.245
176.264
176.282
F
D
OH
O
5a
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H and ^{13}C NMR spectra for compound 5b (DMSO-d_6)

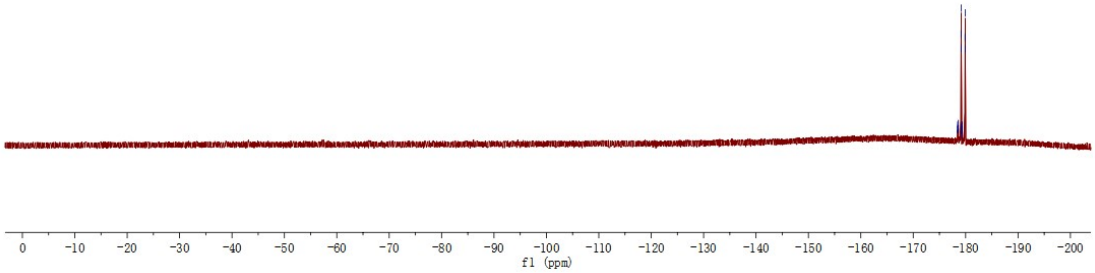


^{1}H, ^{13}C NMR and ^{19}F spectra for compound 6 (Chloroform-d)

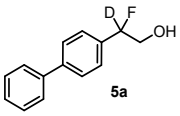




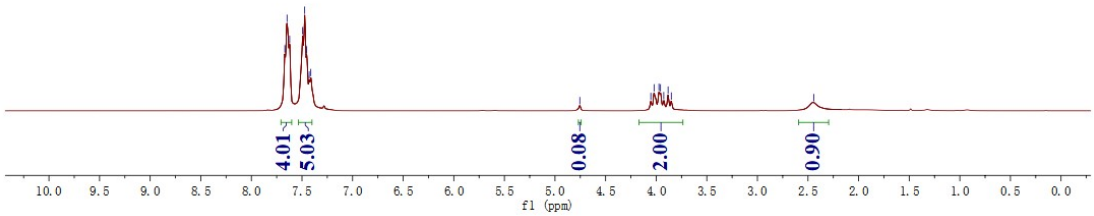
6



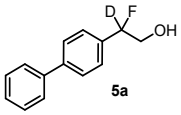
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 5a (Chloroform-d)



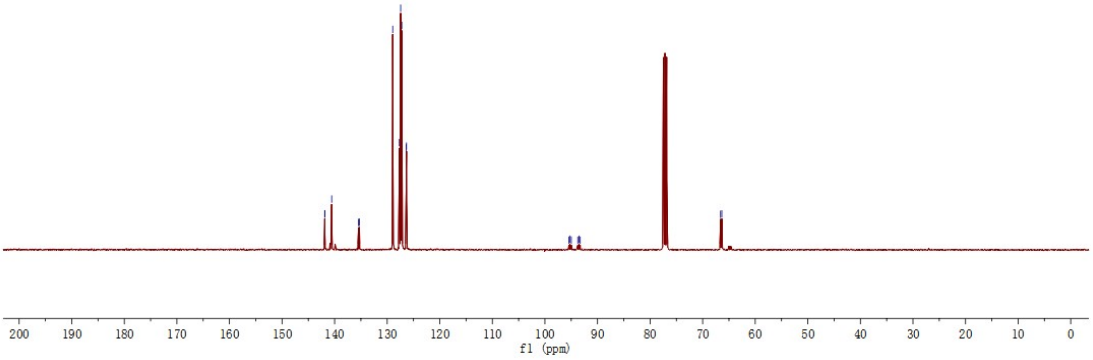
5a

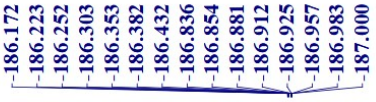


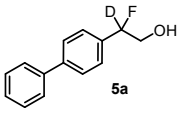

141.885
141.872
140.556
135.464
135.267
128.950
127.684
127.437
127.225
126.395
126.328
95.454
95.219
94.983
93.753
93.519
93.282
66.598
66.352


D
F
OH

5a


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

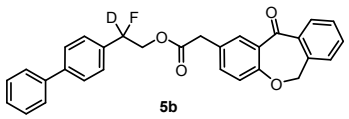

186.172
186.223
186.252
186.303
186.353
186.382
186.432
186.836
186.854
186.881
186.912
186.925
186.957
186.983
187.000


D
F
OH

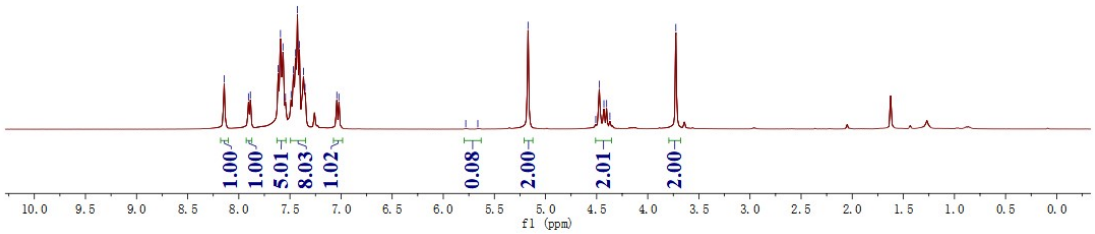
5a

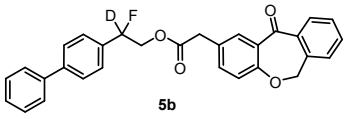
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

^{1}H, ^{13}C NMR and ^{19}F spectra for compound 5b (Chloroform-d)

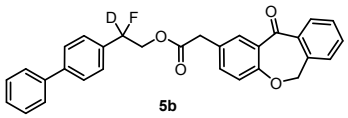


5b

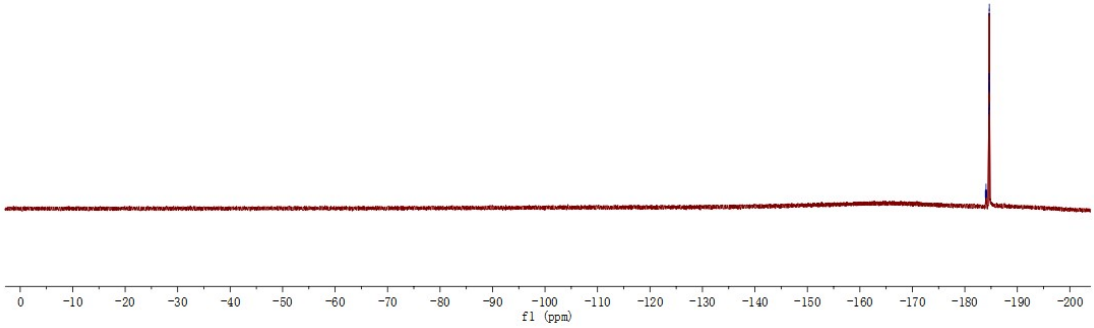




5b

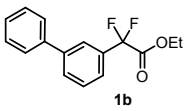


5b

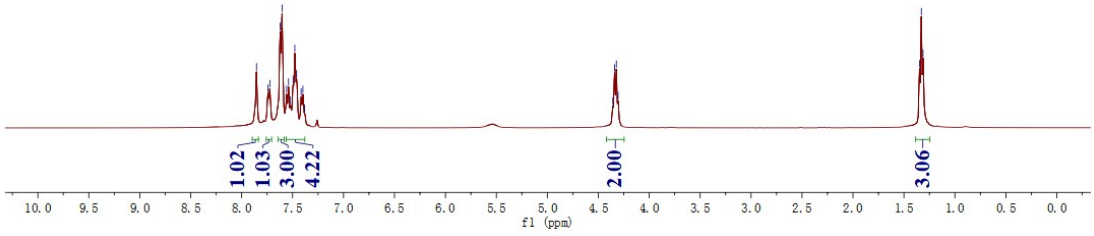


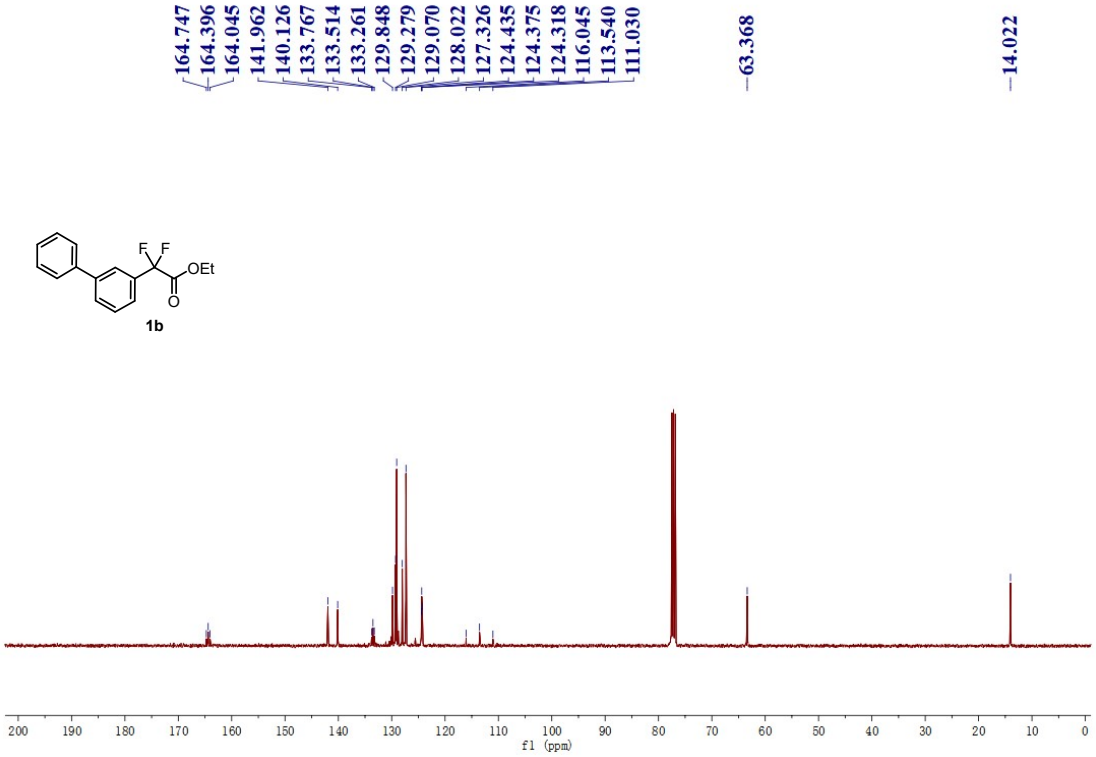
11.2 ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of material 1

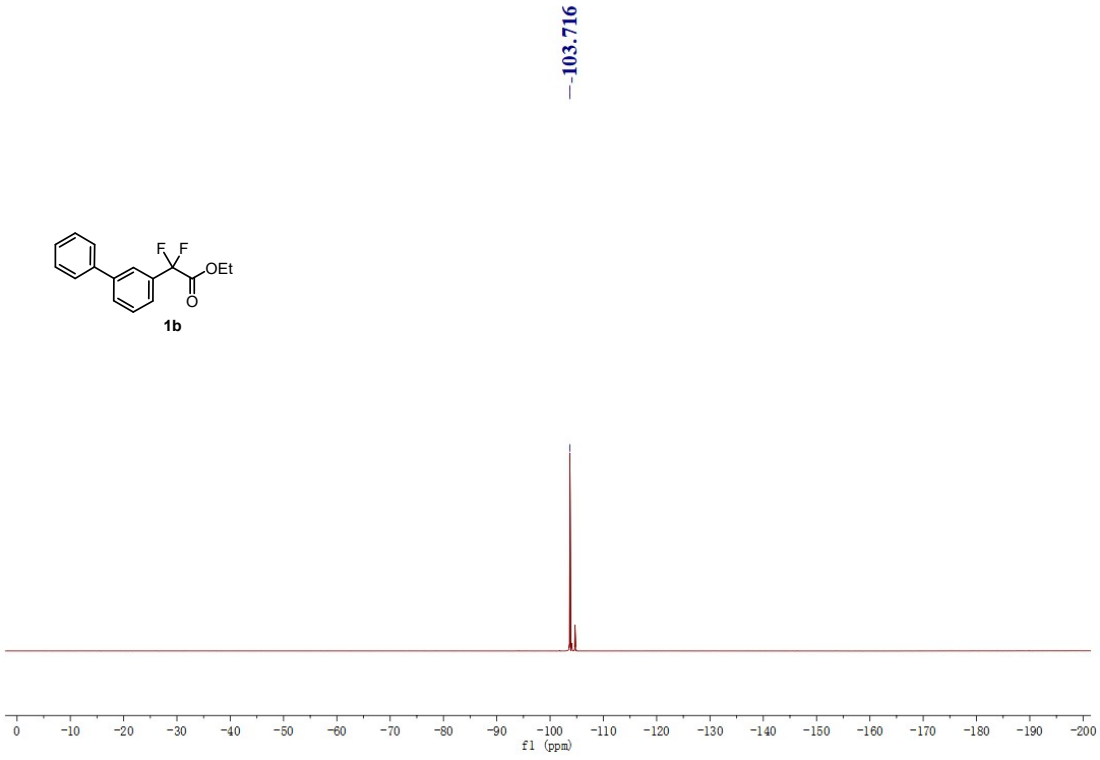
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1b (Chloroform-d)



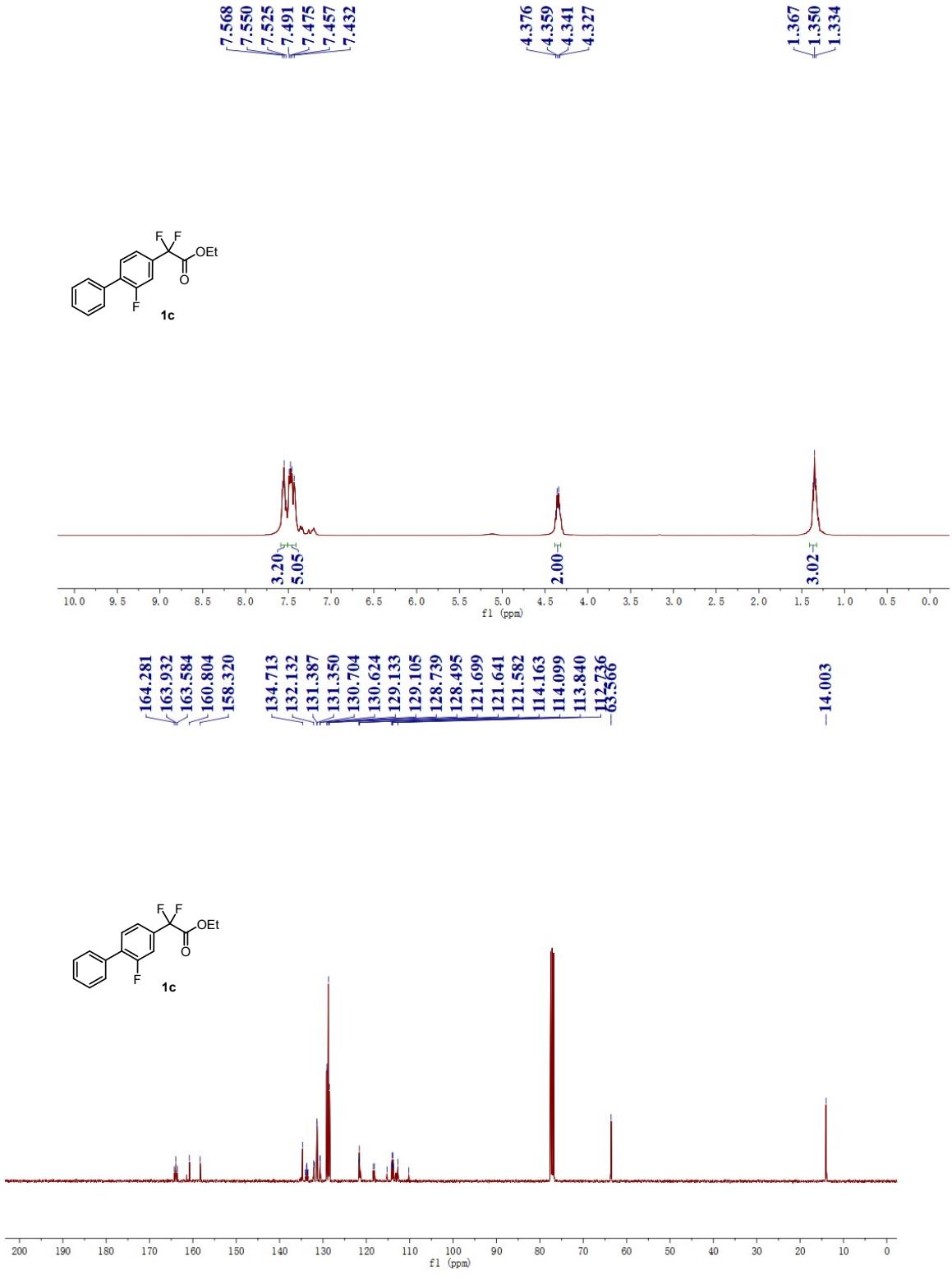
1b

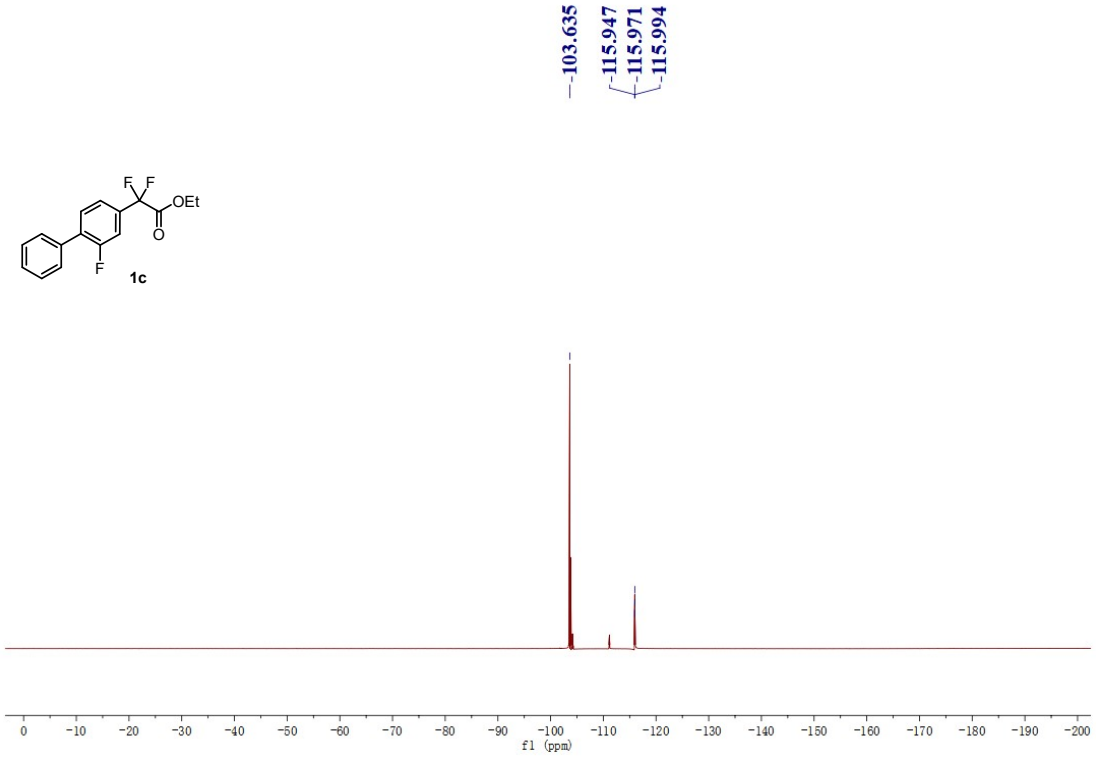



164.747
164.396
164.045
141.962
140.126
133.767
133.514
133.261
129.848
129.279
129.070
128.022
127.326
124.435
124.375
124.318
116.045
113.540
111.030
63.368
14.022
F F
OEt
O
1b
f1 (ppm)

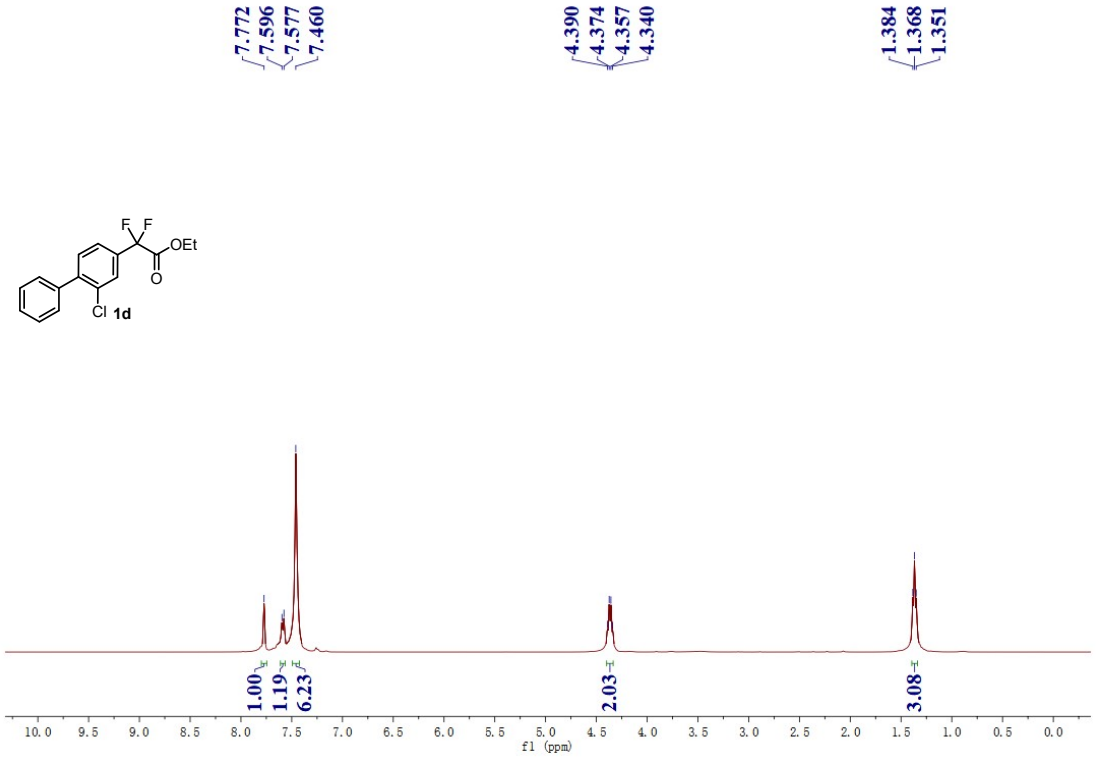

-103.716
F F
OEt
O
1b
f1 (ppm)

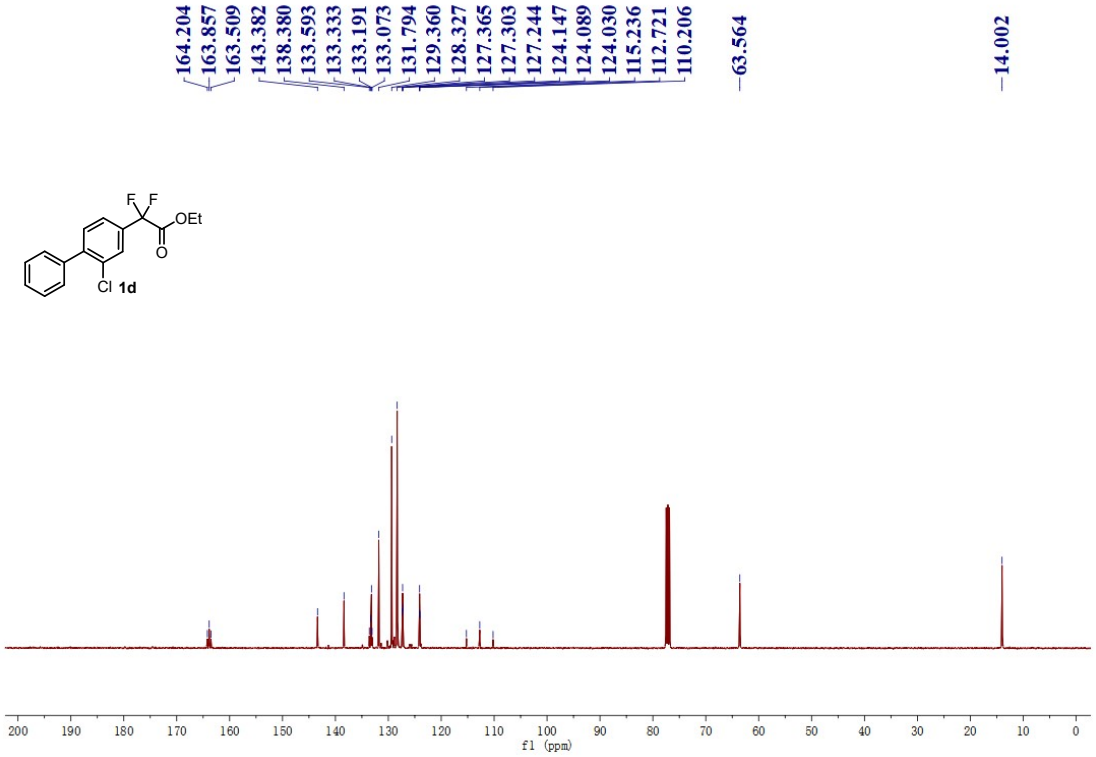
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1c (Chloroform-d)

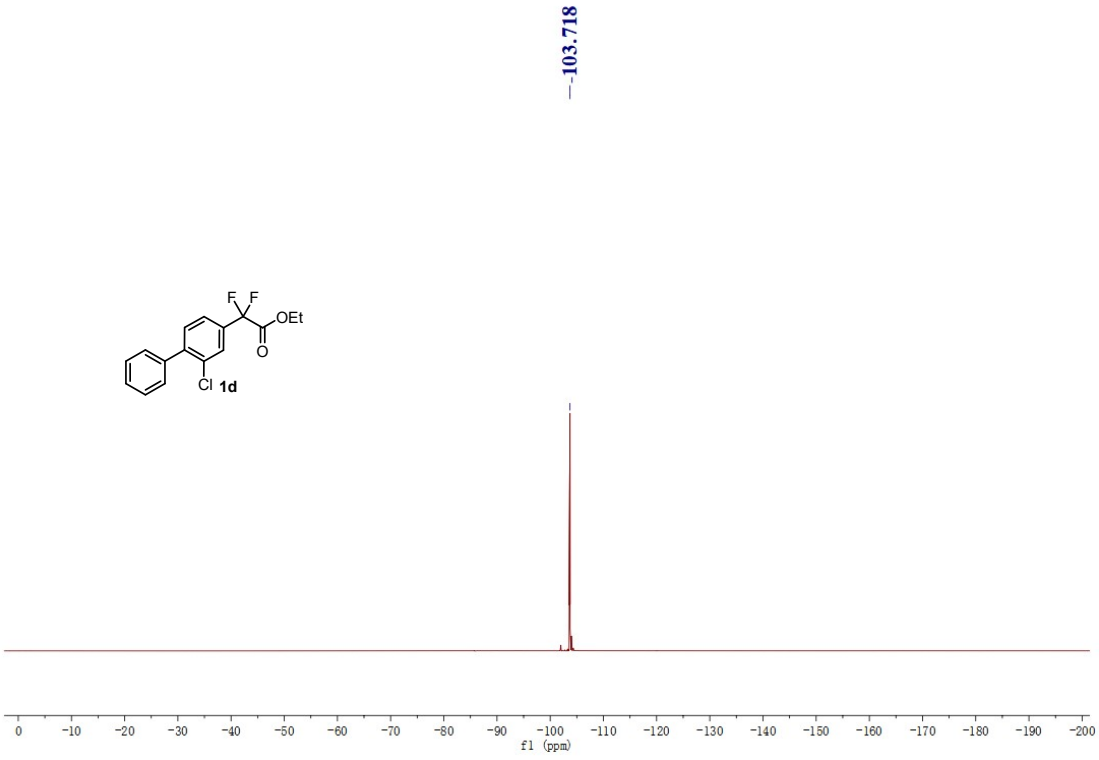




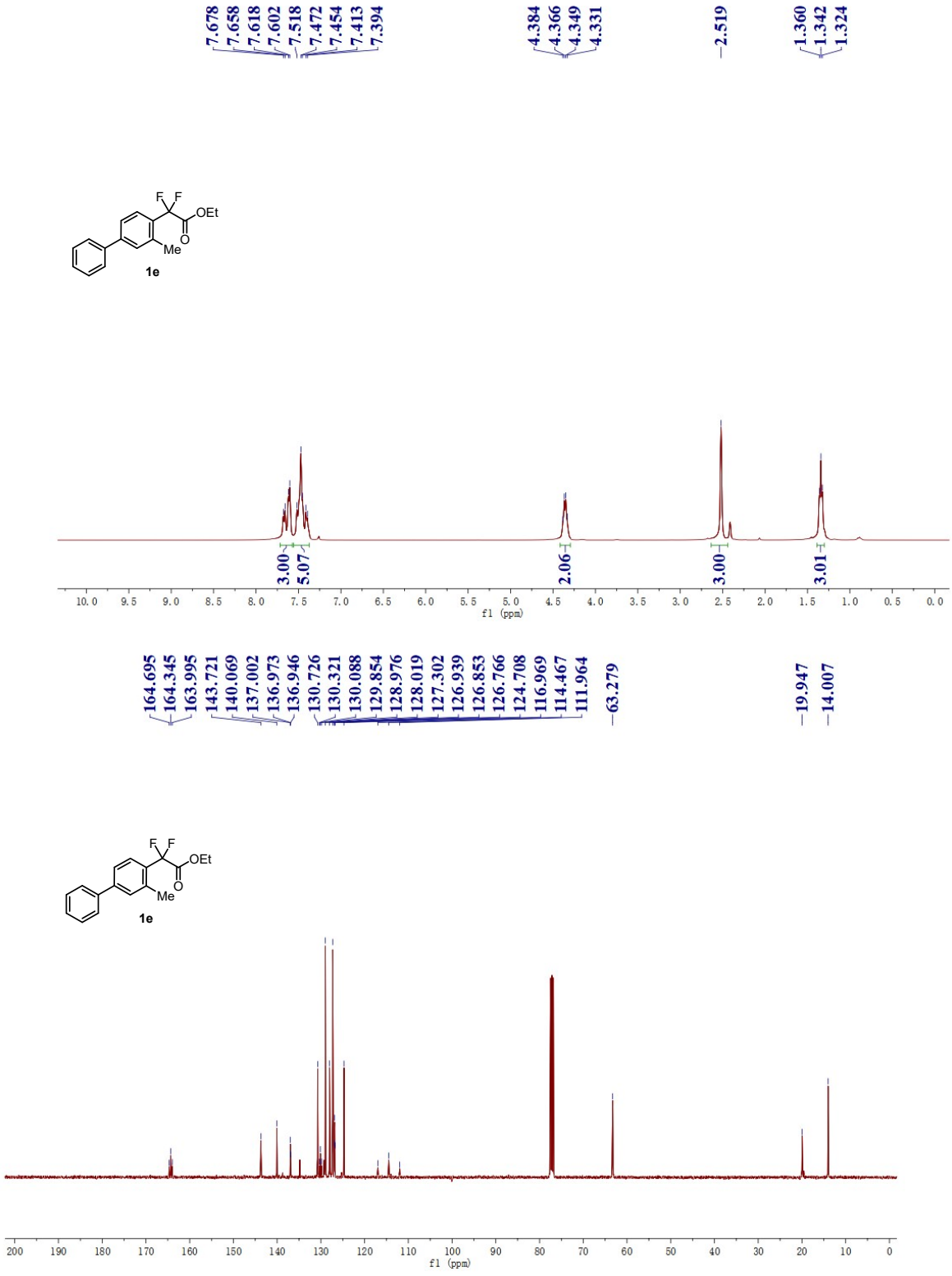
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1d (Chloroform-d)

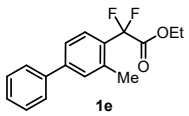



164.204
163.857
163.509
143.382
138.380
133.593
133.333
133.191
133.073
131.794
129.360
128.327
127.365
127.303
127.244
124.147
124.089
124.030
115.236
112.721
110.206
63.564
14.002
F F
OEt
O
Cl 1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.718
F F
OEt
O
Cl 1d
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

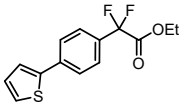
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1e (Chloroform-d)



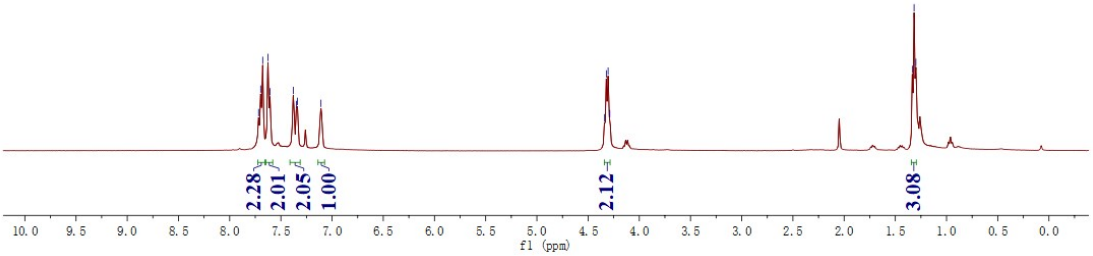


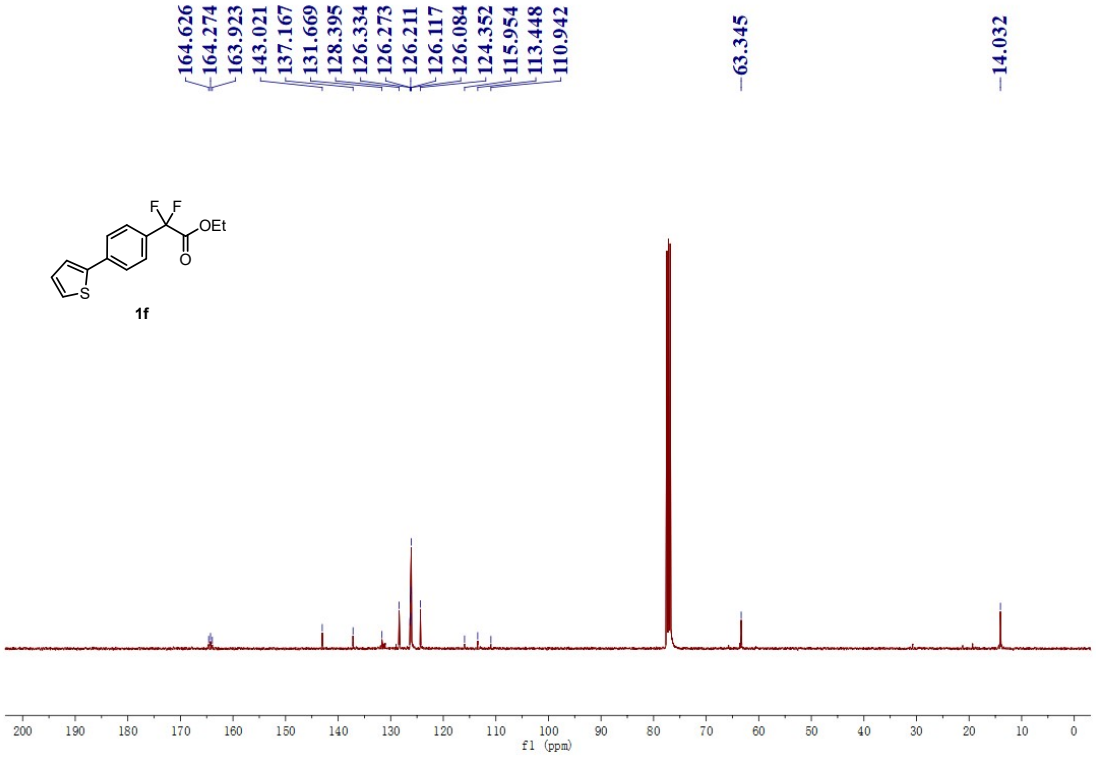
1e

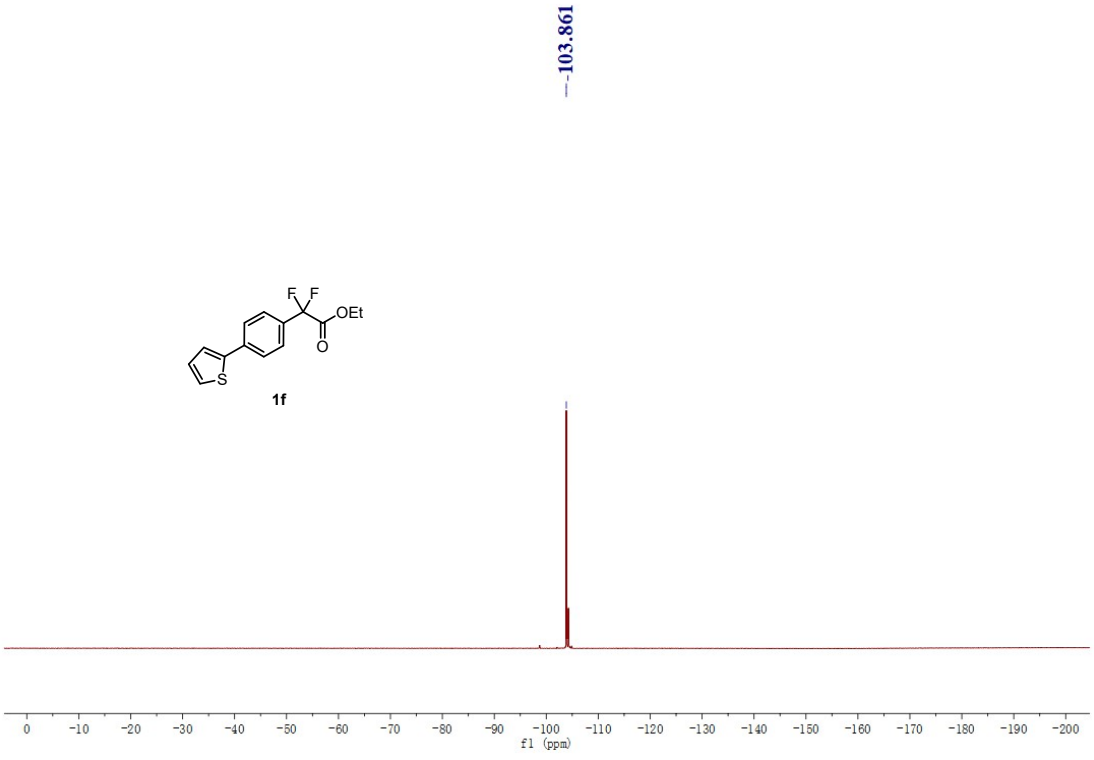
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1f (Chloroform-d)



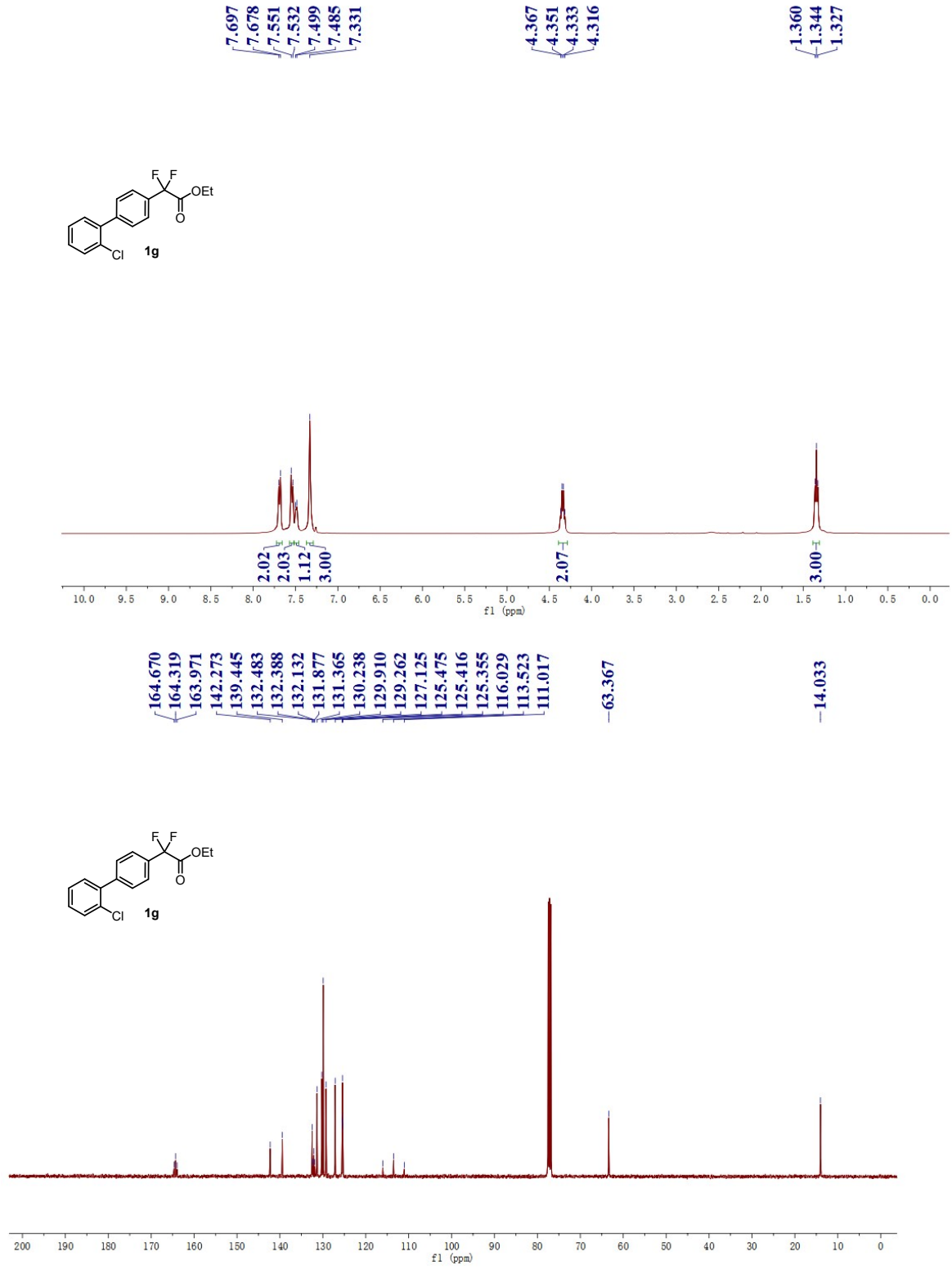
1f

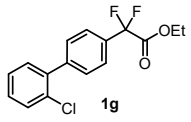



164.626
164.274
163.923
143.021
137.167
131.669
128.395
126.334
126.273
126.211
126.117
126.084
124.352
115.954
113.448
110.942
63.345
14.032
F
F
OEt
O
S
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-103.861
F
F
OEt
O
S
1f
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

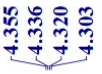
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1g (Chloroform-d)

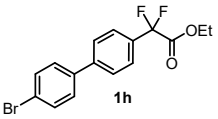




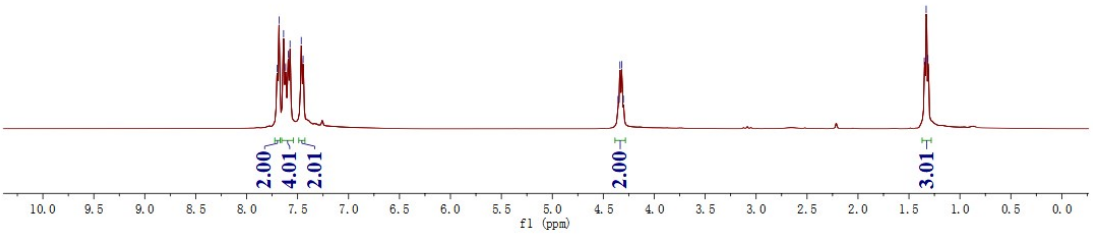
1g

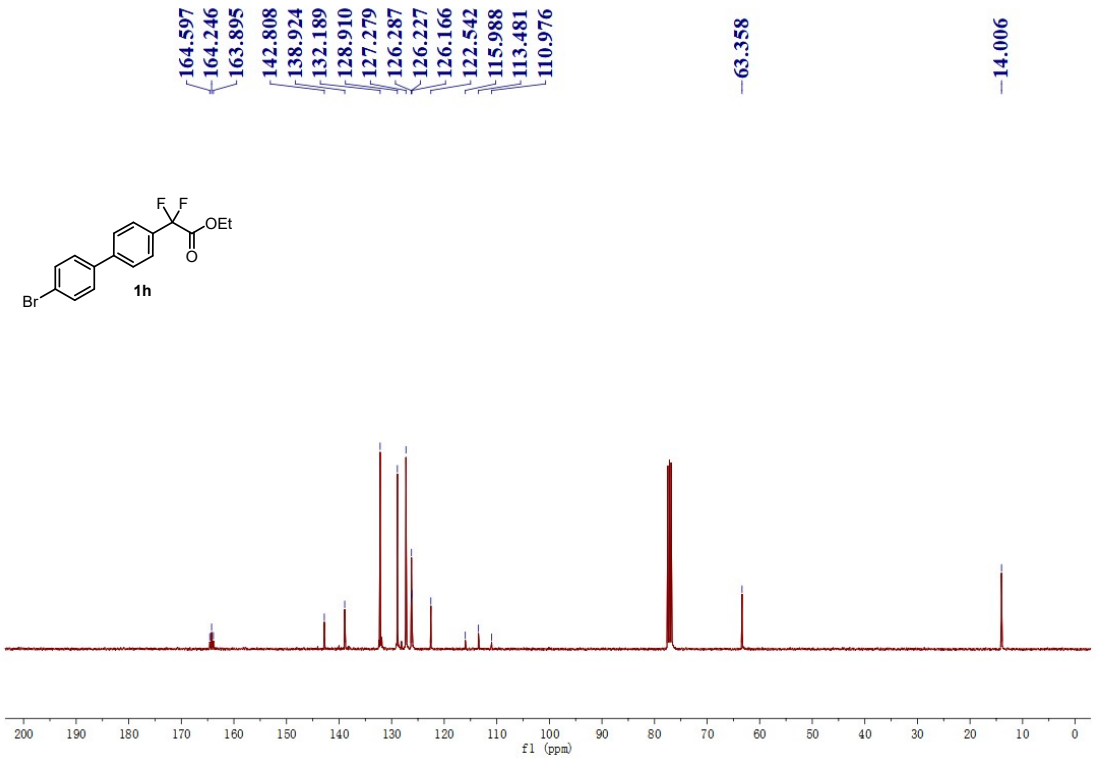
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1h (Chloroform-d)

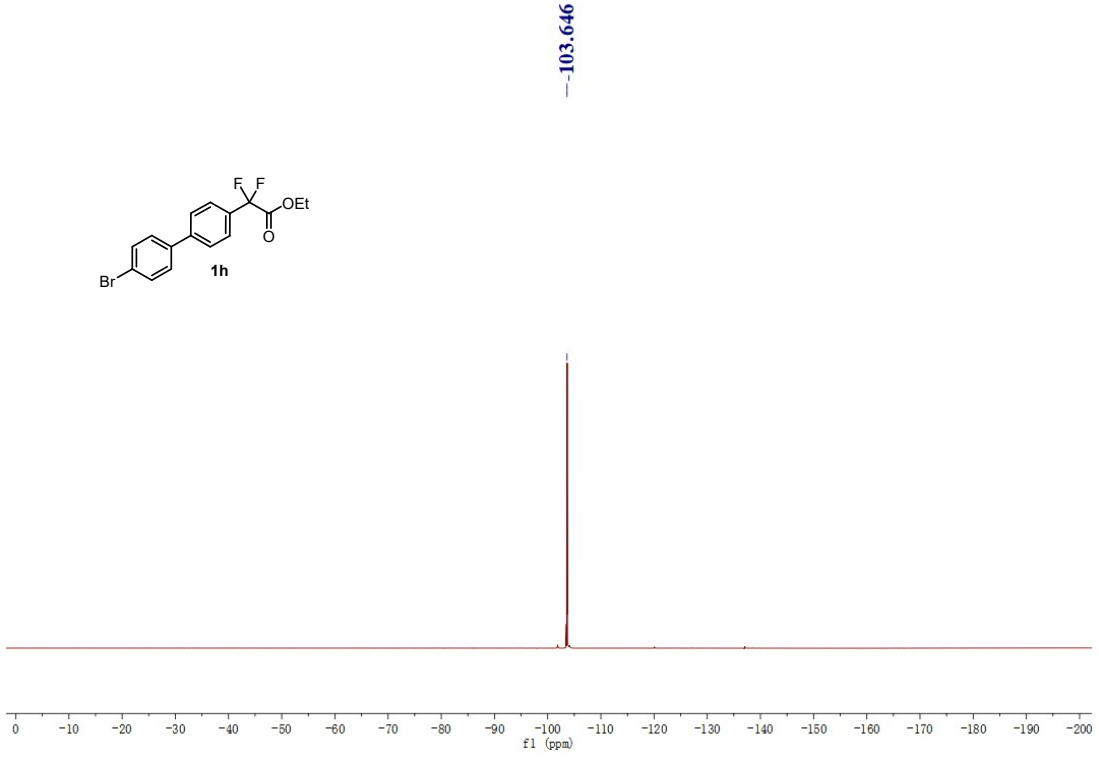




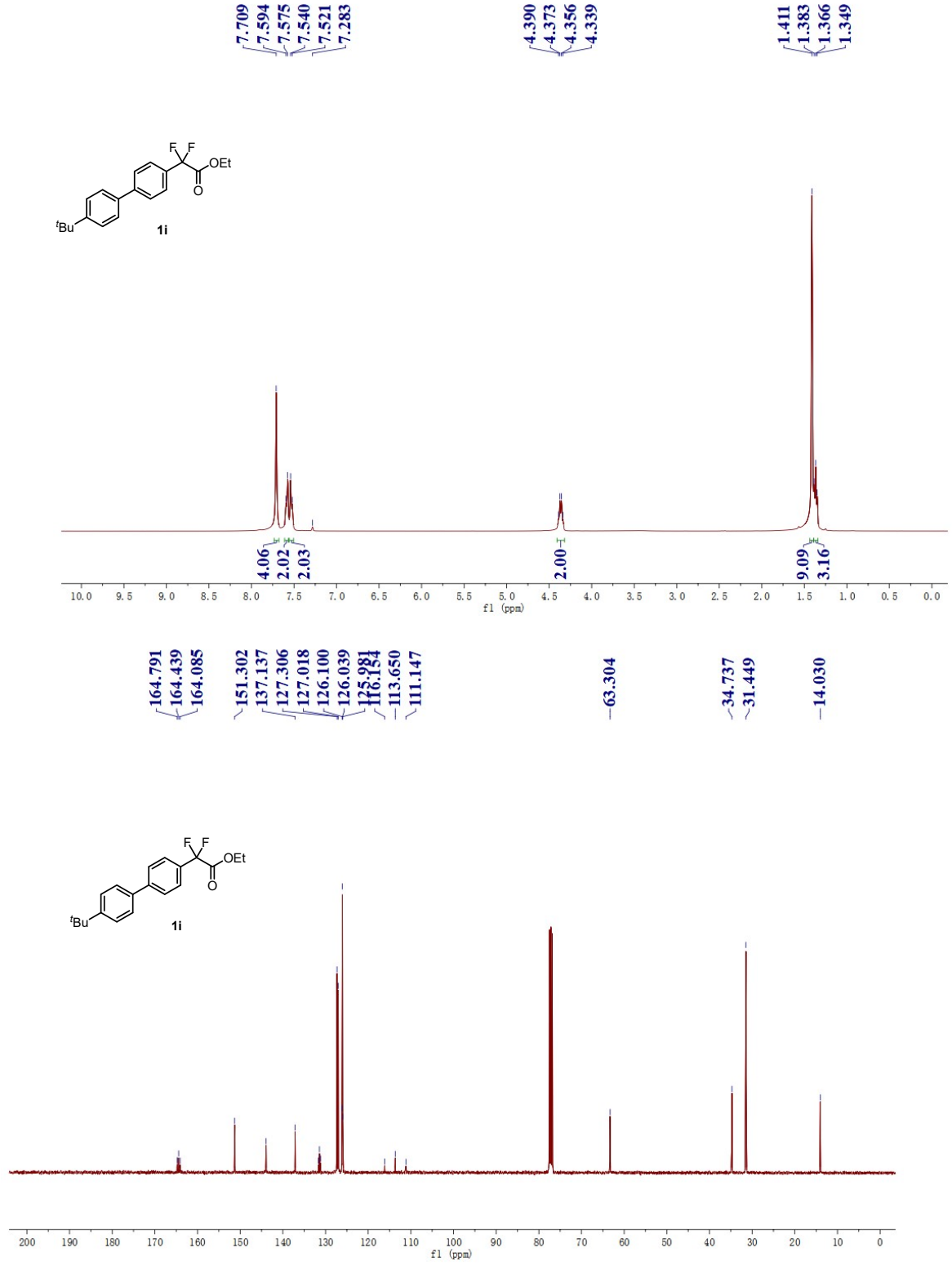
1h

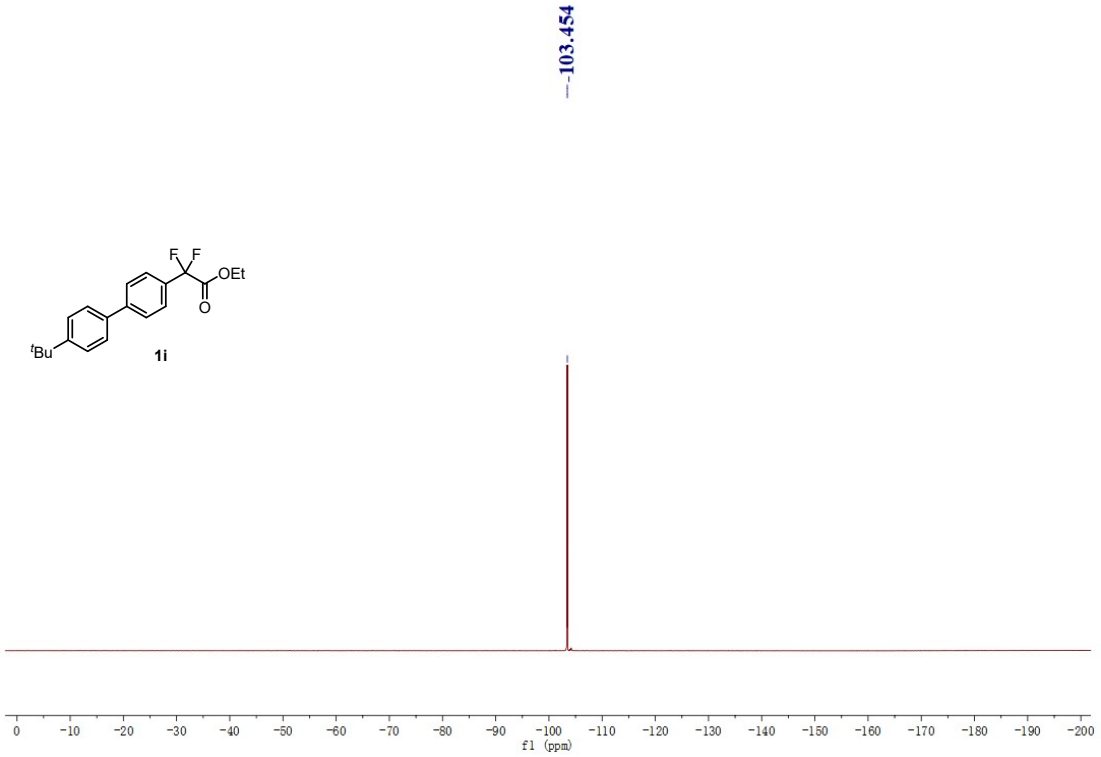



164.597
164.246
163.895
142.808
138.924
132.189
128.910
127.279
126.287
126.227
126.166
122.542
115.988
113.481
110.976
63.358
14.006
F F
OEt
O
Br
1h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

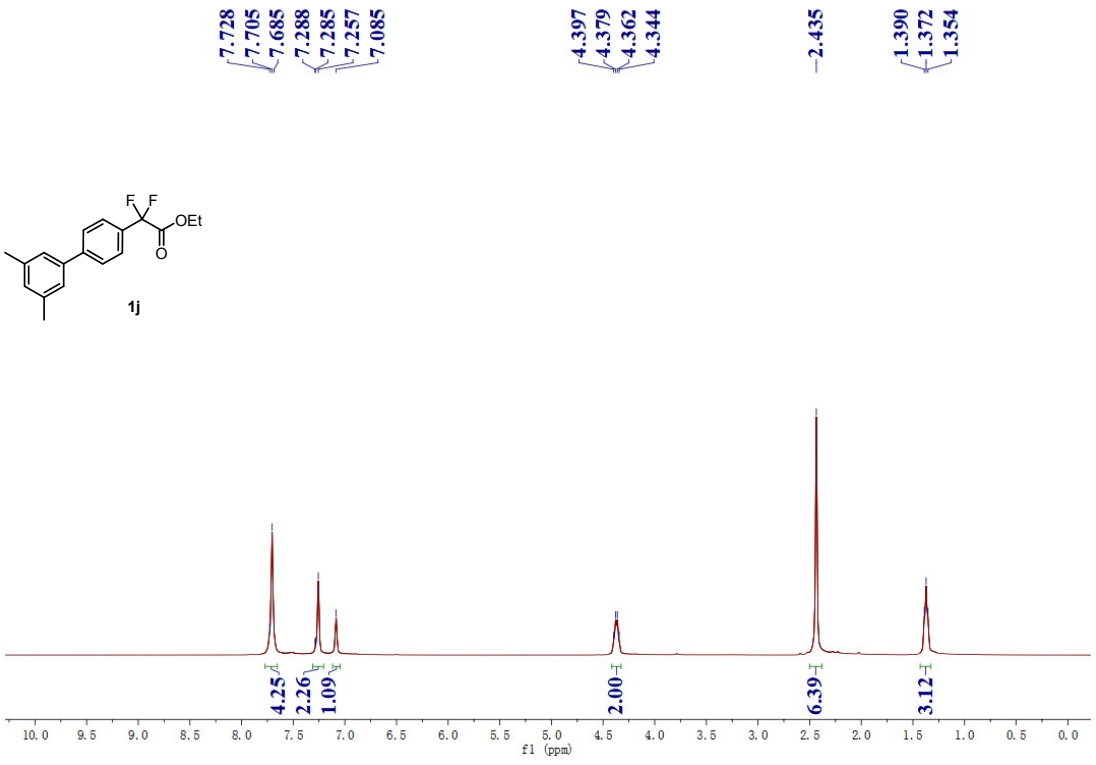

-103.646
F F
OEt
O
Br
1h
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

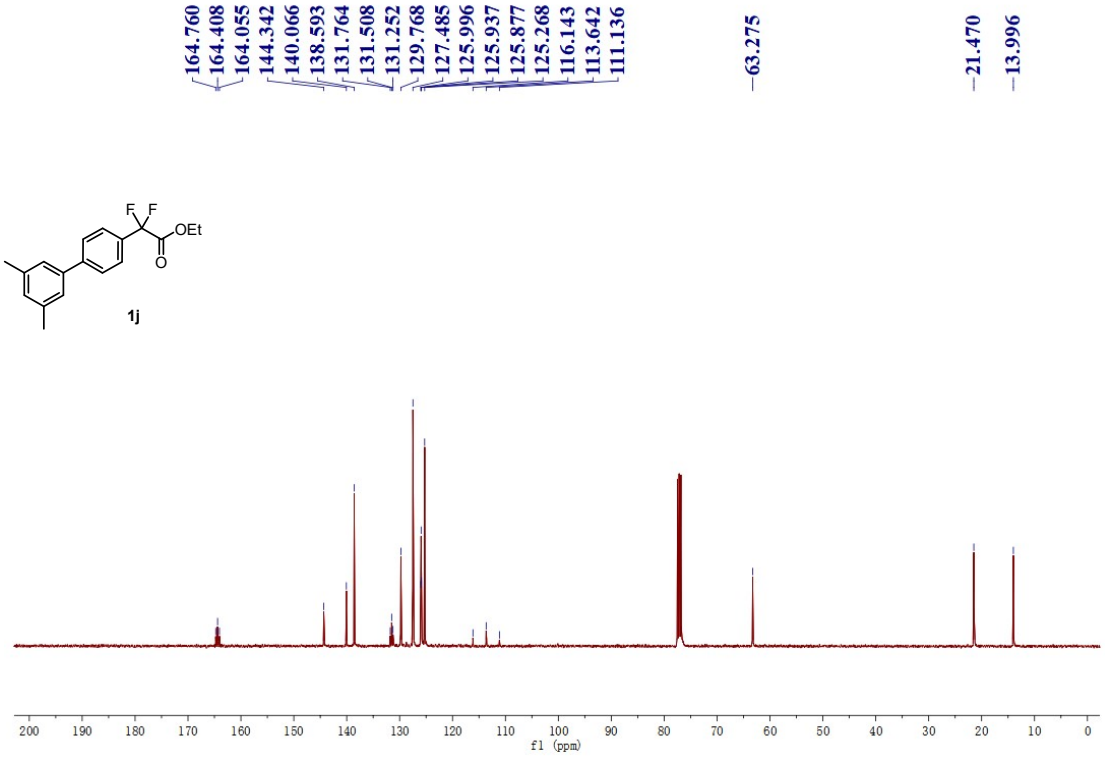
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1i (Chloroform-d)

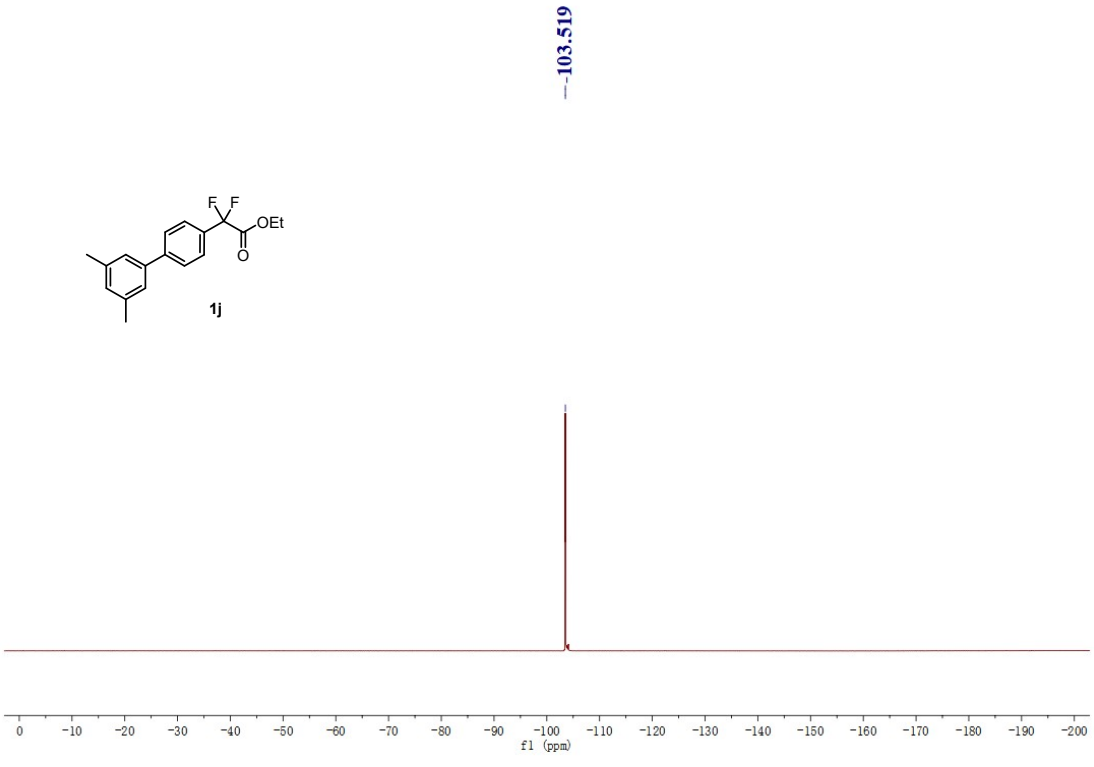




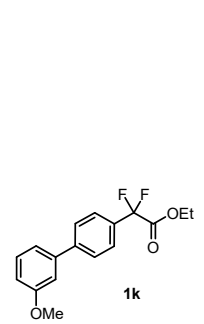
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1j (Chloroform-d)




164.760
164.408
164.055
144.342
140.066
138.593
131.764
131.508
131.252
129.768
127.485
125.996
125.937
125.877
125.268
116.143
113.642
111.136
63.275
21.470
13.996
F
F
OEt
O
1j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.519
F
F
OEt
O
1j
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

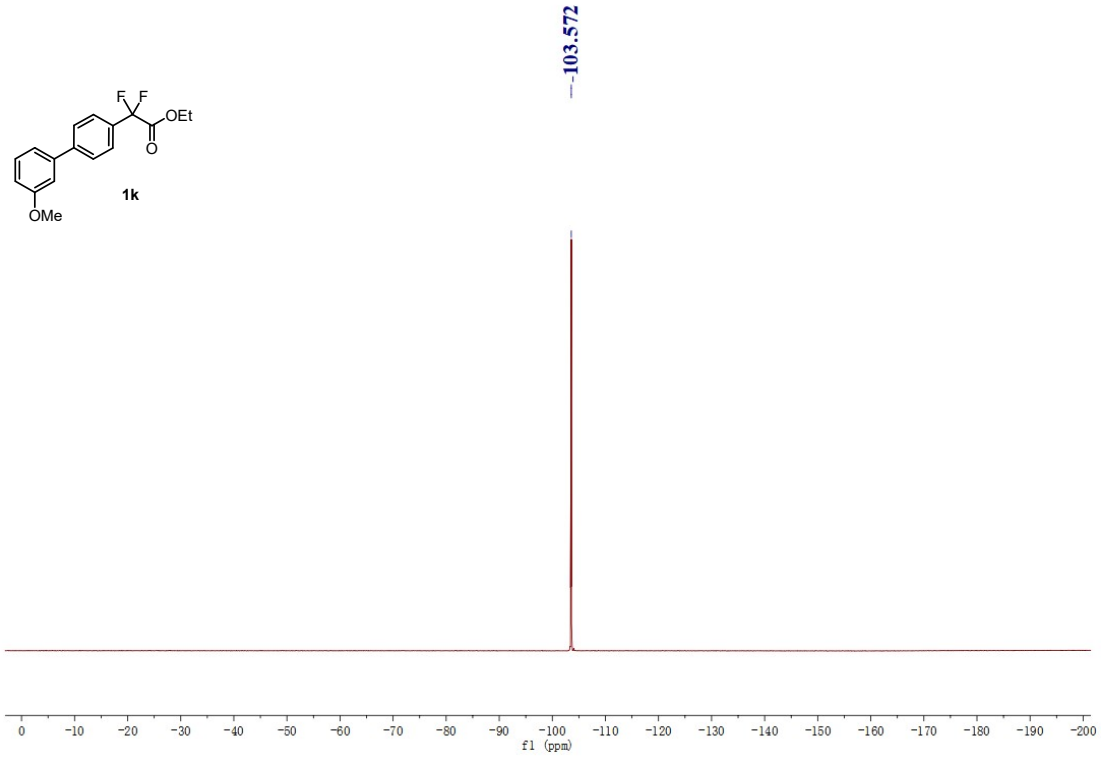
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1k (Chloroform-d)



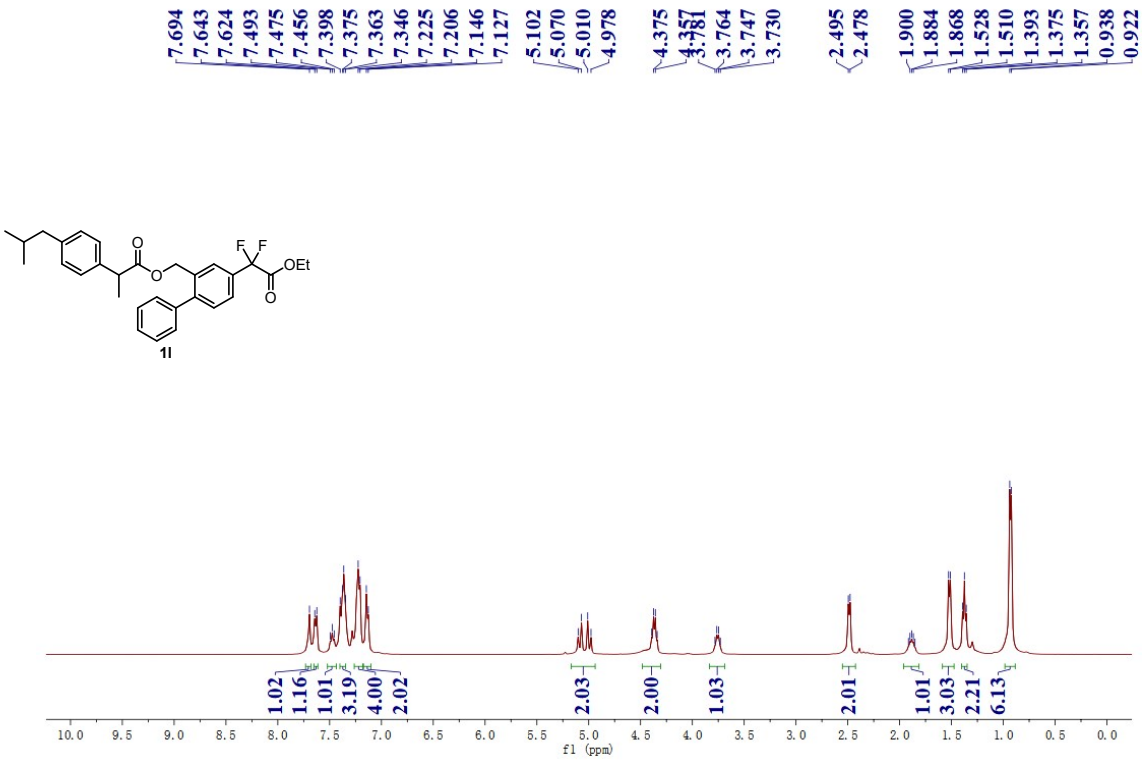
1k

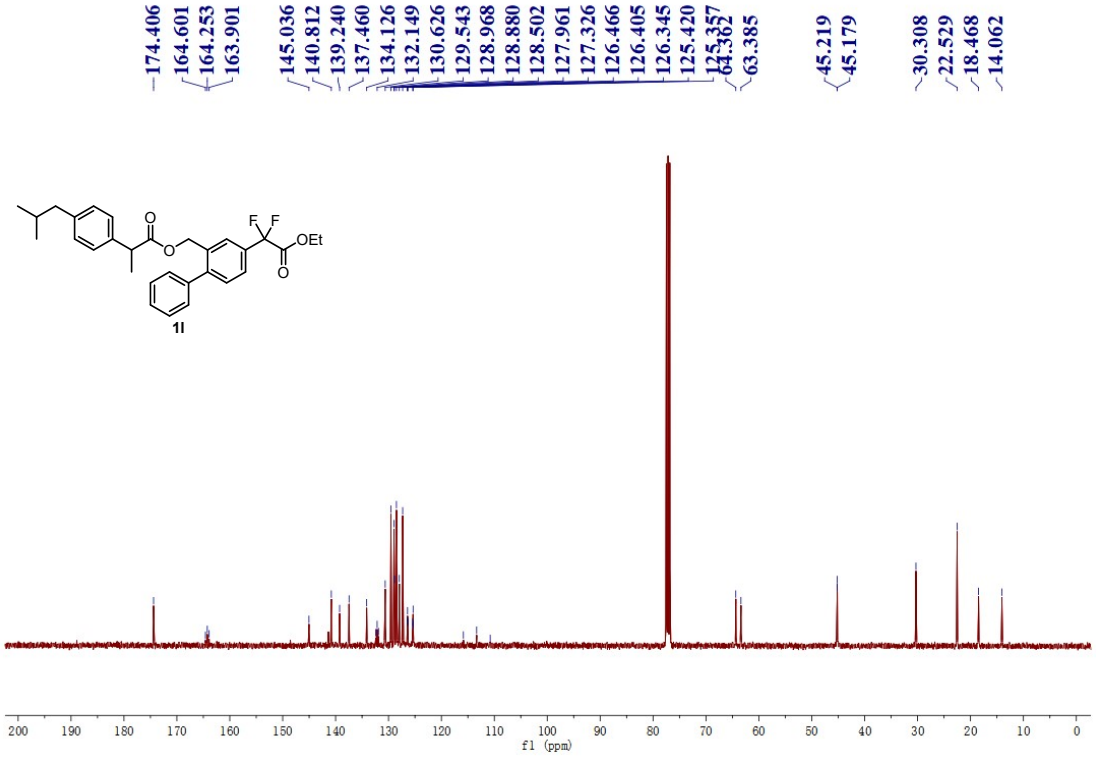
F
F
OEt
O
OMe

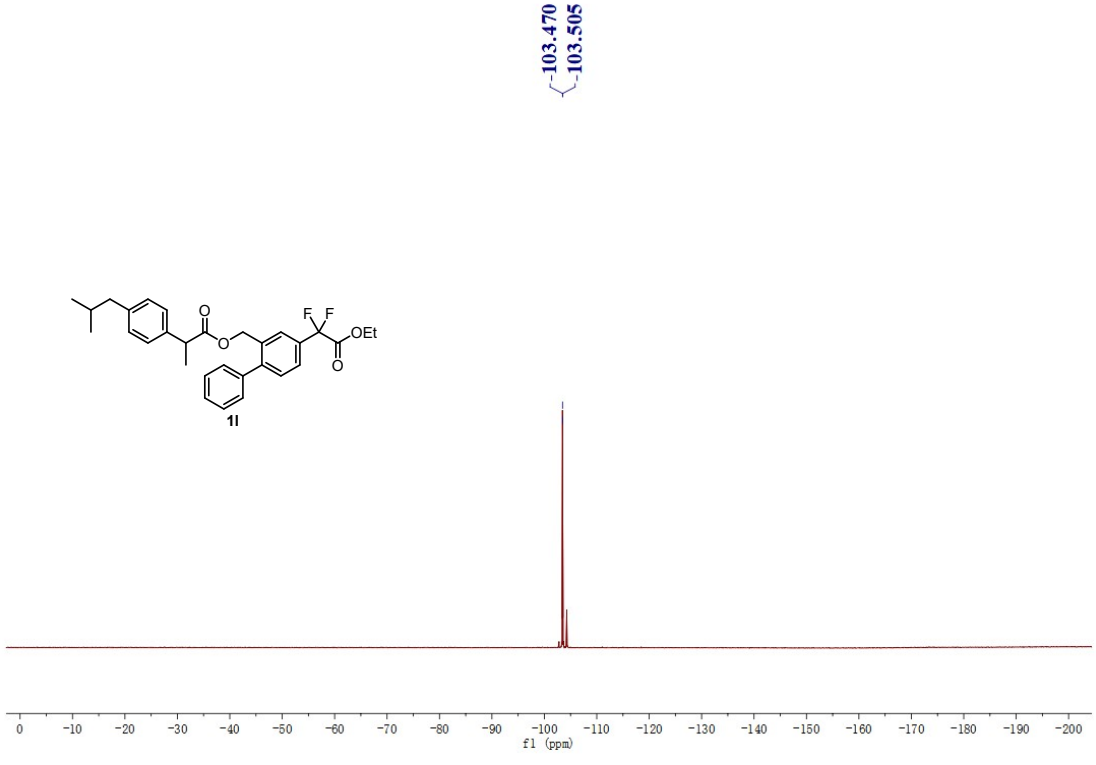
1k



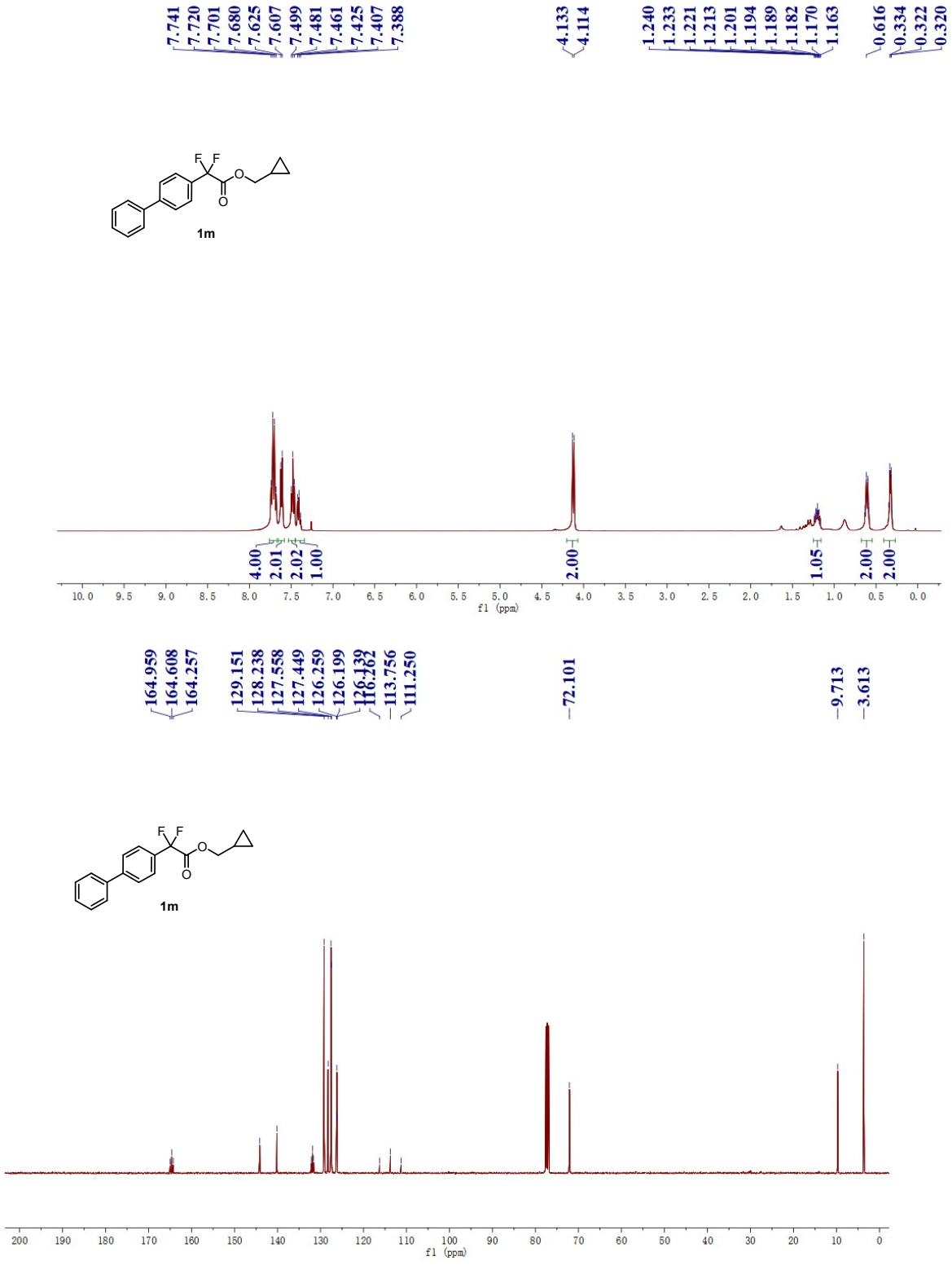
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1l (Chloroform-d)

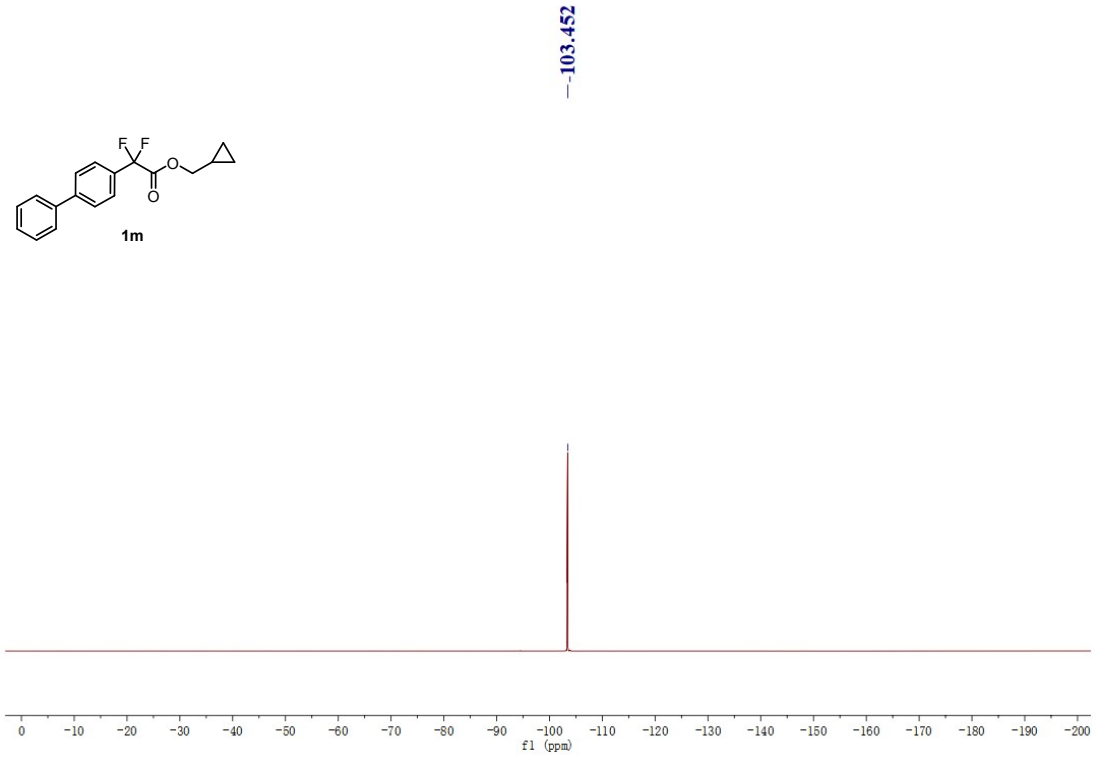



174.406
164.601
164.253
163.901
145.036
140.812
139.240
137.460
134.126
132.149
130.626
129.543
128.968
128.880
128.502
127.961
127.326
126.466
126.405
126.345
125.420
125.357
64.362
63.385
45.219
45.179
30.308
22.529
18.468
14.062
O
O
F F
OEt
O
1l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

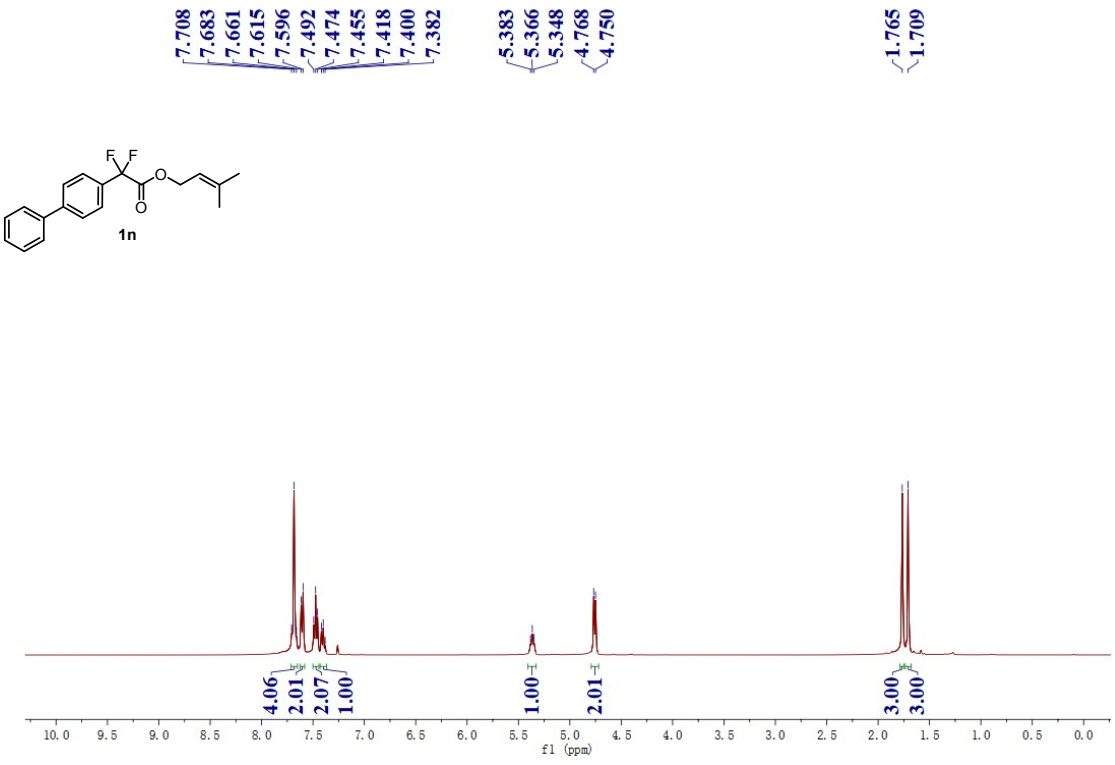

103.470
103.505
O
O
F F
OEt
O
1l
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

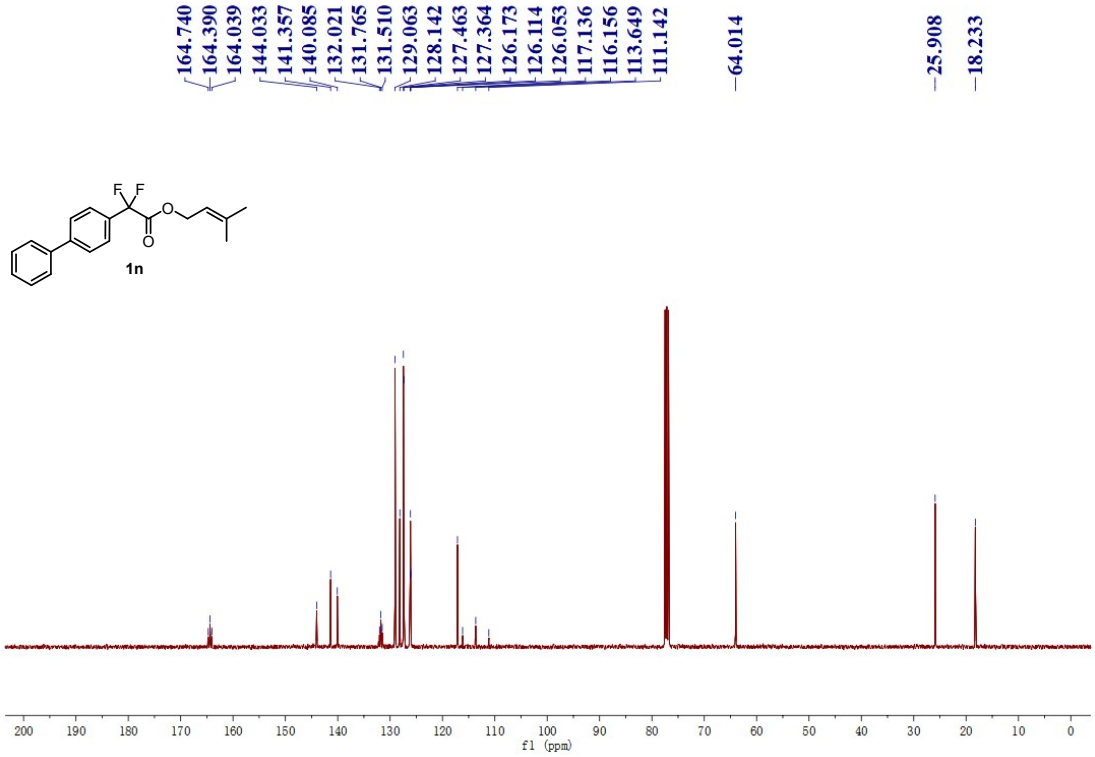
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1m (Chloroform-d)

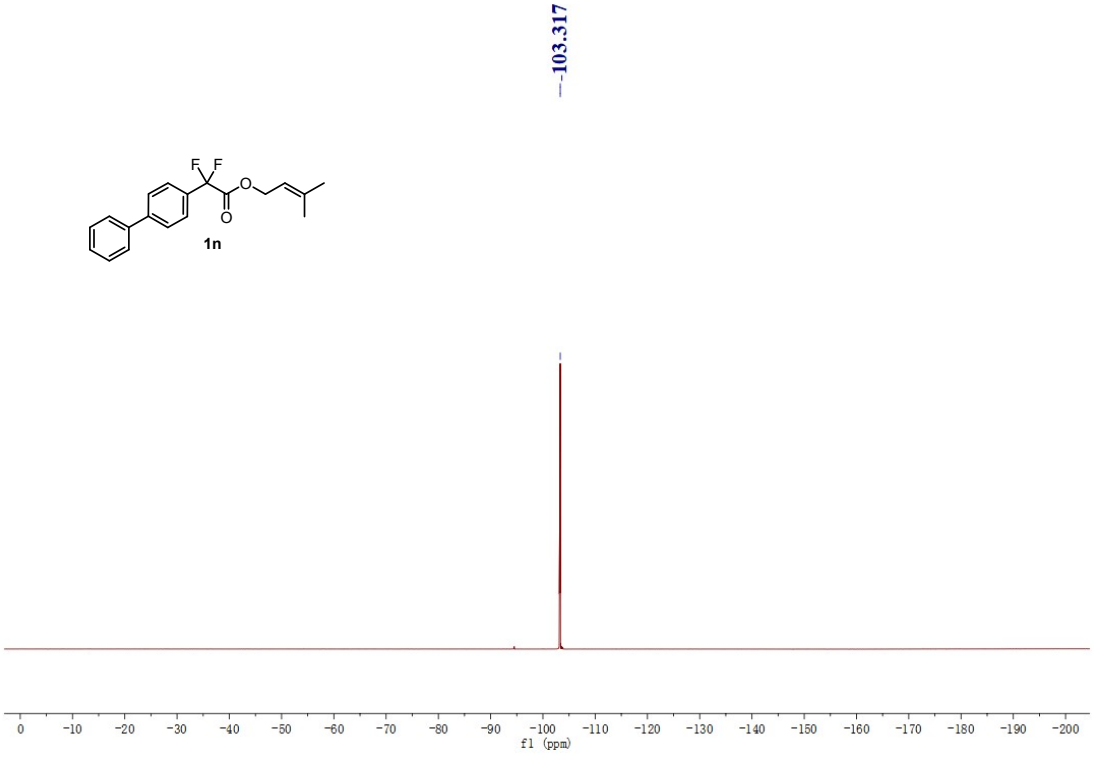




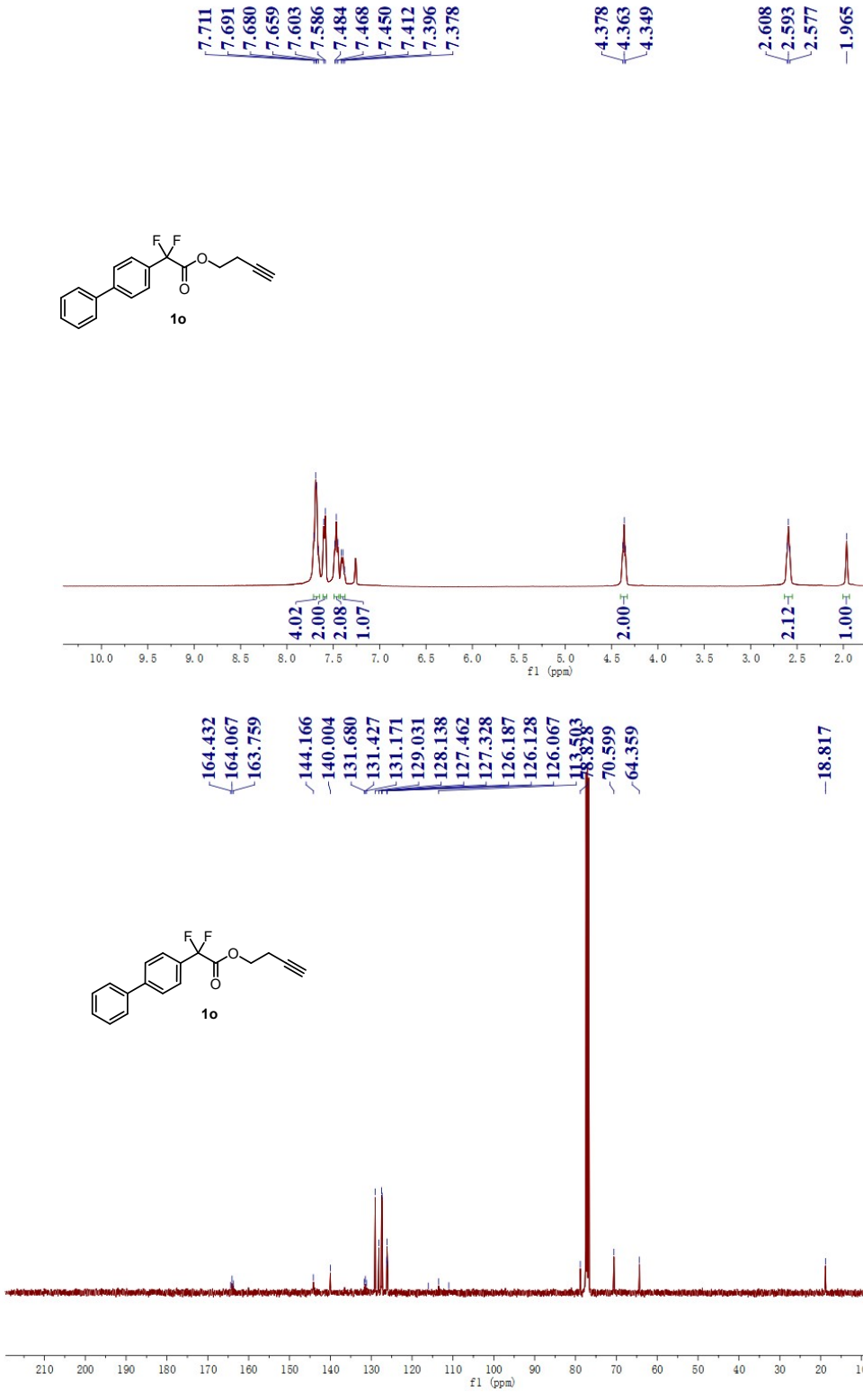
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1n (Chloroform-d)

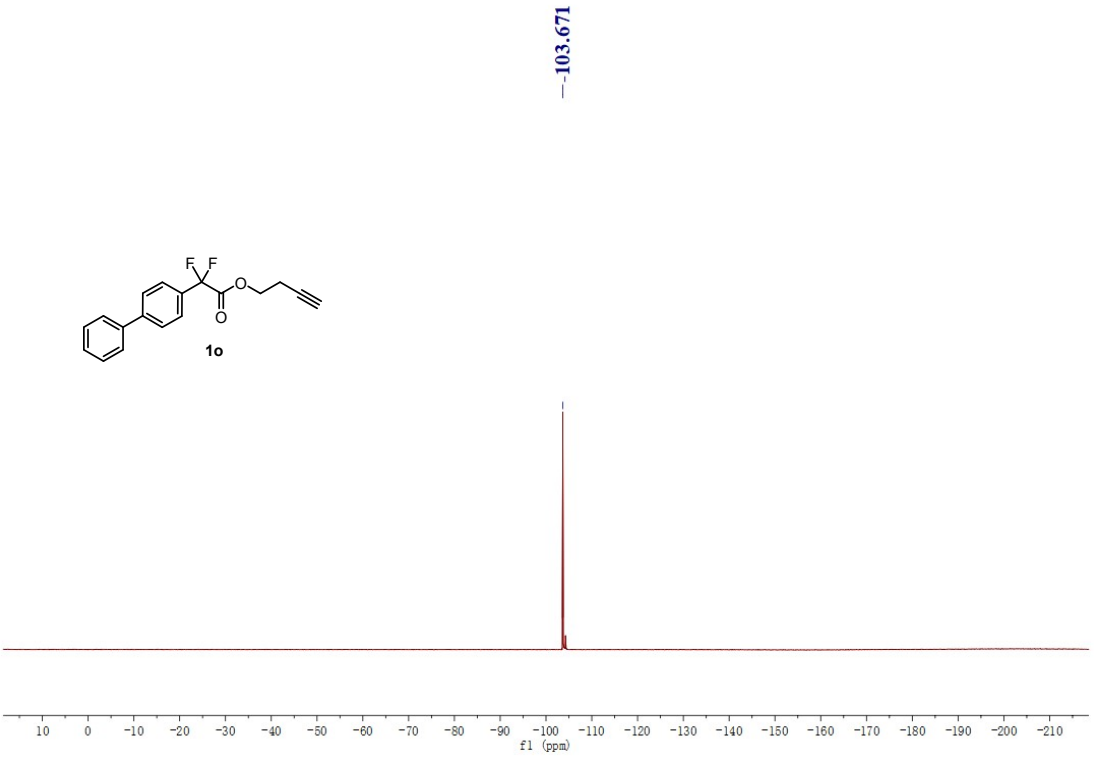



164.740
164.390
164.039
144.033
141.357
140.085
132.021
131.765
131.510
129.063
128.142
127.463
127.364
126.173
126.114
126.053
117.136
116.156
113.649
111.142
64.014
25.908
18.233
F F
O
O
1n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

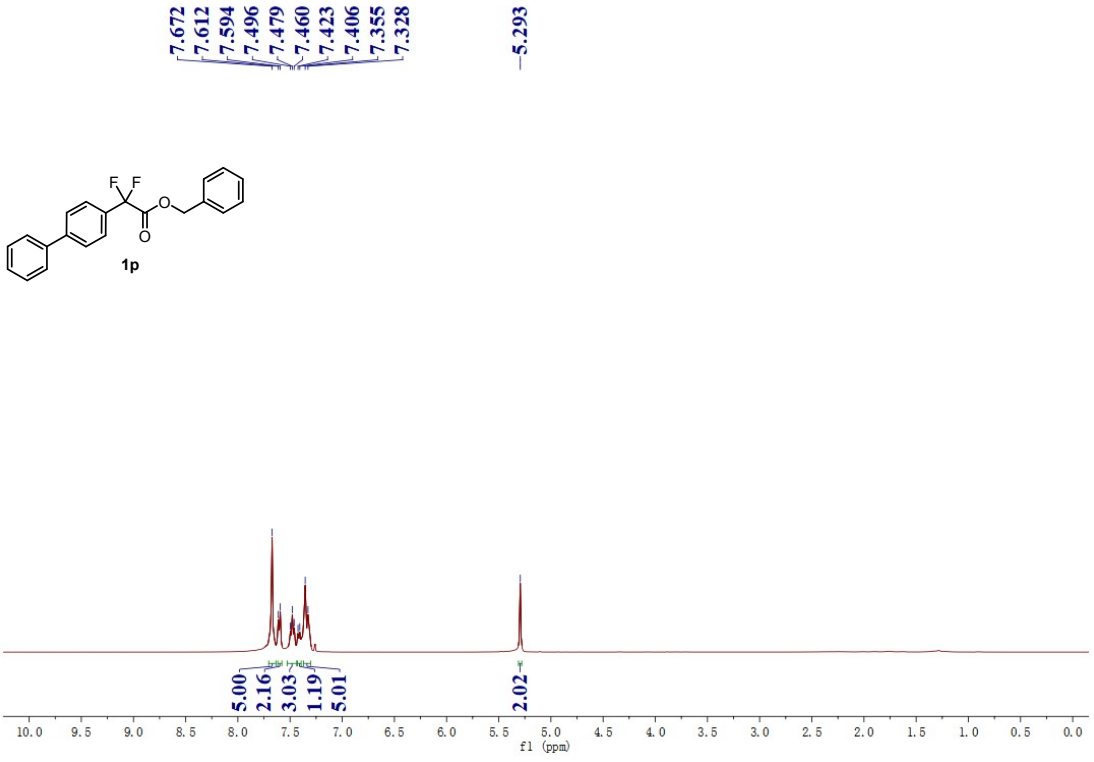

-103.317
F F
O
O
1n
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

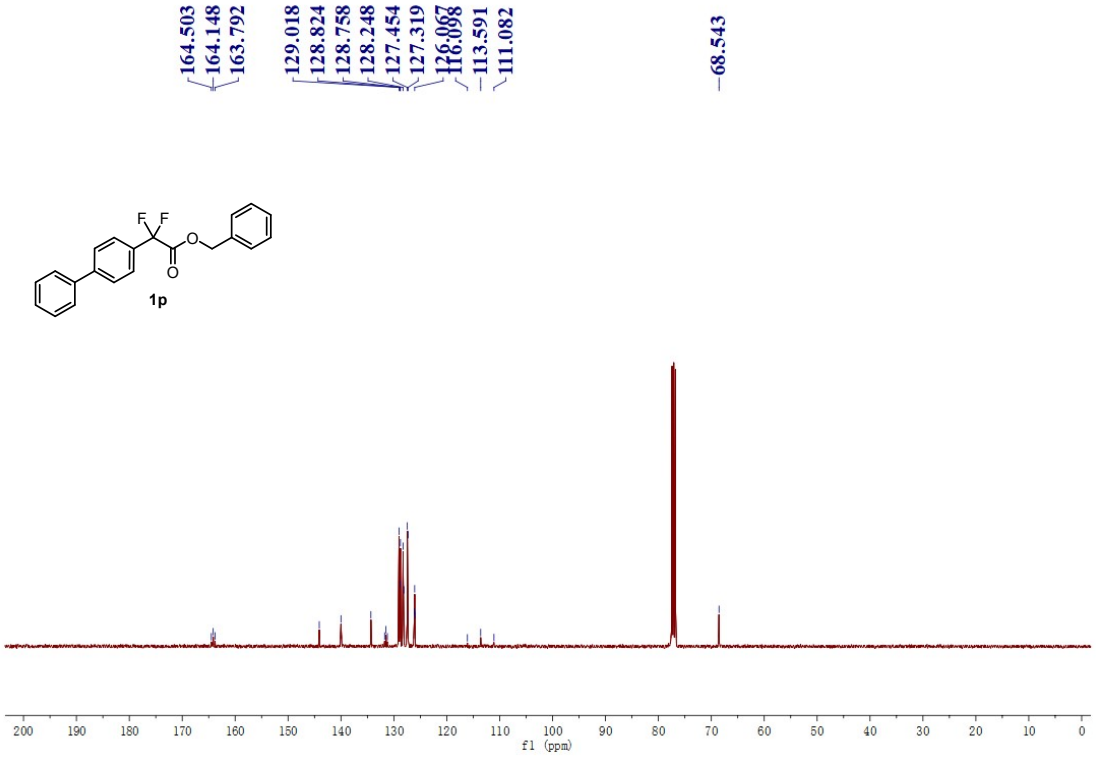
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1o (Chloroform-d)

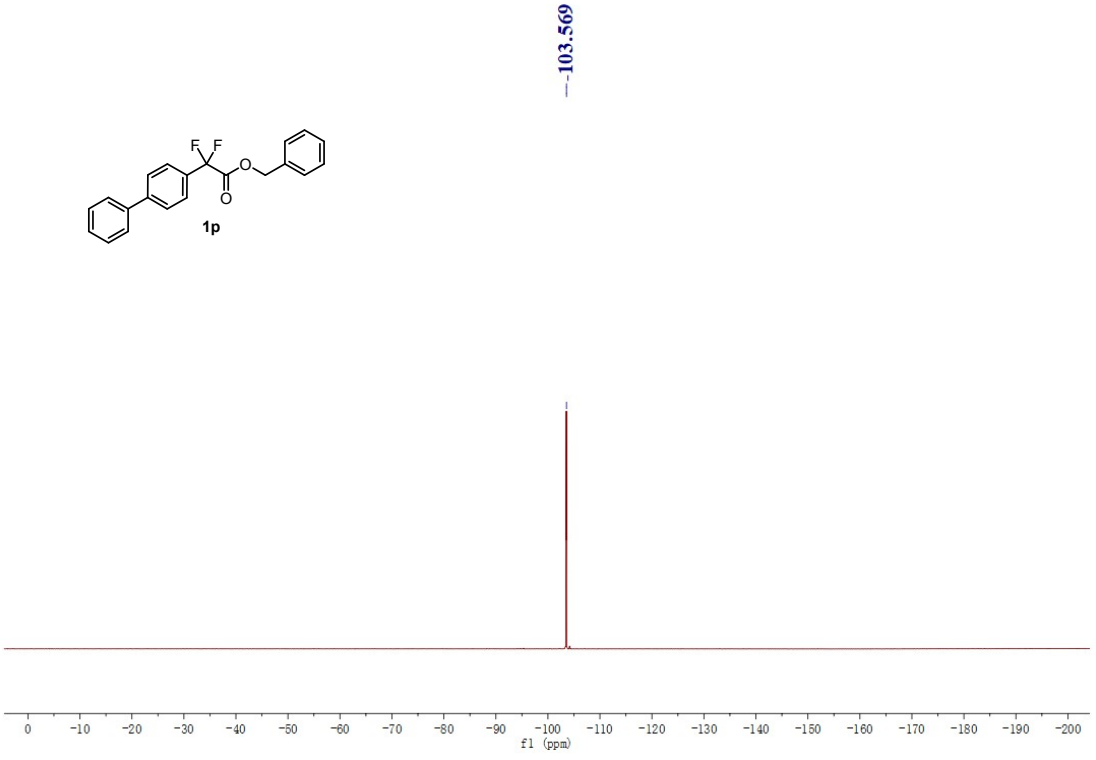




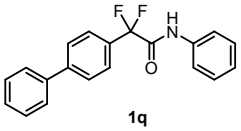
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1p (Chloroform-d)



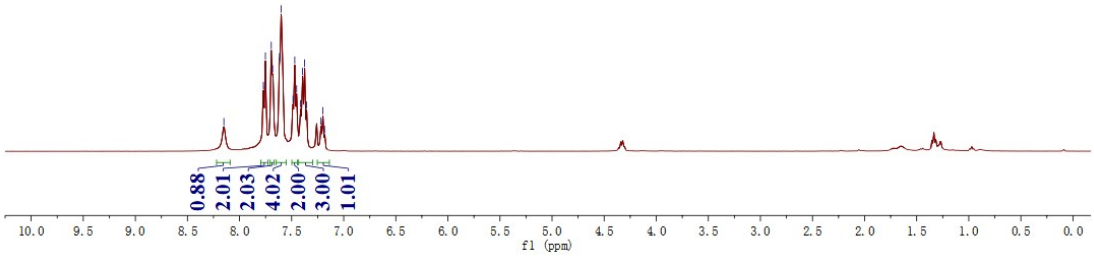

164.503
164.148
163.792
129.018
128.824
128.758
128.248
127.454
127.319
126.067
116.098
113.591
111.082
68.543
F
F
O
O
1p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

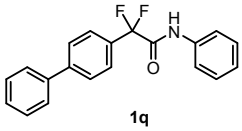

-103.569
F
F
O
O
1p
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1q (Chloroform-d)

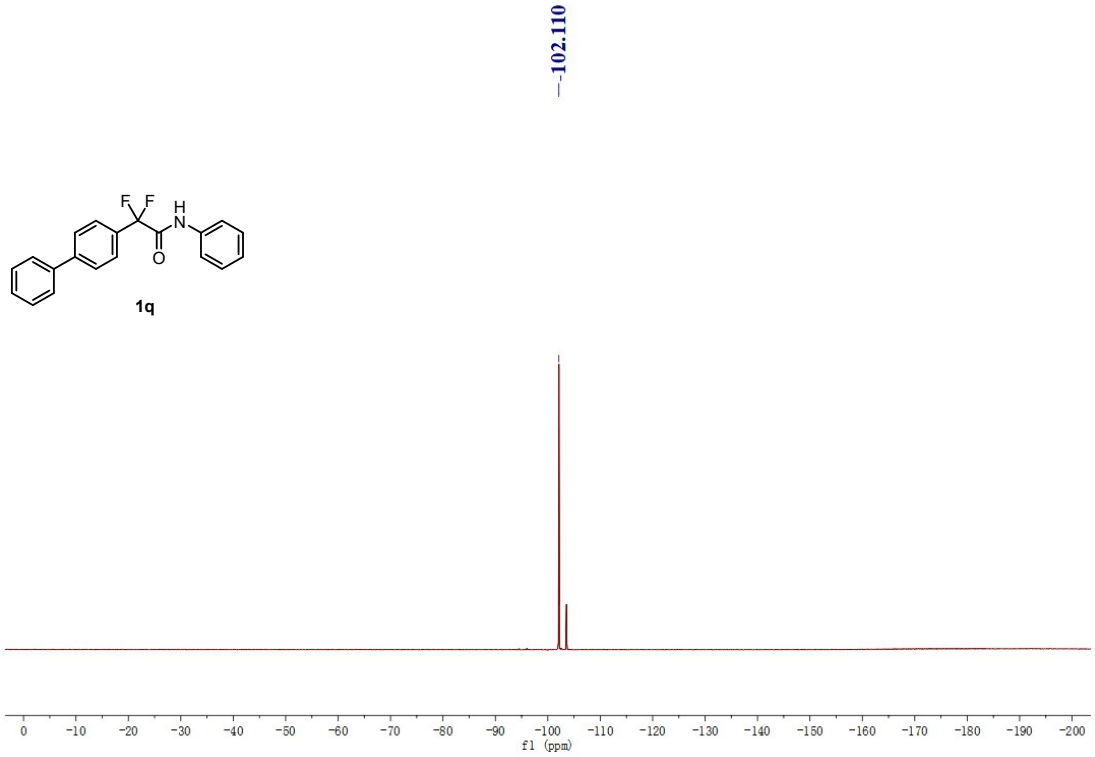


1q

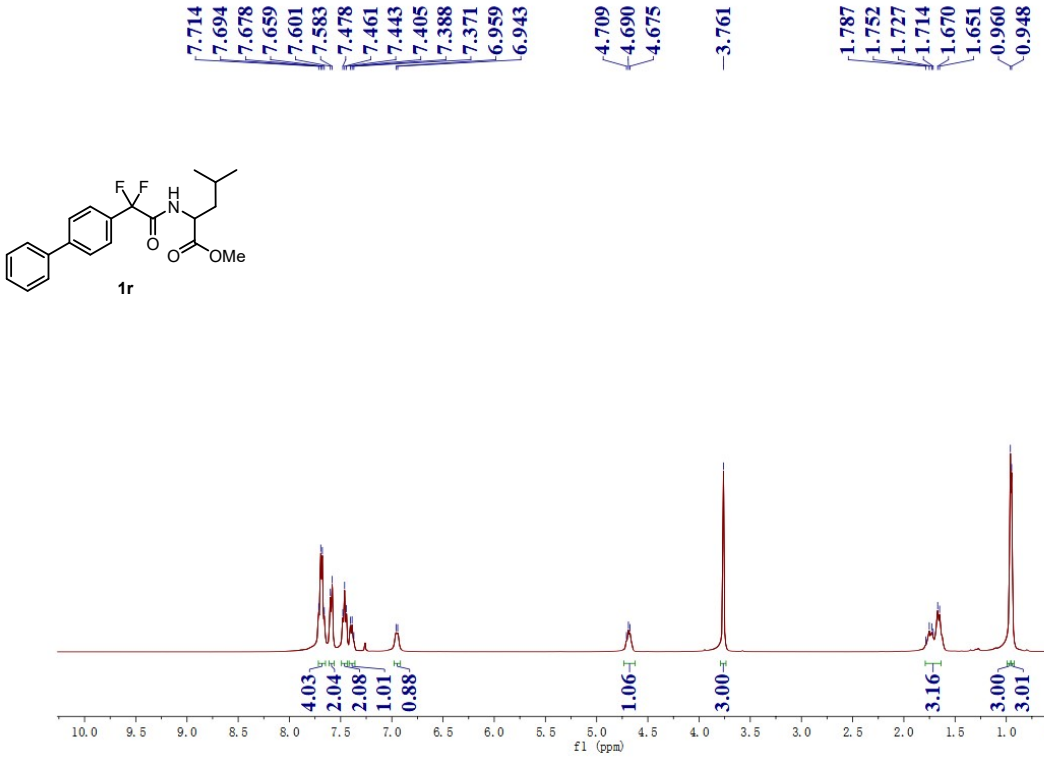


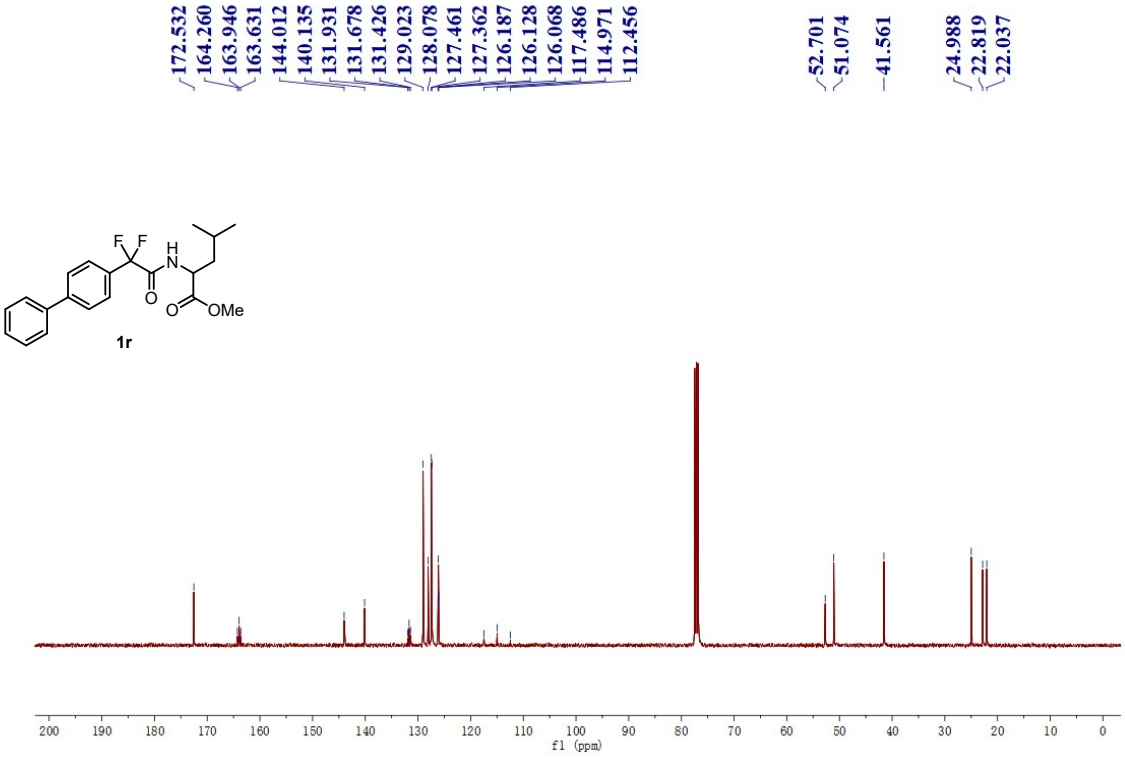


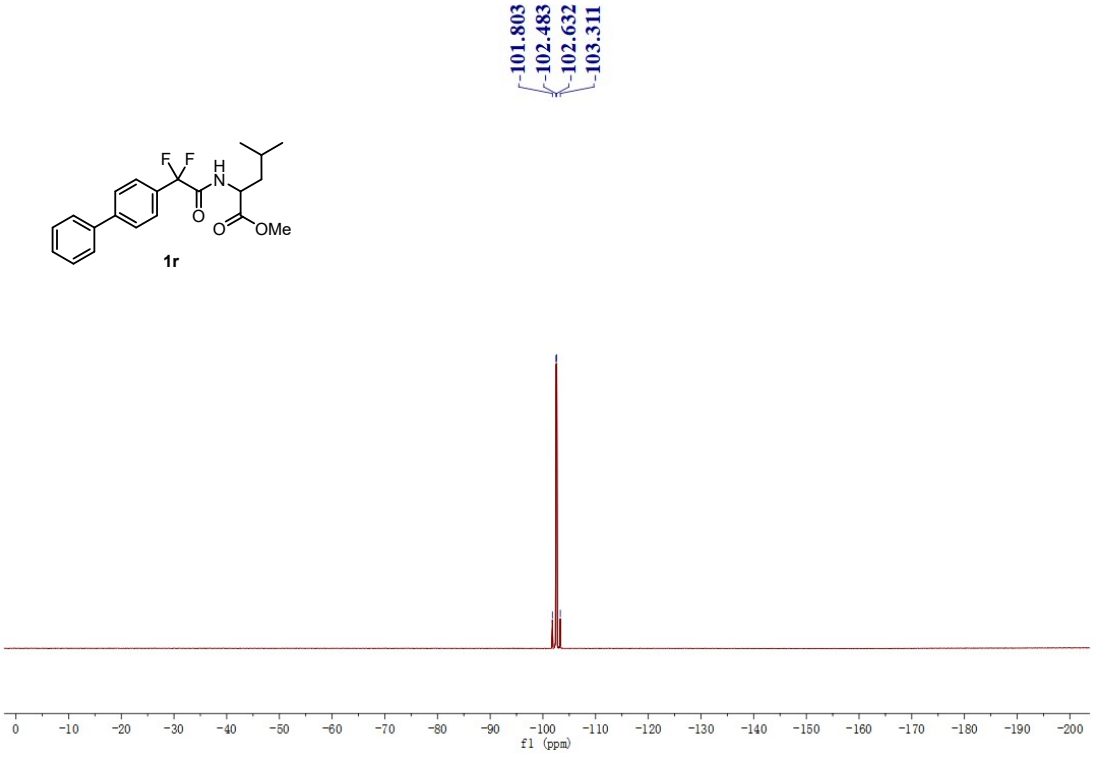
1q



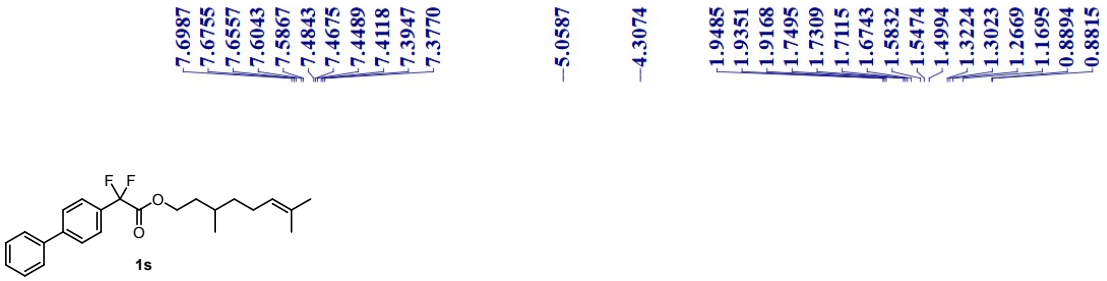
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1r (Chloroform-d)

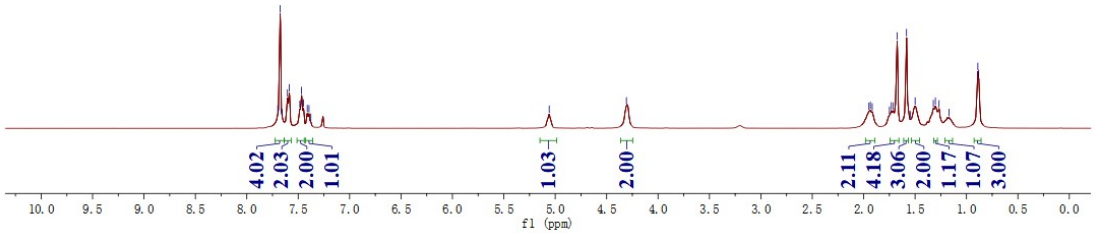


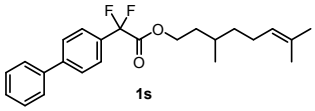

172.532
164.260
163.946
163.631
144.012
140.135
131.931
131.678
131.426
129.023
128.078
127.461
127.362
126.187
126.128
126.068
117.486
114.971
112.456
52.701
51.074
41.561
24.988
22.819
22.037
F
F
H
N
O
O
OMe
1r
f1 (ppm)

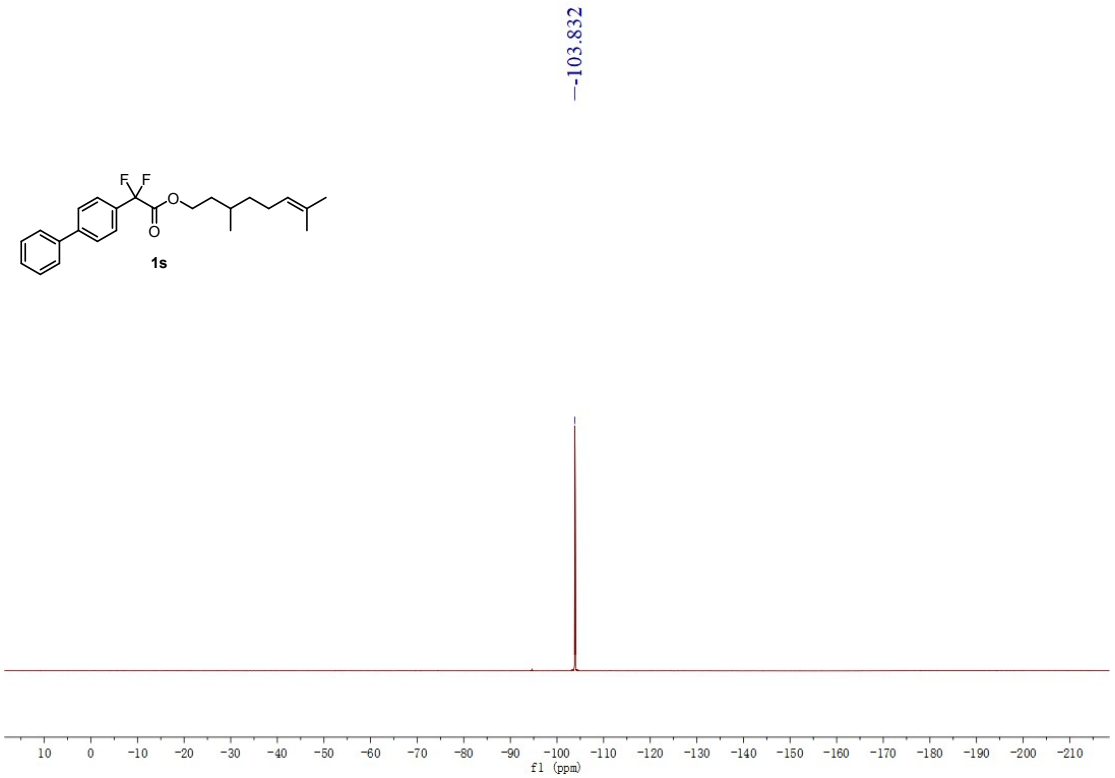

101.803
102.483
102.632
103.311
F
F
H
N
O
O
OMe
1r
f1 (ppm)

^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1s (Chloroform-d)

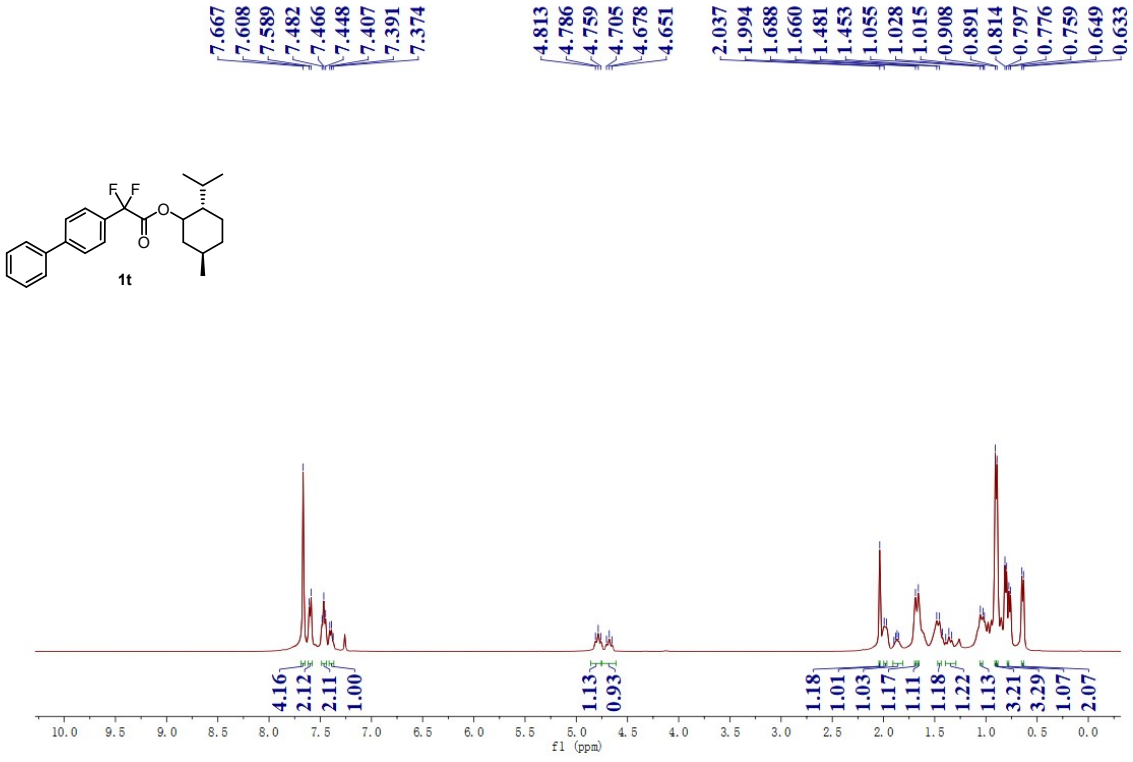


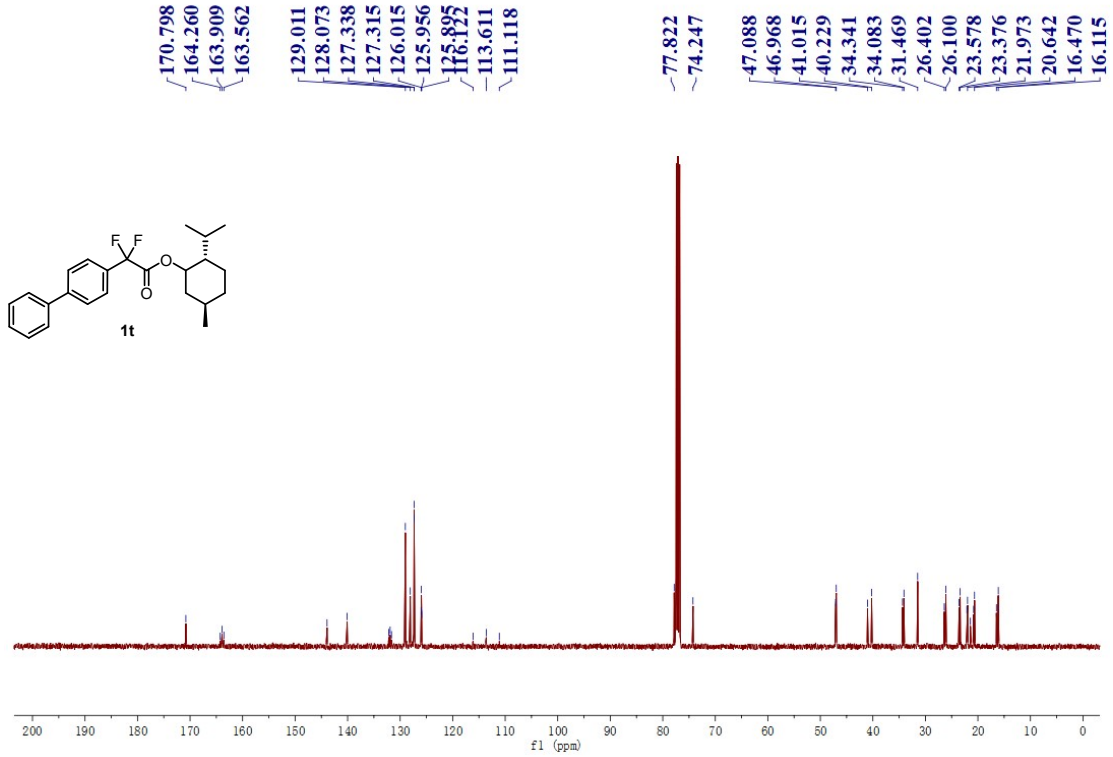


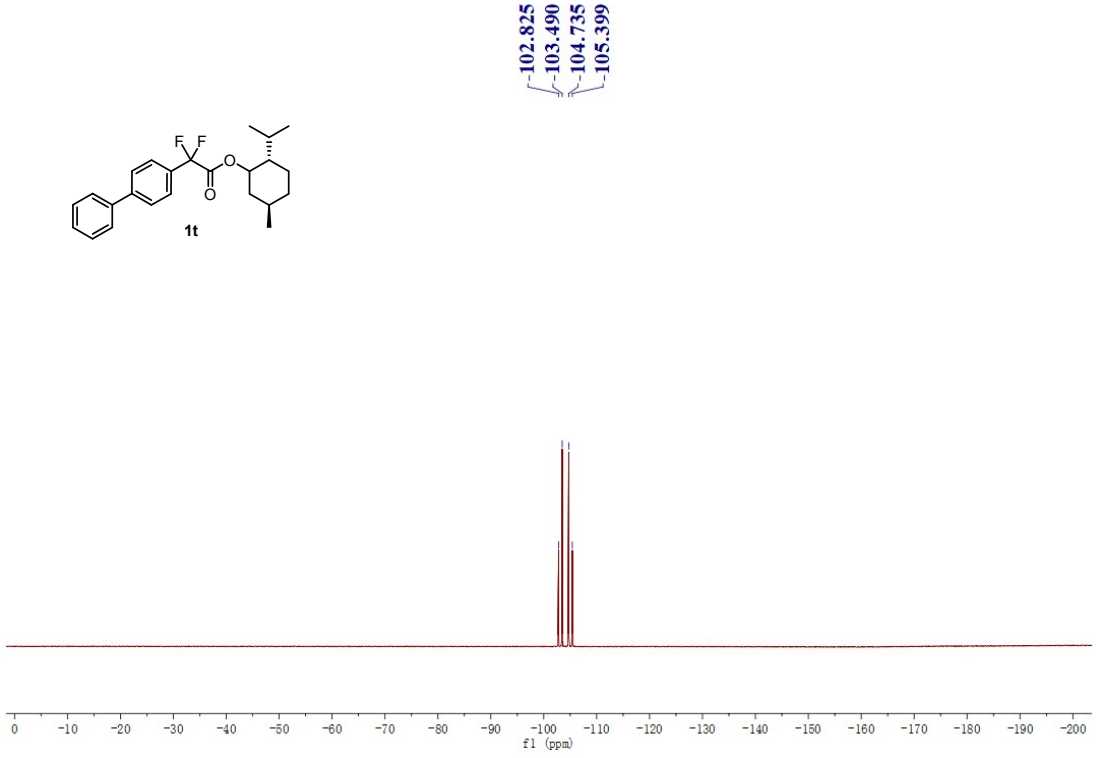




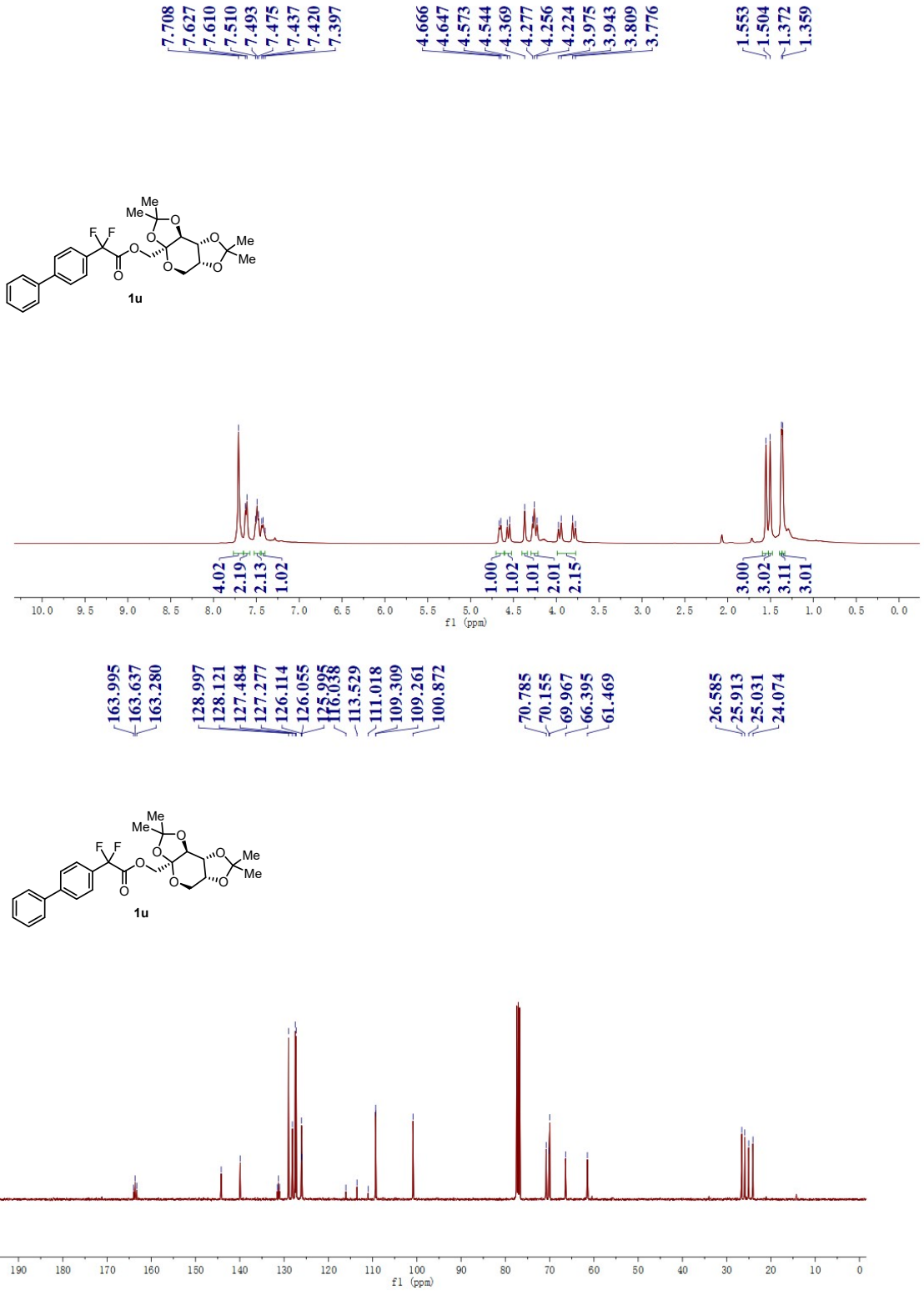
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1t (Chloroform-d)

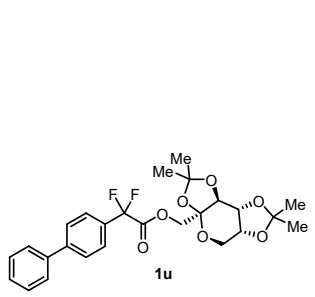


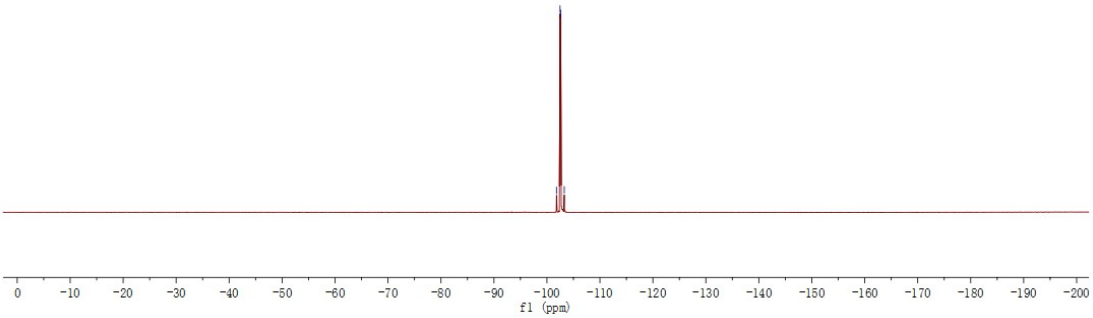

170.798
164.260
163.909
163.562
129.011
128.073
127.338
127.315
126.015
125.956
125.895
116.122
113.611
111.118
77.822
74.247
47.088
46.968
41.015
40.229
34.341
34.083
31.469
26.402
26.100
23.578
23.376
21.973
20.642
16.470
16.115
F
F
O
O
1t
f1 (ppm)


102.825
103.490
104.735
105.399
F
F
O
O
1t
f1 (ppm)

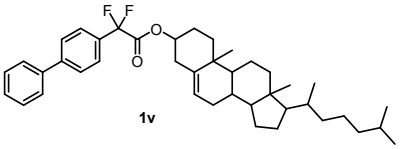
^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1u (Chloroform-d)

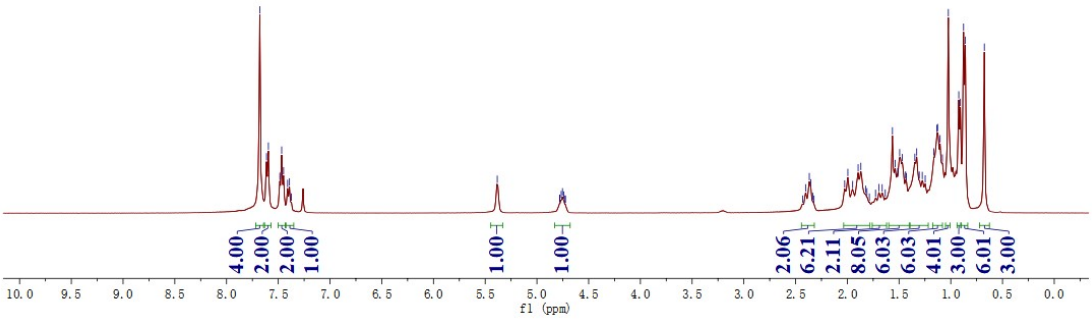


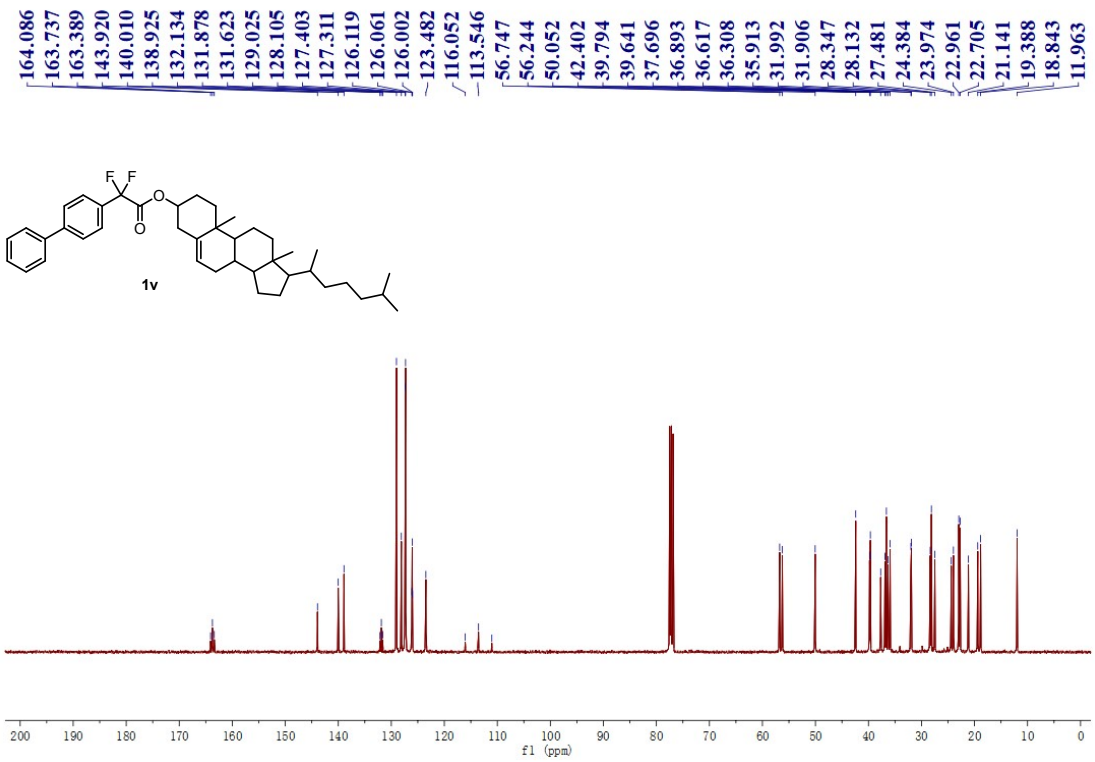


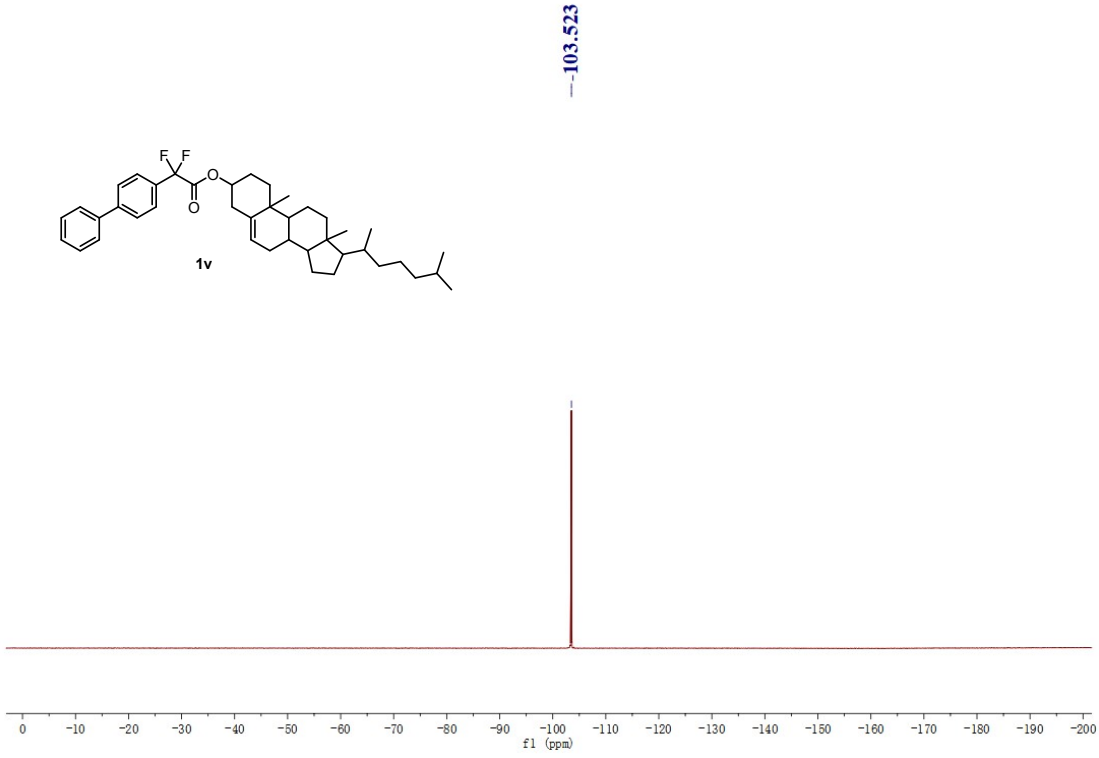


^{1}H, ^{13}C NMR and ^{19}F spectra for compound 1v (Chloroform-d)






164.086
163.737
163.389
143.920
140.010
138.925
132.134
131.878
131.623
129.025
128.105
127.403
127.311
126.119
126.061
126.002
123.482
116.052
113.546
56.747
56.244
50.052
42.402
39.794
39.641
37.696
36.893
36.617
36.308
35.913
31.992
31.906
28.347
28.132
27.481
24.384
23.974
22.961
22.705
21.141
19.388
18.843
11.963
F F
O
O
1v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.523
F F
O
O
1v
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)