Supporting Information

Organocatalytic Enantioselective α-Difluoromethylketone Thiolation of β-Keto Esters Using Phthalimide-SCF_2COAr

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1. General information

All reagents and solvents were obtained commercially sources and used without further purification unless otherwise noted. Reactions monitoring was achieved by analytical thin layer chromatorgraphy (TLC), and the GF254 plates (0.25 mm layer thickness) are visualized by exposure to ultraviolet light. Flash chromatography columns were packed with 200-300 silica gel in petroleum (b.p. 60-90 °C).

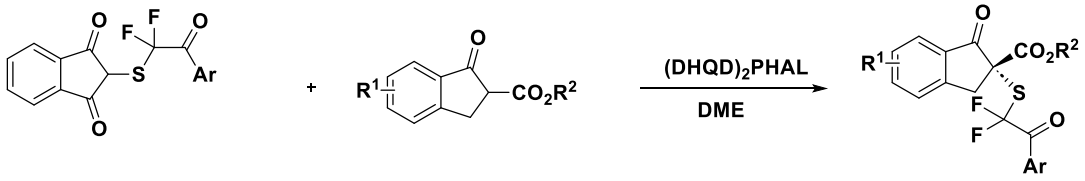
^{1}H, ^{13}C and ^{19}F NMR were collected 400 or 600 MHz spectrometer (Bruker AVANCE). Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity, coupling constants (Hz), and assignment. The resonance multiplicity is abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), tt (triplet of triplet), m (multiplet), and br (broad resonance).

Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode.

The HPLC measurements were carried out on a Thermo UltiMate 3000 apparatus. The used solvents were hexane and 2-propanol and were bought from Titan and Energy as HPLC grade. The chiral columns used for the separation of the enantiomers were Daicel Chiralpak AD-H (0.46 cm i.d. x 25 cm), Daicel Chiralpak IF-H (0.46 cm i.d. x 25 cm), Chiralpak IG-H (0.46 cm i.d. x 25 cm), and Daicel Chiralcel OD-H (0.46 cm i.d. x 25 cm).

The Phthalimide-SCF_2COAr reagents were prepared by referring to the literature.[1] Racemic α-difluorothiomethylated ketones were prepared according to the literature procedures.[1]

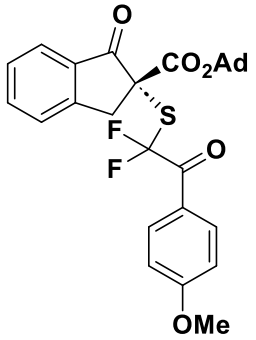
2. General procedure for the enantioselective α-difluoromethylketone thiolation of β-keto esters.



1 2 3

In a screw capped reaction tube, a mixture of β-keto ester **2** (0.12 mmol, 1.2 eq) and $(DHQD)_2PHAL$ (20 mol%) was dissolved in DME (1.0 mL) and reagents **1** (0.1 mmol, 1 eq) was added. The resulting solution was stirred at 25 °C until reagents **1** was fully consumed (TLC monitoring). The crude reaction mixture was directly subjected to silica gel and purified by column chromatography to give compound **3**.

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3a) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (32 mg, 0.061 mmol, 61% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 7.7 Hz, 1H), 7.67 (m, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.42 (m, 1H), 6.95 (d, J = 8.6 Hz, 2H), 4.16 (d, J = 17.9 Hz, 1H), 3.88 (s, 3H), 3.81 (d, J = 17.7 Hz, 1H), 2.11 (s, 3H), 2.02 (s, 6H), 1.59 (s, 6H).

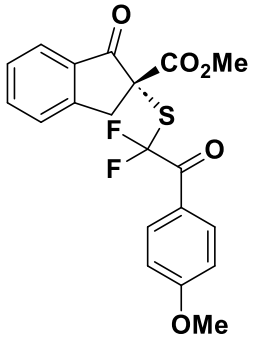
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.21, 182.87 (t, $^2J_{C\text{-}F}$ = 27.1 Hz), 165.51, 164.90, 152.33, 135.96, 133.32, 133.14, 128.00, 126.07, 125.32, 124.43 (t, $^1J_{C\text{-}F}$ = 292.5 Hz), 123.54, 114.07, 84.37, 64.96, 60.33, 40.94, 40.67, 35.90, 30.84, 14.16.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.14 (d, J = 220.2 Hz, 1F), -74.75 (d, J = 220.1 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{28}F_2O_5S$ $(M + Na)^+$ 549.1518, found 549.1528.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 9.313 min; major enantiomer: t_R = 10.609 min (93% ee); $[\alpha]_D^{22}$ = +187 (c = 0.10, CH_2Cl_2).

(*R*)-Methyl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3b) :



Petroleum ether/EtOAc = 5/1, Yellow oil (17.1 mg, 0.042 mmol, 42% yield).

NMR Spectroscopy:

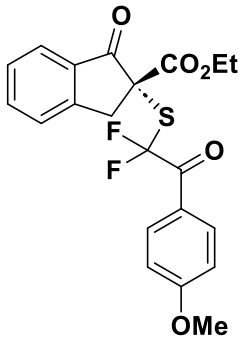
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.75-7.66 (m, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.48-7.40 (m, 1H), 6.96 (d, J = 9.0, 2.1 Hz, 2H), 4.31 (d, J = 17.8 Hz, 1H), 3.89 (s, 3H), 3.83 (d, J = 17.9 Hz, 1H), 3.74 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.86 (dd, J = 222.7, 11.0 Hz, 1F), -75.03 (dd, J = 222.7, 9.1 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{20}H_{16}F_2O_5S$ $(M+H)^+$ 407.0759, found 407.0763.

HPLC conditions: IG-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 28.356 min; major enantiomer: t_R = 34.096 min (49% ee).

(*R*)-Ethyl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3c) :



Petroleum ether/EtOAc = 5/1, Yellow oil (20.2 mg, 0.048 mmol, 48% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 7.7 Hz, 1H), 7.73-7.66 (m, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.48-7.40 (m, 1H), 7.01-6.93 (m, 2H), 4.29 (d, J = 17.8 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.83 (d, J = 17.8 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.61, 182.78 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 167.11, 164.99, 136.30, 133.13, 132.98, 128.20, 126.24, 125.53, 124.59 (t, $^1J_{C\text{-}F}$= 292.9 Hz), 123.43, 114.14, 63.92, 63.46, 55.63, 40.86, 13.81.

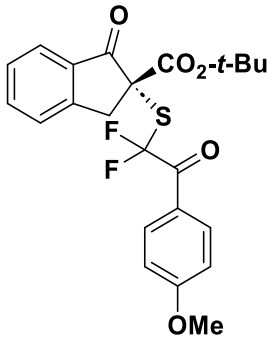
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.92 (dd, J = 221.5, 10.0 Hz, 1F), -74.97 (dd, J = 221.3, 6.8 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{21}H_{18}F_2O_5S$ $(M+H)^+$ 421.0916, found 421.0919.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ

= 220 nm, minor enantiomer: t_R = 12.236 min; major enantiomer: t_R = 13.131 min (56% ee); $[\alpha]_D^{22}$ = +34 (*c* = 0.10, CH_3OH).

(*R*)-*Tert*-butyl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3d) :



Petroleum ether/EtOAc = 5/1, White solid (18.8mg, 0.042 mmol, 42% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.75-7.64 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.49-7.38 (m, 1H), 6.98-6.93 (m, 2H), 4.18 (d, *J* = 17.7 Hz, 1H), 3.88 (s, 3H), 3.82 (d, *J* = 17.7 Hz, 1H), 1.40 (s, 9H).

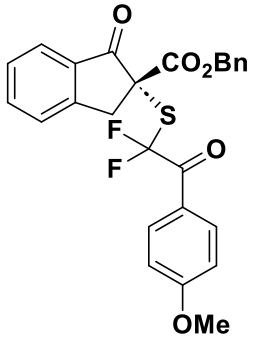
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.17, 182.85 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 165.94, 164.92, 152.36, 136.04, 133.27, 133.12 (t, $^3J_{C\text{-}F}$ = 2.5 Hz), 130.25, 128.05, 126.12, 125.37, 124.41 (t, $^1J_{C\text{-}F}$ = 292.7 Hz), 123.52, 114.10, 84.38, 64.88, 55.61, 40.92, 27.52.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.06 (d, *J* = 219.7 Hz, 1F), -74.91 (d, *J* = 219.5 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{23}H_{22}F_2O_5S$ $(M + Na)^+$ 471.1048, found 471.1050.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.710 min; major enantiomer: t_R = 7.828 min (36% ee); $[\alpha]_D^{22}$ = +157 (*c* = 0.10, CH_2Cl_2).

(*R*)-Benzyl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3e) :



Petroleum ether/EtOAc = 5/1, Yellow oil (19.8 mg, 0.041 mmol, 41% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.79-7.68 (m,

1H), 7.56 (d, J = 7.7 Hz, 1H), 7.50-7.44 (m, 1H), 7.42-7.27 (m, 5H), 5.27-5.15 (m, 2H), 4.33 (d, J = 17.8 Hz, 1H), 3.91 (s, 3H), 3.91 (d, J = 17.8 Hz, 1H).

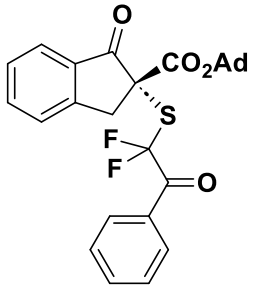
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.27, 182.76 (t, $^2J_{C\text{-}F}$ = 26.8 Hz), 167.05, 164.95, 152.31, 136.34, 134.79, 133.13 (t, $^3J_{C\text{-}F}$ = 2.5 Hz), 132.94, 128.49, 128.28, 128.24, 127.82, 126.25, 125.54, 124.59 (t, $^1J_{C\text{-}F}$ = 292.8 Hz), 123.38, 68.66, 63.91, 55.61, 40.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.96 (dd, J = 220.8, 14.6 Hz, 1F), -74.86 (dd, J = 220.6, 10.0 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{26}H_{20}F_2O_5S$ $(M + H)^+$ 483.1072, found 483.1045.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 21.894 min; major enantiomer: t_R = 23.250 min (42% ee); $[\alpha]_D^{23}$ = -31 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-oxo-2-phenylethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3f) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (35.2 mg, 0.071 mmol, 71% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.9 Hz, 2H), 7.82 (d, J = 7.7 Hz, 1H), 7.73-7.61 (m, 2H), 7.55-7.47 (m, 3H), 7.47-7.40 (m, 1H), 4.18 (d, J = 17.7 Hz, 1H), 3.81 (d, J = 17.7 Hz, 1H), 2.12 (s,3H), 2.02 (s, 6H), 1.60 (s, 6H).

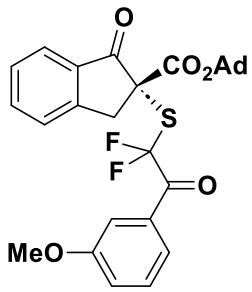
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.17, 184.57 (t, $^2J_{C\text{-}F}$ = 27.7 Hz), 165.52, 152.40, 136.09, 134.89, 133.36, 130.89, 130.59, 128.80, 128.12, 126.15, 125.46, 124.24 (t, $^1J_{C\text{-}F}$ = 292.8 Hz), 84.57, 65.10, 41.04, 40.74, 35.97, 30.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.66 (d, J = 221.9 Hz,1F), -75.19 (d, J = 222.0 Hz,1F).

HRMS (ESI) m/z calcd. for $C_{28}H_{26}F_2O_4S$ $(M + Na)^+$ 519.1412, found 519.1424.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.641 min; major enantiomer: t_R = 7.816 min (91% ee); $[\alpha]_D^{22}$ = +23 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(3-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3g) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (35.8 mg, 0.068 mmol, 68% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.78-7.68 (m, 2H), 7.63 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.49-7.40 (m, 2H), 7.26-7.19 (m, 1H), 4.21 (d, J = 17.7 Hz, 1H), 3.90 (s, 3H), 3.84 (d, J = 17.7 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 6H), 1.64 (s, 6H).

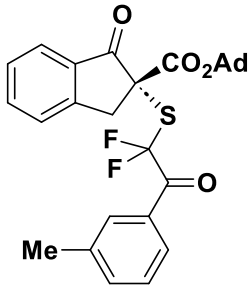
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.10, 184.28 (t, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 165.44, 159.72, 152.31, 136.02, 133.29, 131.95, 129.74, 128.05, 126.09, 125.37, 124.11 (t, $^{1}J_{C\text{-}F}$ = 292.8 Hz), 123.21 (t, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 121.73, 114.33, 84.47, 65.09, 55.53, 40.95, 40.66, 35.90, 30.85.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.46 (d, J = 221.1 Hz, 1F), -75.06 (d, J = 221.0 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{28}F_2O_5S$ $(M + Na)^+$ 549.1518, found 549.1526.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 7.073 min; major enantiomer: t_R = 8.154 min (89% ee); $[\alpha]_D^{21}$ = -264 (c = 0.10, CH_3OH).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-oxo-2-(m-tolyl)ethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3h) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (30.6 mg, 0.060 mmol, 60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.87 (m, 2H), 7.82 (d, J = 7.7 Hz, 1H), 7.72-7.63 (m, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.47-7.42 (m, 2H), 7.41-7.35 (m, 1H), 4.17 (d, J = 17.7 Hz, 1H), 3.80 (d, J = 17.7 Hz, 1H), 2.42 (s, 3H), 2.12 (s, 3H), 2.02 (s, 6H), 1.59 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.17, 184.62 (t, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 165.50, 152.37, 138.72, 136.05, 135.74, 133.30, 130.83, 128.62, 128.07, 127.79 (t, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 126.12, 125.39, 124.23 (t, $^{1}J_{C\text{-}F}$ = 293.0 Hz), 84.46, 65.06, 41.01, 40.67, 35.92, 30.86, 29.69, 21.34.

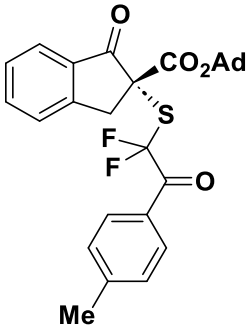
^{19}F NMR (376 MHz, $CDCl_3$) δ -73.49 (d, J = 221.9 Hz, 1F), -75.01 (d, J = 222.0 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{28}F_2O_4S$ $(M + Na)^+$ 533.1569, found 533.1575.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ

= 220 nm, minor enantiomer: t_R = 5.741 min; major enantiomer: t_R = 6.834 min (88% ee); $[\alpha]_D^{22}$ = +30 (*c* = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-oxo-2-(p-tolyl)ethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3i) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (27.5 mg, 0.054 mmol, 54% yield).

NMR Spectroscopy:

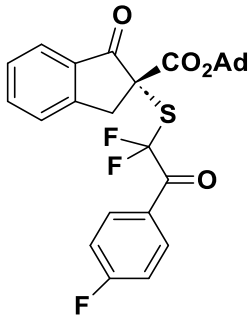
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.72-7.63 (m, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.45-7.37 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.17 (d, *J* = 17.8 Hz, 1H), 3.80 (d, *J* = 17.7 Hz, 1H), 2.43 (s, 3H), 2.12 (s, 3H), 2.02 (s, 6H), 1.60 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.23, 184.13 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 165.57, 152.43, 146.27, 136.07, 133.39, 130.74, 129.54, 128.32, 128.10, 126.16, 125.44, 124.35 (t, $^1J_{C\text{-}F}$ = 291.1 Hz), 84.51, 65.07, 41.05, 40.74, 35.99, 30.93, 21.93.

HRMS (ESI) m/z calcd. for $C_{29}H_{28}F_2O_4S$ $(M + Na)^+$ 533.1569, found 533.1580.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.977 min; major enantiomer: t_R = 7.719 min (91% ee); $[\alpha]_D^{22}$ = +52 (*c* = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-fluorophenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3j) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (27.8 mg, 0.054 mmol, 54% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.72-7.65 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.48-7.40 (m, 1H), 7.21-7.14 (m, 2H), 4.16 (d, *J* = 17.7 Hz, 1H), 3.81 (d, *J* = 17.7 Hz, 1H), 2.13 (s, 3H), 2.01 (s, 6H), 1.60 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.16, 183.13 (t, $^2J_{C\text{-}F}$ = 27.8 Hz), 168.06, 165.48, 152.32,

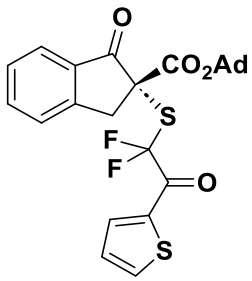
136.14, 133.61 (d, $^{3'}J_{C\text{-}F}$ = 9.7 Hz),133.354, 127.30, 126.83 (d, $^{1'}J_{C\text{-}F}$ = 271.4 Hz), 126.16, 124.18 (t, $^{1}J_{C\text{-}F}$ = 292.4 Hz), 116.21 (d, $^{2'}J_{C\text{-}F}$ = 22.1 Hz), 84.66, 65.16, 40.99, 40.77, 35.97, 30.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.75 (d, J = 222.3 Hz, 1F), -75.17 (d, J = 222.5 Hz, 1F), -100.94--101.06 (m, 1F).

HRMS (ESI) m/z calcd. for $C_{28}H_{25}F_3O_4S$ $(M + Na)^+$ 537.1318, found 537.1325.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 7.047 min; major enantiomer: t_R = 8.437 min (58% ee); $[\alpha]_D^{22}$ = -169 (c = 0.10, CH_3OH).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-oxo-2-(thiophen-2-yl)ethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3k) :



Petroleum ether/EtOAc = 5/1, White solid (26.6 mg, 0.053 mmol, 53% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 3.9, 1.5 Hz, 1H), 7.87-7.79 (m, 2H), 7.74-7.63 (m, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.43 (m, 1H), 7.22-7.18 (m, 1H), 4.15 (d, J = 17.8 Hz, 1H), 3.81 (d, J = 17.8 Hz, 1H), 2.12 (s, 3H), 2.02 (s, 6H), 1.60 (s, 6H).

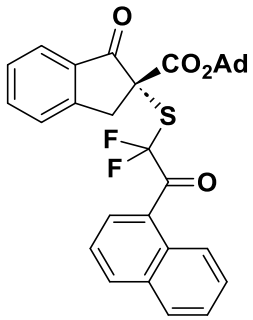
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.23, 177.82 (t, $^{2}J_{C\text{-}F}$ = 28.9 Hz), 165.52, 152.35, 137.40, 136.95, 136.12, 133.38, 128.99, 128.16, 126.18, 125.45, 123.88 (t, $^{1}J_{C\text{-}F}$ = 292.5 Hz), 84.62, 65.13, 40.94, 40.78, 35.99, 30.94.

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.33 (d, J = 218.7 Hz, 1F), -75.97 (d, J = 218.6 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{26}H_{24}F_2O_4S_2$ $(M + Na)^+$ 525.0976, found 525.0983.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.578 min; major enantiomer: t_R = 7.305 min (44% ee); $[\alpha]_D^{21}$ = +67 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(naphthalen-1-yl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3l) :



Petroleum ether/EtOAc = 5/1, White solid (28.8 mg, 0.053 mmol, 53% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 7.3 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.64-7.53 (m, 2H), 7.51-7.41 (m, 3H), 7.40-7.32 (m, 1H), 4.11 (d, J = 17.7 Hz, 1H), 3.77 (d, J = 17.7 Hz, 1H), 2.02 (s, 3H), 1.92 (s, 6H), 1.50 (s, 6H).

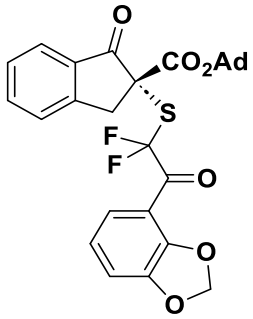
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.22, 187.02 (t, $^{2}J_{C\text{-}F}$ = 27.1 Hz), 165.52, 152.33, 136.02, 134.97, 133.81, 133.27, 131.09, 131.06, 131.02, 128.83, 128.73, 128.03, 126.83, 126.08, 125.38, 125.30, 124.29 (t, $^{1}J_{C\text{-}F}$ = 294.3 Hz), 124.04, 84.43, 65.03, 40.93, 40.63, 35.86, 30.80.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.27 (d, J = 218.5 Hz, 1F), -74.07 (d, J = 218.6 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{32}H_{28}F_2O_4S$ $(M + Na)^+$ 569.1569, found 569.1580.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 90/10, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 14.417 min; major enantiomer: t_R = 15.635 min (92% ee); $[\alpha]_D^{22}$ = +50 (c = 0.01, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((2-(benzo[d][1,3]dioxol-4-yl)-1,1-difluoro-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3m) :



Petroleum ether/EtOAc = 5/1, White solid (29.1 mg, 0.054 mmol, 54% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.75 (m, 2H), 7.72-7.64 (m, 1H), 7.57-7.48 (m, 2H), 7.47 -7.40 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.08 (s,2H), 4.16 (d, J = 17.7 Hz, 1H), 3.80 (d, J = 17.7 Hz, 1H), 2.13 (s, 3H), 2.03 (s, 6H), 1.61 (s, 6H).

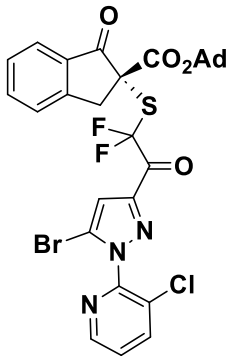
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.23, 182.60 (t, $^{2}J_{C\text{-}F}$ = 27.6 Hz), 165.58, 153.49, 152.41, 148.31, 136.07, 133.40, 128.11, 128.07, 126.16, 125.45, 125.26, 124.43 (t, $^{1}J_{C\text{-}F}$ = 292.8 Hz), 109.91, 108.33, 102.29, 84.54, 65.11, 41.03, 40.77, 36.00, 30.95.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.79 (d, J = 220.2 Hz, 1F), -74.49 (d, J = 219.7 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{26}F_2O_6S$ $(M + Na)^+$ 563.1310, found 563.1320.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 11.028 min; major enantiomer: t_R = 12.925 min (89% ee); $[\alpha]_D^{22}$ = +220 (*c* = 0.01, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((2-(5-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-3-yl)-1,1-difluoro-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3n) :



Petroleum ether/EtOAc = 5/1, White solid (27.7 mg, 0.041 mmol, 41% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.48 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.70-7.65 (m, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.47-7.41 (m, 2H), 7.35 (s, 1H), 4.10 (d, *J* = 17.7 Hz, 1H), 3.72 (d, *J* = 17.7 Hz, 1H),2.13 (s, 3H), 2.01 (s, 6H), 1.60 (s, 6H).

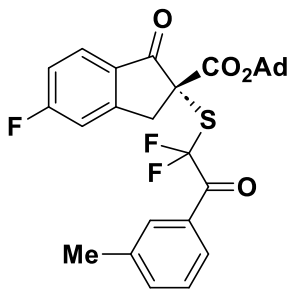
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 195.77, 174.08 (t, $^2J_{C\text{-}F}$ = 30.7 Hz), 165.24, 151.96, 148.36, 147.12, 139.22, 136.12, 135.73, 134.26, 133.13, 128.65, 128.17, 126.177 (t, $^1J_{C\text{-}F}$ = 265.0 Hz), 126.04, 125.44, 123.10, 120.19, 117.05 (t, $^3J_{C\text{-}F}$ = 4.3 Hz), 84.81, 64.97, 40.75, 40.68, 35.84, 30.84.

^{19}F NMR (376 MHz, $CDCl_3$) *δ* -76.14 (d, *J* = 222.7 Hz, 1F), -77.72 (d, *J* = 222.9 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{30}H_{25}BrClF_2N_3O_4S$ $(M + H)^+$ 676.0479, found 676.0438.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 8.208 min; major enantiomer: t_R = 8.876 min (84% ee); $[\alpha]_D^{22}$ = +58 (*c* = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3o) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (33 mg, 0.062 mmol, 62% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.5 Hz, 2H), 7.83 (dd, J = 8.5, 5.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.42-7.34 (m, 1H), 7.21-7.08 (m, 2H), 4.16 (d, J = 17.9 Hz, 1H), 3.79 (d, J = 17.9 Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H), 2.02 (s, 6H), 1.60 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.31, 184.59 (t, $^2J_{C\text{-}F}$ = 27.4 Hz), 167.91 (d, $^{1'}J_{C\text{-}F}$ = 259.1 Hz), 165.26, 155.36 (d, $^{3'}J_{C\text{-}F}$ = 10.5 Hz), 138.77, 135.78, 130.83, 129.74, 128.65, 127.81 (t, $^3J_{C\text{-}F}$ = 5.6 Hz), 124.27 (t, $^1J_{C\text{-}F}$ = 293.2 Hz), 116.57 (d, $^{2'}J_{C\text{-}F}$ = 24.0 Hz), 112.97 (d, $^{2''}J_{C\text{-}F}$ = 22.8 Hz).

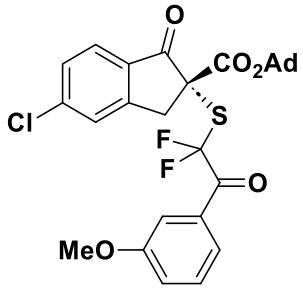
, 84.75, 65.21, 40.83, 40.71, 35.93, 30.90, 21.34.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.42 (d, J = 222.4 Hz, 1F), -74.88 (d, J = 222.6 Hz, 1F), -99.84--99.96 (m, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{27}F_3O_4S$ $(M + Na)^+$ 551.1474, found 551.1481.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.135 min; major enantiomer: t_R = 7.157 min (92% ee); $[\alpha]_D^{21}$ = -31 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 5-chloro-2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3p) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (37.5 mg, 0.067 mmol, 67% yield).

NMR Spectroscopy:

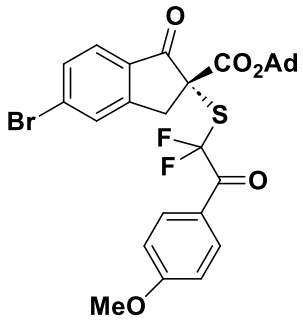
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.59 (s, 1H), 7.52 (s, 1H), 7.45-7.36 (m, 2H), 7.20 (dd, J = 8.2, 2.6 Hz, 1H), 4.13 (d, J = 17.9 Hz, 1H), 3.87 (s, 3H), 3.78 (d, J = 17.9 Hz, 1H), 2.13 (s, 3H), 2.02 (s, 6H), 1.61 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.77, 184.18 (t, $^2J_{C\text{-}F}$ = 27.6 Hz), 165.11, 159.74, 153.62, 142.72, 131.86, 131.80, 129.77, 128.96, 126.39, 126.34, 124.15 (t, $^1J_{C\text{-}F}$ = 293.1 Hz), 123.17 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 121.76, 114.35, 84.83, 65.07, 55.53, 40.68, 40.58, 35.87, 30.86.

HRMS (ESI) m/z calcd. for $C_{29}H_{27}ClF_2O_5S$ $(M + Na)^+$ 583.1128, found 583.1135.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 90/10, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 11.840 min; major enantiomer: t_R = 13.924 min (93% ee); $[\alpha]_D^{21}$ = +6 (c = 0.01, CH_3OH).

(*R*)-Adamantan-1-yl 5-bromo-2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3q) :



Petroleum ether/EtOAc = 5/1, Yellow oil (33 mg, 0.055 mmol, 55% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 2H), 7.76-7.63 (m, 2H), 7.57 (d, J = 8.3 Hz, 1H), 6.99-6.93 (m, 2H), 4.13 (d, J = 17.9 Hz, 1H), 3.89 (s, 3H), 3.80 (d, J = 17.9 Hz, 1H), 2.13 (s, 3H), 2.02 (s, 6H), 1.61 (s, 6H).

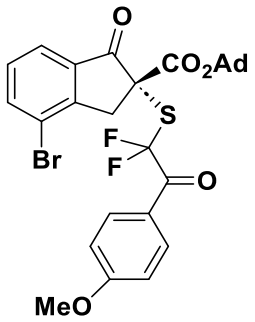
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.23, 182.81 (t, $^2J_{C\text{-}F}$ = 27.1 Hz), 165.20, 165.00, 153.76, 133.18, 132.29, 131.80, 131.63, 129.46, 126.44, 124.53 (t, $^1J_{C\text{-}F}$ = 292.8 Hz), 123.50, 114.16, 84.82, 64.89, 55.65, 40.73, 40.56, 35.92, 30.90, 29.70.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.73 (d, J = 220.9 Hz, 1F), -74.43 (d, J = 221.2 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{27}BrF_2O_5S$ $(M + Na)^+$ 627.0623, found 627.0631.

HPLC conditions: IB-H column, n-hexane/ isopropanol = 85/15, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 6.648 min; major enantiomer: t_R = 7.394 min (90% ee); $[\alpha]_D^{22}$ = +154 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 7-bromo-2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3r) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (44.1mg, 0.073 mmol, 73% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.40-7.30 (m, 1H), 7.01-6.89 (m, 2H), 4.08 (d, J = 18.2 Hz, 1H), 3.89 (s, 3H), 3.73 (d, J = 18.2 Hz, 1H), 2.14 (s, 3H), 2.03 (s, 6H), 1.61 (s, 6H).

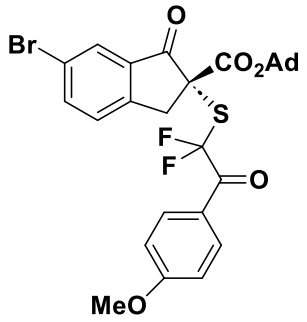
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.79, 182.76 (t,$^2J_{C\text{-}F}$ = 27.0 Hz), 165.14, 165.00, 151.89, 138.67, 135.43, 133.19, 129.78, 124.60 (t,$^1J_{C\text{-}F}$ = 292.9 Hz), 124.14, 123.51, 121.46, 114.16, 84.89, 64.71, 55.65, 41.98, 40.73, 35.92, 30.91, 29.70.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.37 (dd, J = 221.3, 5.0 Hz, 1F), -74.28 (dd, J = 221.2, 4.3 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{27}BrF_2O_5S$ $(M + Na)^+$ 627.0623, found 627.0630.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 8.842 min; major enantiomer: t_R = 9.403 min (89% ee); $[\alpha]_D^{21}$ = +263 (*c* = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 6-bromo-2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3s) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (38 mg, 0.063 mmol, 63% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.48-7.39 (m, 2H), 7.23 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.12 (d, *J* = 17.9 Hz, 1H), 3.90 (s, 3H), 3.78 (d, *J* = 17.9 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 6H), 1.64 (s, 6H).

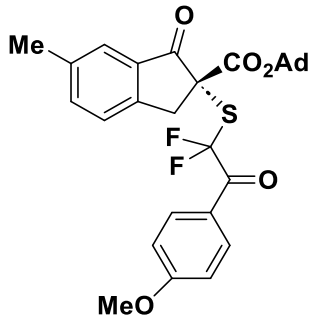
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.89, 184.17 (t, $^2J_{C\text{-}F}$ = 27.5 Hz), 165.03, 159.74, 150.72, 138.73, 135.16, 131.84, 129.77, 128.10, 127.61, 124.14 (t, $^1J_{C\text{-}F}$ = 293.1 Hz), 123.16 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 122.17, 121.76, 114.36, 84.89, 65.20, 55.53, 40.68, 40.58, 35.86, 30.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.18 (d, *J* = 222.1 Hz, 1F), -74.65 (d, *J* = 222.2 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{29}H_{27}BrF_2O_5S$ $(M + Na)^+$ 627.0623, found 627.0625.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 7.252 min; major enantiomer: t_R = 9.553 min (93% ee); $[\alpha]_D^{21}$ = -214 (*c* = 0.10, CH_3OH).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3t) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (32.4 mg, 0.060 mmol, 60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.64 (s, 1H), 7.52 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.14 (d, *J* = 17.6 Hz, 1H), 3.92 (s, 3H),

3.79 (d, J = 17.6 Hz, 1H), 2.45 (s, 3H), 2.16 (s, 3H), 2.07 (s, 6H), 1.64 (s, 6H).

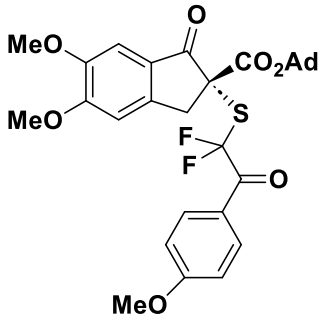
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.34, 184.00 (t, $^2J_{C\text{-}F}$ = 27.3 Hz), 165.73, 164.95, 149.86, 138.14, 137.37, 133.56, 133.25, 125.81, 125.28, 124.49 (t, $^1J_{C\text{-}F}$ = 293.4 Hz), 123.69,114.14, 84.38, 65.39, 55.68, 40.76, 36.01, 30.93, 21.13.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.22 (d, J = 219.9 Hz, 1F), -74.86 (d, J = 219.8 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{30}H_{30}F_2O_5S$ $(M + Na)^+$ 563.1674, found 563.1680.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 8.852 min; major enantiomer: t_R = 11.286 min (90% ee); $[\alpha]_D^{22}$ = +193 (c = 0.10, CH_2Cl_2).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3u) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (25.8 mg, 0.044 mmol, 44% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.7 Hz, 2H), 7.19 (s, 1H), 7.00-6.87 (m, 3H), 4.08 (d, J = 17.4 Hz, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.71 (d, J = 17.4 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 6H), 1.60 (s, 6H).

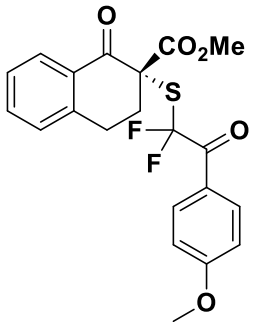
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.59, 183.04 (t, $^2J_{C\text{-}F}$ = 26.9 Hz), 165.92, 164.97, 156.74, 149.98, 148.41, 133.26, 129.08, 128.27, 125.99, 125.35, 124.48 (t, $^1J_{C\text{-}F}$ = 292.4 Hz), 123.68, 114.15, 106.98, 105.48, 84.32, 65.43, 56.47, 56.21, 55.70, 40.79, 36.03, 30.94.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.61 (d, J = 219.2 Hz,1F), -75.23 (d, J = 219.2 Hz,1F).

HRMS (ESI) m/z calcd. for $C_{31}H_{32}F_2O_7S$ $(M + Na)^+$ 609.1729, found 609.1738.

HPLC conditions: AD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 19.437 min; major enantiomer: t_R = 21.962 min (91% ee); $[\alpha]_D^{21}$ = +223 (c = 0.10, CH_2Cl_2).

(*R*)-methyl 2-((1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)thio)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3v) :



Petroleum ether/EtOAc = 5/1, Colorless stick oil (4.2 mg, 0.010 mmol, 10% yield).

NMR Spectroscopy:

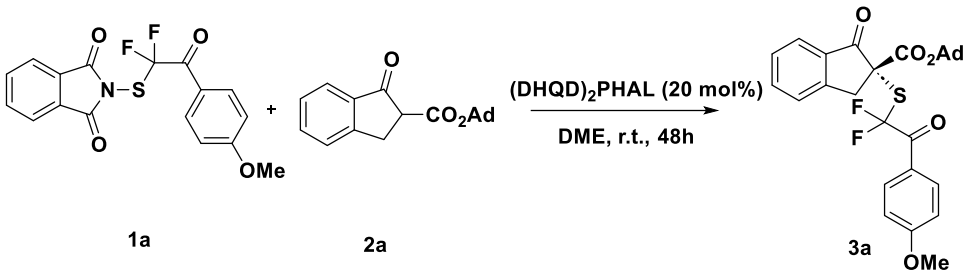
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 8.03 (dd, J = 8.0, 1.4 Hz, 1H), 7.57-7.48 (m, 1H), 7.37-7.29 (m, 1H), 7.29-7.22 (m, 1H), 7.02-6.90 (m, 2H), 3.89 (s, 3H), 3.75 (s, 3H), 3.22 (t, J = 6.0 Hz, 2H), 3.20-3.12 (m, 1H), 2.75-2.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.18, 183.06 (t, $^{2}J_{C\text{-}F}$ = 27.2 Hz), 168.30, 164.95, 143.02, 134.51, 133.29, 130.65, 128.87, 128.81, 127.12, 124.41 (t, $^{1}J_{C\text{-}F}$ = 292.2 Hz), 123.68, 114.13, 65.01, 55.69, 53.63, 32.99, 26.34.

HRMS (ESI) m/z calcd. for $C_{21}H_{18}F_2O_5S$ $(M + H)^+$ 421.0916, found 421.0889.

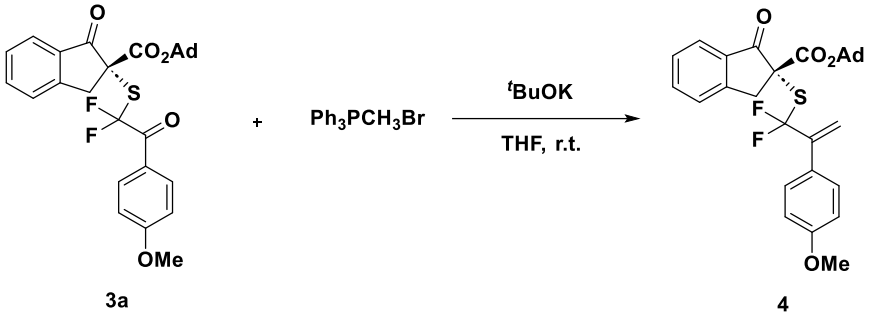
HPLC conditions: OD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 10.902 min; major enantiomer: t_R = 13.069 min (18% ee)

3. Gram-scale preparation of product 3a



In a screw capped reaction flask, a mixture of β-keto ester **2a** (6 mmol, 1.2 eq) and $(DHQD)_2PHAL$ (20 mol%) was dissolved in DME (20.0 mL) and reagents **1a** (5 mmol, 1 eq) was added. The resulting solution was stirred at 25 °C until reagents **1a** was fully consumed (TLC monitoring). The crude reaction mixture was directly subjected to silica gel and purified by column chromatography (PE/EA= 5/1) to give compound **3a** in 56% yield (1.54 g, 93% ee).

4. Synthetic transformation of product 3a



To a solution of the corresponding methyltriphenylphosphonium bromide (0.2 mmol, 2.0 eq.) in dried THF under N_2 atmosphere, a solution of ^{t}BuOK (0.2 mmol, 2 equiv.) dissolved in THF was added dropwise at room temperature. The mixture was allowed to stir for 1 h. Then, the **3a** (0.1 mmol, 1.0 equiv.) dissolved in THF and the wittig reagent were added dropwise, and the mixture was allowed to stir overnight. After completion of the reaction, the reaction was quenched with saturated solution of NH_4Cl. The mixture was extracted with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by column chromatography (PE/EA= 10/1) to afford the product **4** in 50% yield (26.2 mg, 91% ee).

(*R*)-Adamantan-1-yl 2-((1,1-difluoro-2-(4-methoxyphenyl)allyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4) :

Petroleum ether/EtOAc = 10/1, Colorless stick oil (26.2 mg, 0.050 mmol, 50% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.7 Hz, 1H), 7.68-7.60 (m, 1H), 7.49 (d, J = 7.6 Hz,

1H), 7.43 (dd, J = 9.4, 2.6 Hz, 2H), 7.39 (d, J = 7.5 Hz, 1H), 5.70 (s, 1H), 5.49 (s, 1H), 4.14 (d, J = 17.7 Hz, 1H), 3.85 (d, J = 17.7 Hz, 1H), 3.81 (s, 3H), 2.12 (s, 3H), 2.02 (s, 6H), 1.60 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.84, 166.04, 159.97, 152.55, 143.66 (t, $^2J_{C\text{-}F}$ = 22.6 Hz), 135.81, 133.62, 129.70, 128.35 (t, $^1J_{C\text{-}F}$ = 282.3 Hz), 127.91, 127.48, 126.11, 125.30, 118.52 (t, $^3J_{C\text{-}F}$ = 6.9 Hz), 113.69, 83.96, 65.14, 55.31, 40.76, 40.61, 36.03, 30.91.

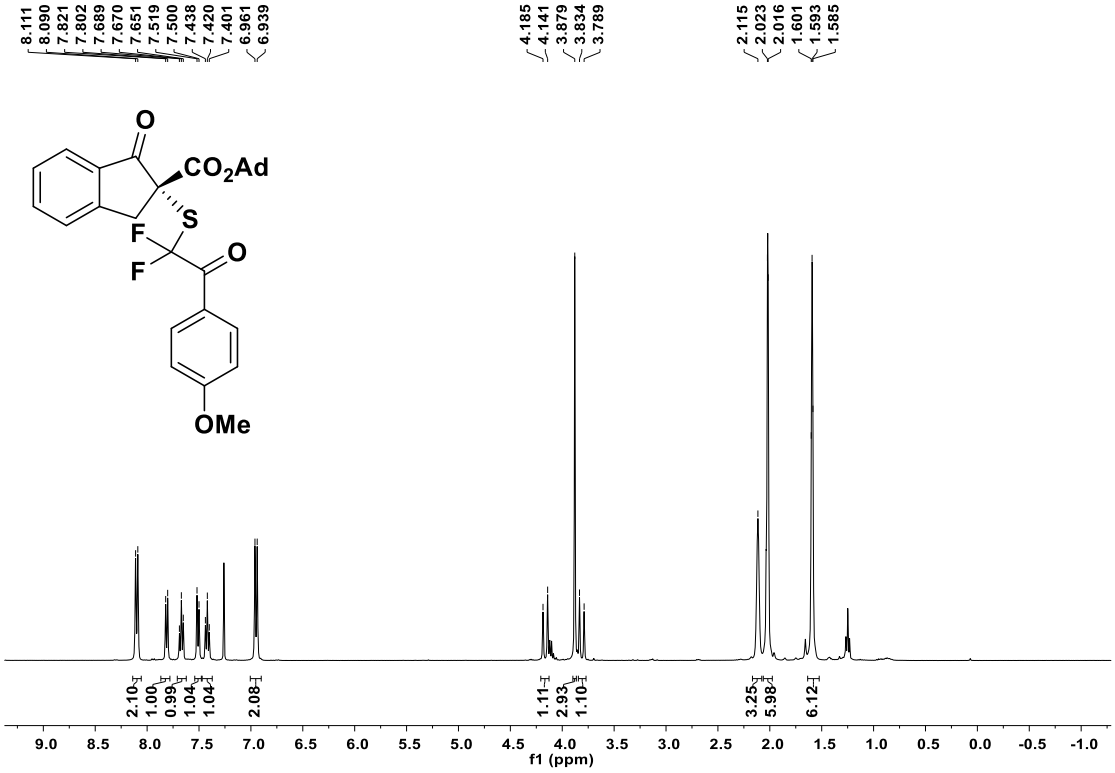
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.21 (d, J = 200.1 Hz, 1F), -69.39 (d, J = 199.7 Hz, 1F).

HRMS (ESI) m/z calcd. for $C_{30}H_{30}F_2O_4S$ $(M + Na)^+$ 547.1725, found 547.1696.

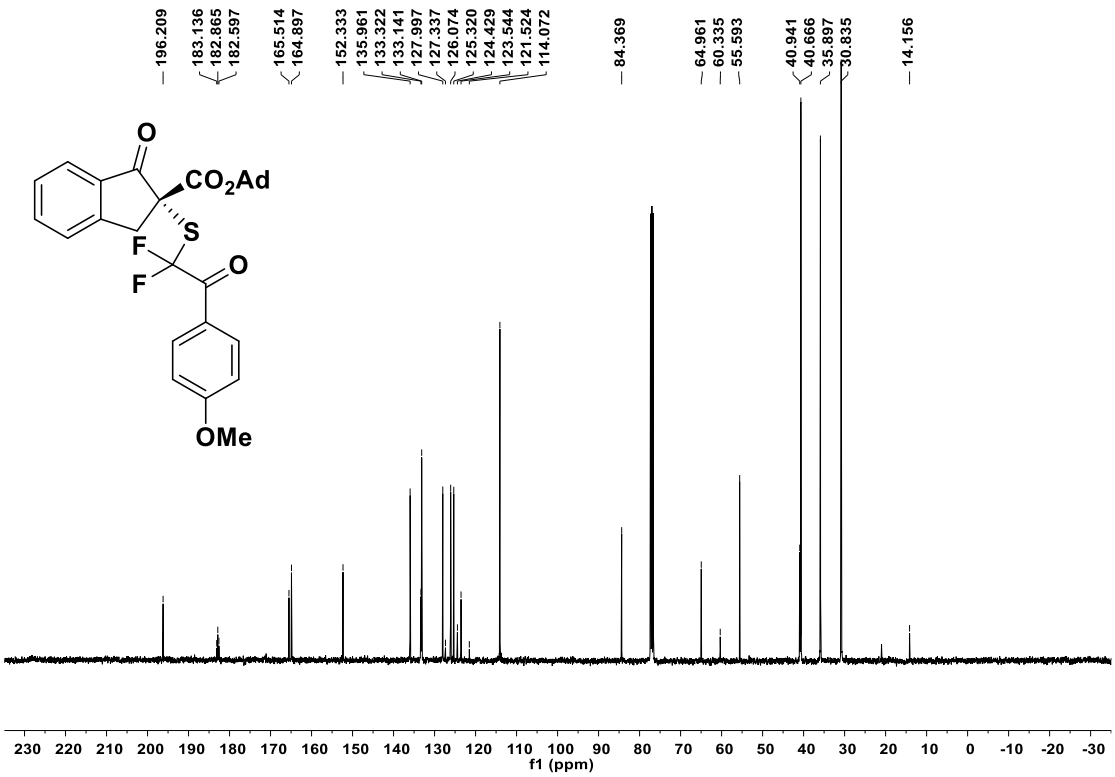
HPLC conditions: OD-H column, n-hexane/ isopropanol = 80/20, flow rate = 1.0 mL min^{-1}, λ = 220 nm, minor enantiomer: t_R = 5.252 min; major enantiomer: t_R = 6.154 min (91% ee).

5. NMR spectra

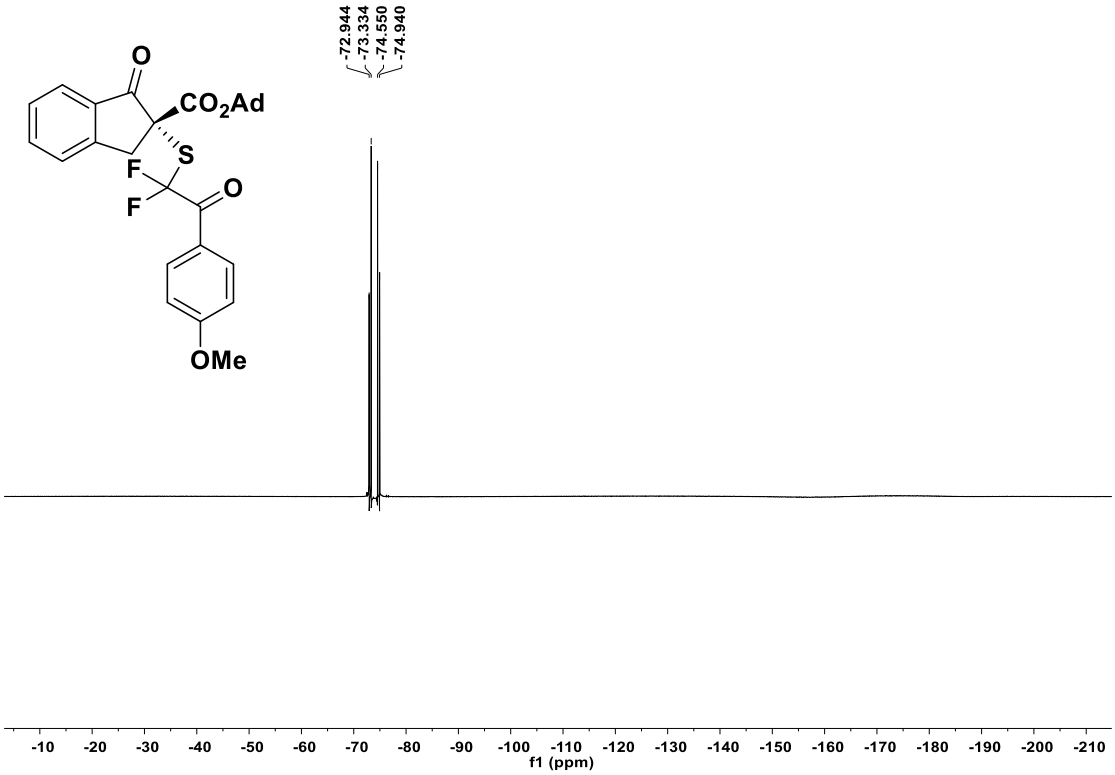
^{1}H NMR (400 MHz) of **3a** in $CDCl_3$



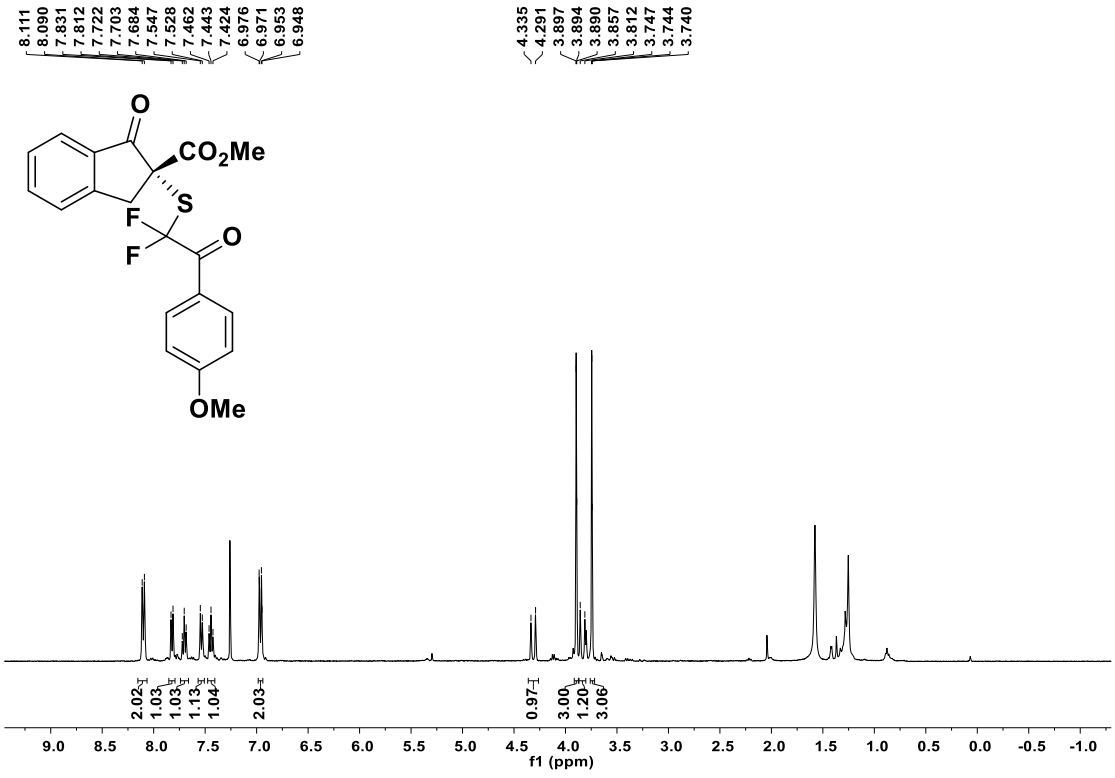
^{13}C NMR (101 MHz) of **3a** in $CDCl_3$



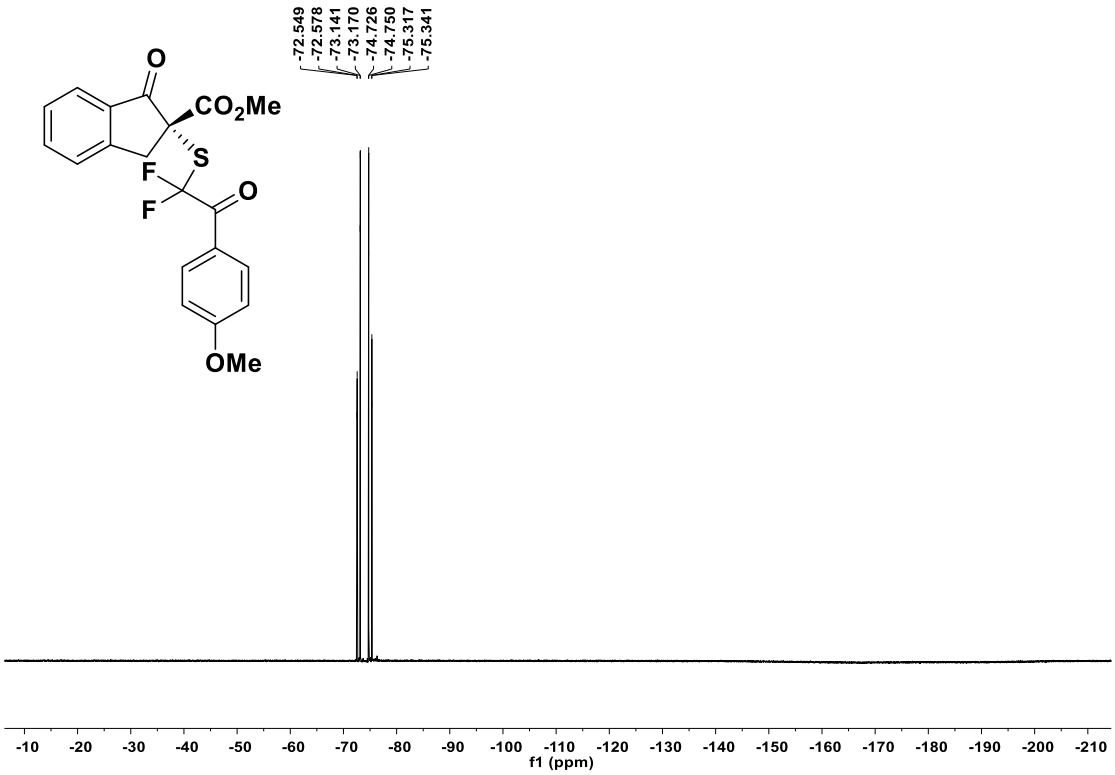
^{19}F NMR (376 MHz) of **3a** in $CDCl_3$



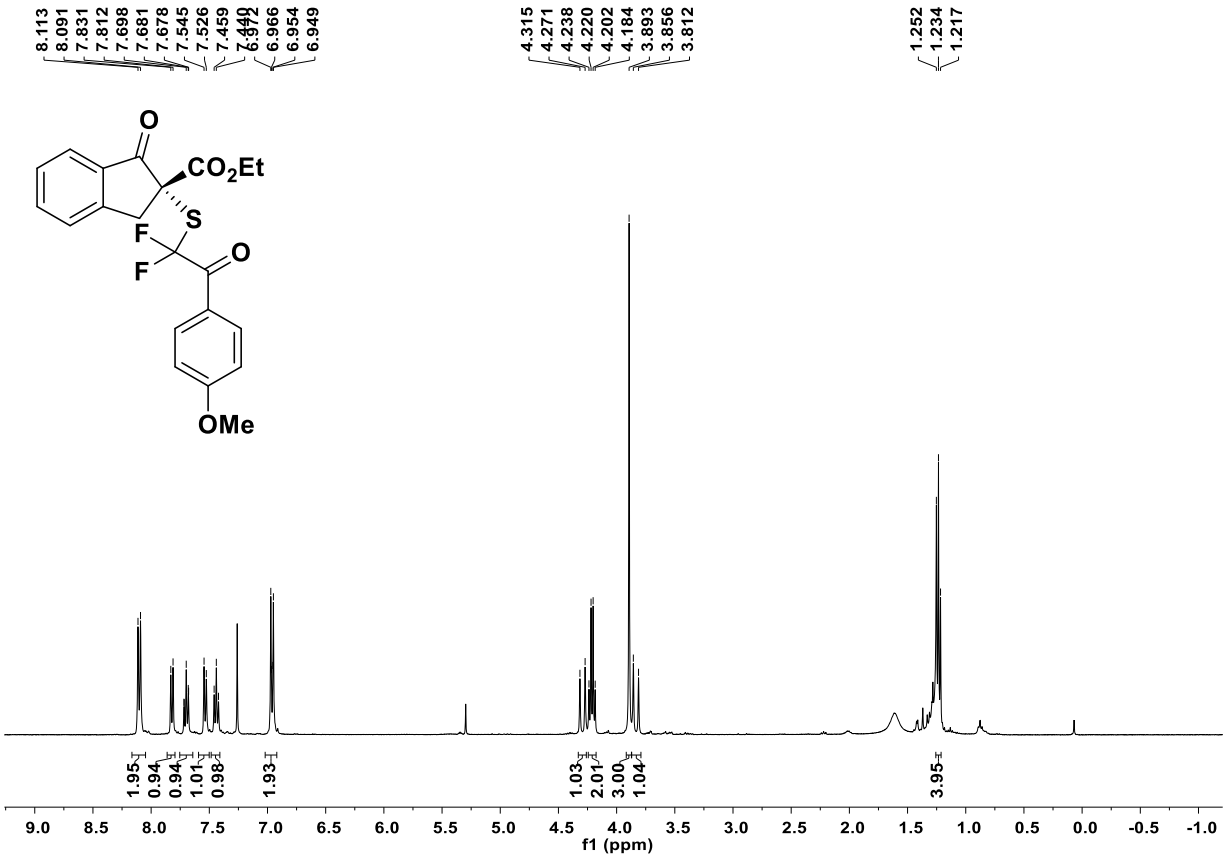
^{1}H NMR (400 MHz) of **3b** in $CDCl_3$



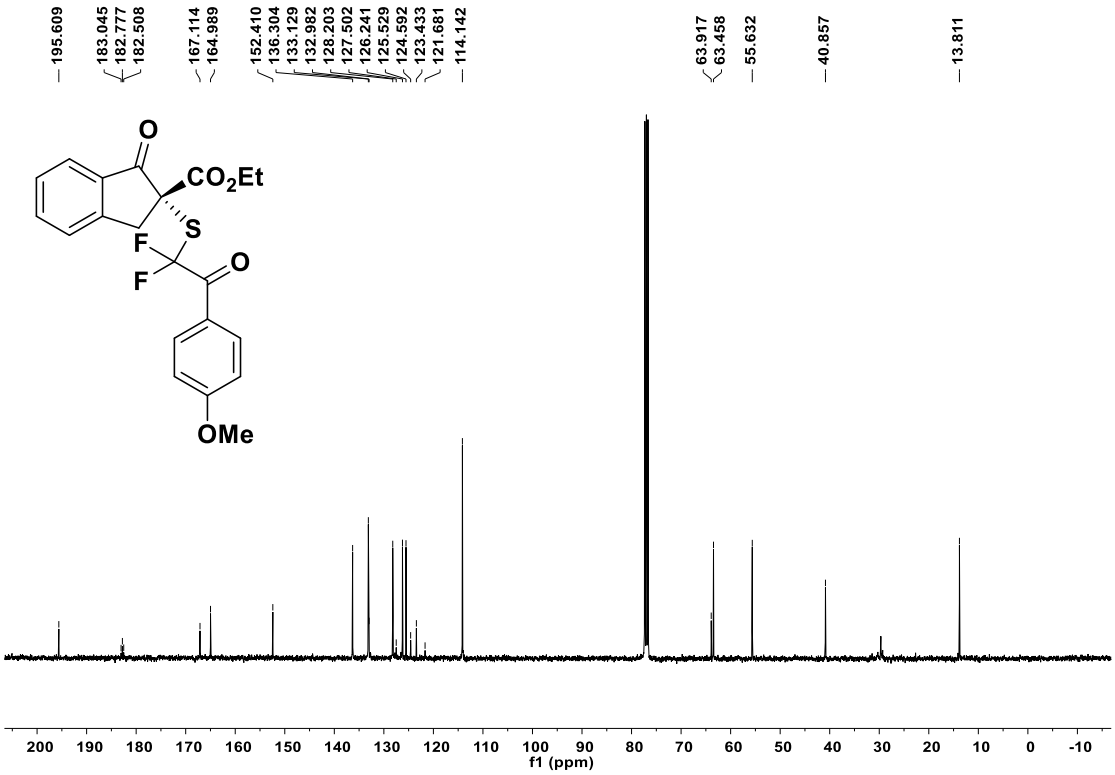
^{19}F NMR (376 MHz) of **3b** in $CDCl_3$



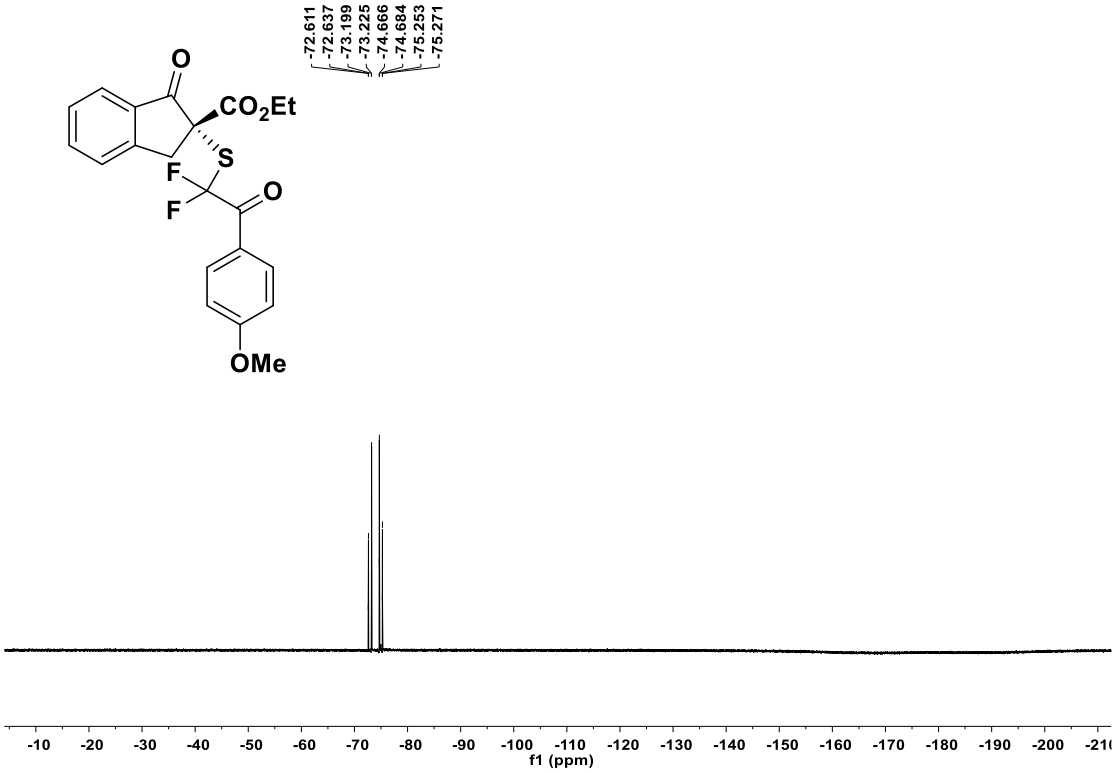
^{1}H NMR (400 MHz) of **3c** in CDCl3



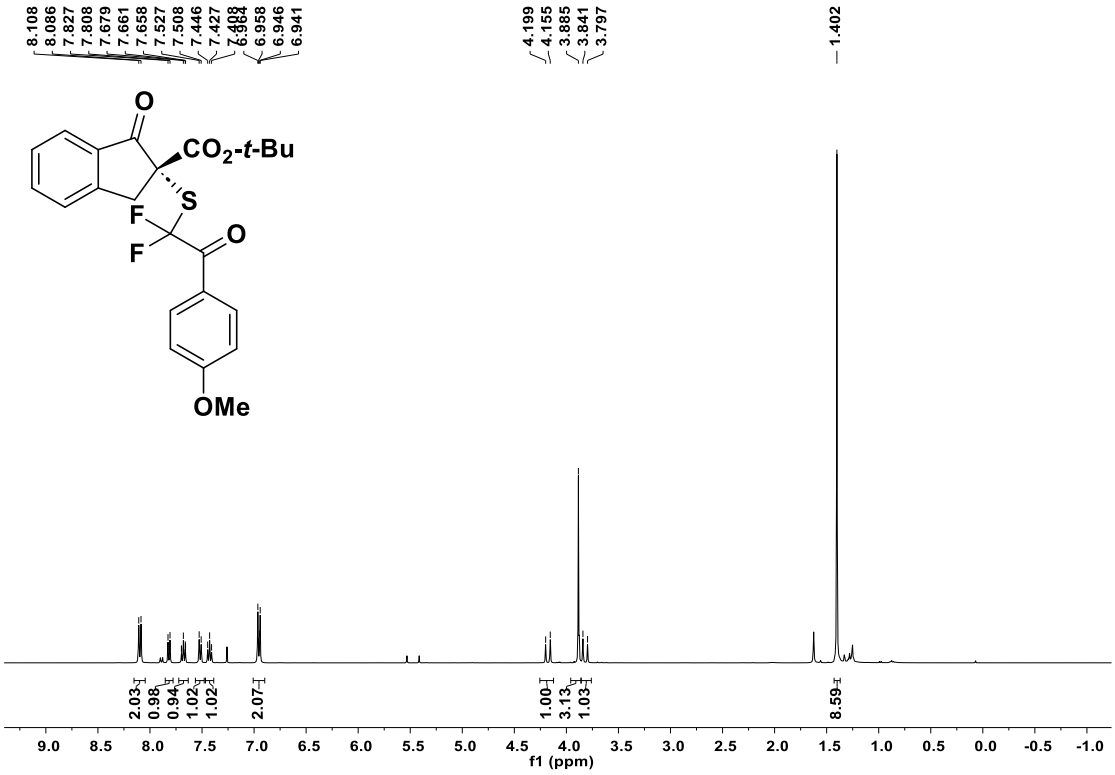
^{13}C NMR (101 MHz) of **3c** in $CDCl_3$



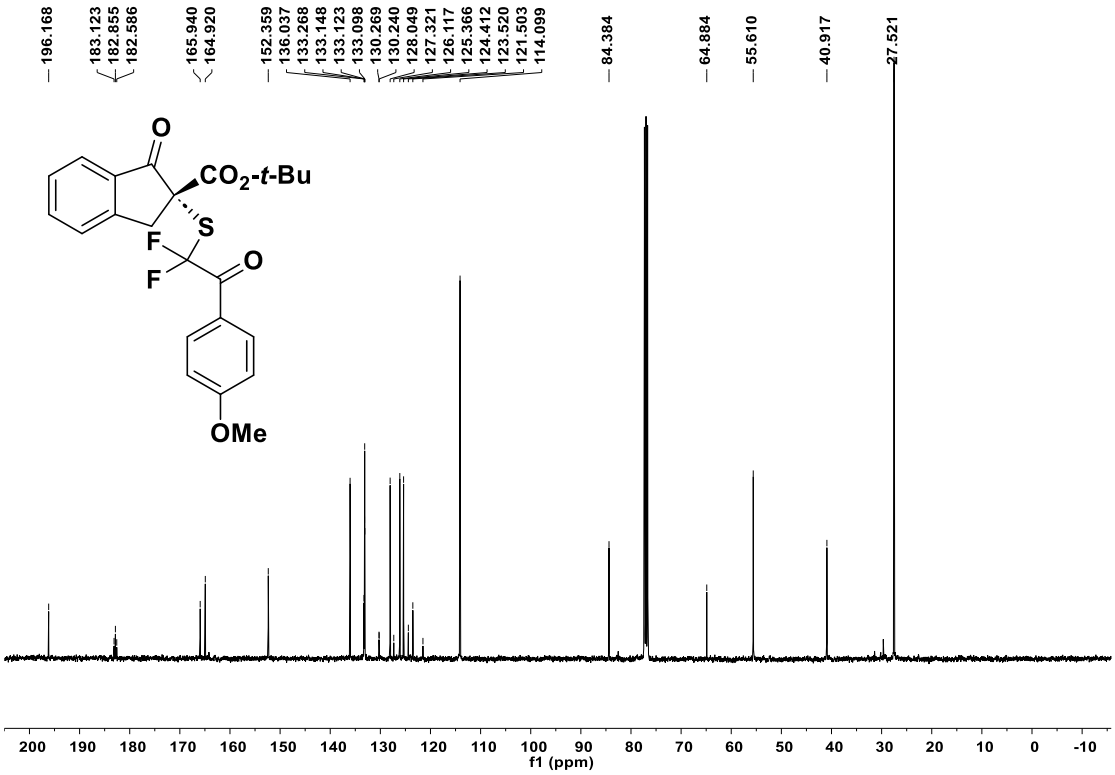
^{19}F NMR (376 MHz) of **3c** in $CDCl_3$



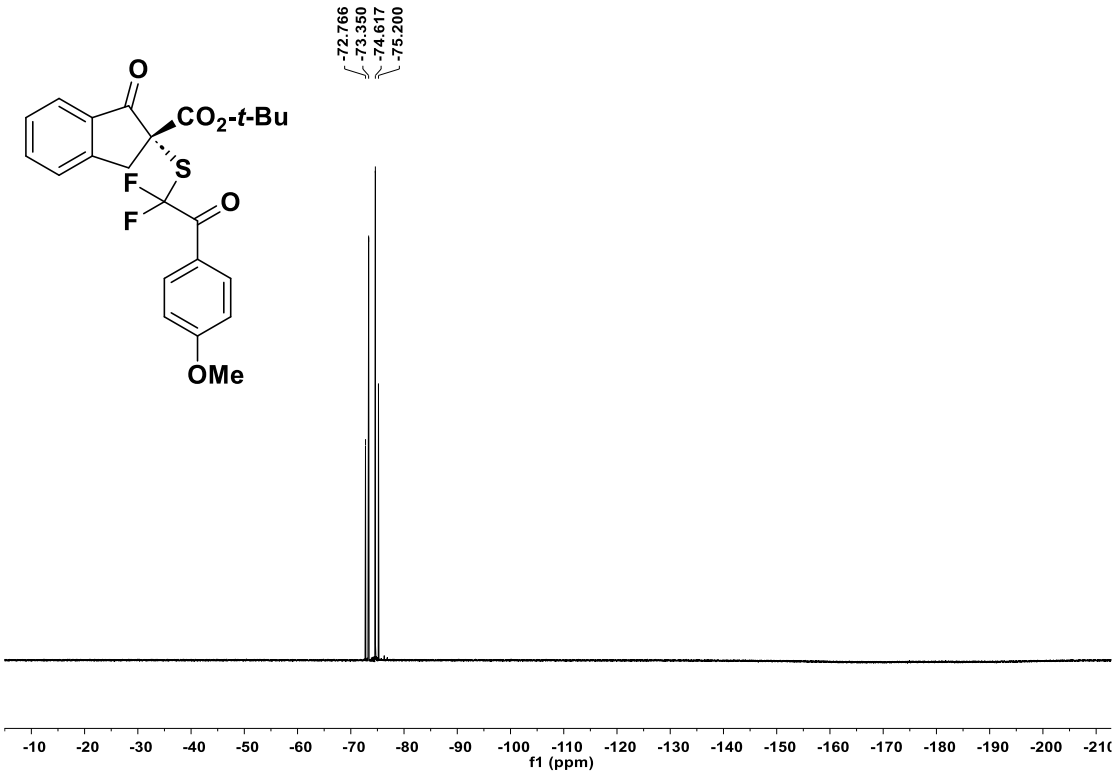
^{1}H NMR (400 MHz) of **3d** in $CDCl_3$



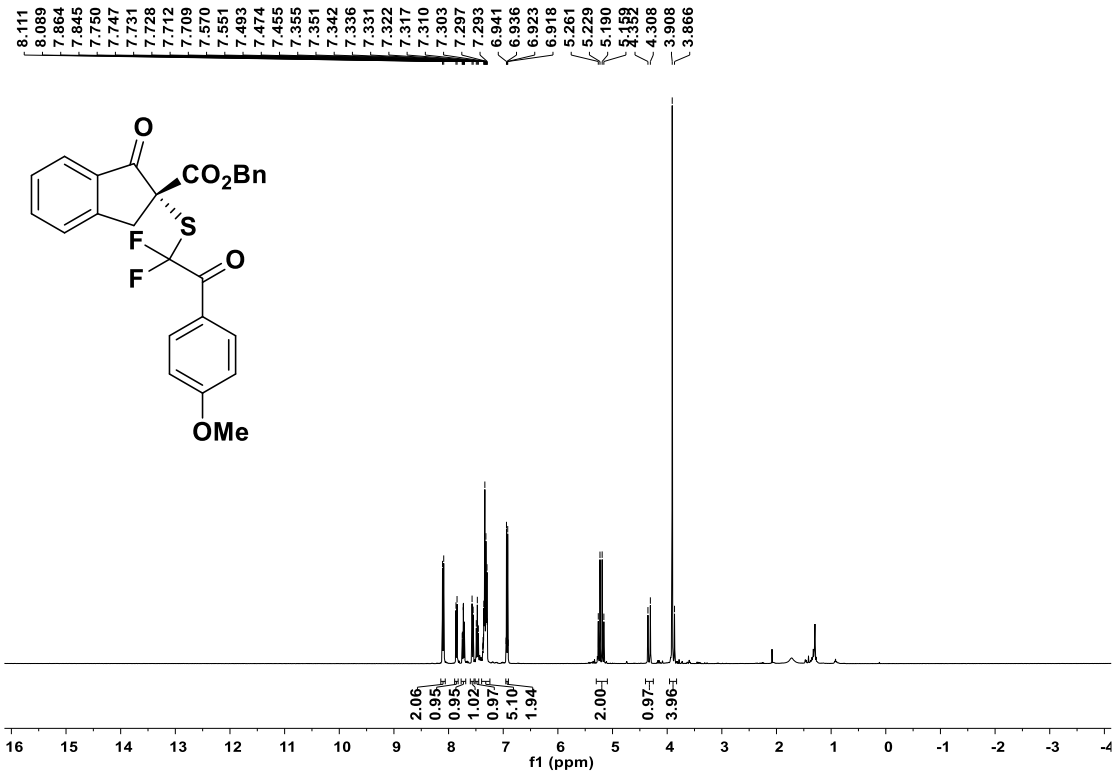
^{13}C NMR (101 MHz) of **3d** in $CDCl_3$



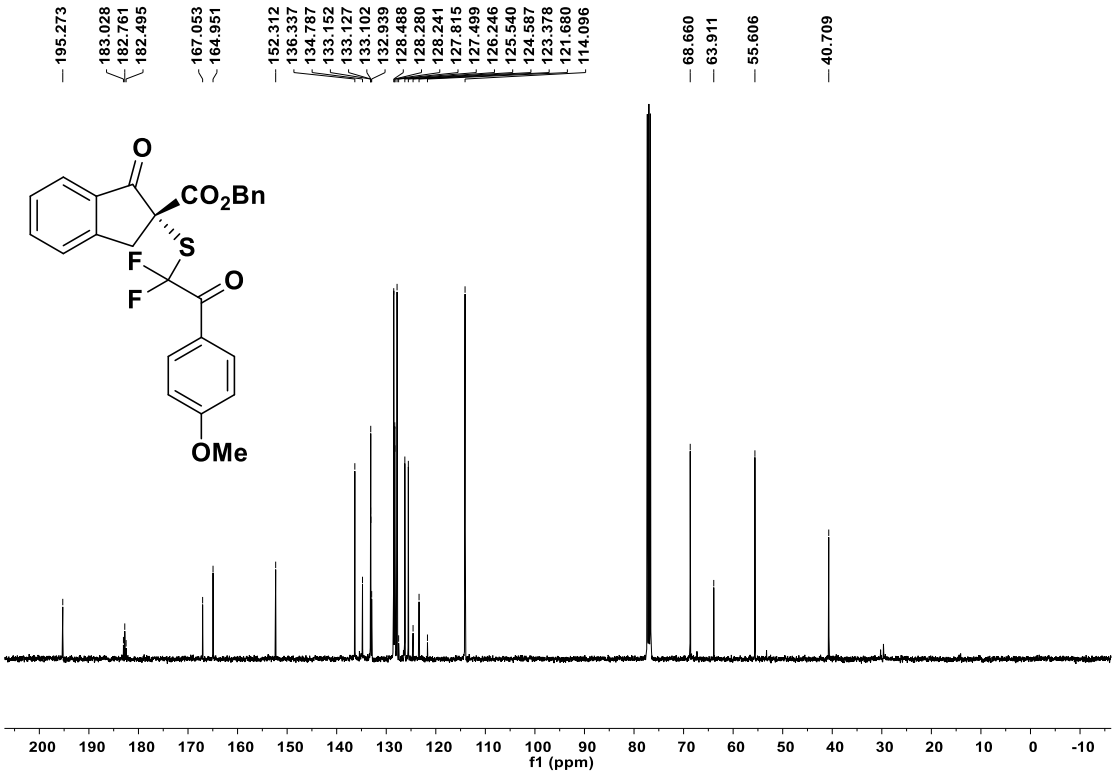
^{19}F NMR (376 MHz) of **3d** in $CDCl_3$



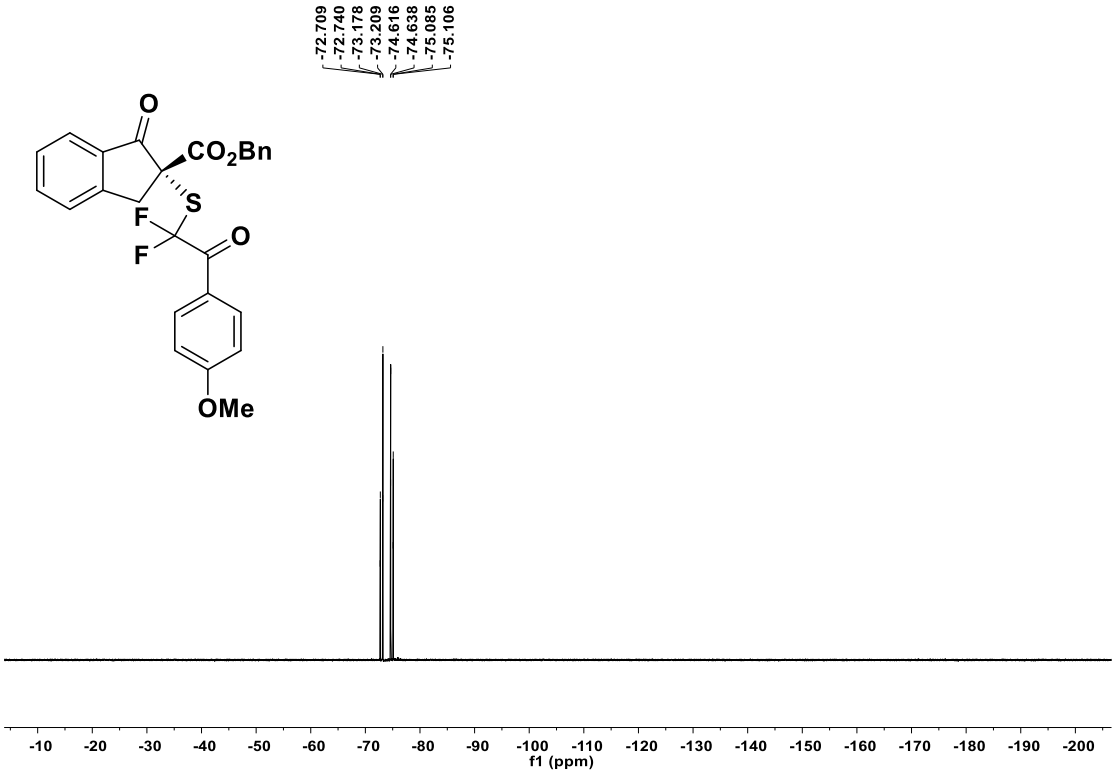
H NMR (400 MHz) of **3e** in $CDCl_3$



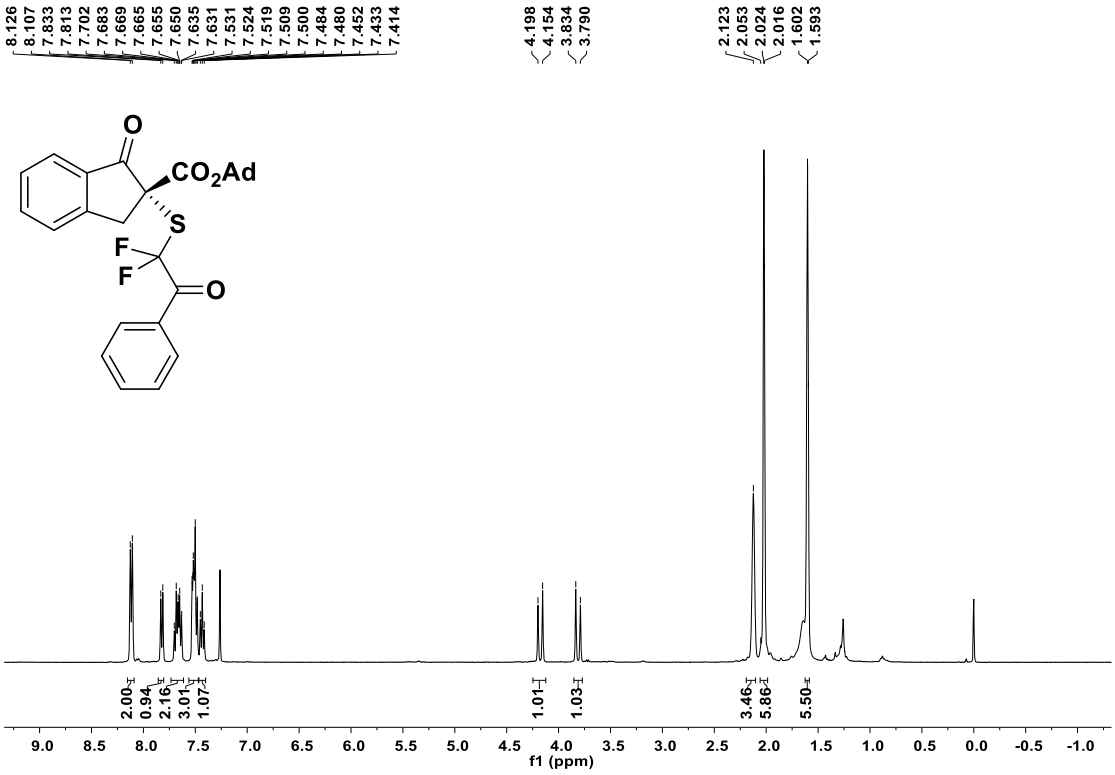
^{13}C NMR (101 MHz) of **3e** in $CDCl_3$



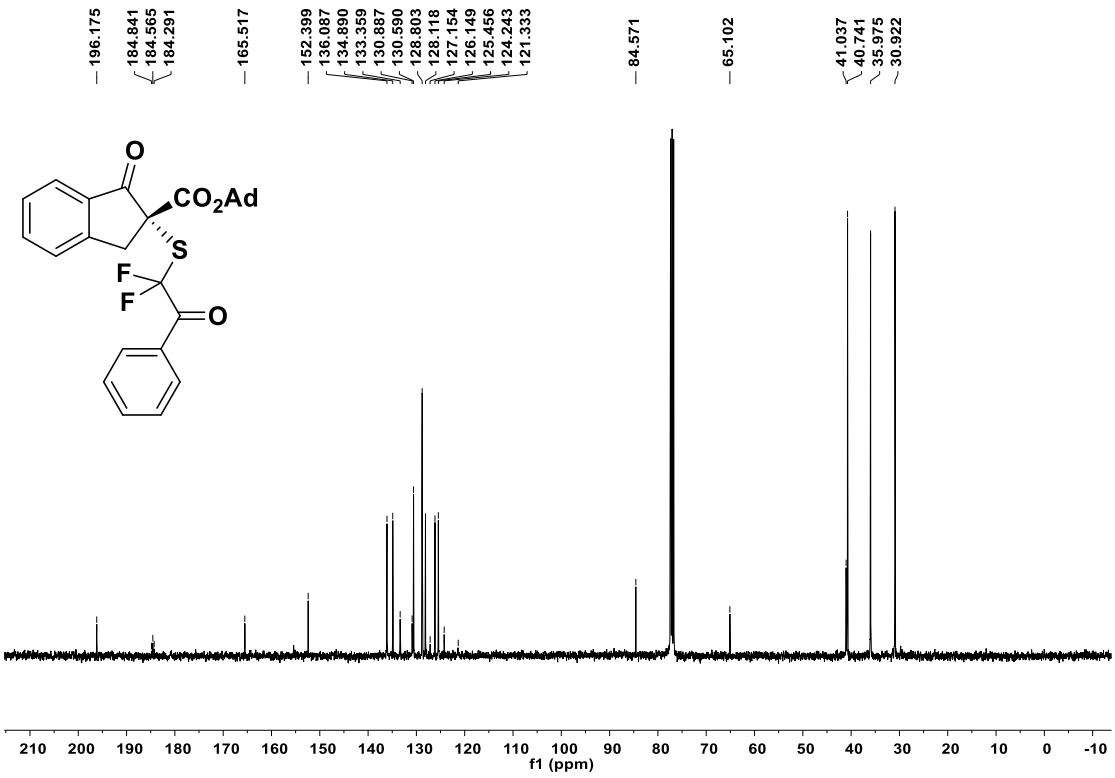
^{19}F NMR (376 MHz) of **3e** in $CDCl_3$



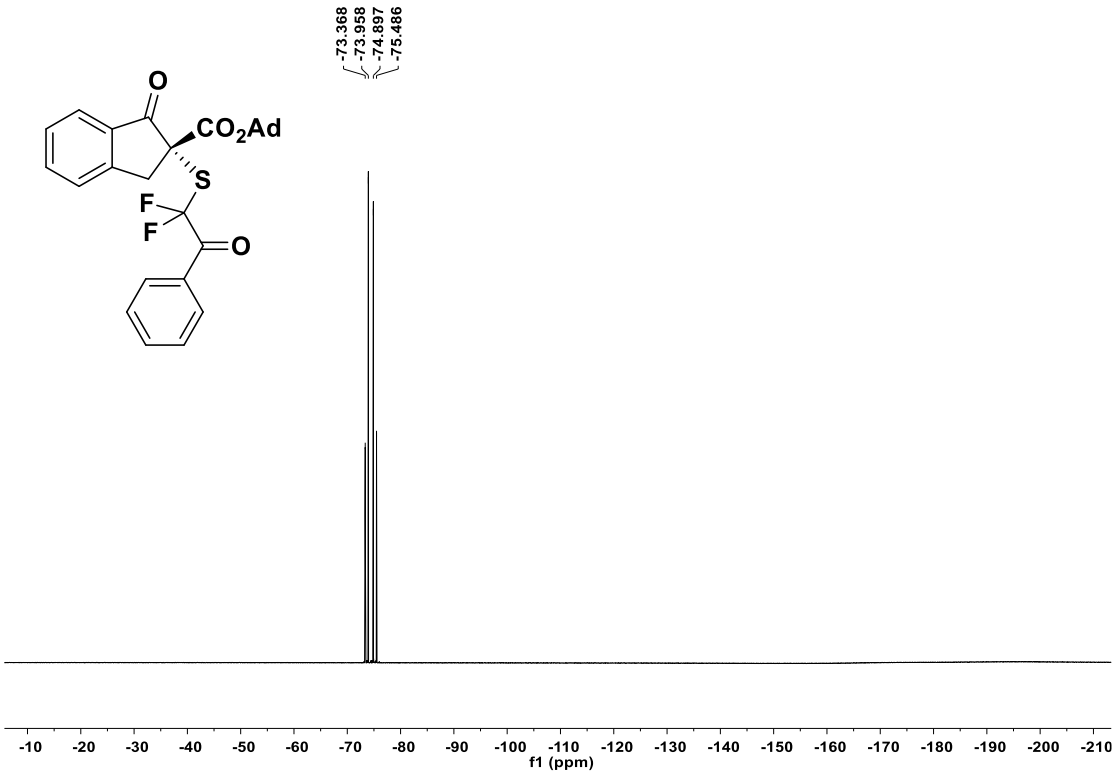
^{1}H NMR (400 MHz) of **3f** in $CDCl_3$



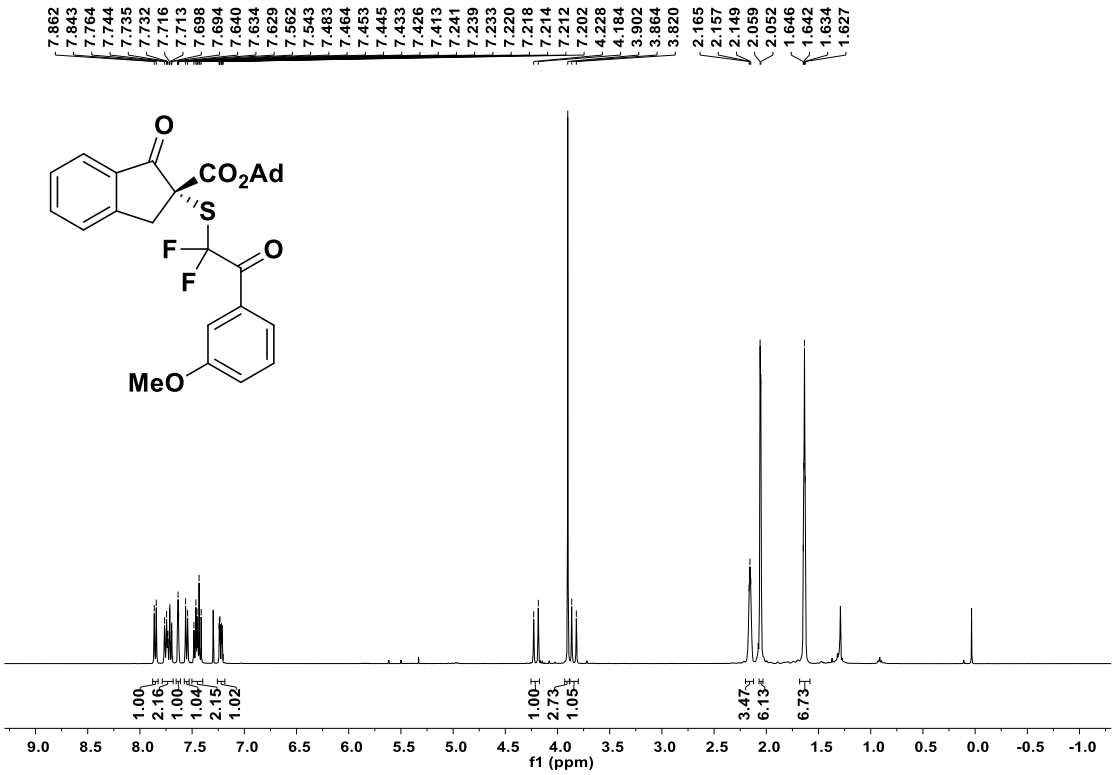
^{13}C NMR (101 MHz) of **3f** in $CDCl_3$



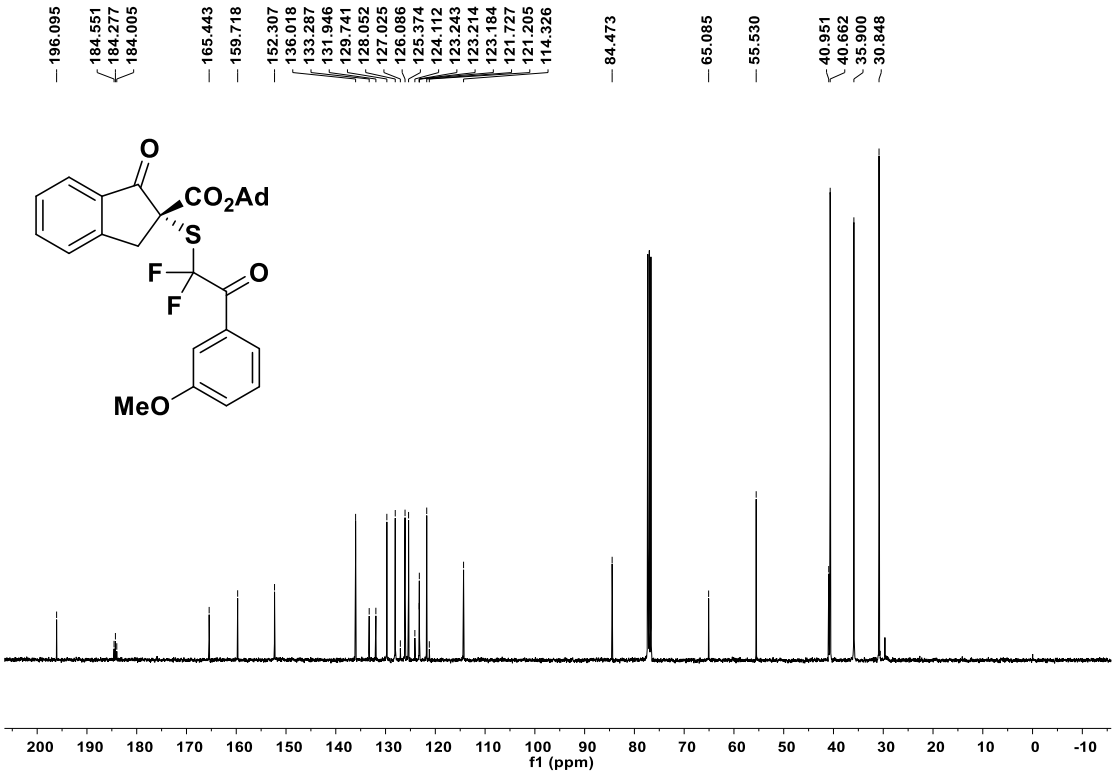
^{19}F NMR (376 MHz) of **3f** in $CDCl_3$



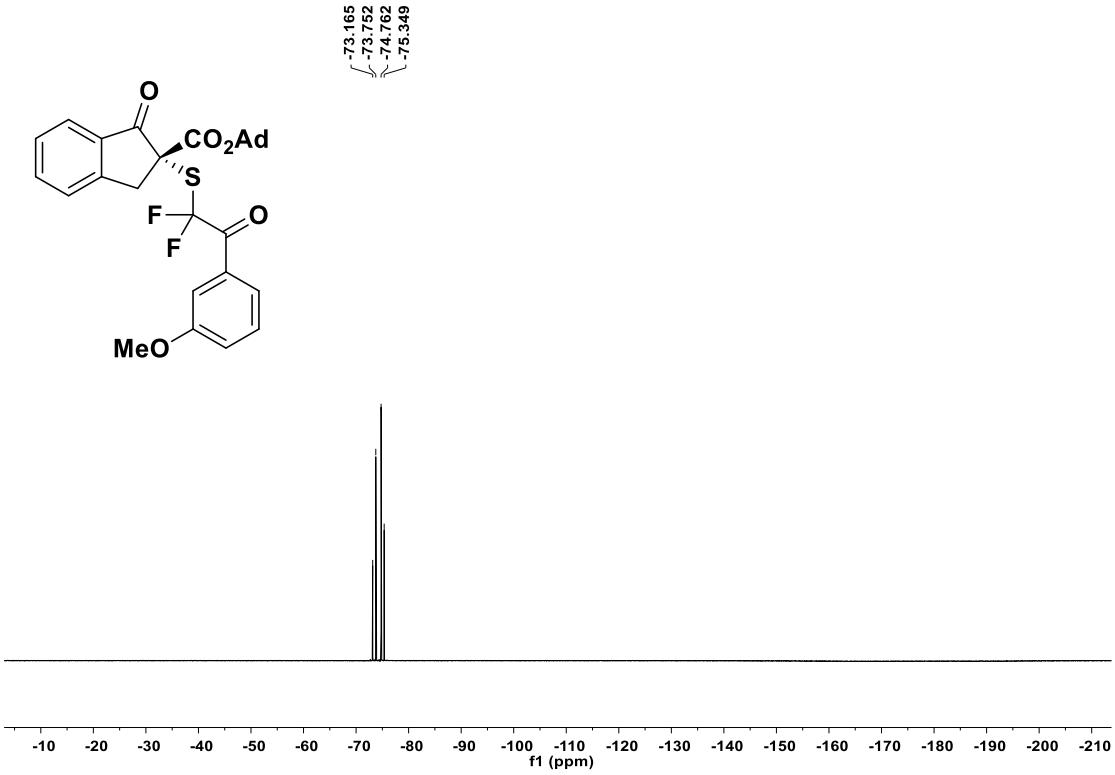
^{1}H NMR (400 MHz) of **3g** in $CDCl_3$



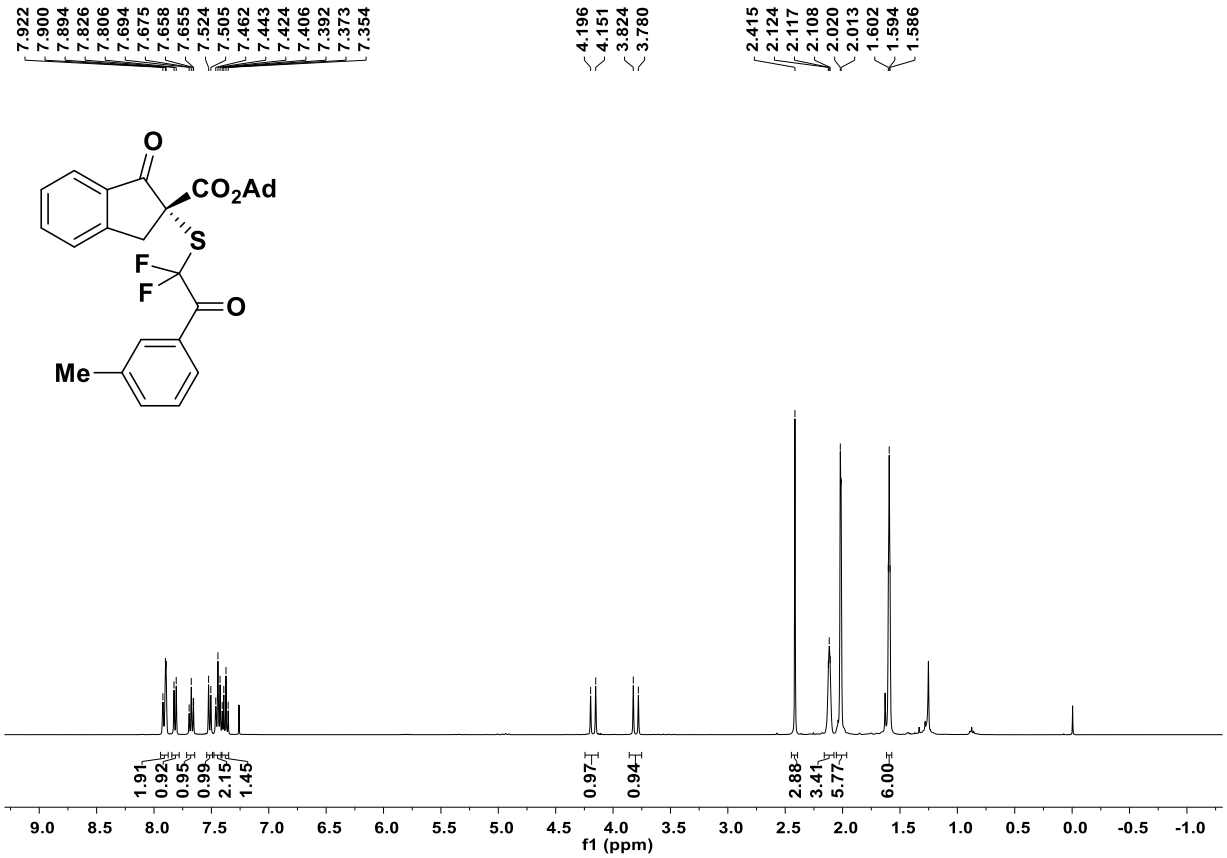
^{13}C NMR (101 MHz) of **3g** in $CDCl_3$



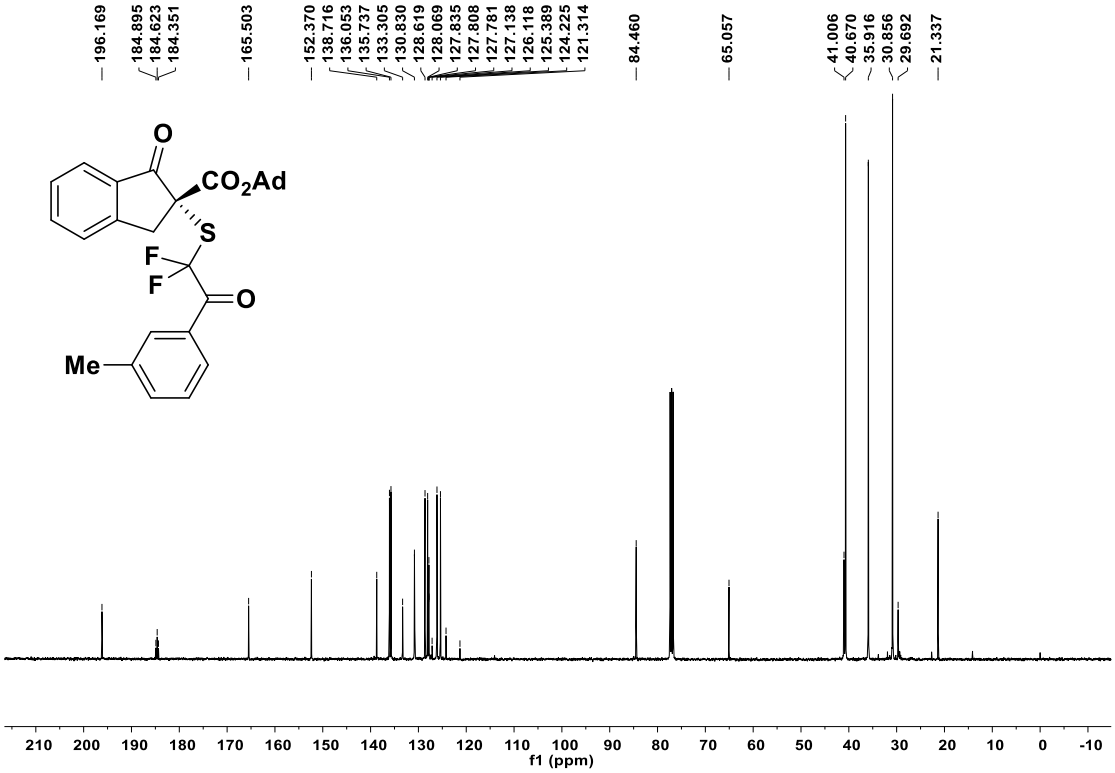
^{19}F NMR (376 MHz) of **3g** in $CDCl_3$



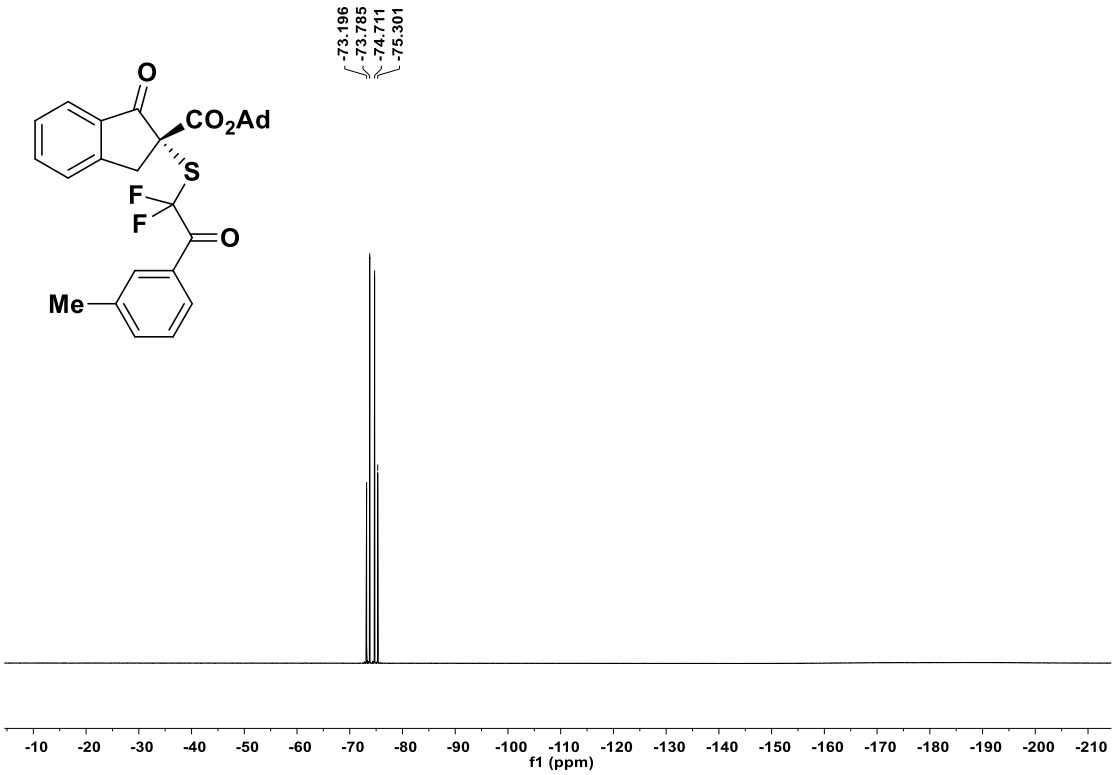
^{1}H NMR (400 MHz) of **3h** in $CDCl_3$



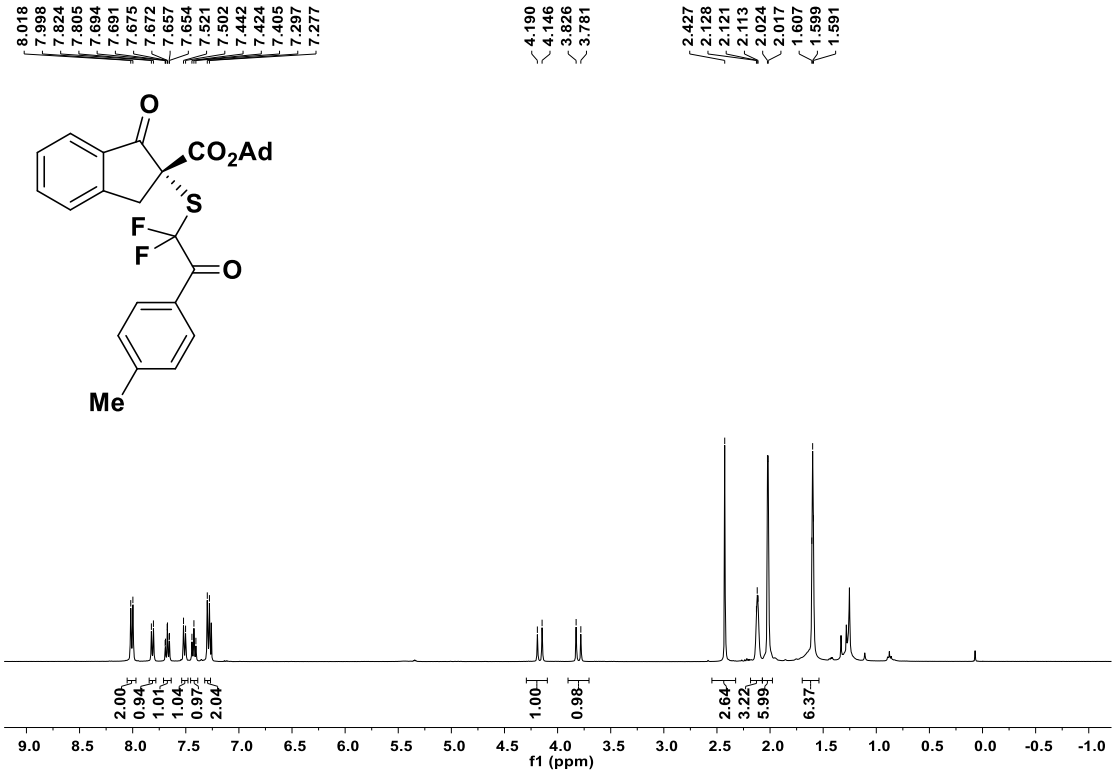
^{13}C NMR (101 MHz) of **3h** in $CDCl_3$



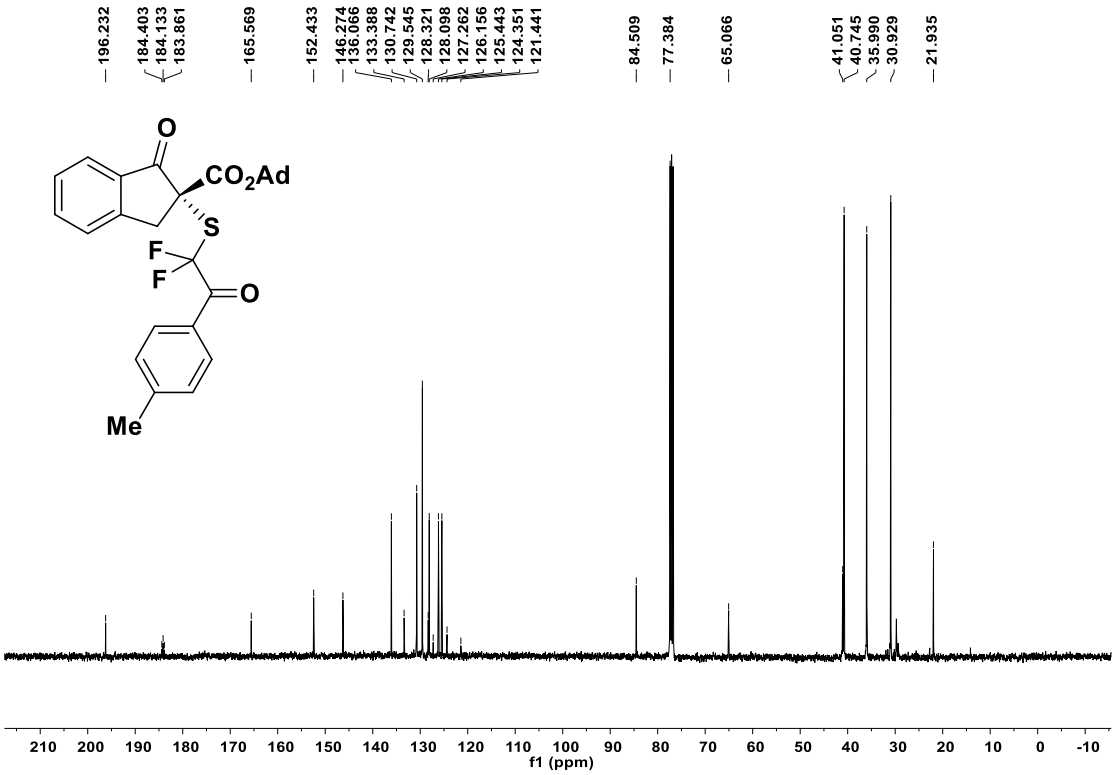
^{19}F NMR (376 MHz) of **3h** in $CDCl_3$



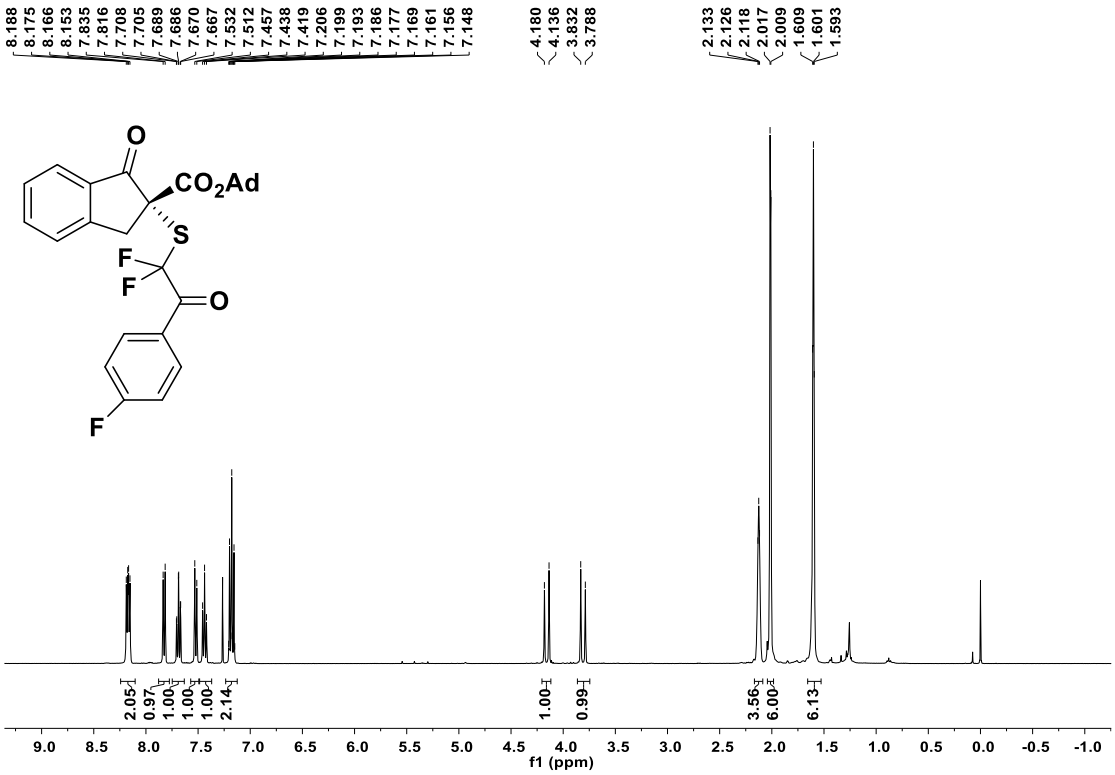
^{1}H NMR (400 MHz) of **3i** in $CDCl_3$



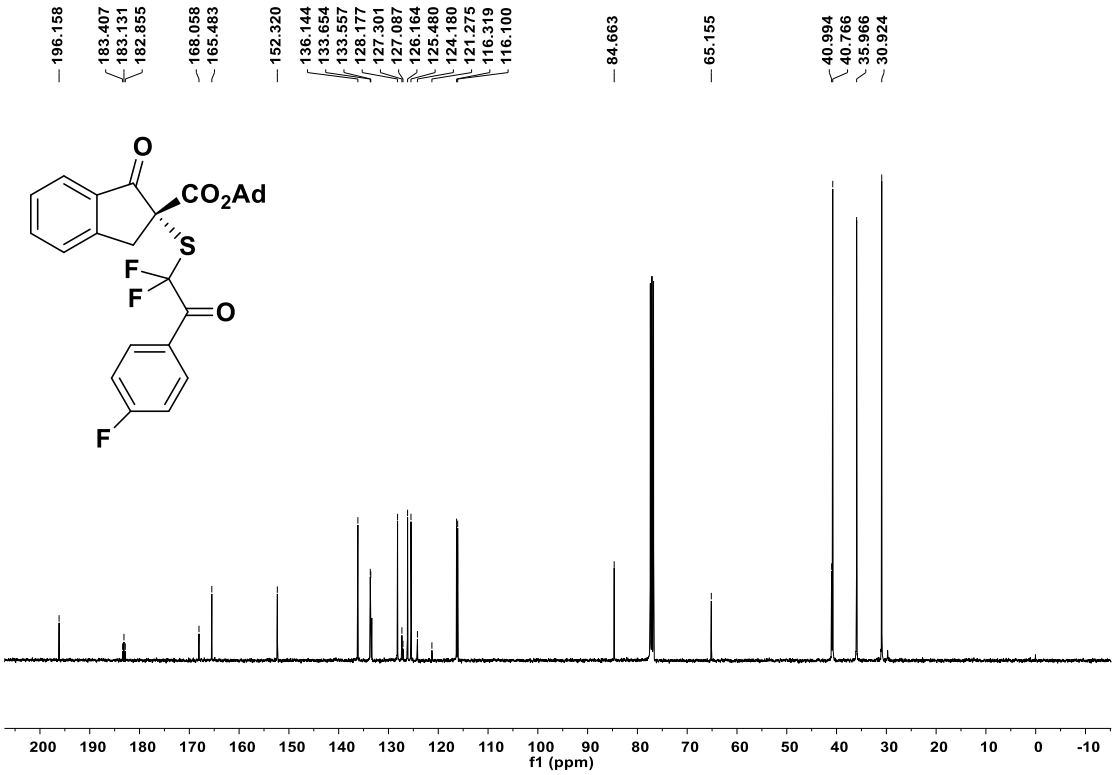
^{13}C NMR (101 MHz) of **3i** in $CDCl_3$



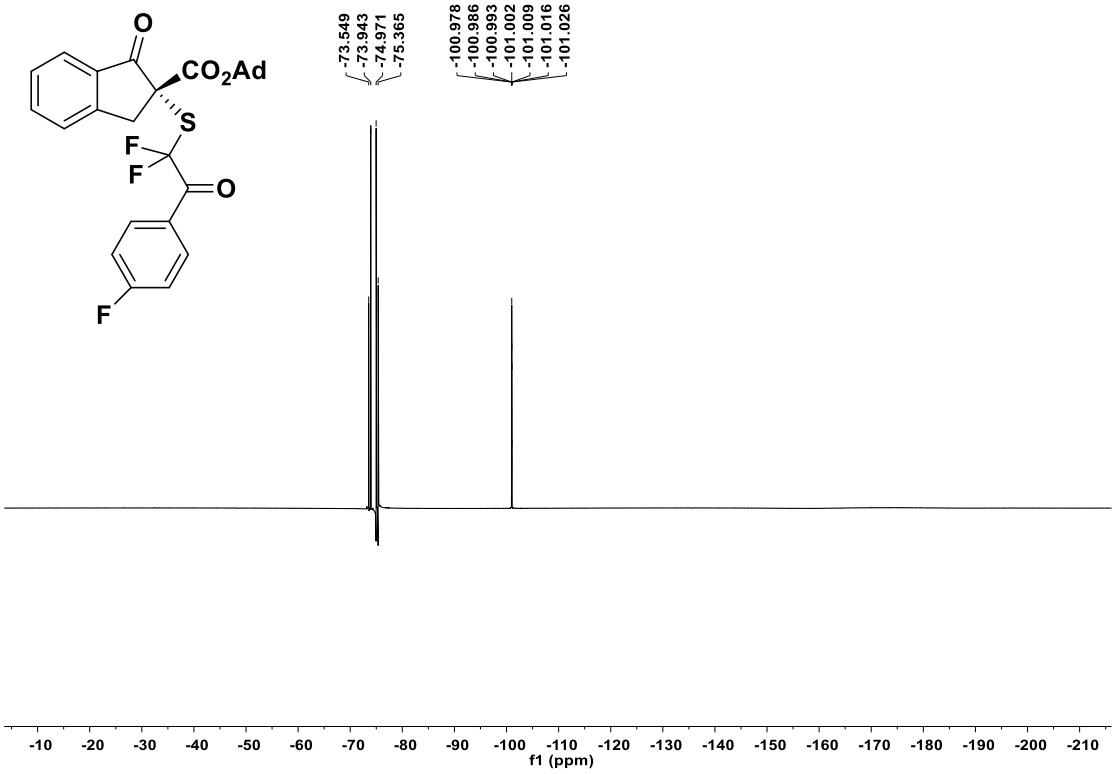
^{1}H NMR (400 MHz) of **3j** in $CDCl_3$



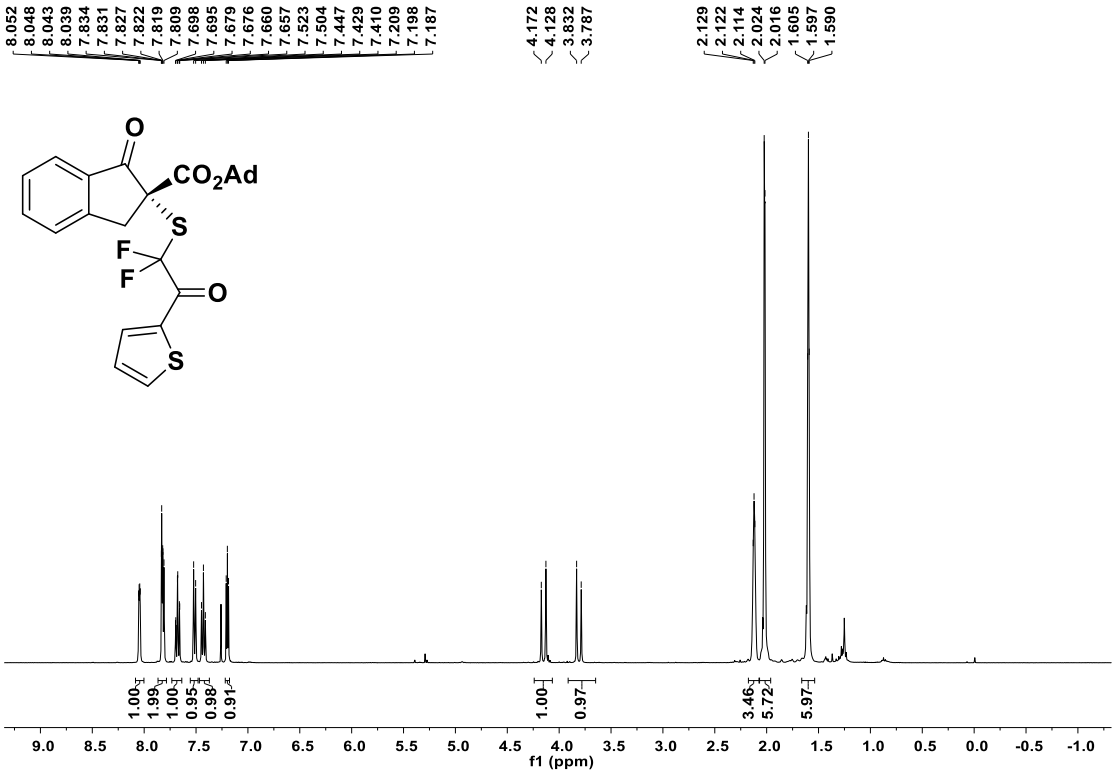
^{13}C NMR (101 MHz) of **3j** in $CDCl_3$



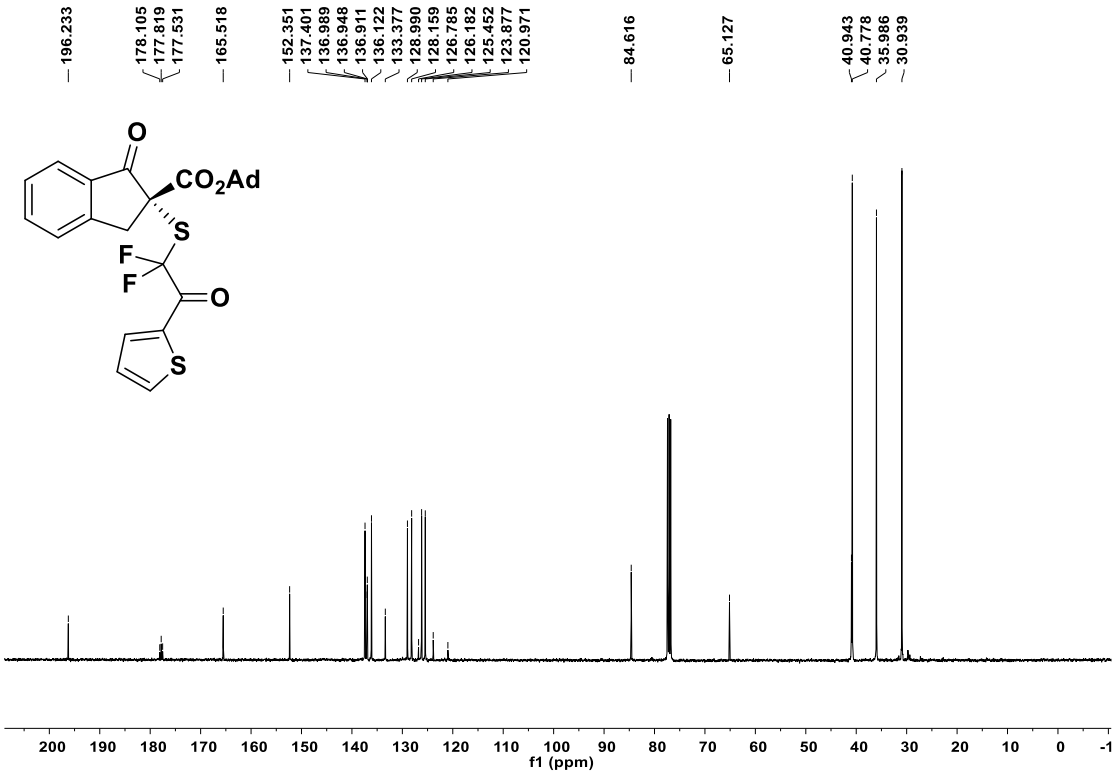
^{19}F NMR (376 MHz) of **3j** in $CDCl_3$



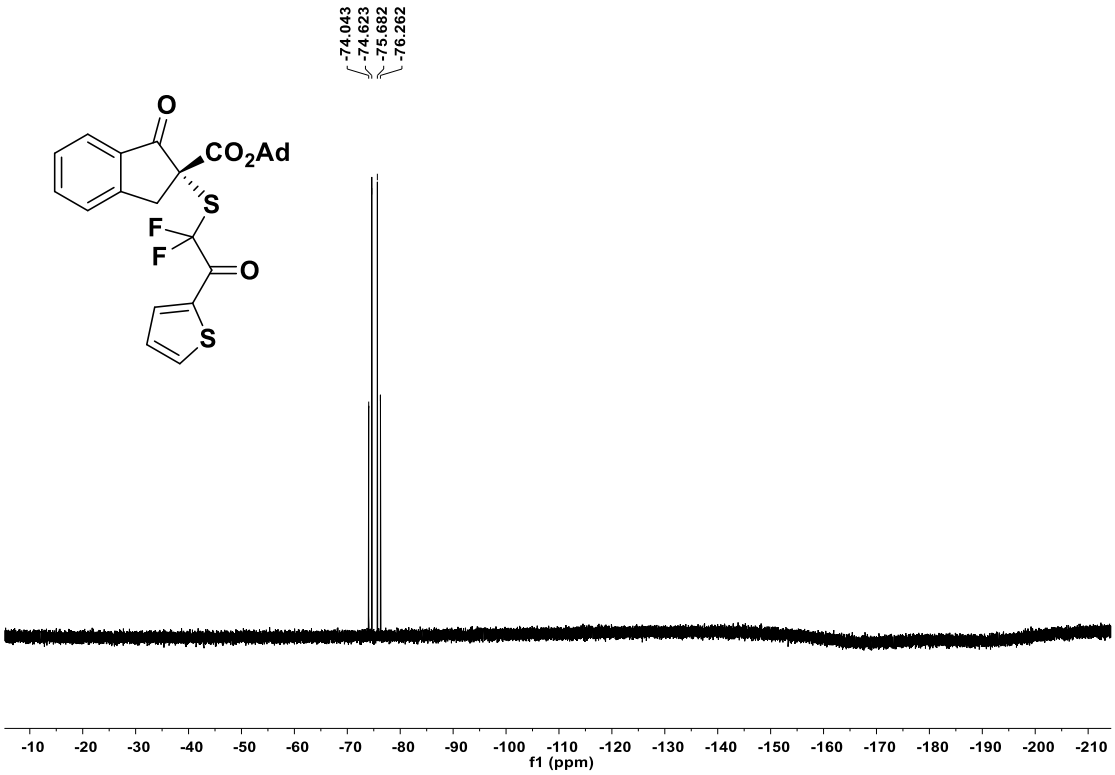
^{1}H NMR (400 MHz) of **3k** in $CDCl_3$



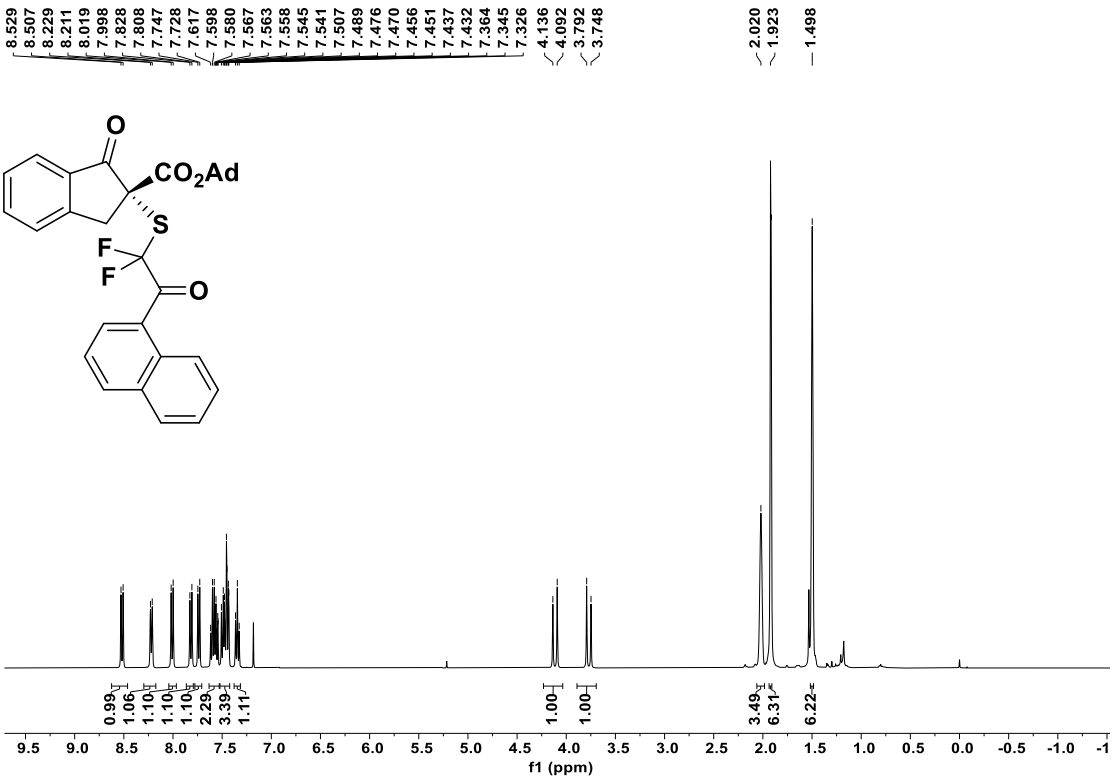
^{13}C NMR (101 MHz) of **3k** in $CDCl_3$



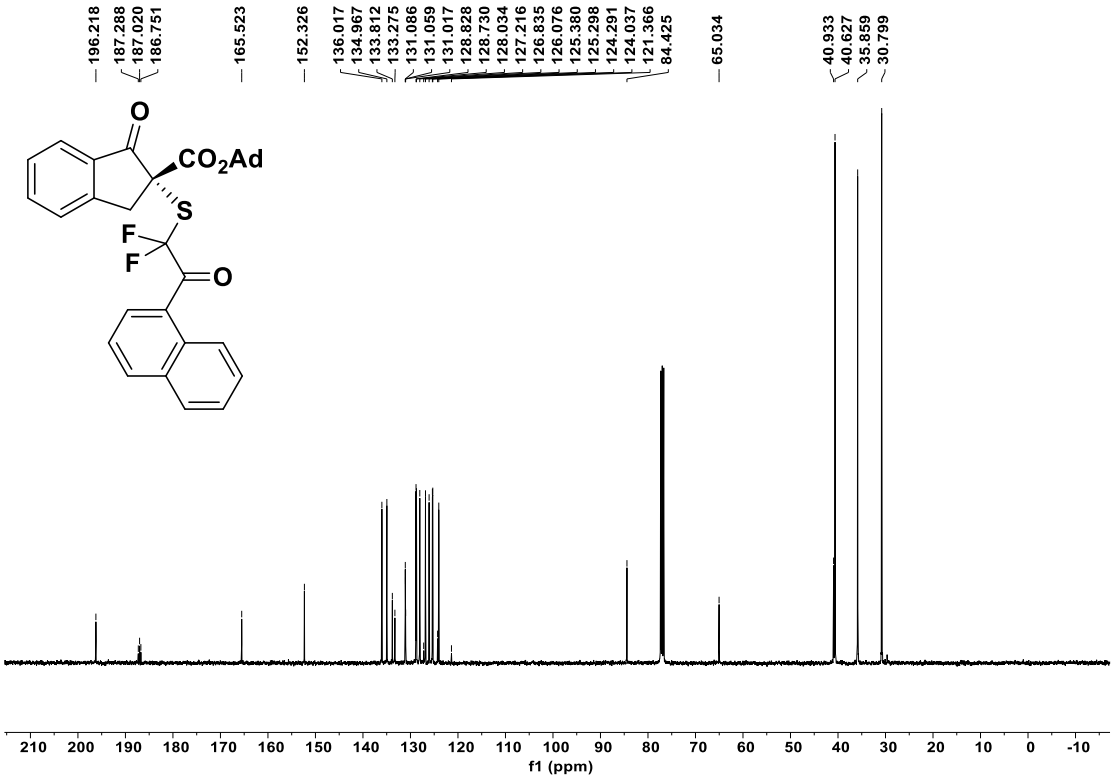
^{19}F NMR (376 MHz) of **3k** in $CDCl_3$



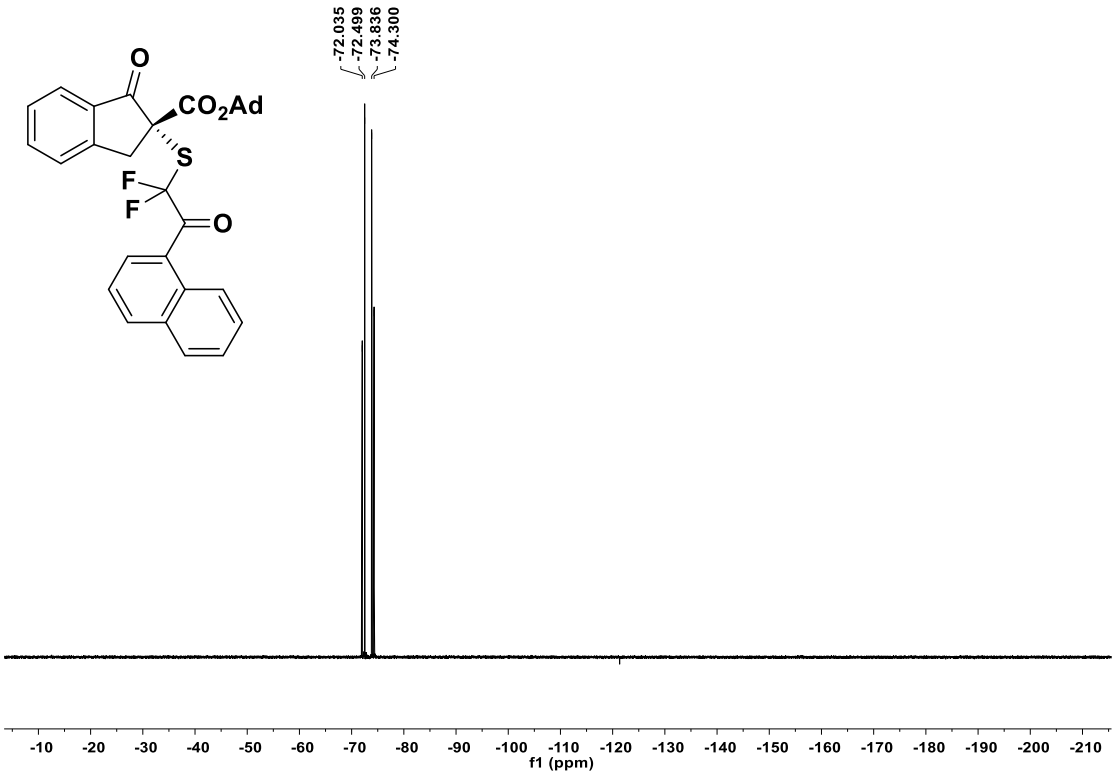
^{1}H NMR (400 MHz) of **3l** in $CDCl_3$



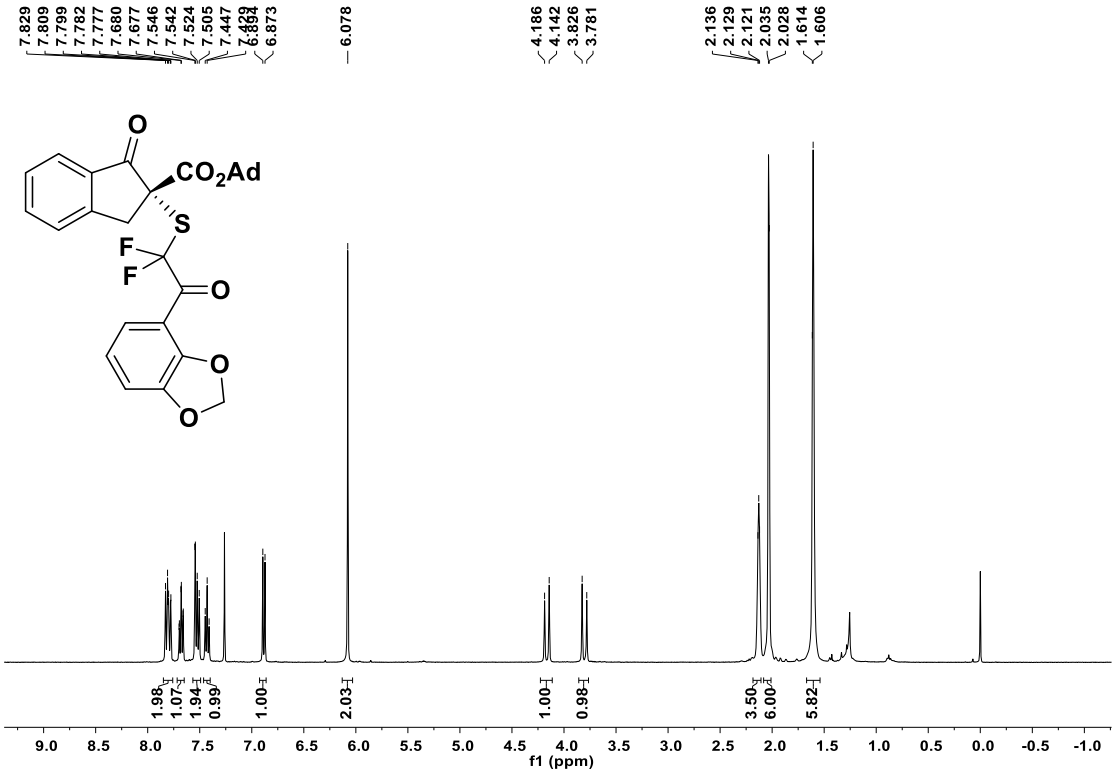
^{13}C NMR (101 MHz) of **3l** in $CDCl_3$



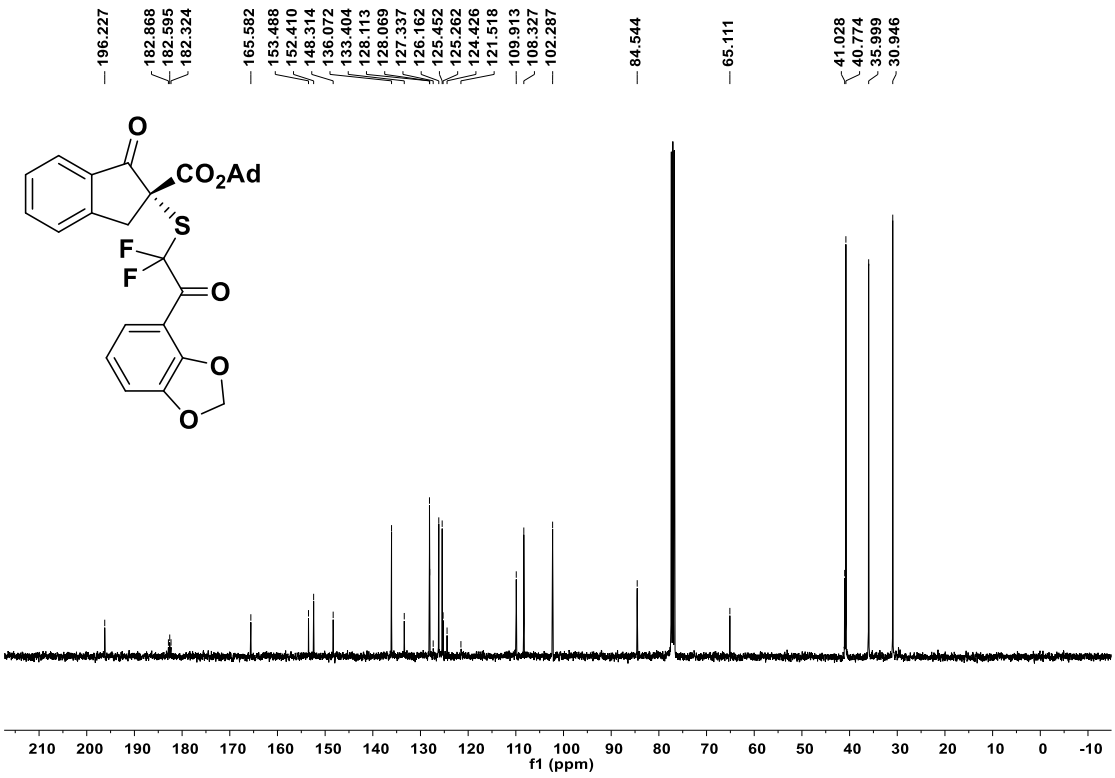
^{13}F NMR (376 MHz) of **3l** in $CDCl_3$



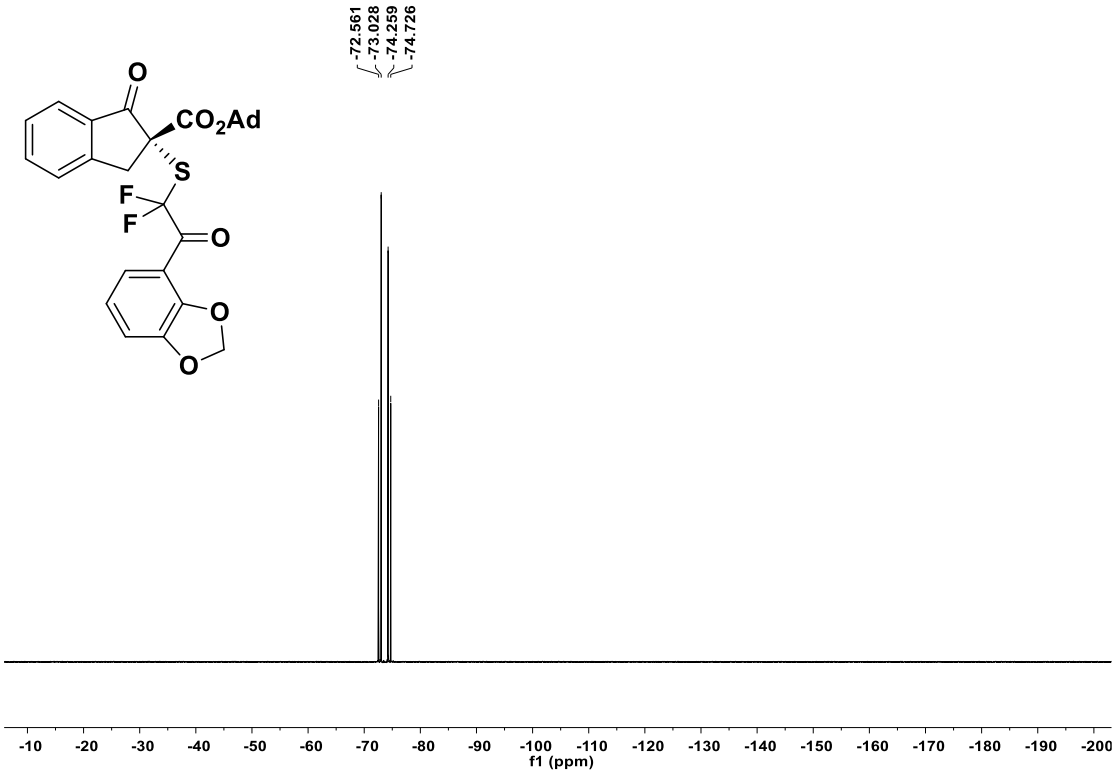
^{1}H NMR (400 MHz) of **3m** in $CDCl_3$



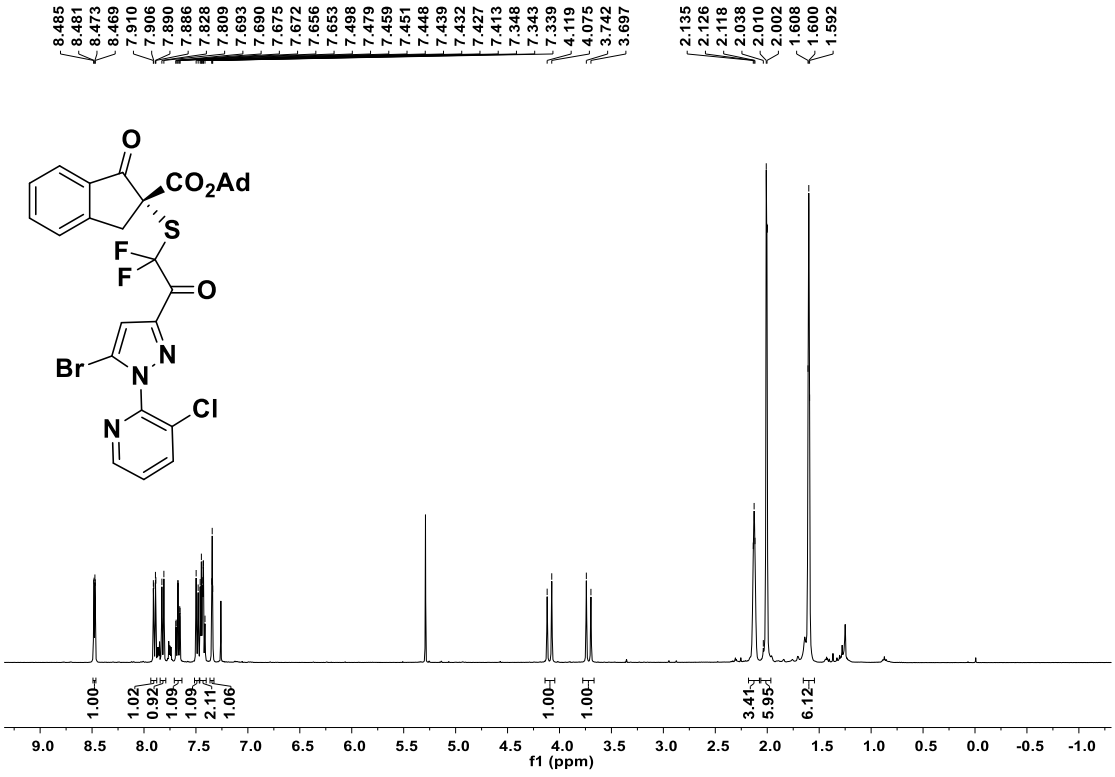
^{13}C NMR (101 MHz) of **3m** in $CDCl_3$



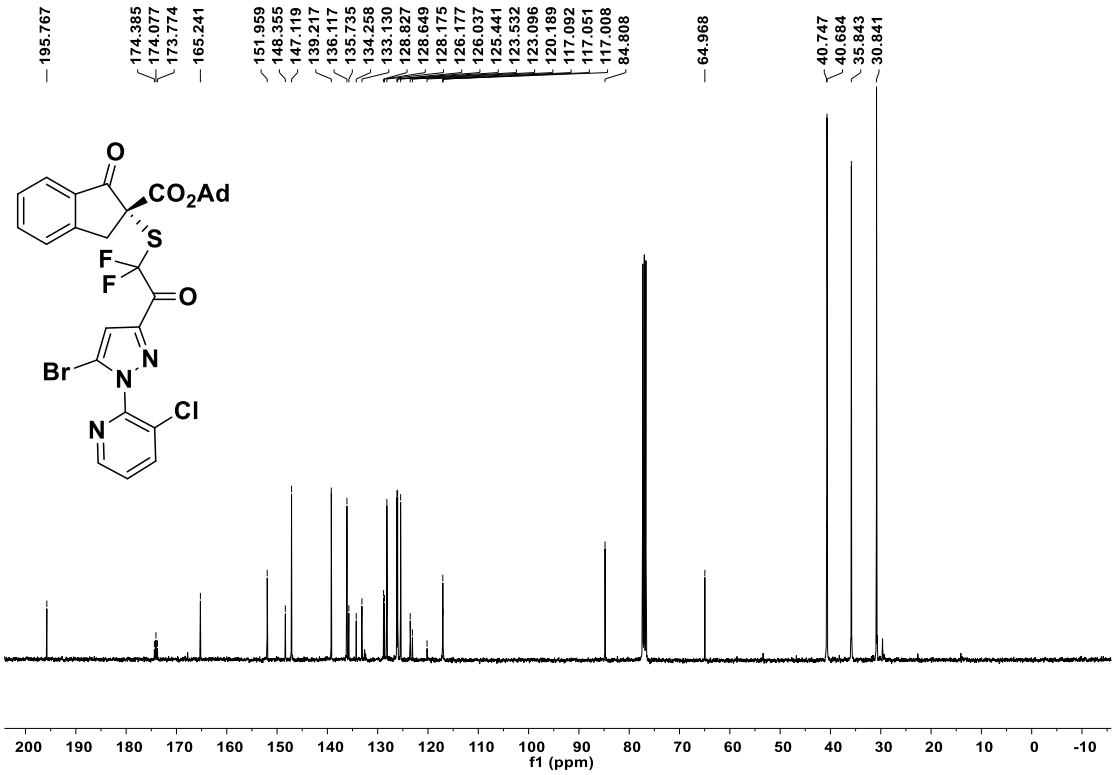
^{19}F NMR (376 MHz) of **3m** in $CDCl_3$



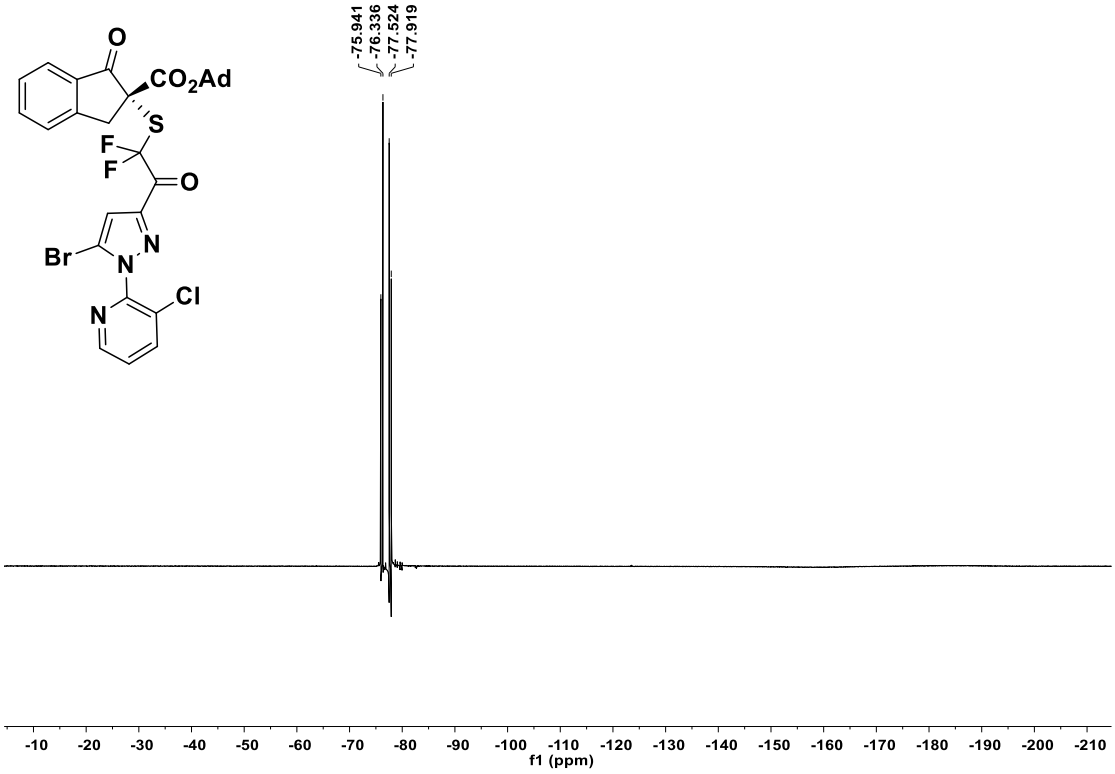
^{1}H NMR (400 MHz) of **3n** in $CDCl_3$



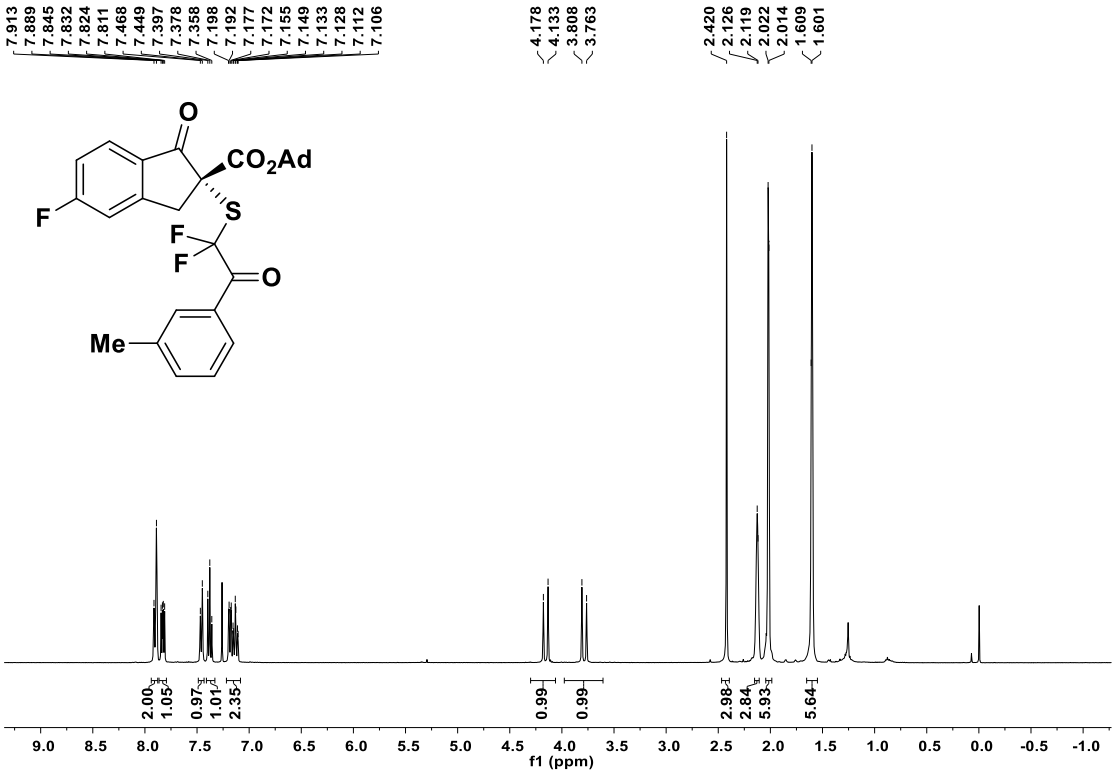
^{13}C NMR (101 MHz) of **3n** in $CDCl_3$



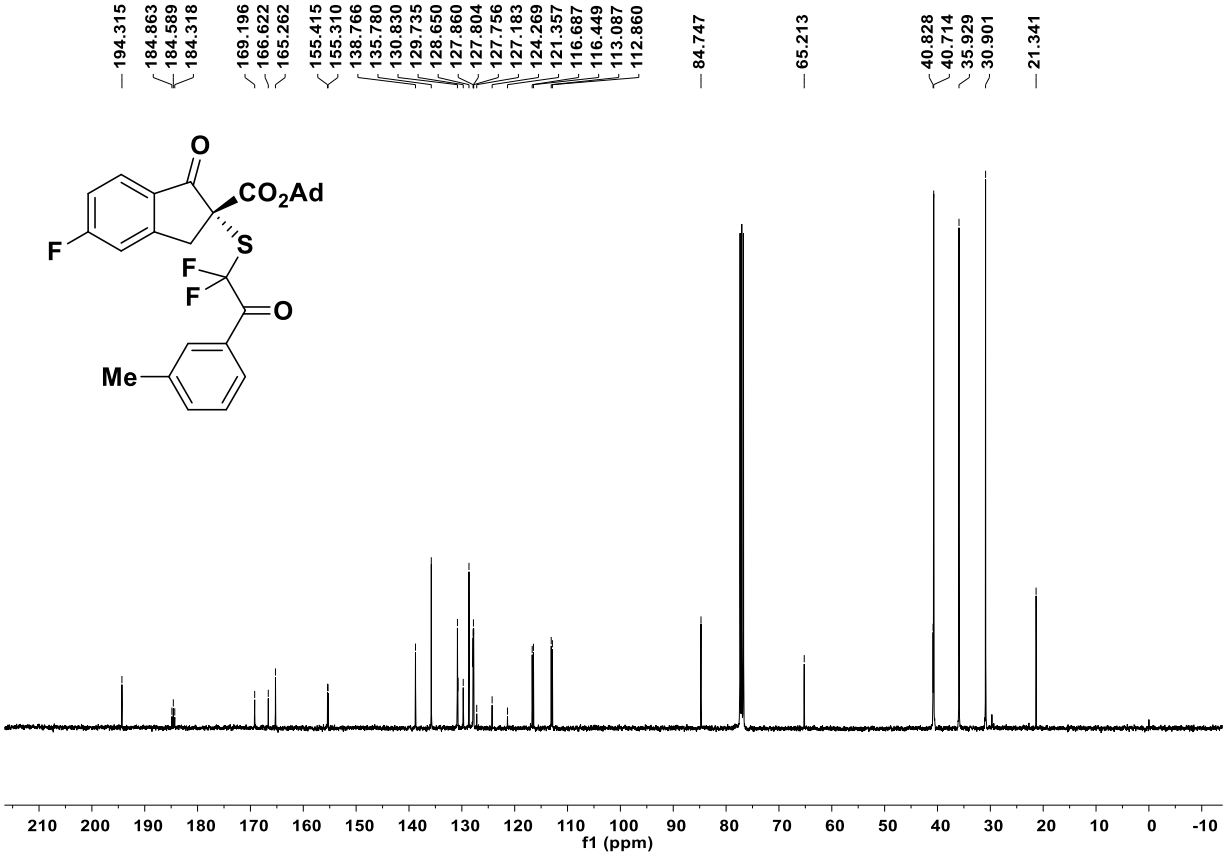
^{19}F NMR (376 MHz) of **3n** in $CDCl_3$



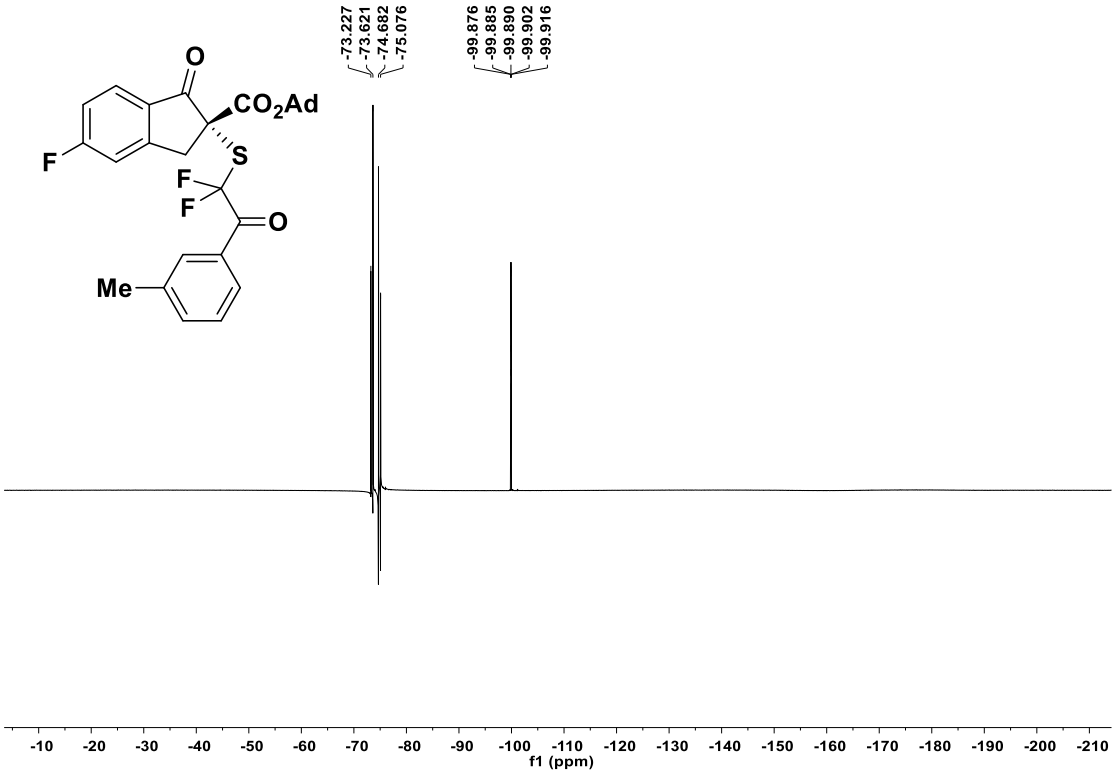
^{1}H NMR (400 MHz) of **3o** in $CDCl_3$



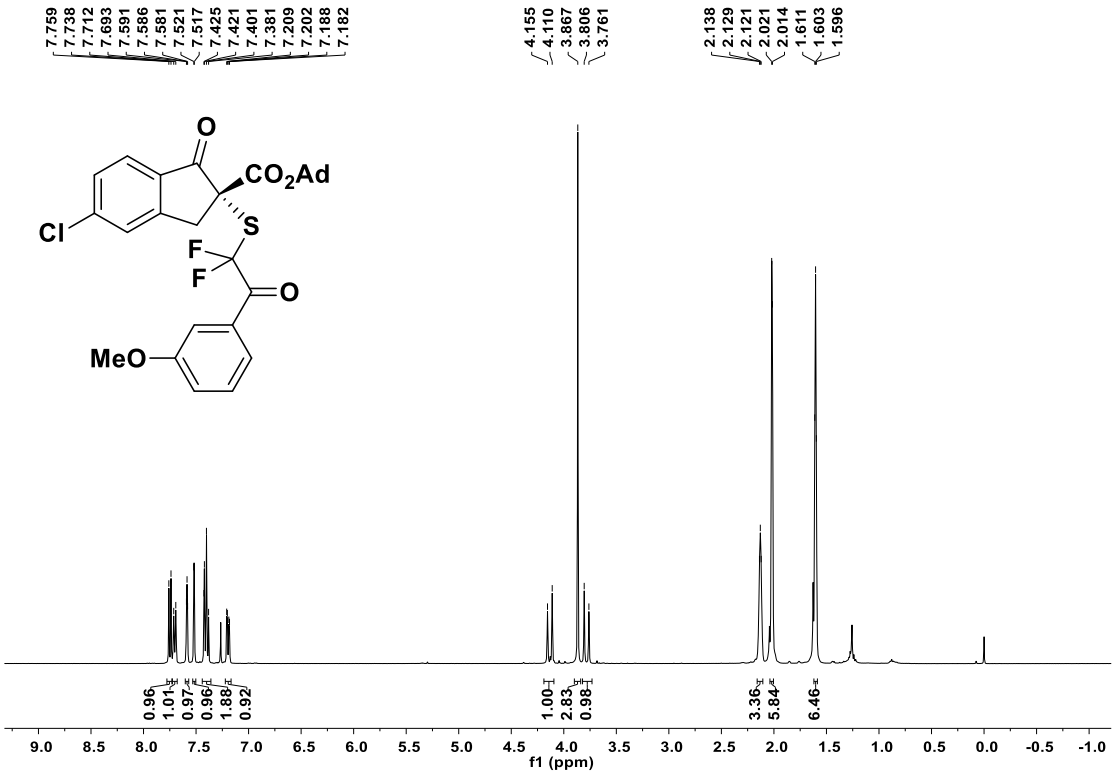
^{13}C NMR (101 MHz) of **3o** in $CDCl_3$



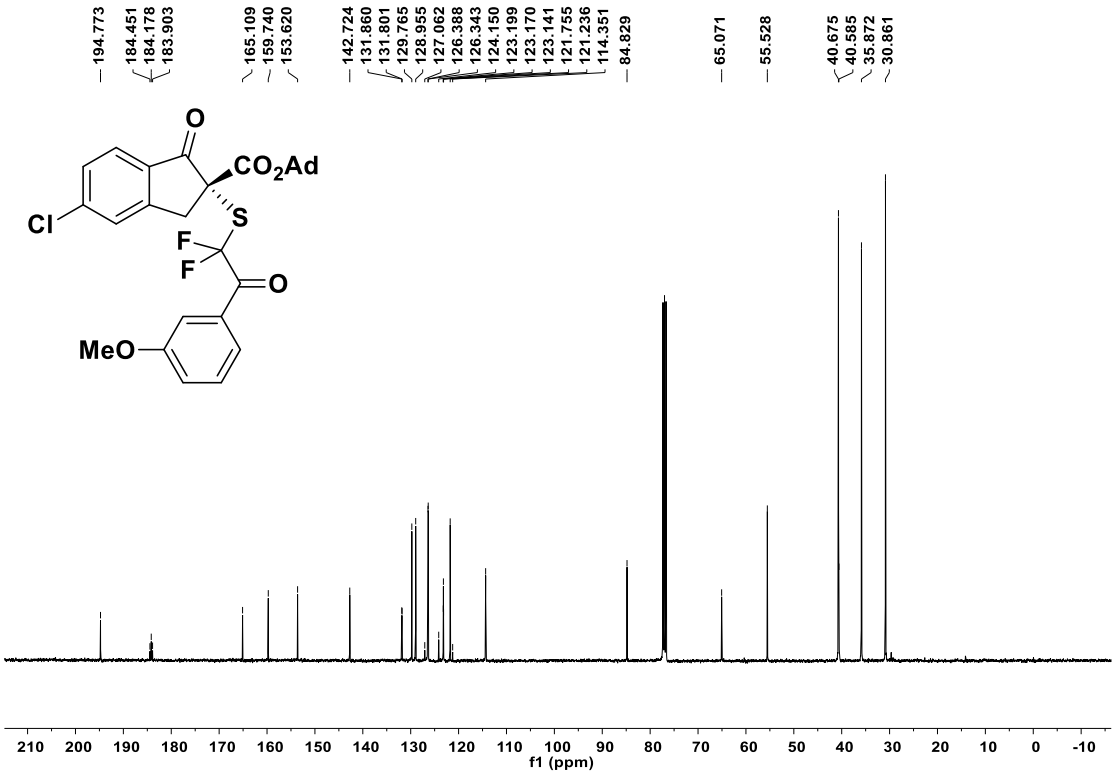
^{19}F NMR (376 MHz) of **3o** in $CDCl_3$



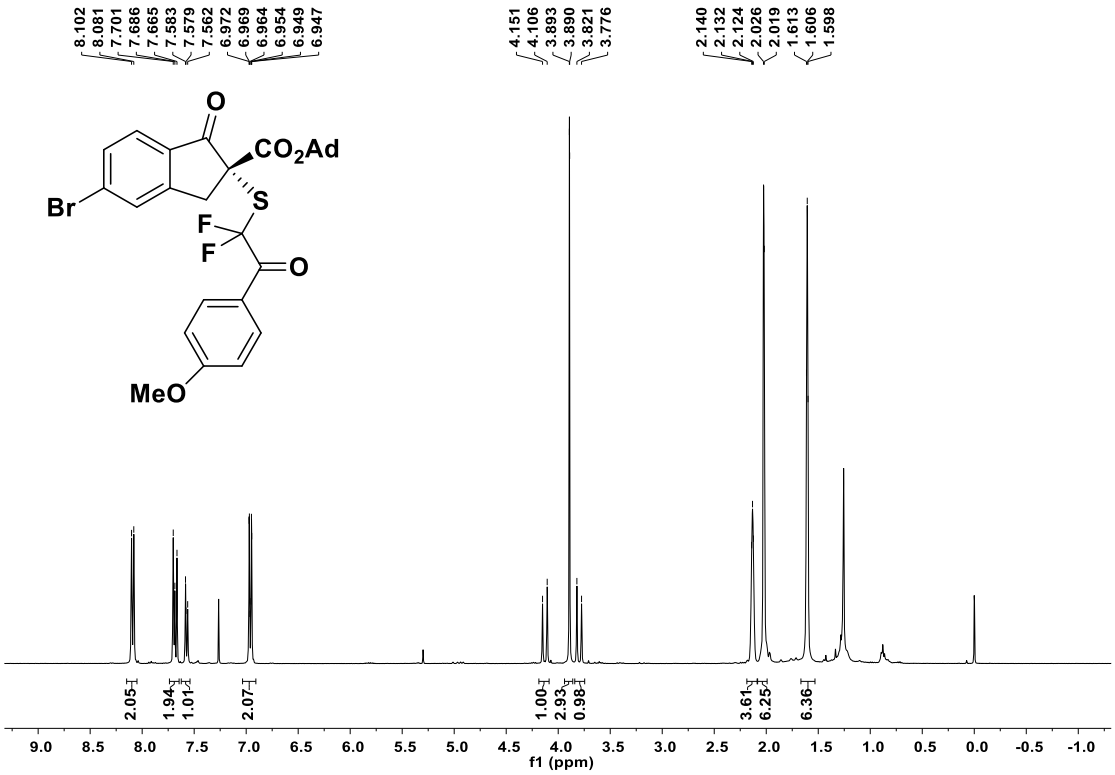
^{1}H NMR (400 MHz) of **3p** in $CDCl_3$



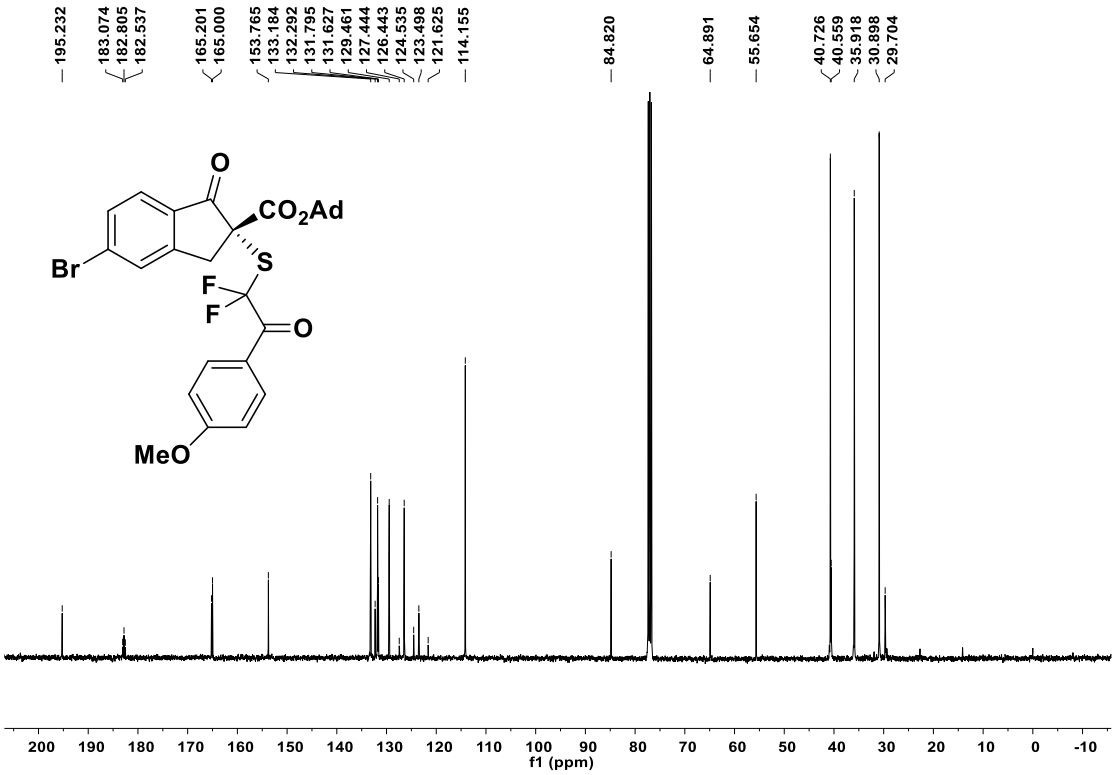
^{13}C NMR (101 MHz) of **3p** in $CDCl_3$



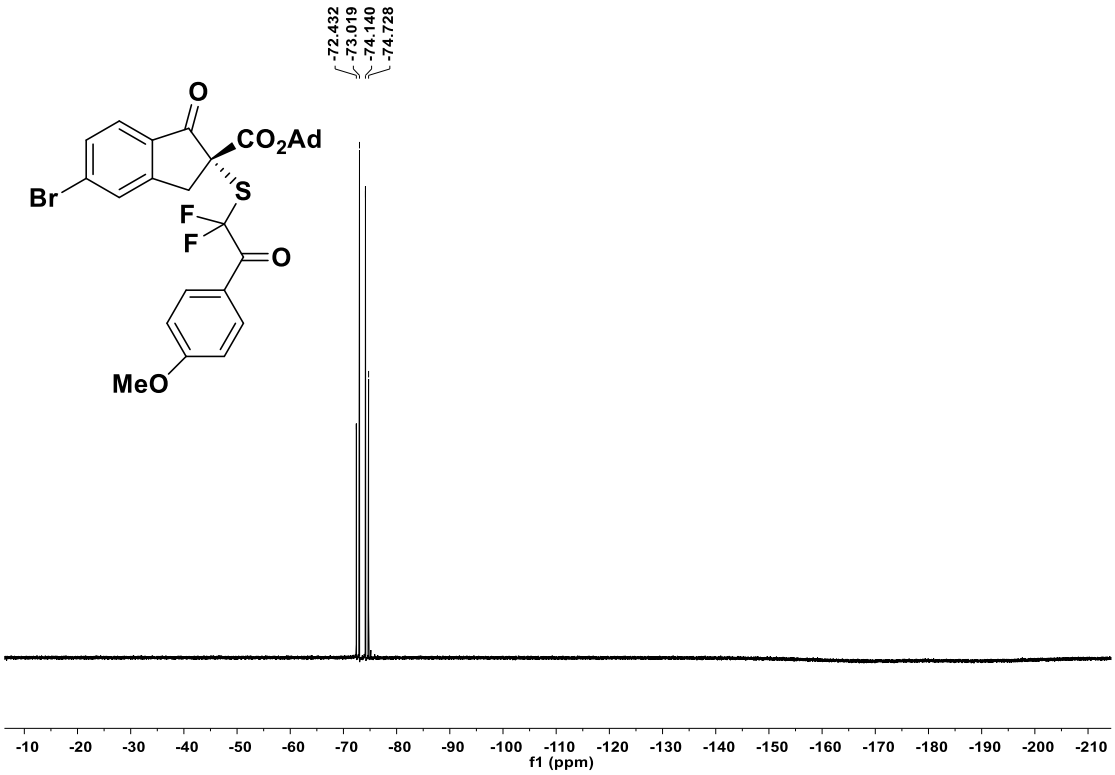
^{1}H NMR (400 MHz) of **3q** in $CDCl_3$



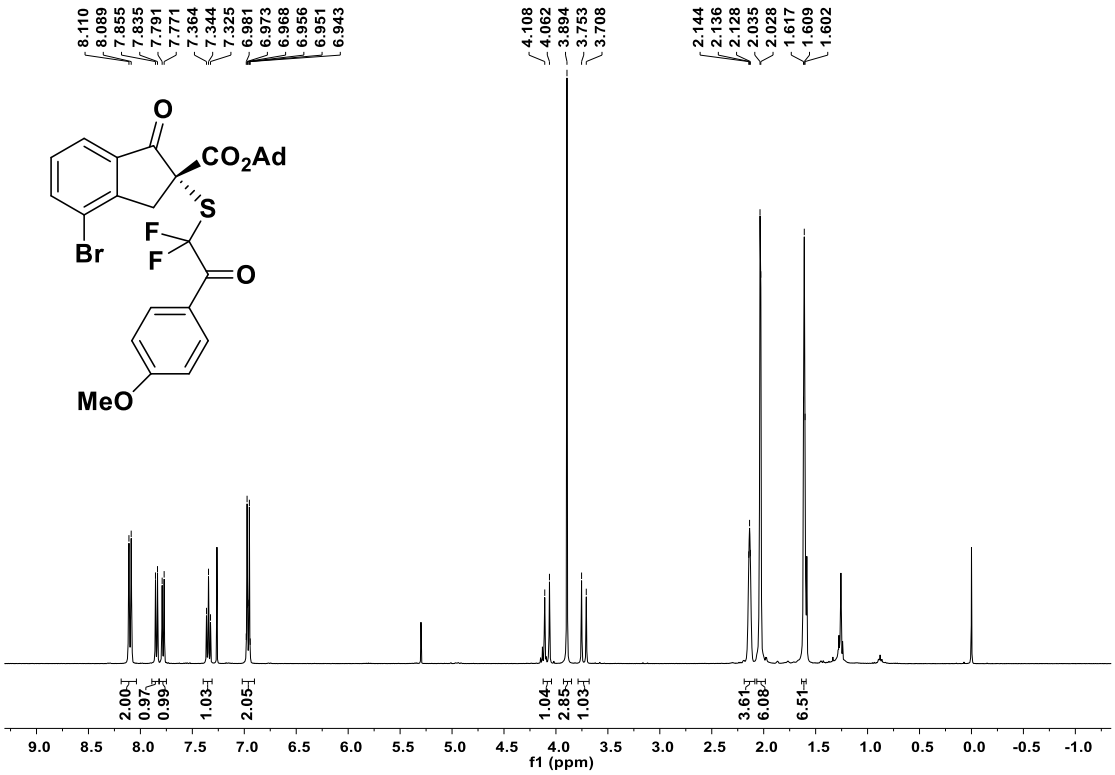
^{13}C NMR (101 MHz) of **3q** in $CDCl_3$



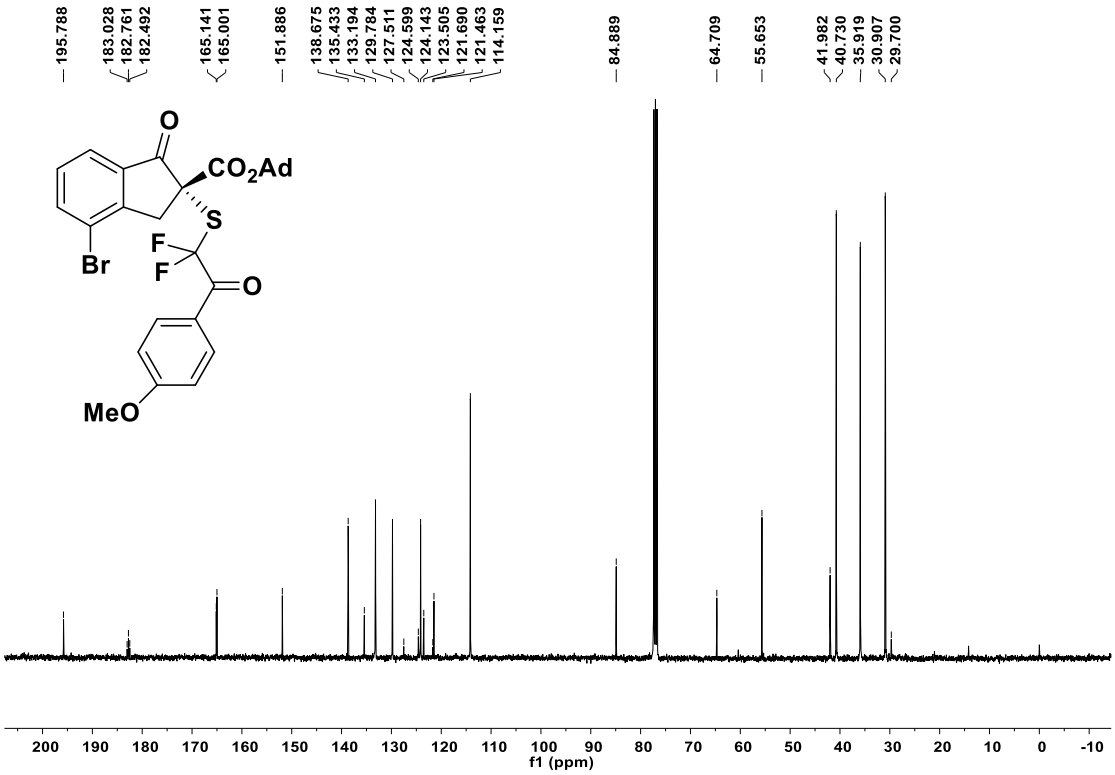
^{19}F NMR (376 MHz) of **3q** in $CDCl_3$



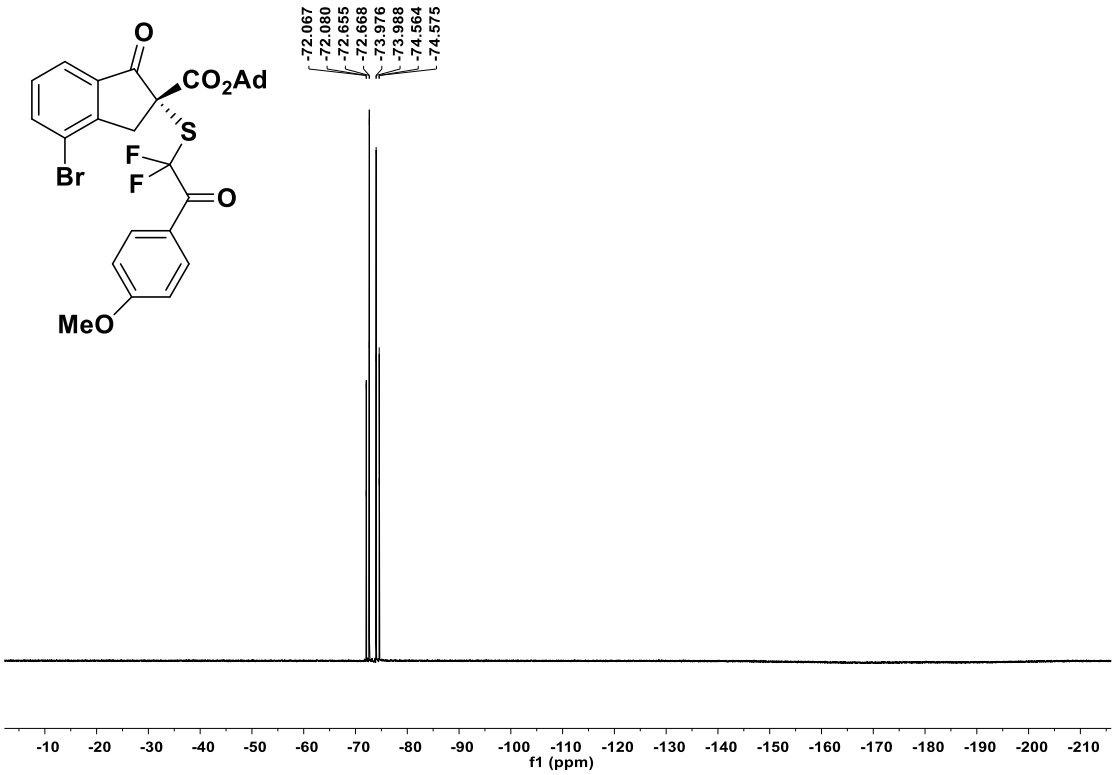
^{1}H NMR (400 MHz) of **3r** in $CDCl_3$



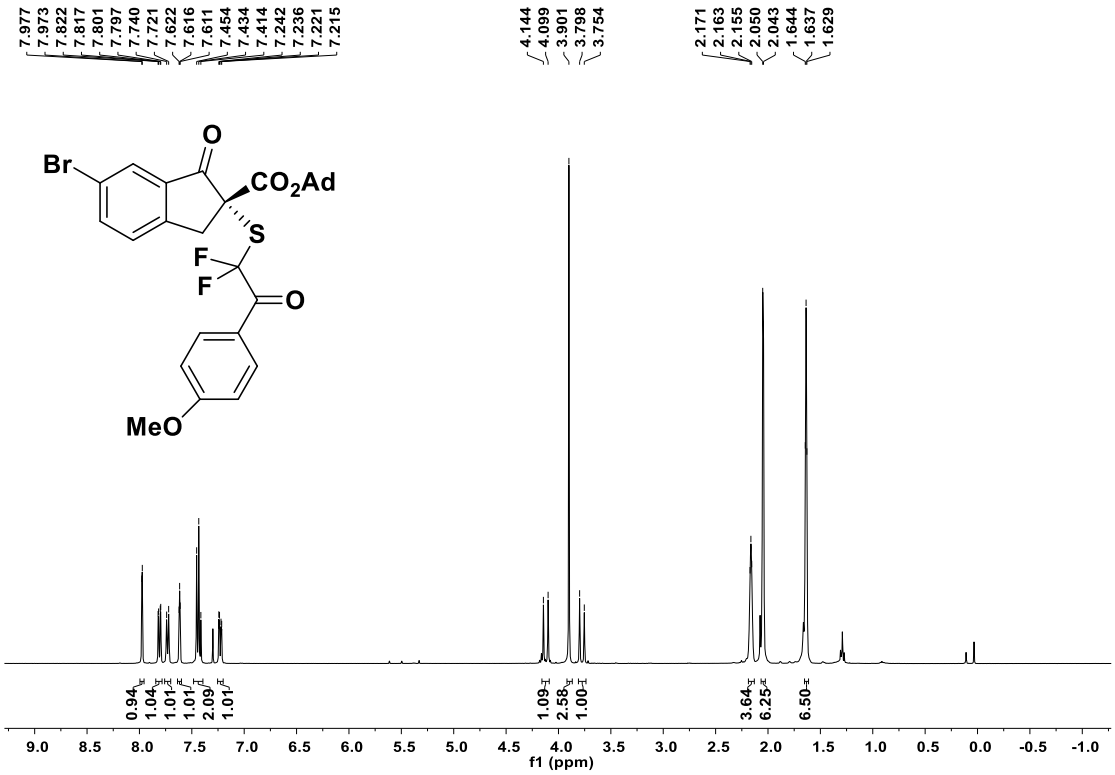
^{13}C NMR (101 MHz) of **3r** in $CDCl_3$



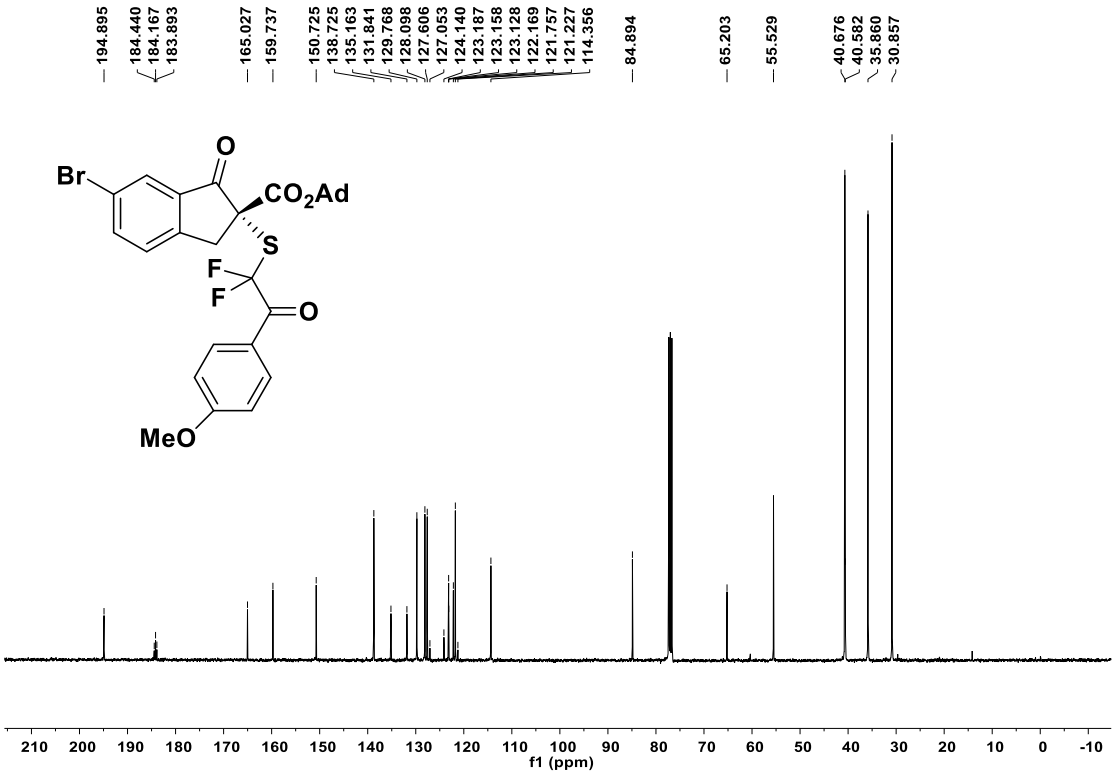
^{19}F NMR (376 MHz) of **3r** in $CDCl_3$



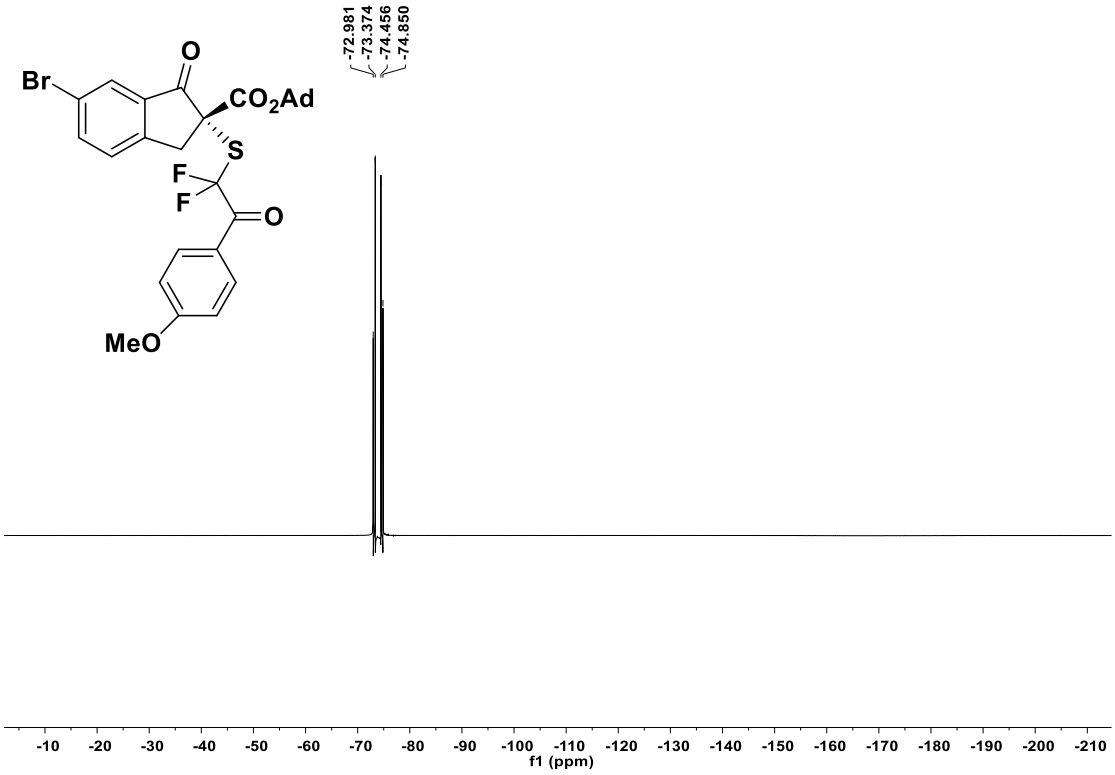
^{1}H NMR (400 MHz) of **3s** in $CDCl_3$



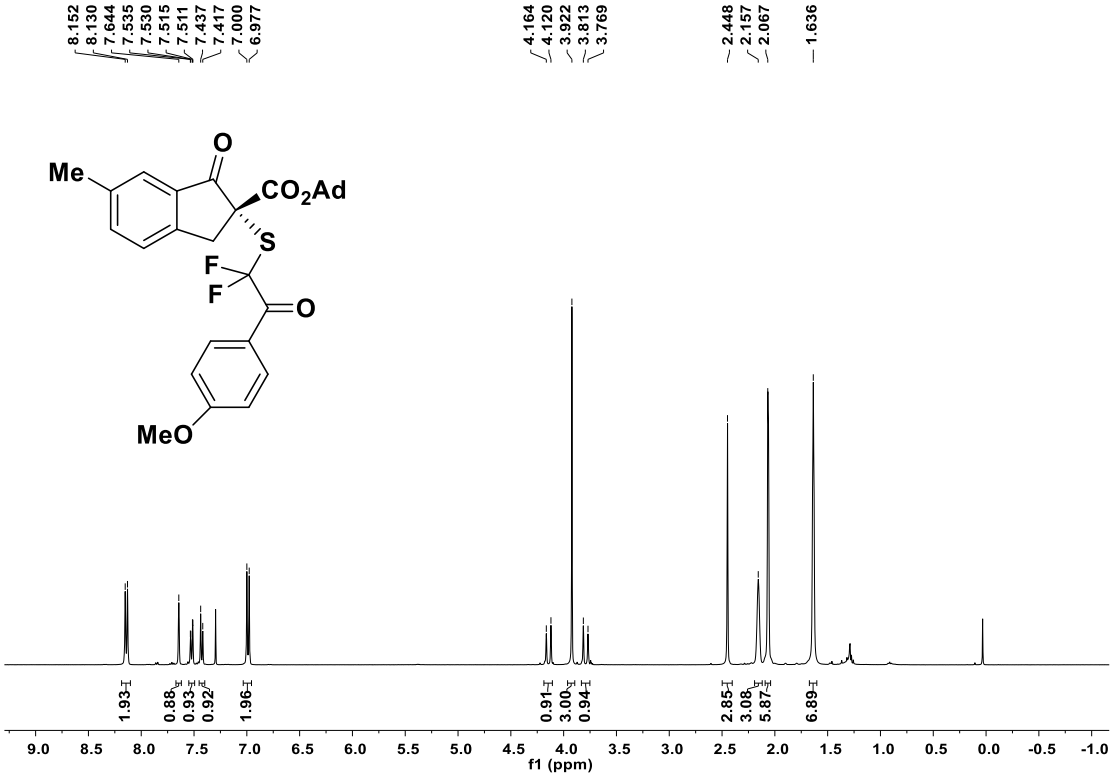
^{13}C NMR (101 MHz) of **3s** in $CDCl_3$



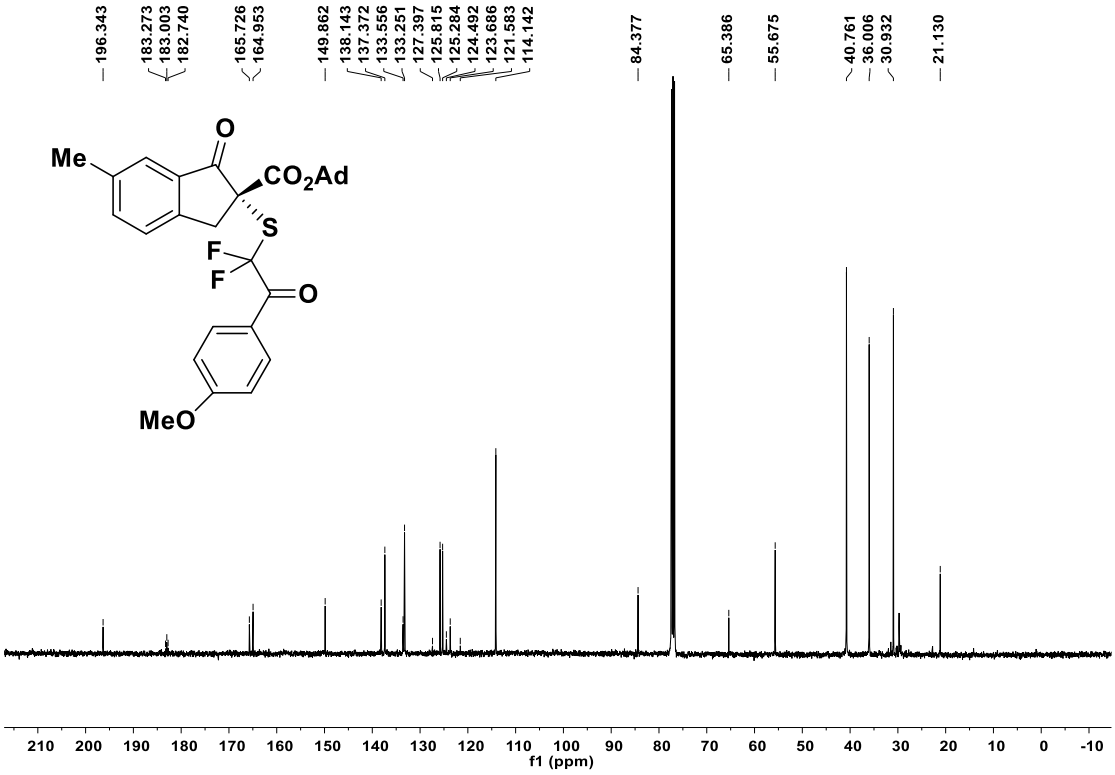
^{19}F NMR (376 MHz) of **3s** in $CDCl_3$



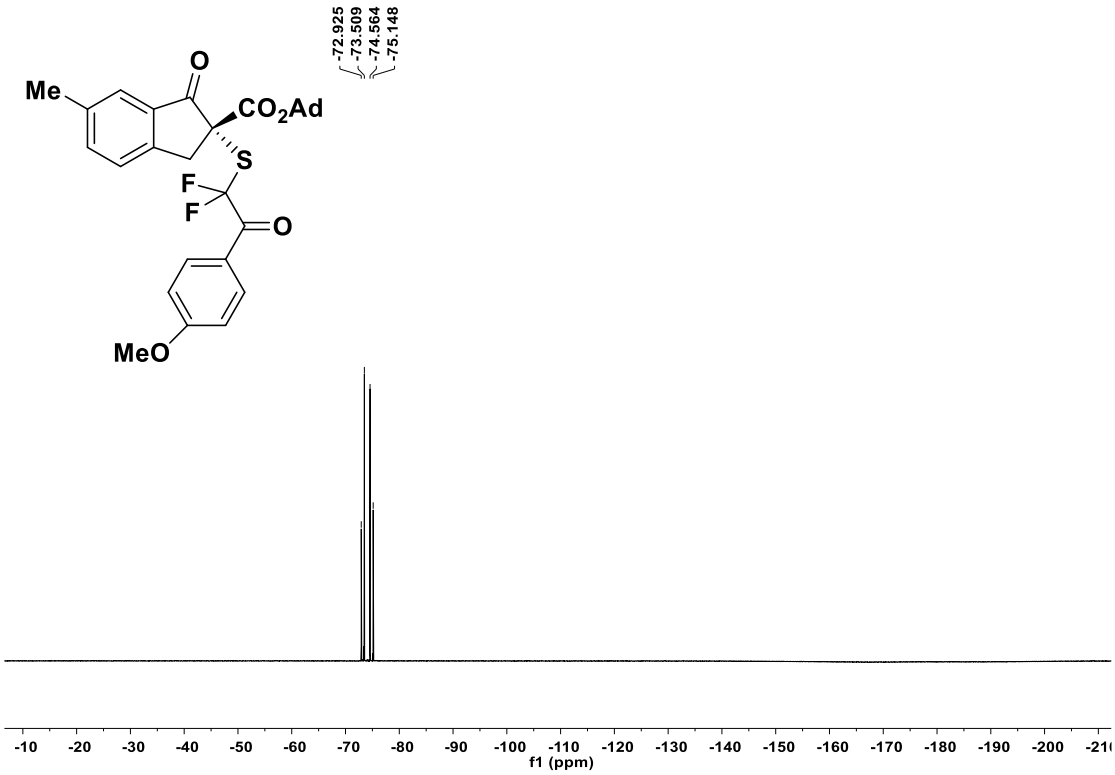
^{1}H NMR (400 MHz) of **3t** in $CDCl_3$



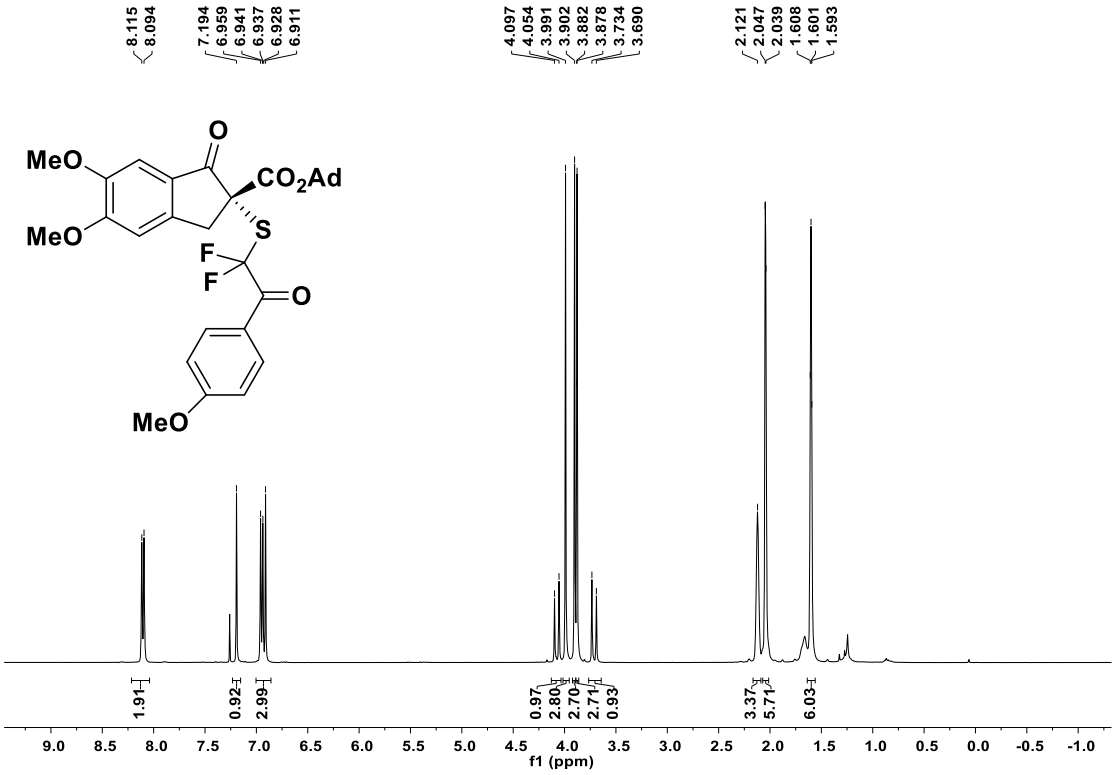
^{13}C NMR (101 MHz) of **3t** in $CDCl_3$



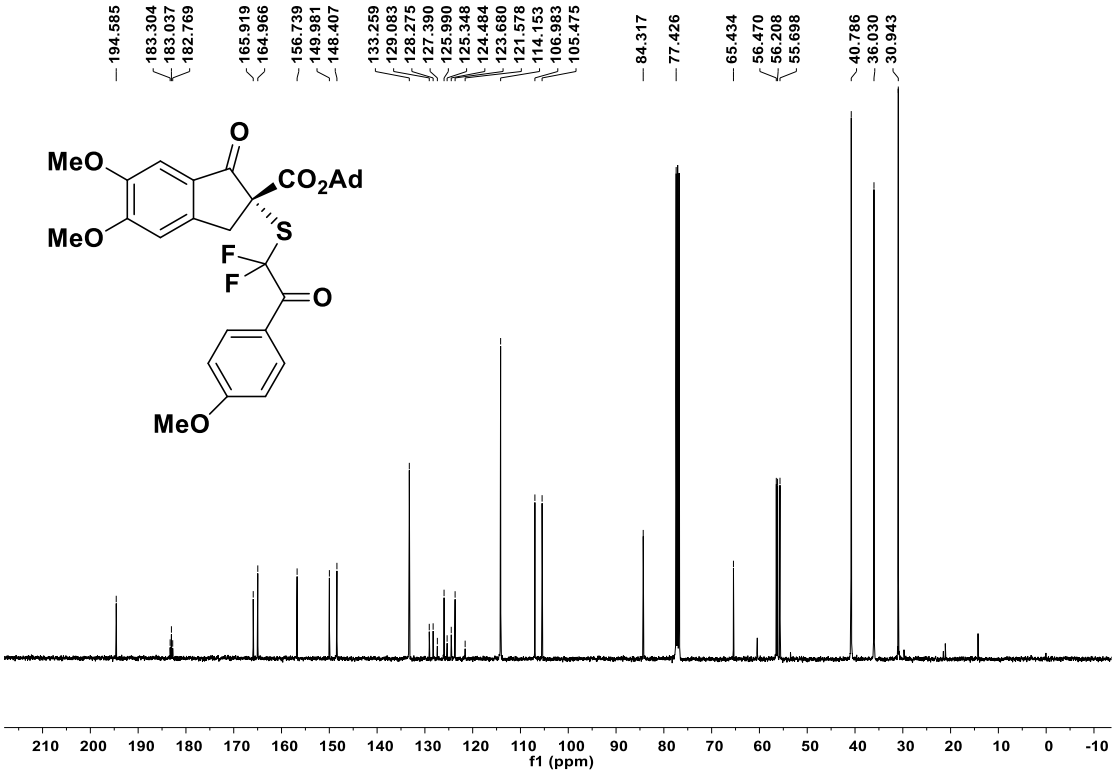
^{19}F NMR (376 MHz) of **3t** in $CDCl_3$



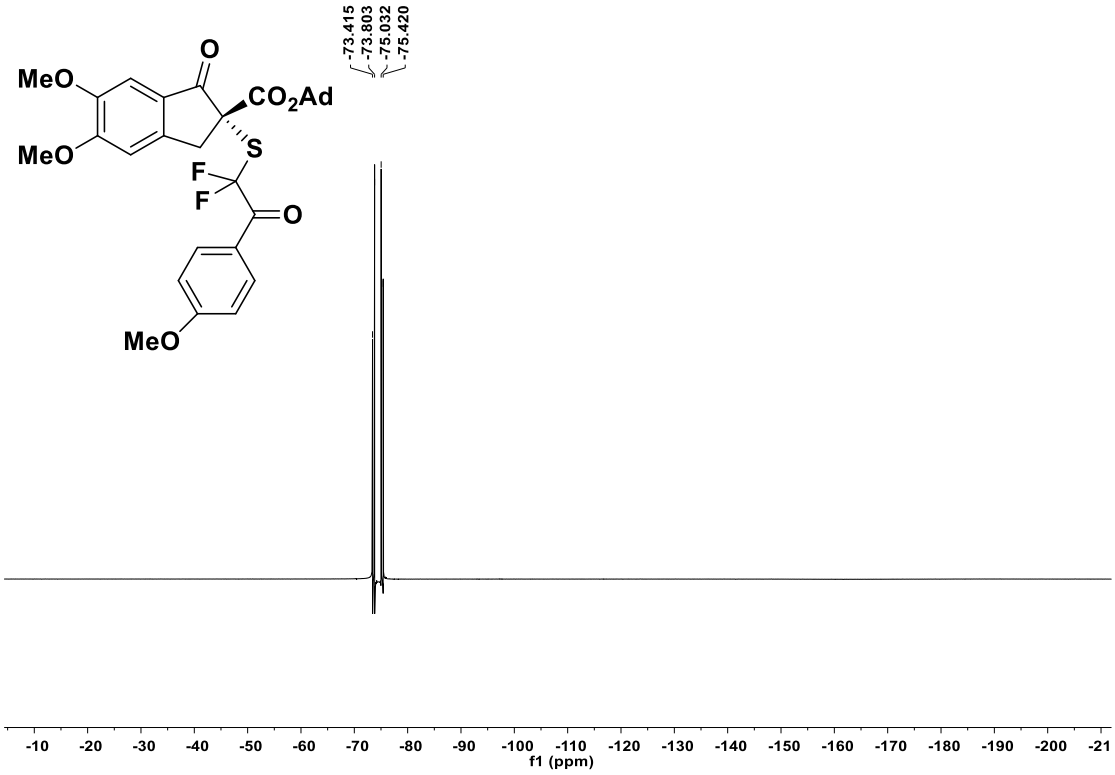
^{1}H NMR (400 MHz) of **3u** in $CDCl_3$



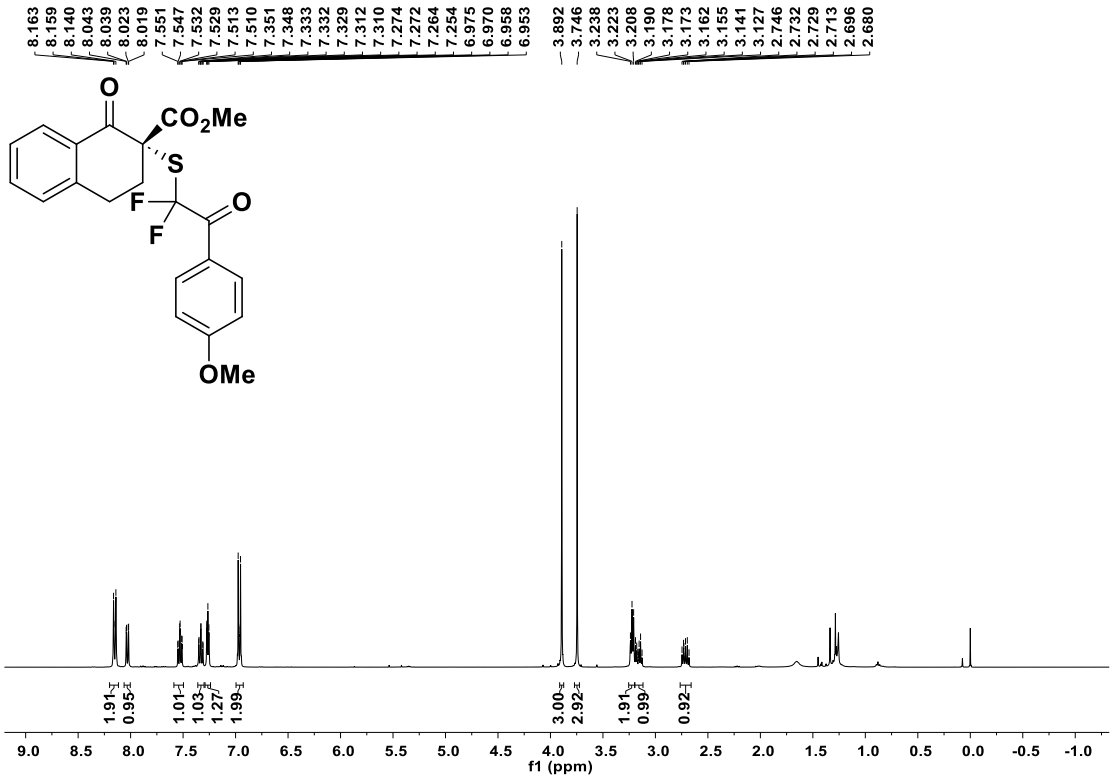
^{13}C NMR (101 MHz) of **3u** in $CDCl_3$



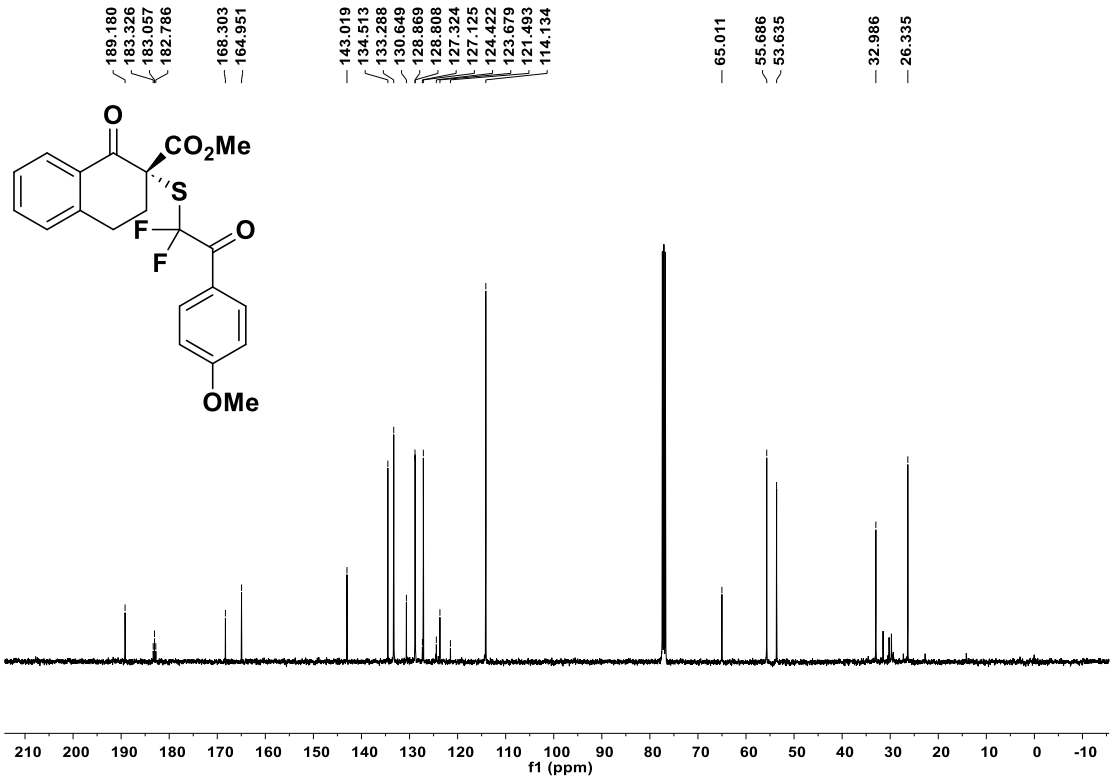
^{19}F NMR (376 MHz) of **3u** in $CDCl_3$



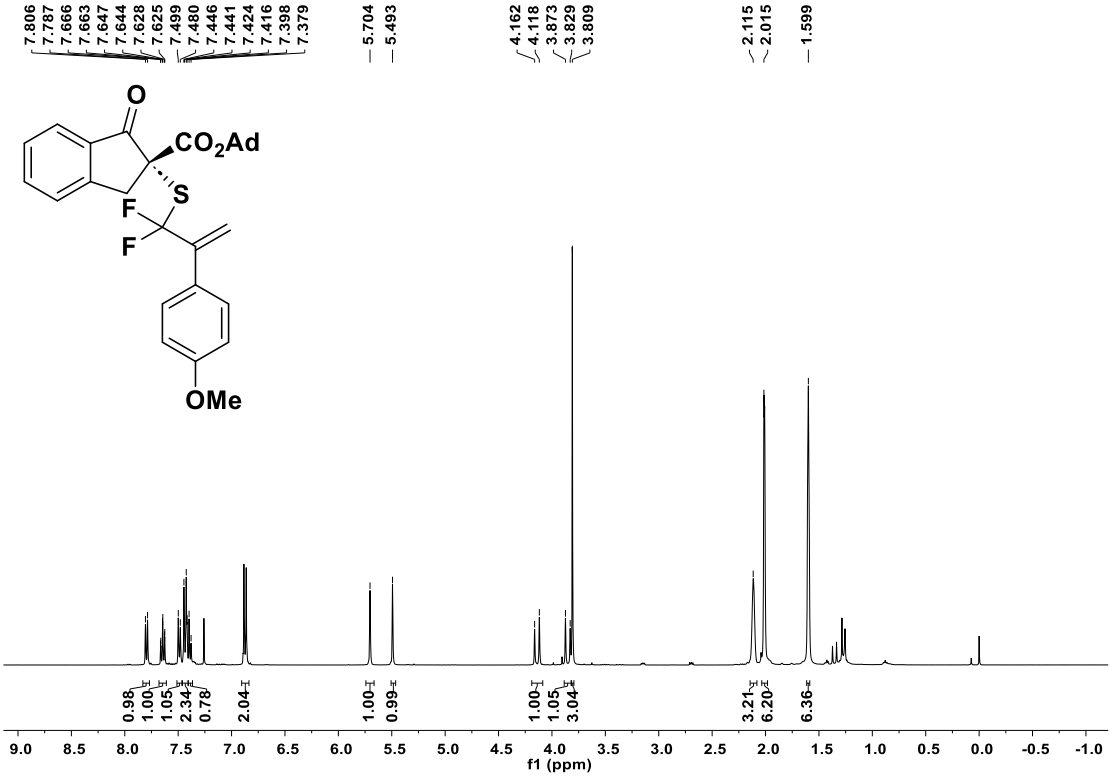
^{1}H NMR (400 MHz) of **3v** in $CDCl_3$



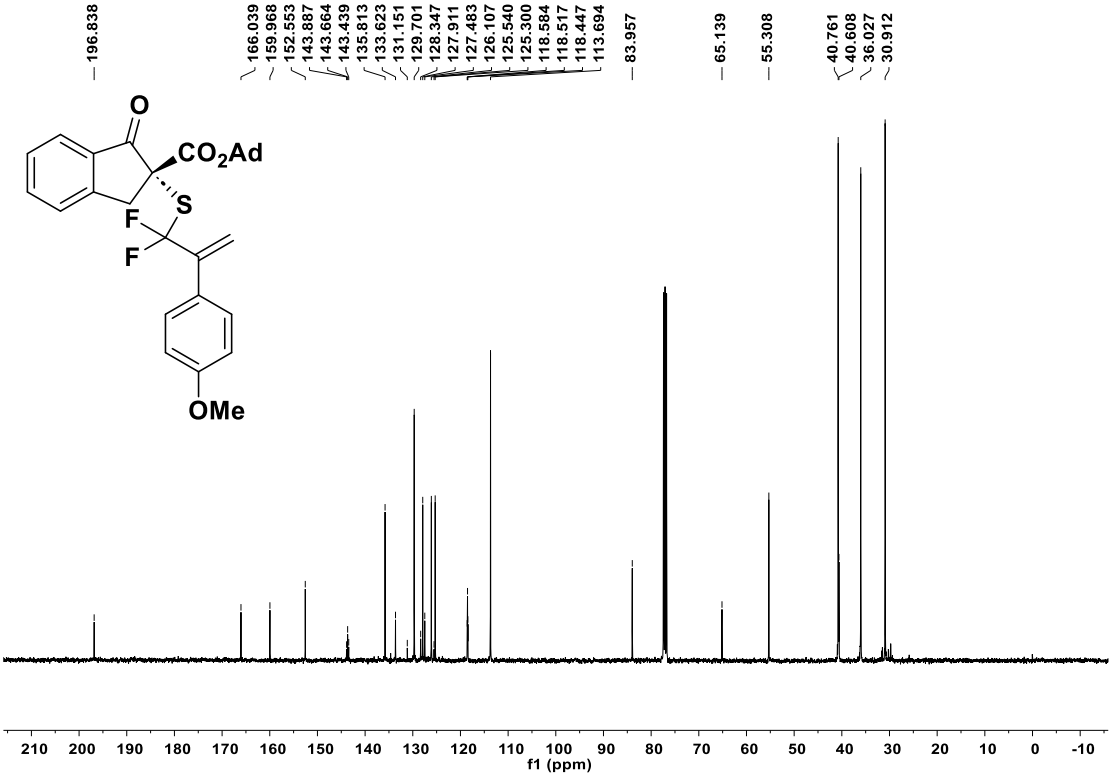
^{13}C NMR (101 MHz) of **3v** in $CDCl_3$



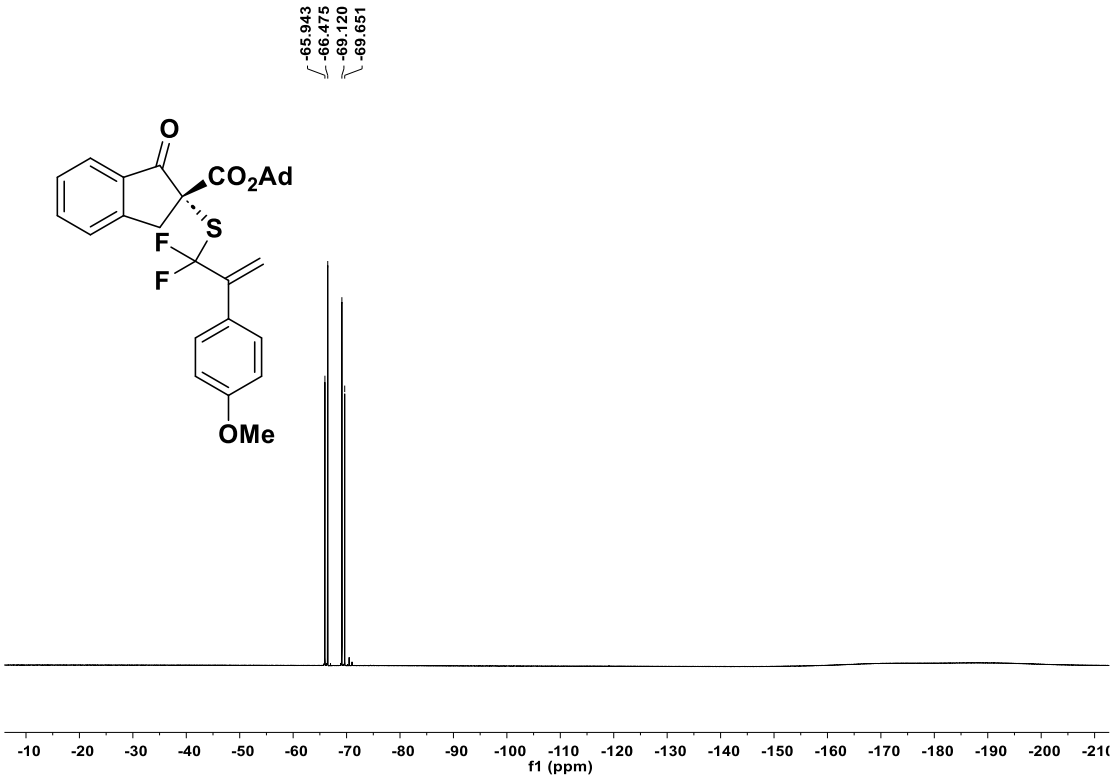
^{1}H NMR (400 MHz) of **4** in $CDCl_3$



^{13}C NMR (101 MHz) of **4** in $CDCl_3$

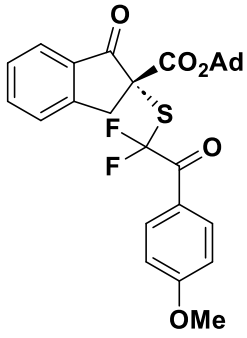


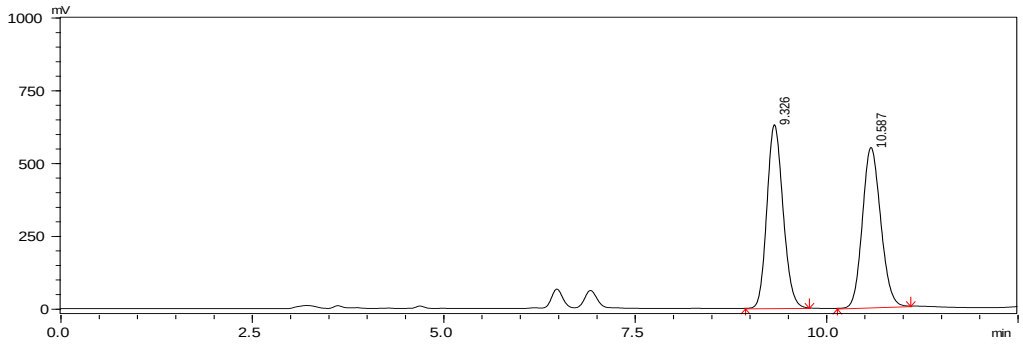
^{19}F NMR (376 MHz) of **4** in $CDCl_3$



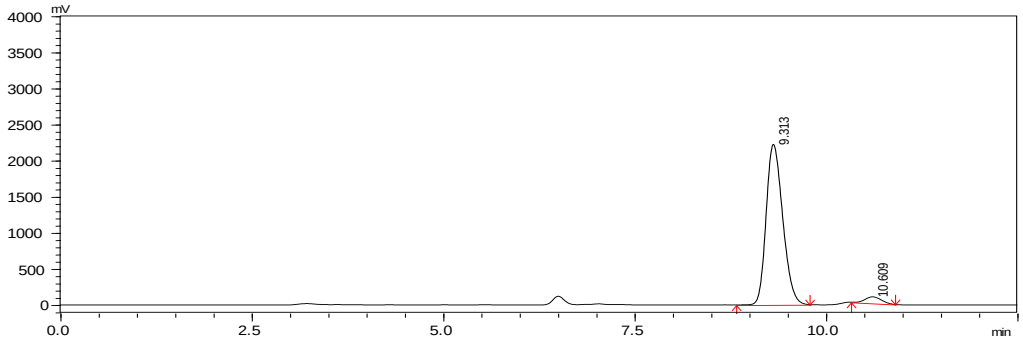
6. HPLC chromatograms

HPLC chromatogram of compound **3a** (93% ee)



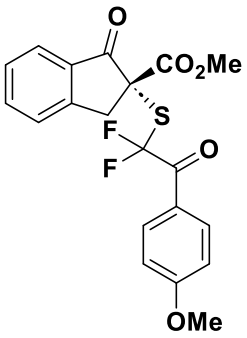


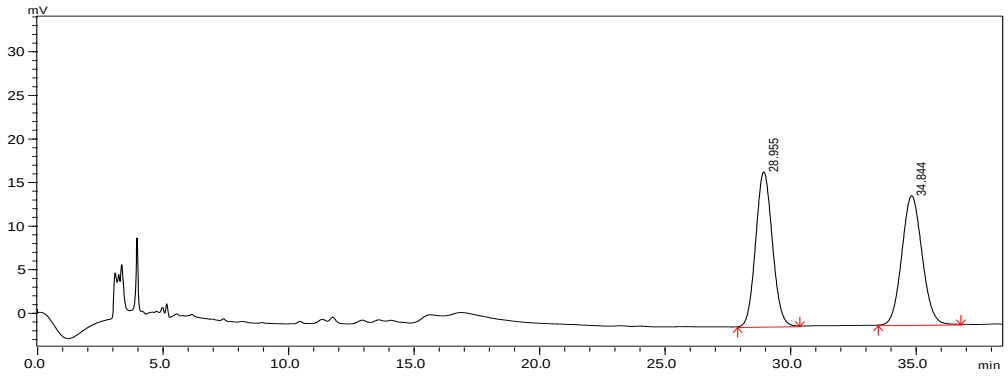
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.326	630258	9209367	50.299
2	10.587	548678	9099790	49.701
total		1178936	18309157	100.000



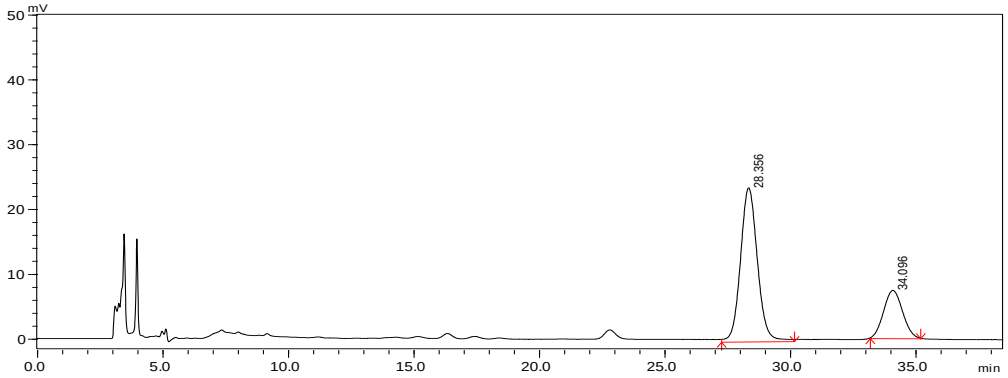
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.313	2220084	33418864	96.279
2	10.609	89257	1291493	3.721
total		2309341	34710357	100.000

HPLC chromatogram of compound **3b** (49% ee)



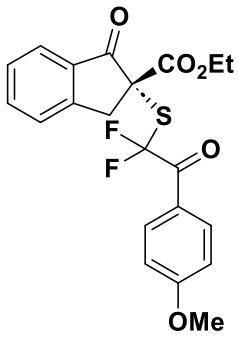


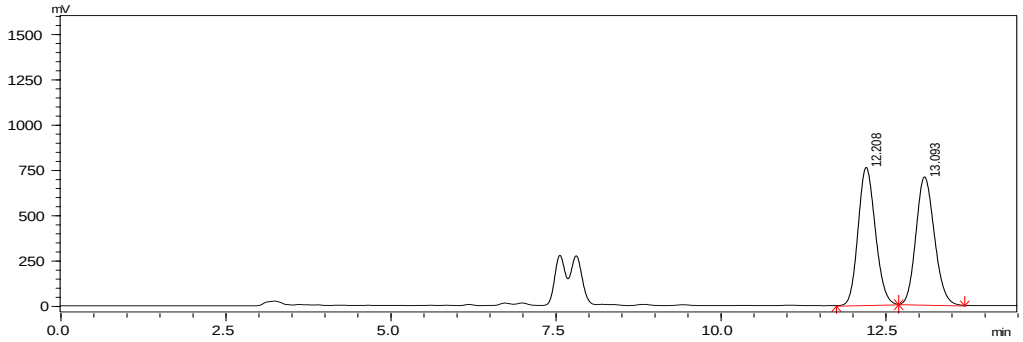
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	28.955	17736	818984	49.691
2	34.844	14800	829167	50.3309
total		32536	1648151	100.000



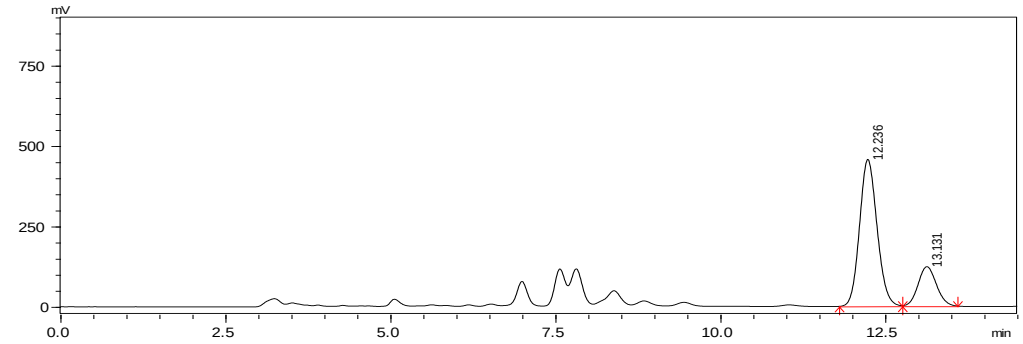
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	28.356	23686	1108006	74.339
2	34.096	7343	382468	25.661
total		31029	1490474	100.000

HPLC chromatogram of compound **3c** (56% ee)



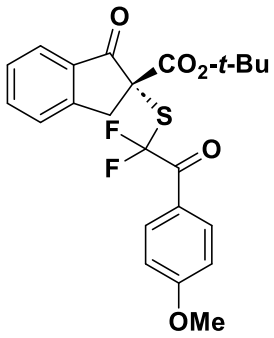


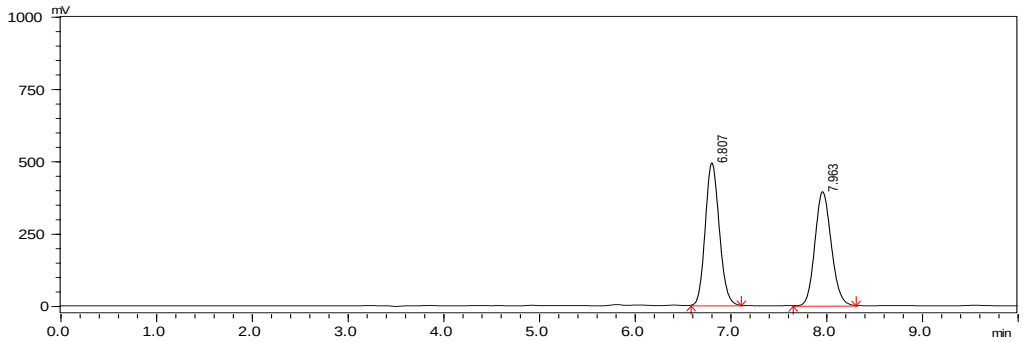
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.208	759007	13762377	50.148
2	13.093	704918	13681186	49.852
total		1463924	27443562	100.000



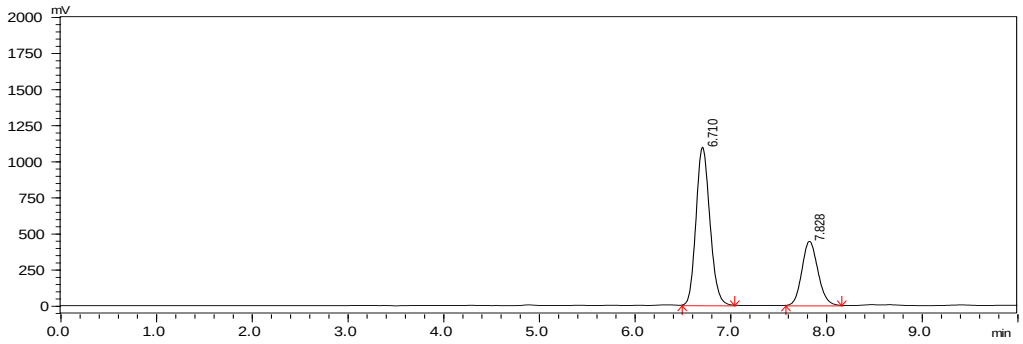
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.236	456706	8429637	78.078
2	13.131	122618	2366781	21.922
total		579324	10796419	100.000

HPLC chromatogram of compound **3d** (36% ee)



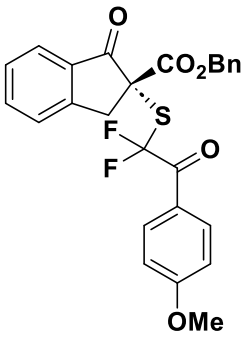


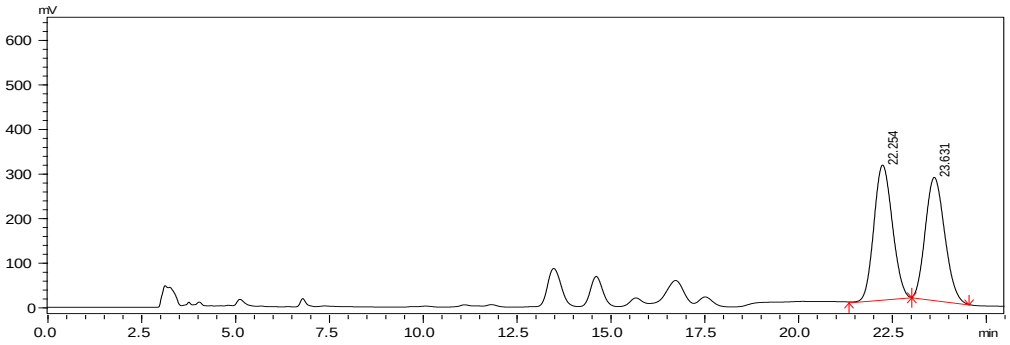
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.807	492321	5015576	51.789
2	7.963	393768	4669006	48.211
total		886089	9684582	100.000



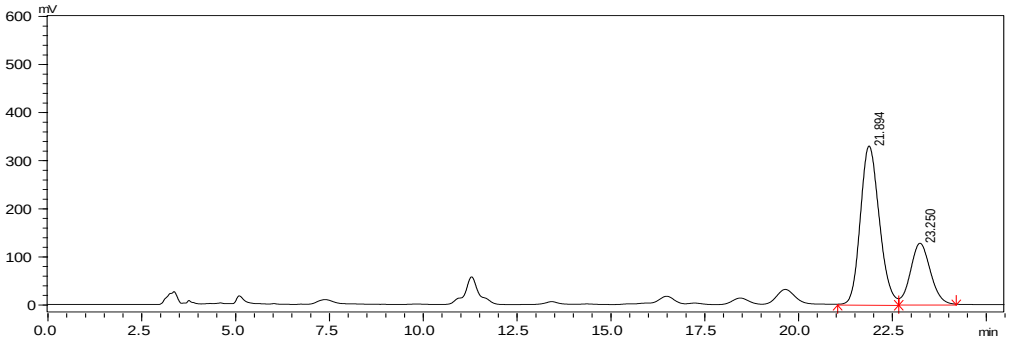
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.710	1094329	11031303	68.222
2	7.828	443376	5138487	31.778
total		1537705	16169789	100.000

HPLC chromatogram of compound **3e** (42% ee)



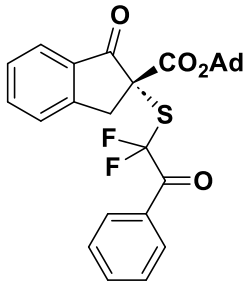


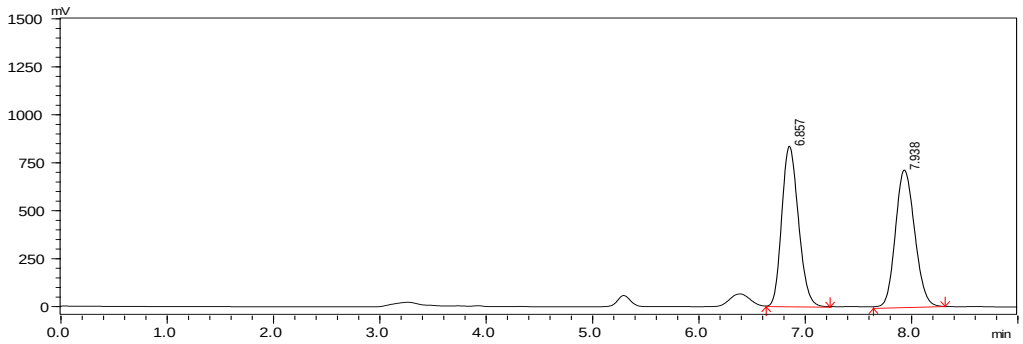
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	22.254	301676	10260781	50.955
2	23.631	275225	9876189	49.045
total		576901	20136971	100.000



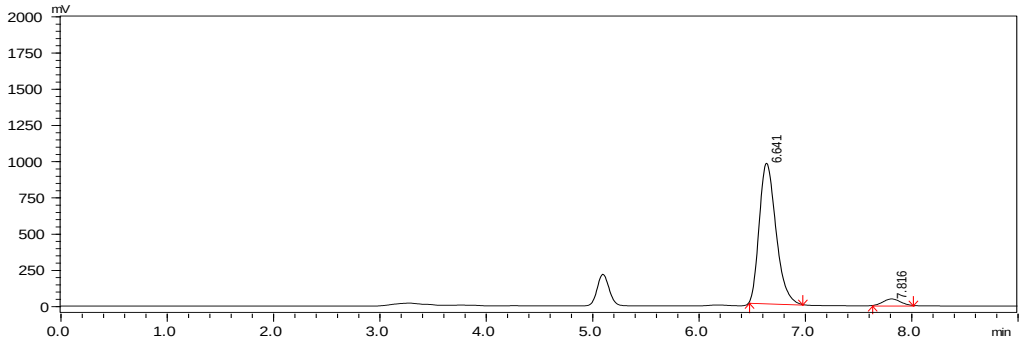
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	21.894	329801	11577991	71.075
2	23.250	127396	4711832	28.925
total		457197	16289823	100.000

HPLC chromatogram of compound **3f** (91% ee)



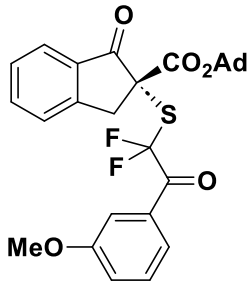


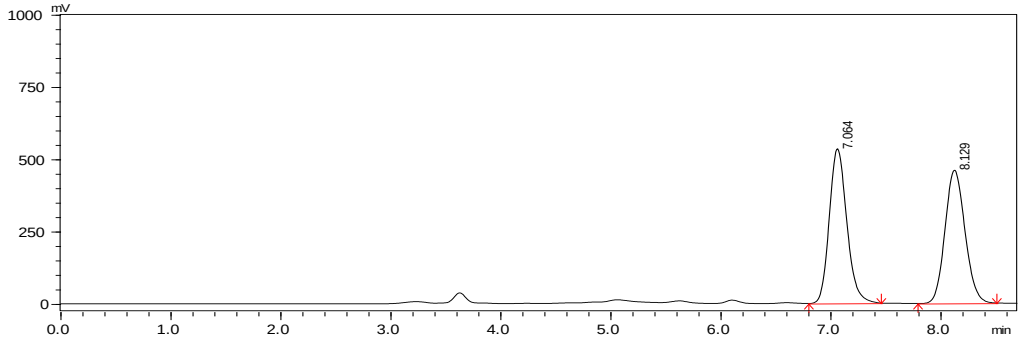
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.857	834366	9071871	50.262
2	7.938	713730	8977148	49.738
total		1548095	18049019	100.000



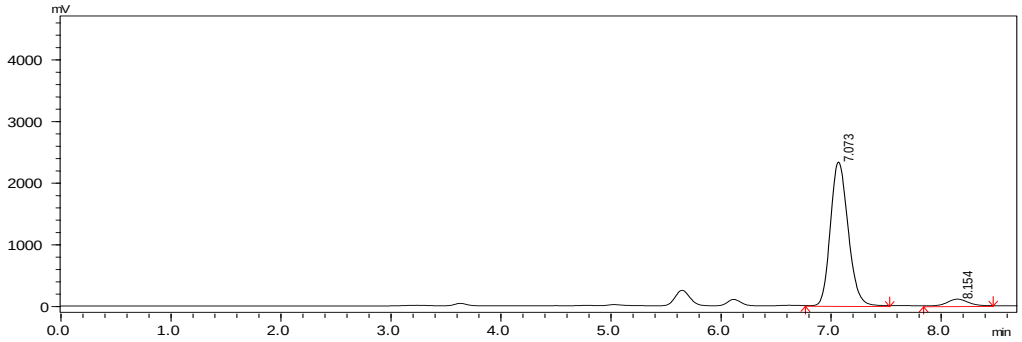
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.641	966729	10522553	95.477
2	7.816	45159	498454	4.523
total		1011888	11021007	100.000

HPLC chromatogram of compound **3g** (89% ee)



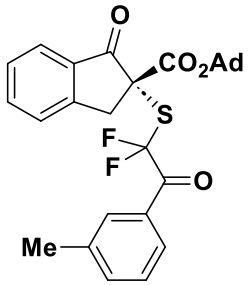


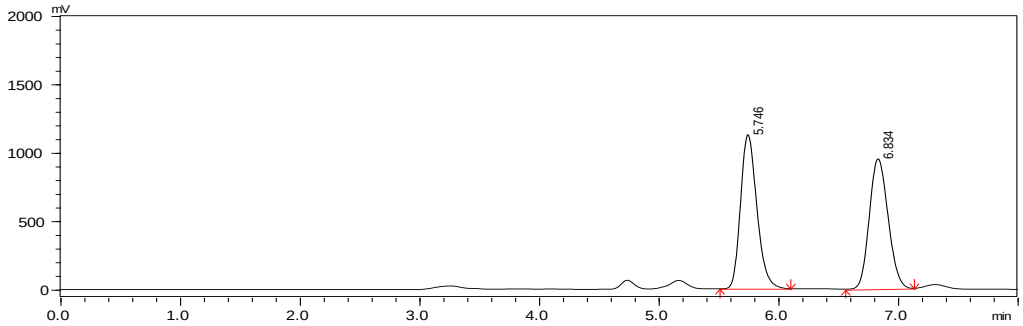
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.064	534552	5923671	50.453
2	8.129	460020	5817319	49.547
total		994572	11740990	100.000



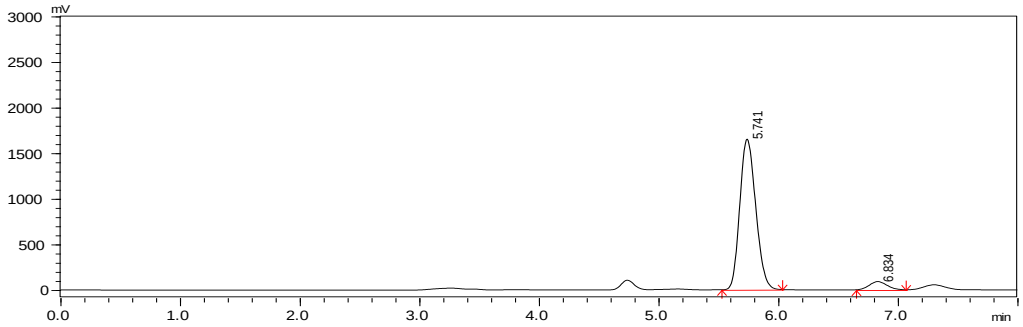
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.073	2331455	26062142	94.610
2	8.154	110811	1484896	5.390
total		2442266	27547037	100.000

HPLC chromatogram of compound **3h** (88% ee)



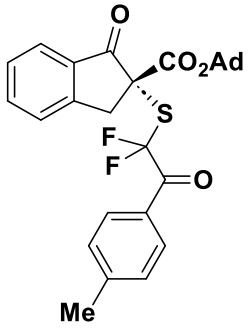


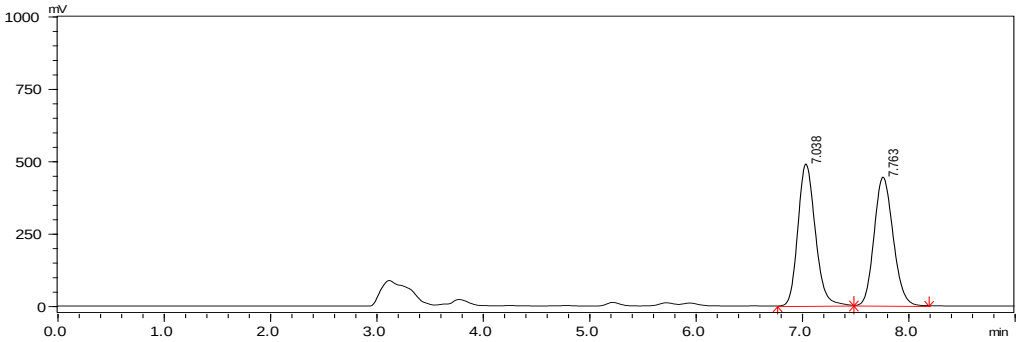
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.746	1124504	10698238	50.686
2	6.834	951791	10408536	49.314
total		2076295	21106774	100.000



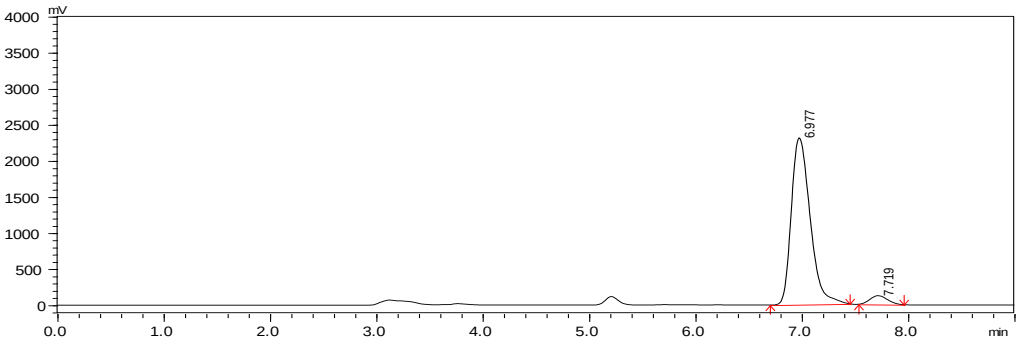
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.741	1651391	15317958	94.210
2	6.834	90263	941390	5.790
total		1741655	16259348	100.000

HPLC chromatogram of compound **3i** (91% ee)



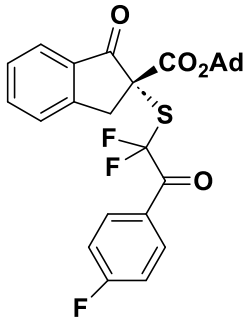


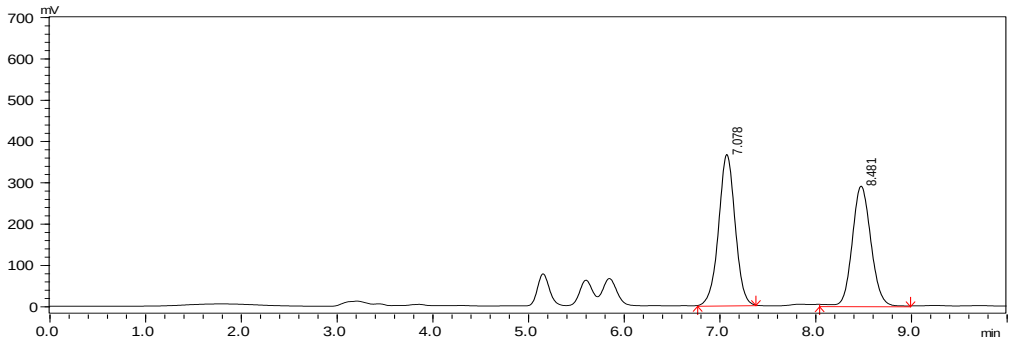
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.038	489531	5566146	50.350
2	7.763	443028	5488744	49.650
total		932559	11054890	100.000



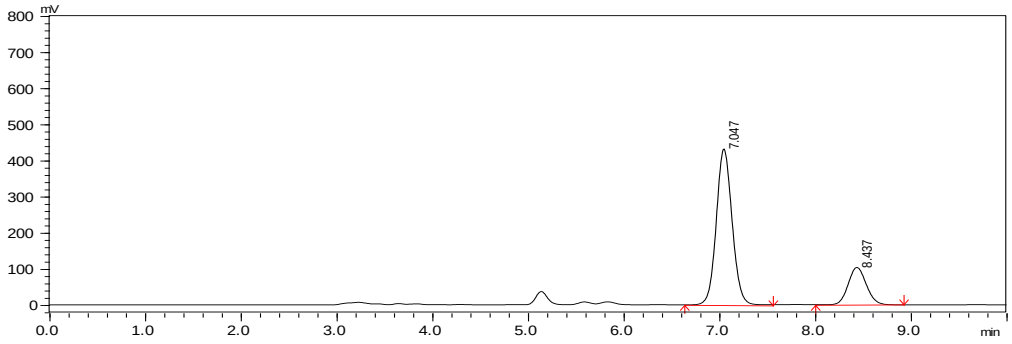
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.977	2311464	28444507	95.349
2	7.719	121558	1387379	4.651
total		2433021	29831886	100.000

HPLC chromatogram of compound **3j** (58% ee)



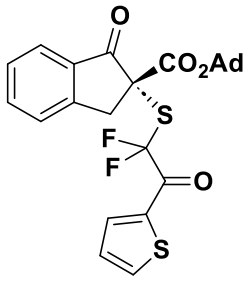


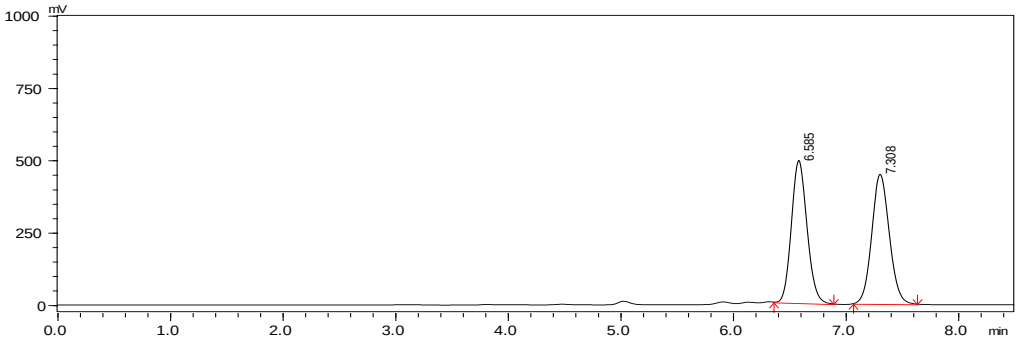
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.078	364844	4361049	52.487
2	8.481	290425	3947789	47.513
total		655269	8308838	100.000



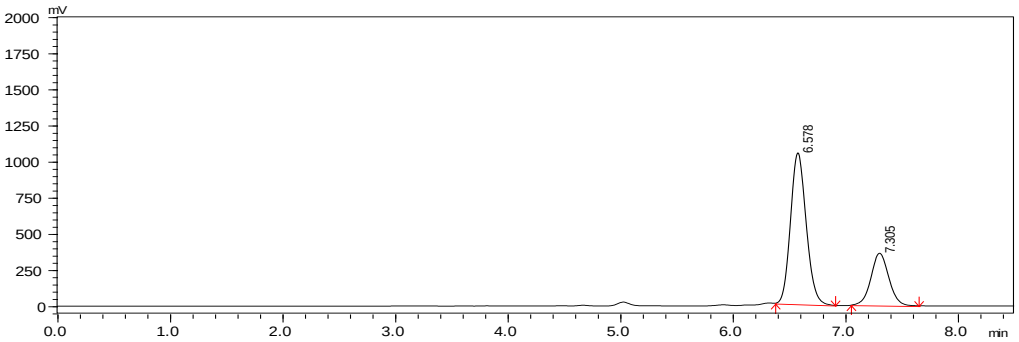
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.047	431516	4965995	78.966
2	8.437	102663	1322773	21.034
total		534179	6288767	100.000

HPLC chromatogram of compound **3k** (44% ee)



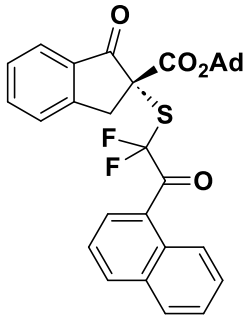


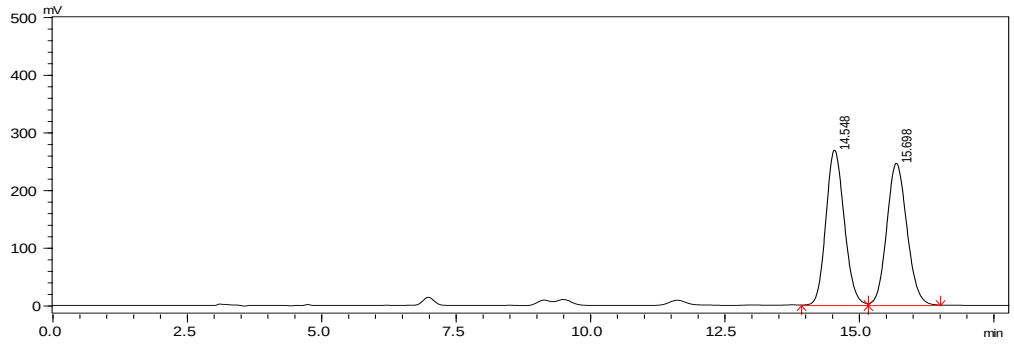
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.585	492631	4754759	49.492
2	7.308	448247	4852397	50.508
total		940878	9607156	100.000



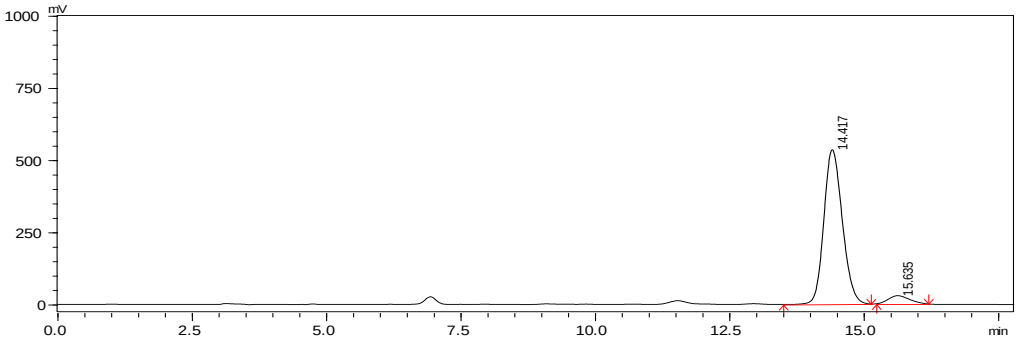
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.578	1046609	10167002	71.931
2	7.305	360795	3967319	28.069
total		1407404	14134321	100.000

HPLC chromatogram of compound **3l** (92% ee)



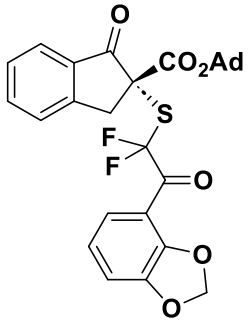


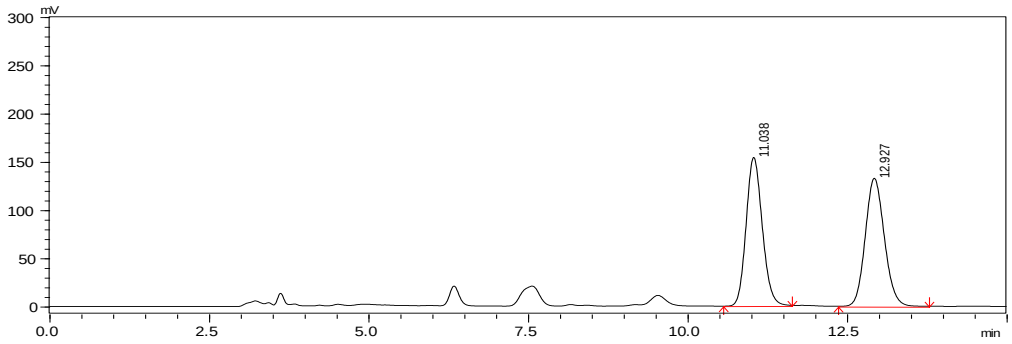
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	14.548	268410	6381782	49.858
2	15.698	245702	6418151	50.142
total		514112	12799932	100.000



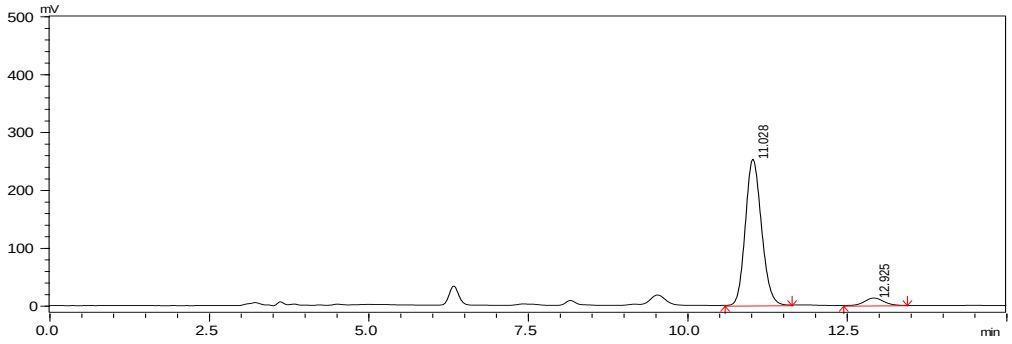
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	14.417	541051	13331623	95.759
2	15.635	24775	590506	4.241
total		565826	13922130	100.000

HPLC chromatogram of compound **3m** (89% ee)



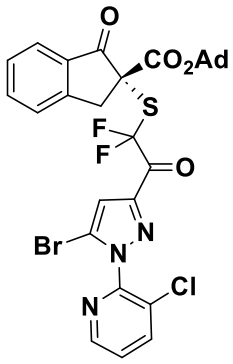


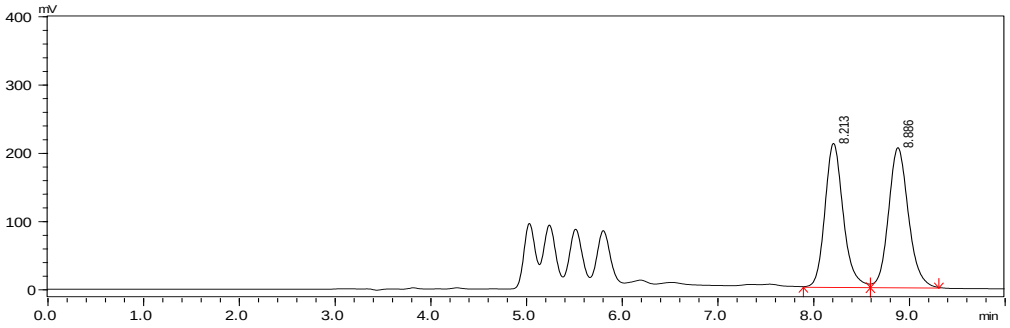
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.038	153965	2709379	49.410
2	12.927	132882	2774119	50.590
total		286847	5483498	100.000



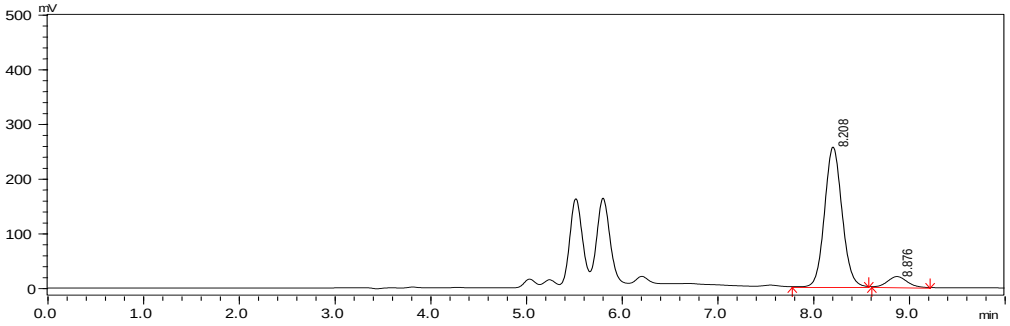
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.028	252113	4435810	94.564
2	12.925	12746	254977	5.436
total		264860	4690787	100.000

HPLC chromatogram of compound **3n** (84% ee)



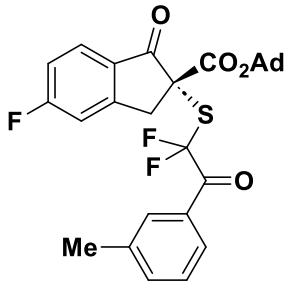


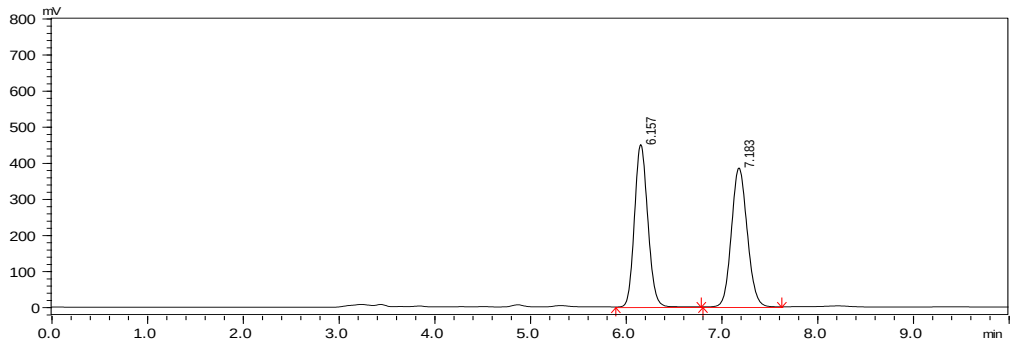
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.213	209908	2774381	48.592
2	8.886	204297	2935140	51.408
total		414205	5709521	100.000



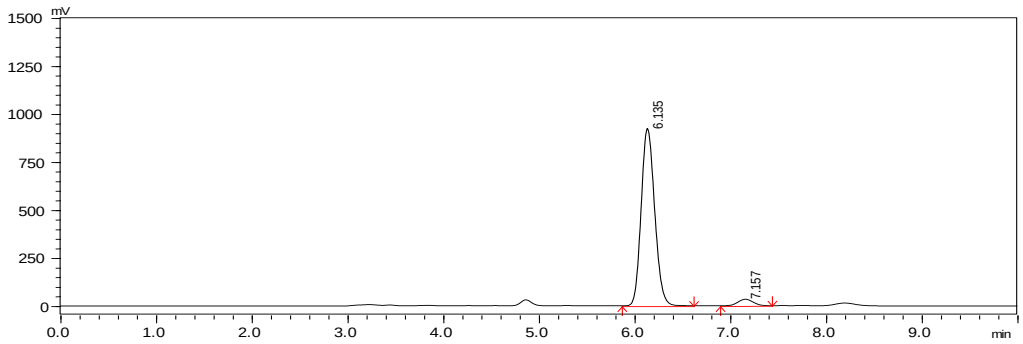
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.208	255434	3227820	92.140
2	8.876	19504	275343	7.860
total		274938	3503163	100.000

HPLC chromatogram of compound **3o** (92% ee)



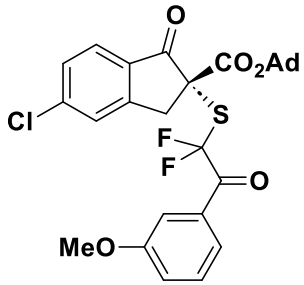


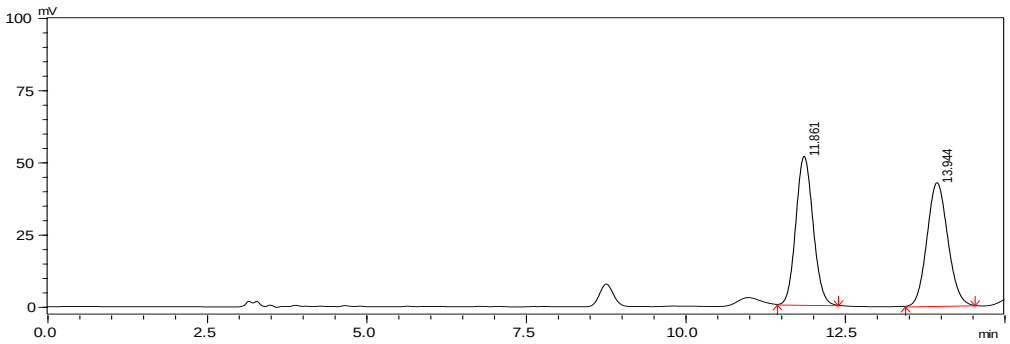
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.157	449825	4341115	49.621
2	7.183	384848	4407445	50.379
total		834672	8748560	100.000



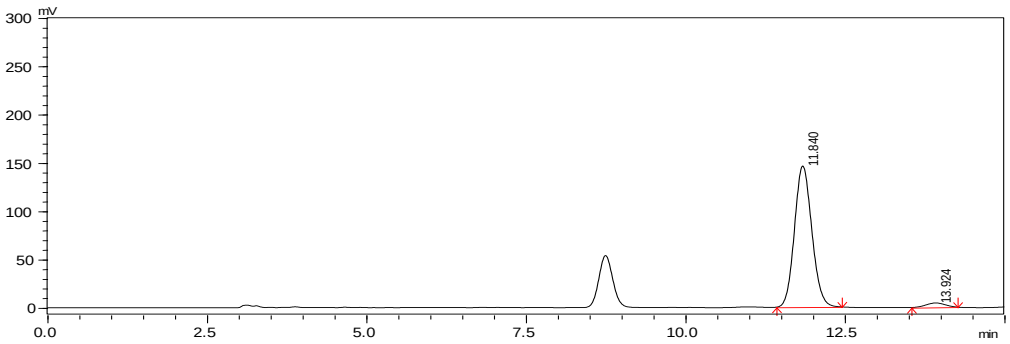
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.135	925230	9101482	95.790
2	7.157	34789	400060	4.210
total		960019	9501543	100.000

HPLC chromatogram of compound **3p** (93% ee)



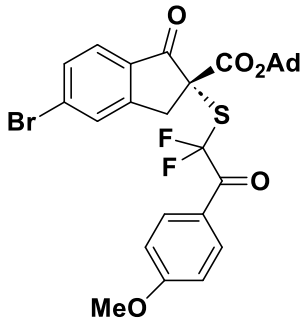


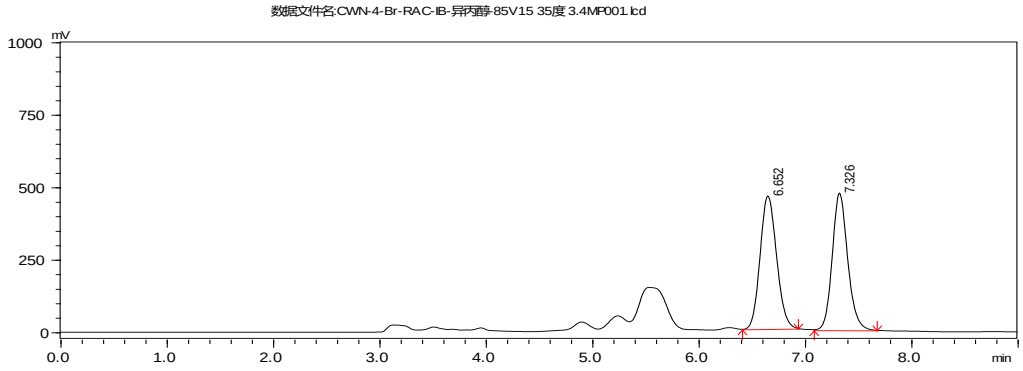
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.861	51436	965949	49.892
2	13.944	42672	970144	50.108
total		94107	1936094	100.000



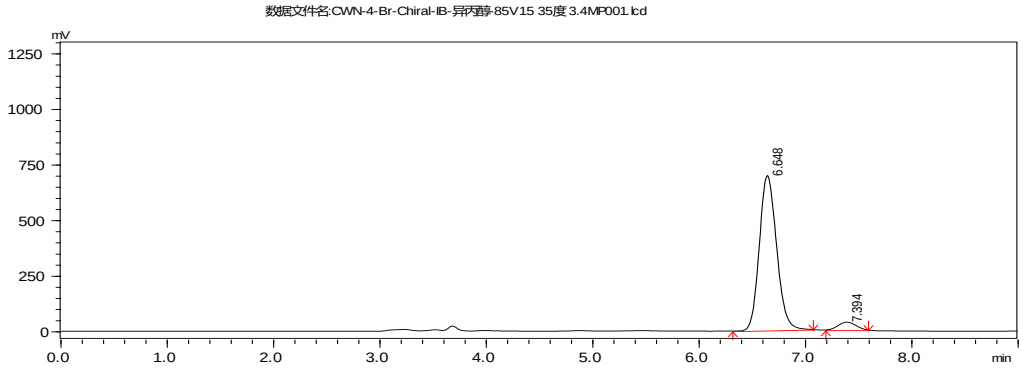
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.840	145996	2766628	96.748
2	13.924	4501	92999	3.252
total		150497	2859626	100.000

HPLC chromatogram of compound **3q** (90% ee)



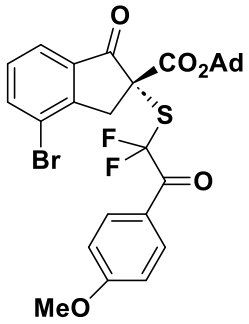


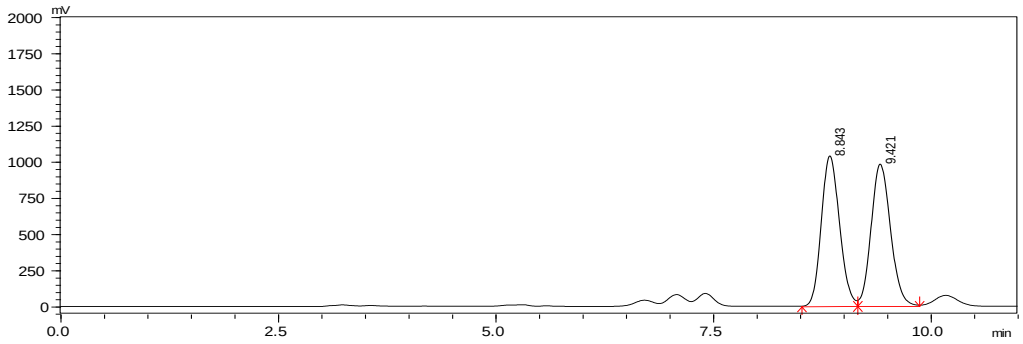
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.652	458749	4929215	50.799
2	7.326	472813	4774141	49.201
total		931562	9703356	100.000



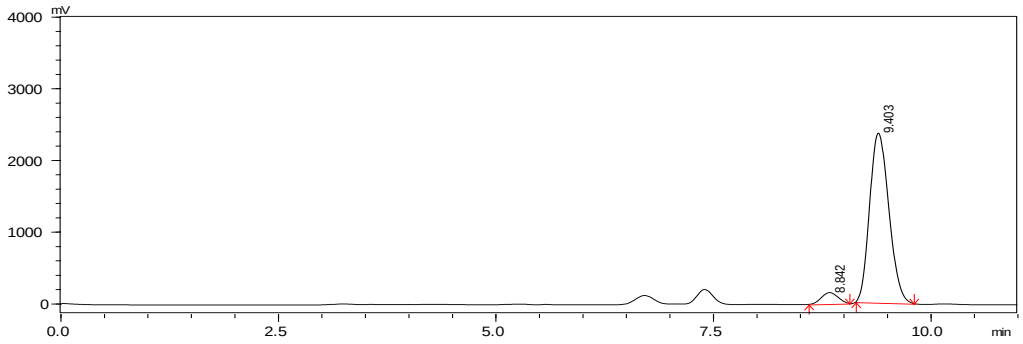
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.648	696314	7859172	95.043
2	7.394	35524	409868	4.957
total		731837	8269040	100.000

HPLC chromatogram of compound **3r** (89% ee)



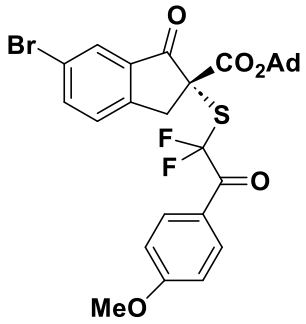


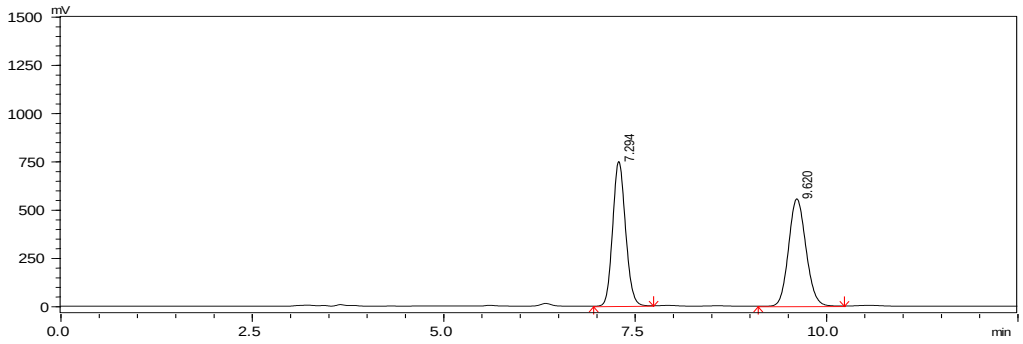
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.843	1038189	15109291	49.856
2	9.421	979653	15196557	50.144
total		2017841	30305848	100.000



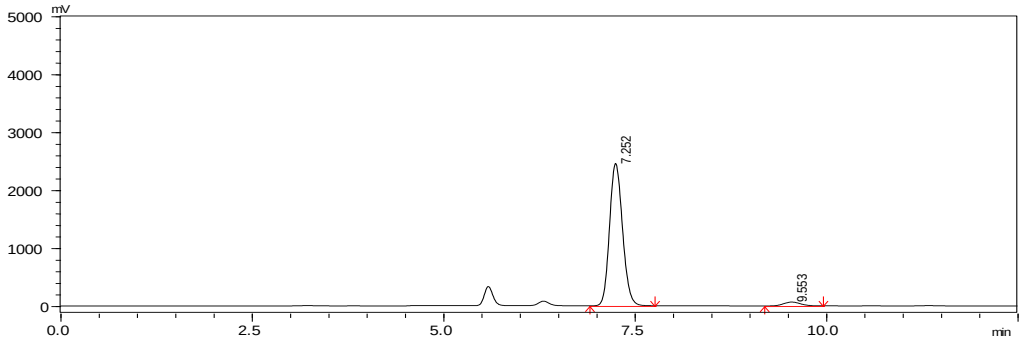
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.842	157531	2073261	5.383
2	9.403	2364811	36441090	94.617
total		2522342	38514351	100.000

HPLC chromatogram of compound **3s** (93% ee)



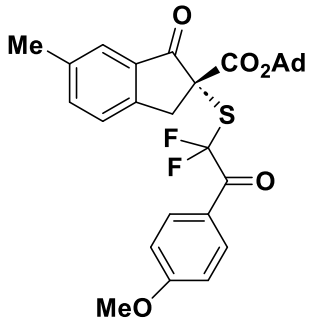


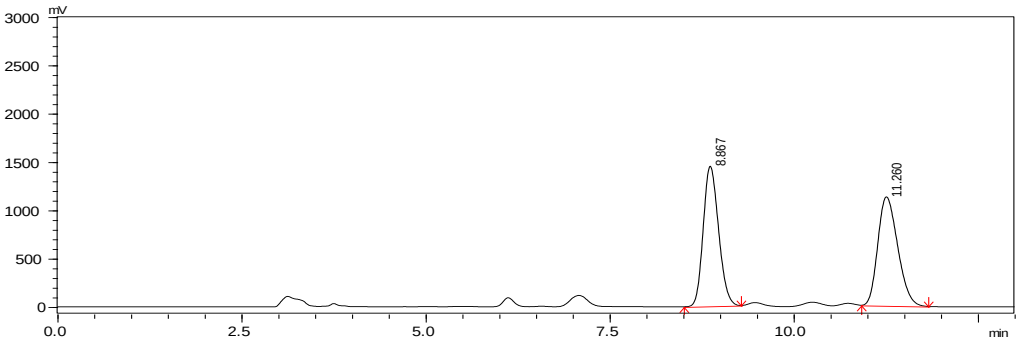
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.294	748347	8726690	49.923
2	9.620	555624	8753530	50.077
total		1303970	17480220	100.000



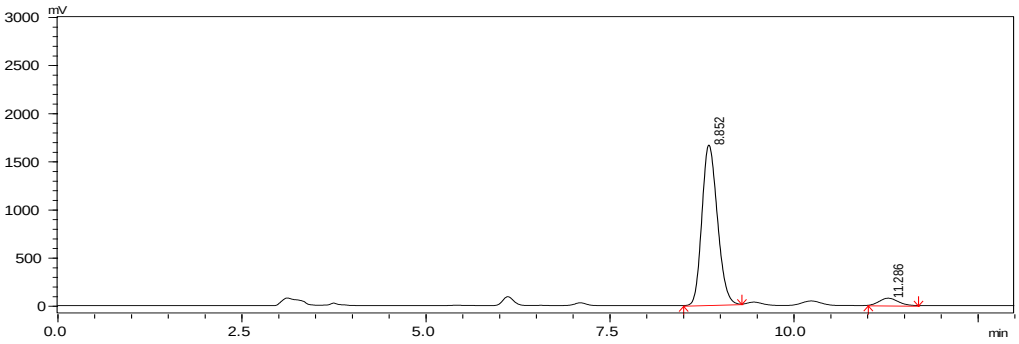
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.252	2458003	29046345	96.539
2	9.553	67172	1041195	3.461
total		2525175	30087540	100.000

HPLC chromatogram of compound **3t** (90% ee)



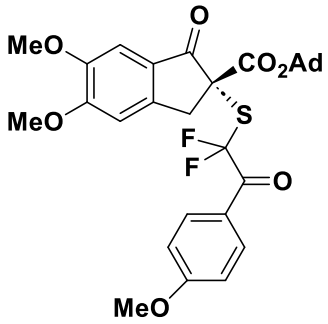


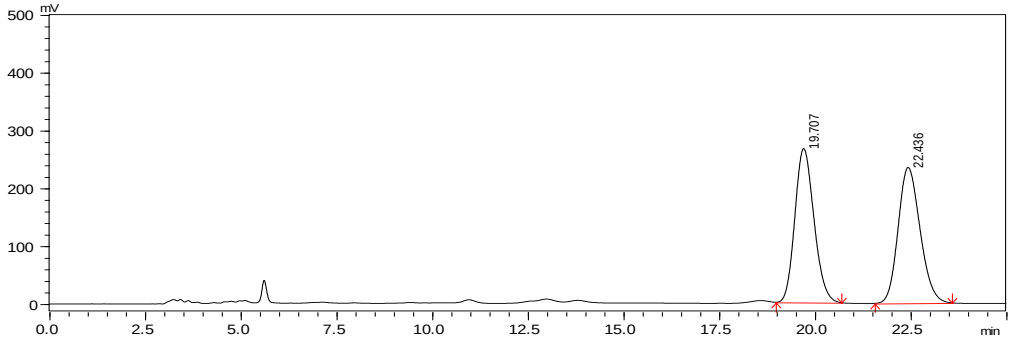
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.867	1448357	20991239	49.844
2	11.260	1126308	21122758	50.156
total		2574665	42113997	100.000



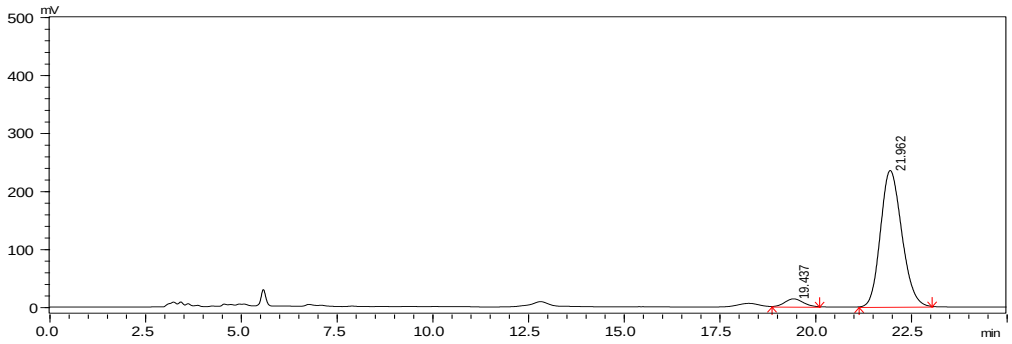
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.852	1660364	24242380	94.924
2	11.286	74934	1296257	5.076
total		1735297	25538637	100.000

HPLC chromatogram of compound **3u** (91% ee)



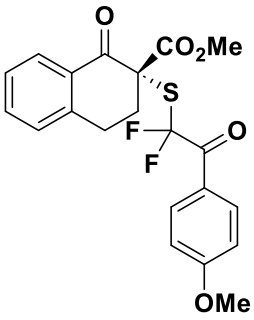


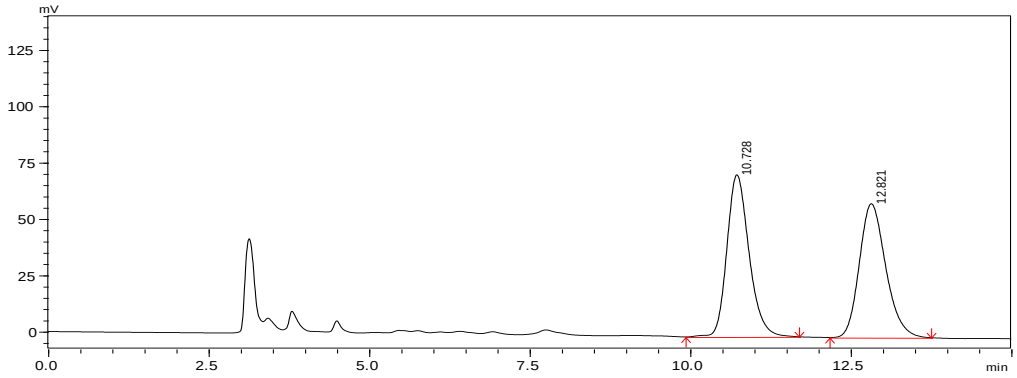
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	19.707	266135	9238170	49.688
2	22.436	234673	9354062	50.312
total		500808	18592233	100.000



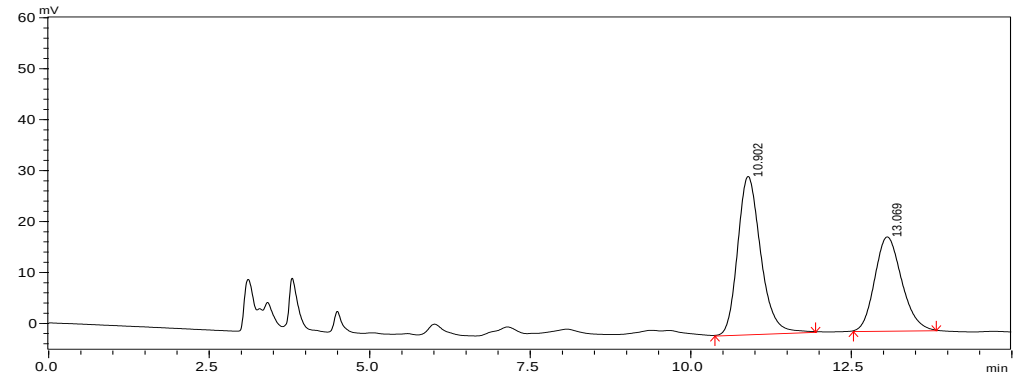
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	19.437	13311	426414	4.485
2	21.962	234751	9080192	95.515
total		248062	9506606	100.000

HPLC chromatogram of compound **3v** (18% ee)



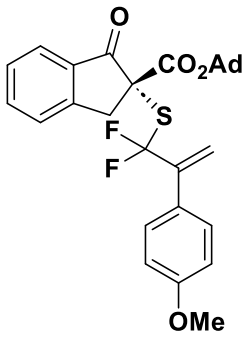


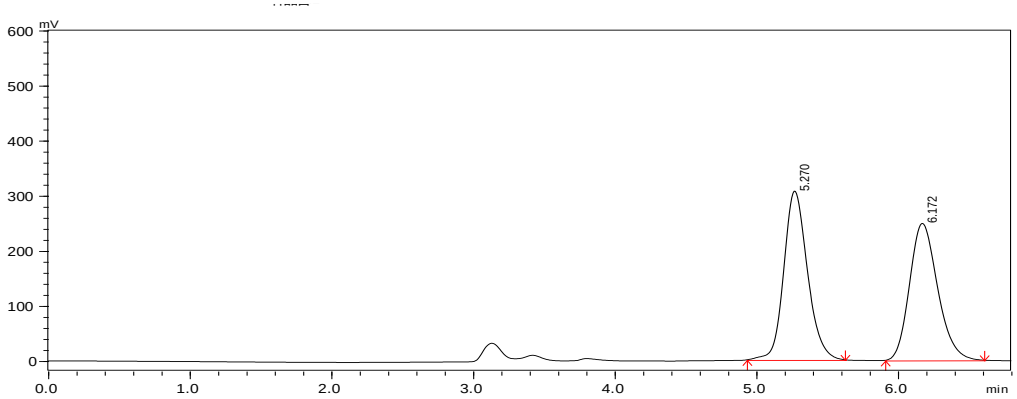
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.728	71893	1728274	50.387
2	12.821	59372	1701718	49.613
total		131264	3429992	100.000



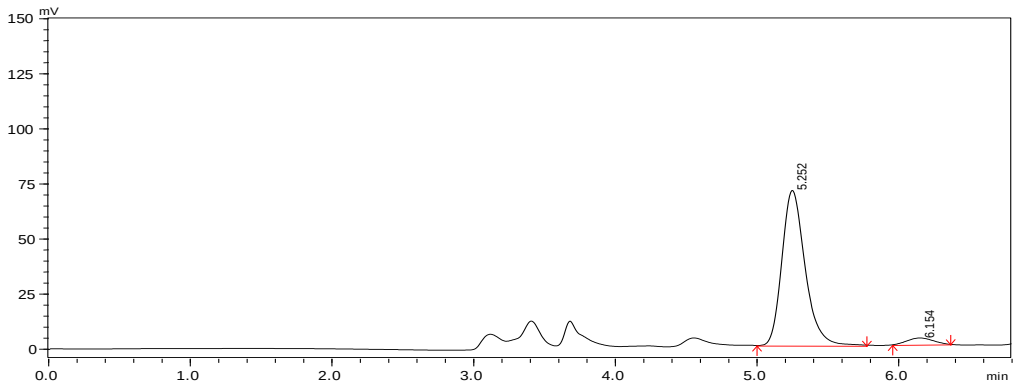
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.902	30956	767802	58.990
2	13.069	18384	533774	41.010
total		49340	1301576	100.000

HPLC chromatogram of compound **4** (91% ee)





#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.270	306266	3566578	50.563
2	6.172	250132	3487195	49.437
total		556398	7053774	100.000



#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.252	70393	799553	95.490
2	6.154	3014	37767	4.510
total		73407	837320	100.000

7. X-ray crystallographic data

X-ray Crystallographic Data for compound 3l (CCDC:2428901)

Compound **3l** (10.0 mg) was weighed into a sample bottle and dissolved in 1.0 ml ether. Hexane was then added dropwise until a small amount of solid precipitated out. A small amount of ether was added to re-dissolve the precipitate. The bottle was sealed with a Parafilm and placed in a fume hood for several days to allow crystal formation by slow solvent evaporation. Applied with multi-scan absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. CCDC 2428901 contains the supplementary crystallographic data, and can be obtained free of charge via: www.ccdc.cam.ac.uk/conts/retrieving.html. The measurements were taken in a Bruker D8 Venture diffractometer. The data was integrated by Bruker D8 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3).

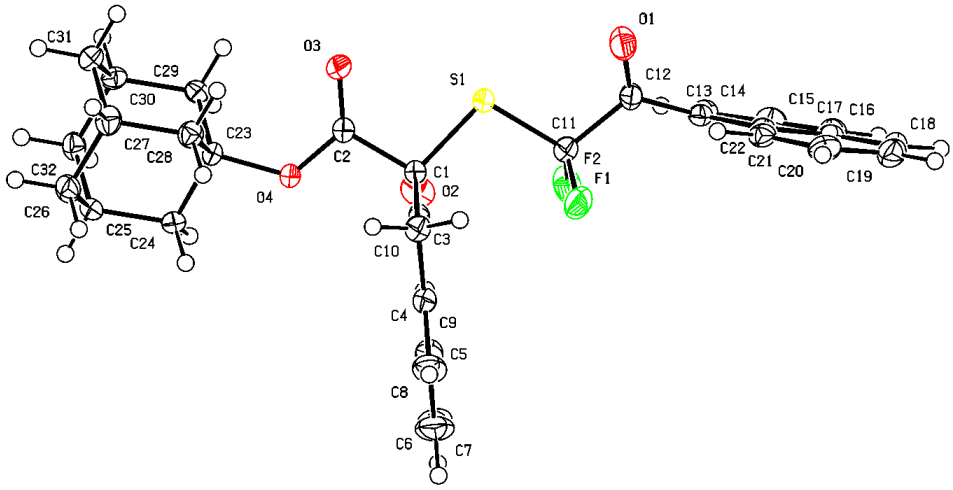


***Table S1*. Crystal data for Compound 3l.**

Compound	**3l**
Empirical formula	$C_{32}H_{28}F_2O_4S$
Formula weight	546.60
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 9.9024(2) Å, a= 90°. b = 12.6959(2) Å, b= 97.0660(10) °. c = 10.5735(2) Å, g = 90°.
Volume	1319.20(4) $Å^3$
Z	2
Density (calculated)	1.376 Mg/m^3
Absorption coefficient	0.993 mm^{-1}
F (000)	572
Crystal size	0.17 x 0.17 x 0.05 mm^3
Theta range for data collection	3.665 to 54.896°.
Index ranges	-11<=h<=12, -15<=k<=14, -12<=l<=12
Reflections collected	18509
Independent reflections	4862 [R(int) = 0.0457]
Completeness to theta = 53.594°	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.6340
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4862 / 1 / 352
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0284, wR2 = 0.0714
R indices (all data)	R1 = 0.0310, wR2 = 0.0724
Absolute structure parameter	0.034(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.234 and -0.174 $e.Å^{-3}$

8. References

[1] J. Liang, W. Fu, L. Dong, C. Zhou, Q. Yuan,W. Chang, W. Yang, X. Xu, X. Shao,Z. Li, N-Difluoromethylthiophthalimide Reagents for Modular Synthesis of Diversified α-Difluoromethylthiolated Ketones, Org. Lett., 2023, 25, 4797–4802.