Supporting Information

Synthesis of Difluoromethanesulfinate Esters by the Difluoromethanesulfinylation of Alcohols

Yuji Sumii,[†&] Kenta Sasaki,[†&] Okiya Matsubara,[†] and Norio Shibata*[†,‡,#]

[†]Department of Life Science and Applied Chemistry, [‡]Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

[#]Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, 688 Yingbin Avenue, 321004 Jinhua, China.

[&]Contributed equally to this work.

*E-mail: nozshiba@nitech.ac.jp.

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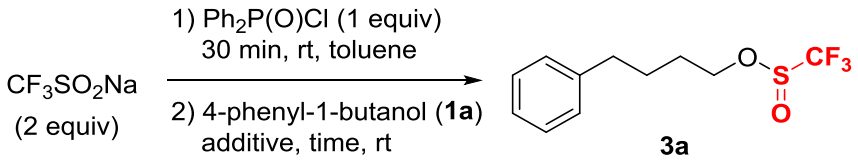
Table S1. Prediction of log P, and pKa valuesa

$MeOS(O)_xCF_2H$	log *P*	pK_a (XGBoost/neural network)
$PhCH_2OSCF_2H$	3.0740	8.52/8.22
$PhCH_2OS(O)CF_2H$	2.0895	7.91/6.19
$PhCH_2OSO_2CF_2H$	1.7556	8.20/7.03

[a]Log *P* and p*K*a were estimated by the p*K*a prediction platform by Luo group.[1]

Table S2. Optimization of the Trifluoromethanesulfinylation of 1a[a]



3a

run	additive	time	yield (%)[b]
1	-	3 h	61
2	-	6 h	70
3	-	12 h	76
4	-	24 h	84
5	Me_3SiCl (0.1 equiv)	3 h	99 (89[c])

[a]$Ph_2P(O)Cl$ (1.0 equiv) was added to a solution of CF_3SO_2Na (2.0 equiv) in toluene (1.0 mL) and stirred at rt for 30 min. A solution of 4-phenyl-1-butanol (**1a**, 0.2 mmol) in toluene (1.0 mL) and the desired additive (0.02 mmol, 0.1 equiv) were added separately to the mixture, and stirred at rt. [b]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c]Isolated yield.

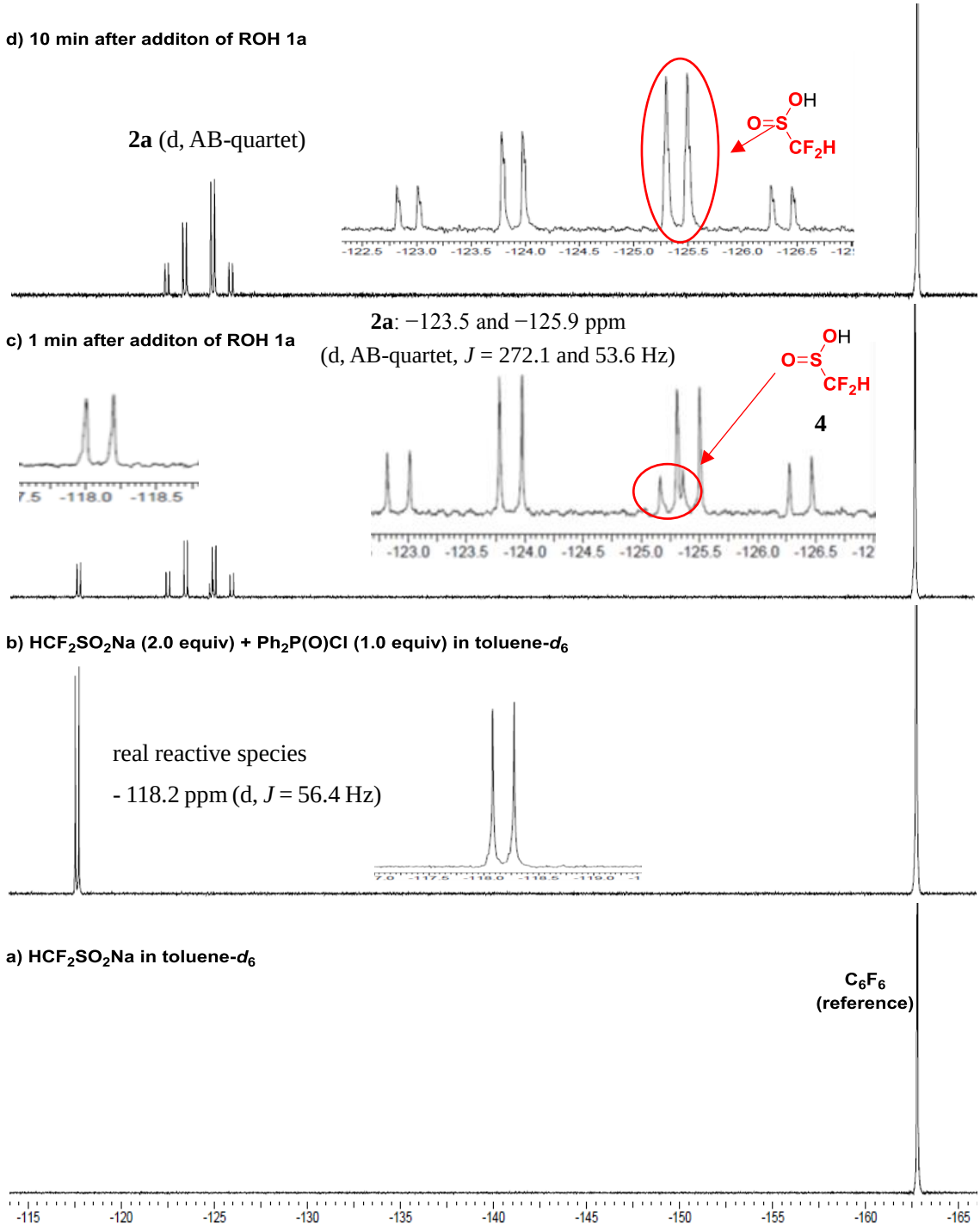


Figure S1. ^{19}F NMR experiments in toluene-d_6. a) HCF_2SO_2Na (2.0 equiv), b) HCF_2SO_2Na (2.0 equiv) + $Ph_2P(O)Cl$ (1.0 equiv), stirred for 30 min, c) 1 min after addition of **1a** to b), d) 10 min after addition of **1a** to b).

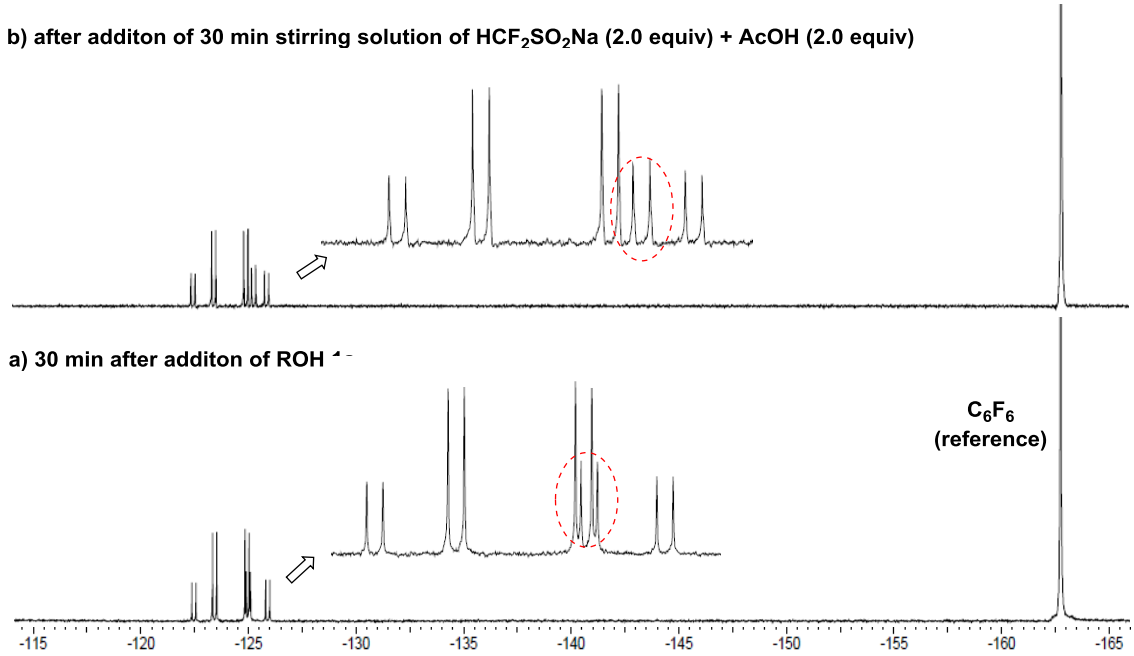


Figure S2. ^{19}F NMR experiments. a) HCF_2SO_2Na (2.0 equiv) in toluene-d_6, b) 30 min after addition of AcOH (2.0 equiv) to HCF_2SO_2Na (2.0 equiv) in toluene-d_6.

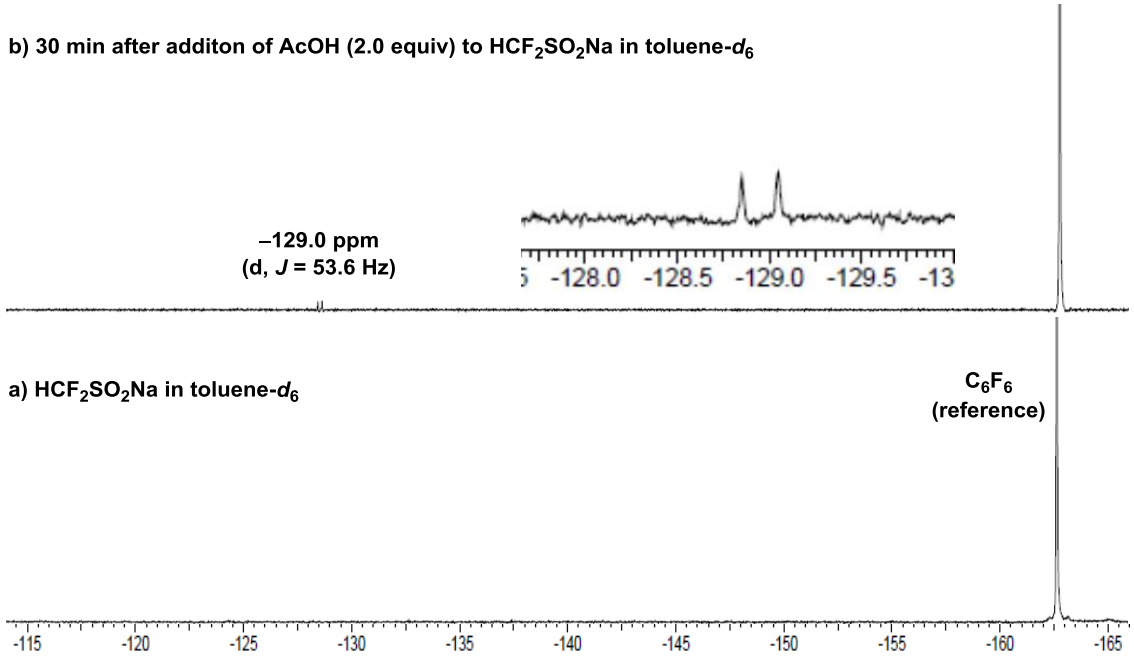
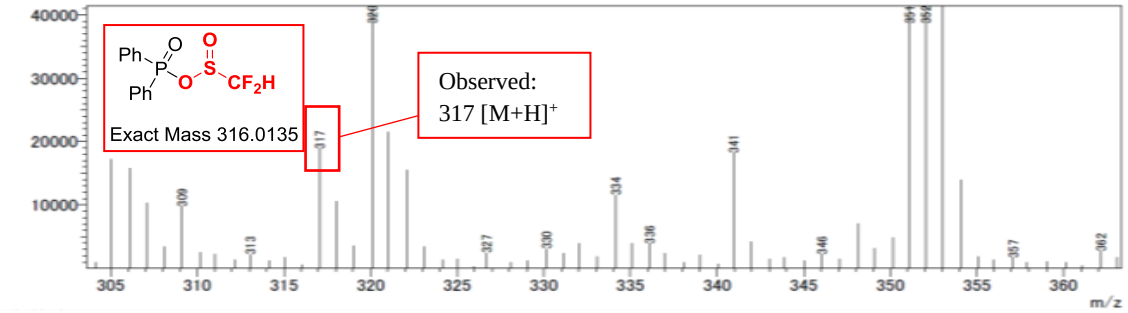
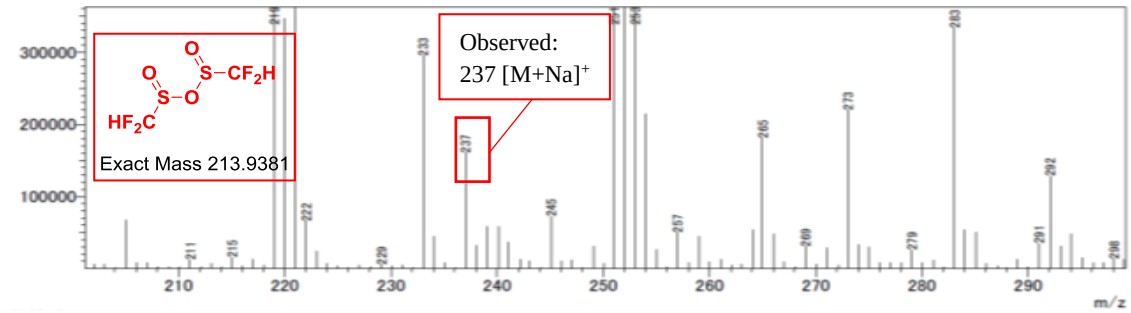


Figure S3. ^{19}F NMR experiments. a) HCF_2SO_2Na (2.0 equiv) in toluene-d_6, b) 30 min after addition of AcOH (2.0 equiv) to HCF_2SO_2Na (2.0 equiv) in toluene-d_6.

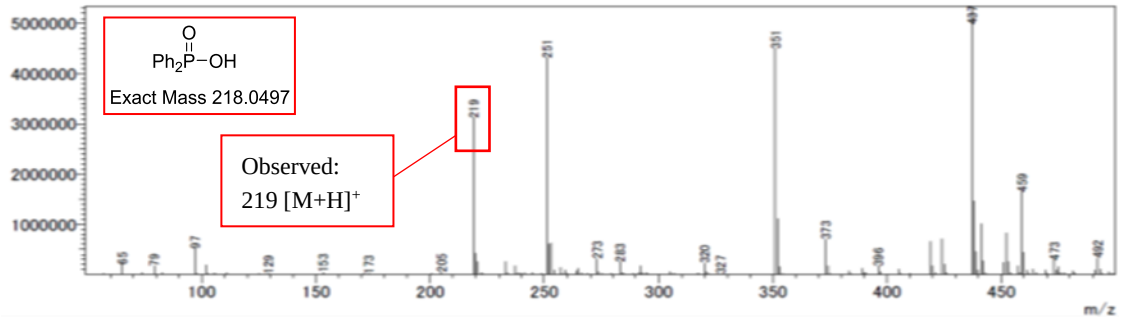
a) LC-MS spectra of intermediate Ph_2P-O-S(O)CF_2H **II**



b) LC-MS spectra of $(HCF_2S(O))_2O$ **III**



c) LC-MS spectra of $Ph_2P(O)OH$ (positive mode)



c) LC-MS spectra of $Ph_2P(O)OH$ (negative mode)

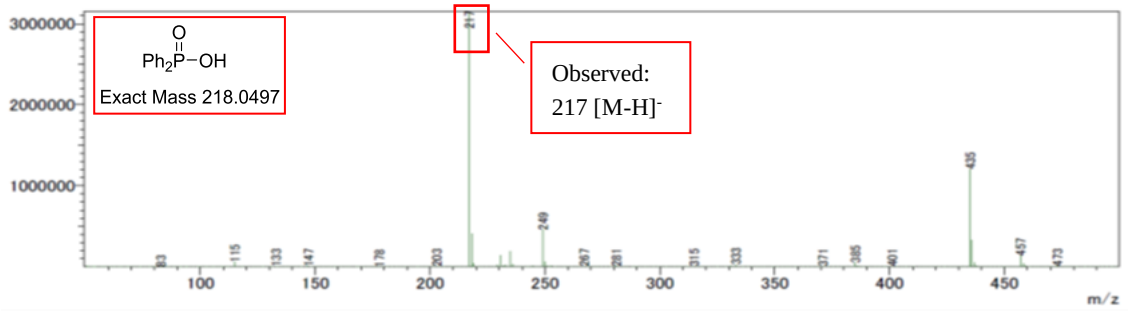


Figure S4. LC-MS analysis of reaction intermediates. a) Intermediate Ph_2P-O-S(O)CF_2H II. b) $(HCF_2S(O))_2O$ **III**. c) $Ph_2P(O)OH$ (positive mode). d) $Ph_2P(O)OH$ (negative mode).

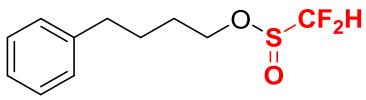
1. General information.

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels though a rubber septum. All solvents were purified by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F_{254}). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 50-63 μm). The ^1H NMR (300 MHz), ^{19}F NMR (282 MHz) and ^{13}C NMR (126 MHz) spectra for solution in $CDCl_3$ or toluene-d_8 were recorded on a Varian Mercury 300 and Bruker Avance 500 NMR spectrometers. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane (0.0 ppm) for ^1H NMR and C_6F_6 (–162.2 ppm) for ^{19}F NMR. UV-vis spectra were recorded on a JASCO V-530 spectrometer. High resolution mass spectrometries were recorded on a Waters Synapt G2 HDMS (ESI-MS) and a SHIMADZU GCMS-QP5050A (EI-MS). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Fluorescence spectroscopy was recorded on a JASCO FP-6200. Melting point were recorded on a BUCHI M-565. X-ray measurements were carried out on a Rigaku R-AXIS RAPID or Rigaku Mercury70 diffractometer with graphite monochromated Mo Kα radiation at –100 °C.

2. General Procedure for the difluoromethanesulfinylation of alcohols

$Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv)was added to a suspension of HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv) in toluene (1.0 mL) under nitrogen atmosphere, and the reaction was stirred at room temperature for 30 min. A solution of the desired alcohol **1** (0.2 mmol, 1.0 equiv) in toluene (1.0 mL) was then added to the mixture, and the reaction was stirred at room temperature for 3 h. After this time, the reaction mixture was diluted with diethyl ether and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography using hexane/ethyl acetate (9:1) as the eluent.

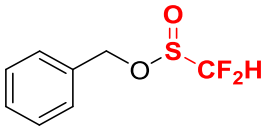
4-Phenylbutyl difluoromethanesulfinate (2a)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1a** (30.0 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2a** (44.2 mg, 89%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32−7.26 (m, 2H), 7.22−7.16 (m, 3H), 5.83 (t, *J* = 55.5 Hz, 1H), 4.23 (t, *J* = 4.5 Hz, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 1.85−1.68 (m, 4H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.2 and –125.6 (d-AB quartet, *J* = 272.1, 54.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 141.2, 128.4, 128.3 (2C), 126.0 (2C), 120.3 (t, *J* = 284.8 Hz), 70.5, 35.2, 29.5, 27.1 ppm. IR (neat): 3853, 3778, 3689, 3629, 3084, 3064, 3024, 2949, 2858, 2328, 2197, 1950, 1873, 1815, 1741, 1603, 1502, 1464, 1371, 1329, 1281, 1157, 1097 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_{11}H_{14}F_2O_2S$ 248.0683; found 248.0695.

Benzyl difluoromethanesulfinate (2b)

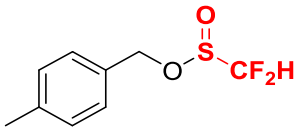


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1b** (21.6 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2b** (34.0 mg, 82%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40 (br s, 5H), 5.87 (t, *J* = 54.0 Hz, 1H), 5.21 (s, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.8 and –125.4 (d-AB quartet, *J* = 271.9, 53.3 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 134.2, 129.3, 128.9 (2C), 128.7 (2C), 120.2 (t, *J* = 285.4 Hz), 71.5 ppm. IR (neat): 3602,

3419, 3060, 3032, 2925, 2841, 2746, 2495, 2368. 1722, 1639, 1491, 1456, 1352, 1161, 1065, 1026 cm^{-1}. MS (ESI) *m/z*: 229 $[M+Na]^+$. Anal. Calcd for $C_8H_8F_2O_2S$: C, 46.60; H, 3.91; S, 15.55; found: C, 46.59; H, 3.91; S, 15.55.

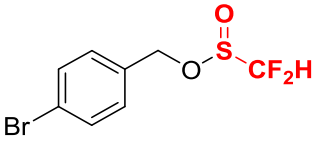
4-Methylbenzyl difluoromethanesulfinate (2c)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1c** (24.4 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2c** (35.2 mg, 80%) as colorless oil.

^1H NMR (300 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 5.85 (t, *J* = 55.5 Hz, 1H), 5.16 (s, 2H), 2.37 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.6 and –125.3 (d-AB quartet, *J* = 271.7, 53.6 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 139.4, 131.1, 129.6 (2C), 128.9 (2C), 120.3 (t, *J* = 286.0 Hz), 71.6, 21.3 ppm. IR (neat): 3622, 3498, 3300, 2866, 2542, 2443, 2368, 2299, 1890, 1738, 1631, 1512, 1427, 1383, 1315, 1184, 1076, 1034 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_9H_{10}F_2O_2NaS$ 243.0267; found 243.0258.

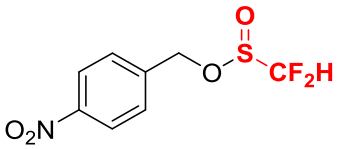
4-Bromobenzyl difluoromethanesulfinate (2d)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1d** (37.4 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2d** (49.1 mg, 86%) as brown oil.

^1H NMR (300 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.88 (t, *J* = 54.6 Hz, 1H), 5.16 (s, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.7 and –125.3 (d-AB quartet, *J* = 271.7, 53.6 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 133.2, 132.1 (2C), 130.2 (2C), 123.6, 120.3 (t, *J* = 286.0 Hz), 70.6 ppm. IR (KBr): 3824, 3730, 3666, 3101, 2960, 2877, 2582, 2447, 2283, 2200, 1897, 1782, 1595, 1495, 1448, 1412, 1360, 1284, 1169, 1093 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_8H_7BrF_2O_2S$ 283.9318; found 283.9331.

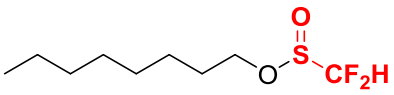
4-Nitrobenzyl difluoromethanesulfinate (2e)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1e** (30.6 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2e** (44.0 mg, 88%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 6.0 Hz, 2H), 5.96 (t, *J* = 54.0 Hz, 1H), 5.31 (s, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.6 and –125.0 (d-AB quartet, *J* = 272.1, 54.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 148.2, 141.4, 128.7 (2C), 124.0 (2C), 120.2 (t, *J* = 286.7 Hz), 69.5 ppm. IR (KBr): 3905, 3845, 3737, 3651, 3435, 3078, 2326, 1836, 1724, 1649, 1533, 1338, 1095 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_8H_7F_2NO_4S$ 251.0064; found 251.0065.

Octyl difluoromethanesulfinate (2f)

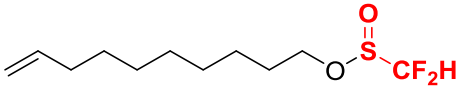


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1f** (26.0 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2f** (36.0 mg, 79%) as colorless oil.

Gram scale: Following general procedure, $Ph_2P(O)Cl$ (1.5 mL, 7.7 mmol, 1.0 equiv) and HF_2CSO_2Na (2.1 g, 15.4 mmol, 2.0 equiv) in toluene (38.5 mL) was reacted with alcohol **1f** (1.0 g, 7.7 mmol, 1.0 equiv) in toluene (38.5 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2f** (1.7 g, 7.5 mmol, 98%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.83 (t, *J* = 54.7 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 1.79−1.70 (m, 2H), 1.40−1.27 (m, 10H), 0.89−0.85 (m, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.3 and –125.7 (d-AB quartet, *J* = 272.1, 54.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 120.3 (t, *J* = 285.4 Hz), 70.9, 31.7, 30.0, 29.1, 29.0, 25.4, 22.6, 14.1 ppm. IR (neat): 3897, 3778, 3649, 2964, 2866, 2185, 1734, 1603, 1379, 1176, 1018 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_9H_{18}F_2O_2NaS$ 251.0893; found 251.0891.

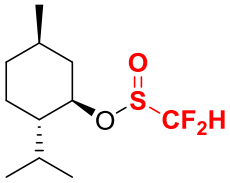
Dec-9-en-1-yl difluoromethanesulfinate (2g)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1g** (31.3 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2g** (49.8 mg, 98%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.86−5.73 (m, 1H), 5.83 (t, *J* = 55.5 Hz, 1H), 4.96 (t, *J* = 15.0 Hz, 2H), 4.21 (t, *J* = 7.5 Hz, 2H), 2.04−2.00 (m, 2H), 1.76−1.72 (m, 2H), 1.36−1.30 (m, 10H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.3 and –125.6 (d-AB quartet, *J* = 271.3, 54.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 139.1, 120.3 (t, *J* = 284.8 Hz), 114.2, 70.9, 33.7, 30.0, 29.2, 28.93, 28.91, 28.8, 25.3 ppm. IR (neat): 3745, 3606, 3462, 3008, 2933, 2858, 2503, 2312, 1730, 1448, 1236, 1153, 1045 cm^{-1}. HRMS (ESI) *m*/*z*: $[M-H]^+$ calcd. for $C_{11}H_{19}F_2O_2S$ 253.1074; found 253.1099.

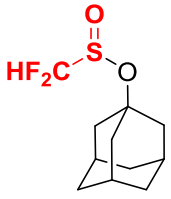
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl difluoromethanesulfinate (2h)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1h** (31.3 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2h** (46.1 mg, 91%, inseparable mixture of isomers; major:minor = 1:1) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.82 (t, *J* = 54.8 Hz, 0.5H), 5.79 (t, *J* = 54.9 Hz, 0.5H), 4.22−4.12 (m, 1H), 2.23−2.01 (m, 2H), 1.77−1.67 (m, 2H), 1.51−0.76 (m, 14H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.6− –125.6 (m, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 120.48 (t, *J* = 287.3 Hz), 120.47 (t, *J* = 281.6 Hz), 85.1, 83.3, 48.0, 47.8, 43.3, 42.2, 33.70, 33.65, 31.8, 31.7, 25.3, 25.2, 23.1, 22.9, 21.9, 21.8, 20.68, 20.66, 15.5, 15.4 ppm. IR (neat): 3842, 3757, 3016, 2960, 2933, 2866, 2735, 2185, 1666, 1464, 1348, 1165, 1097, 1038 cm^{-1}. HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{11}H_{20}F_2O_2NaS$ 277.1050; found 277.1054.

(3*S*,5*S*,7*S*)-Adamantan-1-yl difluoromethanesulfinate (2i)

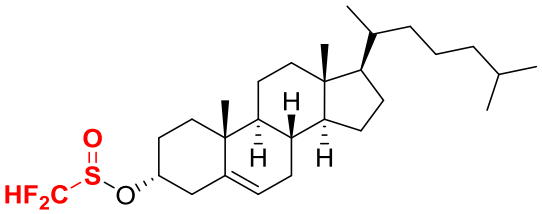


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), alcohol **1i** (30.5 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude

product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2i** (39.0 mg, 78%) as a white semi-solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.77 (t, *J* = 55.5Hz, 1H), 2.25 (br s, 3H), 2.02 (br s, 6H), 1.66 (br s, 6H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.8 and –125.8 (d- AB quartet, *J* = 267.1, 54.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 120.7 (t, *J* = 283.5 Hz), 84.7, 43.4, 35.5, 31.1 ppm. IR (KBr): 3969, 3869, 3745, 3685, 3566, 3471, 3307, 3199, 3072, 2848, 2646, 2355, 1703, 1442, 1304, 1169, 1090 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_{11}H_{16}F_2O_2S$ 250.0839; found 250.0842.

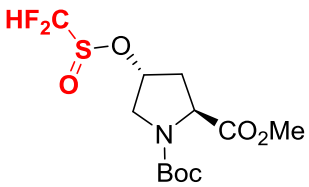
_O_-Difluoromethanesulfinyl 5-cholesten-3β-ol (2j)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.4 mmol, 2.0 equiv), 5-cholesten-3β-ol **1j** (77.3 mg, 0.2 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **2j** (85.9 mg, 89%, inseparable mixture of isomers; major:minor = 1:1) as a white solid.

Mp: 118.5–121.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.80 (t, *J* = 54.9 Hz, 1H), 5.41 (br s, 1H), 4.29−4.18 (m, 1H), 2.59−2.40 (m, 2H), 2.03−1.73 (m, 6H), 1.60−0.85 (m, 32H), 0.67 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.7 and –125.7 (d-AB quartet, *J* = 270.1, 53.3 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 138.71, 138.69, 123.7, 123.6, 120.4 (t, *J* = 285.4 Hz), 82.8, 82.7, 56.6, 56.1, 49.9, 42.3, 40.1, 39.6, 39.5, 37.0, 36.9, 36.42, 36.37, 36.1, 35.8, 31.8, 31.7, 29.8, 29.3, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.2, 18.7, 11.8 ppm. IR (KBr): 3980, 3884, 3797, 3705, 3562, 3458, 3319, 3045, 2867, 2713, 2351, 2193, 1666, 1360, 1161, 1105 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_{28}H_{46}F_2O_2S$ 484.3187; found 484.3202.

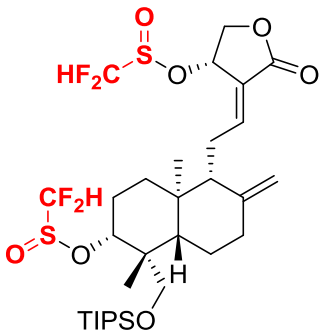
Difluoromethanesulfinate mono-ester of Proline derivative (2k)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), HF_2CSO_2Na (55.2 mg, 0.20 mmol, 2.0 equiv), alcohol **1k** (49.1 mg, 0.20 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (6:1) to give the

product **2k** (33.0 mg, 48%, inseparable mixture of isomers, major:minor = 1:1) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.87 (t, *J* = 54.0 Hz, 1H), 5.06 (s, 1H), 4.50–4.33 (s, 1H), 3.88–3.57 (m, 2H), 3.75 (s, 3H), 2.79–2.50 (m, 1H), 2.30–2.22 (m, 1H), 1.46 (s, 4.5H, minor isomer), 1.41 (s, 4.5H, major isomer) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.6–−127.2 (m, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ:172.7, 172.5, 153.5, 153.3, 120.2 (t, *J* = 288.5 Hz), 81.1, 79.5, 79.4, 79.0, 78.2, 57.9, 57.5, 57.4, 57.1, 57.0, 54.7, 54.6, 53.0, 52.7, 52.7, 52.5, 52.3, 52.1, 39.1, 38.5, 37.9, 37.5, 36.9, 36.6, 28.2 (3C) ppm. IR (KBr): 2980, 1751, 1705, 1404, 1163 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{12}H_{19}F_2NO_6NaS$ 366.0799; found 366.0807.

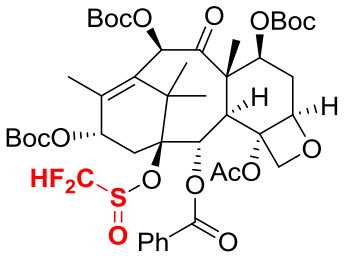
Difluoromethanesulfinate di-ester of 19-*O*-TIPS-andrographolide (2l)



Following general procedure with $Ph_2P(O)Cl$ (111.8 μL, 0.6 mmol, 4.0 equiv), HF_2CSO_2Na (82.8 mg, 0.6 mmol, 4.0 equiv), alcohol **1l** (77.9 mg, 0.15 mmol, 1.0 equiv) and toluene (0.75 + 0.75 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (7:3) to give the product **2l** (51.7 mg, 49%) as a white solid.

Mp: 58.3–59.6 °C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (s, 1H), 5.81 (t, *J* = 54.0 Hz, 1H), 5.76 (t, *J* = 55.5 Hz, 1H), 4.96 (s, 1H), 4.88−4.86 (m, 3H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.11−4.05 (m, 1H), 3.89 (t, *J* = 10.5, 1H), 3.73 (d, *J* = 9.0 Hz, 1H), 2.46−2.42 (m, 2H), 2.29-2.12 (m, 2H), 2.02-1.65 (m, 7H), 1.39-1.25 (m, 3H), 1.13 (s, 3H), 1.05 (s, 18H), 0.88-0.84 (m, 1H), 0.77 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –122.3, –125.0 (d, AB quartet, *J* = 270.7, 53.6 Hz, 2F), –123.1, –125.5 (d, AB quartet, *J* = 269.3, 56.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 171.2, 147.3, 146.2, 145.0, 135.8, 120.5 (t, *J* = 285.4 Hz), 120.4 (t, *J* = 284.1 Hz), 108.2, 92.1, 90.1, 70.2, 63.0, 55.6, 54.2, 52.9, 44.2, 38.6, 37.0, 32.3, 27.3, 26.1, 25.5, 23.0, 22.6, 18.1 (6C), 15.1, 11.9 (3C) ppm. IR (KBr): 2943, 1760, 1645, 1462, 1105, 810 cm^{-1}. MS (ESI) *m/z*: 725 $[M+Na]^+$ Calcd. Chemical formula: $C_{31}H_{50}F_4O_7S_2Si$, Mass = 702.27.

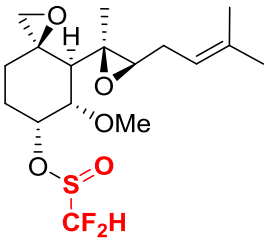
Difluoromethanesulfinate mono-ester of 7, 10, 13-triBoc-10-Deacetylbaccatin III (2m)



Following general procedure with $Ph_2P(O)Cl$ (33.5 μL, 0.18 mmol, 2.0 equiv), HF_2CSO_2Na (24.9 mg, 0.18 mmol, 2.0 equiv), alcohol **1m** (74.7 mg, 0.09 mmol, 1.0 equiv) and toluene (1.0 + 1.0 mL). A part of crude product was purified by silica gel column chromatography with hexane/ethyl acetate (4:1) to give the product **2m** (54%, yield was determined by ^{19}F NMR, because the product **2m** was unstable and decomposed within a few days in the fridge).

Mp: 213.8–215.0 °C ($CHCl_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.7, –125.5 (d, AB quartet, J = 266.5, 53.6 Hz, 2F) ppm. IR (KBr): 2985, 1713, 1654, 1087, 963, 799 cm^{-1}. MS (ESI) m/z: 965 $[M+Na]^+$. Calcd. Chemical formula: $C_{45}H_{60}F_2O_{17}S$, Mass = 942.35.

Difluoromethanesulfinate mono-ester of Fumagillol (2n)



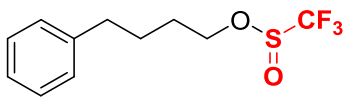
Following general procedure with $Ph_2P(O)Cl$ (22.4 μL, 0.12 mmol, 2.0 equiv), HF_2CSO_2Na (16.6 mg, 0.12 mmol, 2.0 equiv), alcohol **1n** (16.6 mg, 0.06 mmol, 1.0 equiv) and toluene (0.3 + 0.3 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (4:1) to give the product **2n** (9.0 mg, 40%) as a white solid.

Mp: 106.2–107.5 °C ($CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 6.20 (t, J = 52.5 Hz, 0.25H, minor isomer), 5.93 (t, J = 55.0 Hz, 0.75H, major isomer), 5.20 (t, J = 7.5 Hz, 1H), 5.05 (s, 1H), 3.70 (dd, J = 10.0, 5.0 Hz, 1H), 3.49 (s, 3H), 2.98 (d, J = 4.3 Hz, 1H), 2.60-2.57 (m, 2H), 2.39–2.34 (m, 1H), 2.22–2.04 (m, 3H), 1.98 (d, J = 10.0 Hz, 2H), 1.74 (s, 3H), 1.65 (s, 3H), 1.23 (s, 3H), 1.19–1.10 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –123.7, –125.3 (d, AB quartet, J = 272.1, 56.4 Hz, 2F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 134.9, 120.7 (t, J = 294.2 Hz), 118.5, 80.3, 79.5, 75.8, 74.1, 60.7, 59.1, 58.2, 56.7, 51.1, 47.7, 28.6, 27.3, 26.5, 25.7, 18.0, 14.2 ppm. IR (KBr): 3144, 2943, 1104, 922, 833 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{17}H_{26}F_2O_5NaS$ 403.1367; found 403.1353.

3. General Procedure for the trifluoromethylsulfinylation of alcohols

$Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv) was added to a suspension of F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv) in toluene (1.0 mL) under nitrogen atmosphere, and the reaction was stirred at room temperature for 30 min. A solution of the alcohol **1** (0.2 mmol, 1.0 equiv) in toluene (1.0 mL) was then added to the mixture followed by TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv), and the reaction was stirred at room temperature for 3 h. After this time, the reaction mixture was diluted with diethyl ether and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography using hexane/ethyl acetate (9:1) as the eluent.

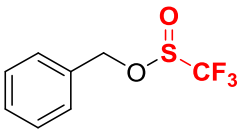
4-Phenylbutyl trifluoromethanesulfinate (3a)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1a** (30.0 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3a** (49.0 mg, 92%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32−7.25 (m, 2H), 7.22−7.16 (m, 3H), 4.39−4.34 (m, 1H), 4.15−4.10 (m, 1H), 2.66 (t, *J* = 6.9 Hz, 2H), 1.78−1.76 (m, 4H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –78.9 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 141.4, 128.41 (2C), 128.35 (2C), 126.0, 122.8 (q, *J* = 339.4 Hz), 68.8, 35.1, 29.2, 27.1 ppm. IR (neat): 3816, 3697, 3084, 3060, 3024, 2960, 2862, 1946, 1815, 1603, 1495, 1465, 1383, 1213, 1136 cm^{-1}. HRMS (EI) *m*/*z*: $[M]^+$ calcd. for $C_{11}H_{13}F_3O_2S$ 266.0588; found 266.0590.

Benzyl trifluoromethanesulfinate (3b) [2]

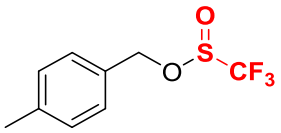


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1b** (21.6 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3b** (38.6 mg, 86%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41 (br s, 5H), 5.39 (d, *J* = 9.0 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –78.4 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 133.6, 129.5, 129.0 (2C), 128.9 (2C), 123.0 (q, *J* = 339.8 Hz), 69.8 ppm. IR (neat): 3076, 2964, 2925, 2852, 2308, 1894, 1726, 1498, 1464, 1367, 1192, 1120 cm^{-1}. HRMS (EI) *m*/*z*: $[M+Na]^+$ calcd. for $C_8H_7F_3O_2S$

224.0119; found 224.0126.

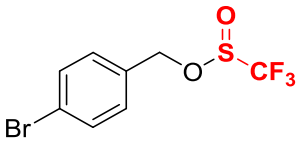
4-Methylbenzyl trifluoromethanesulfinate (3c) [2]



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1c** (24.4 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3c** (95%, yield was determied by ^{19}F NMR, unstable under silica gel column chromatography) as pale yellow solid.

Mp: 56.1–57.3 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 2H), 5.34 (d, *J* = 12.0 Hz, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 2.38 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –78.8 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 140.2, 131.1 (2C), 130.0 (2C), 119.8, 119.7 (q, *J* = 328.9 Hz), 55.8, 21.3 ppm. IR (KBr): 3973, 3820, 3678, 3535, 3427, 3224, 3045, 2885, 2721, 2362, 1913, 1610, 1519, 1360, 1192, 1120 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_9H_9F_3O_2S$ 238.0275; found 238.0277.

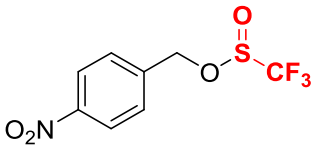
4-Bromobenzyl trifluoromethanesulfinate (3d)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1d** (37.4 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3d** (56.0 mg, 92%) as brown oil.

^1H NMR (300 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –78.6 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 132.6, 132.2 (2C), 130.4 (2C), 123.7, 122.9 (q, *J* = 339.8 Hz), 68.6 ppm. IR (KBr): 3714, 3570, 3041, 2885, 2395, 1894, 1595, 1491, 1404, 1367, 1304, 1277, 1217, 1128, 1065 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_8H_6BrF_3O_2S$ 301.9224; found 301.9233.

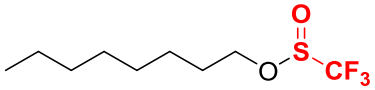
4-Nitrobenzyl trifluoromethanesulfinate (3e)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1e** (30.6 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL) crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3e** (49.2 mg, 91%) as a white solid.

Mp: 56.1−57.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 5.49 (d, *J* = 15.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –78.2 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 148.3, 140.7, 128.9 (2C), 124.1 (2C), 122.9 (q, *J* = 340.2 Hz), 67.1 ppm. IR (KBr): 3965, 3849, 3674, 3610, 3479, 3352, 3195, 3020, 2862, 2654, 2436, 2305, 1738, 1512, 1196, 1113 cm^{-1}. HRMS (ESI) *m/z*: $[M–H]^+$ calcd. for $C_8H_5F_3NO_4S$ 267.9891; found 267.9889.

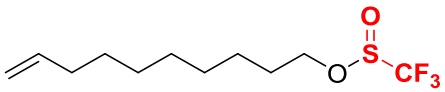
Octyl trifluoromethanesulfinate (3f) [3]



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1f** (26.0 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3f** (43.1 mg, 87%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.37 (d, *J* = 7.1 Hz, 1H), 4.15 (d, *J* = 6.2 Hz, 1H), 1.76 (br s, 2H), 1.38−1.29 (m, 10H), 0.89 (br s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –79.0 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 122.8 (q, *J* = 339.8 Hz), 69.2, 31.7, 29.7, 29.0, 28.9, 25.3, 22.6, 14.1 ppm. IR (neat): 3001, 2952, 2929, 2848, 2359, 2312, 1468, 1379, 1200, 1132 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_9H_{17}F_3O_2NaS$ 269.0799; found 269.0790.

Dec-9-en-1-yl trifluoromethanesulfinate (3g)

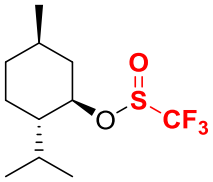


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1g** (31.2 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3g** (51.2 mg, 94%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.87−5.74 (m, 1H), 5.01−4.91 (m, 2H), 4.39−4.32 (m, 1H), 4.17−4.10

(m, 1H), 2.05−2.00 (m, 2H), 1.77−1.71 (m, 2H), 1.36−1.30 (m, 10H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –79.0 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 139.1, 122.8 (q, *J* = 339.8 Hz), 114.2, 69.2, 33.7, 29.7, 29.2, 28.92, 28.91, 28.8, 25.3 ppm. IR (neat): 3080, 2929, 2852, 2376, 2316, 1815, 1734, 1643, 1460, 1435, 1371, 1284, 1205, 1128 cm^{-1}. HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{11}H_{19}F_3O_2NaS$ 295.0956; found 295.0959.

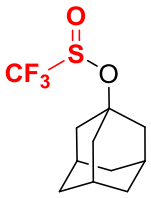
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl trifluoromethanesulfinate (3h)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1h** (31.2 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3h** (44.2 mg, 81%, major:minor = 5:4) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.31−4.20 (m, 1H), 2.23−1.98 (m, 2H), 1.79−1.68 (m, 2H), 1.57−0.74 (m, 14H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –80.4 (s, 3F, major), –81.0 (s, 3F, minor) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 122.62 (q, *J* = 336.0 Hz), 122.61 (q, *J* = 335.2 Hz), 85.4, 84.5, 47.9, 47.7, 42.8, 42.1, 33.61, 33.59, 31.9, 31.7, 25.4, 25.2, 23.1, 22.9, 21.84, 21.78, 20.7, 20.6, 15.5, 15.4 ppm. IR (neat): 2952, 2933, 2866, 2725, 2376, 2305, 1464, 1383, 1188, 1128 cm^{-1}. HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{11}H_{19}F_3O_2NaS$ 295.0956; found 295.0954.

(3*S*,5*S*,7*S*)-Adamantan-1-yl trifluoromethanesulfinate (3i)

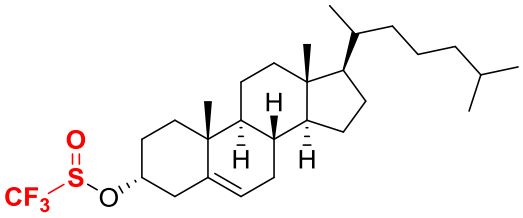


Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), alcohol **1i** (30.4 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3i** (37.2 mg, 69%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.06 (br s, 6H), 1.68 (br s, 6H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –81.1 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 122.8 (q, *J* = 334.3 Hz), 86.5, 43.3, 35.4, 31.2 ppm. IR (neat): 3726, 3626, 3539, 3375, 3236, 2937, 2866, 2368, 2081, 1670, 1558, 1456, 1363,

1213, 1173, 1124, 1049 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_{11}H_{15}F_3O_2S$ 268.0745; found 268.0737.

Difluoromethanesulfinyl 5-cholesten-3β-ol (3j)



Following general procedure with $Ph_2P(O)Cl$ (37.3 μL, 0.2 mmol, 1.0 equiv), F_3CSO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv), 5-cholesten-3β-ol **1j** (77.3 mg, 0.2 mmol, 1.0 equiv), TMSCl (2.5 μL, 0.02 mmol, 0.1 equiv) and toluene (1.0 + 1.0 mL), crude product was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) to give the product **3j** (76.5 mg, 76%, major:minor = 6:5) as a white solid.

Mp: 145.0−147.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.41 (br s, 1H), 4.42−4.31 (m, 1H), 2.62−2.37 (m, 2H), 2.04−1.77 (m, 6H), 1.60−0.85 (m, 32H), 0.67 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –80.5 (s, 3F, minor), –80.5 (s, 3F, major) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 138.53, 138.51, 123.9, 122.7 (q. *J* = 336.8 Hz), 83.1, 83.0, 56.6, 56.1, 49.9, 42.3, 39.8, 39.6, 39.5, 37.0, 36.9, 36.40, 36.37, 36.1, 35.8, 31.9, 31.7, 29.5, 29.4, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.2, 18.7, 11.8 ppm. IR (KBr): 3965, 3880, 3797, 3670, 3606, 3518, 3394, 3203, 3089, 2881, 2619, 2320, 1714, 1367, 1176, 1132 cm^{-1}. HRMS (EI) *m/z*: $[M]^+$ calcd. for $C_{28}H_{45}F_3O_2S$ 502.3092; found 502.3094.

4. Crystal data collection and structure refinement for 4-Nitrobenzyl trifluoromethanesulfinate (3e)

Data Collection

A colorless block crystal of $C_8H_6F_3NO_4S$ prepared from **3e** in Hexane having approximate dimensions of 0.250 x 0.150 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Ka radiation.

The data were collected at a temperature of -100 ± 1 °C to a maximum 2q value of 54.9°. A total of 44 oscillation images were collected. A sweep of data was done using w scans from 130.0 to 190.0° in 5.0° step, at c=45.0° and f = 0.0°. The exposure rate was 10.0 [sec./°]. A second sweep was performed using w scans from 0.0 to 160.0° in 5.0° step, at c=45.0° and f = 180.0°. The exposure rate was 10.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

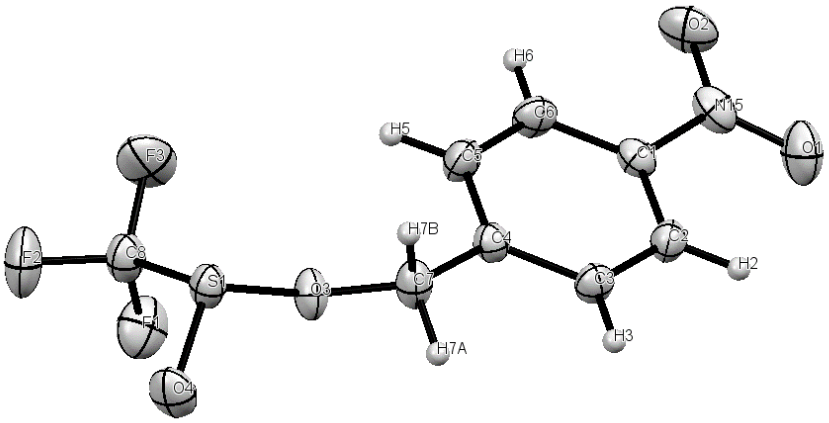


Figure S1. Thermal ellipsoid plot of the molecular structure of **3e**. Thermal ellipsoid probability set to 50%, only one molecule of the asymmetric unit shown.

A. Crystal Data

Empirical Formula	$C_8H_6BrF_3NO_4S$
Formula Weight	269.119
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.250 X 0.150 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 4.9106(2) Å
	b = 19.7529(6) Å
	c = 10.8754(4) Å
	b = 103.8638(9) ^{o}
	V = 1024.16(5) Å^3
Space Group	$P2_1$ (#14)
Z value	4
D_{calc}	1.746 g/cm^3
F_{000}	544.00
m(MoKa)	3.636 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKa (l = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 24mA

Temperature	-100.0 °C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
w oscillation Range (c=45.0, f=0.0)	130.0 - 190.0°
Exposure Rate	10.0 sec./°
w oscillation Range (c=45.0, f=180.0)	0.0 - 160.0°
Exposure Rate	10.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2q_{max}$	54.9°
No. of Reflections Measured	Total: 9834
	Unique: 2338 (R_{int} = 0.0.146)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.728 - 0.964)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	S w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [s^2 (Fo^2) + (0.0435 \cdot P)^2$
	$+ 0.3535 \cdot P]$
	where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2q_{max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2338
No. Variables	154
Reflection/Parameter Ratio	15.18
Residuals: R1 (I>2.00s(I))	0.0291
Residuals: R (All reflections)	0.0323
Residuals: wR2 (All reflections)	0.0829
Goodness of Fit Indicator	1.098
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.32 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.31 $e^-/Å^3$

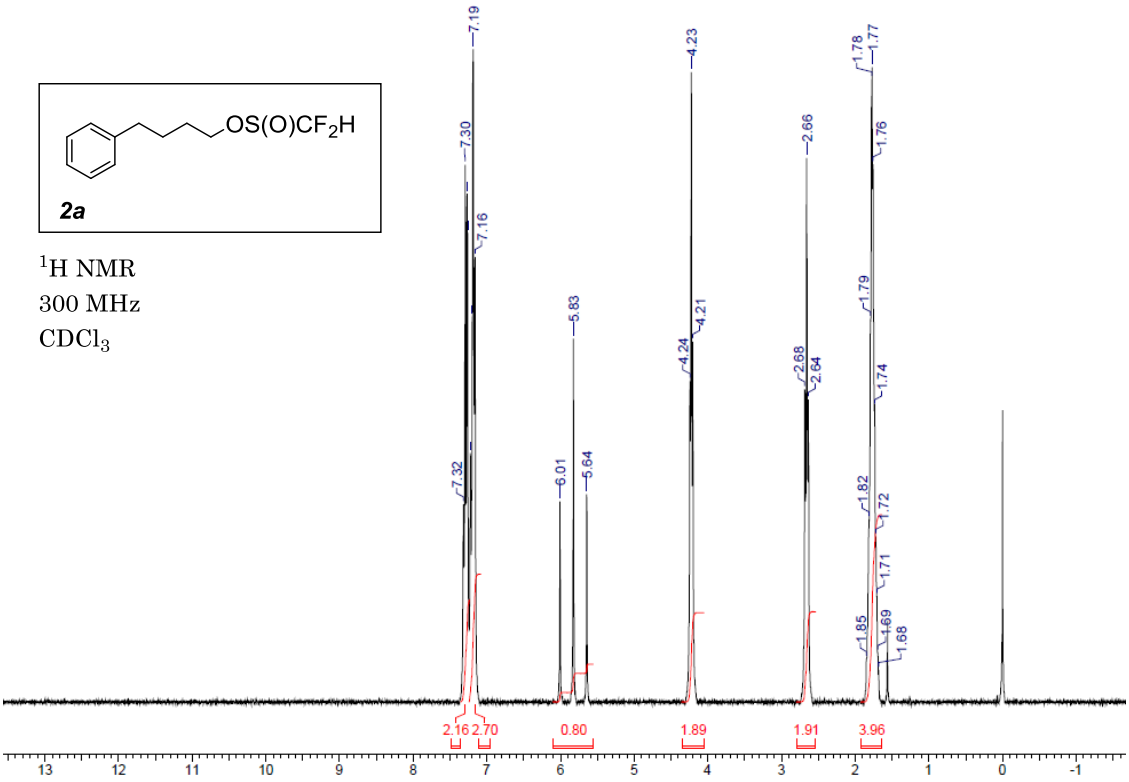
5. References

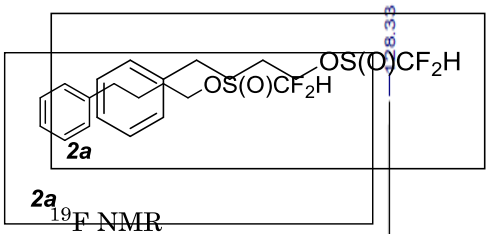
1. Yang, Q.; Li, Y.; Yang, J.-D.; Liu, Y.; Zhang, L.; Luo, S.; Cheng. J.-P. *Angew. Chem., Int. Ed.* **2020**, *19*, 19282–19291.

2. Braverman, S.; Manor, H. *Phosphorur, Sulfur, and Silicon* **1990**, *53*, 357.

3. Hasegawa, A.; Ishikawa, T.; Ishihara, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1401.

6. ^{1}H, ^{19}F and ^{13}C NMR spectra of compound 2 and 3





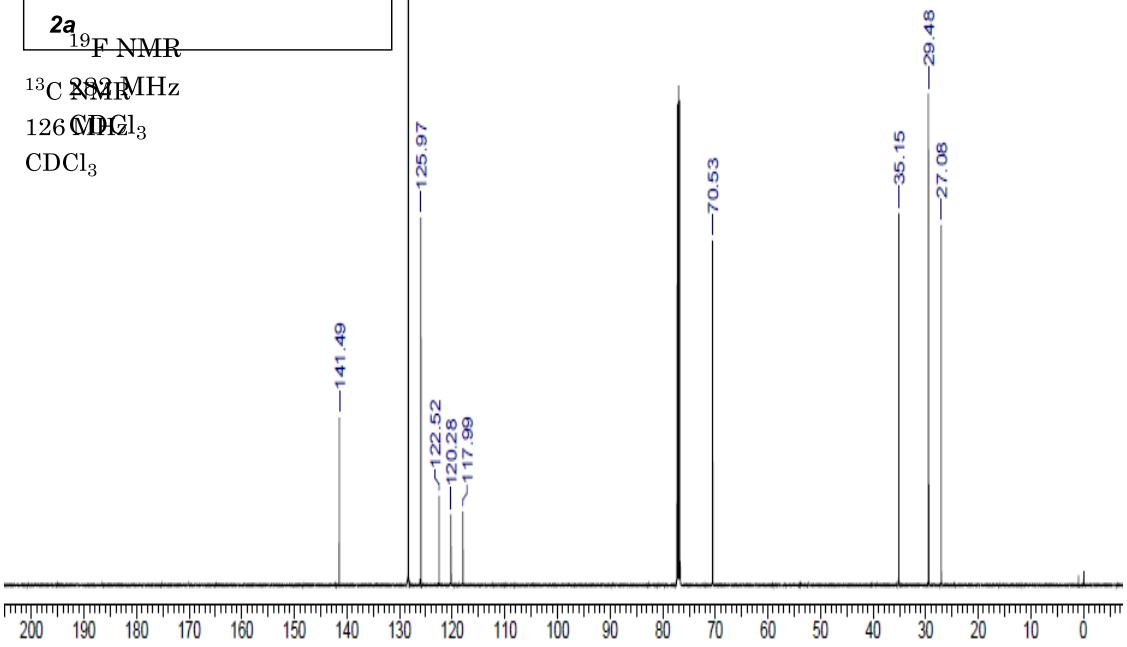
2a

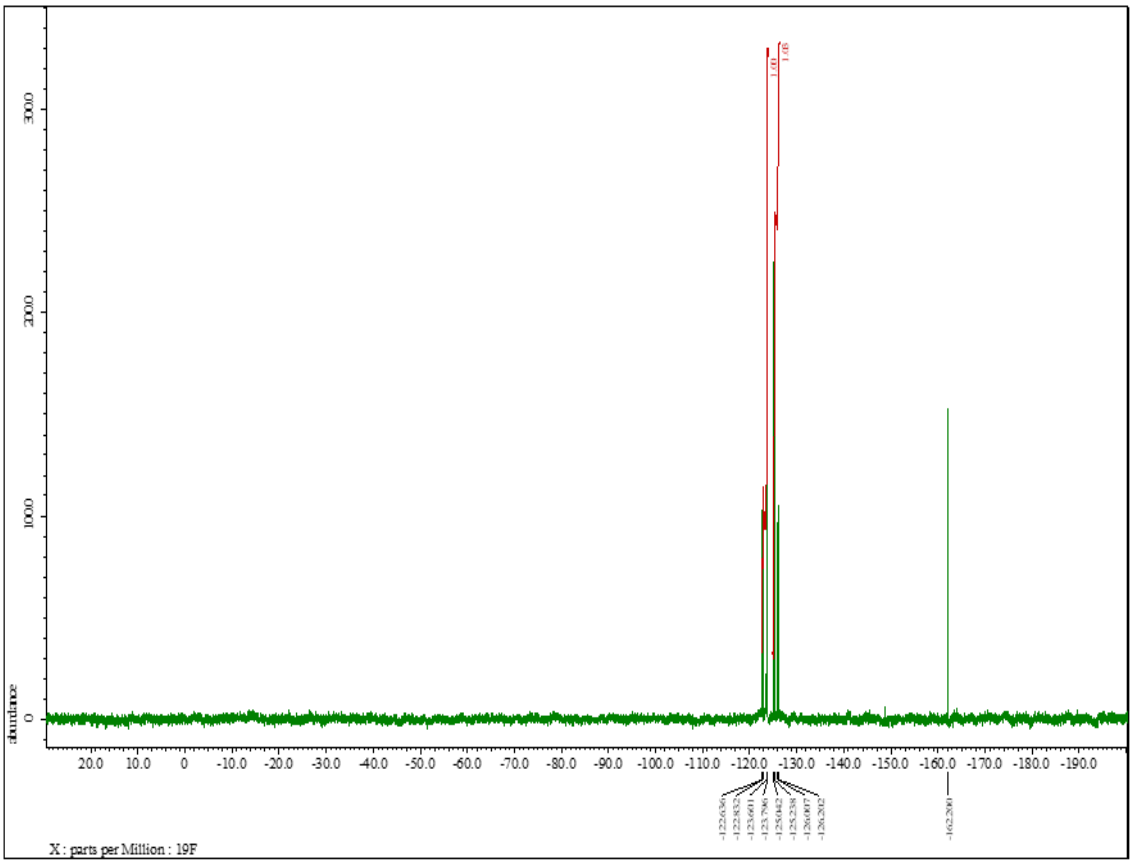
^{19}F NMR

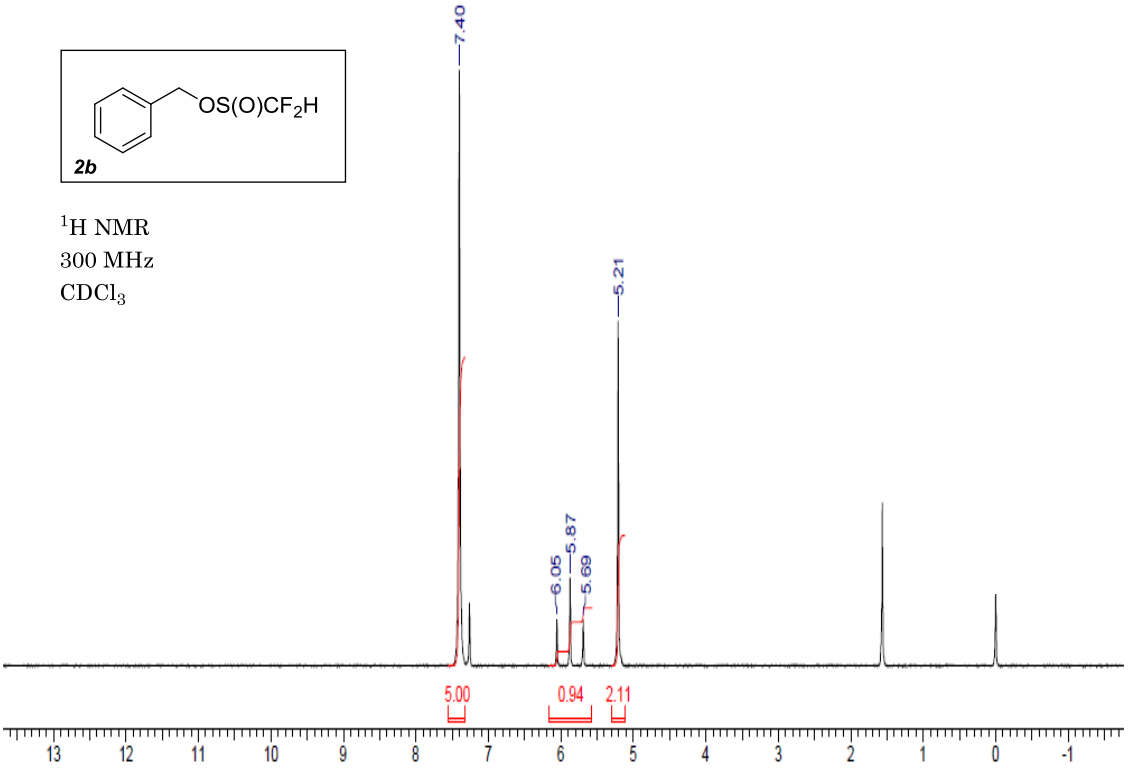
^{13}C NMR

126 MHz

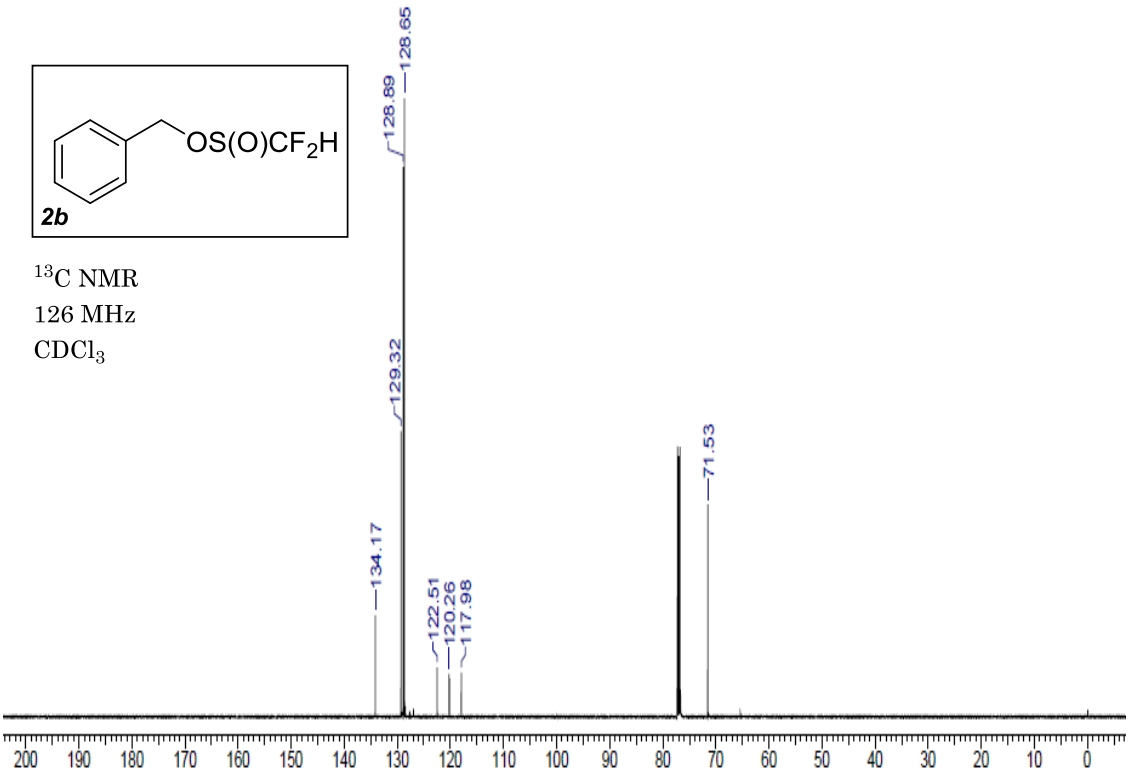
$CDCl_3$



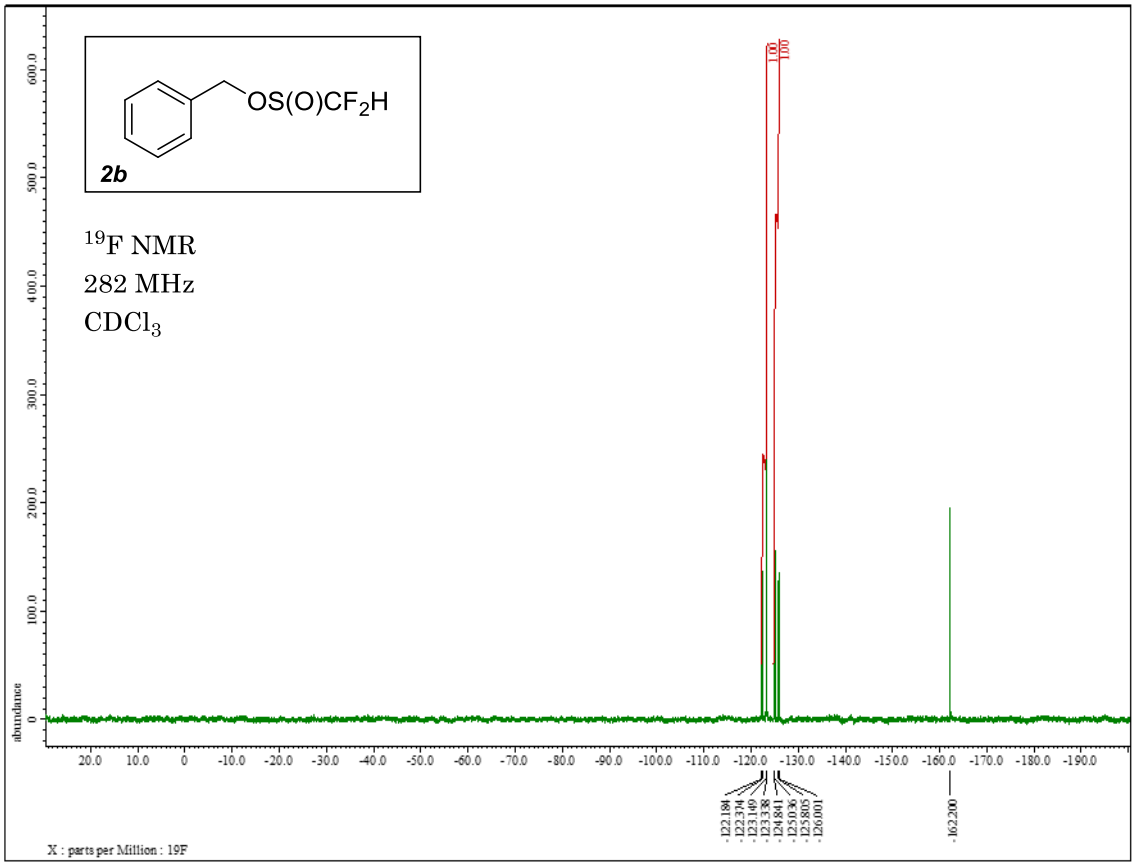




^{1}H NMR
300 MHz
$CDCl_3$



^{13}C NMR
126 MHz
$CDCl_3$


OS(O)CF2H
2b
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F
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-122.374
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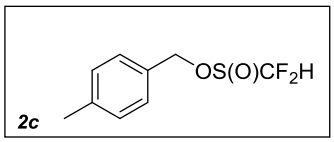
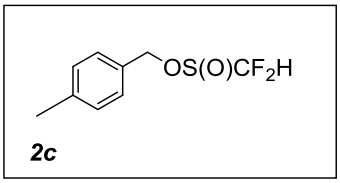
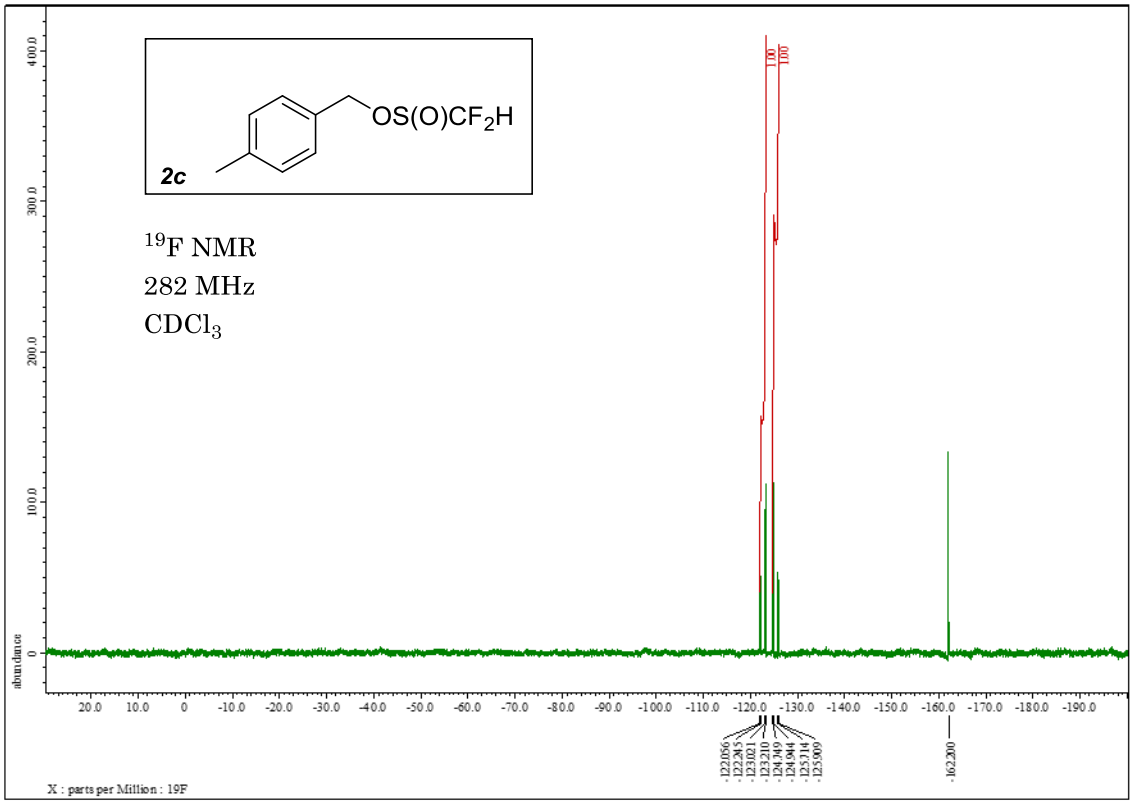
-123.338
-124.841
-125.036
-125.805
-126.001
-162.200



^{1}H NMR
300 MHz
$CDCl_3$



^{13}C NMR
126 MHz
$CDCl_3$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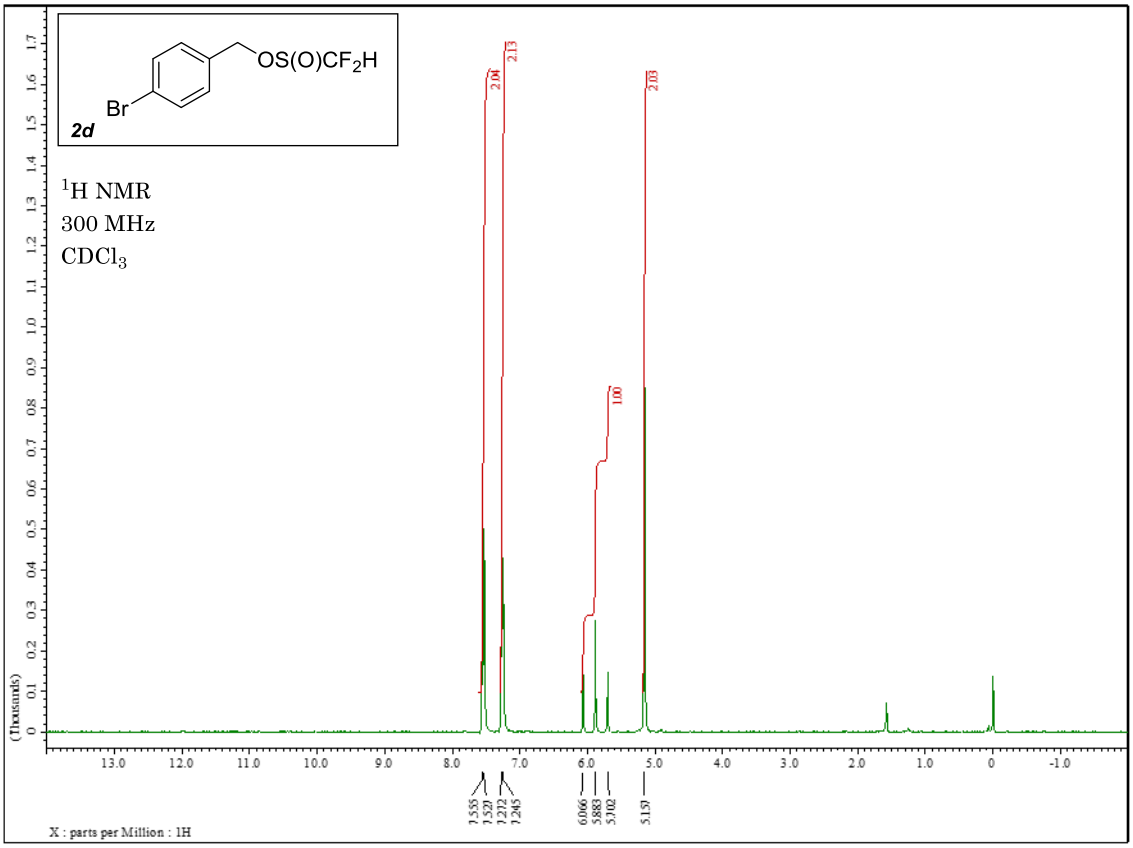
2c
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F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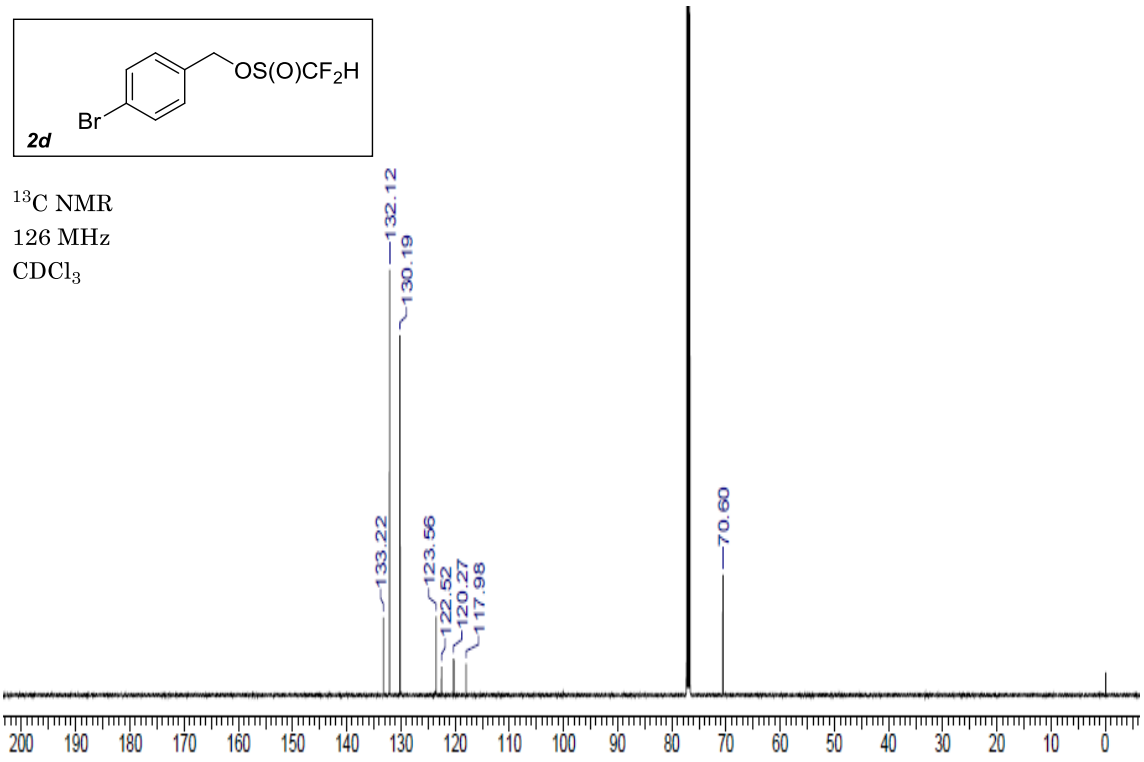
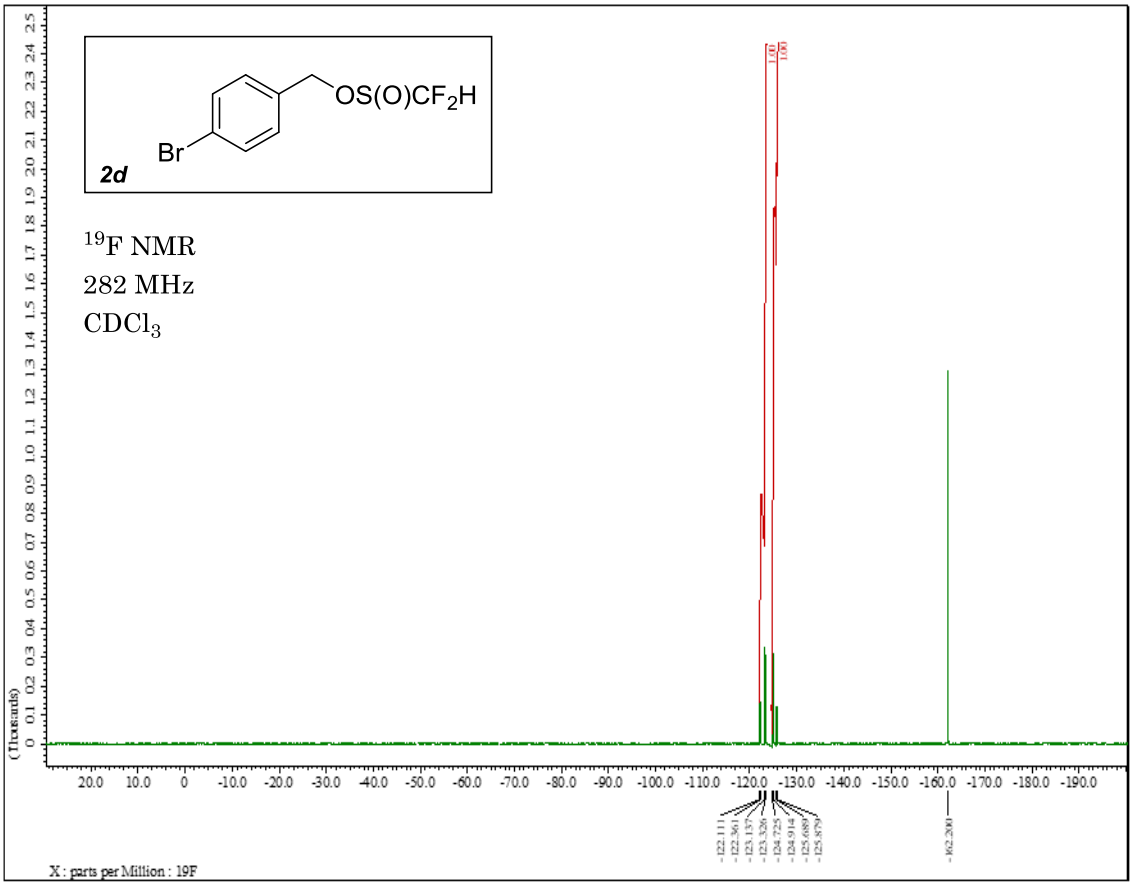
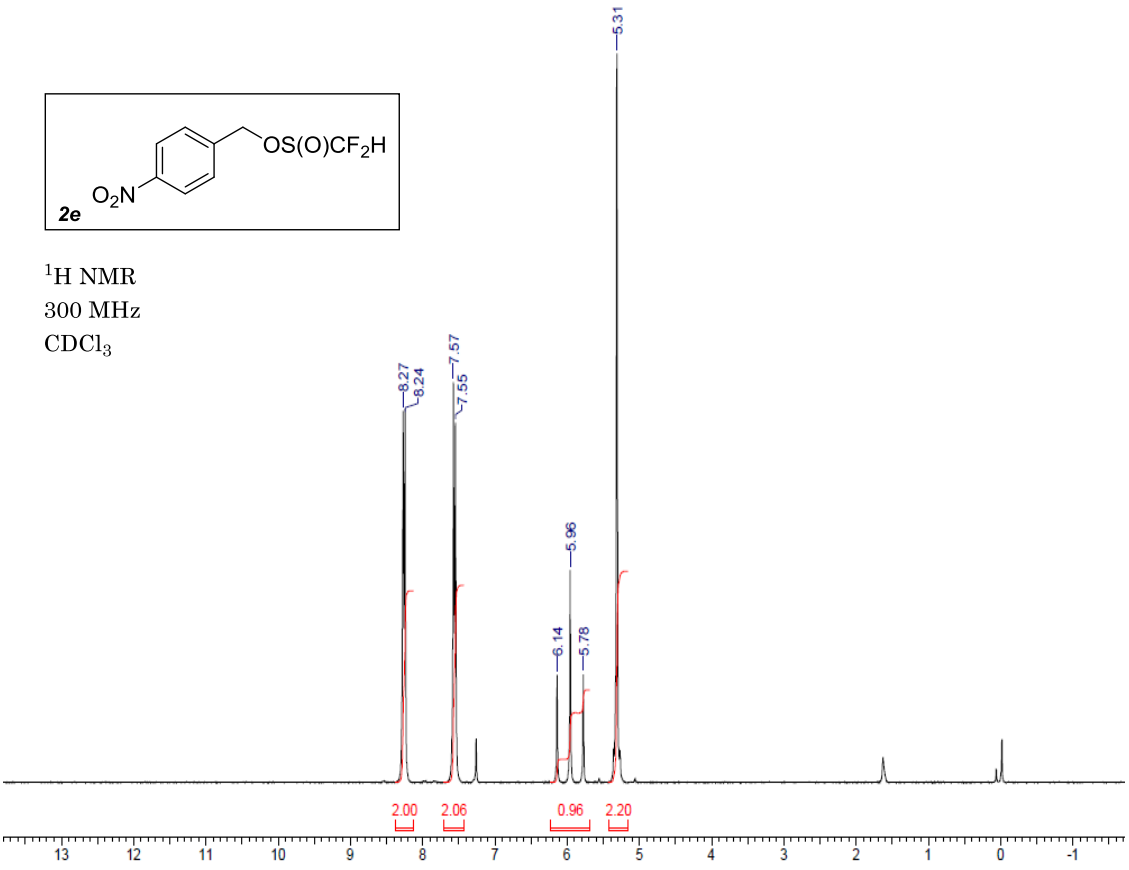
Br
2d
1H NMR
300 MHz
CDCl3
(Thousands)
X : parts per Million : 1H



^{13}C NMR
126 MHz
$CDCl_3$



^{19}F NMR
282 MHz
$CDCl_3$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2e
1H NMR
300 MHz
CDCl3
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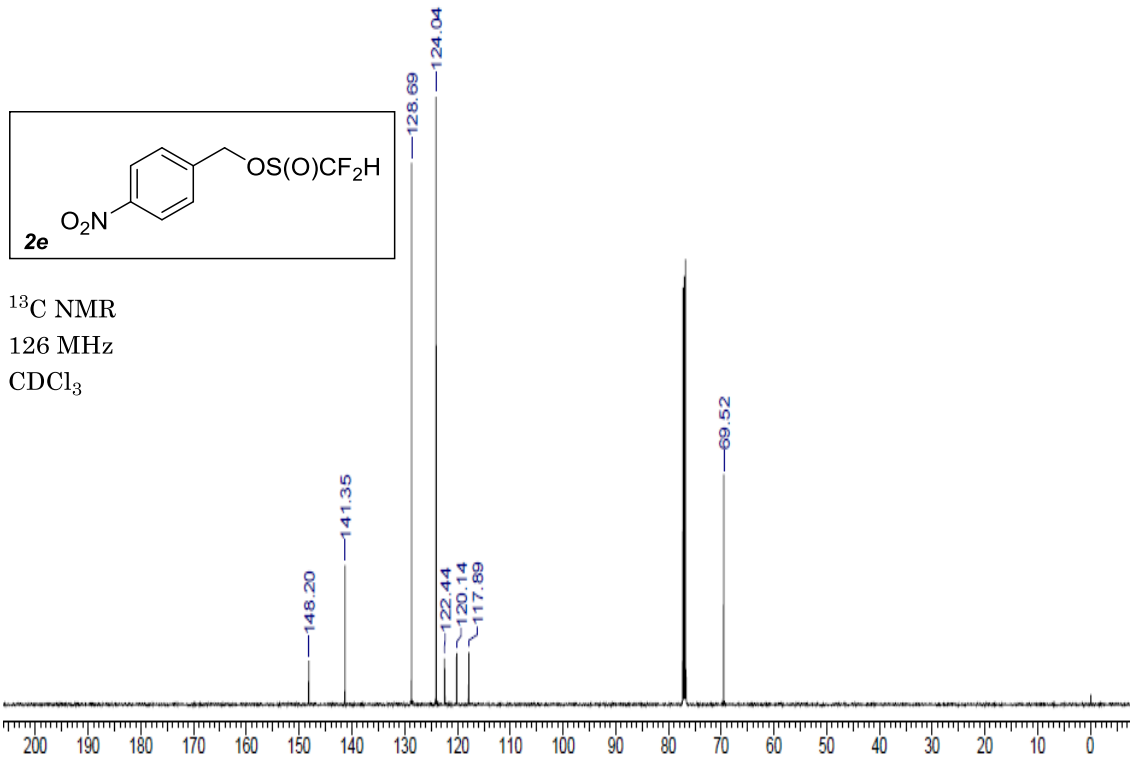
5.31
2.00
2.06
0.96
2.20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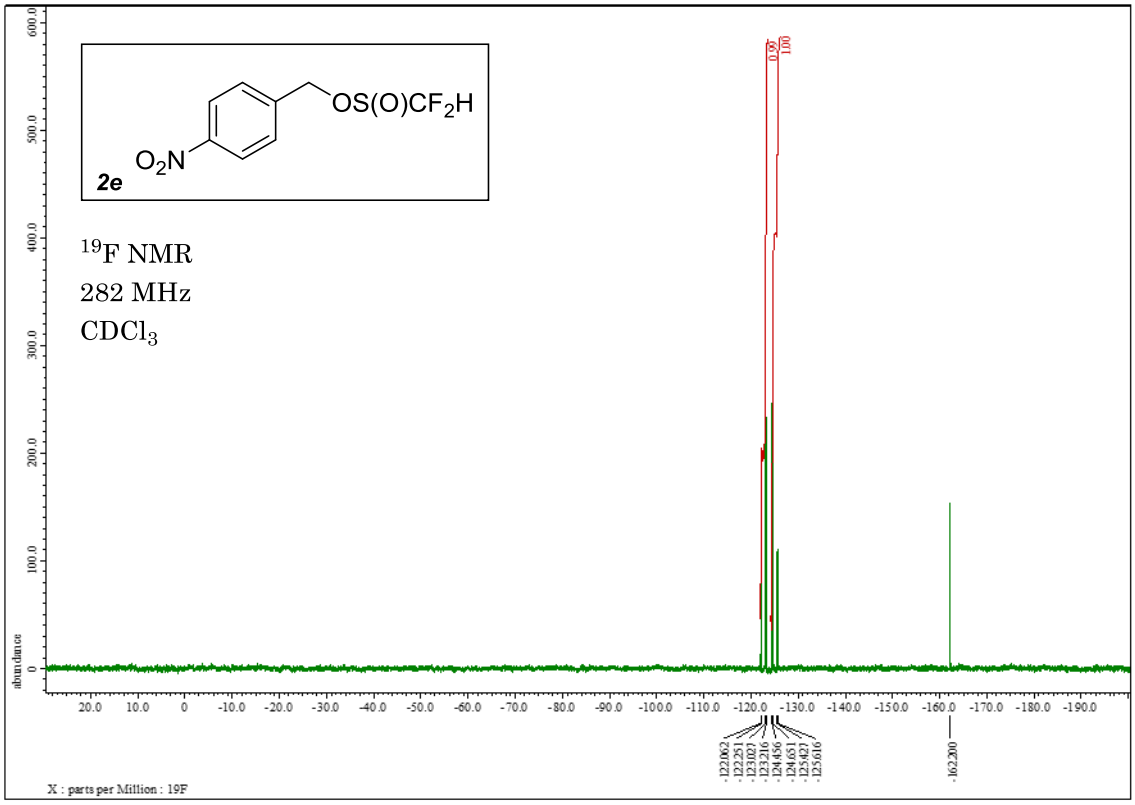
69.52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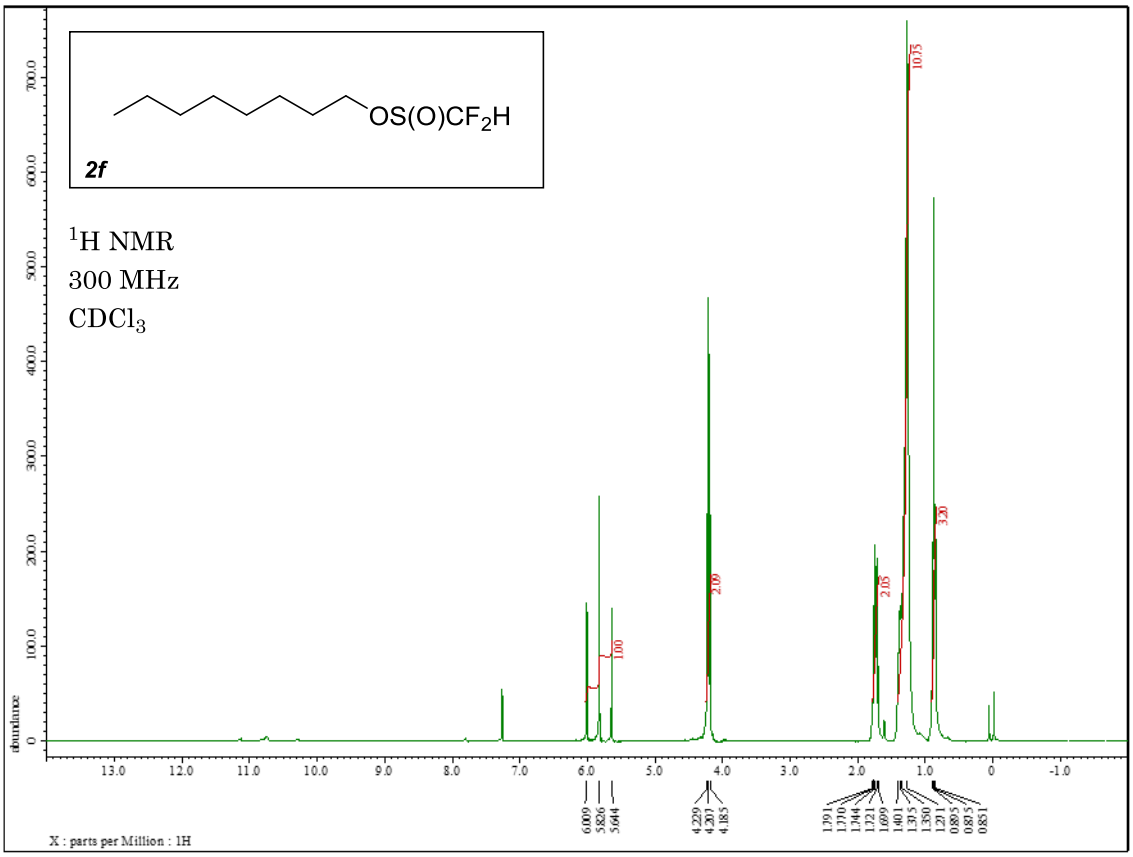
O2N
2e
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F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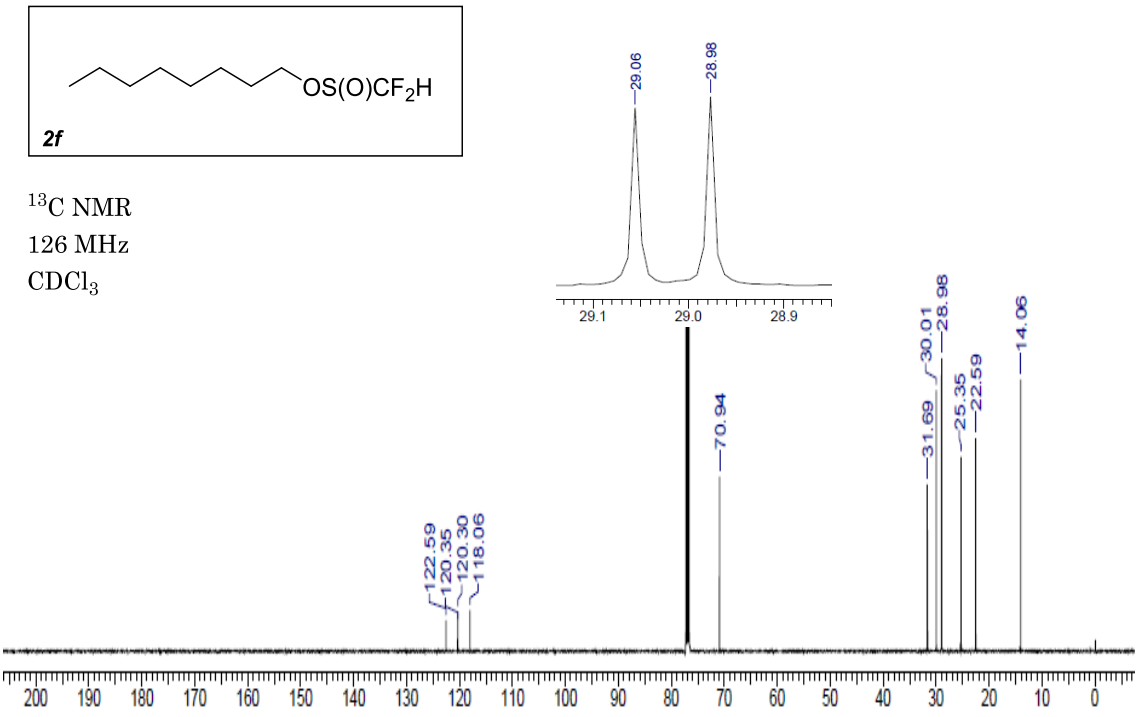
2f
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H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2f
13C NMR
126 MHz
CDCl3
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29.1
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28.9
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14.06
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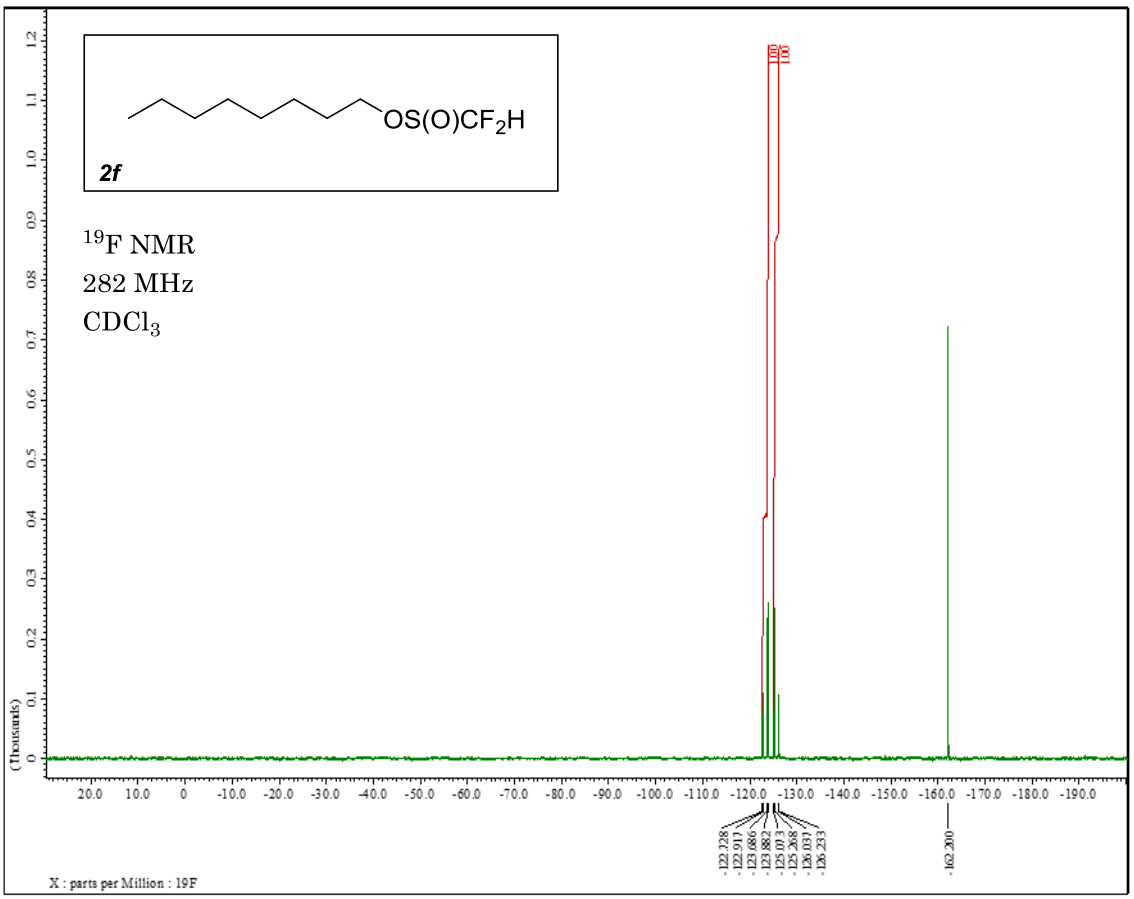
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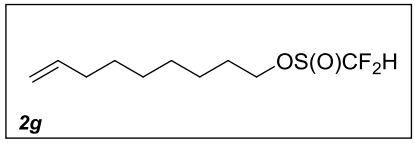
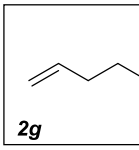
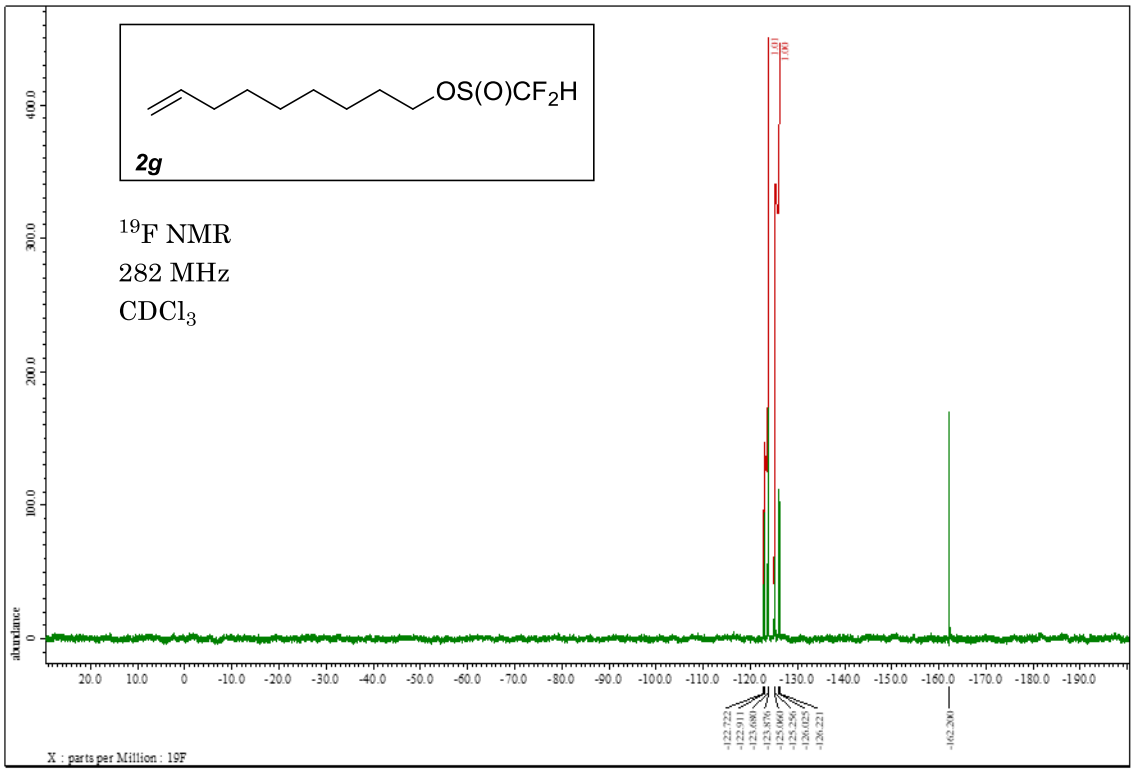
2f
19F NMR
282 MHz
CDCl3
(Thousands)
X : parts per Million : 19F



^{1}H NMR
300 MHz
$CDCl_3$



^{13}C NMR
126 MHz
$CDCl_3$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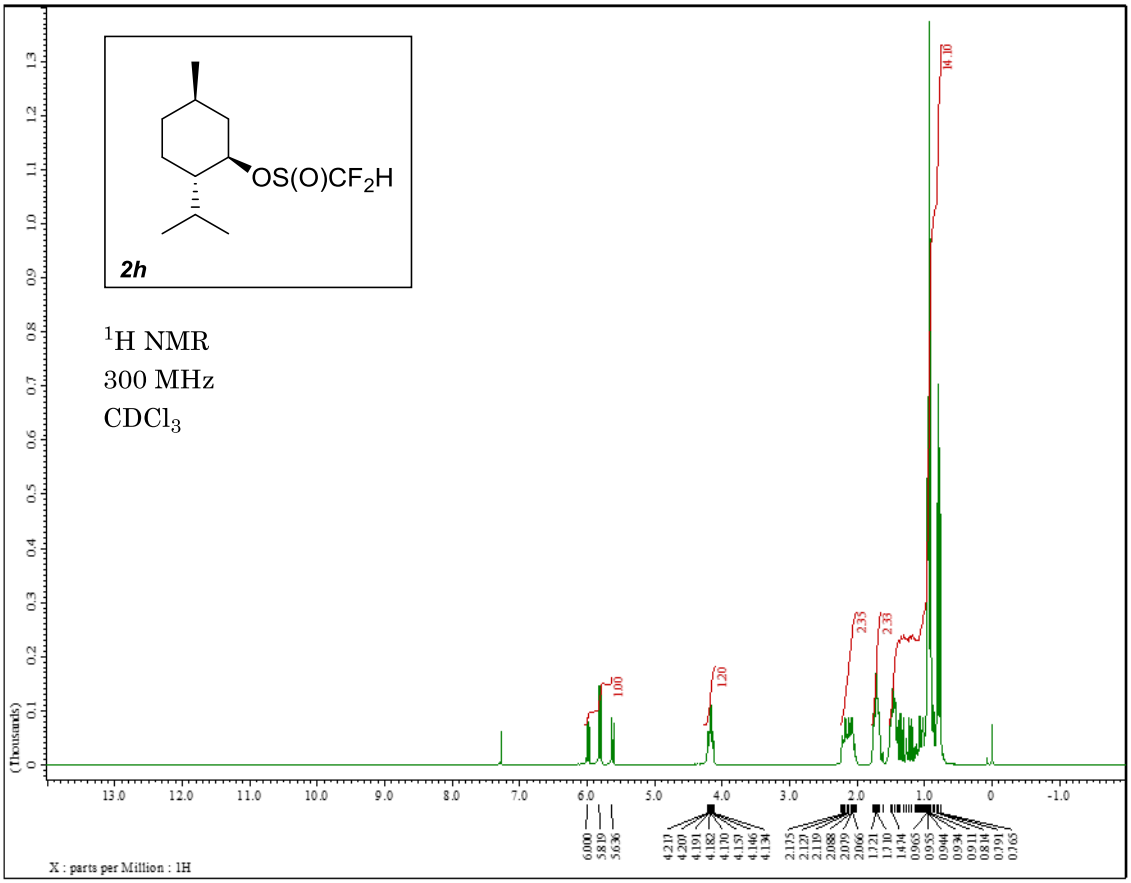
2g
19F NMR
282 MHz
CDCl3
X : parts per Million : 19F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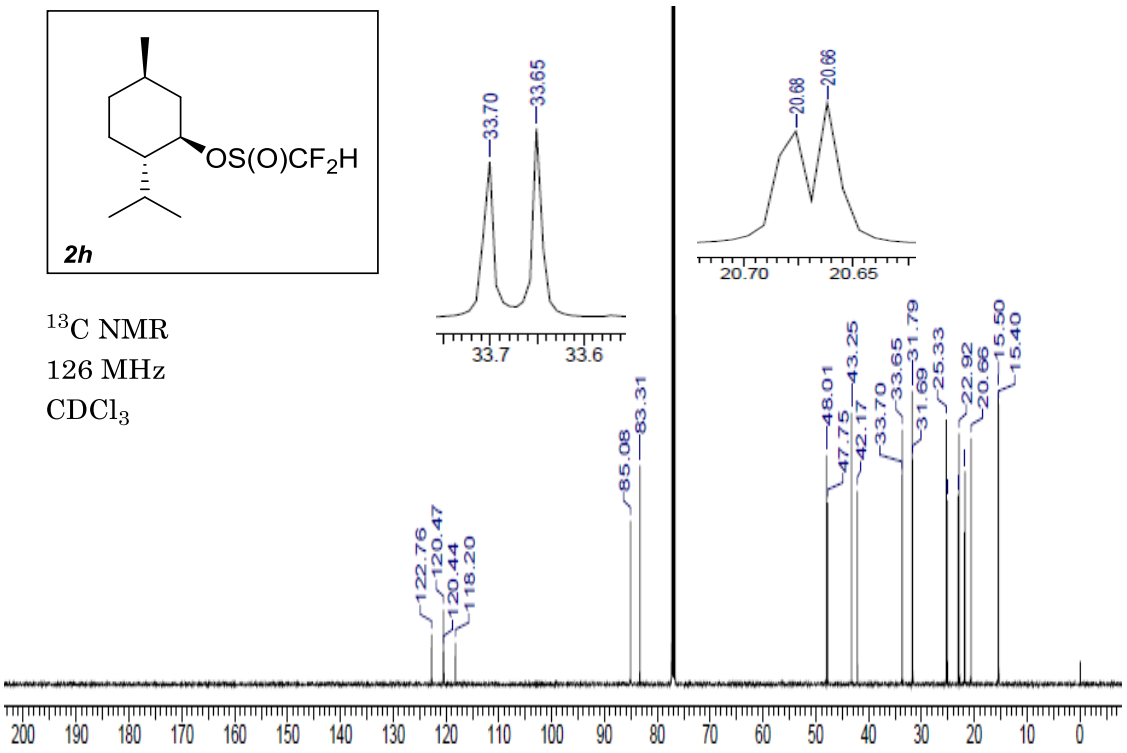
2h
1H NMR
300 MHz
CDCl3
X : parts per Million : 1H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33.65
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122.76
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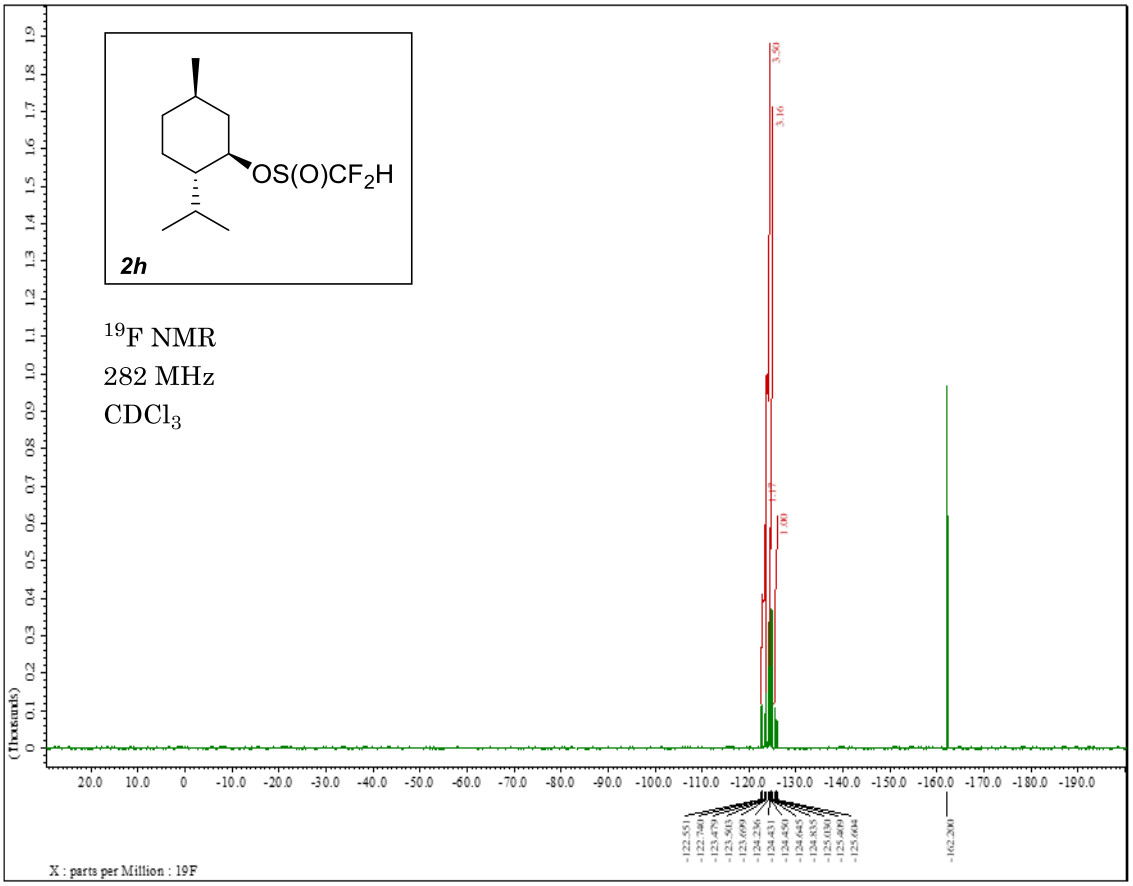
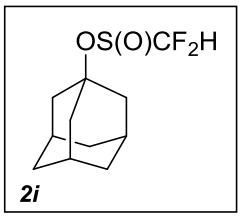
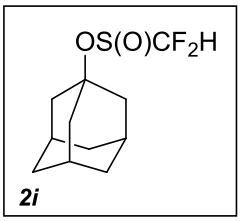
48.01
47.75
43.25
42.17
33.70
33.65
31.79
31.69
25.33
22.92
20.66
15.50
15.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

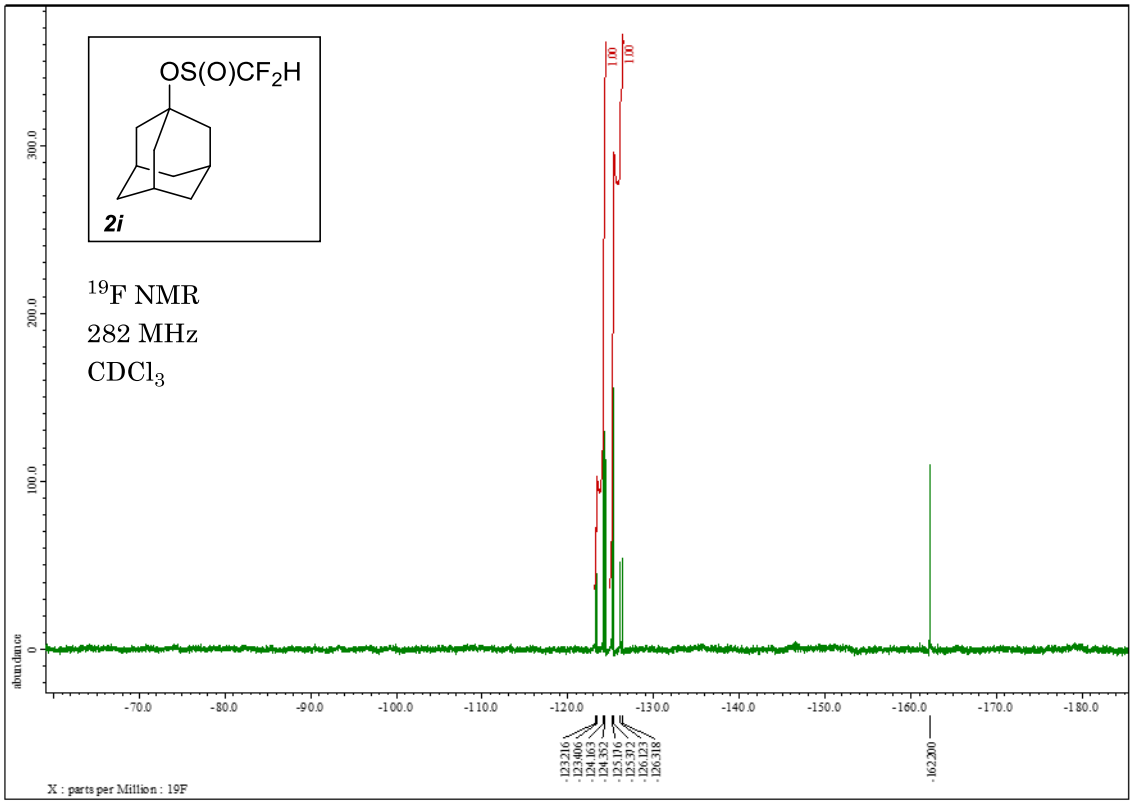

OS(O)CF2H
2h
19F NMR
282 MHz
CDCl3
3.50
3.16
1.17
1.00
(Thousands)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : 19F

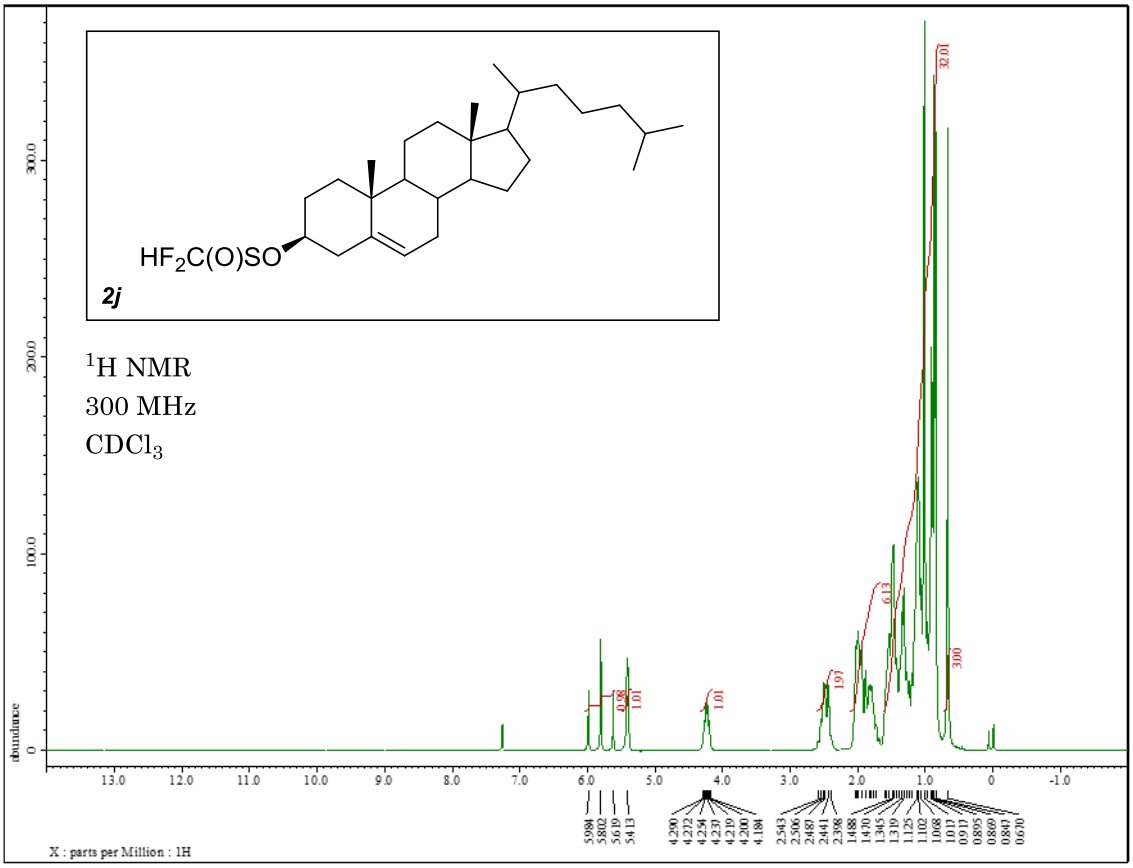


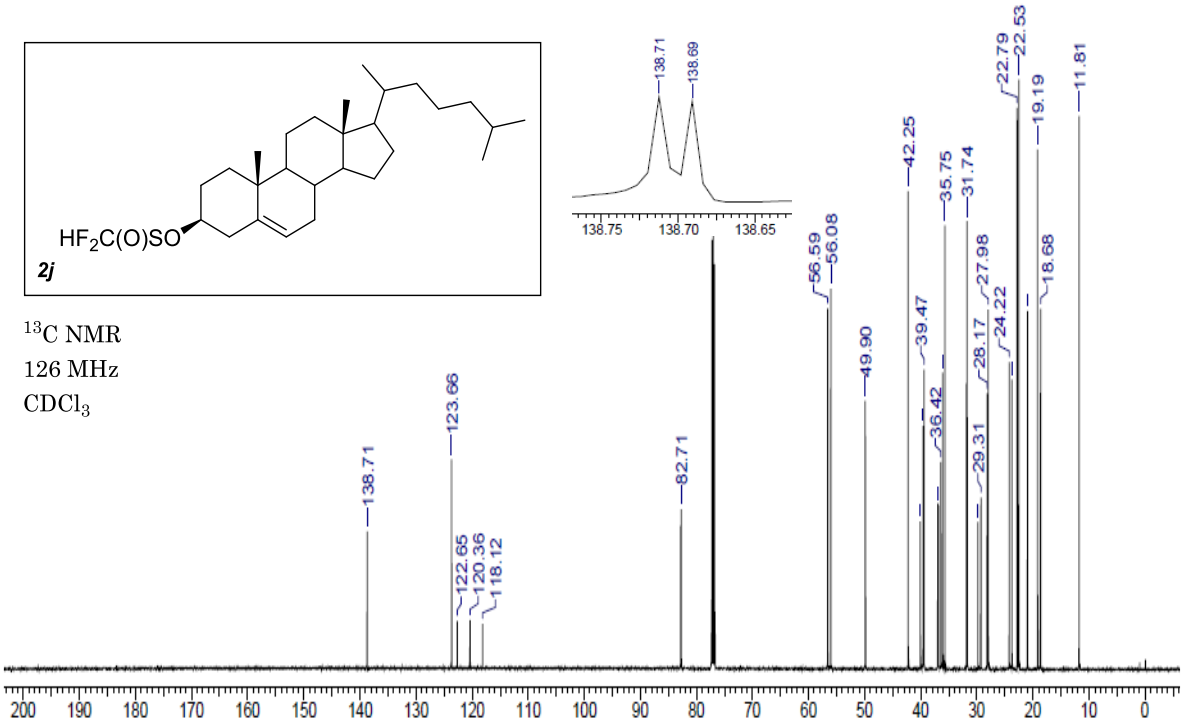
^{1}H NMR
300 MHz
$CDCl_3$

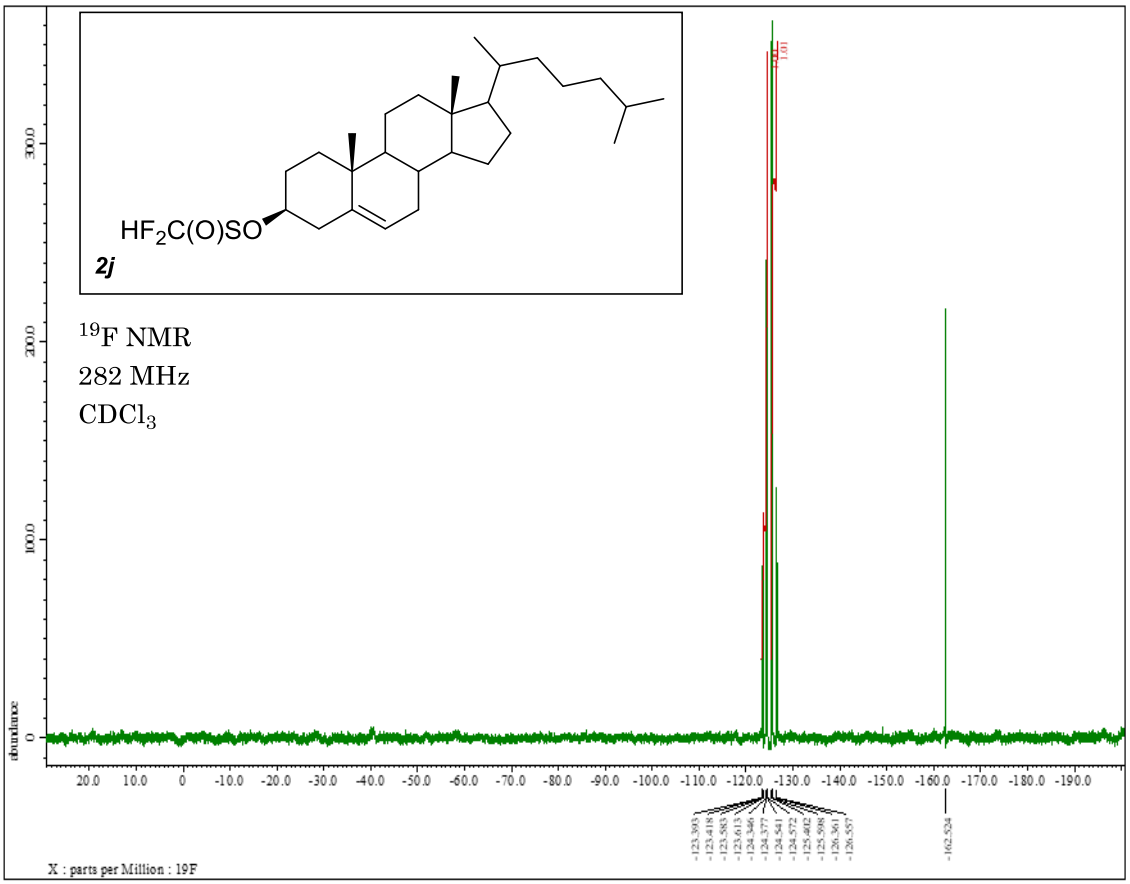


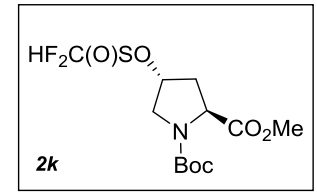
^{13}C NMR
126 MHz
$CDCl_3$


OS(O)CF2H
2i
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F

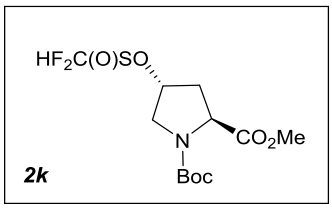

HF2C(O)SO
2j
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H


HF2C(O)SO
2j
13C NMR
126 MHz
CDCl3
138.71
138.69
138.75
138.70
138.65
42.25
35.75
31.74
22.79
22.53
19.19
11.81
56.59
56.08
49.90
39.47
36.42
29.31
28.17
27.98
24.22
18.68
138.71
123.66
122.65
120.36
118.12
82.71
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

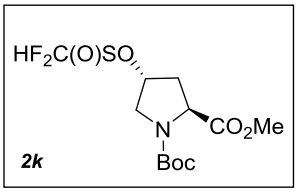

HF2C(O)SO
2j
19F NMR
282 MHz
CDCl3
abundance
300.0
200.0
100.0
0
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : 19F



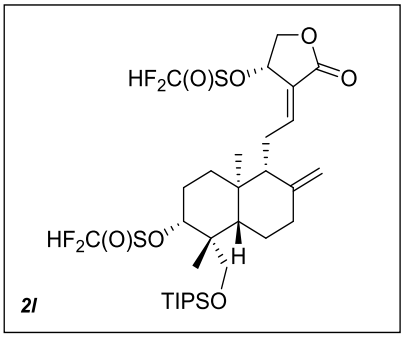
^{1}H NMR
300 MHz
$CDCl_3$



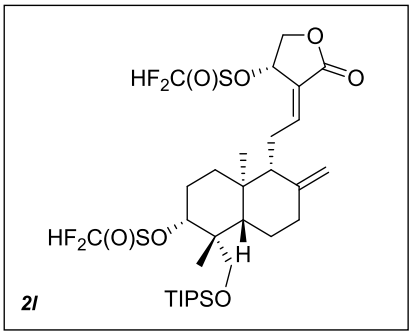
^{13}C NMR
126 MHz
$CDCl_3$



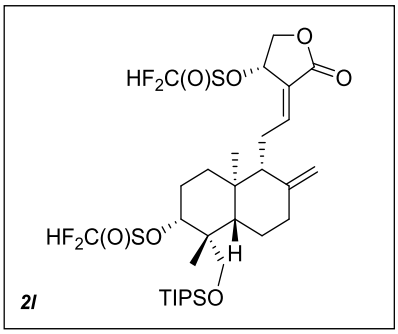
^{19}F NMR
282 MHz
$CDCl_3$



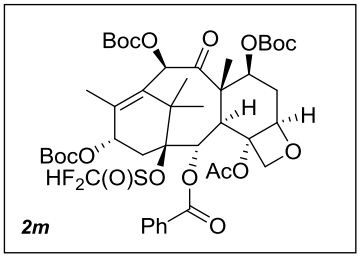
^{1}H NMR
300 MHz
$CDCl_3$



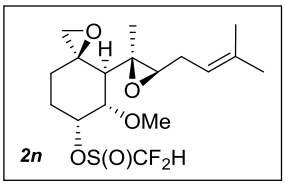
^{13}C NMR
126 MHz
$CDCl_3$



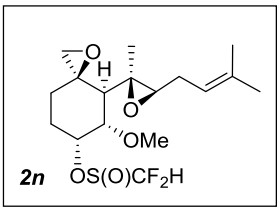
^{19}F NMR
282 MHz
$CDCl_3$



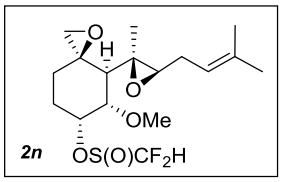
^{19}F NMR
282 MHz
$CDCl_3$



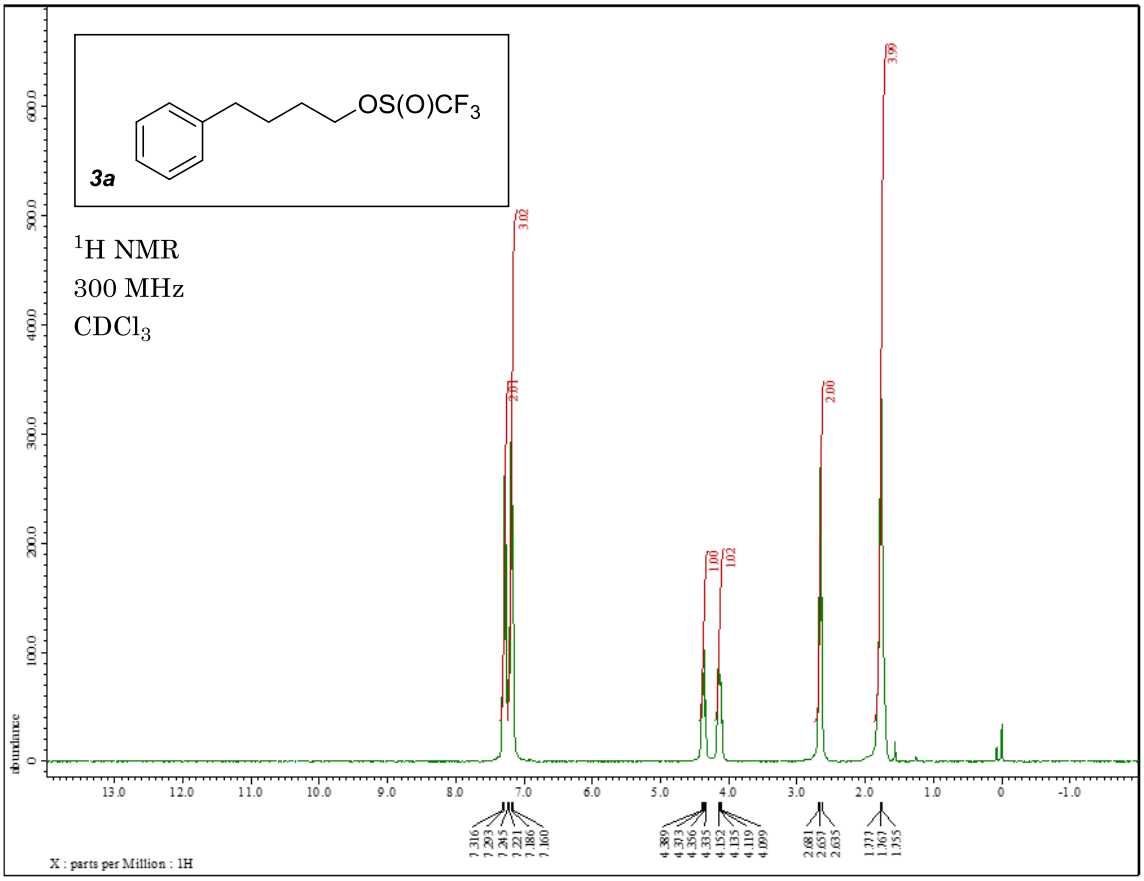
^{1}H NMR
500 MHz
$CDCl_3$

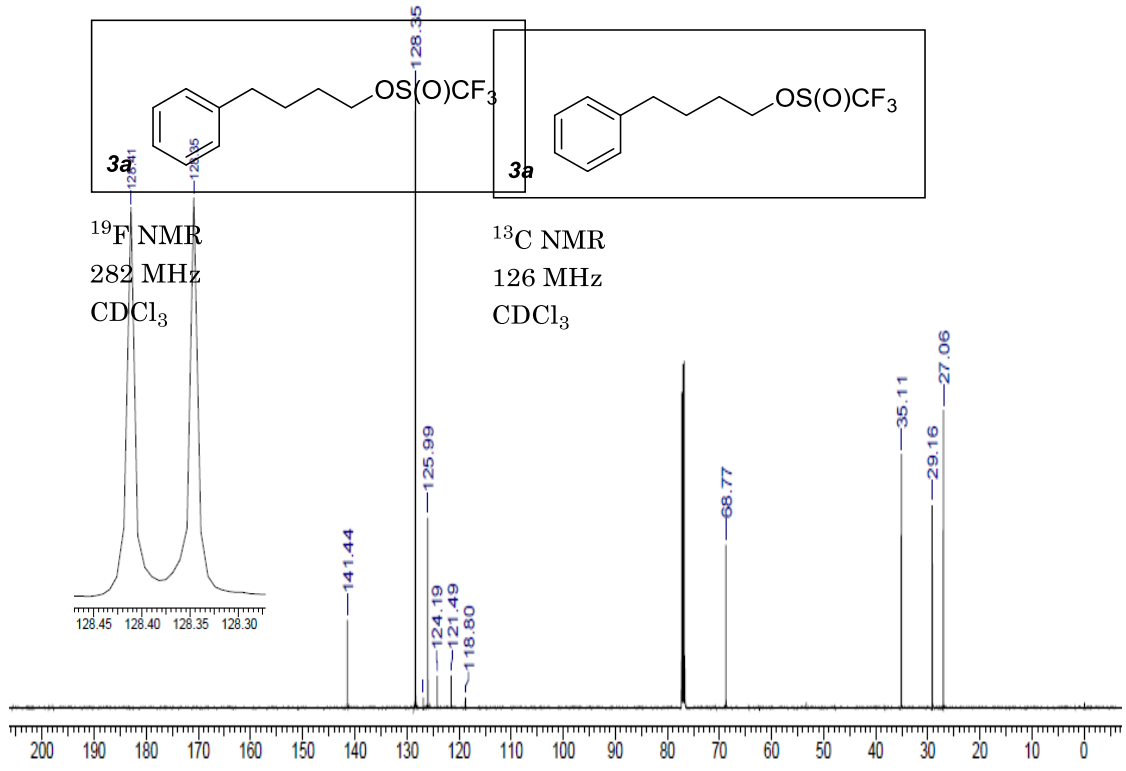


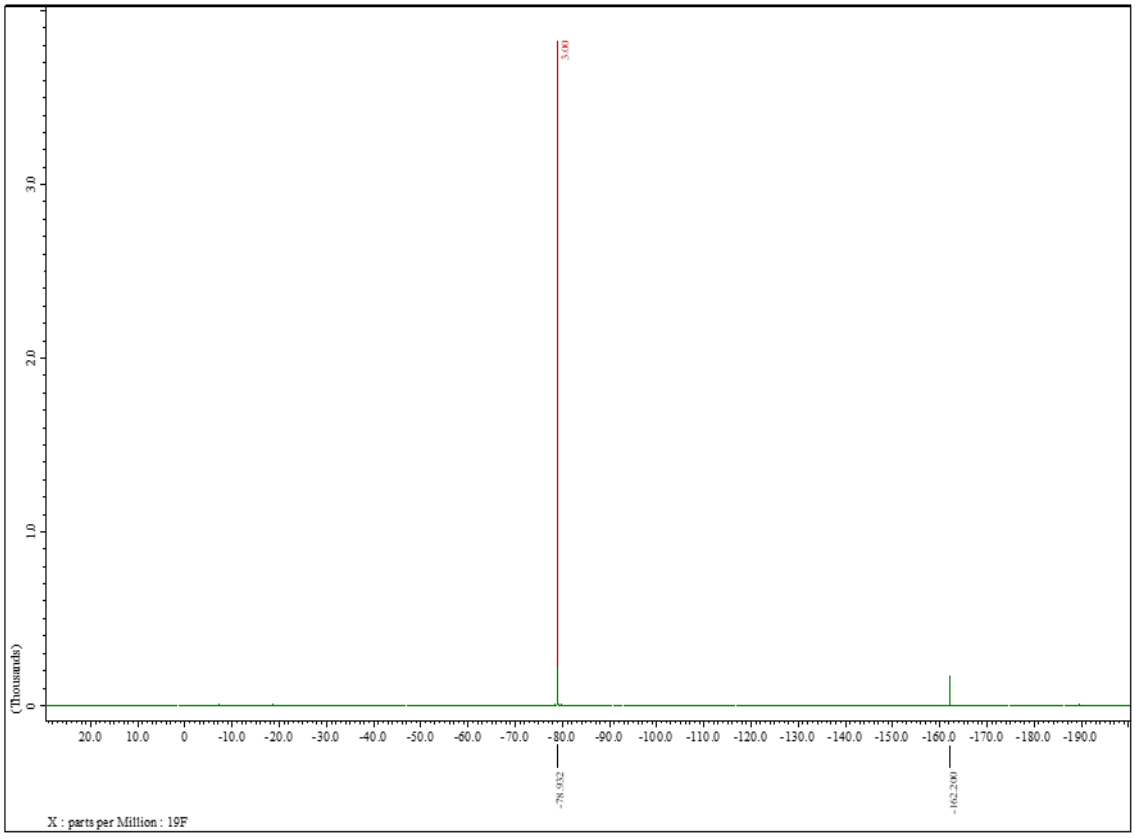
^{13}C NMR
126 MHz
$CDCl_3$

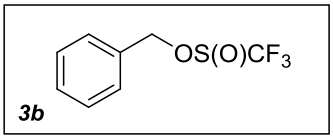


^{19}F NMR
282 MHz
$CDCl_3$

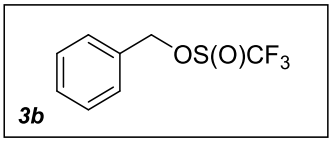

OS(O)CF3
3a
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H


OS(O)CF3
3a
128.35
128.11
128.35
19F NMR
282 MHz
CDCl3
13C NMR
126 MHz
CDCl3
141.44
125.99
124.19
121.49
118.80
68.77
35.11
29.16
27.06
128.45 128.40 128.35 128.30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

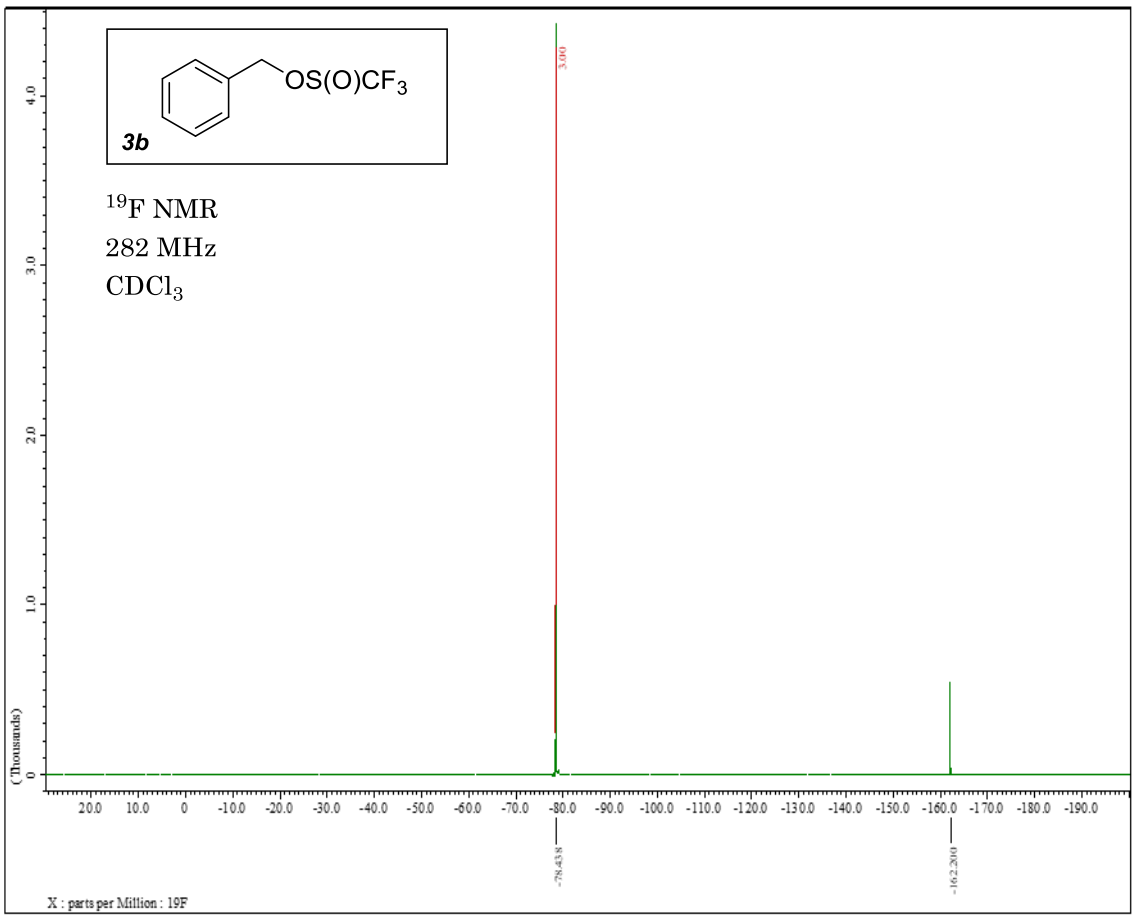

3.00
(Thousands)
3.0
2.0
1.0
0
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-78.932
-162.200
X : parts per Million : 19F

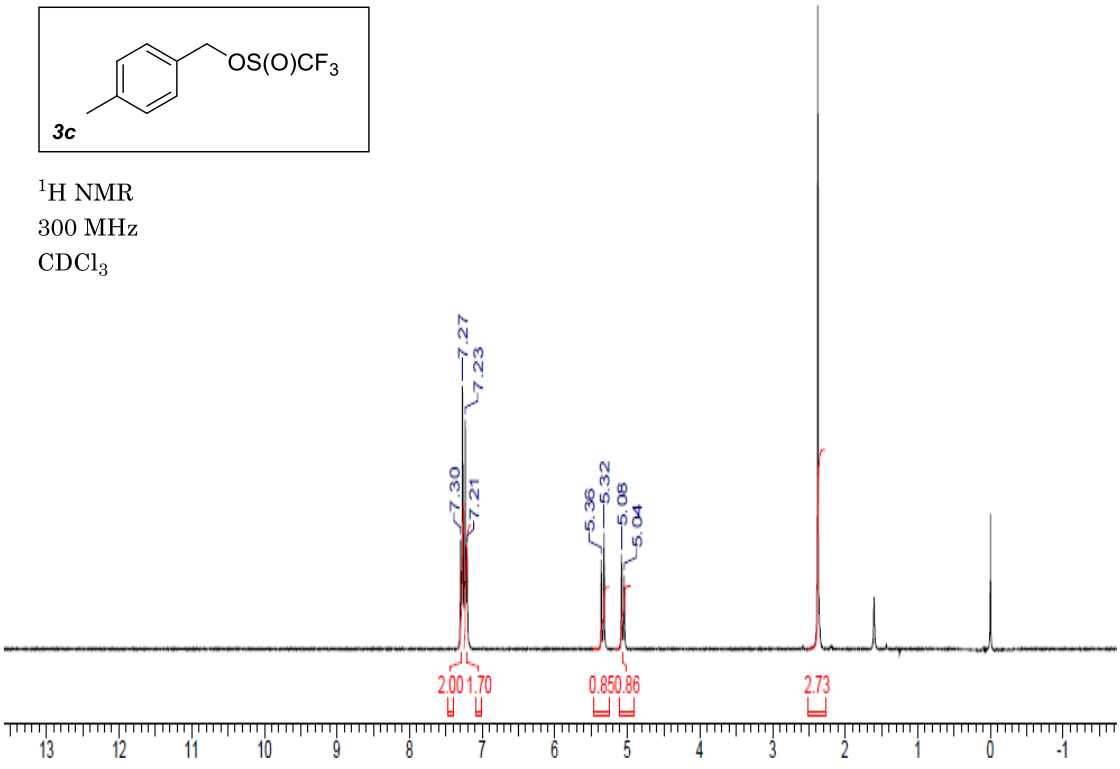


^{1}H NMR
300 MHz
$CDCl_3$

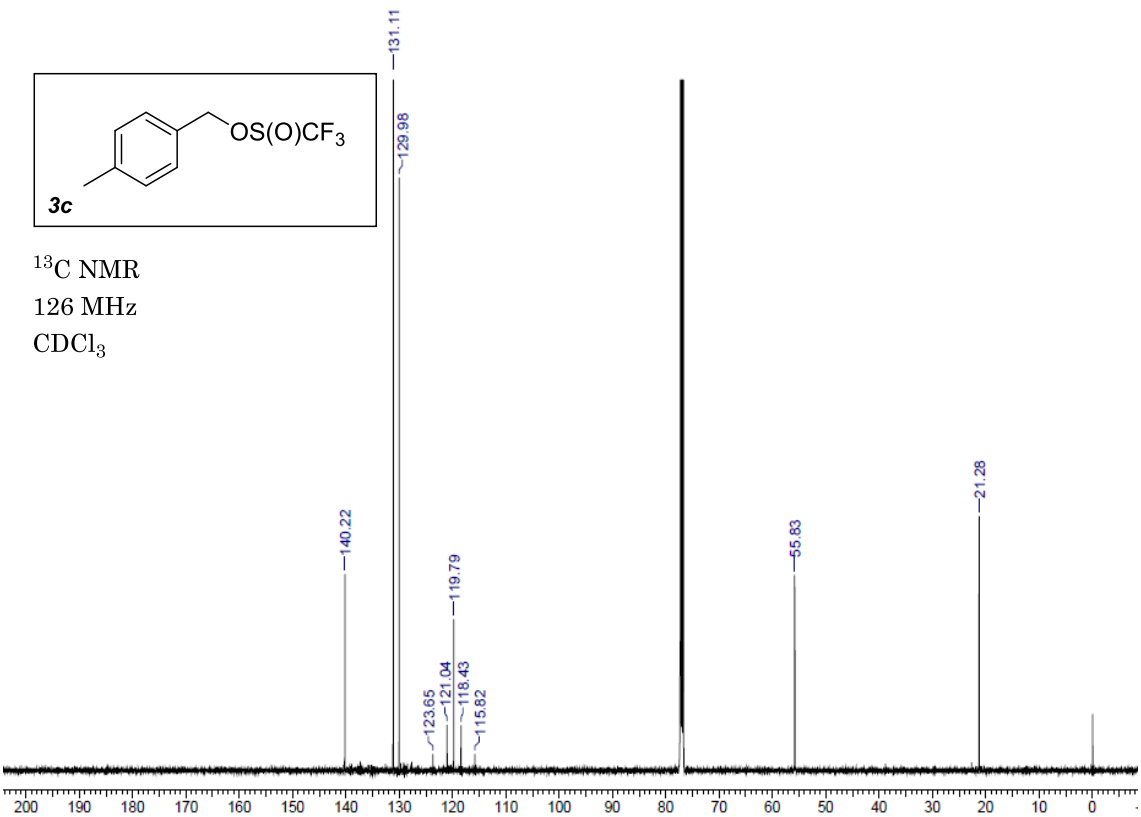


^{13}C NMR
126 MHz
$CDCl_3$

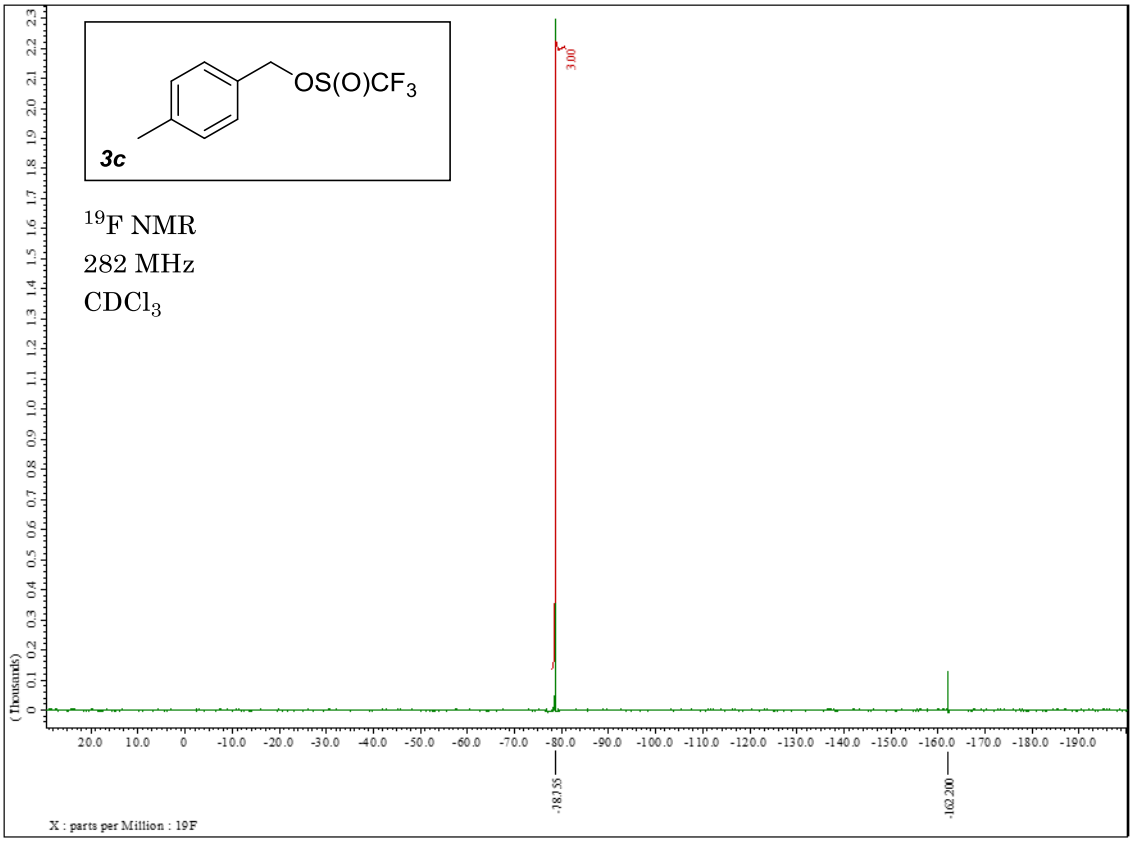

OS(O)CF3
3b
19F NMR
282 MHz
CDCl3
3.00
(Thousands)
4.0
3.0
2.0
1.0
0
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-78.438
-162.200
X : parts per Million : 19F

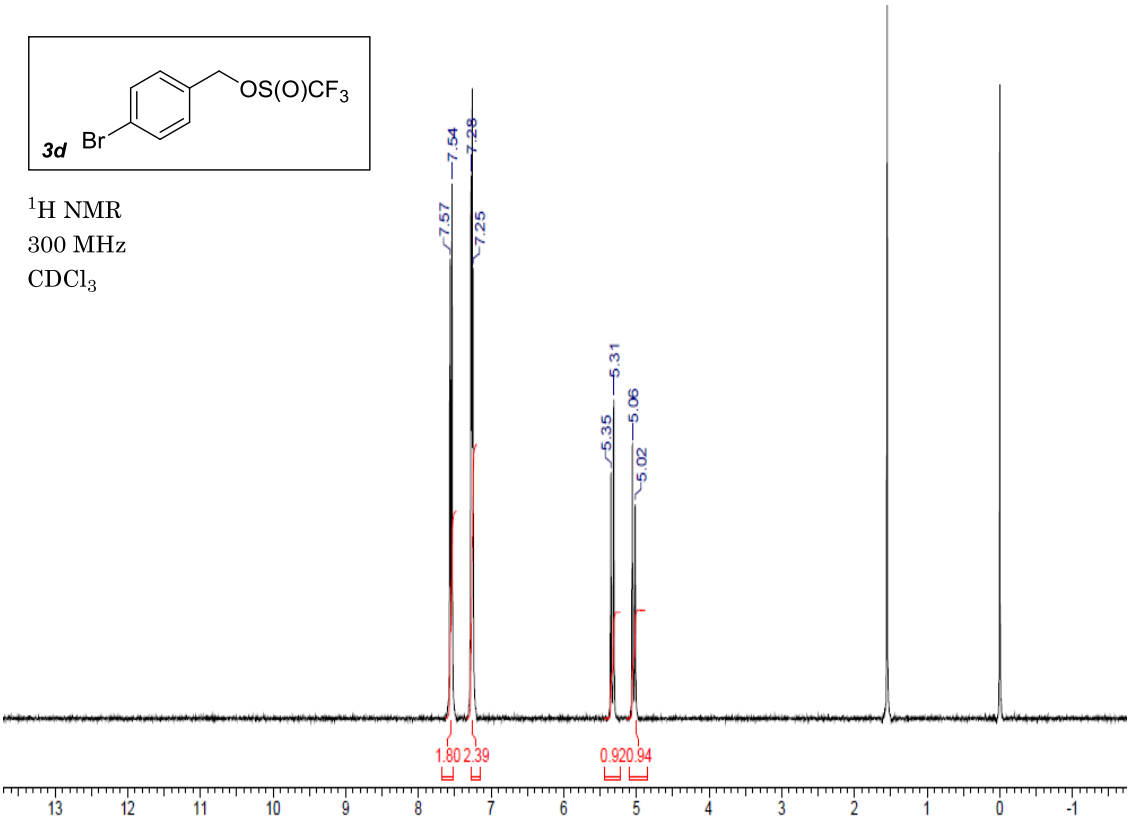


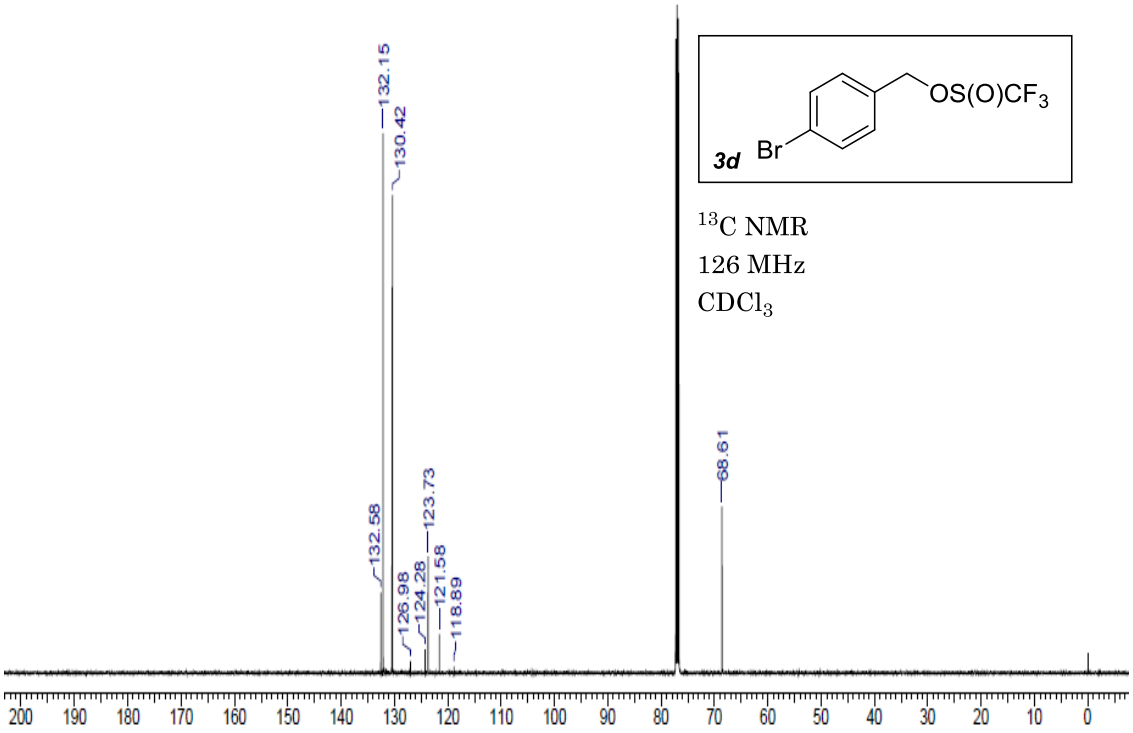
^{1}H NMR
300 MHz
$CDCl_3$



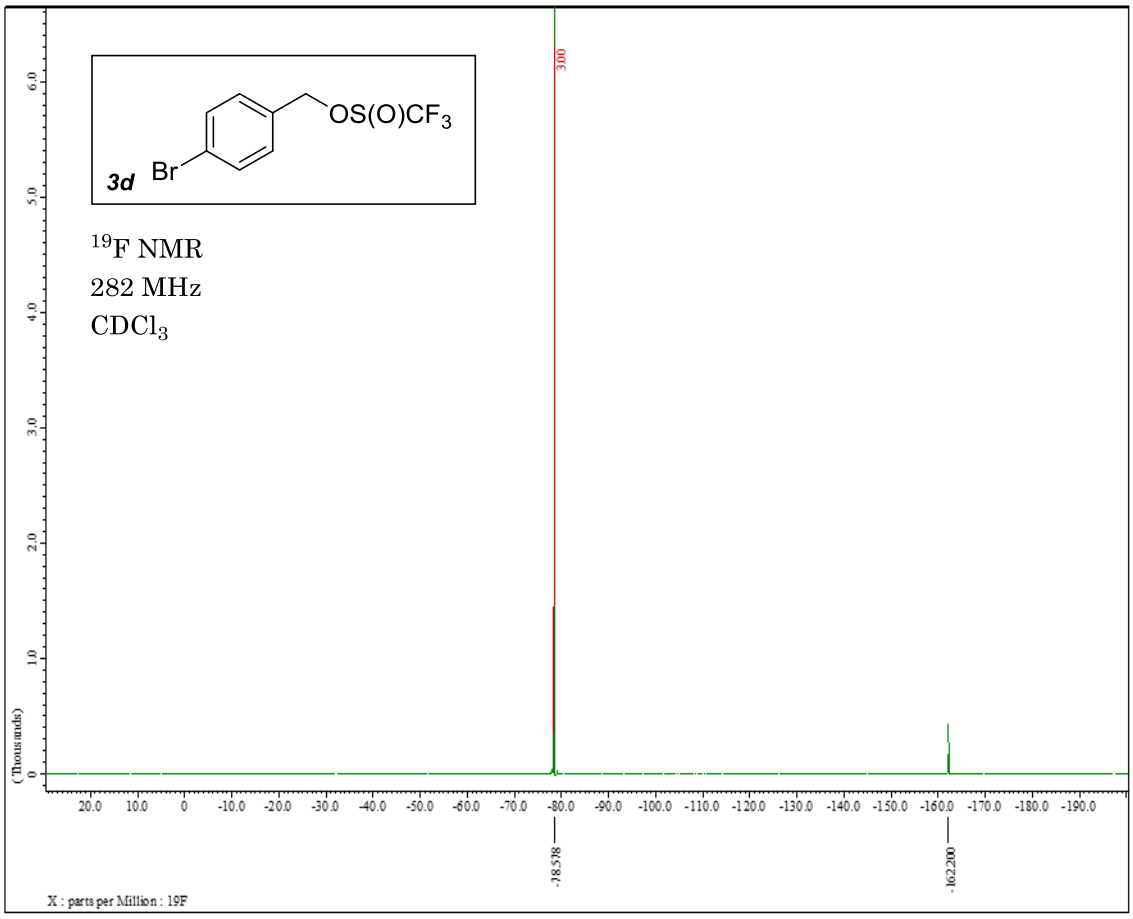
^{13}C NMR
126 MHz
$CDCl_3$


OS(O)CF3
3c
19F NMR
282 MHz
CDCl3
3.00
-78.55
-162.200
X : parts per Million : 19F

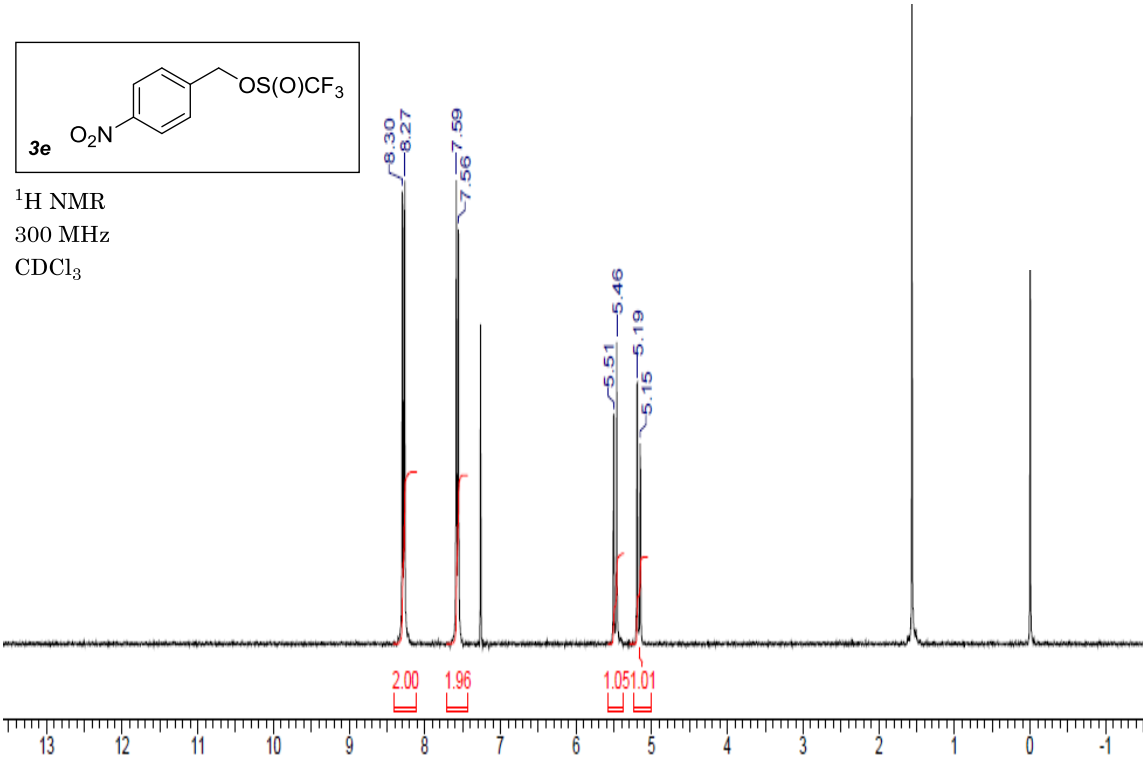

OS(O)CF3
Br
3d
1H NMR
300 MHz
CDCl3
7.57
7.54
7.28
7.25
5.35
5.31
5.06
5.02
1.80
2.39
0.92
0.94



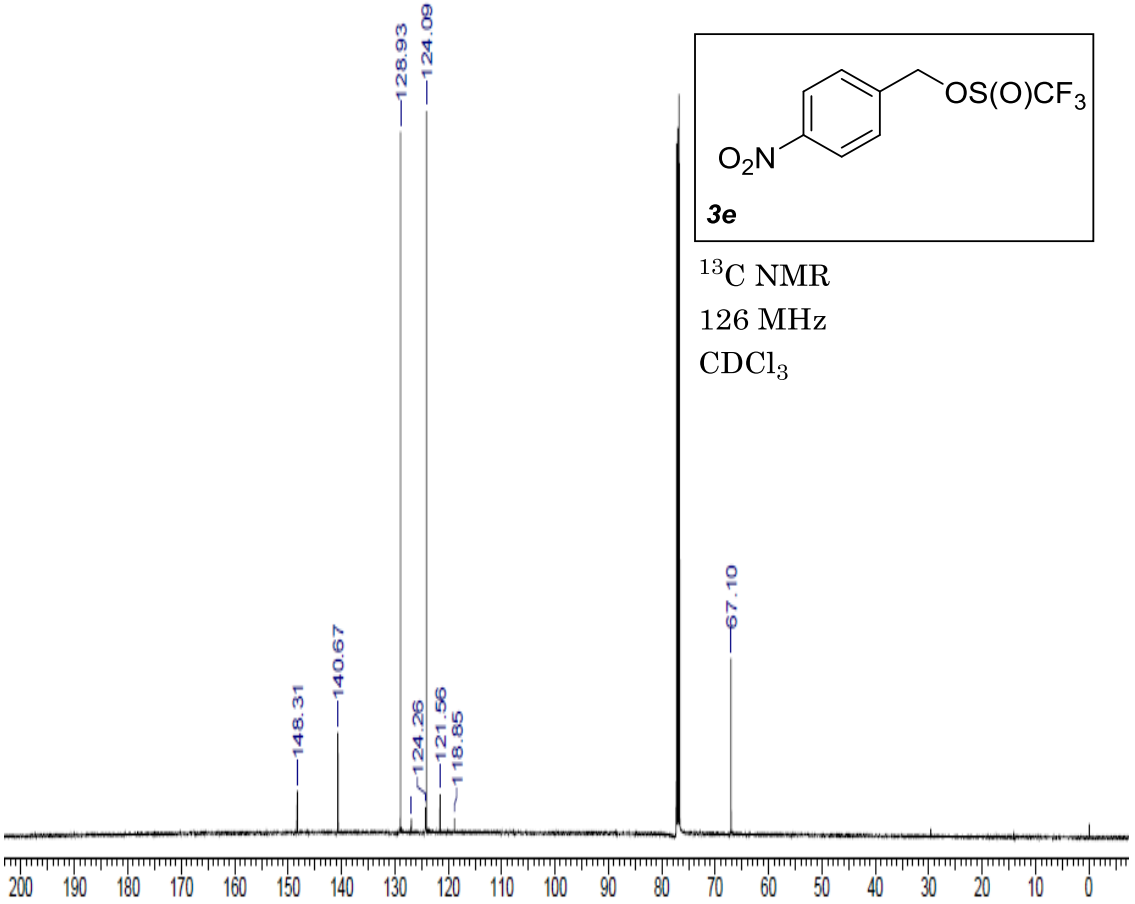
^{13}C NMR
126 MHz
$CDCl_3$



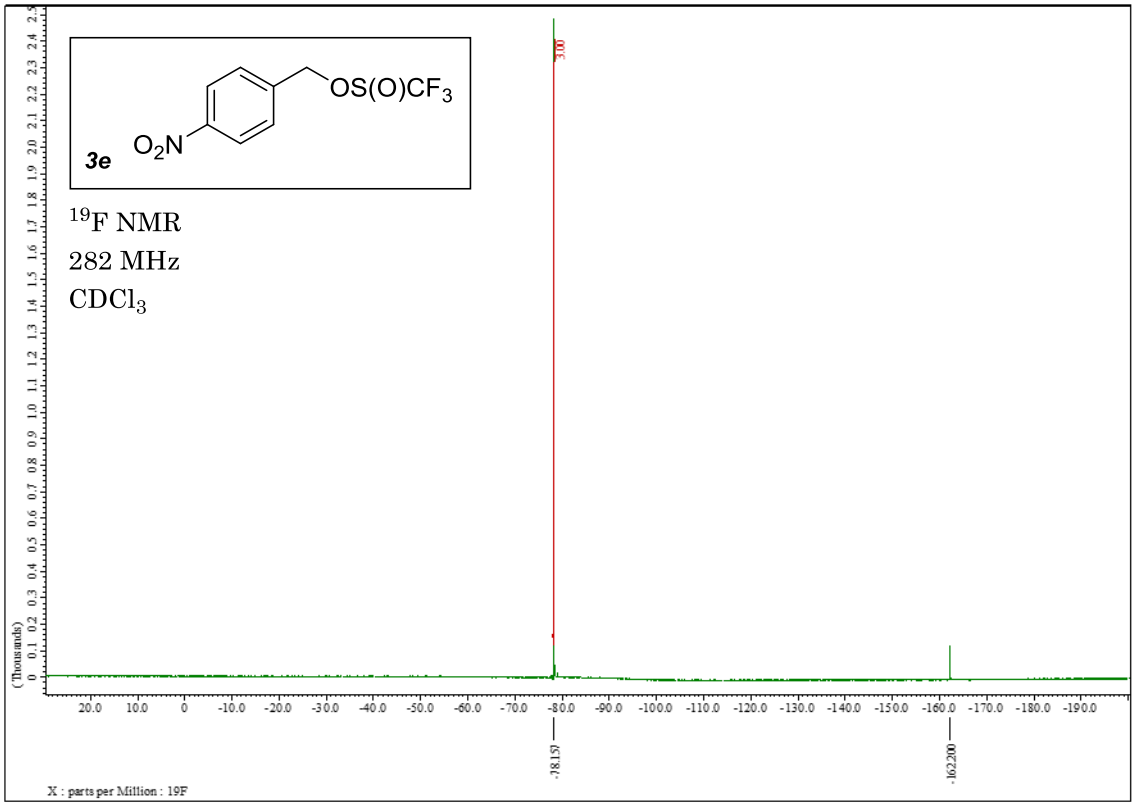
^{19}F NMR
282 MHz
$CDCl_3$

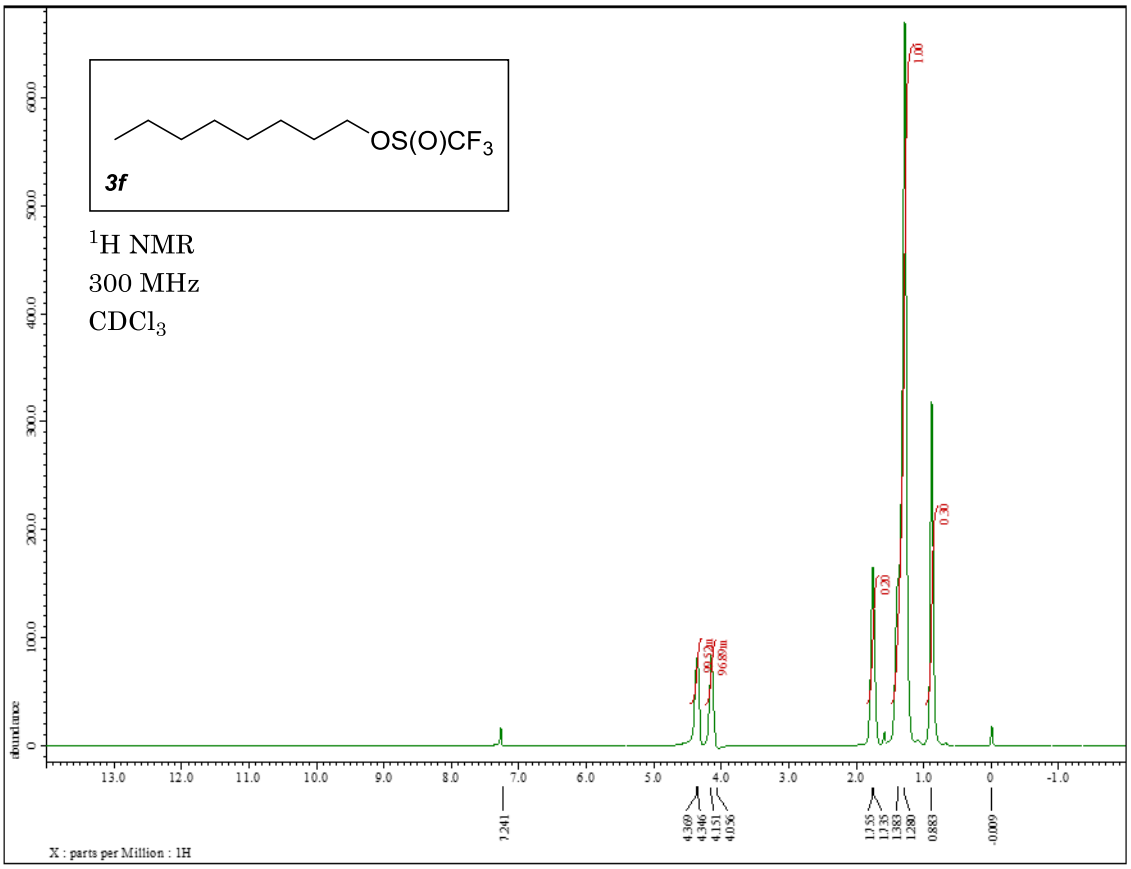


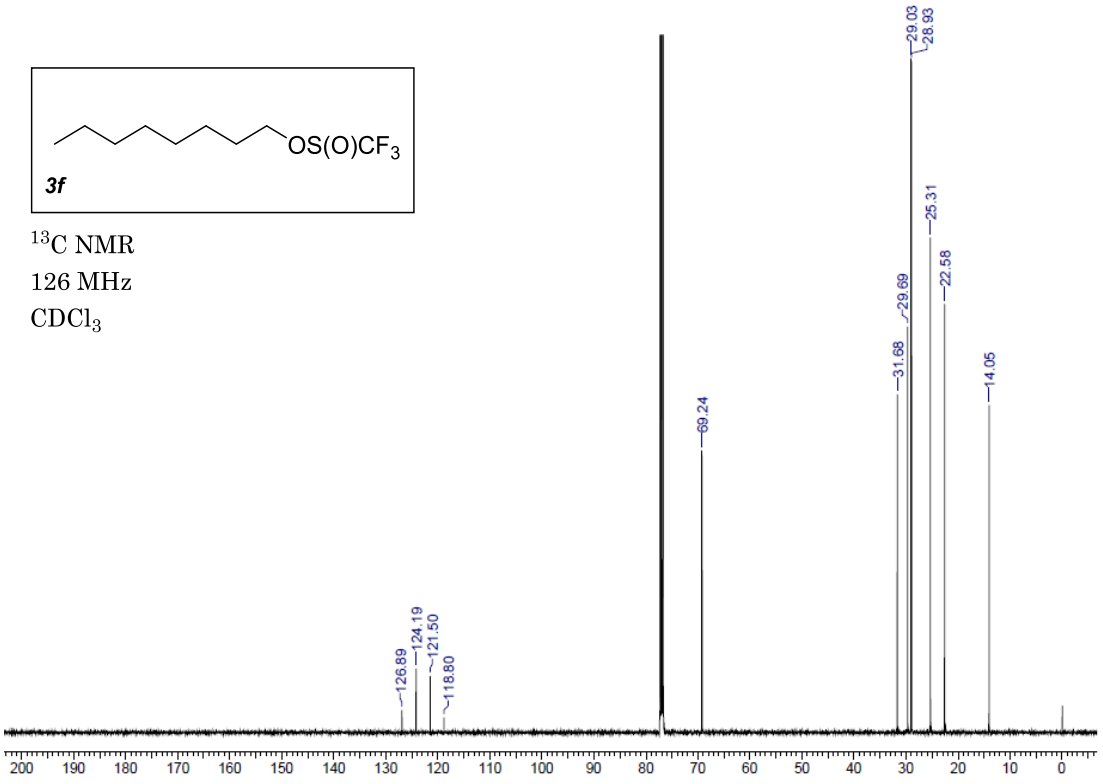
^{1}H NMR
300 MHz
$CDCl_3$

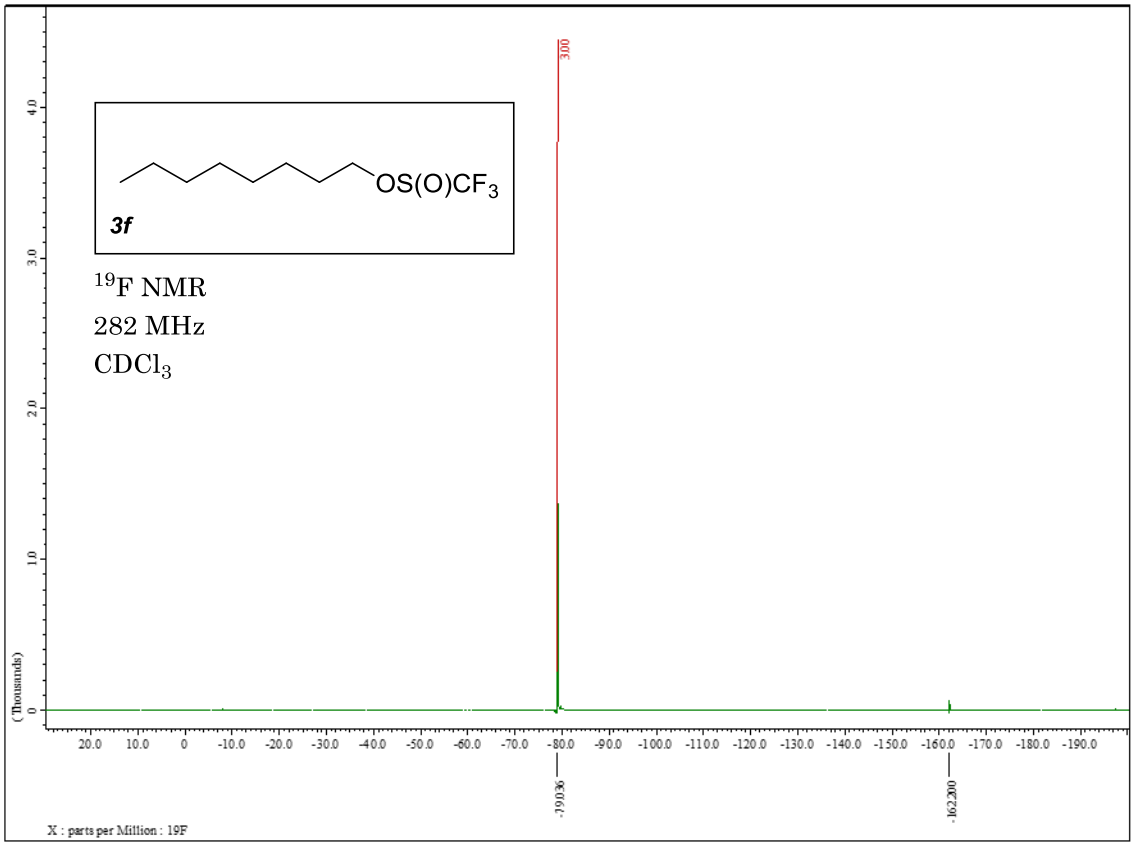


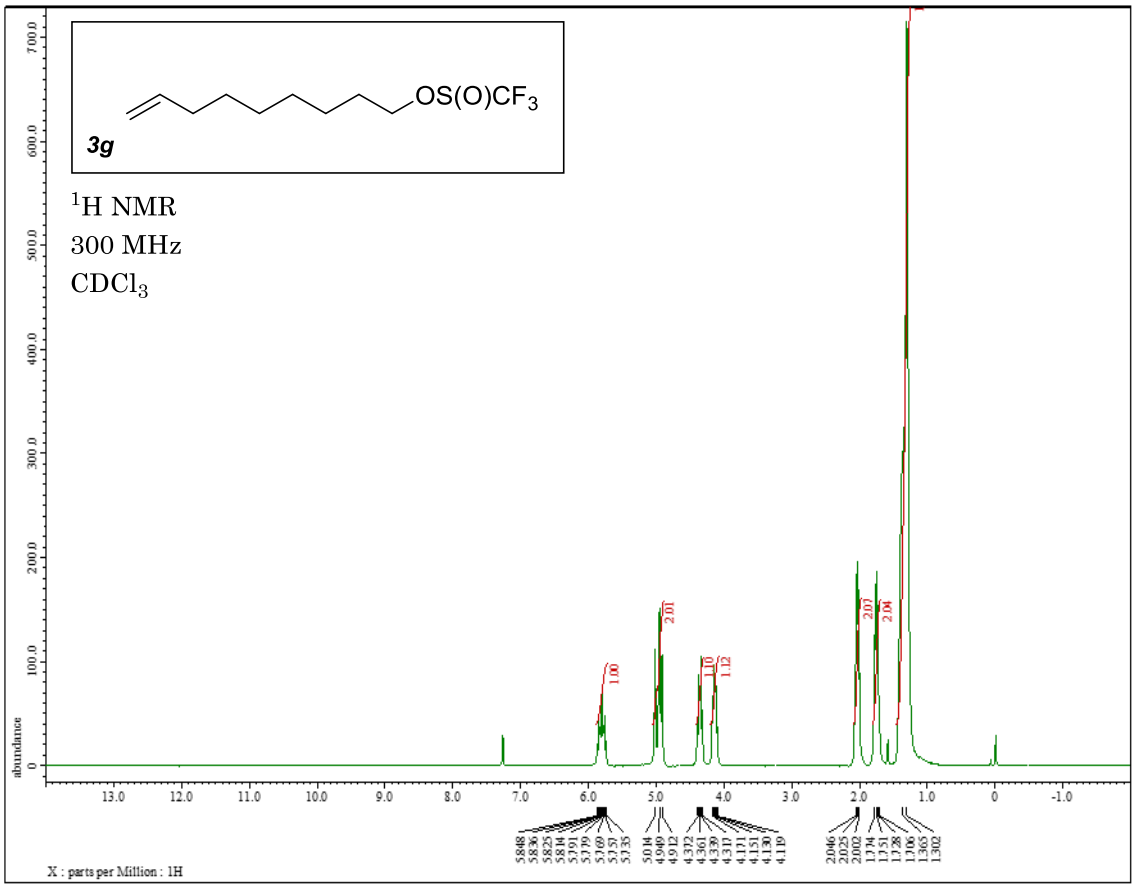
^{13}C NMR
126 MHz
$CDCl_3$

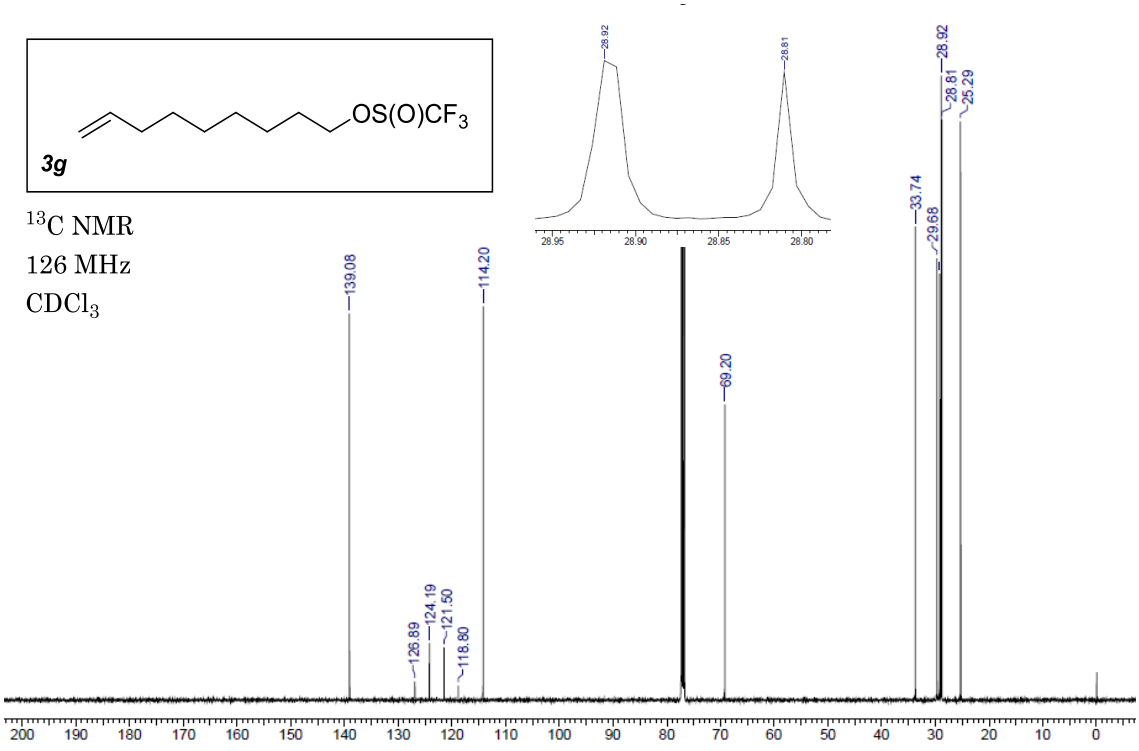

OS(O)CF3
O2N
3e
19F NMR
282 MHz
CDCl3
X : parts per Million : 19F

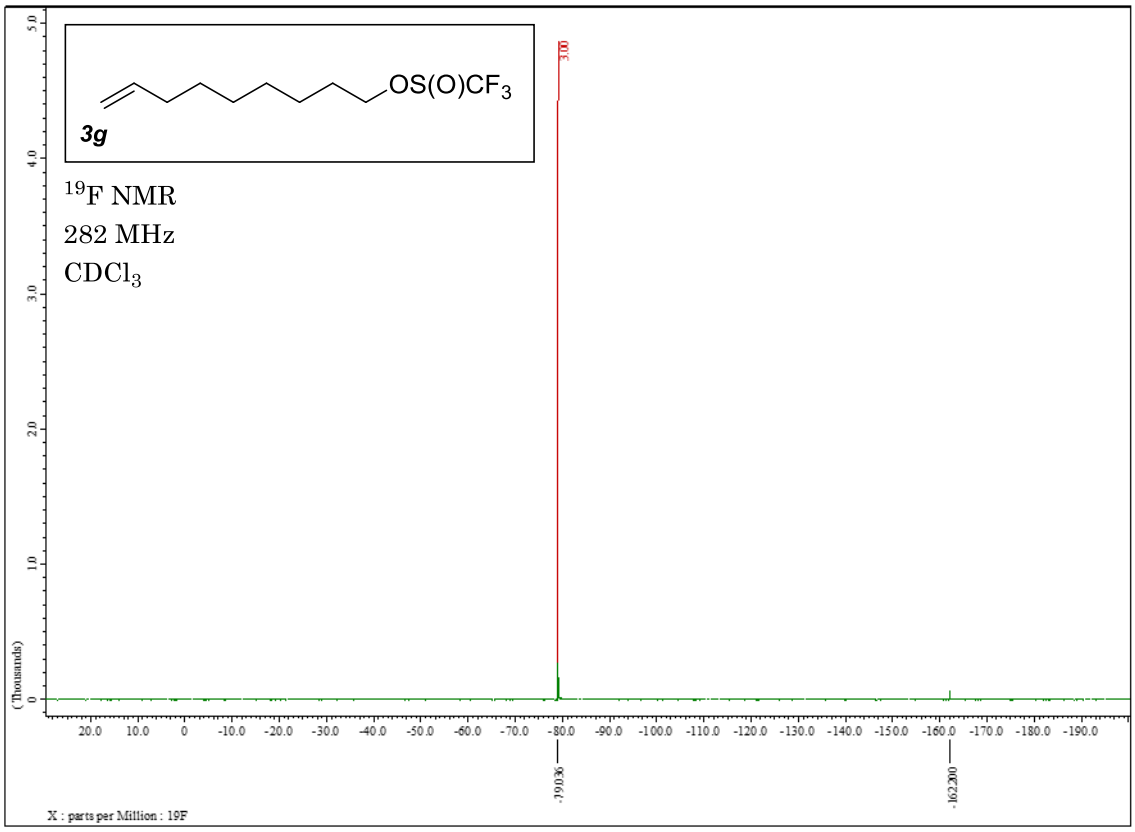

OS(O)CF3
3f
1H NMR
300 MHz
CDCl3
X : parts per Million : 1H

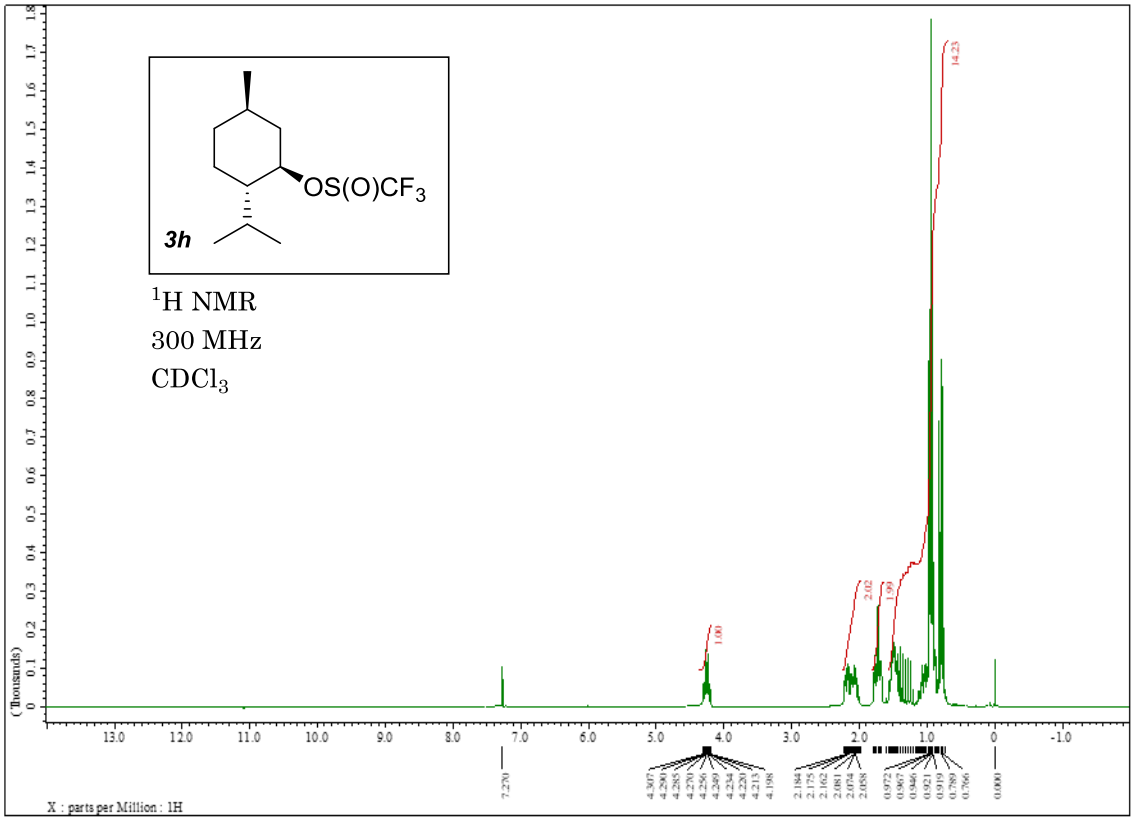

OS(O)CF3
3f
13C NMR
126 MHz
CDCl3
29.03
28.93
25.31
22.58
29.69
31.68
14.05
69.24
126.89
124.19
121.50
118.80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

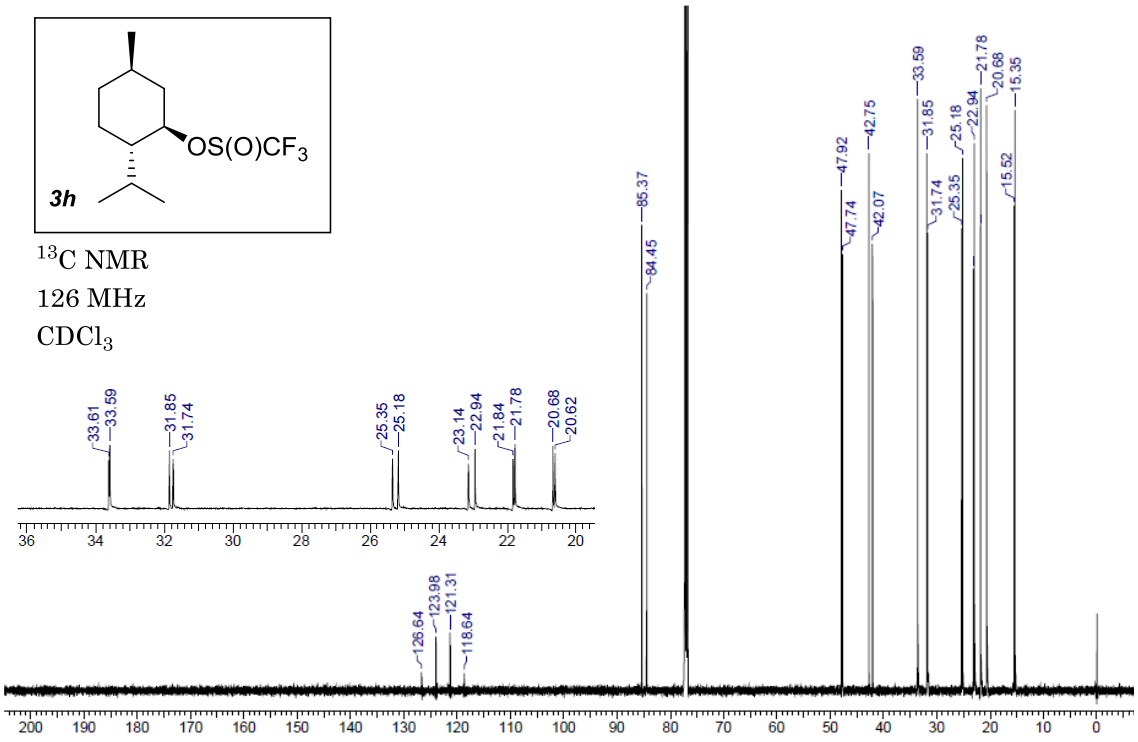

OS(O)CF3
3f
19F NMR
282 MHz
CDCl3
3.00
(Thousands)
4.0
3.0
2.0
1.0
0
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-79.936
-162.200
X : parts per Million : 19F

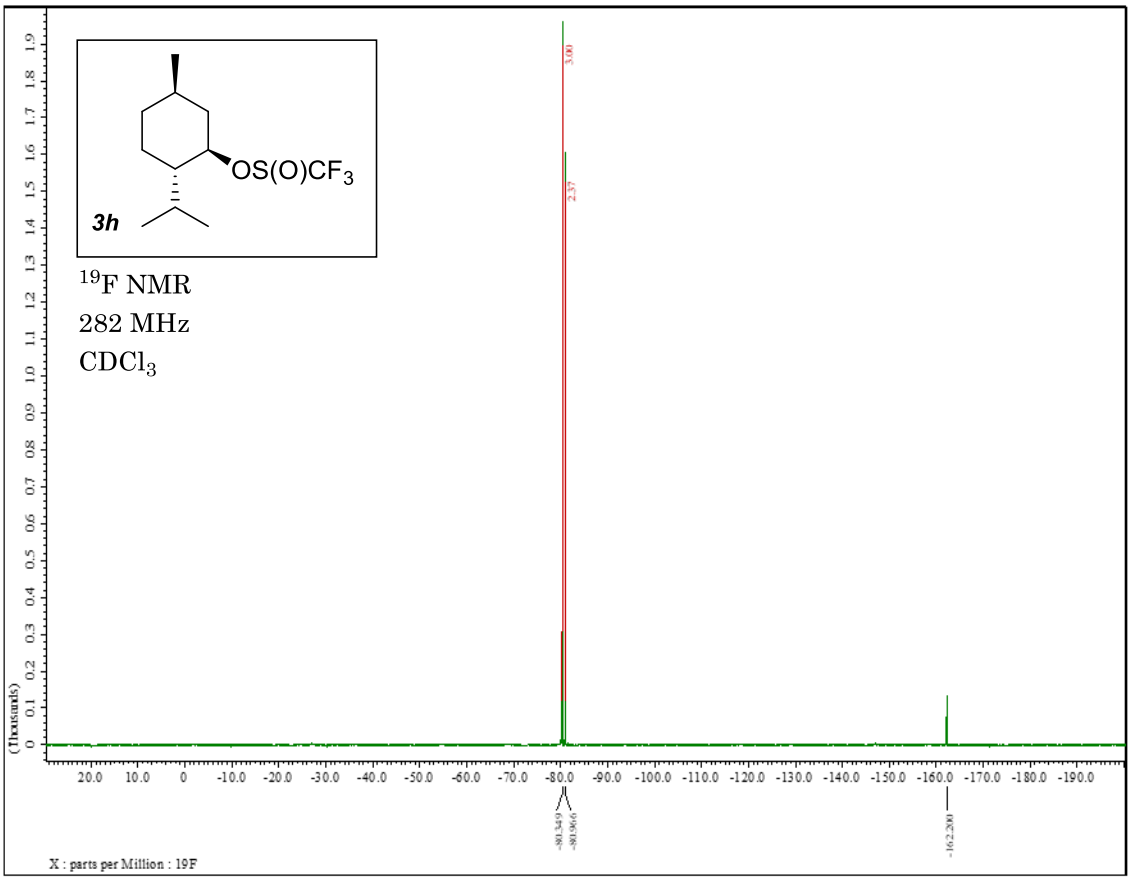

OS(O)CF3
3g
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H

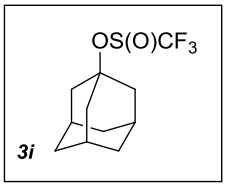

OS(O)CF3
3g
13C NMR
126 MHz
CDCl3
139.08
114.20
69.20
126.89
124.19
121.50
118.80
33.74
29.68
28.92
28.81
25.29


OS(O)CF3
3g
19F NMR
282 MHz
CDCl3
X : parts per Million : 19F

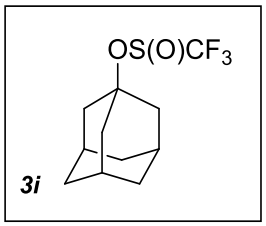

OS(O)CF3
3h
1H NMR
300 MHz
CDCl3
X : parts per Million : 1H


OS(O)CF3
3h
13C NMR
126 MHz
CDCl3
86.37
84.45
47.92
47.74
42.75
42.07
33.59
31.85
31.74
25.35
25.18
22.94
21.78
20.68
15.52
15.35
126.64
123.98
121.31
118.64

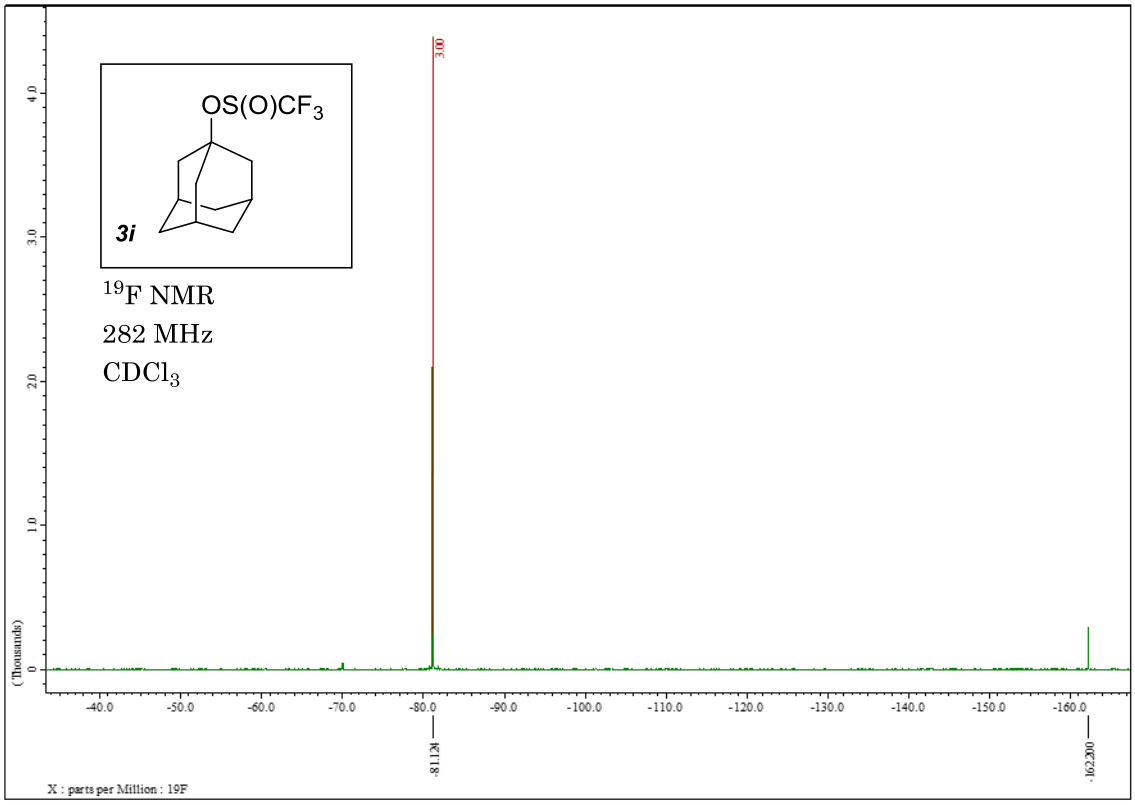

OS(O)CF3
3h
19F NMR
282 MHz
CDCl3
X : parts per Million : 19F

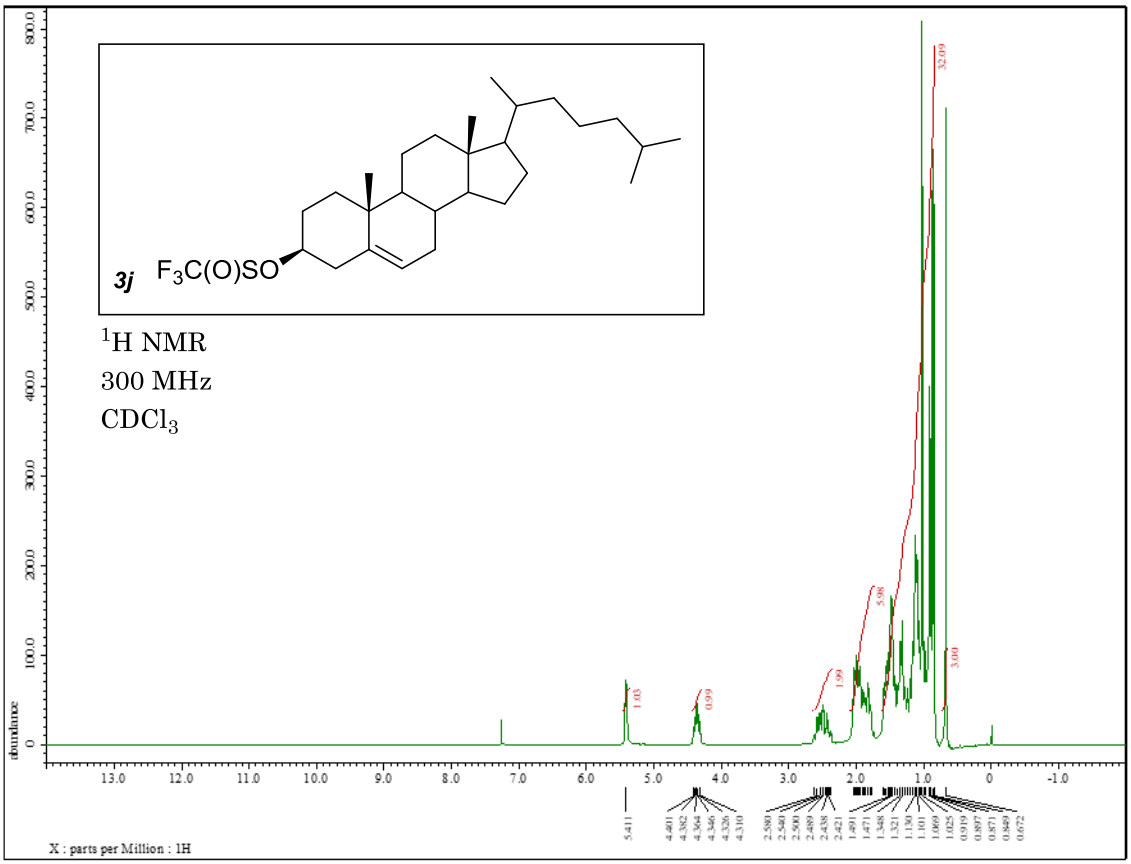


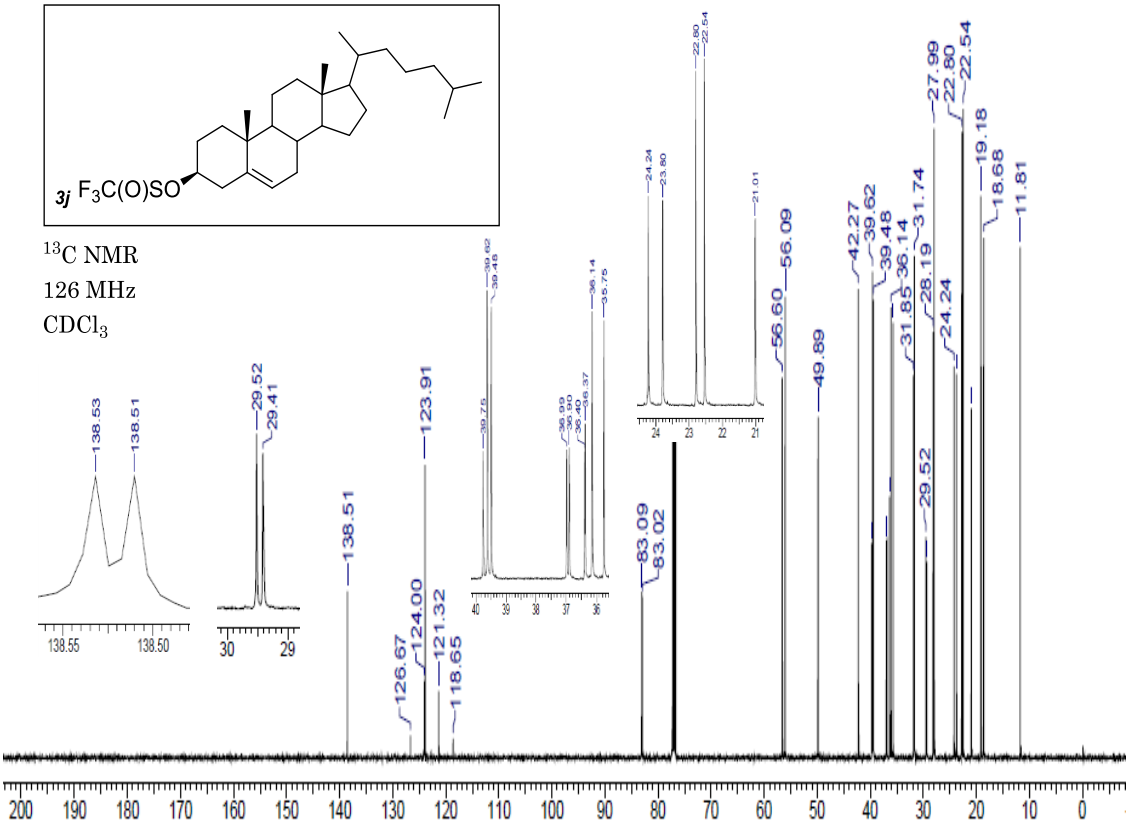
^{1}H NMR
300 MHz
$CDCl_3$

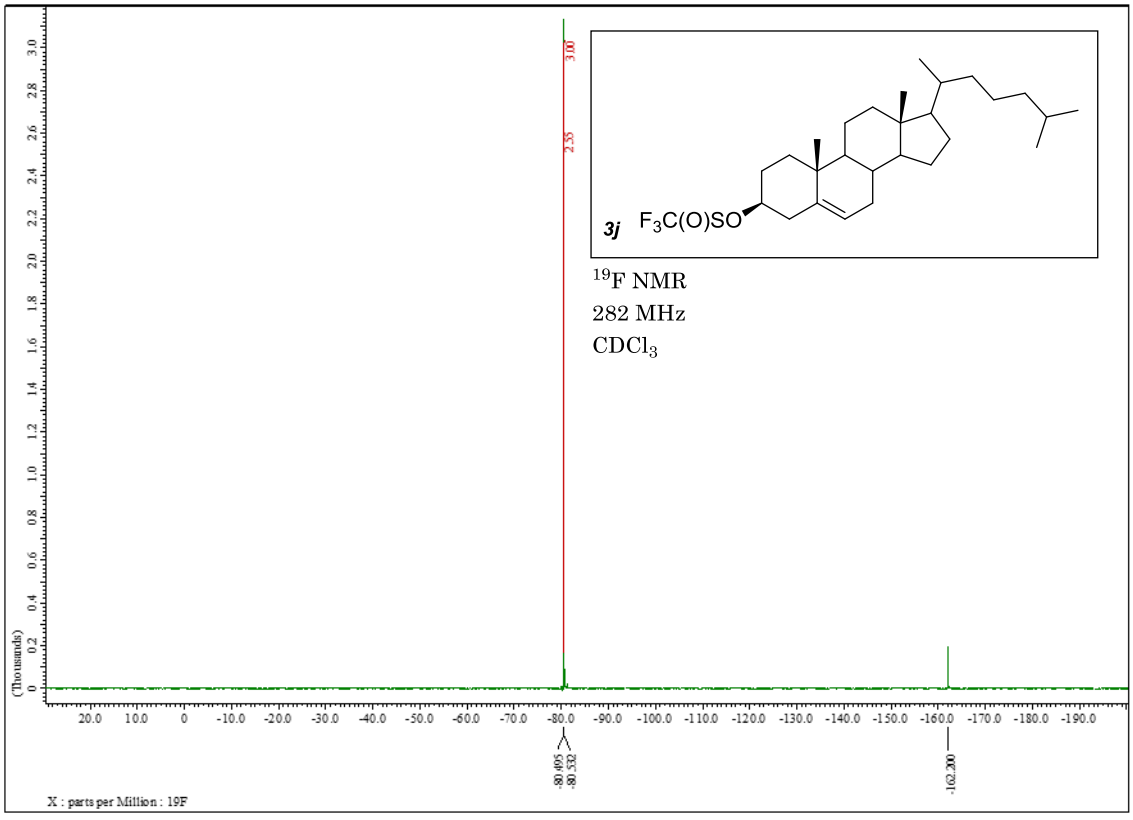


^{13}C NMR
126 MHz
$CDCl_3$


OS(O)CF3
3i
19F NMR
282 MHz
CDCl3
3.00
-81.124
-162.200
X : parts per Million : 19F


3j
F3C(O)SO
1H NMR
300 MHz
CDCl3
32.09
5.08
3.00
1.99
1.68
0.99
X : parts per Million : 1H


3j F3C(O)SO
13C NMR
126 MHz
CDCl3
138.53
138.51
29.52
29.41
138.51
123.91
126.67
124.00
121.32
118.65
83.09
83.02
56.60
56.09
49.89
42.27
39.62
39.48
36.14
31.85
31.74
28.19
27.99
24.24
22.80
22.54
19.18
18.68
11.81


3j F3C(O)SO
19F NMR
282 MHz
CDCl3
3.00
2.35
(Thousands)
-80.495
-80.532
-162.200
X : parts per Million : 19F