Supporting Information

Fast, solvent-free and highly enantioselective fluorination of β-keto esters catalyzed by chiral copper complexes in a ball mill

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1. General methods

Flash chromatography (FC) was carried out using silica gel (200-300 mesh). Monitoring of reactions was performed by TLC on silica gel precoated on glass plates, and spots were visualized with UV light at 254nm.^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker AVANCE III (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR and $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR; ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. HPLC experiments were carried out using a JASCO LC-2000 Plus system with MD-2010 HPLC diode array detector. Electrospray ionization (ESI) mass experiments were performed on a Thermo LCQ fleet. All experiments were carried out under air. Reactions in the ball mill were conducted using a Fritsch Planetary Micro Mill model "Pulverisette 7". The milling instrument consists of a main disk which can rotate at a speed of 100-800 rpm and accommodates two grinding bowls (45 mL). Both bowls and balls (2 mm diameter) are made of stainless steel. GC analyses were performed on Supelco β-*DEX* 120 (30 m) columns; carrier gas: N_2; flow rate, 1 ml min^{-1}; injector, 200°C; FID detector, air/H2 400/40 ml min-1, 250°C.

Ligands **II**, substrates **1** and **3** were synthesized according to the reported procedures.[1] Commercially available fluorination reagent (NFSI), ligands **I** , **7a-e** and solvents were used without further purification or drying. All reactions were carried out in oven-dried stainless steel milling vessel.

The absolute configurations of **2f**[2] and **4j**[3] were assigned by comparing the retention times of the HPLC analysis reported in the literature.

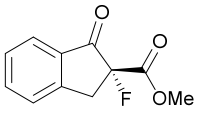
2. General procedure for the asymmetric fluorination of β-Ketoesters:

A clean, dry ball milling vessel was charged with 60 stainless steel grinding balls (2 mm diameter), the Lewis acid and the chiral ligands was grinded firstly for 5 minute to form the metal complexes, and then 1,3-dicarbonyl compounds **1a** (1 mol) and NFSI (1.2 equiv.) were added sequentially. After 4 min milling at 200 rpm and monitoring by TLC, the mixture was obtained by washing the vessel and the balls

with 3 × 30 mL ethyl acetate. The organic solution was concentrated and purified by Flash chromatography to afford the fluorinated product (gradient: pentane: ethyl acetate=5:1). The enantiomeric excess was determined by chiral-phase HPLC analysis.

3. Characterization results

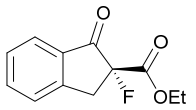
methyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2a**)



2a

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.53-7.46 (m, 2H), 3.82 (s, 3H), 3.81 (dd, *J* = 11.7, 17.7 Hz, 1H), 3.45 (dd, *J* = 23.3, 17.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.02 (d, J_{CF} = 18.2 Hz), 167.74 (d, J_{CF} = 27.9 Hz), 150.80 (d, J_{CF} = 3.6 Hz), 136.72, 133.32, 128.67, 126.61, 125.68, 94.64 (d, J_{CF} = 201.8 Hz), 53.17, 38.29 (d, J_{CF} = 24.0 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm) t_R = 11.2 min (major), t_R = 13.3 min (minor). MS (ES^+): m/z =209.15 ($[M+H]^+$)

ethyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2b**)

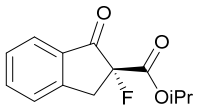


2b

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.77 (dd, *J* = 17.7, 11.6 Hz, 1H), 3.40 (dd, *J* = 23.4, 17.7 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.13 (d, J_{CF} = 18.1 Hz), 167.16 (d, J_{CF} = 27.8 Hz), 150.80 (d, J_{CF} = 3.5 Hz), 136.59, 133.19, 128.50, 126.54, 125.37, 94.42 (d, J_{CF} = 201.3 Hz), 62.38, 38.16 (d, J_{CF} = 23.9 Hz), 13.85. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 9.4 min (major), t_R = 10.9 min (minor). MS (ES^+): m/z

=223.04 ([M+H]$^+$)

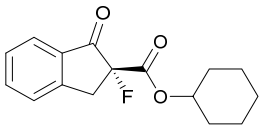
isopropyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2c**)



2c

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 5.13-5.18 (m, 1H), 3.77 (dd, *J* = 17.6, 11.8 Hz, 1H), 3.43 (dd, *J* = 23.3, 17.6 Hz, 1H), 1.25 (dd, *J* = 12.0, 6.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.29 (d, J_{CF} = 18.4 Hz), 166.88 (d, J_{CF} = 27.4 Hz), 150.92 (d, J_{CF} = 3.5 Hz), 136.55, 133.47, 128.56, 126.55, 125.57, 94.47 (d, J_{CF} = 201.7 Hz), 70.66, 38.30 (d, J_{CF} = 24.0 Hz), 21.51 (d, J_{CF} = 13.3 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, Hexane: iPrOH= 99: 1, flow rate 0.5ml/min, 254nm): t_R = 34.8 min (minor), t_R = 43.7 min (major). MS (ES$^+$): m/z =237.85 ([M+H]$^+$)

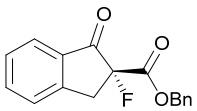
cyclohexyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2d**)



2d

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 4.94-4.89 (m, 1H), 3.76 (dd, *J* = 17.5, 10.9 Hz, 1H), 3.43 (dd, *J* = 22.9, 17.5 Hz, 1H), 1.76 (dd, *J* = 10.9, 7.9 Hz, 2H), 1.53 (dd, *J* = 14.0, 9.1 Hz, 2H), 1.47-1.38 (m, 3H), 1.36-1.28 (m, 2H), 1.24-1.18 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.33 (d, J_{CF} = 18.3 Hz), 166.60 (d, J_{CF} = 27.8 Hz), 150.79 (d, J_{CF} = 3.8 Hz), 136.49, 133.51, 128.51, 126.50, 125.42, 94.55 (d, J_{CF} = 201.7 Hz), 74.94, 38.34 (d, J_{CF} = 24.0 Hz), 31.00 (d, J_{CF} = 15.5 Hz), 25.09, 23.08 (d, J_{CF} = 6.0 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: iPrOH= 98: 2, flow rate 1.0ml/min, 254nm): t_R = 15.6 min (major), t_R = 17.4 min (minor). MS (ES$^+$): m/z =277.15 ([M+H]$^+$)

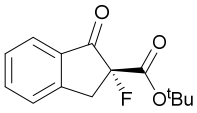
benzyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2e**)



2e

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.34 (d, *J* = 6.9 Hz, 3H), 5.27 (dd, *J* = 30.5 Hz, 12 Hz 2H), 3.79 (dd, *J* = 17.6, 11.5 Hz, 1H), 3.49-3.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.96 (d, J_{CF} = 17.5 Hz), 167.17 (d, J_{CF} = 28.0 Hz), 150.78 (d, J_{CF} = 3.8 Hz), 136.67, 135.80, 134.77, 133.41, 128.67, 128.65, 128.56, 128.02, 126.59, 125.70, 94.66 (d, J_{CF} = 202.4 Hz), 67.85, 38.29 (d, J_{CF} = 23.8 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 18.3 min (major), t_R = 24.1 min (minor). MS (ES^+): m/z =285.37 ($[M+H]^+$)

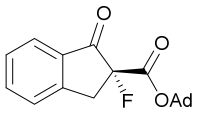
tert-butyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2f**)



2f

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 3.74 (dd, *J* = 17.5, 10.8 Hz, 1H), 3.41 (dd, *J* = 22.9, 17.5 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.70 (d, J_{CF} = 18.4 Hz), 166.26 (d, J_{CF} = 27.6 Hz), 150.94 (d, J_{CF} = 3.7 Hz), 136.39, 133.68, 128.46, 126.47, 125.43, 94.41 (d, J_{CF} = 201.9 Hz), 84.08, 38.37 (d, J_{CF} = 24.1 Hz), 27.85. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, Hexane: *i*PrOH= 99: 1, flow rate 0.5ml/min, 254nm): t_R = 29.0 min (minor), t_R = 40.6 min (major). MS (ES^+): m/z =272.95 ($[M+Na]^+$)

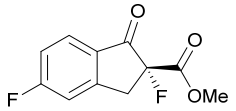
(3r)-adamantan-1-yl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2g**)



2g

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 3.74 (dd, *J* = 17.5, 10.5 Hz, 1H), 3.40 (dd, *J* = 22.8, 17.5 Hz, 1H), 2.15 (s, 3H), 2.05 (d, *J* = 2.9 Hz, 6H), 1.63 (t, *J* = 2.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.75 (d, J_{CF} = 18.4 Hz), 165.82 (d, J_{CF} = 27.8 Hz), 150.95 (d, J_{CF} = 3.9 Hz), 136.32, 133.75, 128.41, 126.44, 125.39, 94.34 (d, J_{CF} = 201.9 Hz), 84.10, 41.12, 38.47 (d, J_{CF} = 24.2 Hz), 35.95, 30.93. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 7.6 min (major), t_R = 10.5 min (minor). MS (ES^+): m/z =329.17 ($[M+H]^+$)

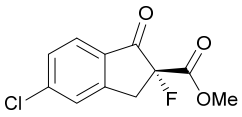
methyl (*R*)-2,5-difluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2h**)



2h

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.75 (m, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 13.2, 5.3 Hz, 1H), 3.83 (s, 3H), 3.81 (dd, *J* = 17.8, 10.9 Hz, 1H), 3.44 (dd, *J* = 22.9, 17.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.08 (d, J_{CF} = 18.3 Hz), 169.23, 167.53, 167.23 (d, J_{CF} = 17.9 Hz), 153.79 (dd, J_{CF} = 10.6, 3.8 Hz), 128.18 (d, J_{CF} = 10.7 Hz), 117.17 (d, J_{CF} = 23.9 Hz), 113.54 (d, J_{CF} = 23.0 Hz), 94.61 (d, J_{CF} = 202.6 Hz), 53.26, 38.11 (dd, J_{CF} = 24.3, 1.9 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 14.9 min (major), t_R= 18.3 min (minor). MS (ES^+): m/z =227.04 ($[M+H]^+$)

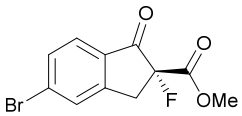
methyl (*R*)-5-chloro-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2i**)



2i

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.52 (s, 1H), 7.47-7.45 (m, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 17.9, 11.1 Hz, 1H), 3.43 (dd, *J* = 22.9, 17.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.58 (d, J_{CF} = 18.4 Hz), 167.36 (d, J_{CF} = 27.7 Hz), 152.13 (d, J_{CF} = 3.8 Hz), 143.52, 131.73, 129.60, 126.90, 126.72, 94.53 (d, J_{CF} = 202.9 Hz), 53.30, 37.98 (d, J_{CF} = 24.3 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 99: 1, flow rate 1.0ml/min, 254nm): t_R = 35.2 min (major), t_R = 49.9 min (minor). MS (ES^+): m/z =243.75 ($[M+H]^+$)

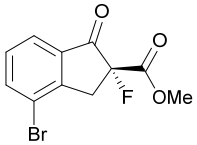
methyl (*R*)-5-bromo-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2j**)



2j

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.62 (dd, *J* = 8.2, 0.7 Hz, 1H), 3.82 (s, 3H), 3.78 (dd, *J* = 10.5, 17.5 Hz 1H), 3.43 (dd, *J* = 22.9, 17.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.82 (d, J_{CF} = 18.3 Hz), 167.28 (d, J_{CF} = 27.8 Hz), 152.15 (d, J_{CF} = 3.7 Hz), 132.42, 132.38, 132.08, 129.97, 126.68, 94.41 (d, J_{CF} = 202.9 Hz), 53.28, 37.86 (d, J_{CF} = 24.2 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 36.9 min (major), t_R = 50.9 min (minor). MS (ES^+): m/z =287.45 ($[M+H]^+$)

methyl (*R*)-4-bromo-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2k**)

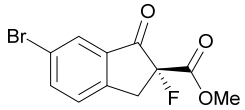


2k

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.6

Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 3.84 (s, 3H), 3.75 (dd, J = 18.1, 11.6 Hz, 1H), 3.38 (dd, J = 23.2, 18.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.48 (d, J_{CF} = 18.5 Hz), 167.27 (d, J_{CF} = 27.8 Hz), 150.65 (d, J_{CF}= 3.7 Hz), 139.39, 135.15, 130.37, 124.39, 121.86, 94.07 (d, J_{CF} = 202.7 Hz), 53.38, 39.32 (d, J_{CF} = 24.8 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 17.0 min (major), t_R = 20.1 min (minor). MS (ES^+): m/z =287.49 ($[M+H]^+$)

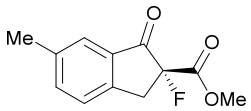
methyl (*R*)-6-bromo-2-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2l**)



2l

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 3.83 (s, 3H), 3.74 (dd, J = 18.1, 11.6 Hz, 1H), 3.37 (dd, J = 23.2, 18.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.39 (d, J_{CF} = 18.3 Hz), 167.24 (d, J_{CF} = 27.8 Hz), 150.60 (d, J_{CF} = 3.8 Hz), 139.34, 135.19, 130.35, 124.34, 121.85, 94.07 (d, J_{CF} = 202.7 Hz), 53.29, 39.32 (d, J_{CF} = 24.8 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 11.9 min (major), t_R = 14.5 min (minor). MS (ES^+): m/z =287.46 ($[M+H]^+$)

methyl (*R*)-2-fluoro-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2m**)

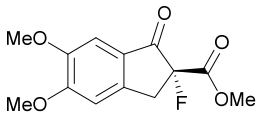


2m

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.52 (dd, J = 7.9, 1.1 Hz, 1H), 7.39 (d, J = 7.9 Hz, 1H), 3.79 (s, 3H), 3.74 (dd, J = 17.5, 11.1 Hz, 1H), 3.37 (dd, J = 23.3, 17.5 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.03 (d, J_{CF} = 18.2 Hz), 167.75 (d, J_{CF} = 28.0 Hz), 148.19 (d, J_{CF} = 3.7 Hz), 138.80, 137.98, 133.36, 126.24, 125.36, 94.94 (d, J_{CF} = 201.4 Hz), 53.02, 37.89 (d, J_{CF} = 23.8 Hz), 20.95. The

enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 9.3 min (major), t_R = 10.7 min (minor). MS (ES^+): m/z =223.20 ($[M+H]^+$)

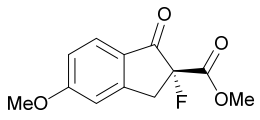
methyl (*R*)-2-fluoro-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2n**)



2n

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (s, 1H), 6.89 (s, 1H), 3.98 (s, 3H), 3.89 (s, 3H), 3.79 (s, 3H), 3.69 (dd, *J* = 17.4, 10.4 Hz, 1H), 3.32 (dd, *J* = 22.5, 17.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.25 (d, J_{CF} = 18.5 Hz), 167.97 (d, J_{CF} = 28.1 Hz), 157.27, 150.39, 146.79 (d, J_{CF} = 4.1 Hz), 125.95, 107.36, 105.49, 95.05 (d, J_{CF} = 201.2 Hz), 56.41, 56.13, 53.04, 37.92 (d, J_{CF} = 24.1 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 44.7 min (major), t_R = 59.6 min (minor). MS (ES^+): m/z =269.21 ($[M+H]^+$)

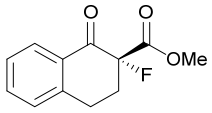
methyl (*R*)-2-fluoro-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2o**)



2o

Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.92 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.74 (dd, *J* = 17.6, 11.1 Hz, 1H), 3.36 (dd, *J* = 23.1, 17.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.82 (d, *J* = 18.3 Hz), 168.03, 166.92, 153.94 (d, *J* = 3.8 Hz), 127.41, 126.30, 116.73, 109.81, 95.04 (d, *J* = 201.1 Hz), 55.87, 53.05, 38.21 (d, *J* = 24.1 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 21.3 min (major), t_R = 24.9 min (minor). MS (ES^+): m/z =239.08 ($[M+H]^+$)

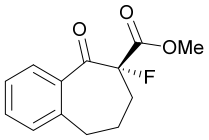
methyl (*R*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2p**)



2p

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 7.9 Hz, 1H), 7.56-7.53 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 3.82 (s, 3H), 3.22-3.14 (m, 1H), 3.10-3.04 (m, 1H), 2.77-2.67 (m, 1H), 2.58-2.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.40 (d, J_{CF} = 18.7 Hz), 167.76 (d, J_{CF} = 26.1 Hz), 143.12, 134.55, 130.46, 128.74, 128.38, 127.22, 93.25 (d, J_{CF} = 194.0 Hz), 52.90, 31.84 (d, J_{CF} = 22.2 Hz), 24.77 (d, J_{CF} = 7.3 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 12.4 min (major), t_R = 13.7 min (minor). MS (ES^+): m/z =223.25 ($[M+H]^+$)

methyl (*R*)-6-fluoro-5-oxo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate (**2q**)

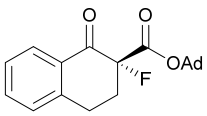


2q

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.7, 1.2 Hz, 1H), 7.43 (td, J = 7.5, 1.3 Hz, 1H), 7.30 (dd, J = 14.3, 7.0 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.14-3.07 (m, 1H), 2.96-2.90 (m, 1H), 2.68-2.56 (m, 1H), 2.33-2.24 (m, 1H), 2.18-2.10 (m, 1H), 1.95-1.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.59 (d, J_{CF} = 26.7 Hz), 167.60 (d, J_{CF} = 25.2 Hz), 140.60, 136.44, 132.26, 129.54, 129.26, 126.62, 99.10 (d, J_{CF} = 195.9 Hz), 52.93, 33.40 (d, J_{CF} = 1.3 Hz), 32.66 (d, J_{CF} = 21.25 Hz), 22.38 (d, J_{CF} = 2.1 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 12.2 min (minor), t_R = 13.6 min (major). MS (ES^+): m/z =237.15 ($[M+H]^+$)

(3r)-adamantan-1-yl (*R*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate

(**2r**)

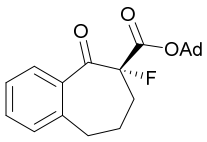


2r

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 3.19-3.04 (m, 2H), 2.72-2.63 (m, 1H), 2.53-2.43 (m, 1H), 2.13 (s, 3H), 2.04 (d, *J* = 2.8 Hz, 6H), 1.61 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.25 (d, J_{CF} = 18.4 Hz), 165.72 (d, J_{CF} = 26.4 Hz), 142.84, 134.14, 131.14, 128.59, 128.03 (d, J_{CF} = 0.8 Hz), 127.04, 93.03 (d, J_{CF} = 194.0 Hz), 83.96, 41.02, 35.86, 31.97 (d, J_{CF} = 22.3 Hz), 30.81, 25.29 (d, J_{CF} = 8.1 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 7.8 min (major), t_R = 13.1 min (minor). MS (ES^+): m/z =343.20 ($[M+H]^+$)

(3r)-adamantan-1-yl

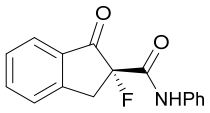
(*R*)-6-fluoro-5-oxo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate (**2s**)



2s

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.43 (td, *J* = 7.5, 1.3 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 3.09-3.03 (m, 1H), 2.96-2.91 (m, 1H), 2.69-2.47 (m, 2H), 2.23 (d, *J* = 3.9 Hz, 2H), 2.16 (s, 3H), 2.06 (dd, *J* = 5.0, 3.1 Hz, 6H), 1.65 (t, *J* = 2.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.21 (d, J_{CF} = 24.1 Hz), 165.64 (d, J_{CF} = 25.1 Hz), 140.06, 137.30, 132.04, 129.46, 129.21, 126.61, 98.32 (d, J_{CF} = 195.0 Hz), 83.67, 41.02, 36.03, 33.29, 32.62 (d, J_{CF} = 22.4 Hz), 30.92, 22.29 (d, J_{CF} = 3.9 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 11.9 min (minor), t_R = 14.3 min (major). MS (ES^+): m/z =357.25 ($[M+H]^+$)

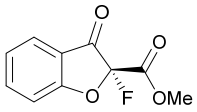
(*R*)-2-fluoro-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (**2t**)



2t

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.08 (dd, *J* = 17.4, 11.3 Hz, 1H), 3.42 (dd, *J* = 24.0, 17.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.30 (d, J_{CF} = 18.1 Hz), 164.75 (d, J_{CF} = 21.8 Hz), 151.83 (d, J_{CF} = 4.0 Hz), 136.84, 136.63, 133.25, 129.11, 128.54, 126.56, 125.58, 125.22, 120.13, 97.03 (d, J_{CF} = 204.7 Hz), 37.39 (d, J_{CF} = 22.6 Hz). The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 90: 10, flow rate 1.0ml/min, 254nm): t_R = 17.3 min (major), t_R = 25.0 min (minor). MS (ES^+): m/z =270.16 ($[M+H]^+$)

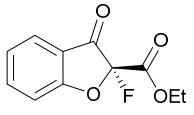
methyl (*R*)-2-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5a**)



5a

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.72 (m, 2H), 7.30-7.20 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.63 (d, J_{CF} = 18.1 Hz), 171.14 (d, J_{CF}= 1.2 Hz), 162.64 (d, J_{CF} = 36.7 Hz), 139.70, 125.88, 124.47, 117.46, 113.61, 103.36 (d, J_{CF} = 249.3 Hz), 53.81. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, column at Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =18.3 min (minor), t_R = 20.7. min (major). MS (ES^+): m/z =211.15 ($[M+H]^+$)

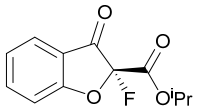
ethyl (*R*)-2-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5b**)



5b

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.72 (m, 2H), 7.28-7.21 (m, 2H), 4.35 (dd, J = 7.1, 3.9 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.83 (d, J_{CF} = 18.2 Hz), 171.20 (d, J_{CF} = 1.3 Hz), 162.22 (d, J_{CF} = 36.4 Hz), 139.66, 125.83, 124.40, 117.46, 113.58, 103.28 (d, J_{CF} = 249.5 Hz), 63.51, 13.87. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =15.6 min (minor), t_R =18.8 min (major). MS (ES^+): m/z =225.05 ($[M+H]^+$)

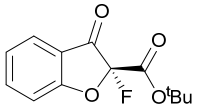
isopropyl (*R*)-2-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5c**)



5c

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.72 (m, 2H), 7.28-7.22 (m, 2H), 5.24-5.16 (m, 1H), 1.30 (t, J = 5.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.98 (d, J_{CF} = 18.4 Hz), 171.27 (d, J_{CF} = 1.4 Hz), 161.80 (d, J_{CF} = 35.9 Hz), 139.57, 125.83, 124.33, 117.54, 113.58, 103.24 (d, J_{CF} = 249.9 Hz), 72.03, 21.45. The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 95:5, flow rate 1.0 mL/min, 254nm): t_R =8.7 (minor), t_R = 9.1 min (major). MS (ES^+): m/z =239.08 ($[M+H]^+$)

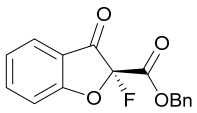
tert-butyl (*R*)-2-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5d**)



5d

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.70 (m, 2H), 7.25-7.19 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.32 (d, J_{CF} = 18.4 Hz), 171.27 (d, J_{CF} = 1.6 Hz), 161.08 (d, J_{CF} = 35.9 Hz), 139.42, 125.66, 124.18, 117.64, 113.48, 103.19 (d, J_{CF} = 250.4 Hz), 85.60, 27.70. The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =5.6 min (minor), t_R =5.9 min (major). MS (ES^+): m/z =253.15 ($[M+H]^+$)

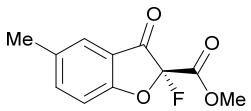
benzyl (*R*)-2-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5e**)



5e

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.39-7.35 (m, 3H), 7.34-7.31 (m, 2H), 7.28-7.21 (m, 2H), 5.33 (d, J = 3.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.65 (d, J_{CF} = 18.3 Hz), 171.19 (d, J_{CF} = 1.5 Hz), 162.18 (d, J_{CF} = 36.6 Hz), 139.69, 134.07, 128.76, 128.68, 128.16, 125.91, 124.46, 117.47, 113.60, 103.35 (d, J_{CF} = 250.1 Hz), 68.70. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 99:1, flow rate 1.0 mL/min, 254nm): t_R =12.0 min (major), t_R =13.3 min (minor). MS (ES^+): m/z =287.07 ($[M+H]^+$)

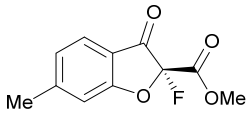
methyl (*R*)-2-fluoro-5-methyl-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5f**)



5f

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, J = 8.5, 1.9 Hz, 1H), 7.50 (s, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.68 (d, J_{CF} = 18.2 Hz), 169.56 (d, J_{CF} = 1.2 Hz), 162.72 (d, J_{CF} = 37.3 Hz), 140.80, 134.45, 125.23, 117.29, 113.12, 103.66 (d, J_{CF} = 248.5 Hz), 53.69, 20.52. The enantiomeric excess was determined by HPLC (Daicel ChiralpakOJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =15.3 min (minor), t_R = 19.7 min (major). MS (ES^+): m/z =225.17 ($[M+H]^+$)

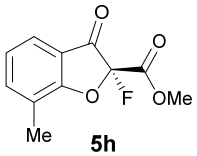
methyl (*R*)-2-fluoro-6-methyl-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5g**)



5g

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H), 7.02 (s, 1H), 3.88 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.90 (d, J_{CF} = 18.4 Hz), 171.66 (d, J_{CF} = 1.4 Hz), 162.79 (d, J_{CF} = 37.0 Hz), 152.53, 125.84, 125.49, 115.09, 113.74, 103.83 (d, J_{CF}=249.0 Hz), 53.75, 22.78. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =17.1 min (minor), t_R =24.3 min (major). MS (ES^+): m/z =225.15 ($[M+H]^+$)

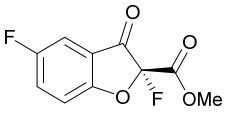
methyl (*R*)-2-fluoro-7-methyl-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5h**)



5h

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.15 (t, J = 7.5 Hz, 1H), 3.89 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.18 (d, J_{CF} = 18.1 Hz), 169.85 (d, J_{CF} = 1.6 Hz), 162.86 (d, J_{CF} = 37.0 Hz), 140.58, 124.28, 123.91, 123.04, 116.94, 103.36 (d, J = 248.6 Hz), 53.76, 13.99. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 95:5, flow rate 1.0 mL/min, 254nm): t_R=11.5 min (major), t_R = 12.0 min (minor). MS (ES^+): m/z =225.16 ($[M+H]^+$)

methyl (*R*)-2-fluoro-5-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5i**)

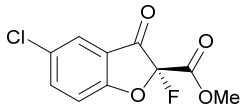


5i

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.45 (m, 1H), 7.39 (dd, J = 6.3, 2.8 Hz, 1H), 7.22 (dd, J = 9.0, 3.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.15 (dd, J_{CF} = 18.4, 3.0 Hz), 167.20, 162.27 (d, J_{CF} = 36.7 Hz), 158.99 (d, J_{CF} =

245 Hz), 127.16 (d, J_{CF} = 25.7 Hz), 118.18 (d, J_{CF} = 8.3 Hz), 114.92 (d, J_{CF} = 7.8 Hz), 111.25 (d, J_{CF} = 24.8 Hz), 104.07 (d, J_{CF} = 250.3 Hz), 53.92. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 99:1, flow rate 1.0 mL/min, 254nm): t_R =36.5 min (major). MS (ES^+): m/z =251.03 ($[M+Na]^+$)

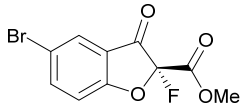
methyl (*R*)-2-fluoro-5-chloro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5j**)



5j

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.67 (m, 2H), 7.20 (d, *J* = 9.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.49 (d, J_{CF} = 18.4 Hz), 169.38 (d, J_{CF} = 1.4 Hz), 162.14 (d, J_{CF} = 36.6 Hz), 139.44, 130.14, 125.18, 118.63, 114.95, 103.74 (d, J_{CF} = 250.9 Hz), 53.93. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R = 7.6 min (major), t_R = 8.9 min (minor). MS (ES^+): m/z =245.04 ($[M+H]^+$)

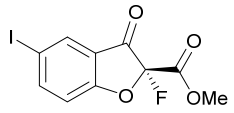
methyl (*R*)-2-fluoro-5-bromo-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5k**)



5k

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.31 (d, J_{CF} = 18.1 Hz), 169.85 (d, J_{CF} = 1.2 Hz), 162.14 (d, J_{CF} = 36.6 Hz), 142.18, 128.34, 119.17, 117.12, 115.35, 103.58 (d, J_{CF} = 251.2 Hz), 53.97. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =17.6 min (major), t_R = 19.3 min (minor). MS (ES^+): m/z =288.95 ($[M+H]^+$)

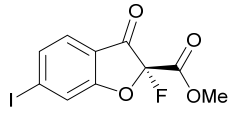
methyl (*R*)-2-fluoro-5-iodo-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5l**)



5l

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 1.8 Hz, 1H), 8.00 (dd, J = 8.7, 1.9 Hz, 1H), 7.05 (d, J = 8.6 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.02 (d, J_{CF} = 18.3 Hz), 170.56 (d, J_{CF} = 1.1 Hz), 162.14 (d, J_{CF} = 36.5 Hz), 147.83, 134.42, 119.71, 115.75, 103.24 (d, J_{CF} = 251.0 Hz), 86.71, 53.96. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =21.3 min (major), t_R = 27.1 min (minor). MS (ES^+): m/z =336.93 ($[M+H]^+$)

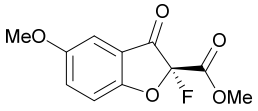
methyl (*R*)-2-fluoro-6-iodo-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5m**)



5m

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 1.1 Hz, 1H), 7.63 (dd, J = 8.0, 1.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.64 (d, J_{CF} = 18.2 Hz), 170.50 (d, J_{CF} = 1.1 Hz), 162.12 (d, J_{CF} = 36.7 Hz), 134.18, 126.27, 123.22, 116.95, 107.82, 103.34 (d, J_{CF} = 251.1 Hz), 53.91. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =17.2 min (minor), t_R = 28.8 min (major). MS (ES^+): m/z =337.03 ($[M+H]^+$)

methyl (*R*)-2-fluoro-5-methoxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5n**)

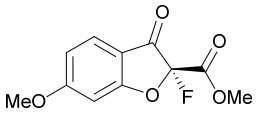


5n

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 9.0, 2.8 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 2.8 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.87 (d, J_{CF} = 18.1 Hz), 166.28 (d, J_{CF} = 1.7 Hz), 162.65 (d, J_{CF} = 37.4

Hz), 156.57, 128.92, 117.51, 114.39, 105.94, 104.06 (d, J_{CF} = 248.5 Hz), 55.98, 53.72. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =27.4 min (minor), t_R = 30.7 min (major). MS (ES^+): m/z =263.04 ($[M+Na]^+$)

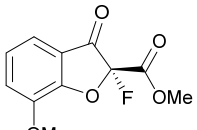
methyl (*R*)-2-fluoro-6-methoxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5o**)



5o

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 187.07 (d, J_{CF} = 18.0 Hz), 173.82, 169.60, 162.84 (d, J_{CF} = 36.9 Hz), 127.07, 113.34, 110.34, 104.46 (d, J_{CF} = 249.6 Hz), 97.21, 56.31, 53.76. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =28.9 min (minor), t_R = 41.3 min (major). MS (ES^+): m/z =263.05 ($[M+Na]^+$)

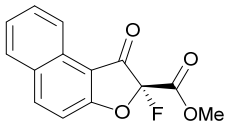
methyl (*R*)- 2-fluoro-7-methoxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (**5p**)



5p

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.81 (d, J_{CF} = 18.0 Hz), 162.43 (d, J_{CF} = 36.9 Hz), 160.79 (d, J_{CF} = 1.7 Hz), 146.16, 125.09, 121.24, 118.57, 116.59, 103.36 (d, J_{CF} = 250.2 Hz), 56.50, 53.78. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =46.3 min (minor), t_R = 60.4 min (major). MS (ES^+): m/z =263.08 ($[M+Na]^+$)

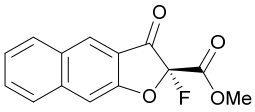
methyl (*R*)-2-fluoro-1-oxo-1,2-dihydronaphtho[2,1-*b*]furan-2-carboxylate (**5q**)



5q

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.76-7.72 (m, 1H), 7.59-7.55 (m, 1H), 7.35 (d, J = 8.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.27 (d, J_{CF} = 17.9 Hz), 174.38 (d, J_{CF} = 0.9 Hz), 162.72 (d, J_{CF} = 36.6 Hz), 141.95, 130.92, 130.26, 128.96, 128.94, 126.55, 123.39, 113.10, 110.25, 103.73 (d, J_{CF} = 249.7 Hz), 53.84. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =21.4 min (major), t_R = 31.4 min (minor). MS (ES^+): m/z =261.06 ($[M+H]^+$)

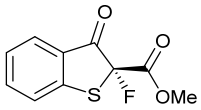
methyl (*R*)-2-fluoro-3-oxo-2,3-dihydronaphtho[2,3-*b*]furan-2-carboxylate (**5r**)



5r

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.68-7.65 (m, 1H), 7.52-7.48 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.60 (d, J_{CF} = 19.1 Hz), 174.38 (d, J_{CF} = 0.9 Hz), 162.93 (d, J_{CF} = 39.2 Hz), 139.55, 131.10, 130.95, 130.12, 128.58, 127.85, 126.00, 117.36, 108.42, 104.03 (d, J_{CF} = 248.7 Hz), 53.82. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 90:10, flow rate 1.0 mL/min, 254nm): t_R =29.3 min (minor), t_R = 42,2 min (major). MS (ES^+): m/z =261.05 ($[M+H]^+$)

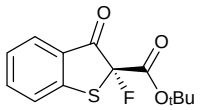
methyl 2-fluoro-3-oxo-2,3-dihydrobenzo[b]thiophene-2-carboxylate (6a)



6a

The product was synthesized according to the general procedure as yellow oil in 80% overall yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.67-7.63 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.47 (d, J_{CF} = 19.0 Hz), 178.24, 161.98 (d, J_{CF} = 35.0 Hz), 149.23, 131.30, 125.98, 124.91, 123.22, 109.68 (d, J_{CF} = 258.1 Hz), 54.02.The enantiomeric excess was determined by HPLC with an IC-H column at 254nm (2-propanol:hexane=5: 95), 1.0 mL/min; t_R =11.0 min (major), 12.3 min (minor). 99% *ee.*

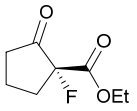
tert-butyl 2-fluoro-3-oxo-2,3-dihydrobenzo[b]thiophene-2-carboxylate (6b)



6b

The product was synthesized according to the general procedure as yellow oil in 88% overall yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 1H), 7.67 – 7.61 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34-7.28 (m, 1H), 1.47 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.18 (d, J_{CF} = 16.0 Hz), 163.73 (d, J_{CF} = 32.2 Hz), 149.00, 137.25, 128.06, 126.35, 124.33, 124.31, 98.31 (d, J_{CF} = 240.8 Hz), 85.32, 27.71. The enantiomeric excess was determined by HPLC with an OJ-H column at 254nm (2-propanol: hexane=10: 90), 1.0 mL/min; t_R =17.9 min (minor), 19.8 min (major). 93% *ee.*

ethyl 1-fluoro-2-oxocyclopentane-1-carboxylate (8a)

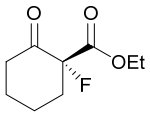


8a

Coloreless oil. ^{1}H NMR (500 MHz, Chloroform-d) δ = 4.26-4.19 (m, 2H), 2.53 – 2.45 (m, 1H), 2.44-2.40 (m, 2H), 2.30-2.20 (m, 1H), 2.14-2.03 (m, 2H), 1.24 (t, *J* = 7.1 Hz,

3H) ppm. ^{13}C NMR (125 MHz, Chloroform-d) δ = 207.51 (d, J_{CF} = 17.1 Hz), 167.22 (d, J_{CF} = 27.5 Hz), 94.51(d, J_{CF} = 199.5 Hz), 62.13, 35.53, 33.70 (d, J_{CF} = 20.8 Hz), 17.85 (d, J_{CF} = 3.5 Hz), 13.81ppm. The enantiomeric excess was determined by GC (β−DEX, 70 °C): t_R =23.4 min (minor), t_R = 23,8 min (major).

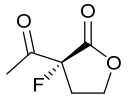
ethyl 1-fluoro-2-oxocyclohexane-1-carboxylate (8b)



8b

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32-4.27 (m, 2H), 2.75-2.57 (m, 2H), 2.52-2.42 (m, 1H), 2.20-2.09 (m, 1H), 1.99-1.79 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.79 (d, J_{CF} = 20.0 Hz), 166.89 (d, J_{CF} = 24.8 Hz), 96.30 (d, J_{CF} = 196.6 Hz), 62.31, 39.58, 35.98 (d, J_{CF} = 21.7 Hz), 26.50, 20.91 (d, J_{CF} = 5.9 Hz), 13.95. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AS-H, Hexane: *i*PrOH= 98:2, flow rate 0.5ml/min, 220nm): t_R = 68.4 min (minor), t_R = 142.4 min (major). MS (ES^+): m/z = 189.07 ($[M+H]^+$)

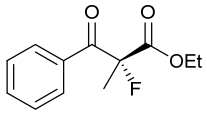
3-acetyl-3-fluorodihydrofuran-2(3H)-one (8c)



8c

Coloreless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 4.44-4.29 (m, 2H), 2.77-2.70 (m, 1H), 2.55-2.44 (m, 1H), 2.33 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ = 203.08 (d, J_{CF} = 31.2 Hz), 169.14 (d, J_{CF} = 24.2 Hz), 96.15 (d, J_{CF} = 204.0 Hz), 65.59 (d, J_{CF} = 4.6 Hz), 31.78 (d, J_{CF} = 21.3 Hz), 25.45. The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC-H, Hexane: *i*PrOH= 95:5, flow rate 1.0 mL/min, 210nm): t_R =14.1 min (minor), t_R = 15.0 min (major).

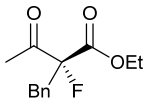
ethyl 2-fluoro-2-methyl-3-oxo-3-phenylpropanoate (8d)



8d

Coloreless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.07-8.04 (m, 2H), 7.62-7.58 (m, 1H), 7.49-7.46 (m, 2H), 4.30-4.23 (m, 2H), 1.88 (d, *J* = 22.5 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, Chloroform-*d*) δ = 191.68(d, J_{CF} = 25.3 Hz), 168.43(d, J_{CF} = 25.5 Hz), 133.89, 133.37, 133.35, 129.72, 129.67, 128.61, 96.99(d, J_{CF} = 194.7 Hz), 62.56, 20.96(d, J_{CF} = 23.5 Hz), 13.86. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OB-H, Hexane: *i*PrOH= 96:4, flow rate 0.7 mL/min, 254nm): t_R =14.4min (minor), t_R = 17.0 min (major).

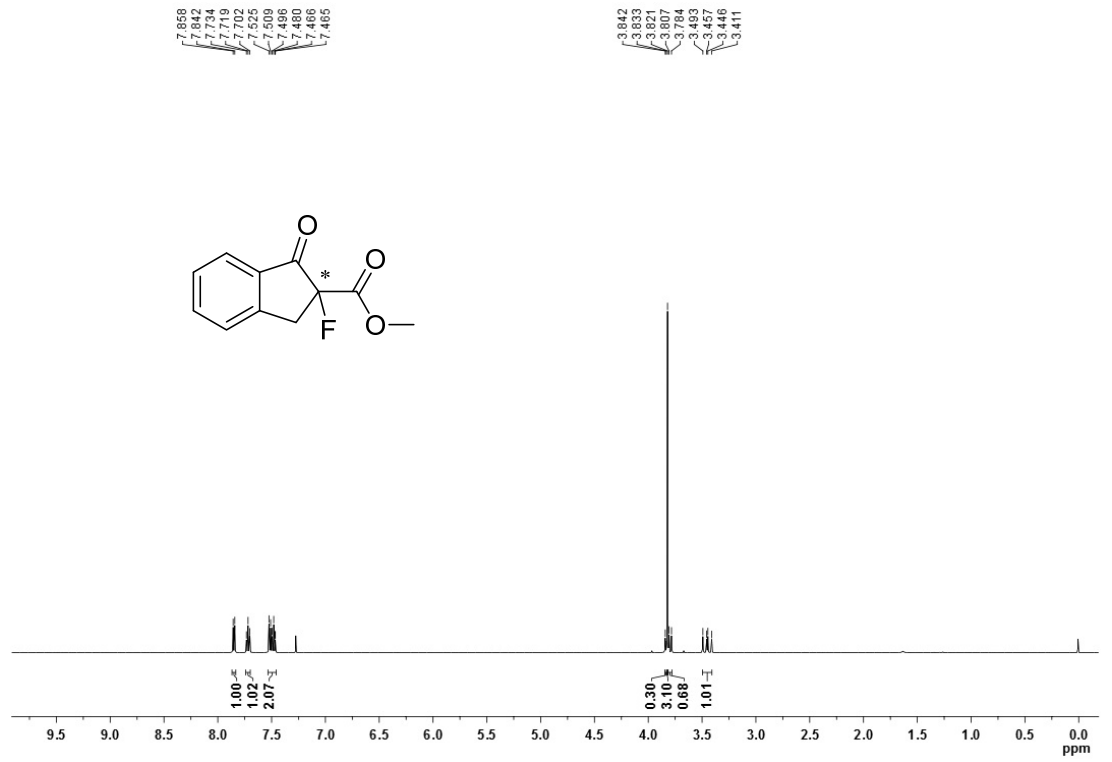
ethyl 2-benzyl-2-fluoro-3-oxobutanoate (8e)

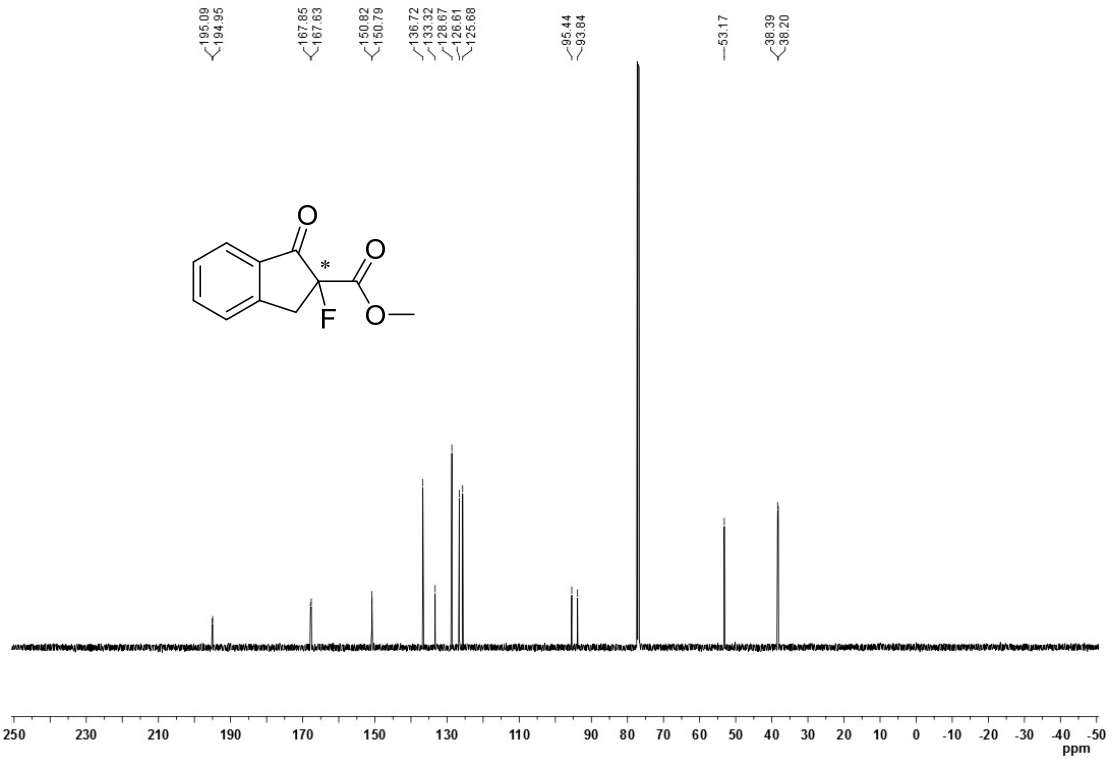


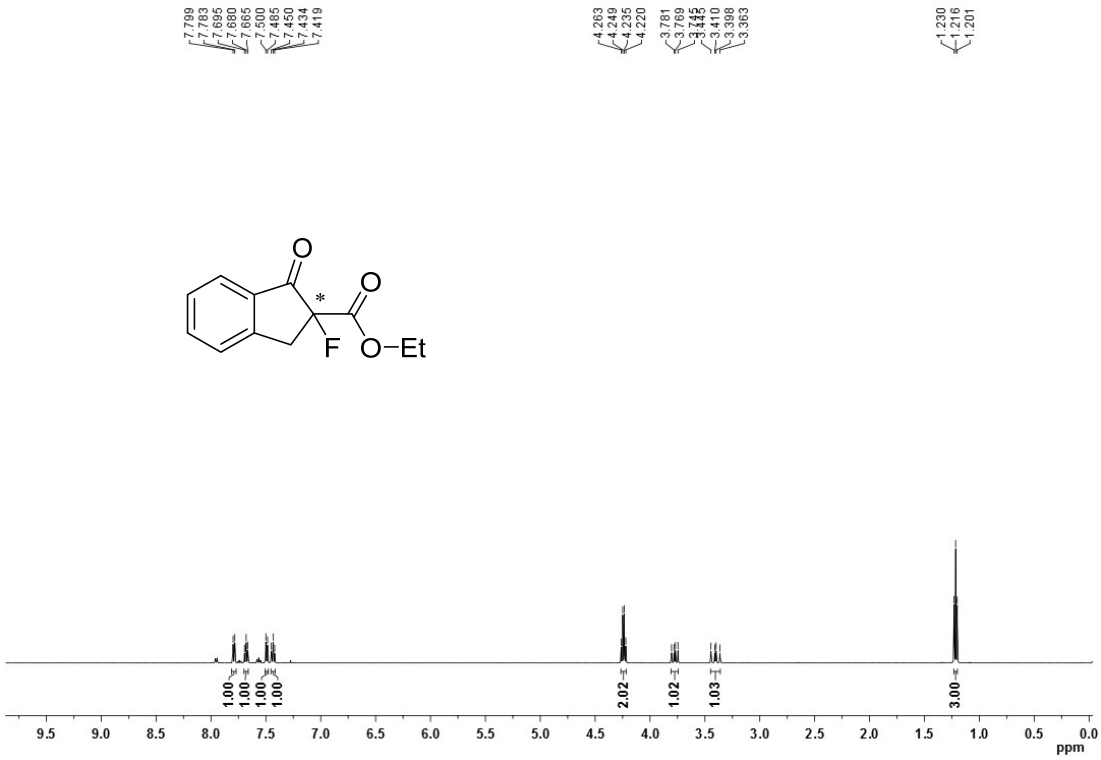
8e

Coloreless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.31-7.21 (m, 5H), 4.23 (q, *J*=7.1, 2H), 3.41 (dd, *J* = 25.8, 7.6 Hz, 2H), 2.13 (d, *J* = 5.1 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ = 202.27 (d, J_{CF} = 29.5 Hz), 165.63 (d, J_{CF} = 25.4 Hz), 133.02, 130.30, 128.33, 127.35, 99.91 (d, J_{CF} = 200.1 Hz), 62.57, 39.66 (d, J_{CF} = 20.2 Hz), 26.15, 13.86. The enantiomeric excess was determined by HPLC (Daicel Chiralpak OJ-H, Hexane: *i*PrOH= 95:5, flow rate 1.0 mL/min, 210nm): t_R =23.0 min (minor), t_R = 37.1 min (major).

3. NMR spectra



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4.220
3.781
3.769
3.445
3.410
3.398
3.363
1.230
1.216
1.201
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O
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F
O−Et
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1.00
1.00
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2.02
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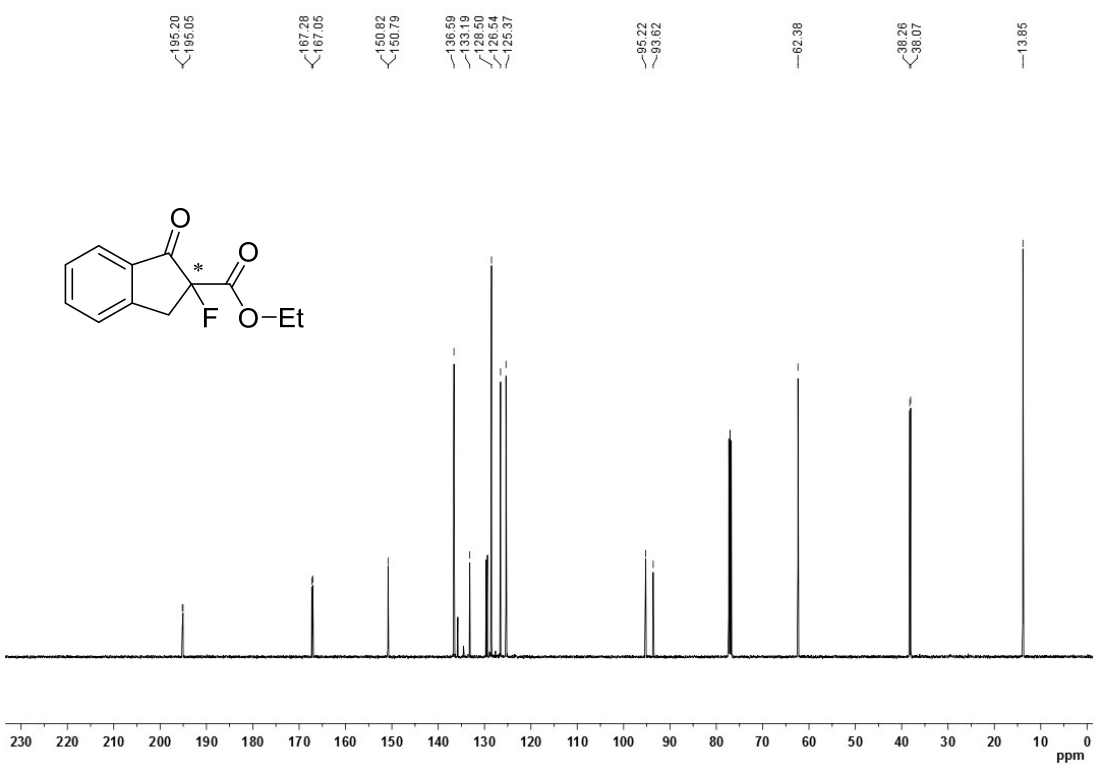
1.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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125.37
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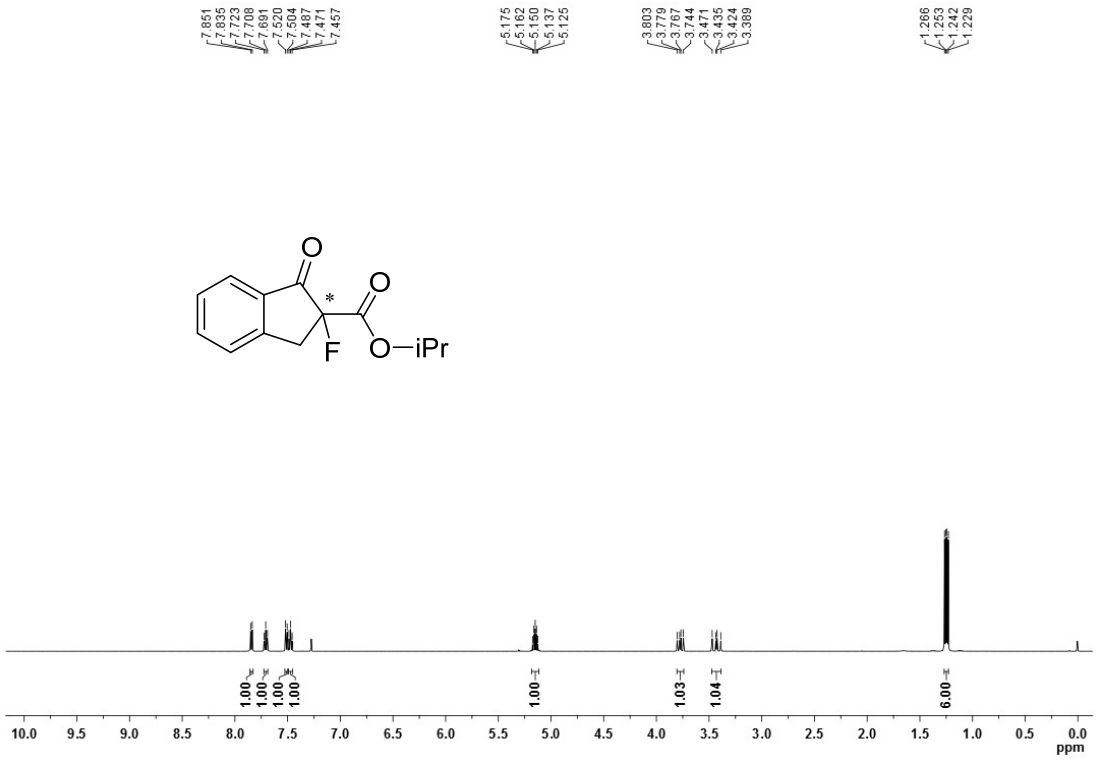
38.26
38.07
13.85
O
O
*
F
O−Et
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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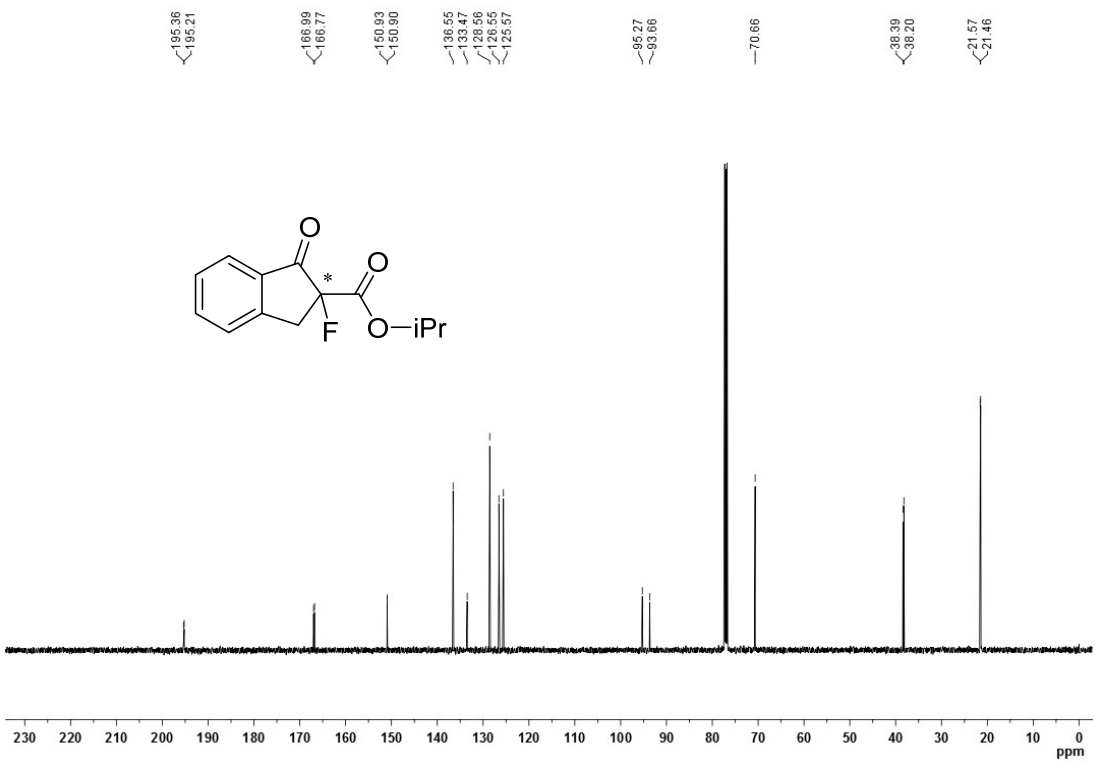
7.708
7.691
7.520
7.504
7.487
7.471
7.457
5.175
5.162
5.150
5.137
5.125
3.803
3.779
3.767
3.744
3.471
3.435
3.424
3.389
1.266
1.253
1.242
1.229
O
O
*
F
O—iPr
1.00
1.00
1.00
1.00
1.00
1.03
1.04
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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166.99
166.77
150.93
150.90
136.55
133.47
128.56
126.55
125.57
95.27
93.66
70.66
38.39
38.20
21.57
21.46
O
O
*
F
O—iPr
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.836
7.820
7.713
7.698
7.681
7.515
7.500
7.475
7.459
7.445
4.939
4.932
4.923
4.915
4.907
4.898
4.890
3.792
3.770
3.757
3.735
3.471
3.436
3.425
3.390
1.772
1.766
1.760
1.530
1.520
1.507
1.454
1.447
1.439
1.429
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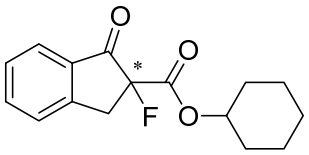
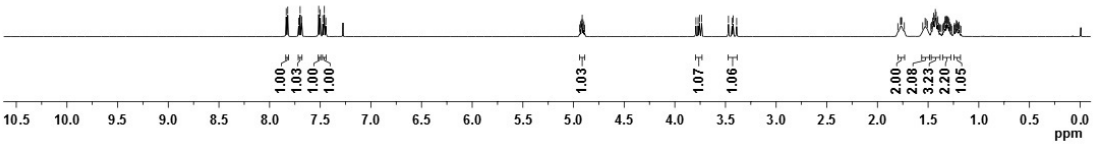
1.333
1.326
1.318
1.313
1.306
1.299
1.292
1.221


O
O
*
F
O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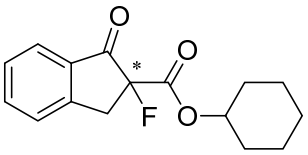
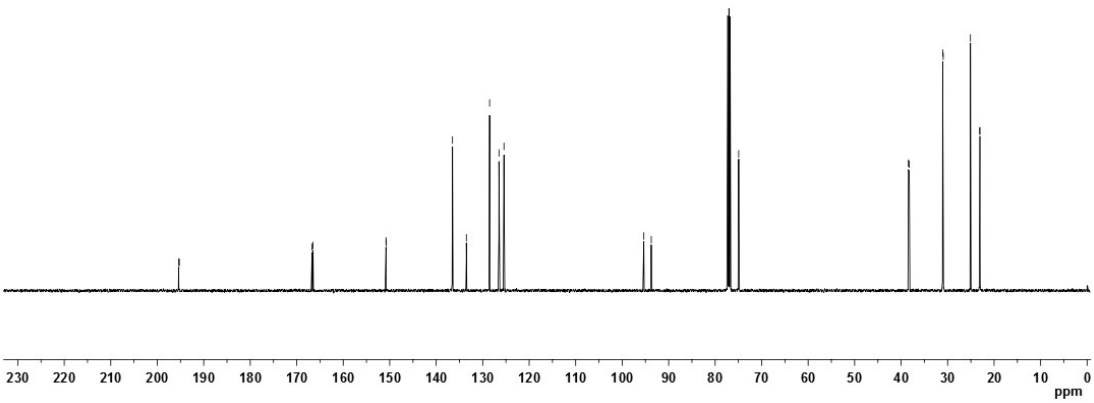
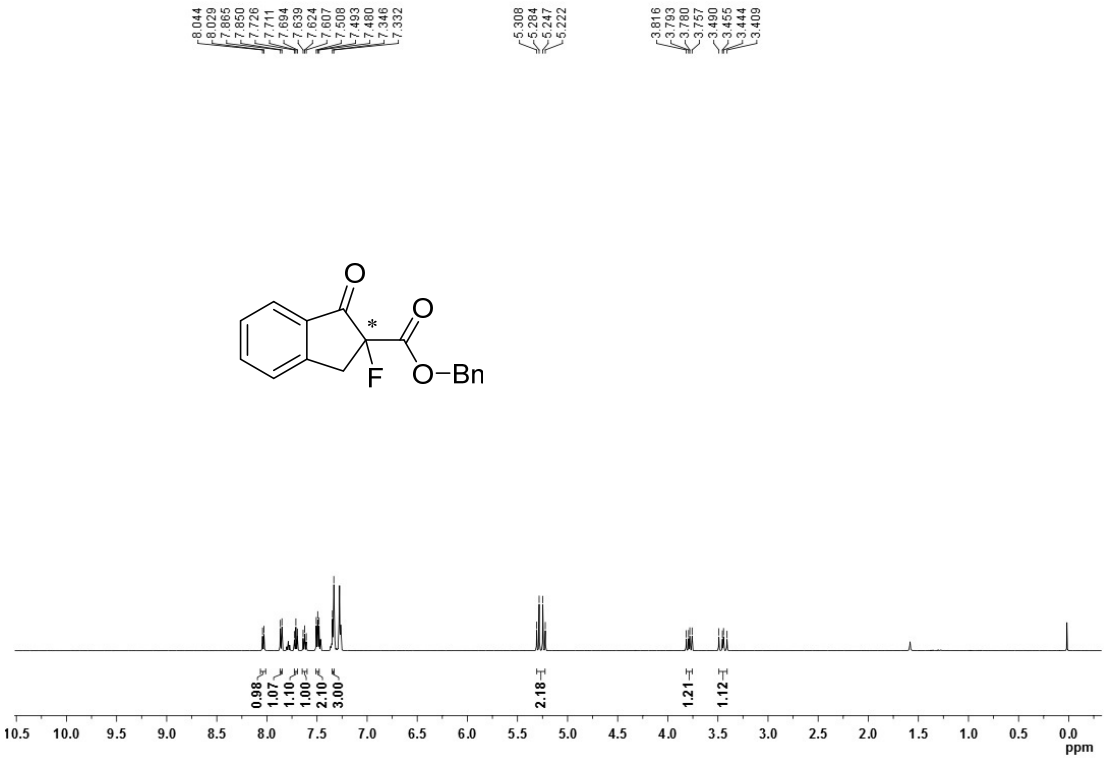
1.00
1.00
1.03
1.07
1.06
2.00
2.08
3.23
2.20
1.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


195.40
195.25
166.71
166.49
150.80
150.77
136.49
133.51
128.51
126.50
125.42
95.35
93.74
74.94
38.43
38.24
31.06
30.94
25.09
23.10
23.05


O
O
*
F
O


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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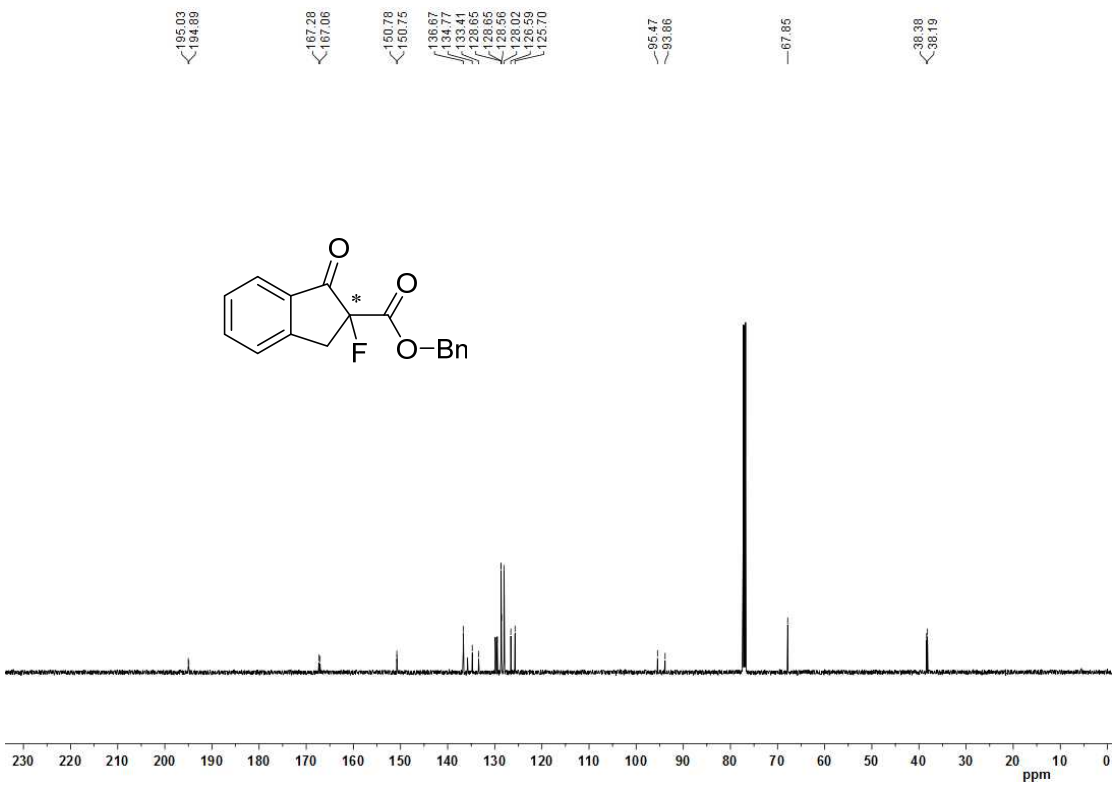
8.029
7.865
7.850
7.726
7.711
7.694
7.639
7.624
7.607
7.508
7.493
7.480
7.346
7.332
5.308
5.284
5.247
5.222
3.816
3.793
3.780
3.757
3.490
3.455
3.444
3.409
O
O
*
F
O−Bn
0.98
1.07
1.10
1.00
2.10
3.00
2.18
1.21
1.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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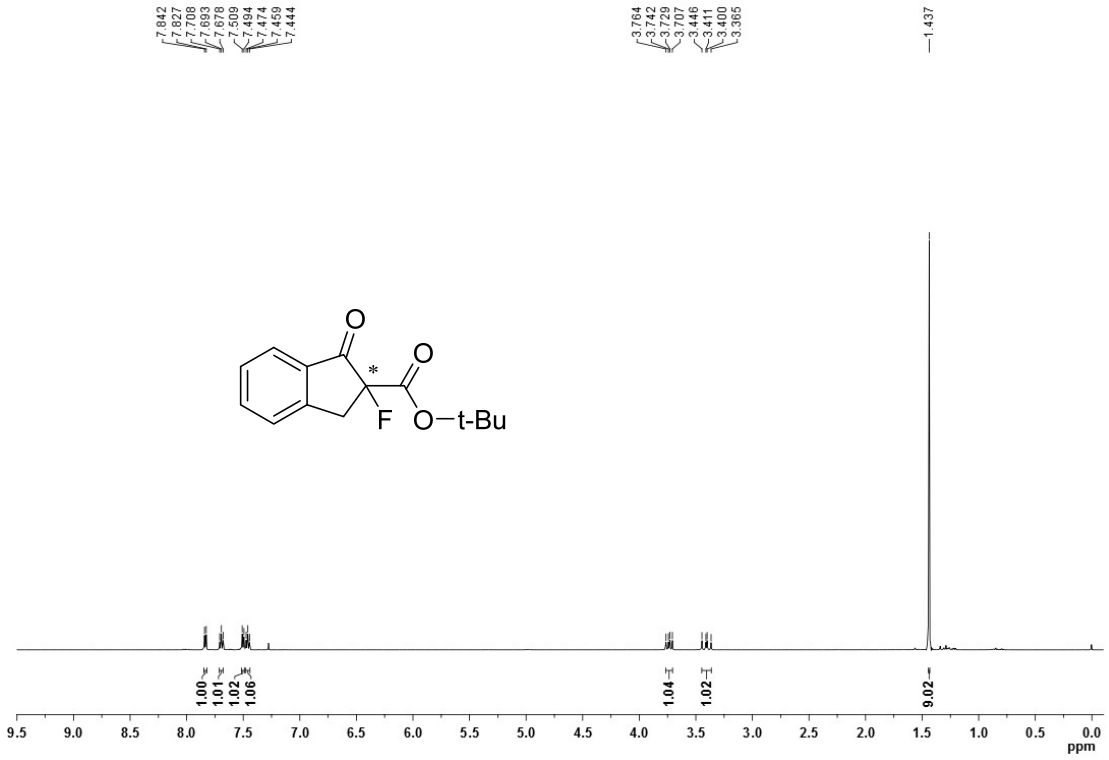
194.89
167.28
167.06
150.78
150.75
136.67
134.77
133.41
128.65
128.65
128.56
128.02
126.59
125.70
95.47
93.86
67.85
38.38
38.19
O
O
*
F
O−Bn
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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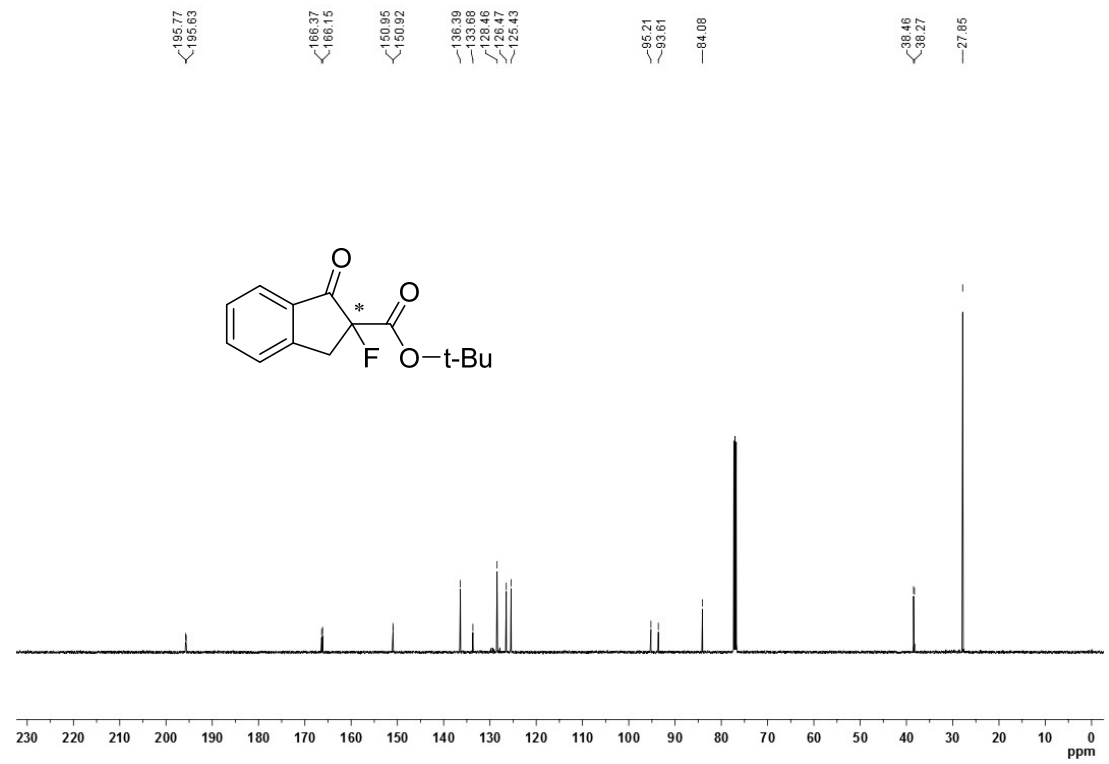
7.827
7.708
7.693
7.678
7.509
7.494
7.474
7.459
7.444
3.764
3.742
3.729
3.707
3.446
3.411
3.400
3.365
1.437
O
O
*
F
O−t-Bu
1.00
1.01
1.02
1.06
1.04
1.02
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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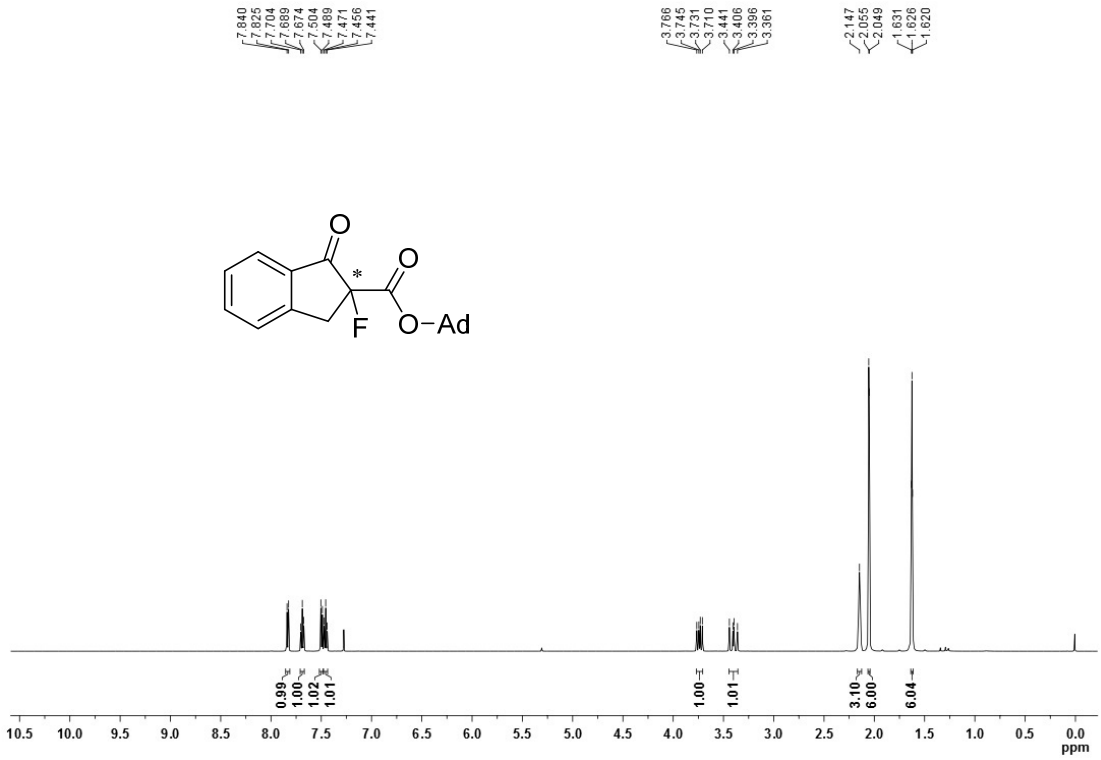
195.63
166.37
166.15
150.95
150.92
136.39
133.68
128.46
126.47
125.43
95.21
93.61
84.08
38.46
38.27
27.85
O
O
*
F
O−t-Bu
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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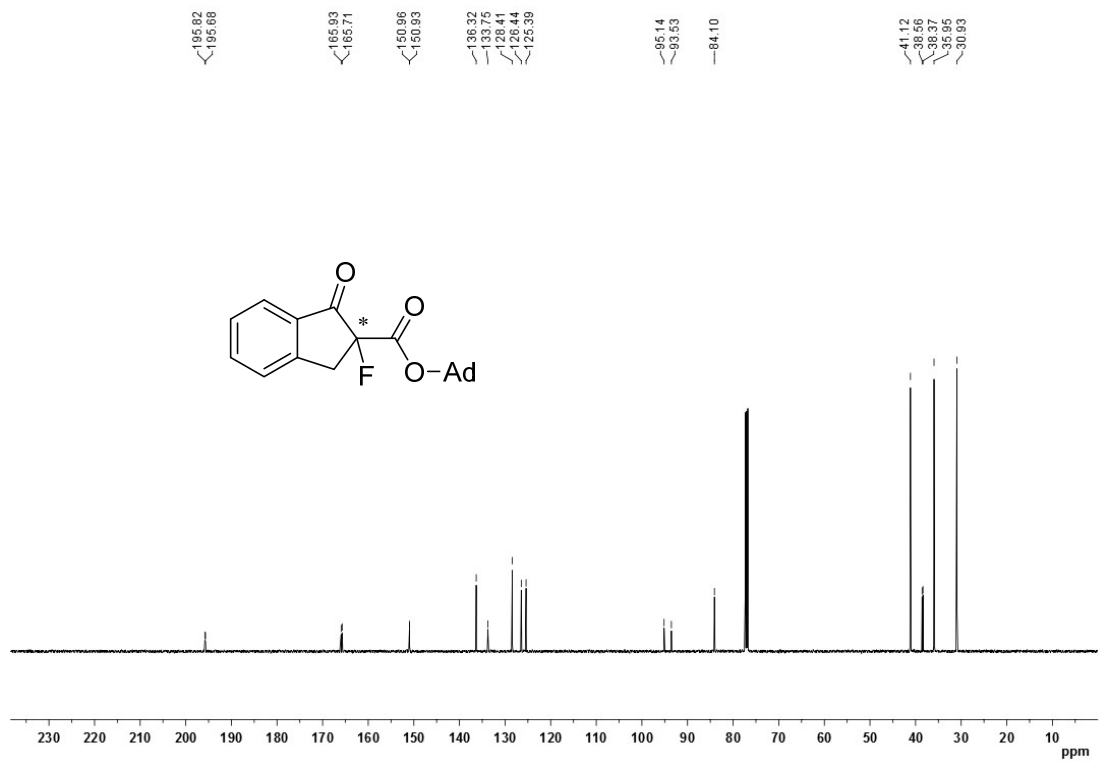
7.825
7.704
7.689
7.674
7.504
7.489
7.471
7.456
7.441
3.766
3.745
3.731
3.710
3.441
3.406
3.396
3.361
2.147
2.055
2.049
1.631
1.626
1.620
O
O
*
F
O−Ad
0.99
1.00
1.02
1.01
1.00
1.01
3.10
6.00
6.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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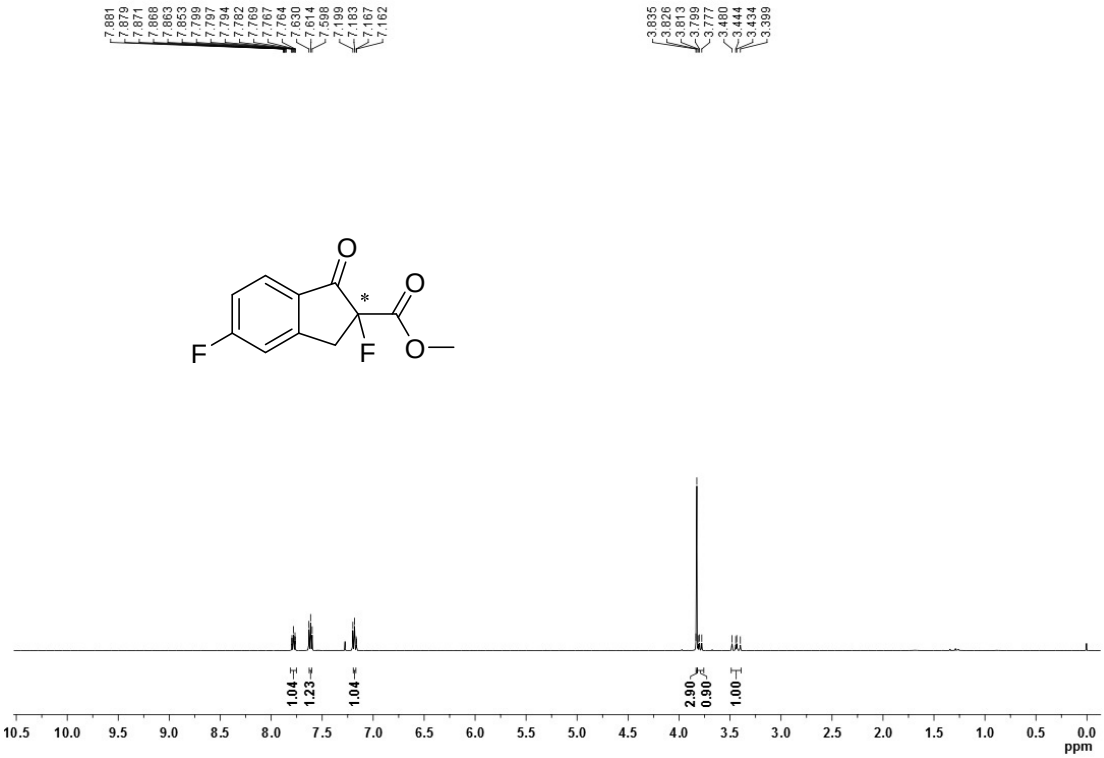
195.68
165.93
165.71
150.96
150.93
136.32
133.75
128.41
126.44
125.39
95.14
93.53
84.10
41.12
38.56
38.37
35.95
30.93
O
O
*
F
O−Ad
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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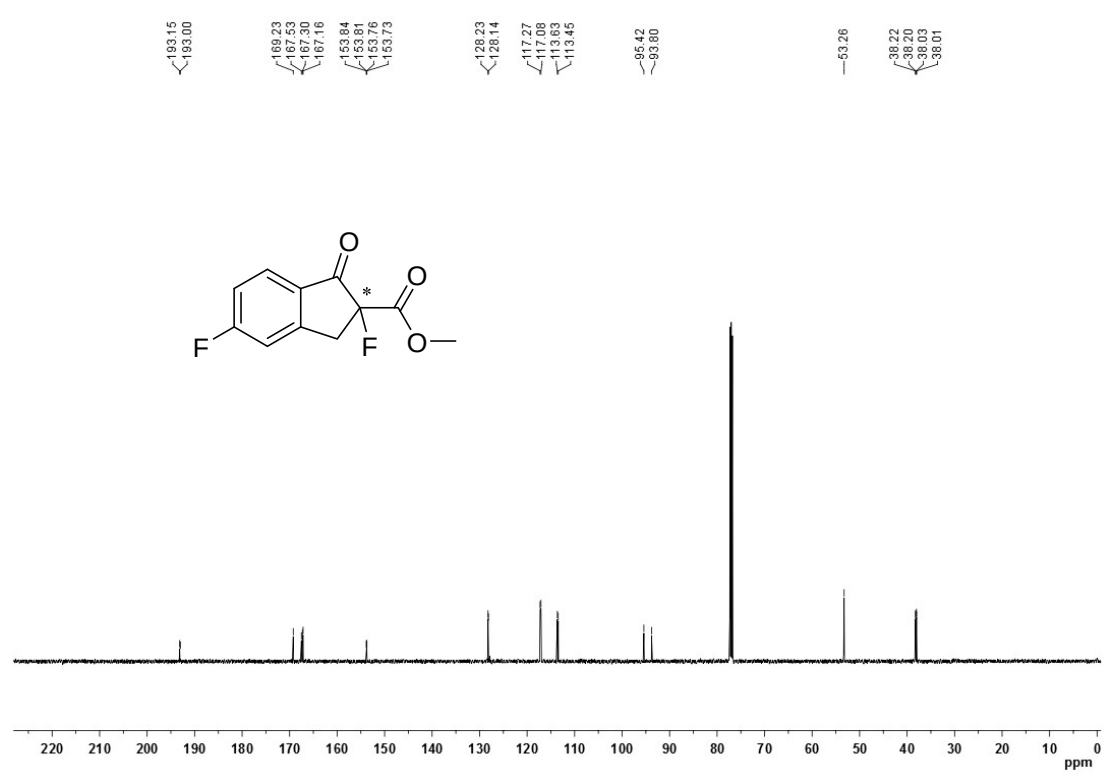
7.871
7.868
7.863
7.853
7.799
7.797
7.794
7.782
7.769
7.767
7.764
7.630
7.614
7.598
7.199
7.183
7.167
7.162
3.835
3.826
3.813
3.799
3.777
3.480
3.444
3.434
3.399
O
O
*
F
F
O—
1.04
1.23
1.04
2.90
0.90
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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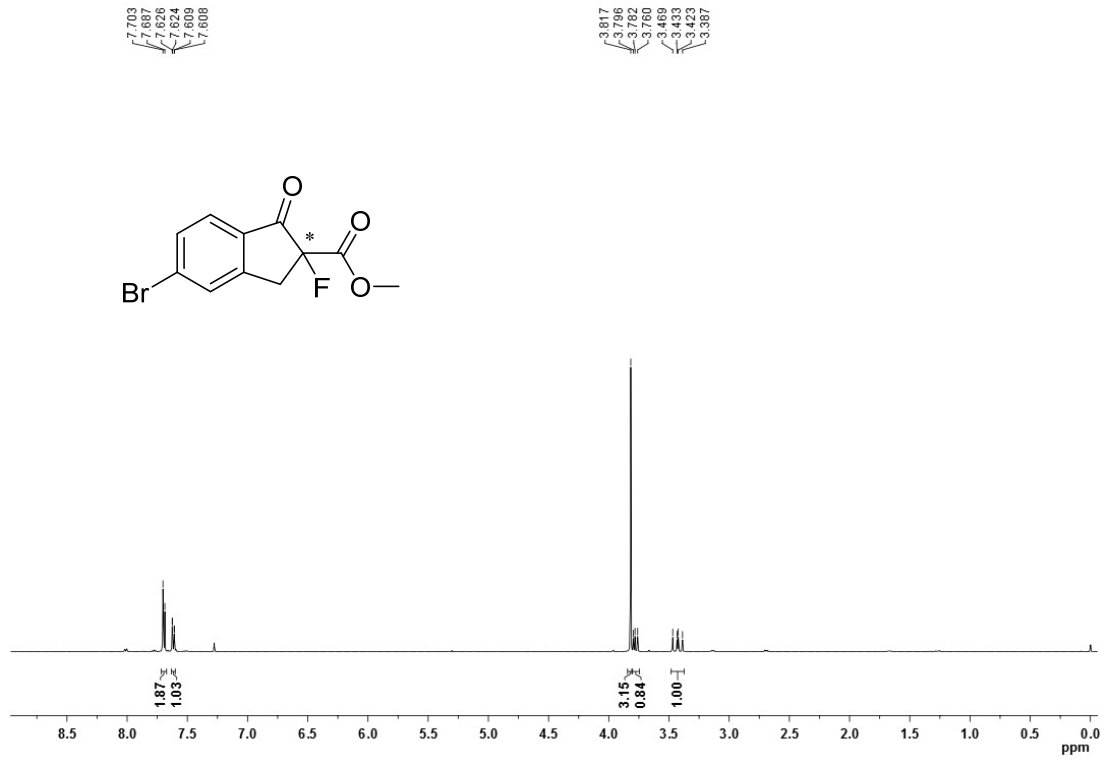
193.00
169.23
167.53
167.30
167.16
153.84
153.81
153.76
153.73
128.23
128.14
117.27
117.08
113.63
113.45
95.42
93.80
53.26
38.22
38.20
38.03
38.01
O
O
*
F
F
O—
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.791
7.775
7.521
7.519
7.472
7.471
7.469
7.456
7.454
7.452
3.828
3.820
3.798
3.785
3.763
3.471
3.435
3.425
3.389
O
O
*
Cl
F
O—
1.00
1.00
1.00
3.03
1.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


193.65
193.51
167.47
167.25
152.15
152.12
143.52
131.73
129.60
126.90
126.72
95.33
93.72
53.30
38.08
37.88
O
O
*
Cl
F
O—
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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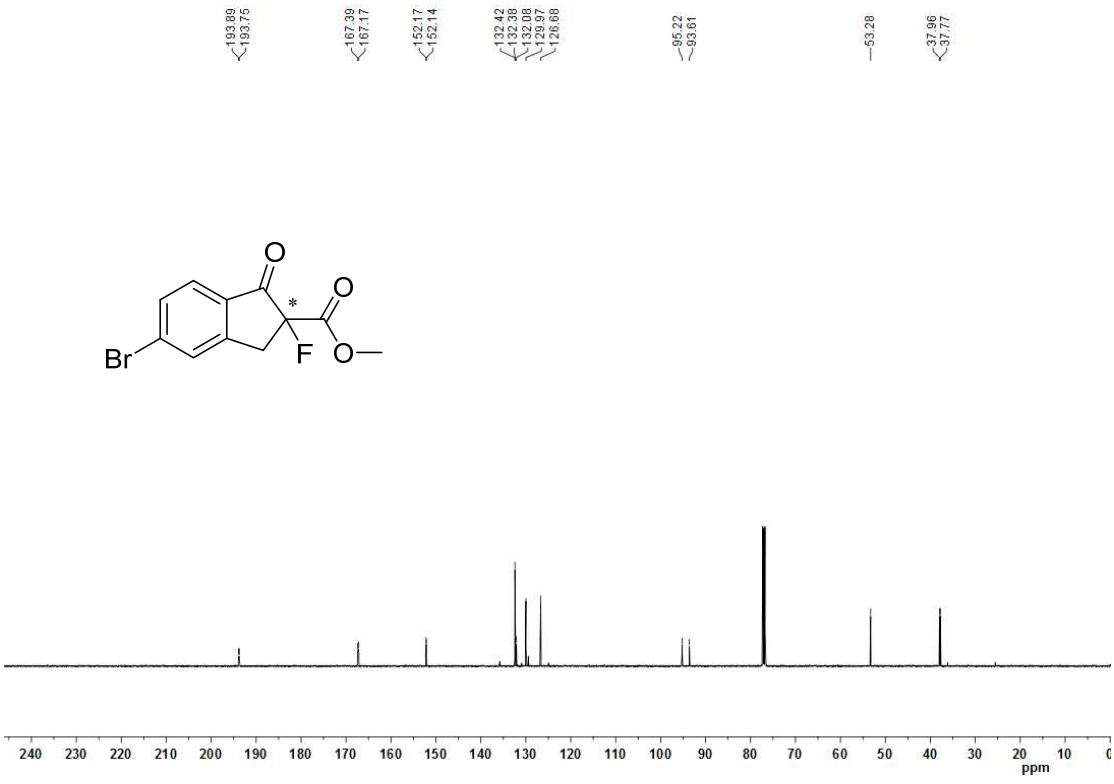
7.626
7.624
7.609
7.608
3.817
3.796
3.782
3.760
3.469
3.433
3.423
3.387
O
O
*
Br
F
O—
1.87
1.03
3.15
0.84
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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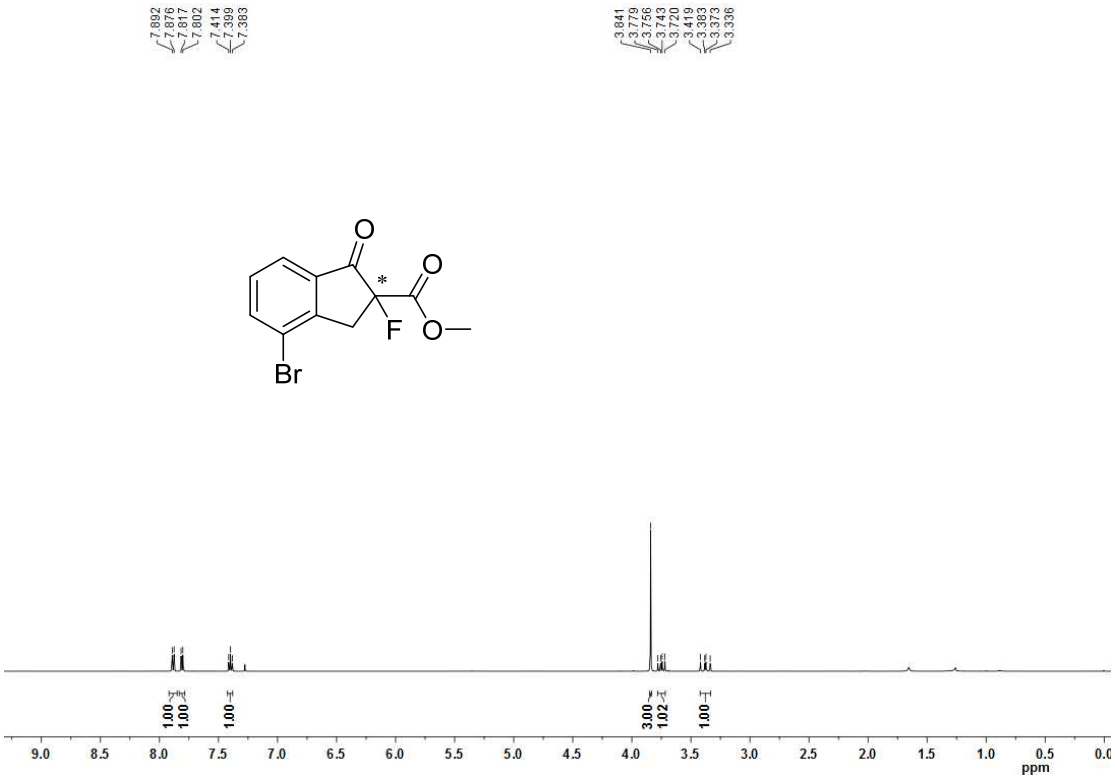
167.17
152.17
152.14
132.42
132.38
132.08
129.97
126.68
95.22
93.61
53.28
37.96
37.77
O
O
*
Br
F
O—
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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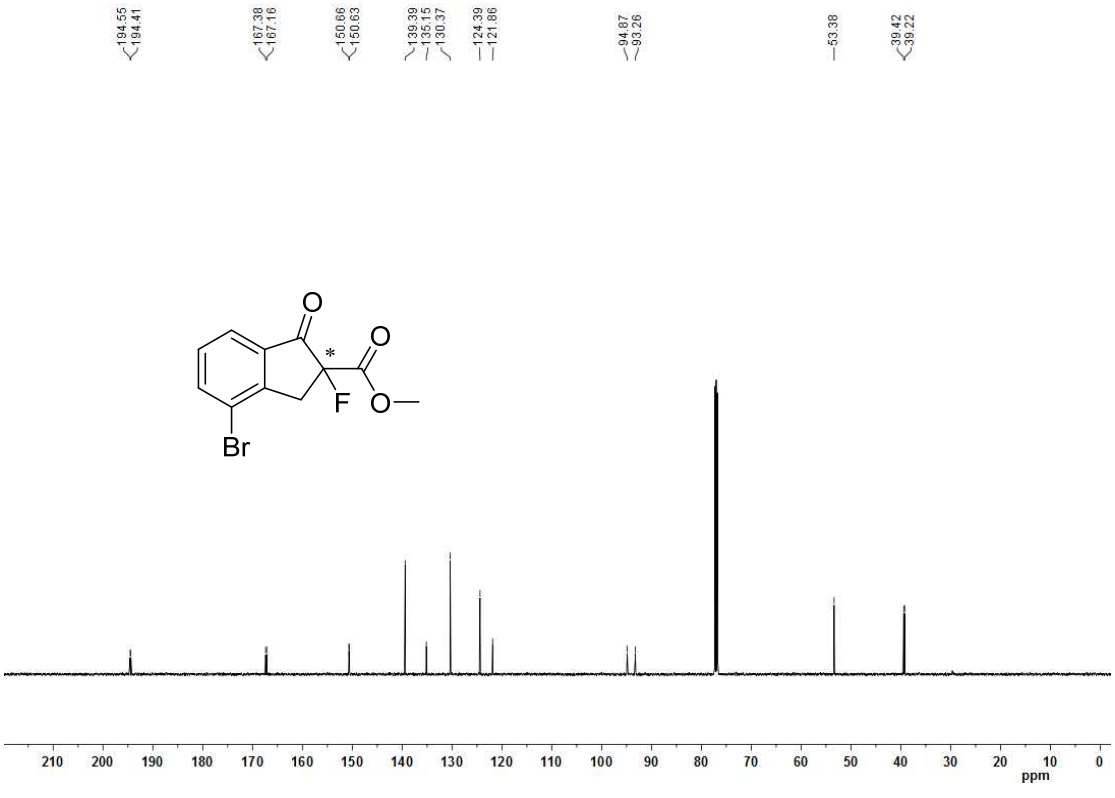
7.802
7.414
7.399
7.383
3.841
3.779
3.756
3.743
3.720
3.419
3.393
3.373
3.336
O
O
*
F
O
Br
1.00
1.00
1.00
3.00
1.02
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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167.16
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150.63
139.39
135.15
130.37
124.39
121.86
94.87
93.26
53.38
39.42
39.22
O
O
*
F
O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.882
7.867
7.804
7.789
7.406
7.391
7.375
3.831
3.771
3.748
3.735
3.712
3.407
3.371
3.361
3.324
Br
O
*
O
F
O
1.00
1.00
1.02
3.00
1.01
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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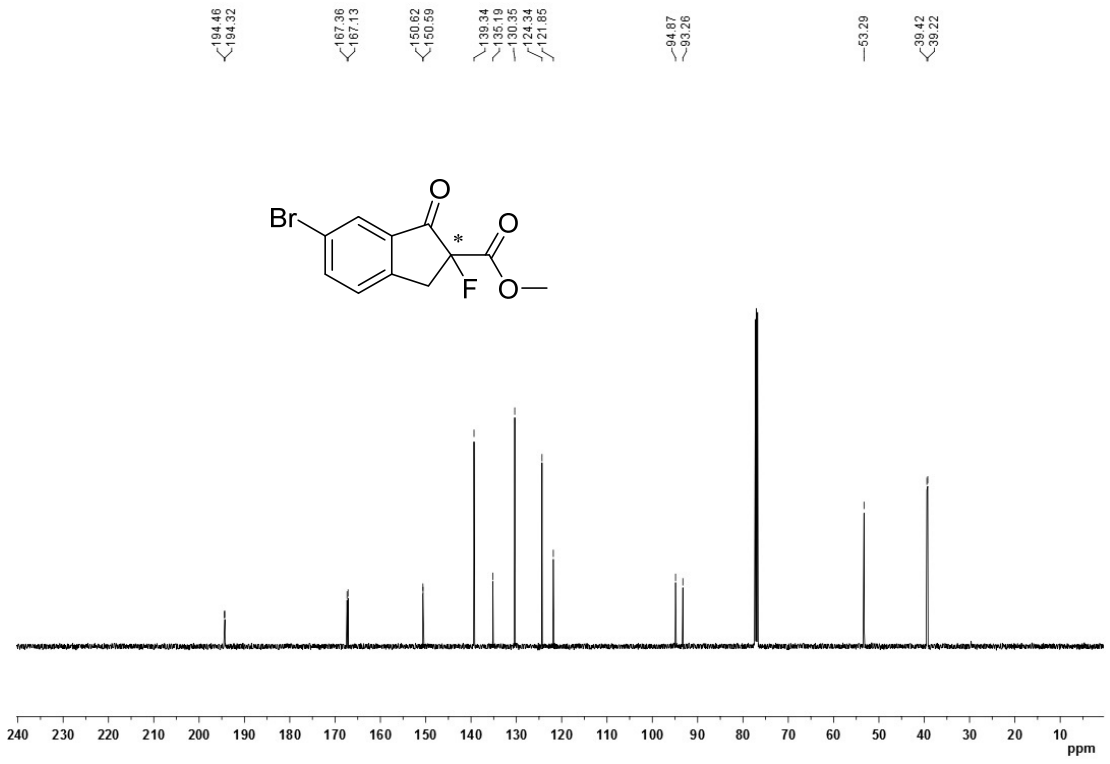
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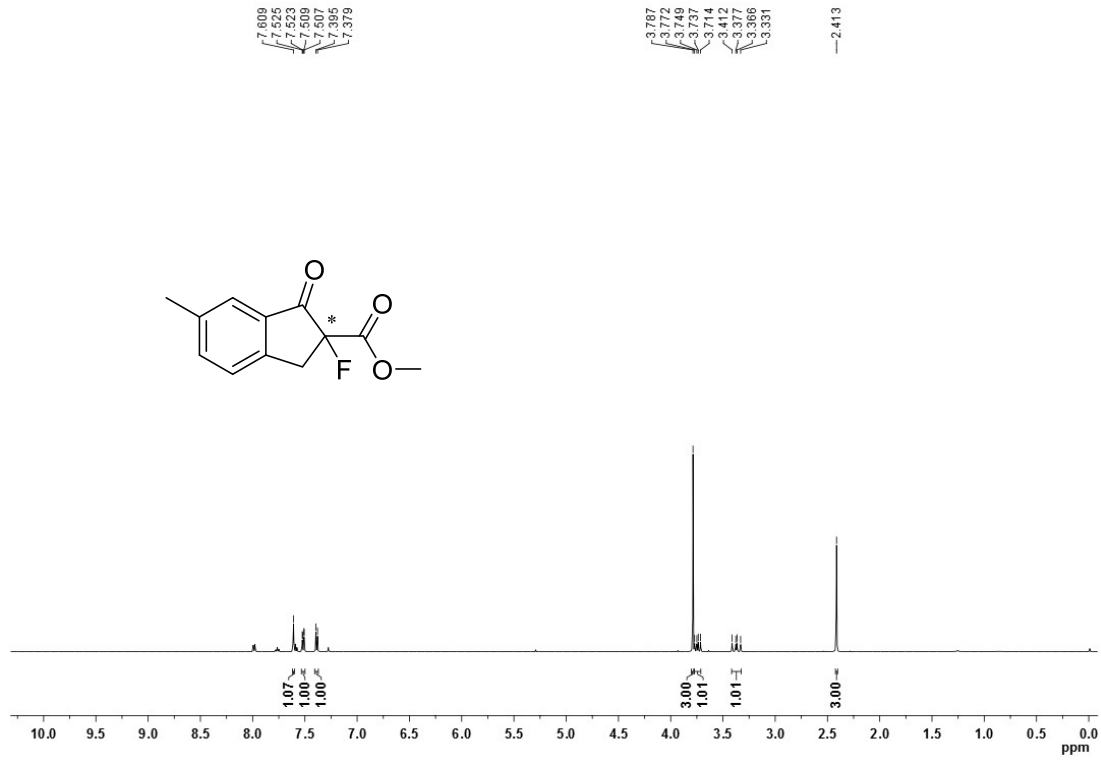
150.59
139.34
135.19
130.35
124.34
121.85
94.87
93.26
53.29
39.42
39.22
Br
O
*
O
F
O
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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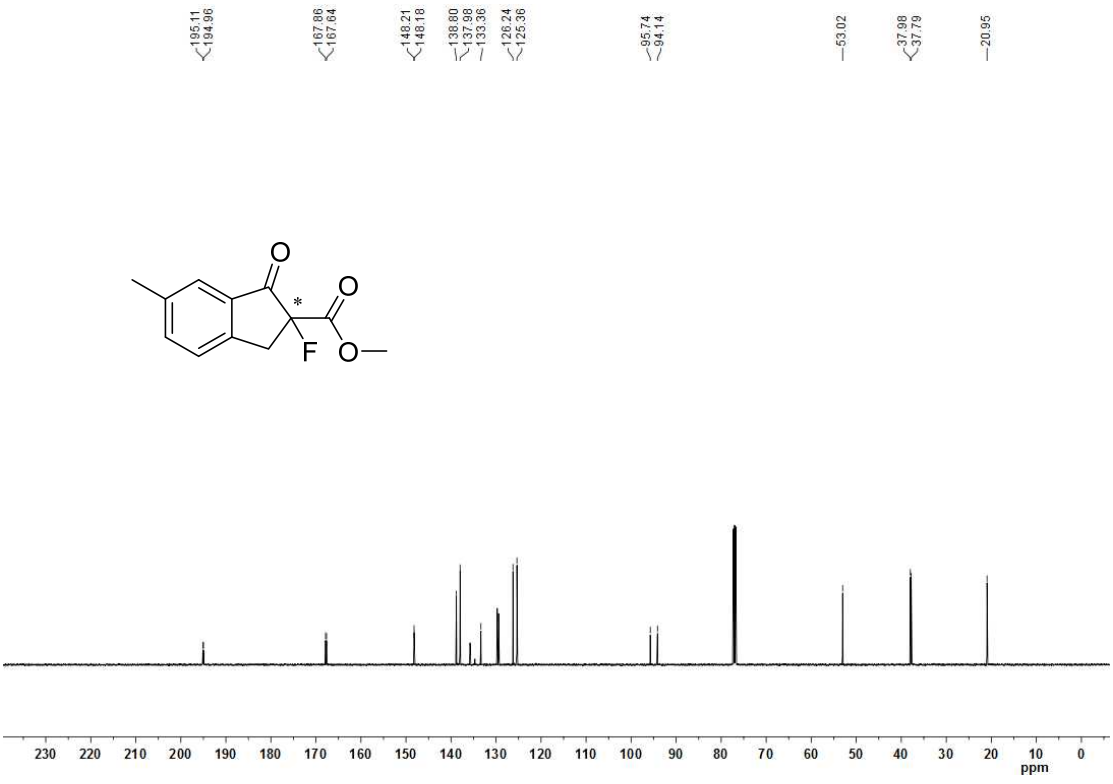
7.395
7.379
3.787
3.772
3.749
3.737
3.714
3.412
3.377
3.366
3.331
2.413
O
O
*
F
O
1.07
1.00
1.00
3.00
1.01
1.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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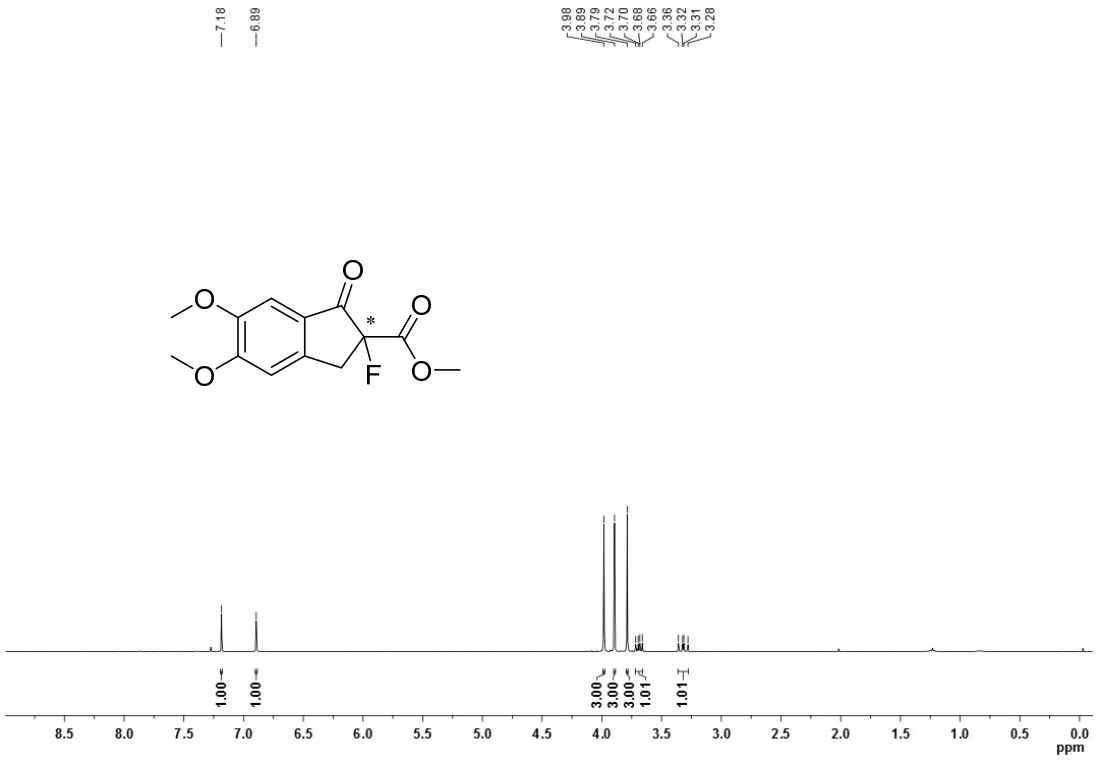
148.21
148.18
138.80
137.98
133.36
126.24
125.36
95.74
94.14
53.02
37.98
37.79
20.95
O
O
*
F
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.89
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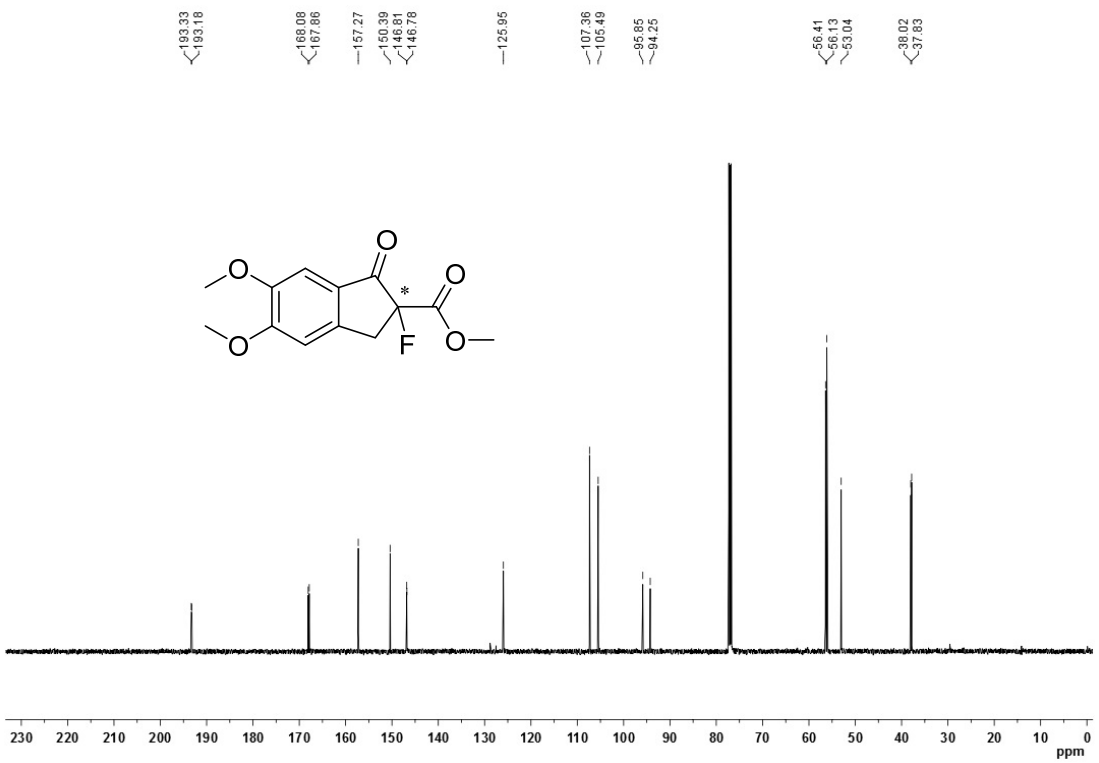
3.89
3.79
3.72
3.70
3.68
3.66
3.36
3.32
3.31
3.28
O
O
O
*
F
O
1.00
1.00
3.00
3.00
3.00
1.01
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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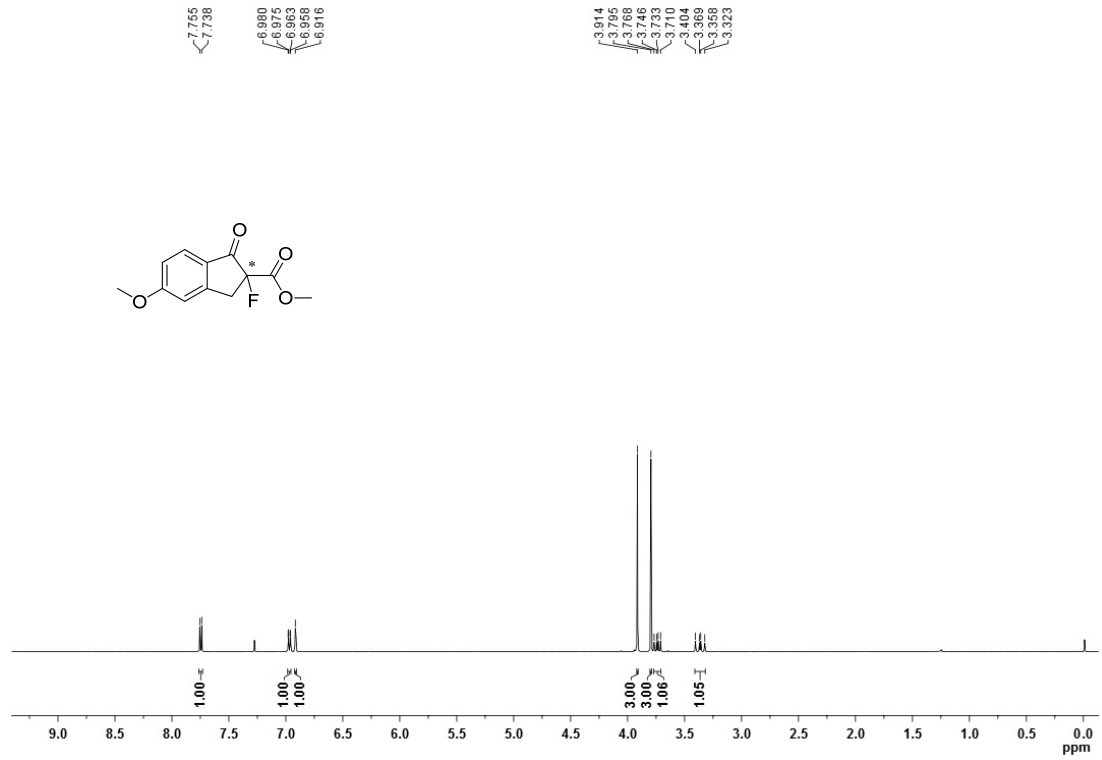
193.18
168.08
167.86
157.27
150.39
146.81
146.78
125.95
107.36
105.49
95.85
94.25
56.41
56.13
53.04
38.02
37.83
O
O
O
*
F
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.975
6.963
6.958
6.916
3.914
3.795
3.768
3.746
3.733
3.710
3.404
3.369
3.358
3.323
O
O
O
O
F
1.00
1.00
1.00
3.00
3.00
1.06
1.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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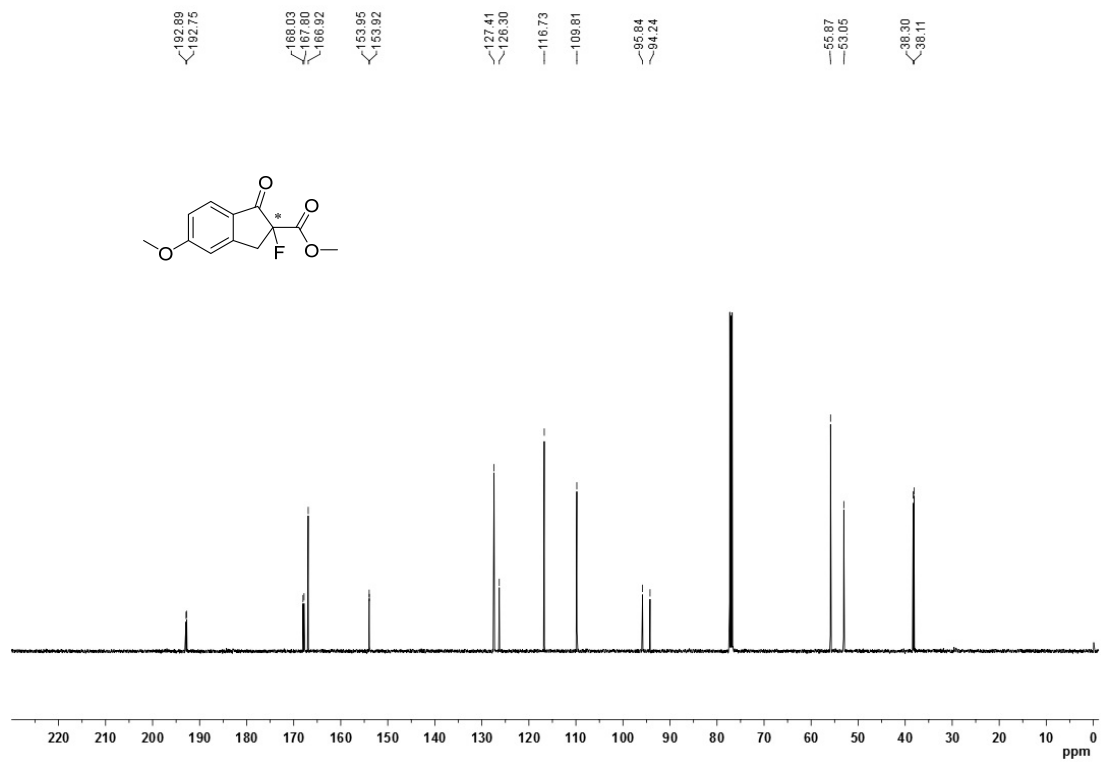
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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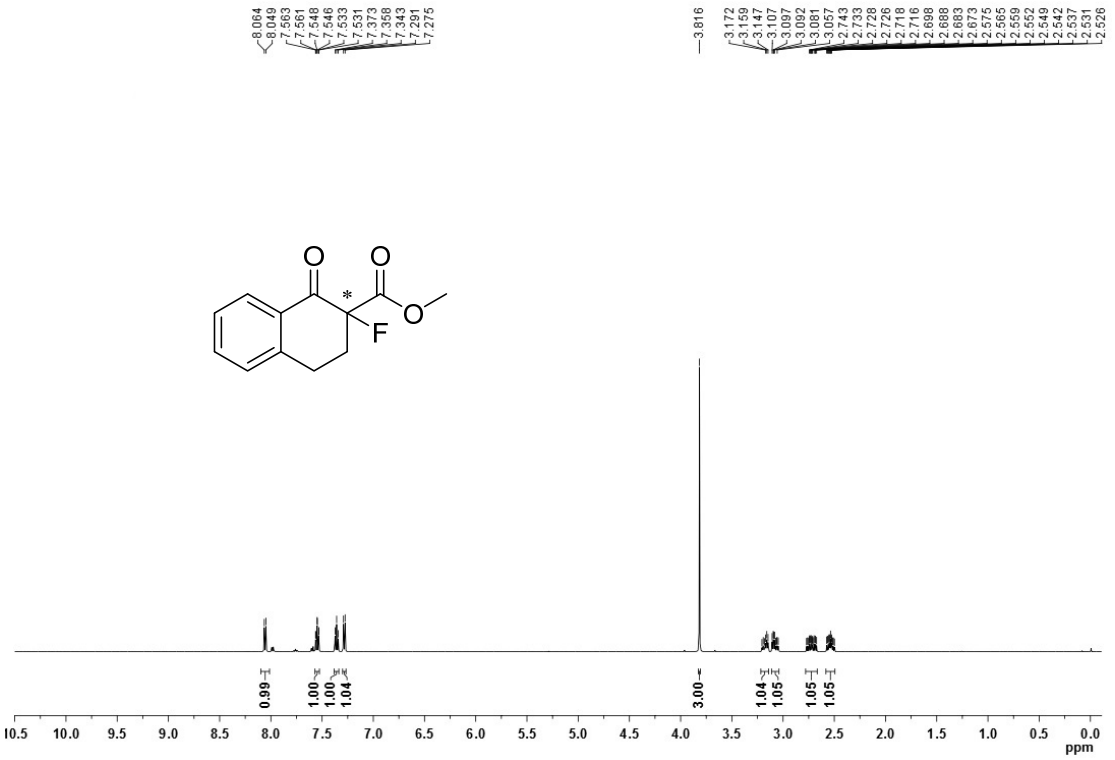
192.75
168.03
167.80
166.92
153.95
153.92
127.41
126.30
116.73
109.81
95.84
94.24
55.87
53.05
38.30
38.11
O
O
O
O
F
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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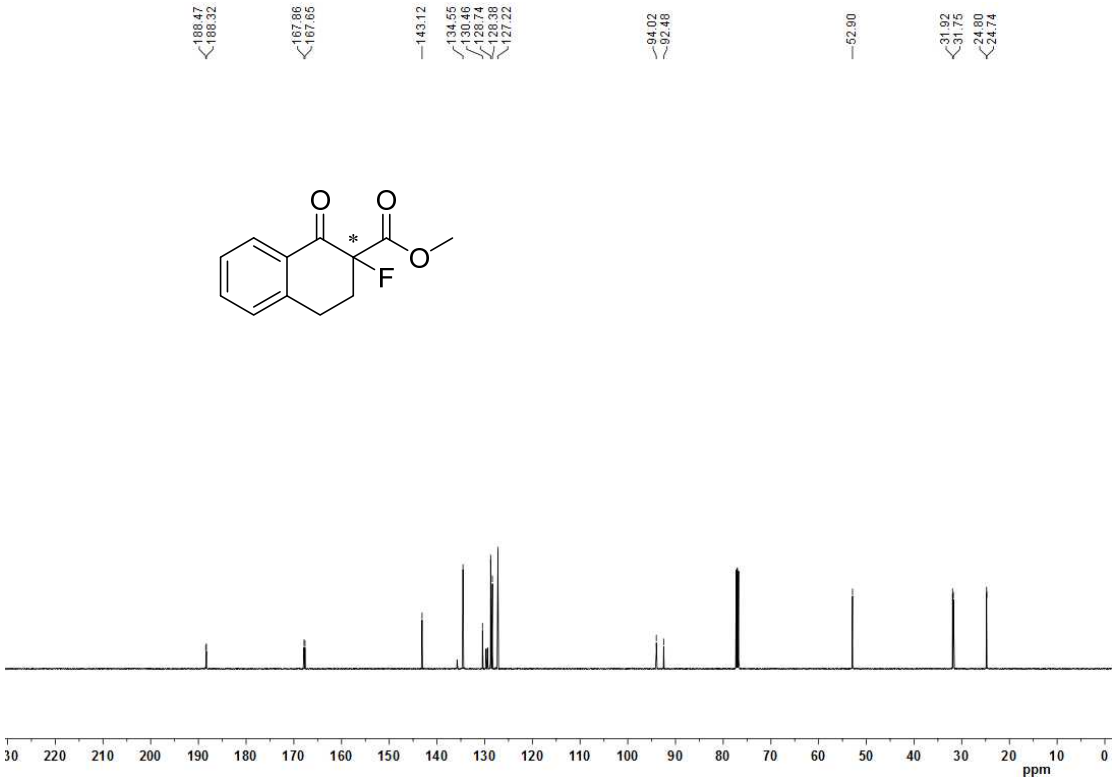
7.546
7.533
7.531
7.373
7.358
7.343
7.291
7.275
3.816
3.172
3.159
3.147
3.107
3.097
3.092
3.081
3.057
2.743
2.733
2.728
2.726
2.718
2.716
2.698
2.688
2.683
2.673
2.575
2.565
2.559
2.552
2.549
2.542
2.537
2.531
2.526
O
O
*
O
F
0.99
1.00
1.00
1.04
3.00
1.04
1.05
1.05
1.05
ppm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188.32
167.86
167.65
143.12
134.55
130.46
128.74
128.38
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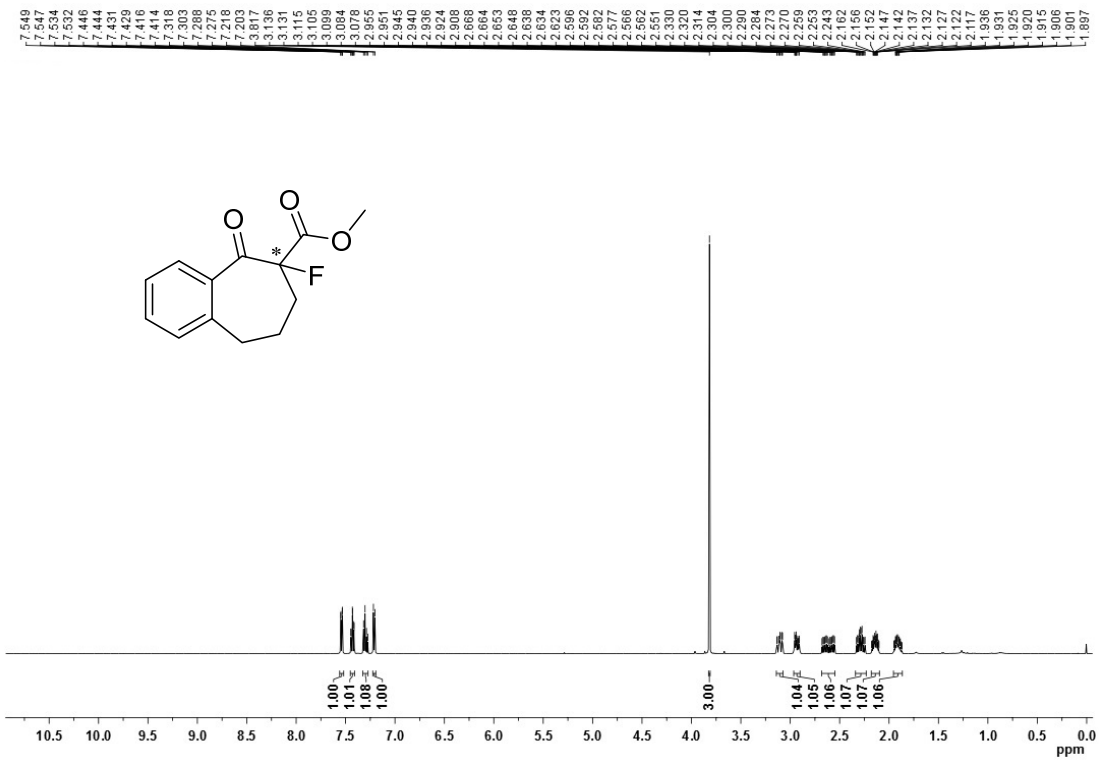
92.48
52.90
31.92
31.75
24.80
24.74
O
O
*
O
F
ppm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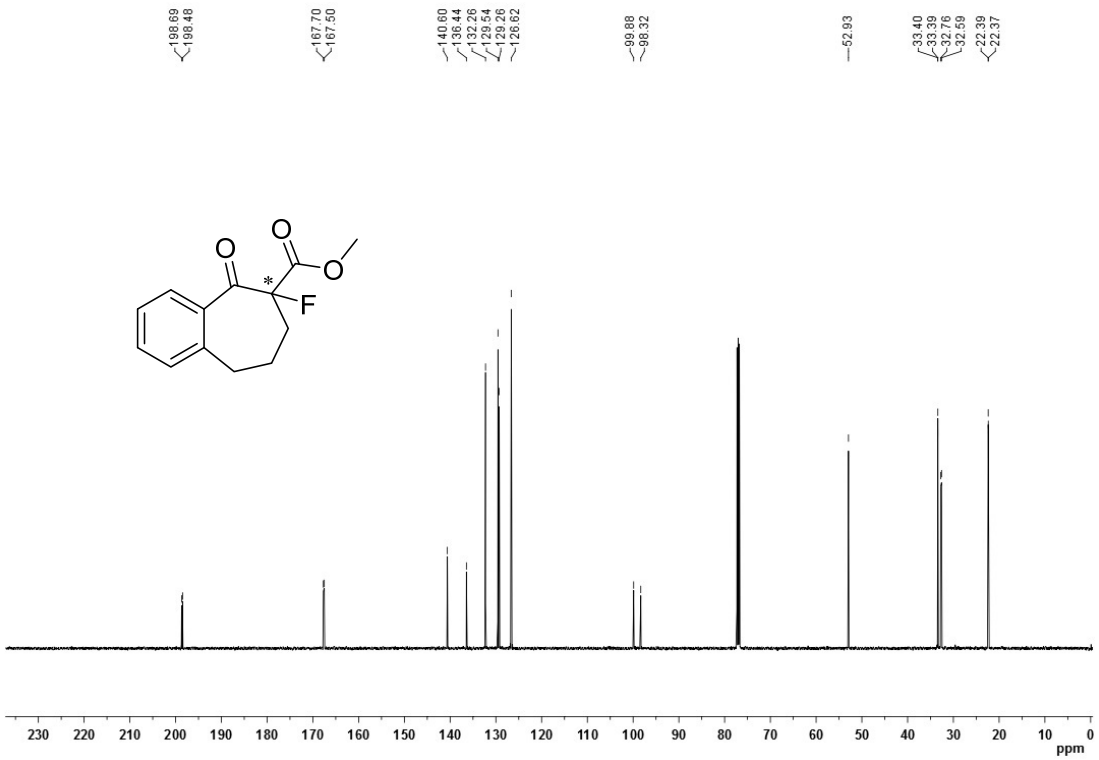
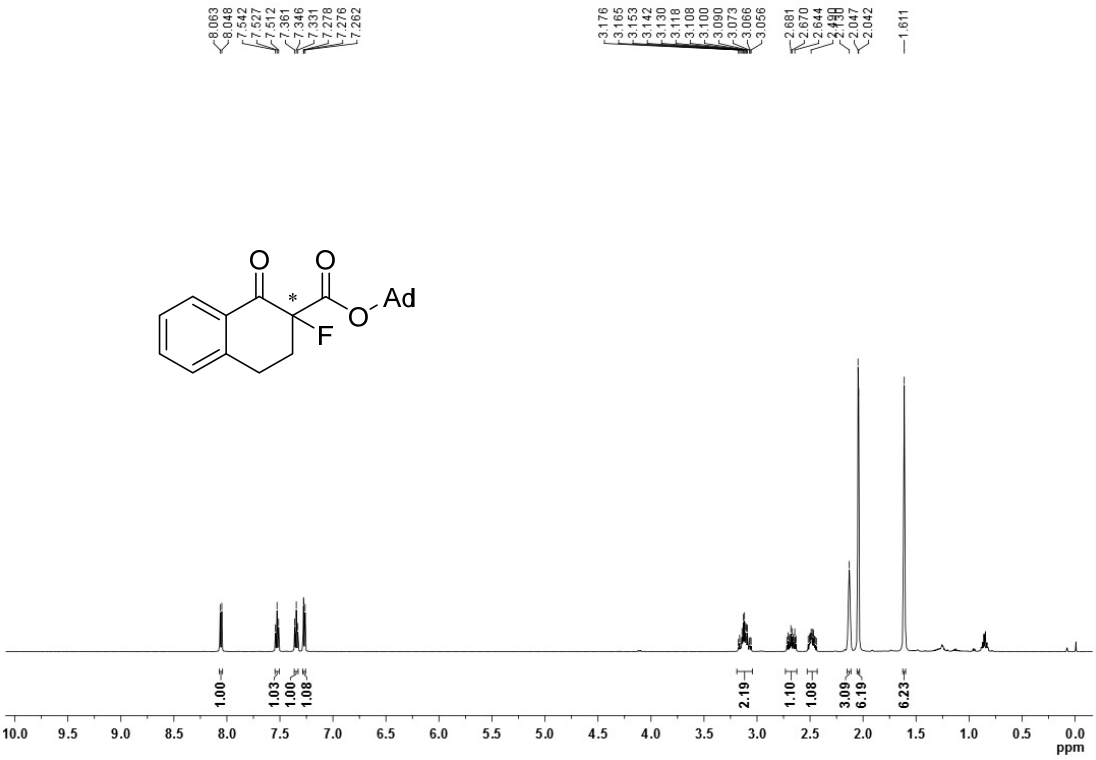
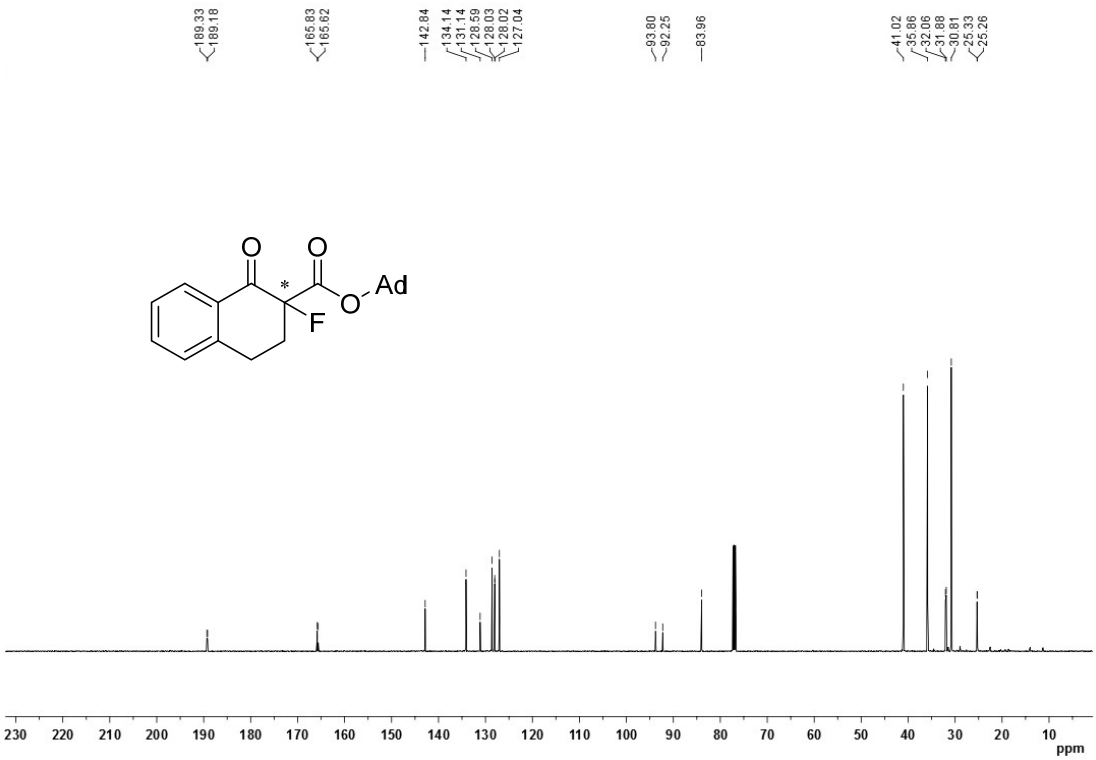
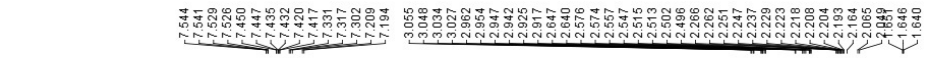
7.534
7.532
7.446
7.444
7.431
7.429
7.416
7.414
7.318
7.303
7.288
7.275
7.218
7.203
3.817
3.136
3.131
3.115
3.105
3.099
3.084
3.078
2.955
2.951
2.945
2.940
2.936
2.924
2.908
2.668
2.664
2.653
2.648
2.638
2.634
2.623
2.596
2.592
2.582
2.577
2.566
2.562
2.551
2.330
2.320
2.314
2.304
2.300
2.290
2.284
2.273
2.270
2.259
2.253
2.243
2.162
2.156
2.152
2.147
2.142
2.137
2.132
2.127
2.122
2.117
1.936
1.931
1.925
1.920
1.915
1.906
1.901
1.897
O
O
O
*
F
1.00
1.01
1.08
1.00
3.00
1.04
1.05
1.06
1.07
1.07
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


198.69
198.48
167.70
167.50
140.60
138.44
132.26
129.54
129.26
126.62
99.88
98.32
52.93
33.40
33.39
32.76
32.59
22.39
22.37
O
O
O
*
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.063
8.048
7.542
7.527
7.512
7.361
7.346
7.331
7.278
7.276
7.262
3.176
3.165
3.153
3.142
3.130
3.118
3.108
3.100
3.090
3.073
3.066
3.056
2.681
2.670
2.644
2.490
2.130
2.047
2.042
1.611
O
O
*
O
Ad
F
1.00
1.03
1.00
1.08
2.19
1.10
1.08
3.09
6.19
6.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


189.33
189.18
165.83
165.62
142.84
134.14
131.14
128.59
128.03
128.02
127.04
93.80
92.25
83.96
41.02
35.86
32.06
31.88
30.81
25.33
25.26
O
O
*
O
Ad
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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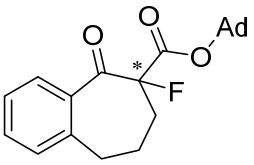
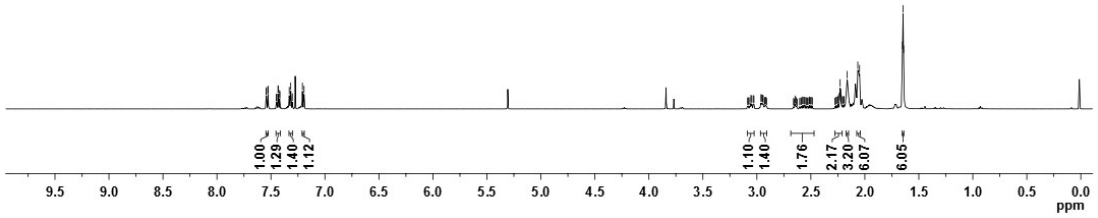
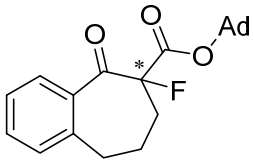
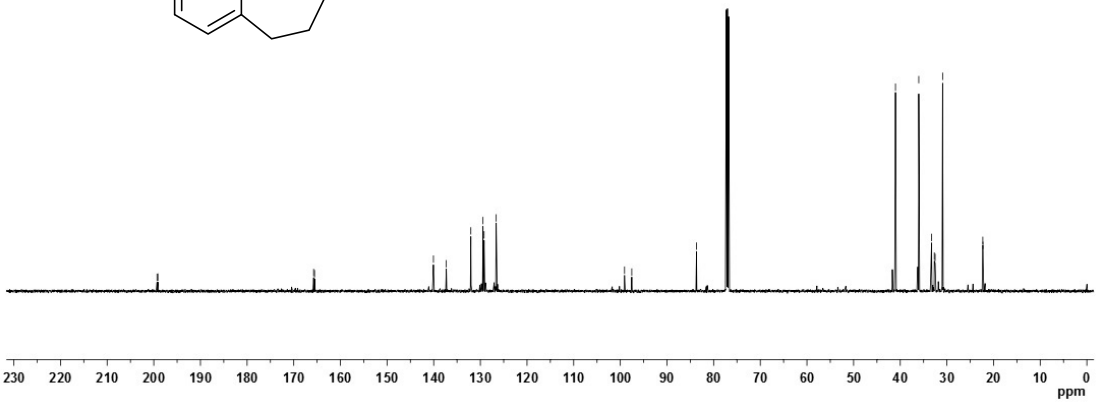
7.541
7.529
7.526
7.450
7.447
7.435
7.432
7.420
7.417
7.331
7.317
7.302
7.209
7.194
3.055
3.048
3.034
3.027
2.962
2.954
2.947
2.942
2.925
2.917
2.647
2.640
2.576
2.574
2.557
2.547
2.515
2.513
2.502
2.496
2.266
2.262
2.251
2.247
2.237
2.229
2.223
2.218
2.208
2.204
2.193
2.164
2.065
1.646
1.640


O
O
Ad
O
*
F

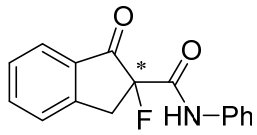

1.00
1.29
1.40
1.12
1.10
1.40
1.76
2.17
3.20
6.07
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

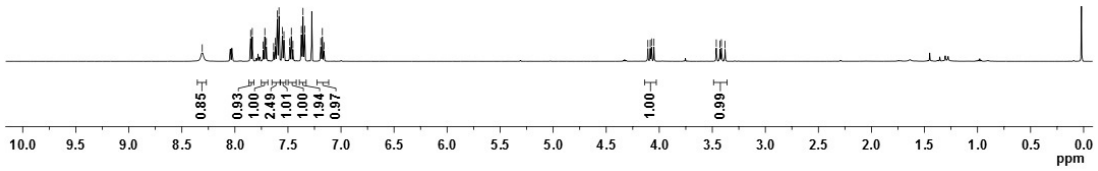

199.31
199.11
165.74
165.54
140.06
137.30
132.04
129.44
129.21
126.61
99.10
97.55
83.67
41.02
36.03
33.29
32.70
32.53
30.92
22.31
22.28


O
O
Ad
O
*
F

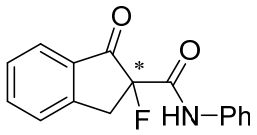

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.308
7.852
7.836
7.733
7.718
7.703
7.635
7.619
7.600
7.584
7.553
7.538
7.483
7.468
7.453
7.373
7.358
7.342
7.190
7.176
7.161
4.107
4.085
4.073
4.050
3.462
3.428
3.414
3.380

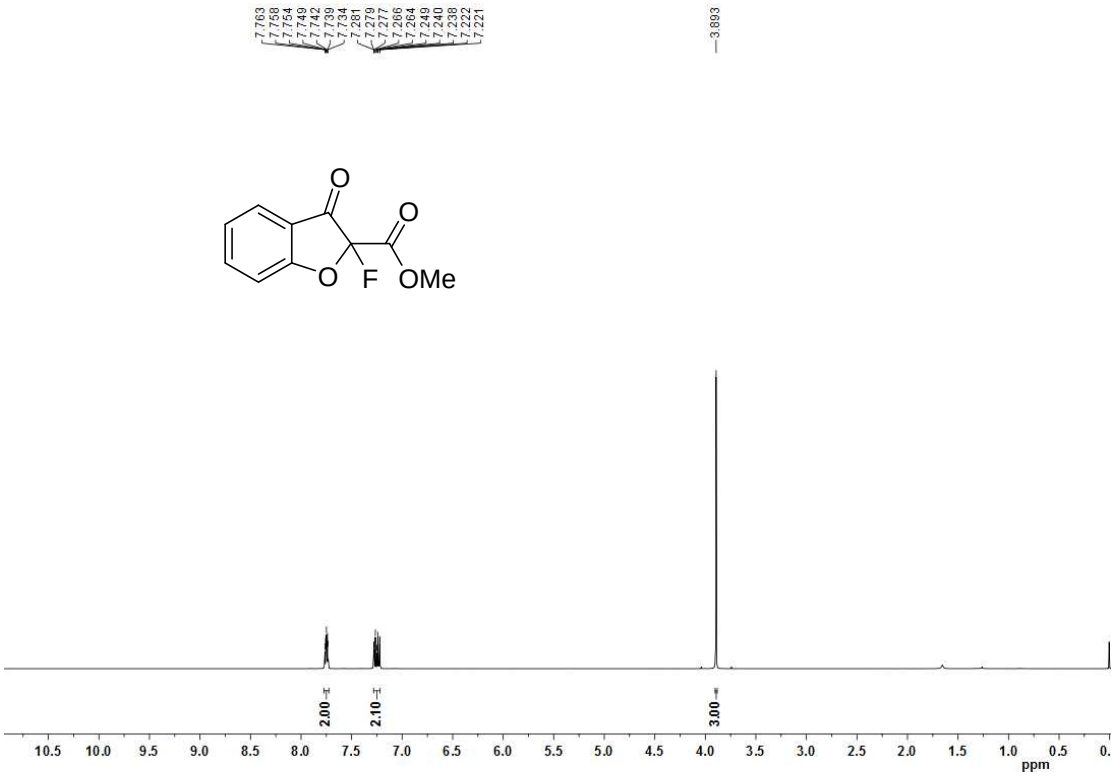

O
O
*
F HN−Ph


0.85
0.93
1.00
2.49
1.01
1.00
1.94
0.97
1.00
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


196.37
196.23
164.84
164.67
151.85
151.81
136.84
129.11
128.54
126.56
125.58
125.22
120.13
97.84
96.22
37.48
37.30


O
O
*
F HN−Ph

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.754
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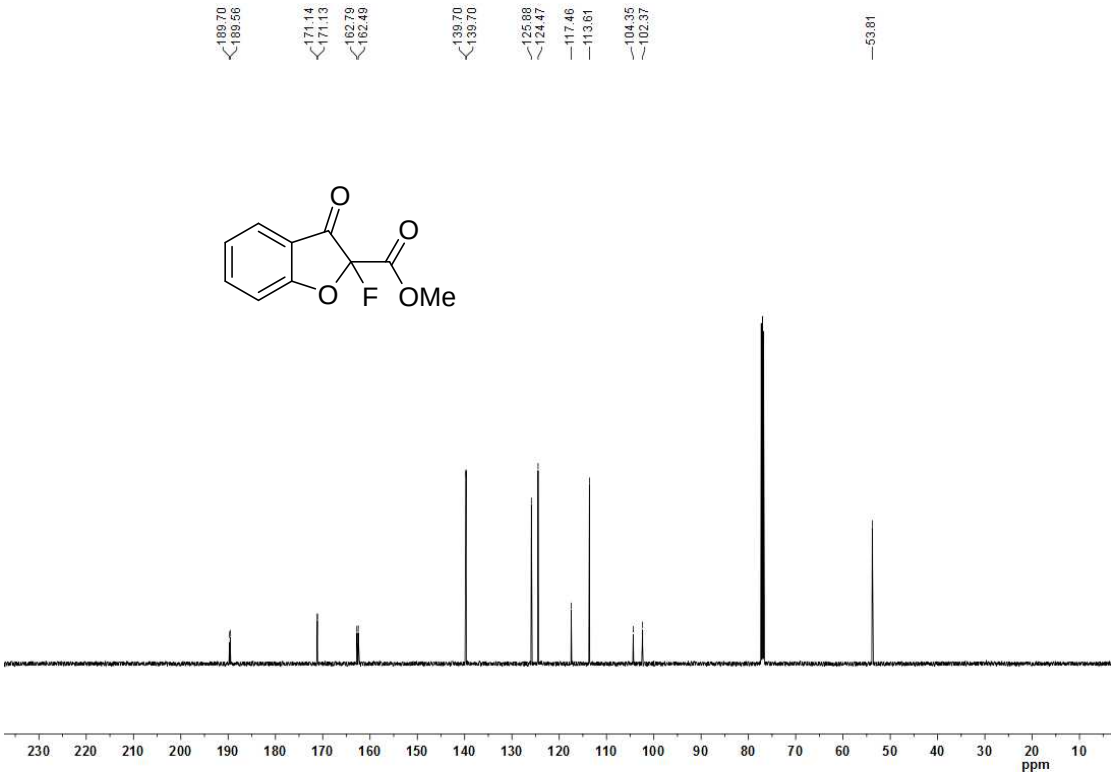
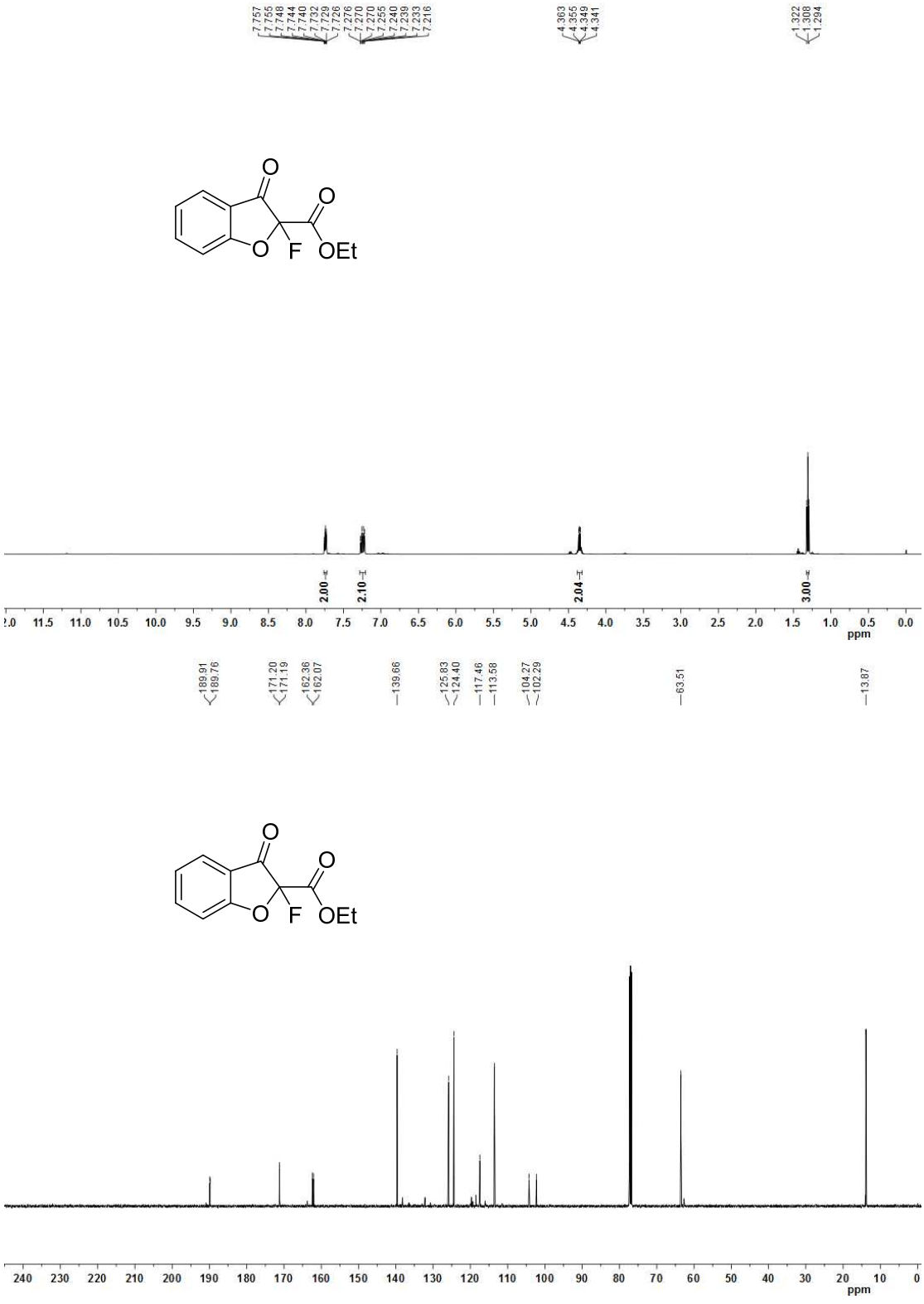
7.742
7.739
7.734
7.281
7.279
7.277
7.266
7.264
7.249
7.240
7.238
7.222
7.221
3.893
O
O
O
F
OMe
2.00
2.10
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm


189.70
189.56
171.14
171.13
162.79
162.49
139.70
139.70
125.88
124.47
117.46
113.61
104.35
102.37
53.81
O
O
O
F
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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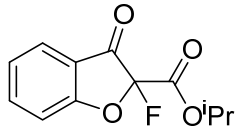
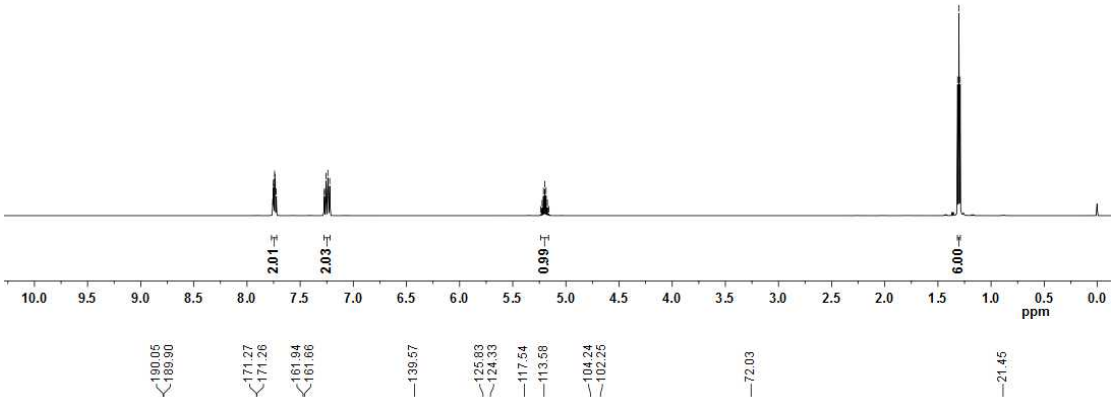
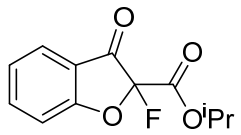
7.756
7.748
7.744
7.740
7.732
7.729
7.726
7.276
7.270
7.270
7.255
7.240
7.239
7.233
7.216
4.363
4.355
4.349
4.341
1.322
1.308
1.294
O
O
O
F
OEt
2.00
2.10
2.04
3.00
ppm
189.91
189.76
171.20
171.19
162.36
162.07
139.66
125.83
124.40
117.46
113.58
104.27
102.29
63.51
13.87
O
O
O
F
OEt
ppm

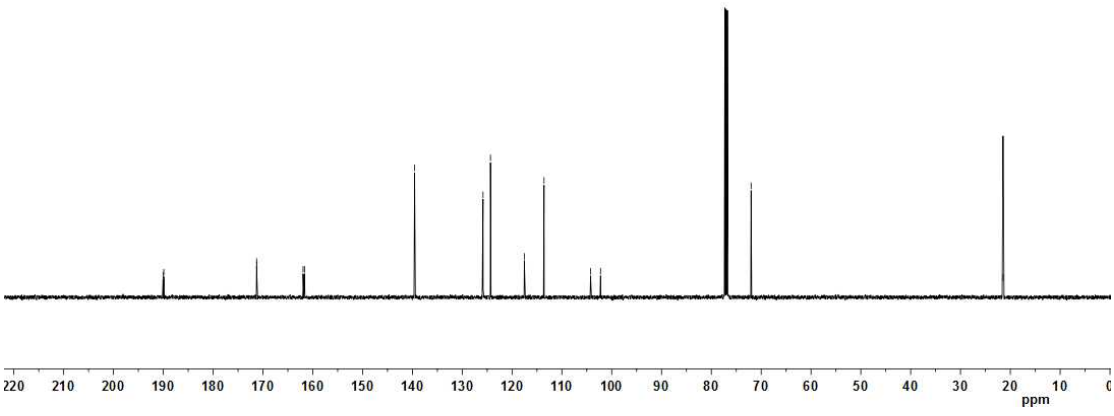

7.759
7.756
7.752
7.749
7.744
7.741
7.737
7.734
7.727
7.724
7.276
7.272
7.271
7.256
7.240
7.229
7.222
5.237
5.224
5.212
5.199
5.186
5.174
5.162
1.315
1.303
1.291

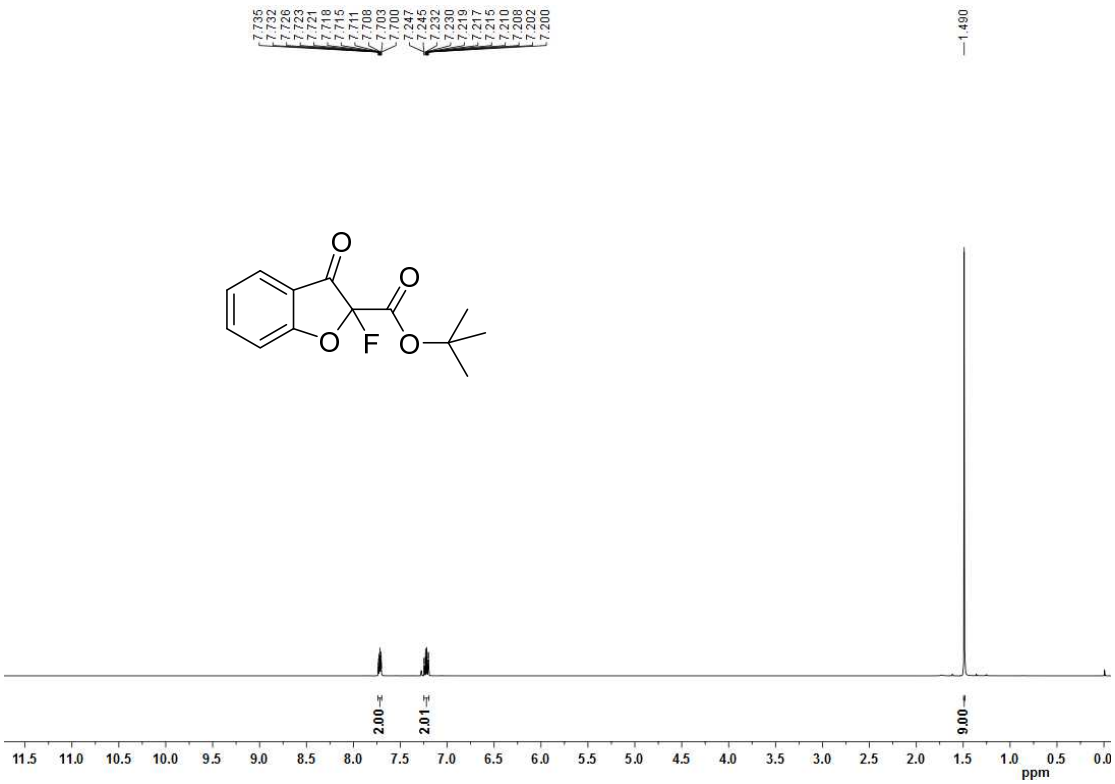

O
O
O
F
O^{i}Pr

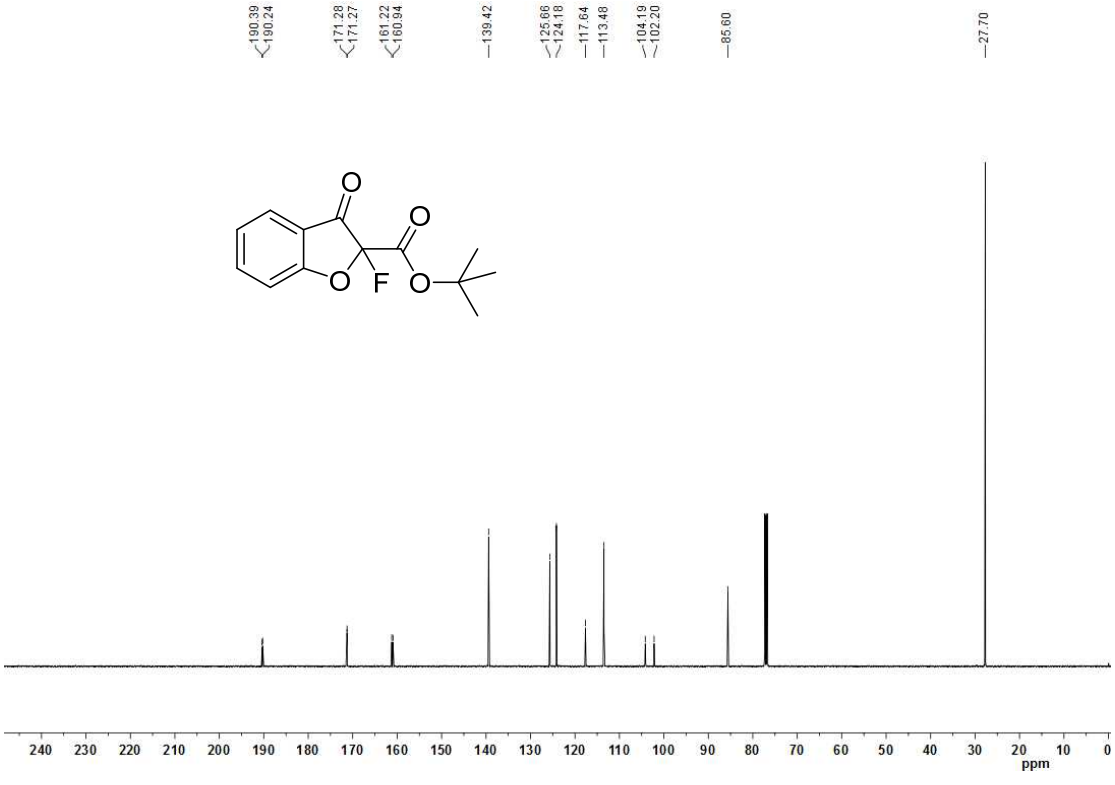

2.01
2.03
0.99
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

190.05
189.90
171.27
171.26
161.94
161.66
139.57
125.83
124.33
117.54
113.58
104.24
102.25
72.03
21.45


O
O
O
F
O^{i}Pr


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.735
7.732
7.726
7.723
7.721
7.718
7.715
7.711
7.708
7.703
7.700
7.247
7.245
7.232
7.230
7.219
7.217
7.215
7.210
7.208
7.202
7.200
1.490
O
O
O
F
O
2.00
2.01
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


190.39
190.24
171.28
171.27
161.22
160.94
139.42
125.66
124.18
117.64
113.48
104.19
102.20
85.60
27.70
O
O
O
F
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.751
7.735
7.731
7.719
7.716
7.391
7.385
7.381
7.373
7.370
7.366
7.363
7.359
7.354
7.347
7.337
7.332
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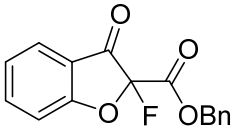
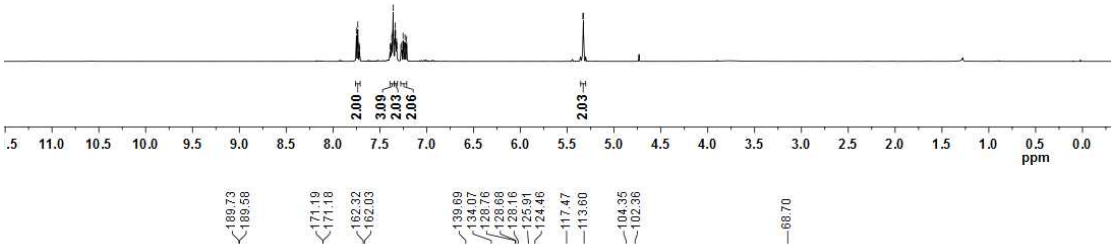
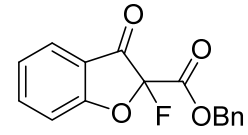
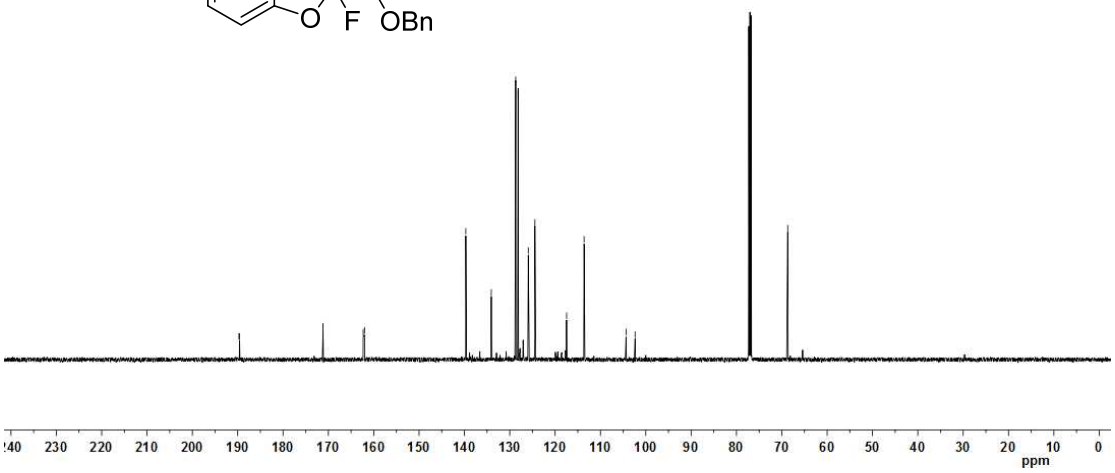
7.237
7.231
7.215
7.213
5.334
5.328

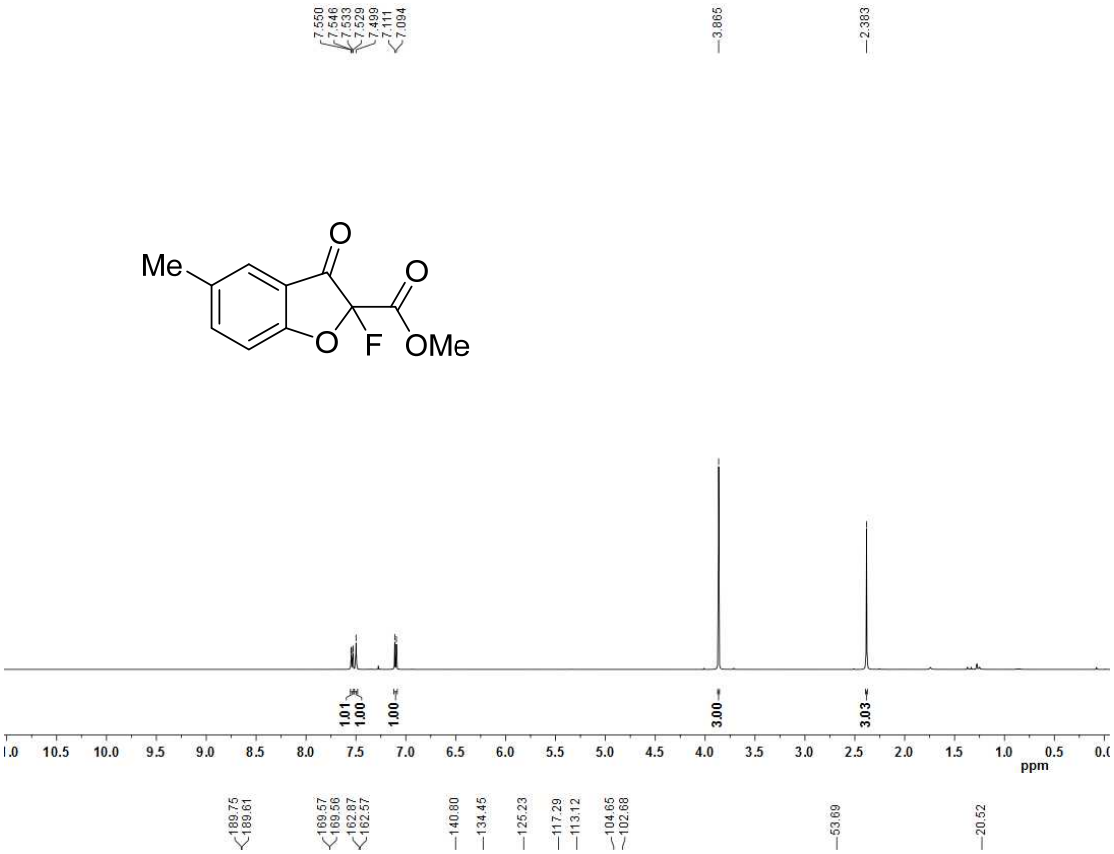

O
O
O
F
OBn


2.00
3.09
2.03
2.06
2.03
ppm

189.73
189.58
171.19
171.18
162.32
162.03
139.69
134.07
128.76
128.68
128.16
125.91
124.46
117.47
113.60
104.35
102.36
68.70


O
O
O
F
OBn


ppm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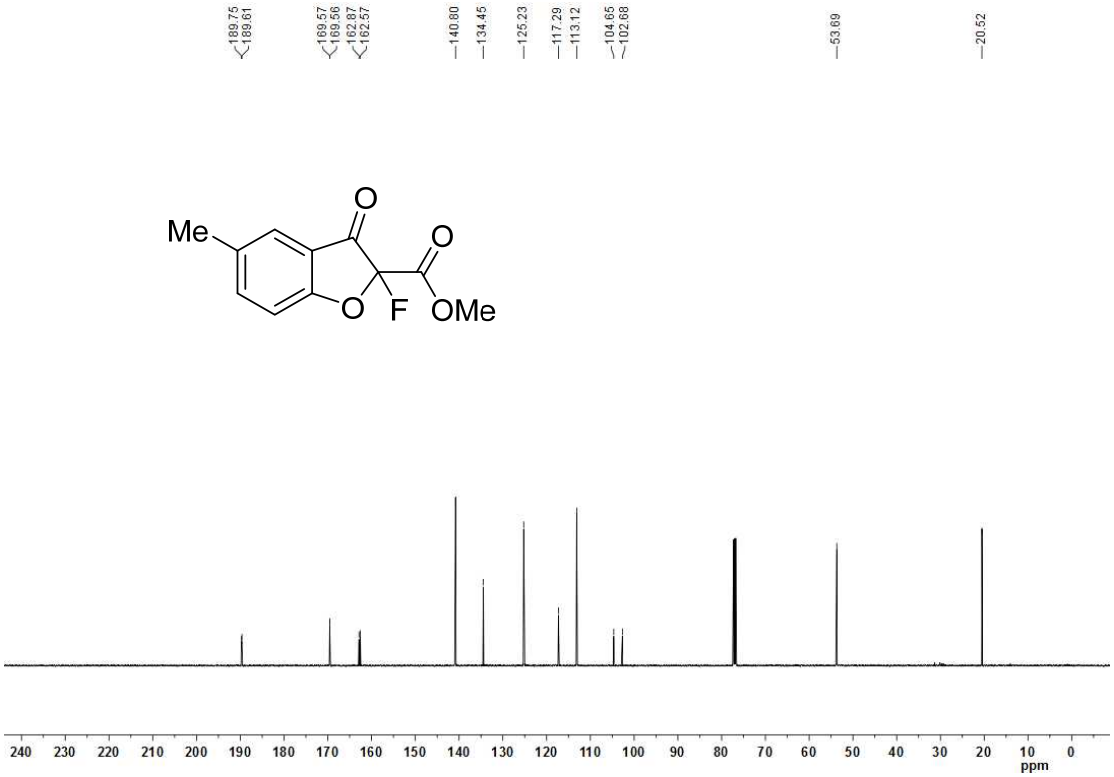
7.546
7.533
7.529
7.499
7.111
7.094
3.865
2.383
Me
O
O
O
F
OMe
1.01
1.00
1.00
3.00
3.03
ppm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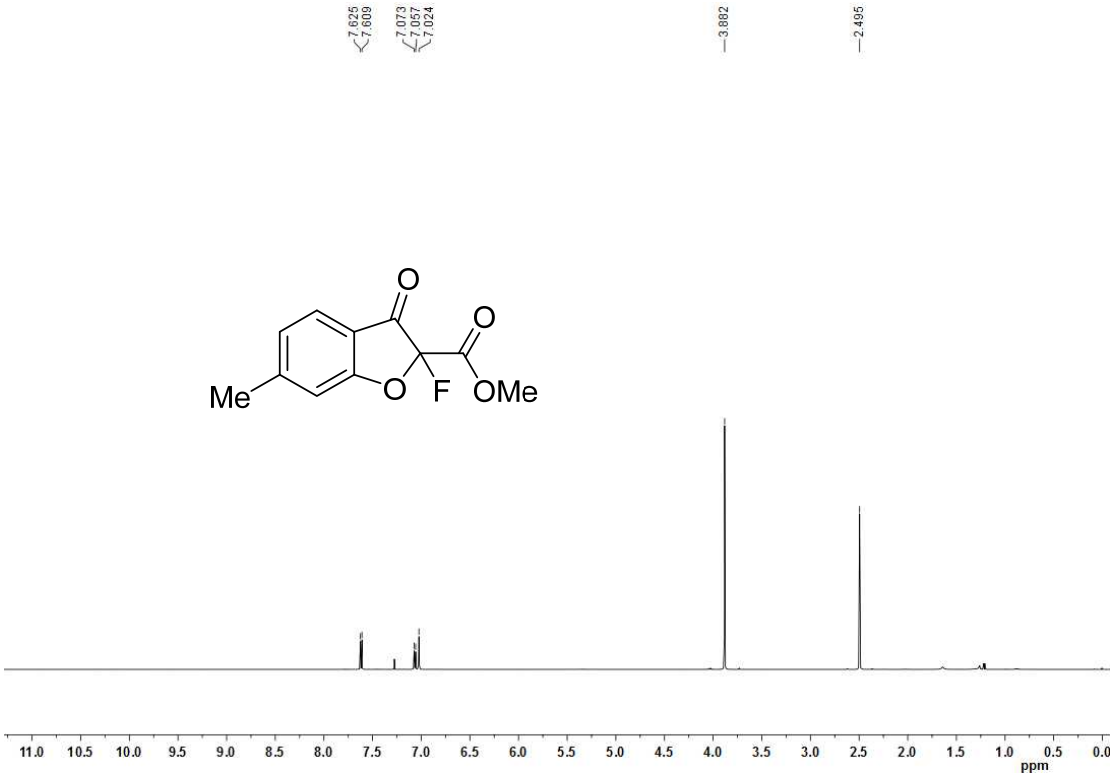
169.57
169.56
162.87
162.57
140.80
134.45
125.23
117.29
113.12
104.65
102.68
53.69
20.52
Me
O
O
O
F
OMe
ppm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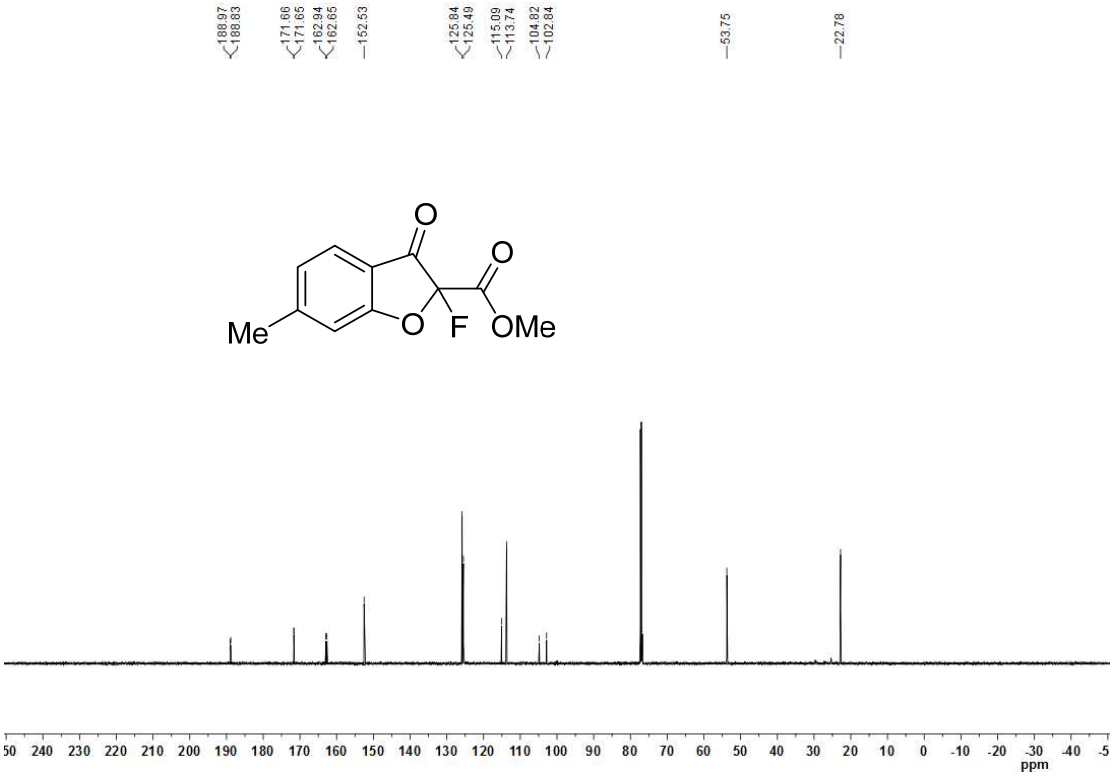
7.609
7.073
7.057
7.024
3.882
2.495
O
O
Me
O
F
OMe
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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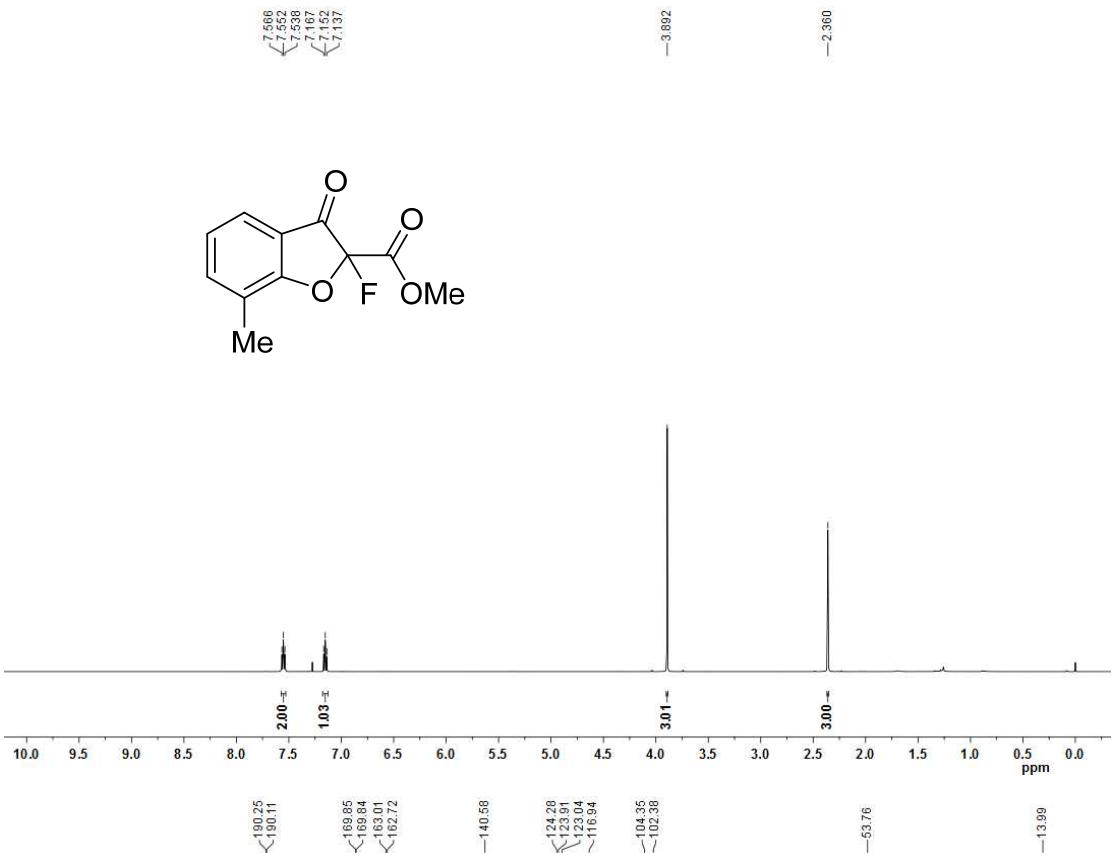
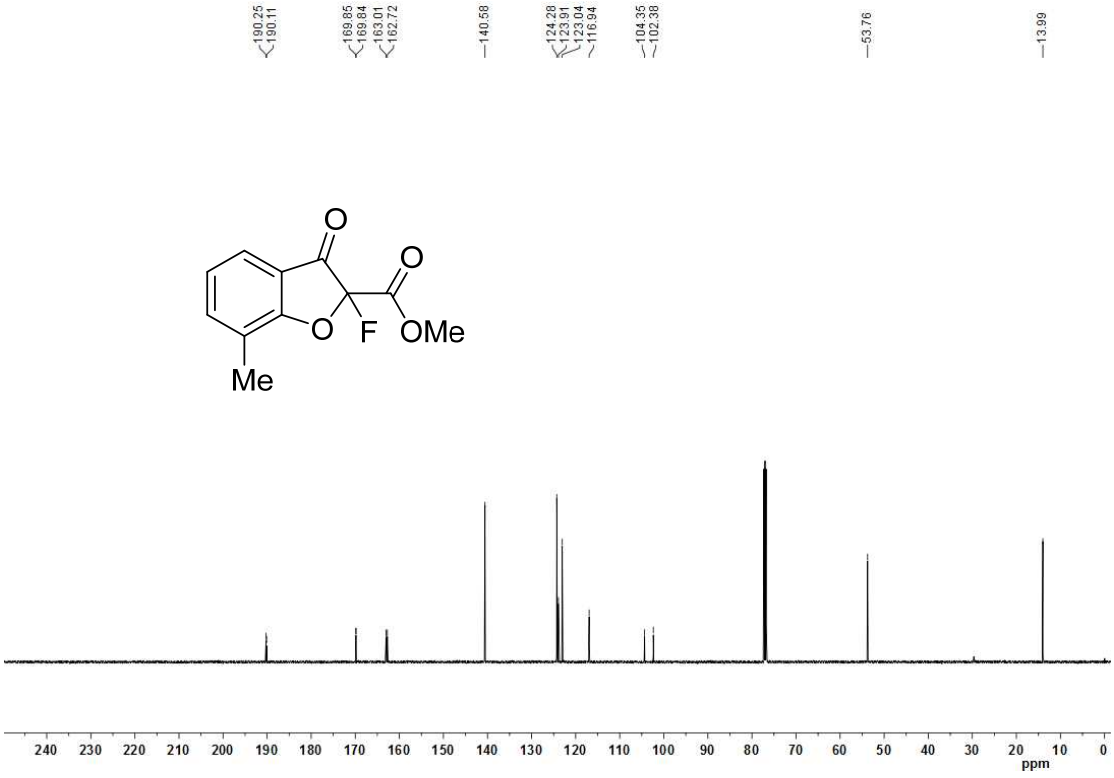
188.83
171.66
171.65
162.94
162.65
152.53
125.84
125.49
115.09
113.74
104.82
102.84
53.75
22.78
O
O
Me
O
F
OMe
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
ppm


7.666
7.552
7.538
7.167
7.152
7.137
3.892
2.360
O
O
O
F
OMe
Me
2.00
1.03
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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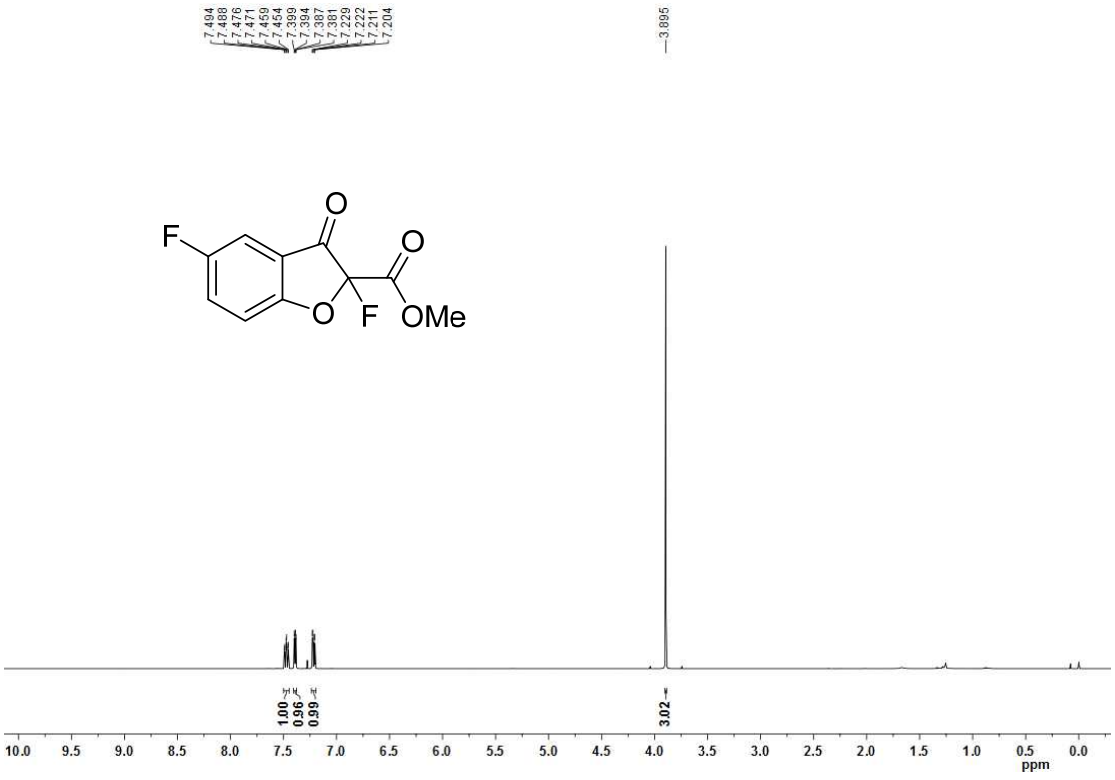
190.11
169.85
169.84
163.01
162.72
140.58
124.28
123.91
123.04
116.94
104.35
102.38
53.76
13.99
O
O
O
F
OMe
Me
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.476
7.471
7.459
7.454
7.399
7.394
7.387
7.381
7.229
7.222
7.211
7.204
3.895
O
F
O
O
F
OMe
1.00
0.96
0.99
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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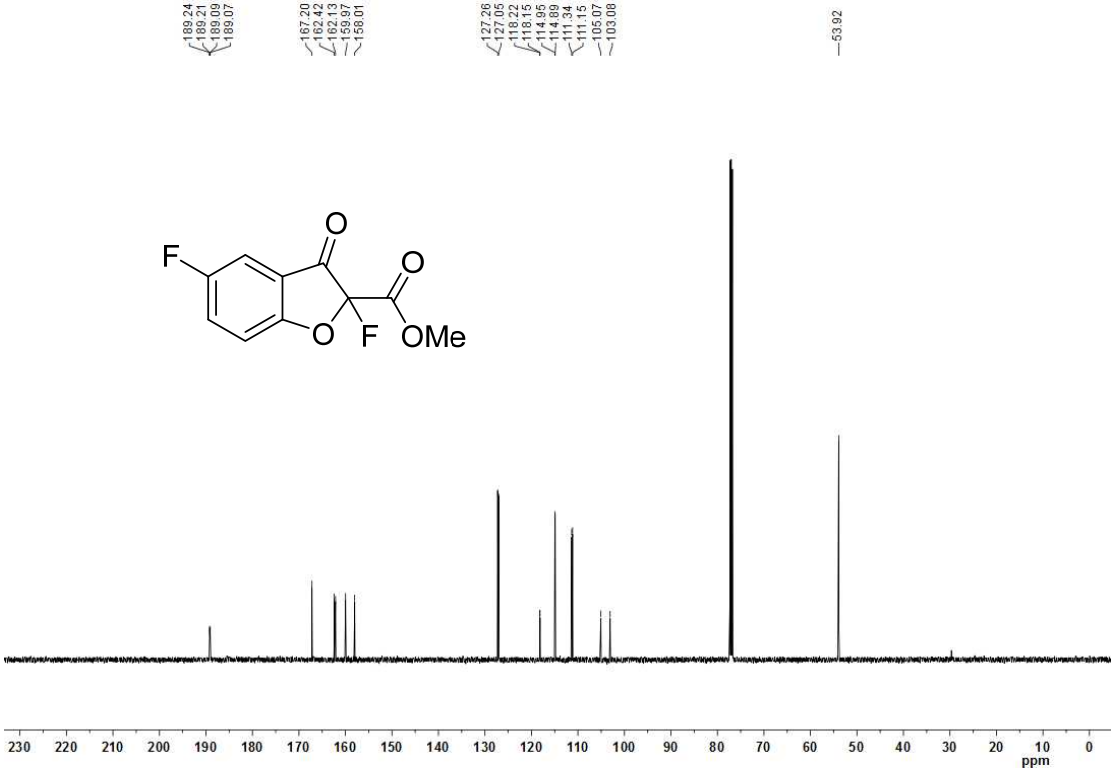
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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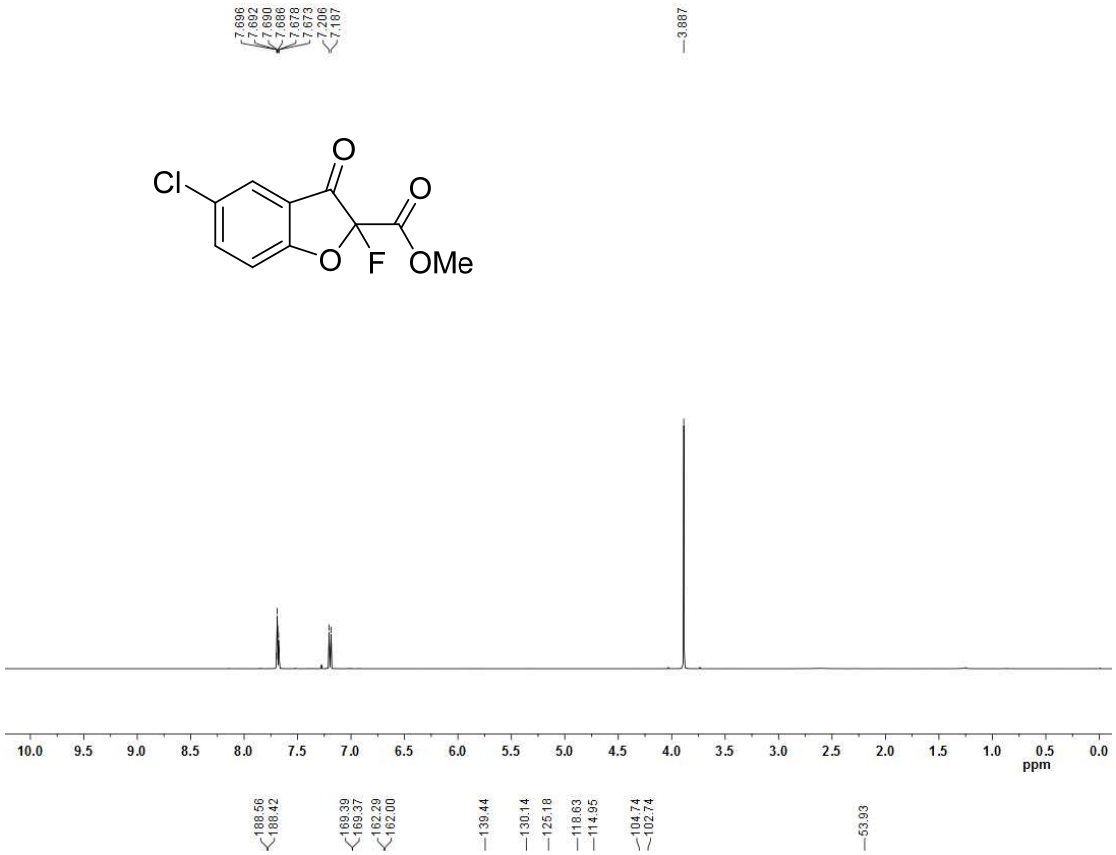
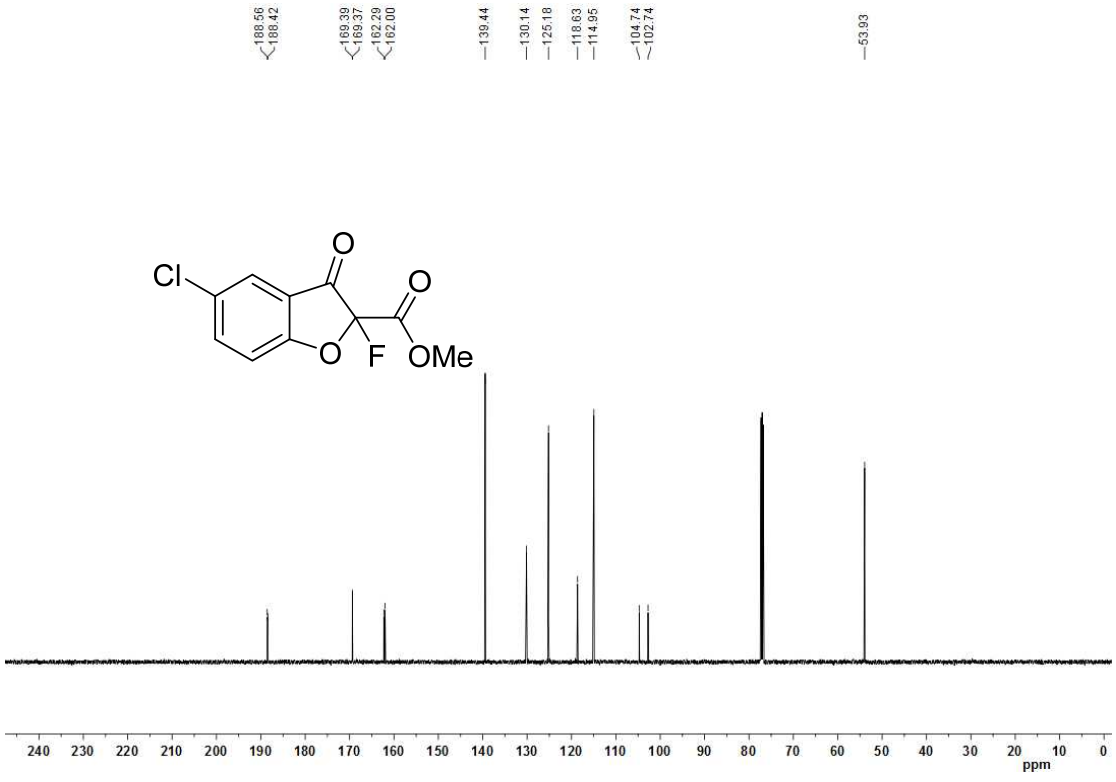
189.21
189.09
189.07
167.20
162.42
162.13
159.97
158.01
127.26
127.05
118.22
118.15
114.95
114.89
111.34
111.15
105.07
103.08
53.92
O
F
O
O
F
OMe
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.696
7.692
7.690
7.686
7.678
7.673
7.206
7.187
3.887
Cl
O
O
O
F
OMe
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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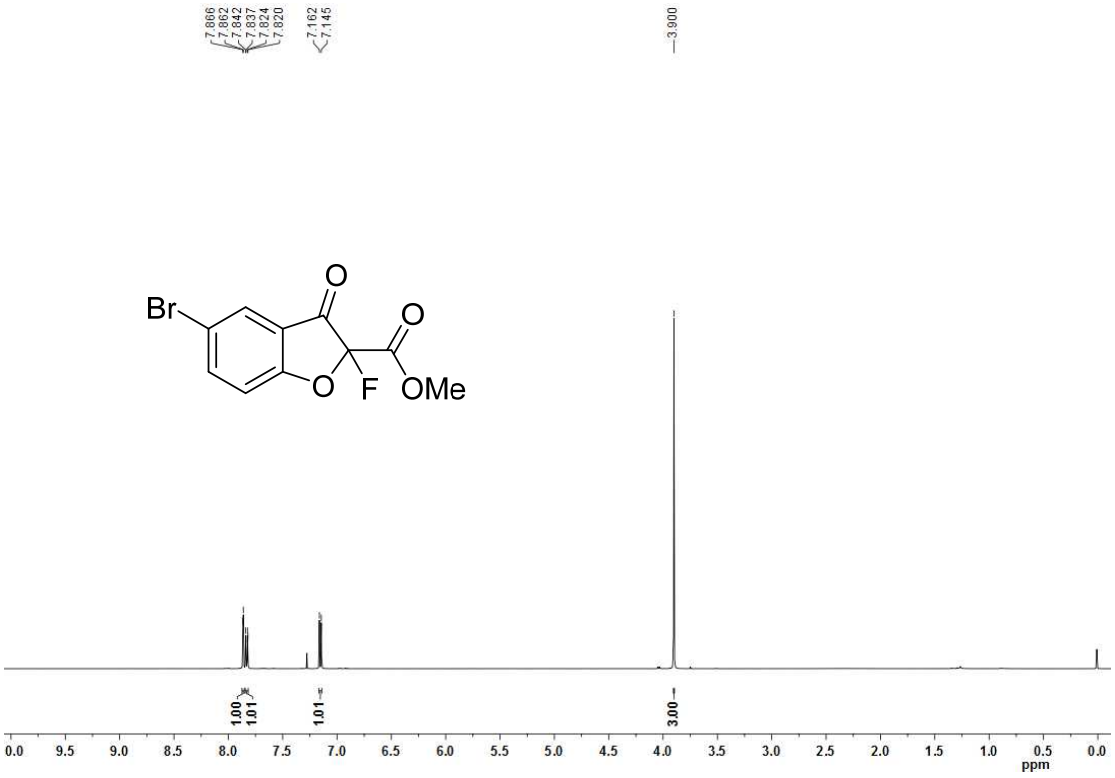
188.42
169.39
169.37
162.29
162.00
139.44
130.14
125.18
118.63
114.95
104.74
102.74
53.93
Cl
O
O
O
F
OMe
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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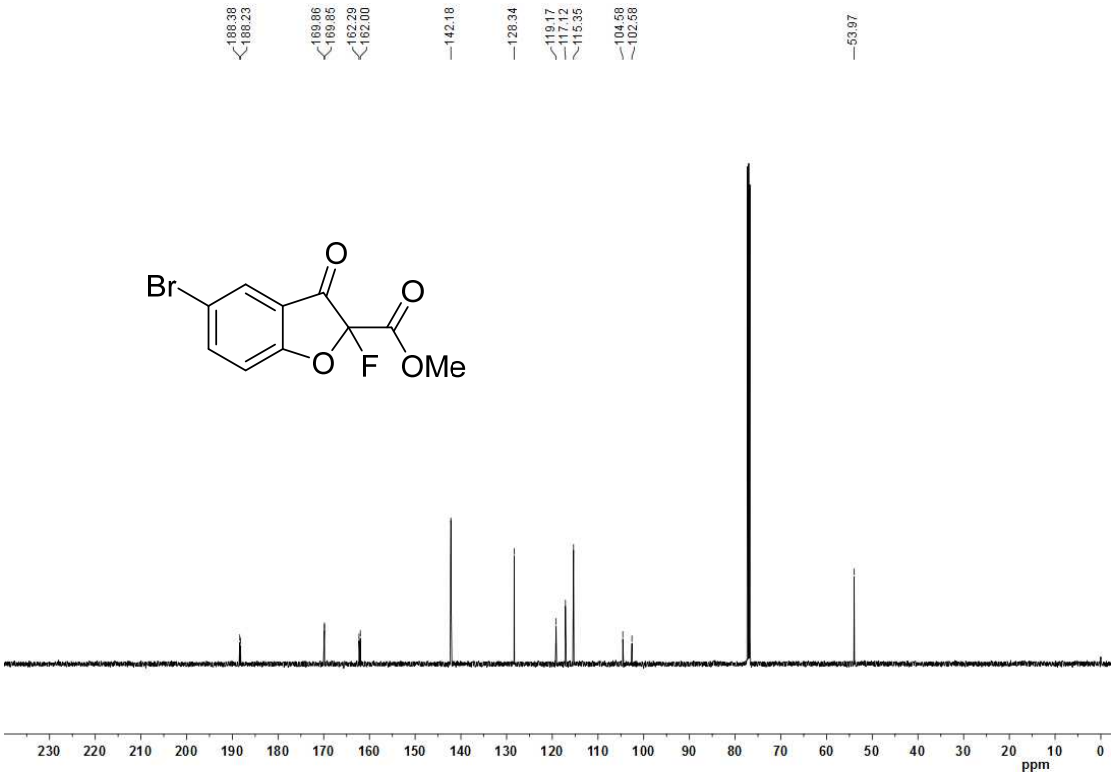
7.862
7.842
7.837
7.824
7.820
7.162
7.145
3.900
Br
O
O
O
F
OMe
1.00
1.01
1.01
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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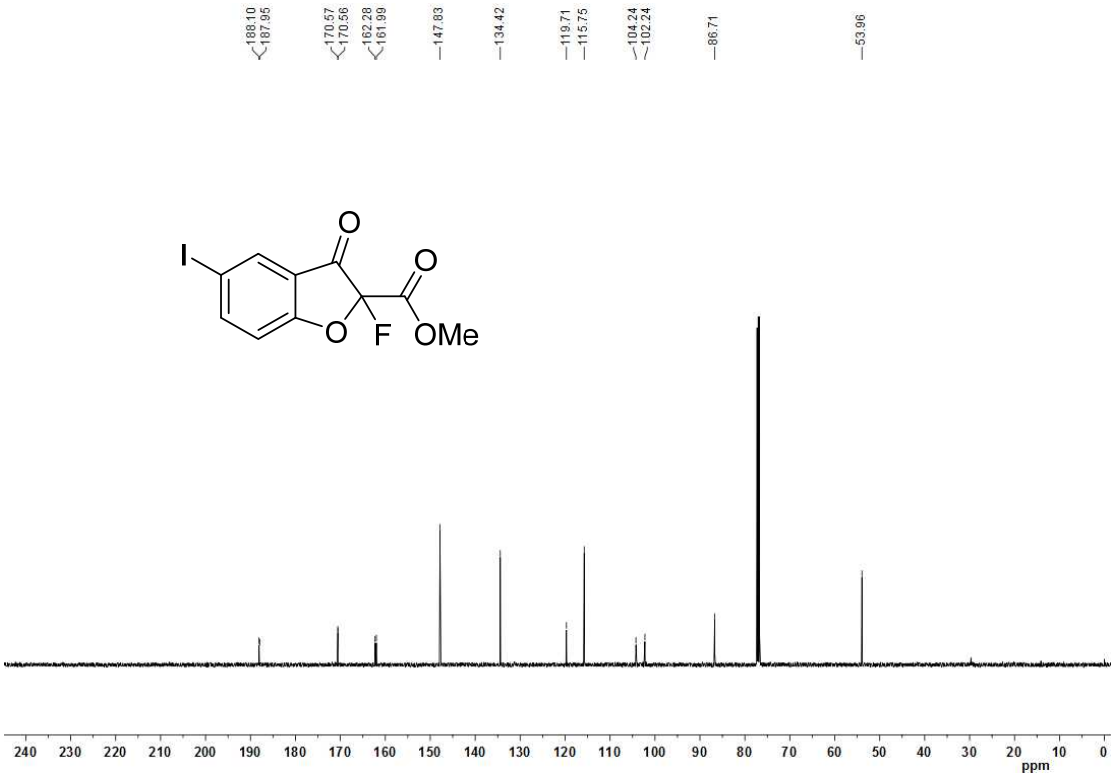
188.23
169.86
169.85
162.29
162.00
142.18
128.34
119.17
117.12
115.35
104.58
102.58
53.97
Br
O
O
O
F
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.055
8.051
8.007
8.003
7.989
7.986
7.054
7.037
3.895
I
O
O
O
F
OMe
1.00
1.05
1.03
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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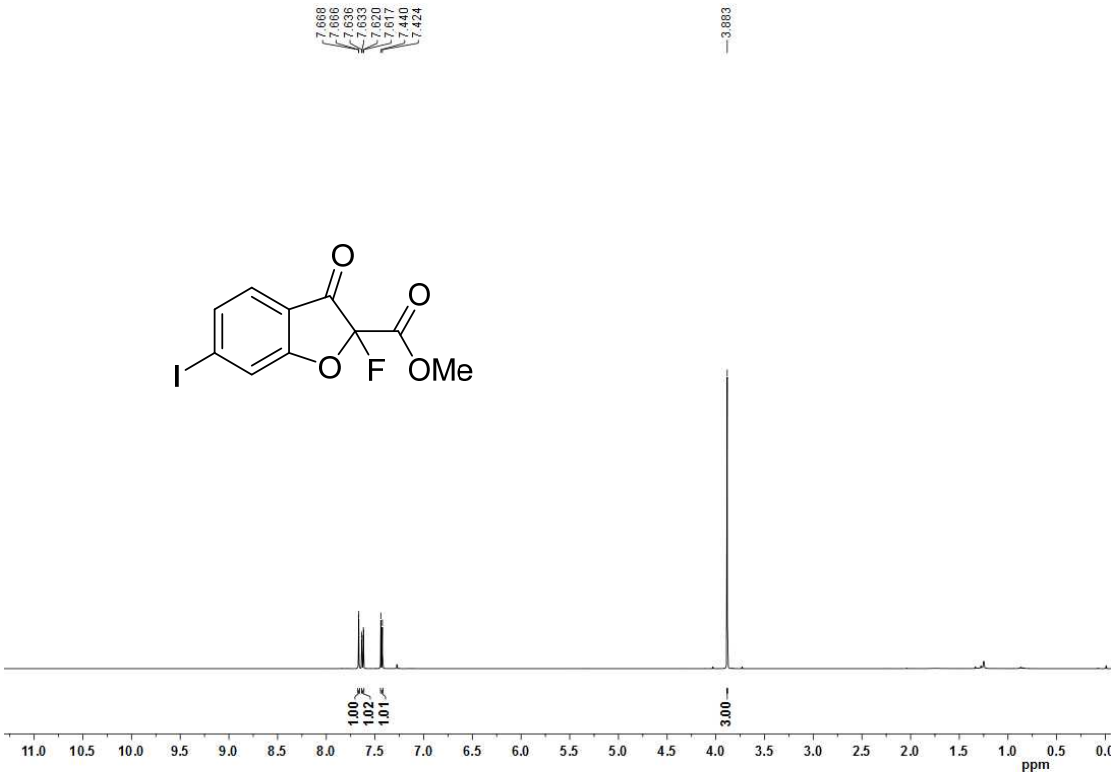
187.95
170.57
170.58
162.28
161.99
147.83
134.42
119.71
115.75
104.24
102.24
86.71
53.96
I
O
O
O
F
OMe
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.636
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7.617
7.440
7.424
3.883
O
O
I
O
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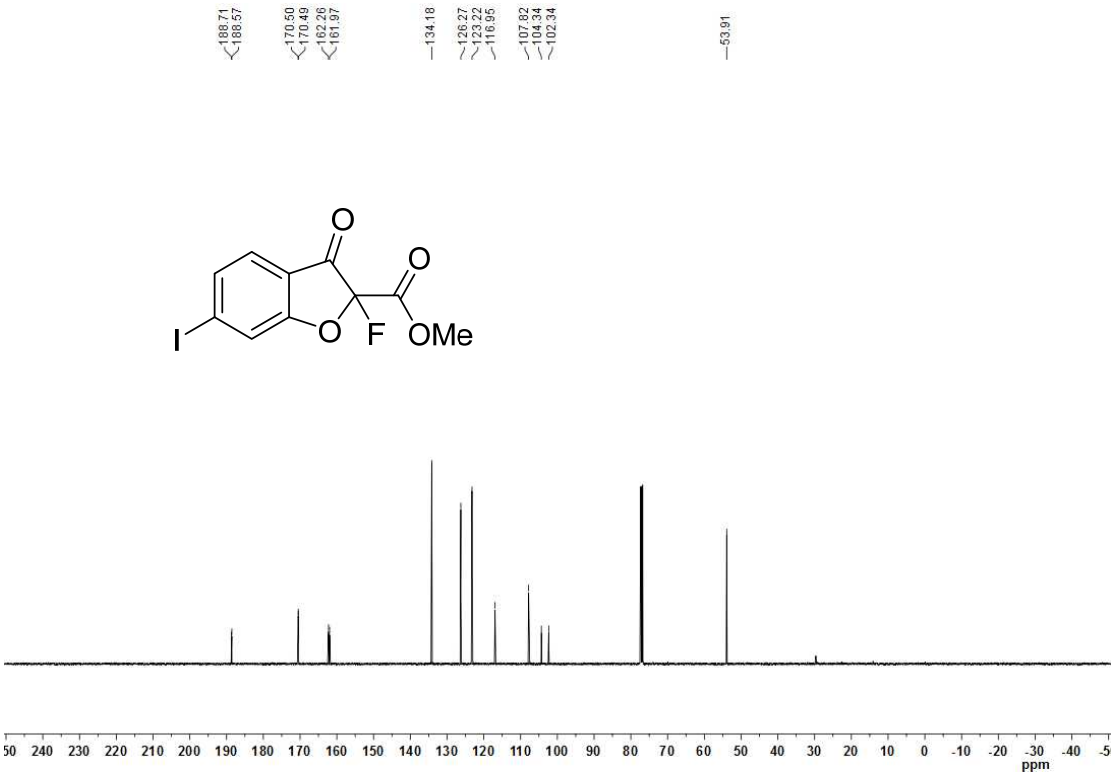
1.00
1.02
1.01
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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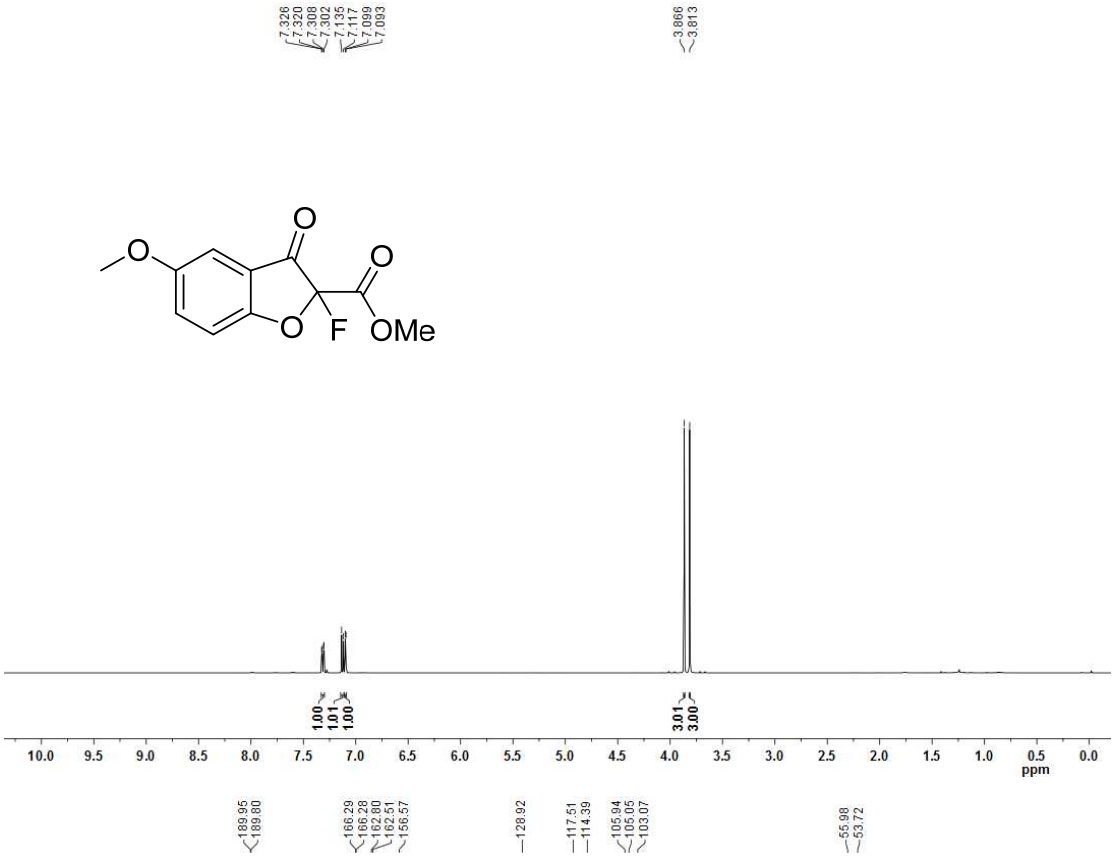
170.50
170.49
162.26
161.97
134.18
126.27
123.22
116.95
107.82
104.34
102.34
53.91
O
O
I
O
F
OMe
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
ppm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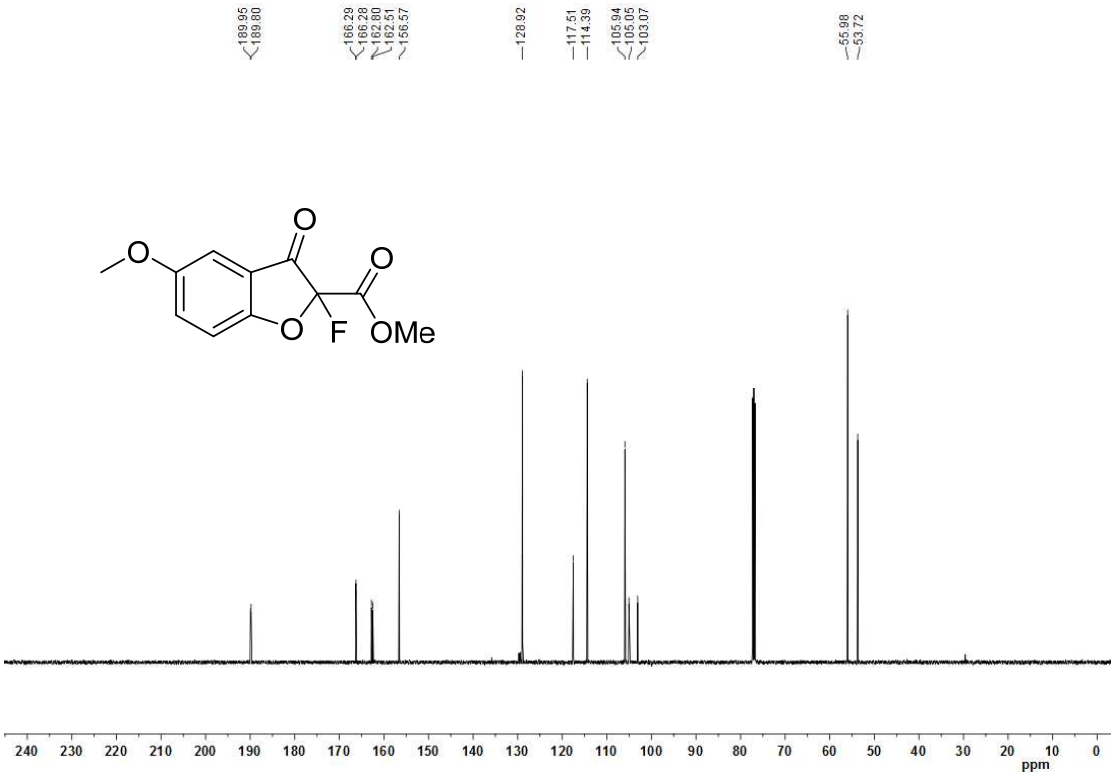
7.320
7.308
7.302
7.135
7.117
7.099
7.093
3.866
3.813
O
O
O
O
F
OMe
1.00
1.01
1.00
3.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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189.80
166.29
166.28
162.80
162.51
156.57
128.92
117.51
114.39
105.94
105.05
103.07
55.98
53.72
O
O
O
O
F
OMe
240
230
220
210
200
190
180
170
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150
140
130
120
110
100
90
80
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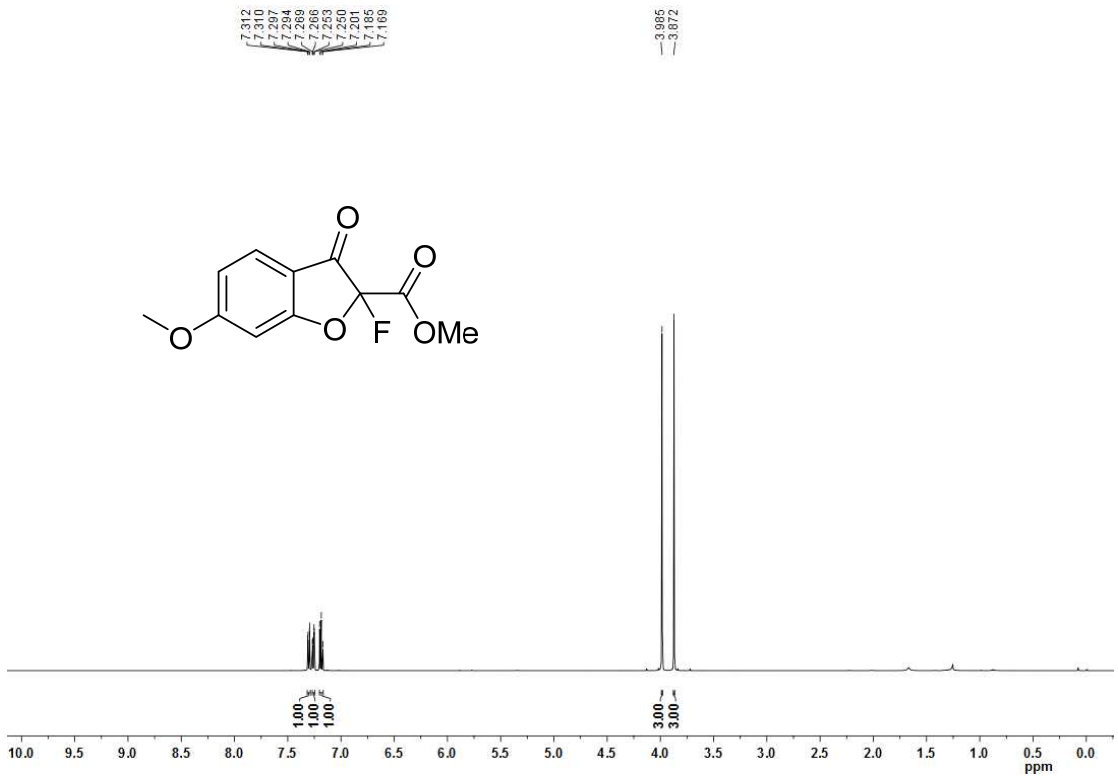
60
50
40
30
20
10
0
ppm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7.310
7.297
7.294
7.289
7.286
7.253
7.250
7.201
7.195
7.169
3.985
3.872
O
O
O
O
F
OMe
1.00
1.00
1.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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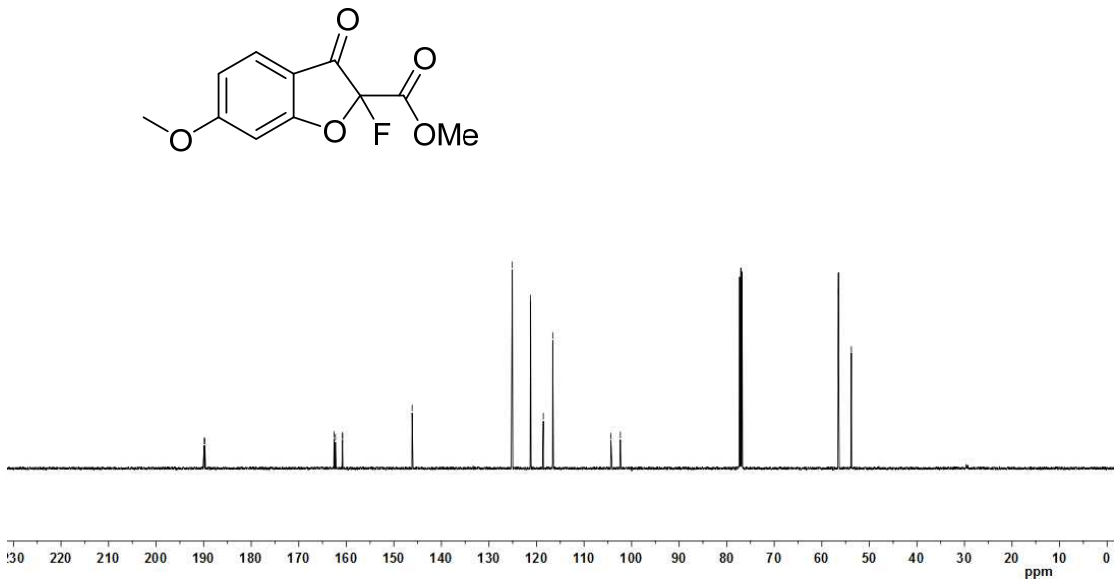
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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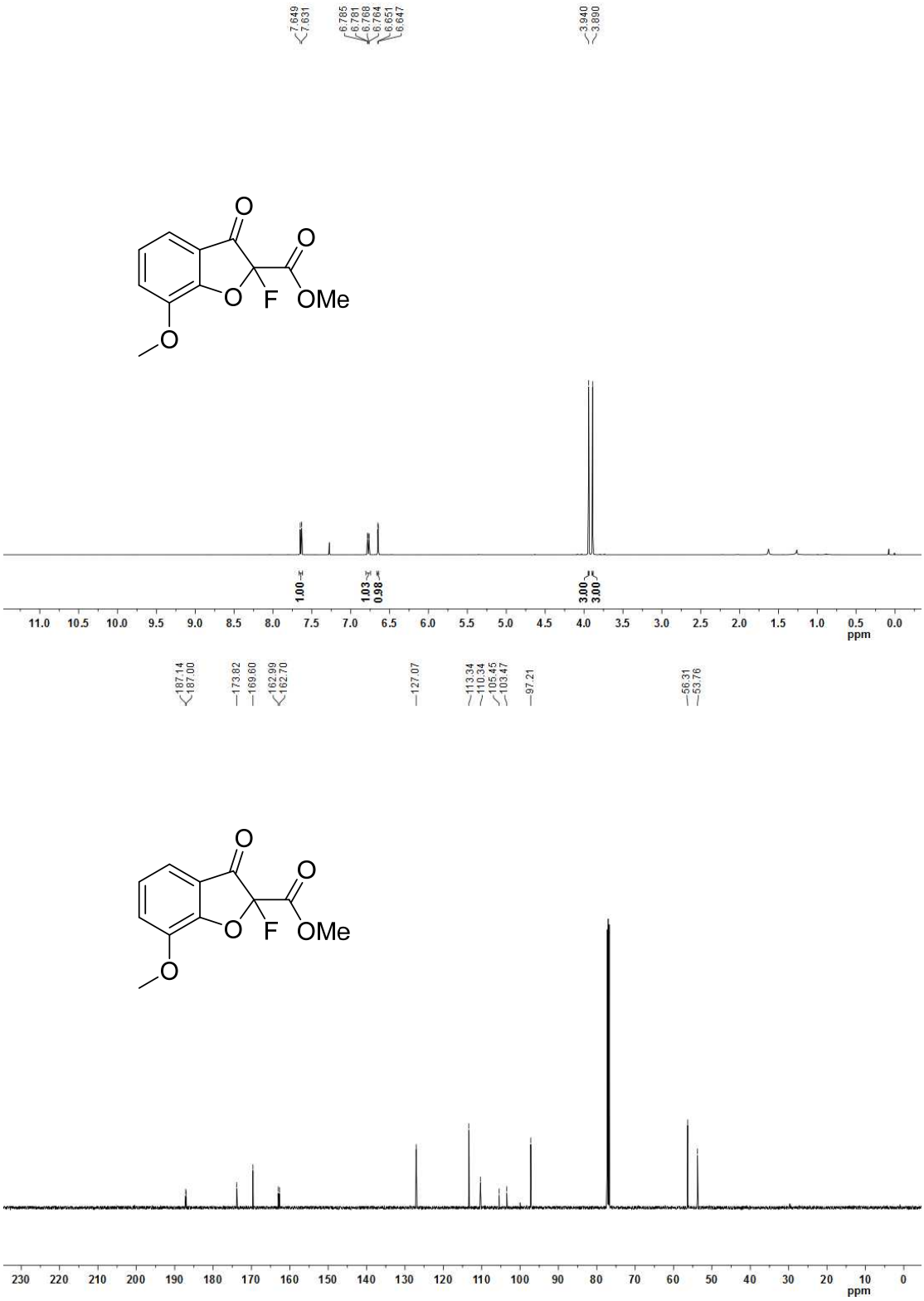
160.79
146.16
125.09
121.24
118.57
116.59
104.36
102.37
56.50
53.78
O
O
O
O
F
OMe
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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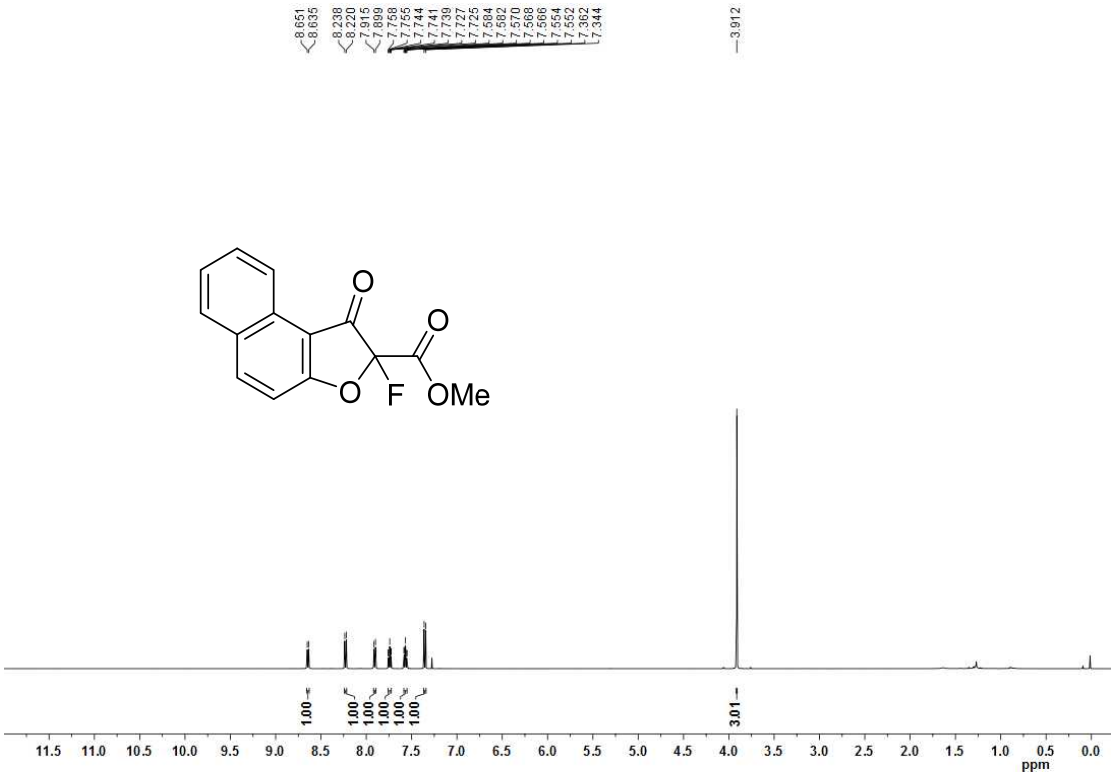
6.785
6.781
6.768
6.764
6.651
6.647
3.940
3.890
O
O
O
F
OMe
O
1.00
1.03
0.98
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
187.14
187.00
173.82
169.60
162.99
162.70
127.07
113.34
110.34
105.45
103.47
97.21
56.31
53.76
O
O
O
F
OMe
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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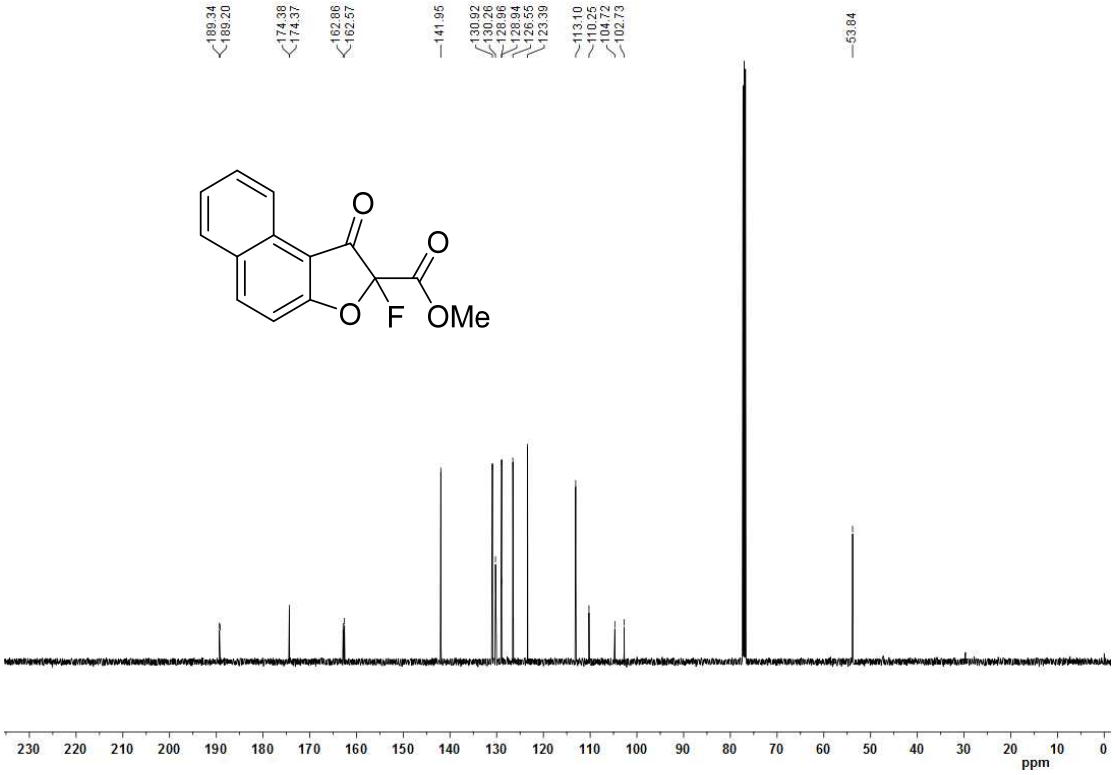
7.899
7.758
7.755
7.744
7.741
7.739
7.727
7.725
7.584
7.582
7.570
7.568
7.566
7.554
7.552
7.362
7.344
3.912
O
O
O
F
OMe
1.00
1.00
1.00
1.00
1.00
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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174.37
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130.26
128.96
128.94
126.55
123.39
113.10
110.25
104.72
102.73
53.84
O
O
O
F
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.367
7.982
7.966
7.850
7.834
7.679
7.677
7.666
7.663
7.660
7.649
7.647
7.515
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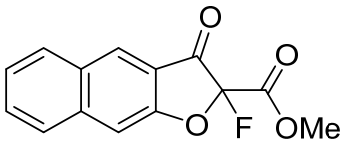
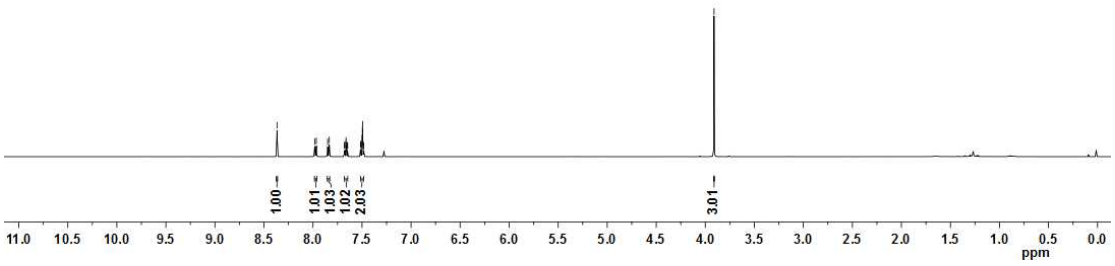
7.502
7.499
7.496
7.494
7.485
7.483
3.911


O
O
O
F
OMe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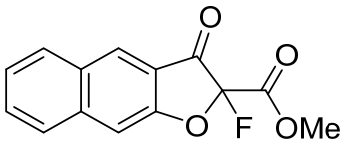
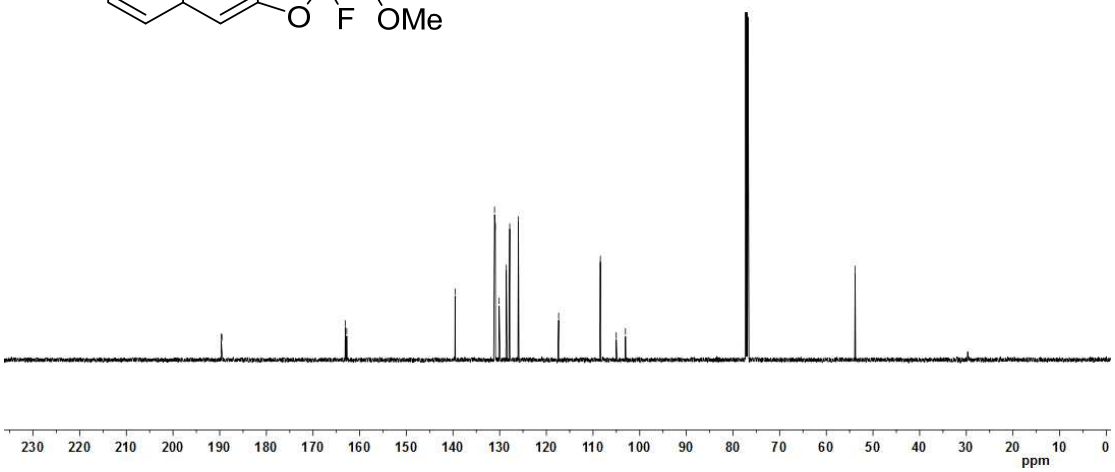
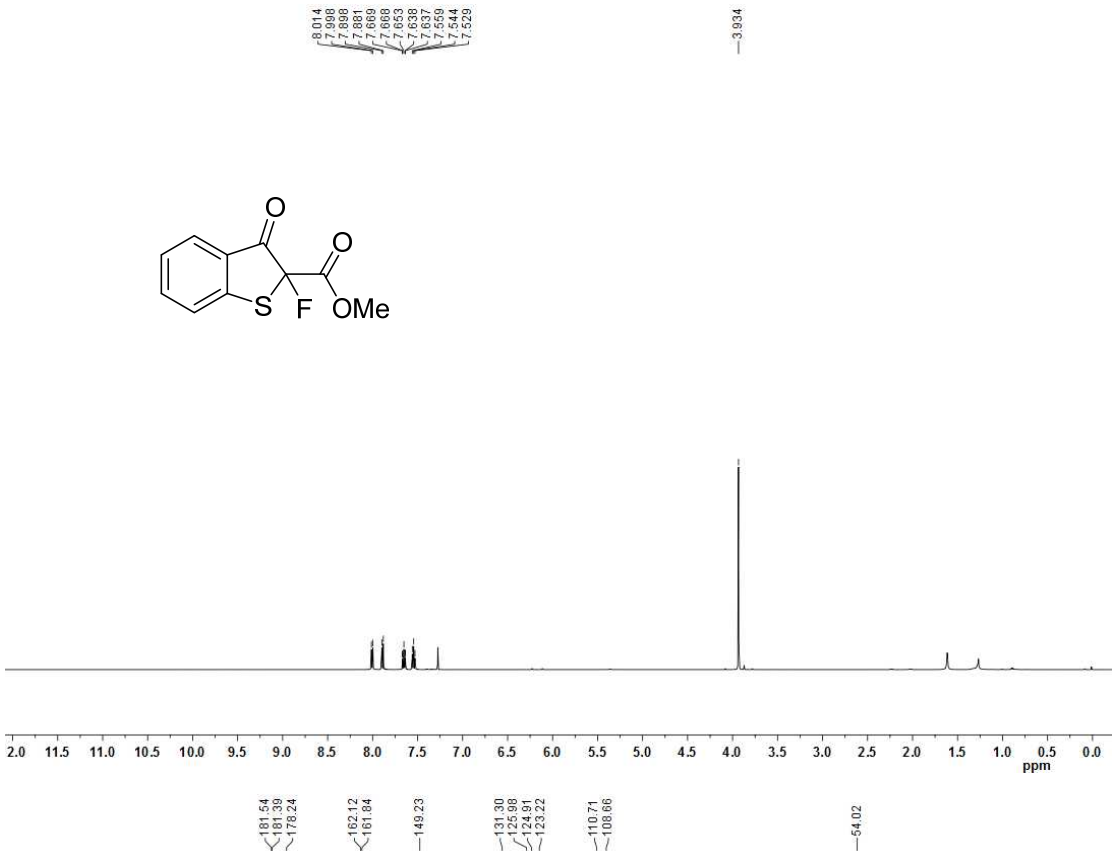
1.01
1.03
1.02
2.03
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


189.67
189.52
163.09
162.78
139.55
131.10
130.95
130.12
128.58
127.85
126.00
117.36
108.42
105.02
103.04
53.82


O
O
O
F
OMe


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.638
7.637
7.559
7.544
7.529
3.934
O
O
S
F
OMe
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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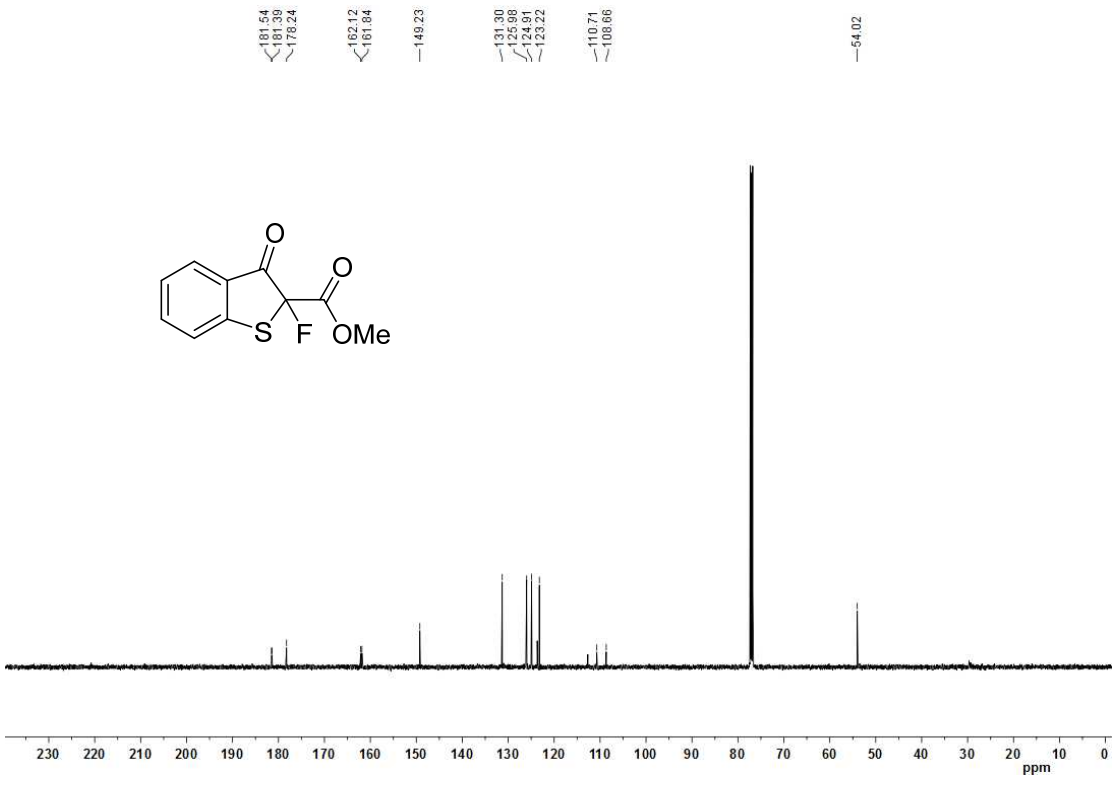
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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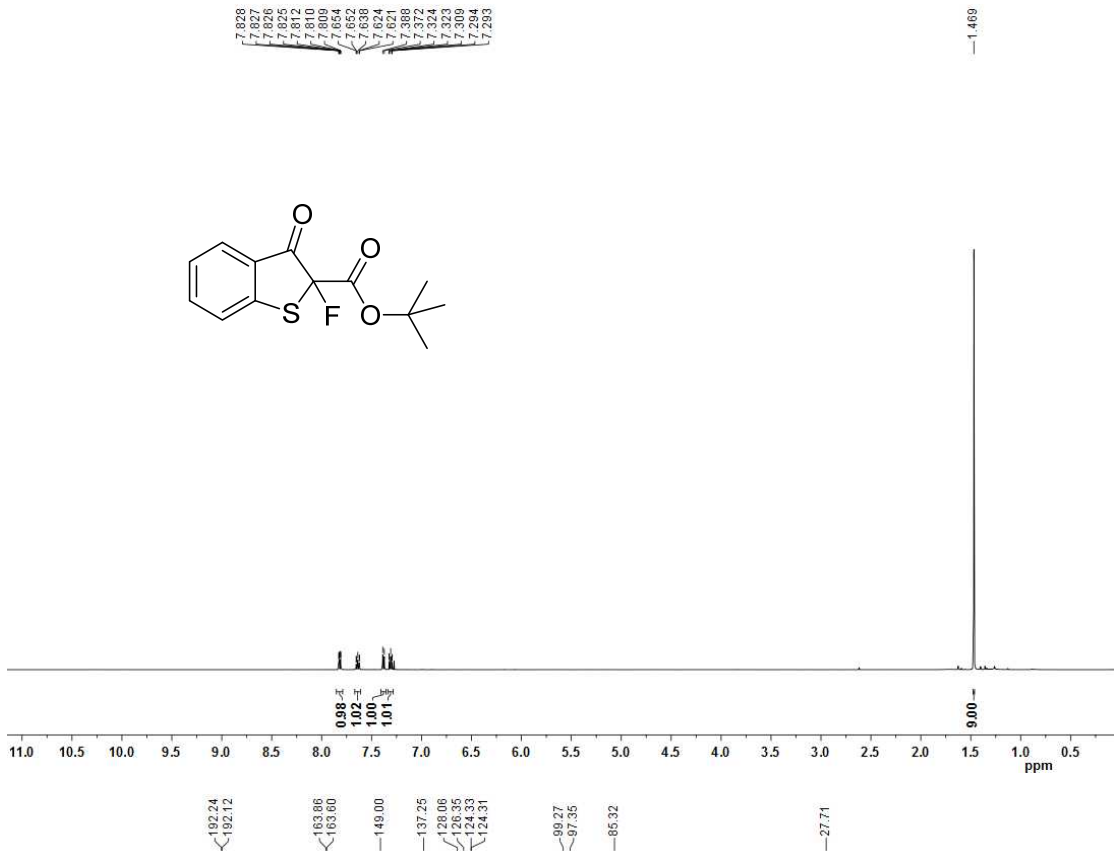
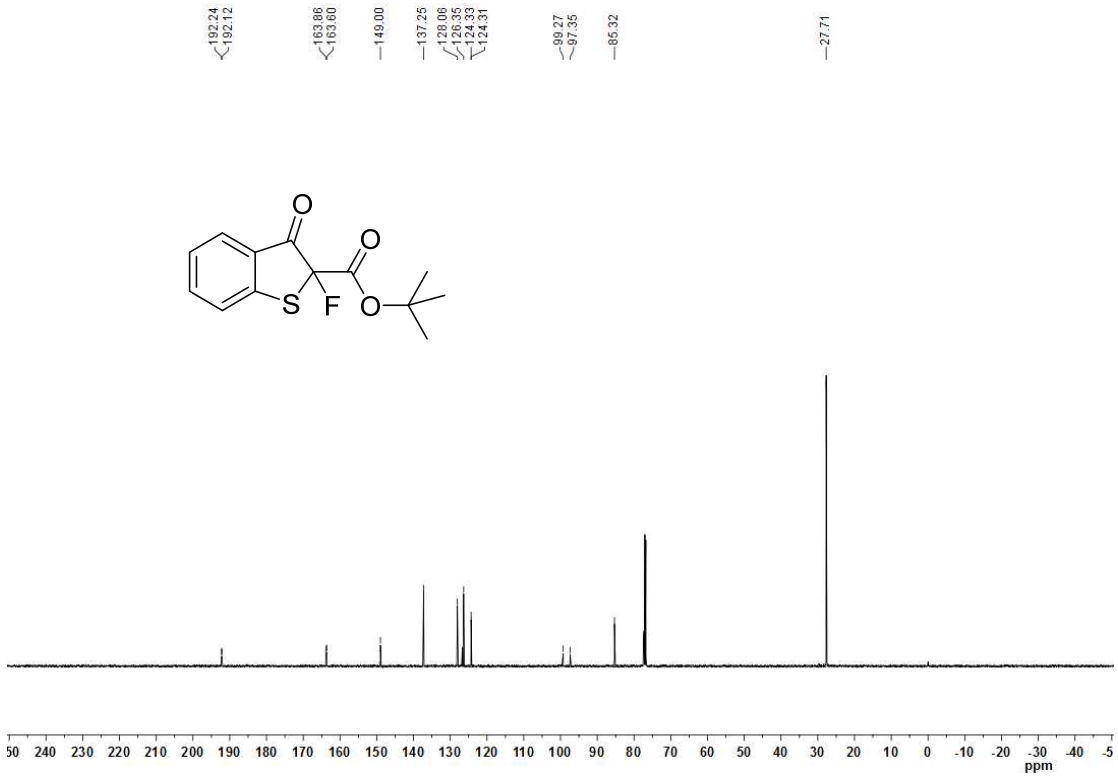
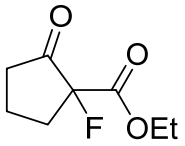
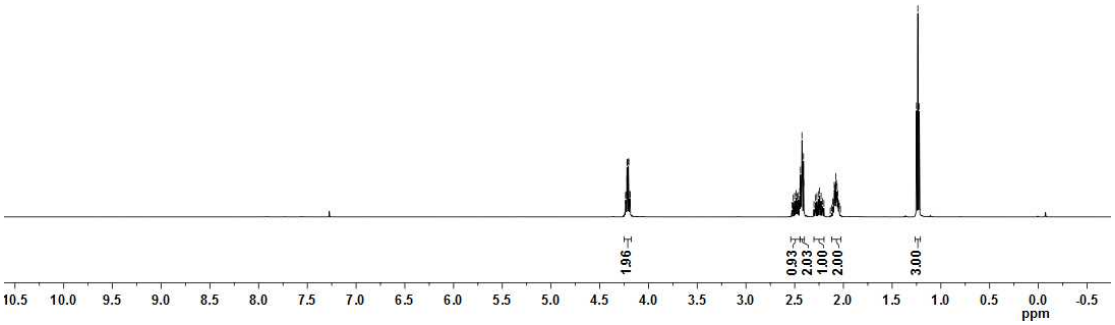
181.39
178.24
162.12
161.84
149.23
131.30
125.98
124.91
123.22
110.71
108.66
54.02
O
O
S
F
OMe
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.828
7.827
7.826
7.825
7.812
7.810
7.809
7.654
7.652
7.638
7.624
7.621
7.388
7.372
7.324
7.323
7.309
7.294
7.293
1.469
O
O
S
F
O
0.98
1.02
1.00
1.01
9.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

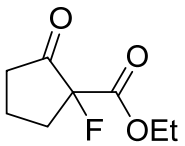

192.24
192.12
163.86
163.60
149.00
137.25
128.06
126.35
124.33
124.31
99.27
97.35
85.32
27.71
O
O
S
F
O
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
ppm


4.235
4.231
4.222
4.221
4.217
4.208
4.206
4.203
4.192
4.188
2.529
2.515
2.500
2.492
2.491
2.486
2.477
2.472
2.462
2.448
2.441
2.438
2.433
2.425
2.413
2.410
2.407
2.302
2.288
2.273
2.258
2.244
2.229
2.215
2.200
2.135
2.120
2.108
2.103
2.094
2.087
2.079
2.072
2.065
2.057
2.050
2.046
2.042
2.031
1.251
1.236
1.222


O
O
F
OEt


1.96
0.93
2.03
1.00
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


207.58
207.44
167.33
167.11
95.30
93.71
62.13
35.53
33.78
33.62
17.87
17.84
13.81


O
O
F
OEt

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm


4.321
4.306
4.306
4.292
4.277
2.741
2.730
2.727
2.723
2.717
2.713
2.710
2.705
2.702
2.699
2.695
2.685
2.634
2.628
2.624
2.622
2.618
2.615
2.608
2.598
2.595
2.590
2.580
2.493
2.491
2.483
2.478
2.473
2.469
2.465
2.451
2.449
2.441
2.437
2.162
2.153
2.151
2.147
2.134
2.129
2.126
1.943
1.940
1.930
1.925
1.922
1.918
1.913
1.910
1.906
1.903
1.899
1.896
1.887
1.879
1.877
1.872
1.870
1.867
1.863
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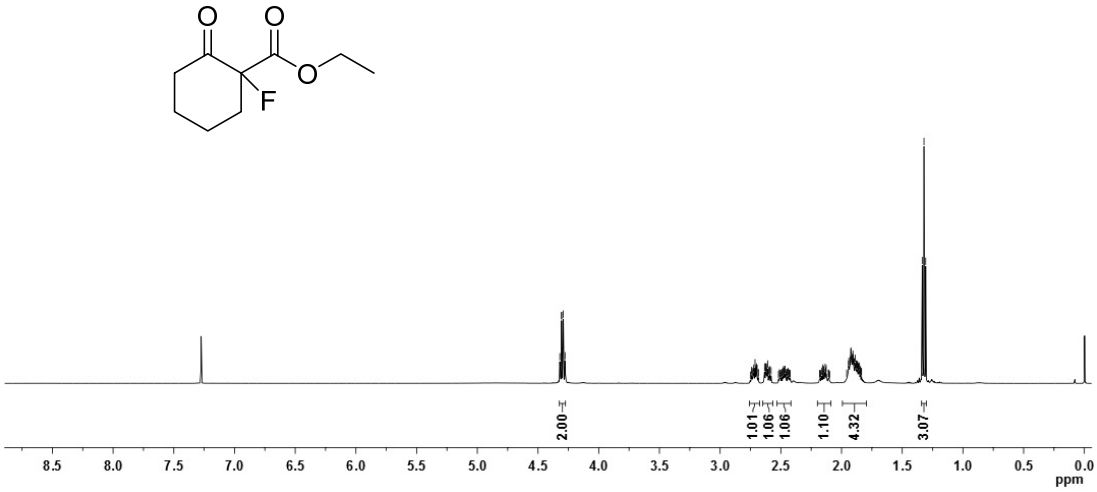
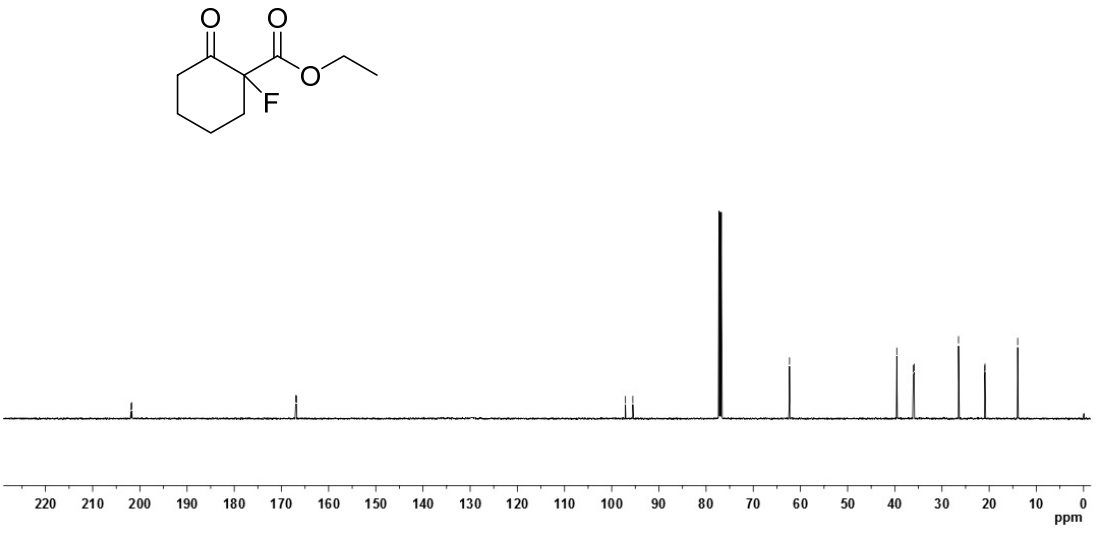
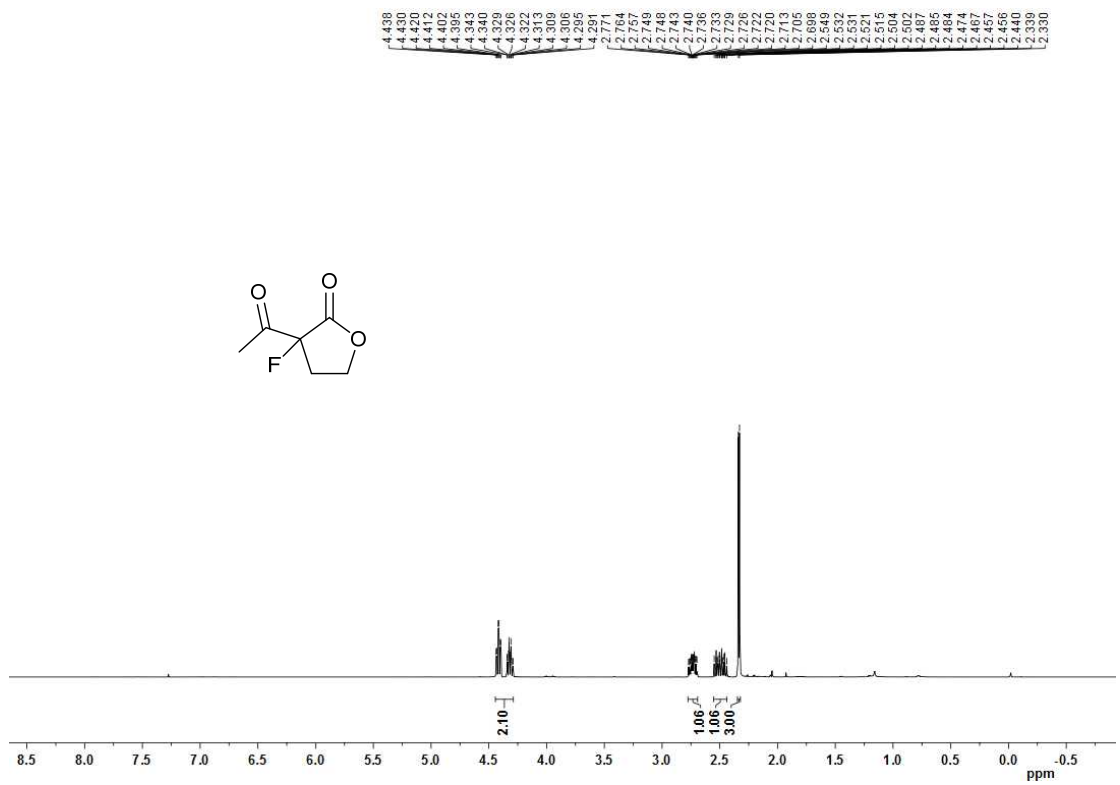
1.856
1.852
1.846
1.844
1.836
1.835
1.335
1.321
1.307


O
O
O
F
2.00
1.01
1.06
1.06
1.10
4.32
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


201.87
201.71
166.99
166.79
97.09
95.52
62.31
39.58
36.07
35.89
26.50
20.93
20.89
13.95


O
O
O
F
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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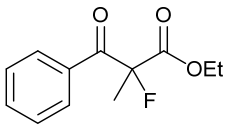
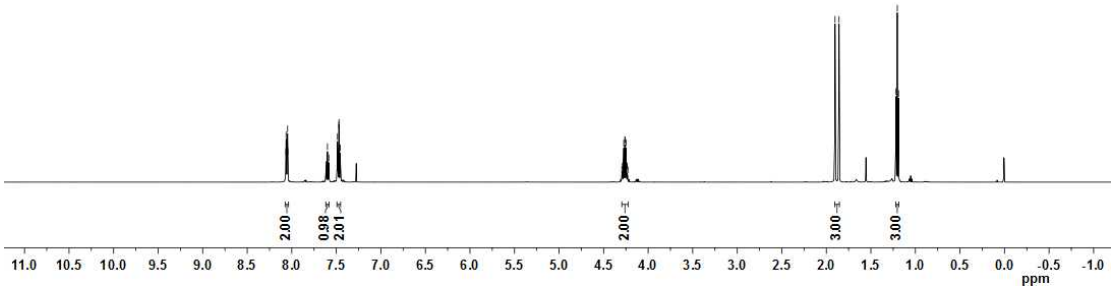
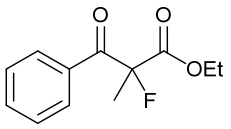
4.420
4.412
4.402
4.395
4.343
4.340
4.329
4.326
4.322
4.313
4.309
4.306
4.295
4.291
2.771
2.764
2.757
2.749
2.748
2.743
2.740
2.736
2.733
2.729
2.726
2.722
2.720
2.713
2.705
2.698
2.549
2.532
2.531
2.521
2.515
2.504
2.502
2.487
2.485
2.484
2.474
2.467
2.457
2.456
2.440
2.339
2.330
O
O
O
F
2.10
1.06
1.06
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm
203.21
202.96
169.23
169.04
96.96
95.34
65.61
65.57
31.86
31.69
25.45
O
O
O
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
ppm

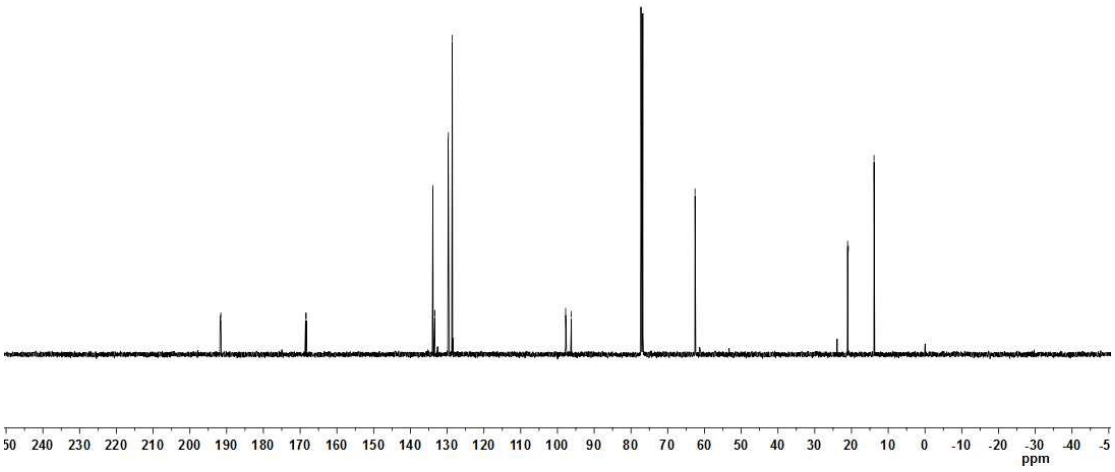

8.067
8.064
8.061
8.050
8.047
8.044
7.617
7.614
7.612
7.603
7.599
7.596
7.587
7.584
7.492
7.490
7.487
7.484
7.472
7.470
7.459
7.456
4.296
4.288
4.282
4.277
4.274
4.267
4.263
4.260
4.255
4.249
4.246
4.241
4.234
4.227
1.902
1.857
1.218
1.203
1.189


O
O
OEt
F

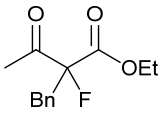

2.00
0.98
2.01
2.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

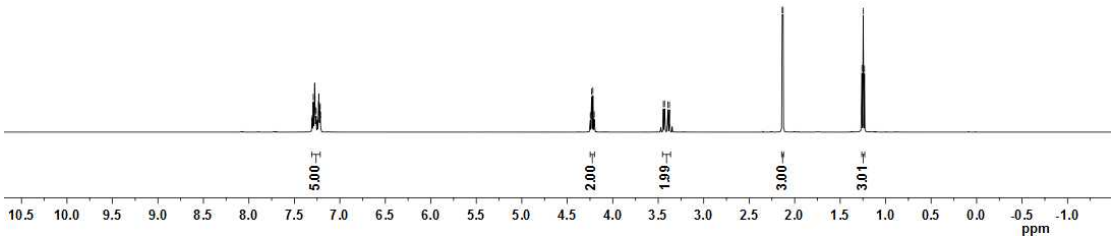

191.78
191.58
168.53
168.33
133.89
133.37
133.35
129.72
129.67
128.61
97.77
96.22
62.56
21.05
20.87
13.86

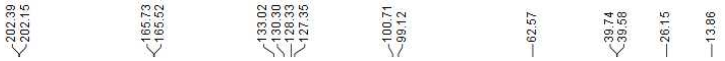

O
O
OEt
F

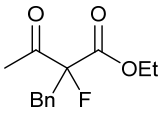

50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
ppm

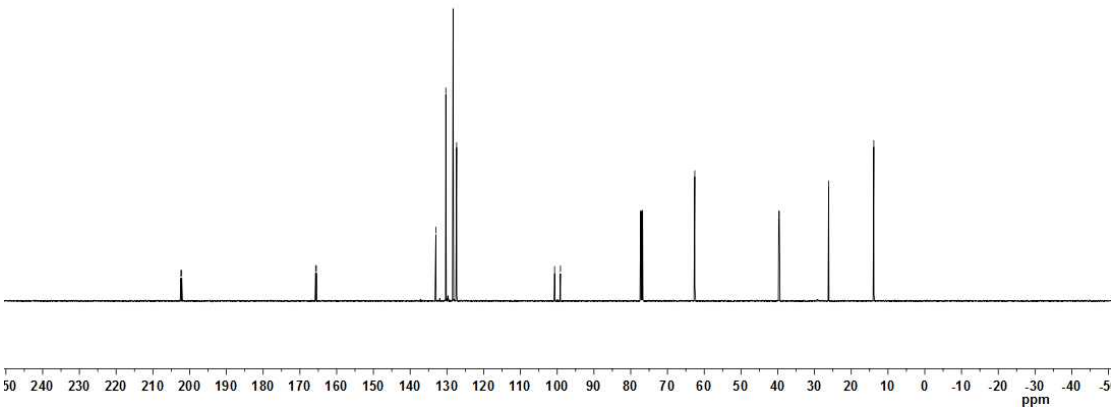

7.310
7.305
7.301
7.297
7.292
7.289
7.287
7.281
7.278
7.276
7.273
7.269
7.265
7.259
7.250
7.248
7.244
7.241
7.235
7.232
7.231
7.229
7.219
7.216
7.213
4.247
4.233
4.218
4.204
3.443
3.430
3.394
3.377
2.137
2.127
1.261
1.246
1.232


O
O
OEt
Bn
F


5.00
2.00
1.99
3.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


202.39
202.15
165.73
165.52
133.02
130.30
128.33
127.35
100.71
99.12
62.57
39.74
39.58
26.15
13.86


O
O
OEt
Bn
F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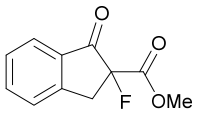
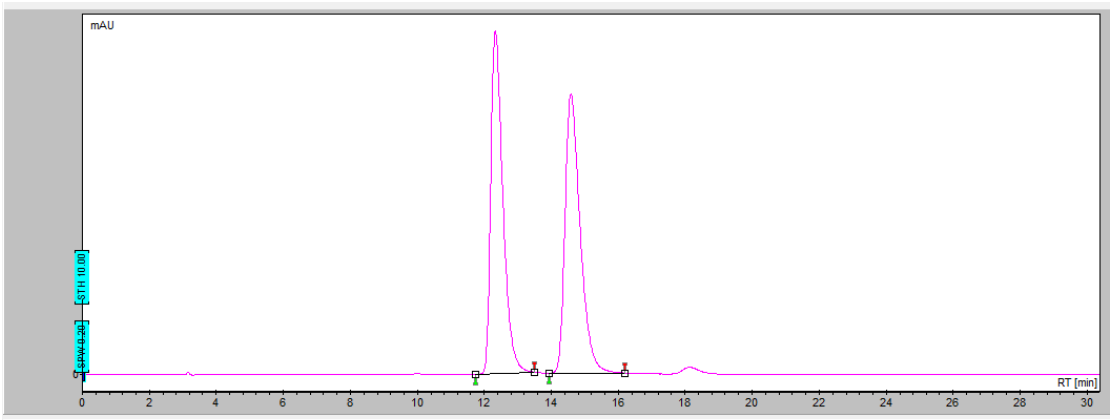
ppm

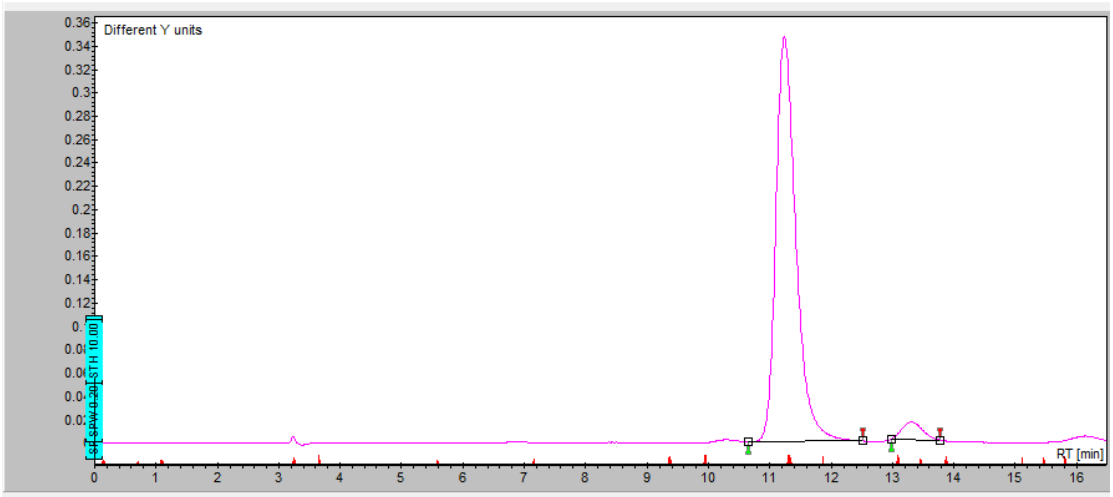
4. HPLC analysis



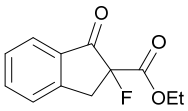
2a



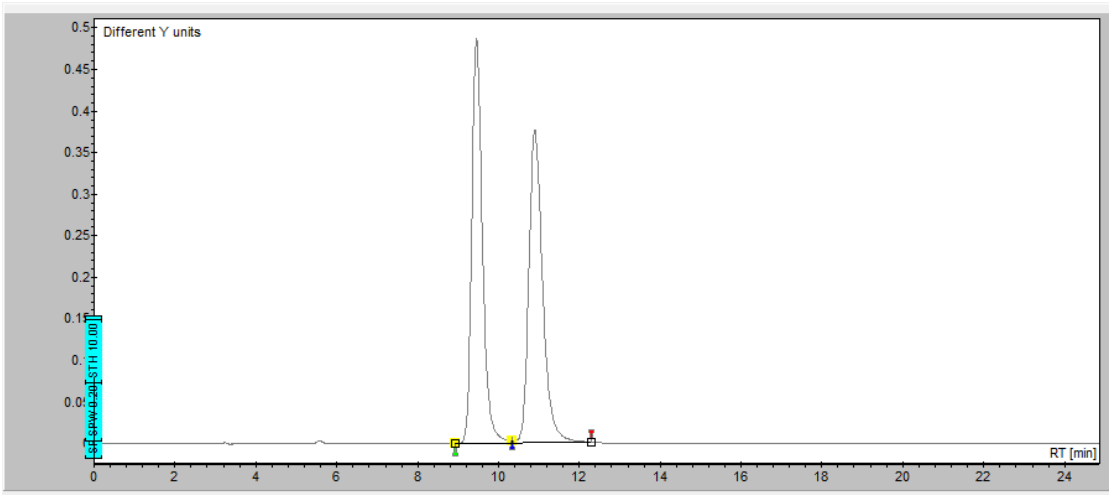
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.332	49.427
2	UNKNOWN	14.586	50.573
Total			100.000



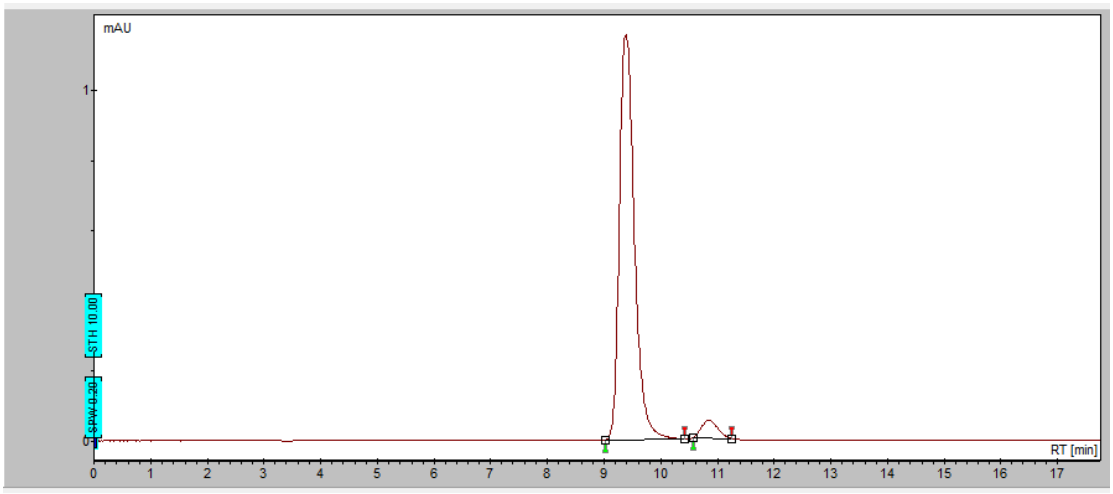
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.239	95.799
2	UNKNOWN	13.306	4.201
Total			100.000



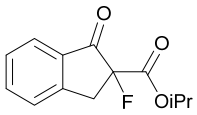
2b



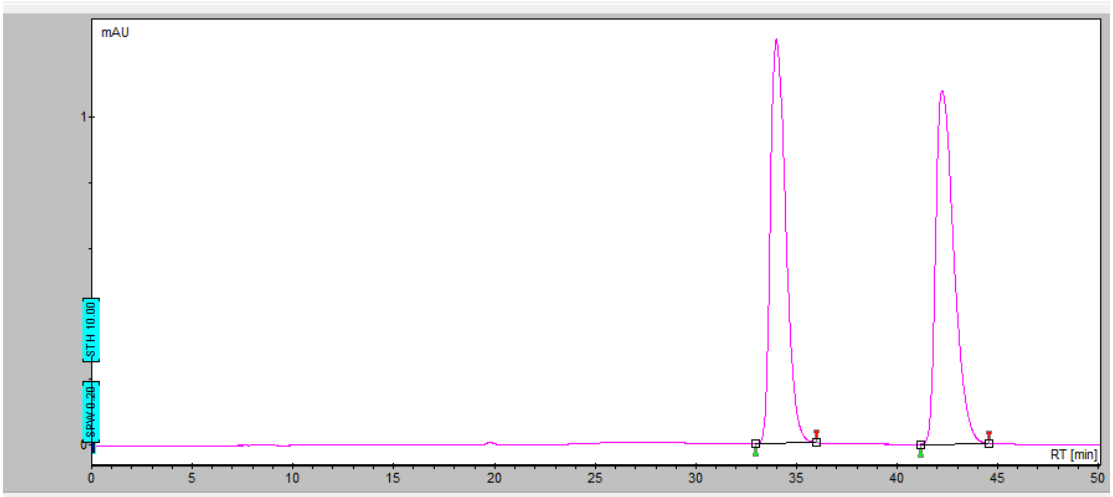
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	9.453	50.058
2	UNKNOWN	10.893	49.942
Total			100.000



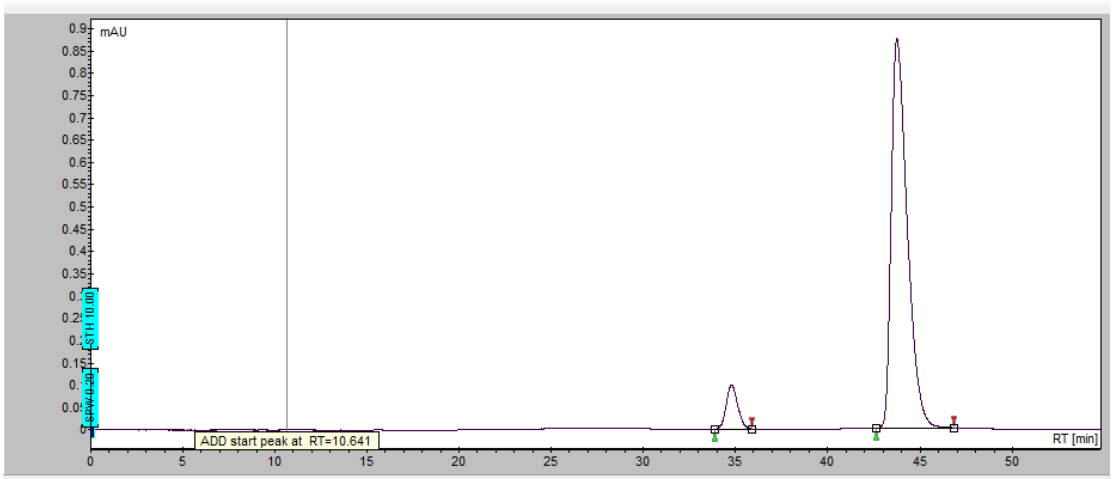
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	9.386	95.581
2	UNKNOWN	10.853	4.419
Total			100.000



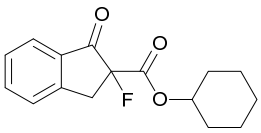
2c



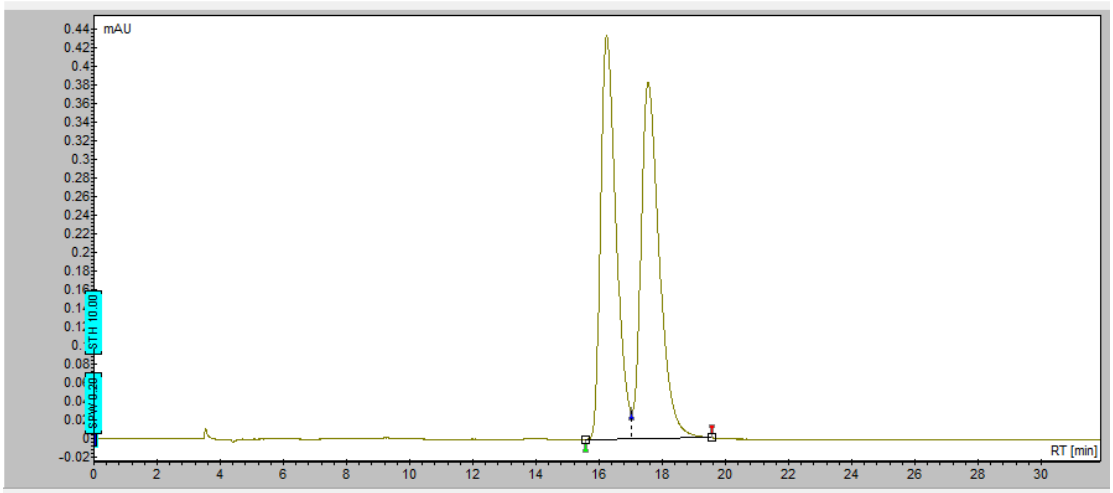
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	33.984	49.106
2	UNKNOWN	42.224	50.894
Total			100.000



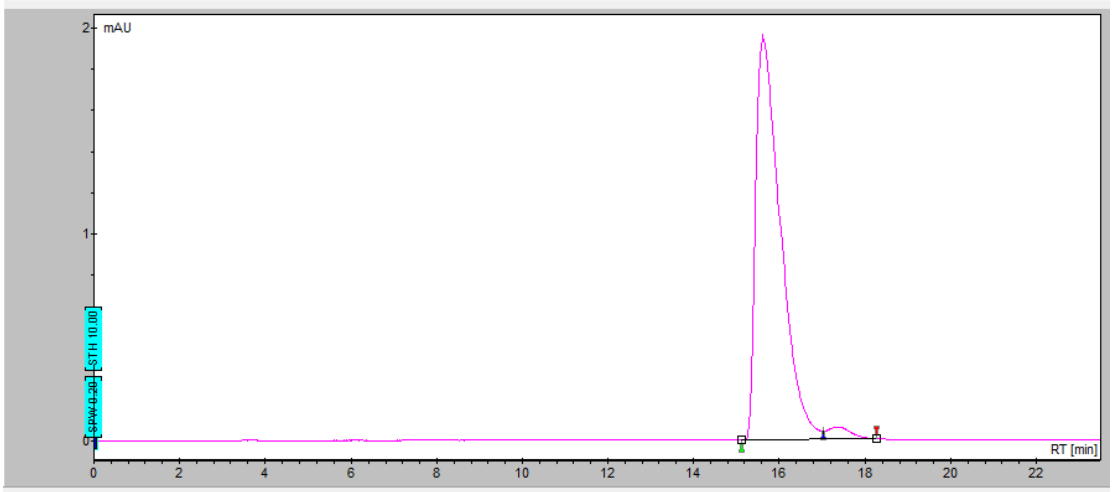
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	34.771	7.585
2	UNKNOWN	43.743	92.415
Total			100.000



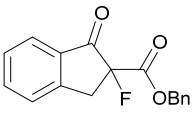
2d



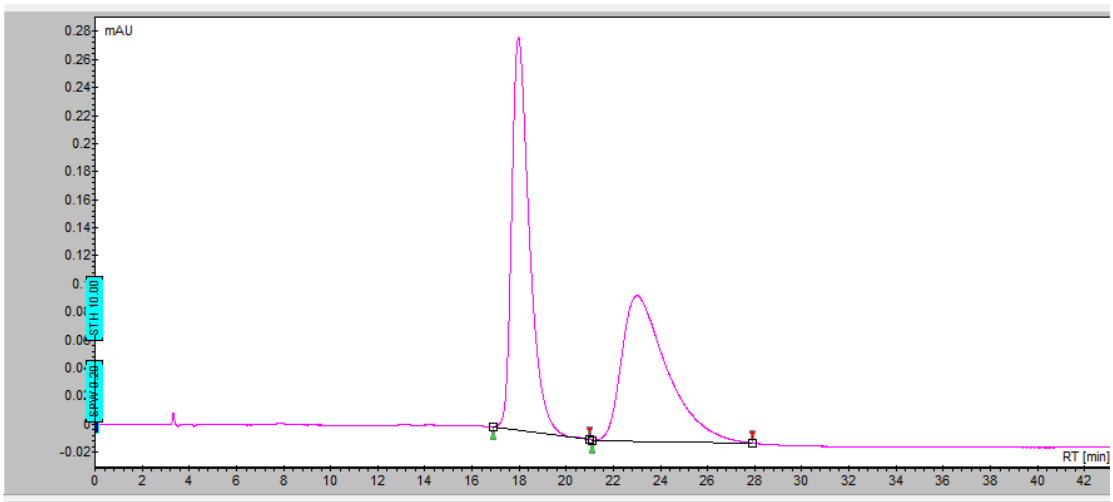
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	16.239	48.899
2	UNKNOWN	17.559	51.101
Total			100.000



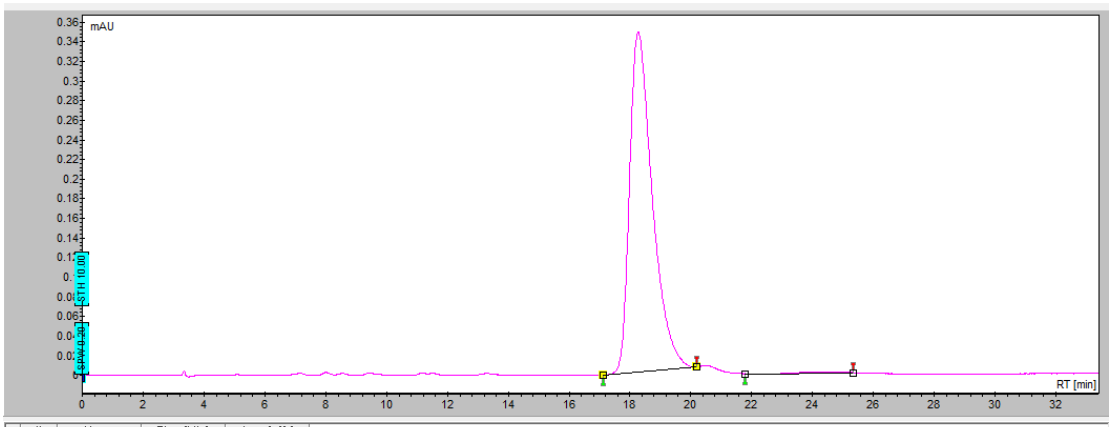
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	15.612	97.168
2	UNKNOWN	17.359	2.832
Total			100.000



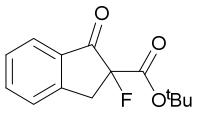
2e



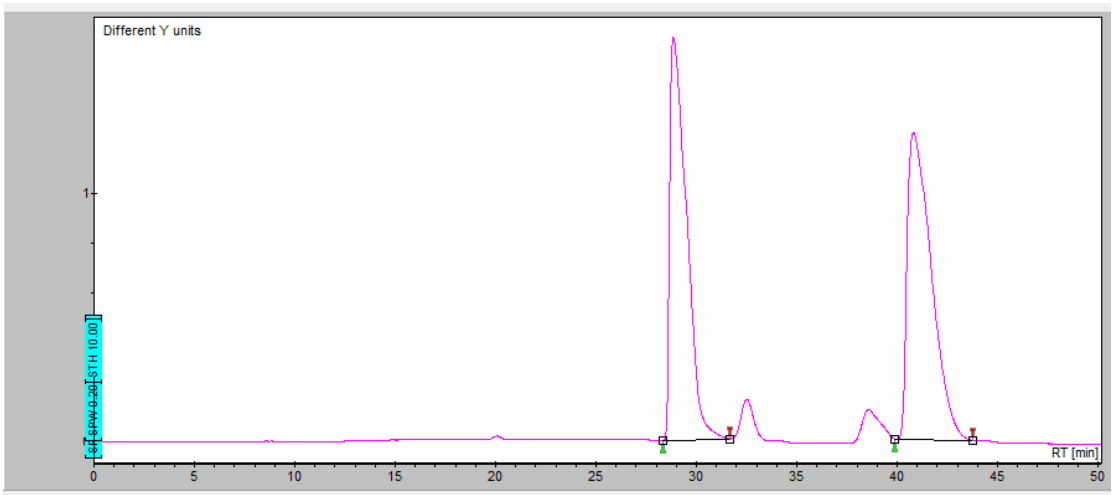
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.972	51.466
2	UNKNOWN	22.998	48.534
Total			100.000



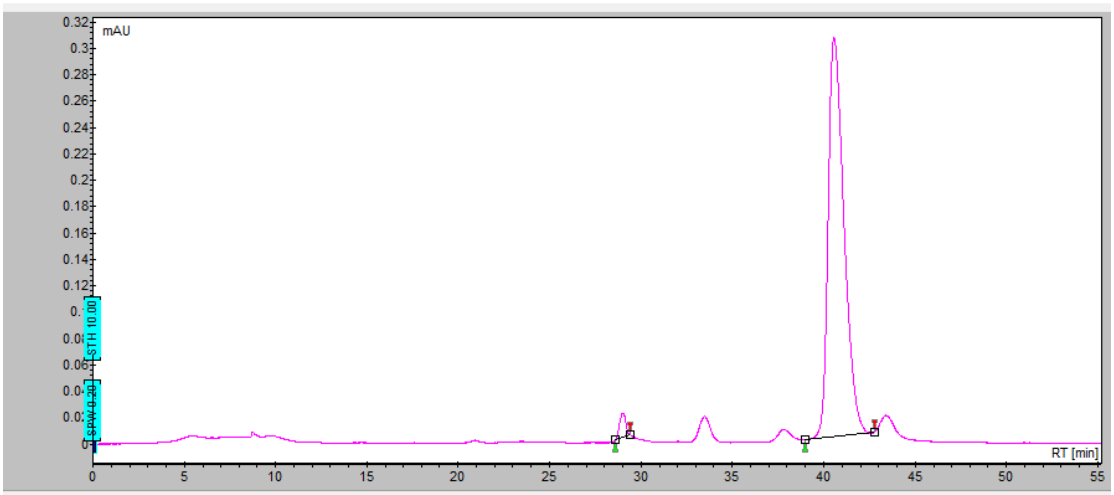
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.265	99.636
2	UNKNOWN	24.092	0.364
Total			100.000



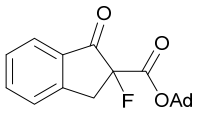
2f



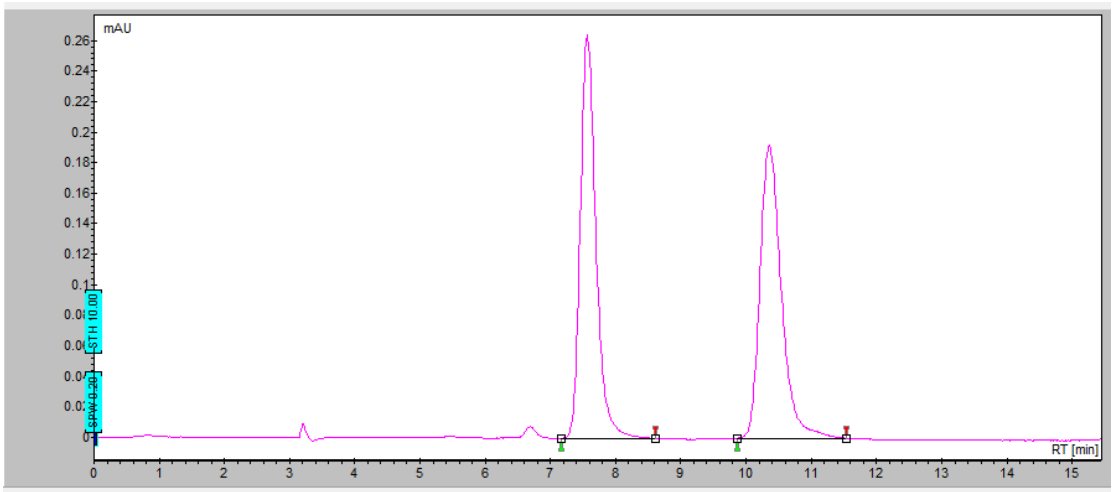
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	28.838	47.835
2	UNKNOWN	40.784	52.165
Total			100.000



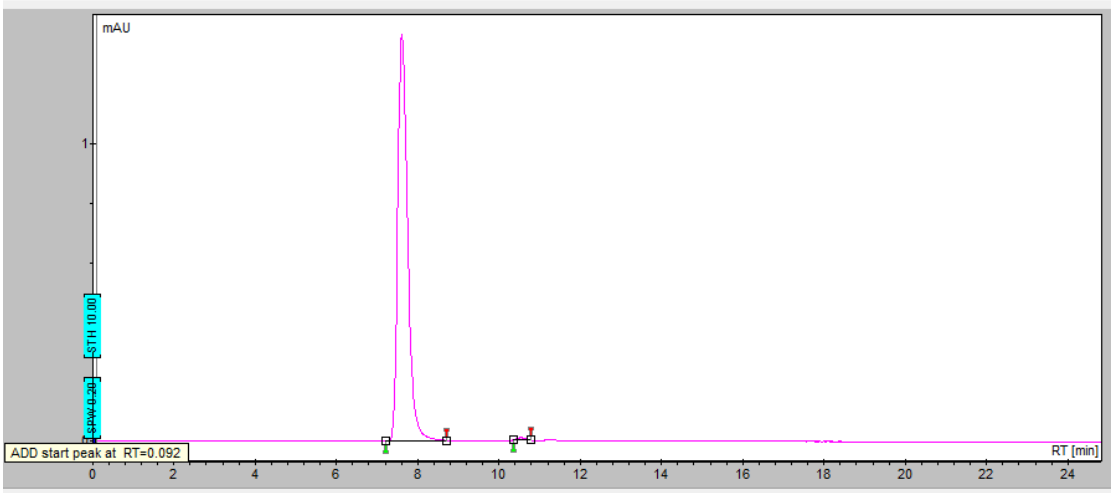
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	28.998	2.306
2	UNKNOWN	40.570	97.694
Total			100.000



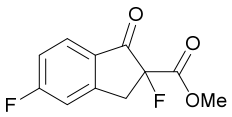
2g



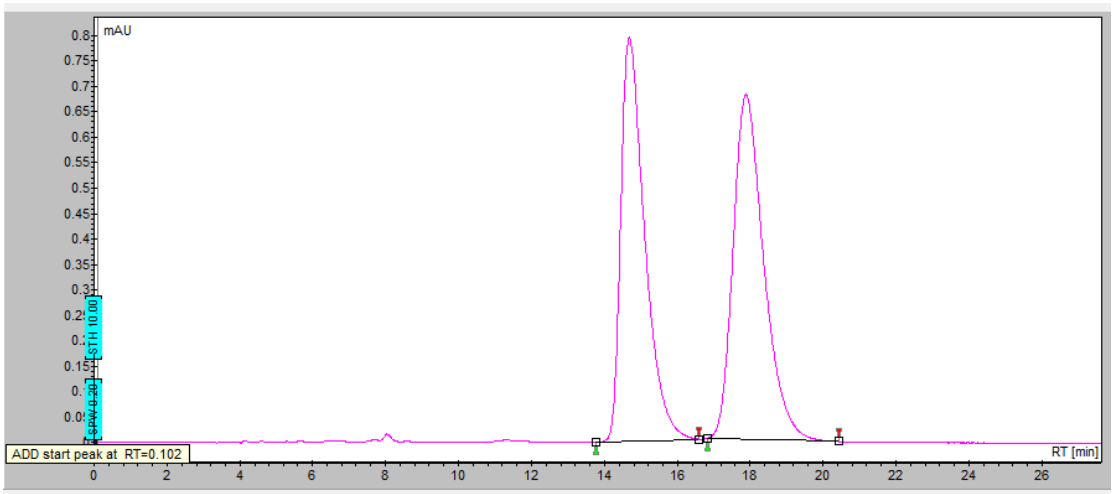
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.560	50.218
2	UNKNOWN	10.360	49.782
Total			100.000



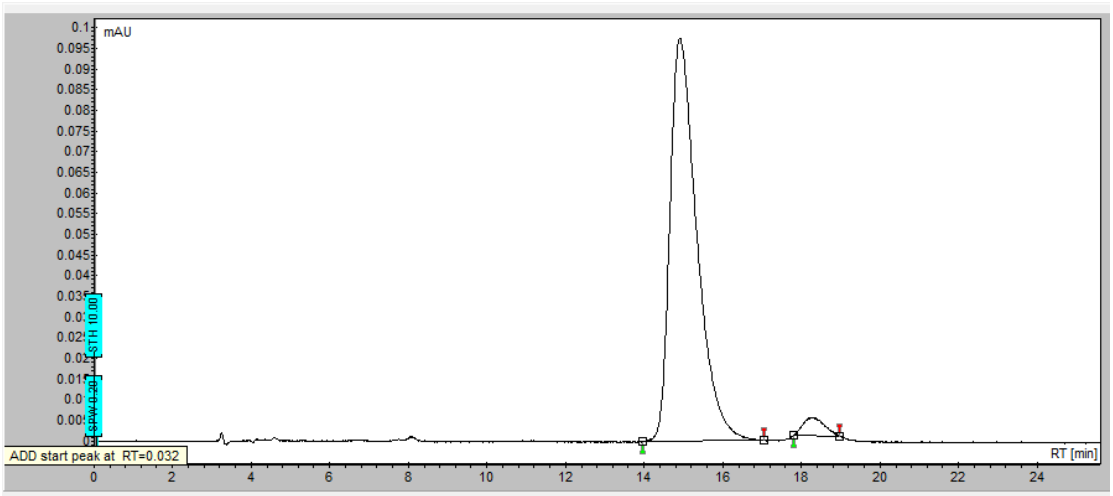
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.599	99.524
2	UNKNOWN	10.533	0.476
Total			100.000



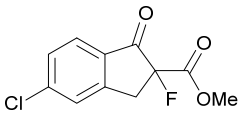
2h



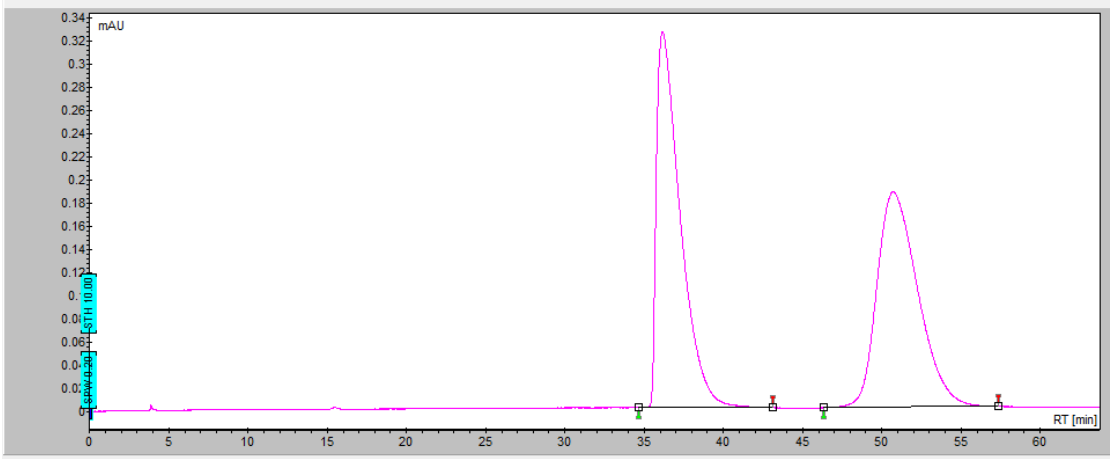
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.679	47.736
2	UNKNOWN	17.892	52.264
Total			100.000



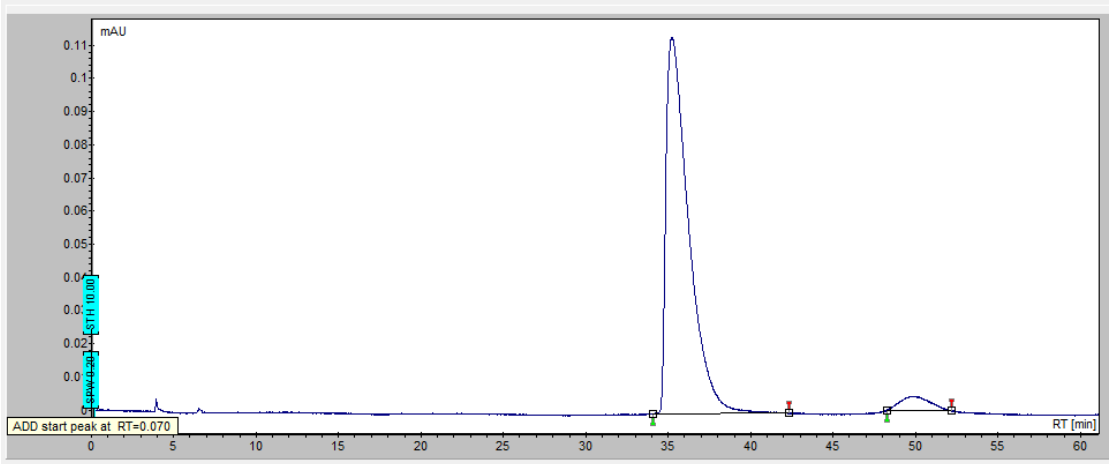
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.906	96.584
2	UNKNOWN	18.265	3.416
Total			100.000



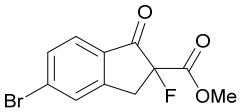
2i



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	36.171	50.451
2	UNKNOWN	50.730	49.549
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	35.211	95.238
2	UNKNOWN	49.863	4.762
Total			100.000



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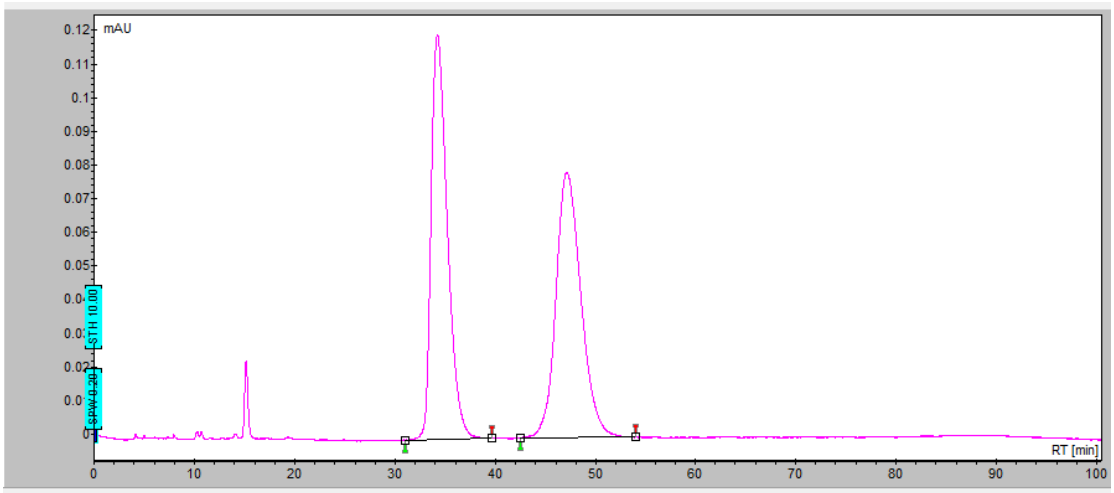
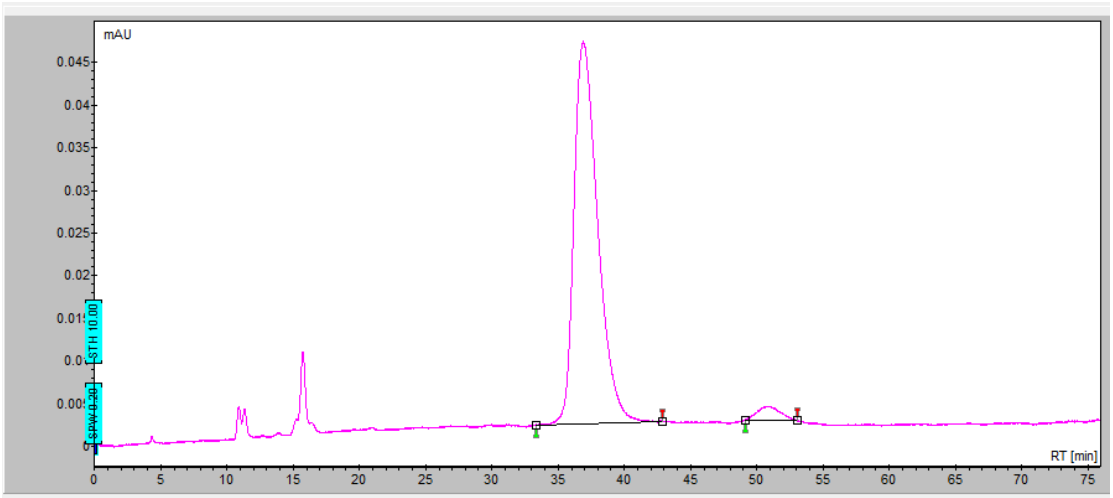
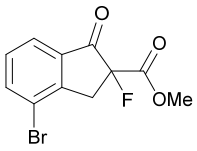


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	34.254	49.691
2	UNKNOWN	47.156	50.309
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	36.920	96.568
2	UNKNOWN	50.888	3.432
Total			100.000



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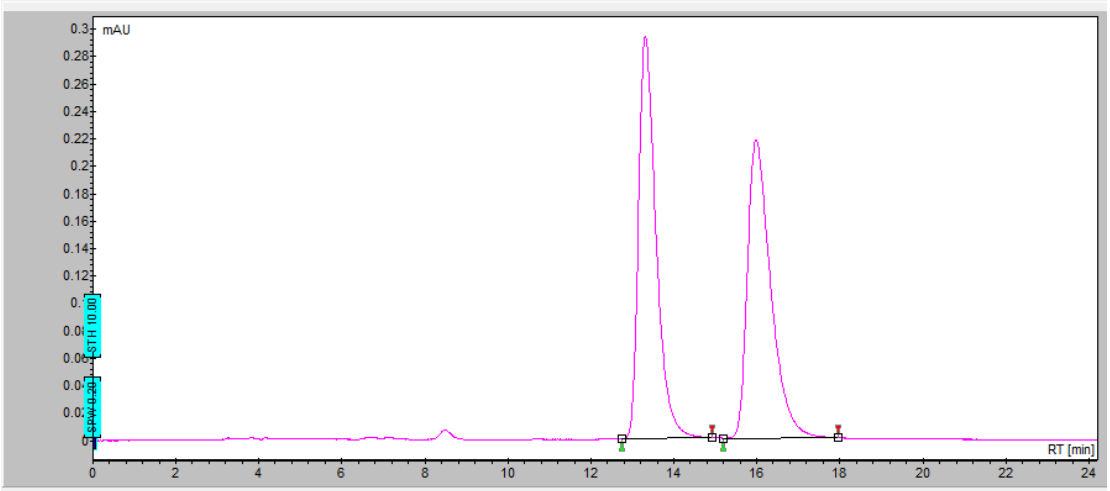
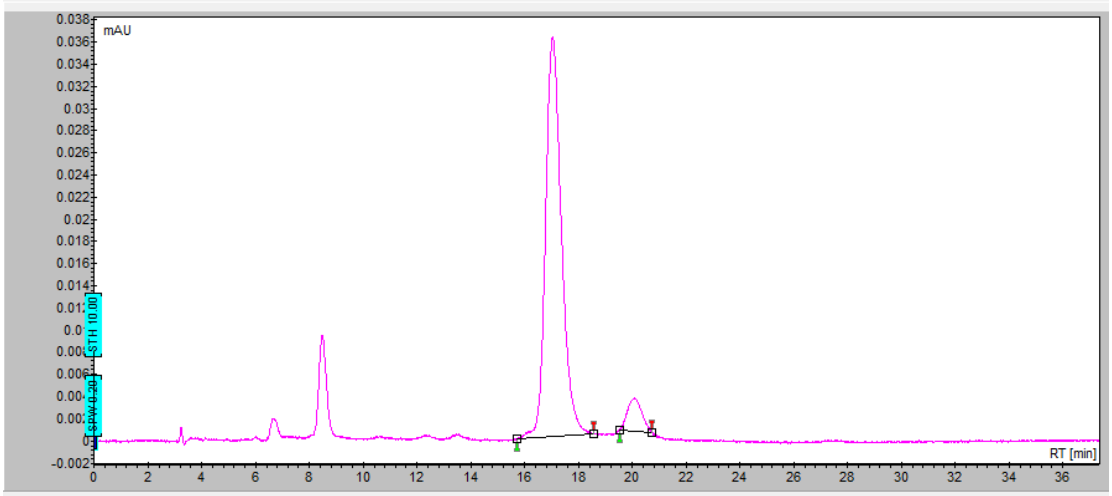
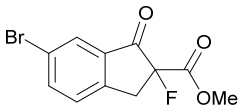


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	13.306	50.173
2	UNKNOWN	15.986	49.827
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.039	93.093
2	UNKNOWN	20.079	6.907
Total			100.000



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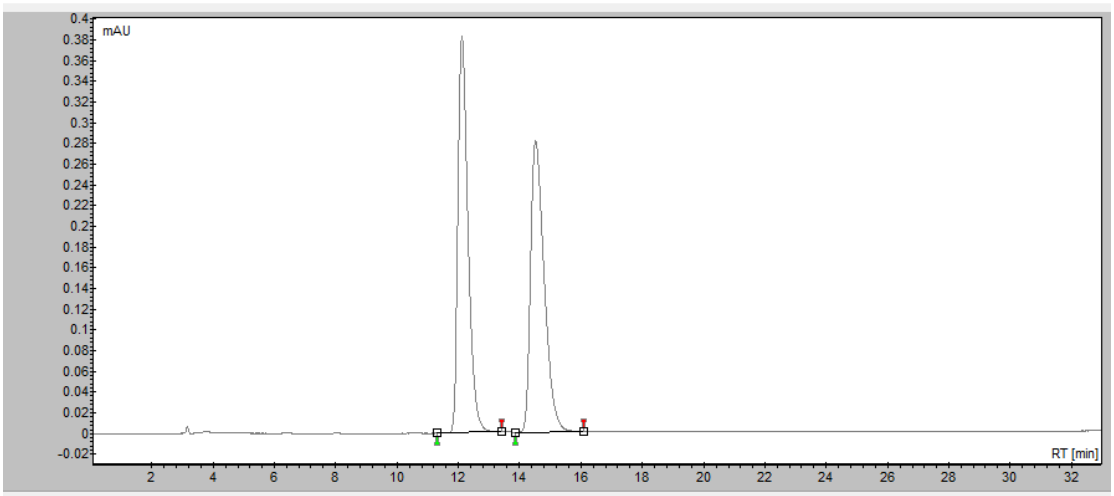
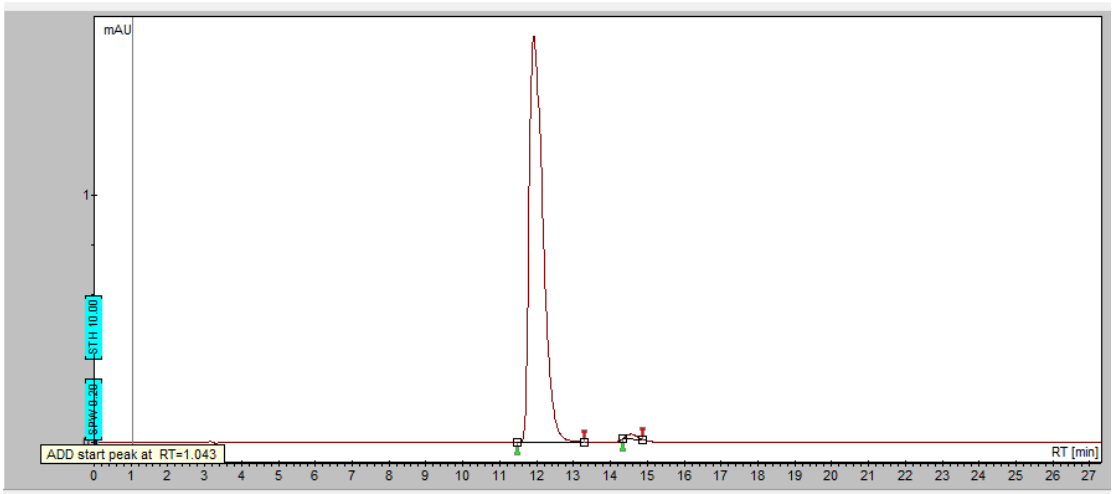
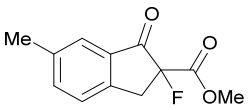


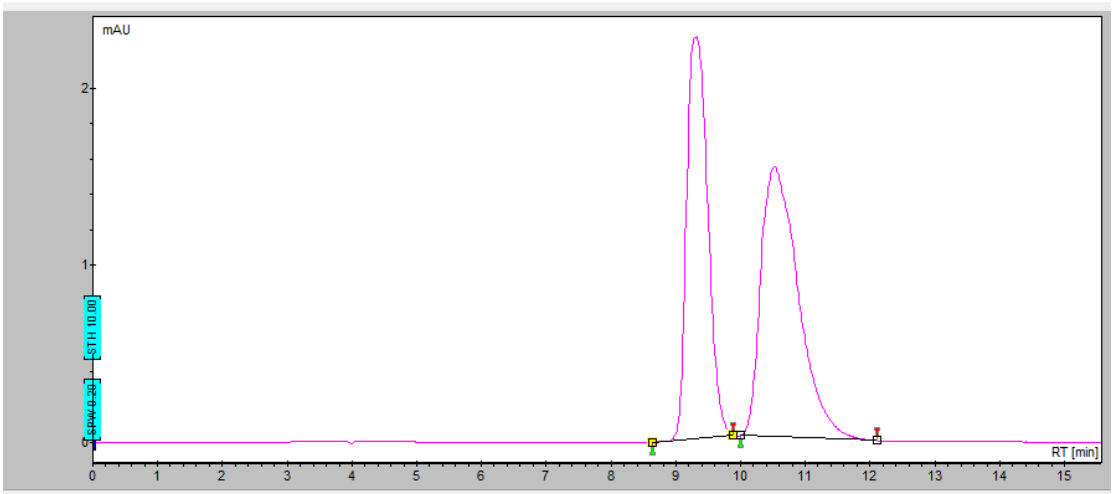
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.119	50.223
2	UNKNOWN	14.519	49.777
Total			100.000



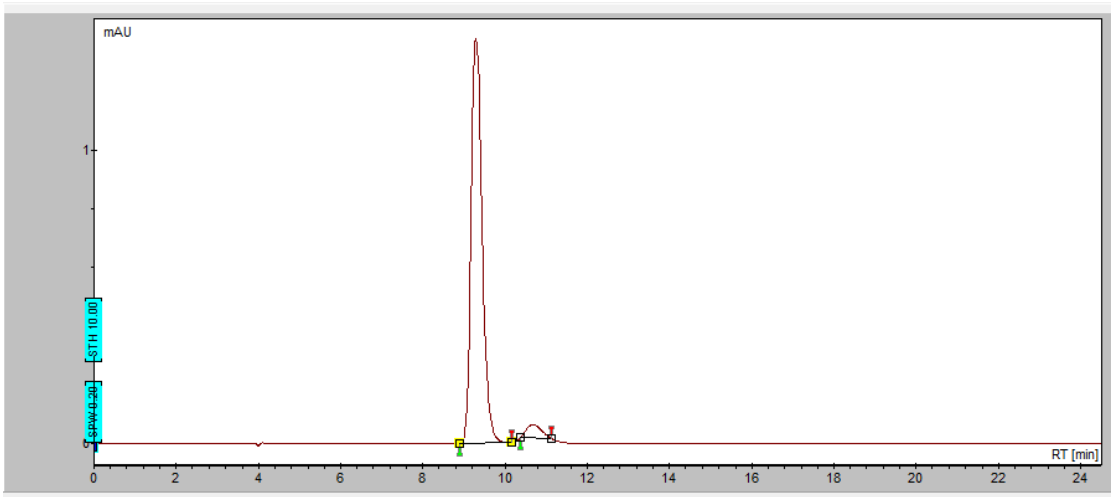
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.919	99.155
2	UNKNOWN	14.546	0.845
Total			100.000



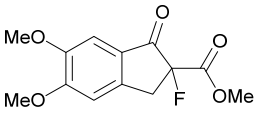
2m



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	9.320	45.477
2	UNKNOWN	10.520	54.523
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	9.279	95.673
2	UNKNOWN	10.666	4.327
Total			100.000



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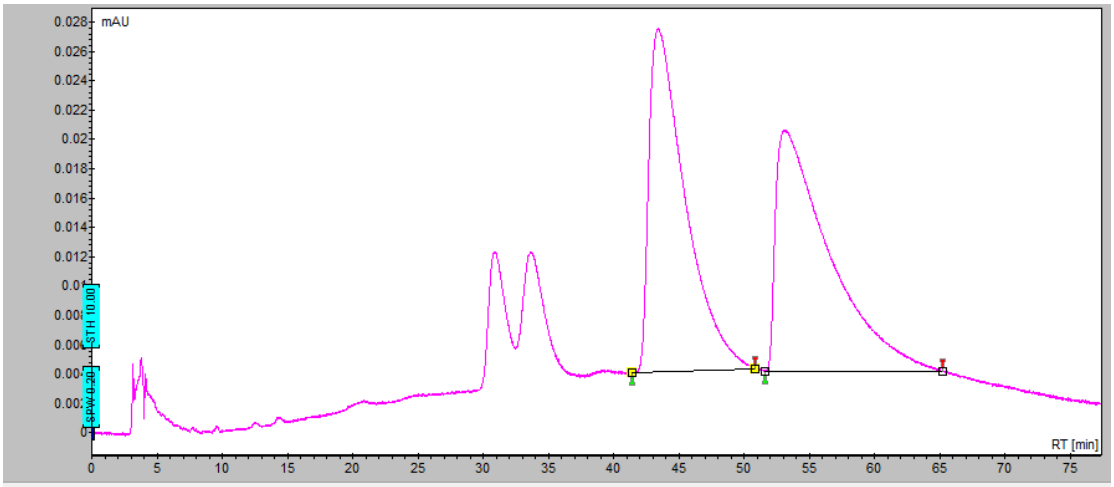
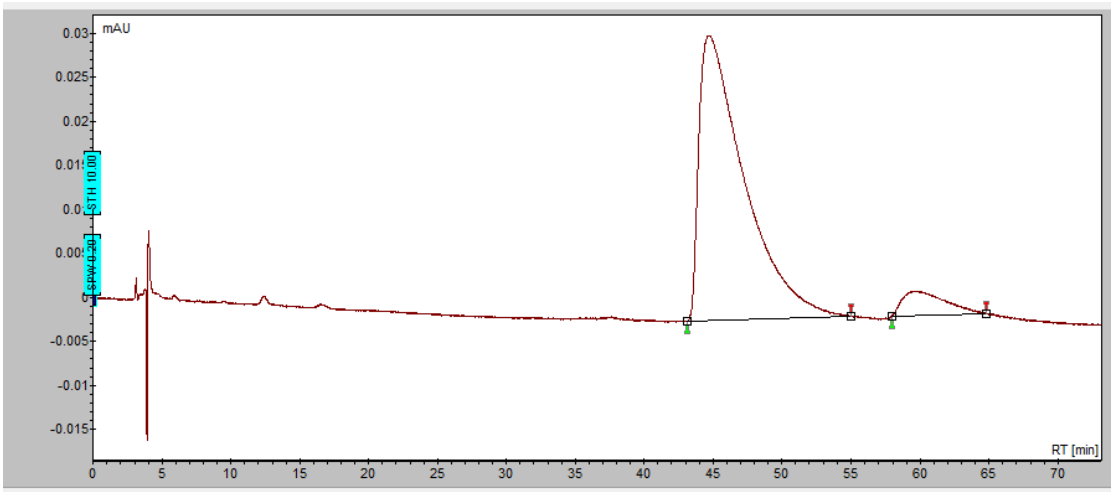
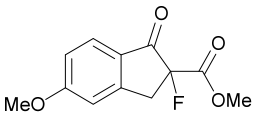


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	43.384	48.918
2	UNKNOWN	53.141	51.082
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	44.677	92.557
2	UNKNOWN	59.619	7.443
Total			100.000



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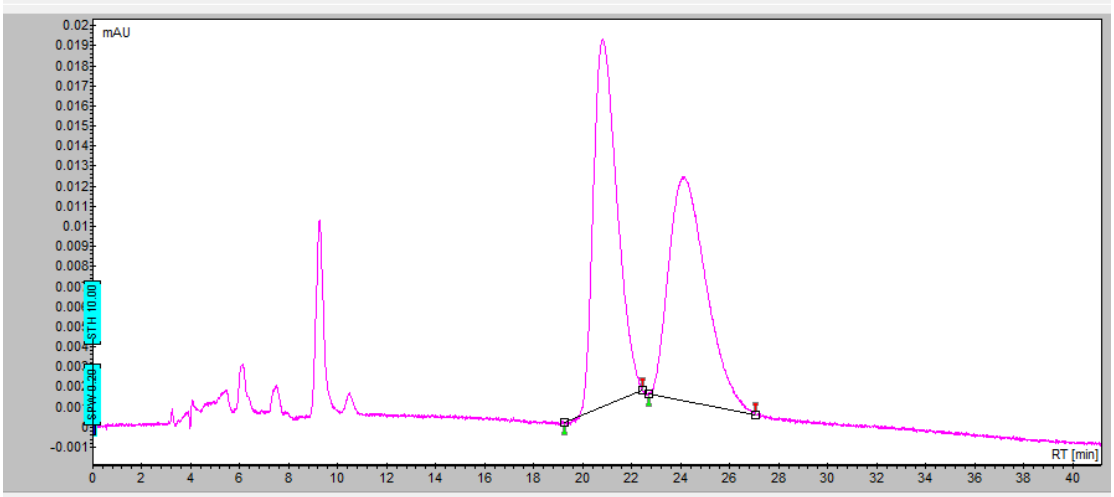
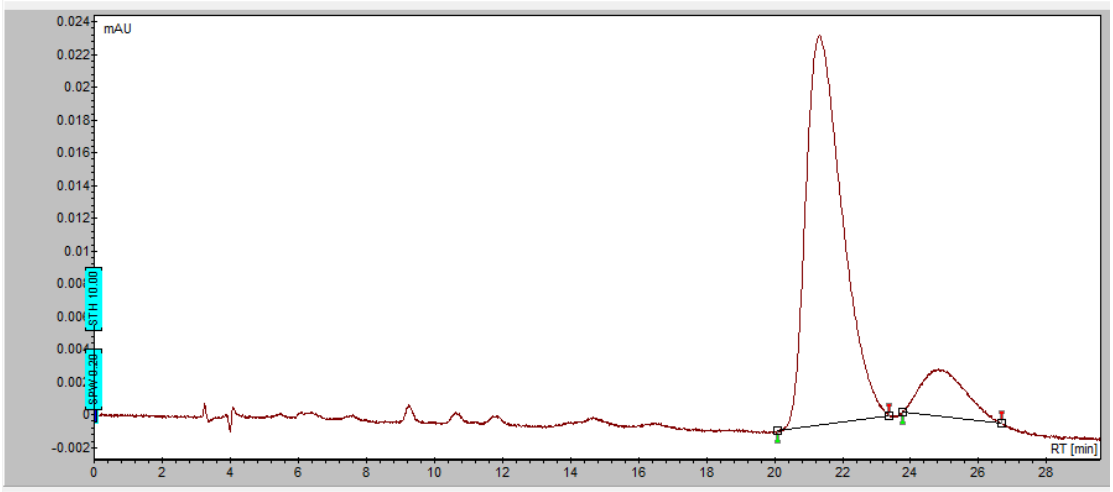
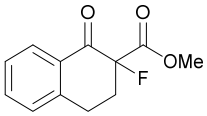


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	20.812	50.752
2	UNKNOWN	24.118	49.248
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.305	86.942
2	UNKNOWN	24.878	13.058
Total			100.000



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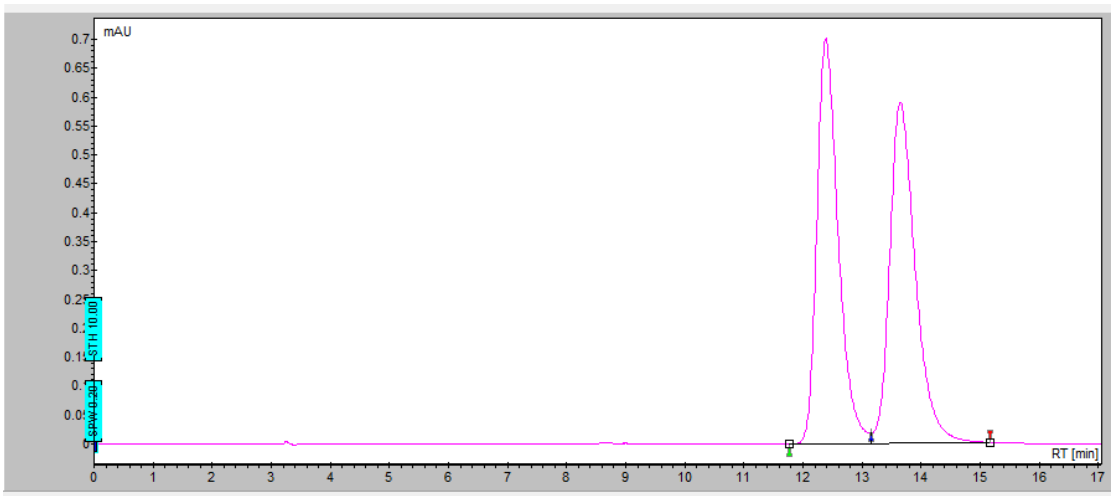
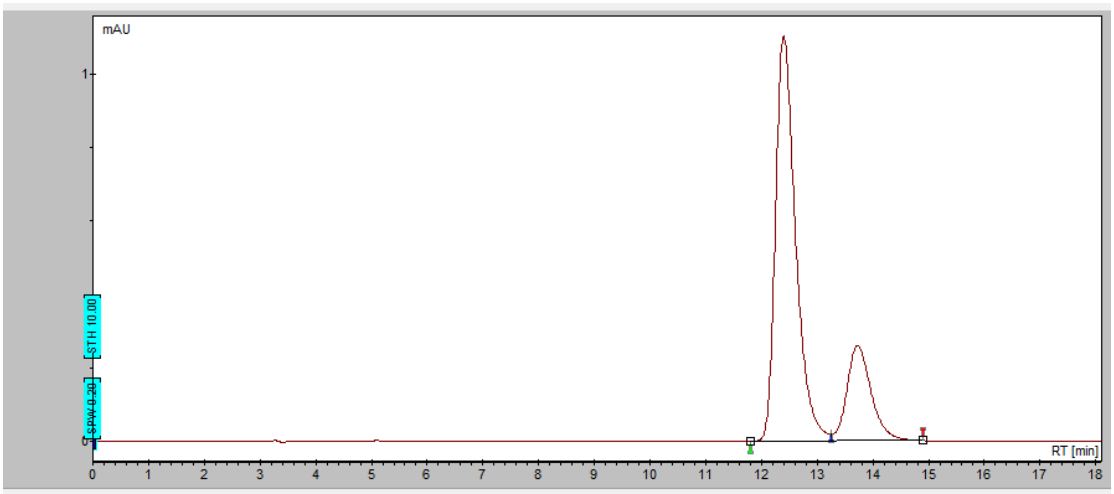
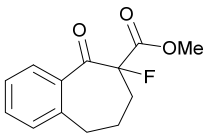


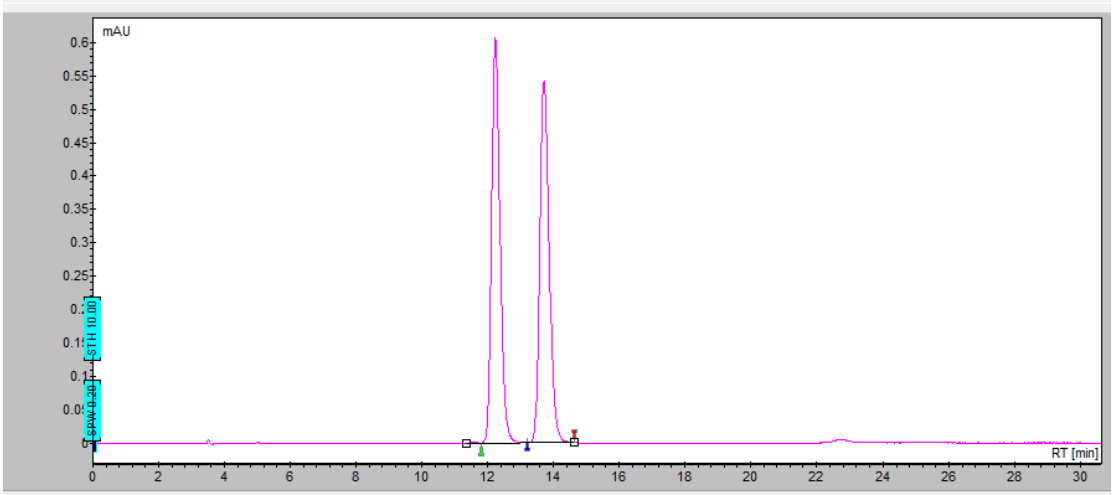
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.386	49.667
2	UNKNOWN	13.652	50.333
Total			100.000



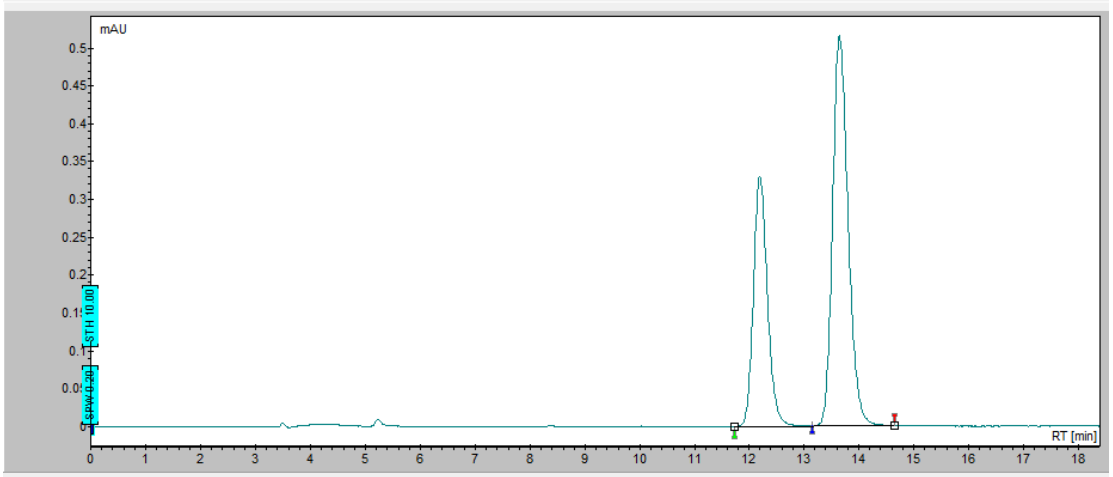
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.399	77.822
2	UNKNOWN	13.732	22.178
Total			100.000



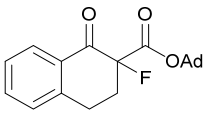
2q



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.226	50.093
2	UNKNOWN	13.706	49.907
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.186	36.542
2	UNKNOWN	13.639	63.458
Total			100.000



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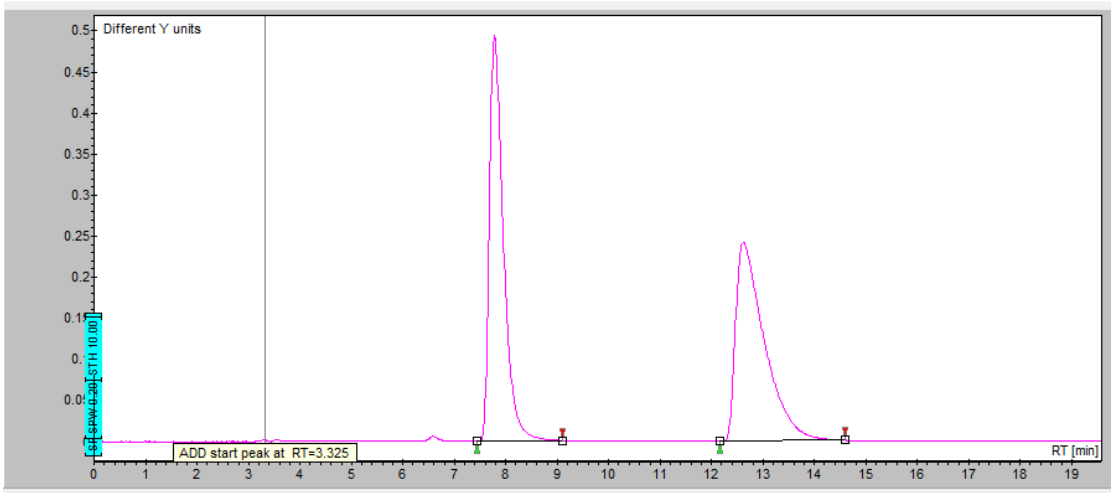
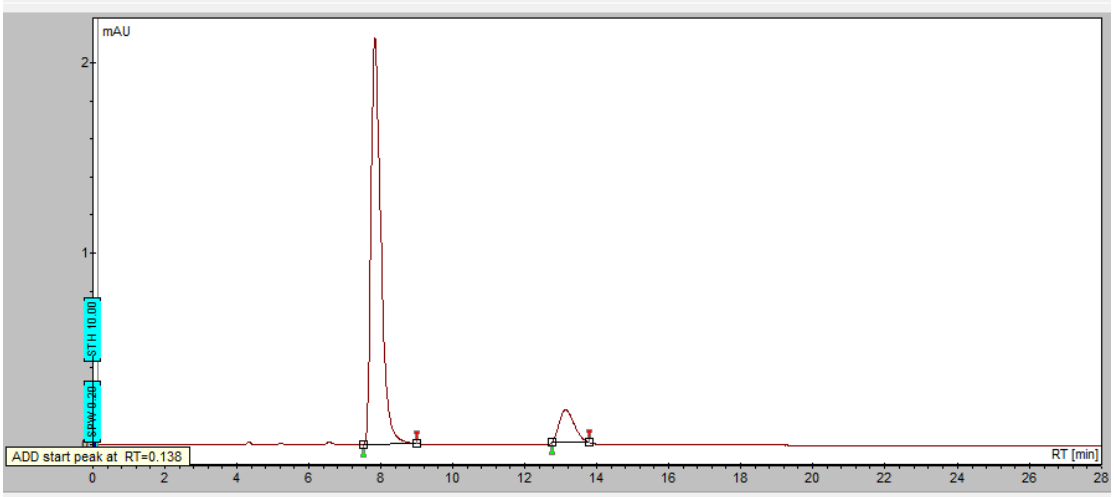
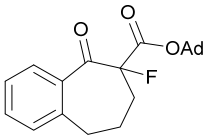


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.786	49.956
2	UNKNOWN	12.626	50.044
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.826	89.208
2	UNKNOWN	13.119	10.792
Total			100.000



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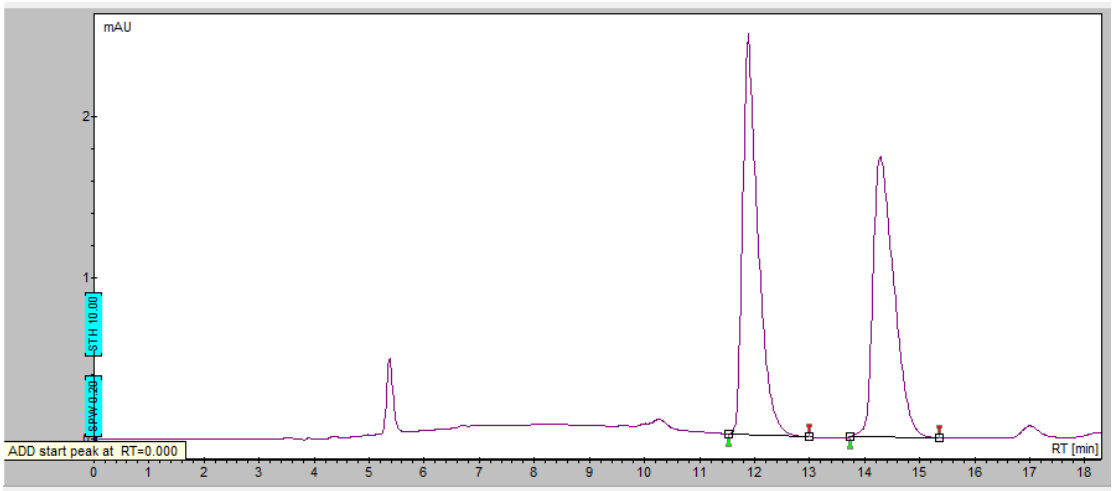
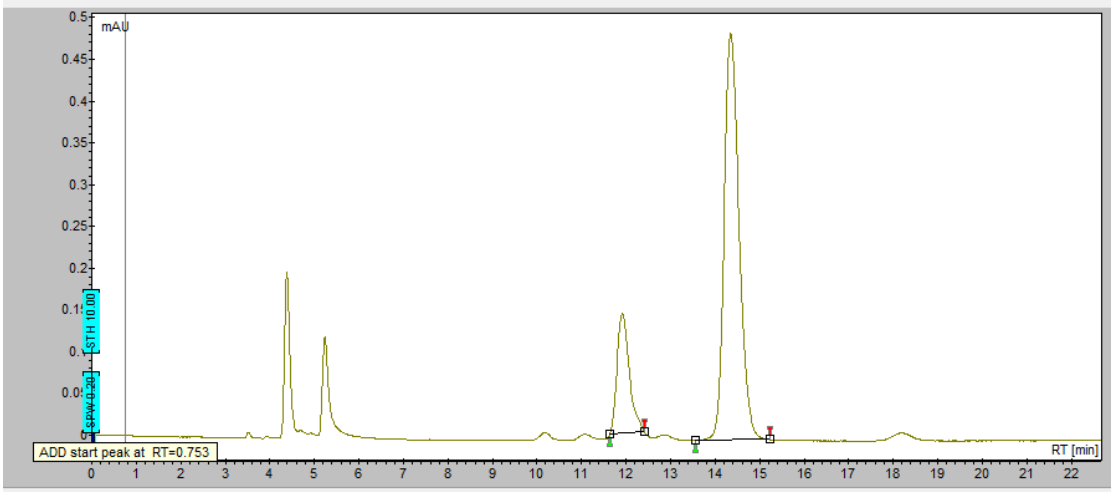
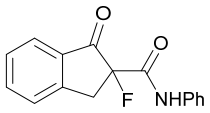


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.879	50.955
2	UNKNOWN	14.292	49.045
Total			100.000



#	Name	Time [Min]	Area % [%]
2	UNKNOWN	11.919	19.596
1	UNKNOWN	14.346	80.404
Total			100.000



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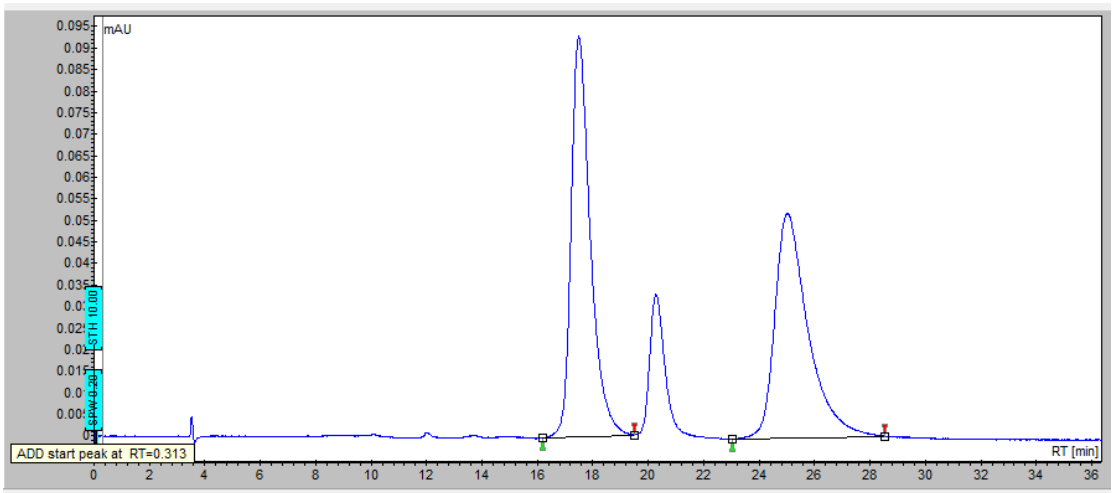
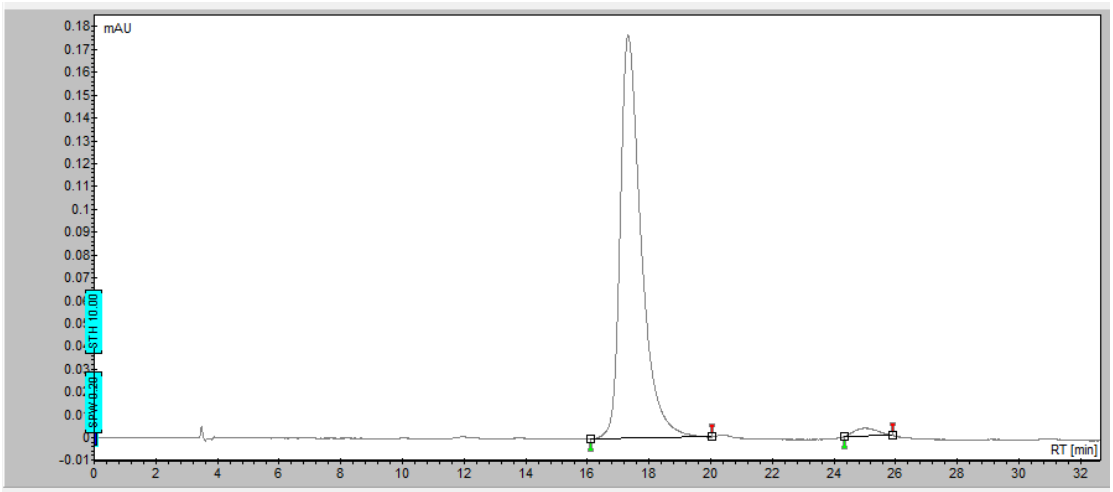
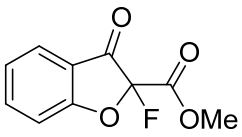


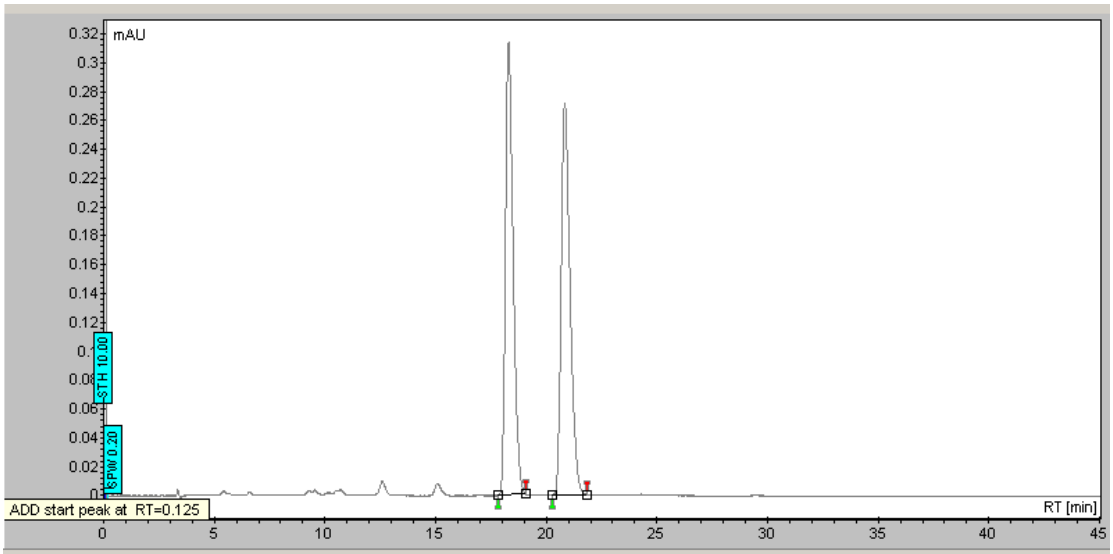
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.492	50.789
2	UNKNOWN	25.012	49.211
Total			100.000



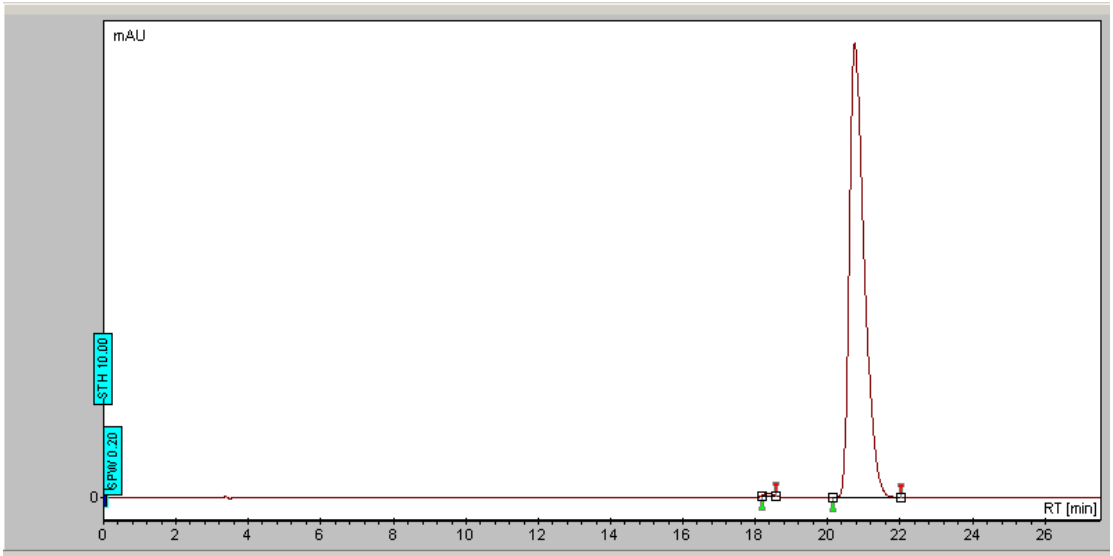
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.319	97.834
2	UNKNOWN	24.998	2.166
Total			100.000



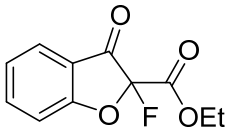
5a



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.292	49.754
2	UNKNOWN	20.825	50.246
Total			100.000



#	Name	Time [Min]	Area % [%]
2	UNKNOWN	18.345	0.240
1	UNKNOWN	20.745	99.760
Total			100.000



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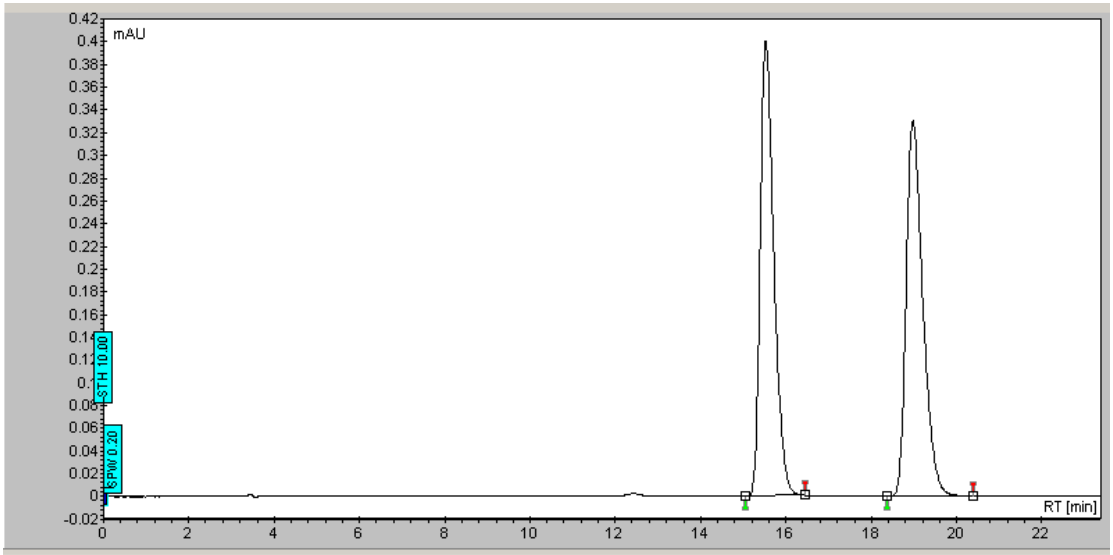
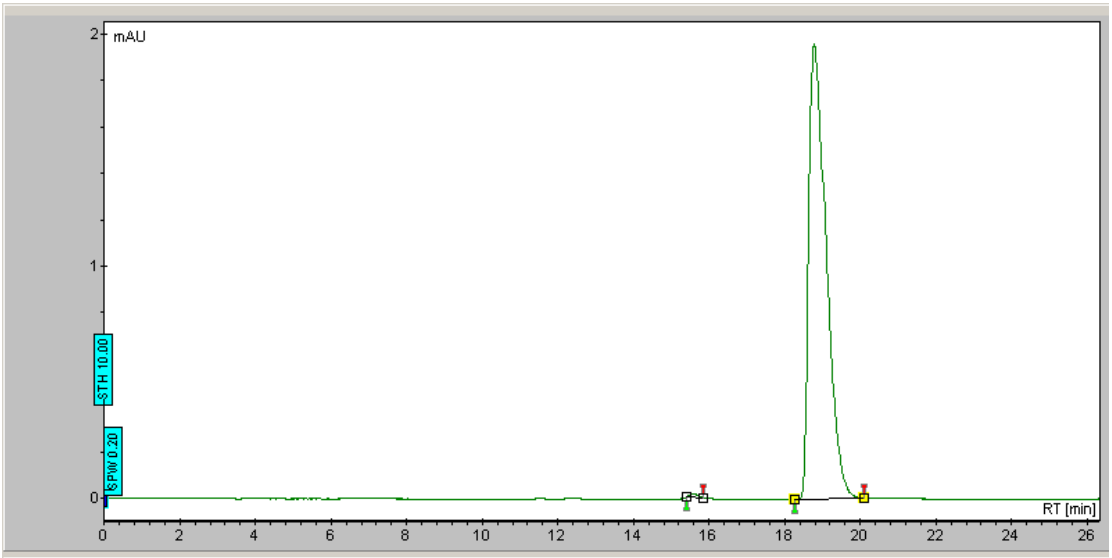
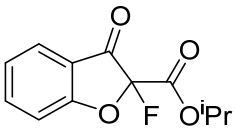


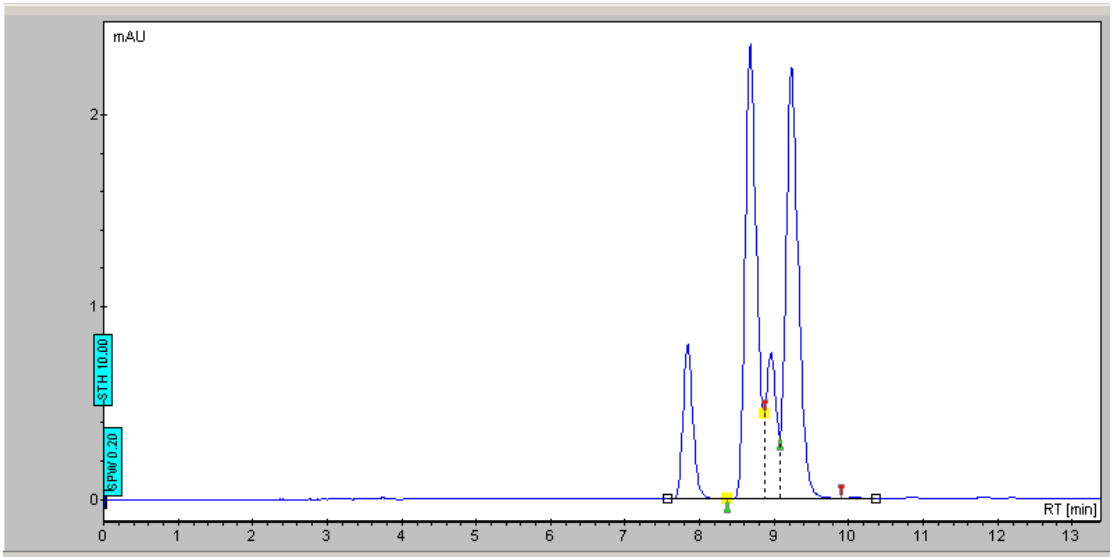
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	15.532	49.869
2	UNKNOWN	18.972	50.131
Total			100.000



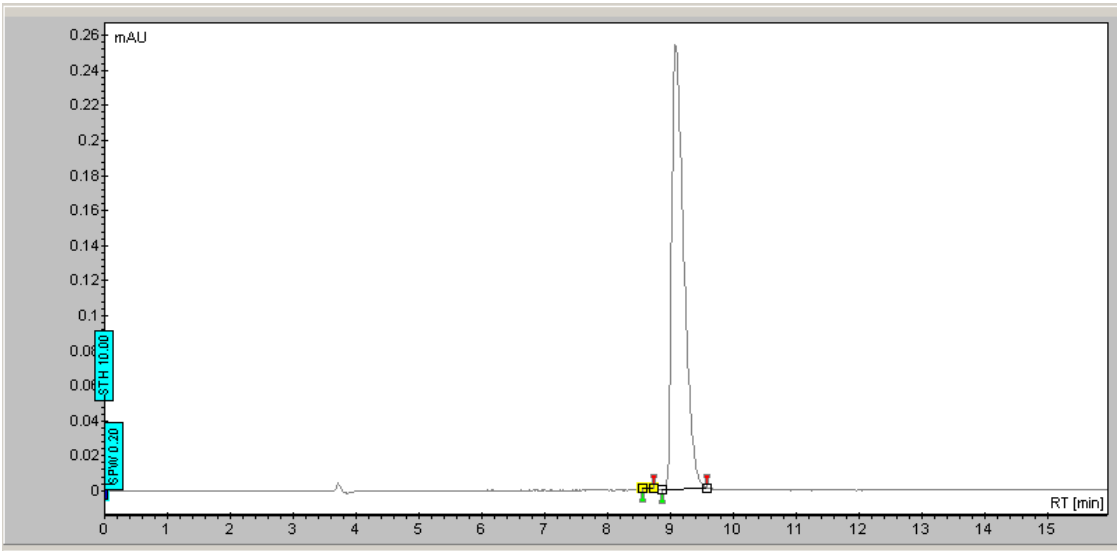
#	Name	Time [Min]	Area % [%]
2	UNKNOWN	15.599	0.344
1	UNKNOWN	18.799	99.656
Total			100.000



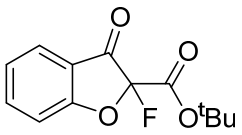
5c



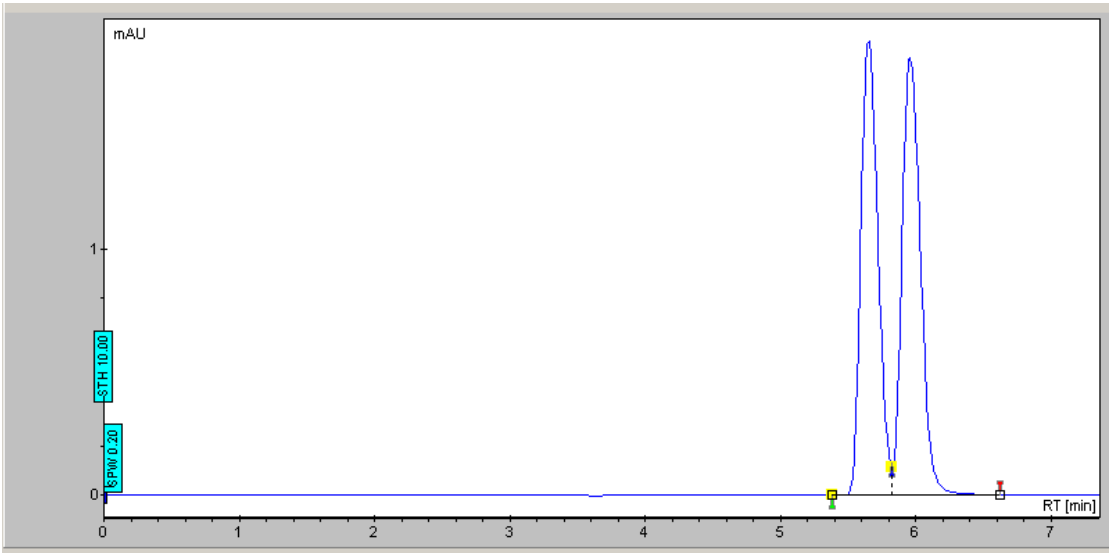
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	8.680	49.000
2	UNKNOWN	9.227	51.000
Total			100.000



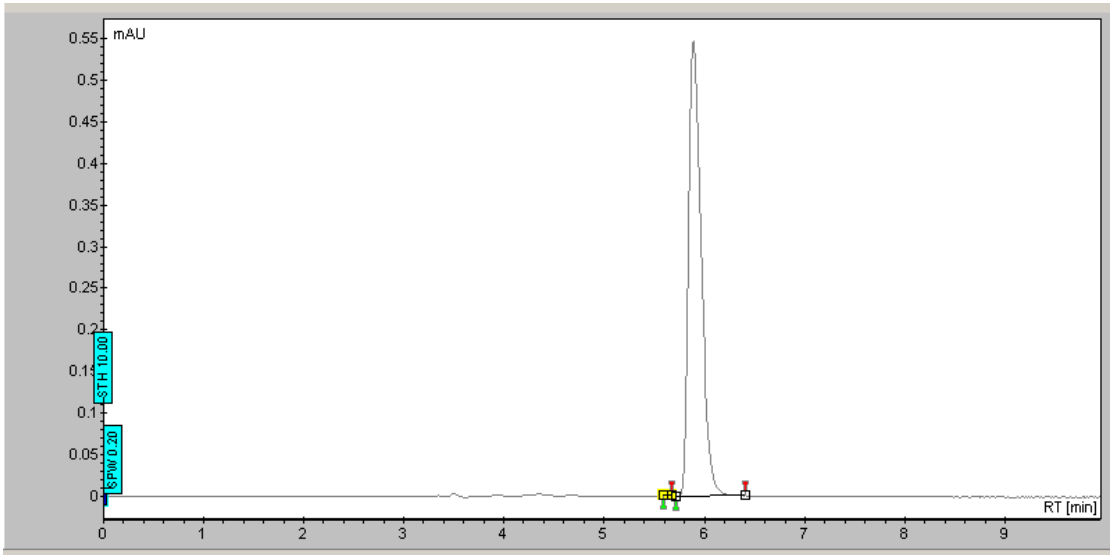
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	8.653	0.264
2	UNKNOWN	9.080	99.736
Total			100.000



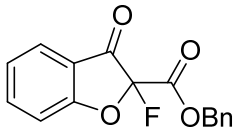
5d



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	5.653	48.788
2	UNKNOWN	5.960	51.212
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	5.627	0.043
2	UNKNOWN	5.893	99.957
Total			100.000



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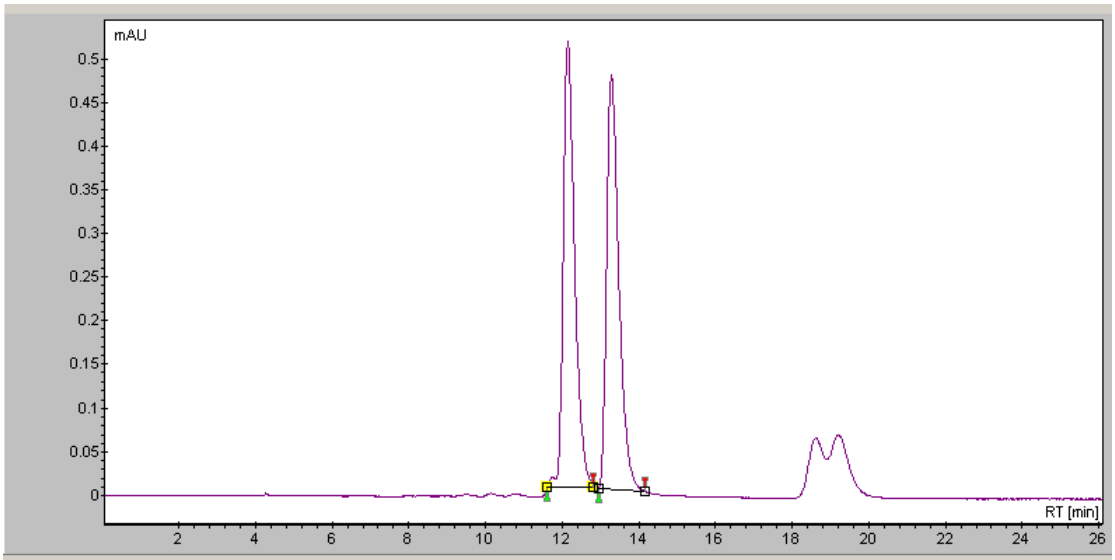
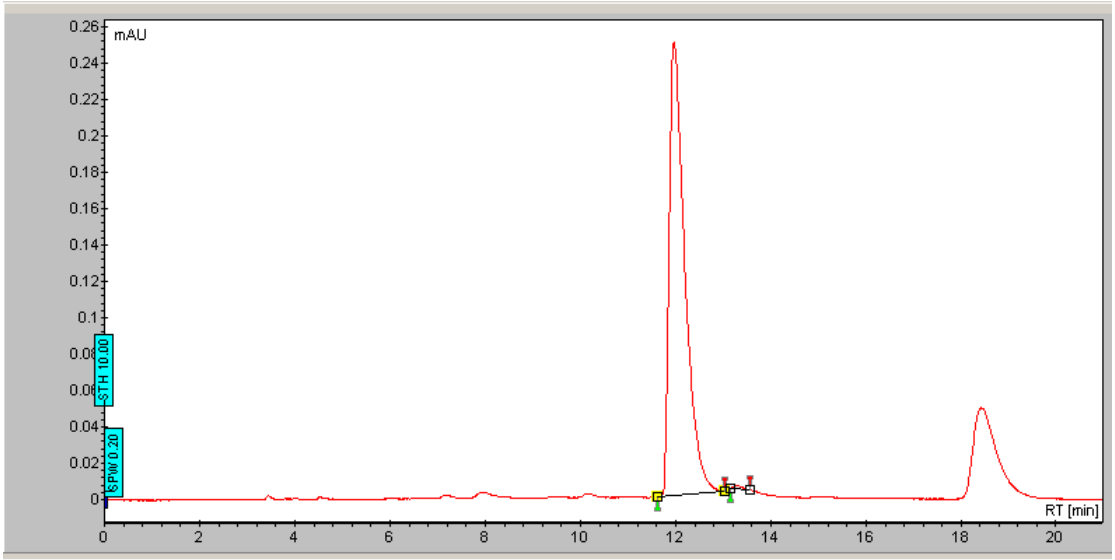
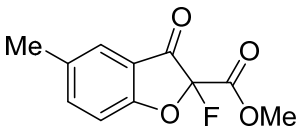


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	12.146	50.086
2	UNKNOWN	13.279	49.914
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.972	99.559
2	UNKNOWN	13.292	0.441
Total			100.000



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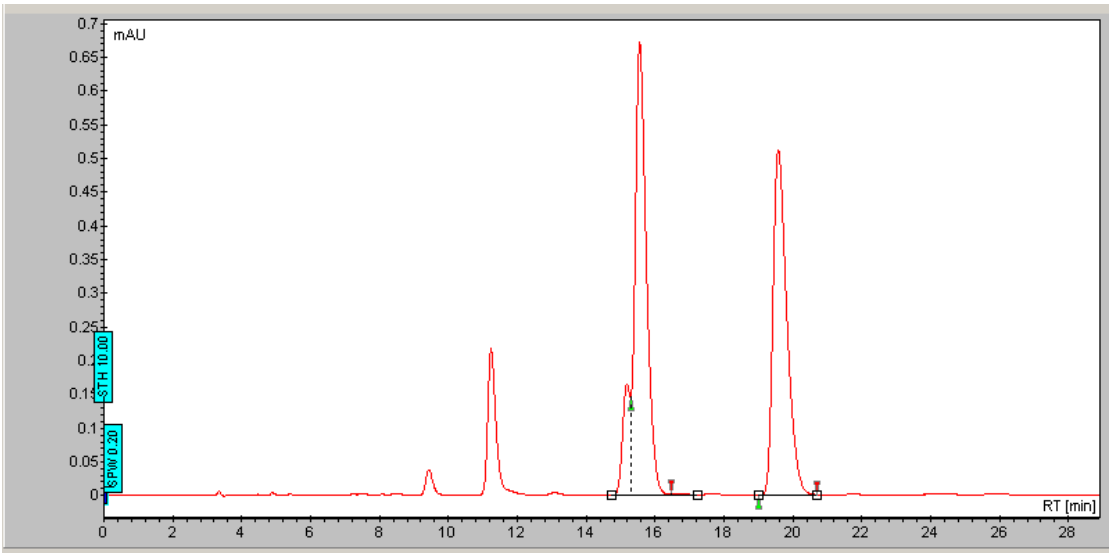
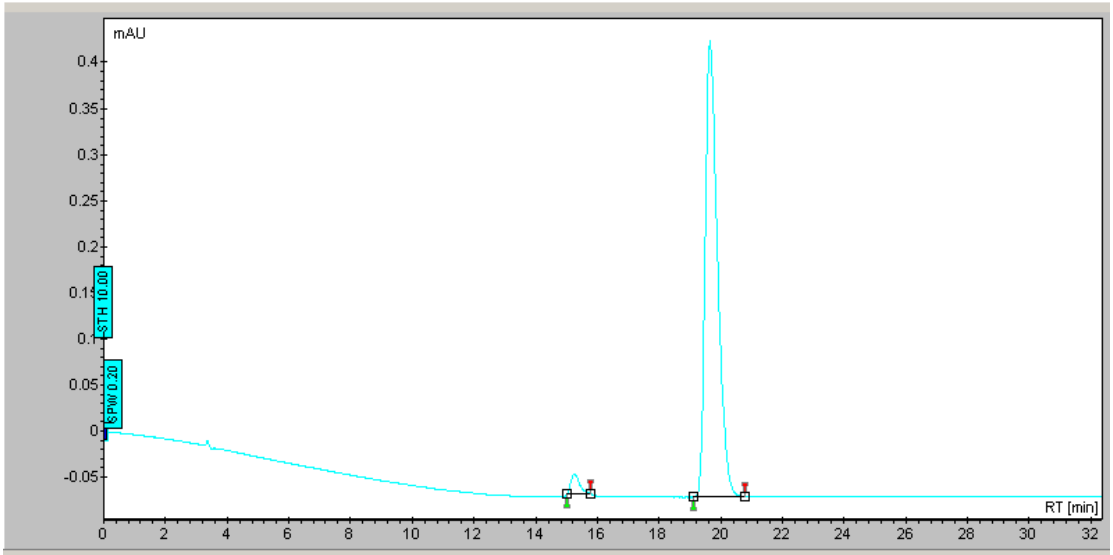
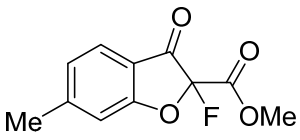


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	15.559	51.733
2	UNKNOWN	19.572	48.267
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	15.252	3.031
2	UNKNOWN	19.652	96.969
Total			100.000



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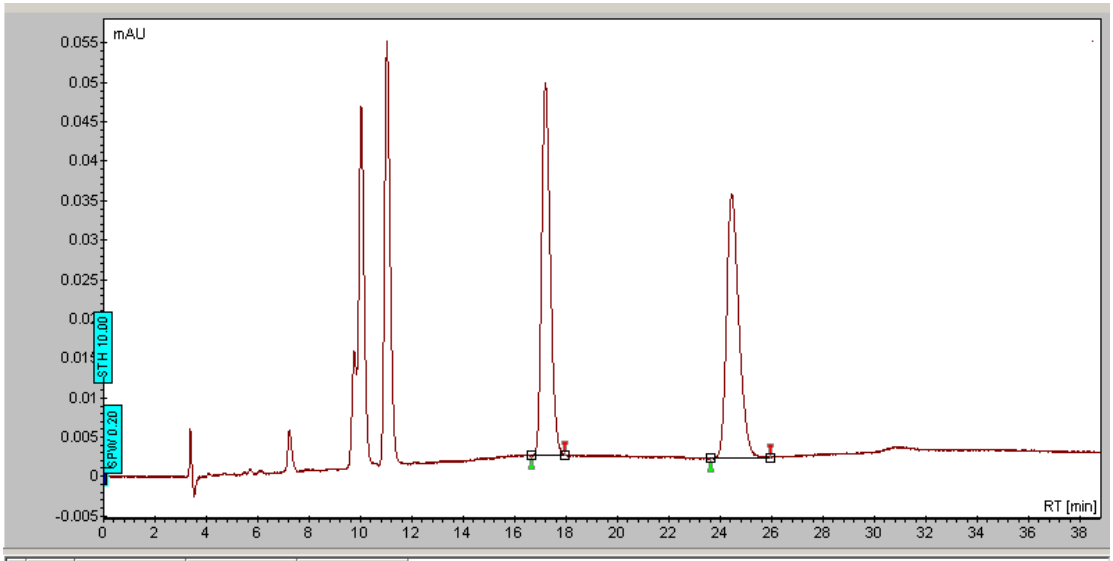
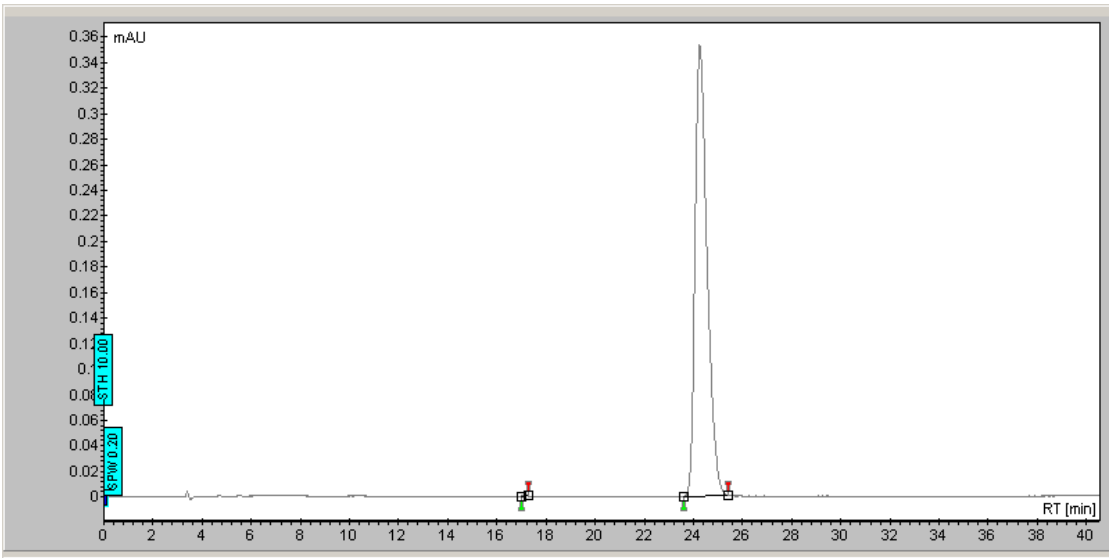
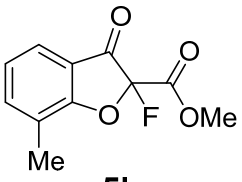


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.199	49.472
2	UNKNOWN	24.452	50.528
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.119	0.058
2	UNKNOWN	24.252	99.942
Total			100.000



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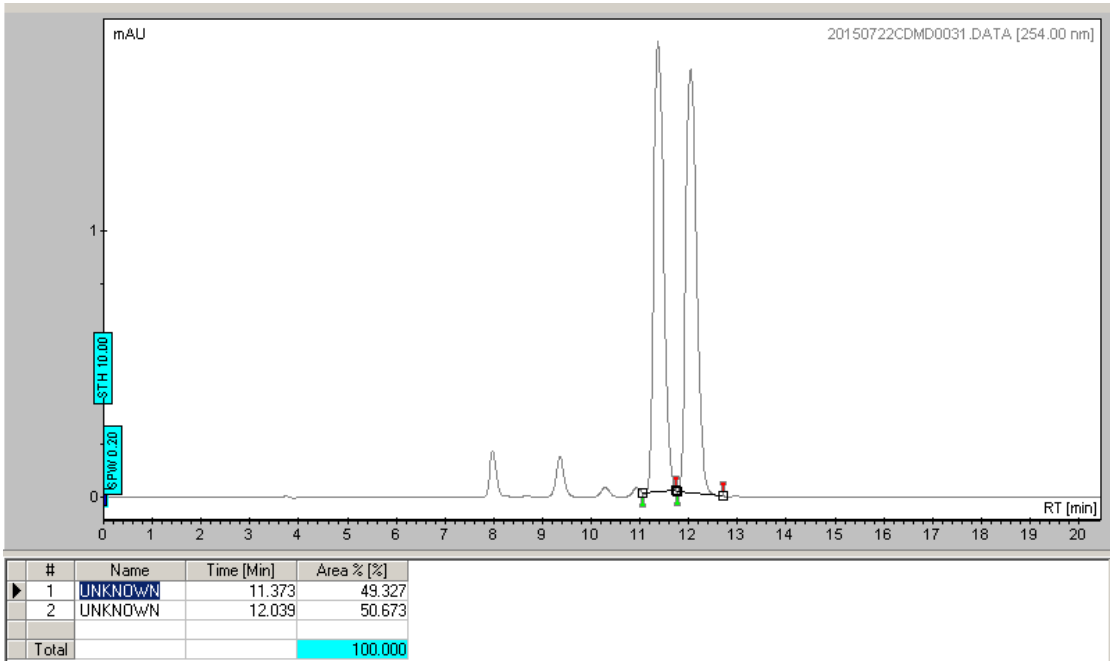
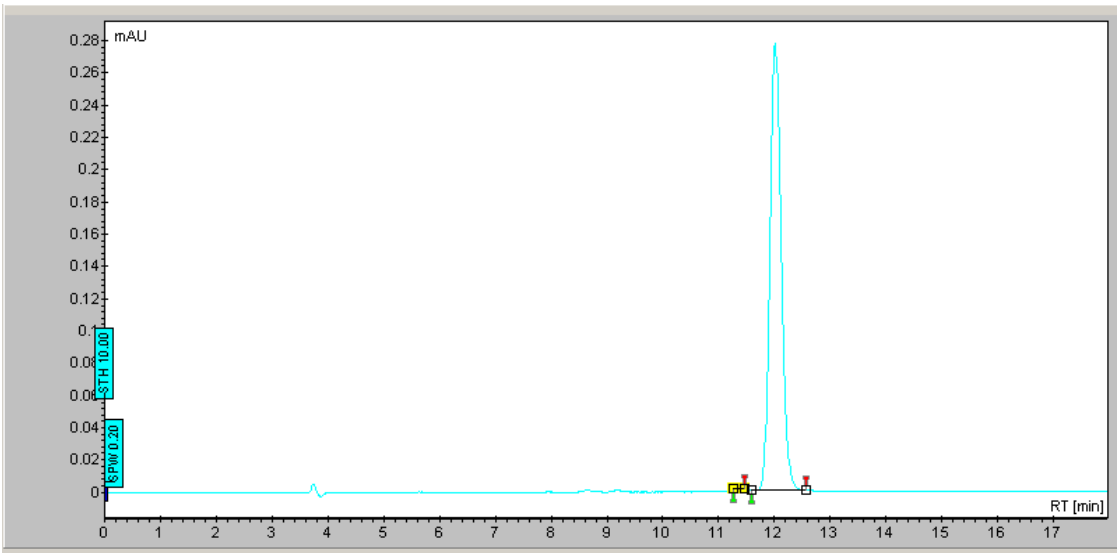
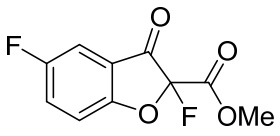


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.373	49.327
2	UNKNOWN	12.039	50.673
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	11.359	0.197
2	UNKNOWN	12.012	99.803
Total			100.000



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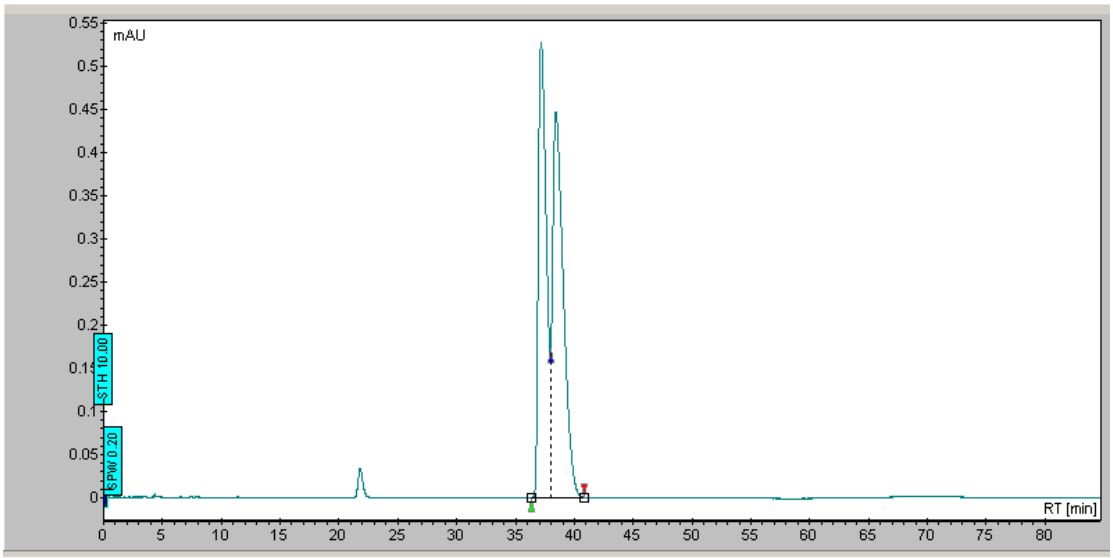
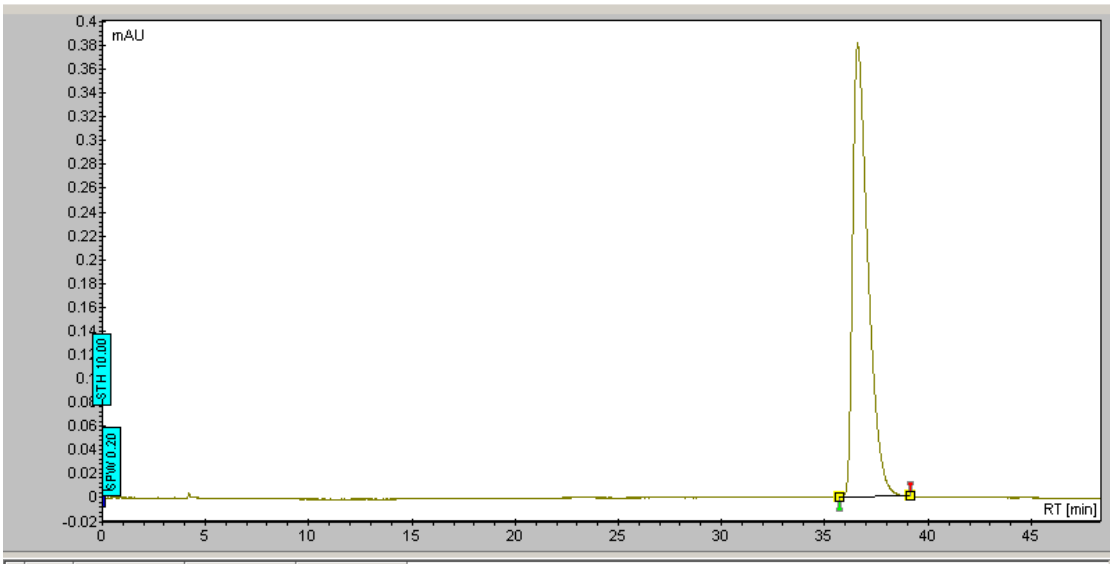
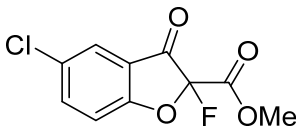


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	37.187	46.301
2	UNKNOWN	38.440	53.699
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	36.597	100.000
Total			100.000



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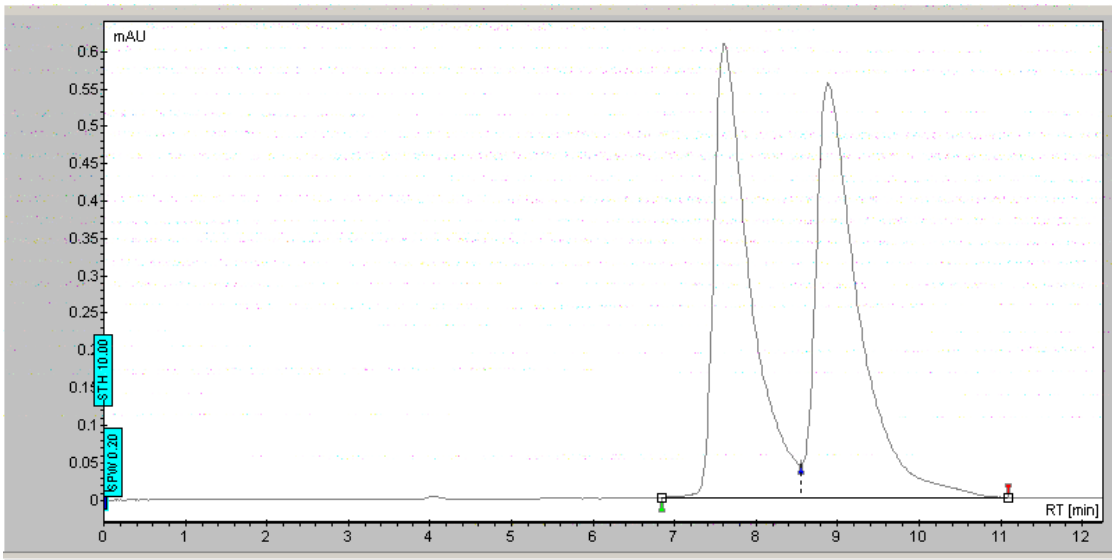
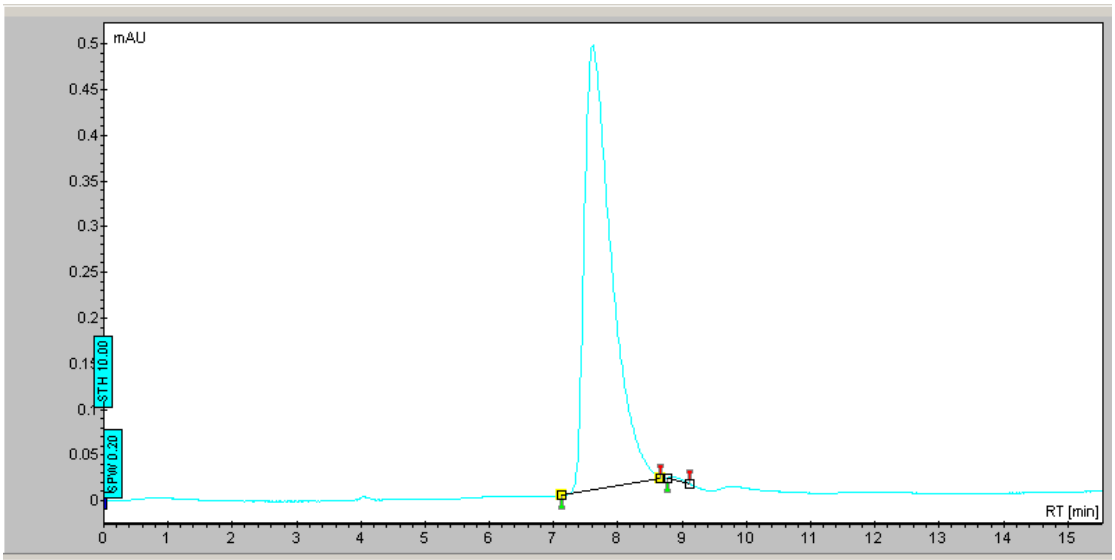
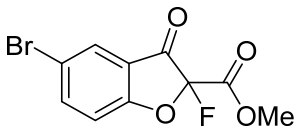


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.613	48.203
2	UNKNOWN	8.880	51.797
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	7.613	99.736
2	UNKNOWN	8.907	0.264
Total			100.000



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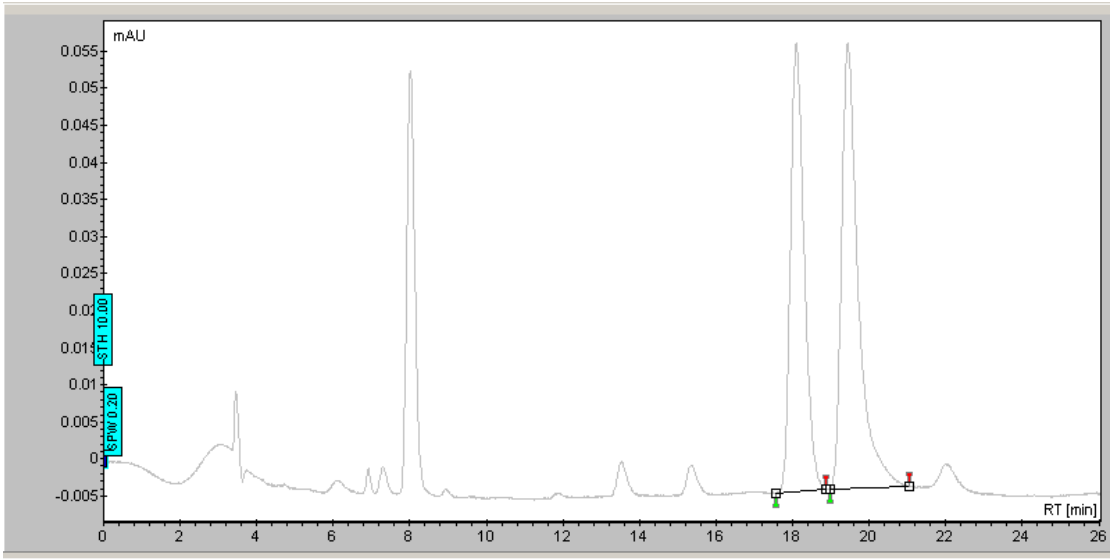
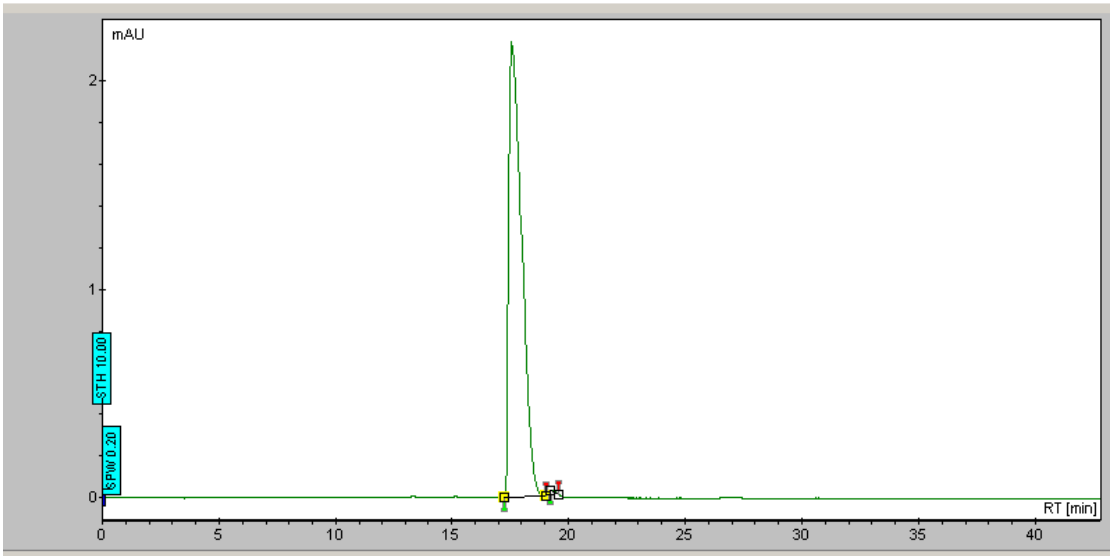
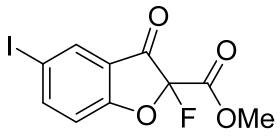


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.092	45.130
2	UNKNOWN	19.439	54.870
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.559	99.834
2	UNKNOWN	19.345	0.166
Total			100.000



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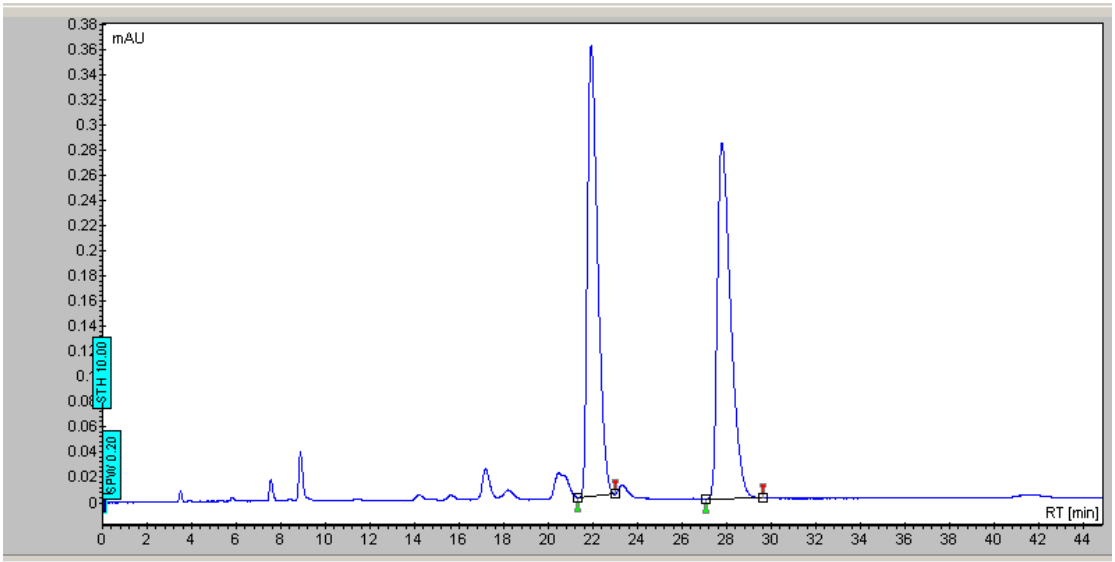
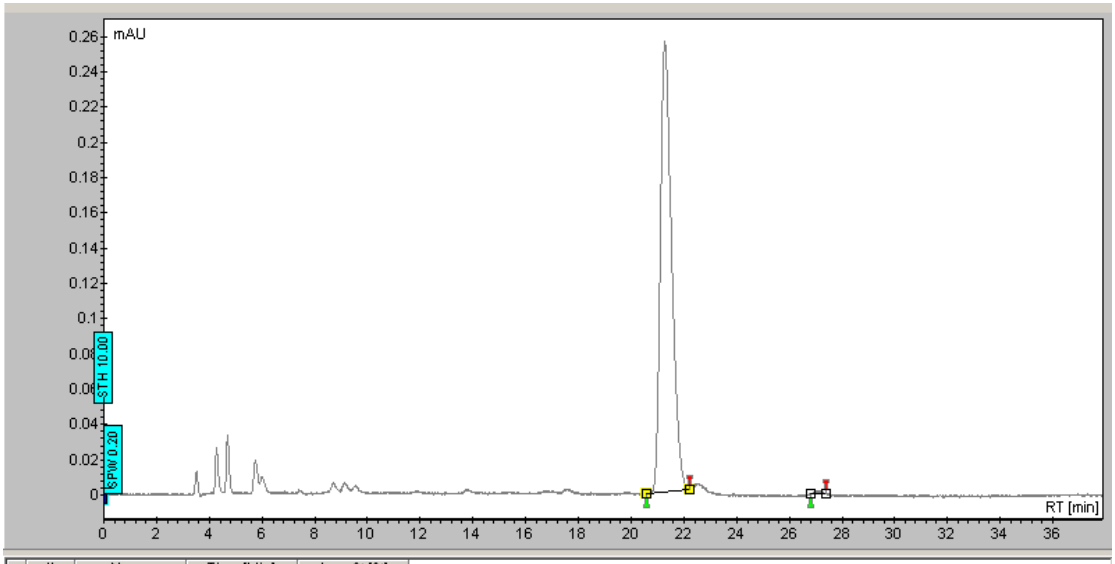
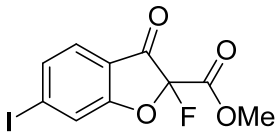


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.918	49.402
2	UNKNOWN	27.785	50.598
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.278	99.609
2	UNKNOWN	27.105	0.391
Total			100.000



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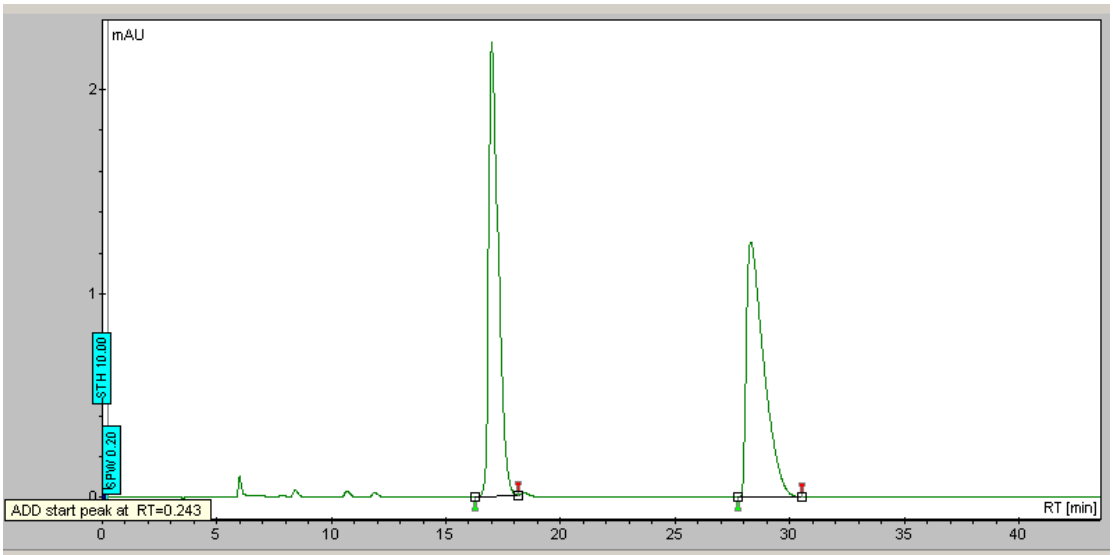
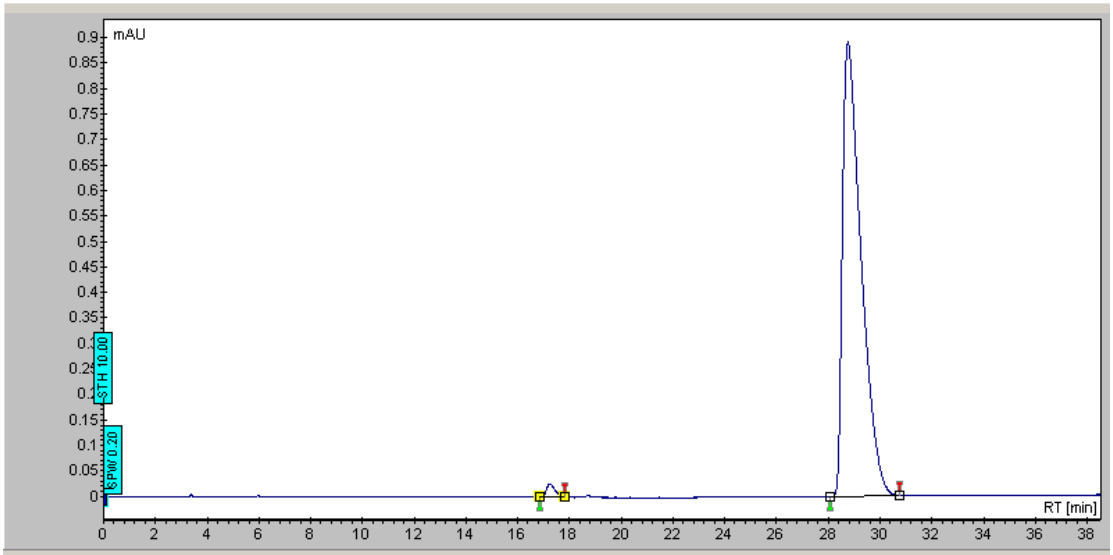
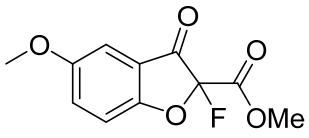


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	16.999	49.472
2	UNKNOWN	28.305	50.528
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	17.252	1.277
2	UNKNOWN	28.758	98.723
Total			100.000



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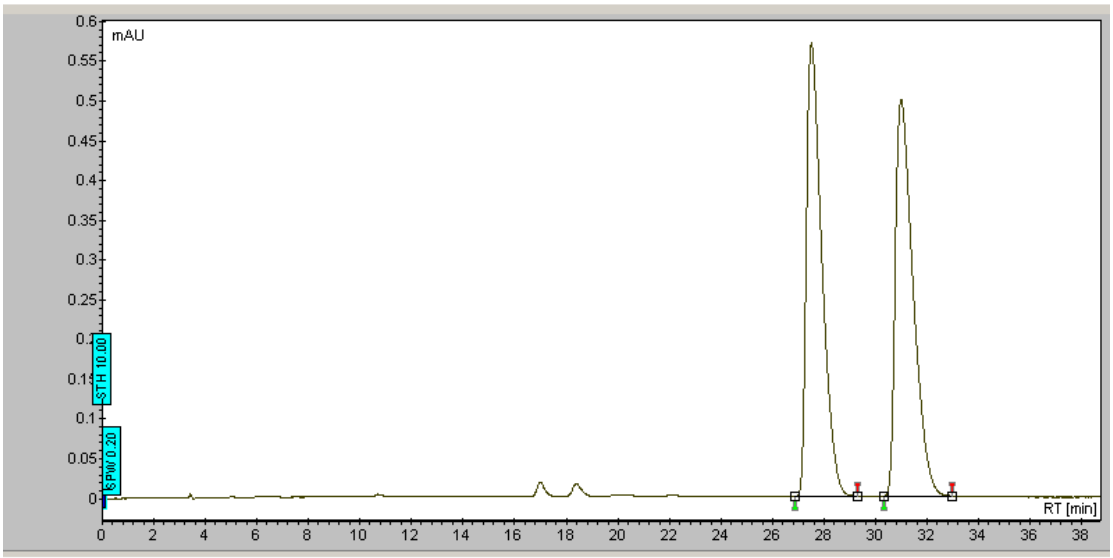
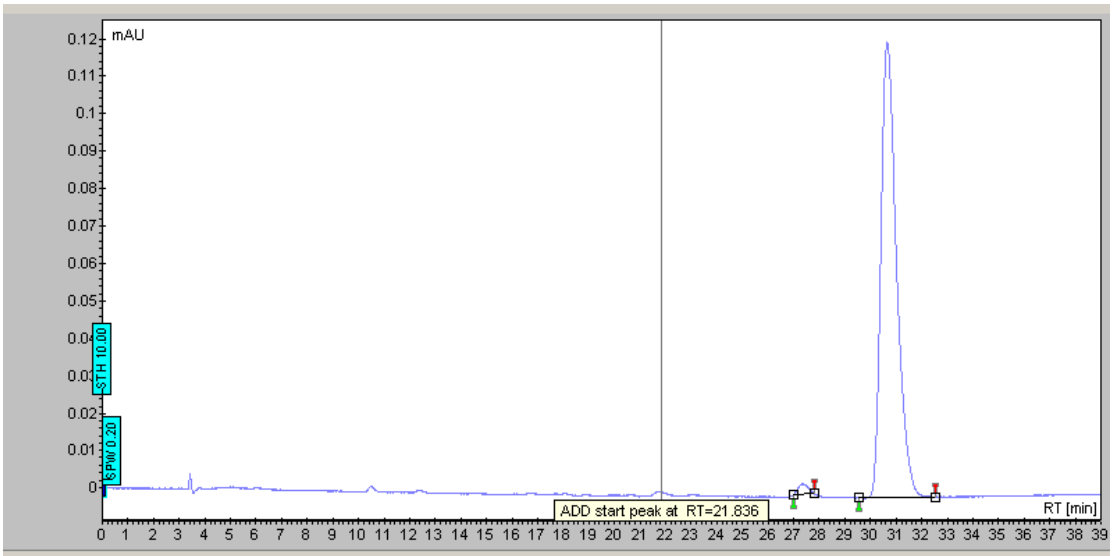
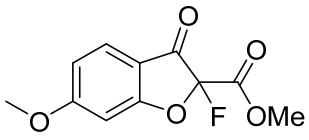


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	27.518	50.022
2	UNKNOWN	30.998	49.978
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	27.358	1.392
2	UNKNOWN	30.651	98.608
Total			100.000



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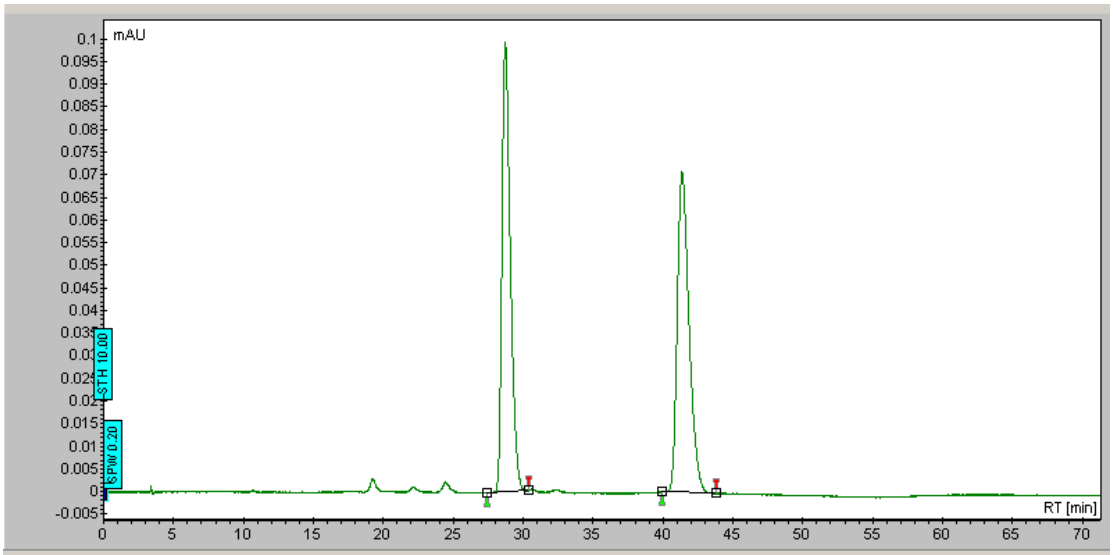
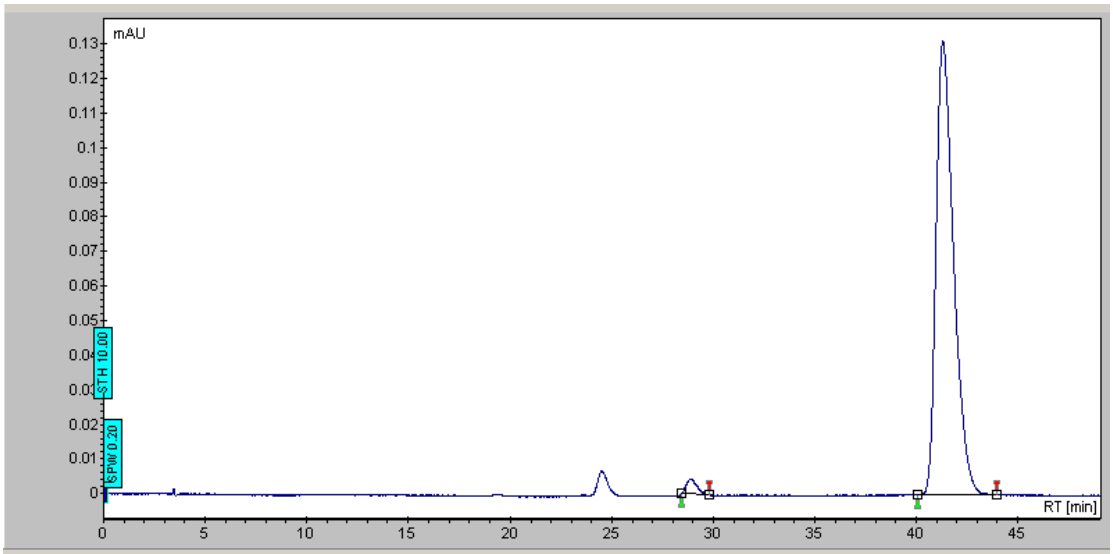
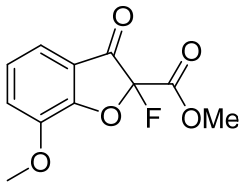


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	28.723	50.026
2	UNKNOWN	41.358	49.974
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	28.891	1.963
2	UNKNOWN	41.317	98.037
Total			100.000



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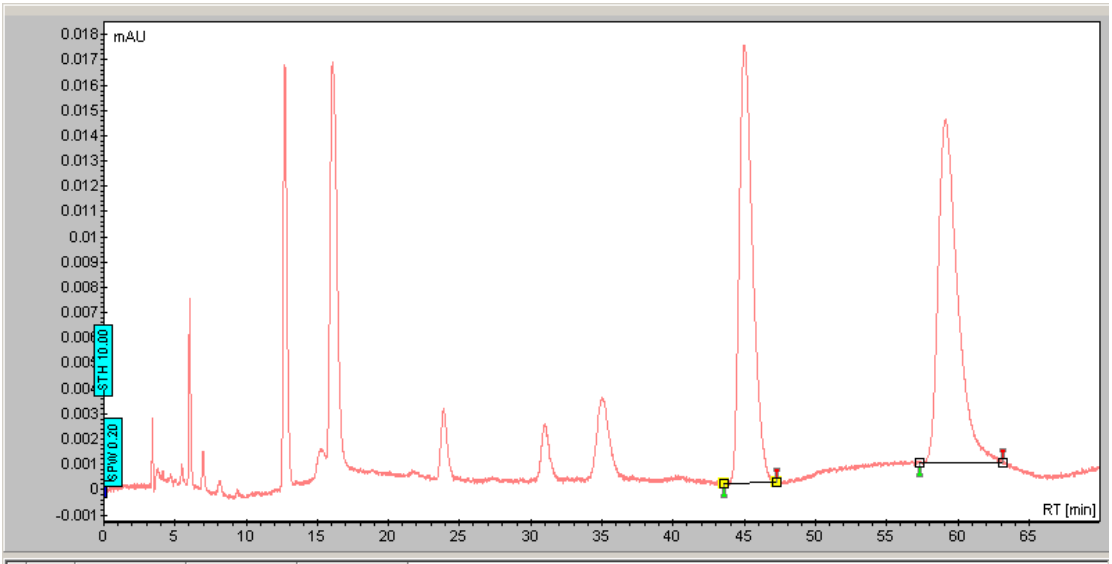
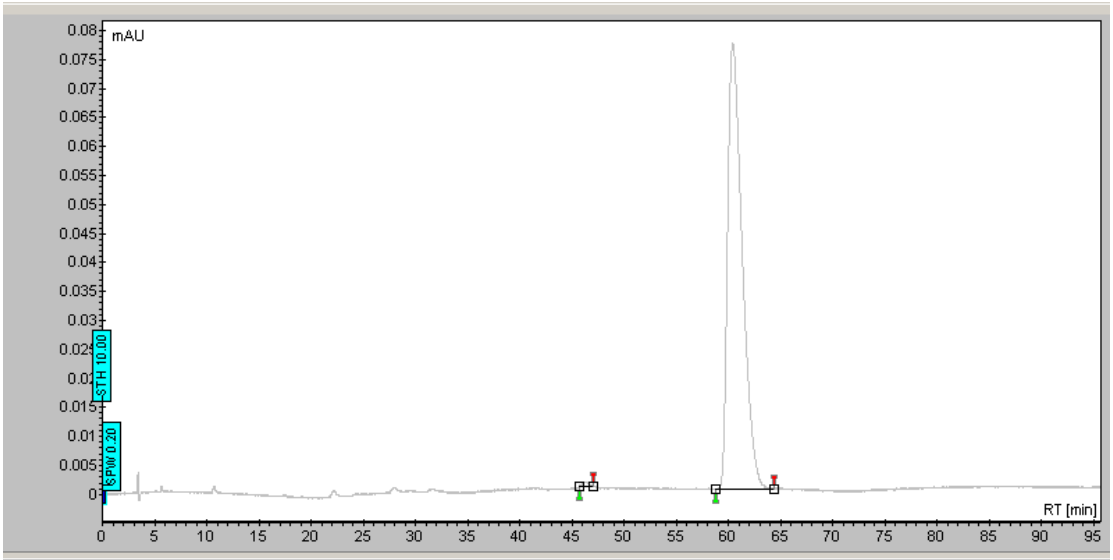
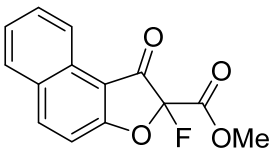


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	45.011	46.830
2	UNKNOWN	59.125	53.170
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	46.277	0.450
2	UNKNOWN	60.405	99.550
Total			100.000



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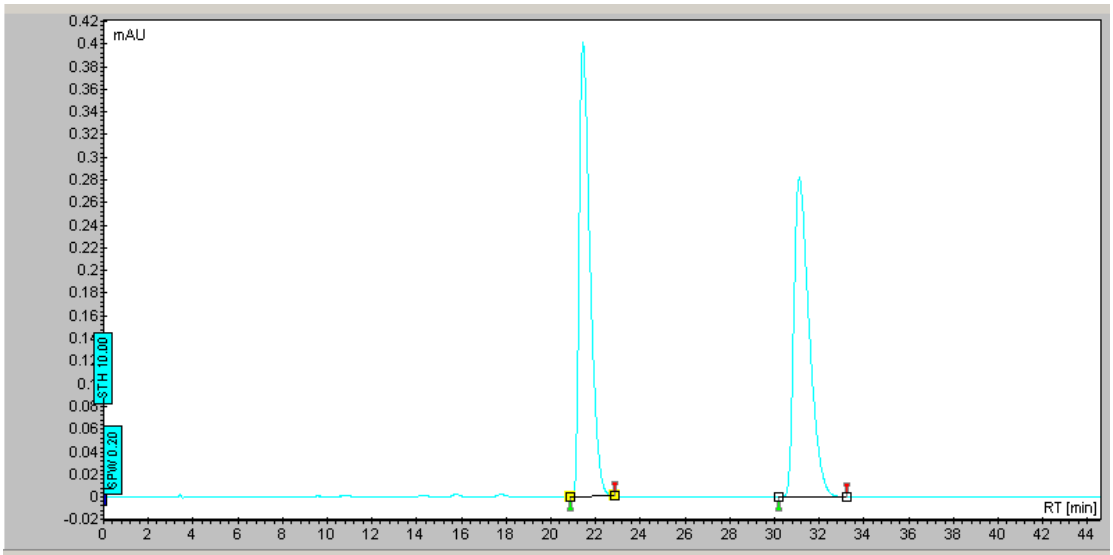
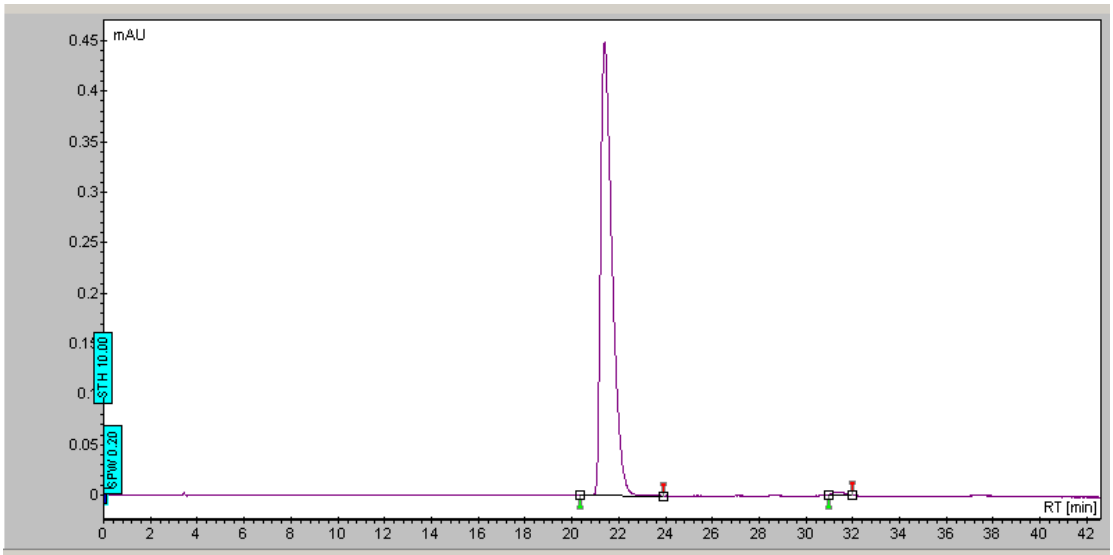
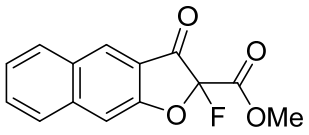


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.438	50.112
2	UNKNOWN	31.118	49.888
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.398	99.371
2	UNKNOWN	31.411	0.629
Total			100.000



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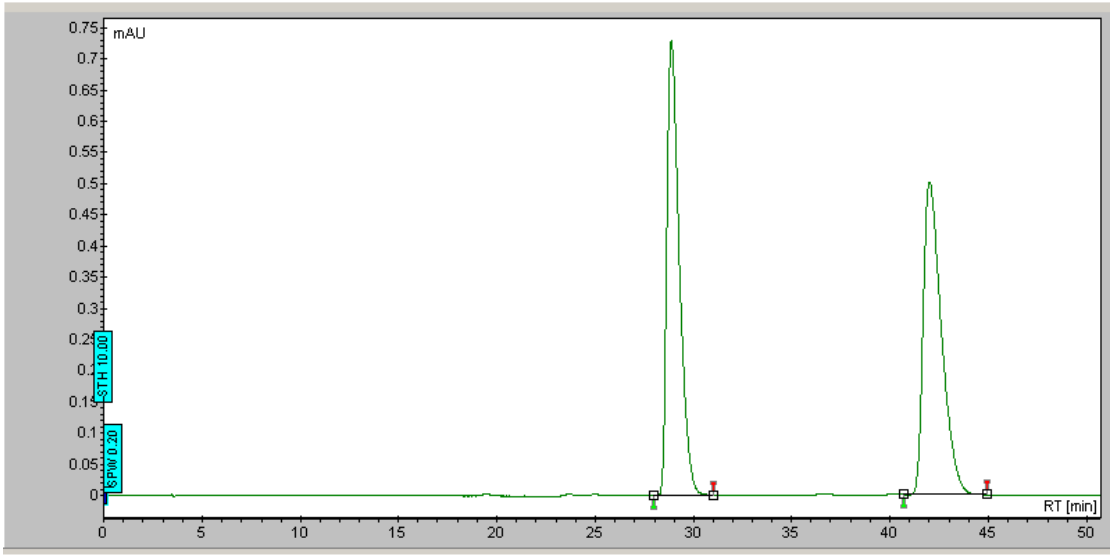
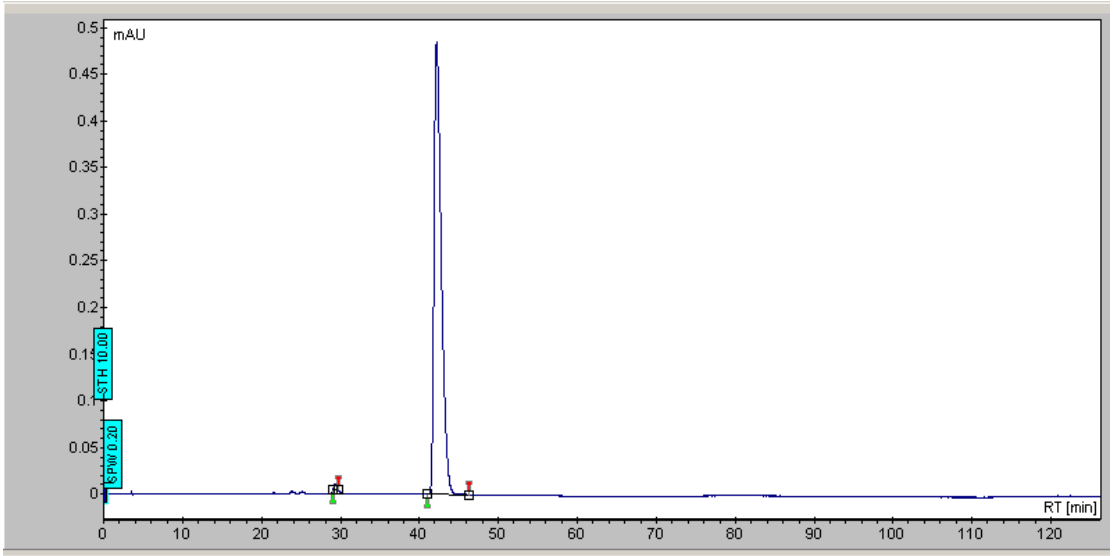
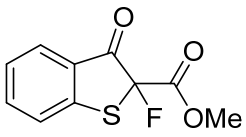


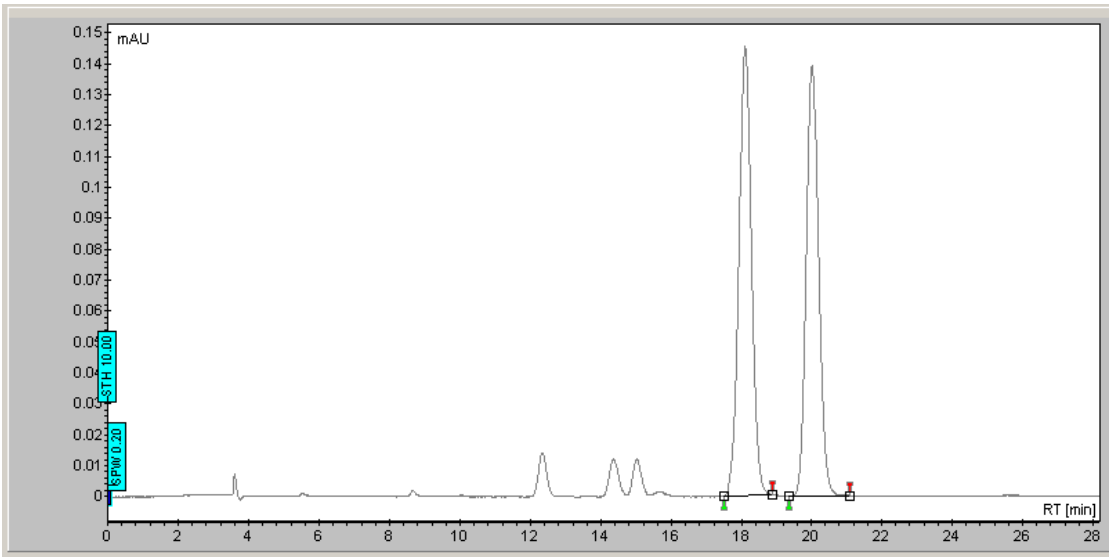
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	28.865	49.886
2	UNKNOWN	42.010	50.114
Total			100.000



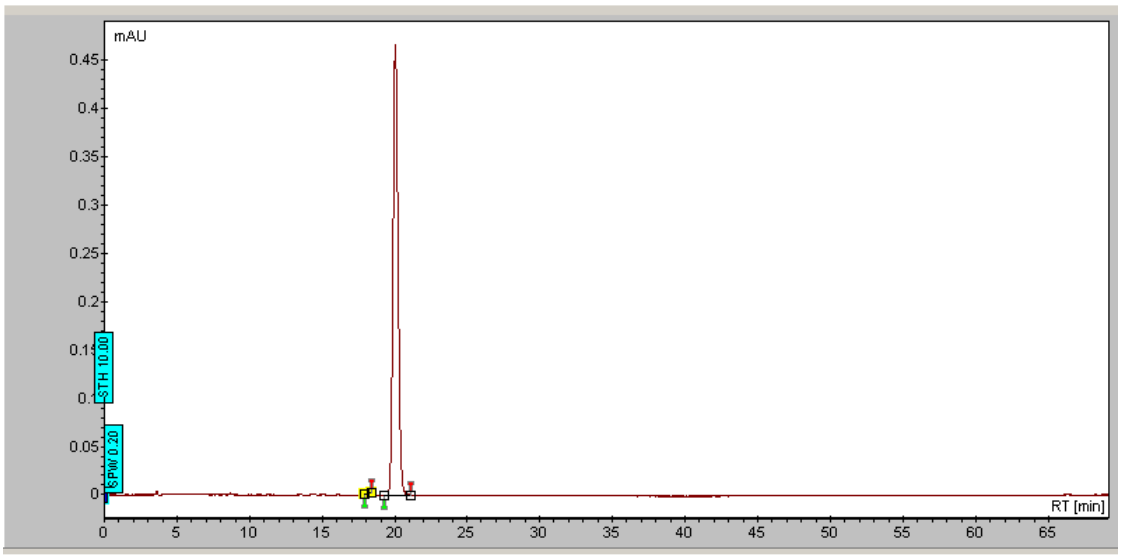
#	Name	Time [Min]	Area % [%]
2	UNKNOWN	29.349	0.496
1	UNKNOWN	42.185	99.504
Total			100.000



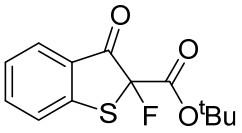
6a



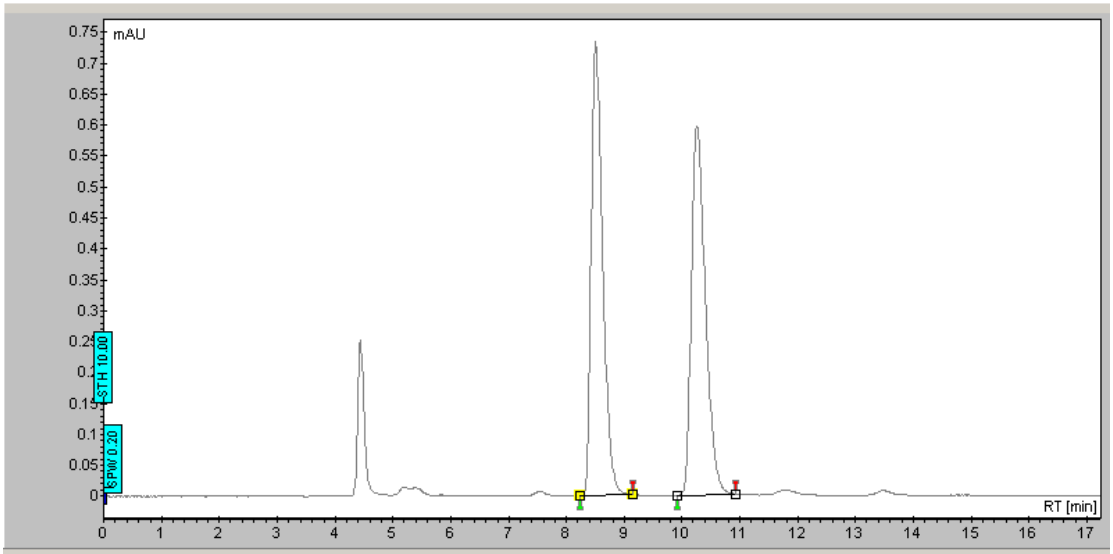
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.105	51.338
2	UNKNOWN	20.012	48.662
Total			100.000



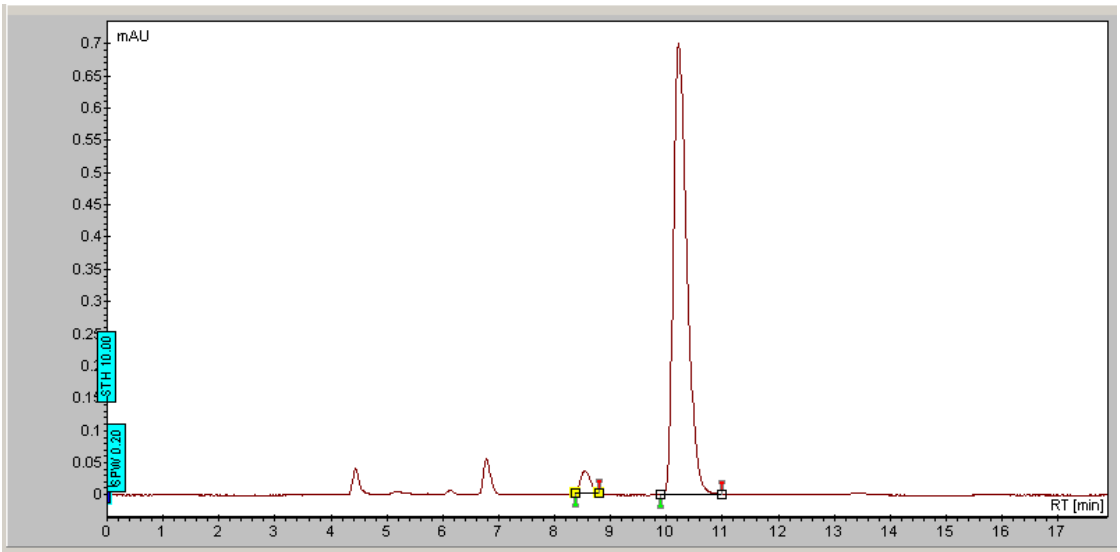
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.220	0.388
2	UNKNOWN	20.046	99.612
Total			100.000



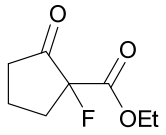
6b



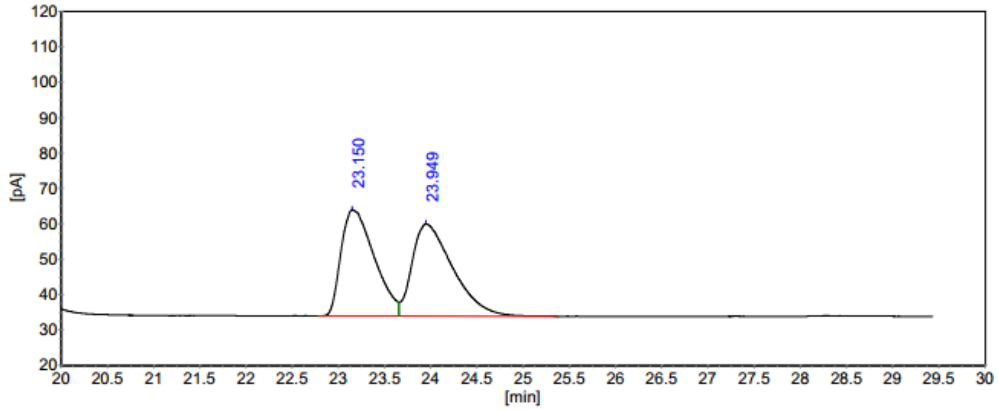
#	Name	Time [Min]	Area % [%]
1	UNKNOWN	8.506	50.239
2	UNKNOWN	10.253	49.761
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	8.546	3.469
2	UNKNOWN	10.213	96.531
Total			100.000

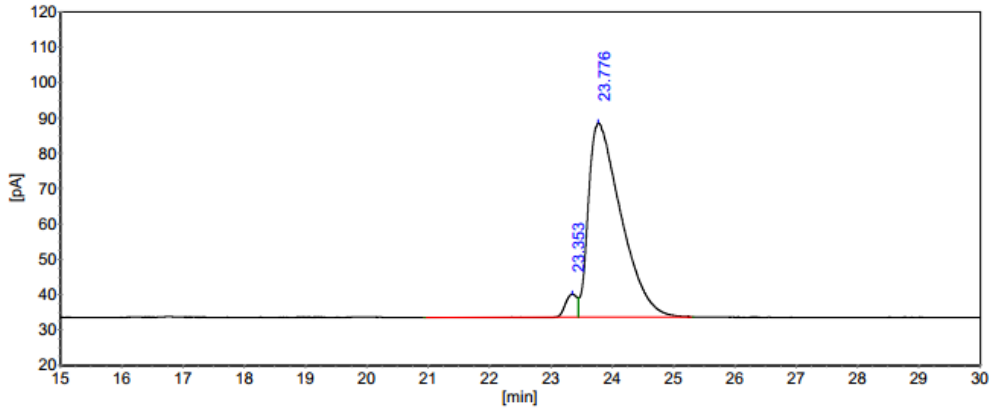


8a



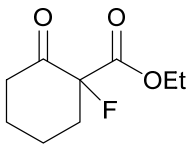
分析结果表

峰序	组分名	保留时间 [min]	峰高 [pA]	峰面积 [pA*s]	面积%	含量 [%]	峰型
1		23.150	30.08	749.66	48.4905	48.4905	BV
2		23.949	26.16	796.34	51.5095	51.5095	VB
	总计:		**56.24**	**1546.00**	**100.0000**	**100.0000**	



分析结果表

峰序	组分名	保留时间 [min]	峰高 [pA]	峰面积 [pA*s]	面积%	含量 [%]	峰型
1		23.353	6.52	83.82	3.9708	3.9708	TPV
2		23.776	54.97	2027.07	96.0292	96.0292	TVB
	总计:		**61.49**	**2110.88**	**100.0000**	**100.0000**	



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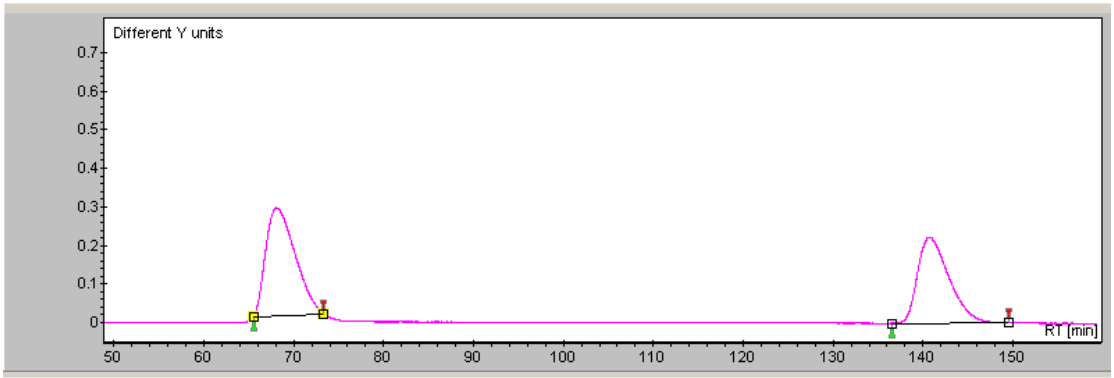
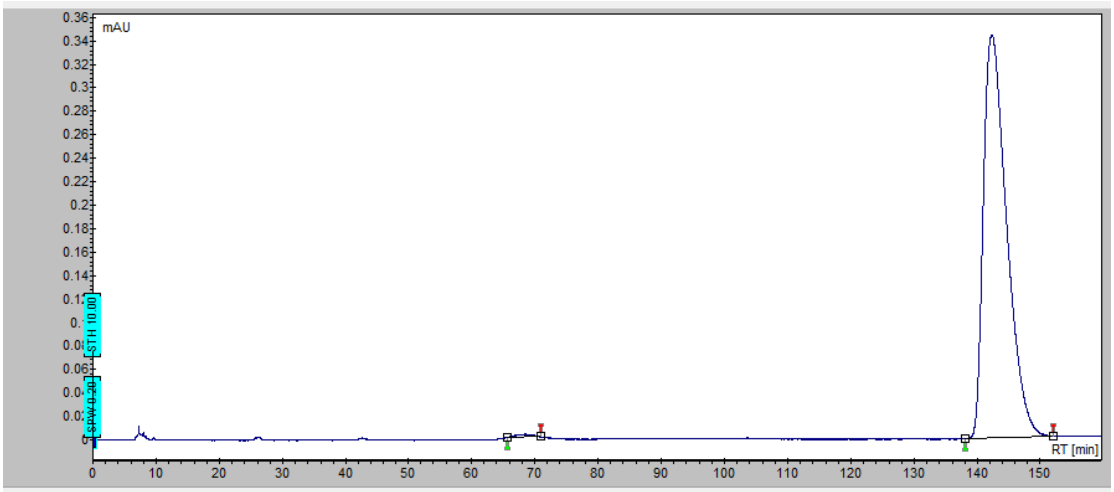
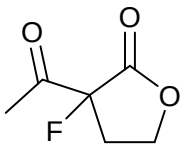


#	Name	Time [Min]	Area % [%]
2	UNKNOWN	68.083	53.829
1	UNKNOWN	140.709	46.171
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	68.350	0.446
2	UNKNOWN	142.401	99.554
Total			100.000



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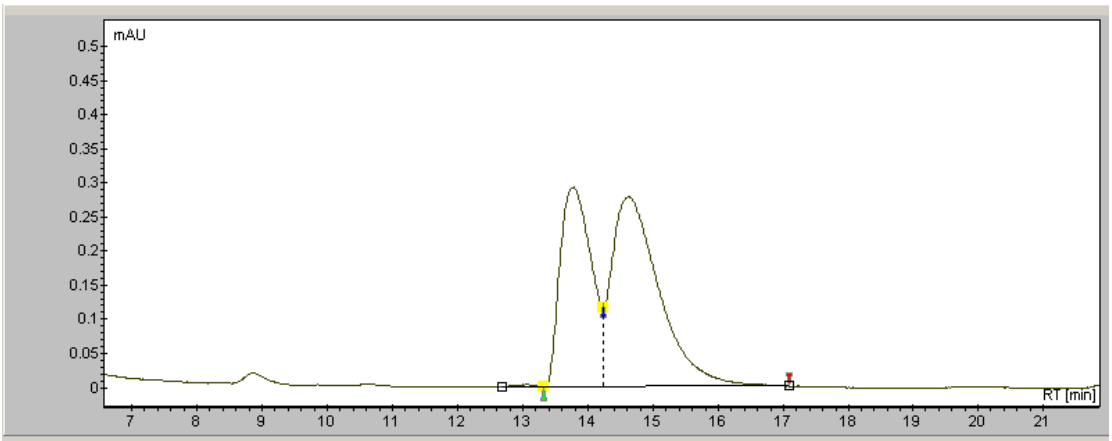
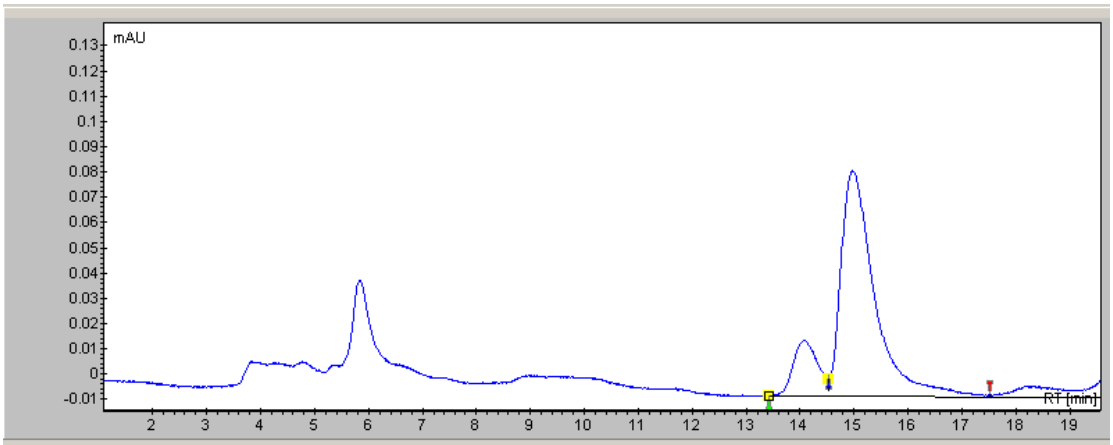
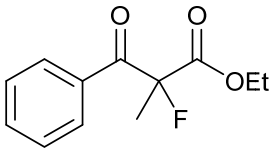


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	13.772	40.807
2	UNKNOWN	14.626	59.193
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.079	15.137
2	UNKNOWN	14.972	84.863
Total			100.000



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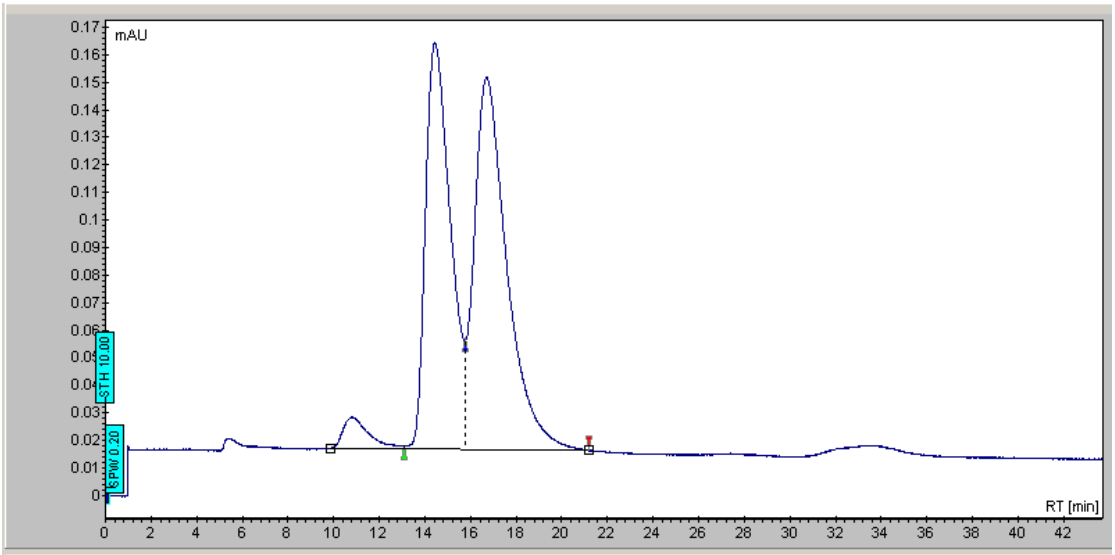
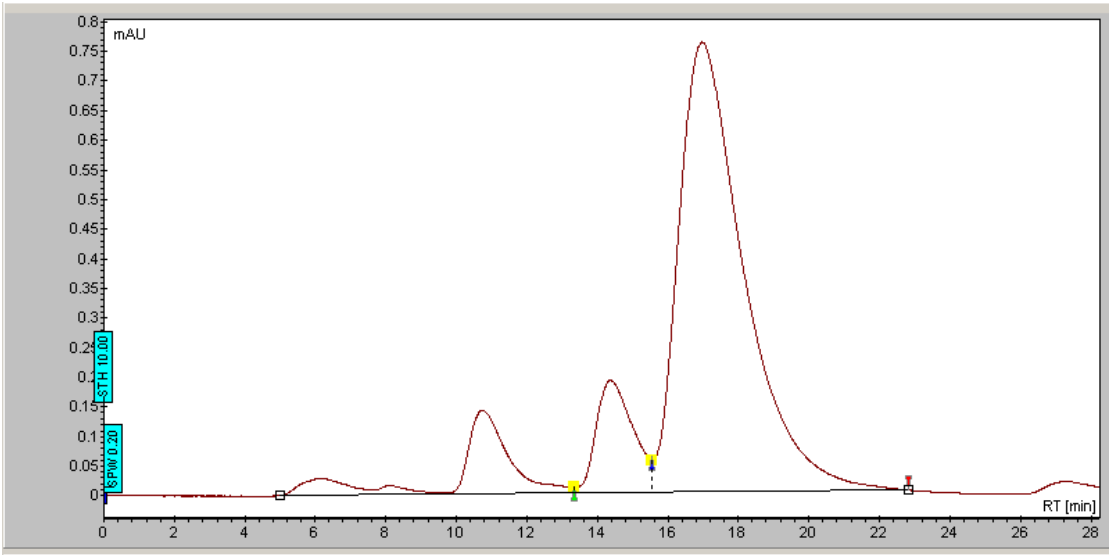
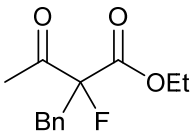


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.439	45.249
2	UNKNOWN	16.705	54.751
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.372	12.411
2	UNKNOWN	16.972	87.589
Total			100.000



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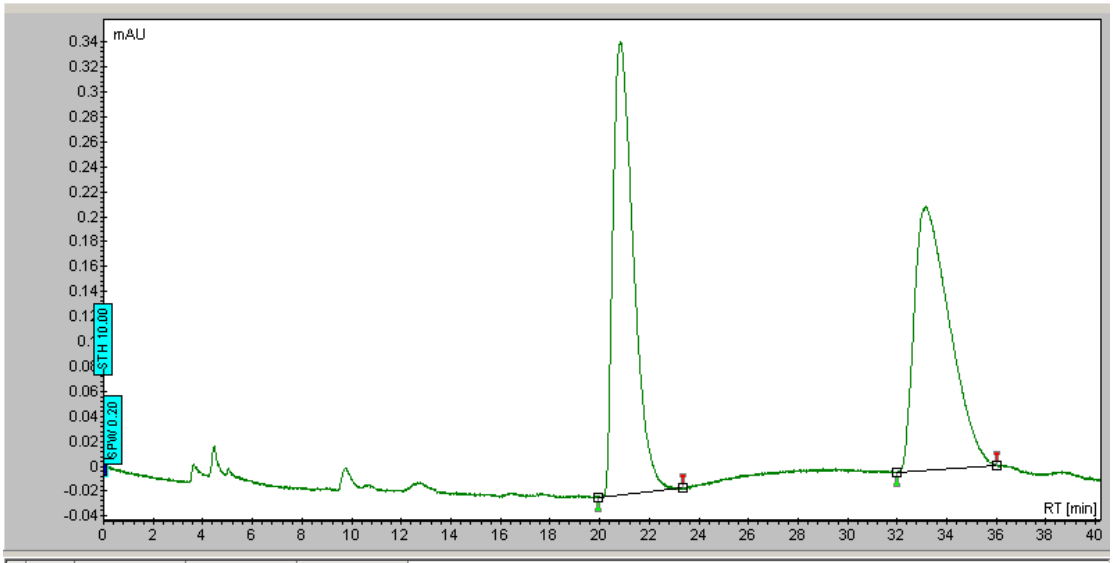
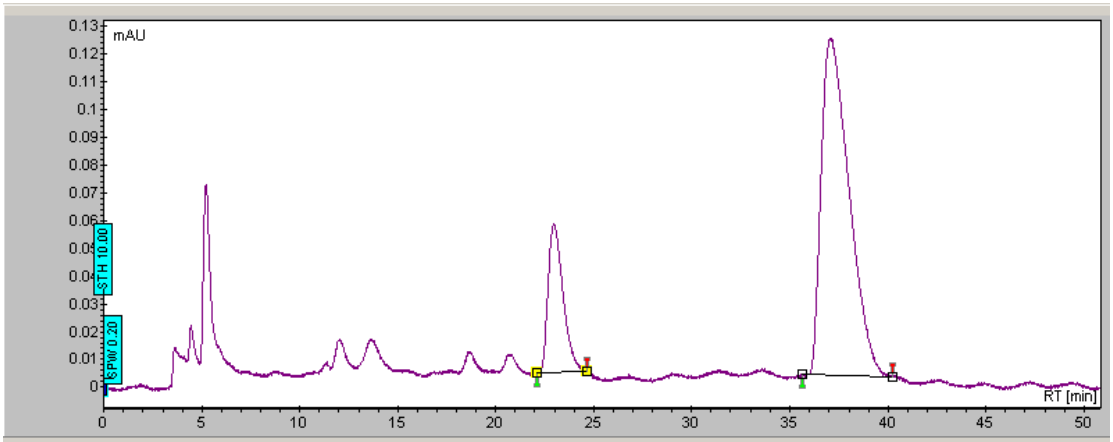


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	20.825	49.764
2	UNKNOWN	33.131	50.236
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	22.958	19.193
2	UNKNOWN	37.064	80.807
Total			100.000

[1] a) J. Peng, D.-M. Du, *RSC Adv*. 2014, **4**, 2061-2067; b) L. Zhao, G. Huang, B. Guo, L. Xu, J. Chen, W. Cao, G. Zhao and X. Wu, *Org. Lett*., 2014, **16**, 5584-5587.

[2] a) Y. Hamashima, K. Yagi, H. Takano, L. Tamas and M. Sodeoka, *J. Am. Chem. Soc.*, 2002, **124**, 14530-14531; b) X. Wang, Q. Lan, S. Shirakawa and K. Maruoka, *Chem. Commun.* 2010, **46**, 321-323.

[3] K. Mori, A. Miyake and T. Akiyama, *Chem. Lett.*, 2014, **43**, 137-139