Supporting Information

ortho-Cyanomethylation of Aryl Fluoroalkyl Sulfoxides via Sulfonium-Claisen Rearrangement

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1 General information

Unless otherwise indicated, all glassware was oven dried before use and all reactions were performed under an atmosphere of Nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Compound isolation was performed on chromatography column using silica gel 60 (160-200 mesh). Neat infrared spectra were recorded using a NEXUS670 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. MS (EI) analysis was performed on Agilent GC-MS instrument. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with ESI or APCI source. All ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz).

2 General procedure for the synthesis of starting matericals

Acetonitrile is commercially available. Aryl fluoroalkyl sulfoxides **1a**[1],**1b**[2], **1c**[3], **1f**[1], **1g**[4], **1i**[5],**1k**[6], **1l**[7], **1w**[8] and **1x**[9] are known compounds.

References:

[1] A. Sperga, R. Melngaile, A. Kazia, S. Belyakov and J. Veliks, *J. Org. Chem.,* 2021, **86**, 3196.

[2] Y. Nakayama, G. Ando, M. Abe, T. Koike and M. Akita, *ACS Catal*, 2019, **9**, 6555.

[3] R. P. Singh, G. Cao, R. L. Kirchmeier and J. M. *J. Org. Chem.*, 1999, **64**, 2873.

[4] W. Lu, W. Li, Y. Zhou, Y. Xie and W.-B. Chen, *Chinese Chemical Letters*, 2022, **33**, 4865.

[5] C. Batisse, A. Panossian, G. Hanquet, F. R. Leroux, *Chem. Commun.*, 2018, **54**, 10423.

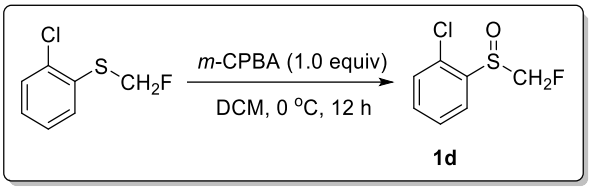
[6] C. Batisse, M. F. Cespedes Davila, M. Castello, A. Messara, B. Vivet, G. Marciniak, A. Panossian, G. Hanquet and F. R Leroux, *Tetrahedron,* 2019, **75**, 3063.

[7] A. Messara, A. Panossian, K. Mikami, G. Hanquet and F. R. Leroux, *Angew. Chem. Int. Ed.,* 2023, **62**, e202215899.

[8] M. Hu, J.-N. He, Y. Liu, T. Dong, M. Chen, C. Yan, Y. Ye and B. Peng, *Eur. J. Org. Chem.,* 2020, 193.

[9] G. K. S. Prakash, J. Hu, T. Mathew, G. A. Olah, *Angew. Chem., Int. Ed.,* 2003, **42**, 5216

(2-chlorophenyl)(fluoromethyl)sulfane (1d)



To a solution of aryl sulfide (5 mmol) in DCM (0.3 M) was added a solution of *m*-CPBA (1.0 equiv) in DCM (0.3 M) dropwise at 0 °C. Progress of the oxidation was checked by TLC. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was further purified by column chromatography on silica gel to afford compound **1n** in 90% (0.87 g) as colorless oil. (Rf = 0.3 eluent: Petroleum ether /EtOAc = 5/1).

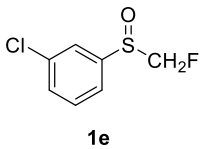
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.50 (m, 1H), 7.44 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.46 (dd, *J* = 47.5, 8.4 Hz, 1H), 5.10 (dd, *J* = 48.4, 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ136.2 (d, *J* = 8.4 Hz), 133.1, 130.6, 130.1, 128.4, 127.4, 97.5 (d, *J* = 221.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -213.9

IR (neat): 3066, 2922, 1572, 1449, 1105, 1012, 934, 875, 730, 522.

HRMS (ESI-TOF): calculated for [$C_7H_6ClFOSNa$ (M + Na^+)]: 214.9704, found: 214.9699.



1e

1-chloro-3-((fluoromethyl)sulfinyl)benzene (1e)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.7 g, 90% yield. (Rf = 0.21, eluent: PE/EtOAc =2/1)

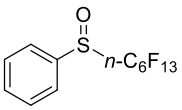
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 1.6 Hz, 1H), 7.57 – 7.47 (m, 3H), 5.10 (d, *J* = 47.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9 (d, *J* = 6.4 Hz), 136.2, 132.4, 130.9, 124.8, 122.9, 97.9 (d, *J* = 223.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -212.6

IR (neat): 3058, 2928, 1575, 1461, 1022, 994, 781, 735, 675.

HRMS (ESI-TOF): calculated for [$C_7H_6ClFOSNa$ (M + Na^+)]: 214.9704, found: 214.9699.



1j

((perfluorohexyl)sulfinyl)benzene (1j)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 3.1 g, 70% yield. (Rf = 0.49, eluent: PE/EtOAc = 5/1)

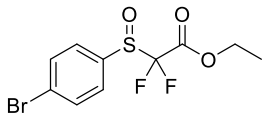
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.64 – 7.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, C-F decoupling): δ 135.2, 134.0, 131.3, 129.9, 129.6, 129.6, 129.6, 126.9, 117.3, 111.9, 110.9, 110.3.

^{19}F NMR (377 MHz, $CDCl_3$): δ -81.0, -111.4 (d, *J* = 245.3 Hz), -119.3–121.3 (m), -122.4 (d, *J* = 323.4 Hz), -122.7 (d, *J* = 245.3 Hz), -126.3.

IR (neat): 2367, 1447, 1233, 1198, 1128, 883, 747, 686, 531.

HRMS (ESI-TOF): calculated for [$C_{12}H_5OF_{13}SNa$ (M + Na^+)]: 466.9746, found: 466.9747.



1n

ethyl 2-((4-bromophenyl)sulfinyl)-2,2-difluoroacetate (1n)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.8 g, 55% yield. (Rf = 0.44, eluent: PE/EtOAc =5/1)

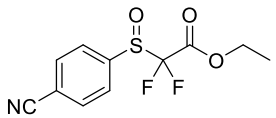
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.33 – 4.25 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ159.2 (t, *J* = 27.5 Hz), 135.2, 132.8, 128.4, 127.6, 117.8 (t, *J* = 303.8 Hz), 64.5, 13.9.

^{19}F NMR (565MHz, $CDCl_3$): δ -108.4 (d, *J* = 233.0 Hz), -111.4 (d, *J* = 237.1 Hz)

IR (neat): 3085, 2986, 1758, 1570, 1473, 1300, 1130, 1065, 819, 728

HRMS (ESI-TOF): calculated for [$C_{10}H_9BrF_2O_3SNa$ (M + Na^+)]: 348.9316, found: 348.9317.



1o

ethyl 2-((4-cyanophenyl)sulfinyl)-2,2-difluoroacetate (1o)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.7 g, 62% yield. (Rf = 0.5, eluent: PE/EtOAc =5/1)

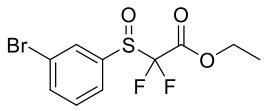
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 – 7.80 (m, 4H), 4.36 – 4.31 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9 (t, *J* = 27.2 Hz), 141.7, 133.0, 126.9, 118.0 (t, *J* = 304.1 Hz), 117.4, 117.0, 64.8, 14.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -106.7 (d, *J* = 248.3.0 Hz), -110.6 (d, *J* = 237.6 Hz)

IR (neat): 2916, 2234, 1759, 1301, 1132, 1090, 904, 724, 648, 551.

HRMS (ESI-TOF): calculated for [$C_{11}H_9F_2NO_3SNa$ (M + Na^+)]: 296.0163, found: 296.0166



1p

ethyl 2-((3-bromophenyl)sulfinyl)-2,2-difluoroacetate (1p)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 2.3 g, 70% yield. (Rf = 0.26, eluent: PE/EtOAc = 10/1)

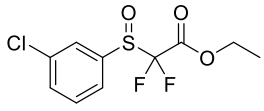
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.75 – 7.73 (m, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 4.31 – 4.27 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.1(t, *J* = 28.1 Hz), 138.3, 136.4, 130.9, 128.8, 124.7, 123.7, 118.1(t, *J* = 303.2 Hz), 64.5, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -108.3 (d, *J* = 221.6 Hz), -110.6 (d, *J* = 231.2 Hz)

IR (neat): 2990, 2252, 1758, 1460, 1296, 1095, 904, 784, 725, 676, 545.

HRMS (ESI-TOF): calculated for [$C_{10}H_9BrF_2O_3SNa$ (M + Na^+)]: 348.9316, found: 348.9317.



1q

ethyl 2-((3-chlorophenyl)sulfinyl)-2,2-difluoroacetate (1q)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.8 g, 65% yield. (Rf = 0.21 eluent: PE/EtOAc = 10/1)

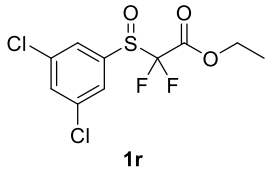
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.61 – 7.56 (m, 2H), 7.53 – 7.50 (m, 1H), 4.32 – 4.25 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1(t, *J* = 28.5 Hz), 138.2, 135.9, 133.5, 130.7, 126.0, 124.3, 118.0 (t, *J* = 302.6 Hz), 64.5, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -108.3 (d, *J* = 228.2 Hz), -110.7 (d, *J* = 231.9 Hz)

IR (neat): 3063, 2986, 1760, 1463, 1300, 1131, 1011, 963, 786, 678.

HRMS (ESI-TOF): calculated for [$C_{10}H_9ClF_2O_3SNa$ (M + Na^+)]: 304.9821, found: 304.9824.



1r

ethyl 2-((3,5-dichlorophenyl)sulfinyl)-2,2-difluoroacetate (1r)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.5 g, 48% yield. (Rf = 0.33, eluent: PE/EtOAc = 10/1)

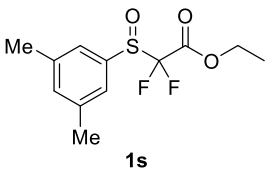
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 – 7.56 (m, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.9 (t, *J* = 27.8 Hz), 139.8, 136.6, 133.3, 124.3, 118.0 (t, *J* = 302.8 Hz), 64.7, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -107.4 (d, *J* = 230.0 Hz), -110.3 (d, *J* = 231.6 Hz).

IR (neat): 3069, 2988, 1761, 1567, 1304, 1139, 1107, 962, 801, 667, 554.

HRMS (ESI-TOF): calculated for [$C_{10}H_8Cl_2F_2O_3SNa$ (M + Na^+)]: 338.9431, found: 338.9438.



1s

ethyl 2-((3,5-dimethylphenyl)sulfinyl)-2,2-difluoroacetate (1s)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.7 g, 62% yield. (Rf = 0.24, eluent: PE/EtOAc = 10/1)

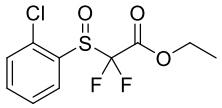
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 2H), 7.22 (d, *J* = 0.6 Hz, 1H), 4.28 – 4.22 (m, 2H), 2.38 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5 (t, *J* = 28.4 Hz), 139.5, 135.8, 135.1, 123.5, 118.1(t, *J* = 303.1 Hz), 64.1, 21.3, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -109.4 (d, *J* = 222.7 Hz), -111.3 (d, *J* = 228.7 Hz).

IR (neat): 2985, 1759, 1607, 1447, 1303, 1128, 1081, 963, 853, 683, 560.

HRMS (ESI-TOF): calculated for [$C_{12}H_{14}F_2O_3SNa$ (M + Na^+)]: 299.0524, found: 299.0524.



1t

ethyl 2-((2-chlorophenyl)sulfinyl)-2,2-difluoroacetate (1t)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 2.0 g, 70% yield. (Rf = 0.44, eluent: PE/EtOAc = 5/1)

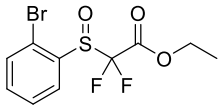
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 – 7.90 (m, 1H), 7.57 – 7.51 (m, 2H), 7.47 – 7.43 (m, 1H), 4.37 – 4.26 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ159.3 (t, *J* = 28.3 Hz), 135.2, 134.3, 133.3, 130.2, 128.2, 127.9, 119.0 (t, *J* = 302.4 Hz), 64.5, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -106.5 (d, *J* = 219.3 Hz), -108.9 (d, *J* = 219.3 Hz)

IR (neat): 2987, 1759, 1452, 1303, 1132, 1084, 957, 760, 698, 459.

HRMS (ESI-TOF): calculated for [$C_{10}H_9ClF_2O_3SNa$ (M + Na^+)]: 304.9821, found: 304.9824.



1u

ethyl 2-((2-bromophenyl)sulfinyl)-2,2-difluoroacetate (1u)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 2.2 g, 68% yield. (Rf = 0.27, eluent: PE/EtOAc = 10/1)

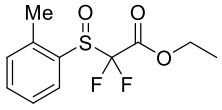
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.50 – 7.47 (m, 1H), 4.40 – 4.27 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.4 (t, *J* = 29.2 Hz), 137.2, 134.5, 133.5, 128.8, 128.5, 121.8, 119.2 (t, *J* = 303.8 Hz), 64.5, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -105.5 (d, *J* = 218.1 Hz), -108.3 (d, *J* = 218.3 Hz).

IR (neat): 2988, 1762, 1568, 1449, 1304, 1134, 1017, 955, 760, 537, 452.

HRMS (ESI-TOF): calculated for [$C_{10}H_9BrF_2O_3SNa$ (M + Na^+)]: 348.9316, found: 348.9317.



1v

ethyl 2,2-difluoro-2-(*o*-tolylsulfinyl)acetate (1v)

Following a procedure similar to the synthesis of **1d**, the title compound was prepared from 10 mmol of corresponding aryl sulfide and obtained as colorless oil, 1.8g, 70% yield. (Rf = 0.35, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.47 – 7.42 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 4.30 – 4.21 (m, 2H), 2.46 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

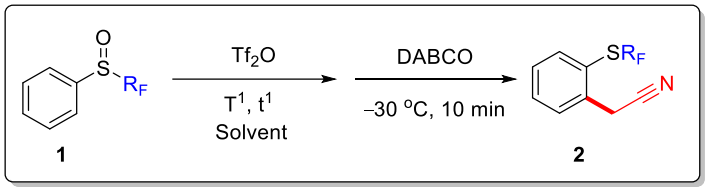
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6 (t, *J* = 27.6 Hz), 138.4, 134.9, 133.0, 131.3, 127.1, 126.2, 119.0 (t, *J* = 303.6 Hz), 64.3, 18.6, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -106.2 (d, *J* = 226.1 Hz), -110.7 (d, *J* = 230.9 Hz)

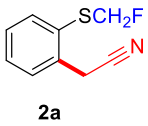
IR (neat): 2987, 1759, 1473, 1300, 1130, 1011, 962, 759, 562, 457.

HRMS (ESI-TOF): calculated for [$C_{11}H_{12}F_2O_3SNa$ (M + Na^+)]: 285.0367, found: 285.0371.

3 General procedure for the synthesis of *ortho*-cyanomethylated fluoroalkylthio arenes 2



To a mixture of aryl fluoroalkyl sulfoxides (**1**, 0.5 mmol) in solvent (3 mL) was added Tf_2O (126 μL, 0.75 mmol) at T^1(–30 to 50 °C). After stirring for t^1(10 min to 5 h), DABCO (112 mg, 1.0 mmol) was added to the mixture under the same temperature. The mixture was then stirred for another 10 min. After that, the mixture was passed through a short silica gel colum and concentrated under vacuum. The resulting residue was further purified by silica gel column chromatography to give compounds **2**.



2a

2-(2-((fluoromethyl)thio)phenyl)acetonitrile (2a)

Following the general procedure, using acetonitrile as solvent, T^1 (–30 °C), t^1 (10 min), the title compound was obtained as colorless oil, 63 mg, 70% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1)

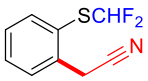
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.43 – 7.35 (m, 2H), 5.66 (d, *J* = 52.3 Hz, 2H), 3.96 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.1(d, *J* = 1.5 Hz), 133.0 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 2.2 Hz), 129.7, 129.6, 129.4, 117.7, 89.0 (d, *J* = 220.2 Hz), 22.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -182.5 (t, *J* = 52.3 Hz).

IR (neat): 2923, 2252, 1721, 1473, 1321, 962, 905, 728, 752, 649.

HRMS (ESI-TOF): calculated for [C_9H_8FNSNa (M + Na^+)]: 204.0254, found: 204.0255.



2b

2-(2-((difluoromethyl)thio)phenyl)acetonitrile (2b)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 76 mg, 76% yield. (Rf = 0.3, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.41 – 7.39 (m, 1H), 6.81 (t, *J* = 56.3 Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.7, 135.9, 131.6, 129.8, 129.4, 124.6, 120.2 (t, *J* = 276.8 Hz), 117.6, 23.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -91.4 (d, *J* = 57.2 Hz).

IR (neat): 2920, 2249, 1474, 1316, 1068, 1032, 904, 794, 748, 439.

HRMS (ESI-TOF): calculated for [$C_9H_7F_2NSNa$ (M + Na^+)]: 222.0159, found: 222.0157.

2c

2-(2-((trifluoromethyl)thio)phenyl)acetonitrile (2c)

Following the general procedure, using acetonitrile as solvent, T[1] (50 °C), t[1](5 h), the title compound was obtained as colorless oil, 87 mg, 80% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

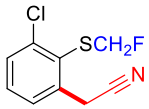
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.45 – 7.42 (m, 1H), 4.07 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 139.4, 136.2, 132.7, 130.0, 129.7, 129.3 (q, *J* = 310.0 Hz), 123.4, 117.3, 23.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -42.3.

IR (neat): 2917, 2360, 2253, 1475, 1130, 1103, 905, 760, 729, 649, 462.

HRMS (ESI-TOF): calculated for [$C_9H_6F_3NSNa$ (M + Na^+)]: 240.0065, found: 240.0066.



2d

2-(3-chloro-2-((fluoromethyl)thio)phenyl)acetonitrile (2d)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 70 mg, 65% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

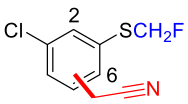
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.52 (m, 2H), 7.40 (dd, *J* = 10.0, 5.8 Hz, 1H), 5.62 (d, *J* = 52.0 Hz, 2H), 4.15 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.9 (d, *J* = 2.3 Hz), 138.3, 131.5, 130.6, 130.1, 127.8, 117.6, 88.7 (d, *J* = 222.2 Hz), 24.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -185.1 (t, *J* = 52.3 Hz).

IR (neat): 2947,2254, 1562, 1445, 1319, 1152, 966, 905, 779, 720, 648.

HRMS (ESI-TOF): calculated for [$C_9H_7ClFNSNa$ (M + Na^+)]: 237.9864, found: 237.9868.



2e

C2/C6 = 25/75

2-(4-chloro-2-((fluoromethyl)thio)phenyl)acetonitrile (2e)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 86 mg, 80% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

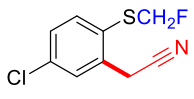
^{1}H NMR (400 MHz, $CDCl_3$) (Reio-isomers of **2e** (C2/C6 = 25/75) were obtained): δ 7.64 (d, *J* = 2.2 Hz, 0.75H, C6), 7.61 (dd, *J* = 7.8, 1.2 Hz, 0.25H, C2), 7.47 – 7.45 (m, 1H), 7.37 (dd, *J* = 8.3, 2.2 Hz, 0.75H, C6), 7.32 (t, *J* = 8.0 Hz, 0.25H, C2), 5.69 (d, *J* = 51.7 Hz, 0.5H), 5.68 (d, *J* = 52.5 Hz, 1.5H), 4.13 (s, 0.5H, C2), 3.90 (s, 1.5H, C6).

^{13}C NMR (101 MHz, $CDCl_3$): δ 136.0 (d, *J* = 2.9 Hz), 135.6, 135.1, 134.7 (d, *J* = 2.7 Hz), 133.0 (d, *J* = 1.6 Hz), 132.5 (d, *J* = 1.6 Hz), 130.8 (d, *J* = 2.2 Hz) , 130.6, 130.4, 130.3 (d, *J* = 2.9 Hz), 129.6, 117.1, 116.3, 88.6 (d, *J* = 219.1 Hz), 88.3 (d, *J* = 219.1 Hz), 22.4, 20.7.

^{19}F NMR (377 MHz, $CDCl_3$): δ -183.1(t, *J* = 52.6 Hz) , -183.4 (t, *J* = 51.2 Hz).

IR (neat): 2948, 2252, 1584, 1471, 1321, 1103, 964, 906, 814,.725.

HRMS (ESI-TOF): calculated for [$C_9H_7ClFNSNa$ (M + Na^+)]: 237.9864, found: 237.9868.



2f

2-(5-chloro-2-((fluoromethyl)thio)phenyl)acetonitrile (2f)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 78 mg, 73% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

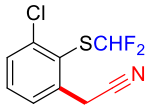
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.62 (d, *J* = 52.1 Hz, 2H), 3.94 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 135.9, 135.4 (d, *J* = 2.1 Hz), 134.5 (d, *J* = 2.3 Hz), 131.3 (d, *J* = 2.8 Hz), 129.7, 129.4, 117.0, 88.9 (d, *J* = 219.5 Hz), 22.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -182.9 (t, *J* = 52.6 Hz).

IR (neat): 2945, 2253, 1582, 1466, 1106, 904, 820, 724, 648.

HRMS (ESI-TOF): calculated for [$C_9H_7ClFNSNa$ (M + Na^+)]: 237.9864, found: 237.9868.



2g

2-(3-chloro-2-((difluoromethyl)thio)phenyl)acetonitrile (2g)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 40 mg, 34% yield. (Rf = 0.27, eluent: PE/EtOAc = 10/1)

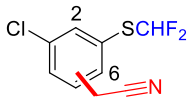
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.45 (m, 1H), 6.85 (t, *J* = 57.1 Hz, 1H), 4.12 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 139.1, 132.5, 130.6, 128.2, 124.3 (d, *J* = 2.8 Hz), 120.0 (t, *J* = 277.9 Hz), 117.2, 24.4.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.7

IR (neat): 2924, 2252, 1562, 1447, 1297, 1153, 1036, 905, 782, 759.

HRMS (ESI-TOF): calculated for [$C_9H_6ClF_2NSNa$ (M + Na^+)]: 255.9770, found: 255.9767.



2h

C2/C6 = 25/75

2-(4-chloro-2-((difluoromethyl)thio)phenyl)acetonitrile (2h)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 90 mg, 77% yield. (Rf = 0.28, eluent: PE/EtOAc = 10/1)

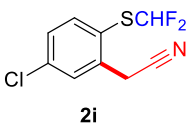
^{1}H NMR (400 MHz, $CDCl_3$) (Reio-isomers of **2h** (C2/C6 = 25/75) were obtained): δ 7.70 (d, *J* = 2.2 Hz, 0.75H, C6), 7.66 (dd, *J* = 7.8, 1.1 Hz, 0.25H, C2), 7.59 – 7.54 (m, 1H), 7.51 – 7.48 (m, 0.75H, C6), 7.36 (t, *J* = 8.0 Hz, 0.25H, C2), 6.85 (t, *J* = 54.9 Hz, 0.25H, C2), 6.85 (t, *J* = 55.4 Hz, 0.75H, C6), 4.19 (s, 0.5H, C2), 3.99 (s, 1.5H, C6).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.0, 137.3, 136.1, 134.9, 134.3, 132.6, 131.7, 130.8, 130.2, 127.5 (d, *J* = 3.1 Hz), 126.1(d, *J* = 3.1 Hz), 122.5, 119.7 (t, *J* = 277.4 Hz), 117.2, 116.1, 22.8, 21.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.2, -91.5.

IR (neat): 2968, 2257, 1585, 1473, 1412, 1315, 1035, 911, 819, 753.

HRMS (ESI-TOF): calculated for [$C_9H_6ClF_2NSNa$ (M + Na^+)]: 255.9770, found: 255.9767.



2i

2-(5-chloro-2-((difluoromethyl)thio)phenyl)acetonitrile (2i)

Following the procedure of **2a**, the title compound was obtained as colorless oil, 82 mg, 70% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

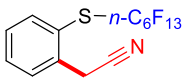
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.62 (m, 2H), 7.39 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.79 (t, *J* = 56.0 Hz, 1H), 4.01 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 138.2, 137.7, 130.0, 129.7, 122.7 (d, *J* = 3.3 Hz), 119.7 (t, *J* = 279.7 Hz), 116.7, 23.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.5.

IR (neat): 2926, 2256, 1581, 1466, 1314, 1187, 1065, 1027, 824, 754.

HRMS (ESI-TOF): calculated for [$C_9H_6ClF_2NSNa$ (M + Na^+)]: 255.9770, found: 255.9767.



2j

2-(2-((perfluorohexyl)thio)phenyl)acetonitrile (2j)

Following the procedure of **2c**, the title compound was obtained as colorless oil, 210 mg, 90% yield. (Rf = 0.5, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.45 – 7.43 (m, 1H), 4.06 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, C-F decoupling): δ 140.2, 137.0, 132.9, 130.1, 129.6, 123.4, 121.8, 117.3, 117.2, 111.1, 111.0, 110.4, 108.6, 23.1.

^{19}F NMR (377 MHz, $CDCl_3$, F-F decoupling): δ -80.8, -86.1, -119.3, -121.4, -122.8, -126.1.

IR (neat): 2917, 2257, 1475, 1234, 1195, 1144, 909, 735, 707, 636, 447.

HRMS (ESI-TOF): calculated for [$C_{14}H_6F_{13}NSNa$ (M + Na^+)]: 489.9906, found: 489.9912.

2k

ethyl 2-((2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2k):

Following the general procedure, using DCM/MeCN (volume ratio: 2:1) as solvent, T[1] (–30 °C), t[1](1 h). the title compound was obtained as colorless oil, 117 mg, 86% yield. (Rf = 0.25, eluent: PE/EtOAc = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.66 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.42 – 7.38 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3 (t, *J* = 31.3 Hz), 161.0, 139.5, 136.6, 132.3, 129.8, 129.3, 120.3 (t, *J* = 288.6 Hz), 117.5, 64.1, 23.1, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.8.

IR (neat): 2985, 2253, 1760, 1473, 1443, 1292, 1098,1056, 972, 757.

HRMS (ESI-TOF): calculated for [$C_{12}H_{11}F_2O_2NSNa$ (M + Na^+)]:294.0371, found: 294.0373.

ethyl 2-((2-(cyanomethyl)-4-methylphenyl)thio)-2,2-difluoroacetate (2l)

2l

Following the procedure of **2k**, the title compound was obtained as colorless oil, 107 mg, 75% yield. (Rf = 0.25, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.46 (s, 1H), 7.22 – 7.17 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 2.42 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.4 (t, *J* = 31.8 Hz), 143.2, 139.4, 136.3, 130.5, 130.1, 123.1, 120.3 (t, *J* = 287.3 Hz), 117.7, 64.1, 23.0, 21.5, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -81.2.

IR (neat): 2985, 2250,1760, 1479,1446,1291,1100, 972, 820, 723.

HRMS (ESI-TOF): calculated for [$C_{13}H_{13}F_2O_2NSNa$ (M + Na^+)]: 308.0527, found: 308.0528.

2m

ethyl 2-((4-chloro-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2m)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 110 mg, 72% yield. (Rf = 0.27, eluent: PE/EtOAc = 20/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 8.3, 2.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.1(t, *J* = 31.8 Hz), 140.5, 138.9, 138.2, 130.0, 129.6, 122.2, 120.0 (t, *J* = 289.4 Hz), 116.9, 64.3, 23.1, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.6.

IR (neat): 2983, 2265, 1759, 1582, 1466, 1298, 1103, 970, 823, 717.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}ClF_2O_2NSNa$ (M + Na^+)]: 327.9981, found: 327.9984.

2n

ethyl 2-((4-bromo-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2n)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 122 mg, 70% yield. (Rf = 0.26, eluent: PE/EtOAc = 20/1).

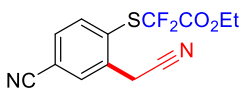
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.55 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.03 (s, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ161.1(t, *J* = 31.2 Hz), 140.6, 138.3, 132.9, 132.6, 127.1, 122.8, 119.9 (t, *J* = 287.5 Hz), 116.9, 64.4, 23.0, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -80.6.

IR (neat): 2988, 2261, 1759, 1465, 1295, 1091, 1007, 971, 821, 715.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}BrF_2O_2NSNa$ (M + Na^+)]: 371.9476, found: 371.9474.



2o

ethyl 2-((4-cyano-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2o)

Following the procedure of **2k**, the title compound was obtained as light yellow oil, 44 mg, 30% yield. (Rf = 0.24, eluent: PE/EtOAc = 10/1).

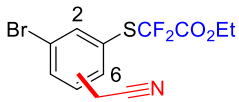
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.08 (s, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.7 (t, *J* = 31.2 Hz), 139.8, 137.9, 132.8, 132.4, 130.0, 119.9 (t, *J* = 291.4 Hz), 117.1, 116.3, 116.2, 64.6, 23.2, 14.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -79.4.

IR (neat): 2923, 2235, 2210, 1762, 1474, 1301, 1131, 1095, 973, 837, 723.

HRMS (ESI-TOF): calculated for [$C_{13}H_{10}F_2N_2O_2NSNa$ (M + Na^+)]: 319.0323, found: 319.0330.



2p

C2/C6 = 7/93

ethyl 2-((5-bromo-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2p)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 108 mg, 62% yield. (Rf = 0.26, eluent: PE/EtOAc = 10/1).

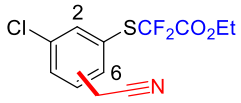
^{1}H NMR (600 MHz, $CDCl_3$) (Reio-isomers of **2p** (C2/C6 = 7/93) were obtained): δ 7.86 (d, *J* = 2.0 Hz, 0.93H, C6), 7.79 – 7.77 (m, 0.07H, C2), 7.73 – 7.66 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 0.93H, C6), 7.29 (t, *J* = 7.9 Hz, 0.07H, C2), 4.36 – 4.29 (m, 2H), 4.24 (s, 0.14H, C2), 4.01 (s, 1.86H, C6), 1.34 – 1.31 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ161.0 (t, *J* = 31.0 Hz), 141.7, 136.7, 135.5, 135.3, 131.0, 130.4, 125.8, 122.6, 120.1 (t, *J* = 288.9 Hz), 117.0, 115.6, 64.4, 53.6, 22.8, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -80.4, -80.5.

IR (neat): 2985, 2385, 2257, 1760, 1470, 1293, 1099, 972, 815, 784, 717.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}BrF_2O_2NSNa$ (M + Na^+)]: 371.9476, found: 371.9474.



2q

C2/C6 = 12:88

ethyl 2-((5-chloro-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2q)

Following the procedure of **2k**, the title compound was obtained as light yellow oil, 124 mg, 81% yield. (Rf = 0.22, eluent: PE/EtOAc = 10/1).

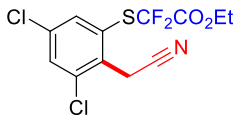
^{1}H NMR (600 MHz, $CDCl_3$) (Reio-isomers of **2q** (C2/C6 = 12/88) were obtained): δ 7.73 (s, 0.12H, C2), 7.71 (d, *J* = 2.1 Hz, 0.88H, C6), 7.67 (d, *J* = 7.8 Hz, 0.12H, C2), 7.60 (d, *J* = 8.3 Hz, 0.88H, C6), 7.53 (dd, *J* = 8.3, 2.1 Hz, 0.88H, C6), 7.37 (t, *J* = 8.0 Hz, 0.12H, C2), 4.34 – 4.30 (m, 2H), 4.20 (s, 0.24H, C2), 4.02 (s, 0.76H, C6), 1.34 – 1.31 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ, 161.00 (t, *J* = 31.4 Hz), 138.9, 138.1, 135.0, 134.8, 133.5, 133.2, 132.4, 130.8, 130.7, 130.1, 126.0, 125.5, 124.3, 120.1(t, *J* = 288.5 Hz), 117.1, 115.9, 64.4, 53.6, 22.7, 21.3, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -80.4, -80.5.

IR (neat): 2985, 2365, 2255, 1760, 1473, 1293, 1102, 1010, 972, 822, 718.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}ClF_2O_2NSNa$ (M + Na^+)]: 327.9981, found: 327.9984.



2r

ethyl 2-((3,5-dichloro-2-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate（2r）

Following the procedure of **2k**, the title compound was obtained as colorless oil 42 mg, 25% yield. (Rf = 0.33, eluent: PE/EtOAc = 10/1)

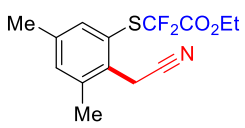
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.1 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.14 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8 (t, *J* = 31.1 Hz), 137.6, 136.7, 135.4, 133.5, 133.0, 128.1, 119.8 (t, *J* = 294.0 Hz), 115.5, 64.6, 21.0, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -80.0.

IR (neat): 3067, 2984, 2339, 1759, 1566, 1137, 1009, 854, 799, 666.

HRMS (ESI-TOF): calculated for [$C_{12}H_9Cl_2F_2NO_2Na$ (M + Na^+)]: 361.9591, found: 361.9594.



2s

ethyl 2-((2-(cyanomethyl)-3,5-dimethylphenyl)thio)-2,2-difluoroacetate (2s)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 135 mg, 90% yield. (Rf = 0.25, eluent: PE/EtOAc = 10/1)

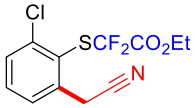
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.19 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 2H), 2.46 (s, 3H), 2.33 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4 (t, *J* = 31.7 Hz), 139.1, 138.7, 137.8, 135.0, 132.0, 124.4, 120.1 (t, *J* = 288.8 Hz), 117.0, 64.0, 20.8, 20.6, 19.8, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -81.3.

IR (neat): 2983, 2252, 1761, 1604, 1470, 1288, 1098, 975, 861, 723, 708.

HRMS (ESI-TOF): calculated for [$C_{14}H_{15}F_2NO_2SNa$ (M + Na^+)]:322.0684, found: 322.0684.



2t

ethyl 2-((2-chloro-6-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2t)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 43 mg, 28% yield. (Rf = 0.33, eluent: PE/EtOAc = 5/1)

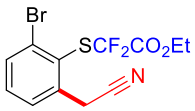
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 1H), 7.56 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.50 – 7.46 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.16 (s, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.0 (t, *J* = 31.6 Hz), 143.7, 139.8, 133.0, 130.6, 128.1, 123.7, 119.8(t, *J* = 290.9 Hz), 117.3, 64.3, 24.4, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -80.6.

IR (neat): 2924, 2360, 1761, 1574, 1452, 1165, 1134, 968, 783, 759.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}ClF_2O_2NSNa$ (M + Na^+)]: 327.9981, found: 327.9984.



2u

ethyl 2-((2-bromo-6-(cyanomethyl)phenyl)thio)-2,2-difluoroacetate (2u)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 52 mg, 30% yield. (Rf = 0.28, eluent: PE/EtOAc = 10/1)

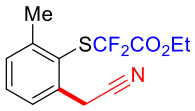
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 – 7.73 (m, 1H), 7.64 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.41 – 7.38 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.18 (s, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9 (t, *J* = 31.6 Hz), 139.8, 135.1, 134.1, 133.2, 128.8, 125.7, 119.8 (t, *J* = 291.6 Hz), 117.3, 64.4, 24.9, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.4

IR (neat): 2923, 2358, 2262, 1761, 1444, 1299, 1129, 970, 780, 725.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}BrF_2O_2NSNa$ ($M + Na^+$)]: 371.9476, found: 371.9474.



2v

ethyl 2-((2-(cyanomethyl)-6-methylphenyl)thio)-2,2-difluoroacetate (2v)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 47 mg, 33% yield. (Rf = 0.37, eluent: PE/EtOAc = 10/1)

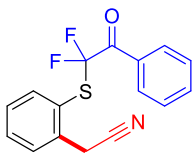
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.11 (s, 2H), 2.57 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3 (t, *J* = 31.2 Hz), 147.1, 137.7, 131.8, 131.1, 127.3, 123.4, 120.8 (t, *J* = 289.0 Hz), 117.9, 64.1, 23.9, 22.4, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -79.7.

IR (neat): 2929, 2247, 1760, 1462, 1297, 1091, 968, 854, 769, 711.

HRMS (ESI-TOF): calculated for [$C_{13}H_{13}F_2O_2NSNa$ ($M + Na^+$)]:308.0527, found: 308.0528.



2w

2-(2-((1,1-difluoro-2-oxo-2-phenylethyl)thio)phenyl)acetonitrile (2w)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 88 mg, 58% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1)

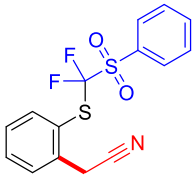
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.07 (m, 2H), 7.72 – 7.64 (m, 3H), 7.58 – 7.49 (m, 3H), 7.41 – 7.37 (m, 1H), 4.04 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 185.0 (t, *J* = 28.2 Hz), 139.6, 136.5, 135.2, 132.1, 130.8, 130.5, 129.8, 129.3 129.0, 124.5 (t, *J* = 292.3 Hz) , 124.1, 117.6, 23.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -75.4.

IR (neat): 2982, 2250, 1700, 1596, 1449, 1241, 1073, 987, 823, 757.

HRMS (ESI-TOF): calculated for [$C_{16}H_{11}F_2NOSNa$ ($M + Na^+$)]:326.0422, found: 326.0422.



2x

2-(2-((difluoro(phenylsulfonyl)methyl)thio)phenyl)acetonitrile (2x)

Following the general procedure, using DCM/MeCN (volume ratio: 2:1) as solvent, T[1] (room temperature), t[1](5 h). the title compound was obtained as colorless oil, 139 mg, 82% yield. (Rf = 0.2, eluent: PE/EtOAc = 5/1)

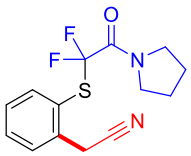
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.93 (m, 2H), 7.81 – 7.75 (m, 2H), 7.68 – 7.54 (m, 4H), 7.42 – 7.38 (m, 1H), 4.14 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 137.0, 136.0, 132.6, 132.0, 131.0, 129.9, 129.7, 129.4, 128.1 (t, *J* = 325.9 Hz), 122.8 (t, *J* = 3.2 Hz), 117.5, 23.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -78.0.

IR (neat): 3066, 2359, 2252, 1582, 1448, 1348, 1169, 903, 725, 682, 577.

HRMS (ESI-TOF): calculated for [$C_{15}H_{11}F_2NO_2S_2Na$ (M + Na^+)]:362.0091, found: 362.0094.



2y

2-(2-((1,1-difluoro-2-oxo-2-(pyrrolidin-1-yl)ethyl)thio)phenyl)acetonitrile (2y)

Following the procedure of **2k**, the title compound was obtained as colorless oil, 120 mg, 81% yield. (Rf = 0.2, eluent: PE/EtOAc = 5/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 – 7.69 (m, 1H), 7.65 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.40 – 7.37 (m, 1H), 4.09 (s, 2H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.54 (t, *J* = 7.0 Hz, 2H), 1.98 – 1.94 (m, 2H), 1.90 – 1.85 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.4 (t, *J* = 28.1 Hz), 139.7, 136.7, 131.9, 129.6, 129.0, 124.8, 124.6 (t, *J* = 290.5 Hz), 117.8, 47.9, 46.8, 26.5, 23.5, 23.1.

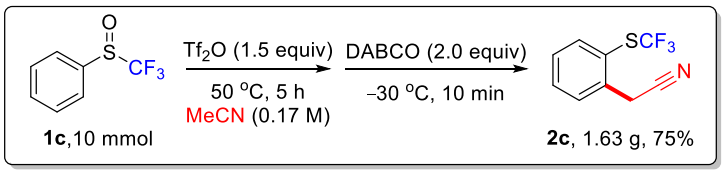
^{19}F NMR (565 MHz, $CDCl_3$): δ -76.5.

IR (neat): 2979, 2252, 1661, 1461, 1342, 1131, 904, 722, 647, 545.

HRMS (ESI-TOF): calculated for [$C_{14}H_{14}F_2N_2OSNa$ (M + Na^+)]:319.0687, found: 319.0688.

4 Gram-Scale reaction and elaboration of product 2c

Gram-Scale reaction

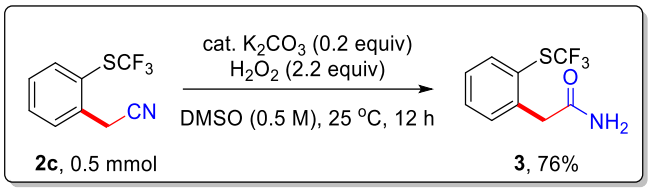


To a mixture of aryl trifluoromethyl sulfoxide (**1c**, 10.0 mmol) in acetonitrile (60 mL) was added Tf_2O(2.5 mL, 15 mmol) at 50 °C. After stirring for 5 h, DABCO (2.2 g, 20 mmol) was added to the mixture under the same temperature. The mixture was then stirred for another

10 min. After that, the mixture was passed through a short silica gel colum and concentrated under vacuum. The resulting residue was further purified by silica gel column chromatography to give compounds **2c** in 75% yield (1.63 g) as colorless oil.

Elaboration of product 2c:

2-(2-((trifluoromethyl)thio)phenyl)acetamide (3)



To a solution of **2c** (109 mg, 0.5 mmol) in DMSO (1 mL) were sequentially added H_2O_2 (30% aq., 140μL) and K_2CO_3 (14 mg, 0.1 mmol) at 25 °C. After stirring for 12 h, the mixture was diluted with H_2O, extracted with DCM and dried with Na_2SO_4. Then the mixture was filtered and concentrated under vacuum. The resulting residue was further purified by column chromatography on silica gel to afford compound **3** in 76% yield (89 mg) as white solid, m.p. 83-84 °C (Rf = 0.19, eluent: PE/EtOAc = 1/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.45 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 – 7.35 (m, 1H), 5.97 (brs, 1H), 5.50 (brs, 1H), 3.88 (s, 2H).

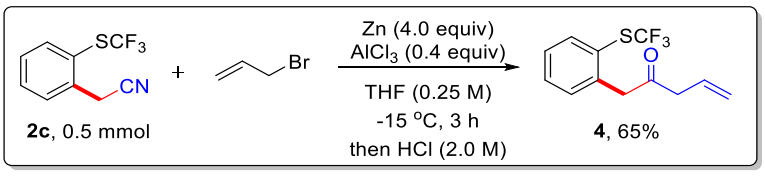
^{13}C NMR (151 MHz, $CDCl_3$): δ 172.5, 140.5, 138.7, 132.0, 131.7, 129.5 (q, *J* = 308.8 Hz), 128.8, 124.7, 41.5.

^{19}F NMR (377 MHz, $CDCl_3$): δ -42.4.

IR (neat): 3392, 3200, 2933, 1660, 1288, 1143, 1058, 935, 762, 594.

HRMS (ESI-TOF): calculated for [$C_9H_8F_3NOSNa$ ($M + Na^+$)]: 258.0171, found: 258.0173.

1-(2-((trifluoromethyl)thio)phenyl)pent-4-en-2-one (4)



To a mixture of **2c** (109 mg, 0.5 mmol), allyl bromide (91 mg, 0.75 mmol) and Zn (powder, 131 mg, 2.0 mmol) in THF (2.0 mL) was added anhydrous $AlCl_3$ (27 mg, 0.2 mmol) at –

15 °C under N_2 atmosphere. The mixture was stirred for 3 h at the same temperature. Then to the mixture was added HCl (1.0 M, 5 mL) dropwise. After stirring for another 30 min, the mixture was neutralized with $NaHCO_3$ (sat.), extracted with DCM. The organic layer was separated, dried over Na_2SO_4, and concentrated. The resulting residue was further purified by column chromatography on silica gel to afford compound **4** in 65% (85 mg) as colorless oil. (Rf = 0.58, eluent: Petroleum ether /EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.37 – 7.33 (m, 1H), 7.28 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.01 – 5.91 (m, 1H), 5.26 – 5.17 (m, 2H), 4.09 (s, 2H), 3.31 – 3.29 (m, 2H).

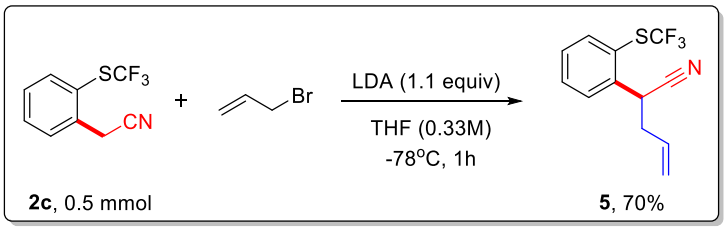
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.8, 140.1, 138.5, 131.8, 131.7, 130.2, 128.5, 129.6 (q, *J* = 309.8 Hz), 124.7, 119.5, 47.74, 47.73.

^{19}F NMR (377 MHz, $CDCl_3$): δ -42.6.

IR (neat): 3420, 2929, 2362, 1720, 1475, 1109, 1056, 923, 759, 476.

HRMS (ESI-TOF): calculated for [$C_{12}H_{11}F_3OSNa$ (M + Na^+)]: 283.0375, found: 283.0381.

2-(2-((trifluoromethyl)thio)phenyl)pent-4-enenitrile (5)



To the solution of (*i*-pr)$_2$NH (84 µL, 0.6 mmol) in THF (1.5 mL) was added *n*-BuLi (1.6 M, 0.37 mL) slowly at –78 °C. After stirring for 10 min, **2c** (109 mg, 0.5 mmol) was added dropwise to the mixture at –78 °C. After 5 min, allyl bromide (50 µL, 0.6 mmol) was added. After stirring for 1 h, the mixture was quenched with NH_4Cl (sat.), extracted with DCM. The organic layer was separated, dried over Na_2SO_4, and concentrated. The resulting residue was further purified by column chromatography on silica gel to afford compound **5** in 70% (90 mg) as colorless oil. (Rf = 0.41, eluent: Petroleum ether /EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.43 – 7.41 (m, 1H), 7.86 – 7.79 (m, 1H), 5.24 – 5.16 (m, 2H), 4.68 (dd, *J* = 8.6, 5.9 Hz, 1H), 2.66 – 2.54 (m, 2H).

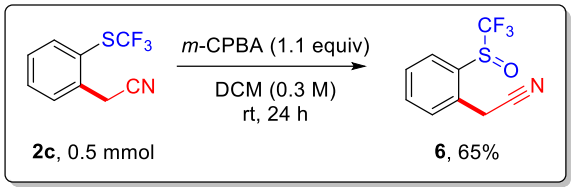
^{13}C NMR (151 MHz, $CDCl_3$): δ 141.1, 139.1, 132.6, 132.1, 129.5, 129.3, 129.1 (q, *J* = 309.9 Hz), 122.9, 120.11, 120.08, 39.6, 35.3.

^{19}F NMR (565 MHz, $CDCl_3$): δ -42.3.

IR (neat): 2923, 2852, 2243, 1644, 1472, 1106, 1055, 761, 649, 499.

HRMS (ESI-TOF): calculated for [$C_{12}H_{10}F_3NSNa$ (M + Na^+)]:280.0378, found: 280.0378.

2-(2-((trifluoromethyl)sulfinyl)phenyl)acetonitrile (6)



To a solution of **2c** (109 mg, 0.5 mmol) in DCM (0.3 M) was added *m*-CPBA (112 mg, 0.55 mmol). The resulting solution was stirred at room temperature for 24 h. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was further purified by column chromatography on silica gel to afford compound **6** in 65% (76 mg) as colorless oil. (Rf = 0.15, eluent: Petroleum ether /EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.67 – 7.61 (m, 1H), 4.05 (d, *J* = 3.3 Hz, 2H).

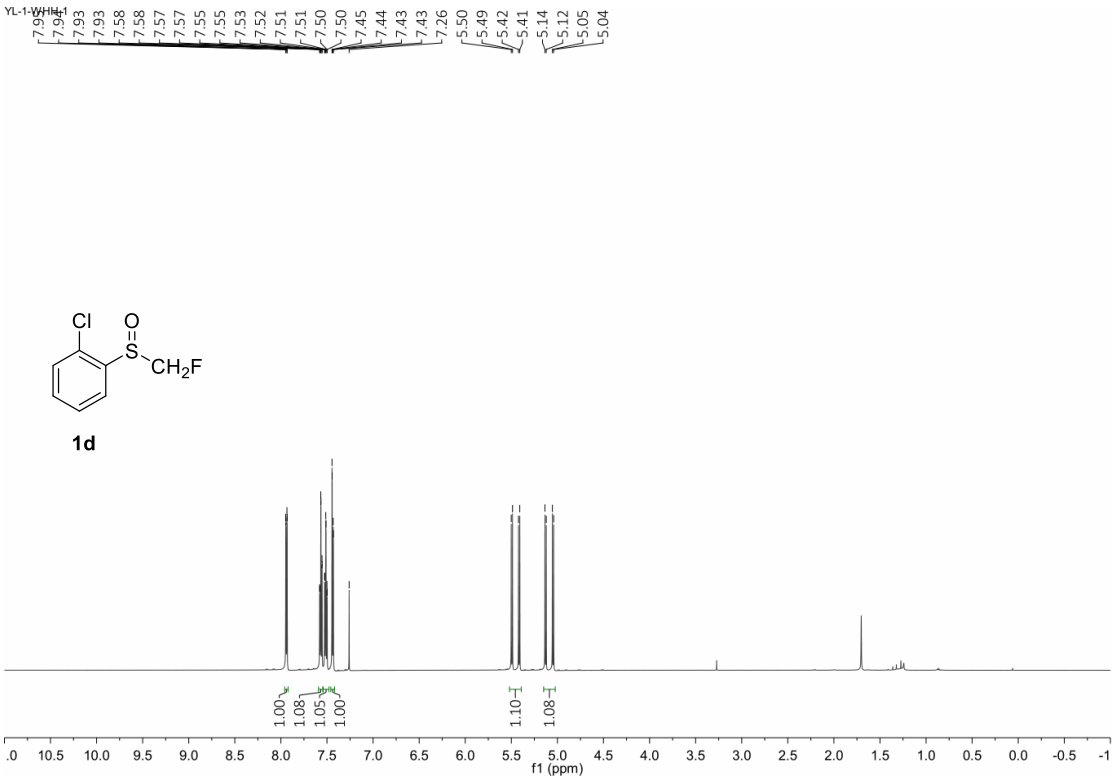
^{13}C NMR (101 MHz, $CDCl_3$): δ 134.4, 133.6, 130.8, 130.7, 129.7, 127.7, 125.1 (q, *J* = 336.5 Hz), 116.2, 20.2.

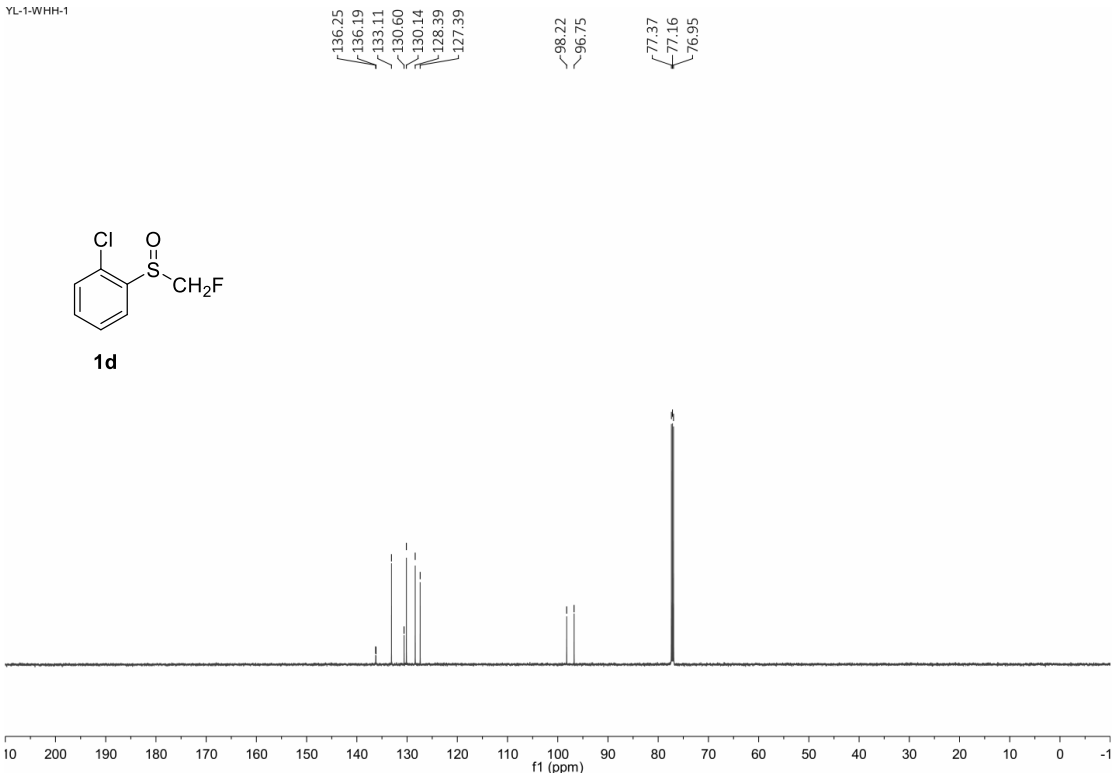
^{19}F NMR (377 MHz, $CDCl_3$): δ -72.8.

IR (neat): 2254, 1476, 1187, 1077, 905, 726, 648, 575, 458, 436.

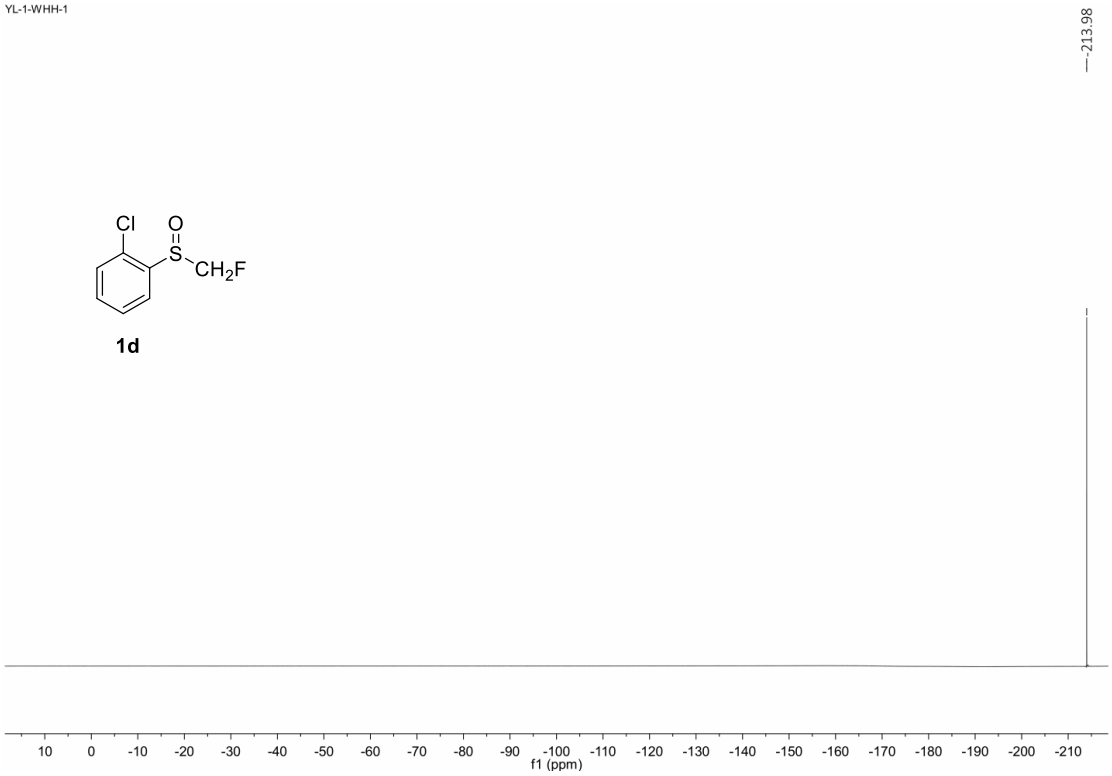
HRMS (ESI-TOF): calculated for [$C_9H_6F_3NOSNa$ (M + Na^+)]:256.0014, found: 256.0013.

5 NMR spectra



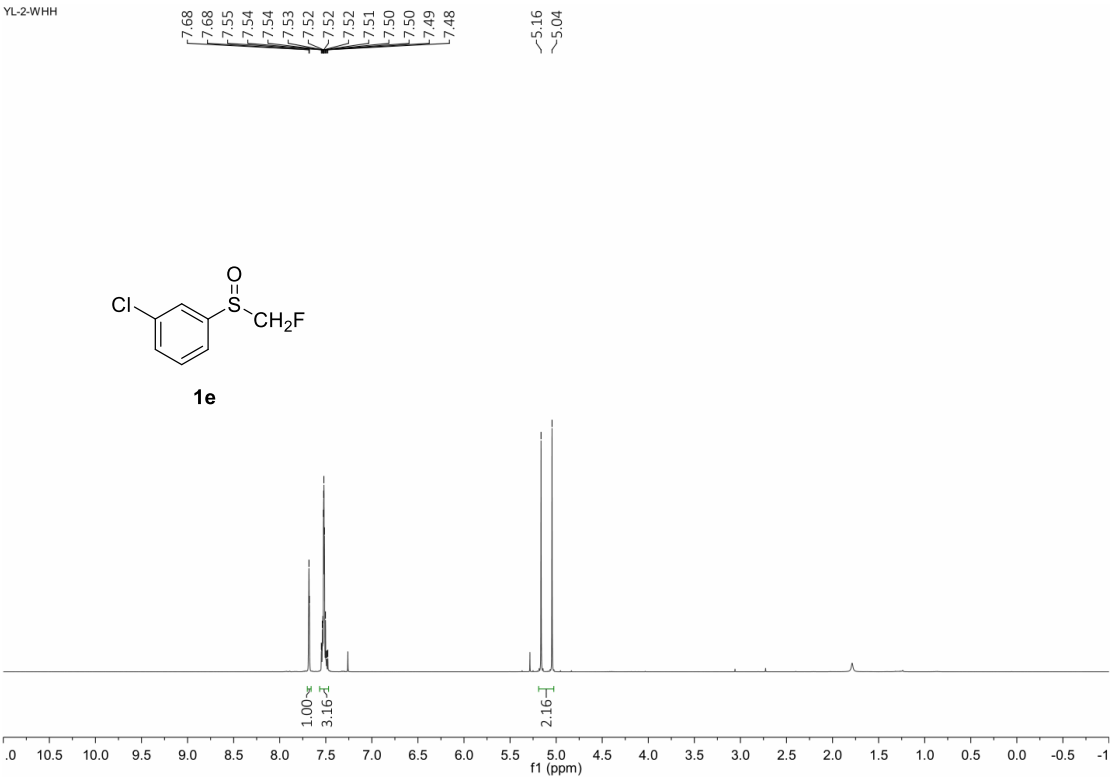


YL-1-WHH-1

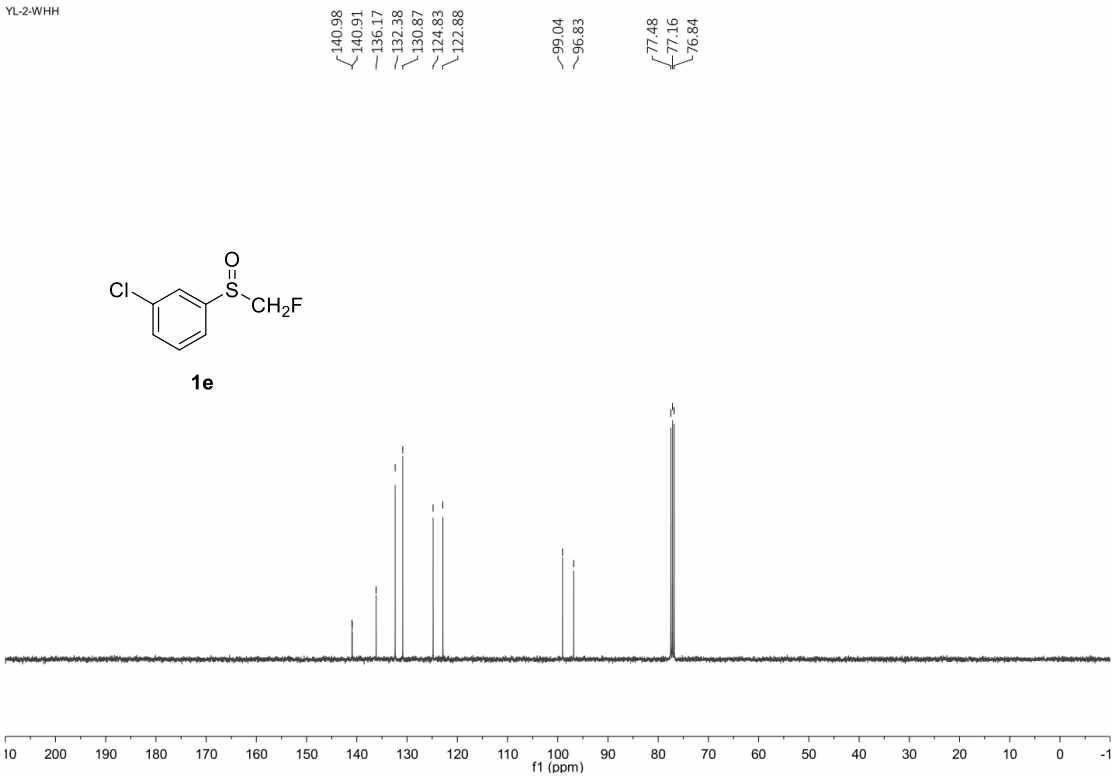


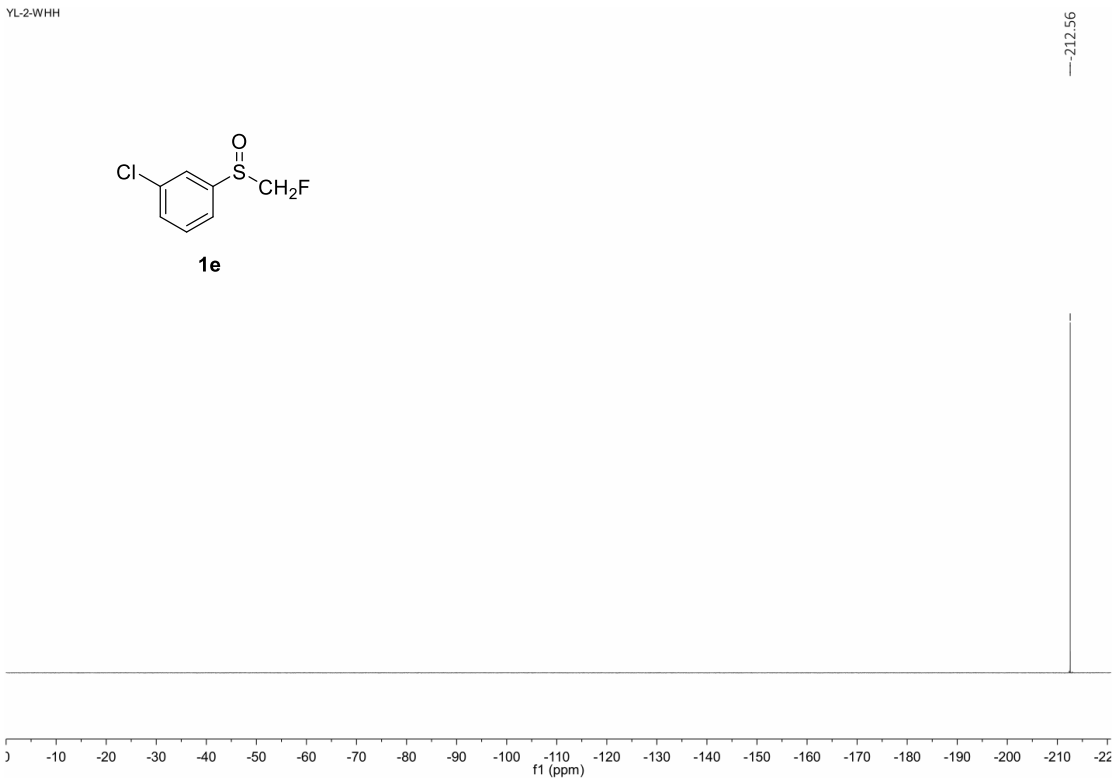
1d

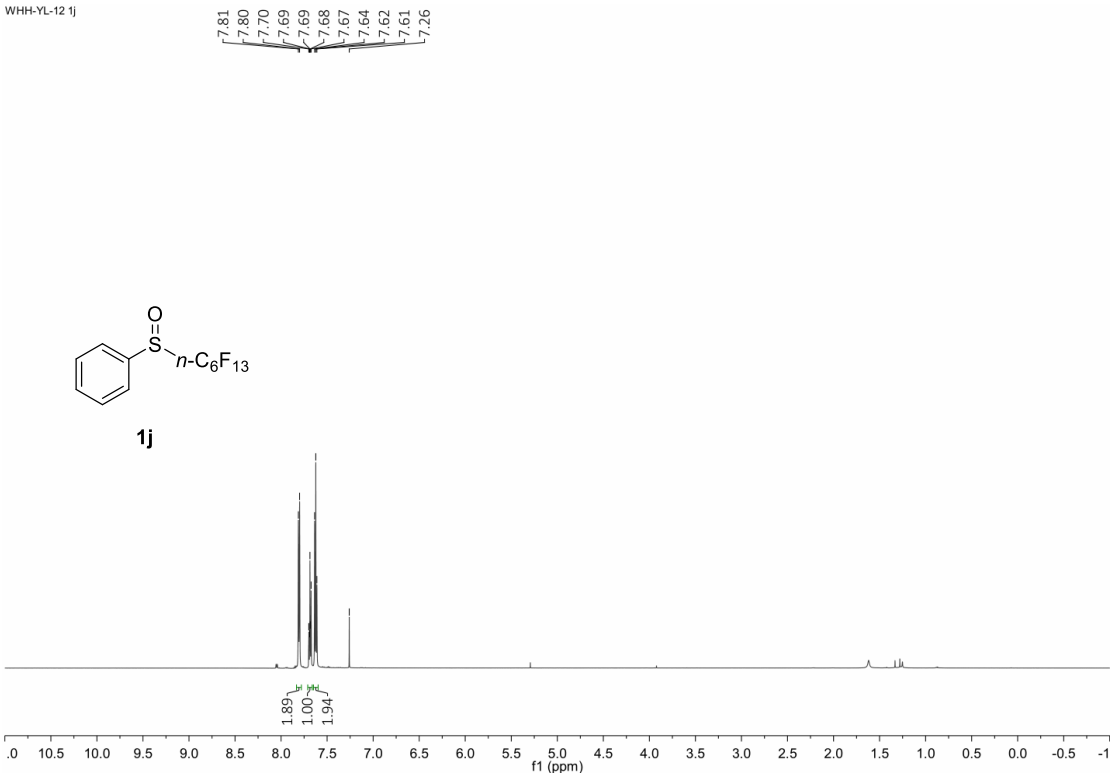
YL-2-WHH

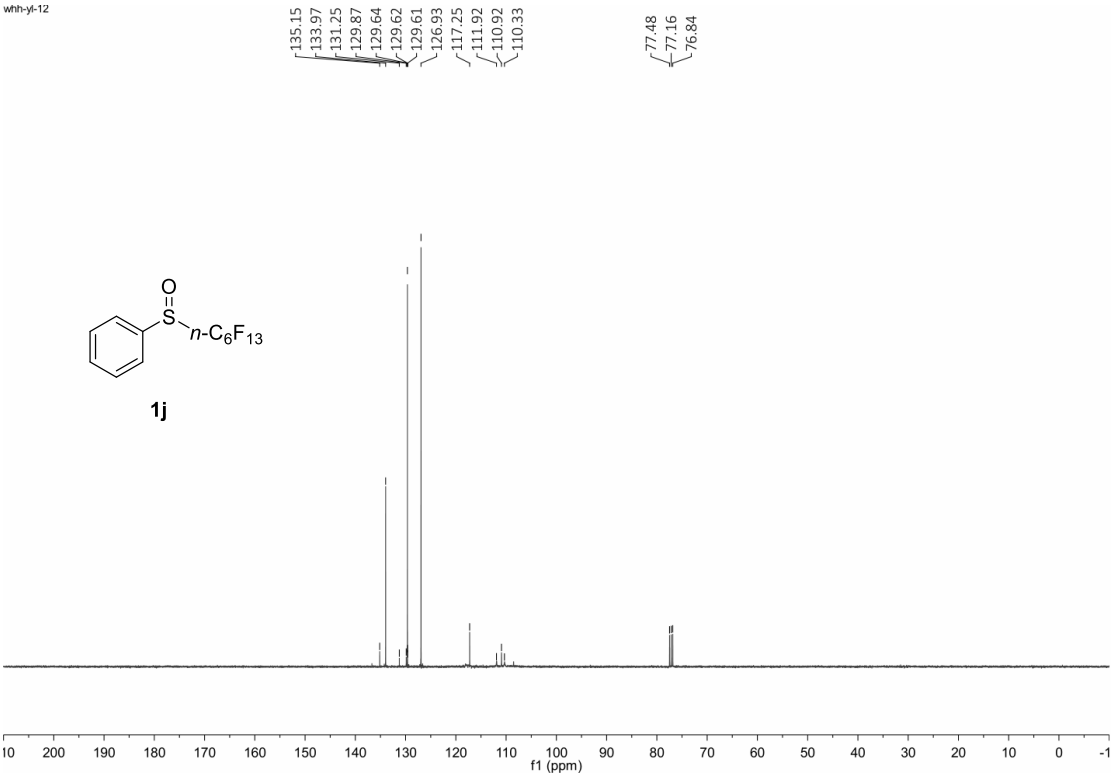


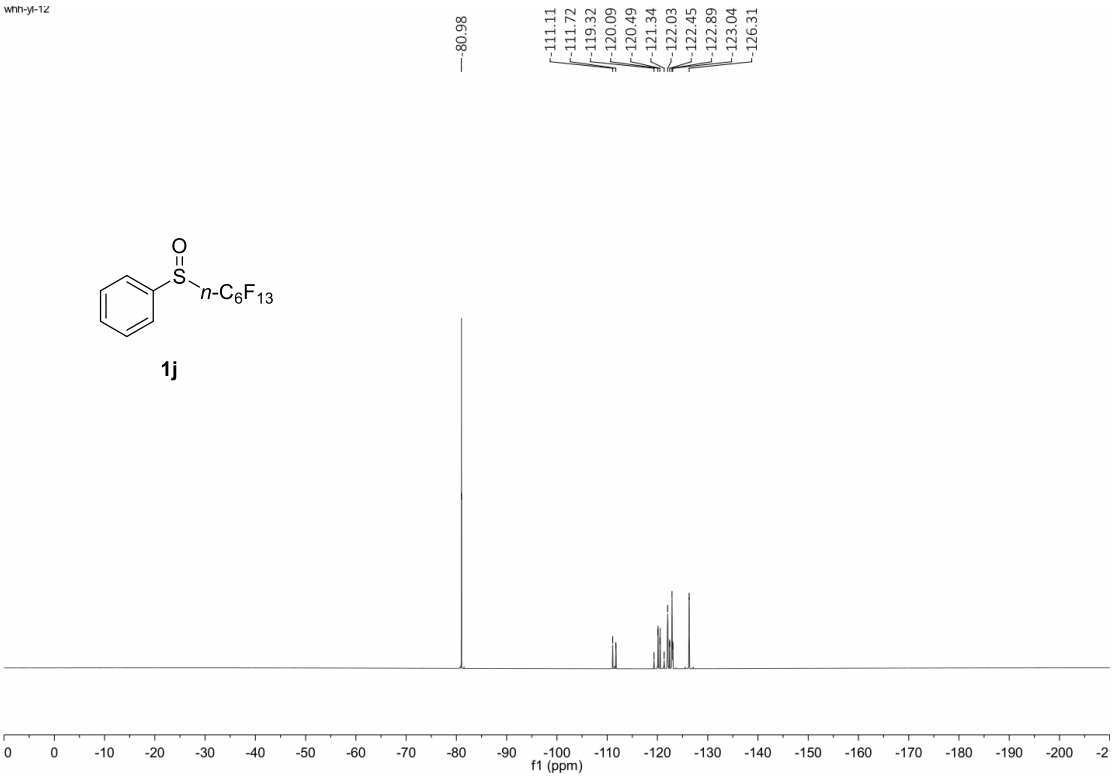
1e

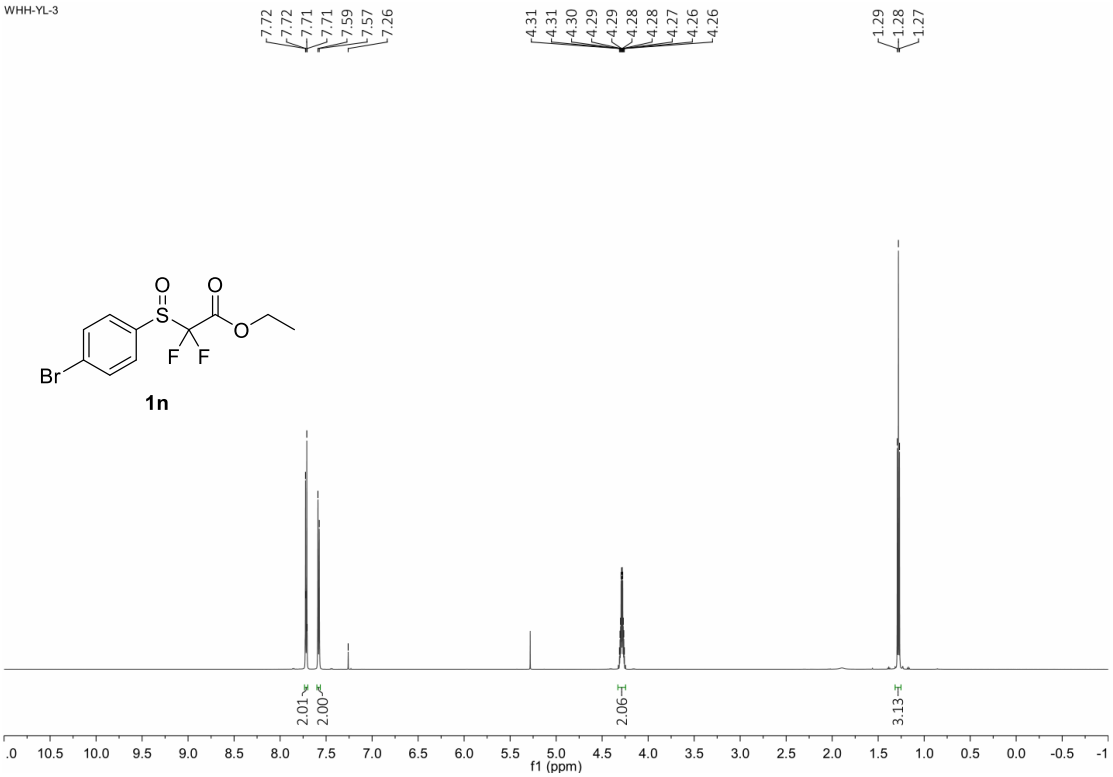

YL-2-WHH
140.98
140.91
136.17
132.38
130.87
124.83
122.88
99.04
96.83
77.48
77.16
76.84
Cl
O
S
CH2F
1e
f1 (ppm)

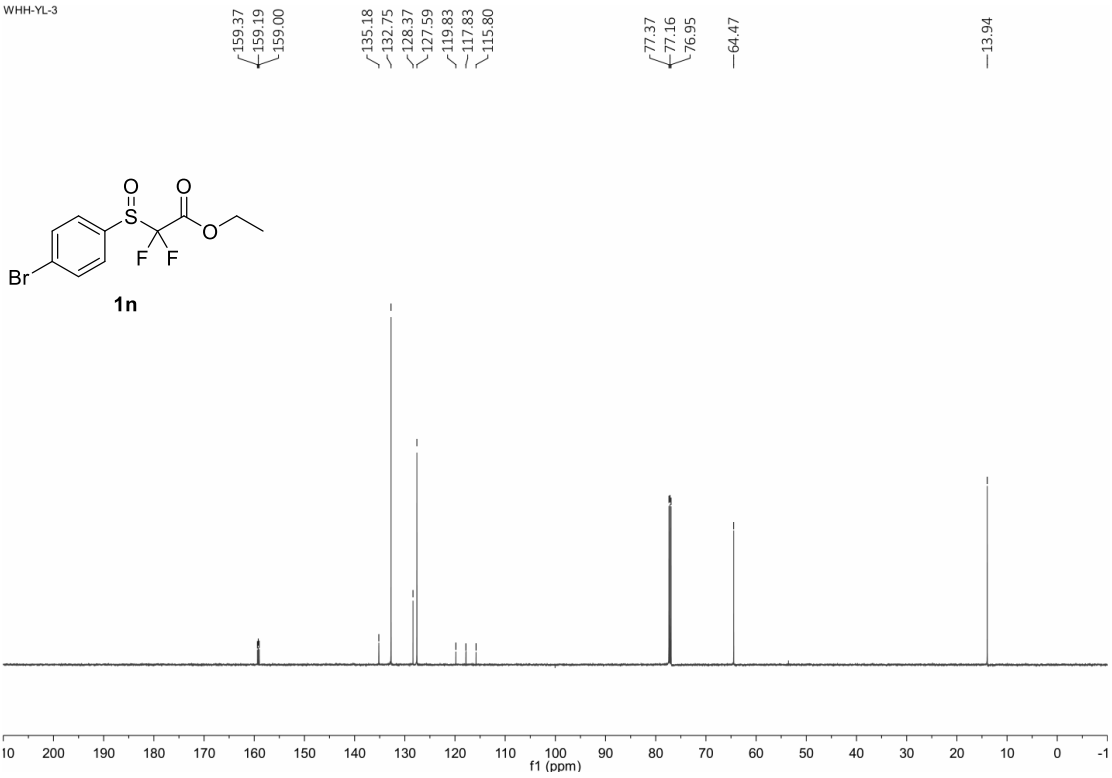

YL-2-WHH
212.56
Cl
O
S
CH2F
1e
f1 (ppm)

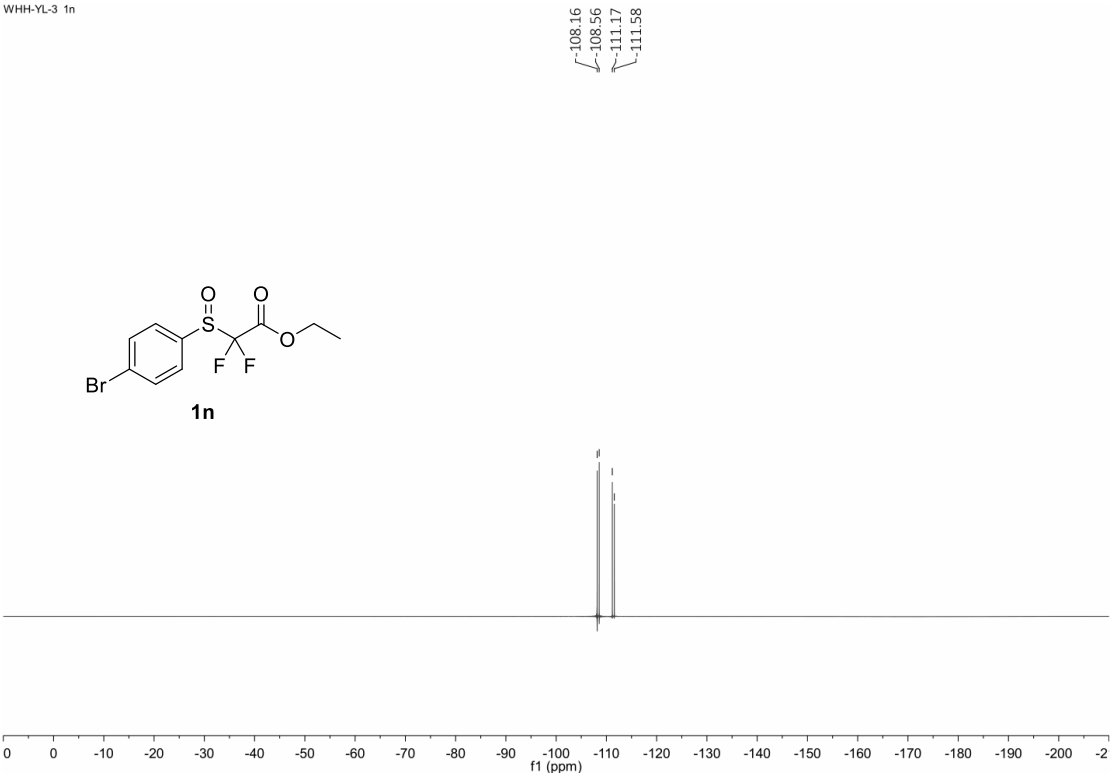

WHH-YL-12 1j
7.81
7.80
7.70
7.69
7.69
7.68
7.67
7.64
7.62
7.61
7.26
O
S
n-C6F13
1j
1.89
1.00
1.94
f1 (ppm)

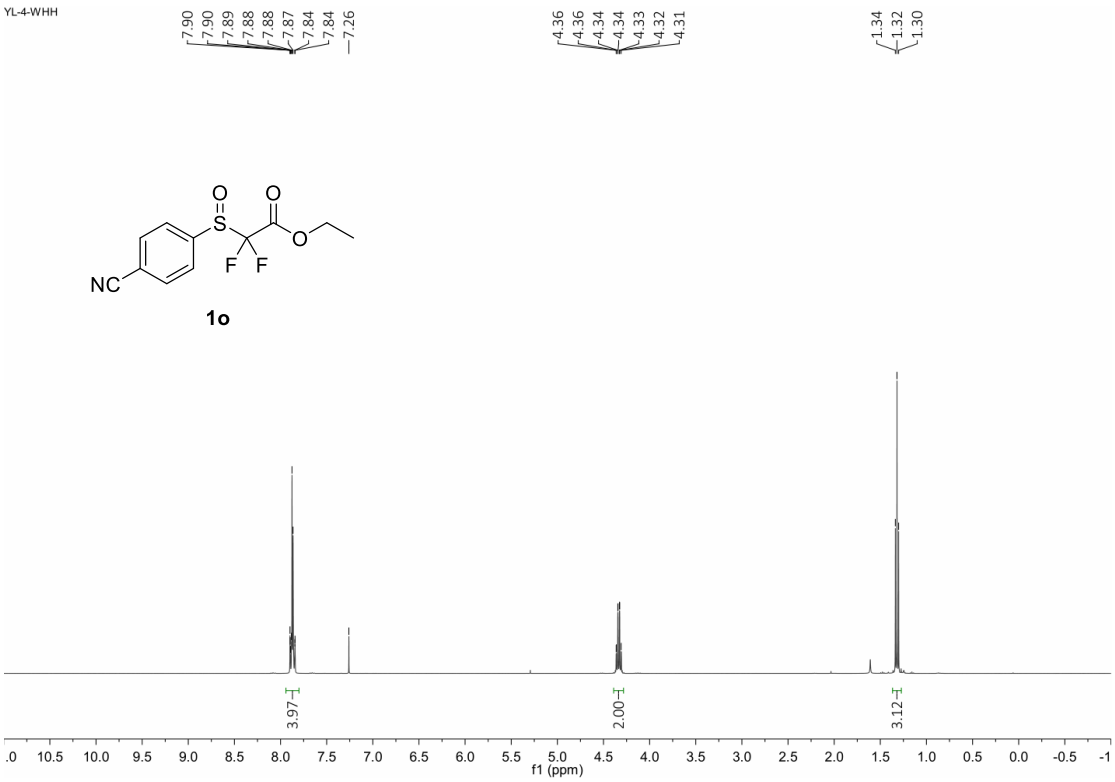

whh-yl-12
135.15
133.97
131.25
129.87
129.64
129.62
129.61
126.93
117.25
111.92
110.92
110.33
77.48
77.16
76.84
O
S
n-C6F13
1j
f1 (ppm)

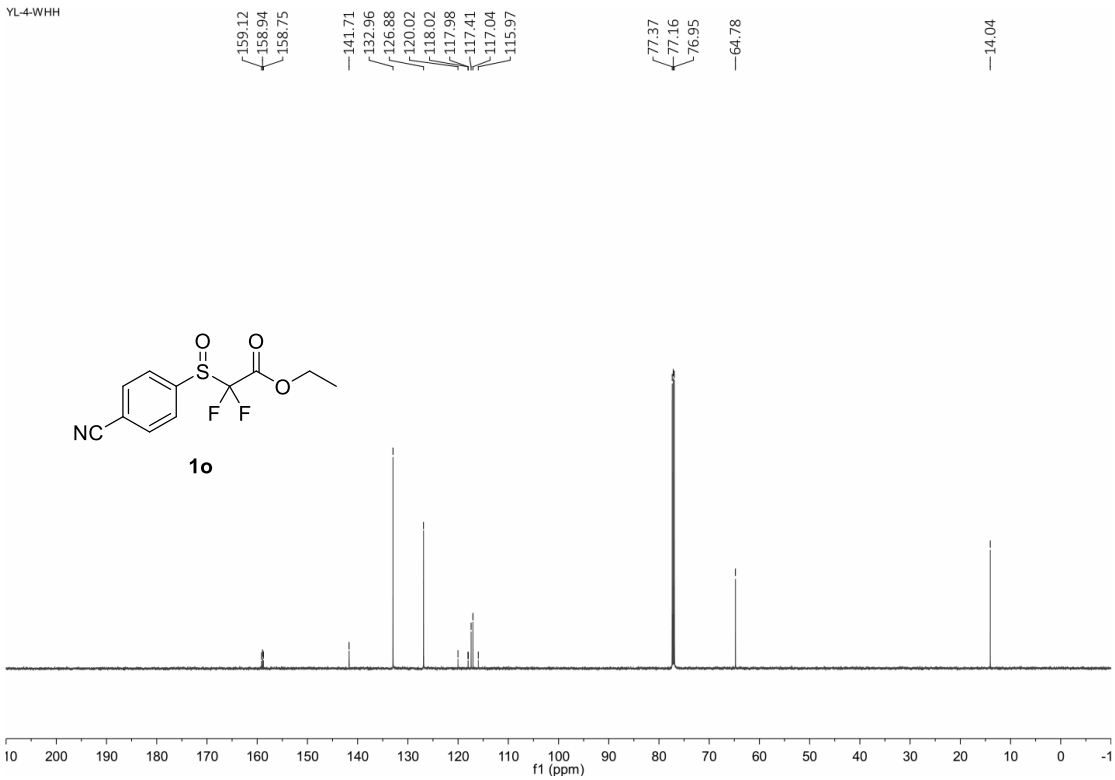

WHH-YL-12
-80.98
-111.11
-111.72
-119.32
-120.09
-120.49
-121.34
-122.03
-122.45
-122.89
-123.04
-126.31
O
S
n-C6F13
1j
f1 (ppm)


WHH-YL-3
7.72
7.72
7.71
7.71
7.59
7.57
7.26
4.31
4.31
4.30
4.29
4.29
4.28
4.28
4.27
4.26
4.26
1.29
1.28
1.27
O
O
S
O
F
F
Br
1n
2.01
2.00
2.06
3.13
f1 (ppm)


WHH-YL-3
159.37
159.19
159.00
135.18
132.75
128.37
127.59
119.83
117.83
115.80
77.37
77.16
76.95
64.47
13.94
O
O
S
O
F
F
Br
1n
f1 (ppm)


WHH-YL-3 1n
-108.16
-108.56
-111.17
-111.58
O
O
S
O
F
F
Br
1n
f1 (ppm)

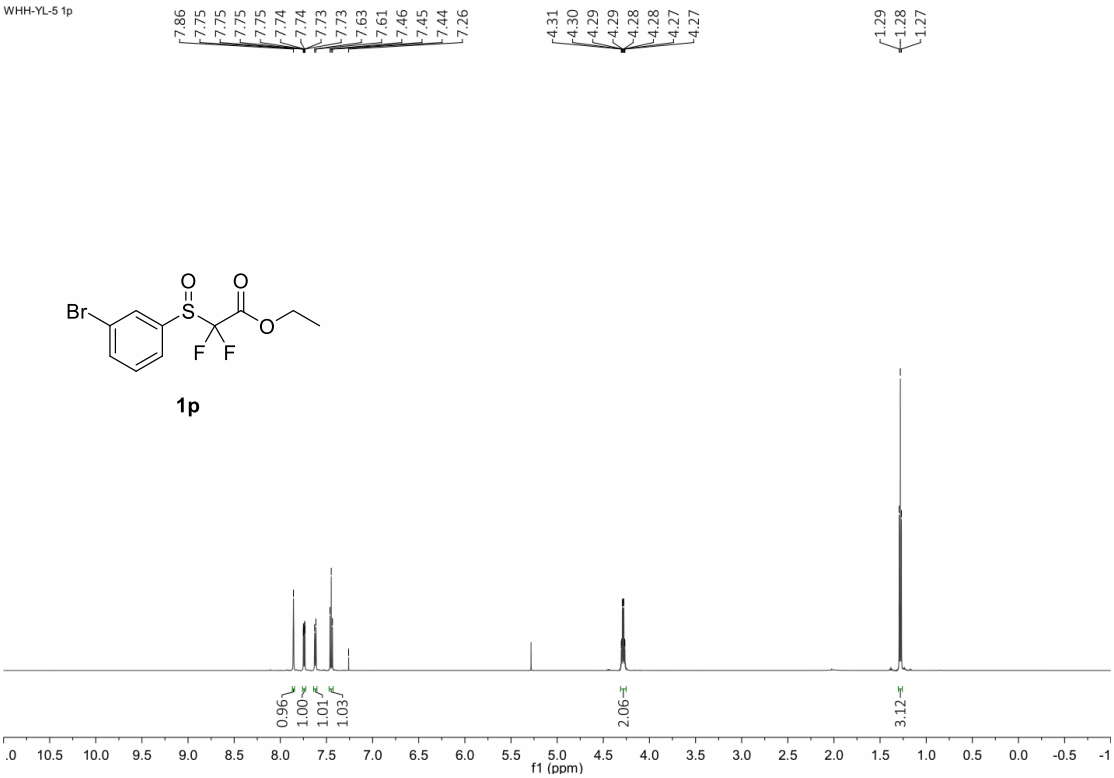

YL-4-WHH
7.90
7.90
7.89
7.88
7.88
7.87
7.84
7.84
7.26
4.36
4.36
4.34
4.34
4.33
4.32
4.31
1.34
1.32
1.30
O
O
S
O
F
F
NC
1o
3.97
2.00
3.12
f1 (ppm)


YL-4-WHH
159.12
158.94
158.75
141.71
132.96
126.88
120.02
118.02
117.98
117.41
117.04
115.97
77.37
77.16
76.95
64.78
14.04
O
O
S
O
F
F
NC
1o
f1 (ppm)

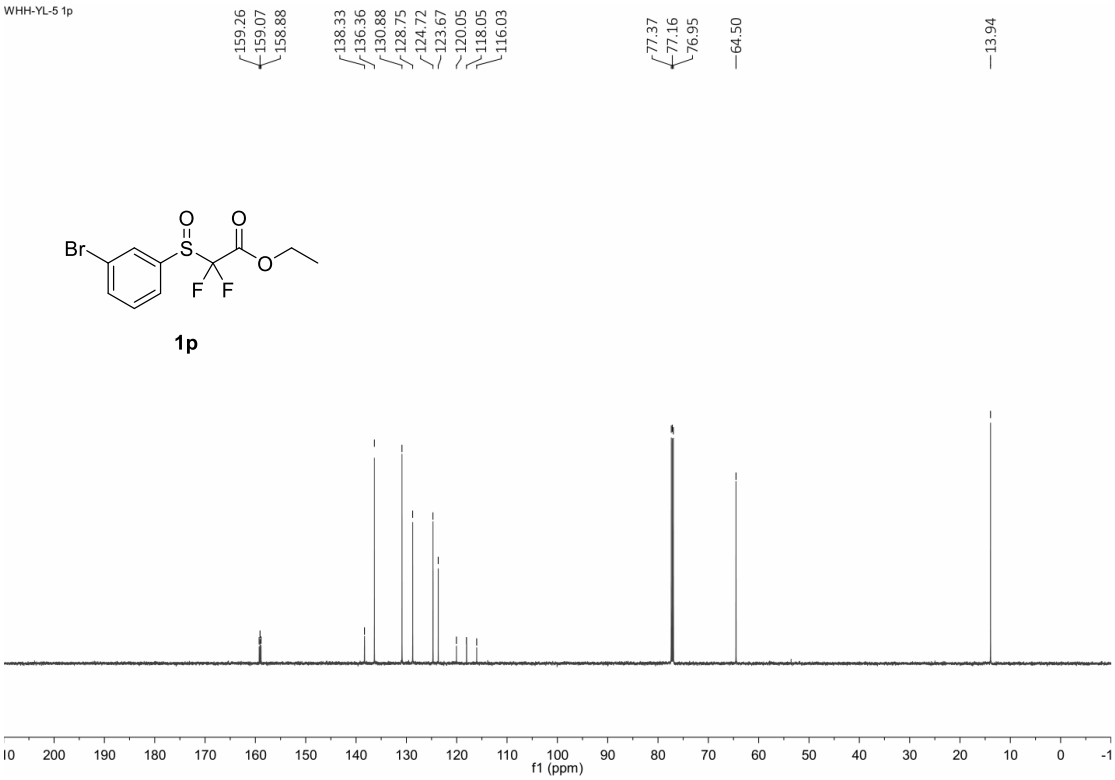
YL-4-WHH

1o

WHH-YL-5 1p



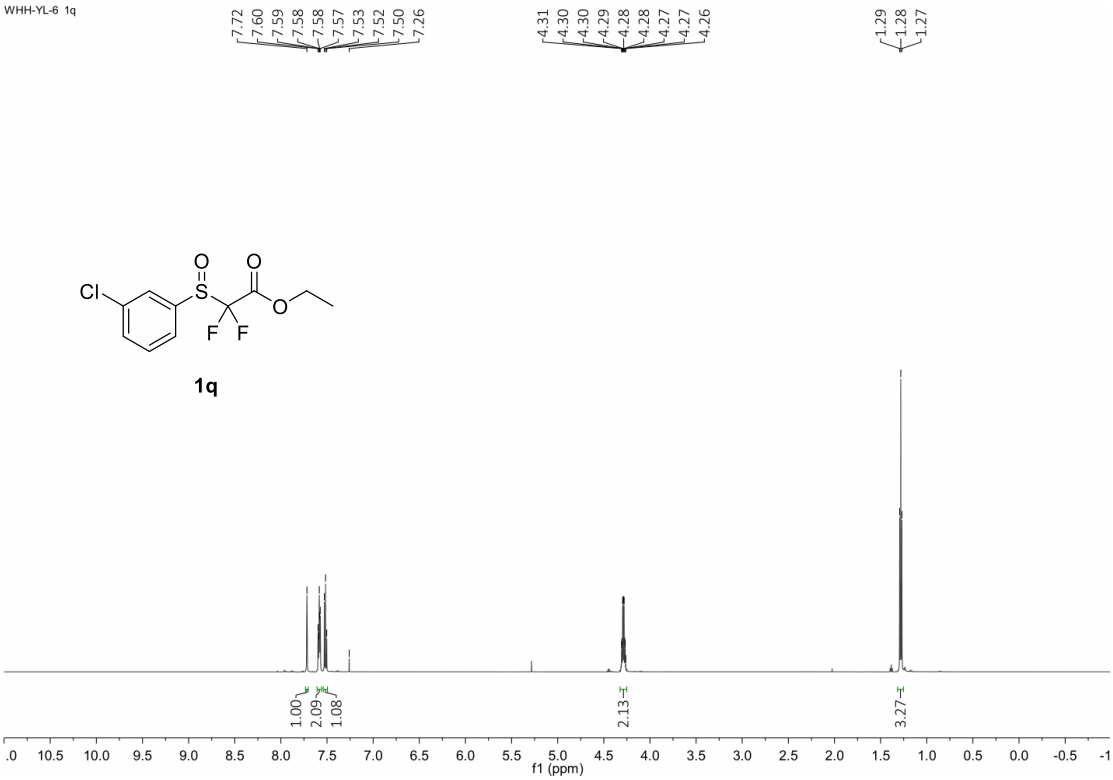
1p

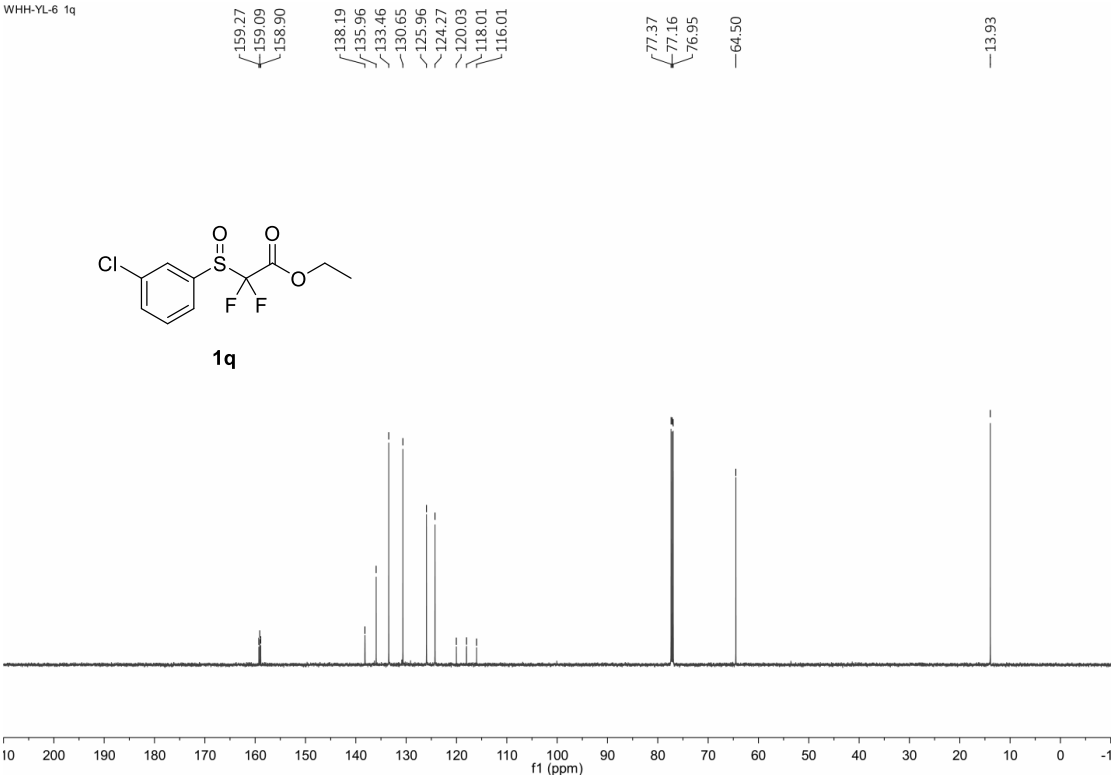

WHH-YL-5 1p
159.26
159.07
158.88
138.33
136.36
130.88
128.75
124.72
123.67
120.05
118.05
116.03
77.37
77.16
76.95
64.50
13.94
Br
O
S
O
O
F
F
f1 (ppm)

1p

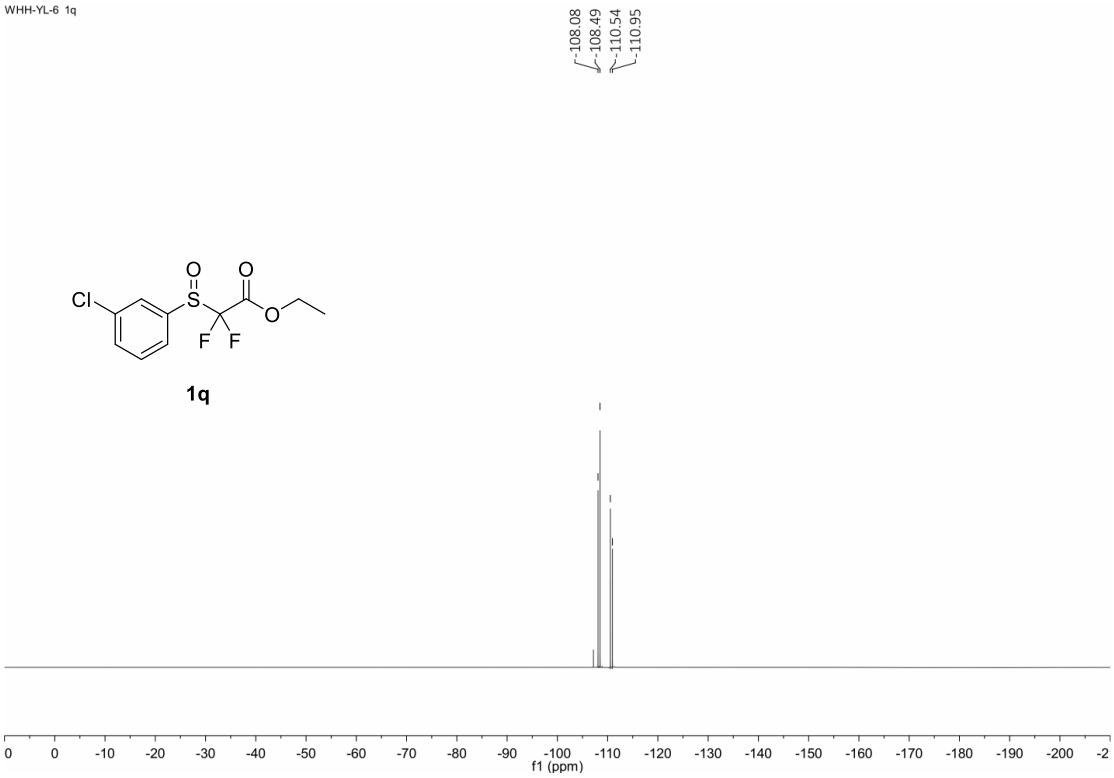

WHH-YL-5 1p
-108.09
-108.49
-110.45
-110.86
Br
O
S
O
O
F
F
f1 (ppm)

1p


WHH-YL-6 1q
7.72
7.60
7.59
7.58
7.58
7.57
7.53
7.52
7.50
7.26
4.31
4.30
4.30
4.29
4.28
4.28
4.27
4.27
4.26
1.29
1.28
1.27
Cl
O
S
O
O
F
F
1q
1.00
2.09
1.08
2.13
3.27
f1 (ppm)

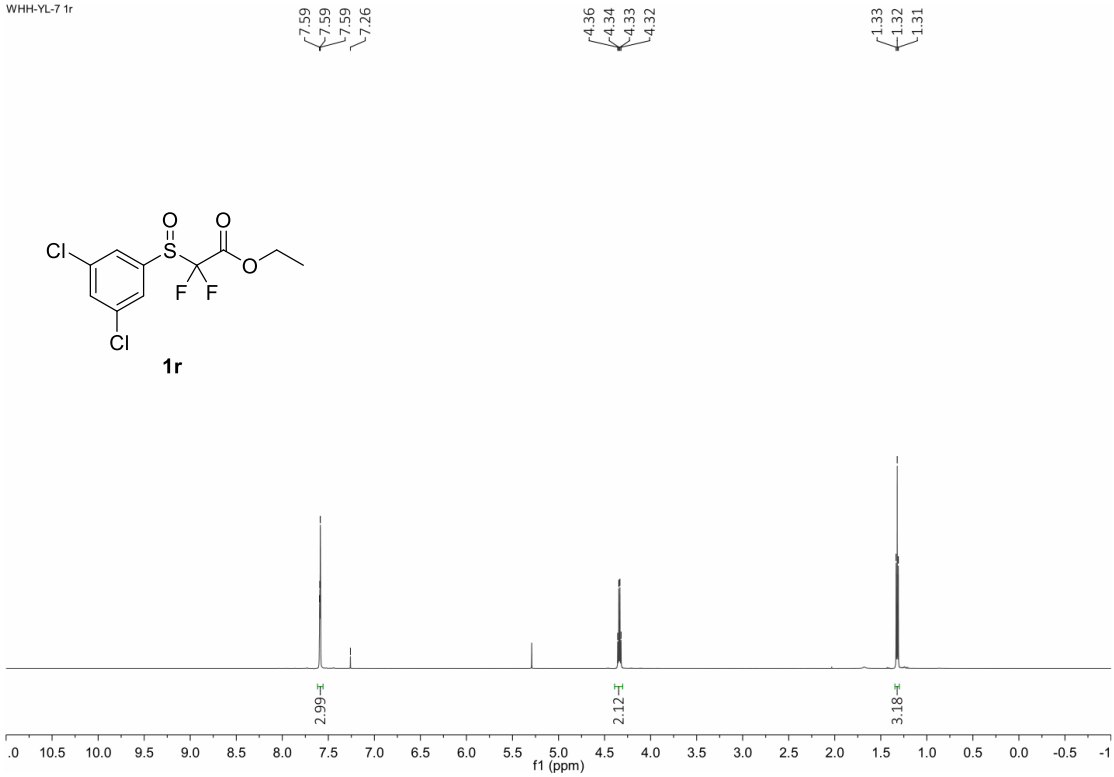

WHH-YL-6 1q
159.27
159.09
158.90
138.19
135.96
133.46
130.65
125.96
124.27
120.03
118.01
116.01
77.37
77.16
76.95
64.50
13.93
Cl
O
S
O
O
F
F
1q
f1 (ppm)

WHH-YL-6 1q

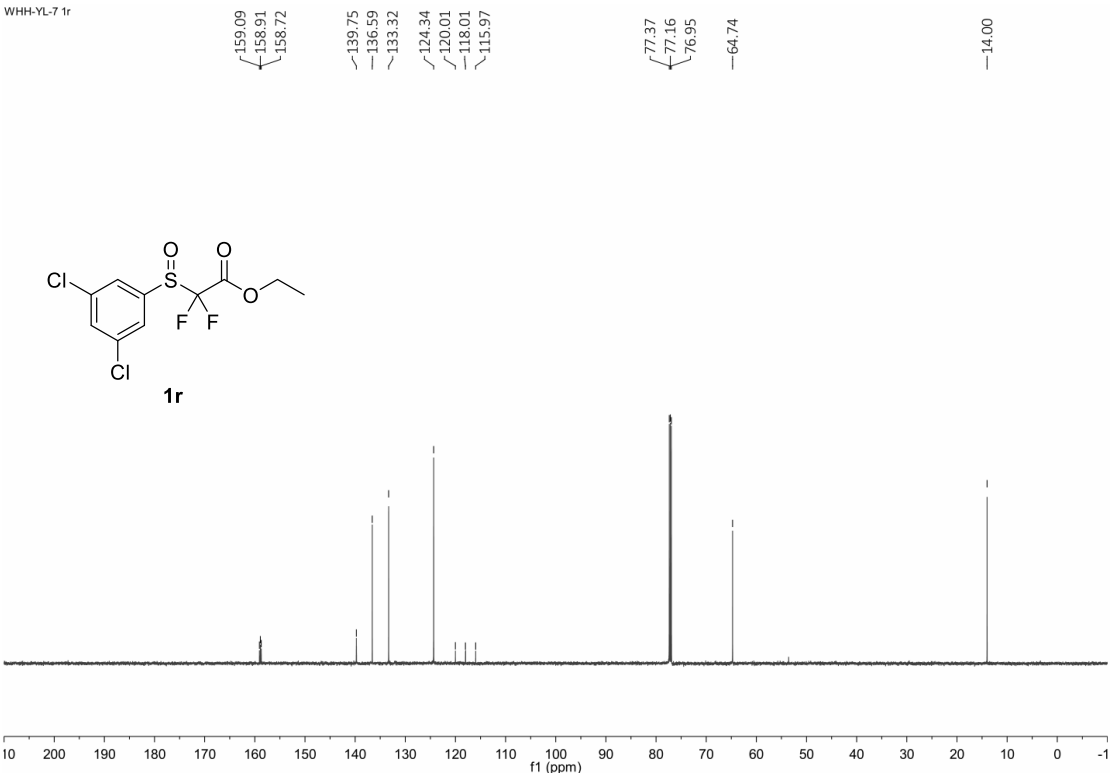


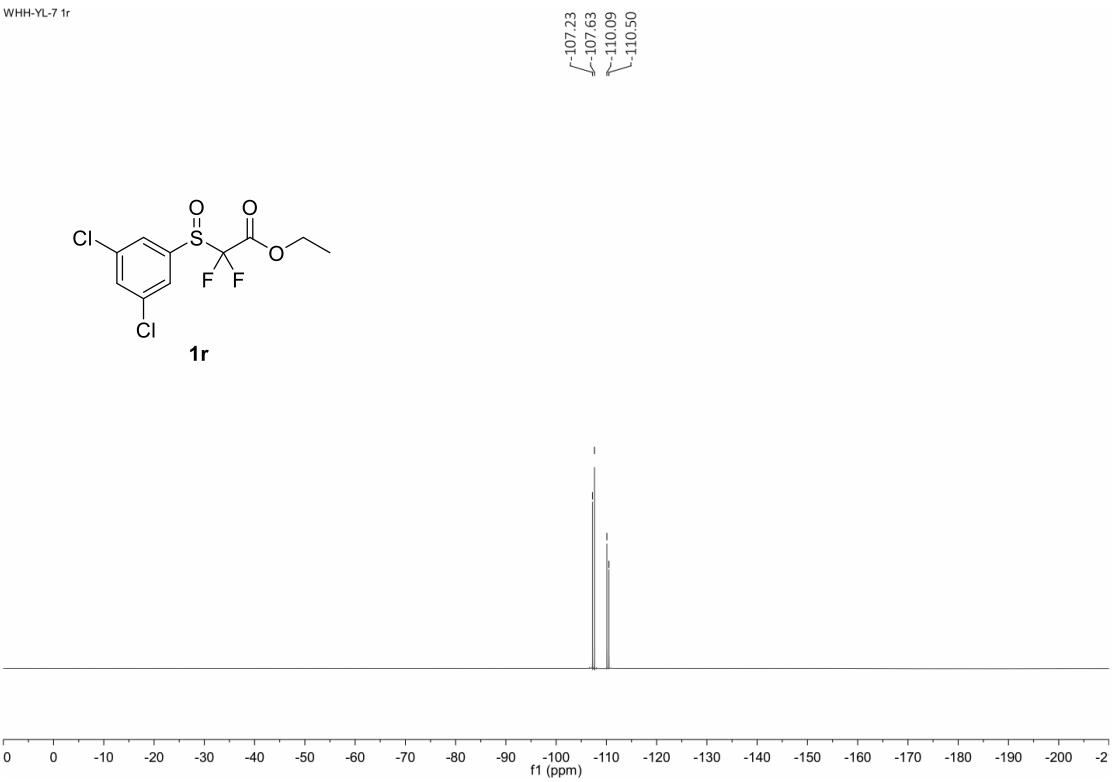
1q

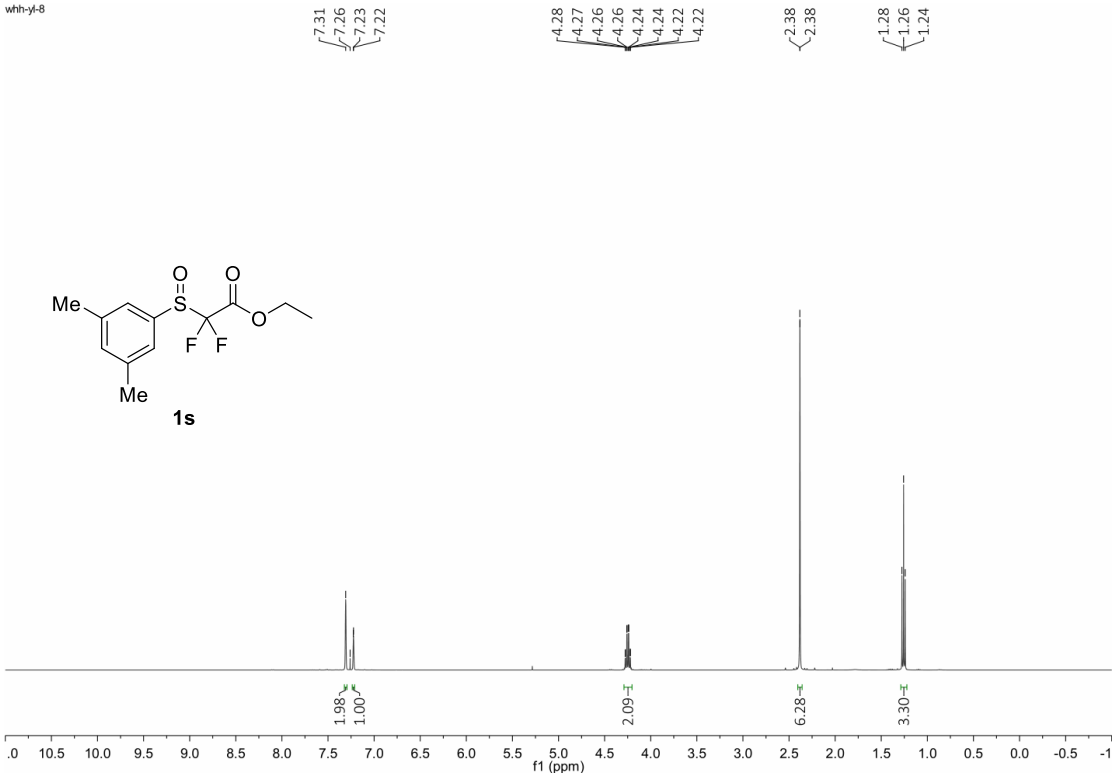
WHH-YL-7 1r

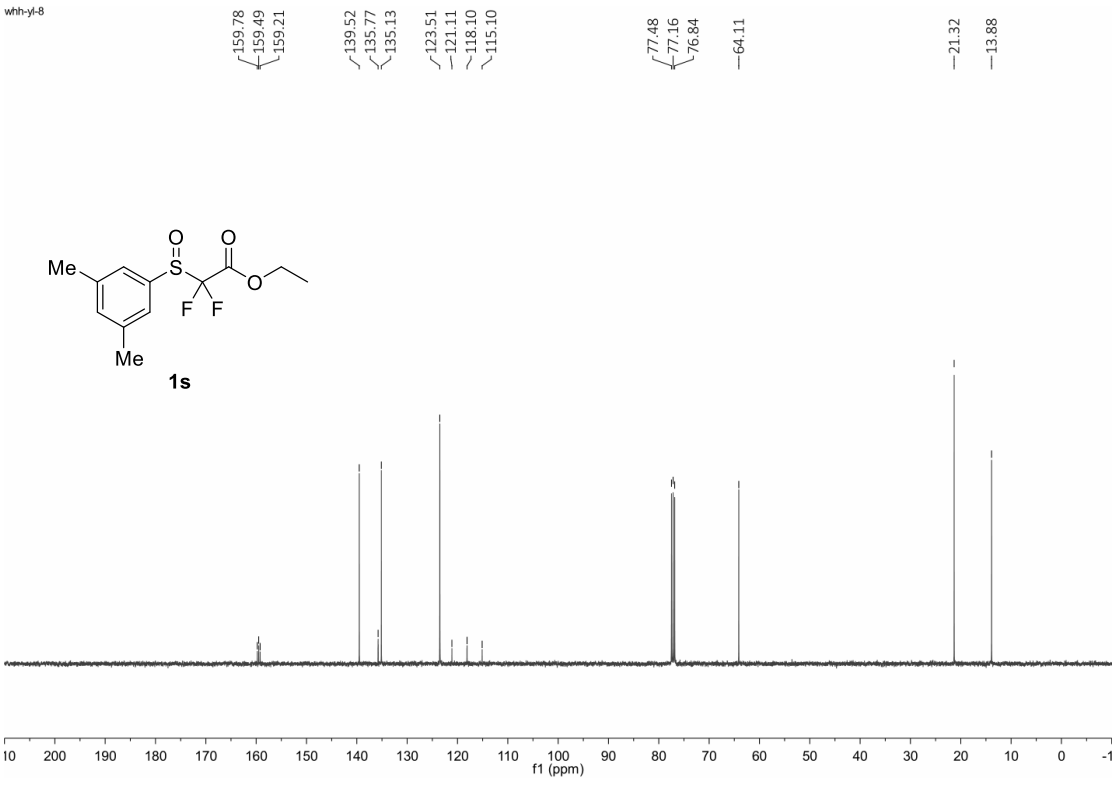


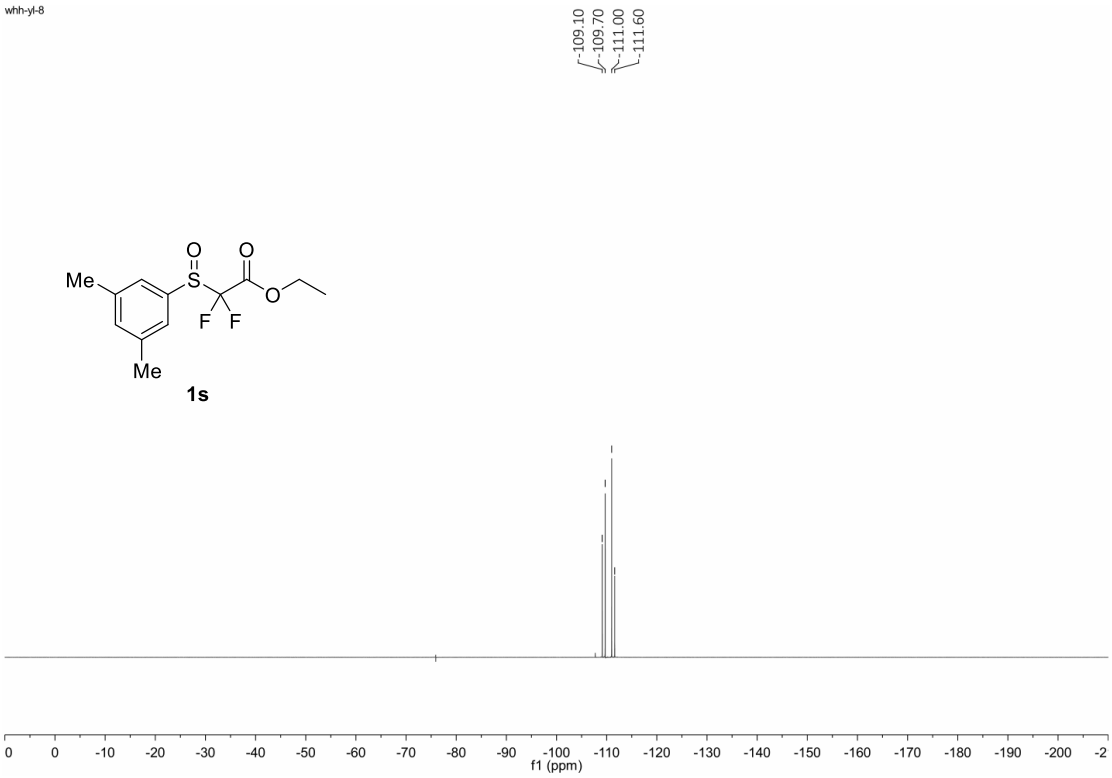
1r


WHH-YL-7 1r
159.09
158.91
158.72
139.75
136.59
133.32
124.34
120.01
118.01
115.97
77.37
77.16
76.95
64.74
14.00
Cl
O
S
O
O
F
F
Cl
1r
f1 (ppm)

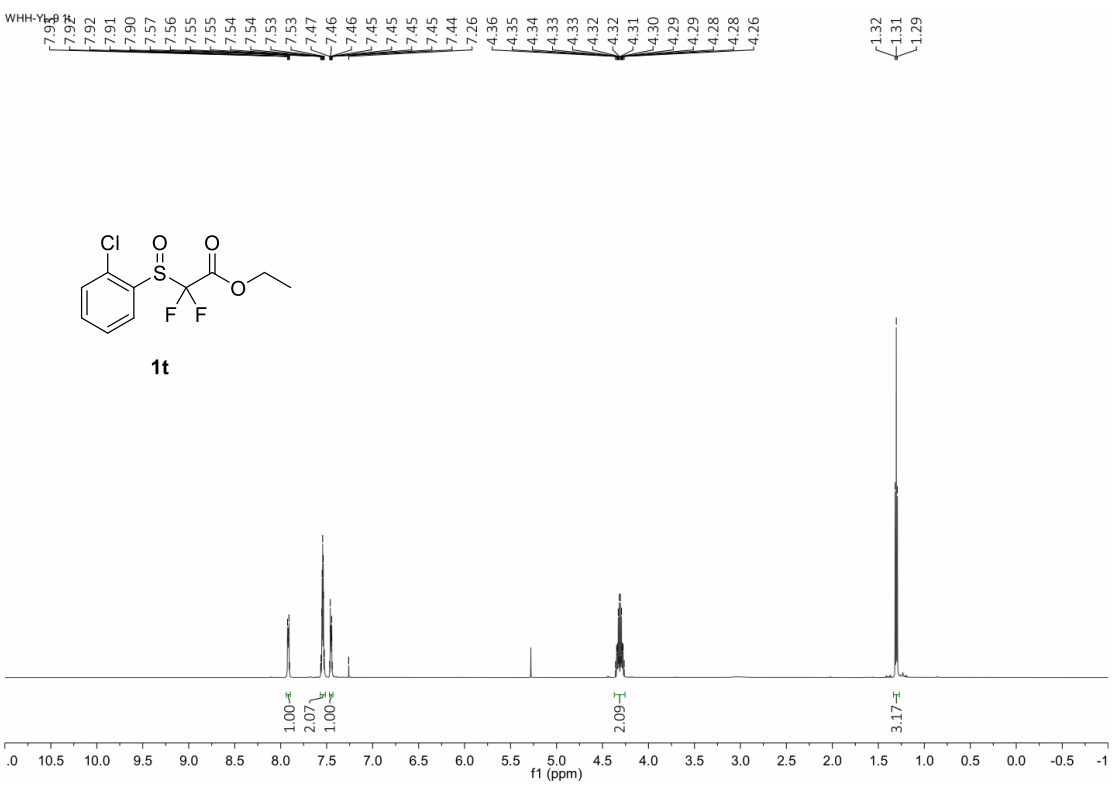

WHH-YL-7 1r
-107.23
-107.63
-110.09
-110.50
Cl
O
S
O
O
F
F
Cl
1r
f1 (ppm)


whh-yl-8
7.31
7.26
7.23
7.22
4.28
4.27
4.26
4.26
4.24
4.24
4.22
4.22
2.38
2.38
1.28
1.26
1.24
Me
Me
1s
1.98
1.00
2.09
6.28
3.30
f1 (ppm)

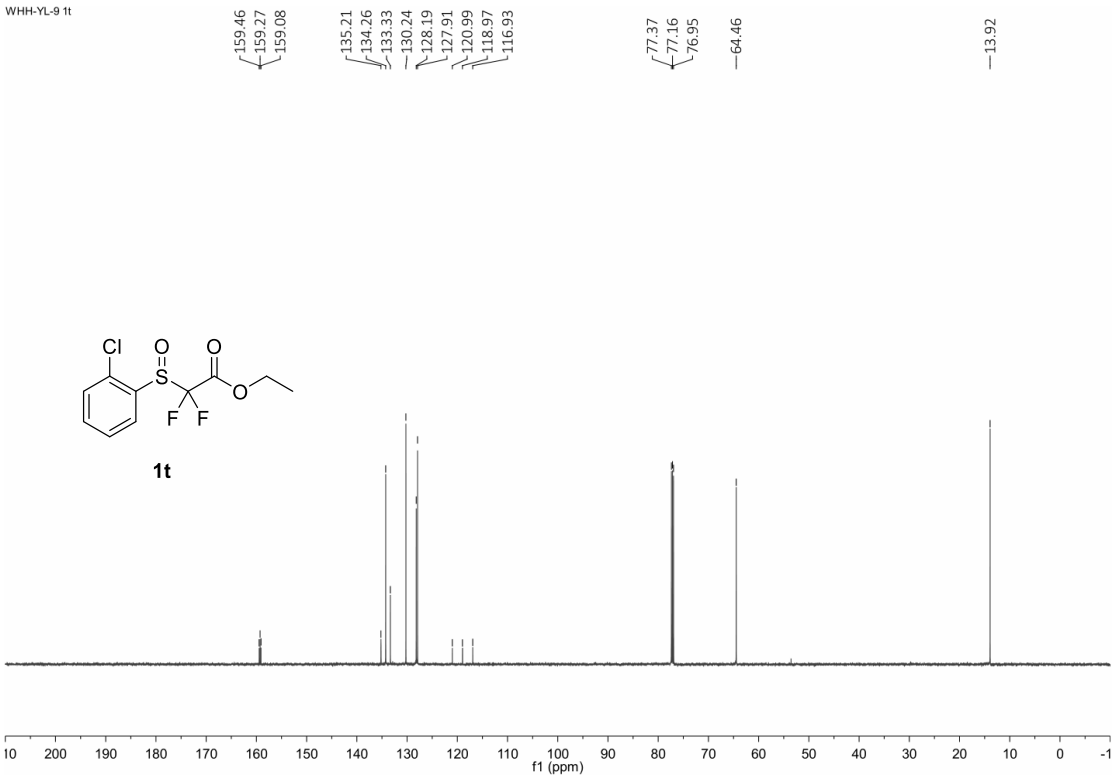

whh-yl-8
159.78
159.49
159.21
139.52
135.77
135.13
123.51
121.11
118.10
115.10
77.48
77.16
76.84
64.11
21.32
13.88
Me
Me
1s
f1 (ppm)


whh-yl-8
-109.10
-109.70
-111.00
-111.60
Me
Me
O
O
S
O
F
F
f1 (ppm)

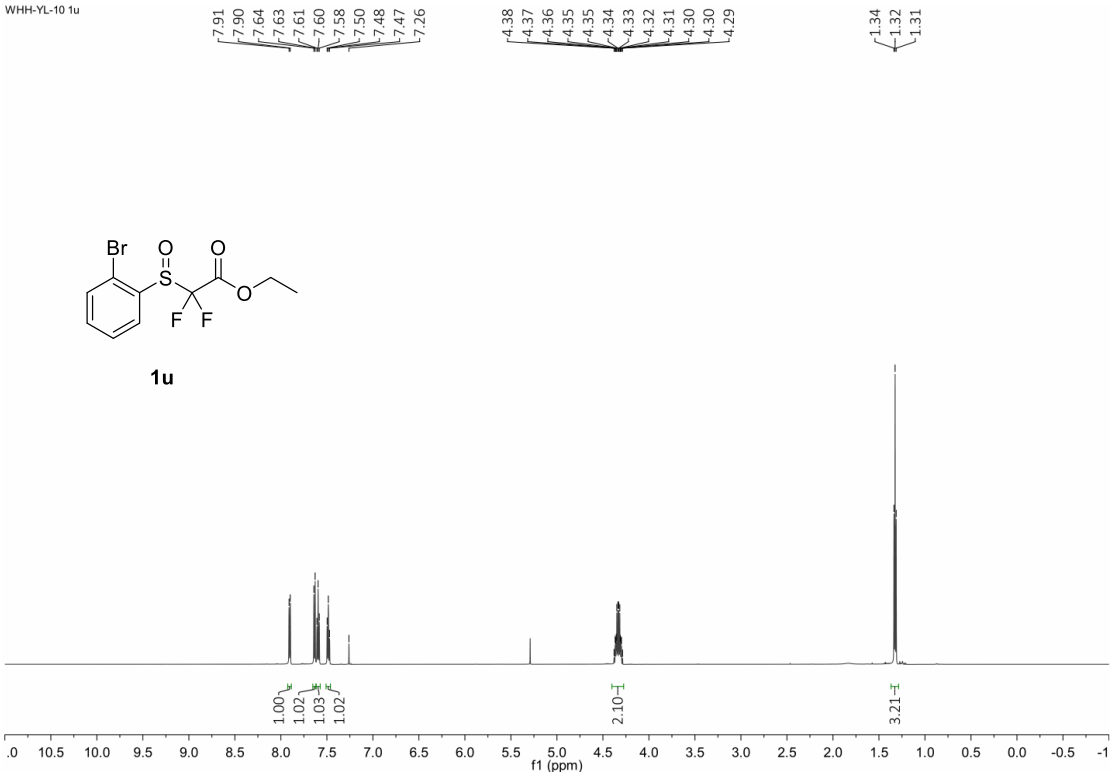
1s

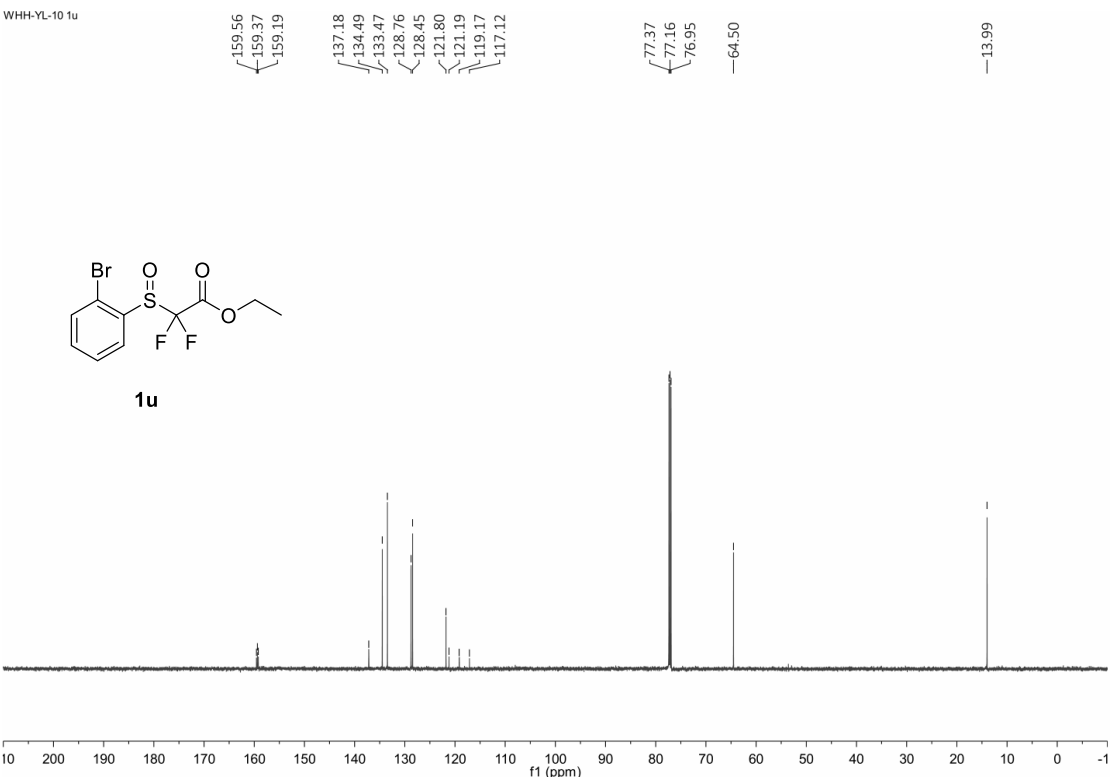

WHH-YL-9
7.93
7.92
7.92
7.91
7.90
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.47
7.46
7.46
7.45
7.45
7.45
7.45
7.44
7.26
4.36
4.35
4.34
4.33
4.33
4.32
4.32
4.31
4.30
4.29
4.29
4.28
4.28
4.26
1.32
1.31
1.29
Cl
O
S
O
O
F
F
1.00
2.07
1.00
2.09
3.17
f1 (ppm)

1t

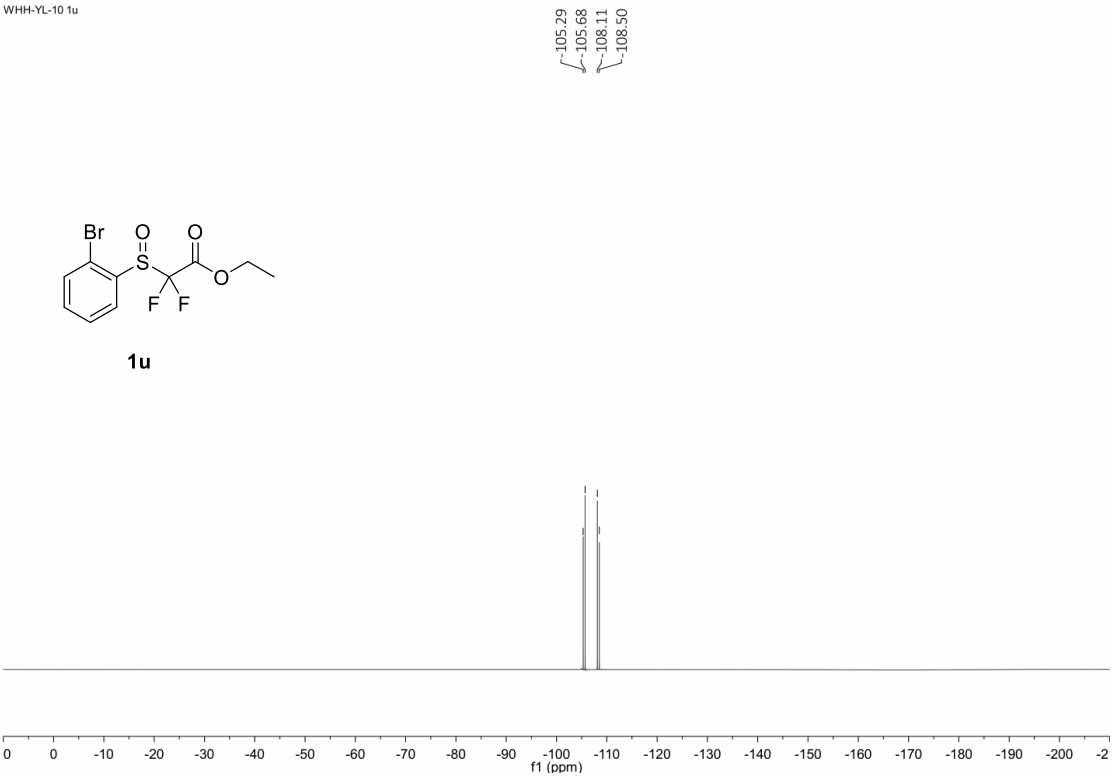

WHH-YL-9 1t
159.46
159.27
159.08
135.21
134.26
133.33
130.24
128.19
127.91
120.99
118.97
116.93
77.37
77.16
76.95
64.46
13.92
Cl
O
S
O
O
F
F
1t
f1 (ppm)


WHH-YL-9 1t
-106.32
-106.71
-108.66
-109.05
Cl
O
S
O
O
F
F
1t
f1 (ppm)


WHH-YL-10 1u
7.91
7.90
7.64
7.63
7.61
7.60
7.58
7.50
7.48
7.47
7.26
4.38
4.37
4.36
4.35
4.35
4.34
4.33
4.32
4.31
4.30
4.30
4.29
1.34
1.32
1.31
Br
O
S
O
O
F
F
1u
1.00
1.02
1.03
1.02
2.10
3.21
f1 (ppm)

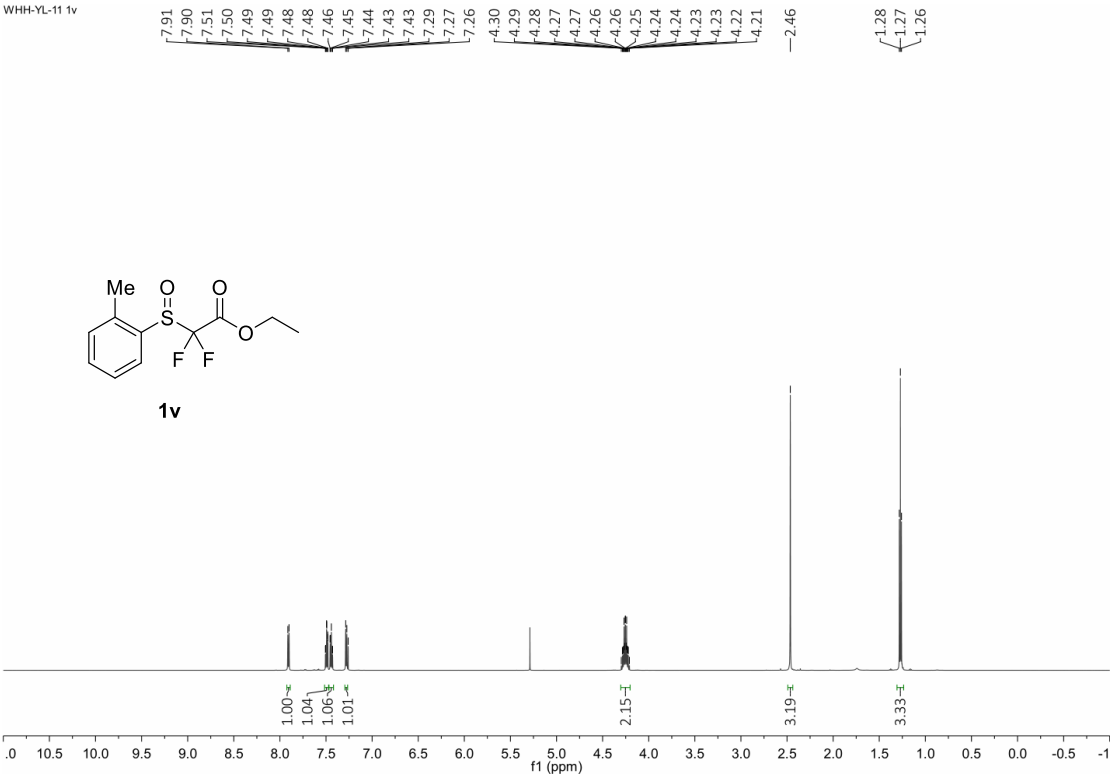

WHH-YL-10 1u
159.56
159.37
159.19
137.18
134.49
133.47
128.76
128.45
121.80
121.19
119.17
117.12
77.37
77.16
76.95
64.50
13.99
Br
O
S
O
O
F
F
1u
f1 (ppm)

WHH-YL-10 1u

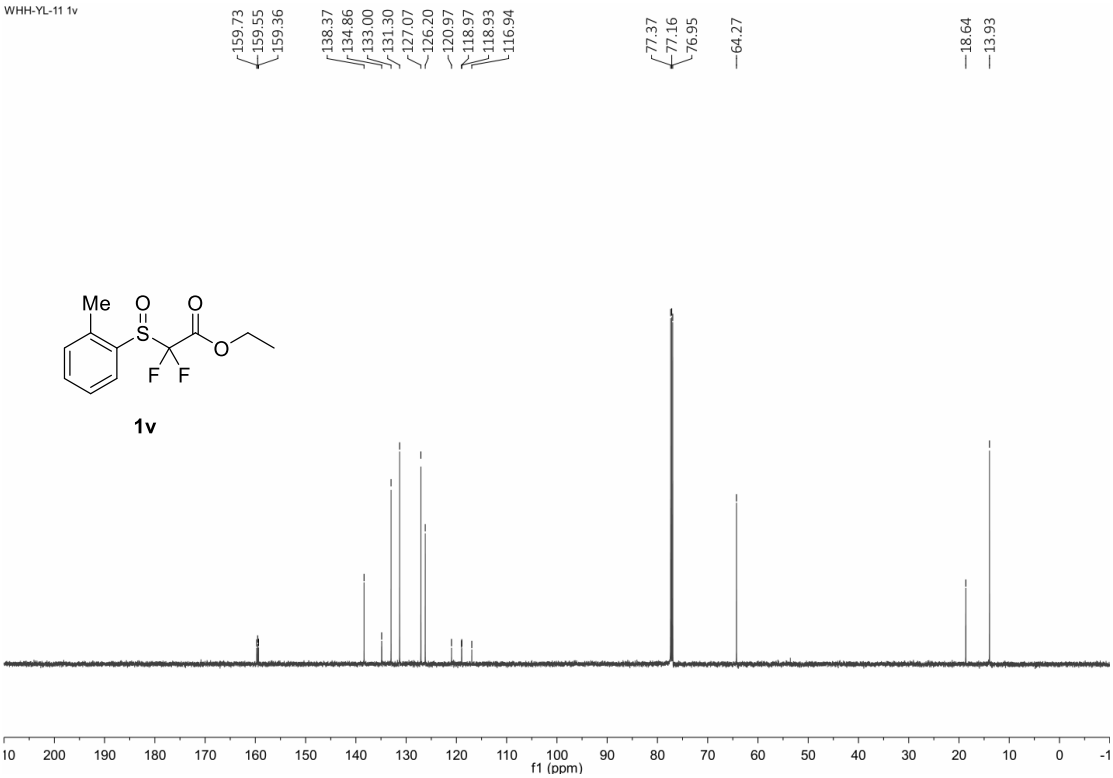


1u

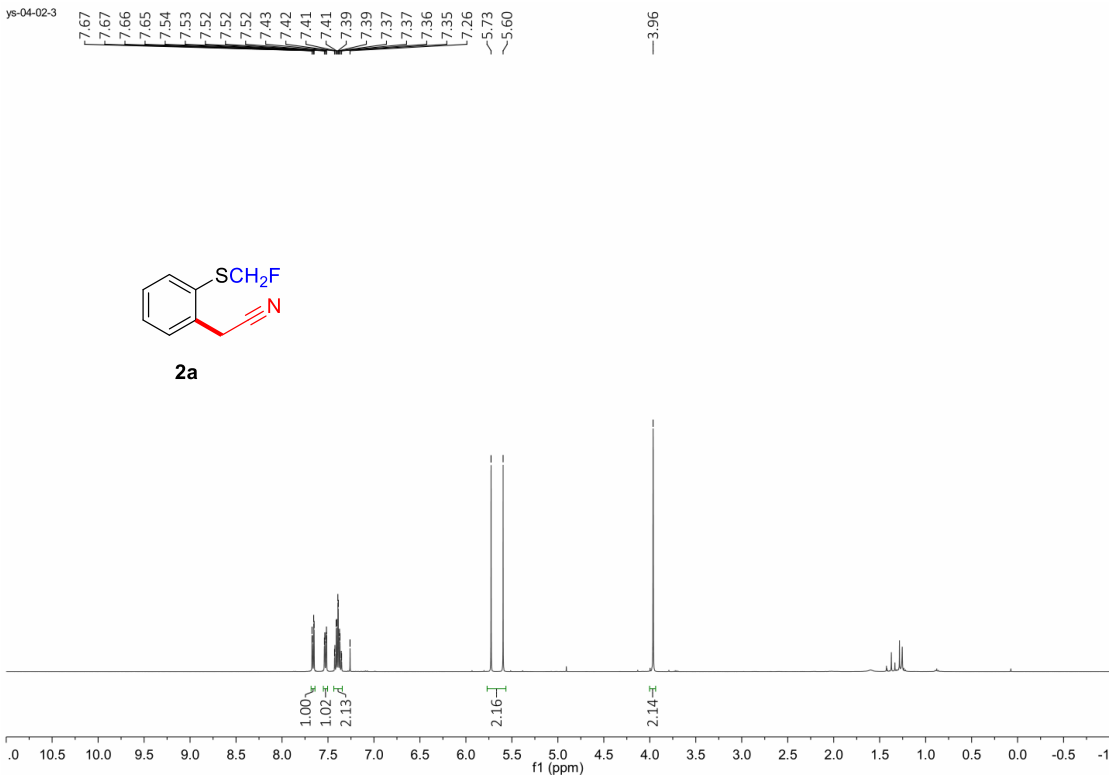
WHH-YL-11 1v



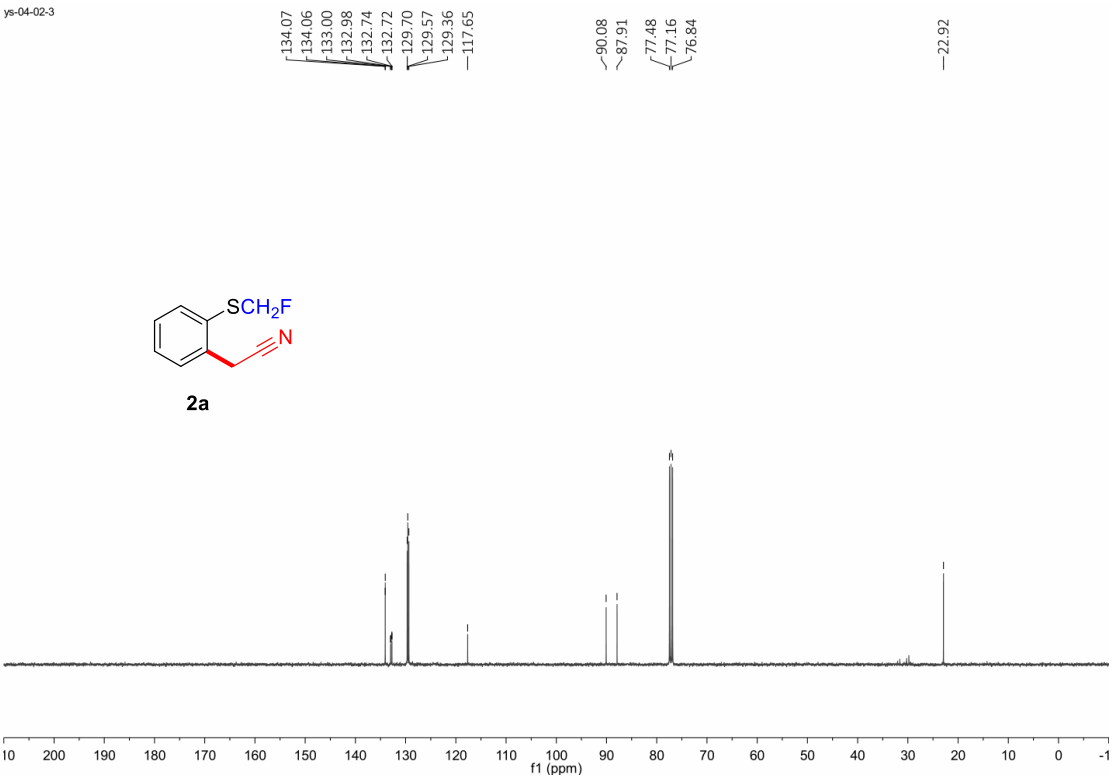
1v


WHH-YL-11 1v
159.73
159.55
159.36
138.37
134.86
133.00
131.30
127.07
126.20
120.97
118.97
118.93
116.94
77.37
77.16
76.95
64.27
18.64
13.93
Me
O
S
O
O
F
F
1v
f1 (ppm)

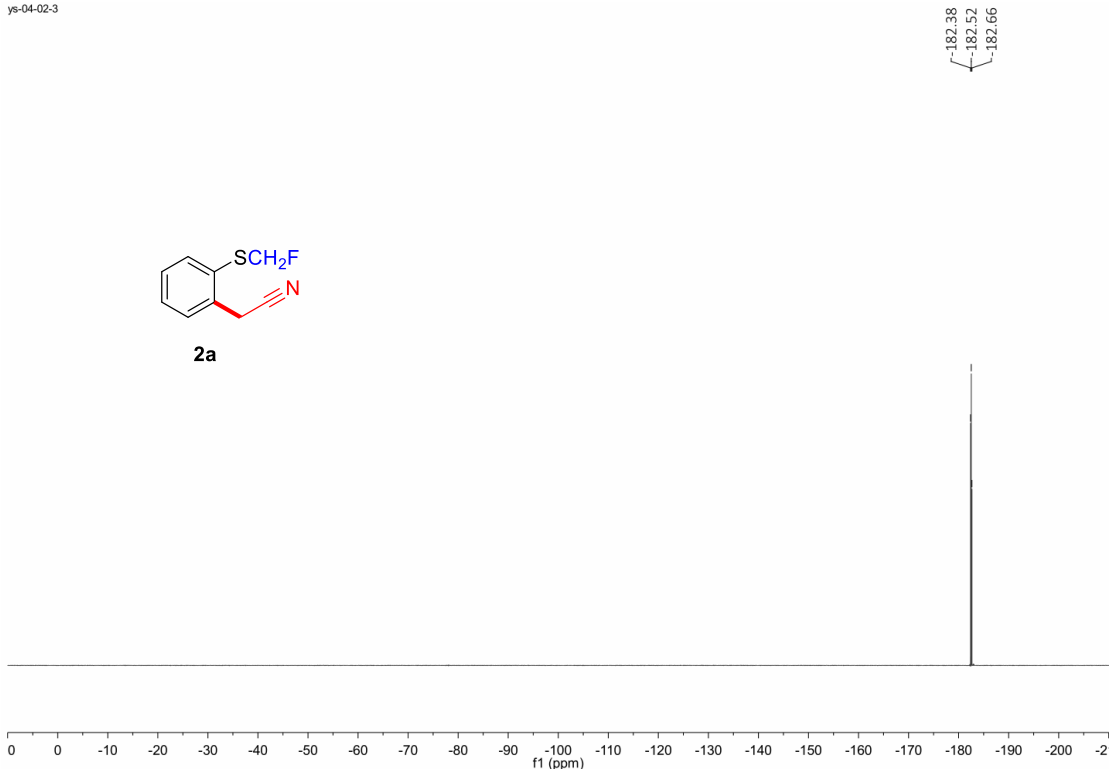

WHH-YL-11 1v
-106.01
-106.41
-110.47
-110.87
Me
O
S
O
O
F
F
1v
f1 (ppm)

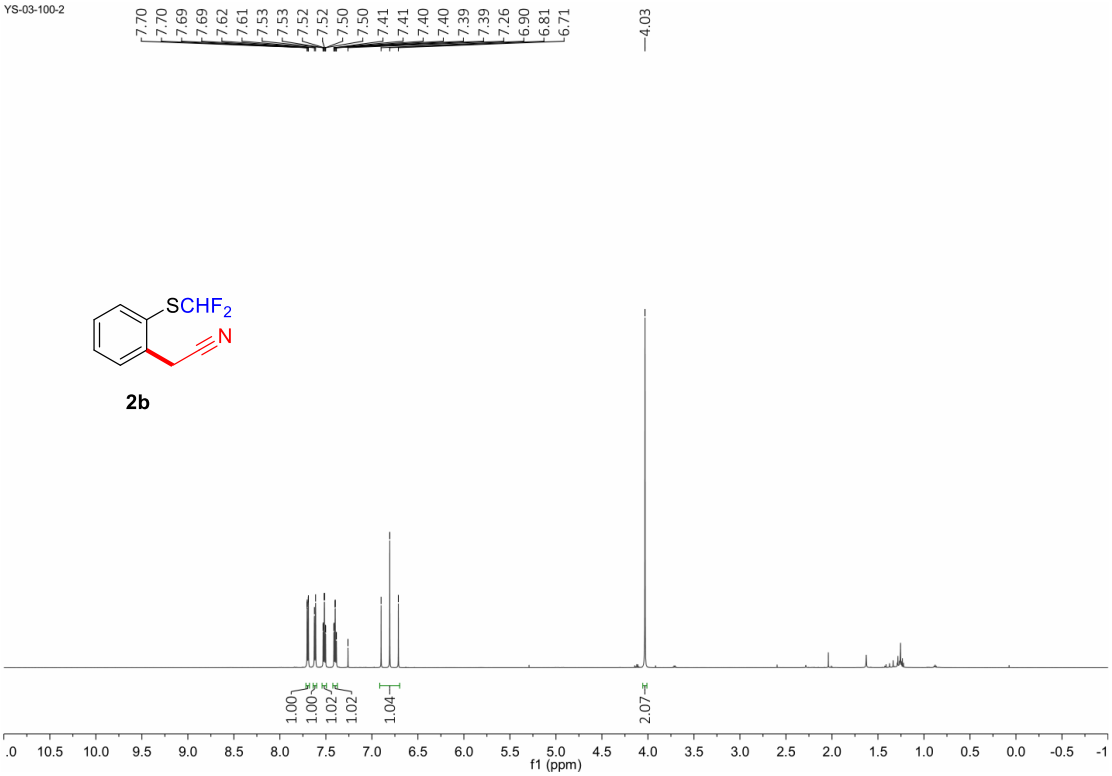

ys-04-02-3
7.67
7.67
7.66
7.65
7.54
7.53
7.52
7.52
7.52
7.43
7.42
7.41
7.41
7.39
7.39
7.37
7.37
7.36
7.35
7.26
5.73
5.60
3.96
SCH2F
N
1.00
1.02
2.13
2.16
2.14
f1 (ppm)

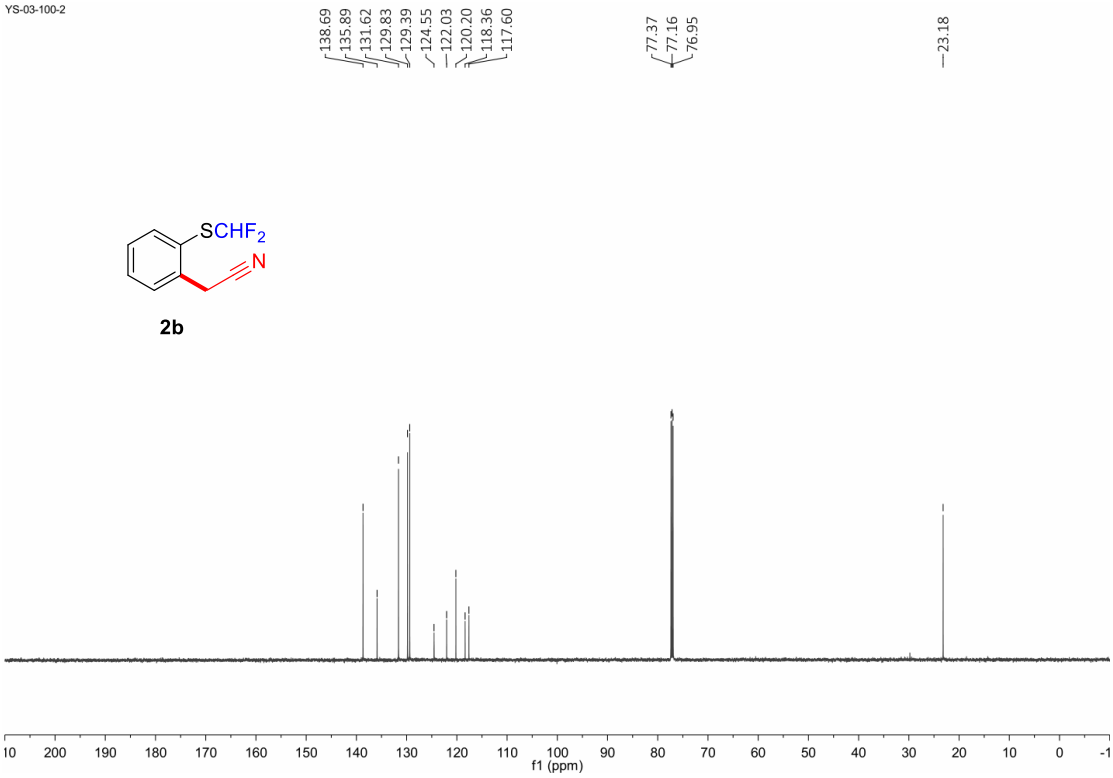
2a

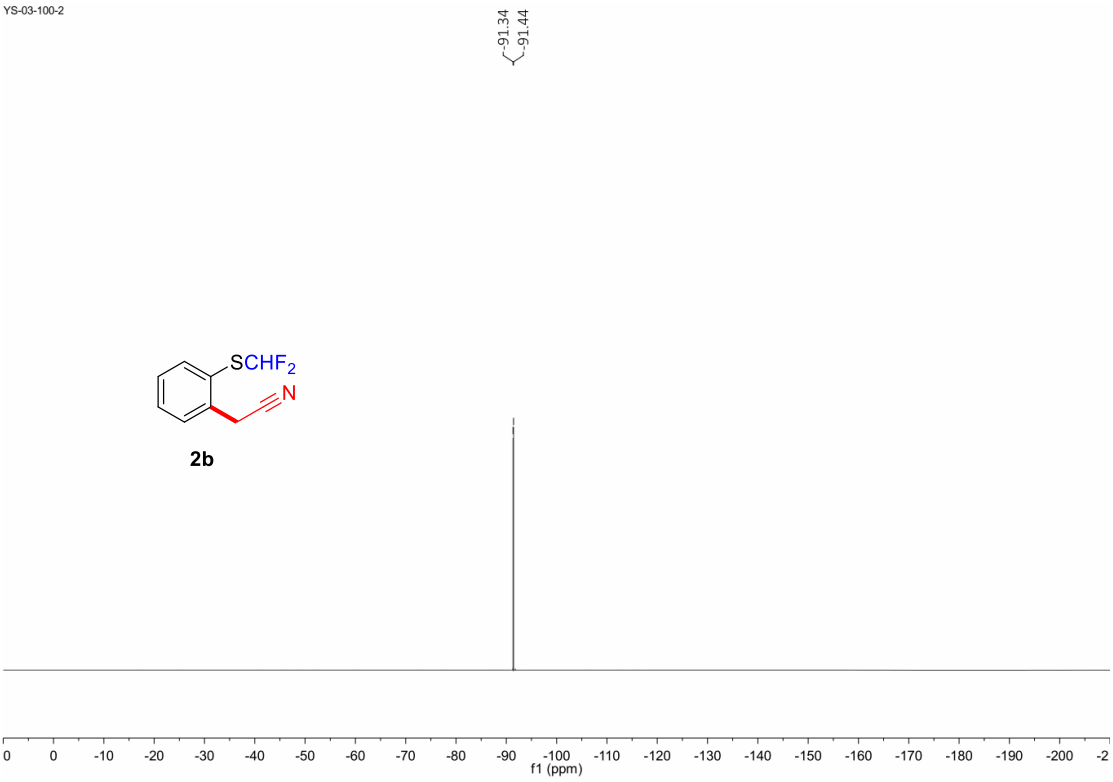

ys-04-02-3
134.07
134.06
133.00
132.98
132.74
132.72
129.70
129.57
129.36
117.65
90.08
87.91
77.48
77.16
76.84
22.92
SCH2F
N
f1 (ppm)

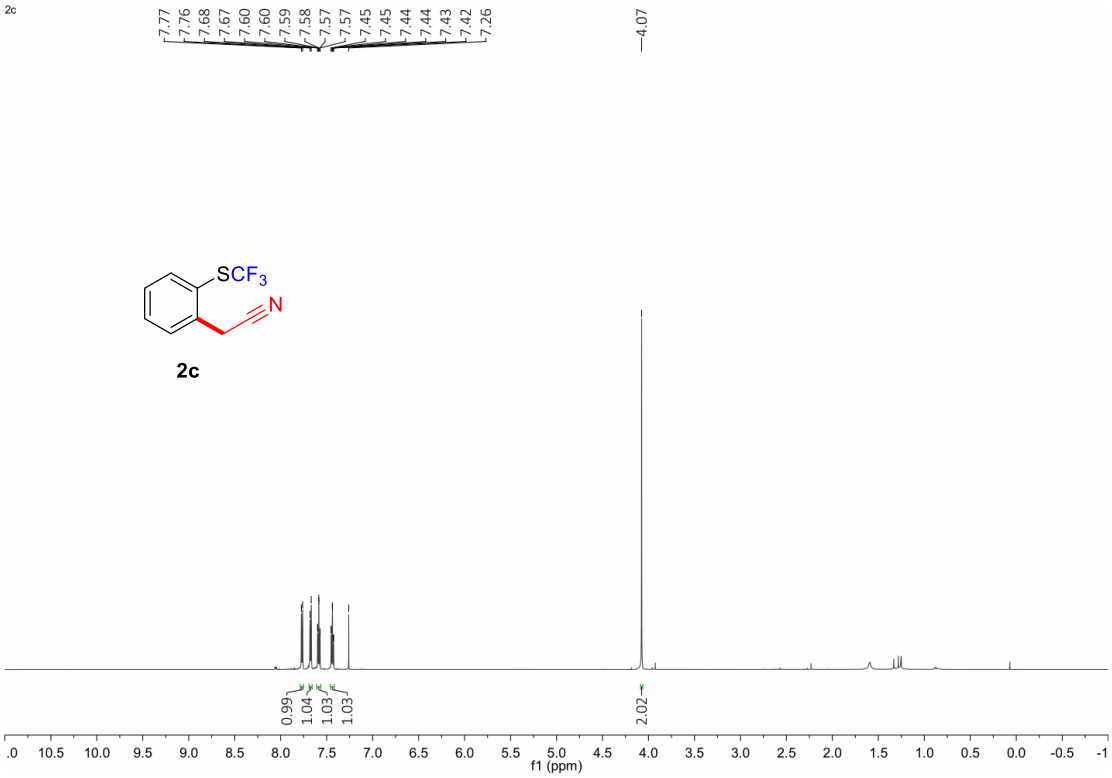
2a

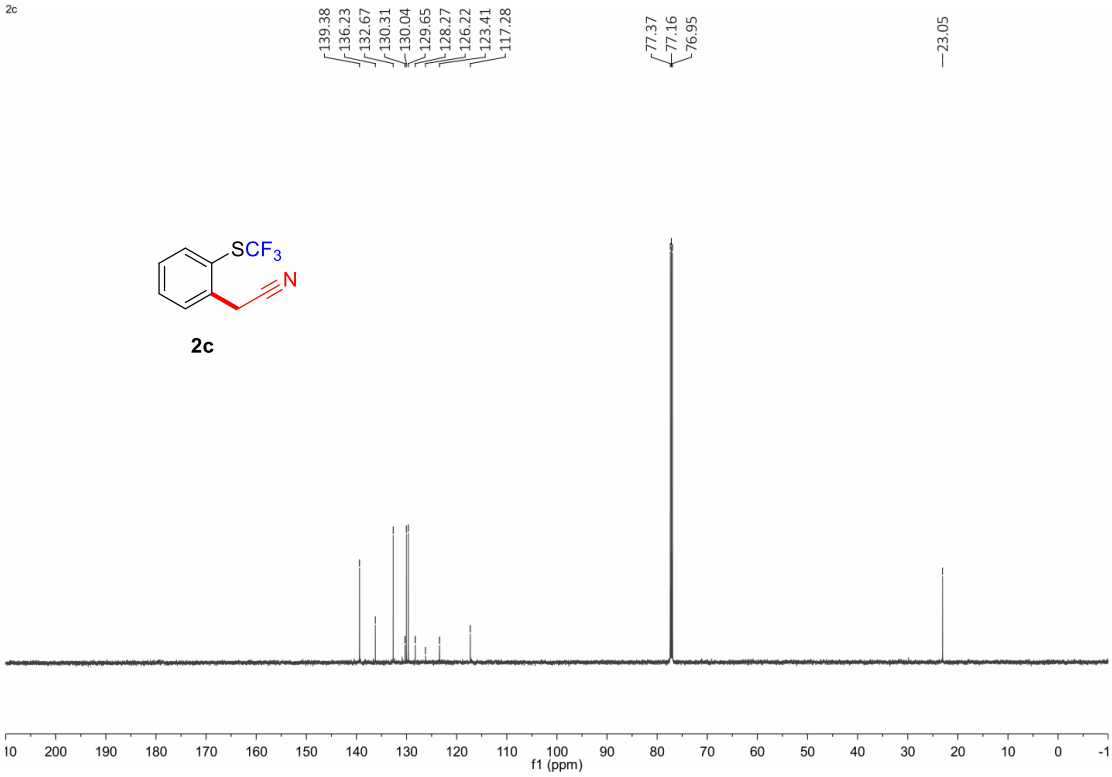

ys-04-02-3
-182.38
-182.52
-182.66
SCH2F
N
2a
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

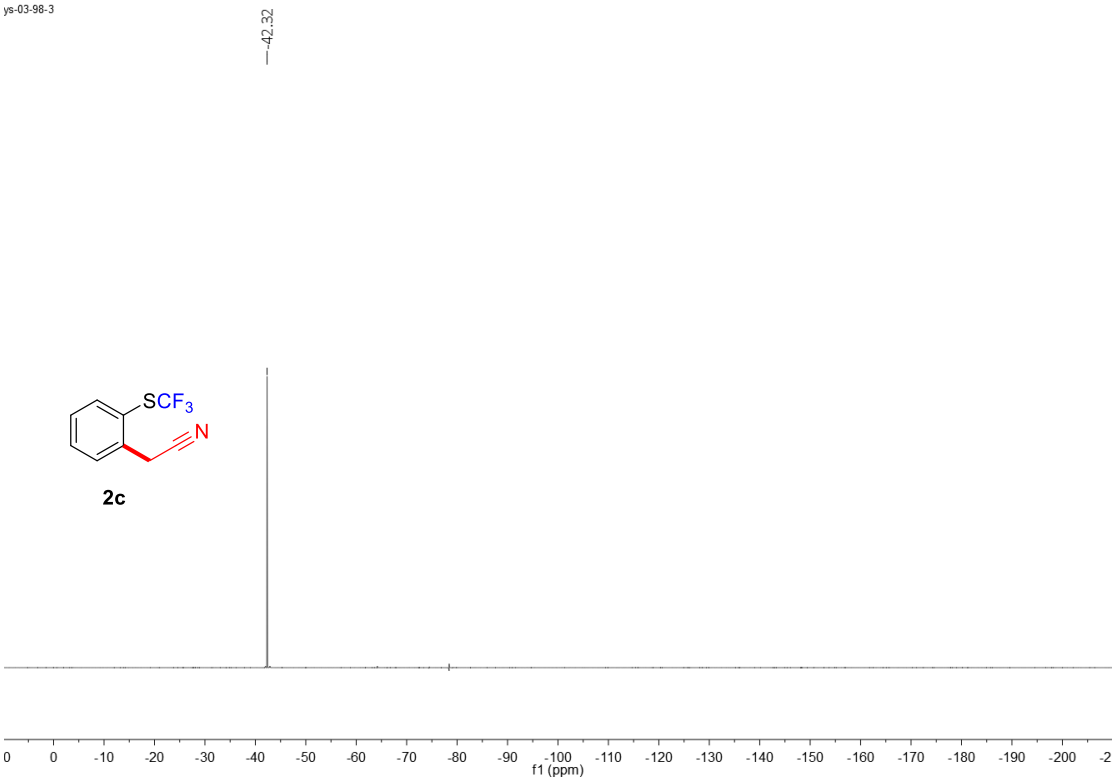

YS-03-100-2
7.70 7.70 7.69 7.69 7.62 7.61 7.53 7.53 7.52 7.52 7.50 7.50 7.41 7.41 7.40 7.40 7.39 7.39 7.26 6.90 6.81 6.71
4.03
SCHF2
N
2b
1.00 1.00 1.02 1.02 1.04 2.07
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

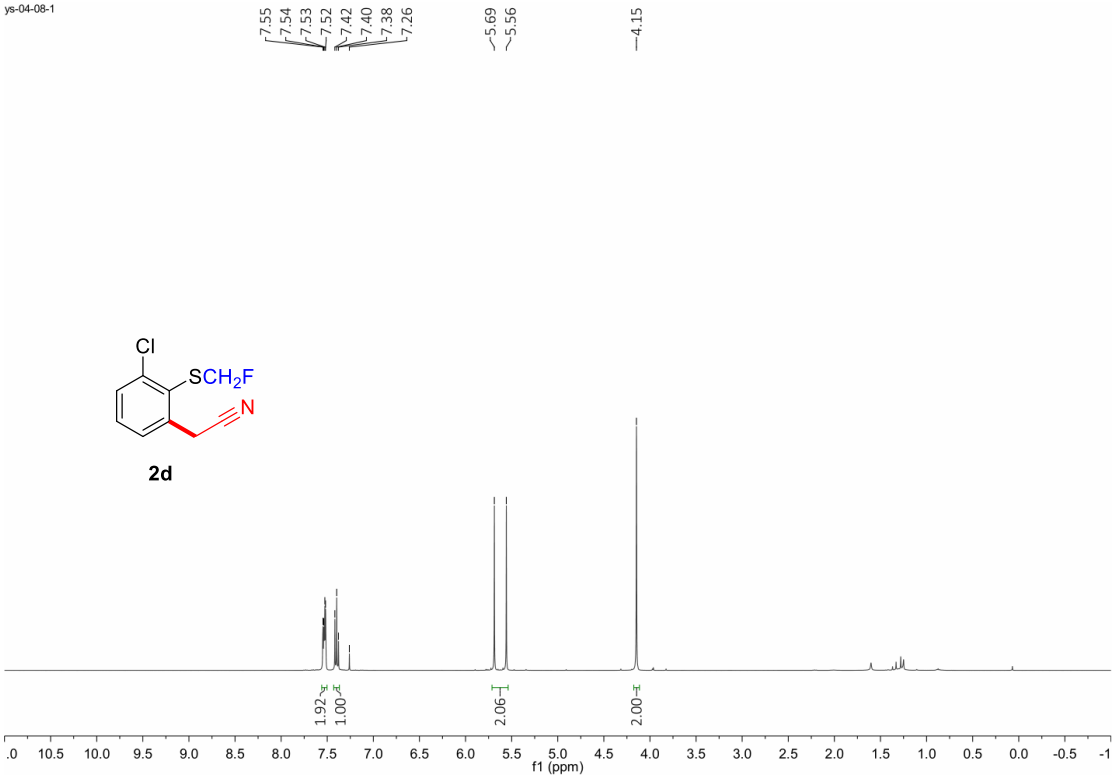

YS-03-100-2
138.69
135.89
131.62
129.83
129.39
124.55
122.03
120.20
118.36
117.60
77.37
77.16
76.95
23.18
SCHF2
N
2b
f1 (ppm)

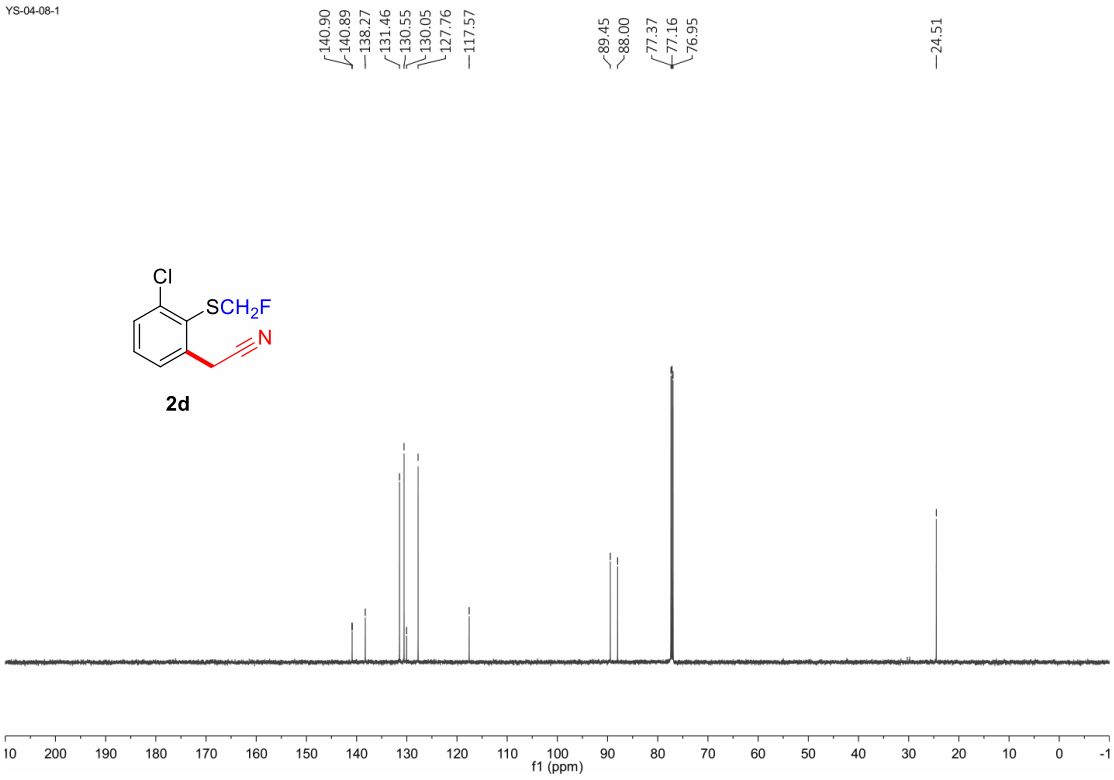

YS-03-100-2
-91.34
-91.44
SCHF2
N
2b
f1 (ppm)

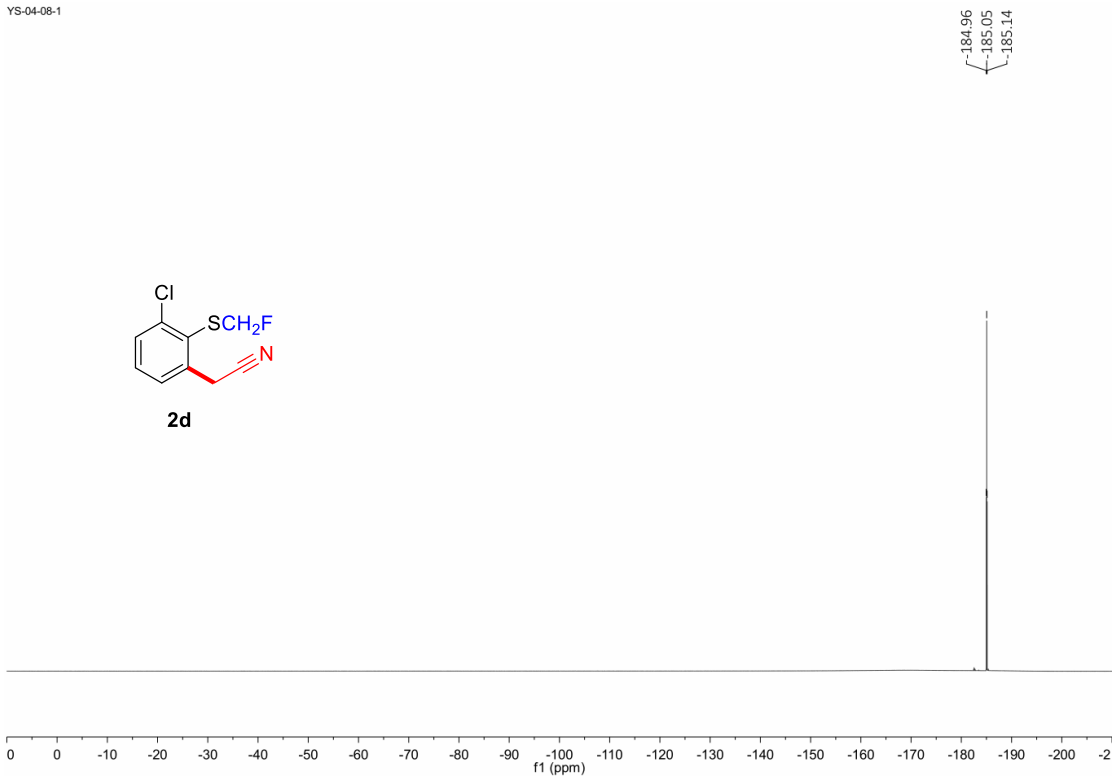

2c
7.77
7.76
7.68
7.67
7.60
7.60
7.59
7.58
7.57
7.57
7.45
7.45
7.44
7.44
7.43
7.42
7.26
4.07
SCF3
N
2c
0.99
1.04
1.03
1.03
2.02
f1 (ppm)

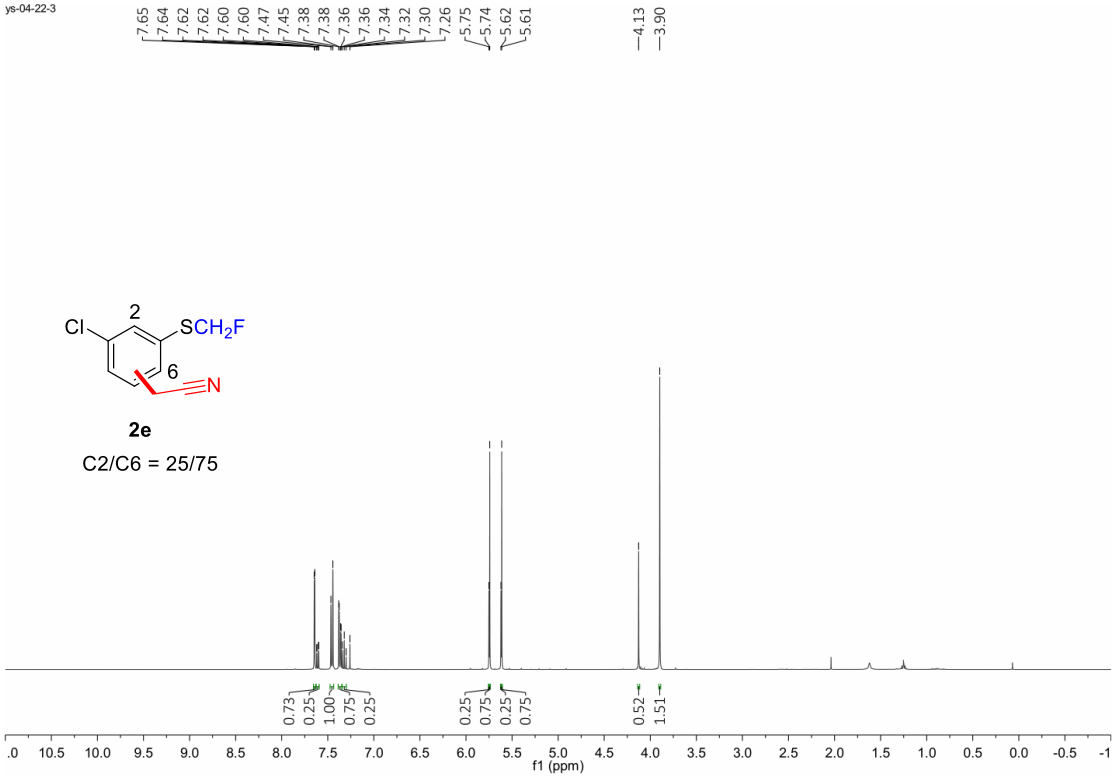

2c
139.38
136.23
132.67
130.31
130.04
129.65
128.27
126.22
123.41
117.28
77.37
77.16
76.95
23.05
SCF3
N
2c
f1 (ppm)

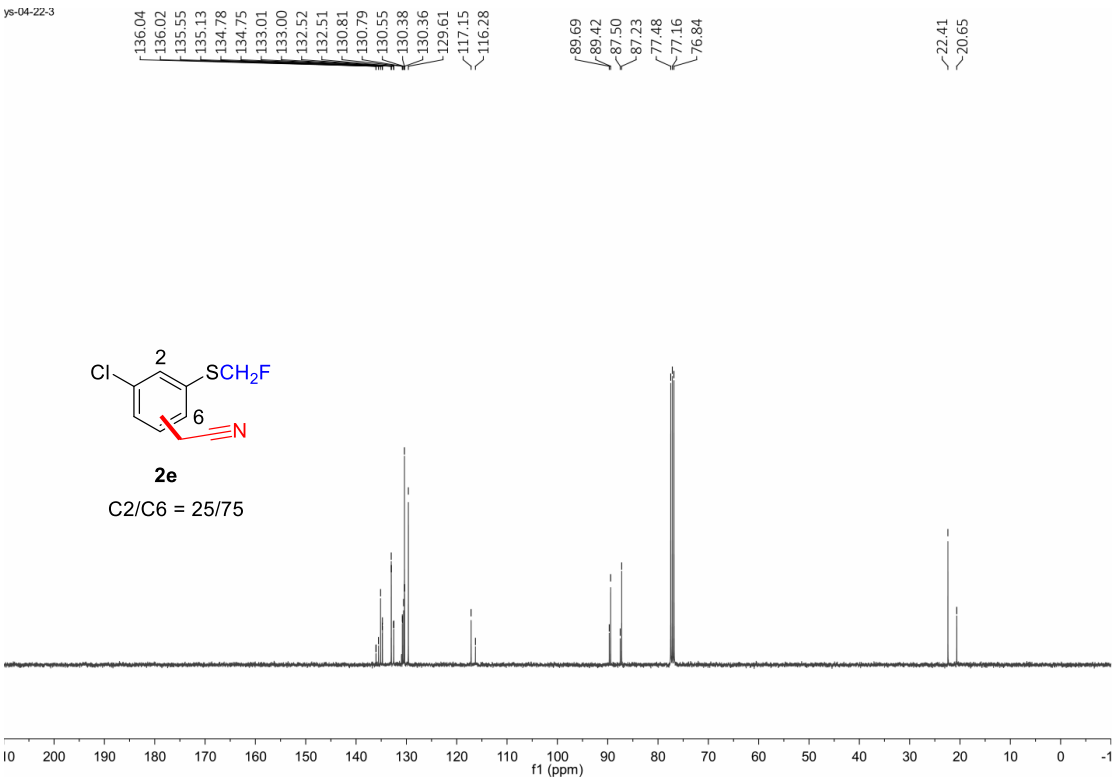

ys-03-98-3
-42.32
SCF3
N
2c
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

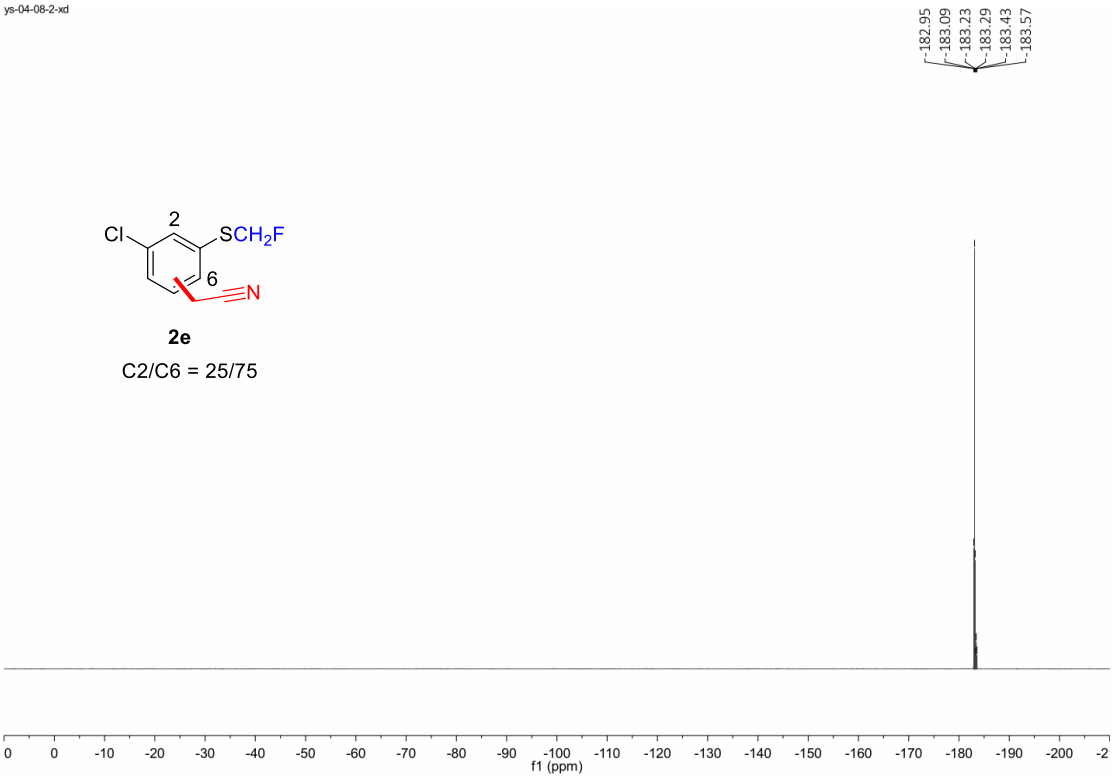

ys-04-08-1
7.55
7.54
7.53
7.52
7.42
7.40
7.38
7.26
5.69
5.56
4.15
Cl
SCH2F
N
2d
1.92
1.00
2.06
2.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

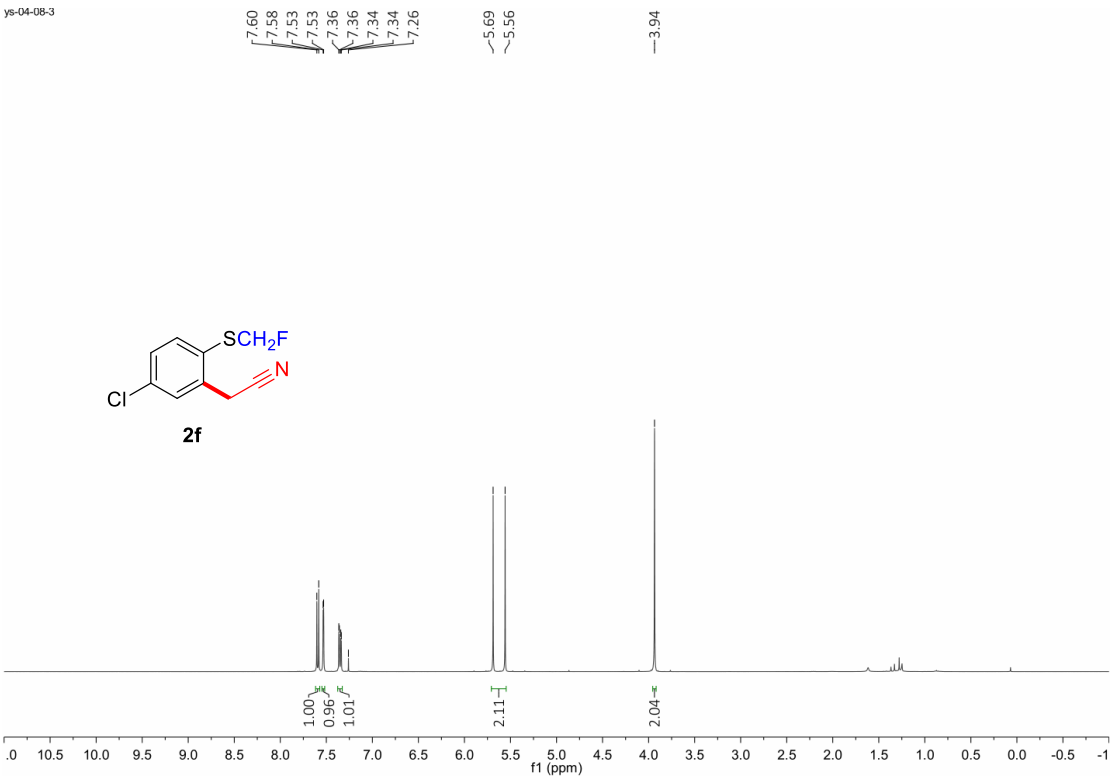

YS-04-08-1
140.90
140.89
138.27
131.46
130.55
130.05
127.76
117.57
89.45
88.00
77.37
77.16
76.95
24.51
Cl
SCH2F
N
2d
f1 (ppm)

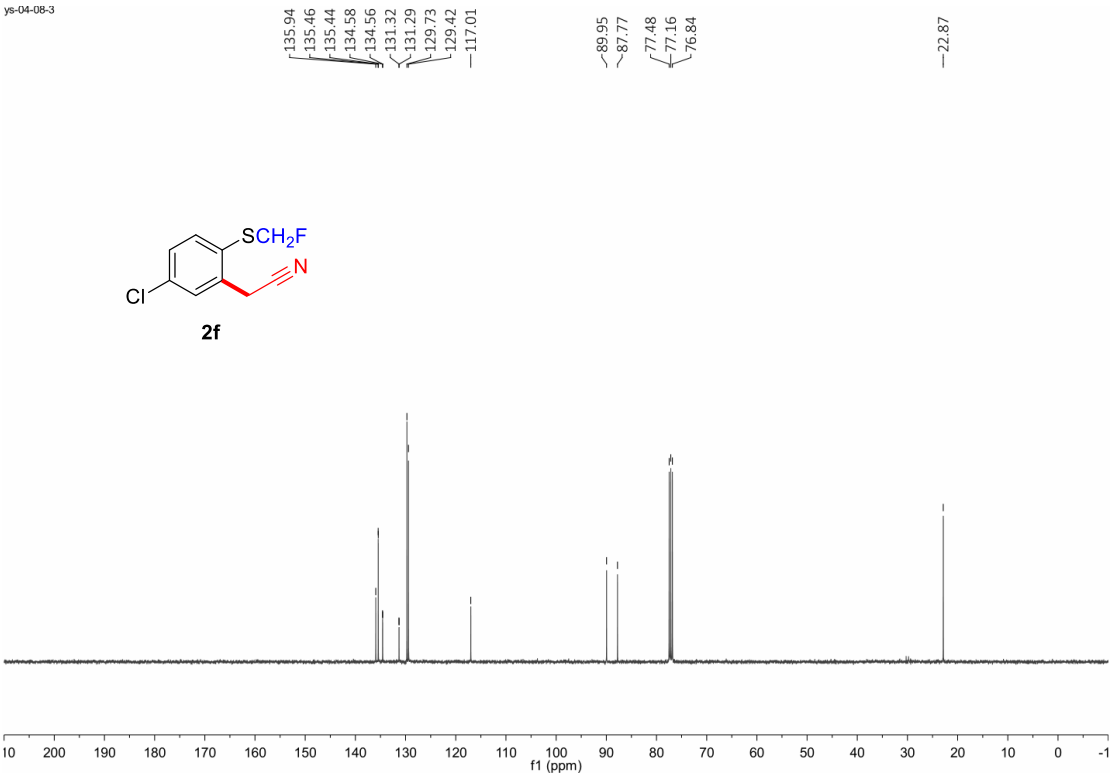

YS-04-08-1
-184.96
-185.05
-185.14
Cl
SCH2F
N
2d
f1 (ppm)

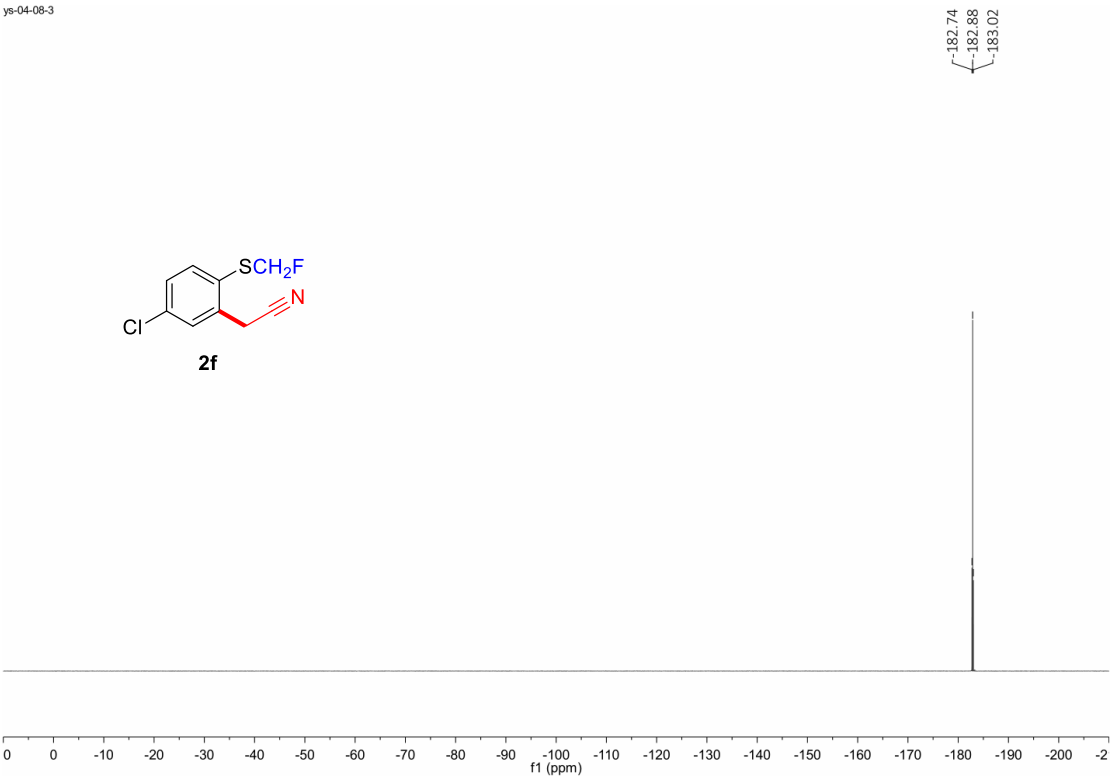

ys-04-22-3
7.65
7.64
7.62
7.62
7.60
7.60
7.47
7.45
7.38
7.38
7.36
7.36
7.34
7.32
7.30
7.26
5.75
5.74
5.62
5.61
4.13
3.90
Cl
2
SCH2F
6
N
2e
C2/C6 = 25/75
0.73
0.25
1.00
0.75
0.25
0.25
0.75
0.25
0.75
0.52
1.51
f1 (ppm)

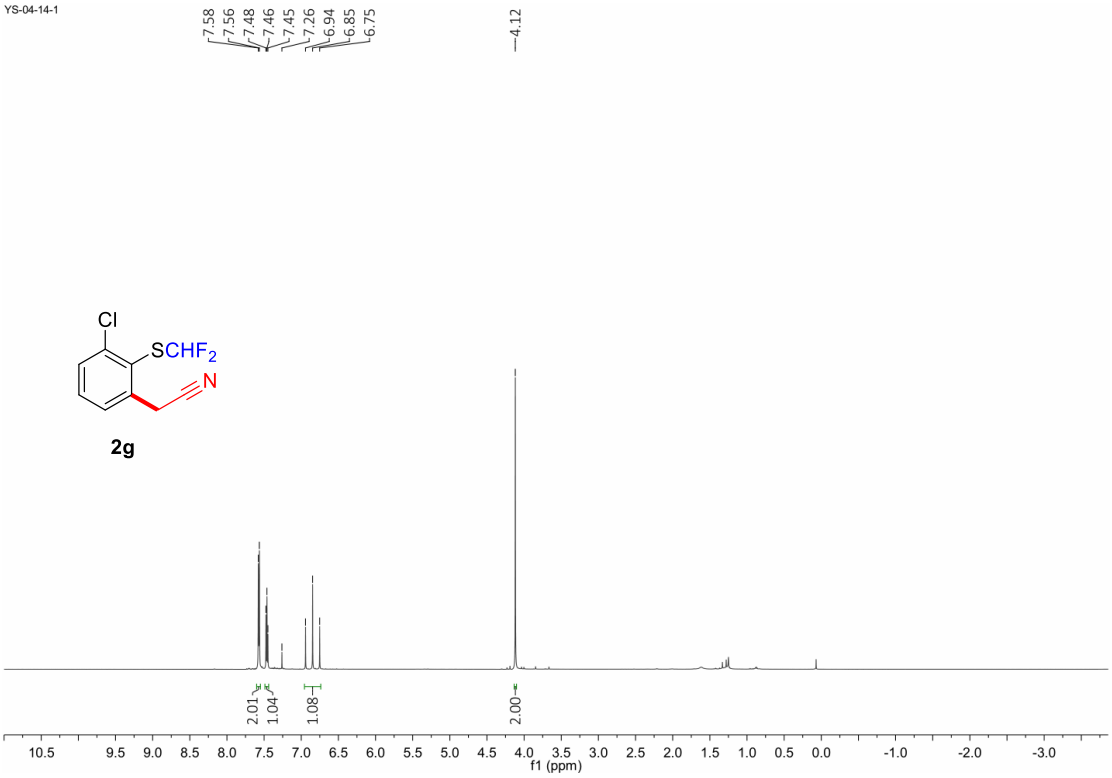

ys-04-22-3
136.04
136.02
135.55
135.13
134.78
134.75
133.01
133.00
132.52
132.51
130.81
130.79
130.55
130.38
130.36
129.61
117.15
116.28
89.69
89.42
87.50
87.23
77.48
77.16
76.84
22.41
20.65
Cl
2
SCH2F
6
N
2e
C2/C6 = 25/75
f1 (ppm)

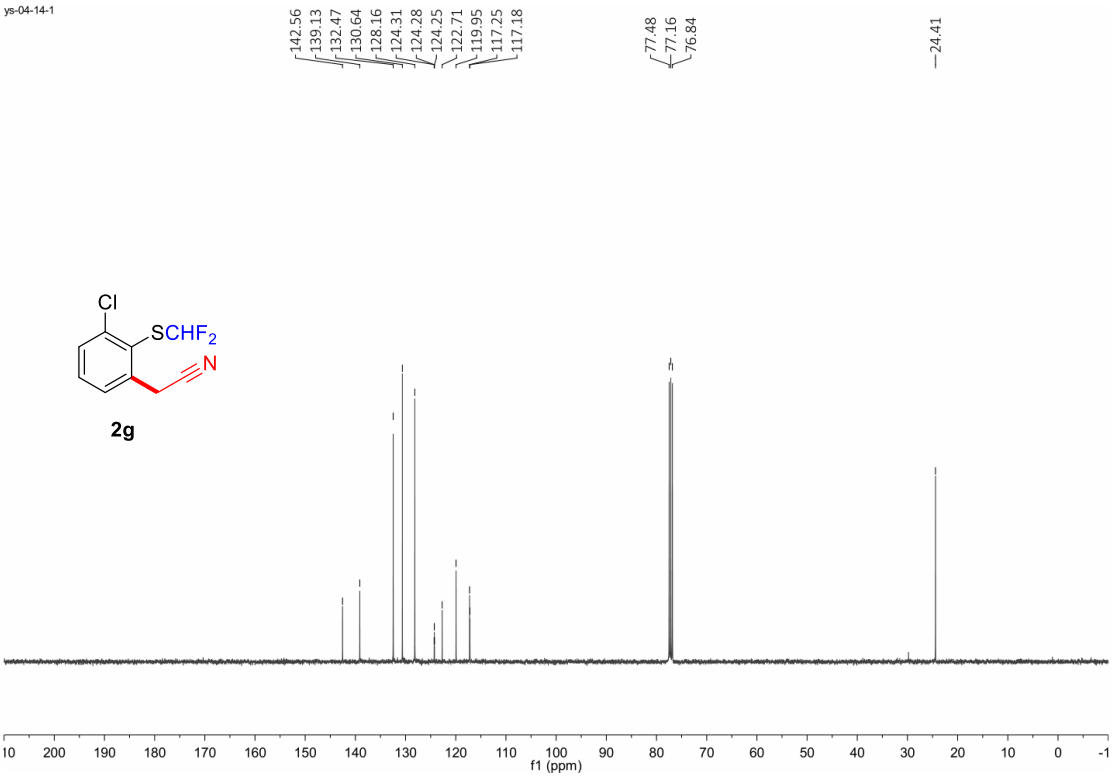

ys-04-08-2-xd
182.95
183.09
183.23
183.29
183.43
183.57
Cl
2
SCH2F
6
N
2e
C2/C6 = 25/75
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

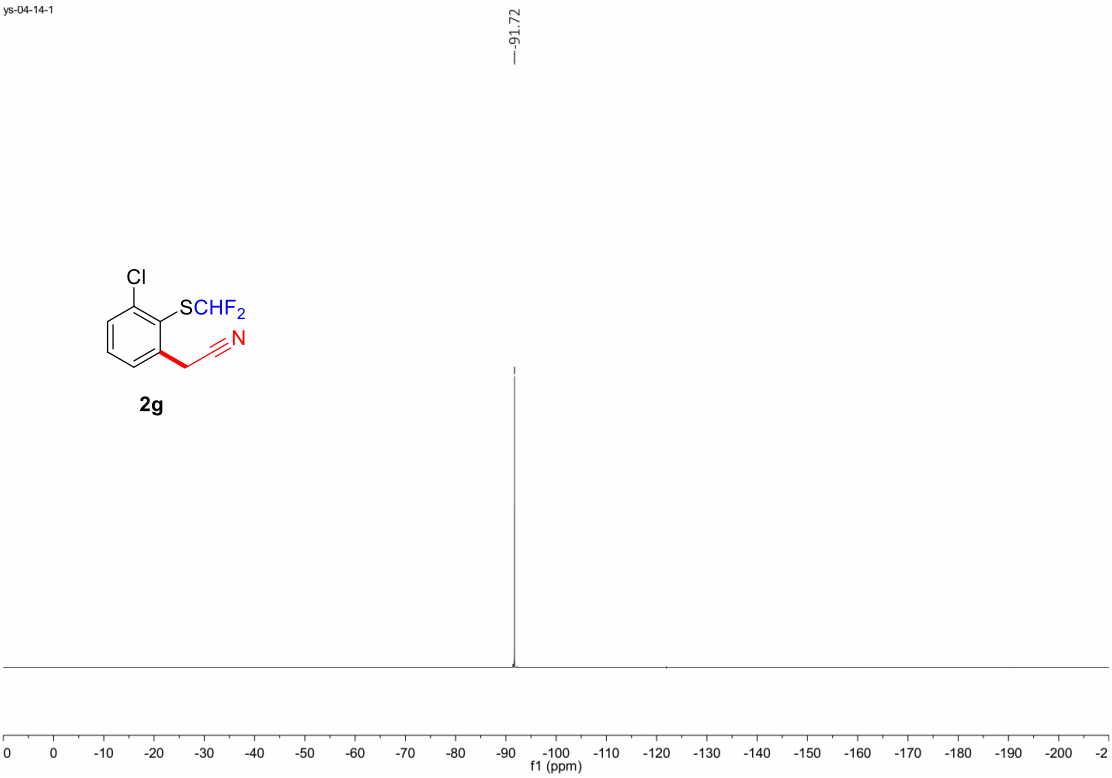

ys-04-08-3
7.60
7.58
7.53
7.53
7.36
7.36
7.34
7.34
7.26
5.69
5.56
3.94
SCH2F
N
Cl
2f
1.00
0.96
1.01
2.11
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

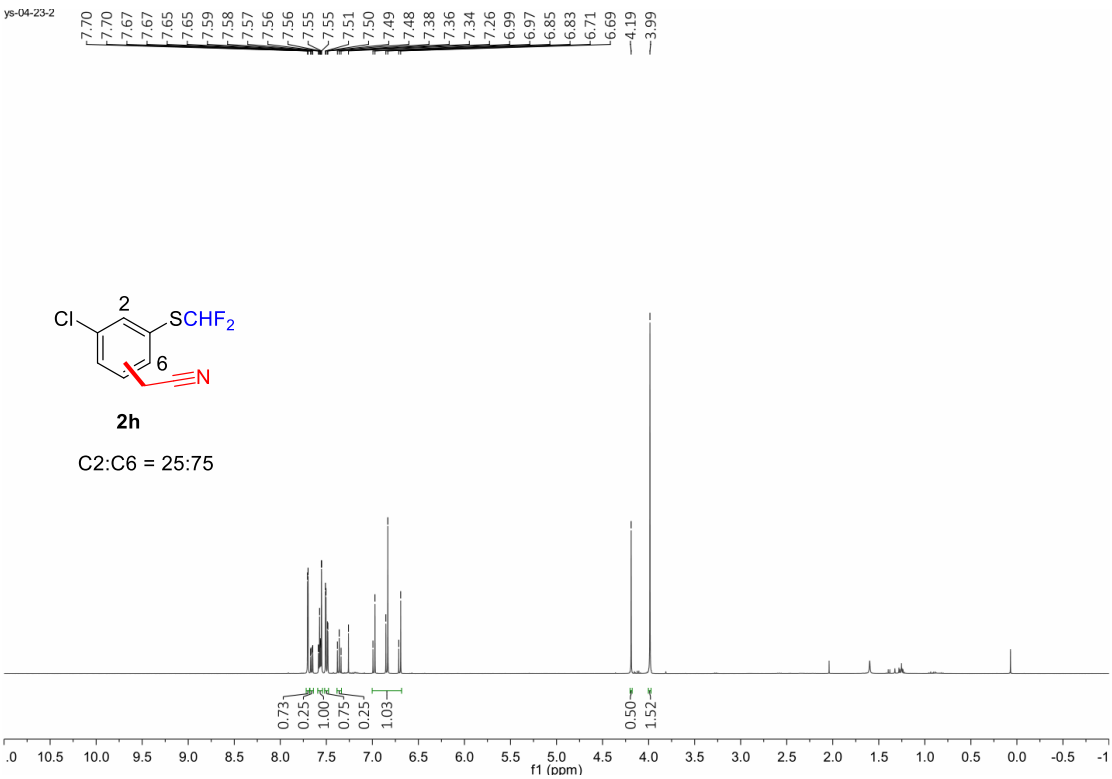

ys-04-08-3
135.94
135.46
135.44
134.58
134.56
131.32
131.29
129.73
129.42
117.01
89.95
87.77
77.48
77.16
76.84
22.87
SCH2F
N
Cl
2f
f1 (ppm)

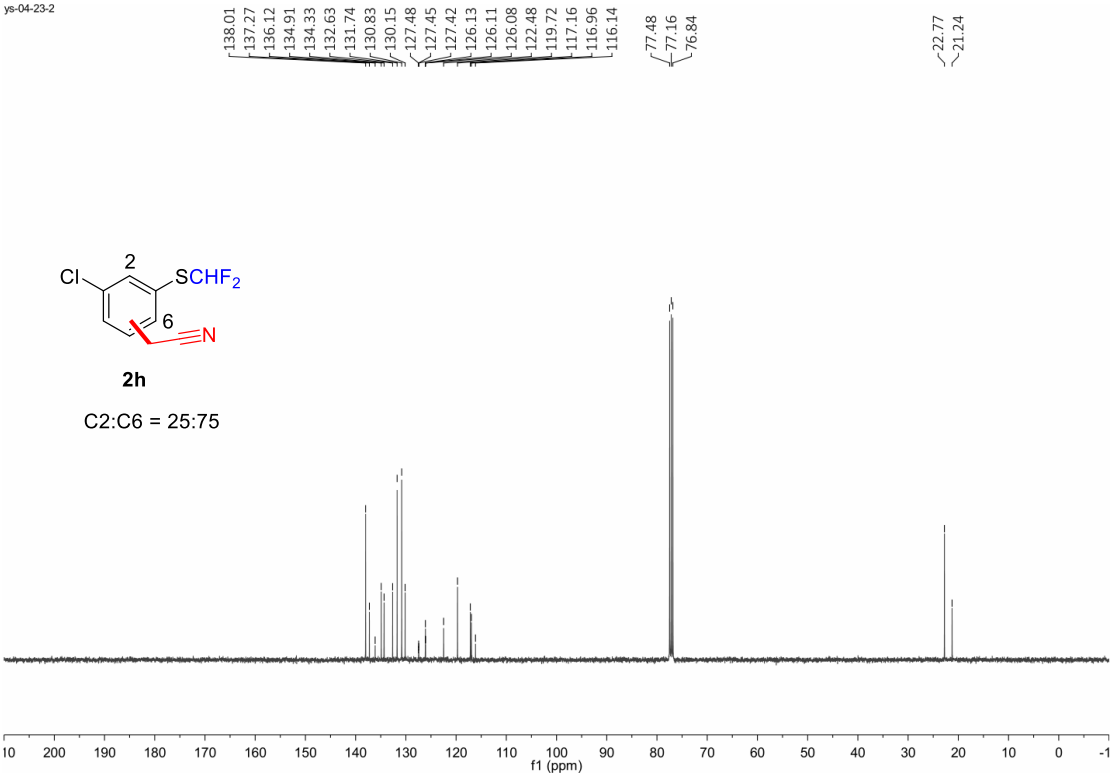

ys-04-08-3
-182.74
-182.88
-183.02
SCH2F
N
Cl
2f
f1 (ppm)

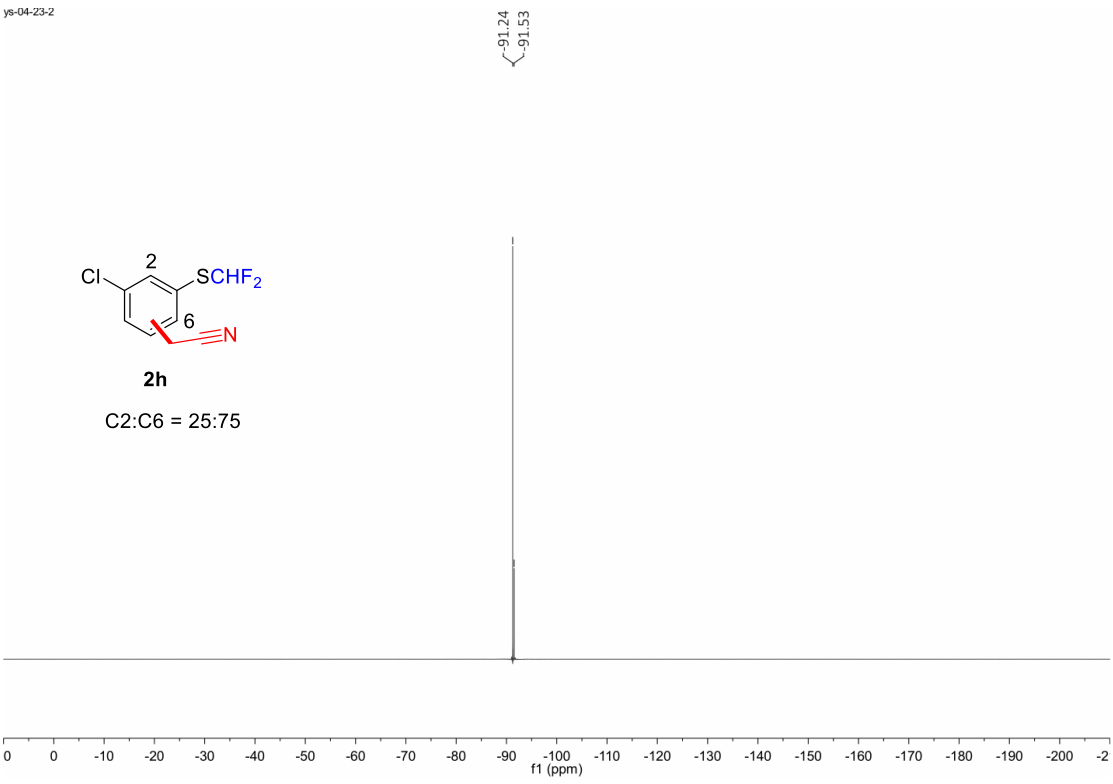

YS-04-14-1
7.58
7.56
7.48
7.46
7.45
7.26
6.94
6.85
6.75
4.12
Cl
SCHF2
N
2g
2.01
1.04
1.08
2.00
f1 (ppm)

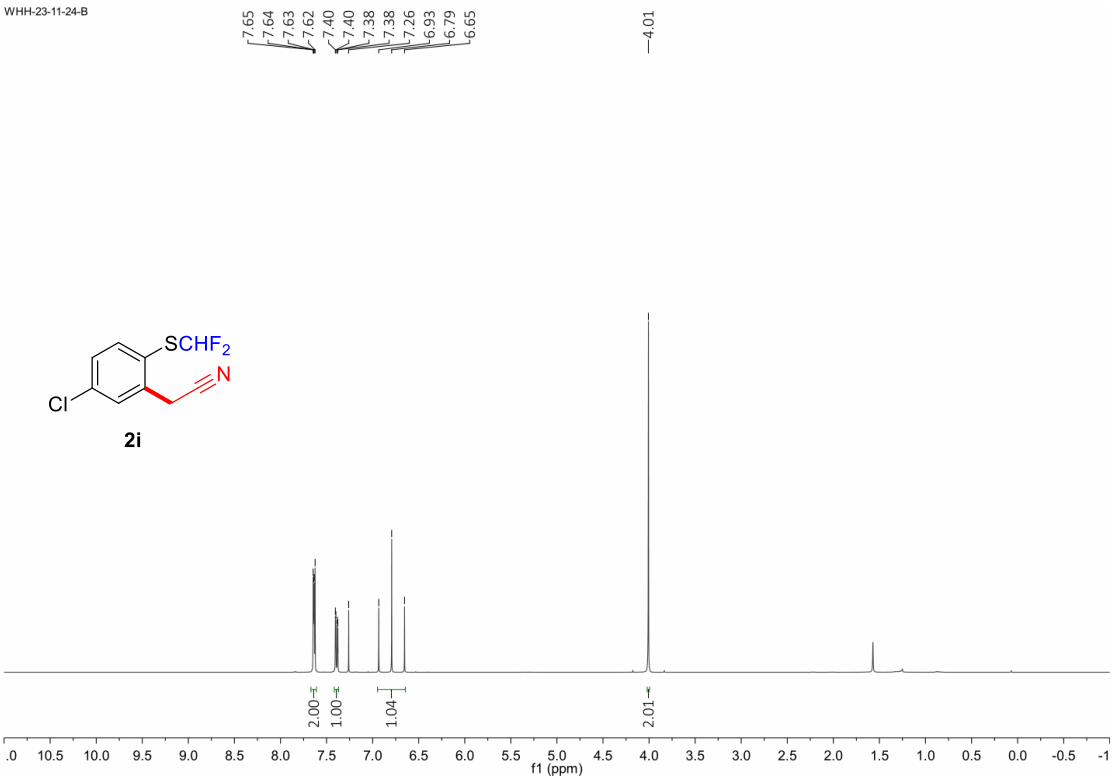

ys-04-14-1
142.56
139.13
132.47
130.64
128.16
124.31
124.28
124.25
122.71
119.95
117.25
117.18
77.48
77.16
76.84
24.41
Cl
SCHF2
N
2g
f1 (ppm)

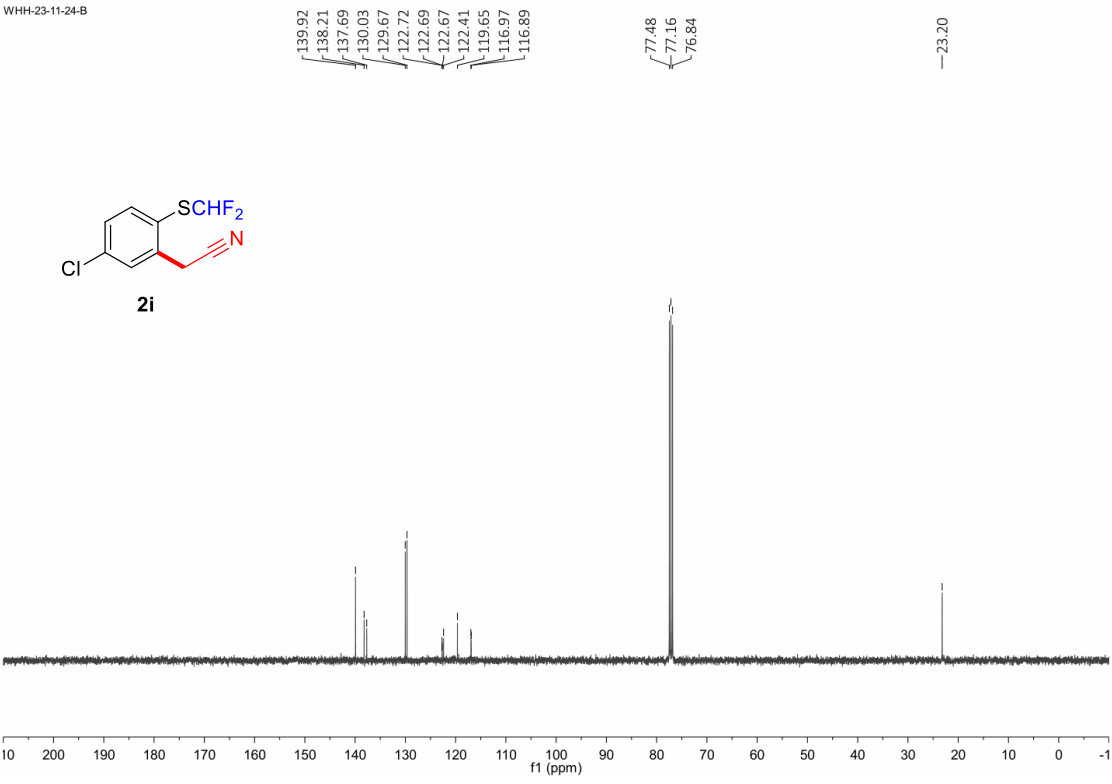

ys-04-14-1
-91.72
Cl
SCHF2
N
2g
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)


ys-04-23-2
7.70 7.70 7.67 7.67 7.65 7.65 7.59 7.58 7.57 7.56 7.56 7.55 7.55 7.51 7.50 7.49 7.48 7.38 7.36 7.34 7.26 6.99 6.97 6.85 6.83 6.71 6.69 4.19 3.99
Cl
2
SCHF2
6
N
2h
C2:C6 = 25:75
0.73 0.25 1.00 0.75 0.25 1.03 0.50 1.52
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

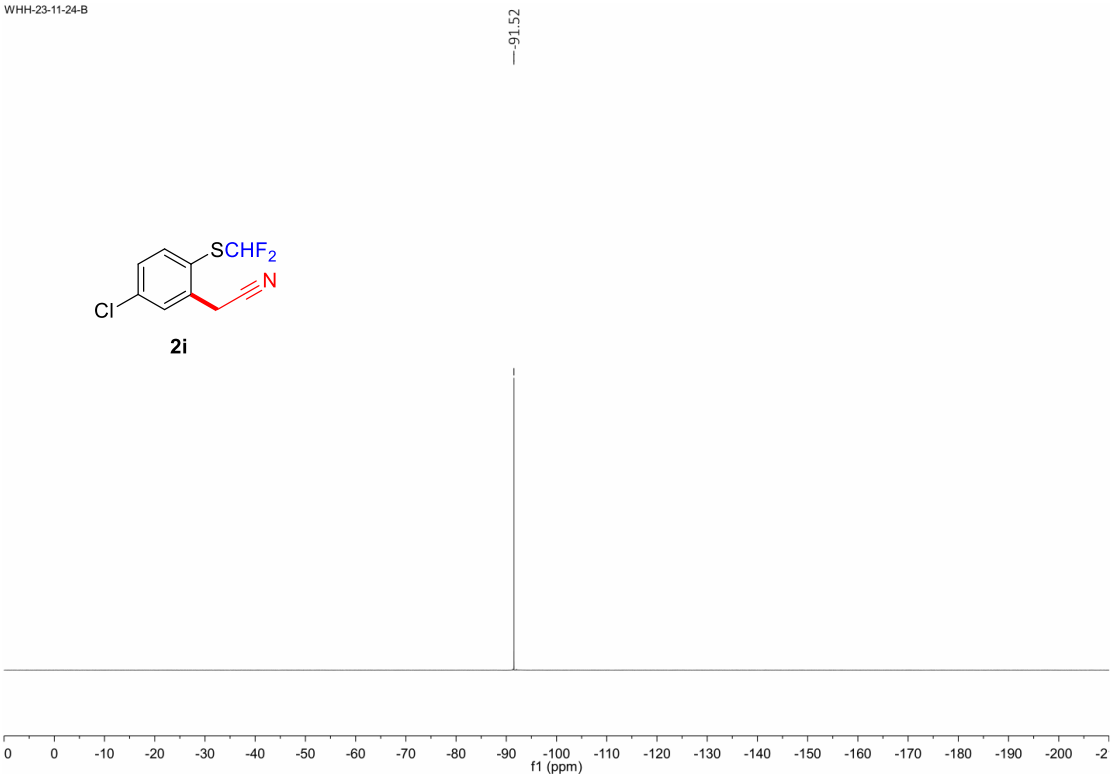

ys-04-23-2
138.01
137.27
136.12
134.91
134.33
132.63
131.74
130.83
130.15
127.48
127.45
127.42
126.13
126.11
126.08
122.48
119.72
117.16
116.96
116.14
77.48
77.16
76.84
22.77
21.24
Cl
2
SCHF2
6
N
2h
C2:C6 = 25:75
f1 (ppm)


ys-04-23-2
-91.24
-91.53
Cl
2
SCHF2
6
N
2h
C2:C6 = 25:75
f1 (ppm)


WHH-23-11-24-B
7.65
7.64
7.63
7.62
7.40
7.40
7.38
7.38
7.26
6.93
6.79
6.65
4.01
SCHF2
N
Cl
2i
2.00
1.00
1.04
2.01
f1 (ppm)

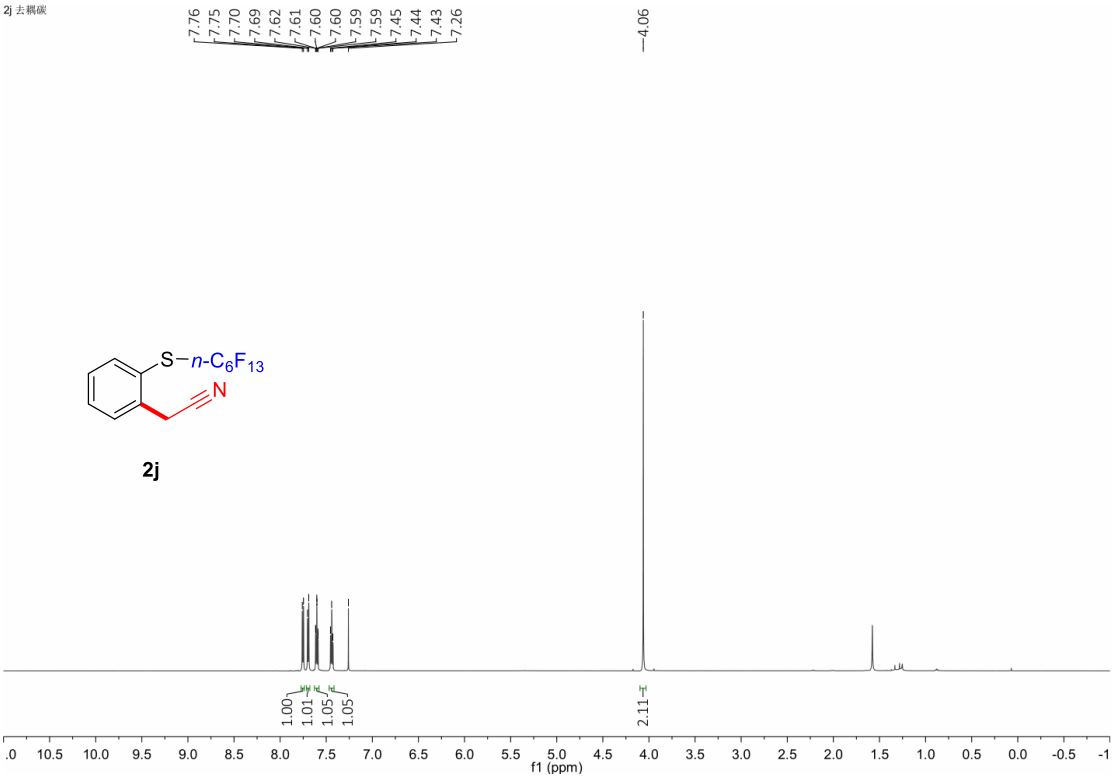

WHH-23-11-24-B
139.92
138.21
137.69
130.03
129.67
122.72
122.69
122.67
122.41
119.65
116.97
116.89
77.48
77.16
76.84
23.20
SCHF2
N
Cl
2i
f1 (ppm)

WHH-23-11-24-B

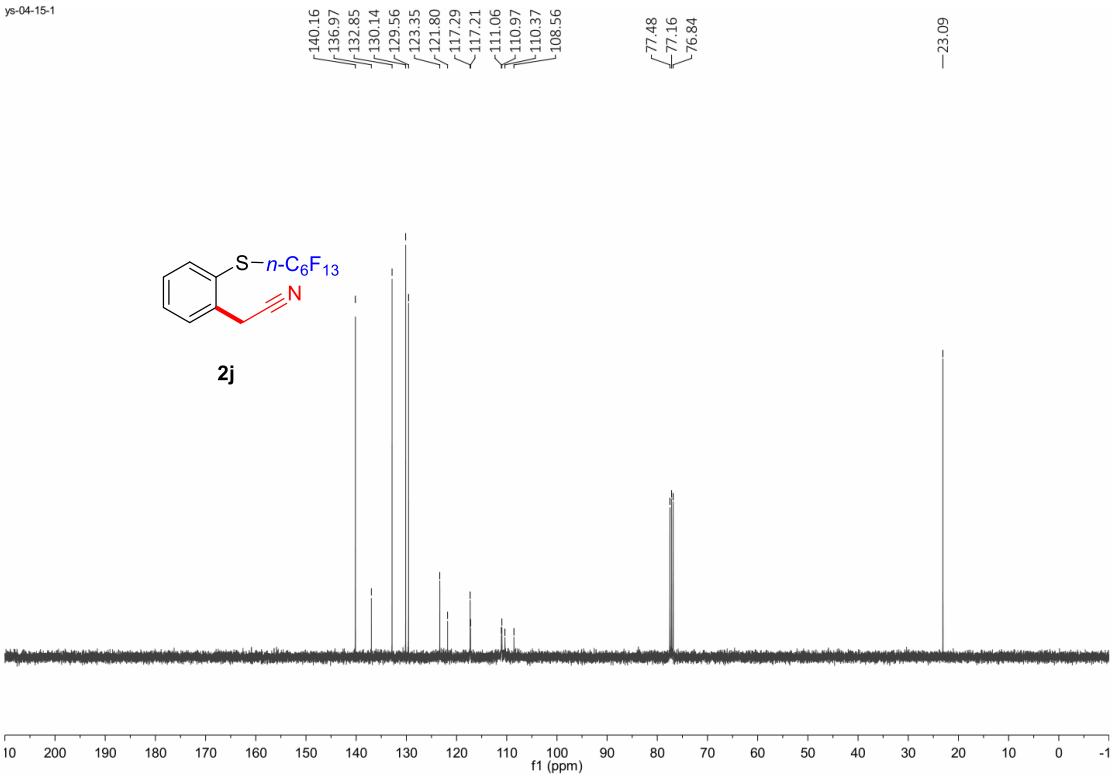


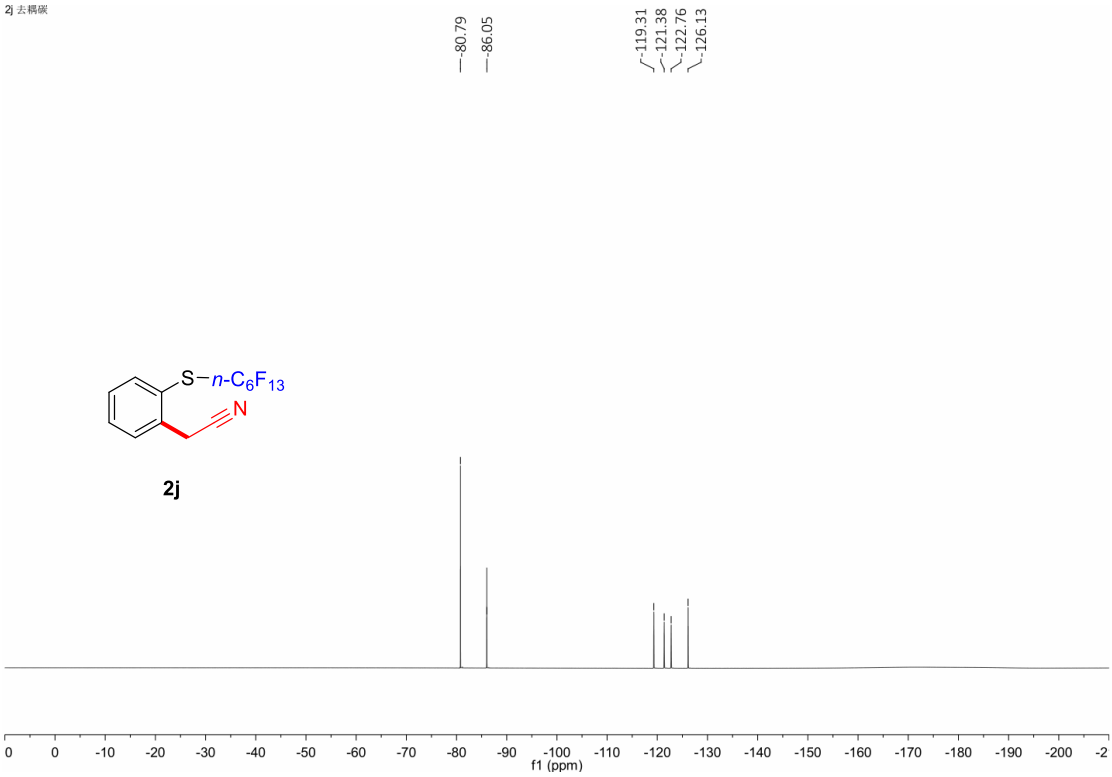
2i

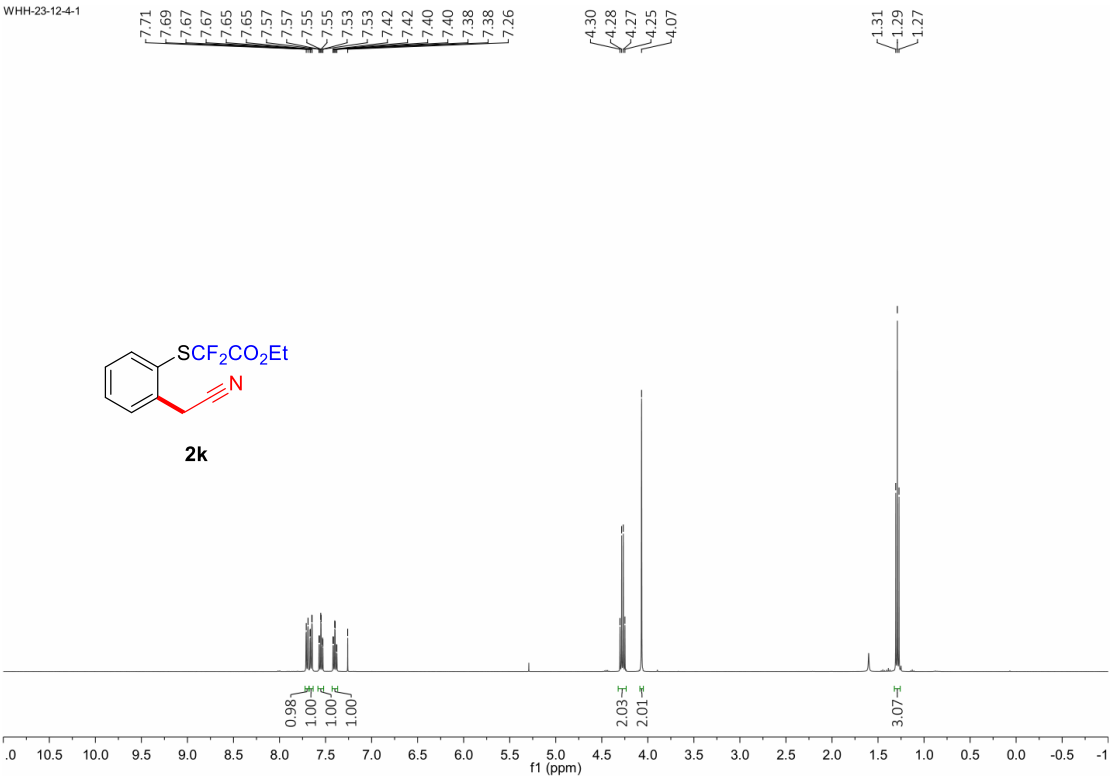
2j 去耦碳

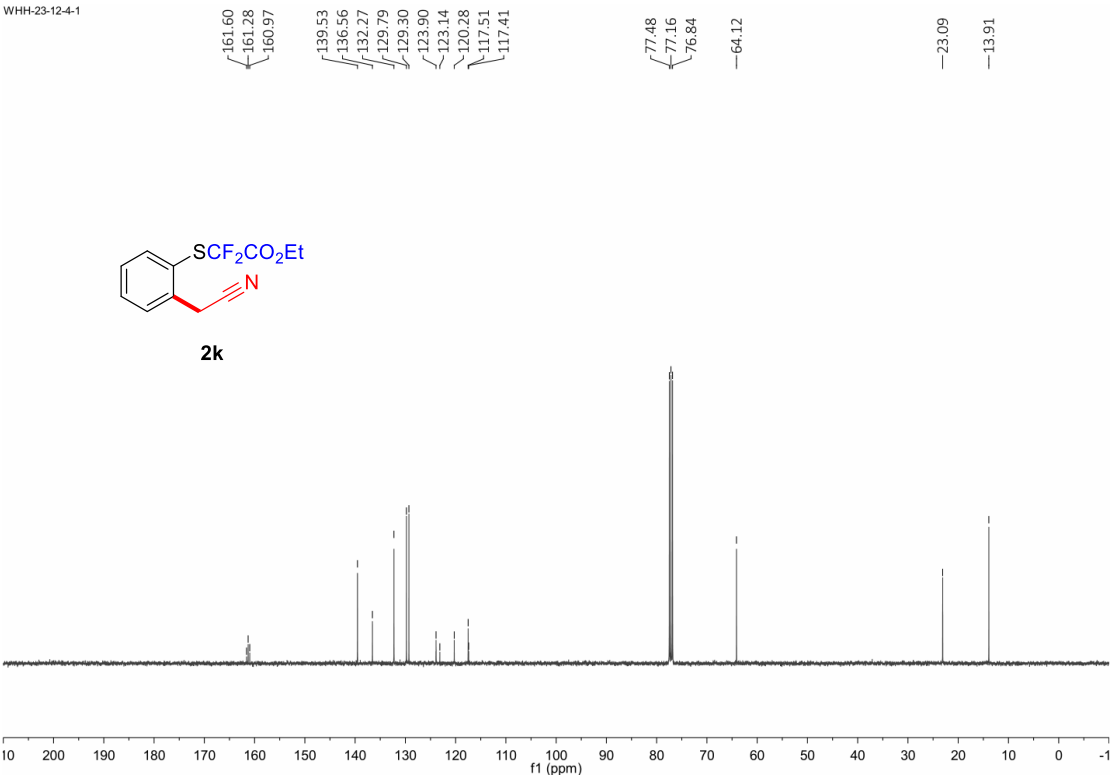


2j

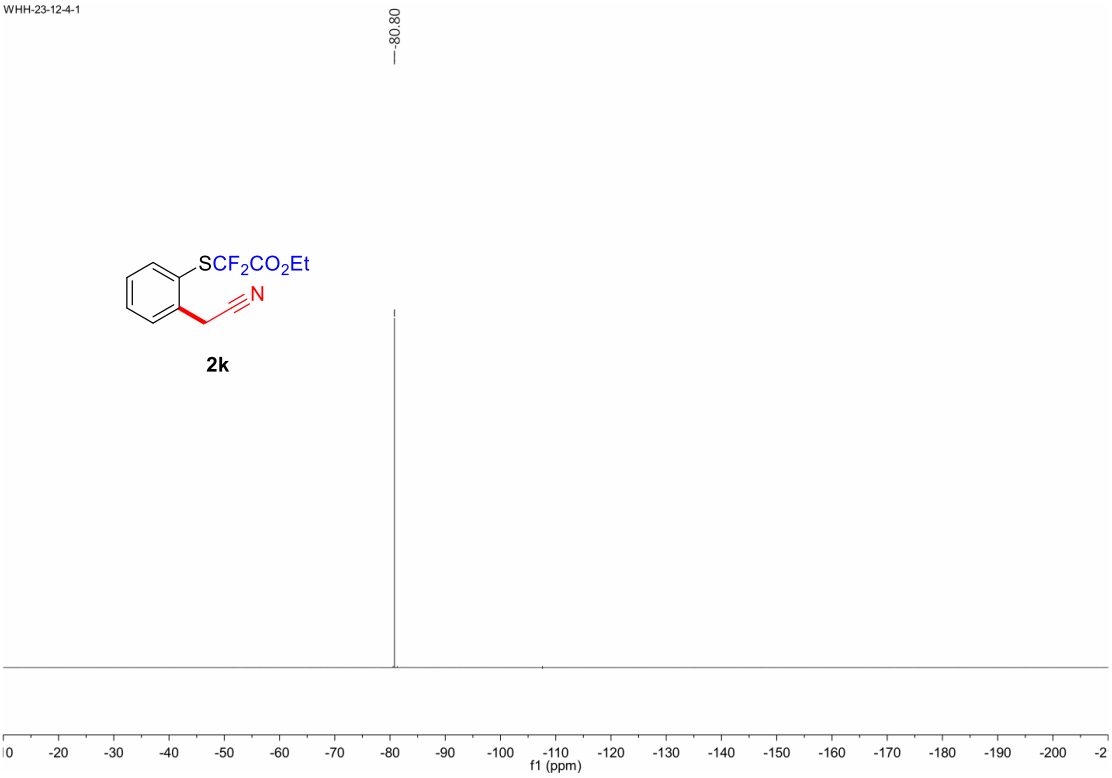

ys-04-15-1
140.16
136.97
132.85
130.14
129.56
123.35
121.80
117.29
117.21
111.06
110.97
110.37
108.56
77.48
77.16
76.84
23.09
S−n-C6F13
N
2j
f1 (ppm)


2j 去耦碳
-80.79
-86.05
-119.31
-121.38
-122.76
-126.13
S−n-C6F13
N
2j
f1 (ppm)


WHH-23-12-4-1
7.71
7.69
7.67
7.67
7.65
7.65
7.57
7.57
7.55
7.55
7.53
7.53
7.42
7.42
7.40
7.40
7.38
7.38
7.26
4.30
4.28
4.27
4.25
4.07
1.31
1.29
1.27
SCF2CO2Et
N
2k
0.98
1.00
1.00
1.00
2.03
2.01
3.07
f1 (ppm)

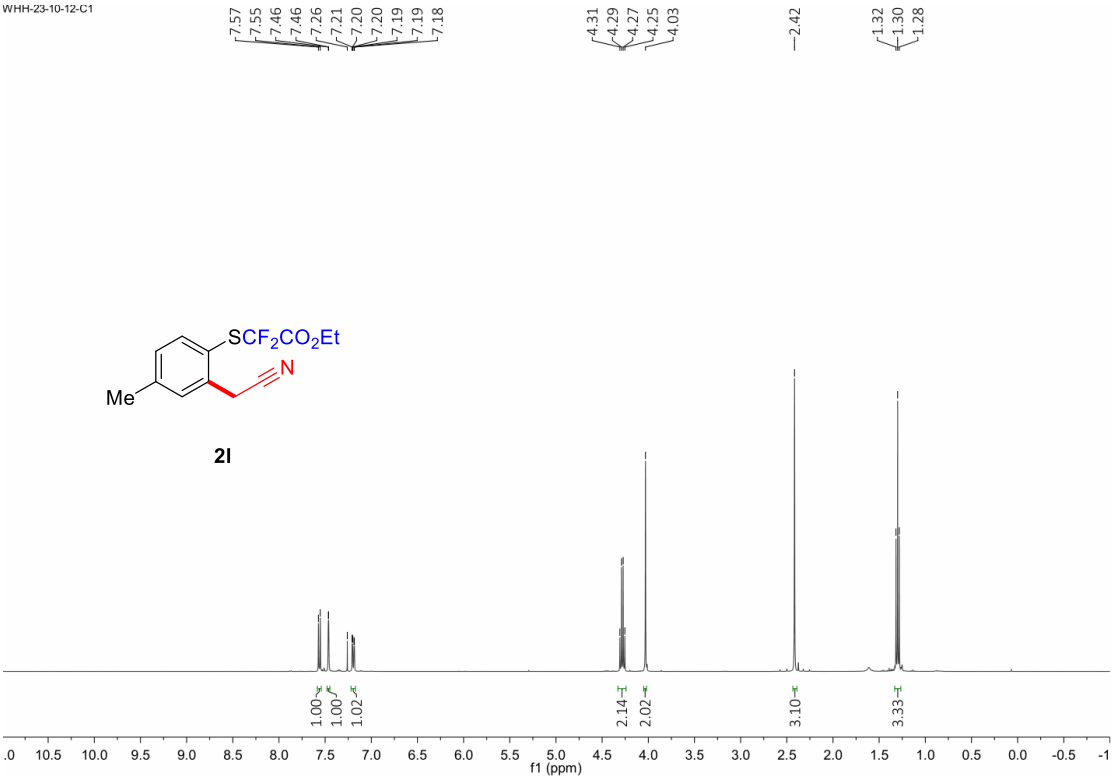

WHH-23-12-4-1
161.60
161.28
160.97
139.53
136.56
132.27
129.79
129.30
123.90
123.14
120.28
117.51
117.41
77.48
77.16
76.84
64.12
23.09
13.91
SCF2CO2Et
N
2k
f1 (ppm)

WHH-23-12-4-1

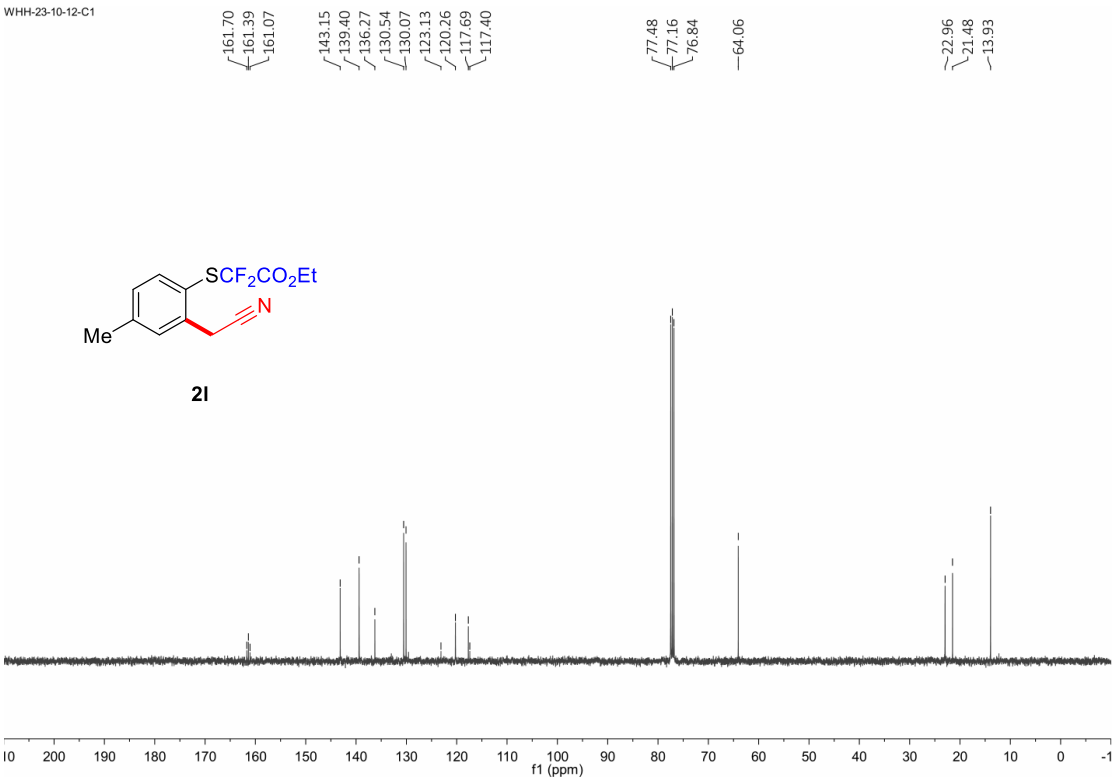


2k

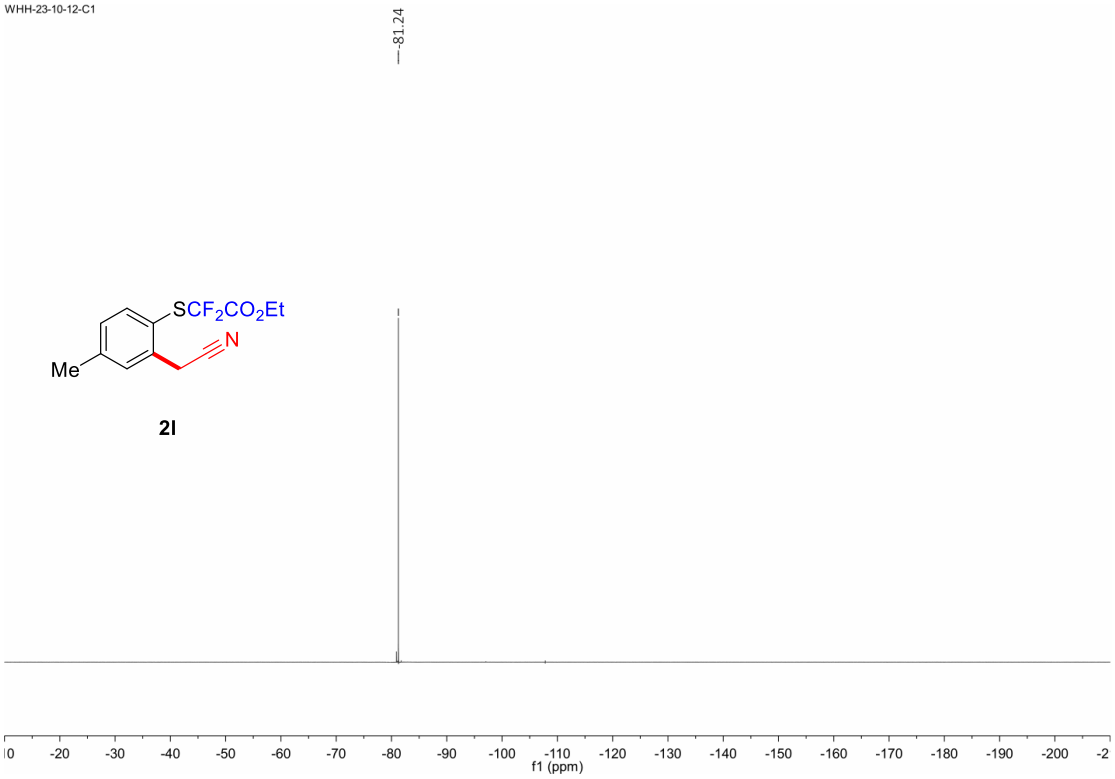
WHH-23-10-12-C1



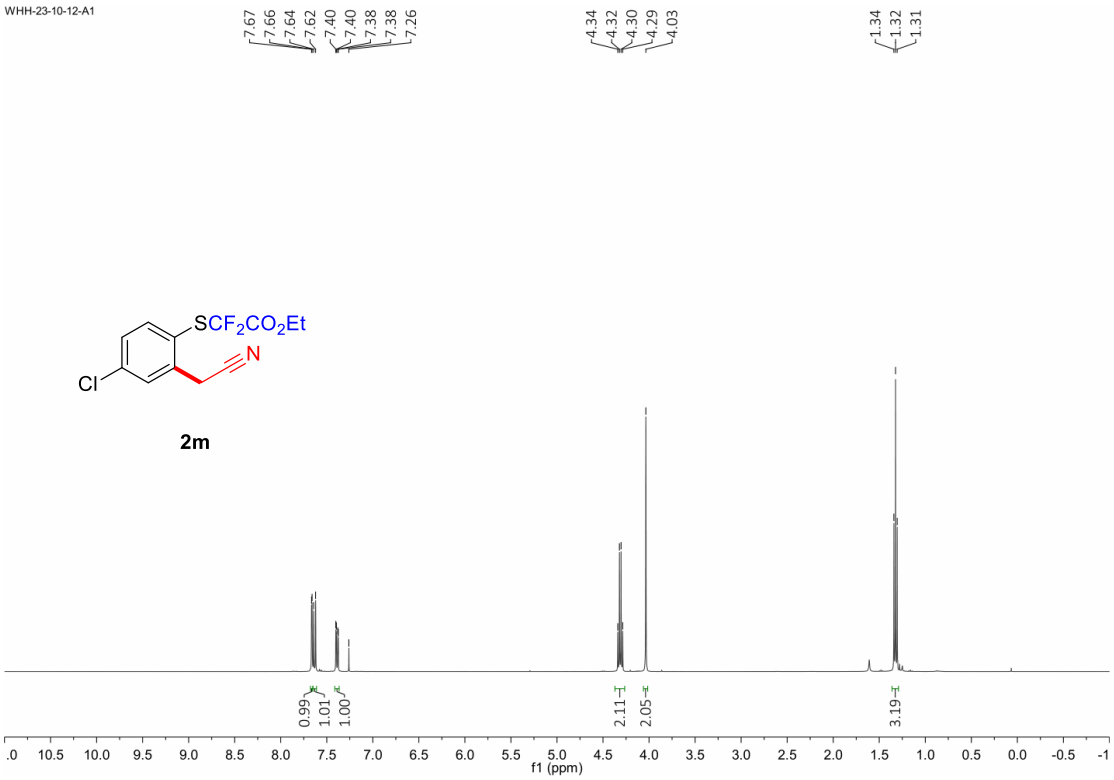
2l

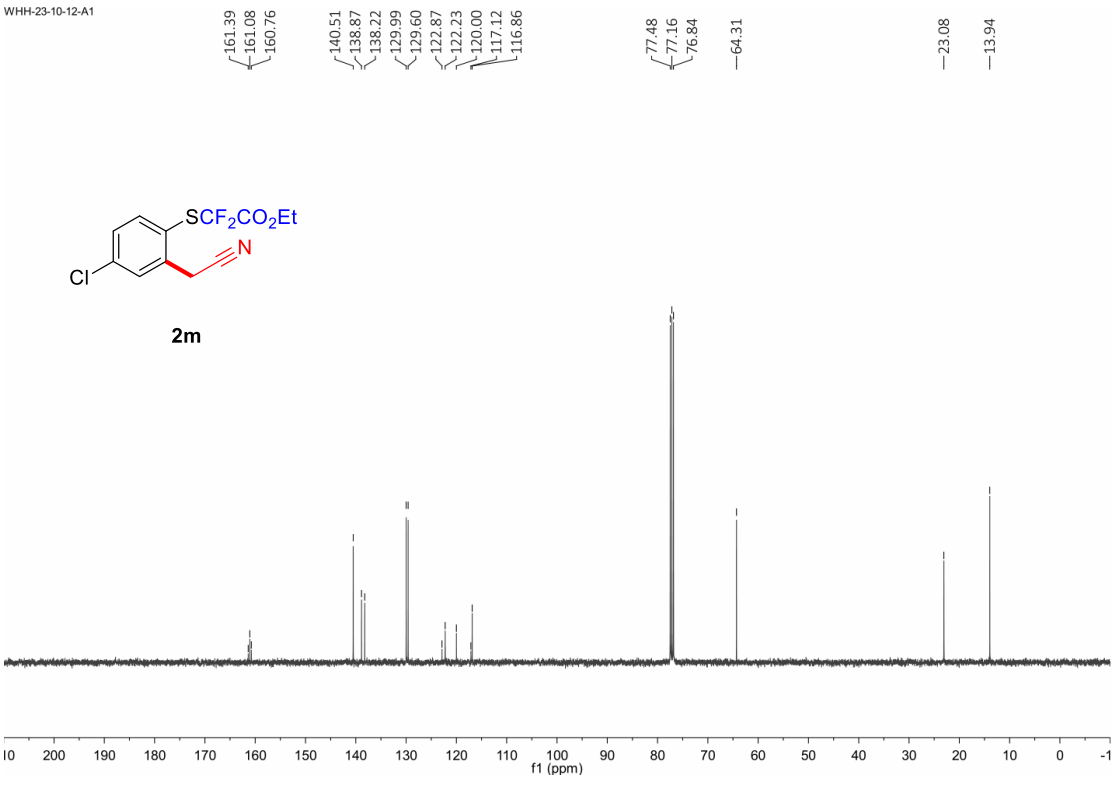

WHH-23-10-12-C1
161.70
161.39
161.07
143.15
139.40
136.27
130.54
130.07
123.13
120.26
117.69
117.40
77.48
77.16
76.84
64.06
22.96
21.48
13.93
SCF2CO2Et
N
Me
f1 (ppm)

2l

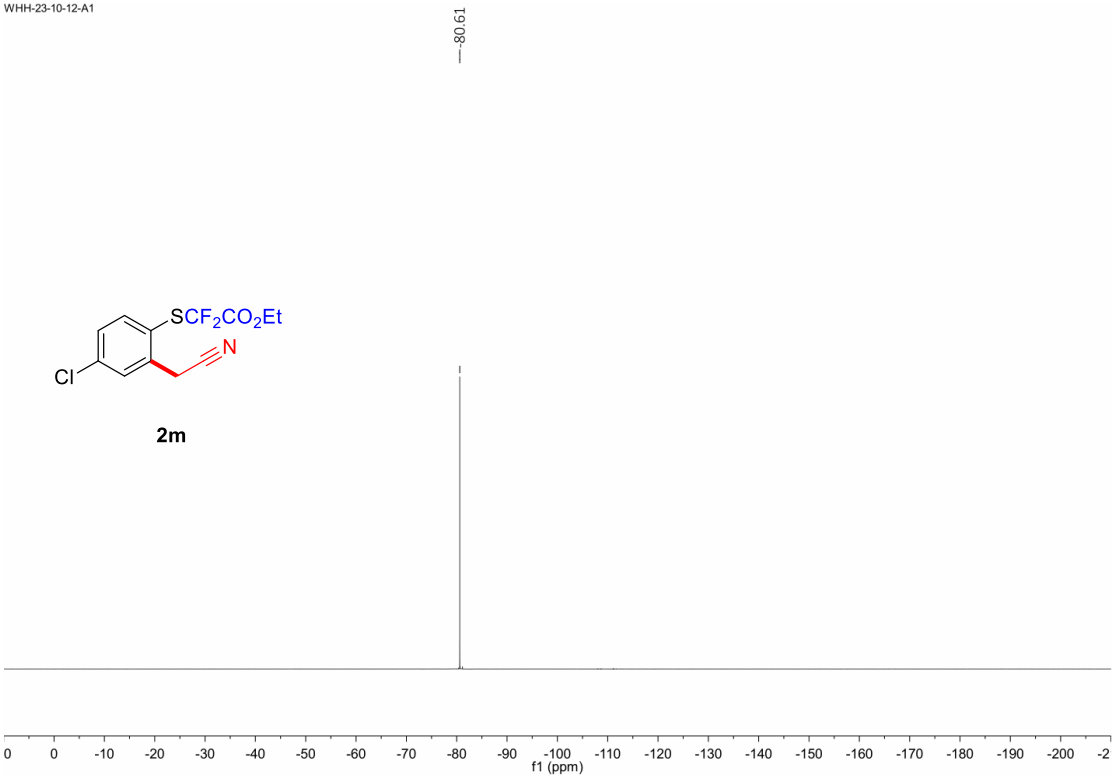

WHH-23-10-12-C1
-81.24
SCF2CO2Et
N
Me
f1 (ppm)

2l


WHH-23-10-12-A1
7.67
7.66
7.64
7.62
7.40
7.40
7.38
7.38
7.26
4.34
4.32
4.30
4.29
4.03
1.34
1.32
1.31
SCF2CO2Et
N
Cl
2m
0.99
1.01
1.00
2.11
2.05
3.19
f1 (ppm)

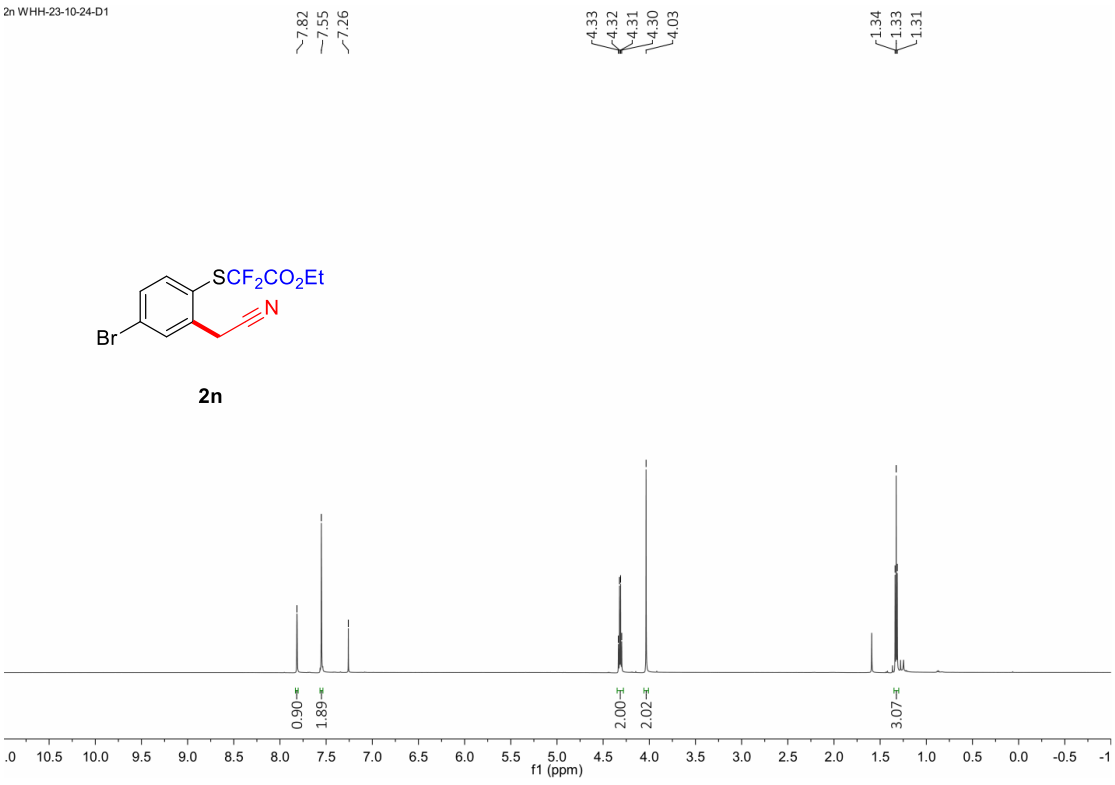

WHH-23-10-12-A1
161.39
161.08
160.76
140.51
138.87
138.22
129.99
129.60
122.87
122.23
120.00
117.12
116.86
77.48
77.16
76.84
64.31
23.08
13.94
SCF2CO2Et
N
Cl
2m
f1 (ppm)

WHH-23-10-12-A1

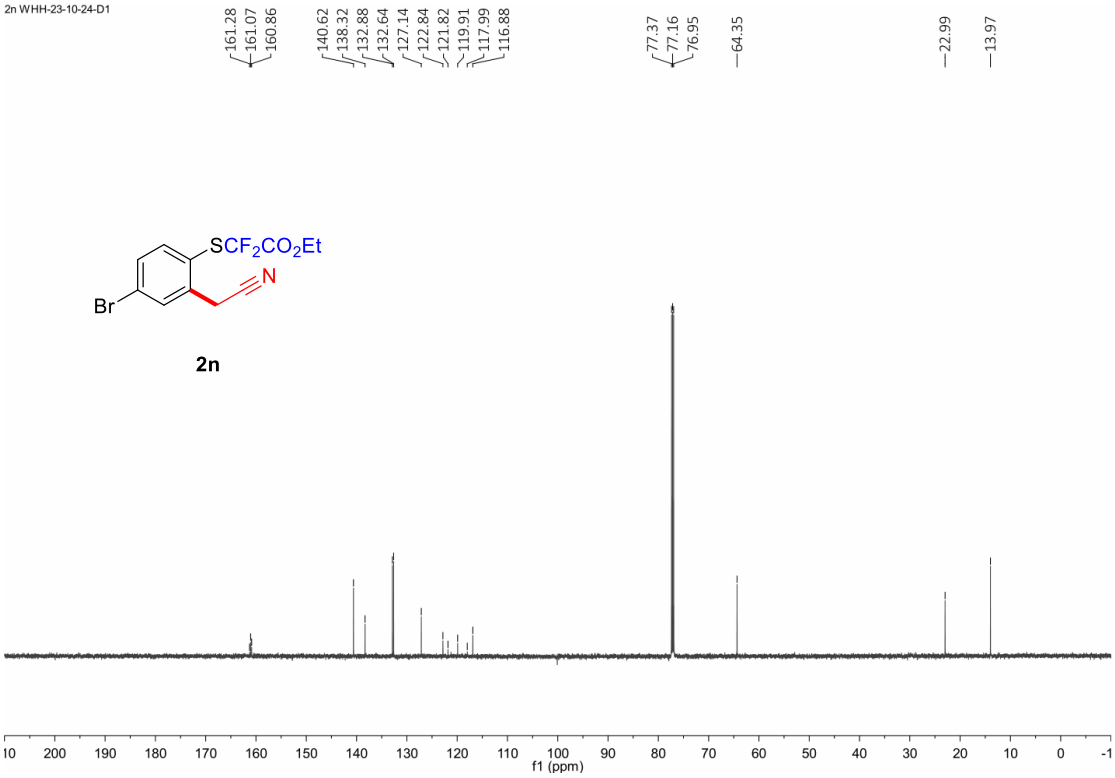


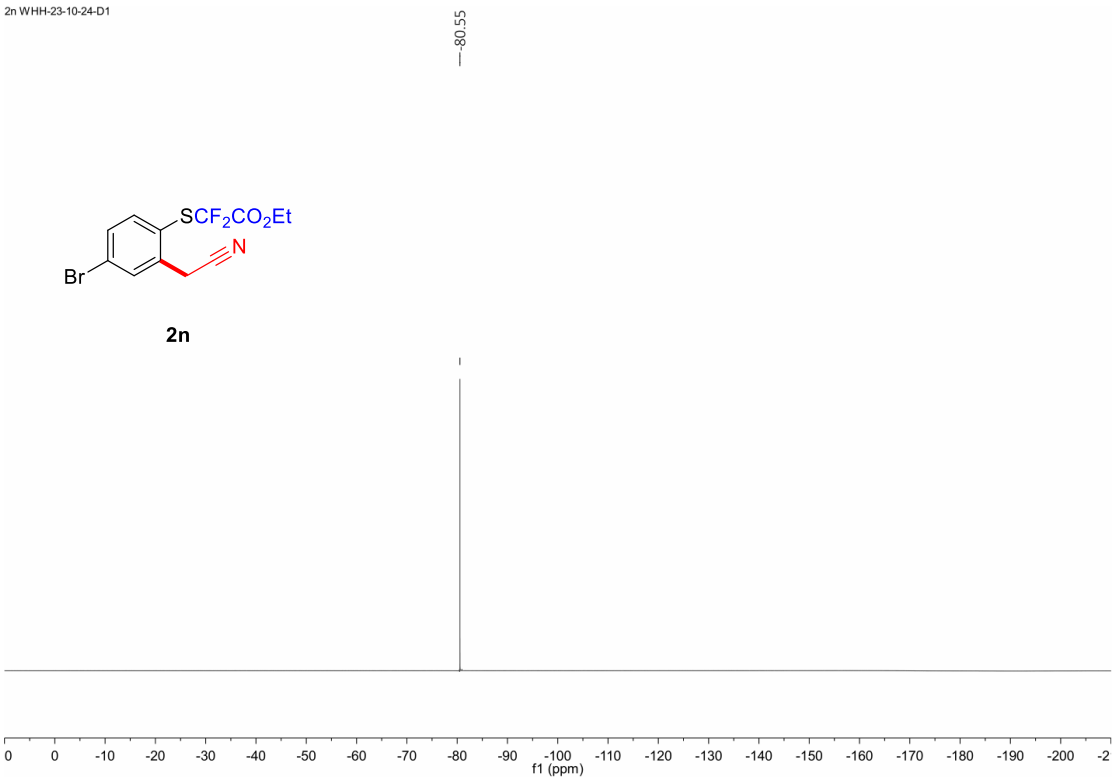
2m

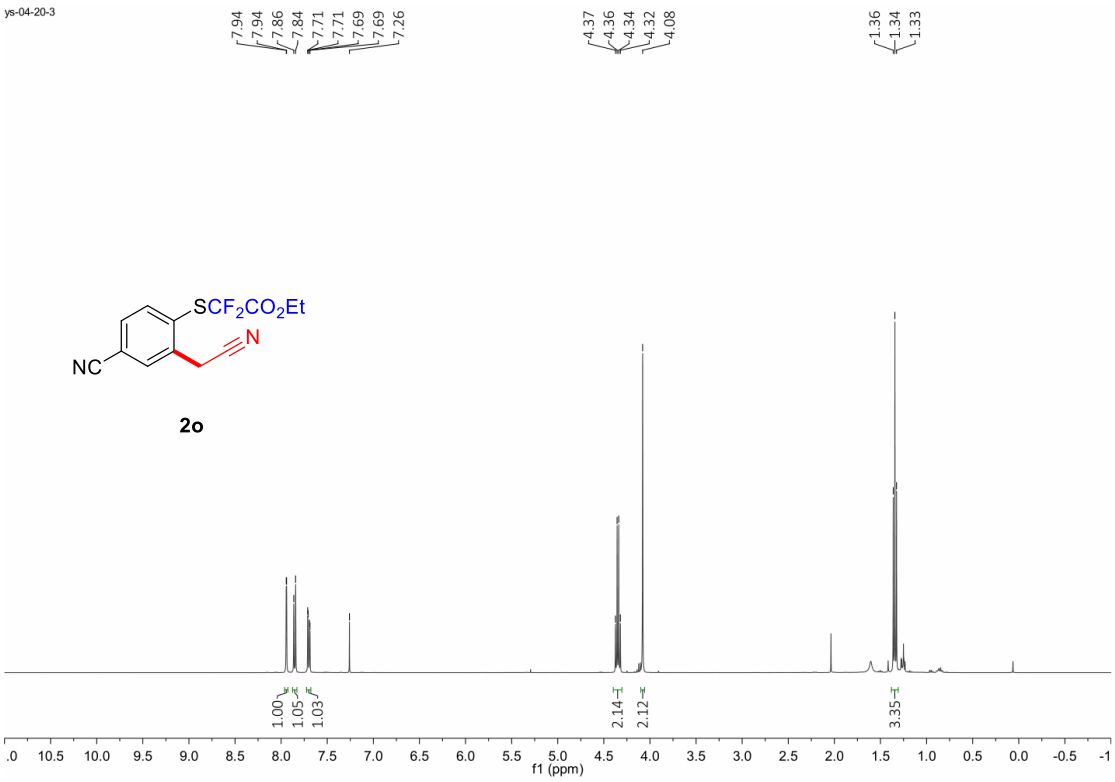
2n WHH-23-10-24-D1



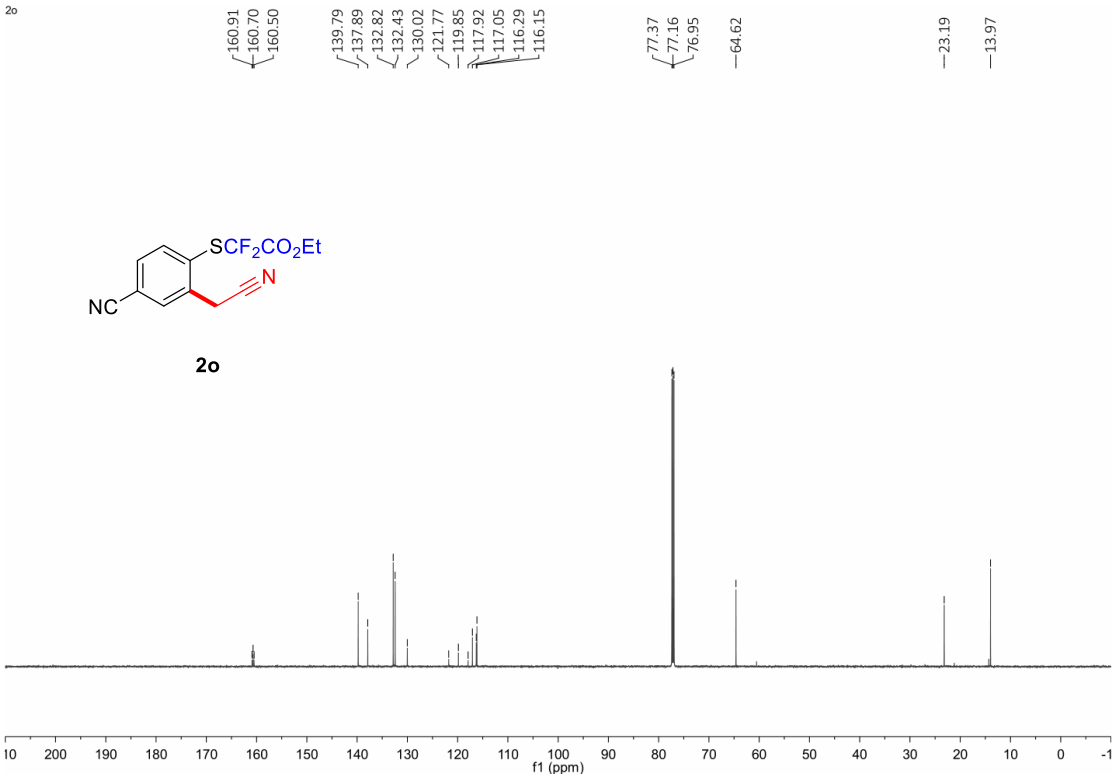
2n


2n WHH-23-10-24-D1
161.28
161.07
160.86
140.62
138.32
132.88
132.64
127.14
122.84
121.82
119.91
117.99
116.88
77.37
77.16
76.95
64.35
22.99
13.97
SCF2CO2Et
N
Br
2n
f1 (ppm)

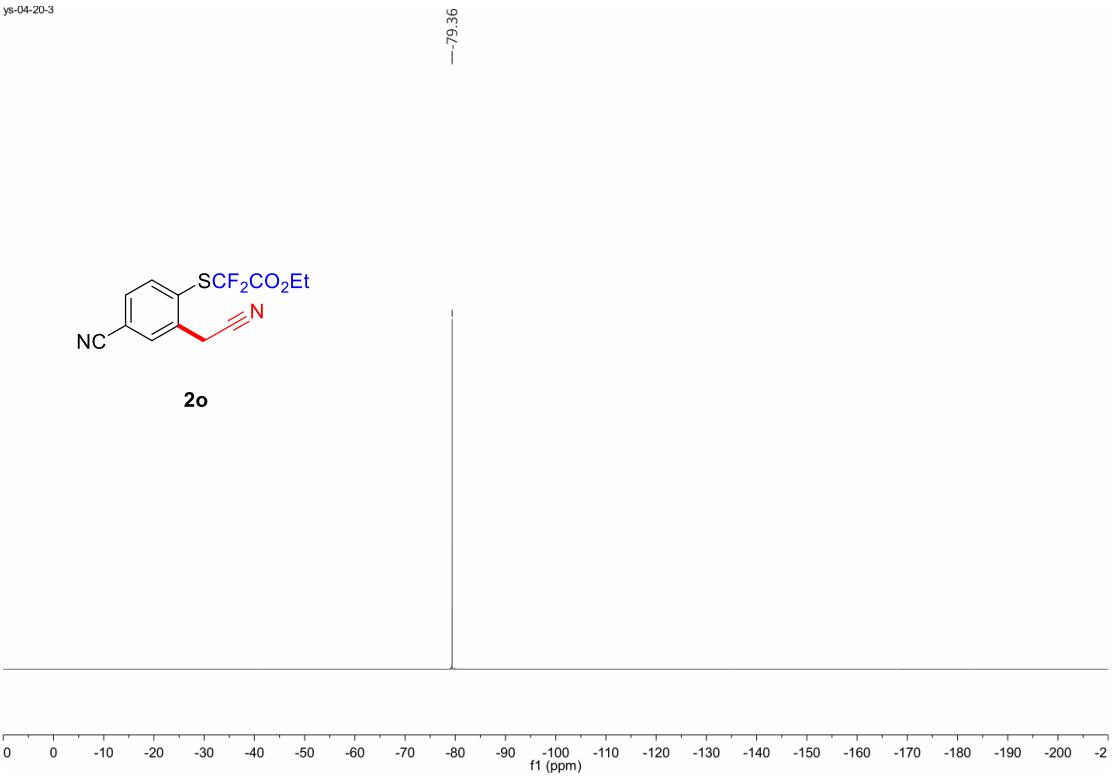

2n WHH-23-10-24-D1
-80.55
SCF2CO2Et
N
Br
2n
f1 (ppm)


ys-04-20-3
7.94
7.94
7.86
7.84
7.71
7.71
7.69
7.69
7.26
4.37
4.36
4.34
4.32
4.08
1.36
1.34
1.33
SCF2CO2Et
N
NC
1.00
1.05
1.03
2.14
2.12
3.35
f1 (ppm)

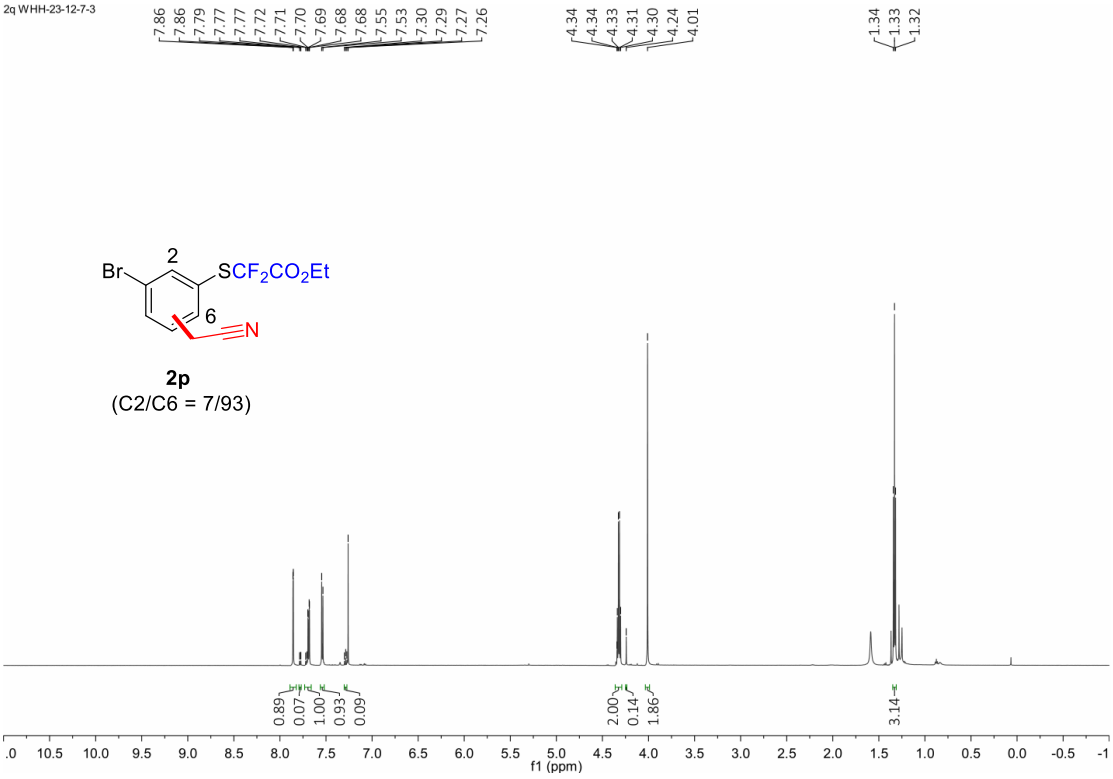
2o


2o
160.91
160.70
160.50
139.79
137.89
132.82
132.43
130.02
121.77
119.85
117.92
117.05
116.29
116.15
77.37
77.16
76.95
64.62
23.19
13.97
SCF2CO2Et
N
NC
f1 (ppm)

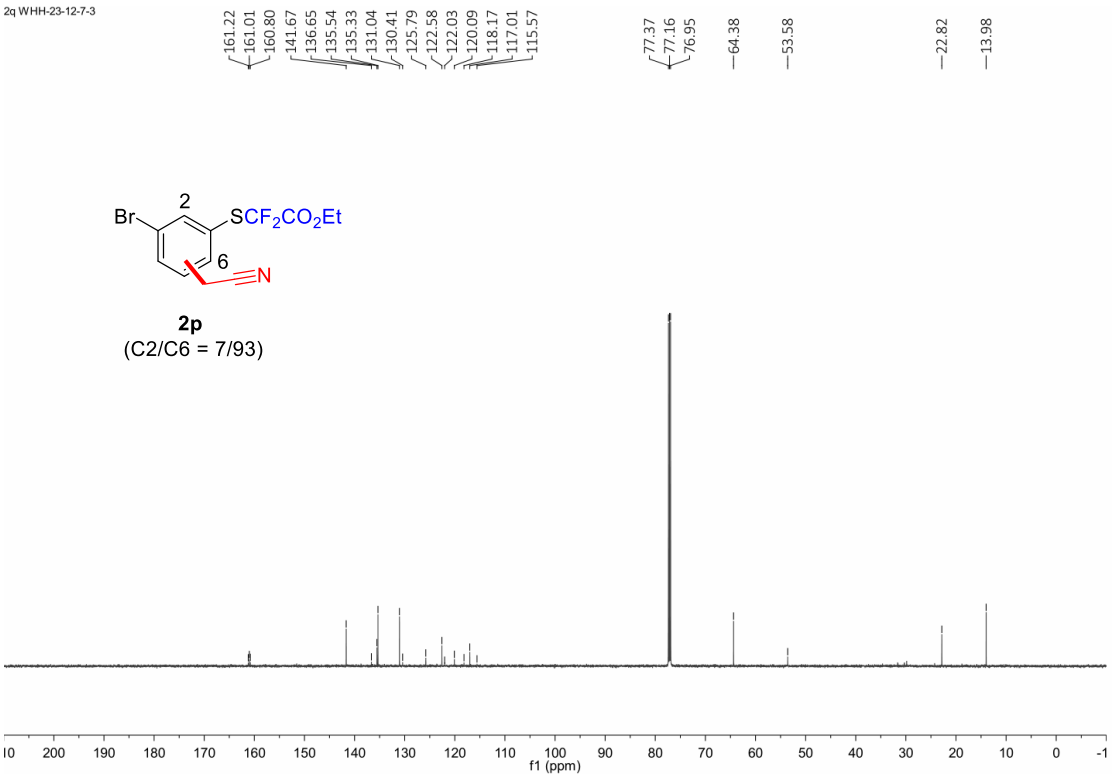
2o

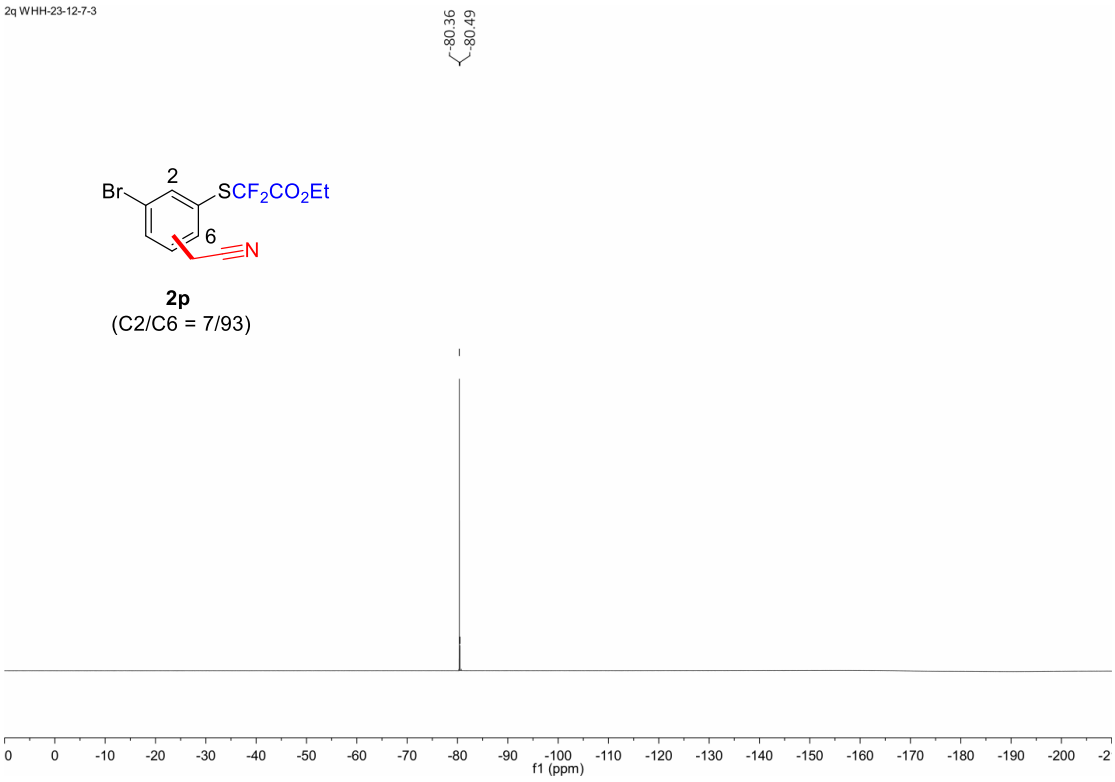


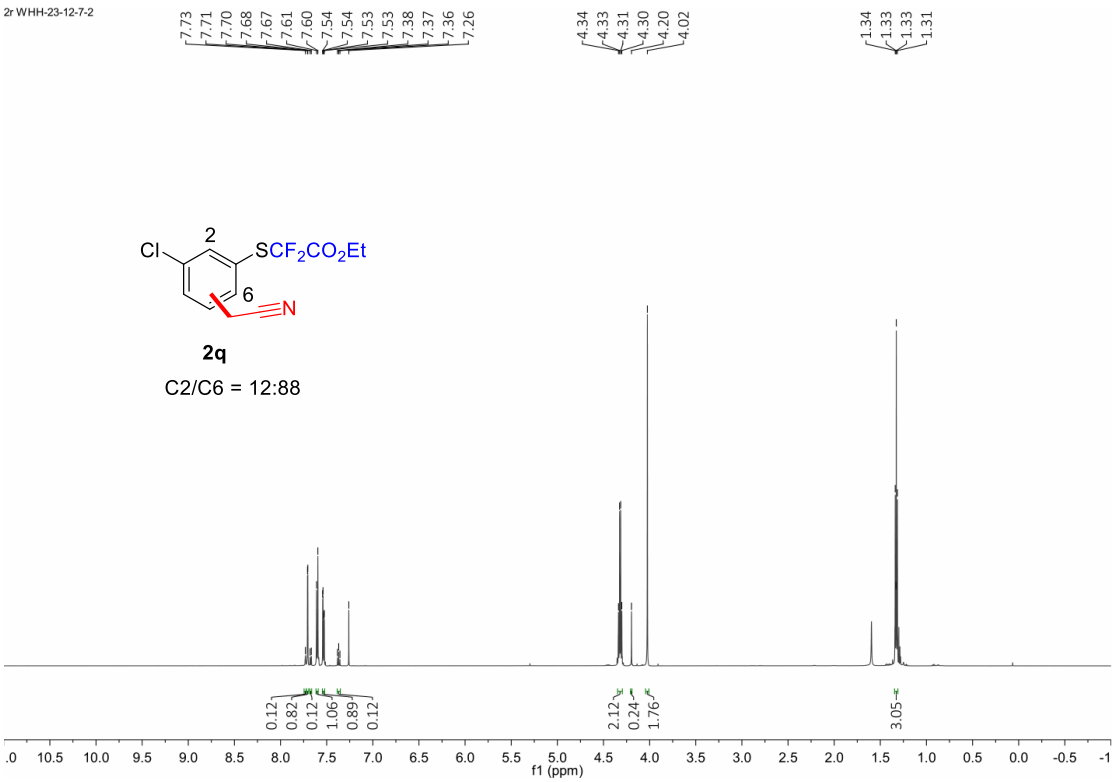
2o

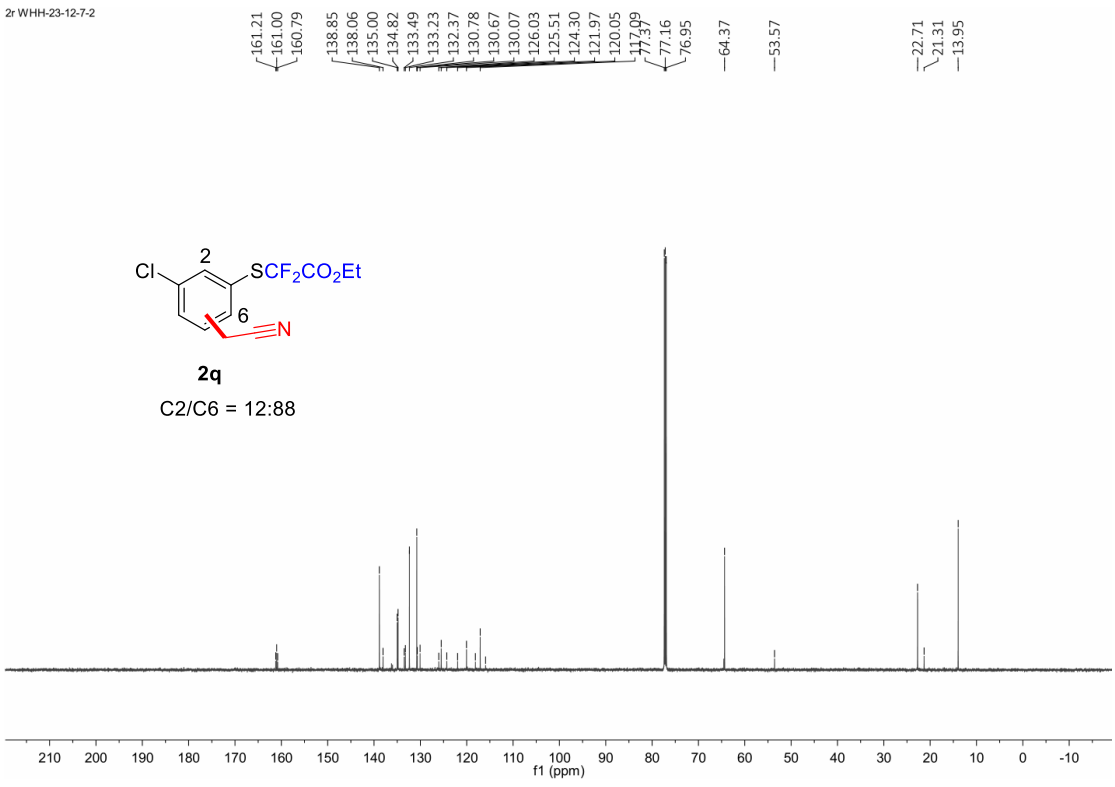


2p
(C2/C6 = 7/93)

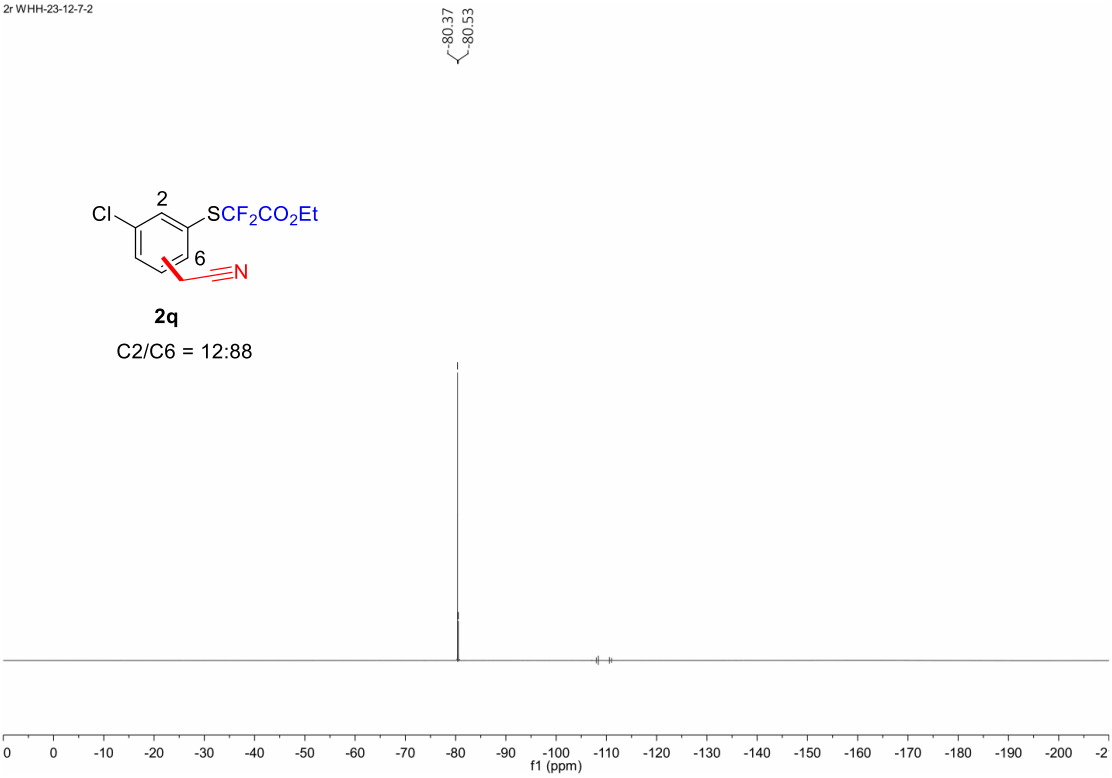

2q WHH-23-12-7-3
161.22
161.01
160.80
141.67
136.65
135.54
135.33
131.04
130.41
125.79
122.58
122.03
120.09
118.17
117.01
115.57
77.37
77.16
76.95
64.38
53.58
22.82
13.98
Br
2
SCF2CO2Et
6
N
2p
(C2/C6 = 7/93)
f1 (ppm)


2q WHH-23-12-7-3
-80.36
-80.49
Br
2
SCF2CO2Et
6
N
2p
(C2/C6 = 7/93)
f1 (ppm)


2r WHH-23-12-7-2
7.73
7.71
7.70
7.68
7.67
7.61
7.60
7.54
7.54
7.53
7.53
7.38
7.37
7.36
7.26
4.34
4.33
4.31
4.30
4.20
4.02
1.34
1.33
1.33
1.31
Cl
2
SCF2CO2Et
6
N
2q
C2/C6 = 12:88
0.12
0.82
0.12
1.06
0.89
0.12
2.12
0.24
1.76
3.05
f1 (ppm)


2r WHH-23-12-7-2
161.21
161.00
160.79
138.85
138.06
135.00
134.82
133.49
133.23
132.37
130.78
130.67
130.07
126.03
125.51
124.30
121.97
120.05
77.37
77.16
76.95
64.37
53.57
22.71
21.31
13.95
Cl
2
SCF2CO2Et
6
N
2q
C2/C6 = 12:88
f1 (ppm)

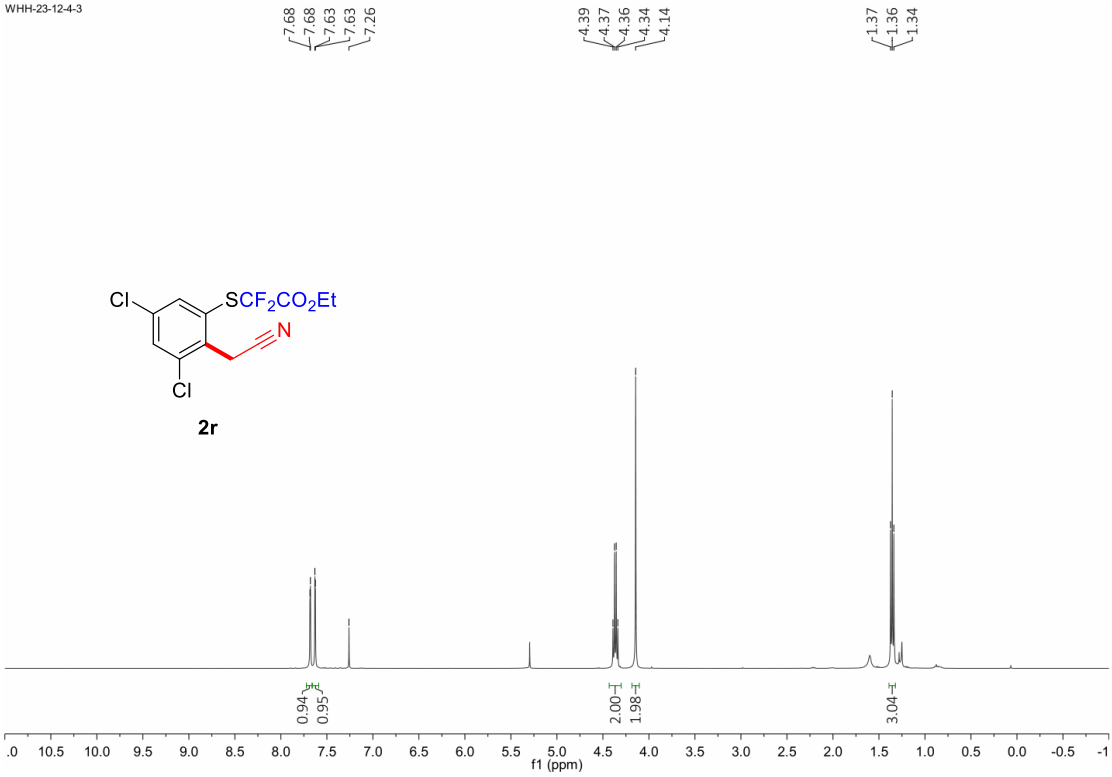
2r WHH-23-12-7-2



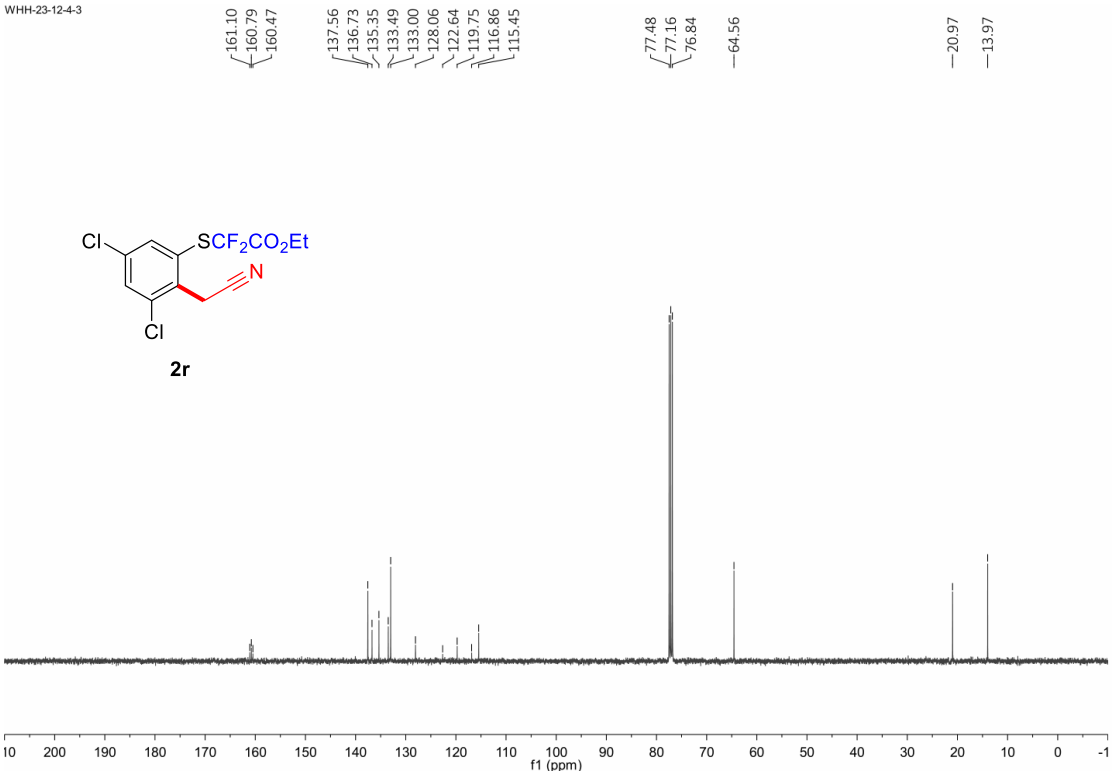
2q

C2/C6 = 12:88

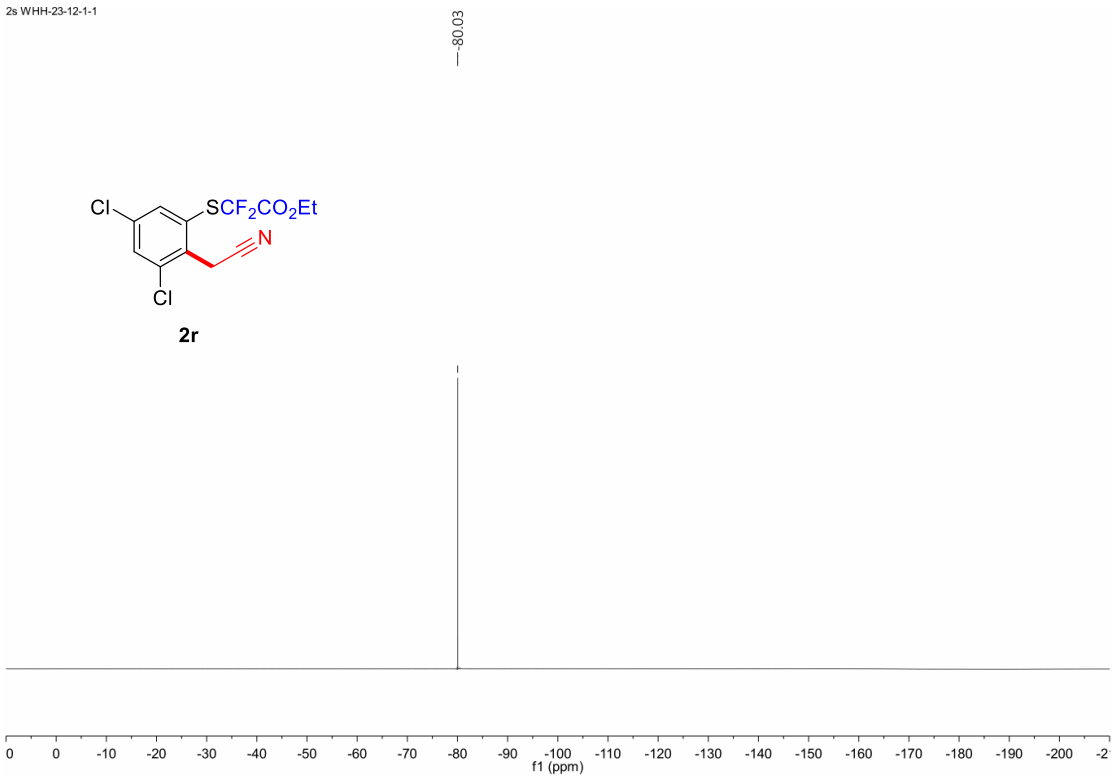
WHH-23-12-4-3



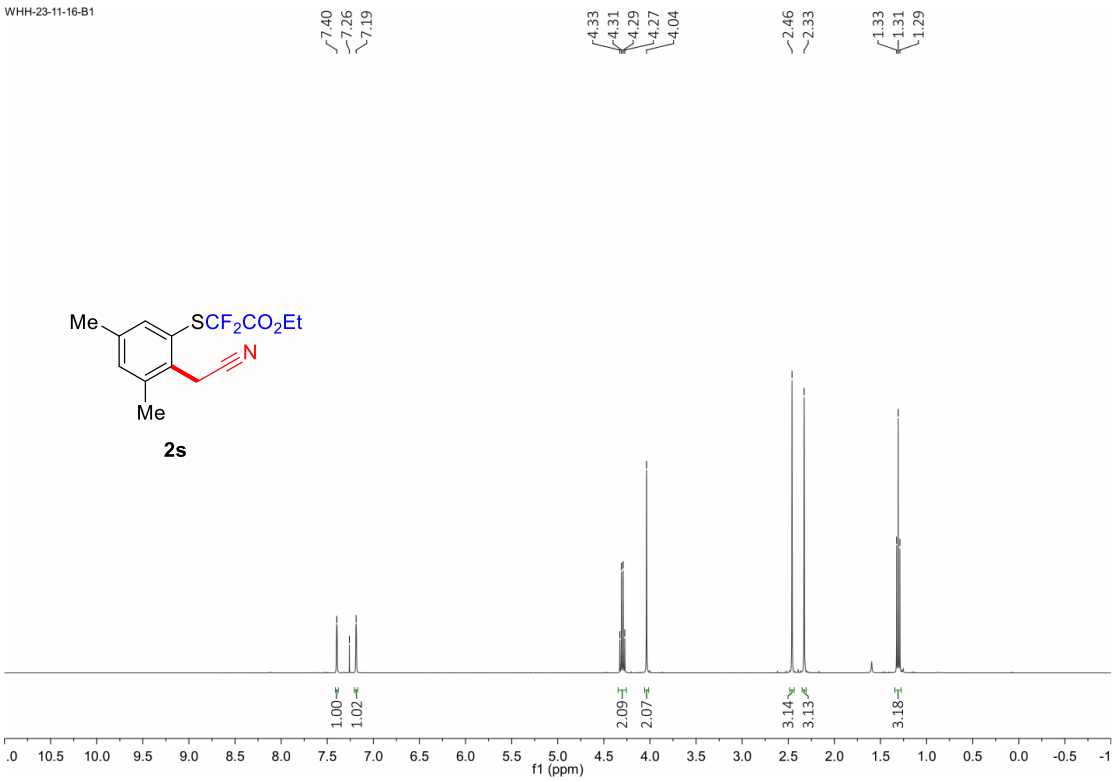
2r


WHH-23-12-4-3
161.10
160.79
160.47
137.56
136.73
135.35
133.49
133.00
128.06
122.64
119.75
116.86
115.45
77.48
77.16
76.84
64.56
20.97
13.97
Cl
SCF2CO2Et
N
Cl
f1 (ppm)

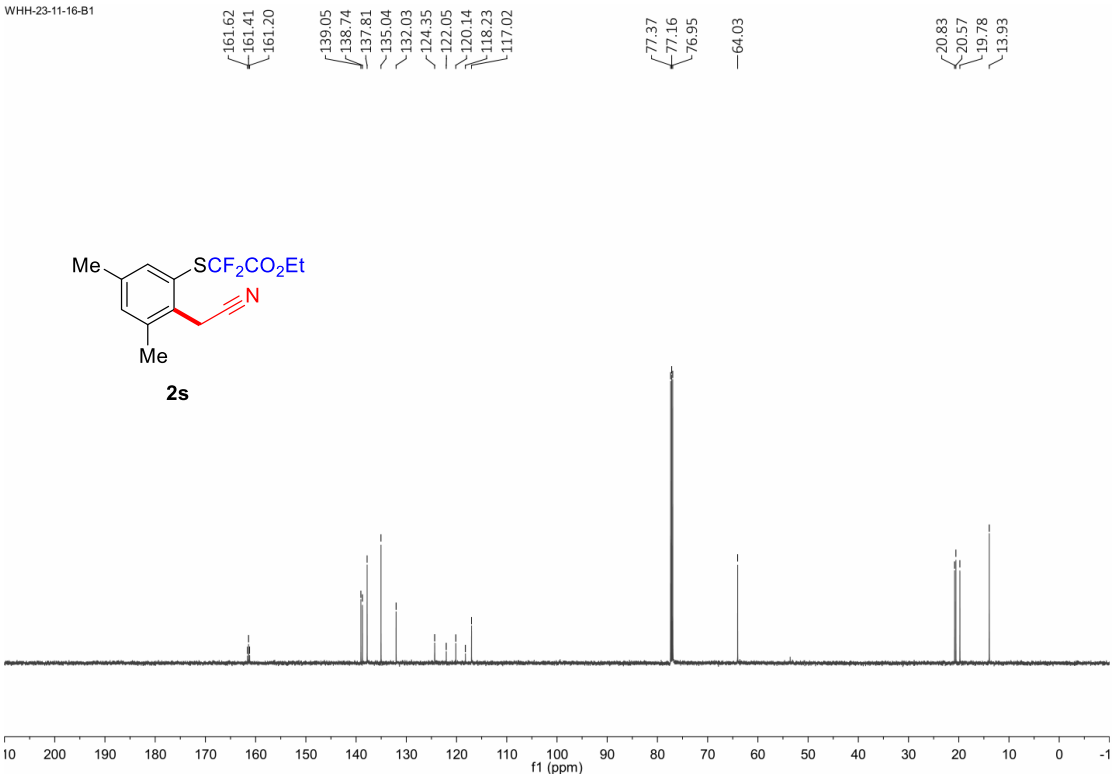
2r


2s WHH-23-12-1-1
-80.03
Cl
SCF2CO2Et
N
Cl
f1 (ppm)

2r

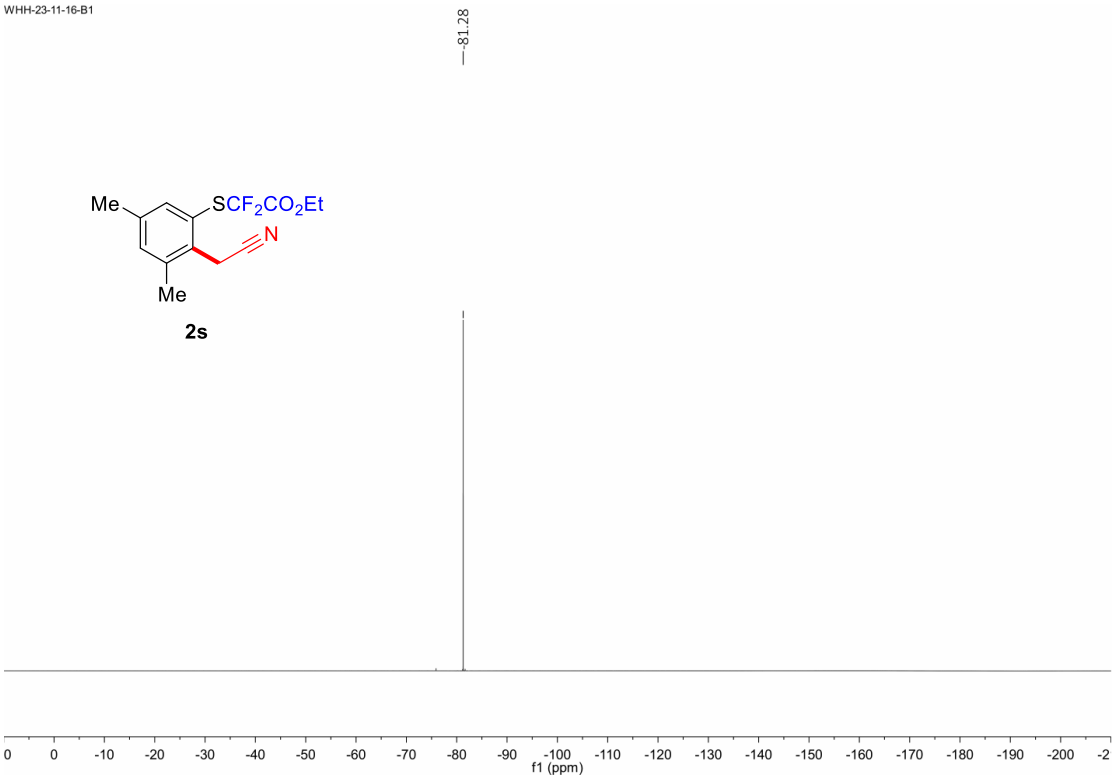

WHH-23-11-16-B1
7.40
7.26
7.19
4.33
4.31
4.29
4.27
4.04
2.46
2.33
1.33
1.31
1.29
Me
SCF2CO2Et
N
Me
1.00
1.02
2.09
2.07
3.14
3.13
3.18
f1 (ppm)

2s


WHH-23-11-16-B1
161.62
161.41
161.20
139.05
138.74
137.81
135.04
132.03
124.35
122.05
120.14
118.23
117.02
77.37
77.16
76.95
64.03
20.83
20.57
19.78
13.93
Me
SCF2CO2Et
N
Me
f1 (ppm)

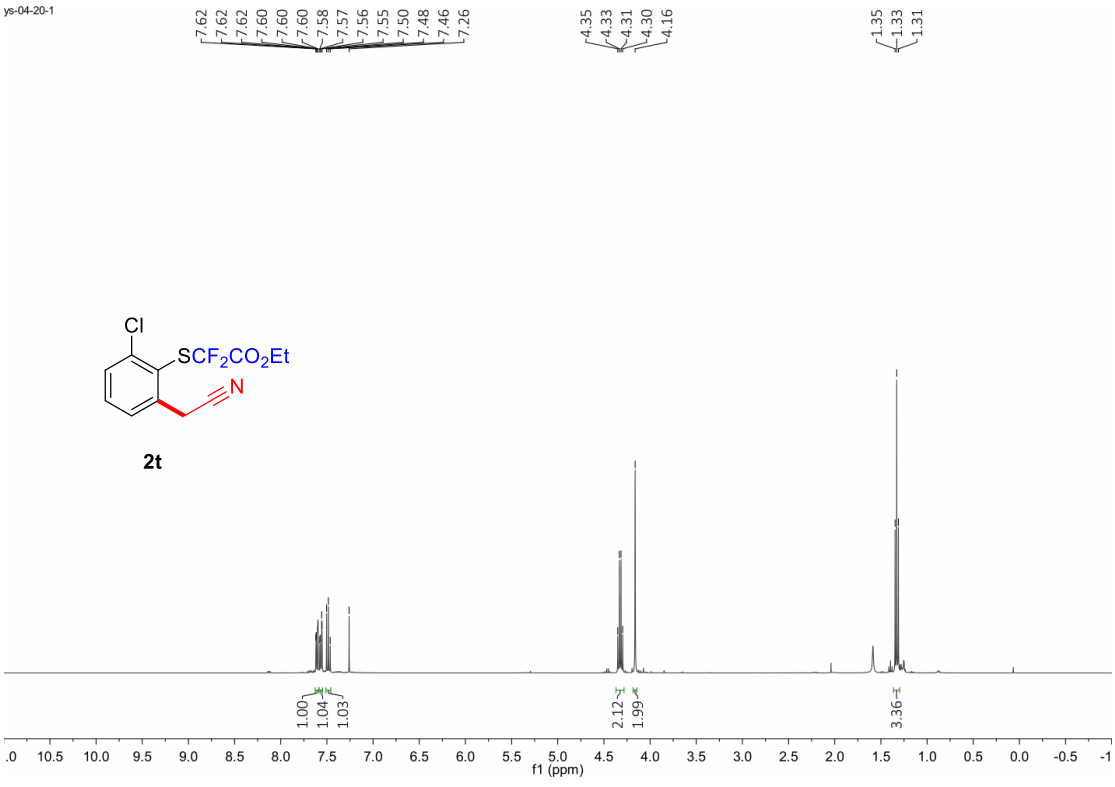
2s

WHH-23-11-16-B1

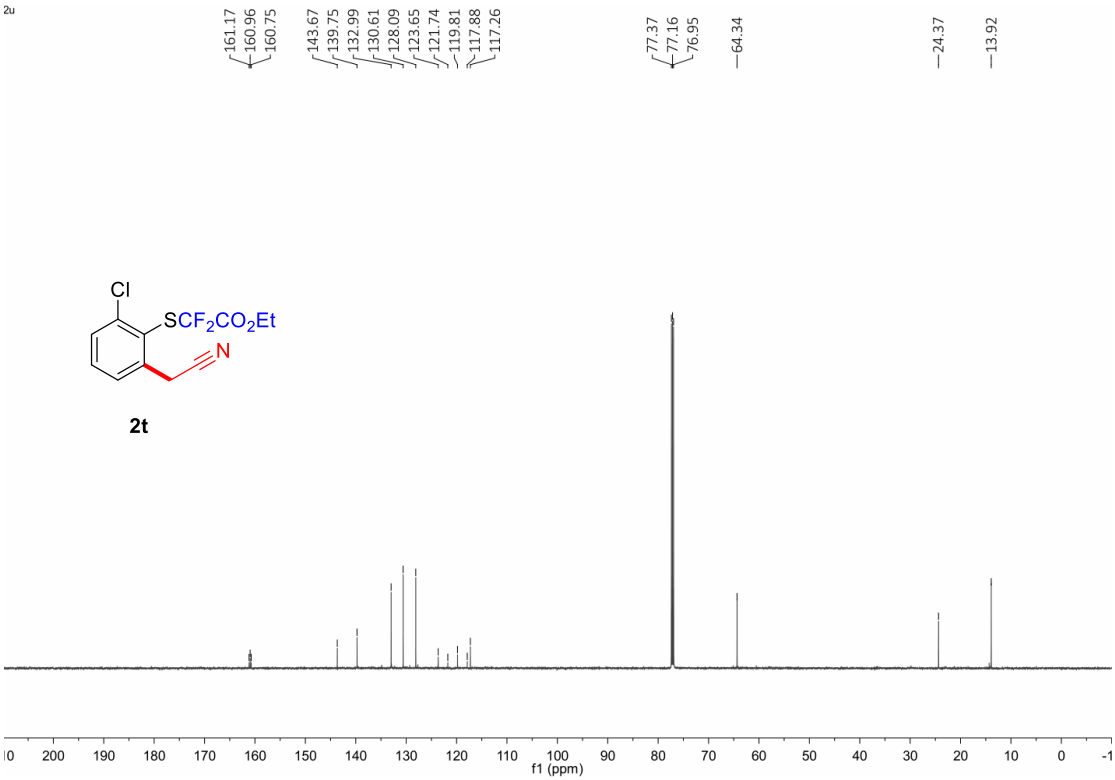


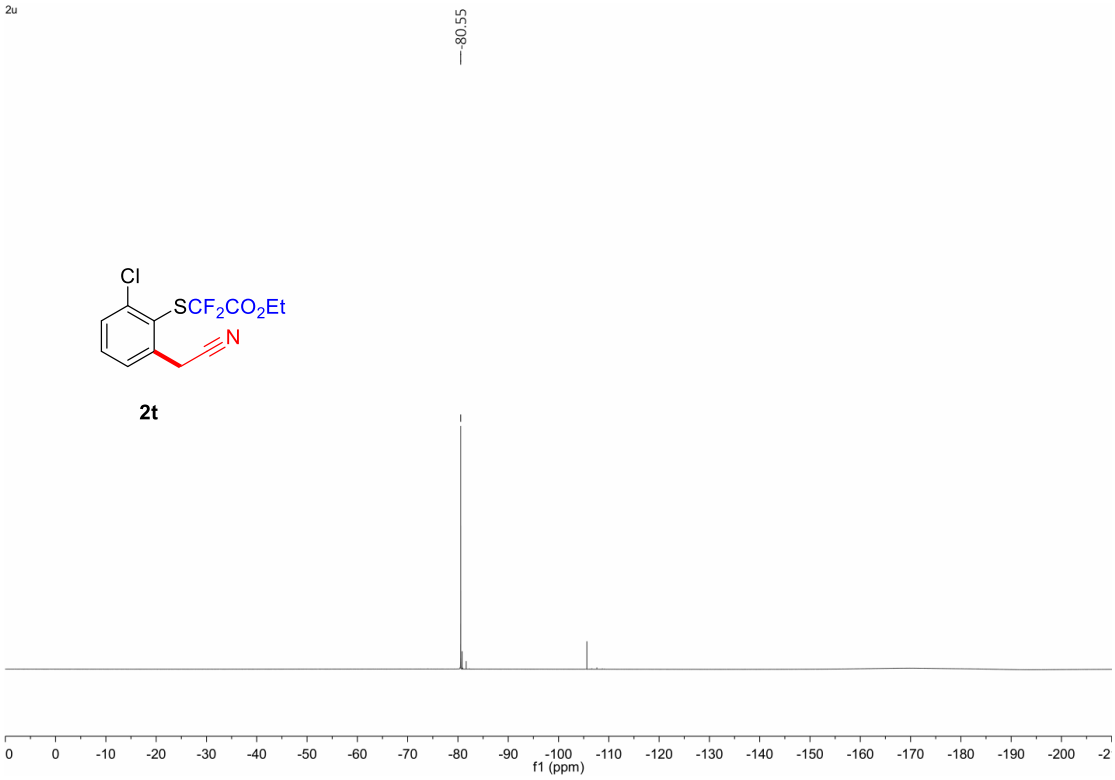
2s

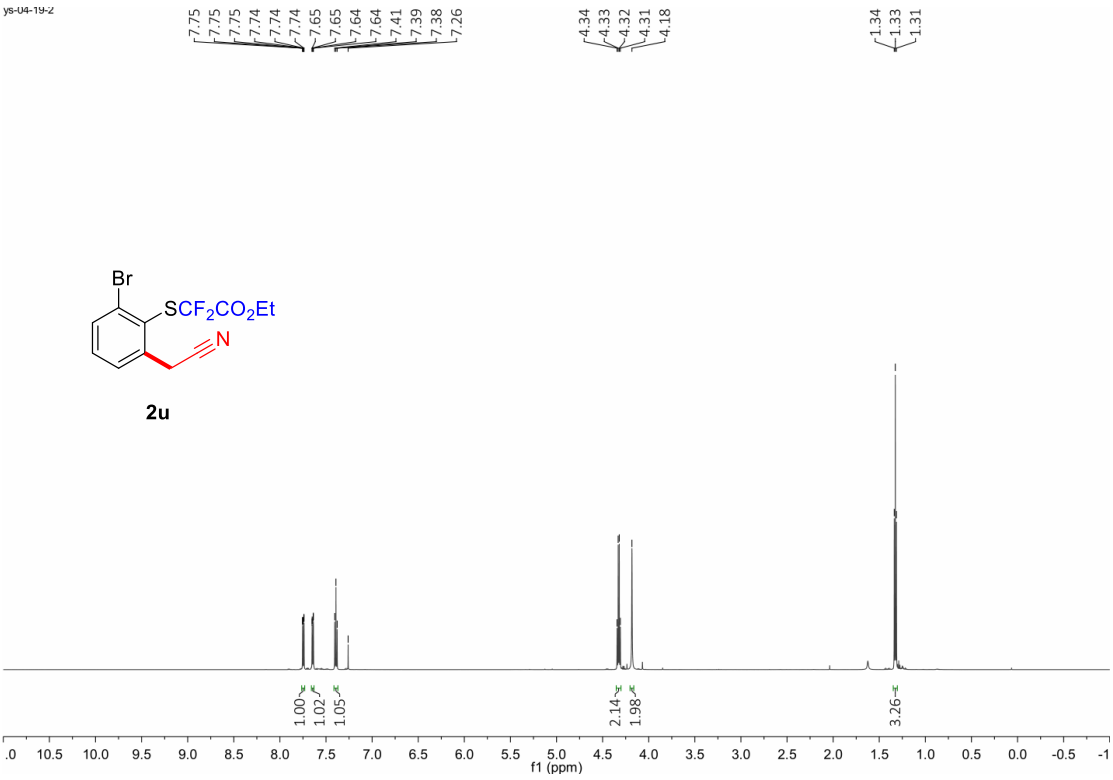
ys-04-20-1

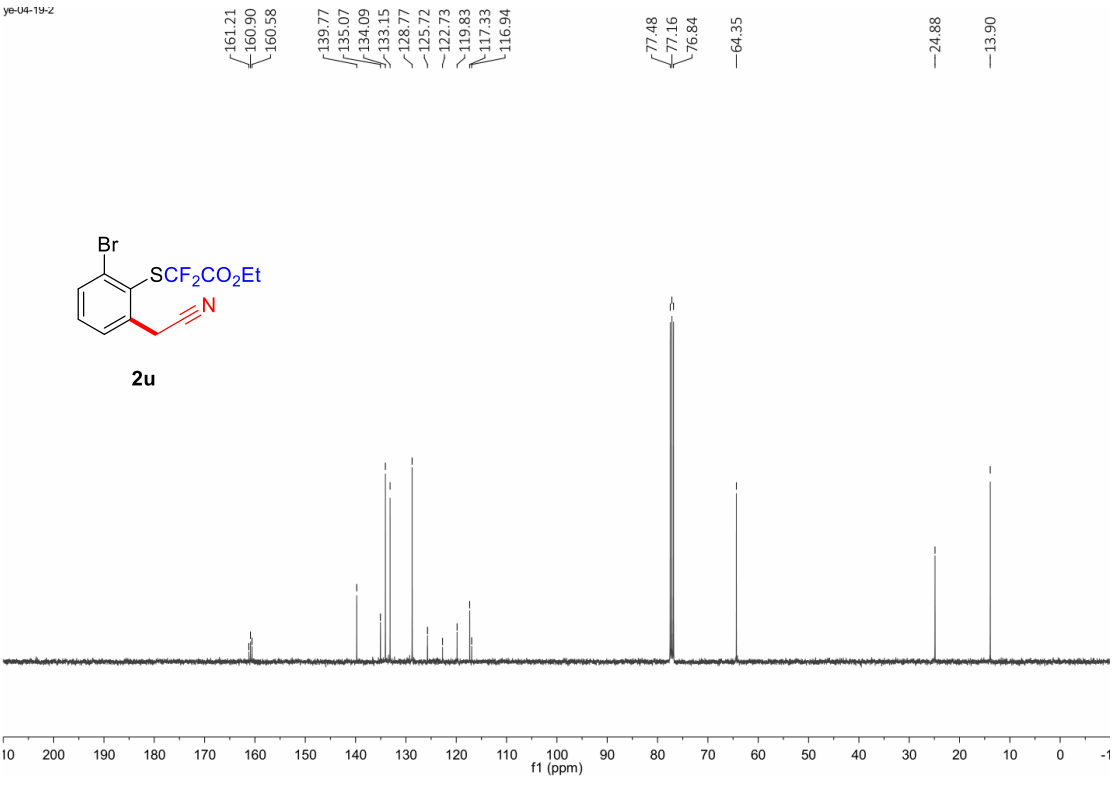


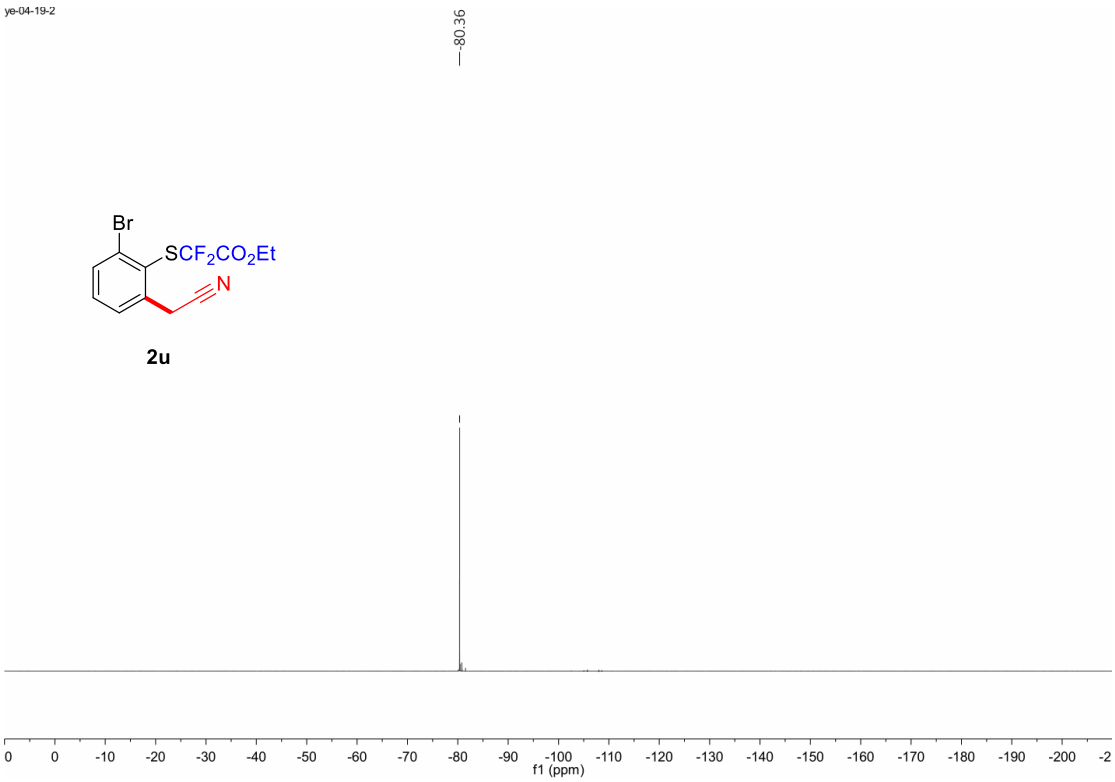
2t


2u
161.17
160.96
160.75
143.67
139.75
132.99
130.61
128.09
123.65
121.74
119.81
117.88
117.26
77.37
77.16
76.95
64.34
24.37
13.92
Cl
SCF2CO2Et
N
2t
f1 (ppm)

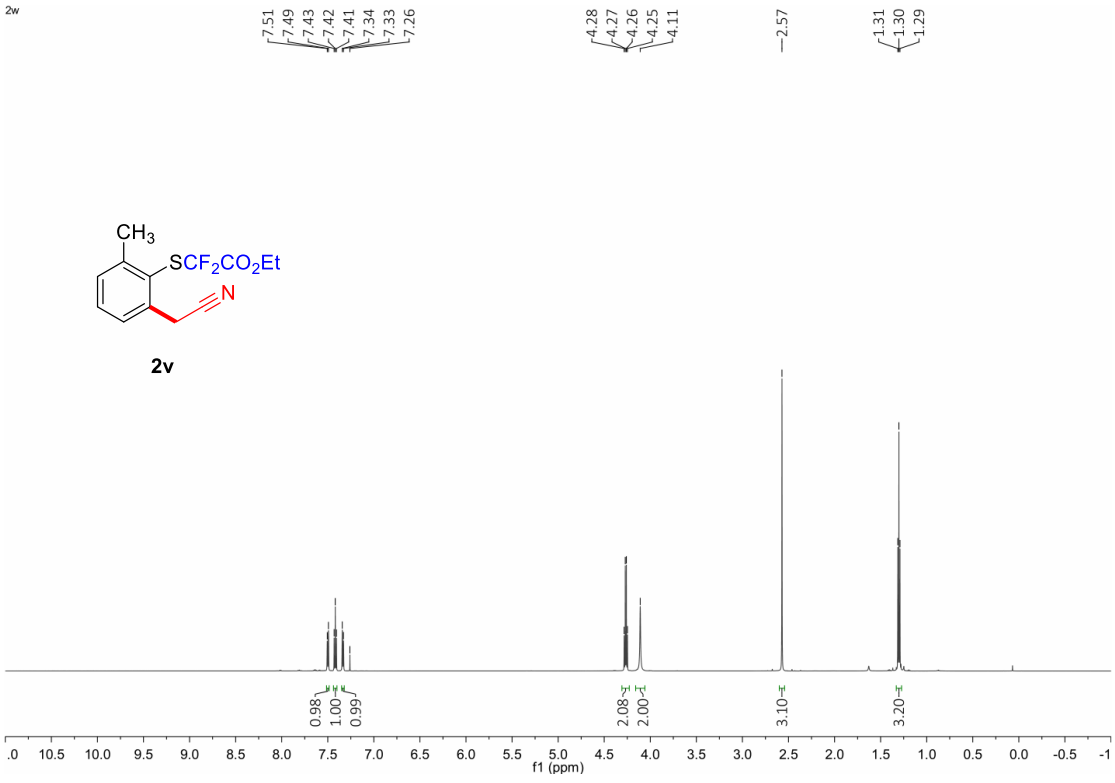

2u
-80.55
Cl
SCF2CO2Et
N
2t
f1 (ppm)


ys-04-19-z
7.75
7.75
7.75
7.74
7.74
7.74
7.65
7.65
7.64
7.64
7.41
7.39
7.38
7.26
4.34
4.33
4.32
4.31
4.18
1.34
1.33
1.31
Br
SCF2CO2Et
N
2u
1.00
1.02
1.05
2.14
1.98
3.26
f1 (ppm)

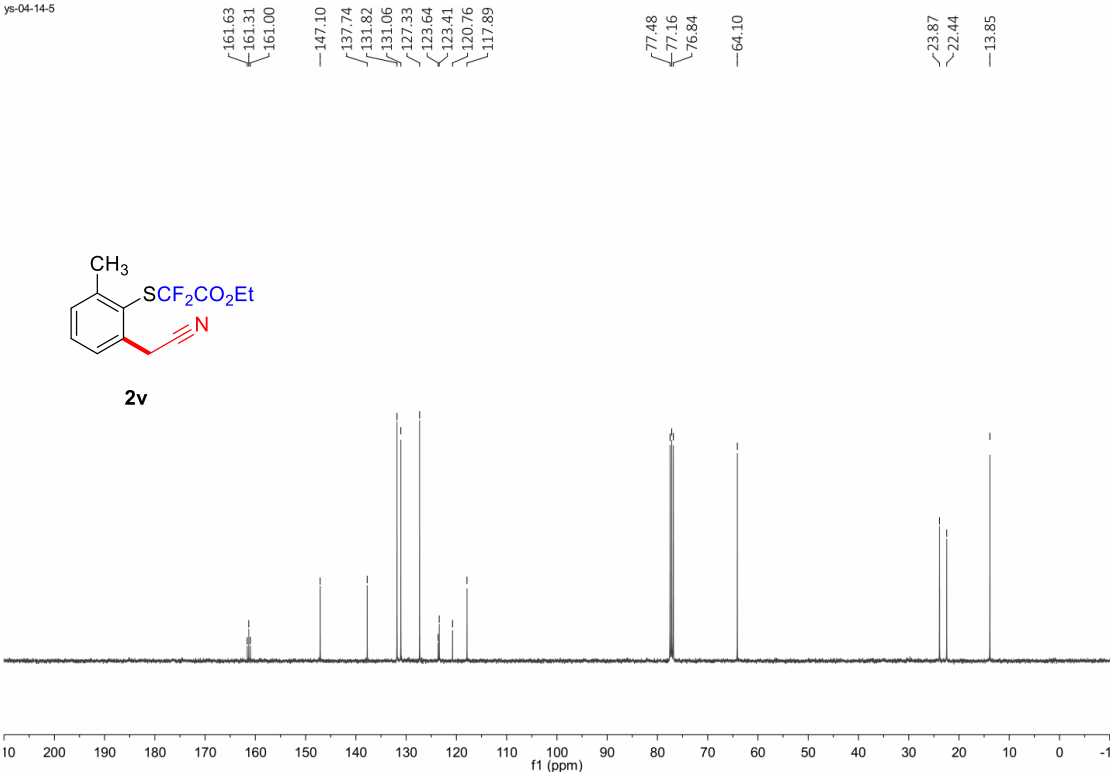

ye-04-19-z
161.21
160.90
160.58
139.77
135.07
134.09
133.15
128.77
125.72
122.73
119.83
117.33
116.94
77.48
77.16
76.84
64.35
24.88
13.90
Br
SCF2CO2Et
N
2u
f1 (ppm)

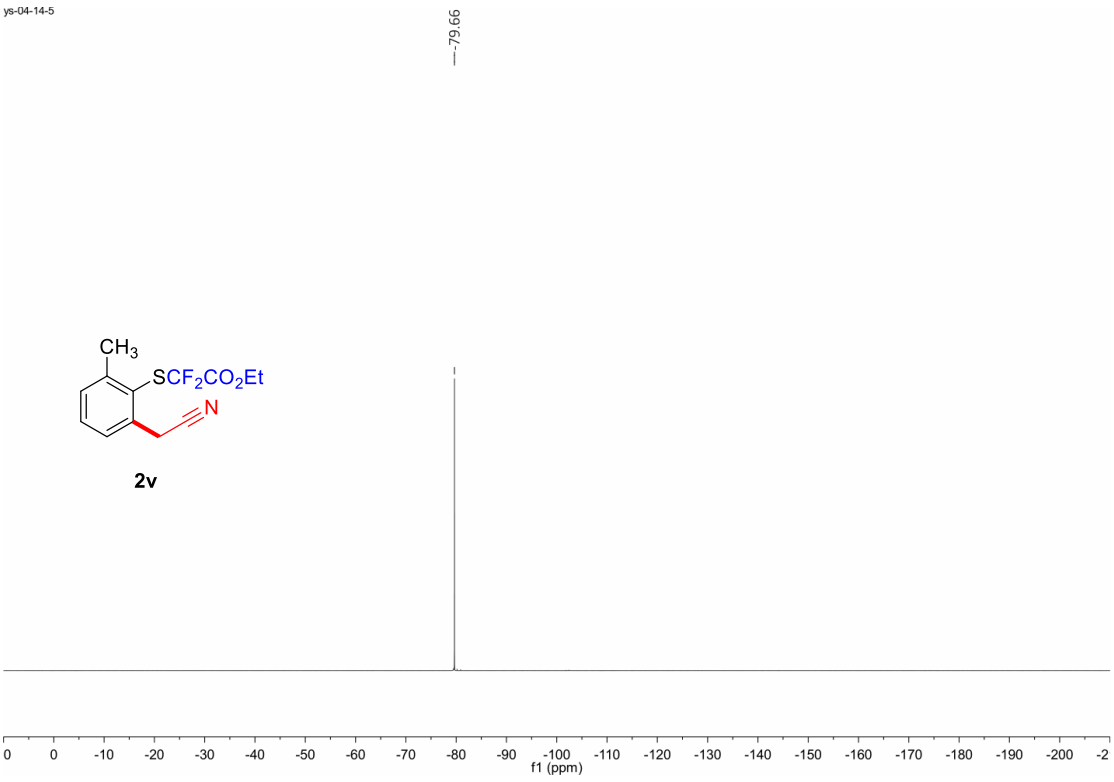

ye-04-19-2
-80.36
Br
SCF2CO2Et
N
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

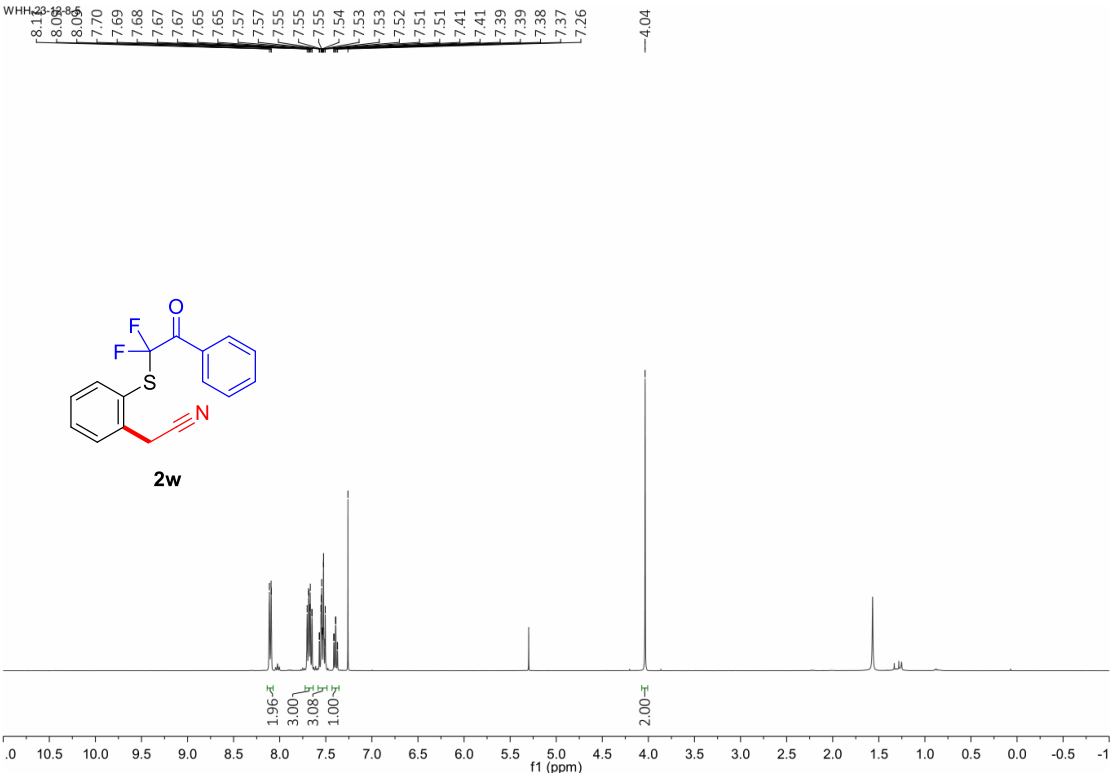
2u

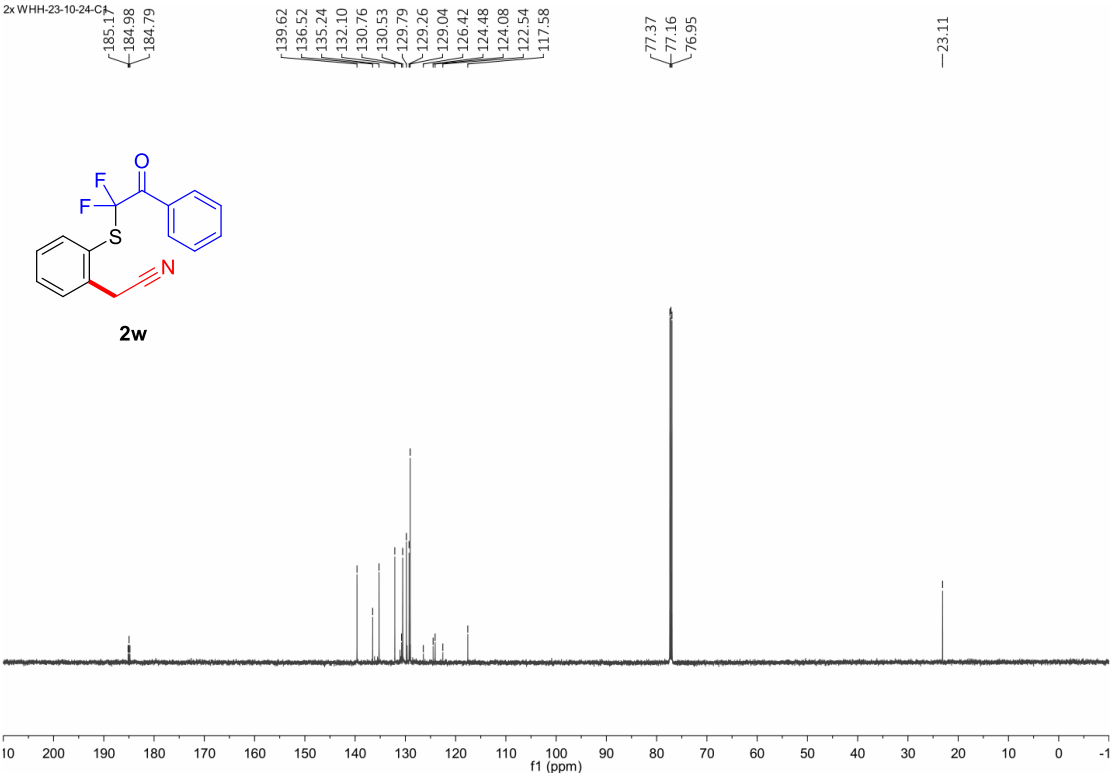

2w
7.51
7.49
7.43
7.42
7.41
7.34
7.33
7.26
4.28
4.27
4.26
4.25
4.11
2.57
1.31
1.30
1.29
CH3
SCF2CO2Et
N
0.98
1.00
0.99
2.08
2.00
3.10
3.20
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

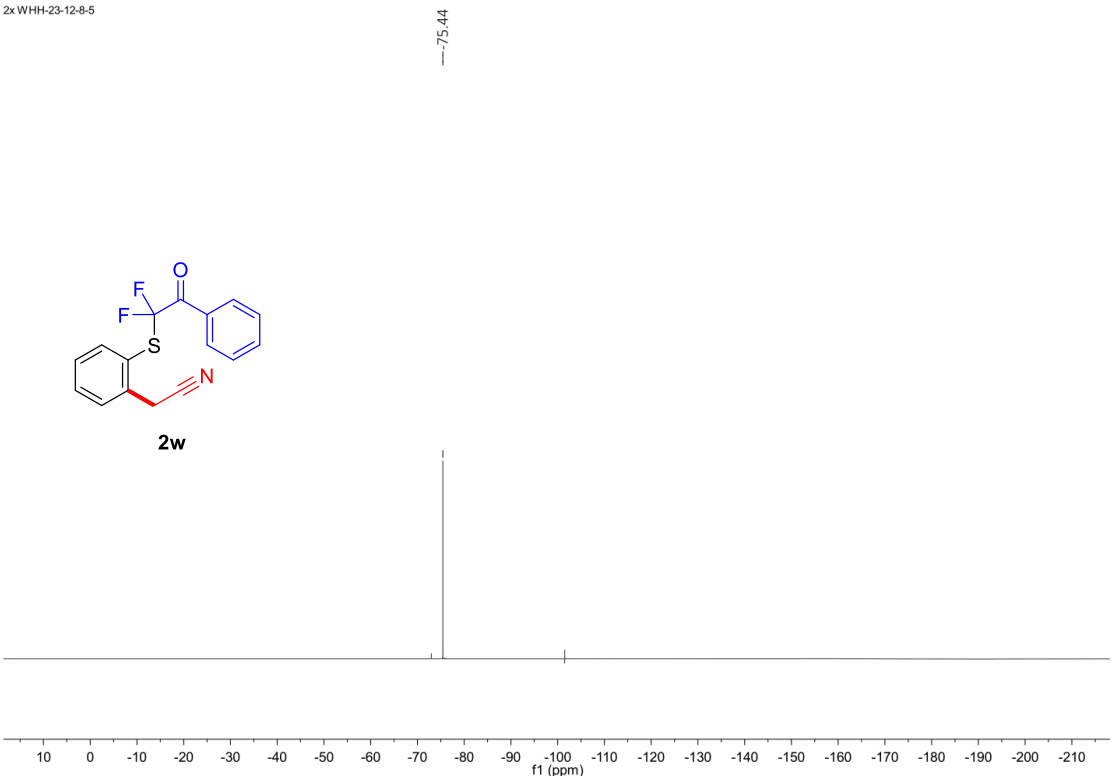
2v


ys-04-14-5
161.63
161.31
161.00
147.10
137.74
131.82
131.06
127.33
123.64
123.41
120.76
117.89
77.48
77.16
76.84
64.10
23.87
22.44
13.85
CH3
SCF2CO2Et
N
2v
f1 (ppm)

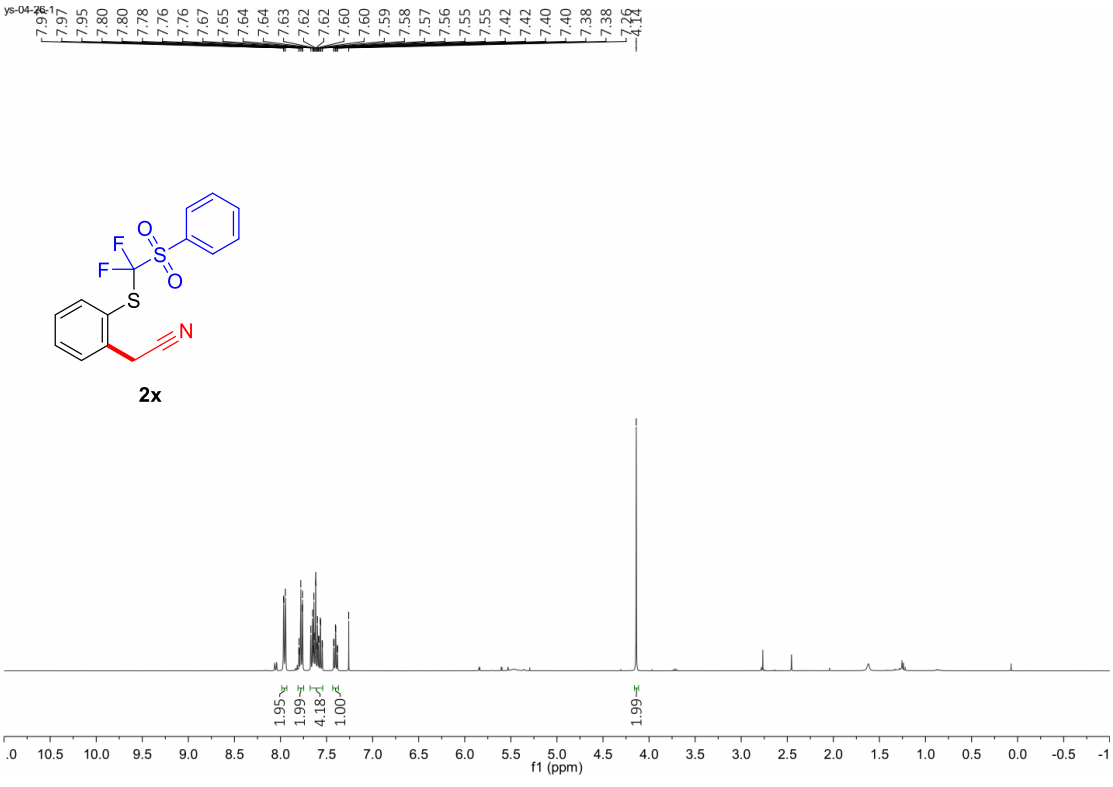

ys-04-14-5
-79.66
CH3
SCF2CO2Et
N
2v
f1 (ppm)


WHH-23-12-8-f
8.11
8.05
8.04
8.03
7.70
7.69
7.68
7.67
7.67
7.65
7.65
7.57
7.57
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.41
7.41
7.39
7.39
7.38
7.37
7.26
4.04
F
F
O
S
N
2w
1.96
3.00
3.08
1.00
2.00
f1 (ppm)

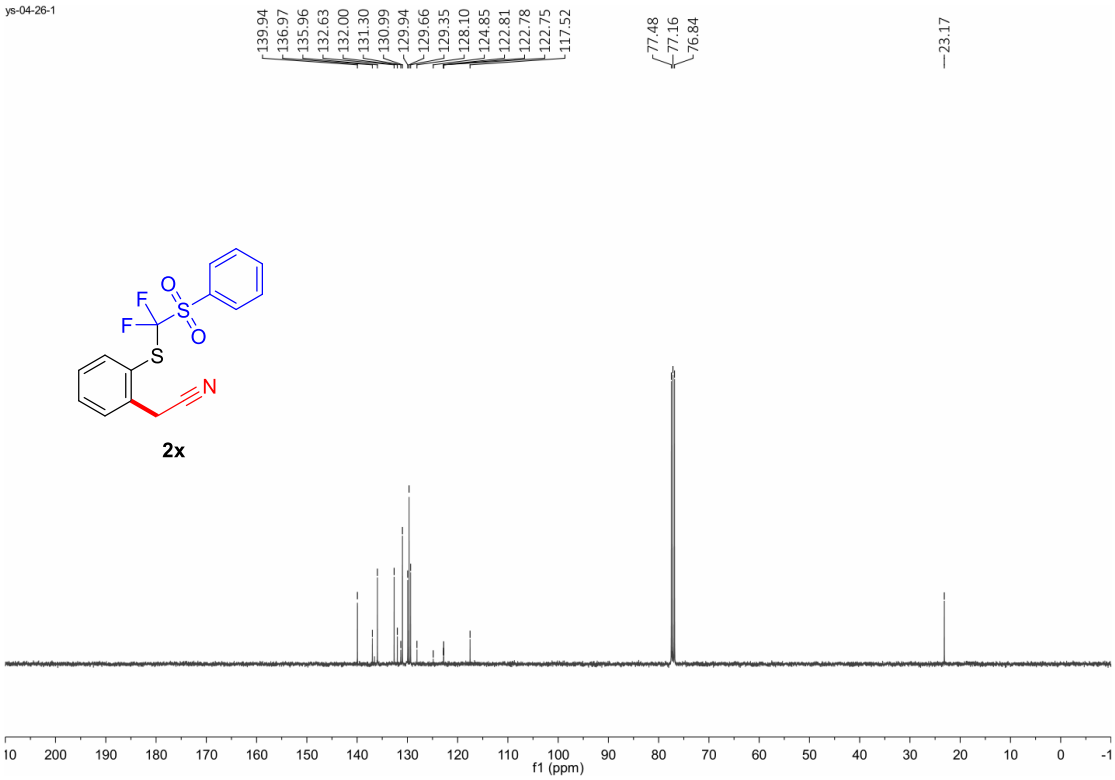

2x WHH-23-10-24-C
185.17
184.98
184.79
139.62
136.52
135.24
132.10
130.76
130.53
129.79
129.26
129.04
126.42
124.48
124.08
122.54
117.58
77.37
77.16
76.95
23.11
F
F
O
S
N
2w
f1 (ppm)

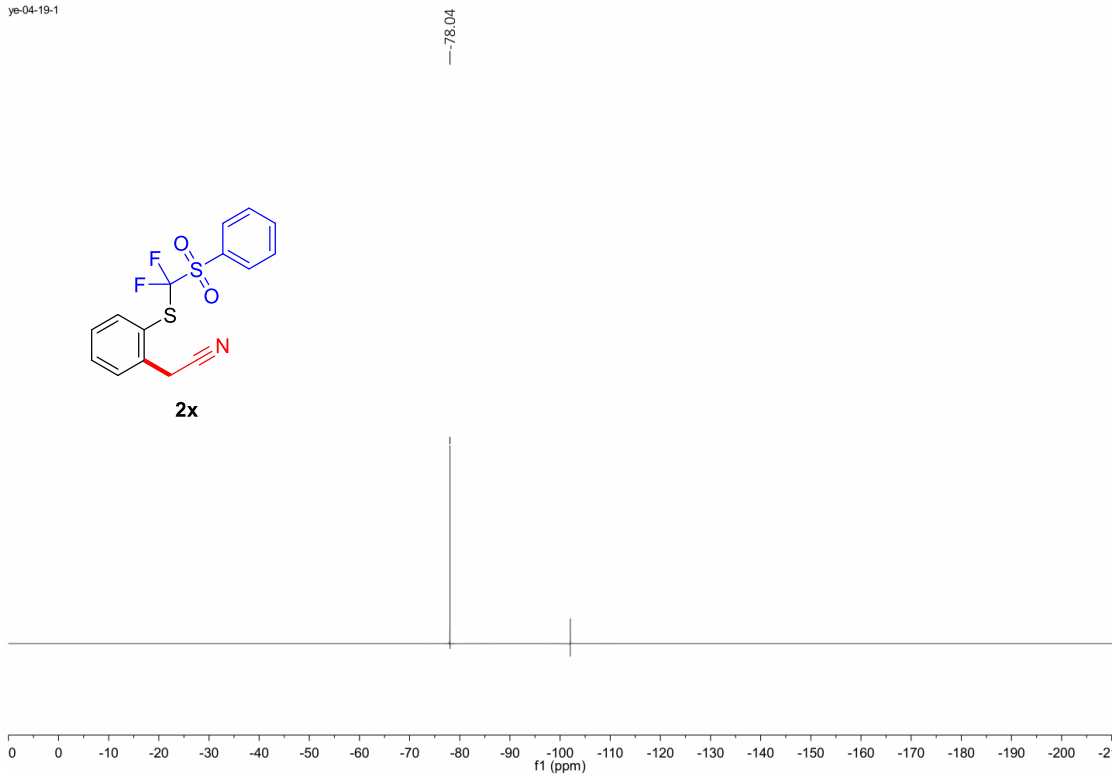

2x WHH-23-12-8-5
-75.44
F
F
O
S
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

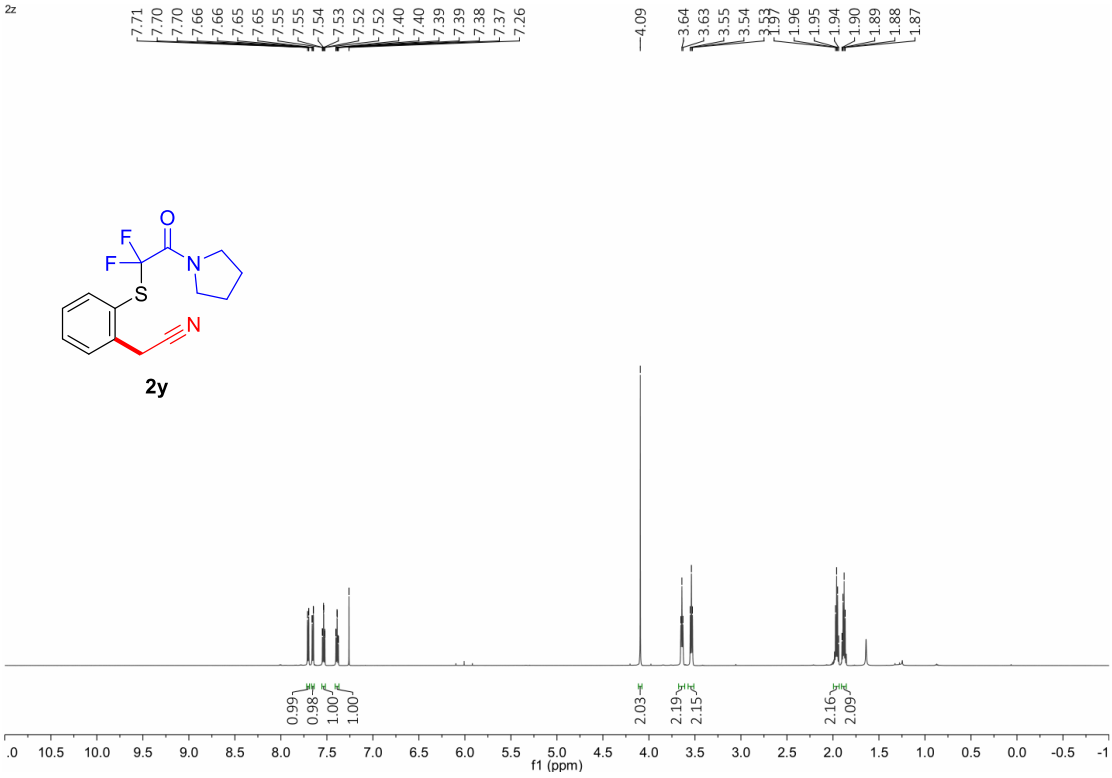
2w

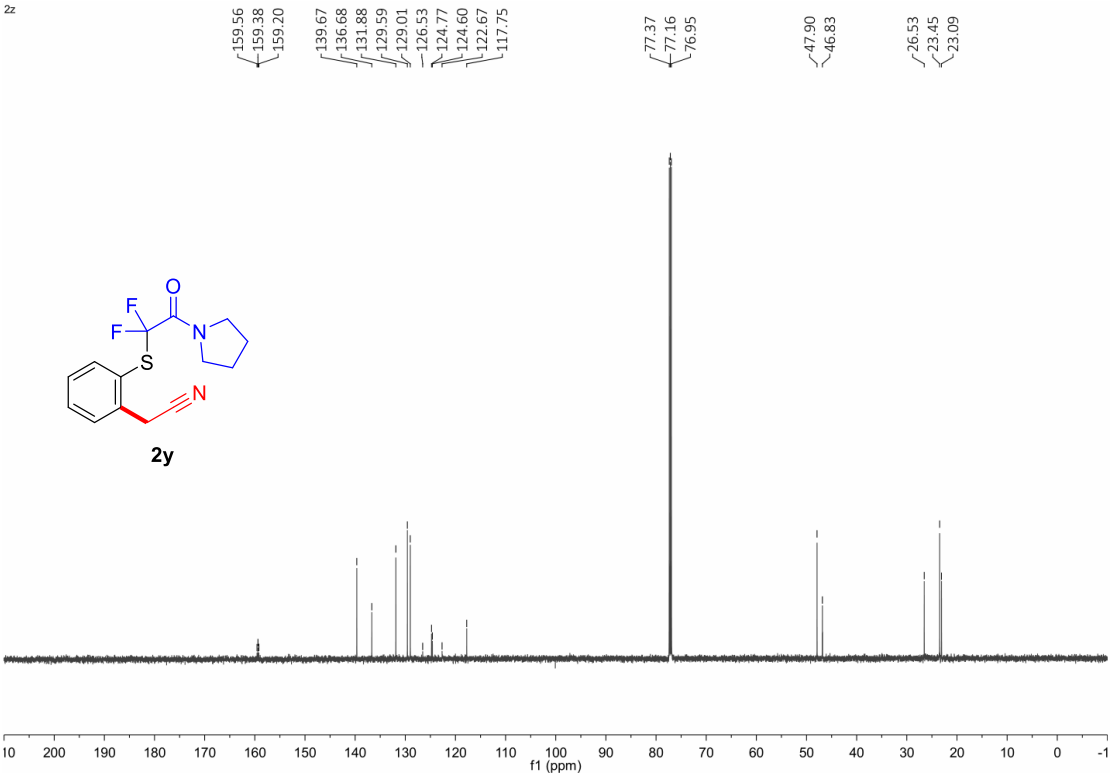

ys-04-26-1
7.98
7.97
7.95
7.80
7.80
7.78
7.76
7.76
7.67
7.65
7.64
7.64
7.63
7.62
7.62
7.60
7.60
7.59
7.58
7.57
7.56
7.55
7.55
7.42
7.42
7.40
7.40
7.38
7.38
7.26
4.14
F
F
O
O
S
S
N
1.95
1.99
4.18
1.00
1.99
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

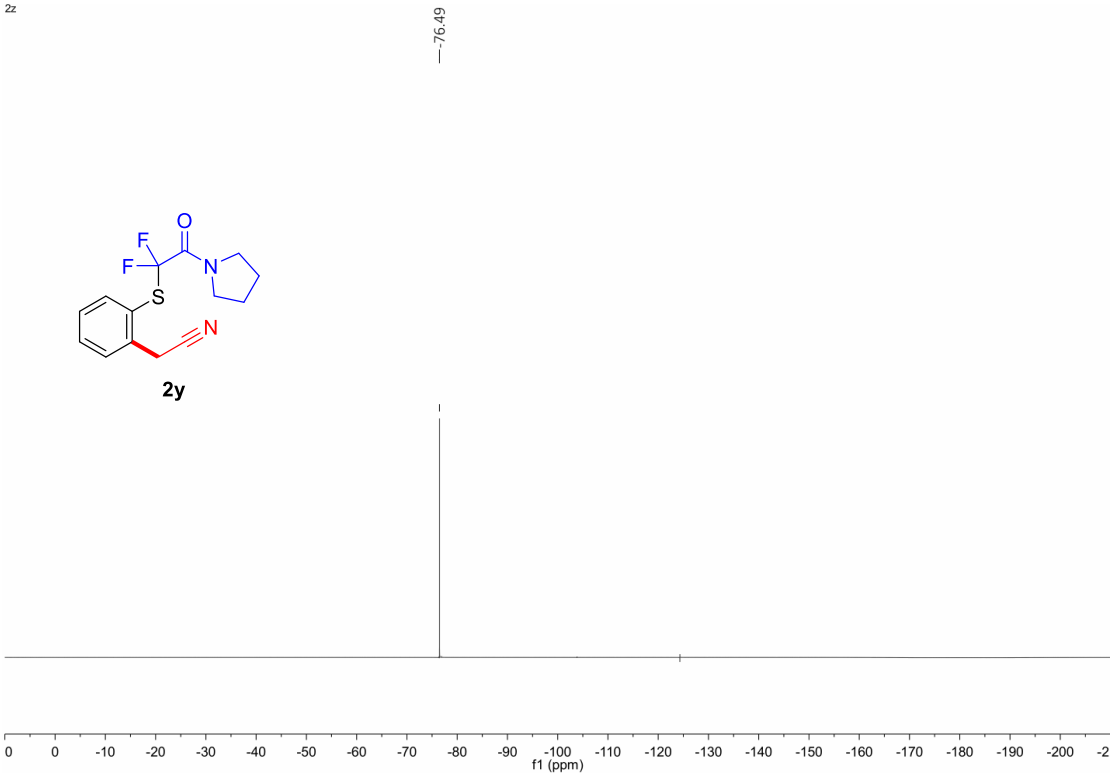
2x

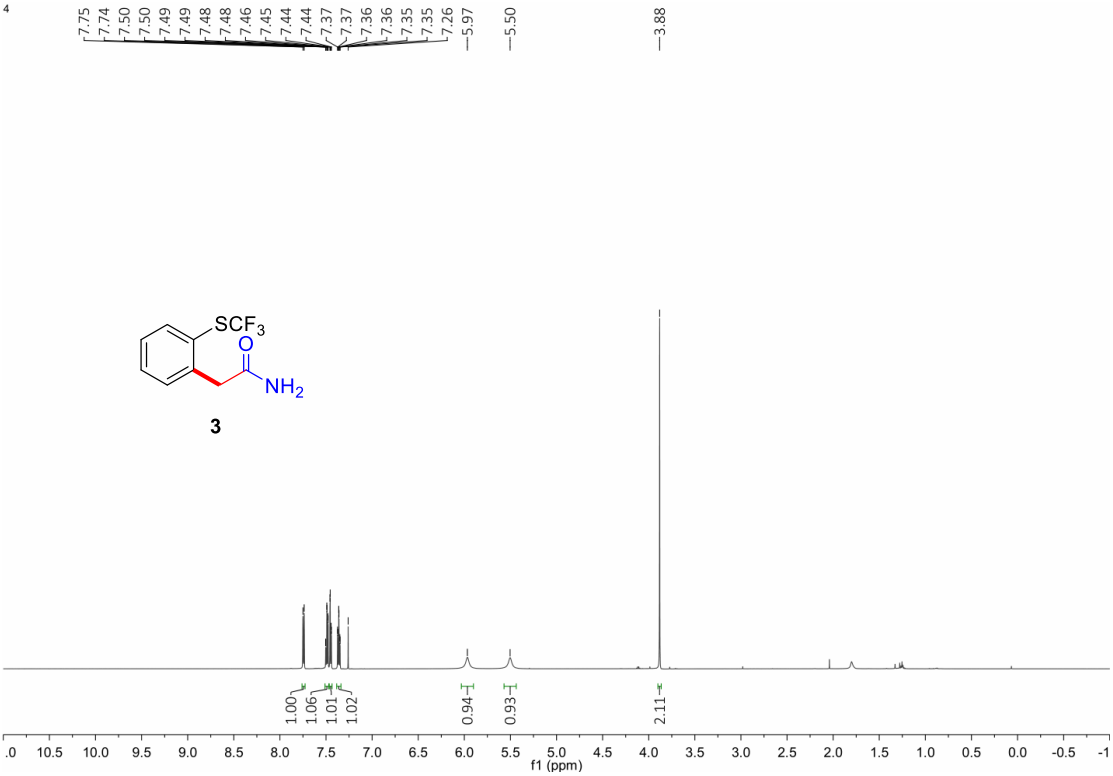

ys-04-26-1
139.94
136.97
135.96
132.63
132.00
131.30
130.99
129.94
129.66
129.35
128.10
124.85
122.81
122.78
122.75
117.52
77.48
77.16
76.84
23.17
F
F
O
S
O
S
N
2x
f1 (ppm)

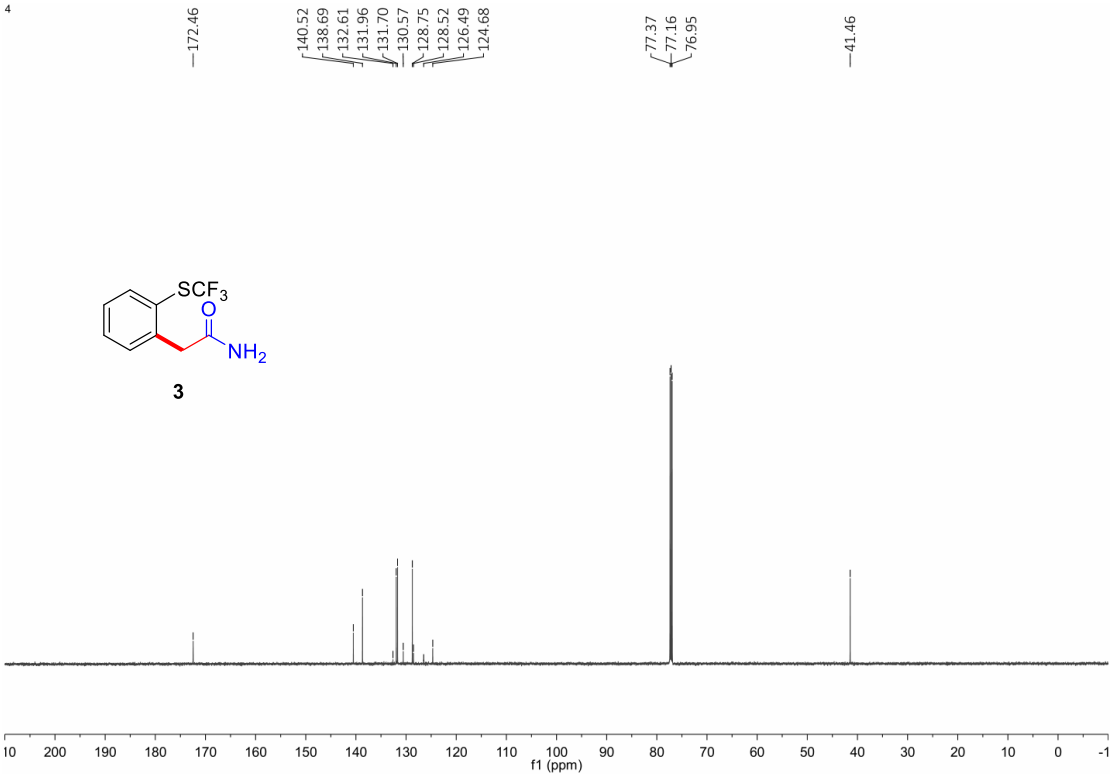

ye-04-19-1
-78.04
F
F
O
S
O
S
N
2x
f1 (ppm)

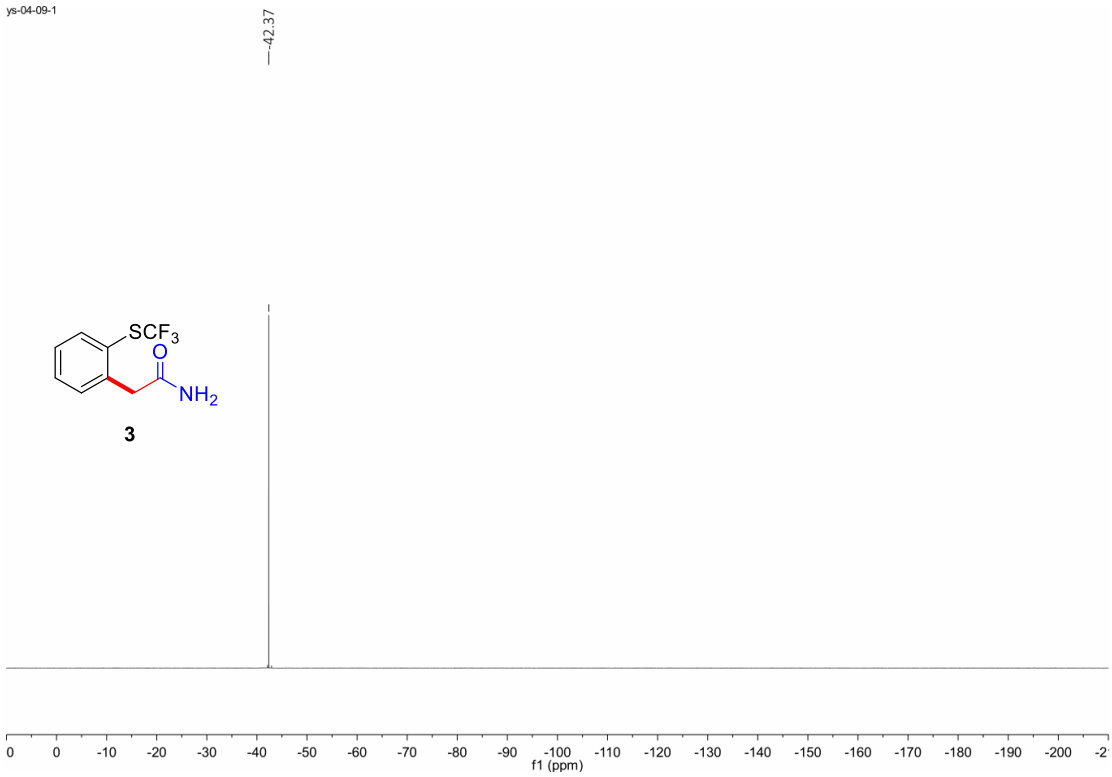

2z
7.71
7.70
7.70
7.66
7.66
7.65
7.65
7.55
7.55
7.54
7.53
7.52
7.52
7.40
7.40
7.39
7.39
7.38
7.37
7.26
4.09
3.64
3.63
3.55
3.54
3.53
1.97
1.96
1.95
1.94
1.90
1.89
1.88
1.87
F
F
O
N
S
N
2y
0.99
0.98
1.00
1.00
2.03
2.19
2.15
2.16
2.09
f1 (ppm)

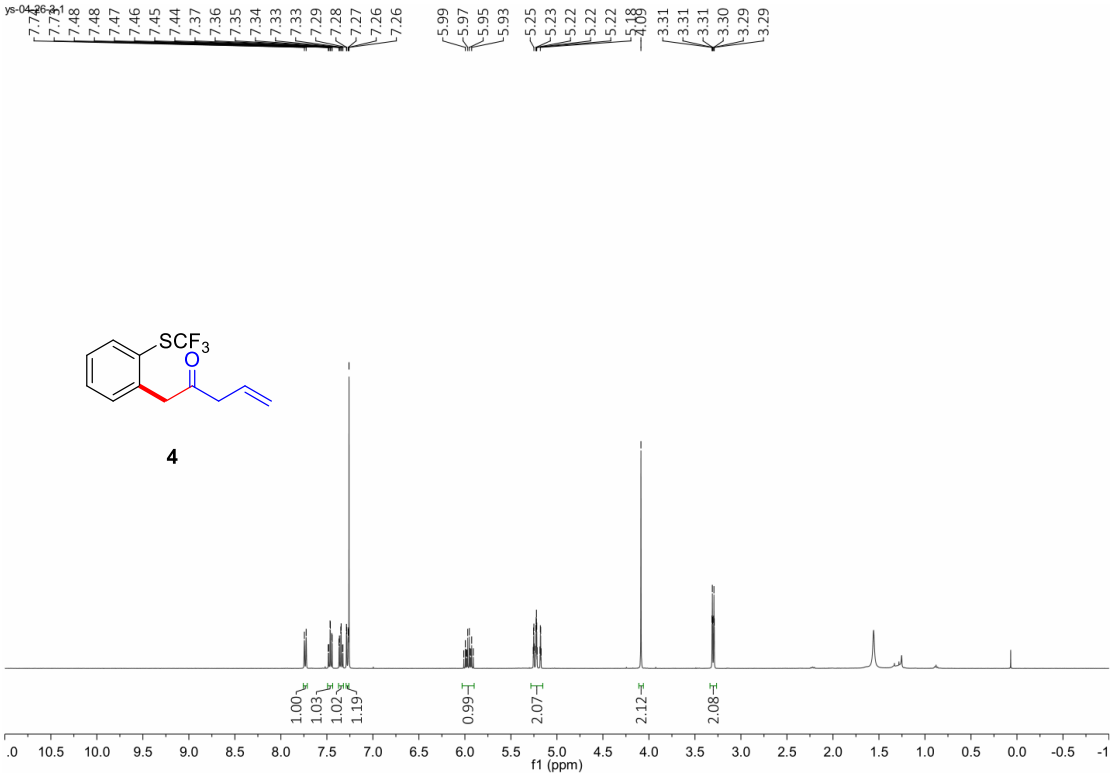

2z
159.56
159.38
159.20
139.67
136.68
131.88
129.59
129.01
126.53
124.77
124.60
122.67
117.75
77.37
77.16
76.95
47.90
46.83
26.53
23.45
23.09
F
F
O
N
S
N
2y
f1 (ppm)

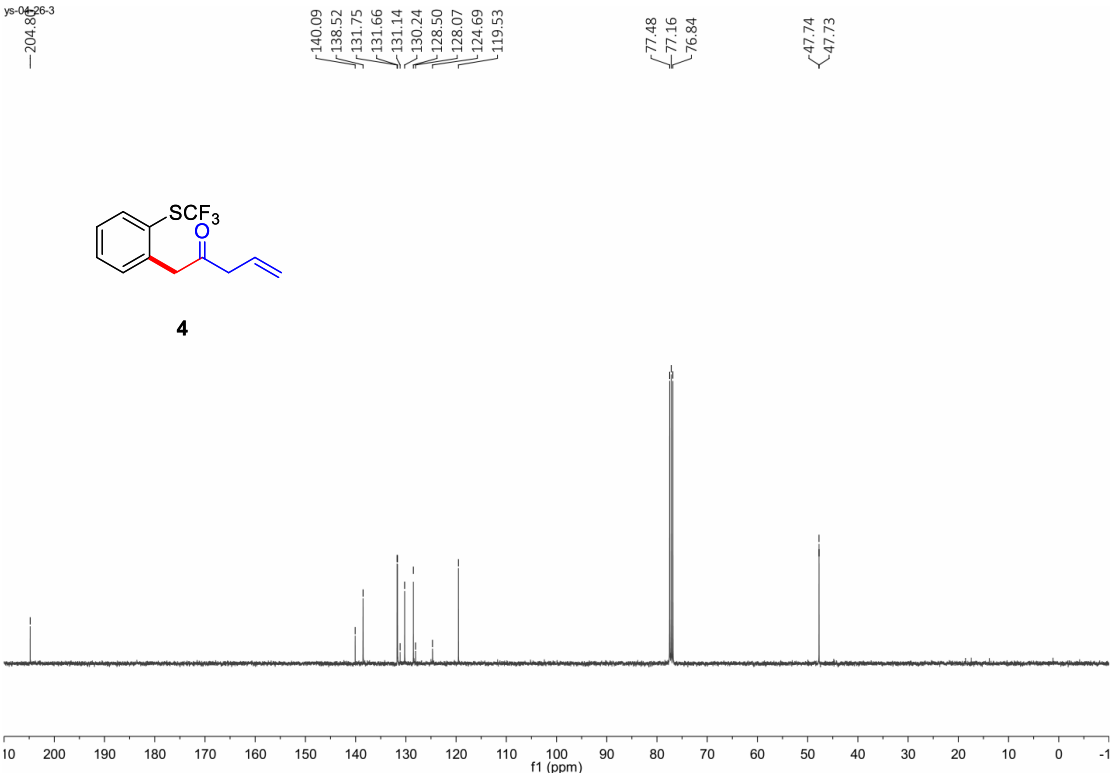

2z
-76.49
F
F
O
N
S
N
2y
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)


4
7.75
7.74
7.50
7.50
7.49
7.49
7.48
7.48
7.46
7.45
7.44
7.44
7.37
7.37
7.36
7.36
7.35
7.35
7.26
5.97
5.50
3.88
SCF3
O
NH2
3
1.00
1.06
1.01
1.02
0.94
0.93
2.11
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


4
172.46
140.52
138.69
132.61
131.96
131.70
130.57
128.75
128.52
126.49
124.68
77.37
77.16
76.95
41.46
SCF3
O
NH2
3
f1 (ppm)

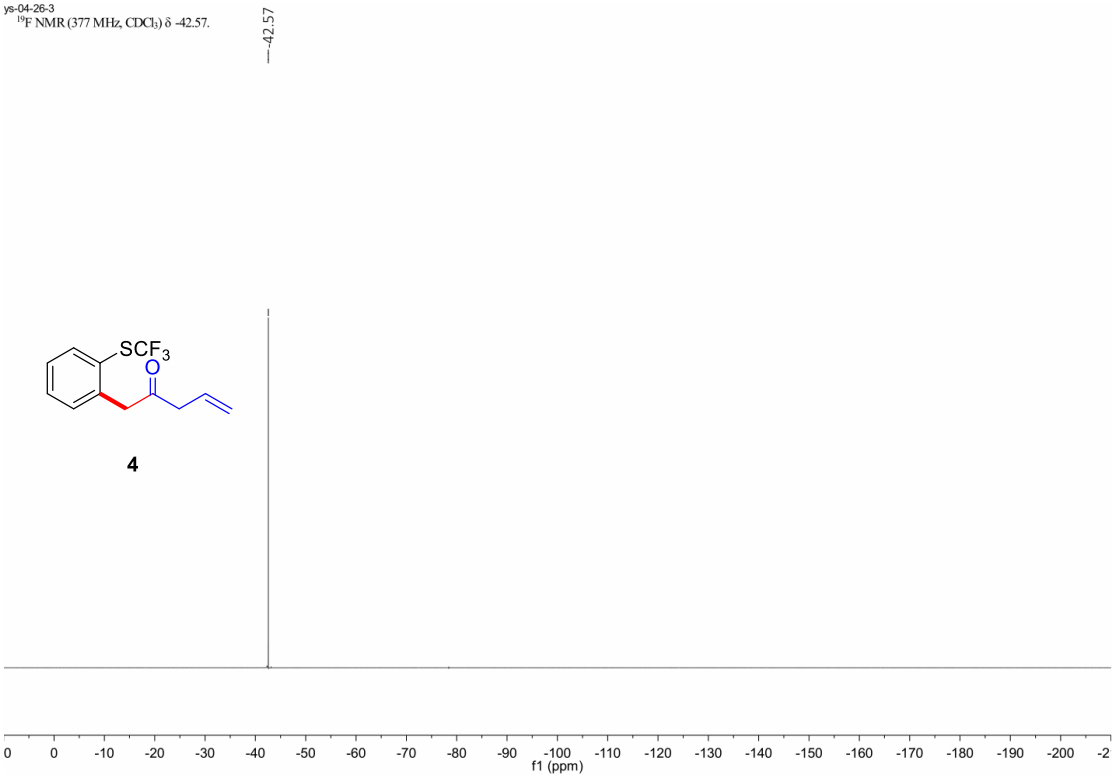

ys-04-09-1
-42.37
SCF3
O
NH2
3
f1 (ppm)


ys-04-26-1
7.74
7.73
7.48
7.48
7.47
7.46
7.45
7.44
7.37
7.36
7.35
7.34
7.33
7.33
7.29
7.28
7.27
7.26
7.26
5.99
5.97
5.95
5.93
5.25
5.23
5.22
5.22
5.22
5.18
4.00
3.31
3.31
3.31
3.30
3.29
3.29
SCF3
O
4
1.00
1.03
1.02
1.19
0.99
2.07
2.12
2.08
f1 (ppm)

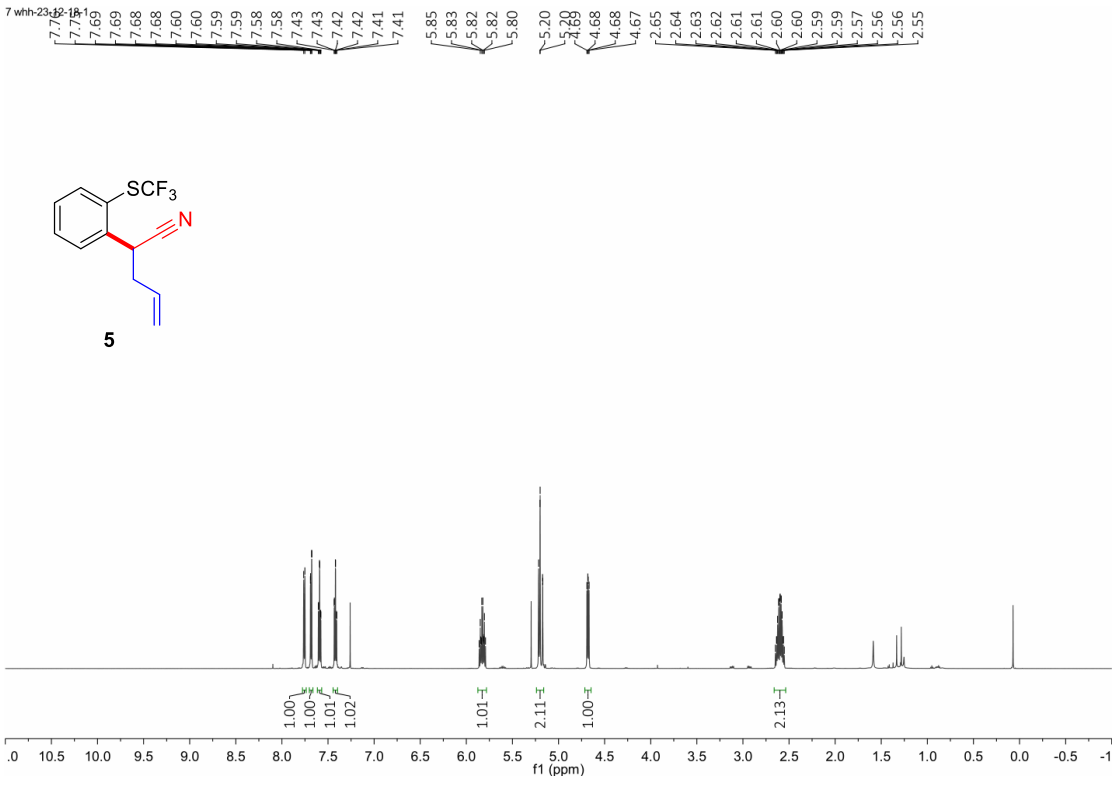

ys-04-26-3
204.80
140.09
138.52
131.75
131.66
131.14
130.24
128.50
128.07
124.69
119.53
77.48
77.16
76.84
47.74
47.73
SCF3
O
4
f1 (ppm)

ys-04-26-3

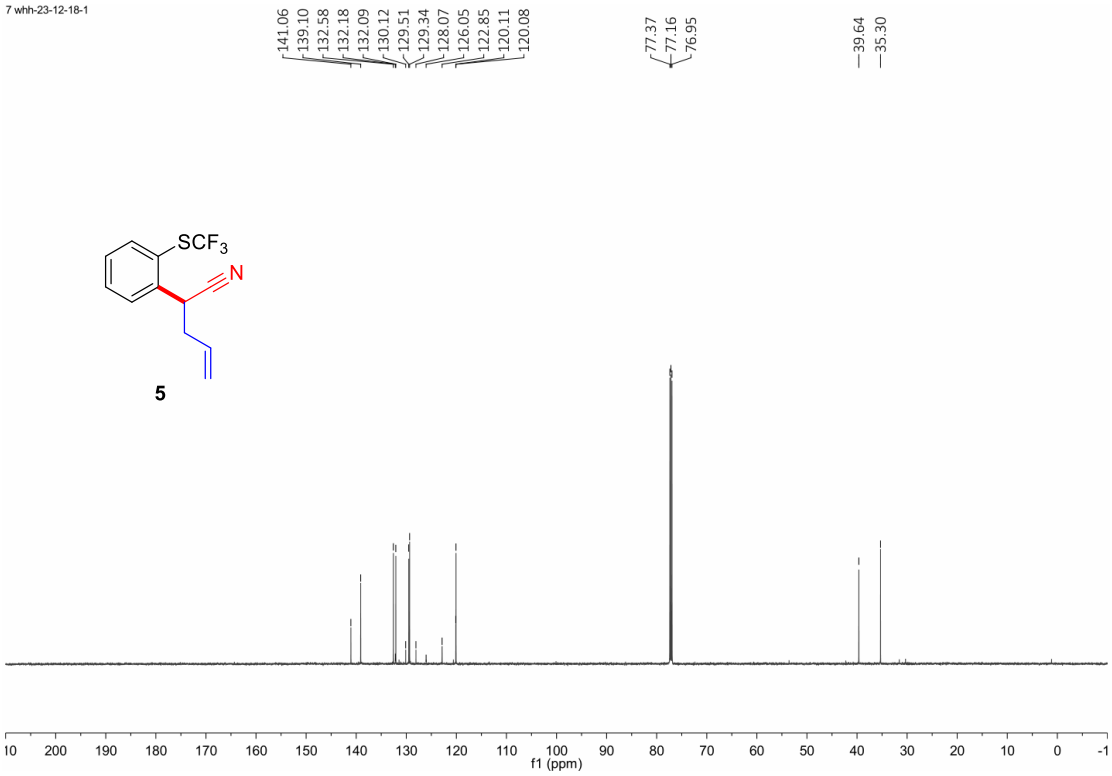
^{19}F NMR (377 MHz, $CDCl_3$) δ -42.57.

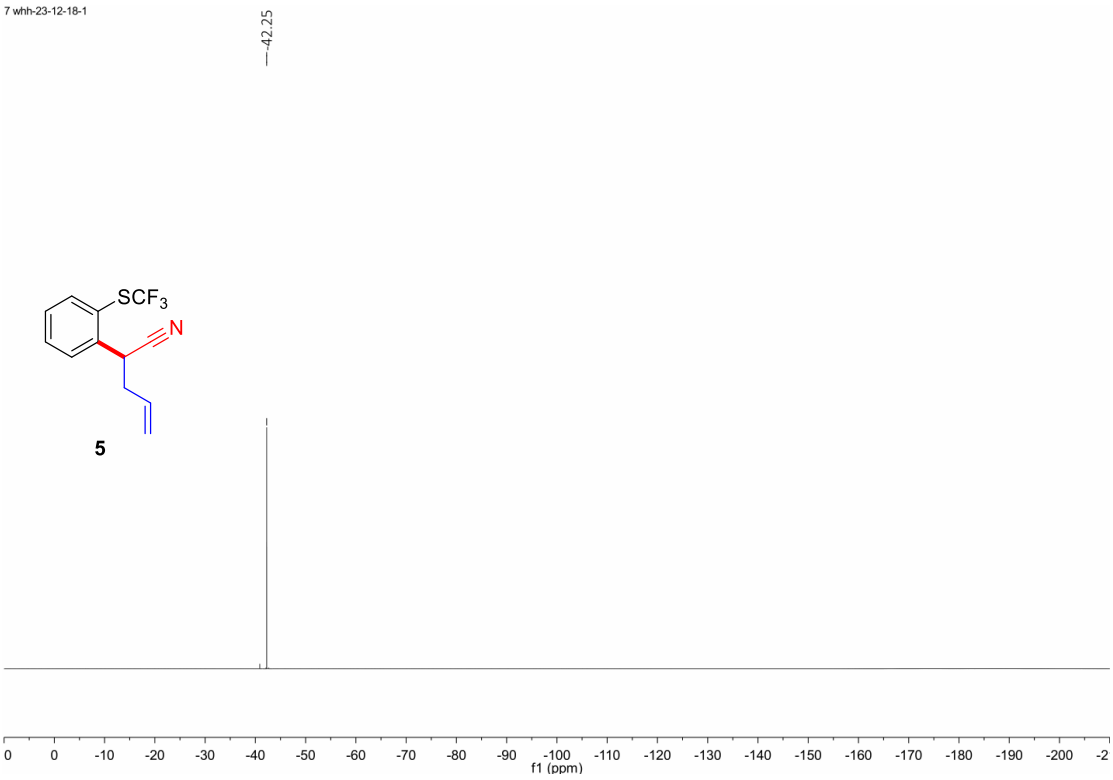


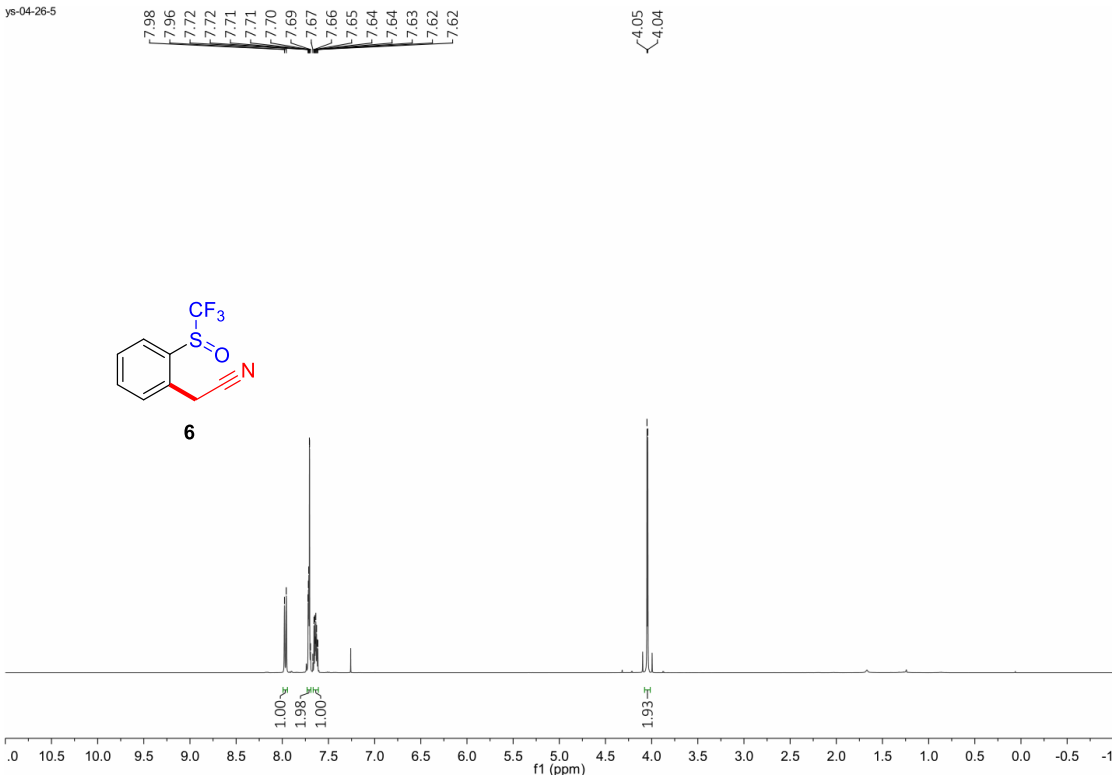
4

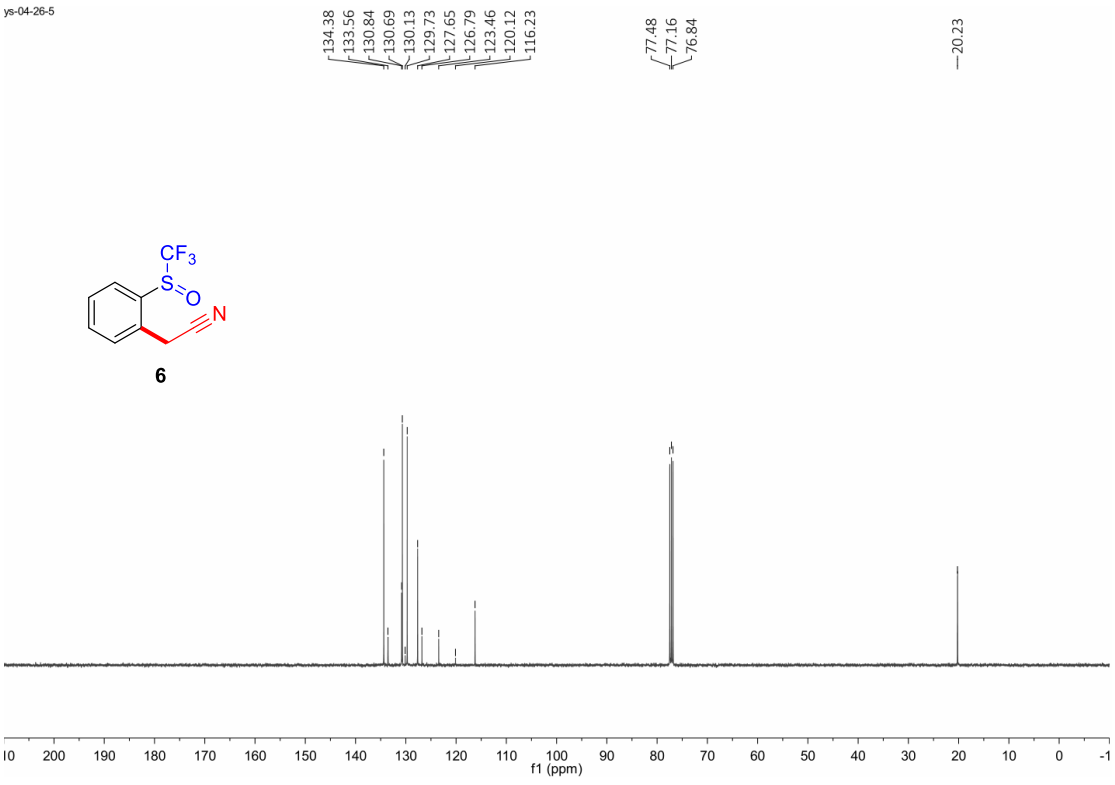


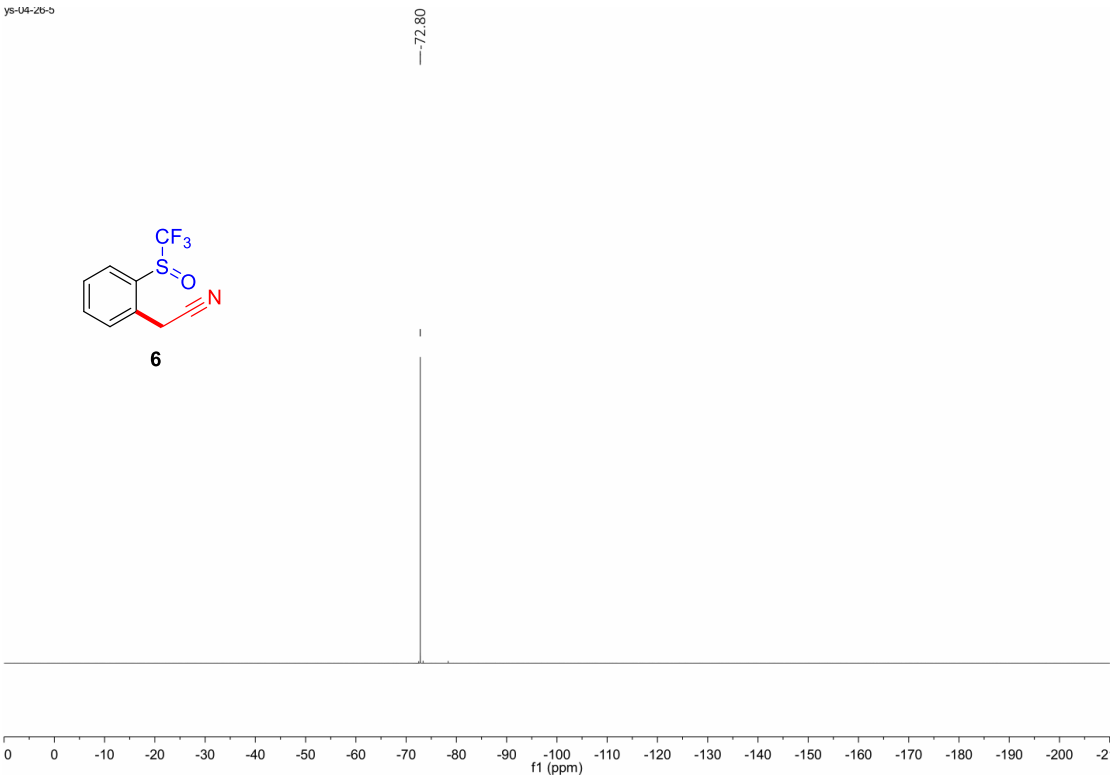
5


7 whh-23-12-18-1
141.06
139.10
132.58
132.18
132.09
130.12
129.51
129.34
128.07
126.05
122.85
120.11
120.08
77.37
77.16
76.95
39.64
35.30
SCF3
N
5
f1 (ppm)


7 whh-23-12-18-1
42.25
SCF3
N
5
f1 (ppm)


ys-04-26-5
7.98
7.96
7.72
7.72
7.71
7.71
7.70
7.69
7.67
7.66
7.65
7.64
7.64
7.63
7.62
7.62
4.05
4.04
CF3
S
O
N
6
1.00
1.98
1.00
1.93
f1 (ppm)


ys-04-26-5
134.38
133.56
130.84
130.69
130.13
129.73
127.65
126.79
123.46
120.12
116.23
77.48
77.16
76.84
20.23
CF3
S
O
N
6
f1 (ppm)


ys-04-zb-5
-72.80
CF3
S
O
N
6
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)