**Supporting Information**

# Electrochemical trifluoromethylation/semipinacol rearrangement sequences of alkenyl alcohols: Synthesis of β-$CF_3$-substituted ketones

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**Contents**

## 1. General information

All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with $F_{254}$ indicator. Visualization was accomplished by UV light (254 nm). Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230-400 mesh). $^{1}H$ NMR,$^{13}C$ NMR, and $^{19}F$ NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz respectively, on a Jeol ECS 400 MHz NMR spectrometer. Chemical shift values (δ) are reported in ppm relative to $Me_4Si$ as the internal references and $PhCF_3$ as the external references. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010. High resolution mass spectra were measured on Jeol HX110/110A using electrospray ionization technique. Cyclic voltammetry experiments were carried out in an IKA ElectraSyn 2.0. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode (d = 3 mm), A platinum electrode served as counter electrode. $Ag/AgNO_3$ was used as the reference electrode. The working electrode was polished before recording each CV curve.

## 2. Preparation of starting materials[1-3]

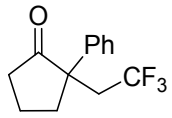
(1-(1-Arylvinyl)cyclobutoxy)trimethyl-silanes **1** were prepared in accordance with literature methods.

## 3. General procedure for the synthesis of β-$CF_3$-substituted ketones

An undivided cell was equipped with a platinum plate (1.0 × 1.0 $cm^2$) as the anode and a platinum plate (1.0 × 1.0 $cm^2$) as the cathode and connected to a DC regulated power supply. A mixture of (1-(1-arylvinyl)cyclobutoxy)trimethyl-silanes **1** (0.1 mmol), Sodium trifluoromethanesulfinate **2** (31.2 mg, 0.2 mmol), $LiClO_4$ (53.2 mg, 0.5 mmol) and $H_2O$ (1 equiv.) in $CH_3CN$ (2.5 mL) was added to an undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under room temperature for 1 h. When the reaction was finished, the residue was diluted with EtOAc and washed with brine, dried over $Na_2SO_4$, concentrated under reduced pressure concentrated, and purified by flash chromatography (EtOAc:Hex, 1:30) to afford β-trifluoromethylated cyclic ketone derivatives **3**.

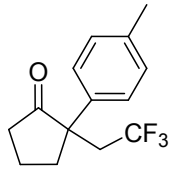
## 4. Characterization data of β-trifluoromethylated cycloalkanone derivatives

**2-phenyl-2-(2,2,2-trifluoroethyl)cyclopentanone (3a)**[2,3]




Yield: 83%; pale oil; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 4 H), 7.30-7.28 (m, 1 H), 2.93 (dd, *J* = 13.6 Hz, 5.6 Hz, 1 H), 2.80 (dq, *J* = 15.6 Hz, 11.2 Hz, 1 H), 2.49 (dq, *J* = 15.6 Hz, 11.2 Hz, 1 H), 2.36-1.97 (m, 4 H), 1.86-1.73 (m, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 216.2, 136.0, 128.9, 126.7, 126.8, 126.2 (q, *J* = 277.4 Hz), 53.4, 42.0 (q, *J* = 26.7 Hz), 35.5, 32.4, 18.3; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -60.4; IR (film): ν ($cm^{-1}$): 2922, 1738; HRMS (ESI) m/z calcd for $C_{13}H_{13}F_3NaO$ $[M+Na]^+$: 265.0816; found : 265.0812.

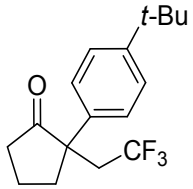
**2-(*p*-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3b)**[2,3]




Yield: 87%; pale oil; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.4 Hz, 2 H), 7.16 (d, *J* = 8 Hz, 2 H), 2.90 (dd, *J* = 13.2 Hz, 6 Hz, 1 H), 2.78 (dq, *J* = 15.4 Hz, 11.6 Hz, 1 H), 2.46 (dq, *J* = 15.6 Hz, 11.2 Hz, 1 H), 2.35-1.95 (m, 4 H), 2.33 (s, 3H), 1.85-1.73 (m, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 216.3, 137.5, 132.8, 129.7, 126.7,

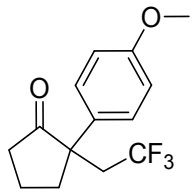
126.3 (q, $J$ = 276.5 Hz), 53.0, 42.0 (q, $J$ = 27.6 Hz), 35.4, 32.4, 21.0, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.3; IR (film): ν ($cm^{-1}$): 2972, 1738; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$ : 279.0937; found : 279.0935.

**2-(4-(*tert*-butyl)phenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3c )**



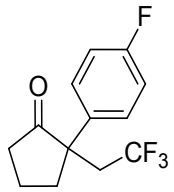

Yield: 82%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, $J$ = 8.8 Hz, 2H), 7.29 (d, $J$ = 8.8 Hz, 2H), 2.89 (dd, $J$ = 14 Hz, 6 Hz, 1H), 2.75 (dq, $J$ = 15.2 Hz, 11.2 Hz, 1 H), 2.52 (dq, $J$ = 15.4 Hz, 11.6 Hz, 1 H), 2.36-1.95 (m, 4H), 1.86-1.74 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 216.4, 132.9, 128.4, 126.4, 126.2 (q, $J$ = 276.5 Hz), 125.9, 125.8, 53.0, 41.9 (q, $J$ = 26.7 Hz), 35.6, 34.4, 32.3, 31.2, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.4; IR (film): ν ($cm^{-1}$): 2963, 1740; HRMS (ESI) m/z calcd for $C_{17}H_{21}F_3NaO$ $[M+Na]^+$ : 321.1442; found : 321.1445.

**2-(4-methoxyphenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3d)**[2]



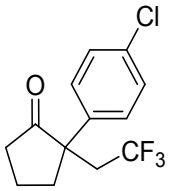

Yield: 86%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2 H), 6.90-6.86 (m, 2 H), 3.80 (s, 3H), 2.89 (dd, $J$ = 13.2 Hz, 5.6 Hz, 1 H), 2.78 (dq, $J$ = 15.6 Hz, 11.2 Hz, 1 H), 2.43 (dq, $J$ = 15.5 Hz, 11.2 Hz, 1 H), 2.36-2.14 (m, 2 H), 2.10-1.96 (s, 2H), 1.87-1.73 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 216.2, 159.0, 128.1, 127.4, 126.3 (q, $J$ = 277.4 Hz ), 114.3, 55.2, 52.6, 42.0 (q, $J$ = 27.6 Hz), 35.4, 32.6, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.4; IR (film): ν ($cm^{-1}$): 2972, 1738; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO_2$ $[M+Na]^+$ : 295.0922; found : 295.0927.

**2-(4-fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3e)**[2,3]



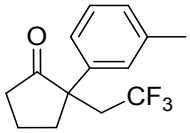

Yield: 75%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.07-7.02 (m, 2H), 2.90 (dd, $J$ =13.4 Hz, 5.8 Hz, 1H), 2.85-2.73 (m, 1H), 2.49-2.17 (m, 3H), 2.14-1.98 (m, 2H), 1.89-1.72 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 215.9, 162.2 (d, J = 246 Hz), 131.4 (d, J = 2.9 Hz), 128.7 (d, J = 8.6 Hz), 126.2 (q, J = 276.5 Hz), 115.9 (d, J = 21.0 Hz), 52.7, 42.1 (q, J = 27.7 Hz), 35.4, 32.7, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.4, -115.6; IR (film): ν ($cm^{-1}$): 2976, 1739; HRMS (ESI) m/z calcd for $C_{13}H_{12}F_4NaO$ $[M+Na]^+$: 283.0722; found : 283.0720.

**2-(4-chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3f)**[2,3]



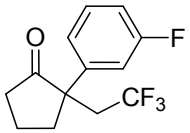
Yield: 70%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4 H), 2.90 (dd, *J*= 13.2 Hz, 6.4 Hz, 1H), 2.80 (dq, *J* = 15.6 Hz, 11.2 Hz, 1 H), 2.43 (dq, *J* = 15.6 Hz, 10.8 Hz, 1 H), 2.36-2.18 (m, 2H), 2.13-200 (m, 2H), 1.85-1.68 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 215.9, 134.3, 133.8, 129.1, 128.3, 126.1 (q, *J* = 276.5 Hz), 52.8, 42.0 (q, *J* = 26.7 Hz), 35.4, 32.5, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -60.3; IR (film) ν ($cm^{-1}$): 2966, 1740; MS (EI) m/z calcd for $C_{13}H_{12}ClF_3O$ $[M]^+$ : 276.1, found: 276.1

**2-(*m*-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3g)**[2]



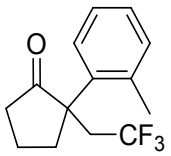
Yield: 72%; pale oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 6.8 Hz, 1 H), 2.90 (dd, *J* = 14 Hz, 6 Hz, 1 H), 2.79 (dq, *J* = 15.4 Hz, 11.2 Hz, 1 H), 2.50 (dq, *J* = 15.4 Hz, 11.2 Hz, 1 H), 2.37-1.95 (m, 4 H), 2.35 (s, 3H), 1.85-1.73 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 216.3, 138.6, 136.0, 128.8, 128.5,127.5, 126.2 (q, *J* = 276.5 Hz), 123.7, 53.3, 42.0 (q, *J* = 26.7 Hz), 35.5, 32.4, 21.6, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ −61.3; IR (film): ν ($cm^{-1}$): 2962, 1738; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$ : 279.0937; found : 279.0939.

**2-(3-fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3h)**[3]



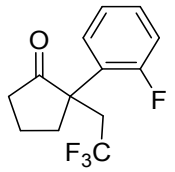
Yield: 72%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (d, J = 10.8 Hz, 1H), 6.99 (t, *J* = 8 Hz, 1H), 2.91-2.74 (m, 2H), 2.46 (dq, *J* = 15.6 Hz, 10.8 Hz, 1 H), 2.38-2.18 (m, 2H), 2.15-2.00 (m, 2H), 1.86 -1.77 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 215.7, 163.0 (d, *J* = 259.3 Hz), 138.6 (d, *J* = 6.6 Hz), 130.4 (d, *J* = 7.7 Hz), 126.1 (q, *J* = 276.5 Hz), 122.5 (d, *J* = 2.9 Hz), 114.8 (d, *J* = 21 Hz), 114.1 (d, *J* = 22.9 Hz), 53.1, 42.0 (q, *J* = 27.7 Hz), 35.5, 32.6, 18.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ −60.4, −111.6; IR (film): ν ($cm^{-1}$): 2963, 1742; HRMS (ESI) m/z calcd for $C_{13}H_{12}F_4NaO$ $[M+Na]^+$: 283.0722; found : 283.0725.

**2-(*o*-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3i)**[2]



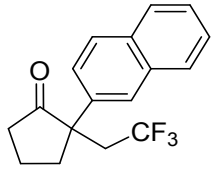
Yield: 59%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 1 H), 7.11 (t, *J* = 7.8 Hz, 1.6Hz, 1 H), 7.02(d, *J* = 8 Hz, 1 H), 2.95-2.71 (m, 3 H), 2.46 (s, 3H), 2.46-2.39 (m, 1 H), 2.31-2.17 (m, 2 H), 1.96-1.88 (m, 1 H), 1.72-1.59 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 217.4, 136.6, 136.2, 133.6, 127.7, 127.2, 126.1 (q, *J* = 276.5 Hz), 126.1, 54.2, 38.6 (q, *J* = 26.7 Hz), 36.1, 33.2, 21.2, 18.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.4; IR (film): ν ($cm^{-1}$): 2962, 1742; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$ : 279.0937; found : 279.0933.

**2-(2-fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3j)**



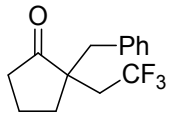

Yield: 66%; pale oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 1H), 7.14-7.07 (m, 3H), 2.92 (dq, *J* = 15.6 Hz, 11.2 Hz, 1 H), 2.81-2.63 (m, 2H), 2.48-2.18 (m, 3H), 2.05-1.95 (m, 1H), 1.78-1.65 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 216.0, 161.2 (d, *J* = 247.9 Hz), 129.8 (d, *J* = 8.6 Hz), 128.5 (d, *J* = 3.8 Hz), 126.0 (q, *J* = 276.5 Hz), 125.9 (d, *J* = 11.5 Hz), 124.3 (d, *J* = 3.8 Hz), 117.2 (d, *J* = 22.9 Hz), 52.1, 38.5 (qd, *J* = 27.6 Hz, 3.8 Hz), 36.3, 33.3 (d, *J* = 3.8 Hz), 18.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.8, -114.8; IR (film): ν ($cm^{-1}$): 2963, 1746; HRMS (ESI) m/z calcd for $C_{13}H_{12}F_4NaO$ $[M+Na]^+$: 283.0722; found : 283.0723.

**2-(naphthalen-2-yl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3k)**



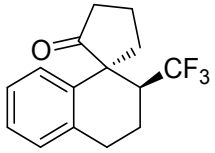

Yield: 66%; pale oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4 H), 7.54-7.48 (m, 3 H), 3.06 (dd, *J* = 14 Hz, 6 Hz, 1 H), 2.91 (dq, *J* = 15.6 Hz, 10.8 Hz, 1 H), 2.57 (dq, *J* = 15.4 Hz, 11.6 Hz, 1 H), 2.38-2.14 (m, 3 H), 2.08-2.01 (m, 1H), 1.90-1.78 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 216.1, 133.3, 133.2, 132.5, 128.9, 128.1, 127.5, 126.5, 126.4, 126.2, 126.2 (q, *J* = 277.4 Hz), 124.3, 53.4, 42.0 (q, *J* = 26.7 Hz), 35.5, 32.4, 18.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.3; IR (film): ν ($cm^{-1}$): 2974, 1737; HRMS (ESI) m/z calcd for $C_{17}H_{15}F_3NaO$ $[M+Na]^+$ : 315.0973; found : 315.0971.

**2-benzyl-2-(2,2,2-trifluoroethyl)cyclopentanone (3l)**




Yield: 68%; pale oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 3 H), 7.09 (d, *J* = 7Hz, 2 H), 2.84 (d, *J* = 13.6 Hz, 1 H), 2.62 (d, *J* = 13.6 Hz, 1 H), 2.46 (dq, *J* = 15.4 Hz, 12 Hz, 1 H), 2.36-2.07 (m, 5 H), 1.91-1.82 (m, 1 H), 1.63-1.51 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 220.1, 135.9, 130.4, 128.5, 127.1, 126.4 (q, *J* = 276.5 Hz), 49.8, 41.8, 38.9 (q, *J* = 26.7 Hz), 37.4, 30.4, 18.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -60.0; IR (film): ν ($cm^{-1}$): 2967, 1739; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$ : 279.0937; found : 279.0935.

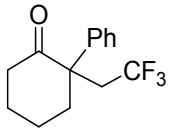
**2'-(trifluoromethyl)-3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalen]-2-one (5)**[2,3]




Yield: 54%; 2:1 d.r.; pale oil; major diastereomer: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 7.13-7.09 (m, 1H), 6.97-6.95 (m, 1H), 3.03-2.95 (m, 1H), 2.85-2.77 (m, 1H), 2.72-2.64 (m, 2H), 2.61-2.34 (m, 4H), 2.21-2.12 (m, 2H), 2.08-2.05 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 218.6, 138.7, 136.2, 129.0, 127.9, 127.1 (q, *J* =

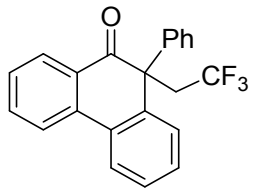
281.3 Hz), 126.7, 126.6, 52.9, 46.3 (q, $J$ = 24.7 Hz), 41.4, 38.1, 26.9, 20.0, 18.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.3; IR (film): ν ($cm^{-1}$): 2960, 1741; HRMS (ESI) m/z calcd for $C_{15}H_{15}F_3NaO$ $[M+Na]^+$ : 291.0973; found : 291.0969.

**2-phenyl-2-(2,2,2-trifluoroethyl)cyclohexanone (7)**



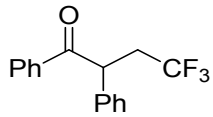

Yield: 35%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, $J$ = 7.2 Hz, 2 H), 7.30 (d, $J$ = 7.2 Hz, 1 H), 7.21 (d, $J$ = 7.2 Hz, 2 H), 3.04 (d, $J$ = 7.6 Hz, 1 H ), 2.77-2.57 (m, 2H), 2.34-2.30 (m, 2H), 2.00-1.95 (m, 1H), 1.88-1.69 (m, 4 H); $^{13}$C NMR (100 MHz, CDCl3) δ 210.4, 138.2, 129.1, 127.5, 126.9, 126.5 (q, $J$ = 276.5 Hz), 54.4, 43.0 (q, $J$ = 26.7 Hz), 39.2, 43.2, 28.0, 21.4;$^{19}$F NMR (376 MHz, $CDCl_3$) δ -59.7; IR (film): ν ($cm^{-1}$): 2943, 2868, 1710; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$ : 279.0937; found : 279.0939.

**10-phenyl-10-(2,2,2-trifluoroethyl)phenanthren-9(10*H*)-one (9)**[3]



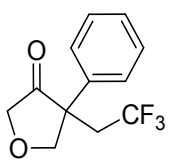

Yield: 34%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18-8.08 (m, 3 H), 7.72-7.68 (m, 1 H), 7.50-7.46 (m, 1 H), 7.43-7.38 (m, 2 H), 7.21-7.15 (m , 4 H), 7.05 (dd, $J$ = 8 Hz, 2 Hz, 2 H), 4.20-4.12 (m, 1 H), 3.26-3.15 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.6, 141.5, 138.4, 136.9, 135.0, 130.3, 130.1, 128.9, 128.9, 128.8, 128.5, 128.1, 128.0, 127.6, 126.8, 125.6 (q, $J$ = 278.5 Hz), 123.8, 123.2, 55.0, 42.1 (q, $J$ = 27.6 Hz);$^{19}$F NMR (376 MHz, $CDCl_3$) δ -59.0; IR (film): ν ($cm^{-1}$): 2921, 2852, 1734; HRMS (ESI) m/z calcd for $C_{22}H_{15}F_3NaO$ $[M+Na]^+$ : 375.0973; found 375.0976.

**4,4,4-trifluoro-1,2-diphenylbutan-1-one (11)**[3]




Yield: 53%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J$ = 8 Hz, 2 H), 7.53-7.47 (m, 1 H), 7.40 (t, $J$ = 7.6 Hz, 2 H), 7.31 (d, $J$ = 4Hz, 4 H),7.26-7.21(m, 1 H), 4.92-4.89 (m, 1 H ), 3.38-3.24 (m, 1H), 2.61-2.48 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.4, 135.6, 133.4, 129.3, 128.8, 128.7, 128.0, 127.8, 126.4 (q, $J$ = 275.6 Hz), 47.2, 37.3 (q, $J$ = 28.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -65.6; IR (film): ν ($cm^{-1}$): 3064, 1684; HRMS (ESI) m/z calcd for $C_{16}H_{13}F_3NaO$ $[M+Na]^+$ : 301.0816; found : 301.0815.

**4-phenyl-4-(2,2,2-trifluoroethyl)dihydrofuran-3(2*H*)-one (13)**[2,3]




Yield: 38%; pale oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, $J$ = 7.6 Hz, 2H), 7.40 (t, $J$ = 6.8 Hz, 2H), 7.32 (t, $J$ = 7.6 Hz, 1H), 5.06 (d, $J$ = 10.4 Hz, 1H), 4.22 (d, $J$ = 11.2 Hz, 1H), 4.12 (d, $J$ = 17.6 Hz, 1H), 3.92 (d, $J$ = 17.2

Hz, 1H), 3.04 (dq, $J$ = 15.6 Hz, 11.2 Hz, 1H), 2.53 (dq, $J$ = 15.6 Hz, 10.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.6, 134.0, 129.1, 128.2, 126.6, 125.8 (q, $J$ = 276.5 Hz), 74.0, 69.4, 52.0, 38.7 (q, $J$ = 28.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -60.8; IR (film): ν ($cm^{-1}$): 2873, 1764; HRMS (ESI) m/z calcd for $C_{12}H_{11}F_3NaO_2$ $[M+Na]^+$ : 267.0609; found : 267.0605.

## 5. Cyclic voltammograms

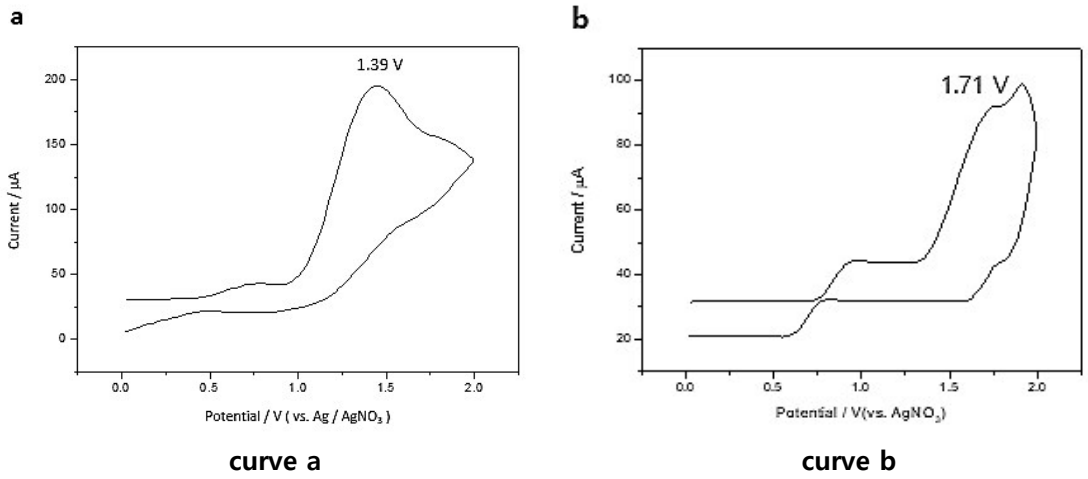


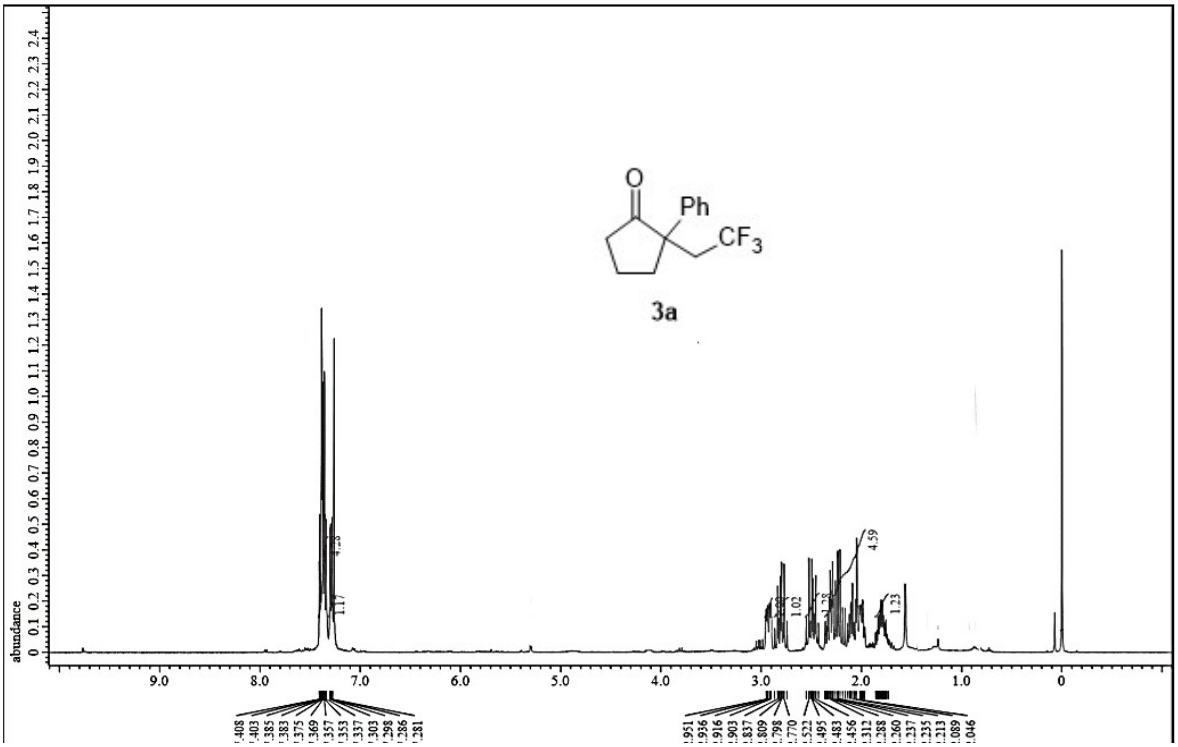

**Figure S1**. Cyclic voltammograms of 0.1 M $LiClO_4$ solution in $CH_3CN$, using glassy carbon electrode as working electrode (d = 3 mm), a platinum electrode as counter electrode, and $Ag/AgNO_3$ as a reference electrode, at a scan rate of 200 mV/s: (a) $CF_3SO_2Na$ **2** (0.0015 M); (b) trimethyl(1-(1 -phenylvinyl)cyclobutoxy)silane **1a** (0.015 M).

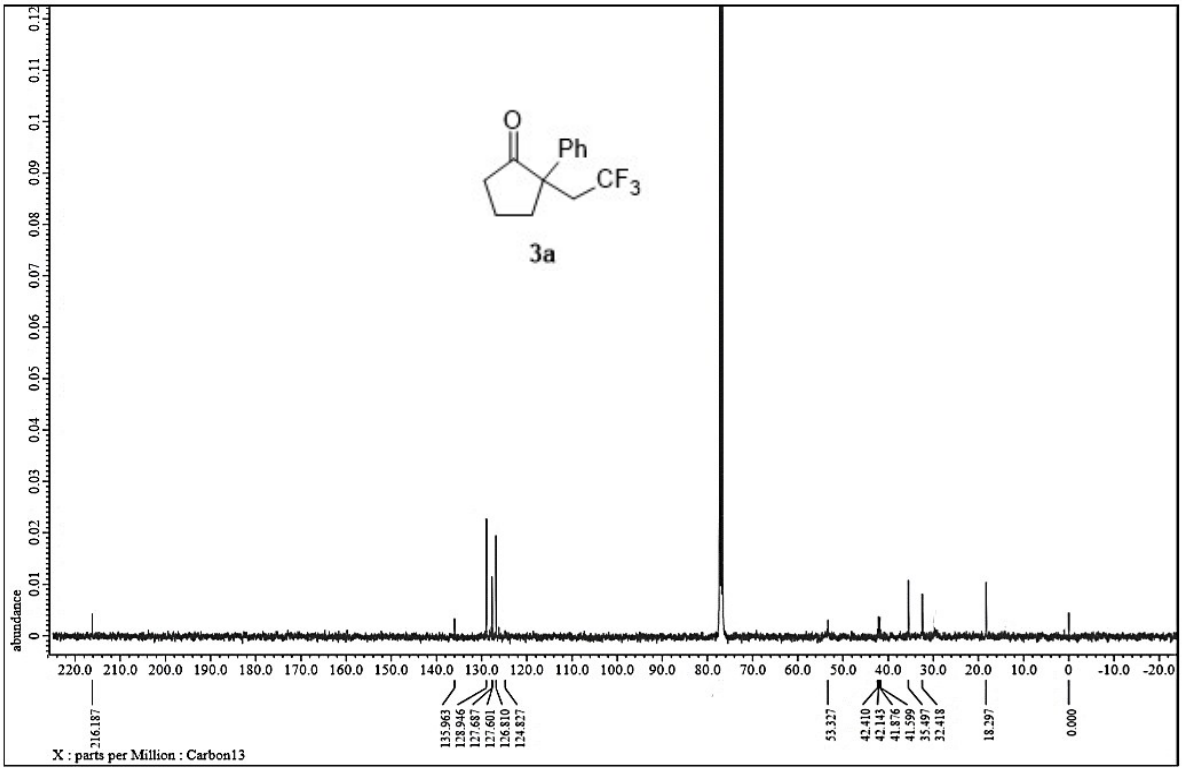
In **Figure S1**, curve a, the oxidation peak of $CF_3SO_2Na$ **2** (*Ep* = 1.39 V vs. $Ag/AgNO_3$)*;* curve b, the oxidation peak of trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane **1a** (*Ep* = 1.71 V vs. $Ag/AgNO_3$).

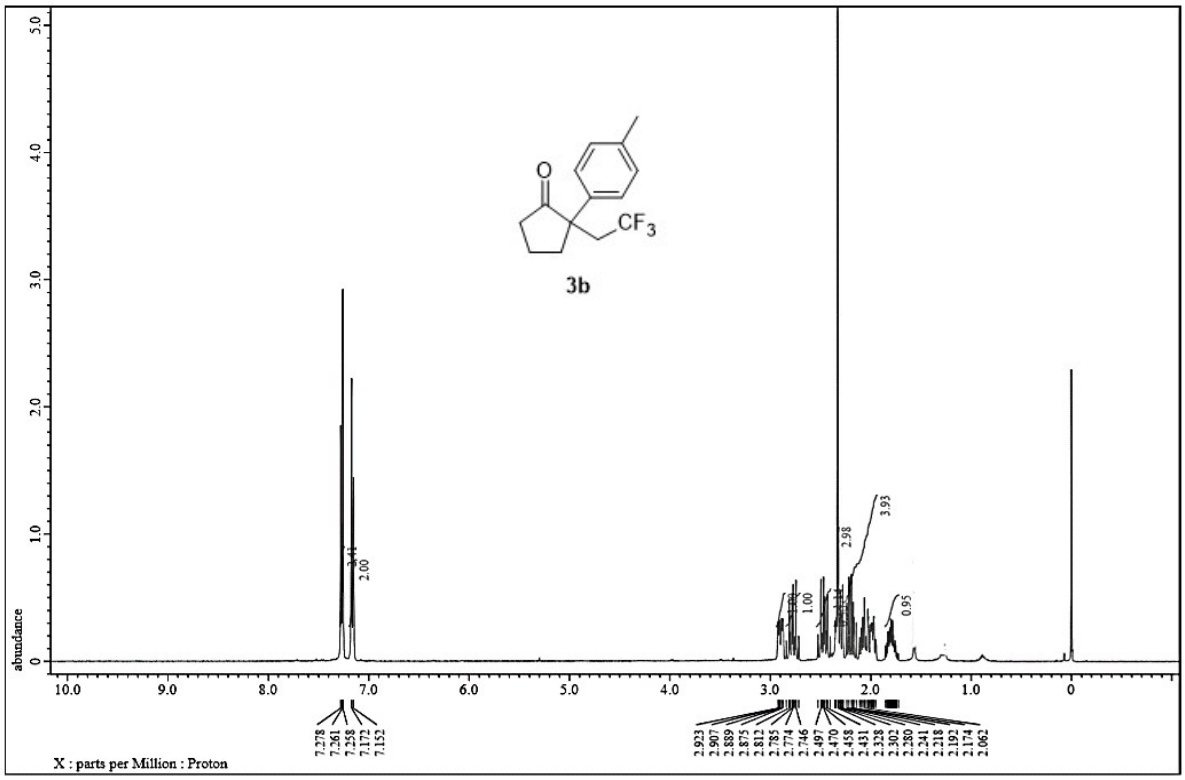
## 6. References

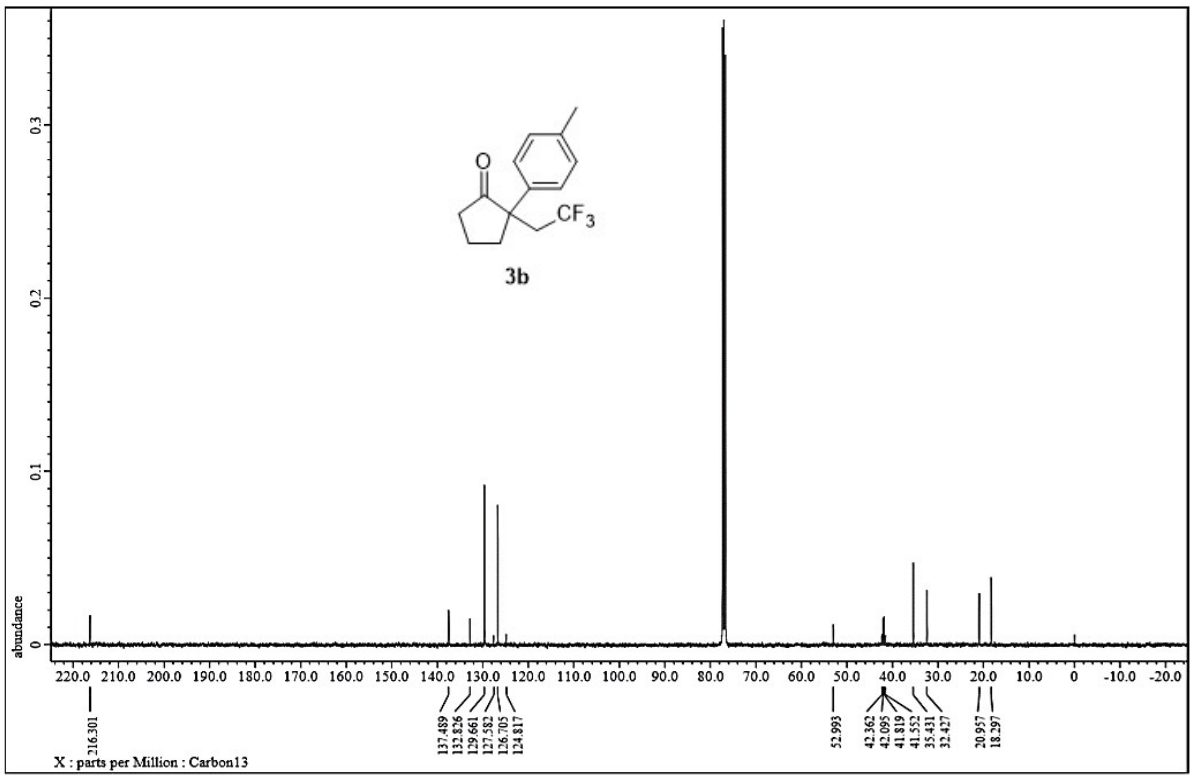

1. (a) X. Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc*. **2014**, *136*, 5844; (b) C. W. Suh, D. Y. Kim, *Tetrahedron Lett*. **2015**, *56*, 5661. (c) Q. Yin, S.-L. You, *Org. Lett.* **2014**, *16*, 1810.
2. B. Sahoo, J. L. Li, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 11577.
3. S. B. Woo, D. Y. Kim, *J. Fluorine Chem*. **2015**, *178*, 214.

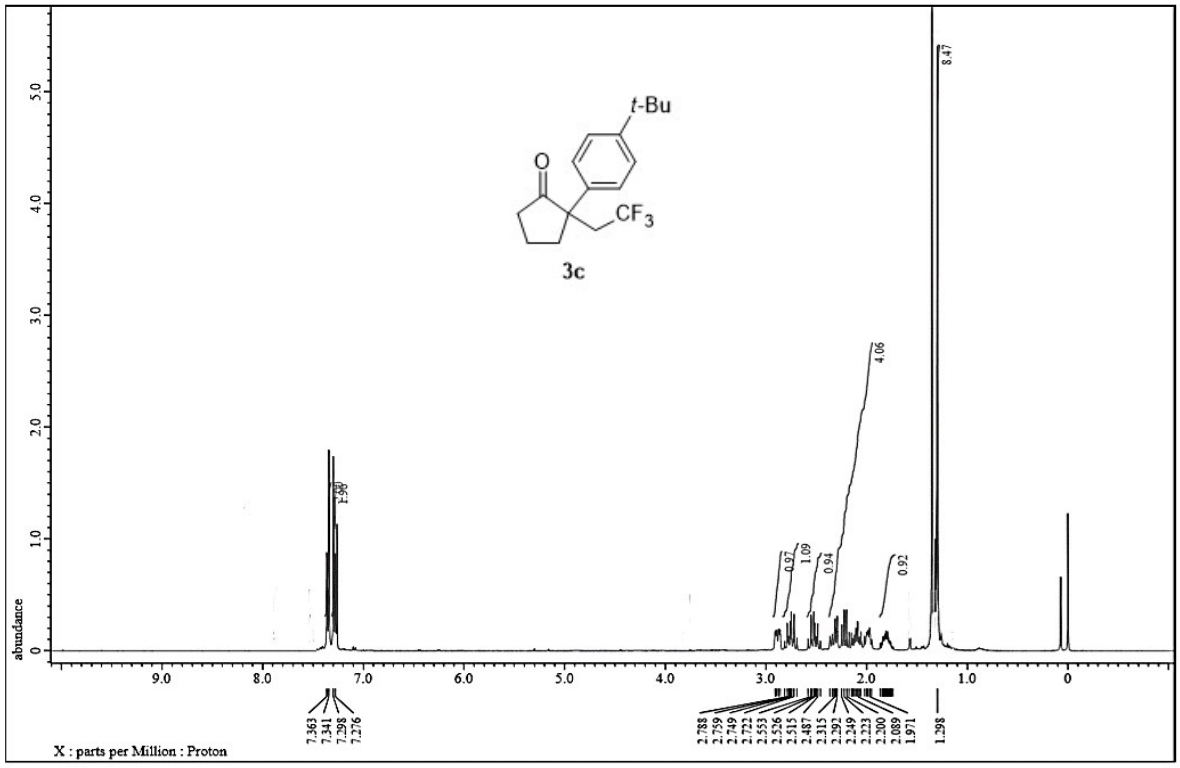
## 7. NMR spectra

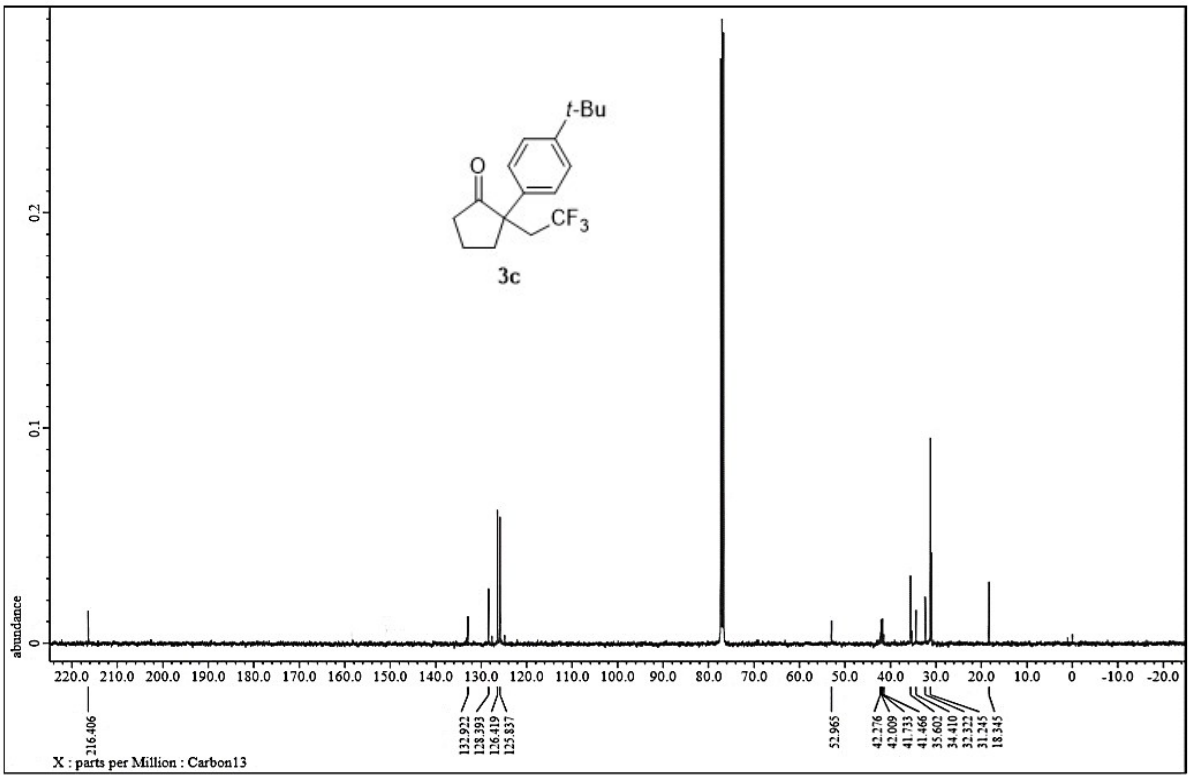


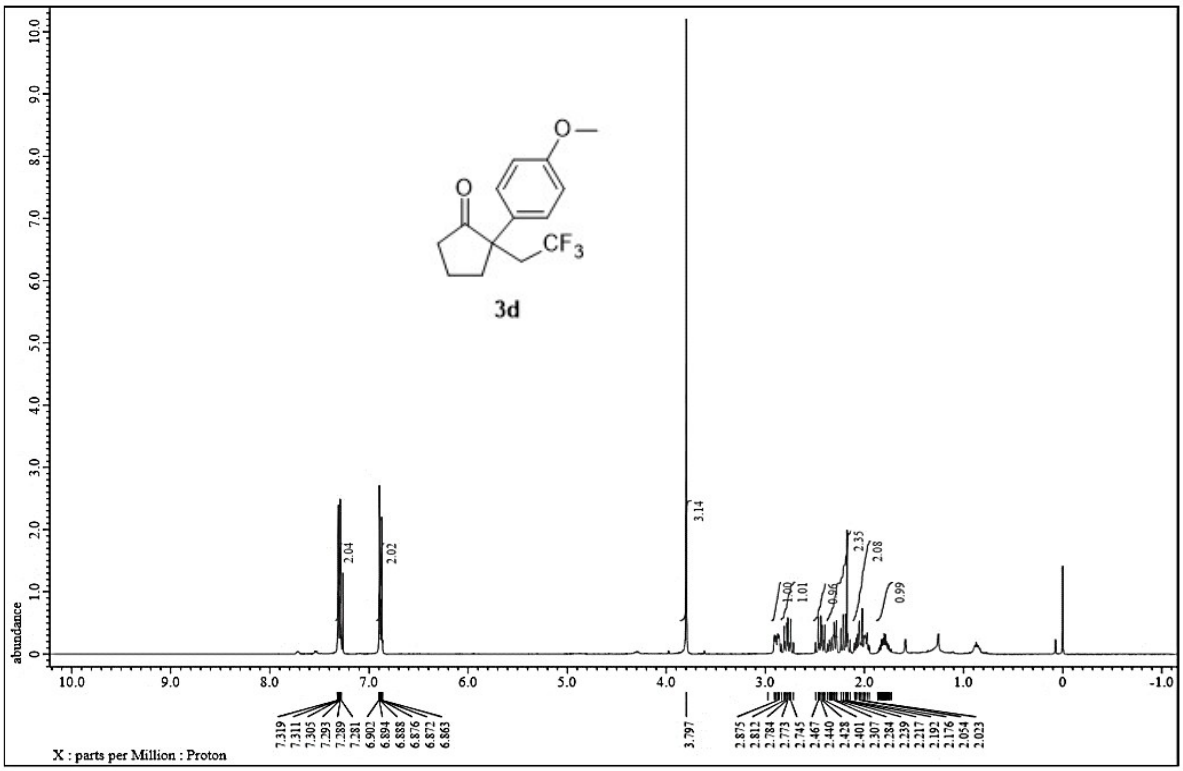



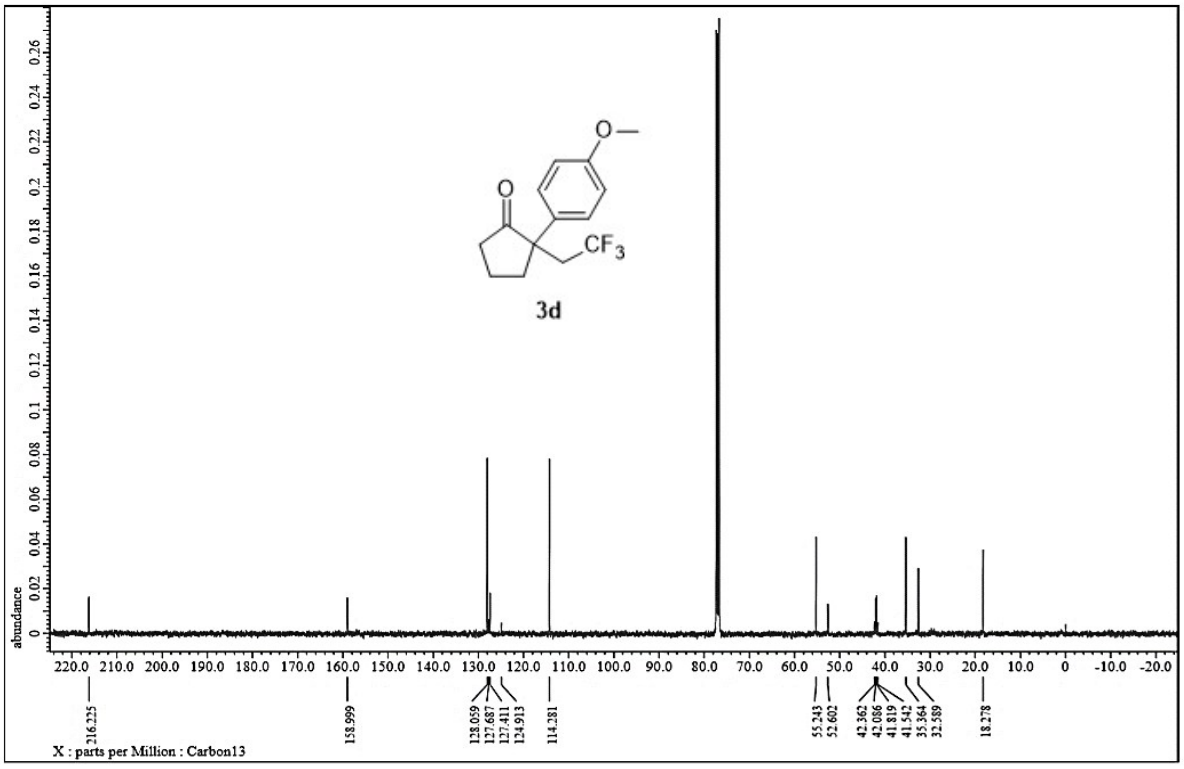

O
CF3
3b
abundance
X : parts per Million : Proton

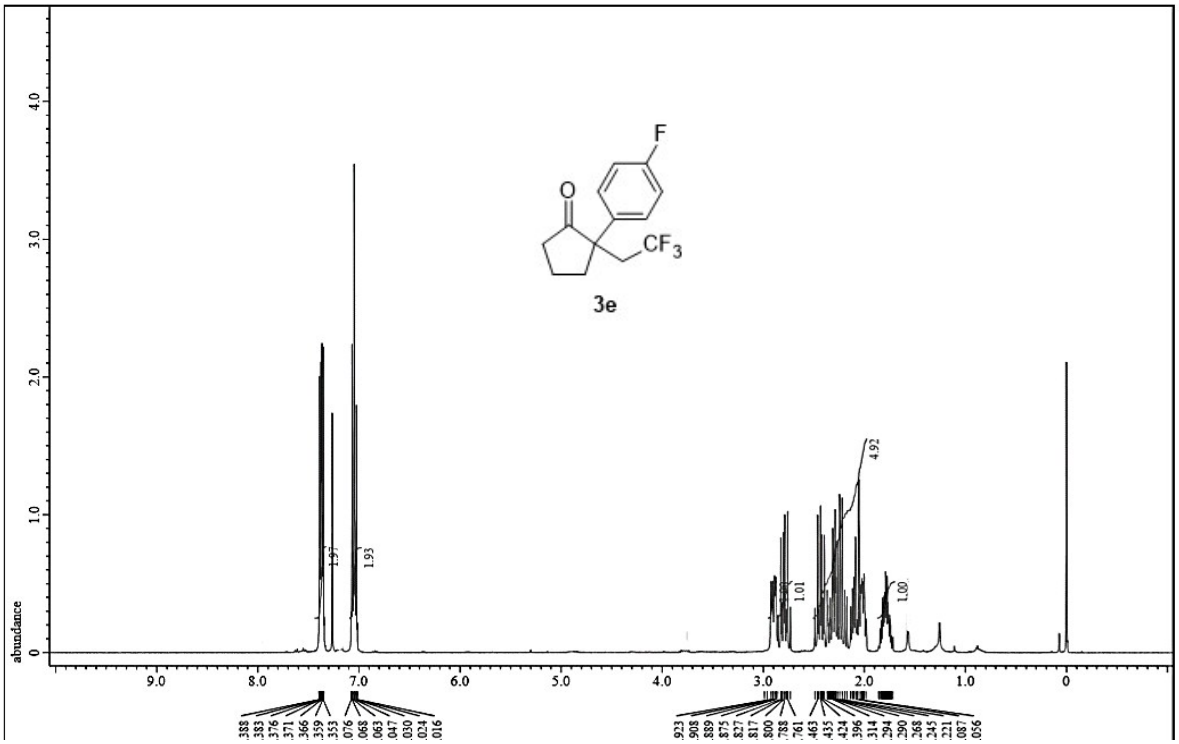

O
CF3
3b
abundance
X : parts per Million : Carbon13

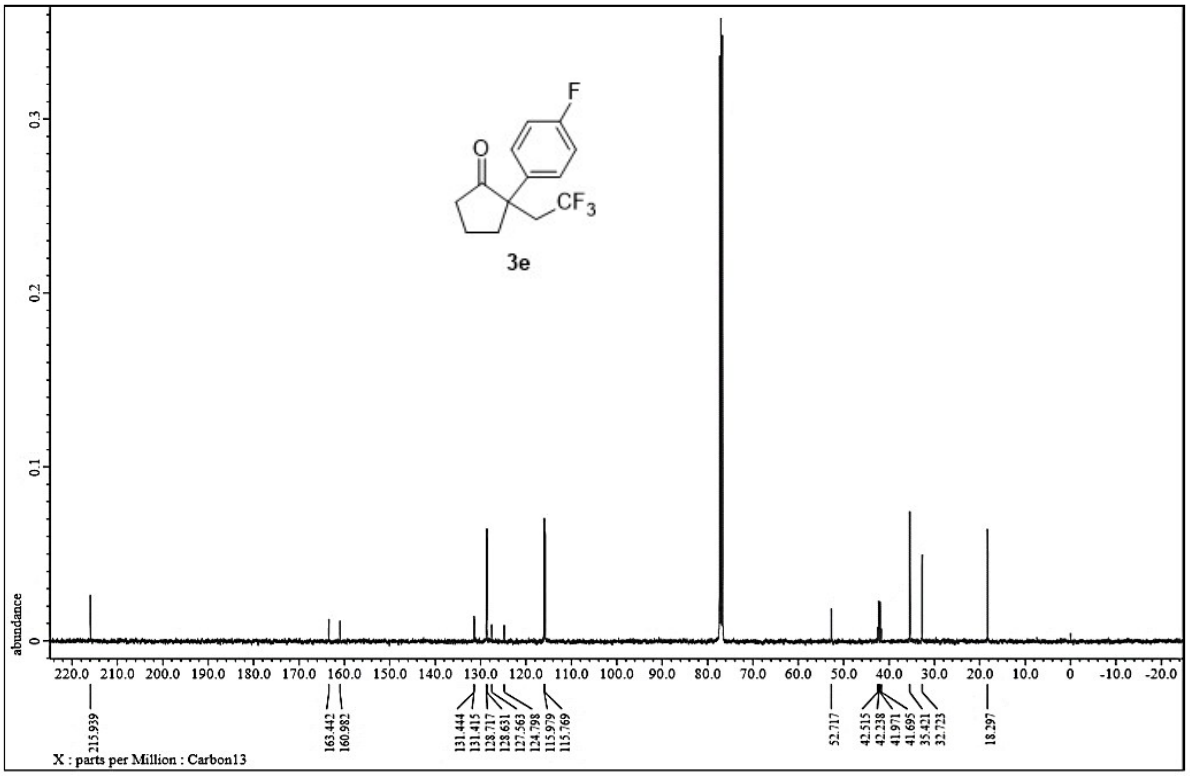

t-Bu
O
CF3
3c
8.47
4.06
0.97
1.09
0.94
0.92
abundance
X : parts per Million : Proton

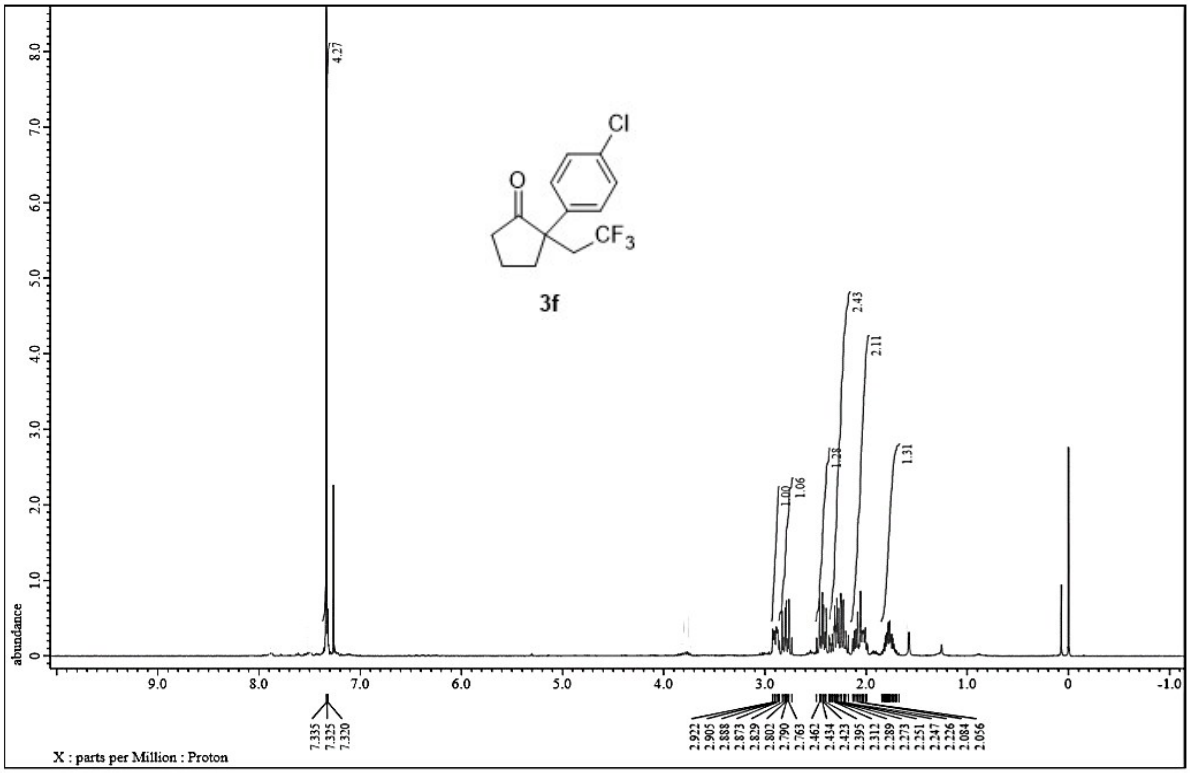

t-Bu
O
CF3
3c
abundance
X : parts per Million : Carbon13

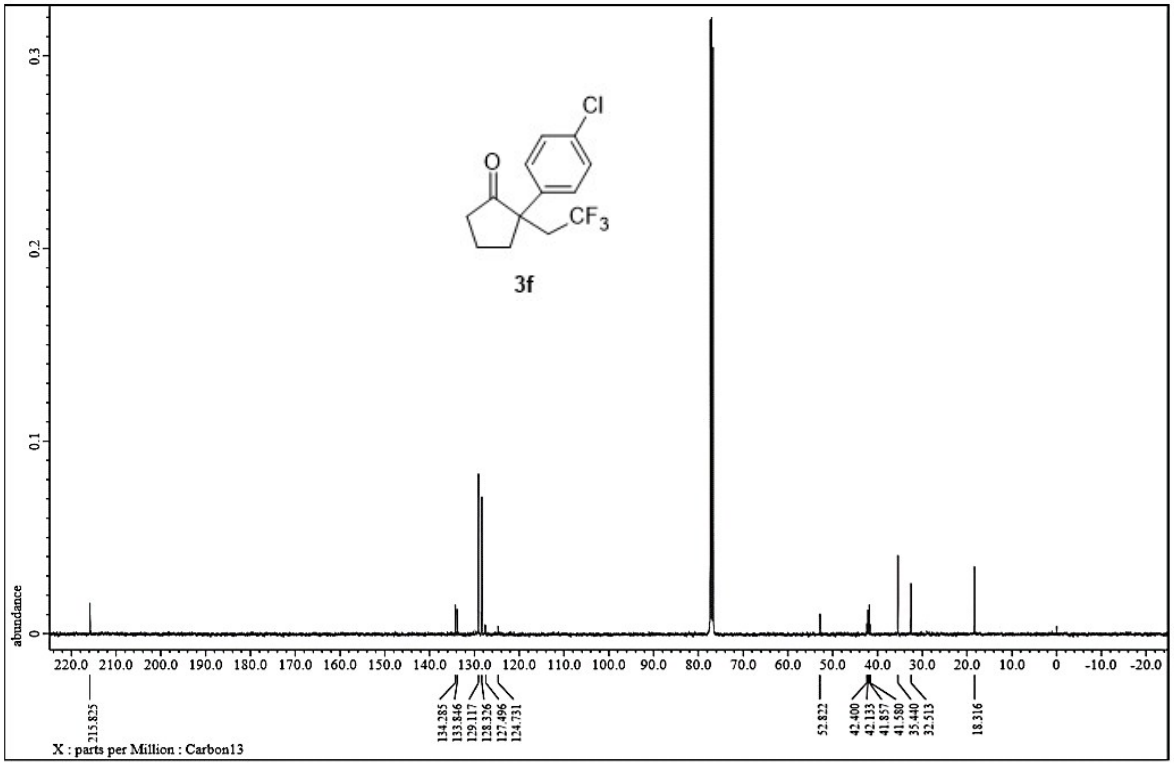

3d
abundance
X : parts per Million : Proton

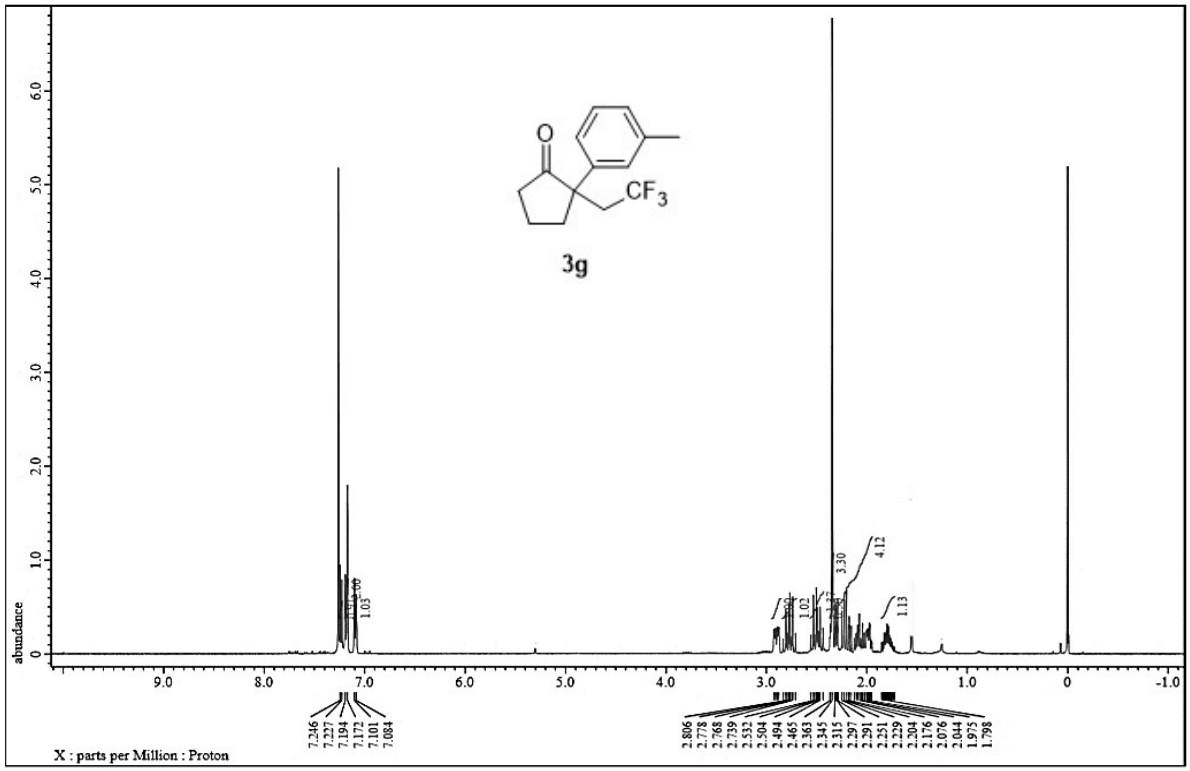

3d
abundance
X : parts per Million : Carbon13


F
O
CF3
3e
abundance
1.97
1.93
1.01
4.92
1.00


F
O
CF3
3e
abundance
215.939
163.442
160.982
131.444
131.415
128.717
128.651
127.563
124.798
115.979
115.769
52.717
42.515
42.238
41.971
41.695
35.421
32.723
18.397
X : parts per Million : Carbon13


Cl
O
CF3
3f
4.27
2.43
2.11
1.38
1.31
1.00
1.06
abundance
X : parts per Million : Proton


Cl
O
CF3
3f
abundance
X : parts per Million : Carbon13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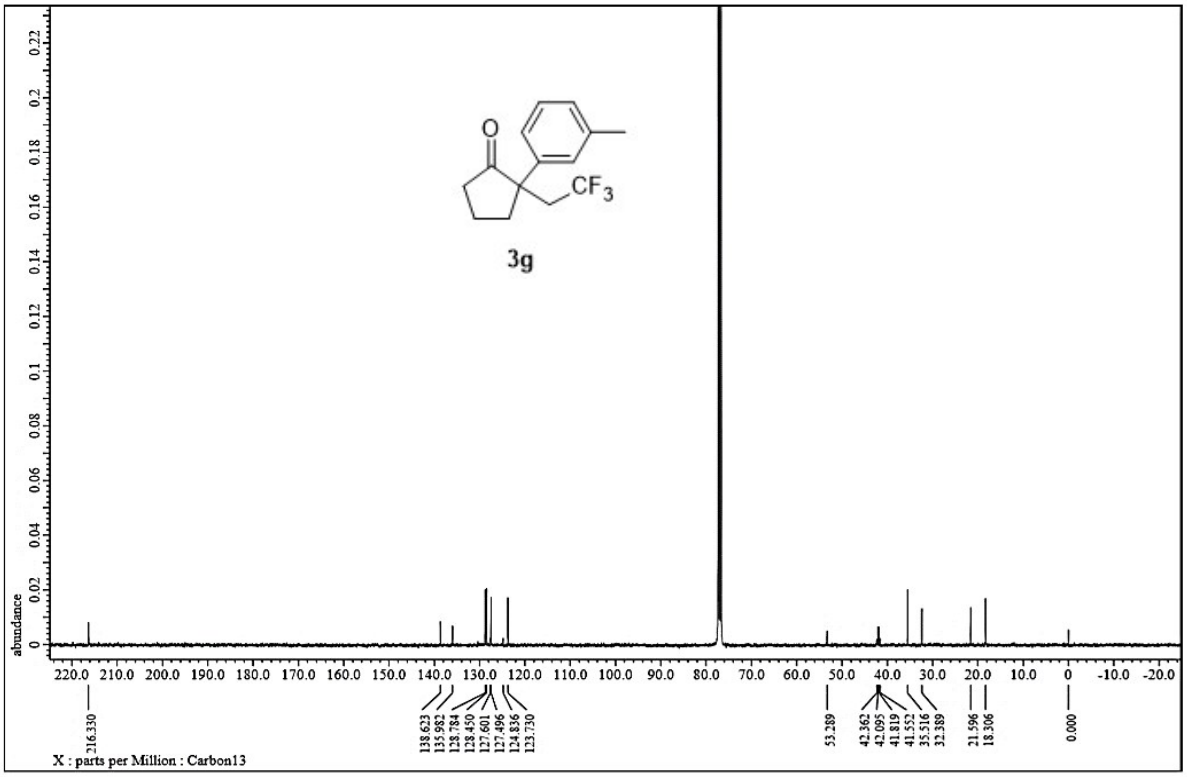
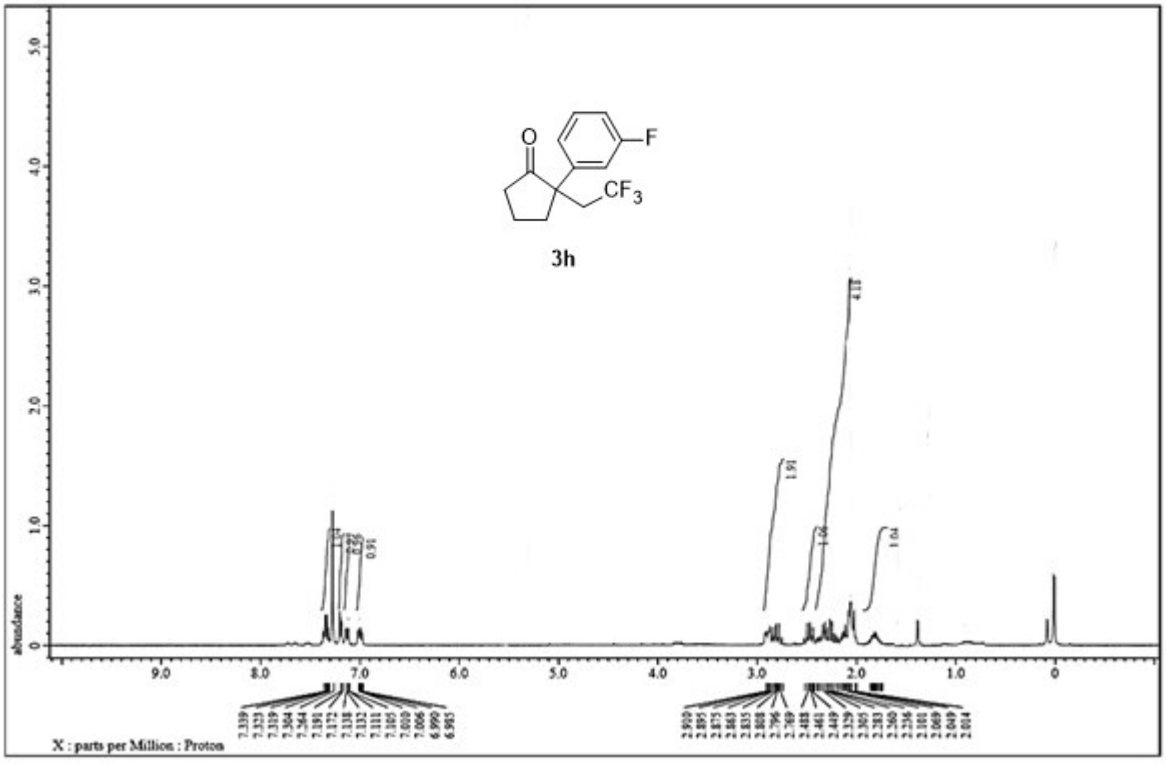
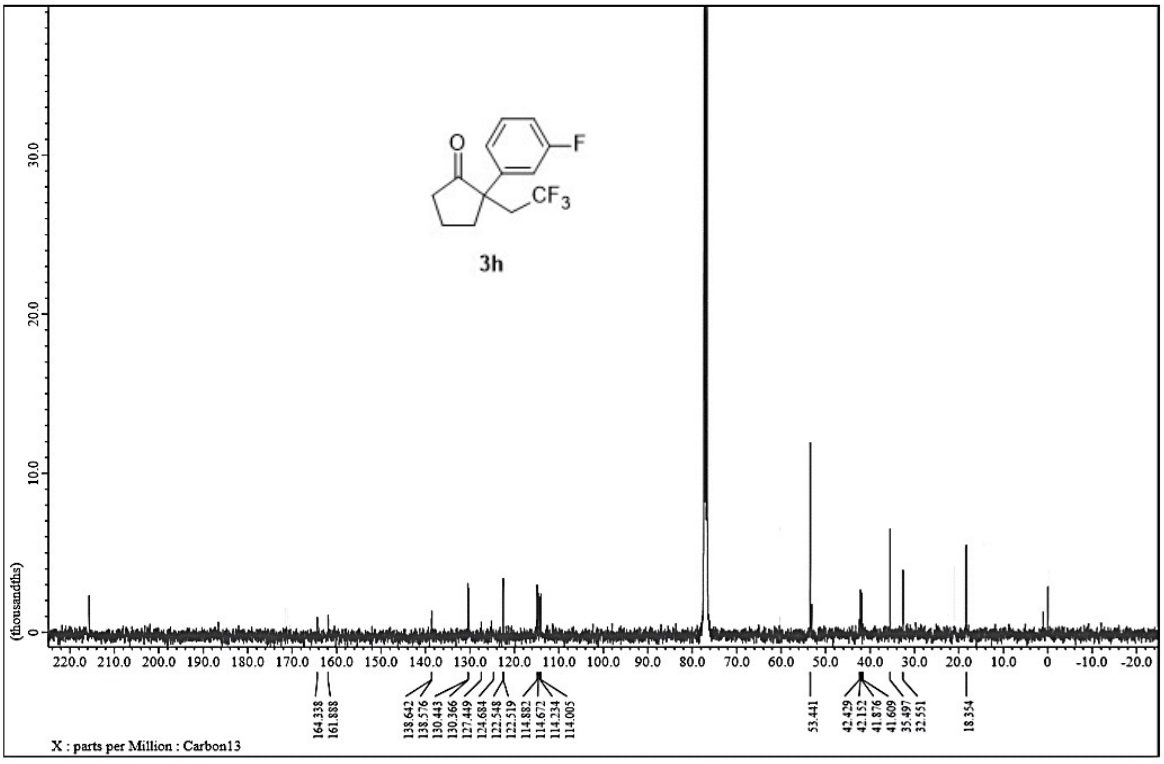
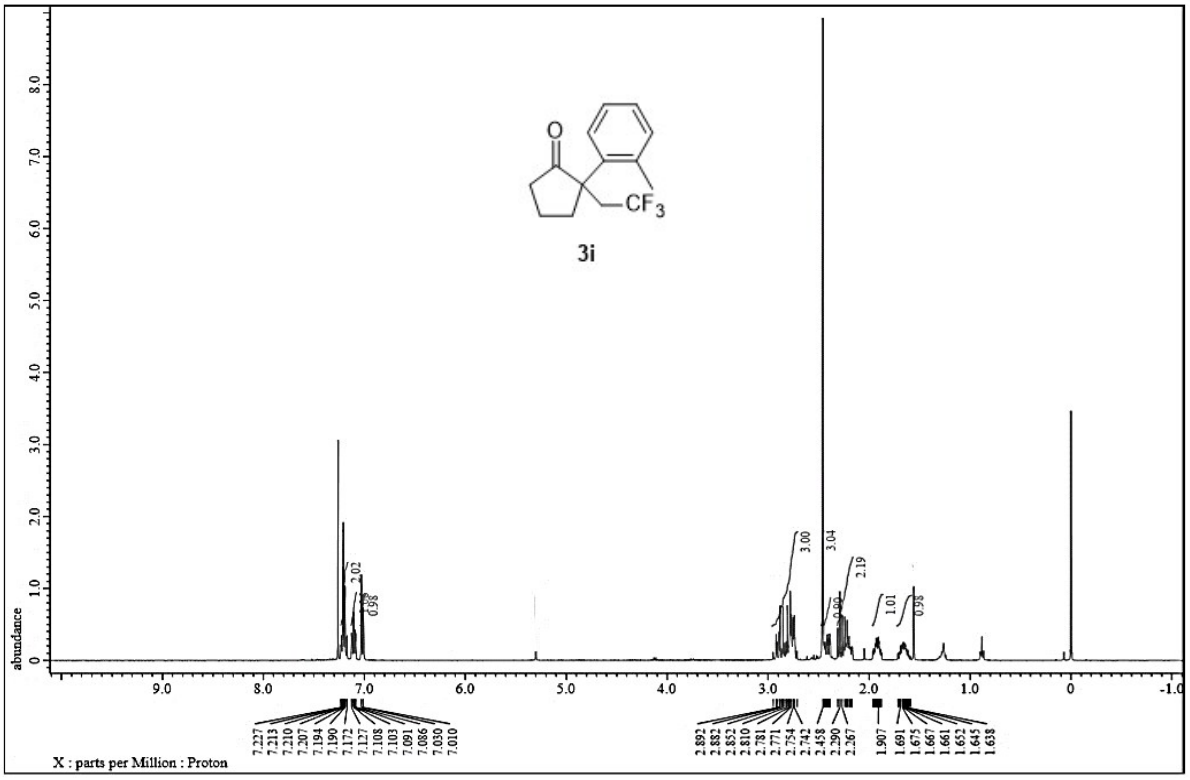
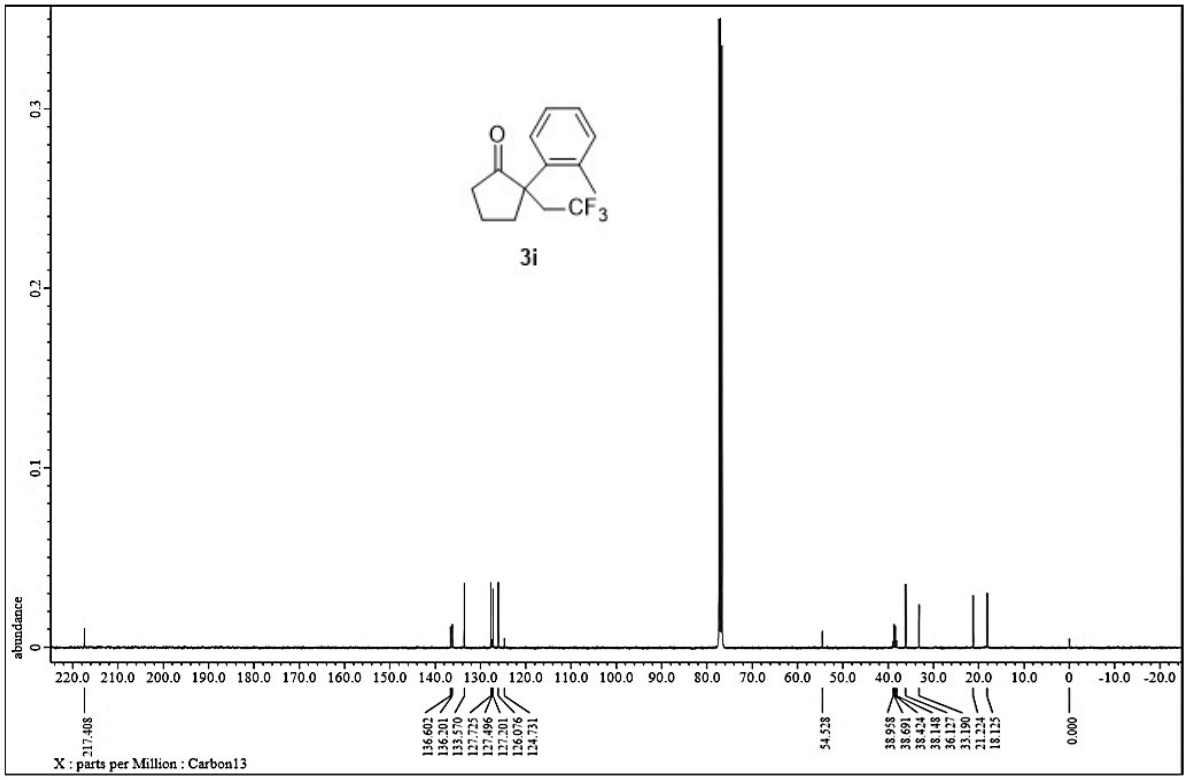
CF3
3g
abundance
X : parts per Million : Proton

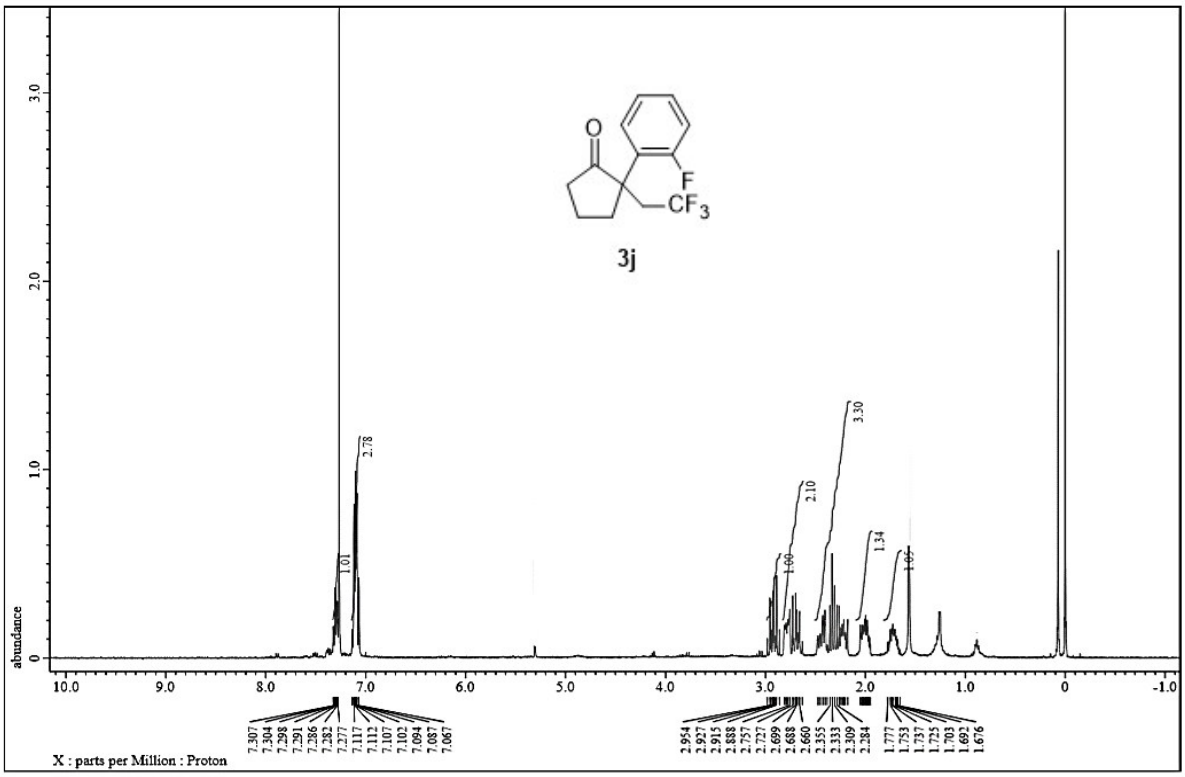

O
CF3
3g
abundance
X : parts per Million : Carbon13


O
F
CF3
3h
abundance
X : parts per Million : Proton


O
F
CF3
3h
(thousandths)
X : parts per Million : Carbon13


O
CF3
3i
abundance
X : parts per Million : Proton


O
CF3
3i
abundance
X : parts per Million : Carbon13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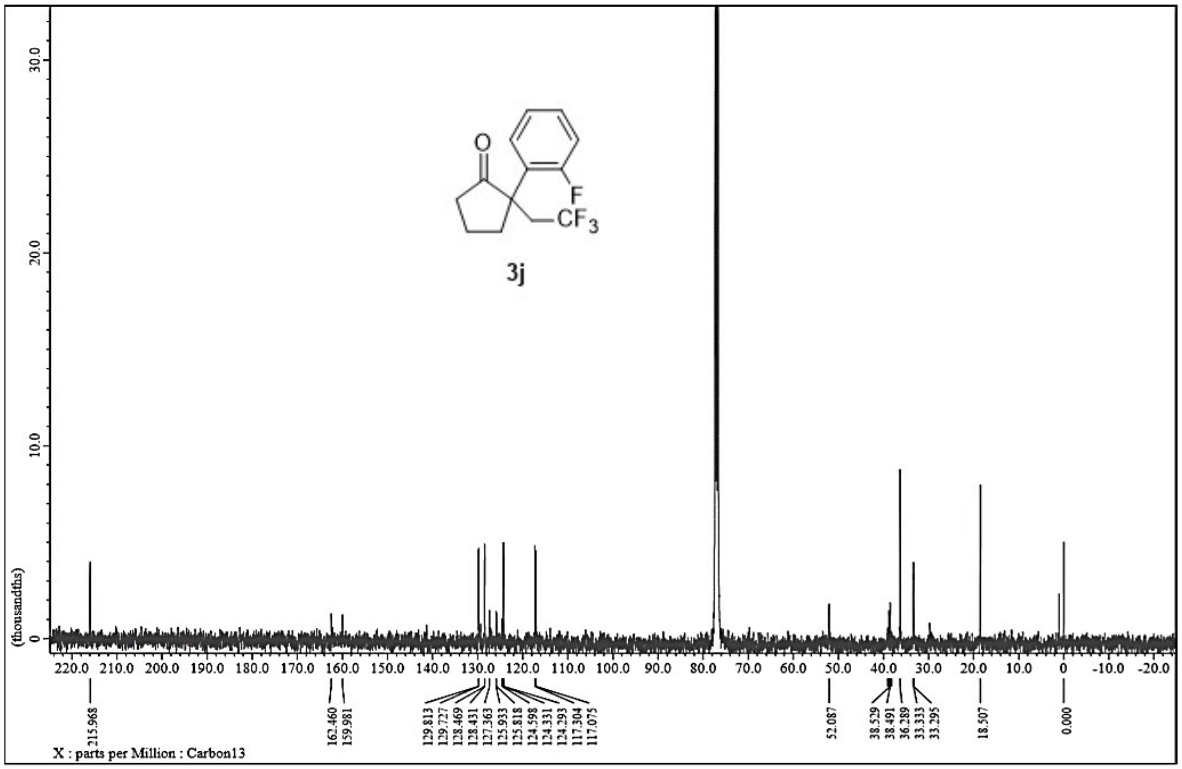
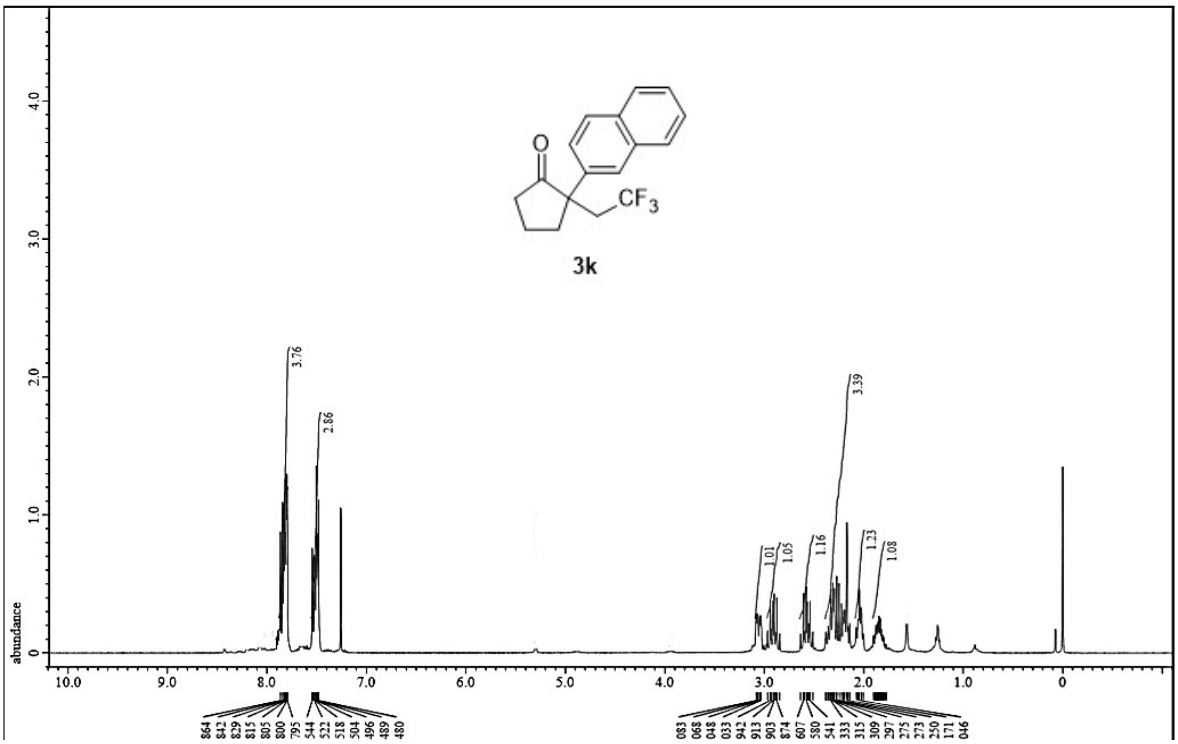
F
CF3
3j
abundance
X : parts per Million : Proton


O
F
CF3
3j
(thousandths)
X : parts per Million : Carbon13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CF3
3k
abundance
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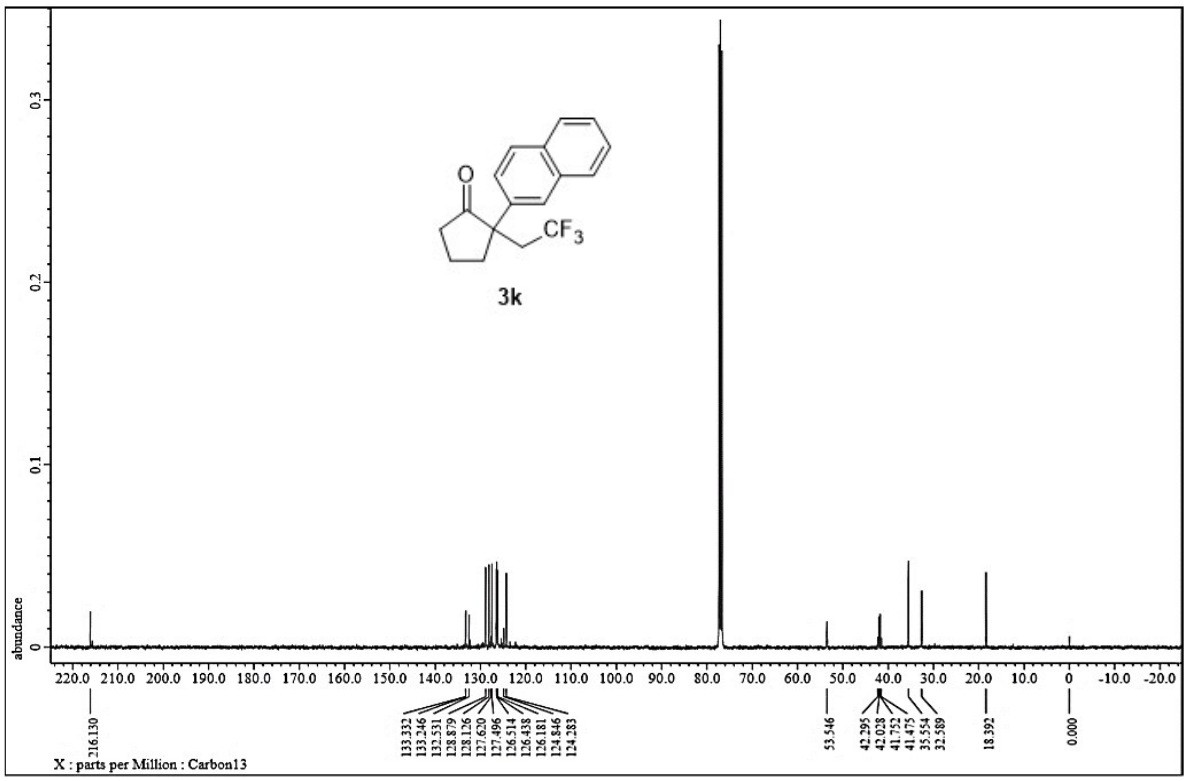
3.39
1.01
1.05
1.16
1.33
1.08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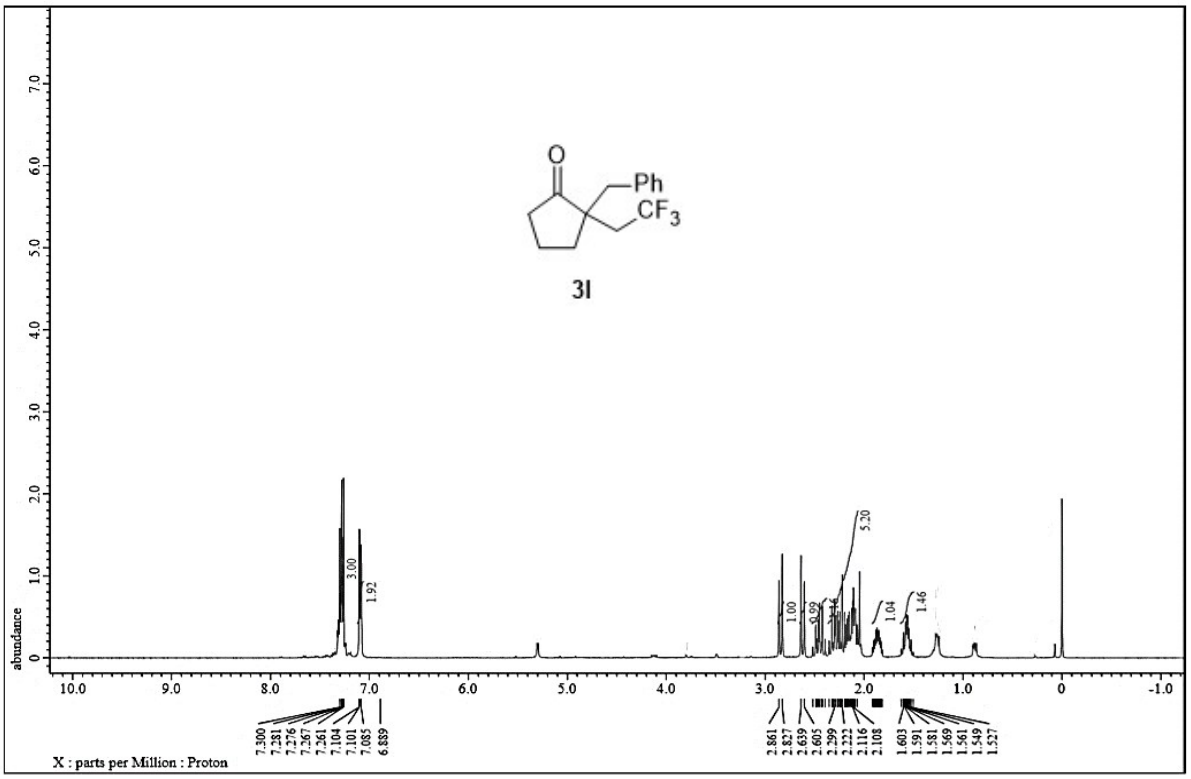
CF3
3k
abundance
X : parts per Million : Carbon13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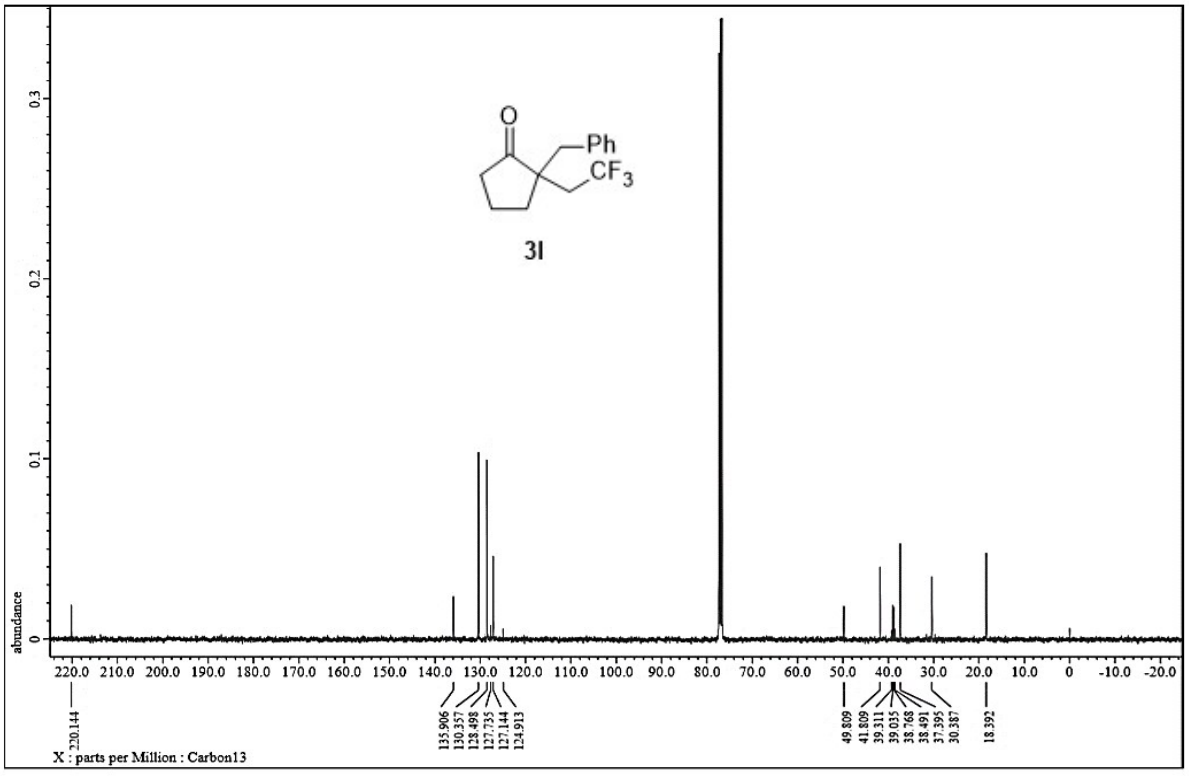
Ph
CF3
3l
abundance
X : parts per Million : Proton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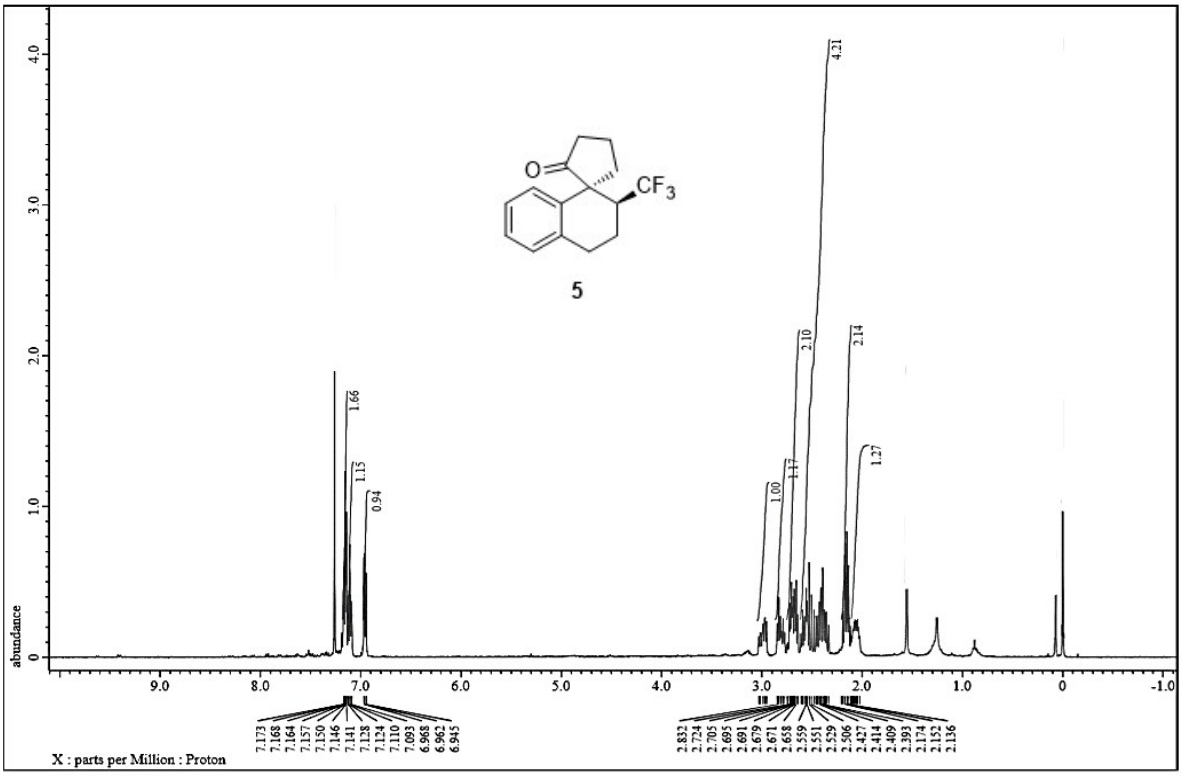
Ph
CF3
3l
abundance
X : parts per Million : Carbon13


O
CF3
5
abundance
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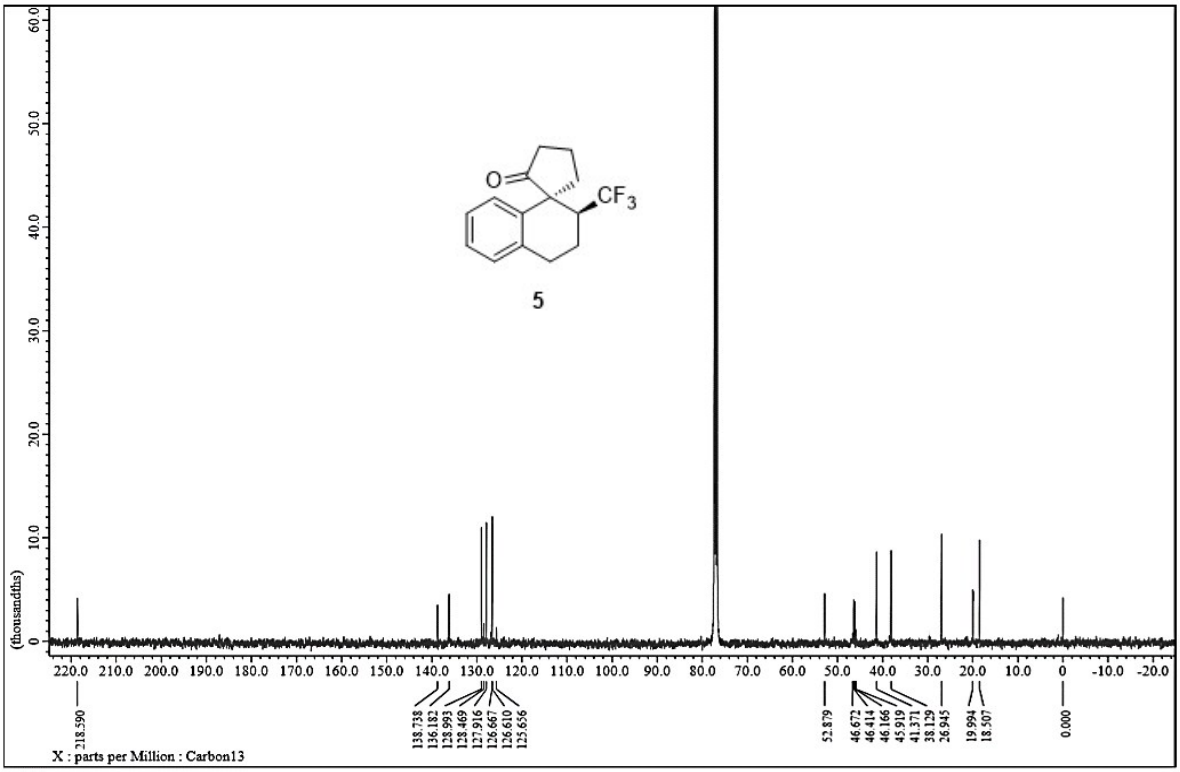
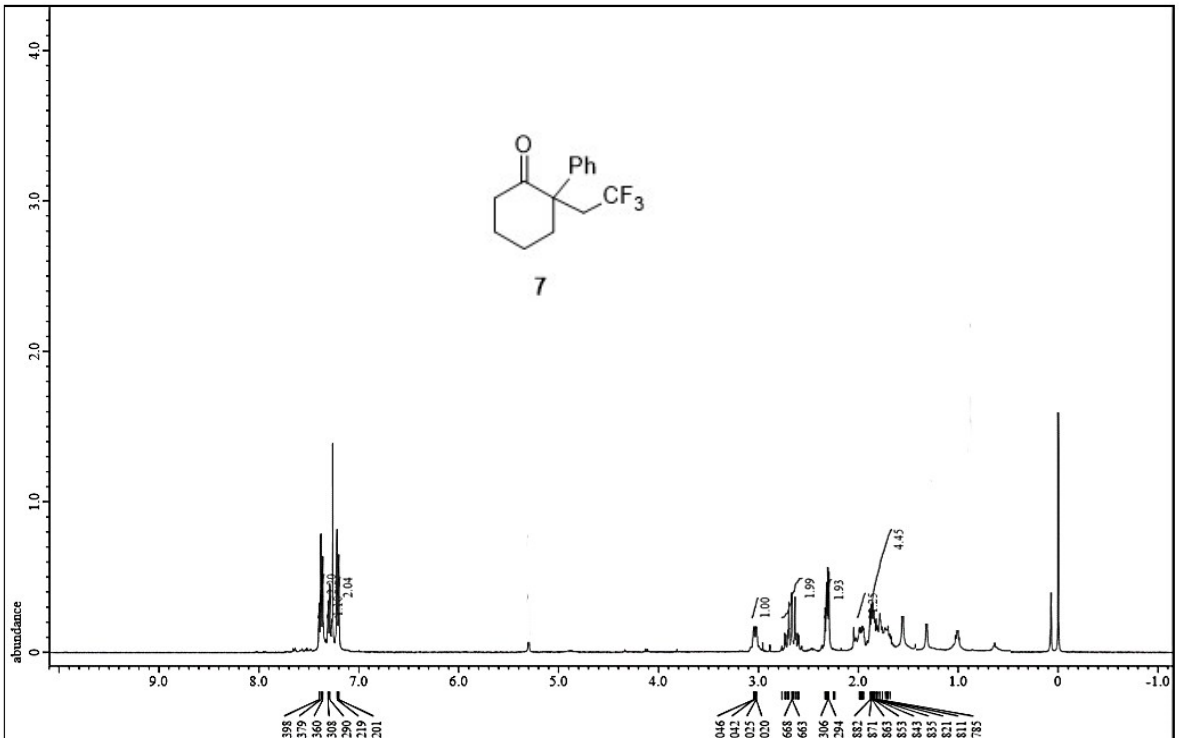

O
CF3
5
(thousandths)
X : parts per Million : Carbon13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Ph
CF3
7
abundance
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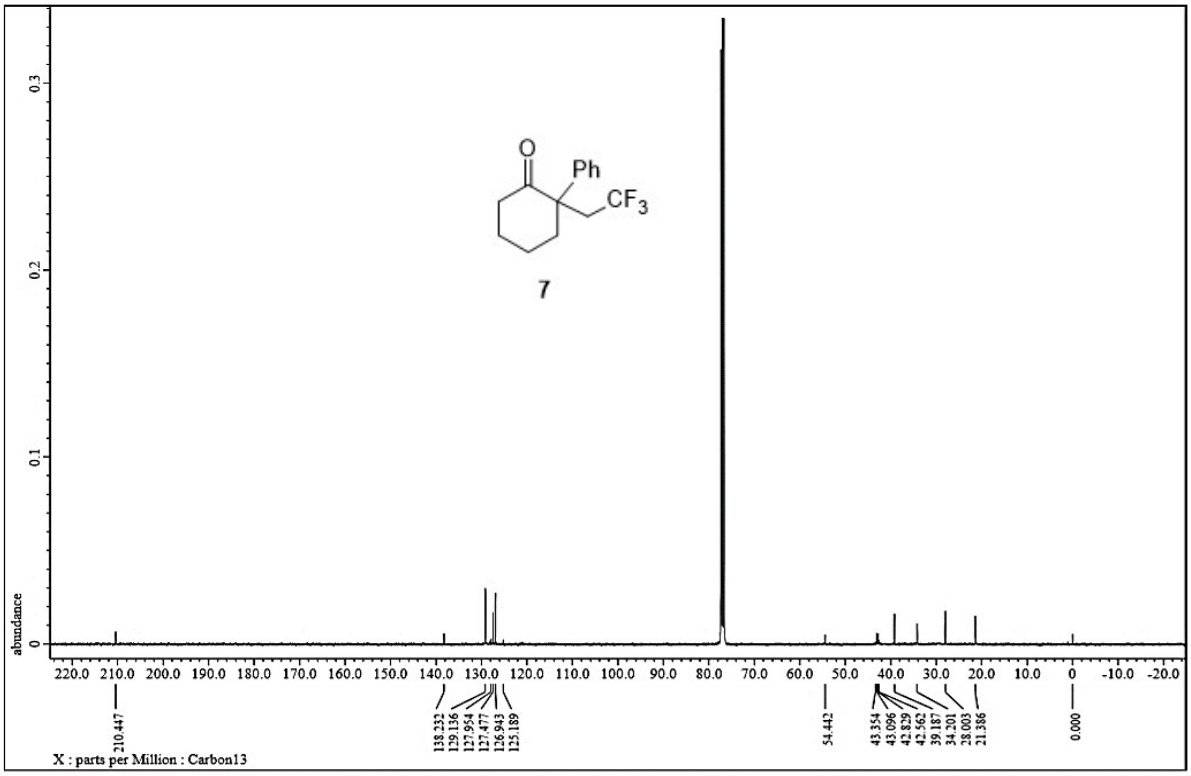
2.04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Ph
CF3
7
abundance
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127.477
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28.003
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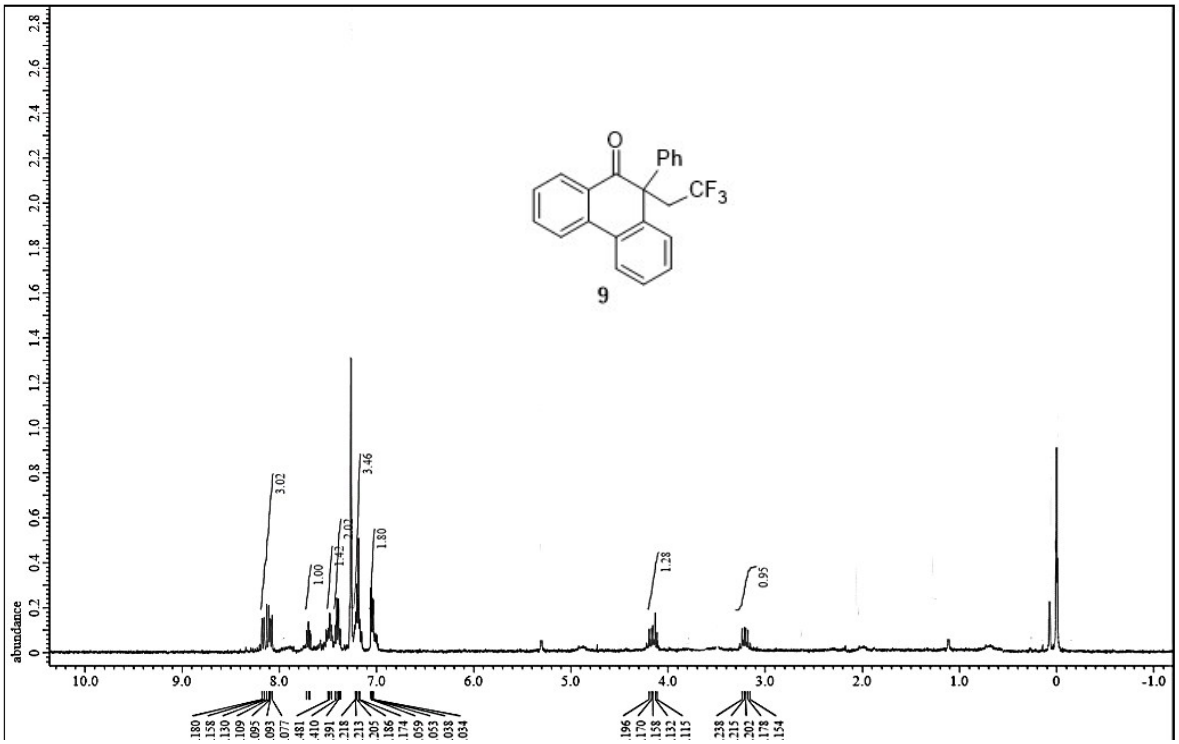
0.000
X : parts per Million : Carbon13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Ph
CF3
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abundance
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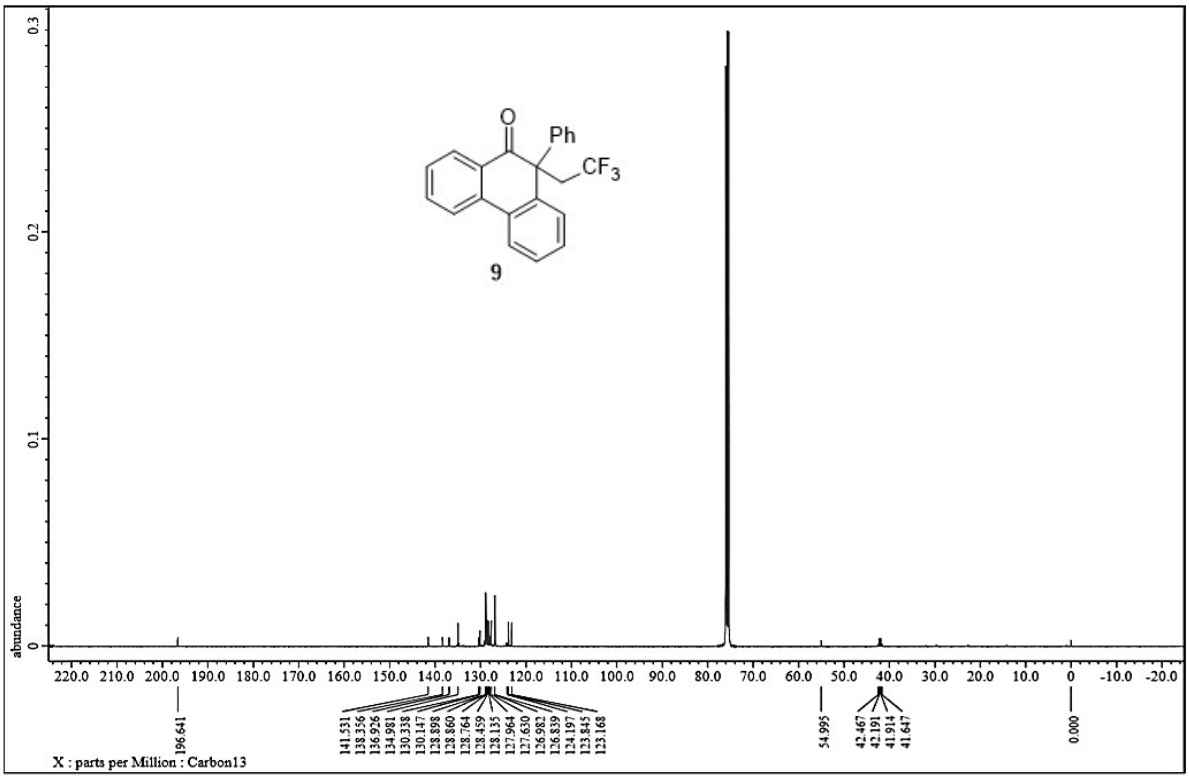
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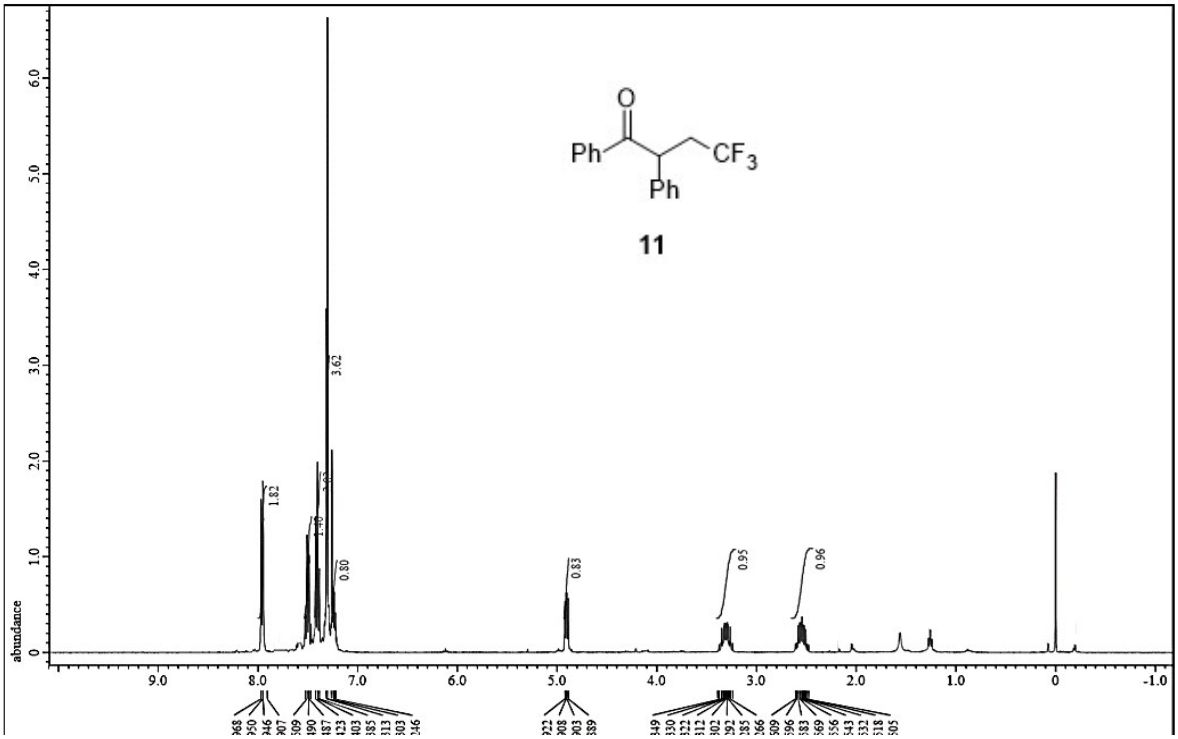
Ph
CF3
9
abundance
X : parts per Million : Carbon13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Ph
CF3
Ph
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abundance
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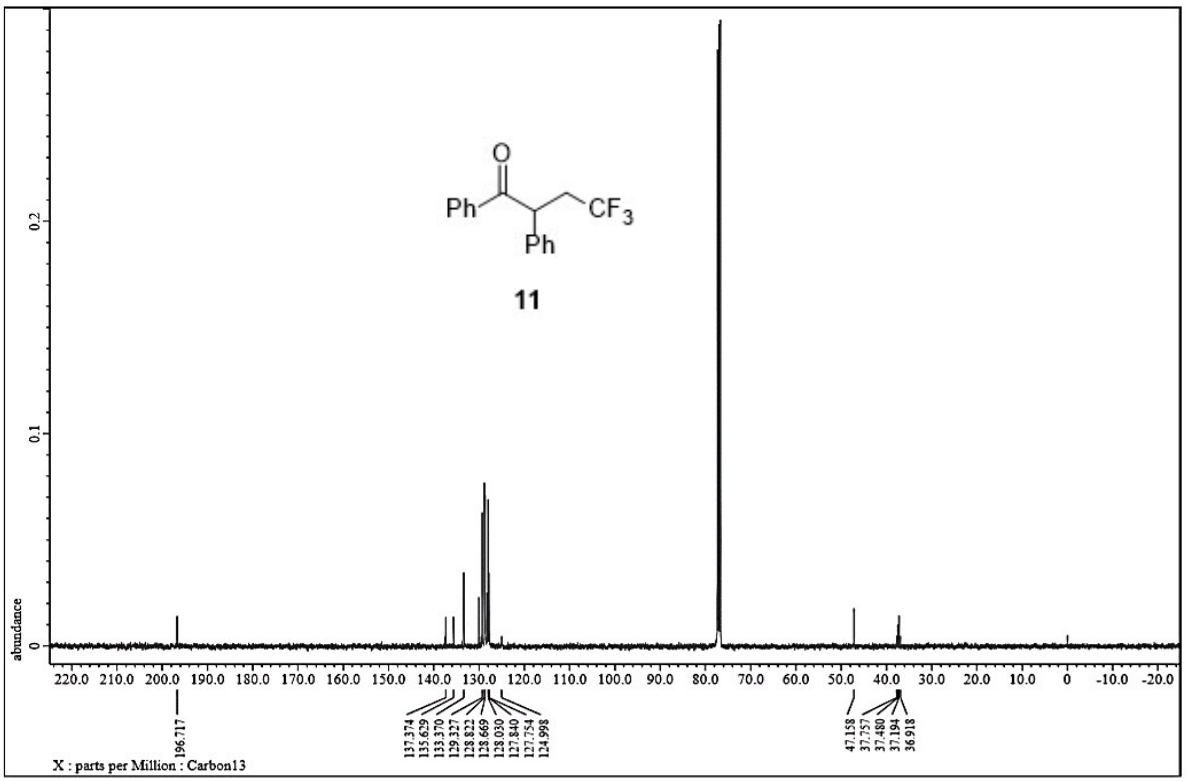
0.83
0.95
0.96


O
Ph
CF3
Ph
11
abundance
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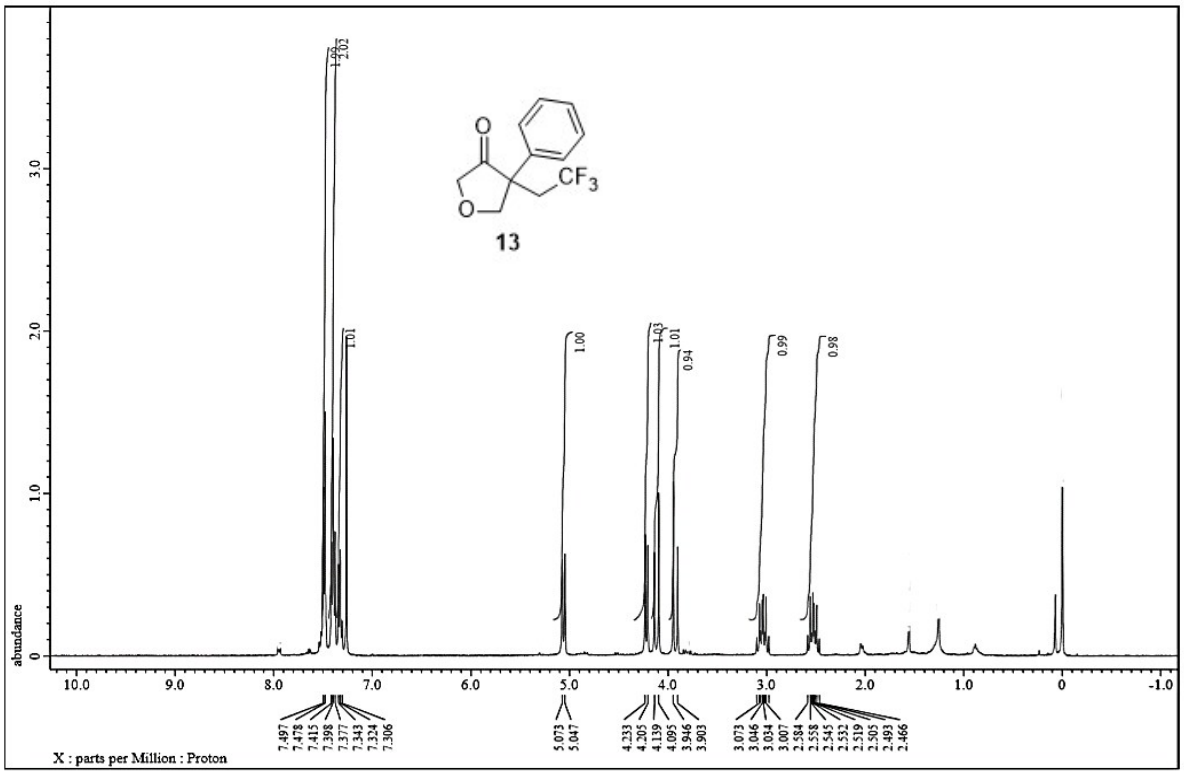
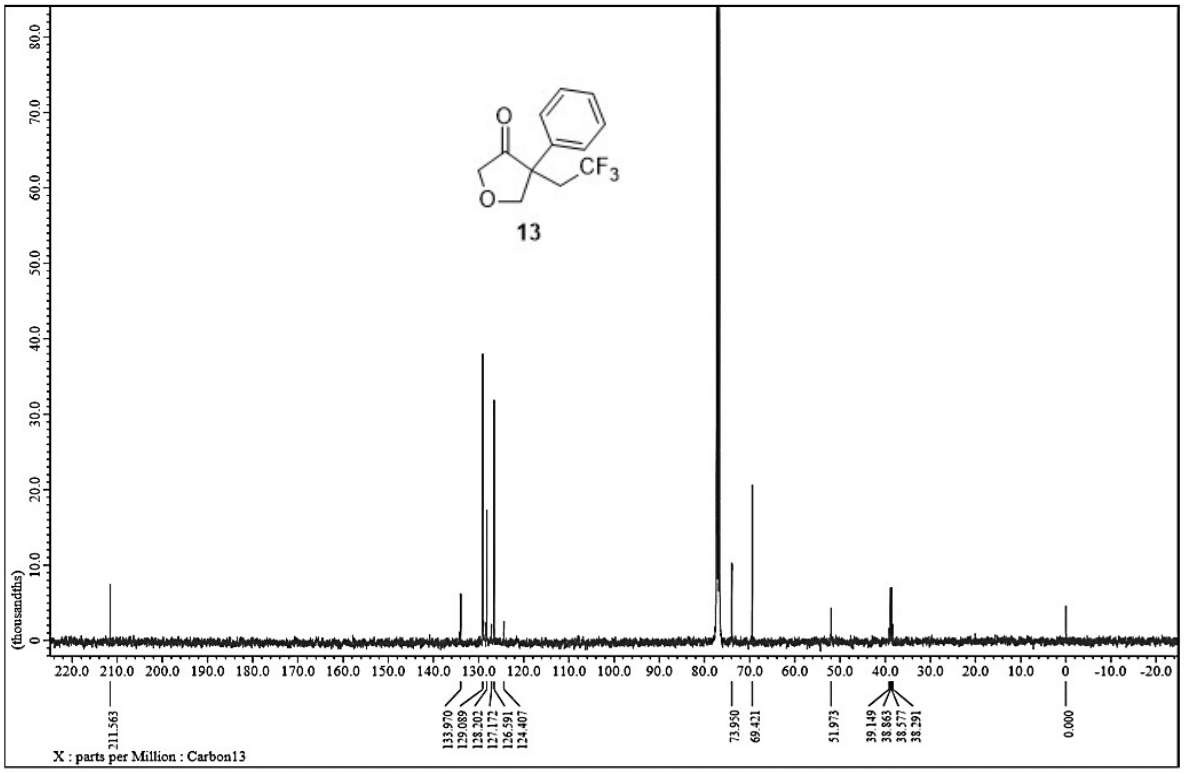
137.374
135.629
133.370
129.327
128.822
128.669
128.030
127.840
127.754
124.998
47.158
37.757
37.480
37.194
36.918
X : parts per Million : Carbon13


13
abundance
X : parts per Million : Proton


13
(thousandths)
X : parts per Million : Carbon13