Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper-Catalysed Synthesis of Trifluoromethyl Allenes via Fluoro-carboalkynylation of Alkenes

(Supporting Information)

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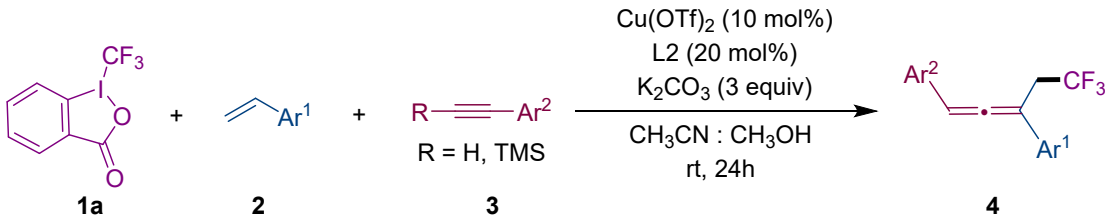
1. General Information.

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on ARX-400 MHz or a ARX-600 Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL Schlenk tubes with Teflon screw caps under argon. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

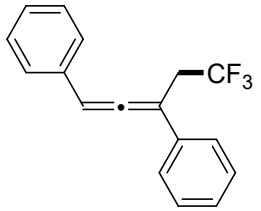
2. General Procedures for the Synthesis of Trifluoromethyl Allenes.



Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), alkenes **2** (0.2 mmol, 1.0 equiv), alkynes **3** (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (0.04 mmol, 20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h as monitored by TLC. The solvent was removed under vaccum directly.

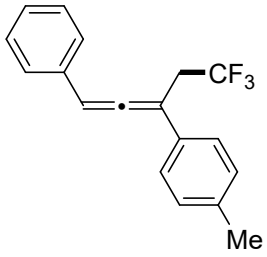
The crude product was purified by flash column chromatography on silica gel (eluent: PE/EA) to afford the product **4**.

3. Characterization Data of the Products 4.



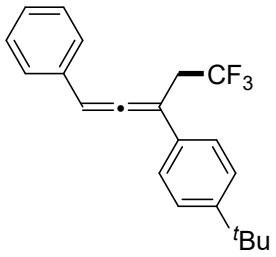
4a

(5,5,5-Trifluoropenta-1,2-diene-1,3-diyl)dibenzene (4a): colorless oil, 39.8 mg (73% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.44 (m, 2H), 7.40 – 7.33 (m, 6H), 7.30 – 7.27 (m, 2H), 6.67 (s, 1H), 3.50 – 3.30 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.7, 134.5, 132.9, 128.8, 128.7, 127.7, 127.6, 127.2, 126.0, 125.9 (q, J = 277.5 Hz), 100.3 (q, J = 3.0 Hz), 98.6, 35.3 (q, J = 29.7 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{14}F_3$ $(M + H)^+$ 275.1042, found 275.1045.



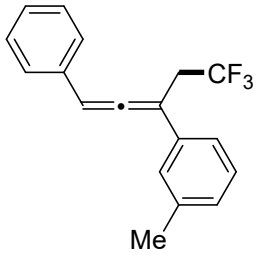
4b

1-Methyl-4-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4b): colorless oil, 45.4 mg (79% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.35 (m, 6H), 7.31 – 7.25 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.66 (s, 1H), 7.47 – 7.33 (m, 2H), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.5, 137.5, 133.1, 131.5, 129.4, 128.8, 127.6, 127.2, 125.9 (d, J = 277.5 Hz), 125.9, 100.2 (q, J = 3.1 Hz), 98.5, 35.3 (q, J = 29.7 Hz), 21.1; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}F_3Na$ $(M + Na)^+$ 331.1018, found 331.1022.



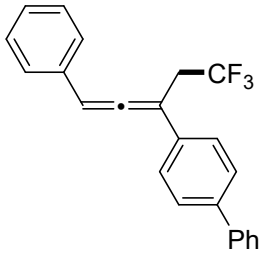
4c

1-(*tert*-Butyl)-4-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4c): colorless oil, 52.3 mg (79% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.32 (m, 8H), 7.27 (dd, *J* = 8.7, 5.1 Hz, 1H), 6.66 (s, 1H), 3.50 – 3.29 (m, 2H), 1.34 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.6, 150.8, 133.1, 131.4, 128.8, 127.6, 127.2, 125.9 (d, *J* = 277.5 Hz), 125.7, 125.7, 100.0 (q, *J* = 3.2 Hz), 98.6, 35.3 (q, *J* = 29.7 Hz), 34.5, 31.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{21}H_{22}F_3$ $(M + H)^+$ 331.1668, found 331.1673.



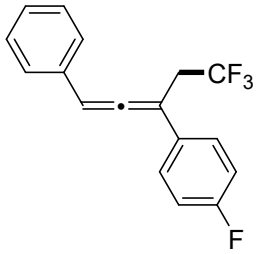
4d

1-Methyl-3-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4d): colorless oil, 46.2 mg (80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.34 (m, 4H), 7.30 – 7.26 (m, 4H), 7.12 – 7.10 (m, 1H), 6.67 (s, 1H), 3.49 – 3.28 (m, 2H), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.6, 138.4, 134.4, 133.0, 128.8, 128.6, 128.5, 127.7, 127.2, 126.7, 125.9 (q, *J* = 277.5 Hz), 123.1, 100.3 (q, *J* = 3.1 Hz), 98.5, 35.4 (q, *J* = 29.7 Hz), 21.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}F_3$ $(M + H)^+$ 289.1199, found 289.1203.



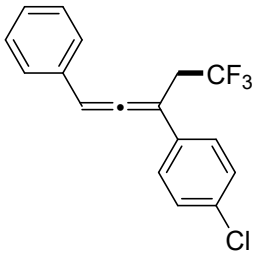
4e

4-(5,5,5-Trifluoro-1-phenylpenta-1,2-dien-3-yl)-1,1'-biphenyl (4e): colorless oil, 44.2 mg (63% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.58 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 5H), 7.29 (t, *J* = 6.9 Hz, 1H), 6.71 (s, 1H), 3.52 – 3.35 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.0, 140.5, 140.4, 133.3, 132.8, 128.9, 128.8, 127.8, 127.5, 127.4, 127.2, 127.0, 126.4, 125.9 (q, *J* = 277.4 Hz), 100.1 (q, *J* = 3.0 Hz), 98.8, 35.3 (q, *J* = 29.7 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.4; **HRMS m/z (ESI)** calcd for $C_{23}H_{18}F_3$ $(M + H)^+$ 351.1355, found 351.1356.



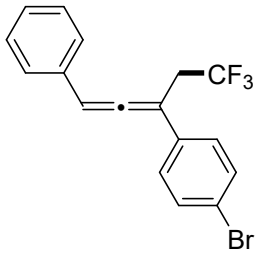
4f

1-Fluoro-4-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4f): colorless oil, 35.7 mg (61% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.32 (m, 6H), 7.30 – 7.25 (m, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.65 (s, 1H), 3.45 – 3.27 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.5 (d, *J* = 1.5 Hz), 162.3 (d, *J* = 247.5 Hz), 132.7, 130.5 (d, *J* = 3.5 Hz), 128.8, 127.8, 127.7 (d, *J* = 8.1 Hz), 127.2, 125.8 (q, *J* = 277.8 Hz), 115.7 (d, *J* = 21.8 Hz), 99.5 (q, *J* = 3.3 Hz), 98.7, 35.6 (q, *J* = 29.8 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.4, -114.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{12}F_4Na$ $(M + Na)^+$ 315.0767, found 315.0769.



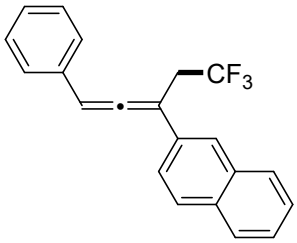
4g

1-Chloro-4-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4g): colorless oil, 31.8 mg (52% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.25 (m, 9H), 6.70 (s, 1H), 3.47 – 3.29 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.8, 133.5, 133.0, 132.5, 128.9, 128.9, 127.9, 127.3, 127.2, 125.7 (q, J = 277.6 Hz), 99.6 (q, J = 3.4 Hz), 98.9, 35.3 (q, J = 29.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{12}ClF_3Na$ $(M + Na)^+$ 331.0472, found 331.0475.



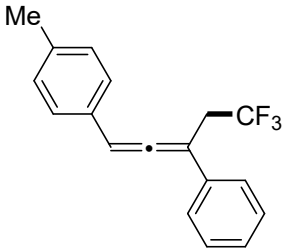
4h

1-Bromo-4-(5,5,5-trifluoro-1-phenylpenta-1,2-dien-3-yl)benzene (4h): colorless oil, 30.2 mg (43% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.43 (m, 2H), 7.35 (d, J = 4.3 Hz, 4H), 7.31 – 7.25 (m, 3H), 6.66 (s, 1H), 3.44 – 3.26 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.8, 133.5, 132.4, 131.8, 128.9, 127.9, 127.6, 127.2, 125.7 (q, J = 277.6 Hz), 121.6, 99.6 (q, J = 3.4 Hz), 99.0, 35.3 (q, J = 29.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{13}ClF_3$ $(M + H)^+$ 353.0147, found 353.0148.



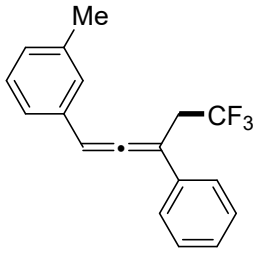
4i

2-(5,5,5-Trifluoro-1-phenylpenta-1,2-dien-3-yl)naphthalene (4i): colorless oil, 41.6 mg (64% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 – 7.76 (m, 4H), 7.61 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 – 7.26 (m, 1H), 6.75 (s, 1H), 3.61 – 3.44 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.3, 133.5, 132.9, 132.7, 131.8, 128.9, 128.3, 128.1, 127.8, 127.6, 127.3, 126.4, 126.2, 125.9 (q, *J* = 277.5 Hz), 124.7, 124.1, 100.5 (q, *J* = 3.2 Hz), 99.0, 35.3 (q, *J* = 29.8 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.3; **HRMS m/z (ESI)** calcd for $C_{21}H_{16}F_3$ $(M + H)^+$ 325.1199, found 325.1203.



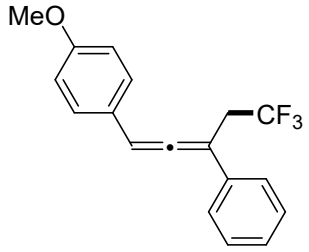
4j

1-Methyl-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4j): colorless oil, 40.4 mg (70% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.65 (s, 1H), 3.48 – 3.26 (m, 2H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.6, 137.6, 134.7, 132.4, 129.6, 128.7, 127.5, 127.1, 126.0, 125.9 (q, *J* = 277.5 Hz), 100.1 (q, *J* = 3.1 Hz), 98.4, 35.3 (q, *J* = 29.7 Hz), 21.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}F_3$ $(M + H)^+$ 289.1199, found 289.1203.



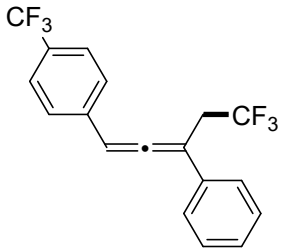
4k

1-Methyl-3-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4k): colorless oil, 41.6 mg (72% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.19 (d, *J* = 6.2 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.65 (s, 1H), 3.49 – 3.32 (m, 2H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δδ 208.8, 138.5, 134.6, 132.8, 128.72, 128.68, 128.6, 127.9, 127.6, 126.0, 125.9 (q, *J* = 277.5 Hz), 124.3, 100.1 (q, *J* = 3.0 Hz), 98.6, 35.3 (q, *J* = 29.7 Hz), 21.3; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}F_3$ $(M + H)^+$ 289.1199, found 289.1200.



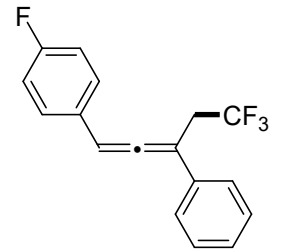
4l

1-Methoxy-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4l): colorless oil, 37.8 mg (62% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.26 (m, 3H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.63 (s, 1H), 3.82 (s, 3H), 3.45 – 3.31 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.3, 159.3, 134.8, 128.7, 128.4, 127.5, 126.0, 125.9 (q, *J* = 277.5 Hz), 125.1, 114.3, 100.1 (q, *J* = 3.2 Hz), 98.1, 55.3, 35.4 (q, *J* = 29.6 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}F_3NaO$ $(M + Na)^+$ 327.0967, found 327.0968.



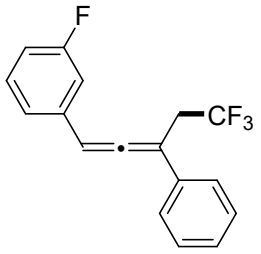
4m

1-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (4m): colorless oil, 50.1 mg (73% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 3.47 – 3.32 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 209.3, 136.9, 133.8, 129.6 (q, *J* = 32.9 Hz), 128.8, 128.0, 127.3, 126.0, 125.8 (q, *J* = 3.5 Hz), 125.7 (d, *J* = 277.4 Hz), 124.1 (d, *J* = 271.9 Hz), 101.1 (q, *J* = 3.1 Hz), 97.8, 35.2 (q, *J* = 29.9 Hz); **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.6, -64.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{12}F_6Na$ $(M + Na)^+$ 365.0735, found 365.0736.



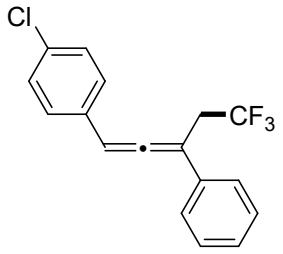
4n

1-Fluoro-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4n): colorless oil, 58.8 mg (76% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.26 (m, 5H), 7.04 (t, *J* = 8.6 Hz, 2H), 3.49 – 3.27 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.4 (d, *J* = 2.3 Hz), 162.4 (d, *J* = 247.3 Hz), 134.4 , 128.9 (d, *J* = 3.4 Hz), 128.7, 128.6, 127.7, 126.0, 125.8 (q, *J* = 277.5 Hz), 115.8 (d, *J* = 21.9 Hz), 100.5 (q, *J* = 3.1 Hz), 97.7, 35.3 (q, *J* = 29.7 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ-64.5, -114.0; **HRMS m/z (ESI)** calcd for $C_{17}H_{12}F_4Na$ $(M + Na)^+$ 315.0767, found 315.0769.



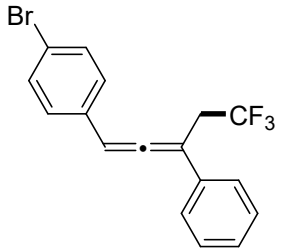
4o

1-Fluoro-3-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4o): colorless oil, 37.2 mg (64% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.42 (m, 2H), 7.39 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.07 (dt, *J* = 9.9, 2.0 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.64 (s, 1H), 3.46 – 3.33 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.8, 163.2 (d, *J* = 245.7 Hz), 135.4 (d, *J* = 7.6 Hz), 134.1, 130.2 (d, *J* = 8.5 Hz), 128.8, 127.9, 126.0, 125.8 (q, *J* = 277.5 Hz), 122.9 (d, *J* = 2.7 Hz), 114.6 (d, *J* = 21.3 Hz), 113.7 (d, *J* = 22.3 Hz), 100.8 (q, *J* = 3.1 Hz), 98.0 (d, *J* = 2.5 Hz), 35.3 (q, *J* = 29.8 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ-64.5, -113.0; **HRMS m/z (ESI)** calcd for $C_{17}H_{13}F_4$ $(M + H)^+$ 293.0948, found 293.0947.



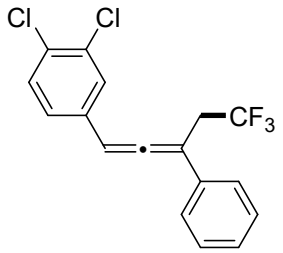
4p

1-Chloro-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4p): colorless oil, 43.1 mg (70% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.28 (m, 5H), 6.63 (s, 1H), 3.45 – 3.32 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.7, 134.2, 133.4, 131.5, 129.0, 128.8, 128.3, 127.8, 126.0, 125.8 (q, *J* = 277.5 Hz), 100.7 (q, *J* = 3.1 Hz), 97.8, 35.3 (q, *J* = 29.8 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{12}ClF_3Na$ $(M + Na)^+$ 331.0472, found 331.0475.



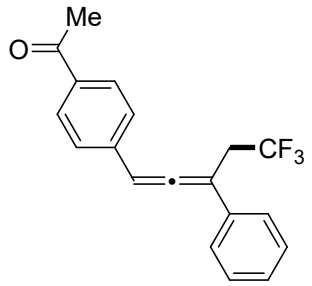
4q

1-Bromo-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4q): colorless oil, 49.1 mg (70% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.40 (m, 4H), 7.38 – 7.35 (m, 2H), 7.31 – 7.26 (m, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 3.48 – 3.29 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.7, 134.1, 132.0, 128.8, 128.6, 127.8, 126.0, 125.8 (q, *J* = 277.5 Hz), 121.5, 100.8, 97.9, 35.2 (q, *J* = 29.7 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{13}BrF_3$ $(M + H)^+$ 353.1047, found 353.1053.



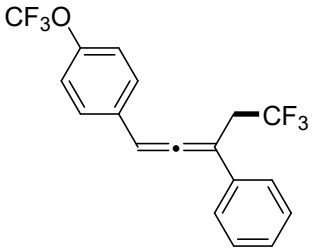
4r

1,2-Dichloro-4-(5,5,5-trifluoro-3-phenylpenta-1,2-dien-1-yl)benzene (4r): colorless oil, 52.8 mg (77% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 7.25 (t, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 2H), 6.56 (s, 1H), 3.49 – 3.31 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.9, 136.3, 135.4, 133.5, 128.9, 128.1, 127.6, 126.1, 125.6 (q, *J* = 277.4 Hz), 125.3, 101.5 (q, *J* = 3.0 Hz), 97.0, 35.2 (q, *J* = 29.9 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{12}Cl_2F_3$ $(M + H)^+$ 343.0263, found 343.0266.



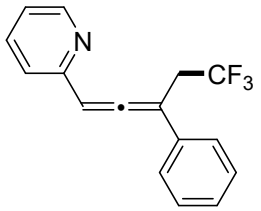
4s

1-(4-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)phenyl)ethan-1-one (4s): colorless oil, 28.6 mg (45% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 7.7, 5.7 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.69 (s, 1H), 3.47 – 3.30 (m, 2H), 2.59 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.7, 197.4, 138.1, 136.2, 133.8, 129.0, 128.8, 128.0, 127.2, 126.0, 125.7 (q, *J* = 277.4 Hz), 98.1, 35.2 (q, *J* = 29.8 Hz), 26.6; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{19}H_{16}F_3O$ $(M + H)^+$ 317.1148, found 317.1152.



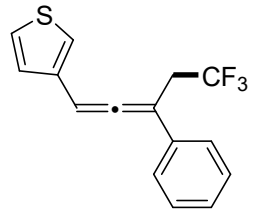
4t

1-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)-4-(trifluoromethoxy)benzene (4t): colorless oil, 28.6 mg (45% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.34 (m, 6H), 7.32 – 7.27 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 3.53 – 3.26 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.7, 148.6, 134.1, 131.8, 129.3, 128.8, 128.4, 127.9, 125.8 (q, *J* = 277.6 Hz), 120.5 (d, *J* = 257.0 Hz), 100.8 (d, *J* = 2.8 Hz), 97.6, 35.3 (q, *J* = 29.8 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -57.9, -64.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{13}F_6O$ $(M + H)^+$ 359.0865, found 359.0863.



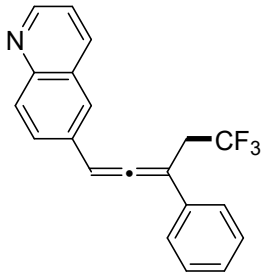
4u

2-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)pyridine (4u): colorless oil, 34.5 mg (63% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.62 (td, *J* = 7.7, 1.7 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.18 – 7.07 (m, 1H), 6.85 (s, 1H), 3.51 – 3.31 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 210.2, 153.3, 149.7, 136.5, 133.8, 128.8, 127.9, 126.1, 125.7 (q, *J* = 277.5 Hz), 122.1, 121.8, 100.8 (q, *J* = 3.1 Hz), 100.3, 35.2 (q, *J* = 30.0 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{16}H_{13}F_3N$ $(M + H)^+$ 276.2817, found 276.2818.



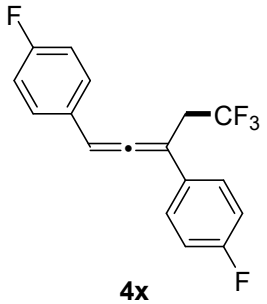
4v

3-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)thiophene (4v): yellow oil, 37.4 mg (67% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 6.74 (s, 1H), 3.48 – 3.27 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.9, 134.6, 134.0, 128.7, 127.6, 126.3, 126.1, 125.9 (q, *J* = 277.5 Hz), 122.2, 99.4 (q, *J* = 3.2 Hz), 93.0, 35.4 (q, *J* = 29.6 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{15}H_{11}F_3NaS$ $(M + Na)^+$ 303.0426, found 303.0422.



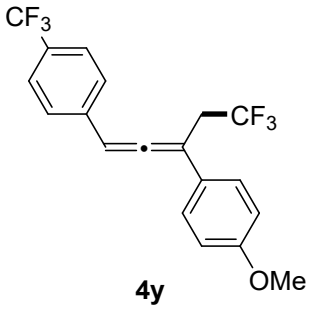
4w

6-(5,5,5-Trifluoro-3-phenylpenta-1,2-dien-1-yl)quinoline (4w): grey oil, 39.8 mg (61% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 6.74 (s, 1H), 3.48 – 3.27 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.9, 134.6, 134.0, 128.7, 127.6, 126.3, 126.1, 125.9 (q, *J* = 277.5 Hz), 122.2, 99.4 (q, *J* = 3.2 Hz), 93.0, 35.4 (q, *J* = 29.6 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.5; **HRMS m/z (ESI)** calcd for $C_{20}H_{15}F_3N$ $(M + H)^+$ 326.1151, found 326.1154.



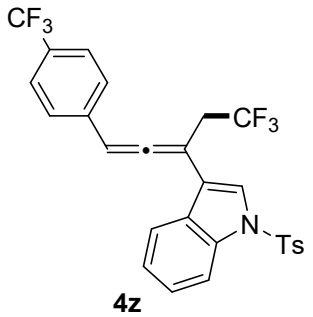
4x

4,4'-(5,5,5-Trifluoropenta-1,2-diene-1,3-diyl)bis(fluorobenzene) (4x): colorless oil, 44.5 mg (72% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.32 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.08 – 7.01 (m, 5H), 6.63 (s, 1H), 3.42 – 3.29 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 208.2 (d, *J* = 1.9 Hz), 162.4 (d, *J* = 247.1Hz), 162.3 (d, *J* = 247.7Hz), 134.5 (d, *J* = 8.7 Hz), 130.4 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 7.9 Hz), 127.7 (d, *J* = 8.2 Hz), 125.8 (d, *J* = 277.5 Hz), 115.9 (d, *J* = 27.7 Hz), 115.7 (d, *J* = 27.7 Hz), 99.8 (d, *J* = 3.1 Hz), 97.8, 35.6 (q, *J* = 29.8 Hz); **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.6, -113.8, -114.3; **HRMS m/z (ESI)** calcd for $C_{17}H_{11}F_5Na$ $(M + Na)^+$ 333.0673, found 333.0674.



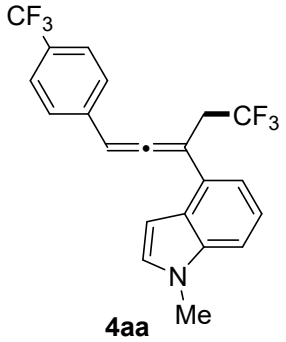
4y

1-Methoxy-4-(5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)penta-1,2-dien-3-yl)benzene (4y): colorless oil, 53.3 mg (72% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 1H), 3.82 (s, 3H), 3.44 – 3.29 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 208.9, 159.5, 137.2, 129.5 (q, *J* = 32.6 Hz), 127.3, 127.2, 125.9, 125.8 (q, *J* = 277.5 Hz), 125.7 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 272.0 Hz), 114.3, 100.6 (q, *J* = 3.1 Hz), 97.7, 55.3, 35.4 (q, *J* = 29.8 Hz); **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.5, -64.5; **HRMS m/z (ESI)** calcd for $C_{19}H_{14}F_6NaO$ $(M + Na)^+$ 395.0841, found 395.0842.



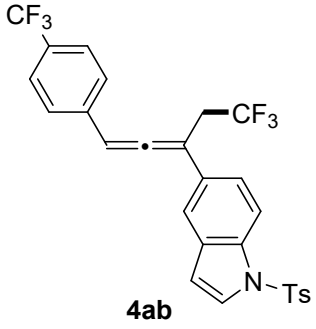
4z

1-Tosyl-3-(5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)penta-1,2-dien-3-yl)-1H-indole (4z): colorless oil, 80.2 mg (75% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.28 (m, 1H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.17 – 7.10 (m, 1H), 6.75 (s, 1H), 3.45 – 3.27 (m, 2H), 2.35 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.8, 145.3, 137.0, 135.4, 134.8, 130.0, 128.4, 127.6, 126.9, 125.8 (q, *J* = 4.0 Hz), 125.6 (q, *J* = 277.5 Hz), 125.4, 124.0 (q, *J* = 272.2 Hz), 123.8, 123.6, 120.6, 116.1, 113.7, 98.0, 94.3 (q, *J* = 3.0 Hz), 37.1 (q, *J* = 30.1 Hz), 21.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ-62.6, -64.3; **HRMS m/z (ESI)** calcd for $C_{27}H_{20}F_6NO_2S$ $(M + H)^+$ 536.1113, found 536.1115.



4aa

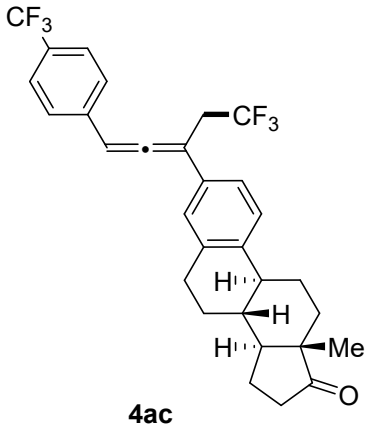
1-Methyl-4-(5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)penta-1,2-dien-3-yl)-1H-indole (4aa): colorless oil, 40.9 mg (52% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.64 (s, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 3.79 (s, 3H), 3.62 – 3.46 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.6, 137.7, 137.1, 129.3, 127.5, 125.9 (q, *J* = 277.7 Hz), 125.7 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 271.9 Hz),121.5, 117.5, 109.6, 100.2, 96.5, 36.9 (q, *J* = 29.4 Hz), 33.0; **^{19}F NMR (376 MHz, $CDCl_3$)** δ-62.4, -64.4; **HRMS m/z (ESI)** calcd for $C_{21}H_{15}F_6NNa$ $(M + Na)^+$ 418.1001, found 418.1006.



4ab

1-Tosyl-5-(5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)penta-1,2-dien-3-yl)-1H-indole (4ab): colorless oil, 67.6 mg (63% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.52 (m, 4H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.38 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 3.51 – 3.31 (m, 2H), 2.34 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.2, 145.1, 136.9, 135.1, 134.3, 131.2, 129.9, 129.1, 127.3, 127.1, 126.8, 125.8 (q, *J* = 3.0 Hz), 125.7 (q, *J* = 276.5 Hz), 124.1 (q, *J* = 271.6 Hz), 123.0, 118.6, 113.82 , 108.94 ,

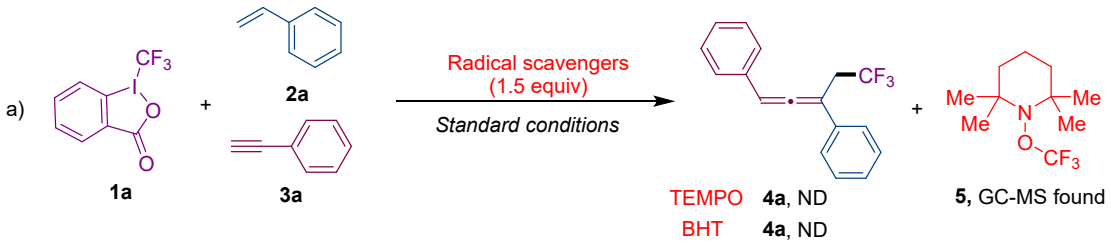
101.1 (q, *J* = 3.0 Hz), 97.7, 35.5 (q, *J* = 29.8 Hz), 21.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.5, -64.5; **HRMS m/z (ESI)** calcd for $C_{27}H_{20}F_6NO_2S$ $(M + H)^+$ 536.1113, found 536.1113.



4ac

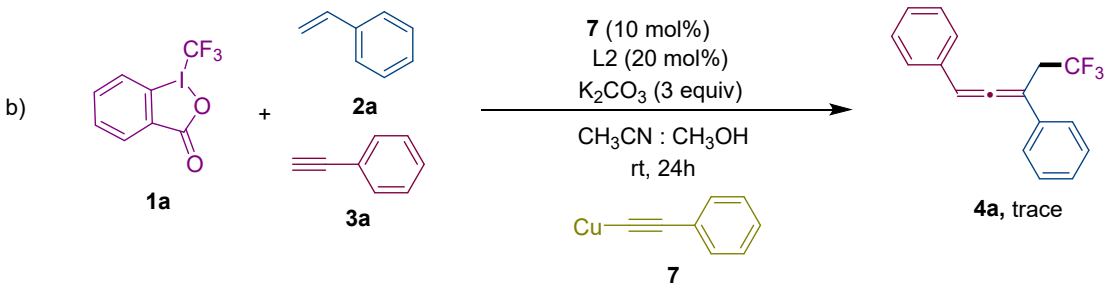
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)penta-1,2-dien-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a] phenanthren-17-one (4ac): colorless oil, 54.8 mg (53% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 6.66 (s, 1H), 3.44 – 3.30 (m, 1H), 2.91 (dd, *J* = 8.0, 3.2 Hz, 2H), 2.51 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.41 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.15 (dt, *J* = 18.7, 8.9 Hz, 1H), 2.05 (ddt, *J* = 19.2, 7.8, 4.3 Hz, 2H), 2.00 – 1.94 (m, 1H), 1.67 – 1.42 (m, 8H), 0.91 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 209.21, 209.20, 139.9, 137.1, 137.0, 131.2, 129.5 (q, *J* = 32.2 Hz), 127.3, 126.5, 125.9, 125.8 (q, *J* = 277.3 Hz), 125.7 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 271.8 Hz), 123.5, 100.8 (q, *J* = 7.4 Hz), 97.7, 50.5, 47.9, 44.4, 38.1, 35.8, 35.2 (q, *J* = 29.6 Hz), 31.5, 29.5, 26.4, 25.6, 21.6, 13.8; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.5, -64.5; **HRMS m/z (ESI)** calcd for $C_{30}H_{29}F_6O$ $(M + H)^+$ 519.2117, found 519.2123.

4. Mechanistic Experiments



TEMPO: Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), styrene (**2a**) (0.2 mmol, 1.0 equiv), phenylacetylene (**3a**) (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (0.04 mmol, 20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), TEMPO (0.3 mmol, 1.5 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by GC-MS showing that no desired product **4a** was formed and CF_3-TEMPO adduct **5** was detected.

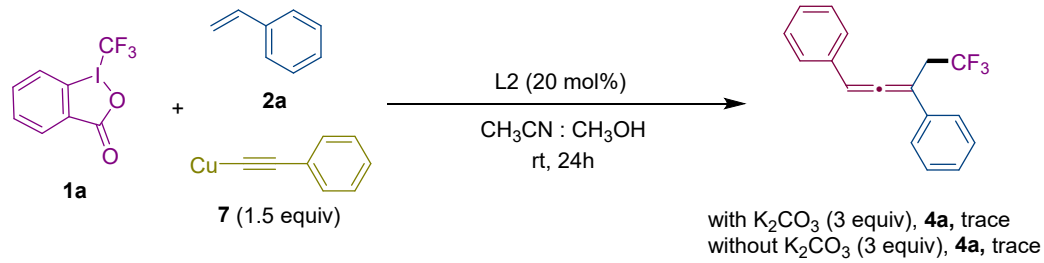
BHT: Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), styrene (**2a**) (0.2 mmol, 1.0 equiv), phenylacetylene (**3a**) (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (0.04 mmol, 20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), BHT (0.3 mmol, 1.5 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by GC-MS showing that no desired product **4a** was formed.



Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), styrene (**2a**) (0.2 mmol, 1.0 equiv), phenylacetylene (**3a**) (0.3 mmol, 1.5 equiv), copper acetylide **7** (0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (0.04 mmol,

20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by GC-MS showing that trace amount of desired product **4a** was detected.

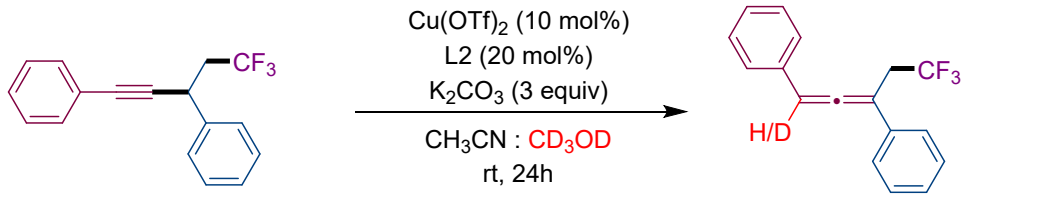
c)



With K_2CO_3: Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), styrene (**2a**) (0.2 mmol, 1.0 equiv), copper acetylide **7** (0.3 mmol, 1.5 equiv), 2,2':6',2''-terpyridine (0.04 mmol, 20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by GC-MS showing that trace amount of desired product **4a** was detected.

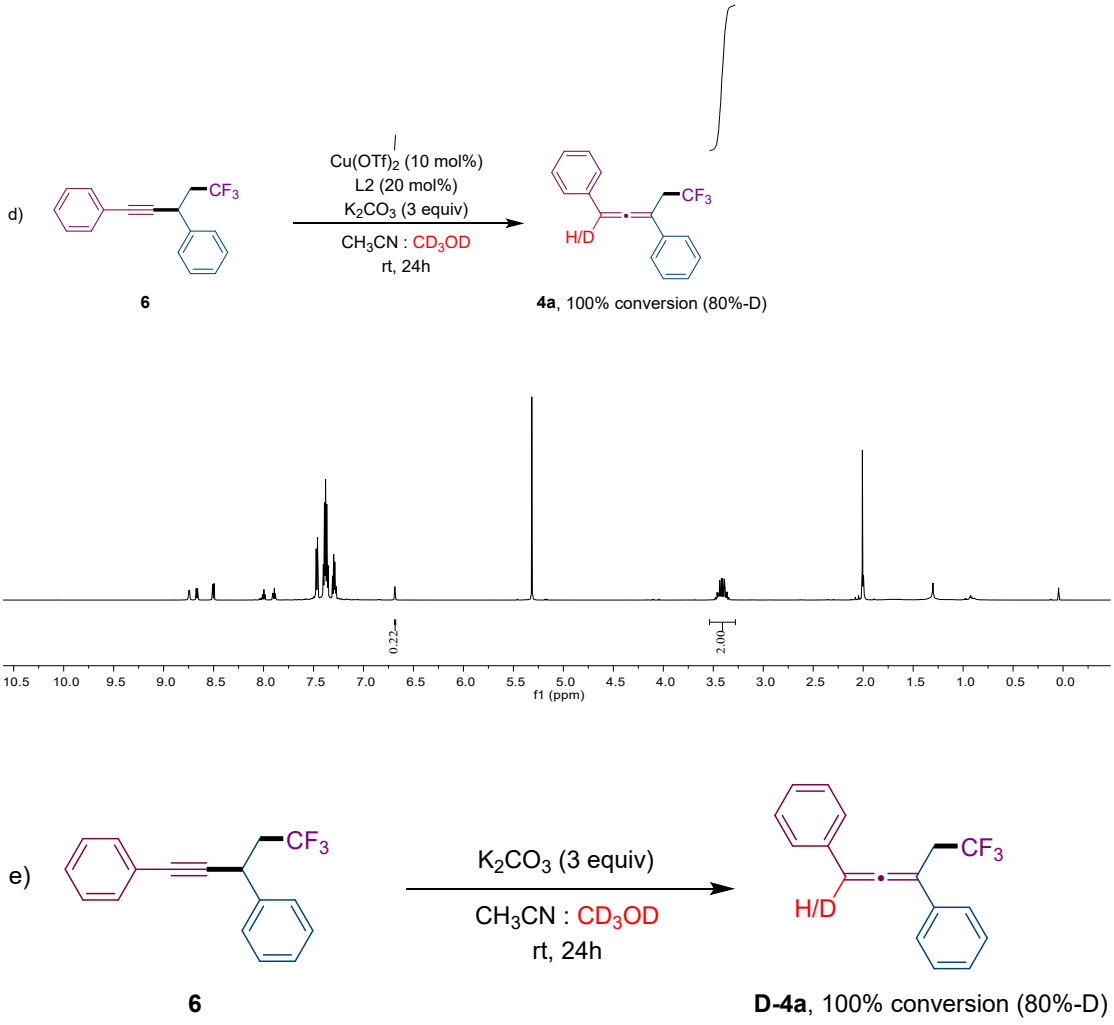
Without K_2CO_3: Flame-dried 10 mL Schlenk tube filled with argon, Togni's reagent II (**1a**) (0.3 mmol, 1.5 equiv), styrene (**2a**) (0.2 mmol, 1.0 equiv), copper acetylide **7** (0.3 mmol, 1.5 equiv), 2,2':6',2''-terpyridine (0.04 mmol, 20 mol%), absolute dry CH_3CN (0.3 mL) and absolute dry CH_3OH (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by GC-MS showing that trace amount of desired product **4a** was detected.

d)

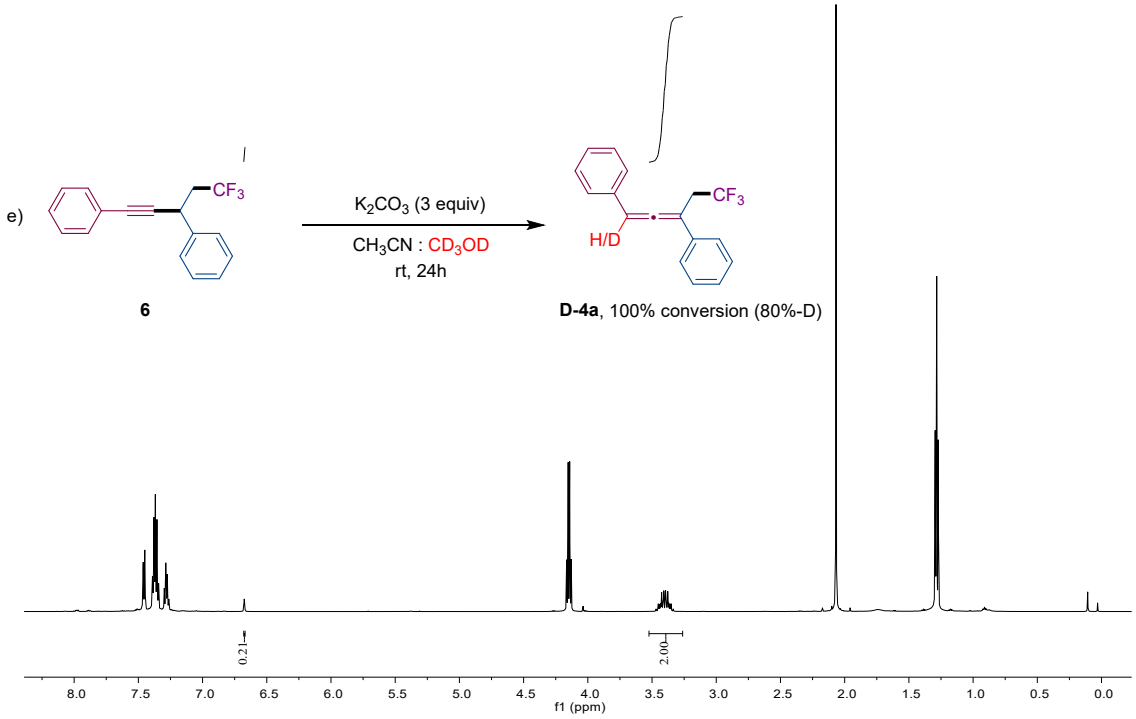


6 **4a**, 100% conversion (80%-D)

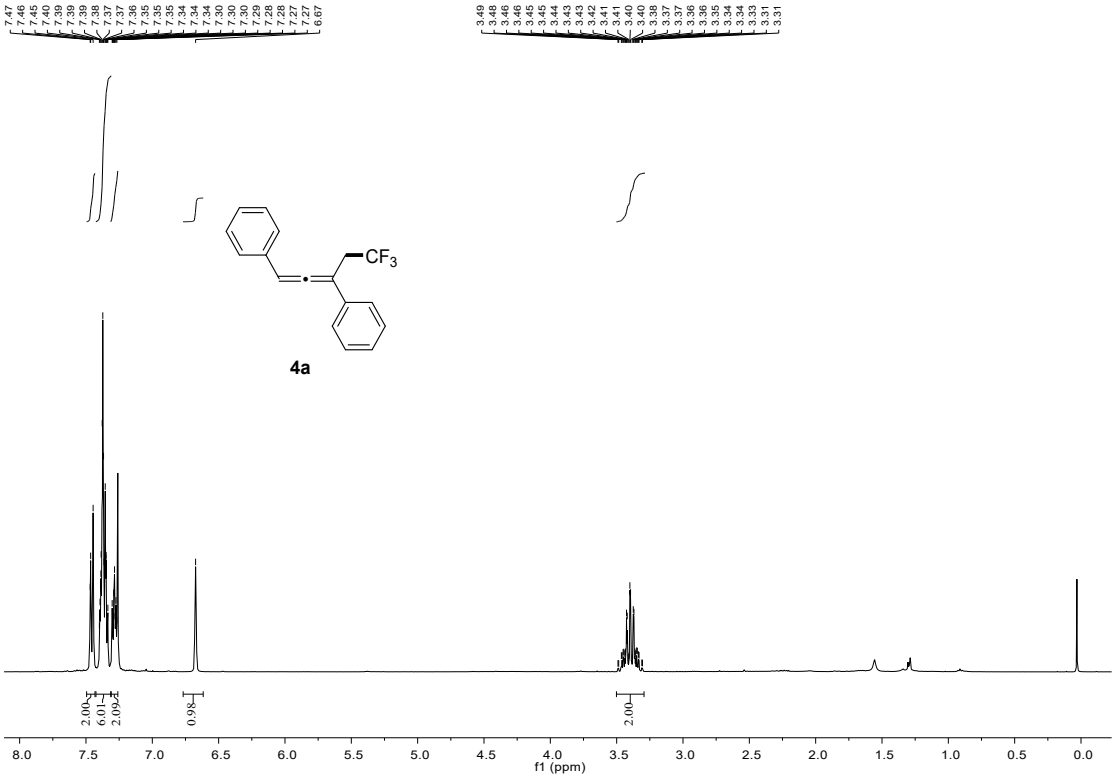
Flame-dried 10 mL Schlenk tube filled with argon, β-CF_3 alkyne **6** (0.2 mmol, 1.0 equiv), $Cu(OTf)_2$ (0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (0.04 mmol, 20 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CD_3OD (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by ^1H NMR showing that 78% deuterated **D-4a** was obtained with 100% conversion.

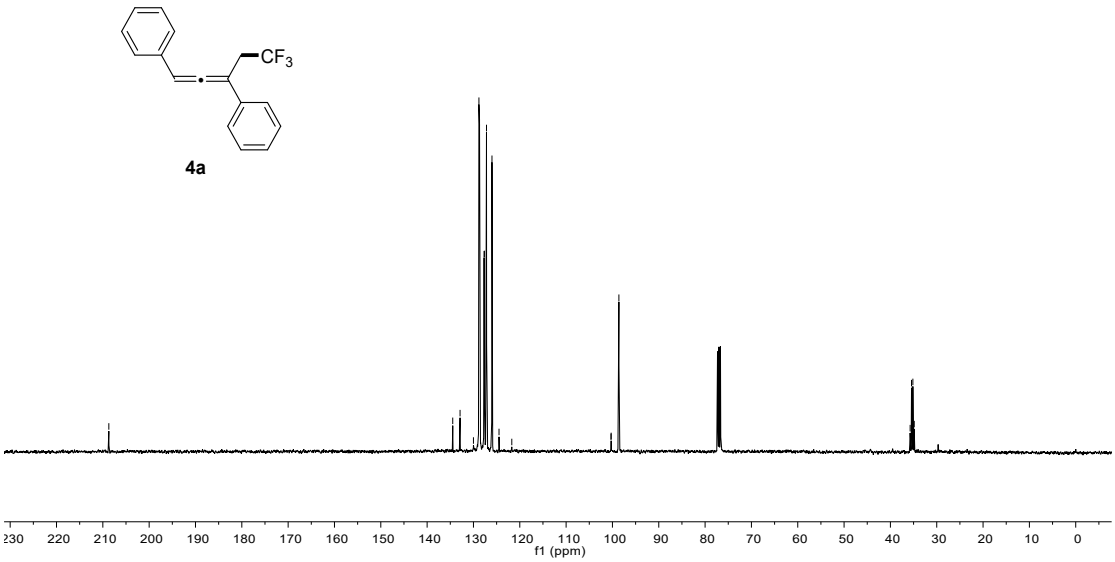


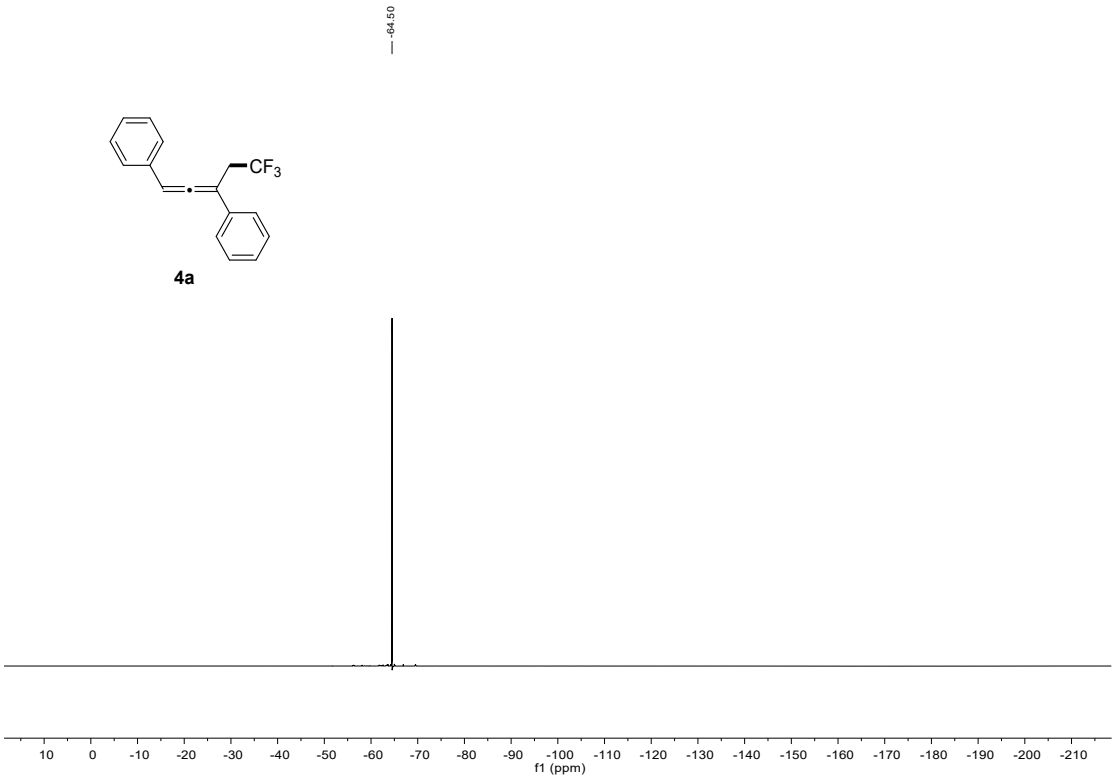
Flame-dried 10 mL Schlenk tube filled with argon, β-CF_3 alkyne **6** (0.2 mmol, 1.0 equiv), K_2CO_3 (0.6 mmol, 3.0 equiv), absolute dry CH_3CN (0.3 mL) and absolute dry CD_3OD (0.7 mL) were added under N_2. The formed mixture was stirred at room temperature under N_2 for 24 h. The reaction mixture was analyzed by ^1H NMR showing that 79% deuterated **D-4a** was obtained with 100% conversion.


e)
CF3
6
K2CO3 (3 equiv)
CH3CN : CD3OD
rt, 24h
H/D
CF3
D-4a, 100% conversion (80%-D)
0.21
2.00
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)

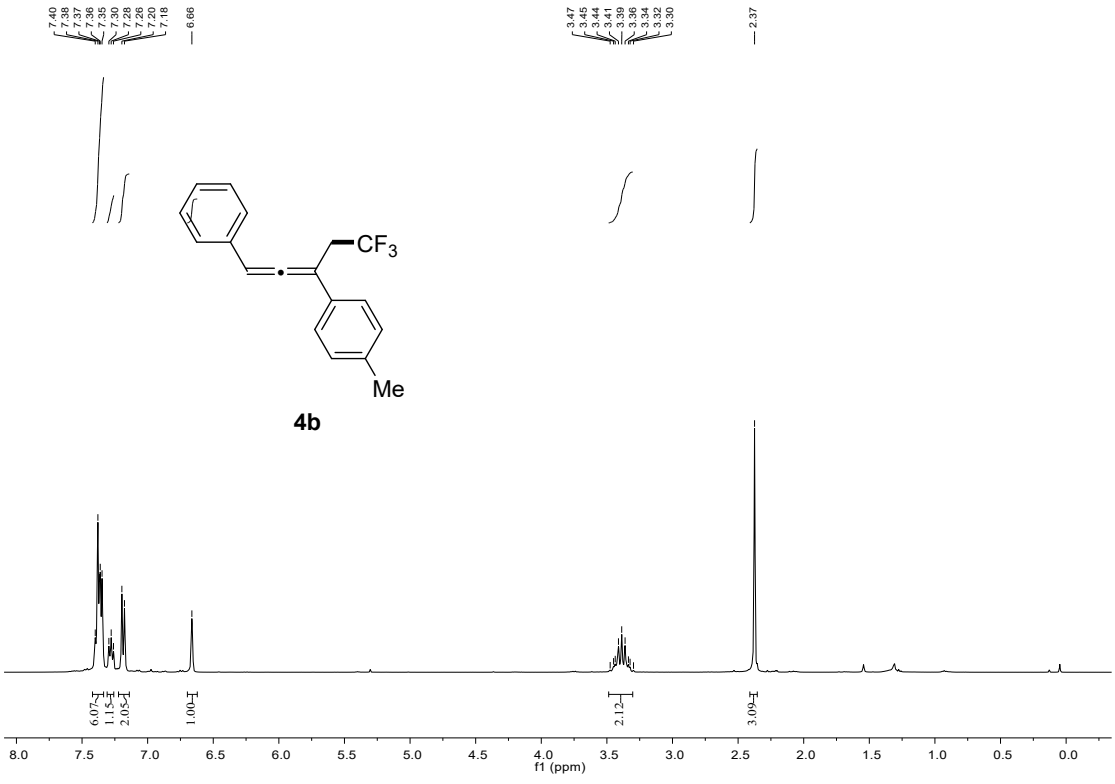
5. Copies of NMR Spectra



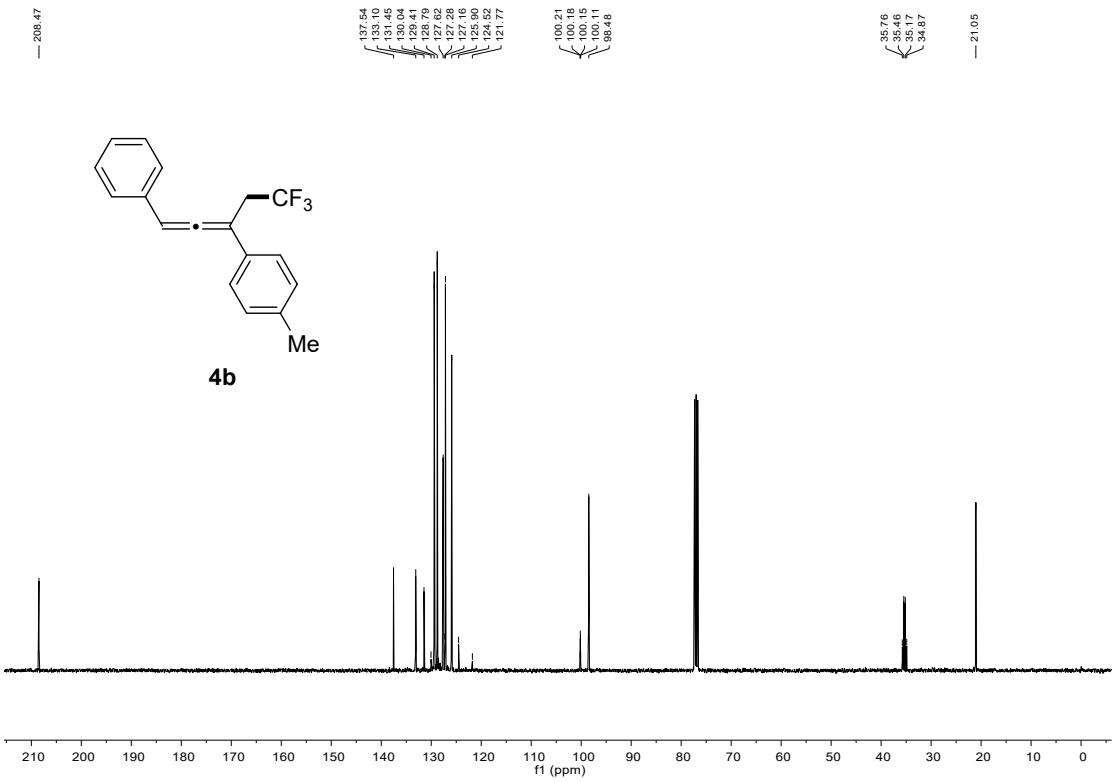


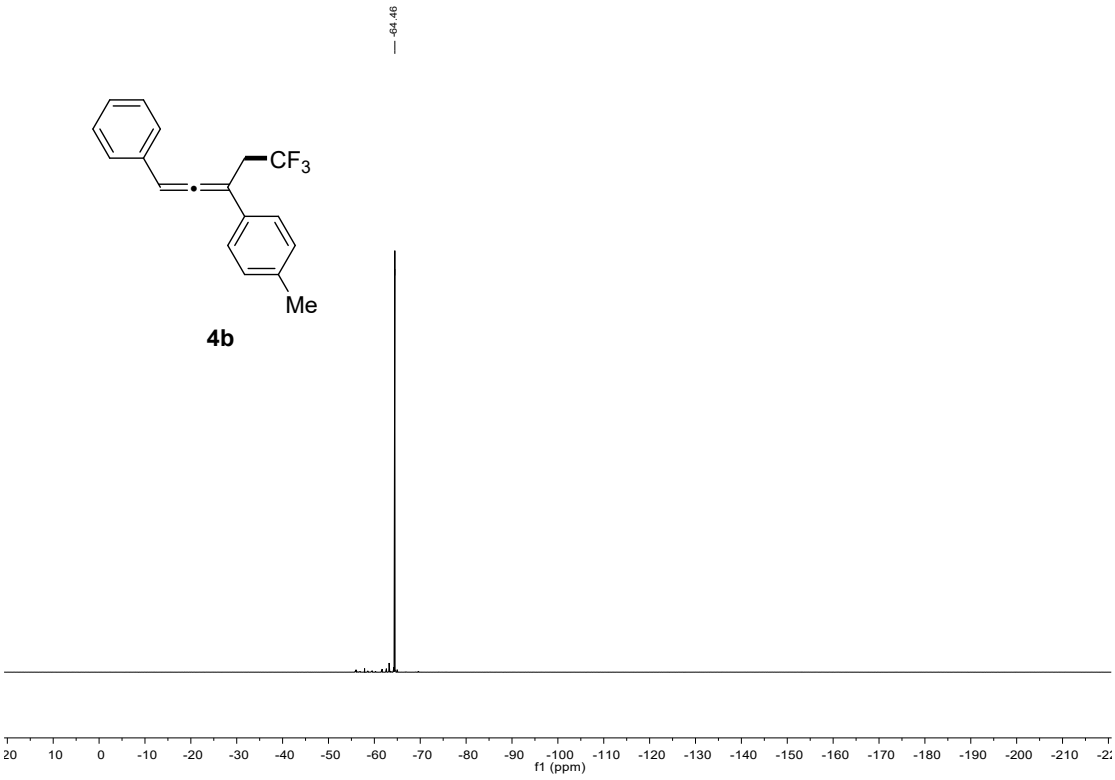

-64.50
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

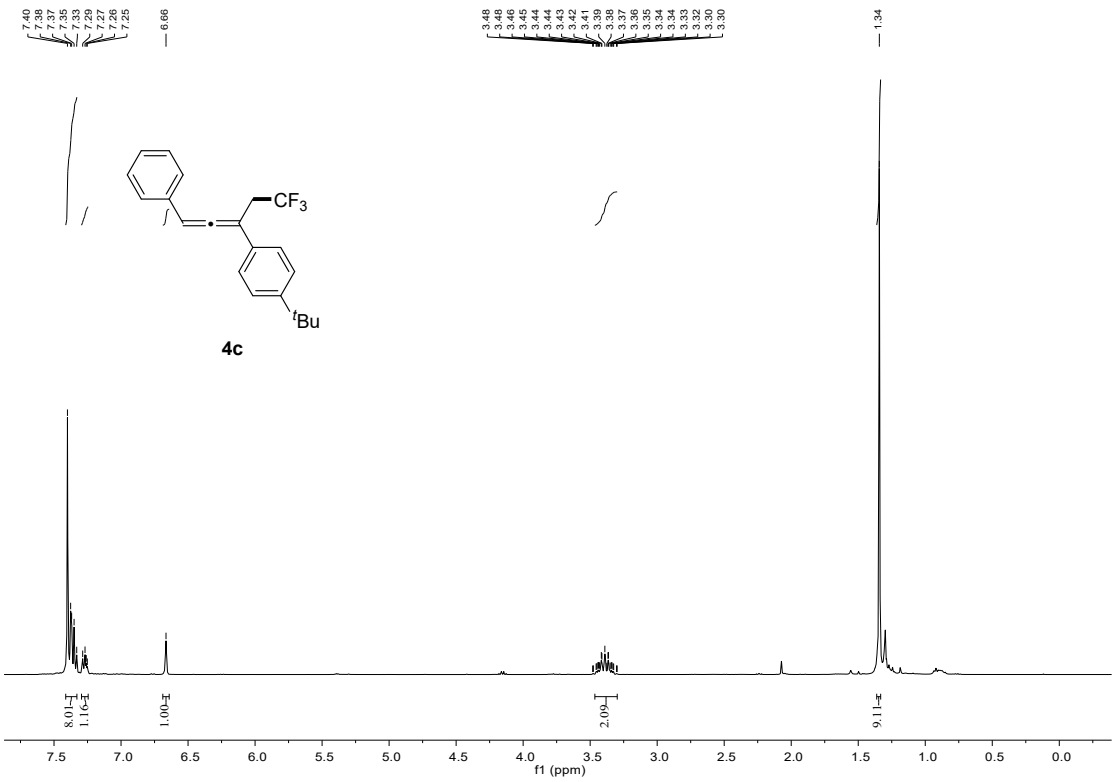
4a

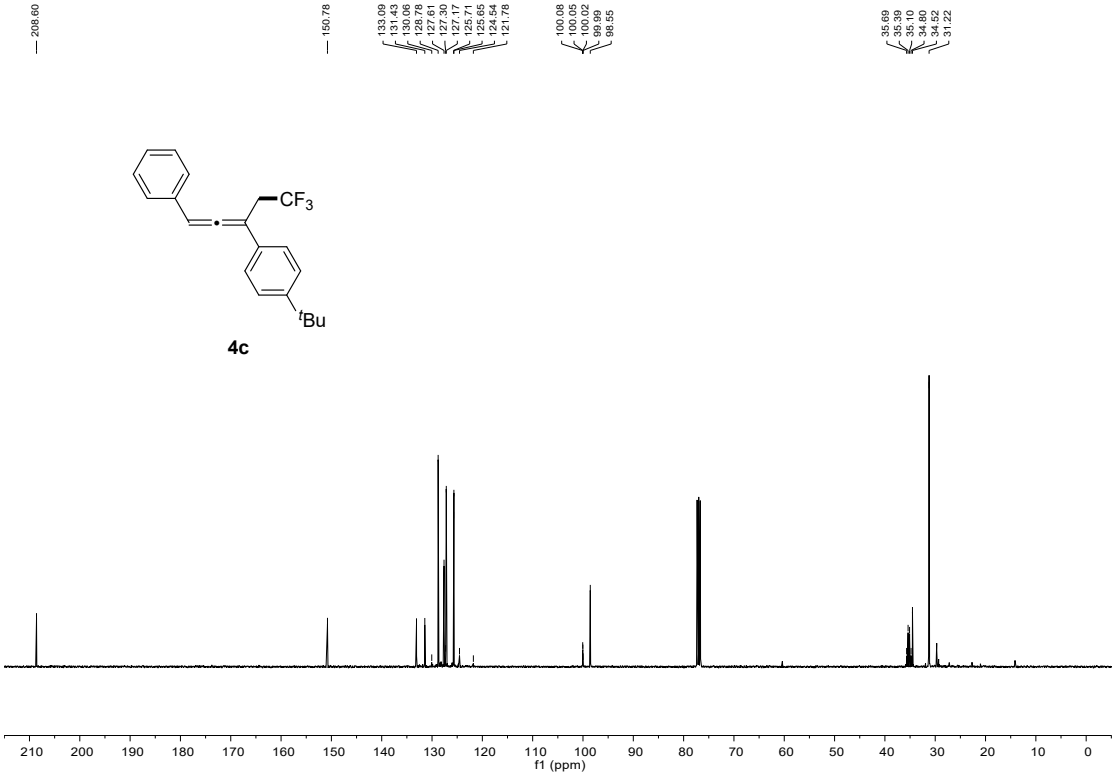

7.40
7.38
7.37
7.36
7.35
7.30
7.28
7.26
7.20
7.18
6.66
3.47
3.45
3.44
3.41
3.39
3.36
3.34
3.32
3.30
2.37
CF3
Me
6.07
1.15
2.05
1.00
2.12
3.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

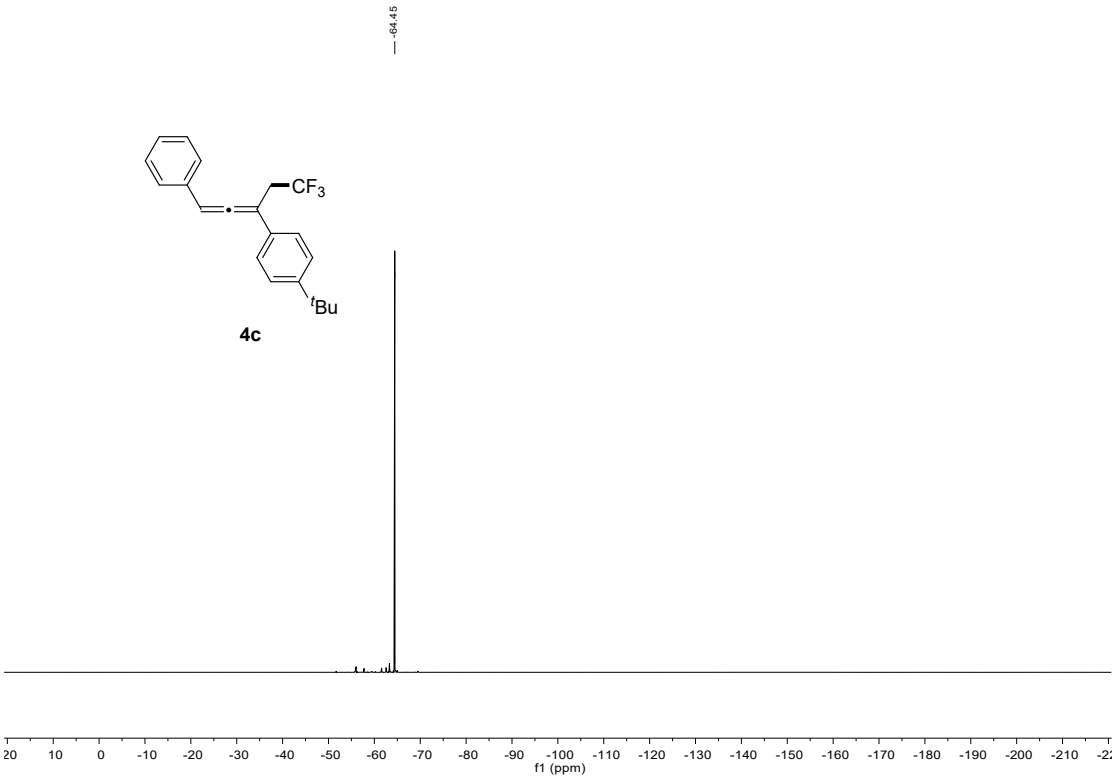
4b

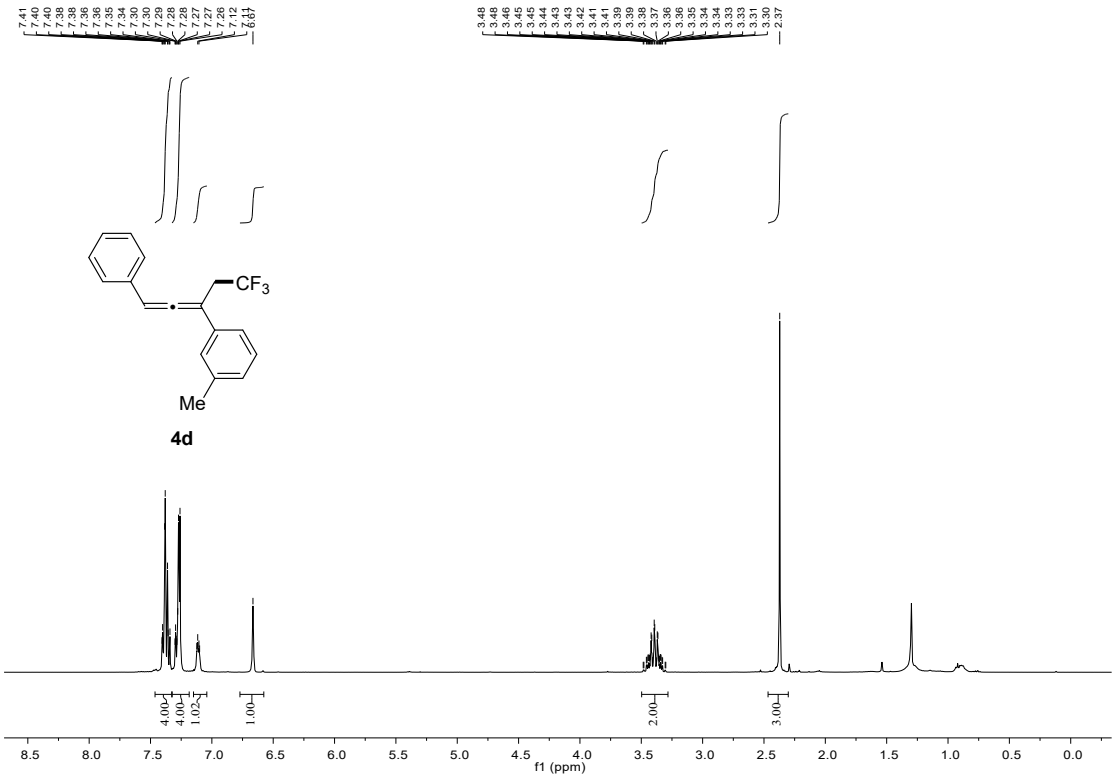

208.47
137.54
133.10
131.45
130.04
129.41
128.79
127.62
127.28
127.16
125.90
124.52
121.77
100.21
100.18
100.15
100.11
98.48
35.76
35.46
35.17
34.87
21.05
CF3
Me
4b
f1 (ppm)

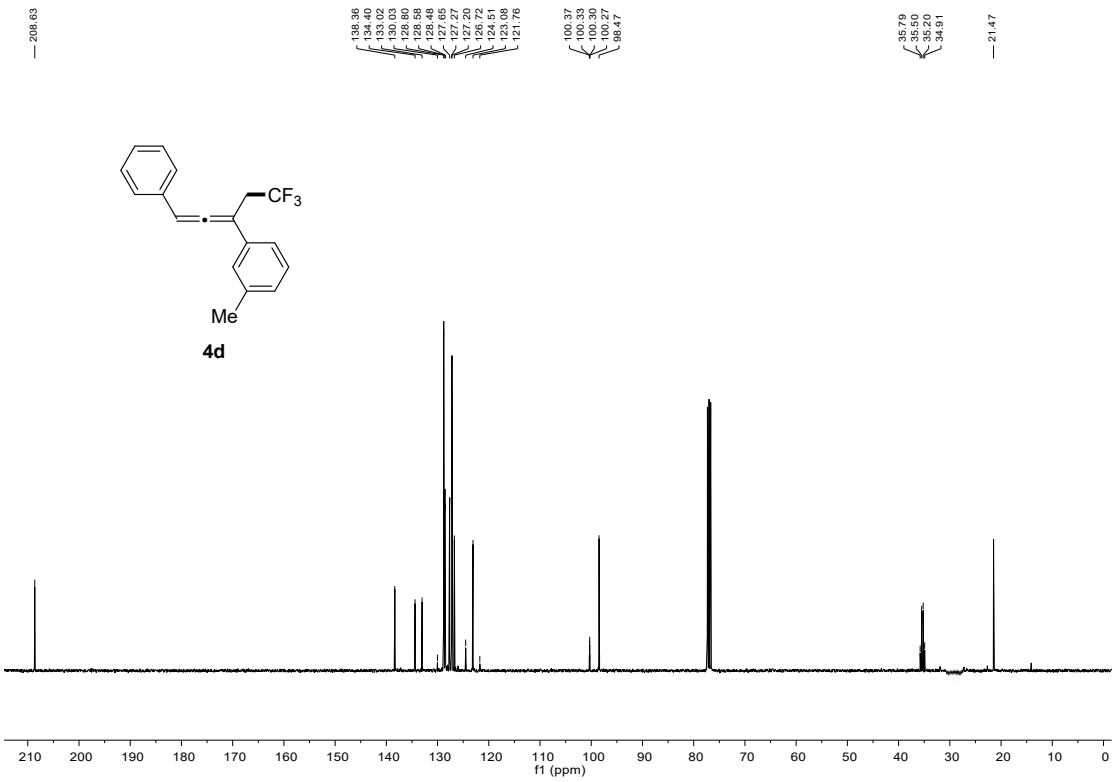

64.46
CF3
Me
4b
f1 (ppm)


7.40
7.38
7.37
7.35
7.33
7.29
7.27
7.26
7.25
6.66
3.48
3.48
3.46
3.45
3.44
3.44
3.43
3.42
3.41
3.39
3.38
3.37
3.36
3.35
3.34
3.34
3.33
3.32
3.30
3.30
1.34
CF3
tBu
4c
8.01
1.16
1.00
2.09
9.11
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)


208.60
150.78
133.09
131.43
130.06
128.78
127.61
127.30
127.17
125.71
125.65
124.54
121.78
100.08
100.05
100.02
99.99
98.55
35.69
35.59
35.10
34.80
34.52
31.22
CF3
tBu
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-64.45
CF3
tBu
4c
20 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)


7.41 7.40 7.40 7.38 7.38 7.36 7.36 7.35 7.34 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 7.12 6.61
3.48 3.48 3.46 3.46 3.45 3.45 3.44 3.43 3.43 3.42 3.41 3.41 3.39 3.39 3.38 3.37 3.36 3.36 3.35 3.34 3.34 3.33 3.33 3.31 3.30 2.37
CF3
Me
4d
4.00 4.00 1.02 1.00 2.00 3.00
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)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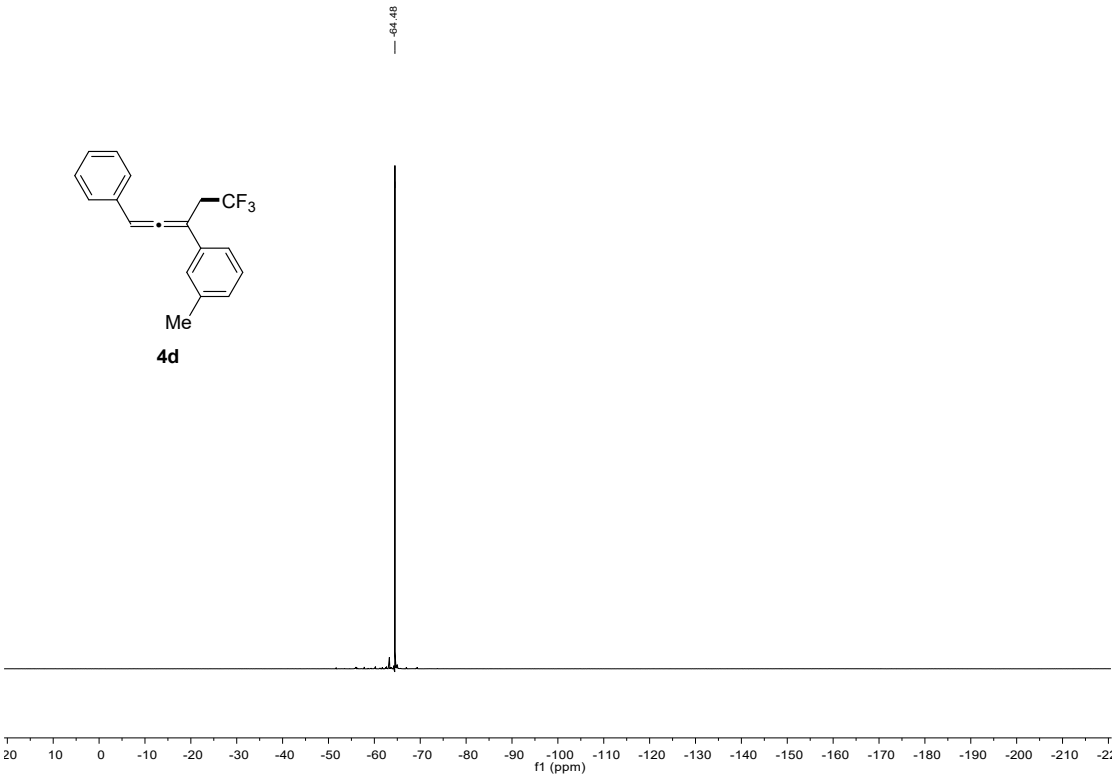
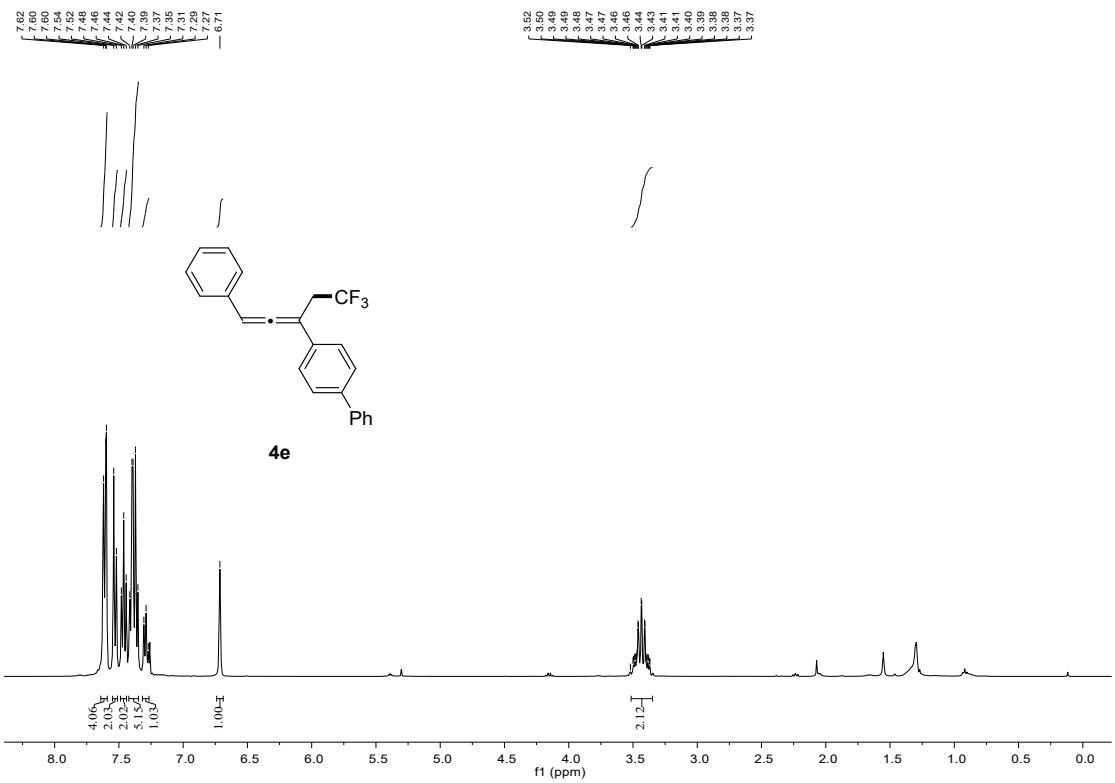
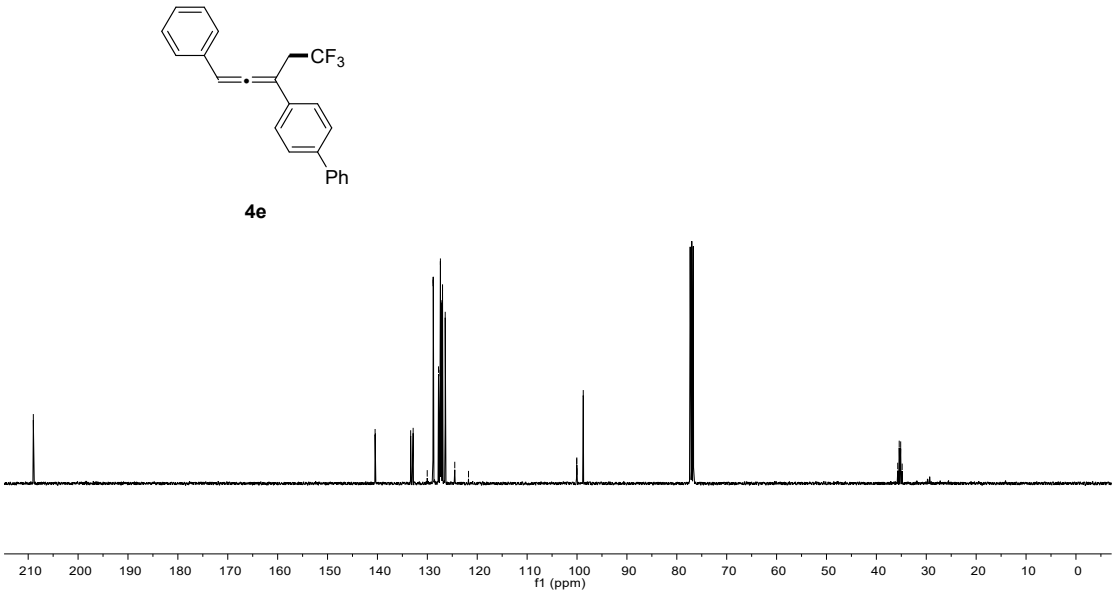
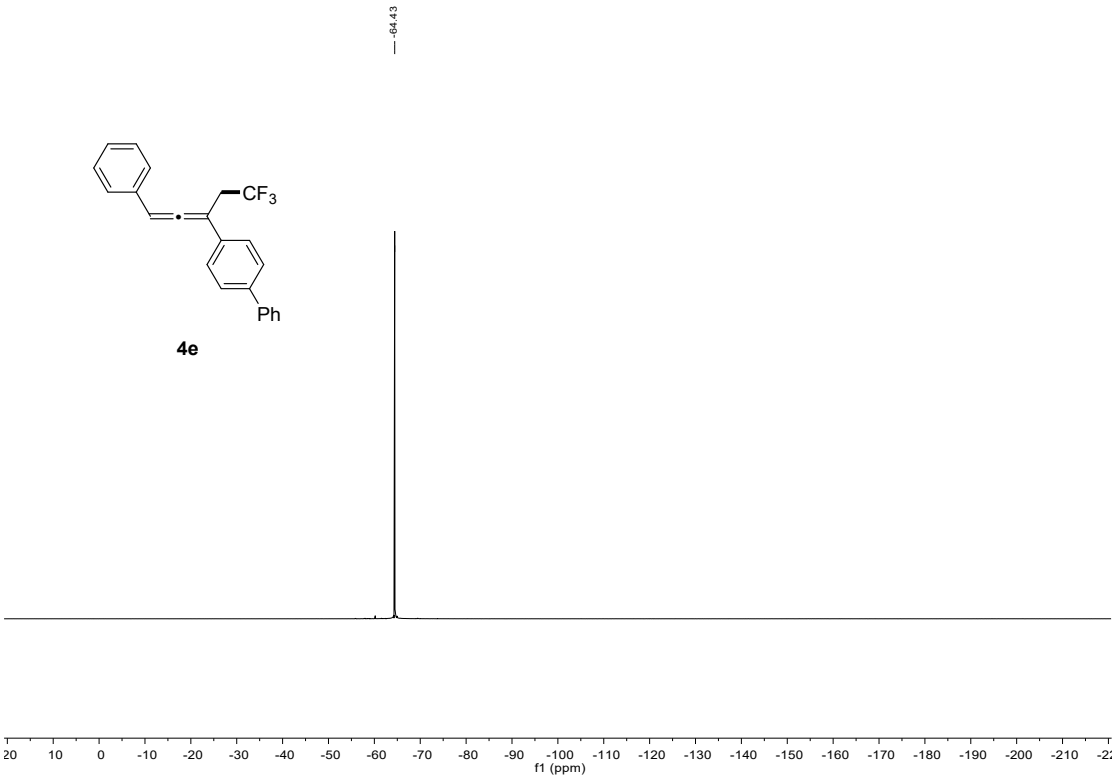
138.36
134.40
133.02
130.05
128.80
128.58
128.48
127.65
127.27
127.20
126.72
124.51
123.08
121.76
100.37
100.33
100.30
100.27
98.47
35.79
35.50
35.20
34.91
21.47
CF3
Me
4d
f1 (ppm)

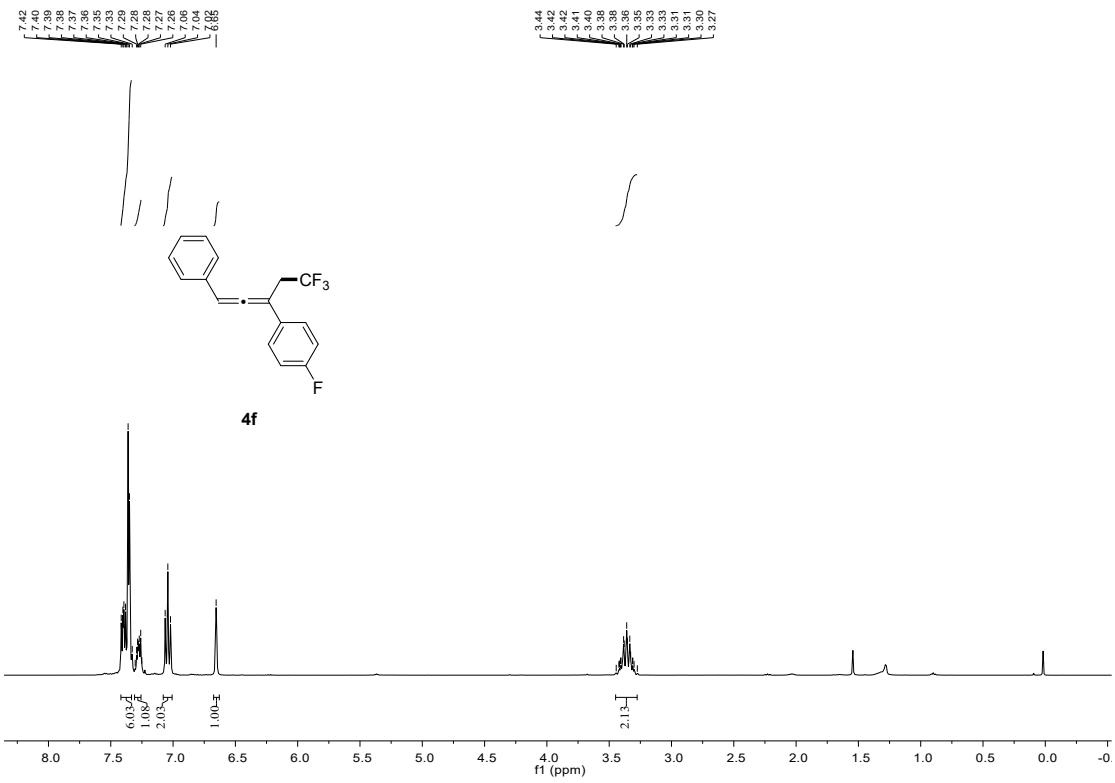

64.48
CF3
Me
4d
f1 (ppm)


CF3
Ph
4e
f1 (ppm)


CF3
Ph
4e
f1 (ppm)


-64.43
CF3
Ph
f1 (ppm)

4e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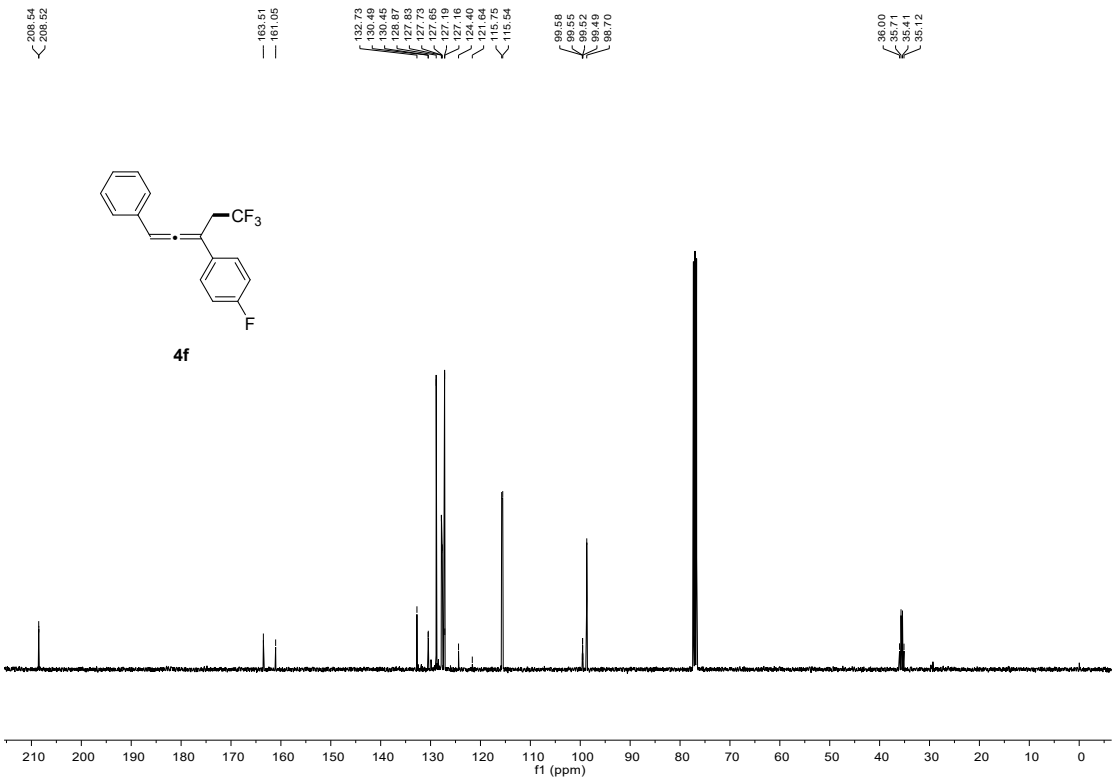
7.27
7.26
7.06
7.04
7.02
6.85
3.44
3.42
3.42
3.41
3.40
3.38
3.38
3.36
3.35
3.33
3.33
3.31
3.31
3.30
3.27
CF3
F
6.03
1.09
2.03
1.00
2.13
f1 (ppm)

4f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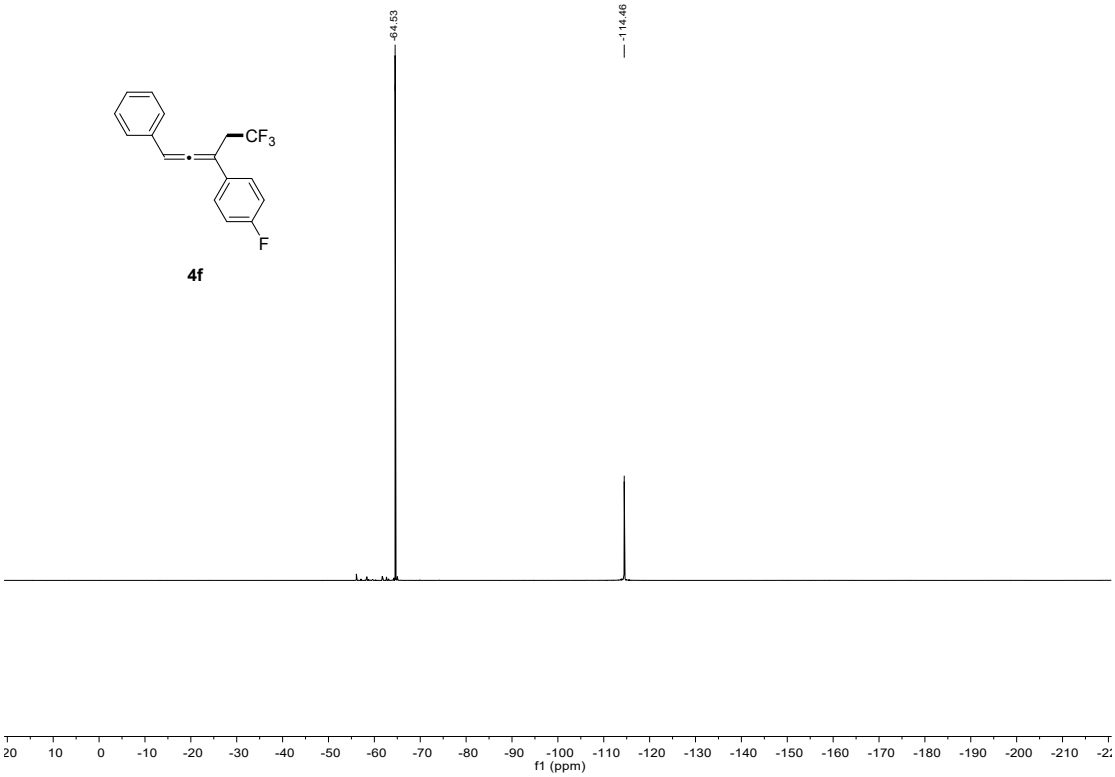
130.49
130.45
128.87
127.83
127.73
127.65
127.19
127.16
124.40
121.64
115.75
115.54
99.58
99.55
99.52
99.49
98.70
36.00
35.71
35.41
35.12
CF3
F
4f
f1 (ppm)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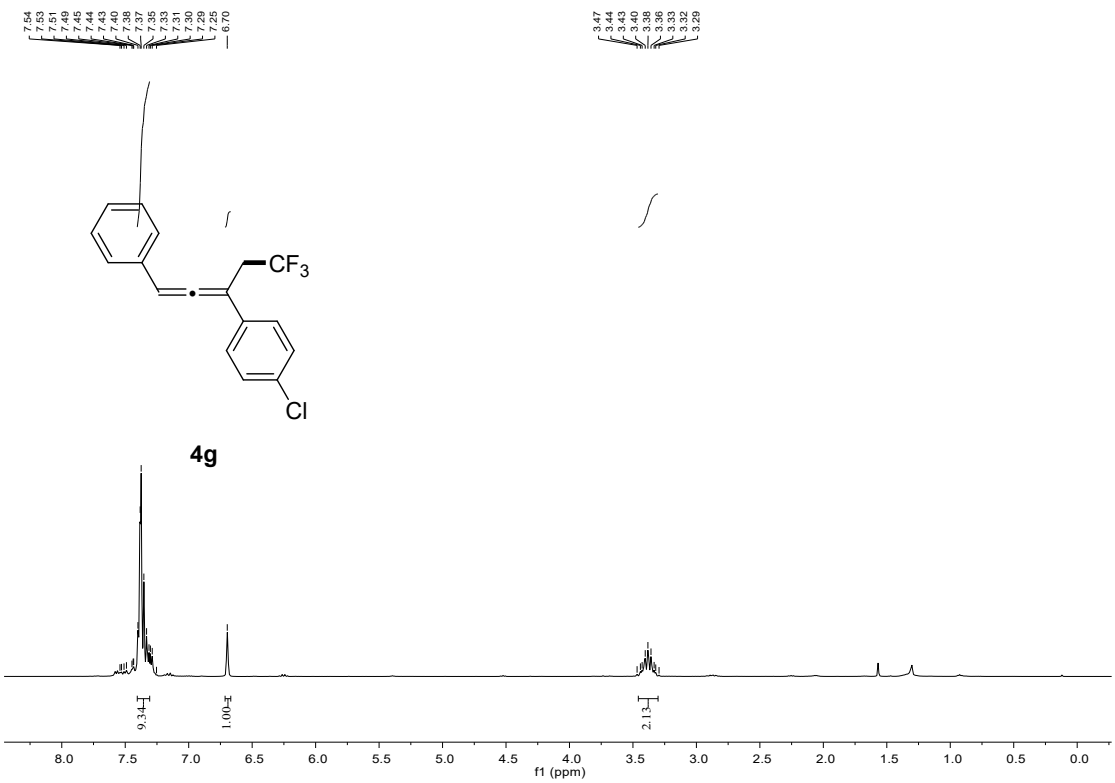
-114.46
CF3
F
4f
f1 (ppm)


7.54
7.53
7.51
7.49
7.45
7.44
7.43
7.40
7.38
7.37
7.35
7.33
7.31
7.30
7.29
7.25
6.70
3.47
3.44
3.43
3.40
3.38
3.36
3.33
3.32
3.29
CF3
Cl
4g
9.34
1.00
2.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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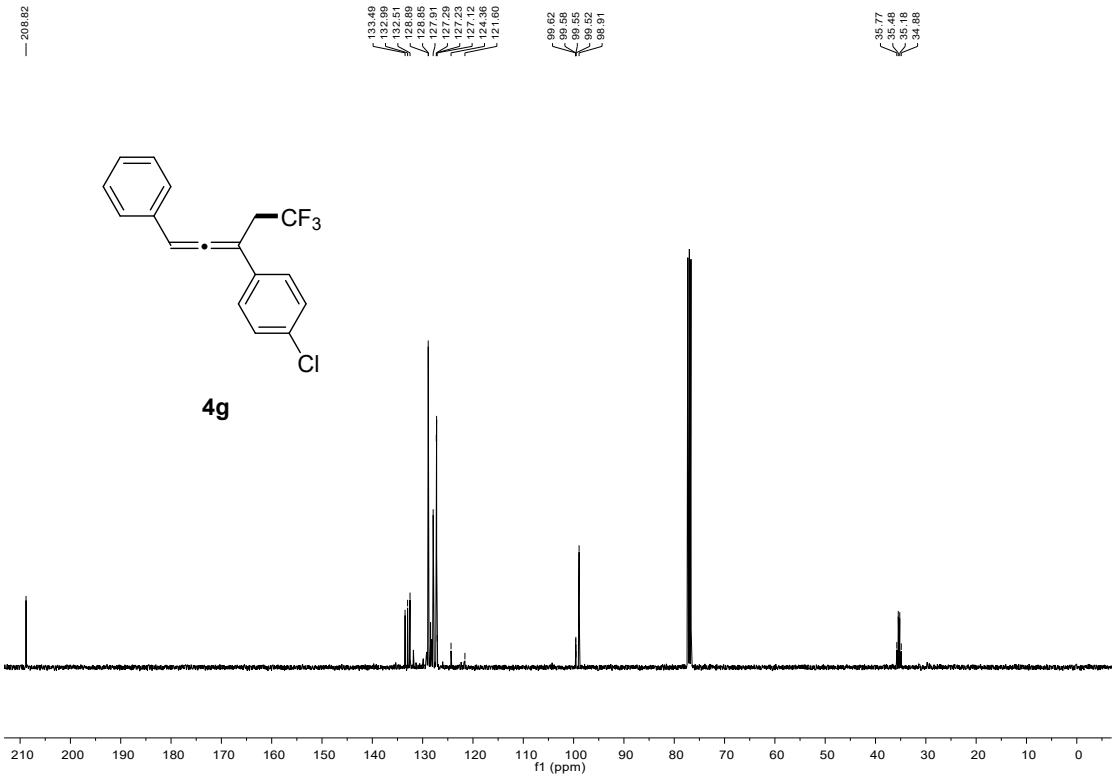
0.0
f1 (ppm)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128.85
127.91
127.29
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127.12
124.36
121.60
99.62
99.58
99.55
99.52
98.91
35.77
35.48
35.18
34.88
CF3
Cl
4g
210
200
190
180
170
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130
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110
100
90
80
70
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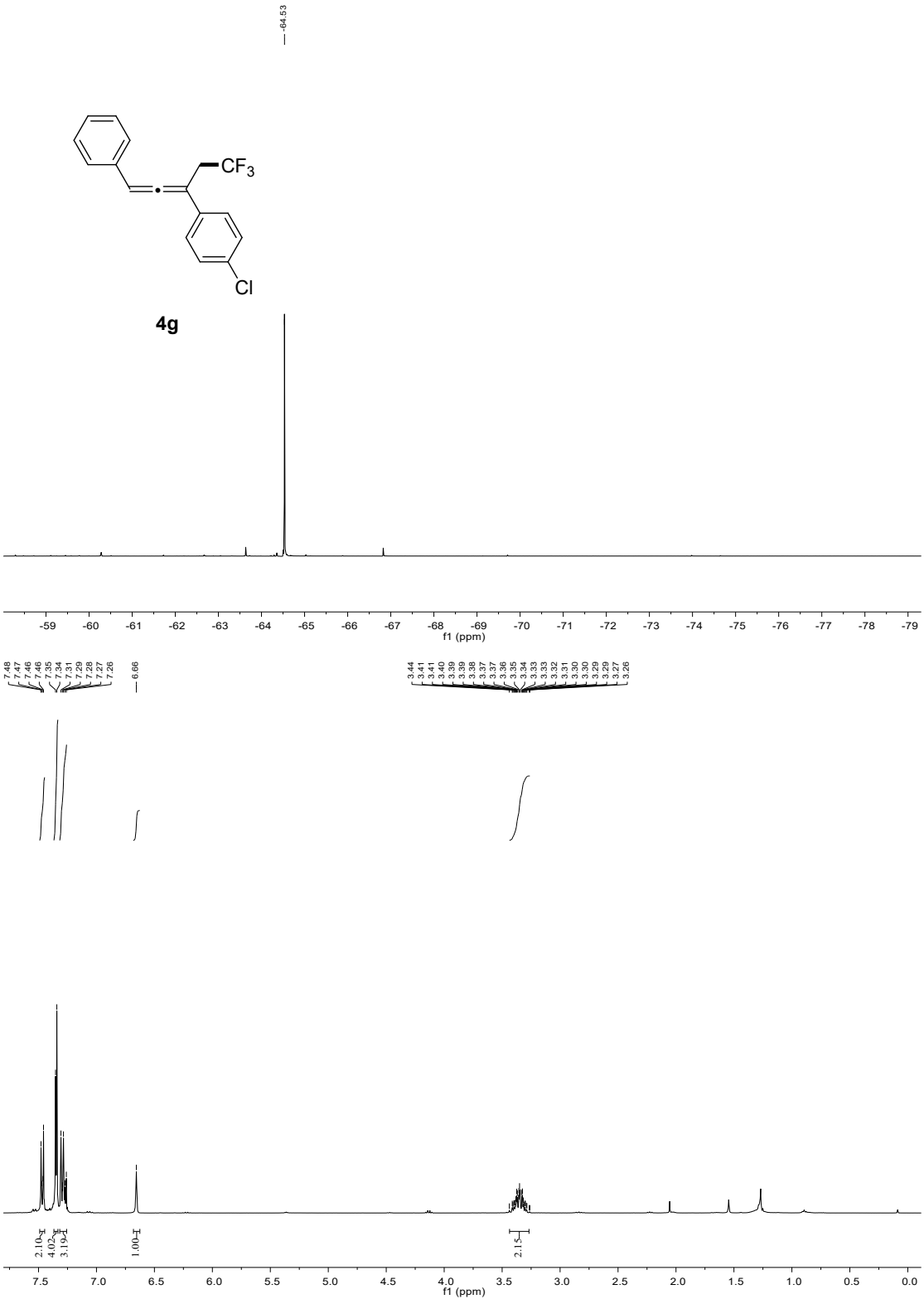
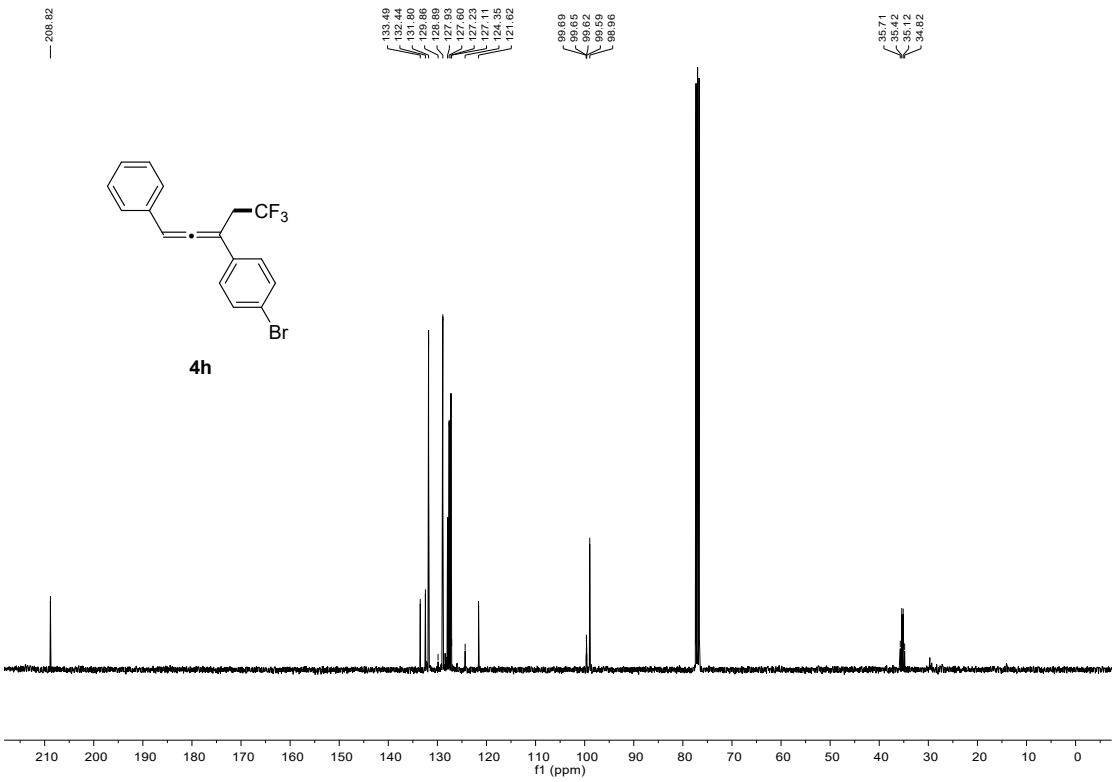
50
40
30
20
10
0
f1 (ppm)


-64.53
CF3
Cl
4g
-59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79
f1 (ppm)
7.48 7.47 7.46 7.46 7.35 7.34 7.31 7.29 7.28 7.27 7.26
6.66
3.44 3.41 3.41 3.40 3.39 3.39 3.38 3.37 3.37 3.36 3.35 3.34 3.33 3.32 3.31 3.30 3.30 3.29 3.29 3.27 3.26
2.10
4.02
3.19
1.00
2.15
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)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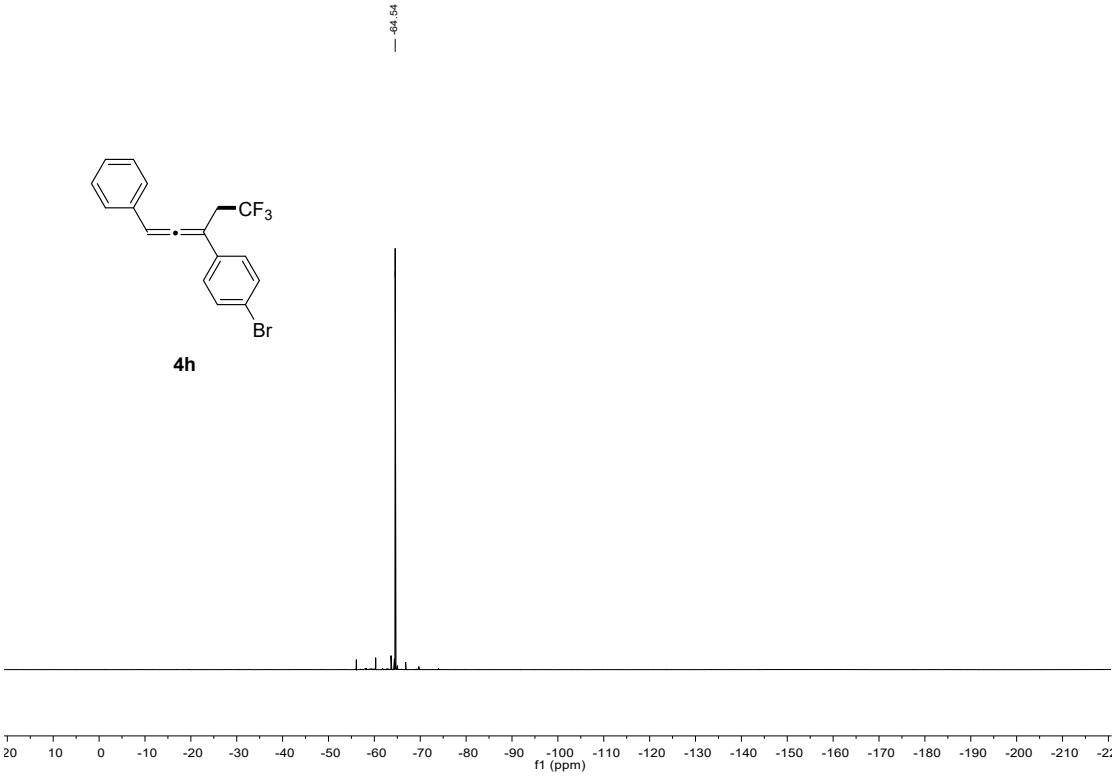
131.80
129.86
129.69
127.95
127.60
127.23
127.11
124.35
121.62
99.69
99.65
99.62
99.59
98.96
35.71
35.42
35.12
34.82
CF3
Br
4h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


64.54
CF3
Br
4h
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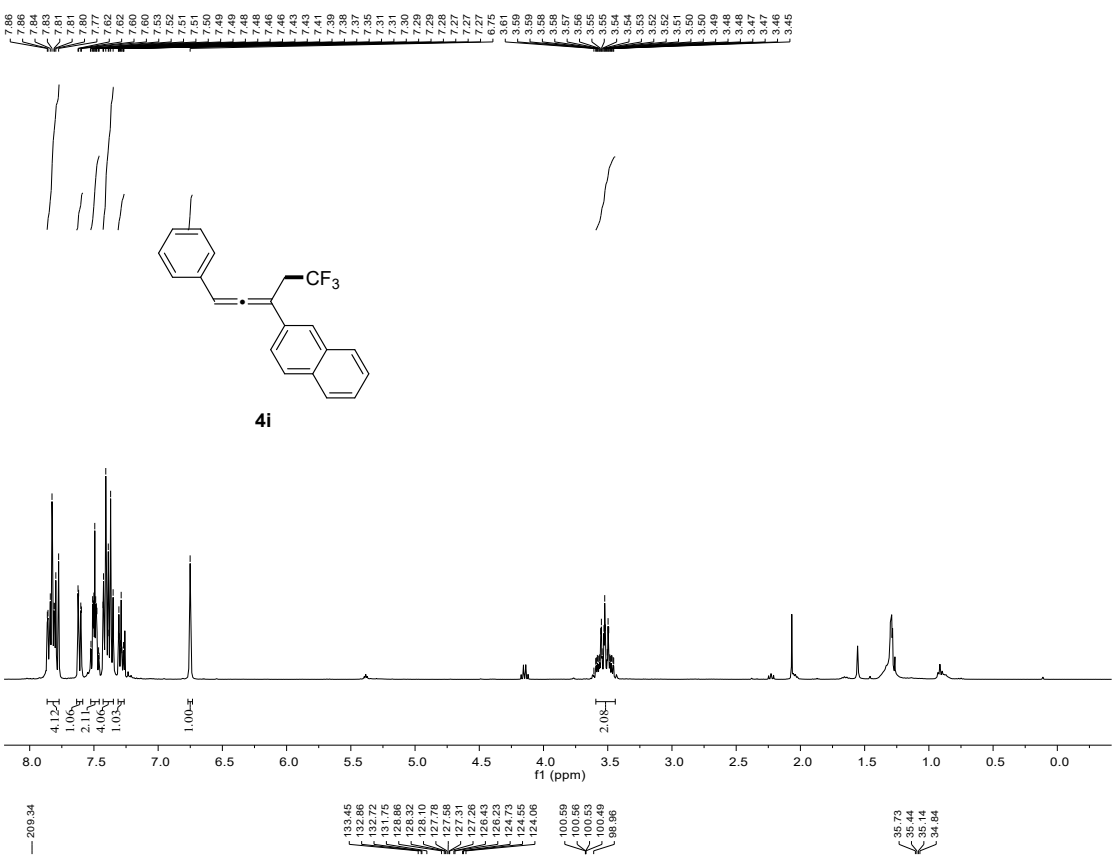
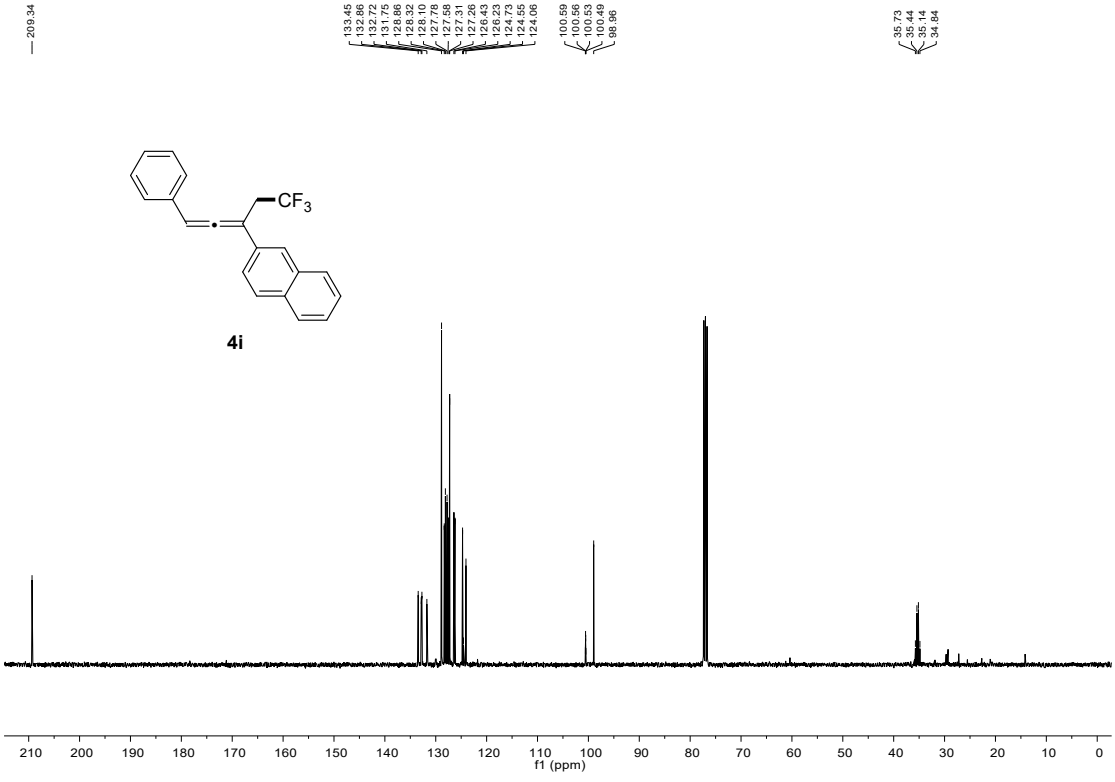
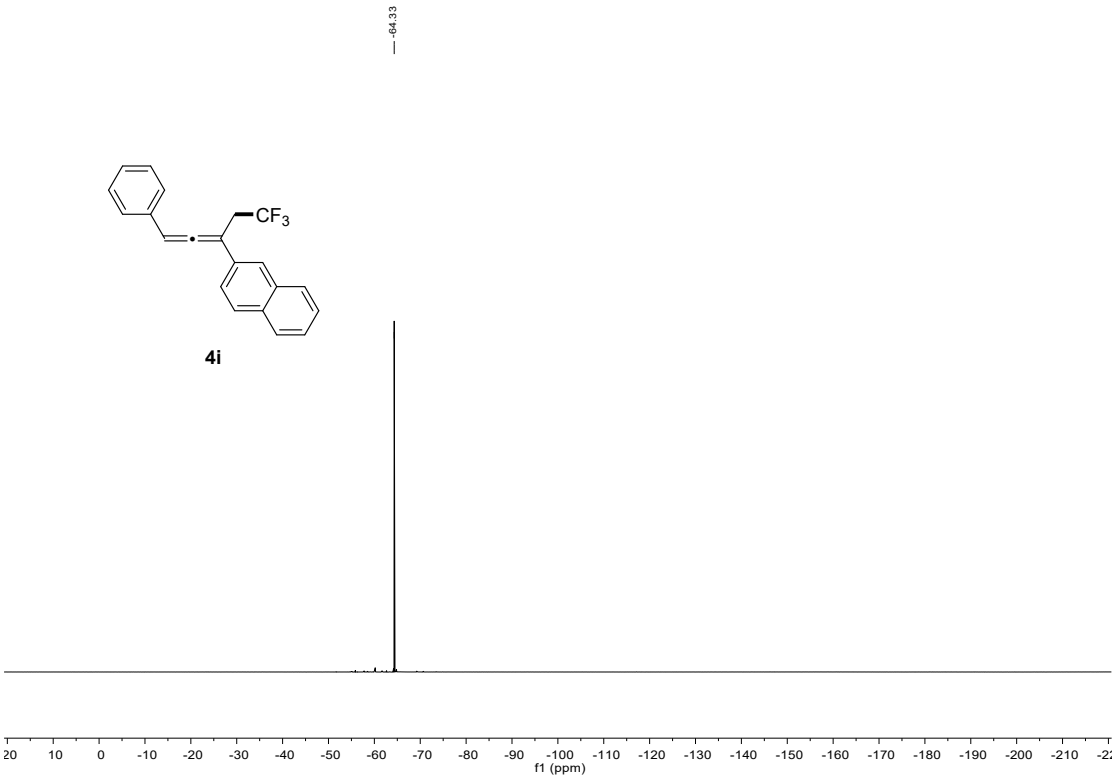
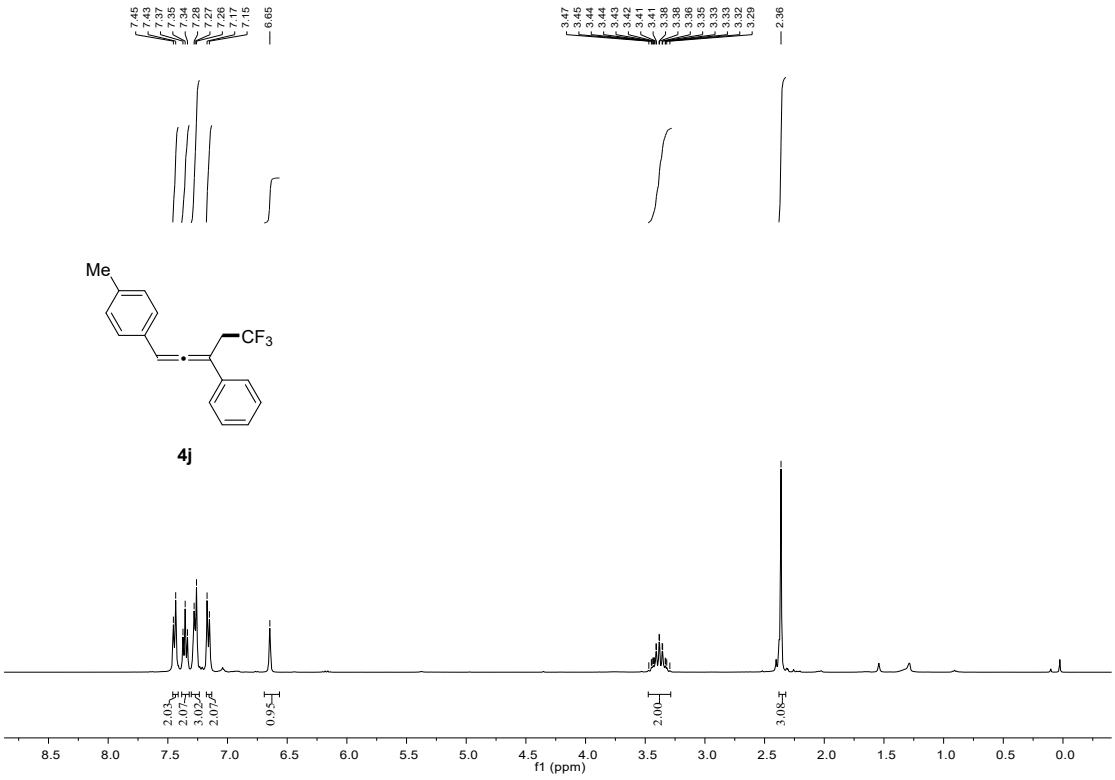
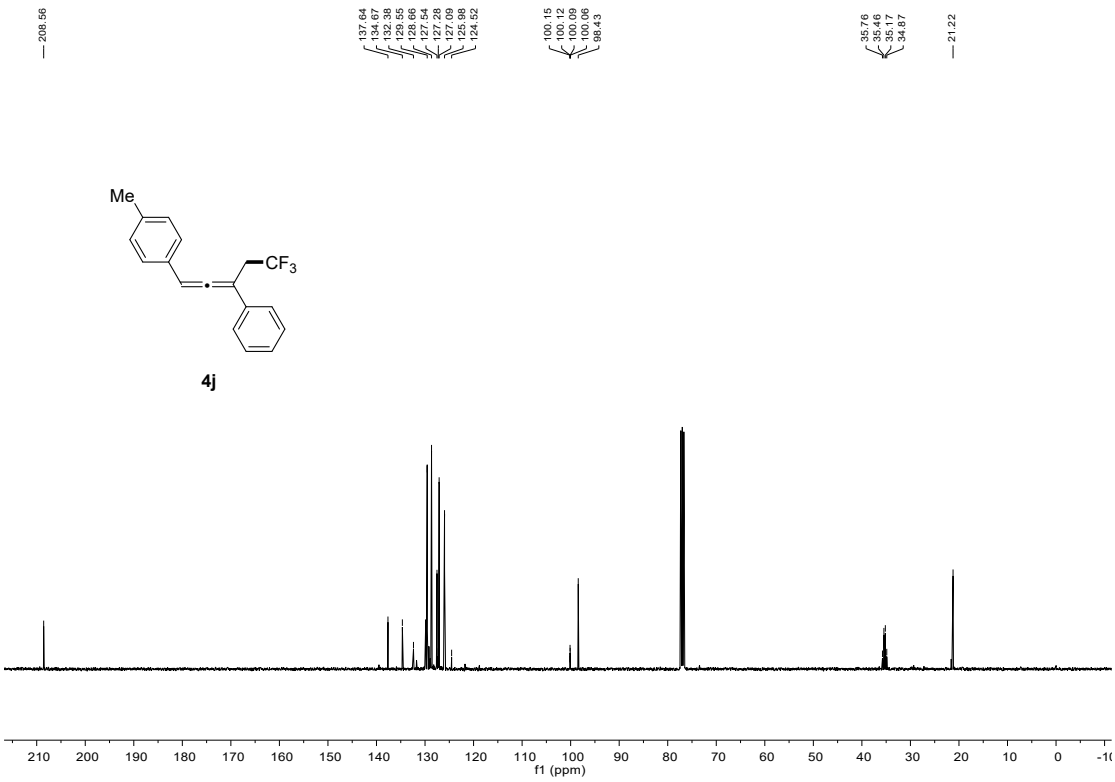
f1 (ppm)


CF3
4i
4.12
1.06
2.11
4.06
1.03
1.00
2.08
f1 (ppm)


CF3
4i
f1 (ppm)


-64.33
CF3
4i
f1 (ppm)


7.45
7.43
7.37
7.35
7.34
7.28
7.27
7.26
7.17
7.15
6.65
3.47
3.45
3.44
3.44
3.43
3.42
3.41
3.41
3.38
3.38
3.36
3.35
3.33
3.32
3.29
2.36
Me
CF3
4j
2.03
2.07
3.02
2.07
0.95
2.00
3.08
f1 (ppm)


208.56
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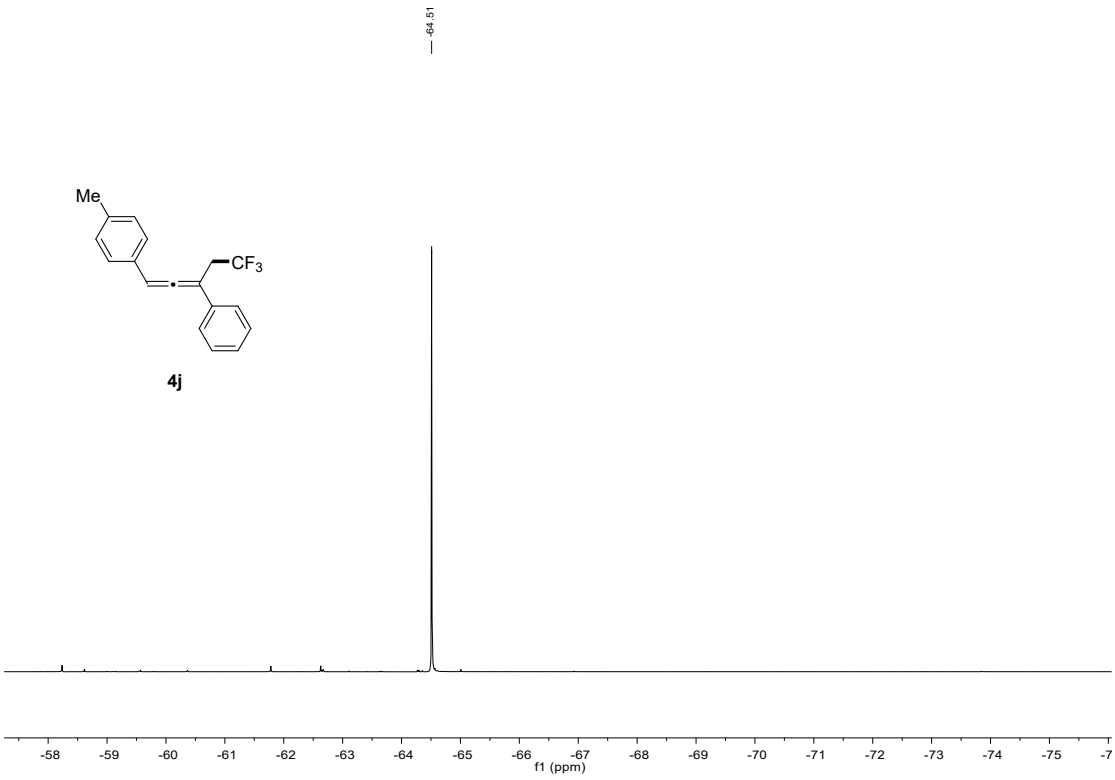
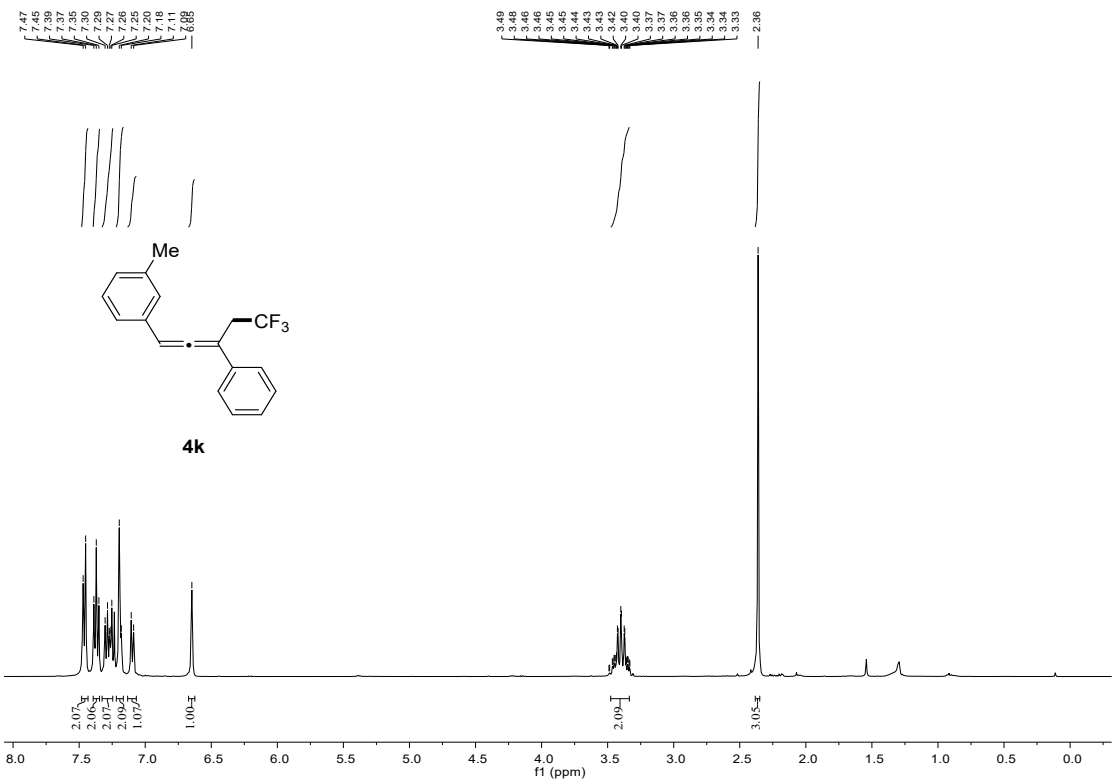
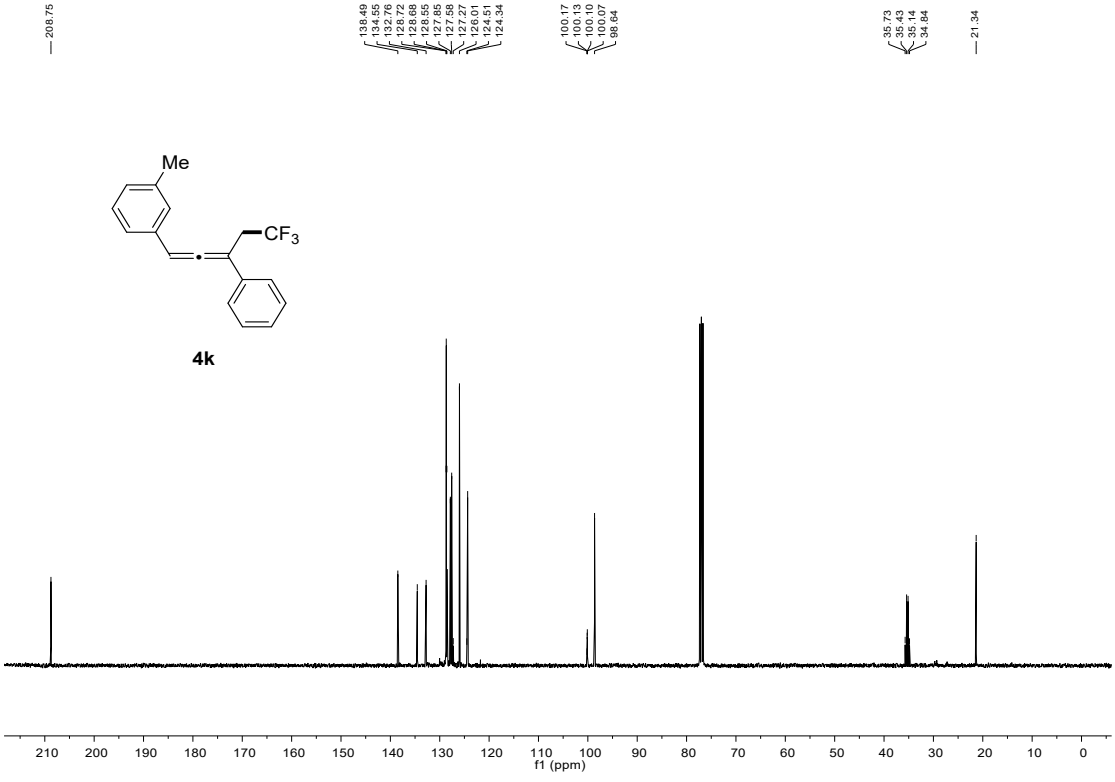
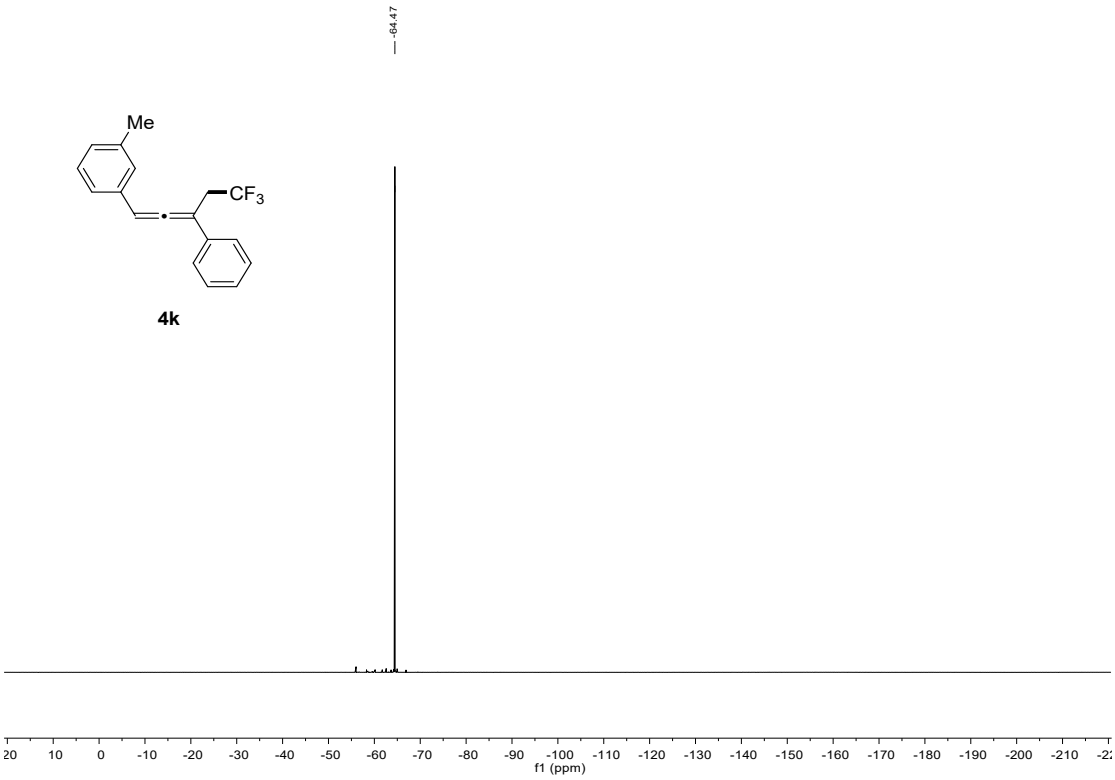
132.38
129.55
128.66
127.54
127.28
127.09
125.98
124.52
100.15
100.12
100.09
100.06
98.43
35.76
35.46
35.17
34.87
21.22
Me
CF3
4j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-64.51
Me
CF3
4j
-58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75
f1 (ppm)


Me
CF3
4k
f1 (ppm)


Me
CF3
4k
f1 (ppm)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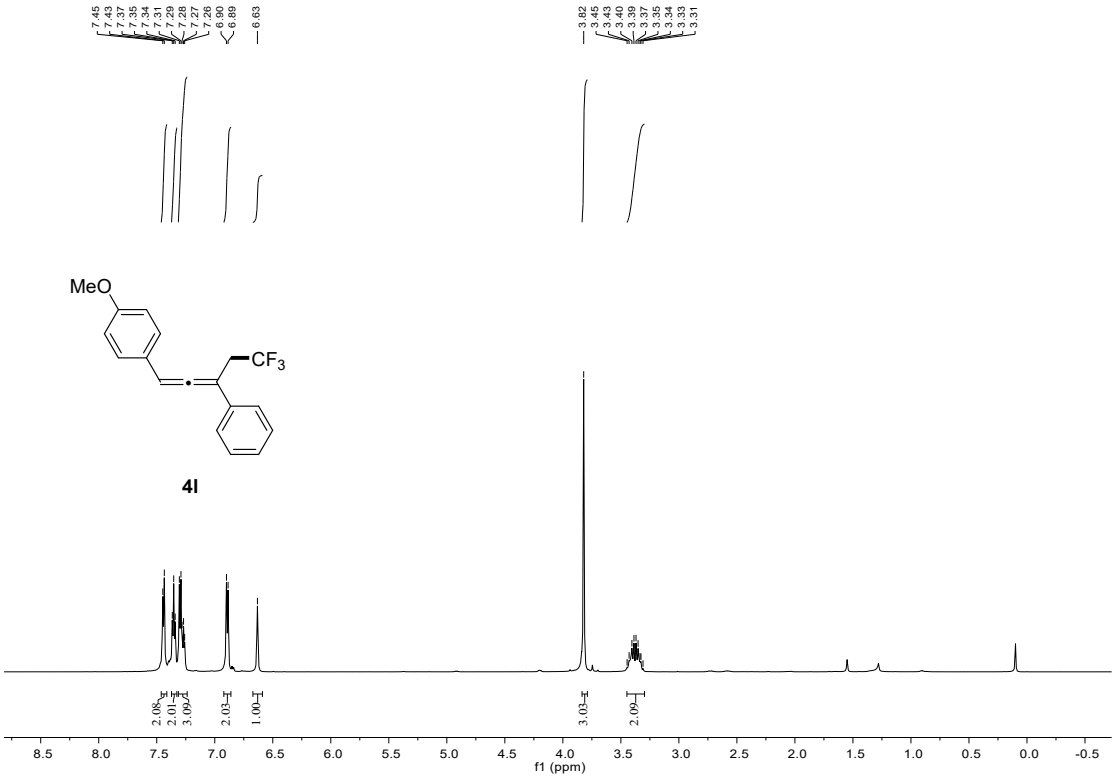
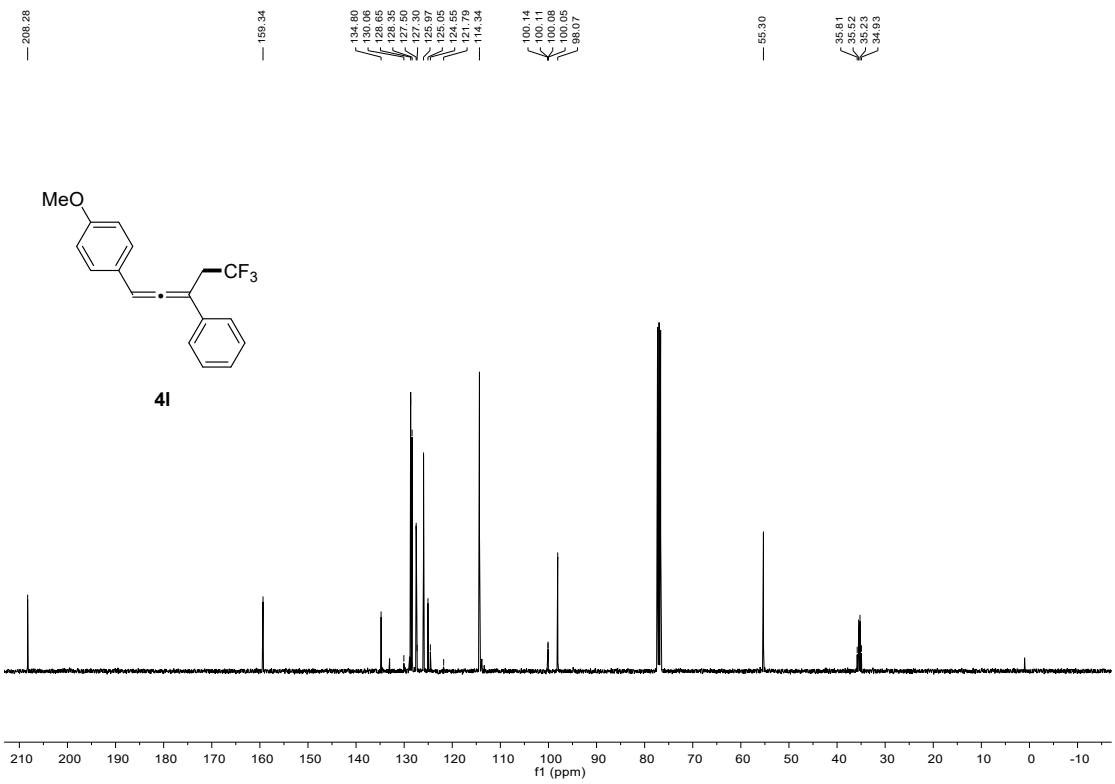
CF3
4k
f1 (ppm)


7.45
7.43
7.37
7.35
7.34
7.31
7.29
7.28
7.27
7.26
6.90
6.89
6.63
3.82
3.45
3.43
3.40
3.39
3.37
3.35
3.34
3.33
3.31
MeO
CF3
4l
2.08
2.01
3.00
2.03
1.00
3.03
2.09
f1 (ppm)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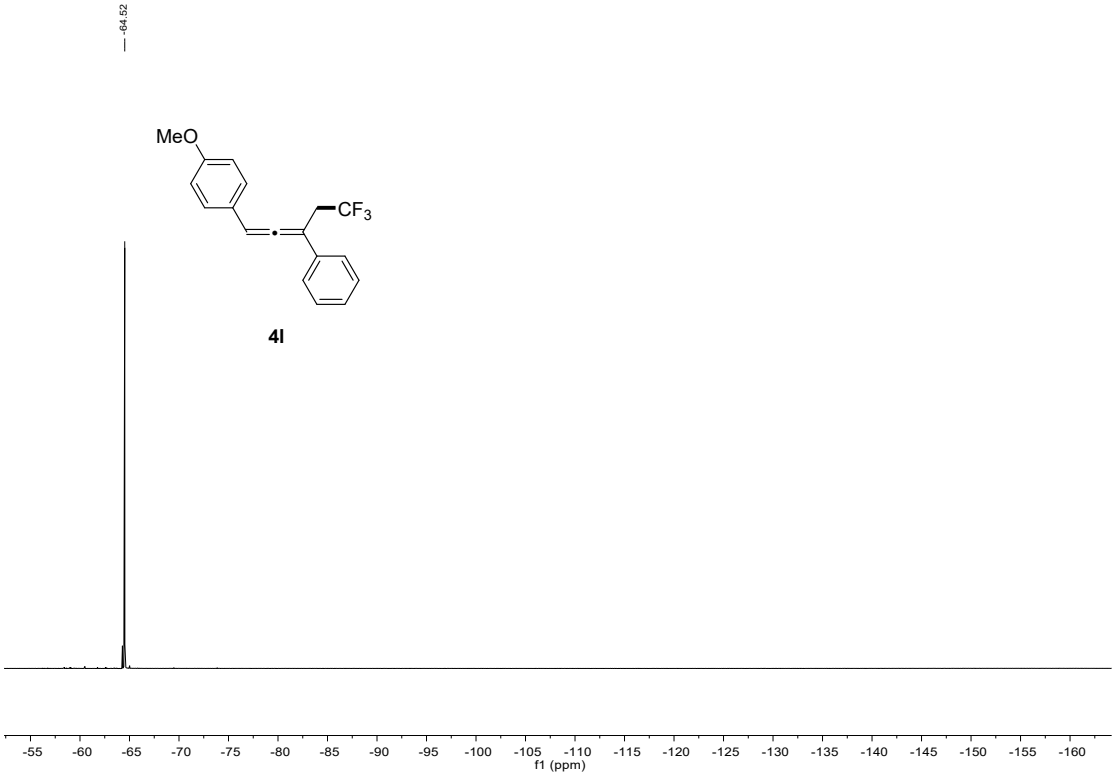
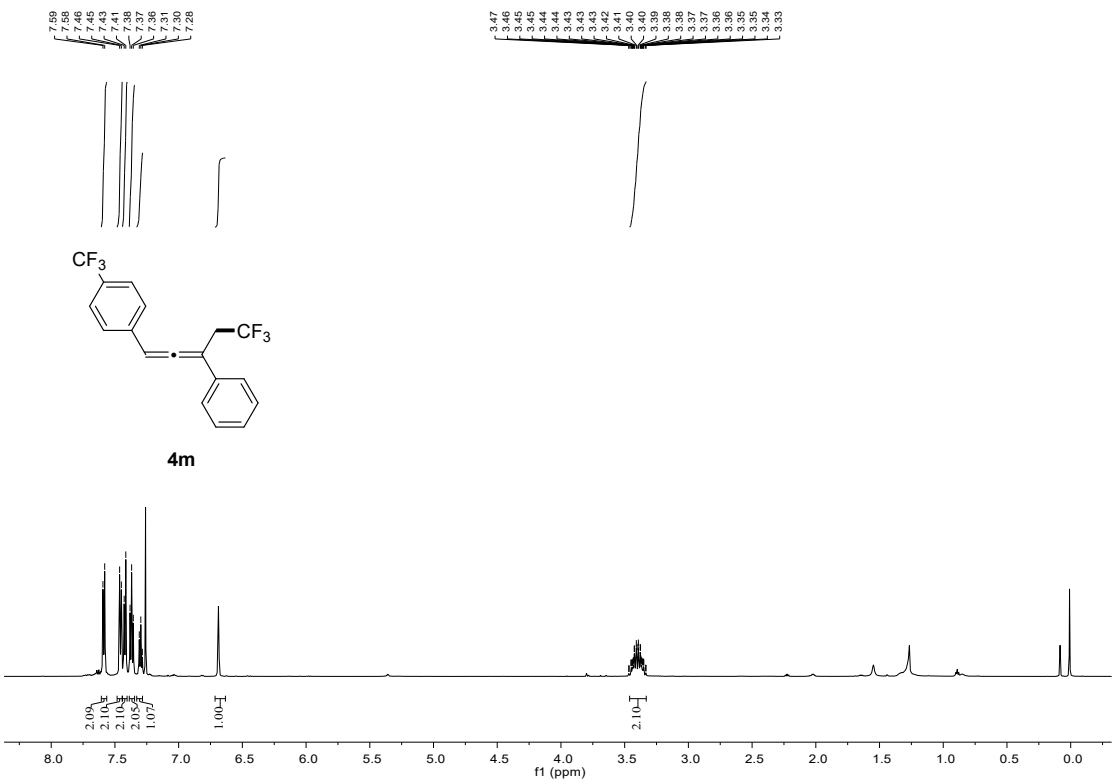
159.34
134.80
130.66
128.65
128.35
127.50
127.30
125.97
125.05
124.55
121.79
114.34
100.14
100.11
100.08
100.05
98.07
55.30
35.81
35.52
35.23
34.93
MeO
CF3
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.52
MeO
CF3
4l
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160
f1 (ppm)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7.37
7.36
7.31
7.30
7.28
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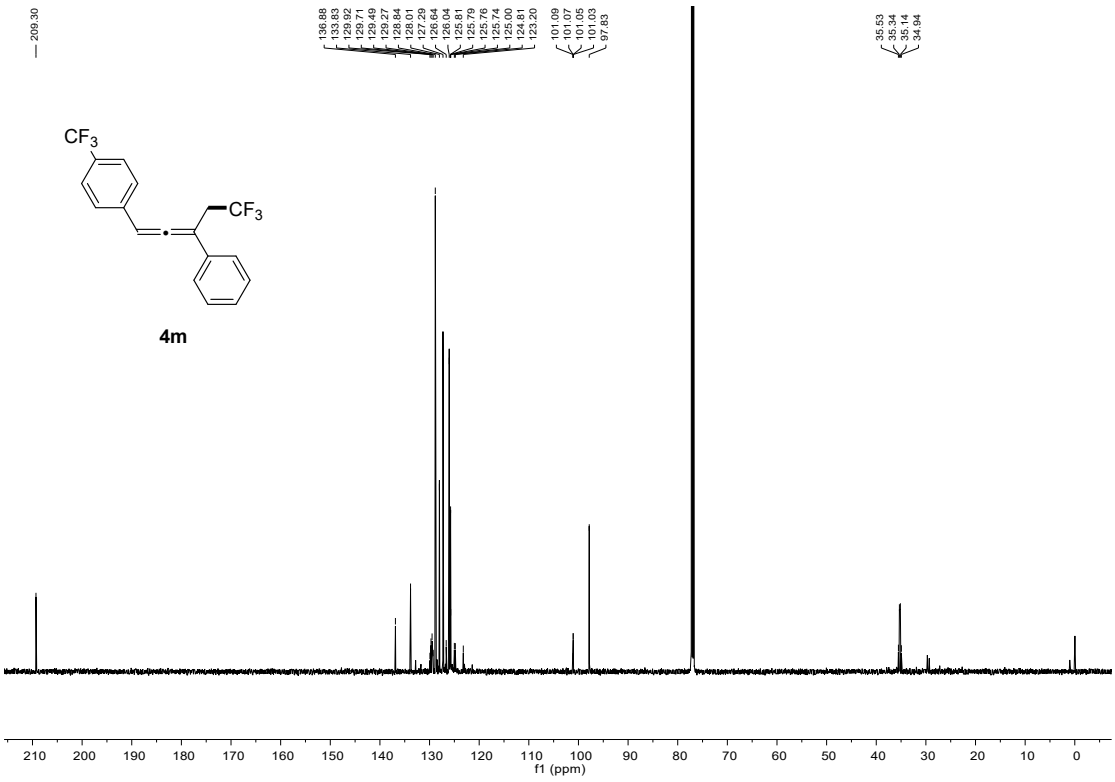
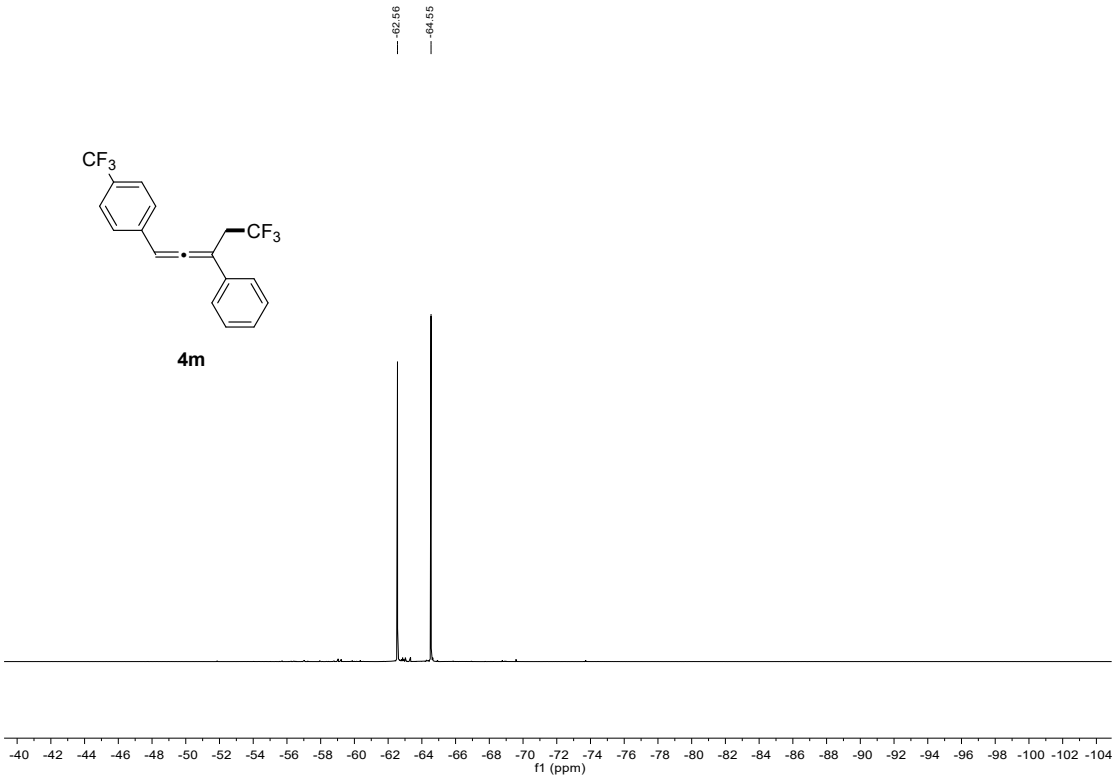
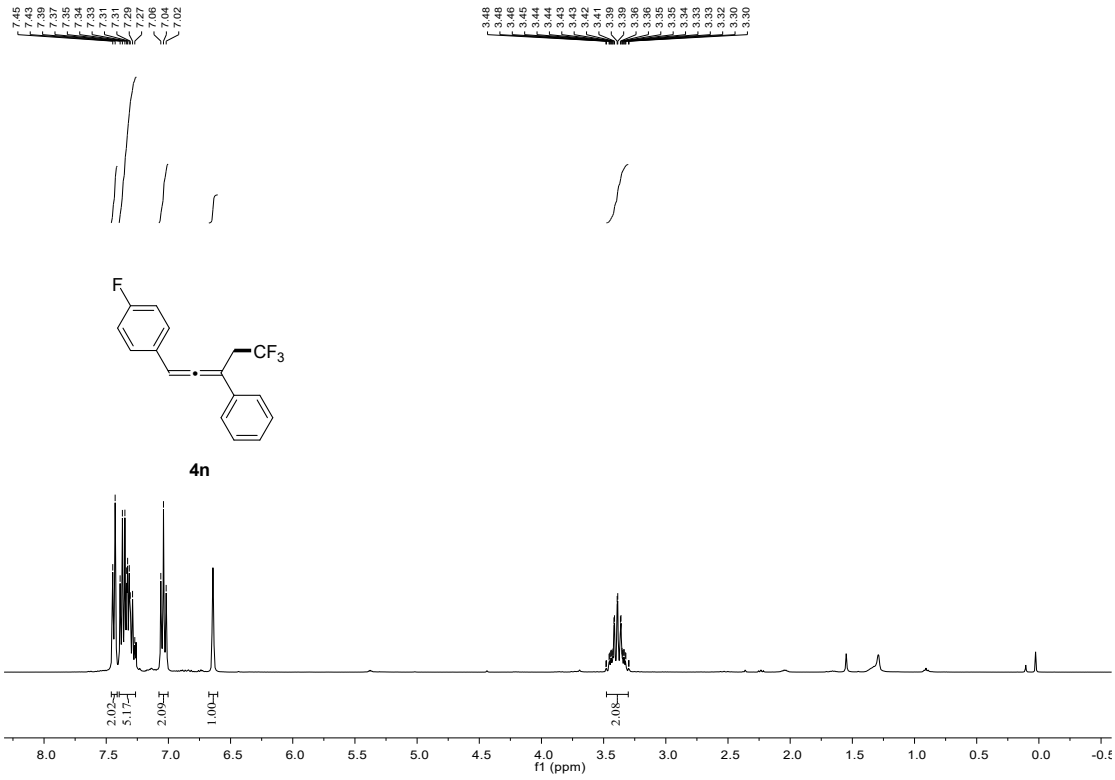
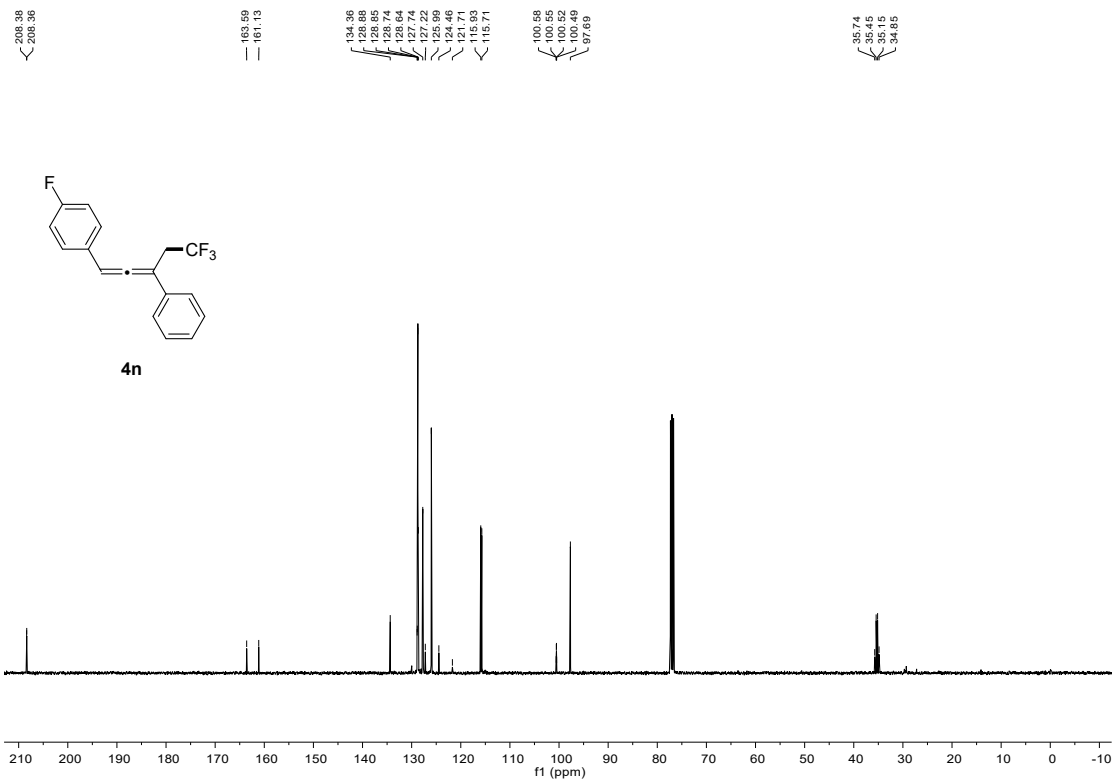
3.46
3.45
3.45
3.44
3.44
3.43
3.43
3.43
3.42
3.41
3.40
3.40
3.39
3.38
3.38
3.37
3.37
3.36
3.36
3.35
3.35
3.34
3.33
CF3
CF3
4m
2.09
2.10
2.10
2.05
1.07
1.00
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.30
136.88
133.83
129.92
129.71
129.49
129.27
128.84
128.01
127.29
126.64
126.04
125.81
125.79
125.76
125.74
125.00
124.81
123.20
101.09
101.07
101.05
101.03
97.83
35.53
35.34
35.14
34.94
CF3
CF3
4m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.56
-64.55
CF3
CF3
4m
-40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104
f1 (ppm)


7.45
7.43
7.39
7.37
7.35
7.34
7.33
7.31
7.31
7.29
7.27
7.06
7.04
7.02
3.48
3.48
3.46
3.45
3.44
3.44
3.43
3.43
3.42
3.41
3.39
3.39
3.36
3.36
3.35
3.35
3.34
3.33
3.33
3.32
3.30
3.30
F
CF3
4n
2.02
5.17
2.09
1.00
2.08
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)


208.38
208.36
163.59
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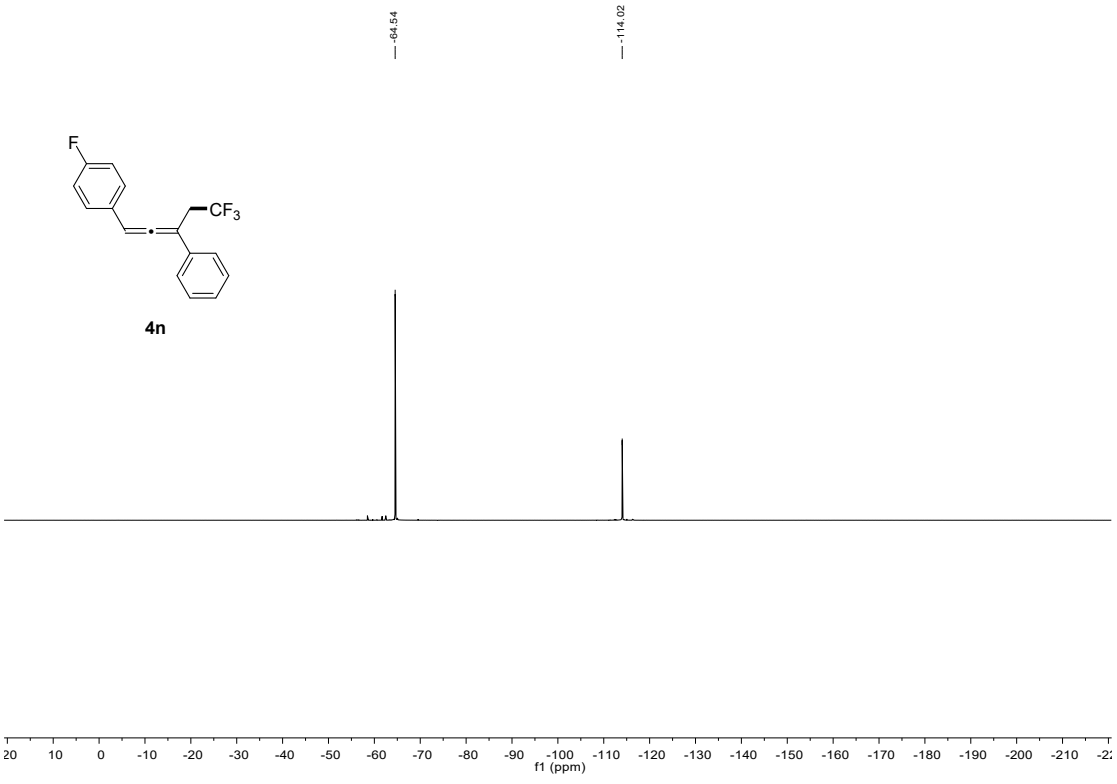
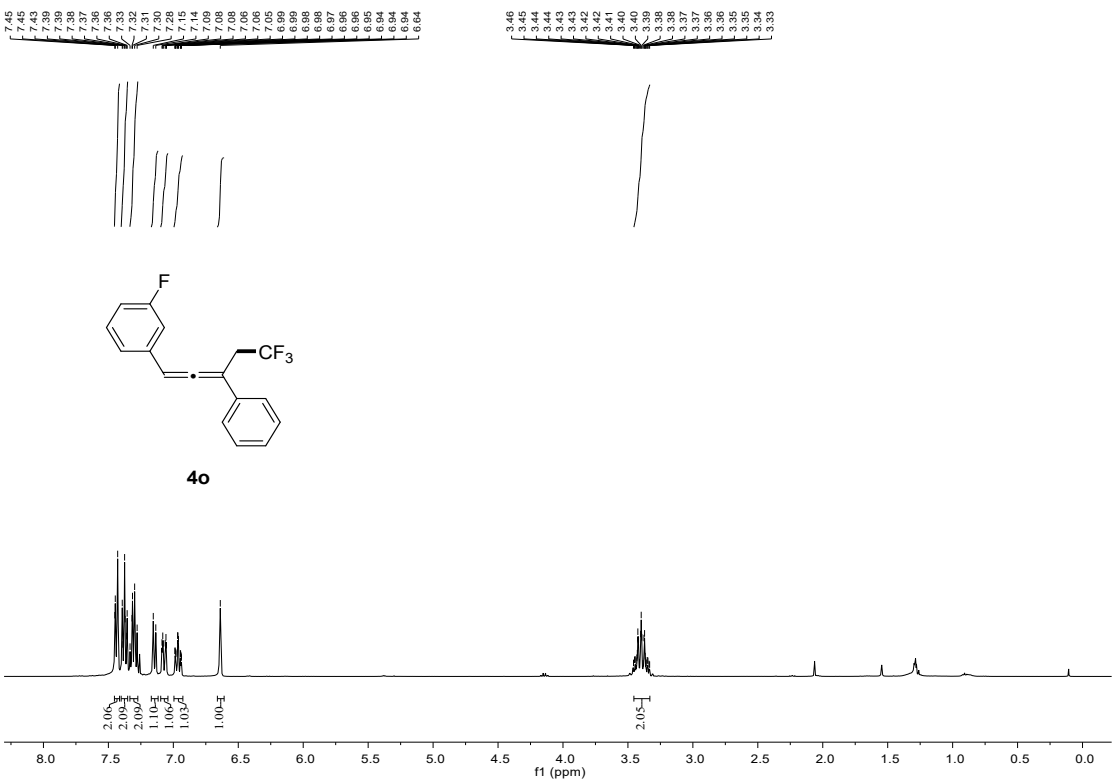
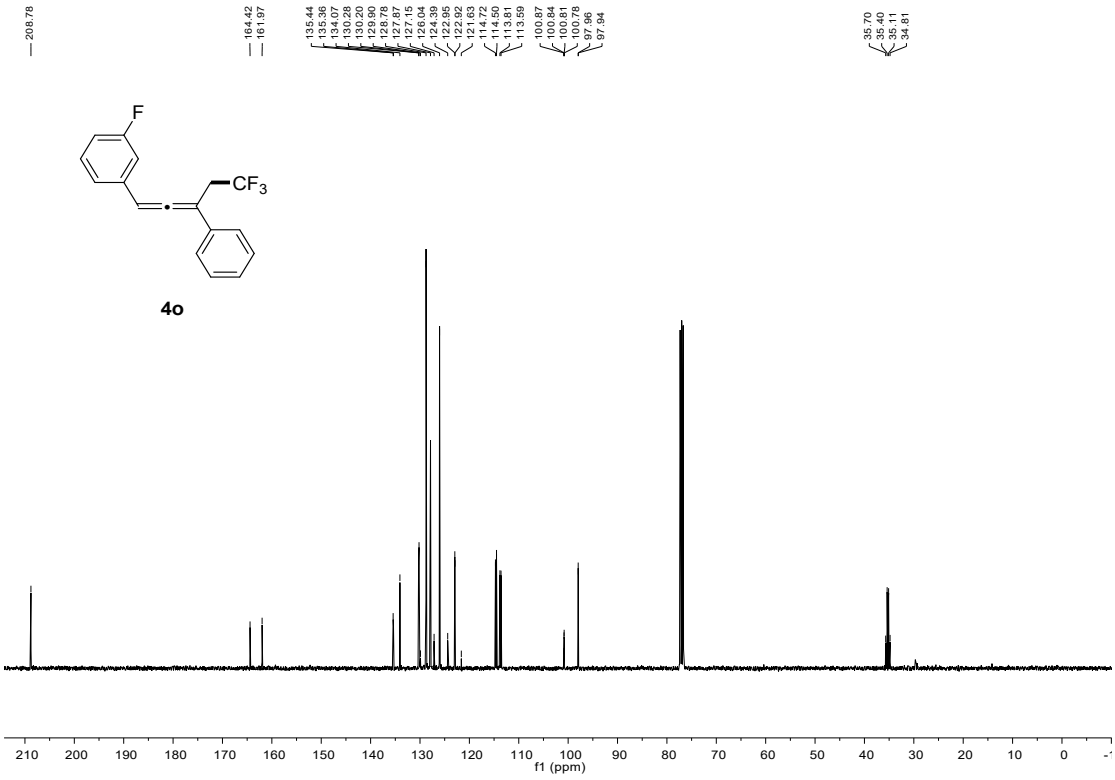
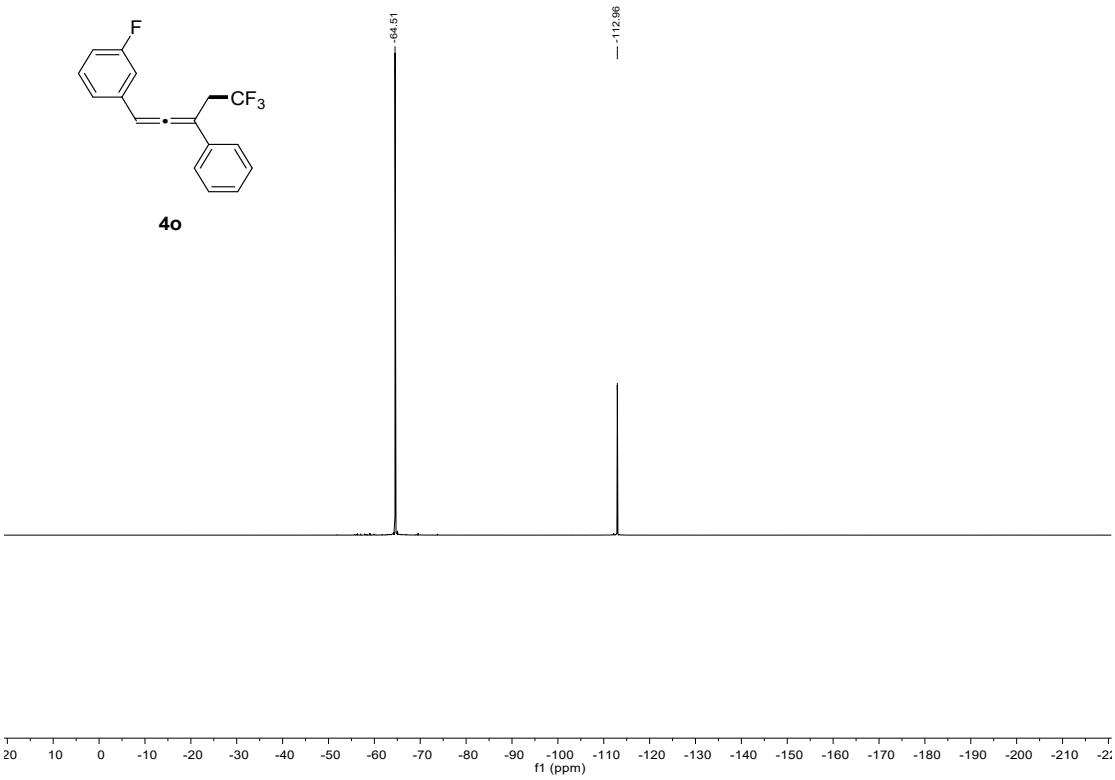
134.36
128.88
128.85
128.74
128.64
127.74
127.22
125.99
124.46
121.71
115.93
115.71
100.58
100.55
100.53
100.49
97.69
35.74
35.45
35.15
34.85
F
CF3
4n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

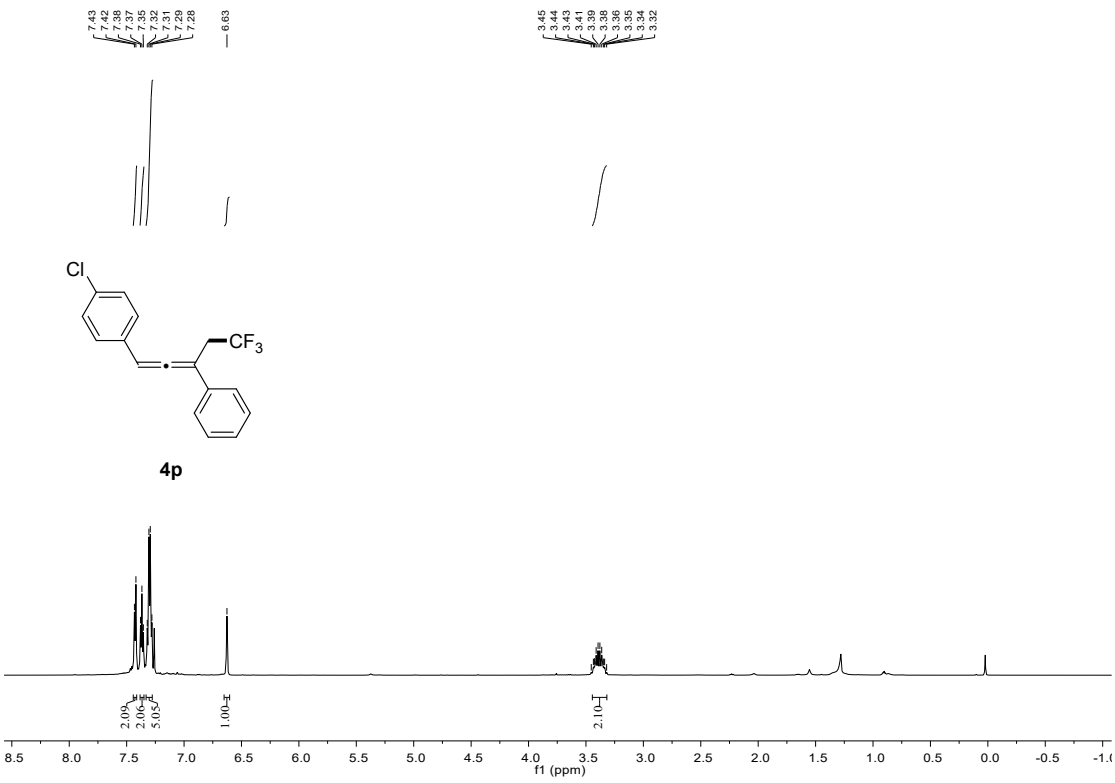

-64.54
-114.02
F
CF3
4n
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


F
CF3
4o
2.06
2.09
2.09
1.10
1.06
1.03
1.00
2.05
f1 (ppm)

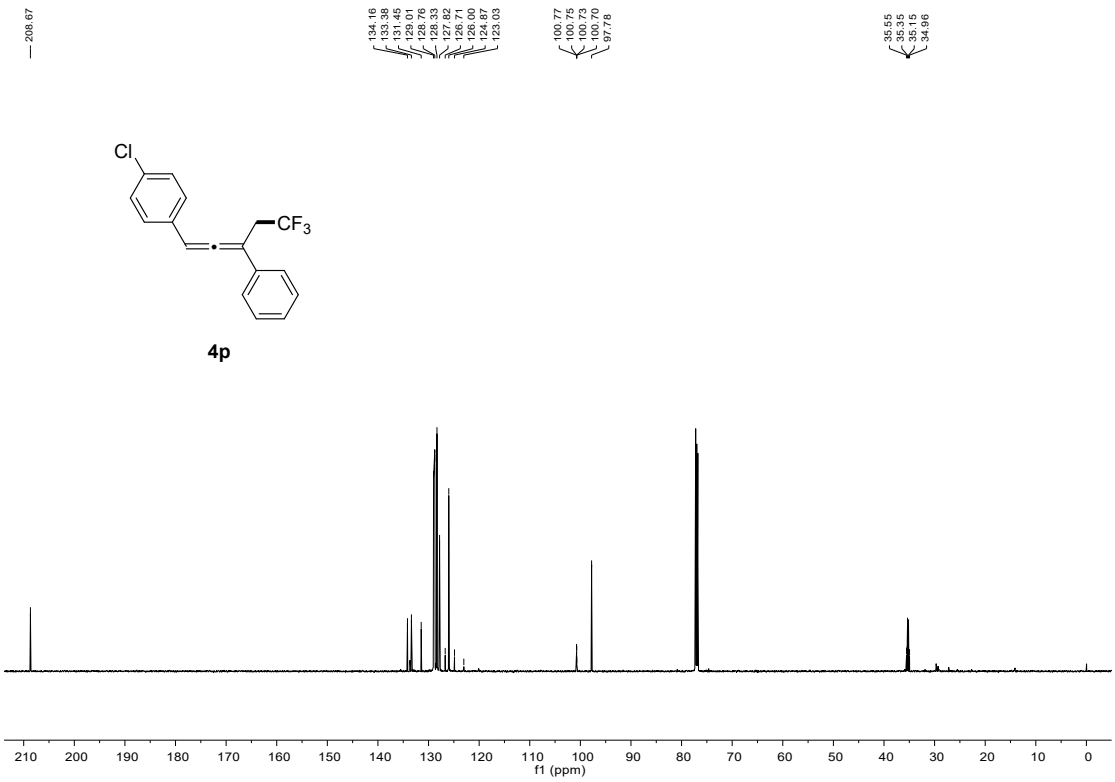

F
CF3
4o
f1 (ppm)


F
CF3
-64.51
-112.96
f1 (ppm)

4o


7.43
7.42
7.38
7.37
7.35
7.32
7.31
7.29
7.28
6.63
3.45
3.44
3.43
3.41
3.39
3.38
3.36
3.35
3.34
3.32
Cl
CF3
2.09
2.06
5.05
1.00
2.10
f1 (ppm)

4p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128.33
127.82
126.71
126.00
124.87
123.03
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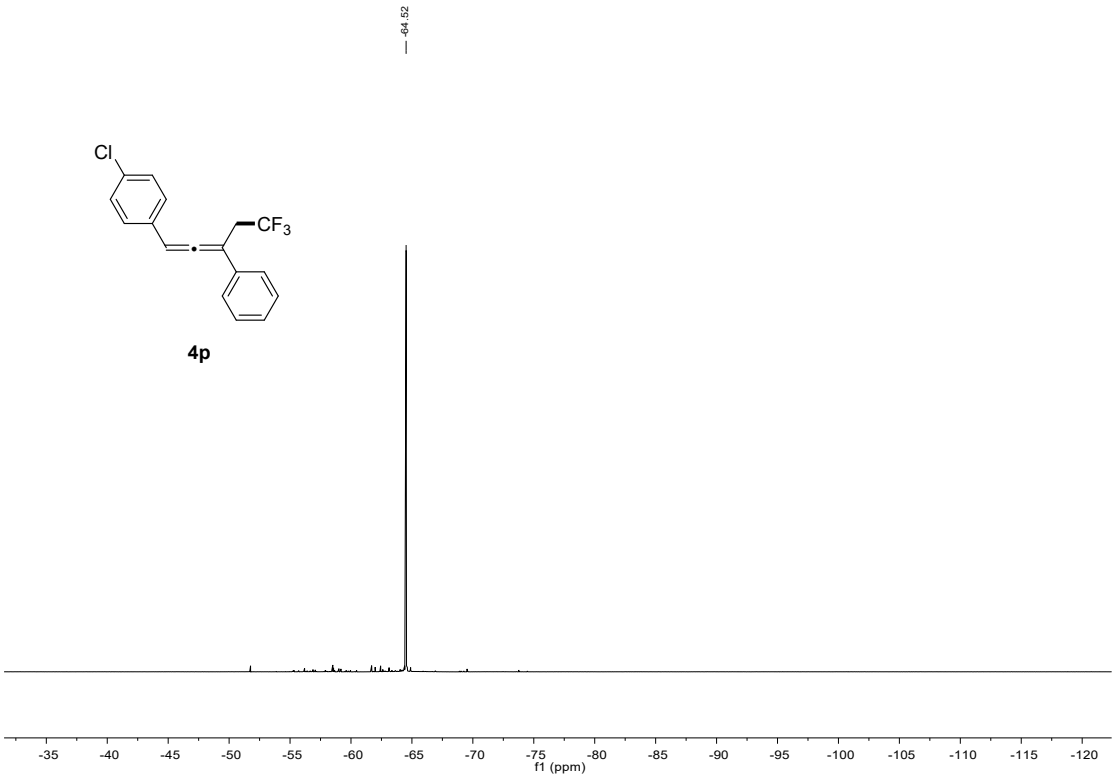
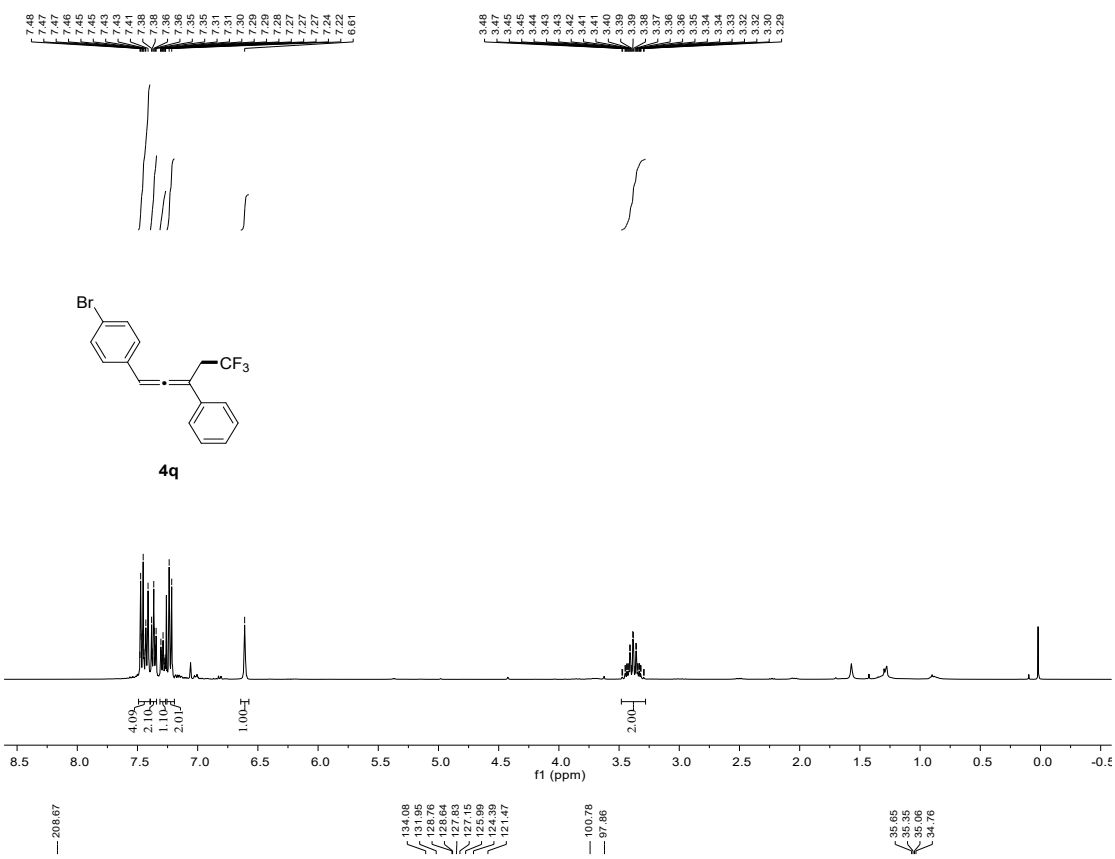
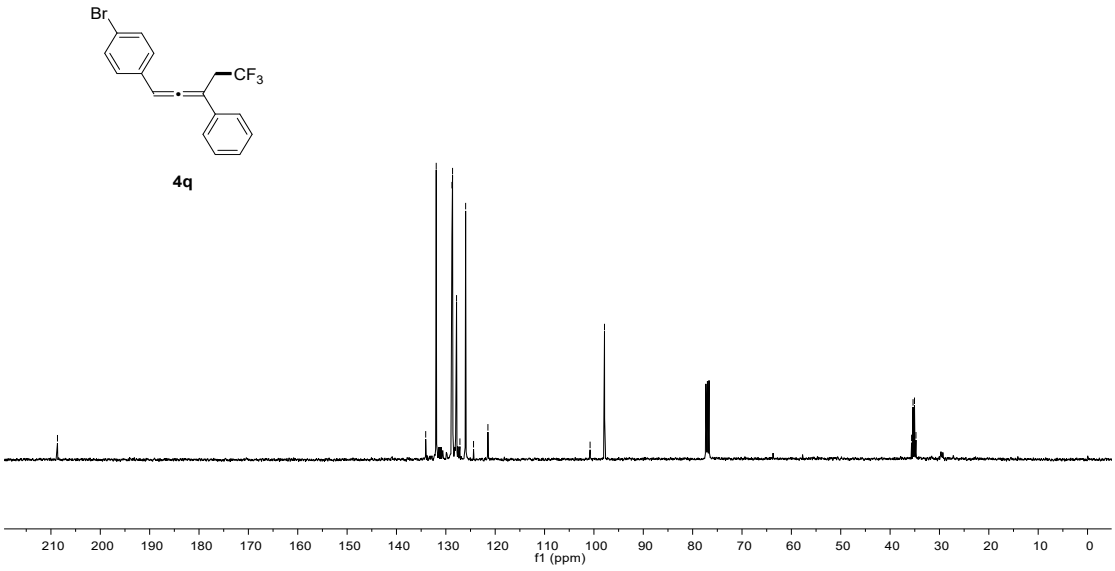
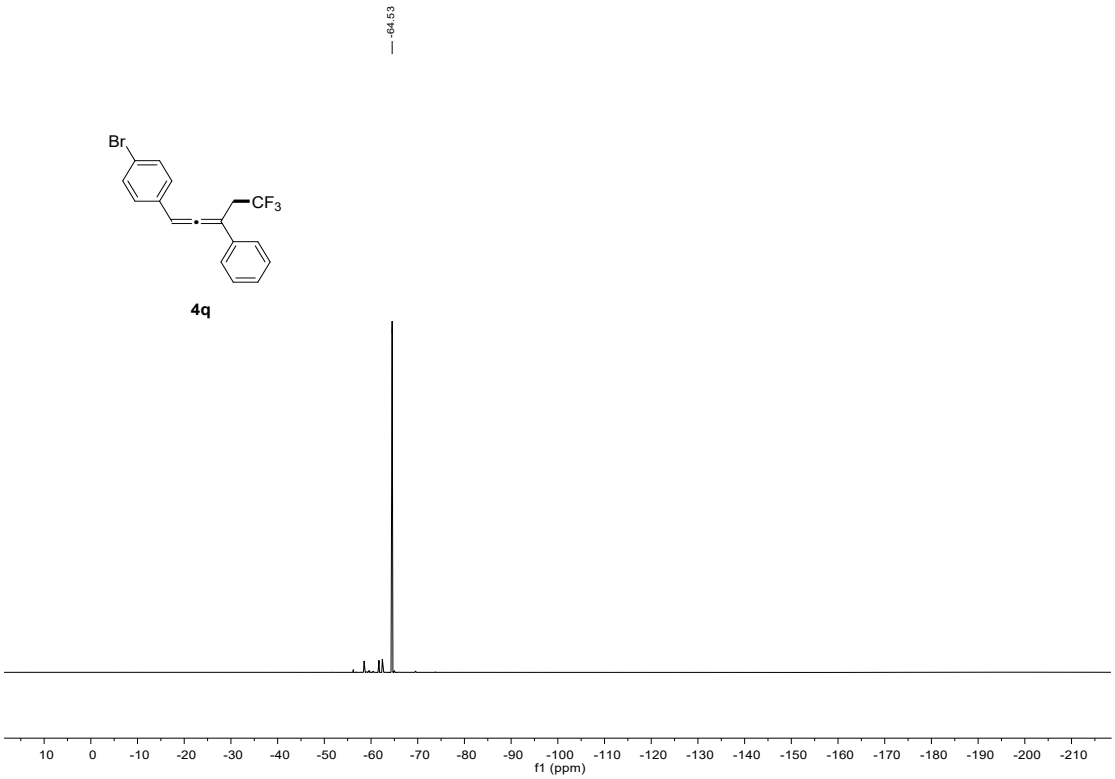
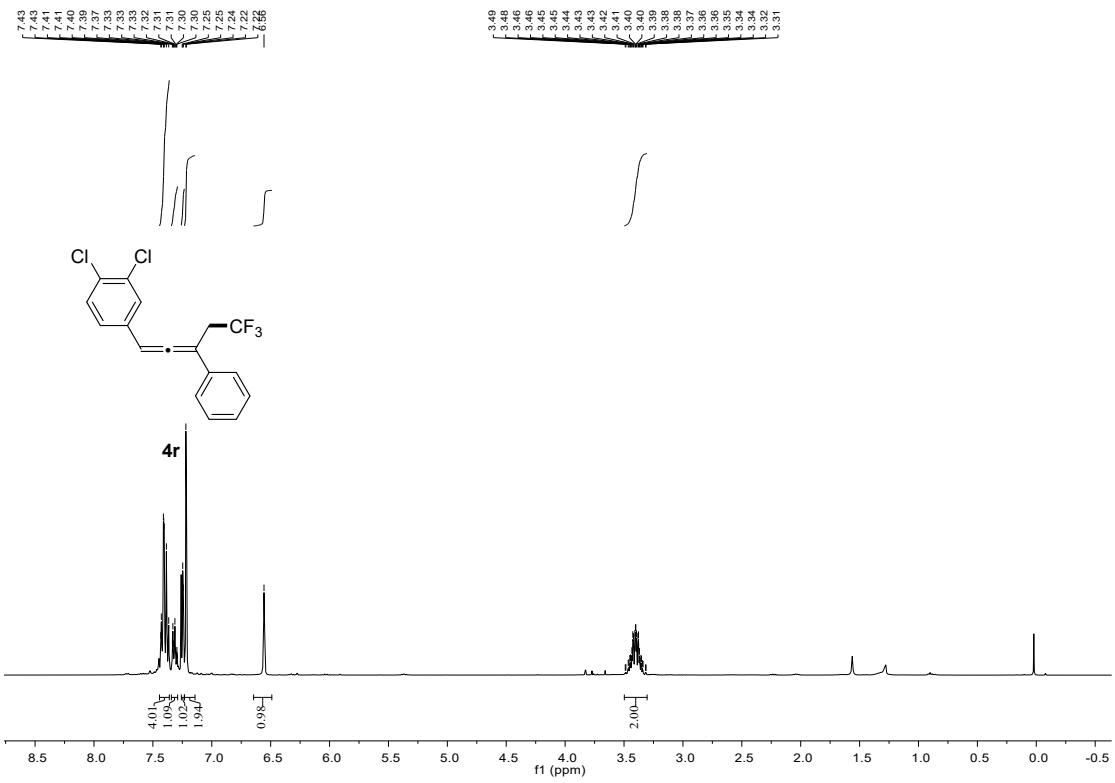
100.75
100.73
100.70
97.78
35.55
35.35
35.15
34.96
Cl
CF3
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

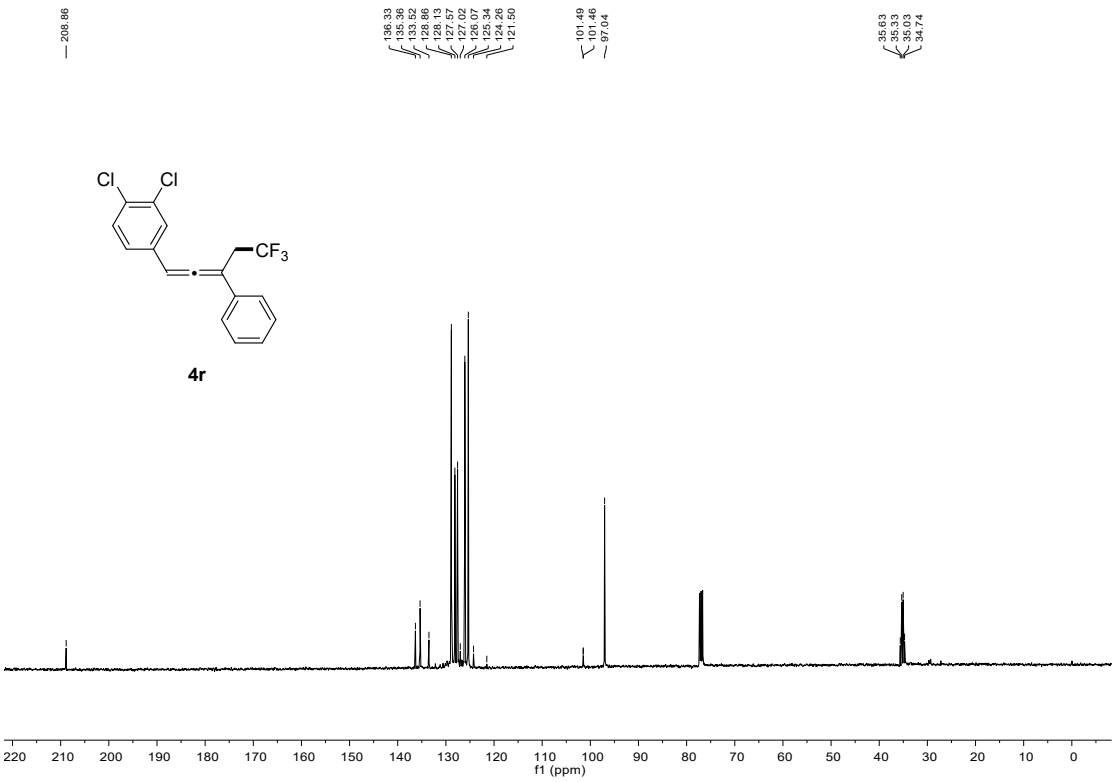

-64.52
Cl
CF3
4p
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

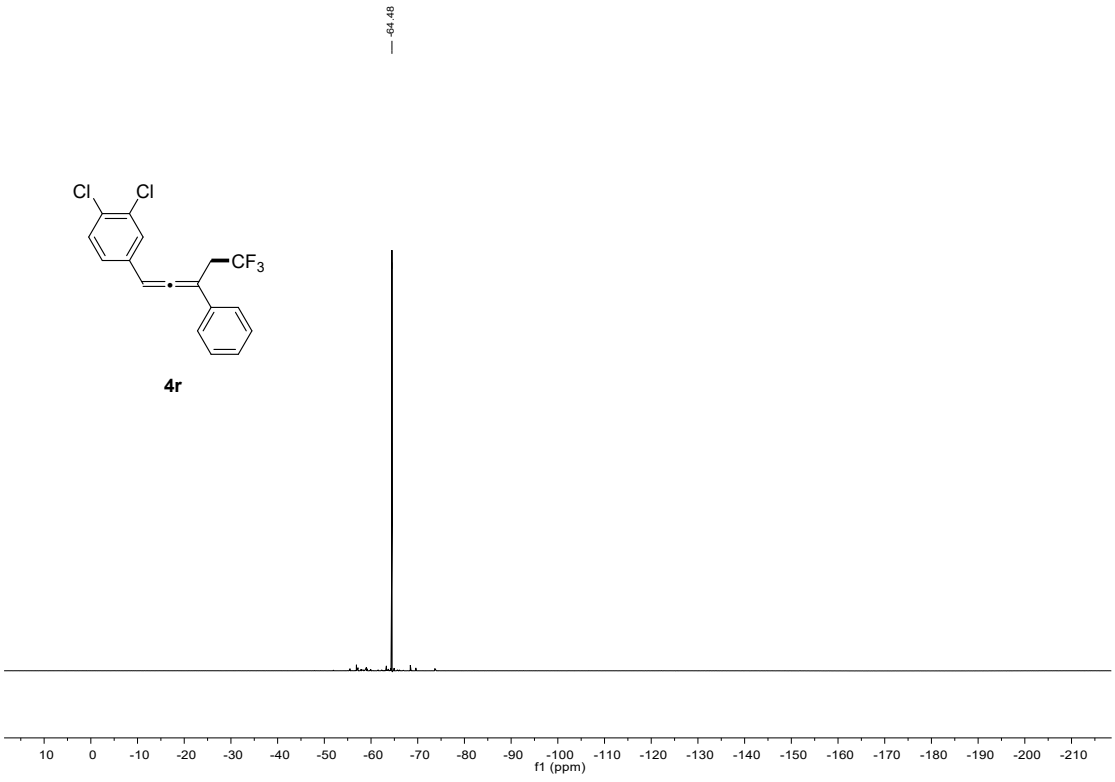

Br
CF3
4q
f1 (ppm)

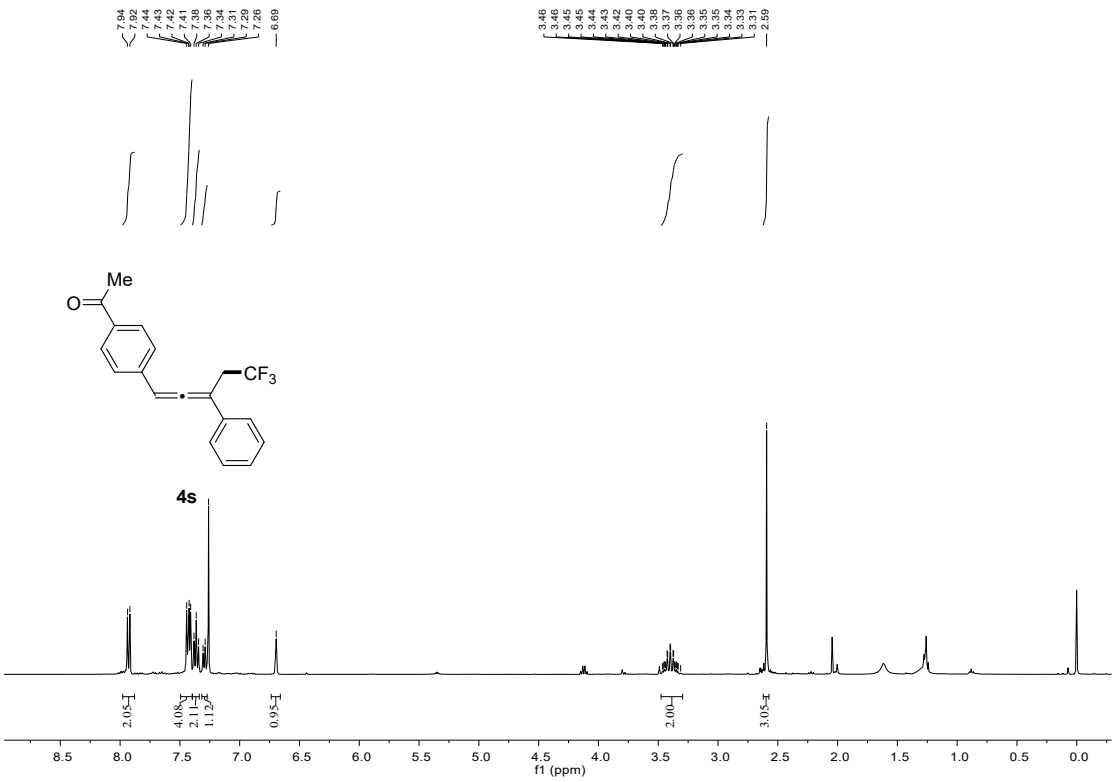

Br
CF3
4q
f1 (ppm)

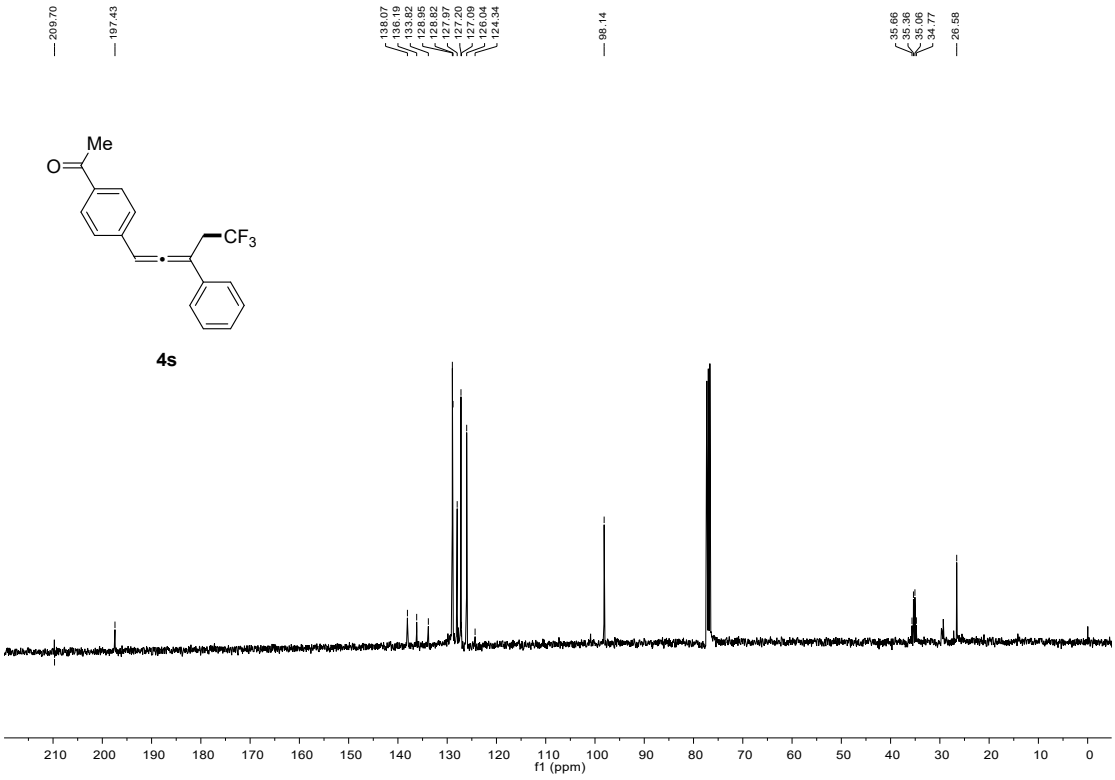

-64.53
Br
CF3
4q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

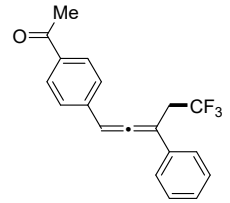

7.43 7.43 7.41 7.41 7.40 7.39 7.37 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.25 7.25 7.24 7.22 6.56 6.56
3.49 3.48 3.46 3.46 3.45 3.45 3.44 3.43 3.43 3.42 3.41 3.40 3.40 3.39 3.38 3.38 3.37 3.36 3.36 3.35 3.34 3.34 3.32 3.31
Cl Cl
CF3
4r
4.01 1.09 1.02 1.94 0.98 2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


208.86
136.33
135.36
133.52
128.86
128.13
127.77
127.02
126.07
125.34
124.26
121.50
101.49
101.46
97.04
35.63
35.33
35.03
34.74
Cl
Cl
CF3
4r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-64.48
Cl
Cl
CF3
4r
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)

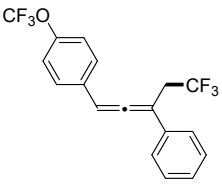

7.94
7.92
7.44
7.43
7.42
7.41
7.38
7.36
7.34
7.31
7.29
7.26
6.69
3.46
3.46
3.45
3.45
3.44
3.43
3.42
3.40
3.40
3.38
3.37
3.36
3.36
3.35
3.35
3.34
3.33
3.31
2.59
Me
O
CF3
4s
2.05
4.08
2.11
1.12
0.95
2.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.70
197.43
138.07
136.19
133.82
129.85
128.82
127.97
127.20
127.09
126.04
124.34
98.14
35.66
35.36
35.06
34.77
26.58
Me
O
CF3
4s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

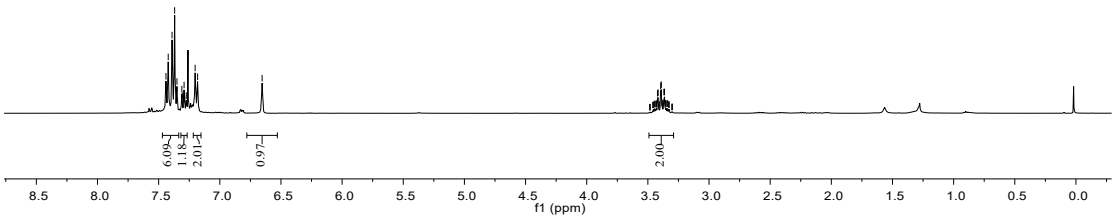

Me
O
CF3

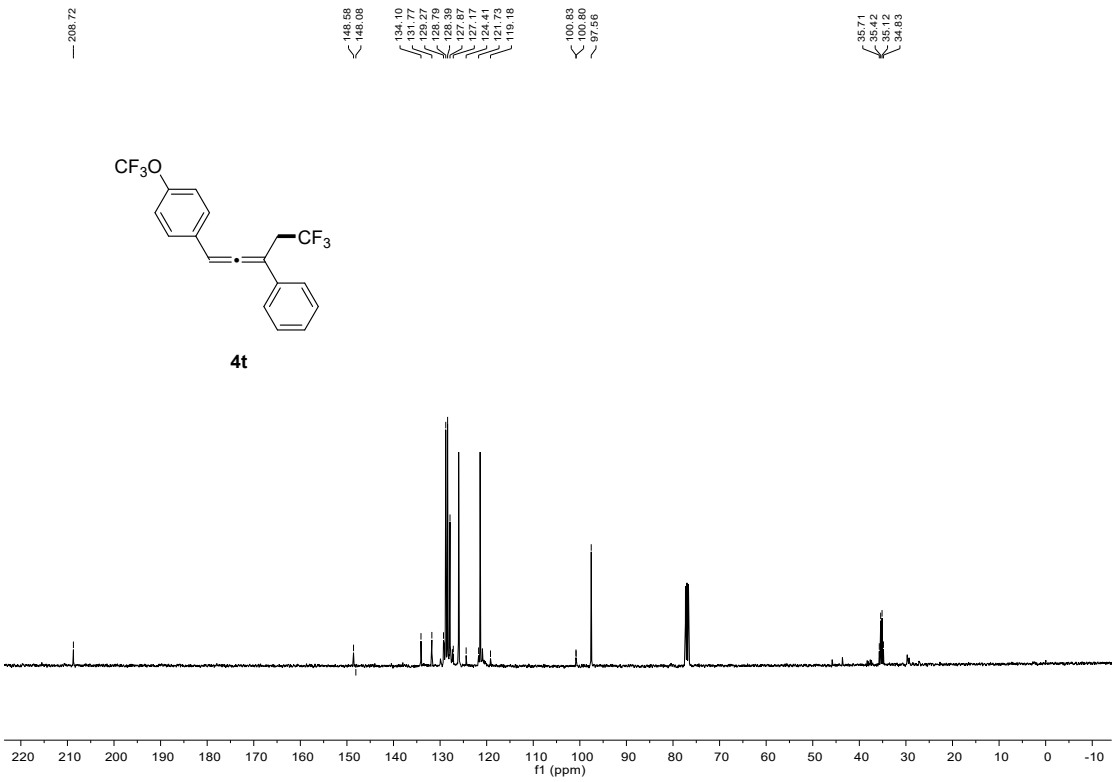
4s

-64.53
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)
7.44 7.44 7.42 7.42 7.39 7.37 7.35 7.35 7.31 7.31 7.30 7.29 7.29 7.27 7.20 7.18 6.65
3.49 3.48 3.46 3.45 3.45 3.44 3.43 3.43 3.42 3.42 3.40 3.40 3.39 3.38 3.38 3.37 3.36 3.36 3.35 3.34 3.34 3.33 3.33 3.30 3.30


CF3O
CF3

4t


6.09
1.18
2.01
0.97
2.00
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)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148.58
148.08
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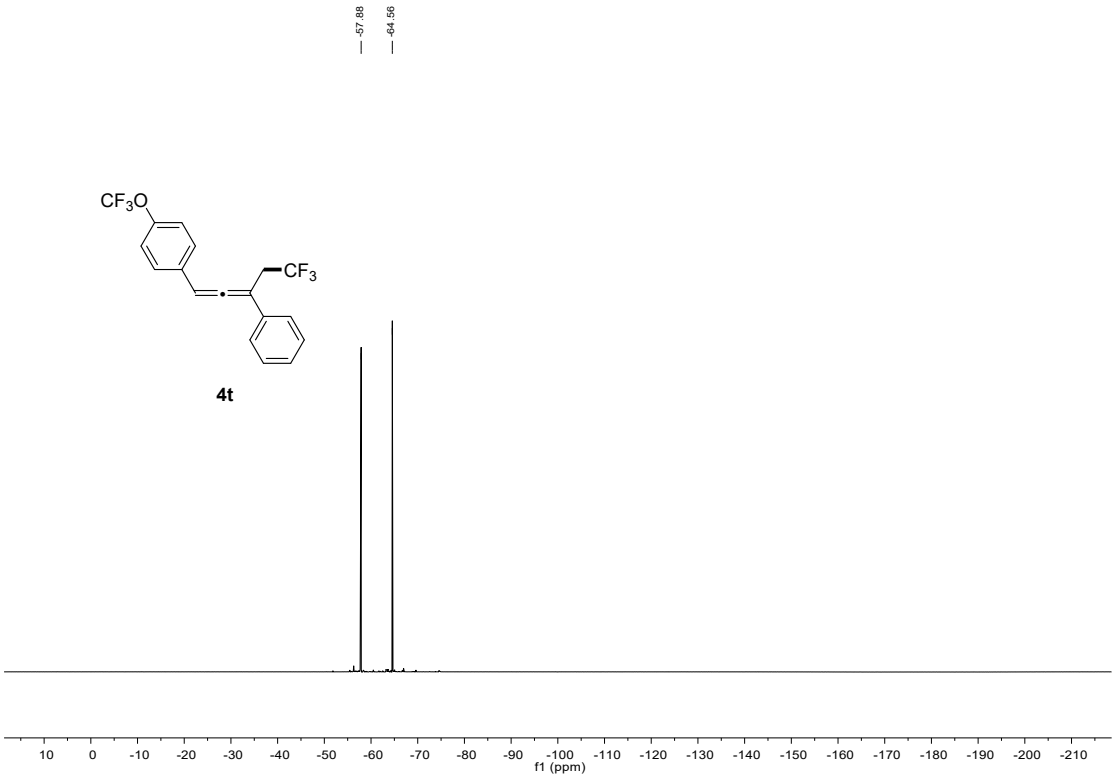
129.27
128.79
128.39
127.87
127.17
124.41
121.73
119.18
100.83
100.80
97.56
35.71
35.42
35.12
34.83
CF3O
CF3
4t
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-57.88
-64.56
CF3O
CF3
4t
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)


8.58
8.57
7.64
7.64
7.62
7.62
7.60
7.60
7.46
7.45
7.43
7.38
7.36
7.34
7.30
7.28
7.26
7.15
7.14
7.13
7.12
7.12
6.85
3.50
3.50
3.48
3.47
3.46
3.46
3.45
3.45
3.44
3.43
3.41
3.41
3.39
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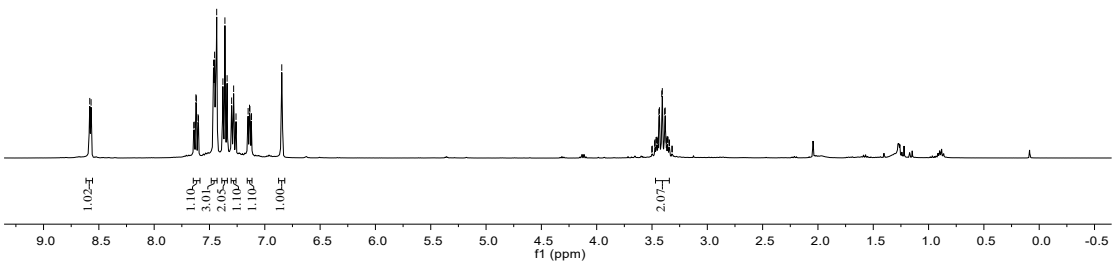
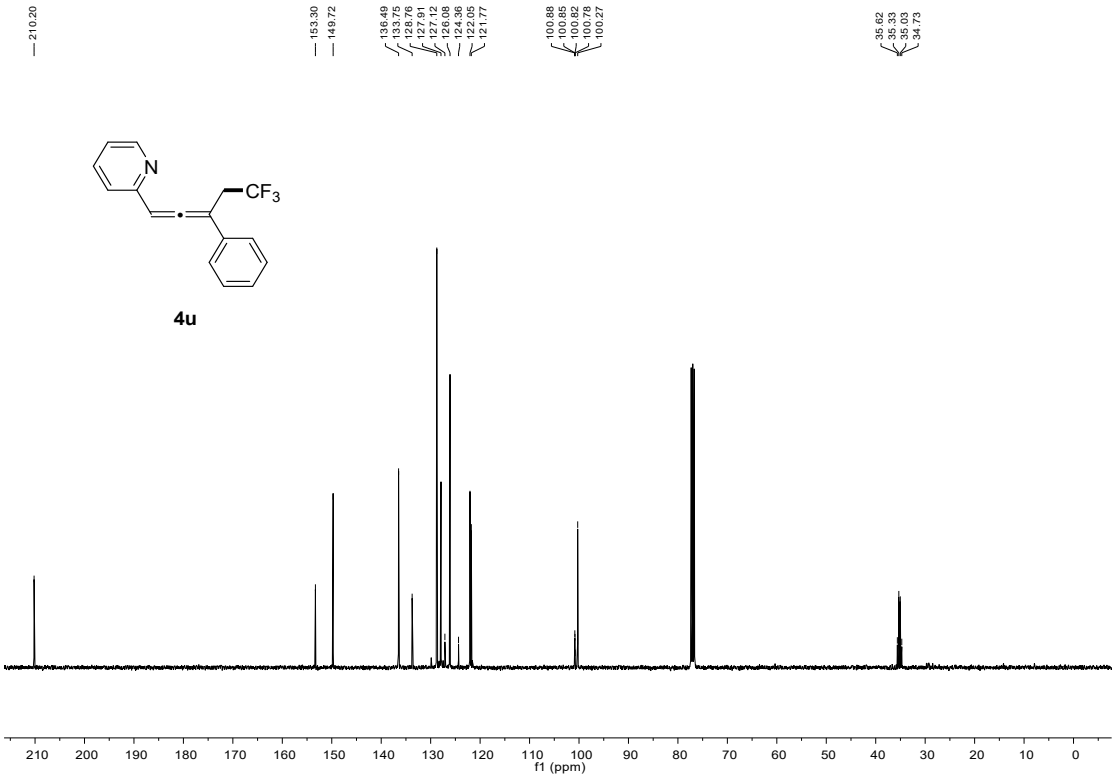
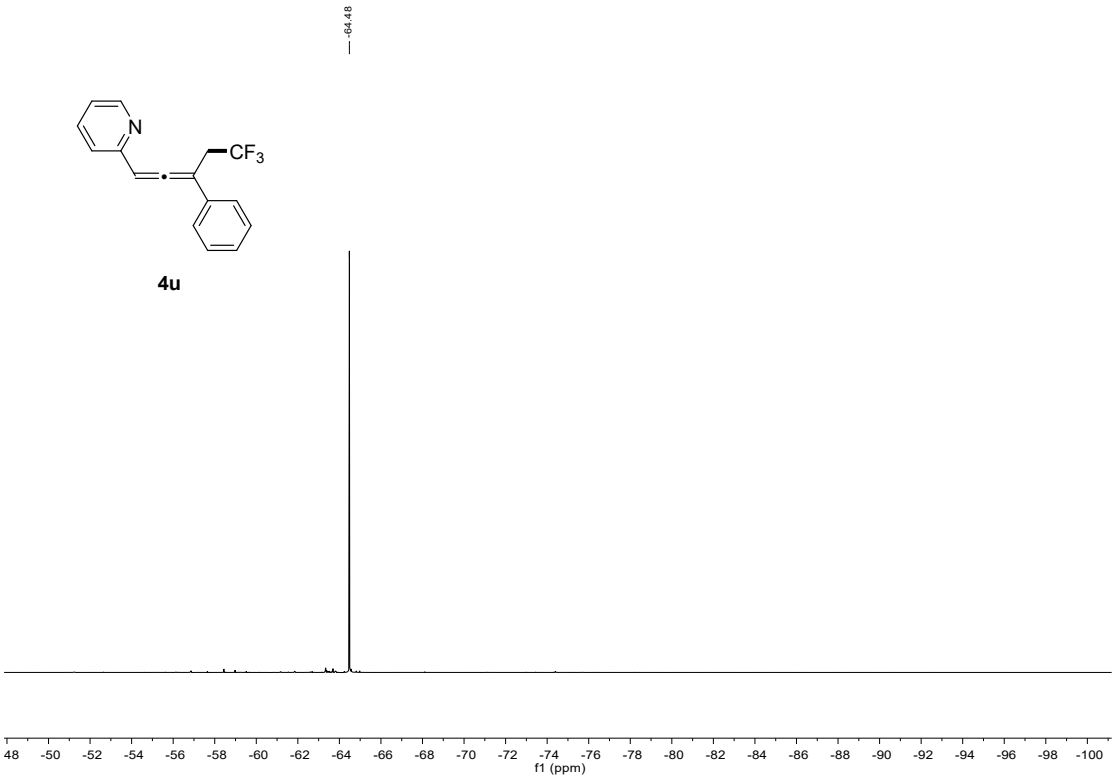
3.37
3.37
3.36
3.35
3.35
3.34
3.32
3.32
N
CF3

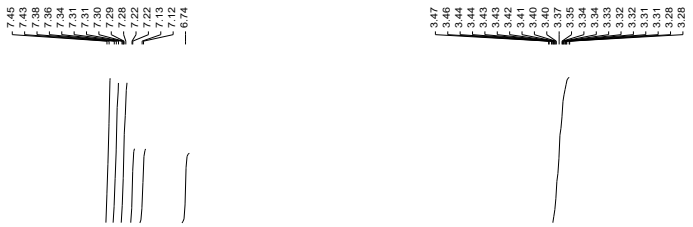
4u


1.02
1.10
3.01
2.05
1.10
1.10
1.00
2.07
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)


210.20
153.30
149.72
136.49
133.75
129.76
127.91
127.12
126.08
124.36
122.05
121.77
100.88
100.85
100.82
100.78
100.27
35.62
35.33
35.03
34.73
N
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4u


-64.48
N
CF3
4u
48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100
f1 (ppm)


7.45
7.43
7.38
7.36
7.34
7.31
7.30
7.29
7.28
7.22
7.22
7.13
7.12
6.74
3.47
3.46
3.44
3.44
3.43
3.42
3.41
3.40
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3.35
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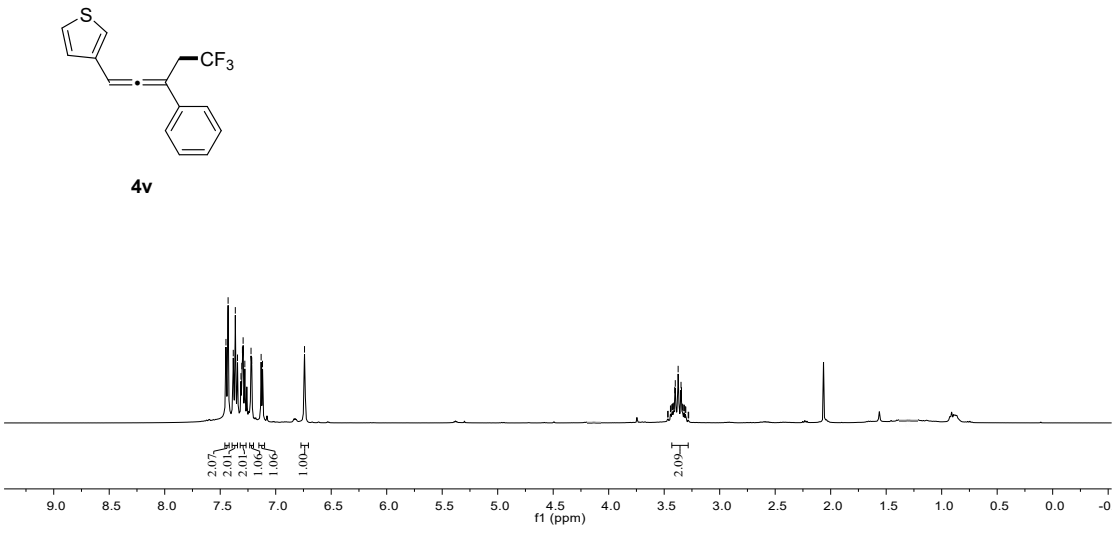
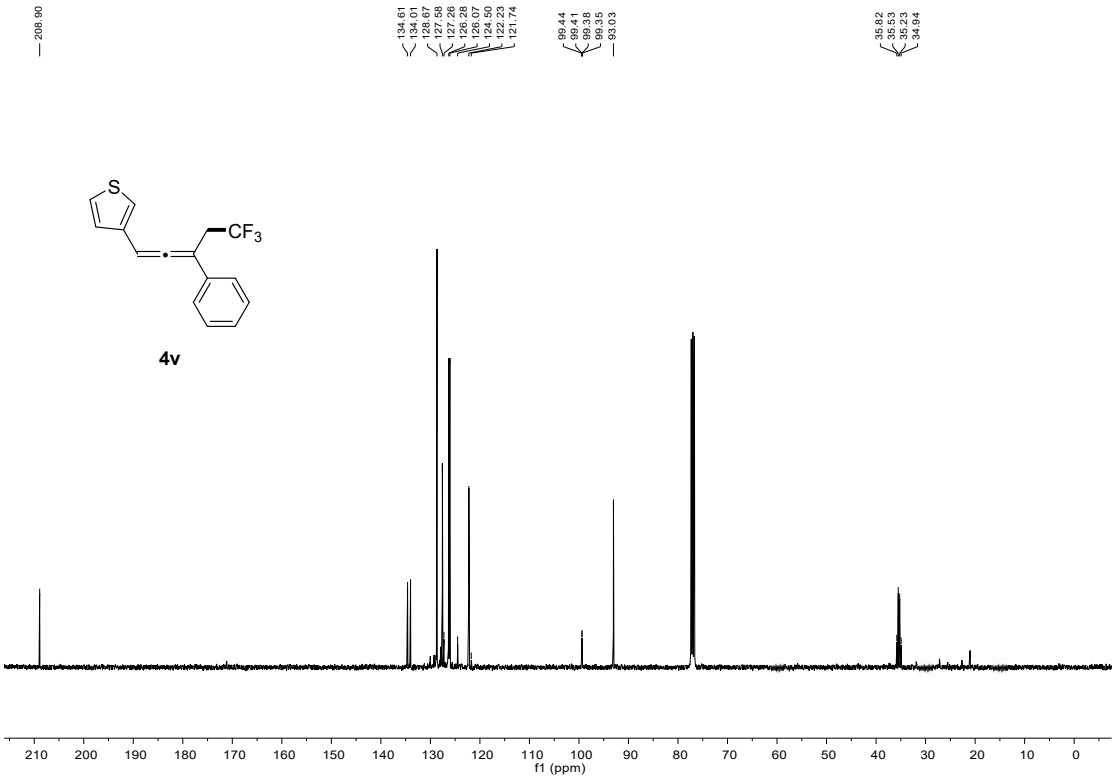
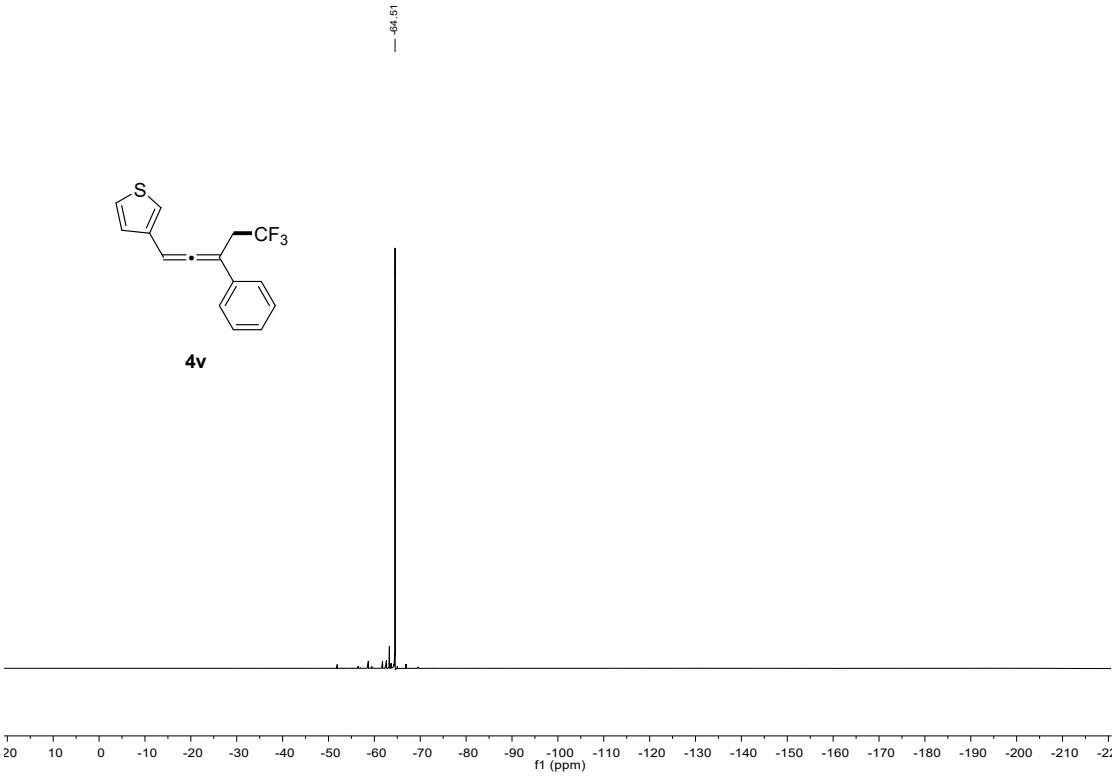
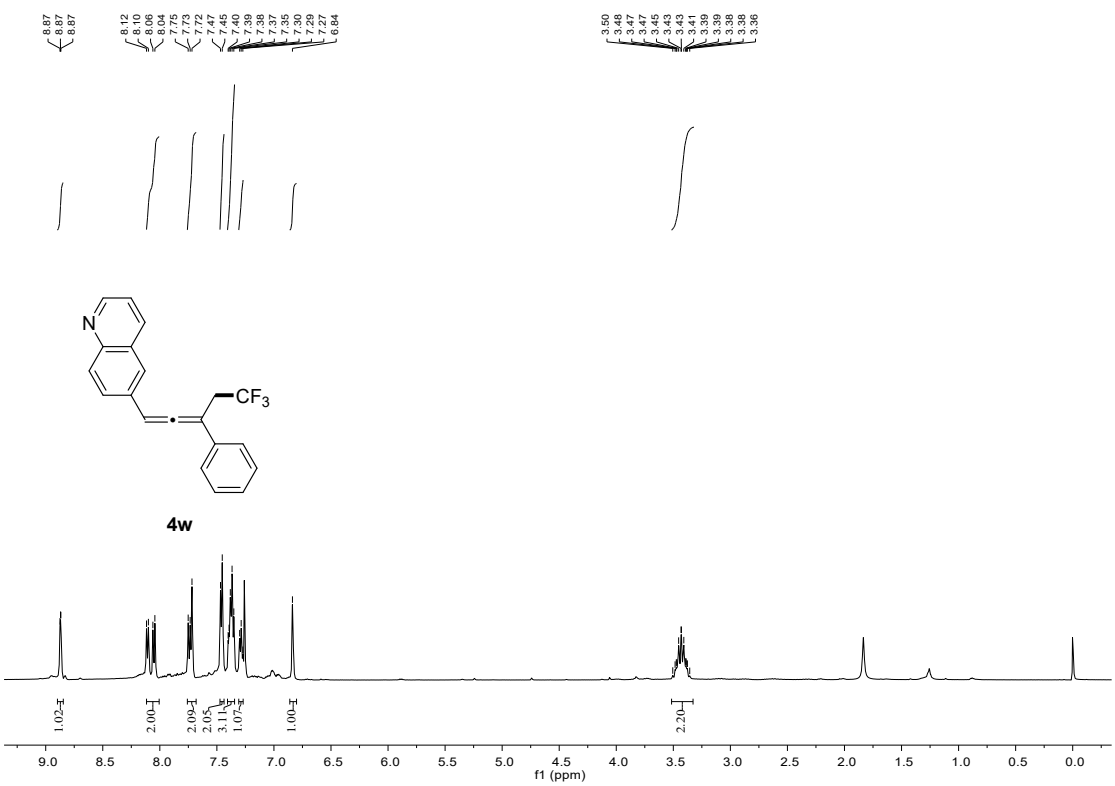
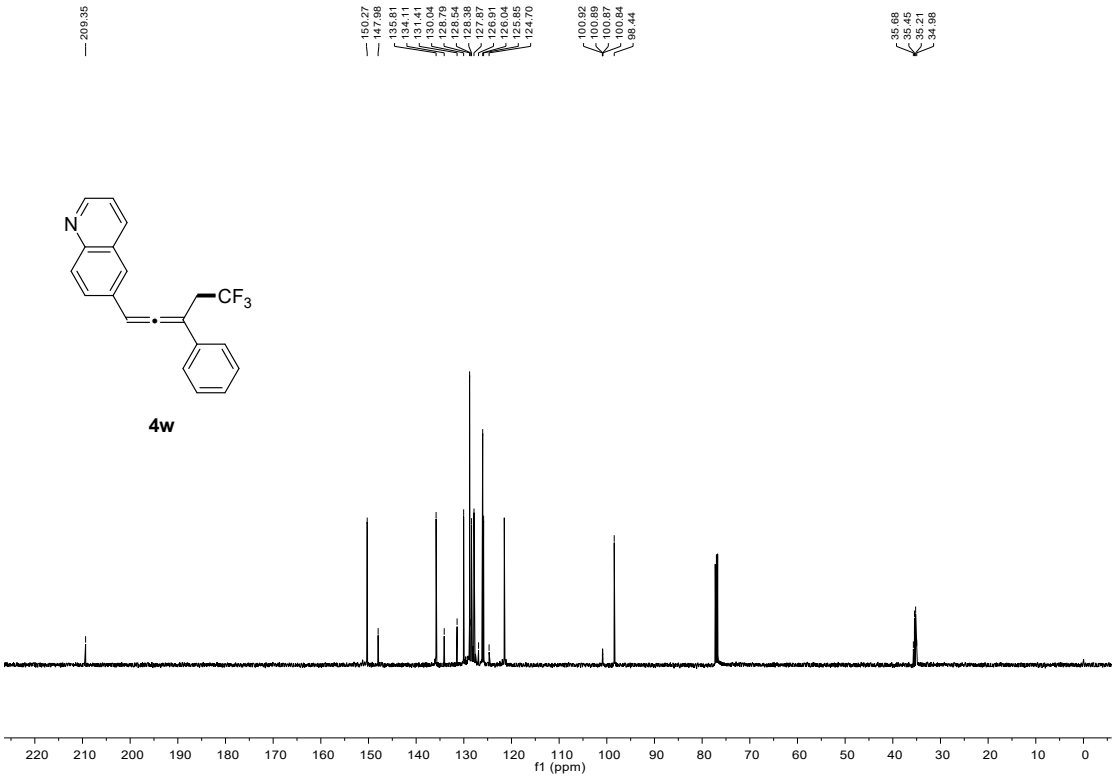
3.33
3.32
3.31
3.31
3.28
3.28

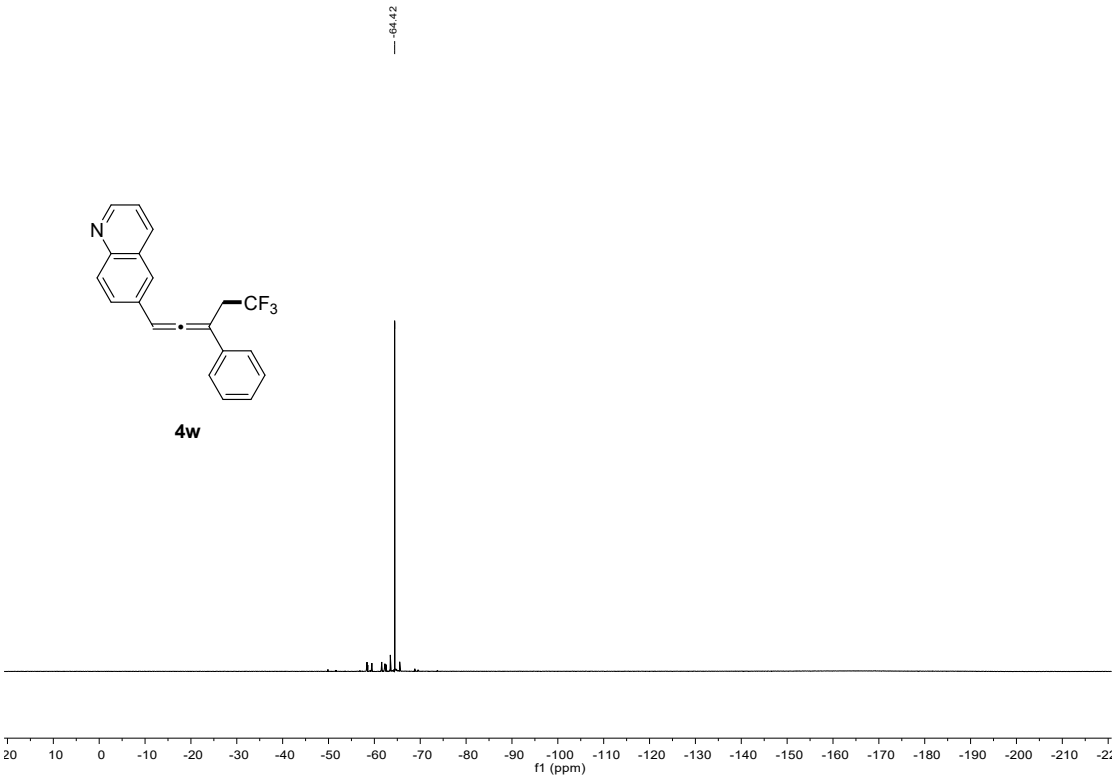

S
CF3
4v
2.07
2.01
2.01
1.06
1.06
1.00
2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

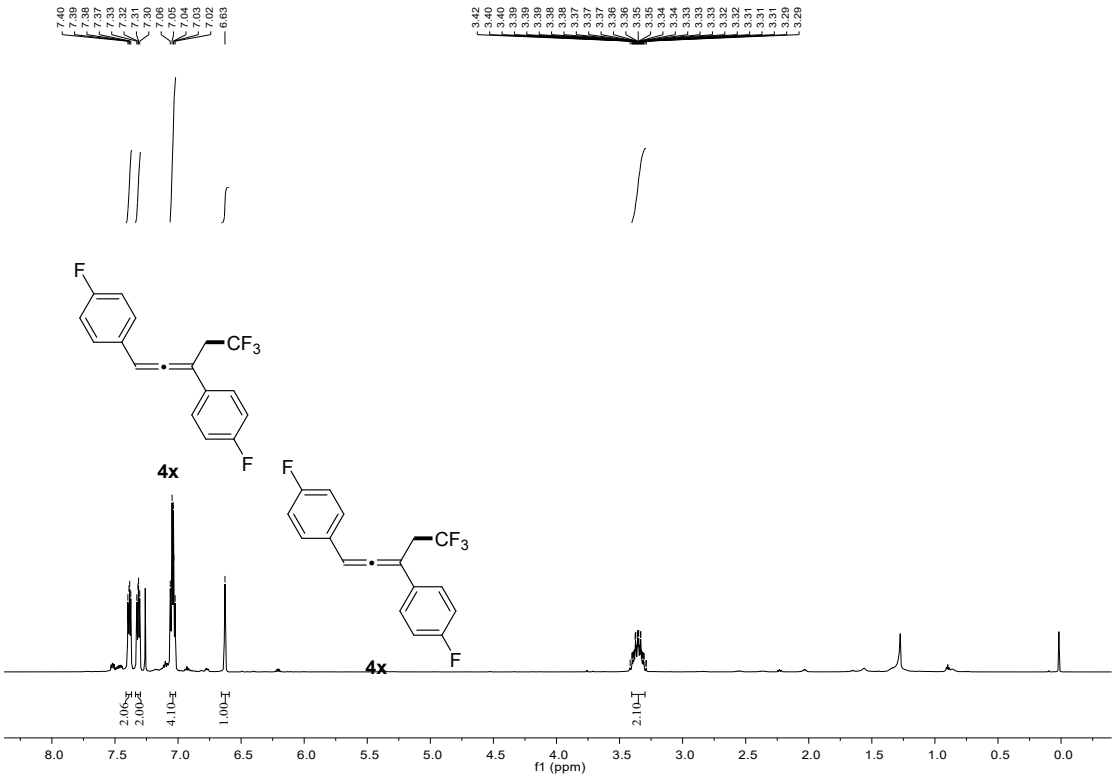

208.90
134.61
134.01
128.67
127.58
127.26
126.28
126.07
124.50
122.23
121.74
99.44
99.41
99.38
99.35
93.03
35.82
35.53
35.23
34.94
S
CF3
4v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

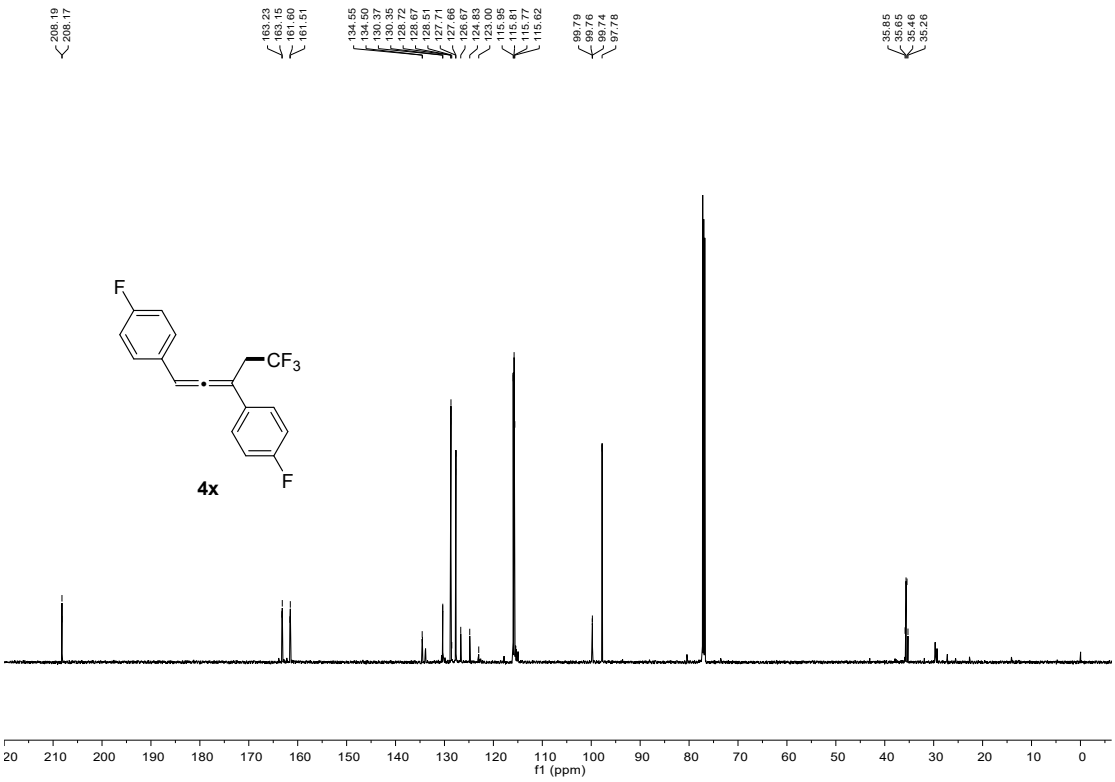

64.51
S
CF3
4v
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

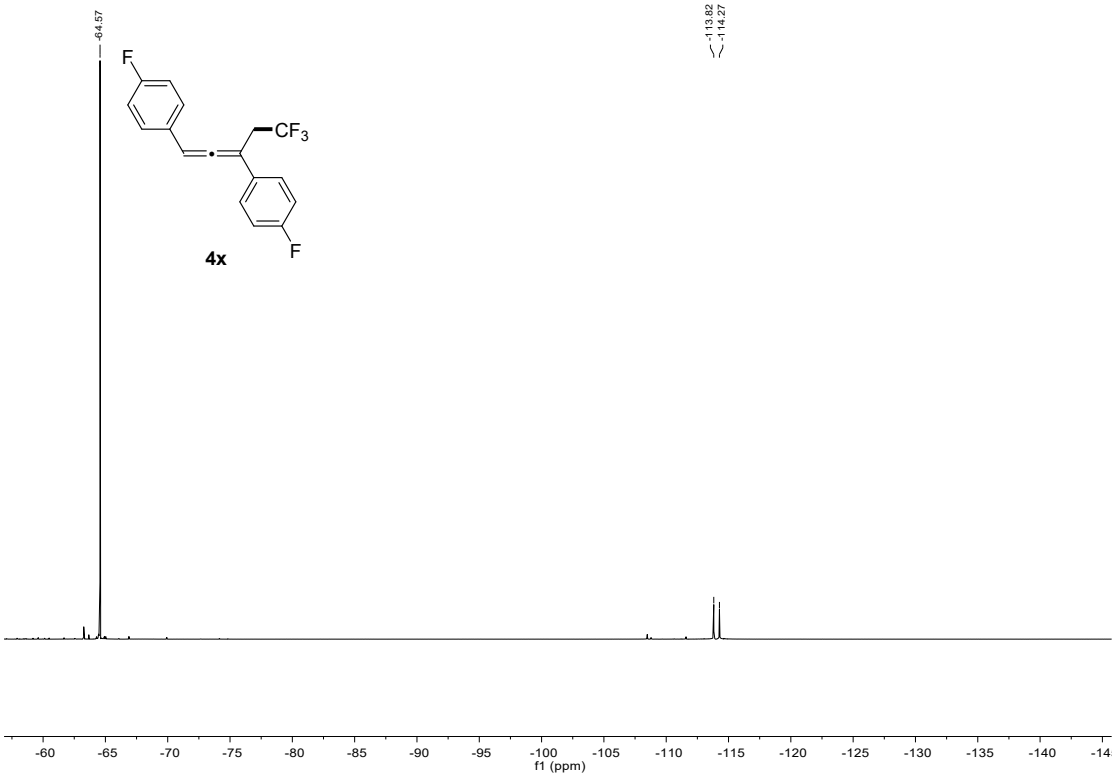

8.87
8.87
8.87
8.12
8.10
8.06
8.04
7.75
7.73
7.72
7.47
7.45
7.40
7.39
7.38
7.37
7.35
7.30
7.29
7.27
6.84
3.50
3.48
3.47
3.47
3.45
3.43
3.41
3.39
3.39
3.38
3.38
3.36
N
CF3
4w
1.02
2.00
2.09
2.05
3.11
1.07
1.00
2.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

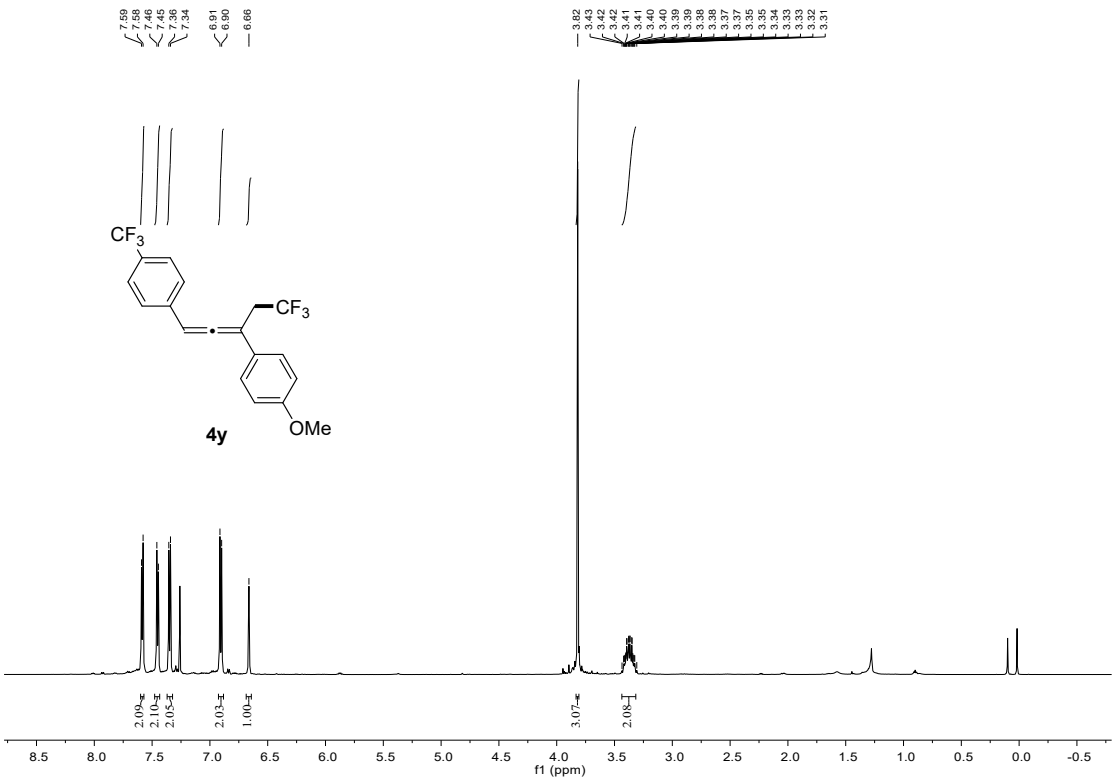

209.35
150.27
147.98
135.81
134.11
131.41
130.04
128.79
128.54
128.38
127.87
126.91
126.04
125.85
124.70
100.92
100.89
100.87
100.84
98.44
35.68
35.45
35.21
34.98
N
CF3
4w
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

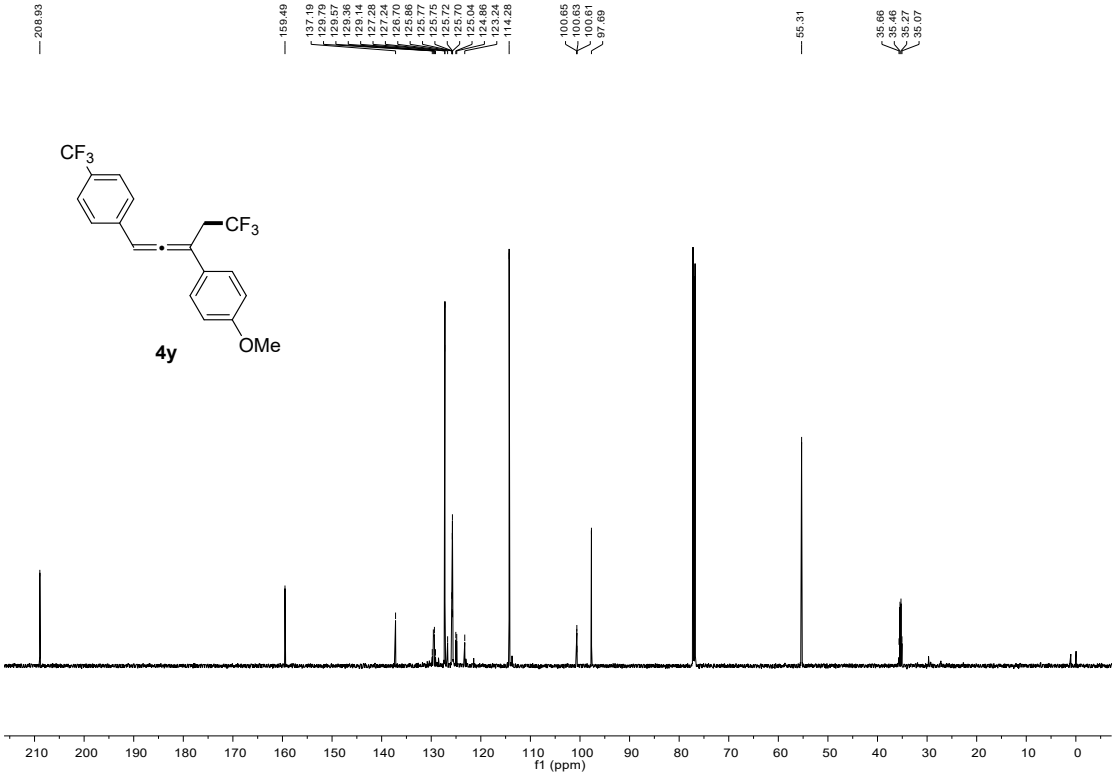

-64.42
N
CF3
4w
f1 (ppm)

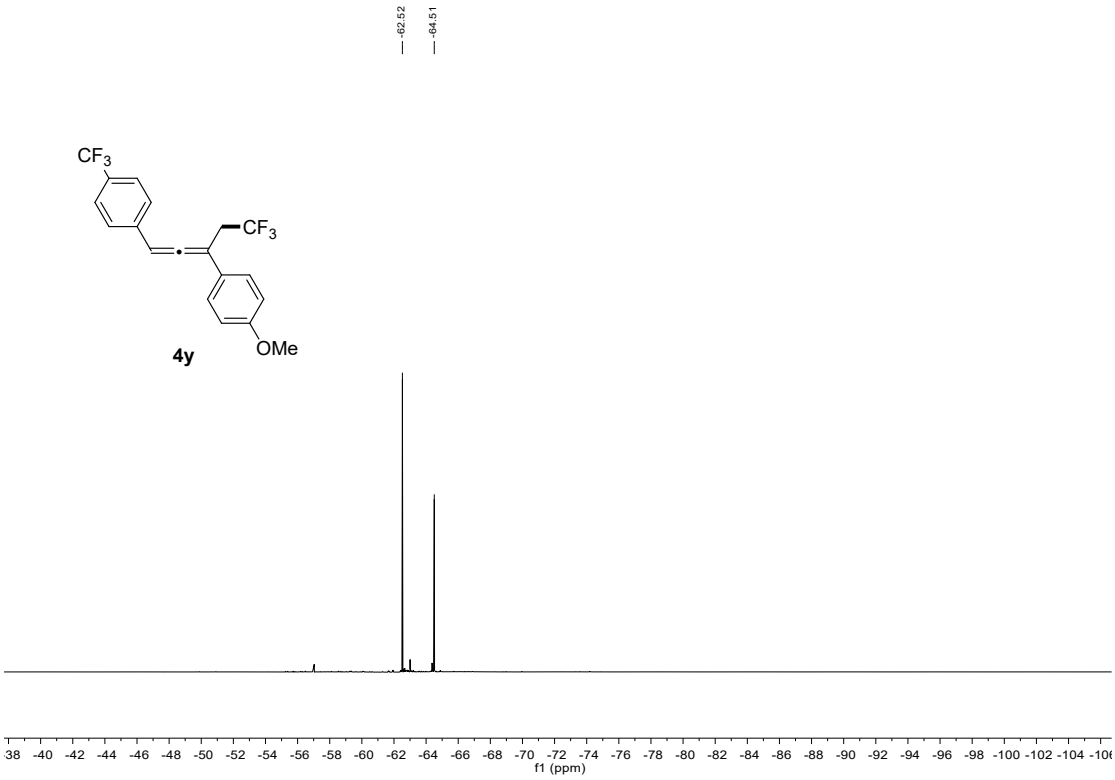

7.40
7.39
7.38
7.37
7.33
7.32
7.31
7.30
7.06
7.05
7.04
7.03
7.02
6.63
3.42
3.40
3.40
3.39
3.39
3.39
3.38
3.38
3.37
3.37
3.37
3.36
3.36
3.35
3.35
3.34
3.34
3.33
3.33
3.32
3.32
3.31
3.31
3.31
3.29
3.29
F
CF3
F
4x
F
CF3
F
4x
2.06
2.00
4.10
1.00
2.10
f1 (ppm)

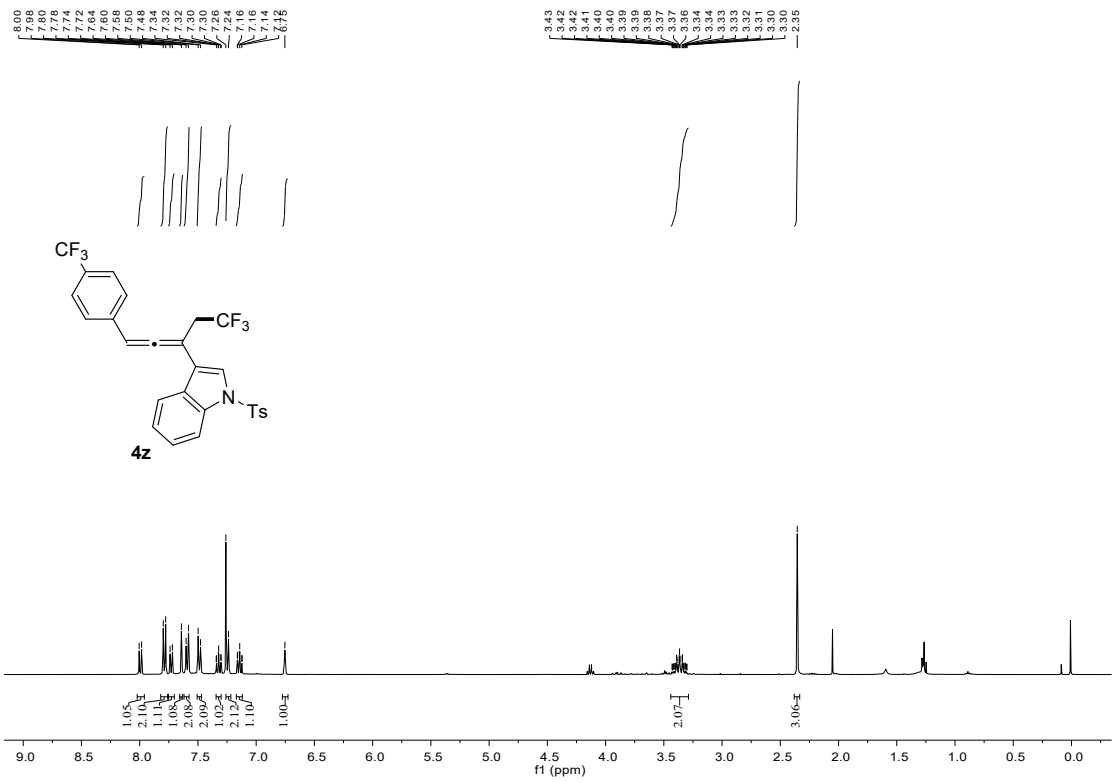

208.19
208.17
163.23
163.15
161.60
161.51
134.55
134.50
130.37
130.35
128.72
128.67
128.51
127.71
127.66
124.87
124.83
123.00
115.95
115.81
115.77
115.62
99.79
99.76
99.74
97.78
35.85
35.65
35.46
35.26
F
CF3
F
4x
f1 (ppm)

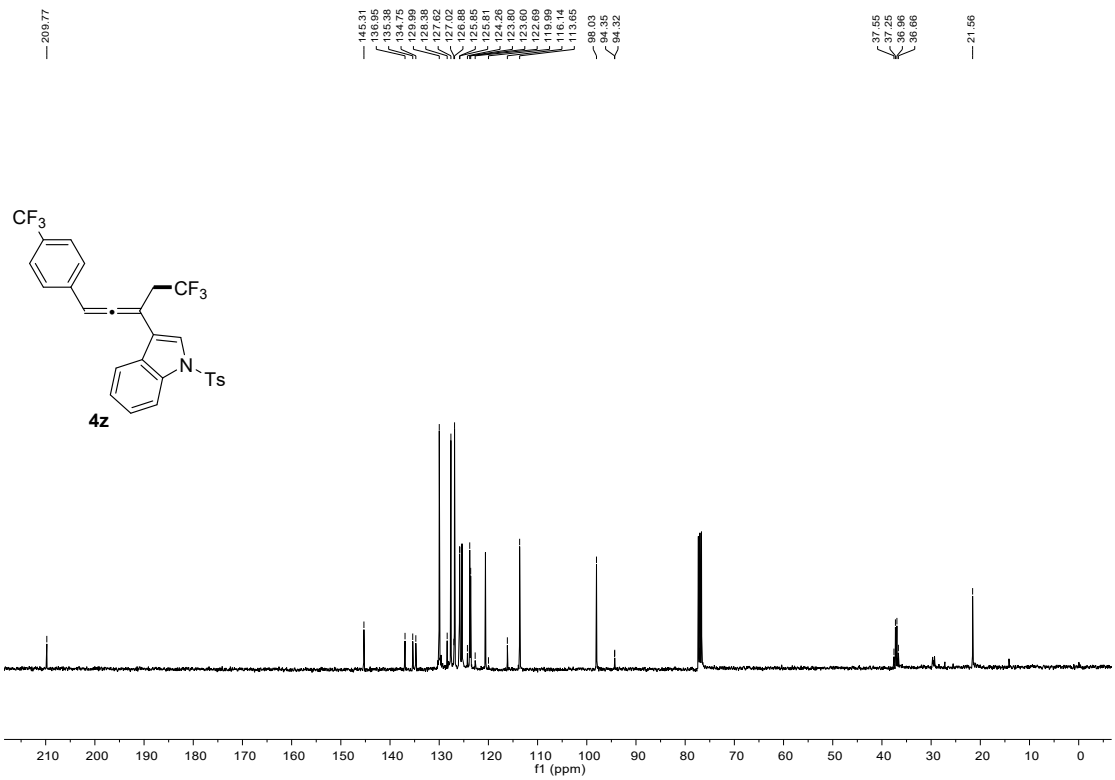

-64.57
-113.82
-114.27
F
CF3
F
4x
f1 (ppm)


7.59
7.58
7.46
7.45
7.36
7.34
6.91
6.90
6.66
3.82
3.43
3.42
3.42
3.41
3.41
3.40
3.40
3.39
3.39
3.38
3.38
3.38
3.37
3.37
3.35
3.35
3.34
3.33
3.33
3.32
3.31
CF3
CF3
OMe
4y
2.09
2.10
2.05
2.03
1.00
3.07
2.08
f1 (ppm)


208.93
159.49
137.19
129.79
129.57
129.36
129.14
127.24
126.70
125.86
125.77
125.75
125.72
125.70
125.04
124.86
123.24
114.28
100.65
100.63
100.61
97.69
55.31
35.66
35.46
35.27
35.07
CF3
CF3
OMe
4y
f1 (ppm)


-62.52
-64.51
CF3
CF3
OMe
4y
f1 (ppm)


CF3
CF3
N
Ts
4z
1.05
2.10
1.11
1.05
2.09
1.02
2.12
1.10
1.00
2.07
3.06
f1 (ppm)


209.77
145.31
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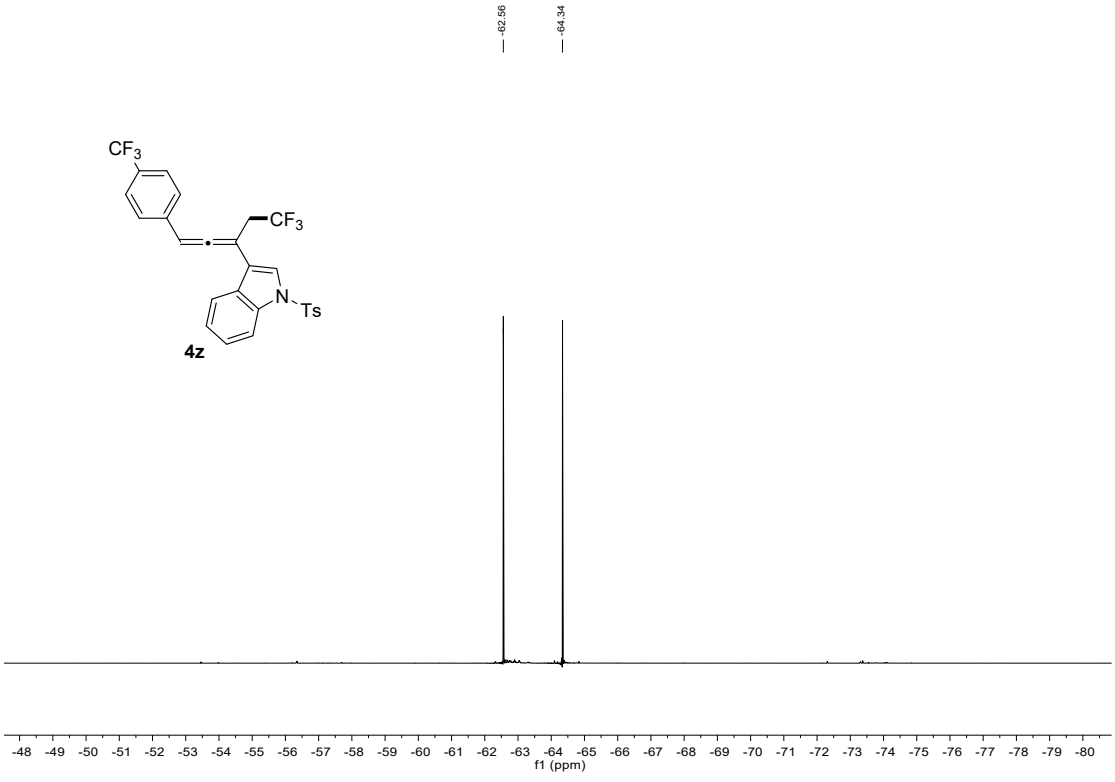
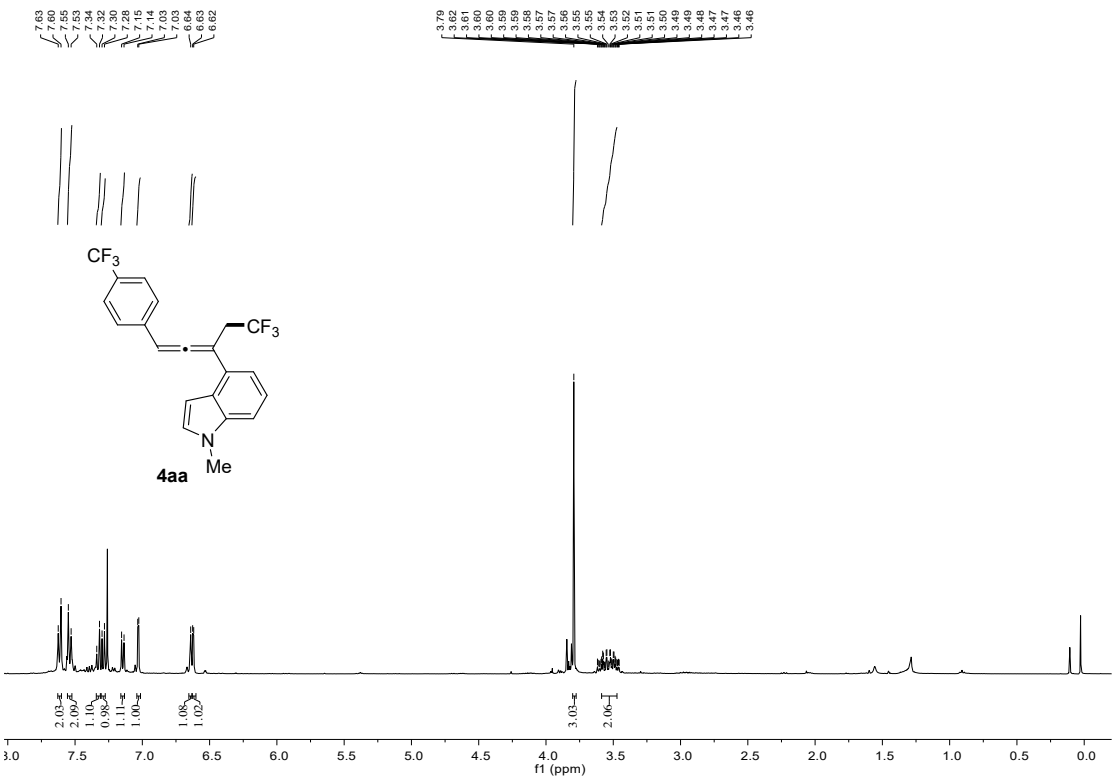
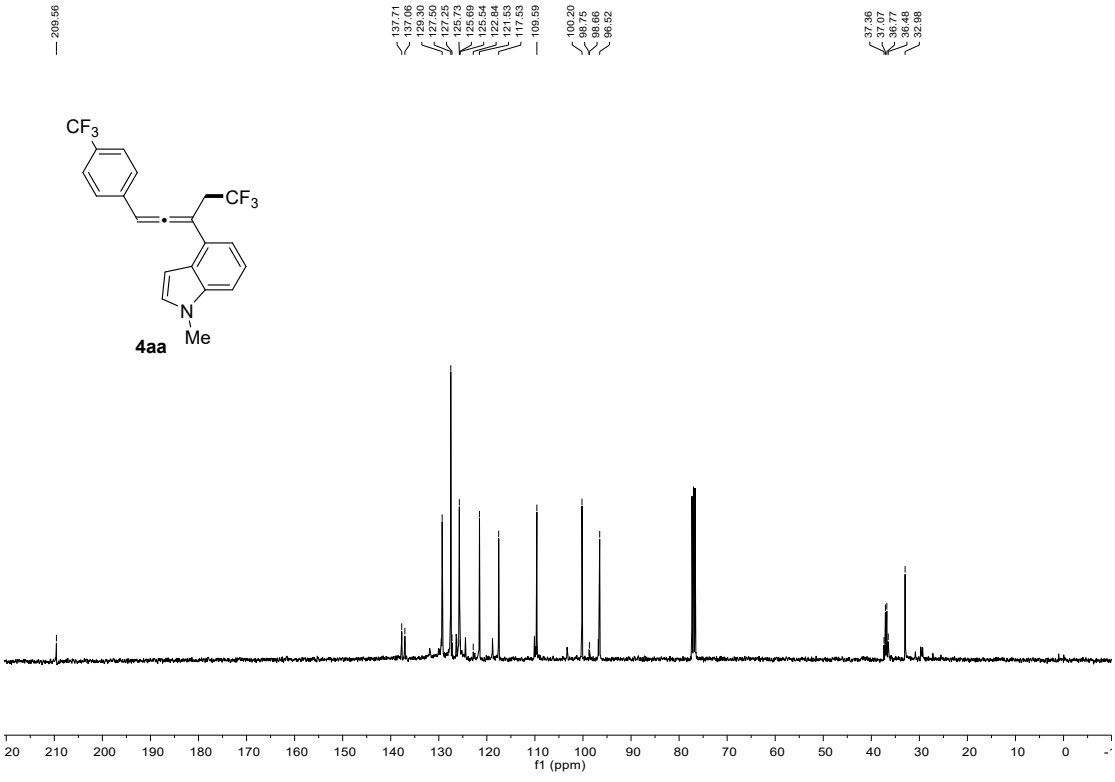
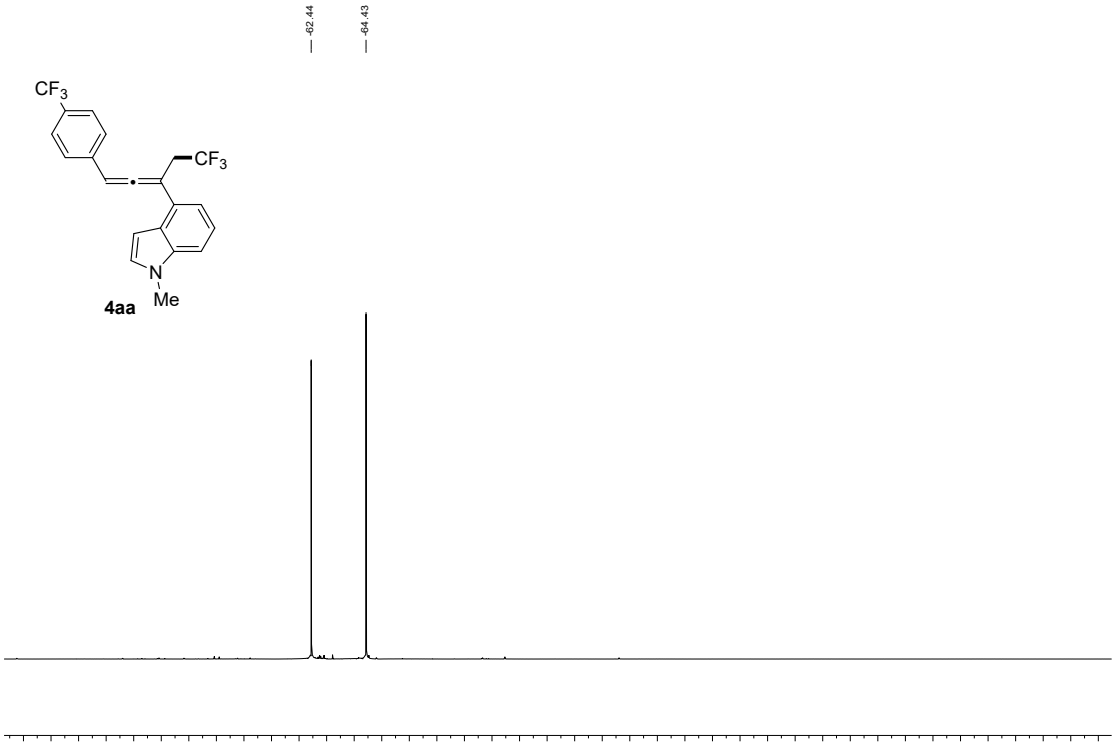
135.38
134.75
129.99
128.38
127.62
127.02
126.88
125.85
125.81
124.26
123.80
123.60
122.69
116.09
113.14
113.65
98.03
84.55
84.32
37.55
37.25
36.96
36.66
21.56
CF3
CF3
N
Ts
4z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.56
-64.34
CF3
CF3
N
Ts
4z
-48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80
f1 (ppm)


CF3
CF3
N
Me
4aa
f1 (ppm)


CF3
CF3
N
Me
4aa
f1 (ppm)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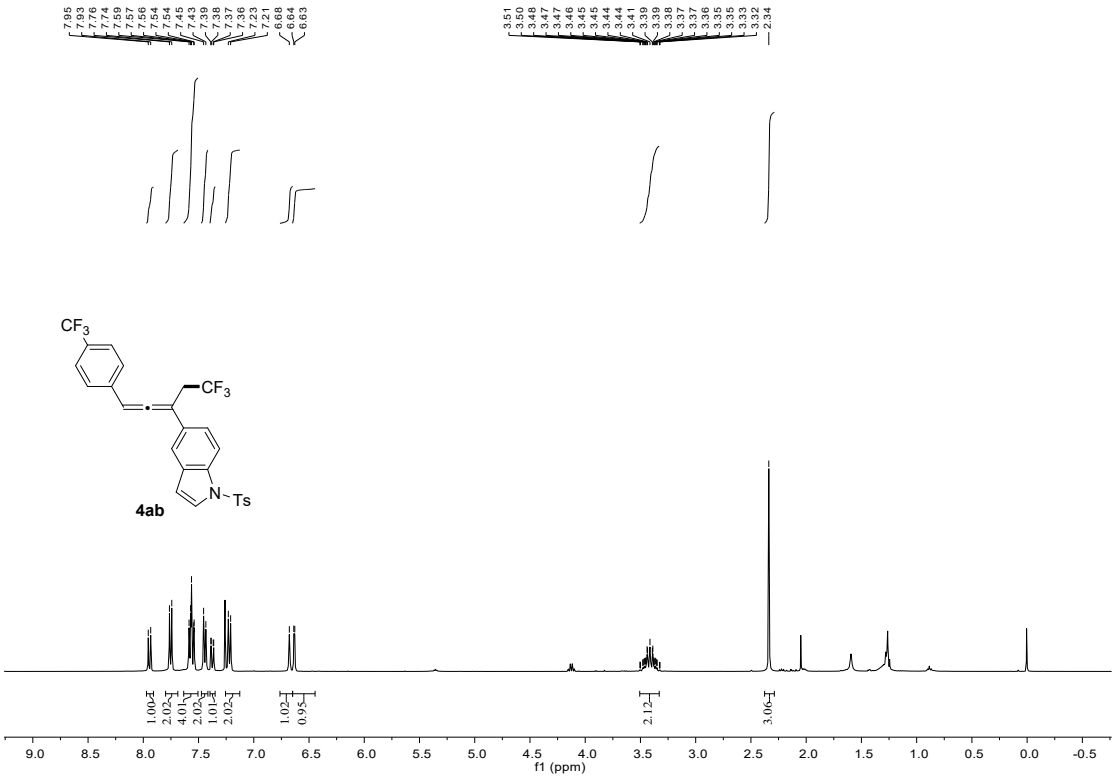
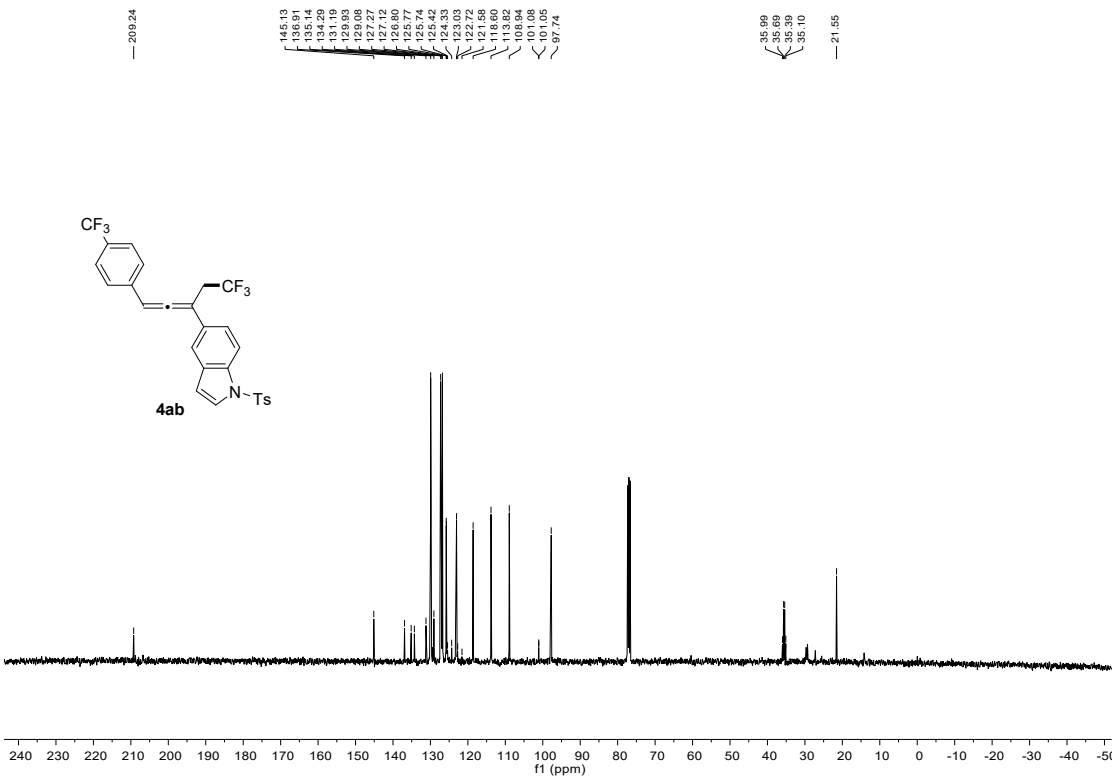
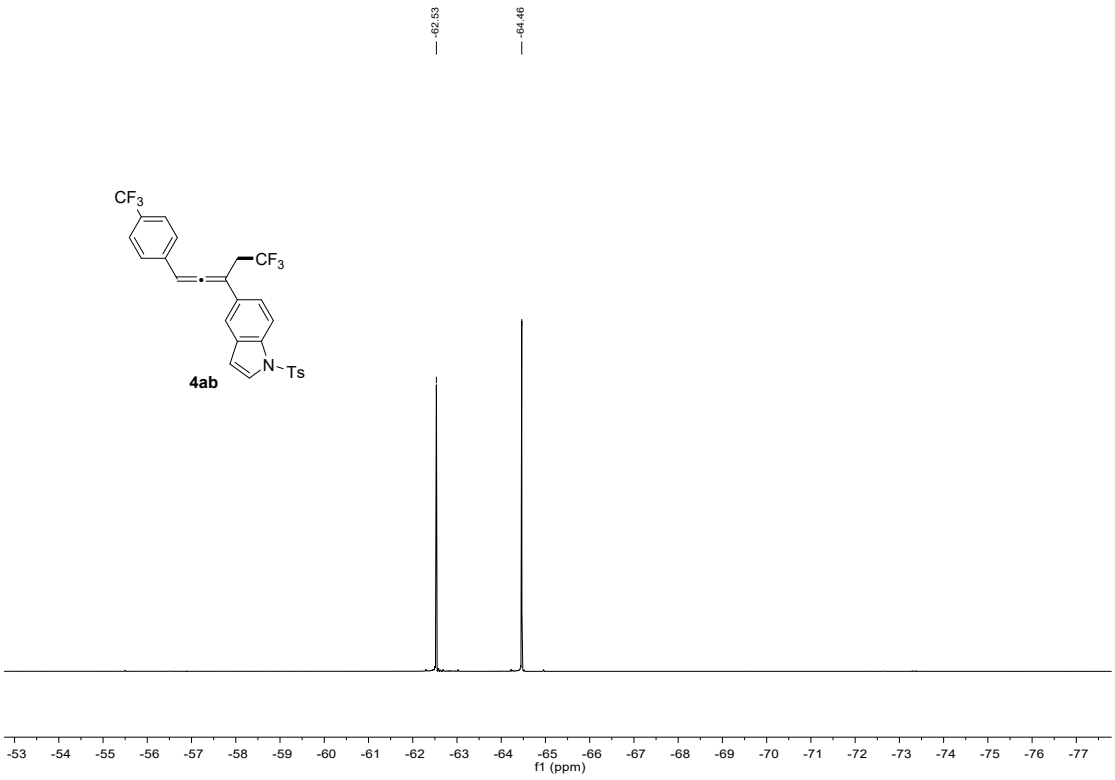
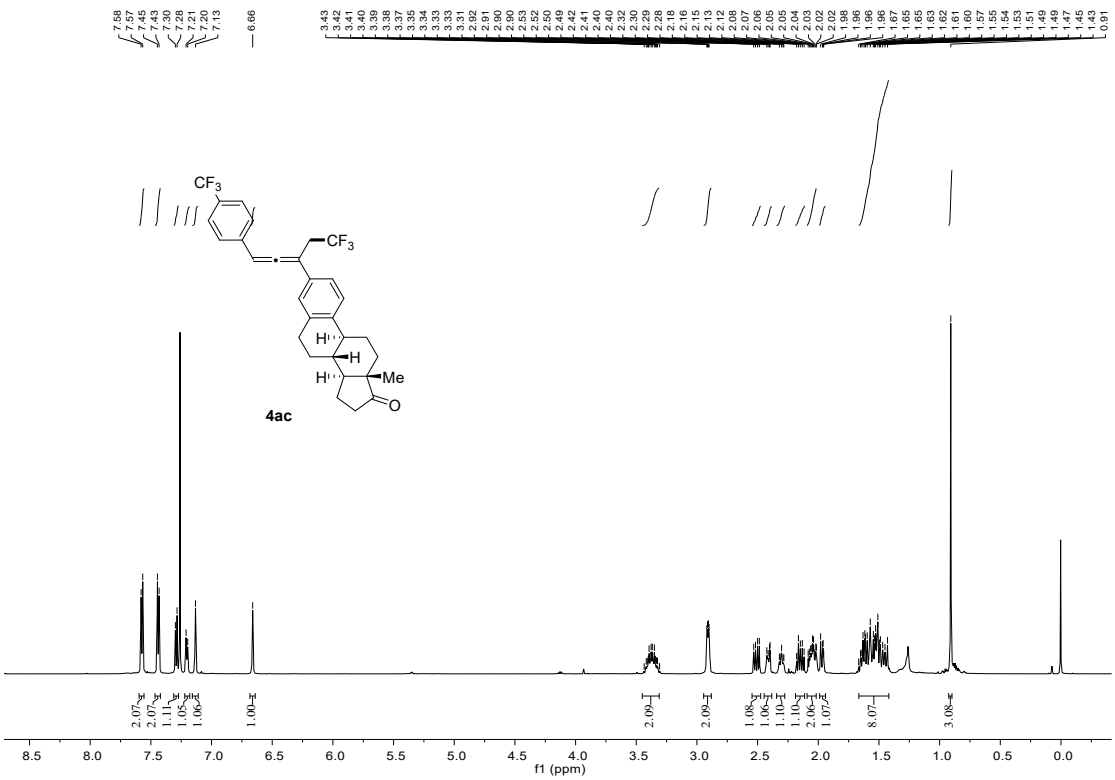
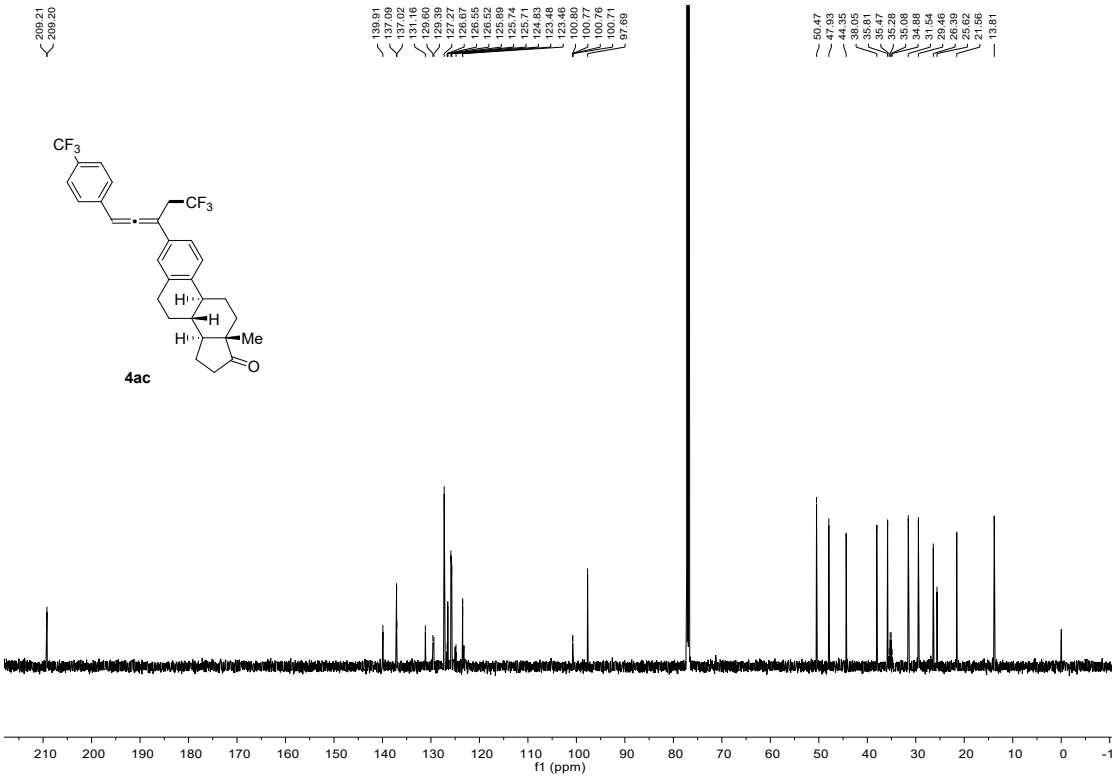
-64.43
CF3
CF3
N
Me
4aa
f1 (ppm)

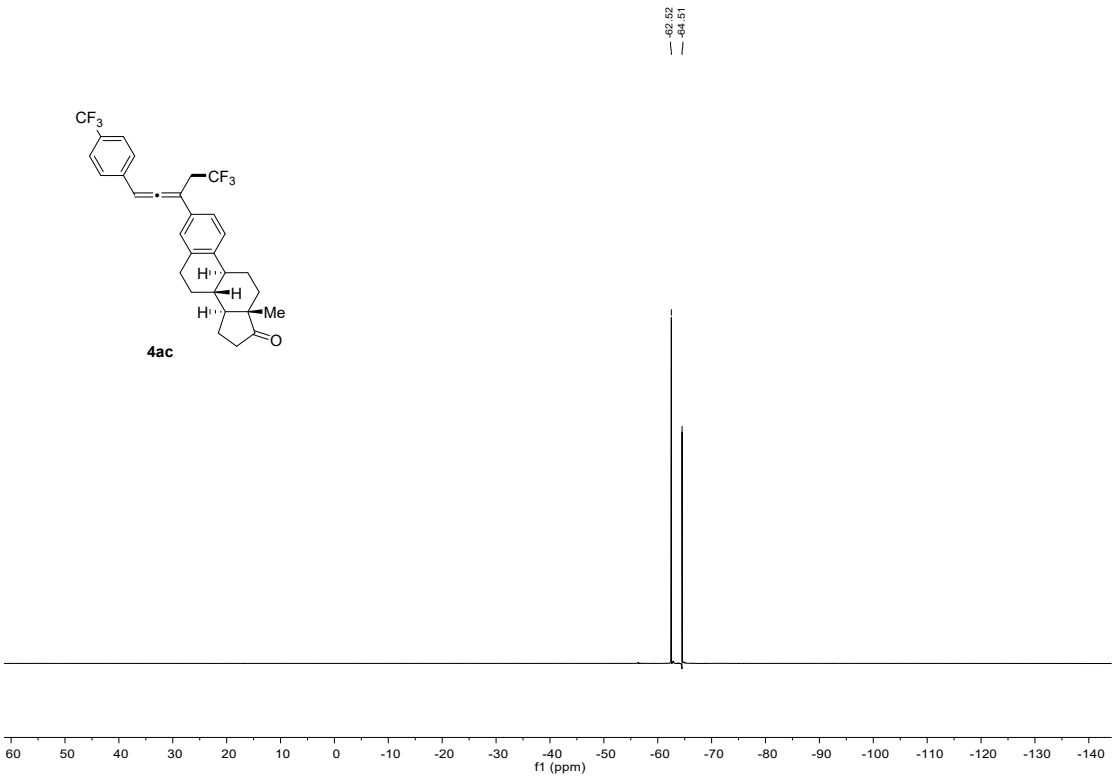

CF3
CF3
N
Ts
4ab
1.00
2.02
4.01
2.03
1.01
2.02
1.02
0.95
2.12
3.06
f1 (ppm)


209.24
145.13
136.61
135.14
134.29
131.19
129.93
129.08
127.27
127.12
126.80
125.77
125.74
125.42
124.33
123.03
122.72
121.58
118.60
111.92
109.84
101.08
101.05
97.74
35.99
35.69
35.39
35.10
21.55
CF3
CF3
N
Ts
4ab
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


-62.53
-64.46
CF3
CF3
N
Ts
4ab
-53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)


CF3
CF3
H
H
H
Me
O
4ac
f1 (ppm)


CF3
CF3
H
H
H
Me
O
4ac
f1 (ppm)


-62.52
-64.51
CF3
CF3
H
H
H
Me
O
4ac
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)