Electronic Supplementary Material (ESI) for Green Chemistry.

Selective synthesis of trisubstituted (trifluoromethyl)alkenes via ligand-free Cu-catalyzed syn hydroarylation, hydroalkenylation and hydroallylation of (trifluoromethyl)alkynes

Yoshihiko Yamamoto,* Erina Ohkubo, and Masatoshi Shibuya

Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University, Chikusa, Nagoya 464-8601, Japan

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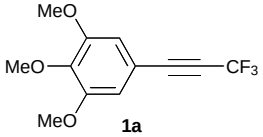
General Experimental

General methods: All air- and moisture-sensitive reactions were performed under an argon (Ar) atmosphere in dried glassware. Analytical thin layer chromatography was performed using 0.25 mm silica gel plate (Merck TLC Silica gel 60 F_{254}). Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. Melting points were recorded on SRS OptiMelt MPA100. NMR spectra were recorded on JEOL ESC-400 spectrometer (^{1}H/400 MHz, ^{13}C/100 MHz, and ^{19}F/376MHz) for samples in $CDCl_3$ solutions at 25 °C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for chloroform. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$. ^{19}F NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ –63.7 ppm for α,α,α-trifluorobenzene as an external standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. Infrared spectra were recorded on JASCO FT/IR-230 spectrometer. High-resolution mass spectra were recorded on JEOL JMS-T100LP mass spectrometer.

Reagents and Solvents: CF_3SiMe_3 (Fluorochem), CuI (Kanto Chemical), and $Cu(OAc)_2$ (Wako), were purchased and used as received. Other orgnoboron reagents were also purchased from Aldrich, TCI, or Wako and used as received. Other solvents and reagents were purchased from chemical suppliers (Aldrich, Kanto Chemical, TCI, and Wako) and used as received.

Experimental Procedures

The required substrates **1** were prepared from terminal alkynes according to the previous report with a slight modification of the reaction conditions.[1]



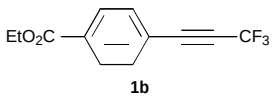
1a

General procedure for preparation of trifluoromethylalkynes. Synthesis of 1a: CuI

[1] C. Tresse, C. Guissart, S. Schweizer, Y. Bouhoute, A.-C. Chany, M.-L. Goddard, N. Blanchard and G. Evano, *Adv. Synth. Catal.*, 2014, **356**, 2051.

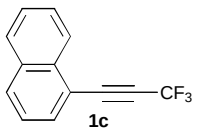
(857 mg, 4.5 mmol), TMEDA (671 μL, 4.5 mmol), and K_2CO_3 (1.24 g, 9.0 mmol) was stirred in dry DMF (13.8 mL) for 15 min at room temperature under an O_2 atmosphere. After the addition of CF_3SiMe_3 (936 μL, 6.0 mmol), the mixture was stirred for 20 min and was cooled to 0 °C. To this mixture was added a solution of 5-ethynyl-1,2,3-trimethoxybenzene (577 mg, 3.0 mmol) and CF_3SiMe_3 (936 μL, 6.0 mmol) in dry DMF (13.8 mL) via a cannula, and the resultant mixture was stirred for 30 min at 0 °C and then for 24 h at room temperature. The reaction was quenched by adding H_2O (30 mL) at 0 °C. The reaction mixture was extracted with Et_2O (3 × 40 mL). The combined organic layer was washed with H_2O (3 × 40 mL) and brine (40 mL) and was dried over $MgSO_4$. The solvents were evaporated *in vacuo*, and the obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 100:0~100:2) to afford **1a** (689 mg, 88% yield) as a colorless solid (mp 65.5–66.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.87 (s, 6 H), 3.88 (s, 3 H), 6.78 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 74.7 (q, J = 52 Hz), 86.7 (q, J = 6 Hz), 109.6, 113.0, 114.8 (q, J = 256 Hz), 140.9, 153.2; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –49.5; HRMS (DART) *m/z* calcd for $C_{12}H_{11}F_3O_3$•H 261.0739, found 261.0752 $[M+H]^+$.

Other trifluoromethylalkynes **1b**–**f** were also obtained according to the above general procedure.



1b

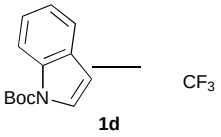
Analytical data for 1b: 71%, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.41 (t, J = 7.0 Hz, 3 H), 4.40 (q, J = 7.0 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 8.07 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 13.9, 61.3, 77.4 (q, J = 52 Hz), 85.2 (q, J = 6 Hz), 114.6 (q, J = 256 Hz), 122.5, 129.5, 132.2, 132.4, 165.2; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –50.3; IR (neat) 2257 (C≡C), 1725 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9F_3O_2$•Na 265.0452, found 265.0462 $[M+Na]^+$.



1c

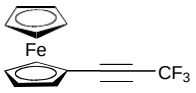
Analytical data for 1c: 73%, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.45 (t, J = 7.8 Hz, 1 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.83 (d, J = 6.8 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$,

25 °C): δ 80.1 (q, *J* = 52 Hz), 85.2 (q, *J* = 6 Hz), 115.1 (q, *J* = 256 Hz), 115.9, 124.9, 125.3, 127.0, 127.8, 128.6, 131.5, 132.5, 132.9, 133.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –49.5; HRMS (ESI) *m/z* calcd for $C_{13}H_7F_3$•Na 243.0398, found 243.0416 $[M+Na]^+$.



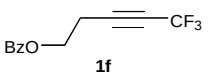
1d

Analytical data for 1d: 77%, pale-yellow solid (mp 87.9–88.6 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.71 (s, 9 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.0 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.98 (s, 1 H), 8.18 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 28.0, 79.2 (q, *J* = 52 Hz), 80.2 (q, *J* = 6 Hz), 85.2, 98.7, 115.0 (q, *J* = 255 Hz), 115.5, 119.8, 123.8, 125.8, 129.4, 132.2, 134.5, 148.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –49.3; IR (neat) 2245 (C≡C), 1743 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{16}H_{14}F_3NO_2$•H 310.1055, found 310.1057 $[M+H]^+$.



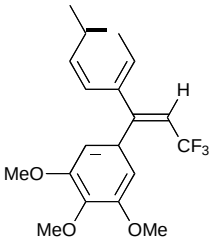
1e

Analytical data for 1e: 91%, red oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.27 (s, 5 H), 4.33 (t, *J* = 1.8 Hz, 2 H), 4.56 (t, *J* = 1.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 59.1, 70.1, 70.4, 72.2, 72.3 (q, *J* = 52 Hz), 87.9 (q, *J* = 6 Hz), 114.9 (q, *J* = 253 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –48.8; HRMS (DART) *m/z* calcd for $C_{13}H_9F_3Fe$•H 279.0084, found 279.0086 $[M+H]^+$.



1f

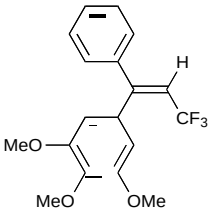
Analytical data for 1f: 40%, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.77–2.84 (tq, *J* = 6.4, 3.2 Hz, 2 H), 4.47 (t, *J* = 6.4 Hz, 2 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.59 (tt, *J* = 7.8, 1.2 Hz, 1 H), 8.06 (dd, *J* = 7.8, 1.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 18.9, 61.0, 69.7 (q, *J* = 52 Hz), 84.8 (q, *J* = 6 Hz), 113.9 (q, *J* = 256 Hz), 128.4, 129.5, 129.6, 133.3, 166.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –50.9; IR (neat) 2275 (C≡C), 1725 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9F_3O_2$•H 243.0633, found 243.0647 $[M+H]^+$.



3ad

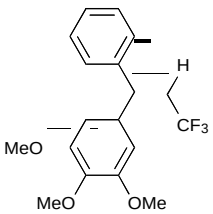
General procedure for hydroarylation. Synthesis of 3ad: A degassed solution of **1a** (130 mg, 0.5 mmol), **2d** (136 mg, 1.0 mmol), and $Cu(OAc)_2$ (0.93 mg, 0.005 mmol) in dry MeOH (1 mL) was stirred at 28 °C under an argon atmosphere for 3 h. The reaction mixture was diluted with AcOEt (3 mL) and filtered through a pad of alumina. The filtrate was concentrated in vacuo and the obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **3ad** (153 mg, 87% yield) as a colorless solid (mp 97.6–98.7 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.36 (s, 3 H), 3.80 (s, 6 H), 3.90 (s, 3 H), 6.06 (q, *J* = 8.4 Hz, 1 H), 6.47 (s, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.1, 56.0, 60.8, 106.6, 114.2 (q, *J* = 33 Hz), 123.2 (q, *J* = 269 Hz), 127.8, 129.1, 132.6, 136.9, 138.1, 139.7, 152.3, 152.7; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.2; HRMS (DART) *m/z* calcd for $C_{19}H_{19}F_3O_3$•NH_4 370.1630, found 370.1610 $[M+NH_4]^+$.

Other hydroarylation, hydroalkenylation, and hydroallylation were also performed according to the above general procedure.



3aa

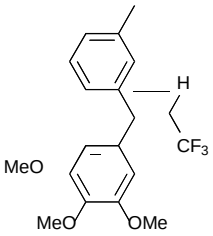
Analytical data for 3aa: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.81 (s, 6 H), 3.91 (s, 3 H), 6.08 (q, *J* = 8.4 Hz, 1 H), 6.46 (s, 2 H), 7.27–7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 106.7, 115.2 (q, *J* = 34 Hz), 123.1 (q, *J* = 269 Hz), 128.0, 128.5, 129.5, 132.5, 138.2, 139.9, 152.5 (q, *J* = 6 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; HRMS (DART) *m/z* calcd for $C_{18}H_{17}F_3O_3$•H 339.1208, found 339.1209 $[M+H]^+$.



3ab

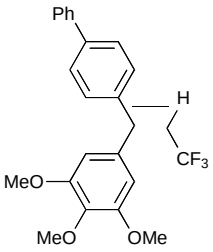
Analytical data for 3ab: colorless solid (mp 68.8–69.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.10 (s, 3 H), 3.77 (s, 6 H), 3.86 (s, 3 H), 5.75 (q, *J* = 8.7 Hz, 1 H), 6.49 (s, 2 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 7.19–7.28 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 20.1, 56.0, 60.8, 106.5, 117.5 (q, *J* = 34 Hz), 122.9 (q, *J* = 270 Hz), 125.8, 128.6, 129.3, 130.7, 132.7, 135.9, 138.5, 140.8, 152.6, 153.3 (q, *J* = 6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; HRMS (DART) *m/z* calcd for $C_{19}H_{19}F_3O_3$•H

353.1365, found 353.1367 $[M+H]^+$.



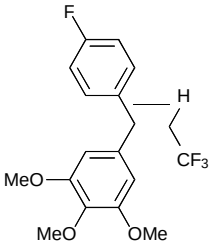
3ac

Analytical data for 3ac: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.35 (s, 3 H), 3.81 (s, 6 H), 3.91 (s, 3 H), 6.06 (q, *J* = 8.4 Hz, 1 H), 6.46 (s, 2 H), 7.07 (d, *J* = 7.2 Hz, 1 H), 7.11 (s, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.22 (dd, *J* = 7.6, 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.3, 56.1, 60.9, 106.6, 115.0 (q, *J* = 34 Hz), 123.1 (q, *J* = 269 Hz), 125.2, 128.3, 128.5, 130.3, 132.6, 138.1, 139.8, 152.6 (q, *J* = 6 Hz), 152.7; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.4; HRMS (DART) *m/z* calcd for $C_{19}H_{19}F_3O_3$•H 353.1365, found 353.1386 $[M+H]^+$.



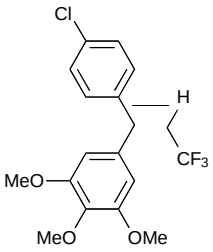
3ae

Analytical data for 3ae: colorless solid (mp 112.2–113.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.84 (s, 6 H), 3.94 (s, 3 H), 6.16 (q, *J* = 8.4 Hz, 1 H), 6.52 (s, 2 H), 7.35–7.41 (m, 3 H), 7.44–7.49 (m, 2 H), 7.57–7.63 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 106.6, 114.9 (q, *J* = 34 Hz), 123.1 (q, *J* = 269 Hz), 127.0, 127.1, 127.8, 128.4, 128.8, 132.4, 138.2, 138.6, 140.0, 142.3, 152.0 (q, *J* = 6 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.2; HRMS (DART) *m/z* calcd for $C_{24}H_{21}F_3O_3$•H 415.1521, found 415.1505 $[M+H]^+$.



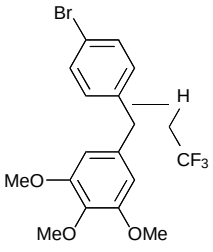
3af

Analytical data for 3af: colorless solid (mp 102.8–105.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.82 (s, 6 H), 3.91 (s, 3 H), 6.04 (q, *J* = 8.3 Hz, 1 H), 6.46 (s, 2 H), 7.03 (t, *J* = 8.6 Hz, 2 H), 7.15 (dd, *J* = 8.8, 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.0, 60.8, 106.5, 114.9 (q, *J* = 34 Hz), 115.4 (d, *J* = 22 Hz), 122.9 (q, *J* = 269 Hz), 129.8 (d, *J* = 9 Hz), 132.2, 135.9 (d, *J* = 3 Hz), 138.3, 151.4 (q, *J* = 5 Hz), 152.8, 163.5 (d, *J* = 249 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –111.4, –55.3; HRMS (DART) *m/z* calcd for $C_{18}H_{16}F_4O_3$•H 357.1114, found 357.1109 $[M+H]^+$.



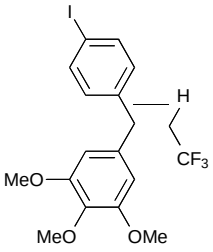
3ag

Analytical data for 3ag: colorless solid (mp 106.7–109.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.81 (s, 6 H), 3.90 (s, 3 H), 6.05 (q, *J* = 8.3 Hz, 1 H), 6.43 (s, 2 H), 7.22 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 55.9, 60.7, 106.5, 115.3 (q, *J* = 34 Hz), 122.8 (q, *J* = 269 Hz), 128.6, 129.2, 131.9, 135.5, 138.2, 138.3, 151.3 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; HRMS (DART) *m/z* calcd for $C_{18}H_{16}ClF_3O_3$•H 373.0818, found 373.0816 $[M+H]^+$.



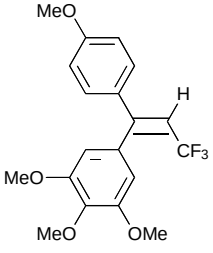
3ah

Analytical data for 3ah: colorless solid (mp 88.4–89.2 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.78 (s, 6 H), 3.88 (s, 3 H), 6.04 (q, *J* = 8.1 Hz, 1 H), 6.42 (s, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.0, 60.8, 106.5, 115.4 (q, *J* = 34 Hz), 122.8 (q, *J* = 269 Hz), 123.8, 129.5, 131.6, 131.9, 138.3, 138.7, 151.4 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.5; HRMS (DART) *m/z* calcd for $C_{18}H_{16}BrF_3O_3$•H 417.0313, found 417.0323 $[M+H]^+$.



3ai

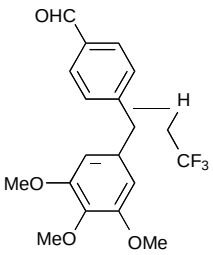
Analytical data for 3ai: pale-yellow solid (mp 73.9–76.9 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.80 (s, 6 H), 3.90 (s, 3 H), 6.06 (q, *J* = 8.3 Hz, 1 H), 6.42 (s, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.0, 60.8, 95.8, 106.5, 115.4 (q, *J* = 34 Hz), 122.8 (q, *J* = 269 Hz), 129.6, 131.8, 137.5, 138.3, 139.3, 151.5 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.6; HRMS (DART) *m/z* calcd for $C_{18}H_{16}F_3IO_3$•NH_4 482.0440, found 482.0429 $[M+NH_4]^+$.



3aj

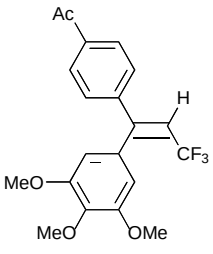
Analytical data for 3aj: colorless solid (mp 68.7–70.1 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.79 (s, 9 H), 3.89 (s, 3 H), 6.00 (q, *J* = 8.4 Hz, 1 H), 6.46 (s, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 55.1, 55.9, 60.8, 113.0 (q, *J* = 34 Hz), 113.7, 123.2 (q, *J* = 269 Hz), 129.3, 132.0,

132.7, 138.0, 151.8 (q, J = 6 Hz), 152.7, 160.7; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.0; HRMS (DART) *m/z* calcd for $C_{19}H_{19}F_3O_4$•H 369.1314, found 369.1311 $[M+H]^+$.



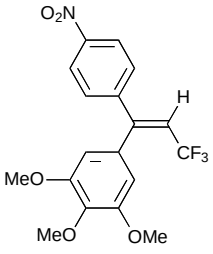
3ak

Analytical data for 3ak: colorless solid (mp 115.1–115.8 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.80 (s, 6 H), 3.90 (s, 3 H), 6.16 (q, J = 8.1 Hz, 1 H), 6.43 (s, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.86 (d, J = 8.0 Hz, 2 H), 10.0 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 106.6, 117.4 (q, J = 34 Hz), 122.7 (q, J = 270 Hz), 128.7, 129.7, 131.6, 136.8, 138.5, 145.6, 151.4 (q, J = 5 Hz), 153.0 191.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; IR (neat) 1704 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{19}H_{17}F_3O_4$•H 367.1157, found 367.1152 $[M+H]^+$.



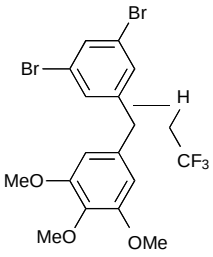
3al

Analytical data for 3al: colorless solid (mp 126.3–127.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.61 (s, 3 H), 3.80 (s, 6 H), 3.90 (s, 3 H), 6.14 (q, J = 8.1 Hz, 1 H), 6.43 (s, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.92 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 26.7, 56.1, 60.9, 106.6, 116.9 (q, J = 34 Hz), 122.8 (q, J = 269 Hz), 128.2, 128.4, 131.8, 137.6, 138.5, 144.3, 151.5 (q, J = 5 Hz), 153.0 197.4; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; IR (neat) 1682 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{20}H_{19}F_3O_4$•NH_4 398.1579, found 398.1577 $[M+NH_4]^+$.



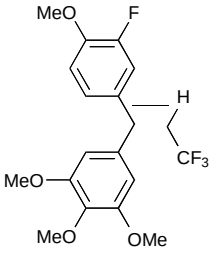
3am

Analytical data for 3am: pale-yellow solid (mp 126.4–127.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.81 (s, 6 H), 3.91 (s, 3 H), 6.17 (q, J = 7.9 Hz, 1 H), 6.42 (s, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 8.21 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.0, 60.8, 106.4, 118.0 (q, J = 34 Hz), 122.4 (q, J = 270 Hz), 128.9, 131.1, 138.6, 146.0, 148.2, 150.5 (q, J = 5 Hz), 153.0; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –57.0; HRMS (DART) *m/z* calcd for $C_{18}H_{16}F_3NO_5$•NH_4 401.1324, found 401.1322 $[M+NH_4]^+$.



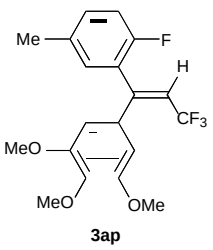
3an

Analytical data for 3an: colorless solid (mp 117.9–118.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.80 (s, 6 H), 3.90 (s, 3 H), 6.03 (q, *J* = 8.1 Hz, 1 H), 6.40 (s, 2 H), 7.34 (d, *J* = 1.6 Hz, 2 H), 7.65 (t, *J* = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.8, 106.4, 117.3 (q, *J* = 34 Hz), 122.4 (q, *J* = 270 Hz), 123.1, 129.7, 130.9, 134.8, 138.6, 143.5, 150.0 (q, *J* = 5 Hz), 153.0; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.9; HRMS (DART) *m/z* calcd for $C_{18}H_{15}Br_2F_3O_5$•H 494.9418, found 494.9411 $[M+H]^+$.



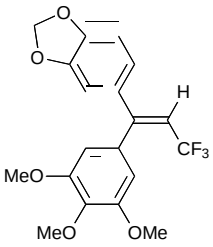
3ao

Analytical data for 3ao: colorless solid (mp 90.5–91.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.81 (s, 6 H), 3.90 (s, 6 H), 6.00 (q, *J* = 8.3 Hz, 1 H), 6.43 (s, 2 H), 6.91 (t, *J* = 8.8 Hz, 1 H), 7.00–7.05 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 56.2, 60.9, 106.5, 112.8, 114.3 (q, *J* = 34 Hz), 115.6 (d, *J* = 19 Hz), 123.1 (q, *J* = 269 Hz), 124.2 (d, *J* = 4 Hz), 132.1, 132.7 (d, *J* = 6 Hz), 138.3, 148.8 (d, *J* = 11 Hz), 150.9 (q, *J* = 5 Hz), 152.0 (d, *J* = 246 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –135.5, –56.3; HRMS (DART) *m/z* calcd for $C_{19}H_{18}F_4O_4$•H 387.1219, found 387.1208 $[M+H]^+$.



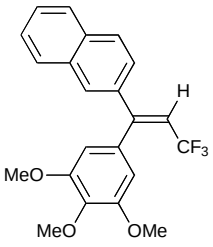
3ap

Analytical data for 3ap: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.28 (s, 3 H), 3.81 (s, 6 H), 3.90 (s, 3 H), 6.06 (q, *J* = 8.4 Hz, 1 H), 6.47 (s, 2 H), 6.90 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.96 (dd, *J* = 10.6, 8.2 Hz, 1 H), 7.11 (ddd, *J* = 7.6, 4.4, 2.0 Hz,1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 20.5, 56.1, 60.9, 106.2, 115.9 (d, *J* = 21 Hz), 119.0 (dq, *J* = 34, 6 Hz), 122.8 (q, *J* = 270 Hz), 127.6 (d, *J* = 12 Hz), 131.2 (d, *J* = 9 Hz), 131.3, 132.5, 133.6 (d, *J* = 4 Hz), 138.3, 147.2 (q, *J* = 6 Hz), 152.8, 158.1 (d, *J* = 247 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –119.0, –55.7; HRMS (DART) *m/z* calcd for $C_{19}H_{18}F_4O_3$•NH_4 388.1536, found 388.1514 $[M+NH_4]^+$.



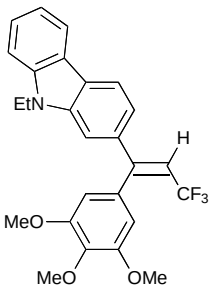
3aq

Analytical data for 3aq: colorless solid (mp 93.4–94.2 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 3.82 (s, 6 H), 3.90 (s, 3 H), 5.98 (q, *J* = 8.4 Hz, 1 H), 5.99 (s, 2 H), 6.44 (s, 2 H), 6.75–6.80 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 101.5, 106.6, 108.01, 108.04, 113.8 (q, *J* = 33 Hz), 122.6, 123.1 (q, *J* = 269 Hz), 132.6, 134.0, 138.2, 147.9, 148.8, 151.9 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –54.9; HRMS (DART) *m/z* calcd for $C_{19}H_{17}F_3O_5$•H 383.1106, found 383.1101 $[M+H]^+$.



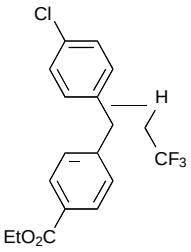
3ar

Analytical data for 3ar: colorless solid (mp 83.0–84.7 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.82 (s, 6 H), 3.97 (s, 3 H), 6.25 (q, *J* = 8.3 Hz, 1 H), 6.57 (s, 2 H), 7.45 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.48–7.55 (m, 2 H), 7.75 (s, 1 H), 7.79–7.86 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 55.9, 60.8, 106.6, 115.4 (q, *J* = 34 Hz), 123.1 (q, *J* = 269 Hz), 124.8, 126.5, 126.9, 127.5, 128.06, 128.10, 128.5, 132.4, 132.8, 133.5, 137.0, 138.1, 152.4 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.1; HRMS (DART) *m/z* calcd for $C_{22}H_{19}F_3O_3$•H 389.1365, found 389.1359 $[M+H]^+$.



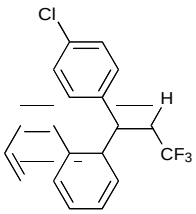
3as

Analytical data for 3as: colorless solid (mp 124.8–126.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.46 (t, *J* = 7.4 Hz, 3 H), 3.84 (s, 6 H), 3.98 (s, 3 H), 4.37 (q, *J* = 7.4 Hz, 2 H), 6.19 (q, *J* = 8.4 Hz, 1 H), 6.59 (s, 2 H), 7.24–7.29 (m, 1 H), 7.36 (d, *J* = 8.8 Hz, 1 H), 7.40–7.45 (m, 2 H), 7.48–7.53 (m, 1 H), 8.05 (d, *J* = 1.2 Hz, 1 H), 8.09 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 13.7, 37.6, 56.1, 60.9, 106.8, 108.2, 108.7, 113.1 (q, *J* = 33 Hz), 119.4, 120.4, 120.5, 122.7, 122.9, 123.5 (q, *J* = 269 Hz), 125.9, 126.2, 130.7, 133.4, 138.1, 140.4, 140.5, 152.7, 153.3 (q, *J* = 6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –54.5; HRMS (DART) *m/z* calcd for $C_{26}H_{24}F_3NO_3$•H 456.1787, found 456.1760 $[M+H]^+$.



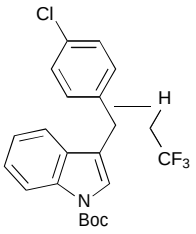
3bg

Analytical data for 3bg: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.41 (t, *J* = 7.0 Hz, 3 H), 4.41 (q, *J* = 7.0 Hz, 2 H), 6.17 (q, *J* = 8.0 Hz, 1 H), 7.13–7.18 (m, 2 H), 7.28–7.33 (m, 4 H), 8.06–8.10 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 14.3, 61.2, 116.4 (q, *J* = 34 Hz), 122.7 (q, *J* = 270 Hz), 128.9, 129.04, 129.09, 129.4, 130.8, 135.9, 137.7, 141.2, 150.3 (q, *J* = 6 Hz), 166.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.7; IR (neat) 1717 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{18}H_{14}ClF_3O_2 \bullet NH_4$ 372.0978, found 372.0973 $[M+NH_4]^+$.



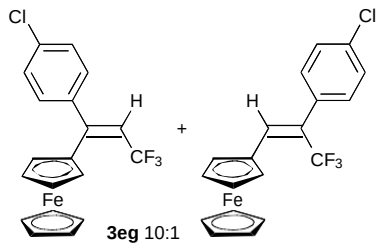
3cg

Analytical data for 3cg: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.49 (q, *J* = 8.0 Hz, 1 H), 7.22–7.29 (m, 4 H), 7.37–7.45 (m, 2 H), 7.45–7.51 (m, 1 H), 7.53–7.62 (m, 2 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.93 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 117.5 (q, *J* = 34 Hz), 122.9 (q, *J* = 269 Hz), 125.0, 125.5, 126.1, 126.5, 126.91, 126.93, 128.3, 128.4, 129.0, 129.1, 131.1, 133.5, 133.6, 135.6, 137.4, 149.7 (q, *J* = 5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.9; HRMS (DART) *m/z* calcd for $C_{19}H_{12}ClF_3 \bullet NH_4$ 350.0923, found 350.0916 $[M+NH_4]^+$.



3dg

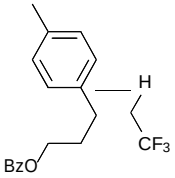
Analytical data for 3dg: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.73 (s, 9 H), 6.22 (q, *J* = 7.9 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 7.28–7.35 (m, 5 H), 7.81 (s, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 28.1, 84.4, 115.3, 115.7, 117.5 (q, *J* = 34 Hz), 120.4, 122.93 (q, *J* = 269 Hz), 122.94, 124.7, 126.1 (q, *J* = 1 Hz), 128.8, 129.0, 129.3, 135.2, 135.7, 137.3, 143.6 (q, *J* = 5 Hz), 149.4; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.5; IR (neat) 1739 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{22}H_{19}ClF_3NO_2 \bullet NH_4$ 439.1400, found 439.1410 $[M+NH_4]^+$.



3eg 10:1

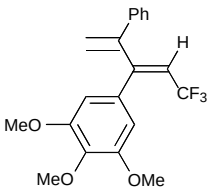
Analytical data for 3ag: red solid (mp 88.2–92.8 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): (major) δ 4.14 (s, 5 H), 4.42 (t, *J* = 1.8 Hz, 2 H), 4.45 (t, *J* = 1.8 Hz, 2 H), 5.56 (q, *J* = 9.9 Hz, 1 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 7.40

(d, *J* = 8.6 Hz, 2 H); (minor) δ 3.87 (t, *J* = 1.8 Hz, 2 H), 4.13 (s, 5 H), 4.22 (t, *J* = 1.8 Hz, 2 H), 7.04 (s, 1 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (major) δ 69.9, 70.6 (q, *J* = 3 Hz), 70.7, 113.8 (q, *J* = 36 Hz), 123.2 (q, *J* = 269 Hz), 128.2, 129.5, 133.9, 140.6, 151.8 (q, *J* = 6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): (major) δ –56.6; (minor) δ –65.1; HRMS (DART) *m/z* calcd for $C_{19}H_{14}ClF_3Fe$•H 391.0164, found 391.0159 $[M+H]^+$.



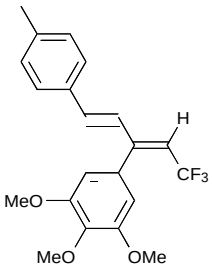
3fc

Analytical data for 3fc: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.35 (s, 3 H), 3.20 (t, *J* = 6.8 Hz, 2 H), 4.33 (t, *J* = 6.8 Hz, 2 H), 5.90 (q, *J* = 8.5 Hz, 1 H), 7.18 (d, *J* = 8.6 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.1, 30.3, 62.8, 117.7 (q, *J* = 34 Hz), 123.4 (q, *J* = 270 Hz), 126.5, 128.2, 129.5, 129.9, 132.9, 136.2, 139.3, 150.0 (q, *J* = 5 Hz), 166.3; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.2; IR (neat) 1722 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{19}H_{17}F_3O_2$•H 335.1259, found 335.1285 $[M+H]^+$.



5aa

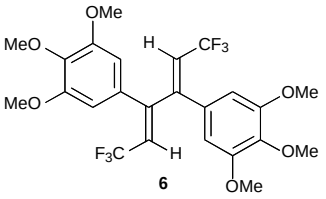
Analytical data for 5aa: pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.84 (s, 6 H), 3.88 (s, 3 H), 5.25 (s, 1 H), 5.49 (s, 1 H), 5.71 (q, *J* = 8.4 Hz, 1 H), 6.52 (s, 2 H), 7.30–7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 106.4, 118.3 (q, *J* = 34 Hz), 121.9, 123.1 (q, *J* = 269 Hz), 128.0, 128.3, 128.4, 131.3, 138.0, 139.4, 149.9, 152.2 (q, *J* = 5 Hz), 152.7; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.6; HRMS (DART) *m/z* calcd for $C_{20}H_{19}F_3O_3$•NH_4 382.1630, found 382.1626 $[M+NH_4]^+$.



5ab

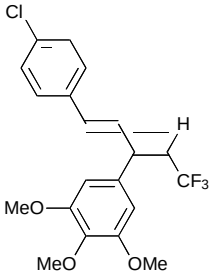
Analytical data for 5ab: colorless solid (mp 92.1–93.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.34 (s, 3 H), 3.85 (s, 6 H), 3.93 (s, 3 H), 5.84 (q, *J* = 8.4 Hz, 1 H), 6.40 (d, *J* = 16.0 Hz, 1 H), 6.47 (s, 2 H), 6.90 (d, *J* = 16.0 Hz, 1 H), 7.14 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.2, 56.1, 60.9, 106.1, 117.0 (q, *J* = 33 Hz), 123.1 (q, *J* = 269 Hz), 127.0, 128.39, 129.4, 130.4, 133.1, 137.5, 137.8, 138.9, 150.4 (q, *J* = 6 Hz),

152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.3; HRMS (DART) *m/z* calcd for $C_{21}H_{21}F_3O_3$•NH_4 396.1787, found 396.1760 $[M+NH_4]^+$.



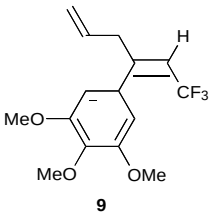
6

Analytical data for 6: pale-yellow solid (mp 177.4–178.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 (C): δ 3.88 (s, 12 H), 3.92 (s, 6 H), 5.67 (q, *J* = 7.7 Hz, 1 H), 6.43 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.2, 60.9, 106.3, 122.5 (q, *J* = 270 Hz), 123.2 (q, *J* = 34 Hz), 129.2, 138.3, 151.3(q, *J* = 5 Hz), 153.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –57.5; HRMS (ESI) *m/z* calcd for $C_{24}H_{24}F_6O_6$•Na 545.1375, found 545.1377 $[M+Na]^+$.



5ac

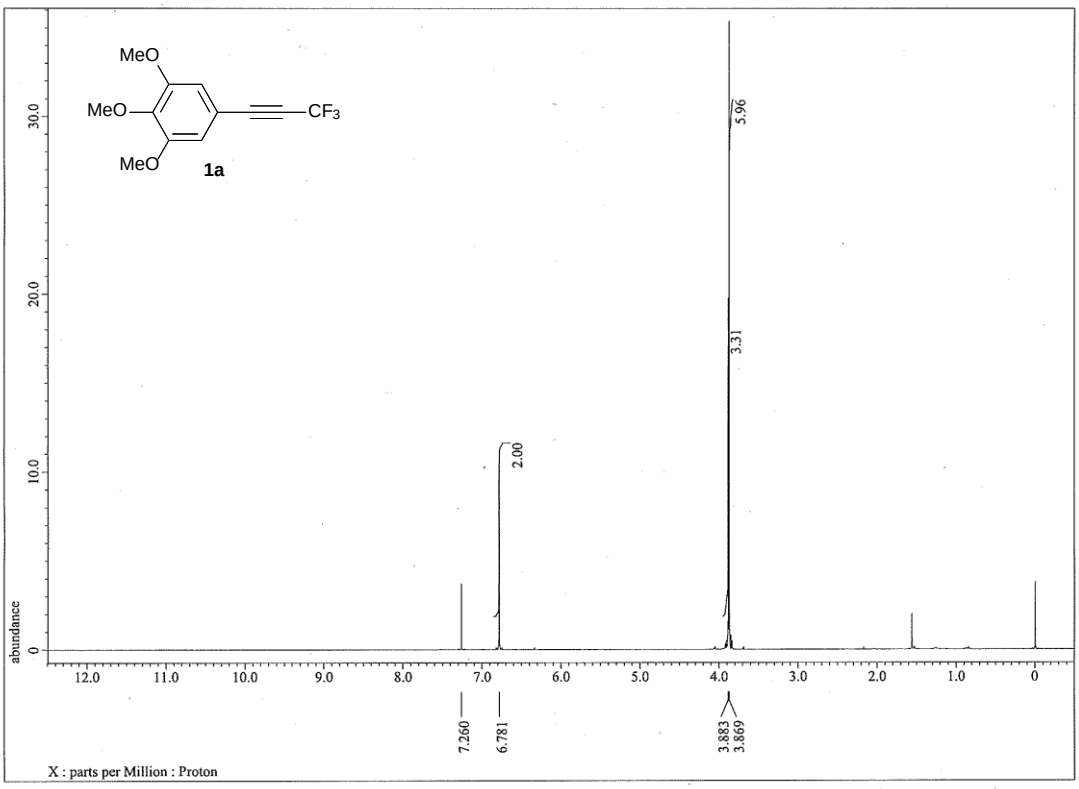
Analytical data for 5ac: colorless solid (mp 110.2–111.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.84 (s, 6 H), 3.91 (s, 3 H), 5.86 (q, *J* = 8.1 Hz, 1 H), 6.35 (d, *J* = 15.8 Hz, 1 H), 6.44 (s, 2 H), 6.89 (d, *J* = 15.8 Hz, 1 H), 7.26–7.33 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 56.1, 60.9, 106.0, 118.0 (q, *J* = 23 Hz), 122.9 (q, *J* = 269 Hz), 128.2, 128.9, 130.0, 130.5, 134.4, 134.5, 136.1, 137.9, 150.0 (q, *J* = 6 Hz), 152.9; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –55.6; HRMS (DART) *m/z* calcd for $C_{20}H_{18}ClF_3O_3$•NH_4 416.1240, found 416.1227 $[M+NH_4]^+$.

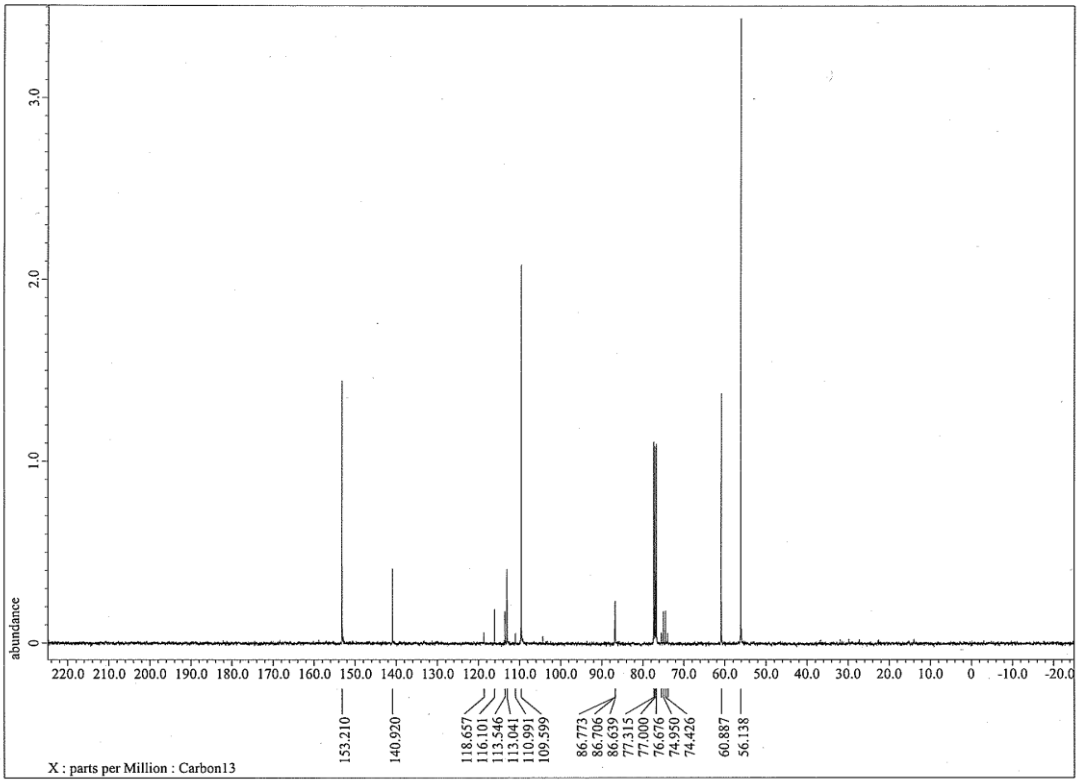


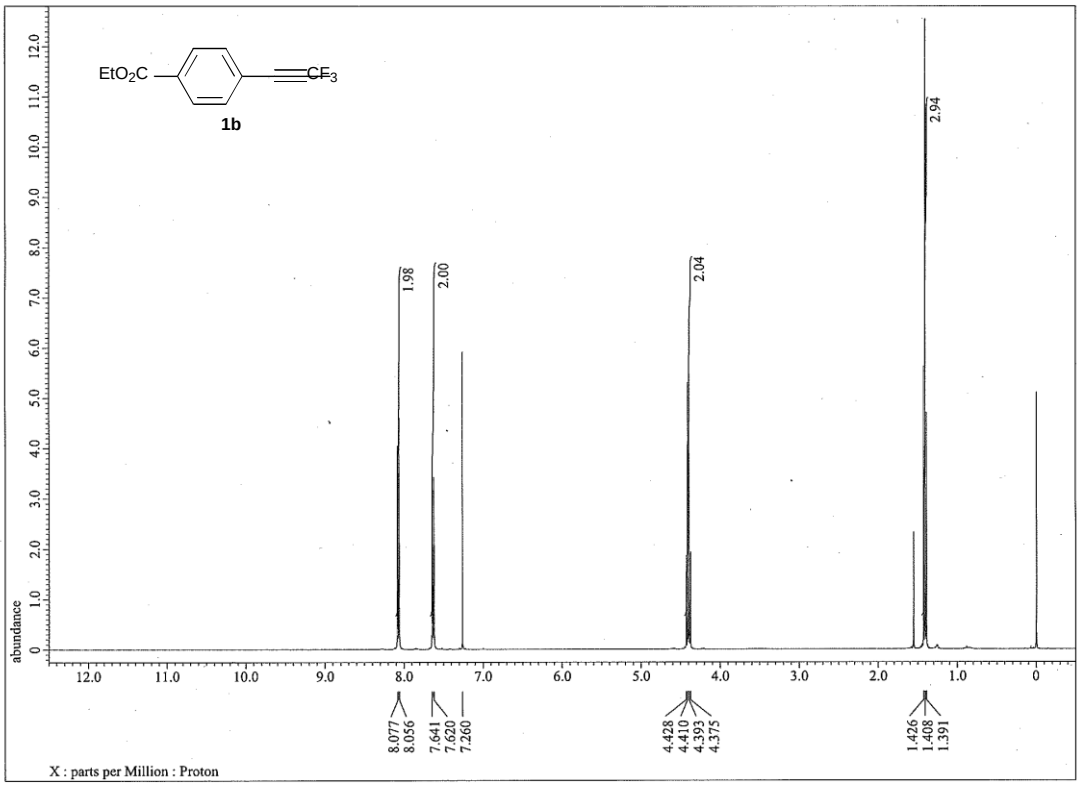
9

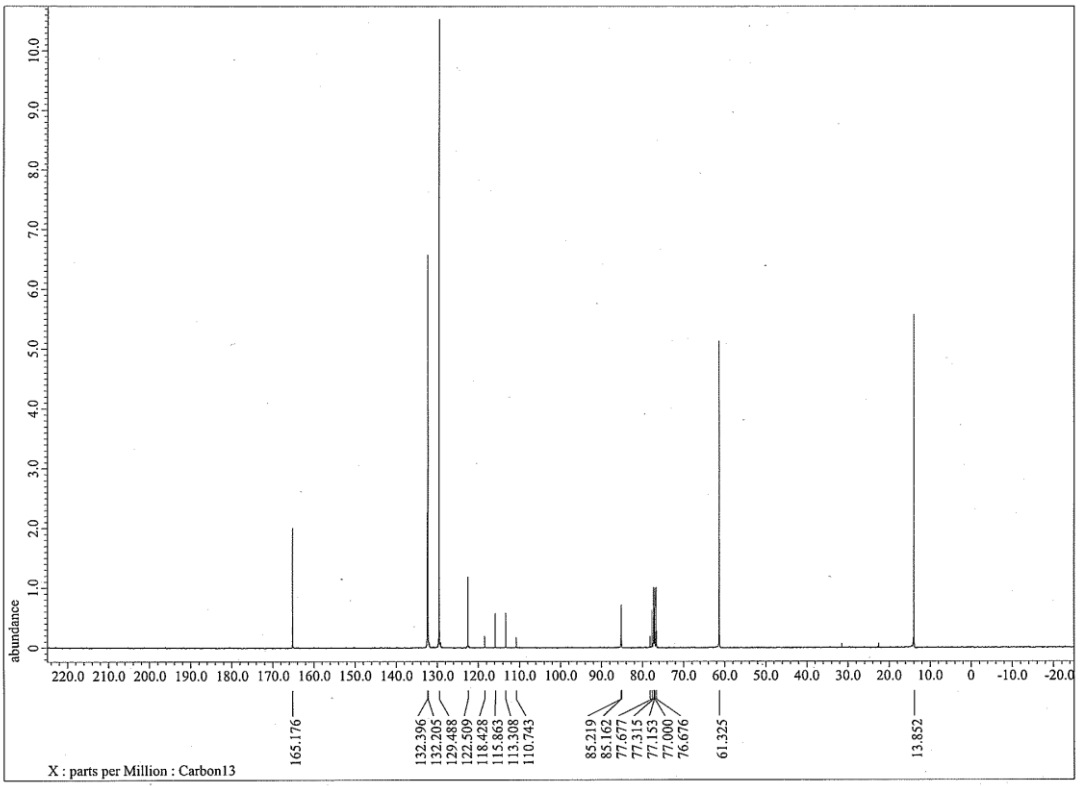
Analytical data for 9: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.12 (d, *J* = 6.8 Hz, 2 H), 3.83 (s, 6 H), 3.85 (s, 3 H), 5.13 (dq, *J* = 16.8, 1.6 Hz, 1 H), 5.15 (dq, *J* = 10.0, 1.0 Hz, 2 H), 5.62 (tq, *J* = 8.0, 1.6 Hz, 1 H), 5.77 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 2 H), 6.41 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 43.7, 56.0, 60.8, 104.5, 115.7 (q, *J* = 33 Hz), 118.6, 122.9 (q, *J* = 269 Hz), 133.3, 133.7, 137.8, 152.4 (q, *J* = 5 Hz), 152.8; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ –56.3; HRMS (DART) *m/z* calcd for $C_{15}H_{17}F_3O_3$•H 303.1208, found 303.1198 $[M+H]^+$.

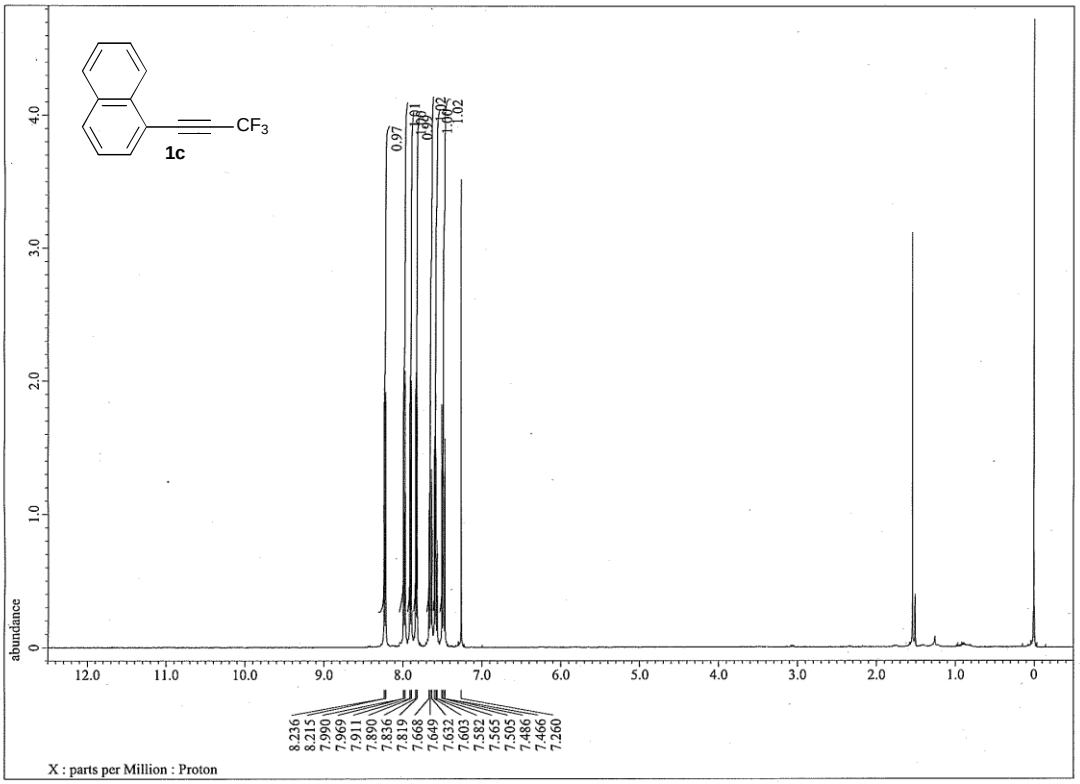
NMR Charts

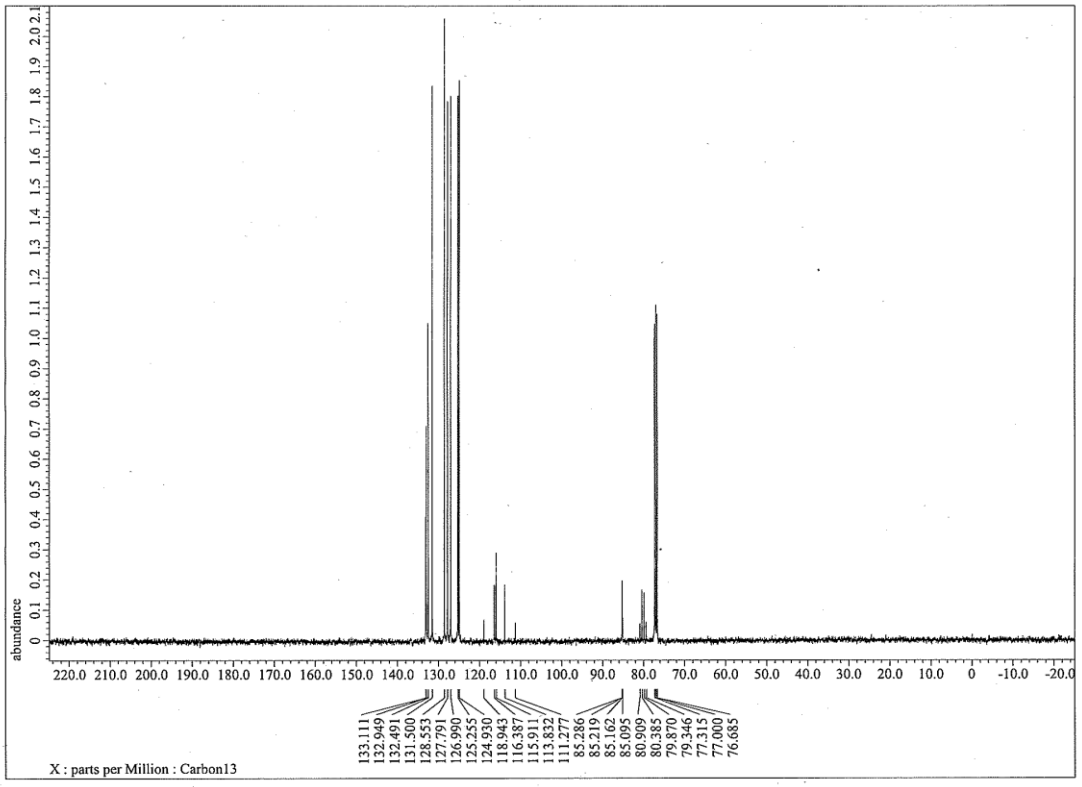

MeO
MeO
MeO
CF3
1a
abundance
30.0
20.0
10.0
0
5.96
3.31
2.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.260
6.781
3.883
3.869
X : parts per Million : Proton

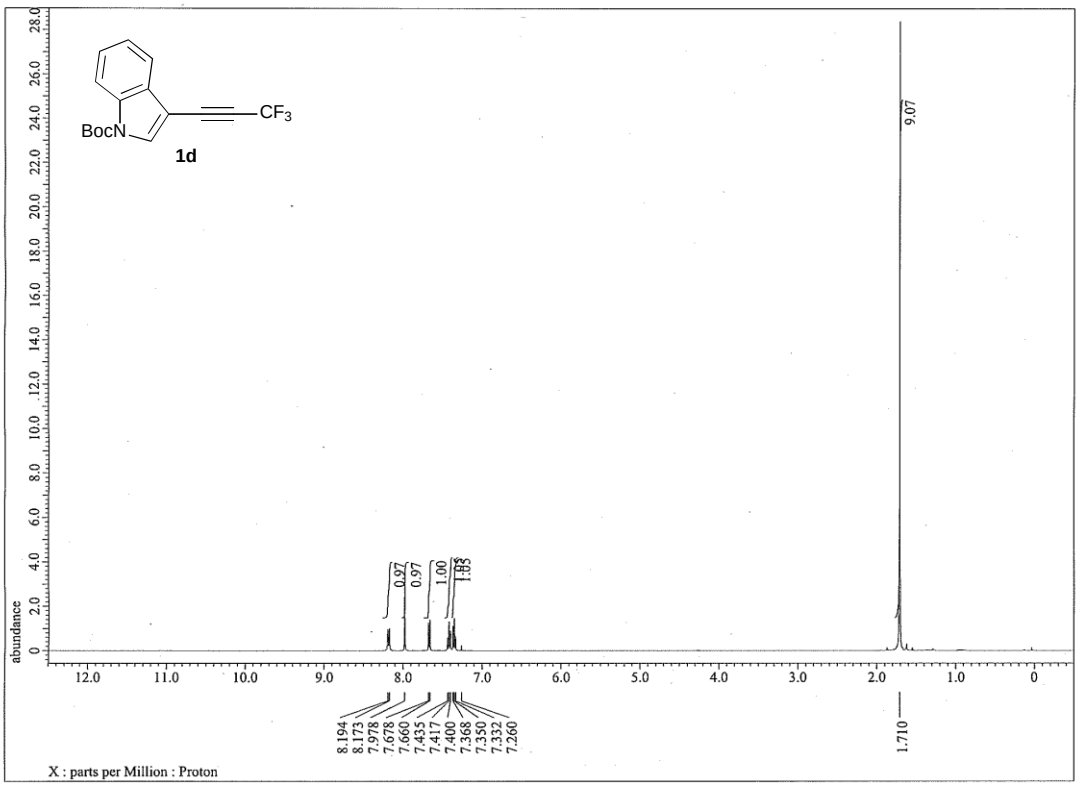

abundance
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
153.210
140.920
118.657
116.101
113.546
113.041
110.991
109.599
86.773
86.706
86.639
77.315
77.000
76.676
74.950
74.426
60.887
56.138
X : parts per Million : Carbon13

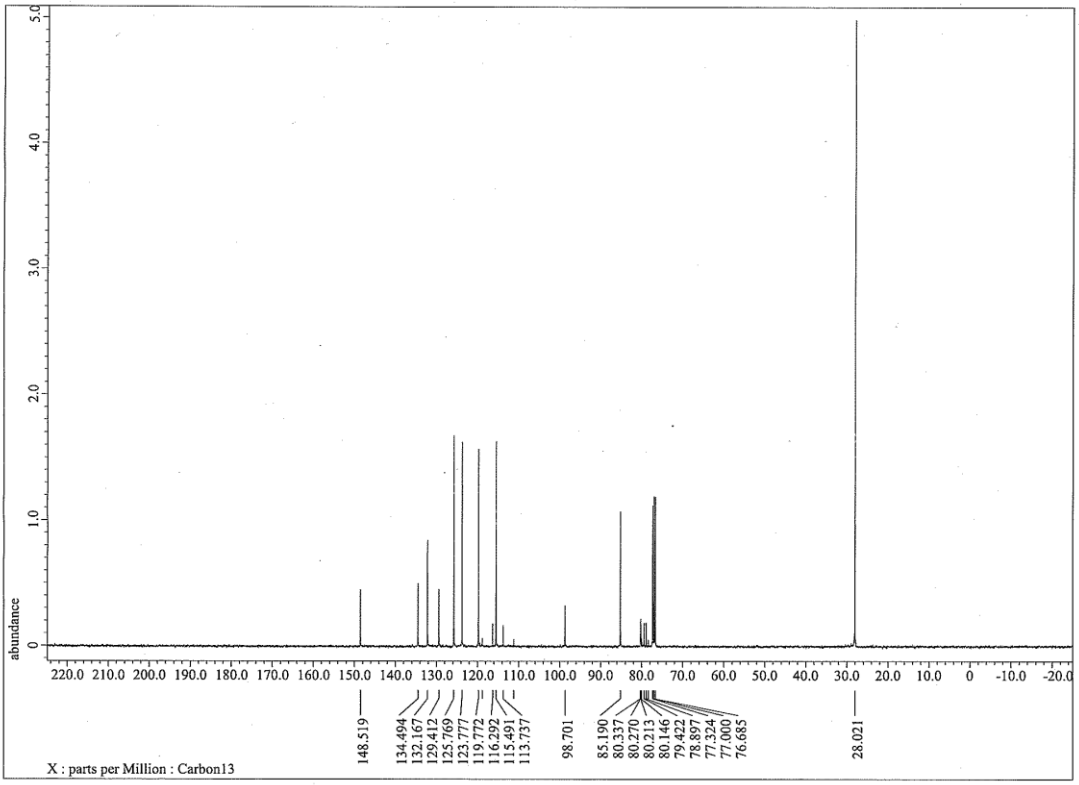

EtO2C
CF3
1b
abundance
1.98
2.00
2.04
2.94
8.077
8.056
7.641
7.620
7.260
4.428
4.410
4.393
4.375
1.426
1.408
1.391
X : parts per Million : Proton

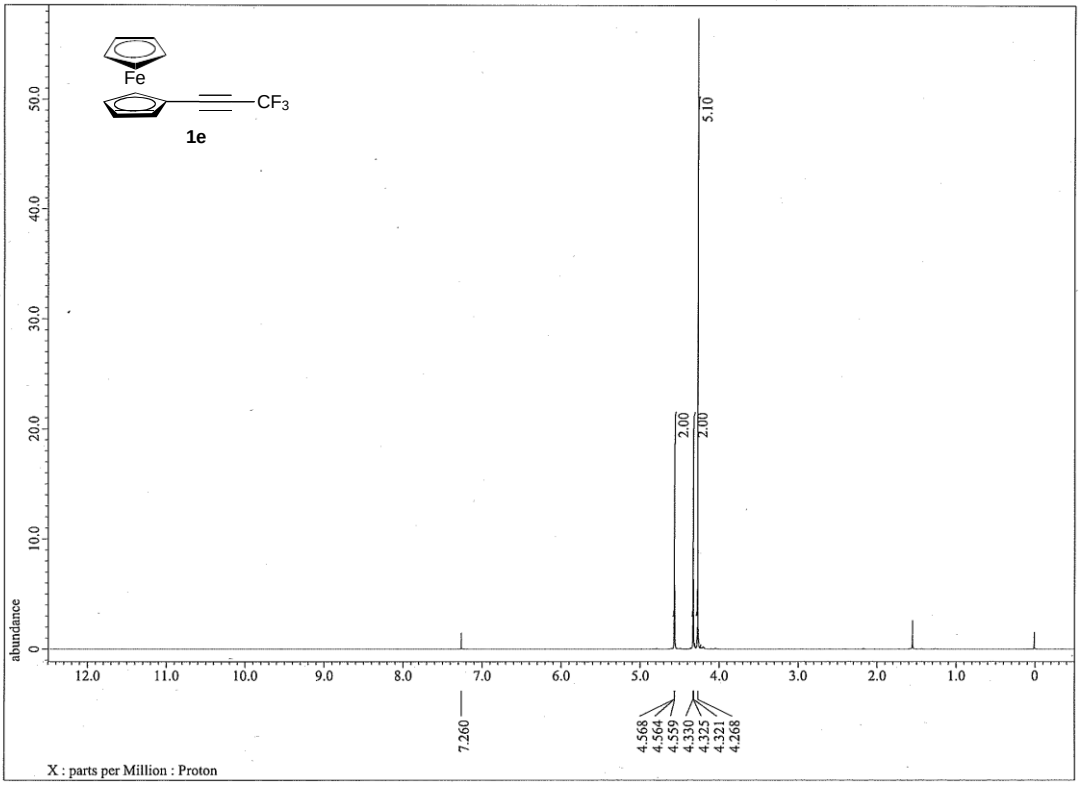

abundance
165.176
132.396
132.205
129.488
122.509
118.428
115.863
113.308
110.743
85.219
85.162
77.677
77.315
77.153
77.000
76.676
61.325
13.852
X : parts per Million : Carbon13

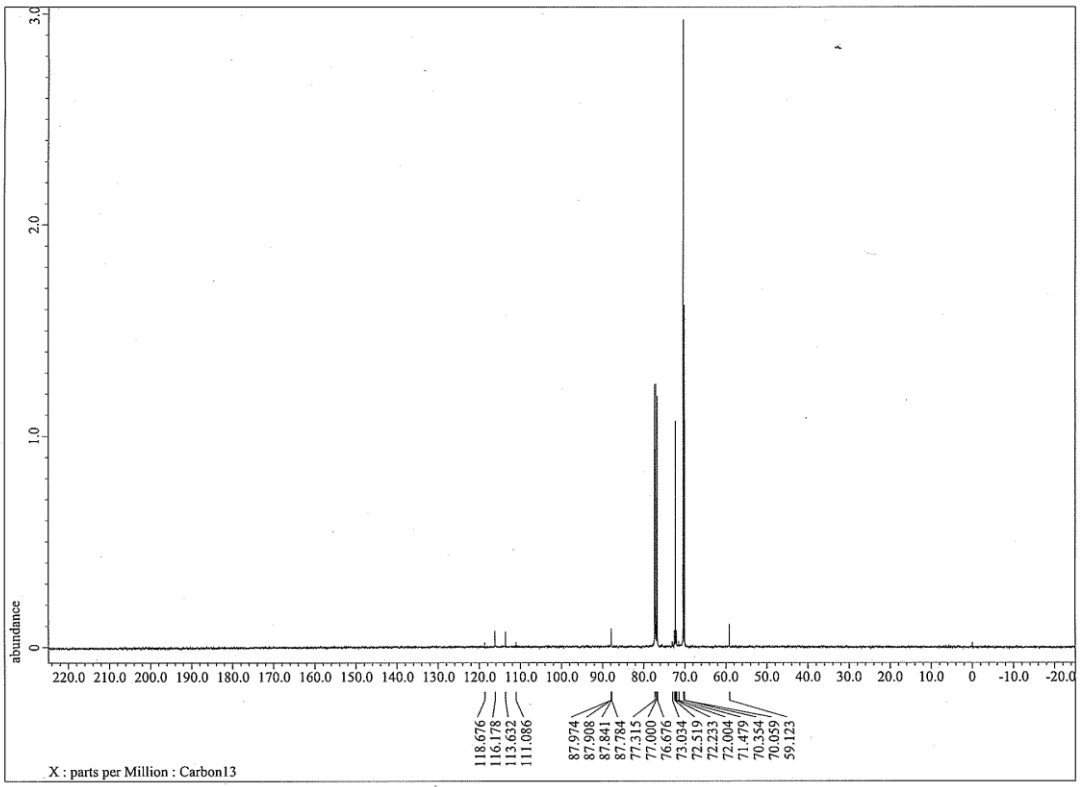

CF3
1c
abundance
X : parts per Million : Proton

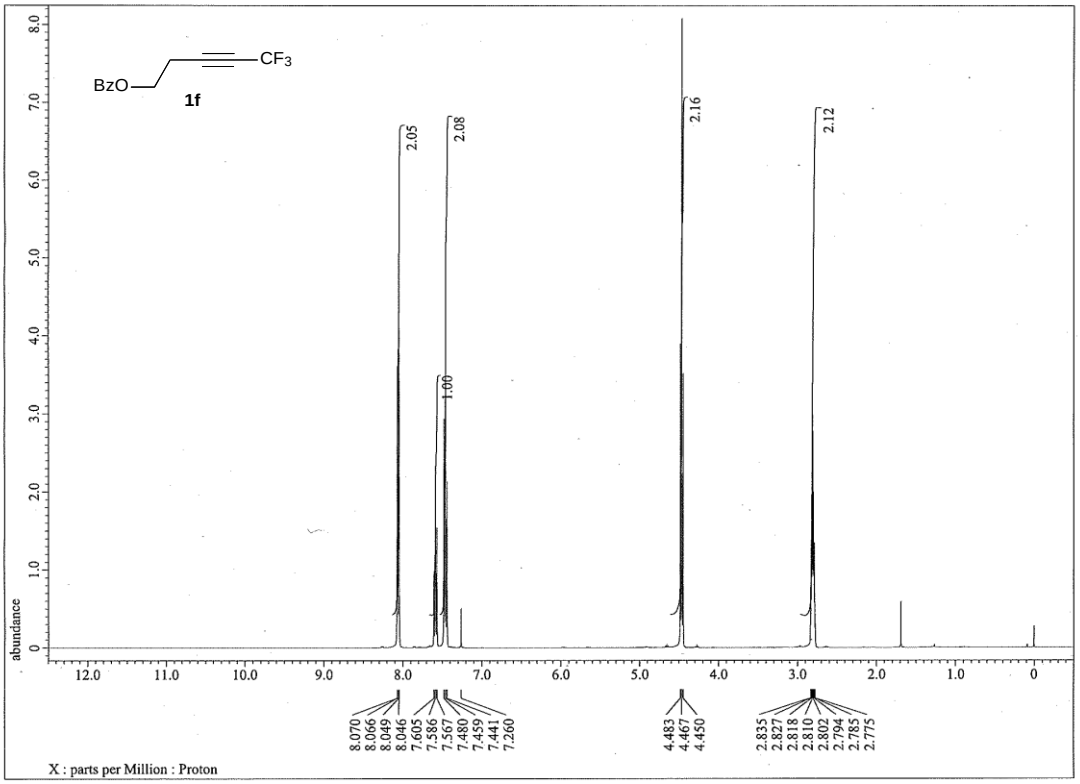

abundance
X : parts per Million : Carbon13

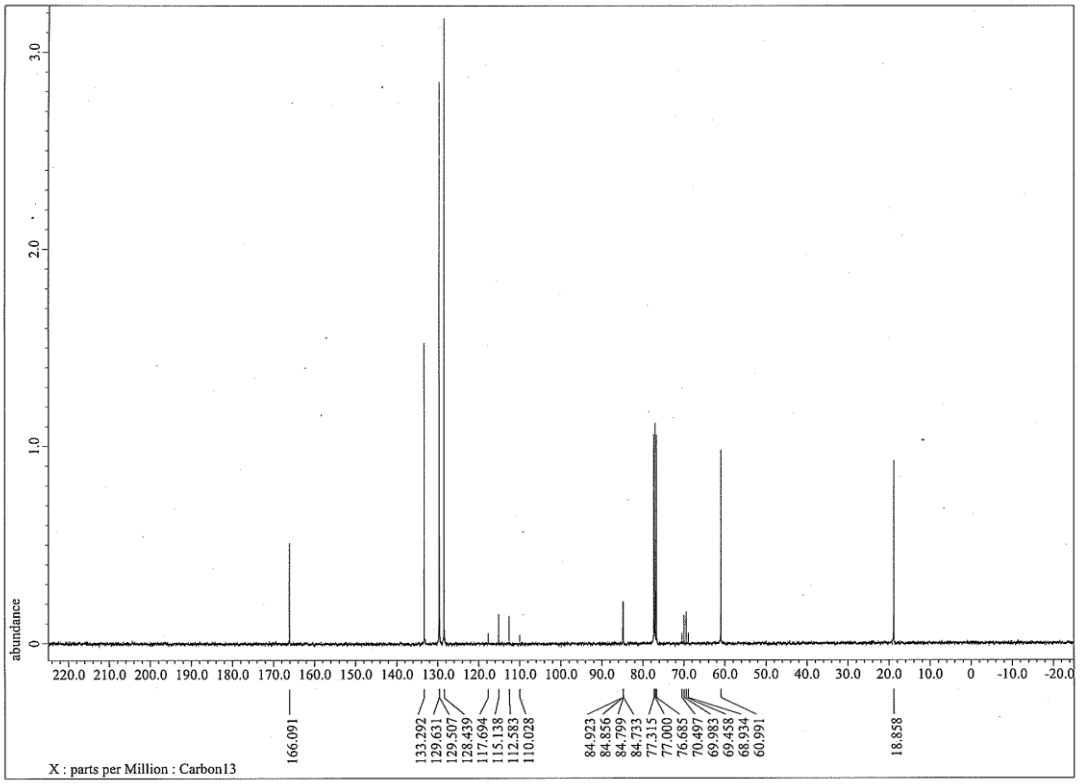

BocN
CF3
1d
abundance
9.07
0.97
0.97
1.00
1.03
8.194
8.173
7.978
7.678
7.660
7.435
7.417
7.400
7.368
7.350
7.332
7.260
1.710
X : parts per Million : Proton

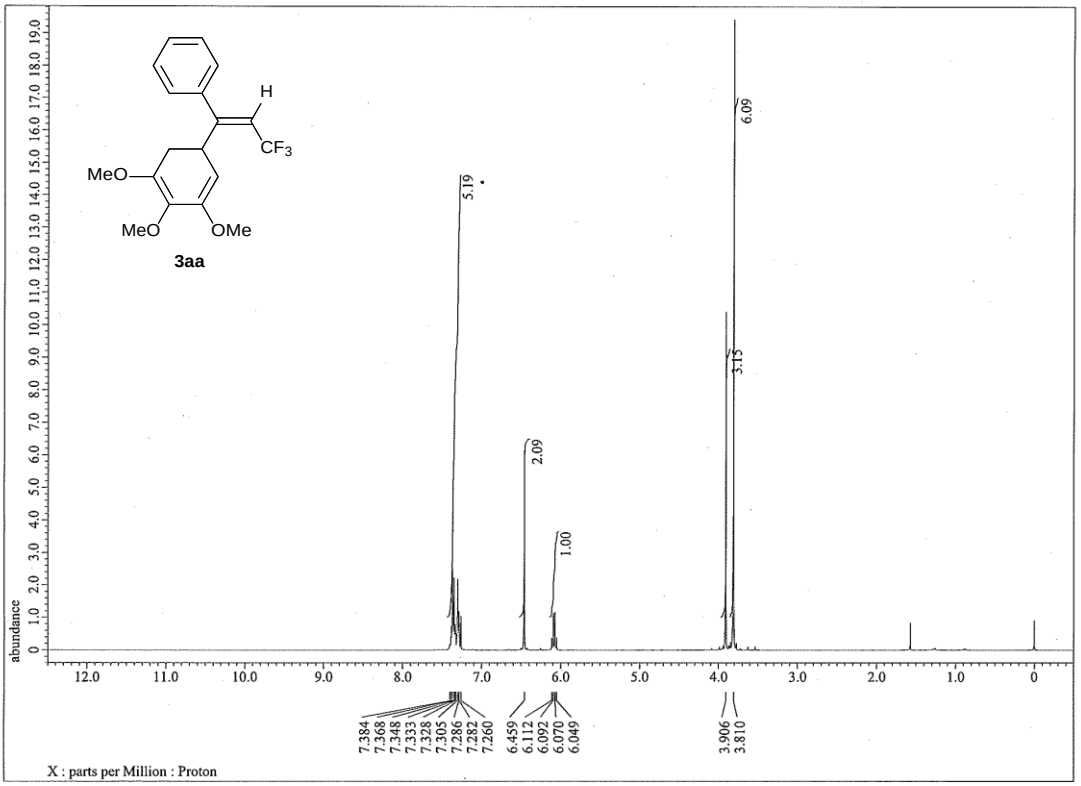

abundance
148.519
134.494
132.167
129.412
125.769
123.777
119.772
116.292
115.491
113.737
98.701
85.190
80.337
80.270
80.213
80.146
79.422
78.897
77.324
77.000
76.685
28.021
X : parts per Million : Carbon13

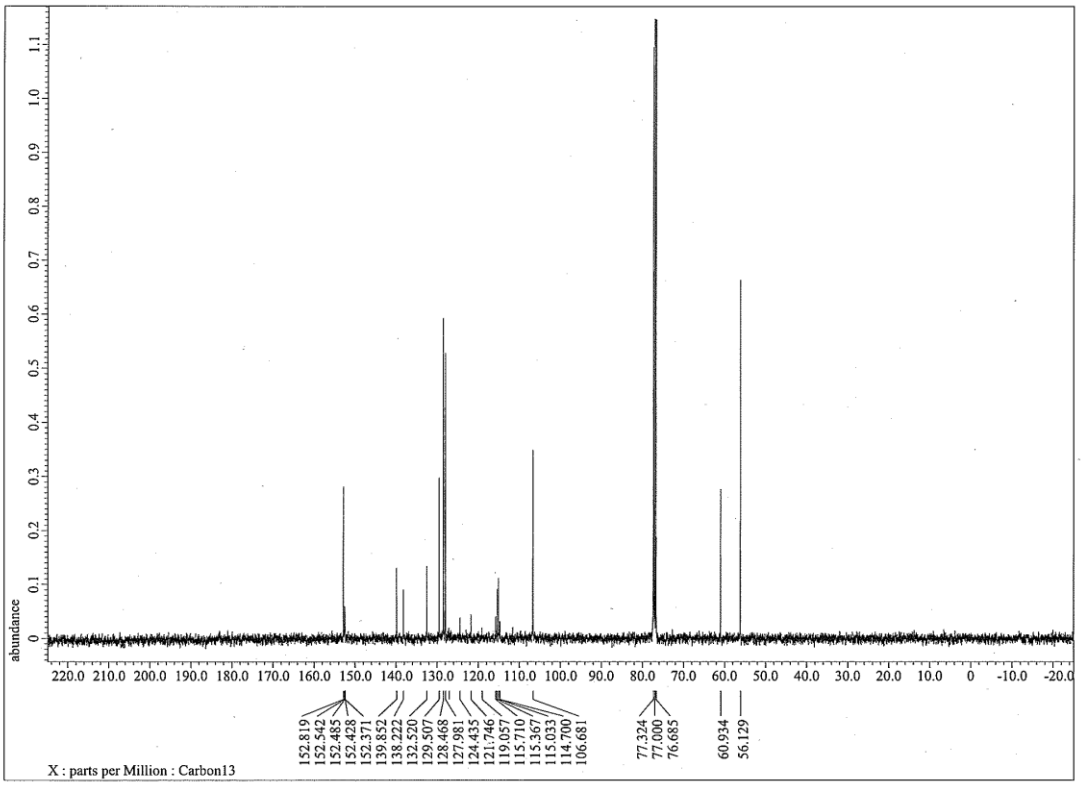

Fe
CF3
1e
abundance
5.10
2.00
2.00
7.260
4.568
4.564
4.559
4.330
4.325
4.321
4.268
X : parts per Million : Proton

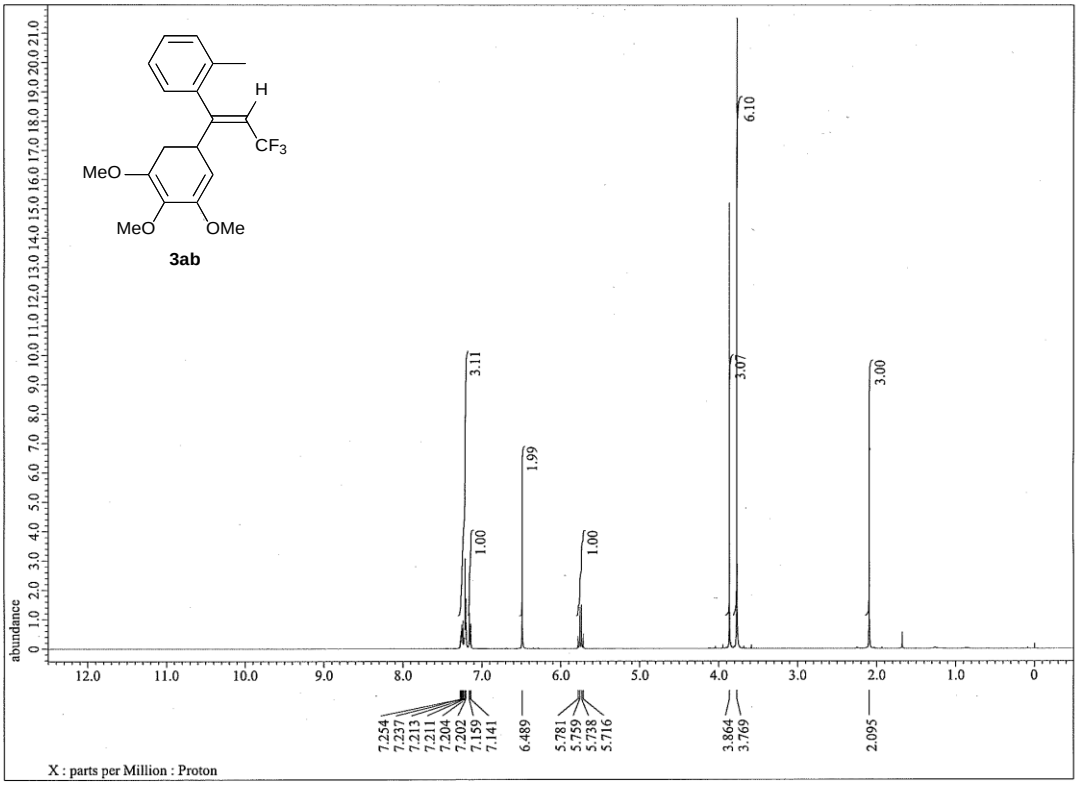

abundance
118.676
116.178
113.632
111.086
87.974
87.908
87.841
87.784
77.315
77.000
76.676
73.034
72.519
72.233
72.004
71.479
70.354
70.059
59.123
X : parts per Million : Carbon13

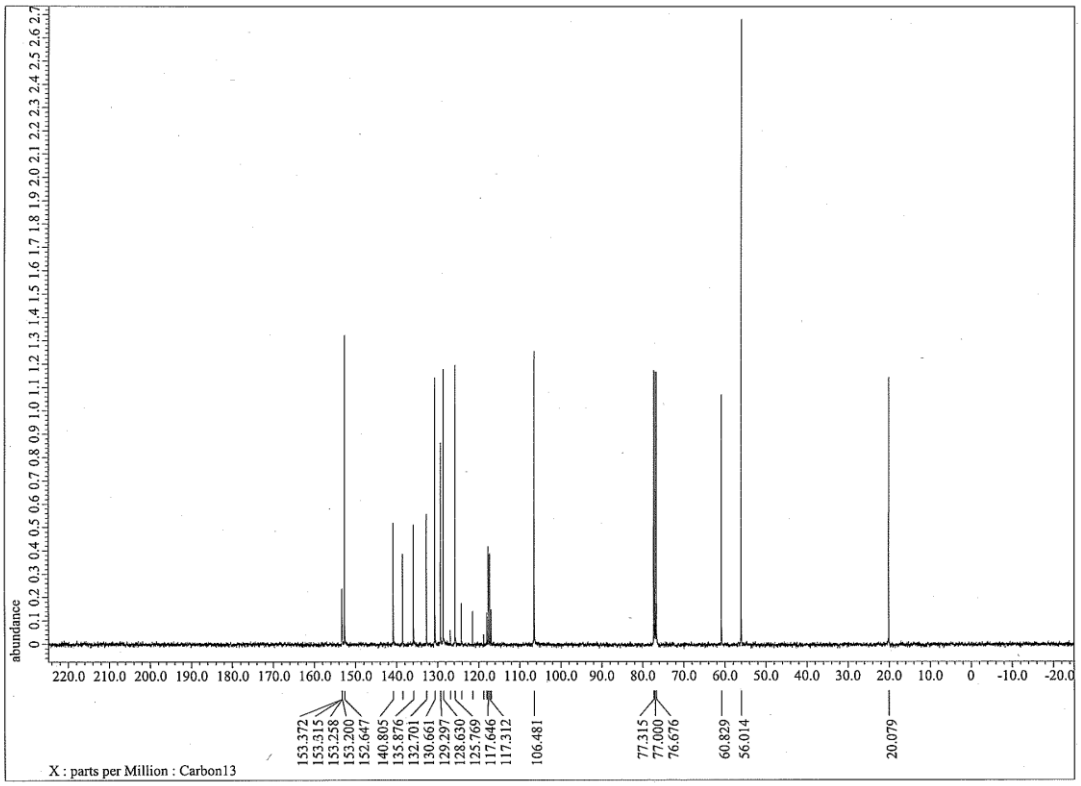

BzO
CF3
1f
2.05
2.08
1.00
2.16
2.12
abundance
8.070
8.066
8.049
8.046
7.605
7.586
7.567
7.480
7.459
7.441
7.260
4.483
4.467
4.450
2.835
2.827
2.818
2.810
2.802
2.794
2.785
2.775
X : parts per Million : Proton

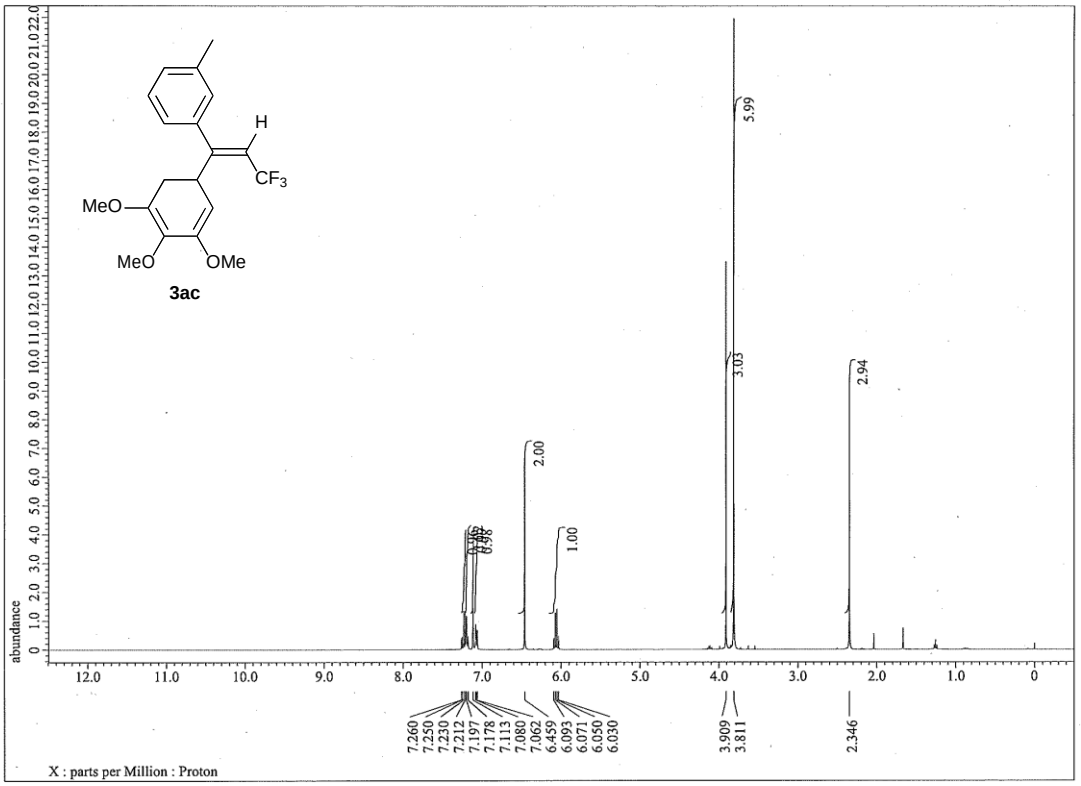

abundance
166.091
133.292
129.631
129.507
128.439
117.694
115.138
112.583
110.028
84.923
84.856
84.799
84.733
77.315
77.000
76.685
70.497
69.983
69.458
68.934
60.991
18.858
X : parts per Million : Carbon13

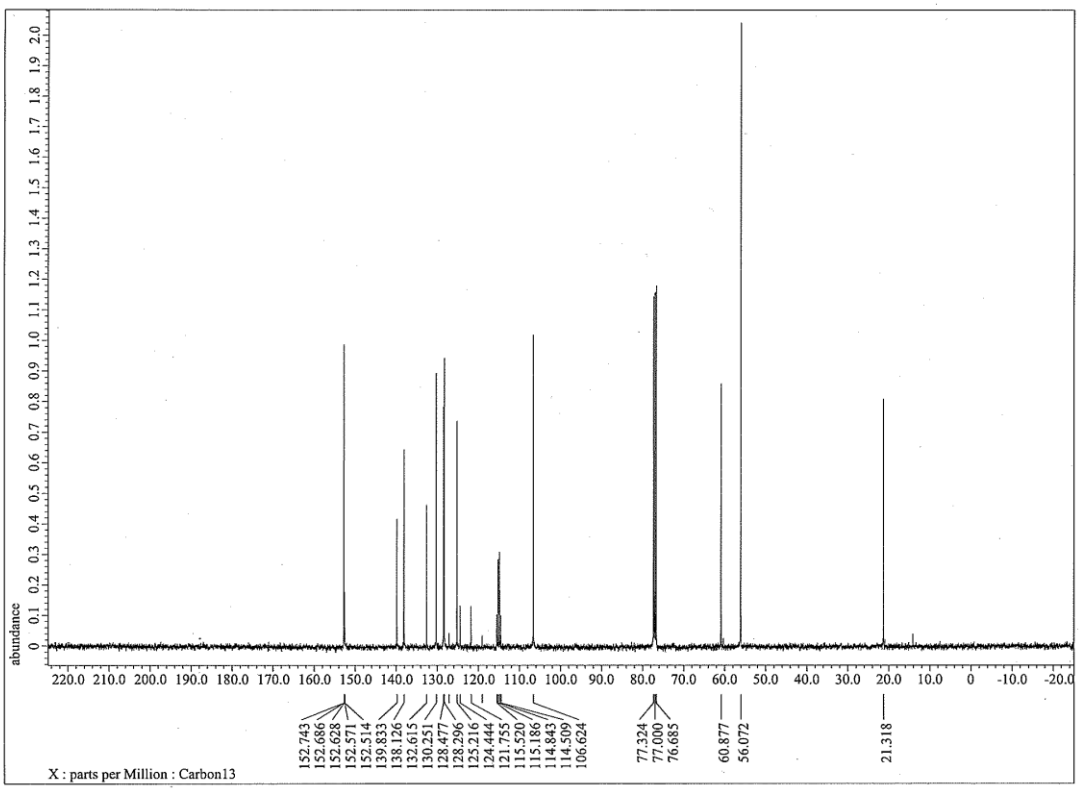

H
CF3
MeO
MeO
OMe
3aa
abundance
5.19
6.09
3.15
2.09
1.00
7.384
7.368
7.348
7.333
7.328
7.305
7.286
7.282
7.260
6.459
6.112
6.092
6.070
6.049
3.906
3.810
X : parts per Million : Proton

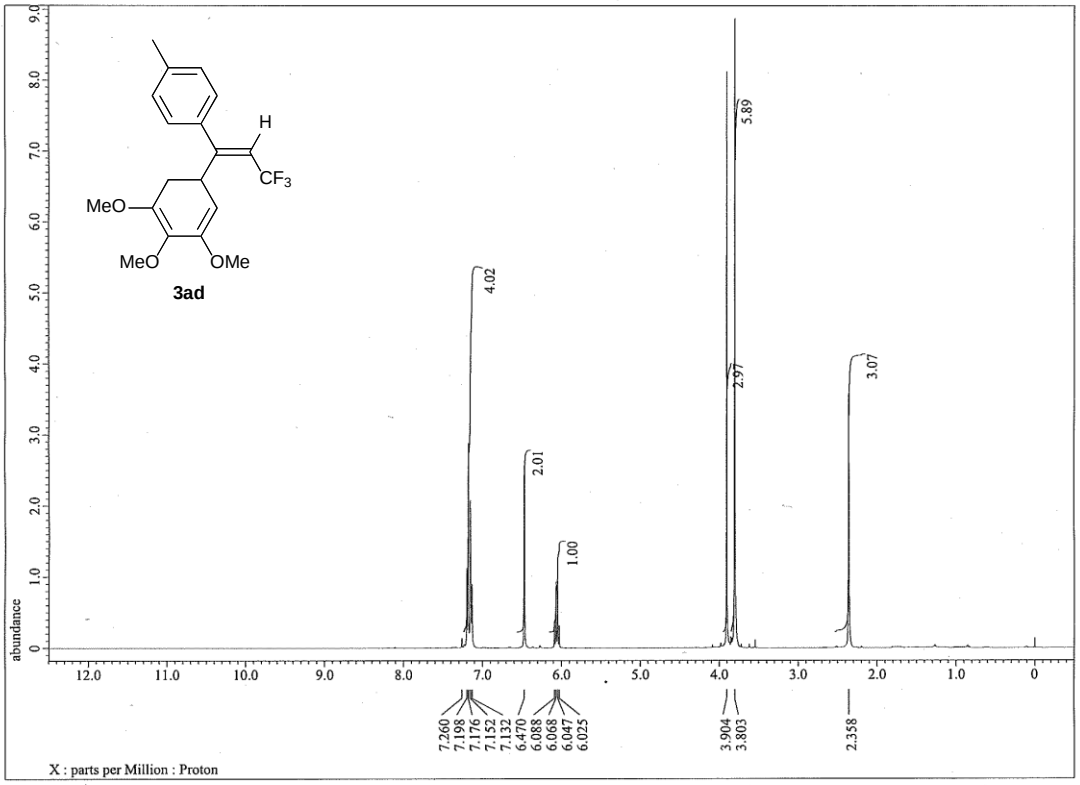

abundance
152.819
152.542
152.485
152.428
152.371
139.852
138.222
132.520
129.507
128.468
127.981
124.435
121.746
119.057
115.710
115.367
115.033
114.700
106.681
77.324
77.000
76.685
60.934
56.129
X : parts per Million : Carbon13

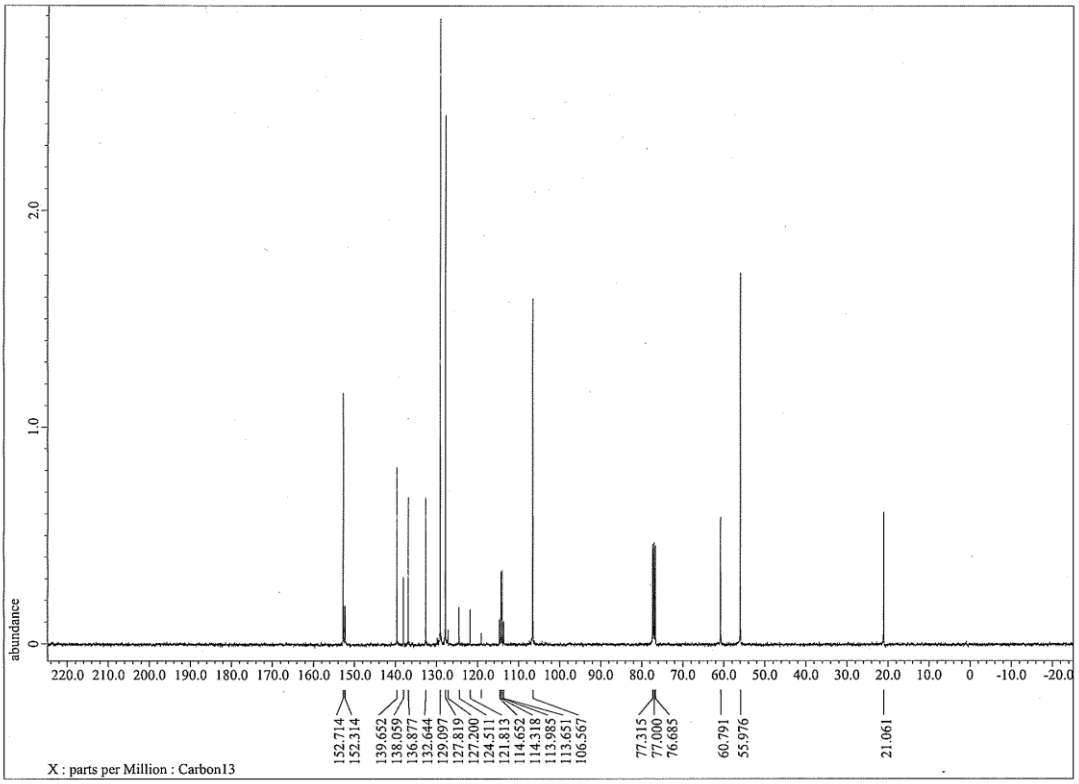

H
CF3
MeO
MeO
OMe
3ab
abundance
3.11
1.00
1.99
1.00
3.07
6.10
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.254
7.237
7.213
7.211
7.204
7.202
7.159
7.141
6.489
5.781
5.759
5.738
5.716
3.864
3.769
2.095
X : parts per Million : Proton

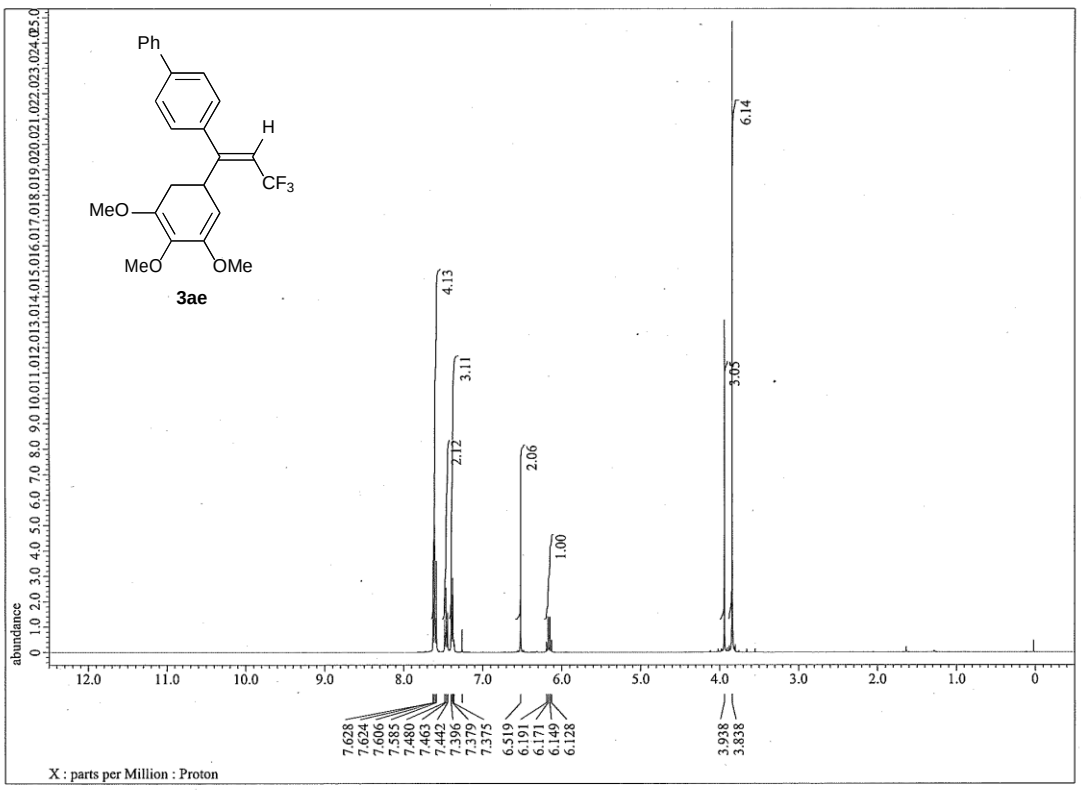

abundance
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
153.372
153.315
153.258
153.200
152.647
140.805
135.876
132.701
130.661
129.297
128.630
125.769
117.646
117.312
106.481
77.315
77.000
76.676
60.829
56.014
20.079
X : parts per Million : Carbon13

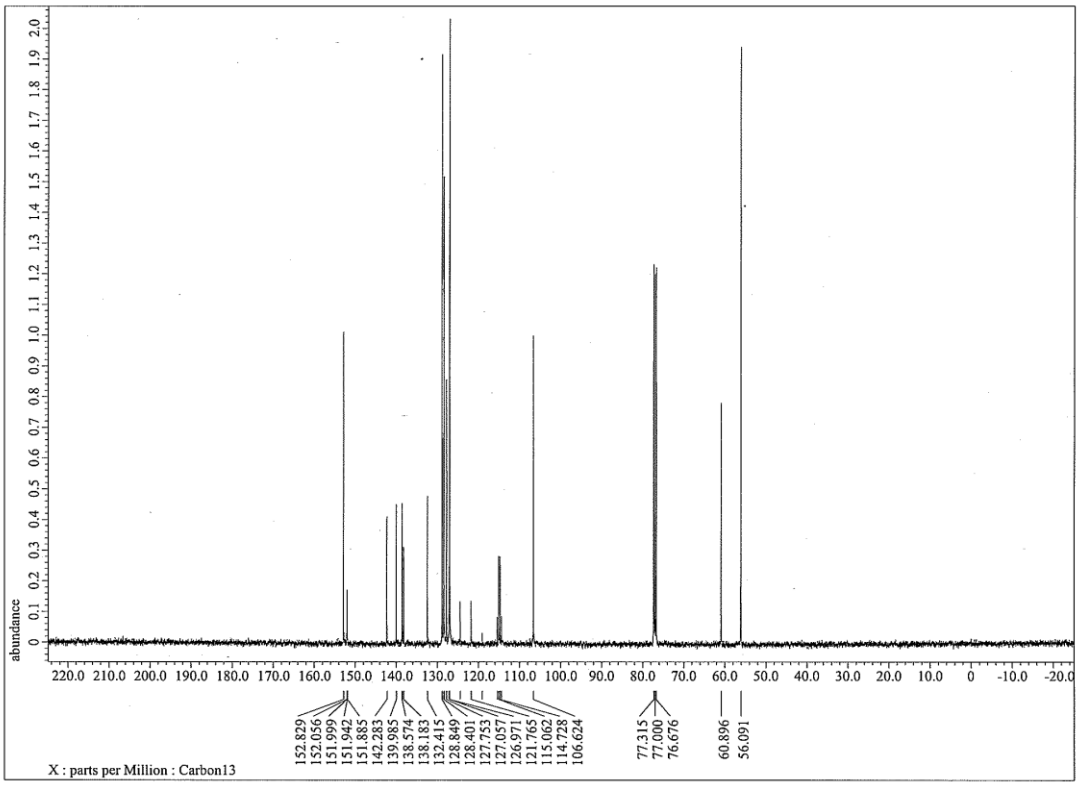

H
CF3
MeO
MeO
OMe
3ac
abundance
5.99
3.03
2.94
2.00
1.00
7.260
7.250
7.230
7.212
7.197
7.178
7.113
7.080
7.062
6.459
6.093
6.071
6.050
6.030
3.909
3.811
2.346
X : parts per Million : Proton

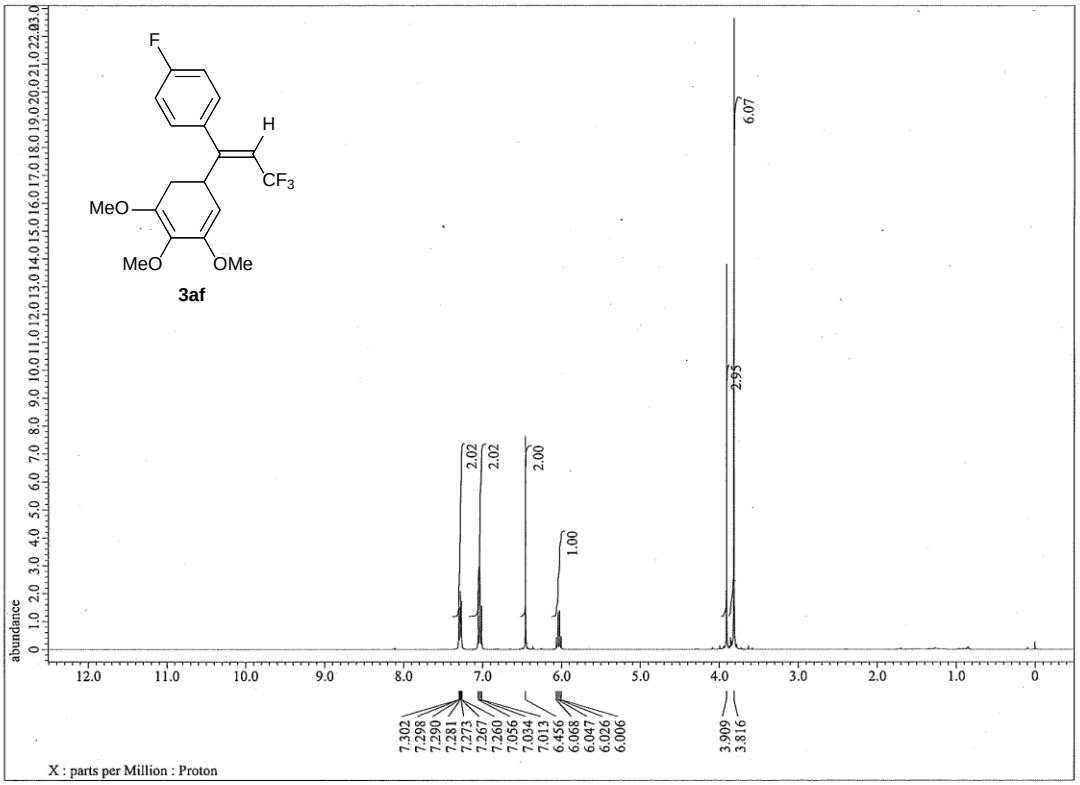

abundance
152.743
152.686
152.628
152.571
152.514
139.833
138.126
132.615
130.251
128.477
128.296
125.216
124.444
121.755
115.520
115.186
114.843
114.509
106.624
77.324
77.000
76.685
60.877
56.072
21.318
X : parts per Million : Carbon13

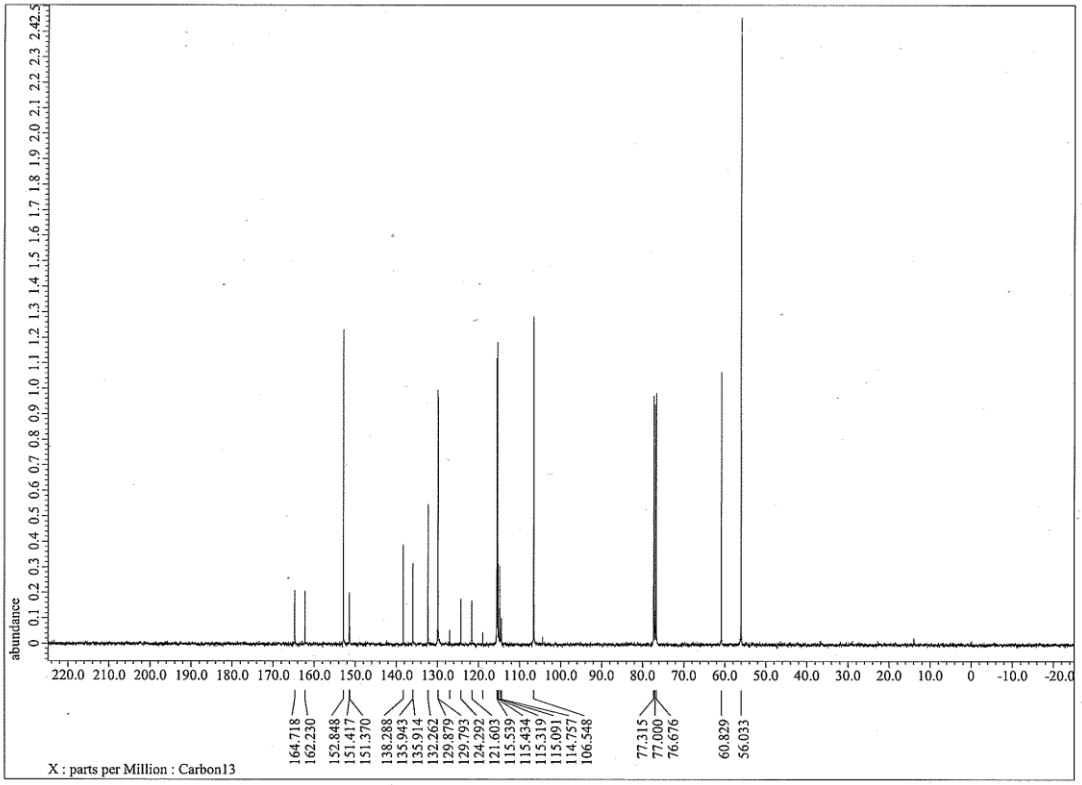

H
CF3
MeO
MeO
OMe
3ad
abundance
4.02
2.01
1.00
5.89
2.97
3.07
7.260
7.198
7.176
7.152
7.132
6.470
6.088
6.068
6.047
6.025
3.904
3.803
2.358
X : parts per Million : Proton

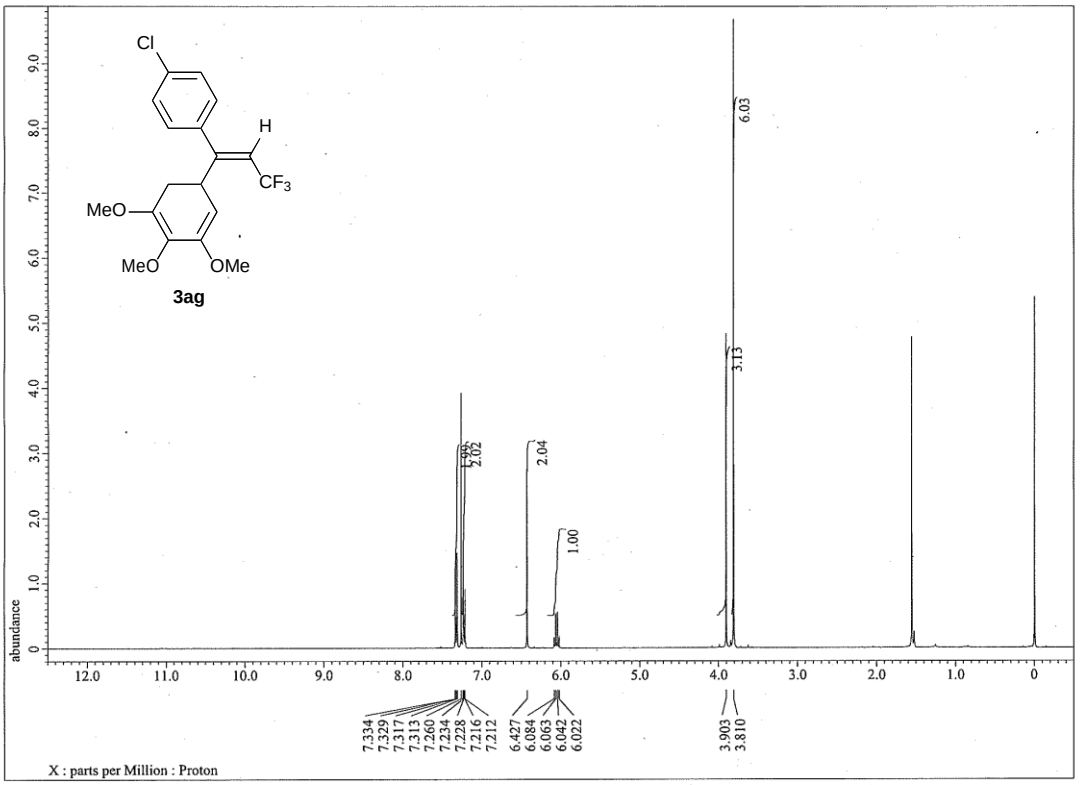

abundance
152.714
152.314
139.652
138.059
136.877
132.644
129.097
127.819
127.200
124.511
121.813
114.652
114.318
113.985
113.651
106.567
77.315
77.000
76.685
60.791
55.976
21.061
X : parts per Million : Carbon13

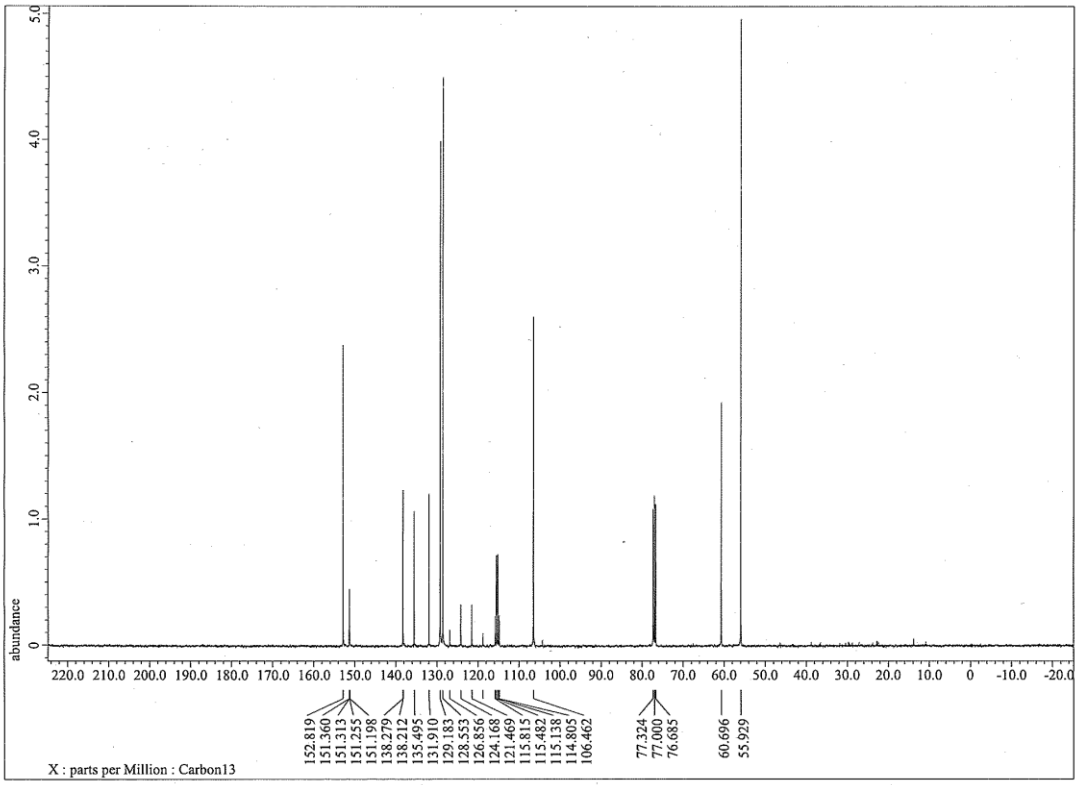

Ph
H
CF3
MeO
MeO
OMe
3ae
abundance
X : parts per Million : Proton

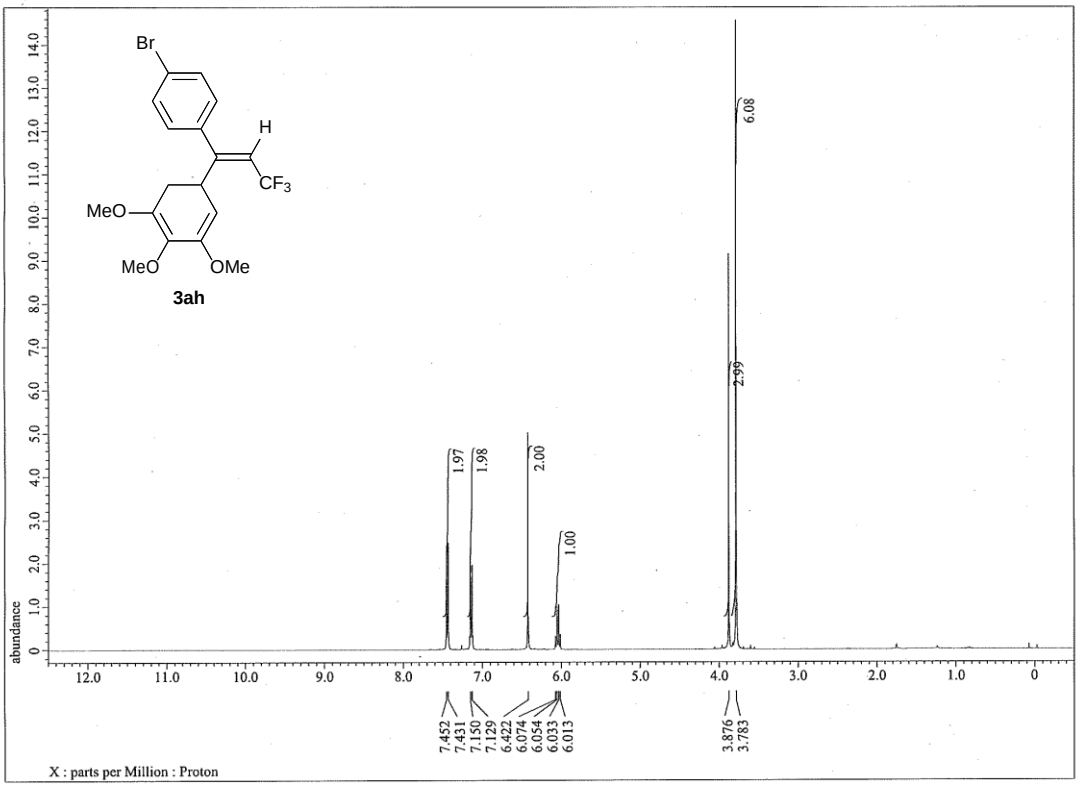

abundance
X : parts per Million : Carbon13

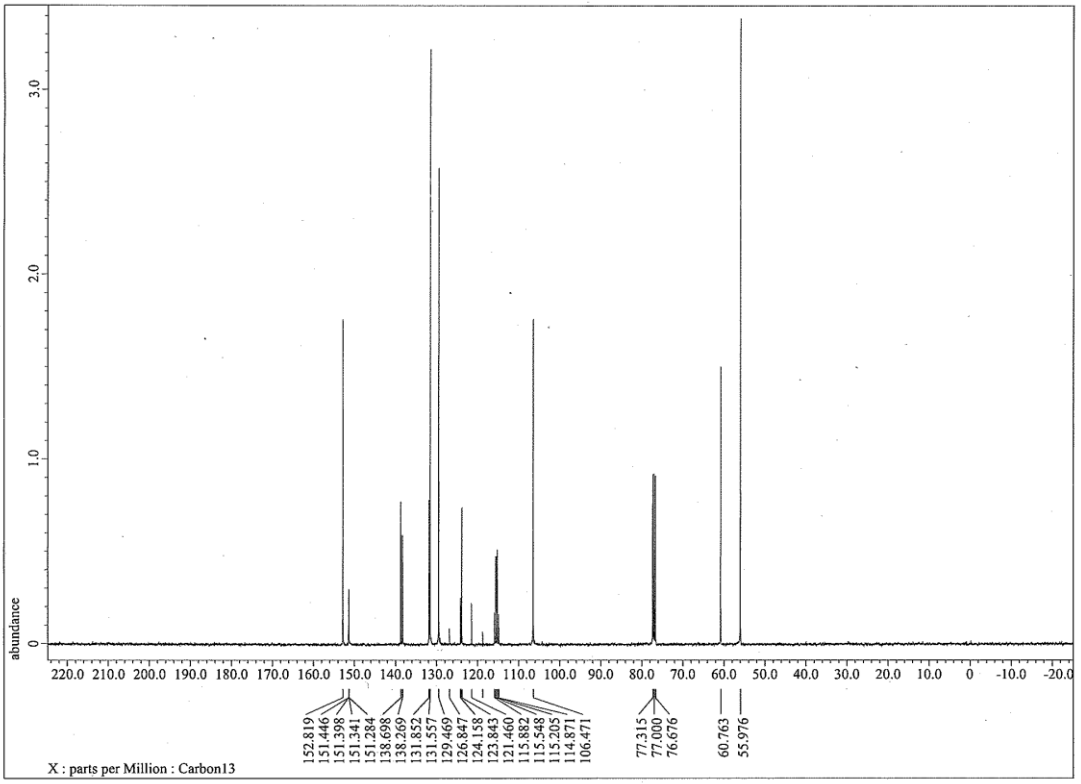

F
H
CF3
MeO
MeO
OMe
3af
abundance
X : parts per Million : Proton
7.302
7.298
7.290
7.281
7.273
7.267
7.260
7.056
7.034
7.013
6.456
6.068
6.047
6.026
6.006
3.909
3.816
2.02
2.02
2.00
1.00
6.07
2.93

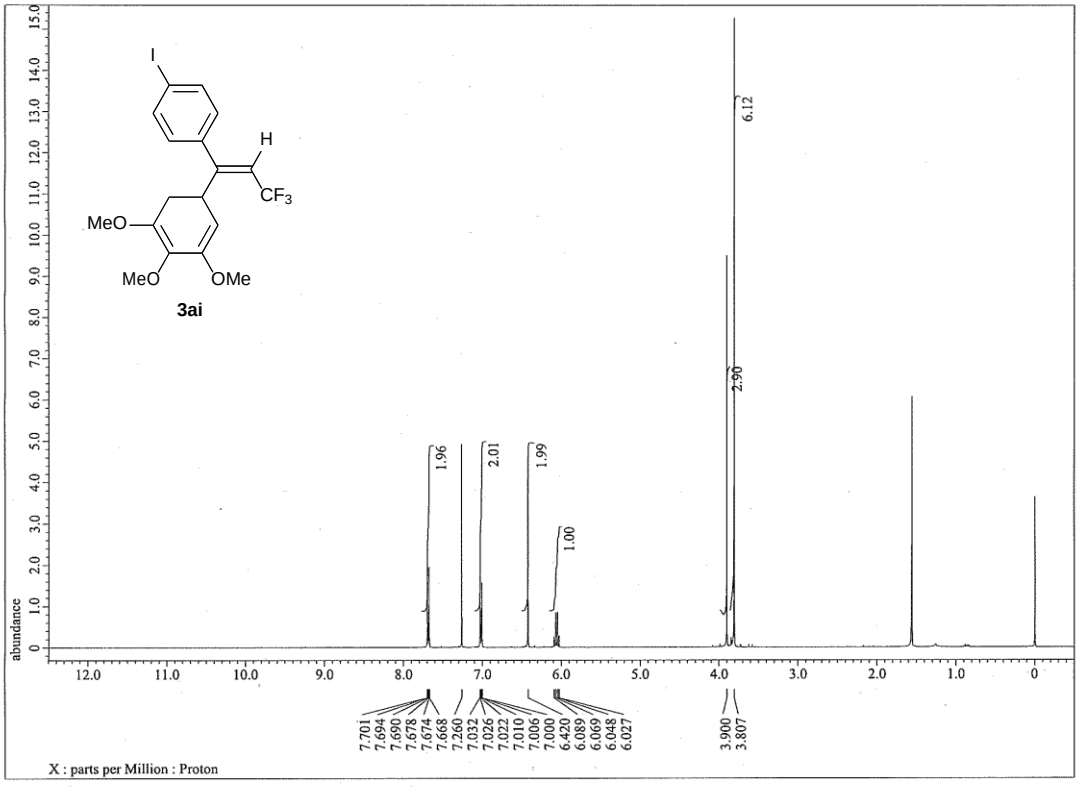

abundance
X : parts per Million : Carbon13
164.718
162.230
152.848
151.417
151.370
138.288
135.943
135.914
132.262
129.879
129.793
124.292
121.603
115.539
115.434
115.319
115.091
114.757
106.548
77.315
77.000
76.676
60.829
56.033

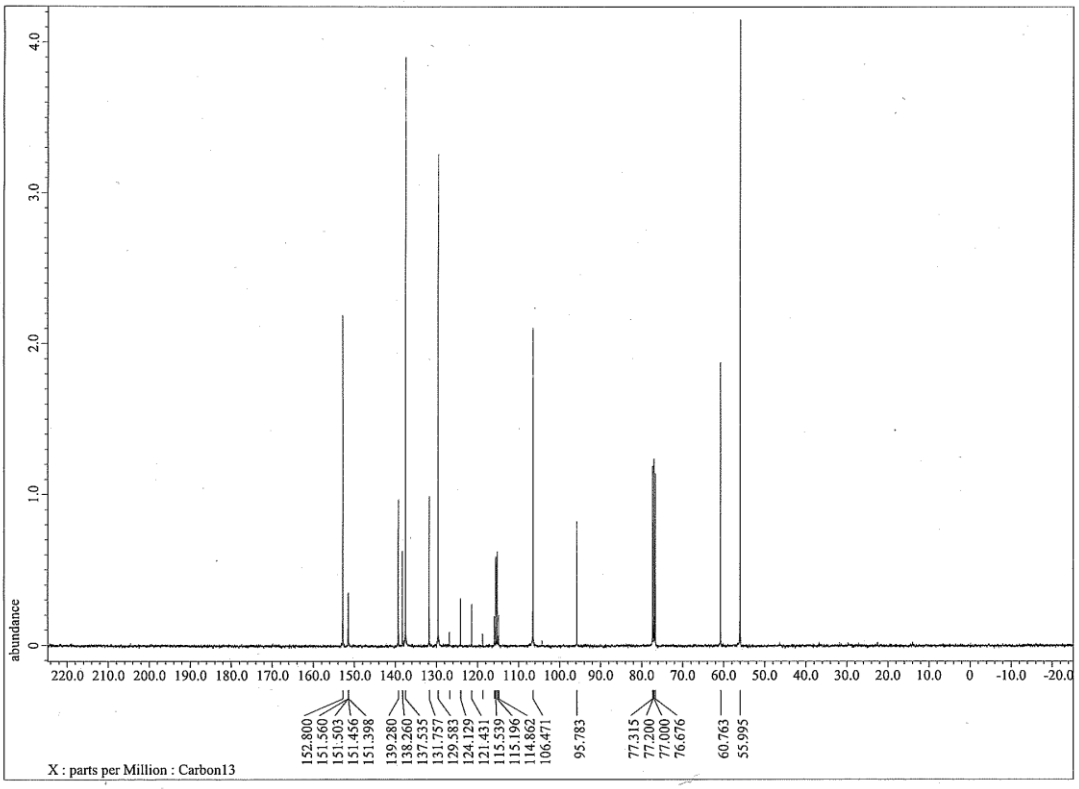

Cl
H
CF3
MeO
MeO
OMe
3ag
6.03
3.13
2.04
2.02
1.00
abundance
7.334
7.329
7.317
7.313
7.260
7.234
7.228
7.216
7.212
6.427
6.084
6.063
6.042
6.022
3.903
3.810
X : parts per Million : Proton

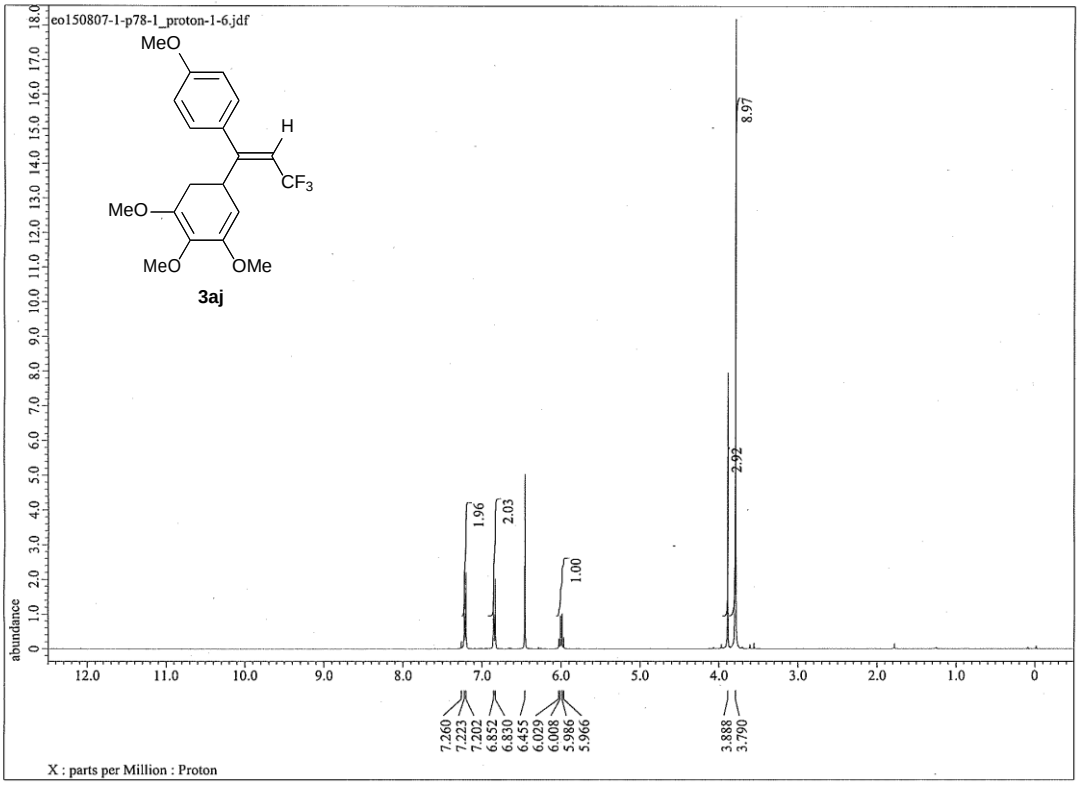

abundance
152.819
151.360
151.313
151.255
151.198
138.279
138.212
135.495
131.910
129.183
128.553
126.856
124.168
121.469
115.815
115.482
115.138
114.805
106.462
77.324
77.000
76.685
60.696
55.929
X : parts per Million : Carbon13

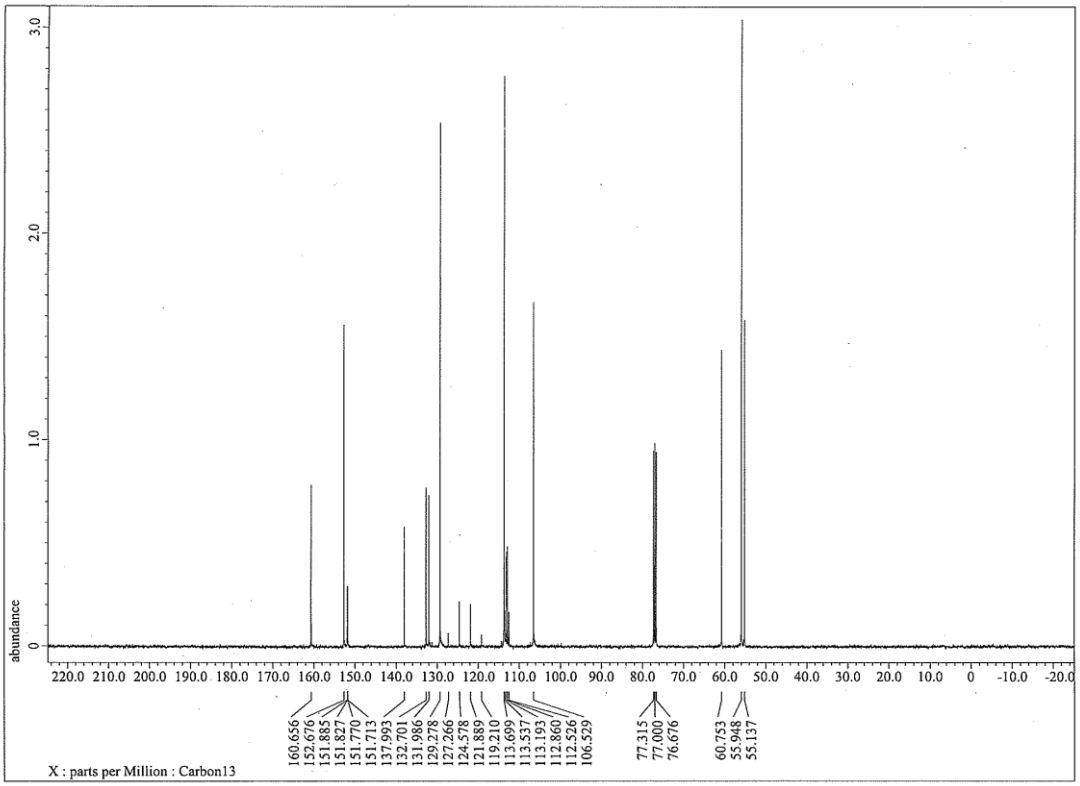

Br
H
CF3
MeO
MeO
OMe
3ah
abundance
6.08
2.99
1.97
1.98
2.00
1.00
7.452
7.431
7.150
7.129
6.422
6.074
6.054
6.033
6.013
3.876
3.783
X : parts per Million : Proton

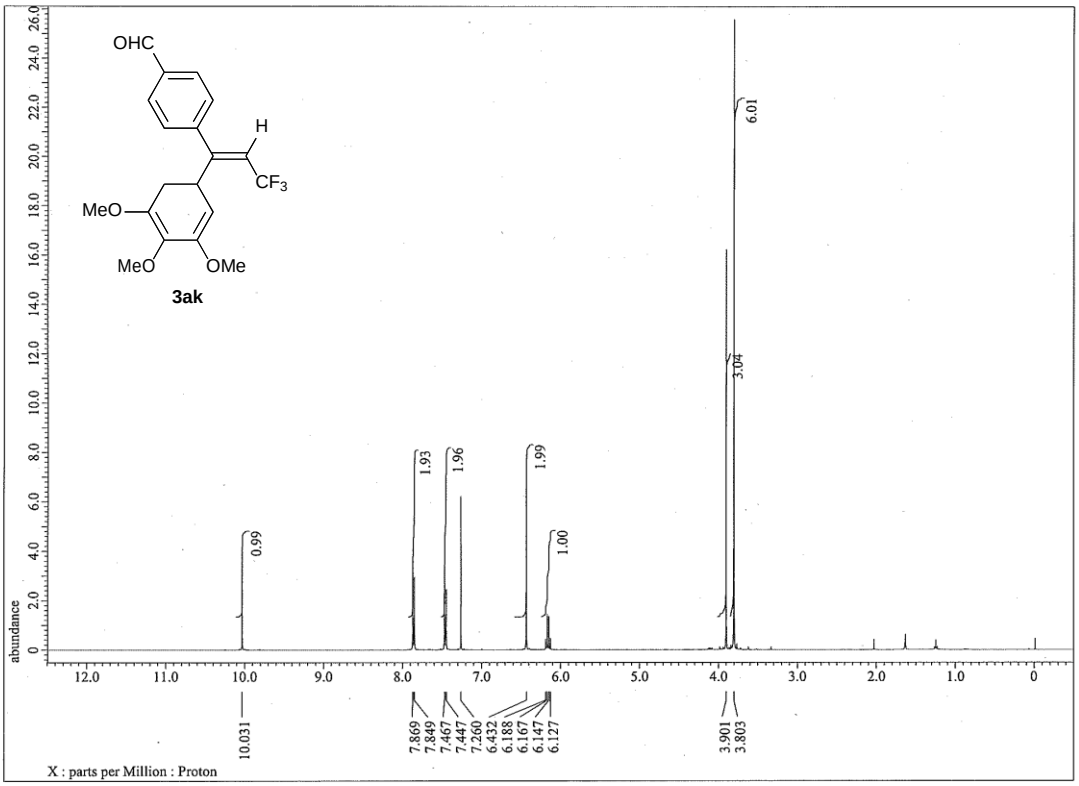

abundance
152.819
151.446
151.398
151.341
151.284
138.698
138.269
131.852
131.557
129.469
126.847
124.158
123.843
121.460
115.882
115.548
115.205
114.871
106.471
77.315
77.000
76.676
60.763
55.976
X : parts per Million : Carbon13

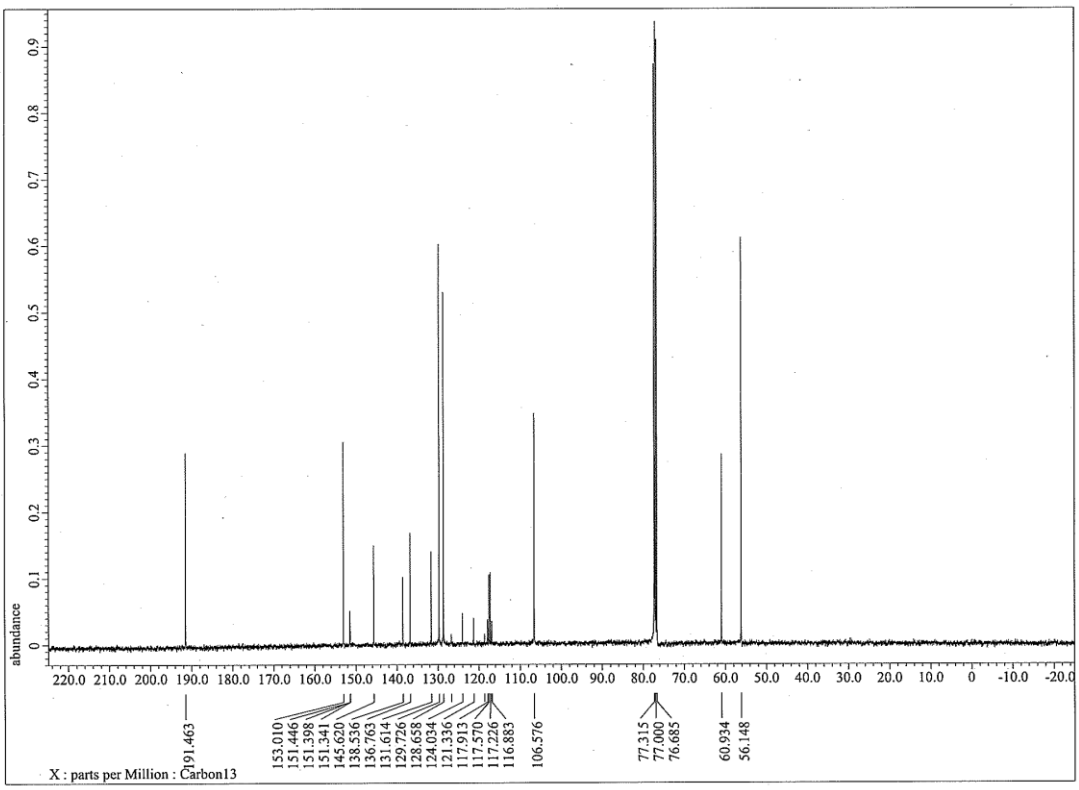

I
H
CF3
MeO
MeO
OMe
3ai
6.12
2.90
1.96
2.01
1.99
1.00
abundance
7.701
7.694
7.690
7.678
7.674
7.668
7.260
7.032
7.026
7.022
7.010
7.006
7.000
6.420
6.089
6.069
6.048
6.027
3.900
3.807
X : parts per Million : Proton

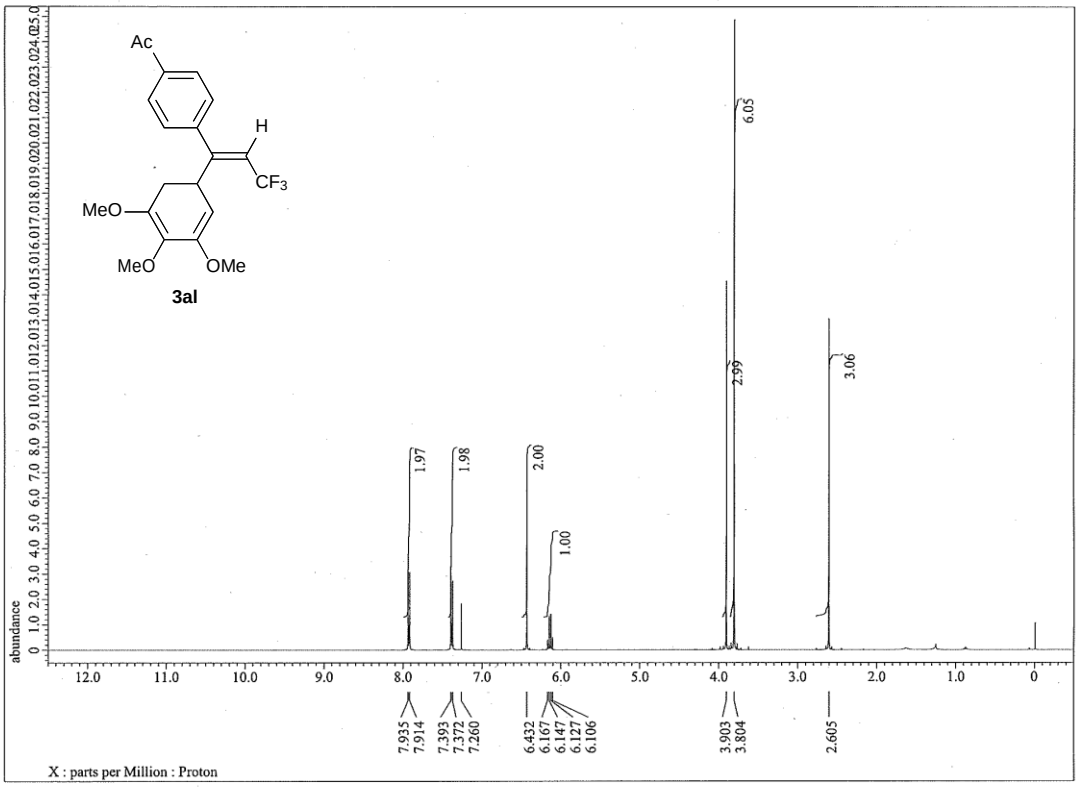

abundance
152.800
151.560
151.503
151.456
151.398
139.280
138.260
137.535
131.757
129.583
124.129
121.431
115.539
115.196
114.862
106.471
95.783
77.315
77.200
77.000
76.676
60.763
55.995
X : parts per Million : Carbon13

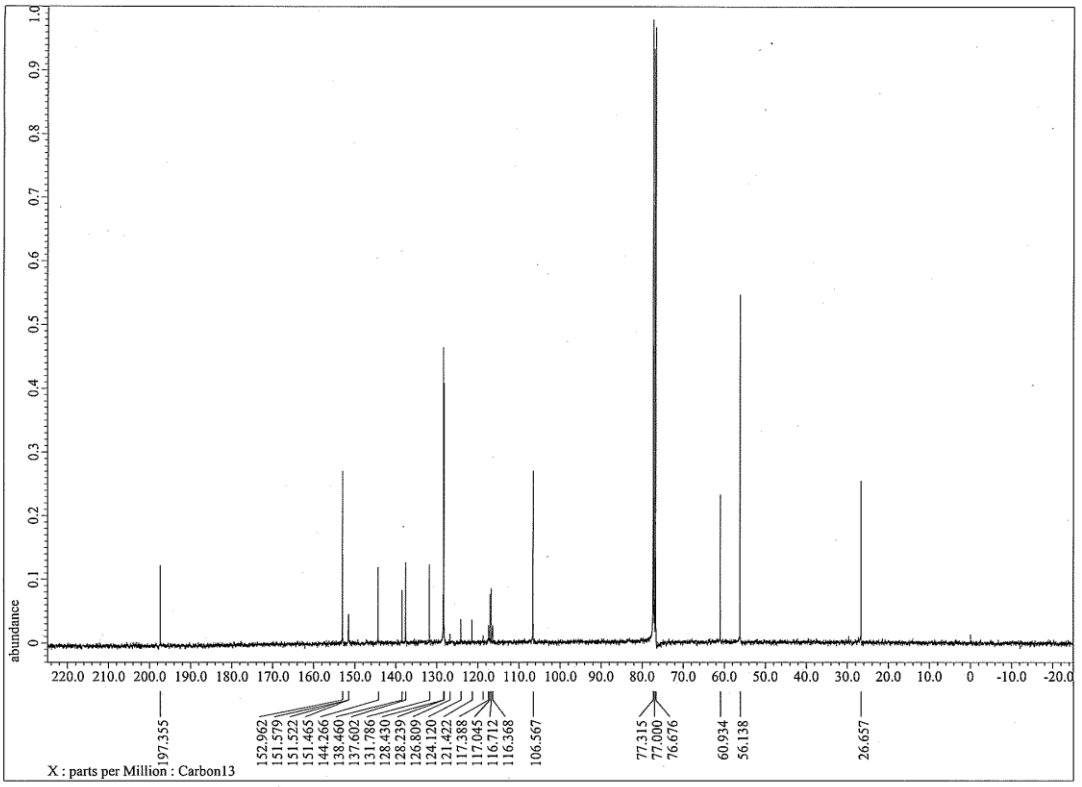

eo150807-1-p78-1_proton-1-6.jdf
MeO
H
CF3
MeO
MeO
OMe
3aj
abundance
8.97
2.92
1.96
2.03
1.00
7.260
7.223
7.202
6.852
6.830
6.455
6.029
6.008
5.986
5.966
3.888
3.790
X : parts per Million : Proton

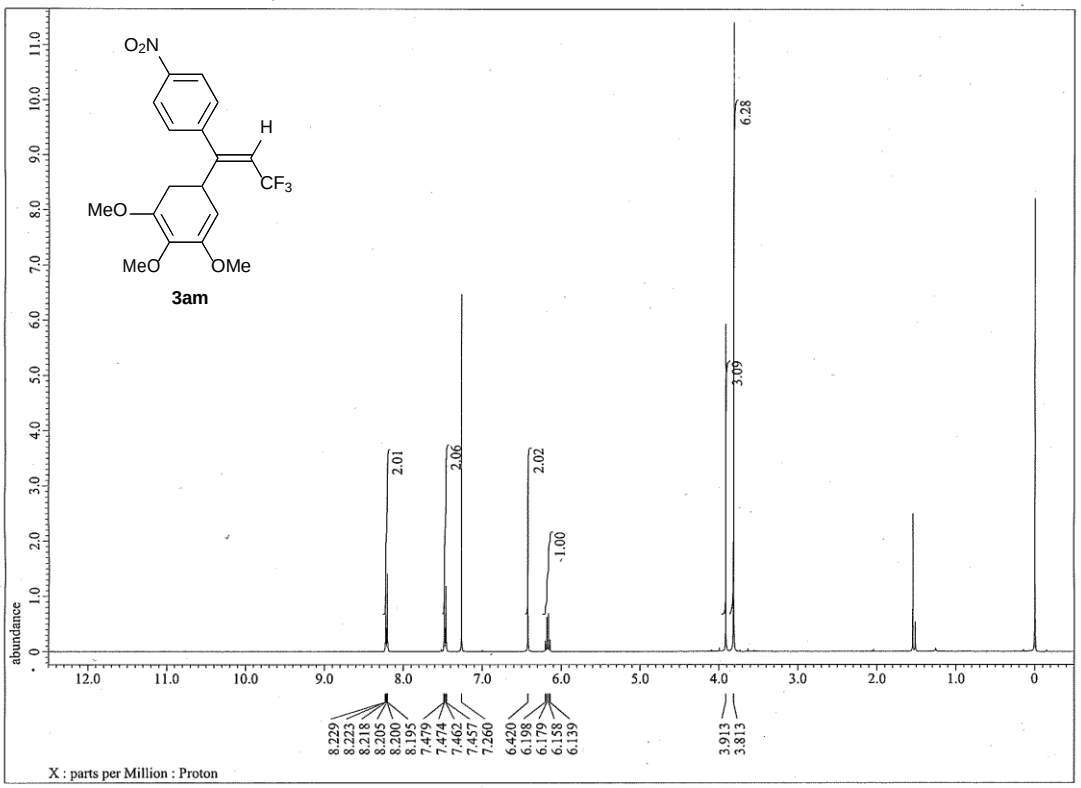

abundance
160.656
152.676
151.885
151.827
151.770
151.713
137.993
132.701
131.986
129.278
127.266
124.578
121.889
119.210
113.699
113.537
113.193
112.860
112.526
106.529
77.315
77.000
76.676
60.753
55.948
55.137
X : parts per Million : Carbon13

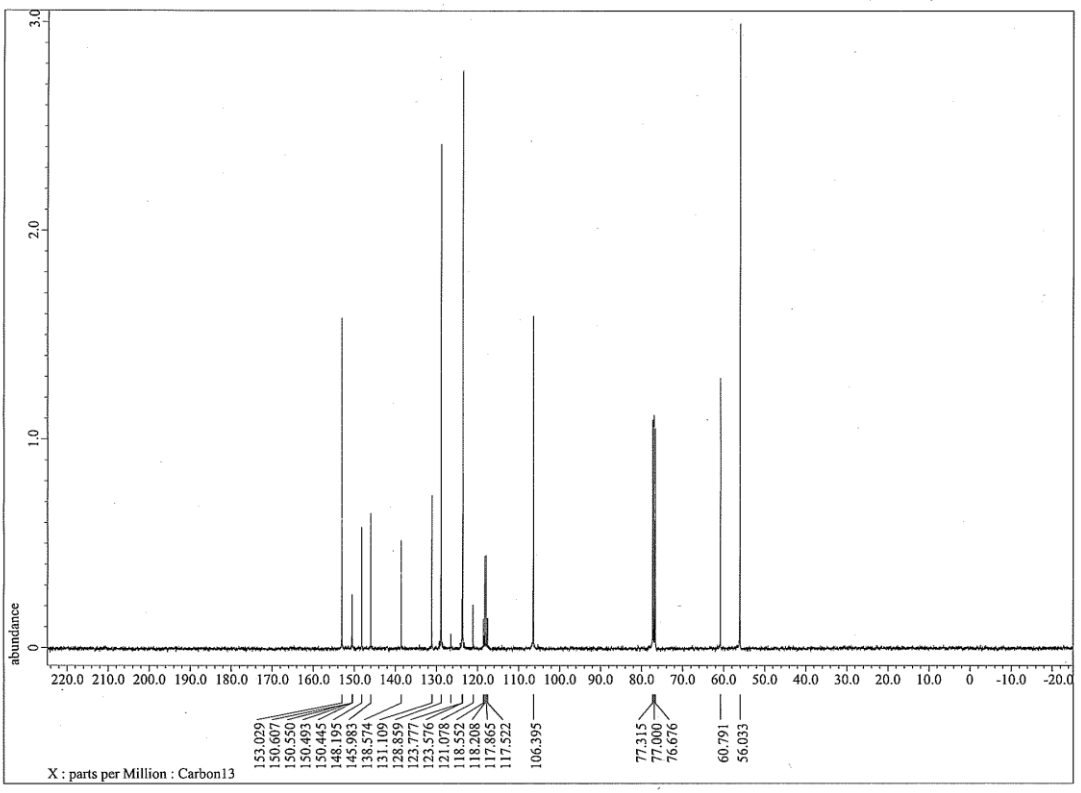

OHC
H
CF3
MeO
MeO
OMe
3ak
abundance
X : parts per Million : Proton

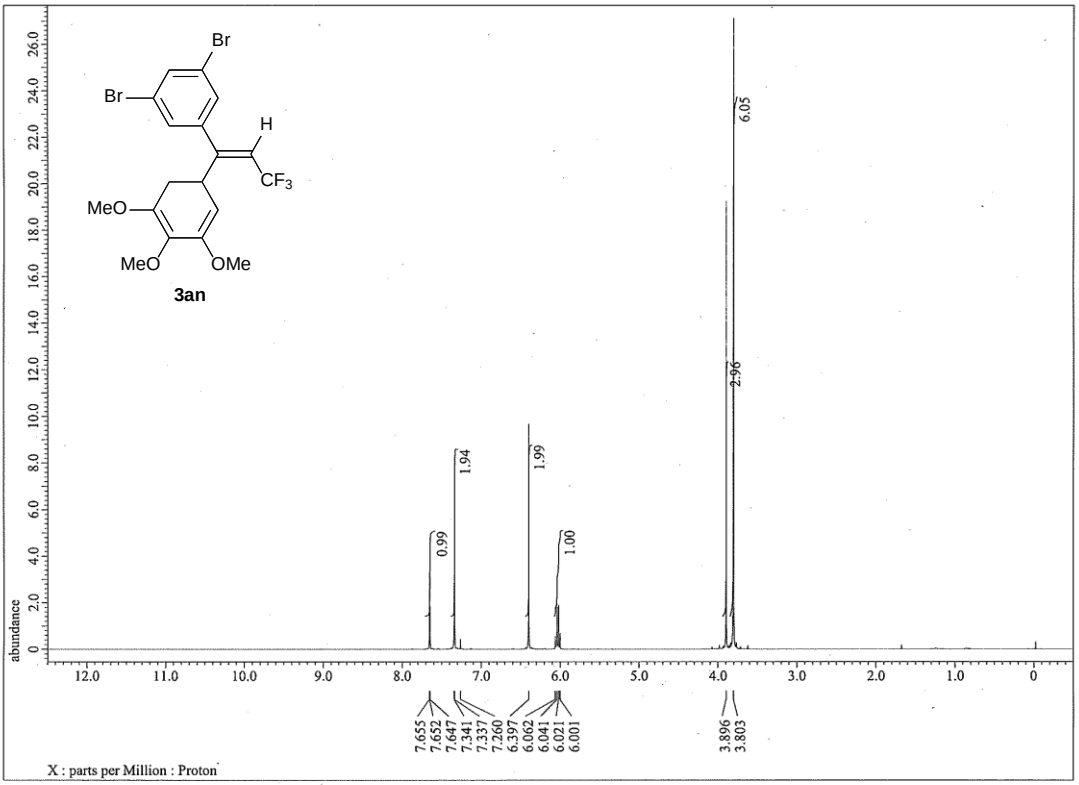

abundance
X : parts per Million : Carbon13

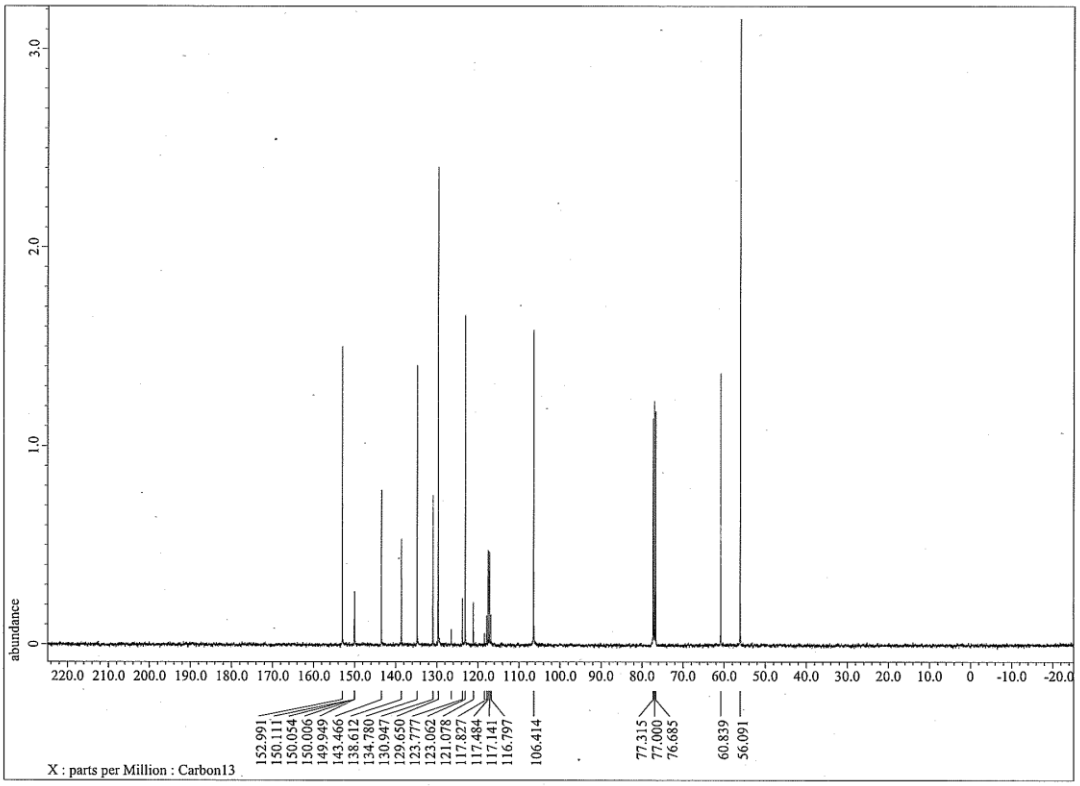

Ac
H
CF3
MeO
MeO
OMe
3aI
abundance
X : parts per Million : Proton
6.05
2.99
3.06
1.97
1.98
2.00
1.00
7.935
7.914
7.393
7.372
7.260
6.432
6.167
6.147
6.127
6.106
3.903
3.804
2.605

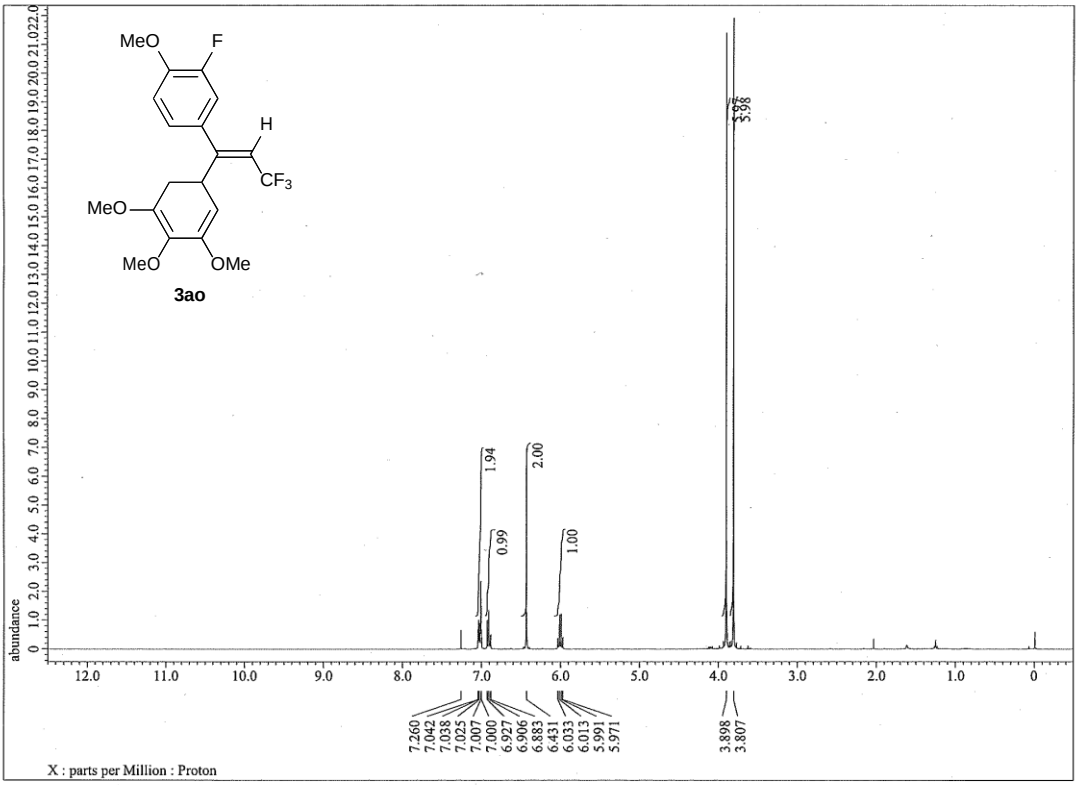

abundance
X : parts per Million : Carbon13
197.355
152.962
151.579
151.522
151.465
144.266
138.460
137.602
131.786
128.430
128.239
126.809
124.120
121.422
117.388
117.045
116.712
116.368
106.567
77.315
77.000
76.676
60.934
56.138
26.657

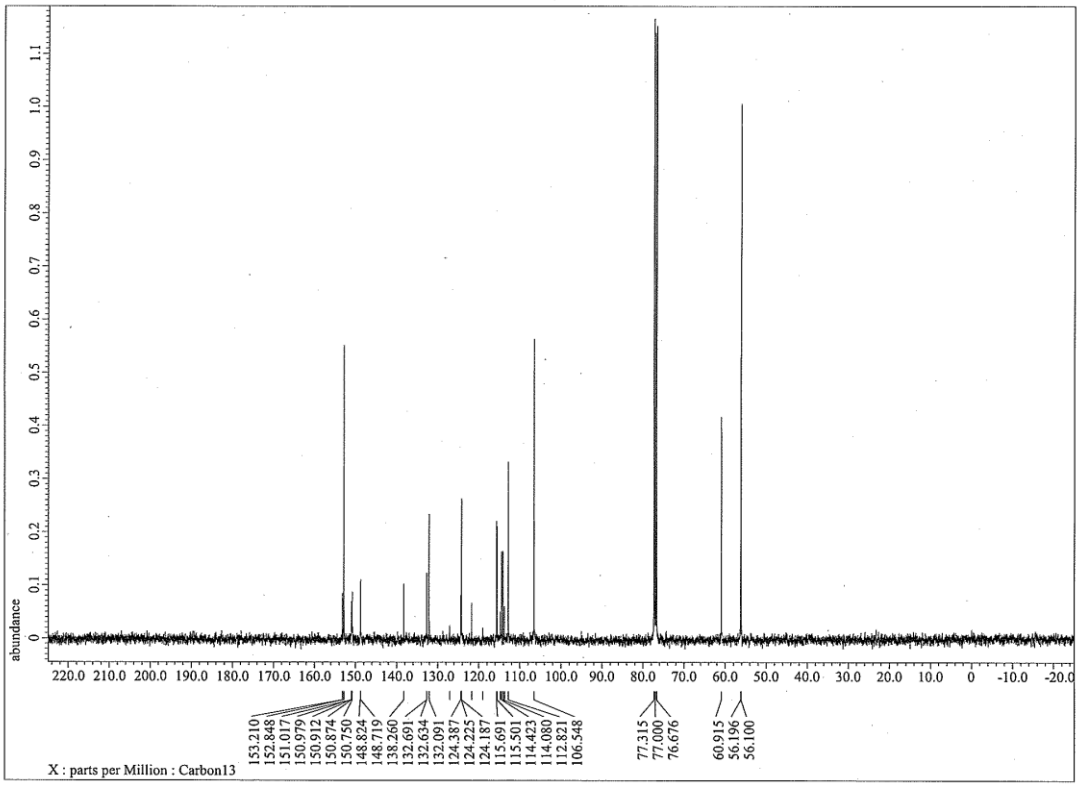

O2N
H
CF3
MeO
MeO
OMe
3am
abundance
6.28
3.09
2.01
2.06
2.02
1.00
8.229
8.223
8.218
8.205
8.200
8.195
7.479
7.474
7.462
7.457
7.260
6.420
6.198
6.179
6.158
6.139
3.913
3.813
X : parts per Million : Proton

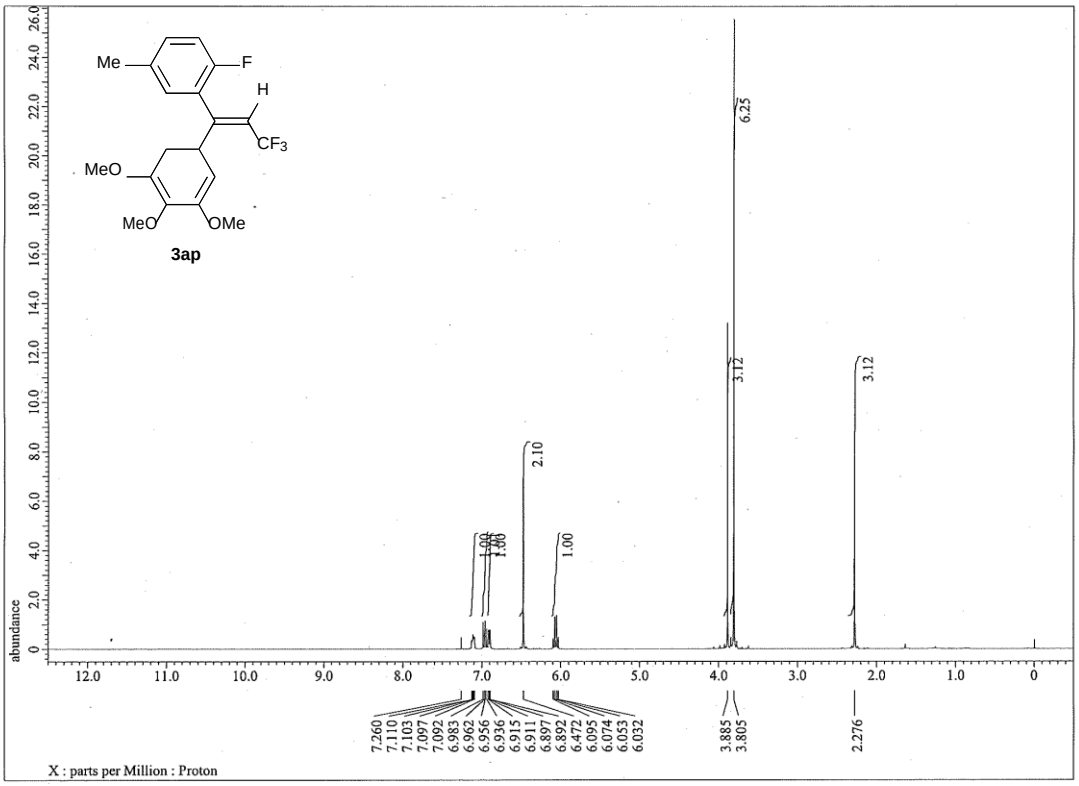

abundance
153.029
150.607
150.550
150.493
150.445
148.195
145.983
138.574
131.109
128.859
123.777
123.576
121.078
118.552
118.208
117.865
117.522
106.395
77.315
77.000
76.676
60.791
56.033
X : parts per Million : Carbon13

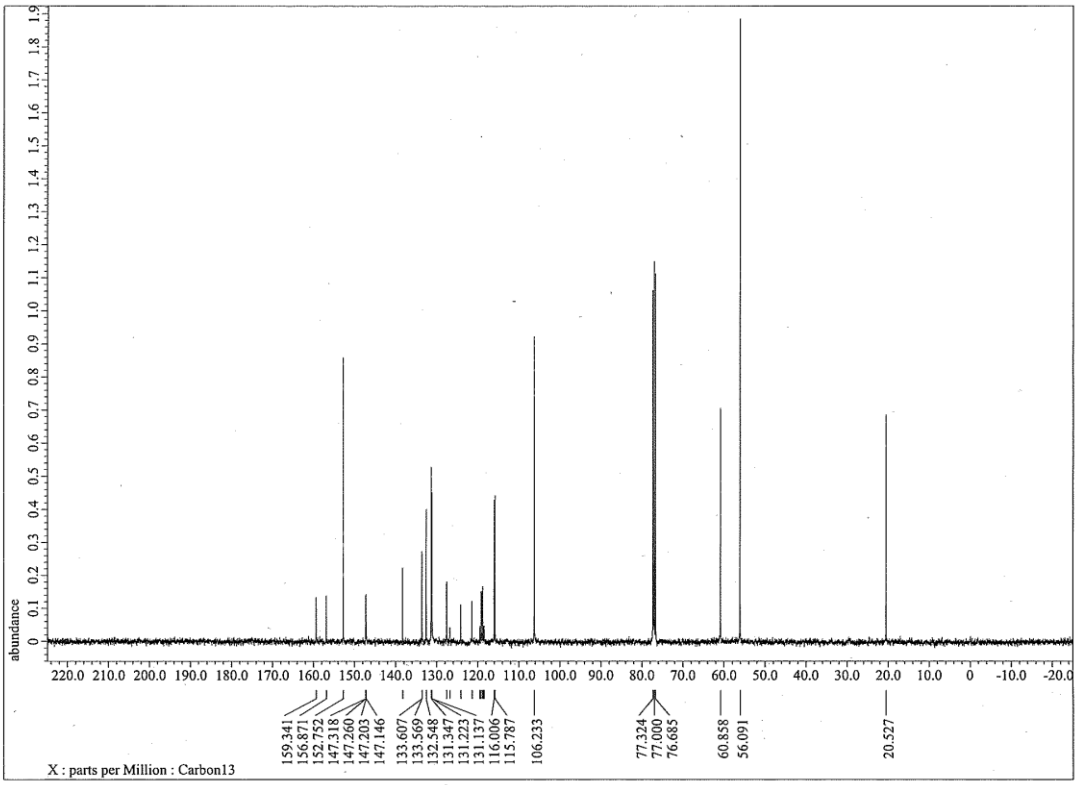

Br
Br
H
CF3
MeO
MeO
OMe
3an
abundance
6.05
2.96
1.94
1.99
0.99
1.00
7.655
7.652
7.647
7.341
7.337
7.260
6.397
6.062
6.041
6.021
6.001
3.896
3.803
X : parts per Million : Proton

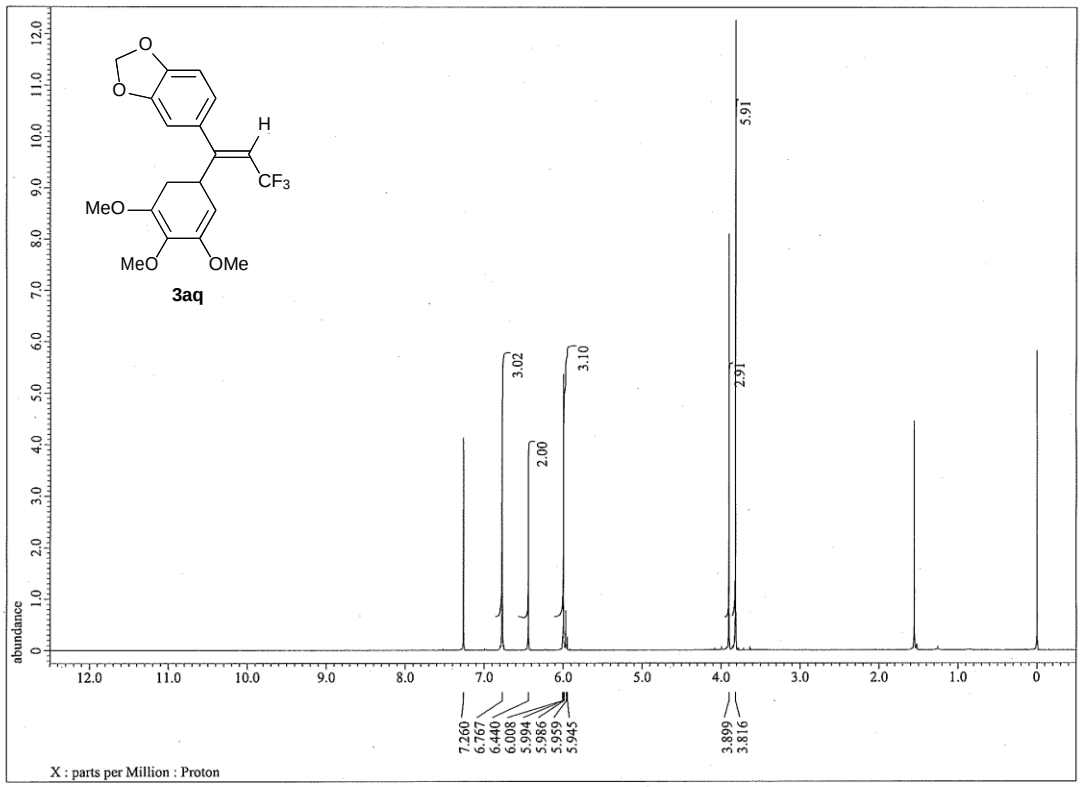

abundance
152.991
150.111
150.054
150.006
149.949
143.466
138.612
134.780
130.947
129.650
123.777
123.062
121.078
117.827
117.484
117.141
116.797
106.414
77.315
77.000
76.685
60.839
56.091
X : parts per Million : Carbon13

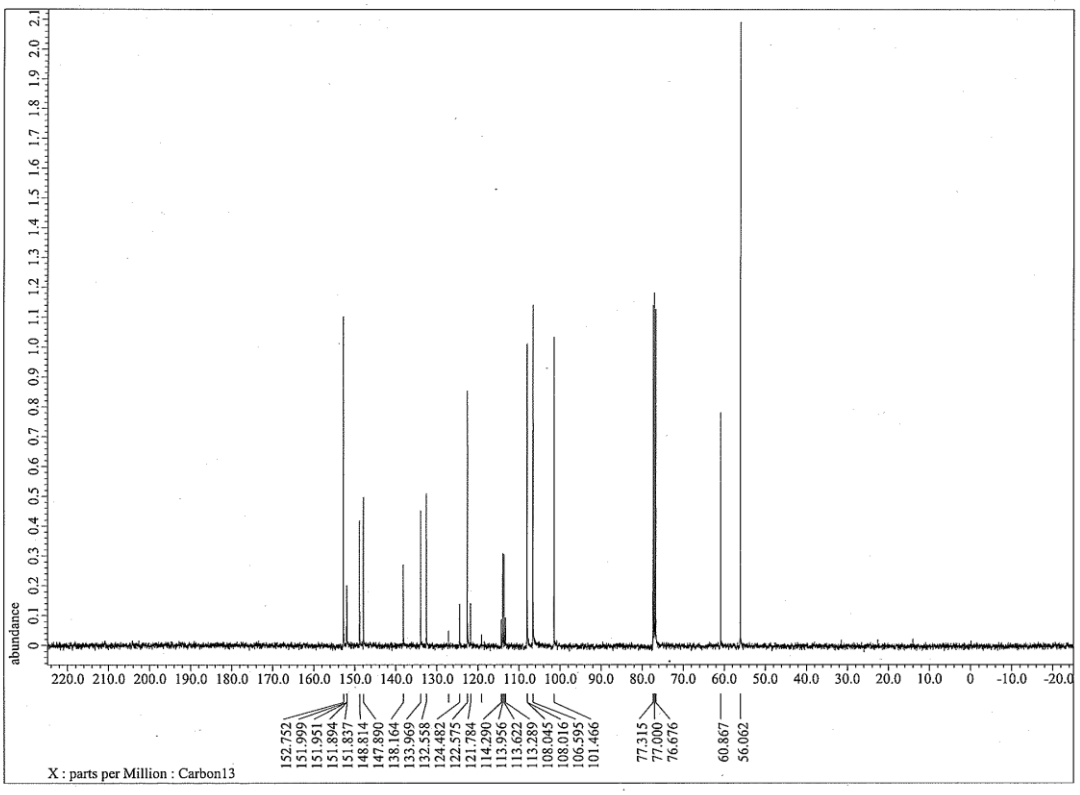

MeO
F
H
CF3
MeO
MeO
OMe
3ao
abundance
1.94
0.99
2.00
1.00
3.00
2.98
7.260
7.042
7.038
7.025
7.007
7.000
6.927
6.906
6.883
6.431
6.033
6.013
5.991
5.971
3.898
3.807
X : parts per Million : Proton

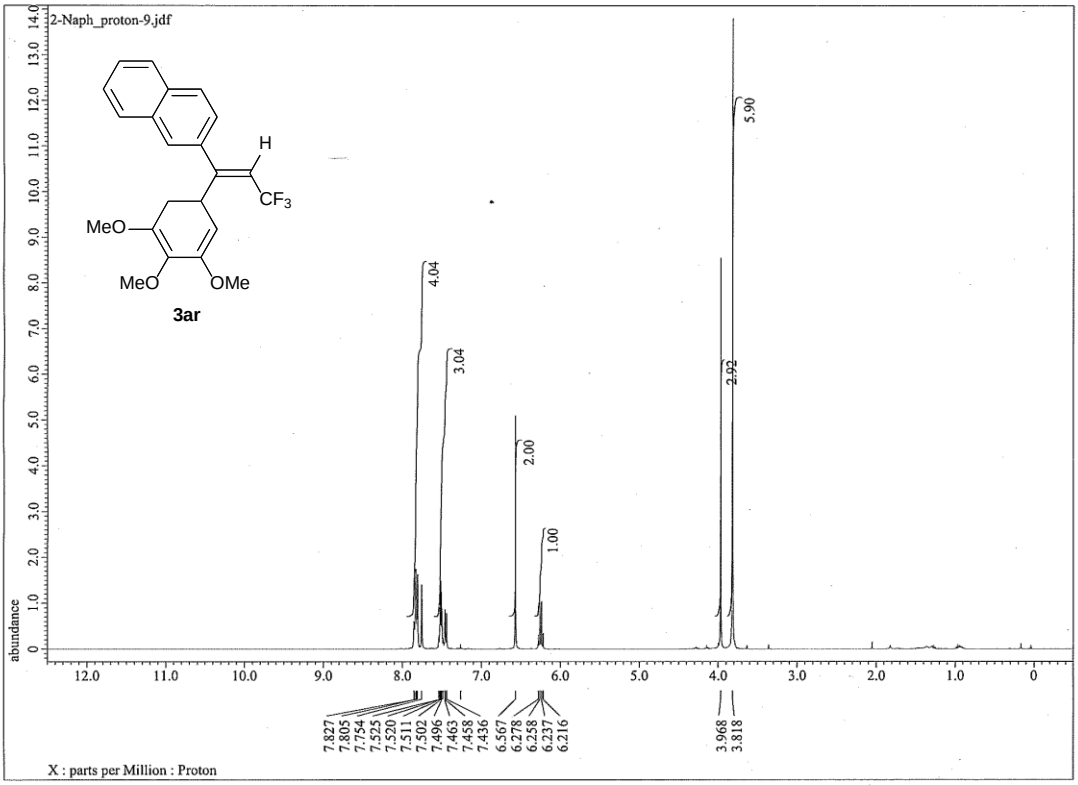

abundance
153.210
152.848
151.017
150.979
150.912
150.874
150.750
148.824
148.719
138.260
132.691
132.634
132.091
124.387
124.225
124.187
115.691
115.501
114.423
114.080
112.821
106.548
77.315
77.000
76.676
60.915
56.196
56.100
X : parts per Million : Carbon13

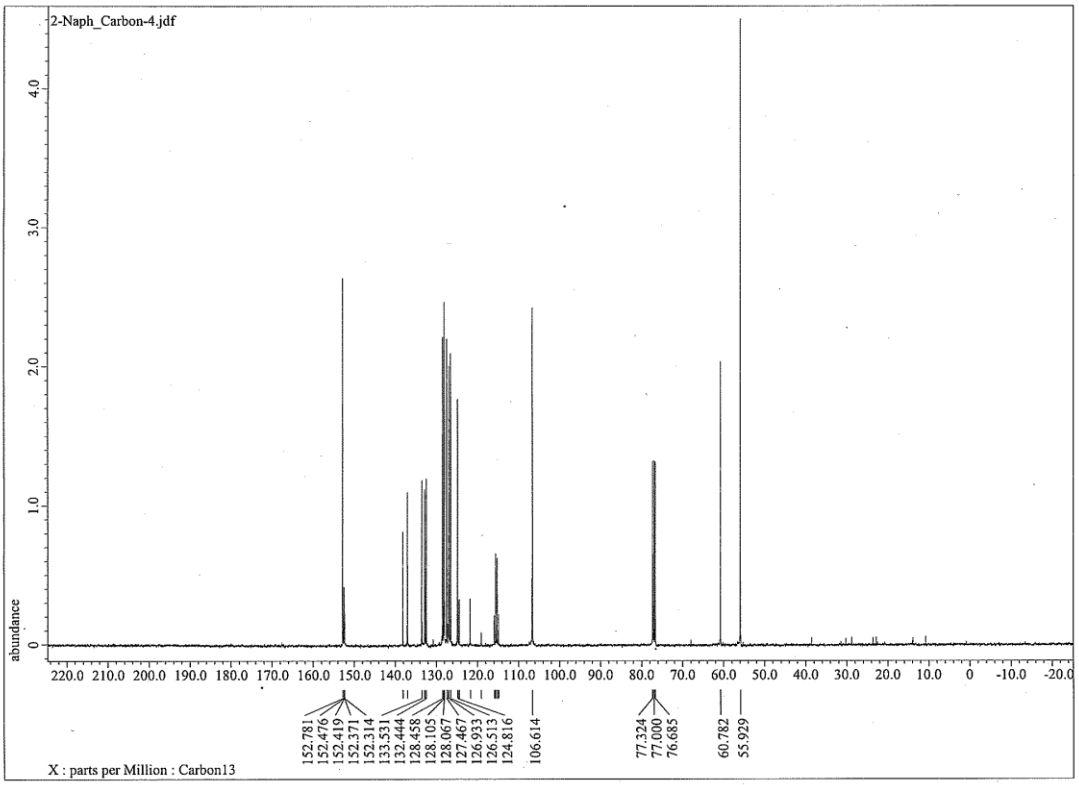

Me
F
H
CF3
MeO
MeO
OMe
3ap
abundance
6.25
3.12
3.12
2.10
1.00
1.00
1.00
1.00
7.260
7.110
7.103
7.097
7.092
6.983
6.962
6.956
6.936
6.915
6.911
6.897
6.892
6.472
6.095
6.074
6.053
6.032
3.885
3.805
2.276
X : parts per Million : Proton

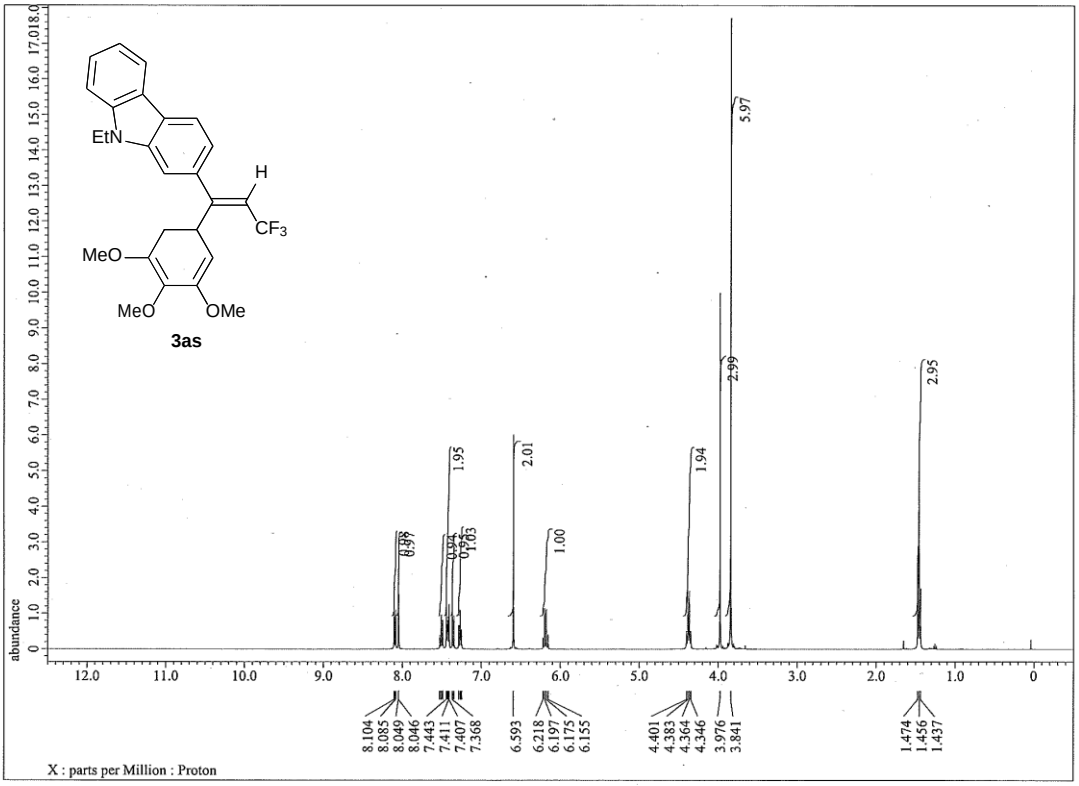

abundance
159.341
156.871
152.752
147.318
147.260
147.203
147.146
133.607
133.569
132.548
131.347
131.223
131.137
116.006
115.787
106.233
77.324
77.000
76.685
60.858
56.091
20.527
X : parts per Million : Carbon13

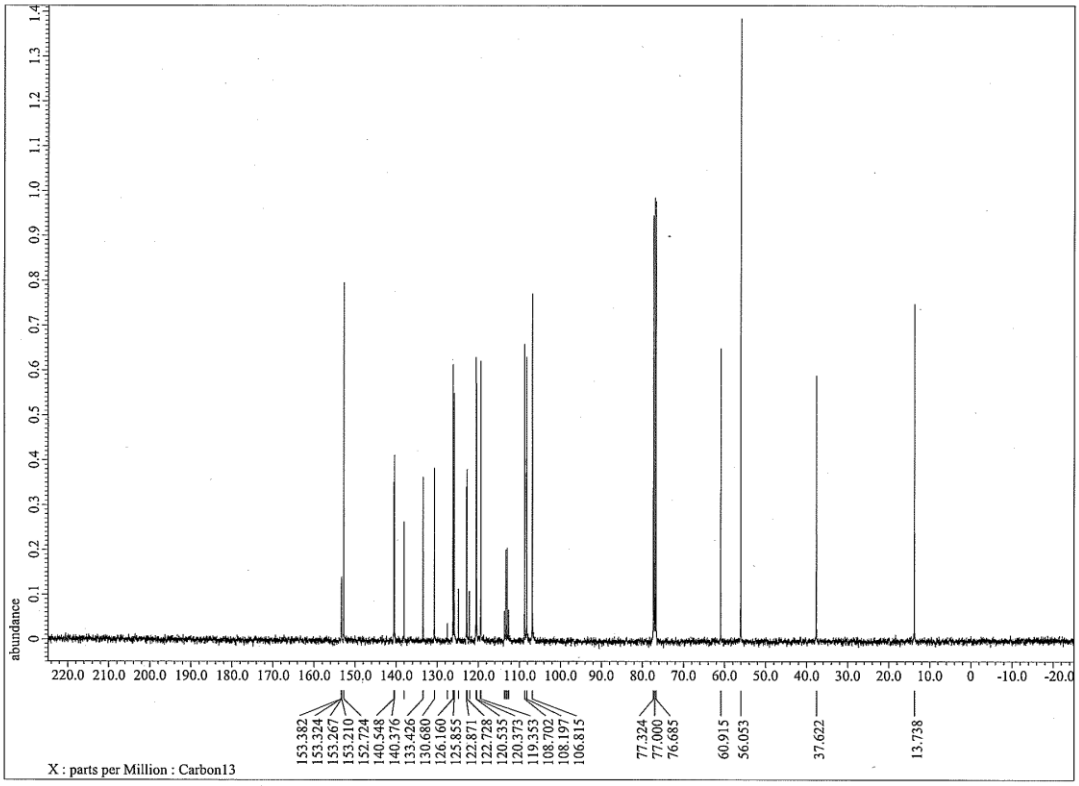

O
O
H
CF3
MeO
MeO
OMe
3aq
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.91
3.02
3.10
2.91
2.00
7.260
6.767
6.440
6.008
5.994
5.986
5.959
5.945
3.899
3.816
X : parts per Million : Proton

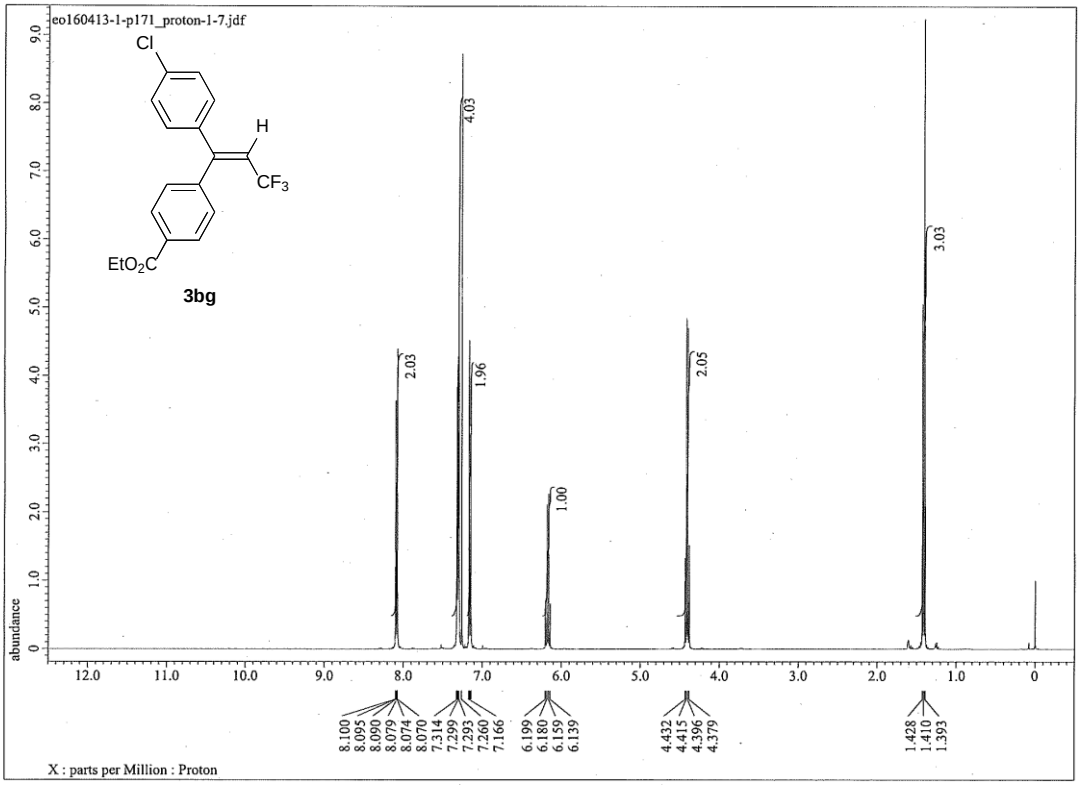

abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
152.752
151.999
151.951
151.894
151.837
148.814
147.890
138.164
133.969
132.558
124.482
122.575
121.784
114.290
113.956
113.622
113.289
108.045
108.016
106.595
101.466
77.315
77.000
76.676
60.867
56.062
X : parts per Million : Carbon13

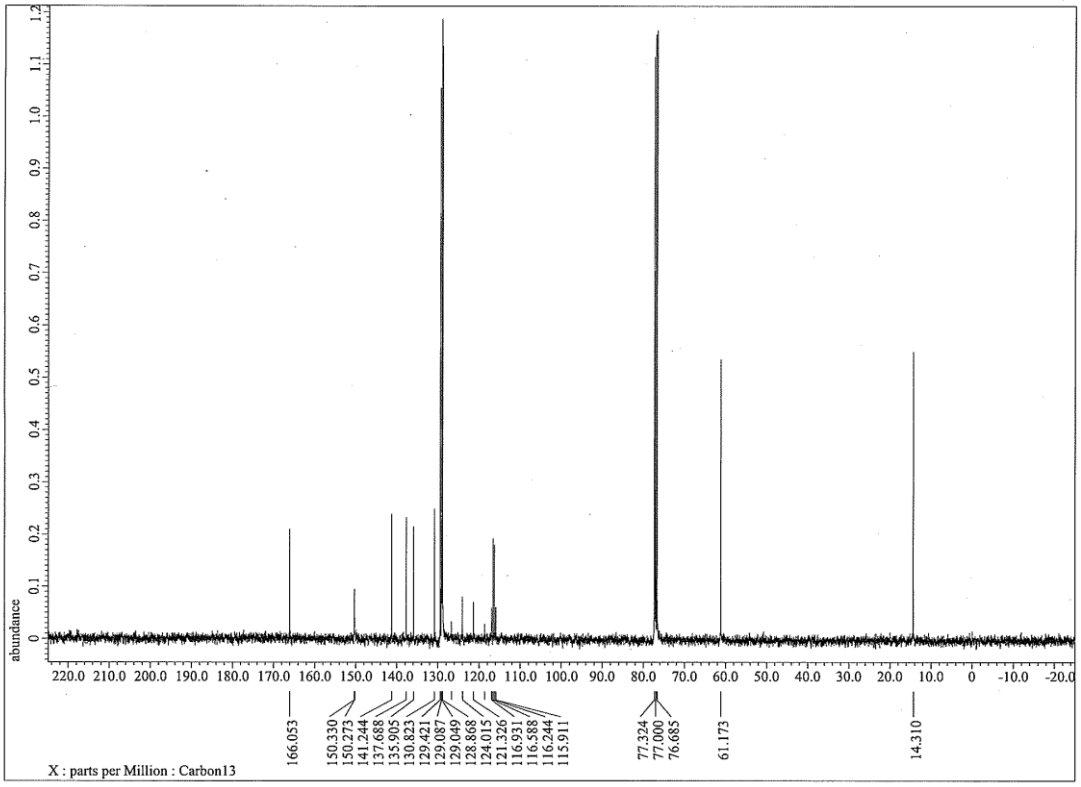

2-Naph_proton-9.jdf
H
CF3
MeO
MeO
OMe
3ar
4.04
3.04
2.00
1.00
2.92
5.90
abundance
7.827
7.805
7.754
7.525
7.520
7.511
7.502
7.496
7.463
7.458
7.436
6.567
6.278
6.258
6.237
6.216
3.968
3.818
X : parts per Million : Proton

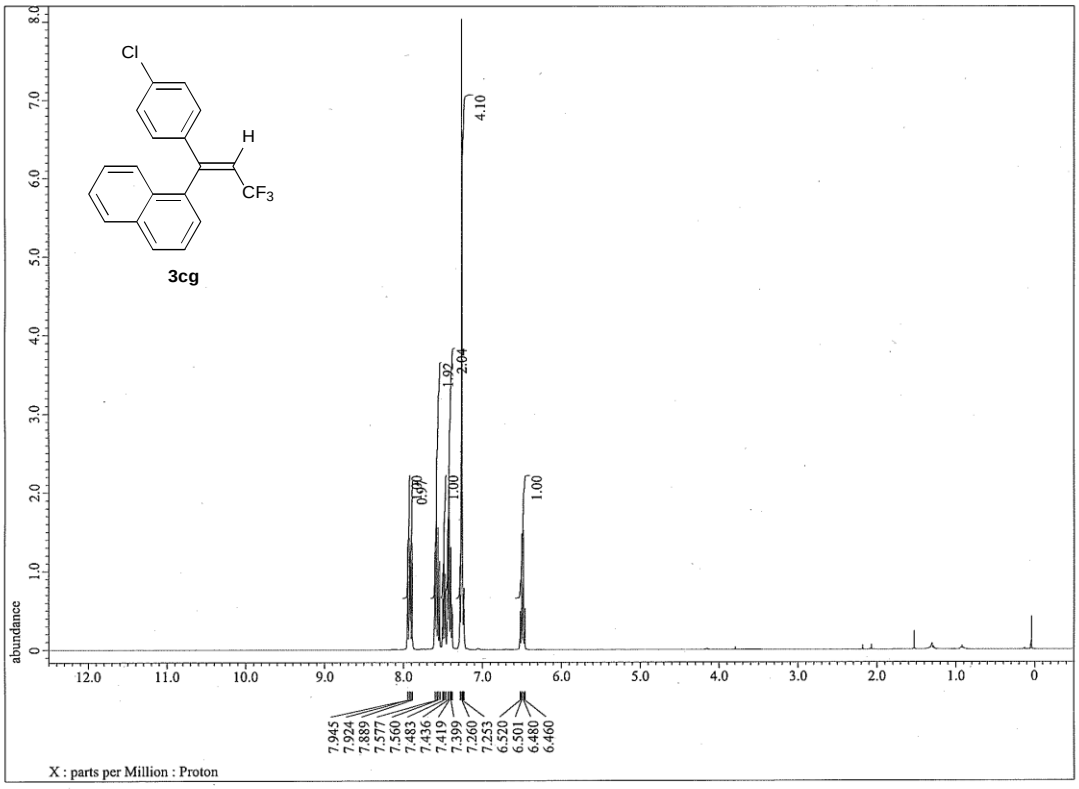

2-Naph_Carbon-4.jdf
abundance
152.781
152.476
152.419
152.371
152.314
133.531
132.444
128.458
128.105
128.067
127.467
126.933
126.513
124.816
106.614
77.324
77.000
76.685
60.782
55.929
X : parts per Million : Carbon13

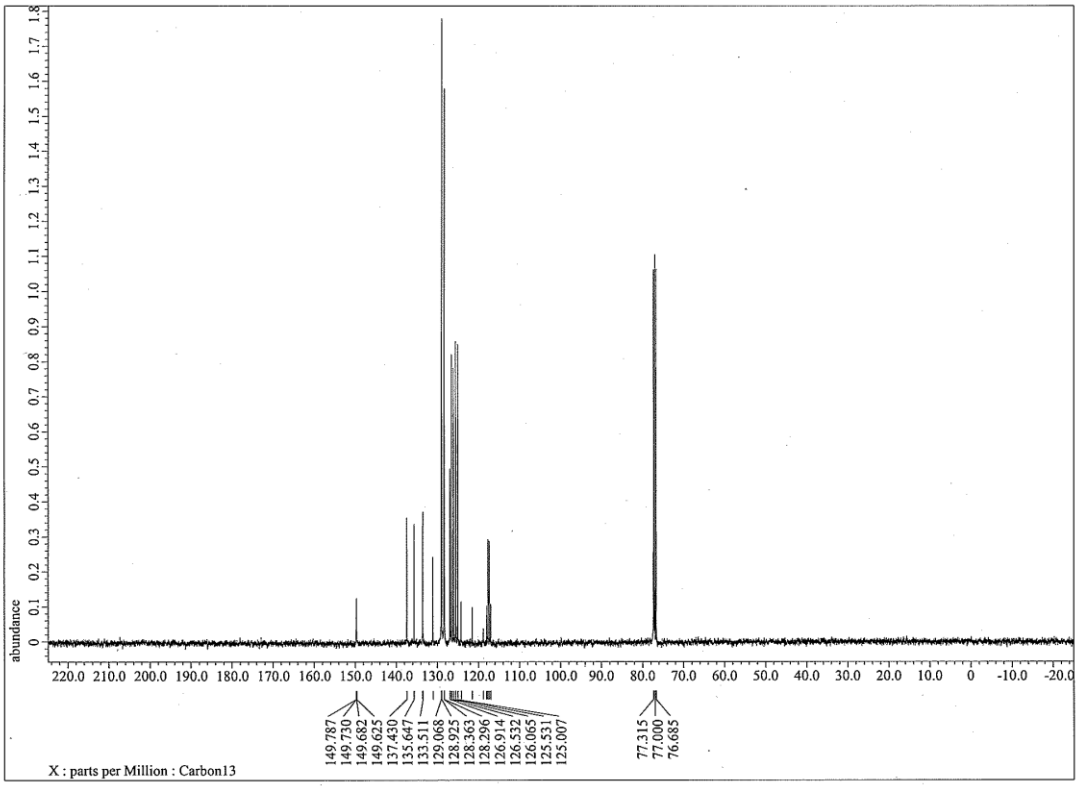

EtN
H
CF3
MeO
MeO
OMe
3as
abundance
X : parts per Million : Proton

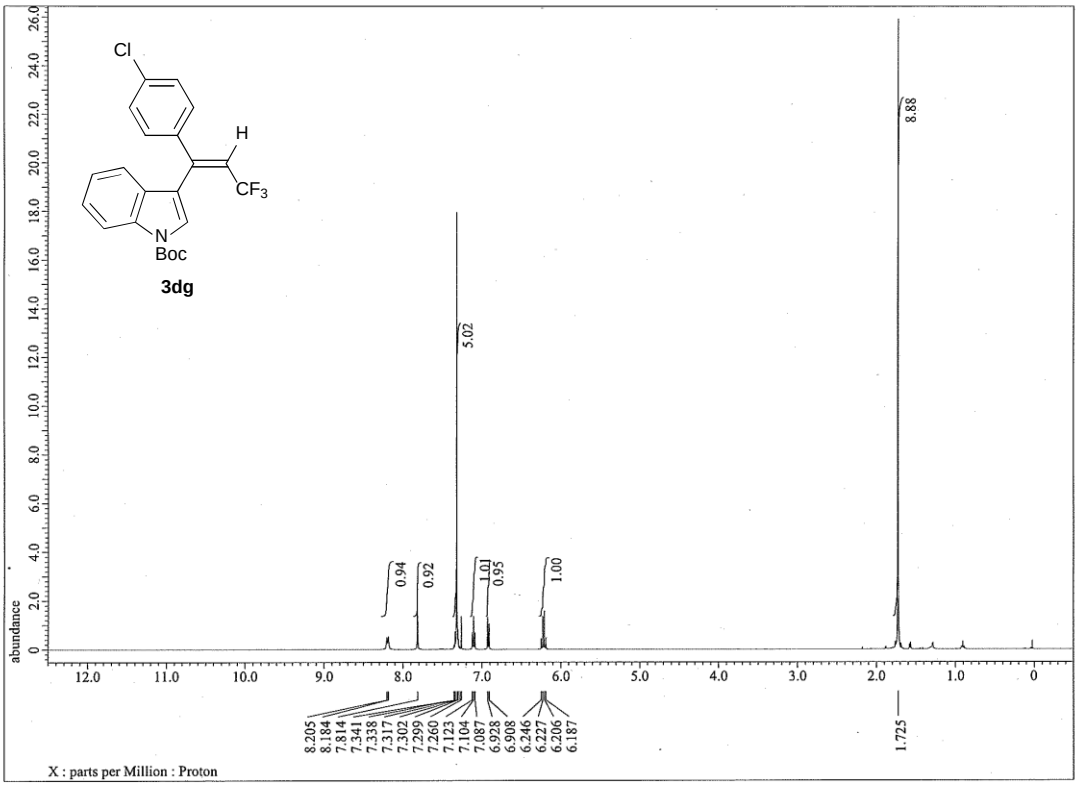

abundance
X : parts per Million : Carbon13

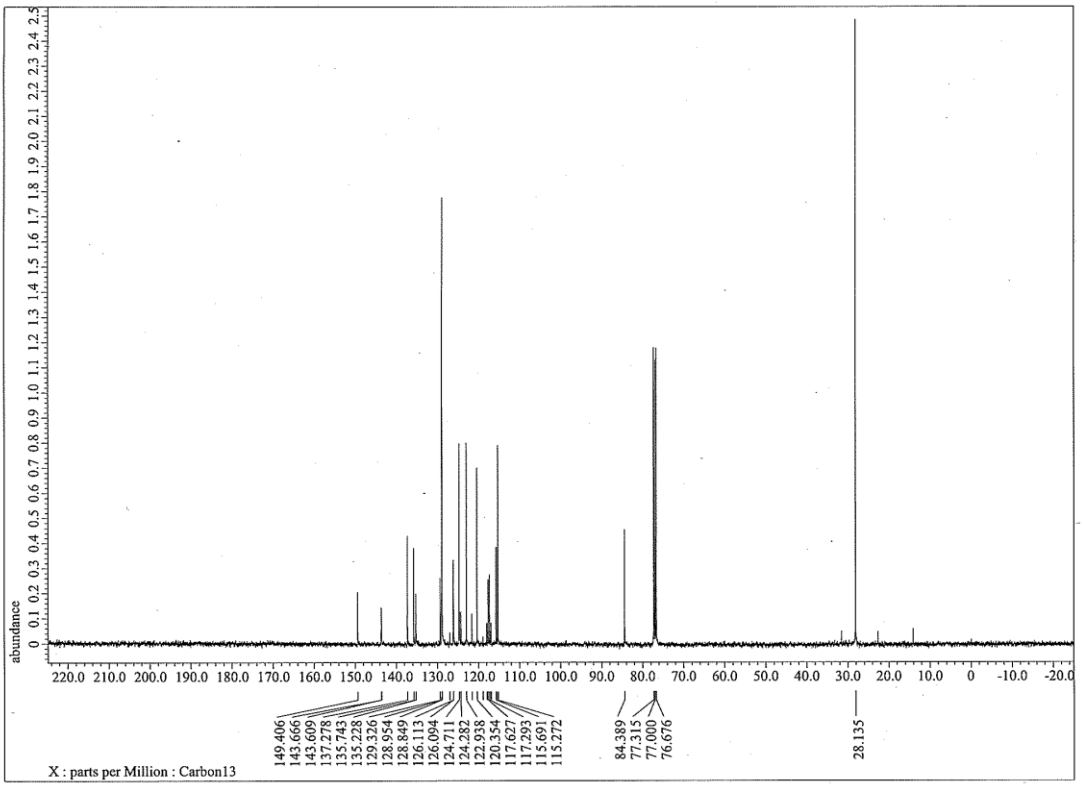

eo160413-1-p171_proton-1-7.jdf
Cl
H
CF3
EtO2C
3bg
abundance
X : parts per Million : Proton

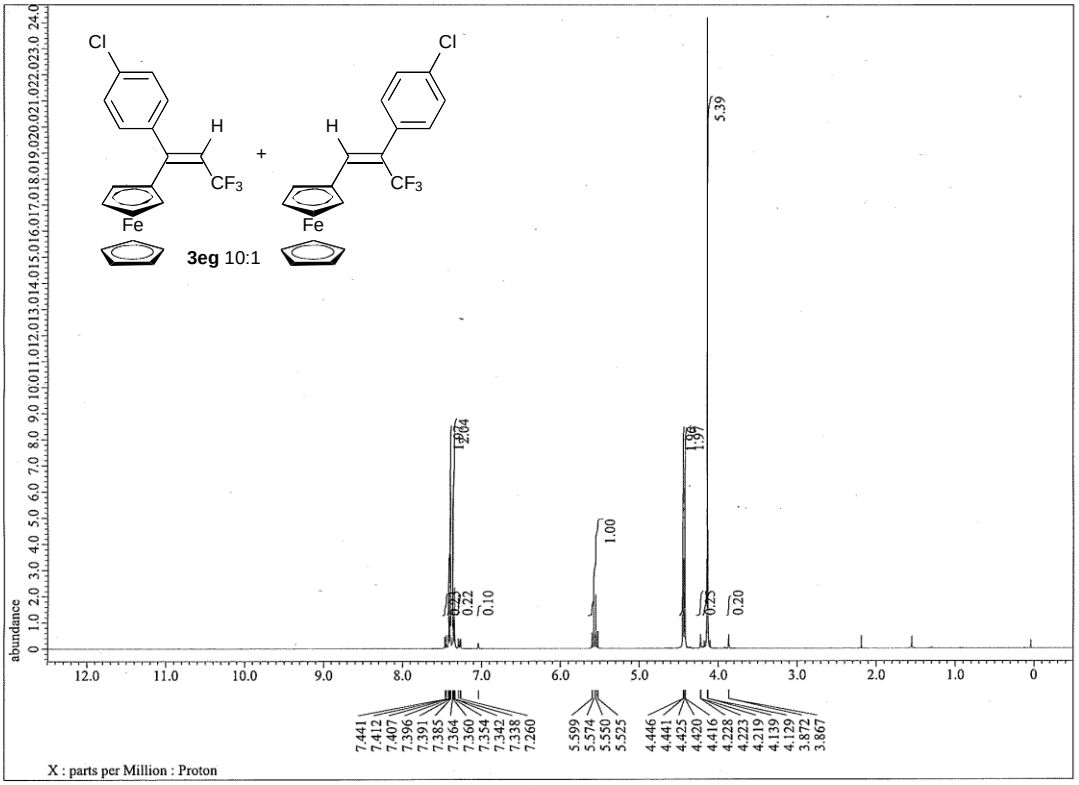

abundance
X : parts per Million : Carbon13

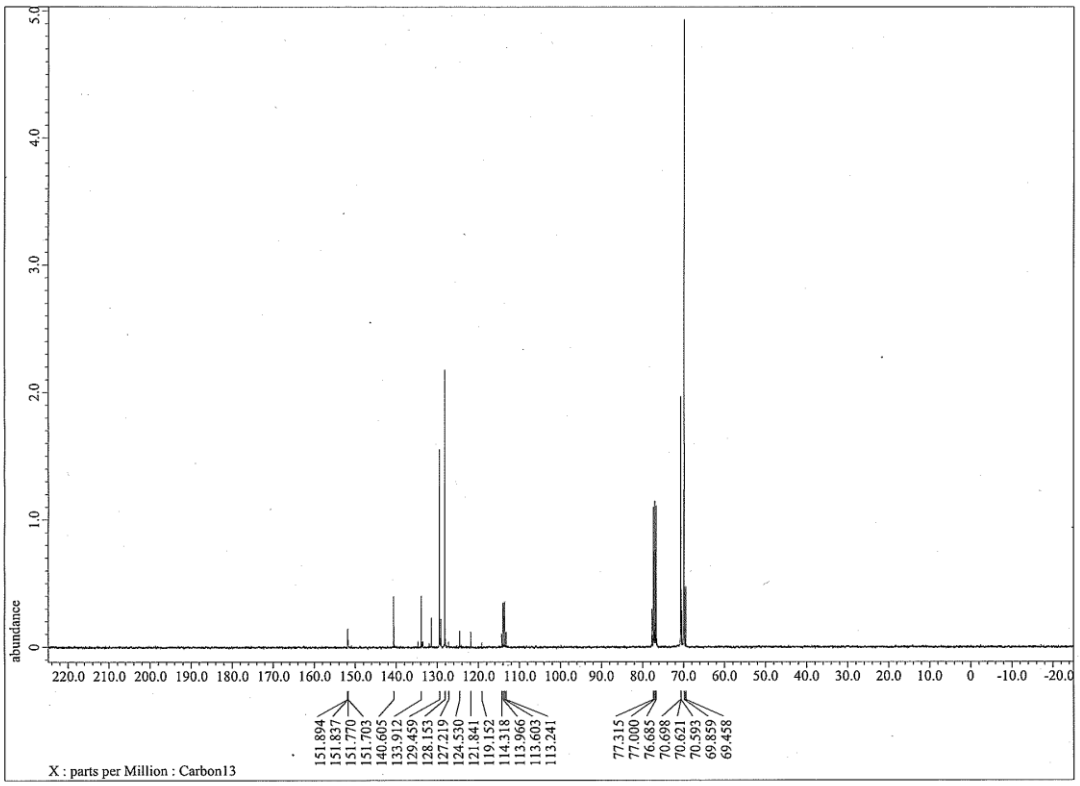

Cl
H
CF3
3cg
4.10
2.04
1.92
1.00
1.00
0.90
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.945
7.924
7.889
7.577
7.560
7.483
7.436
7.419
7.399
7.260
7.253
6.520
6.501
6.480
6.460
X : parts per Million : Proton

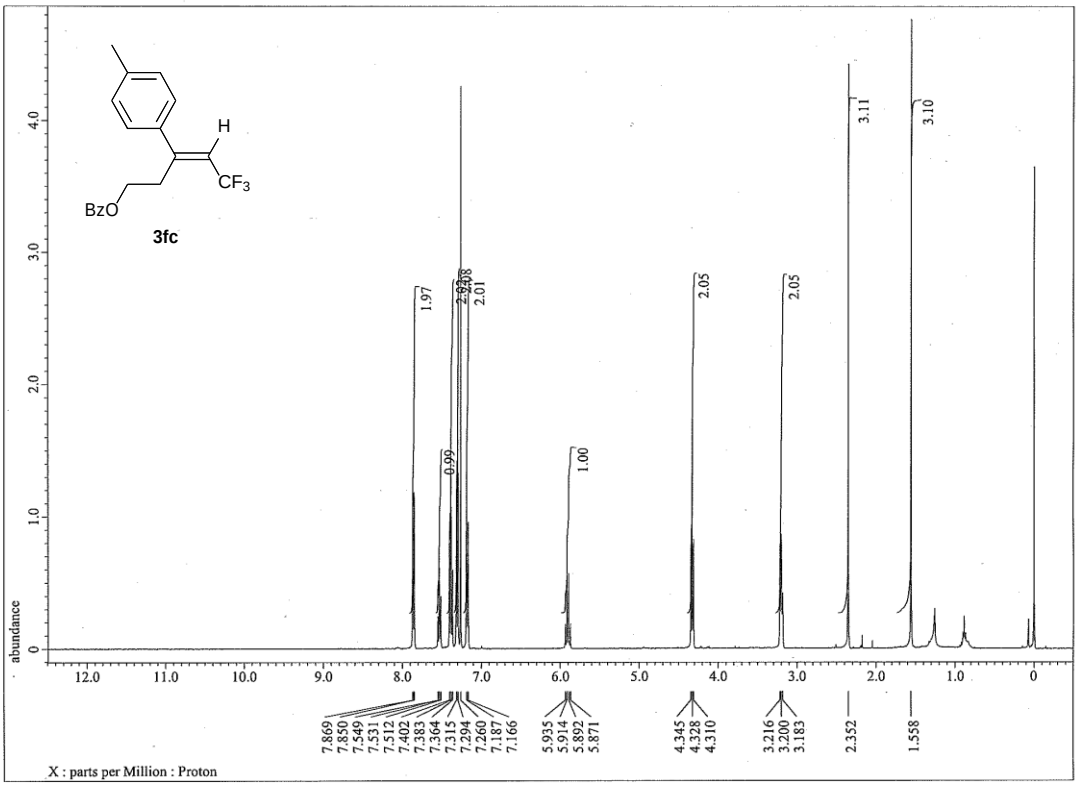

abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
149.787
149.730
149.682
149.625
137.430
135.647
133.511
129.068
128.925
128.363
128.296
126.914
126.532
126.065
125.531
125.007
77.315
77.000
76.685
X : parts per Million : Carbon13

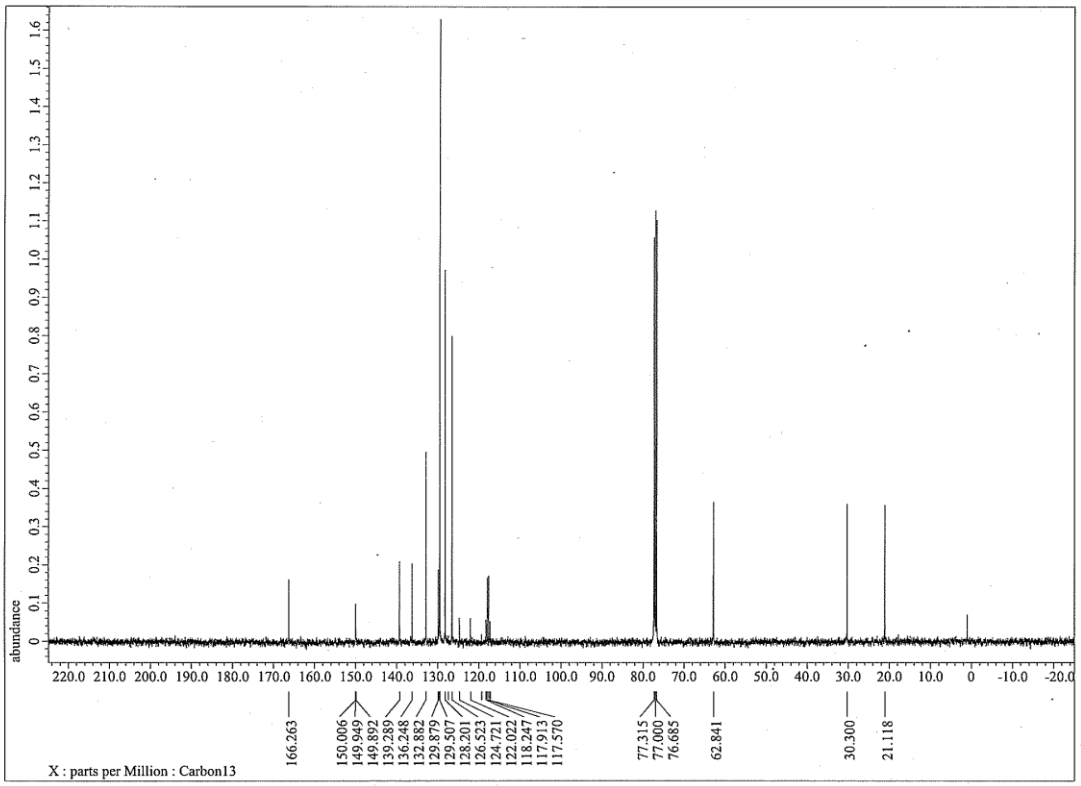

Cl
H
CF3
N
Boc
3dg
abundance
8.88
5.02
0.94
0.92
1.01
0.95
1.00
8.205
8.184
7.814
7.341
7.338
7.317
7.302
7.299
7.260
7.123
7.104
7.087
6.928
6.908
6.246
6.227
6.206
6.187
1.725
X : parts per Million : Proton

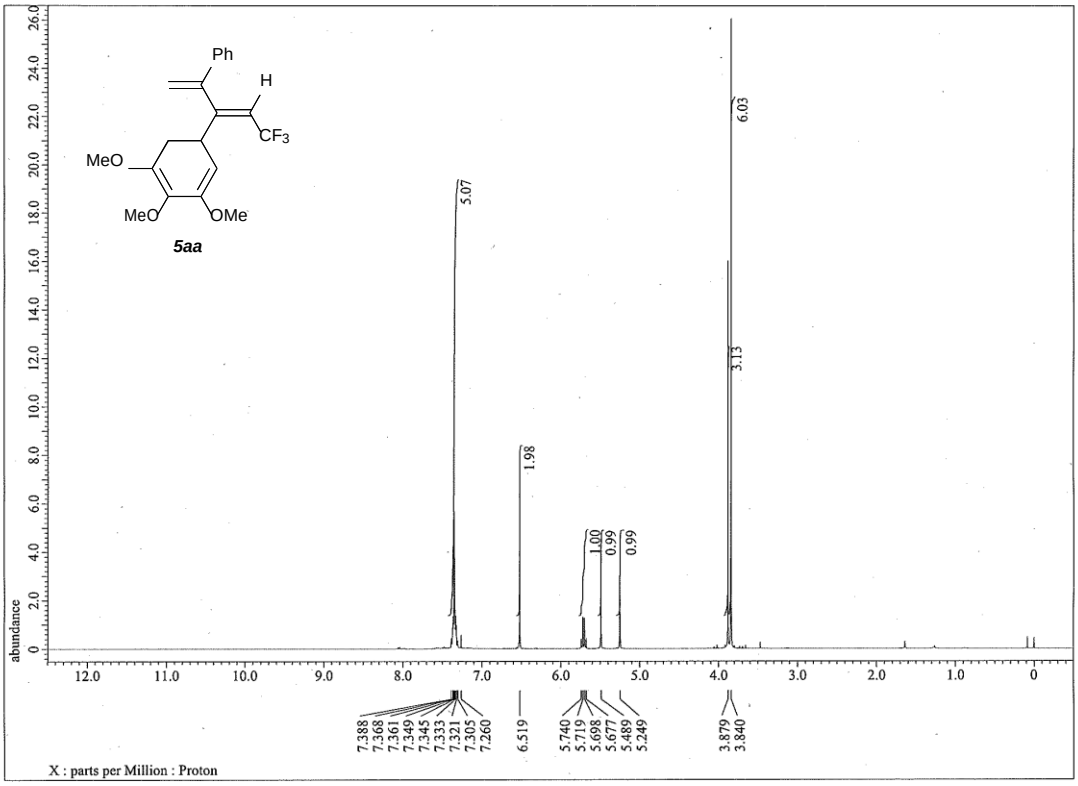

abundance
149.406
143.666
143.609
137.278
135.743
135.228
129.326
128.954
128.849
126.113
126.094
124.711
124.282
122.938
120.354
117.627
117.293
115.691
115.272
84.389
77.315
77.000
76.676
28.135
X : parts per Million : Carbon13

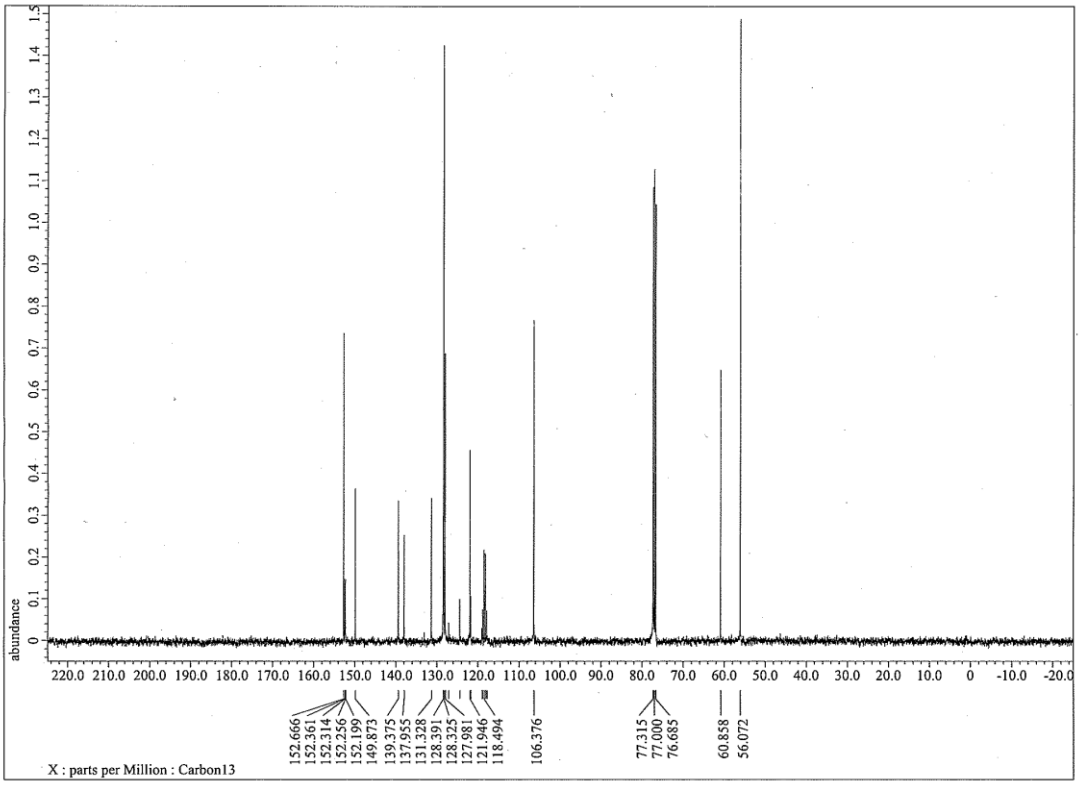

Cl
H
CF3
Fe
+
Cl
H
CF3
Fe
3eg 10:1
abundance
X : parts per Million : Proton

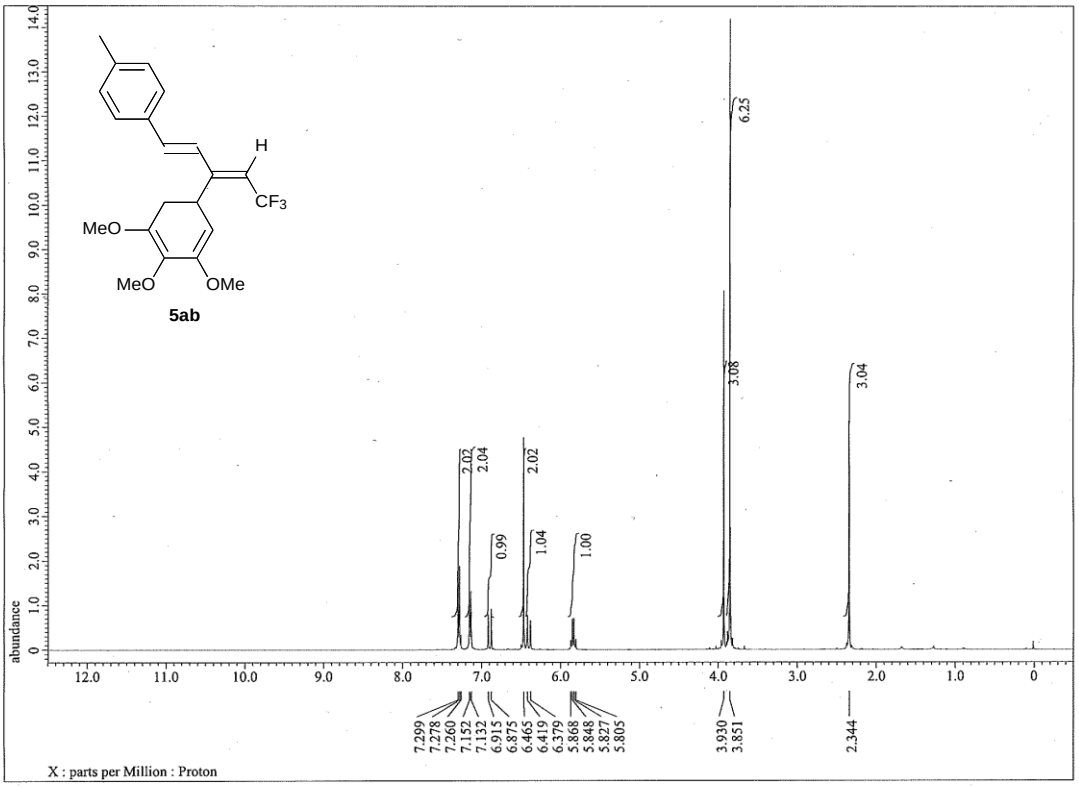

abundance
X : parts per Million : Carbon13

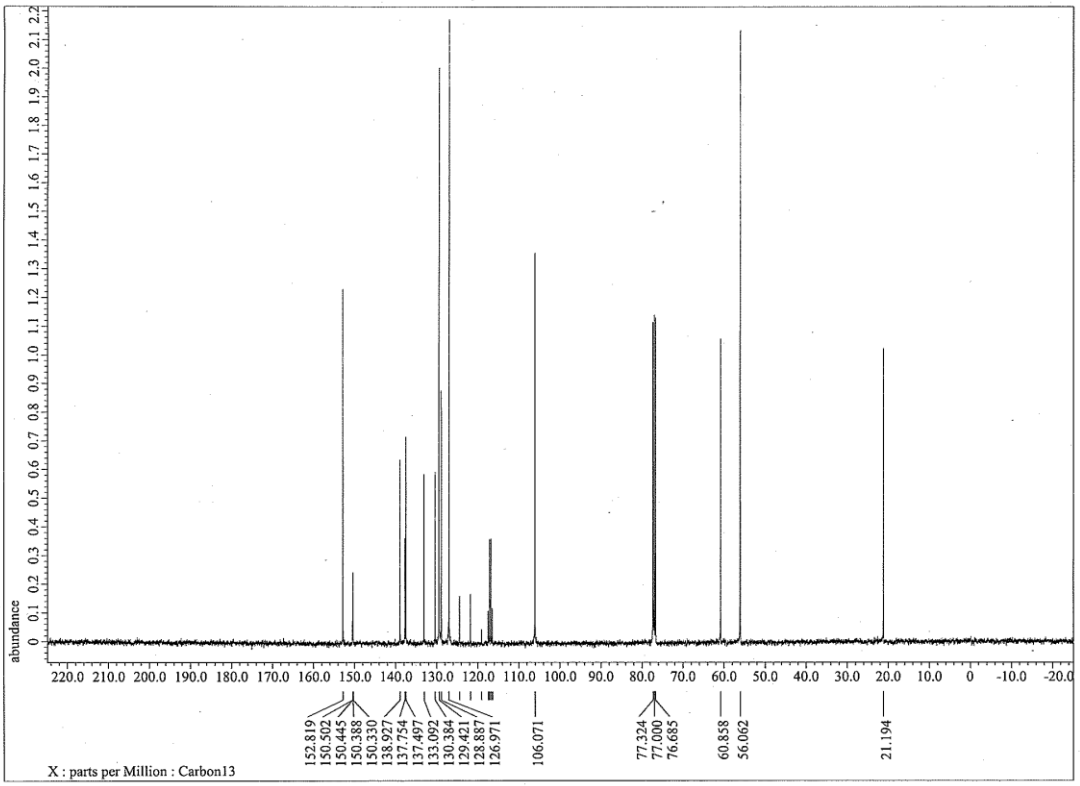

H
CF3
BzO
3fc
abundance
X : parts per Million : Proton

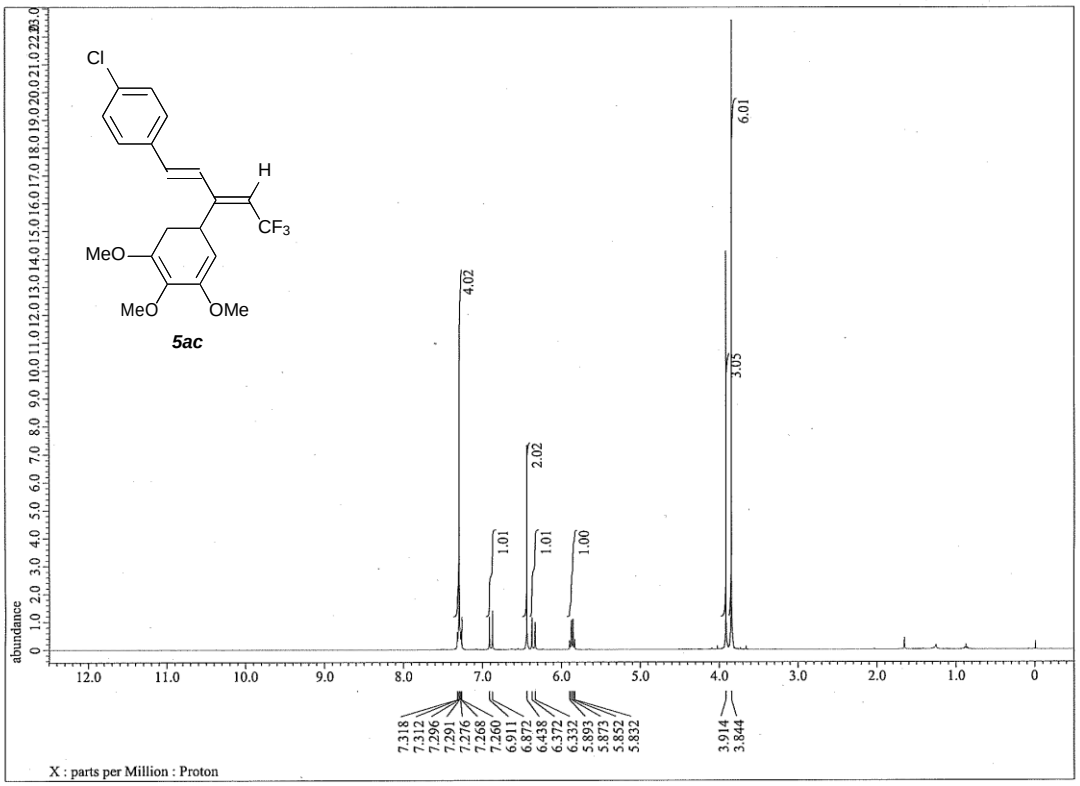

abundance
X : parts per Million : Carbon13

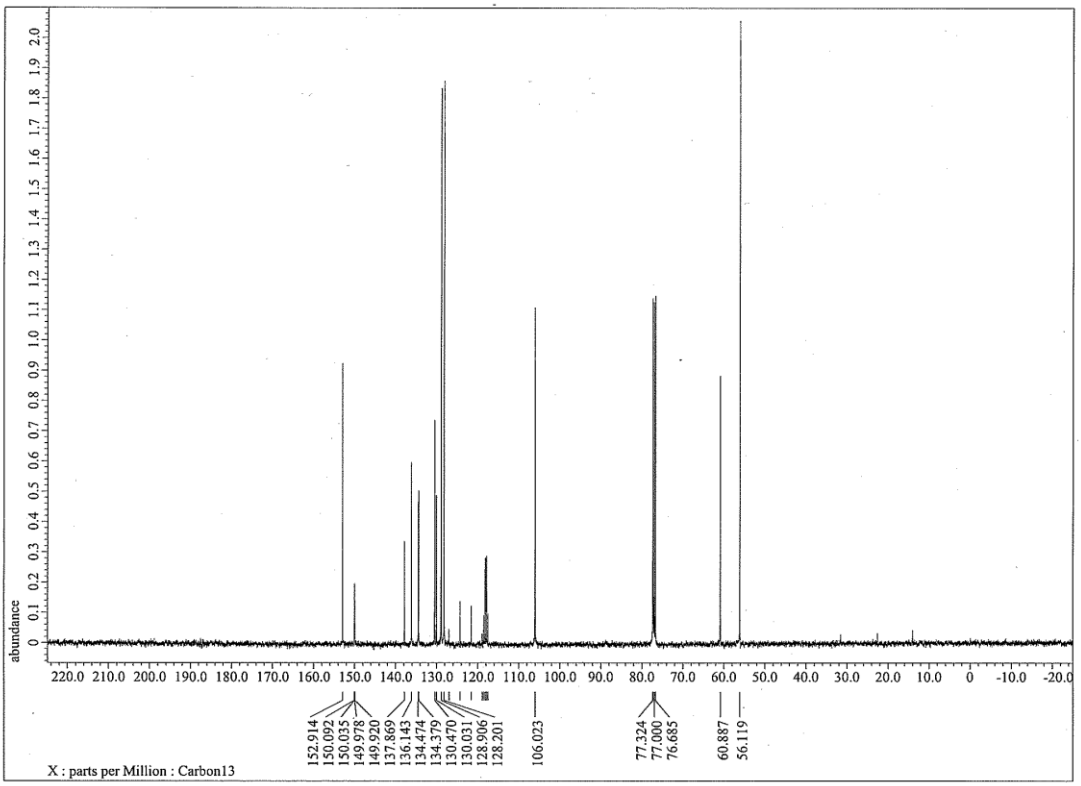

Ph
H
CF3
MeO
MeO
OMe
5aa
abundance
6.03
5.07
3.13
1.98
1.00
0.99
0.99
7.388
7.368
7.361
7.349
7.345
7.333
7.321
7.305
7.260
6.519
5.740
5.719
5.698
5.677
5.489
5.249
3.879
3.840
X : parts per Million : Proton

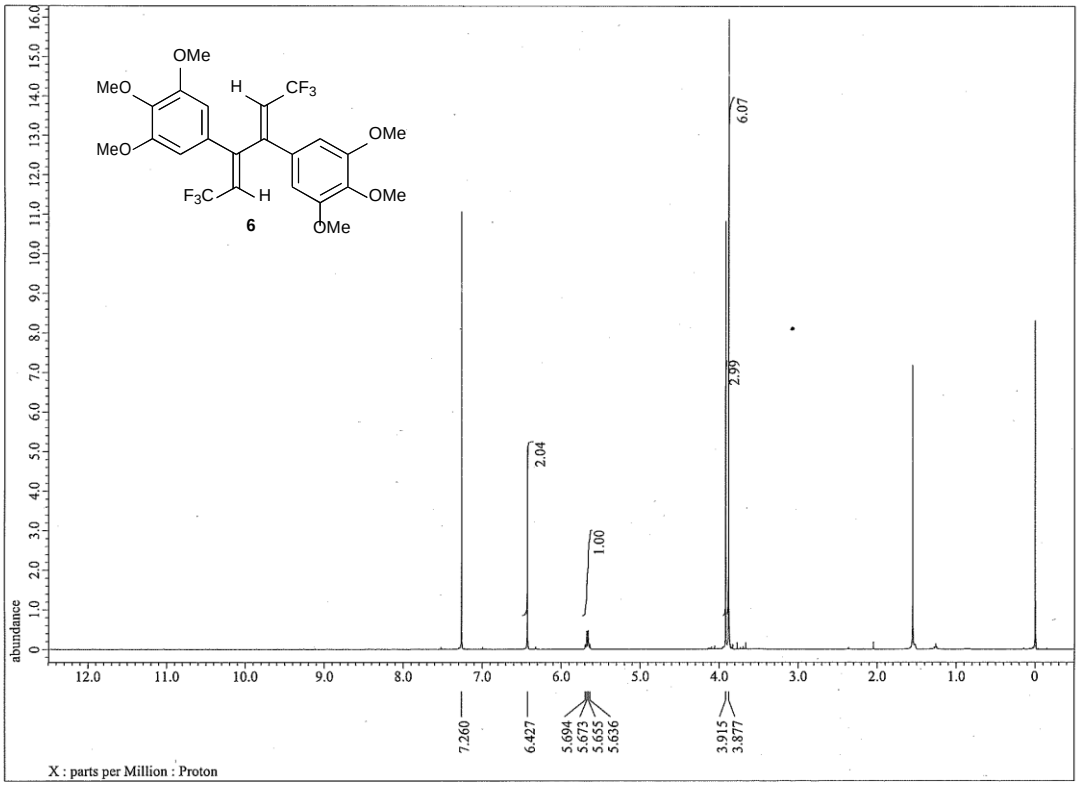

abundance
152.666
152.361
152.314
152.256
152.199
149.873
139.375
137.955
131.328
128.391
128.325
127.981
121.946
118.494
106.376
77.315
77.000
76.685
60.858
56.072
X : parts per Million : Carbon13

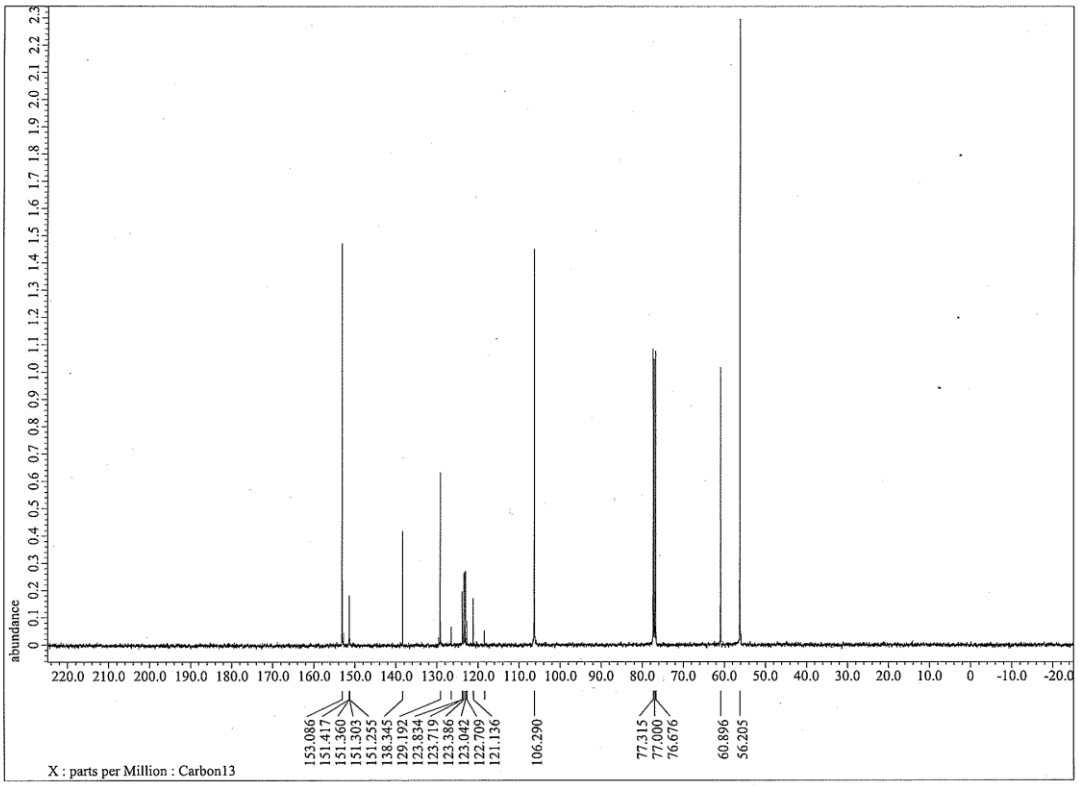

H
CF3
MeO
MeO
OMe
5ab
abundance
X : parts per Million : Proton

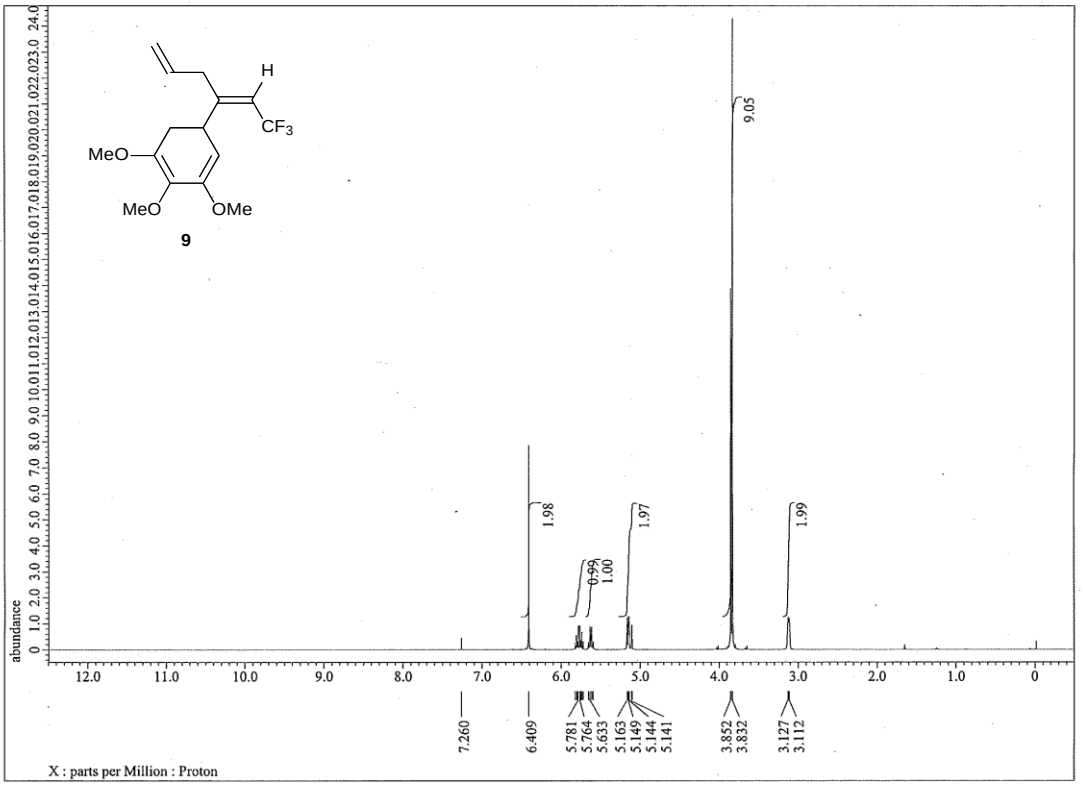

abundance
X : parts per Million : Carbon13

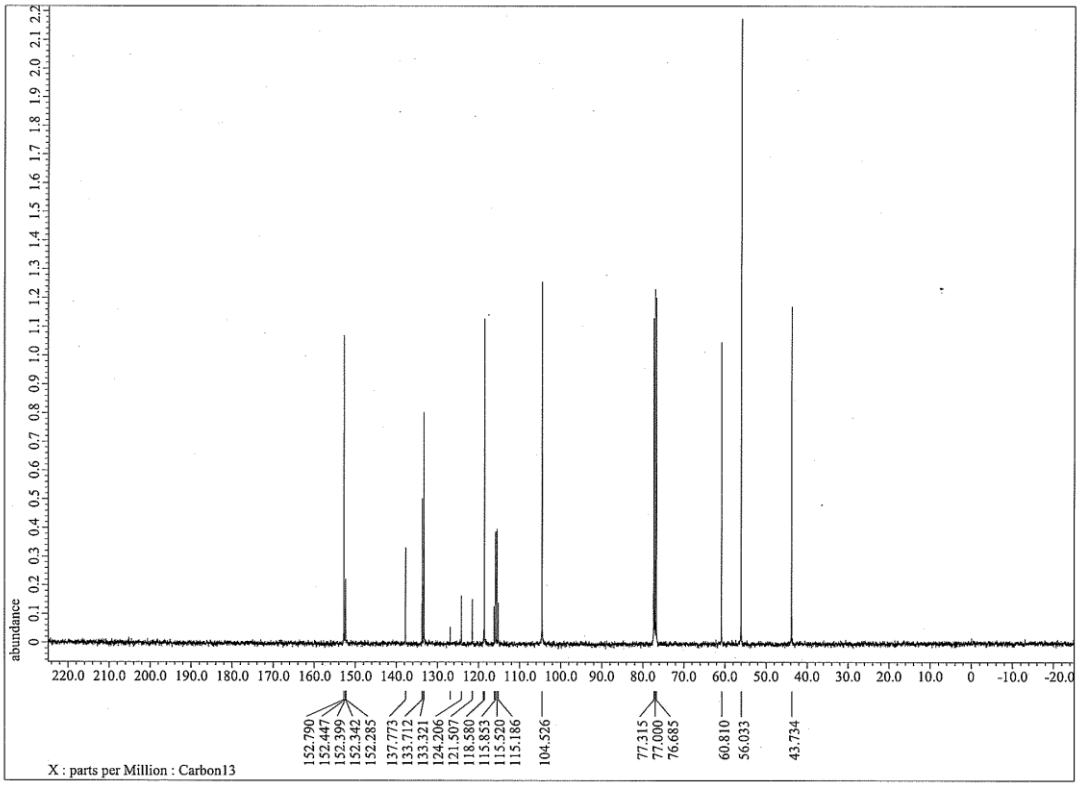

Cl
H
CF3
MeO
MeO
OMe
5ac
abundance
4.02
1.01
2.02
1.01
1.00
6.01
3.05
7.318
7.312
7.296
7.291
7.276
7.268
7.260
6.911
6.872
6.438
6.372
6.332
5.893
5.873
5.852
5.832
3.914
3.844
X : parts per Million : Proton


abundance
152.914
150.092
150.035
149.978
149.920
137.869
136.143
134.474
134.379
130.470
130.031
128.906
128.201
106.023
77.324
77.000
76.685
60.887
56.119
X : parts per Million : Carbon13


OMe
MeO
H
CF3
MeO
OMe
F3C
H
OMe
OMe
6
6.07
2.99
2.04
1.00
abundance
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
7.260
6.427
5.694
5.673
5.655
5.636
3.915
3.877
X : parts per Million : Proton


abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
153.086
151.417
151.360
151.303
151.255
138.345
129.192
123.834
123.719
123.386
123.042
122.709
121.136
106.290
77.315
77.000
76.676
60.896
56.205
X : parts per Million : Carbon13


H
CF3
MeO
MeO
OMe
9
abundance
X : parts per Million : Proton
9.05
1.98
1.97
1.99
0.99
1.00
7.260
6.409
5.781
5.764
5.633
5.163
5.149
5.144
5.141
3.852
3.832
3.127
3.112


abundance
X : parts per Million : Carbon13
152.790
152.447
152.399
152.342
152.285
137.773
133.712
133.321
124.206
121.507
118.580
115.853
115.520
115.186
104.526
77.315
77.000
76.685
60.810
56.033
43.734