Supporting Information

Aerobic Oxidative Hydroxysulfurization of *gem*-Difluoroalkenes towards α,α-Difluoro-β-Hydroxysulfides

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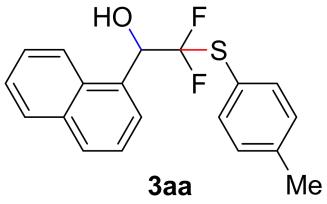
General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra was recoorded on a Bruker DPX-400 spectrometer at room temperature with $CDCl_3$ as the solvent and TMS as an internal standard. GC-MS analysis was performed on Agilent 4890D gas chromatograph. High-resolution mass spectra were collected on MALDI-FTMS or Thermo Scientific Exactive GC Orbitrap GC-MS System. Melting points were measured using a XT4A microscopic apparatus. IR spectra were obtained on a Bruker VECTOR22 spectrophotometer in KBr pellets. *gem*-Difluoroalkenes[1] and (1,1-difluoro-2-(naphthalen-1-yl)ethyl)(p-tolyl)sulfane (**4aa**)[2] were synthesized according to the reported literature. Solvents and chemicals were bought from commercial sources and used directly unless otherwise stated.

General procedure for the synthesis of α,α-difluoro-β-hydroxysulfides

A solution of *gem*-difluoroalkenes (0.2 mmol), thiol (1.0 mmol), $^{n}Bu_3N$ (0.4 mmol) and $K_2S_2O_8$ (0.3 mmol) in DME (1 mL) was stirred in a 10 mL Schlenk tube. Then this Schlenk tube was degassed thoroughly and ensuingly charged with oxygen balloon and the temperature was elevated to 80 ^{o}C for 14 h. The reaction mixture was cooled down with subsequent added into 0.7M HCl (4 mL) and extracted with ethyl acetate (10 mL) for three times. Then the combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent in vacuum, the final residue was purified by flash chromatography on silica gel (ethyl acetate/hexane) to give the pure product.

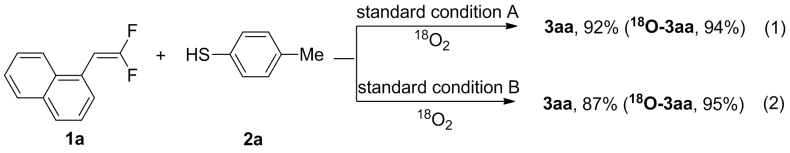


3aa

2,2-difluoro-1-(naphthalen-1-yl)-2-(p-tolylthio)ethanol (3aa)

Pale yellow oil, yield: 90%[a] and 86%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.78 (m, 4H), 7.47–7.41 (m, 5H), 7.08 (d, J=8.0 Hz, 2H), 5.79 (dd, J=11.6 Hz and 6.4 Hz, 1H), 3.14 (s, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 136.6, 133.7, 131.5, 131.5, 130.0, 129.8, 129.5 (t, $^{1}J_{F\text{-}C}$=283.6 Hz), 128.9, 126.5, 126.3, 125.7, 125.3, 123.4, 122.4 (d, $^{3}J_{F\text{-}C}$=1.5 Hz), 71.8 (dd, $^{2}J_{F\text{-}C}$=28.4 Hz and 25.8 Hz), 21.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.9 (d, J=209.4 Hz, 1F), -84.5 (d, J=209.4 Hz, 1F); IR (KBr) 3583, 3426, 3052, 2943, 1595, 1489, 1396, 1037, 973, 794, 730, 512 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2OSNa^+$ 353.0782, found: 353.0783.

Labeling experiments (Scheme 1)

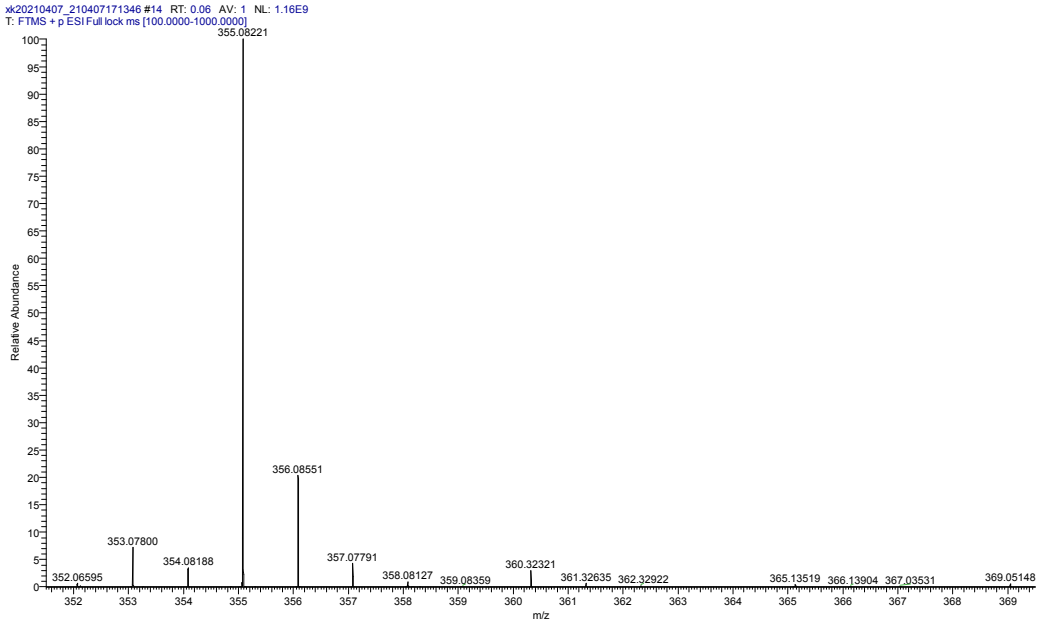


1a **2a**

The reaction was performed in the atmosphere of $^{18}O_2$ (97%), and the typical procedure for labeling experiment was consistent with the general procedure. The isolated products **3aa** was finally analyzed by HRMS. ^{18}O-labled product **3aa** was isolated in 92% yield with 94% isotopic purity under standard condition A and in 87% yield with 95% isotopic purity under standard condition B, respectively (scheme 1).

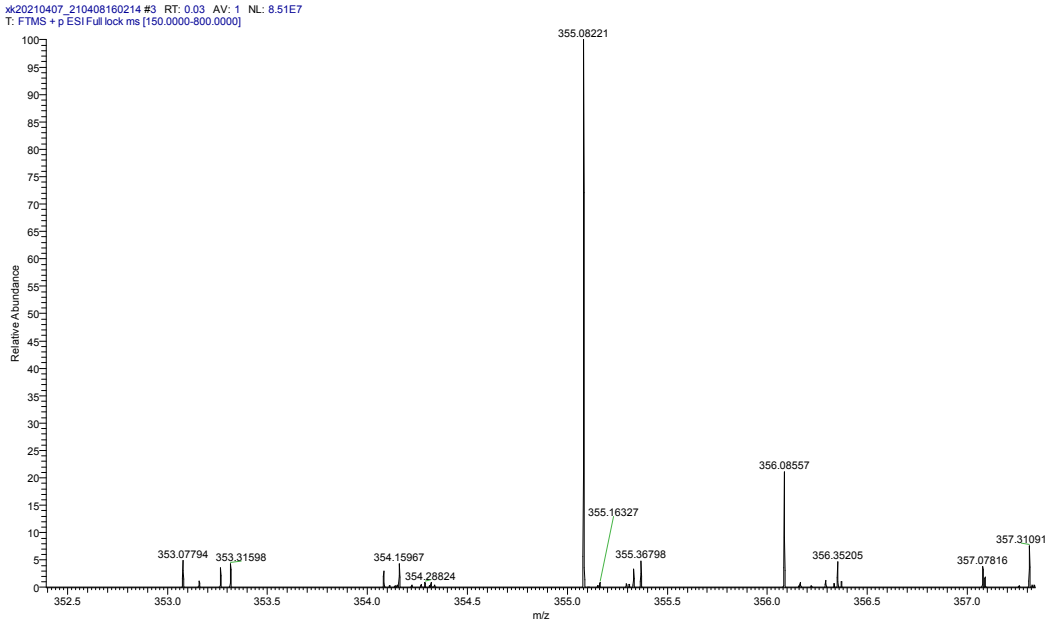
The HRMS spectra of **^{18}O-3aa** (94% purity) (eqn (1))

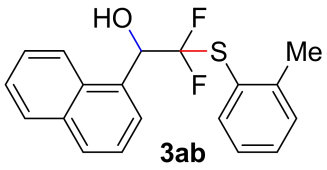
HRMS (ESI): [**^{16}O-3aa**+Na]$^+$ calcd. for $C_{19}H_{16}F_2OSNa^+$ 353.0782, found: 353.0780; HRMS (ESI): [**^{18}O-3aa**+Na]$^+$ calcd. for $C_{19}H_{16}F_2{}^{18}OSNa^+$ 355.0825, found: 353.0822.



The HRMS spectra of **^{18}O-3aa** (95% purity)(eqn (2))

HRMS (ESI): [**^{16}O-3aa**+Na]$^+$ calcd. for $C_{19}H_{16}F_2OSNa^+$ 353.0782, found: 353.0779; HRMS (ESI): [**^{18}O-3aa**+Na]$^+$ calcd. for $C_{19}H_{16}F_2{}^{18}OSNa^+$ 355.0825, found: 353.0822.



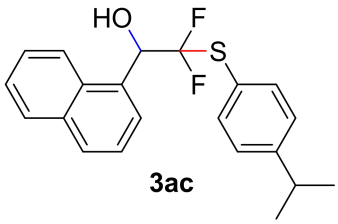


3ab

2,2-difluoro-1-(naphthalen-1-yl)-2-(o-tolylthio)ethanol (3ab)

Pale yellow oil, yield: 91%[a] and 85%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.82 (m, 4H), 7.56 (d, J=7.6 Hz, 1H), 7.51–7.43 (m, 3H), 7.30–7.19 (m, 2H), 7.15–7.10 (m, 1H), 5.85 (t, J=8.6 Hz, 1H), 3.02 (s, 1H), 2.40 (s, 3H); ^{13}C

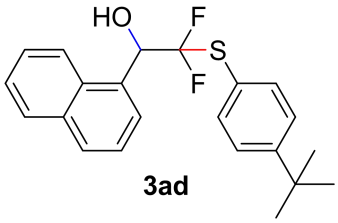
NMR ($CDCl_3$, 100 MHz) δ 144.2, 138.4, 133.6, 131.5, 131.5, 130.8, 130.5, 129.8, 129.8 (t, $^1J_{F\text{-}C}$=284.2 Hz), 128.9, 126.5, 126.5, 126.2, 125.7, 125.3, 125.2, 123.3, 72.2 (dd, $^2J_{F\text{-}C}$=28.0 Hz and 26.0 Hz), 21.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.5 (d, J=207.9 Hz, 1F), -83.3 (d, J=208.3 Hz, 1F). IR (KBr) 3433, 3052, 2927, 1627, 1425, 1153, 1050, 973, 781, 740, 608 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2OSNa^+$ 353.0782, found: 353.0783.



3ac

2,2-difluoro-1-(naphthalen-1-yl)-2-(o-tolylthio)ethanol (3ac)

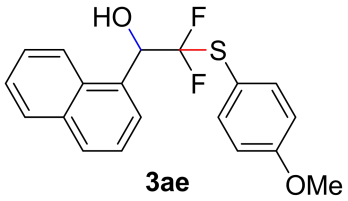
Pale yellow oil, yield: 92%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.81 (m, 4H), 7.51–7.43 (m, 5H), 7.20–7.17 (m, 2H), 5.86–5.79 (m, 1H), 2.98–2.83 (m, 2H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.2, 136.7, 133.6, 131.5, 131.4, 129.7, 129.4 (t, $^1J_{F\text{-}C}$=283.7 Hz), 128.9, 127.4, 126.4, 126.3, 125.7, 125.2, 123.3, 122.7, 71.7 (dd, $^2J_{F\text{-}C}$=28.7 Hz and 25.6 Hz), 34.0, 23.9, 23.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.8 (d, J=209.8 Hz, 1F), -85.1 (d, J=210.2 Hz, 1F). IR (KBr) 3417, 3058, 2965, 2866, 1601, 1457, 1406, 1057, 788, 733, 551 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{21}H_{20}F_2OS^+$ 358.1203, found: 358.1201.



3ad

2-((4-(tert-butyl)phenyl)thio)-2,2-difluoro-1-(naphthalen-1-yl)ethanol (3ad)

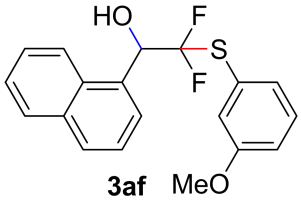
Pale yellow oil, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 4H), 7.49–7.40 (m, 5H), 7.34–7.31 (m, 2H), 5.81 (dd, J=12.0 Hz and 6.0 Hz, 1H), 3.16 (s, 1H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 136.4, 133.6, 131.6, 131.5, 129.8, 129.5 (t, $^1J_{F\text{-}C}$=283.6 Hz), 128.9, 126.5, 126.3, 126.3, 125.7, 125.3, 123.4, 122.5 (d, $^3J_{F\text{-}C}$=2.2 Hz), 71.7 (dd, $^2J_{F\text{-}C}$=28.7 Hz and 25.7 Hz), 34.8, 31.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.5 (d, J=209.8 Hz, 1F), -84.9 (d, J=209.4 Hz, 1F); IR (KBr) 3423, 3052, 2959, 2901, 2866, 1707, 1595, 1463, 1361, 1057, 781, 730, 608 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{22}H_{22}F_2OSNa^+$ 395.1252, found: 395.1254.



3ae

2,2-difluoro-2-((4-methoxyphenyl)thio)-1-(naphthalen-1-yl)ethanol(3ae)

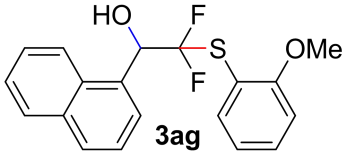
Pale yellow oil, yield: 97%[a] and 89%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.81 (m, 4H), 7.51–7.43 (m, 5H), 6.85–6.80 (m, 2H), 5.82 (dd, J=11.4 Hz and 6.2 Hz, 1H), 3.74 (s, 3H), 3.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.2, 138.4, 133.6, 131.5, 131.5, 129.7, 129.4 (t, $^1J_{F\text{-}C}$=283.4 Hz), 128.9, 126.5, 126.3, 125.7, 125.2, 123.3, 116.3 (d, $^3J_{F\text{-}C}$=1.6 Hz), 114.7, 71.7 (dd, $^2J_{F\text{-}C}$=28.5 Hz and 25.7 Hz), 55.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -79.5 (d, J=209.8 Hz, 1F), -85.4 (d, J=209.8 Hz, 1F); IR (KBr) 3433, 3062, 2940, 2831, 1591, 1489, 1246, 1050, 1025, 791, 733, 525 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2O_2SNa^+$ 369.0731, found: 369.0733.



3af

2,2-difluoro-2-((3-methoxyphenyl)thio)-1-(naphthalen-1-yl)ethanol (3af)

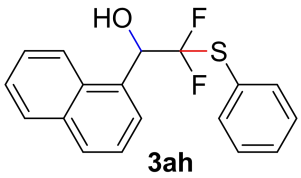
Pale yellow oil, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.83 (m, 4H), 7.52–7.43 (m, 3H), 7.25–7.20 (m, 1H), 7.17–7.14 (m, 1H), 7.10–7.08 (m, 1H), 6.94–6.90 (m, 1H), 5.87–5.81 (m, 1H), 3.72 (s, 3H), 2.99 (d, J=4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 133.6, 131.5, 131.4, 129.8, 129.8, 129.5 (t, $^{1}J_{F\text{-}C}$=284.0 Hz), 128.9, 128.6, 126.9 (d, $^{3}J_{F\text{-}C}$=1.5 Hz), 126.5, 126.3, 125.7, 125.2, 123.3, 121.1, 116.3, 71.9 (dd, $^{2}J_{F\text{-}C}$=28.3 Hz and 25.7 Hz), 55.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.5 (d, J=209.8 Hz, 1F), -84.1 (d, J=209.4 Hz, 1F); IR (KBr) 3433, 3062, 2940, 2837, 1591, 1483, 1419, 1306, 1037, 861, 784, 733, 688 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2O_2SNa^+$ 369.0731, found: 369.0733.



3ag

2,2-difluoro-2-((2-methoxyphenyl)thio)-1-(naphthalen-1-yl)ethanol (3ag)

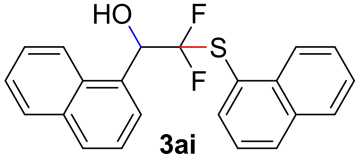
Pale yellow oil, yield: 93%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 3H), 7.72–7.69 (m, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.51–7.34 (m, 4H), 7.07–6,97 (m, 2H), 5.50 (d, J=18.8 Hz, 1H), 4.04 (s, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 140.1, 133.6, 132.8, 131.7, 130.6, 129.6 (dd, $^{1}J_{F\text{-}C}$=290.2 Hz and 281.8 Hz), 129.4, 128.8, 126.6, 126.2, 125.4, 125.2, 123.2, 121.8, 114.3 (d, $^{3}J_{F\text{-}C}$=6.5 Hz), 111.7, 70.4 (dd, $^{2}J_{F\text{-}C}$=33.1 Hz and 23.1 Hz), 56.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -77.4 (d, J=217.7 Hz, 1F), -93.1 (d, J=217.7 Hz, 1F); IR (KBr) 3430, 3068, 2937, 1623, 1582, 1483, 1431, 1069, 970, 794, 746 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2O_2SNa^+$ 369.0731, found: 369.0734.



3ah

2,2-difluoro-1-(naphthalen-1-yl)-2-(phenylthio)ethanol (3ah)

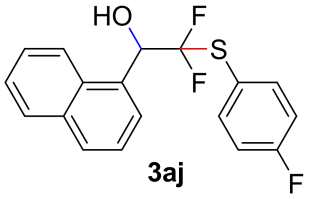
Pale yellow oil, yield: 92%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.92 (m, 1H), 7.89–7.84 (m, 3H), 7.59–7.45 (m, 5H), 7.42–7.31 (m, 3H), 5.89–5.83 (m, 1H), 2.93–2.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.5, 133.6, 131.5, 131.3, 130.0, 129.8, 129.5 (t, $^{1}J_{F\text{-}C}$=283.9 Hz), 129.1, 128.9, 126.5, 126.3, 126.0, 125.7, 125.2, 123.3, 71.9 (dd, $^{2}J_{F\text{-}C}$=28.3 Hz and 25.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.7 (dd, J=209.4 Hz and 3.8Hz, 1F), -84.1 (d, J=209.2 Hz and 7.3 Hz, 1F); IR (KBr) 3420, 3058, 2924, 1598, 1441, 1162, 1053, 973, 861, 794, 746, 691 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{18}H_{14}F_2OSNa^+$ 339.0626, found: 339.0624.



3ai

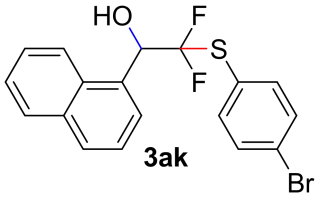
2,2-difluoro-1-(naphthalen-1-yl)-2-(naphthalen-1-ylthio)ethanol (3ai)

Pale yellow oil, yield: 76%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J=8.0 Hz, 1H), 7.94–7.80 (m, 7H), 7.53–7.38 (m, 6H), 5.86 (dd, J=11.2 Hz and 6.8Hz, 1H), 3.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.6, 136.0, 134.2, 133.6, 131.5, 131.5, 131.4, 129.8, 129.7 (t, $^1J_{F\text{-}C}$=285.0 Hz), 128.9, 128.4, 127.3, 126.5, 126.5, 126.3, 126.3, 125.7, 125.5, 125.2, 123.3, 123.3, 72.1 (dd, $^2J_{F\text{-}C}$=28.1 Hz and 26.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.0 (d, J=208.3 Hz, 1F), -83.4 (d, J=208.7 Hz, 1F); IR (KBr) 3401, 3049, 2924, 1620, 1502, 1438, 1146, 1053, 960, 852, 736 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{22}H_{16}F_2OSNa^+$ 389.0782, found: 389.0780.



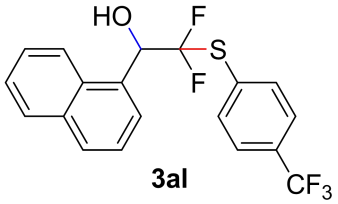
2,2-difluoro-2-((4-fluorophenyl)thio)-1-(naphthalen-1-yl)ethanol (3aj)

Pale yellow oil, yield: 68%[a] and 69%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=8.0 Hz, 1H), 7.88–7.85 (m, 3H), 7.54–7.46 (m, 5H), 7.04–6.98 (m, 2H), 5.87 (t, J=8.2 Hz, 1H), 2.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.0 (d, $^1J_{F\text{-}C}$=249.3 Hz), 138.8 (d, $^3J_{F\text{-}C}$=8.6 Hz), 133.6, 131.4, 131.3, 129.9, 129.3 (t, $^1J_{F\text{-}C}$=283.7 Hz), 129.0, 126.6, 126.2, 125.8, 125.2, 123.2, 121.0, 116.3 (d, $^2J_{F\text{-}C}$=21.9 Hz), 72.0 (dd, $^2J_{F\text{-}C}$=27.7 Hz and 26.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -79.4 (d, J=207.9 Hz, 1F), -83.6 (d, J=208.3 Hz, 1F), -110.4 (s, 1F); IR (KBr) 3423, 3071, 2924, 1588, 1508, 1463, 1393, 1156, 1057, 832, 733 cm^{-1}; HRMS (ESI):$[M+Na]^+$ calcd. for $C_{18}H_{13}F_3OSNa^+$ 357.0531, found: 357.0534.



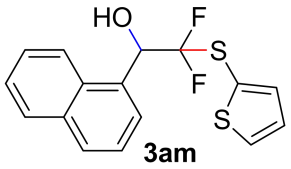
2-((4-bromophenyl)thio)-2,2-difluoro-1-(naphthalen-1-yl)ethanol (3ak)

Pale yellow oil, yield: 79%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J=8.4 Hz, 1H), 7.82–7.81 (m, 3H), 7.46–7.28 (m, 7H), 5.81 (t, J=7.6 Hz, 1H), 3.29 (d, J=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.9, 133.7, 132.3, 131.4, 131.4, 130.0, 129.3 (t, $^1J_{F\text{-}C}$=284.3 Hz), 129.0, 126.6, 126.3, 125.9, 125.2, 125.1, 124.9, 123.3, 72.2 (t, $^2J_{F\text{-}C}$=26.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.7 (d, J=206.8 Hz, 1F), -82.4 (d, J=206.8 Hz, 1F); IR (KBr) 3423, 3058, 2930, 1601, 1508, 1467, 1390, 1063, 1009, 788, 730, 611, 563 cm^{-1}; HRMS (EI and ESI): not detected.



2,2-difluoro-1-(naphthalen-1-yl)-2-((4-(trifluoromethyl)phenyl)thio)ethanol (3al)

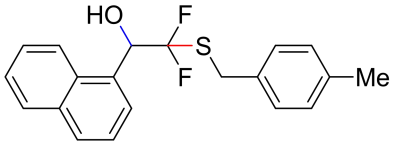
Pale yellow oil, yield: 54%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=8.0 Hz, 1H), 7.88–7.84 (m, 3H), 7.62–7.59 (m, 2H), 7.54–7.46 (m, 5H), 5.93–5.87 (m, 1H), 3.01 (d, J=3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1, 133.7, 131.7 (q, $^2J_{F\text{-}C}$=32.6 Hz), 131.4, 131.2, 130.9, 130.0, 129.5 (t, $^1J_{F\text{-}C}$=285.0 Hz), 129.0, 126.6, 126.3, 125.9, 125.8 (q, $^3J_{F\text{-}C}$=3.7 Hz), 125.2, 123.8 (q, $^1J_{F\text{-}C}$=272.7 Hz), 123.2, 72.4 (t, $^2J_{F\text{-}C}$=26.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.9 (s, 3F), -78.4 (d, J=206.0 Hz, 1F), -81.4 (d, J=206.0 Hz, 1F); IR (KBr) 3417, 3058, 2962, 2930, 1607, 1515, 1399, 1060, 1012, 781, 730, 611 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{19}H_{13}F_5OS^+$ 384.0607, found: 384.0606.



3am

2,2-difluoro-1-(naphthalen-1-yl)-2-(thiophen-2-ylthio)ethanol (3am)

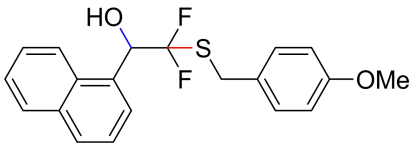
Pale yellow oil, yield: 47%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J=8.4 Hz, 1H), 7.88–7.84 (m, 3H), 7.54–7.45 (m, 4H), 7.29 (dd, J=3.6 Hz and 1.2 Hz, 1H), 7.04 (dd, J=5.6 Hz and 3.6 Hz, 1H), 5.90–5.84 (m, 1H), 2.94 (d, J=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.7, 133.6, 133.1, 131.4, 131.1, 129.9, 128.9, 128.4 (t, $^{1}J_{F\text{-}C}$=285.5 Hz), 127.9, 126.6, 126.2, 125.8, 125.2, 123.2, 122.8, 71.4 (dd, $^{2}J_{F\text{-}C}$=28.6 Hz and 25.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -79.8 (d, J=207.2 Hz, 1F), -86.6 (d, J=207.6 Hz, 1F); IR (KBr) 3423, 3100, 3058, 2927, 1598, 1518, 1402, 1169, 1063, 967, 791, 714 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{16}H_{12}F_2OS_2Na^+$ 345.0190, found: 345.0191.



3an

2,2-difluoro-2-((4-methylbenzyl)thio)-1-(naphthalen-1-yl)ethanol (3an)

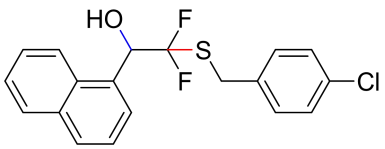
Pale yellow oil, yield: 54%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J=8.4 Hz, 1H), 7.87–7.82 (m, 3H), 7.54–7.45 (m, 3H), 7.15 (d, J=8.0 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 5.85–5.80 (m, 1H), 3.97 (s, 2H), 2.83 (s, 1H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.3, 133.6, 133.1, 131.4, 131.4, 130.7 (t, $^{1}J_{F\text{-}C}$=282.6 Hz), 129.8, 129.4, 129.0, 128.9, 126.5, 126.2, 125.7, 125.2, 123.4, 72.5 (t, $^{2}J_{F\text{-}C}$=26.9 Hz), 32.2 (t, $^{3}J_{F\text{-}C}$=4.3 Hz), 21.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -80.9 (d, J=209.8 Hz, 1F), -82.7 (d, J=209.8 Hz, 1F); IR (KBr) 3670, 3408, 3046, 2920, 2854, 1630, 1508, 1438, 1242, 1149, 1085, 1047, 967, 874, 781, 736, 643 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{20}H_{18}F_2OSNa^+$ 367.0939, found: 367.0935.



3ao

2,2-difluoro-2-((4-methoxybenzyl)thio)-1-(naphthalen-1-yl)ethanol (3ao)

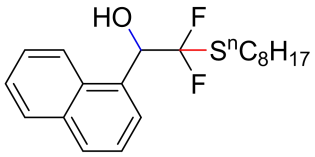
Pale yellow oil, yield: 42%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J=8.4 Hz, 1H), 7.87–7.81 (m, 3H), 7.54–7.45 (m, 3H), 7.17 (d, J=8.8 Hz, 2H), 6.78 (d, J=8.4 Hz, 2H), 5.86–5.80 (m, 1H), 3.96 (s, 2H), 3.73 (s, 3H), 2.92 (d, J=3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 133.6, 131.5, 131.4, 130.7 (t, $^{1}J_{F\text{-}C}$=282.6 Hz), 130.3, 129.8, 128.9, 128.1, 126.5, 126.2, 125.7, 125.2, 123.4, 114.1, 72.5 (t, $^{2}J_{F\text{-}C}$=27.0 Hz), 55.3, 31.9 (t, $^{3}J_{F\text{-}C}$=4.6 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -80.9 (d, J=209.8 Hz, 1F), -82.6 (d, J=210.2 Hz, 1F); IR (KBr) 3443, 3052, 2930, 2834, 1611, 1515, 1463, 1297, 1245, 1175, 1028, 970, 836, 788, 733 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{20}H_{18}F_2O_2SNa^+$ 383.0888, found: 383.0887.



3ap

2-((4-chlorobenzyl)thio)-2,2-difluoro-1-(naphthalen-1-yl)ethanol (3ap)

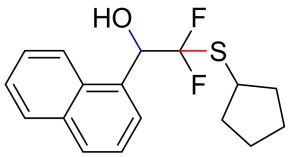
Pale yellow oil, yield: 48%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J=8.4 Hz, 1H), 7.87–7.80 (m, 3H), 7.54–7.46 (m, 3H), 7.23–7.14 (m, 4H), 5.87–5.80 (m, 1H), 3.92 (s, 2H), 2.84 (d, J=4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.0, 133.6, 133.4, 131.4, 131.4, 130.6 (t, $^1J_{F\text{-}C}$=282.9 Hz), 130.4, 129.9, 128.9, 128.8, 126.6, 126.2, 125.8, 125.2, 123.3, 72.5 (t, $^2J_{F\text{-}C}$=26.9 Hz), 31.7 (t, $^3J_{F\text{-}C}$=4.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -80.6 (d, J=208.7 Hz, 1F), -82.2 (d, J=208.3 Hz, 1F); IR (KBr) 3443, 3049, 2924, 1640, 1598, 1489, 1399, 1246, 1143, 1092, 1044, 1015, 970, 788, 736, 506 cm^{-1}; HRMS (EI and ESI): not detected.



3aq

2,2-difluoro-1-(naphthalen-1-yl)-2-(octylthio)ethanol (3aq)

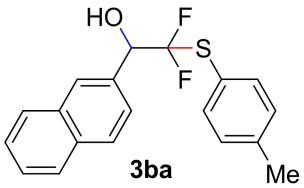
Pale yellow oil, yield: 73%[a] and 27%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=8.4 Hz, 1H), 7.87–7.82 (m, 3H), 7.54–7.45 (m, 3H), 5.83 (t, J=9.0 Hz, 1H), 2.98 (s, 1H), 2.75 (t, J=7.4 Hz, 2H), 1.62–1.53 (m, 2H), 1.32–1.22 (m, 10H), 0.88–0.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.6, 131.7, 131.5, 131.1 (t, $^1J_{F\text{-}C}$=283.5 Hz), 129.7, 128.9, 126.4, 126.2, 125.7, 125.2, 123.4, 72.5 (t, $^2J_{F\text{-}C}$=27.1 Hz), 31.8, 29.8, 29.1, 29.0, 28.8, 28.0 (t, $^3J_{F\text{-}C}$=3.5 Hz), 22.7, 14.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -80.8 (d, J=209.4 Hz, 1F), -83.1 (d, J=209.4 Hz, 1F); IR (KBr) 3427, 3058, 2953, 2924, 2850, 1659, 1598, 1508, 1467, 1041, 791, 733 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{20}H_{26}F_2OSNa^+$ 375.1565, found: 375.1566.



3ar

2-(cyclopentylthio)-2,2-difluoro-1-(naphthalen-1-yl)ethanol (3ar)

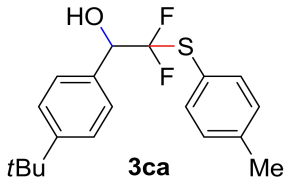
Pale yellow oil, yield: 52%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=8.4 Hz, 1H), 7.86–7.81 (m, 3H), 7.54–7.44 (m, 3H), 5.85–5.79 (m, 1H), 3.52–3.44 (m, 1H), 2.95 (s, 1H), 2.09–2.00 (m, 2H), 1.70–1.47 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.6, 131.7, 131.5, 131.1 (t, $^1J_{F\text{-}C}$=281.6 Hz), 129.7, 128.9, 126.4, 126.2, 125.7, 125.2, 123.5, 72.5 (t, $^2J_{F\text{-}C}$=27.1 Hz), 41.3, 34.6, 34.5, 24.6, 24.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -79.4 (d, J=209.8 Hz, 1F), -81.9 (d, J=210.2 Hz, 1F); IR (KBr) 3427, 3052, 2959, 2866, 1630, 1595, 1511, 1444, 1399, 1354, 1316, 1246, 1153, 1044, 861, 781, 743, 605cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{17}H_{18}F_2OSNa^+$ 331.0939, found: 331.0936.



3ba

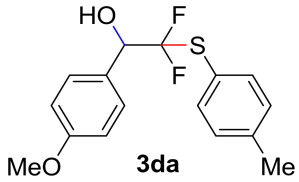
2,2-difluoro-1-(naphthalen-2-yl)-2-(p-tolylthio)ethanol (3ba)

Pale yellow oil, yield: 94%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.85–7.82 (m, 3H), 7.57 (d, J=8.4 Hz, 1H), 7.50–7.43 (m, 4H), 7.13 (d, J=8.0 Hz, 2H), 5.13 (dd, J=10.6 Hz and 8.2 Hz, 1H), 2.98 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 136.6, 133.6, 132.9, 132.7, 130.0, 129.0 (t, $^1J_{F\text{-}C}$=282.9 Hz), 128.3, 128.1, 127.8, 127.6, 126.6, 126.3, 125.0, 122.2, 76.2 (t, $^2J_{F\text{-}C}$=26.6 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.2 (d, J=209.8 Hz, 1F), -84.8 (d, J=209.8 Hz, 1F); IR (KBr) 3366, 3055, 2921, 1598, 1492, 1367, 1156, 1060, 980, 800, 746 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2OSNa^+$ 353.0782, found: 353.0781.



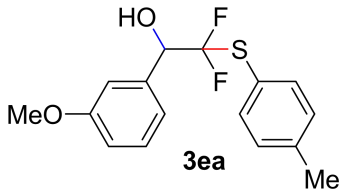
1-(4-(tert-butyl)phenyl)-2,2-difluoro-2-(p-tolylthio)ethanol (3ca)

Pale yellow oil, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.0 Hz, 2H), 7.39 (s, 4H), 7.14 (d, J=8.0 Hz, 2H), 4.93 (dd, J=11.6 Hz and 8.0 Hz, 1H), 2.80 (s, 1H), 2.34 (s, 3H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 140.2, 136.5, 132.4, 129.9, 128.9 (t, $^{1}J_{F\text{-}C}$=284.8 Hz), 127.6, 125.3, 122.4, 76.0 (t, $^{2}J_{F\text{-}C}$=26.7 Hz), 34.7, 31.3, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.5 (d, J=209.0 Hz, 1F), -85.2 (d, J=208.7 Hz, 1F); IR (KBr) 3427, 3026, 2962, 2866, 1620, 1492, 1402, 1162, 1057, 980, 807, 788, 506 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{22}F_2OSNa^+$ 359.1252, found: 359.1253.



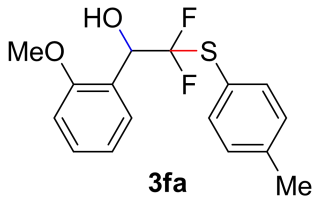
2,2-difluoro-1-(4-methoxyphenyl)-2-(p-tolylthio)ethanol (3da)

Pale yellow solid, mp 61–63 °C, yield: 98%[a] and 88%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.0 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H), 7.15 (d, J=7.6 Hz, 2H), 6.91–6.88 (m, 2H), 4.91 (t, J=9.6 Hz, 1H), 3.79 (s, 3H), 2.85 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.2, 140.3, 136.5, 129.9, 129.1, 129.0 (t, $^{1}J_{F\text{-}C}$=284.4 Hz), 127.4, 122.3, 113.8, 75.7 (t, $^{2}J_{F\text{-}C}$=26.6 Hz), 55.3, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.1 (d, J=208.3 Hz, 1F), -85.2 (d, J=208.3 Hz, 1F); IR (KBr) 3452, 3017, 2988, 2892, 1611, 1515, 1425, 1242, 1053, 1025, 791, 749 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{16}H_{16}F_2O_2SNa^+$ 333.0731, found: 333.0734.



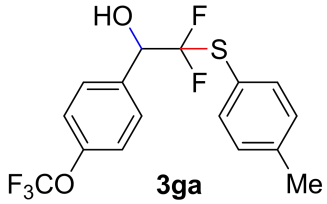
2,2-difluoro-1-(3-methoxyphenyl)-2-(p-tolylthio)ethanol (3ea)

Pale yellow oil, yield: 92%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.0 Hz, 2H), 7.30–7.25 (m, 1H), 7.15 (d, J=8.0 Hz, 2H), 7.05–7.02 (m, 2H), 6.92–6.88 (m, 1H), 4.94 (dd, J=11.2 Hz and 8.0 Hz, 1H), 3.79 (s, 3H), 2.96 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 140.3, 136.8, 136.5, 129.9, 129.3, 128.9 (t, $^{1}J_{F\text{-}C}$=284.9 Hz), 122.2, 120.3, 114.8, 113.3, 76.0 (t, $^{2}J_{F\text{-}C}$=26.6 Hz), 55.3, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.5 (d, J=209.1 Hz, 1F), -85.0 (d, J=208.7 Hz, 1F); IR (KBr) 3436, 2921, 2834, 1604, 1489, 1454, 1255, 1044, 993, 807, 698, 509 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{16}H_{16}F_2O_2SNa^+$ 333.0731, found: 333.0733.



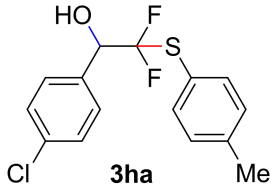
2,2-difluoro-1-(2-methoxyphenyl)-2-(p-tolylthio)ethanol (3fa)

Pale yellow oil, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=8.0 Hz, 2H), 7.40 (d, J=7.6 Hz, 1H), 7.36–7.31 (m, 1H), 7.16 (d, J=8.0 Hz, 2H), 7.02–6.91 (m, 2H), 5.30–5.23 (m, 1H), 3.86 (s, 3H), 3.78 (d, J=7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.7, 140.0, 136.5, 130.1, 129.8, 129.8, 129.3 (t, $^1J_{F\text{-}C}$=285.8 Hz), 123.4, 122.7, 120.9, 111.3, 73.5 (dd, $^2J_{F\text{-}C}$=27.8 Hz and 25.8 Hz), 55.7, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.4 (d, J=205.3 Hz, 1F), -85.1 (d, J=204.9 Hz, 1F); IR (KBr) 3574, 3500, 3026, 2962, 2933, 2834, 1598, 1489, 1457, 1431, 1053, 976, 752 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{16}H_{16}F_2O_2SNa^+$ 333.0731, found: 333.0735.



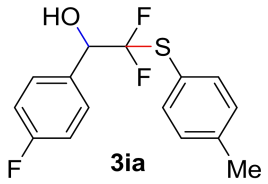
2,2-difluoro-2-(p-tolylthio)-1-(4-(trifluoromethoxy)phenyl)ethanol (3ga)

White solid, mp 57–59 °C, yield: 80%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J=8.4 Hz, 2H), 7.44 (d, J=8.0 Hz, 2H), 7.21 (d, J=8.0 Hz, 2H), 7.16 (d, J=8.0 Hz, 2H), 4.97 (dd, J=11.6 Hz and J=7.2 Hz, 1H), 2.97 (s, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7 (d, $^3J_{F\text{-}C}$=6.0 Hz), 140.6, 136.5, 133.8, 130.0, 129.4, 128.6 (t, $^1J_{F\text{-}C}$=284.7 Hz), 121.8, 120.6, 120.4 (q, $^1J_{F\text{-}C}$=257.4 Hz), 75.2 (dd, $^2J_{F\text{-}C}$=28.1 Hz and 26.3 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -57.8 (s, 1F), -81.4 (d, J=210.9 Hz, 1F), -86.0 (d, J=211.7 Hz, 1F); IR (KBr) 3436, 3052, 3026, 2924, 2866, 1909, 1595, 1508, 1409, 1255, 1047, 791, 717 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{16}H_{13}F_5O_2S^+$ 364.0556, found: 364.0555.



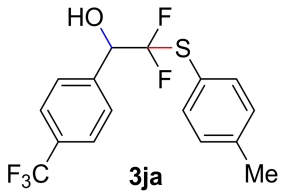
1-(4-chlorophenyl)-2,2-difluoro-2-(p-tolylthio)ethanol (3ha)

Pale yellow solid, mp 85–87 °C, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.32 (m, 6H), 7.16 (d, J=8.0 Hz, 2H), 4.93 (dd, J=11.2 Hz and 7.6 Hz, 1H), 2.94 (s, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 136.5, 135.0, 133.7, 130.0, 129.2, 128.7 (t, $^1J_{F\text{-}C}$=284.6 Hz), 128.5, 121.9, 75.3 (dd, $^2J_{F\text{-}C}$=27.6 Hz and 26.4 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.5 (d, J=210.9 Hz, 1F), -85.8 (d, J=210.6 Hz, 1F); IR (KBr) 3593, 3420, 3055, 2901, 2856, 1595, 1486, 1403, 1040, 989, 768, 701, 541 cm^{-1}; HRMS (EI and ESI): not detected.



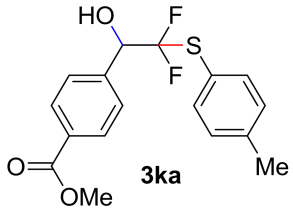
2,2-difluoro-1-(4-fluorophenyl)-2-(p-tolylthio)ethanol (3ia)

Pale yellow solid, mp 58–60 °C, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.43 (m, 4H), 7.17 (d, J=8.0 Hz, 2H), 7.10–7.04 (m, 2H), 4.95 (t, J=9.4 Hz, 1H), 2.84 (s, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.2 (d, $^1J_{F\text{-}C}$=246.2 Hz), 140.5, 136.5, 131.0, 130.0, 129.7 (d, $^3J_{F\text{-}C}$=8.5 Hz), 128.7 (t, $^1J_{F\text{-}C}$=284.2 Hz), 121.9, 115.3 (d, $^2J_{F\text{-}C}$=21.6 Hz), 75.3 (dd, $^2J_{F\text{-}C}$=27.6 Hz and 26.3 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.8 (d, J=210.6 Hz, 1F), -85.9 (d, J=210.2 Hz, 1F), -112.6 (s, 1F); IR (KBr) 3590, 3436, 3074, 2921, 1607, 1511, 1419, 1076, 1044, 980, 810, 756, 701 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{15}H_{13}F_3OS^+$ 298.0639, found: 298.0637.



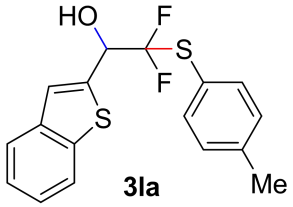
2,2-difluoro-2-(p-tolylthio)-1-(4-(trifluoromethyl)phenyl)ethanol (3ja)

Pale yellow solid, mp 66–68 °C, yield: 81%[a] and 30%[b]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.58 (m, 4H), 7.44 (d, J=8.0 Hz, 2H), 7.17–7.04 (d, J=8.0 Hz, 2H), 5.02 (dd, J=11.6 Hz and 7.2 Hz, 1H), 3.00 (s, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.6, 139.0, 136.5, 131.1 (q, $^{2}J_{F\text{-}C}$=32.5 Hz), 130.1, 128.6 (t, $^{1}J_{F\text{-}C}$=284.3 Hz), 128.3, 125.2 (q, $^{3}J_{F\text{-}C}$=3.73 Hz), 124.0 (q, $^{1}J_{F\text{-}C}$=272.1 Hz), 121.7, 75.3 (t, $^{2}J_{F\text{-}C}$=27.2 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.7 (s, 3F), -81.0 (d, J=212.4 Hz, 1F), -86.0 (d, J=212.4 Hz, 1F); IR (KBr) 3369, 2921, 2853, 1620, 1489, 1422, 1329, 1066, 1015, 961, 791, 720, 502 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{16}H_{13}F_5OS^+$ 348.0607, found: 348.0604.



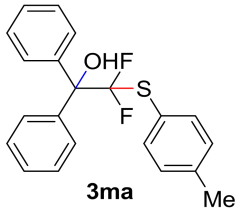
methyl 4-(2,2-difluoro-1-hydroxy-2-(p-tolylthio)ethyl)benzoate (3ka)

Pale yellow solid, mp 75–77 °C, yield: 66%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=8.4 Hz, 2H), 7.56 (d, J=8.0 Hz, 2H), 7.44 (d, J=8.4 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 5.06–4.99 (m, 1H), 3.92 (s, 3H), 2.96 (d, J=3.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 140.5, 140.1, 136.5, 130.7, 130.0, 129.5, 128.7 (t, $^{1}J_{F\text{-}C}$=284.9 Hz), 127.9, 121.8, 75.6 (dd, $^{2}J_{F\text{-}C}$=27.7 Hz and J=26.4 Hz), 52.2, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -81.0 (d, J=211.7 Hz, 1F), -85.7 (d, J=211.3 Hz, 1F); IR (KBr) 3407, 3004, 2953, 2917, 2847, 1787, 1694, 1611, 1585, 1489, 1415, 1303, 1095, 788, 745, 570 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{17}H_{17}F_2O_3S^+$ 339.0861, found: 339.0864.



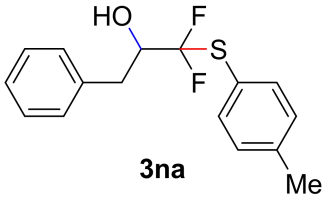
1-(benzo[b]thiophen-2-yl)-2,2-difluoro-2-(p-tolylthio)ethanol (3la)

Pale yellow solid, mp 86–88 °C, yield: 68%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.78 (m, 1H), 7.76–7.70 (m, 1H), 7.47 (d, J=8.0 Hz, 2H), 7.37–7.29 (m, 3H), 7.14 (d, J=8.0 Hz, 2H), 5.27 (dd, J=9.4 Hz and 8.6 Hz, 1H), 3.13 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.6, 140.1, 139.0, 138.5, 136.6, 130.0, 128.4 (t, $^{1}J_{F\text{-}C}$=285.0 Hz), 124.9, 124.5, 124.3, 124.0, 122.4, 121.9, 73.2 (t, $^{2}J_{F\text{-}C}$=28.5 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.0 (d, J=210.6 Hz, 1F), -84.8 (d, J=209.8 Hz, 1F); IR (KBr) 3542, 3423, 3058, 2914, 2850, 1630, 1598, 1492, 1460, 1066, 791, 756 cm^{-1}; HRMS (EI): $[M]^+$ calcd. for $C_{17}H_{14}F_2OS_2^+$ 336.0454, found: 336.0452.



2,2-difluoro-1,1-diphenyl-2-(p-tolylthio)ethanol (3ma)

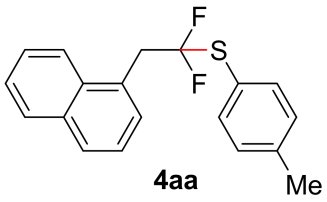
Colorless oil, yield: 99%[a]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=6.8 Hz, 4H), 7.43 (d, J=8.0 Hz, 2H), 7.35–7.26 (m, 6H), 7.13 (d, J=8.0 Hz, 2H), 3.15 (s, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.3, 136.8, 131.2 (t, $^{1}J_{F\text{-}C}$=289.4 Hz), 129.9, 128.3, 128.0, 127.9, 122.7, 81.6 (t, $^{2}J_{F\text{-}C}$=23.8 Hz), 21.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -77.7; IR (KBr) 3526, 3420, 3068, 3033, 2914, 2847, 1640, 1601, 1492, 1444, 1348, 1037, 745 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{21}H_{18}F_2OSNa^+$ 379.0939, found: 379.0940.



3na

1,1-difluoro-3-phenyl-1-(p-tolylthio)propan-2-ol (3na)

Pale yellow oil, yield: 28%; 7.53 (d, J=8.0 Hz, 2H), 7.35–7.30 (m, 2H), 7.27–7.22 (m, 3H), 7.20 (d, J=8.0 Hz, 2H), 4.13–4.03 (m, 1H), 3.17–3.11 (m, 1H), 2.88–2.82 (m, 1H), 2.37 (s, 3H), 2.21 (d, J=4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 136.9, 136.6, 130.0, 129.5, 129.5 (t, $^{1}J_{F\text{-}C}$=281.8 Hz), 128.7, 126.9, 122.1 (t, $^{3}J_{F\text{-}C}$=2.2 Hz), 75.0 ($^{2}J_{F\text{-}C}$, J=26.6 Hz), 36.9 (t, $^{3}J_{F\text{-}C}$=1.8 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.7 (d, J=210.9 Hz, 1F), -87.0 (d, J=210.9 Hz, 1F); IR (KBr) 3516, 3446, 3062, 3030, 2921, 2853, 1636, 1489, 1454, 1383, 1281, 1162, 1101, 1041, 941, 807, 736, 701 cm^{-1}; HRMS (EI): $[M+Na]^+$ calcd. for $C_{16}H_{16}F_2OSNa^+$ 317.0782, found: 317.0782.



4aa

(1,1-difluoro-2-(naphthalen-1-yl)ethyl)(p-tolyl)sulfane (4aa)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=8.4 Hz, 1H), 7.86–7.80 (m, 2H), 7.54–7.41 (m, 6H), 7.15 (d, J=8.0 Hz, 2H), 3.90 (t, J=14.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.2, 136.3, 133.9, 132.7, 129.9, 129.8, 129.0 (t, $^{1}J_{F\text{-}C}$=280.5 Hz), 128.7, 128.7, 128.5 (t, $^{3}J_{F\text{-}C}$=2.5 Hz), 126.3, 125.7, 125.2, 124.3, 123.4, 41.6 (t, $^{2}J_{F\text{-}C}$=24.6 Hz), 21.3; IR (KBr) 3426, 3045, 2917, 1911, 1645, 1591, 1495, 1444, 1396, 1328, 1210, 1143, 1056, 976, 883, 851, 809, 777, 701, 499 cm^{-1}; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -70.7; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{16}F_2SNa^+$ 337.0833, found: 337.0837.

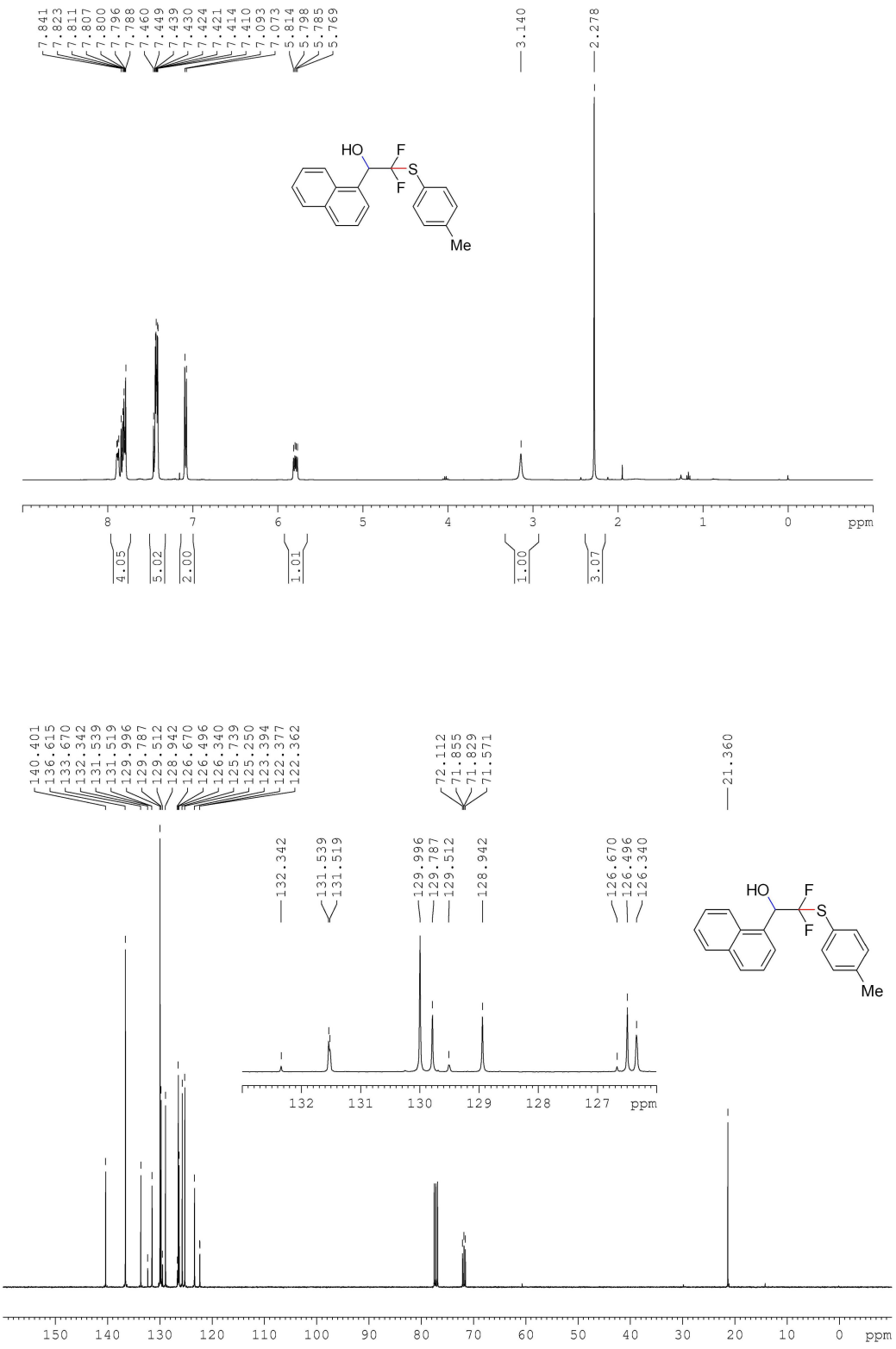
References

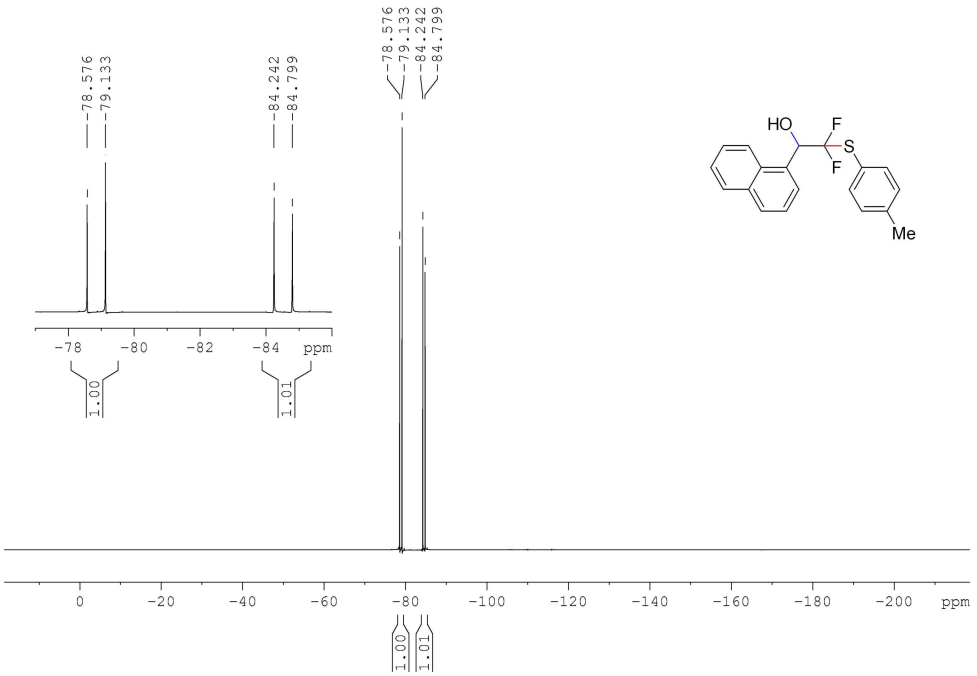
[1] H.Sakaguchi, Y. Uetake, M. Ohashi, T. Niwa, S. Ogoshi and T. Hosoya, *J. Am. Chem. Soc.*, 2017, **139**, 12855.

[2] D. L. Orsi, B. J. Easley, A. M. Lick and R. A. Altman, *Org. Lett.*, 2017, **19**, 1570.

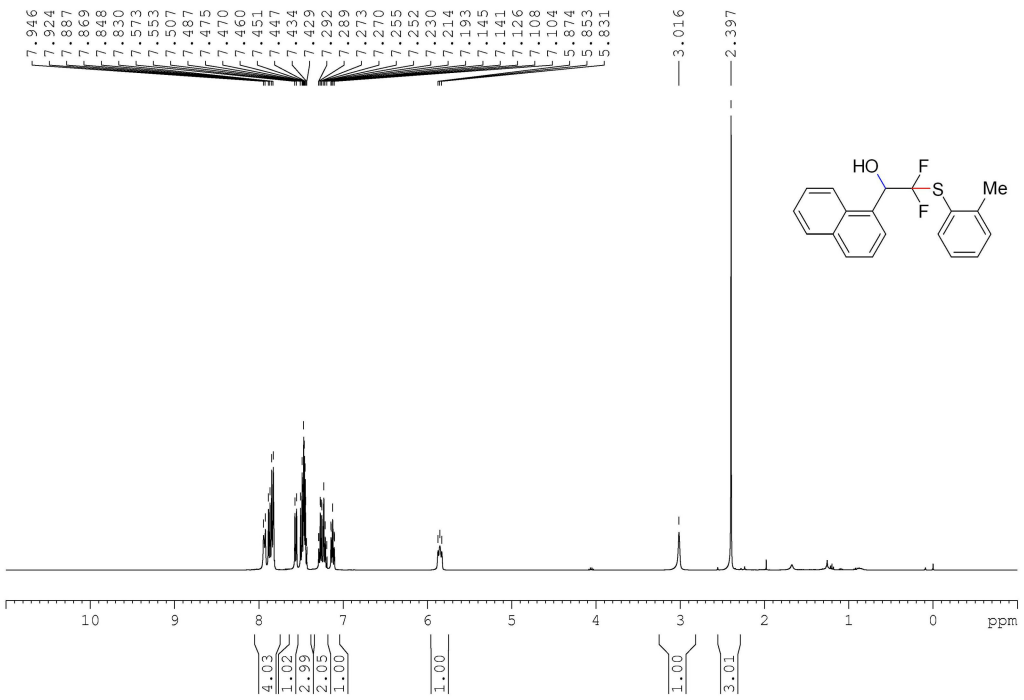
^{1}H, ^{13}C and ^{19}F NMR spectra for all the compounds

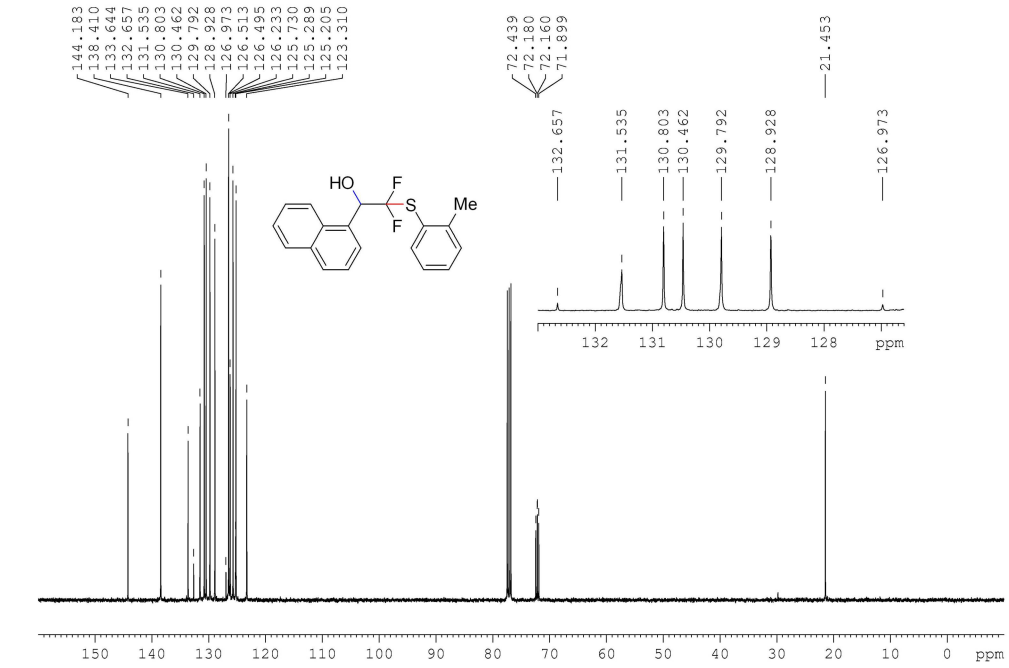
NMR spectra of **3aa**





NMR spectra of **3ab**

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125.730
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125.205
123.310
72.439
72.180
72.160
71.899
21.453
132.657
131.535
130.803
130.462
129.792
128.928
126.973
HO
F
S
F
Me
132
131
130
129
128
ppm
150
140
130
120
110
100
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60
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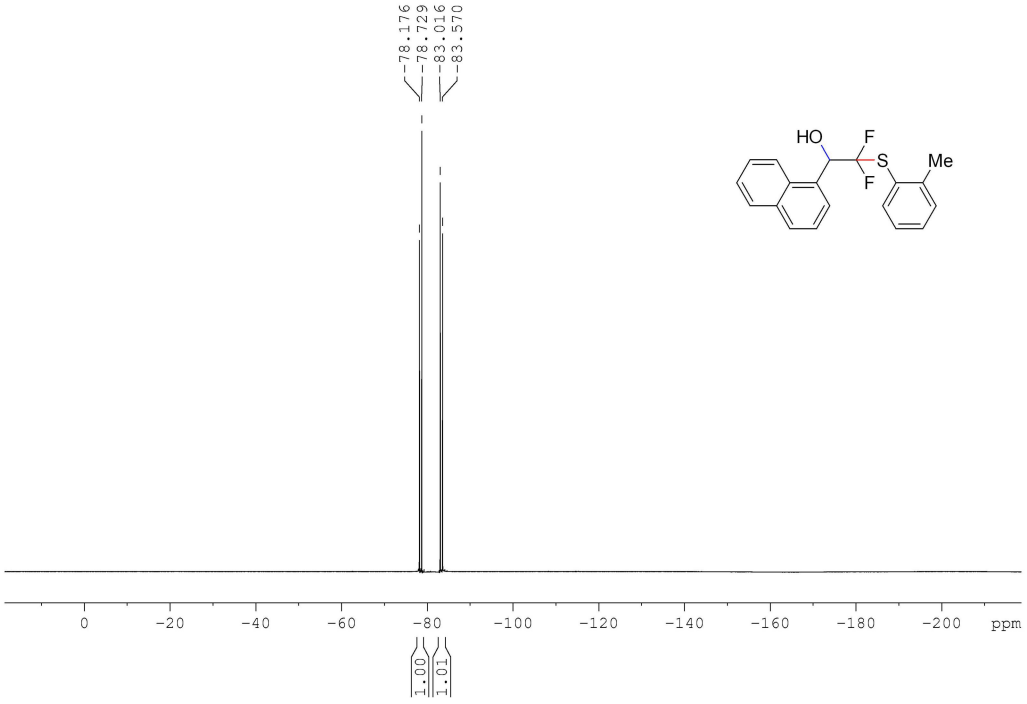
30
20
10
0
ppm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S
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Me
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ppm
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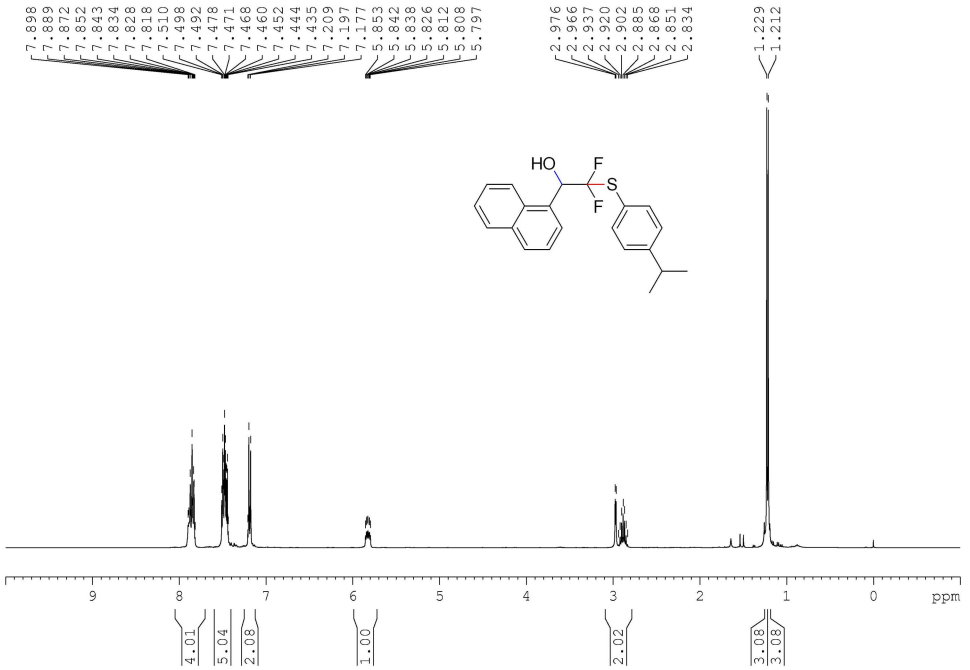
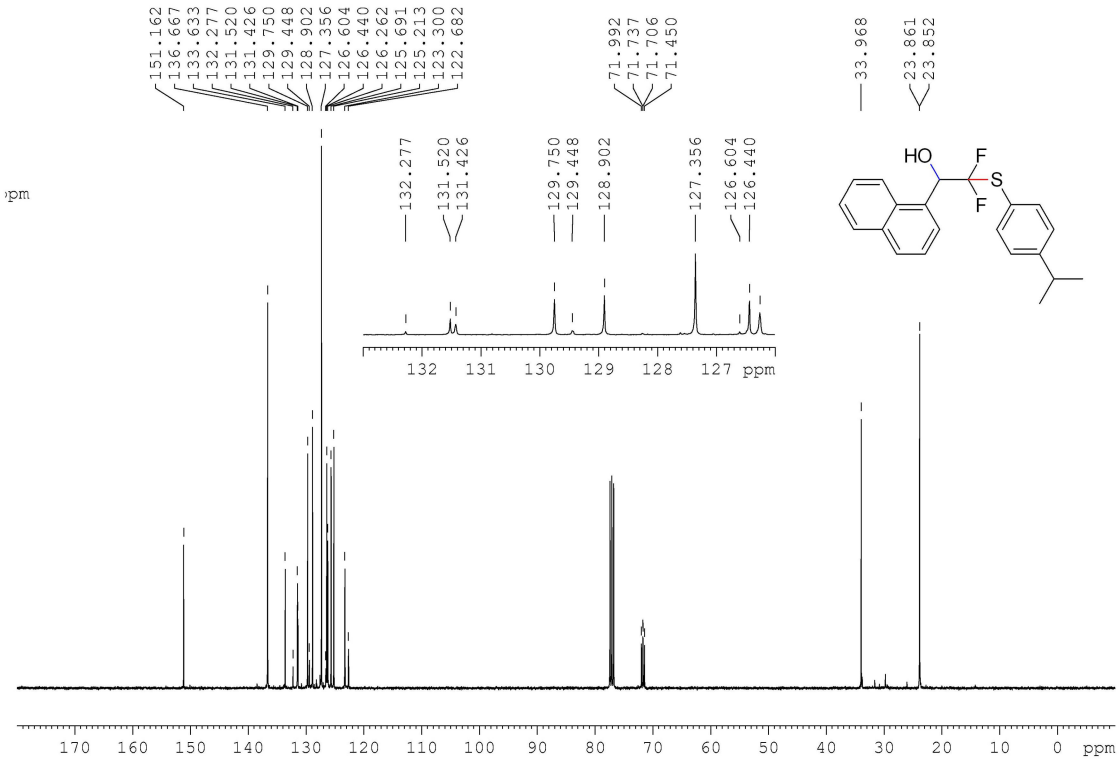
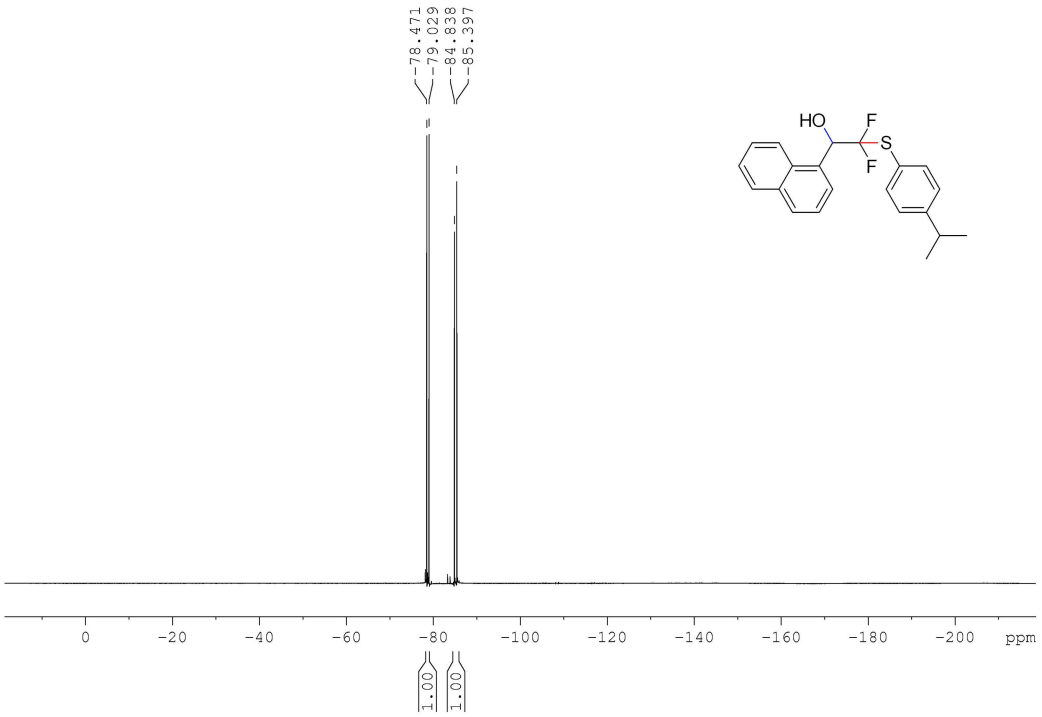
1.01

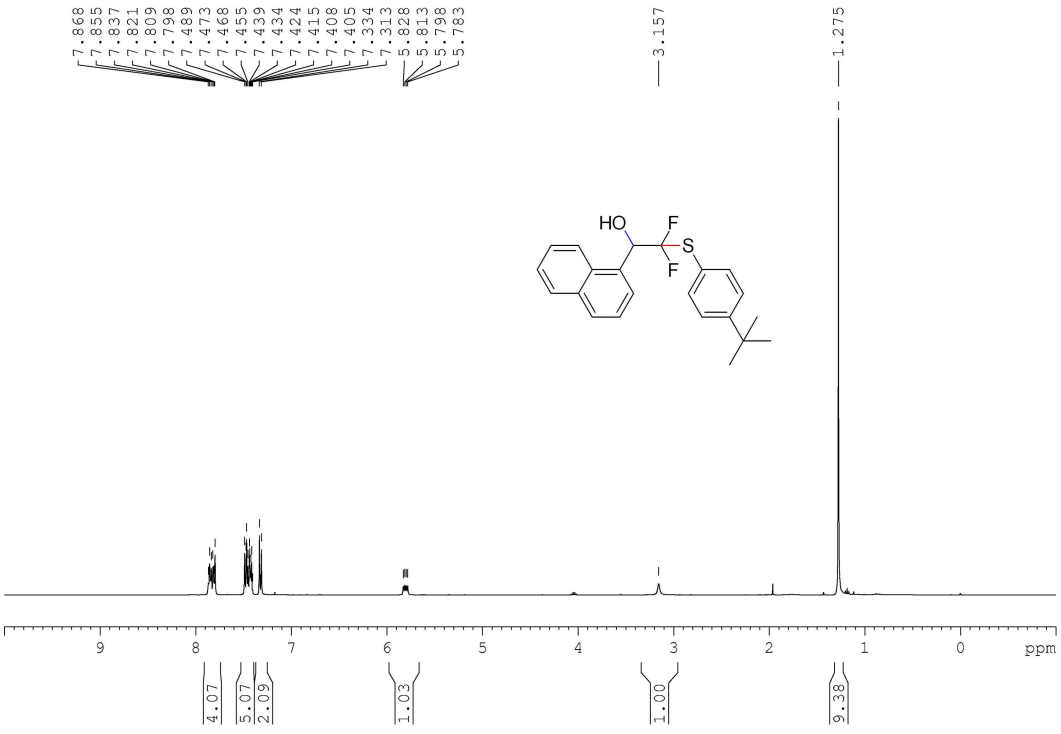
NMR spectra of **3ac**

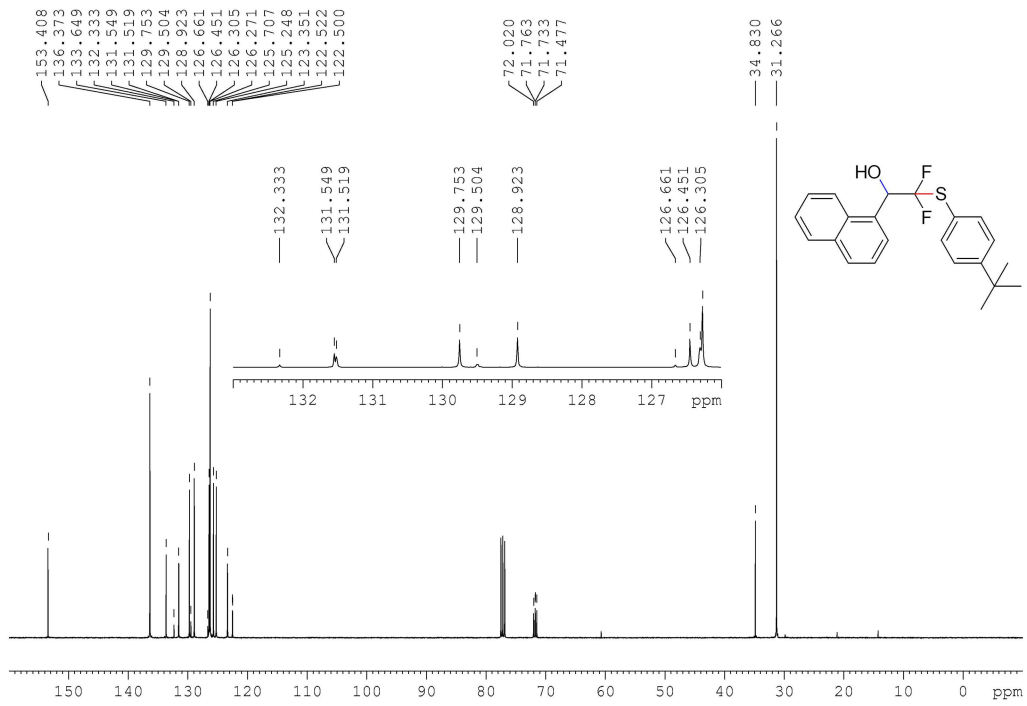






NMR spectra of **3ad**

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S
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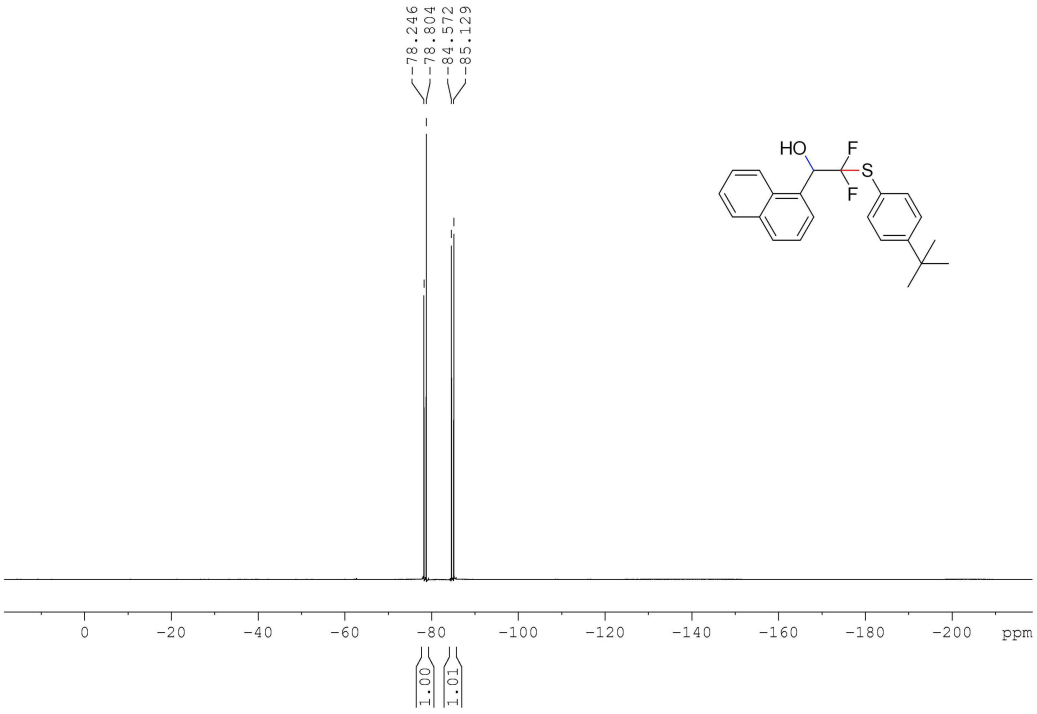
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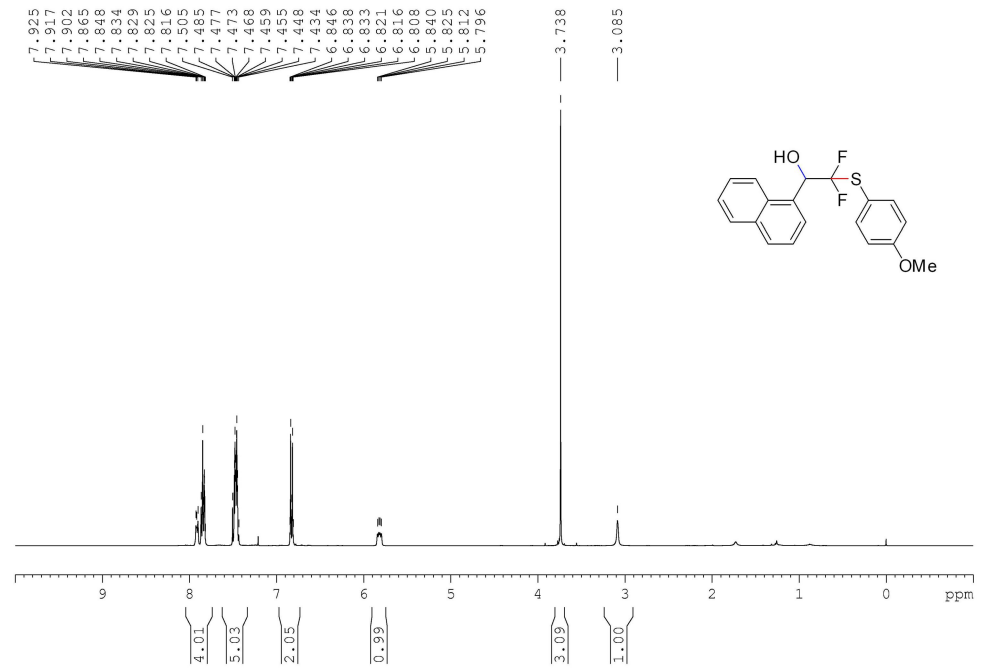
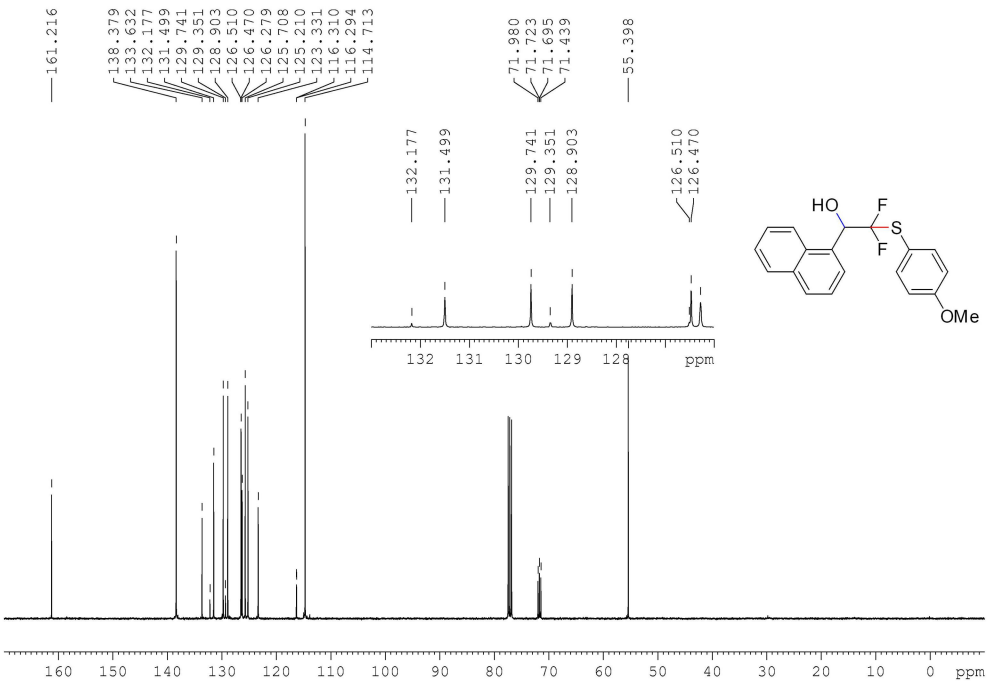
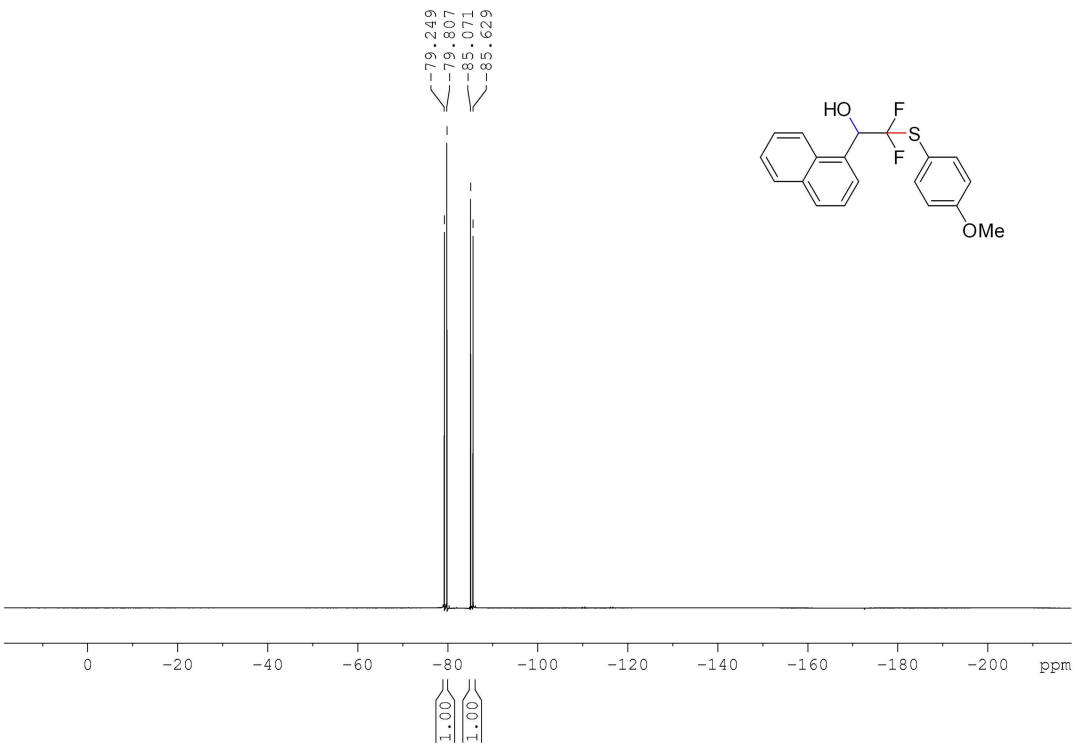
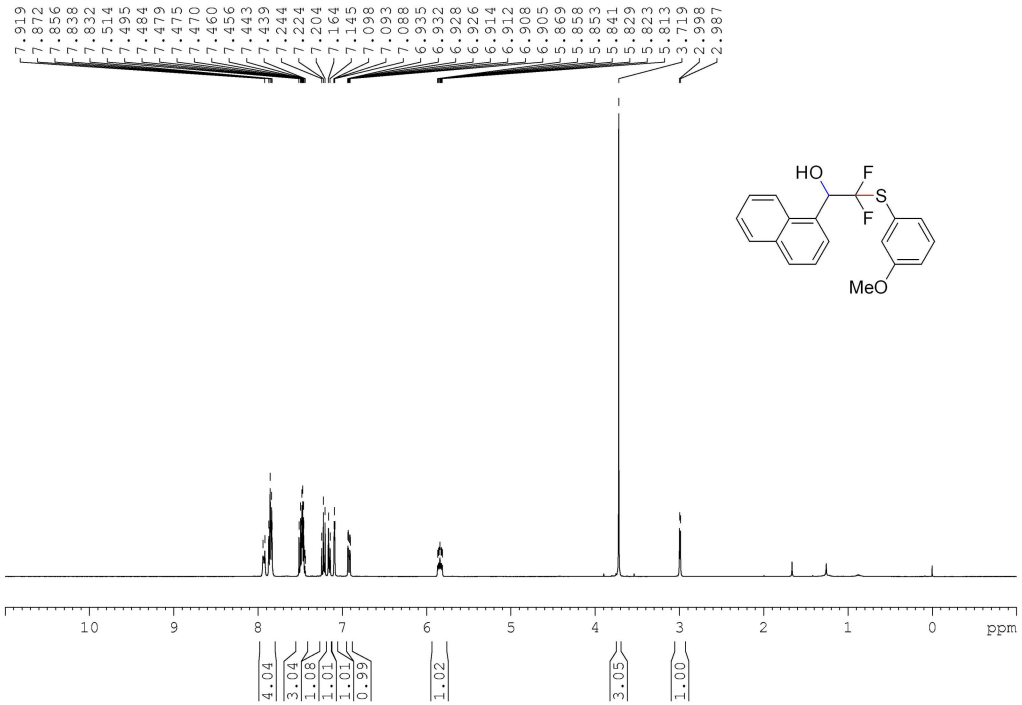
NMR spectra of **3ae**

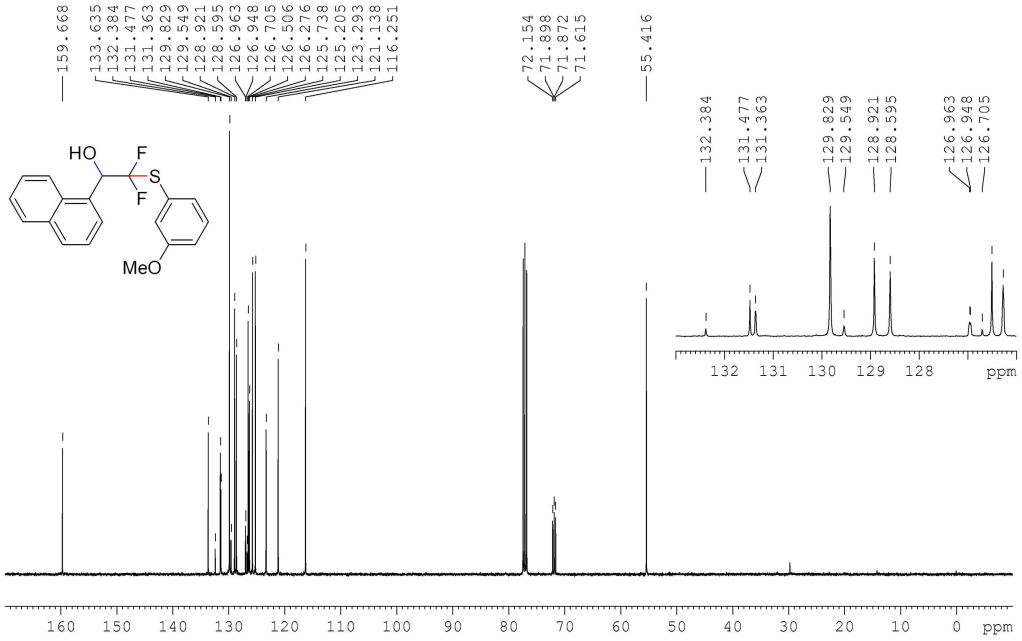






NMR spectra of **3af**

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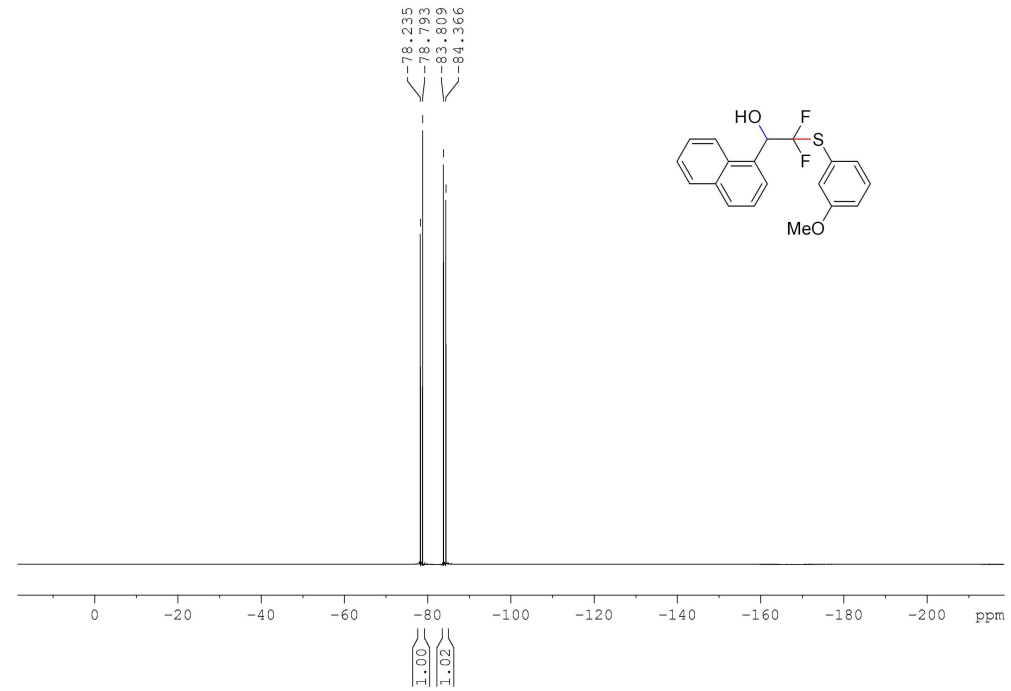
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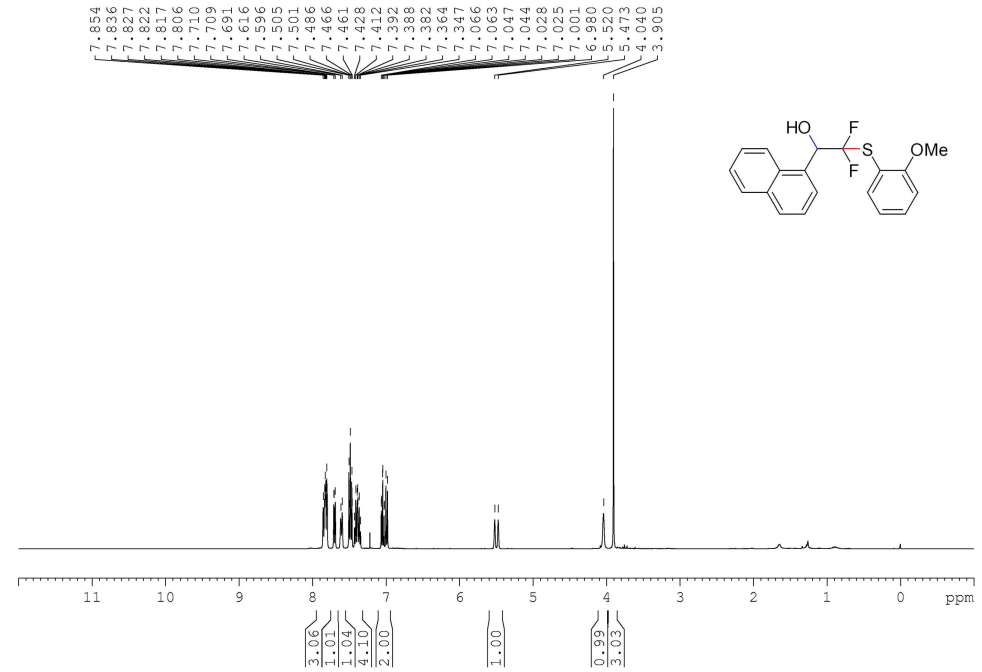
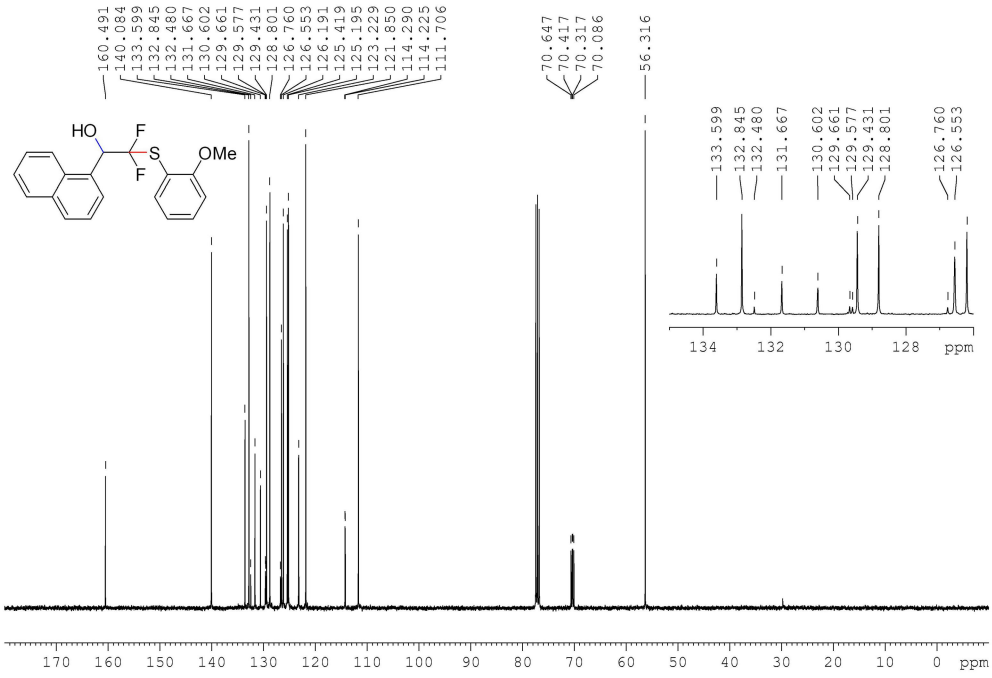
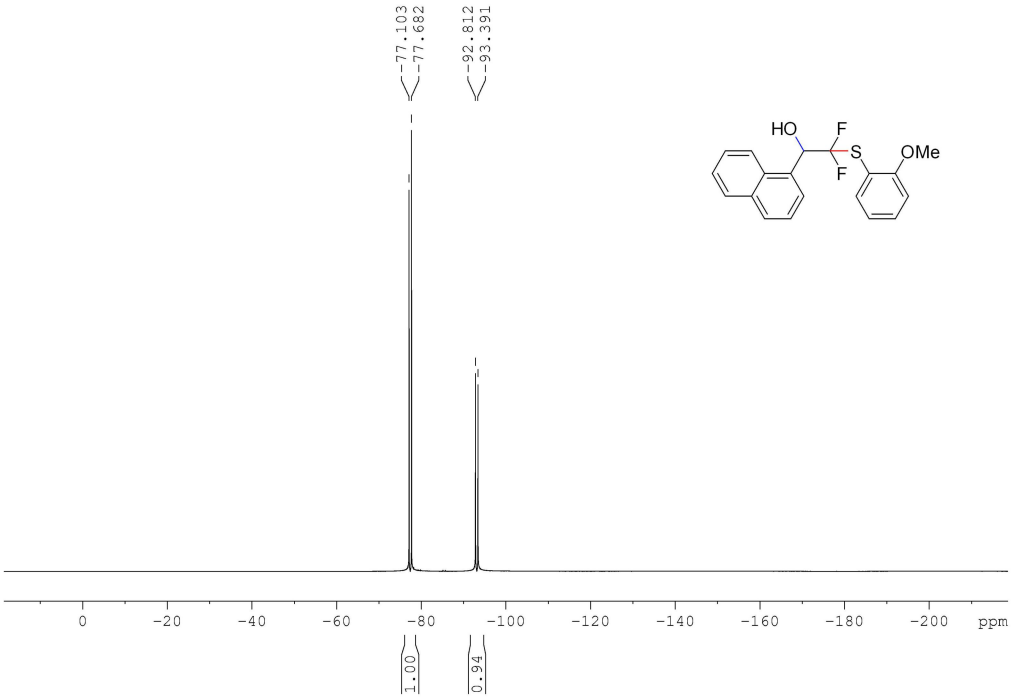
1.00
1.02

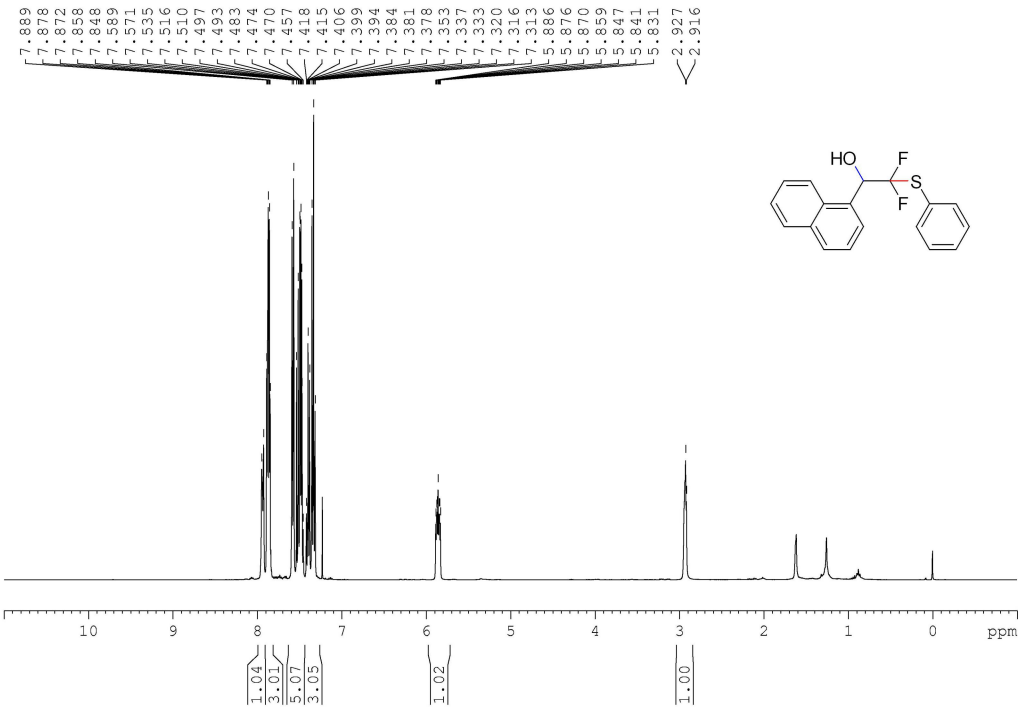
NMR spectra of **3ag**

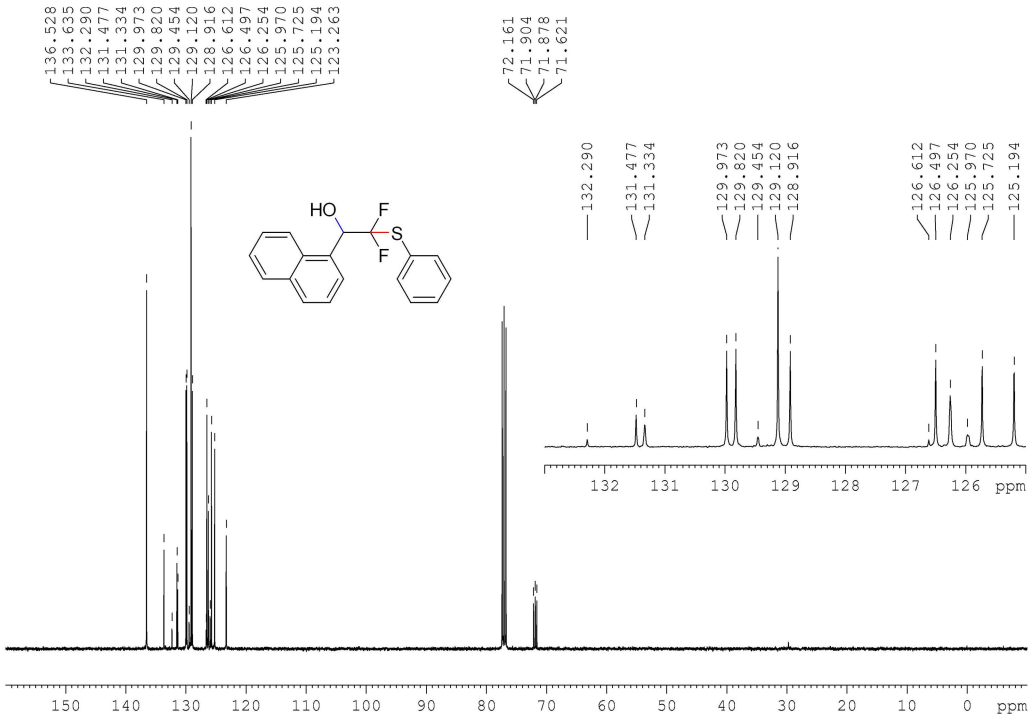






NMR spectra of **3ah**

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71.878
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HO
F
S
F
132.290
131.477
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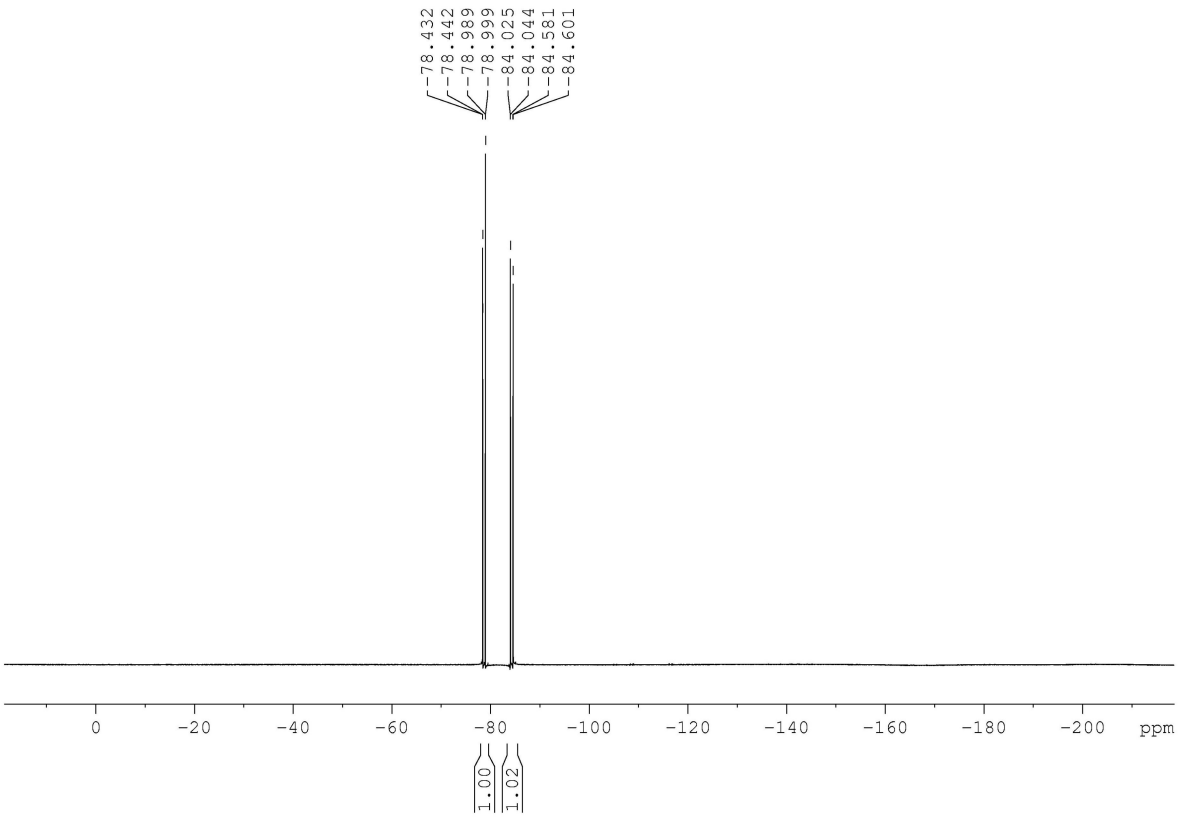
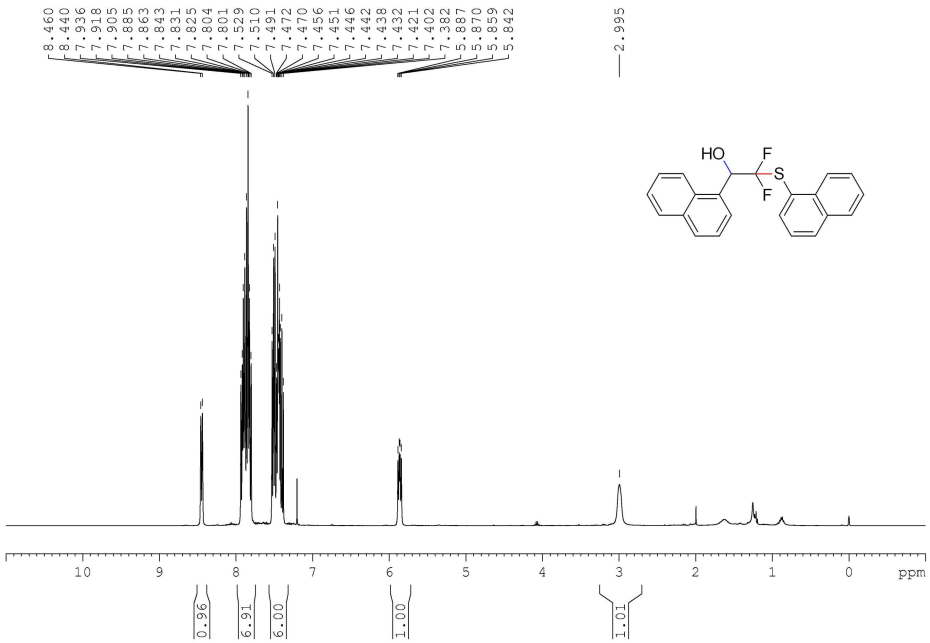
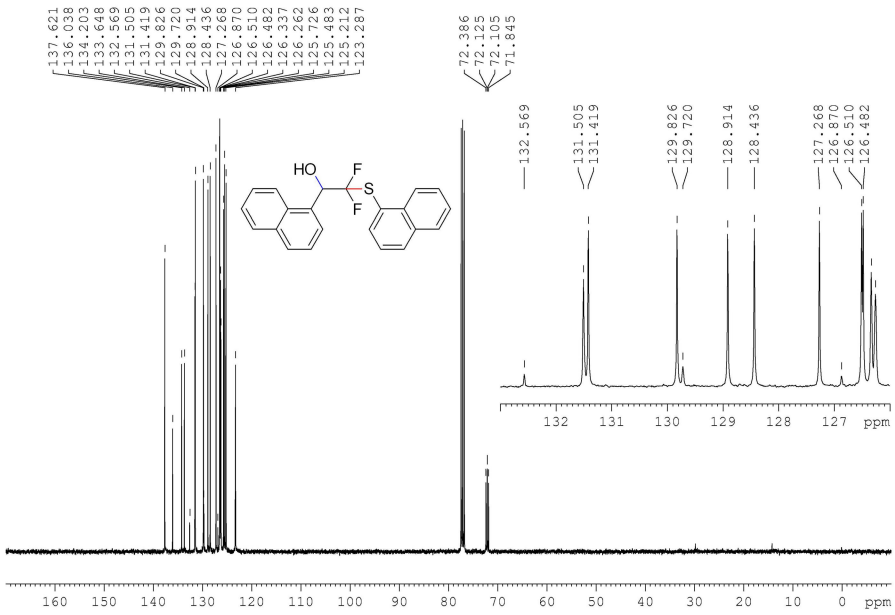
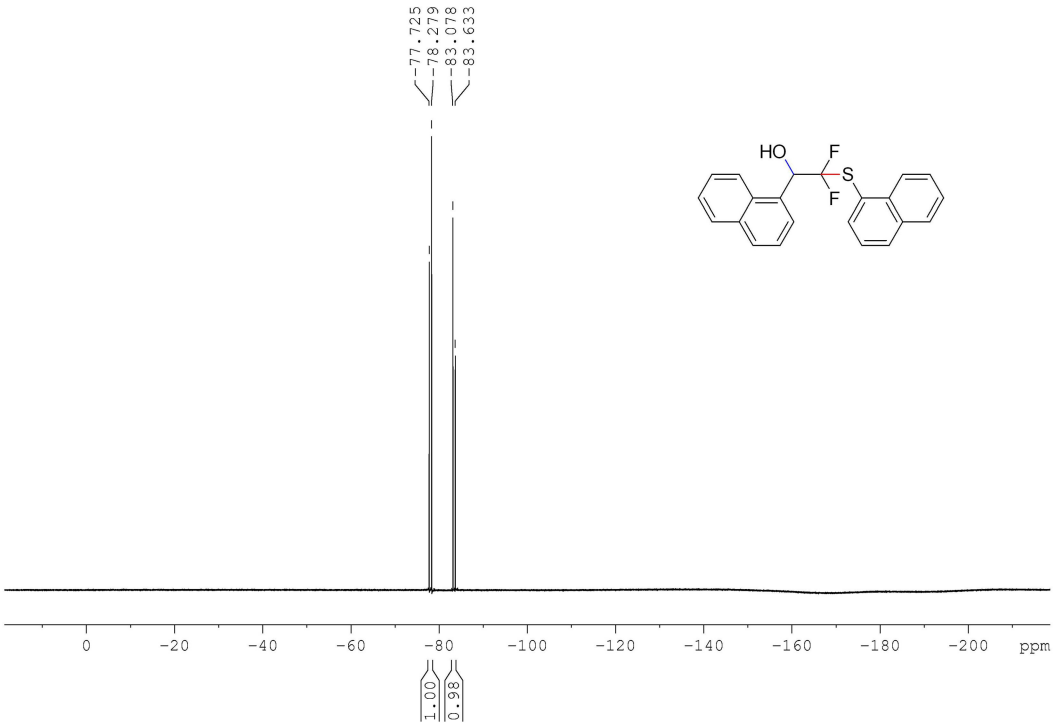
129.973
129.820
129.454
129.120
128.916
126.612
126.497
126.254
125.970
125.725
125.194
132 131 130 129 128 127 126 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-78.432
-78.442
-78.989
-78.999
-84.025
-84.044
-84.581
-84.601
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
1.00
1.02

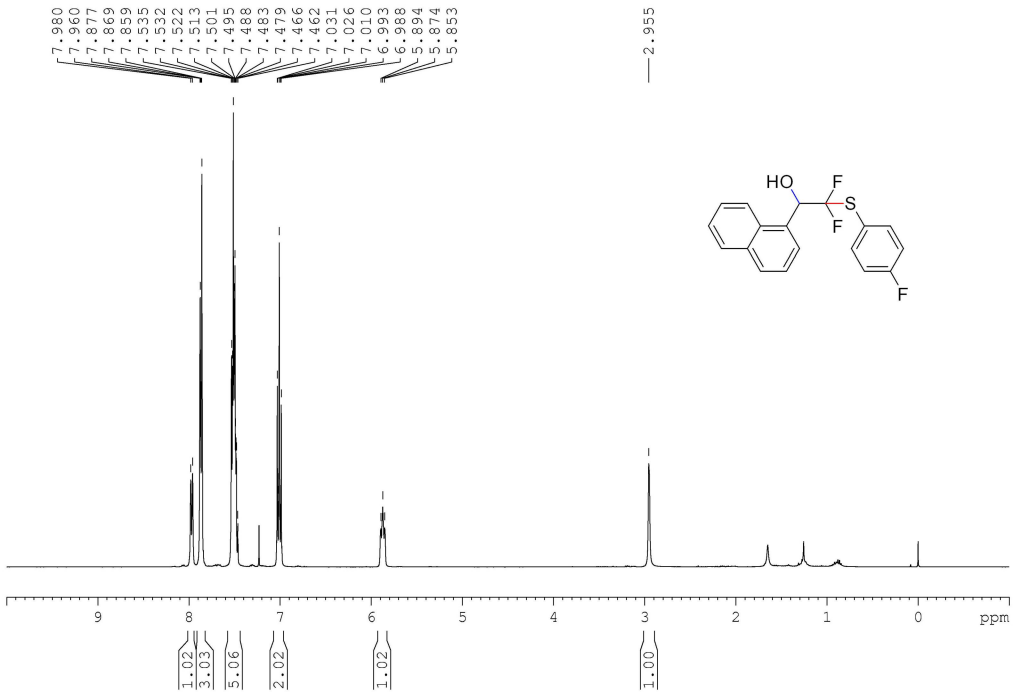
NMR spectra of **3ai**

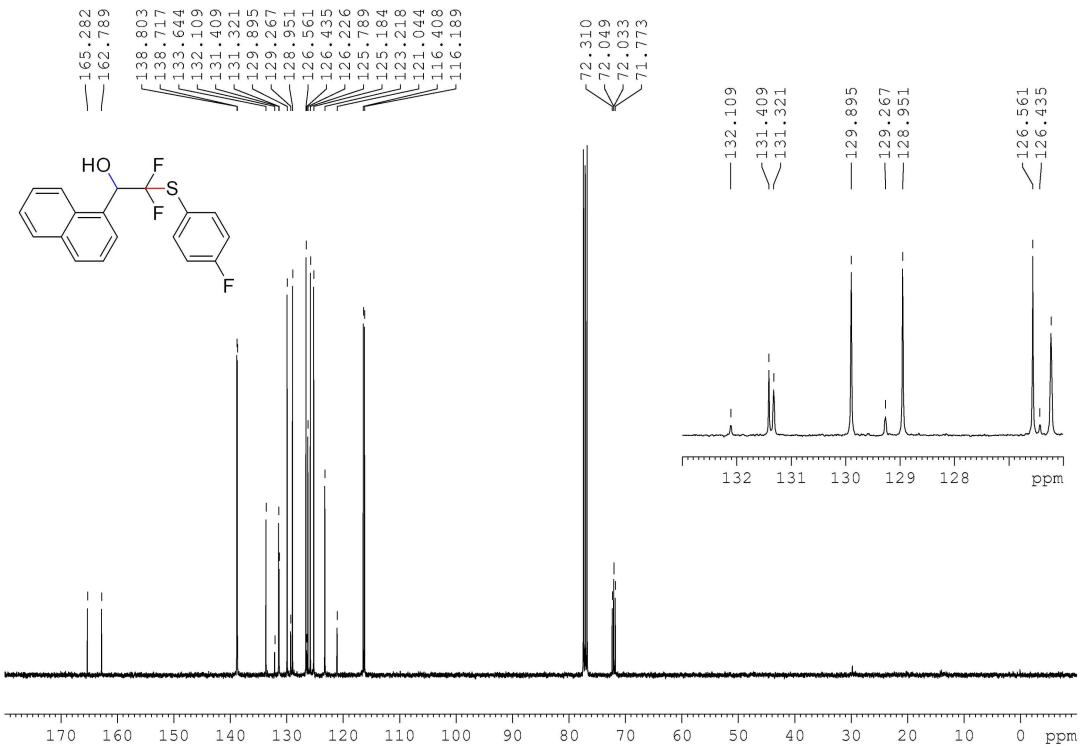


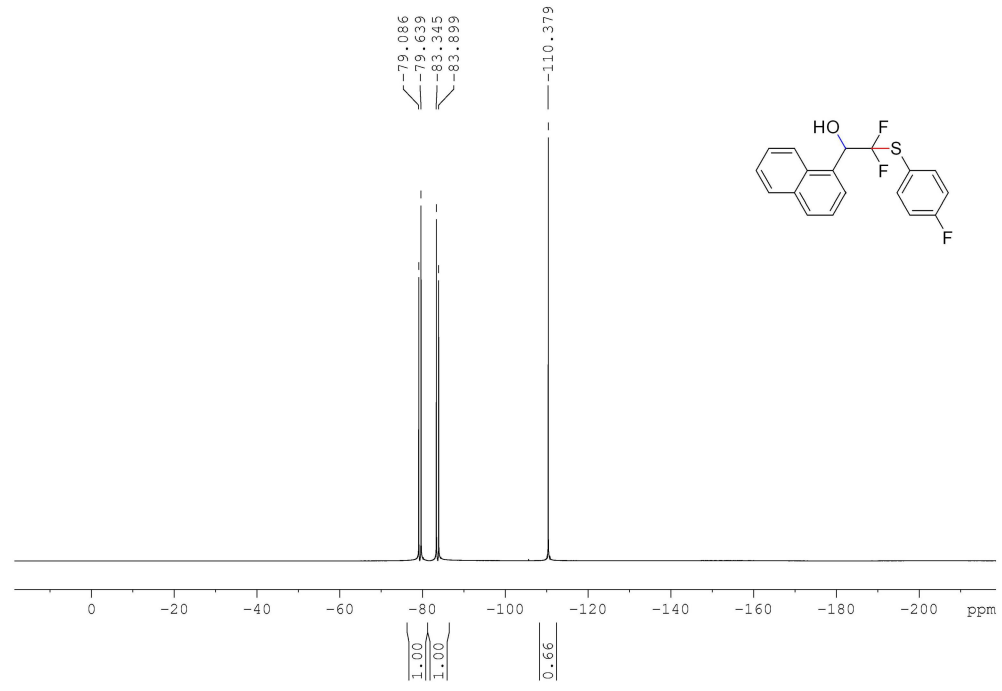




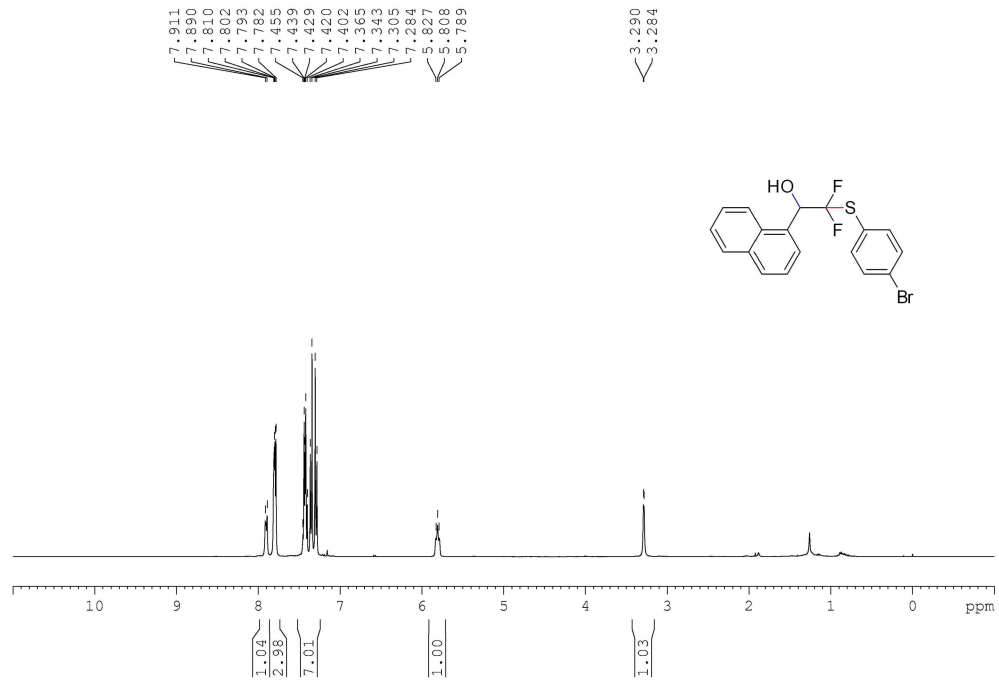
NMR spectra of **3aj**

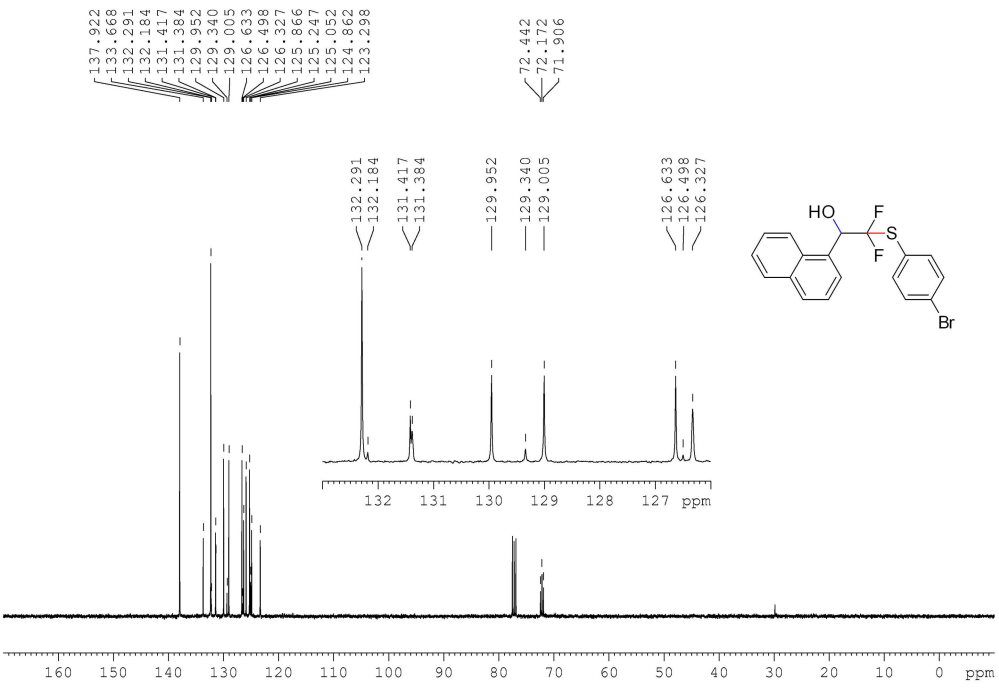


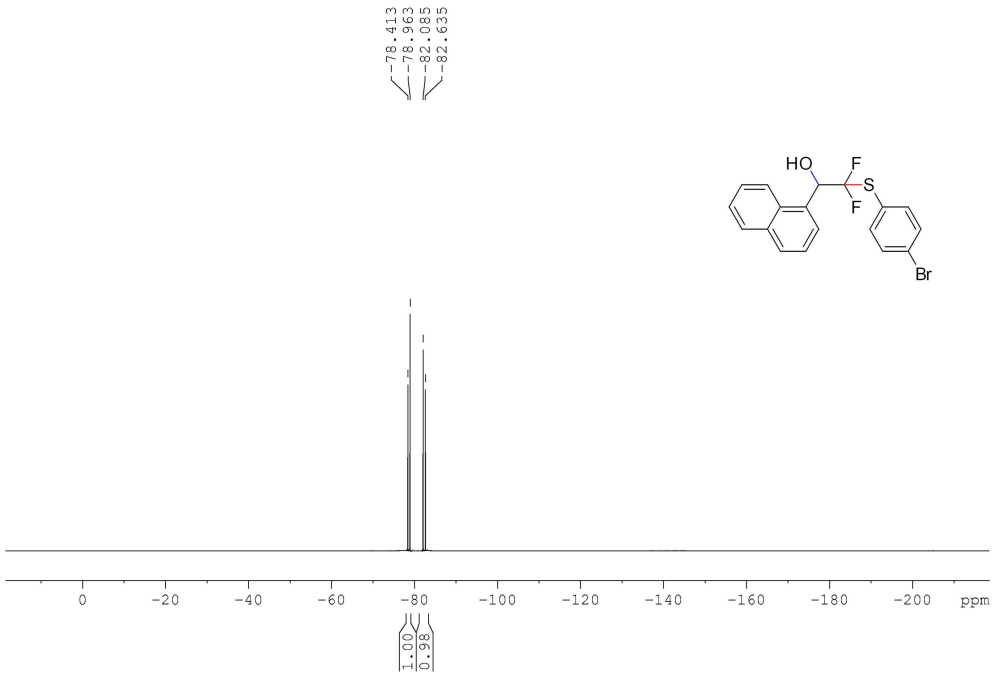

165.282
162.789
138.803
138.717
133.644
132.109
131.409
131.321
129.895
129.267
128.951
126.561
126.435
126.226
125.789
125.184
123.218
121.044
116.408
116.189
72.310
72.049
72.033
71.773
HO
F
S
F
F
132.109
131.409
131.321
129.895
129.267
128.951
126.561
126.435
132 131 130 129 128 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-79.086
-79.639
-83.345
-83.899
-110.379
HO
F
S
F
F
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
1.00
1.00
0.66

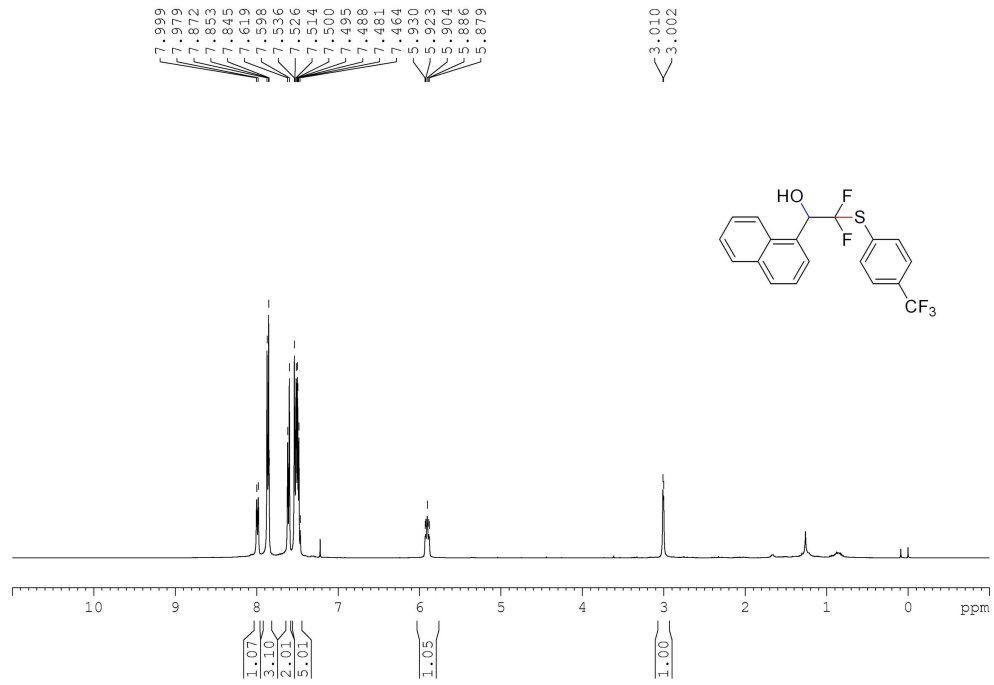
NMR spectra of **3ak**

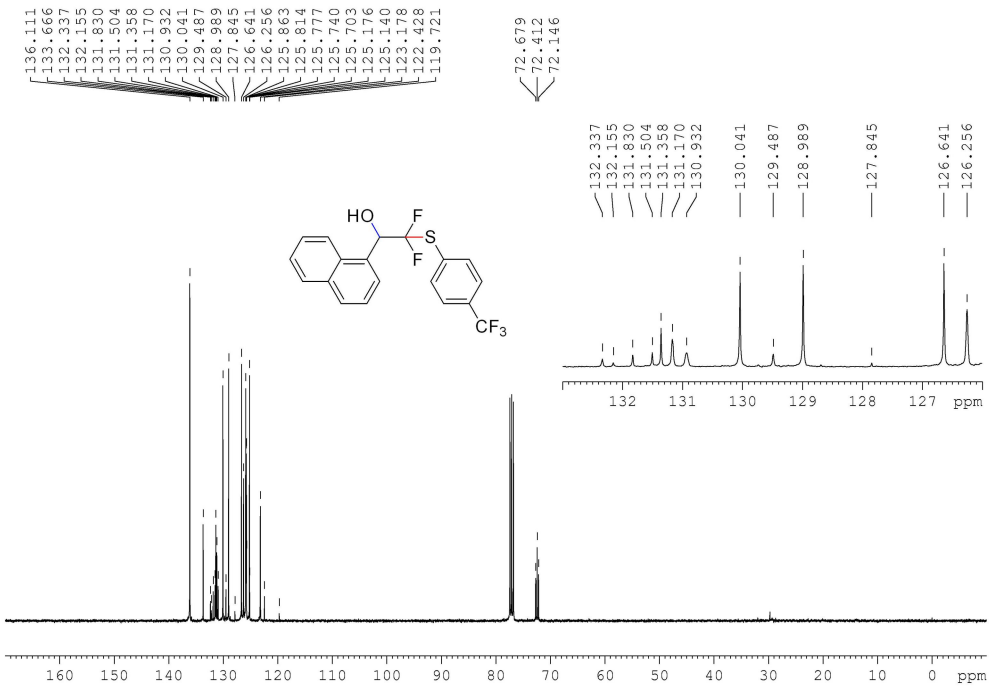


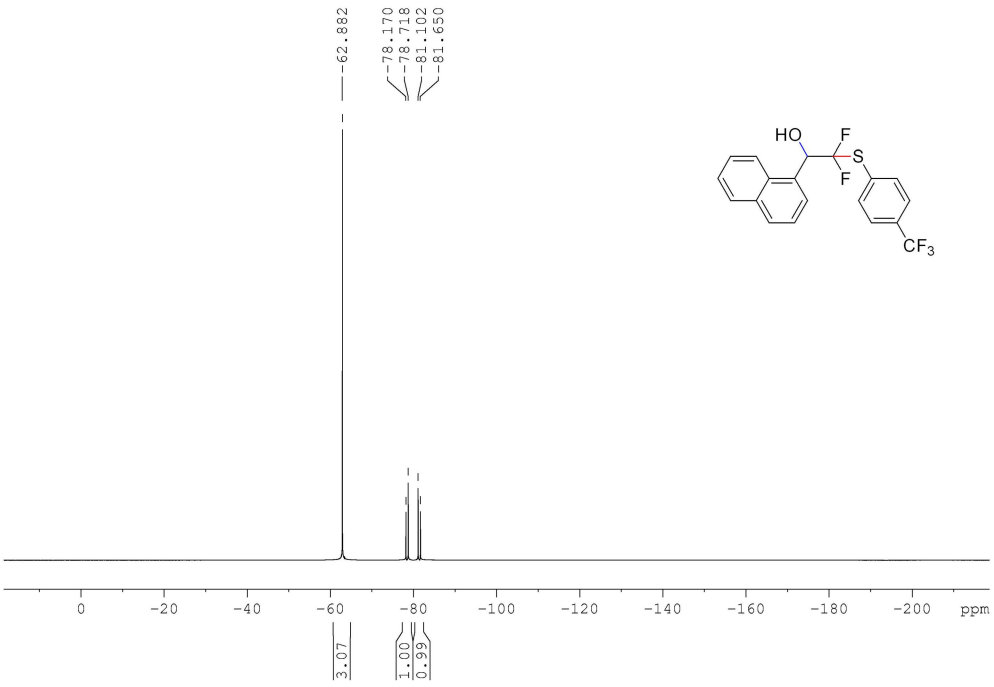




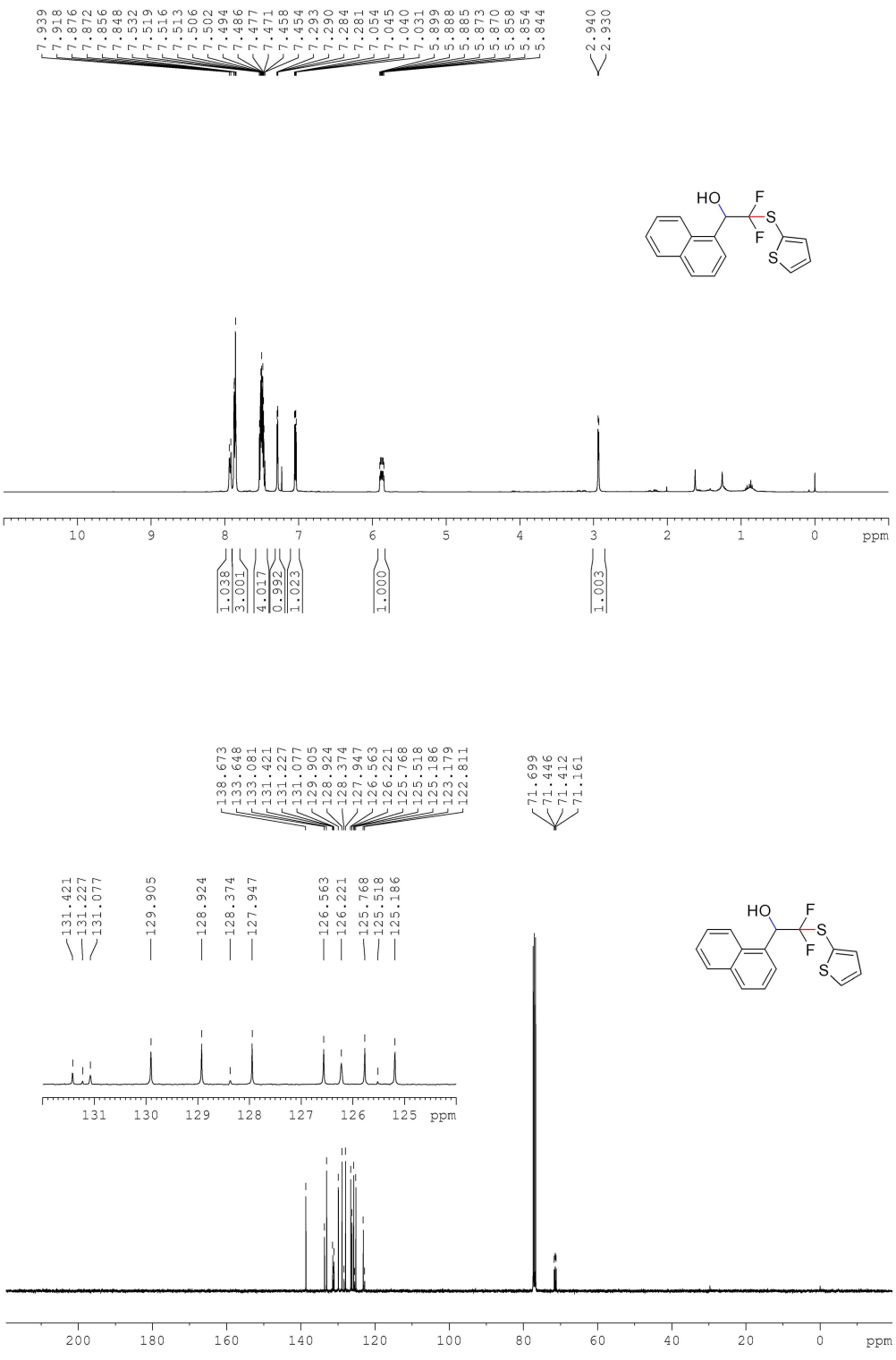
NMR spectra of **3al**

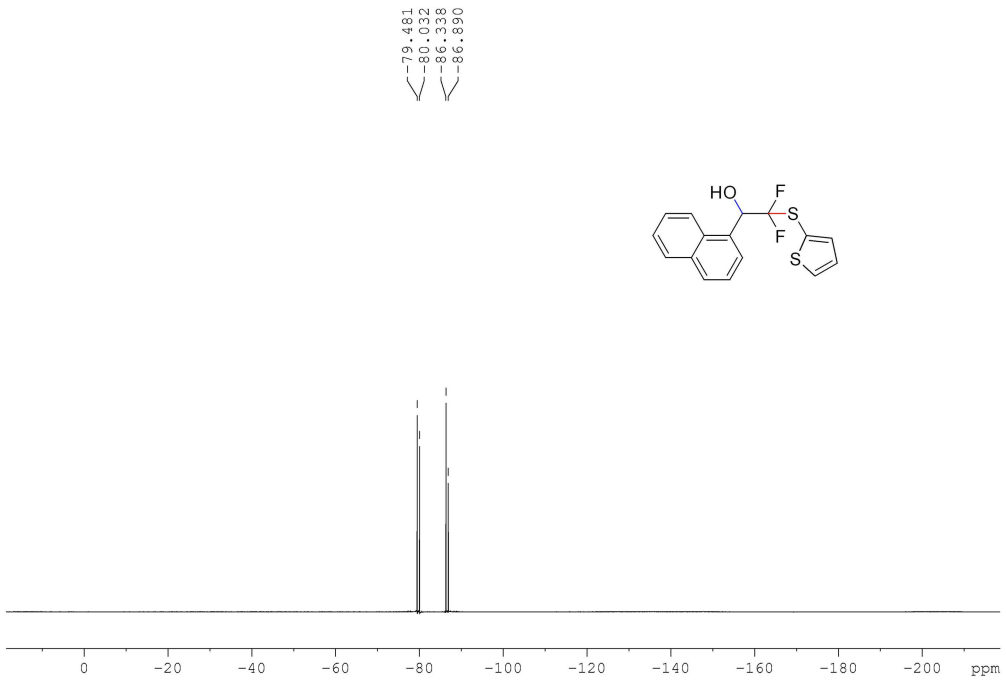



136.111
133.666
132.337
132.155
131.830
131.504
131.358
131.170
130.932
130.041
129.487
128.989
127.845
126.641
126.256
125.863
125.814
125.777
125.740
125.703
125.176
125.140
123.178
122.428
119.721
72.679
72.412
72.146
HO
F
S
F
CF3
132.337
132.155
131.830
131.504
131.358
131.170
130.932
130.041
129.487
128.989
127.845
126.641
126.256
132
131
130
129
128
127
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

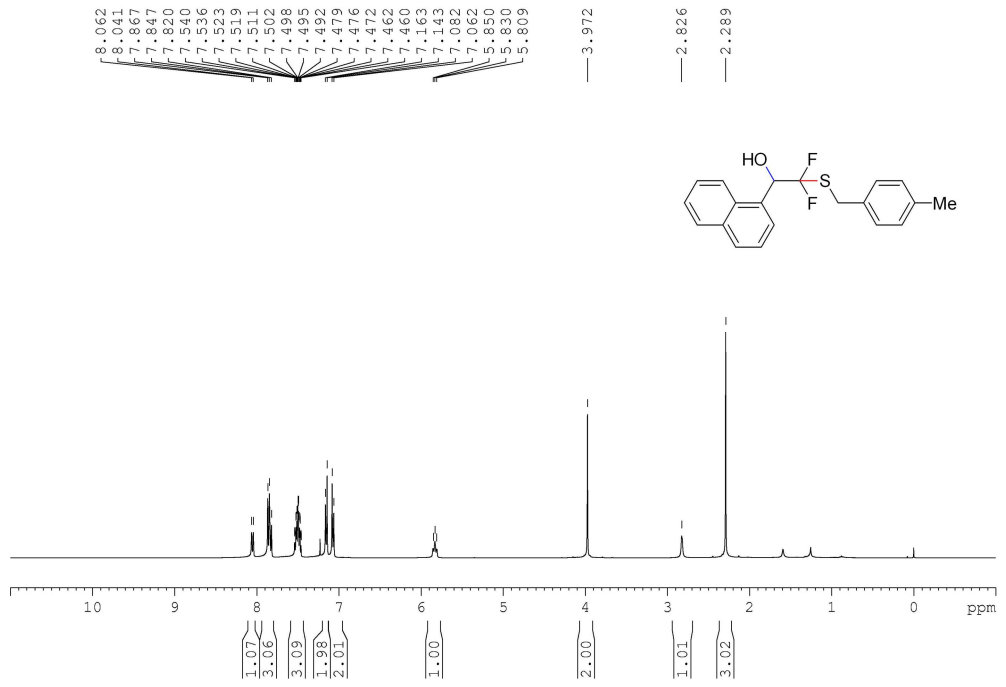

-62.882
-78.170
-78.718
-81.102
-81.650
HO
F
S
F
CF3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
3.07
1.00
0.99

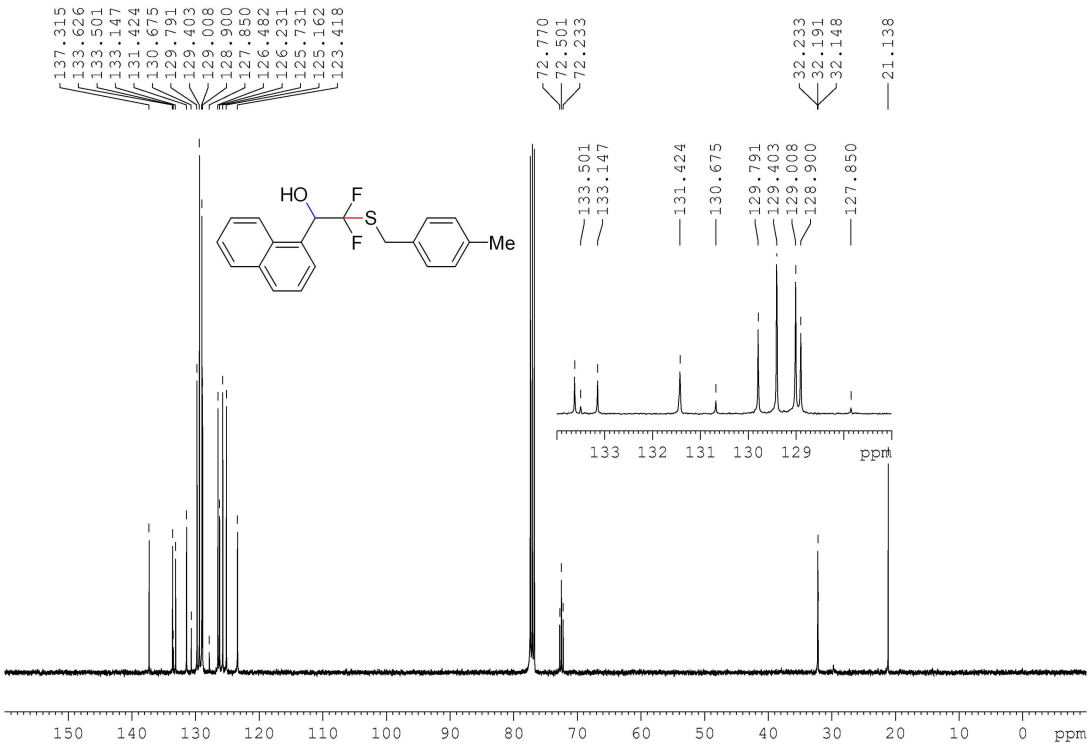
NMR spectra of **3am**

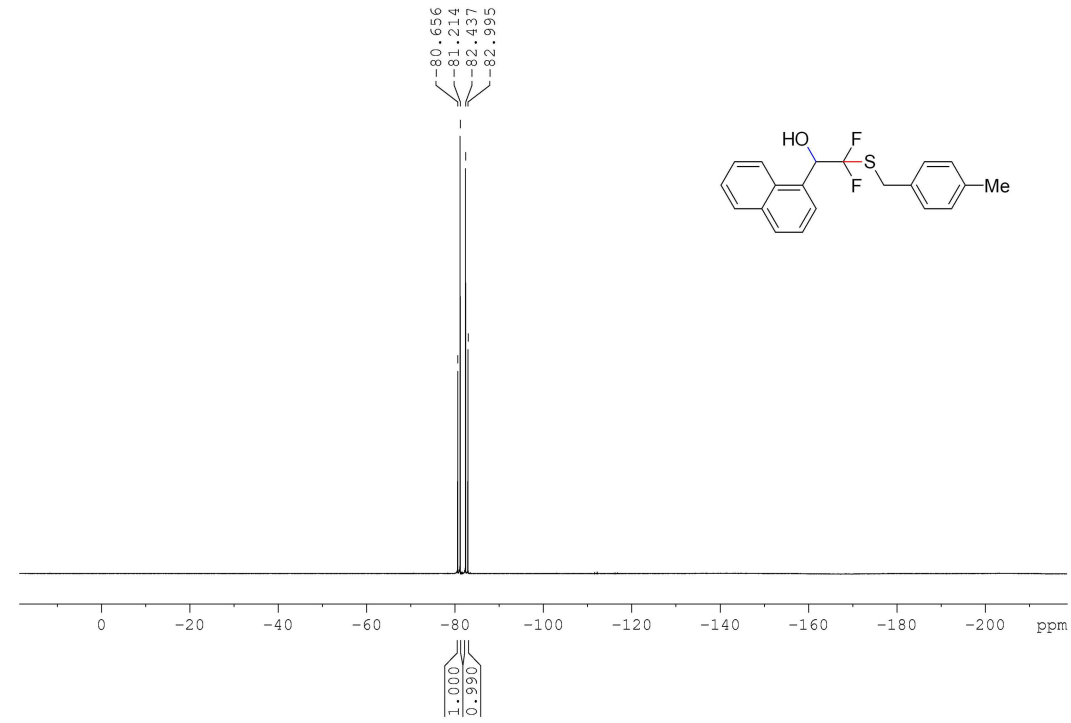




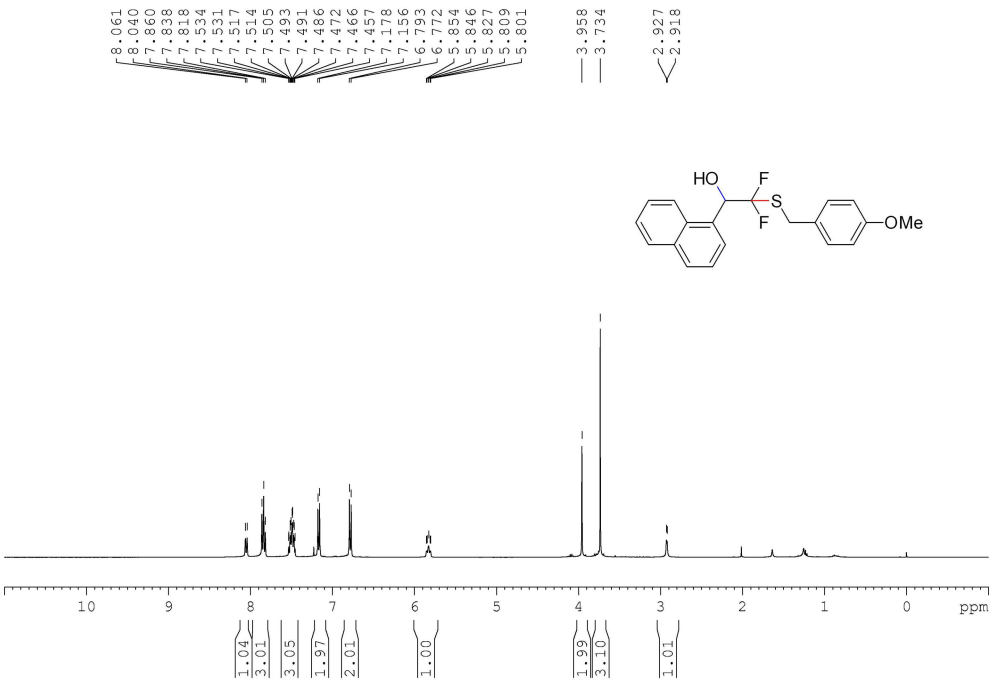
NMR spectra of **3an**

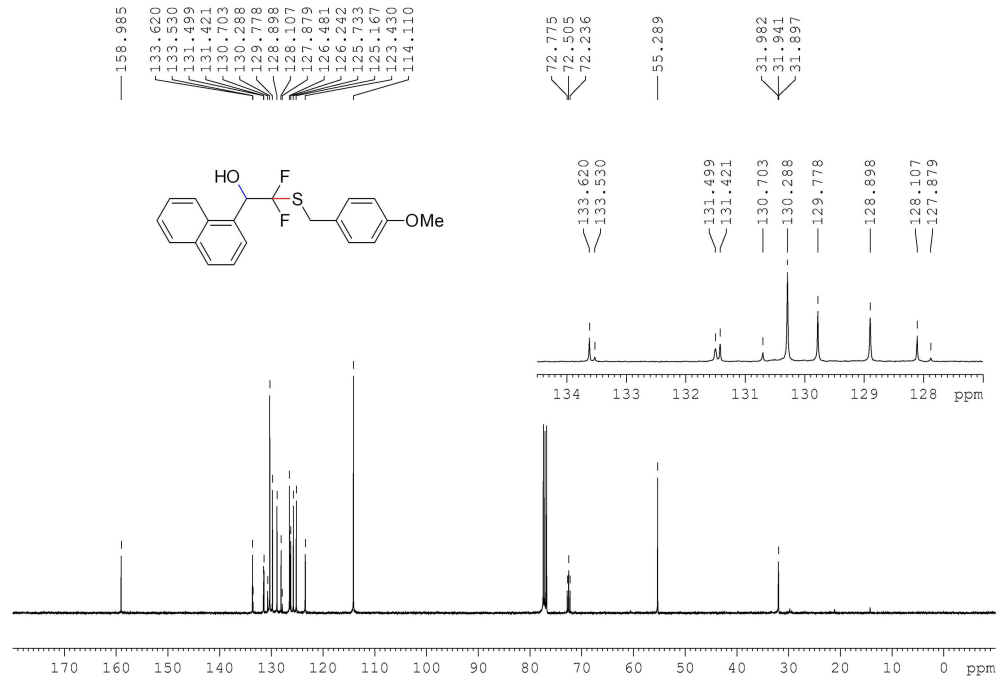


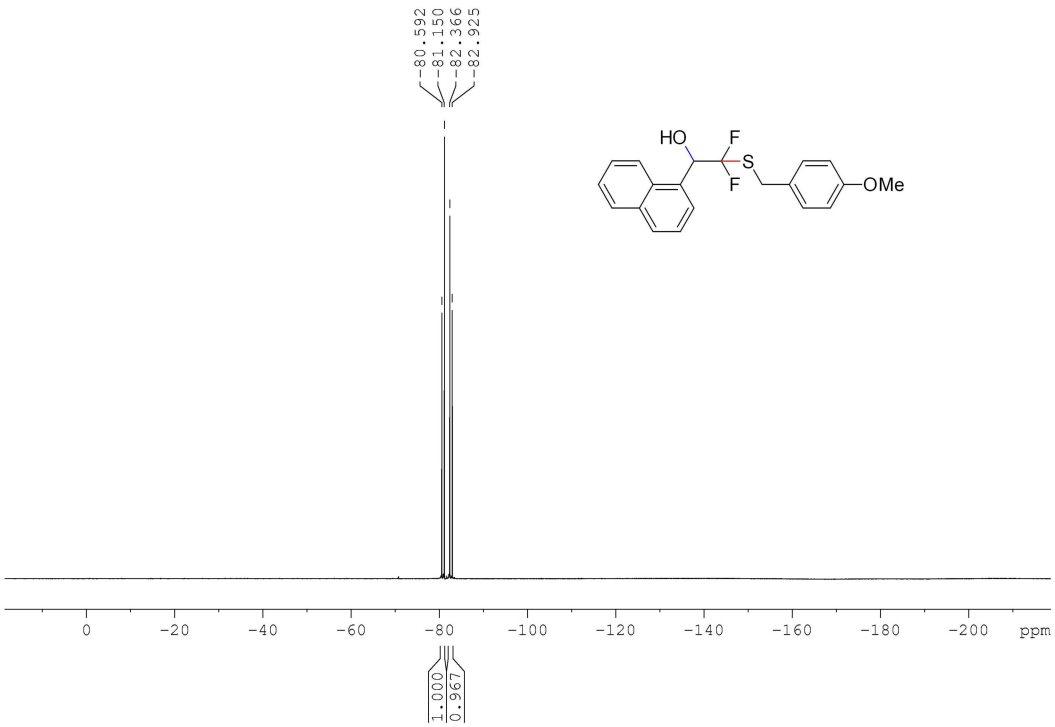

137.315
133.626
133.501
133.147
131.424
130.675
129.791
129.403
129.008
128.900
127.850
126.482
126.231
125.731
125.162
123.418
72.770
72.501
72.233
32.233
32.191
32.148
21.138
HO
F
S
F
Me
133.501
133.147
131.424
130.675
129.791
129.403
129.008
128.900
127.850
133 132 131 130 129 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-80.656
-81.214
-82.437
-82.995
HO
F
S
F
Me
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
1.000
0.990

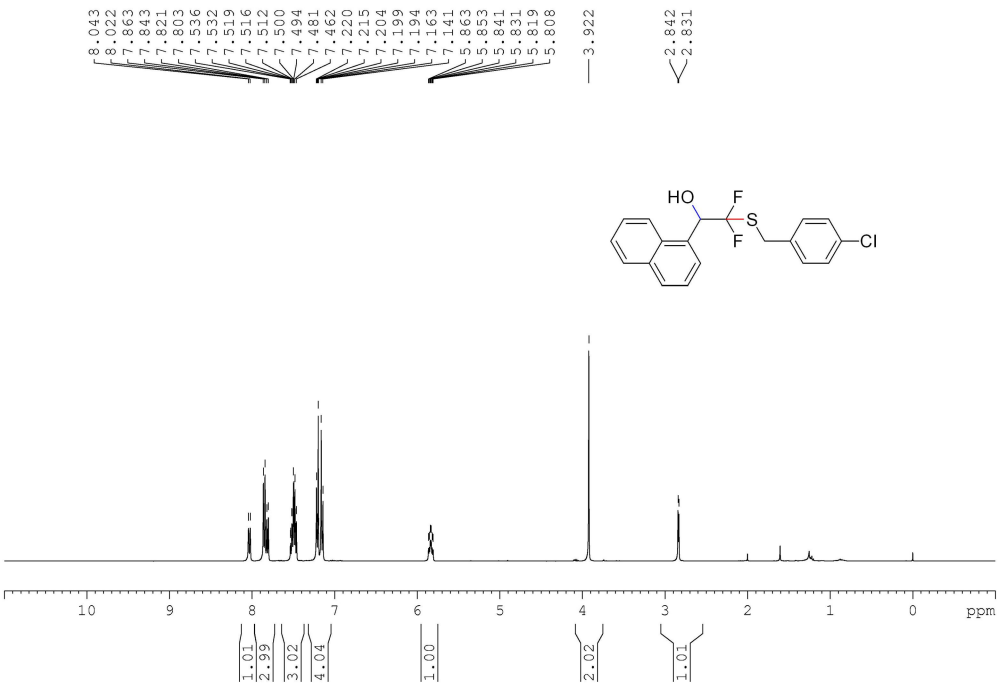
NMR spectra of **3ao**

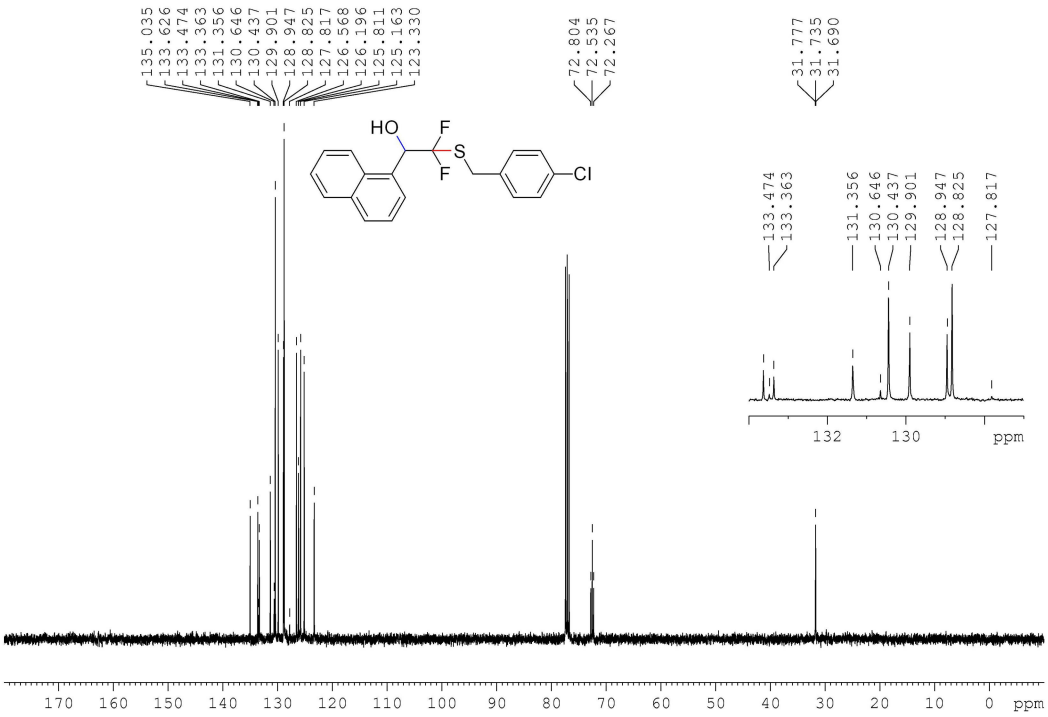


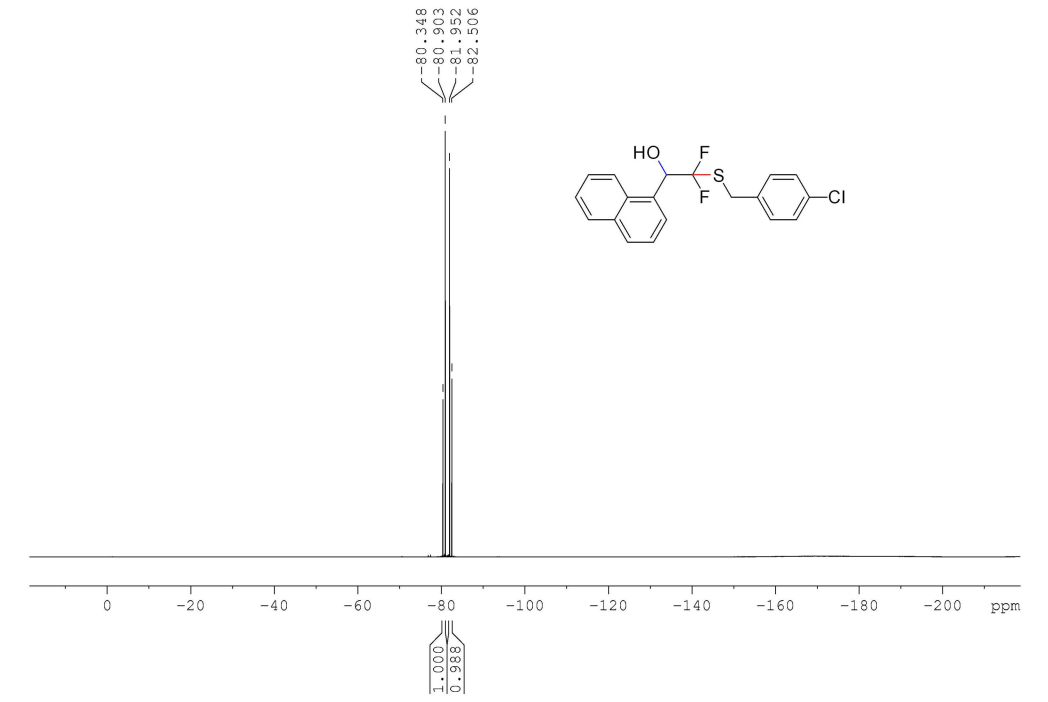




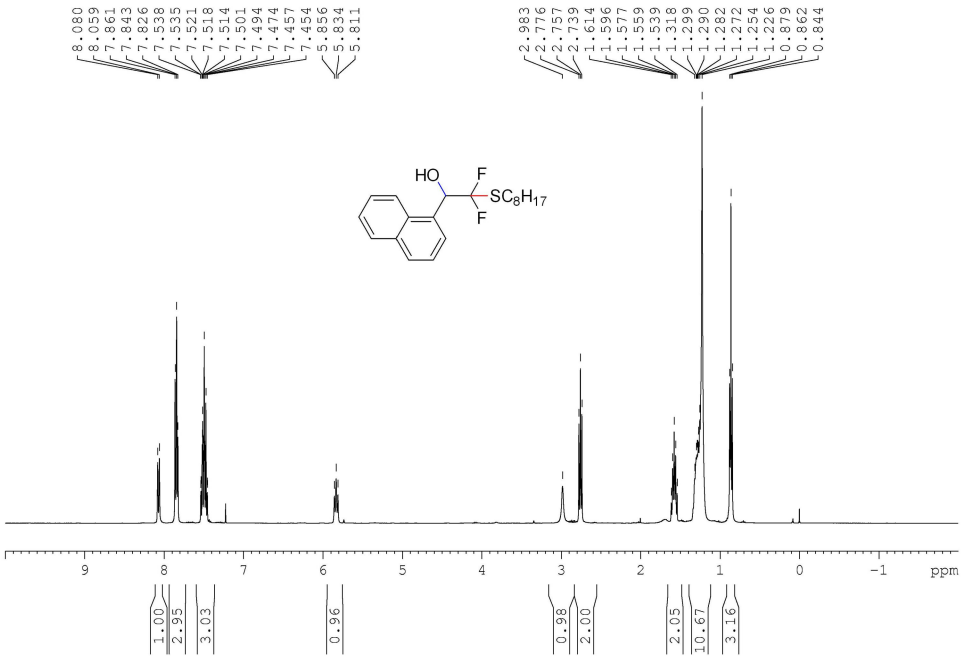
NMR spectra of **3ap**

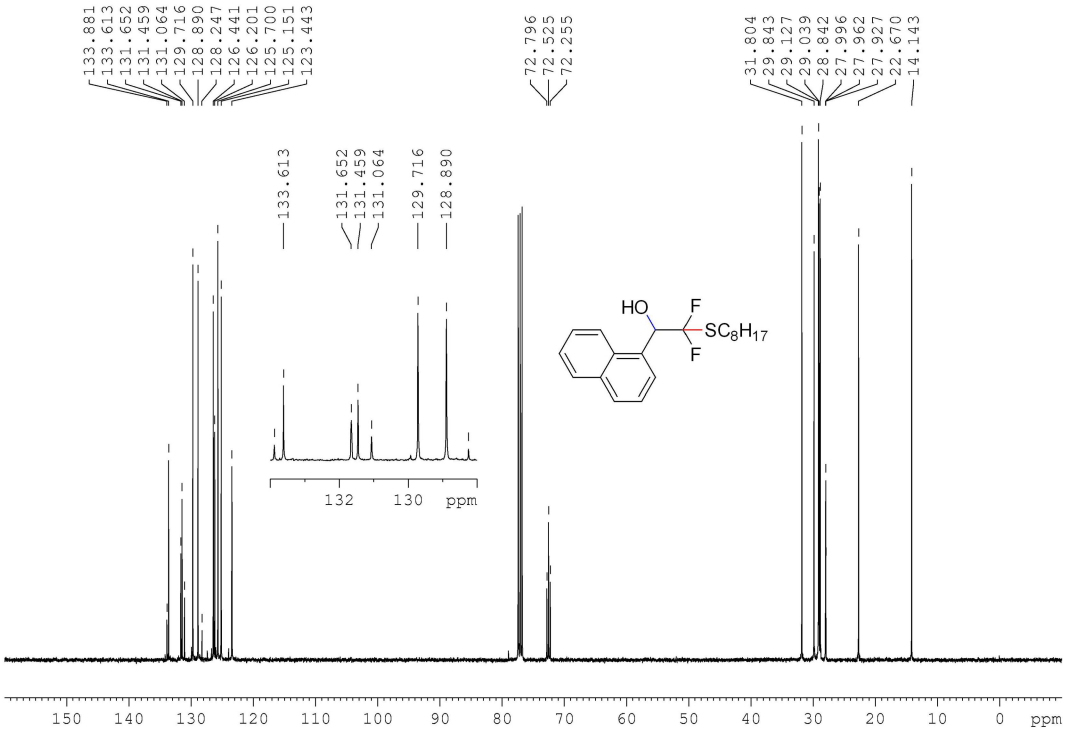


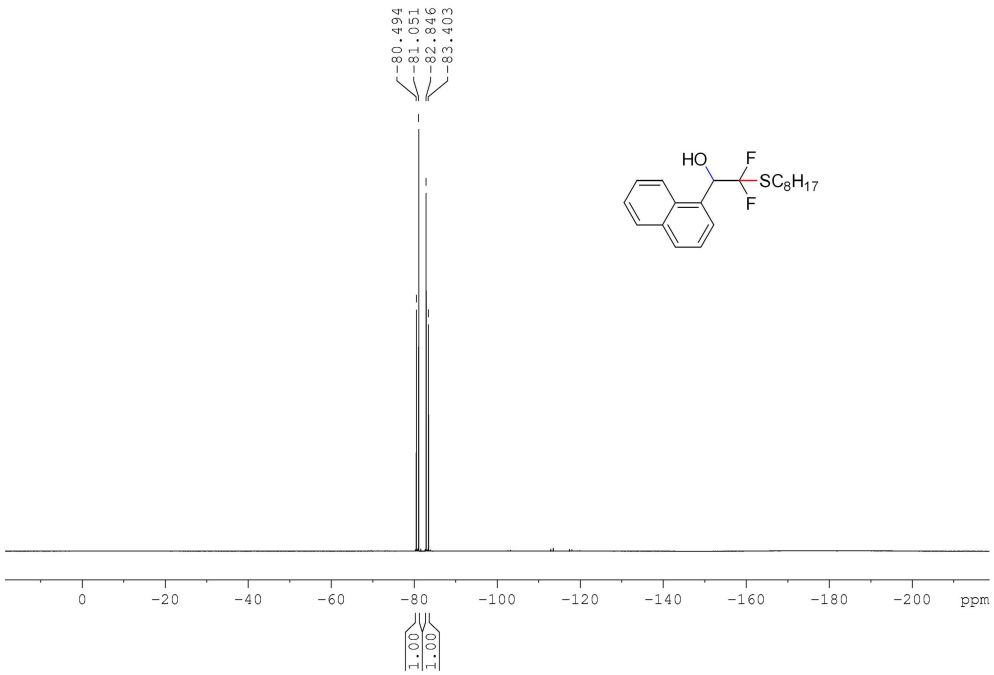

135.035
133.626
133.474
133.363
131.356
130.646
130.437
129.901
128.947
128.825
127.817
126.568
126.196
125.811
125.163
123.330
72.804
72.535
72.267
31.777
31.735
31.690
HO
F
S
F
Cl
133.474
133.363
131.356
130.646
130.437
129.901
128.947
128.825
127.817
132
130
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-80.348
-80.903
-81.952
-82.506
HO
F
S
F
Cl
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
1.000
0.988

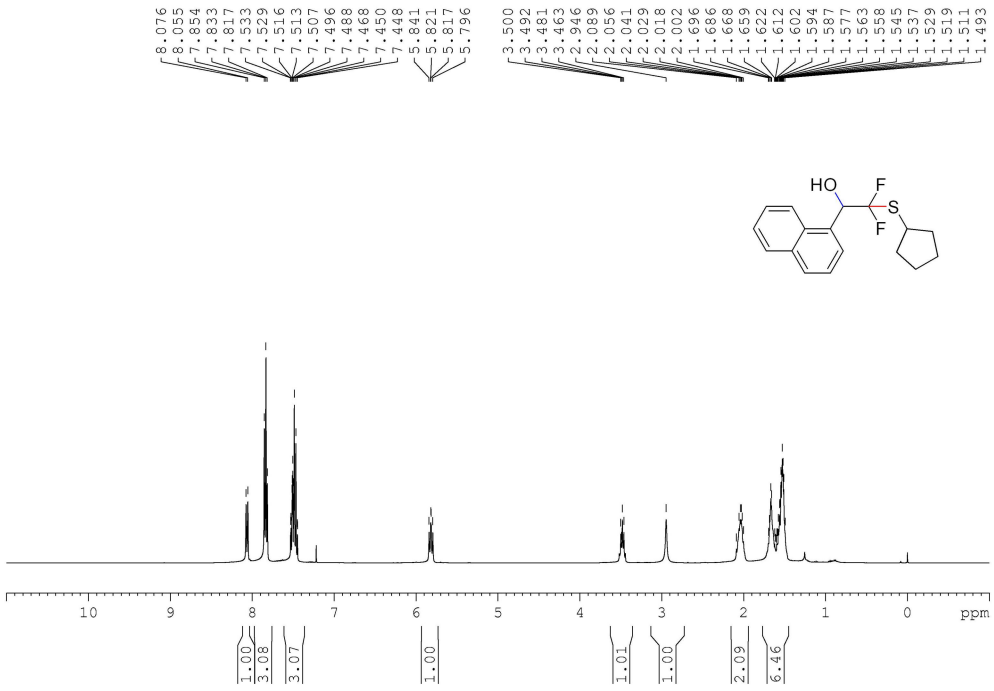
NMR spectra of **3aq**

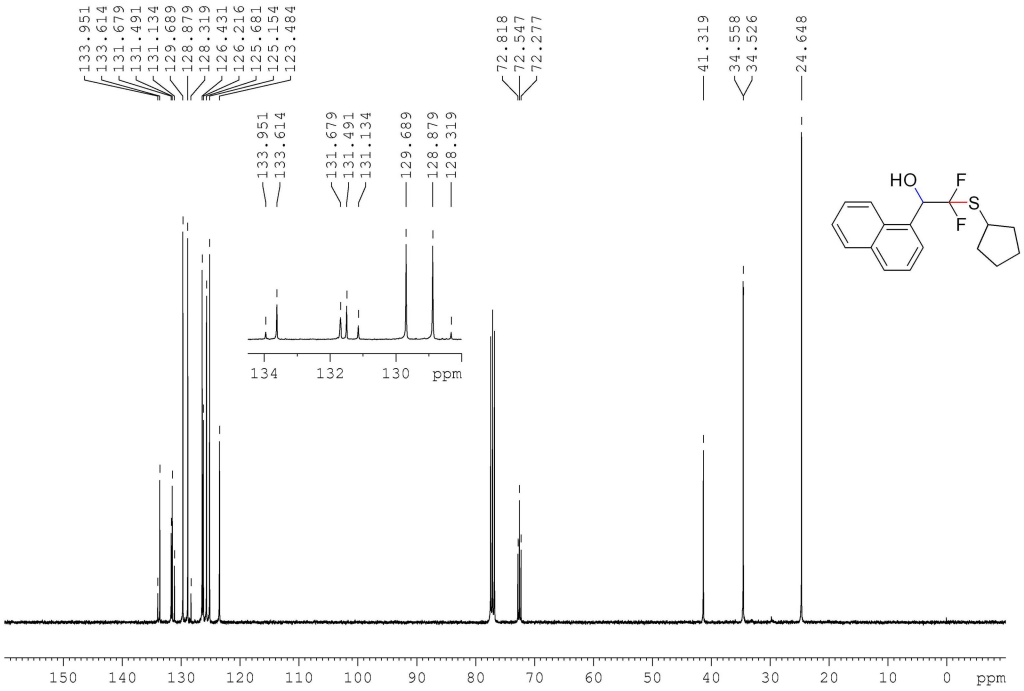


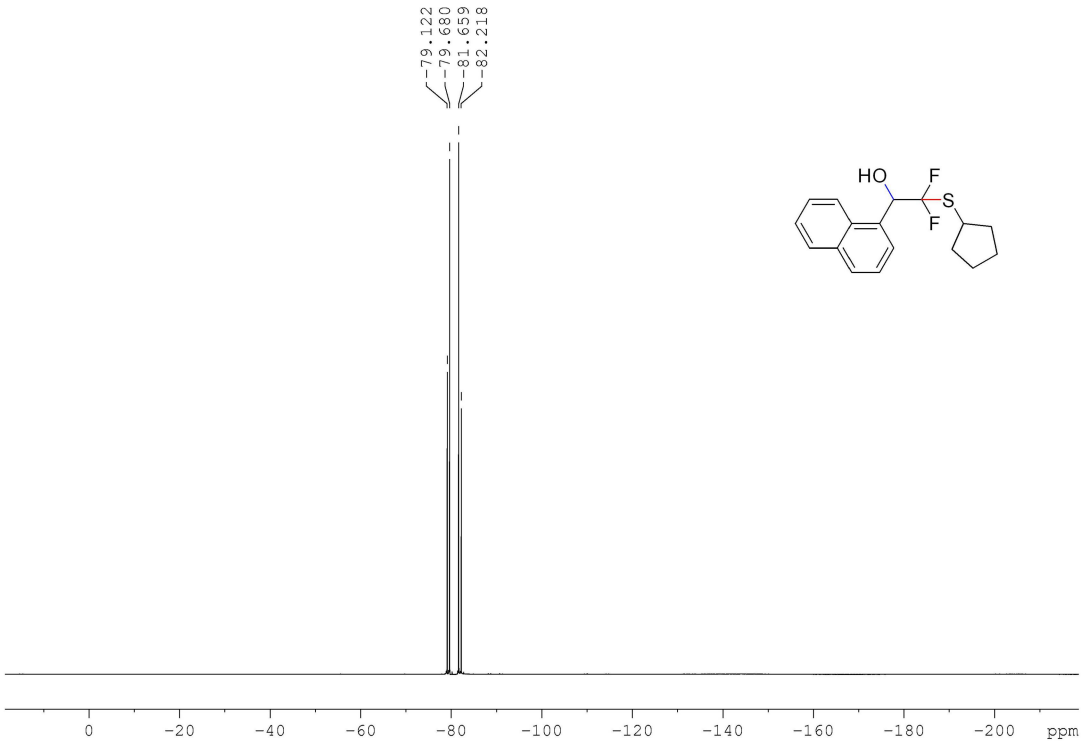




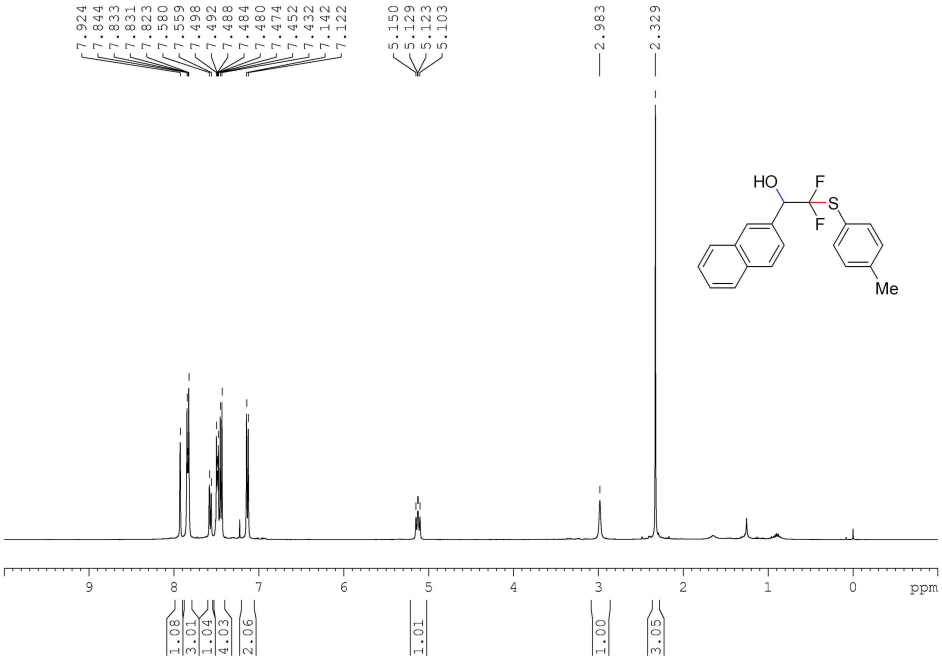
NMR spectra of **3ar**

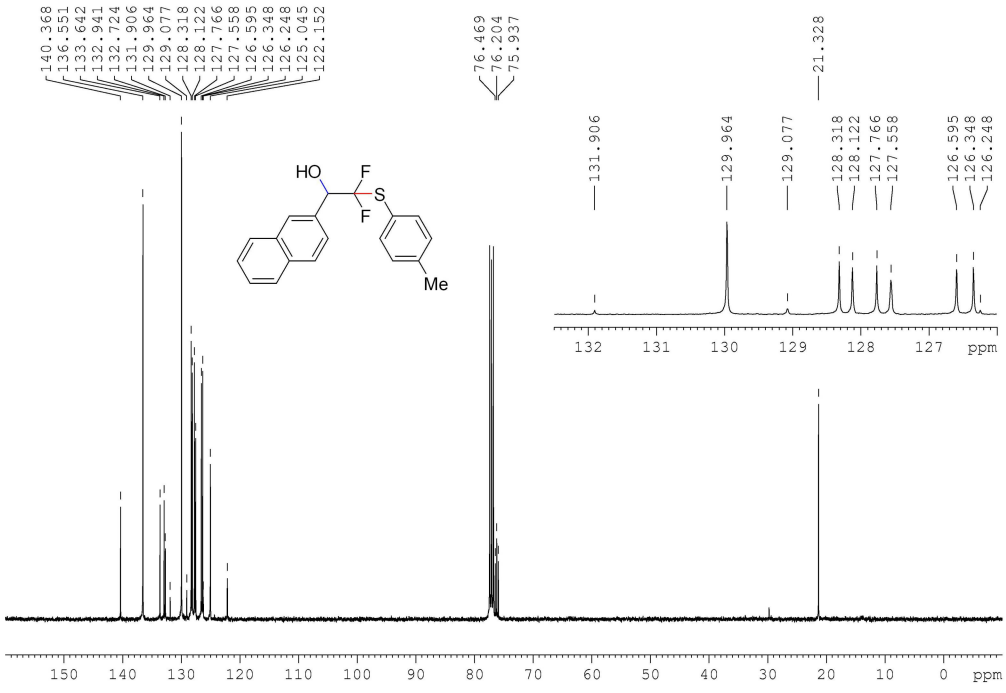


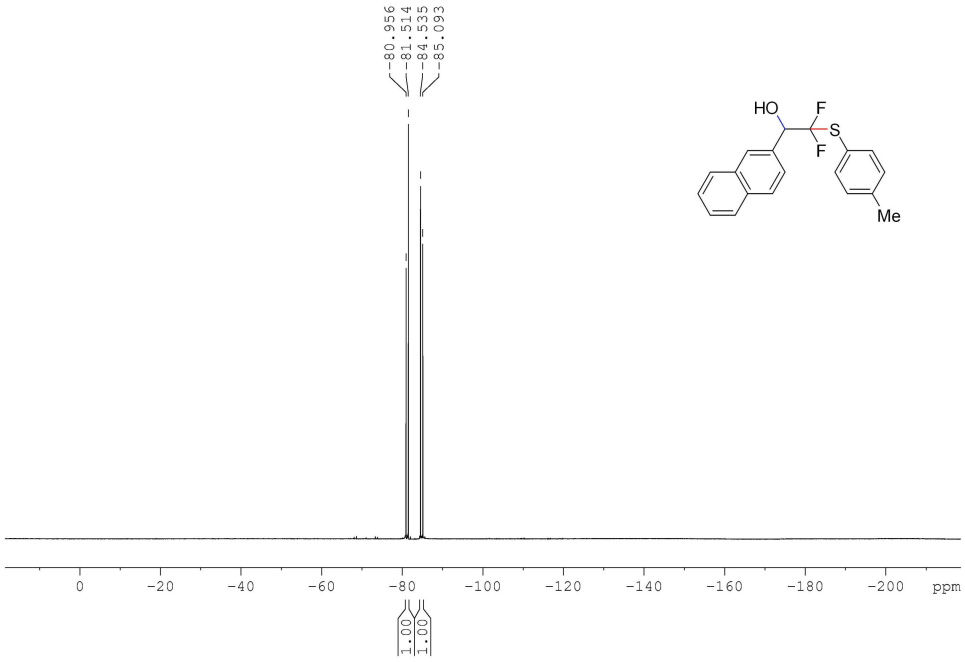

133.951
133.614
131.679
131.491
131.134
129.689
128.879
128.319
126.431
126.216
125.681
125.154
123.484
72.818
72.547
72.277
41.319
34.558
34.526
24.648
HO
F
S
F
134
132
130
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-79.122
-79.680
-81.659
-82.218
HO
F
S
F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

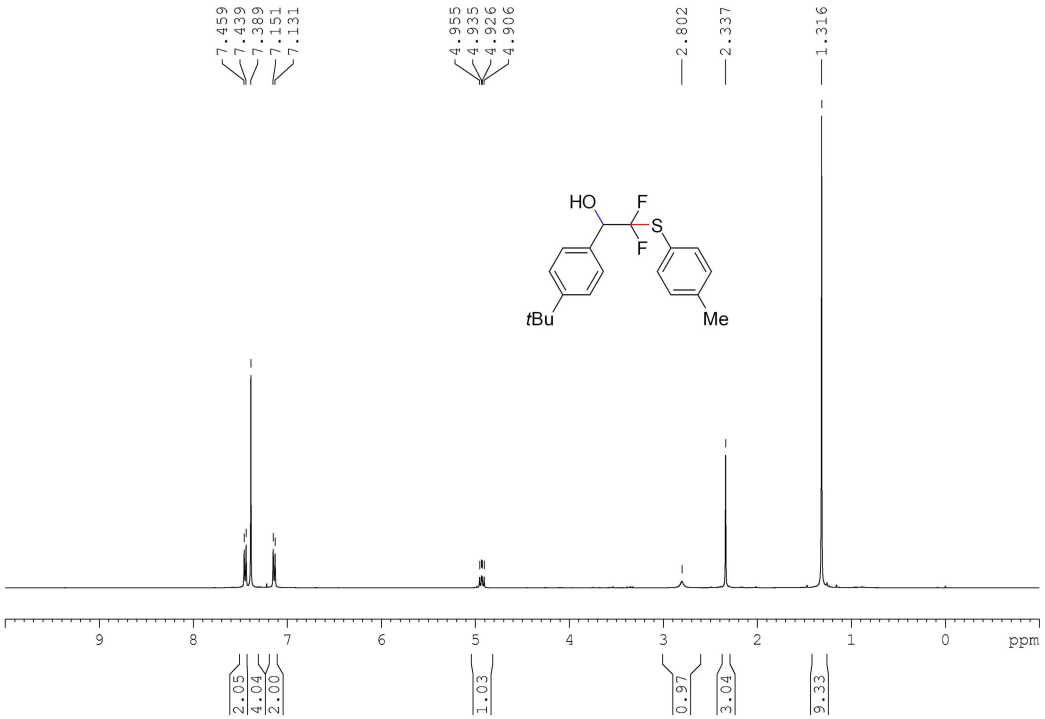
NMR spectra of **3ba**

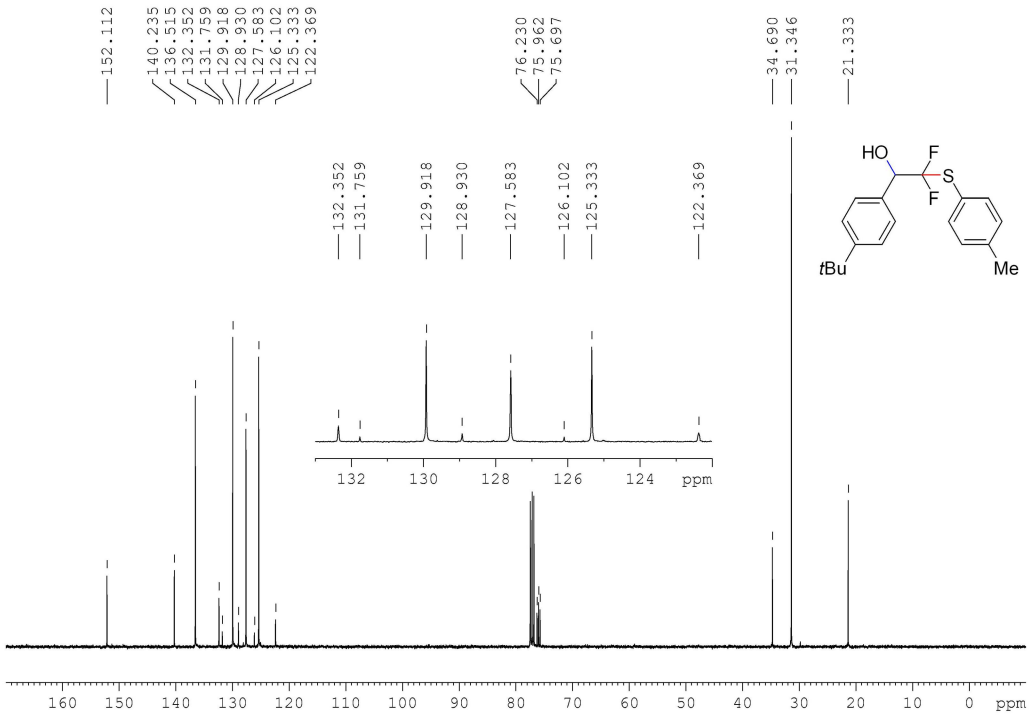


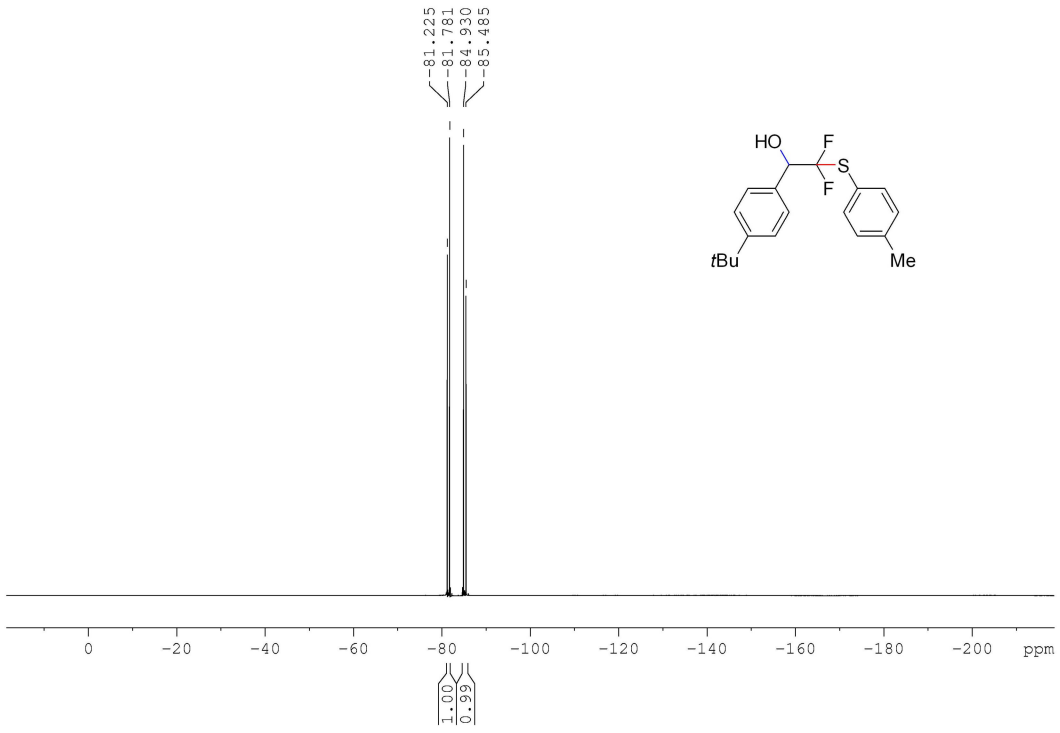




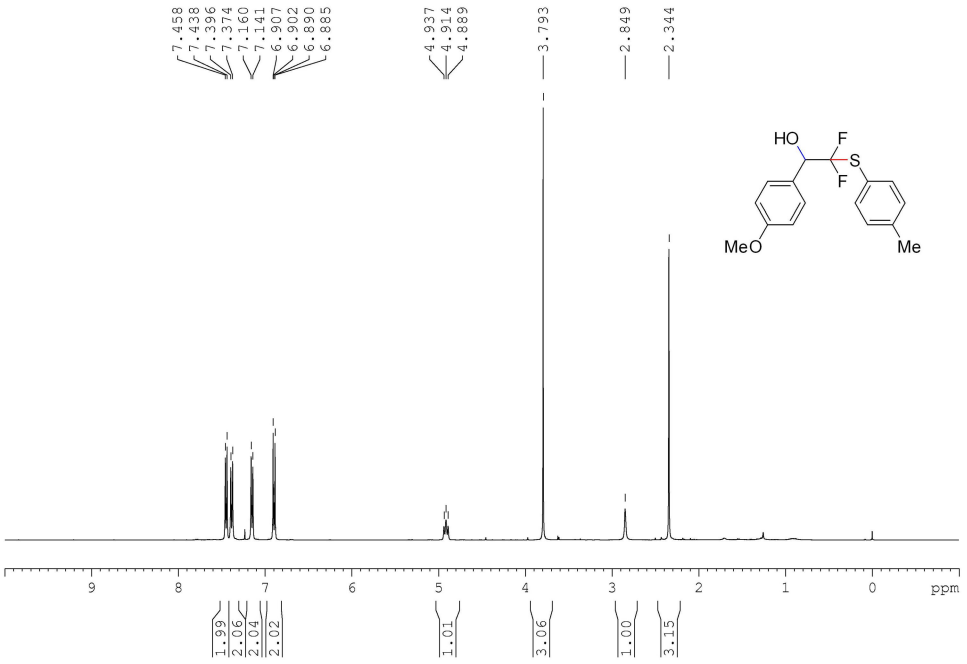
NMR spectra of **3ca**

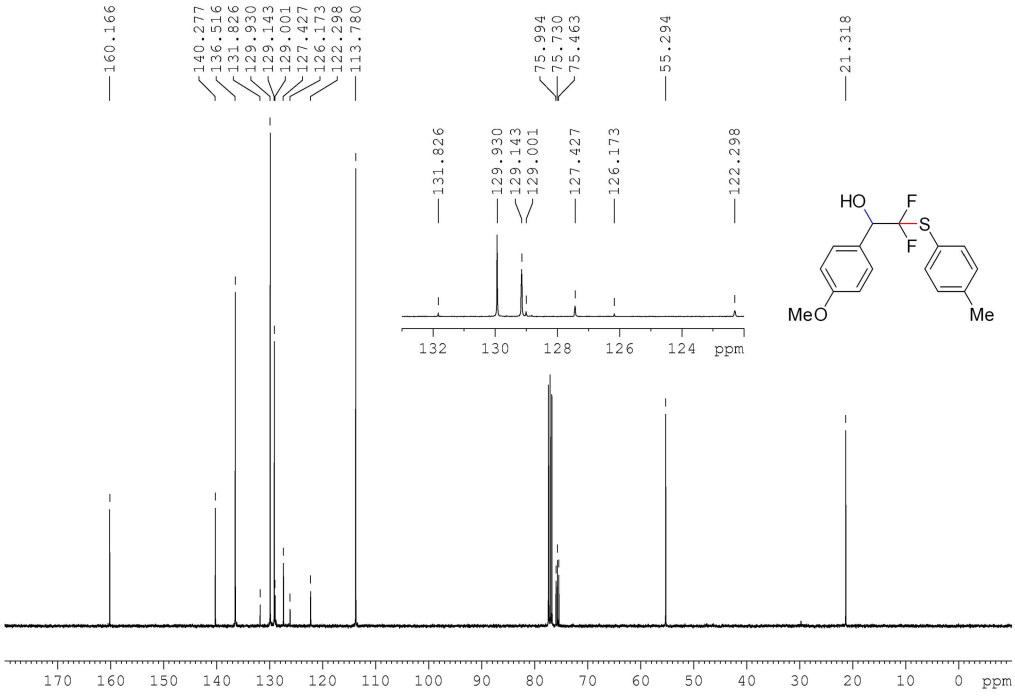


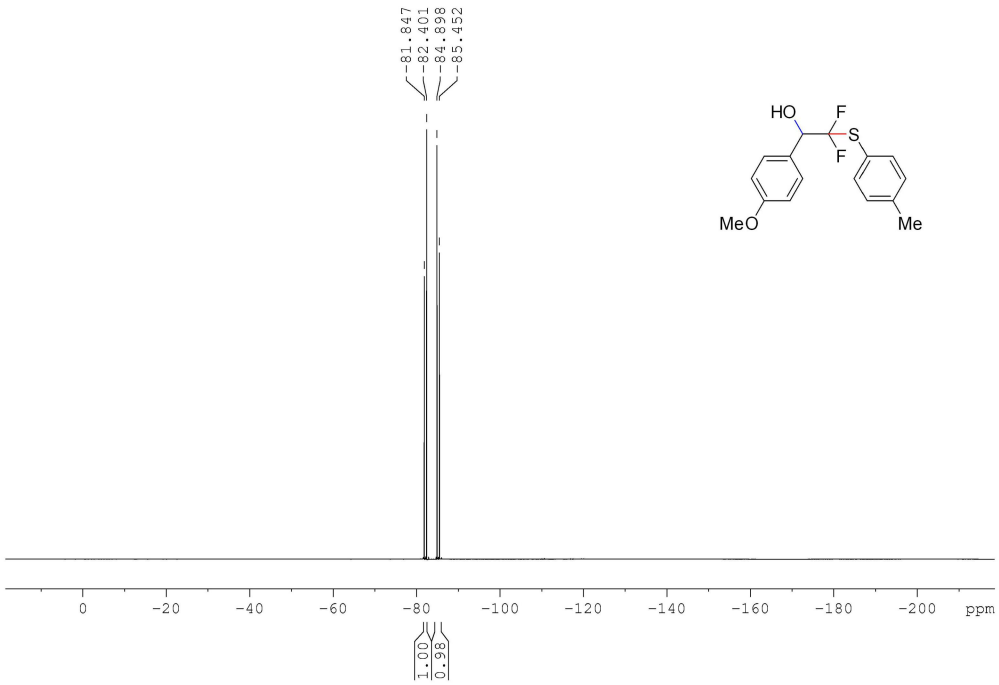

152.112
140.235
136.515
132.352
131.759
129.918
128.930
127.583
126.102
125.333
122.369
76.230
75.962
75.697
34.690
31.346
21.333
HO
F
S
F
tBu
Me
ppm


81.225
81.781
84.930
85.485
HO
F
S
F
tBu
Me
ppm
1.00
0.99

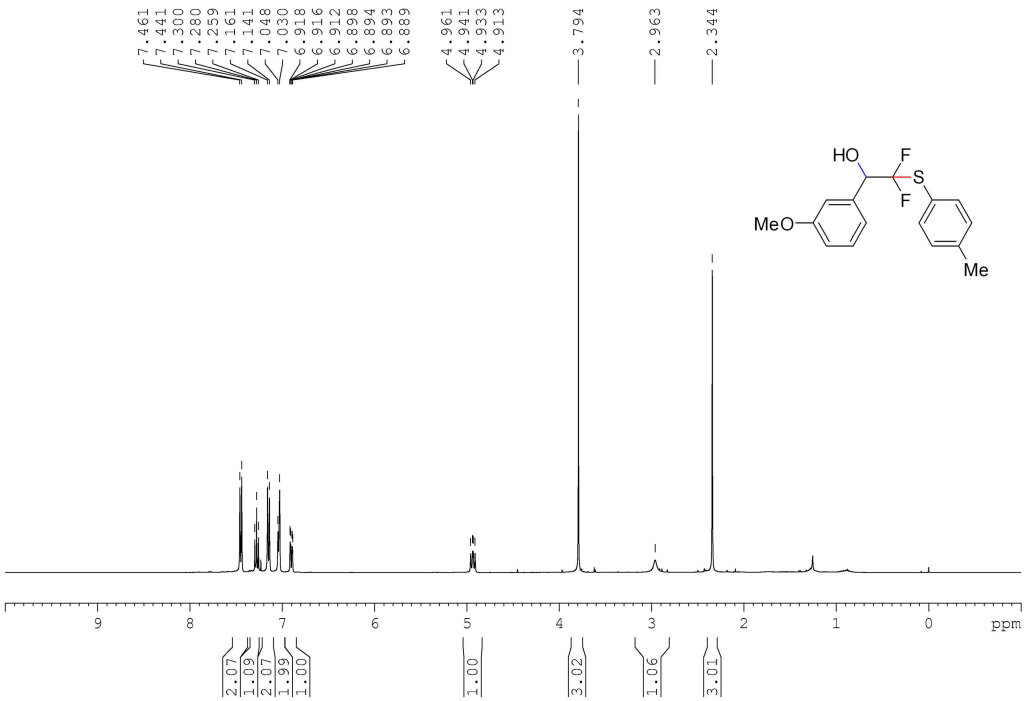
NMR spectra of **3da**

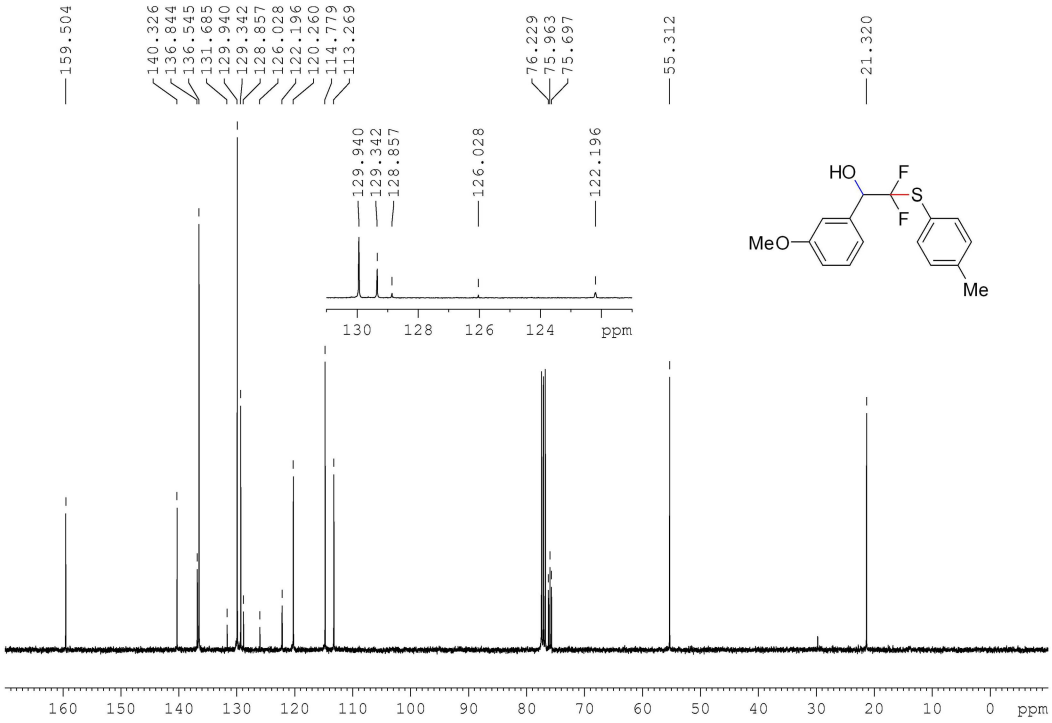


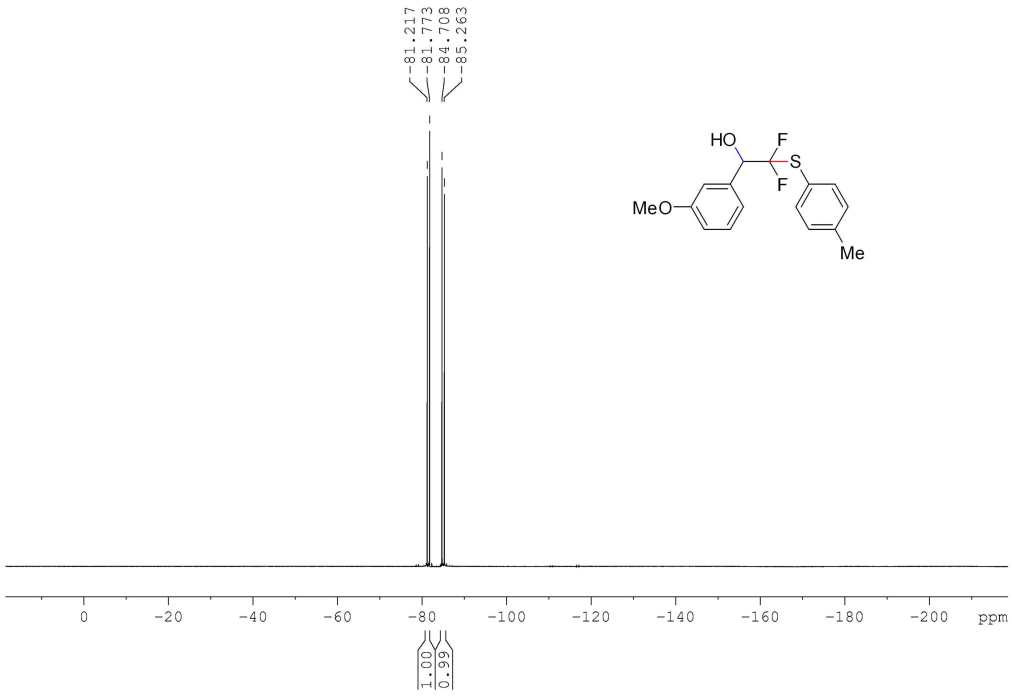




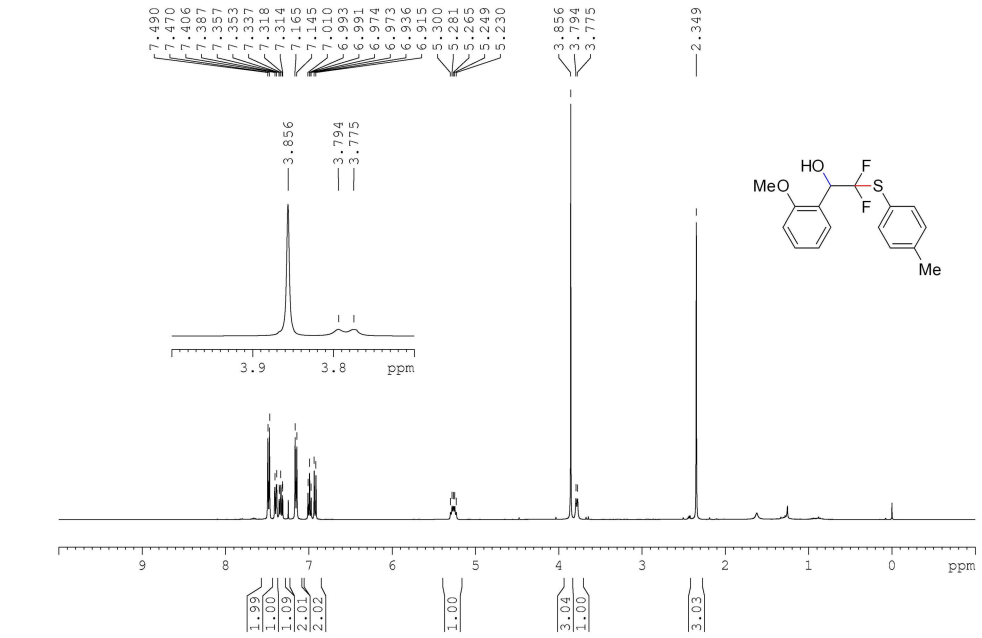
NMR spectra of **3ea**

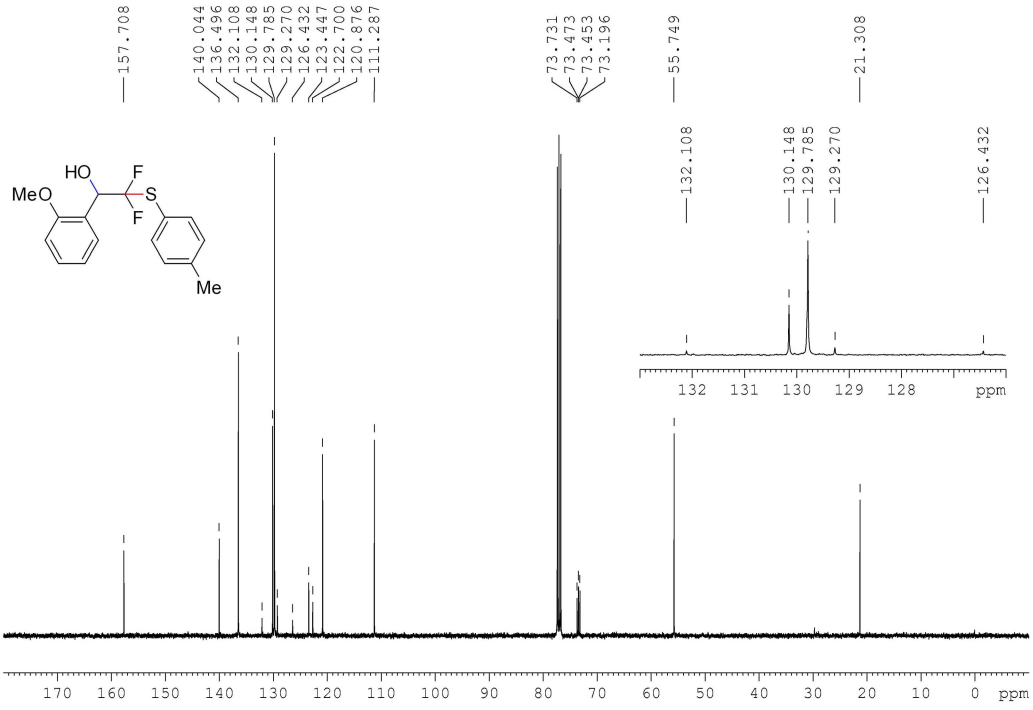


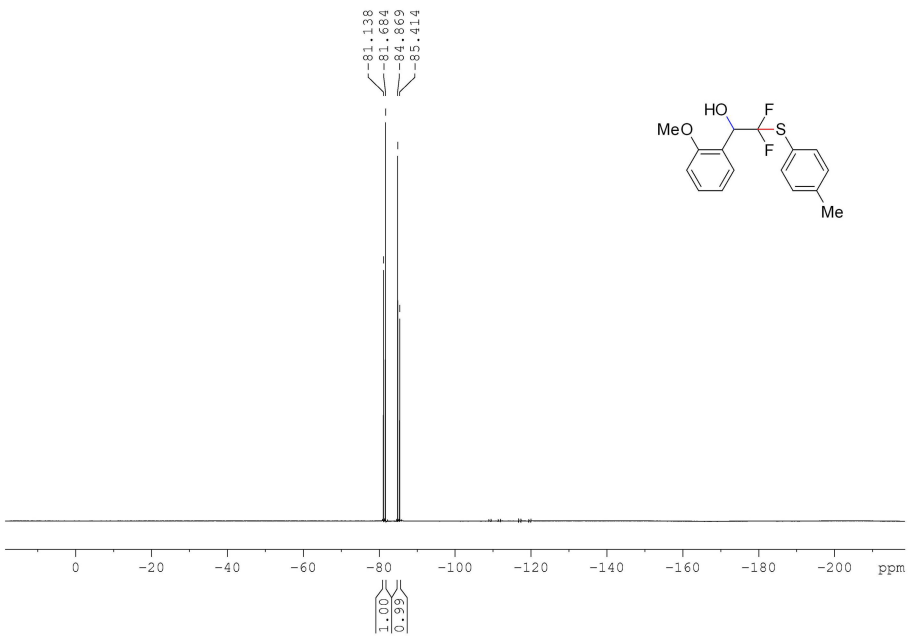

159.504
140.326
136.844
136.545
131.685
129.940
129.342
128.857
126.028
122.196
120.260
114.779
113.269
76.229
75.963
75.697
55.312
21.320
129.940
129.342
128.857
126.028
122.196
130
128
126
124
ppm
HO
F
S
F
MeO
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-81.217
-81.773
-84.708
-85.263
HO
F
S
F
MeO
Me
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
0.99

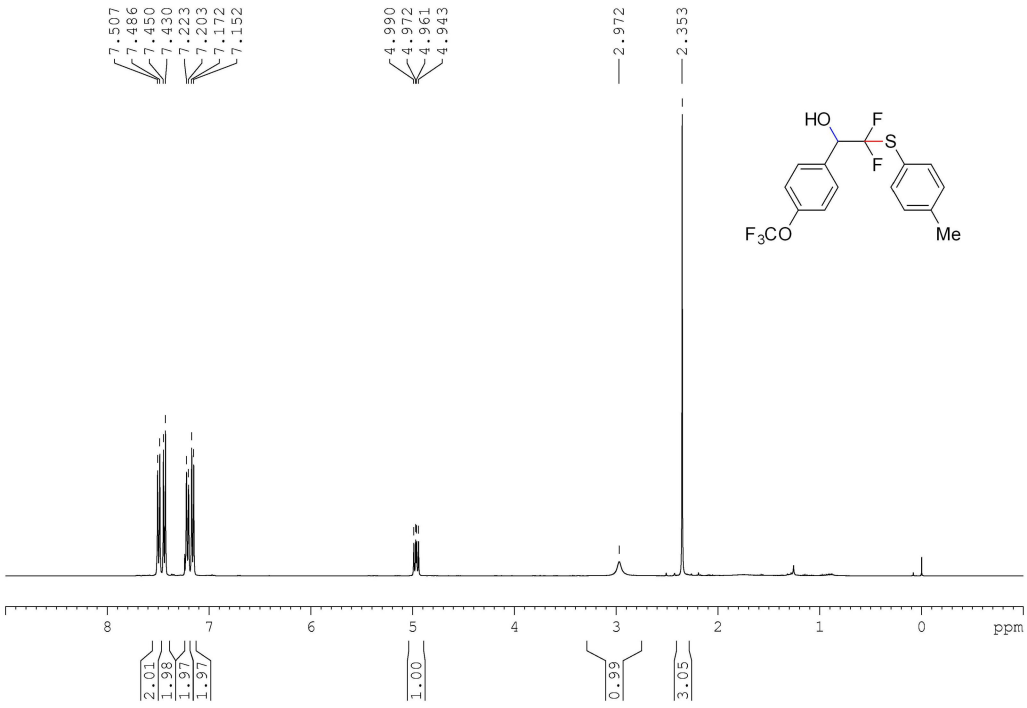
NMR spectra of **3fa**

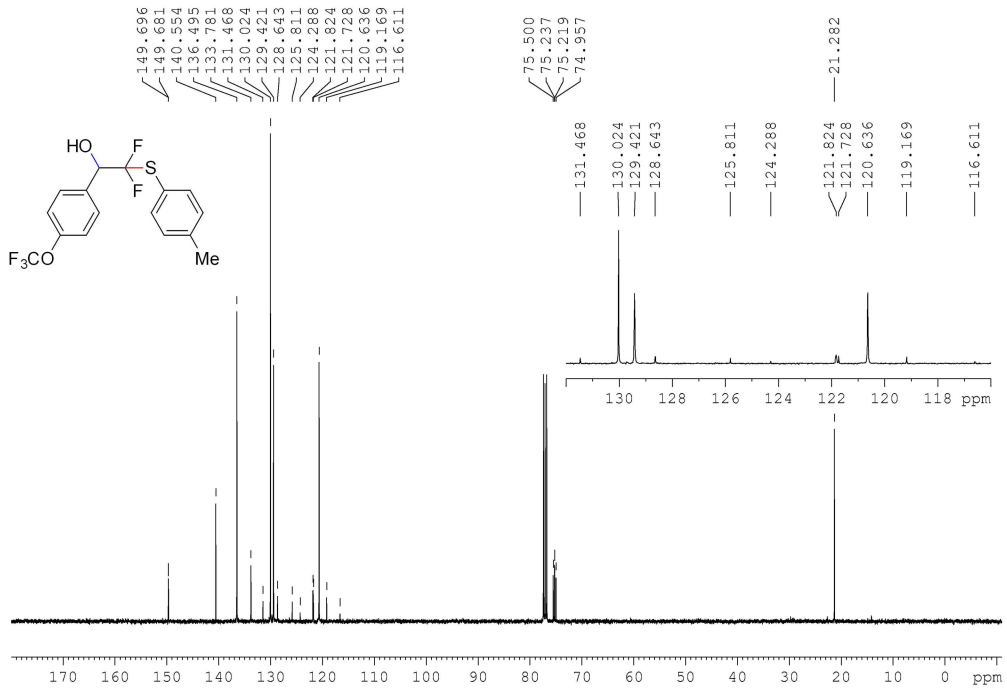


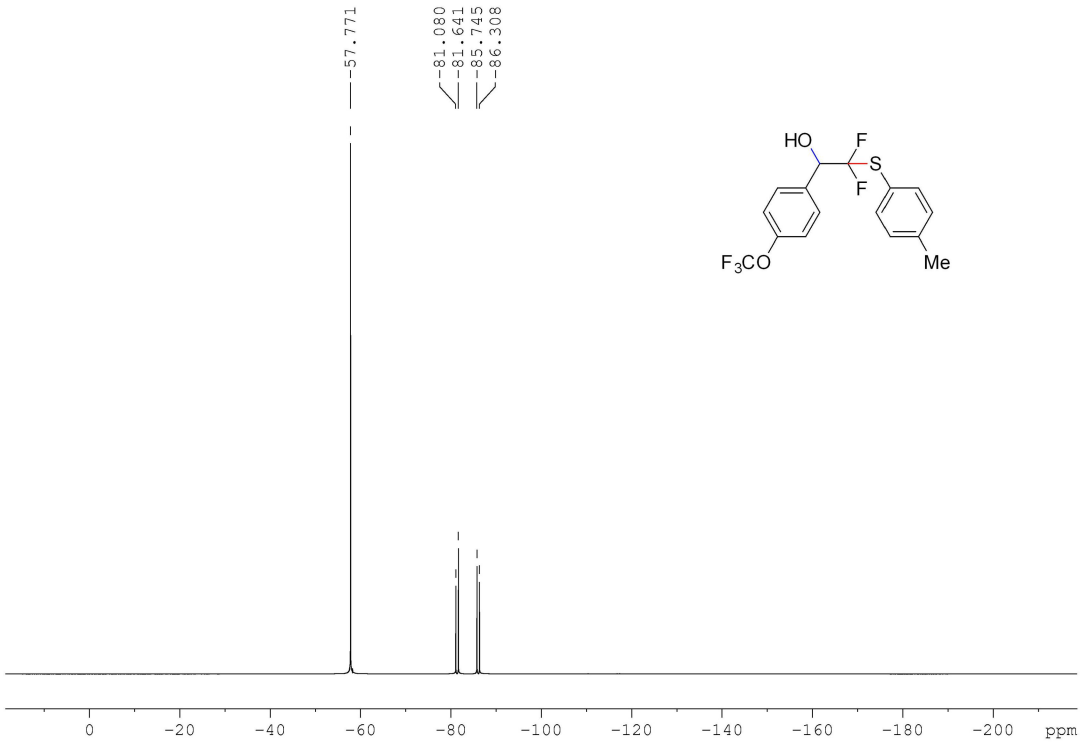




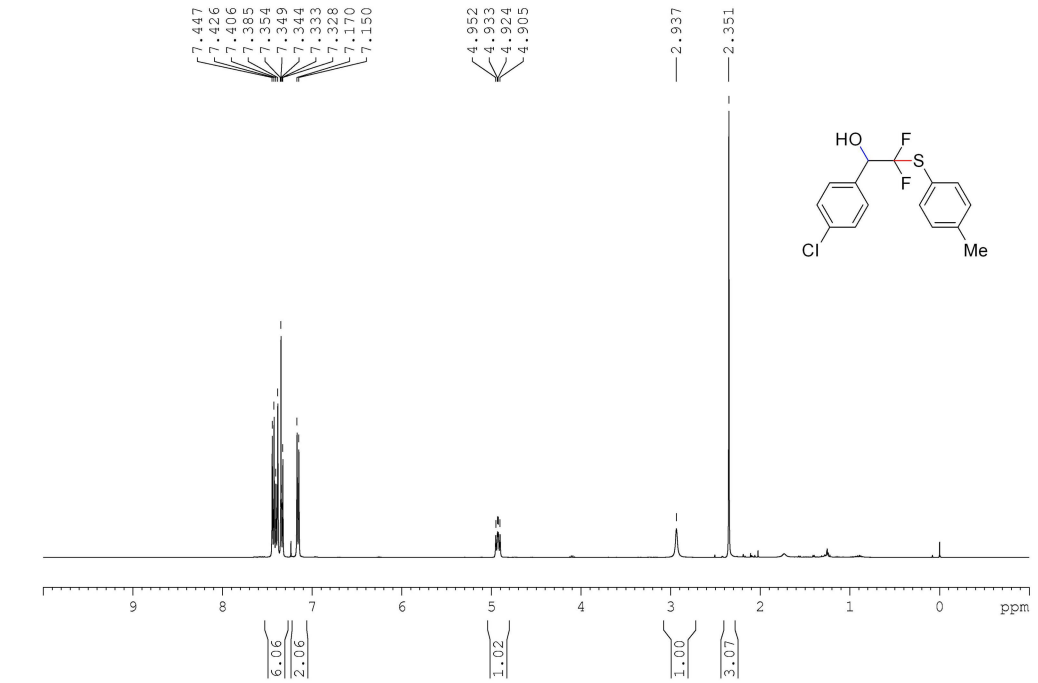
NMR spectra of **3ga**

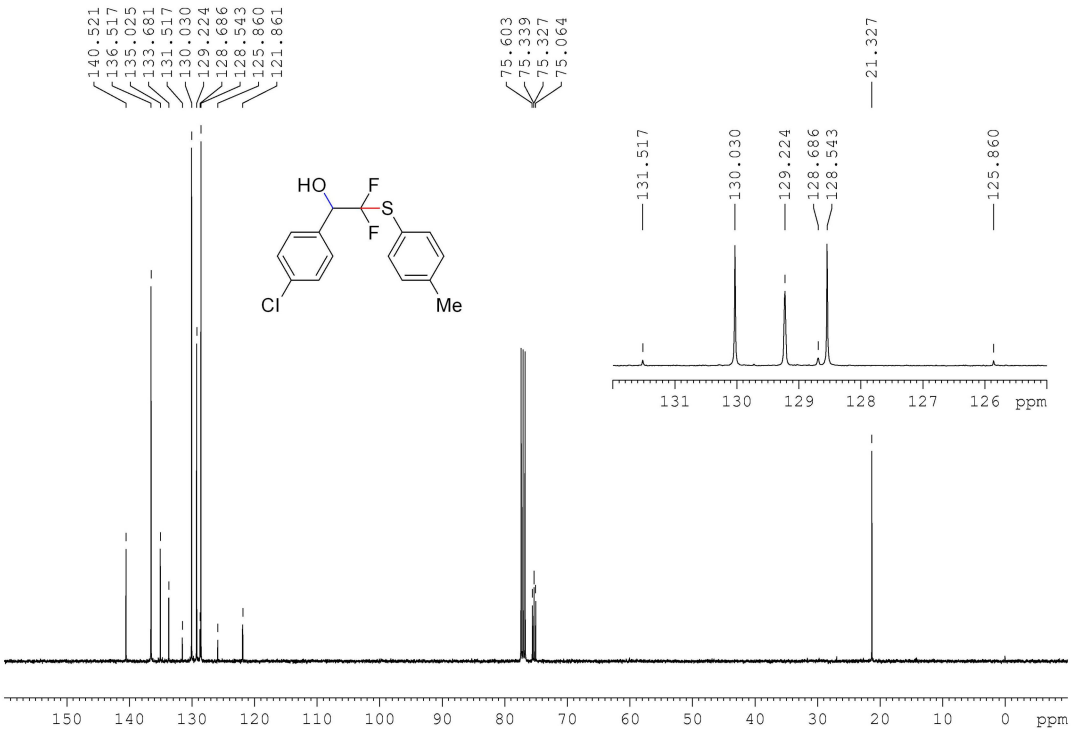


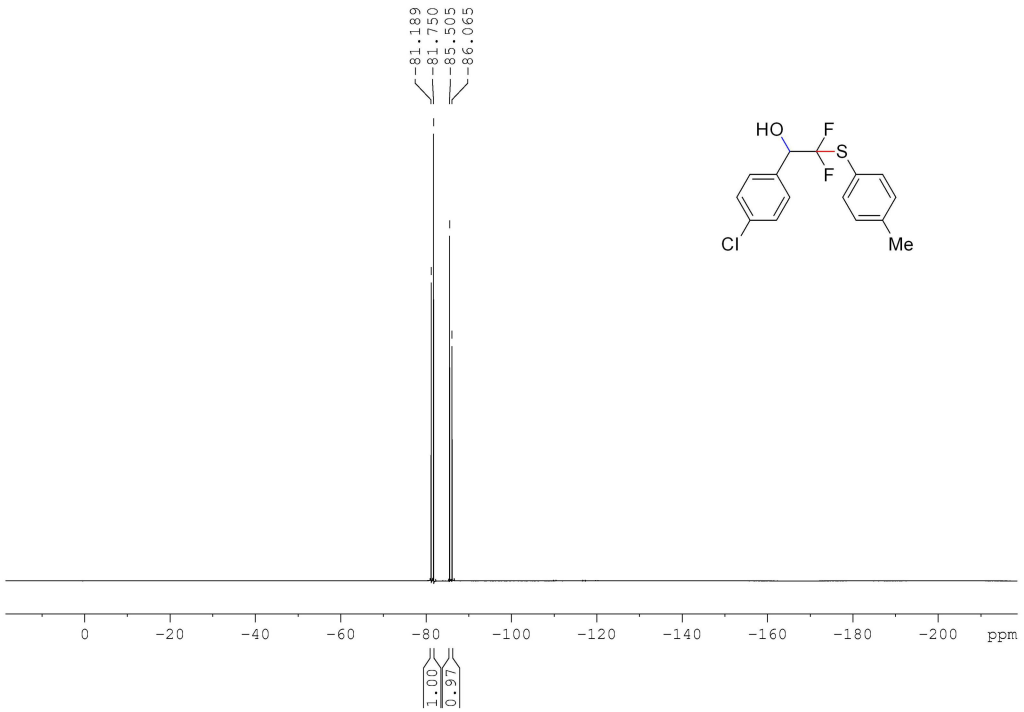

149.696
149.681
140.554
136.495
133.781
131.468
130.024
129.421
128.643
125.811
124.288
121.824
121.728
120.636
119.169
116.611
75.500
75.237
75.219
74.957
21.282
HO
F
S
F
F3CO
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
130 128 126 124 122 120 118 ppm


-57.771
-81.080
-81.641
-85.745
-86.308
HO
F
S
F
F3CO
Me
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

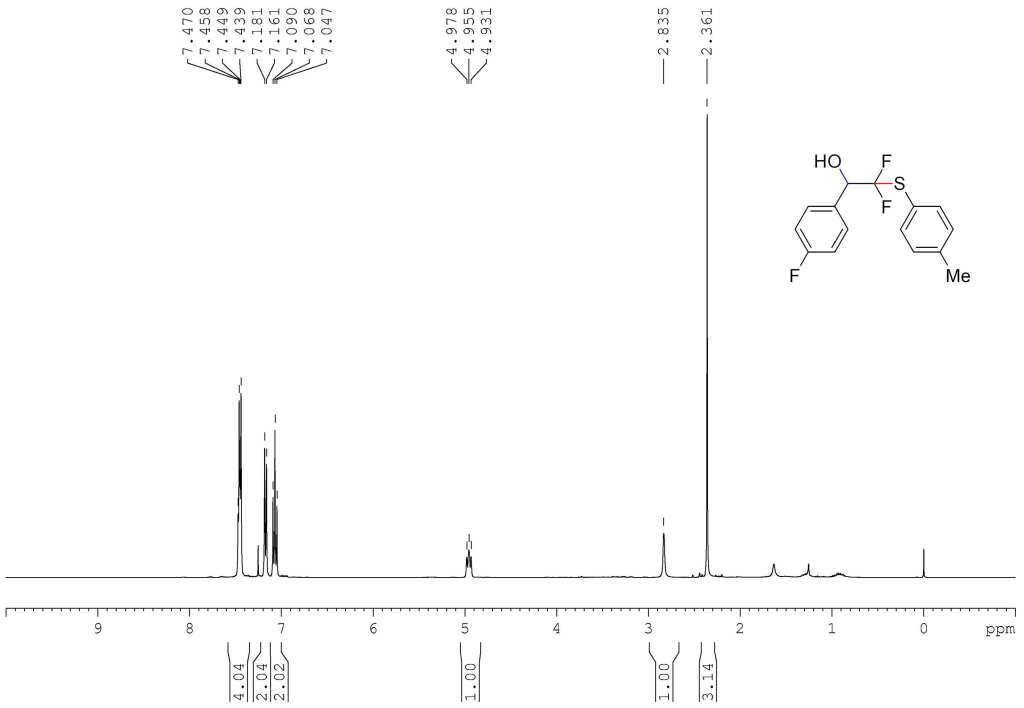
NMR spectra of **3ha**

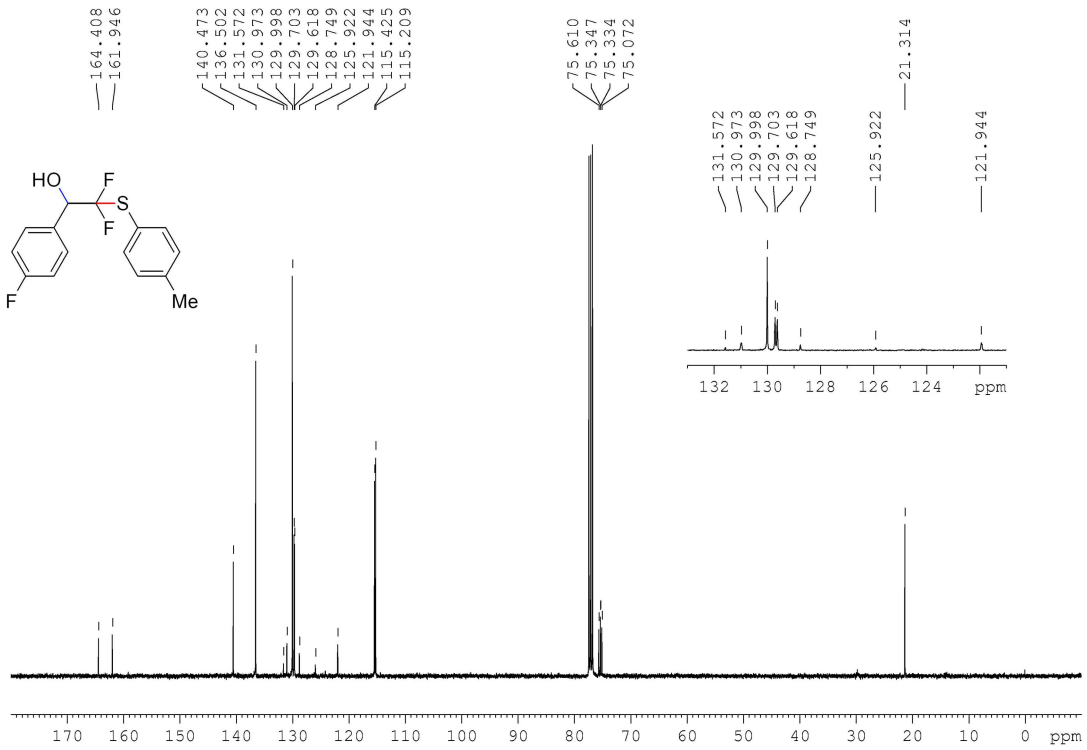


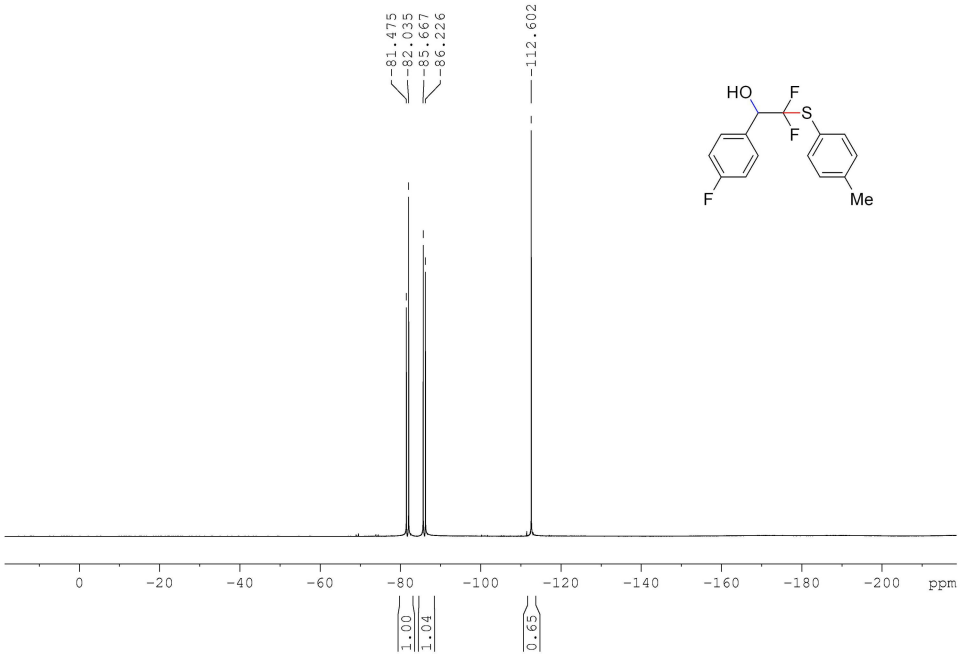




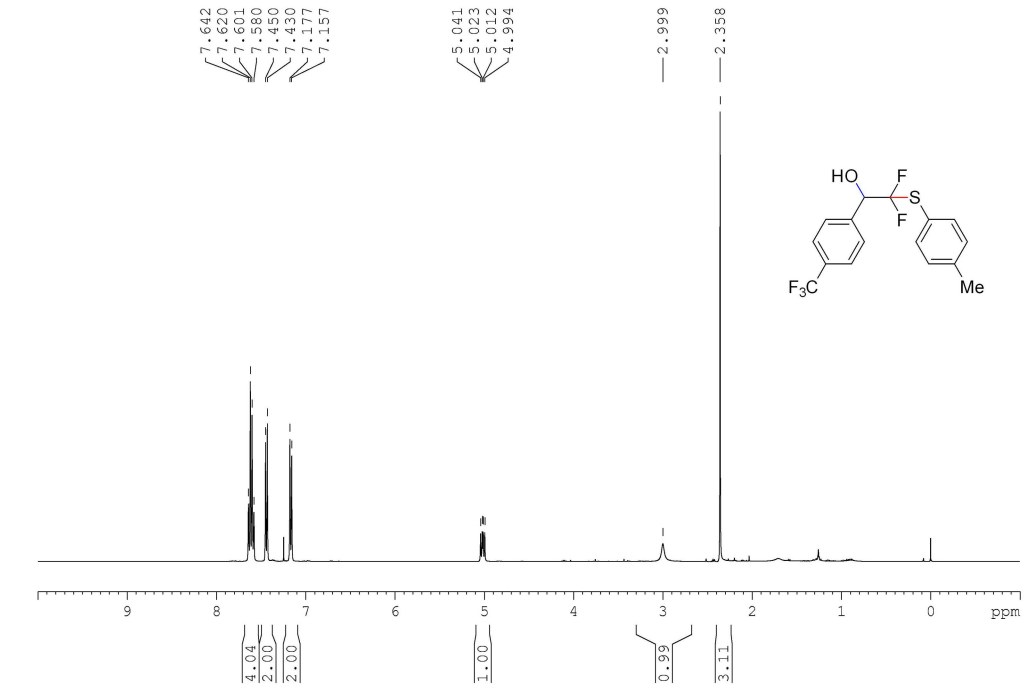
NMR spectra of **3ia**

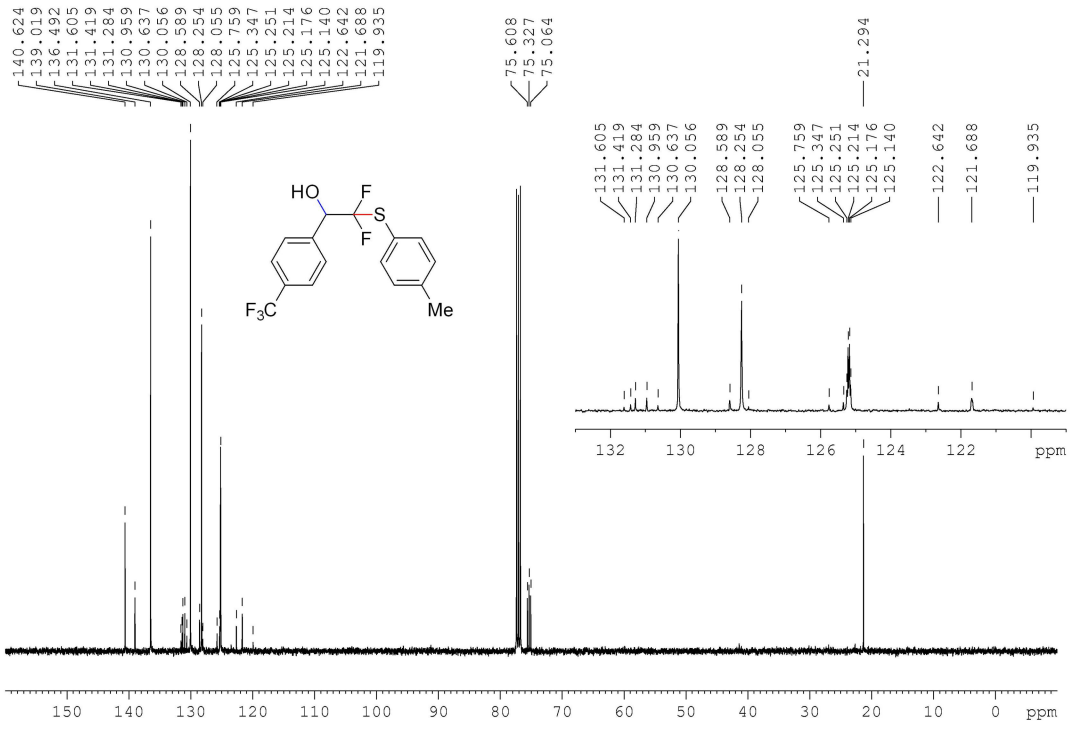


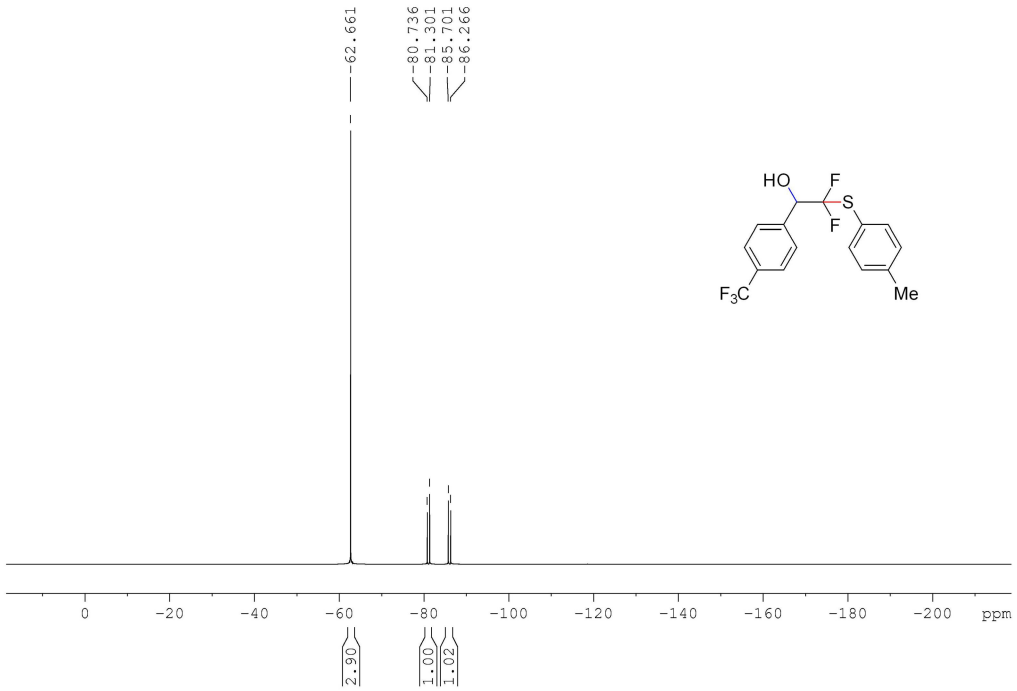

164.408
161.946
140.473
136.502
131.572
130.973
129.998
129.703
129.618
128.749
125.922
121.944
115.425
115.209
75.610
75.347
75.334
75.072
21.314
131.572
130.973
129.998
129.703
129.618
128.749
125.922
121.944
HO
F
S
F
F
Me
132
130
128
126
124
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-81.475
-82.035
-85.667
-86.226
-112.602
HO
F
S
F
F
Me
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.04
0.65

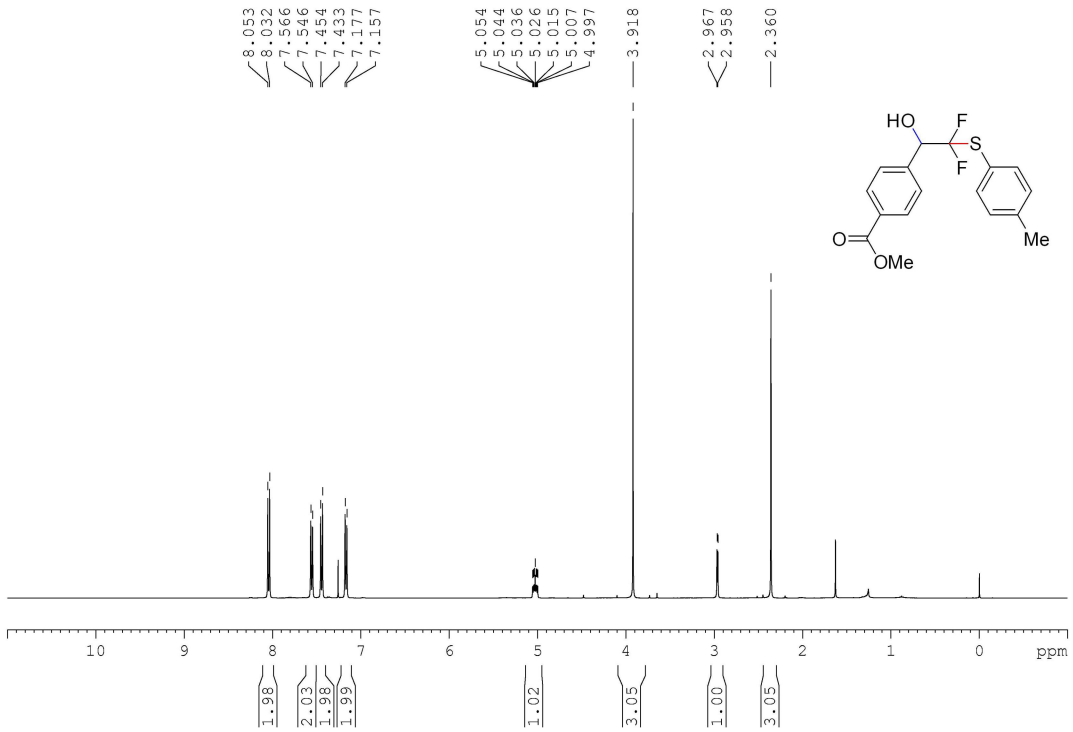
NMR spectra of **3ja**

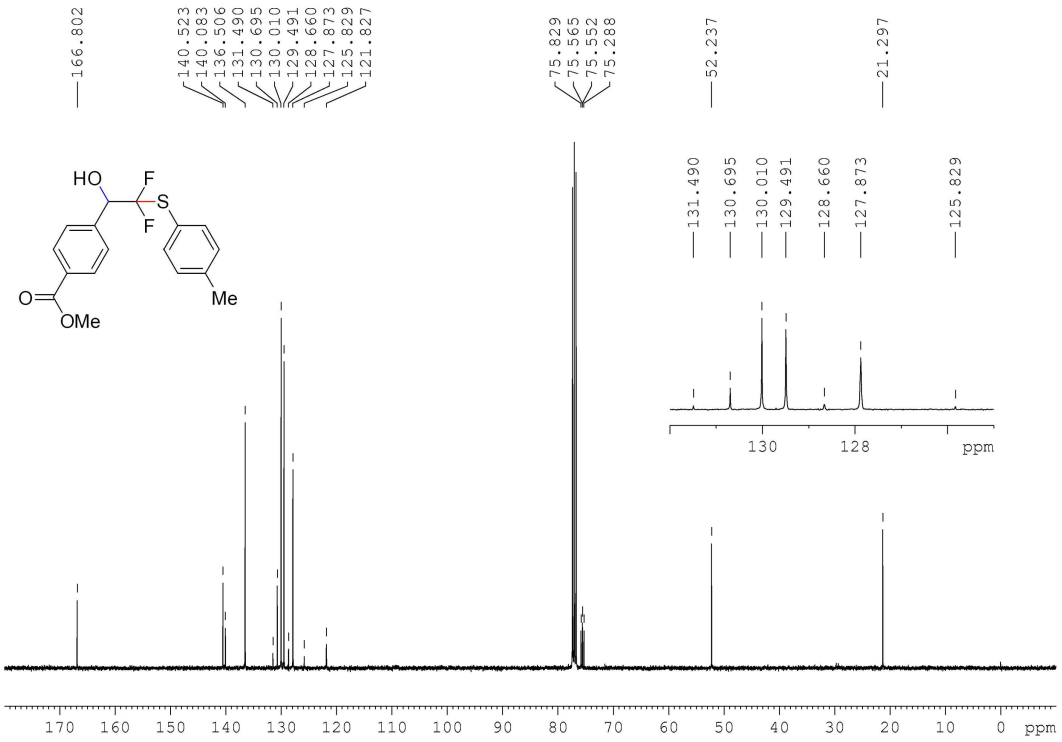


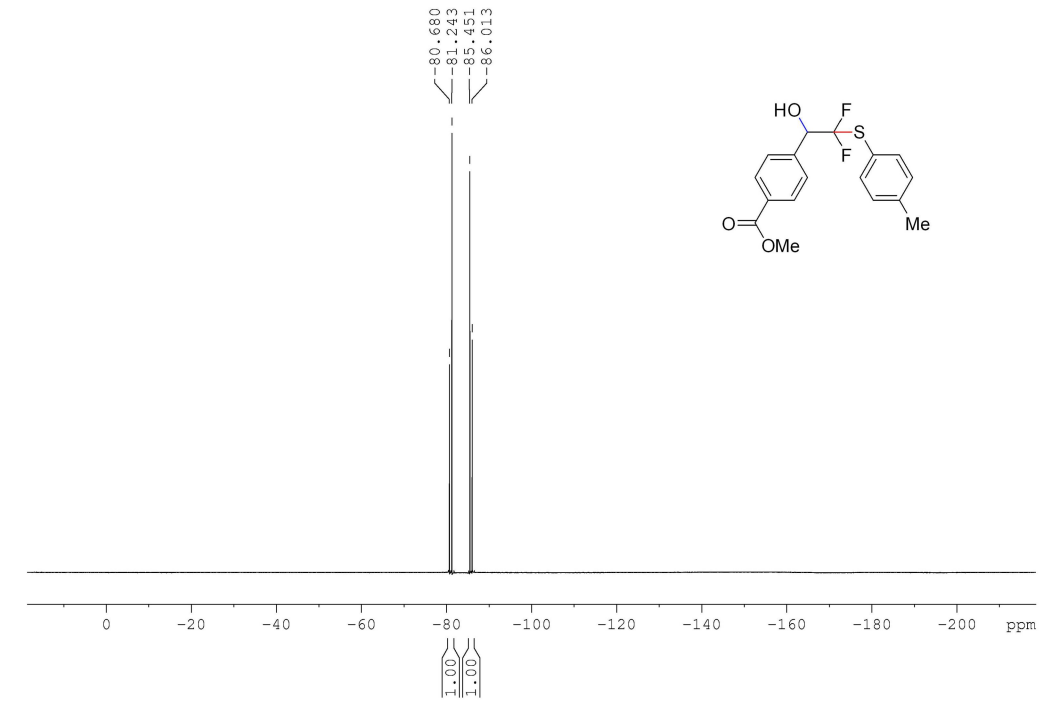




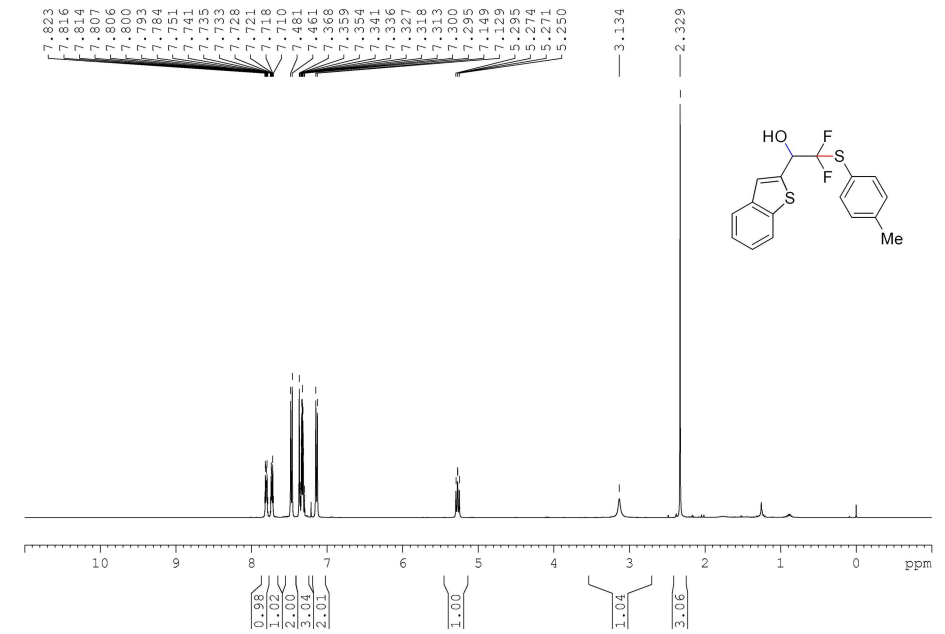
NMR spectra of **3ka**

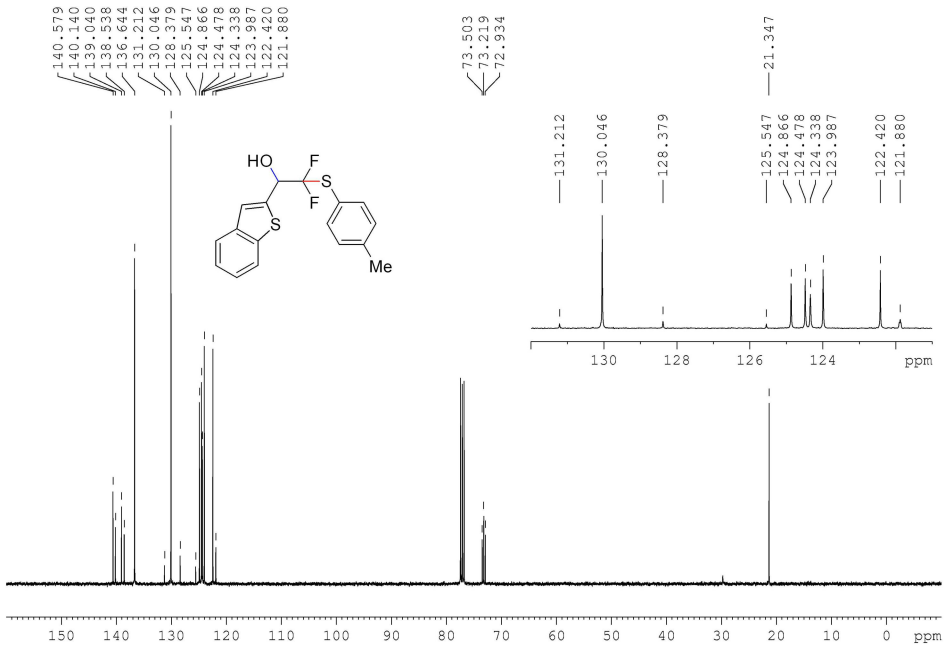


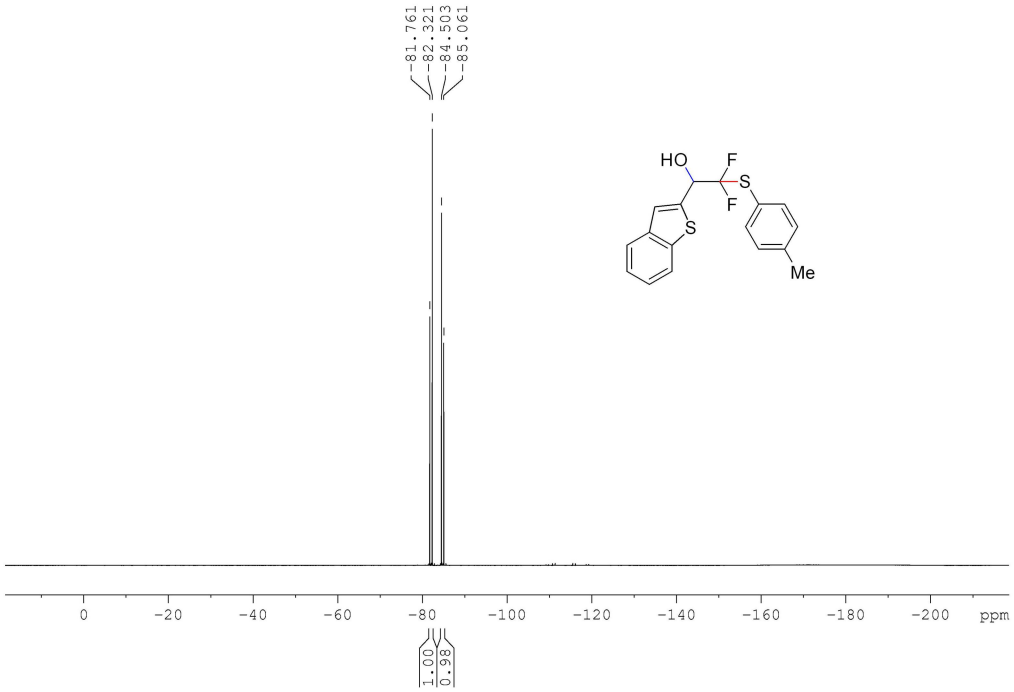

166.802
140.523
140.083
136.506
131.490
130.695
130.010
129.491
128.660
127.873
125.829
121.827
75.829
75.565
75.552
75.288
52.237
21.297
HO
F
S
F
O
OMe
Me
131.490
130.695
130.010
129.491
128.660
127.873
125.829
130
128
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-80.680
-81.243
-85.451
-86.013
HO
F
S
F
O
OMe
Me
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
1.00
1.00

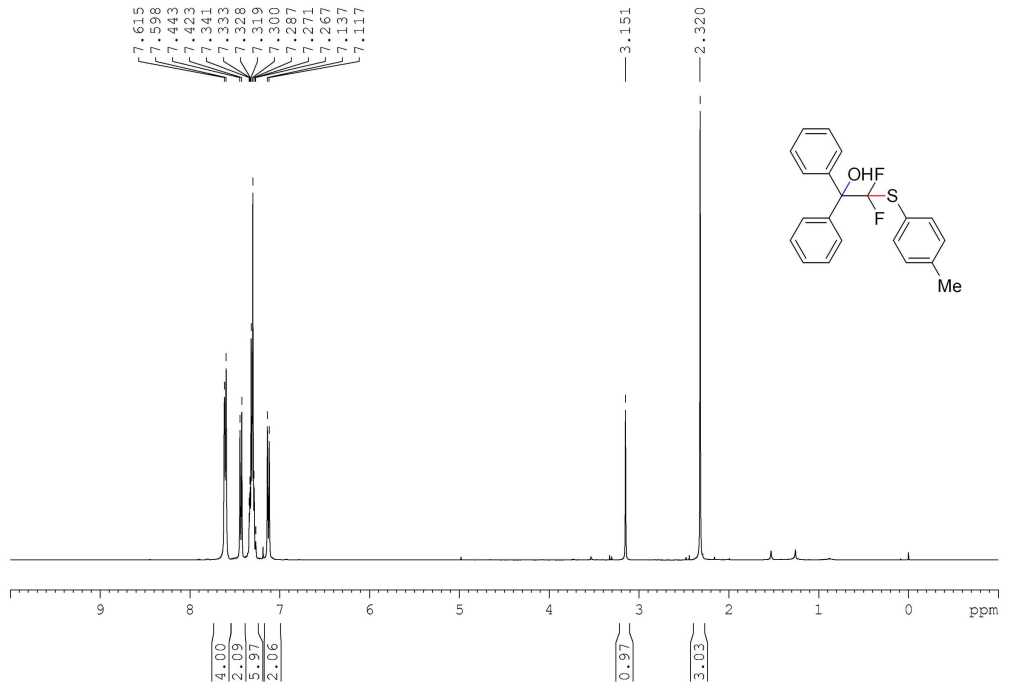
NMR spectra of **3la**

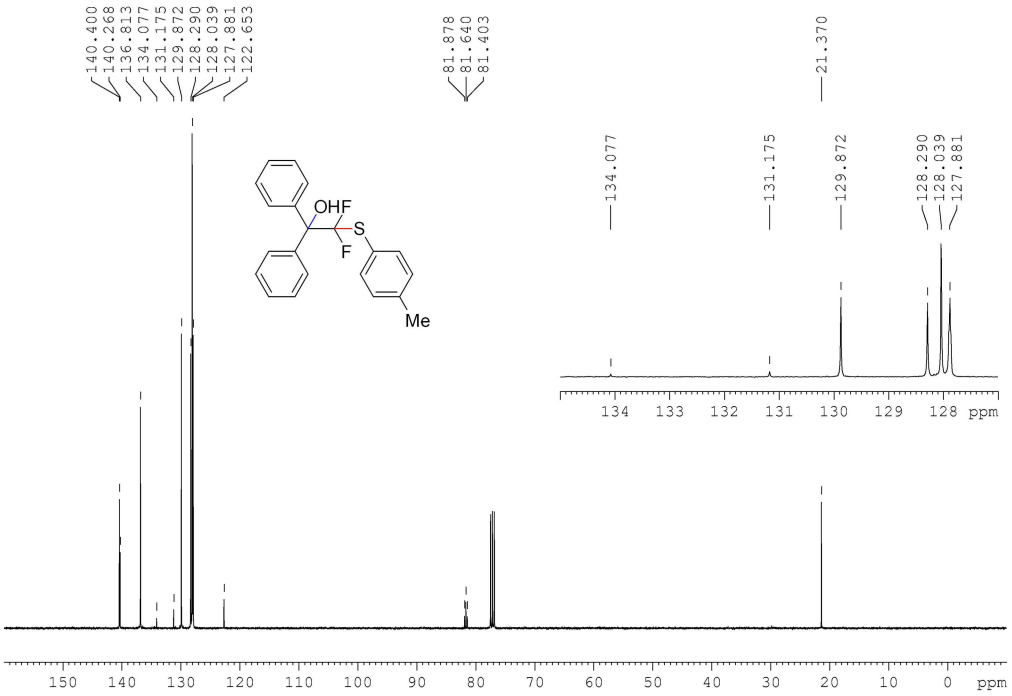


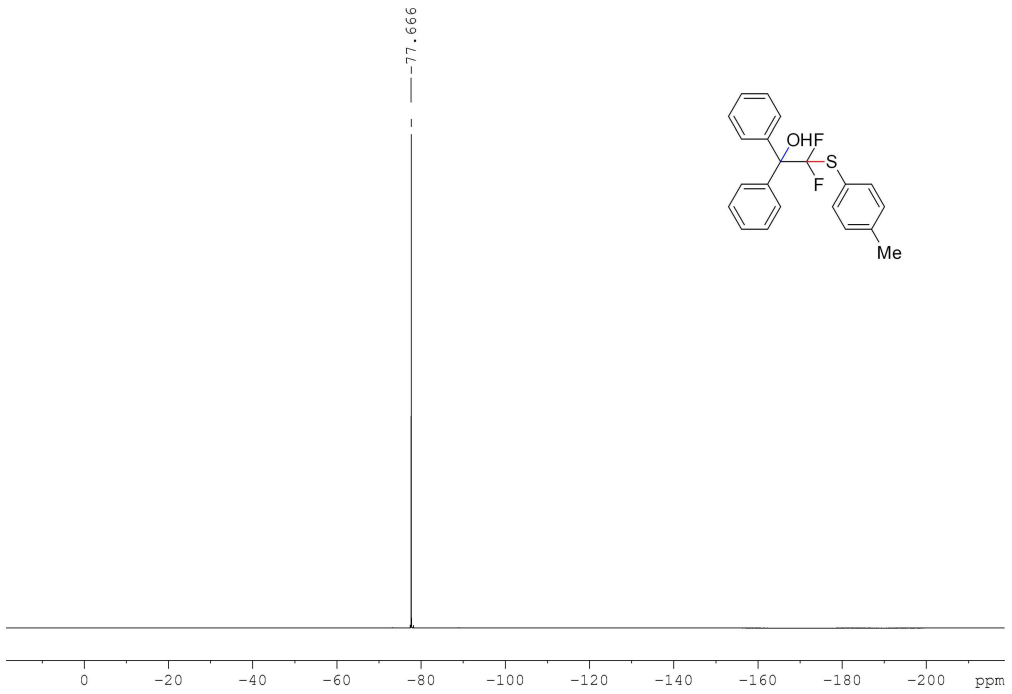




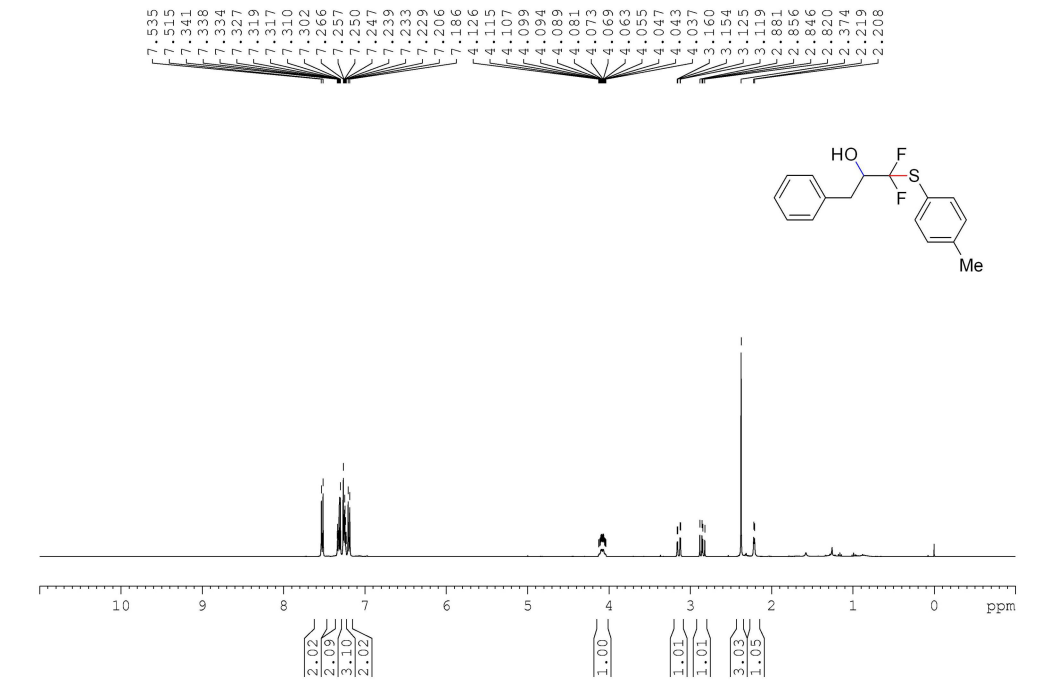
NMR spectra of **3ma**

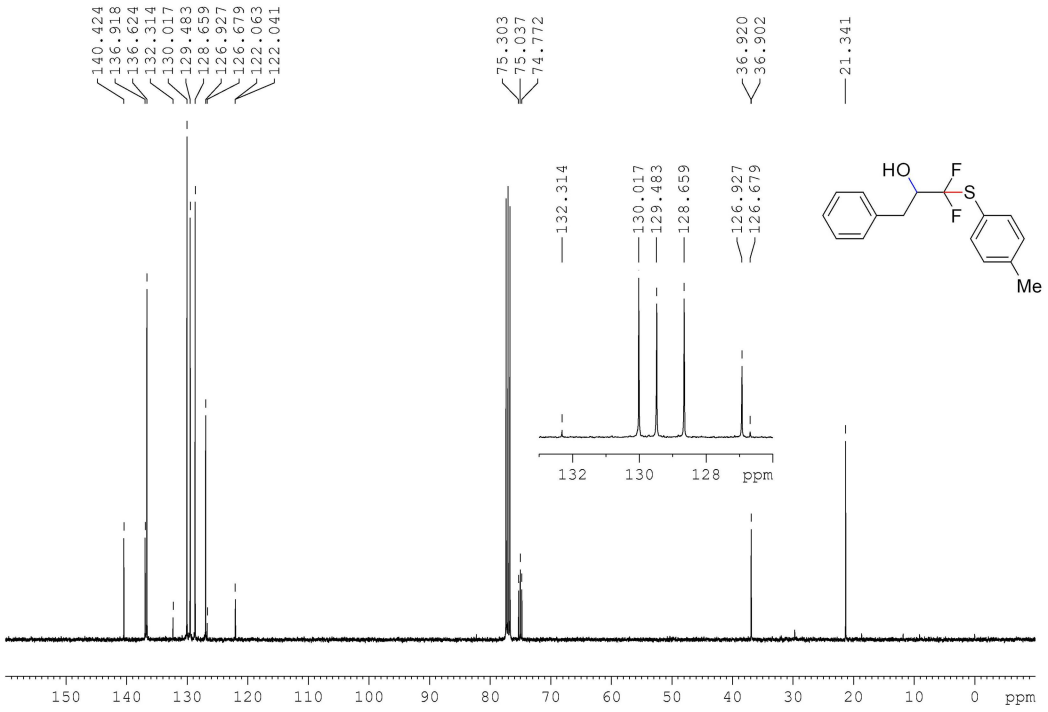


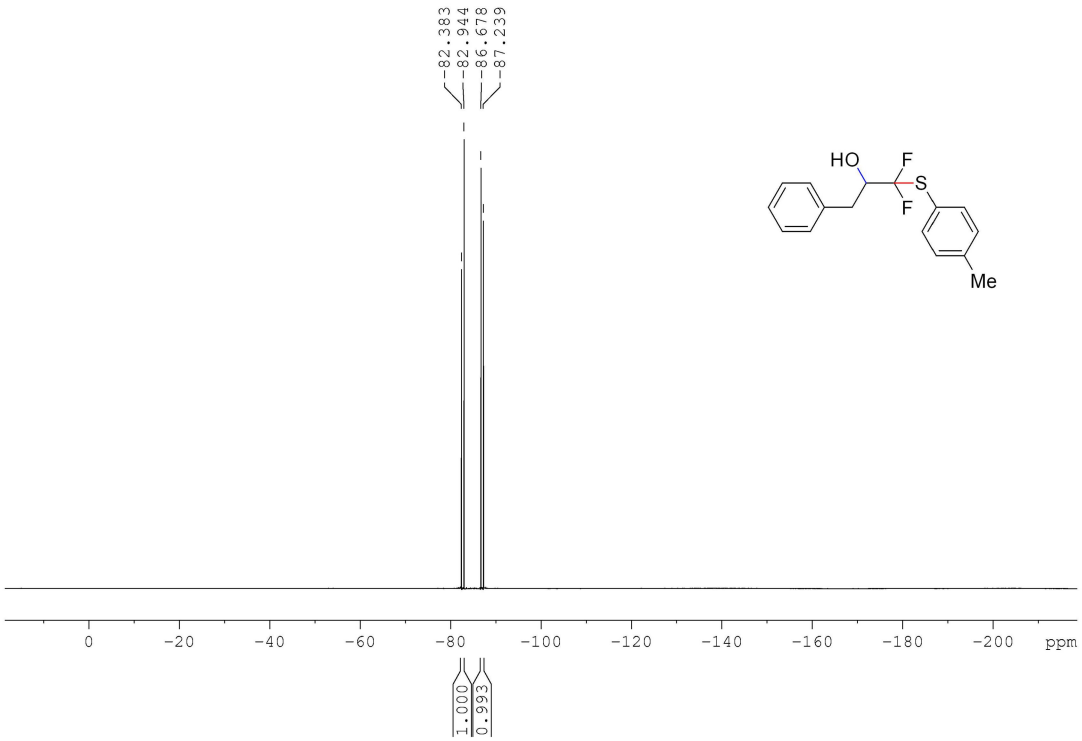

140.400
140.268
136.813
134.077
131.175
129.872
128.290
128.039
127.881
122.653
81.878
81.640
81.403
21.370
134.077
131.175
129.872
128.290
128.039
127.881
OHF
S
F
Me
134 133 132 131 130 129 128 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-77.666
OHF
S
F
Me
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

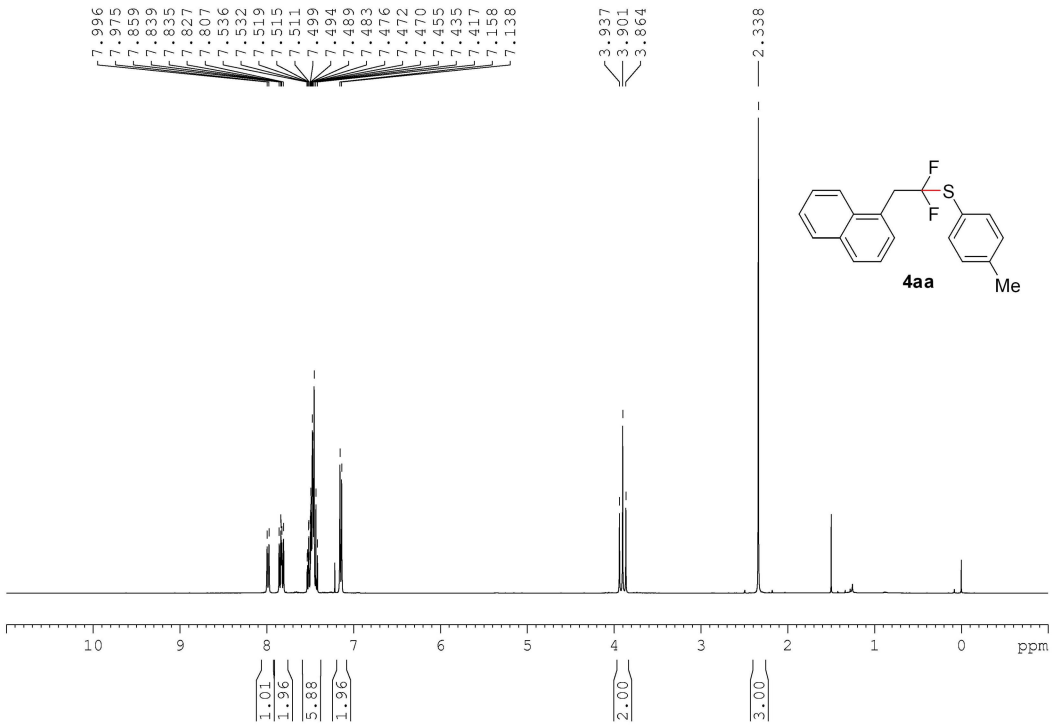
NMR spectra of **3na**

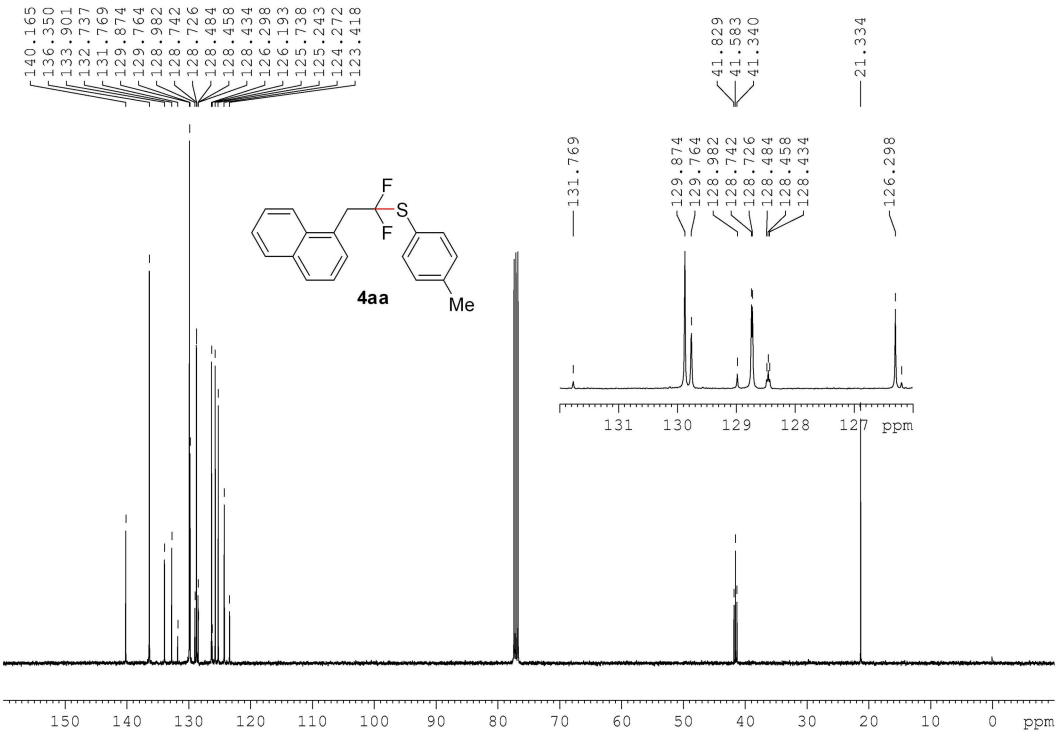


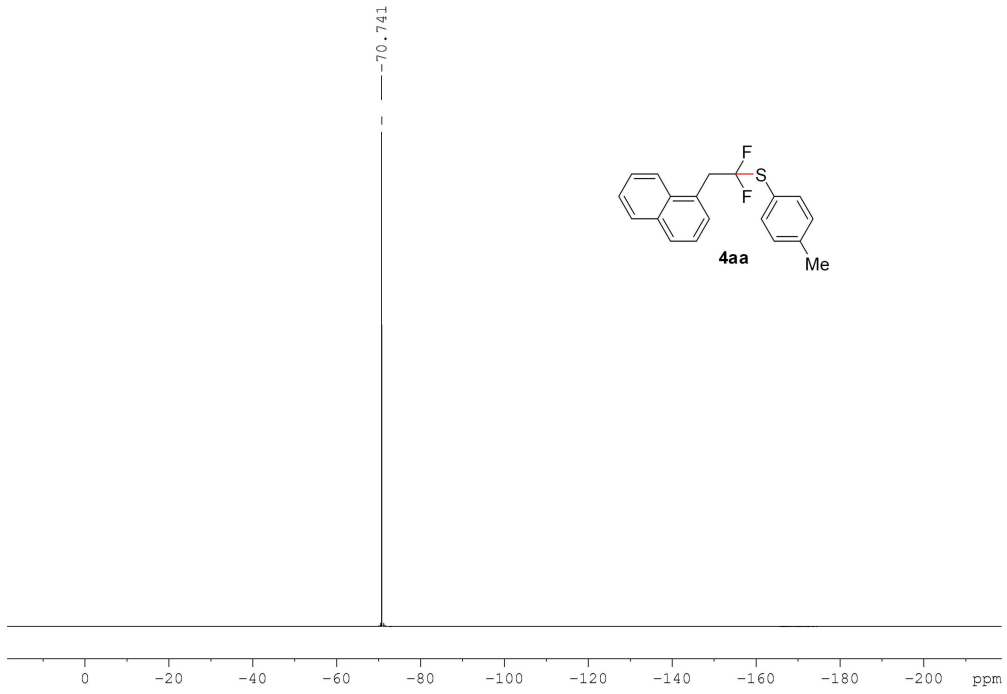




NMR spectra of **4aa**




140.165
136.350
133.901
132.737
131.769
129.874
129.764
128.982
128.742
128.726
128.484
128.458
128.434
126.298
126.193
125.738
125.243
124.272
123.418
41.829
41.583
41.340
21.334
131.769
129.874
129.764
128.982
128.742
128.726
128.484
128.458
128.434
126.298
F
S
F
Me
4aa
131
130
129
128
127 ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


-70.741
F
S
F
Me
4aa
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm