Relay Cooperation of $K_2S_2O_8$ and O_2 in Oxytrifluoromethylation of Alkenes Using CF_3SO_2Na

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Supporting Information

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General information

All reactions were run under a dry air atmosphere with a dry air balloon fitted on a Schlenk tube. All glassware was oven dried at 110 ºC for hours and cooled down under vacuum. All the solvents were purified according to the solvents handbook. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Sodiumtriflinate was purchased from TCI. α-Bromostyrene derivatives and other α-substituted styrene derivatives were all prepared following literature procedures.[1] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 30-60 ºC). GC-MS spectra were recorded on a Varian GCMS-QP2010SE. IR spectra were recorded on a Mettler Toledo React IR TM 15 spectrometer using a diamond comb. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), CD_3OD (3.31 ppm for ^{1}H), DMSO-d_6 (2.50 ppm for ^{1}H), and $CDCl_3$ (77.16 ppm for ^{13}C), respectively.

Experimental section

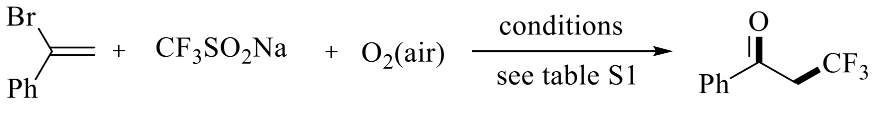
1) Procedure and analytical data of compounds 3a-3r.

1.1) Procedure and analytical data of compounds 3a-3r General procedure for the preparation of α-trifluoromethyl-substituted ketone

Typical procedure: To an oven-dried Schlenk tube was added CF_3SO_2Na (0.60 mmol), $K_2S_2O_8$ (0.05 mmol) and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. α-Bromostyrene (0.20 mmol) and DMSO (2.0 mL) were successively injected into the reaction tube with magnetic stirring. The reaction mixture was vigorous stirred at 45 ºC for 2 h. Thereafter, water was added and the mixture was extracted with diethyl ether (x 4). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was separated on a silica gel column with petroleum ether (30-60 ºC) and ethyl acetate as eluent to afford the desired product.

1.2) Impact of reaction parameters on the oxytrifluoromethylation of alkenes

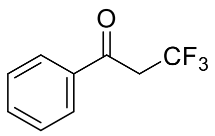
Table S1. Impact of reaction parameters on dioxygen-triggered aerobic difunctionalization of terminal alkynes[a]



Entry	Initiator (%)	Conditions	Solvent	Temp. / ºC	Yield [%][b]
1	TBHP[c] (10%)	air	DMSO	45	39
2	$PhI(OAc)_2$ (10%)	air	DMSO	45	trace
3	$(NH_4)_2S_2O_8$ (10%)	air	DMSO	45	59
4	$Na_2S_2O_8$ (10%)	air	DMSO	45	55
5	$K_2S_2O_8$ (10%)	air	DMSO	45	61
6	**$K_2S_2O_8$ (25%)**	air	**DMSO**	**45**	**88**
7	$K_2S_2O_8$ (25%)	air	DMSO	r.t.	72
8	$K_2S_2O_8$ (25%)	air	DMSO	60	64
9[d]	$K_2S_2O_8$ (25%)	air	DMSO	45	63
10	$K_2S_2O_8$ (25%)	air	DMF	45	54
11	$K_2S_2O_8$ (25%)	air	MeCN	45	10
12	-	air	DMSO	45	trace
13	$K_2S_2O_8$ (25%)	N_2	DMSO	45	0

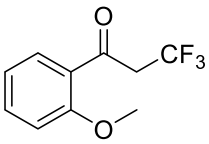
[a]Unless otherwise specified, all reactions were carried out using **1a** (0.20 mmol), **2** (0.60 mmol), and initiator in solvent (2.0 mL) under different conditions for 2 h. [b]Determined by ^{19}F NMR analysis using $PhCF_3$ as internal standard. [c]70% solution in water. [d]**2** (0.40 mmol) was employed.

1.3) Characterization of synthesized compounds 3a-3r.

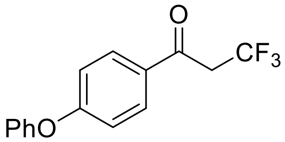


3,3,3-trifluoro-1-phenylpropan-1-one (3a):[2a] Typical procedure: To an oven-dried Schlenk tube was added CF_3SO_2Na (0.60 mmol), $K_2S_2O_8$ (0.05 mmol) and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. α-Bromostyrene (0.20 mmol) and DMSO (2.0 mL) were successively injected into the reaction tube with magnetic stirring. The reaction mixture was vigorous stirred at 45 ºC for 2 h. Thereafter, water was added and the mixture was extracted with diethyl ether (x 4). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was separated on a silica gel column with petroleum ether (30-60 ºC) and ethyl acetate as eluent to afford the desired product.

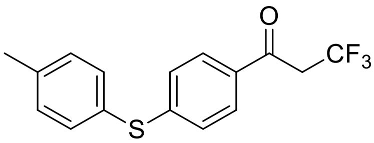
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, J = 10.0 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.64 (tt, J = 7.4, 0.8 Hz, 1H), 7.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 135.9, 134.3, 129.0, 128.4, 124.2 (q, $^{1}J_{C-F}$ = 277.6 Hz), 42.1 (q, $^{2}J_{C-F}$ = 28.3 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.03 ppm.



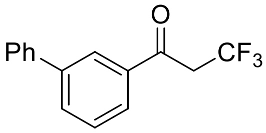
3,3,3-trifluoro-1-(2-methoxyphenyl)propan-1-one (3b):[2b] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (q, J = 10.2 Hz, 2H), 3.95 (s, 3H), 7.00 (d, J = 8.4 Hz, 1H), 7.02-7.05 (t, J = 8.0 Hz, 1H), 7.51-7.55 (m, 1H), 7.82 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1 (q, $^{3}J_{CF}$ = 2.8 Hz), 159.1, 135.1, 131.0, 126.4, 124.3 (q, $^{1}J_{CF}$ = 277.8 Hz), 121.1, 111.8, 55.7, 47.0 (q, $^{2}J_{CF}$ = 27.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57 ppm.



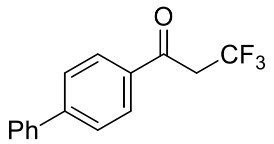
3,3,3-trifluoro-1-(4-phenoxyphenyl)propan-1-one (3c): The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (q, J = 10.2 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.90 (d, J = 9.2 Hz, 2H),. ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (q, $^{3}J_{CF}$ = 2.3 Hz), 163.1, 155.1, 130.9, 130.5, 130.3, 125.1, 124.2 (q, $^{1}J_{CF}$ =278.1 Hz), 120.5, 117.4, 42.0 (q, $^{2}J_{CF}$ = 28.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.94 ppm. HRMS (EI+) calculated for $C_{15}H_{11}O_2F_3$ (M+): 280.0711; found: 280.0710.



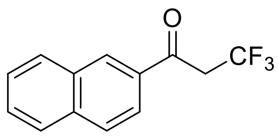
3,3,3-trifluoro-1-(4-(*p*-tolylthio)phenyl)propan-1-one (3d):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.71 (q, J = 10.0 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8 (q, $^{3}J_{CF}$ = 2.4 Hz), 148.3, 140.0, 135.0, 132.6, 130.8, 128.9, 127.0, 126.4, 124.1 (q, $^{1}J_{CF}$ = 278.1 Hz), 42.0 (q, $^{2}J_{CF}$ = 28.3 Hz), 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.95 ppm. HRMS (EI+) calculated for $C_{16}H_{13}OSF_3$ (M+): 310.0639; found: 310.0642.



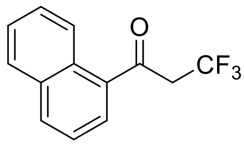
1-([1,1'-biphenyl]-3-yl)-3,3,3-trifluoropropan-1-one (3e):[2c] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (q, *J* = 9.8 Hz, 2H), 7.37–7.31 (tt, *J* = 7.4, 2.2 Hz, 1H), 7.44–7.48 (t, *J* = 7.4 Hz, 2H), 7.53–7.59 (m, 3H), 7.82 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.87 (d, *J* = 7.6, Hz, 1H), 8.12 (t, *J* =3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9 (q, $^{3}J_{CF}$ = 2.4 Hz), 142.2, 139.8, 136.3, 132.9, 129.5, 129.1, 128.2, 127.3, 127.2, 127.0, 124.2 (q, $^{1}J_{CF}$ = 278.0 Hz), 42.3 (q, $^{2}J_{CF}$ = 28.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.93 ppm.



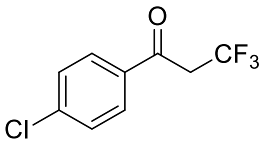
1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropan-1-one (3f):[2b] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (q, *J* = 10.0 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4 (q, $^{3}J_{CF}$ = 2.3 Hz), 147.0, 139.5, 134.6, 129.2, 129.1, 128.7, 127.6, 127.4, 124.2 (q, $^{1}J_{CF}$ = 278.1 Hz), 42.3 (q, $^{2}J_{CF}$ = 28.4 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$) δ -61.94 ppm.



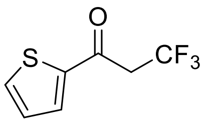
3,3,3-trifluoro-1-(naphthalen-2-yl)propan-1-one (3g):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 4.54 (q, *J* = 10.8 Hz, 2H), 7.63-7.67 (m, 1H), 7.68-7.72 (m, 1H), 7.98-8.06 (m, 3H), 8.13 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8 (q, $^{3}J_{CF}$ = 2.5 Hz), 136.1, 133.3, 132.4, 130.7, 129.8, 129.4, 129.1, 128.4, 128.0, 127.3, 124.2 (q, $^{1}J_{CF}$ = 278.1 Hz), 123.6, 42.3 (q, $^{2}J_{CF}$ = 28.3 Hz). ^{19}F-NMR (376 MHz, DMSO-*d*$_6$) δ -60.88 ppm.



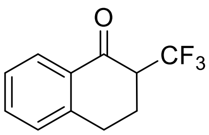
3,3,3-trifluoro-1-(naphthalen-1-yl)propan-1-one (3h):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, CD_3OD) δ 4.15 (q, *J* = 10.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.58 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.89-7.92 (m, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0 (q, $^{3}J_{CF}$ = 2.5 Hz), 134.4, 134.1, 133.8, 130.3, 129.0, 128.9, 128.7, 127.0, 125.7, 124.3, 124.1 (q, $^{1}J_{CF}$ = 278.3 Hz), 45.0 (q, $^{2}J_{CF}$ = 28.0 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$) δ -61.93 ppm.



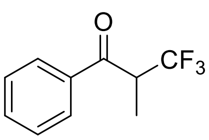
1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one (3i):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (q, *J* = 10.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (q, $^{3}J_{CF}$ = 2.4 Hz), 141.0, 134.2, 129.9, 129.5, 124.0 (q, $^{1}J_{CF}$ = 278.2 Hz), 42.2 (q, $^{2}J_{CF}$ = 28.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.02 ppm.



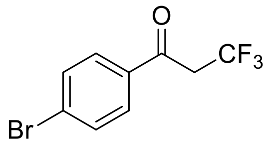
3,3,3-trifluoro-1-(thiophen-2-yl)propan-1-one (3j):[2b] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (q, *J* = 10.0 Hz, 2H), 7.16-7.20 (m, 1H), 7.75-7.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 143.1, 135.9, 133.7, 128.7, 123.9 (q, $^{1}J_{CF}$ = 278.3 Hz), 42.9 (q, $^{2}J_{CF}$ = 28.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.92 ppm.



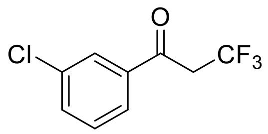
2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (3k):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22-2.32 (m, 1H), 2.47-2.54 (m, 1H), 3.03-3.16 (m, 2H), 3.22-3.33 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.53 (dt, *J* = 7.6, 0.9 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 143.2, 134.4, 132.1, 128.9, 128.0, 127.3, 125.2 (q, $^{1}J_{CF}$ = 280.9 Hz), 51.0 (q, $^{2}J_{CF}$ = 25.7 Hz), 27.7, 23.6 (q, $^{3}J_{CF}$ = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.53 ppm.



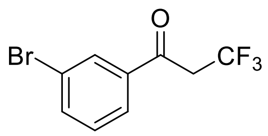
3,3,3-trifluoro-2-methyl-1-phenylpropan-1-one (3l):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 7.2 Hz, 3H), 4.20-4.32 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.95-7.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 135.7, 134.2, 129.1, 128.7, 125.4 (q, $^1J_{CF}$ = 281.2 Hz), 44.4 (q, $^2J_{CF}$ = 26.6 Hz), 11.8 (q, $^3J_{CF}$ = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.27 ppm.



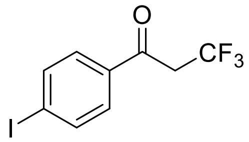
1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one (3m):[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (q, *J* = 9.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9 (q, $^3J_{CF}$ = 2.5 Hz), 134.6, 132.5, 129.9, 129.8, 123.9 (q, $^1J_{CF}$ = 278.0 Hz), 42.3 (q, $^2J_{CF}$ = 28.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.00 ppm.



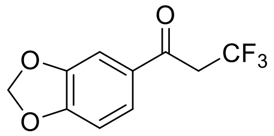
1-(3-chlorophenyl)-3,3,3-trifluoropropan-1-one (3n): The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (q, *J* = 10.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.61 (ddd, *J* = 8.0, 2.0, 0.9 Hz, 1H), 7.79-7.82 (m, 1H), 7.90 (t, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (q, $^3J_{CF}$ = 2.5 Hz), 137.3, 135.5, 134.3, 130.4, 128.5, 126.5, 123.9 (q, $^1J_{CF}$ = 278.0 Hz), 42.3 (q, $^2J_{CF}$ = 28.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.10 ppm. HRMS (EI+) calculated for C9H6ClOF3 (M+): 222.0060; found: 222.0063.



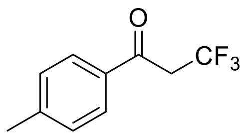
1-(3-bromophenyl)-3,3,3-trifluoropropan-1-one (3o):[2b] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (q, *J* = 9.6 Hz, 2H), 7.40 (dt, *J* = 8.0, 2.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 8.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (q, $^3J_{CF}$ = 2.4 Hz), 137.5, 137.2, 131.5, 130.6, 127.0, 123.9 (q, $^1J_{CF}$ = 278.1 Hz), 123.4, 42.3 (q, $^2J_{CF}$ = 28.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.05 ppm.



3,3,3-trifluoro-1-(4-iodophenyl)propan-1-one (3p):[2d] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (q, *J* = 9.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (q, $^3J_{CF}$ = 2.4 Hz), 138.3, 135.0, 129.6, 123.9 (q, $^1J_{CF}$ = 278.1 Hz), 102.7, 42.0 (q, $^2J_{CF}$ = 28.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.99 ppm.

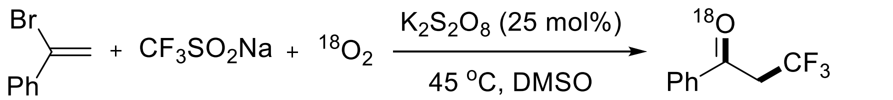


1-(benzo[d][1,3]dioxol-5-yl)-3,3,3-trifluoropropan-1-one (3q): The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (q, *J* = 10.0 Hz, 2H), 6.08 (s, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 152.9, 148.7, 130.8, 125.3, 124.1 (q, $^1J_{CF}$ = 278.0 Hz), 108.2, 108.0, 102.3, 42.1 (q, $^2J_{CF}$ = 28.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.00 ppm. HRMS (EI+) calculated for $C_{10}H_7O_3S_3$ (M+): 232.0347; found: 232.0346.



3,3,3-trifluoro-1-(p-tolyl)propan-1-one (3r:[2a] The synthesis procedure is the same as for **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s), 3.77 (q, *J* = 10.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5 (q, $^3J_{CF}$ = 2.3 Hz), 145.5, 133.5, 129.7, 128.6, 124.2 (q, $^1J_{CF}$ = 278.0 Hz), 42.1 (q, $^2J_{CF}$ = 29.2 Hz), 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.02 ppm.

2) Labeling experiment.



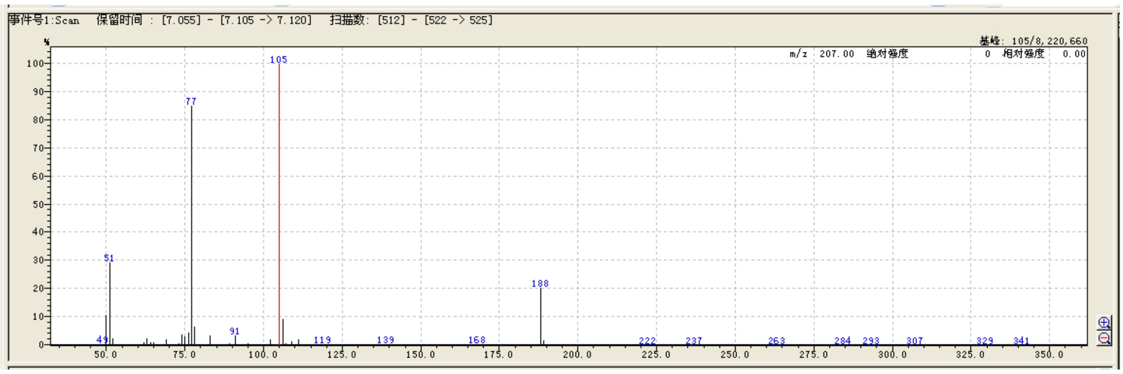
1a **2**

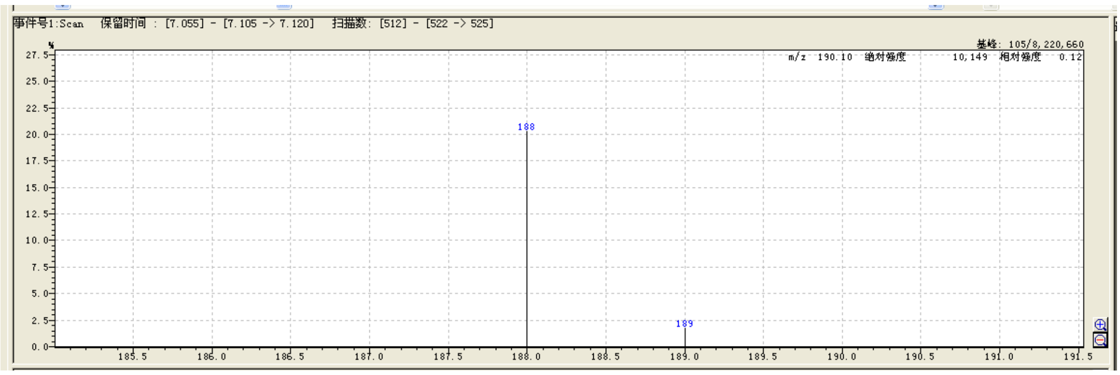
yield: 51%

^{18}O-**3aa'**/^{16}O-**3aa**: 100:8

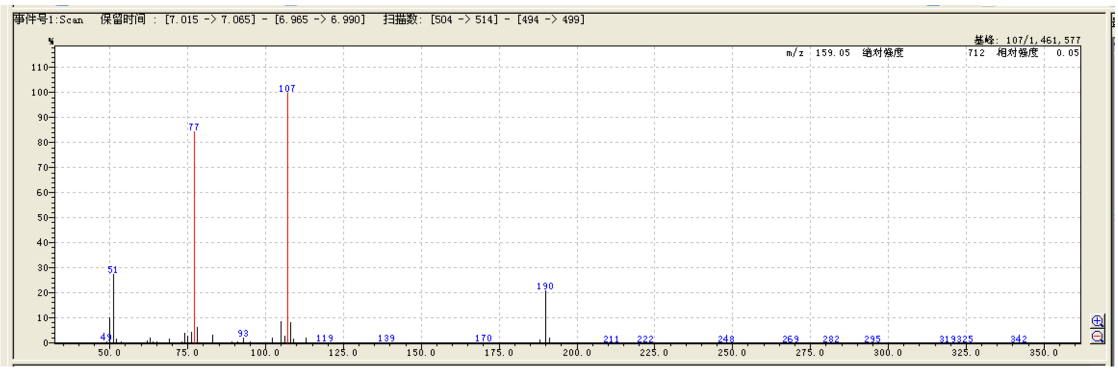
Typical procedure: An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a three way cock which was connected to a nitrogen line and a balloon filled with $^{18}O_2$ respectively. After evacuation under vacuum and flushing with N_2 for one time, CF_3SO_2Na (0.60 mmol), $K_2S_2O_8$ (0.05 mmol) and DMSO (2.0 mL) was quickly added under N_2, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 4 times. Then, $^{18}O_2$ was purged one time, α-Bromostyrene (0.20 mmol) was further injected into the reaction tube with magnetic stirring. The reaction mixture was vigorous stirred at 45 ºC for 2 h. Thereafter, the reaction mixture was analyzed by GC-MS and the yield was determined by ^{19}F NMR analysis using $PhCF_3$ as internal standard.

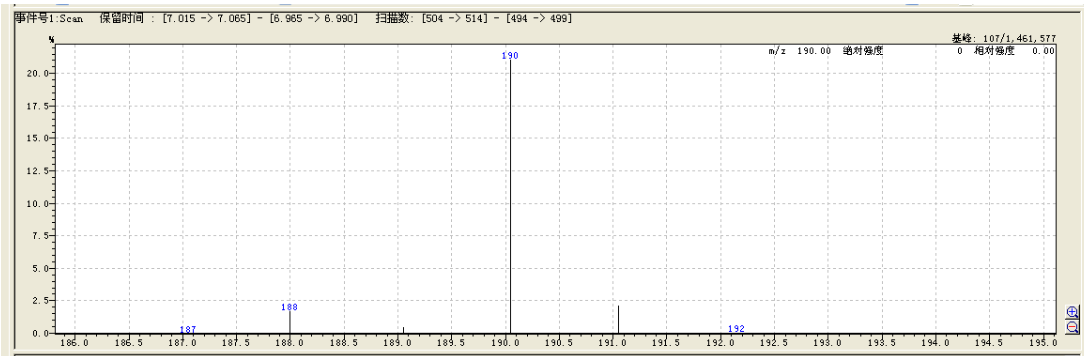
The EI-MS spectral of **3aa**





The EI-MS spectral of **3aa'**





The relative intensity of m/z 190 and m/z 188 are 308548 and 25115 respectively.

3) ReactIR experiments.

3.1 The model reaction between 1a (α-bromostyrene) and 2 (CF_3SO_2Na) in the absence of $K_2S_2O_8$ under air: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a dry air balloon. After evacuation under vacuum and flushing with air through the dry air balloon for three times, DMF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR at 45 °C. Afterwards, **1a** (0.4 mmol) and **2** (1.2 mmol) was added under air and the reaction mixture was allowed to stir vigorously at 45 °C for 2 h. No obvious conversion of **1a** or **2** was observed under present conditions.

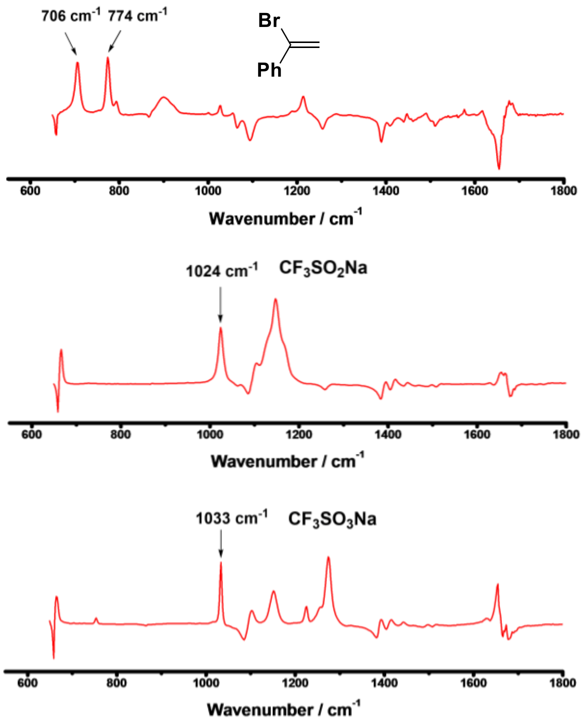


Figure 1. The Characteristic IR band of the different species (in DMF).

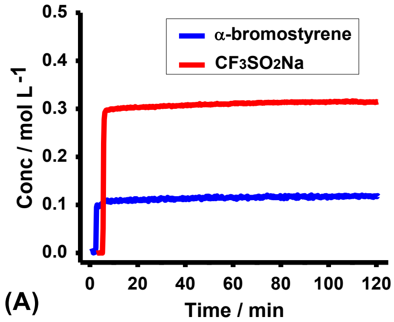


Figure 2. The kinetic profile of the reaction of **1a** (0.40 mmol), **2** (1.20 mmol) in DMF (4.0 mL) at 45 °C for 2 h under 1 atm of air (balloon).

3.2 The reaction between 2 (CF_3SO_2Na) and $K_2S_2O_8$ under N_2: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and nitrogen line. Then, CF_3SO_2Na (0.60 mmol), $K_2S_2O_8$ (0.18 mmol) was added to the reaction vessel. After evacuation under vacuum and flushing with N_2 for three times, degassed DMF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR at 45 °C for 4 h. After the reaction, 42% conversion of CF_3SO_2Na was observed by ^{19}F NMR analysis using $PhCF_3$ as internal standard.

The 2D-kinetic profiles of the reactions:

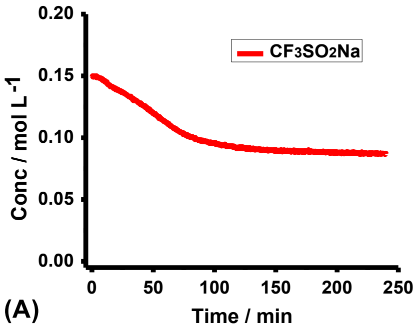


Figure 3. The kinetic profile of the reaction of **2** (0.60 mmol), $K_2S_2O_8$ (0.18 mmol) in DMF (4.0 mL) at 45 °C for 4 h under N_2.

3.3 The reaction between 2 (CF_3SO_2Na) and $K_2S_2O_8$ under air: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a dry air balloon. Then, CF_3SO_2Na (0.60 mmol), $K_2S_2O_8$ (0.18 mmol) was added to the reaction vessel. After evacuation under vacuum and flushing with the dry air balloon for three times, DMF (4.0

mL) was added to the vessel via a springe and the reaction was monitored by operando IR at 45 °C for 4 h. After the reaction, 91% conversion of CF_3SO_2Na was observed and 21% CF_3SO_3Na was obtained by ^{19}F NMR analysis using $PhCF_3$ as internal standard.

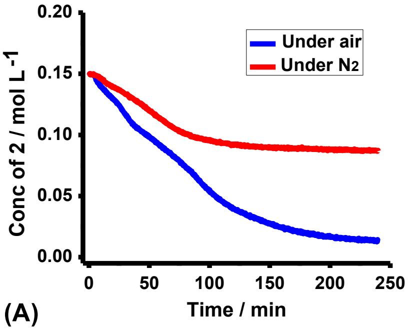


Figure 4. The kinetic profile of the reaction of **2** (0.60 mmol), $K_2S_2O_8$ (0.18 mmol) in DMF (4.0 mL) at 45 °C for 4 h under N_2 or air.

3.4 The model reaction in the absence of 1a: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a dry air balloon. Then, CF_3SO_2Na (1.2 mmol), $K_2S_2O_8$ (0.1 mmol) was added to the reaction vessel. After evacuation under vacuum and flushing with the dry air balloon for three times, DMF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR at 45 °C for 2 h. CF_3SO_3Na was observed during the reaction. After the reaction, 67% conversion of CF_3SO_2Na was observed and 0.26 mmol CF_3SO_3Na was obtained by ^{19}F NMR analysis using $PhCF_3$ as internal standard.

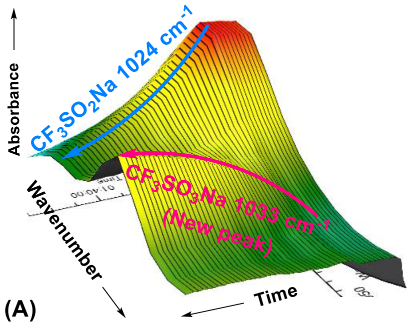


Figure 5. The 3D-FTIR profile of the reaction of **2** (1.20 mmol), $K_2S_2O_8$ (0.10 mmol) in DMF (4.0 mL) at 45 °C for 2 h under 1 atm of air (balloon); CF_3SO_3Na was observed during the reaction.

References

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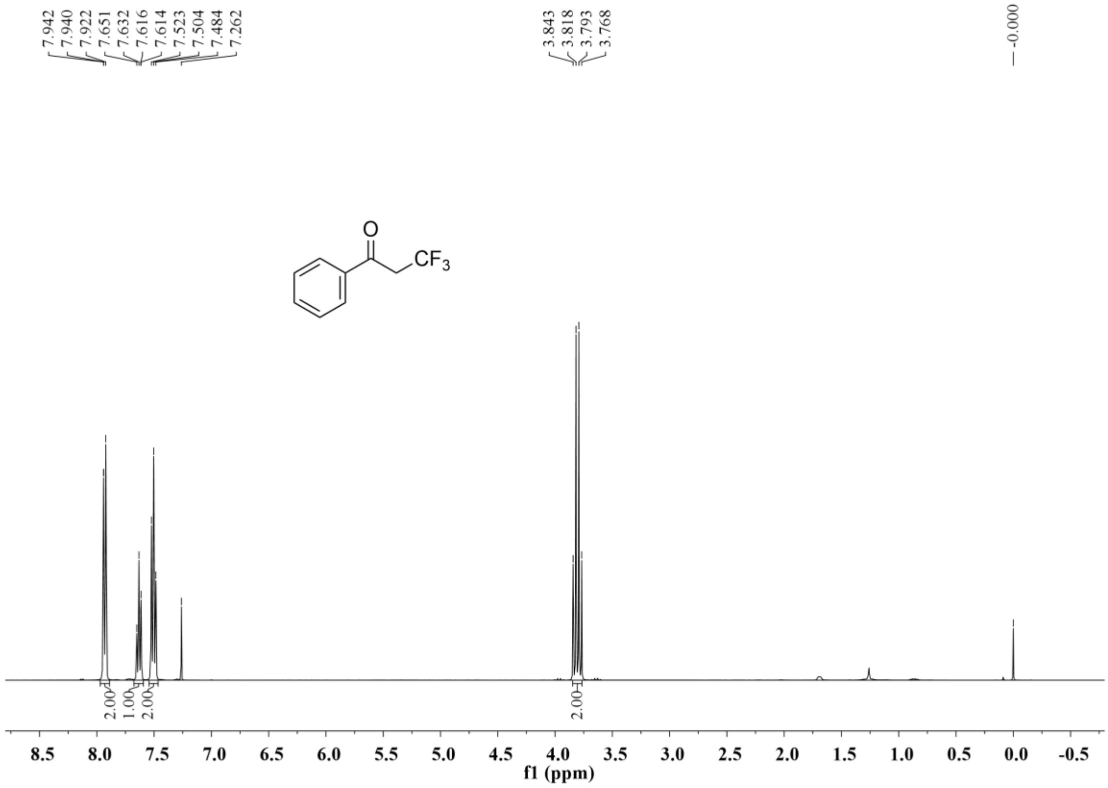
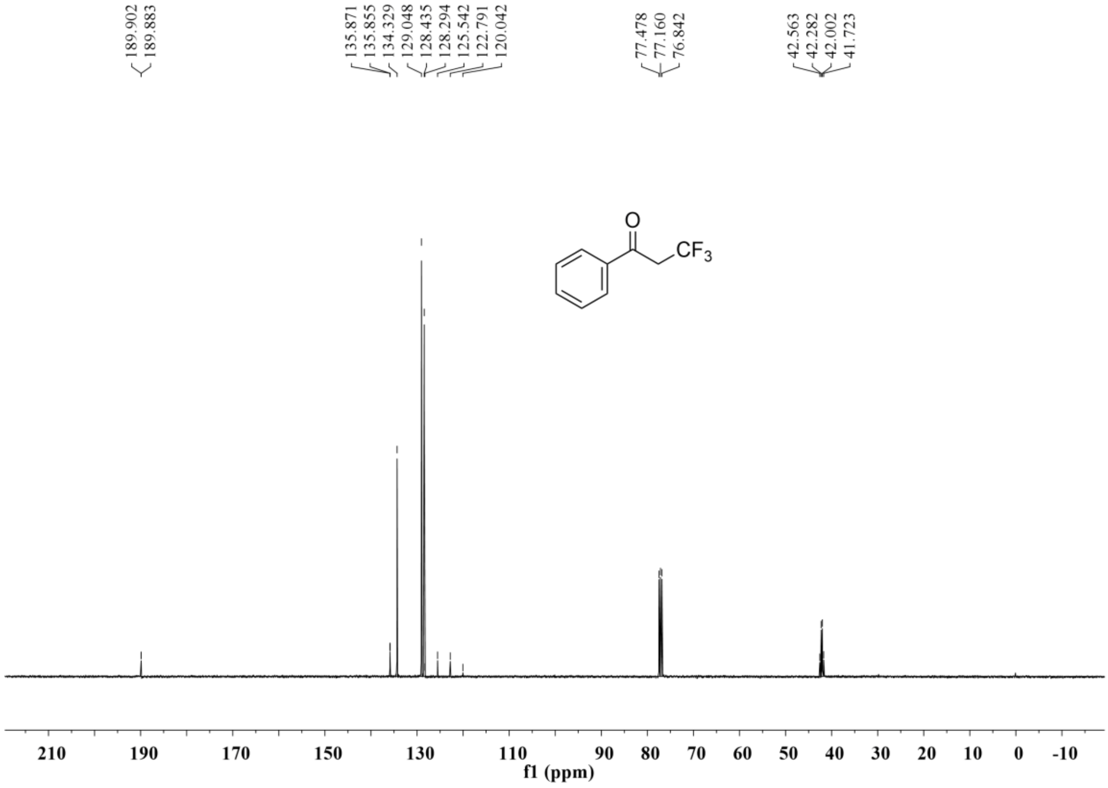
Macharla, R. Chozhiyath Nappunni, N. Nama, *Tetrahedron Lett.* **2012**, *53*, 1401-1405; c) P. B. Silveira, A. L. Monteiro, *Journal of Molecular Catalysis A: Chemical* **2006**, *247*, 1-6; d) M. Kodomari, T. Nagaoka, Y. Furusawa, *Tetrahedron Letters* **2001**, *42*, 3105-3107; e) T. Takeda, R. Sasaki, S. Yamauchi, T. Fujiwara, *Tetrahedron* **1997**, *53*, 557-566; f) A. Hamze, J.-D. Brion, M. Alami, *Org. Lett.* **2012**, *14*, 2782-2785; g) K. Murugan, D.-w. Huang, Y.-T. Chien, S.-T. Liu, *Tetrahedron* **2013**, *69*, 268-273.

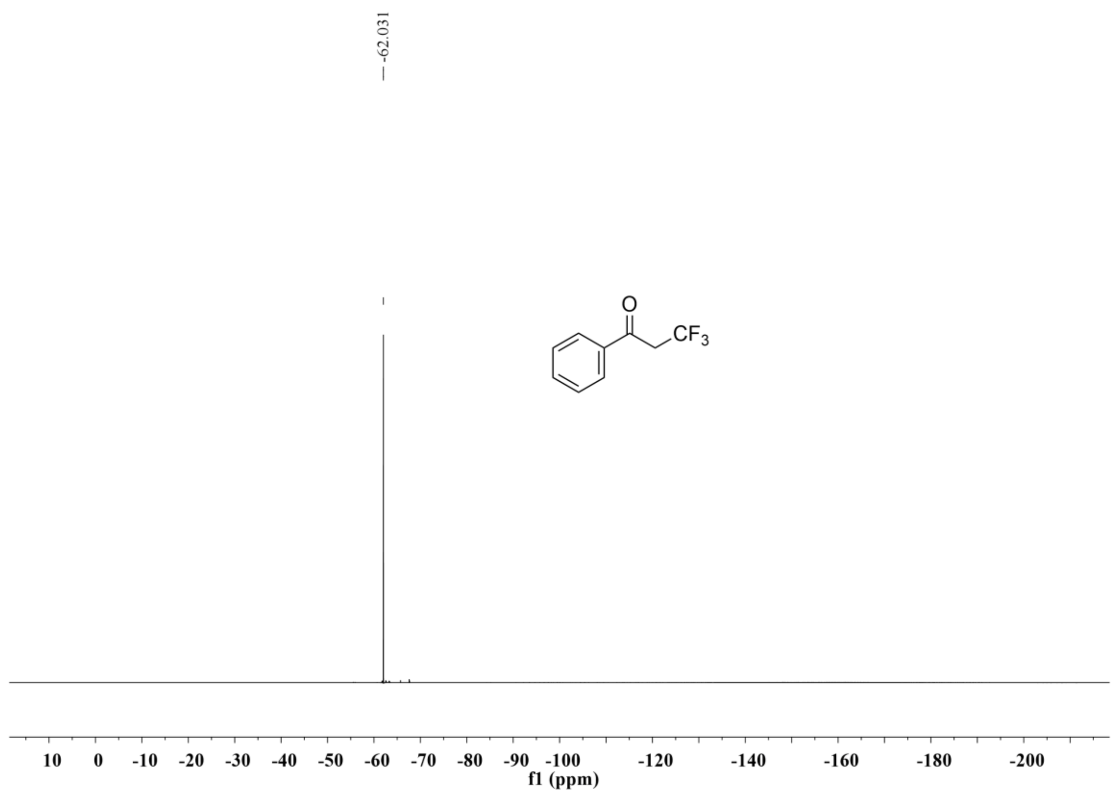
(2) a) A. Deb, S. Manna, A. Modak, T. Patra, S. Maity, D. Maiti, *Angew. Chem. Int. Ed.* **2013**, *52*, 9747-9750; b) P. Novak, A. Lishchynskyi, V. V. Grushin, *J. Am. Chem. Soc.* **2012**, *134*, 16167-16170; c) C. P. Zhang, Z. L. Wang, Q. Y. Chen, C. T. Zhang, Y. C. Gu, J. C. Xiao, *Chem. Commun.* **2011**, *47*, 6632-6634; d) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* **2011**, *50*, 6119-6122.

NMR Spectra of Products

3a



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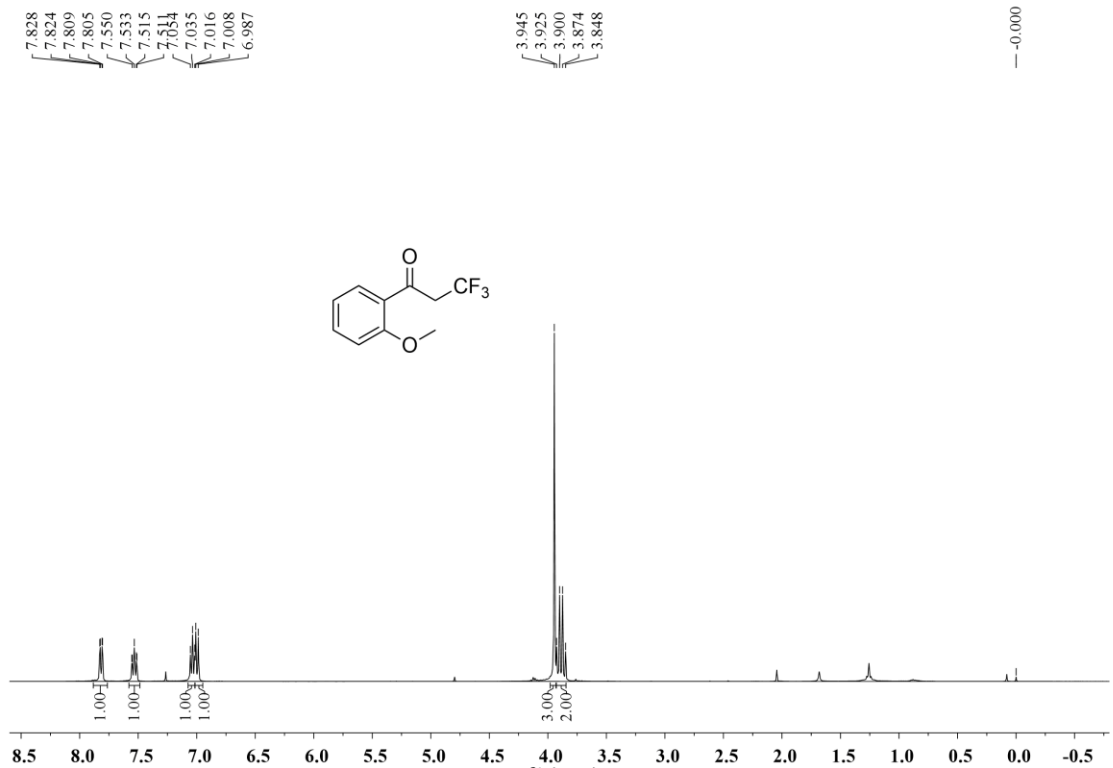
3b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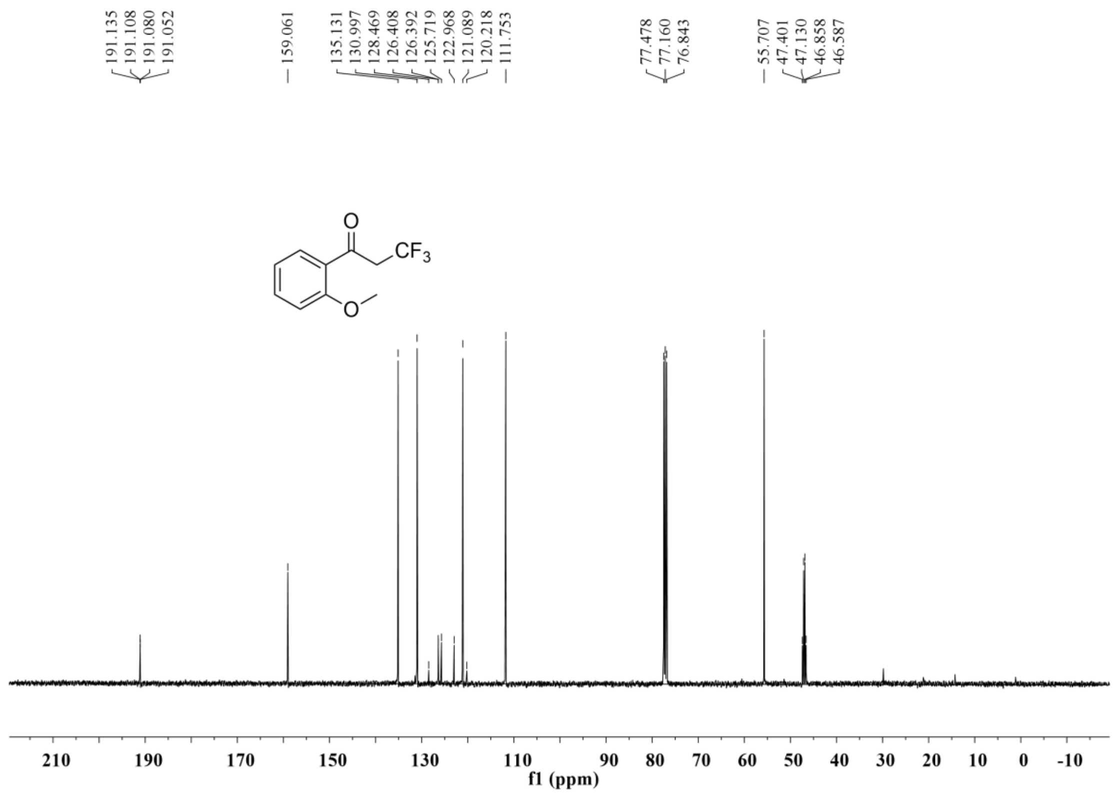
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CF3
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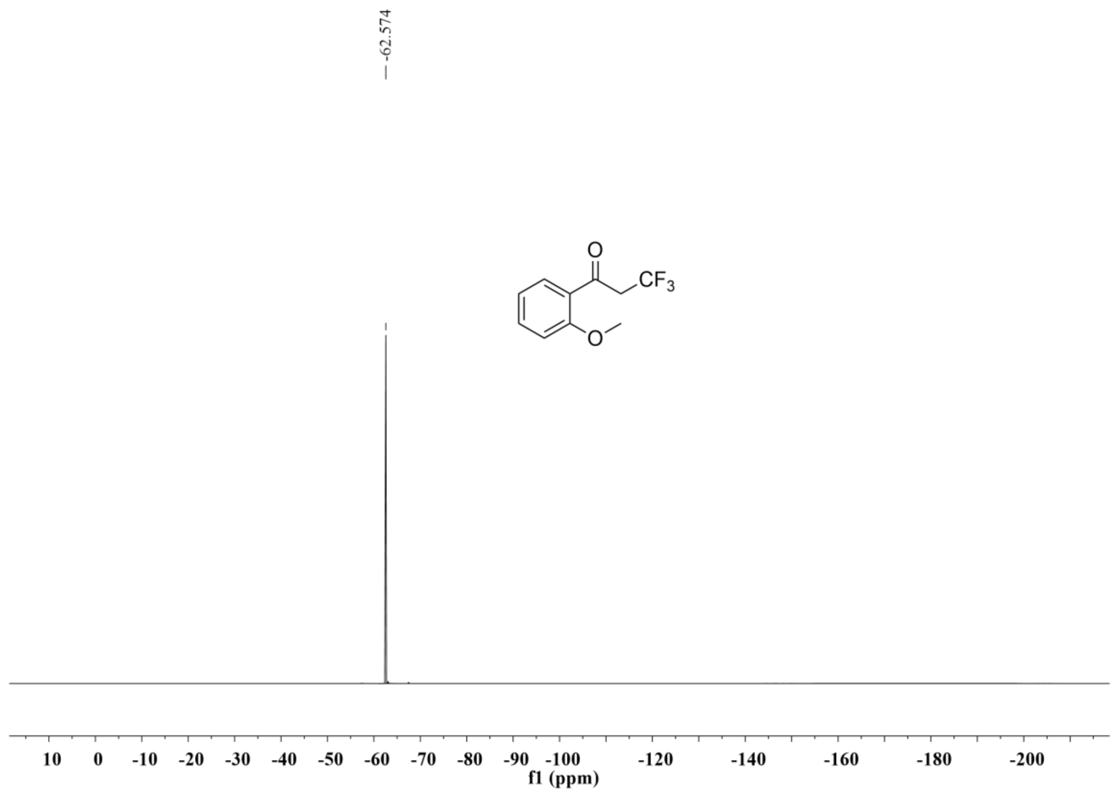
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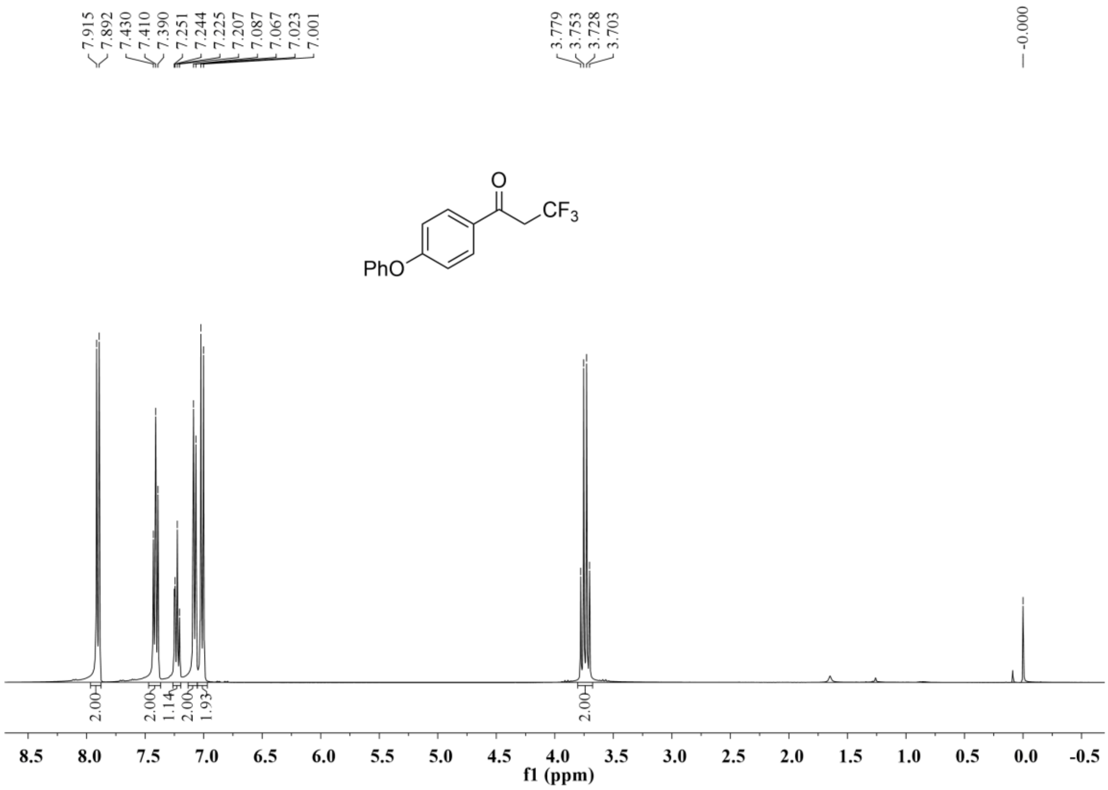
3c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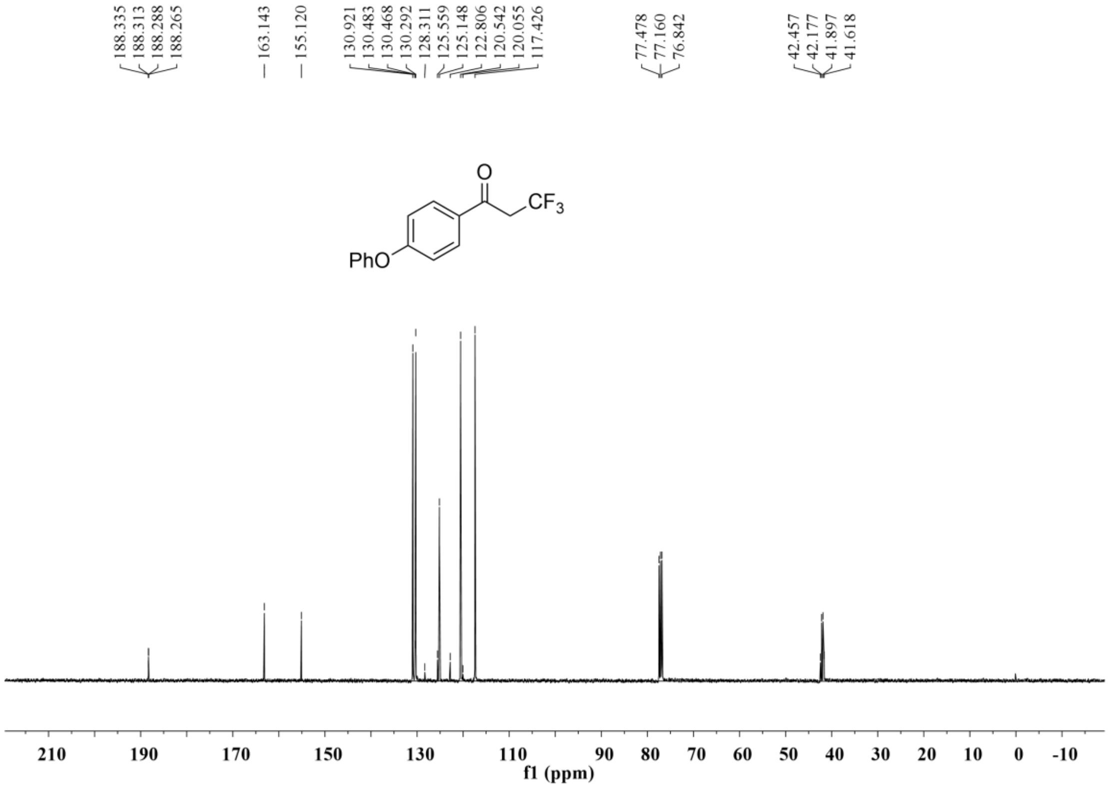
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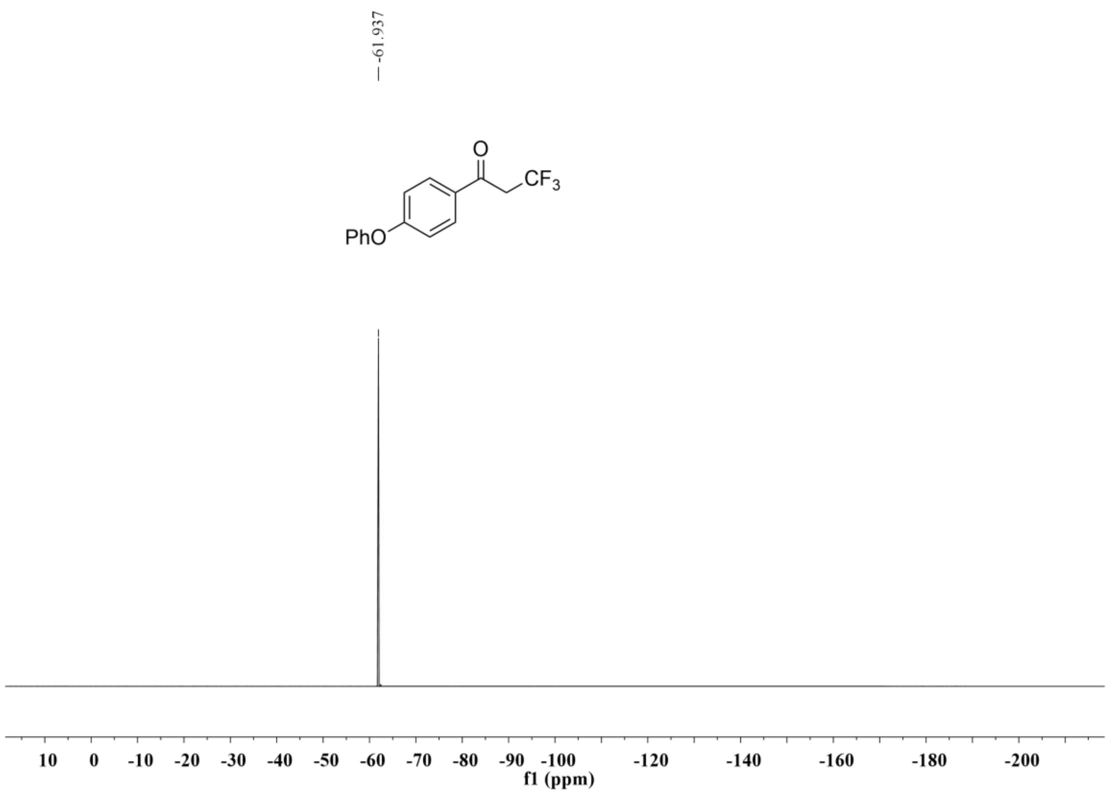
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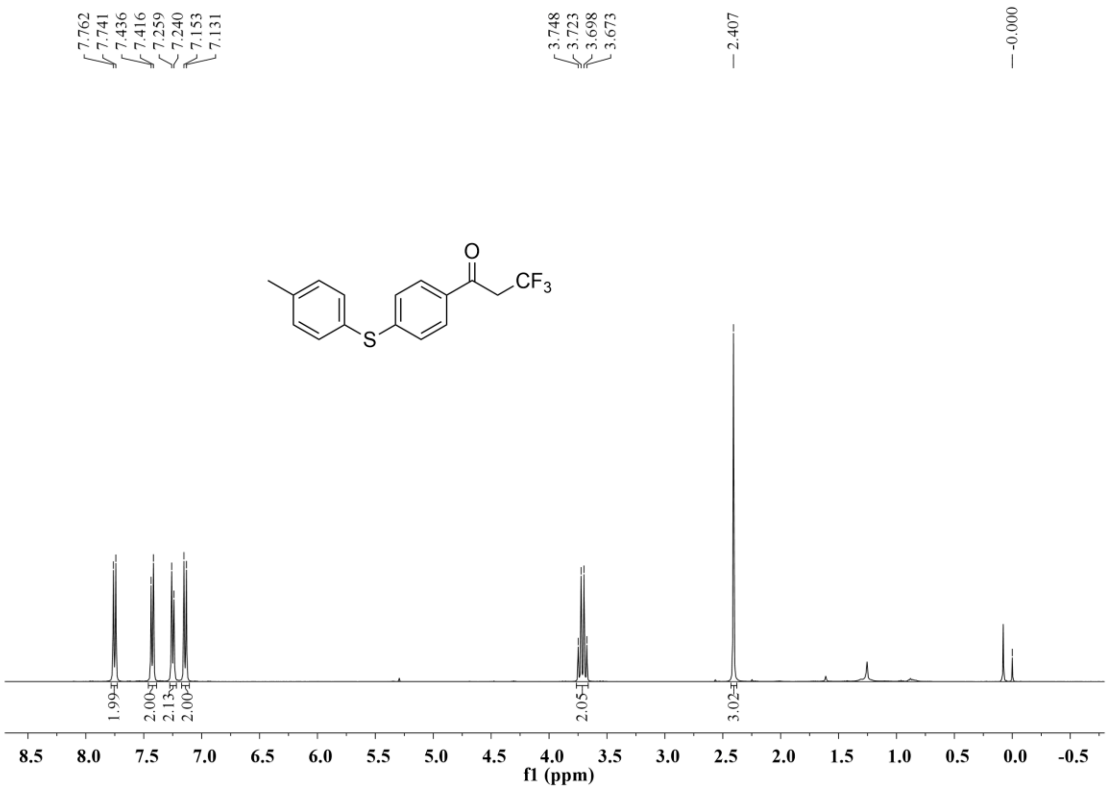
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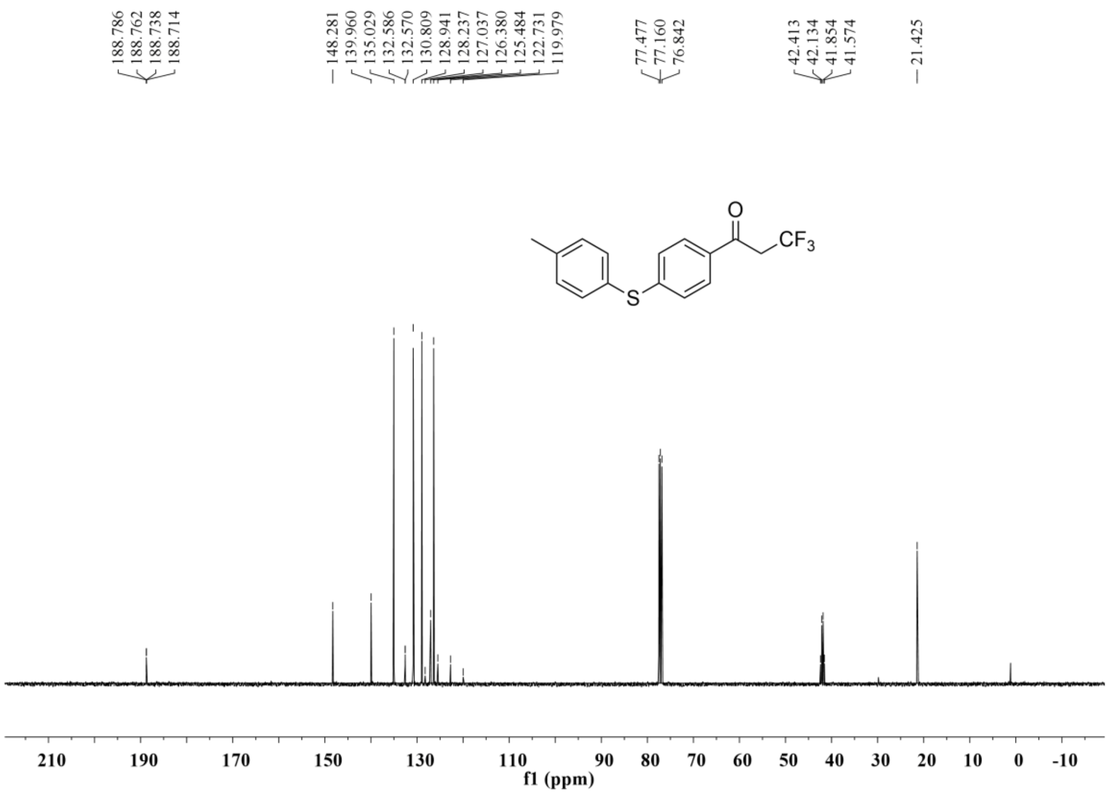
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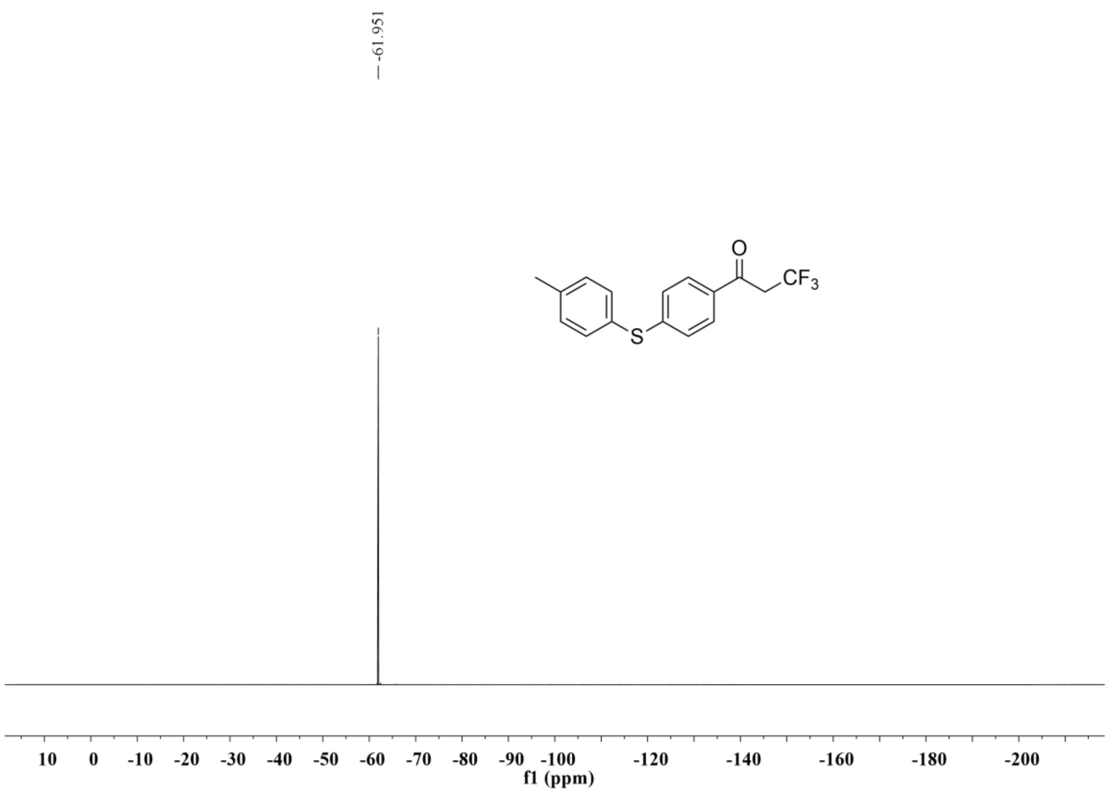
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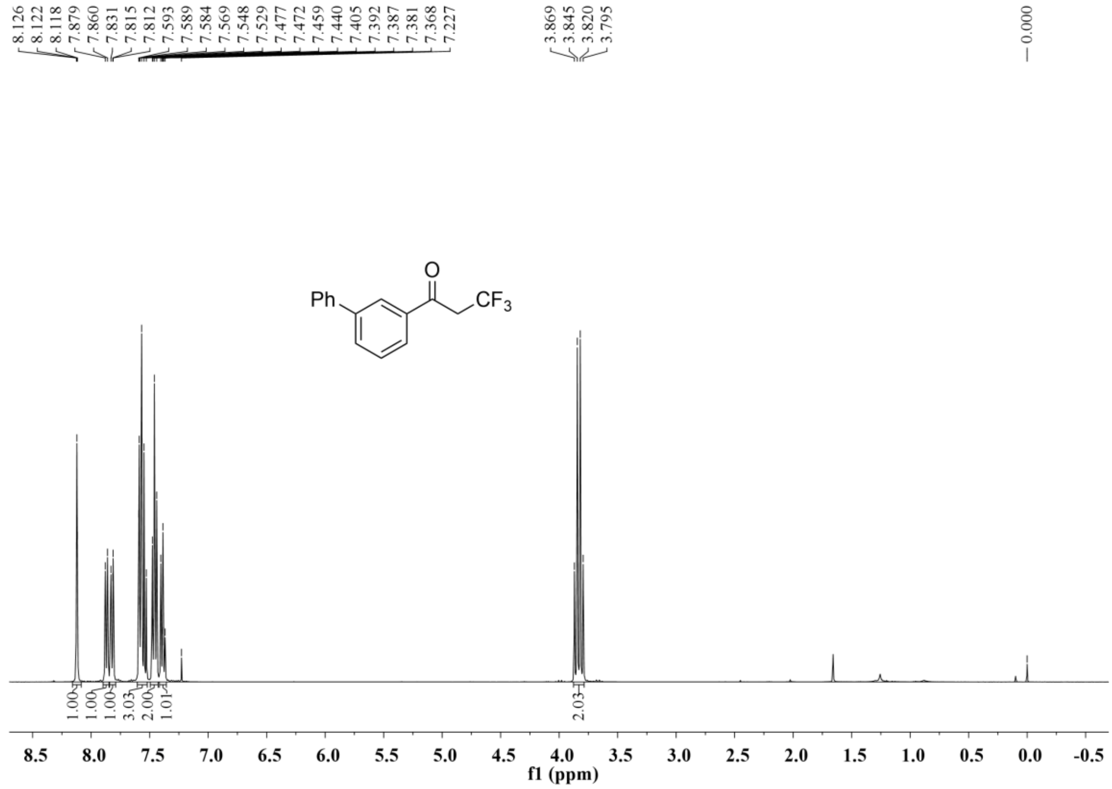
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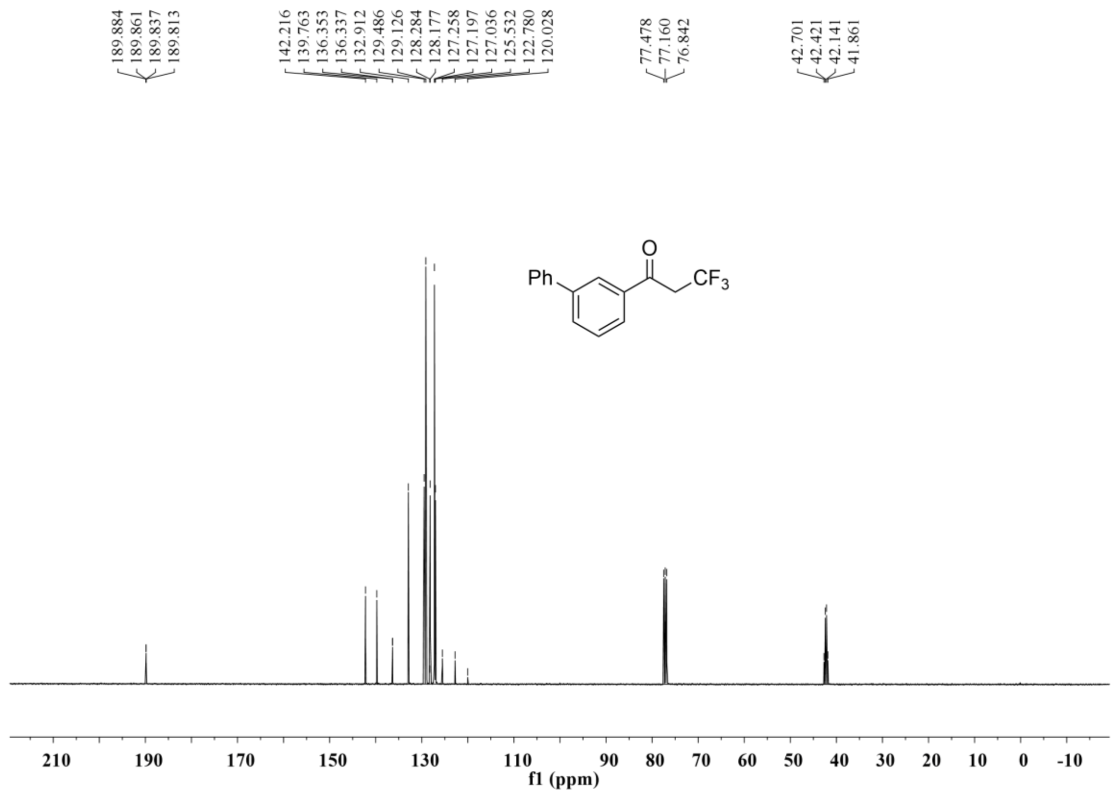
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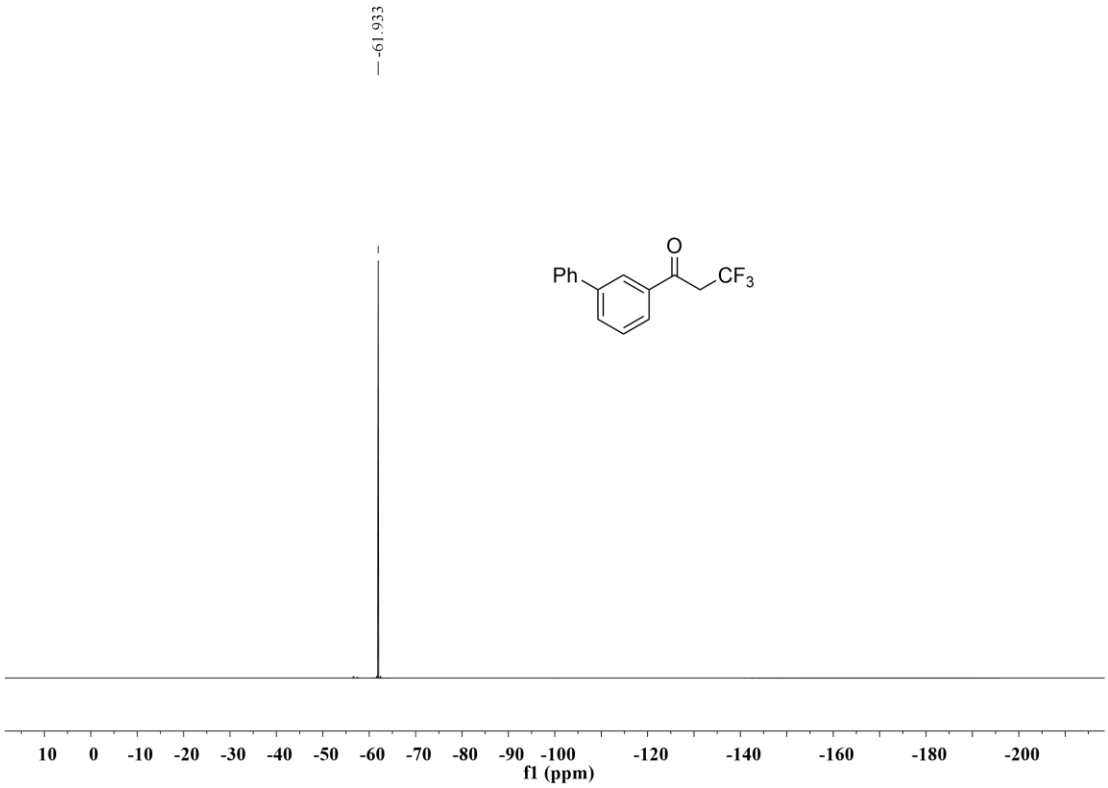
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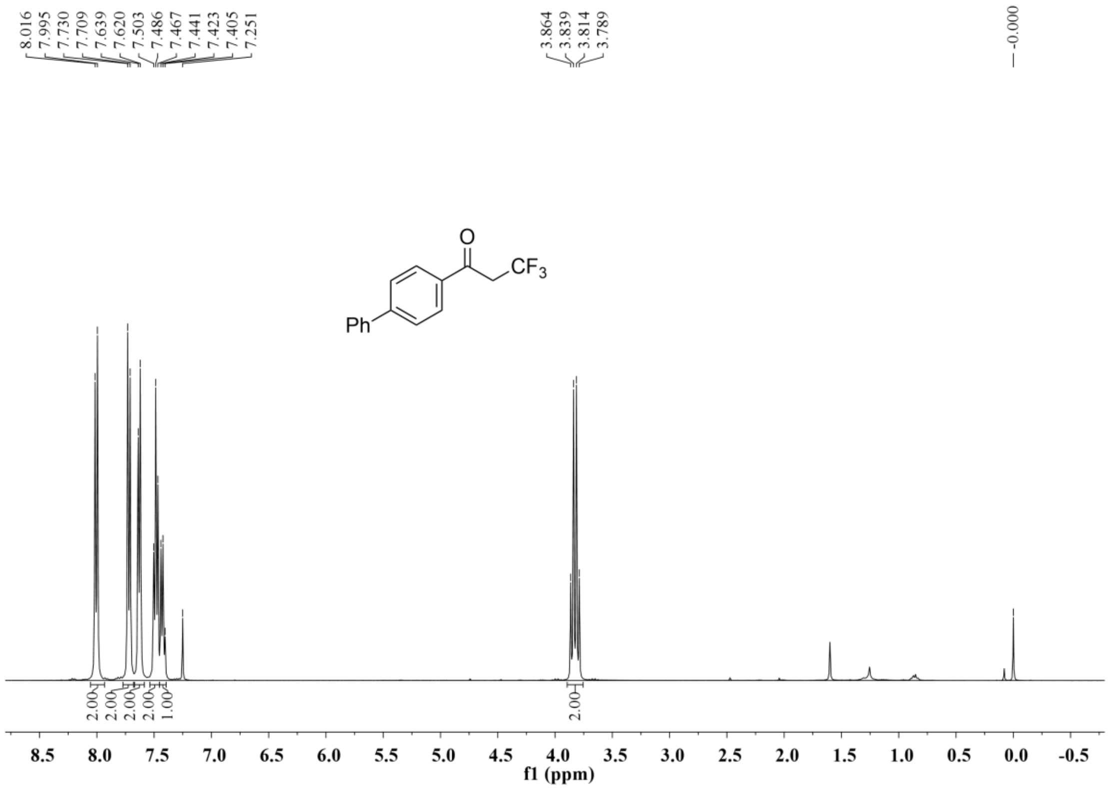
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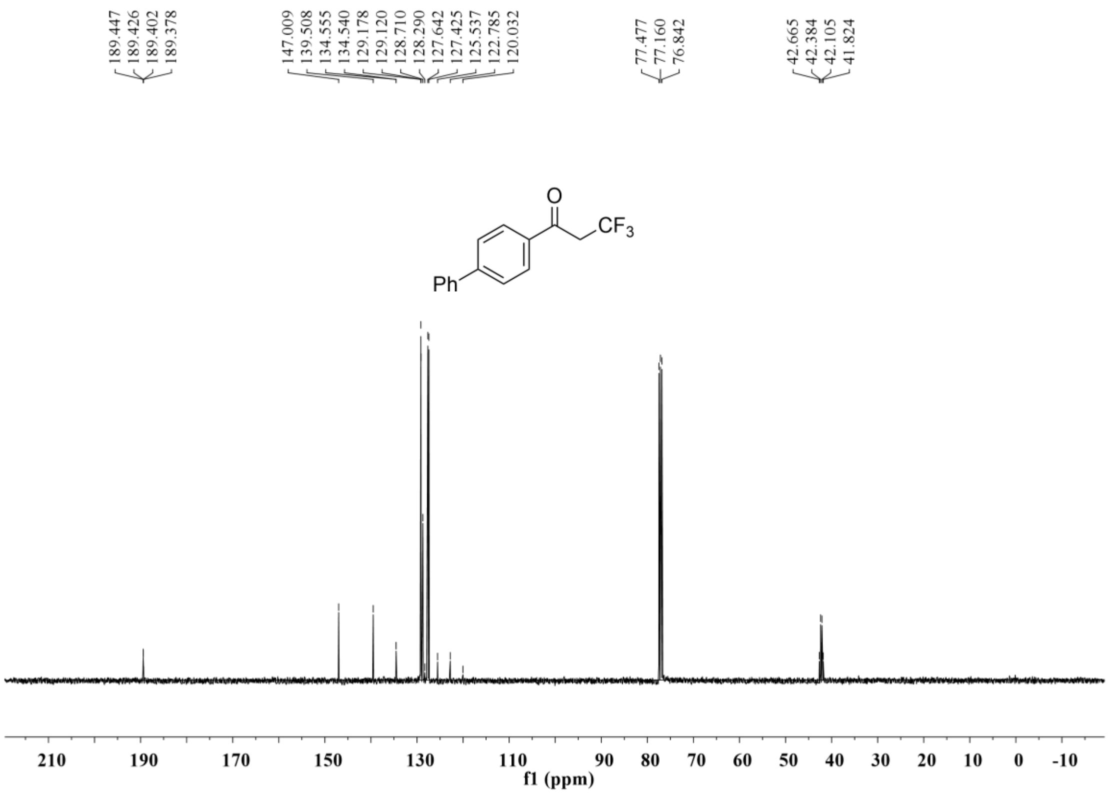
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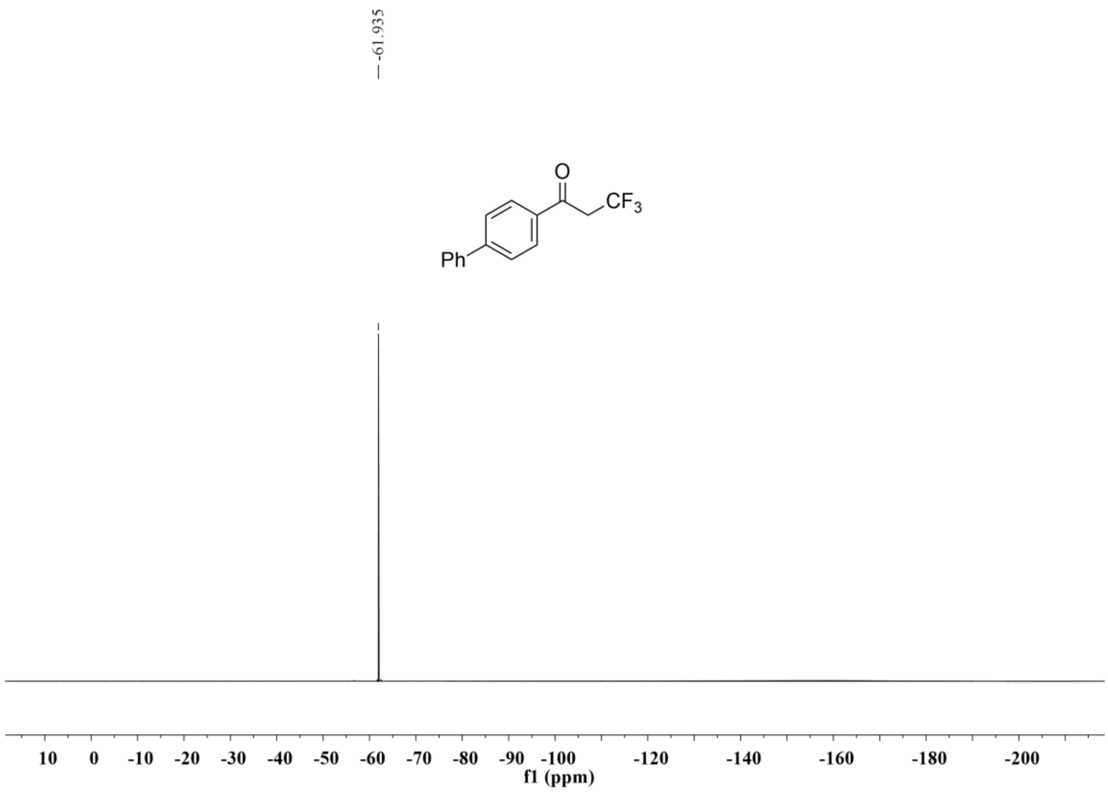
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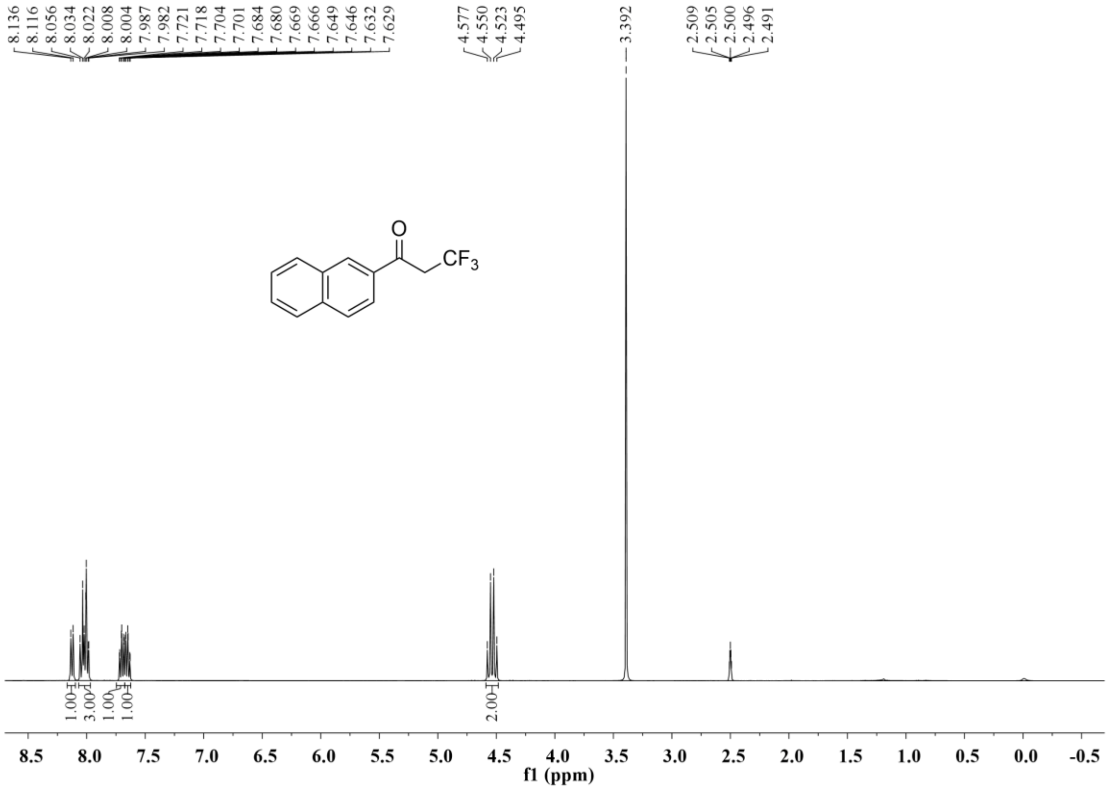

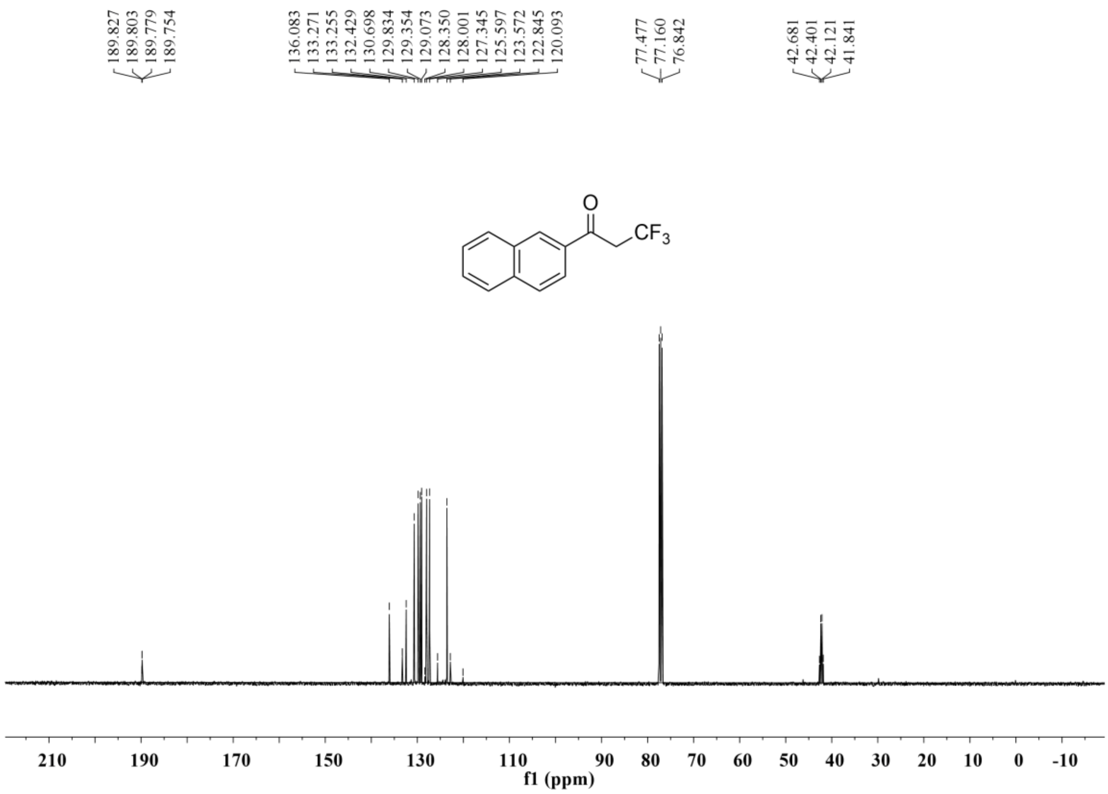

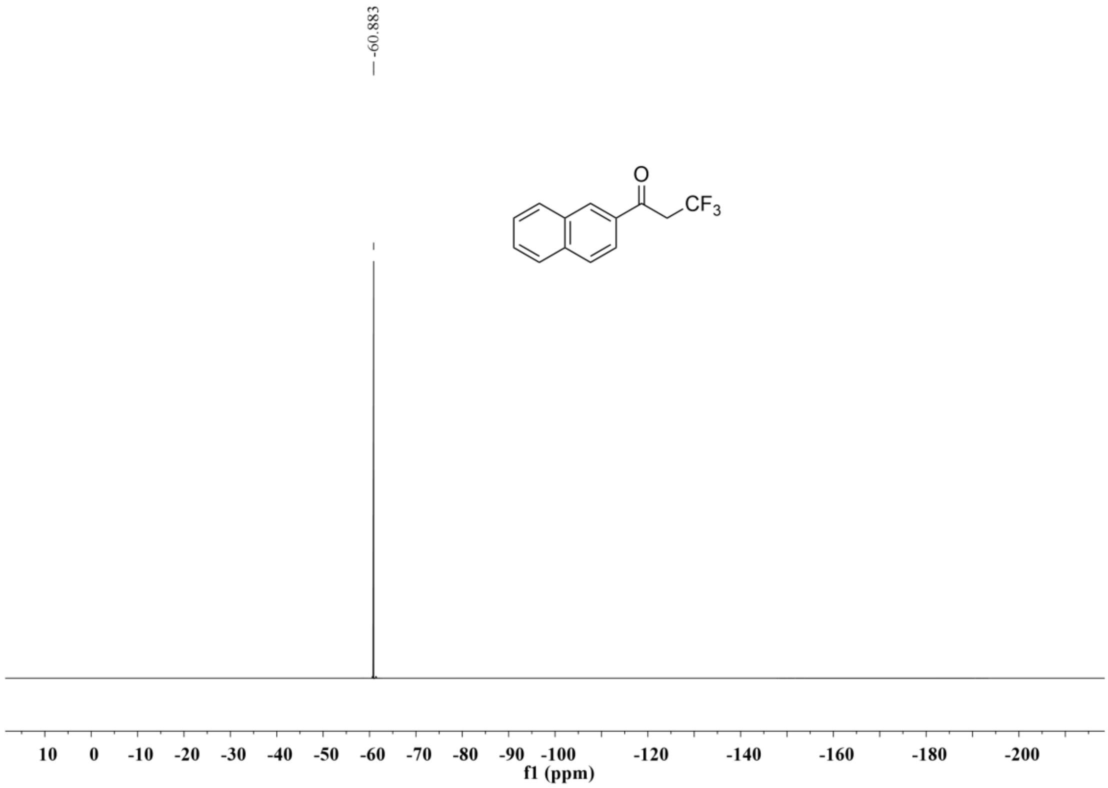
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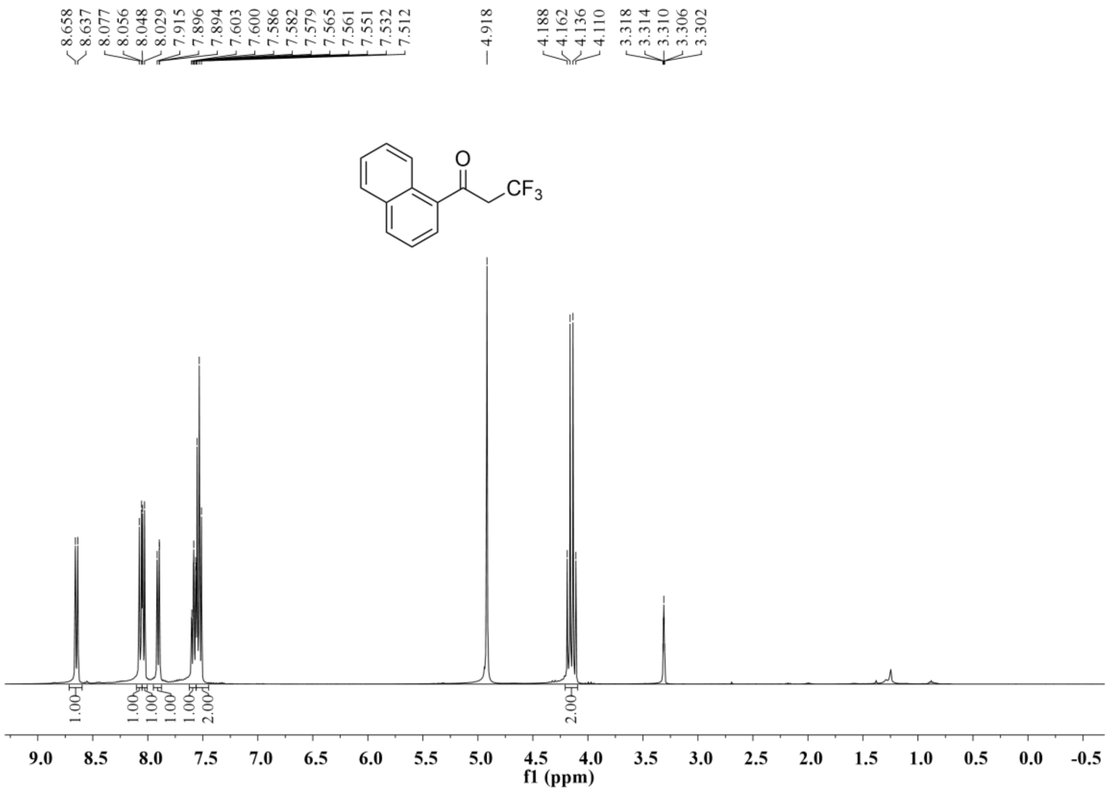
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

3h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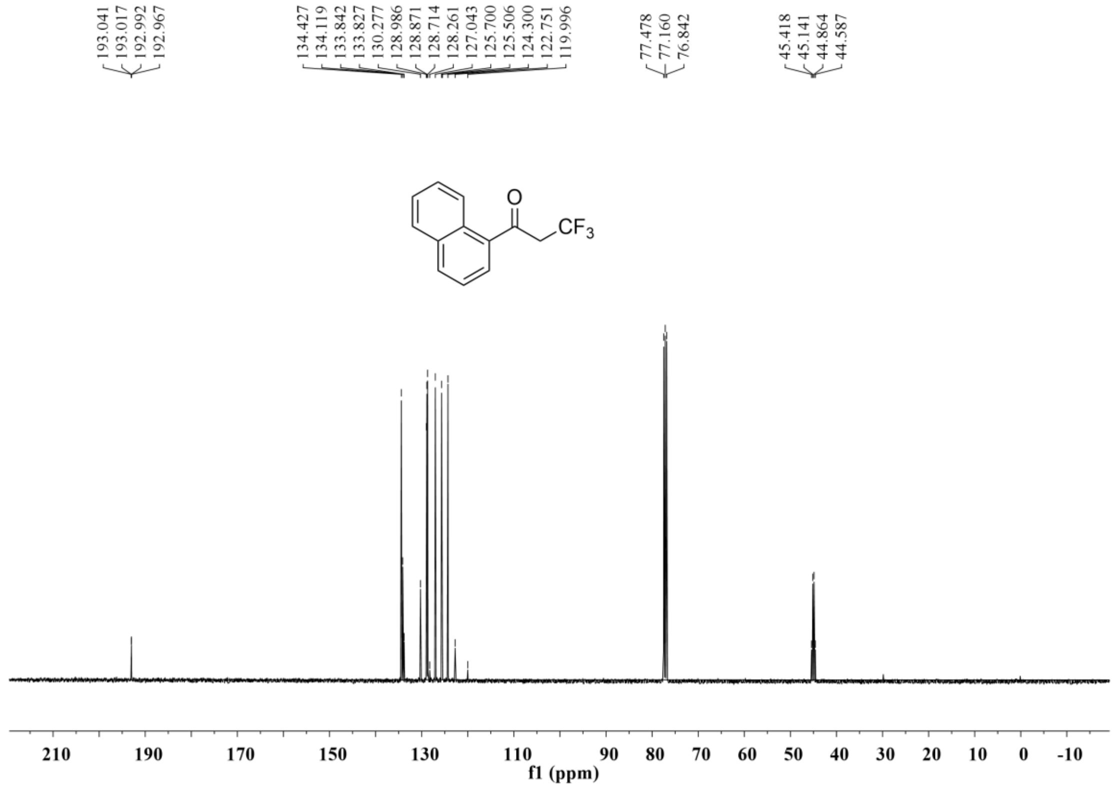
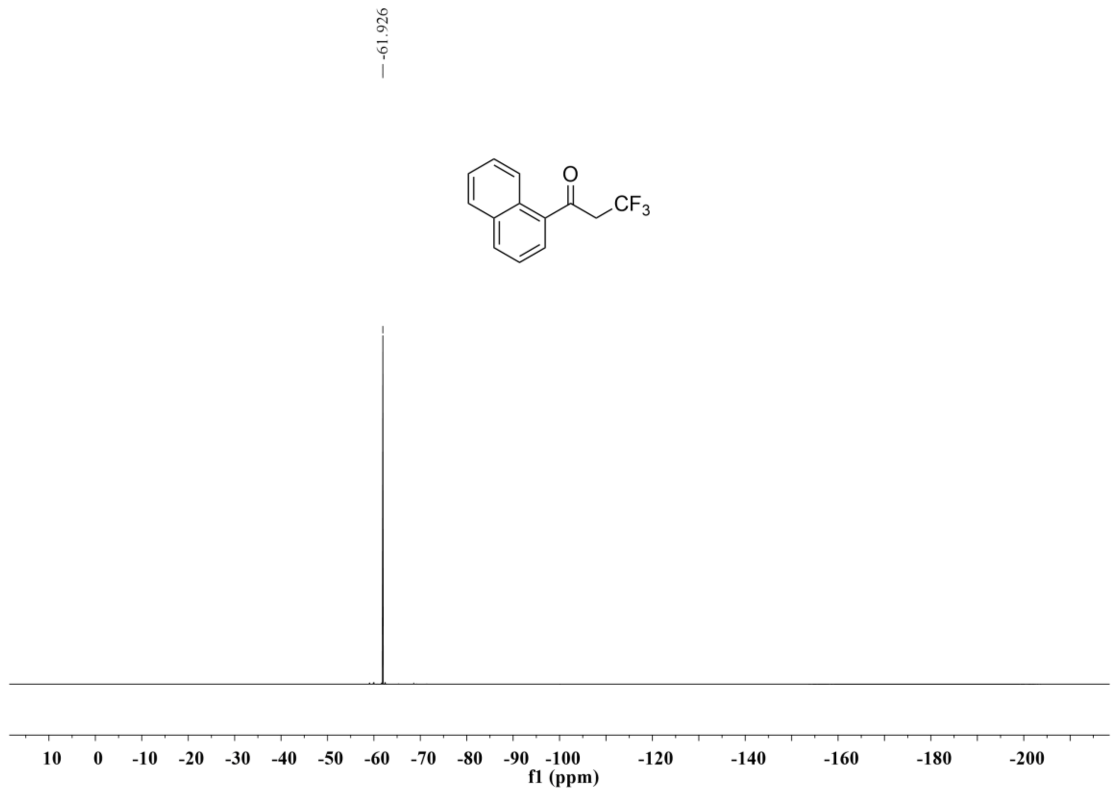
8.637
8.077
8.056
8.048
8.029
7.915
7.896
7.894
7.603
7.600
7.586
7.582
7.579
7.565
7.561
7.551
7.532
7.512
4.918
4.188
4.162
4.136
4.110
3.318
3.314
3.310
3.306
3.302
O
CF3
1.00
1.00
1.00
1.00
1.00
2.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


193.041
193.017
192.992
192.967
134.427
134.119
133.842
133.827
130.277
128.986
128.871
128.714
128.261
127.043
125.700
125.506
124.300
122.751
119.996
77.478
77.160
76.842
45.418
45.141
44.864
44.587
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-61.926
O
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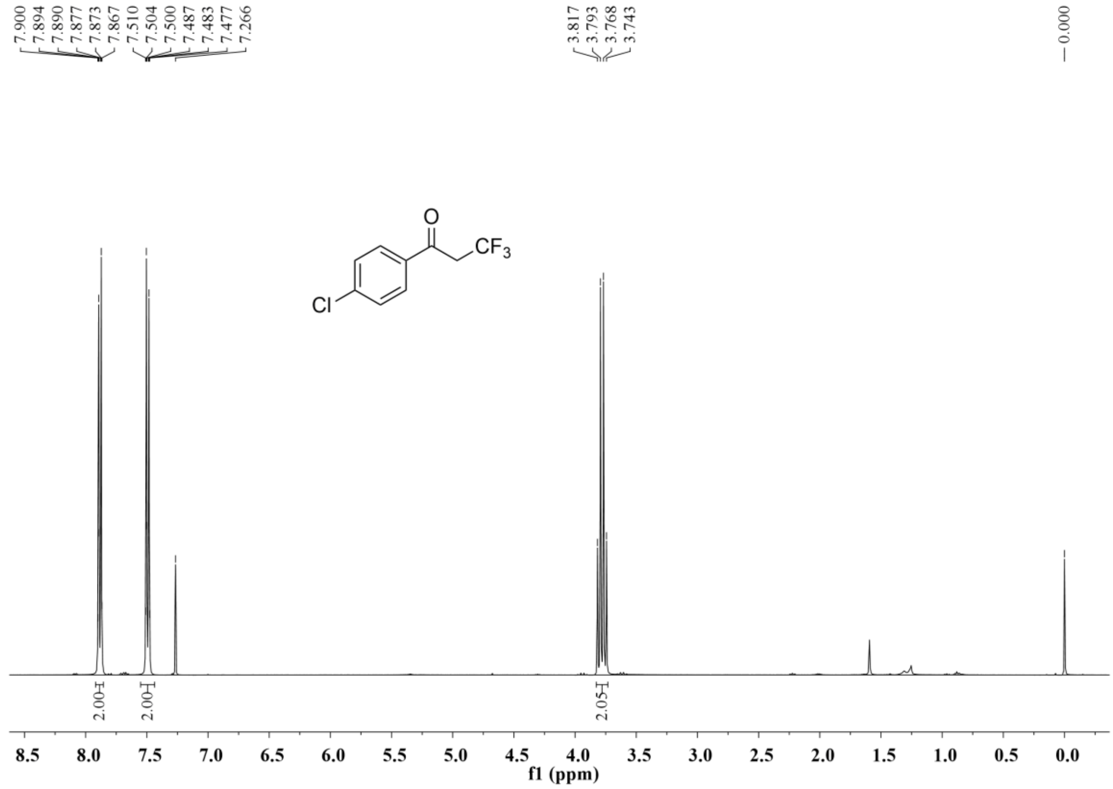
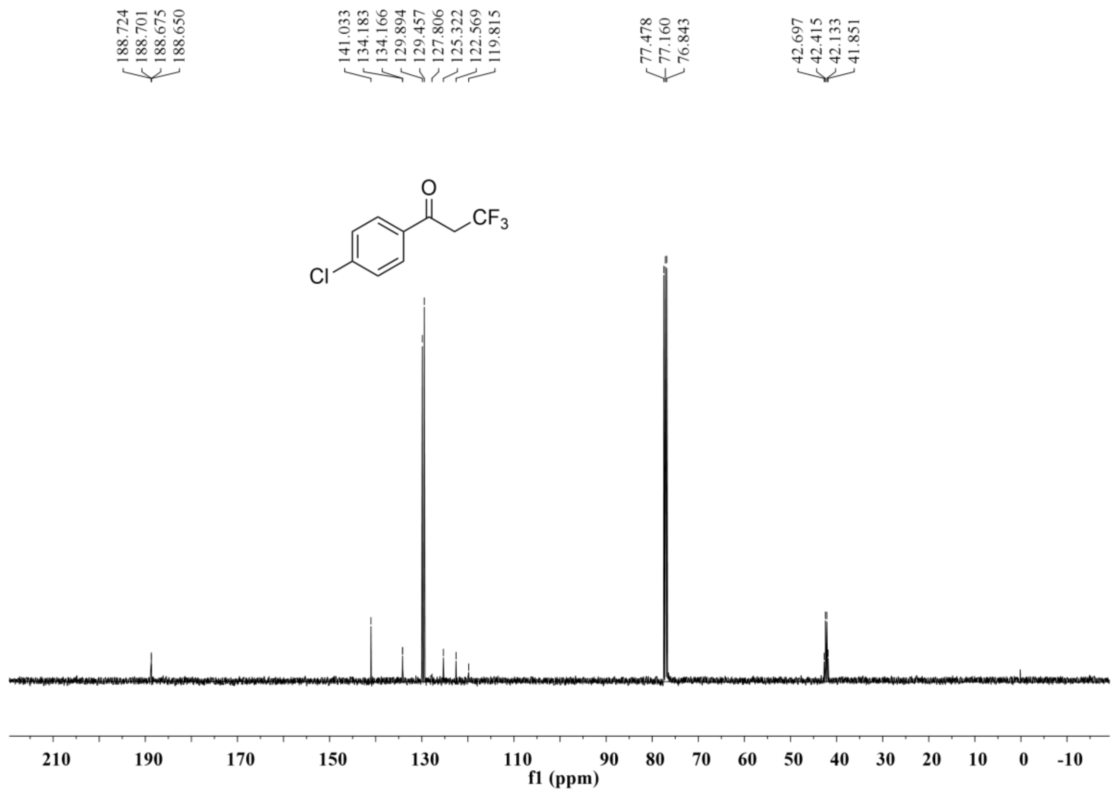
f1 (ppm)

3i


7.900
7.894
7.890
7.877
7.873
7.867
7.510
7.504
7.500
7.487
7.483
7.477
7.266
3.817
3.793
3.768
3.743
0.000
O
CF3
Cl
2.00
2.00
2.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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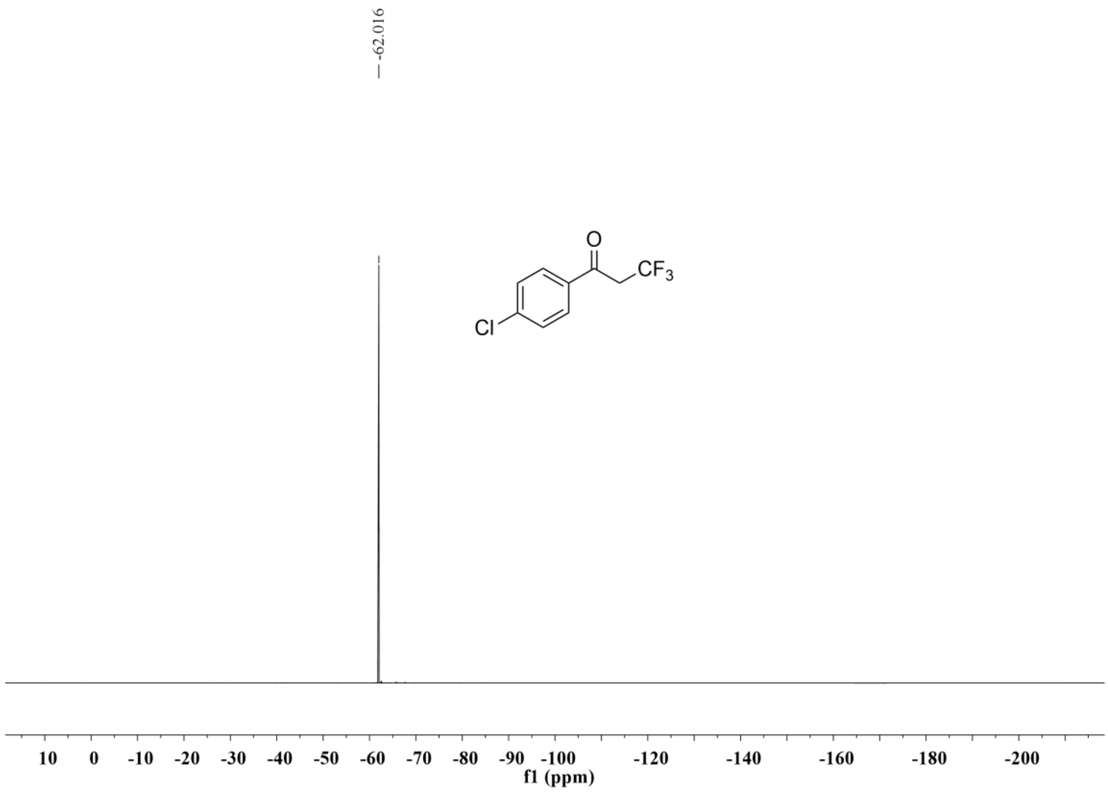
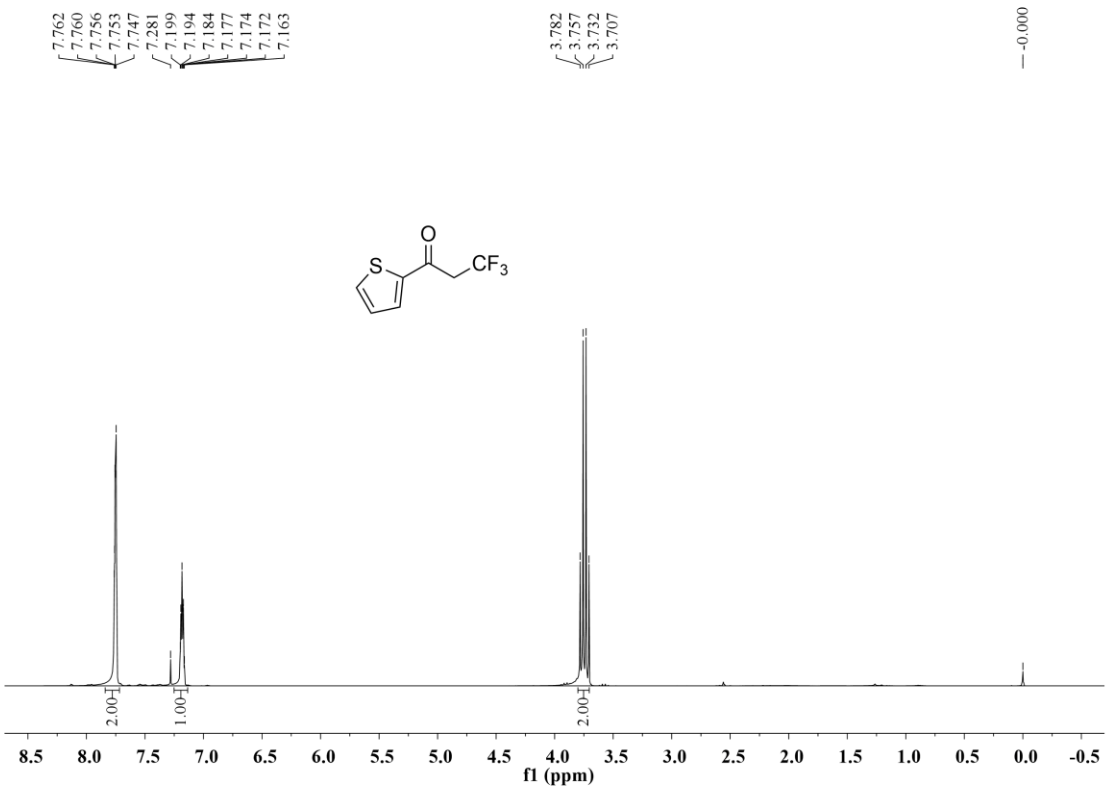
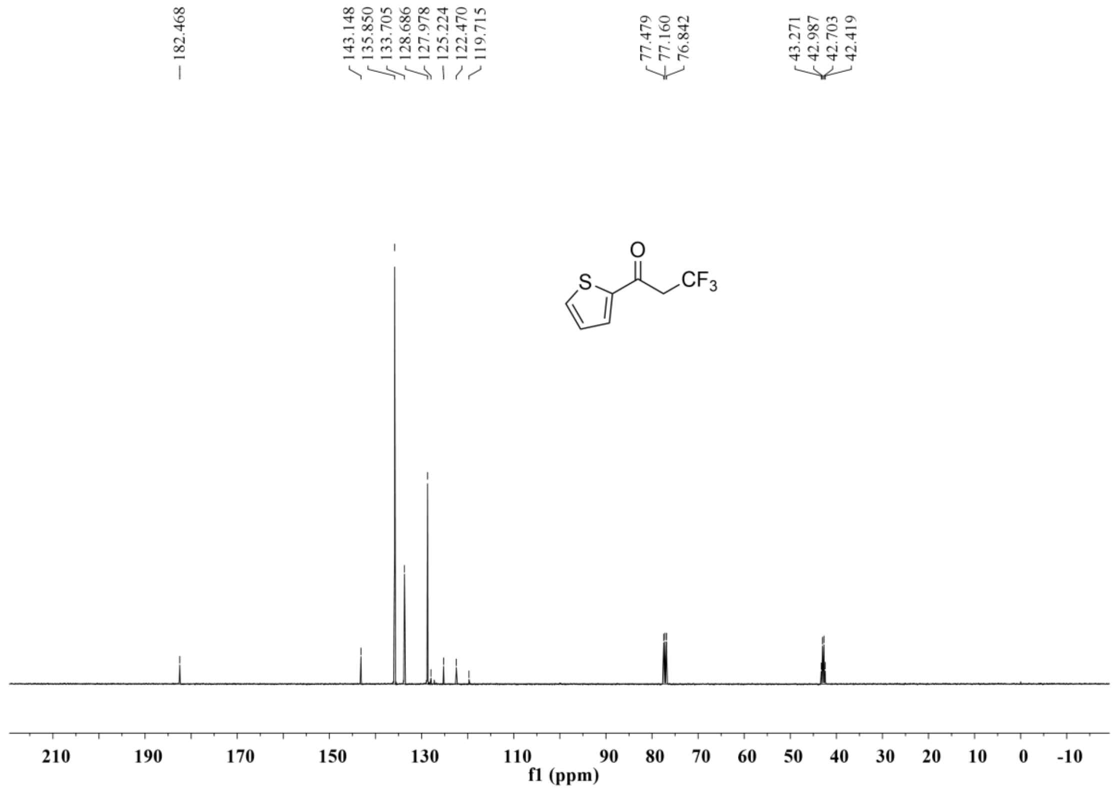
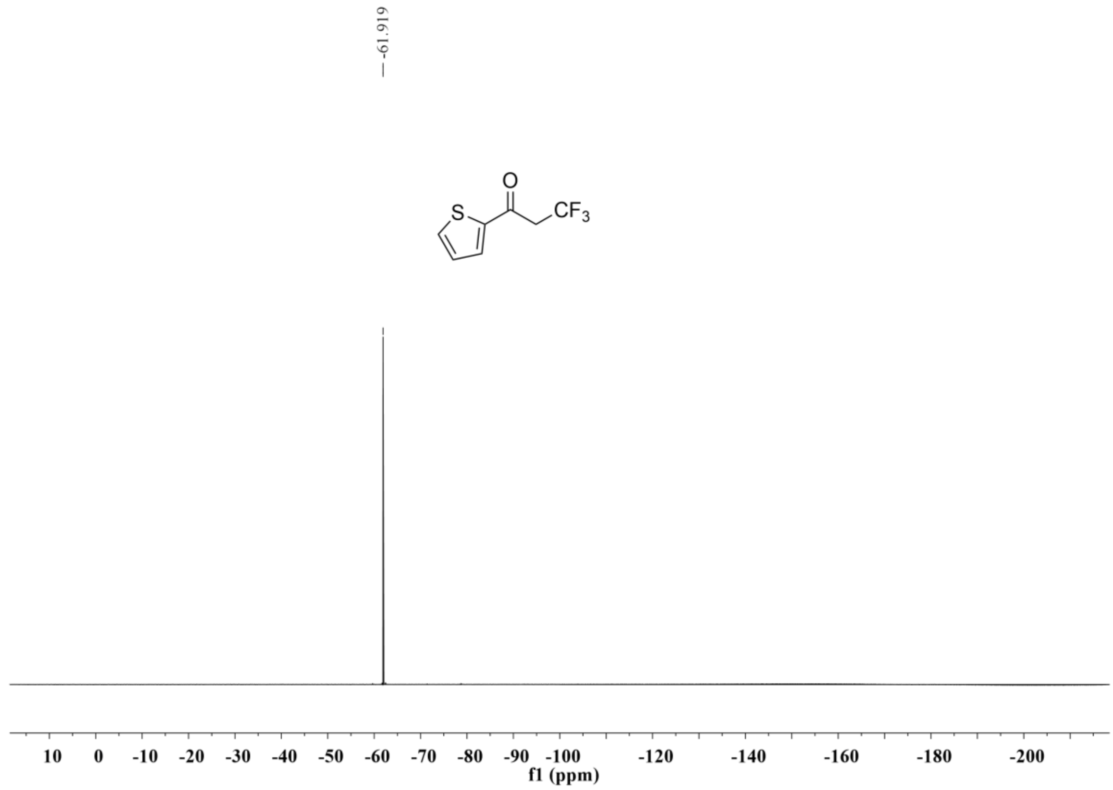
188.701
188.675
188.650
141.033
134.183
134.166
129.894
129.457
127.806
125.322
122.569
119.815
77.478
77.160
76.843
42.697
42.415
42.133
41.851
O
CF3
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.016
Cl
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

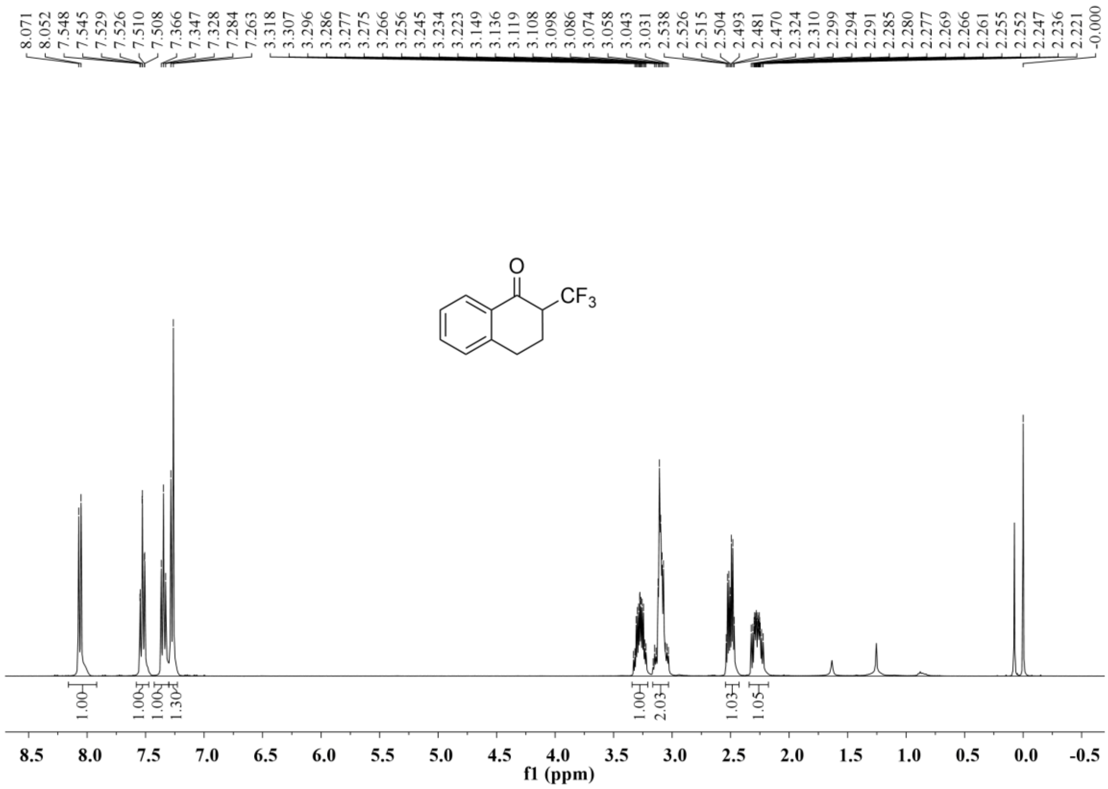
3j

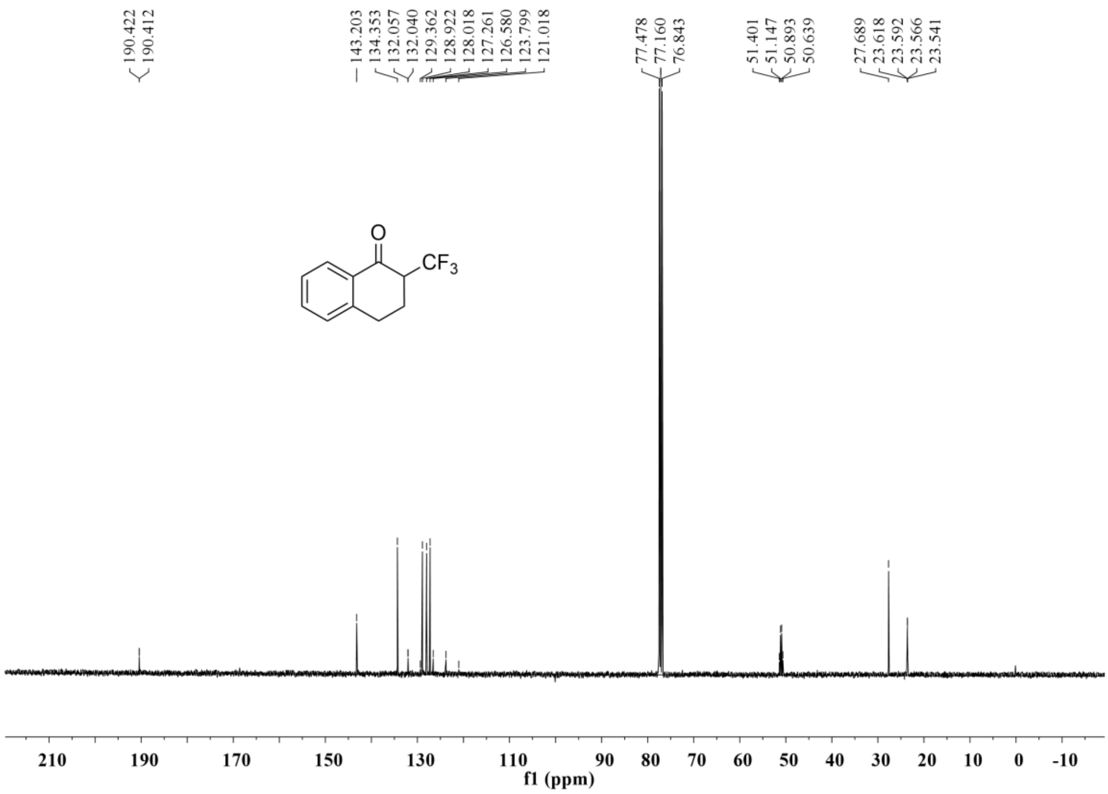

7.762
7.760
7.756
7.753
7.747
7.281
7.199
7.194
7.184
7.177
7.174
7.172
7.163
3.782
3.757
3.732
3.707
-0.000
S
O
CF3
2.00
1.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

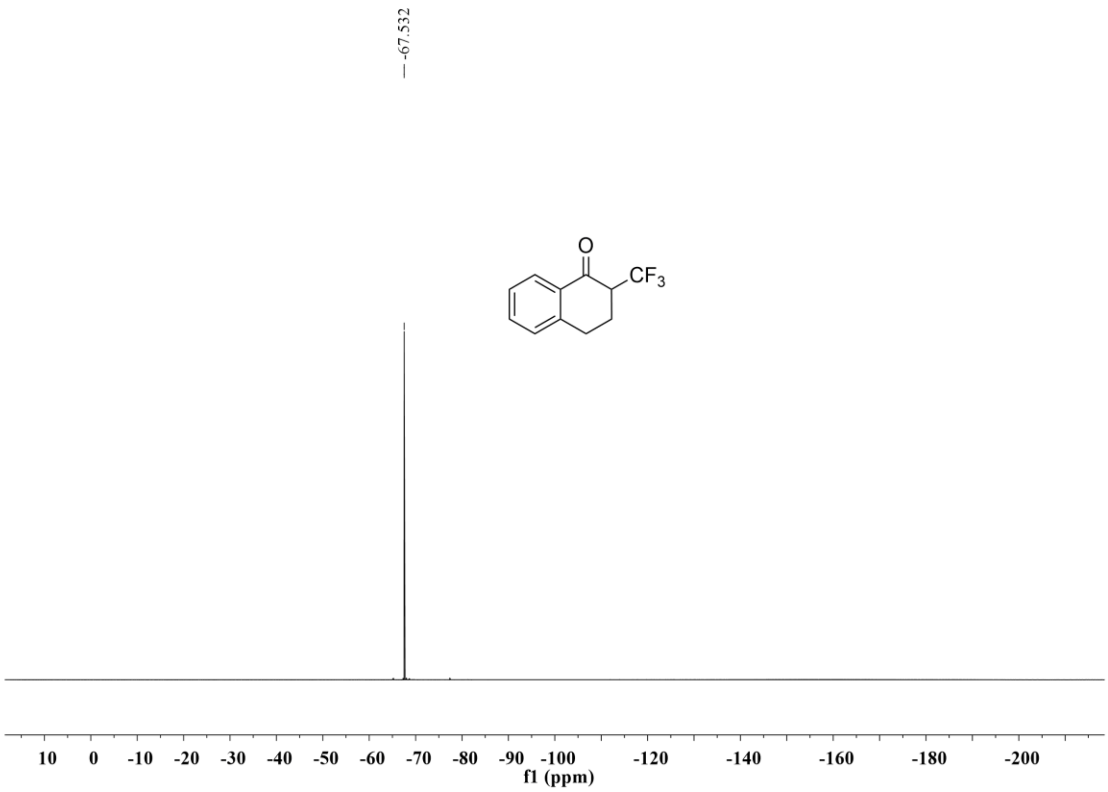

182.468
143.148
135.850
133.705
128.686
127.978
125.224
122.470
119.715
77.479
77.160
76.842
43.271
42.987
42.703
42.419
S
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-61.919
S
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

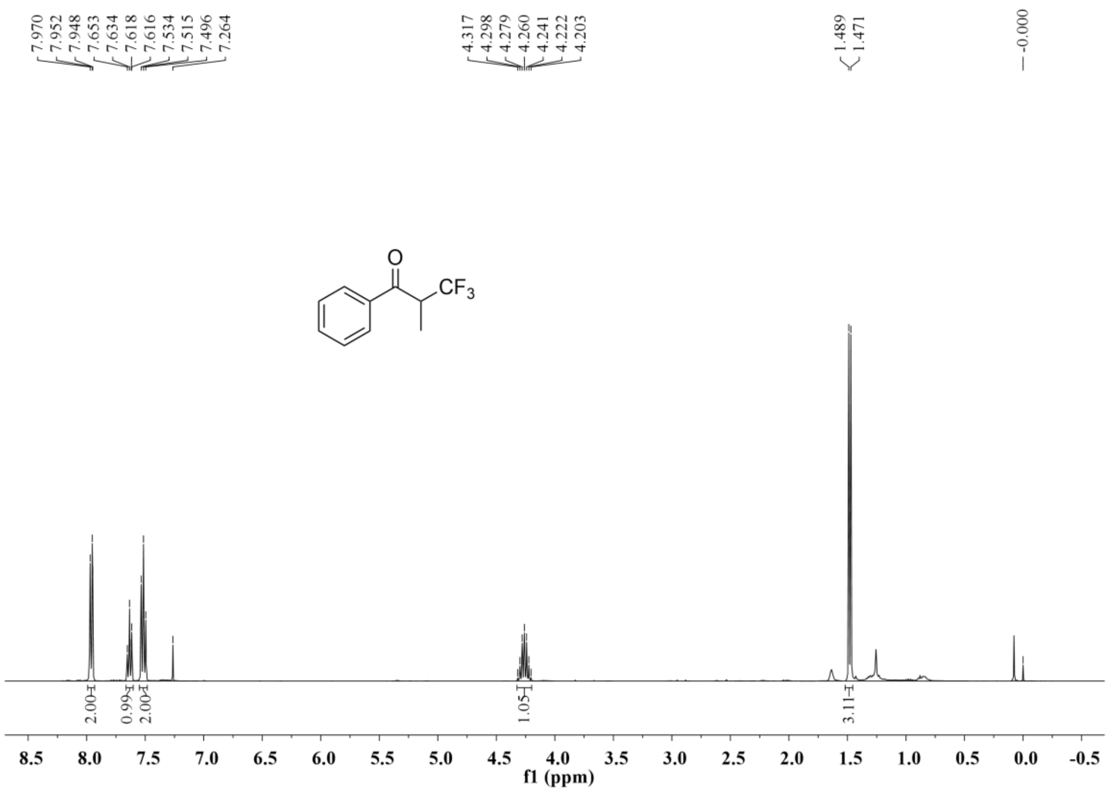
3k

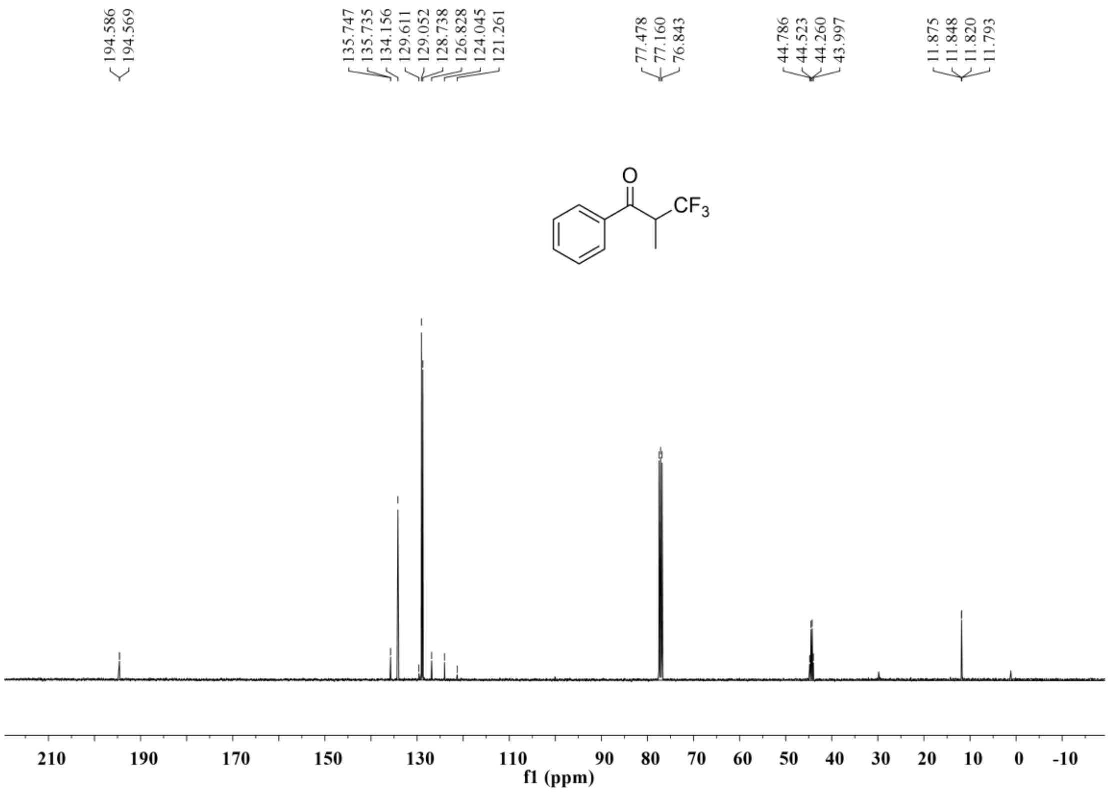


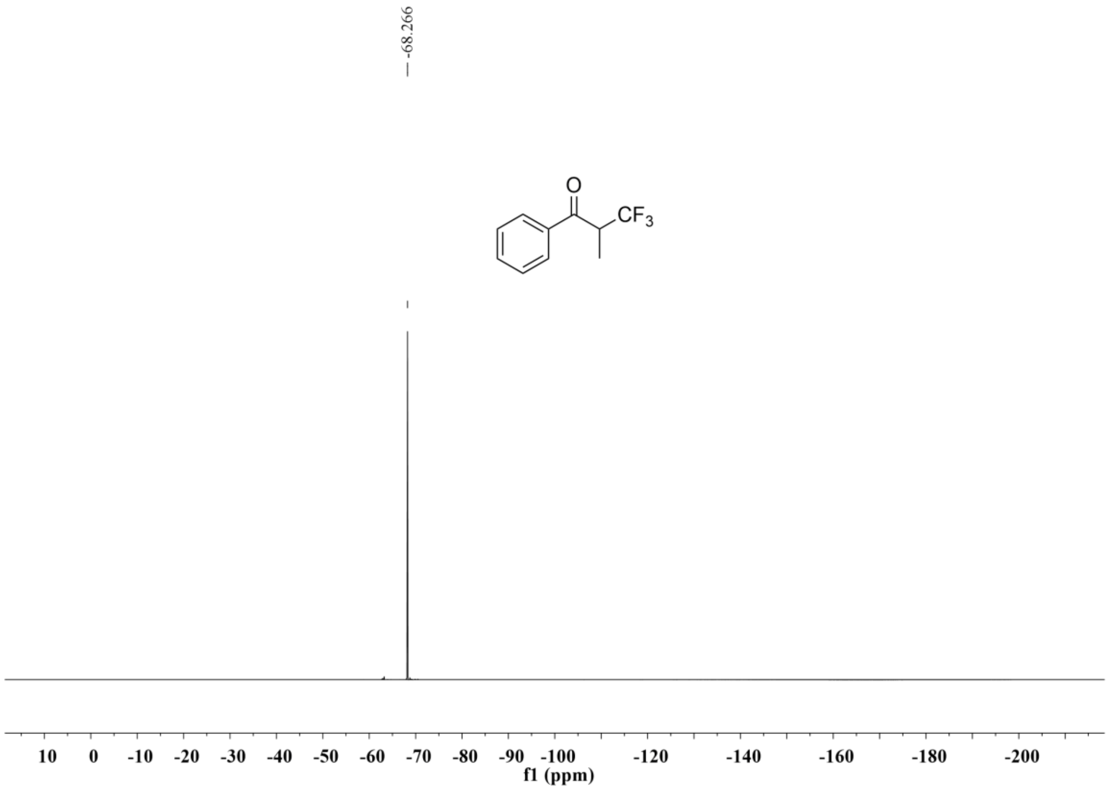



-67.532
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

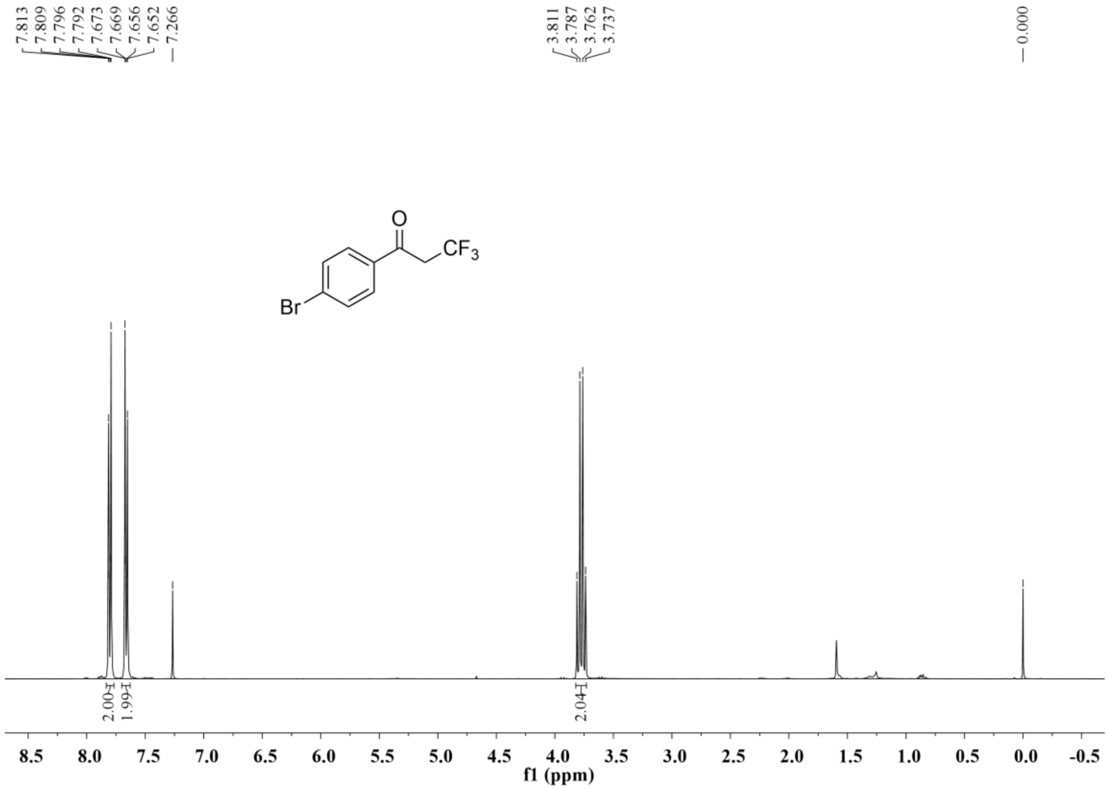
3l


7.970 7.952 7.948 7.653 7.634 7.618 7.616 7.534 7.515 7.496 7.264
4.317 4.298 4.279 4.260 4.241 4.222 4.203
1.489 1.471
-0.000
CF3
2.00 0.99 2.00 1.05 3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

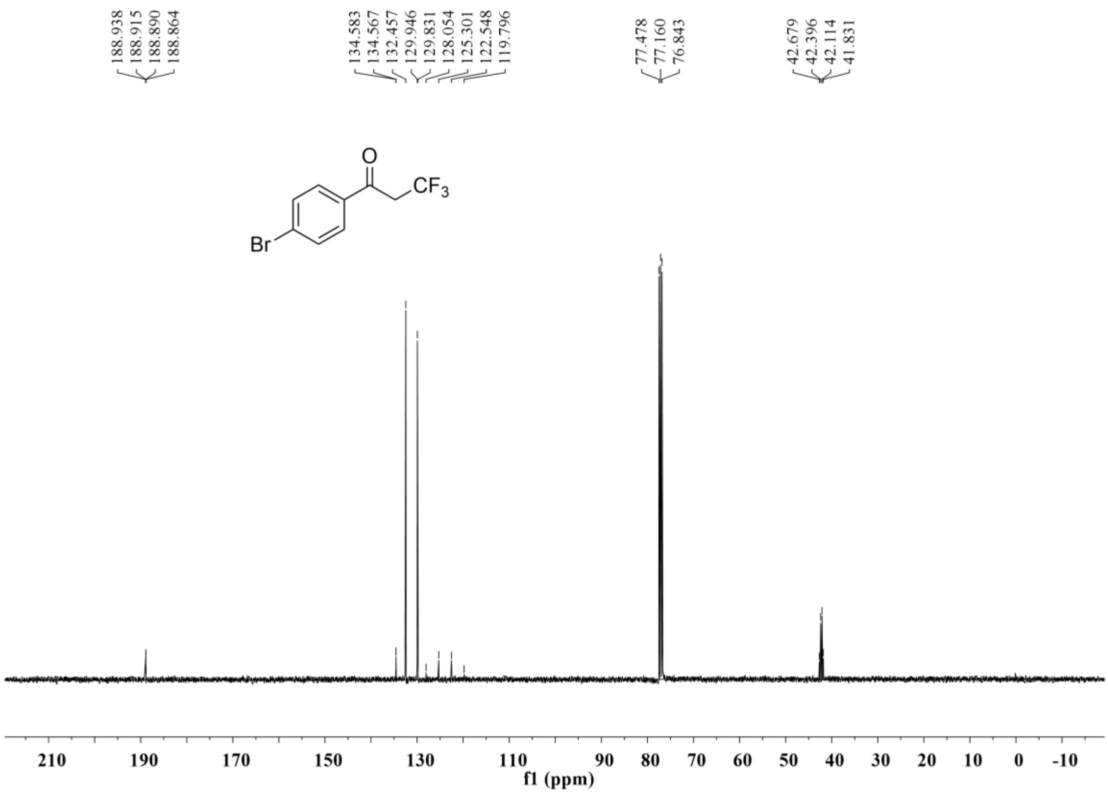

194.586
194.569
135.747
135.735
134.156
129.611
129.052
128.738
126.828
124.045
121.261
77.478
77.160
76.843
44.786
44.523
44.260
43.997
11.875
11.848
11.820
11.793
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.266
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

3m



7.813
7.809
7.796
7.792
7.673
7.669
7.656
7.652
7.266
3.811
3.787
3.762
3.737
0.000
O
CF3
Br
2.00
1.99
2.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



188.938
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188.890
188.864
134.583
134.567
132.457
129.946
129.831
128.054
125.301
122.548
119.796
77.478
77.160
76.843
42.679
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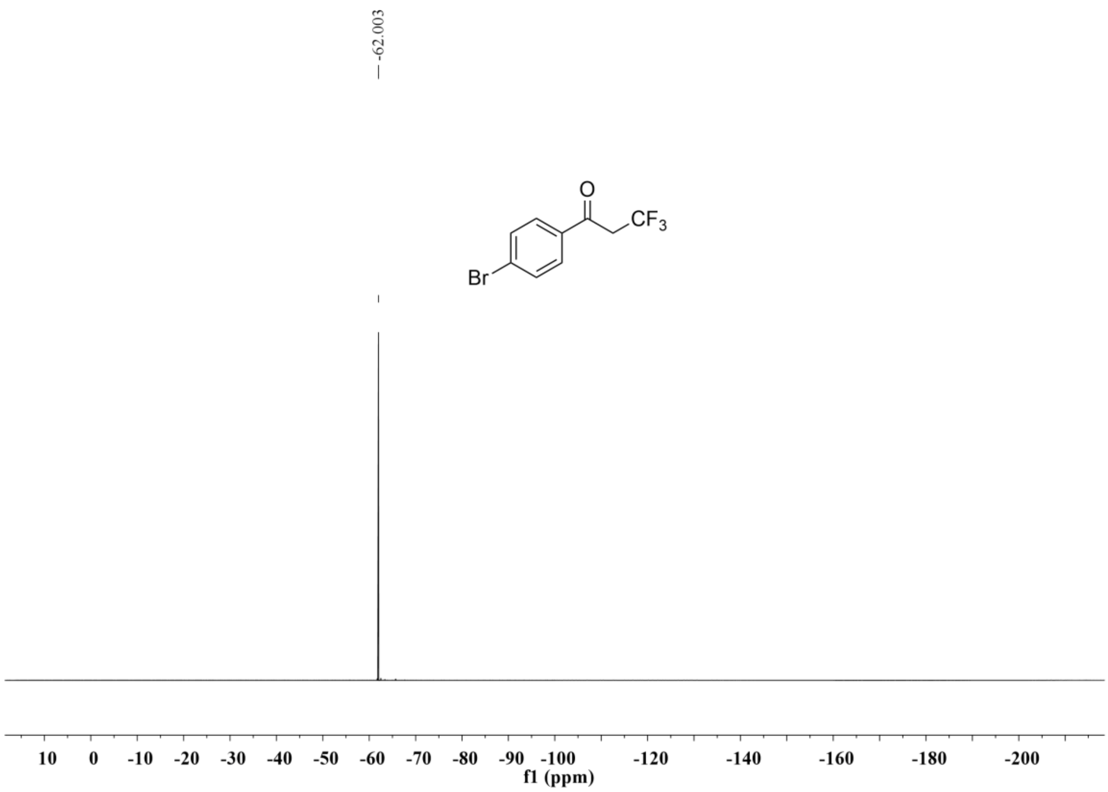
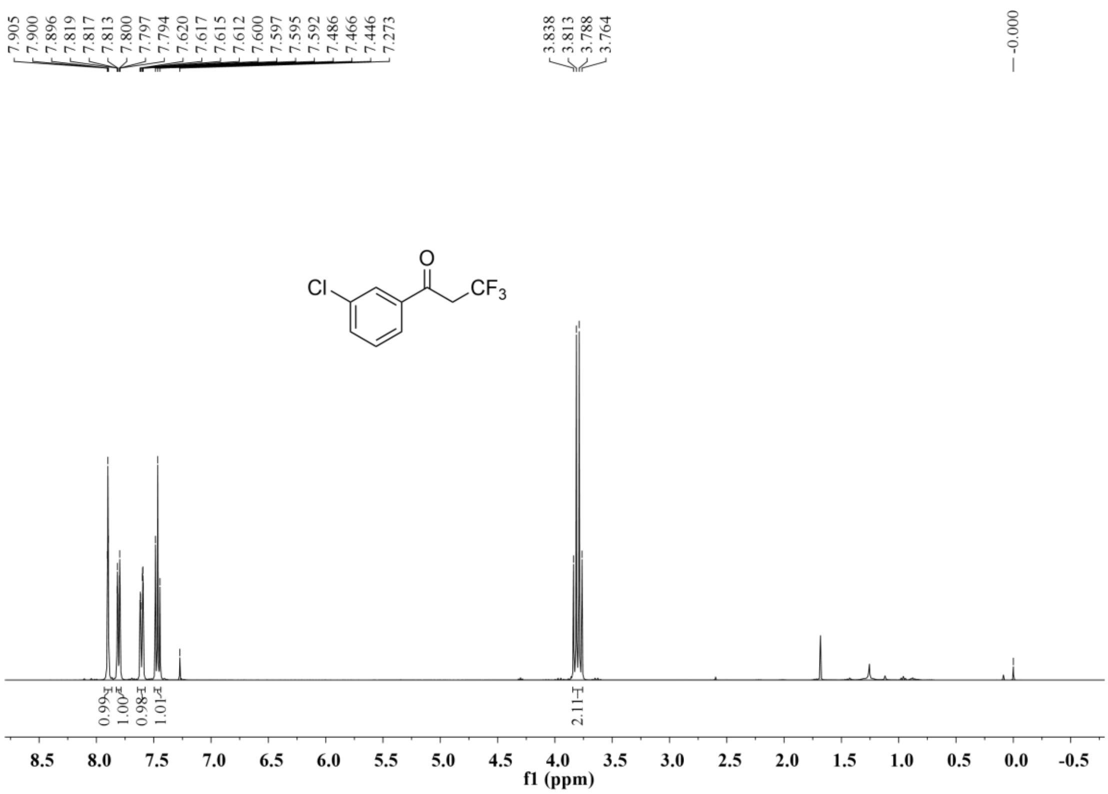
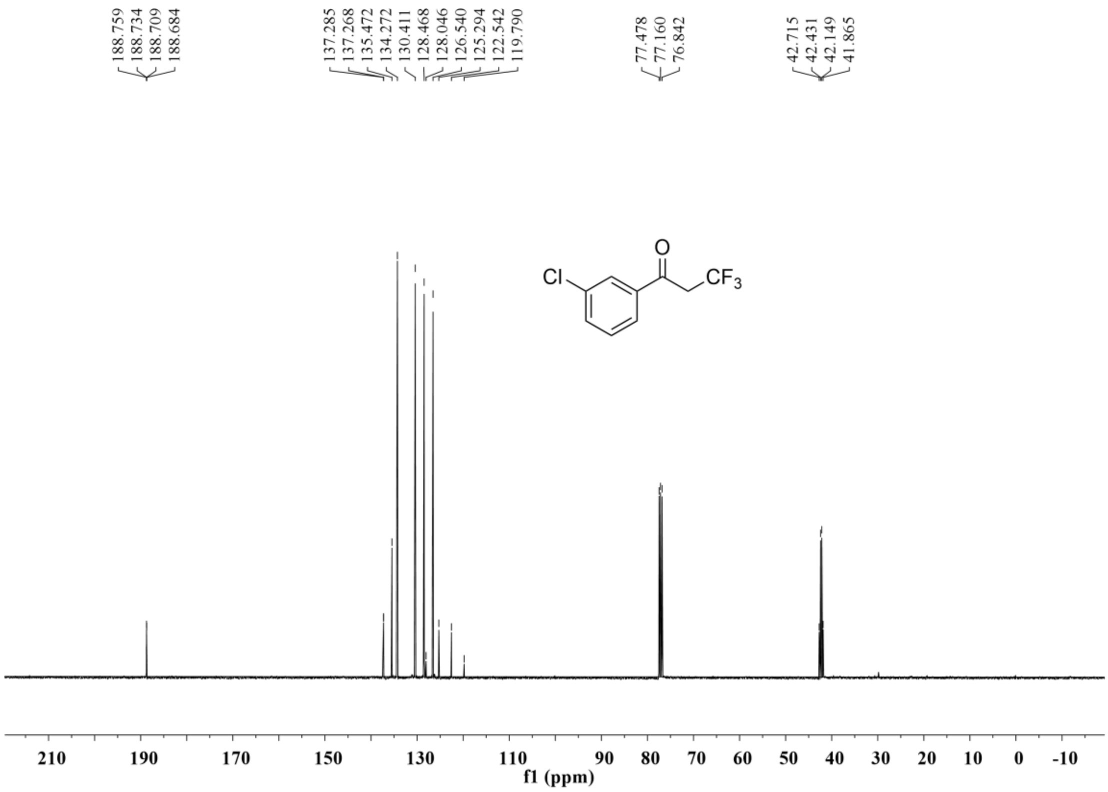
42.114
41.831
O
CF3
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.003
CF3
Br
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

3n


7.905 7.900 7.896 7.819 7.817 7.813 7.800 7.797 7.794 7.620 7.617 7.615 7.612 7.600 7.597 7.595 7.592 7.486 7.466 7.446 7.273
3.838 3.813 3.788 3.764
-0.000
Cl
O
CF3
0.99 1.00 0.98 1.01
2.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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188.709
188.684
137.285
137.268
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134.272
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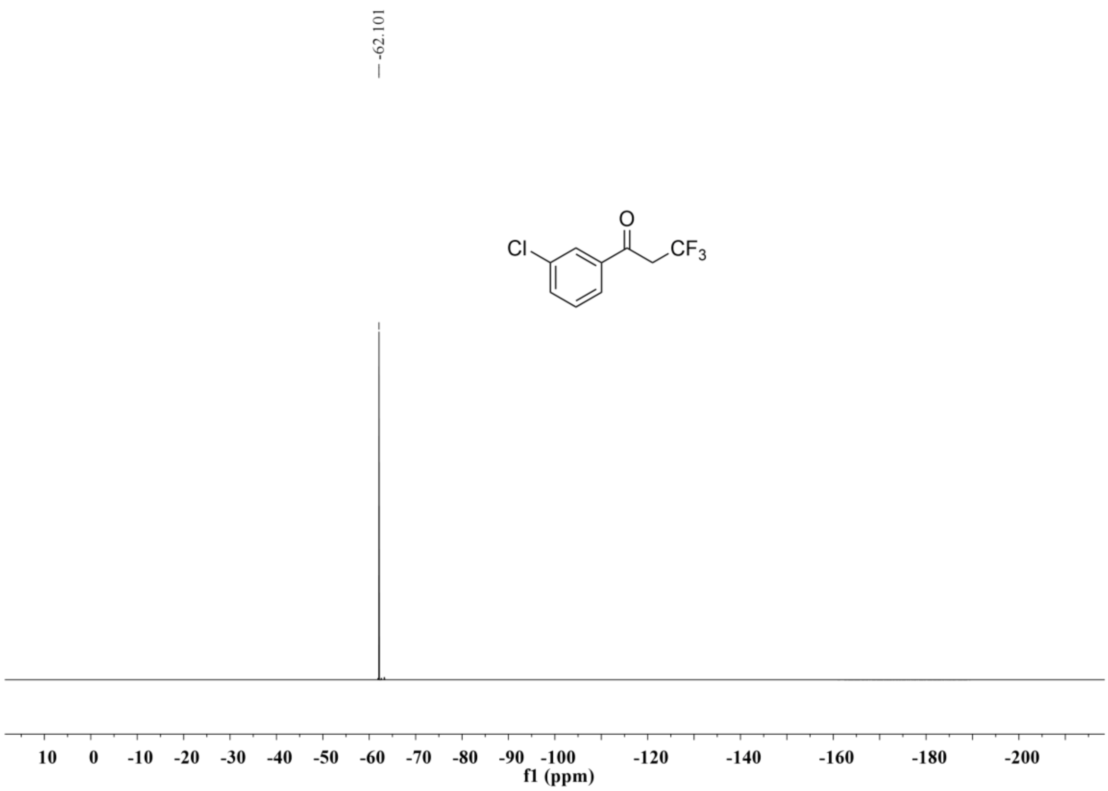
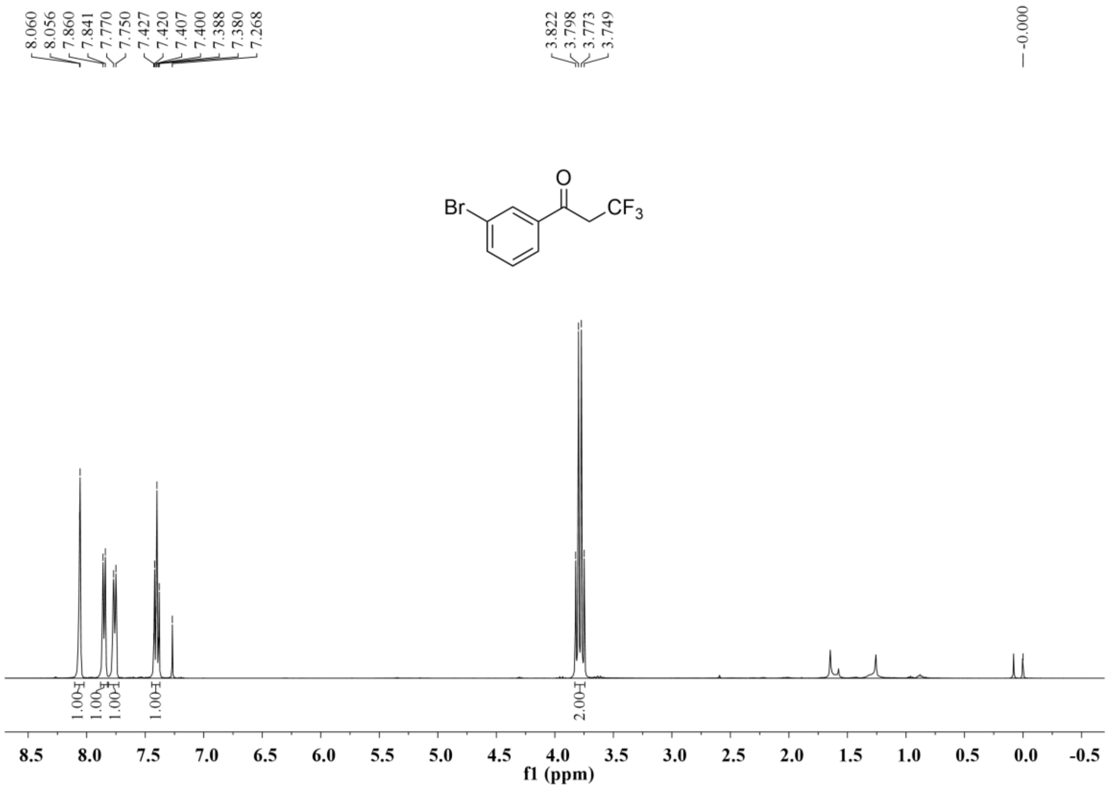
128.468
128.046
126.540
125.294
122.542
119.790
77.478
77.160
76.842
42.715
42.431
42.149
41.865
Cl
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.101
Cl
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

3o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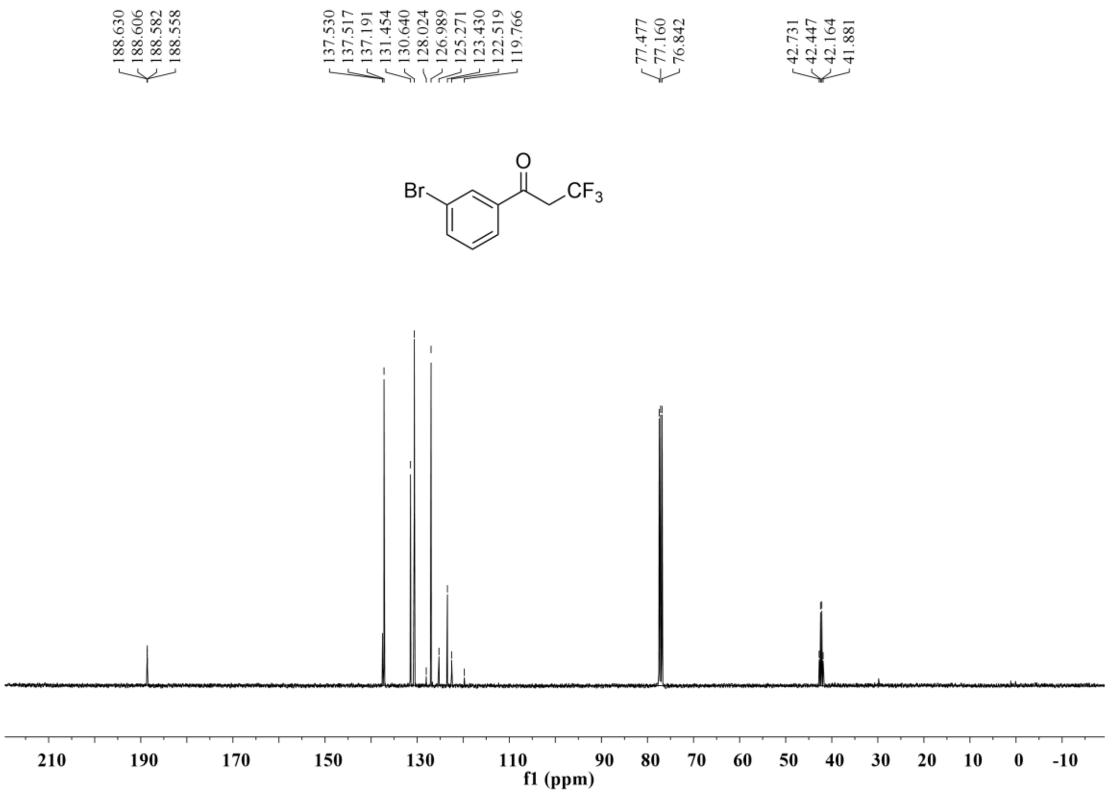
8.056
7.860
7.841
7.770
7.750
7.427
7.420
7.407
7.400
7.388
7.380
7.268
3.822
3.798
3.773
3.749
-0.000
Br
O
CF_3
1.00
1.00
1.00
1.00
2.00
f1 (ppm)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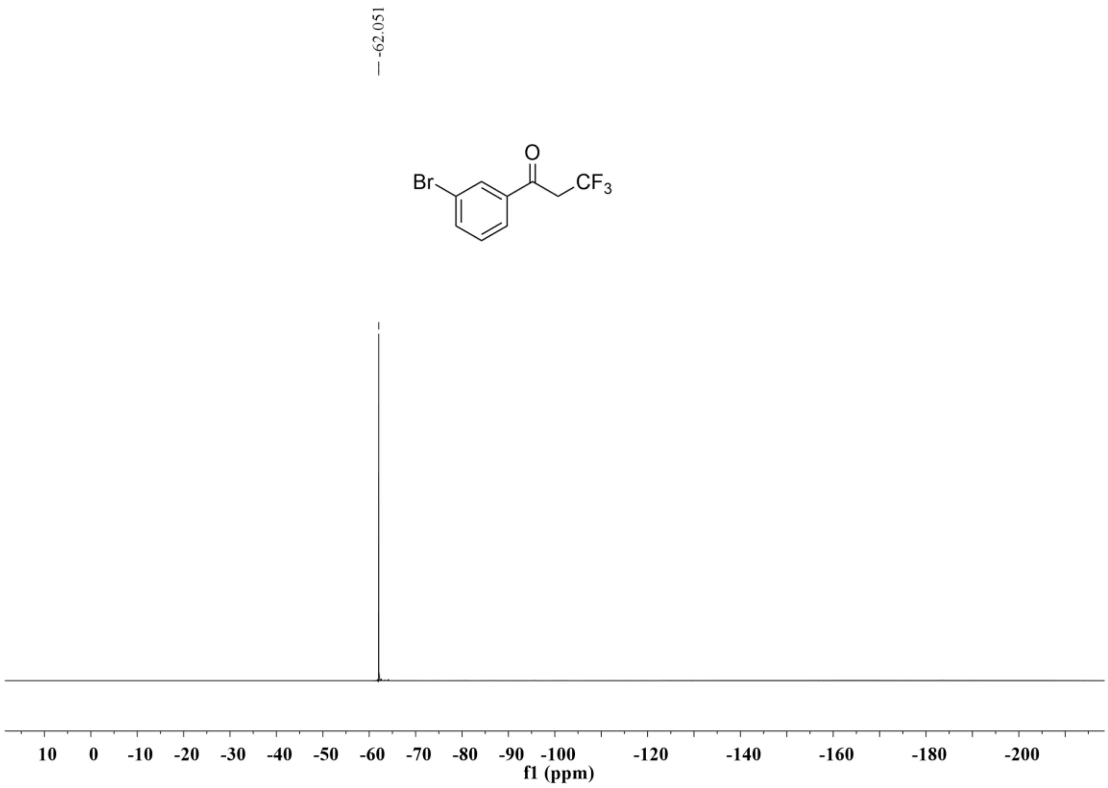
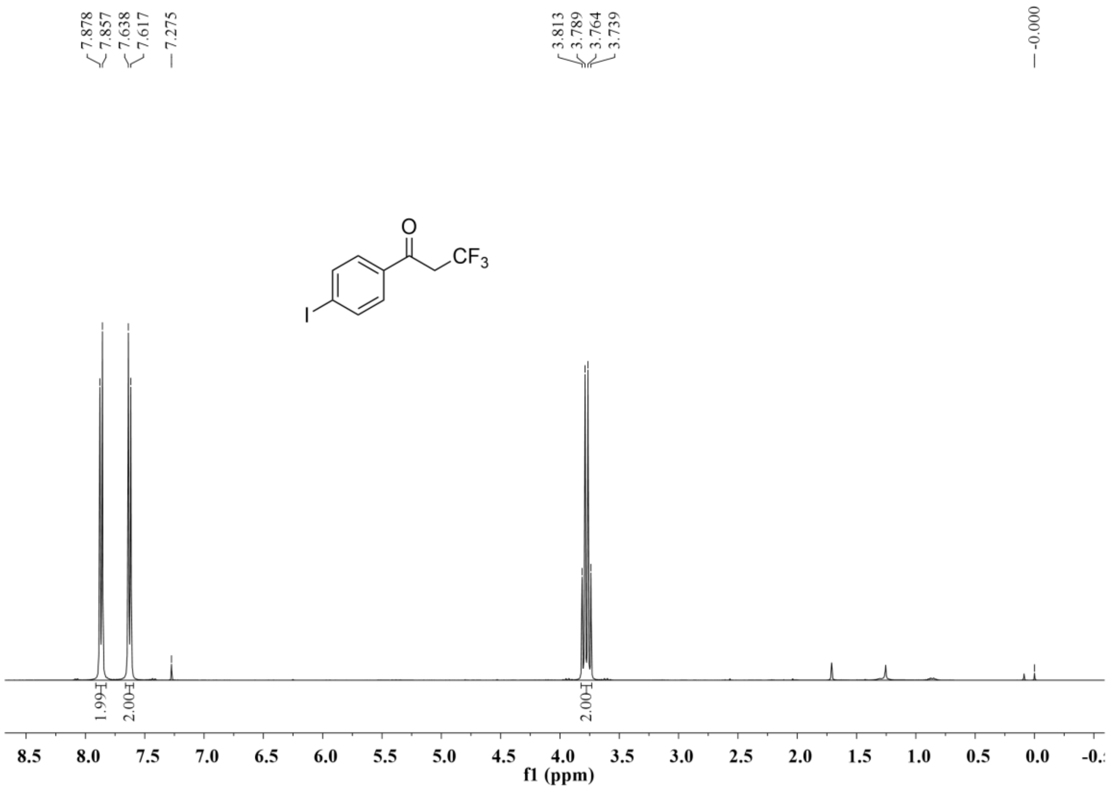
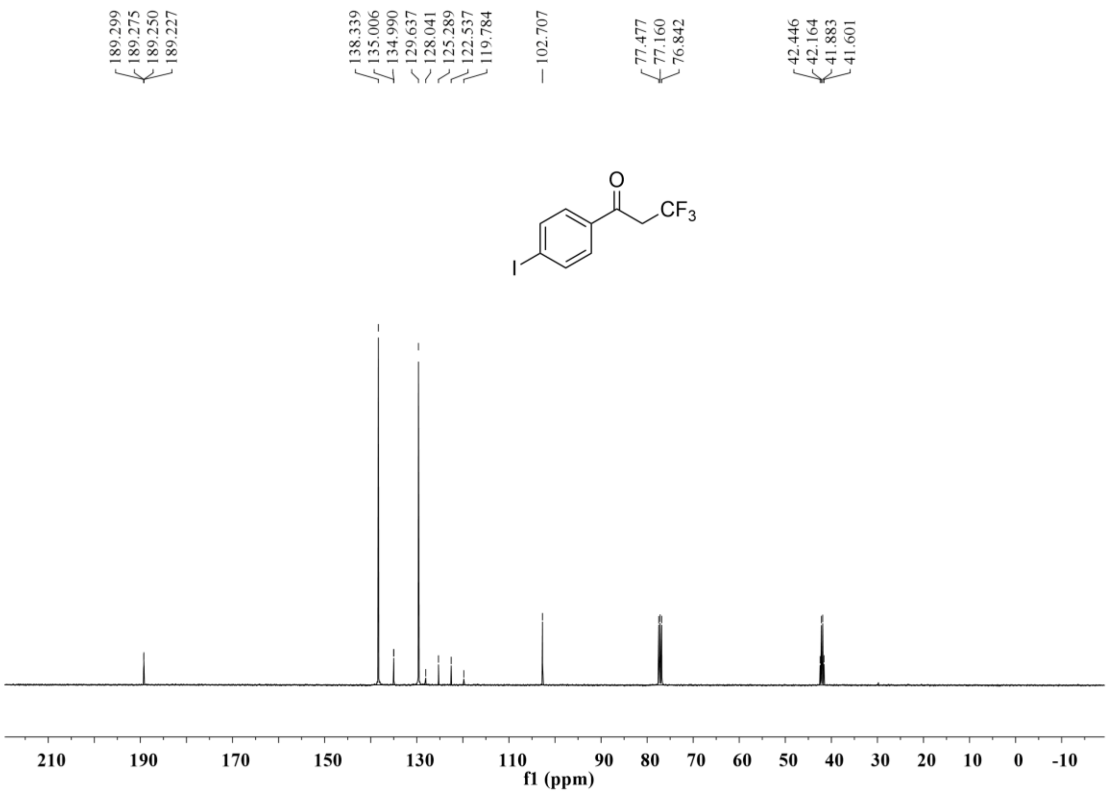
188.558
137.530
137.517
137.191
131.454
130.640
128.024
126.989
125.271
123.430
122.519
119.766
77.477
77.160
76.842
42.731
42.447
42.164
41.881
Br
O
CF_3
f1 (ppm)



3p

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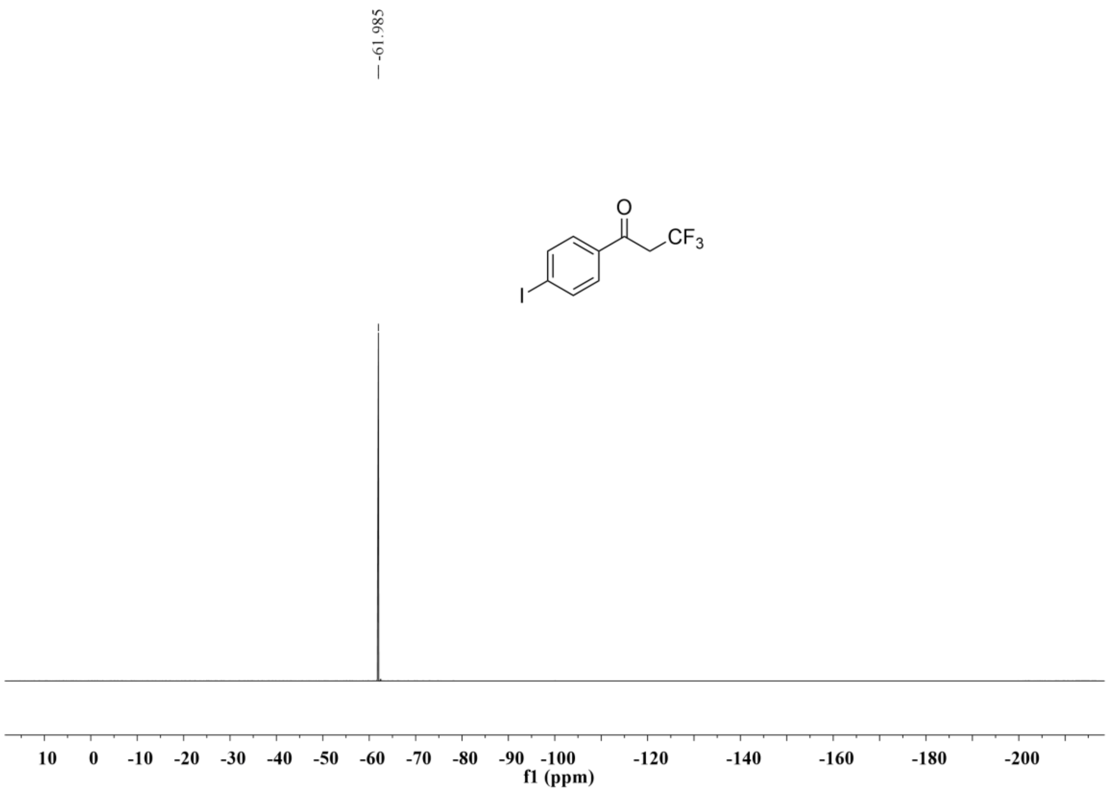
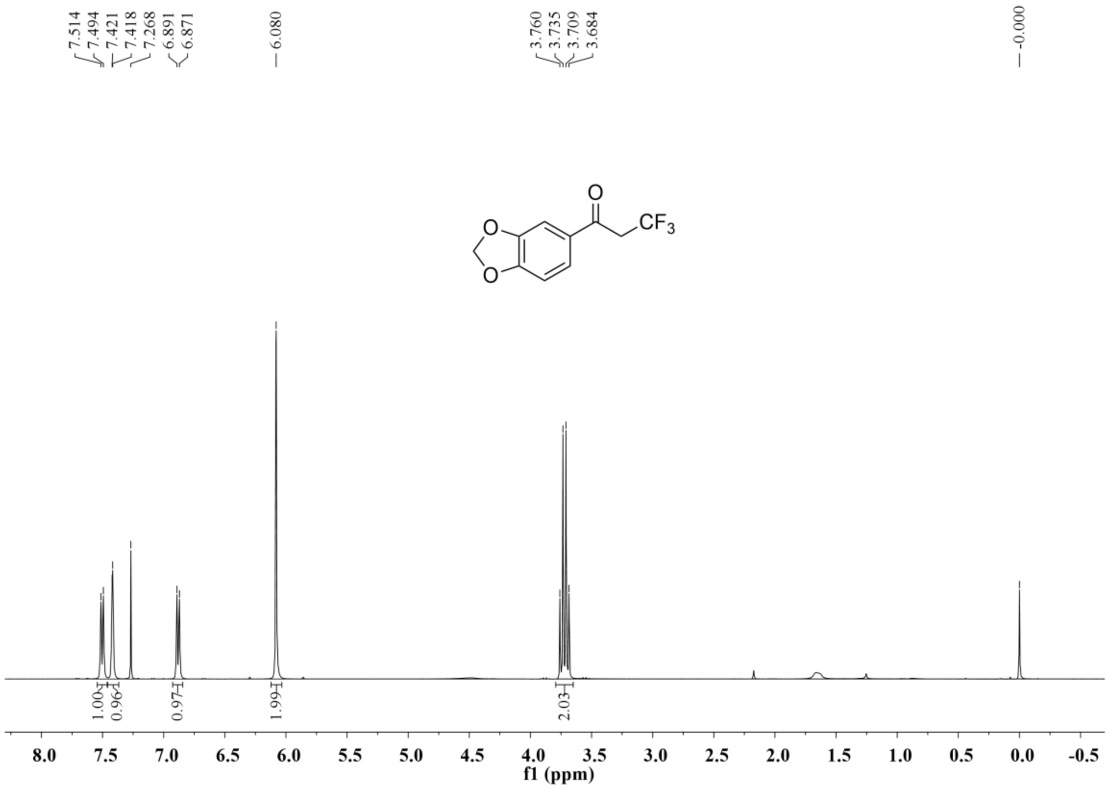
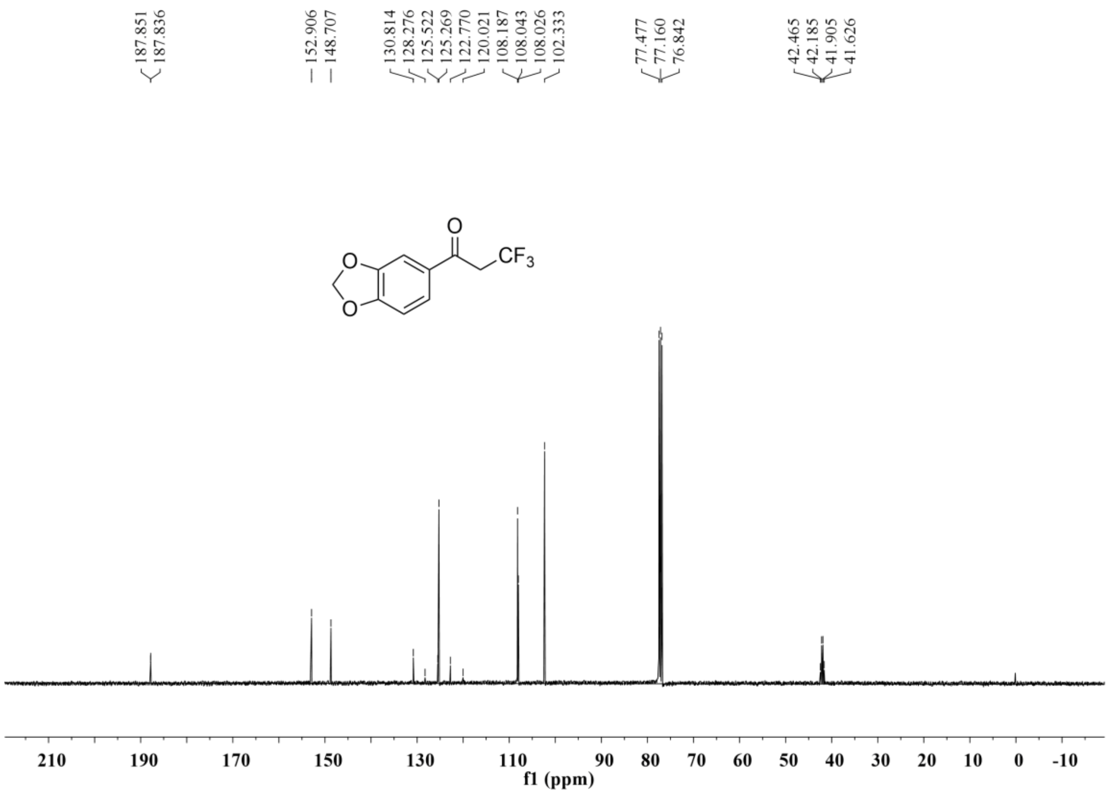
189.275
189.250
189.227
138.339
135.006
134.990
129.637
128.041
125.289
122.537
119.784
102.707
77.477
77.160
76.842
42.446
42.164
41.883
41.601
O
CF3
I
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-61.985
O
CF3
I
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

3q


7.514
7.494
7.421
7.418
7.268
6.891
6.871
6.080
3.760
3.735
3.709
3.684
-0.000
O
O
O
CF3
1.00
0.96
0.97
1.99
2.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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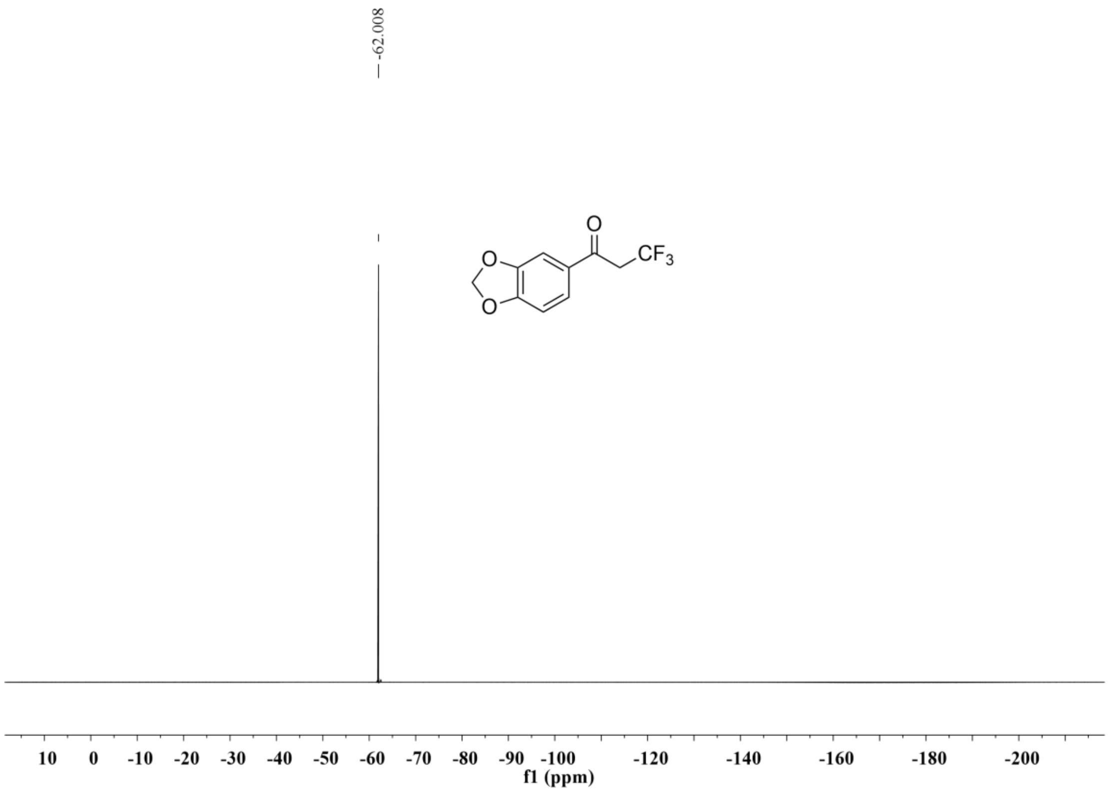
187.836
152.906
148.707
130.814
128.276
125.522
125.269
122.770
120.021
108.187
108.043
108.026
102.333
77.477
77.160
76.842
42.465
42.185
41.905
41.626
O
O
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
O
O
CF3
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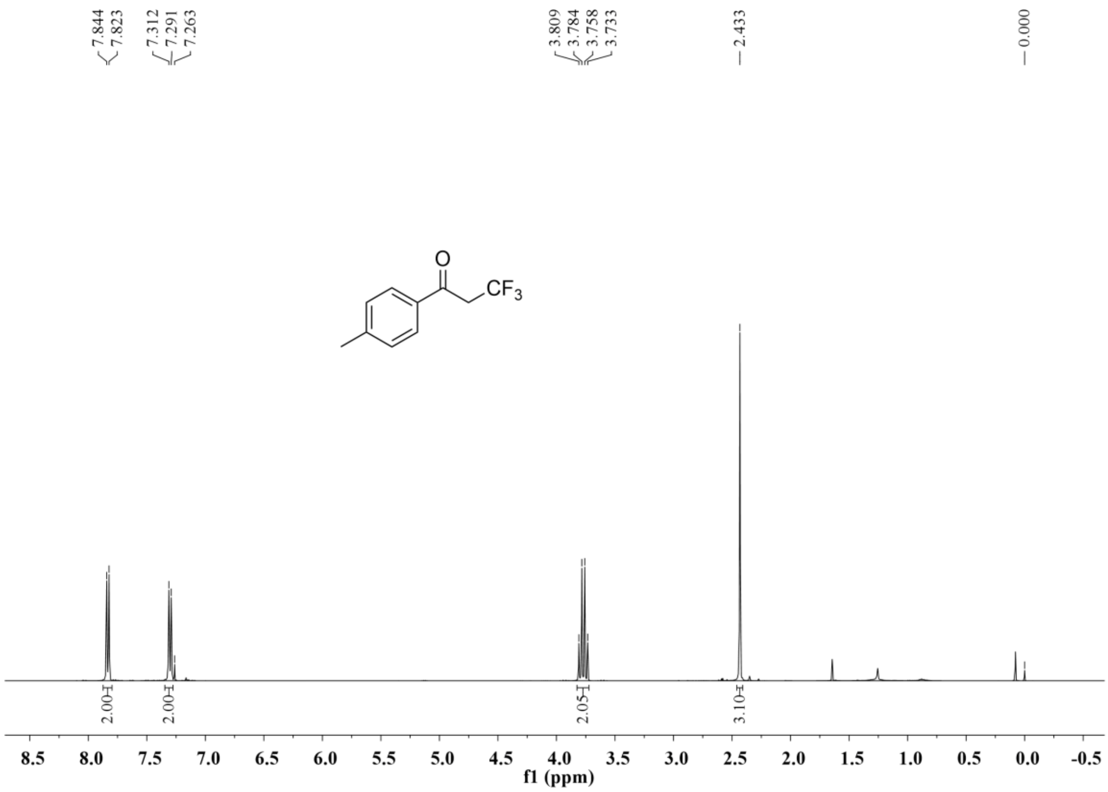
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

3r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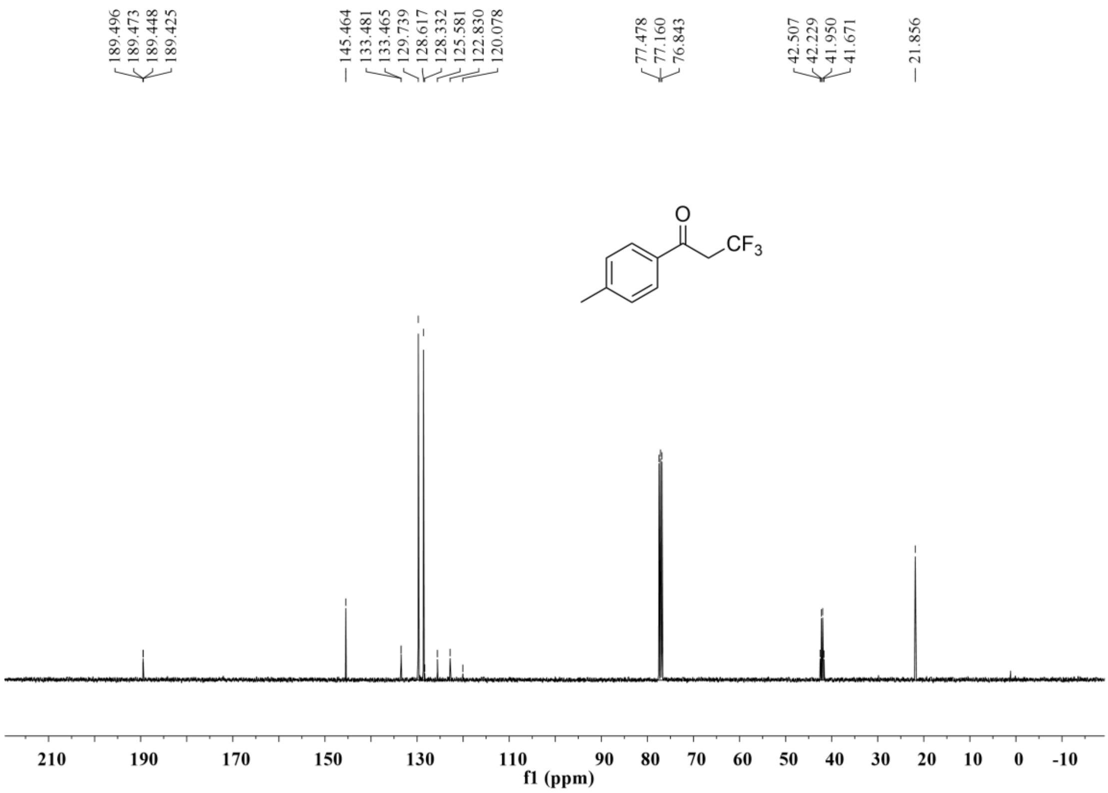
7.823
7.312
7.291
7.263
3.809
3.784
3.758
3.733
2.433
0.000
O
CF3
2.00
2.00
2.05
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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189.473
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145.464
133.481
133.465
129.739
128.617
128.332
125.581
122.830
120.078
77.478
77.160
76.843
42.507
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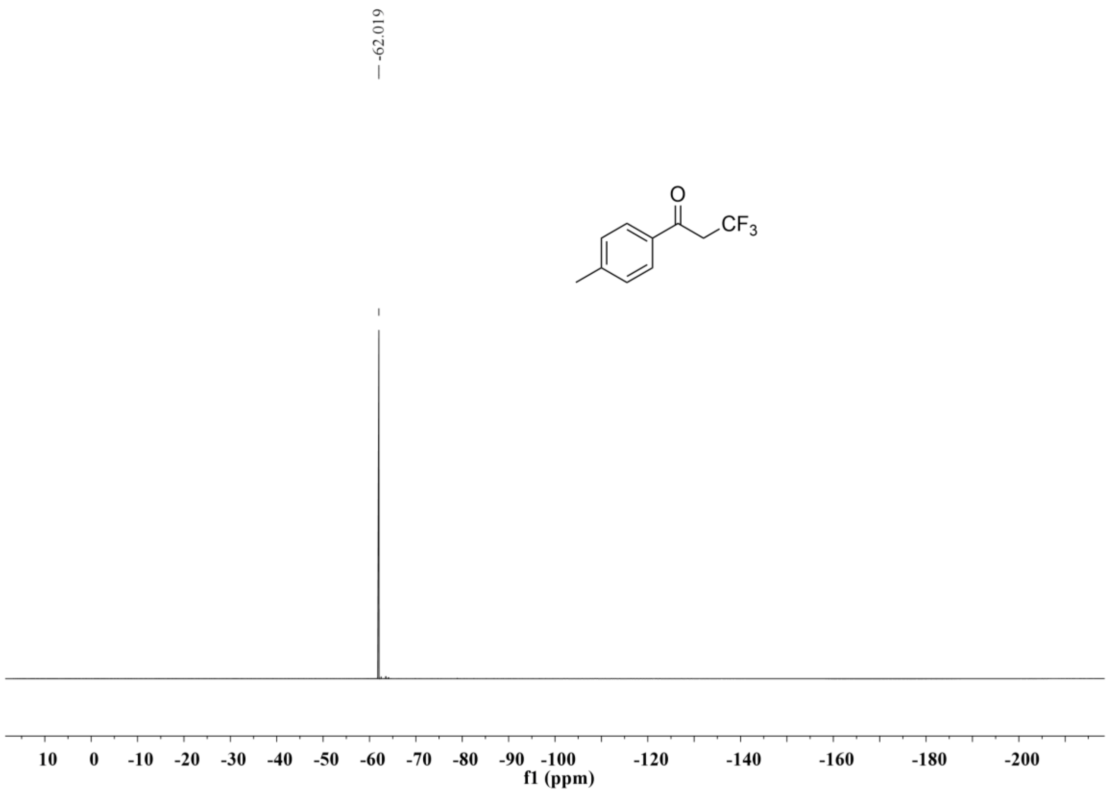
41.950
41.671
21.856
O
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.019
O
CF3
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f1 (ppm)