Supporting Information for

Enantioselective Di-/Perfluoroalkylation of *β*-Ketoesters Enabled by Cooperative Photoredox/Nickel Catalysis

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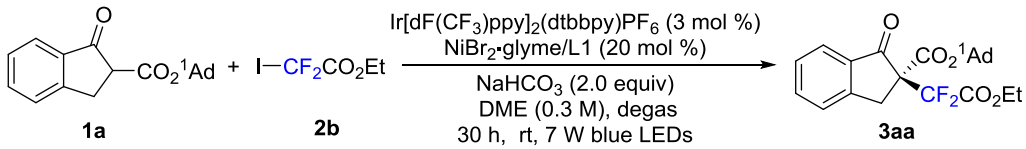
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.[1] Flash column chromatography was performed using 200-300 mesh silica gel.[2] ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 or 150 MHz with complete proton decoupling spectrophotometers. HRMS was recorded on Agilent technologies 6224 TOF LC/MS instrument or Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer. Enantiomeric excesses (ee) were determined by chiral HPLC with chiral columns (chiralpak AD-H column, chiralcel OD-H column) with hexane and *i*-PrOH as solvents. Optical rotations were measured with a polarimeter. All admantyl esters substrates **1** were prepared by transesterification[3] of methyl ester which was prepared according to the previous method.[4] Ligands were synthesised according to the literatures[5] or commerially available. All air- and moisture-sensitive reactions were performed under an atmosphere of Ar in fire dried glassware.

2. General Procedure and Spectral Data of the Products

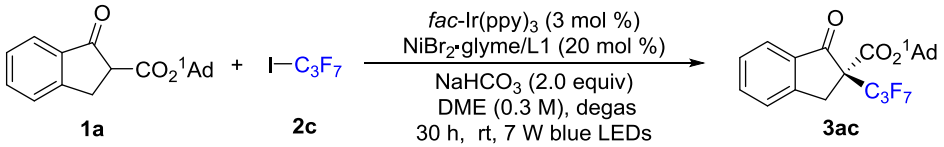
2.1 General procedure for the synthesis of 3aa, 3bb-ob



1a **2b** **3aa**

Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$-glyme (12.34 mg, 0.04 mmol) and **L1** (12.82 mg, 0.04 mmol) and 0.67 mL of DME under Ar. After 0.5 h of stirring at room temperature, substrate **1a** (62.08 mg, 0.2 mmol) was added under Ar. After 10 mins, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (6.73 mg, 0.006 mmol), $NaHCO_3$ (33.6 mg, 0.4 mmol) and substrate **2b** (99.99 mg, 0.4 mmol) were added to the mixture. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 30 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 50/1) to give product **3aa** with 67% yield (58 mg). Other products **3bb-ob** were prepared according to the above procedure.

2.2 General procedure for the synthesis of 3ac, 3kc, 3lc, 3ad

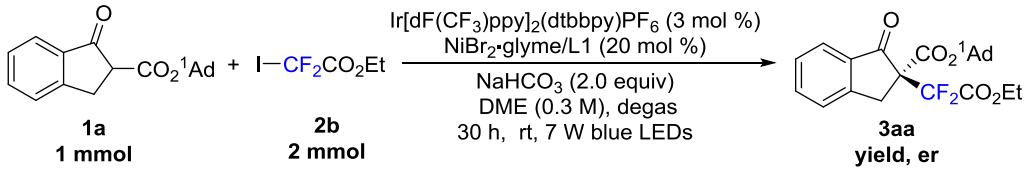


1a **2c** **3ac**

Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$-glyme (12.34 mg, 0.04 mmol) and **L1** (12.82 mg, 0.04 mmol) and 0.67 mL of DME under Ar. After 0.5 h of stirring at room temperature, substrate **1a** (62.08 mg, 0.2 mmol) was added under Ar. After 10 mins, *fac*-$Ir(ppy)_3$ (3.92 mg, 0.006 mmol), $NaHCO_3$ (33.6 mg, 0.4 mmol) and substrate **2c** (118.4 mg, 0.4 mmol) were added to the mixture. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the

solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 30 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 50/1) to give product **3ac** with 43% yield (41 mg). Other products **3kc**, **3lc**, **3ad** were prepared according to the above procedure.

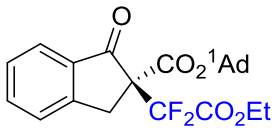
2.3 A 1 mmol-scale reaction



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$-glyme (62 mg, 0.2 mmol) and **L1** (64 mg, 0.2 mmol) and 3.35 mL of DME under Ar. After 1 h of stirring at room temperature, substrate **1a** (310 mg, 1.0 mmol) was added under Ar. After 30 mins, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (34 mg, 0.03 mmol), $NaHCO_3$ (168 mg, 2.0 mmol) and substrate **2b** (500 mg, 2.0 mmol) were added to the mixture. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 30 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 50/1) to give product **3aa** with 60% yield (260 mg) and 93:7 er.

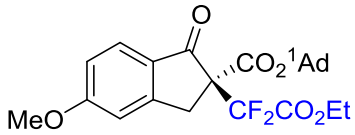
3. Spectral data of the products

(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3aa)



Colorless oil, 30 h, 58 mg, 67% yield. The er value was determined by chiral HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ^{o}C). t_R (major) = 10.443 min, t_R (minor) = 12.717 min, er = 94:6. $[\alpha]_D^{25}$ = 33.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm) = 7.80 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 16.0 Hz, 1H), 3.68 (d, *J* = 16.0 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 6H), 1.61 (s, 6H), 1.35 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 195.1, 165.4 (d, *J* = 6.0 Hz), 162.6 (t, *J* = 32.0), 152.2, 135.6, 135.3, 128.0, 126.1, 125.0, 113.9 (dd, *J* = 263.0, 252.5 Hz) , 84.0, 64.6 (dd, *J* = 23.0, 20.0 Hz), 63.2, 40.9, 36.0, 35.3 (t, *J* = 4.0 Hz) , 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.08 (d, *J* = 278.2 Hz, 1F), -110.08 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{26}O_5F_2$ $[M+Na]^+$: 455.1641, found: 455.1630.

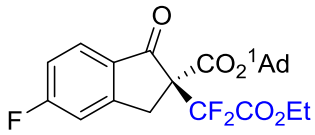
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*- indene-2-carboxylate (3bb)



Colorless oil, 30 h, 51 mg, 55% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ^{o}C). t_R (major) = 20.026 min, t_R (minor) = 34.982 min, er = 93:7. $[\alpha]_D^{25}$ = 71.9 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm) = 7.72 (d, *J* = 8.6 Hz, 1H), 6.98 – 6.87 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 3.72 (d, *J* = 20.0 Hz, 1H), 3.62 (d, *J* = 20.0 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 6H), 1.61 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 193.0, 166.0, 165.7 (d, *J* = 7.0 Hz), 162.7 (t, *J* = 31.5 Hz), 155.3, 128.5, 126.7, 113.9 (dd, *J* = 263.0, 252.0 Hz), 116.1, 109.2, 83.8, 64.8 (dd, *J* = 23.0, 20.0 Hz), 63.1, 55.7, 40.9, 36.0, 35.2 (t, *J* = 3.5 Hz), 30.8,

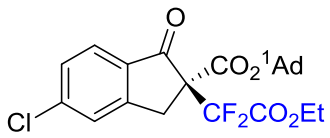
13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.27 (d, *J* = 278.2 Hz, 1F), -110.26 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{25}H_{28}O_6F_2$ $[M+Na]^+$: 485.1746, found: 485.1746.

(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-fluoro-1-oxo-2,3-dihyd -ro-1*H*- indene-2-carboxylate (3cb)



Colorless oil, 30 h, 50 mg, 66% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 10.581 min, t_R (minor) = 12.148 min, er = 91:9. $[\alpha]_D^{25}$ = 36.3 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.81 (dd, *J* = 8.5, 5.2 Hz, 1H), 7.19 – 7.08 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 20.0 Hz, 1H), 3.67 (d, *J* = 20.0 Hz, 1H), 2.14 (s, 3H), 2.05 (s, 6H), 1.62 (s, 6H), 1.36 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm) 193.2, 167.6 (d, *J* = 257.0 Hz), 165.1 (d, *J* = 8.0 Hz), 162.5 (t, *J* = 31.5 Hz), 155.1 (d, *J* = 10.0 Hz), 131.7, 127.4, 127.3, 116.6, 116.3, 113.7 (dd, *J* = 265.5, 255.5 Hz), 113.0, 112.8, 84.2, 76.7, 64.8 (dd, *J* = 23.0, 20.0 Hz), 63.3, 40.9, 35.9, 35.1 (d, *J* = 3.0 Hz), 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) = -100.78 (s, 1F), -107.75 (d, *J* = 278.2 Hz, 1F), -110.19 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_3$ $[M+Na]^+$: 473.1546, found: 473.1547.

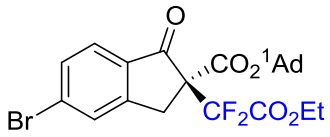
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-chloro-1-oxo-2,3-dihy dro-1*H*- indene-2-carboxylate (3db)



Colorless oil, 30 h, 56 mg, 60% yield. The er value were determined by HPLC (Chiralpak OX column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 11.146 min, t_R (minor) = 11.967 min, er = 90.5:9.5. $[\alpha]_D^{25}$ = 53.2 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.73 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.76 (d, *J* = 18.1 Hz, 1H), 3.65 (d, *J* = 18.0 Hz, 1H), 2.14 (s, 3H), 2.04 (s, 6H), 1.62 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H).

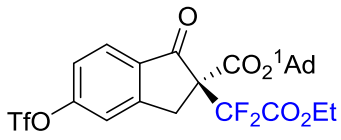
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.6, 165.1 (d, *J* = 7.0 Hz), 162.5 (t, *J* = 32.0 Hz), 153.6, 142.2, 133.8, 128.9, 126.3, 126.0, 113.7(dd, *J* = 264.0, 252.0 Hz), 84.3, 64.7 (dd, *J* = 23.0, 20.0 Hz), 63.3, 40.9, 35.9, 35.0 (t, *J* = 4.0 Hz) , 30.9, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.03 (d, *J* = 278.2 Hz, 1F), -110.10 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Cl$ $[M+Na]^+$: 489.1251, found: 489.1255.

(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-bromo-1-oxo-2,3-dihydro-1*H*- indene-2-carboxylate (3eb)



Colorless oil, 30 h, 69 mg, 67% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 11.029 min, t_R (minor) = 16.846 min, er = 91.5:8.5. $[\alpha]_D^{25}$ = 51.9 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.69 – 7.63 (m, 2H), 7.56 (dd, *J* = 8.2, 1.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 18.1 Hz, 1H), 3.66 (d, *J* = 18.0 Hz, 1H), 2.14 (s, 3H), 2.04 (d, *J* = 3.0 Hz, 6H), 1.62 (s, 6H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 193.9, 165.0 (d, *J* = 7.0 Hz), 162.4 (t, *J* = 32.0 Hz) , 153.6, 134.2, 131.7, 131.1, 129.4, 126.0, 113.7 (dd, *J* = 264.0, 252.0 Hz), 84.3, 64.6 (dd, *J* = 23.0, 20.0 Hz), 63.3, 40.9, 35.9, 34.9 (t, *J* = 4.0 Hz) , 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.03 (d, *J* = 278.2 Hz, 1F), -110.08 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Br$ $[M+Na]^+$: 533.0746, found: 533.0751.

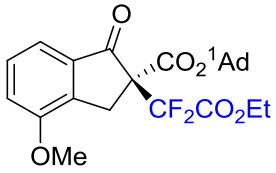
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-(((trifluoromethyl)sulf-onyl)oxy)-1-oxo-2,3-dihydro-1*H*- indene-2-carboxylate (3fb)



Colorless oil, 30 h, 52 mg, 45% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 10.908 min, t_R (minor) = 12.700 min, er = 89:11. $[\alpha]_D^{25}$ = 32.3 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, DMSO) *δ* (ppm) = 7.92 (d, *J* = 8.6 Hz, 1H), 7.86 (s,

1H), 7.61 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.26 (dt, *J* = 7.4, 3.8 Hz, 2H), 3.79 (d, *J* = 18.7 Hz, 1H), 3.71 (d, *J* = 18.7 Hz, 1H), 2.05 (s, 3H), 1.88 (d, *J* = 2.9 Hz, 6H), 1.52 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) *δ* (ppm) 193.5, 164.5 (d, *J* = 7.0 Hz), 161.5 (t, *J* = 32.0 Hz), 154.9, 153.9, 134.34, 127.0, 122.4, 120.3, 118.3 (q, *J* = 319 Hz), 113.7 (dd, *J* = 260.5, 252.5 Hz), 83.8, 64.1 (dd, *J* = 23.5, 19.5 Hz), 63.7, 40.4, 35.4, 35.2, 30.3, 13.5. **^{19}F NMR** (376 MHz, DMSO) δ(ppm) = -72.69 (s, 3F), -107.51 (d, *J* = 278.2 Hz, 1F), -108.69 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{25}H_{25}F_5O_7S$ $[M+H]^+$: 565.1314. Found: 565.1319.

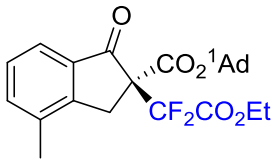
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-4-methoxy-1-oxo-2,3-dih -ydro-1*H*- indene-2-carboxylate (3gb)



Colorless oil, 30 h, 53 mg, 57% yield. The er vaule determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 12.249 min, t_R (minor) = 13.200 min, er = 90.5:9.5. $[\alpha]_D^{25}$ = 44.5 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.48 – 7.34 (m, 2H), 7.07 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.67 (d, *J* = 18.2 Hz, 1H), 3.56 (d, *J* = 18.2 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 6H), 1.61 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 195.3, 165.5 (d, *J* = 7.0 Hz), 162.5 (t, *J* = 32.0 Hz), 156.6, 141.1, 136.8, 129.5, 116.0 (d, *J* = 66 Hz), 115.0 (d, *J* = 56 Hz), 113.8 (dd, *J* = 262.5, 252.5 Hz), 83.9, 64.4 (dd, *J* = 23.0, 20.0 Hz), 63.1, 55.5, 40.9, 36.0, 32.2 (t, *J* = 4.0 Hz), 30.8, 22.5, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.18 (d, *J* = 278.2 Hz, 1F), -109.99 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{25}H_{28}O_6F_2$ $[M+Na]^+$: 485.1746, found: 485.1757.

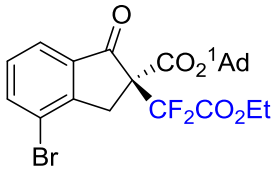
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-4-methyl-1-oxo-2,3-dihy -dro-1*H*- indene-2-carboxylate (3hb)

Colorless oil, 30 h, 49 mg, 55% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25



°C). t_R (major) = 10.232 min, t_R (minor) = 14.158 min, er = 91.5:8.5. $[\alpha]_D^{25}$ = 42.7 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.63 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.64 (d, *J* = 17.9 Hz, 1H), 3.55 (d, *J* = 17.9 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 3H), 2.06 (d, *J* = 2.9 Hz, 6H), 1.62 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 195.3, 165.5 (d, *J* = 7.0 Hz), 162.7 (t, *J* = 32.0 Hz), 151.1, 136.1, 135.4, 135.1, 128.2, 122.4, 113.9 (dd, *J* = 263.5, 252.5 Hz) , 84.0, 64.6 (dd, *J* = 23.0, 20.0 Hz), 63.2, 40.9, 36.0, 34.2 (t, *J* = 3.5 Hz), 30.9, 17.7, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -107.95 (d, *J* = 278.2 Hz, 1F), -109.94 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{25}H_{28}O_5F_2$ $[M+Na]^+$: 469.1797, found: 469.1806.

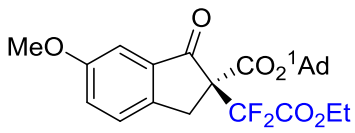
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-4-bromo-1-oxo-2,3-dihydro-1*H*- indene-2-carboxylate (3ib)



Colorless oil, 30 h, 49 mg, 47% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 7.752 min, t_R (minor) = 8.202 min, er = 89:11. $[\alpha]_D^{25}$ = 50.4 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.81 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 3.69 (d, *J* = 18.3 Hz, 1H), 3.60 (d, *J* = 18.3 Hz, 1H), 2.15 (s, 3H), 2.06 (d, *J* = 4.0 Hz, 6H), 1.62 (s, 6H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 194.4, 164.9 (d, *J* = 8.0 Hz), 162.4 (t, *J* = 31.5 Hz), 151.8, 138.3, 137.1, 129.8, 123.7, 121.4, 113.7 (dd, *J* = 263.5, 252.5 Hz), 84.4, 64.6 (dd, *J* = 24.0, 20.0 Hz), 63.3, 40.9, 36.4 (t, *J* = 4.0 Hz), 35.9, 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -107.85 (d, *J* = 278.2 Hz, 1F), -109.85 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Br$ $[M+Na]^+$: 533.0746, found: 533.0741.

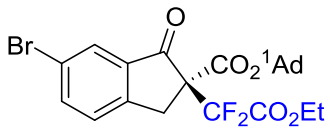
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-6-methoxy-1-oxo-2,3-dih

-ydro-1*H*- indene-2-carboxylate (3jb)



Colorless oil, 30 h, 46 mg, 57% yield. The er value were determined by HPLC (Chiralpak OX column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 14.792 min, t_R (minor) = 15.784 min, er = 94.5:5.5. $[\alpha]_D^{25}$ = 21.1 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.37 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.70 (d, *J* = 17.5 Hz, 1H), 3.58 (d, *J* = 17.5 Hz, 1H), 2.14 (s, 3H), 2.05 (d, *J* = 2.9 Hz, 6H), 1.62 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 195.1, 165.5 (d, *J* = 8.0 Hz), 162.8 (t, *J* = 32.0 Hz) , 159.8, 145.1, 136.5, 126.7, 125.1, 113.9 (dd, *J* = 263, 252 Hz), 105.8, 83.0, 65.3 (dd, *J* = 230.0, 200.0 Hz), 63.1, 55.6, 40.9, 35.9, 34.6 (t, *J* = 4.0 Hz), 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.28 (d, *J* = 278.2 Hz, 1F), -110.08 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{25}H_{28}O_6F_2$ $[M+Na]^+$: 485.1746, found: 485.1746.

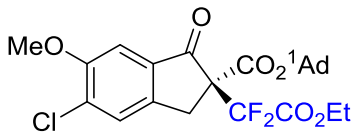
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-6-bromo-1-oxo-2,3-dihy-dro-1*H*- indene-2-carboxylate (3kb)



Colorless oil, 30 h, 64 mg, 61% yield. The er value were determined by HPLC (Chiralpak OX column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 8.473 min, t_R (minor) = 9.060 min, er = 86:14. $[\alpha]_D^{25}$ = 7.8 (c = 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.94 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 18.0 Hz, 1H), 3.64 (d, *J* = 18.0 Hz, 1H), 2.17 (s, 3H), 2.06 (d, *J* = 3.0 Hz, 6H), 1.64 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 193.7, 165.0 (d, *J* = 7.0 Hz), 162.4 (t, *J* = 32.0 Hz), 150.7, 138.3, 137.0, 127.7, 127.6, 122.1, 113.7 (dd, *J* = 263.5, 252.5 Hz) , 84.3, 64.9 (dd, *J* = 23.0, 20.0 Hz), 63.3, 40.8, 35.9, 34.9 (t, *J* = 3.5 Hz), 30.8, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -107.98 (d, *J* = 278.2 Hz, 1F), -109.93 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Br$ $[M+Na]^+$:

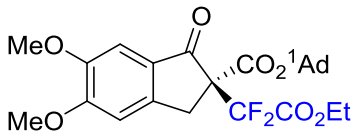
533.0746, found: 533.0745.

(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5-chloro-6-methoxy-1-o-xo-2,3-dihydro-1*H*- indene-2-carboxylate (3lb)



Colorless oil, 30 h, 51 mg, 52% yield. The er value were determined by HPLC (Chiralpak OX column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 13.852 min, t_R (minor) = 15.097 min, er = 94:6. $[\alpha]_D^{25}$ = 38.0 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.52 (s, 1H), 7.26 (s, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 3.94 (s, 3H), 3.69 (d, *J* = 17.7 Hz, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 2.14 (s, 3H), 2.05 (s, 6H), 1.62 (s, 6H), 1.36 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 194.1, 165.2 (d, *J* = 8.0 Hz), 162.5 (t, *J* = 31.5 Hz), 155.4, 145.1, 134.7, 131.9, 127.5, 113.8 (dd, *J* = 263.5, 252Hz), 105.9, 84.2, 64.3 (dd, *J* = 24.0, 20.0 Hz), 63.3, 56.4, 40.9, 35.9, 34.4 (t, *J* = 3.5 Hz), 30.8, 26.9, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -108.22 (d, *J* = 278.2 Hz, 1F), -110.15 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Br$ $[M+Na]^+$: 519.1356, found: 519.1358.

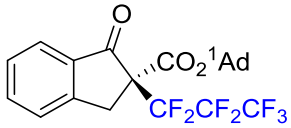
(*S*)-1-Adamantanyl 2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*- indene-2-carboxylate (3mb)



White solid, 30 h, 51 mg, 52% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 33.268 min, t_R (minor) = 49.040 min, er = 94:6. $[\alpha]_D^{25}$ = 56.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.19 (s, 1H), 6.89 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.98 (s, 3H), 3.91 (s, 3H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 6H), 1.62 (s, 6H), 1.36 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 193.5, 165.7 (d, *J* = 9.0 Hz), 162.7 (t, *J* = 32.0 Hz), 156.2, 149.9, 147.9, 128.1, 113.9 (dd, *J* = 263, 251Hz), 106.8, 105.1, 83.7, 64.9 (dd, *J* = 23.0, 20.0 Hz), 64.6, 63.1, 56.3, 56.1, 40.9, 35.9, 34.9 (t, *J* = 4.0 Hz), 30.8, 13.8. **^{19}F**

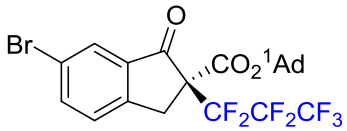
NMR (376 MHz, $CDCl_3$) δ(ppm) -108.44 (d, *J* = 278.2 Hz, 1F), -110.38 (d, *J* = 278.2 Hz, 1F). HRMS (ESI): Calcd for $C_{24}H_{25}O_5F_2Br$ $[M+Na]^+$: 515.1852, found: 515.1862.

(*S*)-1-Adamantanyl 2-(perfluoropropyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3ac)



Colorless oil, 25 h, 41 mg, 43% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 4.234 min, t_R (minor) = 4.625 min, er = 91.5:8.5. $[\alpha]_D^{25}$ = 26.2 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) = 7.81 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.84 (d, *J* = 17.5 Hz, 1H), 3.55 (d, *J* = 17.5 Hz, 1H), 2.15 (s, 3H), 2.07 (d, *J* = 3.0 Hz, 6H), 1.63 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* (ppm) 192.9, 162.7 (d, *J* = 9.0 Hz), 151.9, 136.0, 134.2, 128.2, 126.1, 125.3, 84.7, 63.8 (dd, *J* = 23.0, 19.0 Hz), 40.8, 35.9, 33.5 (t, *J* = 3.5 Hz), 31.0, 30.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -81.10 (dd, *J* = 15.0, 11.3 Hz, 3F), -109.01 ~ -111.69 (m, 2F), -119.54 ~ -119.60 (m, 2F). HRMS (ESI): Calcd for $C_{23}H_{21}O_3F_7$ $[M+Na]^+$: 501.1271. Found: 501.1271.

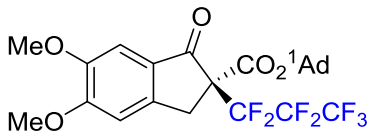
(*S*)-1-Adamantanyl 2-(perfluoropropyl)-6-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3kc)



Colorless oil, 25 h, 45 mg, 40% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 99:1 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 5.826 min, t_R (minor) = 8.955 min, er = 82:18. $[\alpha]_D^{25}$ = 3.1 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) = 7.93 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 3.78 (d, *J* = 17.6 Hz, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 2.16 (s, 3H), 2.06 (d, *J* = 2.9 Hz, 6H), 1.63 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* (ppm) 191.5, 162.3 (d, *J* = 9.0 Hz), 150.4, 138.8, 135.9, 128.1, 127.6, 122.4, 85.1, 64.2 (dd, *J* = 22.5, 18.5 Hz), 40.7, 35.6, 33.2 (t, *J* = 4 Hz), 30.9. **^{19}F NMR**

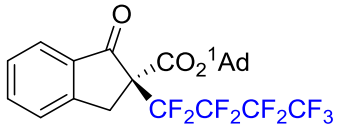
(376 MHz, $CDCl_3$) δ(ppm) -81.07 (dd, *J* = 16.9, 5.6 Hz, 3F), -108.95 ~ -111.75 (m, 2F), -119.61 ~ -119.67 (m, 2F). HRMS (ESI): Calcd for $C_{23}H_{20}BrO_3F_7$ $[M+Na]^+$: 579.0376. Found: 579.0379.

(*S*)-1-Adamantanyl 2-(perfluoropropyl)- 5,6-dimethoxy -1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3mc)



Colorless oil, 25 h, 56 mg, 52% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 9.589 min, t_R (minor) = 10.772 min, er = 95:5. $[\alpha]_D^{25}$ = 42.9 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) = 7.19 (s, 1H), 6.92 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.72 (d, *J* = 17.0 Hz, 1H), 3.42 (d, *J* = 17.1 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 6H), 1.64 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* (ppm) 191.3, 163.1 (d, *J* = 8.0 Hz), 156.6, 150.1, 147.8, 126.9, 106.9, 105.3, 84.5, 64.0 (dd, *J* = 22, 19 Hz), 56.4, 56.2, 40.8, 36.0, 33.2, 30.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -81.12 (dd, *J* = 20.7, 9.4 Hz, 3F), -109.33~ -111.91 (m, 2F), -119.59 ~ -119.67 (m, 2F). HRMS (ESI): Calcd for $C_{25}H_{25}O_5F_7$ $[M+Na]^+$: 561.1482. Found: 561.1492.

(*S*)-1-Adamantanyl 2-(perfluorobutyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3ad)

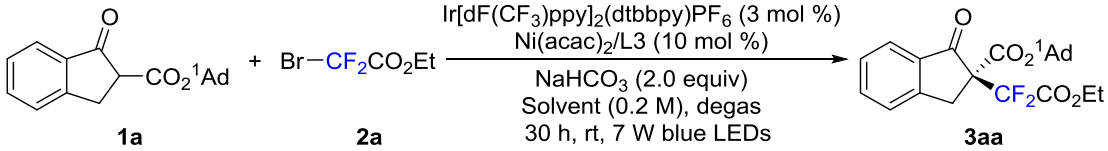


Colorless oil, 25 h, 58 mg, 55% yield. The er value were determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 99:1 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t_R (major) = 6.392 min, t_R (minor) = 8.663 min, er = 95:5. $[\alpha]_D^{25}$ = 25.2 (c = 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) = (d, *J* = 7.7 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.84 (d, *J* = 17.5 Hz, 1H), 3.55 (d, *J* = 17.5 Hz, 1H), 2.15 (s, 3H), 2.07 (d, *J* = 3.0 Hz, 6H), 1.63 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* (ppm) 192.8, 162.6 (d, *J* = 8.0 Hz), 151.9, 136.0, 134.1, 128.2, 126.1, 125.3, 84.6, 64.0 (dd, *J* = 23, 18 Hz), 40.7, 35.9, 33.4 (t, *J* = 4.0 Hz), 30.9. **^{19}F**

NMR (376 MHz, $CDCl_3$) δ(ppm) -80.65 (dd, *J* = 28.2, 9.4 Hz, 3F), -108.56~ -111.39 (m, 2F), -116.45 ~ -116.64 (m, 2F), -126.13 ~ -126.47 (m, 2F). HRMS (ESI): Calcd for $C_{25}H_{25}O_5F_7$ $[M+Na]^+$: 551.1239. Found: 551.1249.

4. Optimization of the Reaction Conditions

4.1 Solvent effect[a]

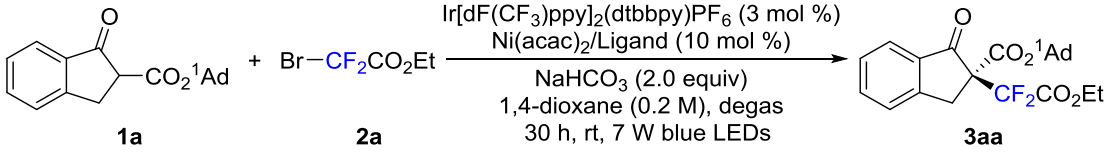


1a **2a** **3aa**

Entry	Solvent	Ligand	Yield/%[b]	er[c]
1	1,4-dioxane	**L3**	39	81:19
2	Toluene	**L3**	15	76:24
3	DCM	**L3**	5	62:38
4	DMF	**L3**	42	51:49
5	DME	**L3**	45	78:22
6	THF	**L3**	33	66:34
7	MTBE	**L3**	34	74:26
8	CH_3OH	**L3**	50	55:45
9	CH_3CN	**L3**	18	64:36
10	Hexane	**L3**	trace	-

[a]Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (3 mol%), Ni(acac)$_2$/**L3** (10 mol%), and $NaHCO_3$ (2.0 equiv) in 1 mL of solvent at rt under irradiation of 7 W blue LEDs for 30 h. [b]Isolated yields. [c]Determined using a chiral HPLC analysis. DCM: dichloromethane; DMF: N,N-dimethylformamide; DME: 1,2-dimethoxyethane; THF: tetrahydrofuran; TBME: methyl *t*-butyl ether.

4.2 Ligand effect[a]

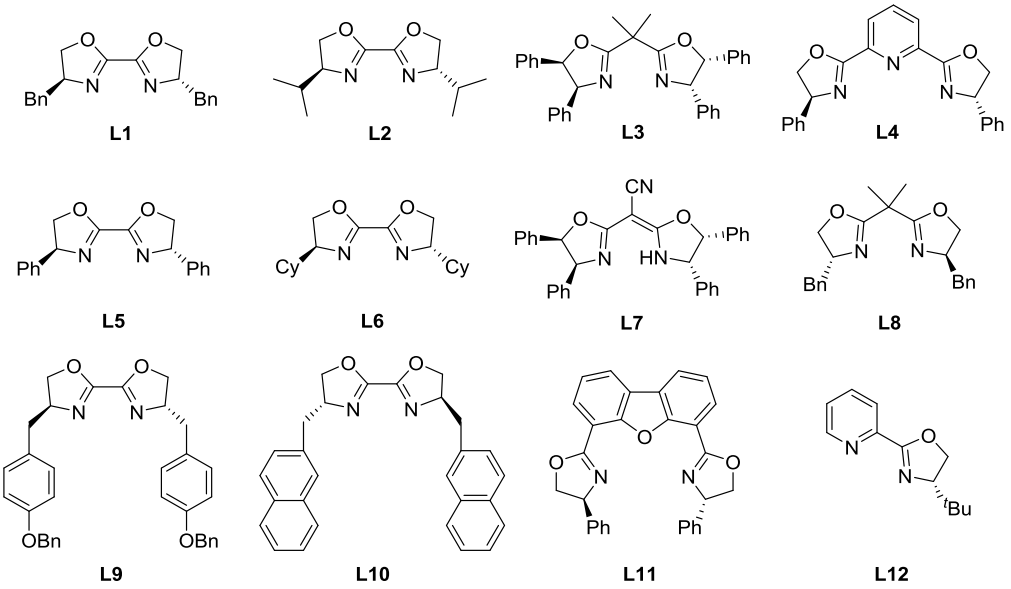


1a **2a** **3aa**

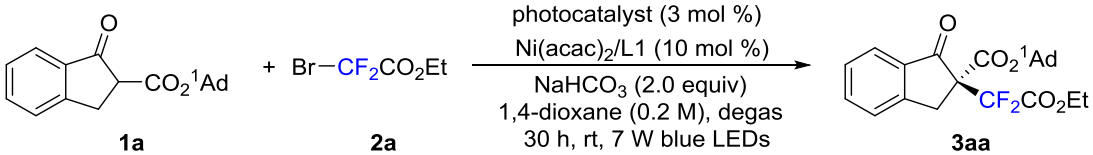
Entry	Solvent	Ligand	Yield/%[b]	er[c]
1	1,4-dioxane	**L1**	48	84:16
2	1,4-dioxane	**L2**	43	77:23
3	1,4-dioxane	**L3**	39	81:19
4	1,4-dioxane	**L4**	30	51:49
5	1,4-dioxane	**L5**	38	72:28
6	1,4-dioxane	**L6**	45	82:18

7	1,4-dioxane	**L7**	17	71:29
8	1,4-dioxane	**L8**	21	69:31
9	1,4-dioxane	**L9**	53	82:18
10	1,4-dioxane	**L10**	40	84:16
11	1,4-dioxane	**L11**	22	50:50
12	1,4-dioxane	**L12**	25	73:27

[a]Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3 mol%), $Ni(acac)_2$/ligand (10 mol%), and $NaHCO_3$ (2.0 equiv) in 1 mL of 1,4-dioxane at rt under irradiation of 7 W blue LEDs for 30 h. [b]Isolated yields. [c]Determined using a chiral HPLC analysis.



4.3 Photocatalyst effect[a]

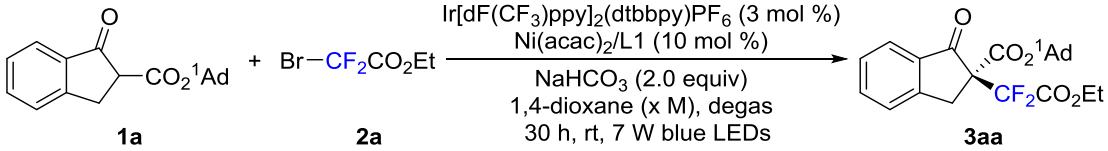


1a 2a 3aa

Entry	Photocatalyst	Yield/%[b]	er[c]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	49	83:17
2	$Ir(ppy)_2dtbbpyPF_6$	47	82:18
3	*fac*-$Ir(ppy)_3$	43	75:25
4	Eosin Y	0	-
5	Rose Bengal	0	-
6	$Ru(bpy)_3Cl_26H_2O$	0	-

[a]Conditions:**1a** (0.2 mmol), **2a** (0.4 mmol), photocatalyst (3 mol%), $Ni(acac)_2$/L1 (10 mol%), and $NaHCO_3$ (2.0 equiv) in 1 mL of 1,4-dioxane at rt under irradiation of 7 W blue LEDs for 30 h. [b]Isolated yields. [c]Determined using a chiral HPLC analysis.

4.4 Concentration effect[a]

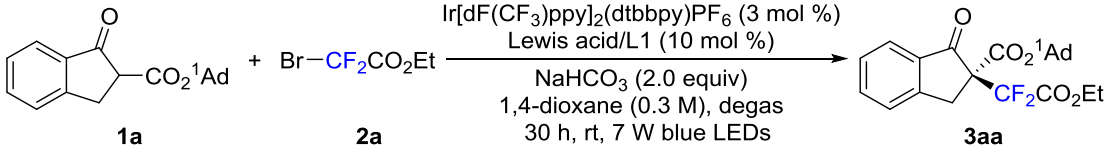


1a 2a 3aa

Entry	Concentration (x)	Yield/%[b]	er[c]
1	0.1	45	81:19
2	0.2	48	83:17
3	0.3	48	84:16
4	0.4	48	84:16

[a]Conditions:**1a** (0.2 mmol), **2a** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (3 mol%), Ni(acac)$_2$/L1 (10 mol%), and NaHCO$_3$ (2.0 equiv) in 1,4-dioxane at rt under irradiation of 7 W blue LEDs for 30 h. [b]Isolated yields. [c]Determined using a chiral HPLC analysis.

4.5 The effect of Lewis acid[a]

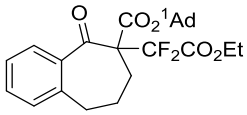


1a 2a 3aa

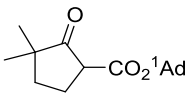
Entry	**Lewis acid**	Yield/%[b]	er[c]
1	Cu(acac)$_2$	trace	-
2	Mg(acac)$_2$	29	50:50
3	Fe(acac)$_3$	4	54:46
4	Zn(acac)$_2$	35	56:44
5	Cr(acac)$_2$	25	51:49
6	Ni(acac)$_2$	48	84:16
7	Ni(OTf)$_2$	42	77:23
8	Ni(ClO$_4$)$_2$	21	85:15
9	NiCl$_2$.glyme	61	87:13
10	NiBr$_2$.glyme	62	89:11
11[d]	NiBr$_2$.glyme	62	90:10
12	NiBr$_2$	60	88:12

[a]Conditions:**1a** (0.2 mmol), **2a** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (3 mol%), Lewis acid/L1 (10 mol%), and NaHCO$_3$ (2.0 equiv) in 0.67 ml of 1,4-dioxane at rt under irradiation of 7 W blue LEDs for 30 h. [b]Isolated yields. [c]Determined using a chiral HPLC analysis. [d]DME as the solvent.

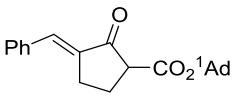
4.6 Unsuccessful substrates[a]



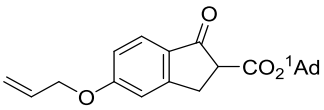
No Reaction



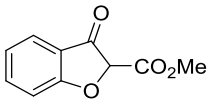
No Reaction



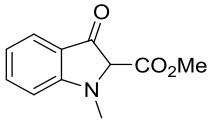
No Reaction



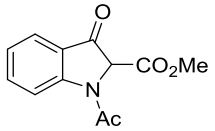
Mixture



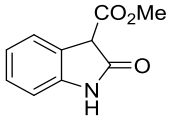
72% yield
0% ee



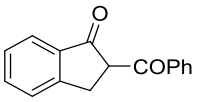
No Reaction



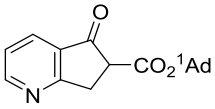
No Reaction



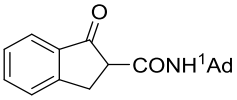
No Reaction



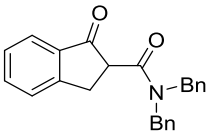
trace



No Reaction



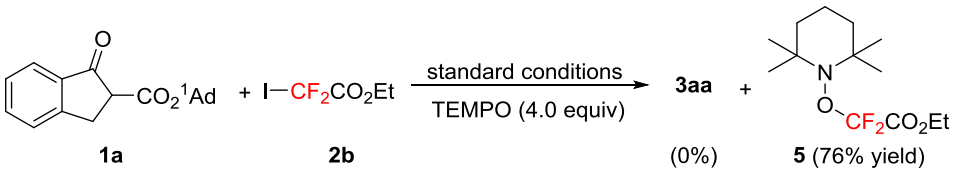
trace



No Reaction

5. Mechanism Investigation

5.1 Control Experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$-glyme (12.34 mg, 0.04 mmol) and L1 (12.82 mg, 0.04 mmol) and 0.67 mL of DME under Ar. After 0.5 h of stirring at room temperature, the substrate **1a** (62.08 mg, 0.2 mmol) was added under Ar. After 10 mins, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (6.73 mg, 0.006 mmol), $NaHCO_3$ (33.6 mg, 0.4 mmol), substrate **2b** (99.99 mg, 0.4 mmol) and TEMPO (124.99 mg, 0.8 mmol) were added to the mixture. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 30 h. Then, the reaction mixture was analyzed by ^{19}F NMR spectroscopy with $PhCF_3$ (7.76 mg, 0.053 mmol) as the internal reference. The ^{19}F NMR spectrum showed that the TEMPO-CF_2COOEt adduct **5** was formed in 76% yield [estimated by ^{19}F NMR (376MHz, $CDCl_3$): δ -73.32]; HRMS (ESI) Calcd for $C_{13}H_{24}NO_3F_2$ $[M+Na]^+$ 302.1538; found 302.1519.

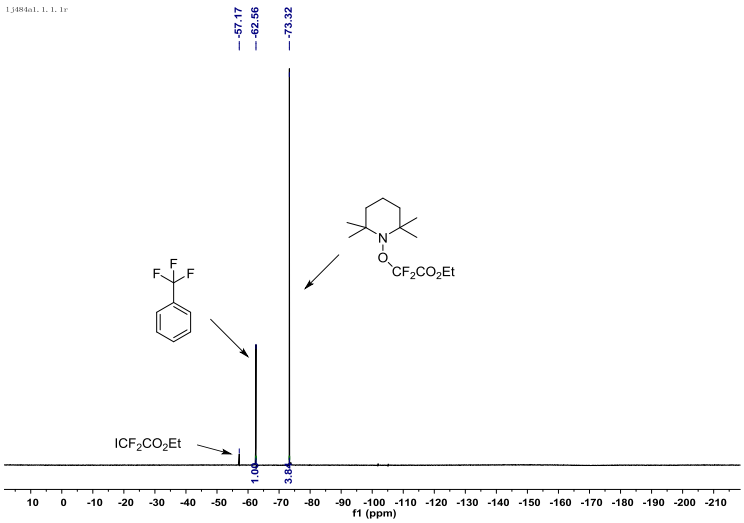
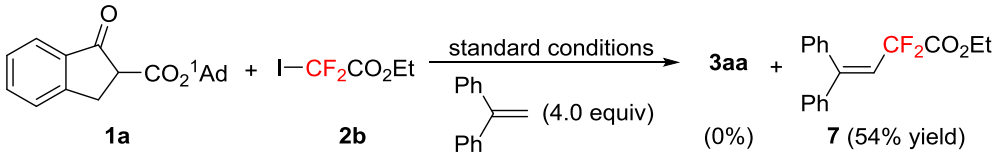


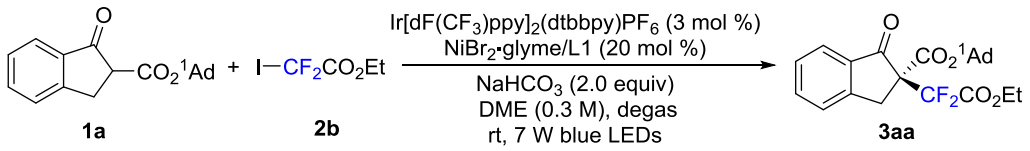
Figure S1. ^{19}F NMR spectrum of the TEMPO-Trapping Experiment

5.2 Control Experiment with 1,1-Diphenylethylene



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$-glyme (12.34 mg, 0.04 mmol) and L1 (12.82 mg, 0.04 mmol) and 0.67 mL of DME under Ar. After 0.5 h of stirring at room temperature, the substrate **1a** (62.08 mg, 0.2 mmol) was added under Ar. After 10 mins, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (6.73 mg, 0.006 mmol), $NaHCO_3$ (33.6 mg, 0.4 mmol), substrate **2b** (99.99 mg, 0.4 mmol) and 1,1-diphenylethylene (144.07 mg, 0.8 mmol) were added to the mixture. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 15 h until the reaction was completed, as monitored by TLC analysis. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 50:1) give colorless product **7** in 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.37 – 7.35 (m, 3H), 7.32 – 7.29 (m, 3H), 7.26 – 7.24 (m, 2H), 7.21 – 7.19 (m, 2H), 6.27 (t, *J* = 11.8 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 163.4 (t, *J* = 33.5 Hz), 151.0 (t, *J* = 10.0 Hz), 140.4, 137.0, 129.8 (t, *J* = 2.5 Hz), 129.1, 128.5, 128.4, 128.0, 127.9, 119.5 (t, *J* = 28.0 Hz), 112.5 (t, *J* = 243.5 Hz), 62.7, 13.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) -90.94 (d, *J* = 15.0 Hz, 2F). HRMS (ESI): Calcd for $C_{18}H_{16}F_2O_2$ [M+Na]+ 325.1011, found: 325.1005.

5.2 Time Profile of the Enantioselective Difluoroalkylation with and without Light Irradiation.



We conducted the experiment about the "on-off" switching of the light source in the reaction of **1a** and **2b** under standard condition with tetradecane as the internal

standard. The yield of **3a**a was determined by GC. The tetradecane was added into the reaction mixture with the substrates. It was found that the desired product can be observed only with the light irradiation. This result indicated that a radical chain process is not the major reaction pathway.

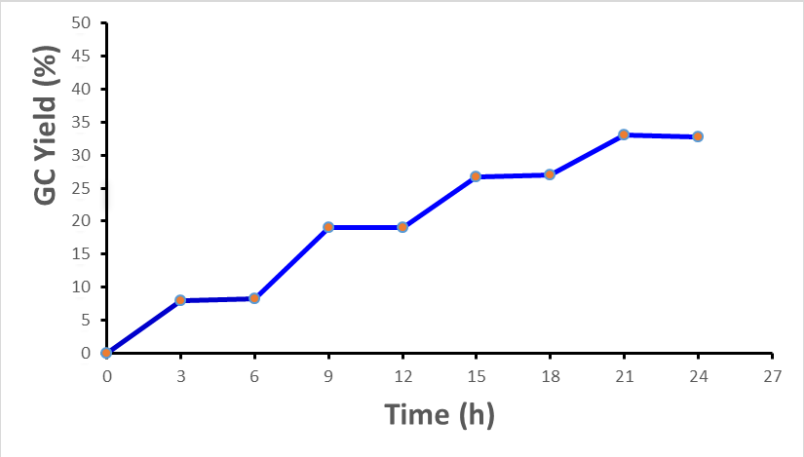
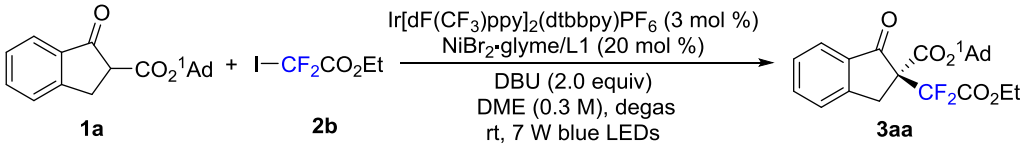


Figure S2. Time Profile of the Enantioselective Difluoroalkylation with and without Light Irradiation.

5.3 Determination of quantum yield



Owing to the frustration of heterogeneity of the reaction mixture when we determine the quantum yield under inorganic base conditions, we chose the DBU as the base.[6] A cuvette was charged with **1a** (0.2 mmol, 1.0 eq.), **2b** (0.4 mmol, 2.0 eq.), photocatalyst (0.006 mmol, 0.03 eq.), $NiBr_2$-glyme/L1 (0.04 mmol, 0.2 eq), DBU (0.4 mmol, 2.0 eq.) and 2.0 ml DME (0.1 M). The sample was irradiated (λ=455 nm, slit width = 3.0 mm, slit height 5.0 mm with intensity of 1.81 mW cm^{-2}) for 13820 s (3 h 50 min 20 s). After irradiation, the 4.3% yield of product formed was determined by GC based on a tetradecane standard. The quantum yield was determined as follows.

ϕ = Mole number for product/Mole number for absorption of photons = 0.854

$$\Phi = \frac{n_{3aa}\, N_A/t}{f\, P\, \lambda/hc}$$

n_{3ab}: the mole number of the product **3aa**; t: reaction time (13820 s, 3 h 50 min 20 s); NA: 6.02×10^{23}/mol; f: $1\text{-}10^{-A}$ (455 nm, A = 0.5317); P: P=E*S (E: illumination

intensity, E = 1.81 mW/cm^2; S: the area that irradiated S = 0.15 cm^2); λ: wavelength (λ = 4.55×10^{-7} m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^8 m/s).

5.4 Cyclic voltammetry profile of Ni(II)/L1 complex

In order to gain some insight into the interaction between the Ni(II) and the excited state of the photoscatalyst, we performed the CV measurements of Ni(II) complex. The result showed an irreversible oxidation at +0.82 V versus Ag/AgCl in CH_3CN corresponding to the oxidation of Ni(II) to Ni(III).

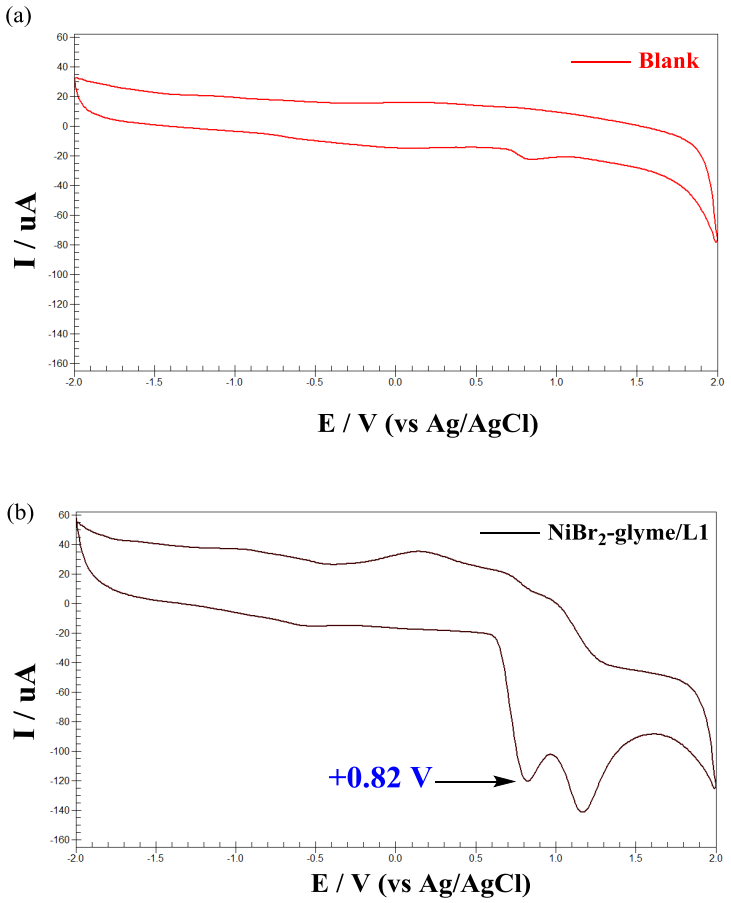


Figure S3. (a) Cyclic Voltammetry Blank Profile of CH_3CN.
(b) Cyclic Voltammetry Profile of Ni(II)/L1 Complex.

5.5 Luminescence quenching experiments

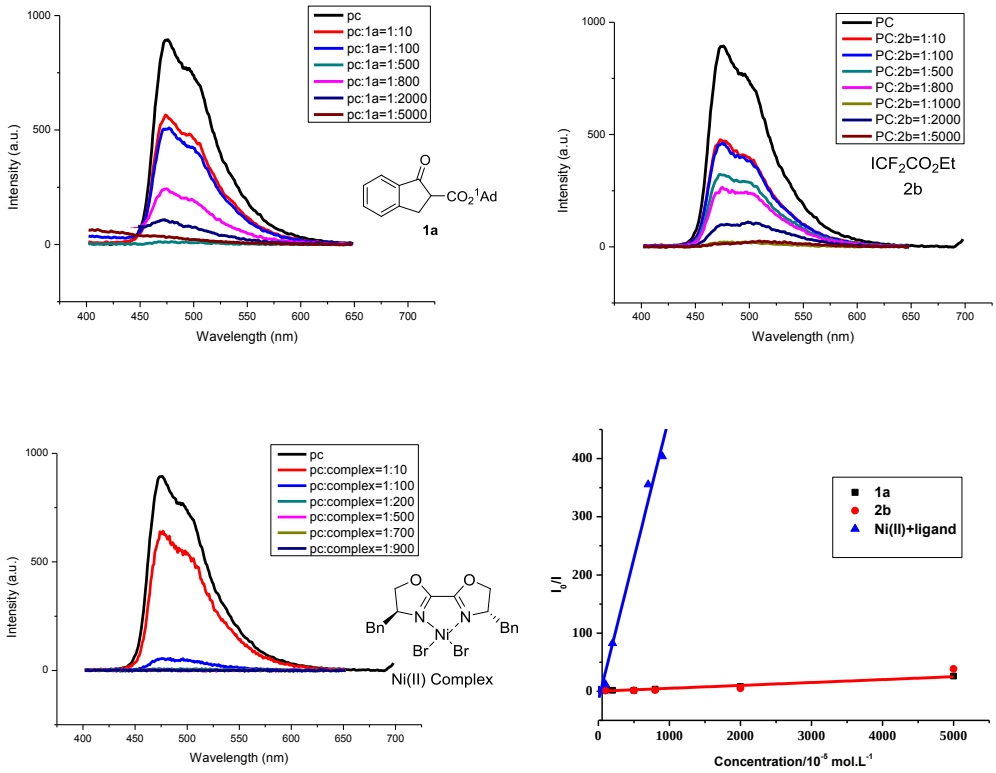


Figure S4. Luminescence Quenching Experiments.

Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All the Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ solutions were excited at 350 nm and the emission intensity at 475 nm was observed. In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ in DME was collected. As shown in **Figure S4,** substrate **1a**, **2b**, and NiBr$_2$-glyme/ligand complex totally could quench the excited state of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$. However, the quenching rate constant of Ni(II) complex is much larger than other two substrates. It might support our hypothesis on the initiation of this enantioselective difluoroalkylation reaction through reductive quenching of the excited state of the photocatalyst by Ni(II) complex.

5.6 Proposed Enantioselective Induction Model

On the basis of experimental results and previous studies, we proposed a possible stereoinduction model in **Figure S5** based on the hypothesis that the ^{1}Ad group was

located away from the ligand L1 to avoid possible steric constraints. The attack of radical from the *Si*-face of enol-formed β-keto ester seems relatively favorable.

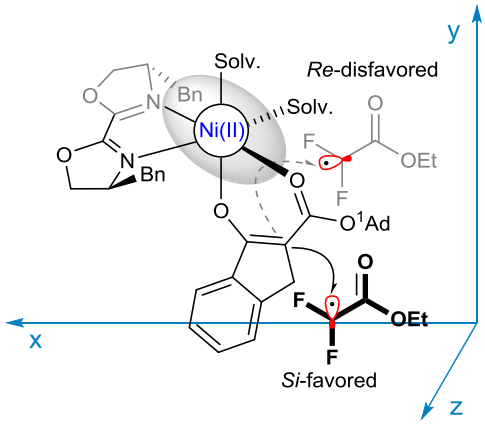
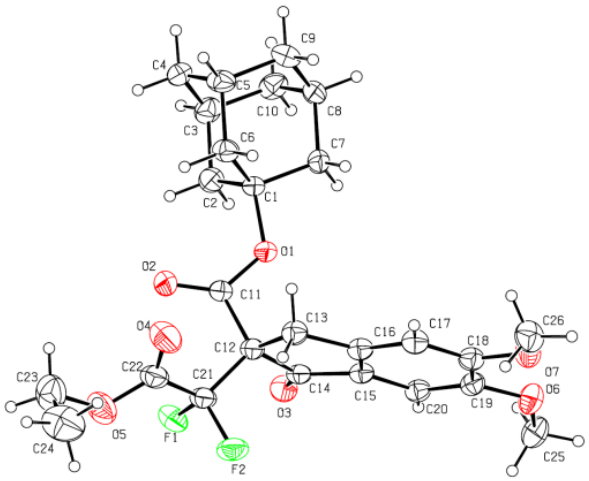
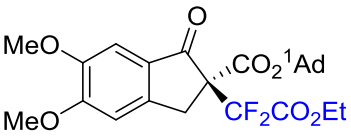


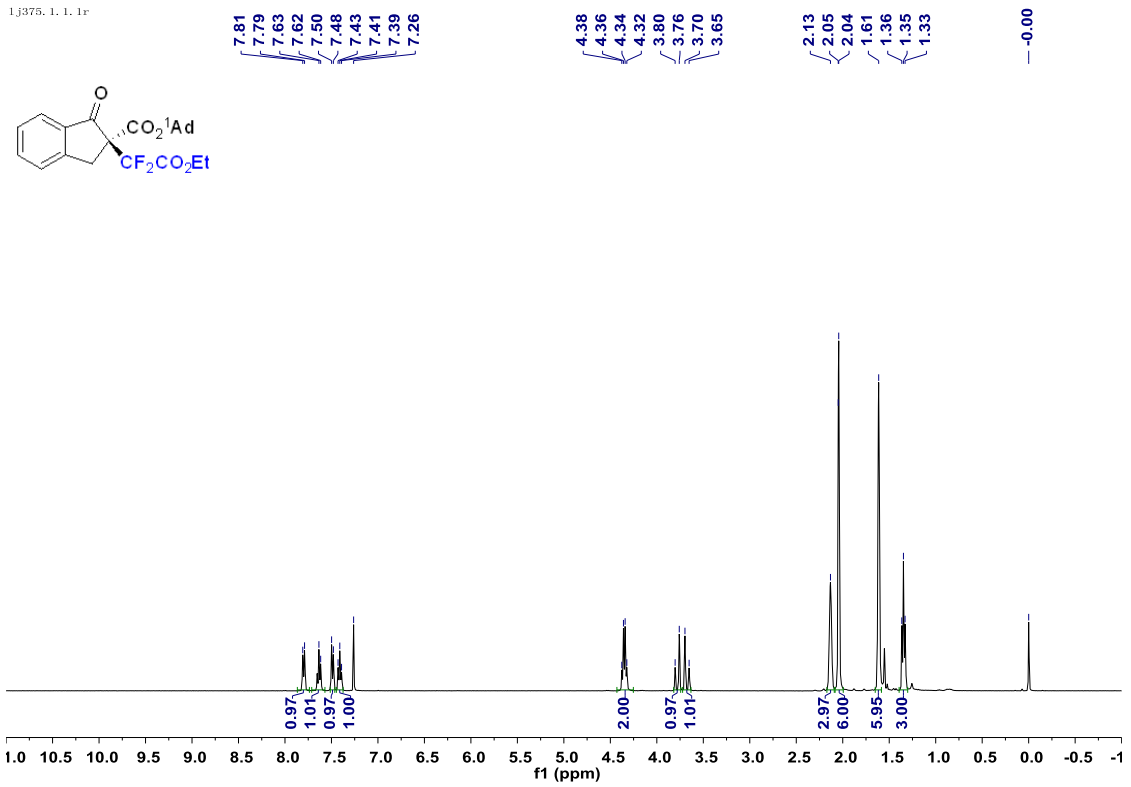
Figure S5. Proposed Enantioselective Induction Model.

6. X-Ray Structure of Products 3mb.

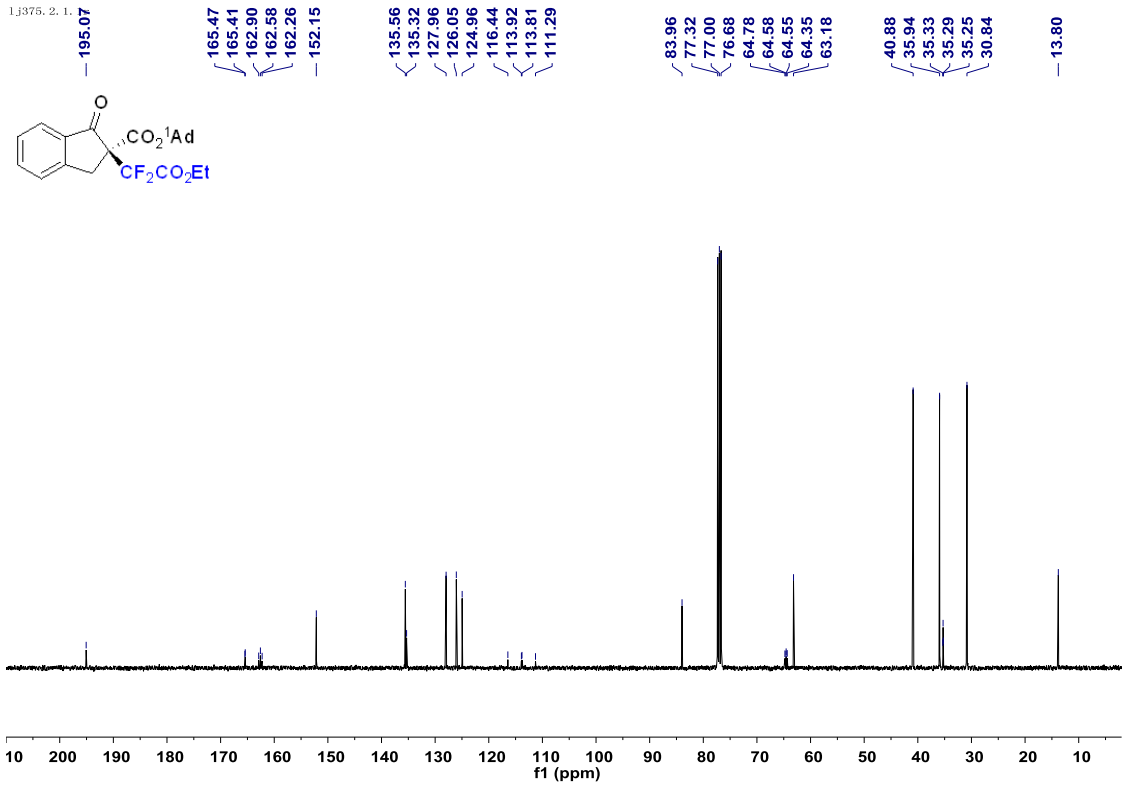
3mb		 **CCDC 1583359**

7. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

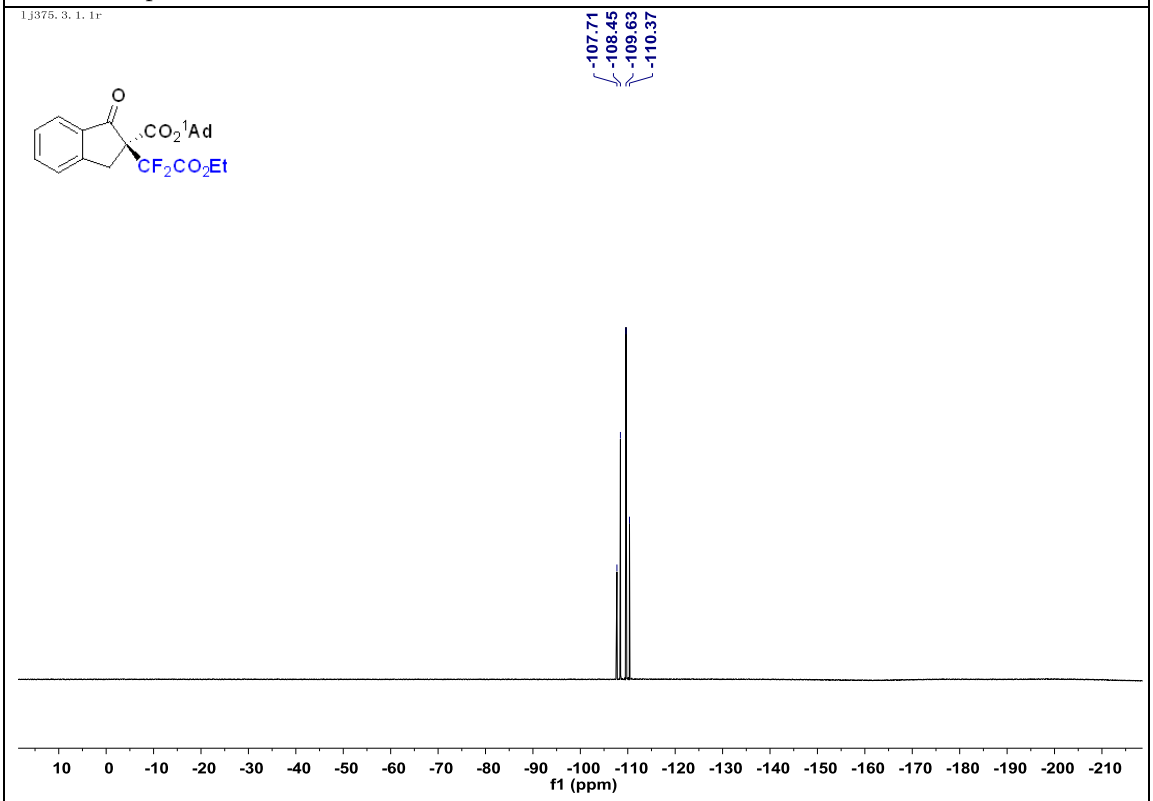
^{1}H NMR Spectrum of **3aa**



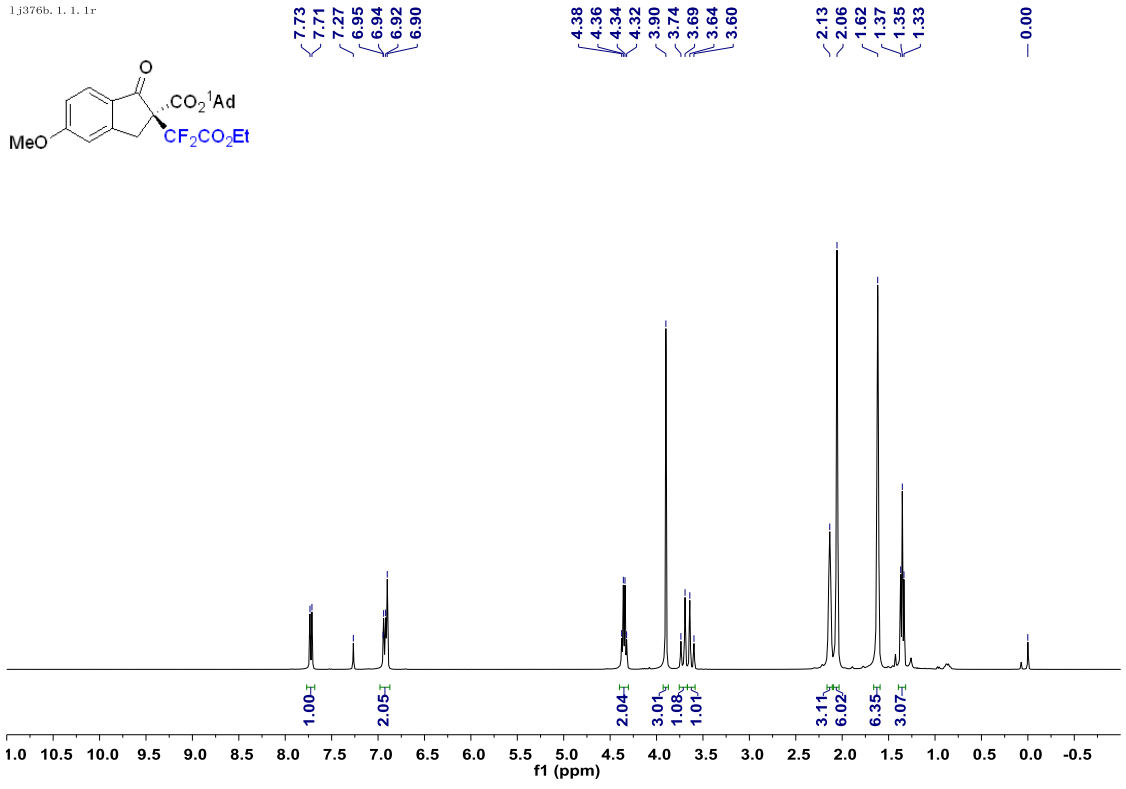
^{13}C NMR Spectrum of **3aa**



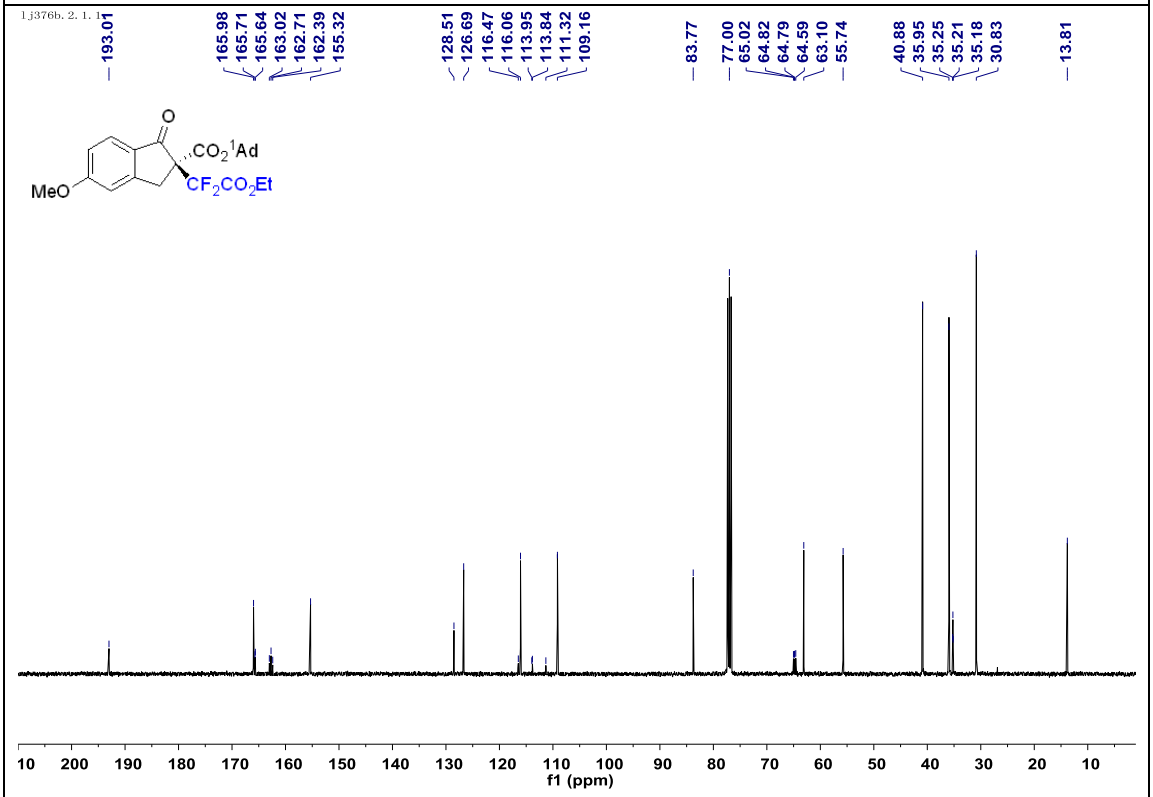
^{19}F NMR Spectrum of **3aa**



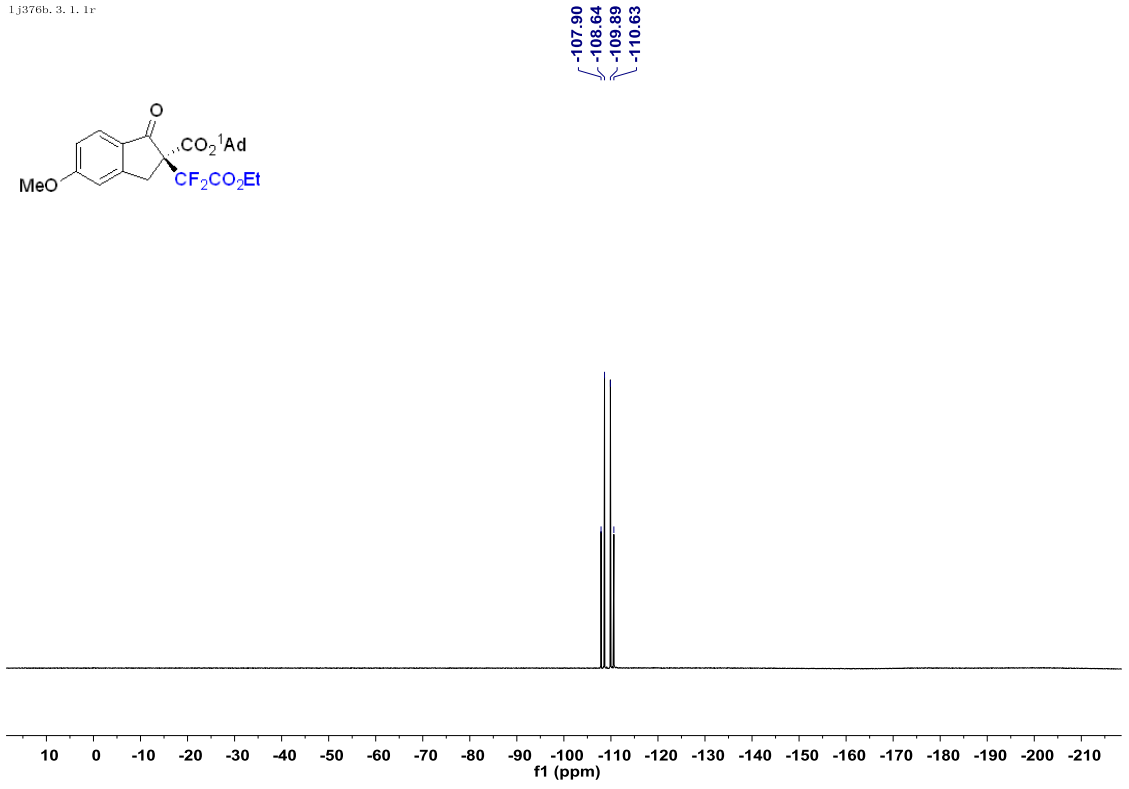
^{1}H NMR Spectrum of **3bb**



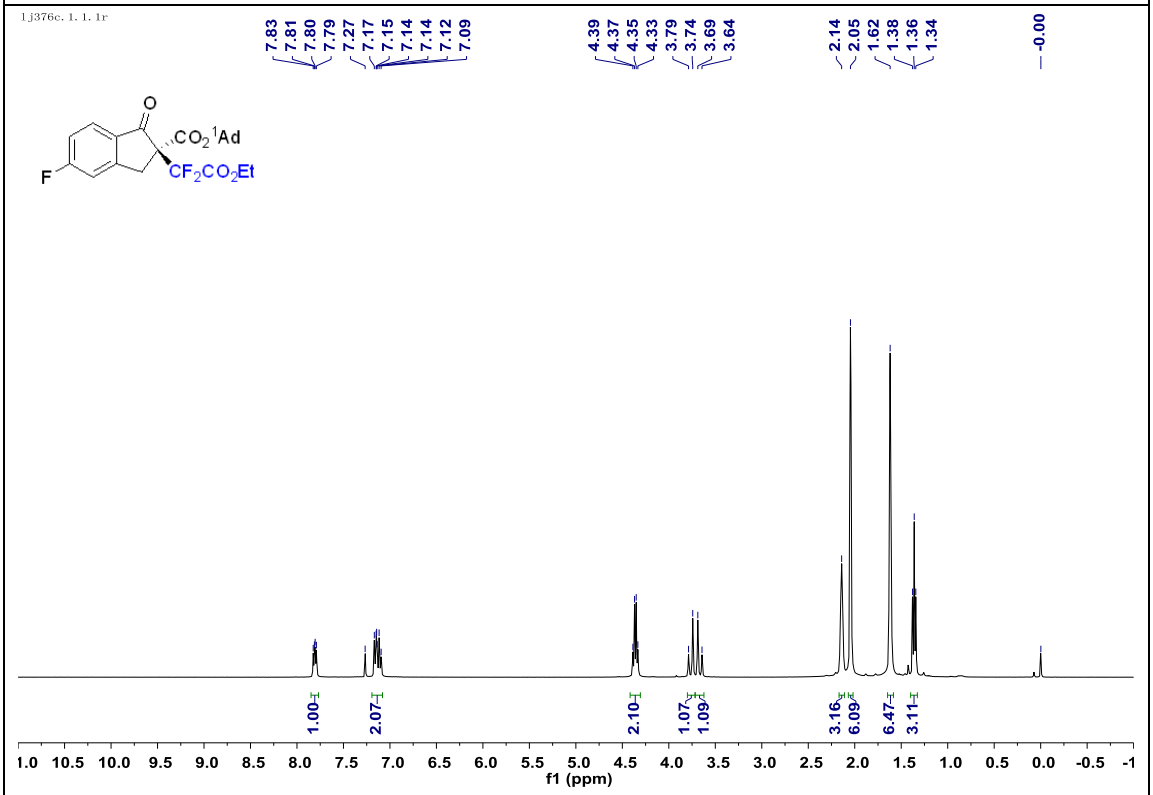
^{13}C NMR Spectrum of **3bb**



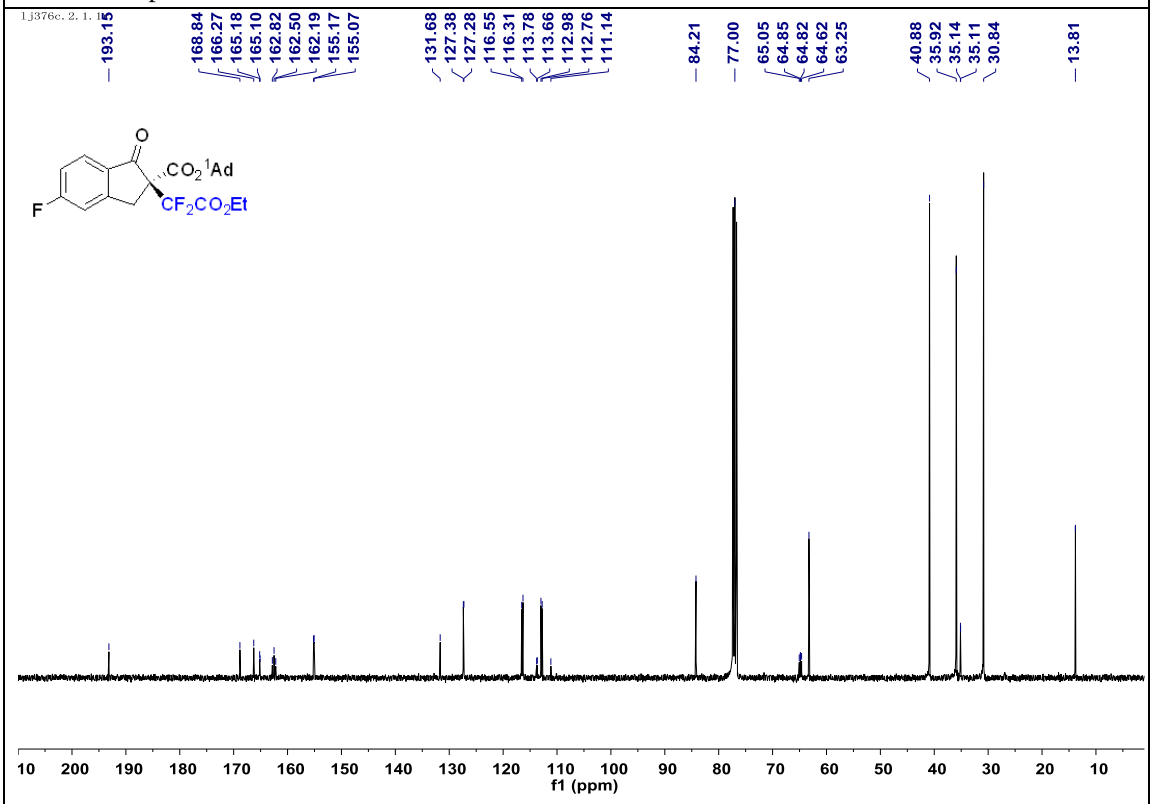
^{19}F NMR Spectrum of **3bb**



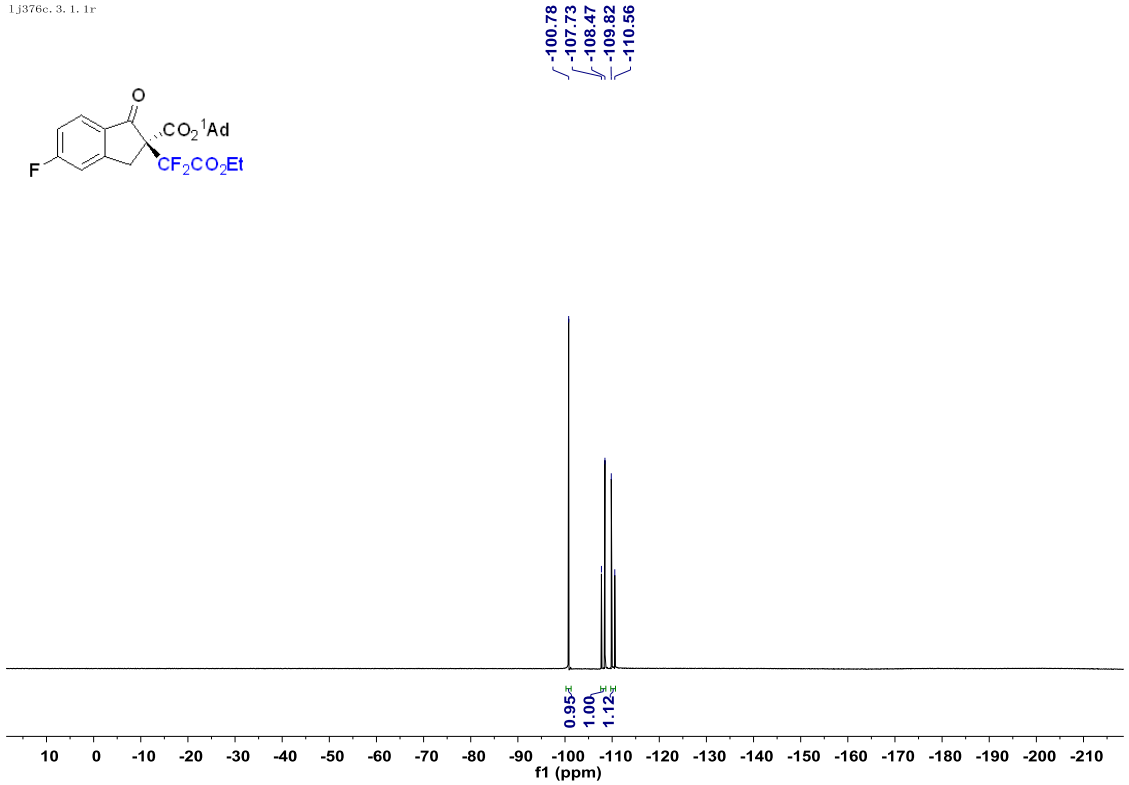
^{1}H NMR Spectrum of **3cb**



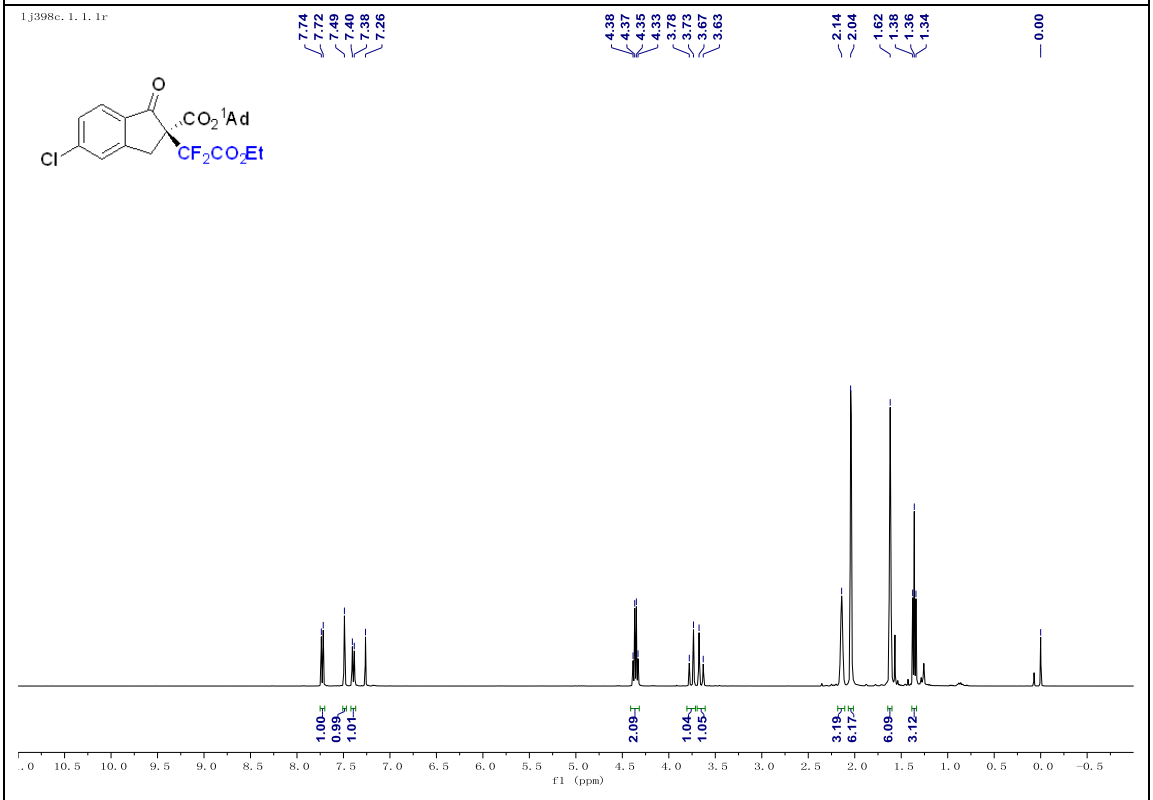
^{13}C NMR Spectrum of **3cb**



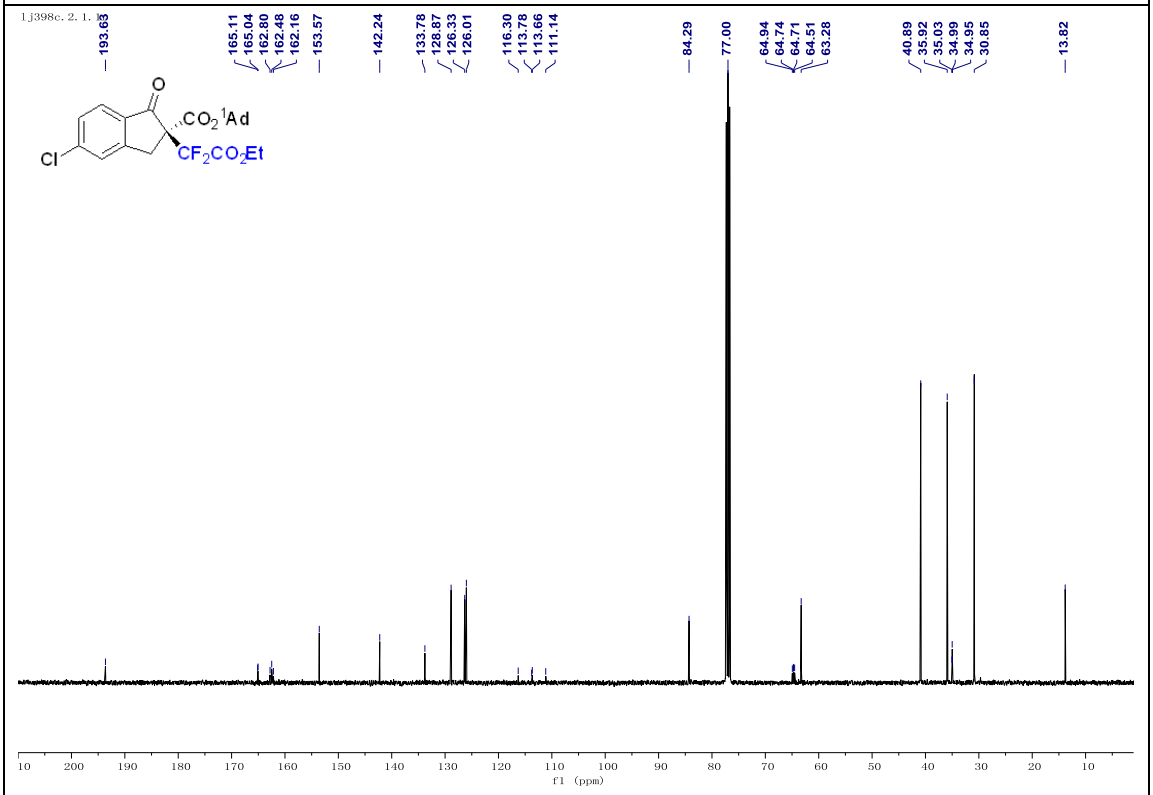
^{19}F NMR Spectrum of **3cb**



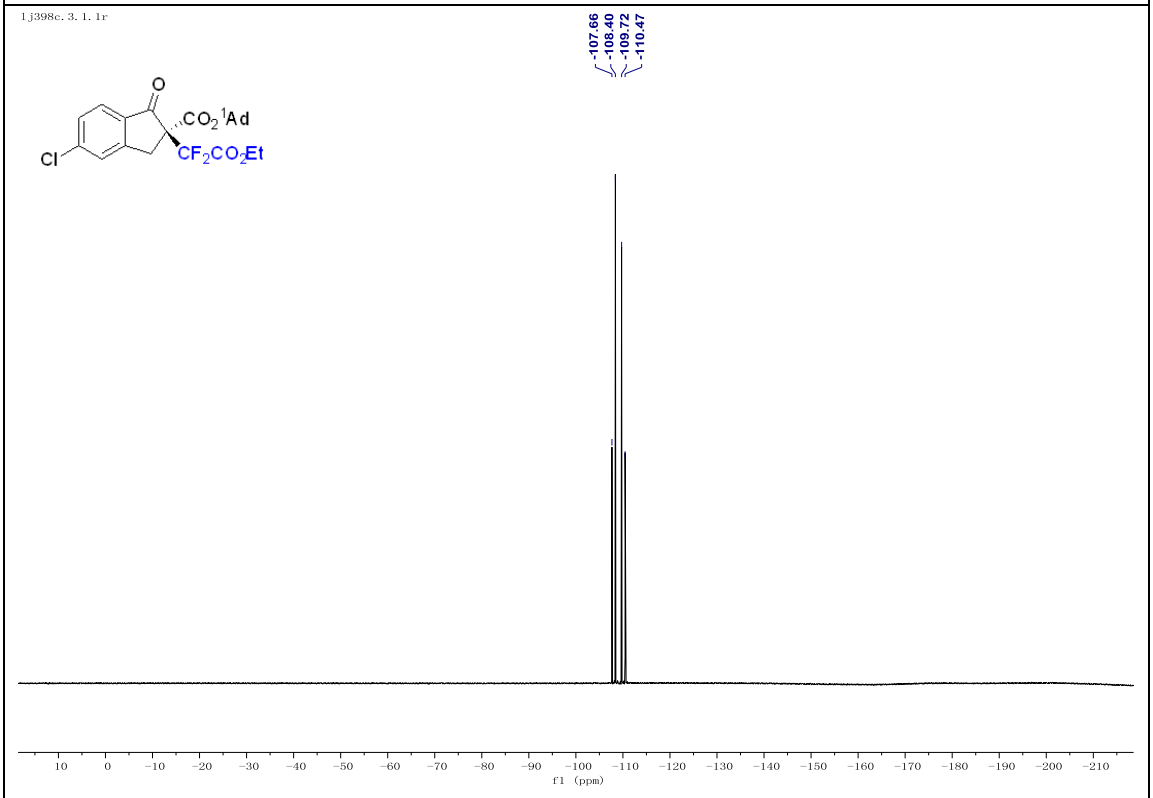
^{1}H NMR Spectrum of **3db**



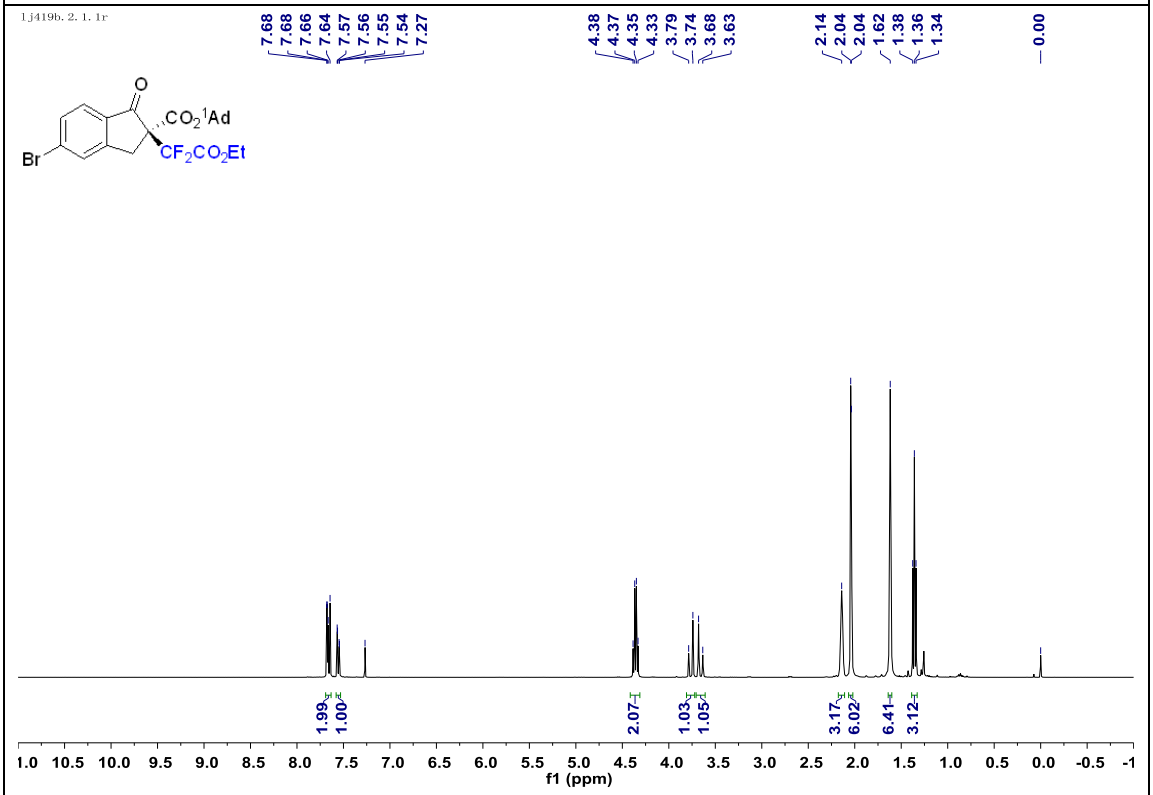
^{13}C NMR Spectrum of **3db**



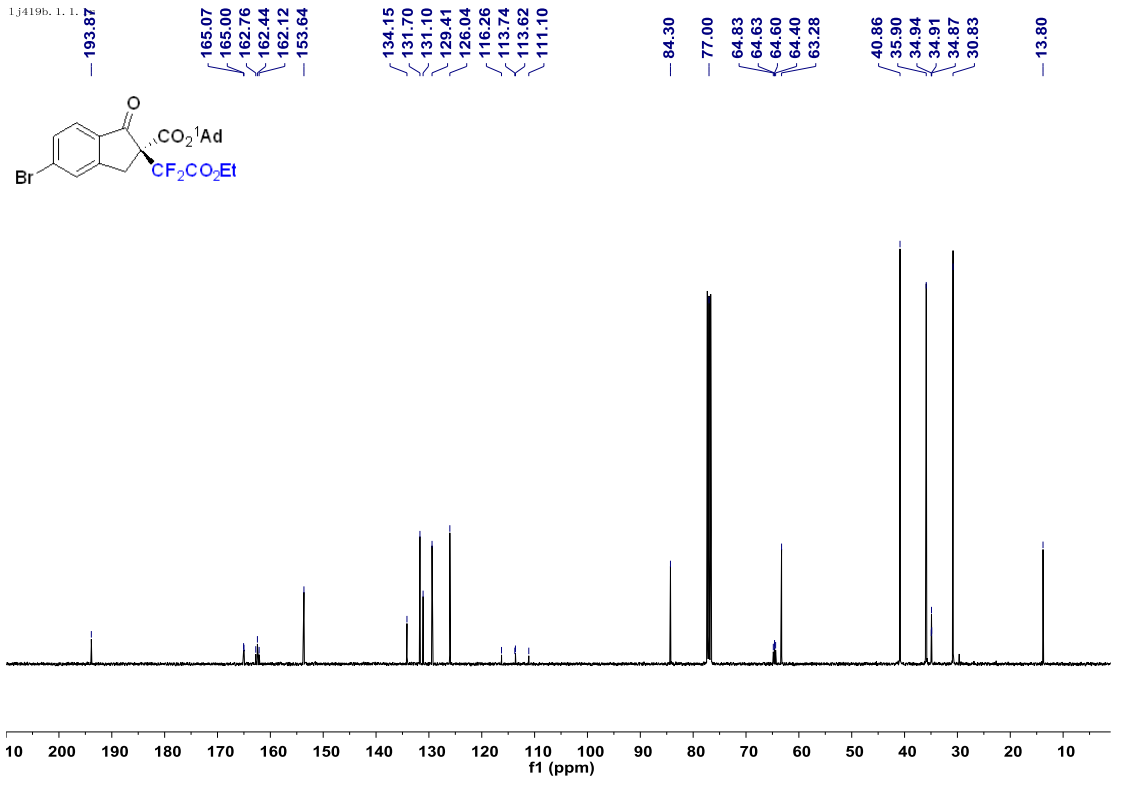
^{19}F NMR Spectrum of **3db**



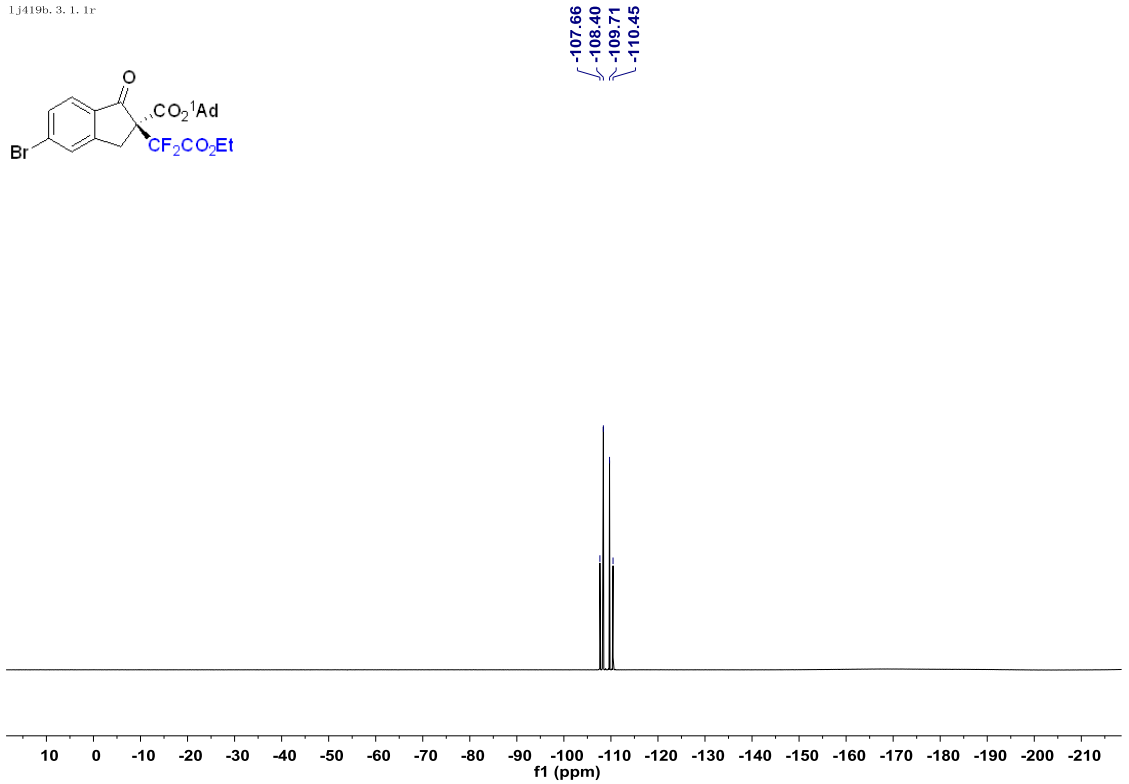
^{1}H NMR Spectrum of **3eb**



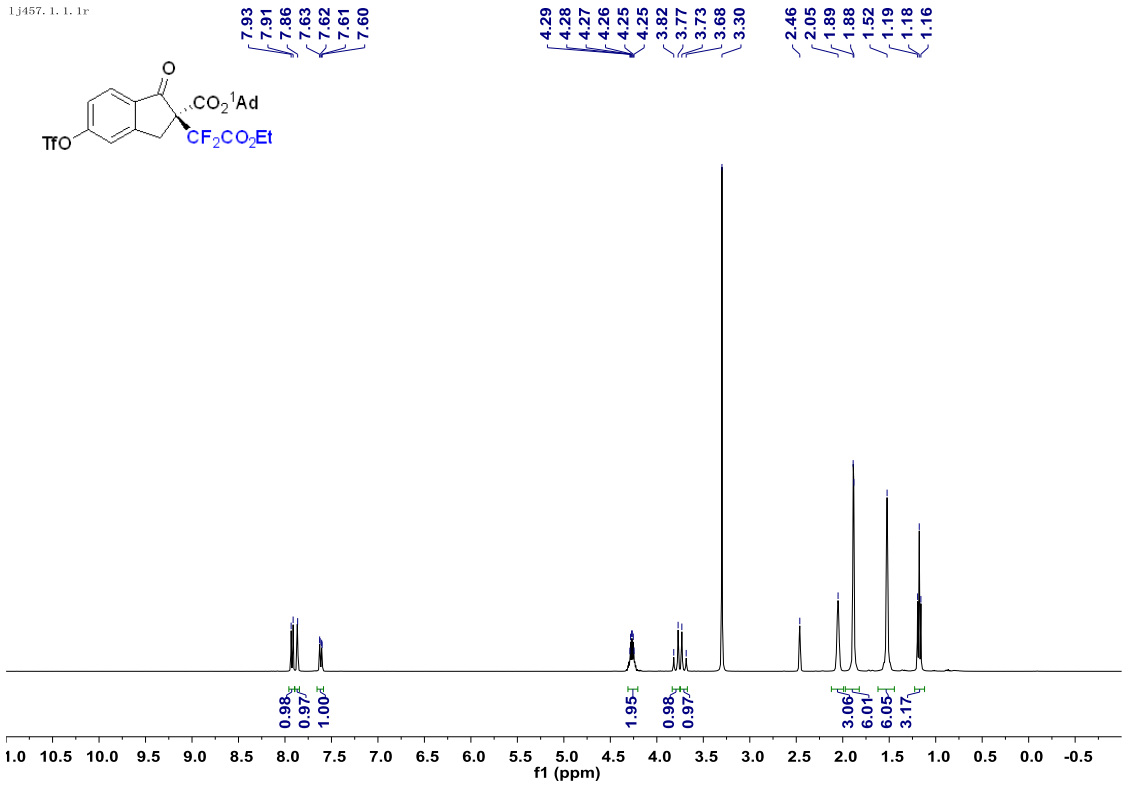
^{13}C NMR Spectrum of **3eb**



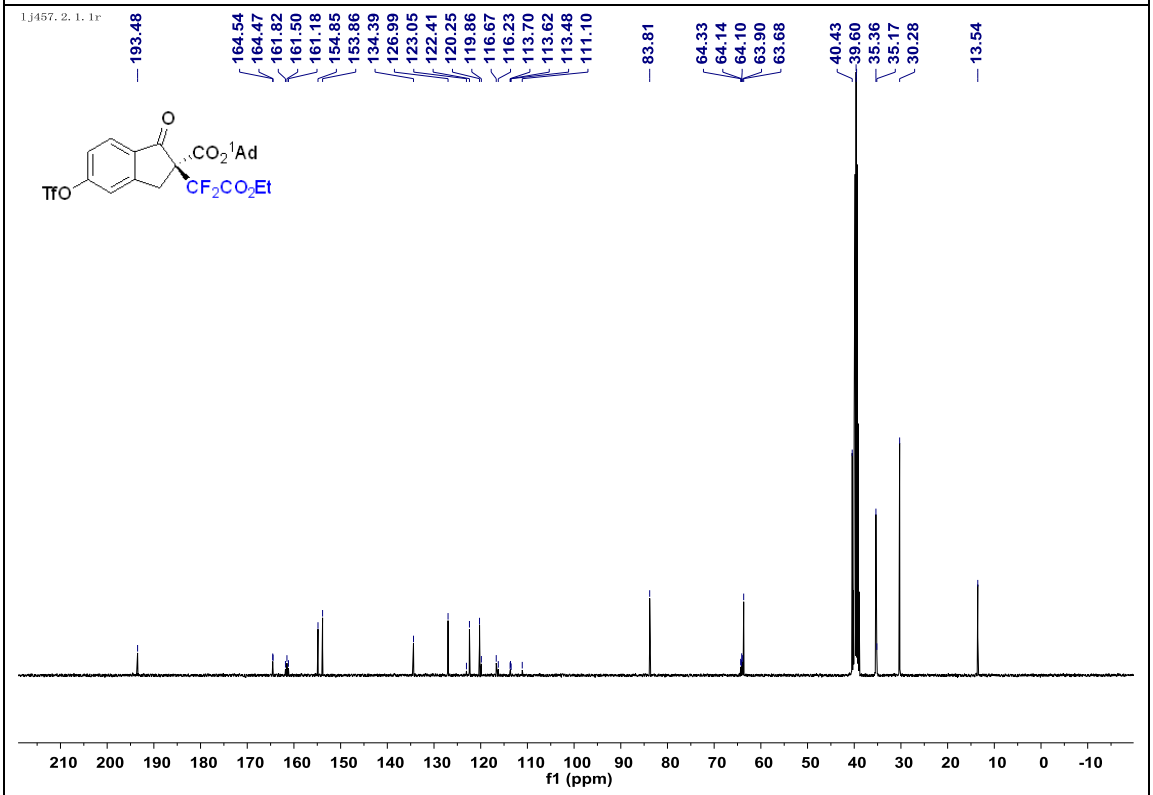
^{19}F NMR Spectrum of **3eb**



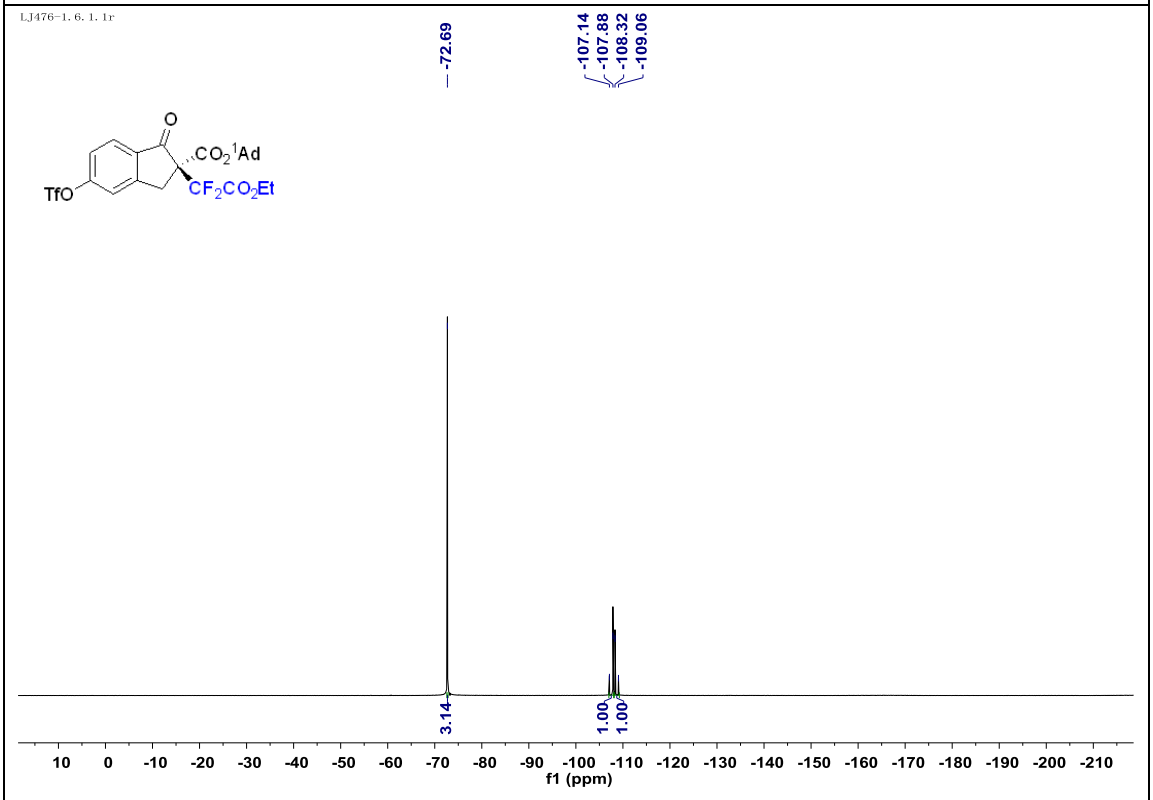
^{1}H NMR Spectrum of **3fb** in DMSO



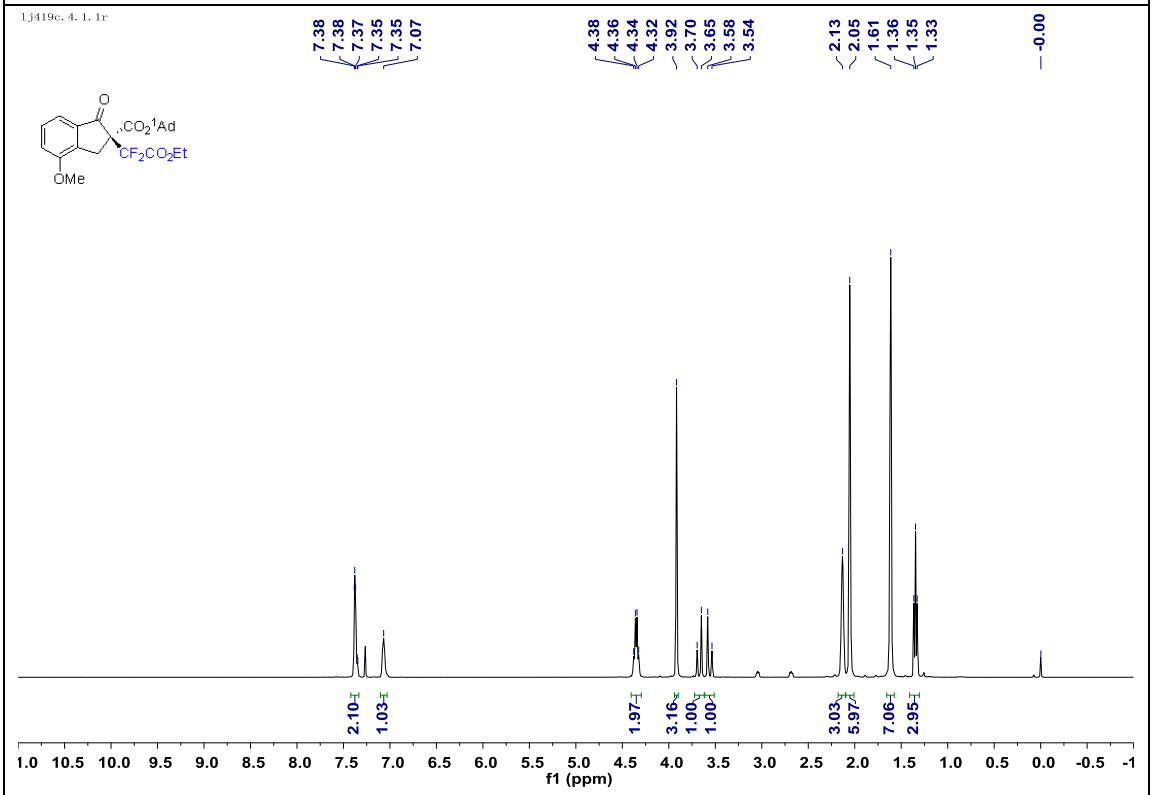
^{13}C NMR Spectrum of **3fb** in DMSO



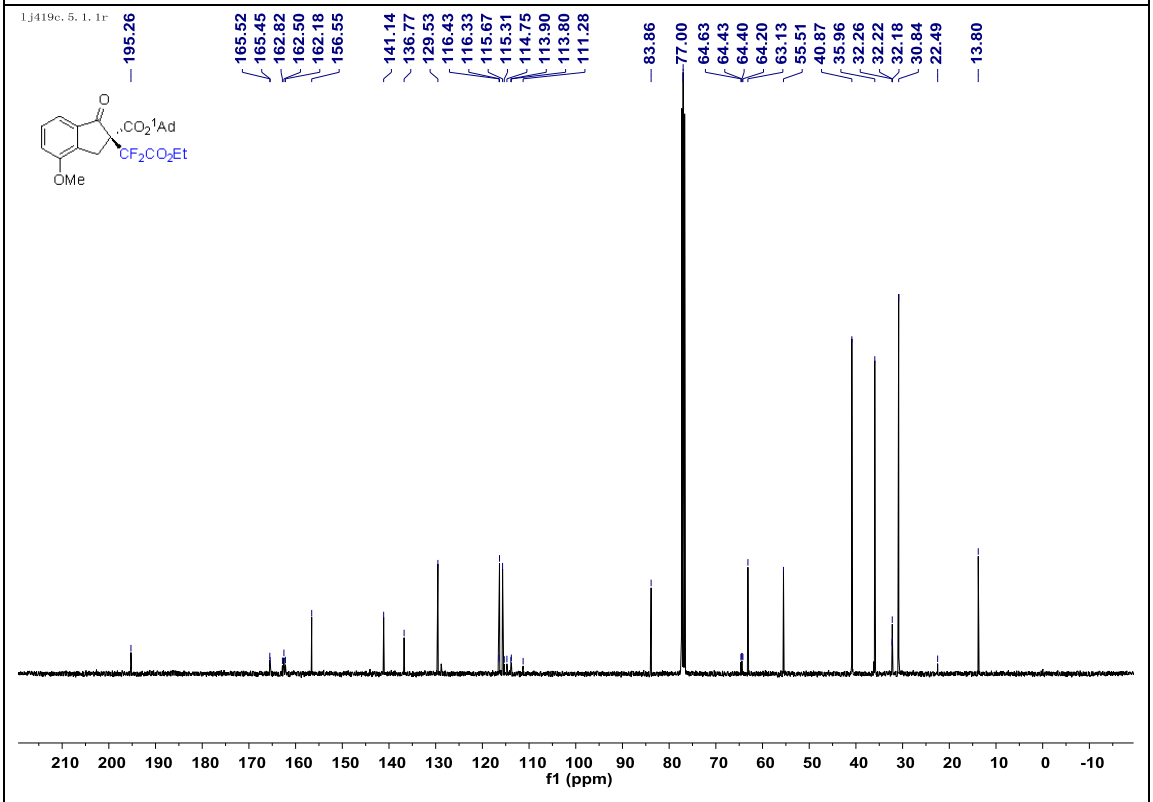
^{19}F NMR Spectrum of **3fb** in DMSO



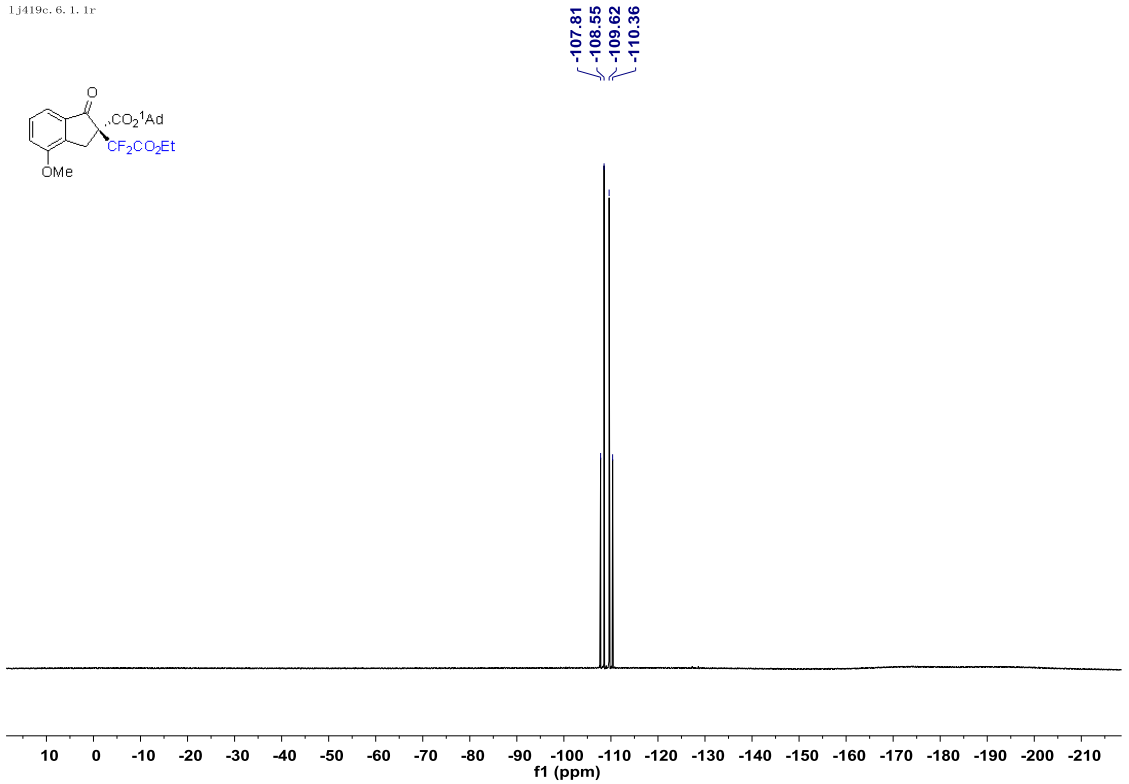
^{1}H NMR Spectrum of **3gb**



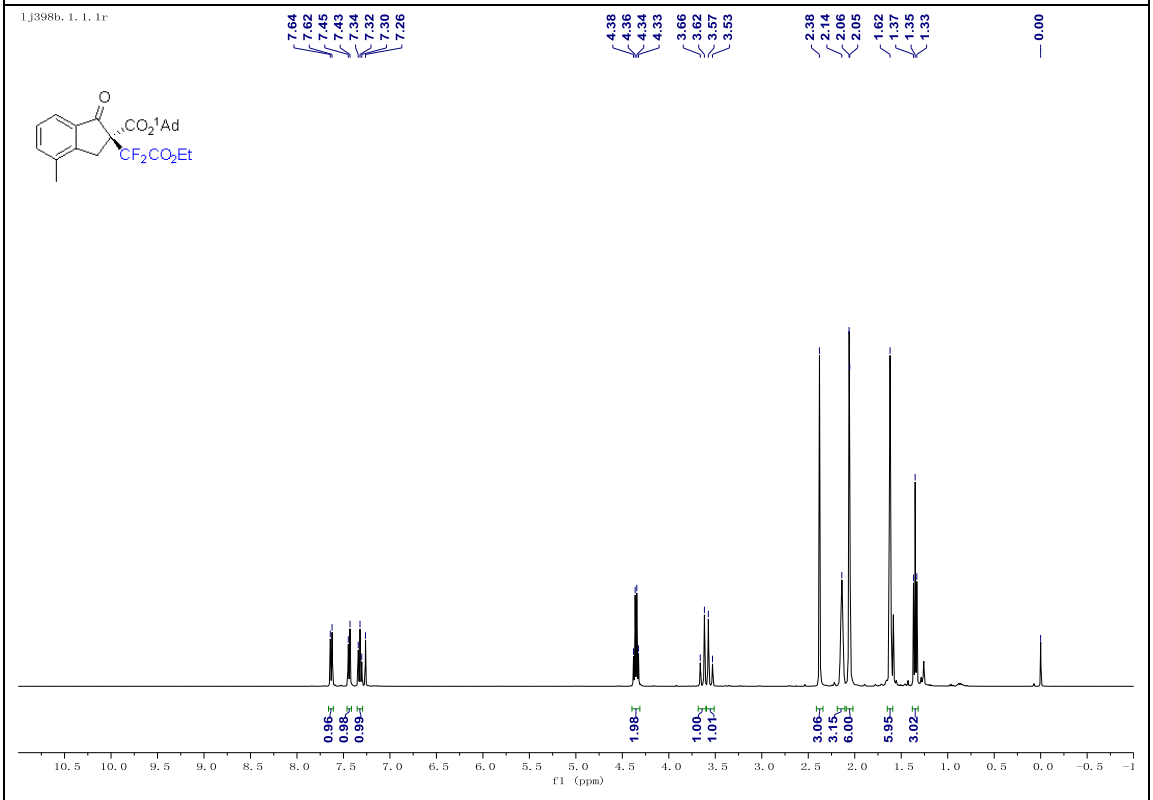
^{13}C NMR Spectrum of **3gb**



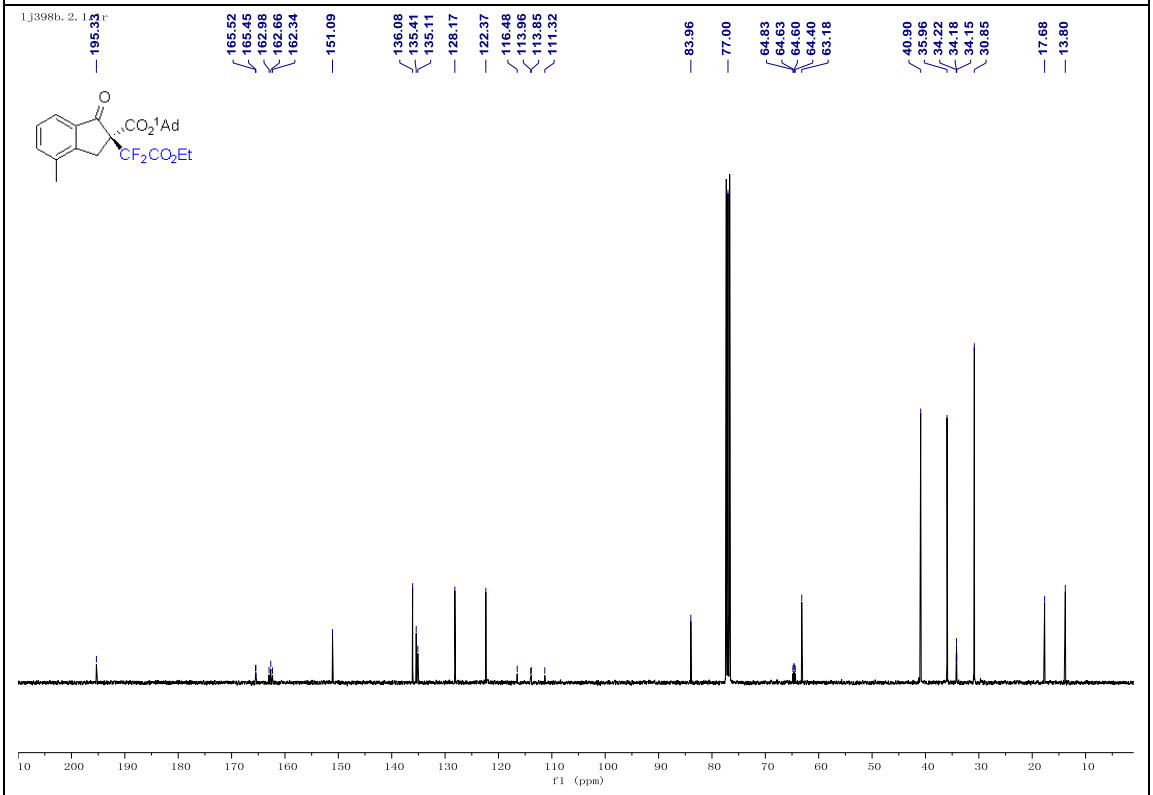
^{19}F NMR Spectrum of **3gb**



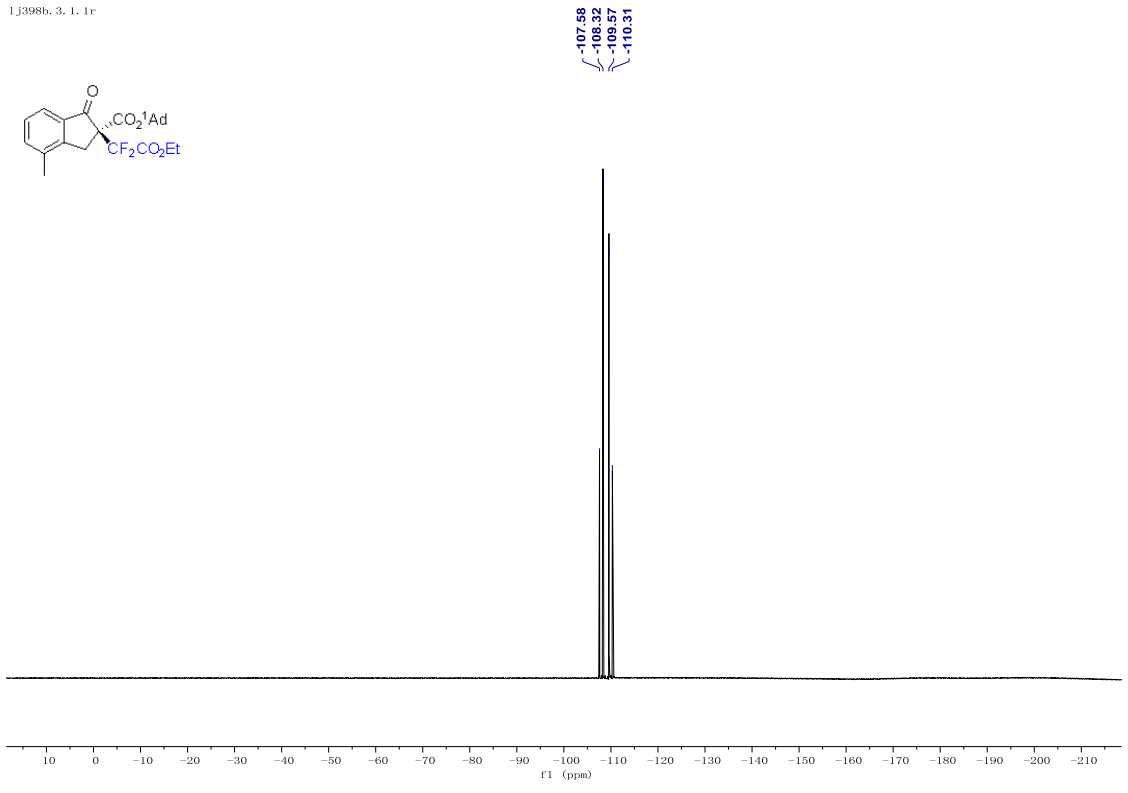
^{1}H NMR Spectrum of **3hb**



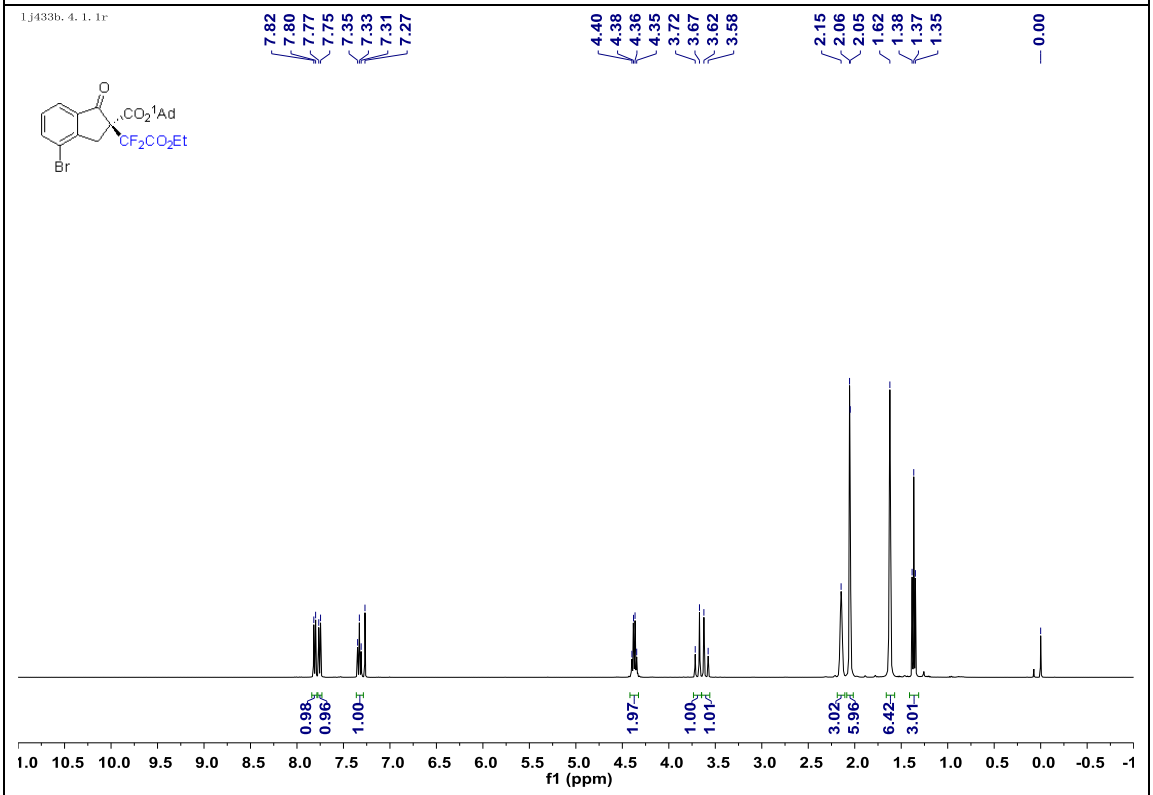
^{13}C NMR Spectrum of **3hb**



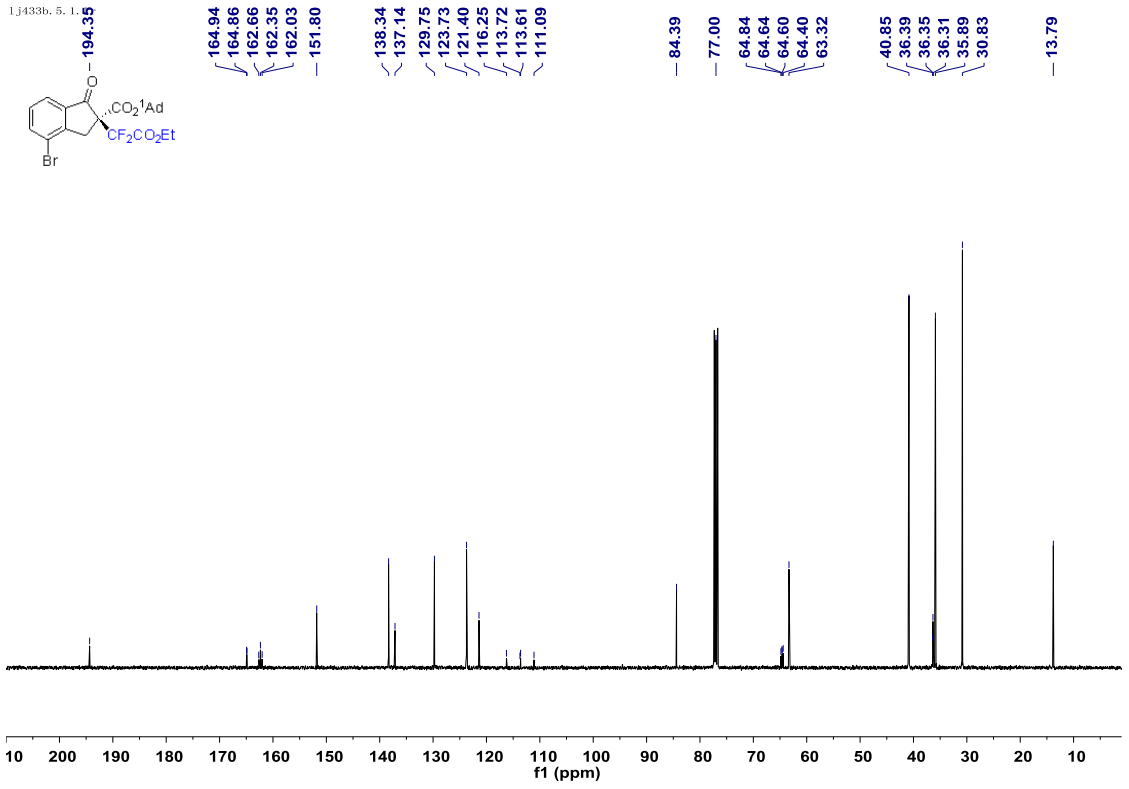
^{19}F NMR Spectrum of **3hb**



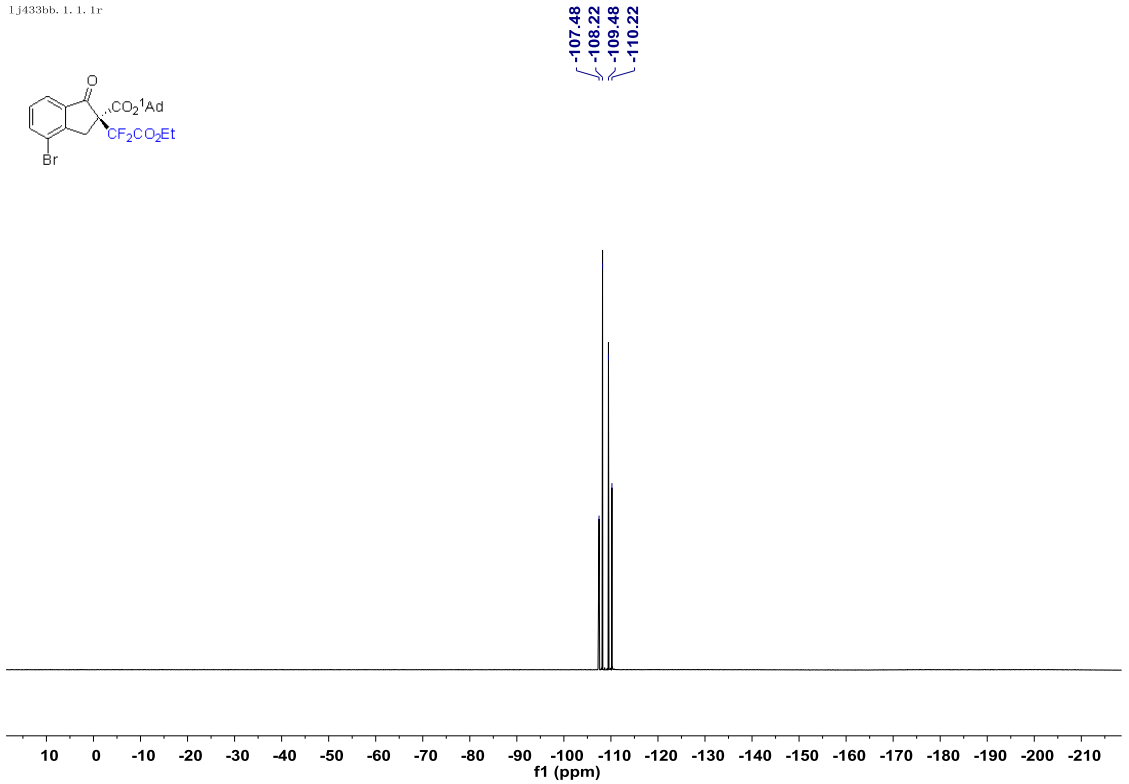
^{1}H NMR Spectrum of **3ib**



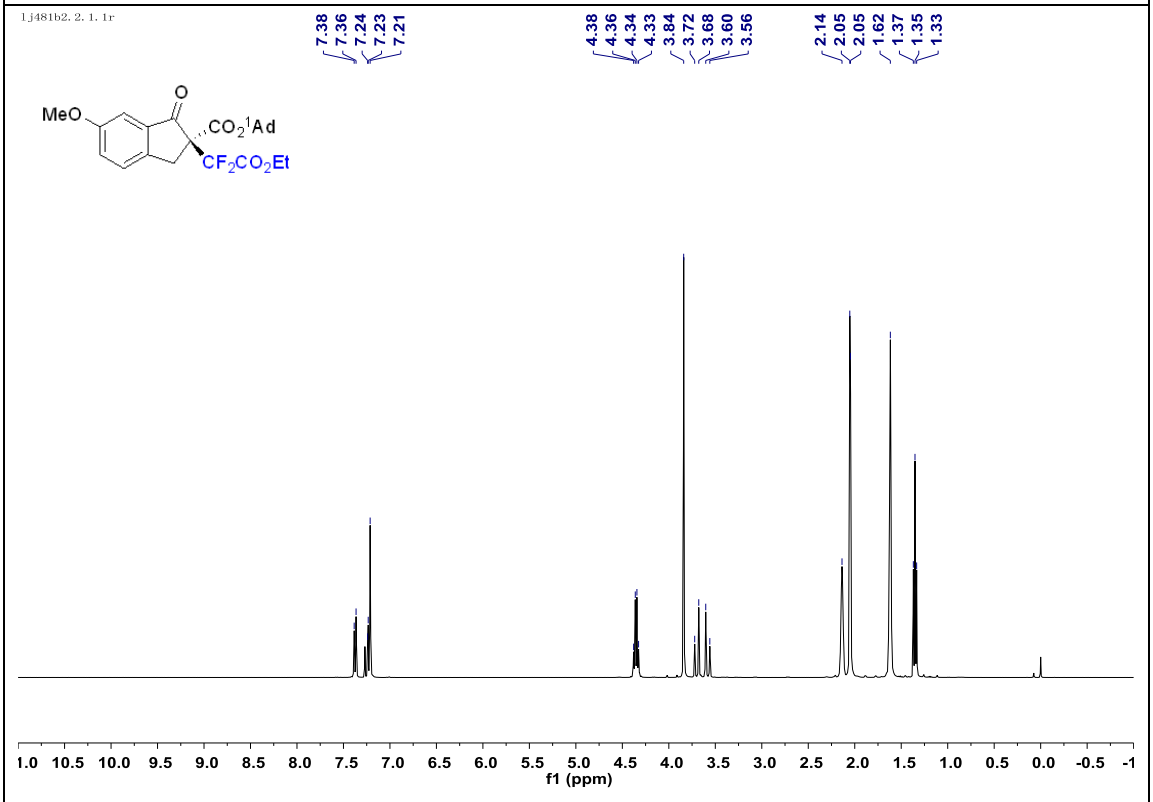
^{13}C NMR Spectrum of **3ib**



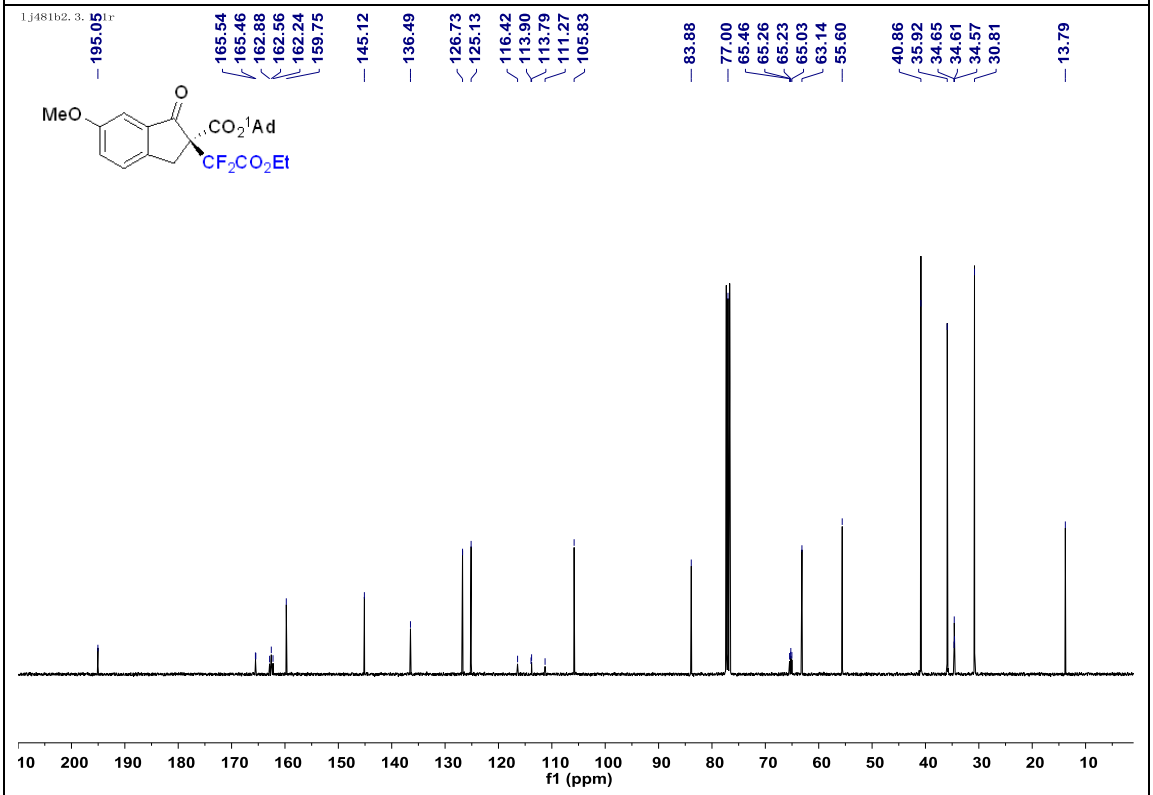
^{19}F NMR Spectrum of **3ib**



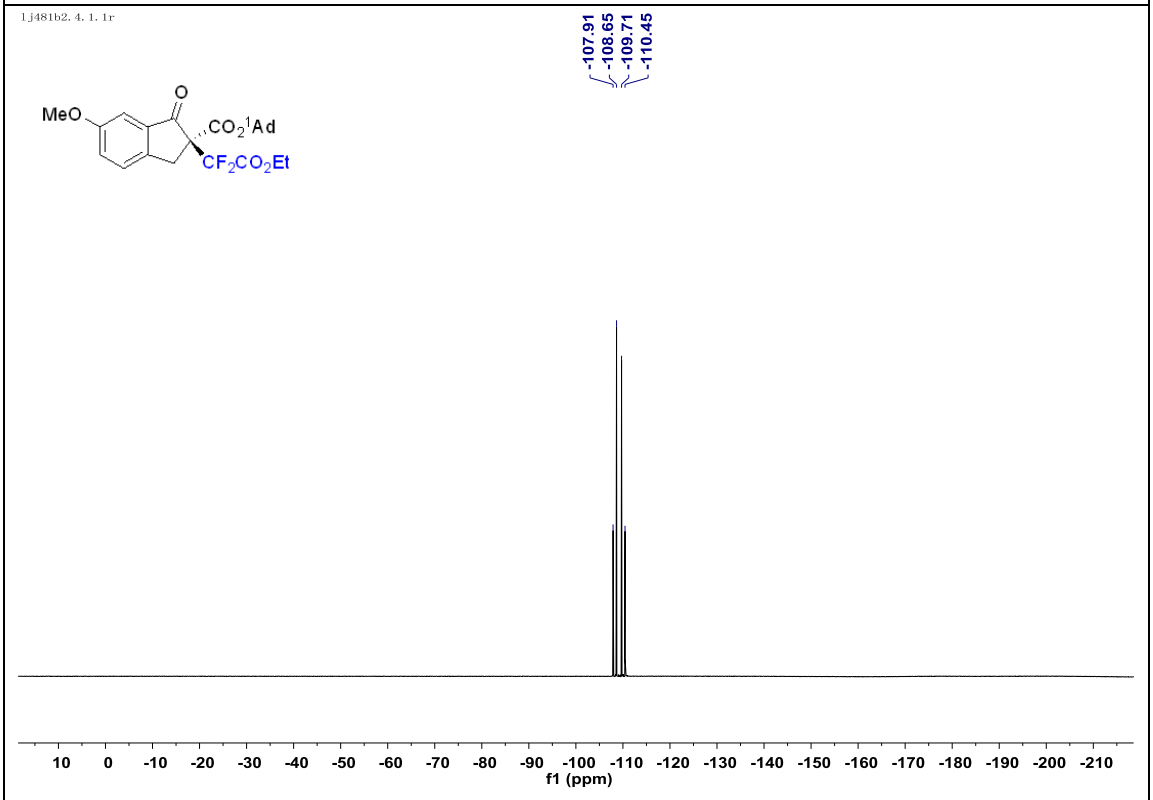
^{1}H NMR Spectrum of **3jb**



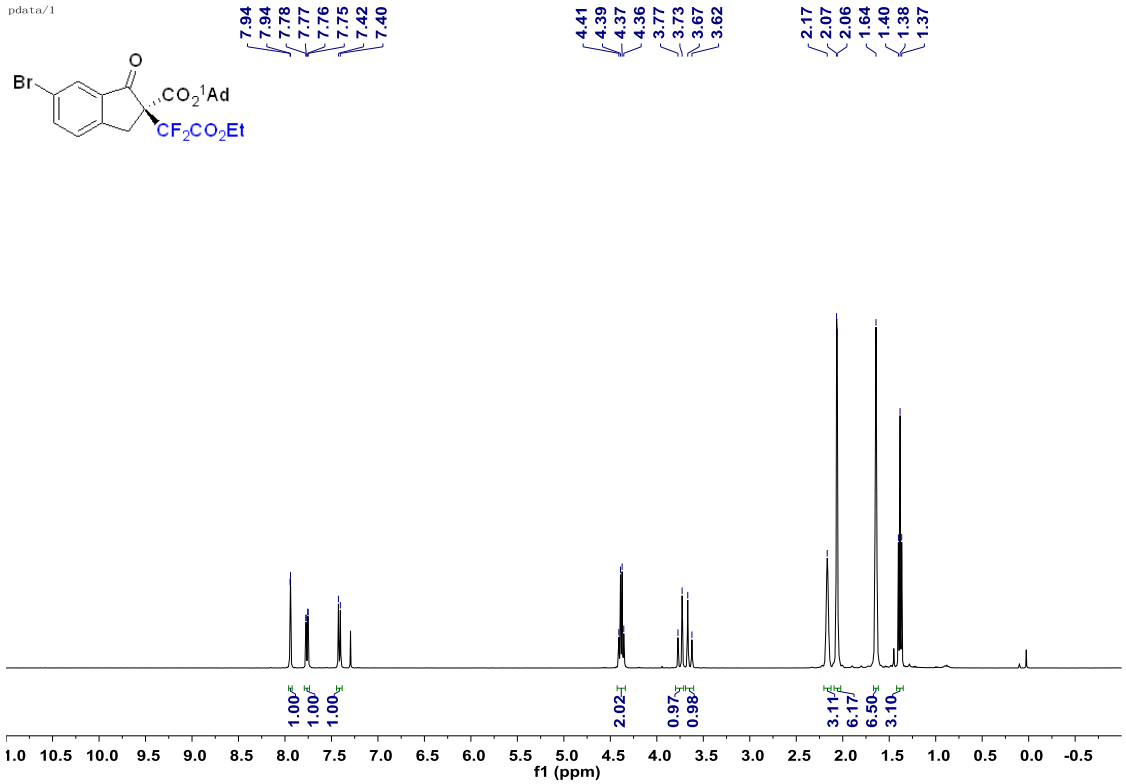
^{13}C NMR Spectrum of **3jb**



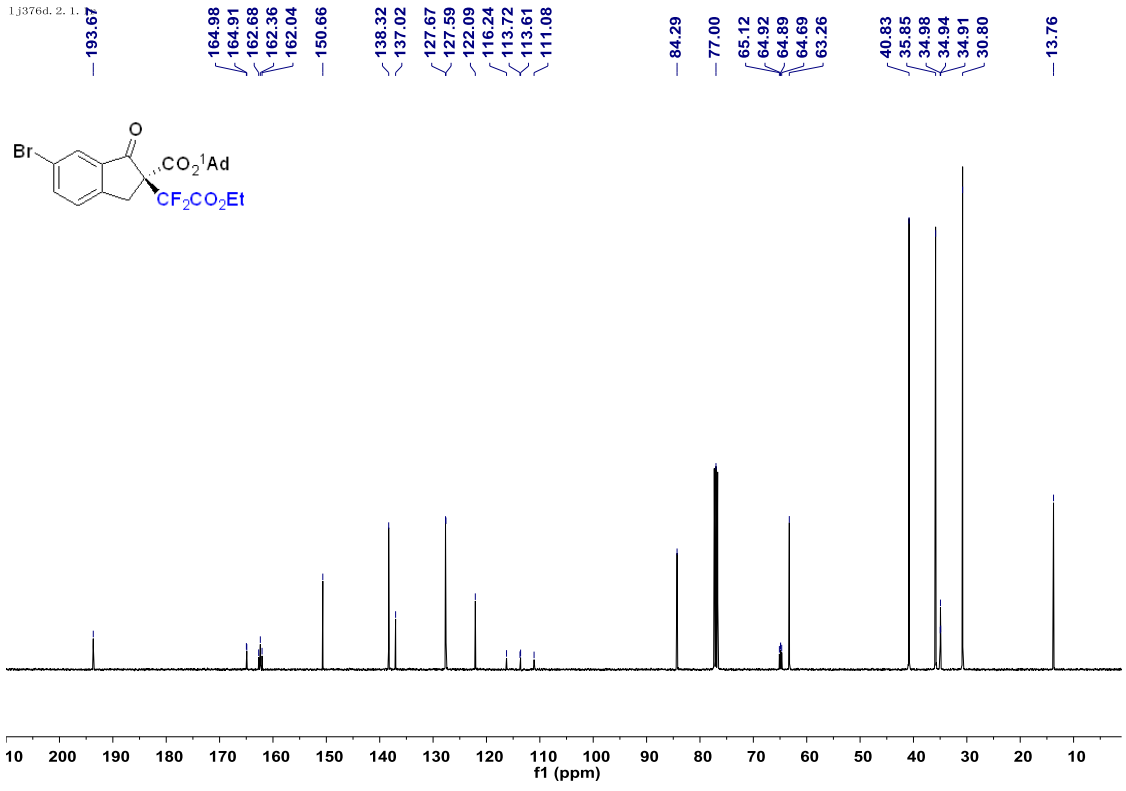
^{19}F NMR Spectrum of **3jb**



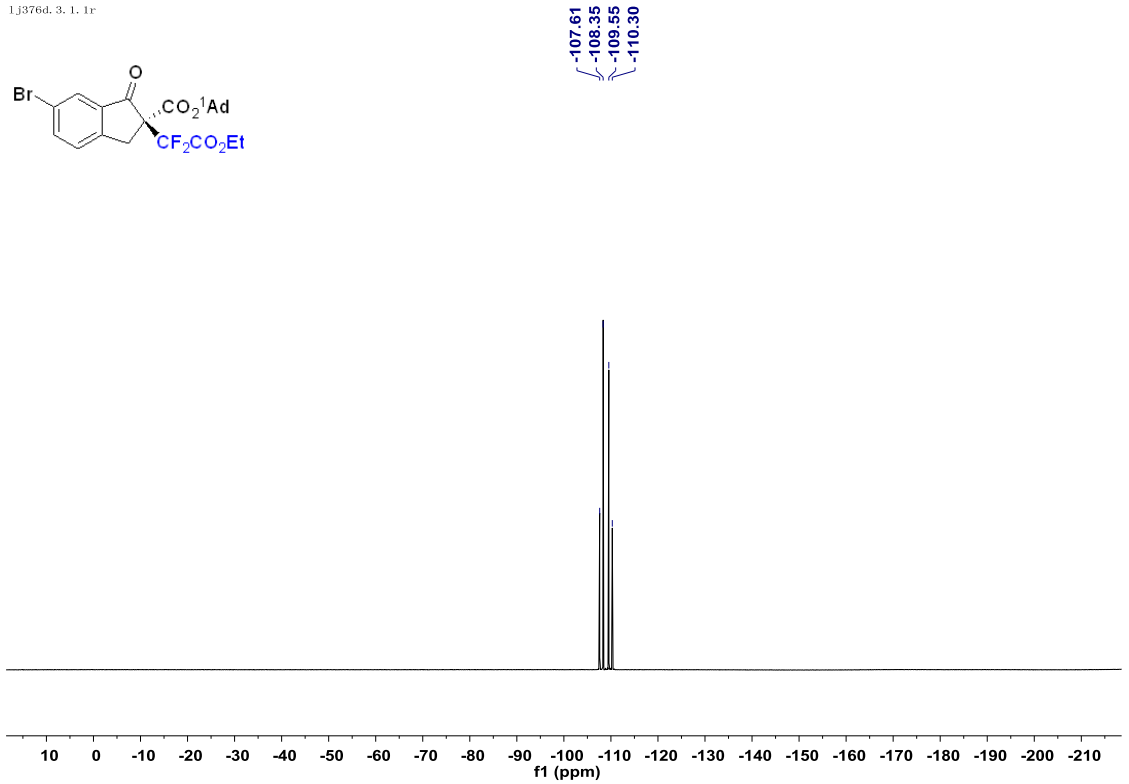
^{1}H NMR Spectrum of **3kb**



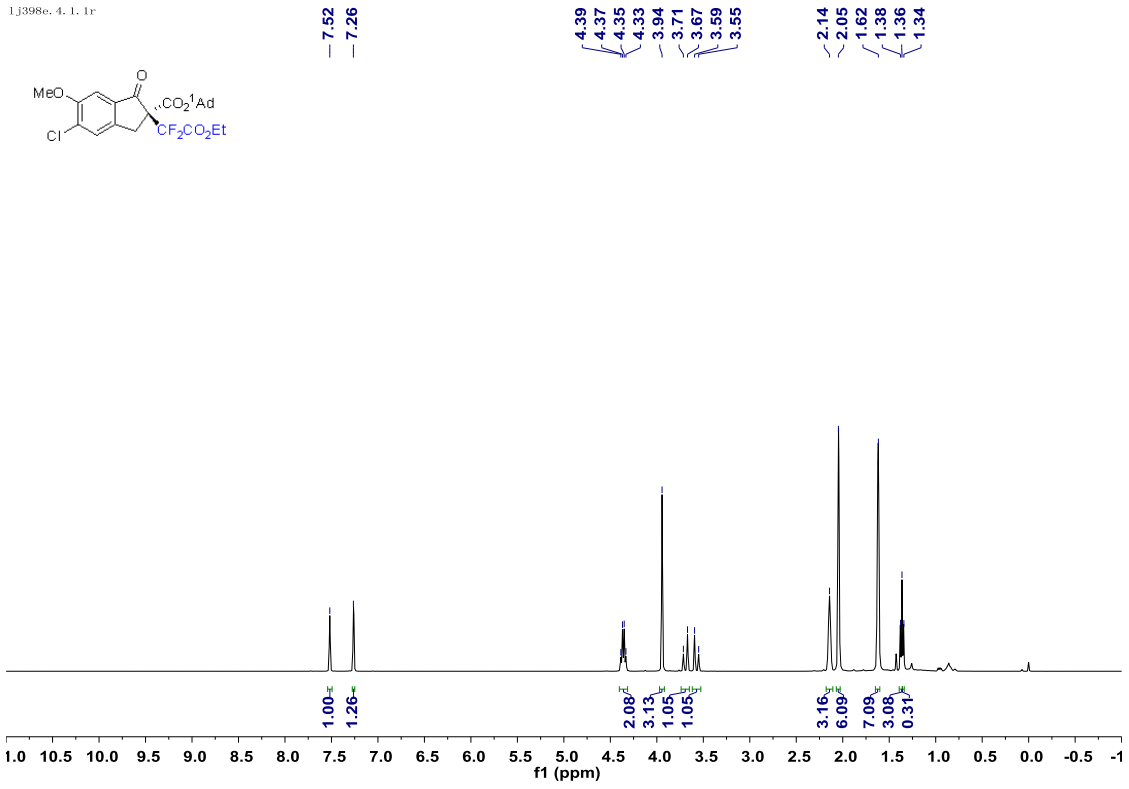
^{13}C NMR Spectrum of **3kb**



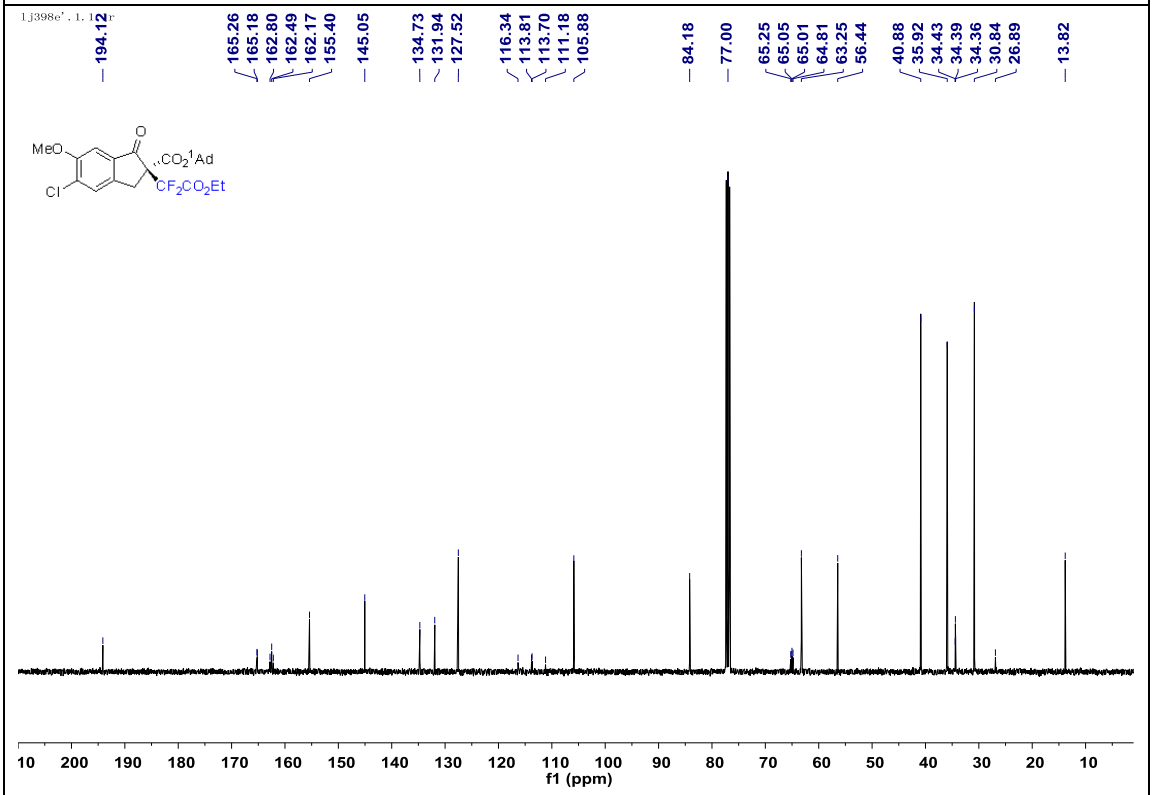
^{19}F NMR Spectrum of **3kb**



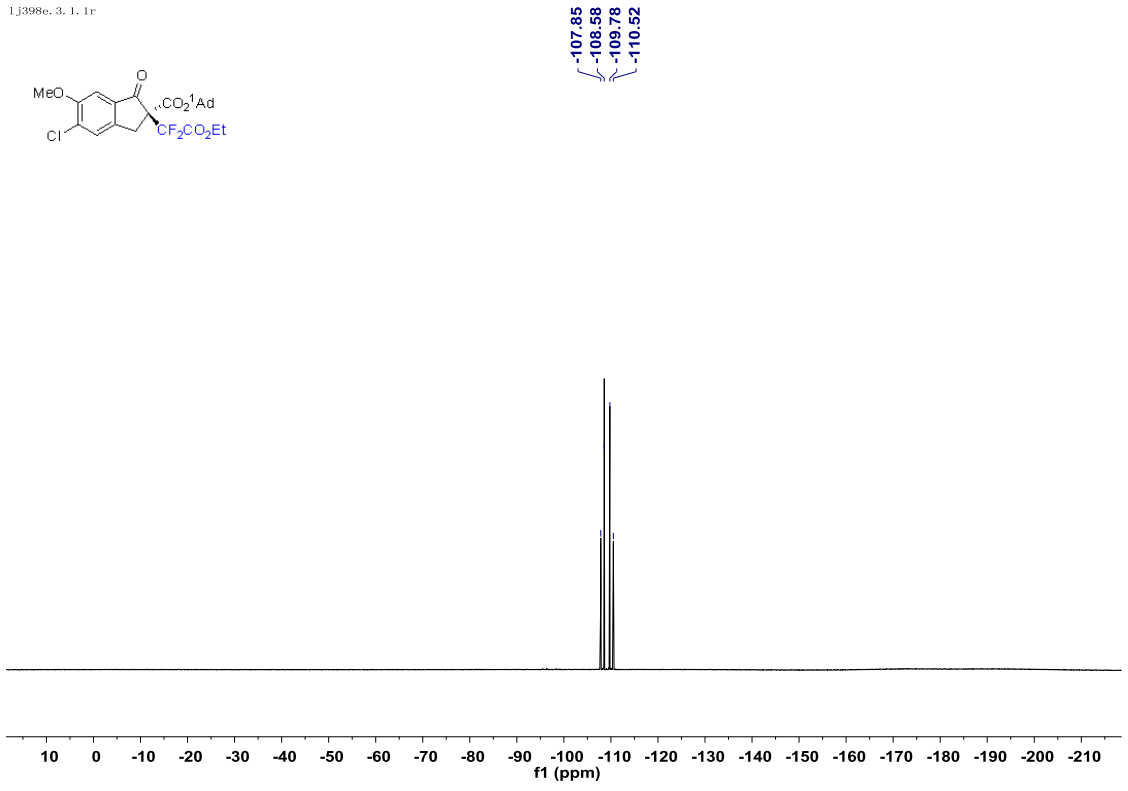
^{1}H NMR Spectrum of **3lb**



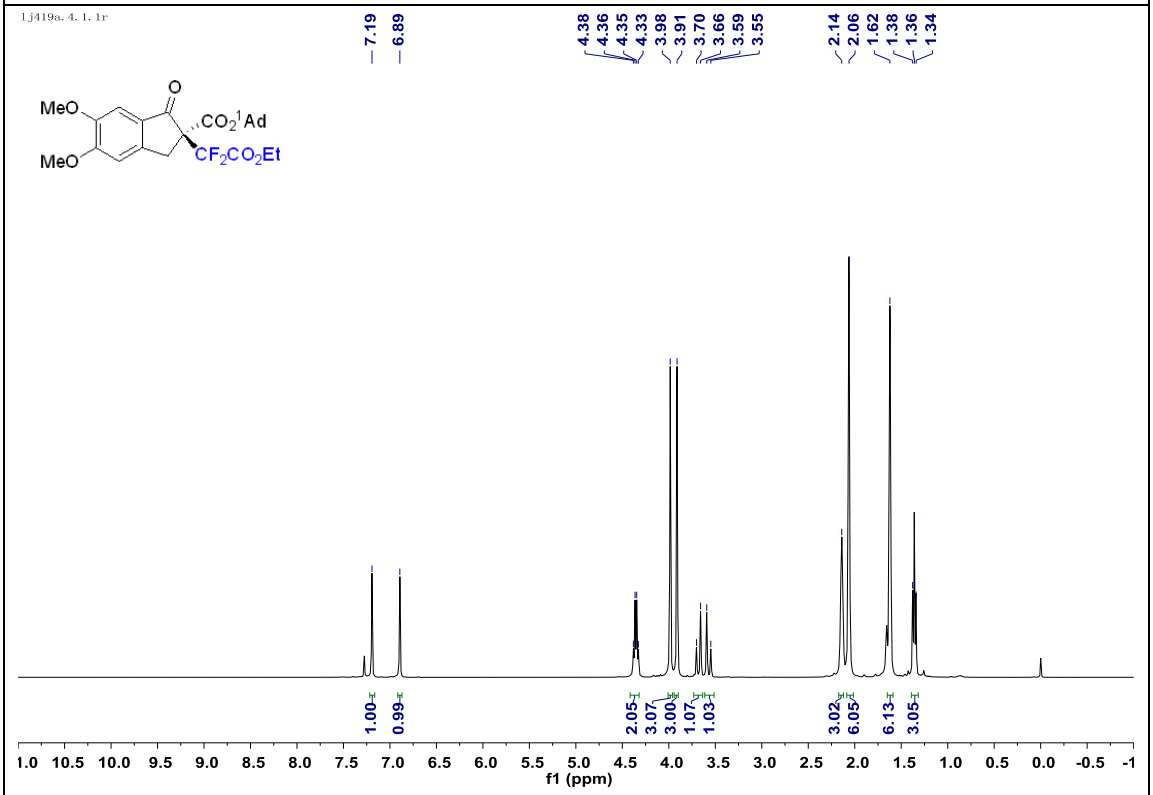
^{13}C NMR Spectrum of **3lb**



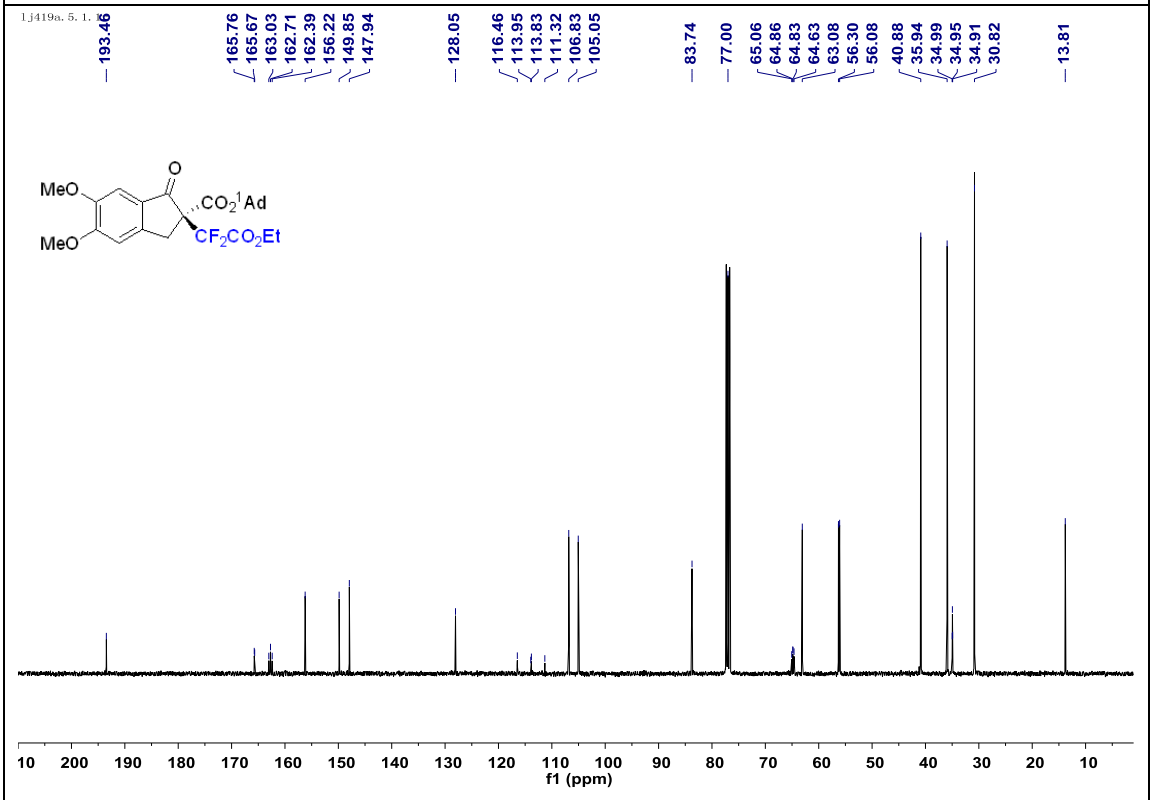
^{19}F NMR Spectrum of **3lb**



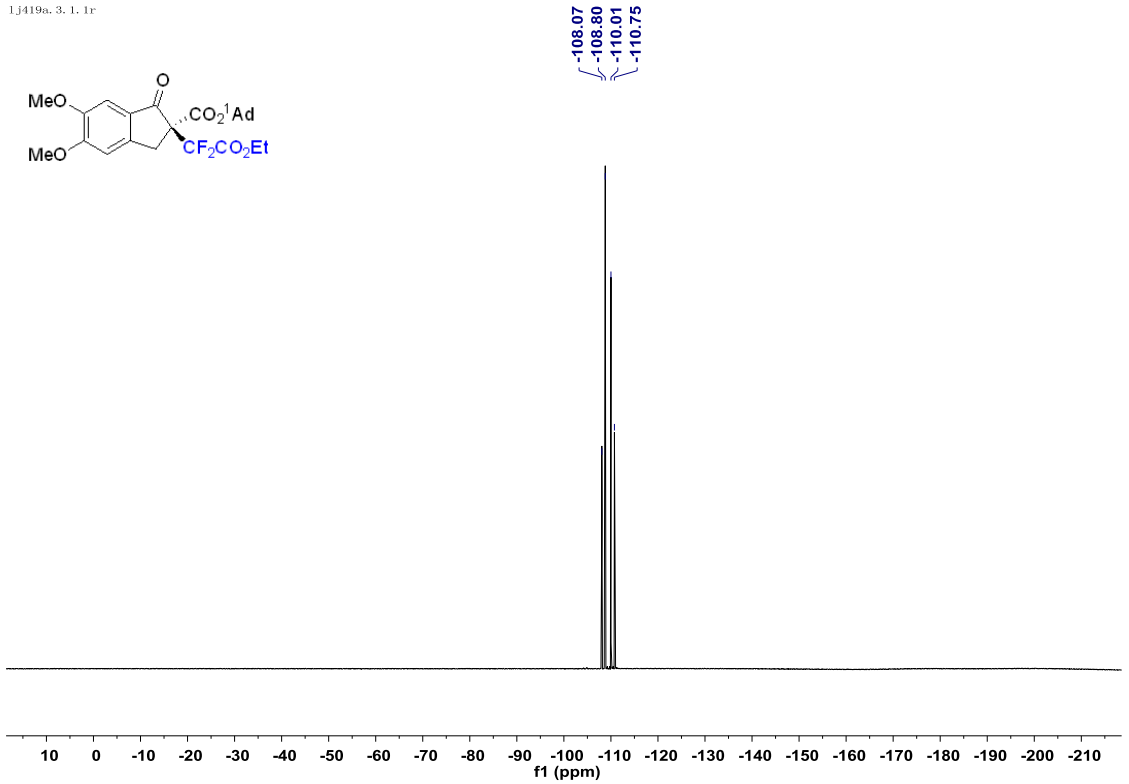
^{1}H NMR Spectrum of **3mb**



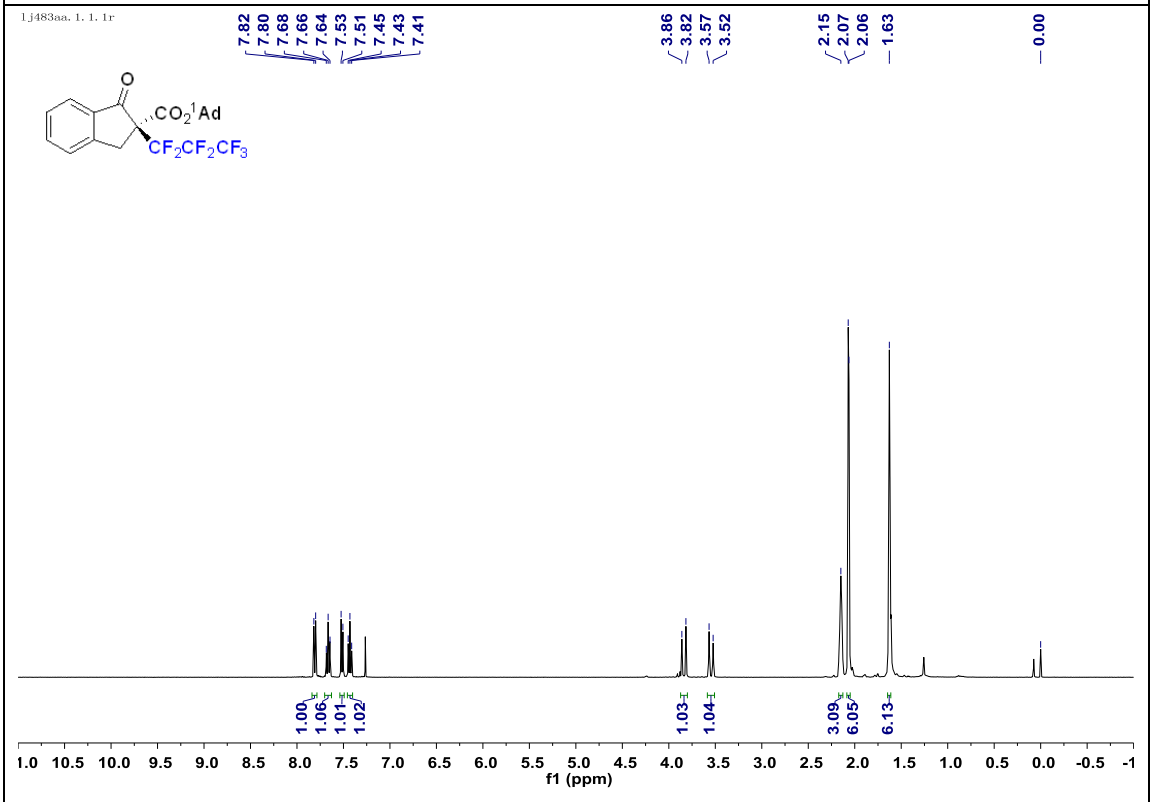
^{13}C NMR Spectrum of **3mb**



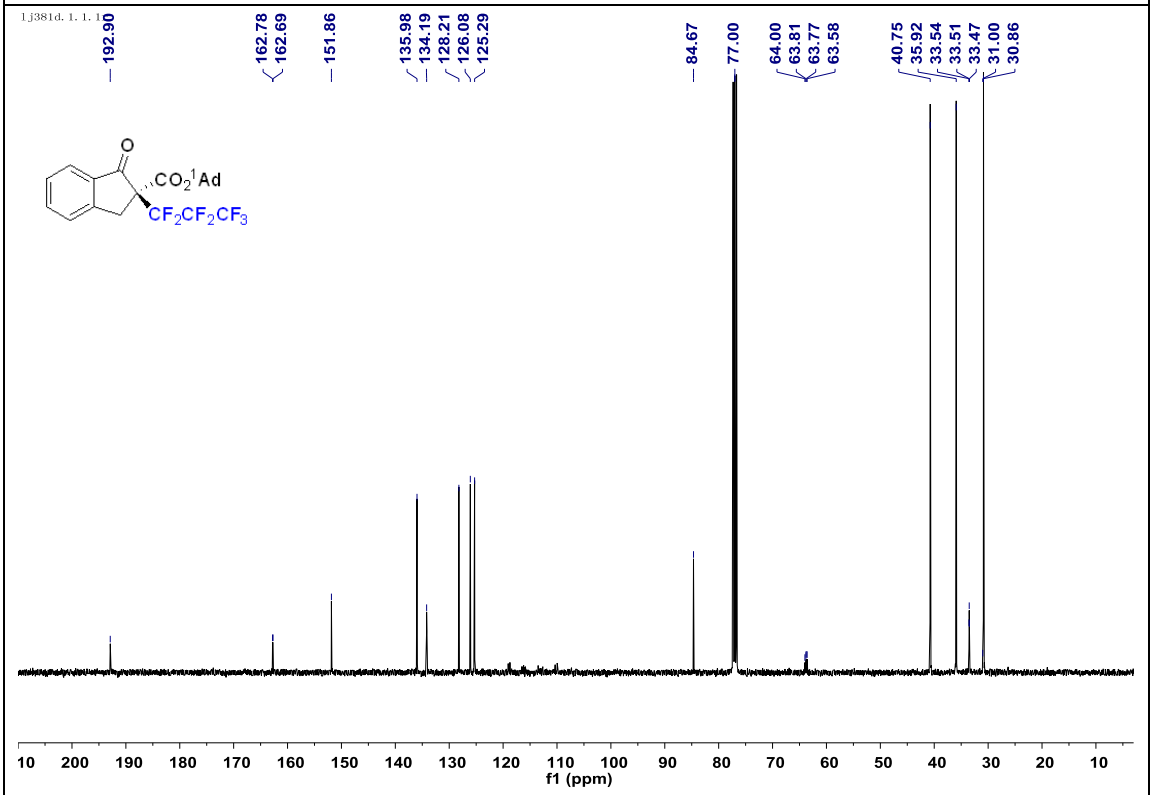
^{19}F NMR Spectrum of **3mb**



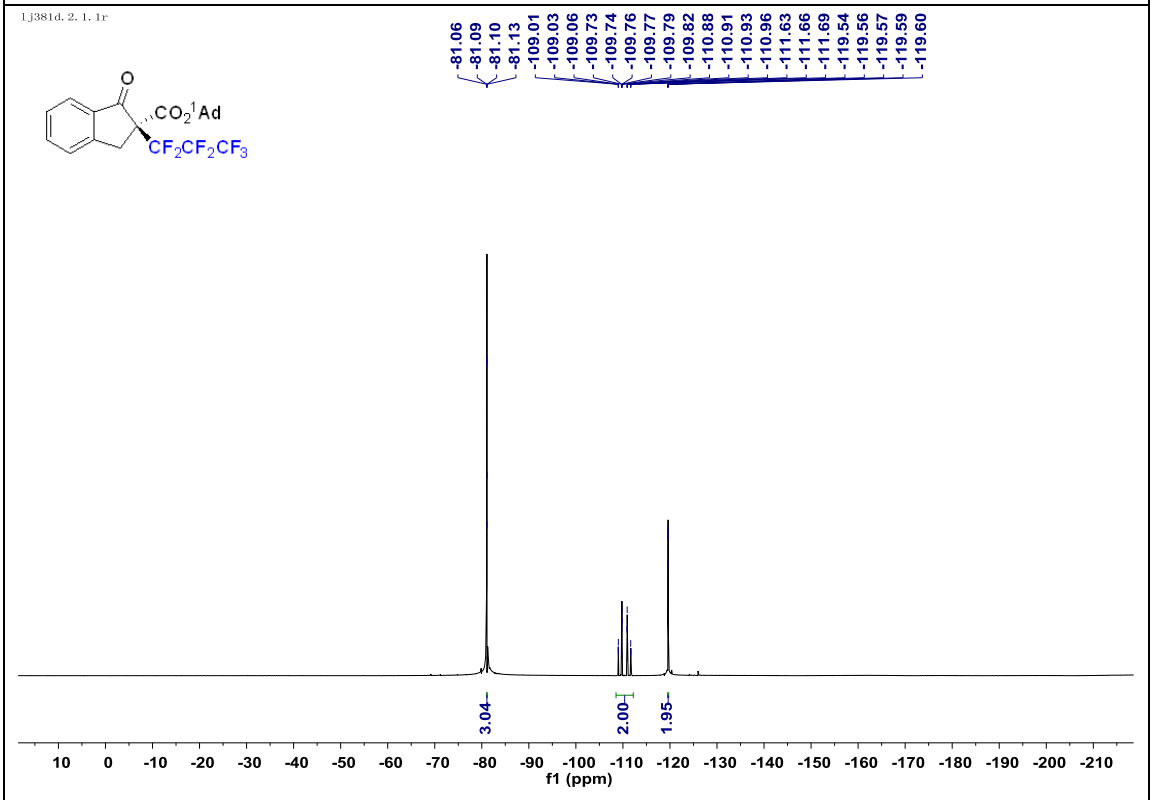
^{1}H NMR Spectrum of **3ac**



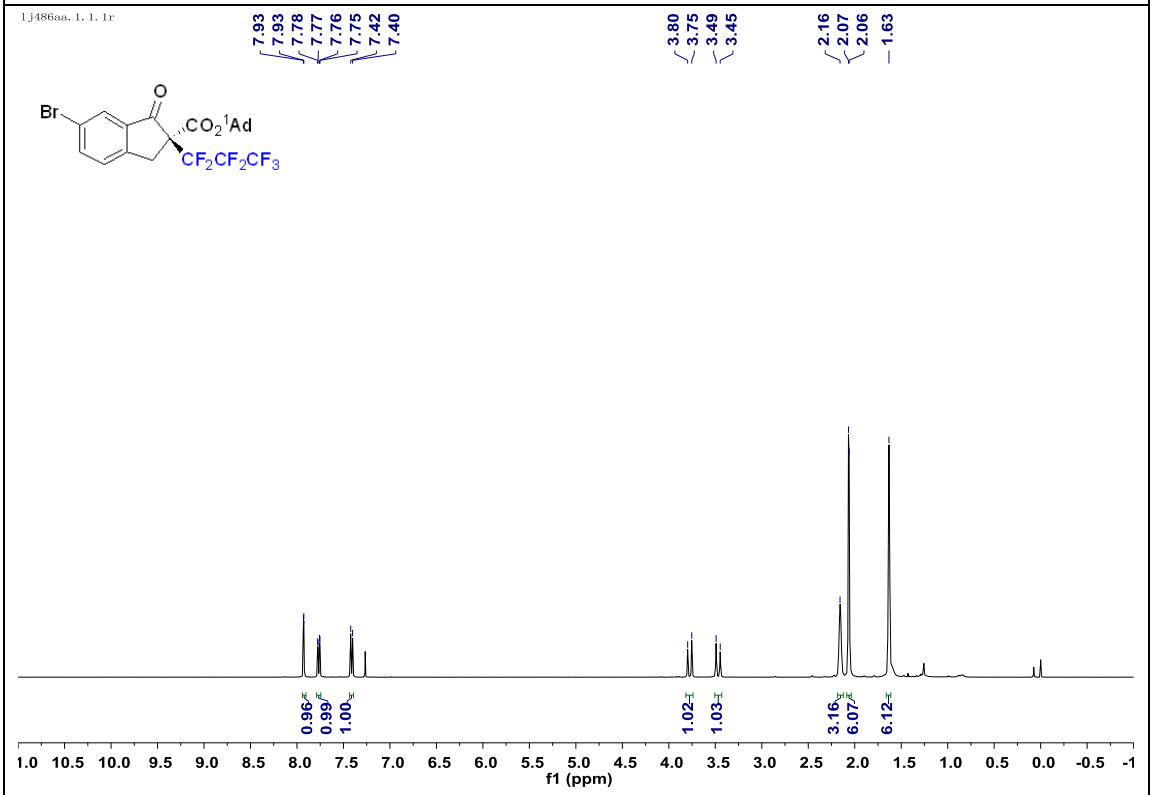
^{13}C NMR Spectrum of **3ac**



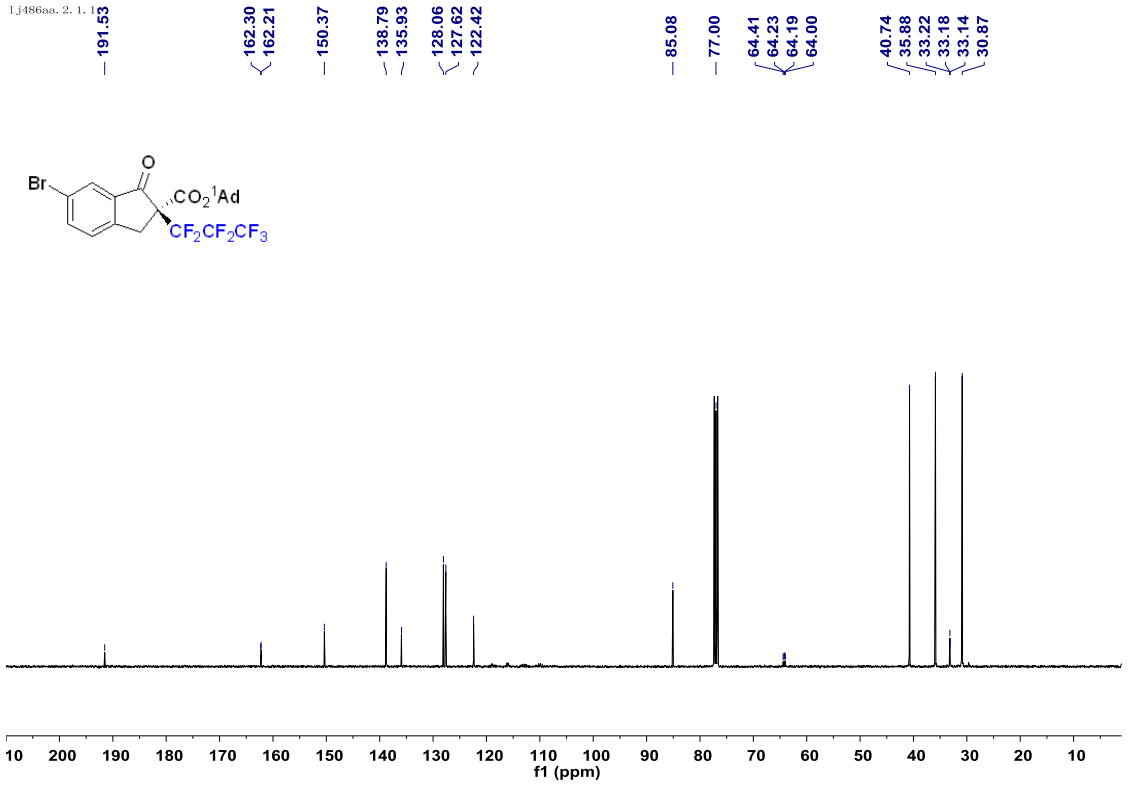
^{19}F NMR Spectrum of **3ac**



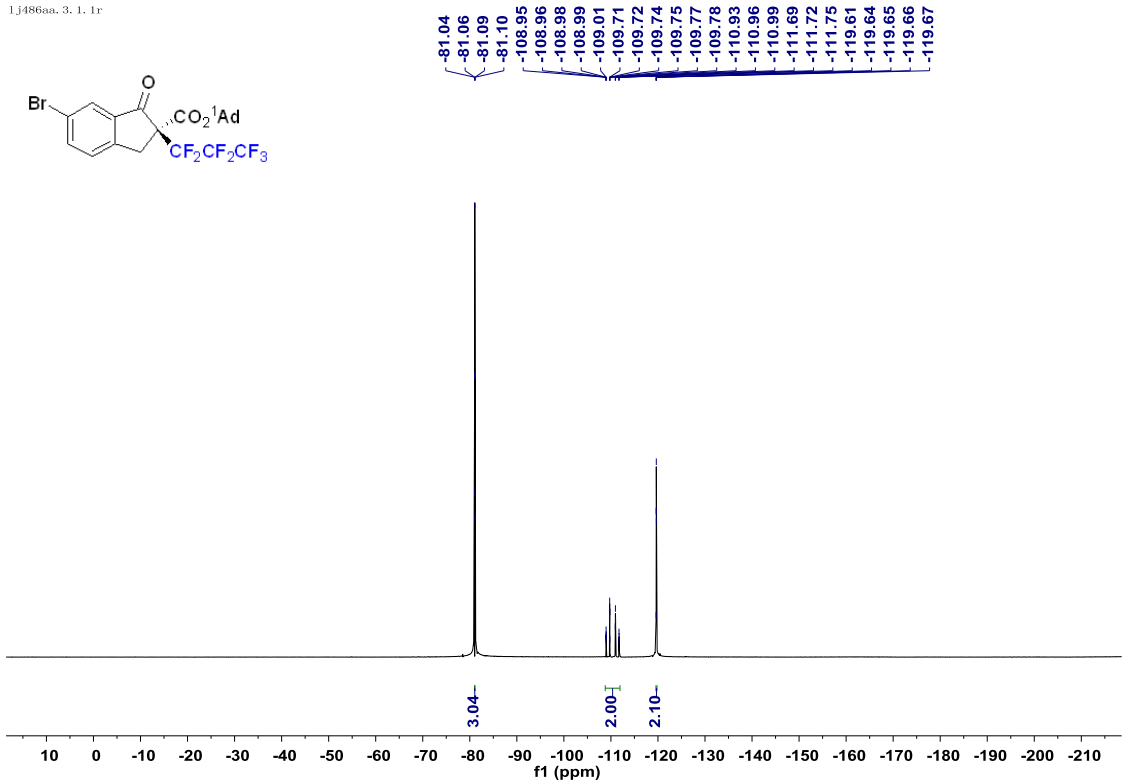
^{1}H NMR Spectrum of **3kc**



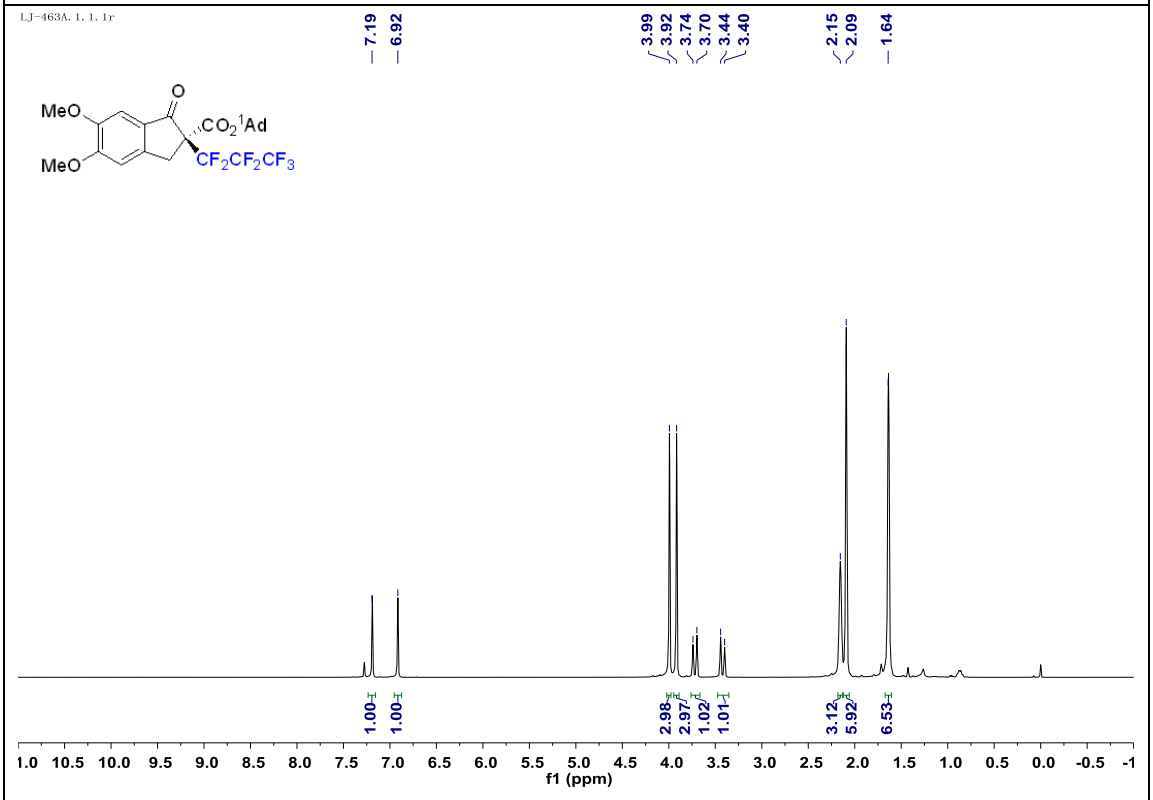
^{13}C NMR Spectrum of **3kc**



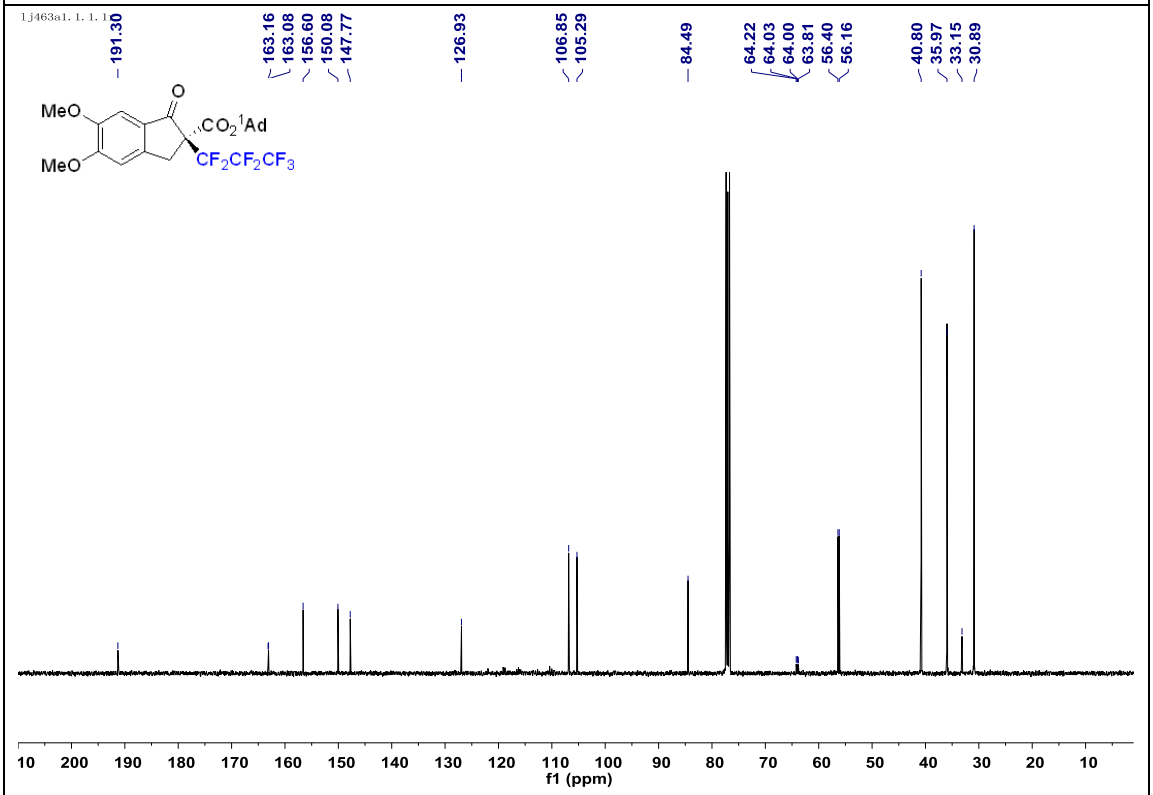
^{19}F NMR Spectrum of **3kc**



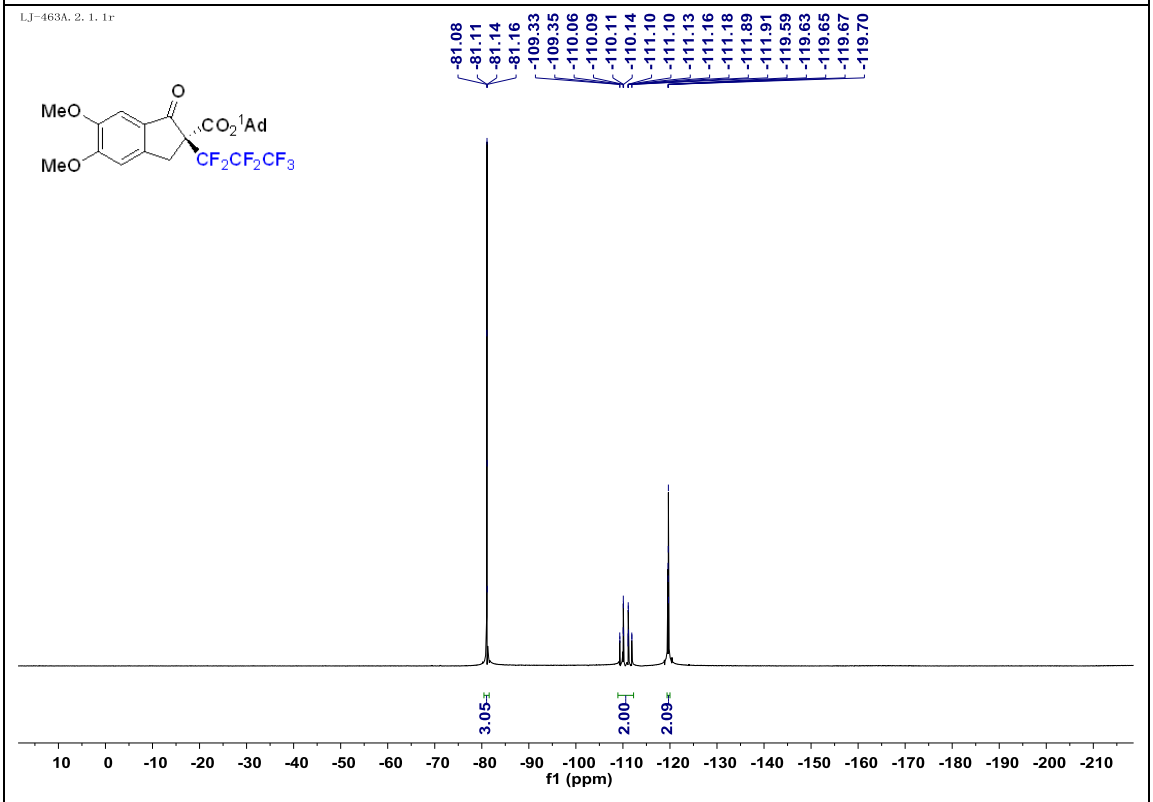
^{1}H NMR Spectrum of **3mc**



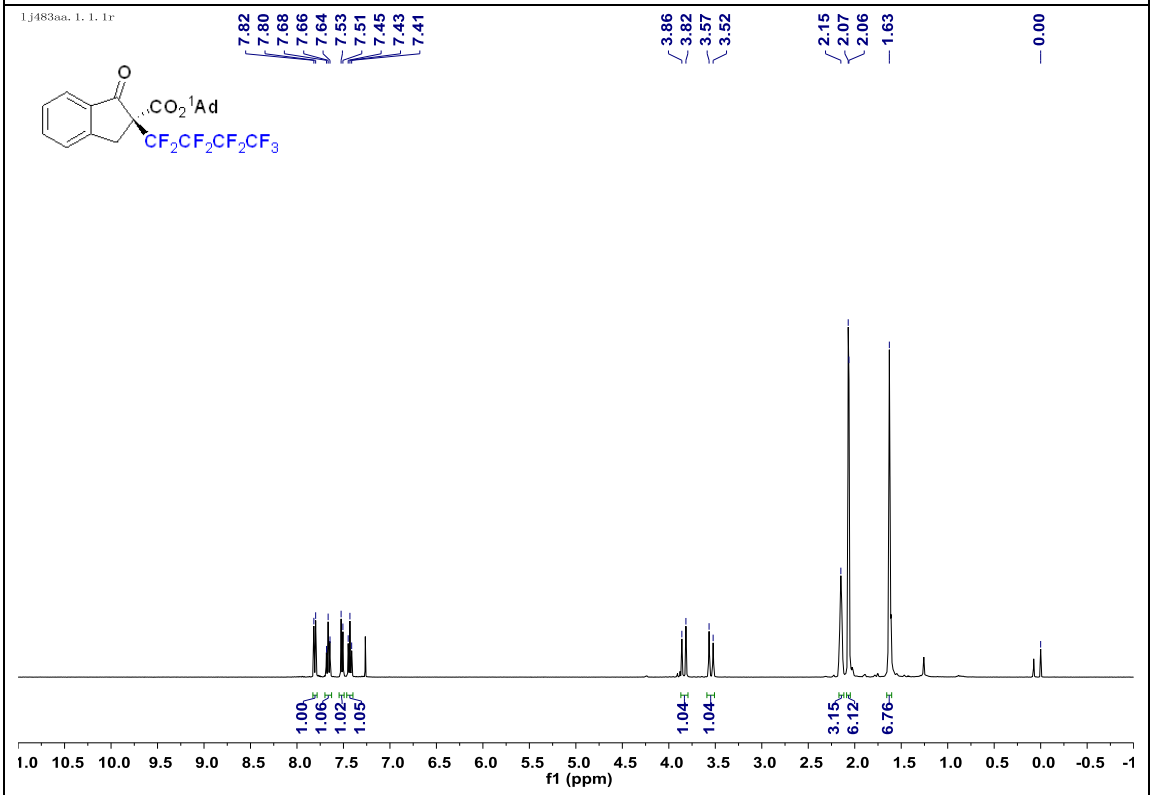
^{13}C NMR Spectrum of **3mc**



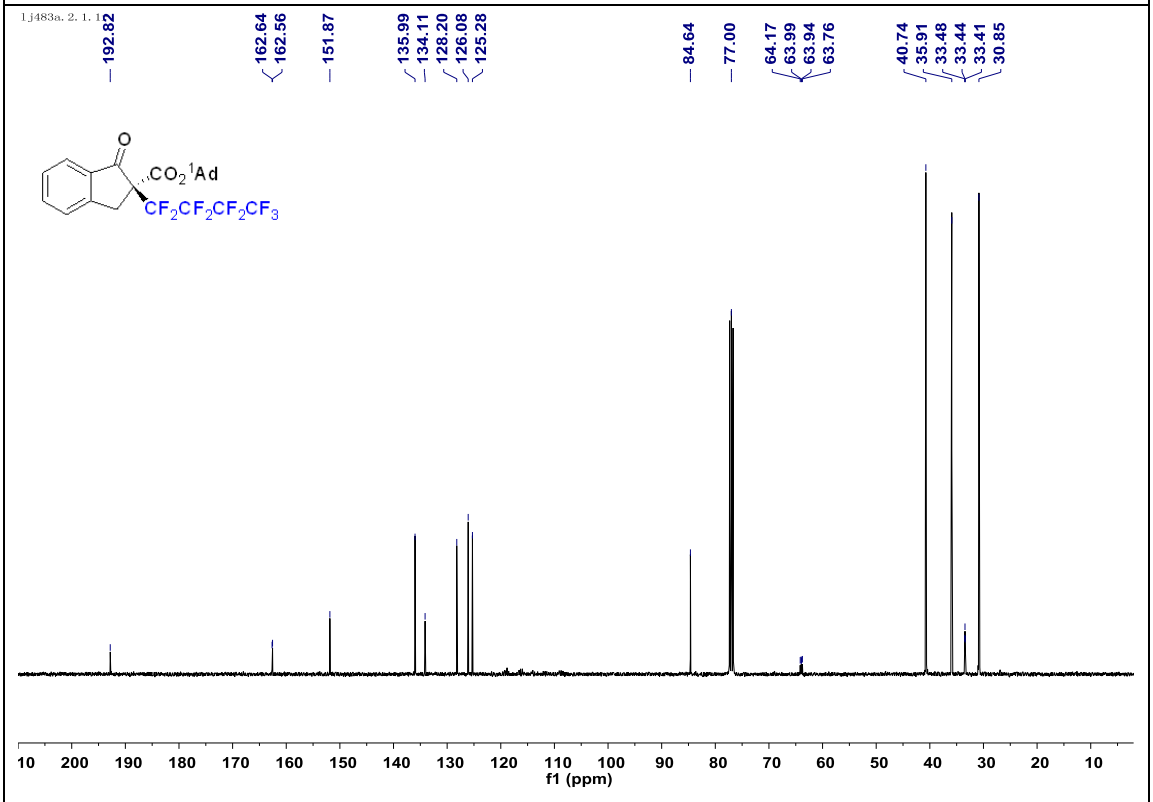
^{19}F NMR Spectrum of **3mc**



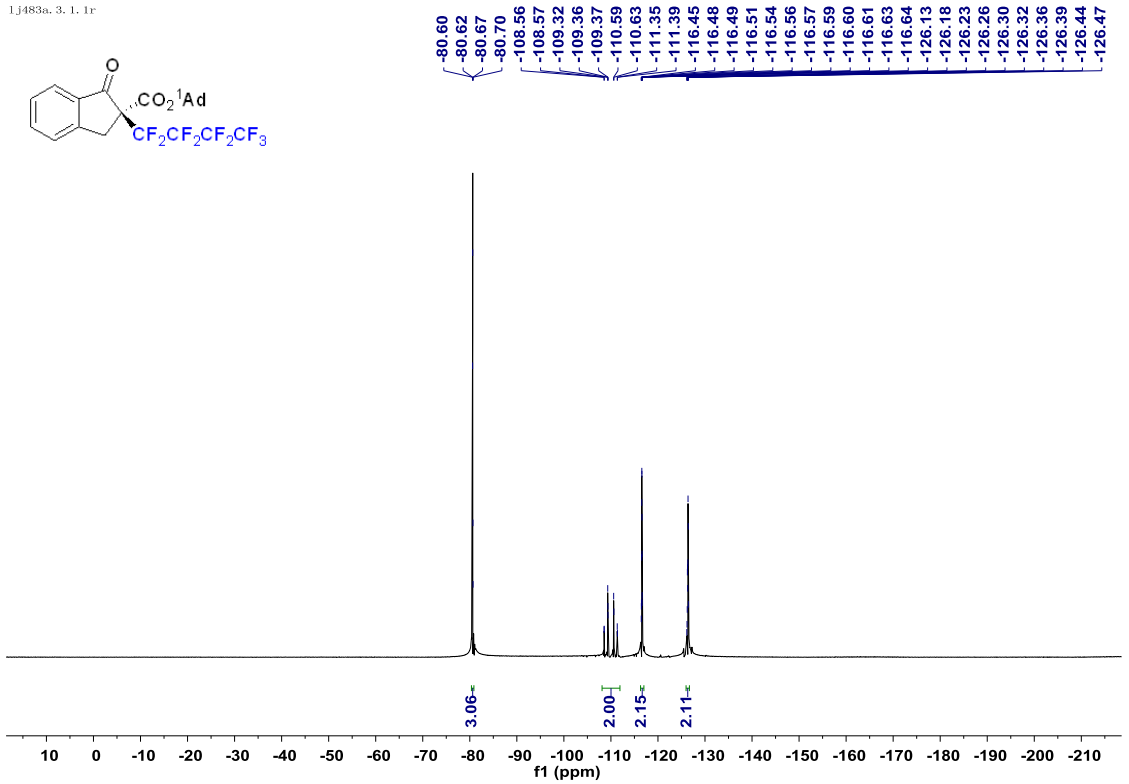
^{1}H NMR Spectrum of **3ad**



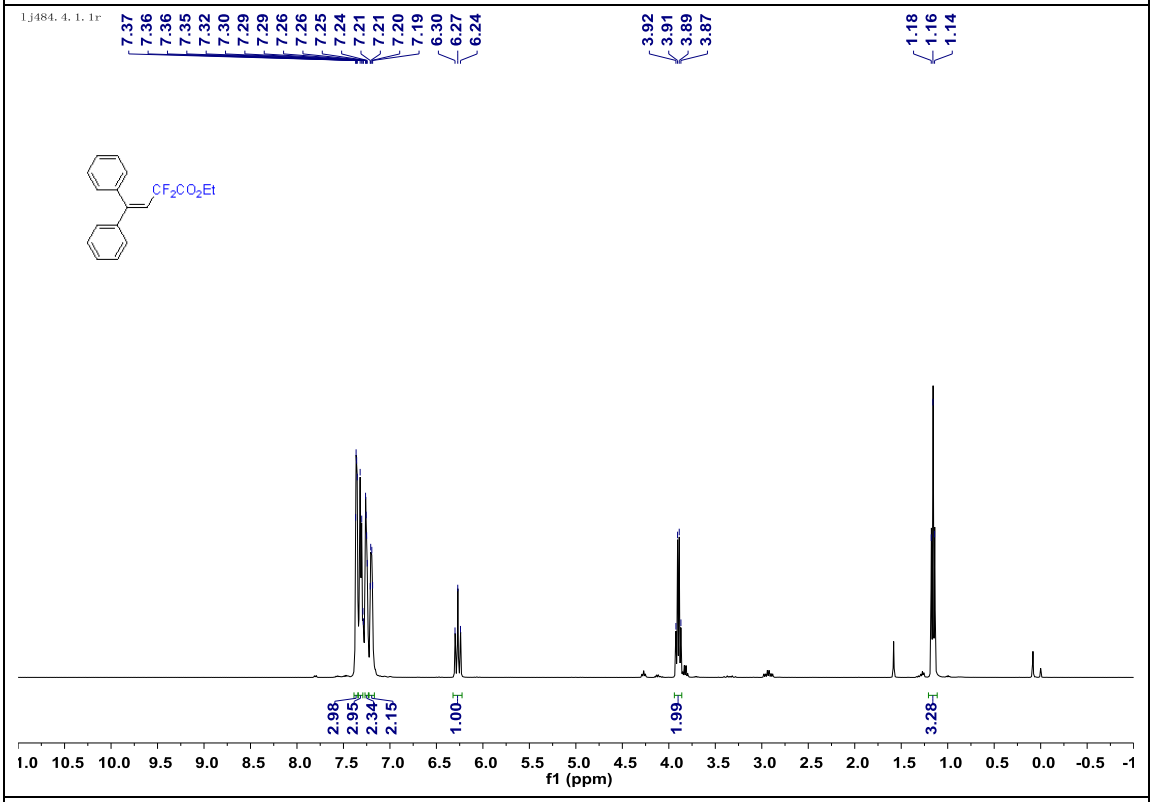
^{13}C NMR Spectrum of **3ad**



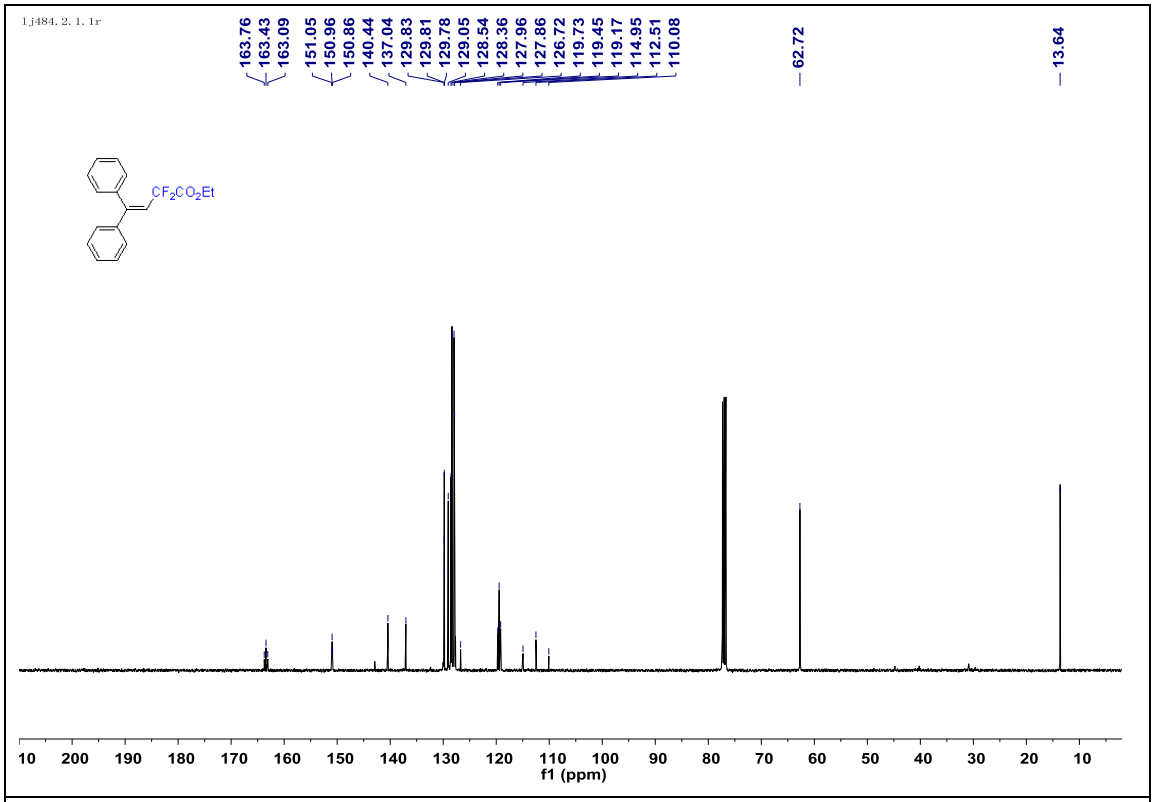
^{19}F NMR Spectrum of **3ad**



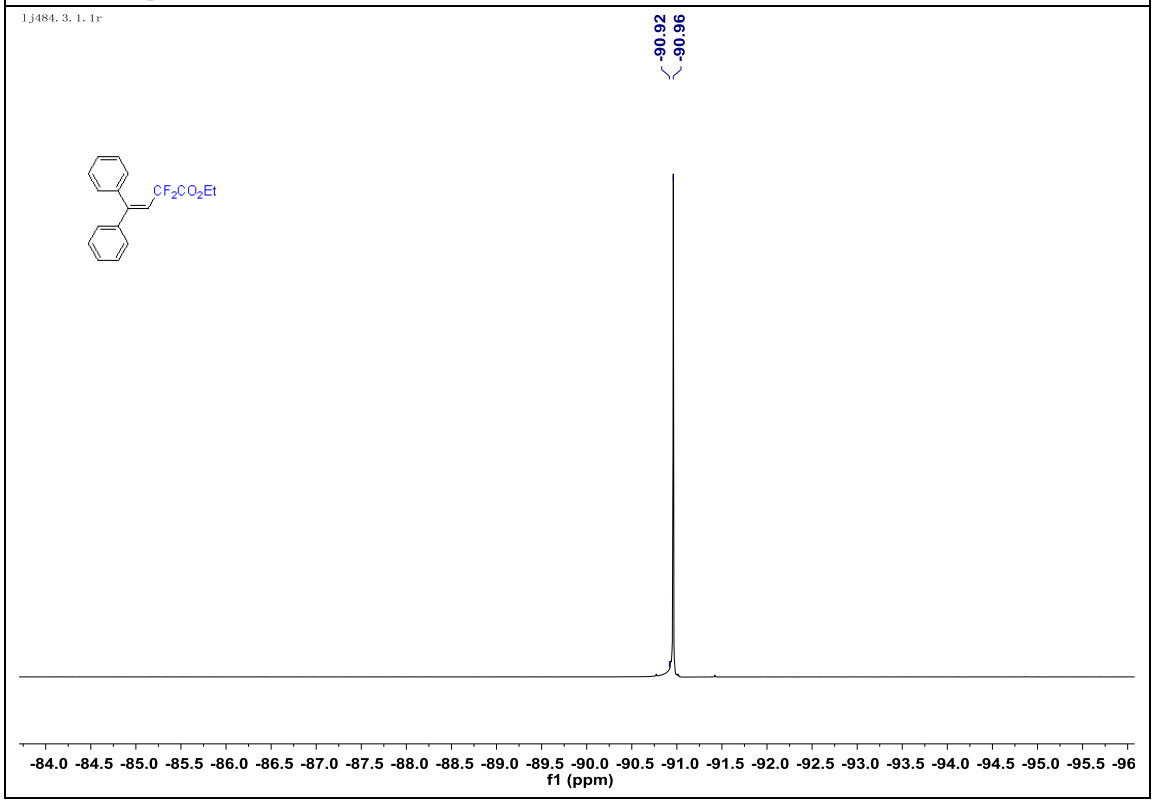
^{1}H NMR Spectrum of **7**



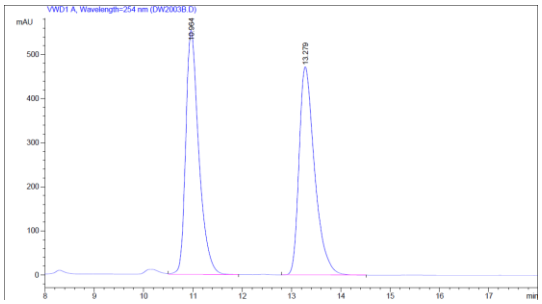
^{13}C NMR Spectrum of **7**

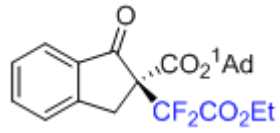


^{19}F NMR Spectrum of **7**



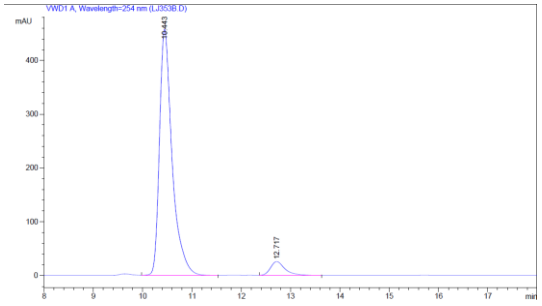
8. Copies of HPLC Chromatograms

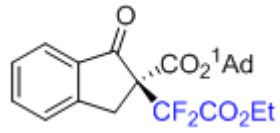




***rac*-3aa**

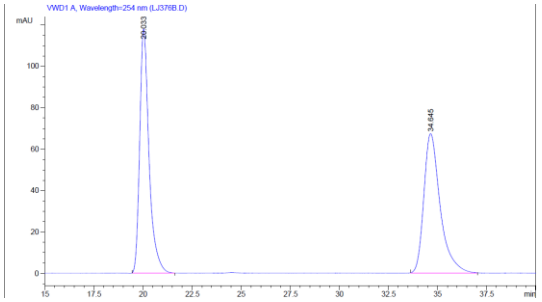
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.964	VB	0.2791	1.02071e4	553.65802	49.6403
2	13.279	VP	0.3379	1.03550e4	471.18463	50.3597

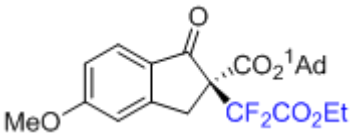




3aa

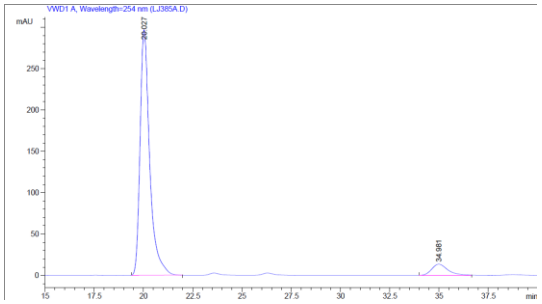
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.443	VB	0.2656	8128.45068	457.31543	93.9455
2	12.717	BB	0.3078	523.85248	25.68356	6.0545

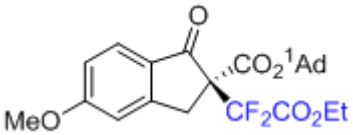




***rac*-3bb**

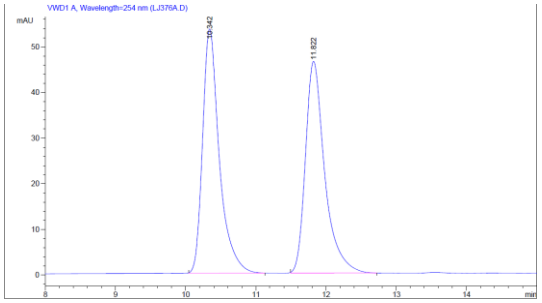
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.033	BB	0.4950	3881.54565	117.80931	49.9043
2	34.645	BB	0.8729	3896.43774	67.35812	50.0957

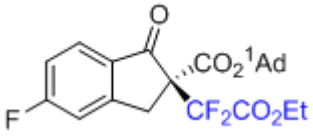




3bb

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.027	BB	0.5074	1.00938e4	296.83789	92.8132
2	34.981	BB	0.8697	781.58661	13.57632	7.1868





***rac*-3cb**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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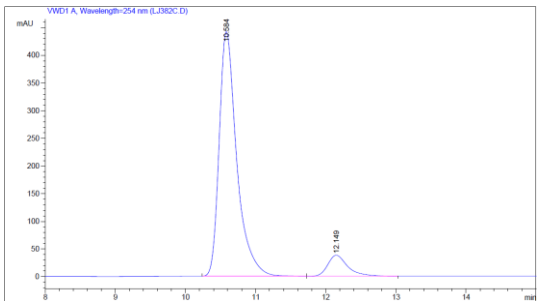
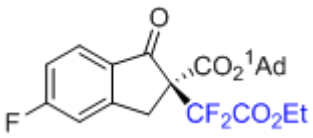
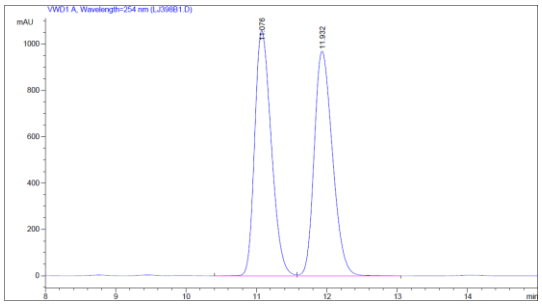
2	11.822	BB	0.2929	884.45184	46.27123	49.9683

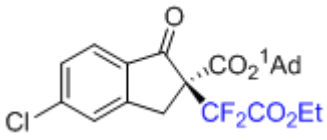




3cb

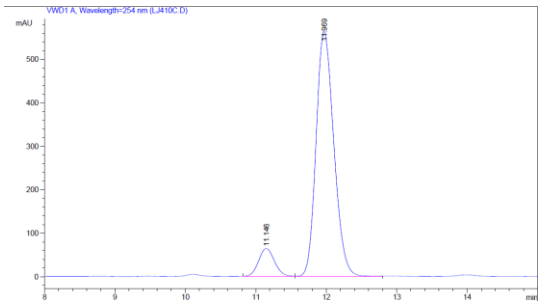
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.584	BV	0.2621	7704.36035	440.95801	91.0944
2	12.149	VB	0.3013	753.19745	37.96884	8.9056

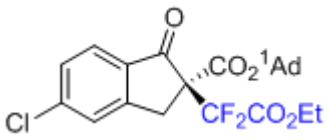




***rac*-3db**

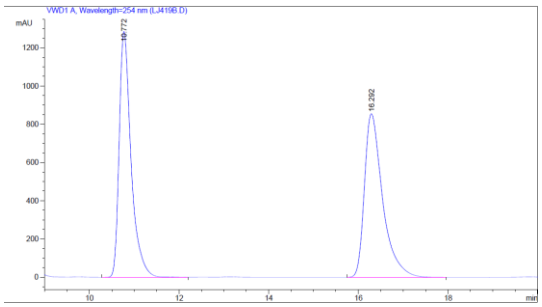
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.076	VV	0.2610	1.73226e4	1057.71582	49.7729
2	11.932	VB	0.2803	1.74807e4	969.20770	50.2271

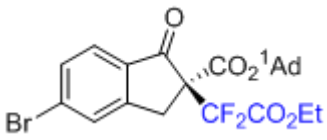




3db

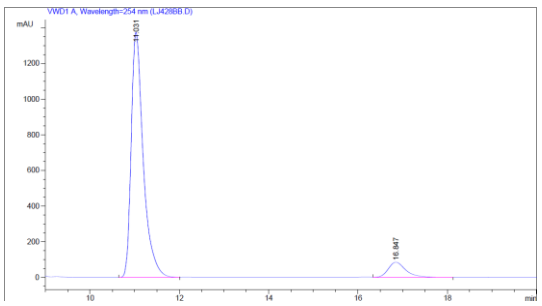
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.146	BV	0.2491	1021.91022	64.42532	9.3635
2	11.969	VB	0.2746	9891.86328	563.84686	90.6365

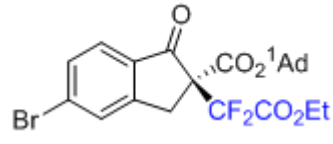




***rac*-3eb**

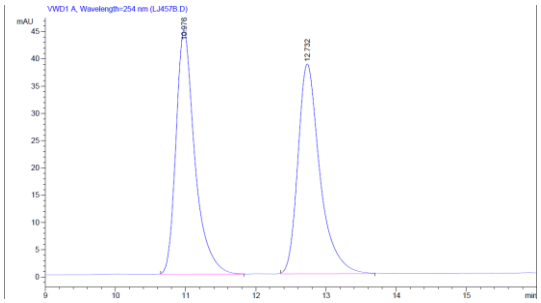
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.772	VB	0.2854	2.36455e4	1280.18530	49.6161
2	16.292	BB	0.4269	2.40114e4	854.40613	50.3839

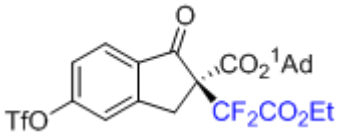




3eb

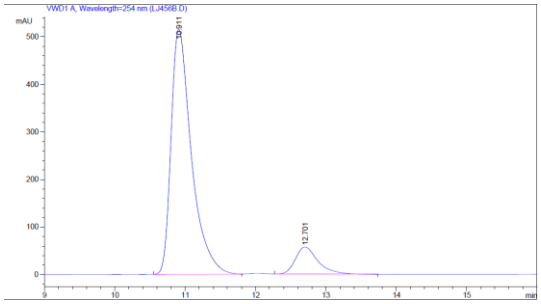
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.031	BV	0.2831	2.57598e4	1371.94080	91.5563
2	16.847	VB	0.4229	2375.67847	85.56526	8.4437

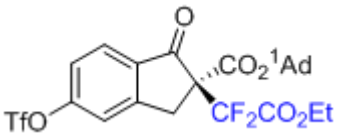




***rac*-3fb**

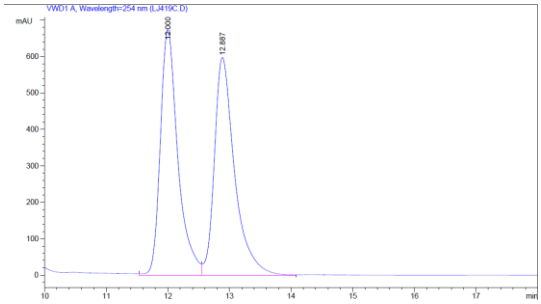
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.976	BB	0.2821	834.96301	44.67686	49.9336
2	12.732	BB	0.3297	837.18494	38.45078	50.0664

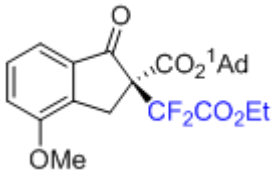




3fb

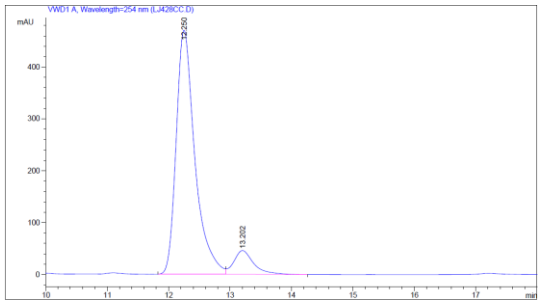
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.911	BV	0.3050	1.03567e4	513.98431	88.7560
2	12.701	VB	0.3473	1312.02539	57.58928	11.2440

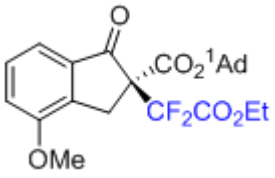




***rac*-3gb**

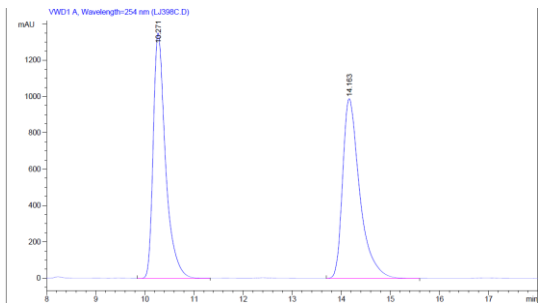
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.000	VV	0.3006	1.32957e4	672.37653	49.4399
2	12.887	VV	0.3469	1.35969e4	597.77112	50.5601

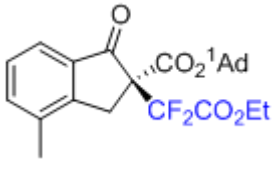




3gb

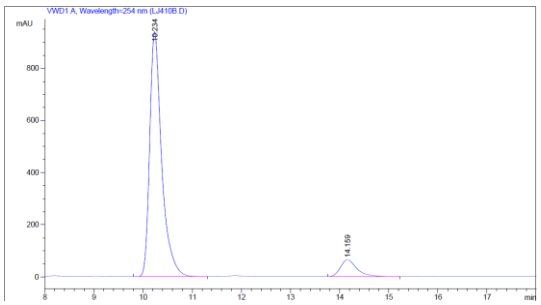
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.250	BV	0.3172	9952.52051	469.54657	90.5257
2	13.202	VP	0.3401	1041.61914	45.95703	9.4743

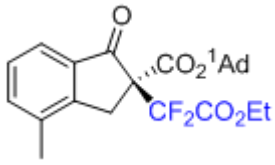




***rac*-3hb**

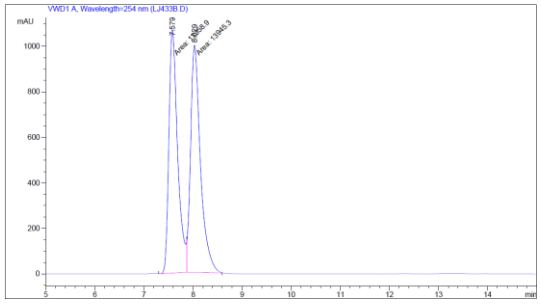
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.271	VB	0.2619	2.34806e4	1345.28186	49.6034
2	14.163	BB	0.3631	2.38561e4	988.64899	50.3966

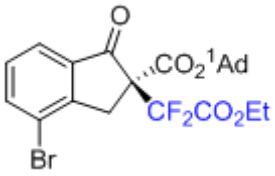




3hb

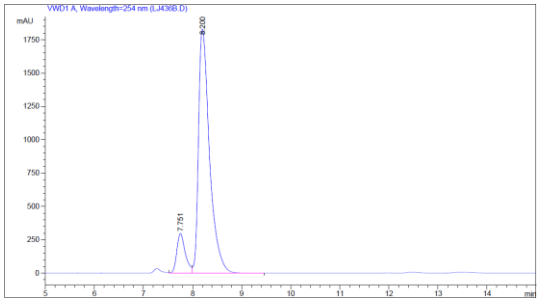
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.234	VB	0.2561	1.58865e4	936.82196	91.4235
2	14.159	BB	0.3519	1490.32129	64.30952	8.5765

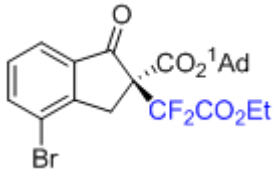




***rac*-3ib**

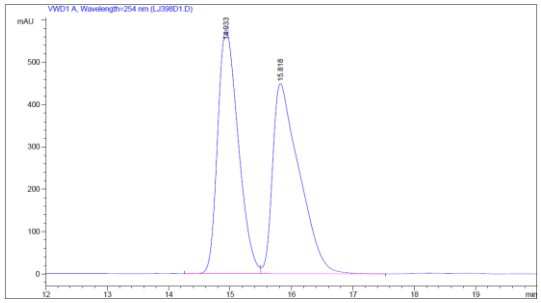
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.591	MM	0.2533	1.69746e4	1117.03027	48.1932
2	10.167	MM	0.2896	1.82474e4	1049.98059	51.8068

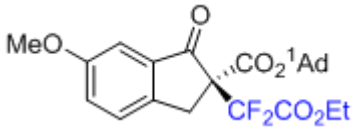




3ib

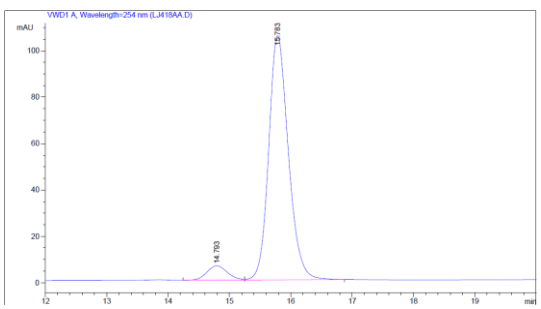
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.751	VV	0.1774	3570.13965	298.45621	11.1374
2	8.200	VB	0.2342	2.84854e4	1828.48145	88.8626

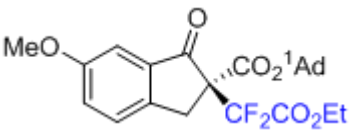




***rac*-3jb**

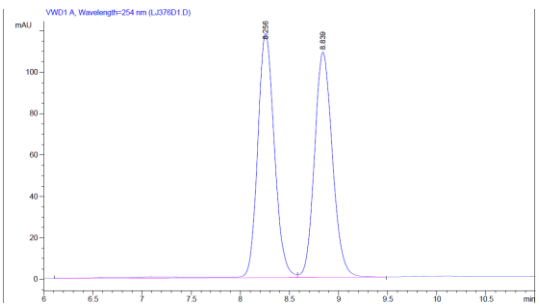
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.933	VV	0.3621	1.34293e4	576.34863	49.8337
2	15.818	VB	0.4235	1.35190e4	449.70761	50.1663

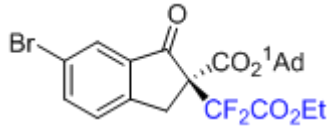




3jb

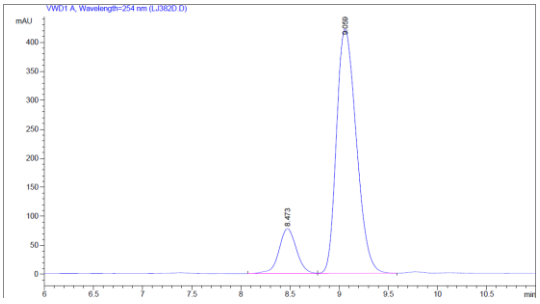
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.792	BV	0.3634	142.80342	6.16545	5.7410
2	15.784	VB	0.3416	2344.63135	105.17419	94.2590

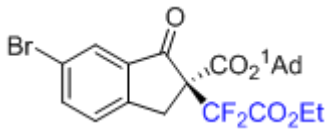




***rac*-3kb**

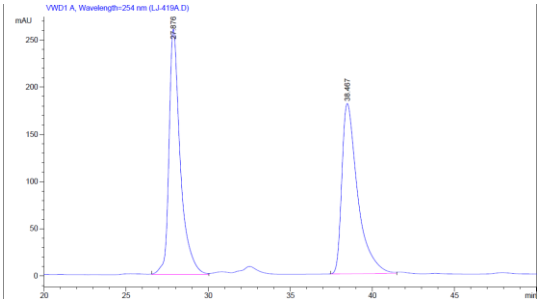
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.256	VV	0.1874	1422.71875	117.84182	50.6005
2	8.839	VB	0.1985	1388.95007	108.76660	49.3995

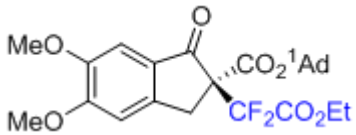




3kb

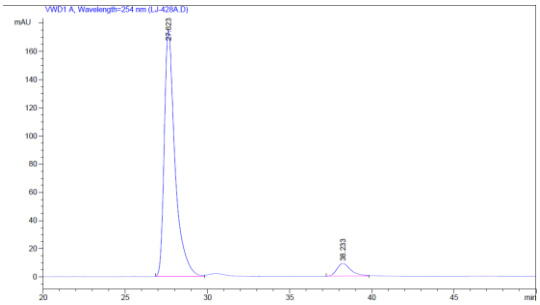
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.473	PV	0.1911	959.43988	77.45181	13.9276
2	9.059	VV	0.2223	5929.34375	421.63919	86.0724

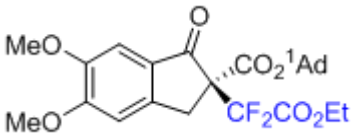




***rac*-3lb**

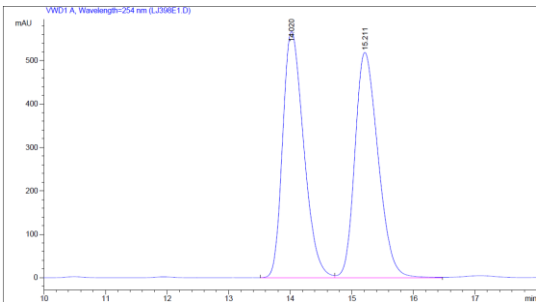
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.876	BV	0.7086	1.24119e4	259.89163	50.6953
2	38.467	BB	0.9958	1.20714e4	180.47589	49.3047

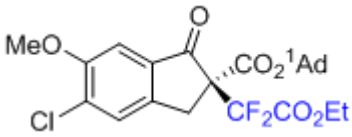




3lb

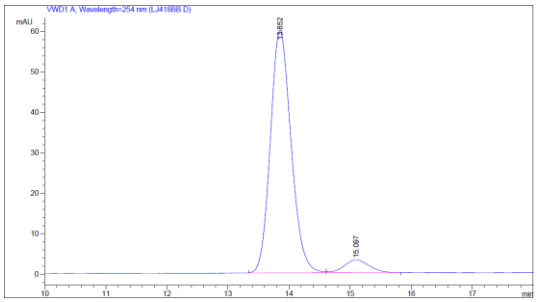
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.623	BB	0.6830	7947.24170	174.42465	93.6141
2	38.233	BB	0.8922	542.12451	9.11070	6.3859

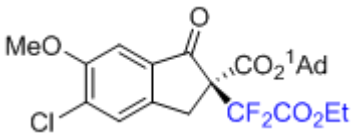




***rac*-3mb**

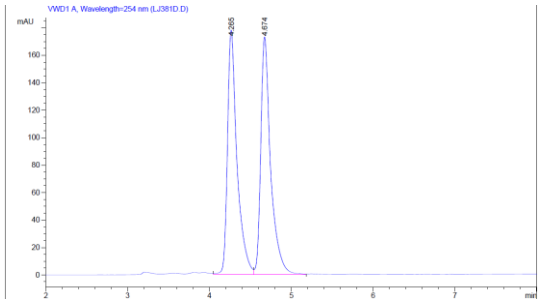
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.020	BV	0.3676	1.34737e4	566.72931	49.8340
2	15.211	VV	0.4070	1.35634e4	518.69470	50.1660

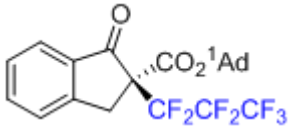




3mb

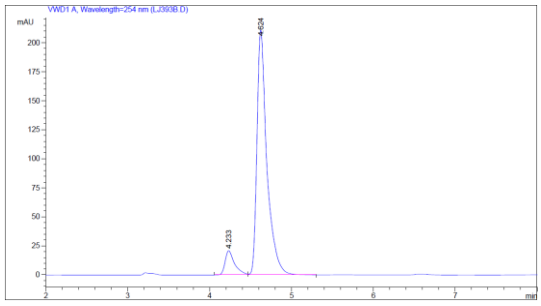
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.853	BV	0.3679	1414.48828	60.07917	93.7956
2	15.099	VB	0.4497	93.56579	3.21979	6.2044

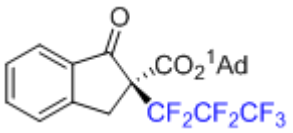




***rac*-3ac**

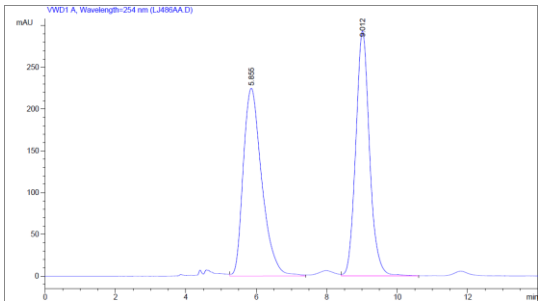
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.265	VV	0.1204	1438.44019	178.10608	49.7863
2	4.674	VV	0.1240	1450.78638	173.13431	50.2137

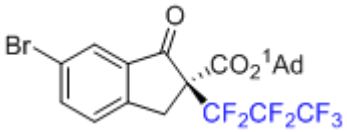




3ac

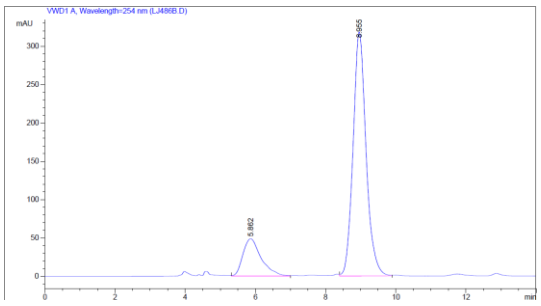
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.233	PV	0.1175	168.86789	20.90545	8.6909
2	4.624	VB	0.1244	1774.17126	210.86391	91.3091

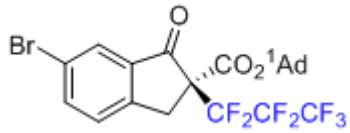




***rac*-3kc**

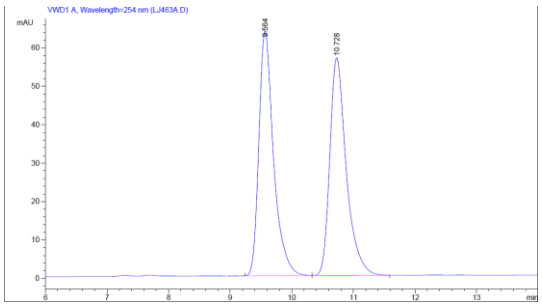
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.855	VV	0.5649	8255.19238	225.00983	50.8336
2	9.012	VB	0.4166	7984.43506	293.35037	49.1664

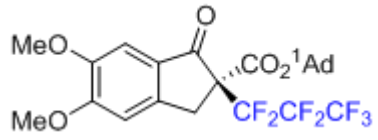




3kc

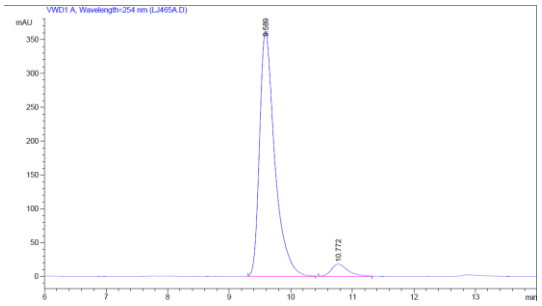
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.862	VV	0.5481	1771.61841	48.87857	17.7588
2	8.955	VV	0.3880	8204.35840	318.39313	82.2412

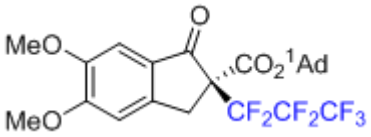




***rac*-3mc**

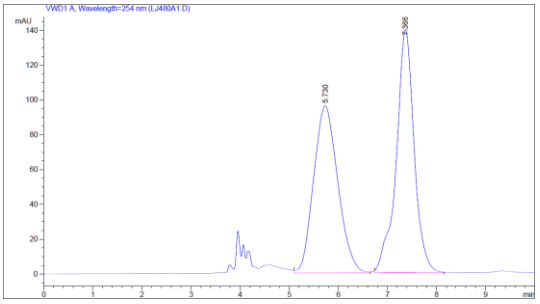
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.564	BV	0.2478	1050.81897	63.68043	49.9365
2	10.728	VB	0.2810	1053.48962	56.65486	50.0635

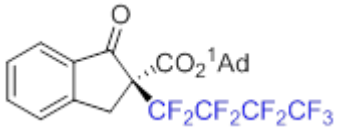




3mc

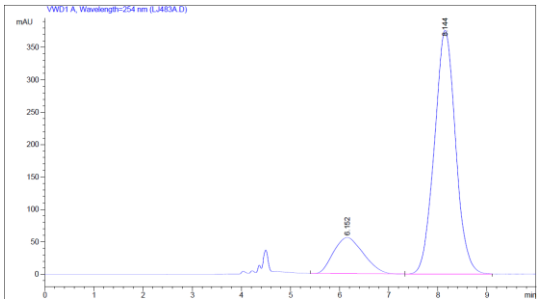
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.589	BB	0.2570	6184.65869	363.06027	94.7314
2	10.772	BB	0.2806	343.96533	18.28708	5.2686

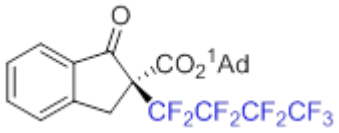




***rac*-3ad**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.730	BB	0.5352	3283.19556	96.15545	48.1943
2	7.366	BB	0.3763	3529.22095	139.67531	51.8057





3ad

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.152	PP	0.6914	2352.59619	55.96210	17.2747
2	8.144	VB	0.4574	1.12661e4	375.91452	82.7253

9. References

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