Supporting Information for

Synthesis of aryl triflones by insertion of arynes into C-SO_2CF_3 bond

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1. General information.

^{1}H and ^{19}F NMR ($CFCl_3$ as outside standard and low field is positive) spectra were recorded on a Bruker AM400 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were performed using a GC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system.

Materials: 2-(trimethylsilyl)phenyltrifluoromethanesulfonate was purchased commercially. 18-Crown-6 was recrystallized from MeCN. THF was distilled from sodium. MeCN and CH_2Cl_2 was distilled from CaH_2 and stored with 4 Å molecular sieves.

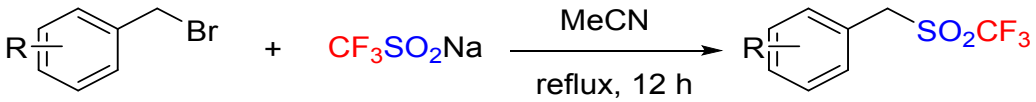
2. Preparation of substrates

2.1 Preparation of 2-(trimethylsilyl)aryltriflates

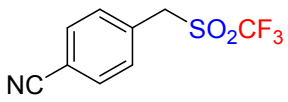
4,5-Dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1b**)[1], and 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1c**)[2] were synthesized according to the litersture procedure.

References
[1] Y. Ueta, K. Mikami, S. Ito, *Angew. Chem., Int. Ed*., **2016**, 55, 7525.
[2] C. Shen, G. Yang, A. Zhang, *Org. Lett*., **2013**, 15, 5722.

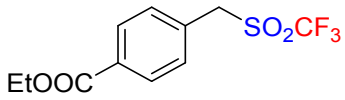
2.2 Preparation of benzyl triflones



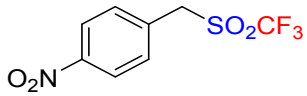
Benzyl bromine (10.0 mmol), CF_3SO_2Na (15.0 mmol, 1.5 eq) and MeCN (20 mL) were added into a 50 mL three-necked bottle equipped with a reflux condenser and a magnetic stirring bar. After refluxing 12 h, the reaction was quenched with H_2O, and extracted with ether. The organic layer was collected and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced vacuum. The crude material was purified by flash column chromatography on silica gel to afford products.



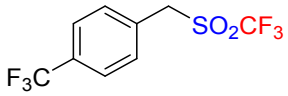
4-(((Trifluoromethyl)sulfonyl)methyl)benzonitrile 2a (1.44 g, 58%)**:** white solid, m.p. 124-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 4.56 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.24 (s, 3F).



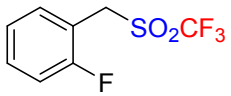
Ethyl 4-(((trifluoromethyl)sulfonyl)methyl)benzoate 2b (1.81 g, 61%)**:** white solid, m.p. 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 4.55 (s, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.30 (s, 3F).



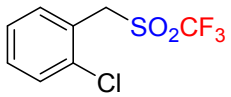
1-Nitro-4-(((trifluoromethyl)sulfonyl)methyl)benzene 2c (1.21 g, 45%)**:** white solid, m.p. 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 4.62 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.21 (s, 3F).



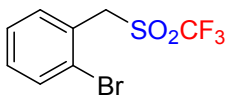
1-(Trifluoromethyl)-4-(((trifluoromethyl)sulfonyl)methyl)benzene 2d (2.34 g, 80%)**:** white solid, m.p.124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 4.56 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.00 (s, 3F), -76.31 (s, 3F).



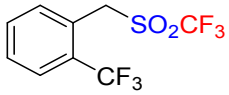
1-Fluoro-2-(((trifluoromethyl)sulfonyl)methyl)benzene 2e (1.74 g, 72%)**:** White solid, m.p. 48-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.0 Hz, 2H), 7.30–7.17 (m, 2H), 4.61 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.86 (s, 3F), -115.59 (s, 1F).



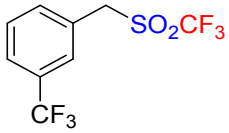
1-Chloro-2-(((trifluoromethyl)sulfonyl)methyl)benzene 2f (1.91 g, 74%)**:** white solid, m.p. 44-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.50 (m, 2H), 7.46–7.34 (m, 2H), 4.77 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.21 (s, 3F).



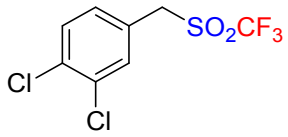
1-Bromo-2-(((trifluoromethyl)sulfonyl)methyl)benzene 2g (1.79 g, 59%)**:** white solid, m.p. 40-42 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 6.7 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 4.81 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.22 (s, 3F).



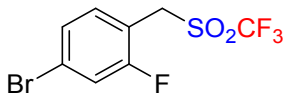
1-(Trifluoromethyl)-2-(((trifluoromethyl)sulfonyl)methyl)benzene 2h (1.20 g, 41%)**:** colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 4.75 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.48 (s, 3F), -77.80 (s, 3F).



1-(Trifluoromethyl)-3-(((trifluoromethyl)sulfonyl)methyl)benzene 2i (1.61 g, 55%)**:** white solid, m.p. 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.71 (s, 1H), 7.69–7.59 (m, 2H), 4.56 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.86 (s, 3F), -76.34 (s, 3F).

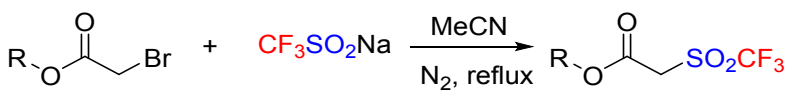


1,2-Dichloro-4-(((trifluoromethyl)sulfonyl)methyl)benzene 2j (1.38 g, 47%)**:** white solid, M.p. 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.52 (m, 2H), 7.30 (s, 1H), 4.45 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.24 (s, 3F).



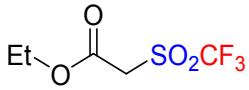
4-Bromo-2-fluoro-1-(((trifluoromethyl)sulfonyl)methyl)benzene 2k (2.31 g, 72%)**:** white solid, m.p. 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.33 (m, 3H), 4.55 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.76 (s, 3F), -112.76 (s, 1F).

2.2 Preparation of *β*-triflyl esters

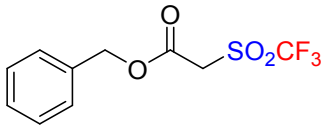


In a 50 ml flask, fitted with a reflux condenser, and a magnetic stirrer, were placed consecutively, under nitrogen, CF_3SO_2Na (4.22 g, 27.1 mmol) and MeCN (30

mL), bromoacetate (27.1 mmol). The stirred reaction mixture was then heated under nitrogen at the 80 °C and maintained at this temperature for the 40 h. After that, water were added. The resulting mixture was extracted with diethyl ether. The organic phase was then washed twice with water, dried over magnesium sulfate, filtered and concentrated at room temperature under reduced pressure. The crude organic residue was purified by flash chromatography.

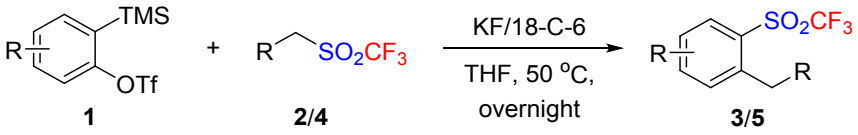


Ethyl 2-((trifluoromethyl)sulfonyl)acetate 4a (2.27 g, 38%)**:** yellow oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, J = 8.0 Hz, 2H), 4.27 (s, 2H), 1.30 (t, J = 6.3 Hz, 3H).^{19}F NMR (377 MHz, $CDCl_3$) δ -77.25 (s, 3F).

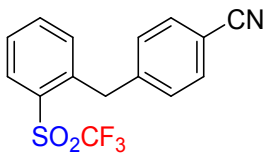


Benzyl 2-((trifluoromethyl)sulfonyl)acetate 4b (3.67 g, 42%)**:** yellow oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 5H), 5.30 (s, 2H), 4.29 (s, 2H).^{19}F NMR (377 MHz, $CDCl_3$) δ -76.93 (s, 3F).

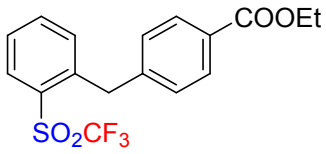
3. General procedure for Synthesis of aryl triflones



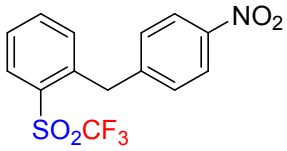
In a 25 mL Schlenk tube equipped with magnetic stirrer bar was charged with KF (34.9 mg, 0.6 mmol, 2.0 equiv), The tube was sealed with a septum in the reduced pressure, then backfilled with nitrogen. The compound **2**/**4** (0.3 mmol, 1.0 equiv) and 18-crown-6 (158.6 mg, 0.6 mmol, 2.0 equiv) was quickly added into the tube, and backfilled with nitrogen three times. The aryne precursor **1** (0.3 mmol, 1.0 equiv) and THF (9.0 mL) was injected into the tube by syringe. The reaction mixture was stirred at 50 °C overnight. Water was added, and extracted with ether, then the combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product **3**/**5**.



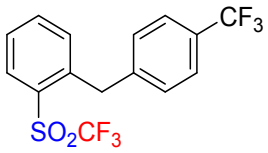
4-(2-((Trifluoromethyl)sulfonyl)benzyl)benzonitrile (3a) (72.2 mg, 74%)**:** white solid, m.p. 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65–7.56 (m, 3H), 7.36–7.29 (m, 3H), 4.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 142.9, 136.8, 133.8, 133.4, 132.5, 129.9, 129.9, 128.3, 119.9 (q, *J* = 326.5 Hz), 118.8, 110.7, 38.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.21 (s, 3F). IR $(KBr)_{max}$ 3080, 2930, 2229, 1604, 1508, 1473, 1357, 1200, 1114, 698 cm^{-1}. MS (ESI): *m/z* (%) 326 $[M+H]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}F_3NO_2S$: 326.0455; Found: 326.0457.



Ethyl 4-(2-((trifluoromethyl)sulfonyl)benzyl)benzoate (3b) (83.8 mg, 75%)**:** white solid, m.p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 8.01 (t, *J* = 11.2 Hz, 2H), 7.71 (t, *J* = 7.1 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 4.60–4.51 (m, 2H), 4.39 (d, *J* = 14.0 Hz, 2H), 1.41 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.2, 144.0, 136.6, 133.6, 133.3, 130.0, 129.8, 129.3, 129.1, 127.9, 120.0 (q, *J* = 326.6 Hz), 61.0, 38.1, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.21 (s, 3F).IR $(KBr)_{max}$ 3058, 2985, 2373, 1712, 1607, 1508, 1463, 1360, 1277, 1207, 1108, 698 cm^{-1}. MS (ESI): *m/z* (%) 373 $[M+H]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}F_3O_4S$: 373.0716; Found: 373.0720.

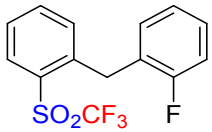


1-(4-Nitrobenzyl)-2-((trifluoromethyl)sulfonyl)benzene (3c) (59.0 mg, 57%)**:** white solid, m.p. 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.19 (m, 3H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.37–7.35 (m, 3H), 4.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 146.7, 142.7, 136.8, 133.9, 133.4, 130.0, 129.9, 128.4, 123.9, 120.0 (q, *J* = 326.5 Hz), 38.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.19 (s, 3F). IR $(KBr)_{max}$ 2965, 2363, 1591, 1517, 1348, 1262, 1207, 1101, 688 cm^{-1}. MS (ESI): *m/z* (%) 346 $[M+H]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}F_3NO_4S$: 346.0355; Found: 346.0356.

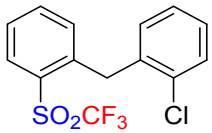


1-(4-(Trifluoromethyl)benzyl)-2-((trifluoromethyl)sulfonyl)benzene (3d) (71.8 mg, 65%): colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.61–7.56 (m, 3H), 7.40–7.32 (m, 3H), 4.60 (s, 2H).

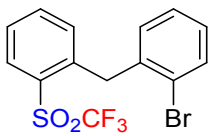
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.3, 136.7, 133.6, 133.4, 129.8, 129.6, 129.0 (q, *J* = 32.6 Hz), 128.1, 125.6 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.7 Hz), 120.1 (q, *J* = 326.5 Hz), 38.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.52 (s, 3F), -78.42 (s, 3F). IR $(KBr)_{max}$ 3065, 2924, 1620, 1575, 1472, 1364, 1210, 1123, 694 cm^{-1}. MS (ESI): *m/z* (%) 391 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{15}H_{14}F_6NO_2S$: 386.0644; Found: 386.0643.



1-Fluoro-2-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3e) (55.4 mg, 58%)**:** colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.3 Hz, 1H), 7.69 (s, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.30 (s, 2H), 7.15 (s, 3H), 4.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 246.1 Hz), 143.8, 136.6, 133.5, 132.3, 131.6 (d, *J* = 4.0 Hz), 129.7, 128.8 (d, *J* = 8.1 Hz), 127.7, 125.8 (d, *J* = 15.7 Hz), 124.5 (d, *J* = 3.5 Hz), 120.1 (q, *J* = 326.4 Hz), 115.6 (d, *J* = 21.8 Hz), 31.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.20 (s, 3F), -117.30 (s, 1F). IR $(KBr)_{max}$ 3065, 2920, 1623, 1578, 1460, 1364, 1287, 1223, 1104, 758 cm^{-1}. MS (ESI): *m/z* (%) 341 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}F_4NO_2S$: 336.0676; Found: 336.0677.

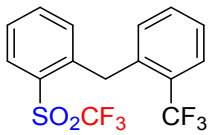


1-Chloro-2-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3f) (79.3 mg, 79%)**:** white solid, m.p. 46-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 7.27 (d, *J* = 5.8 Hz, 2H), 7.12 (d, *J* = 6.7 Hz, 2H), 4.65 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.6, 136.4, 134.5, 133.7, 131.8, 131.6, 129.8, 129.7, 128.5, 127.7, 127.3, 120.1 (q, *J* = 328.0 Hz), 36.07. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.03 (s, 3F). IR $(KBr)_{max}$ 3071, 2924, 1639, 1578, 1473, 1364, 1293, 1207, 1133, 691 cm^{-1}. MS (ESI): *m/z* (%) 357 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{14}H_{14}ClF_3NO_2S$: 352.0380; Found: 352.0382.

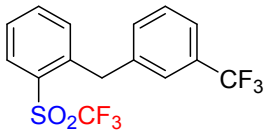


1-Bromo-2-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3g) (91.0 mg, 80%)**:** colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 9.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 6.9 Hz, 2H), 4.67 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.2, 136.7, 133.7, 133.1, 131.9, 131.7, 129.7, 128.7, 127.9, 127.7, 125.2, 120.1 (q, *J*

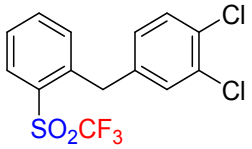
= 326.9 Hz), 38.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.96 (s, 3F). IR $(KBr)_{max}$ 3058, 2923, 1636, 1578, 1469, 1364, 1290, 1210, 1114, 691 cm^{-1}. MS (EI): m/z (%) 378 $[M]^+$. MS (ESI): *m/z* (%) 401 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{14}H_{14}BrF_3NO_4S$: 395.9875; Found: 395.9871.



1-(Trifluoromethyl)-2-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3h) (101.6 mg, 92%)**:** colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 4.73 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 136.1 (d, *J* = 1.5 Hz), 135.6, 132.5, 131.6, 131.2, 131.1, 128.8 (d, *J* = 1.4 Hz), 128.2 (q, *J* = 30.0 Hz), 126.7, 126.1, 125.2 (q, *J* = 5.6 Hz), 123.3 (q, *J* = 273.8 Hz), 119.0 (q, *J* = 326.5 Hz), 33.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.19 (s, 3F), -78.20 (s, 3F). IR $(KBr)_{max}$ 3077, 2923, 1643, 1578, 1444, 1309, 1210, 1041, 909, 694 cm^{-1}. MS (ESI): *m/z* (%) 391 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{15}H_{14}F_6NO_2S$: 386.0644; Found: 386.0644.

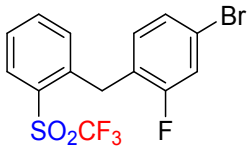


1-(3-(Trifluoromethyl)benzyl)-2-((trifluoromethyl)sulfonyl)benzene (3i) (66.3 mg, 60%): colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.51 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 4.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.0, 136.7, 133.6, 133.3, 132.7, 131.0 (q, *J* = 32.2 Hz), 129.8, 129.2, 128.0, 125.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 3.7 Hz), 120.0 (q, *J* = 326.5 Hz), 37.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.66 (s, 3F), -78.36 (s, 3F). IR $(KBr)_{max}$ 3067, 2924, 1627, 1585, 1437, 1364, 1328, 1210, 1123, 695 cm^{-1}. MS (ESI): *m/z* (%) 391 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{15}H_{14}F_6NO_2S$: 386.0644; Found: 386.0643.

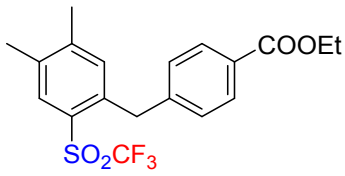


1,2-Dichloro-4-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3j) (45.4 mg, 41%): colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.46 (s, 2H). ^{13}C NMR (101 MHz,

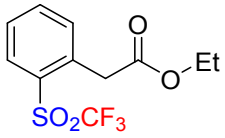
$CDCl_3$) δ 143.4, 139.3, 136.7, 133.7, 133.2, 132.7, 131.1, 130.9, 130.6, 129.8, 128.7, 128.1, 120.0 (q, J = 326.6 Hz), 37.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.22 (s, 3F). IR $(KBr)_{max}$ 3065, 2924, 1636, 1562, 1469, 1357, 1255, 1210, 1107, 691 cm^{-1}. MS (ESI): *m/z* (%) 391 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}Cl_2F_3O_2S$: 368.9725; Found: 368.9724.



4-Bromo-2-fluoro-1-(2-((trifluoromethyl)sulfonyl)benzyl)benzene (3k) (57.2 mg, 48%): colorless oil liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.6 Hz, 1H), 7.71 (t, J = 7.0 Hz, 1H), 7.56 (t, J = 6.9 Hz, 1H), 7.33–7.22 (m, 3H), 7.03 (t, J = 7.3 Hz, 1H), 4.50 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J = 250.8 Hz), 142.9, 136.8, 133.7, 132.5 (d, J = 4.7 Hz), 132.4, 129.8, 128.0, 127.8 (d, J = 3.6 Hz), 125.2 (d, J = 15.7 Hz), 121.0 (d, J = 9.5 Hz), 120.1 (q, J = 326.6 Hz), 119.2 (d, J = 25.3 Hz), 31.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.27 (s, 3F), -114.18 (s, 1F). IR $(KBr)_{max}$ 3065, 2930, 1610, 1575, 1479, 1360, 1271, 1216, 1111, 922 cm^{-1}. MS (ESI): *m/z* (%) 419 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}BrF_4O_2S$: 396.9516; Found: 396.9514.

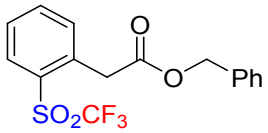


Ethyl 4-(4,5-dimethyl-2-((trifluoromethyl)sulfonyl)benzyl)benzoate (3l) (60.0 mg, 50%): white solid, m.p. 80-82 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.90 (s, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.05 (s, 1H), 4.47 (s, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 147.0, 144.7, 141.0, 136.9, 134.4, 133.9, 129.8, 129.1, 128.8, 126.6, 120.0 (q, J = 326.7 Hz), 60.9, 37.6, 20.1, 19.2, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.46 (s, 3F). IR $(KBr)_{max}$ 3064, 2925, 1720, 1601, 1577, 1465, 1361, 1275, 1209, 1115, 695 cm^{-1}. MS (ESI): *m/z* (%) 401 $[M+H]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}F_3O_4S$: 401.1029; Found: 401.1030.



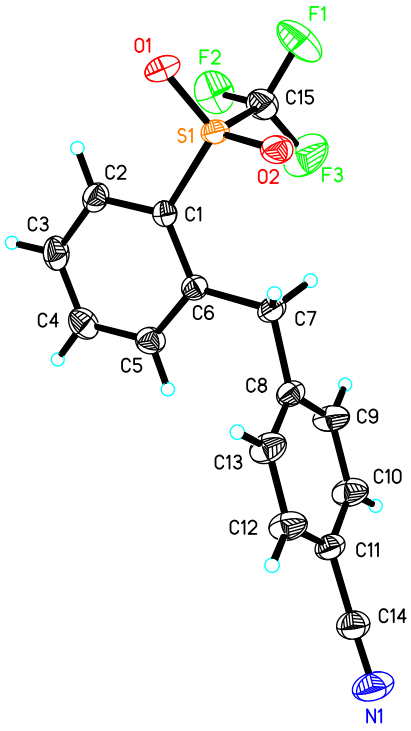
Ethyl 2-(2-((trifluoromethyl)sulfonyl)phenyl)acetate (5a) (32.0 mg, 36%)**:** white solid, m.p. 58-60 °C。 ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.5 Hz, 1H), 7.63–7.53 (m, 2H), 7.47 (d, J = 7.3 Hz, 1H), 5.31 (s, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.32 (s, 3F). ^{13}C NMR (101

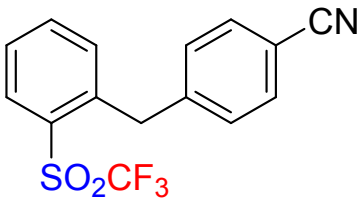
MHz, $CDCl_3$) δ 166.7, 133.5, 132.5, 131.7, 131.5, 130.0, 124.9, 119.8 (q, *J* = 328.1 Hz), 61.7, 53.2, 14.1. IR $(KBr)_{max}$ 3058, 2930, 1718, 1600, 1564, 1470, 1360, 1258, 1205, 1109, 700 cm^{-1}. MS (ESI): *m/z* (%) 319 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}F_3O_4S$: 297.0403; Found: 397.0403.



Benzyl 2-(2-((trifluoromethyl)sulfonyl)phenyl)acetate (5b) (35.7 mg, 33%)**:** white solid, m.p. 38-42 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.52–7.37 (m, 6H), 5.42 (s, 2H), 5.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 135.4, 133.6, 132.8, 131.9, 131.0, 130.1, 128.7, 128.53, 128.50, 125.1, 119.8 (q, *J* = 328.2 Hz), 67.5, 53.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.22 (s, 3F). IR $(KBr)_{max}$ 3016, 2949, 1713, 1590, 1495, 1446, 1360, 1261, 1206, 1120, 956, 703 cm^{-1}. MS (ESI): *m/z* (%) 381 $[M+Na]^+$. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}F_3O_4S$: 359.0559; Found: 359.0563.

4. ORTEP drawing of the X-ray crystallographic structure of 3a



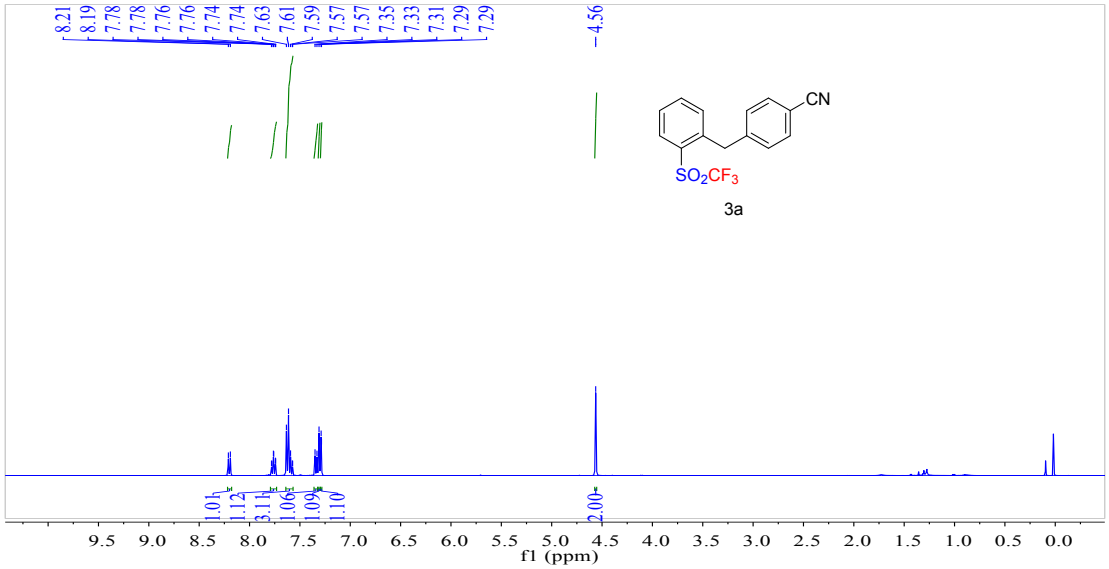


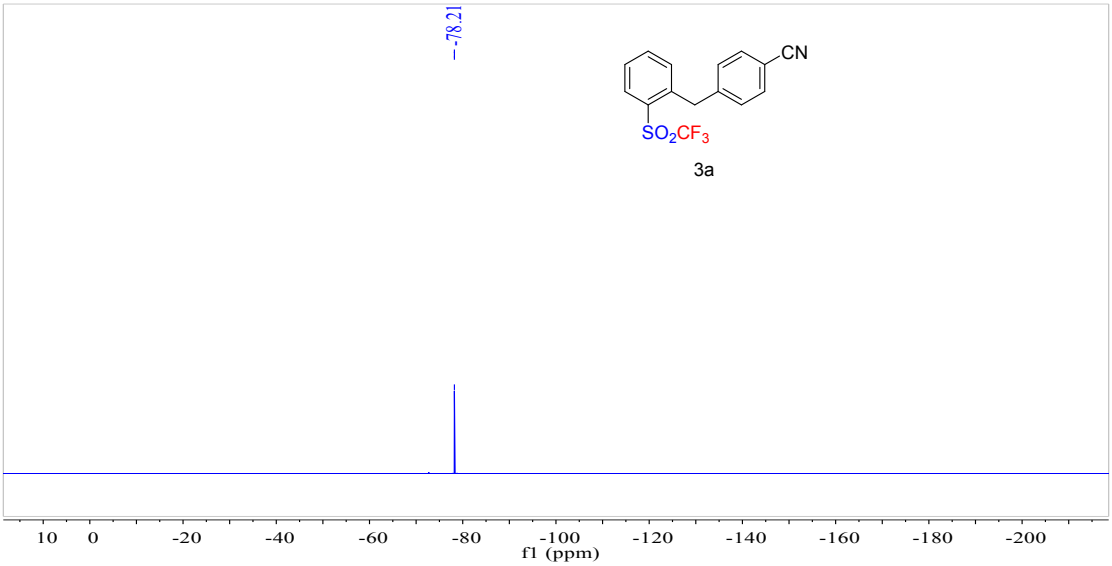
3a

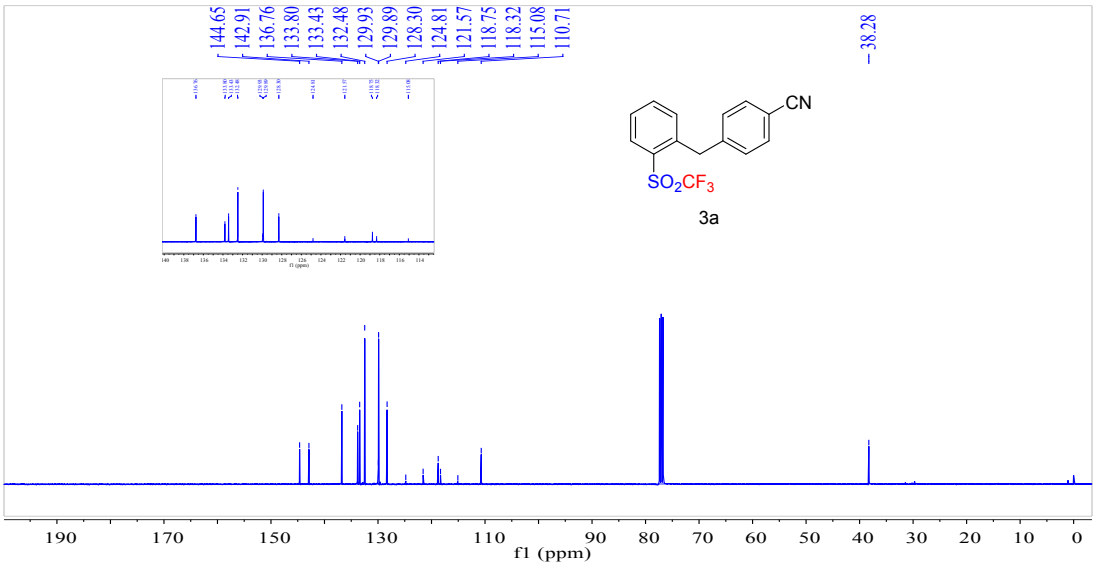
CCDC 1509106 contains the supplementary crystallographic data for the target compound **3a**.

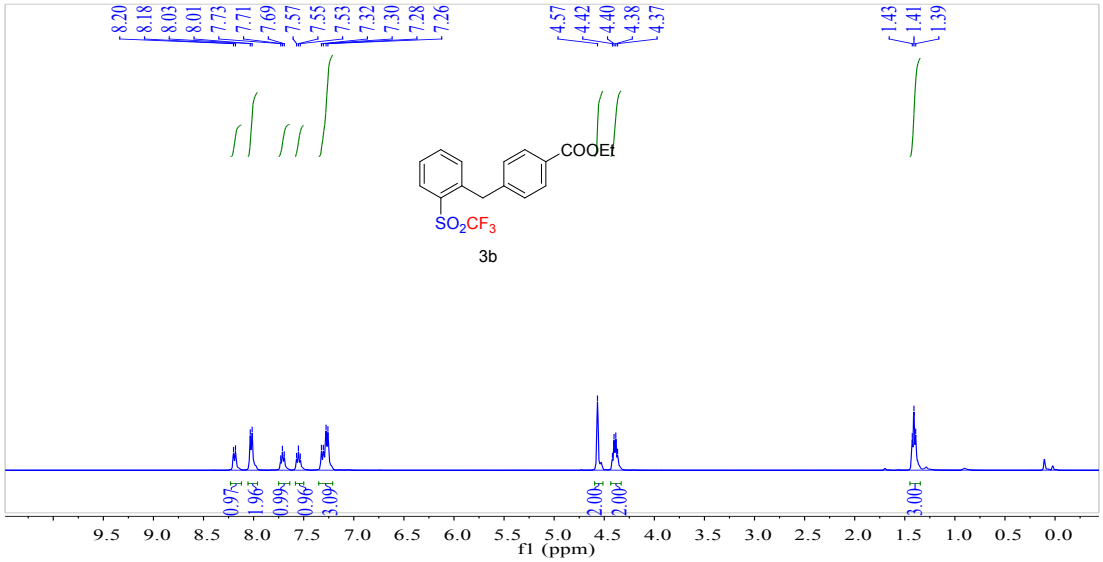
This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra for the products





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4.42
4.40
4.38
4.37
1.43
1.41
1.39
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3b
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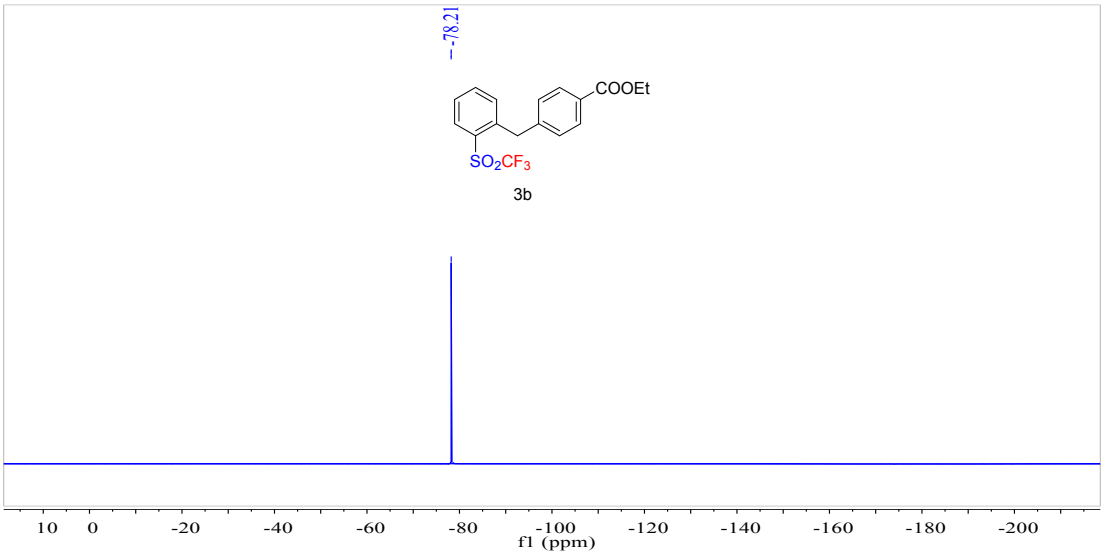
0.99
0.96
3.09
2.00
2.00
3.00
f1 (ppm)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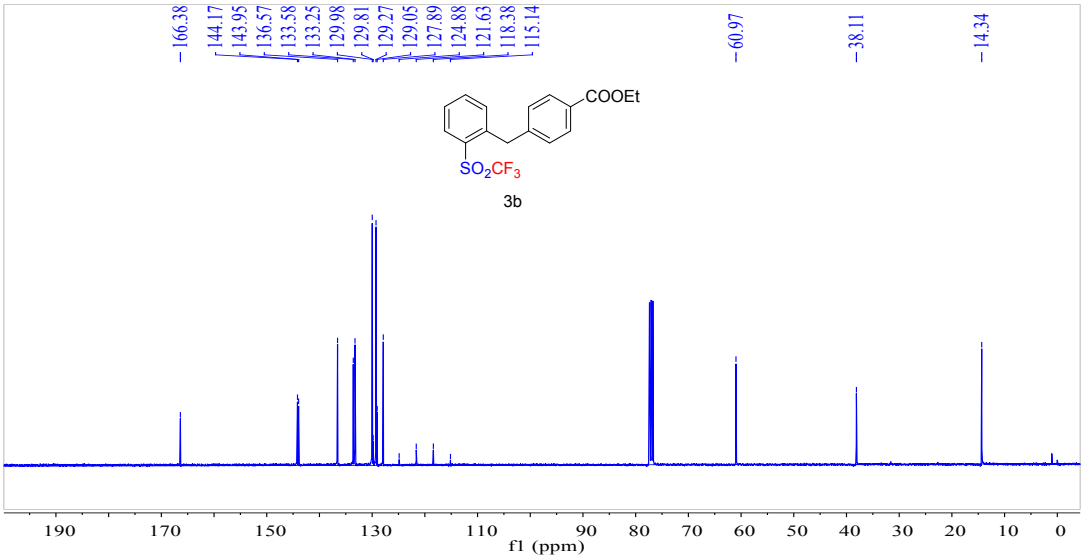
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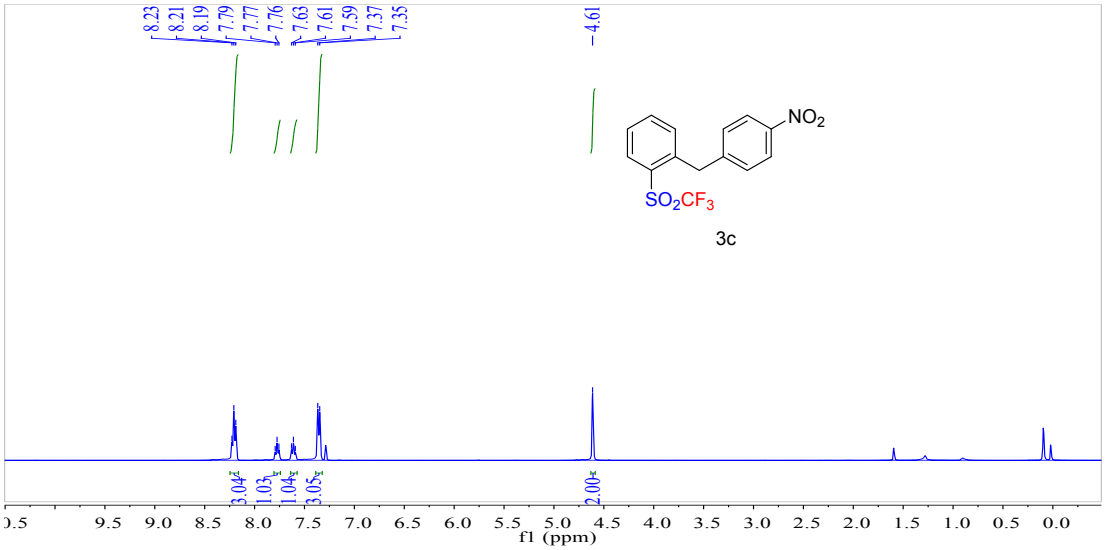
3b
f1 (ppm)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3c
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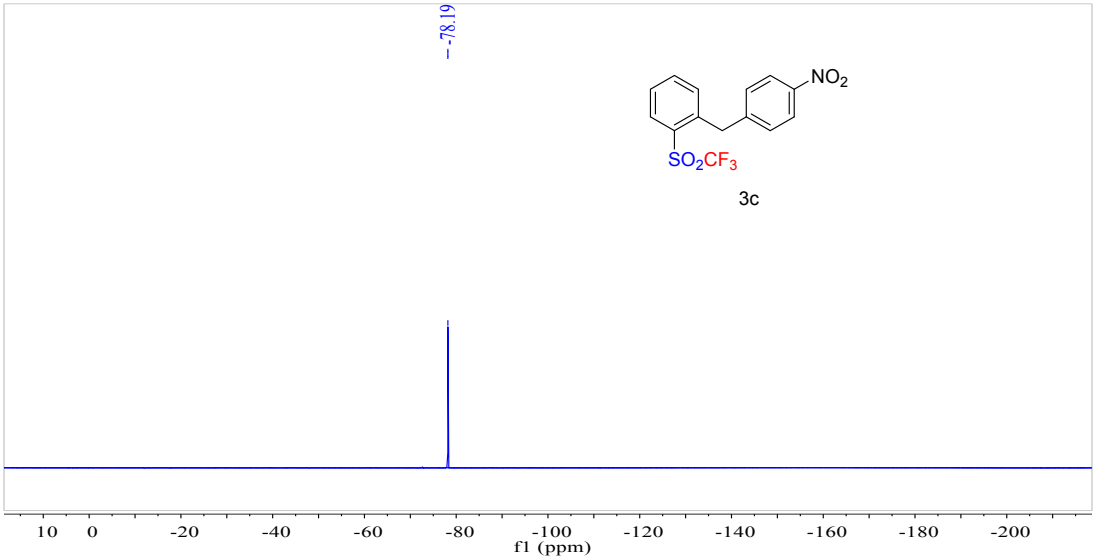
2.00
f1 (ppm)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SO2CF3
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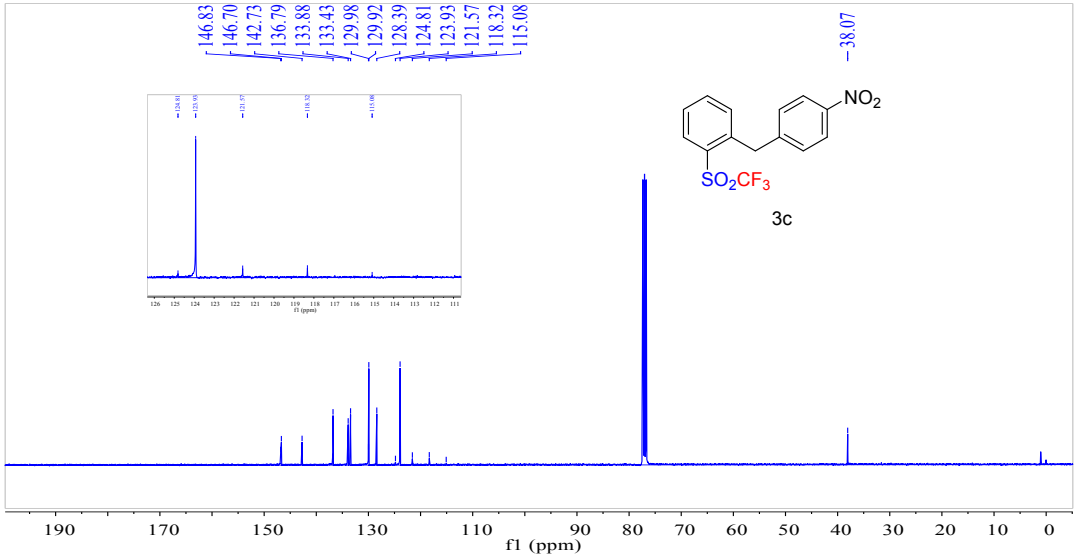
f1 (ppm)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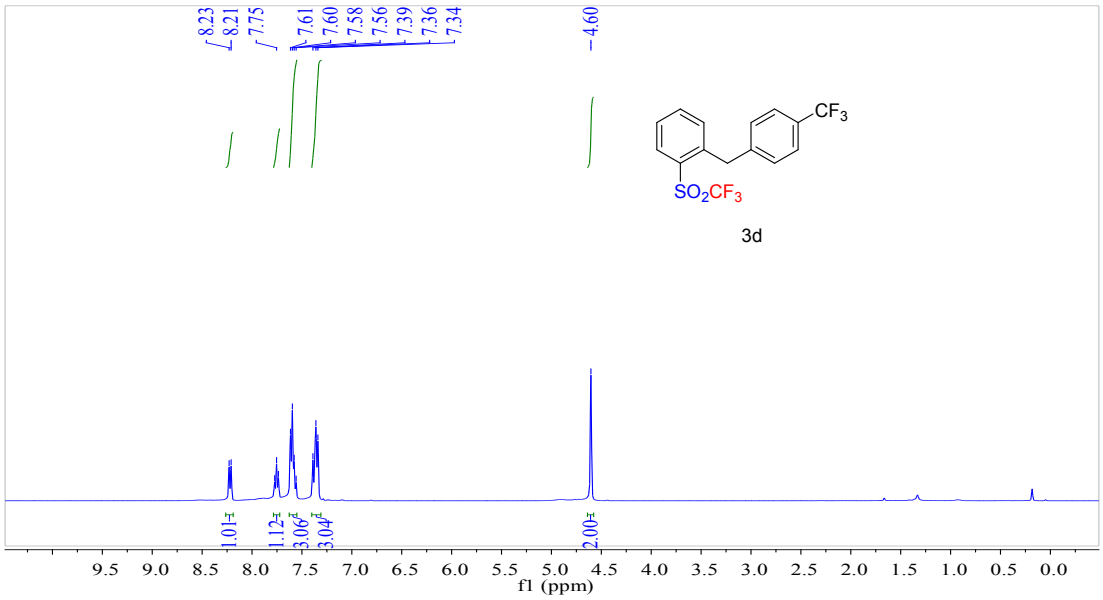
f1 (ppm)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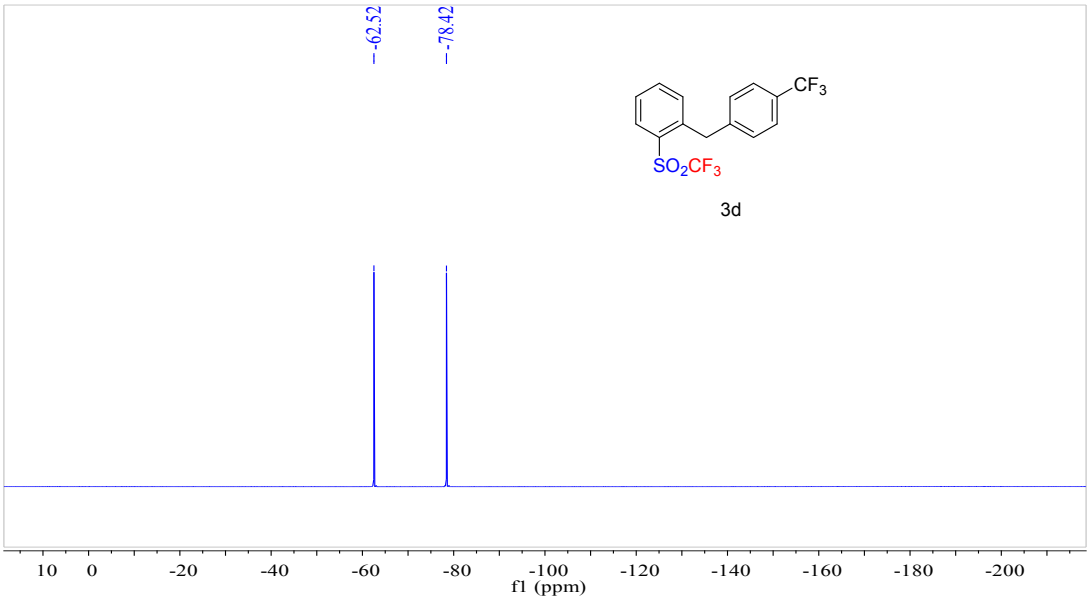
2.00
f1 (ppm)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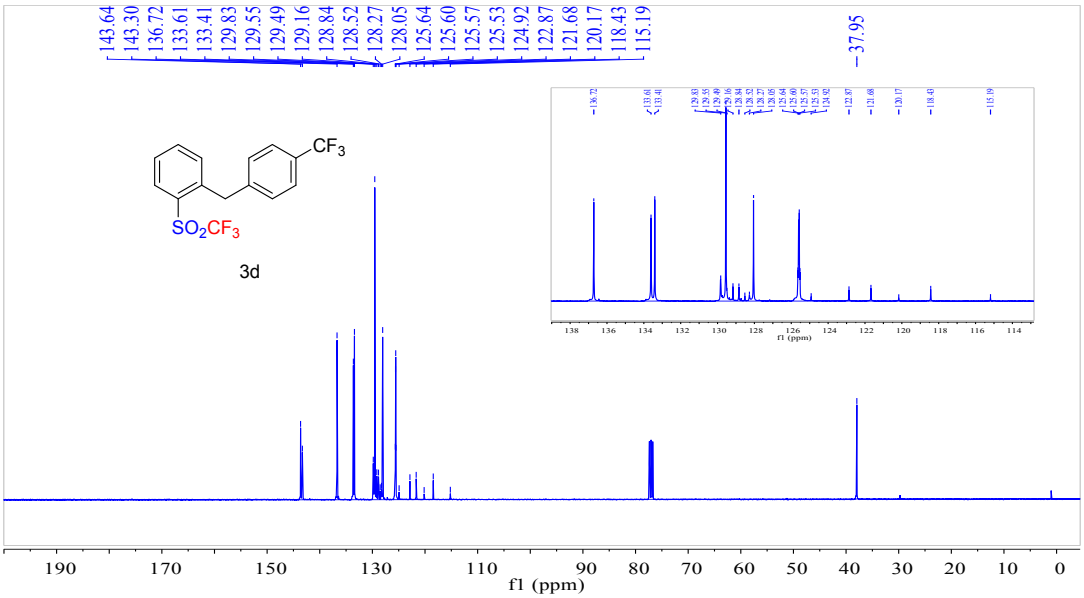
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125.60
125.57
125.53
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CF3
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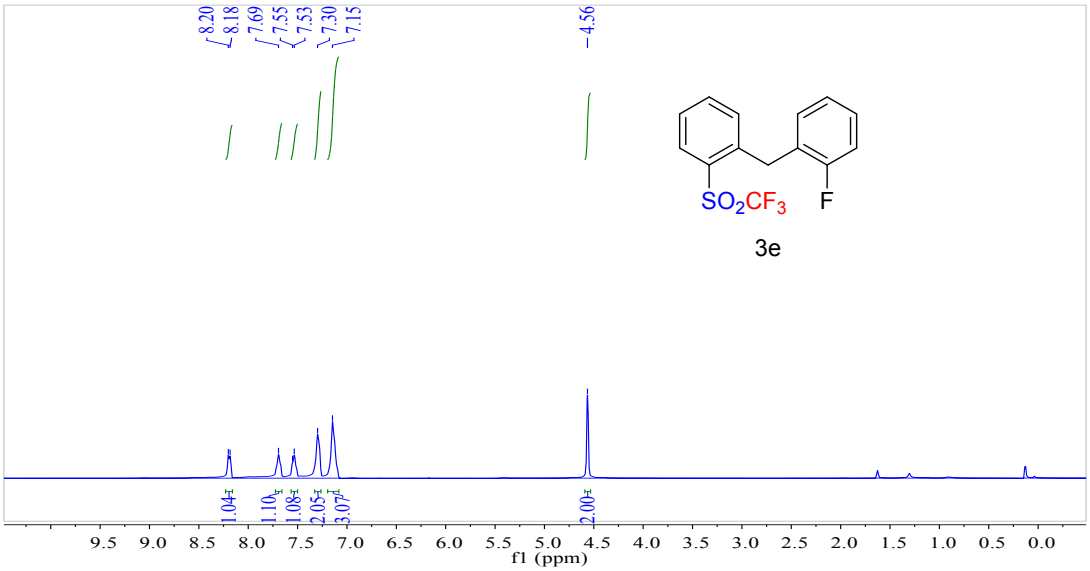
3d
f1 (ppm)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3.07
2.00
SO2CF3
F
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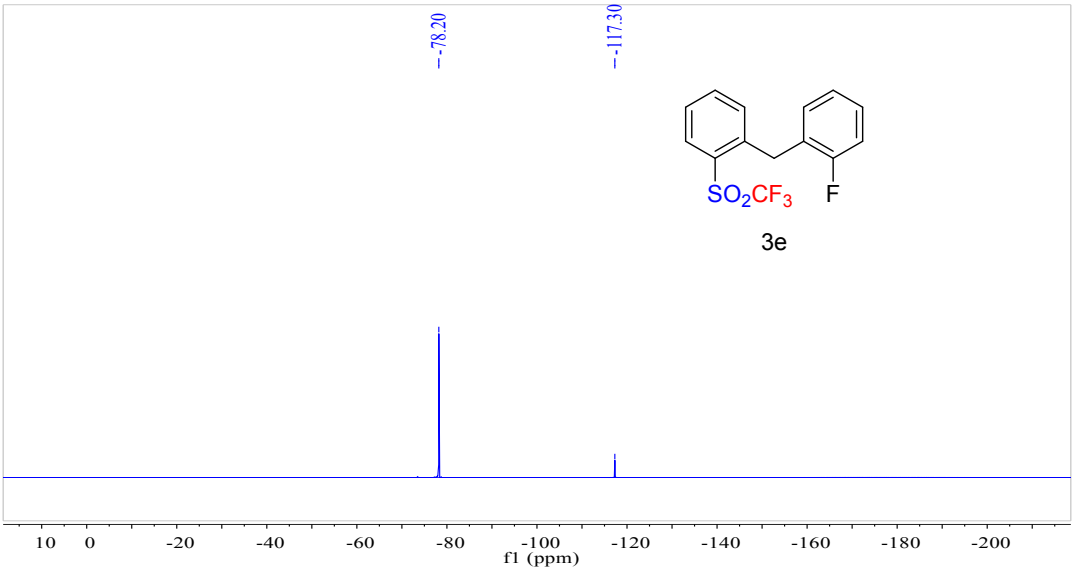
f1 (ppm)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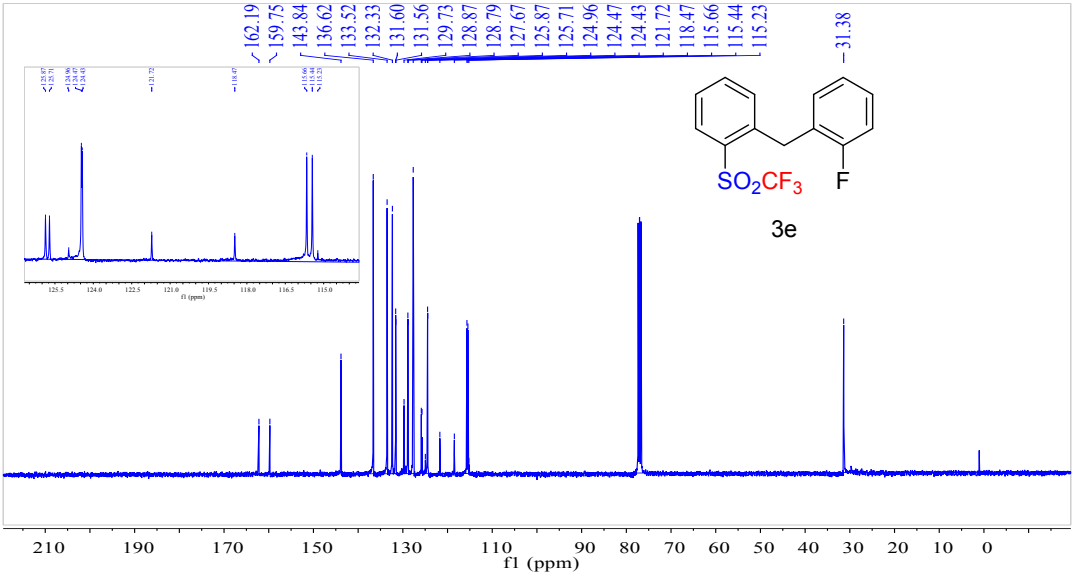
f1 (ppm)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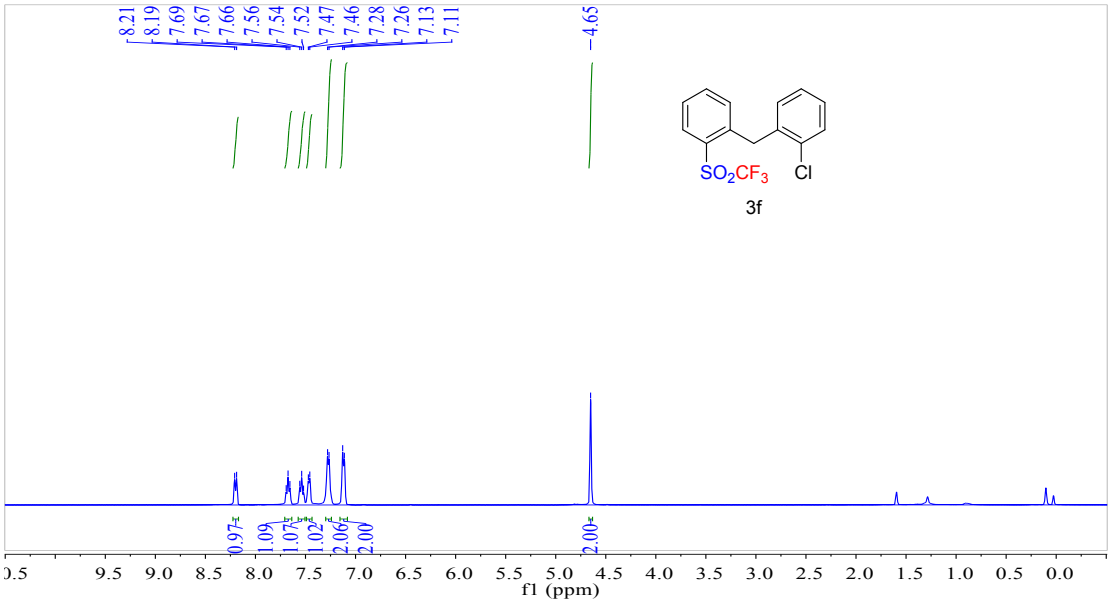
118.47
115.66
115.44
115.23
31.38
SO2CF3
F
3e
f1 (ppm)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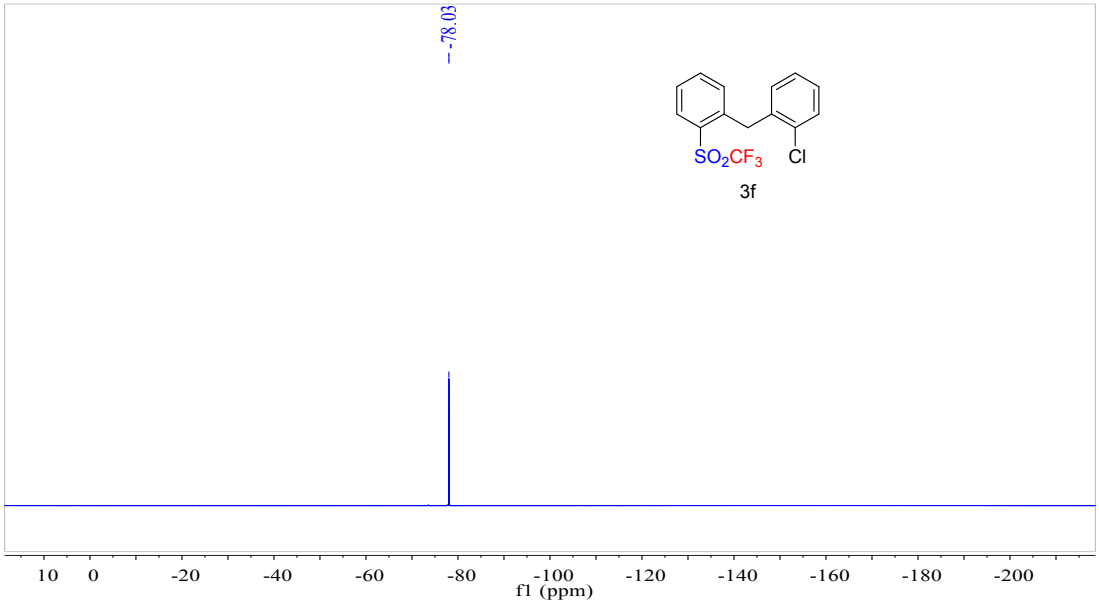
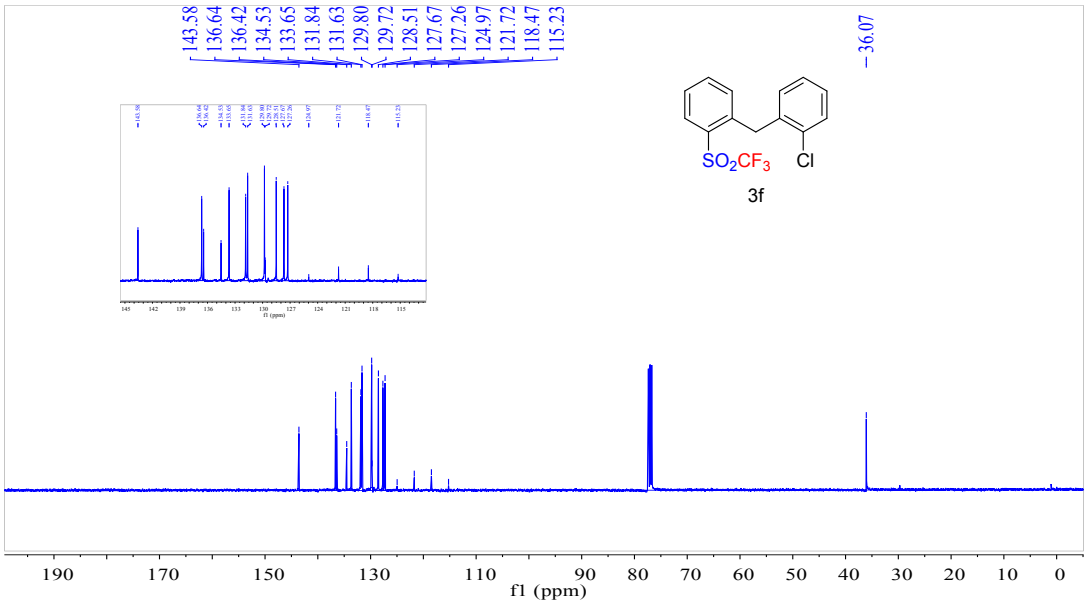
8.19
7.69
7.67
7.66
7.56
7.54
7.52
7.47
7.46
7.28
7.26
7.13
7.11
4.65
SO2CF3
Cl
3f
0.97
1.09
1.07
1.02
2.06
2.00
2.00
f1 (ppm)


-78.03
SO2CF3
Cl
3f
f1 (ppm)


143.58
136.64
136.42
134.53
133.65
131.84
131.63
129.80
129.72
128.51
127.67
127.26
124.97
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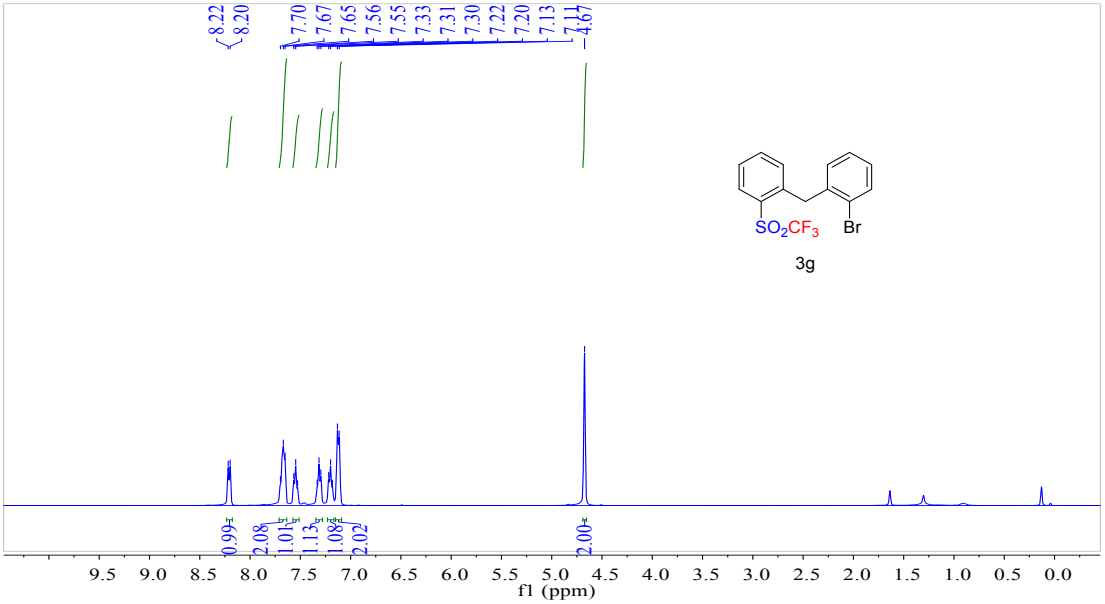
115.23
36.07
SO2CF3
Cl
3f
f1 (ppm)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8.20
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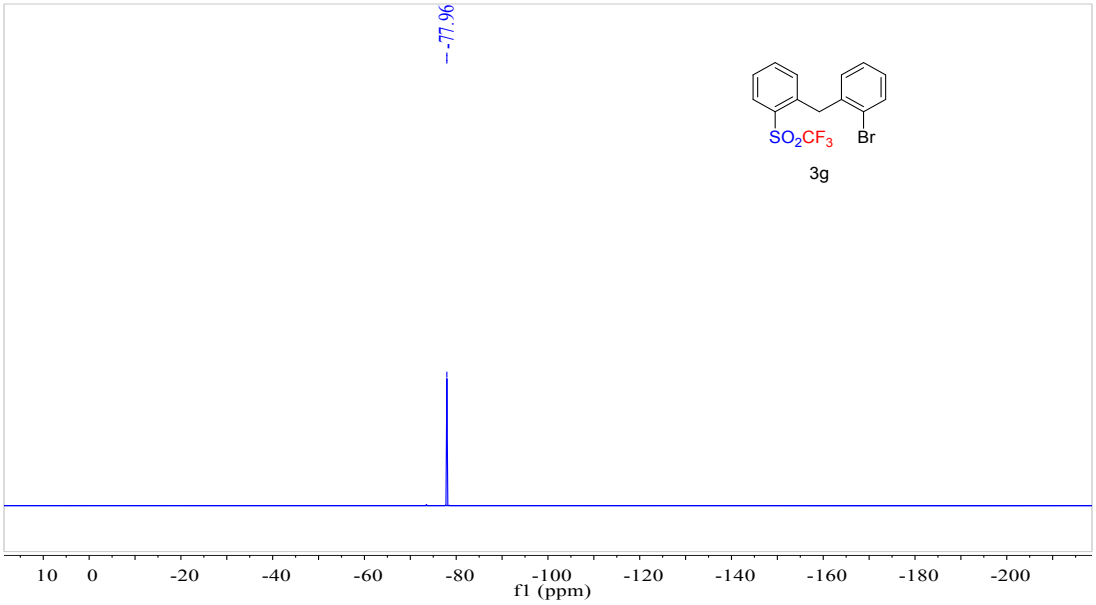
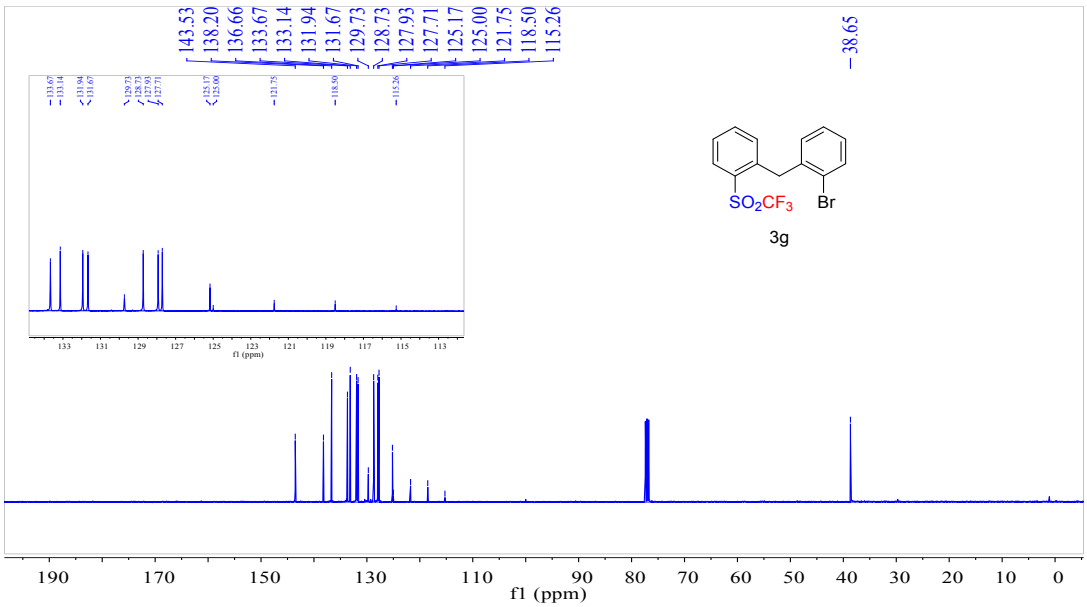
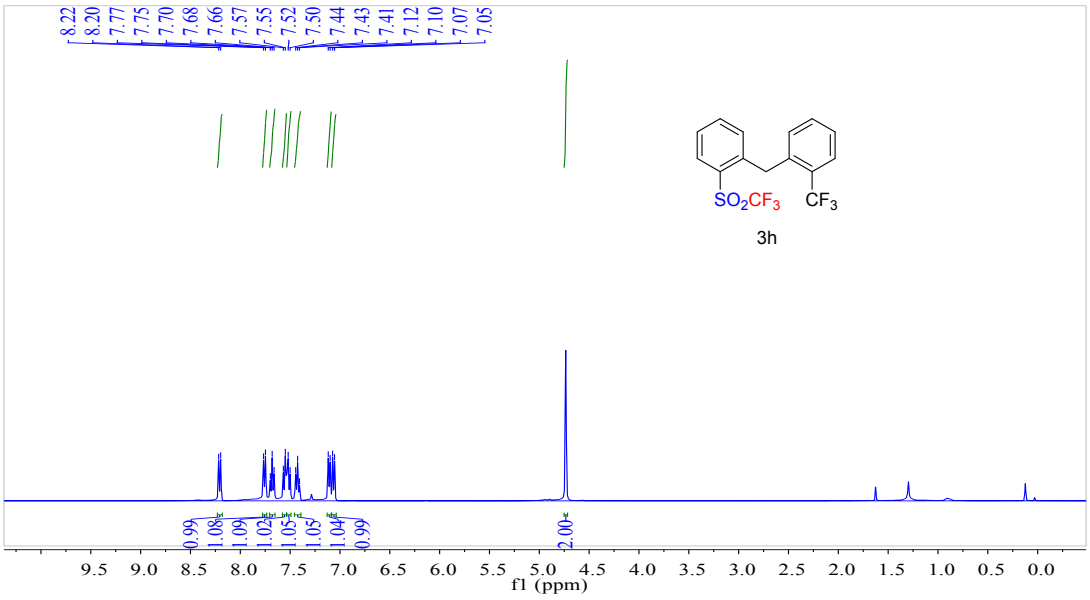
7.65
7.56
7.55
7.33
7.31
7.30
7.22
7.20
7.13
7.11
4.67
0.99
2.08
1.01
1.13
1.08
2.02
2.00
SO2CF3
Br
3g
f1 (ppm)


-77.96
SO2CF3
Br
3g
f1 (ppm)


143.53
138.20
136.66
133.67
133.14
131.94
131.67
129.73
128.73
127.93
127.71
125.17
125.00
121.75
118.50
115.26
38.65
SO2CF3
Br
3g
f1 (ppm)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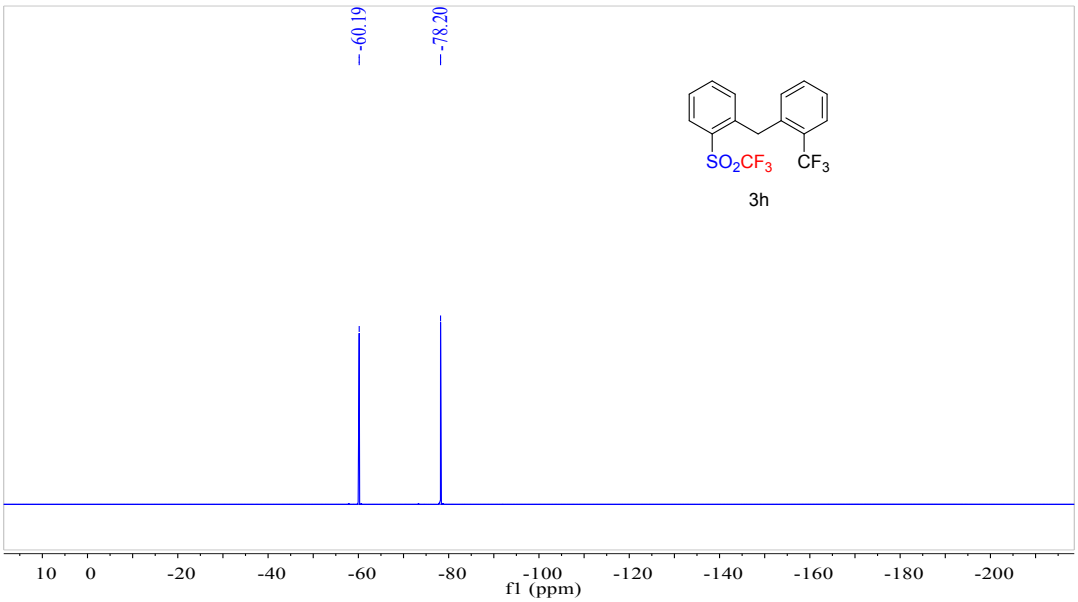
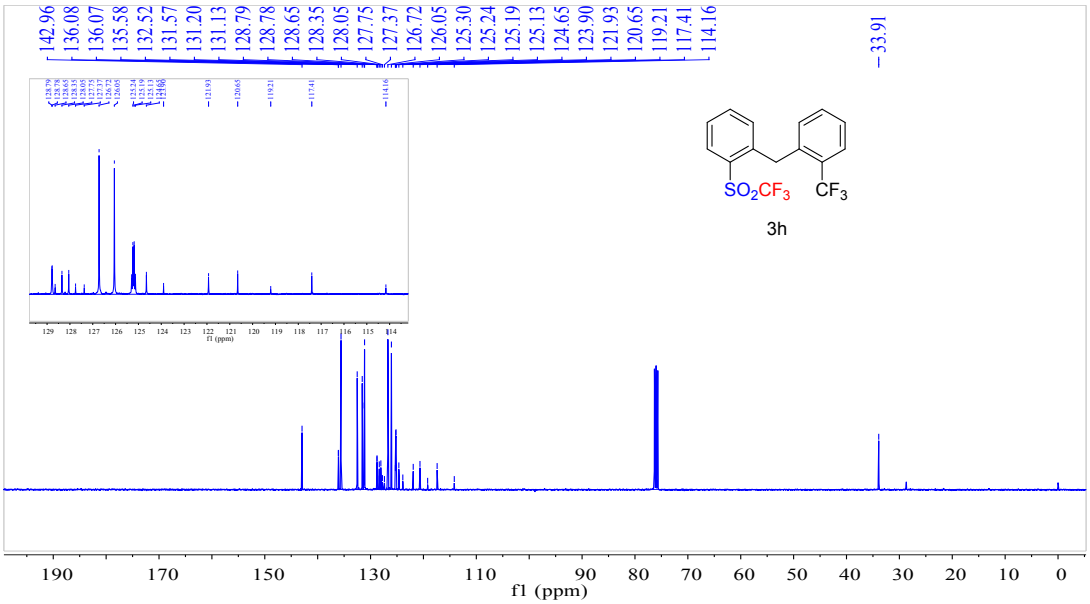
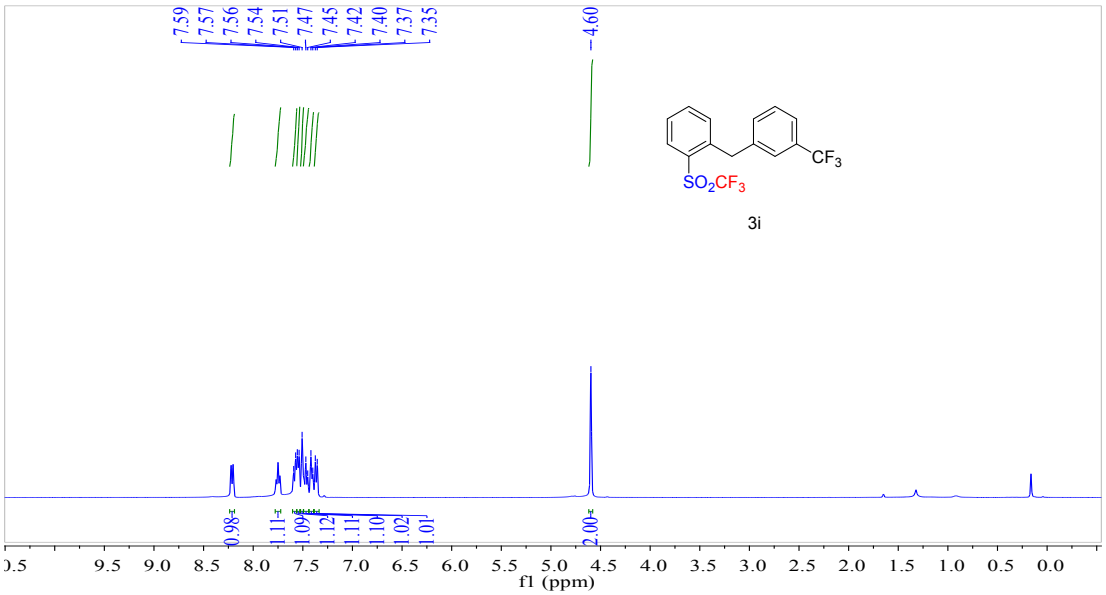
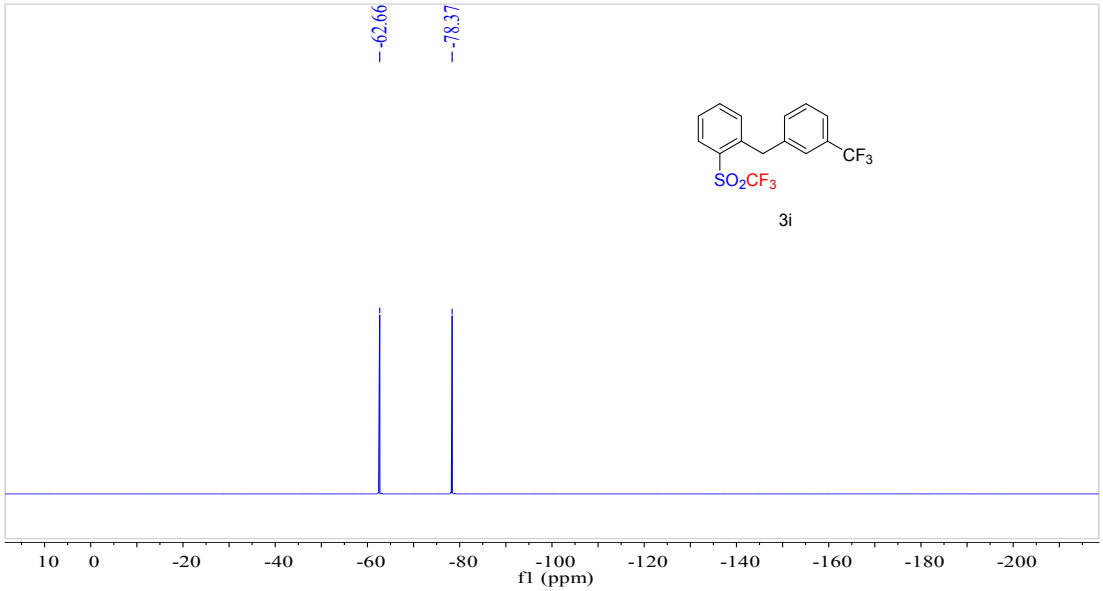
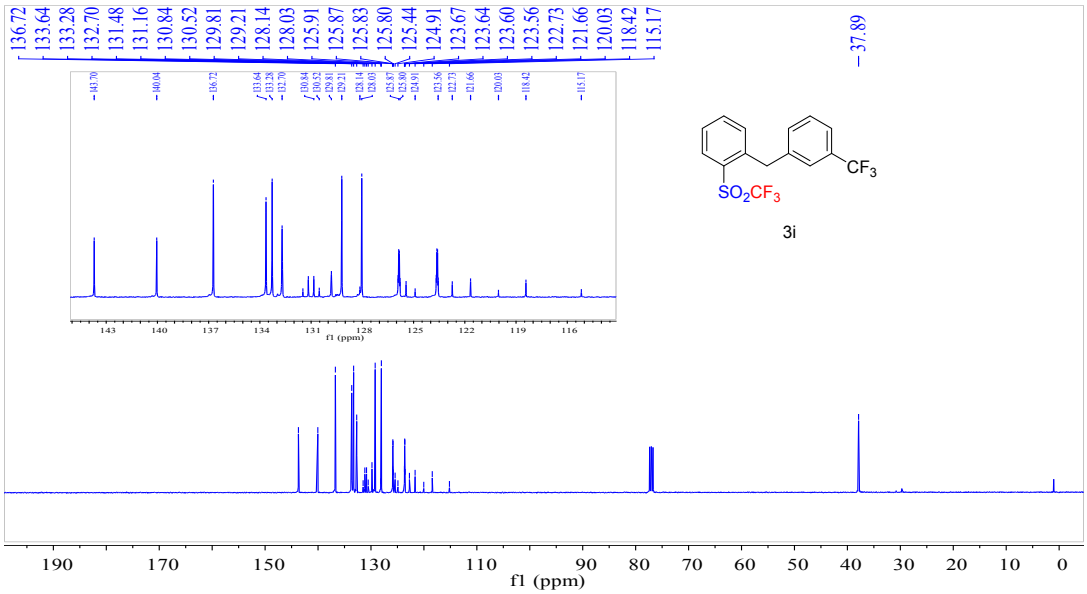
8.20
7.77
7.75
7.70
7.68
7.66
7.57
7.55
7.52
7.50
7.44
7.43
7.41
7.12
7.10
7.07
7.05
SO2CF3
CF3
3h
0.99
1.08
1.09
1.02
1.05
1.05
1.04
0.99
2.00
f1 (ppm)


-60.19
-78.20
SO2CF3
CF3
3h
f1 (ppm)


142.96
136.08
136.07
135.58
132.52
131.57
131.20
131.13
128.79
128.78
128.65
128.35
128.05
127.75
127.37
126.72
126.05
125.30
125.24
125.19
125.13
124.65
123.90
121.93
120.65
119.21
117.41
114.16
33.91
SO2CF3
CF3
3h
f1 (ppm)


7.59
7.57
7.56
7.54
7.51
7.47
7.45
7.42
7.40
7.37
7.35
4.60
CF3
SO2CF3
3i
0.98
1.11
1.09
1.12
1.11
1.10
1.02
1.01
2.00
f1 (ppm)


-62.66
-78.37
CF3
SO2CF3
3i
f1 (ppm)


136.72
133.64
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132.70
131.48
131.16
130.84
130.52
129.81
129.21
128.14
128.03
125.91
125.87
125.83
125.80
125.44
124.91
123.67
123.64
123.60
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122.73
121.66
120.03
118.42
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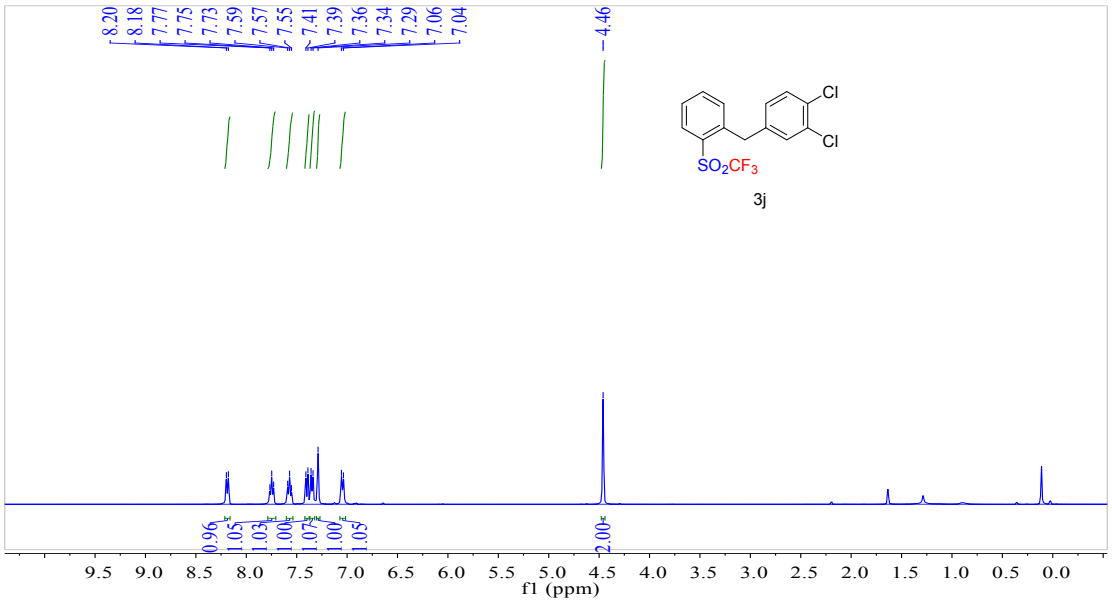
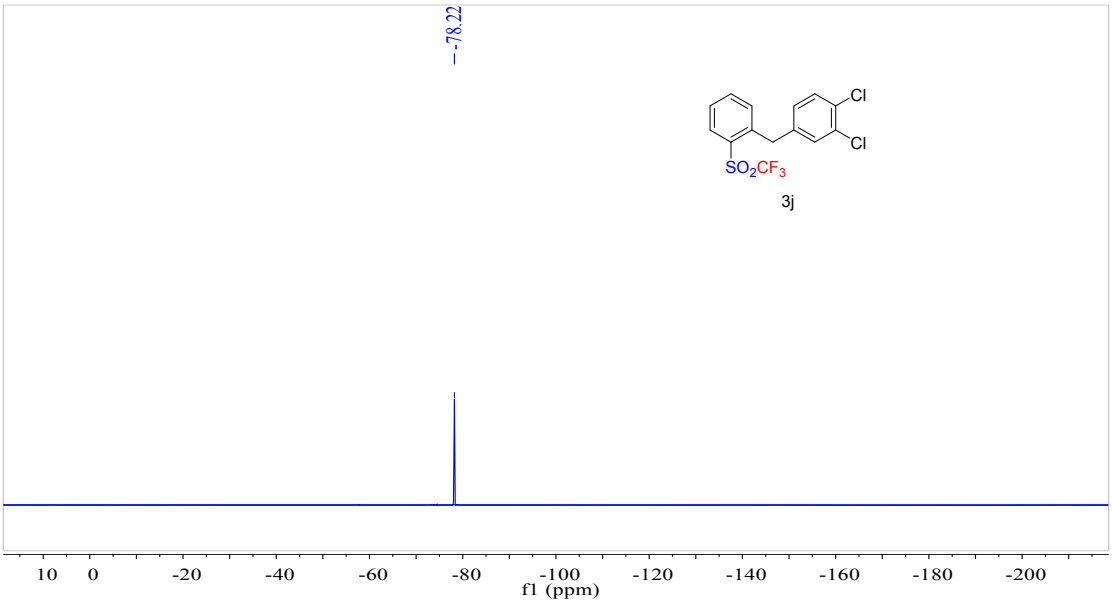
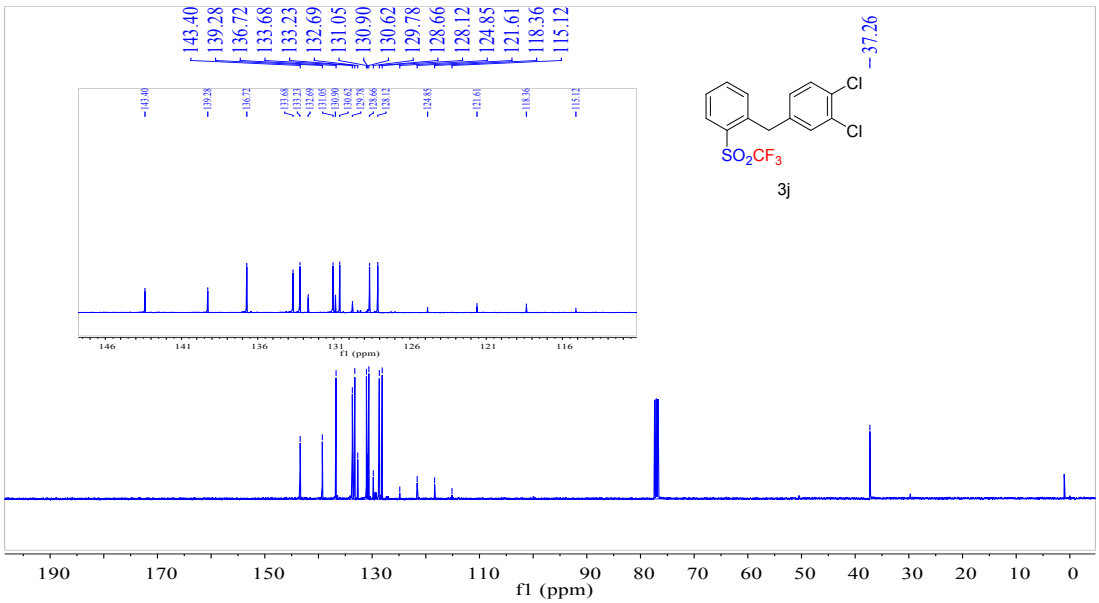
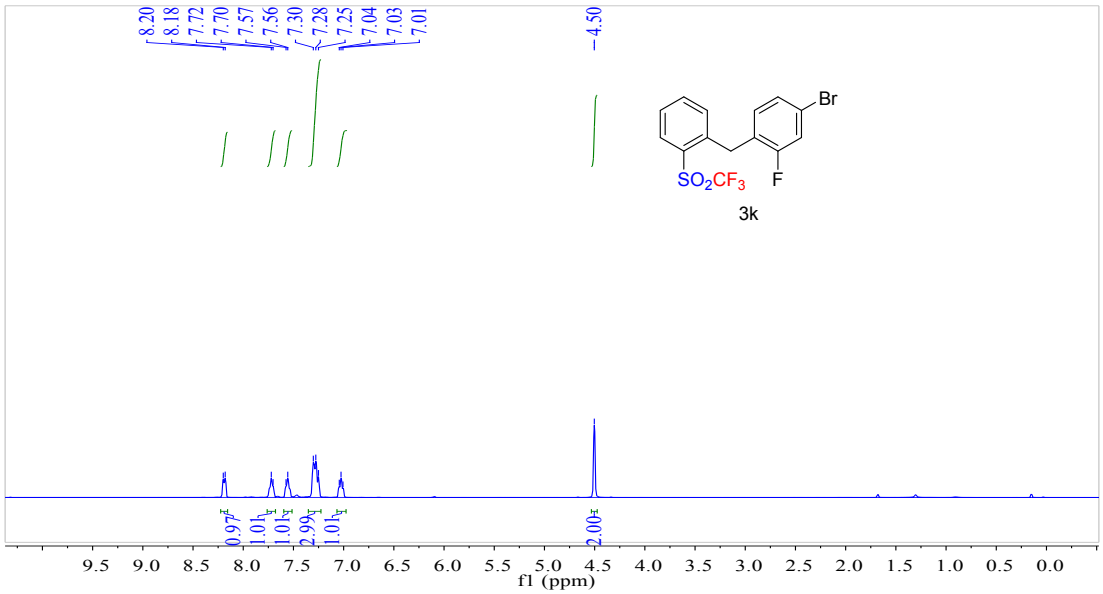
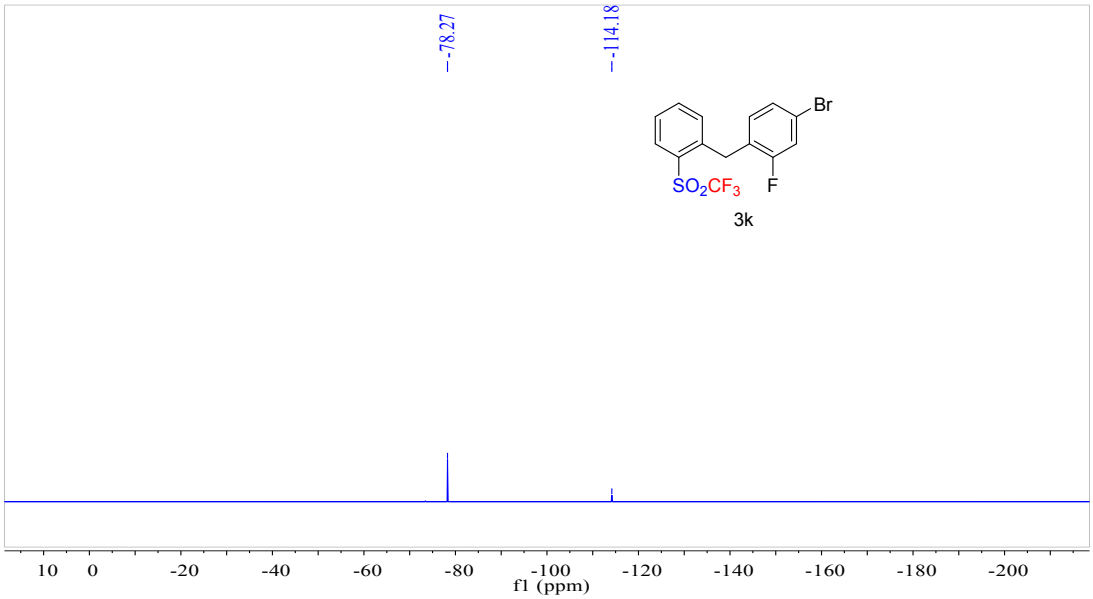
37.89
CF3
SO2CF3
3i
f1 (ppm)

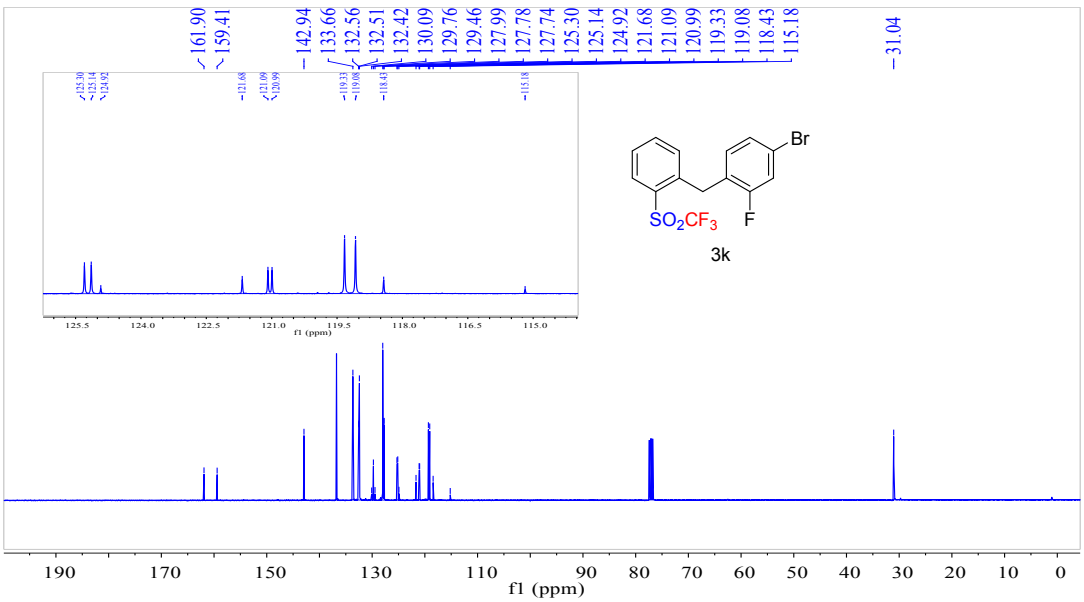

8.20
8.18
7.77
7.75
7.73
7.59
7.57
7.55
7.41
7.39
7.36
7.34
7.29
7.06
7.04
4.46
Cl
Cl
SO2CF3
3j
0.96
1.05
1.03
1.00
1.07
1.00
1.05
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

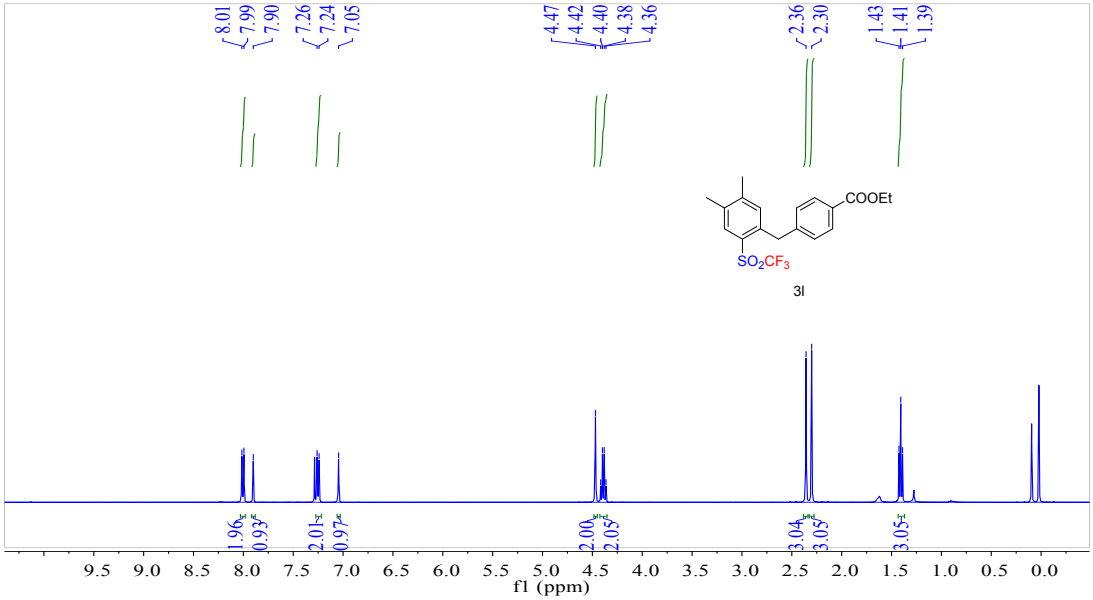

-78.22
Cl
Cl
SO2CF3
3j
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

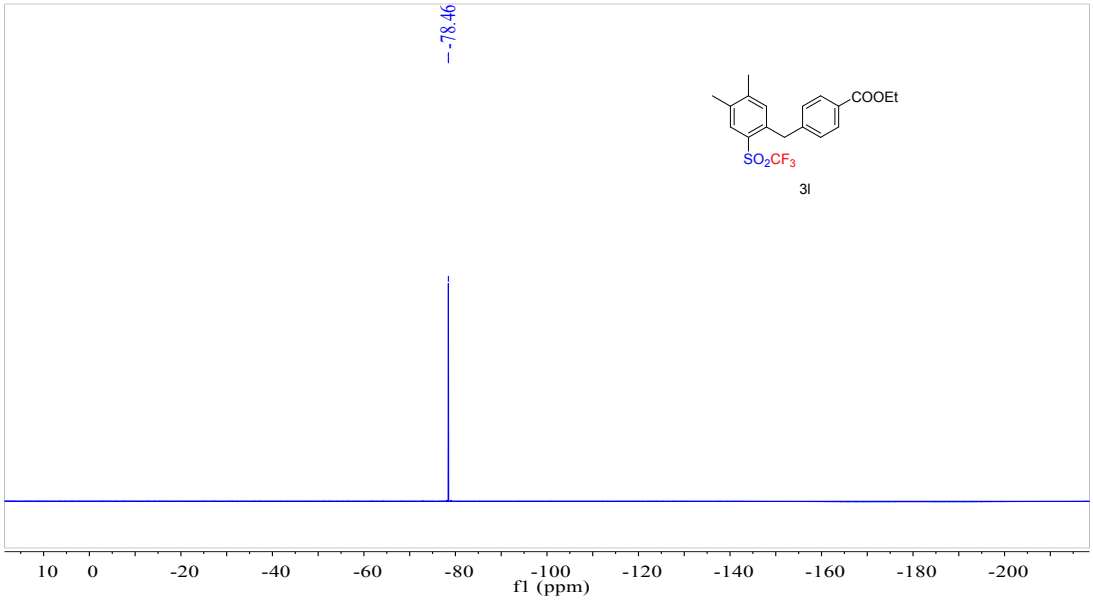

143.40
139.28
136.72
133.68
133.23
132.69
131.05
130.90
130.62
130.62
129.78
129.78
128.66
128.12
124.85
121.61
118.36
115.12
37.26
Cl
Cl
SO2CF3
3j
146 141 136 131 126 121 116
f1 (ppm)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

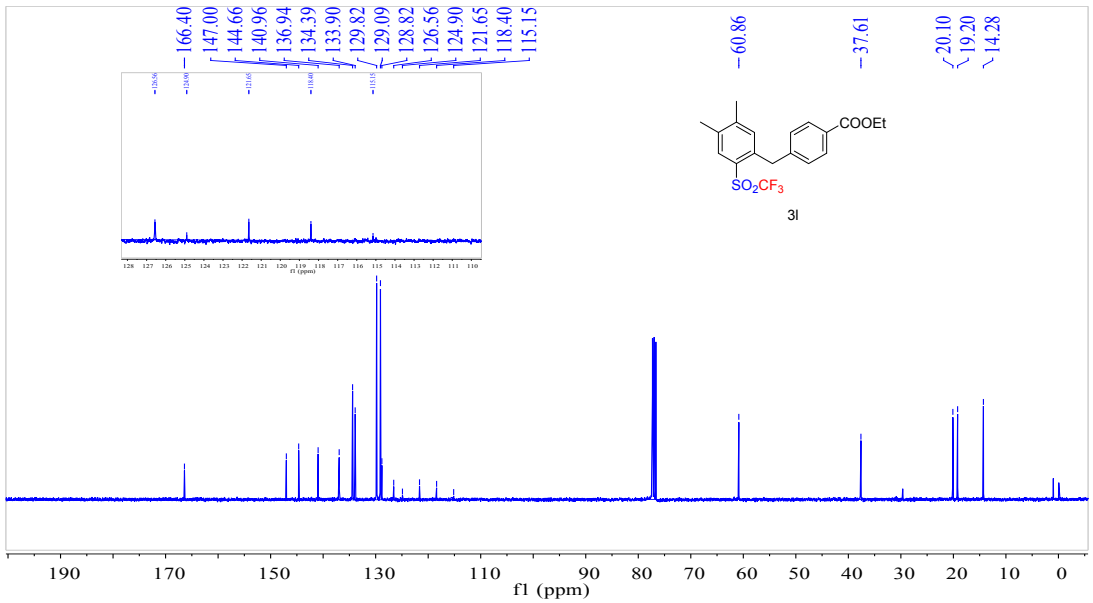

8.20
8.18
7.72
7.70
7.57
7.56
7.30
7.28
7.25
7.04
7.03
7.01
4.50
Br
SO2CF3
F
3k
0.97
1.01
1.01
2.99
1.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-78.27
-114.18
Br
SO2CF3
F
3k
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


161.90
159.41
142.94
133.66
132.56
132.51
132.42
130.09
129.76
129.46
127.99
127.78
127.74
125.30
125.14
124.92
121.68
121.09
120.99
119.33
119.08
118.43
115.18
31.04
Br
SO2CF3
F
3k
125.5 124.0 122.5 121.0 119.5 118.0 116.5 115.0
f1 (ppm)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.01
7.99
7.90
7.26
7.24
7.05
4.47
4.42
4.40
4.38
4.36
2.36
2.30
1.43
1.41
1.39
COOEt
SO2CF3
3l
1.96
0.93
2.01
0.97
2.00
2.05
3.04
3.05
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-78.46
COOEt
SO2CF3
3l
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)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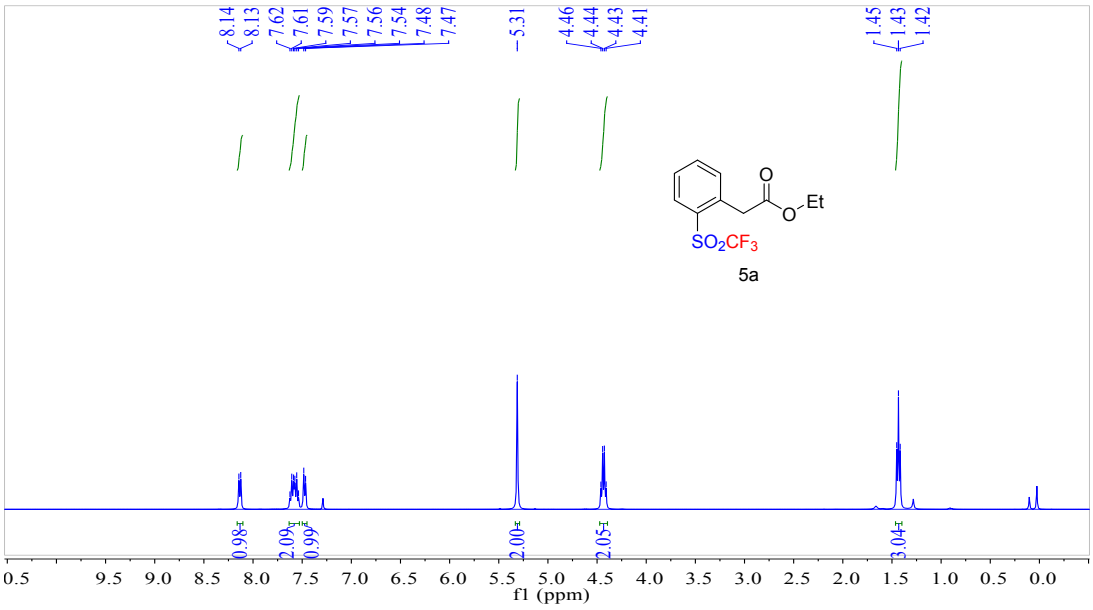
147.00
144.66
140.96
136.94
134.39
133.90
129.82
129.09
128.82
126.56
124.90
121.65
118.40
115.15
60.86
37.61
20.10
19.20
14.28
COOEt
SO2CF3
3l
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.13
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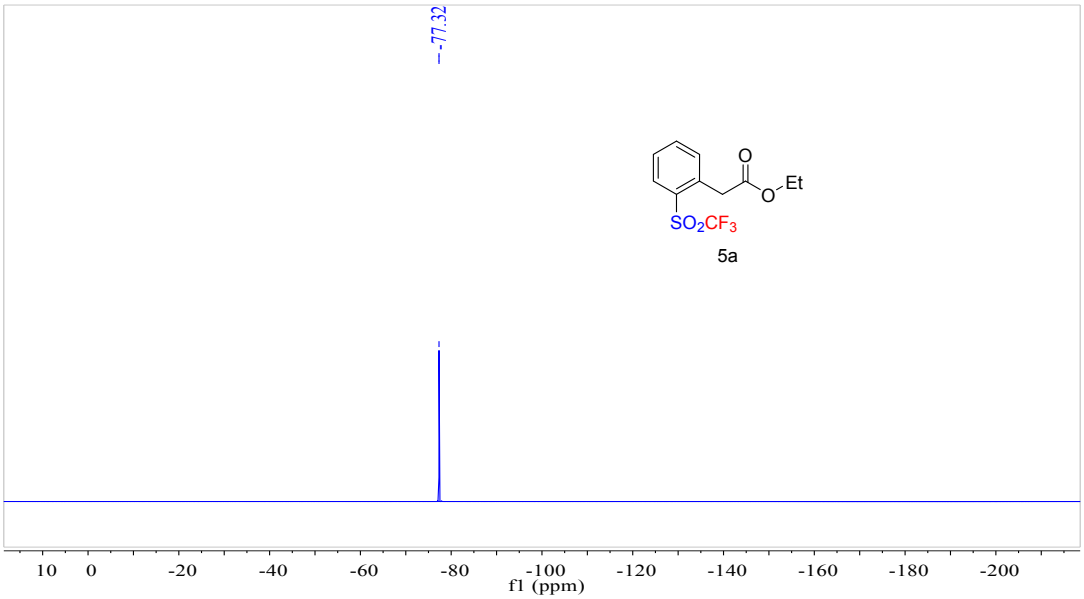
7.61
7.59
7.57
7.56
7.54
7.48
7.47
5.31
4.46
4.44
4.43
4.41
1.45
1.43
1.42
O
O
Et
SO2CF3
5a
0.98
2.09
0.99
2.00
2.05
3.04
f1 (ppm)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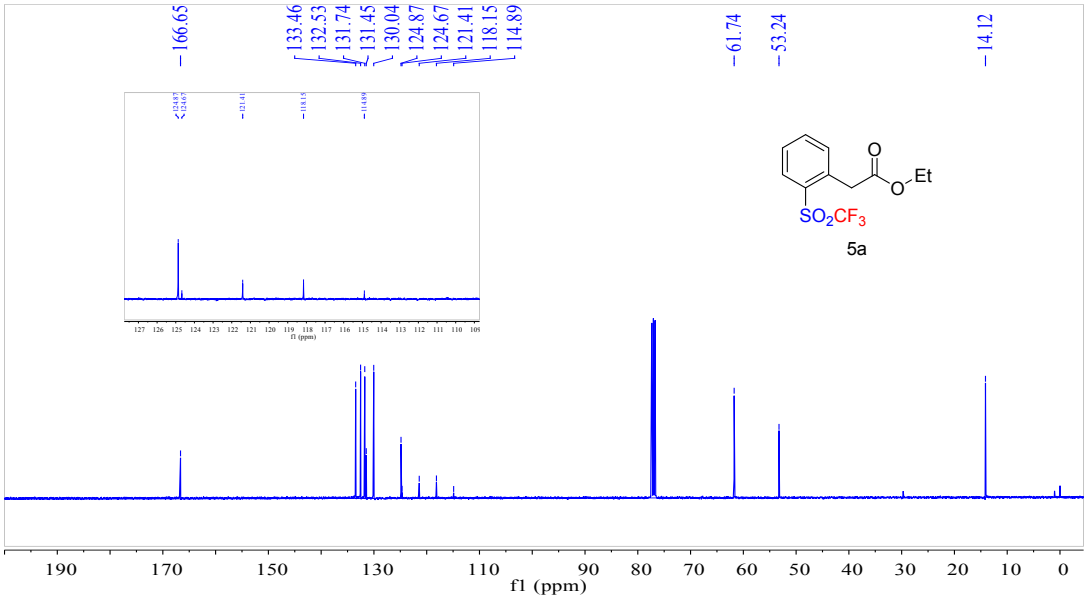
O
Et
SO2CF3
5a
f1 (ppm)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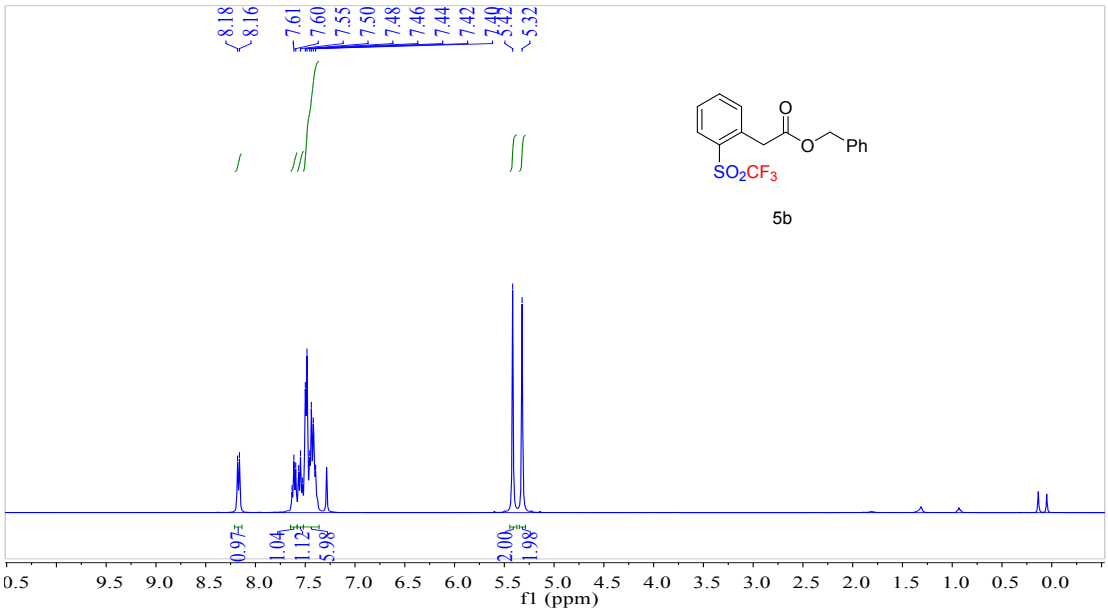
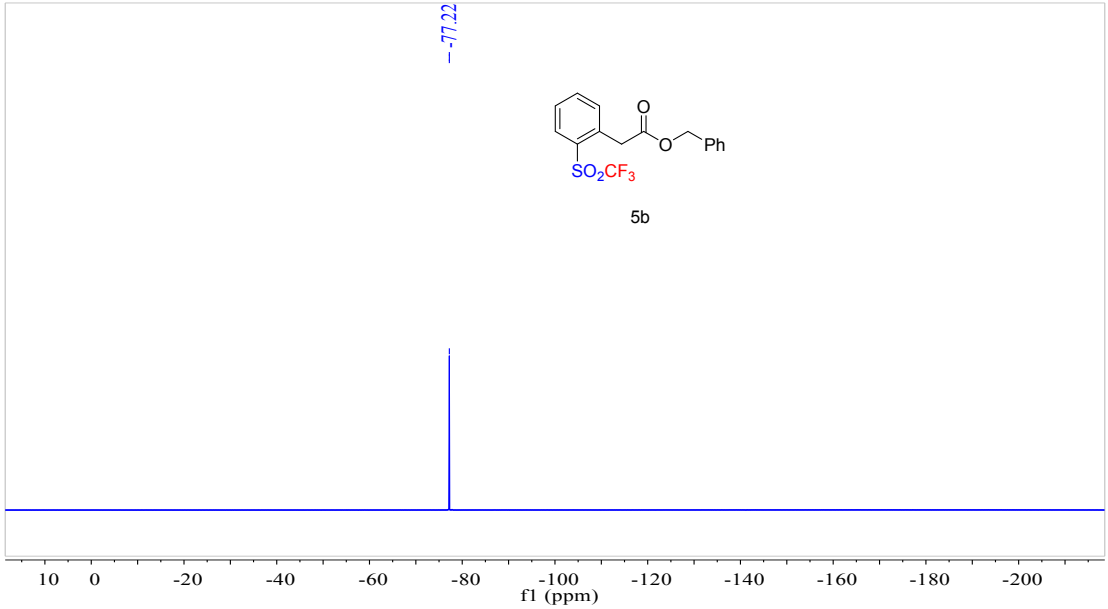
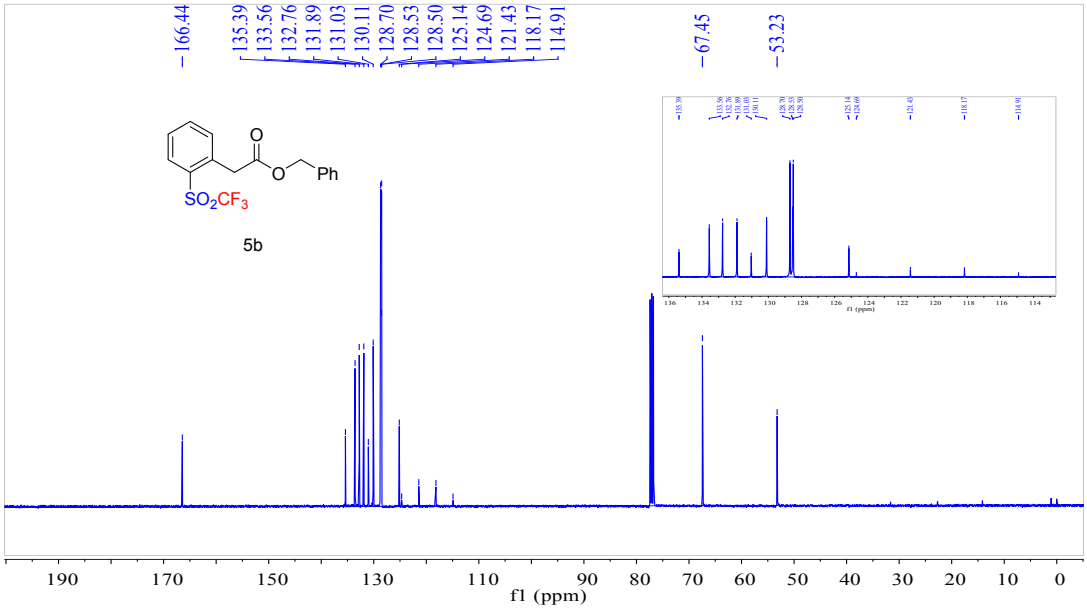
132.53
131.74
131.45
130.04
124.87
124.67
121.41
118.15
114.89
61.74
53.24
14.12
O
O
Et
SO2CF3
5a
f1 (ppm)


8.18
8.16
7.61
7.60
7.55
7.50
7.48
7.46
7.44
7.42
5.42
5.32
O
O
Ph
SO2CF3
5b
0.97
1.04
1.12
5.98
2.00
1.98
f1 (ppm)


-77.22
O
O
Ph
SO2CF3
5b
f1 (ppm)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132.76
131.89
131.03
130.11
128.70
128.53
128.50
125.14
124.69
121.43
118.17
114.91
67.45
53.23
O
O
Ph
SO2CF3
5b
f1 (ppm)