Supporting Information

Tandem Trifluoromethylthiolation/Aryl Migration of Aryl Alkynoates to Trifluoromethylthiolated Alkenes

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Table of Contents

1 General Information……S2

2 Preparation of Aryl Alkynoates……S2

3 Trifluoromethylthiolation/Cyclization of Aryl Alkynoate 1a……S4

4 Trifluoromethylthiolation/Aryl Migration of Aryl Alkynoates……S5

5 Mechanistic Investigation……S13

6. Copies of ^{1}H, ^{19}F, and ^{13}C NMR Spectra for the Products……S16

1. General Information.

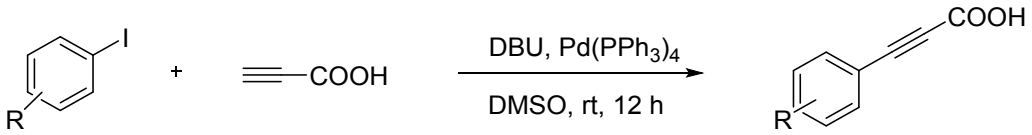
^{1}H and ^{19}F NMR ($CFCl_3$ as outside standard and low field is positive) spectra were recorded on a Bruker AM 400 or 600 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM 400 or 600 spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. DMSO and CH_3CN was distilled from CaH_2 and stored with 4 Å molecular sieves. Reactions were performed using glassware that was flame-dried under vacuum.

2. Preparation of Aryl Alkynoates.

The phenylpropiolic acid **1aa** was purchased and used directly from commercial sources. Substrates **1ab-1ap**[1] and **1a-1u**[2-4] were prepared in accordance with methods described in the references.

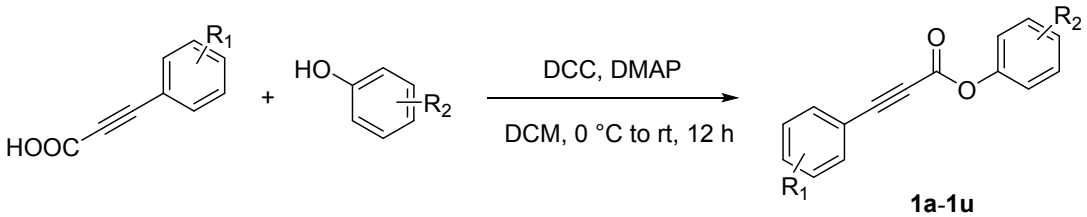
General methods for preparation of aryl alkynyl carboxylic acids (1ab-1ap)[1]



1ab-1ap

Aryl iodides (6.0 mmol, 1.0 equiv), DBU (2.01 g, 13.2 mmol, 2.2 equiv), and $Pd(PPh_3)_4$ (346.7 mg, 0.3 mmol, 5 mol %) were mixed in DMSO (10 mL). A solution of propiolic acid (462.2 mg, 6.6 mmol, 1.1 equiv) in DMSO (5 mL) was added into the flask. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (10 mL) was poured into the reaction mixture. The reaction mixture was extracted with saturated aqueous $NaHCO_3$. The aqueous layer was separated, acidified to pH = 1 by addition of cold HCl (1 N), and extracted with DCM. The combined organic layers were dried with anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel to provide the desired product.

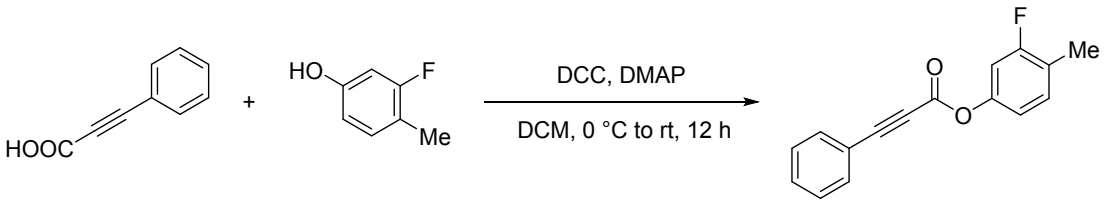
Preparation of aryl alkynoates（1a-1u)[2-4]



1a-1u

To a solution of phenol (3.0 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) was added aryl alkynyl carboxylic acids (3.3 mmol, 1.1 equiv) at 0 °C. Then, a mixture of DCC (873.0 mg, 4.4 mmol, 1.5 equiv) and DMAP (36.0 mg, 1.5 mmol, 0.1 equiv) in CH_2Cl_2 (6 mL) was added dropwise. The resulting mixture was stirred at room temperature for 12 hours. Then the crude mixture was filtered and washed with CH_2Cl_2 (15 mL). The combined organic phase was concentrated under reduced pressure to give a residue which was purified by a silica gel column chromatography to give the desired product.

Preparation of 4-fluoro-3-methylphenyl 3-phenylpropiolate 1t



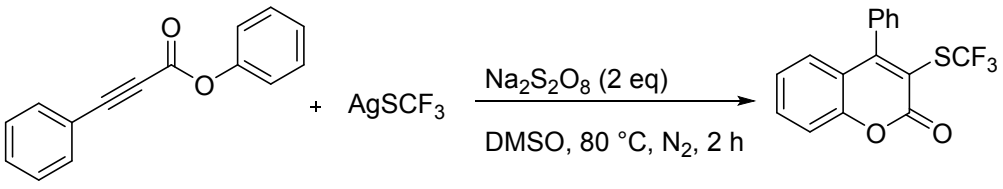
1t

To a solution of 3-fluoro-4-methylphenol (378.4 mg, 3.0 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) was added 3-phenylpropiolic acid (481.8 mg, 3.3 mmol, 1.1 equiv) at 0 °C. Then, a mixture of DCC (873.0 mg, 4.4 mmol, 1.5 equiv) and DMAP (36.0 mg, 1.5 mmol, 0.1 equiv) in CH_2Cl_2 (6 mL) was added dropwise. The resulting mixture was stirred at room temperature for 12 hours. Then the crude mixture was filtered and washed with CH_2Cl_2 (15 mL). The combined organic phase was concentrated under reduced pressure to give a residue which was purified by a silica gel column chromatography (petroleum ether / EtOAc = 100:1) to give product **1t** as a white solid (600.0 mg, 79%). M.p. 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.53 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.13-7.09 (m, 1H), 6.83-6.80 (m, 2H), 2.17 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -113.8--113.9 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.0 (d, J = 246.8 Hz), 152.0, 148.7 (d, J = 10.7 Hz), 133.2, 131.6 (d, J = 6.2 Hz), 131.1, 128.7, 123.1 (d, J = 17.1 Hz), 119.2, 116.9 (d, J = 3.7 Hz), 109.1 (d, J = 25.7 Hz), 89.0, 80.1, 14.1 (d, J = 3.2 Hz). IR (KBr): v 3334, 1380, 1088, 1046, 880, 629, 430 cm^{-1}. MS (EI) m/z: 254 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{11}FO_2$ 254.0743, found $[M]^+$: 254.0747.

Reference:

[1] K. Park, T. Palani, A. Pyo and S. Lee. *Tetrahedron Lett.*, 2012, **53**, 733.
[2] S.-Y. Ni, W. -X. Sha, L.-J. Zhang, C. X., H.-B. Mei, J.-L. He and Y. Pan. *Org. Lett.*, 2016, **18**, 712.
[3] V. Lellek and H.-J. Hansen, *Helv. Chim. Acta*, 2001, **84**, 3548.
[4] W.-C. Gao, T. Liu, B. Zhang, X. Li, W.-L. Wei and H.-H. Chang. *J. Org. Chem.*, 2016, **81**, 11297.

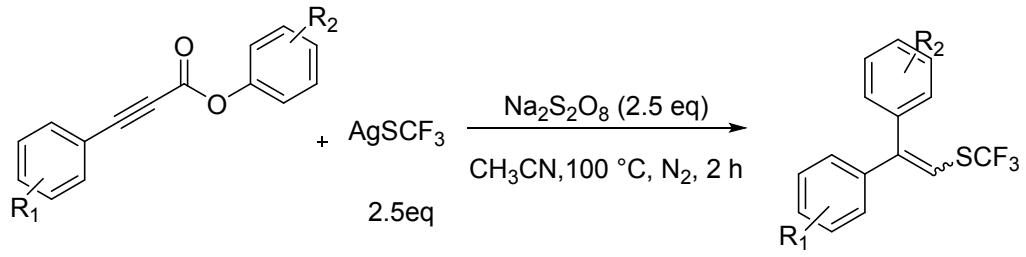
3. Trifluoromethylthiolation/Cyclization of Aryl Alkynoate 1a



1a **2a**

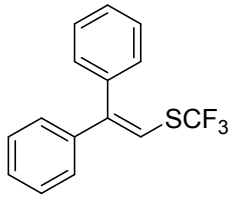
A mixture of **1a** (44.4 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50 mmol, 2.5 equiv) in DMSO (4.0 mL) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. DMSO (4.0 mL) was added to the tube. Then, the tube was stirred at 80 ^oC for 2 h. After the reaction was complete, saturated ammonium chloride solution was added. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with PE:EA=100:1 to give product **2a** as a yellow solid (50.9 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.64 (t, J = 7.7 Hz, 1H), 7.57-7.55 (m, 3H), 7.43 (d, J = 8.3 Hz, 1H), 7.27-7.18 (m, 3H), 7.11 (d, J = 7.9 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -40.40 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 165.6, 159.3, 154.0, 134.2, 134.0, 129.5, 129.4, 128.7 (q, J = 313.1 Hz), 128.6, 128.2, 124.8, 120.2, 117.1, 113.1. MS (EI) m/z: 322 $[M]^+$. These data mathed those previouly reported in reference *Org. Chem. Front.*, 2015, **2**, 1511.

4. Trifluoromethylthiolation/Aryl Migration of Aryl Alkynoates (3a-3u)

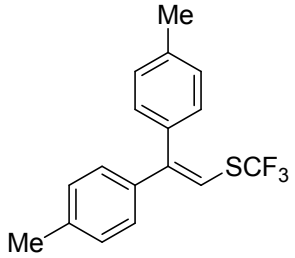


1 **3**

A mixture of **1** (0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50 mmol, 2.5 equiv) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. CH_3CN (4.0 mL) was added to the tube. Then, the tube was stirred at 100 ^oC for 2 h. After the reaction was complete, saturated ammonium chloride solution was added. The resulting mixture was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with PE to give the desired product **(3a-3u)**.

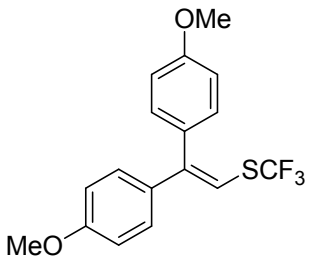


(2,2-Diphenylvinyl)(trifluoromethyl)sulfane (**3a**) (31.0 mg, 52%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.34 (q, *J* = 6.1 Hz, 3H), 7.23-7.13 (m, 7H), 6.69 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.46 (s, 3F). ^{13}C NMR (101MHz, $CDCl_3$): δ ppm 145.5, 139.2, 137.0, 128.7 (q, *J* = 310.1 Hz), 128.3, 127.6, 127.5, 127.4, 127.3, 126.4, 111.0 (q, *J* = 3.3 Hz). IR (KBr): v 1495, 1444, 1285, 1109, 736, 698, 625, 486 cm^{-1}. MS (EI) m/z: 280 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{11}F_3S$ 280.0534, found $[M]^+$: 280.0526. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.

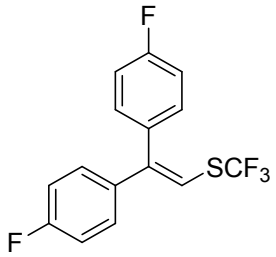


(2,2-Di-p-tolylvinyl)(trifluoromethyl)sulfane (3b) (40.7 mg, 66%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.17-7.13 (m, 2H), 7.07-7.01 (m, 6H), 6.53 (s, 1H), 2.32 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.74 (s, 3F). ^{13}C

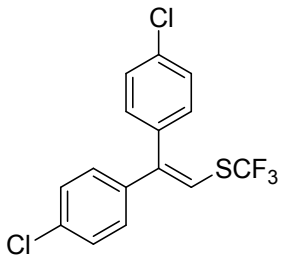
NMR (101 MHz, $CDCl_3$): δ 145.6, 137.4, 137.3, 136.7, 134.2, 128.8 (q, J = 309.1 Hz), 128.3, 128.2, 128.1, 126.4, 109.6 (q, J = 3.2 Hz), 20.3, 20.1. IR (KBr): v 2921, 1612, 1514, 1164, 1110, 929, 822, 771 cm^{-1}. MS (EI) m/z: 308 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{17}H_{15}F_3S$ 308.0847, found $[M]^+$: 308.0838. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.



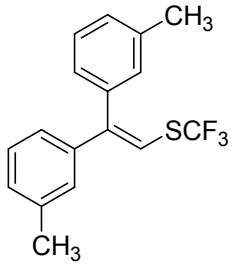
(2,2-Bis(4-methoxyphenyl)vinyl)(trifluoromethyl)sulfane (3c) (39.4 mg, 58%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.11-7.04 (m, 4H), 6.87-6.83 (m, 2H), 6.77-6.73 (m, 2H), 6.43 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.83 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 159.9, 159.7, 146.6, 133.4, 130.8, 130.6, 128.9, 128.8 (q, J = 310.7 Hz), 113.9, 113.8, 109.1 (q, J = 3.2 Hz), 55.34, 55.28. IR (KBr): v 1607, 1511, 1250, 1108, 1034, 835, 816, 584 cm^{-1}. MS (EI) m/z: 340 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{17}H_{15}F_3O_2S$ 340.0745, found $[M]^+$: 340.0736. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.



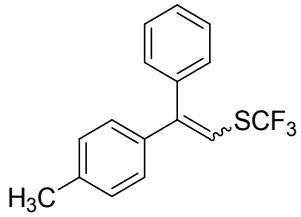
(2,2-Bis(4-fluorophenyl)vinyl)(trifluoromethyl)sulfane (3d) (42.3 mg, 67%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.13-7.09 (m, 4H), 7.05-7.01 (m, 2H), 6.96-6.91 (m, 2H), 6.55 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.56 (s, 3F), -112.09--112.17 (m, 1F), -112.87--112.94 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.9 (d, J = 249.0 Hz), 161.7 (d, J = 248.9 Hz), 143.6, 135.3 (d, J = 3.3 Hz), 132.8 (d, J = 3.4 Hz), 130.2 (d, J = 8.3 Hz), 128.6 (q, J = 309.1 Hz), 128.1 (d, J = 8.2 Hz), 114.8 (d, J = 31.2 Hz), 114.6 (d, J = 31.3 Hz), 111.2. IR (KBr): v 1603, 1511, 1233, 1160, 1111, 841, 733, 576 cm^{-1}. MS (EI) m/z: 316 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_9F_5S$ 316.0345, found $[M]^+$: 316.0334. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.



(2,2-Bis(4-chlorophenyl)vinyl)(trifluoromethyl)sulfane (3e) (39.8 mg, 57%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* =7.6 Hz, 4H), 6.61 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.42 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) : δ ppm 144.1, 138.4, 136.0, 134.9, 134.6, 130.8, 129.6 (q, *J* = 309.1 Hz), 129.1, 128.8, 128.6, 113.3 (q, *J* = 3.4 Hz). IR (KBr): v 2254, 1493, 1114, 1015, 903, 724, 650, 520 cm^{-1}. MS (EI) m/z: 348 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_9Cl_2F_3S$ 347.9754, found $[M]^+$: 347.9760. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.

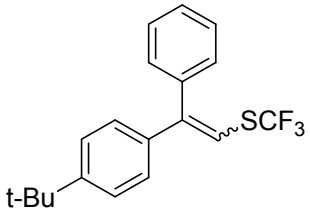


(2, 2-Di-m-tolylvinyl)(trifluoromethyl)sulfane (3f) (32.7 mg, 53%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.20 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 7.4 Hz, 3H), 6.56 (s, 1H), 2.26 (s, 3H), 2.22 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.62 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) : δ ppm 146.7, 140.5, 138.4, 138.21, 138.18, 129.9, 129.6 (q, *J* = 309.1 Hz), 129.4, 129.2, 128.5, 128.4, 128.1, 126.5, 124.7, 111.8 (q, *J* = 3.4 Hz), 21.48, 21.46. IR (KBr): v 1603, 1487, 1158, 1107, 838, 778, 758, 698 cm^{-1}. MS (EI) m/z: 308 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{17}H_{15}F_3S$ 308.0847, found $[M]^+$: 308.0840. These data mathed those previouly reported in reference *Chem. Eur. J.*, 2016, **22**, 4395.

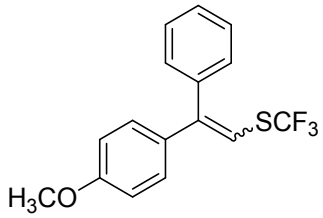


(2-Phenyl-2-(p-tolyl)vinyl)(trifluoromethyl)sulfane (3g) (E/Z = 1:1) (36.5 mg, 62%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39-7.32 (m, 1.5H), 7.28-7.26 (m, 1.5H), 7.23-7.18 (m, 3H), 7.13-7.08 (m, 3H), 6.65 (s, 1H), 2.36 (s, 1.5H), 2.31 (s, 1.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.58 (s, 1.5F), -42.58 (s, 1.5F). ^{13}C

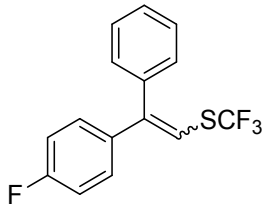
NMR (101 MHz, $CDCl_3$): δ ppm 145.7, 145.4, 139.5, 137.5, 137.3, 137.2, 136.5, 134.1, 128.82 (q, *J* = 309.1 Hz), 128.32, 128.27, 128.2, 128.1, 127.5, 127.4, 127.2, 126.4, 126.3, 110.6 (q, *J* = 3.3 Hz), 110.0 (q, *J* = 3.3 Hz), 20.3, 20.1. IR (KBr): v 3055, 1422, 1265, 898, 731, 703 cm^{-1}. MS (EI) m/z: 294 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{13}F_3S$ 294.0690, found $[M]^+$: 294.0697.



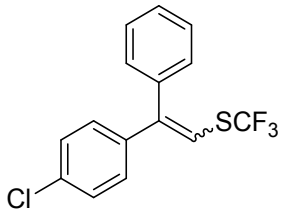
(2-(4-(Tert-butyl)phenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3h) (E/Z = 1:1) (42.4 mg, 63%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.41-7.36 (m, 2.5H), 7.34-7.30 (m, 1.5H), 7.26 (s, 1.5H), 7.24-7.20 (m, 2H), 7.17-7.12 (m, 1.5H), 6.68 (s, 0.5H), 6.64 (s, 0.5H), 1.34 (s, 4.5H), 1.30 (s, 4.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.58 (s, 1.5F), -42.64 (s, 1.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 150.5, 145.6, 145.2, 139.6, 137.2, 136.3, 134.0, 128.9 (q, *J* = 309.1 Hz), 128.8 (q, *J* = 309.1 Hz), 128.3, 128.0, 127.5, 127.39, 127.35, 126.5, 126.0, 124.4, 124.3, 110.7 (q, *J* = 3.3 Hz), 110.1 (q, *J* = 3.2 Hz), 33.6, 33.5, 30.2, 30.1. IR (KBr): v 2964, 1150, 1105, 937, 842, 809, 754, 700, 630 cm^{-1}. MS (EI) m/z: 336 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{19}H_{19}F_3S$ 336.1160, found $[M]^+$: 336.1156.



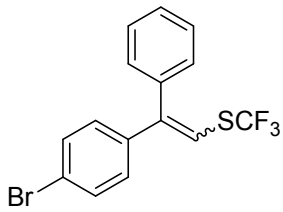
(2-(4-Methoxyphenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3i) (E/Z = 1:1) (42.2 mg, 68%): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.34-7.27 (m, 1.5 H), 7.22-7.21 (m, 1.5H), 7.16-7.11 (m, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 5.6 Hz, 0.5H), 6.83 (s, 0.5H), 6.76 (s, 0.5H), 6.73 (s, 0.5H), 6.53 (s, 0.5H), 6.50 (s, 0.5H), 3.74 (s, 1.5H), 3.70 (s, 1.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.68 (s, 1.5F), -42.73 (s, 1.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 158.8, 158.7, 145.8, 145.2, 139.7, 137.3, 131.9, 129.7, 129.3, 128.8 (q, *J* = 309.7 Hz), 128.4, 127.7, 127.5, 127.44, 127.39, 127.3, 126.5, 112.9, 112.8, 110.2 (q, *J* = 3.2 Hz), 108.6 (q, *J* = 3.2 Hz), 54.3, 54.2. IR (KBr): v 1607, 1510, 1251, 1166, 1108, 1033, 839, 735, 699 cm^{-1}. MS (EI) m/z: 310 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{13}F_3OS$ 310.0639, found $[M]^+$: 310.0636.



(2-(4-Fluorophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3j) (E/Z = 1:1) (30.4 mg, 51%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) : δ ppm 7.36-7.29 (m, 1.5H), 7.25-7.23 (m, 1.5H), 7.16-7.11 (m, 4H), 7.03 (t, *J* = 8.6 Hz, 1H), 6.92 (t, *J* = 8.6 Hz, 1H), 6.61 (s, 0.5H), 6.55 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.51 (s, 1.5F), -42.64 (s, 1.5F), -112.40--112.47 (m, 0.5F), -113.19--113.26 (m, 0.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.8 (d, *J* = 248.7 Hz), 161.6 (d, *J* = 248.6 Hz), 139.1, 135.5 (d, *J* = 3.3 Hz), 132.9 (d, *J* = 3.4 Hz), 136.9, 130.3 (d, *J* = 8.2 Hz), 128.7 (q, *J* = 308.7 Hz), 128.6 (q, *J* = 308.4 Hz), 128.3, 128.2, 128.1, 127.7, 127.52, 127.49, 114.7 (d, *J* = 30.8 Hz), 114.5 (d, *J* = 30.8 Hz), 111.4 (q, *J* = 3.2 Hz), 110.9 (q, *J* = 3.2 Hz). IR (KBr): v 2924, 1603, 1508, 444, 1234, 1165, 1111, 844, 756 cm^{-1}. MS (EI) m/z: 298 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}F_4S$ 298.0439, found $[M]^+$: 298.0447.

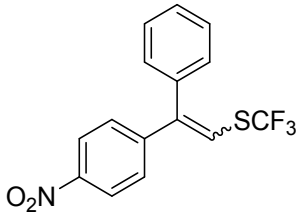


2-(4-Chlorophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3k) (E/Z = 1:1) (29.6 mg, 47%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.41-7.34 (m, 2.5H), 7.28-7.27 (m, 1.5H), 7.24-7.16 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.70 (s, 0.5H), 6.68 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.42 (s, 1.5F), -42.48 (s, 1.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 144.5, 143.9, 138.9, 137.6, 136.6, 135.4, 133.5, 133.3, 129.8, 128.7 (q, *J* = 309.1 Hz), 128.6 (q, *J* = 309.1 Hz), 128.2, 127.9, 127.7, 127.61, 127.58, 127.5, 127.3, 126.3, 111.7 (q, *J* = 3.3 Hz), 111.5 (q, *J* = 3.3 Hz). IR (KBr): v 1489, 1265, 1167, 1107, 1015, 935, 755, 701 cm^{-1}. MS (EI) m/z: 314 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}ClF_3S$ 314.0144, found $[M]^+$: 314.0142.

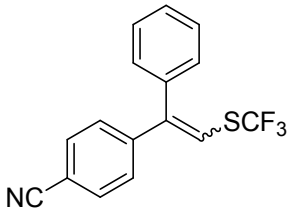


(2-(4-Bromophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3l) (E/Z = 1:1) (37.3 mg, 52%): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.65-7.64 (m, 1H), 7.54-7.49 (m, 2.5H), 7.43-7.41 (m, 1.5H), 7.32-7.30 (m, 2H), 7.22-7.20 (m, 2H), 6.84 (s,

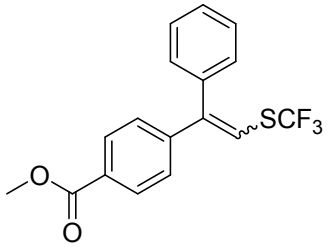
0.5H), 6.83 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$) : δ ppm -42.49 (s, 1.5F), -42.55 (s, 1.5F). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 145.7, 145.1, 139.9, 139.3, 137.6, 137.0, 132.0, 131.7, 131.2, 129.81 (q, *J* = 309.1 Hz), 129.78 (q, *J* = 308.0 Hz), 129.4, 129.0, 128.9, 128.8, 128.70, 128.68, 127.5, 122.9, 122.7, 113.0 (q, *J* = 3.3 Hz), 112.7 (q, *J* = 3.3 Hz). IR (KBr): v 1494, 1167, 1109, 1011, 807, 756, 700 cm^{-1}. MS (EI) m/z: 358 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}BrF_3S$ 357.9639, found $[M]^+$: 357.9637.



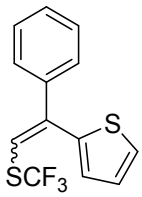
(2-(4-Nitrophenyl)-2-phenylvinyl) (trifluoromethyl)sulfane (3m) (E/Z = 1:1) (36.4 mg, 56%): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 8.32-8.31 (m, 1H), 8.21-8.19 (m, 1H), 7.51-7.45 (m, 2.5H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.39-7.37 (m, 1.5H), 7.24-7.22 (m, 2H), 6.93 (s, 0.5H), 6.85 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.34 (s, 1.5F), -42.35 (s, 1.5F). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 147.7, 147.4, 146.1, 144.9, 144.7, 142.9, 139.2, 136.8, 130.5, 129.5 (q, *J* = 308.0 Hz), 129.4 (q, *J* = 308.0 Hz), 129.23, 129.15, 129.1, 129.0, 128.8, 127.9, 127.3, 124.0, 123.8, 117.1 (q, *J* = 3.4 Hz), 114.1 (q, *J* = 3.3 Hz). IR (KBr): v 1521, 1349, 1265, 1111, 853, 733, 702 cm^{-1}. MS (EI) m/z: 325 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}F_3NO_2S$ 325.0384, found $[M]^+$: 325.0378.



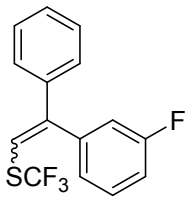
4-(1-Phenyl-2-((trifluoromethyl)thio)vinyl)benzonitrile (3n) (E/Z = 1:1) (27.4 mg, 45%): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) : δ ppm 7.75 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 1.5H), 7.40-7.37 (m, 3.5H), 7.24-7.22 (m, 2H), 6.89 (s, 0.5H), 6.83 (s, 0.5H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -42.34 (s, 1.5F), -42.37 (s, 1.5F). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 145.3, 144.3, 143.5, 142.8, 139.3, 136.8, 132.5, 132.3, 130.3, 129.5 (q, *J* = 308.4 Hz), 129.4 (q, *J* = 308.0 Hz), 129.19, 129.15, 129.1, 129.0, 128.8, 127.8, 127.4, 118.6, 118.4, 116.2 (q, *J* = 3.5 Hz), 113.8 (q, *J* = 3.4 Hz), 112.5, 111.8. IR (KBr): v 3030, 1103, 803, 755, 696, 542 cm^{-1}. MS (EI) m/z: 305 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{10}F_3NS$ 305.0486, found $[M]^+$: 305.0481.



Methyl 4-(1-phenyl-2-((trifluoromethyl)thio)vinyl)benzoate (3o) (E/Z = 1:1) (43.2 mg, 64%): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) : δ ppm 8.15 (d, *J* = 1.8 Hz, 0.5H), 8.14 (d, *J* = 1.8 Hz, 0.5H), 8.03 (d, *J* = 1.8 Hz, 0.5H), 8.02 (d, *J* = 1.8 Hz, 0.5H), 7.49-7.43 (m, 1,5H), 7.36-7.34 (m, 3.5H), 7.27-7.24 (m, 2H), 6.88 (s, 0.5H), 6.81 (s, 0.5H), 3.97 (s, 1.5H), 3.95 (s, 1.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.46 (s, 1.5F), -42.49 (s, 1.5F). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 166.59, 166.55, 145.8, 144.7, 144.4, 142.7, 139.7, 137.5, 130.3, 130.0, 129.82, 129.78, 129.70 (q, *J* = 308.0 Hz), 129.67 (q, *J* = 308.0 Hz), 129.5, 129.3, 128.9, 128.68, 128.65, 127.4, 127.3, 114.8 (q, *J* = 3.3 Hz), 113.1 (q, *J* = 3.3 Hz), 52.21, 52.15. IR (KBr): v 1721, 1436, 1274, 1166, 1099, 1019, 755, 699 cm^{-1}. MS (EI) m/z: 338 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{17}H_{13}F_3O_2S$ 338.0588, found $[M]^+$: 338.0585.

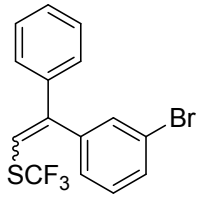


2-(1-Phenyl-2-((trifluoromethyl)thio)vinyl)thiophene (3P) (E/Z = 3:2) (40.0 mg, 54%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.30-7.27 (m, 2.2H), 7.22 (s, 2.2H), 7.17-7.15 (m, 1.2H), 7.08 (t, *J* = 11.0 Hz, 0.8H), 6.94-6.92 (m, 1H), 6.81-6.79 (m, 0.6H), 6.62 (d, *J* = 3.3 Hz, 0.6H), 6.40 (s, 0.4H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.48 (s, 1.8F), -42.63 (s, 1.2F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 144.1, 141.4, 141.0, 139.8, 139.2, 137.4, 129.8 (q, *J* = 309.1 Hz), 129.7 (q, *J* = 309.1 Hz), 129.7, 129.2, 129.0, 128.8, 128.7, 128.5, 128.1, 127.70, 127.66, 127.1, 127.0, 126.3, 111.7 (q, *J* = 3.4 Hz), 109.2 (q, *J* = 3.2 Hz). IR (KBr): v 1237, 1162, 1102, 847, 803, 756, 695, 615 cm^{-1}. MS (EI) m/z: 286 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{13}H_9F_3S_2$ 286.0098, found $[M]^+$: 286.0096.

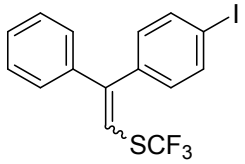


(2-(3-Fluorophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3q) (E/Z = 1:1) (39.8 mg, 58%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.38-7.30 (m, 2H), 7.27 (t, *J* = 6.4 Hz, 1.5H), 7.20-7.16 (m, 2.5H), 7.05-6.96 (m, 1.5H), 6.91 (t, *J* = 8.4 Hz, 1.5H), 6.73 (s, 0.5H), 6.72 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.47 (s, 3F), -

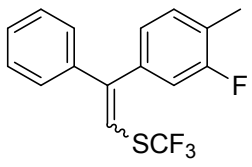
111.68--111.75 (m, 0.5F), -112.41--112.45 (m, 0.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.8 (d, *J* = 246.6 Hz), 144.2, 143.7, 141.3 (d, *J* = 7.5 Hz), 139.1 (d, *J* = 7.6 Hz), 138.7, 136.5, 129.2 (d, *J* = 8.3 Hz), 128.9 (d, *J* = 8.3 Hz), 128.7 (q, *J* = 309.1 Hz), 128.2, 127.8, 127.5, 126.3, 124.1 (d, *J* = 3.0 Hz), 122.0 (d, *J* = 2.8 Hz), 115.4 (d, *J* = 21.8 Hz), 114.4 (d, *J* = 42.4 Hz), 114.2 (d, *J* = 42.7 Hz), 113.3 (d, *J* = 22.5 Hz), 112.6 (q, *J* = 3.3 Hz), 111.8 (q, *J* = 3.3 Hz). IR (KBr): v 3030, 1160, 1103, 783, 803, 755, 694 cm^{-1}. MS (EI) m/z: 298 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}F_4S$ 298.0439, found $[M]^+$: 298.0438.



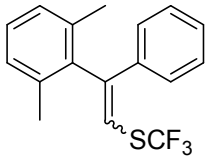
(2-(3-Bromophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3r) (E/Z = 1:1)
^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.68-7.66 (m, 0.5H), 7.61-7.60 (m, 0.5H), 7.59-7.57 (m, 1.5H), 7.56-7.53 (m, 1H), 7.48-7.45 (m, 1.5H), 7.42-7.36 (m, 2.5H), 7.35-7.32 (m, 1 H), 7.29 (t, *J* = 7.8 Hz, 0.5H), 6.94 (s, 0.5H), 6.93 (s, 0.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.45 (s, 1.5F), -42.47 (s, 1.5F). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 145.3, 144.8, 142.5, 140.3, 139.8, 137.6, 132.4, 131.8, 131.4, 130.5, 130.4, 130.1, 129.92 (q, *J* = 308.0 Hz), 129.90 (q, *J* = 308.0 Hz), 129.4, 129.02, 129.00, 128.8, 128.2, 127.5, 126.2, 123.04, 122.99, 114.0 (q, *J* = 3.3 Hz), 113.2 (q, *J* = 3.3 Hz). IR (KBr): v 1540, 1167, 1149, 1103, 947, 774, 754, 699, 473 cm^{-1}. MS (EI) m/z: 358 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}BrF_3S$ 357.9639, found $[M]^+$: 357.9635.



(2-(4-Iodophenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3r) (E/Z = 1:1) (48.7 mg, 60%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.34-7.28 (m, 1.5H), 7.23-7.21 (m, 1.5H), 7.13-7.09 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.61 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.42 (s, 1.5F), -42.46 (s, 1.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 144.5, 144.0, 138.73, 138.68, 136.8, 136.6, 136.43, 136.40, 130.2, 128.60 (q, *J* = 309.1 Hz), 128.57 (q, *J* = 309.1 Hz), 128.2, 128.1, 127.7, 127.6, 127.5, 126.4, 127.3, 111.9 (q, *J* = 3.4 Hz), 111.5 (q, *J* = 3.3 Hz), 93.6, 93.2. IR (KBr): v 1485, 1390, 1168, 1111, 1007, 907, 808, 732 cm^{-1}. MS (EI) m/z: 406 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{10}F_3IS$ 405.9500, found $[M]^+$: 405.9489.



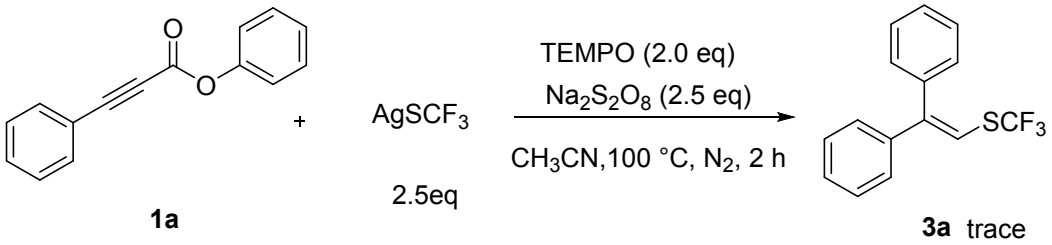
(2-(3-Fluoro-4-methylphenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3t) (E/Z = 1:1) (35.0 mg, 56%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39-7.34 (m, 1.5H), 7.26 (d, *J* = 5.9 Hz, 1.5H), 7.22-7.17 (m, 2.5H), 7.06 (t, *J* = 7.9 Hz, 0.5H), 6.92-6.85 (m, 2H), 6.69 (d, *J* = 3.8 Hz, 1H), 2.28 (s, 1.5H), 2.22 (s, 1.5H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -42.55 (s, 3F), -116.13 (t, *J* = 8.9 Hz, 0.5F), -116.79 (t, *J* = 9.4 Hz, 0.5F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 160.19 (d, *J* = 247.5 Hz), 160.18 (d, *J* = 246.4 Hz), 144.2 (d, *J* = 17.5 Hz), 138.9, 138.7 (d, *J* = 7.5 Hz), 136.6, 136.3 (d, *J* = 7.7 Hz), 130.6 (d, *J* = 5.5 Hz), 130.3 (d, *J* = 5.5 Hz), 128.7 (q, *J* = 309.1 Hz), 128.2, 127.7, 127.5 (d, *J* = 3.8 Hz), 126.4, 124.5, 124.3, 124.1, 124.0, 123.90 (d, *J* = 3.4 Hz), 123.86 (d, *J* = 3.4 Hz), 121.5 (d, *J* = 3.2 Hz), 114.0 (d, *J* = 208.1 Hz), 113.8 (d, *J* = 208.7 Hz), 13.4 (d, *J* = 3.4 Hz), 13.2 (d, *J* = 3.4 Hz). IR (KBr): v 1505, 1161, 1102, 1002, 889, 804, 755, 697 cm^{-1}. MS (EI) m/z: 312 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{12}F_4S$ 312.0596, found $[M]^+$: 312.0590.



(2-(2,6-Dimethylphenyl)-2-phenylvinyl)(trifluoromethyl)sulfane (3u) (E/Z = 1: 0.45) (13.0 mg, 21%): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.34-7.28 (m, 3.0H), 7.24-7.21 (m, 2.0H), 7.17 (d, *J* = 5.4 Hz, 0.8H), 7.12 (d, *J* = 7.5 Hz, 1.5H), 7.07 (d, *J* = 7.5 Hz, 0.7H), 6.95 (s, 0.7H), 6.26 (s, 0.3H), 2.18 (s, 1.9H), 2.12 (s, 4.1H). ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -41.85 (s, 2.1F), -42.91 (s, 0.9F). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 144.6, 142.8, 137.21, 137.17, 136.6, 136.5, 136.1, 129.1 (q, *J* = 309.1 Hz), 129.0 (q, *J* = 309.1 Hz), 128.8, 128.44, 128.41, 128.39, 128.3, 127.9, 127.8, 125.6, 113.4 (q, *J* = 3.3 Hz), 112.8 (q, *J* = 3.3 Hz) , 20.4, 19.5. IR (KBr): v 3326, 1380, 1088, 1046, 880, 635 cm^{-1}. MS (EI) m/z: 308 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{17}H_{15}F_3S$ 308.0847, found $[M]^+$: 308.0836.

5. Mechanistic Investigation

Radical trapping experiments



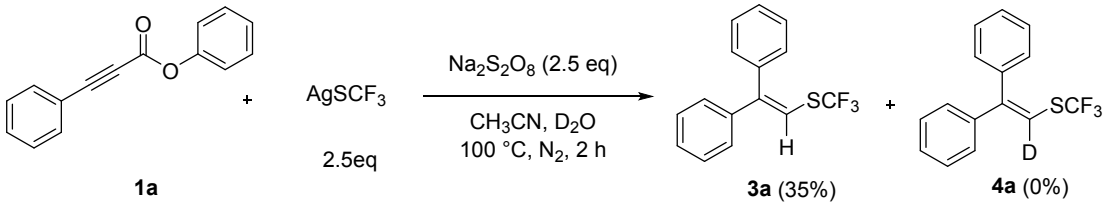
The experimental procedures for radical capture with TEMPO:

A mixture of **1a** (44.4 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv), TEMPO (62.5 mg, 0.40 mmol, 2.0 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50 mmol, 2.5 equiv) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. CH_3CN (4.0 mL) was added to the tube. Then, the tube was

stirred at 100 °C for 2 h. Only trace of the desired product **3a** was detected by ^{19}F NMR.

The deuterium labeling experiments

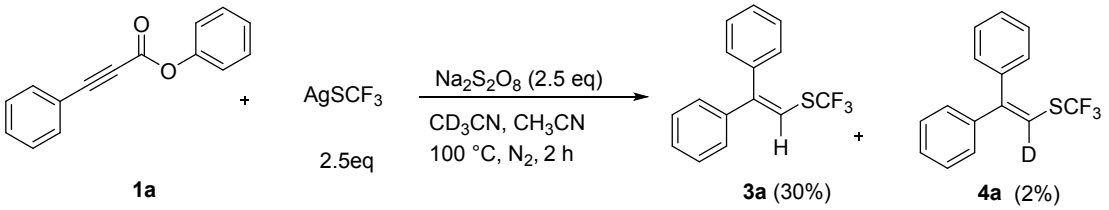
The deuterium labeling experiment in CH_3CN/D_2O



1a **3a** (35%) **4a** (0%)

A mixture of **1** (44.4 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50mmol, 2.5 equiv) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. The mixture of CH_3CN (2.0 mL) and D_2O (2.0 mL) was added to the tube. Then, the tube was stirred at 100 °C for 2 h. Product **3a** was formed in 35% yield (detected by ^{19}F NMR), and no deuterated product **4a** was detected by ^{19}F NMR.

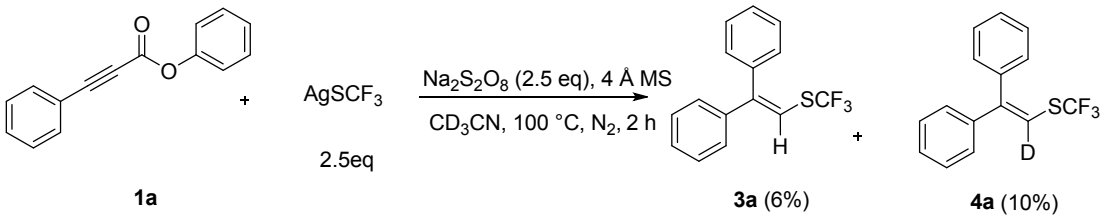
The deuterium labeling experiment in CD_3CN/CH_3CN



1a **3a** (30%) **4a** (2%)

A mixture of **1** (44.4 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50 mmol, 2.5 equiv) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. The mixture of CD_3CN (2.0 mL) and CH_3CN (2.0 mL) was added to the tube. Then, the tube was stirred at 100 °C for 2 h. Product **3a** was formed in 30% yield (detected by ^{19}F NMR), and only trace of deuterated product **4a** (2%) was detected by ^{19}F NMR.

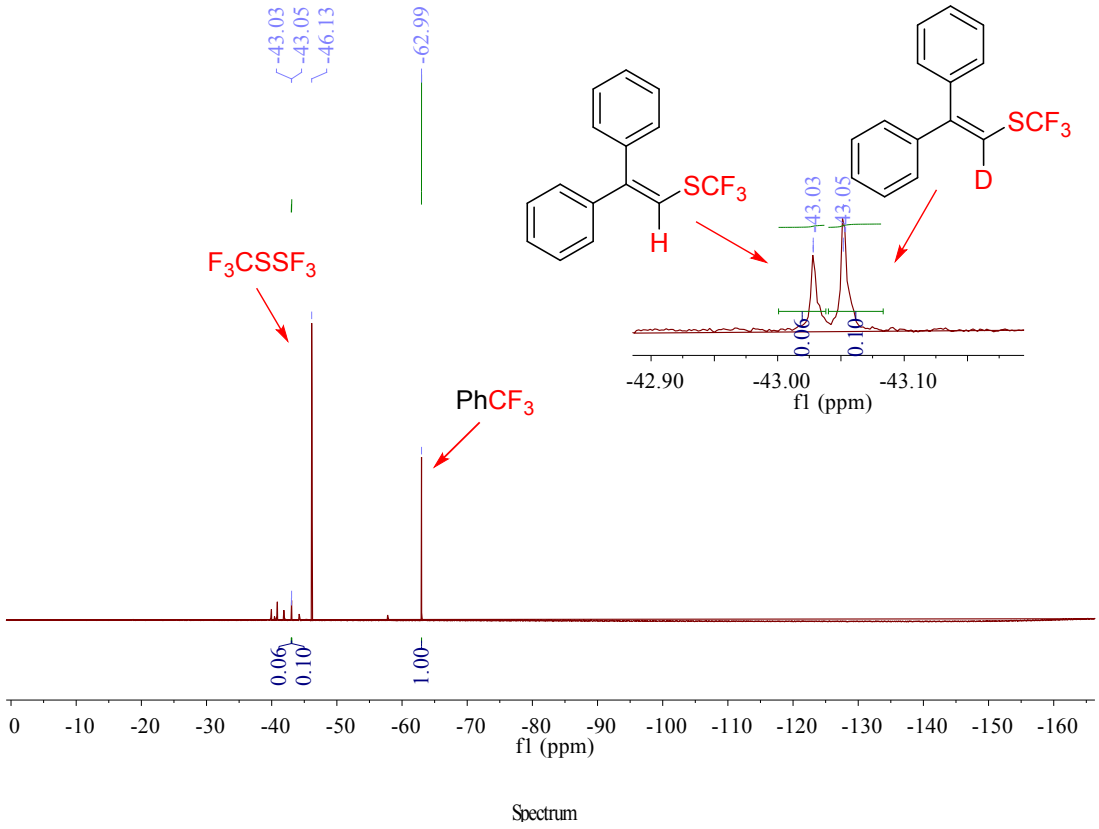
The deuterium labeling experiment in CD_3CN

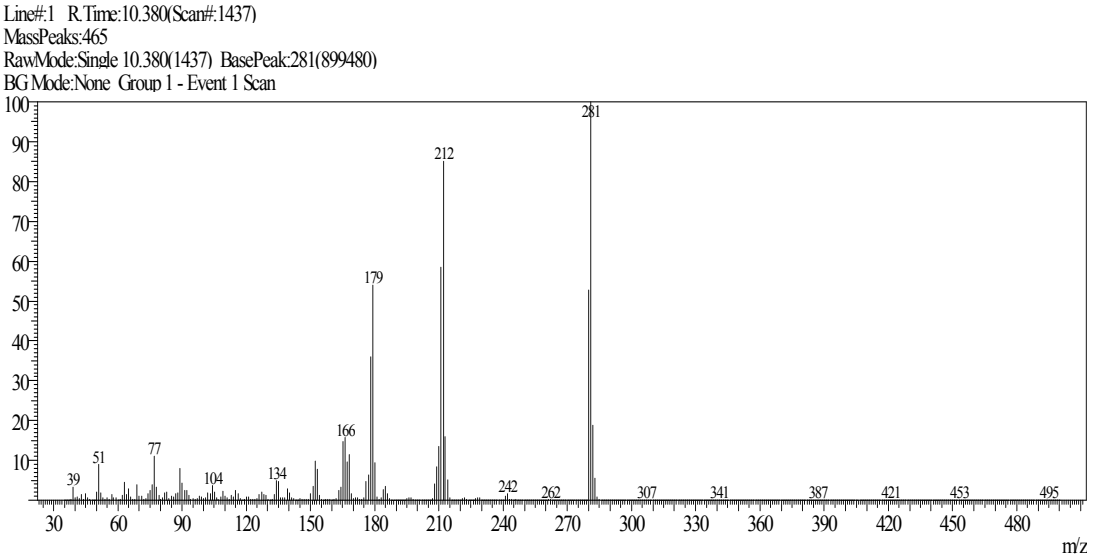


1a **3a** (6%) m/z = 280 **4a** (10%) m/z = 281

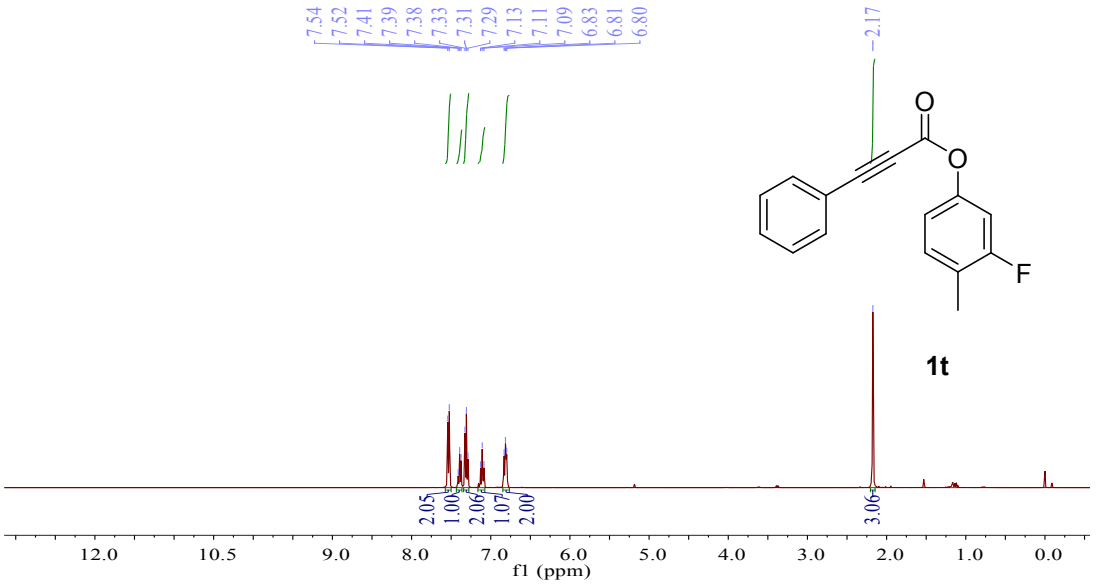
A mixture of **1** (44.4 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (104.0 mg, 0.50 mmol, 2.5 equiv) and $Na_2S_2O_8$ (119.2 mg, 0.50 mmol, 2.5 equiv) was added tube that was sealed with a septum, evacuated, and backfilled with nitrogen three times. CD_3CN (4.0 mL) was added to the tube. Then, the tube was stirred at 100 °C for 2 h. Product **3a** was

formed in 6% yield (detected by ^{19}F NMR). The deuterated product **4a** (10%) was detected by ^{19}F NMR and GC-MS.





6. Copies of ^{1}H, ^{19}F, and ^{13}C NMR Spectra for the Products.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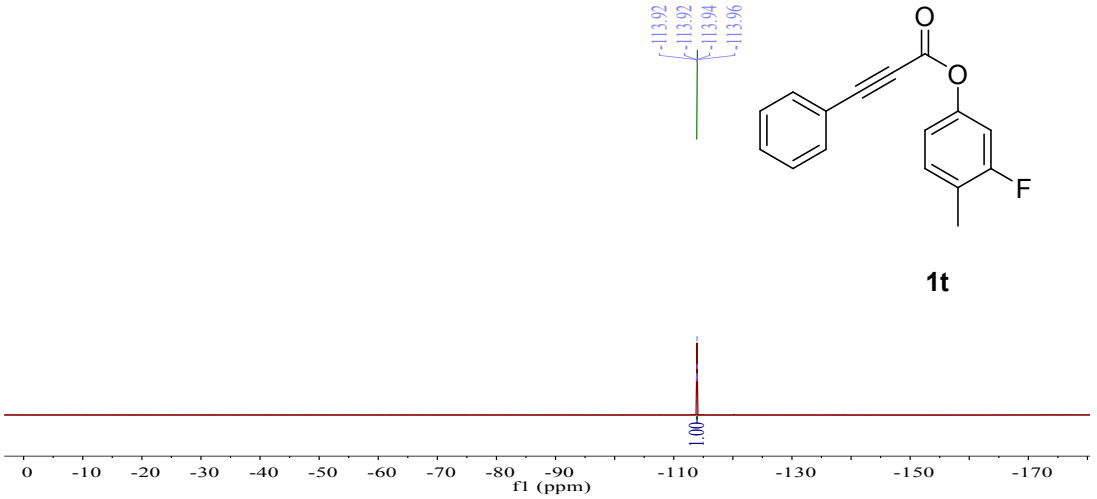
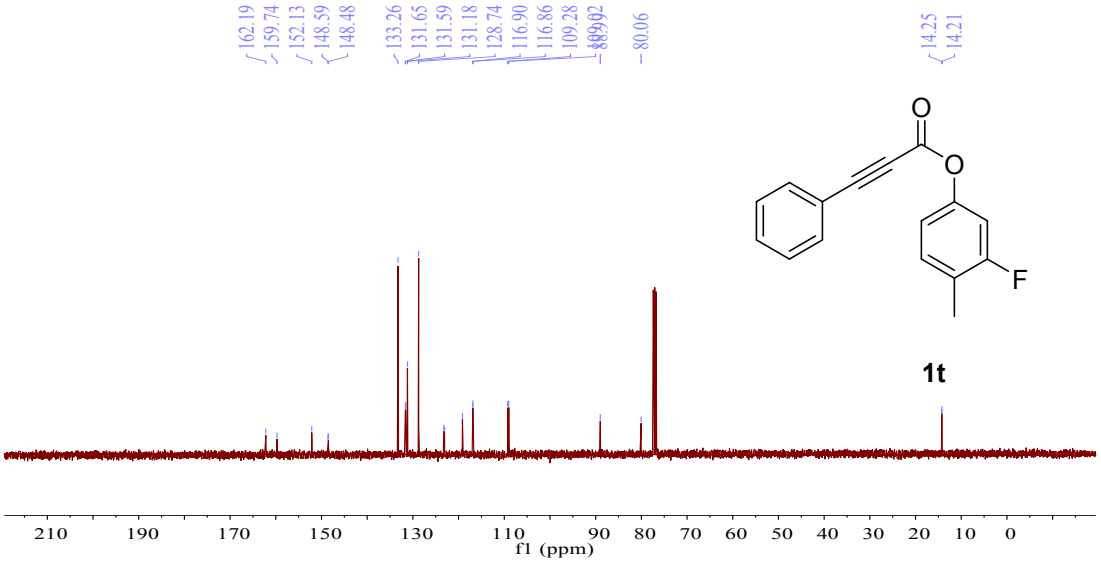
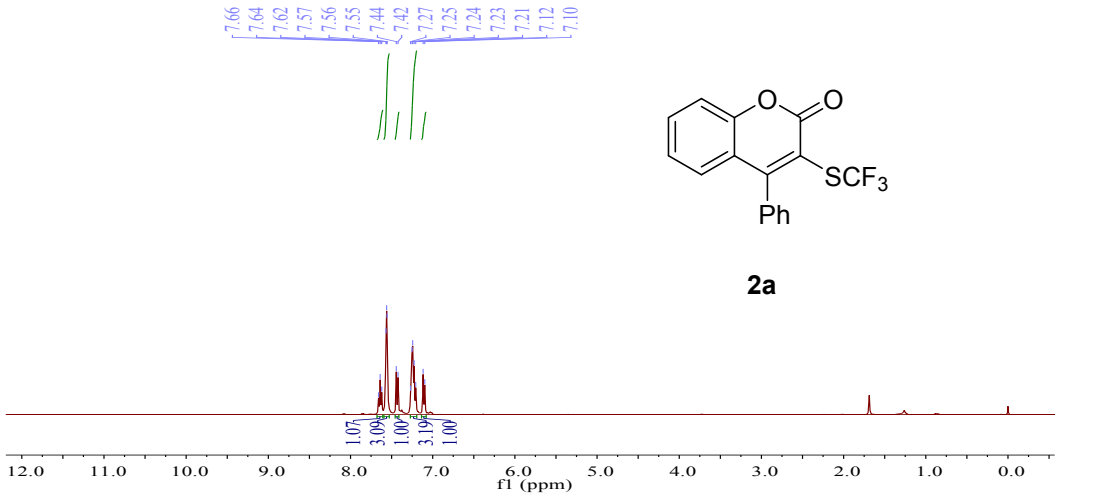
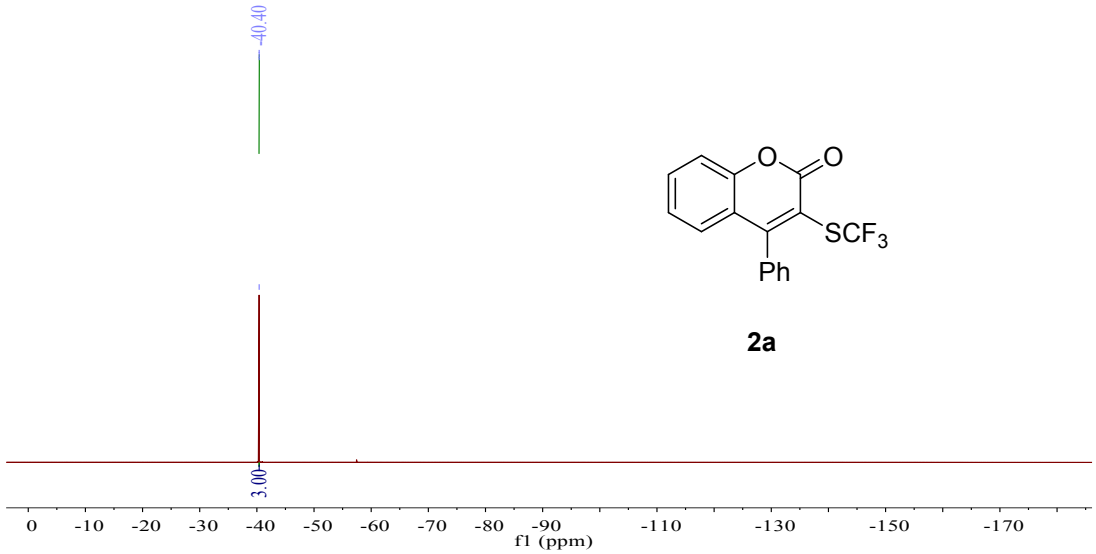
7.52
7.41
7.39
7.38
7.33
7.31
7.29
7.13
7.11
7.09
6.83
6.81
6.80
2.17
O
O
F
1t
2.05
1.00
2.06
1.07
2.00
3.06
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


-113.92
-113.92
-113.94
-113.96
O
O
F
1t
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
f1 (ppm)


162.19
159.74
152.13
148.59
148.48
133.26
131.65
131.59
131.18
128.74
116.90
116.86
109.28
80.06
14.25
14.21
O
O
F
1t
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.66
7.64
7.62
7.57
7.56
7.55
7.44
7.42
7.27
7.25
7.24
7.23
7.21
7.12
7.10
O
O
SCF3
Ph
1.07
3.09
1.00
3.19
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

2a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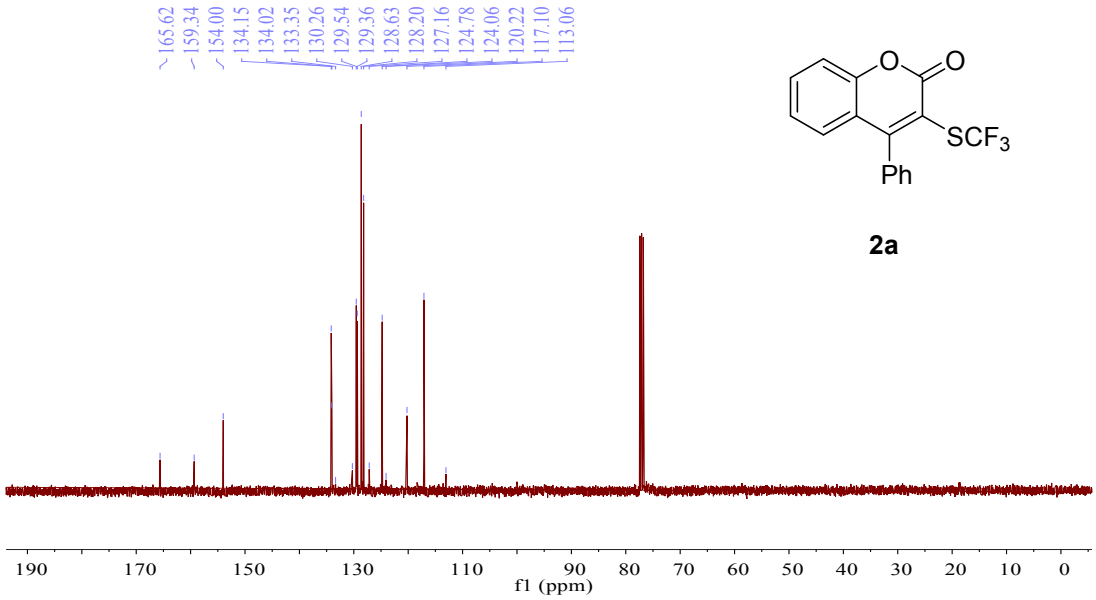
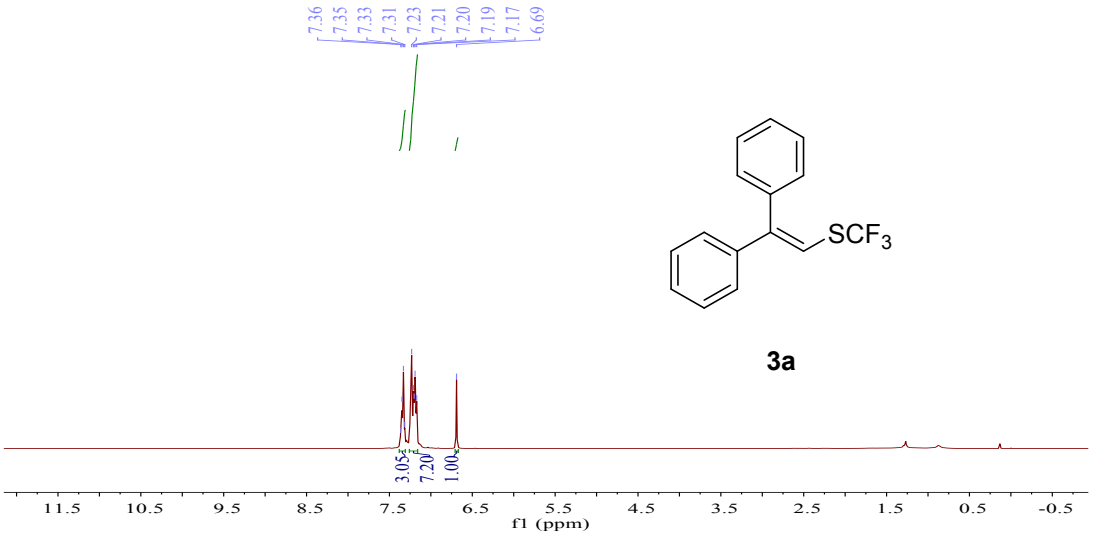
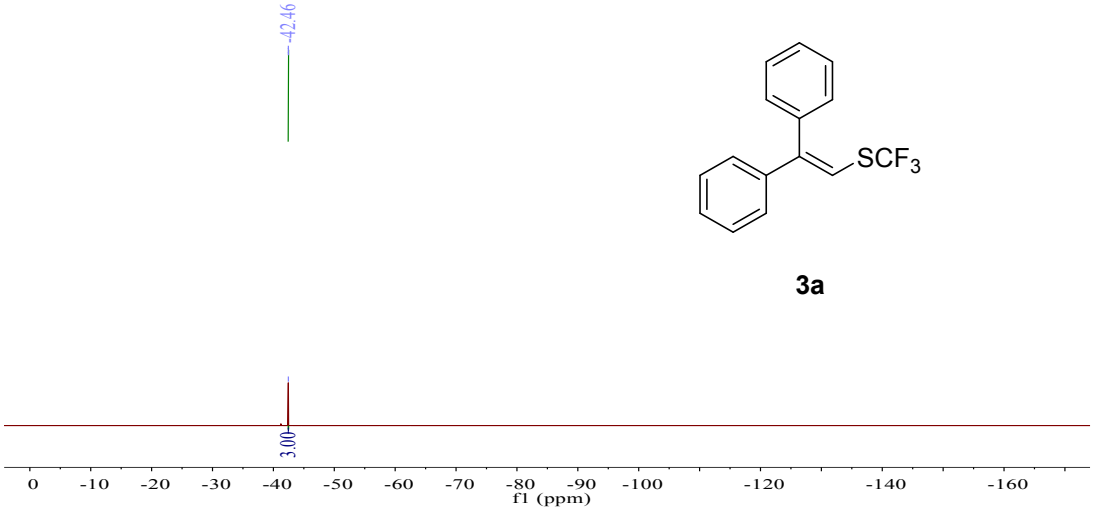
O
O
SCF3
Ph
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
f1 (ppm)

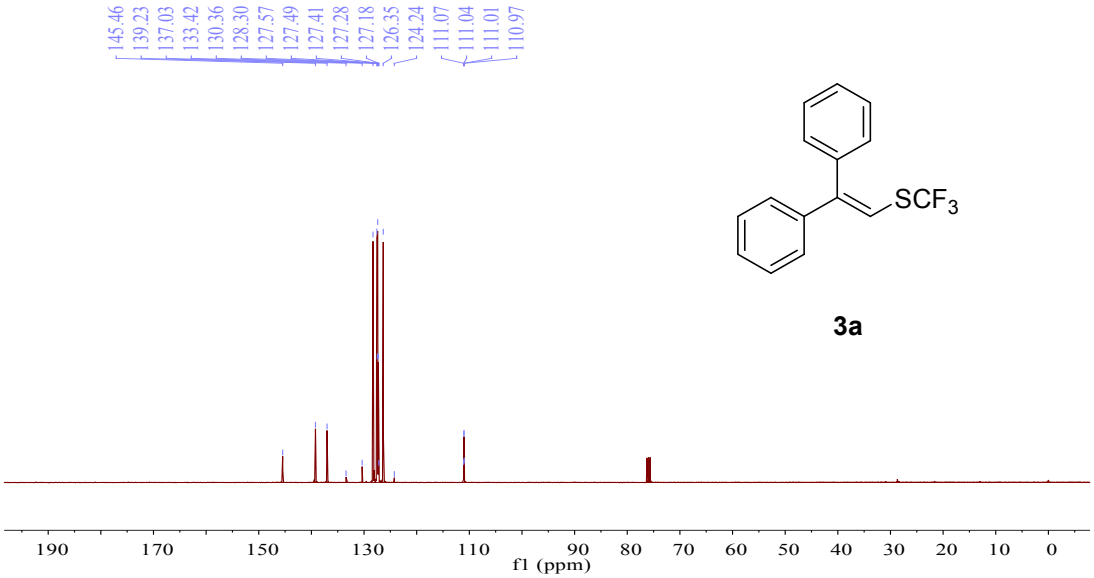
2a


165.62
159.34
154.00
134.15
134.02
133.35
130.26
129.54
129.36
128.63
128.20
127.16
124.78
124.06
120.22
117.10
113.06
O
O
SCF3
Ph
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2a


7.36
7.35
7.33
7.31
7.23
7.21
7.20
7.19
7.17
6.69
SCF3
3a
3.05
2.00
1.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


-42.46
SCF3
3a
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
f1 (ppm)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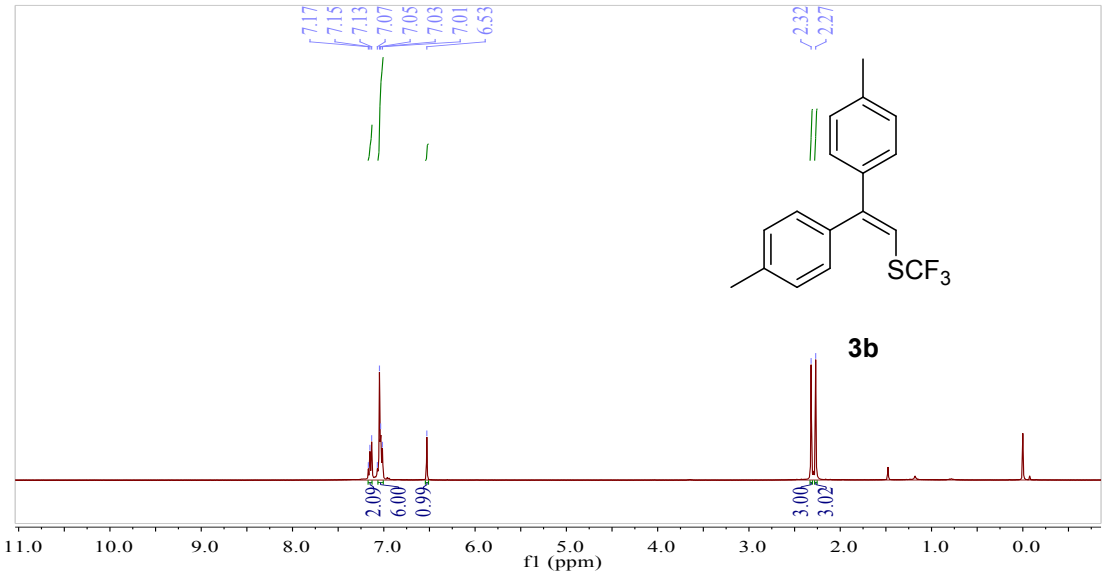
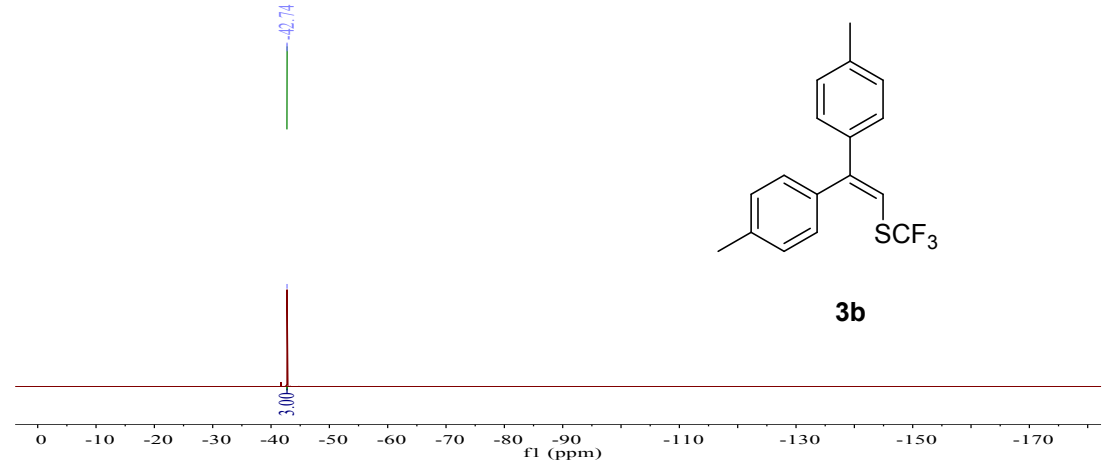
139.23
137.03
133.42
130.36
128.30
127.57
127.49
127.41
127.28
127.18
126.35
124.24
111.07
111.04
111.01
110.97
SCF3
3a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.17
7.15
7.13
7.07
7.05
7.03
7.01
6.53
2.32
2.27
SCF3
3b
2.09
6.00
0.99
3.00
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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3b
3.00
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-30
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-60
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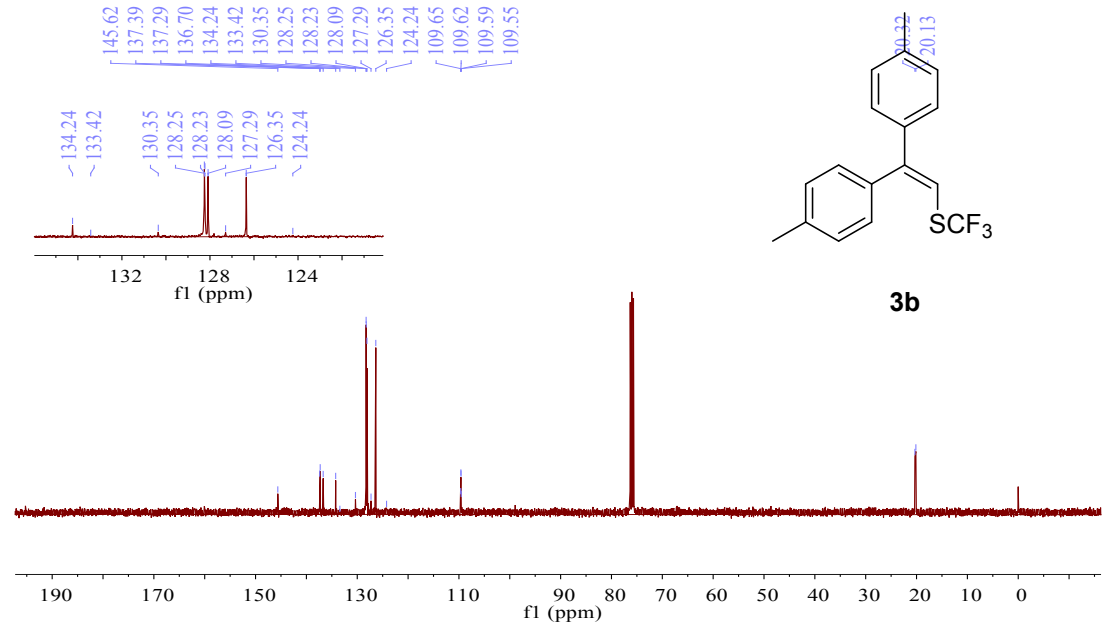
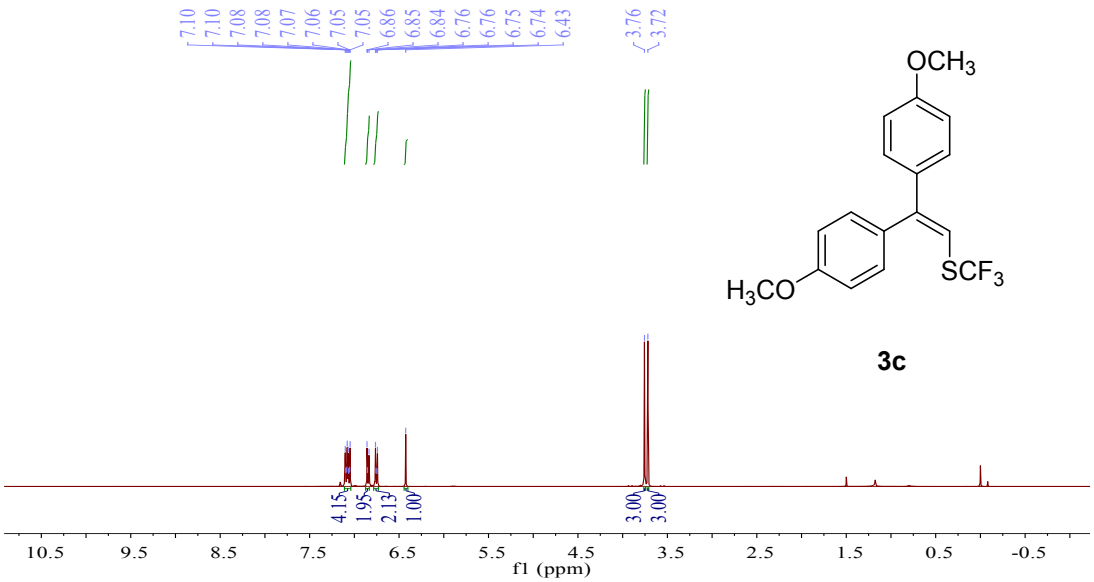
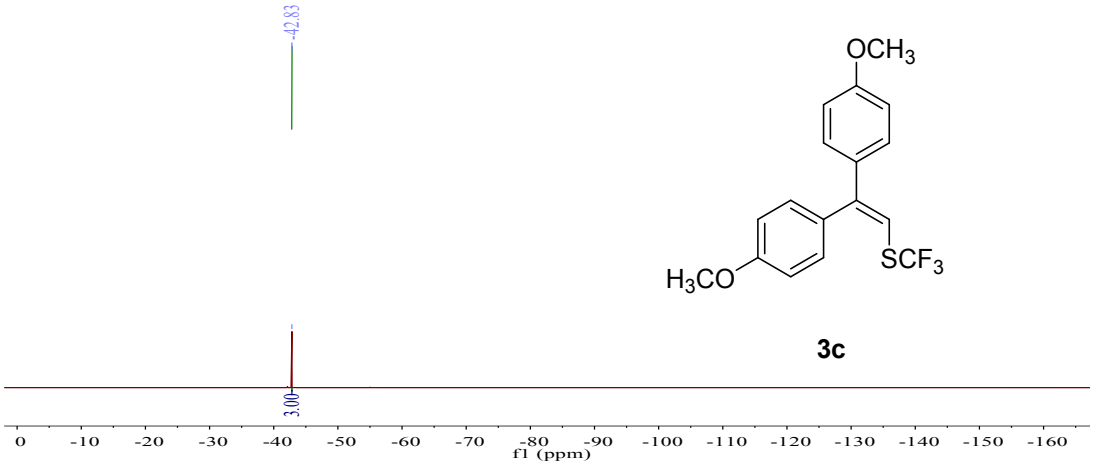
-80
-90
-110
-130
-150
-170
f1 (ppm)


145.62
137.39
137.29
136.70
134.24
133.42
130.35
128.25
128.23
128.09
127.29
126.35
124.24
109.65
109.62
109.59
109.55
30.32
20.13
SCF3
3b
132
128
124
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.10
7.10
7.08
7.08
7.07
7.06
7.05
7.05
6.86
6.85
6.84
6.76
6.76
6.75
6.74
6.43
3.76
3.72
OCH3
H3CO
SCF3
3c
4.15
1.95
2.13
1.00
3.00
3.00
f1 (ppm)


-42.83
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H3CO
SCF3
3c
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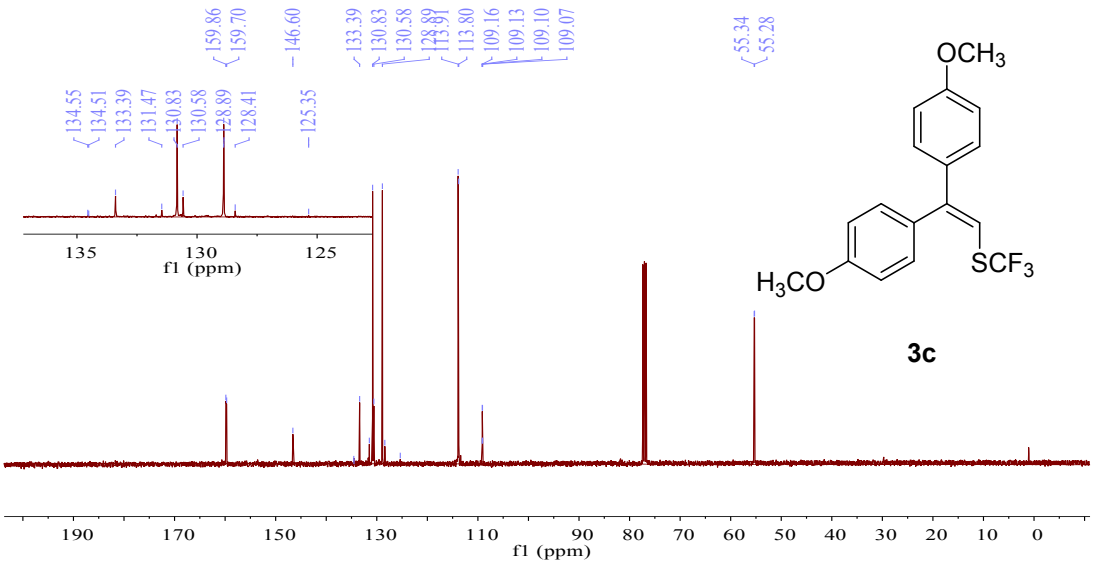
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159.70
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133.39
130.83
130.58
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128.41
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109.16
109.13
109.10
109.07
55.34
55.28
134.55
134.51
133.39
131.47
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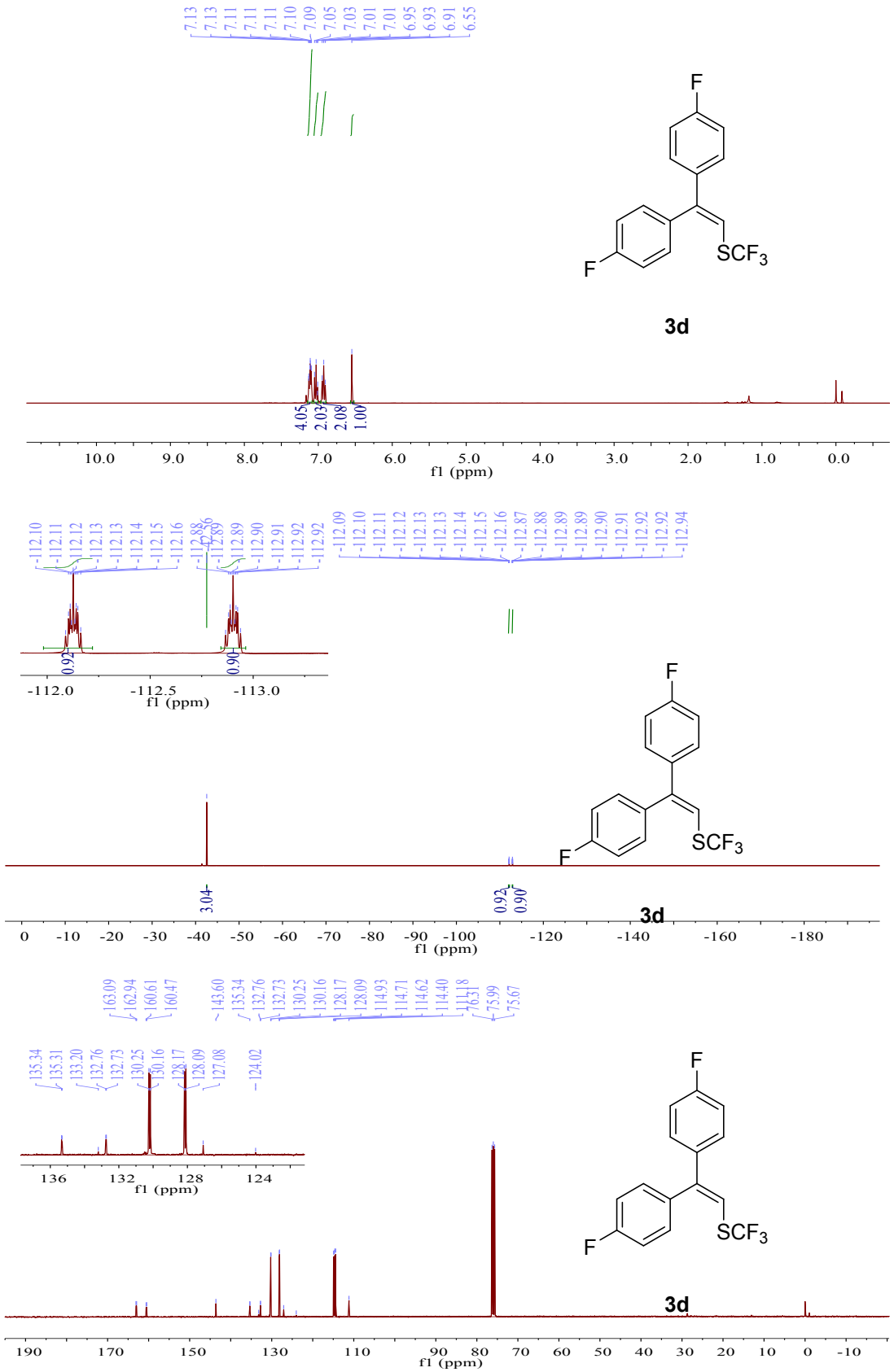
130.58
128.89
128.41
f1 (ppm)
OCH3
H3CO
SCF3
3c
f1 (ppm)


7.13
7.13
7.11
7.11
7.11
7.10
7.09
7.05
7.03
7.01
7.01
6.95
6.93
6.91
6.55
F
F
SCF3
3d
4.05
2.03
2.08
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
-112.10
-112.11
-112.12
-112.13
-112.13
-112.14
-112.15
-112.16
-112.88
-112.89
-112.89
-112.90
-112.91
-112.92
-112.92
-112.09
-112.10
-112.11
-112.12
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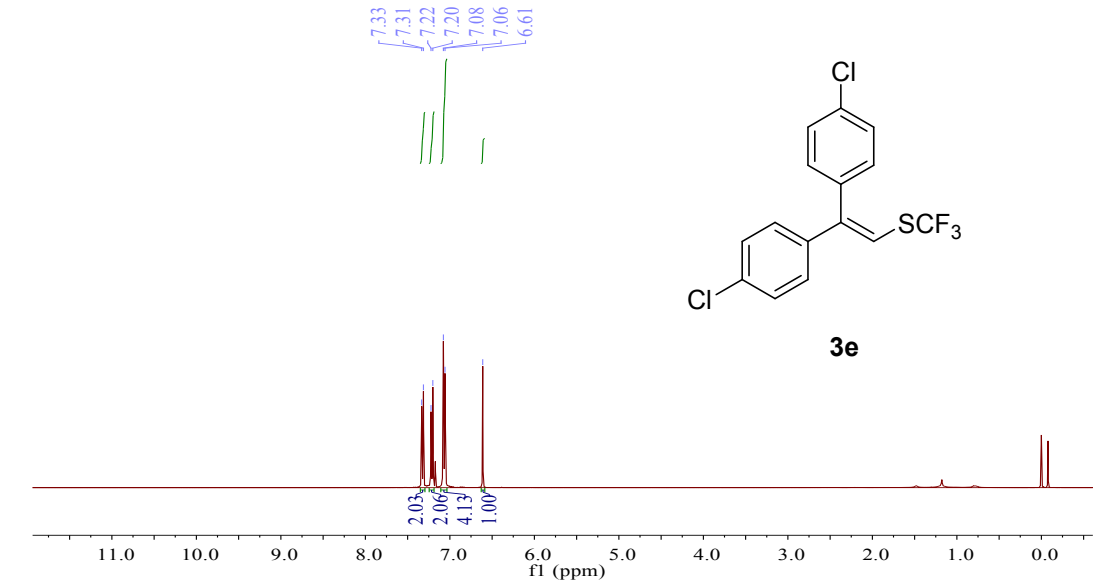
-112.91
-112.92
-112.92
-112.94
0.92
0.90
-112.0
-112.5
-113.0
f1 (ppm)
F
F
SCF3
3.04
0.92
0.90
3d
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
f1 (ppm)
163.09
162.94
160.61
160.47
143.60
135.34
132.76
132.73
130.25
130.16
128.17
128.09
114.93
114.71
114.62
114.40
111.18
76.31
75.99
75.67
135.34
135.31
133.20
132.76
132.73
130.25
130.16
128.17
128.09
127.08
124.02
136
132
128
124
f1 (ppm)
F
F
SCF3
3d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.22
7.20
7.08
7.06
6.61
Cl
SCF3
Cl
3e
2.03
2.06
4.13
1.00
11.0
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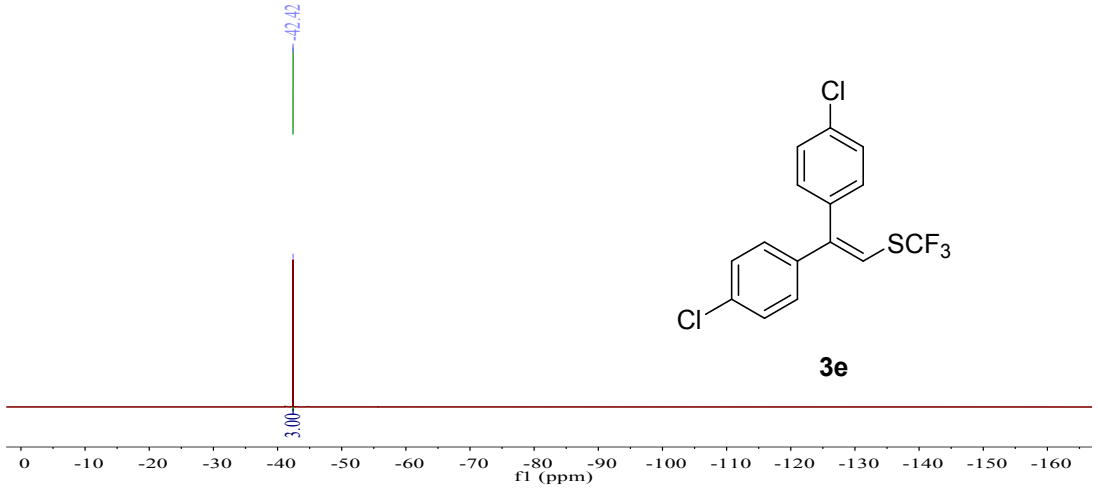
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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Cl
SCF3
Cl
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-20
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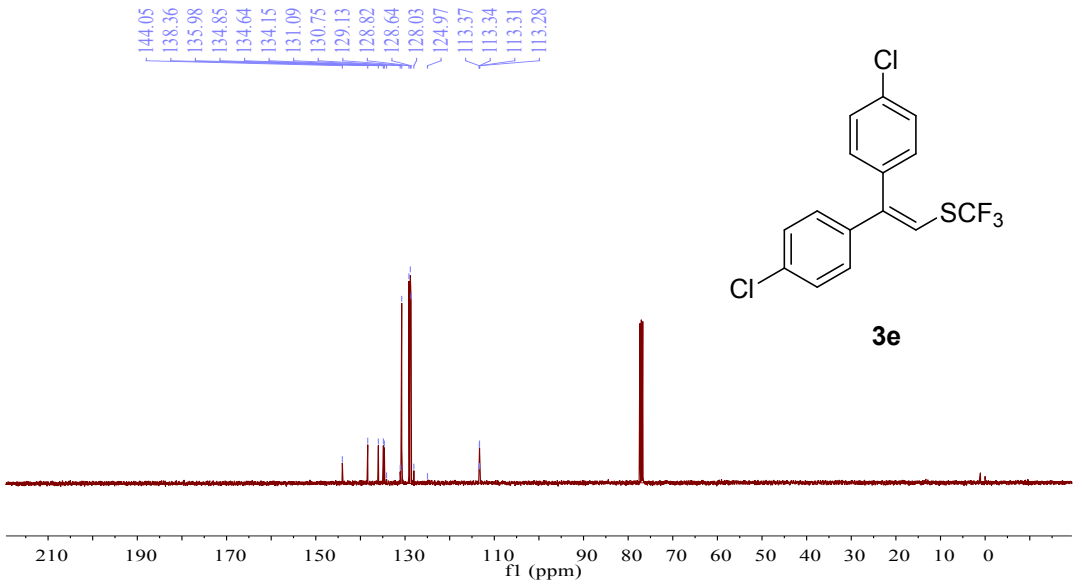
-120
-130
-140
-150
-160
f1 (ppm)


144.05
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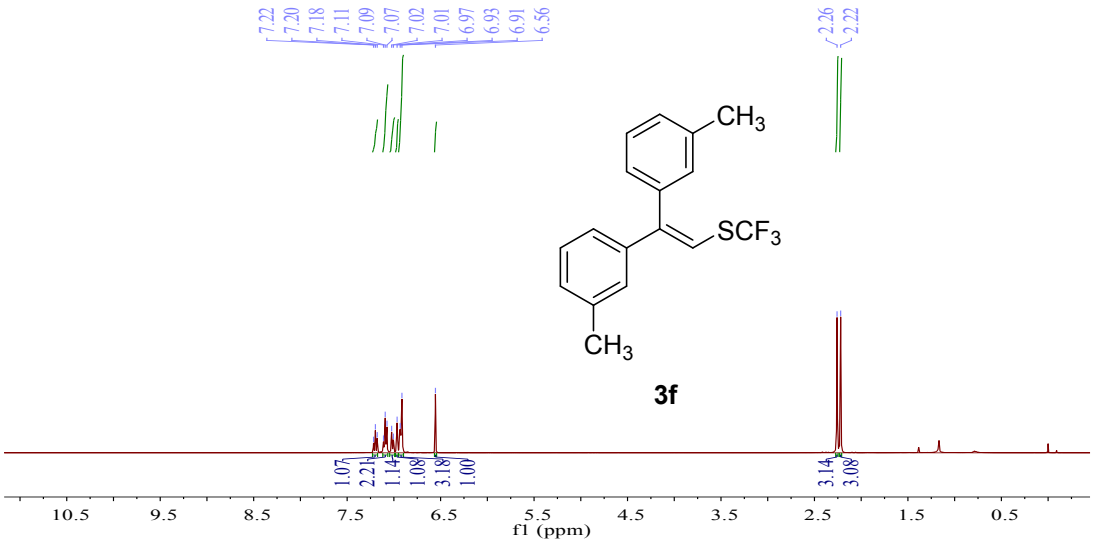
134.64
134.15
131.09
130.75
129.13
128.82
128.64
128.03
124.97
113.37
113.34
113.31
113.28
Cl
SCF3
Cl
3e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.22
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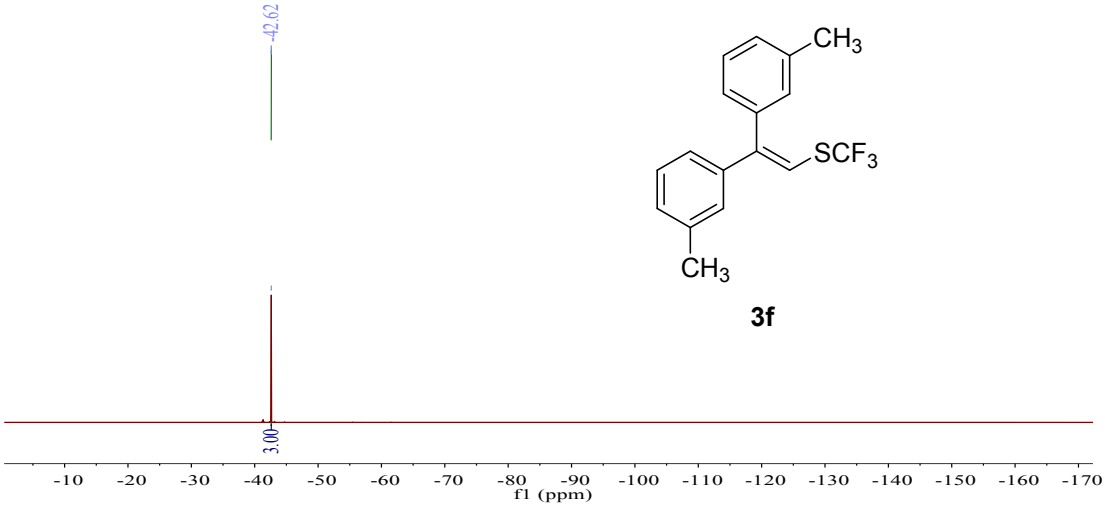
7.09
7.07
7.02
7.01
6.97
6.93
6.91
6.56
2.26
2.22
CH3
SCF3
CH3
3f
1.07
2.21
1.14
1.08
3.18
1.00
3.14
3.08
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


42.62
CH3
SCF3
CH3
3f
3.00
-10
-20
-30
-40
-50
-60
-70
-80
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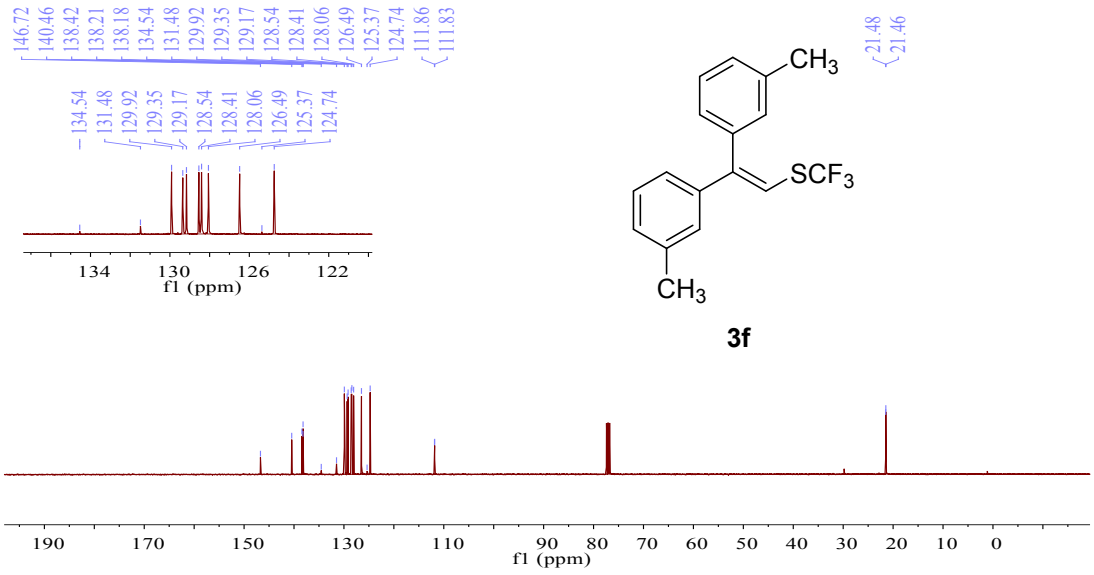
-130
-140
-150
-160
-170
f1 (ppm)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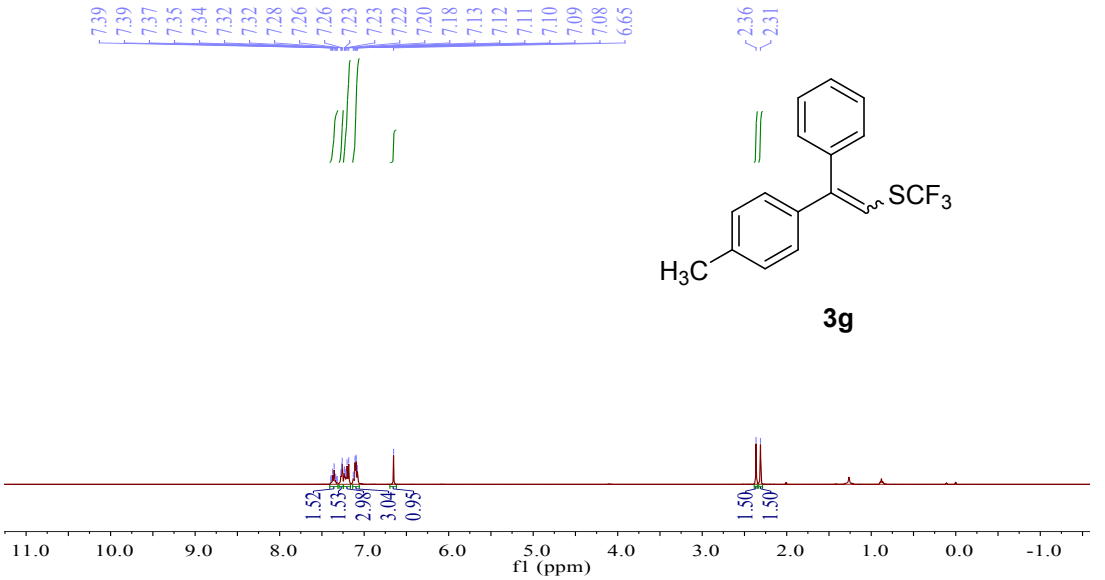
128.41
128.06
126.49
125.37
124.74
111.86
111.83
21.48
21.46
CH3
SCF3
CH3
3f
134
130
126
122
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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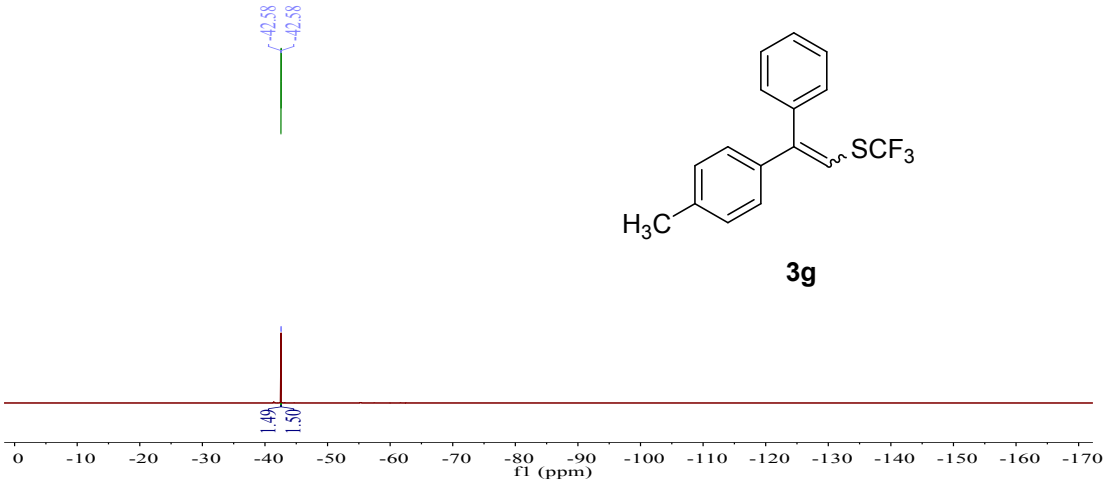
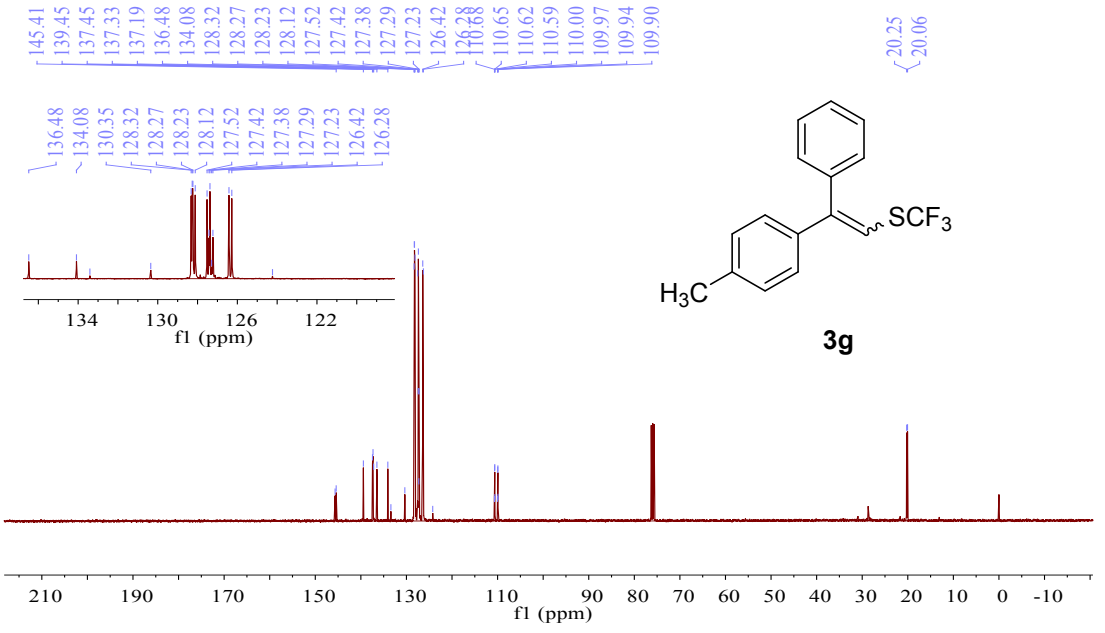
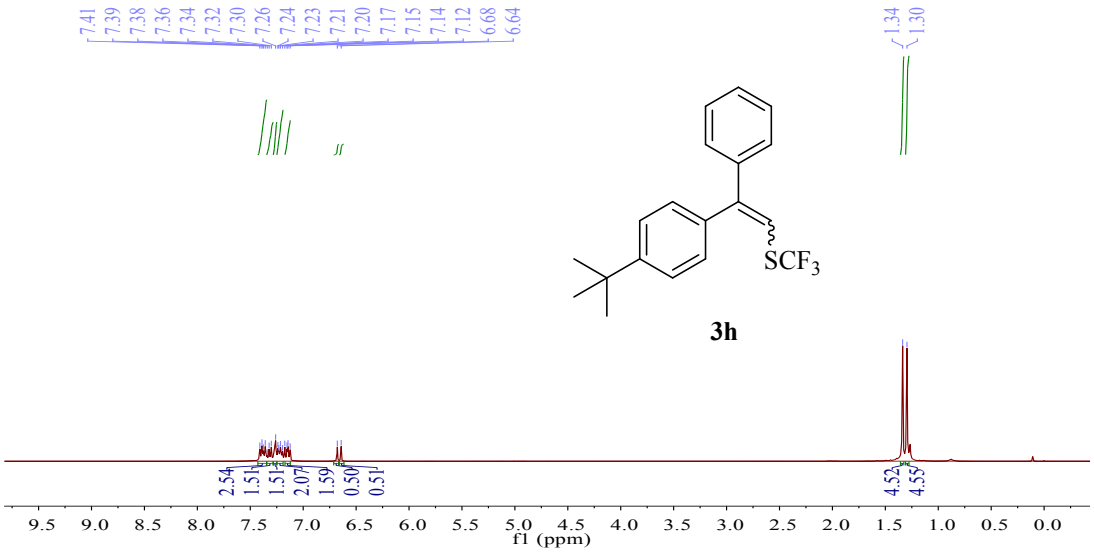
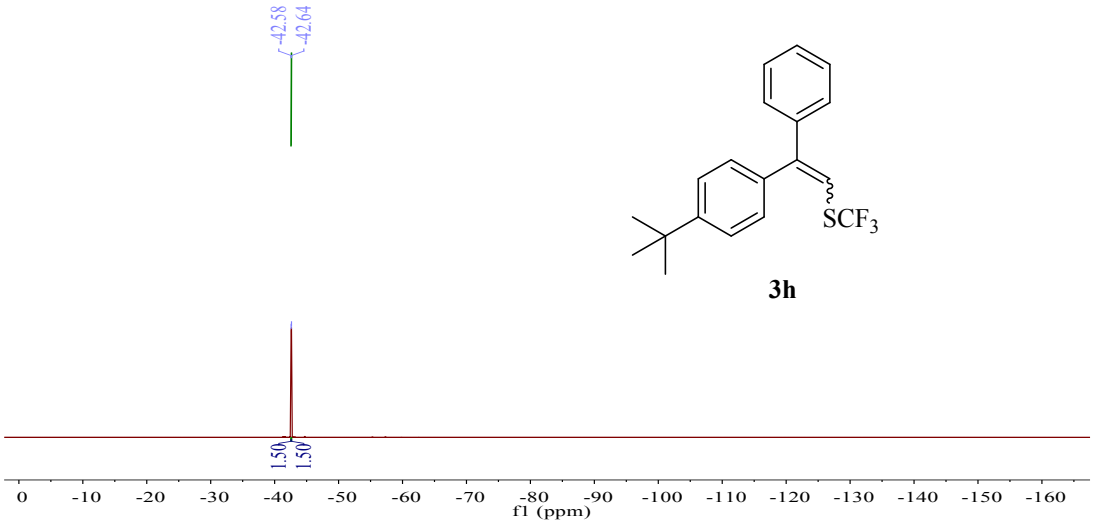
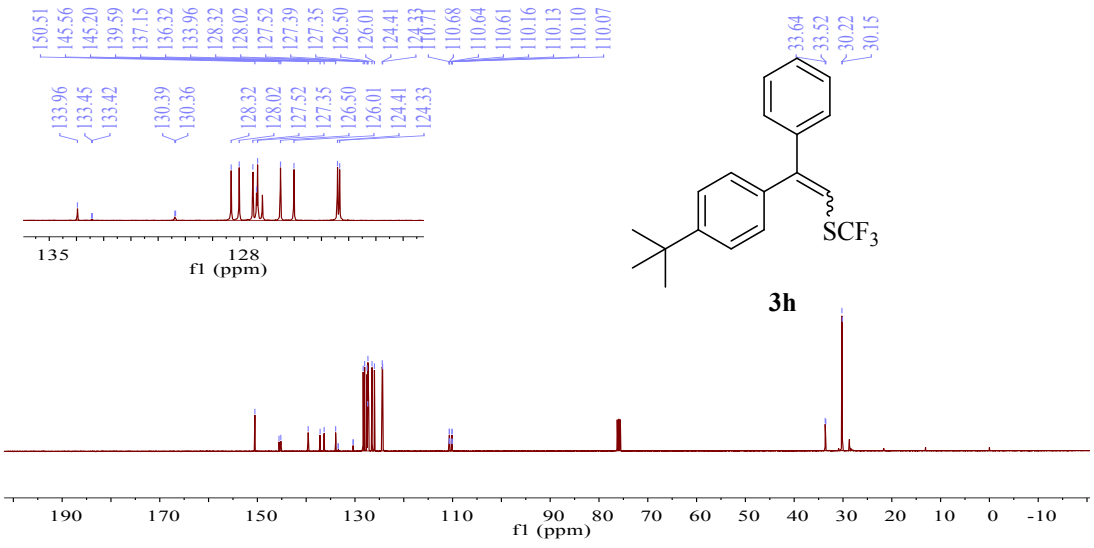
7.39
7.37
7.35
7.34
7.32
7.32
7.28
7.26
7.26
7.23
7.23
7.22
7.20
7.18
7.13
7.12
7.11
7.10
7.09
7.08
6.65
2.36
2.31
SCF3
H3C
3g
1.52
1.53
2.98
3.04
0.95
1.50
1.50
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

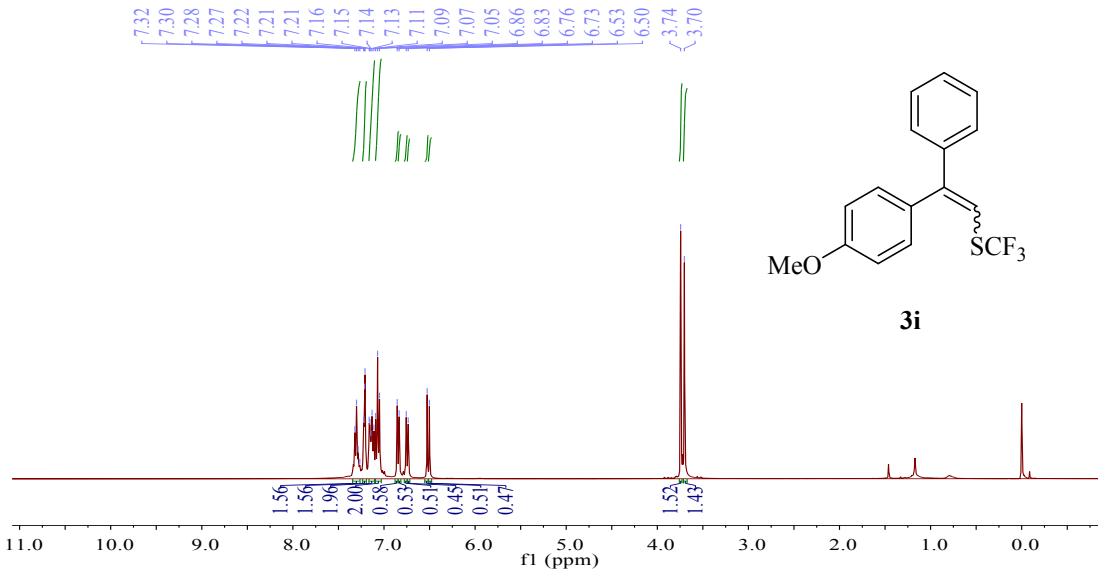

-42.58
-42.58
SCF3
H3C
3g
1.49
1.50
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


145.41
139.45
137.45
137.33
137.19
136.48
134.08
128.32
128.27
128.23
128.12
127.52
127.42
127.38
127.29
127.23
126.42
126.28
110.65
110.62
110.59
110.00
109.97
109.94
109.90
20.25
20.06
136.48
134.08
130.35
128.32
128.27
128.23
128.12
127.52
127.42
127.38
127.29
127.23
126.42
126.28
134
130
126
122
f1 (ppm)
SCF3
H3C
3g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

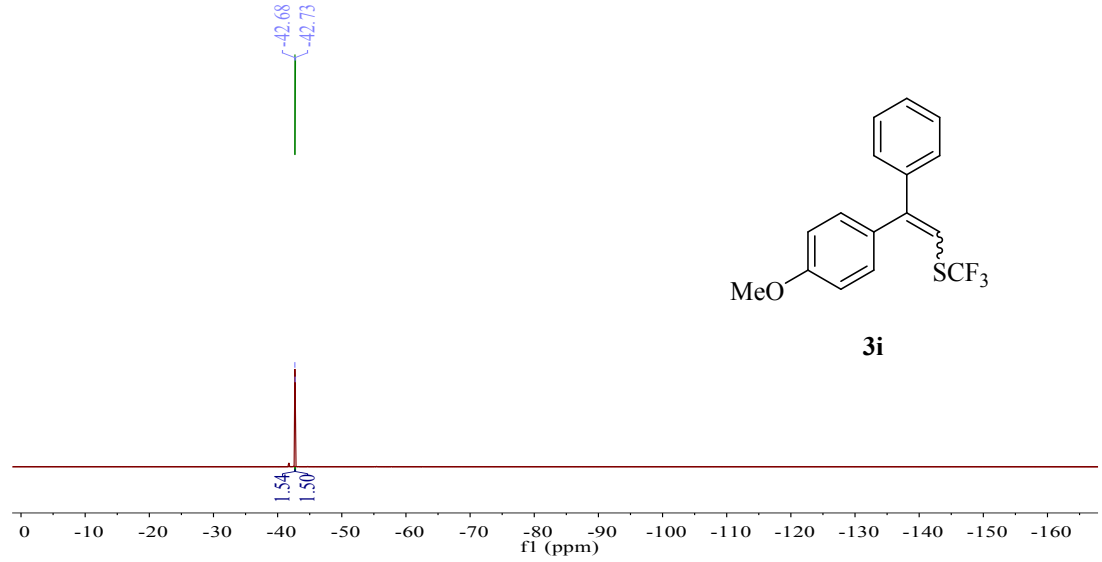

7.41
7.39
7.38
7.36
7.34
7.32
7.30
7.26
7.24
7.23
7.21
7.20
7.17
7.15
7.14
7.12
6.68
6.64
1.34
1.30
SCF3
3h
2.54
1.51
1.51
2.07
1.59
0.50
0.51
4.52
4.55
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-42.58
-42.64
SCF3
3h
1.50
1.50
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

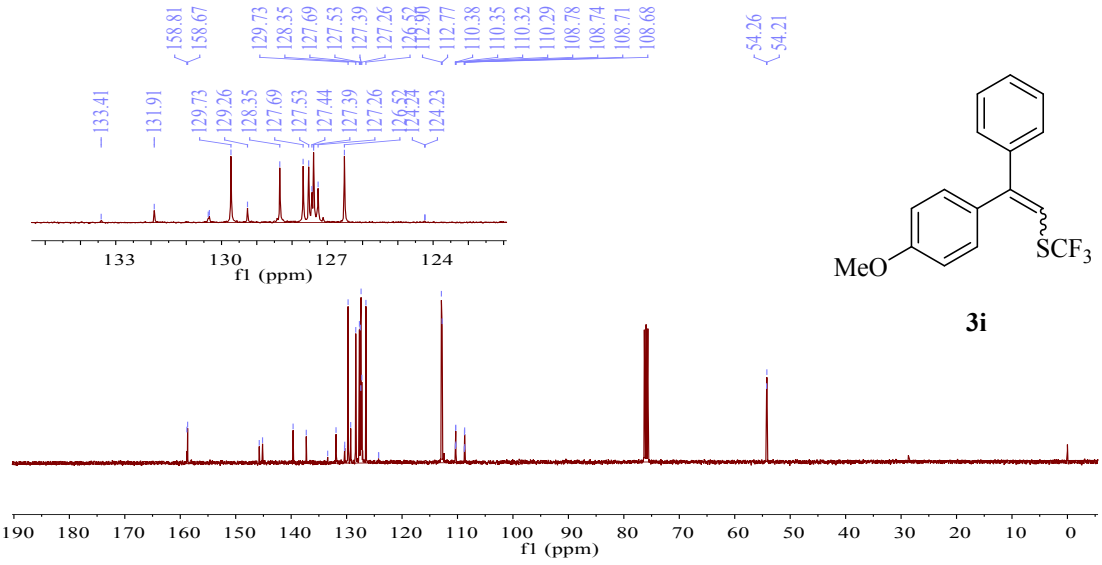

150.51
145.56
145.20
139.59
137.15
136.32
133.96
128.32
128.02
127.52
127.39
127.35
126.50
126.01
124.41
124.33
110.71
110.68
110.64
110.61
110.16
110.13
110.10
110.07
33.64
33.52
30.22
30.15
133.96
133.45
133.42
130.39
130.36
128.32
128.02
127.52
127.35
126.50
126.01
124.41
124.33
135
128
f1 (ppm)
SCF3
3h
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.32
7.30
7.28
7.27
7.22
7.21
7.21
7.16
7.15
7.14
7.13
7.11
7.09
7.07
7.05
6.86
6.83
6.76
6.73
6.53
6.50
3.74
3.70
MeO
SCF3
1.56
1.56
1.96
2.00
0.58
0.53
0.51
0.45
0.51
0.47
1.52
1.43
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

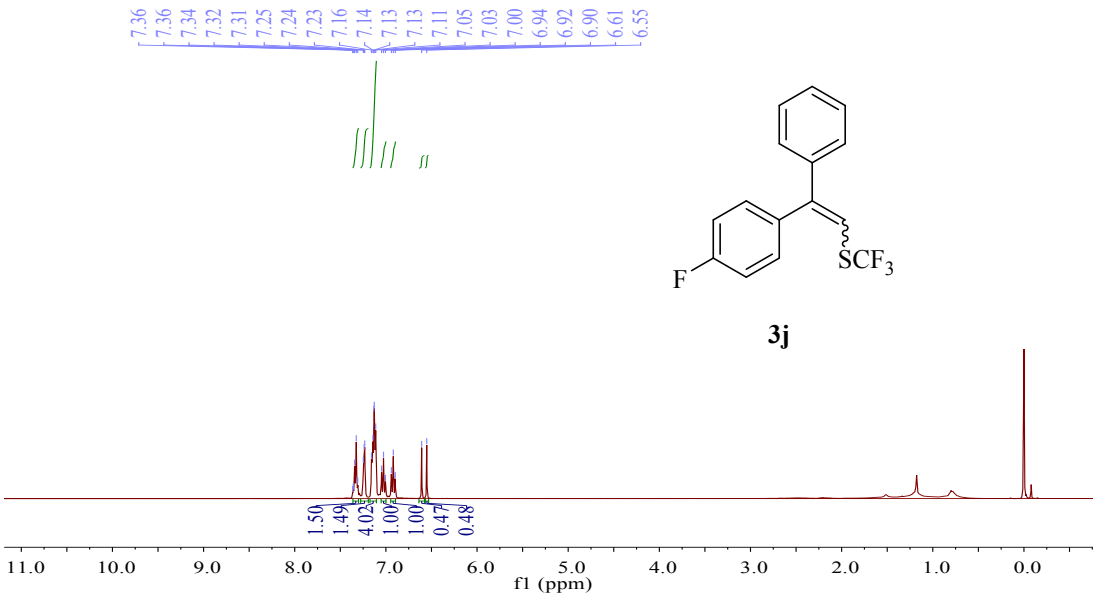
3i

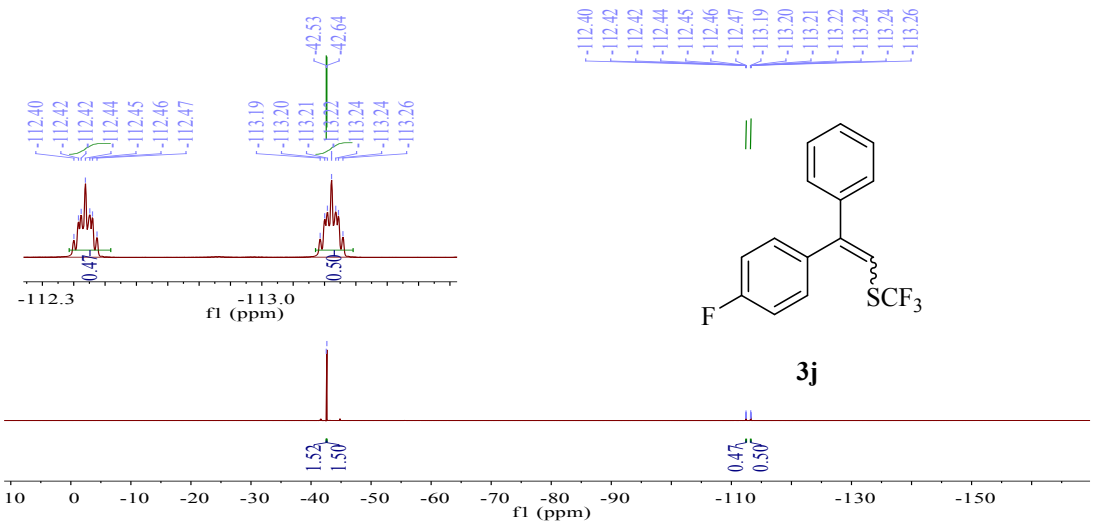

-42.68
-42.73
MeO
SCF3
1.54
1.50
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

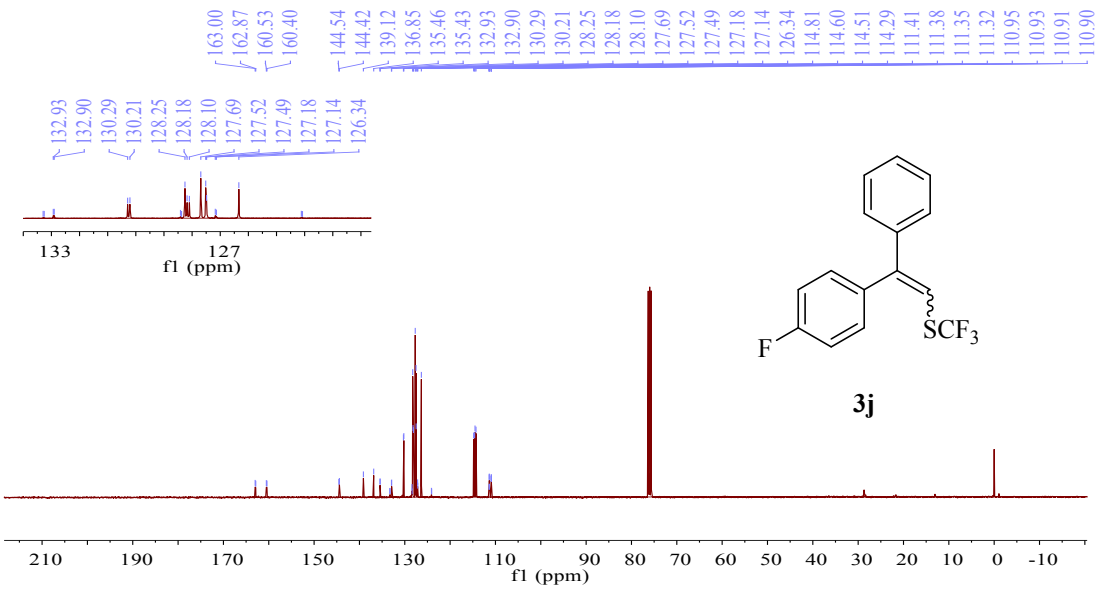
3i

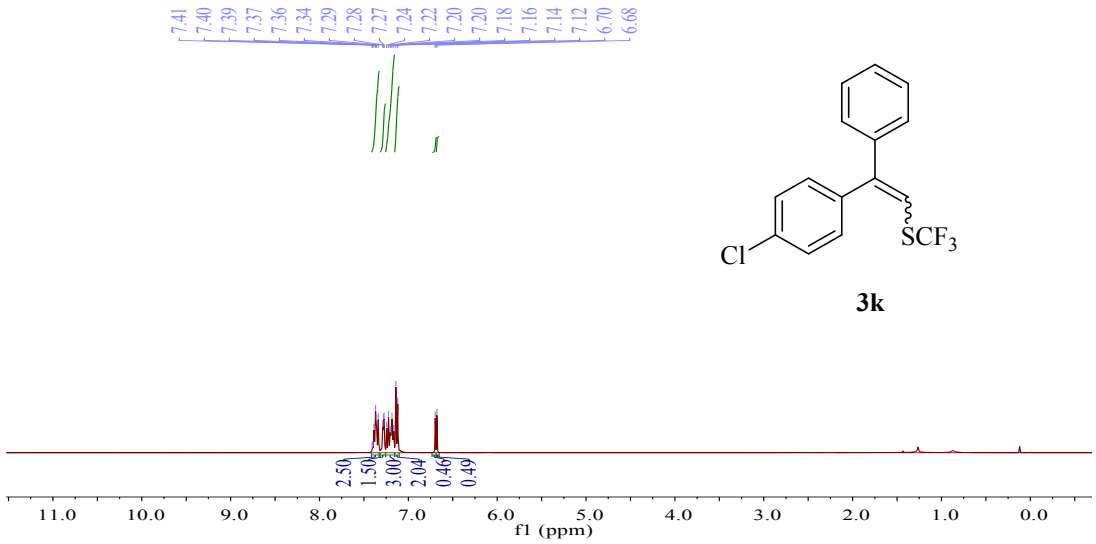

158.81
158.67
129.73
128.35
127.69
127.53
127.39
127.26
126.52
112.90
112.77
110.38
110.35
110.32
110.29
108.78
108.74
108.71
108.68
54.26
54.21
133.41
131.91
129.73
129.26
128.35
127.69
127.53
127.44
127.39
127.26
126.52
124.24
124.23
133
130
127
124
f1 (ppm)
MeO
SCF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3i

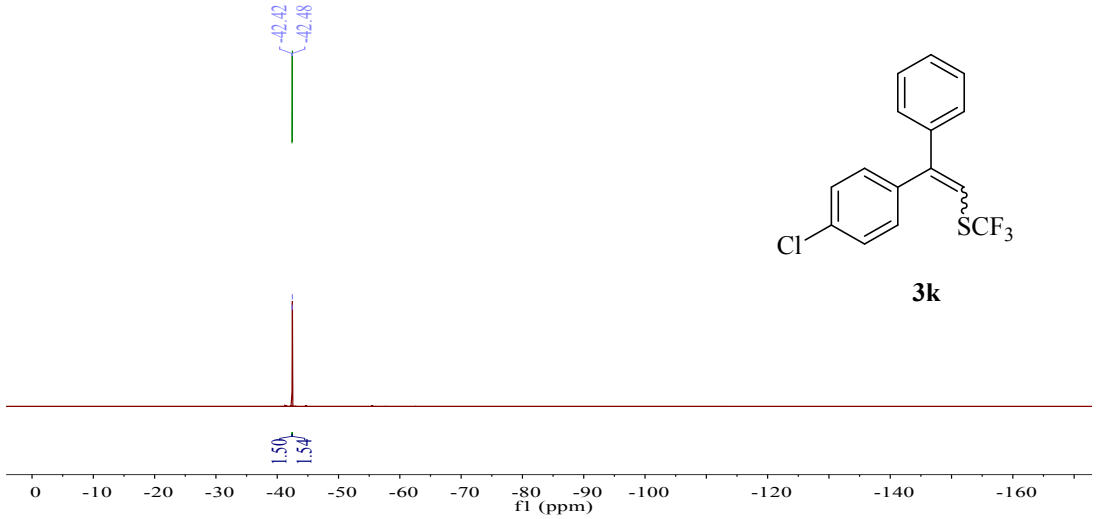

7.36
7.36
7.34
7.32
7.31
7.25
7.24
7.23
7.16
7.14
7.13
7.13
7.11
7.05
7.03
7.00
6.94
6.92
6.90
6.61
6.55
F
SCF3
3j
1.50
1.49
4.02
1.00
1.00
0.47
0.48
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


-112.40
-112.42
-112.42
-112.44
-112.45
-112.46
-112.47
-113.19
-113.20
-113.21
-113.22
-113.24
-113.24
-113.26
42.53
42.64
0.47
0.50
-112.3
-113.0
f1 (ppm)
F
SCF3
3j
1.53
1.50
0.47
0.50
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
f1 (ppm)

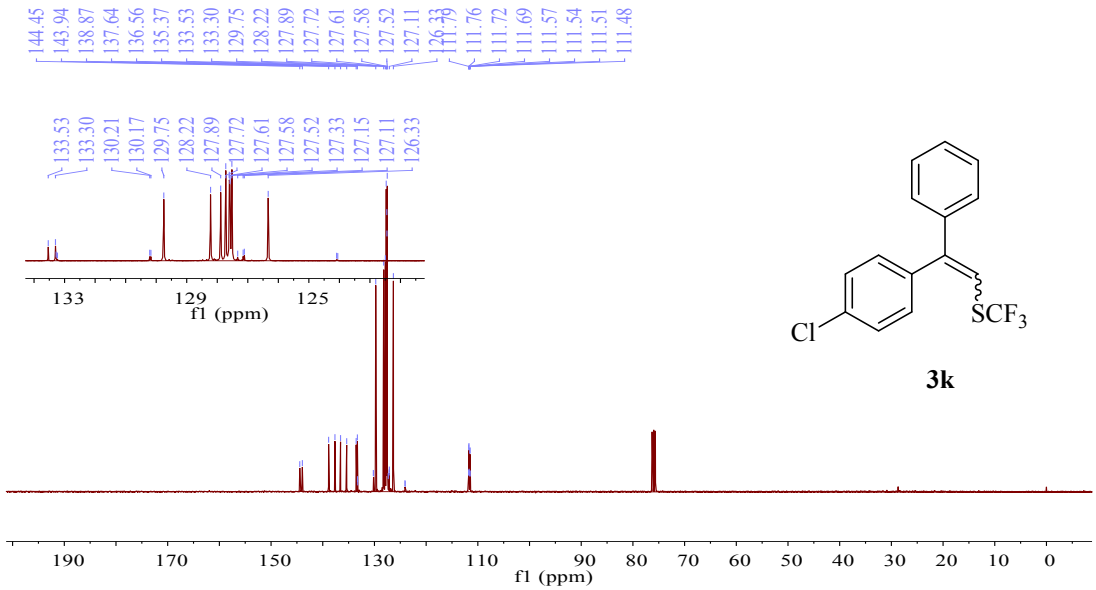

163.00
162.87
160.53
160.40
144.54
144.42
139.12
136.85
135.46
135.43
132.93
132.90
130.29
130.21
128.25
128.18
128.10
127.69
127.52
127.49
127.18
127.14
126.34
114.81
114.60
114.51
114.29
111.41
111.38
111.35
111.32
110.95
110.93
110.91
110.90
133
127
f1 (ppm)
F
SCF3
3j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.41
7.40
7.39
7.37
7.36
7.34
7.29
7.28
7.27
7.24
7.22
7.20
7.20
7.18
7.16
7.14
7.12
6.70
6.68
Cl
SCF3
2.50
1.50
3.00
2.04
0.46
0.49
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

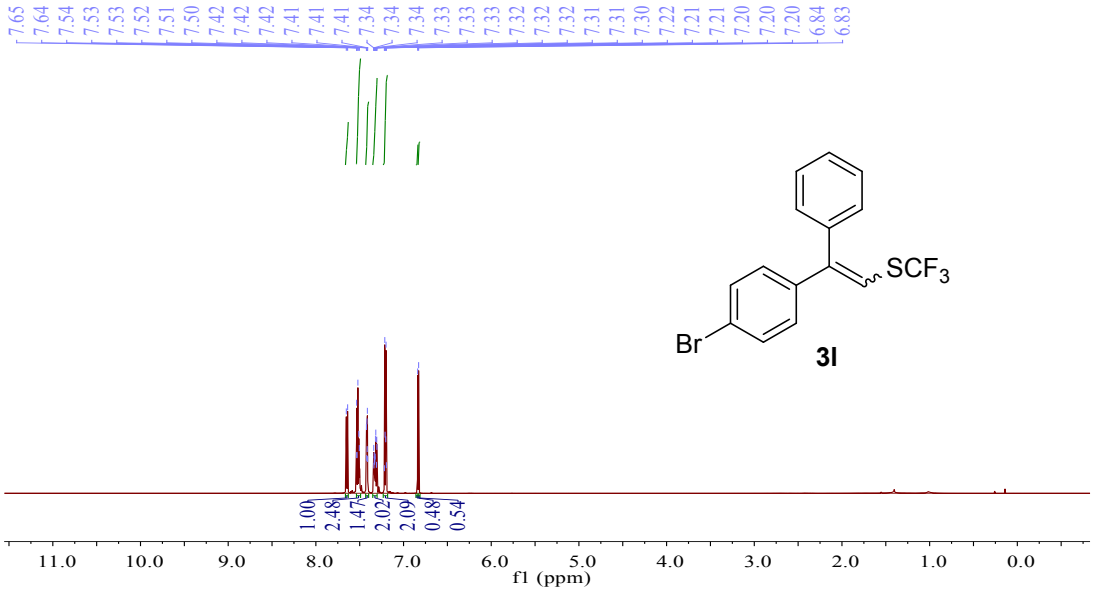
3k

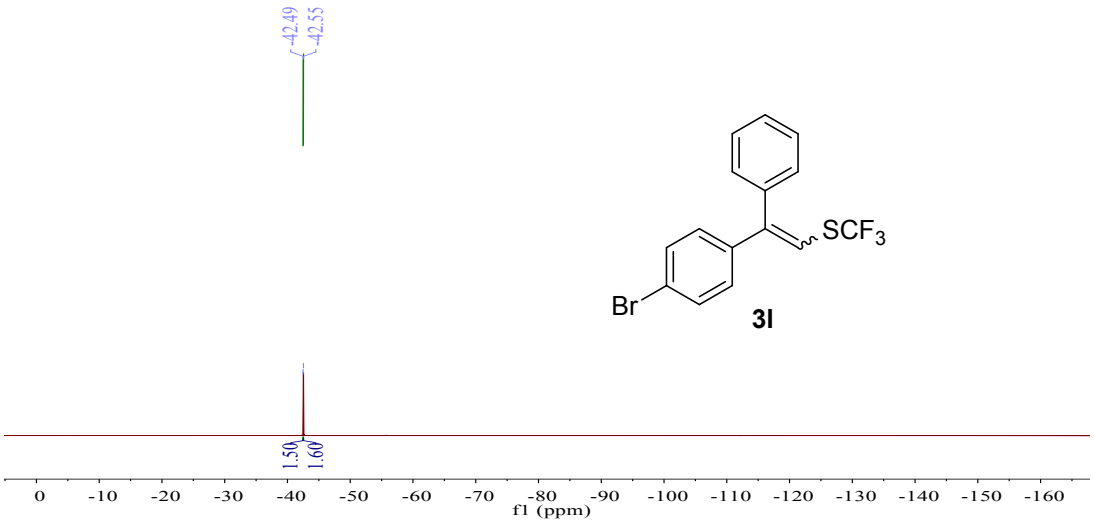

-42.42
-42.48
Cl
SCF3
1.50
1.54
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
f1 (ppm)

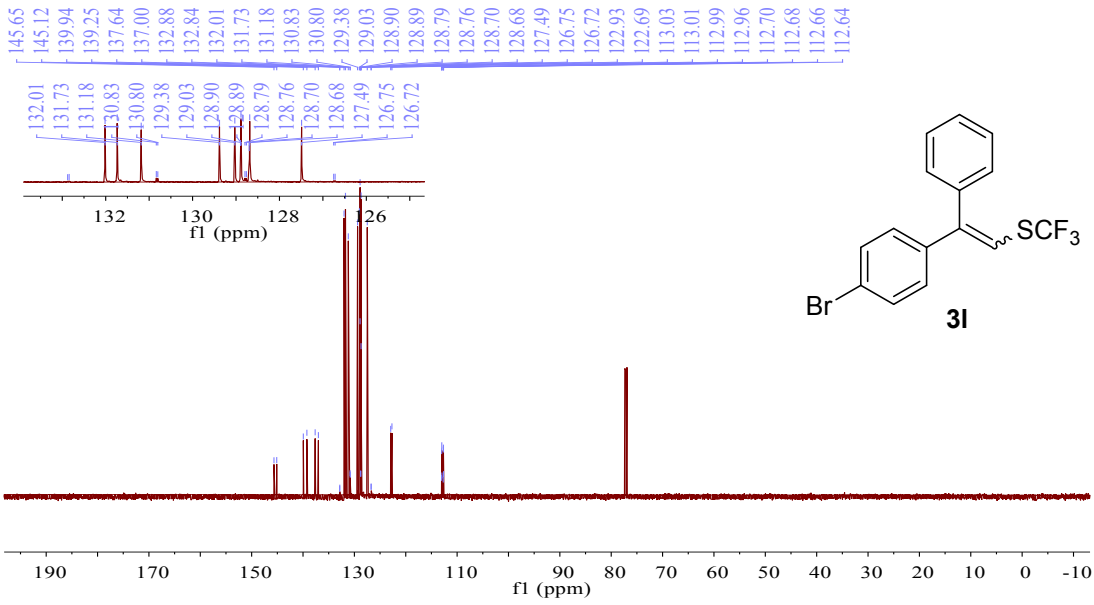
3k

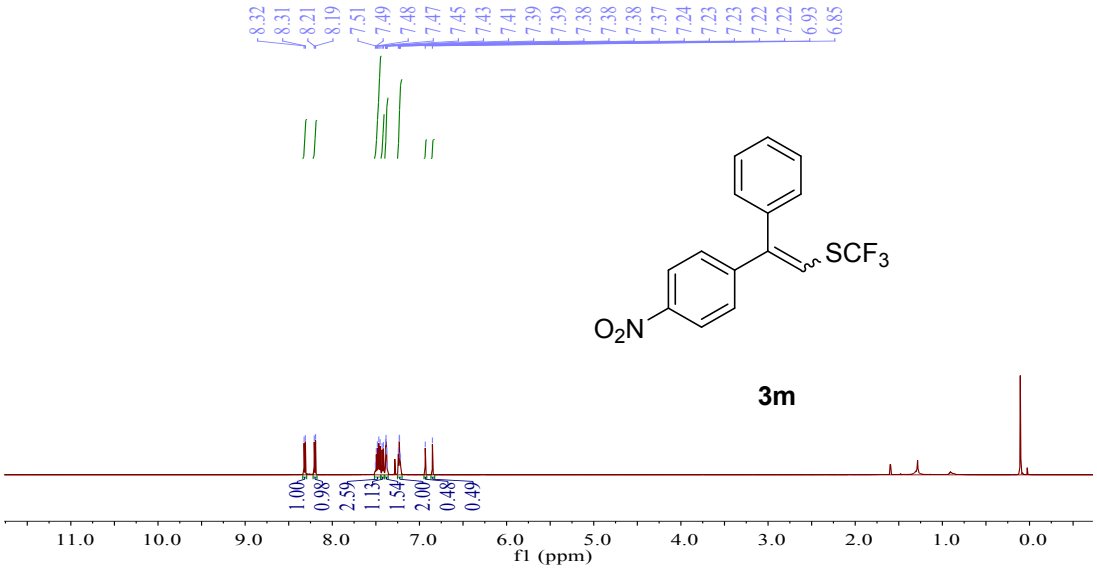

144.45
143.94
138.87
137.64
136.56
135.37
133.53
133.30
129.75
128.22
127.89
127.72
127.61
127.58
127.52
127.11
126.33
111.76
111.72
111.69
111.57
111.54
111.51
111.48
133.53
133.30
130.21
130.17
129.75
128.22
127.89
127.72
127.61
127.58
127.52
127.33
127.15
127.11
126.33
133
129
125
f1 (ppm)
Cl
SCF3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

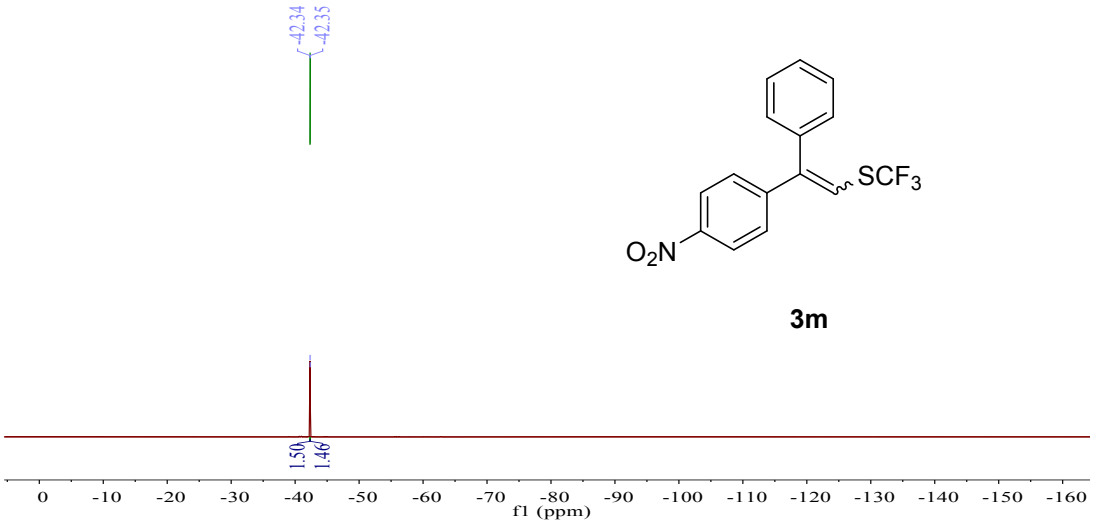
3k

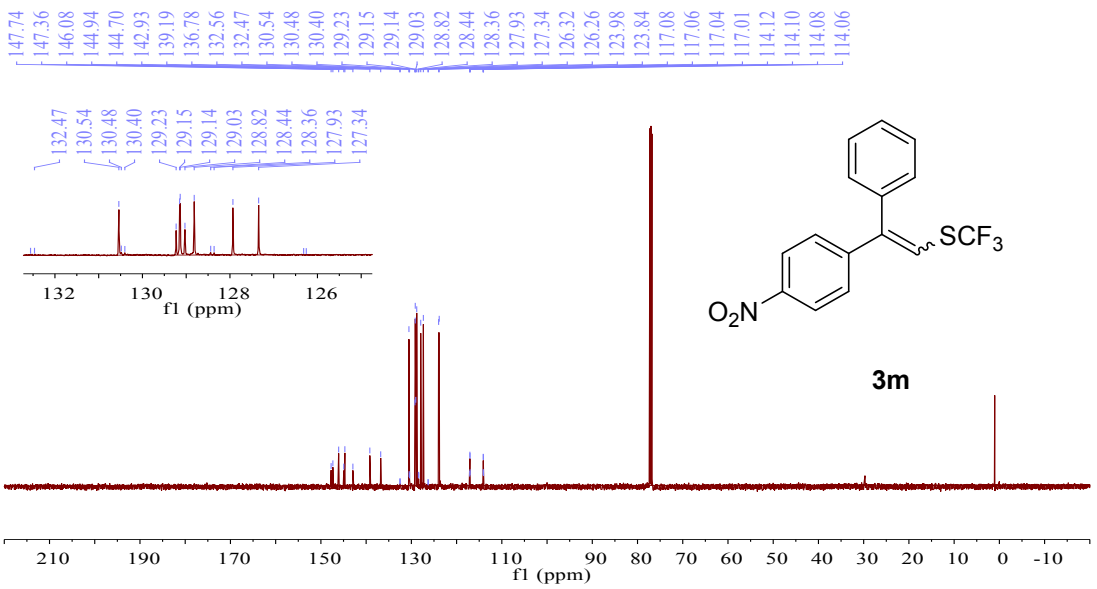

7.65 7.64 7.54 7.53 7.53 7.52 7.51 7.50 7.42 7.42 7.42 7.41 7.41 7.41 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.22 7.21 7.21 7.20 7.20 7.20 6.84 6.83
SCF3
Br
3l
1.00 2.48 1.47 2.02 2.09 0.48 0.54
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


-42.49
-42.55
SCF3
Br
3l
1.50 1.60
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


145.65 145.12 139.94 139.25 137.64 137.00 132.88 132.84 132.01 131.73 131.18 130.83 130.80 129.38 129.03 128.90 128.89 128.79 128.76 128.70 128.68 128.79 128.76 128.70 128.68 127.49 126.75 126.72 122.93 122.69 113.03 113.01 112.99 112.96 112.70 112.68 112.66 112.64
132 130 128 126
f1 (ppm)
SCF3
Br
3l
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.32
8.31
8.21
8.19
7.51
7.49
7.48
7.47
7.45
7.43
7.41
7.39
7.39
7.38
7.38
7.38
7.37
7.24
7.23
7.23
7.22
7.22
6.93
6.85
SCF3
O2N
3m
1.00
0.98
2.59
1.13
1.54
2.00
0.48
0.49
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


-42.34
-42.35
SCF3
O2N
3m
1.50
1.46
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)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146.08
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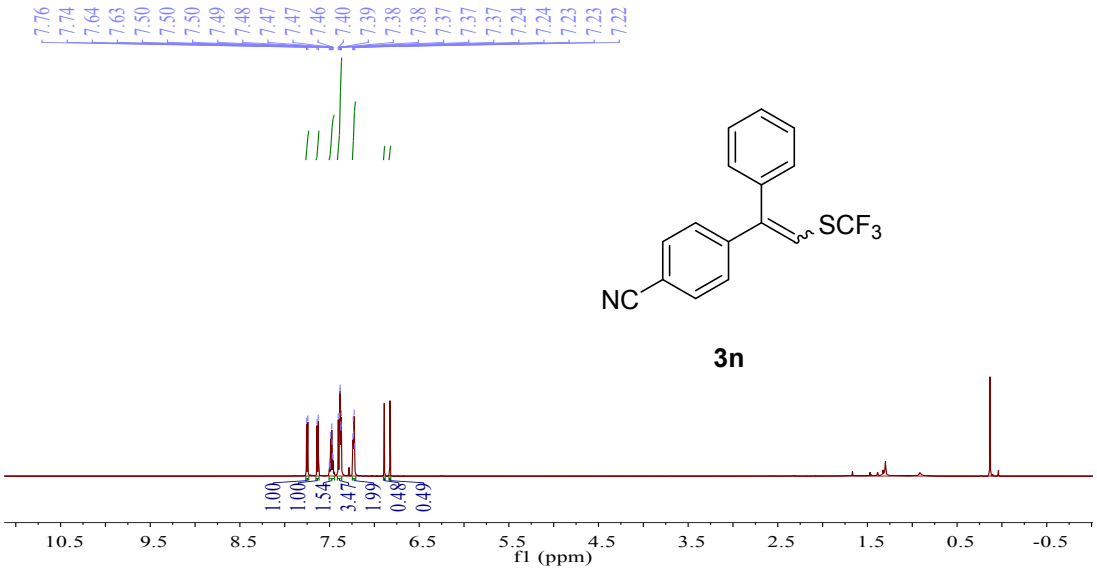
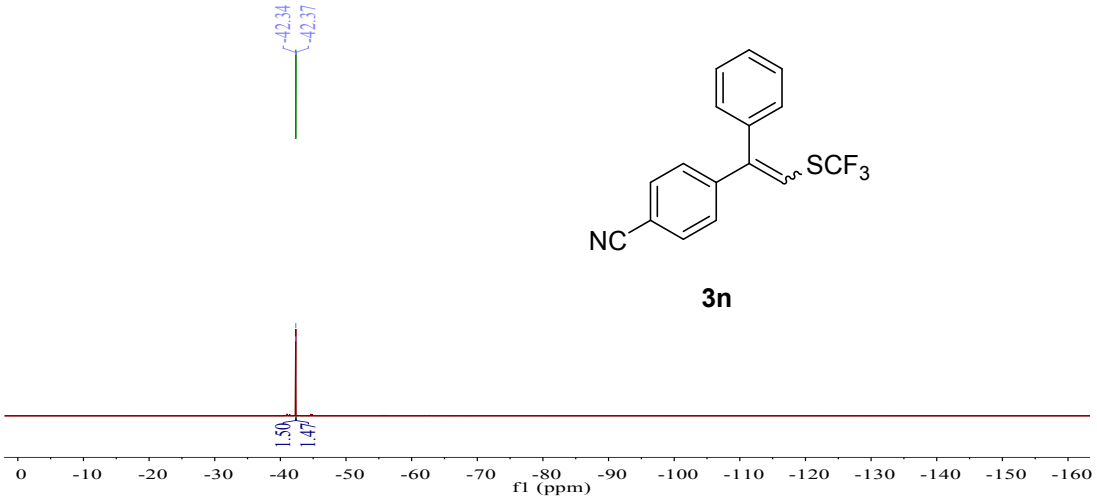
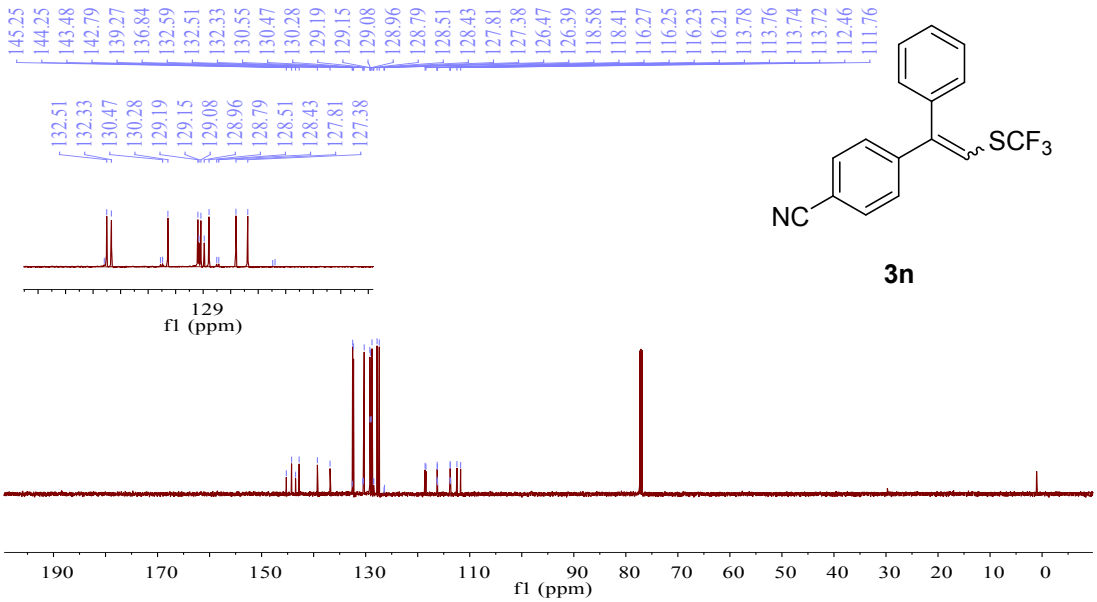
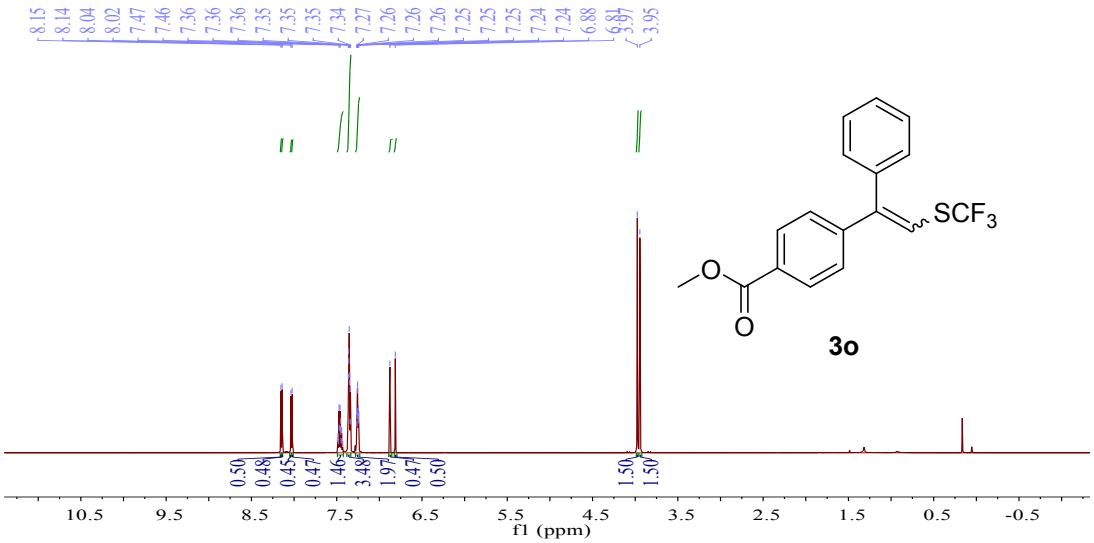
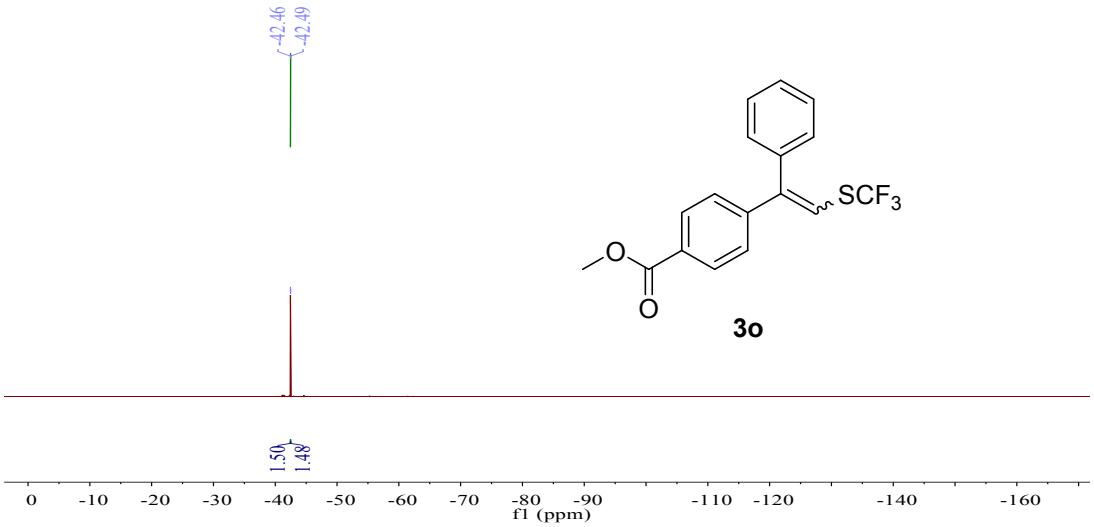
144.70
142.93
139.19
136.78
132.56
132.47
130.54
130.48
130.40
129.23
129.15
129.14
129.03
128.82
128.44
128.36
127.93
127.34
126.32
126.26
123.98
123.84
117.08
117.06
117.04
117.01
114.12
114.10
114.08
114.06
SCF3
O2N
3m
132
130
128
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

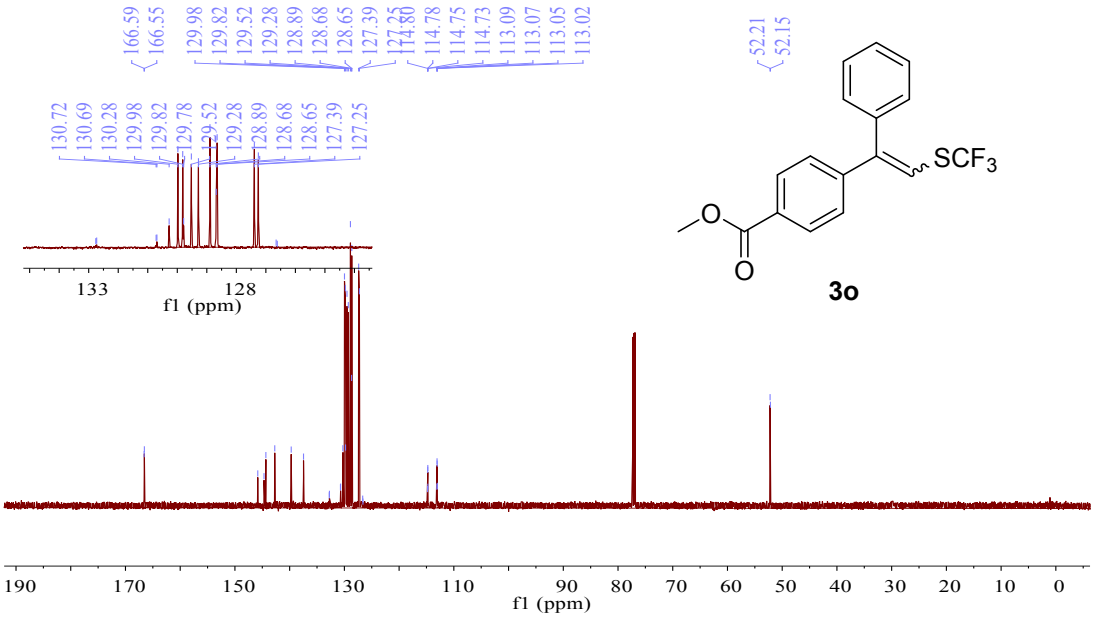

7.76
7.74
7.64
7.63
7.50
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.24
7.24
7.23
7.23
7.22
SCF3
NC
3n
1.00
1.00
1.54
3.47
1.99
0.48
0.49
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

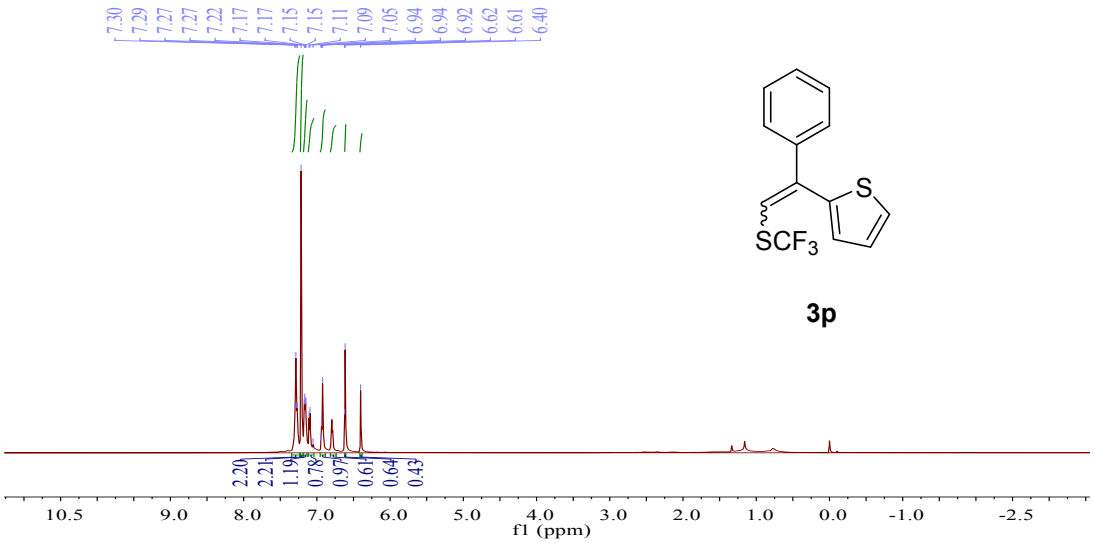

-42.34
-42.37
SCF3
NC
3n
1.50
1.47
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


145.25
144.25
143.48
142.79
139.27
136.84
132.59
132.51
132.33
130.55
130.47
130.28
129.19
129.15
129.08
128.96
128.79
128.51
128.43
127.81
127.38
126.47
126.39
118.58
118.41
116.27
116.25
116.23
116.21
113.78
113.76
113.74
113.72
112.46
111.76
SCF3
NC
3n
129
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

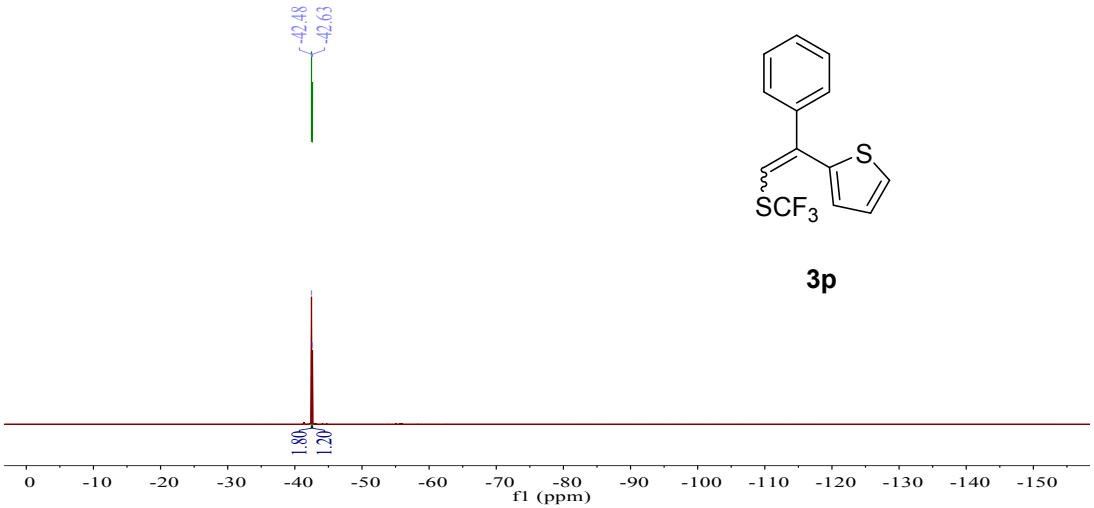

8.15
8.14
8.04
8.02
7.47
7.46
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.24
6.88
6.81
3.97
3.95
SCF3
O
O
3o
0.50
0.48
0.45
0.47
1.46
3.48
1.97
0.47
0.50
1.50
1.50
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


-42.46
-42.49
SCF3
O
O
3o
1.50
1.48
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
f1 (ppm)

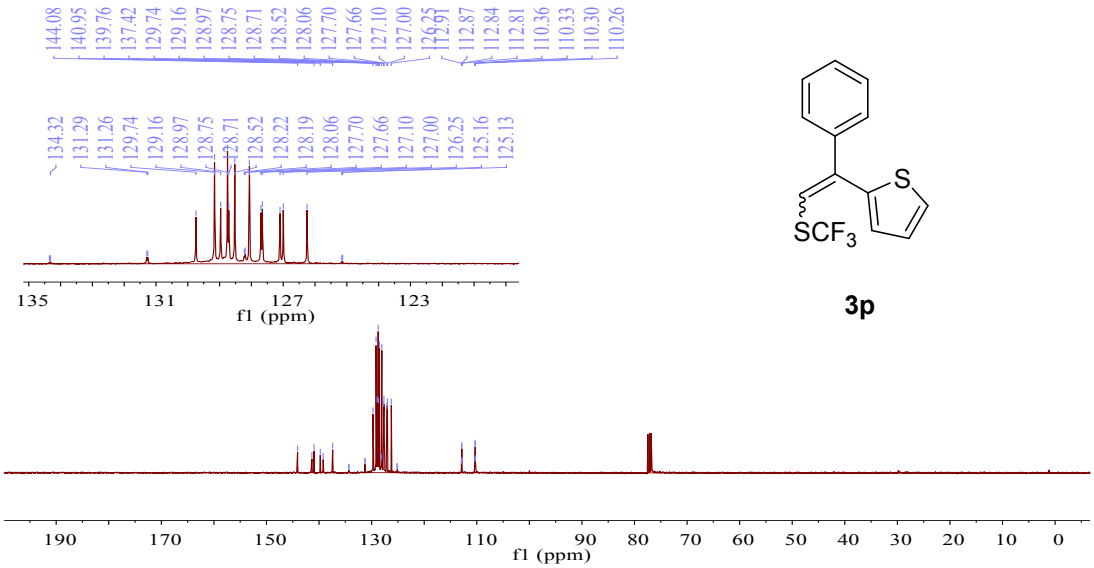

166.59
166.55
129.98
129.82
129.52
129.28
128.89
128.68
128.65
127.39
127.25
114.78
114.75
114.73
113.09
113.07
113.05
113.02
52.21
52.15
130.72
130.69
130.28
129.98
129.82
129.78
129.52
129.28
128.89
128.68
128.65
127.39
127.25
SCF3
O
O
3o
133
128
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.30
7.29
7.27
7.27
7.22
7.17
7.17
7.15
7.15
7.11
7.09
7.05
6.94
6.94
6.92
6.62
6.61
6.40
2.20
2.21
1.19
0.78
0.97
0.61
0.64
0.43
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.5
f1 (ppm)
S
SCF3

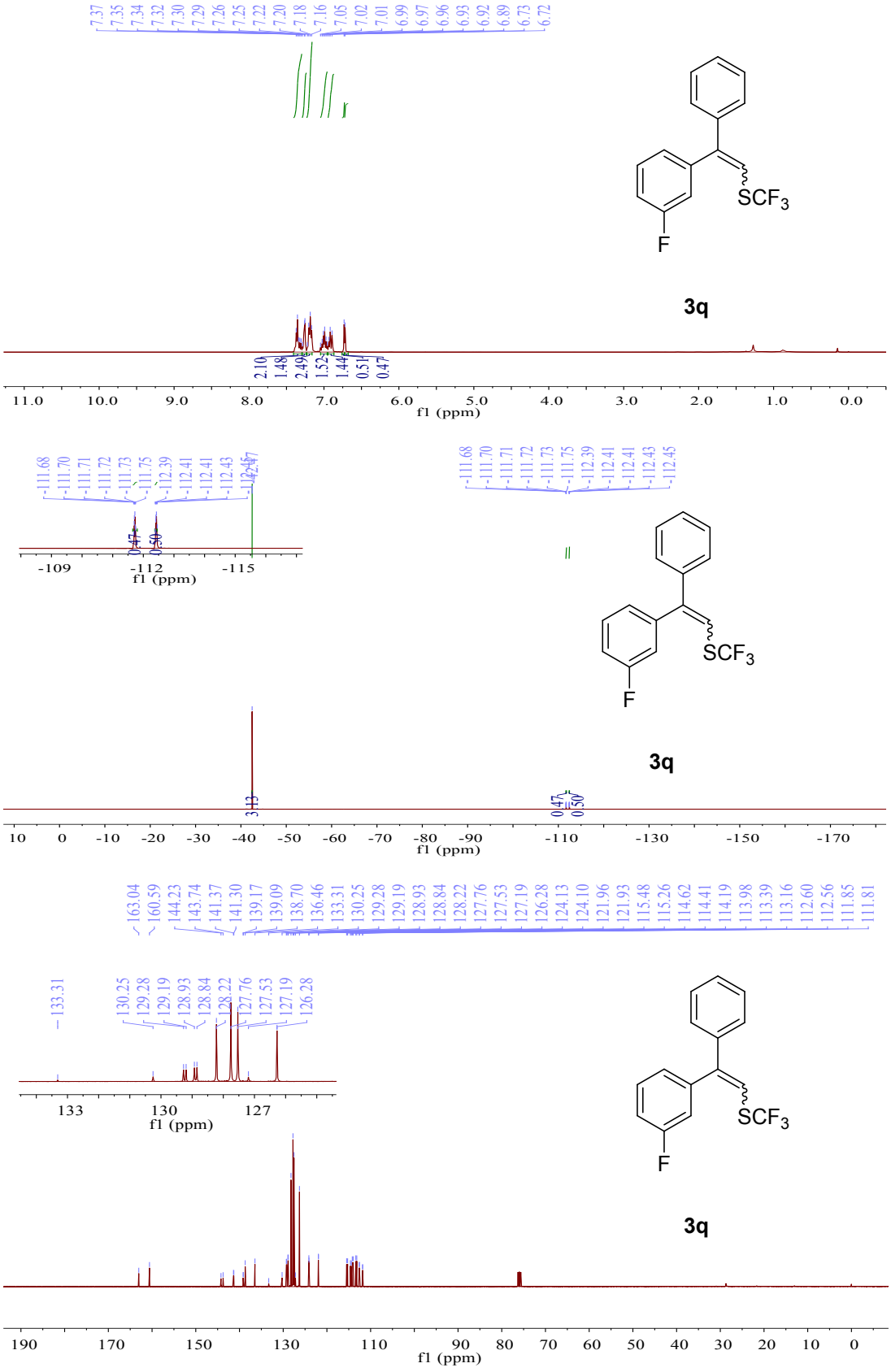
3p

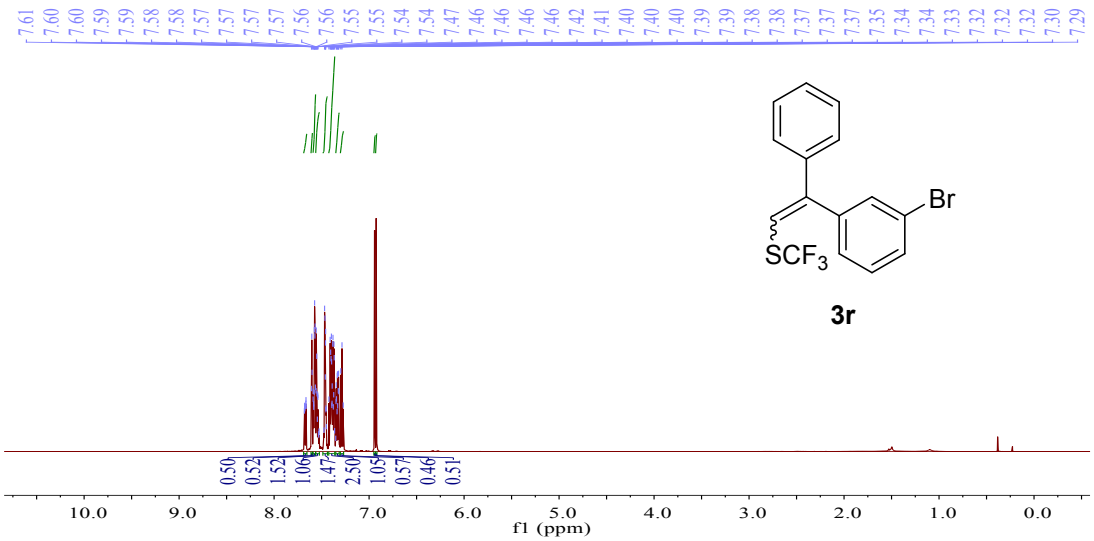

-42.48
-42.63
1.80
1.20
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)
S
SCF3

3p

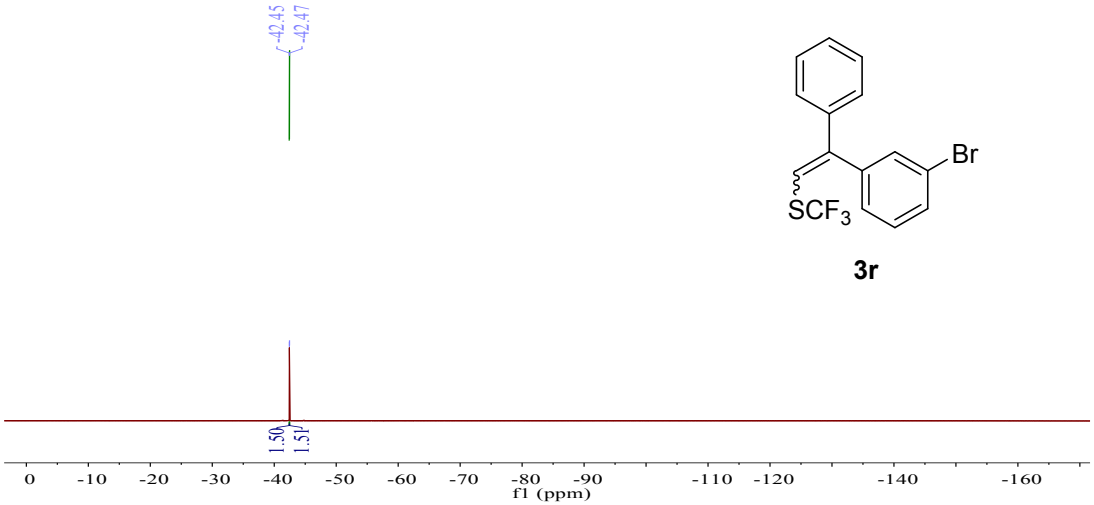

144.08
140.95
139.76
137.42
129.74
129.16
128.97
128.75
128.71
128.52
128.06
127.70
127.66
127.10
127.00
126.25
112.87
112.84
112.81
110.36
110.33
110.30
110.26
134.32
131.29
131.26
129.74
129.16
128.97
128.75
128.71
128.52
128.22
128.19
128.06
127.70
127.66
127.10
127.00
126.25
125.16
125.13
135
131
127
123
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S
SCF3

3p

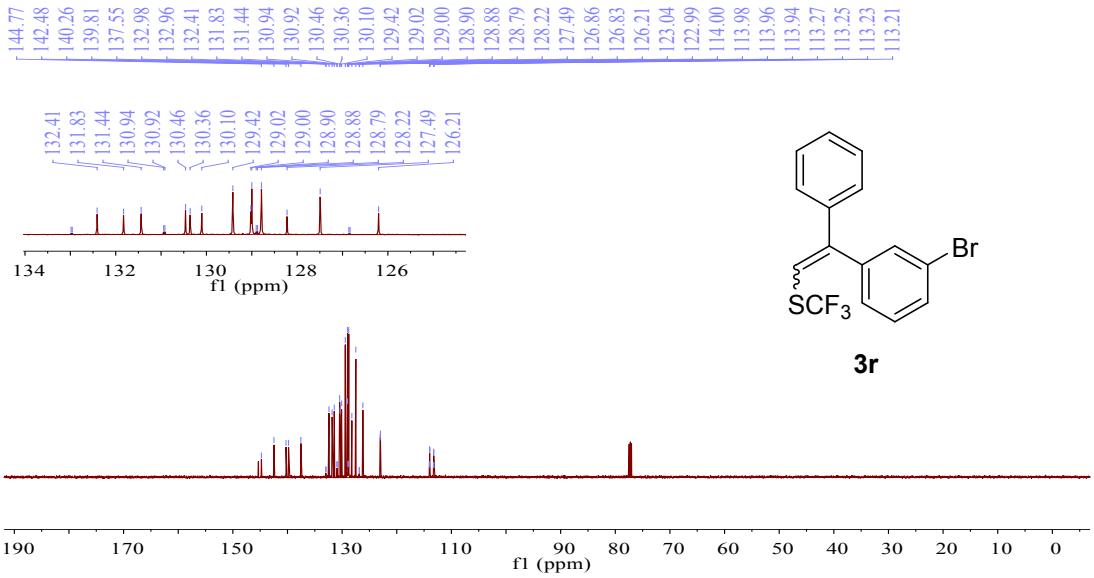

SCF3
F
3q
f1 (ppm)


7.61 7.60 7.60 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.57 7.56 7.56 7.55 7.55 7.54 7.54 7.47 7.46 7.46 7.46 7.46 7.42 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.35 7.34 7.34 7.33 7.32 7.32 7.32 7.30 7.29
Br
SCF3
0.50 0.53 1.52 1.06 1.47 2.50 1.05 0.57 0.46 0.51
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

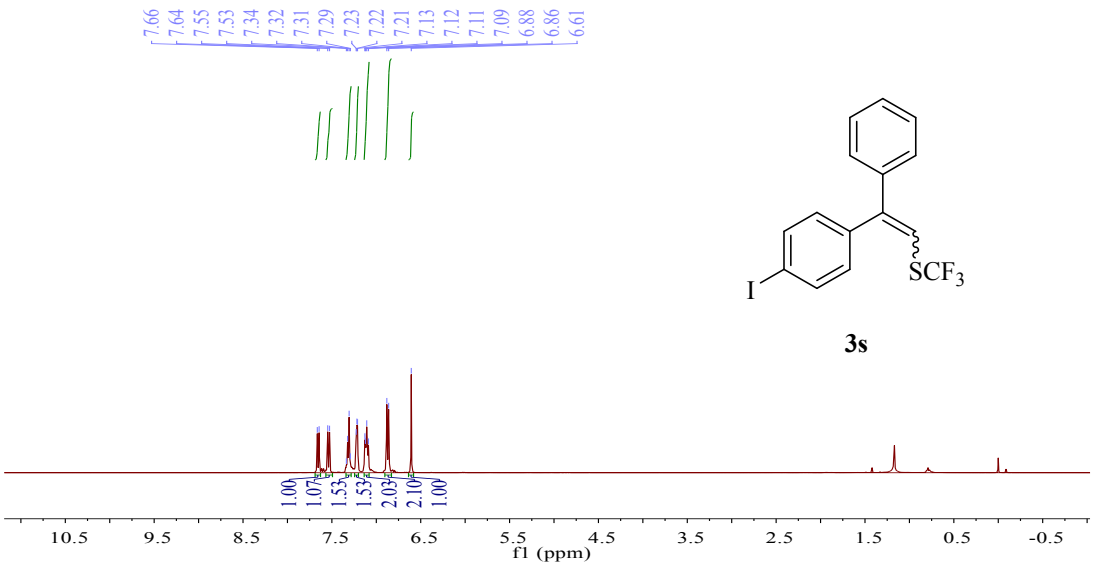
3r


-42.45
-42.47
Br
SCF3
1.50 1.51
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160
f1 (ppm)

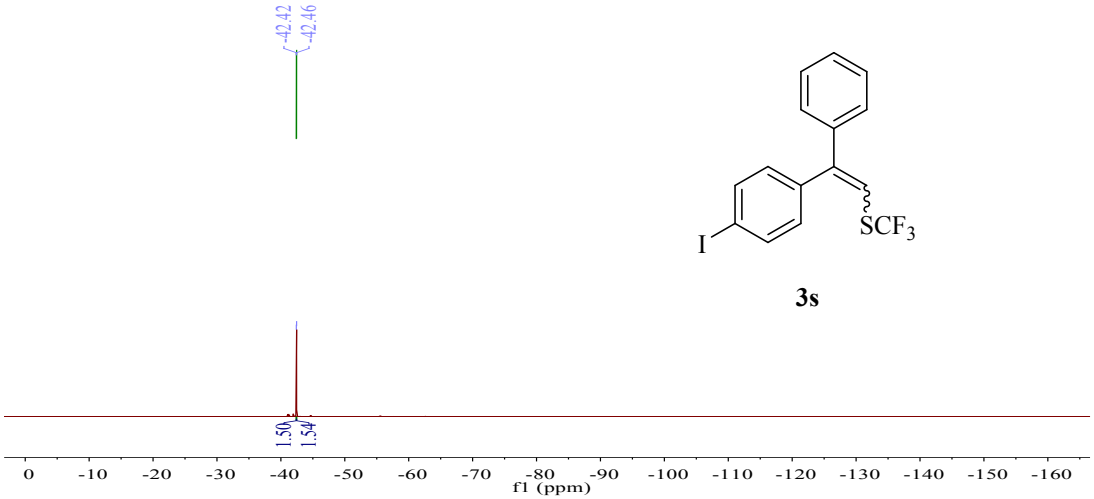
3r


144.77 142.48 140.26 139.81 137.55 132.98 132.96 132.41 131.83 131.44 130.94 130.92 130.46 130.36 130.10 129.42 129.02 129.00 128.90 128.88 128.79 128.22 127.49 126.86 126.83 126.21 123.04 122.99 114.00 113.98 113.96 113.94 113.27 113.25 113.23 113.21
132.41 131.83 131.44 130.94 130.92 130.46 130.36 130.10 129.42 129.02 129.00 128.90 128.88 128.79 128.22 127.49 126.21
134 132 130 128 126
f1 (ppm)
Br
SCF3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

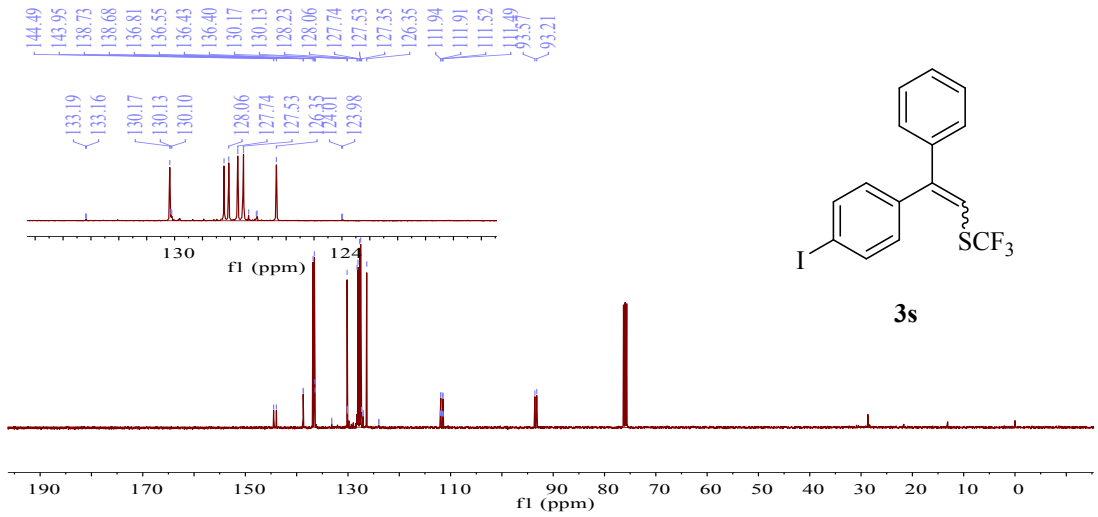
3r


7.66
7.64
7.55
7.53
7.34
7.32
7.31
7.29
7.23
7.22
7.21
7.13
7.12
7.11
7.09
6.88
6.86
6.61
I
SCF3
1.00
1.07
1.53
1.57
2.03
2.10
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

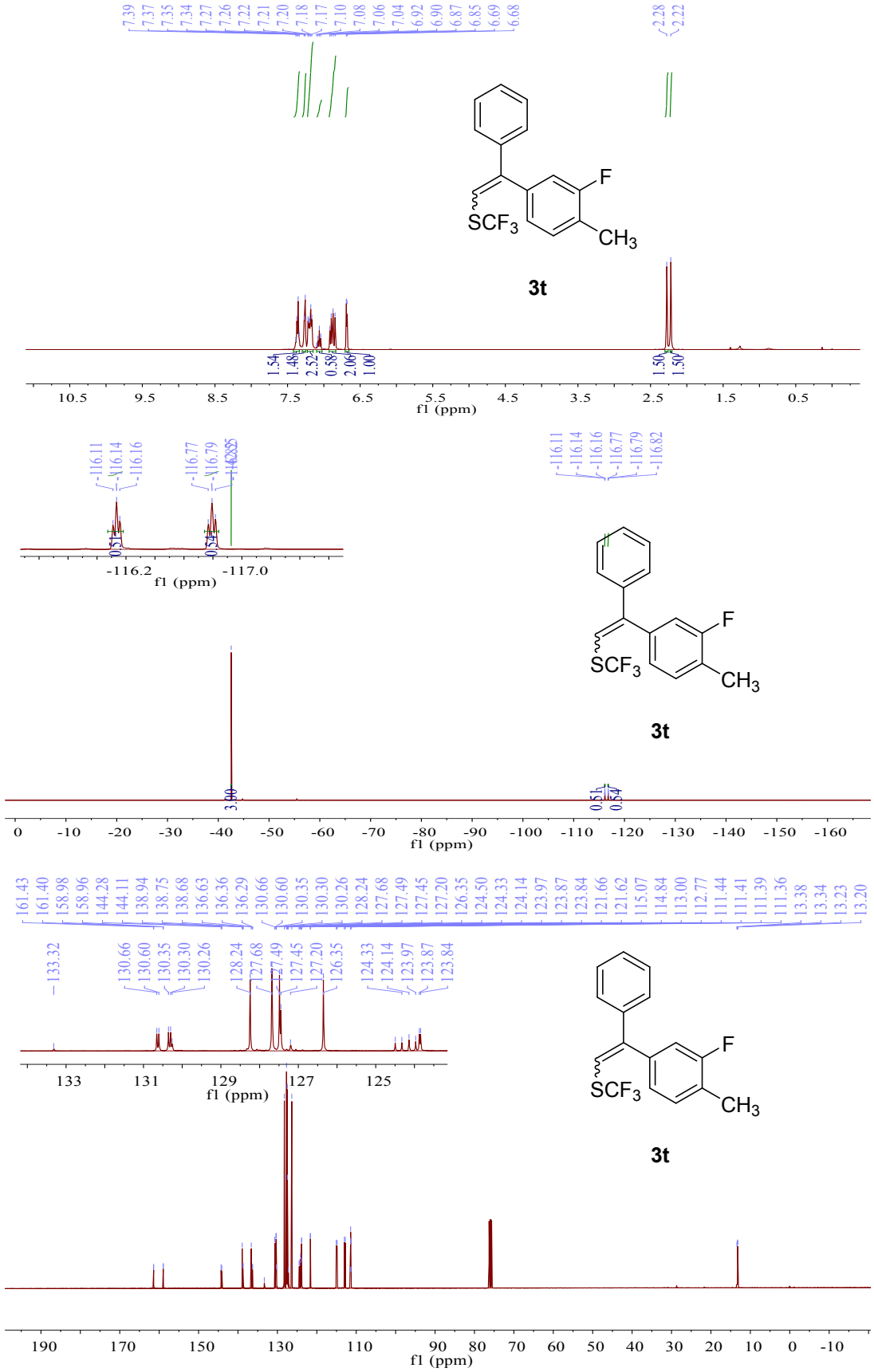
3s

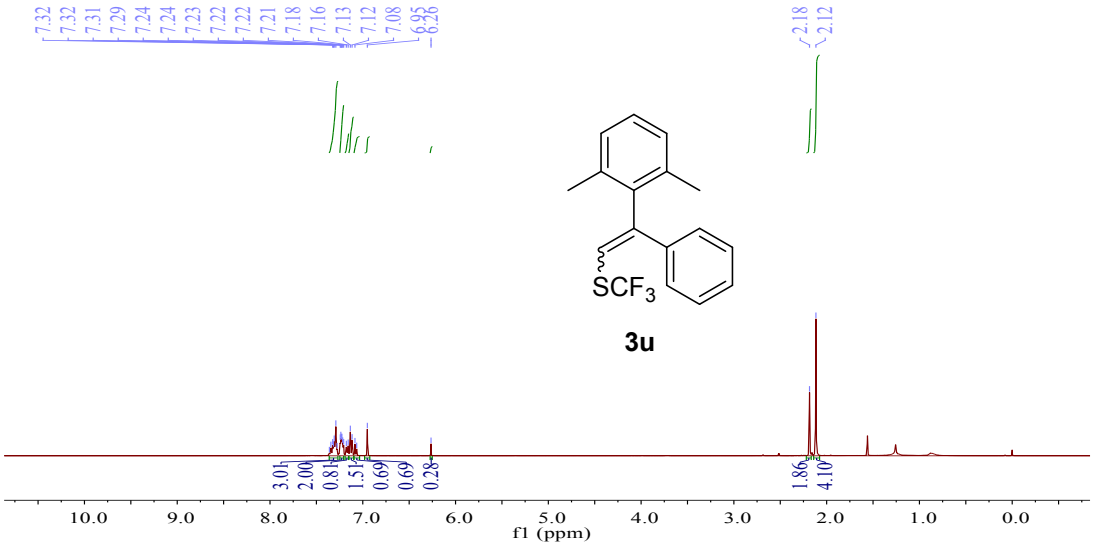

-42.42
-42.46
I
SCF3
1.50
1.54
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

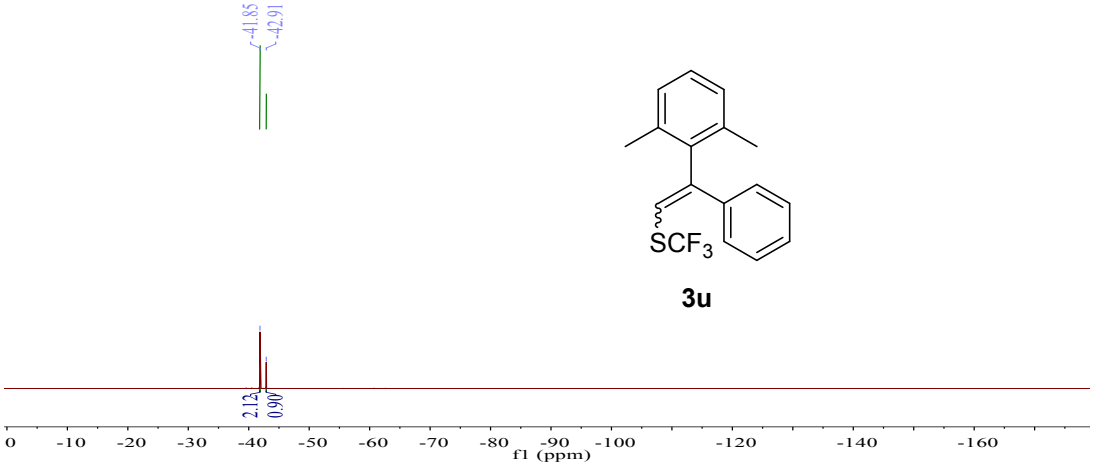
3s

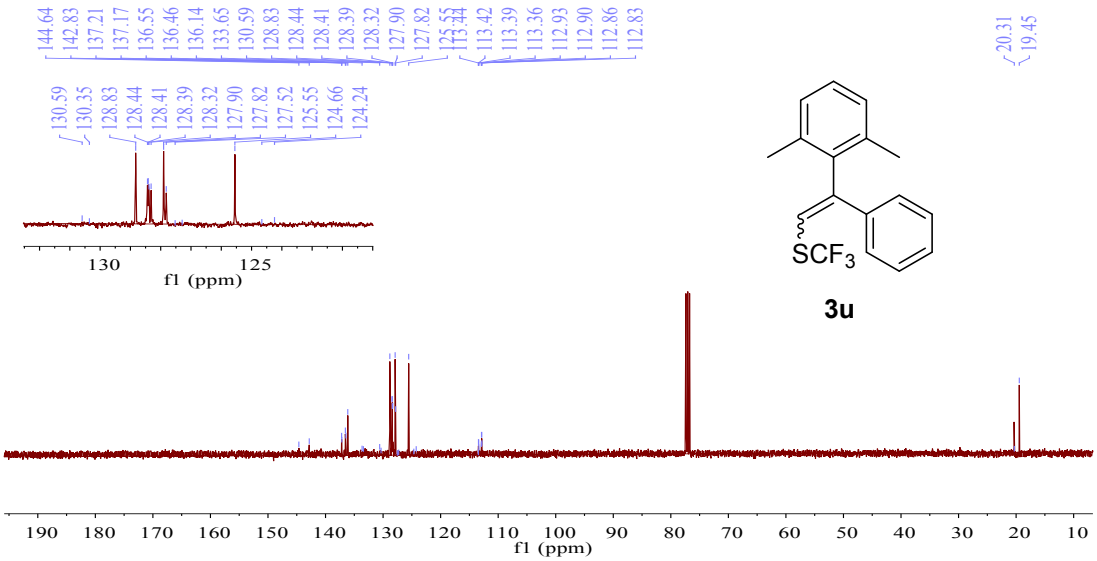

144.49
143.95
138.73
138.68
136.81
136.55
136.43
136.40
130.17
130.13
126.23
128.06
127.74
127.53
127.35
126.35
111.94
111.91
111.52
111.49
93.57
93.21
133.19
133.16
130.17
130.13
130.10
128.06
127.74
127.53
126.35
124.01
123.98
130
124
f1 (ppm)
I
SCF3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3s


7.39
7.37
7.35
7.34
7.27
7.26
7.22
7.21
7.20
7.18
7.17
7.10
7.08
7.06
7.04
6.92
6.90
6.87
6.85
6.69
6.68
2.28
2.22
F
SCF3
CH3
3t
1.54
1.48
2.52
0.58
2.06
1.00
1.50
1.50
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
-116.11
-116.14
-116.16
-116.77
-116.79
-116.2
-117.0
f1 (ppm)
-116.11
-116.14
-116.16
-116.77
-116.79
-116.82
F
SCF3
CH3
3t
3.00
0.51
0.54
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)
161.43
161.40
158.98
158.96
144.28
144.11
138.94
138.75
138.68
136.63
136.36
136.29
130.66
130.60
130.35
130.30
130.26
128.24
127.68
127.49
127.45
127.20
126.35
124.50
124.33
124.14
123.97
123.87
123.84
121.66
121.62
115.07
114.84
113.00
112.77
111.44
111.41
111.39
111.36
13.38
13.34
13.23
13.20
133.32
130.66
130.60
130.35
130.30
130.26
128.24
127.68
127.49
127.45
127.20
126.35
124.33
124.14
123.97
123.87
123.84
133
131
129
127
125
f1 (ppm)
F
SCF3
CH3
3t
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.32
7.32
7.31
7.29
7.24
7.24
7.23
7.22
7.22
7.21
7.18
7.16
7.13
7.12
7.08
6.95
6.26
2.18
2.12
SCF3
3u
3.01
2.00
0.81
1.51
0.69
0.69
0.28
1.86
4.10
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


-41.85
-42.91
SCF3
3u
2.12
0.90
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
f1 (ppm)


144.64
142.83
137.21
137.17
136.55
136.46
136.14
133.65
130.59
128.83
128.44
128.41
128.39
128.32
127.90
127.82
125.55
113.44
113.42
113.39
113.36
112.93
112.90
112.86
112.83
20.31
19.45
130.59
130.35
128.83
128.44
128.41
128.39
128.32
127.90
127.82
127.52
125.55
124.66
124.24
130
125
f1 (ppm)
SCF3
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)