Zinc-Brønsted acid mediated practical hydrotrifluoromethylation of alkenes with CF_3Br

Deqian Peng,[a] Wu Fan,[b] Xueqi Zhao,[a] Wei Chen,[c] Yuan Wen,[a] Li Zhang[a] and Suhua Li*[a,d]

a School of Chemistry, Sun Yat-Sen University, Guangzhou 510006, China

b Key Laboratory of Tobacco Flavor Basic Research, Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, China

c Department of Colorectal Surgery & Guangdong Provincial Key laboratory of Colorectal and Pelvic Floor Disease & Guangdong Research Institute of Gastroenterology, The Sixth Affiliated Hospital of Sun Yat-Sen University, Guangzhou 510655, China.

d Key Lab of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510641, China.

*lisuhua5@mail.sysu.edu.cn

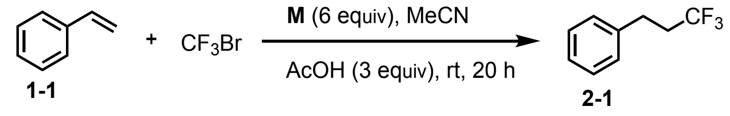
Contents Page

1. General Information

Acetonitrile was dried over CaH_2. All other reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar, Sigma-Aldrich, Energy Chemical, and TCI. The CF_3Br was purchased from Shangfluoro Chemicals. Visualization was accomplished with UV light (254 nm) or $KMnO_4$ stain. Flash column chromatography was performed using silica gel (300-400 mesh). ^1H NMR Spectra were acquired on a Bruker Ascend^{TM} 400 (at 400 MHz) and are reported relative to $SiMe_4$ (δ 0.00) or the residue solvents from the deuterium solvents. ^{13}C NMR spectra were acquired on a Bruker Ascend^{TM} 400 (at 101 MHz) and are reported relative to $CDCl_3$ (δ 77.16) or the residue solvents from the deuterium solvents. ^{19}F NMR spectra were acquired on a Bruker Ascend^{TM} 400 (at 376 MHz) and are reported relative to $CFCl_3$ (δ 0.00). NMR acquisitions were performed at 295 K unless otherwise noted. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; bs, broad singlet; app., approximate peak. Melting points (m.p.) were determined using a WRS-2 microcomputer melting point meter and are uncorrected. All IR spectra were obtained as a film with Perkin Elmer FT-IR Spectrometer Frontier. Low-resolution mass spectrometry data was acquired by SHIMADZU GCMS-QP2010 SE. High-resolution mass spectrometry (HRMS) data was acquired by Synapt G2 Si or Thermo Scientific Q Exactive GC.

2. Reaction Conditions Optimization

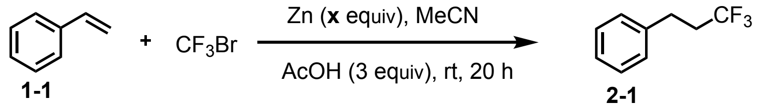
Table S1: Screening of the metals



entry	**Cat.**	yield of **2-1** (%) [a]	rsm (%) [b]
1	**Zn**	**61**	**33**
2	In	10	72
3	Cu	< 1	81
4	Mg	< 1	75
5	Fe	< 1	87
6	Ag	< 1	87
7	Sb	< 1	87
8	Al	< 1	87
9	Mn	3	78

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), M (1.5 mmol), AcOH (43 μL, 0.75 mmol), CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

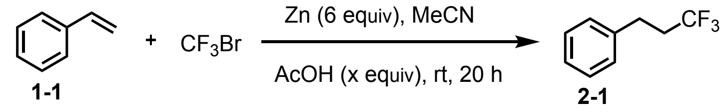
Table S2: **Evaluation of the equivalents of Zn needed in the presence of 3 equiv of AcOH.**



entry	Zn (equiv)	yield of **2-1** (%) [a]	rsm (%) [b]
1	0	0	75
2	1	18	69
3	2	26	57
4	3	27	54
5	4	41	51
6	5	55	36
7	**6**	**61**	**33**
8	7	61	24

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn, AcOH (43 μL, 0.75 mmol), CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

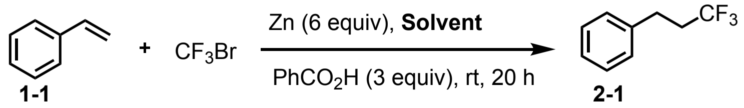
Table S3: **Evaluation of AcOH Needed in the Presence of 6 equiv of Zn.**



entry	**x**	yield of **2-1** (%) [a]	rsm (%) [b]
1	0	0	84
2	1	55	27
3	2	60	33
4	**3**	**61**	**33**
5	4	60	36
6	5	55	36
7	6	51	39

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn (1.5 mmol), AcOH, CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

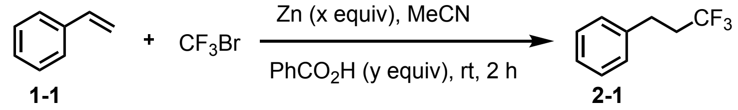
Table S4: **Screening of the solvents**



entry	**Solvents**	yield of **2-1** (%) [a]	rsm (%) [b]
1	NMP	15	69
2	DMA	30	51
3	DMF	22	63
4	Dioxane	76	0
5	PhCN	89	0
6	Xylene	23	60
7	Tol	35	33
8	Glycol dimethyl ether	84	0
9	$CHCl_3$	4	58
10	PE	19	3
11	Cyclooctane	17	45
12	DMSO	2	84
13	MeCN	86	0

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn (1.5 mmol), $PhCO_2H$ (0.75 mmol), CF_3Br (6.2 equiv) and solvent (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

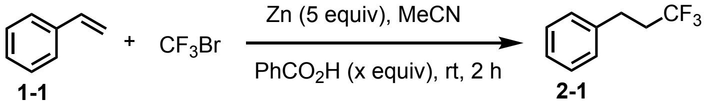
Table S5: **Optimizing the quantity of Zn and $PhCO_2H$ (2:1)**



entry	x	y	yield of **2-1** (%) [a]	rsm (%) [b]
1	5.0	2.5	88	0
2	4.0	2.0	86	6
3	3.0	1.5	74	15
4	2.0	1.0	48	42
5	1.0	0.5	26	66
6	0.5	0.25	4	93

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn, $PhCO_2H$, CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

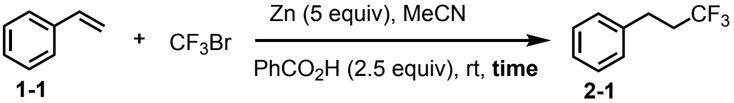
Table S6: **Evaluation of the Equivalents of $PhCO_2H$ Needed in the Presence of 5 equiv of Zn.**



entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1	0.5	0	78
2	1	2	87
3	1.5	74	3
4	2	81	6
5	2.5	88	0

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn (1.25 mmol), $PhCO_2H$, CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Table S7: **Optimization of the Reaction Time**



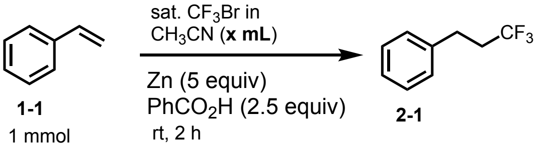
entry	time (h)	yield of **2-1** (%) [a]	rsm (%) [b]
1	0.25	11	84
2	0.5	79	12
3	1.0	87	0
4	2	88	0

The reaction was conducted in 25 mL Schlenk tube with styrene (29 μL, 0.25 mmol), Zn (1.25 mmol), $PhCO_2H$ (0.625 mmol), CF_3Br (6.2 equiv) and MeCN (1 mL) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Hydrotrifluoromethylation of Styrene with Saturated CF_3Br Solution in CH_3CN

Calculating the concentration of saturated CF_3Br in CH_3CN:

Saturated CF_3Br solution in CH_3CN were prepared by stirring of CH_3CN (40 mL) under CF_3Br atmosphere in a 50 mL Schlenk flask with a CF_3Br balloon attached for 10 hours. The amount of CF_3Br dissolved in CH_3CN was calculated through weighing by difference with CF_3Br gas above the solvent deducted. The approximate concentration of CF_3Br was calculated as around 0.12 M (in CH_3CN).

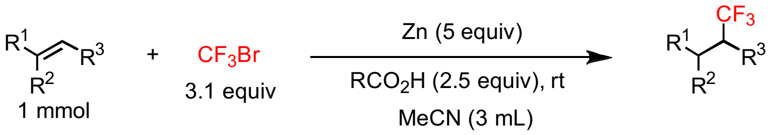


entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1	10	25	69
2	26	54	36

The reaction was conducted in 50 mL Schlenk flask with styrene (1.0 mmol), Zn (5.0 mmol), $PhCO_2H$ (2.5 mmol), sat. CF_3Br in MeCN (10 mL or 26 mL as indicated) at rt; [a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^1H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

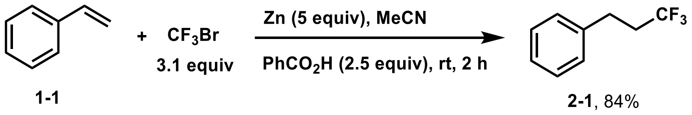
3. Hydroxytrifluoromethylation of Alkenes

General procedure for the hydrotrifluoromethylation of alkenes:



To a 50 mL of Schlenk flask was added Zn powder (5.0 mmol, 5 equiv) and RCO_2H (2.5 mmol, 2.5 equiv), and it was sealed and evacuated for 30 s and backfilled with CF_3Br (3.1 equiv). Then the flask was added MeCN (3 mL) and alkene (1.0 mmol, 1 equiv). After stirring for corresponding time at rt, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated, and the residue was purified by silica gel chromatography.

(3,3,3-trifluoropropyl)benzene (2-1, p4-31)



Prepared according to the general procedure using alkene **1-1** (115 µL, d = 0.906 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.5 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-1**[1] (146.0 mg, 84% yield) as a colorless oil.

TLC: $R_f = 0.79$ in petroleum ether.

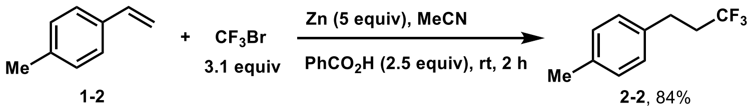
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.24–7.19 (m, 3H), 2.90–2.85 (m, 2H), 2.45–2.33 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.16, 128.87, 128.36, 126.87 (q, J = 276.7 Hz), 126.79, 35.80 (q, J = 28.4 Hz), 28.35 (q, J = 3.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.21.

MS (EI): m/z (%) 174 (M^+, 25.60), 91 (100).

1-methyl-4-(3,3,3-trifluoropropyl)benzene (2-2, p4-33)



Prepared according to the general procedure using alkene **1-2** (132 µL, d = 0.897 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-2** (158.0 mg, 84% yield) as a colorless oil.

TLC: $R_f = 0.78$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.07 (m, 4H), 2.85–2.81 (m, 2H), 2.42–2.30 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.35, 136.13, 129.54, 128.24, 126.94 (q, J = 276.2 Hz), 35.91 (q, J = 28.1 Hz), 27.94 (q, J = 3.6 Hz), 21.09.

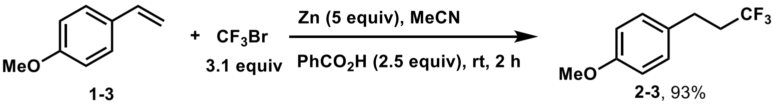
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.21.

IR (neat): 2926, 2856, 1455, 1387, 1307, 1257, 1141, 1809, 808.

MS (EI): *m/z* (%) 188 (M^+, 30.96), 105 (100).

HRMS (EI): m/z calc'd for $C_{10}H_{11}F_3$ $(M)^+$: 188.0807, found 188.0807.

1-methoxy-4-(3,3,3-trifluoropropyl)benzene (2-3, p4-35)



Prepared according to the general procedure using alkene **1-3** (133 μL, d = 1.009 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-3**[2] (190.0 mg, 93% yield) as a colorless oil.

TLC: $R_f = 0.34$ in petroleum ether.

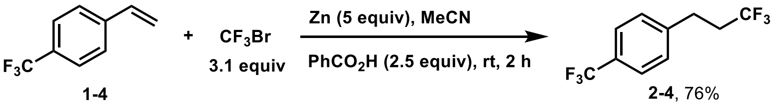
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.09 (m, 2H), 6.87–6.83 (m, 2H), 3.79 (s, 3H), 2.83–2.79 (m, 2H), 2.41–2.29 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.51, 131.18, 129.30, 126.89 (q, J = 276.7 Hz), 114.24, 55.35, 36.02 (q, J = 28.0 Hz), 27.46 (q, J = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.16.

MS (EI): *m/z* (%) 204 (M^+, 27.94), 121 (100).

1-(trifluoromethyl)-4-(3,3,3-trifluoropropyl)benzene (2-4, p4-36)



Prepared according to the general procedure using alkene **1-4** (148 μL, d = 1.165 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-4** (184.0 mg, 76% yield) as a colorless oil.

TLC: $R_f = 0.72$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.96–2.92 (m, 2H), 2.47–2.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.23, 129.36 (q, *J* = 32.7 Hz), 128.78, 126.70 (q, *J* = 276.6 Hz), 125.84 (q, *J* = 3.9 Hz), 124.38 (q, *J* = 271.9 Hz), 35.40 (q, *J* = 28.8 Hz), 28.23 (q, *J* = 3.4 Hz).

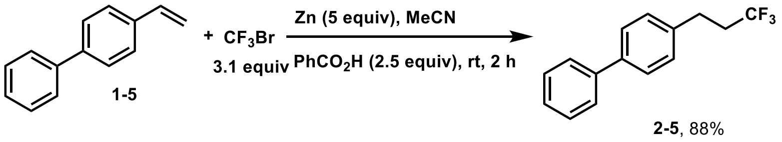
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.05, -67.12.

IR (neat): 2956, 2855, 1327, 1259, 1225, 1168, 1131, 829.

MS (EI): *m/z* (%) 242 (M^+, 42.56), 159 (100).

HRMS (EI): *m/z* calc'd for $C_{10}H_8F_6$ $(M)^+$: 242.0525, found 242.0525.

4-(3,3,3-trifluoropropyl)-1,1'-biphenyl (2-5, p3-195-1)



Prepared according to the general procedure using alkene **1-5** (180.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-5**[3] (220.0 mg, 88% yield) as a white solid.

TLC: R_f = 0.78 in petroleum ether.

m.p.: 82.8~83.7 °C.

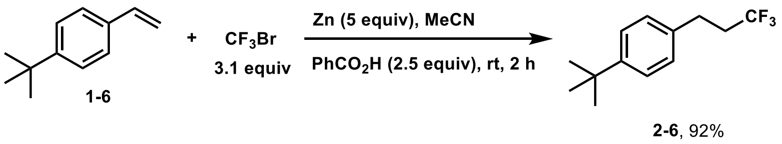
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 4H), 7.45–7.42 (m, 2H), 7.36–7.32 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.94–2.90 (m, 2H), 2.49–2.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.89, 139.82, 138.18, 128.93, 128.78, 127.58, 127.41, 127.16, 126.85 (q, *J* = 277.0 Hz), 35.76 (q, *J* = 28.3 Hz), 27.99 (q, *J* = 3.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.15.

MS (EI): *m/z* (%) 250 (M^+, 48.41), 167 (100).

1-(*tert*-butyl)-4-(3,3,3-trifluoropropyl)benzene (2-6, p4-71)



Prepared according to the general procedure using alkene **1-6** (183 µL, d = 0.875 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.3 mg, 5.0 mmol), $PhCO_2H$ (306.2 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-6**[4] (211.0 mg, 92% yield) as a colorless oil.

TLC: R_f = 0.64 in petroleum ether.

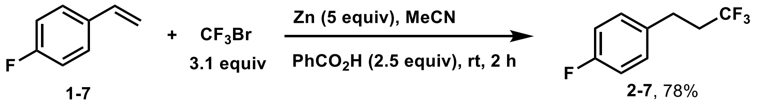
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.86–2.82 (m, 2H), 2.44–2.32 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.73, 136.09, 128.31, 126.93 (q, *J* = 276.7 Hz), 125.76, 35.81 (q, *J* = 28.4 Hz), 34.58, 31.50, 27.78 (q, *J* = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.26.

MS (EI): *m/z* (%) 230 (M^+, 30.86), 215 (100).

1-fluoro-4-(3,3,3-trifluoropropyl)benzene (2-7, p4-58)



Prepared according to the general procedure using alkene **1-7 (**119 µL, d = 1.024 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-7**[4] **(**149.0 mg, 78% yield) as a colorless oil.

TLC: R_f = 0.77 in petroleum.

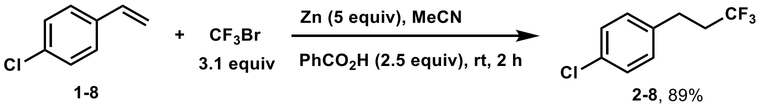
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.14 (m, 2H), 7.02–6.98 (m, 2H), 2.87–2.83 (m, 2H), 2.43–2.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.87 (d, *J* = 244.8 Hz), 134.82 (d, *J* = 3.0 Hz), 129.82 (d, *J* = 8.0 Hz), 126.77 (q, *J* = 276.8 Hz), 115.67 (d, *J* = 21.5 Hz), 35.89 (q, *J* = 28.4 Hz), 27.61 (q, *J* = 3.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.14, -116.93.

MS (EI): *m/z* (%) 192 (M^+, 39.52), 109 (100).

1-chloro-4-(3,3,3-trifluoropropyl)benzene (2-8, p4-38)



Prepared according to the general procedure using alkene **1-8 (**120 µL, d = 1.155 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.6 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-8**[1] **(**185.0 mg, 89% yield) as a colorless oil.

TLC: R_f = 0.77 in petroleum ether.

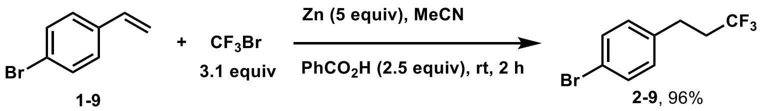
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.15–7.11 (m, 2H), 2.87–2.83 (m, 2H), 2.43–2.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.55, 132.65, 129.72, 128.98, 126.70 (q, *J* = 276.8 Hz), 35.62 (q, *J* = 28.6 Hz), 27.75 (q, *J* = 3.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.11.

MS (EI): *m/z* (%) 208 (M^+, 33.18), 125 (100).

1-bromo-4-(3,3,3-trifluoropropyl)benzene (2-9, p4-32)



Prepared according to the general procedure using alkene **1-9** **(**131 μL, d = 1.40 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.9 mg, 5.0 mmol), $PhCO_2H$ (305.6 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-9**[4] **(**244.0 mg, 96% yield) as a colorless oil.

TLC: R_f = 0.79 in petroleum ether.

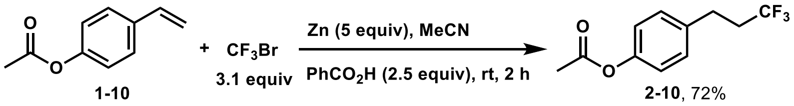
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.85–2.81 (m, 2H), 2.43–2.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.05, 131.94, 130.11, 126.65 (q, *J* = 276.8 Hz), 120.64, 35.56 (q, *J* = 28.6 Hz), 27.82 (q, *J* = 3.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.11.

MS (EI): *m/z* (%) 252 (M^+ (^{79}Br), 59.36), 254 (M^+ (^{81}Br), 57.23), 169 (100).

4-(3,3,3-trifluoropropyl)phenyl acetate (2-10, p4-91)



Prepared according to the general procedure using alkene **1-10** **(**153 μL, d = 1.06 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then filtered through a pad of Celite eluenting with DCM (40 mL). The resulting solution was washed with Na_2CO_3 aq. (2 mL) in H_2O (15 mL) for 3 times. Then the DCM solution was washed with sat. NaCl aq. and dried over anhydrous Na_2SO_4. The solution was concentrated, and the residue was purified by silica gel chromatography (pentane : DCM = 4:1) to afford **2-10**[1] **(**168.0 mg, 72% yield) as a light yellow oil.

TLC: R_f = 0.34 in 10:1 petroleum ether/EtOAc.

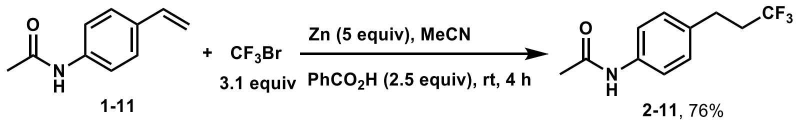
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 2H), 7.05–7.02 (m, 2H), 2.89–2.85 (m, 2H), 2.44–2.31 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.62, 149.49, 136.61, 129.30, 126.73 (q, *J* = 276.6 Hz), 121.91, 35.69 (q, *J* = 28.4 Hz), 27.71 (q, *J* = 3.3 Hz), 21.14.

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.21.

MS (EI): *m/z* (%) 232 (M^+, 5.50), 107 (100).

N-(4-(3,3,3-trifluoropropyl)phenyl)acetamide (2-11, p4-123)



Prepared according to the general procedure using alkene **1-11** (161.2 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.2 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 4 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was purified by silica gel chromatography (DCM : EtOAc = 10 : 1) to afford **2-11** (176.0 mg, 76% yield) as a white solid.

TLC: R_f = 0.30 in 1:1 petroleum ether/EtOAc.

m.p.: 149.1~152.2 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.16–7.14 (m, 3H), 2.86–2.82 (m, 2H), 2.42–2.30 (m, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66, 136.62, 135.06, 128.82, 126.77 (q, *J* = 276.7 Hz), 120.48, 35.73 (q, *J* = 28.1 Hz), 27.74 (q, *J* = 3.4 Hz), 24.59.

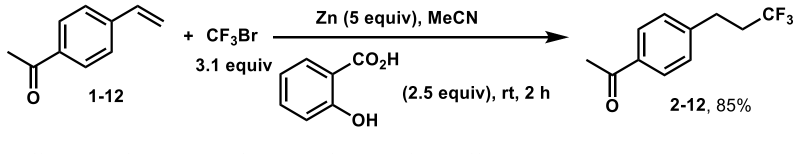
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.14.

IR (neat): 3303, 3264, 3199, 3135, 3085, 2982, 2951, 1686, 1668, 1553, 1516, 1413, 1377, 1324, 1307, 1249, 1212, 1138, 1079, 976, 866, 823, 726.

MS (EI): *m/z* (%) 231 (M^+, 20.40), 106 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{11}H_{13}F_3NO$ $(M + H)^+$: 232.0944, found 232.0946.

1-(4-(3,3,3-trifluoropropyl)phenyl)ethan-1-one (2-12, p6-41)



Prepared according to the general procedure using alkene **1-12** (146.2 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4 and concentrated. The residue was directly purified by silica gel chromatography (petroleum ether : EtOAc = 15:1) to afford **2-12**[5] (184.7 mg, 85% yield) as a light yellow oil.

TLC: R$_f$ = 0.33 in petroleum ether/EtOAc (10:1).

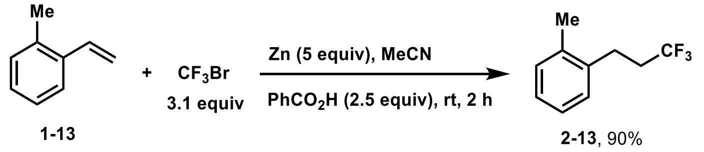
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.96–2.92 (m, 2H), 2.59 (s, 3H), 2.48–2.36 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.59, 144.51, 135.85, 128.85, 128.51, 126.61 (q, *J* = 276.6 Hz), 35.10 (q, *J* = 28.7 Hz), 28.20 (q, *J* = 3.2 Hz), 26.50.

^{19}F NMR (376 MHz, CDCl$_3$): δ -67.09.

MS (EI): *m/z* (%) 216 (M$^+$, 19.15), 201 (100).

1-methyl-2-(3,3,3-trifluoropropyl)benzene (2-13, p4-39)



Prepared according to the general procedure using alkene **1-13 (**129 μL, d = 0.914 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (329.5 mg, 5.0 mmol), PhCO$_2$H (307.6 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-13 (**170.0 mg, 90% yield) as a colorless oil.

TLC: R$_f$ = 0.76 in petroleum ether.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17–7.11 (m, 4H), 2.88–2.84 (m, 2H), 2.39–2.27 (m, 5H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.33, 136.02, 130.67, 128.73, 126.98, 126.96 (q, *J* = 276.6 Hz), 126.50, 34.59 (q, *J* = 28.3 Hz), 25.71 (q, *J* = 3.3 Hz), 19.16.

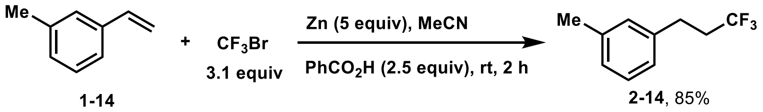
^{19}F NMR (376 MHz, CDCl$_3$): δ -67.38.

IR (neat): 3070, 3026, 2956, 2932, 1497, 1459, 1382, 1309, 1257, 1140, 1081, 810, 758, 743.

MS (EI): *m/z* (%) 188 (M$^+$, 50.44), 105 (100).

HRMS (EI): *m/z* calc'd for $C_{10}H_{11}F_3$ (M)$^+$: 188.0807, found 188.0807.

1-methyl-3-(3,3,3-trifluoropropyl)benzene (2-14, p4-49)



Prepared according to the general procedure using alkene **1-14 (**131 μL, d = 0.901 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (329.5 mg, 5.0 mmol), PhCO$_2$H (306.6 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-14 (**160.0 mg, 85% yield) as a colorless oil.

TLC: R$_f$ = 0.79 in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.5 Hz, 1H), 7.06–6.99 (m, 3H), 2.85–2.81 (m, 2H), 2.44–2.28 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.13, 138.52, 129.17, 128.76, 127.52, 126.93 (q, J = 276.8 Hz), 125.35, 35.84 (q, J = 28.1 Hz), 28.26 (q, J = 3.2 Hz), 21.43.

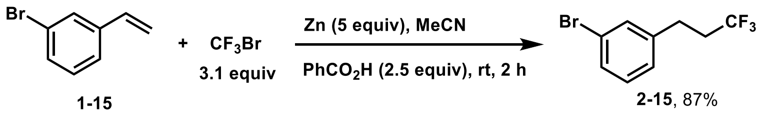
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.25.

IR (neat): 3028, 2951, 2928, 2875, 1612, 1488, 1440, 1384, 1312, 1281, 1261, 1245, 1222, 1110, 847, 700.

MS (EI): *m/z* (%) 188 (M^+, 53.90), 105 (100).

HRMS (ESI^+): *m/z* calc’d for $C_{10}H_{11}F_3$ $(M)^+$: 188.0807, found 188.0805.

1-bromo-3-(3,3,3-trifluoropropyl)benzene (2-15, p4-50)



Prepared according to the general procedure using alkene **1-15** (132 μL, d = 1.406 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (329.3 mg, 5.0 mmol), $PhCO_2H$ (307.5 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-15**[1] (219.0 mg, 87% yield) as a colorless oil.

TLC: R_f = 0.79 in petroleum ether.

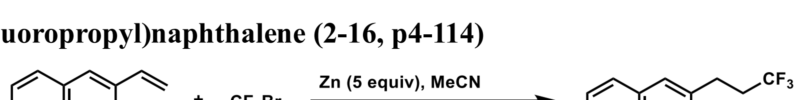
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.21–7.11 (m, 2H), 2.87–2.83 (m, 2H), 2.44–2.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.36, 131.47, 130.41, 129.99, 127.04, 126.64 (q, J = 276.6 Hz), 122.85, 35.50 (q, J = 28.6 Hz), 28.00 (q, J = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.17.

MS (EI): *m/z* (%) 252 (M^+ (^{79}Br), 83.81), 254 (M^+ (^{81}Br), 81.66), 169 (100).

2-(3,3,3-trifluoropropyl)naphthalene (2-16, p4-114)



Prepared according to the general procedure using alkene **1-16** (155.4 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was purified by silica gel chromatography (pentane) to afford **2-16**[1] (130.0 mg, 58% yield) as a white solid.

TLC: R*f* = 0.52 in petroleum ether.

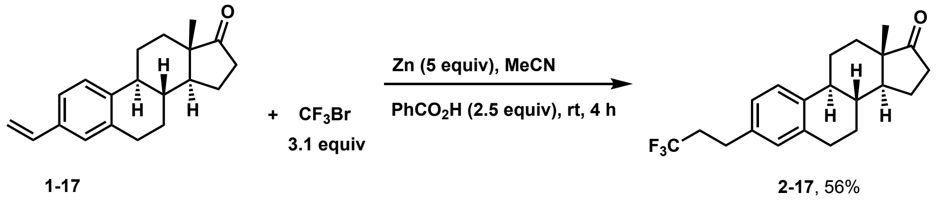
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.78 (m, 3H), 7.65 (s, 1H), 7.50–7.43 (m, 2H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.06–3.02 (m, 2H), 2.55–2.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.56, 133.73, 132.42, 128.56, 127.81, 127.62, 126.89 (q, *J* = 276.7 Hz), 126.74, 126.67, 126.39, 125.80, 35.70 (q, *J* = 28.3 Hz), 28.50 (q, *J* = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -67.10.

MS (EI): *m/z* (%) 224 (M^+, 39.88), 141 (100).

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(3,3,3-trifluoropropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (2-17, p5-18)



Prepared according to the general procedure using alkene **1-17** (283.2 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 4 h at rt, the reaction mixture was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (15 mL × 3), washed with sat. NaCl aq. (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 20:1 to 10:1) to afford **2-17** (196.0 mg, 56% yield) as a white solid.

TLC: R*f* = 0.35 in 10:1 petroleum ether/EtOAc.

m.p.: 59.9~64.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.0 Hz, 1H), 7.01–6.98 (m, 1H), 6.94 (s, 1H), 2.90 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.83–2.79 (m, 2H), 2.54–2.48 (m, 1H), 2.45–2.26 (m, 4H), 2.19–1.93 (m, 4H), 1.68–1.39 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.94, 138.27, 136.99, 136.59, 128.97, 126.86 (q, *J* = 276.5 Hz), 125.84, 125.74, 50.65, 48.12, 44.42, 38.32, 35.98, 35.77 (q, *J* = 28.2 Hz), 31.74, 29.48, 27.76 (q, *J* = 3.3 Hz), 26.62, 25.87, 21.72, 13.97.

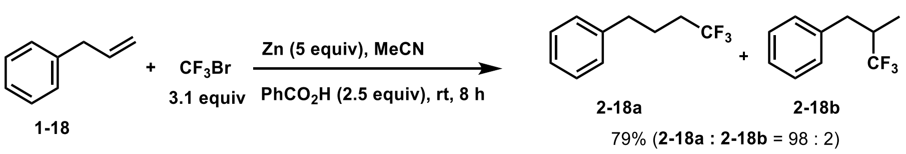
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.25.

IR (neat): 2945, 2922, 2856, 1744, 1500, 1257, 1127, 1096, 975, 888, 823.

MS (ESI): *m/z* (%) 351 ($(M + H)^+$, 5.37), 102 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{21}H_{26}F_3O$ $(M + H)^+$: 351.1930, found 351.1932.

(4,4,4-trifluorobutyl)benzene (2-18a, p4-88)



Prepared according to the general procedure using alkene **1-18 (**133 μL, d = 0.892 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 8 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-18 (**148.0 mg, 79% yield) as a colorless oil. The NMR of **2-18b** is consistent with the literature.[1] The ratio of **2-18a** and **2-18b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-18a[6]

TLC: $R_f = 0.84$ in petroleum ether.

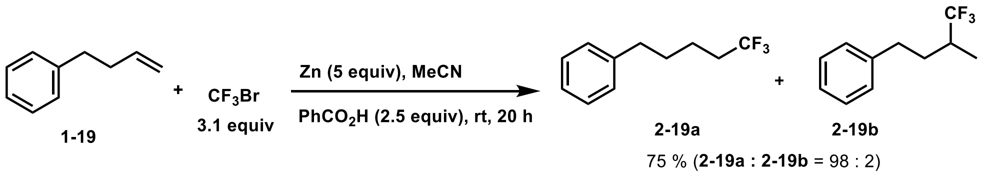
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.23–7.17 (m, 3H), 2.69 (t, $J = 7.6$ Hz, 2H), 2.14–2.02 (m, 2H), 1.94–1.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.84, 128.69, 128.52, 127.37 (q, $J = 276.2$ Hz), 126.40, 34.78, 33.24 (q, $J = 28.3$ Hz), 23.66 (q, $J = 2.8$ Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.70, -74.00 (**2-18b**).

MS (EI): *m/z* (%) 188 (M^+, 21.84), 91 (100).

(5,5,5-trifluoropentyl)benzene (2-19a, p5-59)



Prepared according to the general procedure using alkene **1-19 (**150 μL, d = 0.88 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added basic $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then resulting mixture directly purified by silica gel chromatography (pentane) to afford **2-19 (**151.3 mg, 75% yield) as a colorless oil. The NMR of **2-19b** is consistent with the literature.[7] The ratio of **2-19a** and **2-19b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-19a[8]

TLC: $R_f = 0.75$ in petroleum ether.

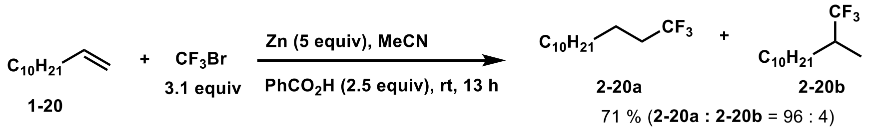
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.22–7.16 (m, 3H), 2.64 (t, $J = 7.5$ Hz, 2H), 2.15–2.03 (m, 2H), 1.74–1.66 (m, 2H), 1.64–1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.85, 128.55, 128.49, 127.35 (q, *J* = 276.4 Hz), 126.09, 35.64, 33.76 (q, *J* = 28.4 Hz), 30.61, 21.69 (q, *J* = 2.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.85, -73.62 (**2-19b**).

MS (EI): *m/z* (%) 202 (M$^+$, 7.14), 91 (100).

1,1,1-trifluorotridecane (2-20a, p4-113)



Prepared according to the general procedure using alkene **1-20 (**222 μL, d = 0.758 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 13 h at rt, the reaction mixture was added basic $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath and sat. Na_2CO_3 aq. (3 mL) for 15 min, then extracted with pentane (15 mL × 3) and concentrated. The residue was purified by silica gel chromatography (pentane) to afford **2-20 (**170.0 mg, 71% yield) as a colorless oil. The ratio of **2-20a** and **2-20b** was calculated as 96:4 by ^{1}H NMR and ^{19}F NMR.

2-20a[9]

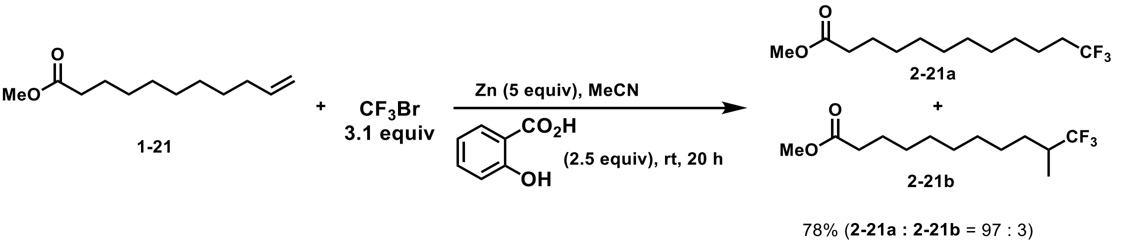
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12–1.99 (m, 2H), 1.58–1.51 (m, 2H), 1.37–1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 127.48 (q, *J* = 276.1 Hz), 33.93 (q, *J* = 28.5 Hz), 32.11, 29.81, 29.75, 29.56, 29.54, 29.38, 28.91, 22.87, 22.03 (q, *J* = 2.9 Hz), 14.25.

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.95, -73.88 (**2-20b**).

MS (EI): *m/z* (%) 238 (M$^+$, 2.37), 57 (100).

methyl 12,12,12-trifluorododecanoate (2-21a, p5-46)



Prepared according to the general procedure using alkene **1-21 (**225 μL, d = 0.882 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with petroleum ether (30 mL). The resulting solution was concentrated, and the residue was dissolved in MeCN (5 mL), and added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath. The resulting solution was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with petroleum ether (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 50:1) to afford **2-21** (209.1 mg, 78% yield) as a light yellow oil. The ratio of **2-21a** and **2-21b** was calculated as 97:3 by ^{1}H NMR and ^{19}F NMR.

2-21a[10]

TLC: R_f = 0.36 in 30:1 petroleum ether/EtOAc.

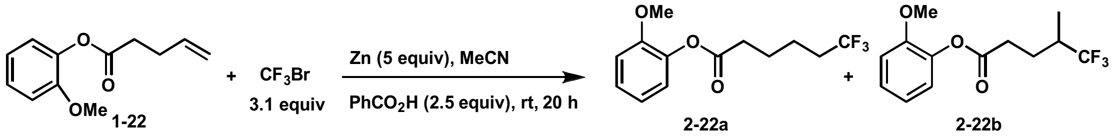
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.12–1.99 (m, 2H), 1.66–1.51 (m, 4H), 1.37–1.28 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 127.34 (q, *J* = 276.3 Hz), 51.31 (t, *J* = 4.3 Hz), 34.06 (t, *J* = 2.7 Hz), 33.74 (q, *J* = 28.4 Hz), 29.37, 29.32, 29.25, 29.20, 29.15, 28.73, 24.97, 21.89.

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.94, -73.87 (**2-21b**).

MS (EI): *m/z* 268 (%) (M^+, 2.28), 74 (100).

2-methoxyphenyl 6,6,6-trifluorohexanoate (2-22a, p4-187)



69% (**2-22a** : **2-22b** = 98 : 2)

Prepared according to the general procedure using alkene **1-22** (214.6 mg, 1.04 mmol), CF_3Br (3.1 mmol), Zn (328.7 mg, 5.0 mmol), $PhCO_2H$ (306.5 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 40:1 to 30:1) to afford **2-22** (198.6 mg, 69% yield) as a light yellow oil. The ratio of **2-22a** and **2-22b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-22a

TLC: R_f = 0.48 in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 1H), 7.02 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.98–6.94 (m, 2H), 3.82 (s, 3H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.24–2.09 (m, 2H), 1.89–1.82 (m, 2H), 1.77–1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 151.20, 139.83, 127.19 (q, *J* = 276.3 Hz), 126.98, 122.81, 120.84, 112.49, 55.77, 33.57, 33.57 (q, *J* = 28.6 Hz), 24.13, 21.40 (q, *J* = 3.1 Hz).

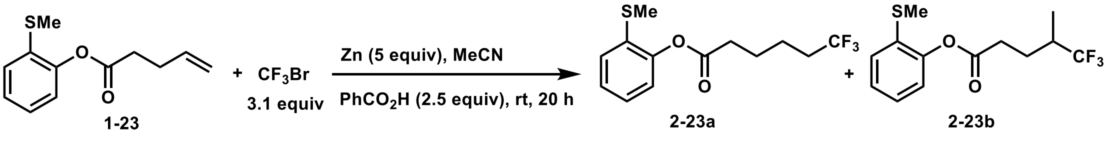
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.89, -73.57 (**2-22b**).

IR (neat): 2957, 2925, 2854, 1763, 1502, 1466, 1458, 1260, 1136, 1112, 1028, 805.

MS (EI): *m/z* (%) 276 (M^+, 2.97), 124 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{13}H_{15}F_3O_3Na$ $(M + Na)^+$: 299.0866, found 299.0871.

2-(methylthio)phenyl 6,6,6-trifluorohexanoate (2-23a, p5-165)



74% (**2-23a** : **2-23b** = 98 : 2)

Prepared according to the general procedure using alkene **1-23** (222.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with EtOAc (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : DCM = 3:1) to afford **2-23** (217.6 mg, 74% yield) as a light yellow oil. The ratio of **2-23a** and **2-23b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-23a

TLC: R_f = 0.33 in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.24–7.17 (m, 2H), 7.03 (dd, *J* = 7.8, 1.7 Hz, 1H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 2.22–2.10 (m, 2H), 1.92–1.84 (m, 2H), 1.77–1.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.98, 148.06, 131.48, 127.23, 127.11 (q, *J* = 276.2 Hz), 126.67, 125.99, 122.36, 33.54, 33.42 (q, *J* = 28.6 Hz), 23.87, 21.44 (q, *J* = 3.2 Hz), 15.09.

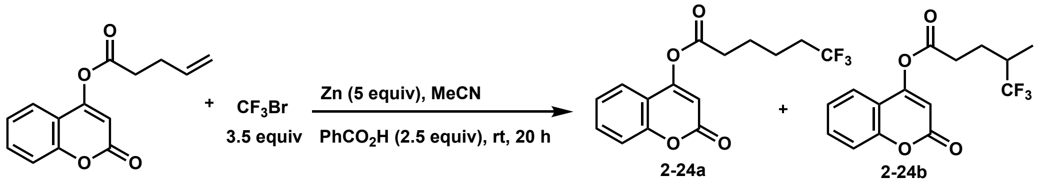
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.85, -73.45 (**2-23b**).

IR (neat): 3068, 2928, 2879, 1763, 1470, 1258, 1201, 1140, 1109, 1071, 1031, 823, 747.

MS (ESI): *m/z* (%) 293 ($(M + H)^+$, 5.90), 102 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{13}H_{15}F_3O_2SNa$ $(M + Na)^+$: 315.0637, found 315.0640.

2-oxo-2*H*-chromen-4-yl 6,6,6-trifluorohexanoate (2-24a, p5-62)



57% (**2-24a** : **2-24b** = 99 : 1)

Prepared according to the general procedure using alkene **1-24** (215.5 mg, 0.88 mmol), CF_3Br (3.5 mmol), Zn (288.6 mg, 4.4 mmol), $PhCO_2H$ (269.1 mg, 2.2 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with EtOAc (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 15:1 (with 5‰ AcOH), 15:1 and 9:1) to afford **2-24** (158.4 mg, 57% yield) as a white solid. The ratio of **2-24a** and **2-24b** was calculated as 99:1 by ^{1}H NMR and ^{19}F NMR.

2-24a

TLC: R$_f$ = 0.66 in 2:1 petroleum ether/EtOAc.

m.p.: 65.6~66.2 ºC.

^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.62 – 7.57 (m, 2H), 7.39 – 7.37 (m, 1H), 7.33 – 7.29 (m, 1H), 6.53 (s, 1H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.24 – 2.12 (m, 2H), 1.93 – 1.86 (m, 2H), 1.77 – 1.69 (m, 2H).

^{13}**C NMR** (101 MHz, CDCl$_3$) δ 168.97, 161.48, 158.29, 153.69, 132.92, 126.98 (q, *J* = 276.2 Hz), 124.46, 122.68, 117.15, 115.42, 105.14, 34.08, 33.47 (q, *J* = 28.9 Hz), 23.64, 21.48 (q, *J* = 2.9 Hz).

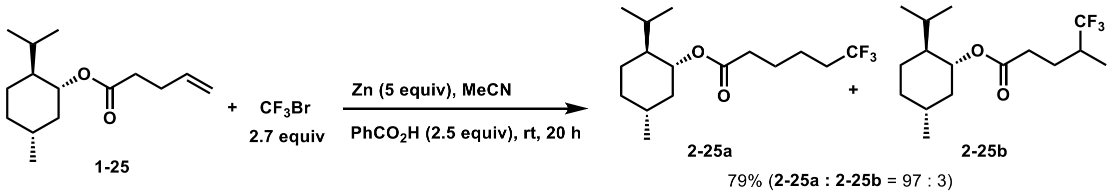
^{19}**F NMR** (376 MHz, CDCl$_3$): δ -66.79, -73.12 (**2-24b**).

IR (neat): 3087, 2959, 2881, 1772, 1733, 1718, 1633, 1377, 1264, 1247, 1207, 1157, 1119, 1105, 1082, 1024, 935, 836, 776, 756.

MS (ESI): *m/z* (%) 315 ((M + H)$^+$, 11.47), 163 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_{15}H_{13}F_3O_4Na$ (M + Na)$^+$: 337.0658, found 337.0659.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 6,6,6-trifluorohexanoate (2-25, p5-63)



Prepared according to the general procedure using alkene **1-25** (272.8 mg, 1.14 mmol), CF$_3$Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. KMnO$_4$ aq. (1 mL) for 15 min in an ice-bath and Na$_2$CO$_3$ aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (15 mL × 3), washed with sat. NaCl aq., dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 50:1) to afford **2-25** (278.1 mg, 79% yield) as a light yellow oil. The ratio of **2-25a** and **2-25b** was calculated as 97:3 by ^{1}H NMR and ^{19}F NMR.

2-25a

TLC: R$_f$ = 0.65 in 1:1 petroleum ether/EtOAc.

^{1}**H NMR** (400 MHz, CDCl$_3$) δ 4.72–4.66 (m, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.16–2.04 (m, 2H), 2.00–1.95 (m, 1H), 1.88–1.80 (m, 1H), 1.75–1.57 (m, 6H), 1.53–1.43 (m, 1H), 1.40–1.33 (m, 1H), 1.08–0.94 (m, 2H), 0.90 (m, 6H), 0.76 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.63, 127.12 (q, *J* = 276.3 Hz), 74.31, 47.14, 41.04, 34.36, 34.22, 33.57 (q, *J* = 28.6 Hz), 31.49, 26.42, 24.21, 23.52, 22.05, 21.53 (q, *J* = 3.1 Hz), 20.78, 16.31.

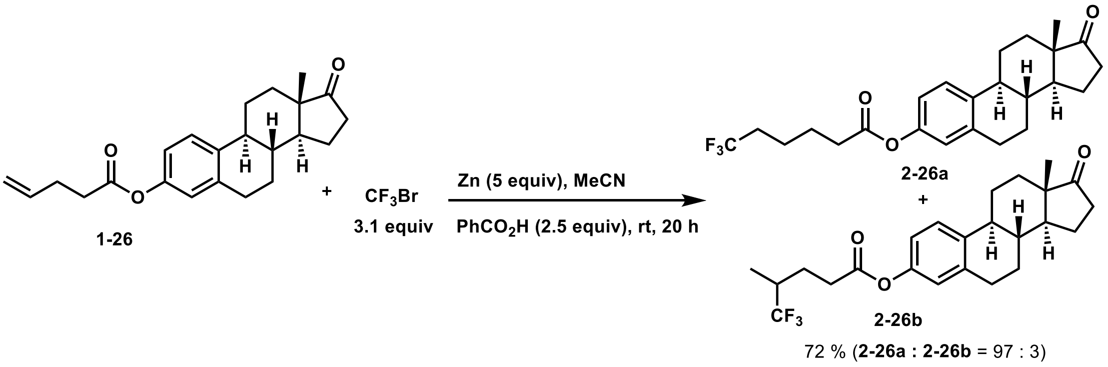
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.95, -73.58 (**2-25b**).

IR (neat): 2959, 2873, 1734, 1458, 1389, 1371, 1256, 1179, 1138, 1115, 1033, 842.

MS (ESI): *m/z* (%) 309 ($(M + H)^+$, 0.20), 102 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{16}H_{27}F_3O_2Na$ $(M + Na)^+$: 331.1855, found 331.1858.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl 6,6,6-trifluorohexanoate (2-26a, p4-178)



Prepared according to the general procedure using alkene **1-26** (350.0 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (329.2 mg, 5.0 mmol), $PhCO_2H$ (308.1 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with EtOAc (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 10:1) to afford **2-26** (304.2 mg, 72% yield) as a white solid. The ratio of **2-26a** and **2-26b** was calculated as 97:3 by ^{1}H NMR and ^{19}F NMR.

2-26a

TLC: R_f = 0.41 in 5:1 petroleum ether/EtOAc.

m.p.: 83.7~85.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 2.93–2,90 (m, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.55–2.48 (m, 1H), 2.44–2.38 (m, 1H), 2.32–2.26 (m, 1H), 2.21–1.93 (m, 6H), 1.87–1.80 (m, 2H), 1.73–1.40 (m, 8H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.73, 171.82, 148.54, 138.10, 137.49, 127.07 (q, *J* = 276.4 Hz), 126.45, 121.54, 118.71, 50.48, 47.98, 44.20, 38.06, 35.88, 33.87, 33.51 (q, *J* = 28.4 Hz), 31.61, 29.45, 26.38, 25.81, 24.00, 21.62, 21.50 (q, *J* = 3.0 Hz), 13.86.

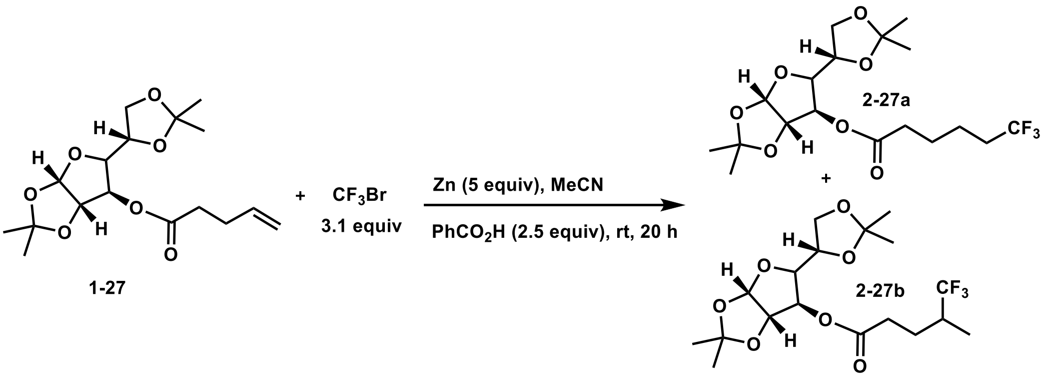
^{19}F NMR (376 MHz, CDCl$_3$): δ -66.86, -73.44 (**2-26b**).

IR (neat): 2956, 2882, 1759, 1735, 1494, 1383, 1321, 1269, 1249, 1224, 1198, 1151, 1087, 1029, 824.

MS (ESI): *m/z* (%) 423 ((M + H)$^+$, 89.54), 280 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_{24}H_{29}F_3O_3Na$ (M + Na)$^+$: 445.1961, found 445.1970.

(3a*S*,6*R*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 6,6,6-trifluorohexanoate (2-27a, p5-84)



59% (**2-27a** : **2-27b** = 97 : 3)

Prepared according to the general procedure using alkene **1-27** (342.4 mg, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. KMnO$_4$ aq. (1 mL) for 15 min in an ice-bath and Na$_2$CO$_3$ aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with EtOAc (15 mL × 3), washed with sat. NaCl aq., dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 20:1 (5 ‰ AcOH), 20:1 and 10:1, respectively) to afford a light yellow oil containing PhCO$_2$H and AcOH. The product was dissolved in DCM (30 mL) and washed with Na$_2$CO$_3$ aq. (0.5 M, 23 mL × 3). The DCM phase was washed with sat. NaCl aq. and dried over Na$_2$SO$_4$. Then solvent was removed to afford **2-27** (243.0 mg, 59% yield) as a light yellow oil. The ratio of **2-27a** and **2-27b** was calculated as 97:3 by ^{1}H NMR and ^{19}F NMR.

2-27a

TLC: R$_f$ = 0.37 in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.87 (d, *J* = 3.7 Hz, 1H), 5.28 (d, *J* = 2.1 Hz, 1H), 4.48 (d, *J* = 3.7 Hz, 1H), 4.21–4.16 (m, 2H), 4.11–4.07 (m, 1H), 4.04–4.00 (m, 1H), 2.45–2.32 (m, 2H), 2.16–2.04 (m, 2H), 1.77–1.68 (m, 2H), 1.66–1.58 (m, 2H), 1.52 (s, 3H), 1.41 (s, 3H), 1.31 (s, 6H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 171.65, 127.06 (q, *J* = 276.2 Hz), 112.41, 109.49, 105.18, 83.50, 79.97, 76.18, 72.55, 67.45, 33.77, 33.51 (q, *J* = 28.6 Hz), 26.93, 26.81, 26.26, 25.25, 23.95, 21.46 (q, *J* = 3.3 Hz).

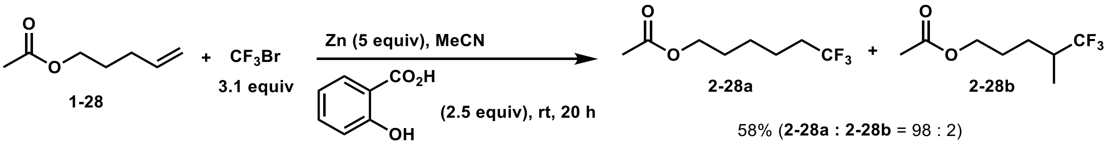
^{19}**F NMR** (376 MHz, $CDCl_3$): δ -66.85, -73.47 (**2-27b**).

IR (neat): 2990, 2941, 2881, 1749, 1458, 1384, 1375, 1259, 1219, 1165, 1138, 1114, 1078, 1026, 847.

MS (ESI): *m/z* (%) 413 ($(M + H)^+$, 0.21), 102 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{18}H_{28}F_3O_7$ $(M + H)^+$: 413.1782, found 413.1775.

6,6,6-trifluorohexyl acetate (2-28a, p5-68)



Prepared according to the general procedure using alkene **1-28** (143 μL, d = 0.911 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was extracted with pentane (20 mL × 4) and the organic phase was concentrated. The residue was dissolved in MeCN (3 mL), added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min. respectively. The resulting solution was washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (pentane) to afford **2-28** (115.2 mg, 58% yield) as a colorless oil. The ratio of **2-28a** and **2-28b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-28a

TLC: R_f = 0.45 in 1:1 petroleum ether/DCM.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.5 Hz, 2H), 2.15–2.03 (m, 4H), 1.70–1.56 (m, 5H), 1.48–1.42 (m, 2H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 171.17, 127.22 (q, *J* = 276.3 Hz), 64.12, 33.67 (q, *J* = 28.6 Hz), 28.31, 25.25, 21.67 (q, *J* = 2.9 Hz), 20.92.

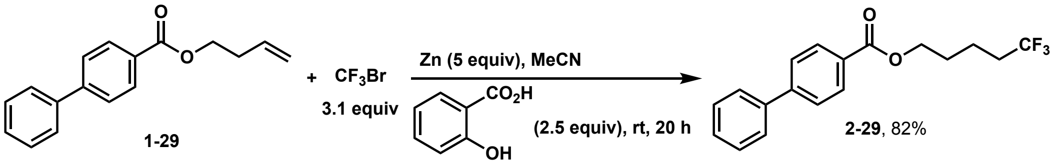
^{19}**F NMR** (376 MHz, $CDCl_3$): δ -66.92, -73.78 (**2-28b**).

IR (neat): 2956, 2928, 2857, 1744, 1391, 1369, 1246, 1144, 1044, 856.

MS (EI): *m/z* (%) 198 (M^+, 0.01), 43 (100).

HRMS (ESI^+): *m/z* calc'd for $C_8H_{13}F_3O_2Na$ $(M + Na)^+$: 221.0760, found 221.0757.

5,5,5-trifluoropentyl [1,1'-biphenyl]-4-carboxylate (2-29, p5-93)



Prepared according to the general procedure using alkene **1-29** (252.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was dissolved in MeCN (5 mL), and added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath. The resulting solution was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether) to afford **2-29** (263.9 mg, 82% yield) as a white solid.

TLC: $R_f = 0.56$ in 10:1 petroleum ether/EtOAc.

m.p.: 56.4~59.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.09 (m, 2H), 7.68–7.62 (m, 2H), 7.63 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.49–7.46 (m, 2H), 7.42–7.38 (m, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 2.25–2.13 (m, 2H), 1.92–1.85 (m, 2H), 1.80–1.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.53, 145.88, 140.09, 130.19, 129.06, 129.01, 128.30, 127.39, 127.21, 127.16 (q, *J* = 276.1 Hz), 64.26, 33.53 (q, *J* = 28.6 Hz), 28.00, 18.95 (q, *J* = 3.0 Hz).

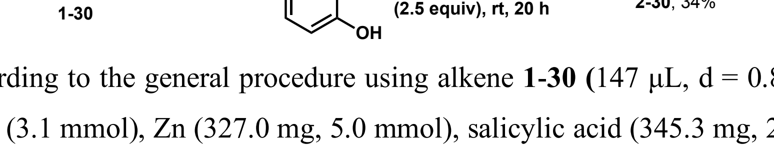
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.86.

IR (neat): 2959, 2926, 2861, 1709, 1610, 1469, 1407, 1295, 1278, 1255, 1072, 1041, 752, 698.

MS (EI): *m/z* (%) 322 (M^+, 7.21), 152 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{18}H_{17}F_3O_2Na$ $(M + Na)^+$: 345.1073, found 345.1075.

3,3,3-trifluoropropyl pivalate (2-30, p5-119)



Prepared according to the general procedure using alkene **1-30** (147 μL, d = 0.866 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with pentane (30 mL). The resulting solution was concentrated, and the residue was dissolved in MeCN (3 mL), and added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath. The resulting solution was filtered through a pad of Celite eluenting with pentane (30 mL) and concentrated. The residue was extracted with pentane (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (pentane) to afford **2-30** **(**66.6 mg, 34% yield) as a colorless oil.

TLC: $R_f = 0.70$ in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30–4.27 (m, 2H), 2.52–2.41 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.27, 126.00 (q, $J = 276.7$ Hz), 57.26 (q, $J = 3.6$ Hz), 38.81, 33.51 (q, $J = 29.1$ Hz), 27.14.

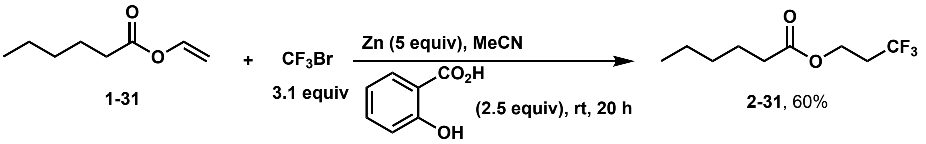
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.47.

IR (neat): 2959, 2922, 2850, 1739, 1662, 1635, 1469, 1378, 1300, 1261, 804.

MS (EI): *m/z* (%) 198 (M^+, 1.03), 57 (100).

HRMS (ESI^+): *m/z* calc'd for $C_8H_{14}F_3O_2$ $(M + H)^+$: 199.0940, found 199.0940.

3,3,3-trifluoropropyl hexanoate (2-31, p5-113)



Prepared according to the general procedure using alkene **1-31** **(**160 μL, d = 0.887 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with pentane (30 mL). The resulting solution was concentrated, and the residue was dissolved in MeCN (5 mL), and added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath. The resulting solution was extracted with pentane (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (pentane) to afford **2-31** **(**127.4 mg, 60% yield) as a colorless oil.

TLC: $R_f = 0.60$ in 1:1 petroleum ether/DCM.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (t, $J = 6.4$ Hz, 2H), 2.52–2.41 (m, 2H), 2.32 (t, $J = 7.5$ Hz, 2H), 1.67–1.59 (m, 2H), 1.35–1.26 (m, 4H), 0.90 (t, $J = 6.7$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54, 125.92 (q, $J = 276.6$ Hz), 57.07 (q, $J = 3.5$ Hz), 34.17, 33.54 (q, $J = 29.2$ Hz), 31.37, 24.62, 22.41, 13.97.

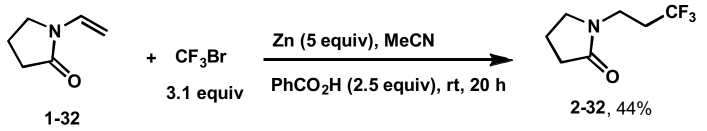
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.54.

IR (neat): 2964, 2936, 2865, 1745, 1388, 1348, 1297, 1260, 1158, 1010, 842.

MS (EI): *m/z* (%) 212 (M^+, 0.64), 43 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_9H_{16}F_3O_2$ $(M + H)^+$: 213.1097, found 213.1095.

1-(3,3,3-trifluoropropyl)pyrrolidin-2-one (2-32, p5-97)



Prepared according to the general procedure using alkene **1-32** (107 µL, d = 1.04 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 (5‰ AcOH), 10:1 and 1:2, respectively) to afford **2-32** (80.5 mg, 44% yield) as a light yellow oil.

TLC: $R_f = 0.31$ in 5:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56–3.51 (m, 2H), 3.46–3.42 (m, 2H), 2.45–2.31 (m, 4H), 2.11–2.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.30, 126.10 (q, $J = 276.8$ Hz), 47.47, 36.31 (q, $J = 3.9$ Hz), 31.68 (q, $J = 28.3$ Hz), 30.70, 18.05.

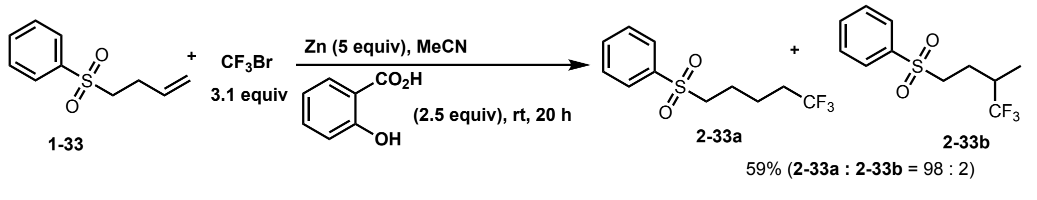
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.96.

IR (neat): 2957, 2938, 2889, 1691, 1255, 1216, 1145, 975, 857.

MS (EI): *m/z* (%) 181 (M$^+$, 59.76), 98 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_7H_{10}F_3NONa$ $(M + Na)^+$: 204.0607, found 204.0605

((5,5,5-trifluoropentyl)sulfonyl)benzene (2-33a, p6-3)



Prepared according to the general procedure using alkene **1-33** (196.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was dissolved in MeCN (3 mL) and added sat. $KMnO_4$ aq. (3 mL) for 15 min in an ice-bath. The reaction mixture was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL

× 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether:DCM = 1:2) to afford **2-33** (158.0 mg, 59% yield) as a light yellow solid. The ratio of **2-33a** and **2-33b** was calculated as 98:2 by ^{1}H NMR and ^{19}F NMR.

2-33a

TLC: R_f = 0.29 in 1:3 petroleum ether/DCM.

m.p.: 48.0~49.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.8 Hz, 2H), 2.14–2.02 (m, 2H), 1.86–1.78 (m, 2H), 1.70–1.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.01, 133.96, 129.48, 128.09, 126.77 (q, *J* = 276.4 Hz), 55.78, 33.30 (q, *J* = 28.8 Hz), 21.96, 20.91 (q, *J* = 3.2 Hz).

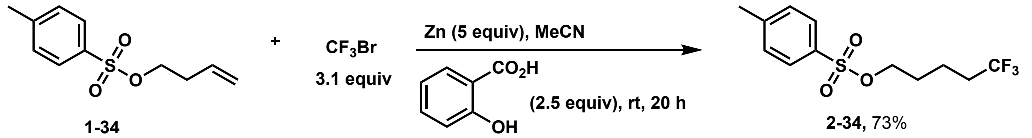
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.79, -73.34 (**2-33b**).

IR (neat): 3062, 2994, 2932, 2877, 1729, 1470, 1448, 1410, 1365, 1320, 1288, 1262, 1233, 1150, 1084, 1058, 1017, 929, 890, 836, 723, 689, 657, 606, 529.

MS (ESI): *m/z* (%) 267 ($(M + H)^+$, 81.42), 102 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{11}H_{13}F_3O_2SNa$ $(M + Na)^+$: 289.0481, found 289.0482.

5,5,5-trifluoropentyl 4-methylbenzenesulfonate (2-34, p5-162)



1-34

2-34, 73%

Prepared according to the general procedure using alkene **1-34** (226.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with EtOAc (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 20:1) to afford **2-34** (216.1 mg, 73% yield) as a light yellow oil. The regio-selectivity is more than 99:1 if 2-CF_3 product was existed based on ^{19}F NMR.

2-34[11]

TLC: R_f = 0.31 in 10:1 petroleum ether/EtOAc.

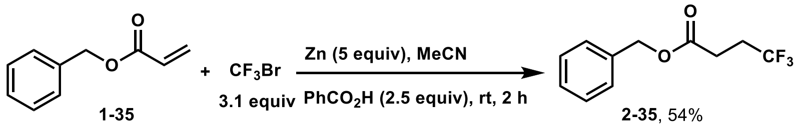
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.37–7.35 (m, 2H), 4.05 (t, *J* = 6.1 Hz, 2H), 2.46 (s, 3H), 2.10–1.97 (m, 2H), 1.77–1.70 (m, 2H), 1.64–1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.12, 133.01, 130.04, 127.97, 126.96 (q, *J* = 276.3 Hz), 69.68, 33.10 (q, *J* = 28.9 Hz) 27.95, 21.68, 18.34 (q, *J* = 3.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.90.

MS (ESI): *m/z* (%) 297 ((M + H)$^+$, 0.20), 274 (100).

benzyl 4,4,4-trifluorobutanoate (2-35, p4-94)



Prepared according to the general procedure using alkene **1-35** (150 μL, d = 1.08 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added basic $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min, then filtered through a pad of Celite eluenting with DCM (30 mL). Then solution dissolved in DCM (40 mL), washed with H_2O (10 mL) containing Na_2CO_3 aq. (2 mL) 3 times, washed with sat. NaCl aq., and dried over Na_2SO_4. The residue was purified by silica gel chromatography (pentane : DCM = 4:1) to afford **2-35** (126.0 mg, 54% yield) as a light yellow oil.

TLC: $R_f = 0.56$ in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 5H), 5.15 (s, 2H), 2.65–2.62 (m, 2H), 2.54–2.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.88, 135.60, 128.76, 128.59, 128.45, 126.59 (q, *J* = 275.7 Hz), 67.04, 29.45 (q, *J* = 30.1 Hz), 27.26 (q, *J* = 3.2 Hz).

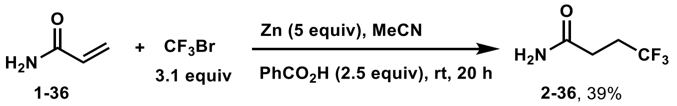
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.54.

IR (neat): 3037, 2965, 2936, 2854, 1744, 1446, 1378, 1330, 1264, 1230, 1187, 1142, 1111, 985, 752, 698.

MS (EI): *m/z* (%) 232 (M$^+$, 22.07), 108 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_{11}H_{11}F_3O_2Na$ $(M + Na)^+$: 255.0603, found 255.0606.

4,4,4-trifluorobutanamide (2-36, p5-146)



Prepared according to the general procedure using alkene **1-36** (71.1 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL). The resulting solution was concentrated, and the residue was extracted with EtOAc (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 (5‰ AcOH), 2:1 and 1:3, respectively) to afford **2-36** (54.7 mg, 39% yield) as a white solid.

TLC: $R_f = 0.75$ in 1:5 petroleum ether/EtOAc.

m.p.: 135.5~136.9 ºC.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (s, 1H), 6.94 (s, 1H), 2.48–2.40 (m, 2H), 2.31 (t, J = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.24, 127.51 (q, J = 276.0 Hz), 28.53 (q, J = 28.5 Hz), 27.29 (q, J = 2.7, 2.3 Hz).

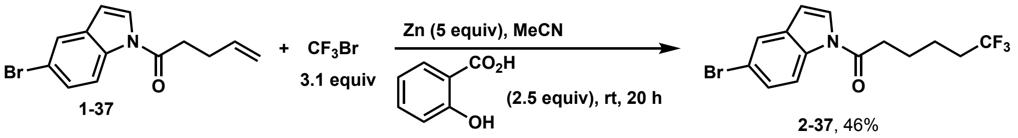
^{19}F NMR (376 MHz, DMSO-d_6): δ -64.79.

IR (neat): 3373, 3204, 2964, 2927, 2855, 1666, 1636, 1447, 1379, 1316, 1291, 1252, 1231, 1148, 1106, 984, 701, 589, 481.

MS (ESI): *m/z* (%) 142 ((M + H)$^+$, 142 (100)).

HRMS (ESI$^+$): *m/z* calc'd for $C_4H_7F_3NO$ (M + H)$^+$: 142.0474, found 142.0474.

1-(5-bromo-1*H*-indol-1-yl)-6,6,6-trifluorohexan-1-one (2-37, p5-179)



Prepared according to the general procedure using alkene **1-37** (278.2 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 25:1 to 20:1) to afford **2-37** (159.0 mg, 46% yield) as a light yellow solid.

TLC: $R_f = 0.33$ in 10:1 petroleum ether/EtOAc.

m.p.: 74.1~75.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 1.9 Hz, 1H), 7.46–7.44 (m, 2H), 6.59 (d, J = 3.8 Hz, 1H), 2.95 (t, J = 7.2 Hz, 2H), 2.24–2.12 (m, 2H), 1.97–1.89 (m, 2H), 1.77–1.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 134.44, 132.15, 128.14, 127.09 (q, J = 276.3 Hz), 125.52, 123.66, 118.10, 117.12, 108.56, 35.24, 33.75 (q, J = 28.8 Hz), 23.51, 21.71 (q, J = 3.0 Hz).

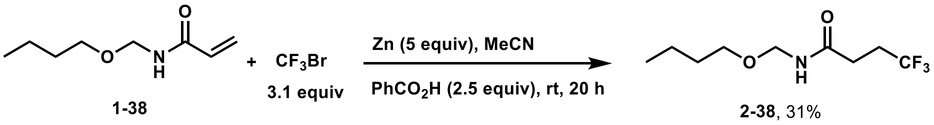
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.82.

IR (neat): 3116, 2953, 2925, 2875, 1704, 1535, 1467, 1445, 1395, 1390, 1309, 1274, 1261, 1245, 1201, 1132, 1114, 1040, 1029, 934, 874, 821, 778, 762, 736, 716.

MS (ESI): *m/z* (%) 347 ((M + H)$^+$ (^{79}Br), 0.21), 349 ((M + H)$^+$ (^{81}Br), 7.21), 102 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_{14}H_{14}BrF_3NO$ [M + H]$^+$: 348.0205 (^{79}Br), found 348.0204; 350.0184 (^{81}Br), found 350.0186.

N-(butoxymethyl)-4,4,4-trifluorobutanamide (2-38, p5-139)



Prepared according to the general procedure using alkene **1-38** (162 μL, d = 0.96 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 (5‰ AcOH), 10:1 and 2:1, respectively) to afford **2-38** (71.3 mg, 31% yield) as a light yellow oil.

TLC: R_f = 0.62 in 1:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.08 (s, 1H), 4.74 (d, *J* = 6.7 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.54–2.47 (m, 4H), 1.58–1.51 (m, 2H), 1.40–1.31 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 170.63, 126.85 (q, *J* = 276.0 Hz), 70.32, 68.71, 31.75, 29.44 (q, *J* = 30.1 Hz), 28.92 (q, *J* = 2.9 Hz), 19.35, 13.93.

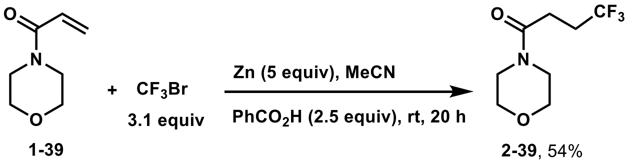
^{19}F NMR (376 MHz, CDCl$_3$): δ -67.33.

IR (neat): 3319, 3079, 2962, 2936, 2876, 1670, 1551, 1449, 1341, 1264, 1142, 1110, 1085, 981, 803.

MS (ESI): *m/z* (%) 228 ((M + H)$^+$, 0.36), 102 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_9H_{16}F_3NO_2Na$ (M + Na)$^+$: 250.1025, found 250.1026.

4,4,4-trifluoro-1-morpholinobutan-1-one (2-39, p5-76)



Prepared according to the general procedure using alkene **1-39** (143 μL, d = 1.122 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was extracted with DCM (15 mL × 3), washed with sat. NaCl aq., dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 (5‰ AcOH), 10:1 and 1:1, respectively) to afford **2-39** (114.0 mg, 54% yield) as a light yellow oil.

TLC: R_f = 0.33 in 1:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71–3.62 (m, 6H), 3.48–3.46 (m, 2H), 2.59–2.46 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.37, 127.04 (q, $J = 275.9$ Hz), 66.74, 66.41, 45.69, 42.16, 29.44 (q, $J = 29.4$ Hz), 25.69 (q, $J = 3.4$ Hz).

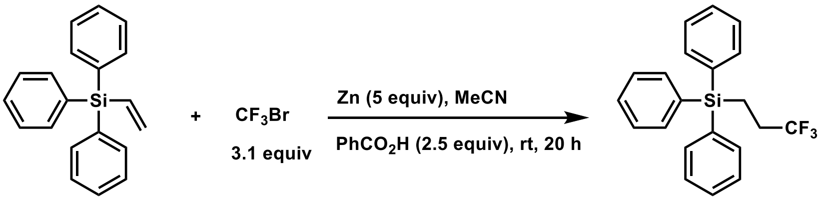
^{19}F NMR (376 MHz, $CDCl_3$): δ -67.14.

IR (neat): 2962, 2923, 2862, 1648, 1466, 1459, 1399, 1315, 1259, 1229, 1136, 1112, 978, 860, 841.

MS (EI): *m/z* (%) 211 (M^+, 0.59), 68 (100).

HRMS (EI): *m/z* calc'd for $C_8H_{12}F_3NO_2$ M^+: 211.0815, found 211.0814.

triphenyl(3,3,3-trifluoropropyl)silane (2-40, p5-191)



1-40 **2-40**, 66%

Prepared according to the general procedure using alkene **1-40** (286.5 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min., and concentrated. The residue was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether) to afford **2-40**[12] (234.6 mg, 66% yield) as a white solid.

TLC: $R_f = 0.63$ in petroleum ether

m.p.: 112.9~113.9 ºC.

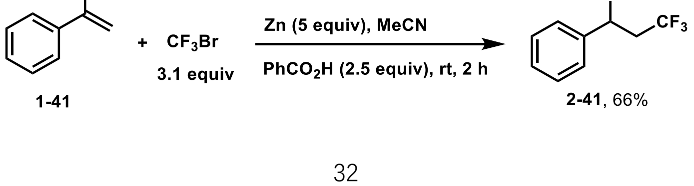
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 6H), 7.46–7.37 (m, 9H), 2.22–2.09 (m, 2H), 1.61–1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.63, 133.67, 130.07, 128.33, 127.81 (q, $J = 276.7$ Hz), 29.18 (q, $J = 30.0$ Hz), 5.47 (q, $J = 2.3$ Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -69.13.

MS (EI): *m/z* (%) 356 (M^+, 0.47), 258 (100).

(4,4,4-trifluorobutan-2-yl)benzene (2-41, p4-87)



1-41 **2-41**, 66%

Prepared according to the general procedure using alkene **1-41** (130 µL, d = 0.909 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.5 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-41**[1] (124.0 mg, 66% yield) as a colorless oil.

TLC: $R_f = 0.86$ in petroleum ether.

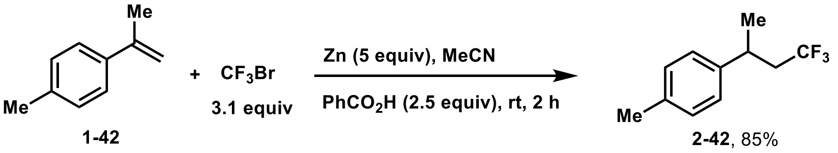
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.25–7.19 (m, 3H), 3.17–3.08 (m, 1H), 2.57–2.26 (m, 2H), 1.36 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.43, 128.82, 126.83, 126.80 (q, *J* = 277.6 Hz), 126.75, 41.81 (q, *J* = 27.2 Hz), 34.32 (q, *J* = 2.6 Hz), 22.26.

^{19}F NMR (376 MHz, $CDCl_3$): δ -64.43.

MS (EI): *m/z* (%) 188 (M^+, 37.33), 105 (100).

1-methyl-4-(4,4,4-trifluorobutan-2-yl)benzene (2-42, p6-56)



Prepared according to the general procedure using alkene **1-42** (152 µL, d = 0.904 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-42** (172.4 mg, 85% yield) as a colorless oil.

TLC: $R_f = 0.50$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.08 (m, 4H), 3.13–3.04 (m, 1H), 2.48–2.24 (m, 5H), 1.34 (dd, *J* = 7.0, 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.48, 136.36, 129.49, 126.85 (q, *J* = 277.5 Hz), 126.61, 41.87 (q, *J* = 27.1 Hz), 33.91 (q, *J* = 2.8 Hz), 22.33, 21.09.

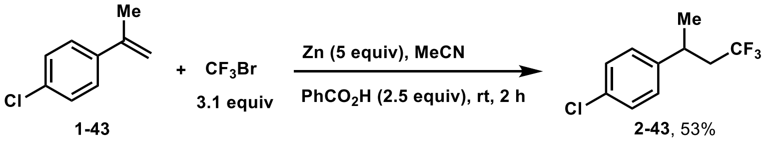
^{19}F NMR (376 MHz, $CDCl_3$): δ -64.41.

IR (neat): 2972, 2927, 2858, 1374, 1277, 1254, 1149, 1085, 1033, 814.

MS (EI): *m/z* (%) 202 (M^+, 30.72), 119 (100).

HRMS (EI): *m/z* calc'd for $C_{11}H_{13}F_3$ $(M)^+$: 202.0964, found 202.0962.

1-chloro-4-(4,4,4-trifluorobutan-2-yl)benzene (2-43, p6-57)



Prepared according to the general procedure using alkene **1-43** (143 μL, d = 1.065 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-43** (117.9 mg, 53% yield) as a colorless oil.

TLC: $R_f = 0.67$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.15–7.12 (m, 2H), 3.15–3.06 (m, 1H), 2.47–2.22 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.76, 132.53, 128.96, 128.15, 126.61 (q, *J* = 277.5 Hz), 41.69 (q, *J* = 27.2 Hz), 33.84 (q, *J* = 2.9 Hz), 22.27.

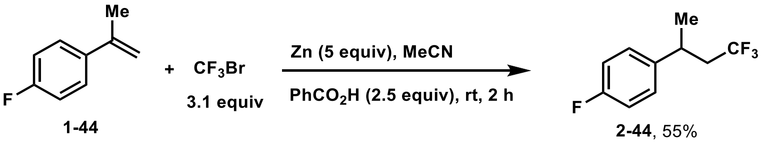
^{19}F NMR (376 MHz, $CDCl_3$): δ -64.41.

IR (neat): 2975, 2934, 2856, 1495, 1374, 1279, 1257, 1149, 1127, 1015, 827.

MS (EI): *m/z* (%) 222 (M^+, 34.81), 139 (100).

HRMS (EI): *m/z* calc'd for $C_{10}H_{10}ClF_3$ $(M)^+$: 222.0418, found 222.0421.

1-fluoro-4-(4,4,4-trifluorobutan-2-yl)benzene (2-44, p6-58)



Prepared according to the general procedure using alkene **1-44** (135 μL, d = 1.01 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-44** (113.7 mg, 55% yield) as a colorless oil.

TLC: $R_f = 0.52$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 2H), 7.03–6.97 (m, 2H), 3.16–3.07 (m, 1H), 2.46–2.25 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.75 (d, *J* = 244.5 Hz), 141.02 (d, *J* = 3.4 Hz), 128.20 (d, *J* = 7.9 Hz), 126.67 (q, *J* = 277.4 Hz), 115.59 (d, *J* = 21.3 Hz), 41.92 (q, *J* = 27.2 Hz), 33.70 (q, *J* = 2.6 Hz), 22.41.

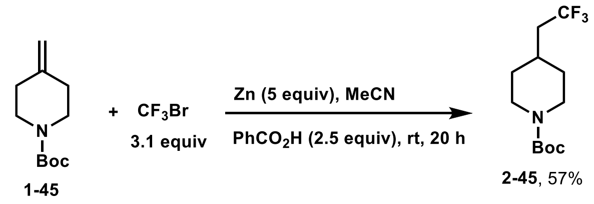
^{19}F NMR (376 MHz, $CDCl_3$): δ -64.42, -116.93.

IR (neat): 2970, 2927, 2857, 1607, 1513, 1374, 1254, 1232, 1148, 834.

MS (EI): *m/z* (%) 206 (M^+, 32.49), 123 (100).

HRMS (EI): *m/z* calc'd for $C_{10}H_{10}F_4$ $(M)^+$: 206.0713, found 206.0711.

tert-butyl 4-(2,2,2-trifluoroethyl)piperidine-1-carboxylate (2-45, p5-79)



Prepared according to the general procedure using alkene **1-45** (197 μL, d = 1.0 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min., and concentrated. The residue was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford **2-45**[10] (151.4 mg, 57% yield) as a light yellow oil.

TLC: R_f = 0.34 in 10:1 petroleum ether/EtOAc.

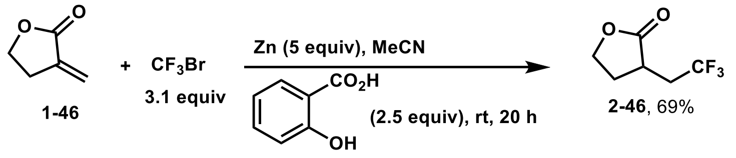
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (br s, 2H), 2.72 (t, *J* = 12.9 Hz, 2H), 2.09–1.99 (m, 2H), 1.88–1.74 (m, 3H), 1.46 (s, 9H), 1.30–1.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.80, 126.90 (q, *J* = 277.3 Hz), 79.56, 43.63, 40.14 (q, *J* = 27.4 Hz), 31.99, 30.66 (q, *J* = 2.8 Hz), 28.49.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.81.

MS (EI): *m/z* (%) 166 ($(M–Boc)^+$, 1.18), 57 (100).

3-(2,2,2-trifluoroethyl)dihydrofuran-2(3*H*)-one (2-46, p5-166)



Prepared according to the general procedure using alkene **1-46** (88 μL, d = 1.119 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL). The resulting solution was concentrated, and the residue was extracted with EtOAc (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 8:1) to afford **2-46** (116.4 mg, 69% yield) as a light yellow oil.

TLC: R_f = 0.36 in 8:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (t, *J* = 9.1 Hz, 1H), 4.26–4.20 (m, 1H), 2.94–2.80 (m, 2H), 2.63–2.56 (m, 1H), 2.22–2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.79, 126.38 (q, *J* = 276.2 Hz), 66.80, 34.90 (q, *J* = 29.9 Hz), 34.61 (q, *J* = 2.8 Hz), 29.35.

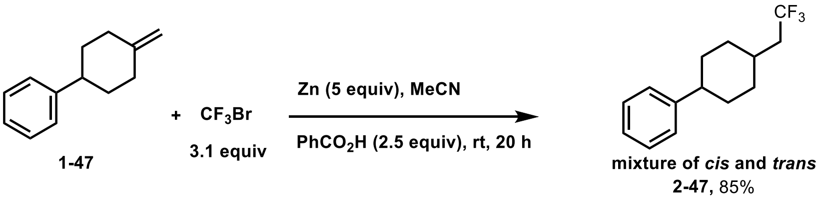
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.96.

IR (neat): 2958, 2922, 2853, 1774, 1727, 1378, 1286, 1255, 1179, 1137, 1043, 1024, 960, 753, 742.

MS (EI): *m/z* (%) 168 (M^+, 0.38), 61 (100).

HRMS (ESI^+): *m/z* calc'd for $C_6H_8F_3O_2$ $(M + H)^+$: 169.0471, found 169.0468.

(4-(2,2,2-trifluoroethyl)cyclohexyl)benzene (2-47, p5-48)



Prepared according to the general procedure using alkene **1-47** (172.9 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then filtered through a pad of Celite eluenting with DCM (30 mL). The resulting solution was concentrated, and the residue was directly purified by silica gel chromatography (petroleum ether) to afford **2-47** (206.3 mg, 85% yield) mixture (*cis* and *trans*) as a colorless oil.

TLC: R_f = 0.55 in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.24–7.17 (m, 3H), 2.63–2.44 (m, 1H), 2.26–2.16 (m, 1H), 2.09–1.91 (m, 4H), 1.81–1.60 (m, 3H), 1.53–1.43 (m, 1H), 1.26–1.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.19, 146.81, 128.51, 127.71 (q, *J* = 277.2 Hz), 127.31 (q, J = 277.3 Hz), 126.96, 126.90, 126.16, 126.11, 127.31 (q, *J* = 277.3 Hz), 44.01, 43.14, 40.89 (q, *J* = 27.1 Hz), 36.24 (q, *J* = 26.9 Hz), 33.92, 33.47, 31.98 (q, *J* = 2.2 Hz), 30.32, 28.74, 27.60 (q, *J* = 2.2 Hz).

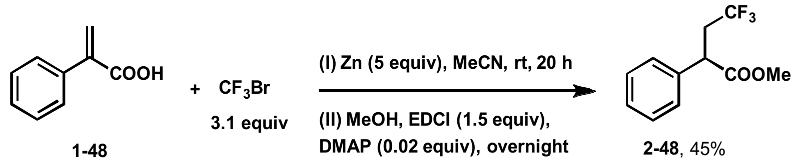
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.72, -64.58.

IR (neat): 3028, 2928, 2858, 1452, 1261, 1233, 1161, 1139, 1113, 1050, 833, 756, 699.

MS (EI): *m/z* (%) 242 (M^+, 2.77), 91 (100).

HRMS (EI): *m/z* calc'd for $C_{14}H_{17}F_3$ $(M)^+$: 242.1282, found 242.2848.

methyl 4,4,4-trifluoro-2-phenylbutanoate (2-48, p7-42)



Step I: Prepared according to the general procedure using alkene **1-48** (148.1 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.2 mg, 5.0 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with EtOAc (30 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated.

Step II: The mixture was dissolved in MeOH (3 mL), added EDCI (290.2 mg, 1.5 mmol) and DMAP (2.6 mg). After stirring for overnight, MeOH was removed by concentration, the mixture was dissolved in MeCN (3 mL), and added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath. The solution was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (30 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The reaction mixture was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford **2-48** (105.4 mg, 45%) as a light yellow oil.

TLC: $R_f = 0.55$ in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 3.90 (dd, J = 8.8, 5.4 Hz, 1H), 3.69 (s, 3H), 3.18–3.05 (m, 1H), 2.55–2.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 137.16, 129.14, 128.14, 127.67, 126.12 (q, J = 277.0 Hz), 52.63, 45.31 (q, J = 2.9 Hz), 37.45 (q, J = 28.8 Hz).

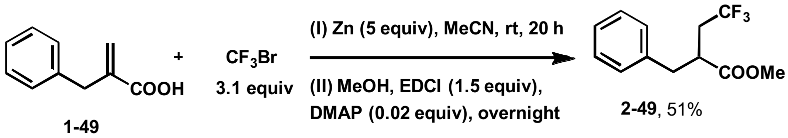
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.92.

IR (neat): 3036, 2958, 2850, 1744, 1457, 1438, 1388, 1341, 1327, 1264, 1208, 1142, 1118, 699.

MS (EI): *m/z* (%) 232 (M^+, 47.45), 109 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{11}H_{11}F_3O_2Na$ $(M + Na)^+$: 255.0603, found 255.0604.

methyl 2-benzyl-4,4,4-trifluorobutanoate (2-49, p7-40)



Step I: Prepared according to the general procedure using alkene **1-49** (162.5 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (329.2 mg, 5.0 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with Et_2O (30 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated.

Step II: The mixture was dissolved in MeOH (3 mL), added EDCI (290.1 mg, 1.5 mmol) and DMAP (2.6 mg). After stirring for overnight, MeOH was removed by concentration, the mixture was dissolved in MeCN (3 mL), and added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath. The solution was filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with Et_2O (30 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford **2-49** (125.6 mg, 51%) as a light yellow oil.

TLC: $R_f = 0.64$ in 10:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 7.4$ Hz, 2H), 3.64 (s, 3H), 3.04–2.96 (m, 2H), 2.85–2.79 (m, 1H), 2.67–2.54 (m, 1H), 2.26–2.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.90, 137.35, 128.97, 128.75, 127.10, 126.31 (q, $J = 276.7$ Hz), 52.04, 41.39 (q, $J = 2.1$ Hz), 38.33, 35.17 (q, $J = 29.1$ Hz).

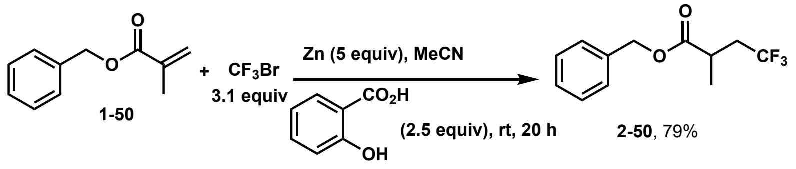
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.67.

IR (neat): 3068, 2958, 2856, 1744, 1438, 1379, 1258, 1169, 1144, 1107, 803, 701.

MS (EI): *m/z* (%) 246 (M^+, 57.19), 90 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{12}H_{13}F_3O_2Na$ $(M + Na)^+$: 269.0760, found 269.0762.

benzyl 4,4,4-trifluoro-2-methylbutanoate (2-50, p5-36)



Prepared according to the general procedure using alkene **1-50** (169 μL, d = 1.04 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min., and concentrated. The residue was extracted with EtOAc (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether) to afford **2-50** (194.7 mg, 79% yield) as a light yellow oil.

TLC: $R_f = 0.38$ in 80:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 5H), 5.15 (s, 2H), 2.89–2.80 (m, 1H), 2.75–2.61 (m, 1H), 2.23–2.10 (m, 1H), 1.31 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.27, 135.75, 128.70, 128.46, 128.27, 126.44 (q, $J = 276.7$ Hz), 66.95, 37.05 (q, $J = 28.8$ Hz), 34.19 (q, $J = 2.7$ Hz), 17.55.

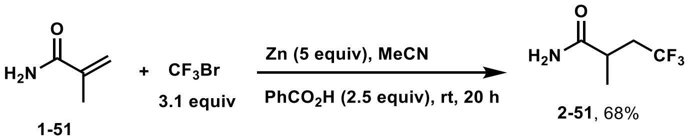
^{19}F NMR (376 MHz, $CDCl_3$): δ -65.34.

IR (neat): 3037, 2957, 2851, 1743, 1258, 1159, 1032, 803, 751, 698.

MS (EI): *m/z* (%) 246 (M^+, 13.62), 91 (100).

HRMS (EI): *m/z* calc'd for $C_{12}H_{13}F_3O_2$ $(M)^+$: 246.0862, found 246.0864.

4,4,4-trifluoro-2-methylbutanamide (2-51, p5-156)



Prepared according to the general procedure using alkene **1-51** (85.1 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL). The resulting solution was concentrated, and the residue was extracted with EtOAc (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 (5‰ AcOH), 2:1 and 1:3, respectively) to afford **2-51** (104.9 mg, 68% yield) as a white solid.

TLC: $R_f = 0.54$ in 1:5 petroleum ether/EtOAc.

m.p.: 91.0~91.8 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (s, 1H), 6.88 (s, 1H), 2.66–2.53 (m, 2H), 2.26–2.14 (m, 1H), 1.10 (d, $J = 6.1$ Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 175.50, 127.06 (q, $J = 276.9$ Hz), 35.92 (q, $J = 27.2$ Hz), 33.62 (q, $J = 2.9$ Hz), 18.46.

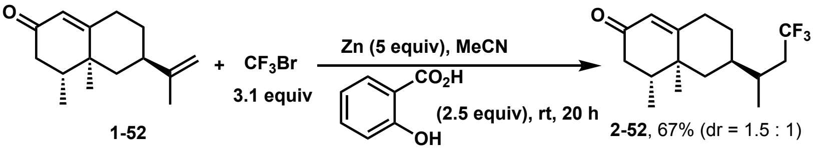
^{19}F NMR (376 MHz, DMSO-d_6): δ -62.98.

IR (neat): 3368, 3184, 2984, 2923, 1669, 1636, 1371, 1325, 1294, 1270, 1246, 1179, 1149, 1131, 1108, 1057, 1023, 836, 661.

MS (ESI): *m/z* (%) 156 ($(M + H)^+$, 156 (100)).

HRMS (ESI^+): *m/z* calc'd for $C_5H_8F_3NONa$ $(M + Na)^+$: 178.0450, found 178.0450.

(4*R*,4a*S*,6*R*)-4,4a-dimethyl-6-((*S*)-4,4,4-trifluorobutan-2-yl)-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (2-52, p6-36)



Prepared according to the general procedure using alkene **1-52** (218.3 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 7:1) to afford **2-52**[13] (193.2 mg, 67% yield, dr 1.5 : 1) as a light yellow oil. Less than 2% of isomer (if any) was observed in ^{19}F NMR.

TLC: $R_f = 0.69$ in 2:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$, dr = 1.5 : 1) δ 5.76 (s, 1H), 2.51–2.33 (m, 2H), 2.30–2.10 (m, 3H), 2.04–1.71 (m, 5H), 1.33–1.11 (m, 3H), 1.09 (d, J = 3.2 Hz, 3H), 1.01–0.97 (m, 6H).

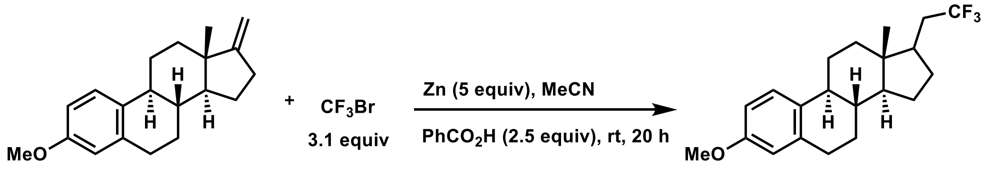
^{13}C NMR (101 MHz, $CDCl_3$, dr = 1.5 : 1) δ 199.43, 170.23, 127.43 (q, J = 277.2 Hz), 124.74, 124.71, 42.39, 42.07, 40.62, 40.59, 40.54, 39.32, 39.20, 38.12 (q, J = 27.1 Hz), 37.67 (q, J = 27.2 Hz), 37.53, 37.40, 32.97, 32.84, 32.09-31.94 (m), 29.82, 28.12, 16.91, 16.90, 16.40, 16.09, 14.95, 14.93.

^{19}F NMR (376 MHz, $CDCl_3$, dr = 1.5 : 1): δ -63.97, -64.05.

MS (EI): *m/z* (%) 288 (M^+, 16.17), 91 (100).

HRMS (ESI^+): *m/z* calc'd for $C_{16}H_{23}F_3ONa$ $(M + Na)^+$: 311.1593, found 311.1590.

(8*S*,9*S*,13*R*,14*S*)-3-methoxy-13-methyl-17-(2,2,2-trifluoroethyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene (2-53, p5-32)



Prepared according to the general procedure using alkene **1-53** (282.2 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min., and filtered through a pad of Celite eluenting with EtOAc (30 mL) and concentrated. The residue was extracted with EtOAc (15 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether) to afford **2-53**[13] (173.7 mg, 49% yield) as a white solid.

TLC: $R_f = 0.67$ in 10:1 petroleum ether/EtOAc.

m.p.: 102.9~105.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, dr = 93 : 7) δ 7.20 (d, J = 8.5 Hz, 1H), 6.71 (dd, J = 8.5, 2.9 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 2.95–2.79 (m, 2H), 2.35–2.15 (m, 3H), 2.09–2.00 (m, 1H), 1.94–1.78 (m, 4H), 1.73–1.65 (m, 1H), 1.51–1.36 (m, 4H), 1.33–1.21 (m, 4H), 0.63 (s, 3H).

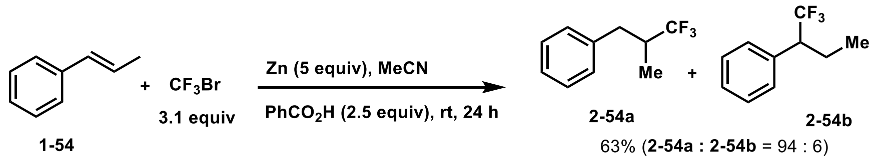
^{13}C NMR (101 MHz, CDCl$_3$, dr = 93 : 7) δ 157.64, 138.11, 132.77, 127.97 (q, *J* = 276.9 Hz), 126.38, 113.98, 111.60, 55.30, 54.22, 44.25 (q, *J* = 2.4 Hz), 44.14, 42.76, 38.98, 37.25, 34.69 (q, *J* = 27.6 Hz), 29.98, 28.65, 27.94, 26.44, 24.58, 12.55.

^{19}F NMR (376 MHz, CDCl$_3$, dr = 93 : 7): δ -59.20, -64.80.

MS (ESI): *m/z* (%) 353 ((M + H)$^+$, 1.89), 102 (100).

HRMS (ESI$^+$): *m/z* calc'd for $C_{21}H_{28}F_3O$ (M + H)$^+$: 353.2087, found 353.2086.

(3,3,3-trifluoro-2-methylpropyl)benzene (2-54a, p4-77)



Prepared according to the general procedure using alkene **1-54** (130 μL, d = 0.911 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.5 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 24 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then filtered through a pad of Celite eluenting with pentane (30 mL). The resulting solution was concentrated, and the residue was purified by silica gel chromatography (pentane) to afford **2-54** (119.0 mg, 63% yield) as a colorless oil. The **2-54b** was consistent with the literature.[14] The ratio of **2-54a** and **2-54b** was calculated as 94:6 by ^{1}H NMR and ^{19}F NMR.

2-54a[1]

TLC: R$_f$ = 0.84 in petroleum ether.

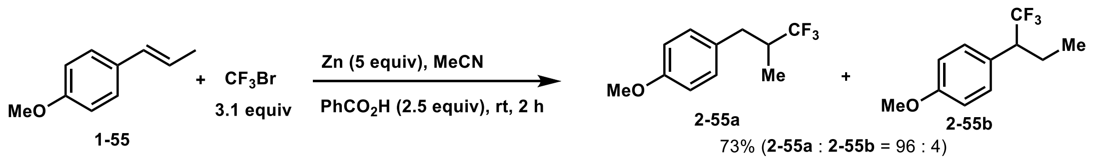
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34–7.30 (m, 2H), 7.25–7.22 (m, 1H), 7.18–7.16 (m, 2H), 3.17–3.08 (m, 1H), 2.49–2.40 (m, 2H), 1.02 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 138.30, 129.24, 128.71, 128.34 (q, *J* = 279.5 Hz), 126.76, 40.20 (q, *J* = 26.3 Hz), 35.79 (q, *J* = 2.7 Hz), 12.21 (q, *J* = 2.9 Hz).

^{19}F NMR (376 MHz, CDCl$_3$): δ -70.22 (**2-54b**), -74.00.

MS (EI): *m/z* (%) 188 (M$^+$, 26.66), 91 (100).

1-methoxy-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2-55, p4-25)



Prepared according to the general procedure using alkene **1-55** (150 μL, d = 0.988 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then filtered through a pad of Celite eluenting with DCM (30 mL).

The resulting solution was concentrated, and extracted with Et_2O (15 mL × 3). The combined Et_2O phase was washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether) to afford **2-55 (**160.0 mg, 73% yield) as a light yellow oil. The ratio of **2-55a** and **2-55b** was calculated as 96:4 by ^{1}H NMR and ^{19}F NMR.

2-55a[15]

TLC: $R_f = 0.46$ in petroleum ether.

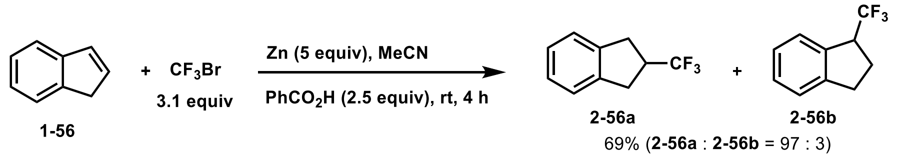
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.06 (m, 2H), 6.87–6.83 (m, 2H), 3.81 (s, 3H), 3.09–3.01 (m, 1H), 2.43–2.33 (m, 2H), 1.01 (d, $J = 6.3$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.49, 130.28, 130.19, 128.36 (q, $J = 279.6$ Hz), 114.11, 55.38, 40.34 (q, $J = 25.9$ Hz), 34.88 (q, $J = 2.5$ Hz), 12.16 (q, $J = 2.6$ Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -70.65 (**2-55b**), -73.93.

MS (EI): *m/z* (%) 218 (M^+, 18.83), 121 (100).

2-(trifluoromethyl)-2,3-dihydro-1H-indene (2-56a, p4-124)



Prepared according to the general procedure using alkene **1-56 (**117 μL, d = 0.996 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 4 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then filtered through a pad of Celite eluenting with pentane (30 mL). The resulting solution was concentrated, and the residue was directly purified by silica gel chromatography (pentane) to afford **2-56 (**129.0 mg, 69% yield) as a colorless oil. The ratio of **2-56a** and **2-56b**[16] was calculated as 97:3 by ^{19}F NMR.

2-56a[1]

TLC: $R_f = 0.67$ in petroleum ether.

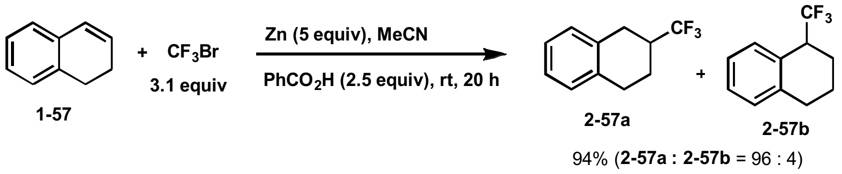
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.17 (m, 4H), 3.23–3.12 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.71, 128.24 (q, $J = 277.0$ Hz), 127.07, 124.60, 42.61 (q, $J = 28.1$ Hz), 33.03 (q, $J = 2.7$ Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -71.17 (**2-56b**), -72.12.

MS (EI): *m/z* (%) 186 (M^+, 58.90), 117 (100).

2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene (2-57a, p4-183)



Prepared according to the general procedure using alkene **1-57** (131 μL, d = 0.997 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (2 mL) for 15 min in an ice-bath, and Na_2CO_3 aq. (3 mL) for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-57** (188.2 mg, 94% yield) as a colorless oil. The **2-57b** is consistent with the literature.[17] The ratio of **2-57a** and **2-57b** was calculated as 96:4 by ^{1}H NMR and ^{19}F NMR.

2-57a

TLC: R_f = 0.72 in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.09 (m, 4H), 3.03–2.80 (m, 4H), 2.52–2.40 (m, 1H), 2.22–2.15 (m, 1H), 1.77–1.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.58, 133.74, 129.30, 128.98, 127.99 (q, J = 278.3 Hz), 126.39, 126.23, 39.42 (q, J = 27.1 Hz), 28.34–28.26 (m), 22.29 (q, J = 2.8 Hz).

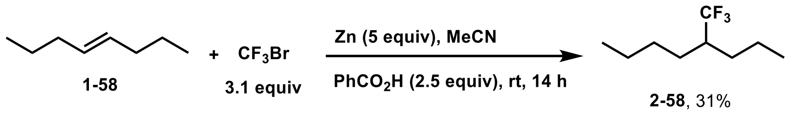
^{19}F NMR (376 MHz, $CDCl_3$): δ -68.24 (**2-57b**), -74.20.

IR (neat): 3025, 2927, 2855, 1498, 1443, 1396, 1330, 1275, 1169, 1143, 1123, 1056, 747.

MS (EI): *m/z* (%) 200 (M^+, 81.07), 104 (100).

HRMS (EI): *m/z* calc'd for $C_{11}H_{11}F_3$ $(M)^+$: 200.0807, found 200.0807.

4-(trifluoromethyl)octane (2-58, p4-116)



Prepared according to the general procedure using alkene **1-58** (157 μL, d = 0.715 g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.0 mg, 5.0 mmol), $PhCO_2H$ (305.8 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 14 h at rt, the reaction mixture was added sat. $KMnO_4$ aq. (1 mL) for 15 min in an ice-bath and Na_2CO_3 aq. (3 mL) for 15 min, then extracted with pentane (15 mL × 3) and concentrated. The residue was purified by silica gel chromatography (pentane) to afford **2-58** (56.0 mg, 31% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05–1.96 (m, 1H), 1.62–1.51 (m, 2H), 1.48–1.23 (m, 8H), 0.94–0.88 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 128.95 (q, J = 280.2 Hz), 42.50 (q, J = 24.6 Hz), 30.20 (q, J = 2.5 Hz), 29.20, 27.73 (q, J = 2.8 Hz), 22.94, 20.26, 14.28, 14.01.

^{19}F NMR (376 MHz, CDCl$_3$): δ -70.74.

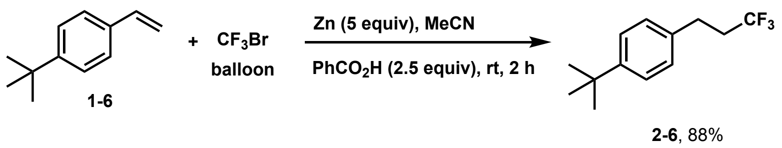
IR (neat): 2960, 2926, 2855, 1465, 1379, 1261, 1168, 1143, 1112, 800.sss

MS (EI): *m/z* (%) 182 (M$^+$, 0.01), 57 (100).

HRMS (EI$^+$): *m/z* calc'd for $C_9H_{17}F_3$ (M)$^+$: 182.1282, found 182.1232.

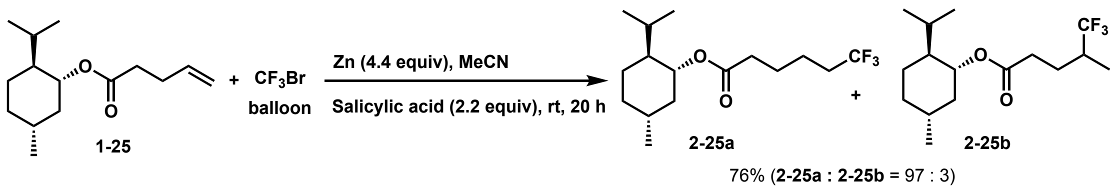
4. Gram-scale Hydrotrifluoromethyltion Reactions

1-(*tert*-butyl)-4-(3,3,3-trifluoropropyl)benzene (2-6, p6-10)



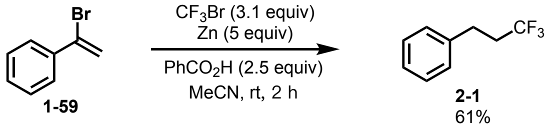
Prepared in 200 mL Schlenk flask according to the general procedure using alkene **1-6** (1.8 mL, 10 mmol), CF$_3$Br balloon, Zn (3.27 g, 50 mmol), PhCO$_2$H (3.05 g, 25 mmol) and MeCN (30 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (15 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-6** (2.04 g, 88% yield) as a colorless oil.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 6,6,6-trifluorohexanoate (2-25a, p6-13)

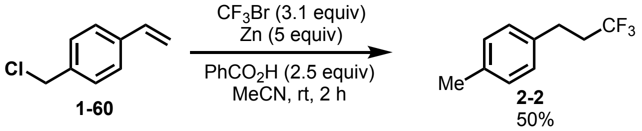


Prepared in 200 mL Schlenk flask according to the general procedure using alkene **1-25** (1.37 g, 5.7 mmol), CF$_3$Br balloon, Zn (1.63 g, 25 mmol), salicylic acid (1.73 g, 12.5 mmol) and MeCN (15 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na$_2$CO$_3$ aq. (15 mL) and stirred for 15 min at rt, and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was added sat. KMnO$_4$ aq. (5 mL) for 15 min in an ice-bath and extracted with DCM (50 mL × 3), washed with sat. NaCl aq., dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 90:1 to 60:1) to afford **2-25** (1.33 g, 76% yield) as a light yellow oil.

5. Hydrotrifluoromethyltion of Alkenes with Vinyl Bromide or Benzyl Chloride



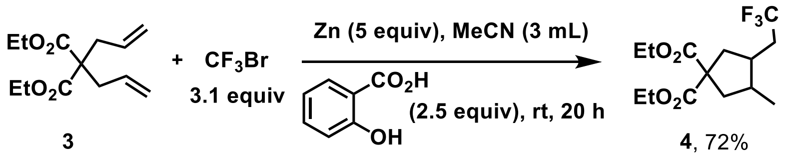
Prepared according to the general procedure using alkene **1-59 (**130 μL, d = 1.387g/mL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-1** (106.0 mg, 61% yield) as a colorless oil.



Prepared according to the general procedure using alkene **1-60 (**141 μL, d = , 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-2** (93.4 mg, 50% yield) as a colorless oil.

6. Mechanism Studies

Preparation of cyclic product 4 (p6-8-3)



Prepared according to the general procedure using alkene **3** (240.4 mg, 1.0 mmol), CF_3Br (3.1 mmol), Zn (327.0 mg, 5.0 mmol), salicylic acid (345.3 mg, 2.5 mmol) and MeCN (3 mL). After stirring for 20 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (15 mL) for 15 min., and filtered through a pad of Celite eluenting with DCM (30 mL) and concentrated. The residue was extracted with DCM (20 mL × 3), washed with sat. NaCl aq., dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (petroleum ether : EtOAc = 20:1 and petroleum ether:DCM = 1:1) to afford **4**[8] (224.0 mg, 72% yield) as a light yellow oil.

TLC: $R_f = 0.33$ in 20:1 petroleum ether/EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$, dr = 9:1, major product) δ 4.19 (q, J = 7.3 Hz, 4H), 2.67–2.43 (m, 2H), 2.34–1.96 (m, 6H), 1.24 (t, J = 7.3 Hz, 6H), 1.03–0.86 (m, 3H).

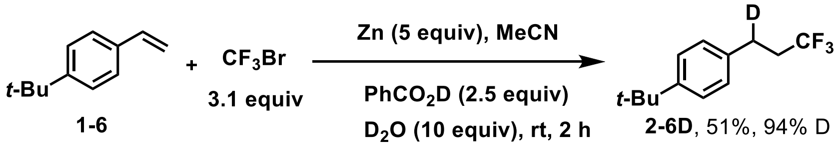
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.63, 172.59, 127.26 (q, J = 276.8 Hz), 61.61, 61.59, 58.77, 41.26, 38.05, 36.59 (q, J = 2.7 Hz), 36.03, 34.03 (q, J = 28.0 Hz), 14.92, 14.04.

^{19}F NMR (376 MHz, $CDCl_3$,): δ -65.12 (mior), -65.16 (major).

MS (ESI): *m/z* (%) 311 ($(M + H)^+$, 59.33), 256 (100).

Preparation of $PhCO_2D$ (p6-34)

To a 50 mL of Schlenk flask was added $PhCO_2Na$ (360.3 mg, 2.5 mmol) in N_2. The flask was added anhydrous THF (6 mL) and DCl (470 μL, 20% in D_2O). After stirring for 0.5 h at rt. The procedure was repeated 3 times to afford $PhCO_2D$. It was directly used for the next step.



Prepared according to the general procedure using alkene **1-6** (183 μL, 1.0 mmol), CF_3Br (3.1 mmol), Zn (328.3 mg, 5.0 mmol), $PhCO_2D$ (307.8 mg, 2.5 mmol), D_2O (181 μL, 10 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was added sat. Na_2CO_3 aq. (3 mL) and stirred for 15 min, then directly purified by silica gel chromatography (pentane) to afford **2-6D** (118.9 mg, 51% yield) as a colorless oil.

TLC: $R_f = 0.66$ in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 2.86–2.80 (m, 1H), 2.46–2.32 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.74, 136.07, 128.04, 131.08–122.83 (m), 125.77, 35.75 (q, *J* = 28.2 Hz), 34.58, 31.51, 27.85–27.24 (m).

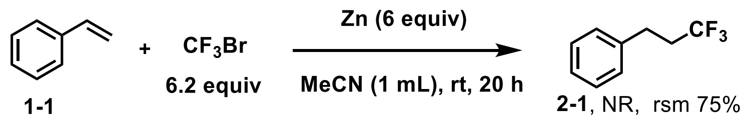
^{19}F NMR (376 MHz, CDCl$_3$): δ -67.23, -67.26.

IR (neat): 2967, 2910, 2871, 1376, 1367, 1266, 1256, 1141, 1115, 822.

MS (EI): *m/z* (%) 231 ((M)$^+$, 2.75), 216 (100).

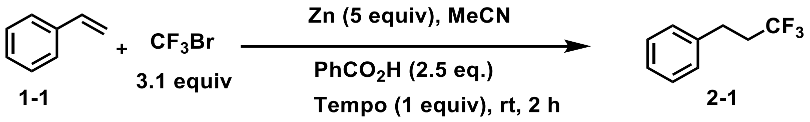
HRMS (ESI$^+$): *m/z* calc'd for $C_{13}H_{17}DF_3$ (M + H)$^+$: 232.1418, found 232.1416.

The Reaction of Styrene with CF$_3$Br and Zn without PhCO$_2$H (P3-142)



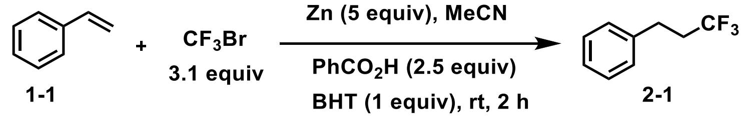
Prepared in 25 mL Schlenk flask according to the general procedure using alkene **1-1** (29 µL, d = 0.906 g/mL, 0.25 mmol), CF$_3$Br (6.2 equiv), Zn (98.1 mg, 1.5 mmol) and MeCN (1 mL). After stirring for 20 h at rt, the reaction mixture was analyzed by NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Test on the Hydrotrifluoromethylation of Styrene in the Standard Condition with 1 equiv of TMEPO (P5-193)



Prepared in 50 mL Schlenk flask according to the general procedure using alkene **1-1** (115 µL, d = 0.906 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (327.5 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol), TEMPO (156.2 mg, 1.0 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S8.

Test on the Hydrotrifluoromethylation of Styrene in the Standard Condition with 1 equiv of BHT (P6-100)



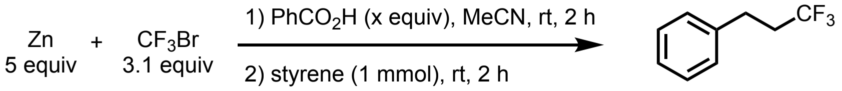
Prepared in 50 mL Schlenk flask according to the general procedure using alkene **1-1** (115 µL, d = 0.906 g/mL, 1.0 mmol), CF$_3$Br (3.1 mmol), Zn (327.5 mg, 5.0 mmol), PhCO$_2$H (305.3 mg, 2.5 mmol), BHT (220.4 mg, 1.0 mmol) and MeCN (3 mL). After stirring for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S8.

Table S8:

entry	additive	yield of **2-1** (%) [a]	rsm (%) [b]
1	TEMPO	0	97
2	BHT	0	96

[a] The yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Tests on the Hydrotrifluoromethylation of Styrene with Premixed Zn, CF_3Br and $PhCO_2H$ (or none) (P6-74, p6-75)



2-1

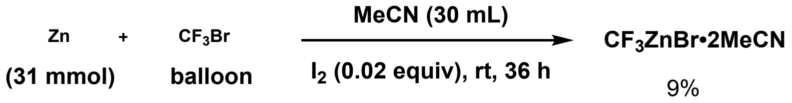
To a 50 mL of Schlenk flask was added Zn (327.0 mg, 5.0 mmol) and $PhCO_2H$ (305.3 mg, 2.5 mmol; or none), CF_3Br (3.1 equiv) and MeCN (3 mL). After stirring for 2 h at rt, the flask was added alkene **1-1** (115 μL, d = 0.906 g/mL, 1.0 mmol) and stirred for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S9.

Table S9:

entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1	0	0	97
2	2.5	0	95

[a] The yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Preparation of CF_3ZnBr•2MeCN (P6-84)[18]



$$\underset{\textbf{(31 mmol)}}{\textbf{Zn}} + \underset{\textbf{balloon}}{\mathbf{CF_3Br}} \xrightarrow[\mathbf{I_2\ (0.02\ equiv),\ rt,\ 36\ h}]{\textbf{MeCN (30 mL)}} \underset{9\%}{\mathbf{CF_3ZnBr{\bullet}2MeCN}}$$

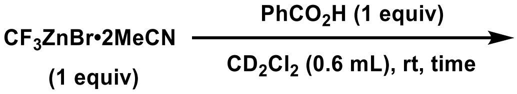
CF_3ZnBr•2MeCN was prepared according to the reference 18 with CF_3Br balloon.

To a 50 mL of Schlenk flask was added Zn powder (2.0 g, 31 mmol) and I_2 (150 mg, 0.6 mmol), and then it was evacuated for 30 s and filled with CF_3Br. The flask was added MeCN (30 mL), and CF_3Br was bubbled to saturate it in the solution for 5 min. Then it was equipped with an CF_3Br balloon for 36 h at rt. The mixture was filtered in glove box. The filtrate was concentrated, and the residue was washed with Cl_3CF and dried to give the CF_3ZnBr•2MeCN (800 mg, 9%) as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.22 (s, 6H).

^{19}F NMR (376 MHz, CD_2Cl_2): δ -45.55.

Tests on the Stability of $CF_3ZnBr•2MeCN$ (P6-94)



$$\underset{\text{(1 equiv)}}{CF_3ZnBr•2MeCN} \xrightarrow[CD_2Cl_2\text{ (0.6 mL), rt, time}]{PhCO_2H\text{ (1 equiv)}}$$

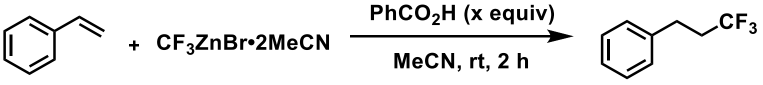
$CF_3ZnBr•2MeCN$ (10.0 mg, 0.034 mmol) and CD_2Cl_2 (0.6 mL) were added to an NMR tube in glove box, and then it was sealed and tested ^{1}H NMR and ^{19}F NMR spectra. After that, $PhCO_2H$ (4.2 mg, 0.034 mmol) was added to the tube in the glove box, and then the remaining $CF_3ZnBr•2MeCN$ was monitored through NMR (^{1}H NMR and ^{19}F NMR). $CF_3ZnBr•2MeCN$ was fully hydrolyzed in 19 min. The results were showed in Table S10.

Table S10: Stability Experiment of $CF_3ZnBr•2MeCN$

entry	time (min)	rsm[a]
1	0	100
2	10.0	28
3	13.0	16
4	14.5	7
5	16.0	2
6	17.5	0.8
7	19.0	0

[a] rsm was determined by ^{19}F NMR analysis of the crude reaction mixture with $CFCl_3$ as the internal standard.

Tests on the Hydrotrifluoromethylation of Styrene with $CF_3ZnBr•2MeCN$ (P6-85, p6-86)



1-1

2-1

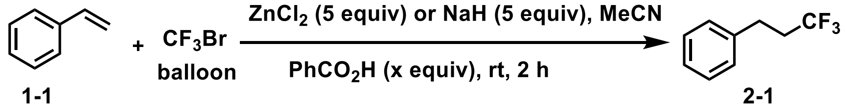
To a 25 mL of Schlenk tube was added $CF_3ZnBr•2MeCN$ (296.4 mg, 1.0 mmol), $PhCO_2H$ (61.1 mg, 0.5 mmol; or 0 mg) in the glove box. The flask was sealed and evacuated for 30 s with an oil pump outside and backfilled with CF_3Br, and then added MeCN (1 mL) and alkene **1-1 (**23 µL, d = 0.906 g/mL, 0.2 mmol). After stirring for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S11.

Table S11:

entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1	0	0	100
2	2.5	0	100

[a] The yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Tests on the Hydrotrifluoromethylation of Styrene with CF_3Br in the Presence of $ZnCl_2$ or NaH (P6-188, P6-189)



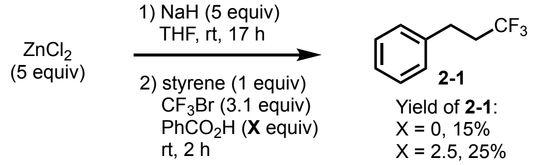
To a 25 mL of Schlenk tube was added NaH (120.0 mg, 5.0 mmol) or $ZnCl_2$ (681.5 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol or 0 mg) in the glove box. The flask was sealed evacuated for 30 s with an oil pump outside and equipped with CF_3Br balloon, and then added MeCN (1 mL) and alkene **1-1** (115 µL, d = 0.906 g/mL, 1.0 mmol). After stirring for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S12.

Table S12:

entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1 ($ZnCl_2$)	0	0	95
2 ($ZnCl_2$)	2.5	0	100
3 (NaH)	0	0	100
4 (NaH)	2.5	0	88

[a] The yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Tests on the Hydrotrifluoromethylation of Styrene with CF_3Br in the Presence of premixed $ZnCl_2$ and NaH (P6-187)



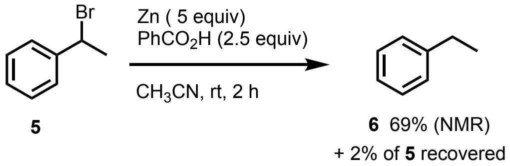
To a 25 mL of Schlenk tube was added sat. NaH (120.0 mg, 5.0 mmol) and $ZnCl_2$ (681.5 mg, 5.0 mmol) and THF (3 mL) in the glove box. After stirring for 17 h at rt, the reaction solvent was removed and then it was added $PhCO_2H$ (305.3 mg, 2.5 mmol or 0 mg). The flask was sealed and evacuated for 30 s with an oil pump and equipped with CF_3Br balloon. Then, MeCN (3 mL) and alkene **1-1** (115 µL, d = 0.906 g/mL, 1.0 mmol) were added. After stirring for 2 h at rt, the reaction mixture was analyzed by NMR. The results were showed in Table S13.

Table S13:

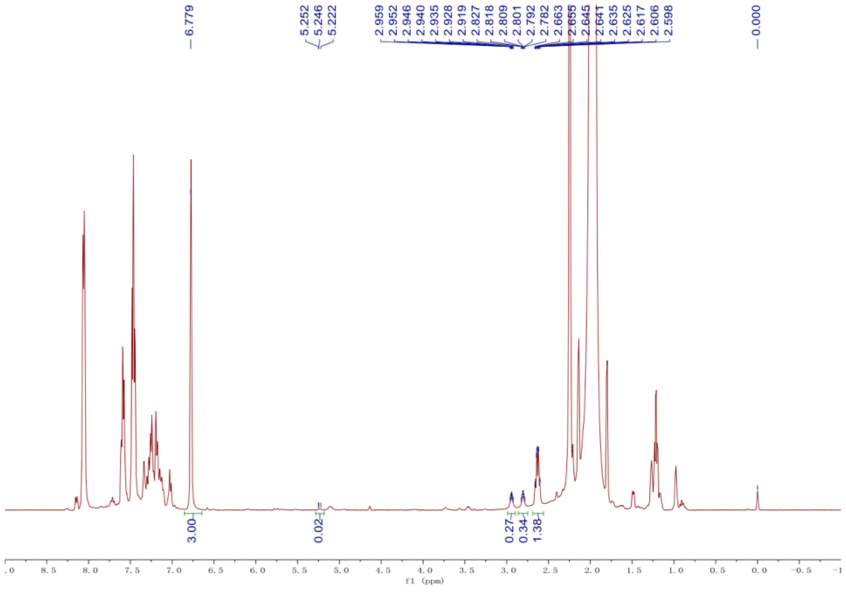
entry	x	yield of **2-1** (%) [a]	rsm (%) [b]
1	0	15	65
2	2.5	25	67

[a] the yield was determined by ^{19}F NMR analysis of the crude reaction mixture with $PhCF_3$ as the internal standard; [b] rsm was determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as the internal standard.

Reduction of (1-bromoethyl)benzene (5) with Zn/$PhCO_2H$



Under N_2 atmosphere, a 25 mL of Schlenk tube was added Zn (327.0 mg, 5.0 mmol), $PhCO_2H$ (305.3 mg, 2.5 mmol) and CH_3CN (3 mL), then (1-bromoethyl)benzene (5) was added. After stirring for 2 h at rt, the reaction mixture was analyzed by ^{1}H NMR with mesitylene as the internal standard, and 69% of ethylbenzene **6** was formed with 2% of **5** recovered. The crude ^{1}H NMR is as follow:

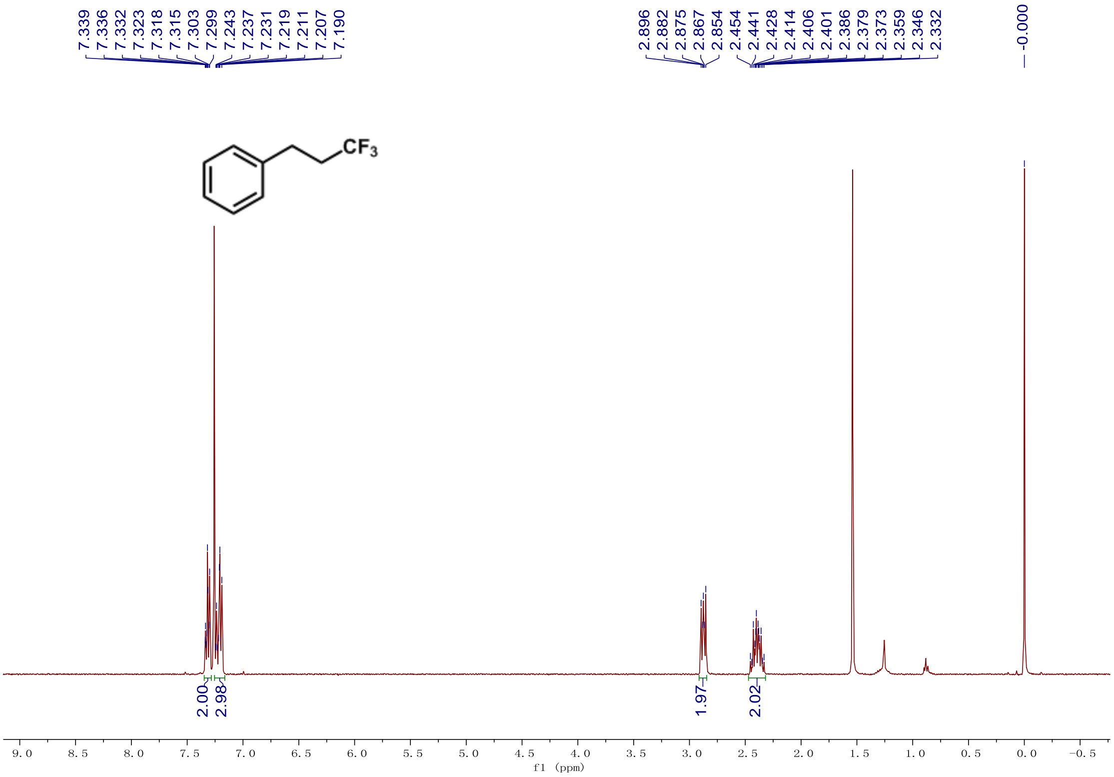


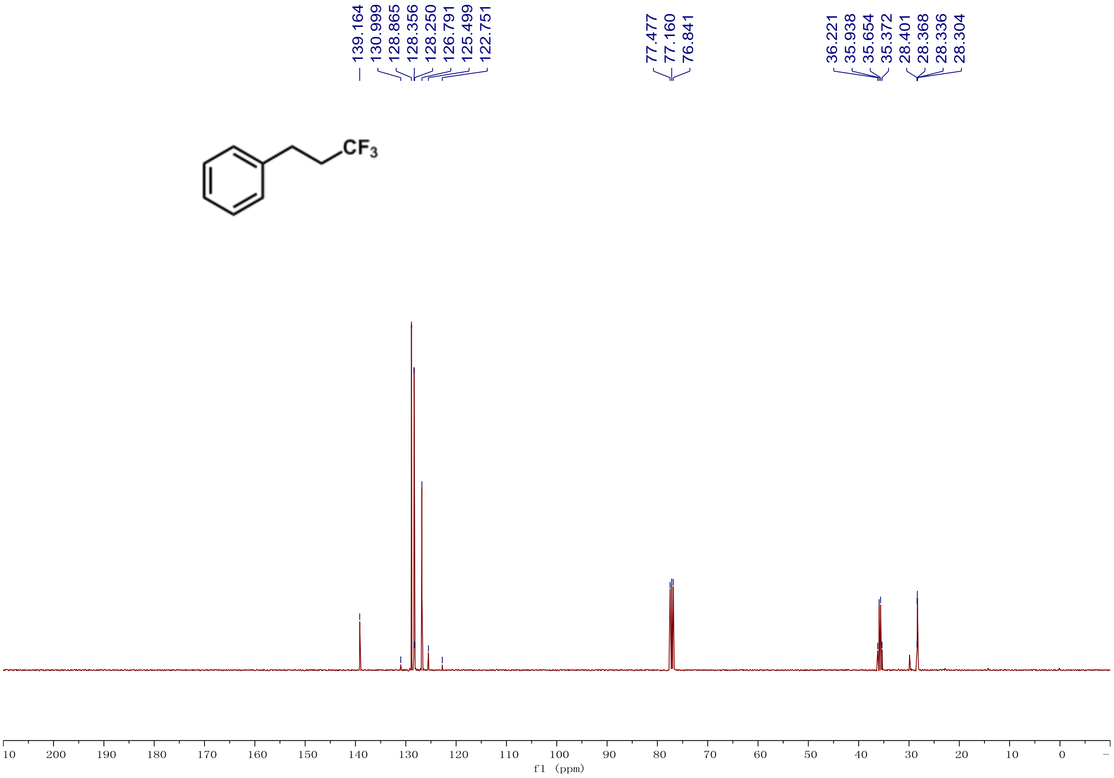
7. References

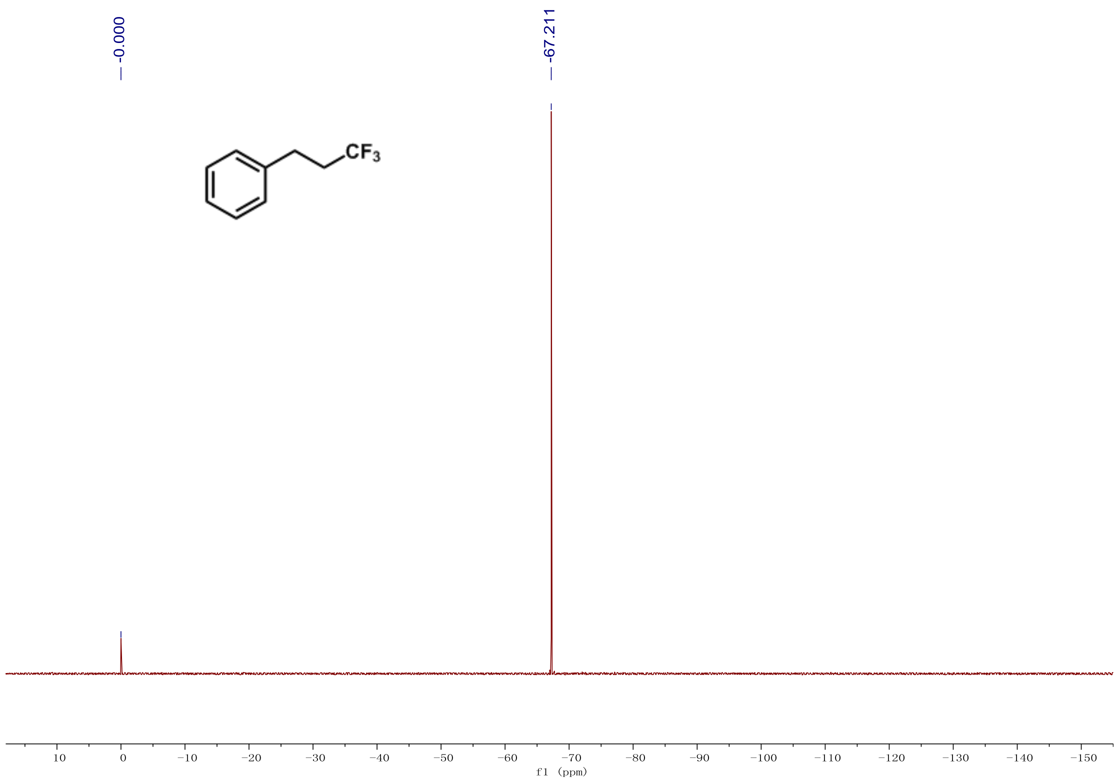
1. N. J. W. Straathof, S. E. Cramer, V. Hessel and T. Noël, *Angew. Chem. Int. Ed.*, 2016, **55**, 15549-15553.
2. X. Zou, J. Zou, L. Yang, G. Li and H. Lu, *J. Org. Chem.*, 2017, **82**, 4677-4688.
3. K.-Y. Ye, G. Pombar, N. Fu, G. S. Sauer, I. Keresztes and S. Lin, *J. Am. Chem. Soc.*, 2018, **140**, 2438-2441.
4. S. Choi, Y. J. Kim, S. M. Kim, J. W. Yang, S. W. Kim and E. J. Cho, *Nat. Commun.*, 2014, **5**, 4881-4887.
5. C. Lévêque, L. Chenneberg, V. Corcé, J.-P. Goddard, C. Ollivier and L. Fensterbank, *Org. Chem. Front.*, 2016, **3**, 462-465.
6. B. He, Q. Pan, Y. Guo, Q.-Y. Chen and C. Liu, *Org. Lett.*, 2020, **22**, 6552-6556.
7. X. Tan, Z. Liu, H. Shen, P. Zhang, Z. Zhang and C. Li, *J. Am. Chem. Soc.*, 2017, **139**, 12430-12433.
8. W. Zhang, Z. Zou, Y. Wang, Y. Wang, Y. Liang, Z. Wu, Y. Zheng and Y. Pan, *Angew. Chem. Int. Ed.*, 2019, **58**, 624-627.
9. Y. Imagawa, S. Yoshikawa, T. Fukuhara and S. Hara, *Chem. Commun.*, 2011, **47**, 9191-9193.
10. J.-X. Xiang, Y. Ouyang, X.-H. Xu and F.-L. Qing, *Angew. Chem. Int. Ed.*, 2019, **58**, 10320-10324.
11. N. Erdeljac, G. Kehr, M. Ahlqvist, L. Knerr and R. Gilmour, *Chem. Commun.*, 2018, **54**, 12002-12005.
12. T. Braun, F. Wehmeier and K. Altenhöner, *Angew. Chem. Int. Ed.*, 2007, **46**, 5321-5324.
13. A.-L. Barthelemy, G. Dagousset and E. Magnier, *Eur. J. Org. Chem.*, 2020, **2020**, 1429-1432.
14. M. Engman, P. Cheruku, P. Tolstoy, J. Bergquist, S. F. Völker and P. G. Andersson, *Adv. Synth. Catal.*, 2009, **351**, 375-378.
15. D. J. Wilger, N. J. Gesmundo and D. A. Nicewicz, *Chem. Sci.*, 2013, **4**, 3160-3165.
16. C. Aubert, J.-P. Bégué, D. Bonnet-Delpon and D. Mesureur, *J. Chem. Soc., Perkin Trans. 1*, 1989, 395-399.
17. D. Bonnet-Delpon, C. Cambillau, M. Charpentier-Morize, R. Jacquot, D. Mesureur and M. Ourevitch, *J. Org. Chem.*, 1988, **53**, 754-759.
18. D. Naumann, W. Tyrra, B. Kock, W. Rudolph and B. Wilkes, *J. Fluorine Chem.*, 1994, **67**, 91-93.

8. NMR spectra

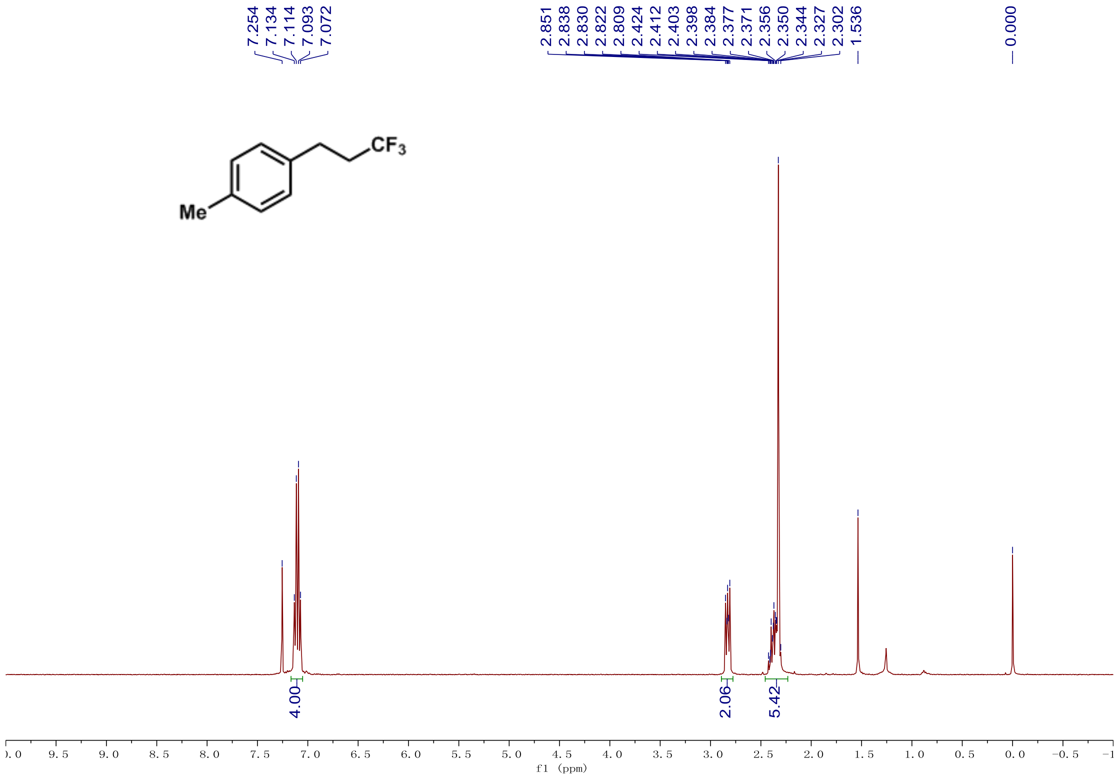
2-1

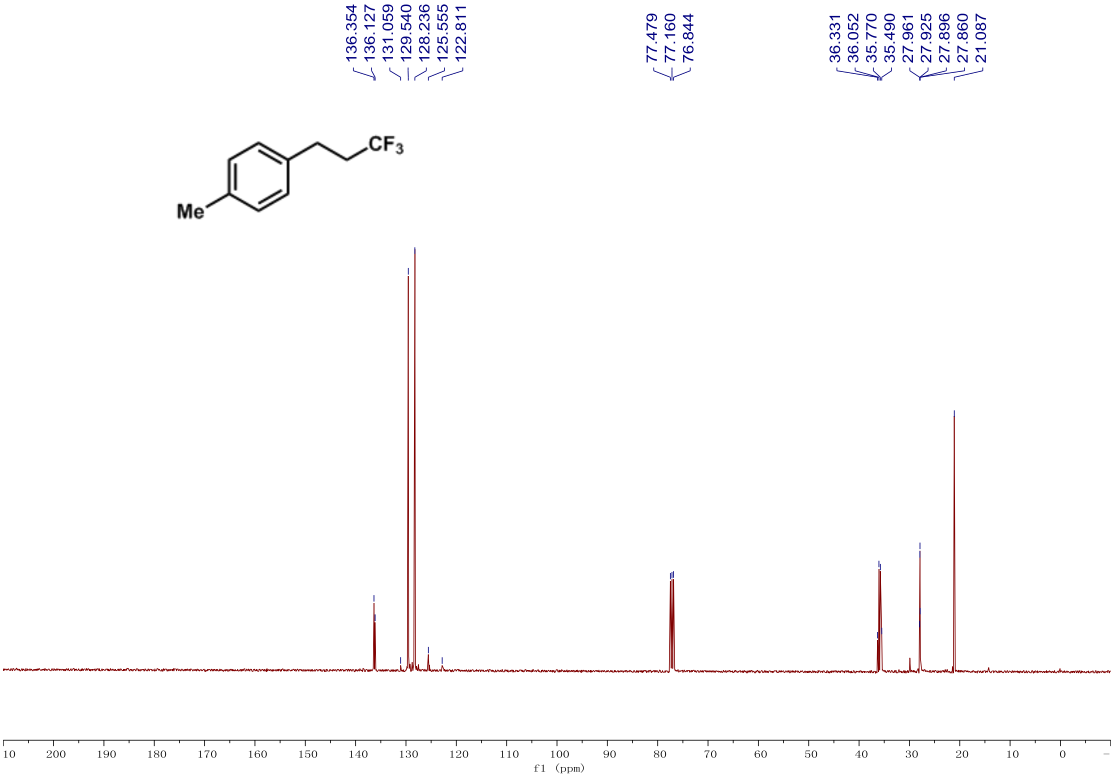


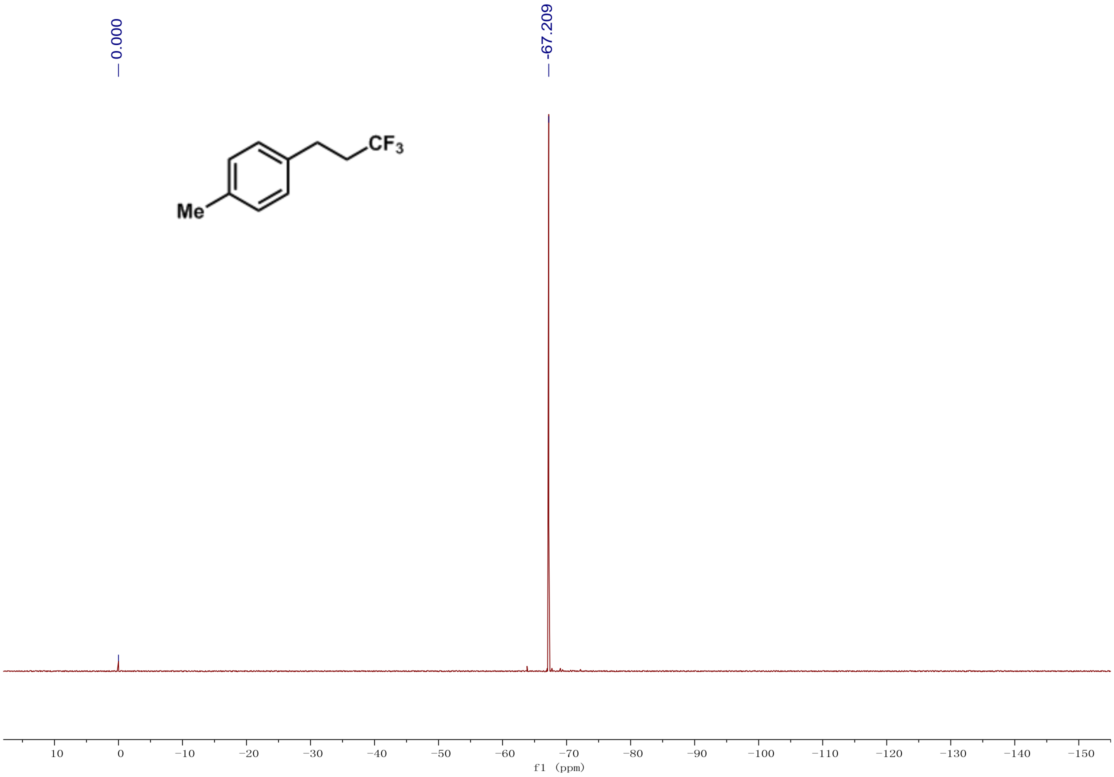



-0.000
-67.211
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

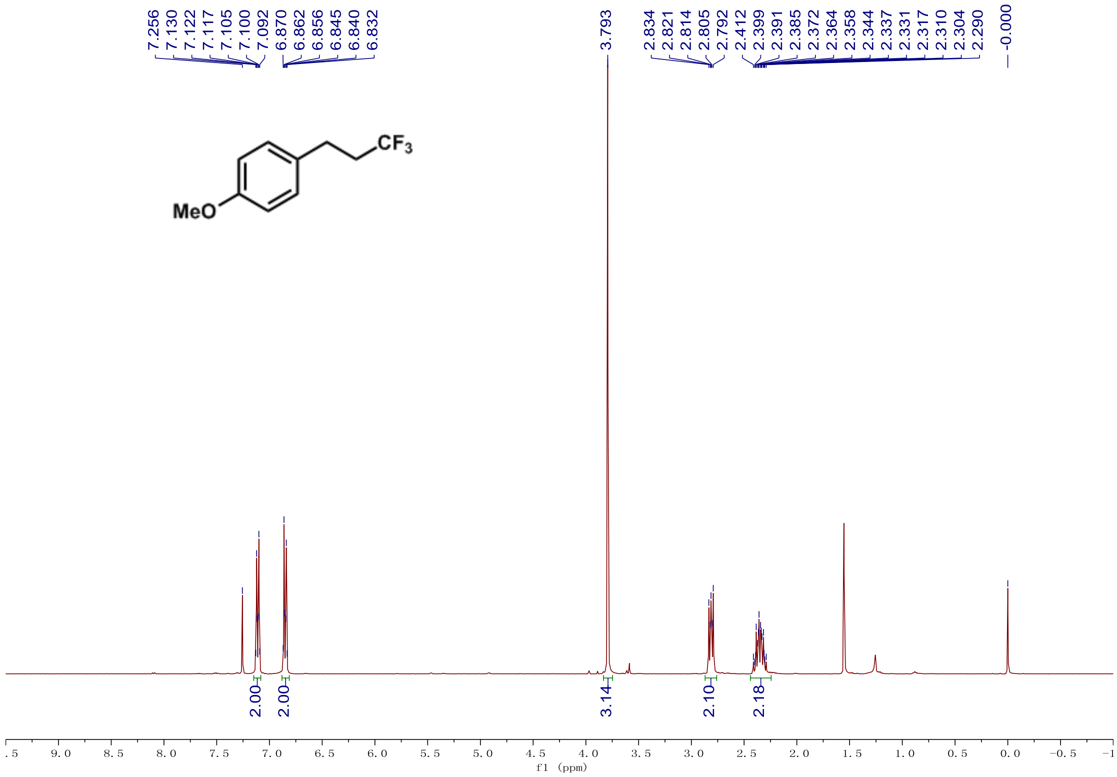
2-2

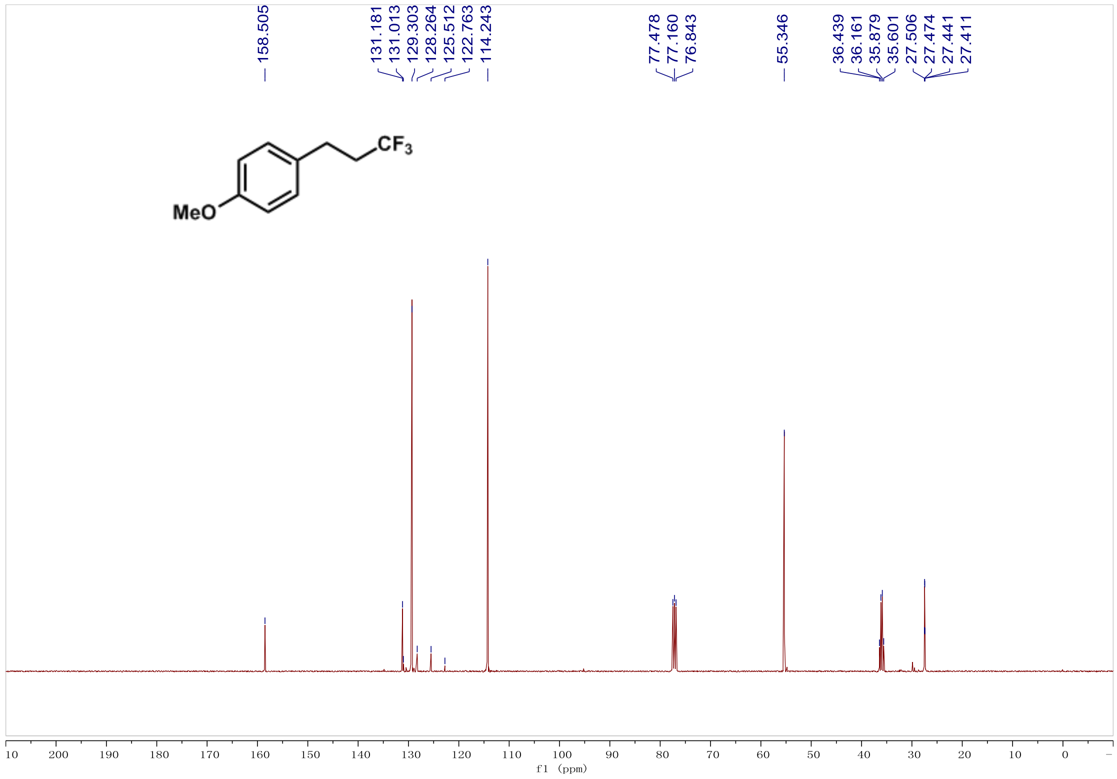

7.254
7.134
7.114
7.093
7.072
2.851
2.838
2.830
2.822
2.809
2.424
2.412
2.403
2.398
2.384
2.377
2.371
2.356
2.350
2.344
2.327
2.302
1.536
0.000
CF3
Me
4.00
2.06
5.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

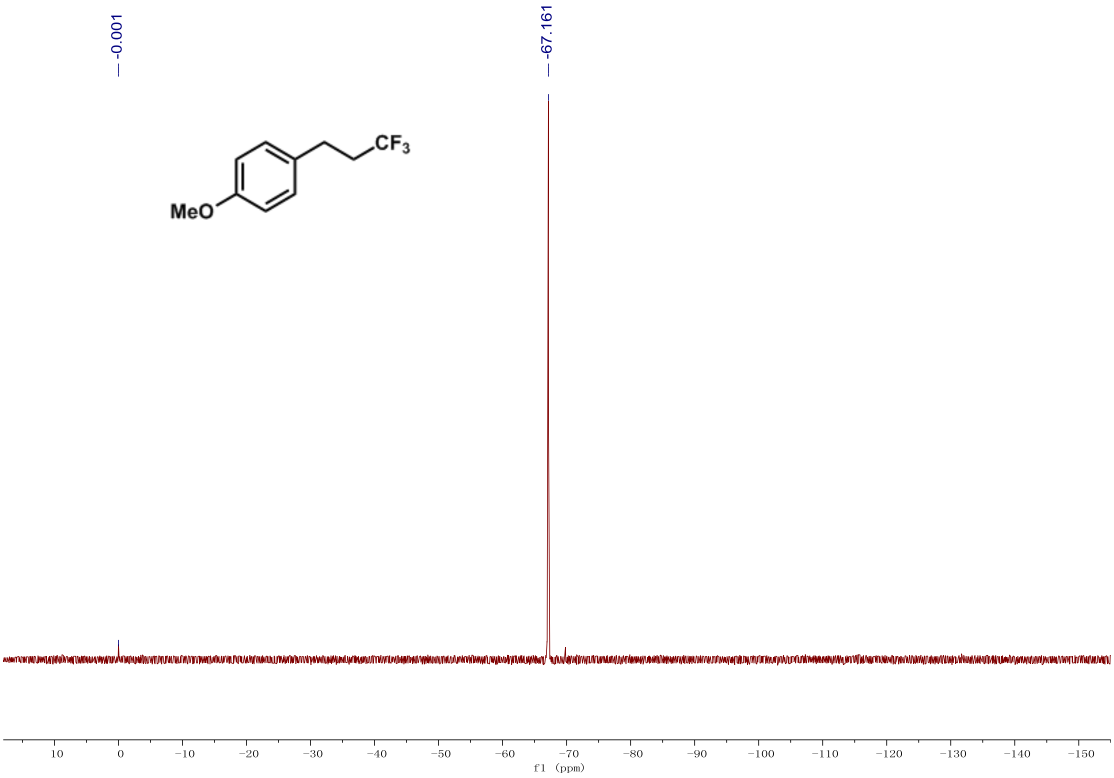

136.354
136.127
131.059
129.540
128.236
125.555
122.811
77.479
77.160
76.844
36.331
36.052
35.770
35.490
27.961
27.925
27.896
27.860
21.087
CF$_3$
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.209
CF$_3$
Me
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

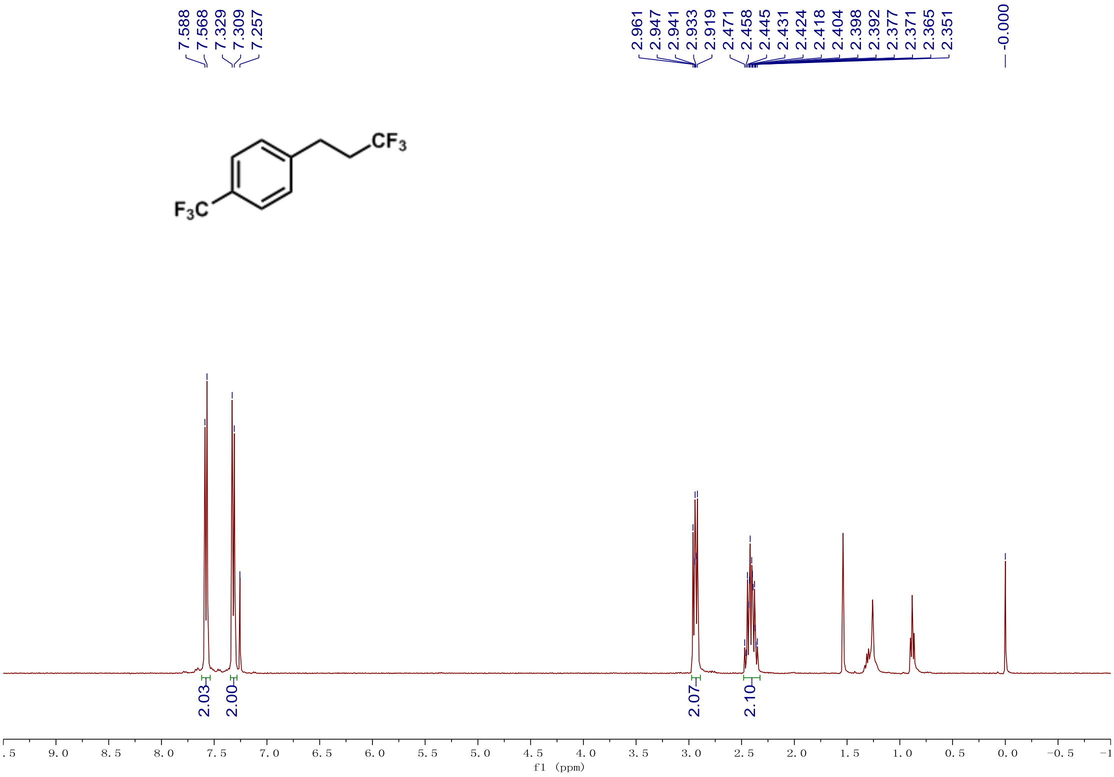
2-3

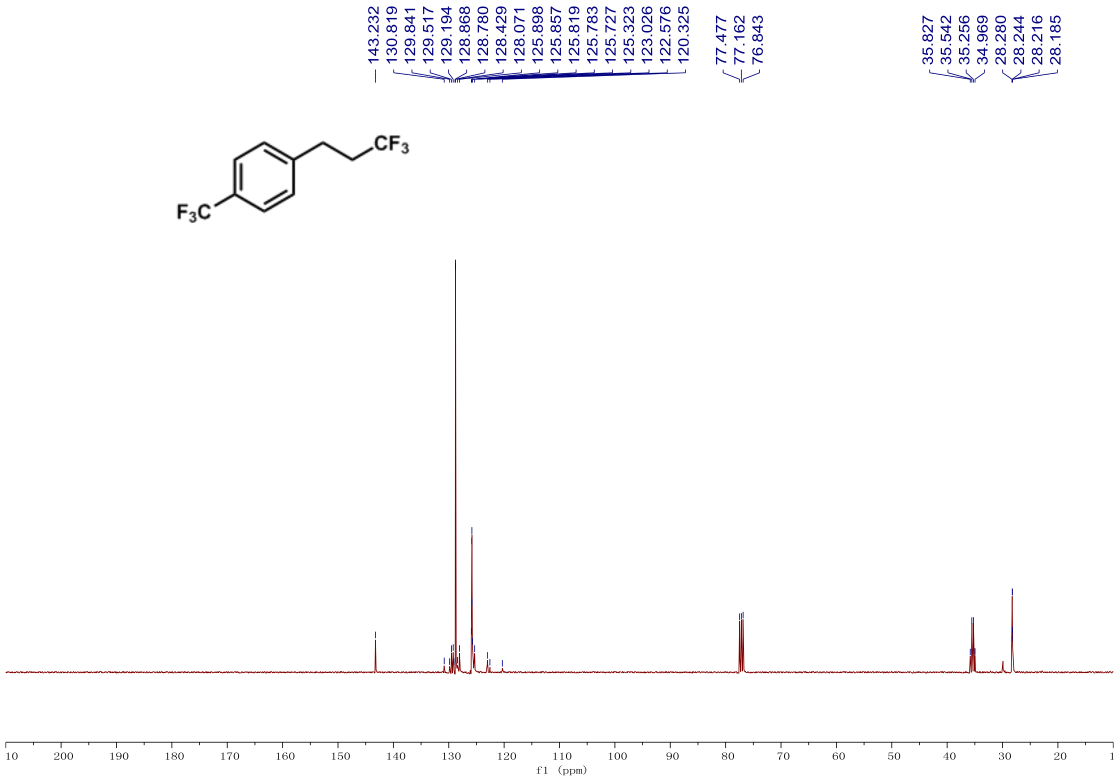

7.256
7.130
7.122
7.117
7.105
7.100
7.092
6.870
6.862
6.856
6.845
6.840
6.832
3.793
2.834
2.821
2.814
2.805
2.792
2.412
2.399
2.391
2.385
2.372
2.364
2.358
2.344
2.337
2.331
2.317
2.310
2.304
2.290
-0.000
CF3
MeO
2.00
2.00
3.14
2.10
2.18
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

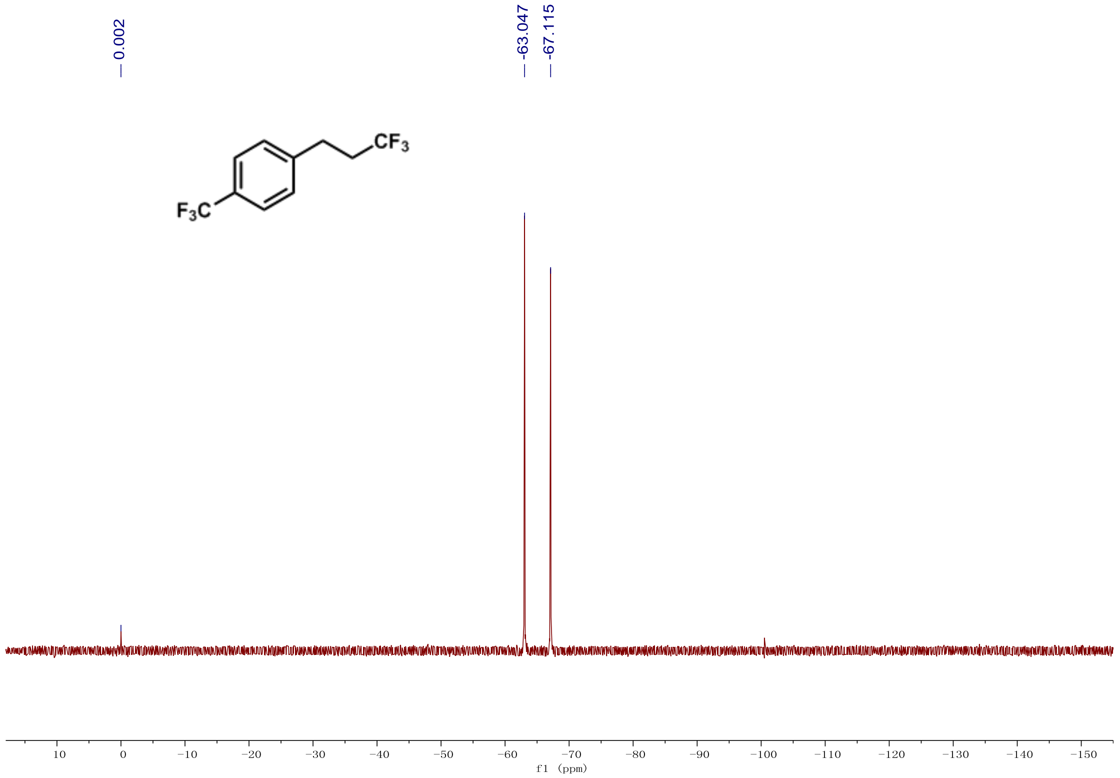

158.505
131.181
131.013
129.303
128.264
125.512
122.763
114.243
77.478
77.160
76.843
55.346
36.439
36.161
35.879
35.601
27.506
27.474
27.441
27.411
CF3
MeO
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.001
-67.161
CF$_3$
MeO
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

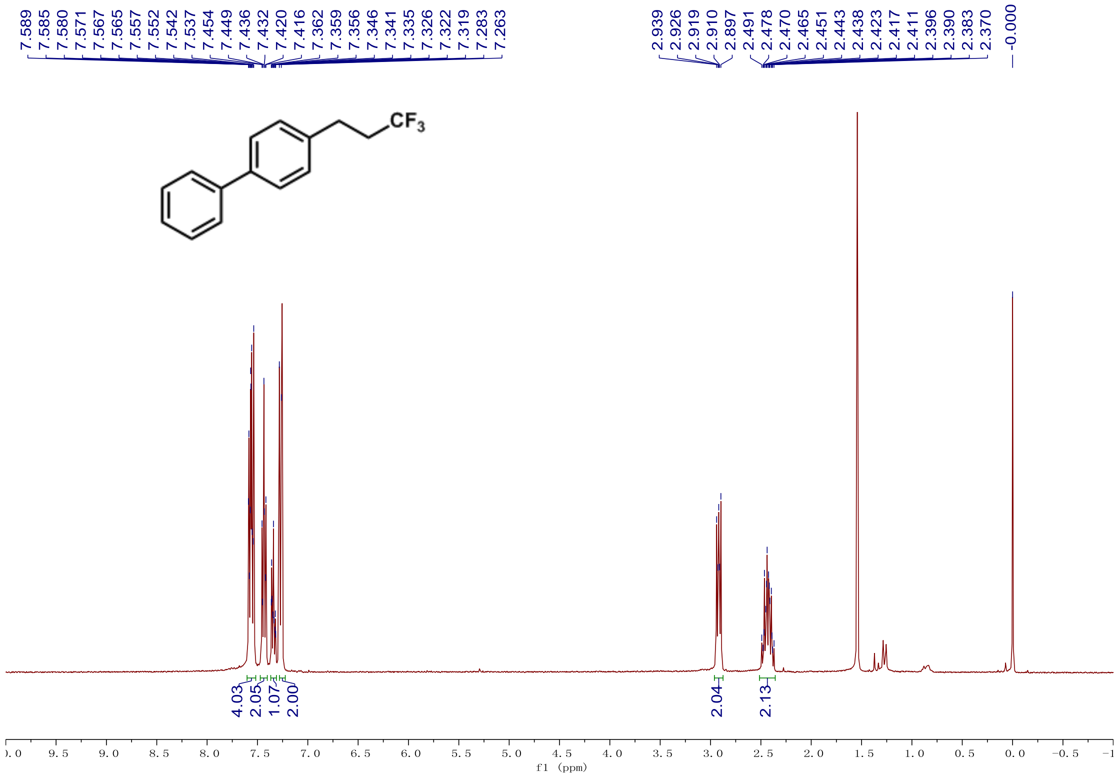
2-4

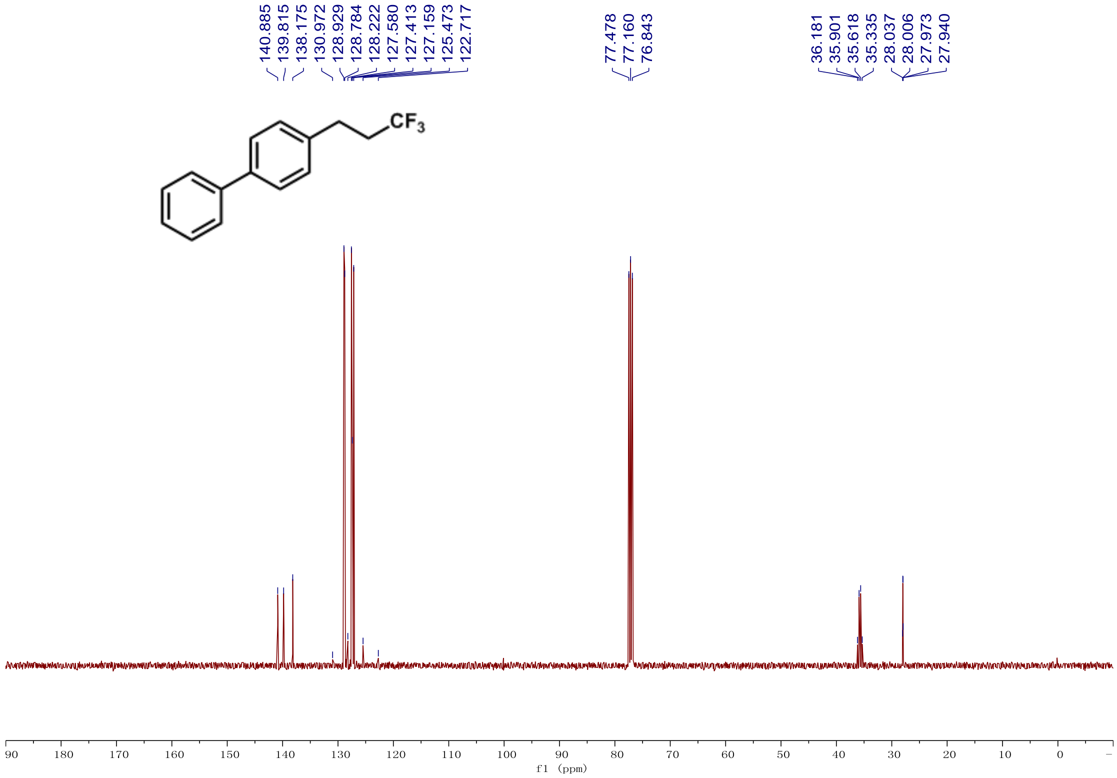

7.588
7.568
7.329
7.309
7.257
2.961
2.947
2.941
2.933
2.919
2.471
2.458
2.445
2.431
2.424
2.418
2.404
2.398
2.392
2.377
2.371
2.365
2.351
-0.000
CF$_3$
F$_3$C
2.03
2.00
2.07
2.10
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

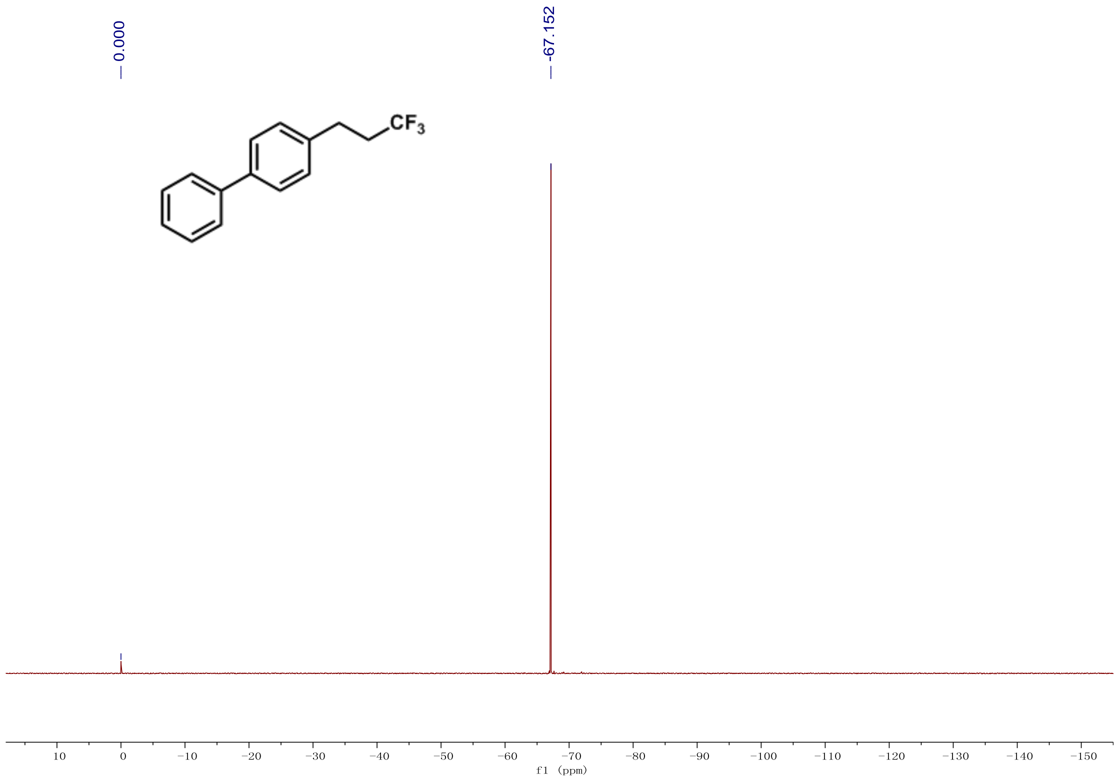

143.232
130.819
129.841
129.517
129.194
128.868
128.780
128.429
128.071
125.898
125.857
125.819
125.783
125.727
125.323
123.026
122.576
120.325
77.477
77.162
76.843
35.827
35.542
35.256
34.969
28.280
28.244
28.216
28.185
CF3
F3C
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)


0.002
-63.047
-67.115
CF3
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

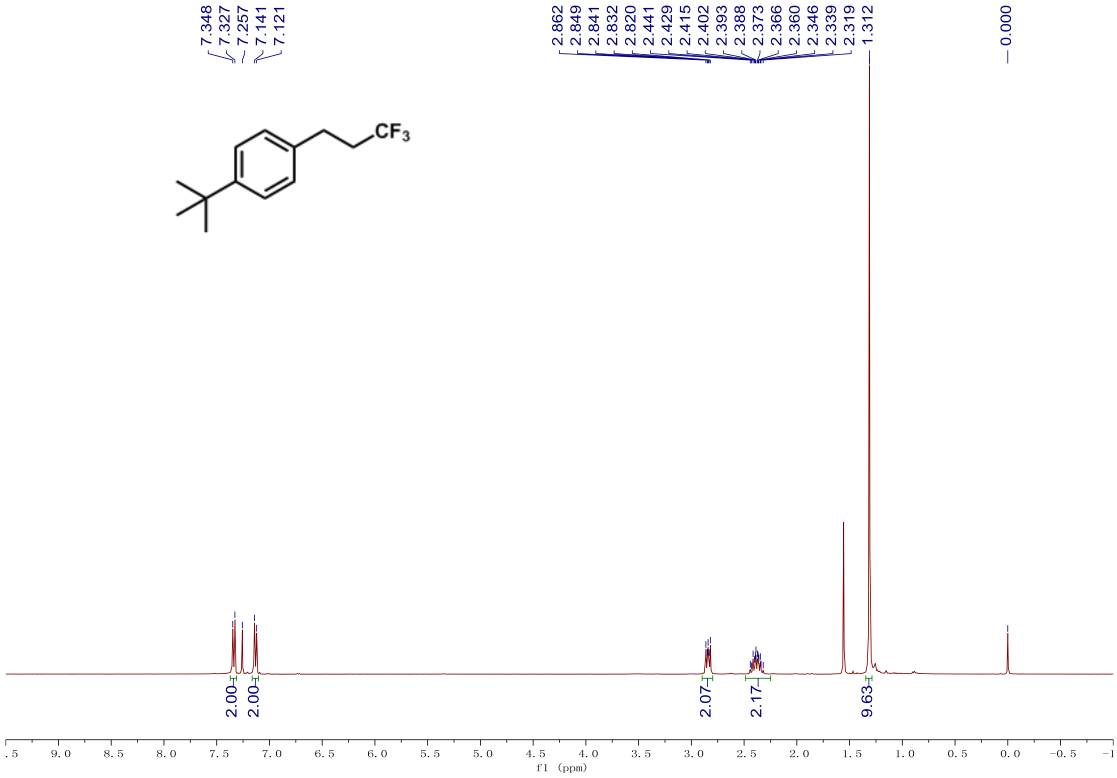
2-5

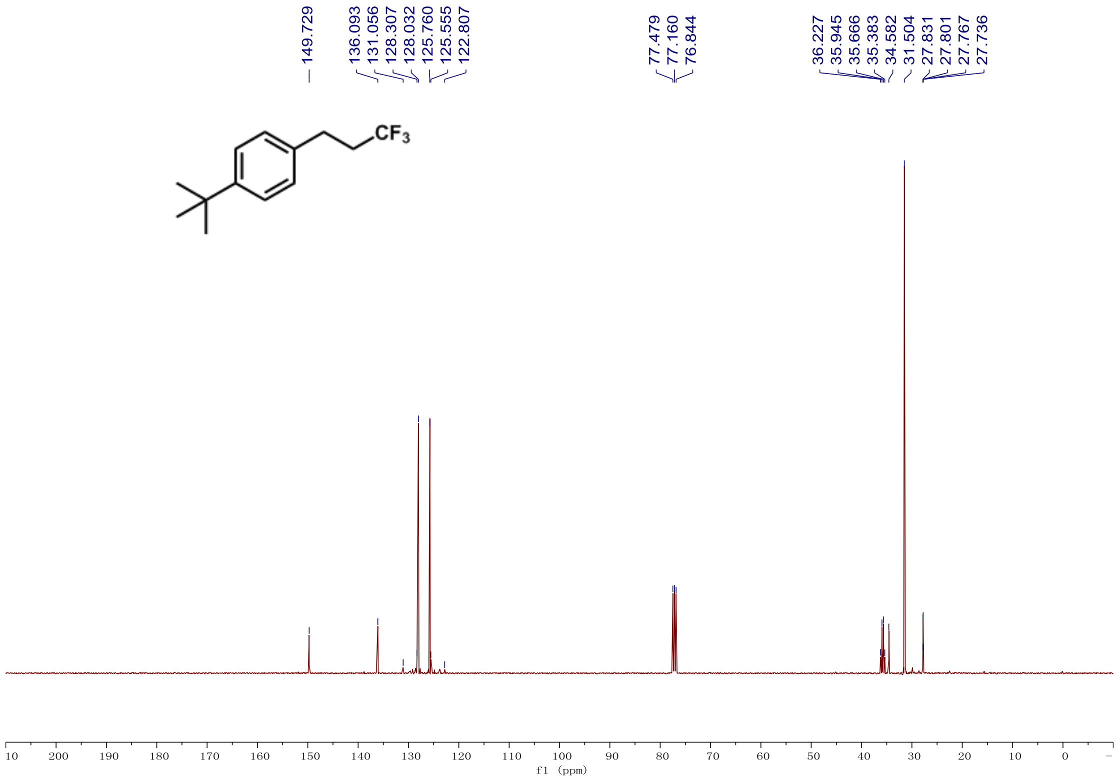

7.589
7.585
7.580
7.571
7.567
7.565
7.557
7.552
7.542
7.537
7.454
7.449
7.436
7.432
7.420
7.416
7.362
7.359
7.356
7.346
7.341
7.335
7.326
7.322
7.319
7.283
7.263
2.939
2.926
2.919
2.910
2.897
2.491
2.478
2.470
2.465
2.451
2.443
2.438
2.423
2.417
2.411
2.396
2.390
2.383
2.370
-0.000
CF3
4.03
2.05
1.07
2.00
2.04
2.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

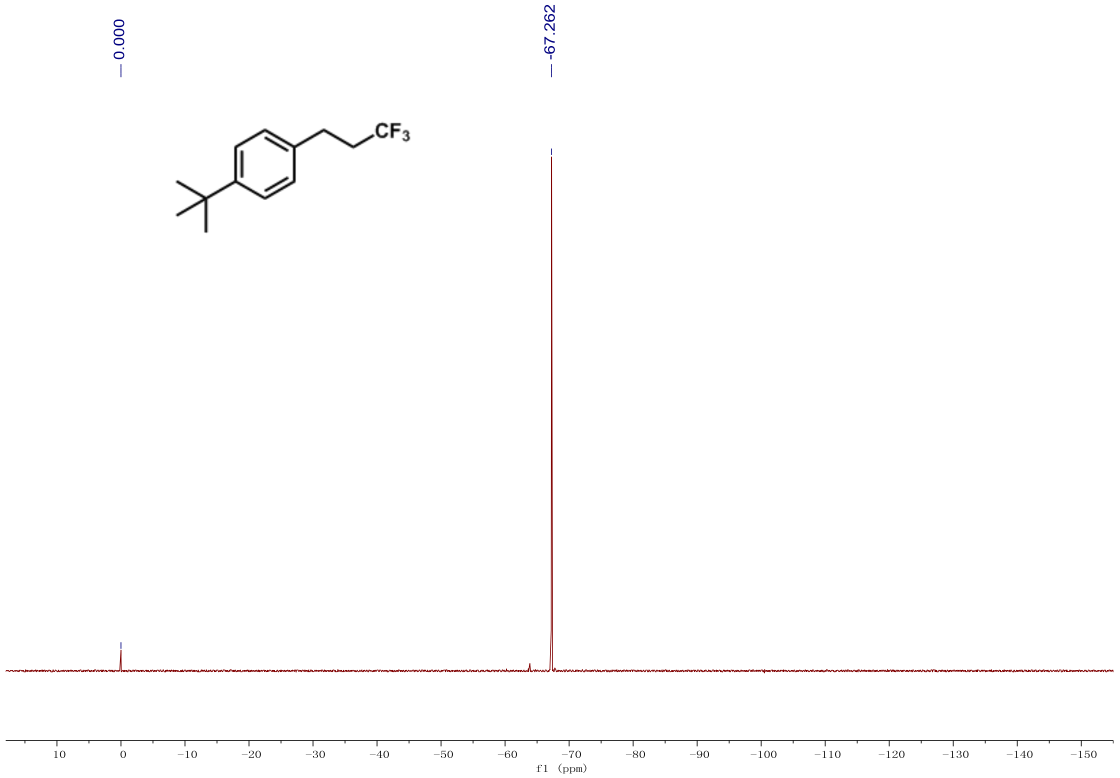

140.885
139.815
138.175
130.972
128.929
128.784
128.222
127.580
127.413
127.159
125.473
122.717
77.478
77.160
76.843
36.181
35.901
35.618
35.335
28.037
28.006
27.973
27.940
CF3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.152
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

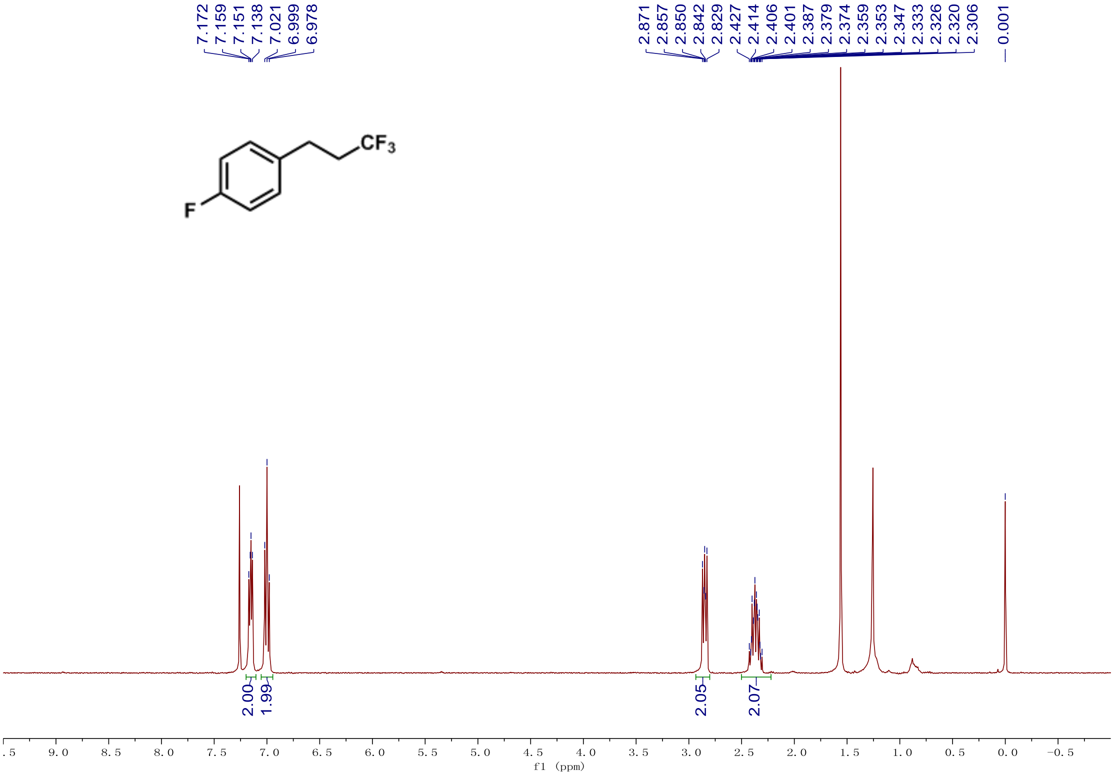
2-6

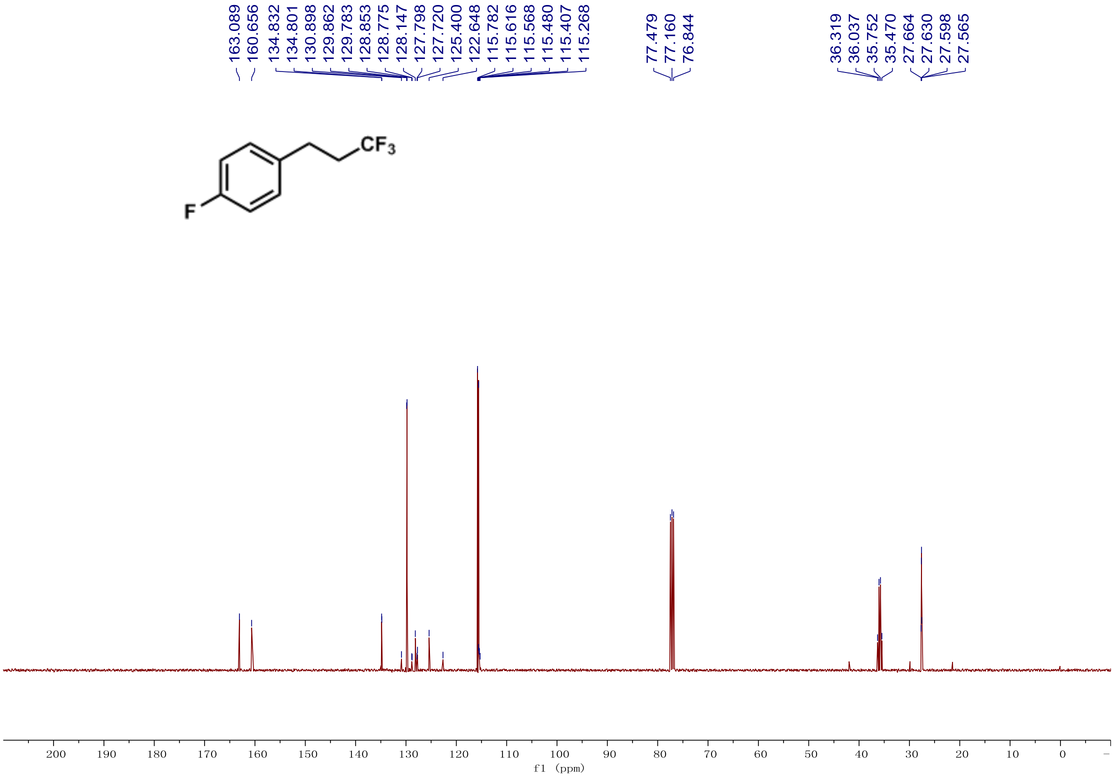

7.348
7.327
7.257
7.141
7.121
2.862
2.849
2.841
2.832
2.820
2.441
2.429
2.415
2.402
2.393
2.388
2.373
2.366
2.360
2.346
2.339
2.319
1.312
0.000
CF3
2.00
2.00
2.07
2.17
9.63
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

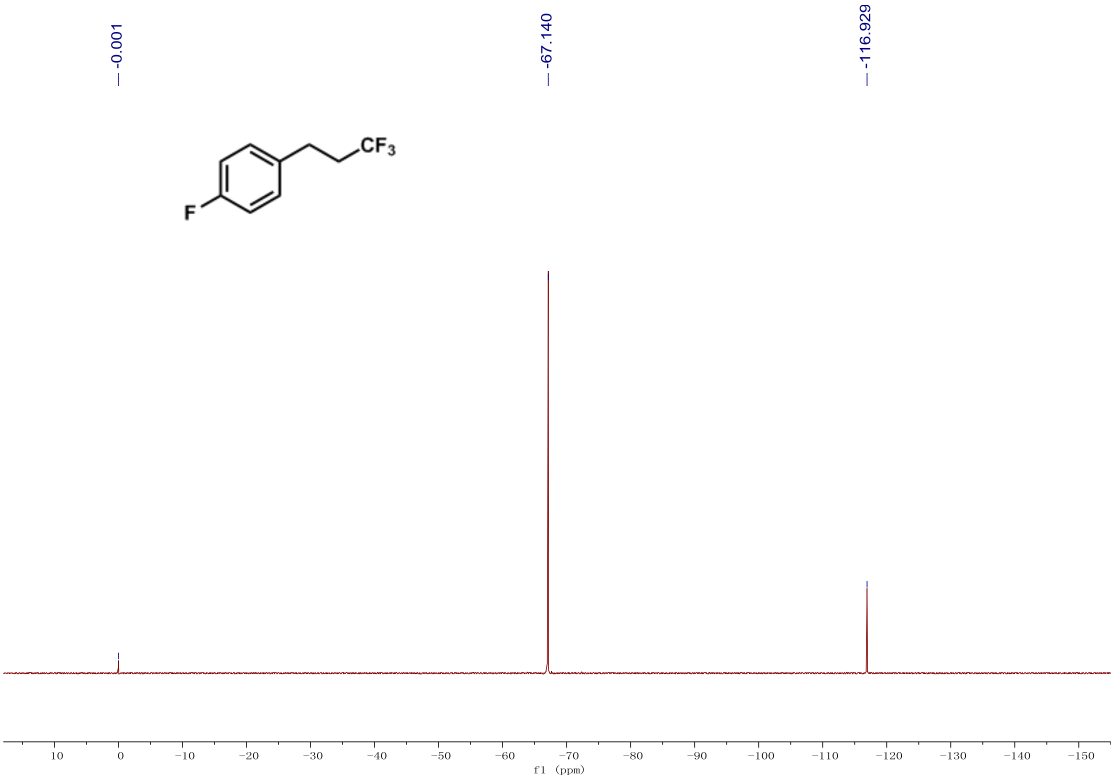

149.729
136.093
131.056
128.307
128.032
125.760
125.555
122.807
77.479
77.160
76.844
36.227
35.945
35.666
35.383
34.582
31.504
27.831
27.801
27.767
27.736
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.262
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

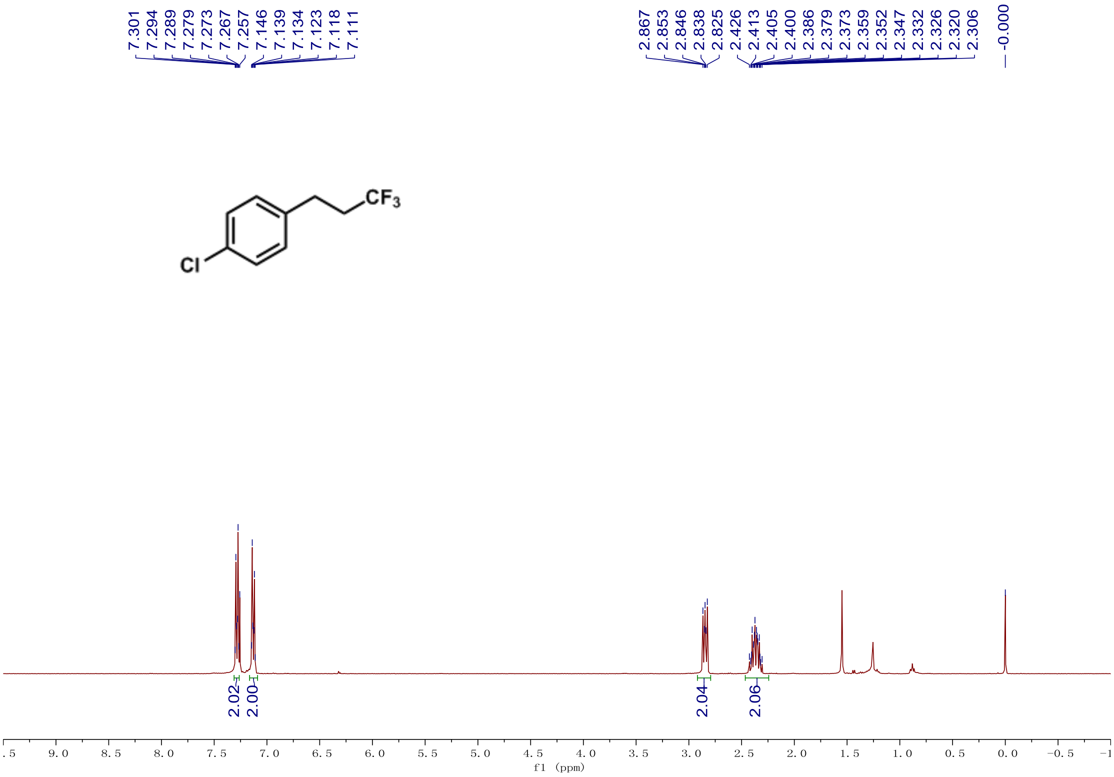
2-7

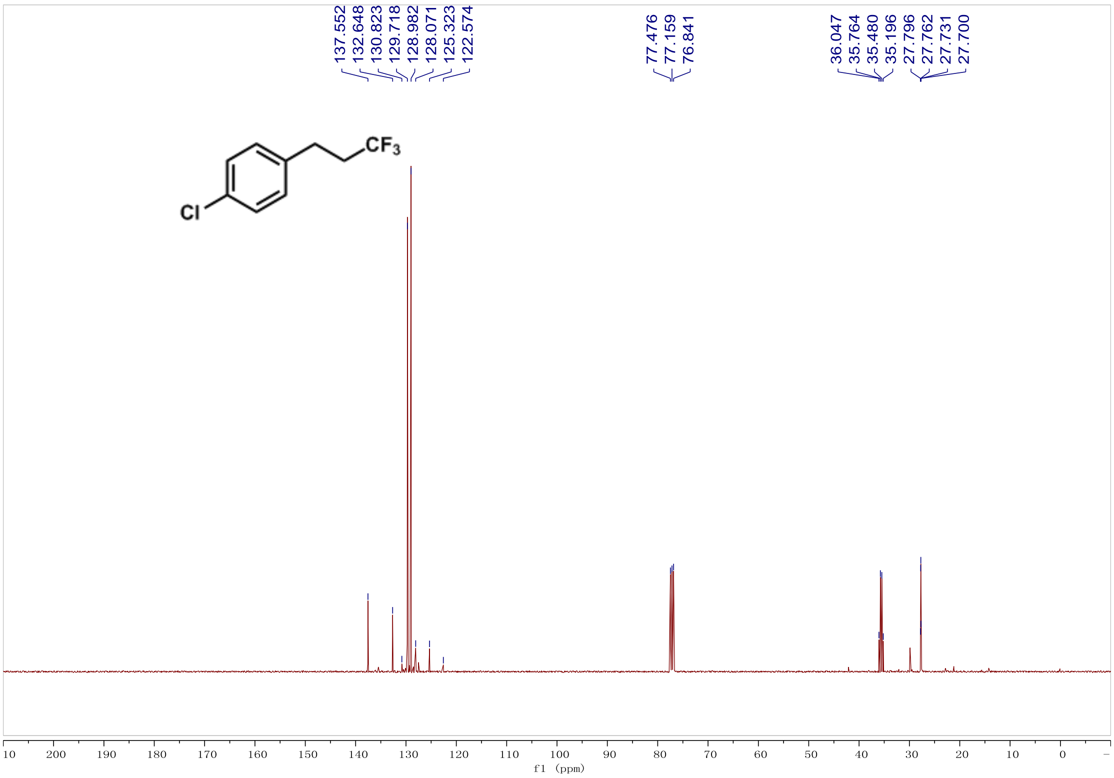

7.172
7.159
7.151
7.138
7.021
6.999
6.978
2.871
2.857
2.850
2.842
2.829
2.427
2.414
2.406
2.401
2.387
2.379
2.374
2.359
2.353
2.347
2.333
2.326
2.320
2.306
0.001
CF3
F
2.00
1.99
2.05
2.07
f1 (ppm)

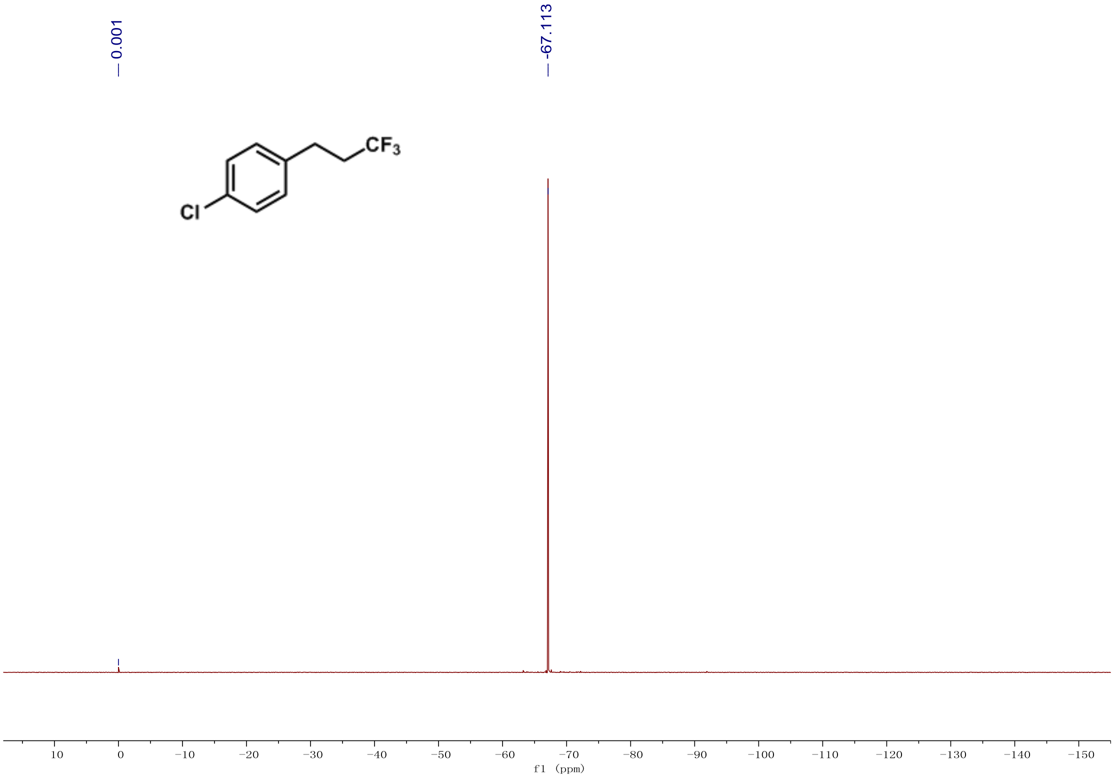

163.089
160.656
134.832
134.801
130.898
129.862
129.783
128.853
128.775
128.147
127.798
127.720
125.400
122.648
115.782
115.616
115.568
115.480
115.407
115.268
77.479
77.160
76.844
36.319
36.037
35.752
35.470
27.664
27.630
27.598
27.565
CF3
F
f1 (ppm)


-0.001
-67.140
-116.929
CF3
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

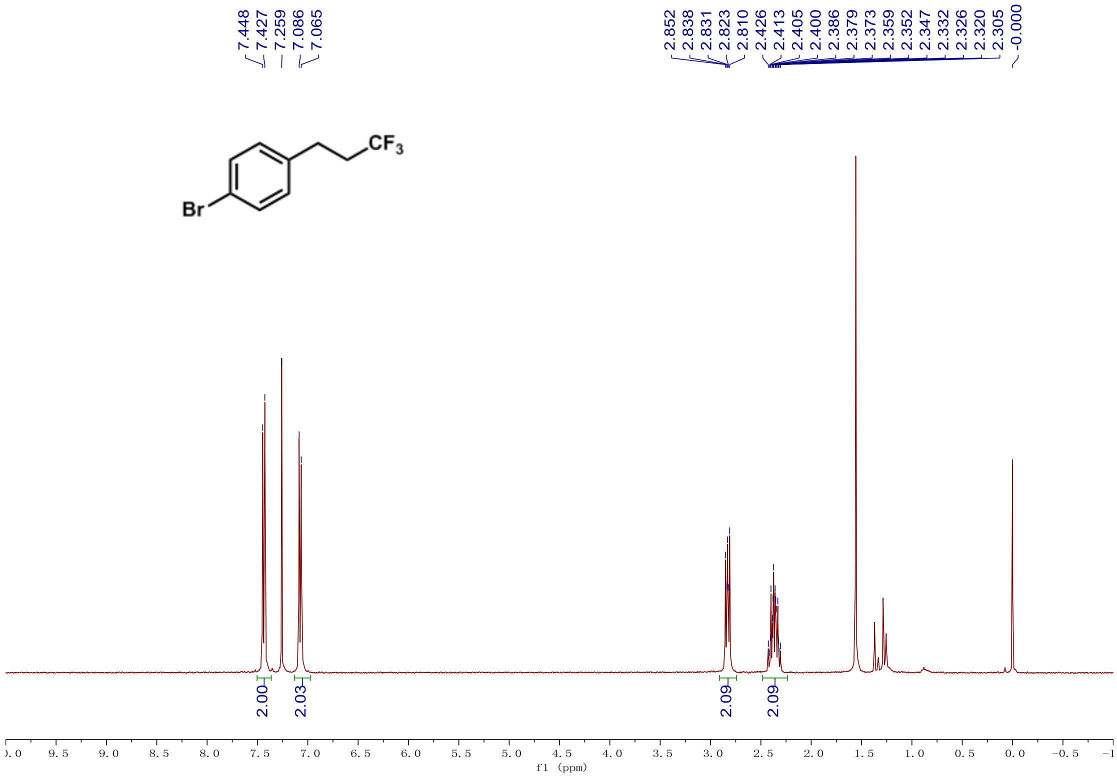
2-8

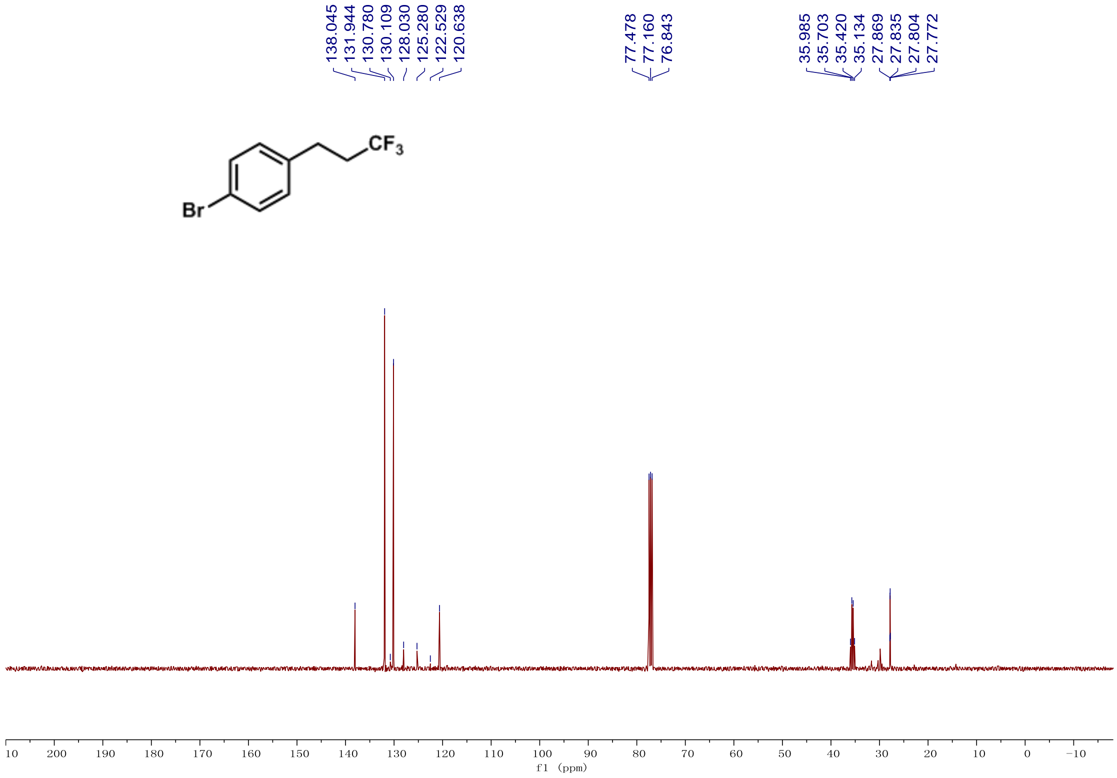

7.301
7.294
7.289
7.279
7.273
7.267
7.257
7.146
7.139
7.134
7.123
7.118
7.111
2.867
2.853
2.846
2.838
2.825
2.426
2.413
2.405
2.400
2.386
2.379
2.373
2.359
2.352
2.347
2.332
2.326
2.320
2.306
-0.000
CF3
Cl
2.02
2.00
2.04
2.06
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

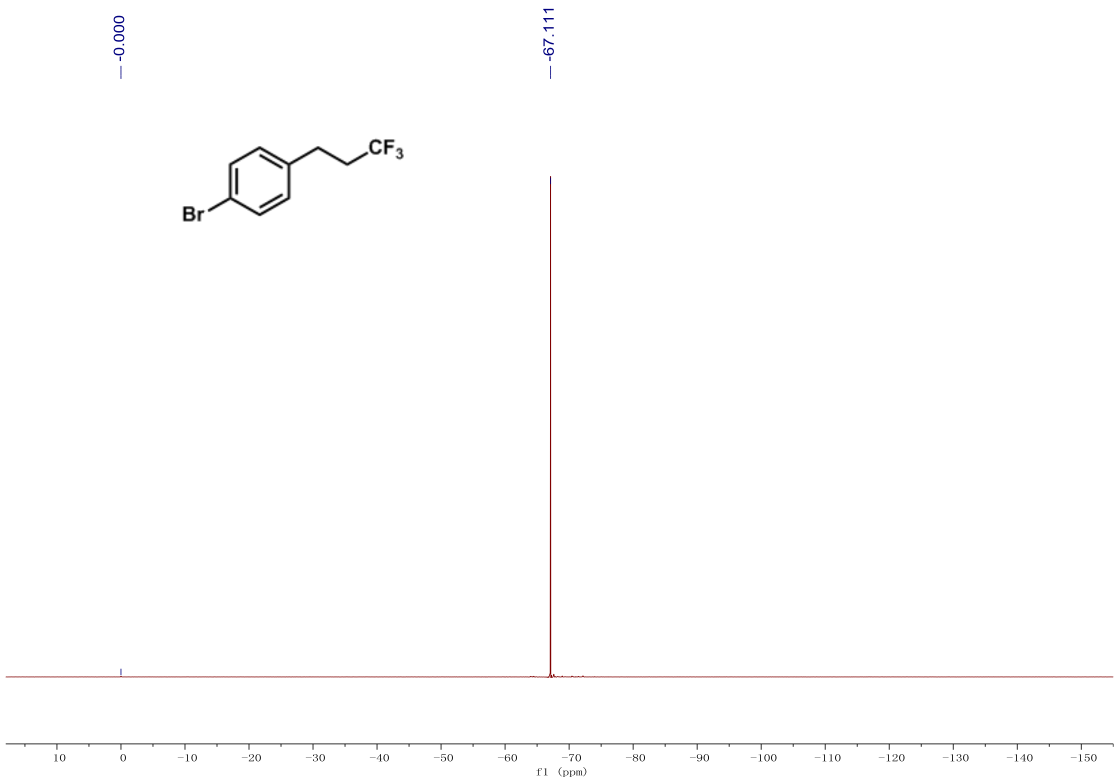

137.552
132.648
130.823
129.718
128.982
128.071
125.323
122.574
77.476
77.159
76.841
36.047
35.764
35.480
35.196
27.796
27.762
27.731
27.700
CF3
Cl
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-67.113
CF3
Cl
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

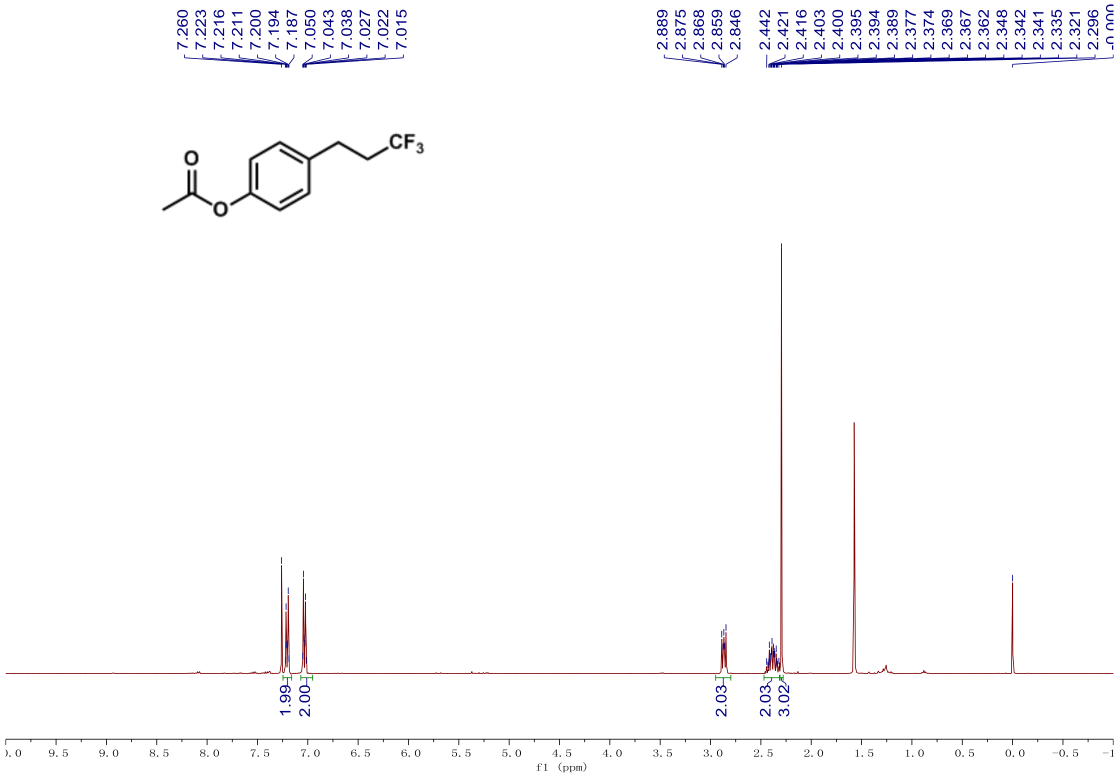
2-9

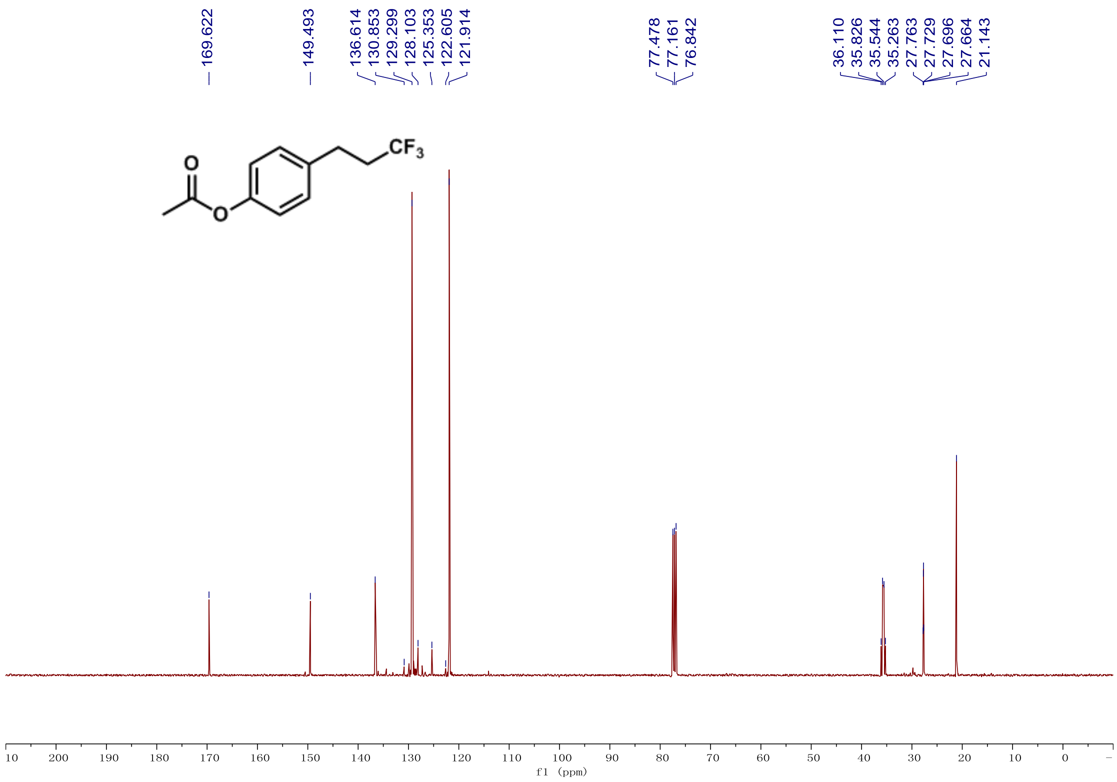

7.448
7.427
7.259
7.086
7.065
2.852
2.838
2.831
2.823
2.810
2.426
2.413
2.405
2.400
2.386
2.379
2.373
2.359
2.352
2.347
2.332
2.326
2.320
2.305
-0.000
CF3
Br
2.00
2.03
2.09
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

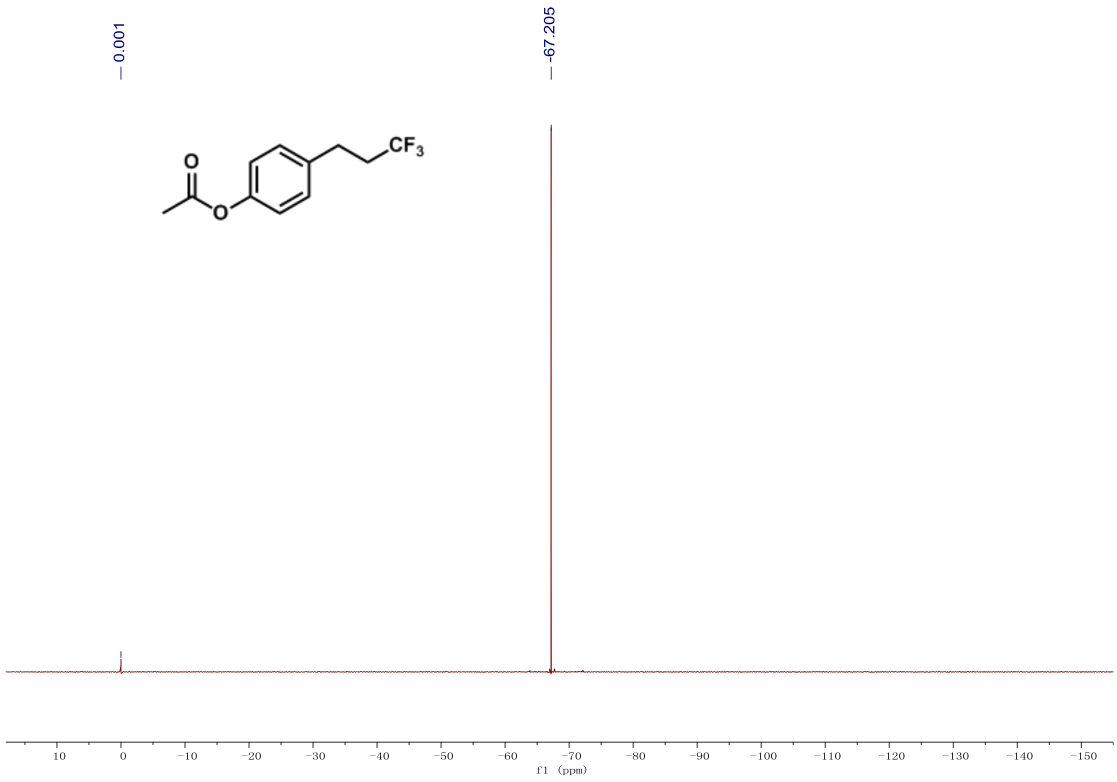

138.045
131.944
130.780
130.109
128.030
125.280
122.529
120.638
77.478
77.160
76.843
35.985
35.703
35.420
35.134
27.869
27.835
27.804
27.772
CF3
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-0.000
-67.111
Br
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

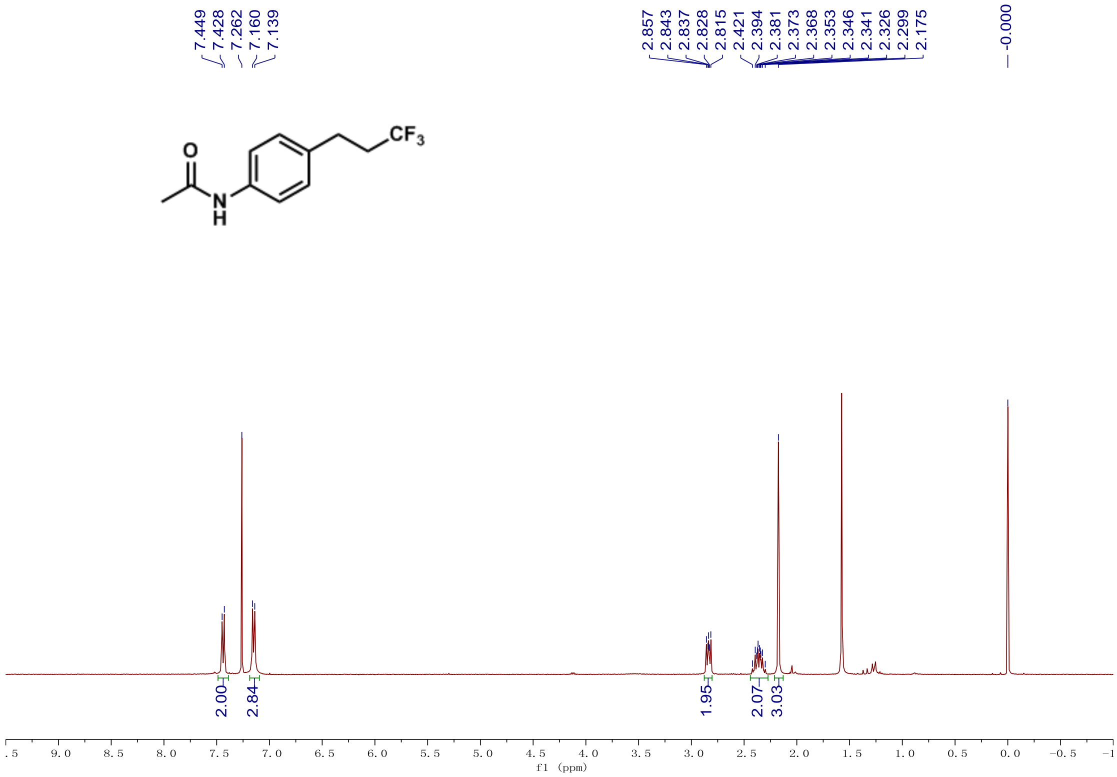
2-10

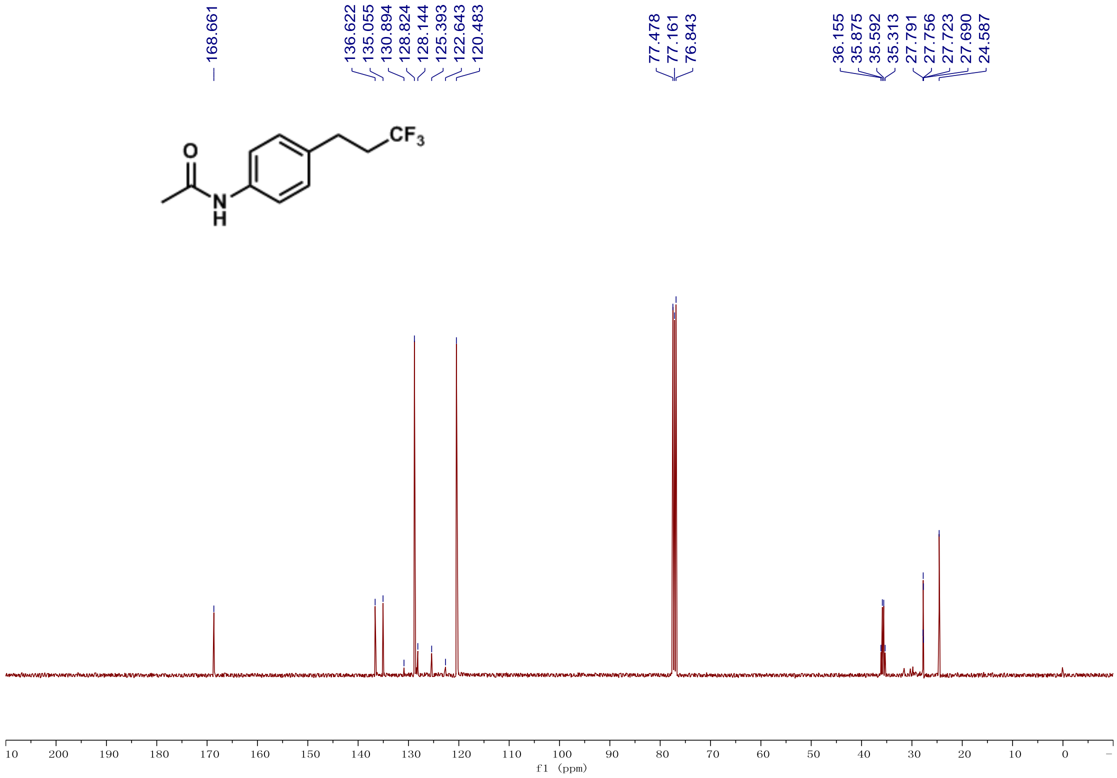

7.260 7.223 7.216 7.211 7.200 7.194 7.187 7.050 7.043 7.038 7.027 7.022 7.015
2.889 2.875 2.868 2.859 2.846 2.442 2.421 2.416 2.403 2.400 2.395 2.394 2.389 2.377 2.374 2.369 2.367 2.362 2.348 2.342 2.341 2.335 2.321 2.296 -0.000
O
O
CF3
1.99
2.00
2.03
2.03
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

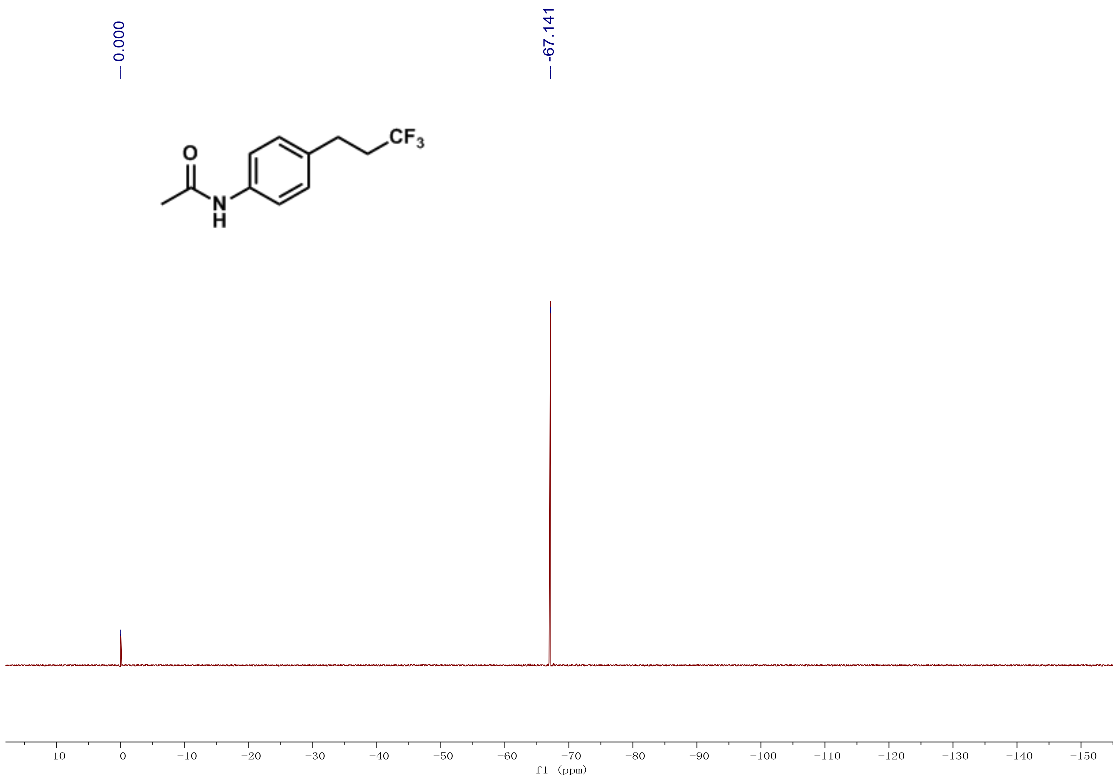

169.622
149.493
136.614
130.853
129.299
128.103
125.353
122.605
121.914
77.478
77.161
76.842
36.110
35.826
35.544
35.263
27.763
27.729
27.696
27.664
21.143
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-67.205
O
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

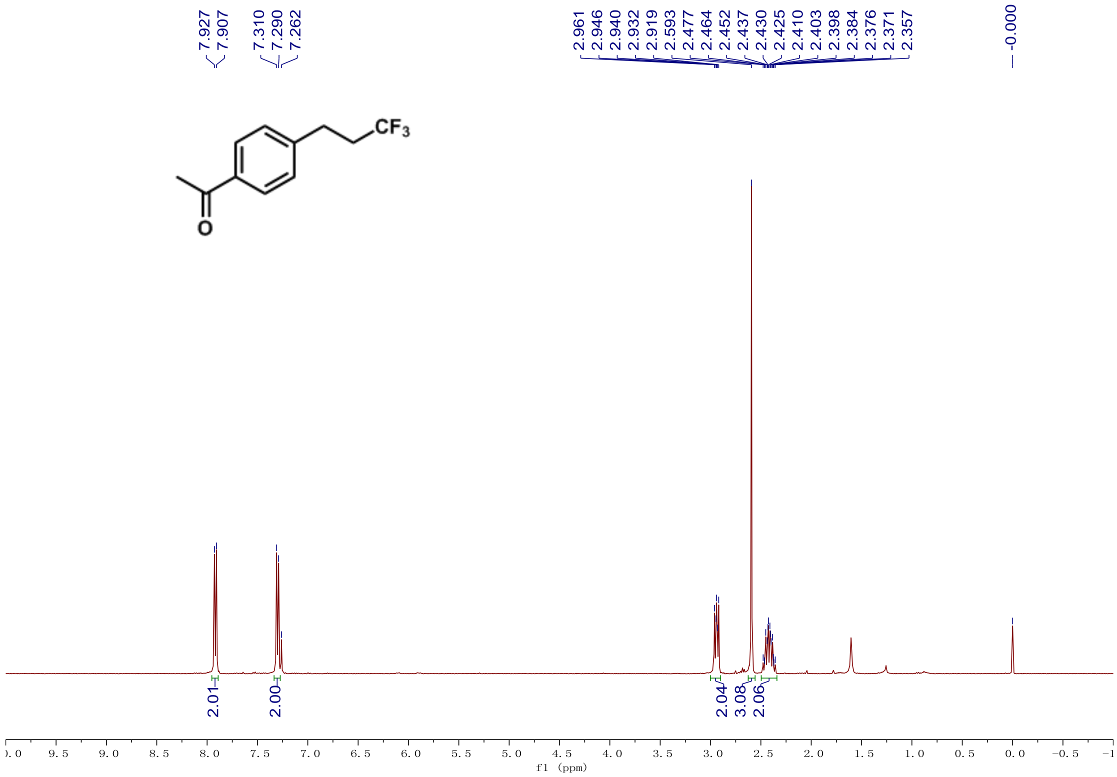
2-11

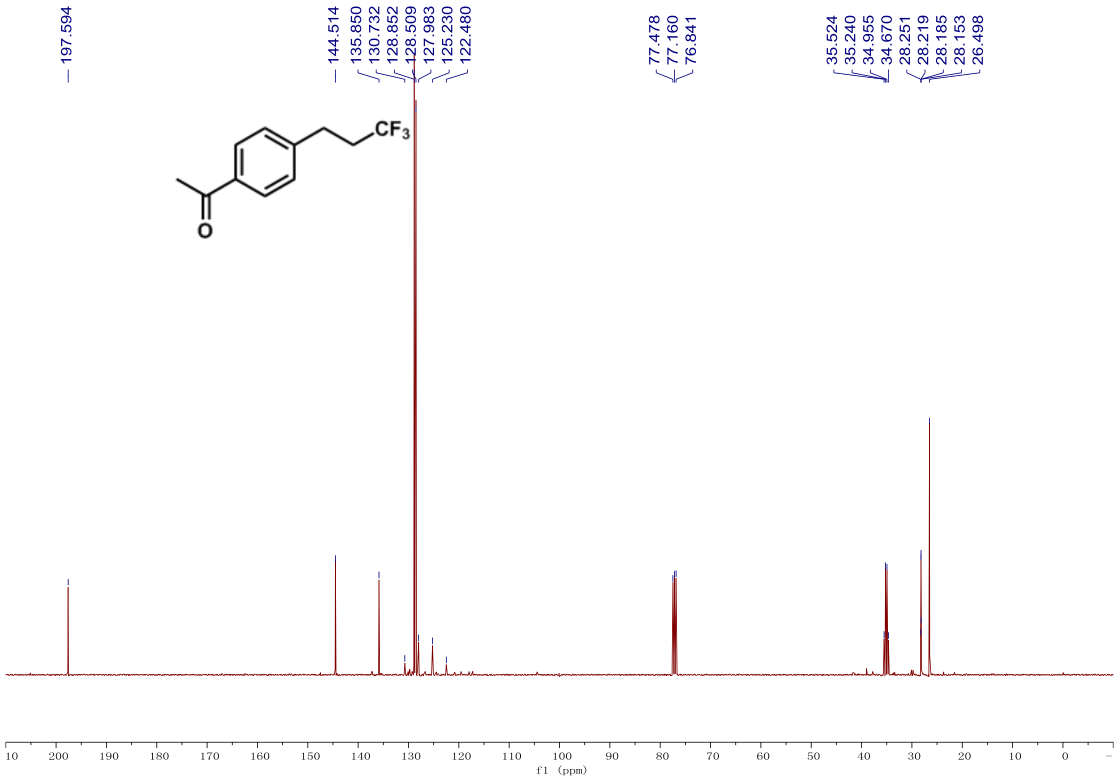

7.449
7.428
7.262
7.160
7.139
2.857
2.843
2.837
2.828
2.815
2.421
2.394
2.381
2.373
2.368
2.353
2.346
2.341
2.326
2.299
2.175
-0.000
O
N
H
CF3
2.00
2.84
1.95
2.07
3.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

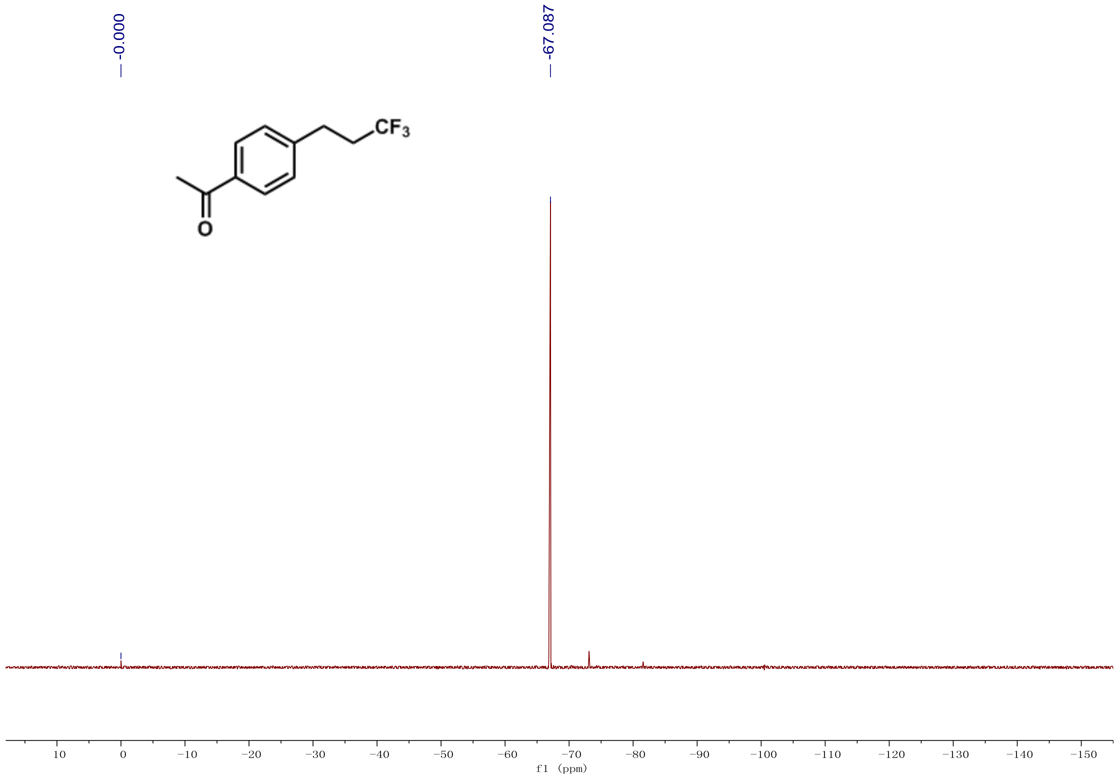

168.661
136.622
135.055
130.894
128.824
128.144
125.393
122.643
120.483
77.478
77.161
76.843
36.155
35.875
35.592
35.313
27.791
27.756
27.723
27.690
24.587
O
N
H
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–
f1 (ppm)


0.000
-67.141
O
N
H
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

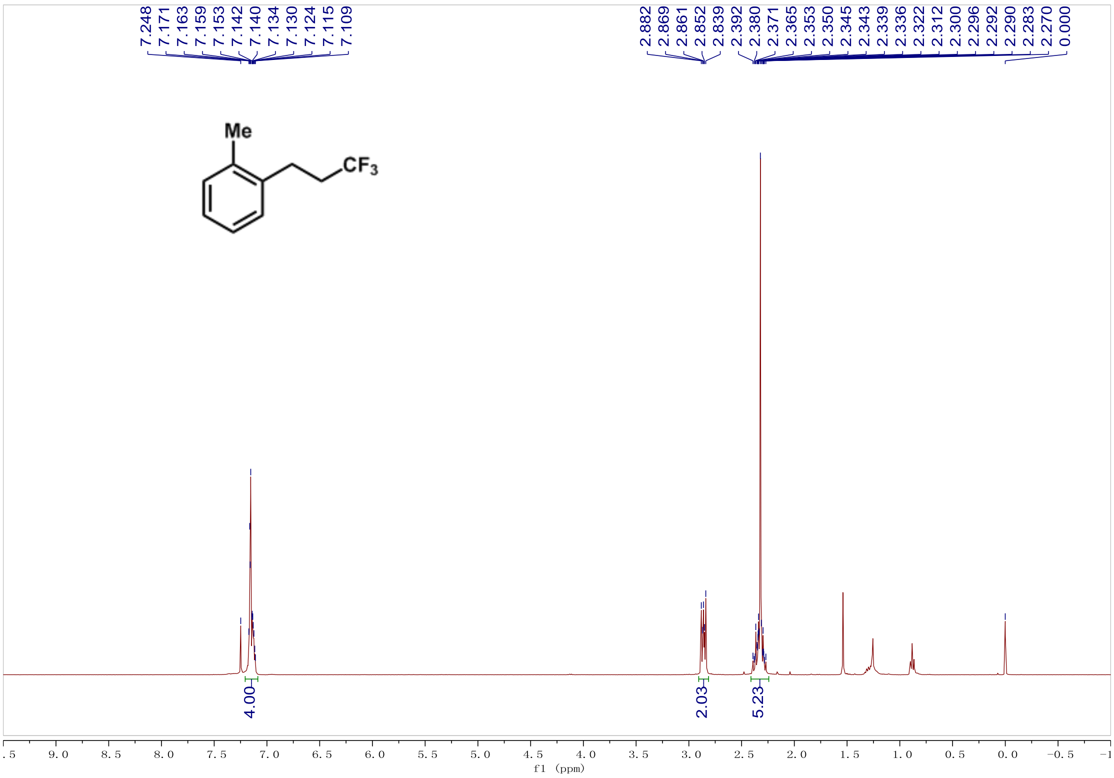
2-12

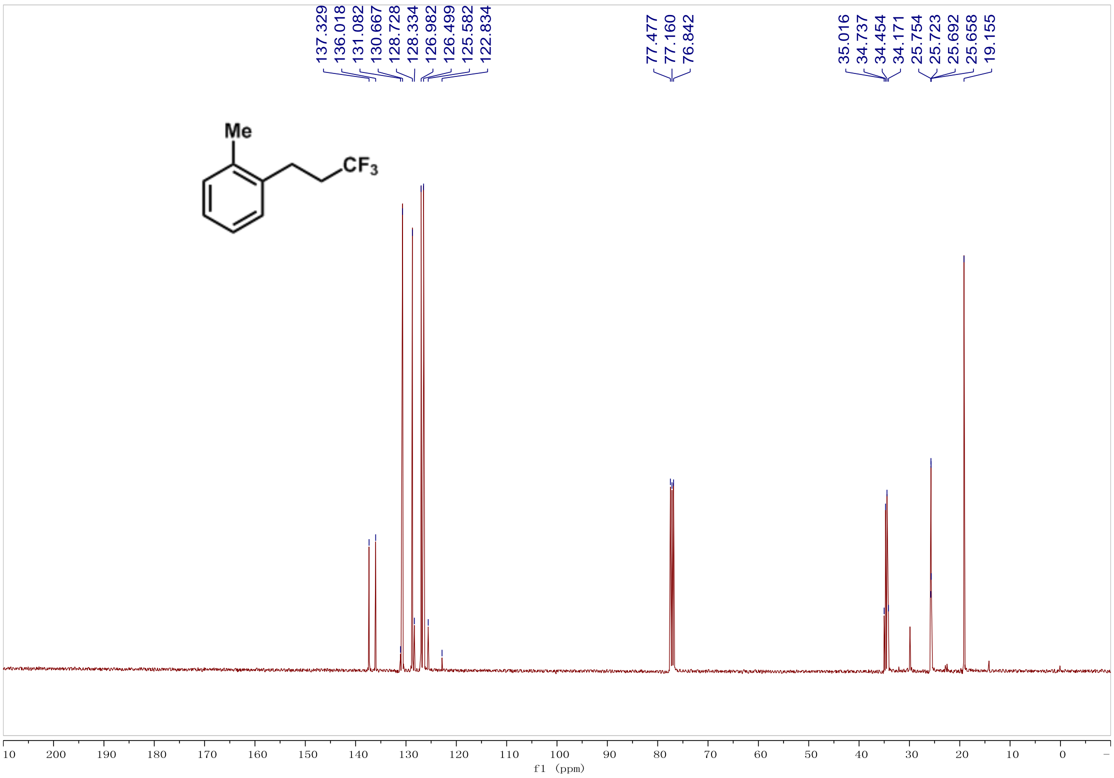

7.927
7.907
7.310
7.290
7.262
2.961
2.946
2.940
2.932
2.919
2.593
2.477
2.464
2.452
2.437
2.430
2.425
2.410
2.403
2.398
2.384
2.376
2.371
2.357
-0.000
CF3
O
2.01
2.00
2.04
3.08
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

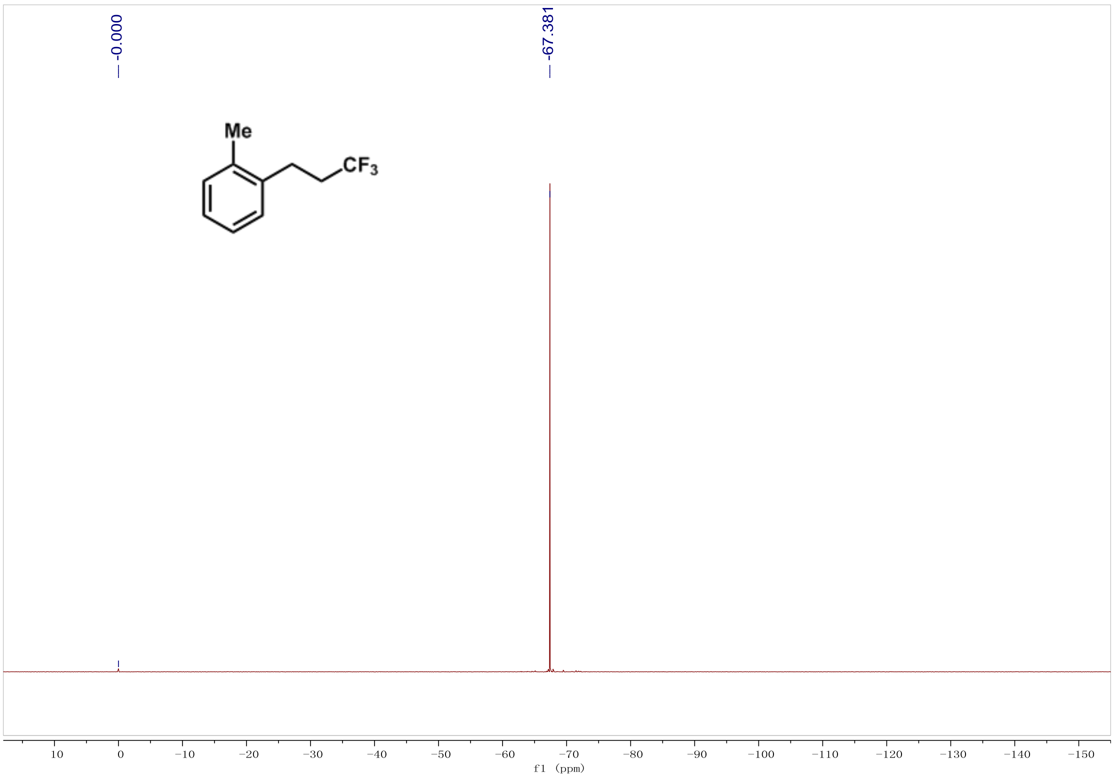

197.594
144.514
135.850
130.732
128.852
128.509
127.983
125.230
122.480
77.478
77.160
76.841
35.524
35.240
34.955
34.670
28.251
28.219
28.185
28.153
26.498
CF3
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-67.087
CF3
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

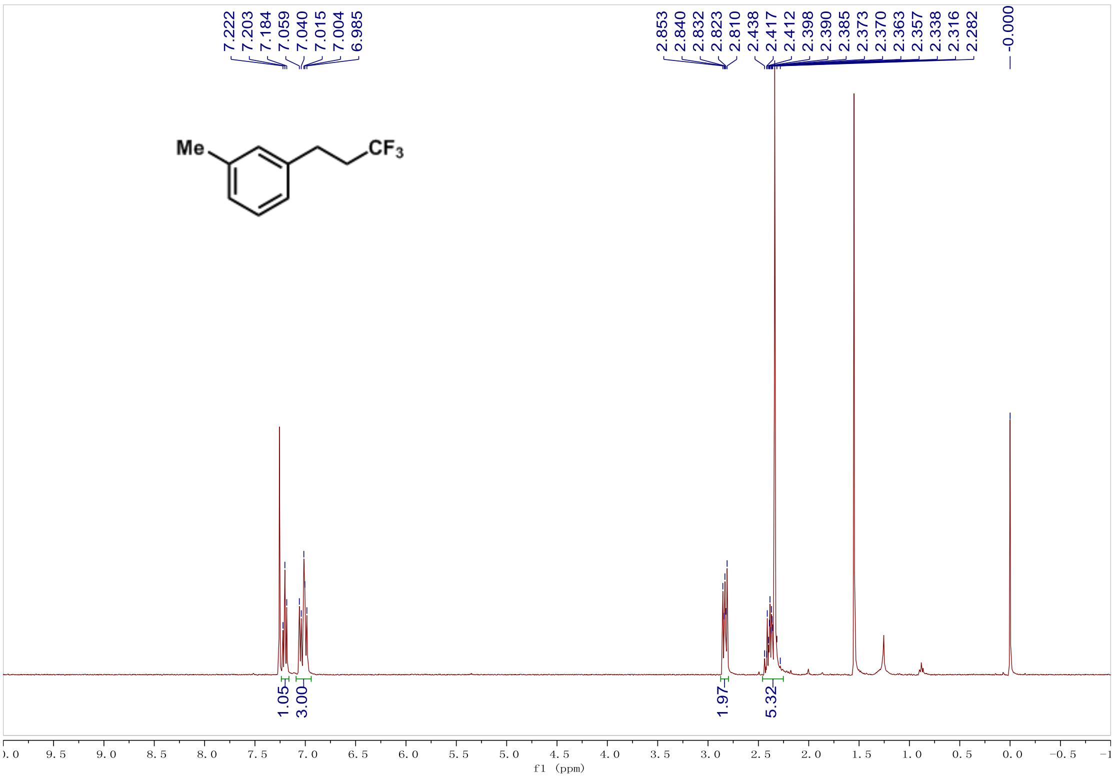
2-13

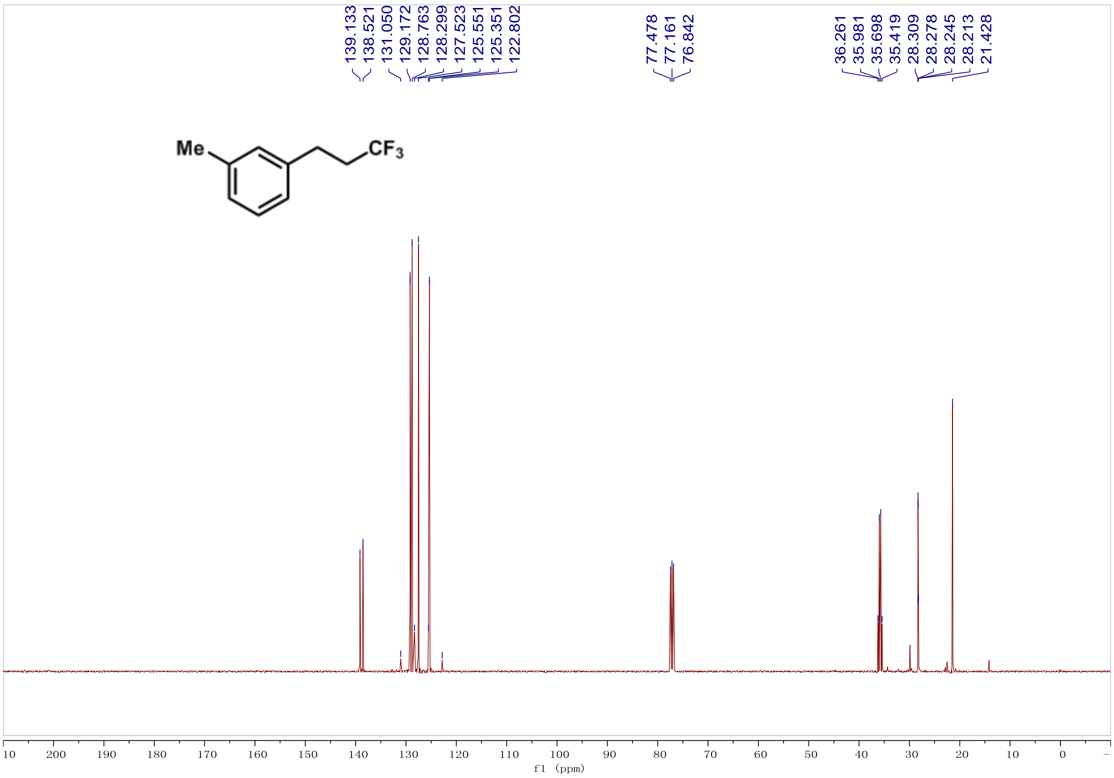

7.248
7.171
7.163
7.159
7.153
7.142
7.140
7.134
7.130
7.124
7.115
7.109
2.882
2.869
2.861
2.852
2.839
2.392
2.380
2.371
2.365
2.353
2.350
2.345
2.343
2.339
2.336
2.322
2.312
2.300
2.296
2.292
2.290
2.283
2.270
0.000
Me
CF3
4.00
2.03
5.23
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

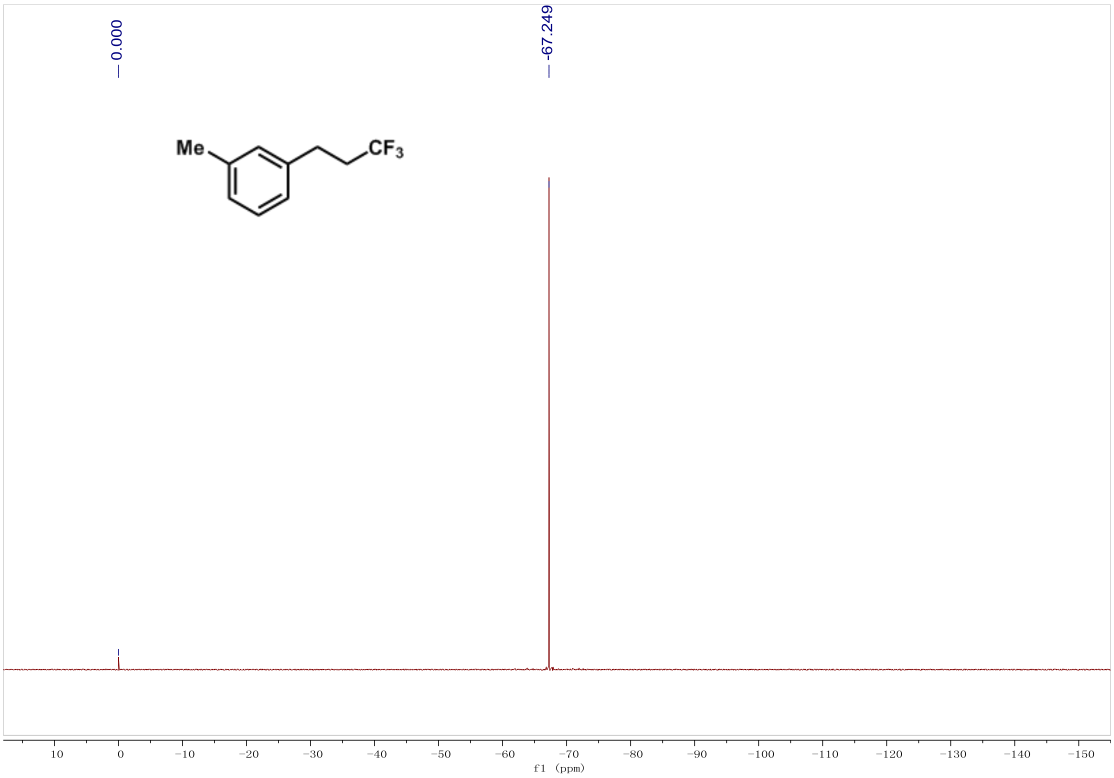

137.329
136.018
131.082
130.667
128.728
128.334
126.982
126.499
125.582
122.834
77.477
77.160
76.842
35.016
34.737
34.454
34.171
25.754
25.723
25.692
25.658
19.155
Me
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)


-0.000
-67.381
Me
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

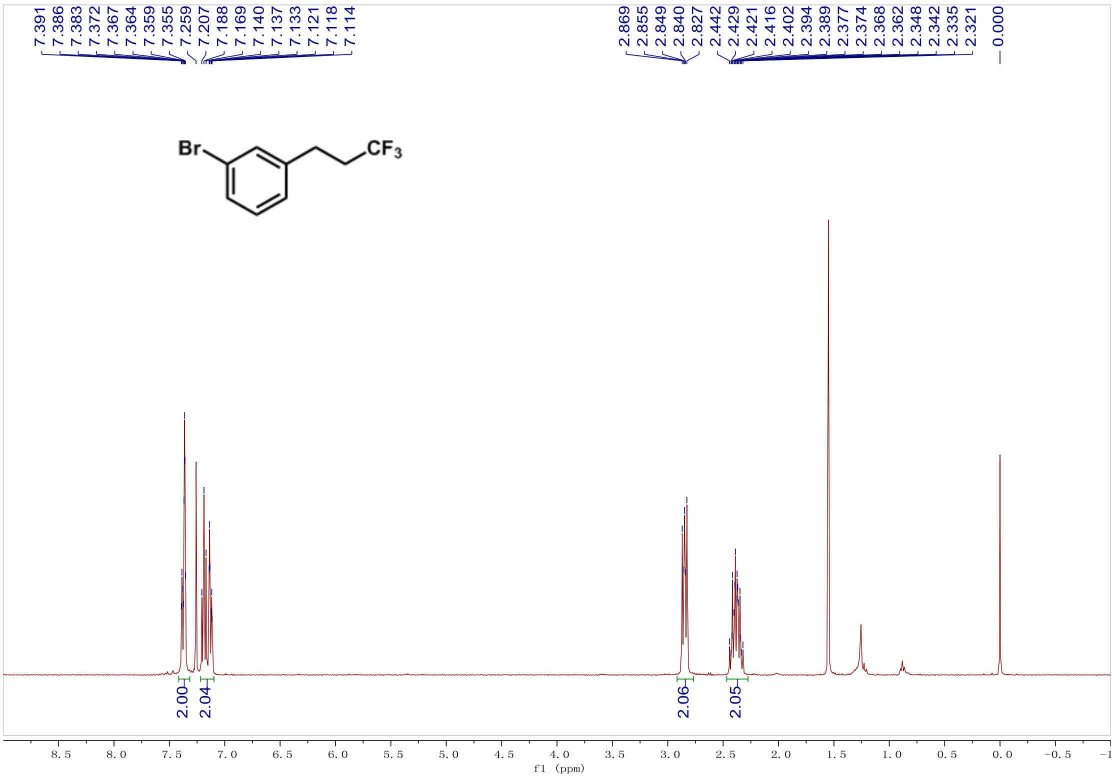
2-14

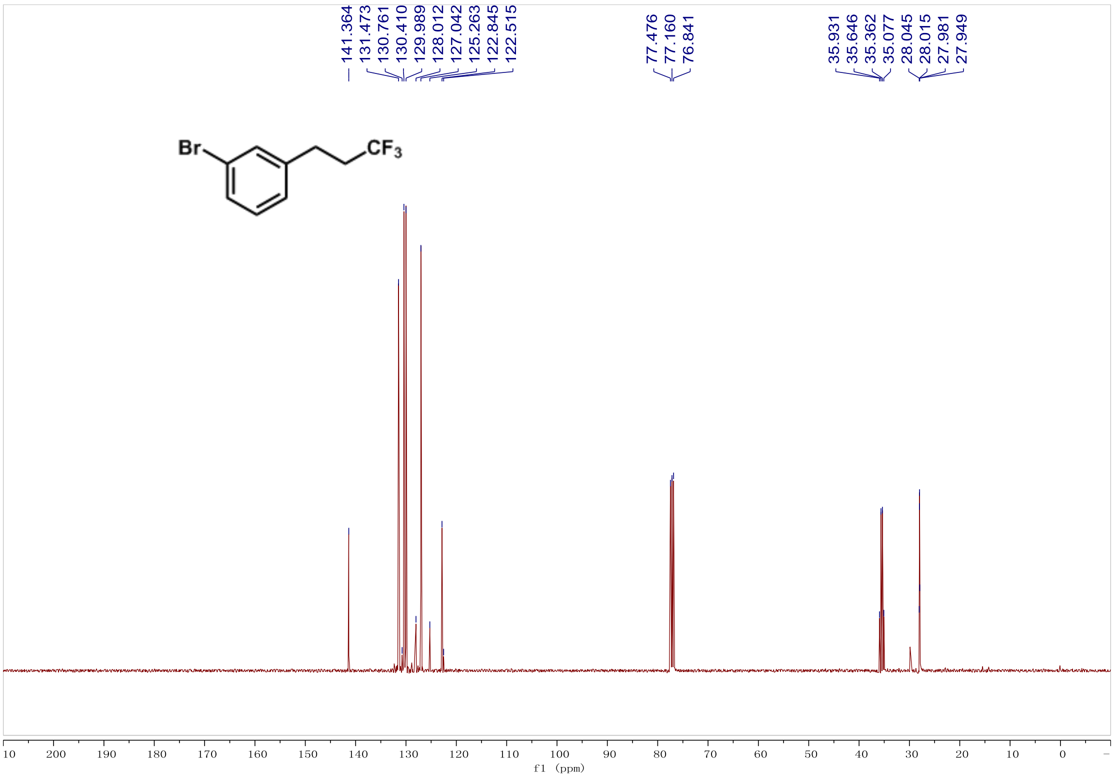

7.222
7.203
7.184
7.059
7.040
7.015
7.004
6.985
2.853
2.840
2.832
2.823
2.810
2.438
2.417
2.412
2.398
2.390
2.385
2.373
2.370
2.363
2.357
2.338
2.316
2.282
-0.000
Me
CF3
1.05
3.00
1.97
5.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

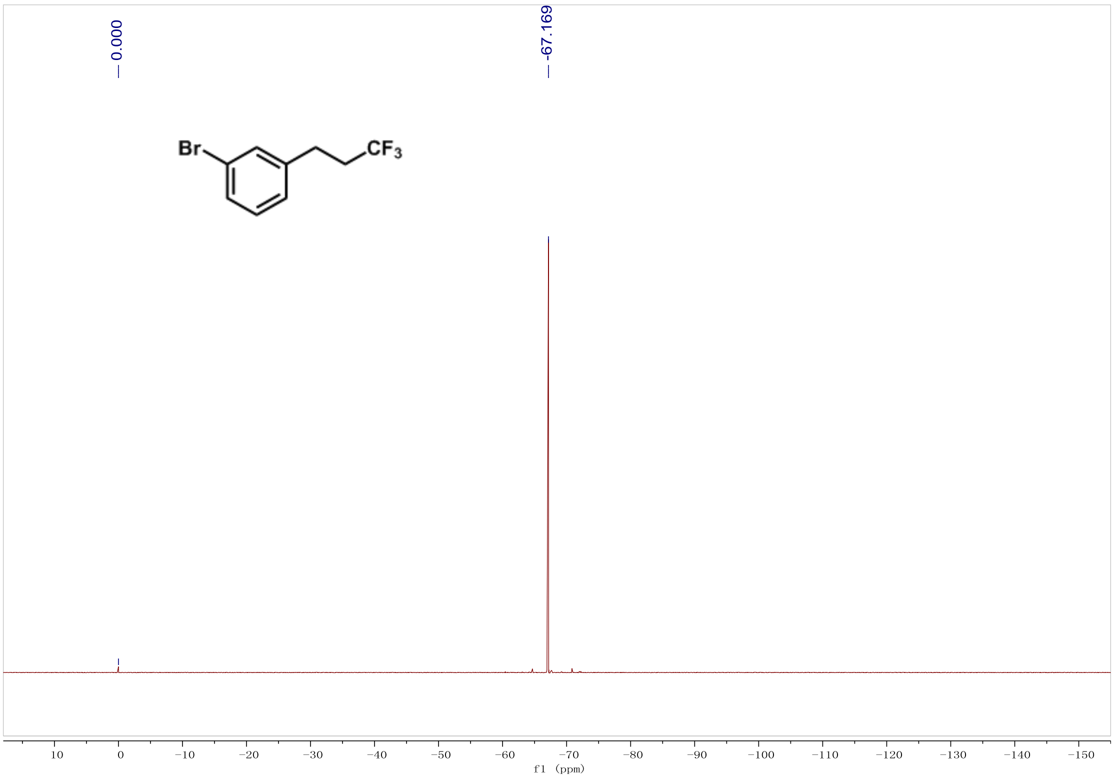

139.133
138.521
131.050
129.172
128.763
128.299
127.523
125.551
125.351
122.802
77.478
77.161
76.842
36.261
35.981
35.698
35.419
28.309
28.278
28.245
28.213
21.428
Me
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.249
Me
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

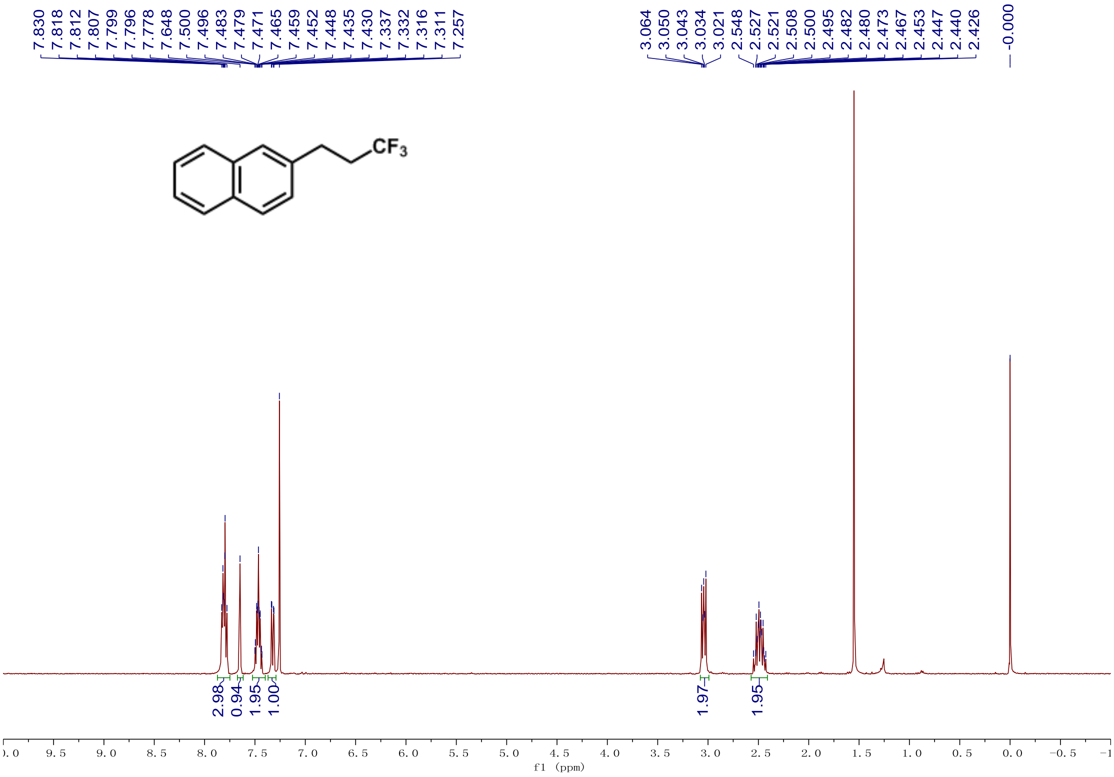
2-15

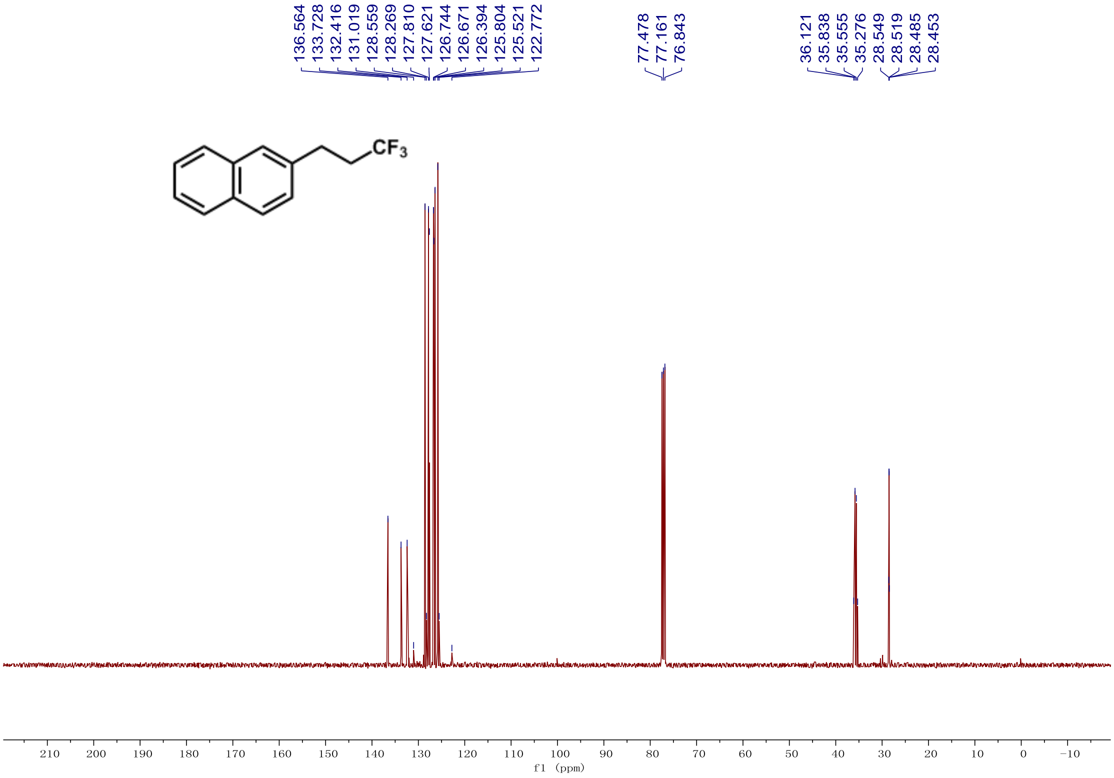

7.391
7.386
7.383
7.372
7.367
7.364
7.359
7.355
7.259
7.207
7.188
7.169
7.140
7.137
7.133
7.121
7.118
7.114
2.869
2.855
2.849
2.840
2.827
2.442
2.429
2.421
2.416
2.402
2.394
2.389
2.377
2.374
2.368
2.362
2.348
2.342
2.335
2.321
0.000
Br
CF3
2.00
2.04
2.06
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

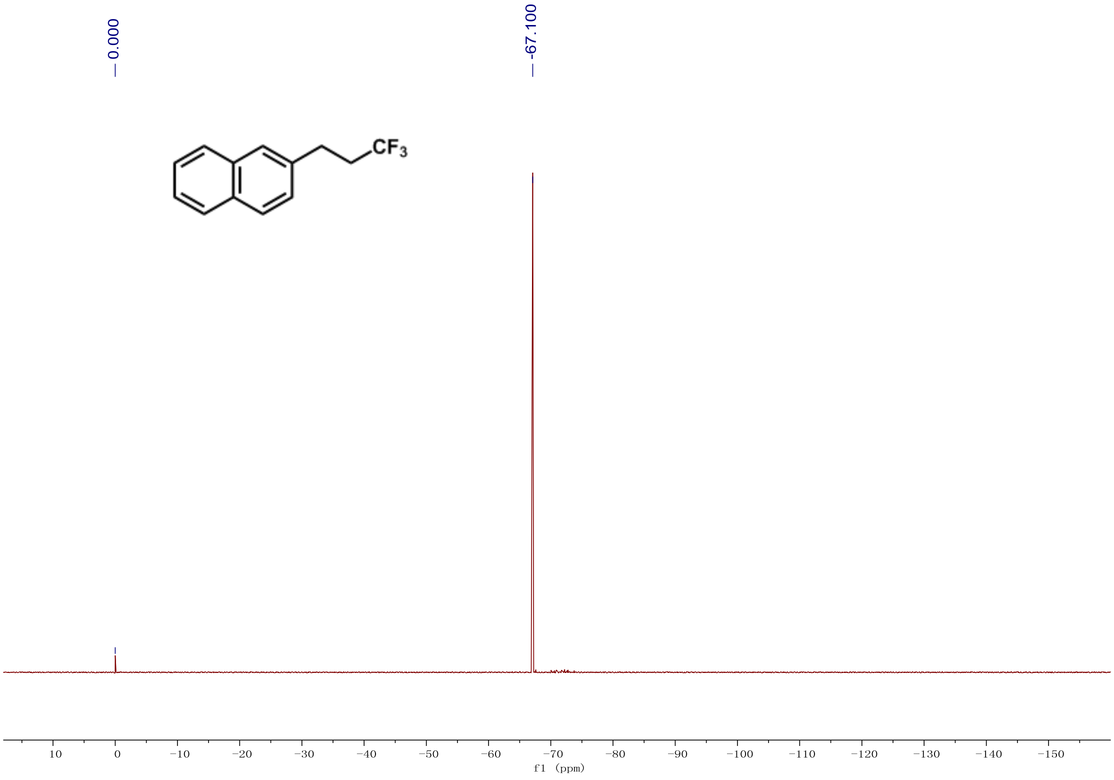

141.364
131.473
130.761
130.410
129.989
128.012
127.042
125.263
122.845
122.515
77.476
77.160
76.841
35.931
35.646
35.362
35.077
28.045
28.015
27.981
27.949
Br
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.169
Br
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

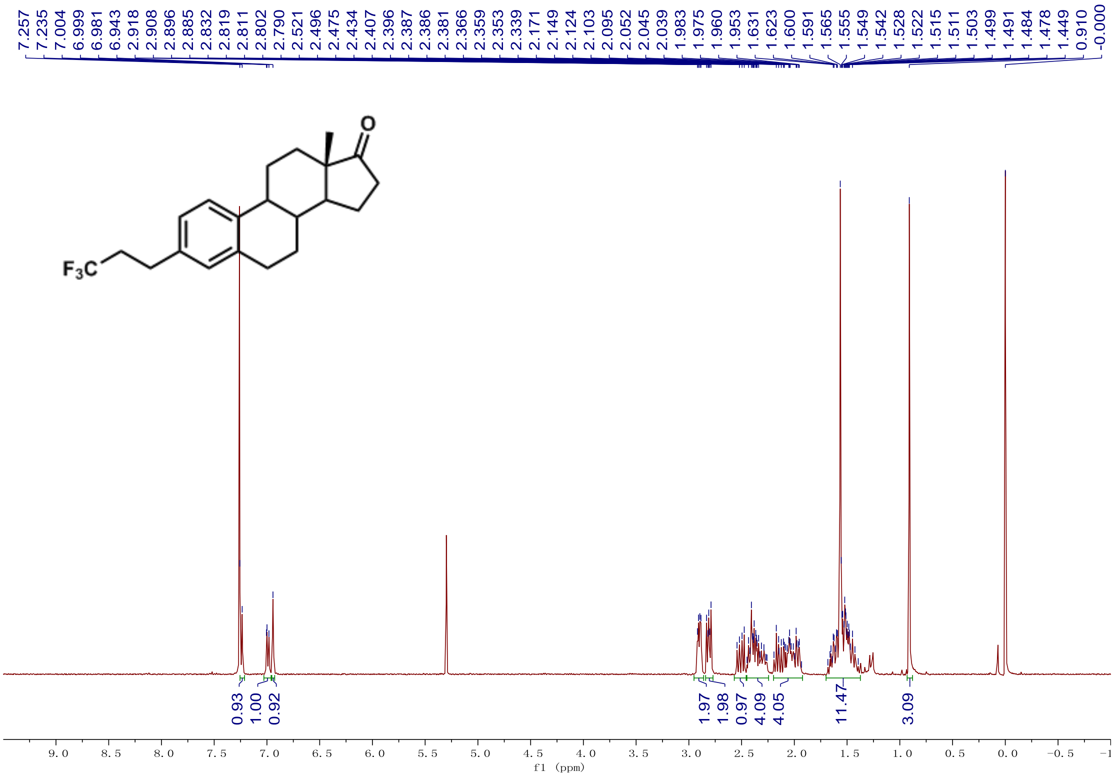
2-16

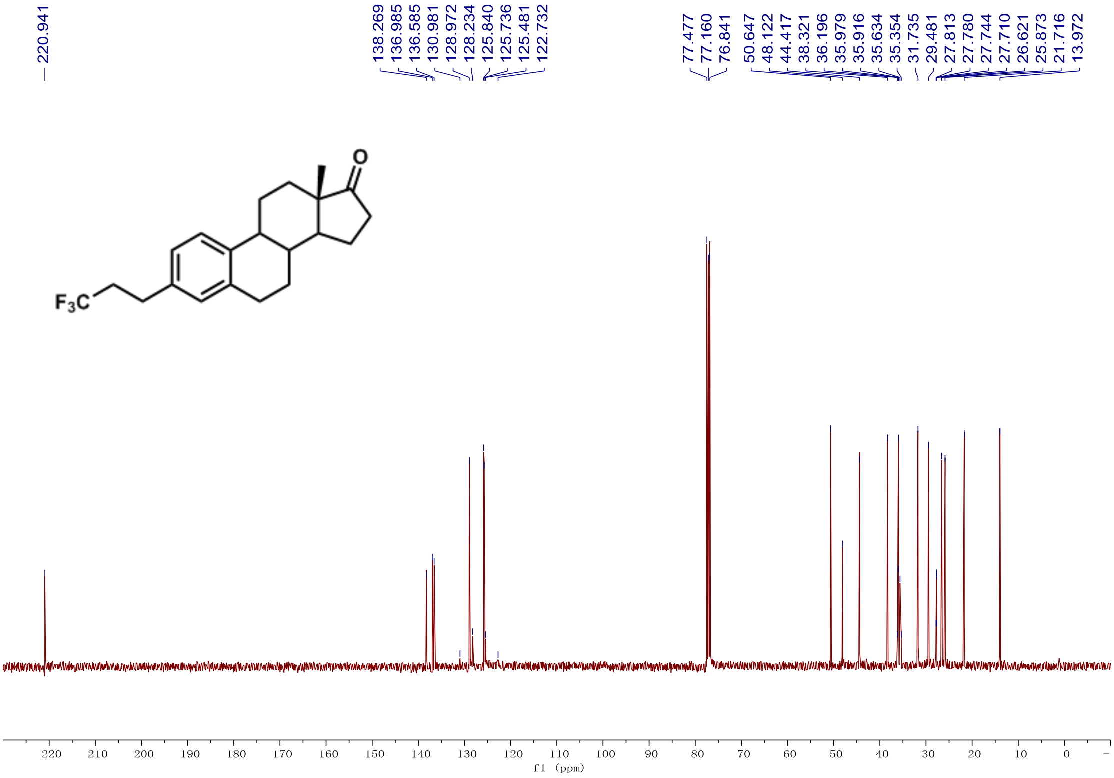

7.830
7.818
7.812
7.807
7.799
7.796
7.778
7.648
7.500
7.496
7.483
7.479
7.471
7.465
7.459
7.452
7.448
7.435
7.430
7.337
7.332
7.316
7.311
7.257
3.064
3.050
3.043
3.034
3.021
2.548
2.527
2.521
2.508
2.500
2.495
2.482
2.480
2.473
2.467
2.453
2.447
2.440
2.426
-0.000
CF3
2.98
0.94
1.95
1.00
1.97
1.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

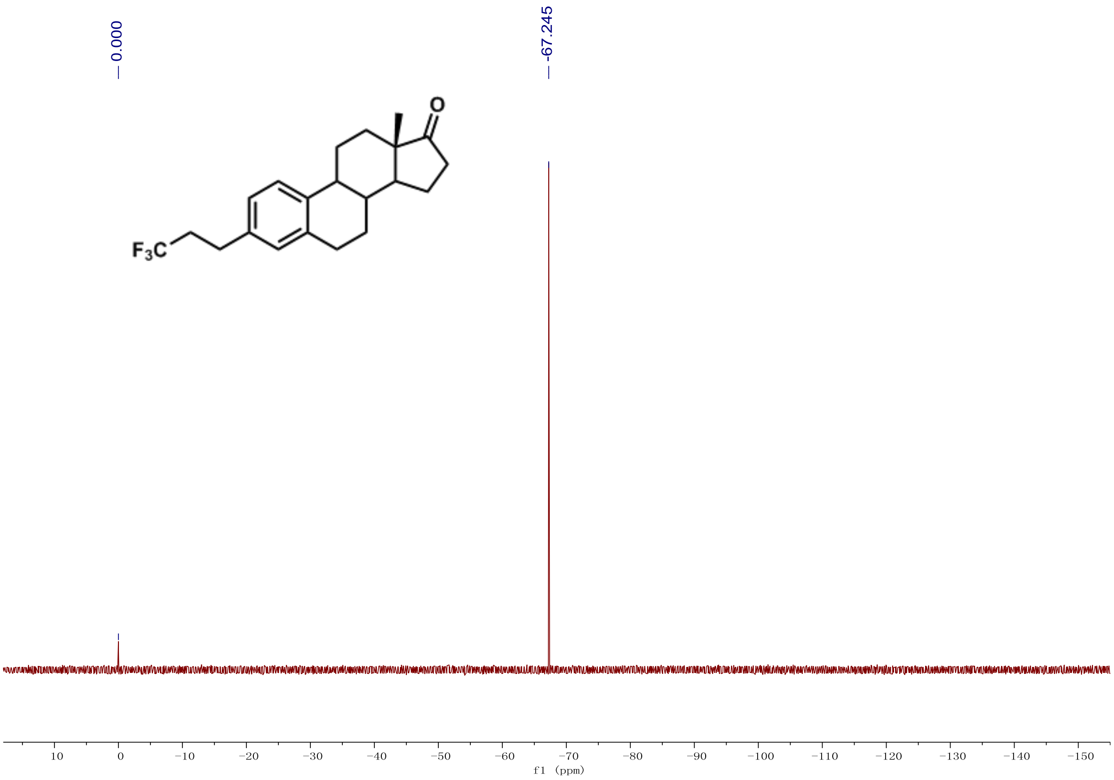

136.564
133.728
132.416
131.019
128.559
128.269
127.810
127.621
126.744
126.671
126.394
125.804
125.521
122.772
77.478
77.161
76.843
36.121
35.838
35.555
35.276
28.549
28.519
28.485
28.453
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


0.000
-67.100
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

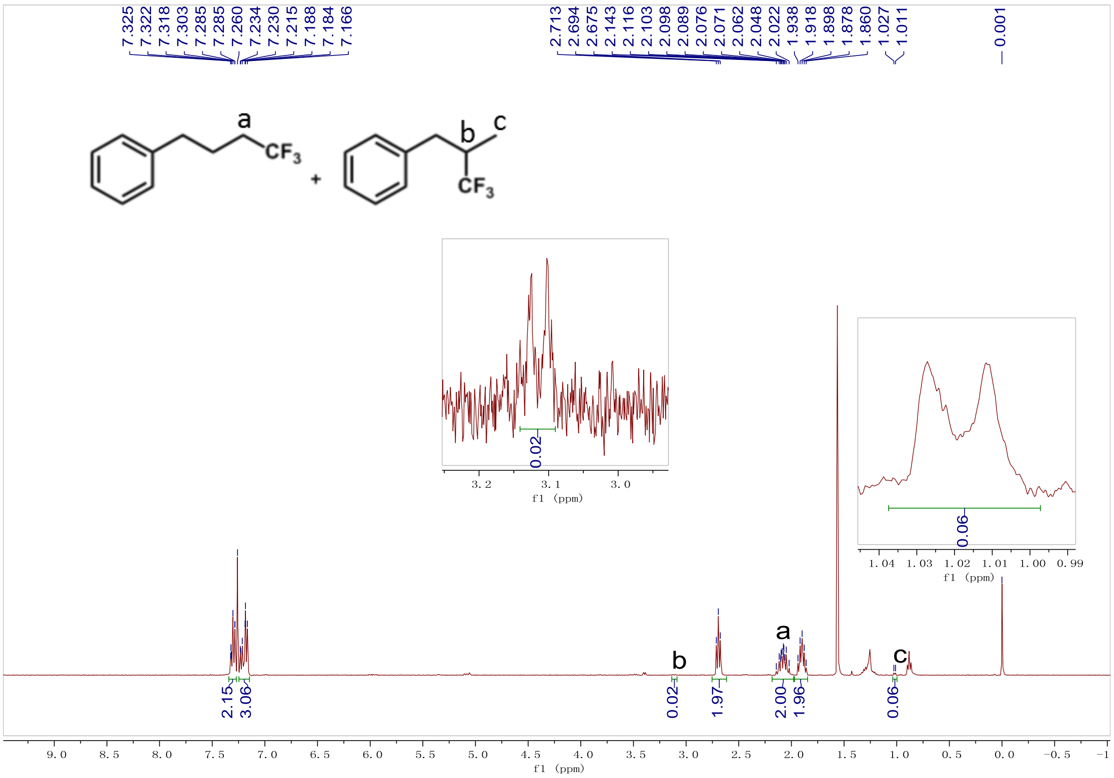
2-17

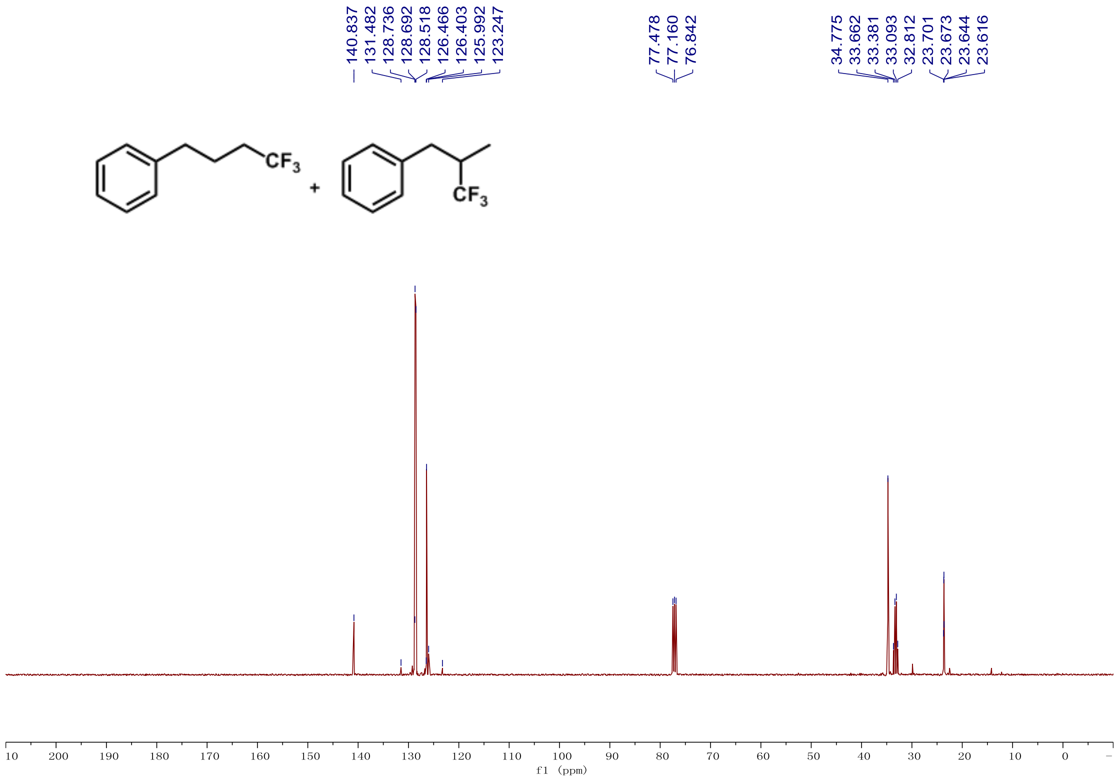

7.257
7.235
7.004
6.999
6.981
6.943
2.918
2.908
2.896
2.885
2.832
2.819
2.811
2.802
2.790
2.521
2.496
2.475
2.434
2.407
2.396
2.387
2.386
2.381
2.366
2.359
2.353
2.339
2.171
2.149
2.124
2.103
2.095
2.052
2.045
2.039
1.983
1.975
1.960
1.953
1.631
1.623
1.600
1.591
1.565
1.555
1.549
1.542
1.528
1.522
1.515
1.511
1.503
1.499
1.491
1.484
1.478
1.449
0.910
-0.000
O
F_3C
0.93
1.00
0.92
1.97
1.98
0.97
4.09
4.05
11.47
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


220.941
138.269
136.985
136.585
130.981
128.972
128.234
125.840
125.736
125.481
122.732
77.477
77.160
76.841
50.647
48.122
44.417
38.321
36.196
35.979
35.916
35.634
35.354
31.735
29.481
27.813
27.780
27.744
27.710
26.621
25.873
21.716
13.972
O
F_3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

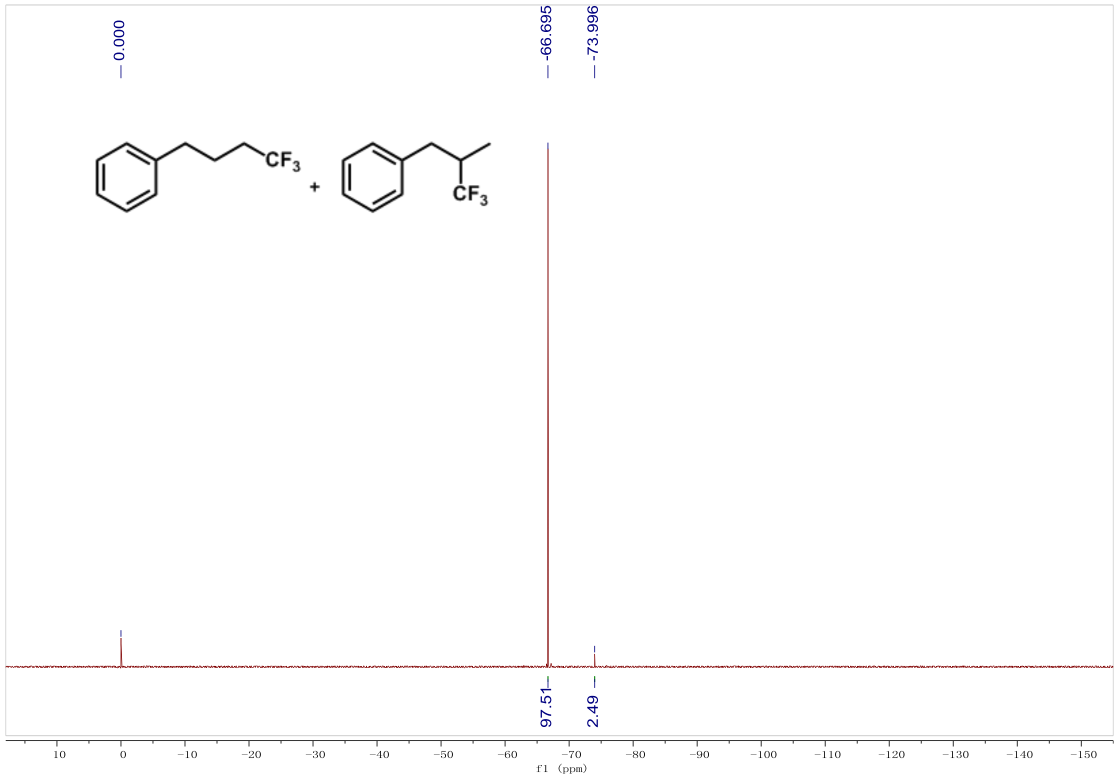

0.000
-67.245
F3C
O
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

2-18


7.325 7.322 7.318 7.303 7.285 7.285 7.260 7.234 7.230 7.215 7.188 7.184 7.166
2.713 2.694 2.675 2.143 2.116 2.103 2.089 2.076 2.071 2.062 2.048 2.022 1.938 1.918 1.898 1.878 1.860 1.027 1.011
0.001
a
CF3
+
b
c
CF3
0.02
3.2 3.1 3.0
f1 (ppm)
0.06
1.04 1.03 1.02 1.01 1.00 0.99
f1 (ppm)
2.15
3.06
b
0.02
1.97
a
2.00
1.96
c
0.06
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 −1
f1 (ppm)

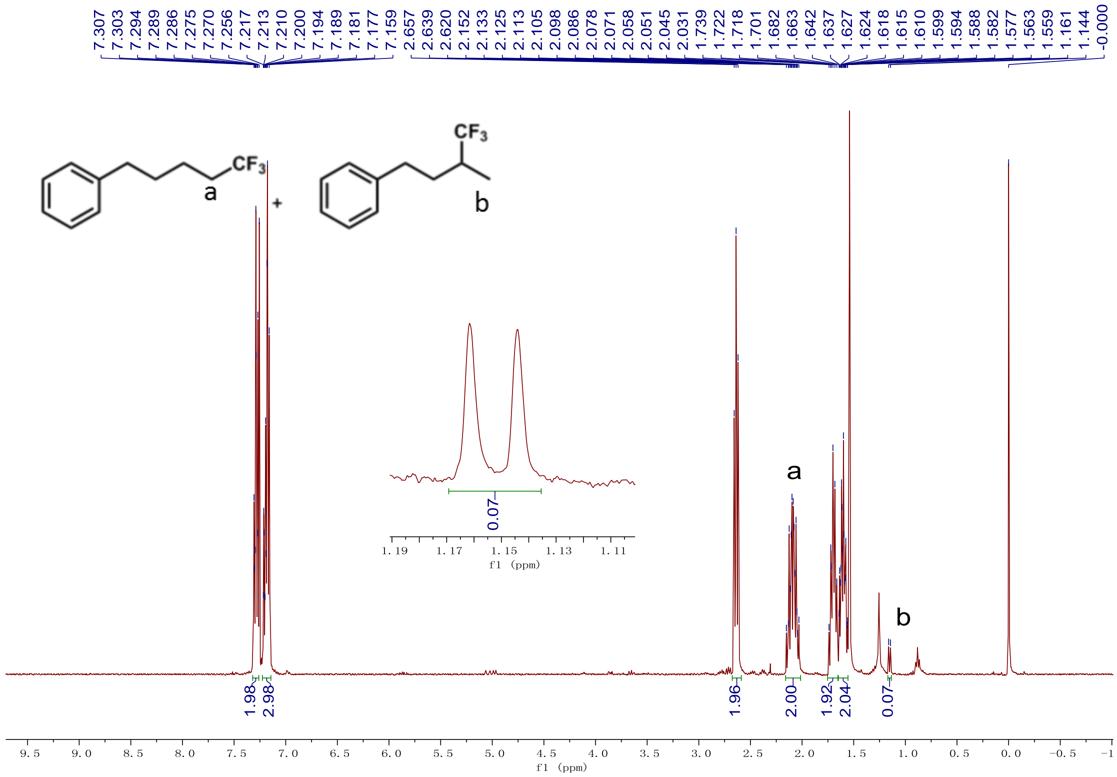


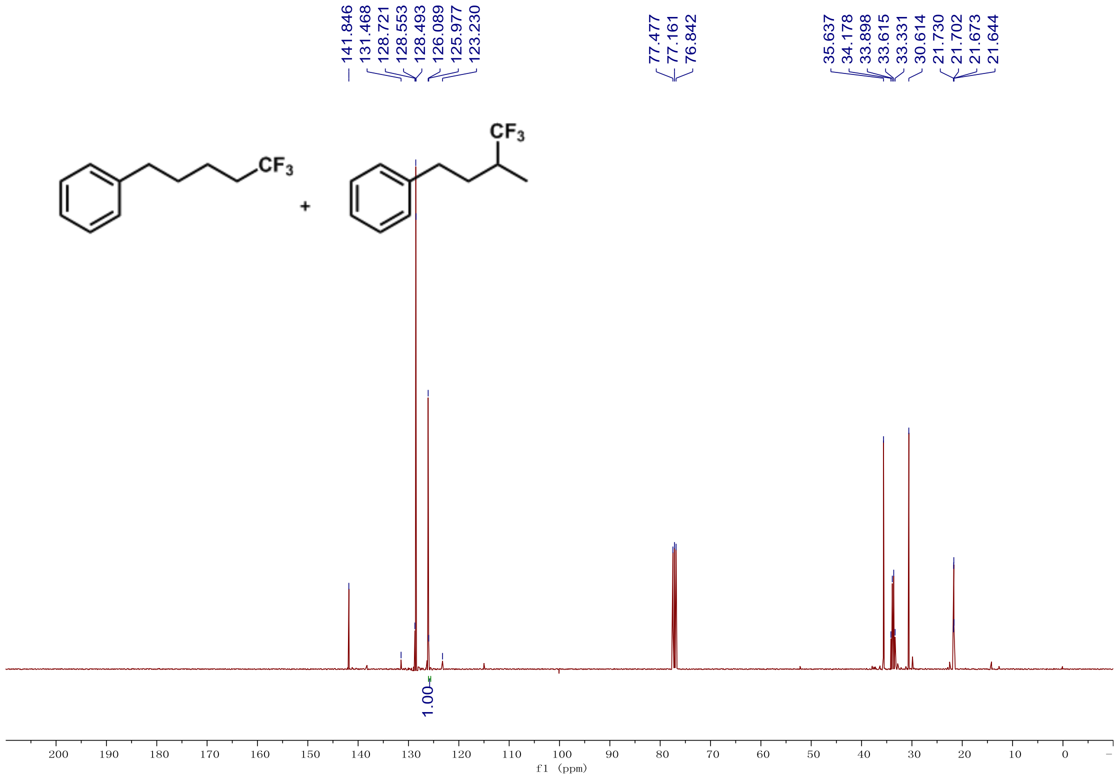
140.837
131.482
128.736
128.692
128.518
126.466
126.403
125.992
123.247
77.478
77.160
76.842
34.775
33.662
33.381
33.093
32.812
23.701
23.673
23.644
23.616
CF3
+
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

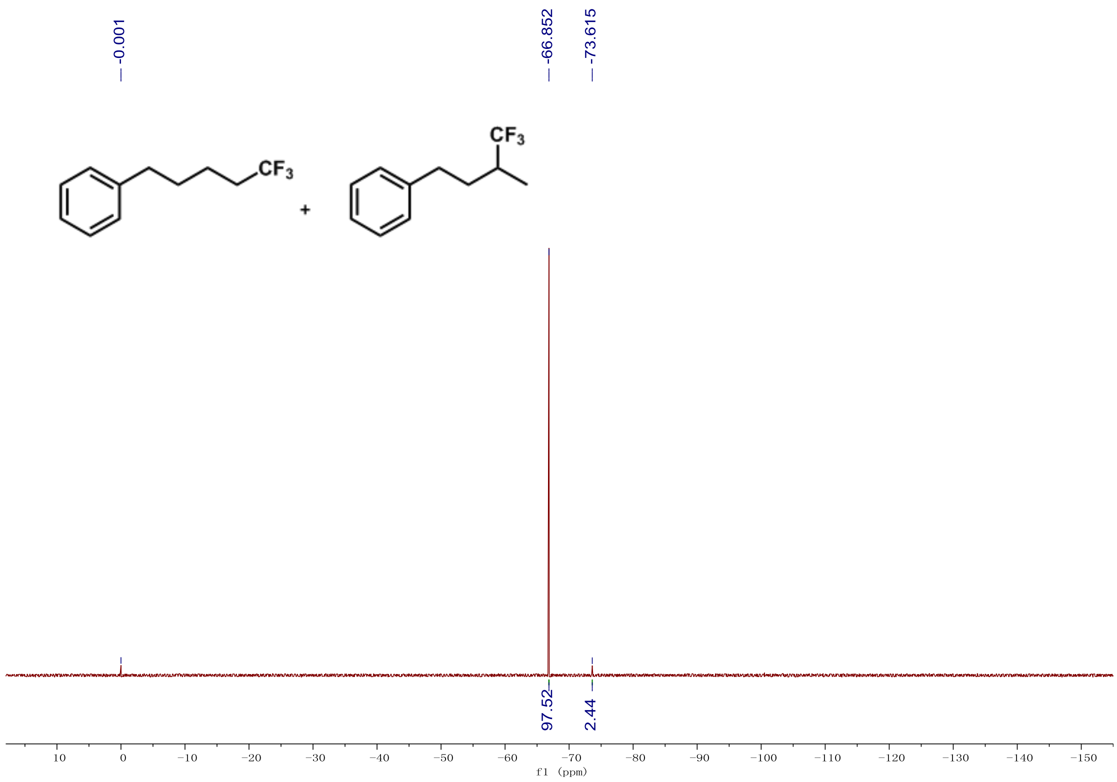


0.000
-66.695
-73.996
CF3
+
CF3
97.51
2.49
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

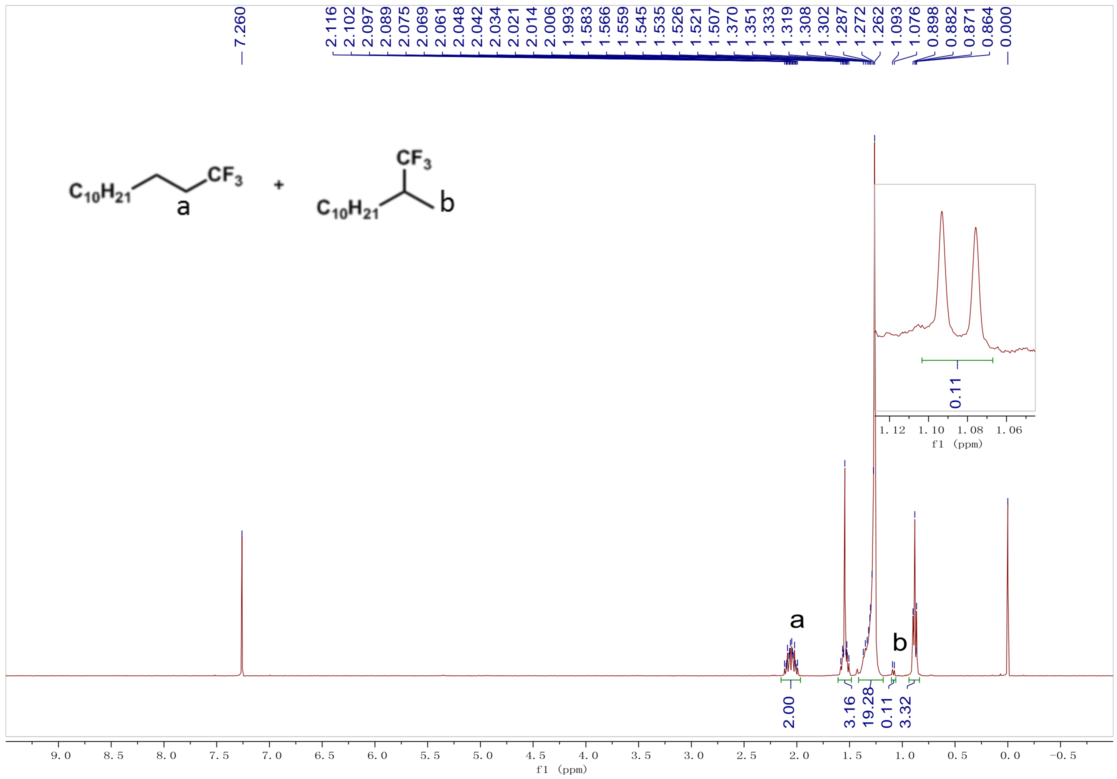
2-19

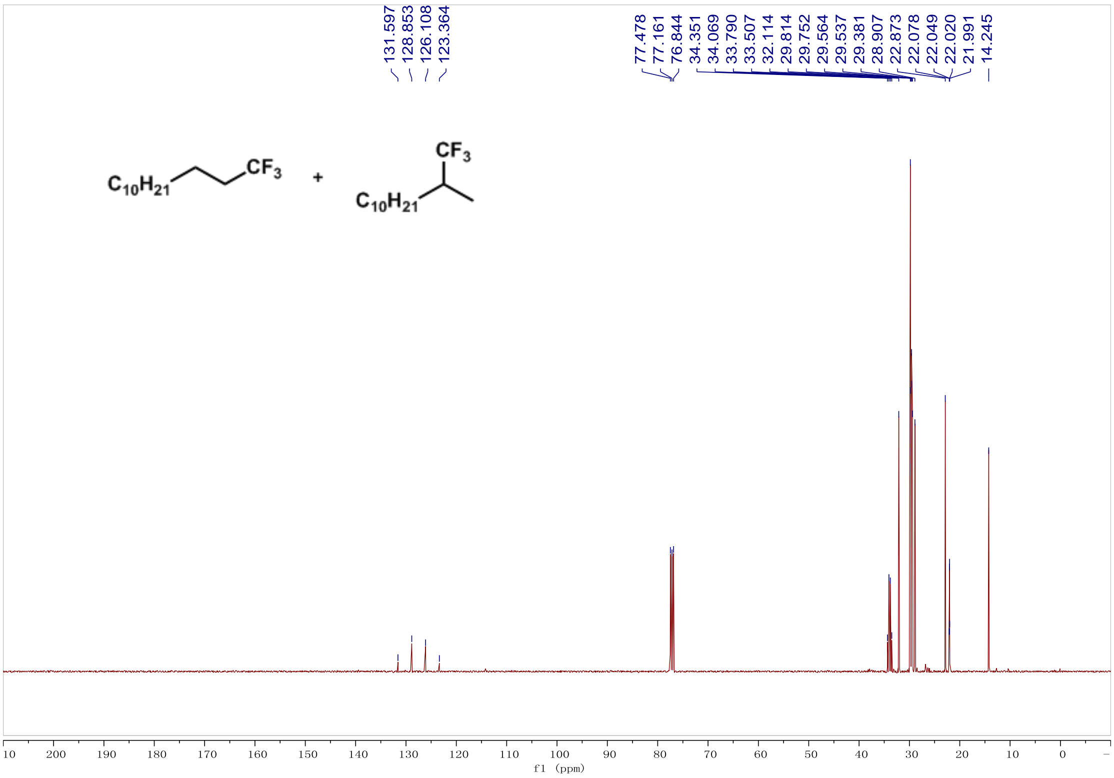

7.307
7.303
7.294
7.289
7.286
7.275
7.270
7.256
7.217
7.213
7.210
7.200
7.194
7.189
7.181
7.177
7.159
2.657
2.639
2.620
2.152
2.133
2.125
2.113
2.105
2.098
2.086
2.078
2.071
2.058
2.051
2.045
2.031
1.739
1.722
1.718
1.701
1.682
1.663
1.642
1.637
1.627
1.624
1.618
1.615
1.610
1.599
1.594
1.588
1.582
1.577
1.563
1.559
1.161
1.144
-0.000
CF3
a
+
CF3
b
0.07
1.19
1.17
1.15
1.13
1.11
f1 (ppm)
a
b
1.98
2.98
1.96
2.00
1.92
2.04
0.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

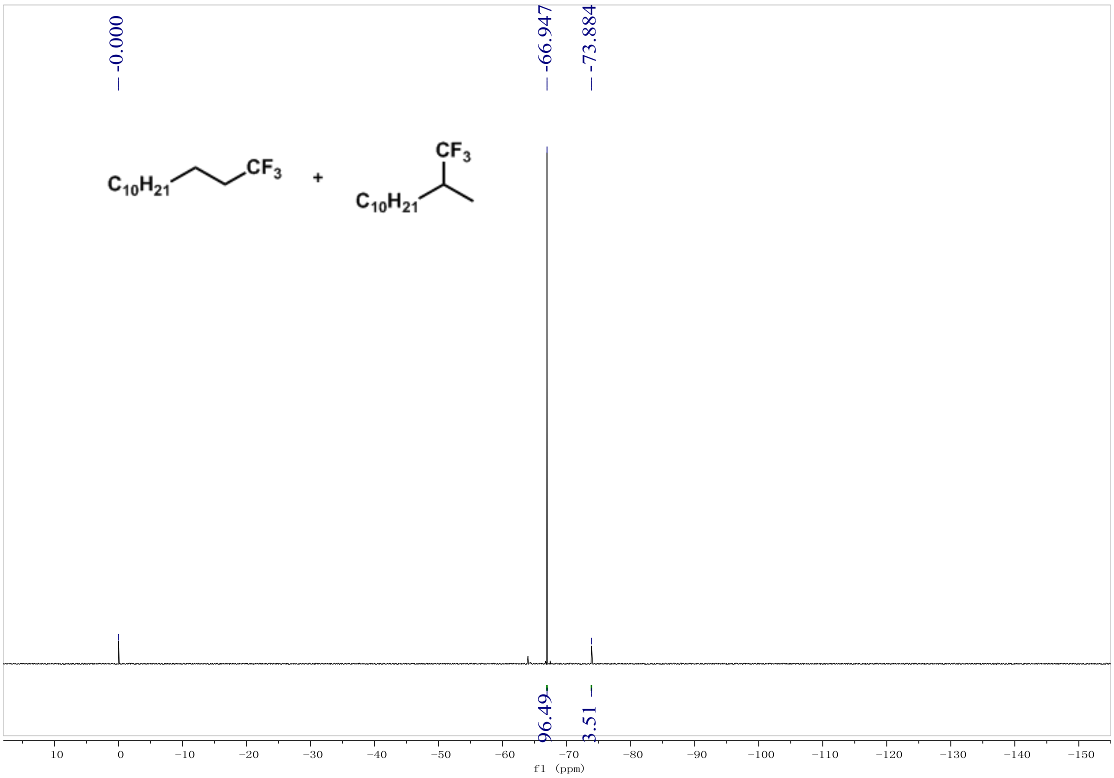

141.846
131.468
128.721
128.553
128.493
126.089
125.977
123.230
77.477
77.161
76.842
35.637
34.178
33.898
33.615
33.331
30.614
21.730
21.702
21.673
21.644
CF3
+
CF3
1.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.001
-66.852
-73.615
CF3
+
CF3
97.52
2.44
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

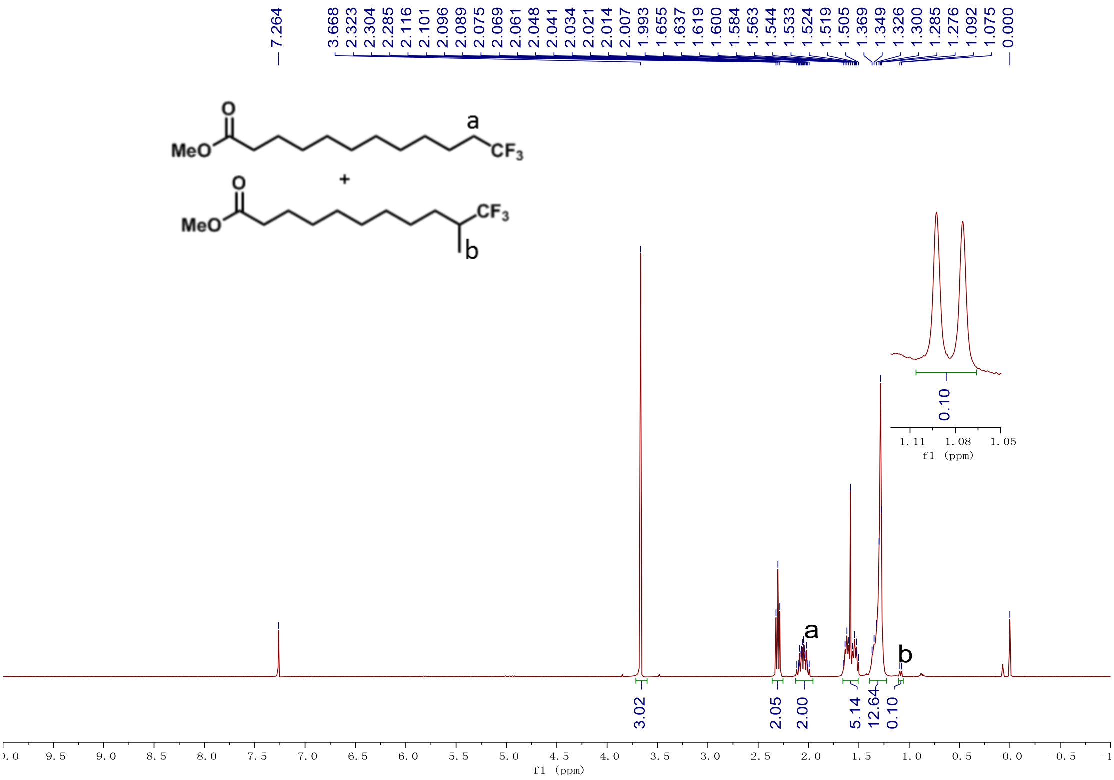
2-20

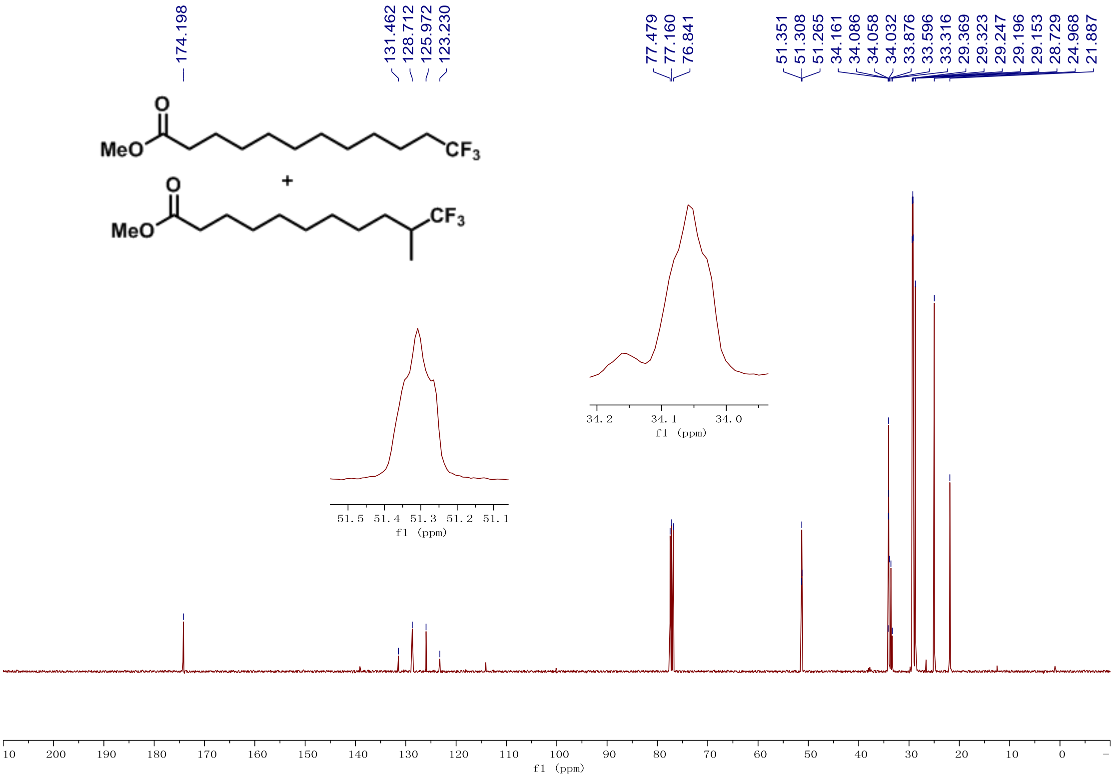

7.260
2.116 2.102 2.097 2.089 2.075 2.069 2.061 2.048 2.042 2.034 2.021 2.014 2.006 1.993 1.583 1.566 1.559 1.545 1.535 1.526 1.521 1.507 1.370 1.351 1.333 1.319 1.308 1.302 1.287 1.272 1.262 1.093 1.076 0.898 0.882 0.871 0.864 0.000
C10H21
CF3
a
+
CF3
C10H21
b
0.11
1.12 1.10 1.08 1.06
f1 (ppm)
a
b
2.00
3.16
19.28
0.11
3.32
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)

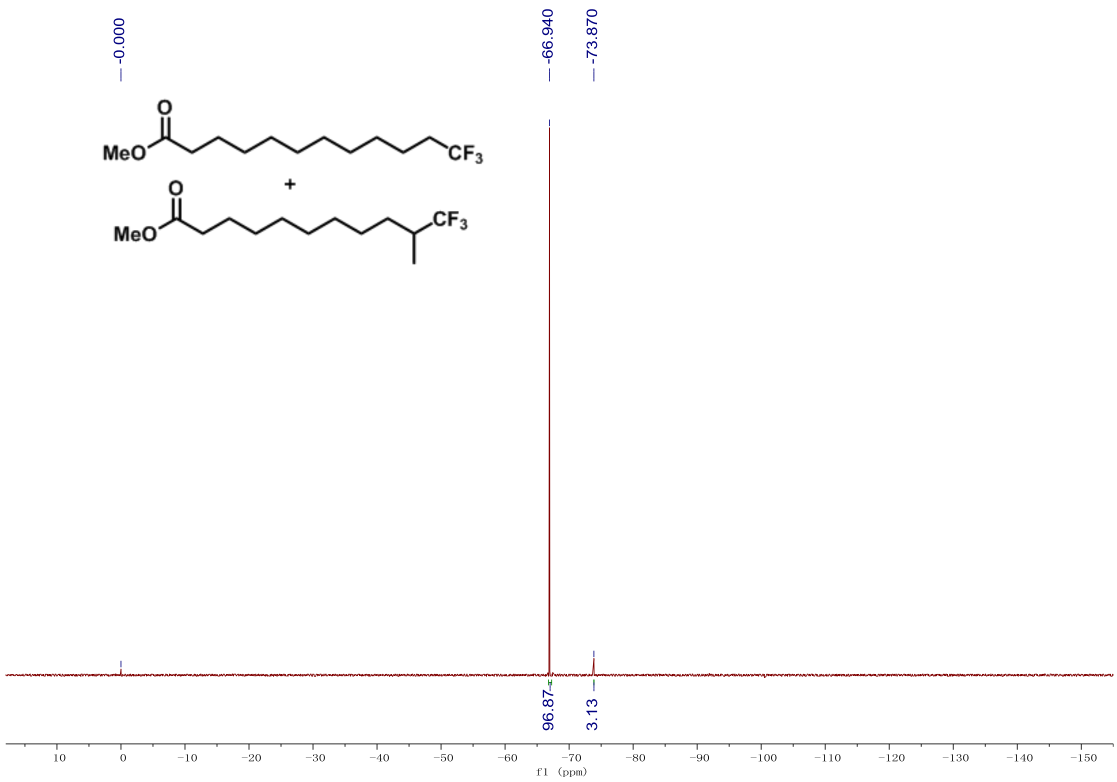

131.597
128.853
126.108
123.364
77.478
77.161
76.844
34.351
34.069
33.790
33.507
32.114
29.814
29.752
29.564
29.537
29.381
28.907
22.873
22.078
22.049
22.020
21.991
14.245
$C_{10}H_{21}$ CF_3 + CF_3 $C_{10}H_{21}$
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-0.000
-66.947
-73.884
$C_{10}H_{21}$ CF_3 + CF_3 $C_{10}H_{21}$
96.49
3.51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

2-21

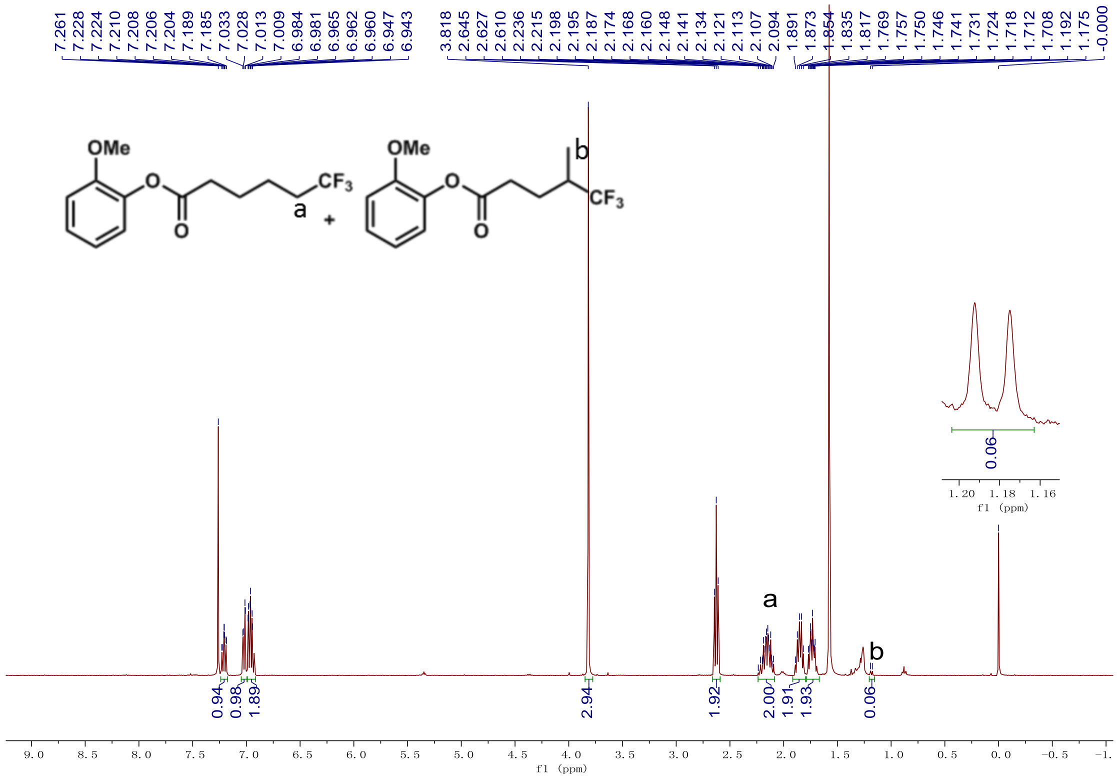

7.264
3.668
2.323
2.304
2.285
2.116
2.101
2.096
2.089
2.075
2.069
2.061
2.048
2.041
2.034
2.021
2.014
2.007
1.993
1.655
1.637
1.619
1.600
1.584
1.563
1.544
1.533
1.524
1.519
1.505
1.369
1.349
1.326
1.300
1.285
1.276
1.092
1.075
0.000
MeO
O
a
CF3
+
b
0.10
1.11
1.08
1.05
f1 (ppm)
3.02
2.05
2.00
5.14
12.64
0.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


174.198
131.462
128.712
125.972
123.230
77.479
77.160
76.841
51.351
51.308
51.265
34.161
34.086
34.058
34.032
33.876
33.596
33.316
29.369
29.323
29.247
29.196
29.153
28.729
24.968
21.887
MeO
O
CF3
+
51.5
51.4
51.3
51.2
51.1
f1 (ppm)
34.2
34.1
34.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

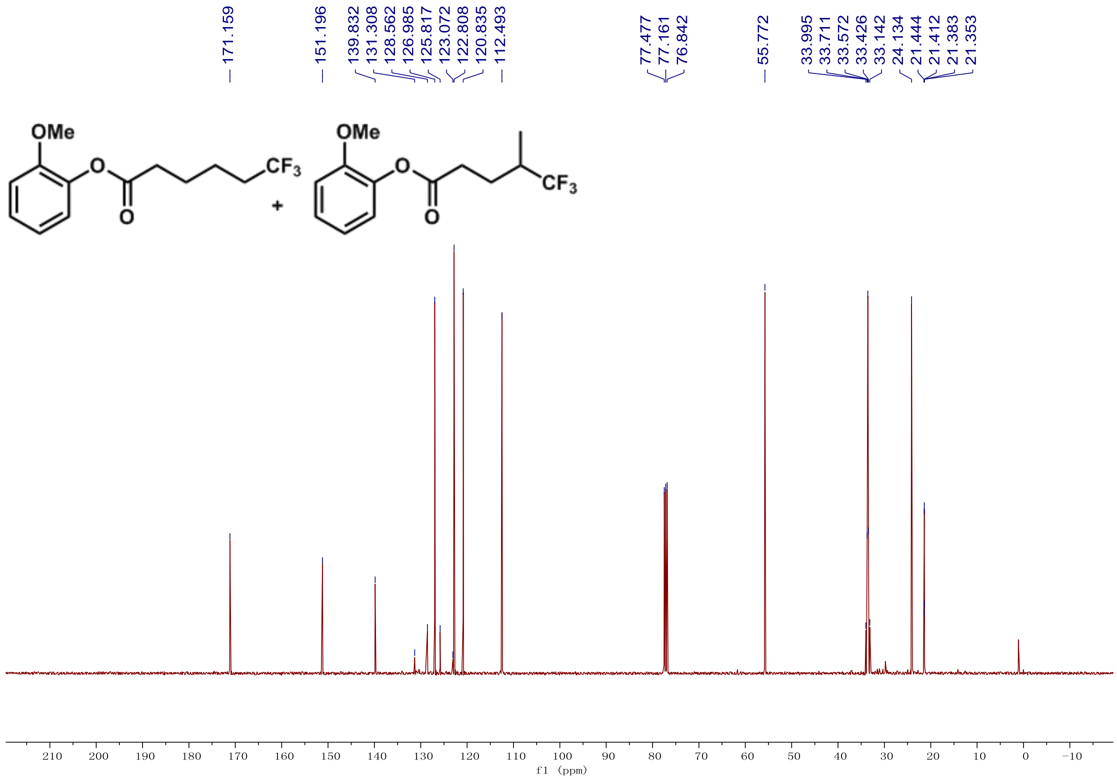


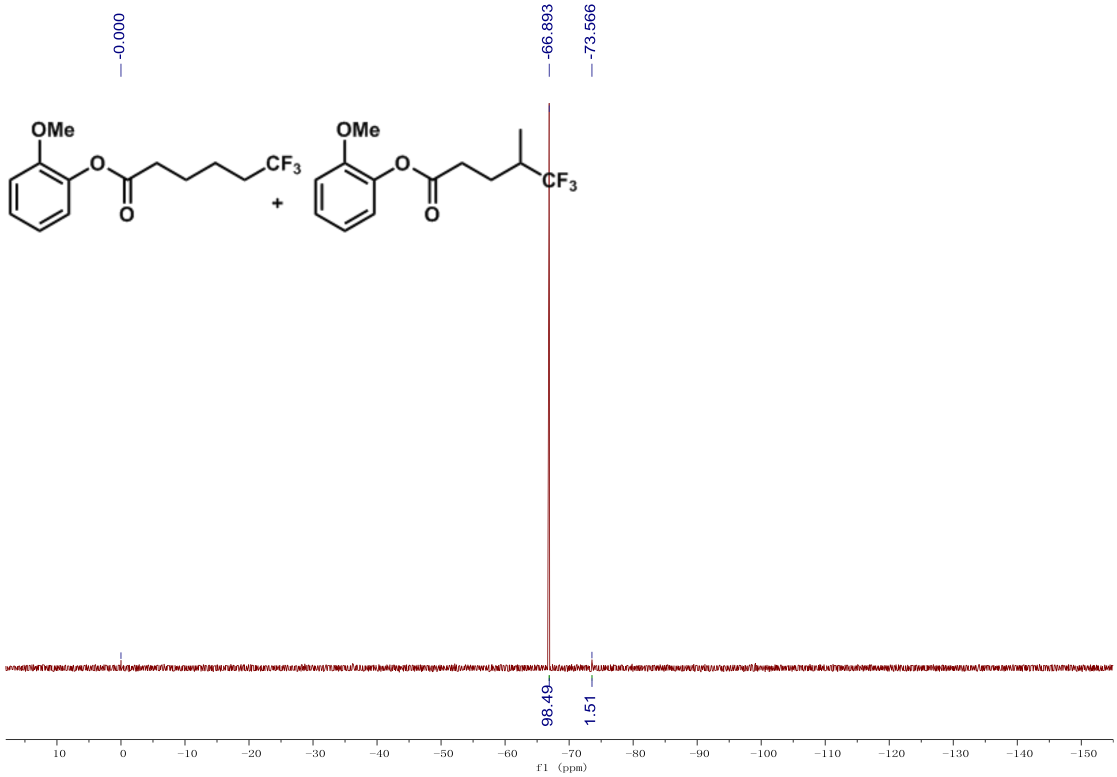
-0.000
-66.940
-73.870
MeO
CF3
+
96.87
3.13
f1 (ppm)

2-22

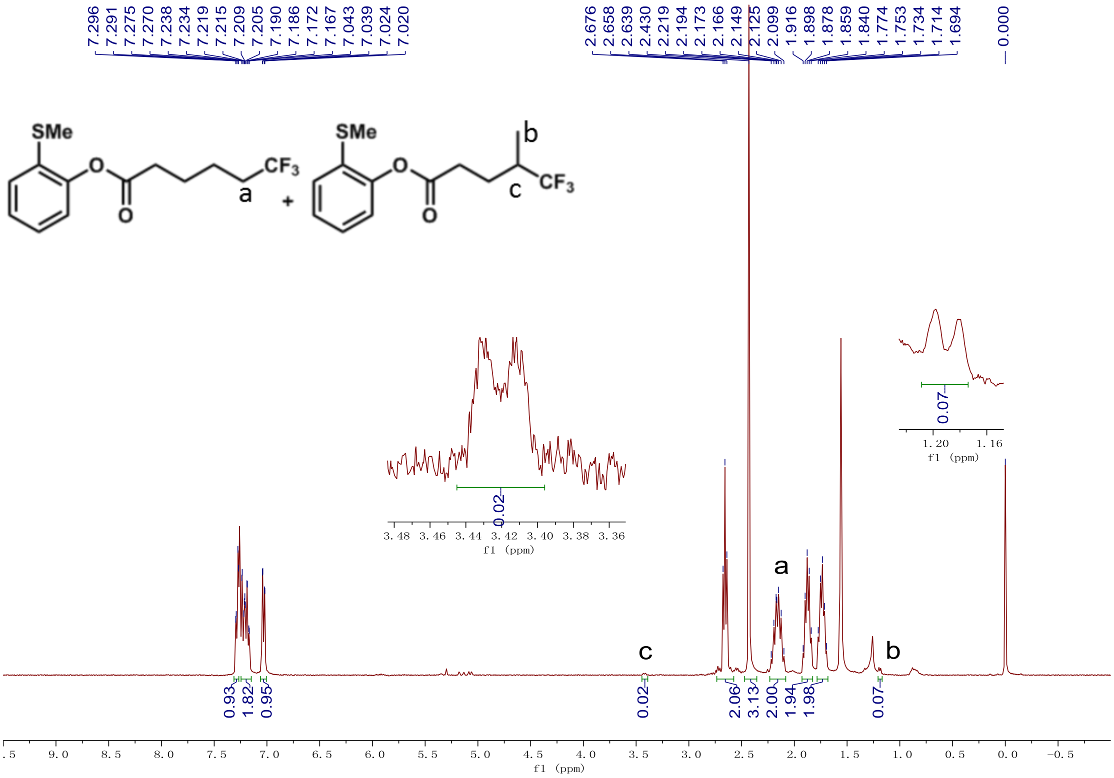


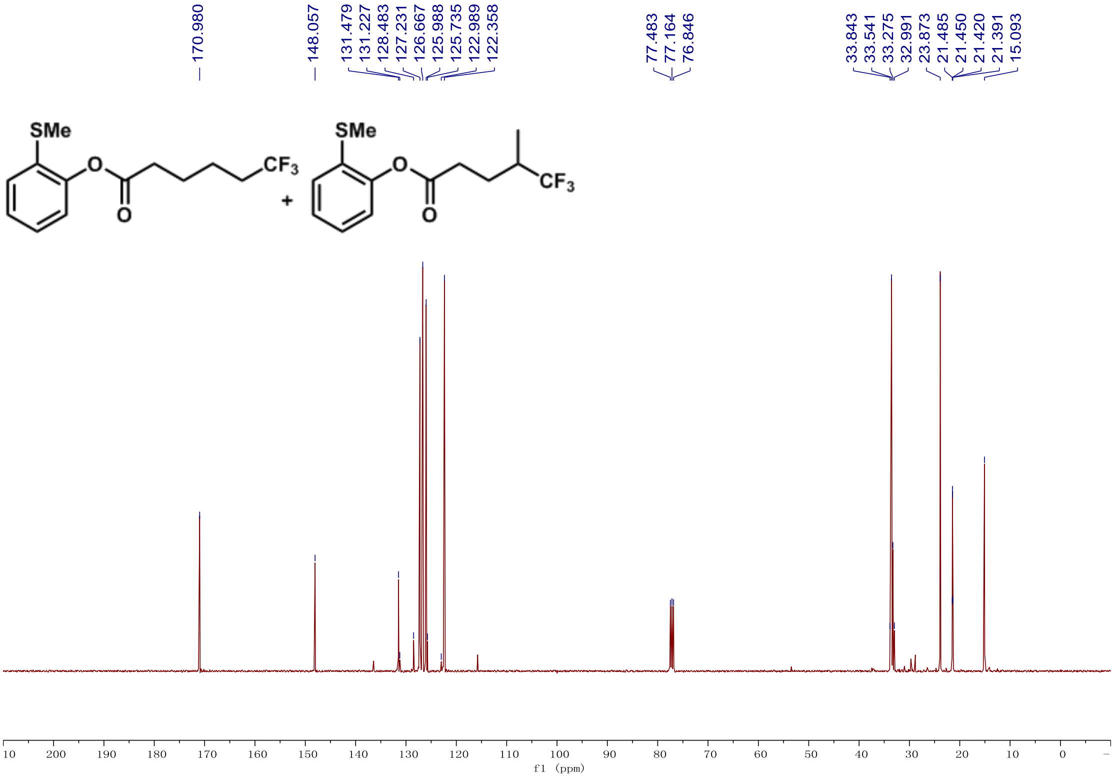
7.261 7.228 7.224 7.210 7.208 7.206 7.204 7.189 7.185 7.033 7.028 7.013 7.009 6.984 6.981 6.965 6.962 6.960 6.947 6.943
3.818 2.645 2.627 2.610 2.236 2.215 2.198 2.195 2.187 2.174 2.168 2.160 2.148 2.141 2.134 2.121 2.113 2.107 2.094 1.891 1.873 1.854 1.835 1.817 1.769 1.757 1.750 1.746 1.741 1.731 1.724 1.718 1.712 1.708 1.192 1.175 -0.000
OMe
CF3
a
b
+
0.94 0.98 1.89 2.94 1.92 2.00 1.91 1.93 0.06
0.06
f1 (ppm)

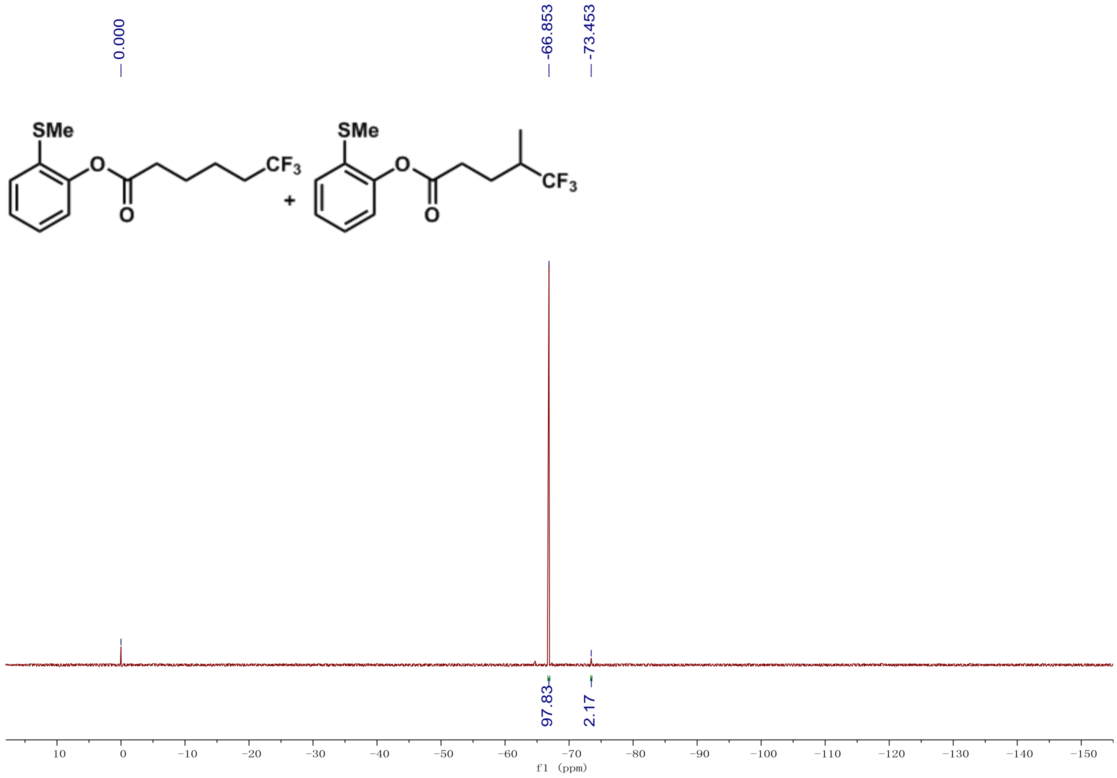

171.159
151.196
139.832
131.308
128.562
126.985
125.817
123.072
122.808
120.835
112.493
77.477
77.161
76.842
55.772
33.995
33.711
33.572
33.426
33.142
24.134
21.444
21.412
21.383
21.353
OMe
O
O
CF3
+
OMe
O
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-0.000
-66.893
-73.566
OMe
O
O
CF3
+
OMe
O
O
CF3
98.49
1.51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

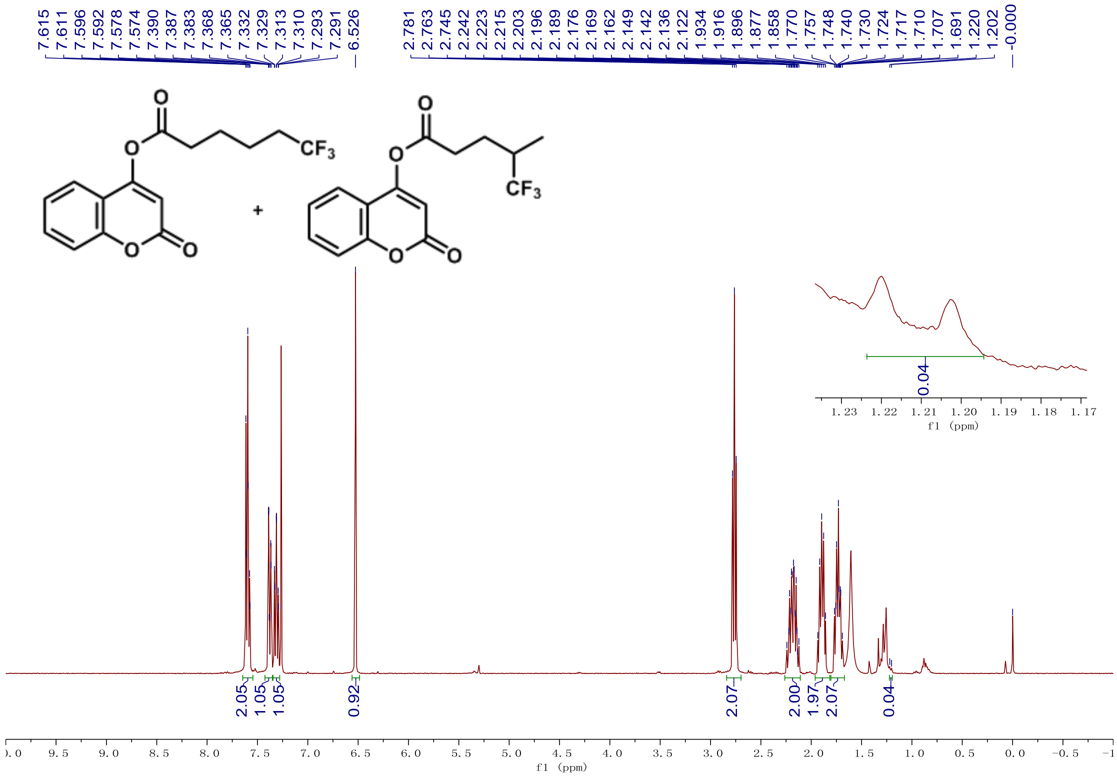
2-23

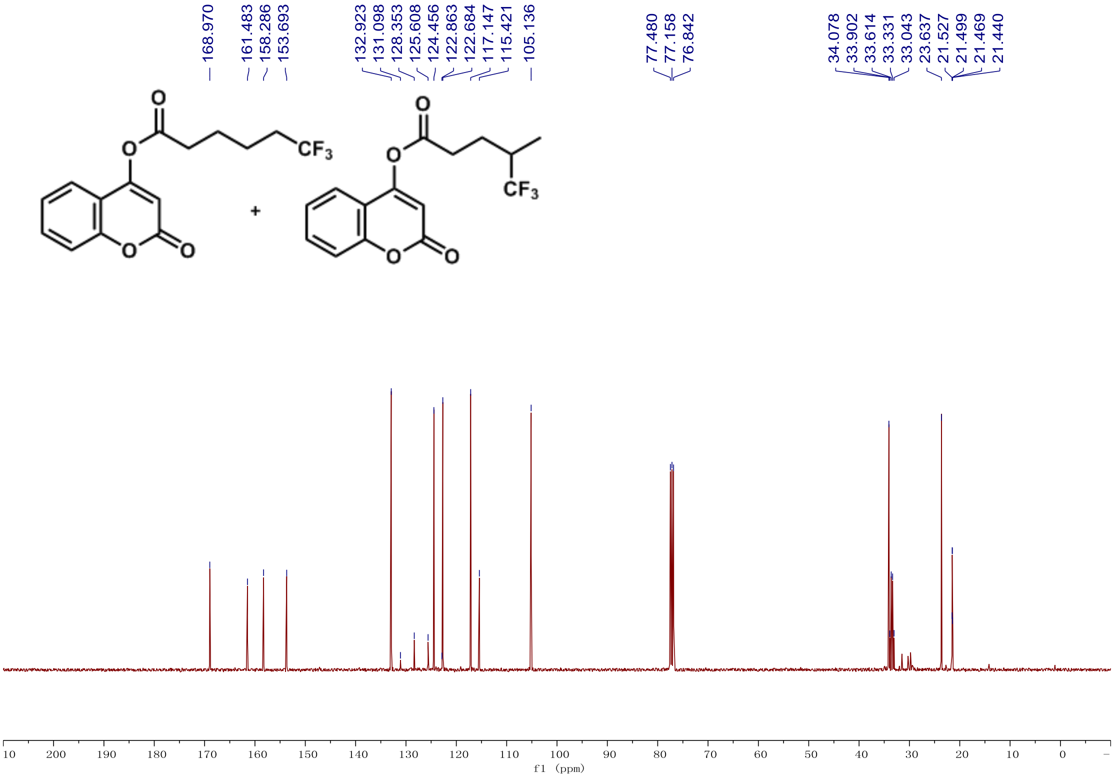

7.296 7.291 7.275 7.270 7.238 7.234 7.219 7.215 7.209 7.205 7.190 7.186 7.172 7.167 7.043 7.039 7.024 7.020
2.676 2.658 2.639 2.430 2.219 2.194 2.173 2.166 2.149 2.125 2.099 1.916 1.898 1.878 1.859 1.840 1.774 1.753 1.734 1.714 1.694
0.000
SMe
O
CF3
a
+
b
c
0.02
3.48 3.46 3.44 3.42 3.40 3.38 3.36
f1 (ppm)
0.07
1.20 1.16
f1 (ppm)
0.93 1.82 0.95
0.02
2.06 3.13 2.00 1.94 1.98
0.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

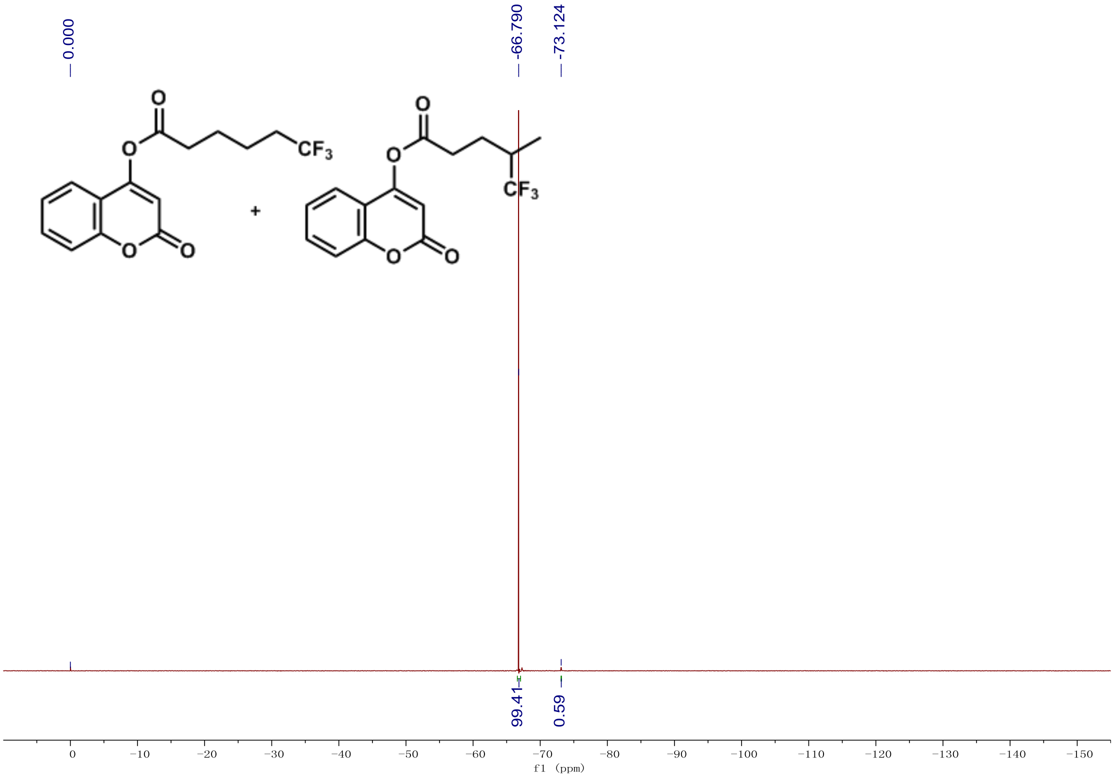

170.980
148.057
131.479 131.227 128.483 127.231 126.667 125.988 125.735 122.989 122.358
77.483 77.164 76.846
33.843 33.541 33.275 32.991 23.873 21.485 21.450 21.420 21.391 15.093
SMe
O
CF3
+
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


0.000
-66.853
-73.453
SMe
O
CF3
O
+
SMe
O
CF3
O
97.83
2.17
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

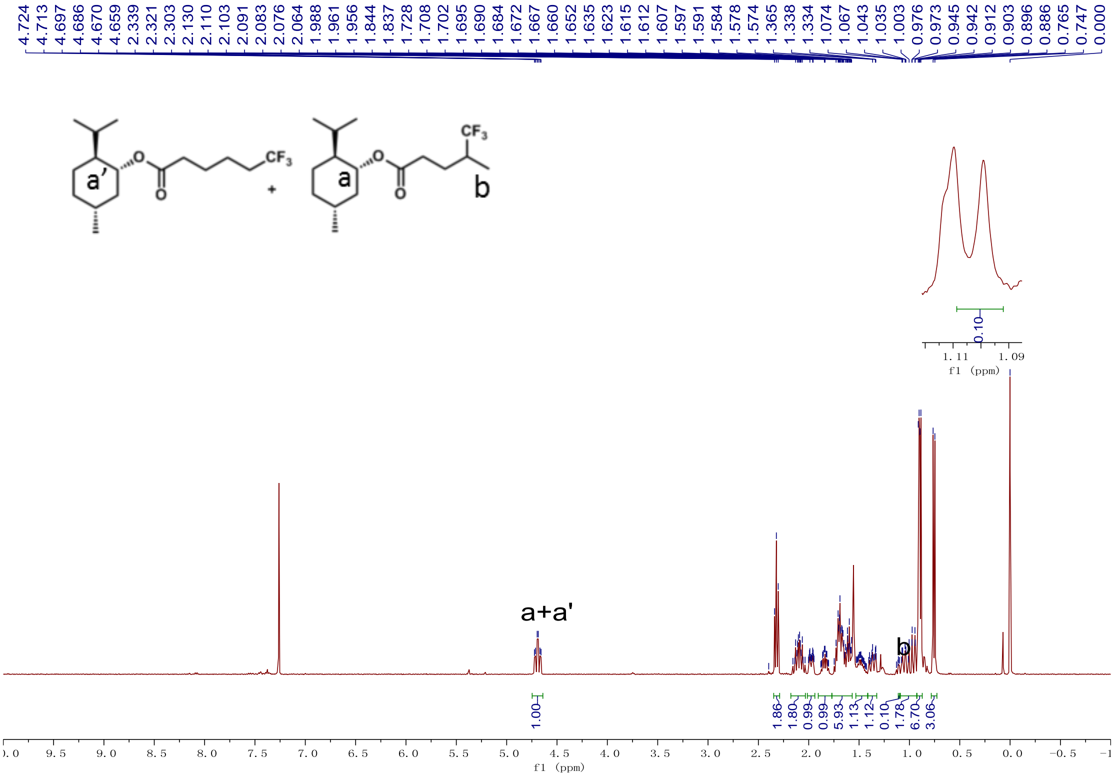
2-24

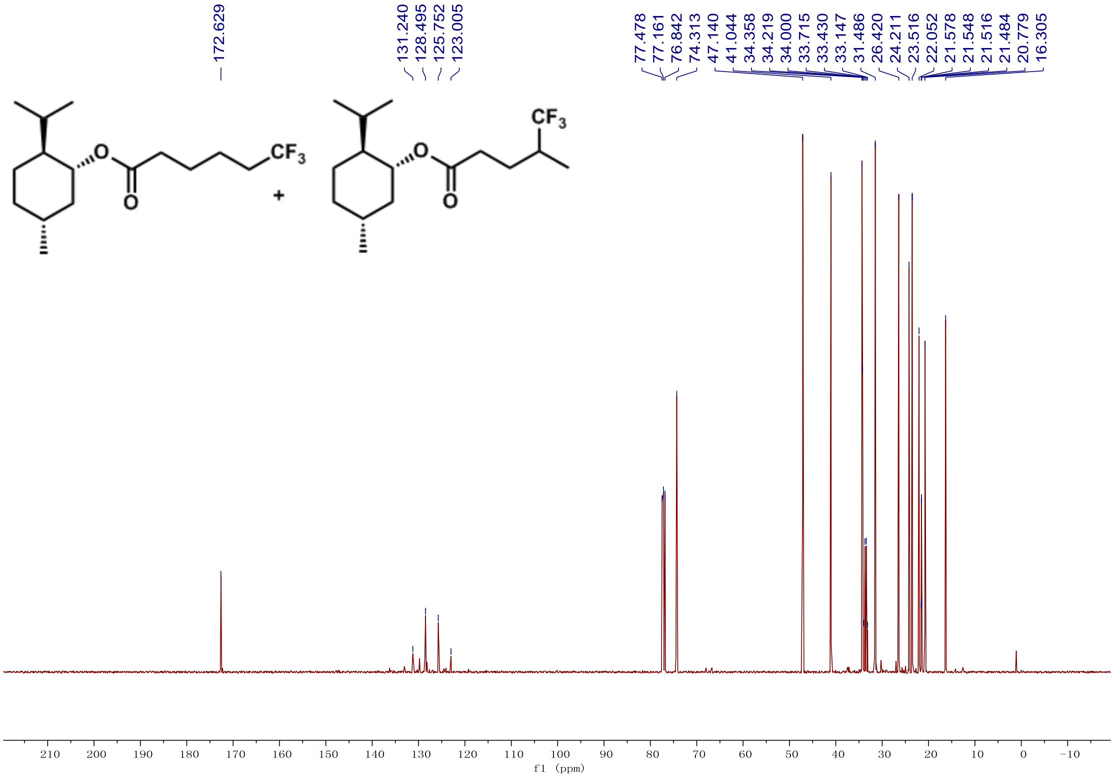

7.615
7.611
7.596
7.592
7.578
7.574
7.390
7.387
7.383
7.368
7.365
7.332
7.329
7.313
7.310
7.293
7.291
6.526
2.781
2.763
2.745
2.242
2.223
2.215
2.203
2.196
2.189
2.176
2.169
2.162
2.149
2.142
2.136
2.122
1.934
1.916
1.896
1.877
1.858
1.770
1.757
1.748
1.740
1.730
1.724
1.717
1.710
1.707
1.691
1.220
1.202
-0.000
O
O
CF3
O
O
+
O
O
CF3
O
O
0.04
1.23
1.22
1.21
1.20
1.19
1.18
1.17
f1 (ppm)
2.05
1.05
1.05
0.92
2.07
2.00
1.97
2.07
0.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

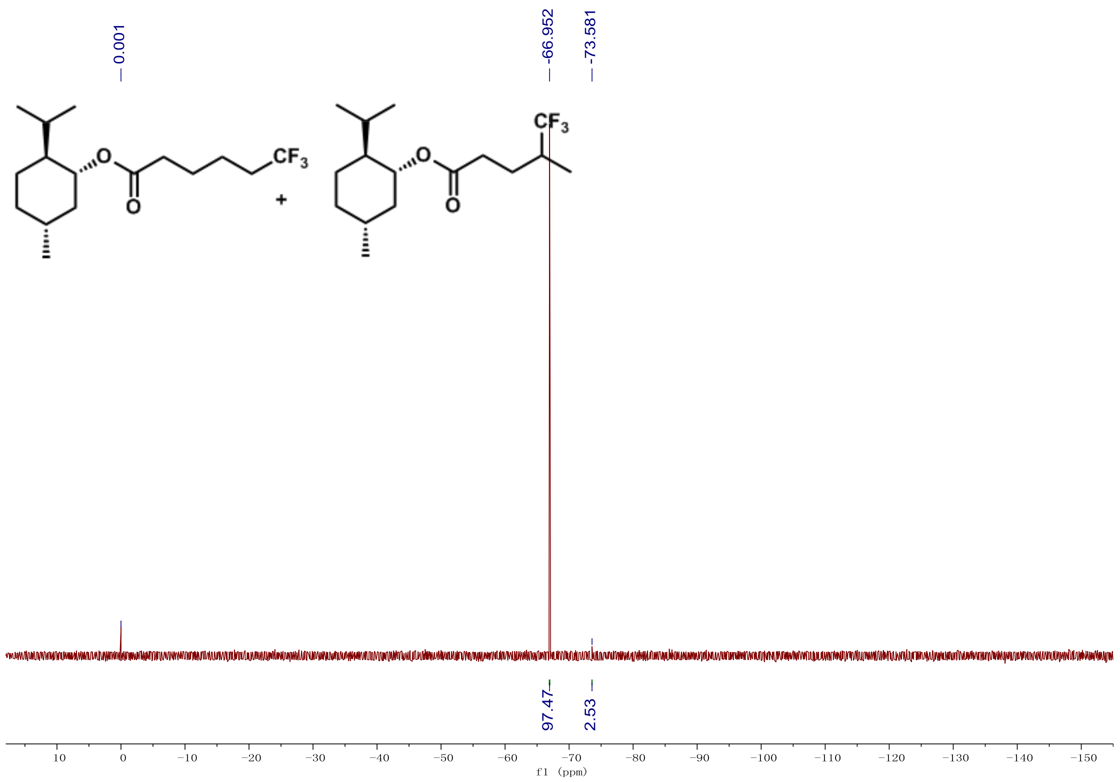

168.970
161.483
158.286
153.693
132.923
131.098
128.353
125.608
124.456
122.863
122.684
117.147
115.421
105.136
77.480
77.158
76.842
34.078
33.902
33.614
33.331
33.043
23.637
21.527
21.499
21.469
21.440
O
O
CF3
+
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-66.790
-73.124
O
O
CF3
+
O
O
CF3
99.41
0.59
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

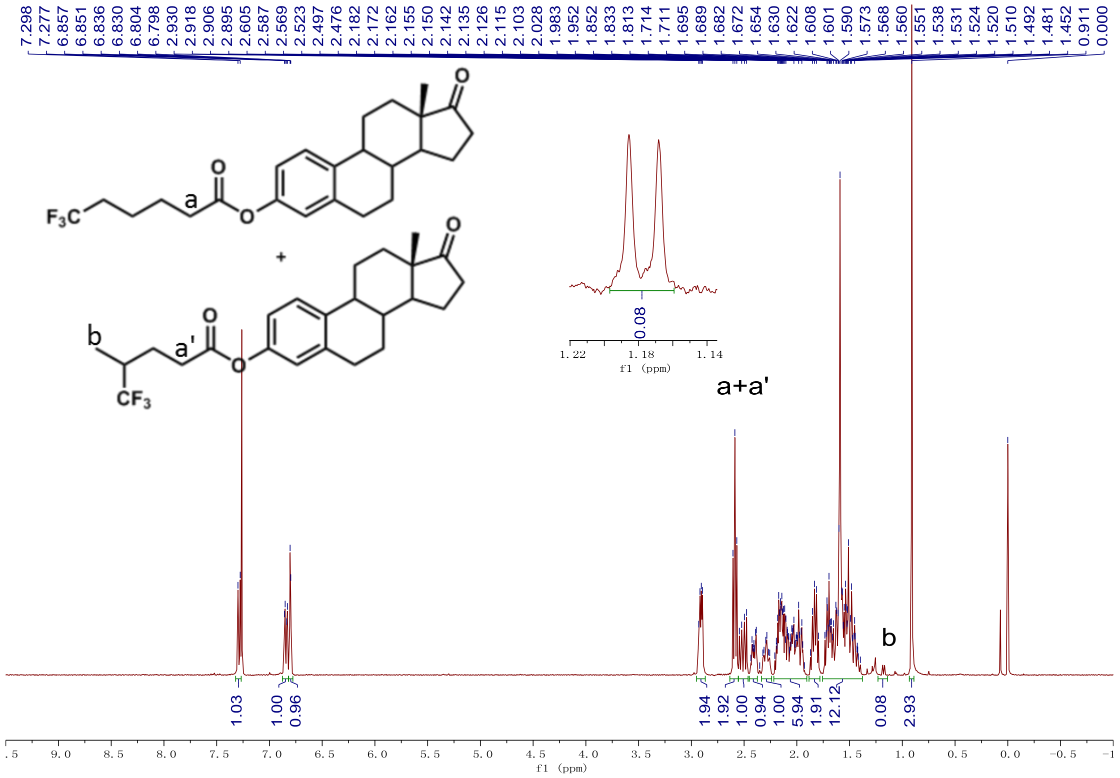
2-25

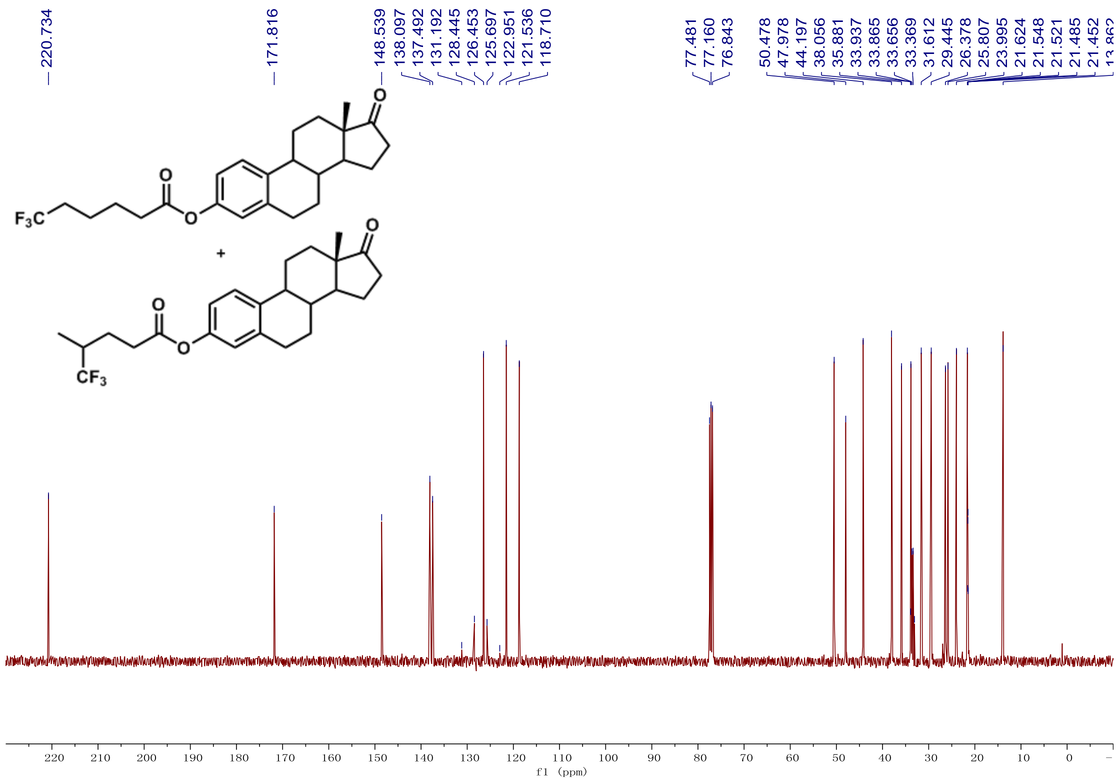

4.724 4.713 4.697 4.686 4.670 4.659 2.339 2.321 2.303 2.130 2.110 2.103 2.091 2.083 2.076 2.064 1.988 1.961 1.956 1.844 1.837 1.728 1.708 1.702 1.695 1.690 1.684 1.672 1.667 1.660 1.652 1.635 1.623 1.615 1.612 1.607 1.597 1.591 1.584 1.578 1.574 1.365 1.338 1.334 1.074 1.067 1.043 1.035 1.003 0.976 0.973 0.945 0.942 0.912 0.903 0.896 0.886 0.765 0.747 0.000
a'
O
CF3
O
+
a
O
CF3
O
b
0.10
1.11
1.09
f1 (ppm)
a+a'
b
1.00
1.86
1.80
0.99
0.99
5.93
1.13
1.12
0.10
1.78
6.70
3.06
f1 (ppm)

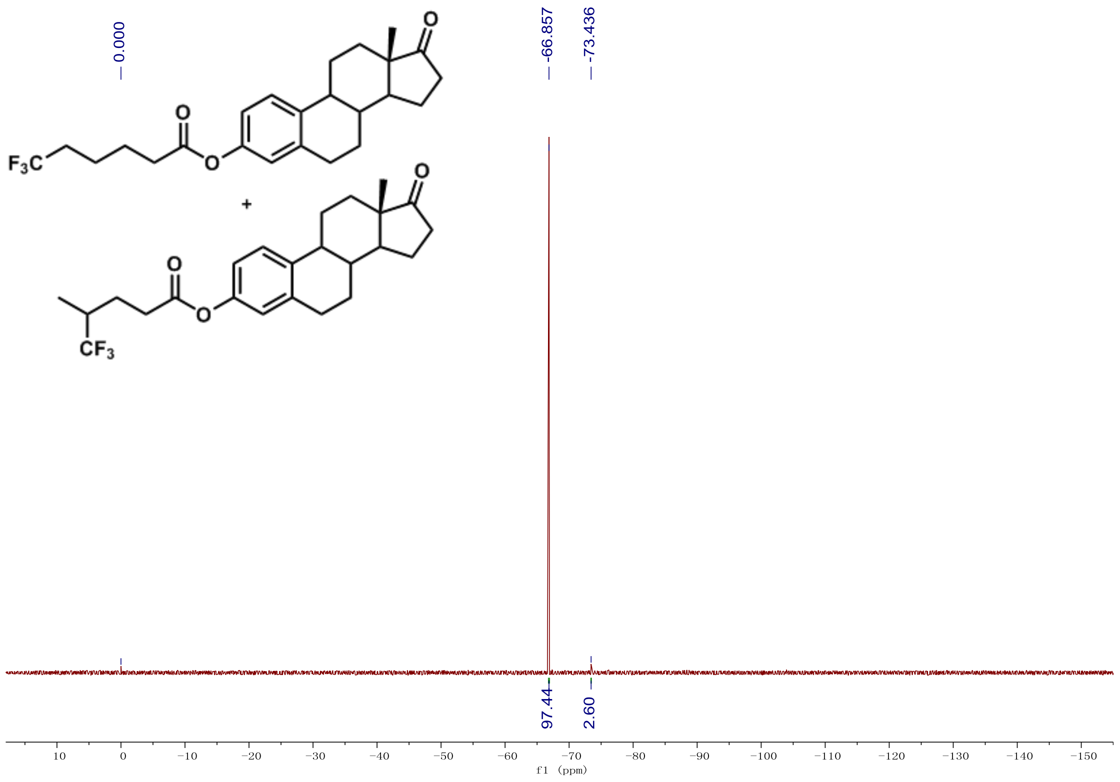

172.629
131.240 128.495 125.752 123.005
77.478 77.161 76.842 74.313 47.140 41.044 34.358 34.219 34.000 33.715 33.430 33.147 31.486 26.420 24.211 23.516 22.052 21.578 21.548 21.516 21.484 20.779 16.305
O
CF3
O
+
O
CF3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


0.001
-66.952
-73.581
CF3
O
O
CF3
+
O
O
97.47
2.53
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

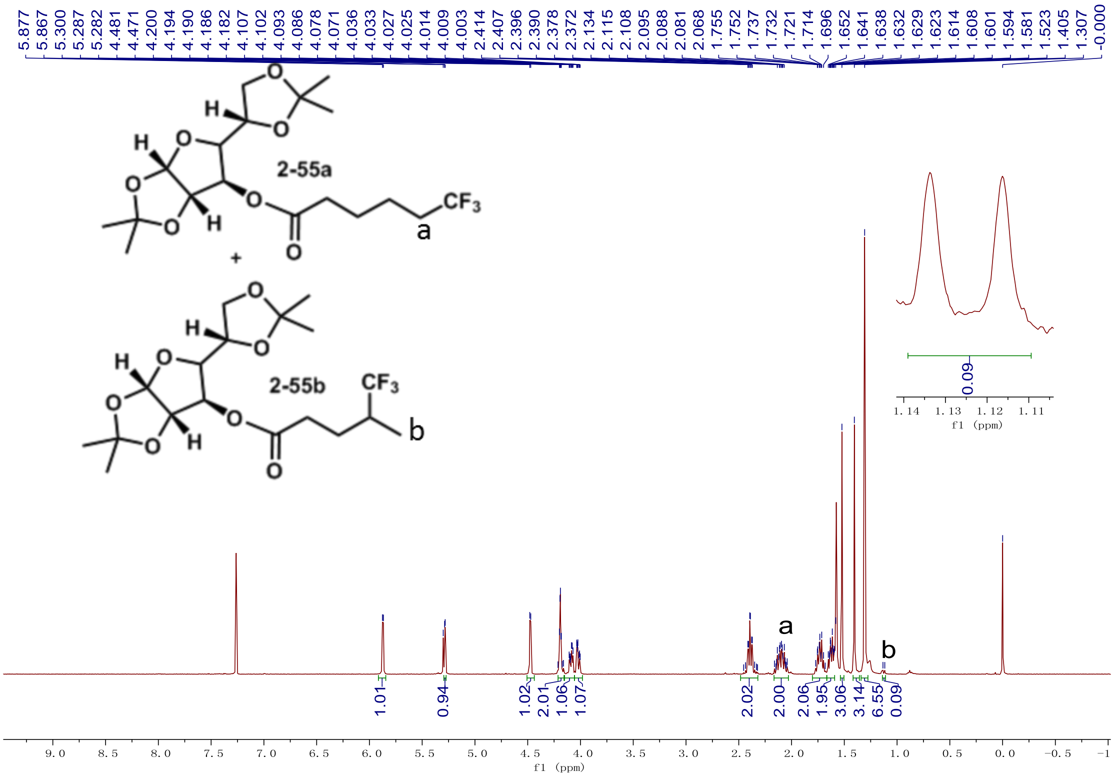
2-26

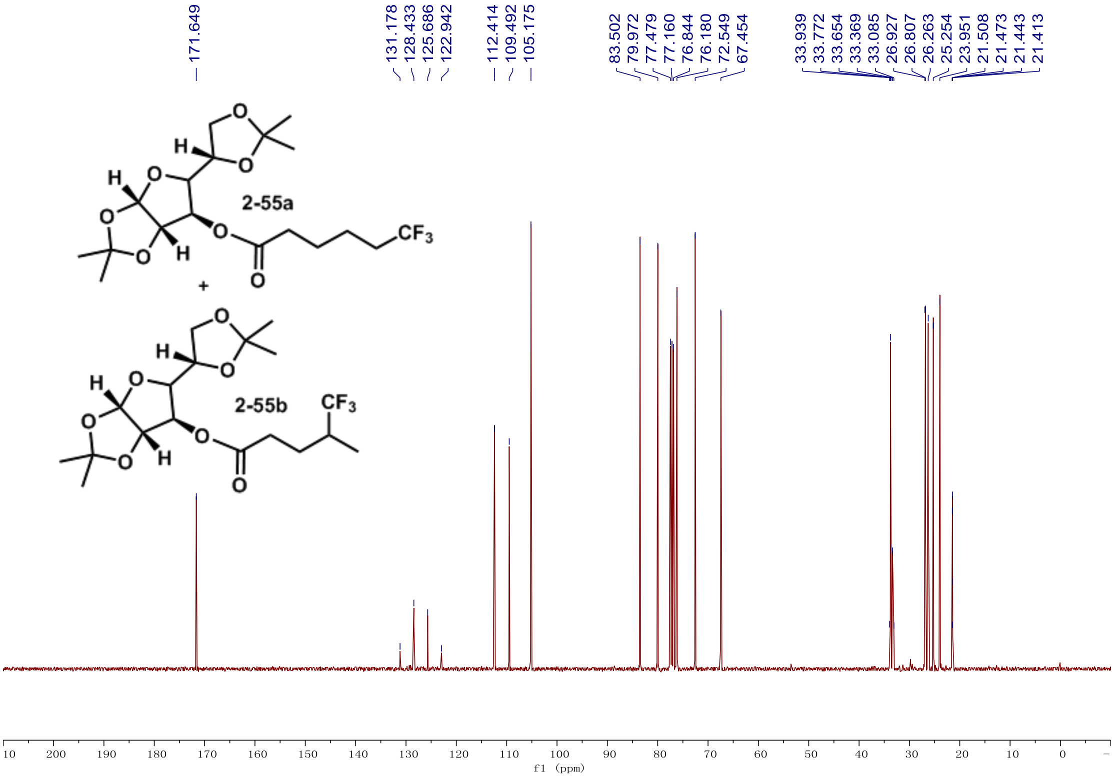

7.298 7.277 6.851 6.836 6.830 6.804 6.798 2.930 2.918 2.906 2.895 2.605 2.587 2.569 2.523 2.497 2.476 2.182 2.172 2.162 2.155 2.150 2.142 2.135 2.126 2.115 2.103 2.028 1.983 1.952 1.852 1.833 1.813 1.714 1.711 1.695 1.689 1.682 1.672 1.654 1.630 1.622 1.608 1.601 1.590 1.573 1.568 1.560 1.551 1.538 1.531 1.524 1.520 1.510 1.492 1.481 1.452 0.911 0.000
F3C
a
O
O
+
b
a'
O
CF3
O
0.08
1.22 1.18 1.14
f1 (ppm)
a+a'
b
1.03
1.00
0.96
1.94
1.92
1.00
0.94
1.00
5.94
1.91
12.12
0.08
2.93
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

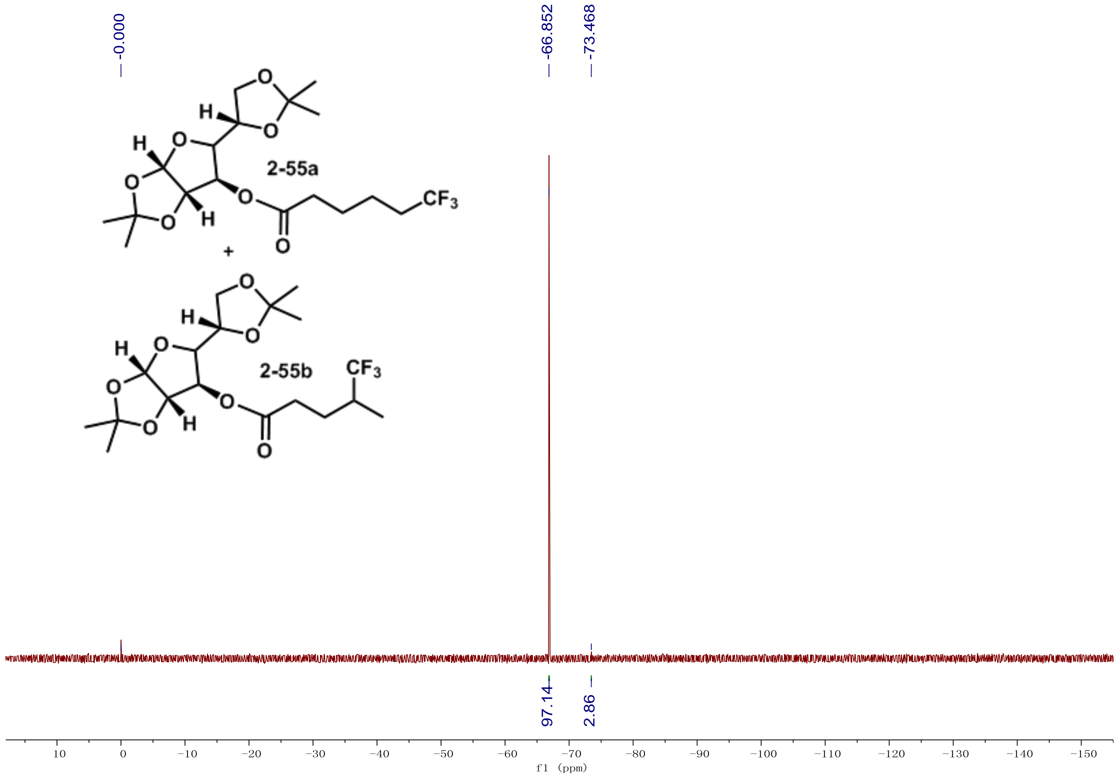

220.734
171.816
148.539
138.097
137.492
131.192
128.445
126.453
125.697
122.951
121.536
118.710
77.481
77.160
76.843
50.478
47.978
44.197
38.056
35.881
33.937
33.865
33.656
33.369
31.612
29.445
26.378
25.807
23.995
21.624
21.548
21.521
21.485
21.452
13.86
F3C
O
O
O
+
O
O
O
CF3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-66.857
-73.436
F3C
O
O
O
+
O
O
O
CF3
97.44
2.60
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

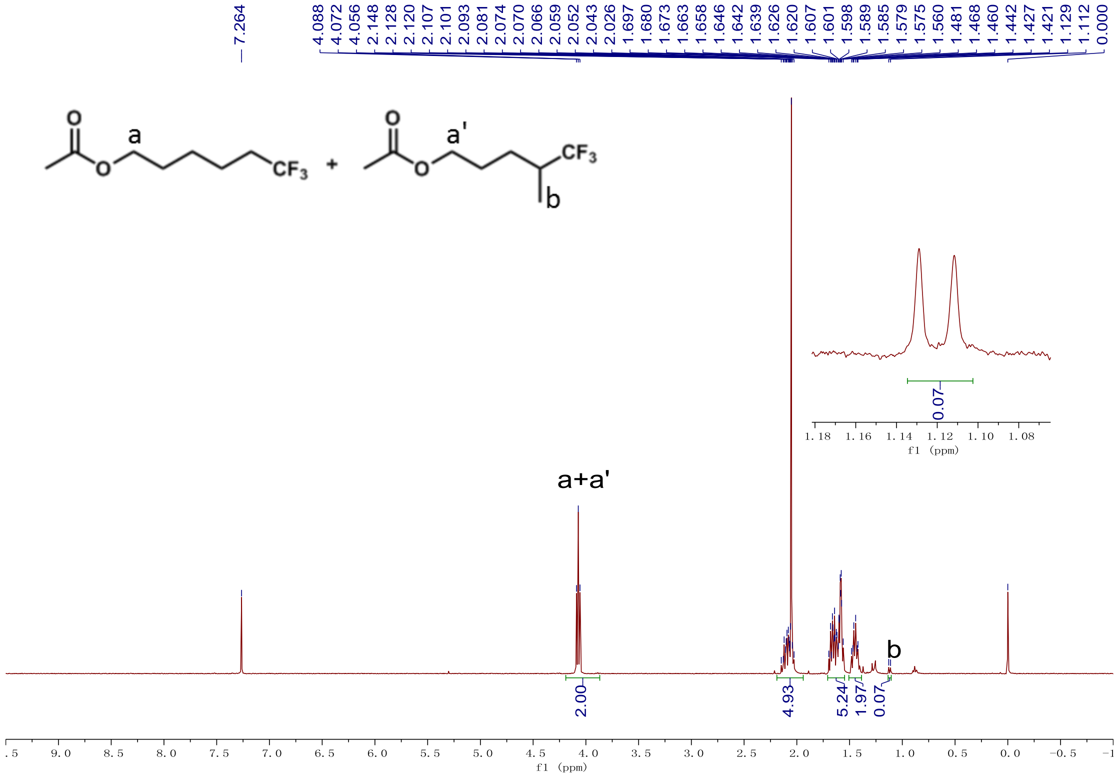
2-27

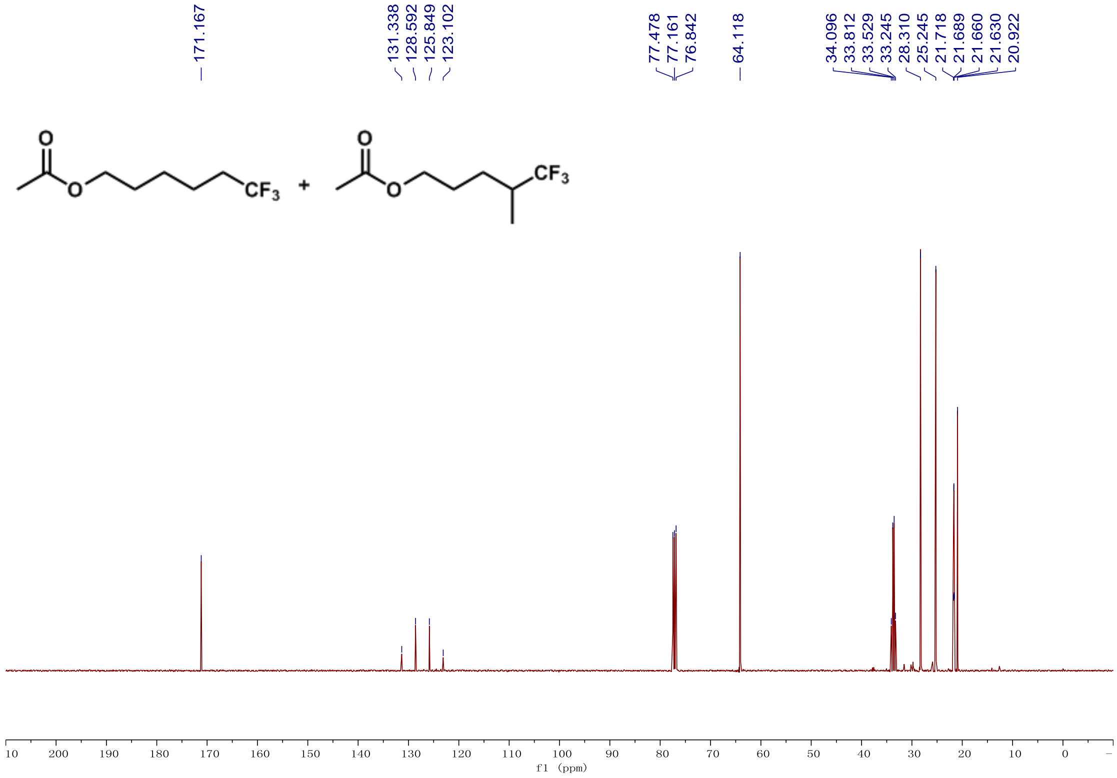

5.877 5.867 5.300 5.287 5.282 4.481 4.471 4.200 4.194 4.190 4.186 4.182 4.107 4.102 4.093 4.086 4.078 4.071 4.036 4.033 4.027 4.025 4.014 4.009 4.003 2.414 2.407 2.396 2.390 2.378 2.372 2.134 2.115 2.108 2.095 2.088 2.081 2.068 1.755 1.752 1.737 1.732 1.721 1.714 1.696 1.652 1.641 1.638 1.632 1.629 1.623 1.614 1.608 1.601 1.594 1.581 1.523 1.405 1.307 -0.000
2-55a
CF3
a
+
2-55b
CF3
b
0.09
1.14 1.13 1.12 1.11
f1 (ppm)
a
b
1.01 0.94 1.02 2.01 1.06 1.07 2.02 2.00 2.06 1.95 3.06 3.14 6.55 0.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

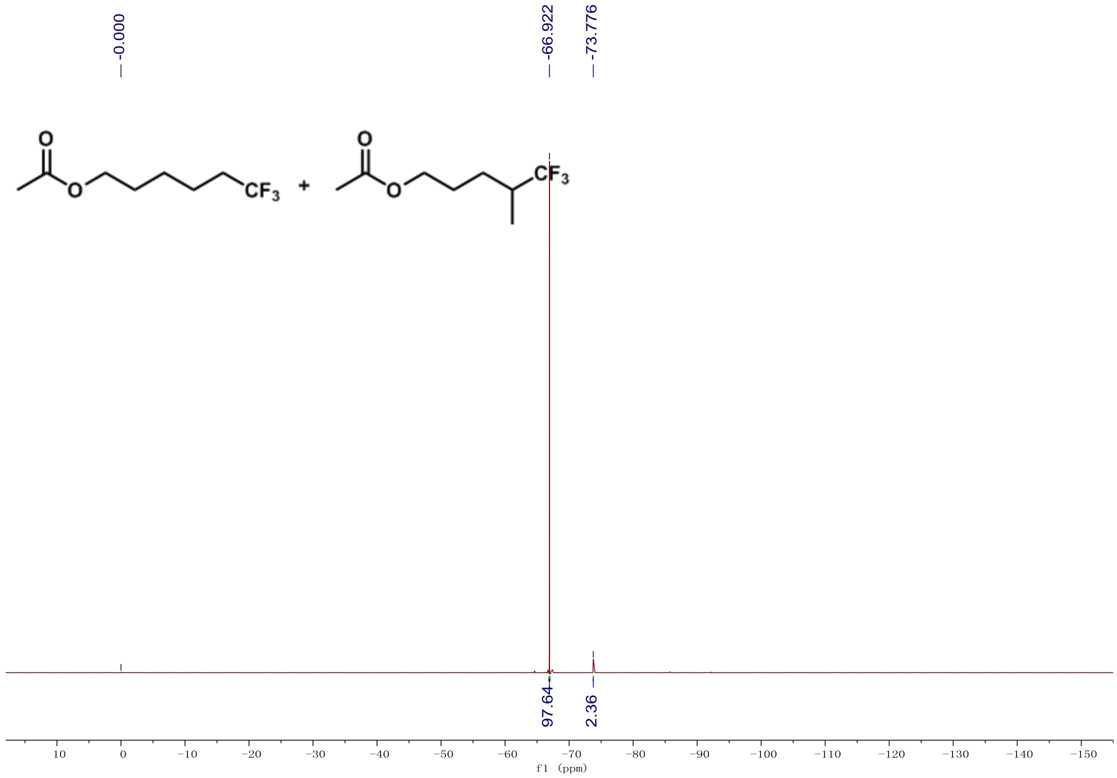

171.649
131.178 128.433 125.686 122.942
112.414 109.492 105.175
83.502 79.972 77.479 77.160 76.844 76.180 72.549 67.454
33.939 33.772 33.654 33.369 33.085 26.927 26.807 26.263 25.254 23.951 21.508 21.473 21.443 21.413
2-55a
CF3
+
2-55b
CF3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-0.000
-66.852
-73.468
2-55a
+
2-55b
CF3
97.14
2.86
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

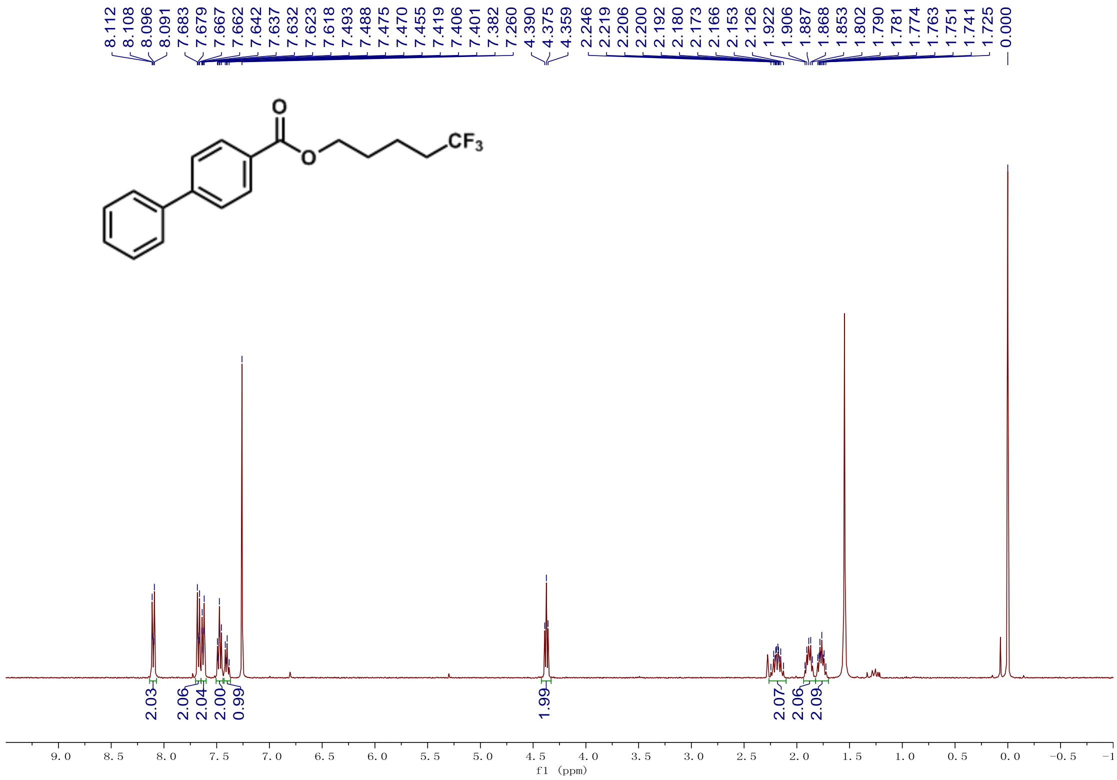
2-28

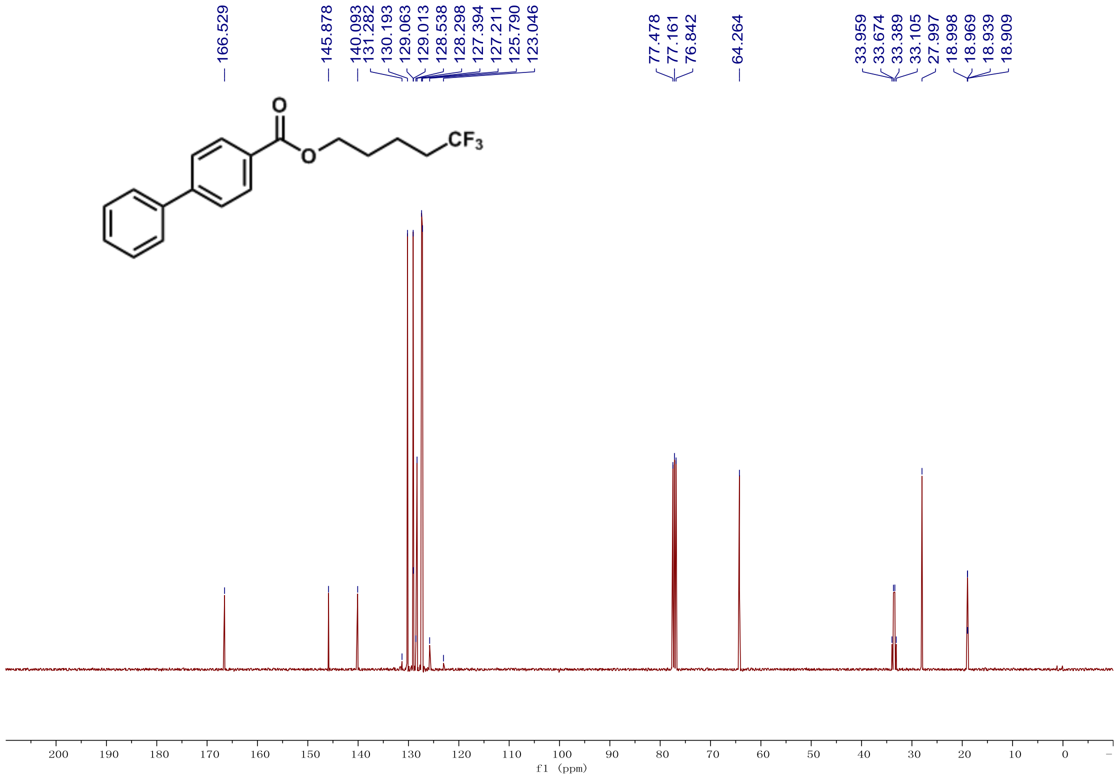

7.264
4.088
4.072
4.056
2.148
2.128
2.120
2.107
2.101
2.093
2.081
2.074
2.070
2.066
2.059
2.052
2.043
2.026
1.697
1.680
1.673
1.663
1.658
1.646
1.642
1.639
1.626
1.620
1.607
1.601
1.598
1.589
1.585
1.579
1.575
1.560
1.481
1.468
1.460
1.442
1.427
1.421
1.129
1.112
0.000
a
CF3
+
a'
CF3
b
a+a'
b
0.07
1.18
1.16
1.14
1.12
1.10
1.08
f1 (ppm)
2.00
4.93
5.24
1.97
0.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

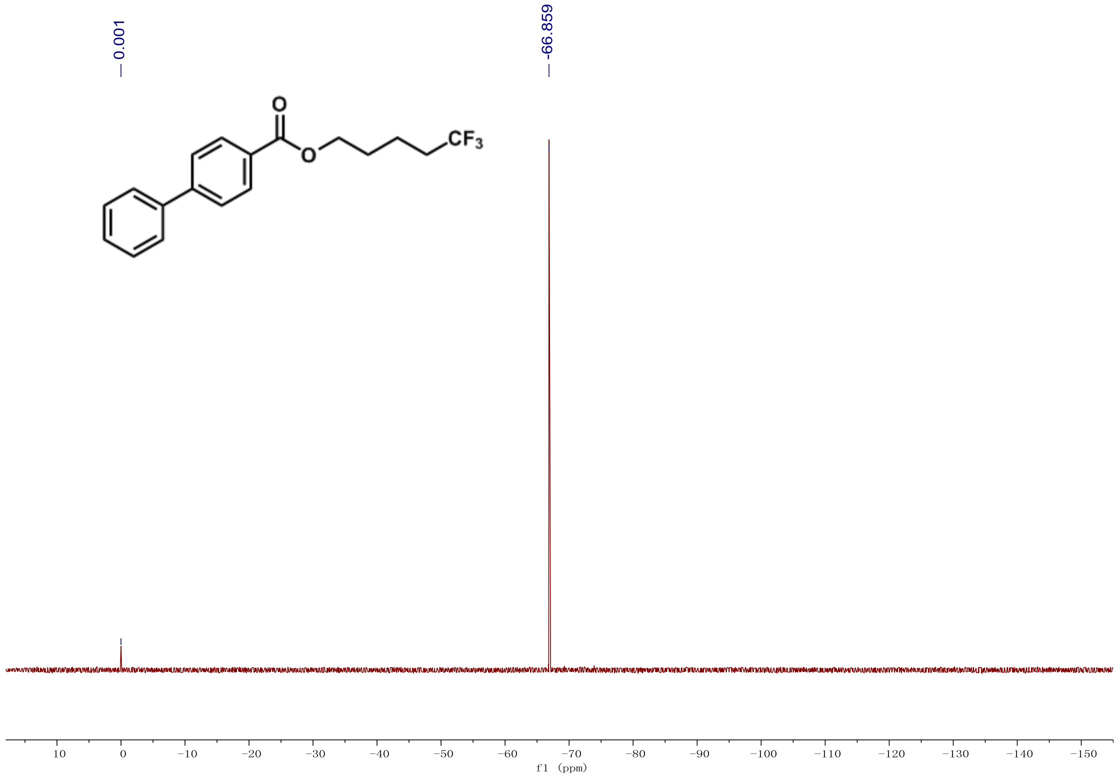

171.167
131.338
128.592
125.849
123.102
77.478
77.161
76.842
64.118
34.096
33.812
33.529
33.245
28.310
25.245
21.718
21.689
21.660
21.630
20.922
O
O
CF3
+
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-66.922
-73.776
O
O
CF3
+
O
O
CF3
97.64
2.36
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

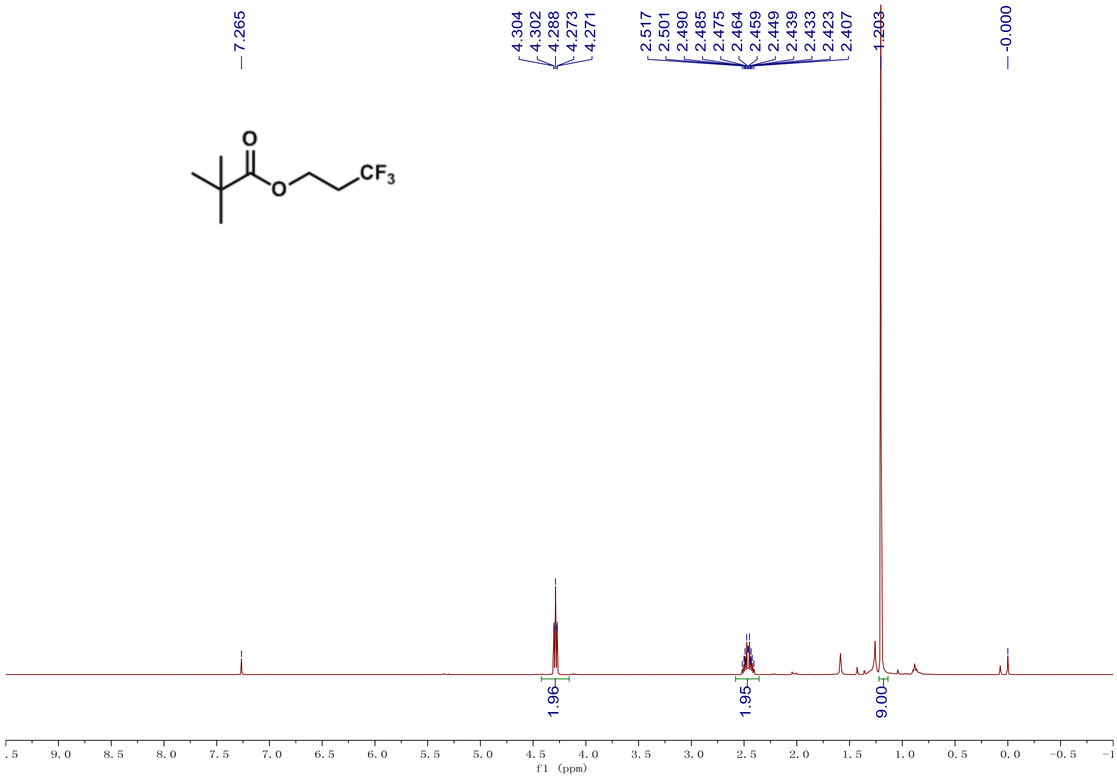
2-29

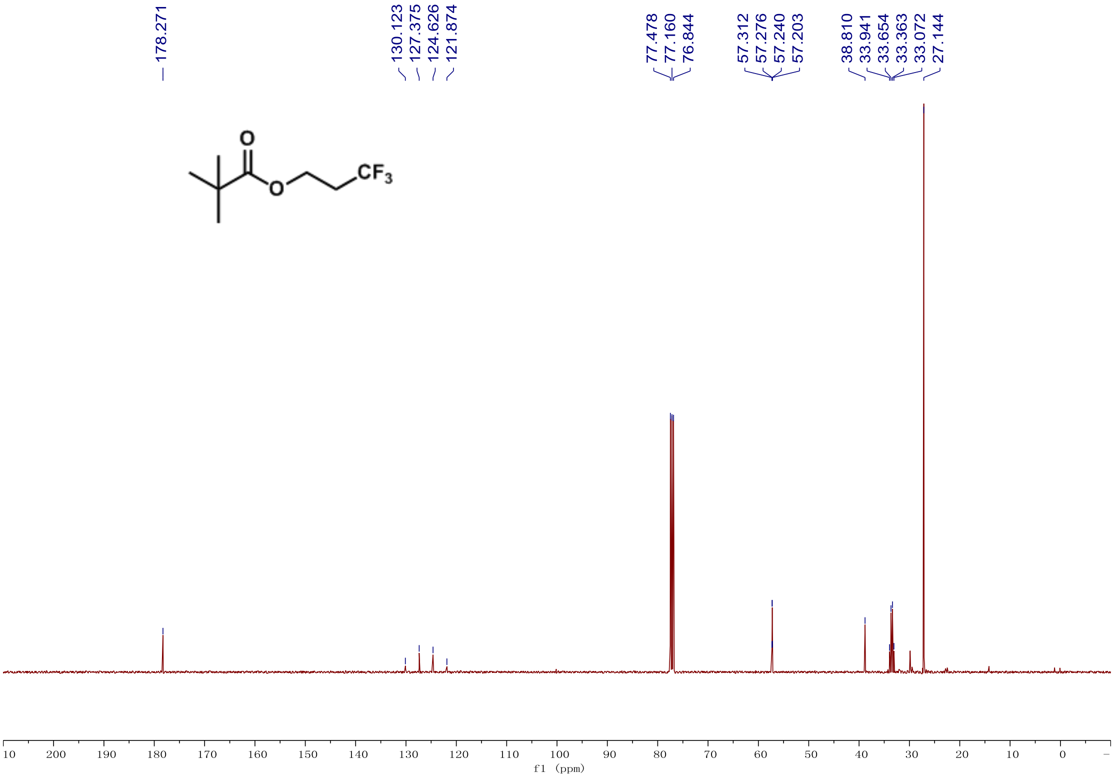

8.112
8.108
8.096
8.091
7.683
7.679
7.667
7.662
7.642
7.637
7.632
7.623
7.618
7.493
7.488
7.475
7.470
7.455
7.419
7.406
7.401
7.382
7.260
4.390
4.375
4.359
2.246
2.219
2.206
2.200
2.192
2.180
2.173
2.166
2.153
2.126
1.922
1.906
1.887
1.868
1.853
1.802
1.790
1.781
1.774
1.763
1.751
1.741
1.725
0.000
O
O
CF3
2.03
2.06
2.04
2.00
0.99
1.99
2.07
2.06
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

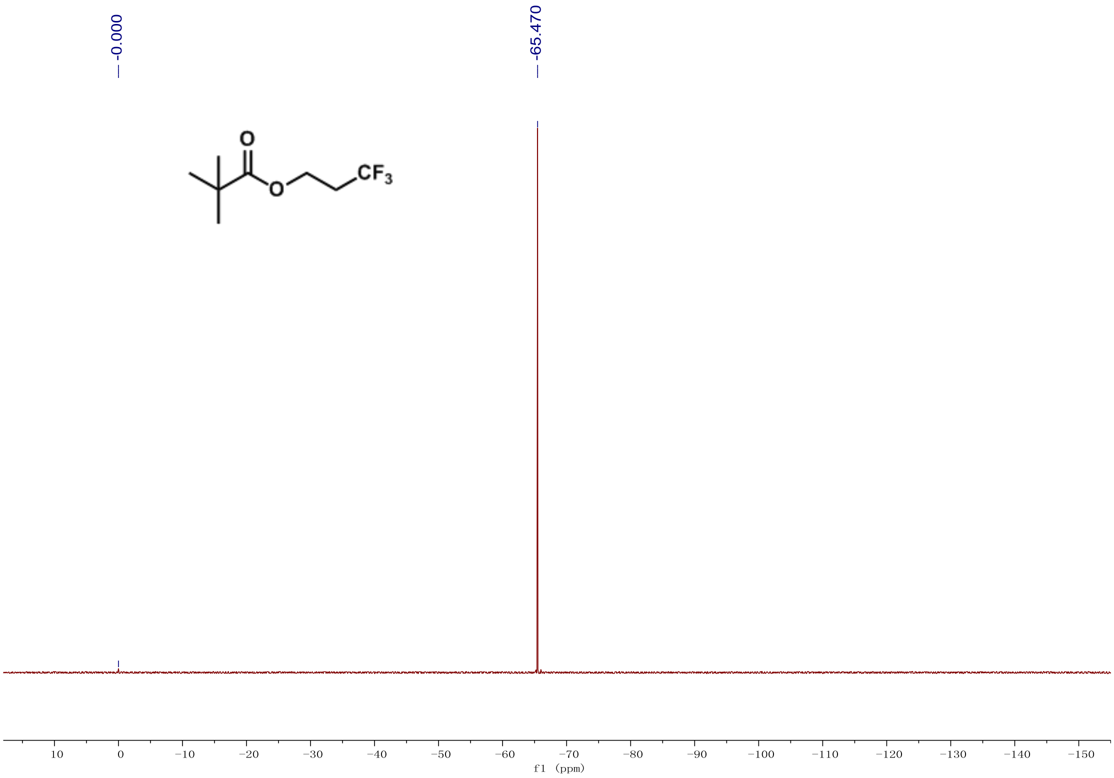

166.529
145.878
140.093
131.282
130.193
129.063
129.013
128.538
128.298
127.394
127.211
125.790
123.046
77.478
77.161
76.842
64.264
33.959
33.674
33.389
33.105
27.997
18.998
18.969
18.939
18.909
O
O
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-66.859
O
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

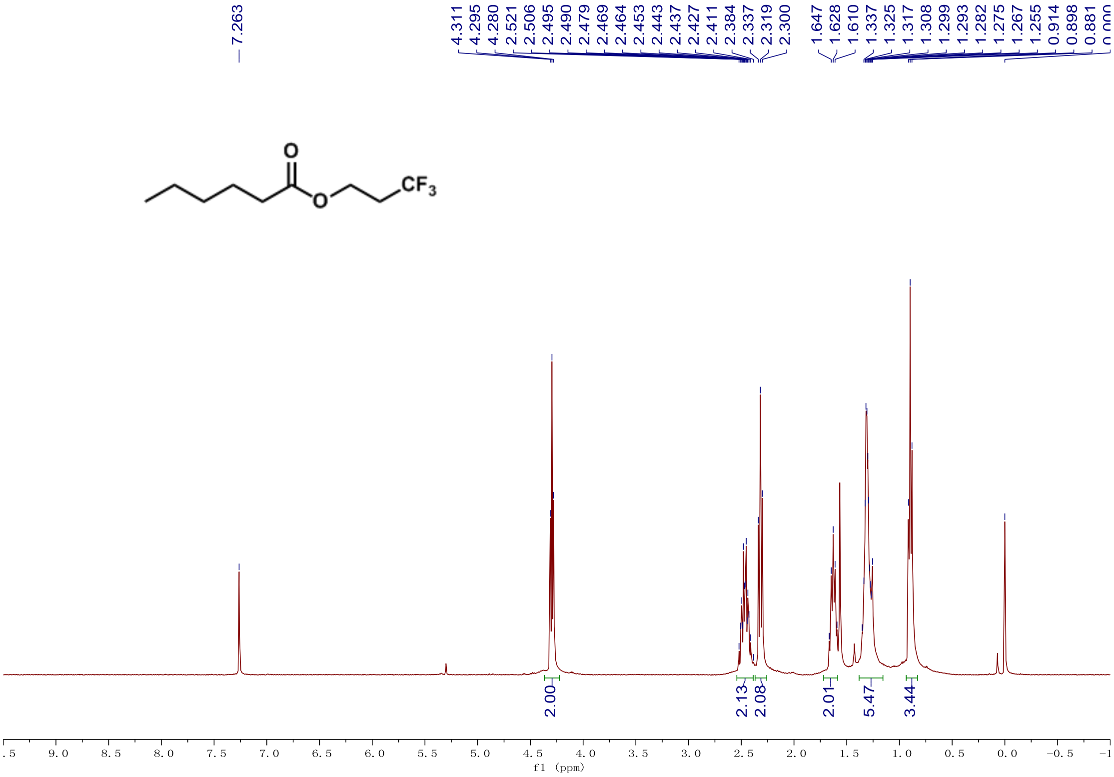
2-30

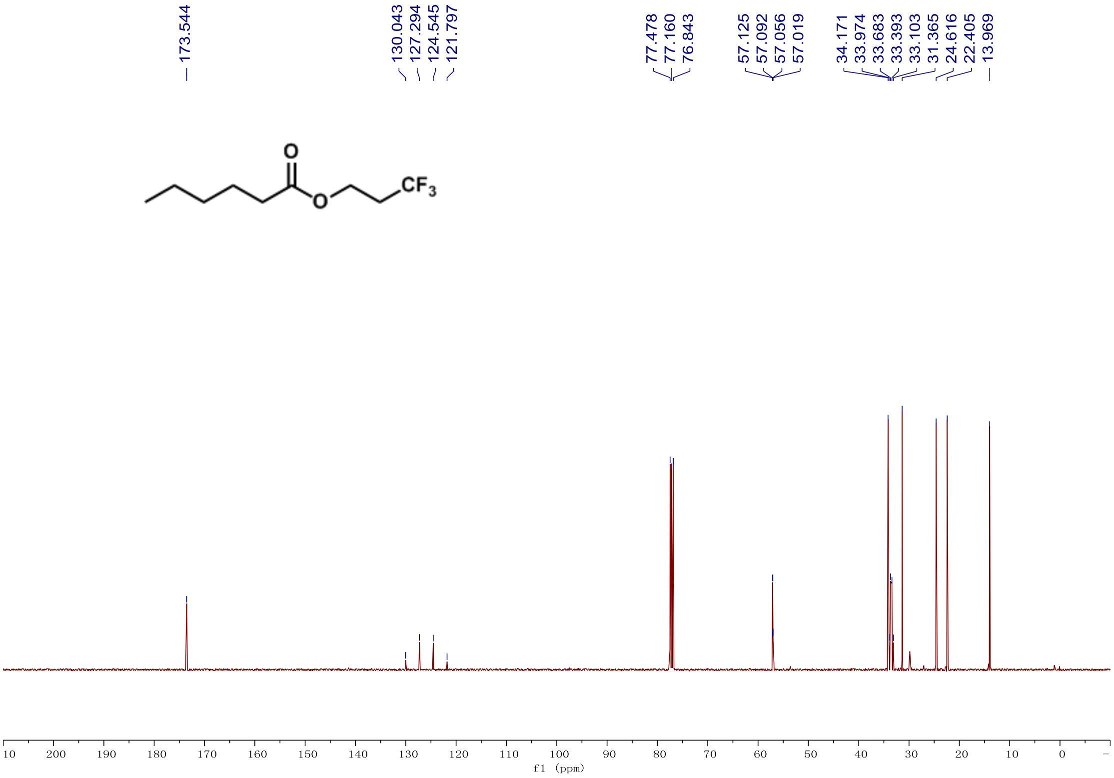

7.265
4.304
4.302
4.288
4.273
4.271
2.517
2.501
2.490
2.485
2.475
2.464
2.459
2.449
2.439
2.433
2.423
2.407
1.203
-0.000
O
O
CF3
1.96
1.95
9.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

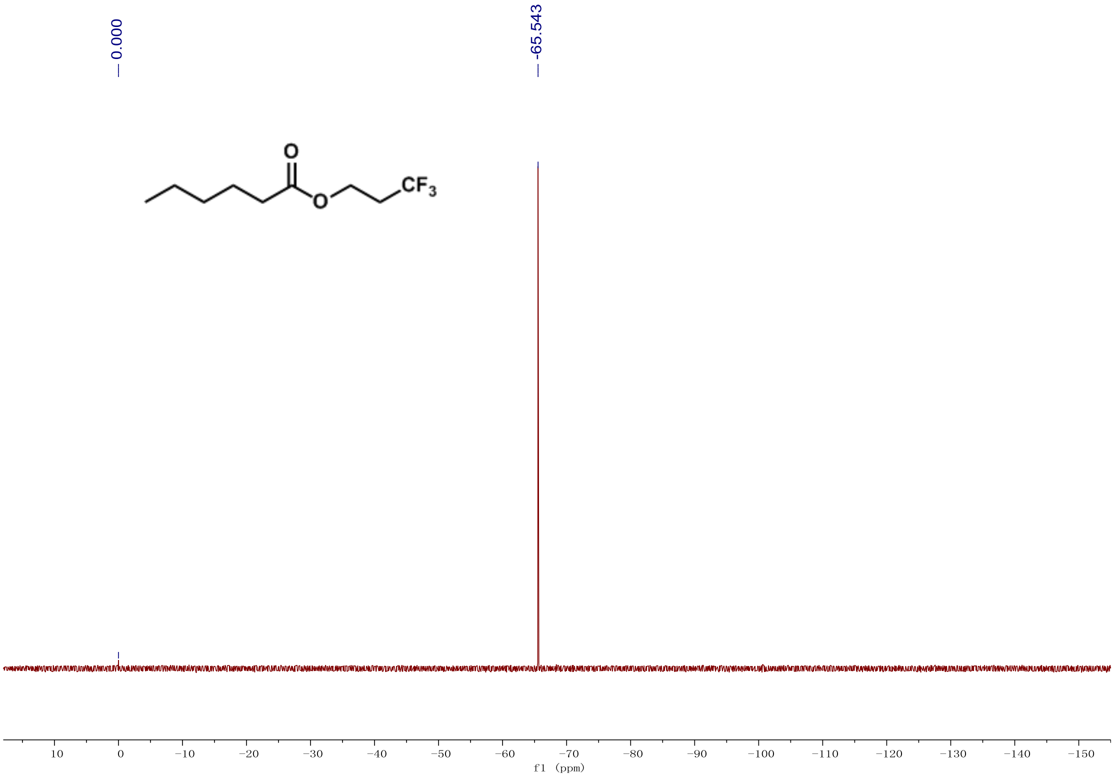

178.271
130.123
127.375
124.626
121.874
77.478
77.160
76.844
57.312
57.276
57.240
57.203
38.810
33.941
33.654
33.363
33.072
27.144
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-65.470
O
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

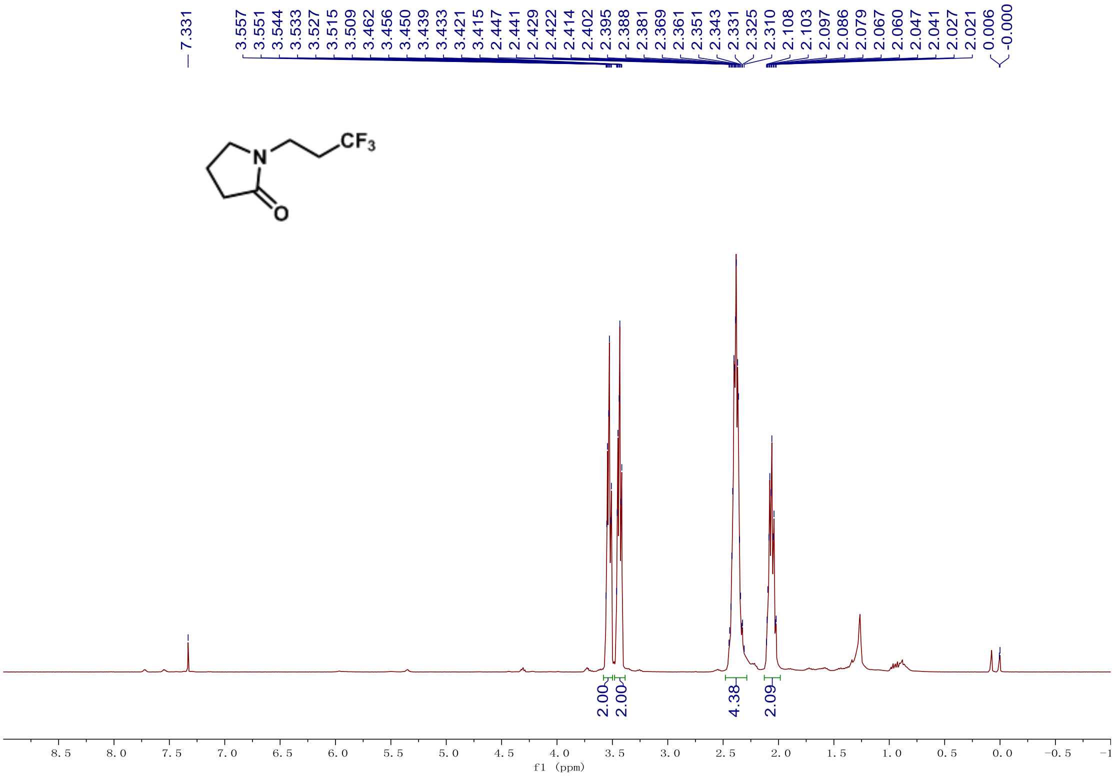
2-31

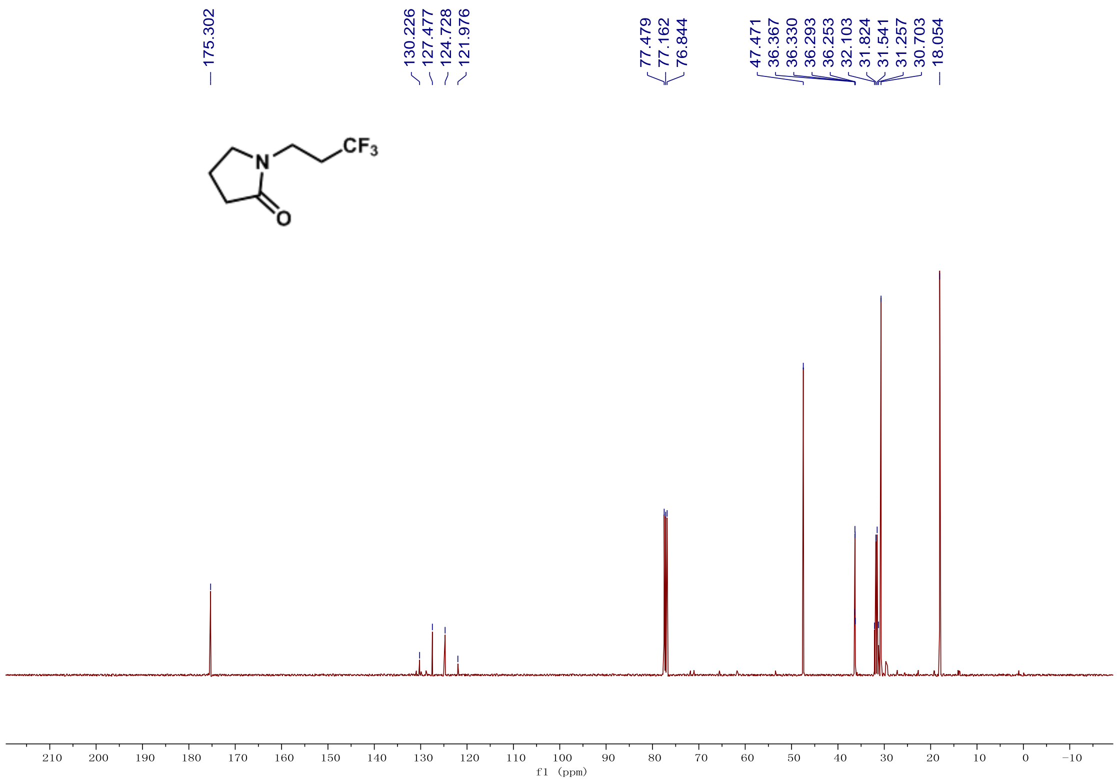

7.263
4.311
4.295
4.280
2.521
2.506
2.495
2.490
2.479
2.469
2.464
2.453
2.443
2.437
2.427
2.411
2.384
2.337
2.319
2.300
1.647
1.628
1.610
1.337
1.325
1.317
1.308
1.299
1.293
1.282
1.275
1.267
1.255
0.914
0.898
0.881
0.000
O
O
CF3
2.00
2.13
2.08
2.01
5.47
3.44
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

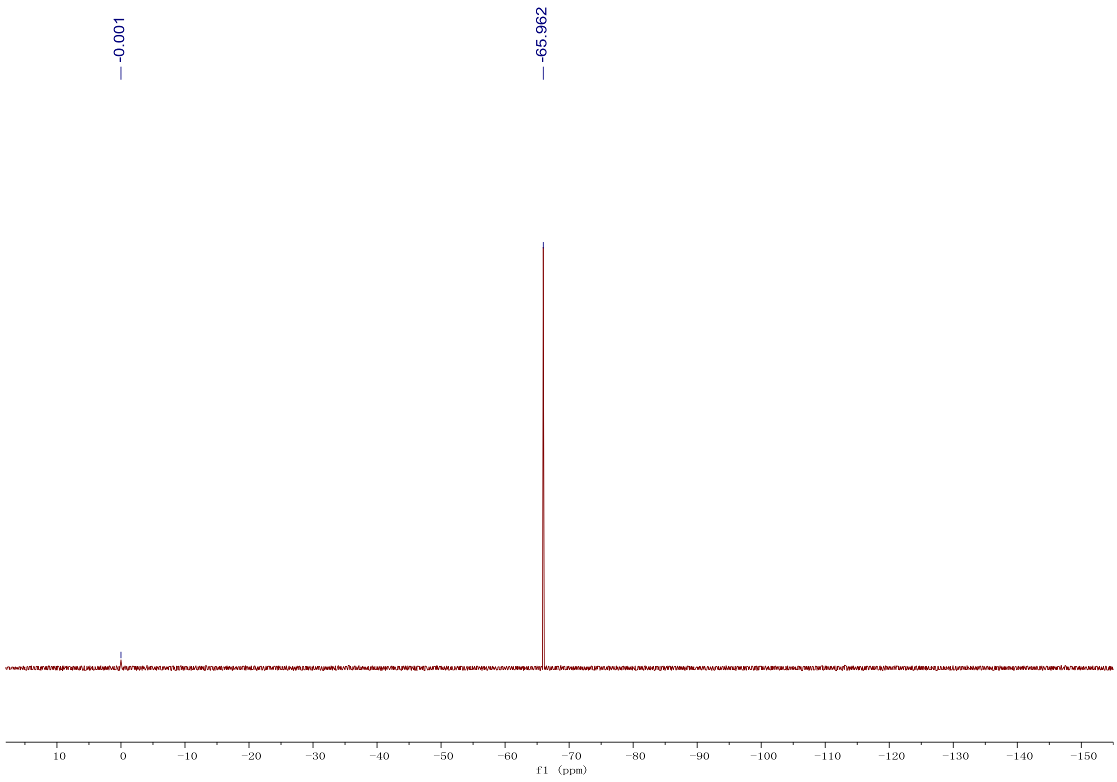

173.544
130.043
127.294
124.545
121.797
77.478
77.160
76.843
57.125
57.092
57.056
57.019
34.171
33.974
33.683
33.393
33.103
31.365
24.616
22.405
13.969
O
O
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


0.000
-65.543
O
O
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

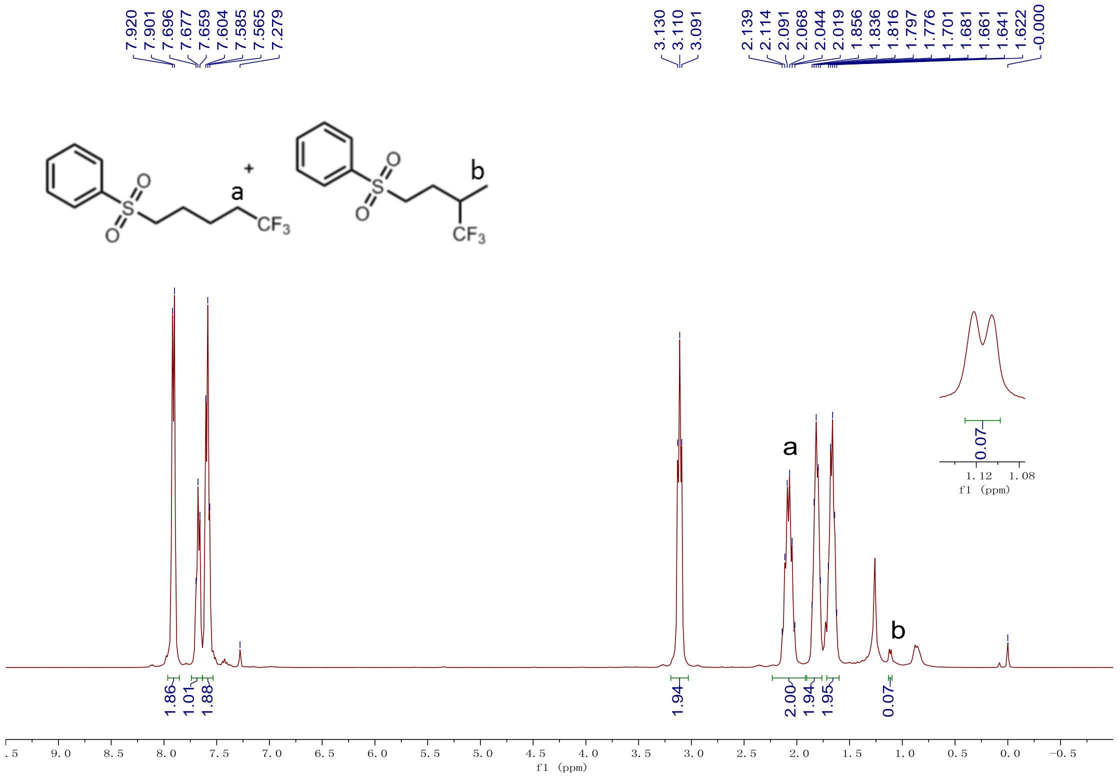
2-32

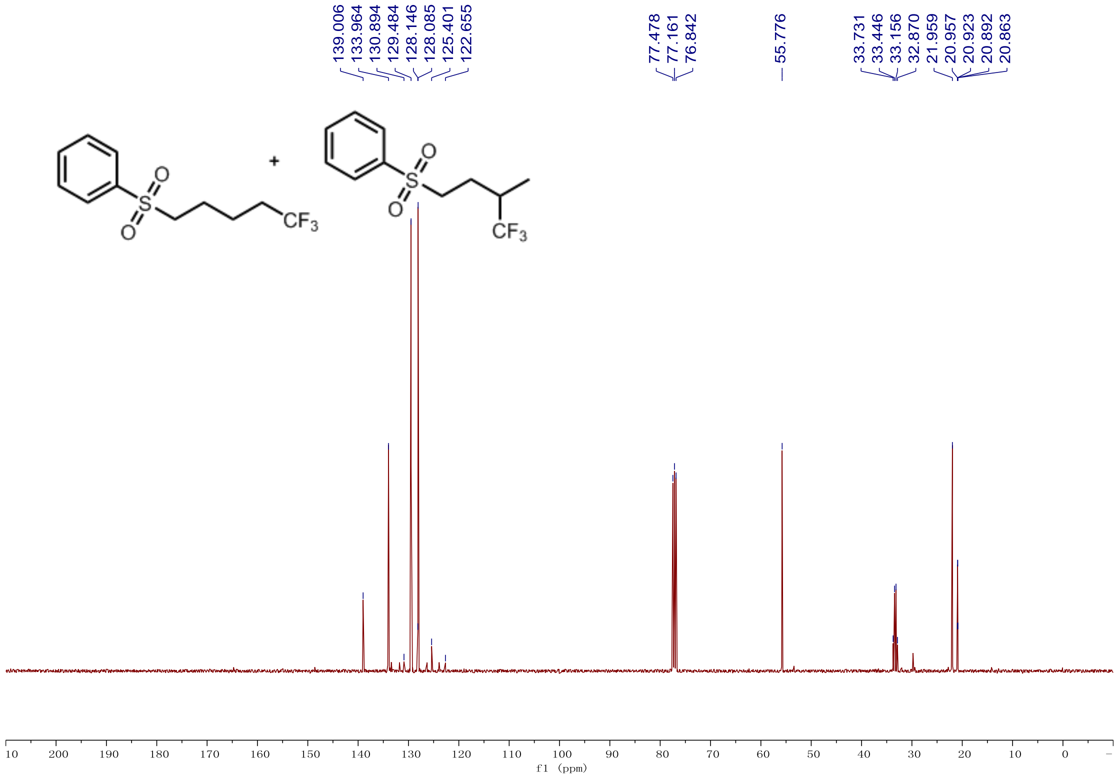

7.331
3.557 3.551 3.544 3.533 3.527 3.515 3.509 3.462 3.456 3.450 3.439 3.433 3.421 3.415 2.447 2.441 2.429 2.422 2.414 2.402 2.395 2.388 2.381 2.369 2.361 2.351 2.343 2.331 2.325 2.310 2.108 2.103 2.097 2.086 2.079 2.067 2.060 2.047 2.041 2.027 2.021 0.006 -0.000
N
CF3
O
2.00
2.00
4.38
2.09
8.5 8.0 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 −1
f1 (ppm)

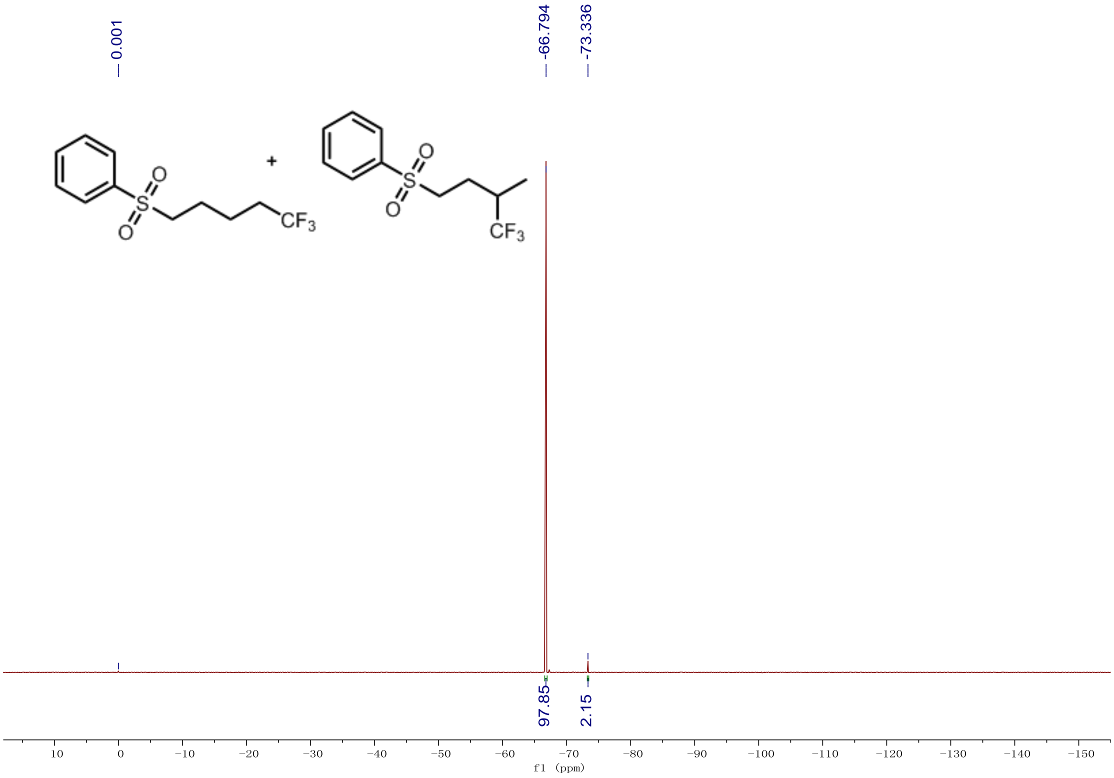

175.302
130.226
127.477
124.728
121.976
77.479
77.162
76.844
47.471
36.367
36.330
36.293
36.253
32.103
31.824
31.541
31.257
30.703
18.054
N
CF3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-0.001
-65.962
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

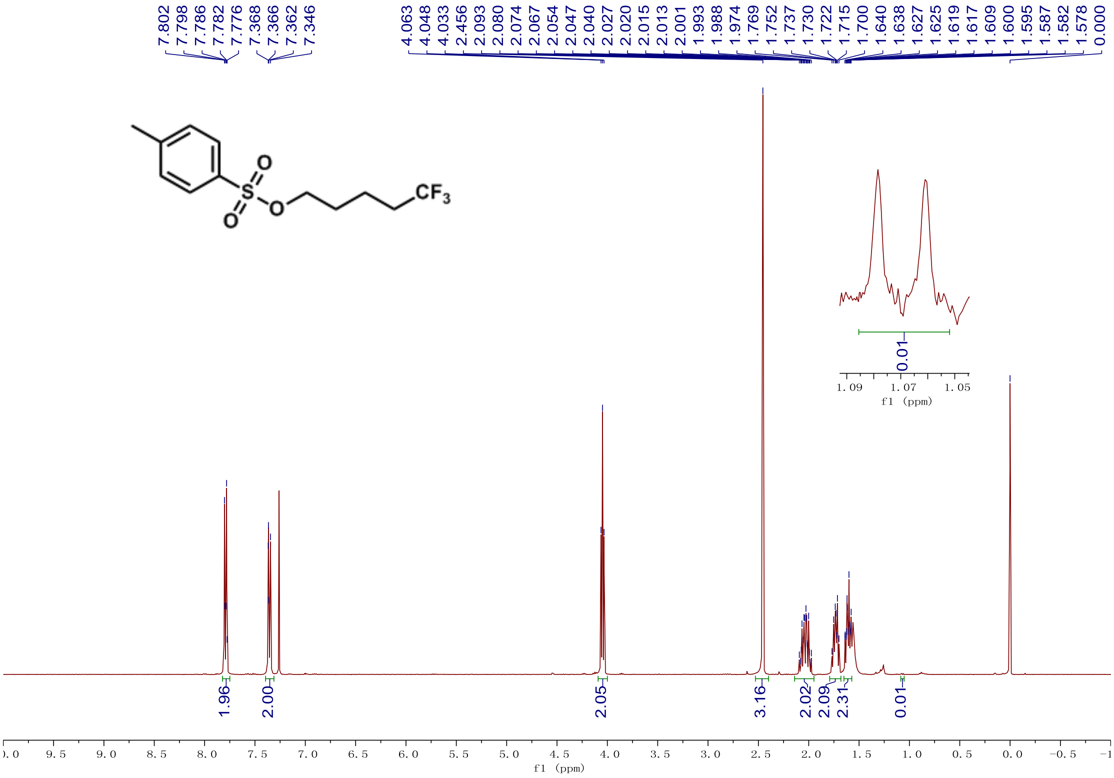
2-33

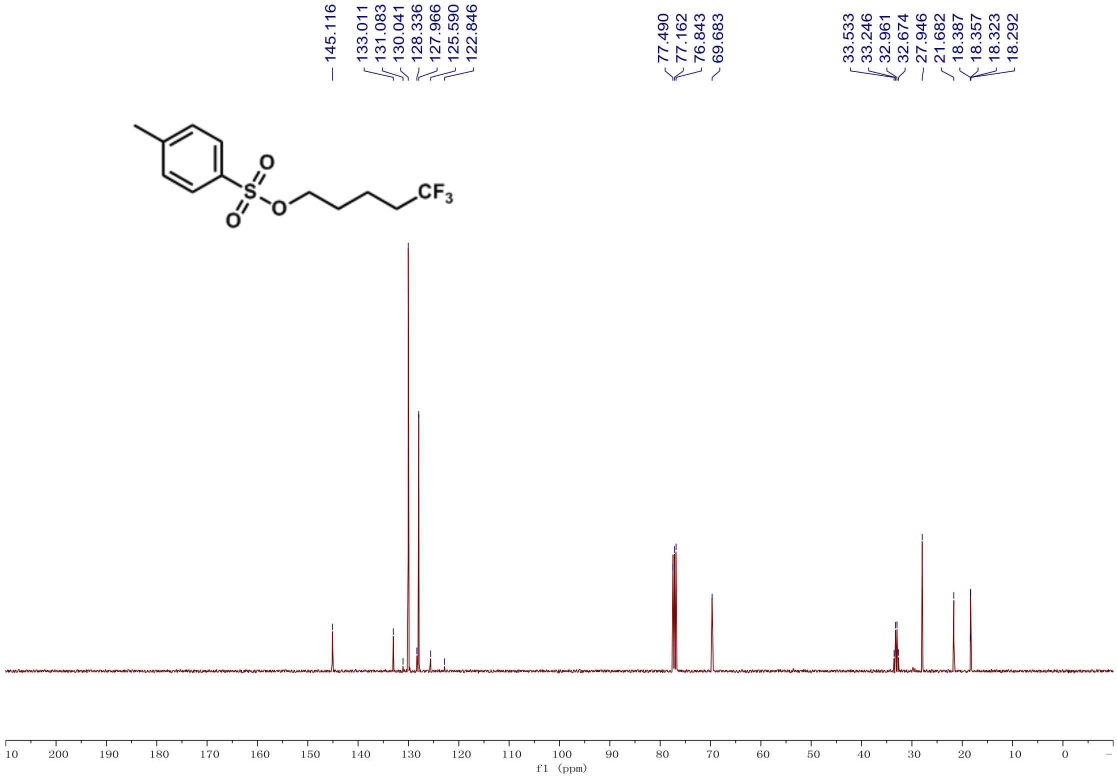

7.920
7.901
7.696
7.677
7.659
7.604
7.585
7.565
7.279
3.130
3.110
3.091
2.139
2.114
2.091
2.068
2.044
2.019
1.856
1.836
1.816
1.797
1.776
1.701
1.681
1.661
1.641
1.622
-0.000
O
S
O
a
CF3
+
O
S
O
b
CF3
a
b
0.07
1.12
1.08
f1 (ppm)
1.86
1.01
1.88
1.94
2.00
1.94
1.95
0.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

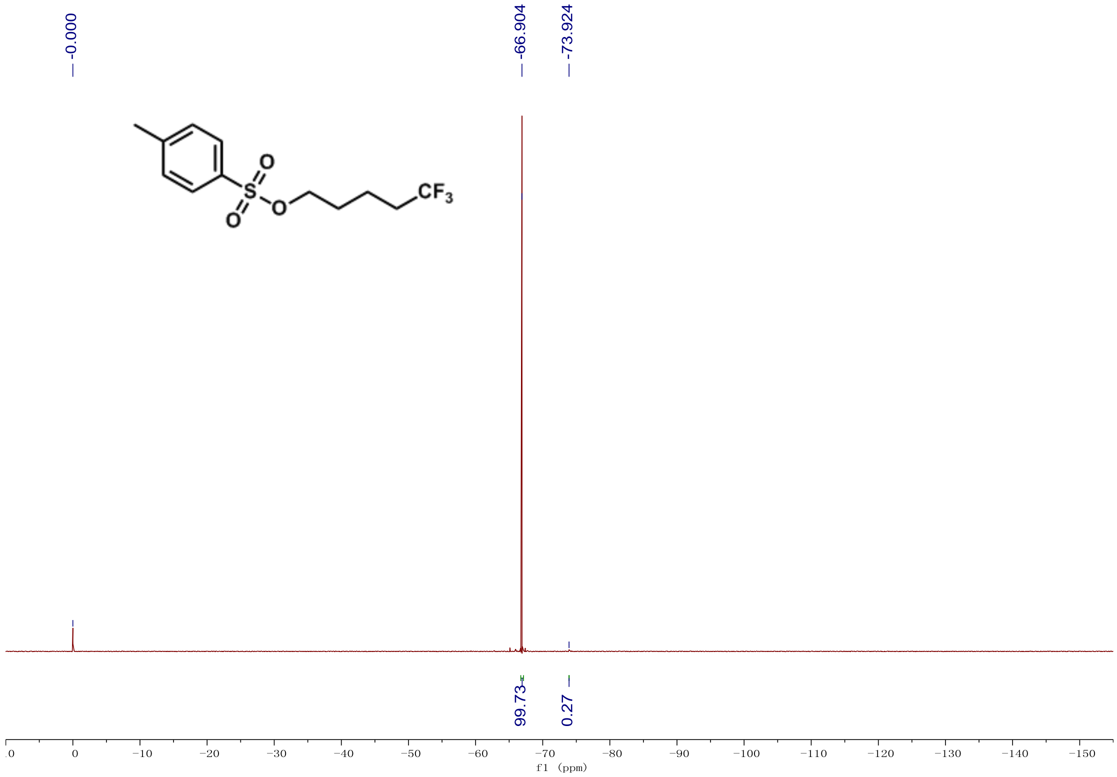

139.006
133.964
130.894
129.484
128.146
128.085
125.401
122.655
77.478
77.161
76.842
55.776
33.731
33.446
33.156
32.870
21.959
20.957
20.923
20.892
20.863
O
S
O
CF3
+
O
S
O
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-66.794
-73.336
+
CF3
CF3
97.85
2.15
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

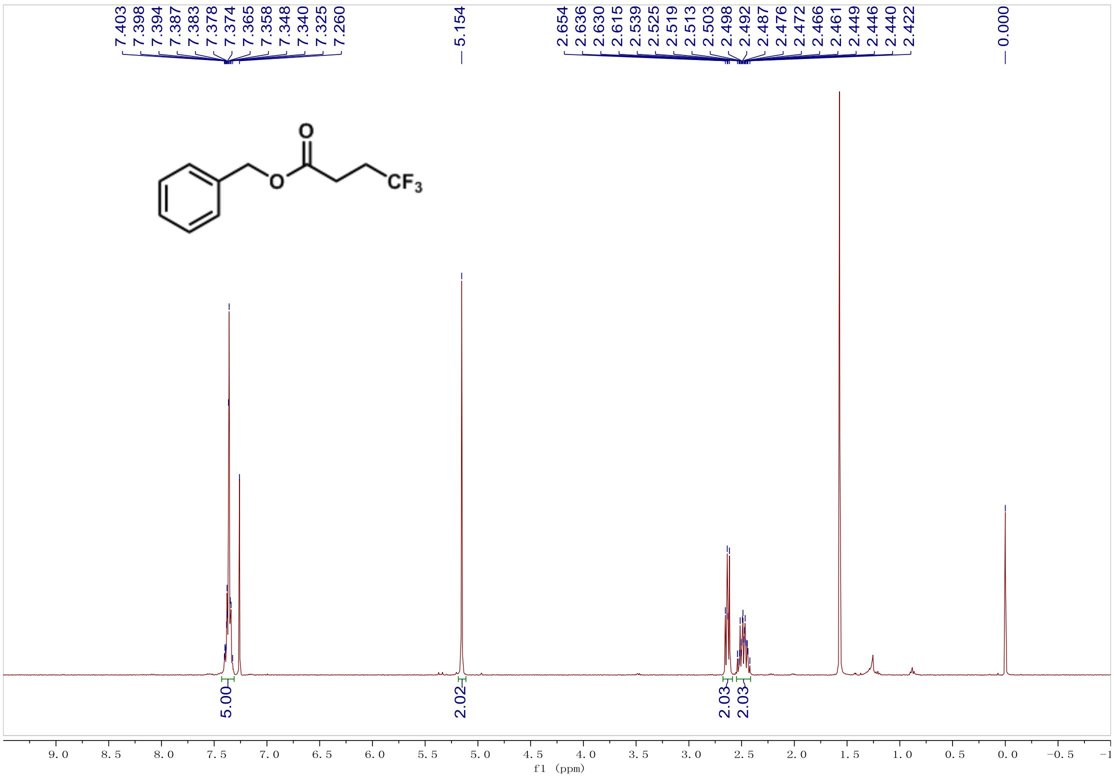
2-34

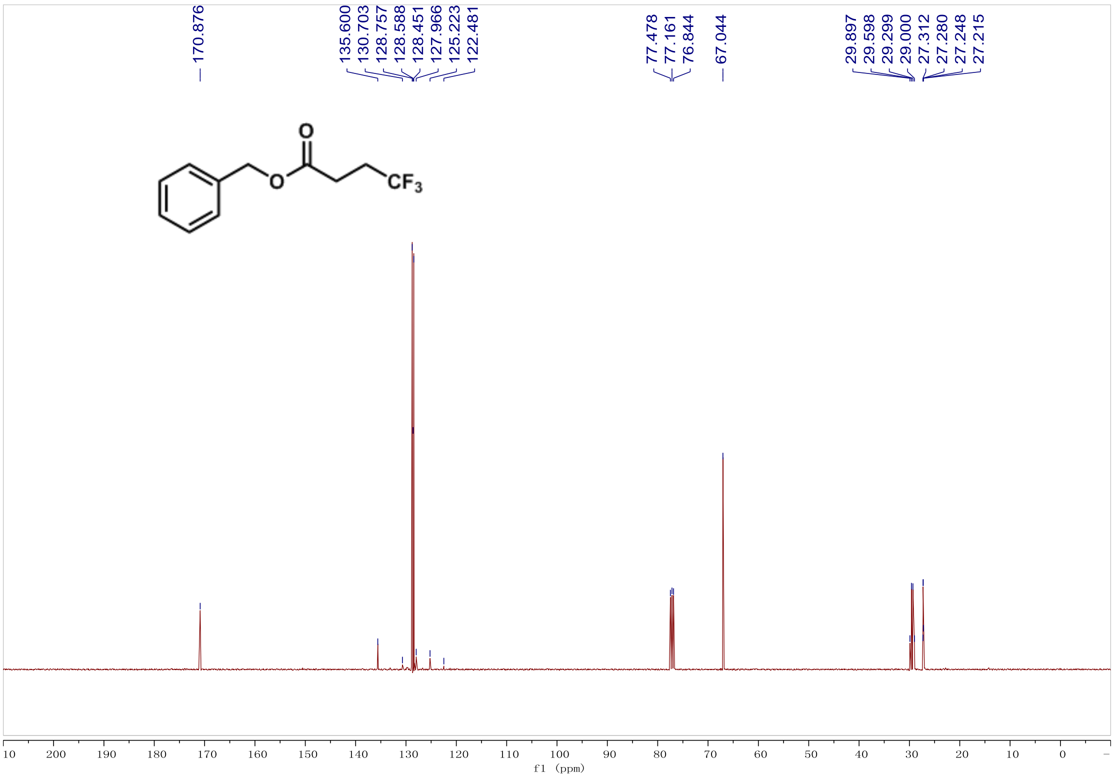

7.802
7.798
7.786
7.782
7.776
7.368
7.366
7.362
7.346
4.063
4.048
4.033
2.456
2.093
2.080
2.074
2.067
2.054
2.047
2.040
2.027
2.020
2.015
2.013
2.001
1.993
1.988
1.974
1.769
1.752
1.737
1.730
1.722
1.715
1.700
1.640
1.638
1.627
1.625
1.619
1.617
1.609
1.600
1.595
1.587
1.582
1.578
0.000
CF3
0.01
1.09 1.07 1.05
f1 (ppm)
1.96
2.00
2.05
3.16
2.02
2.09
2.31
0.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

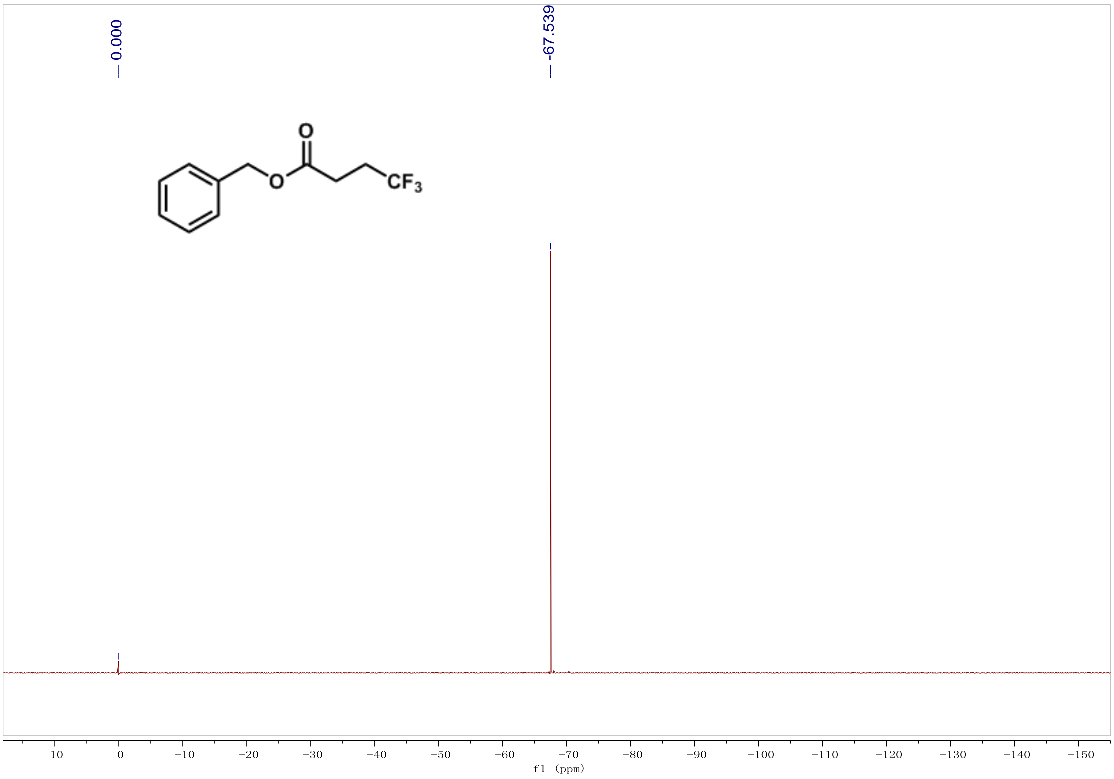

145.116
133.011
131.083
130.041
128.336
127.966
125.590
122.846
77.490
77.162
76.843
69.683
33.533
33.246
32.961
32.674
27.946
21.682
18.387
18.357
18.323
18.292
O
S
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-66.904
-73.924
O
S
O
O
CF3
99.73
0.27
0
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

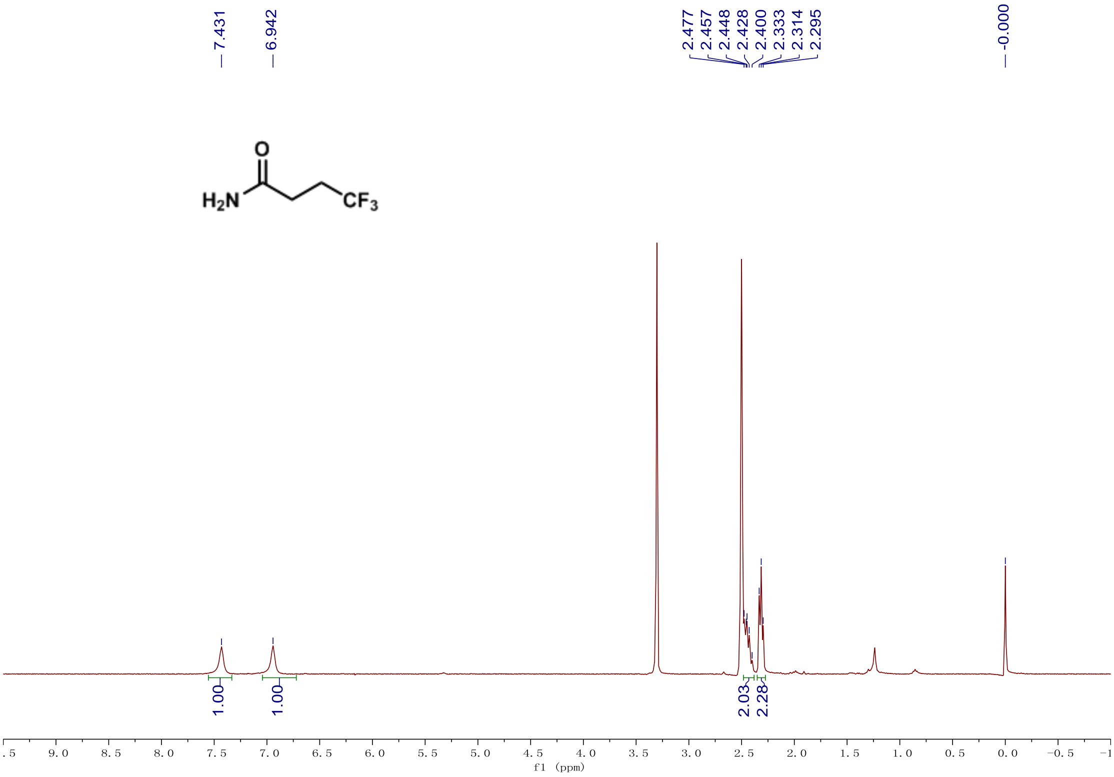
2-35

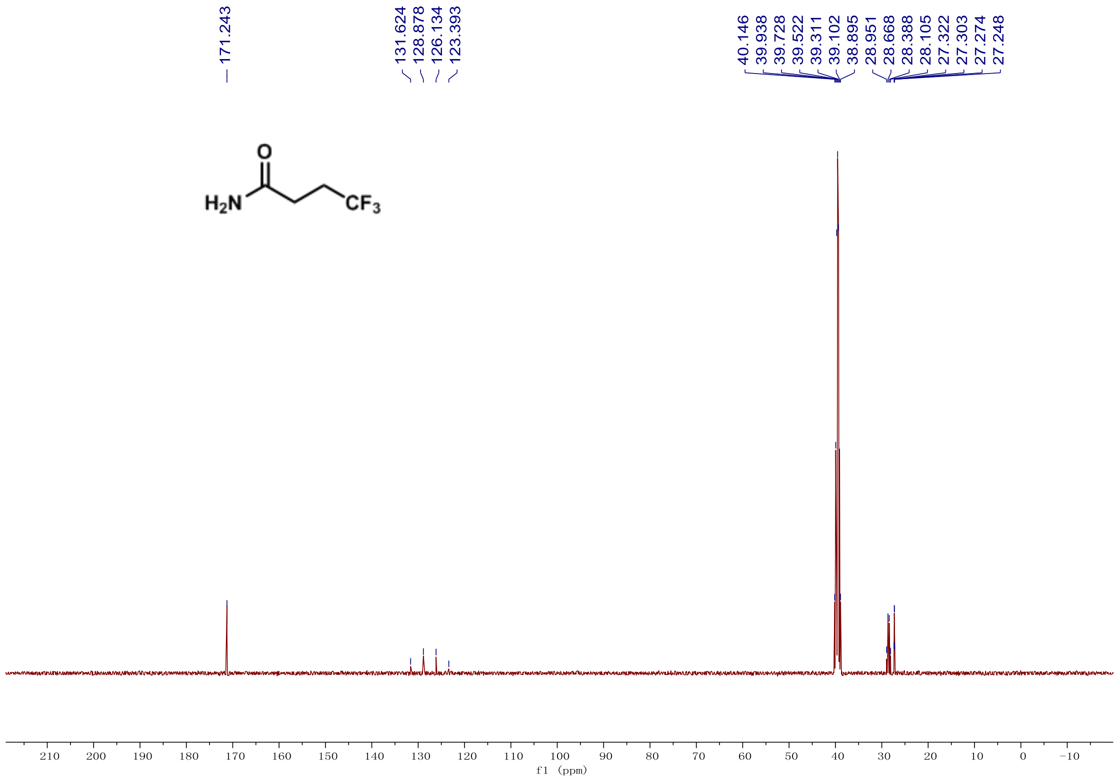

7.403
7.398
7.394
7.387
7.383
7.378
7.374
7.365
7.358
7.348
7.340
7.325
7.260
5.154
2.654
2.636
2.630
2.615
2.539
2.525
2.519
2.513
2.503
2.498
2.492
2.487
2.476
2.472
2.466
2.461
2.449
2.446
2.440
2.422
0.000
O
O
CF3
5.00
2.02
2.03
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

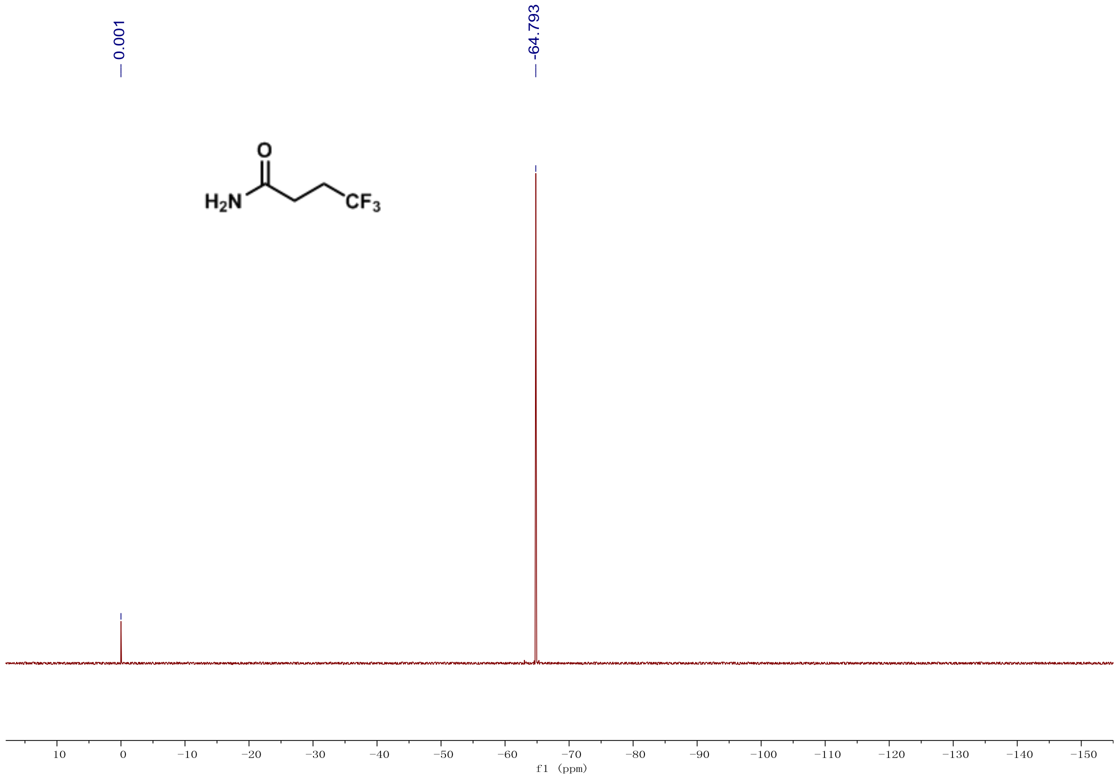

170.876
135.600
130.703
128.757
128.588
128.451
127.966
125.223
122.481
77.478
77.161
76.844
67.044
29.897
29.598
29.299
29.000
27.312
27.280
27.248
27.215
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-67.539
O
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

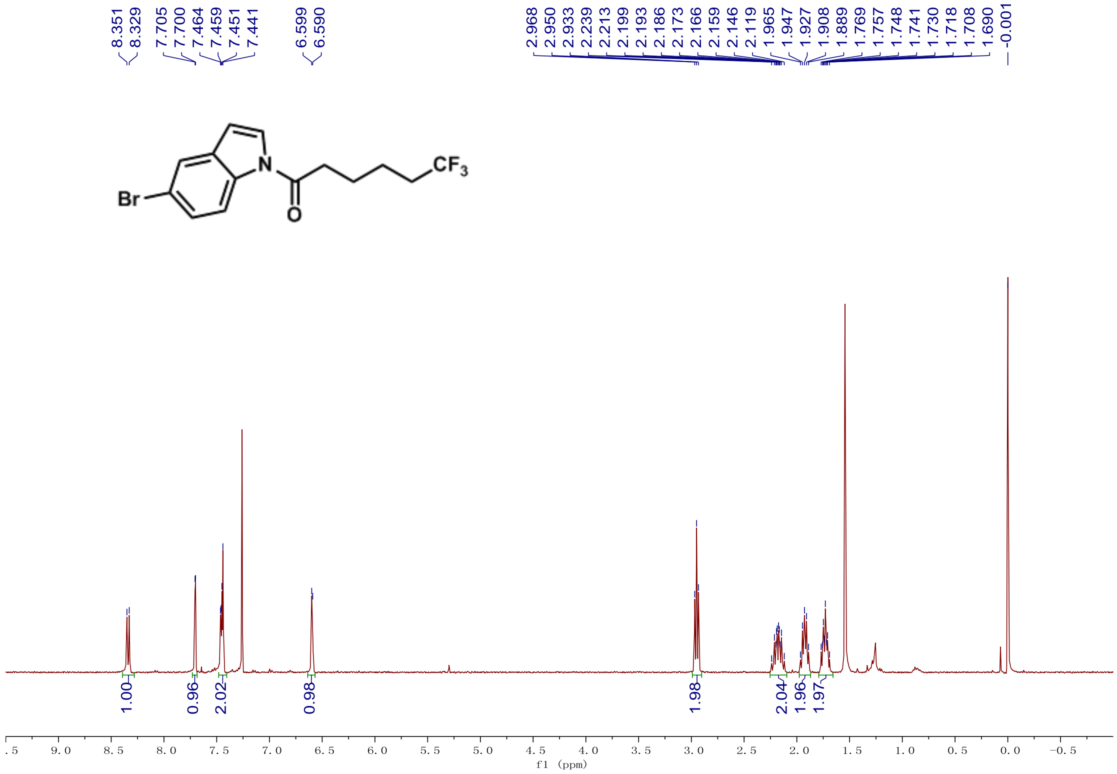
2-36

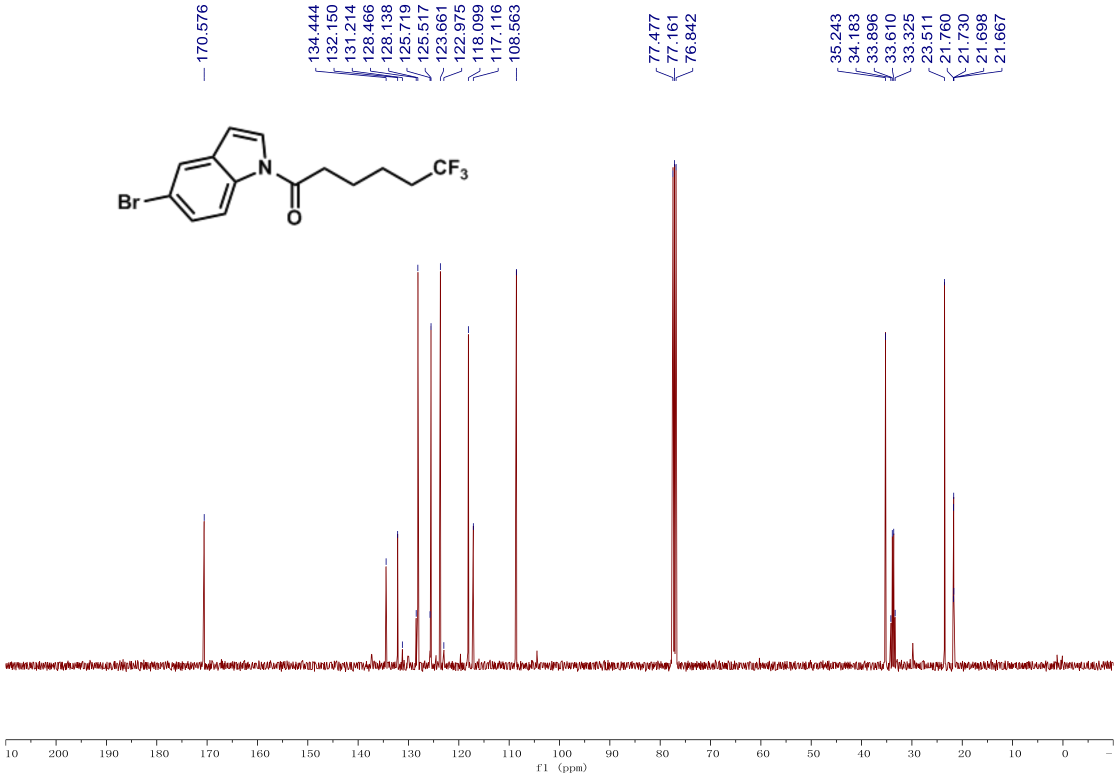

7.431
6.942
2.477
2.457
2.448
2.428
2.400
2.333
2.314
2.295
-0.000
O
H2N
CF3
1.00
1.00
2.03
2.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

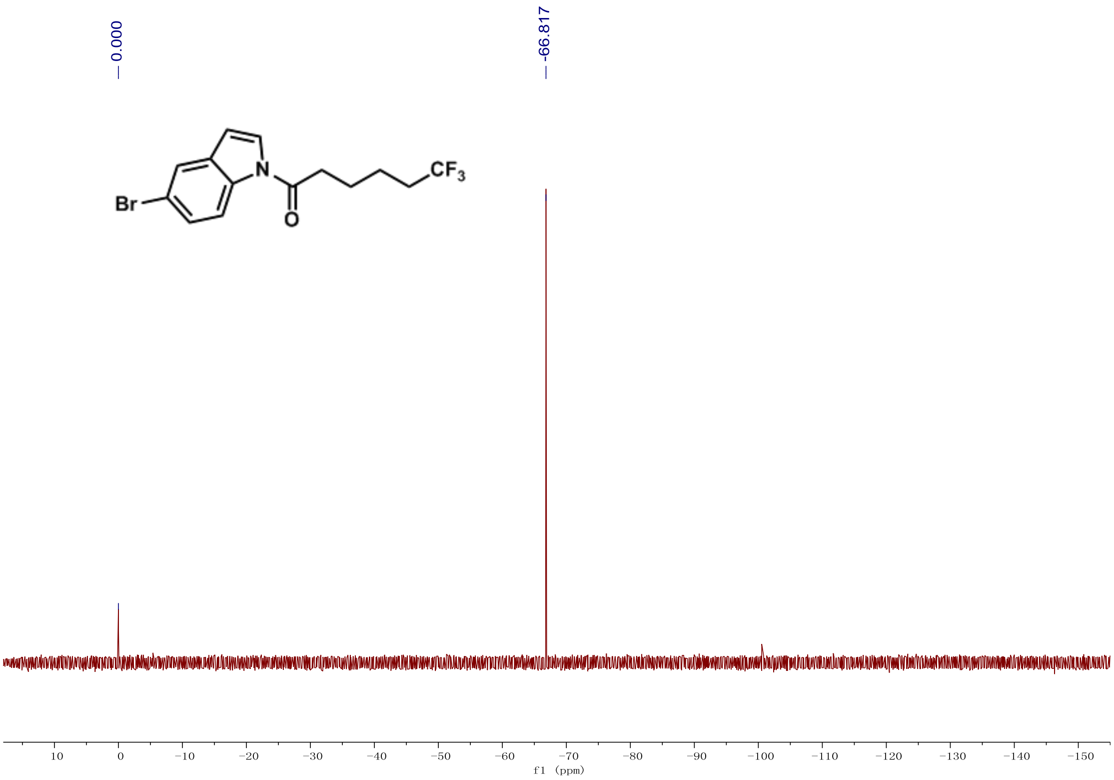

171.243
131.624
128.878
126.134
123.393
40.146
39.938
39.728
39.522
39.311
39.102
38.895
28.951
28.668
28.388
28.105
27.322
27.303
27.274
27.248
O
H2N
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


0.001
-64.793
O
H2N
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

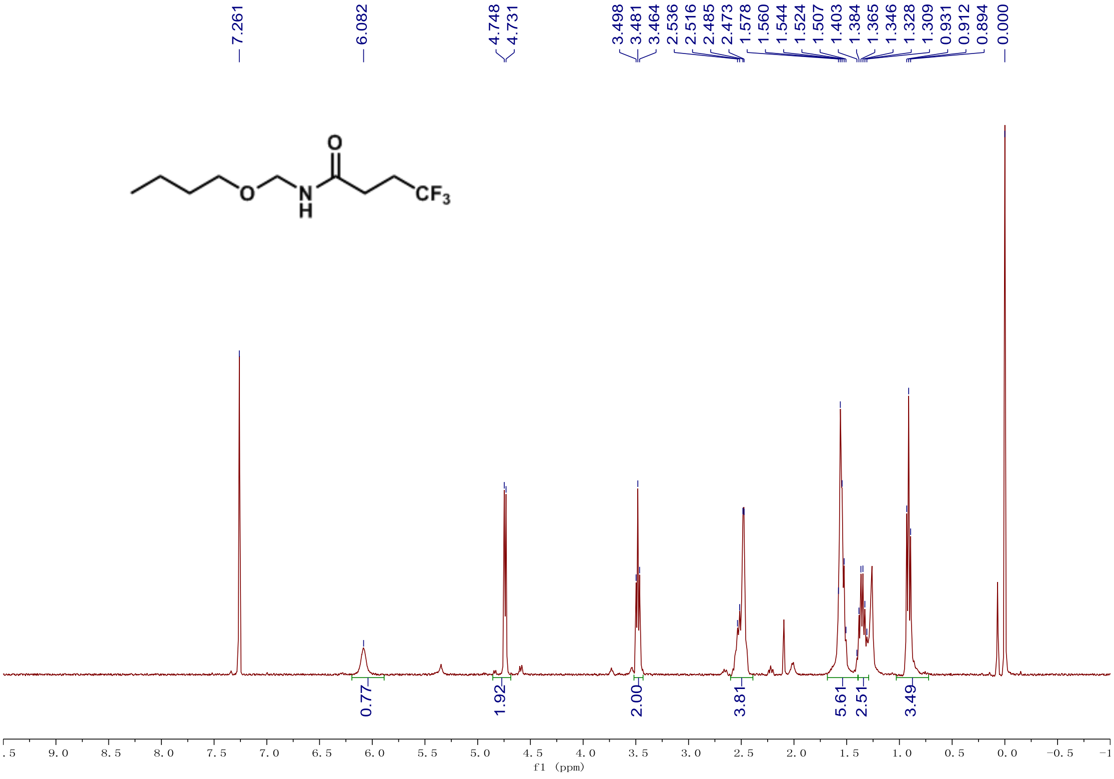
2-37

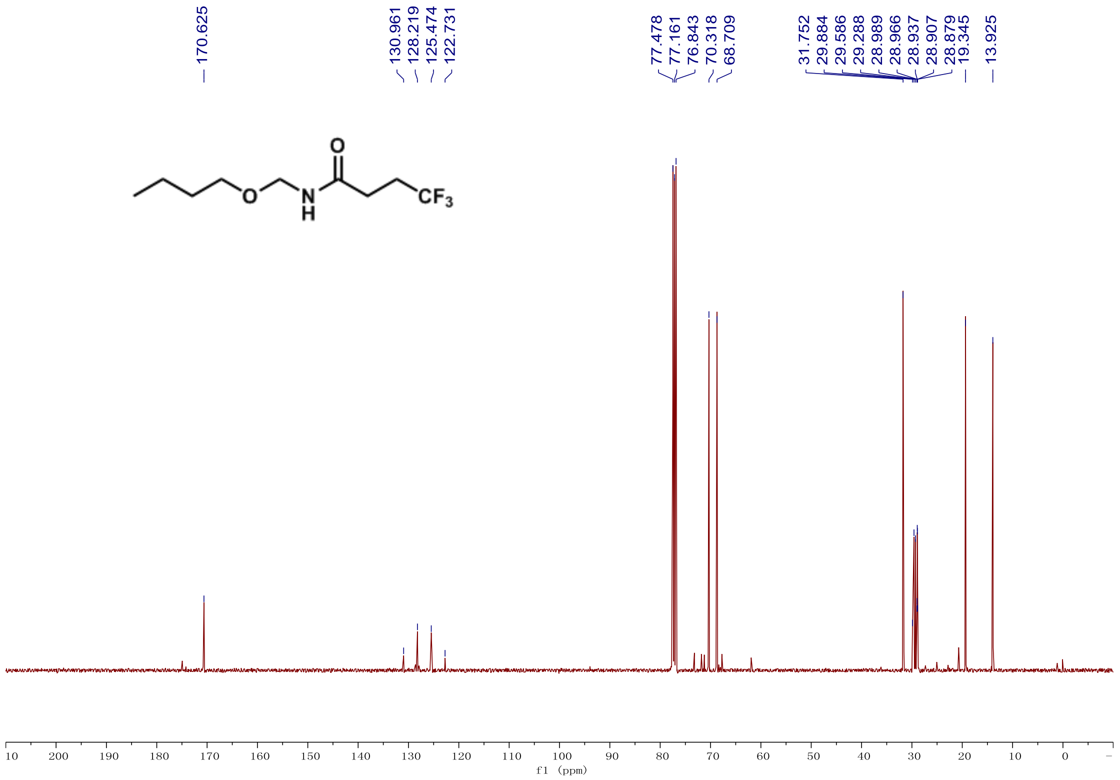

8.351
8.329
7.705
7.700
7.464
7.459
7.451
7.441
6.599
6.590
2.968
2.950
2.933
2.239
2.213
2.199
2.193
2.186
2.173
2.166
2.159
2.146
2.119
1.965
1.947
1.927
1.908
1.889
1.769
1.757
1.748
1.741
1.730
1.718
1.708
1.690
-0.001
Br
N
O
CF3
1.00
0.96
2.02
0.98
1.98
2.04
1.96
1.97
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

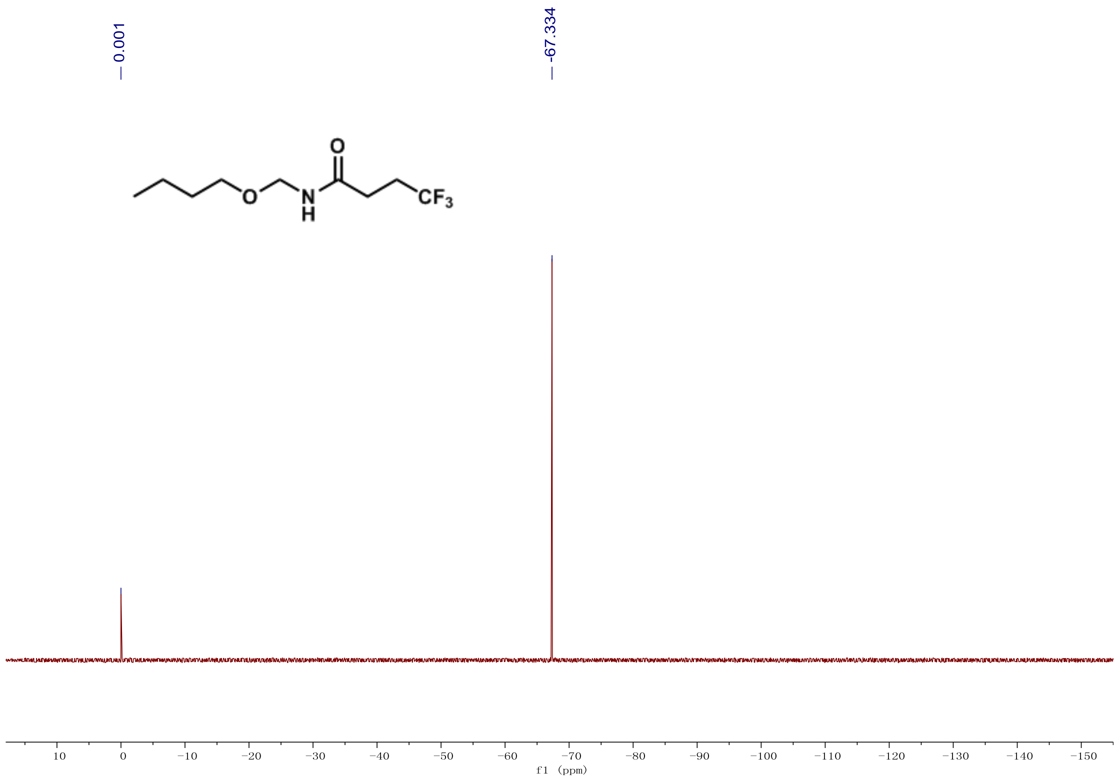

170.576
134.444
132.150
131.214
128.466
128.138
125.719
125.517
123.661
122.975
118.099
117.116
108.563
77.477
77.161
76.842
35.243
34.183
33.896
33.610
33.325
23.511
21.760
21.730
21.698
21.667
Br
N
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-66.817
Br
N
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

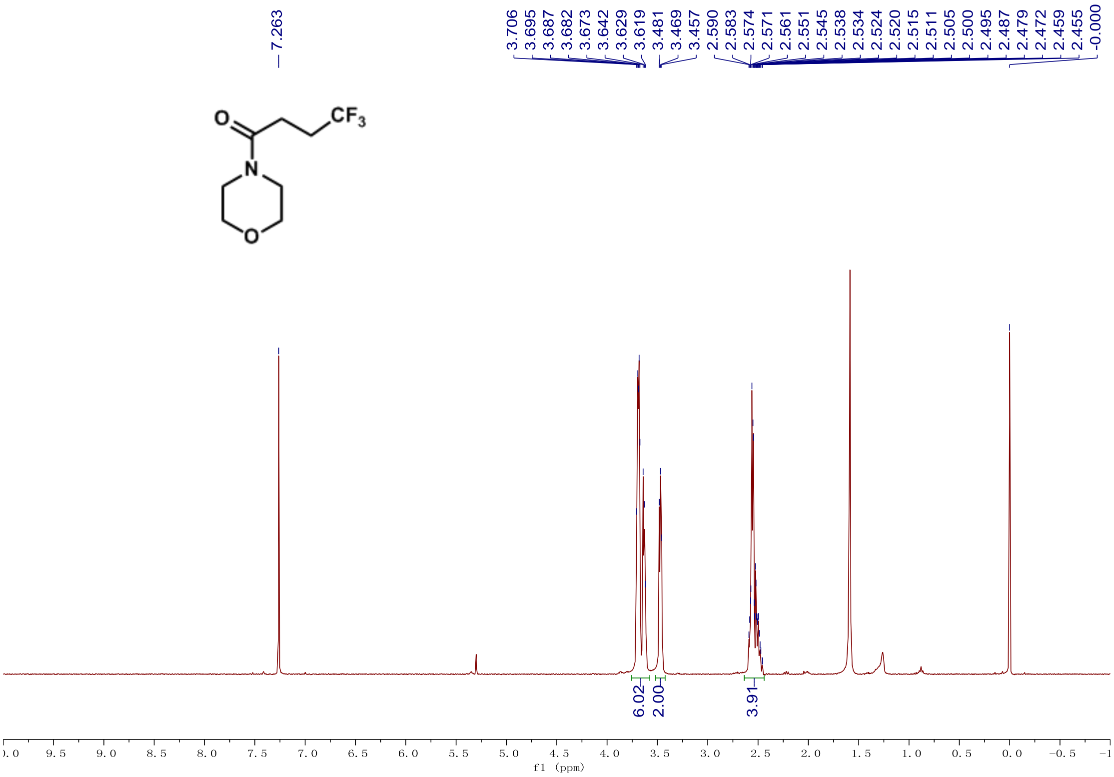
2-38

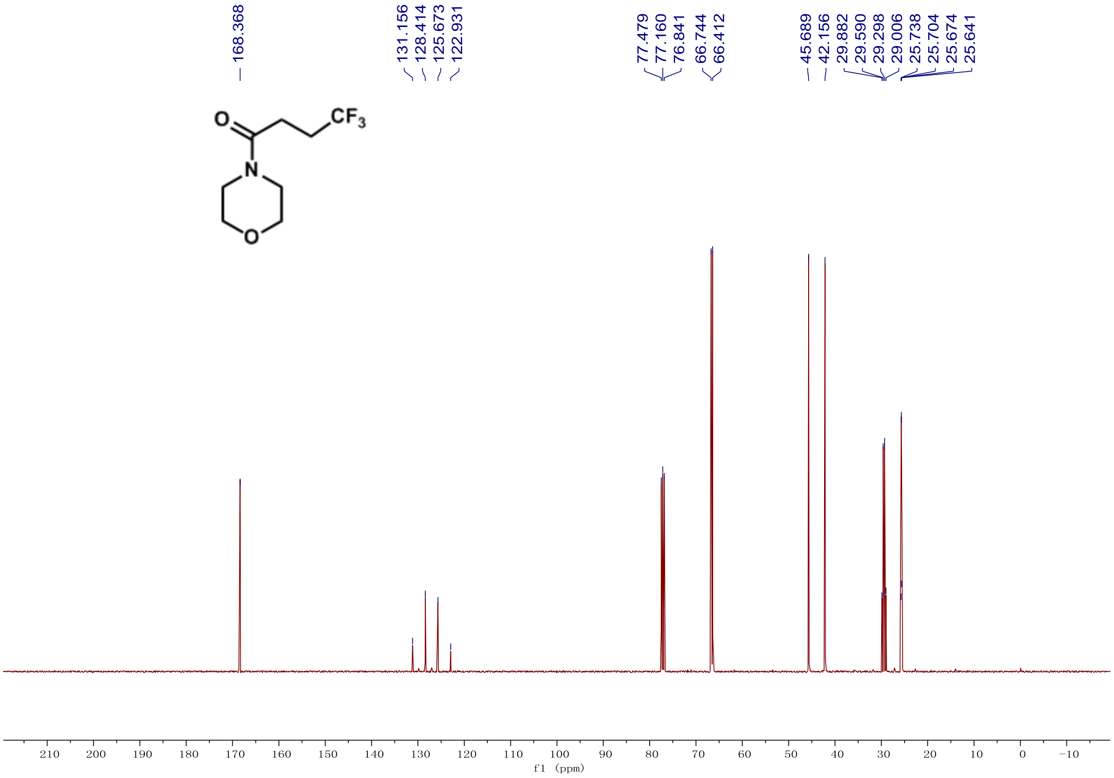

7.261
6.082
4.748
4.731
3.498
3.481
3.464
2.536
2.516
2.485
2.473
1.578
1.560
1.544
1.524
1.507
1.403
1.384
1.365
1.346
1.328
1.309
0.931
0.912
0.894
0.000
O
N
H
CF3
0.77
1.92
2.00
3.81
5.61
2.51
3.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

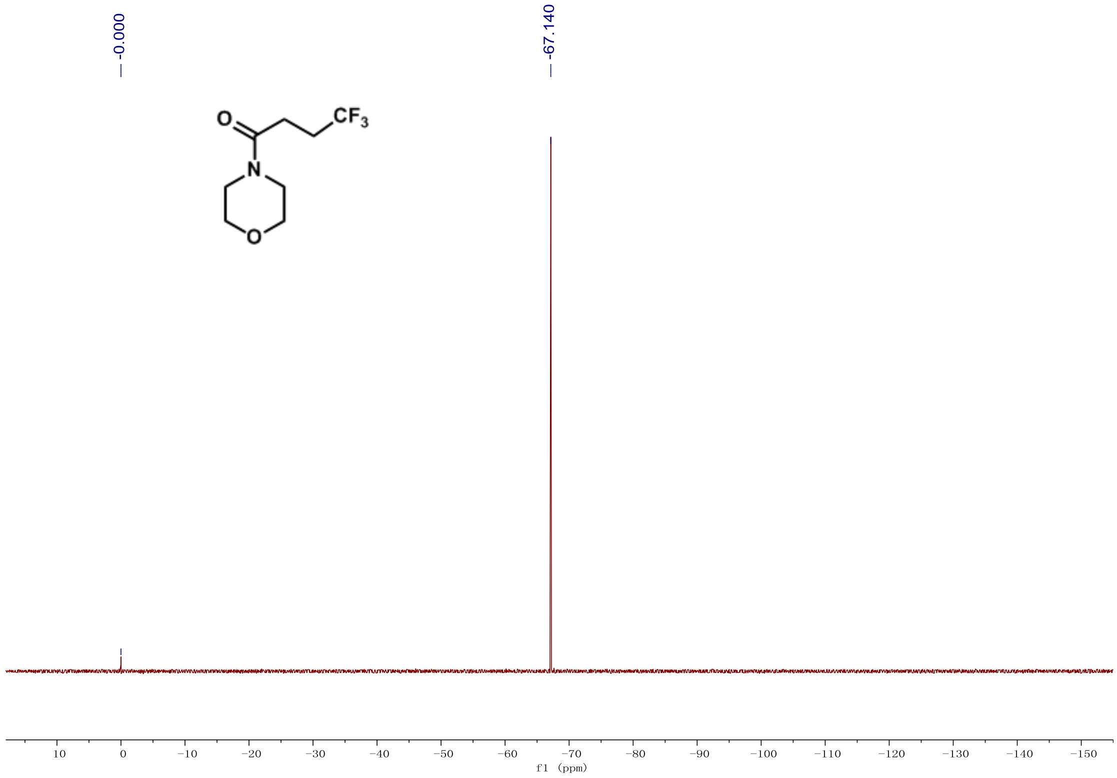

170.625
130.961
128.219
125.474
122.731
77.478
77.161
76.843
70.318
68.709
31.752
29.884
29.586
29.288
28.989
28.966
28.937
28.907
28.879
19.345
13.925
O
O
N
H
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-67.334
O
O
N
H
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

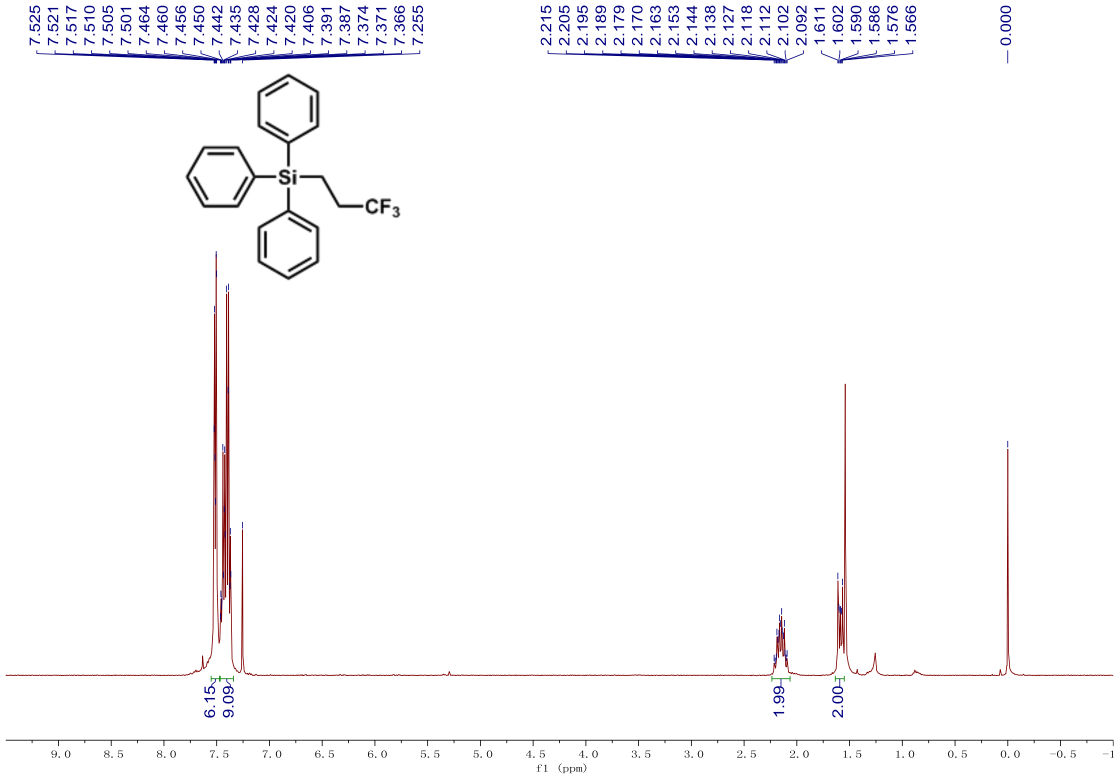
2-39

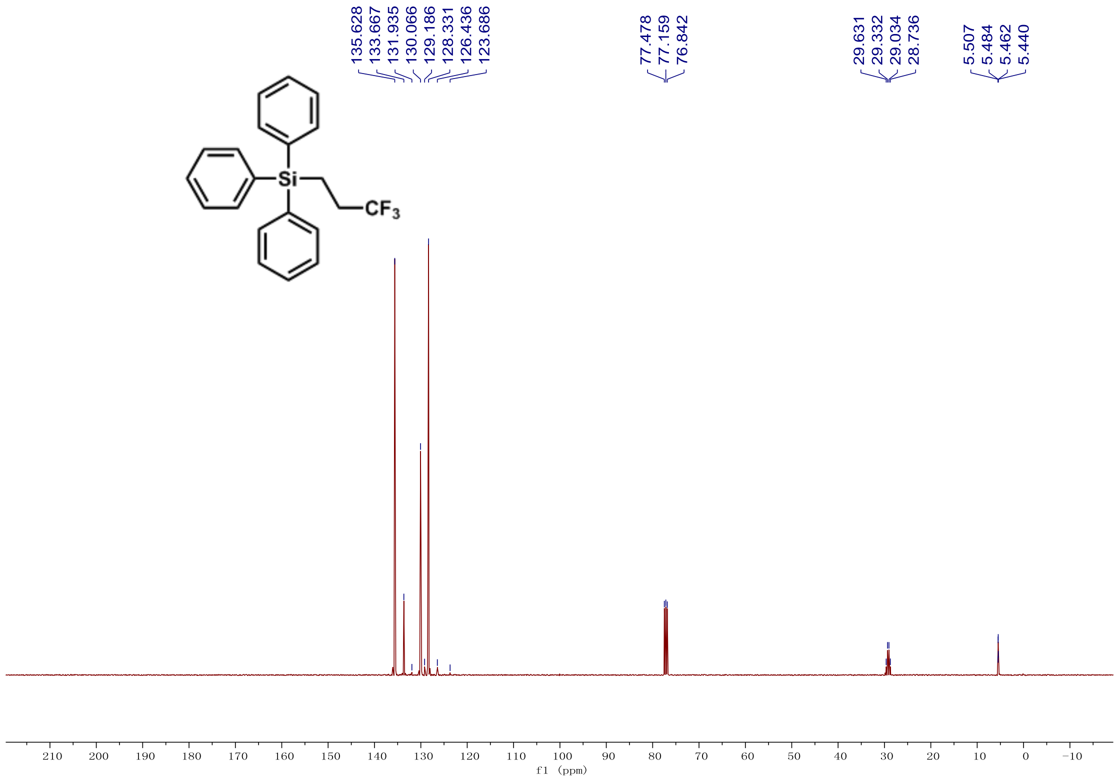

O
CF$_3$
N
O
7.263
3.706
3.695
3.687
3.682
3.673
3.642
3.629
3.619
3.481
3.469
3.457
2.590
2.583
2.574
2.571
2.561
2.551
2.545
2.538
2.534
2.524
2.520
2.515
2.511
2.505
2.500
2.495
2.487
2.479
2.472
2.459
2.455
-0.000
6.02
2.00
3.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

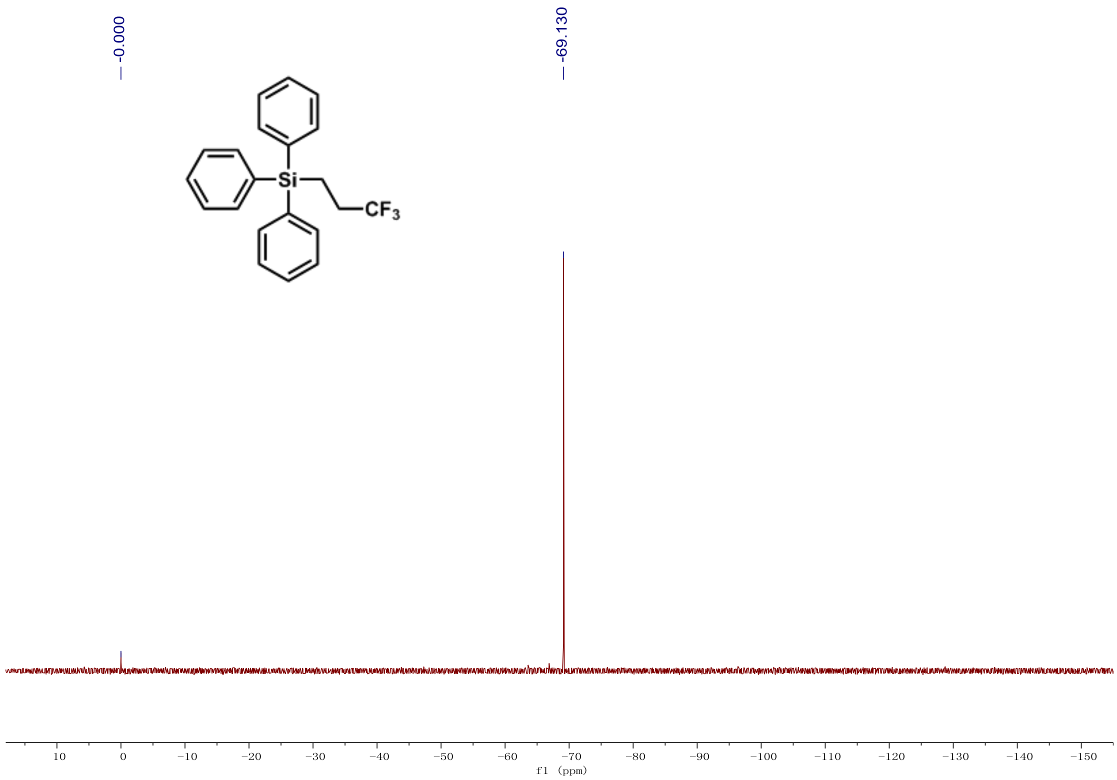

O
CF$_3$
N
O
168.368
131.156
128.414
125.673
122.931
77.479
77.160
76.841
66.744
66.412
45.689
42.156
29.882
29.590
29.298
29.006
25.738
25.704
25.674
25.641
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-0.000
-67.140
O
N
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

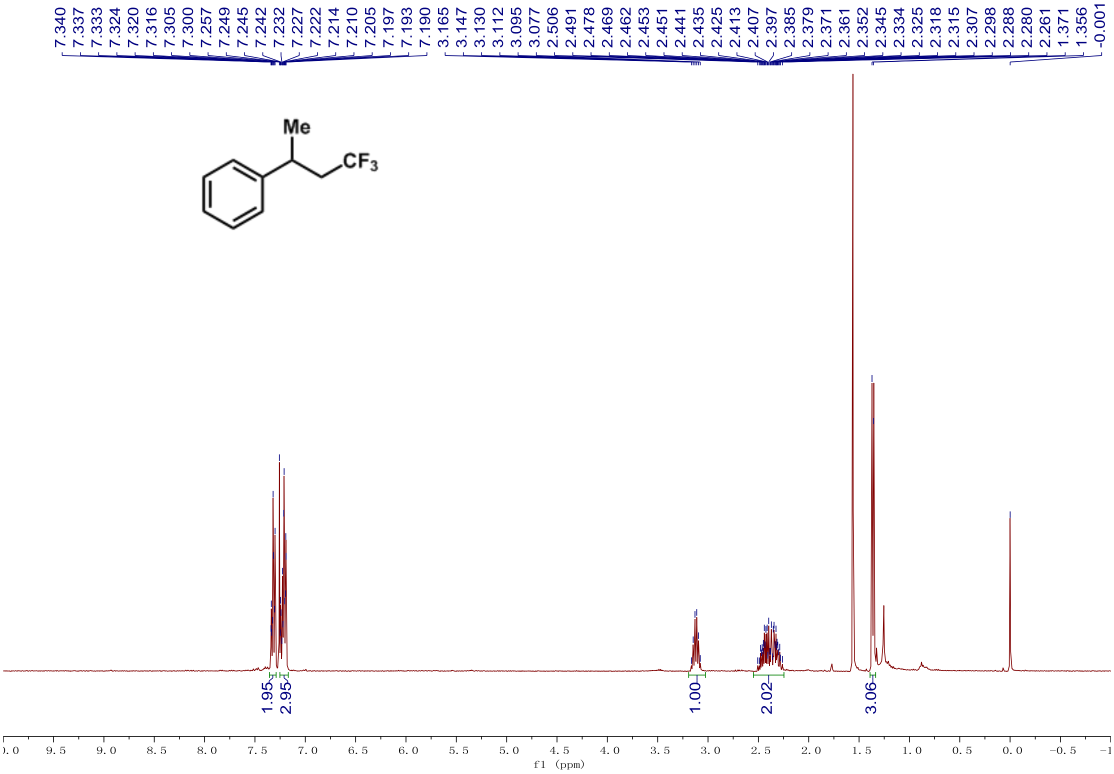
2-40

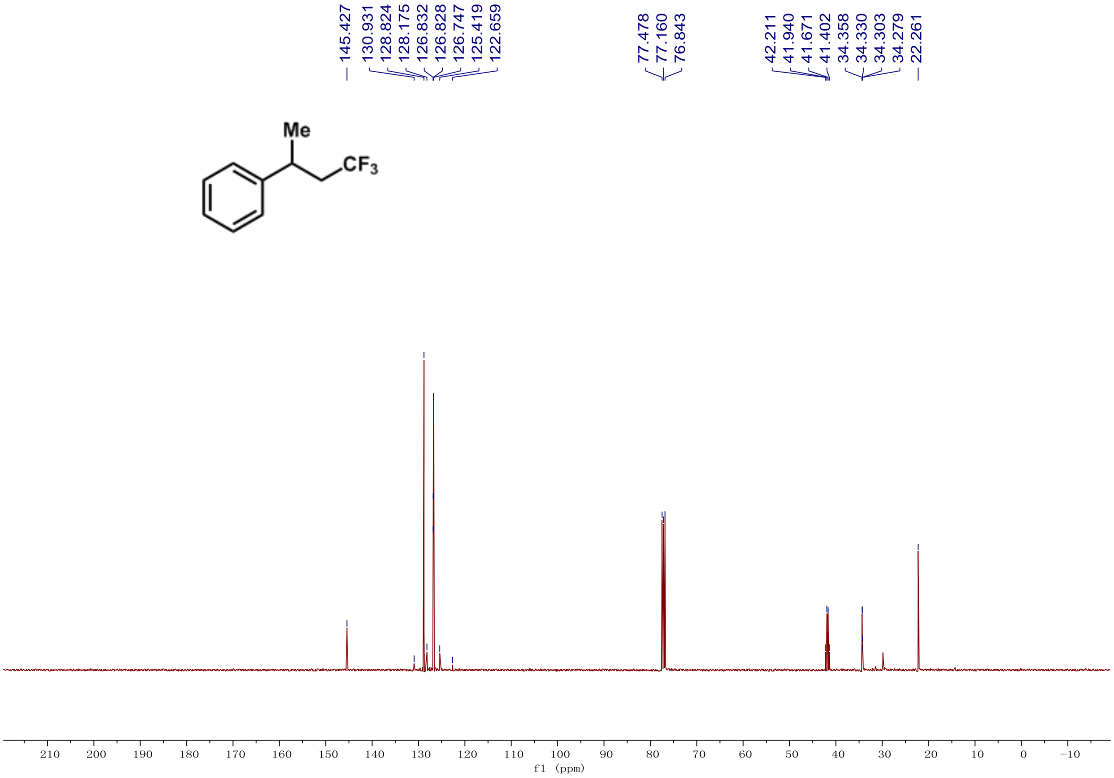

7.525
7.521
7.517
7.510
7.505
7.501
7.464
7.460
7.456
7.450
7.442
7.435
7.428
7.424
7.420
7.406
7.391
7.387
7.374
7.371
7.366
7.255
2.215
2.205
2.195
2.189
2.179
2.170
2.163
2.153
2.144
2.138
2.127
2.118
2.112
2.102
2.092
1.611
1.602
1.590
1.586
1.576
1.566
0.000
Si
CF3
6.15
9.09
1.99
2.00
9.0
8.5
8.0
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
−1
f1 (ppm)

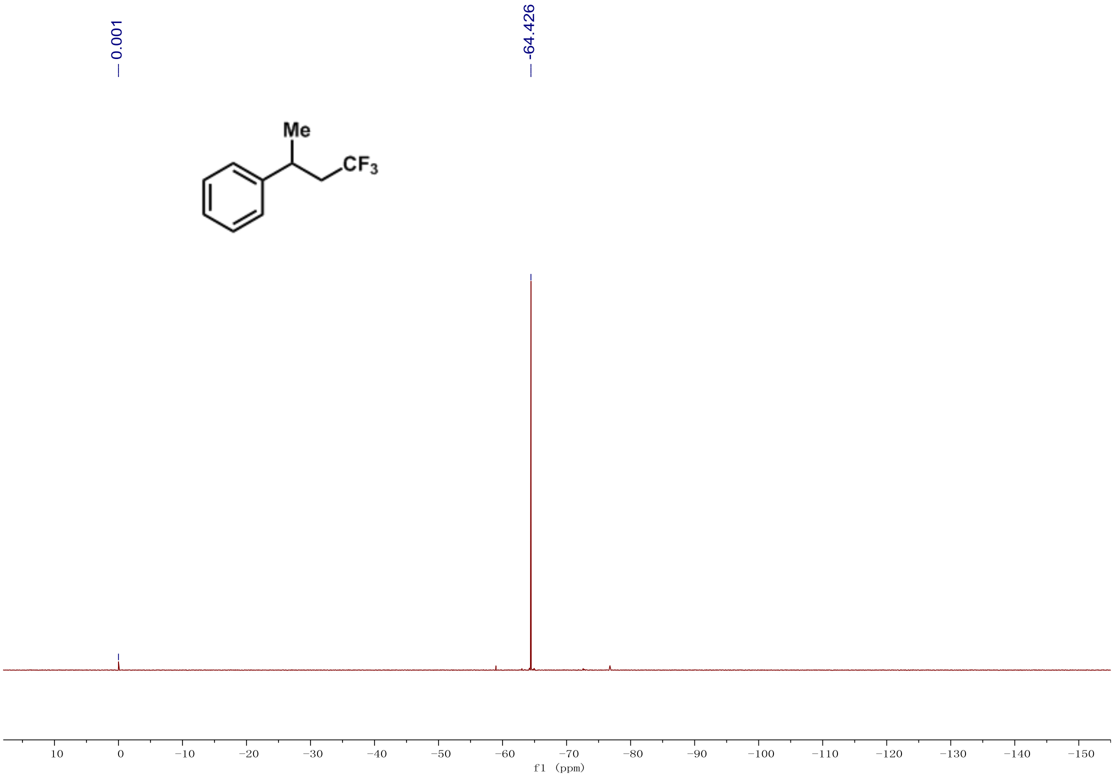

135.628
133.667
131.935
130.066
129.186
128.331
126.436
123.686
77.478
77.159
76.842
29.631
29.332
29.034
28.736
5.507
5.484
5.462
5.440
Si
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-0.000
-69.130
Si
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

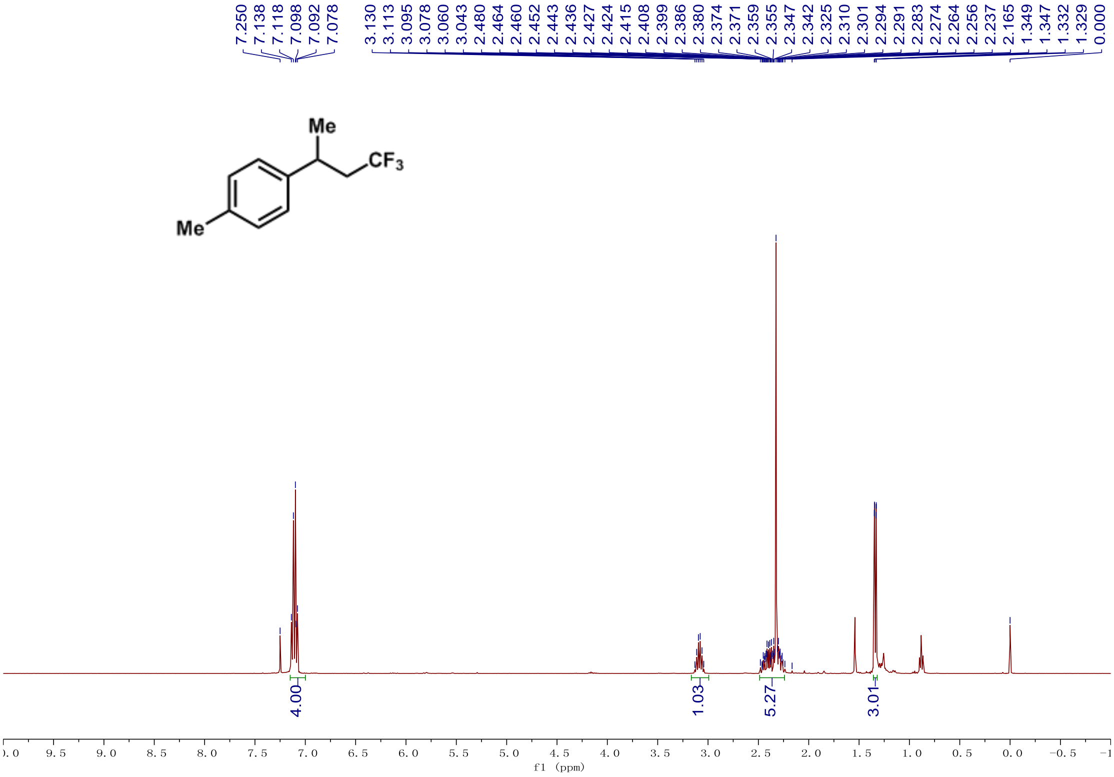
2-41

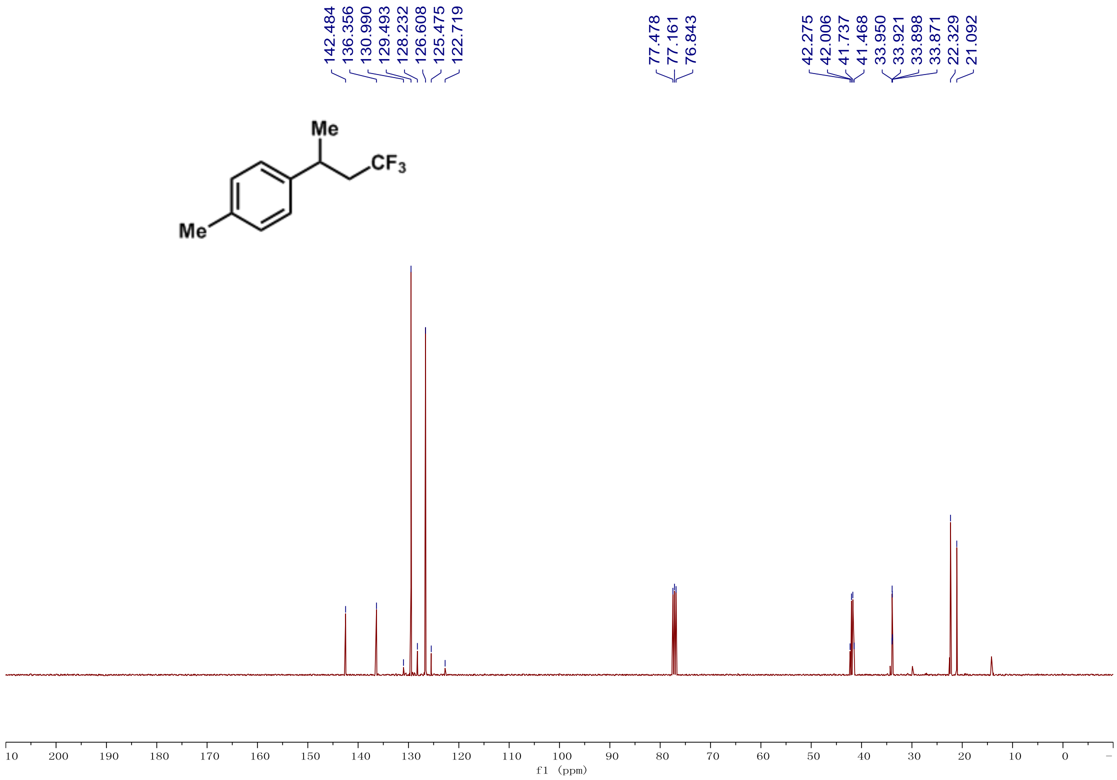

7.340
7.337
7.333
7.324
7.320
7.316
7.305
7.300
7.257
7.249
7.245
7.242
7.232
7.227
7.222
7.214
7.210
7.205
7.197
7.193
7.190
3.165
3.147
3.130
3.112
3.095
3.077
2.506
2.491
2.478
2.469
2.462
2.453
2.451
2.441
2.435
2.425
2.413
2.407
2.397
2.385
2.379
2.371
2.361
2.352
2.345
2.334
2.325
2.318
2.315
2.307
2.298
2.288
2.280
2.261
1.371
1.356
-0.001
Me
CF3
1.95
2.95
1.00
2.02
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

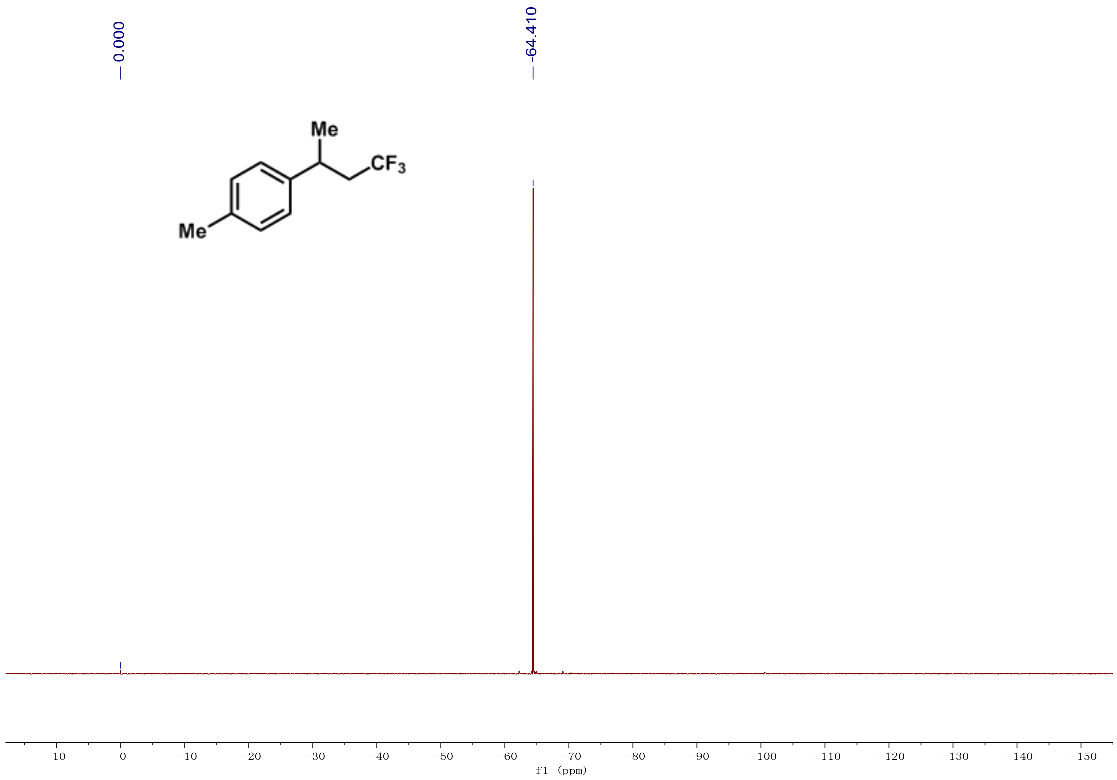

145.427
130.931
128.824
128.175
126.832
126.828
126.747
125.419
122.659
77.478
77.160
76.843
42.211
41.940
41.671
41.402
34.358
34.330
34.303
34.279
22.261
Me
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


0.001
-64.426
Me
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

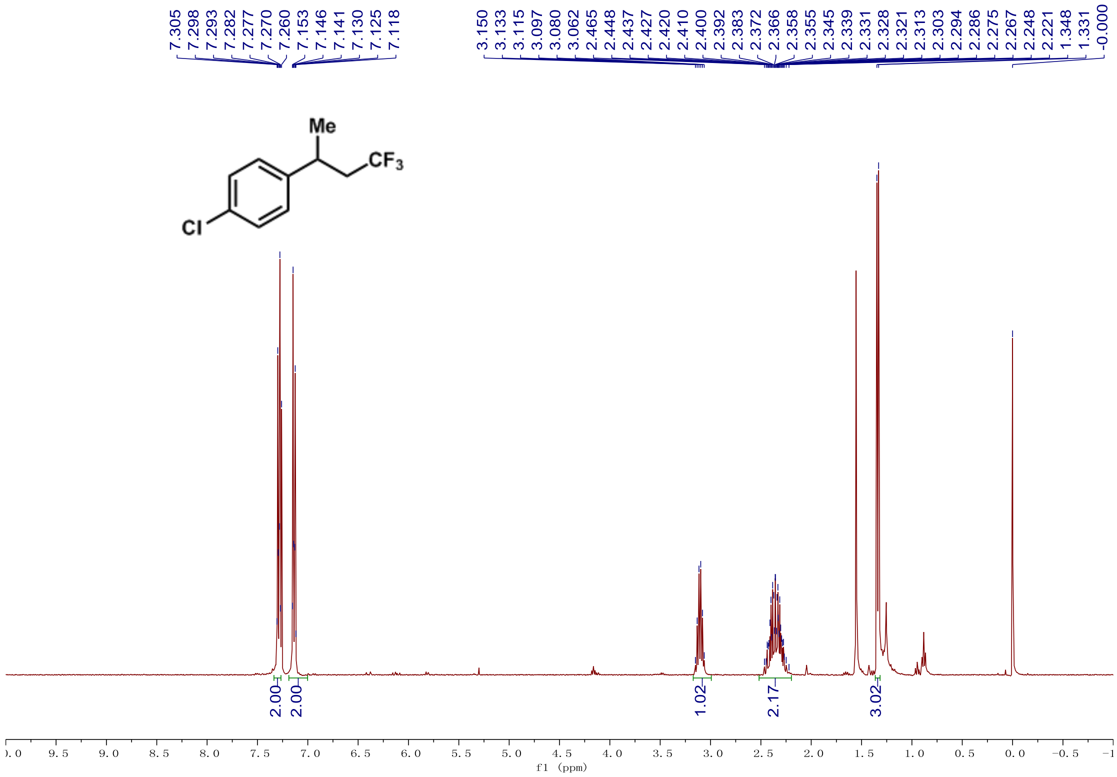
2-42


7.250
7.138
7.118
7.098
7.092
7.078
3.130
3.113
3.095
3.078
3.060
3.043
2.480
2.464
2.460
2.452
2.443
2.436
2.427
2.424
2.415
2.408
2.399
2.386
2.380
2.374
2.371
2.359
2.355
2.347
2.342
2.325
2.310
2.301
2.294
2.291
2.283
2.274
2.264
2.256
2.237
2.165
1.349
1.347
1.332
1.329
0.000
Me
CF3
Me
4.00
1.03
5.27
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

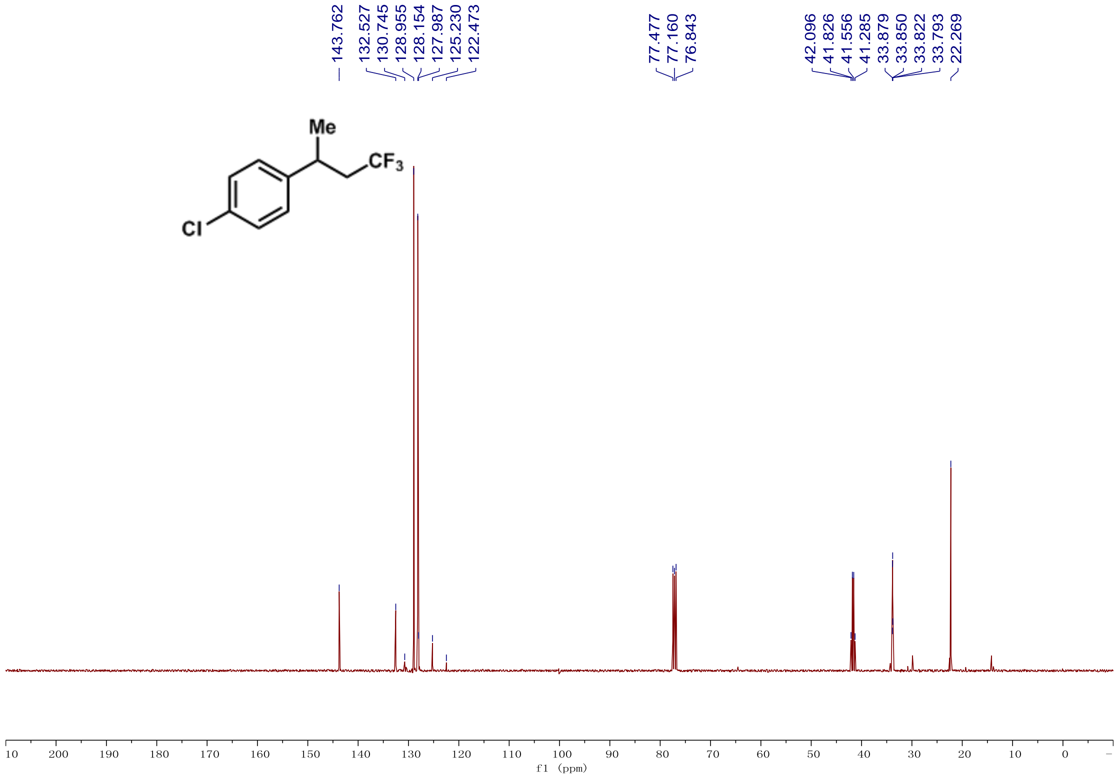

142.484
136.356
130.990
129.493
128.232
126.608
125.475
122.719
77.478
77.161
76.843
42.275
42.006
41.737
41.468
33.950
33.921
33.898
33.871
22.329
21.092
Me
CF$_3$
Me
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–
f1 (ppm)


0.000
-64.410
Me
CF$_3$
Me
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

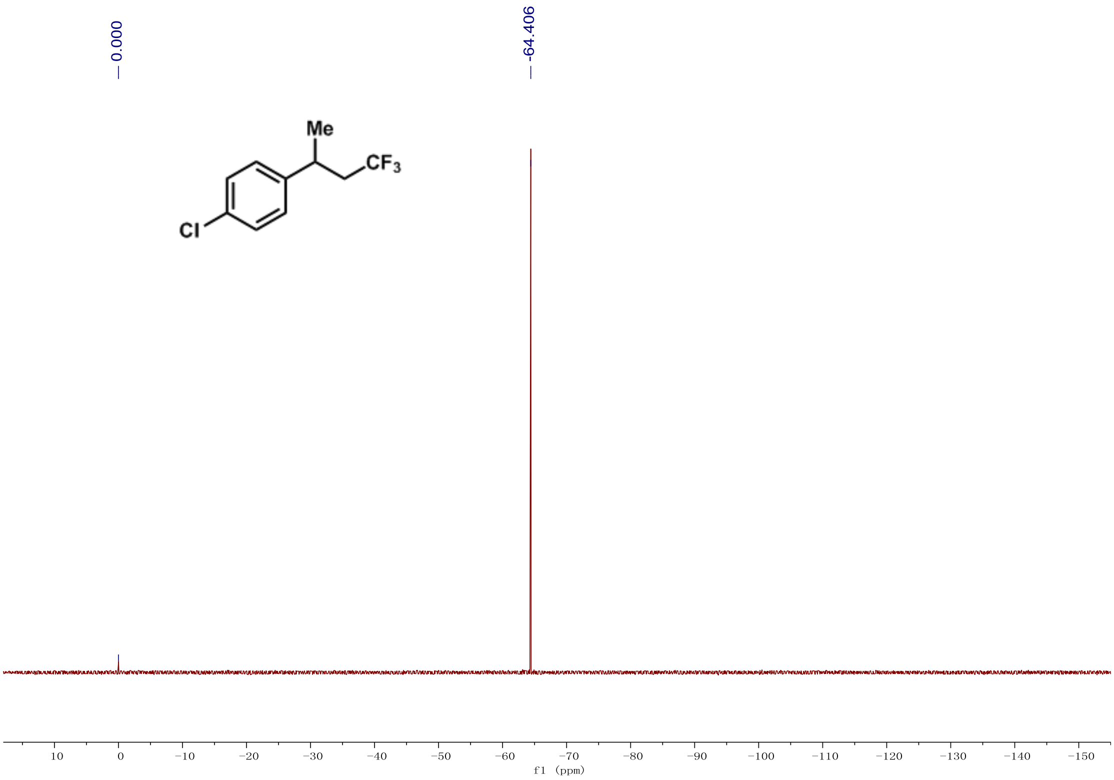
2-43



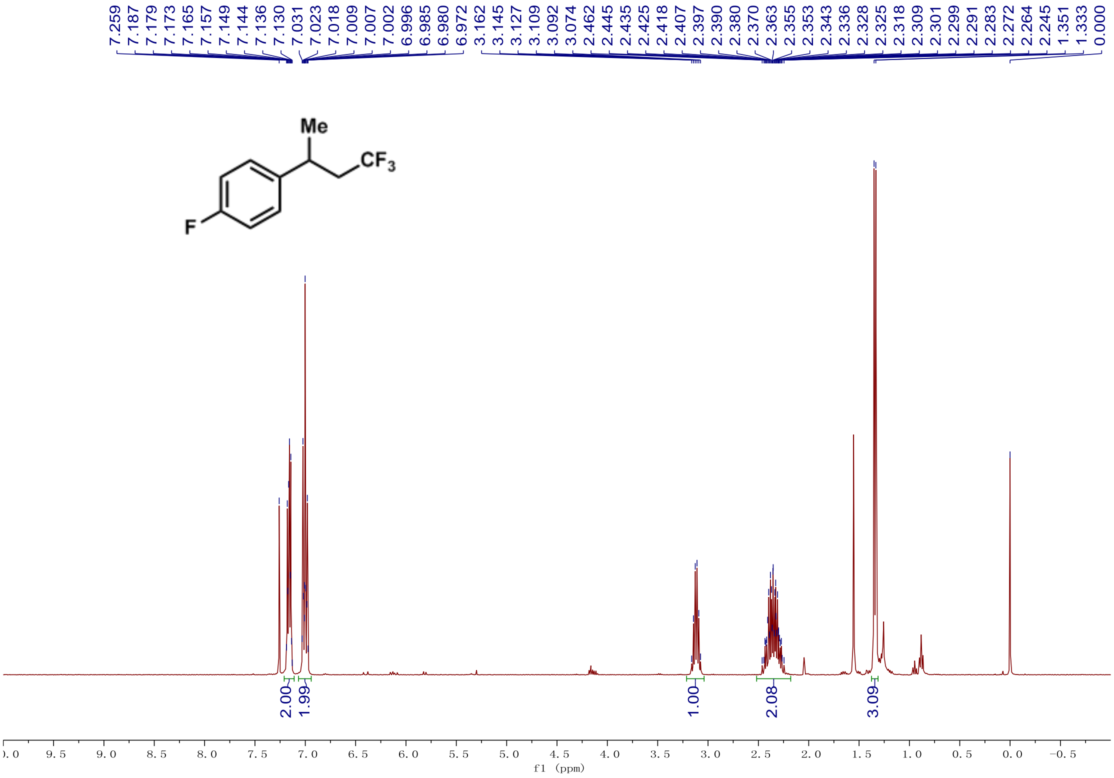
7.305
7.298
7.293
7.282
7.277
7.270
7.260
7.153
7.146
7.141
7.130
7.125
7.118
3.150
3.133
3.115
3.097
3.080
3.062
2.465
2.448
2.437
2.427
2.420
2.410
2.400
2.392
2.383
2.372
2.366
2.358
2.355
2.345
2.339
2.331
2.328
2.321
2.313
2.303
2.294
2.286
2.275
2.267
2.248
2.221
1.348
1.331
-0.000
Me
CF3
Cl
2.00
2.00
1.02
2.17
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

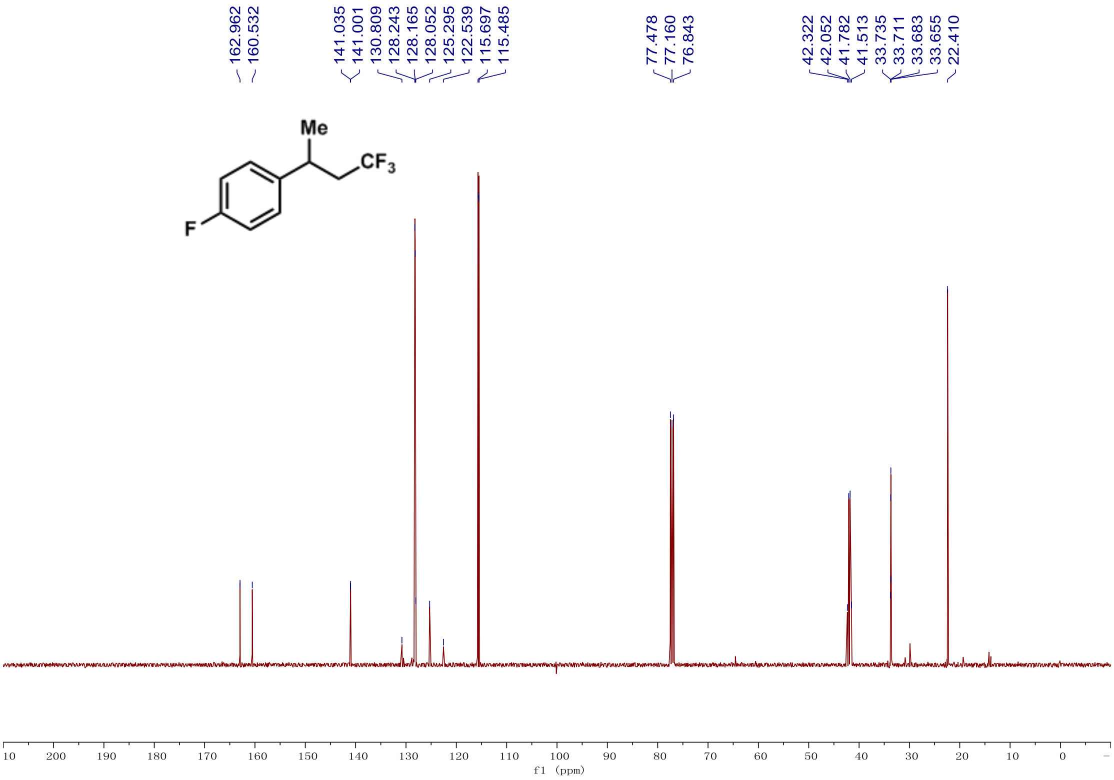


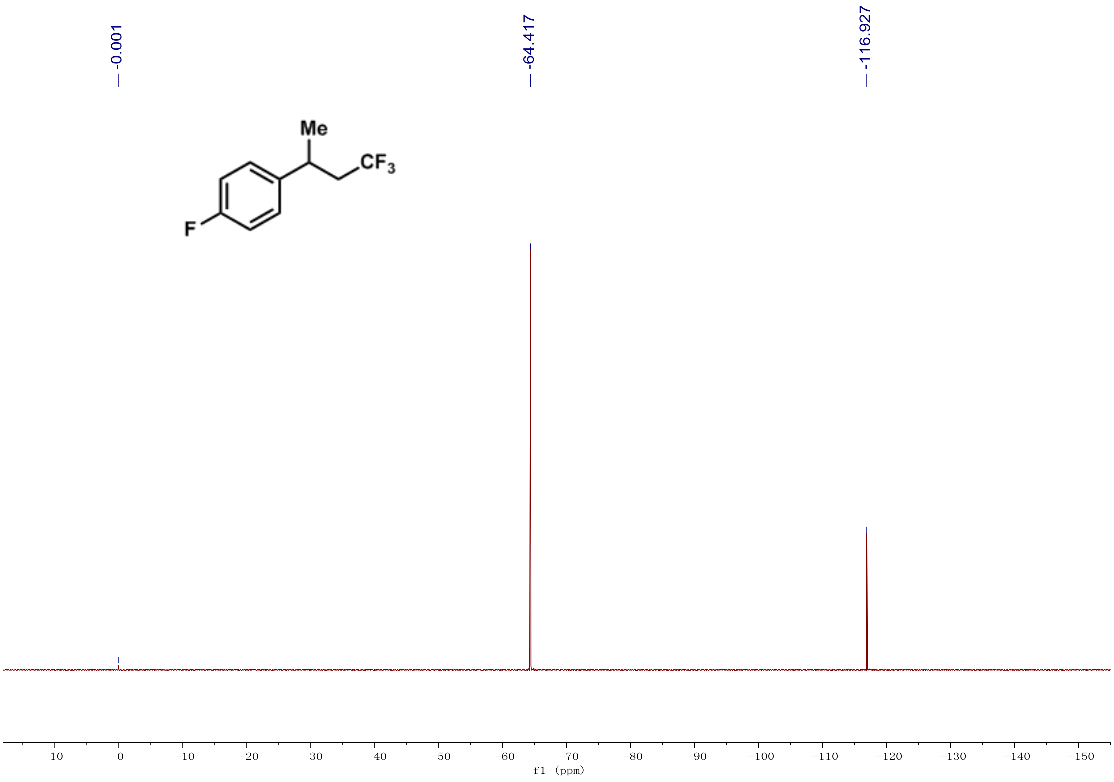
143.762
132.527
130.745
128.955
128.154
127.987
125.230
122.473
77.477
77.160
76.843
42.096
41.826
41.556
41.285
33.879
33.850
33.822
33.793
22.269
Me
CF3
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-64.406
Me
CF3
Cl
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

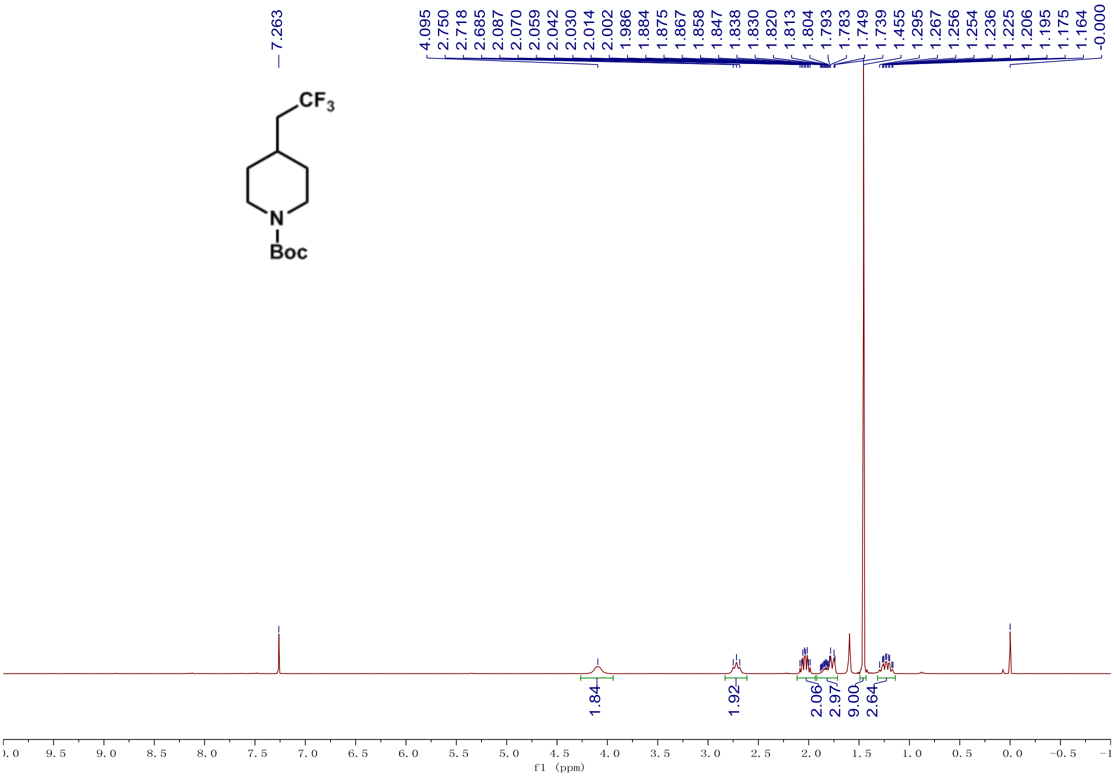
2-44


7.259
7.187
7.179
7.173
7.165
7.157
7.149
7.144
7.136
7.130
7.031
7.023
7.018
7.009
7.007
7.002
6.996
6.985
6.980
6.972
3.162
3.145
3.127
3.109
3.092
3.074
2.462
2.445
2.435
2.425
2.418
2.407
2.397
2.390
2.380
2.370
2.363
2.355
2.353
2.343
2.336
2.328
2.325
2.318
2.309
2.301
2.299
2.291
2.283
2.272
2.264
2.245
1.351
1.333
0.000
Me
CF3
F
2.00
1.99
1.00
2.08
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

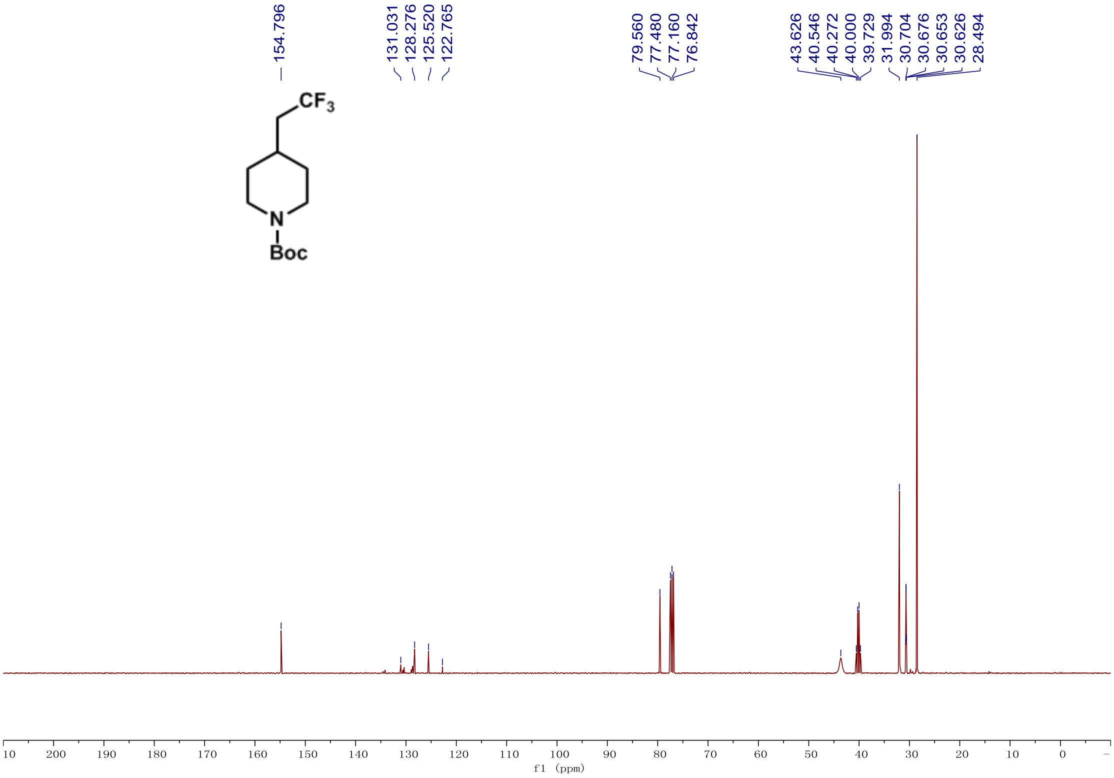

162.962
160.532
141.035
141.001
130.809
128.243
128.165
128.052
125.295
122.539
115.697
115.485
77.478
77.160
76.843
42.322
42.052
41.782
41.513
33.735
33.711
33.683
33.655
22.410
Me
CF3
F
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.001
-64.417
-116.927
Me
CF3
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

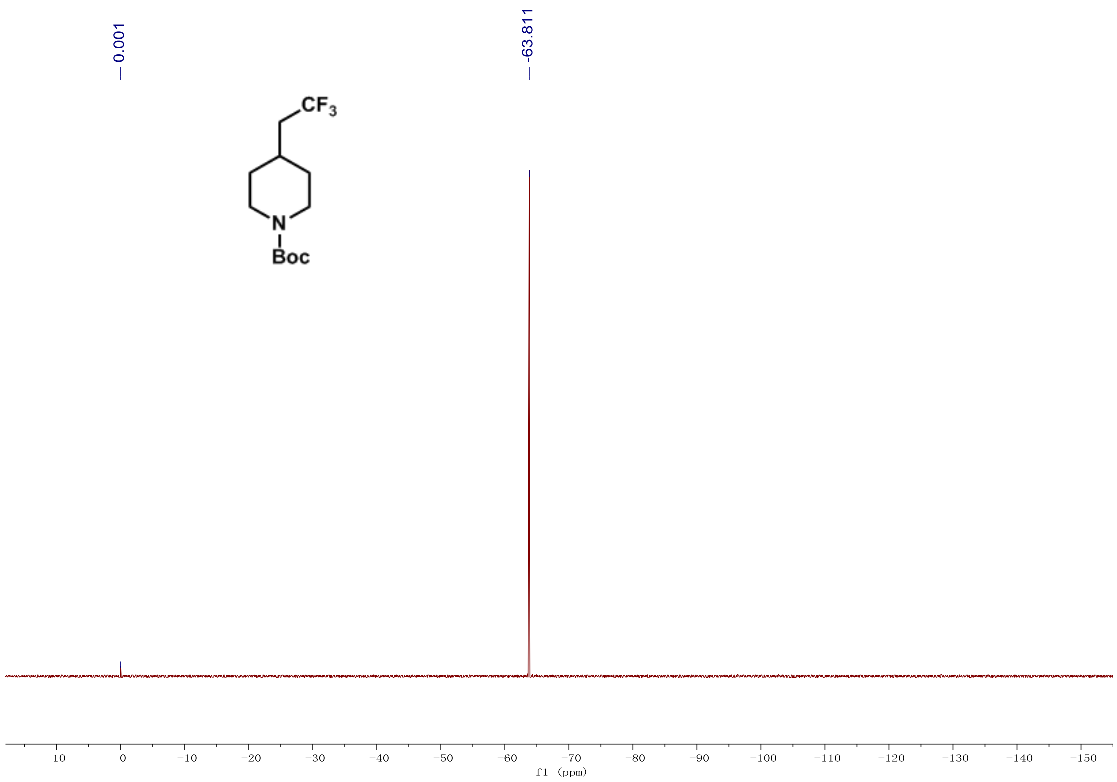
2-45



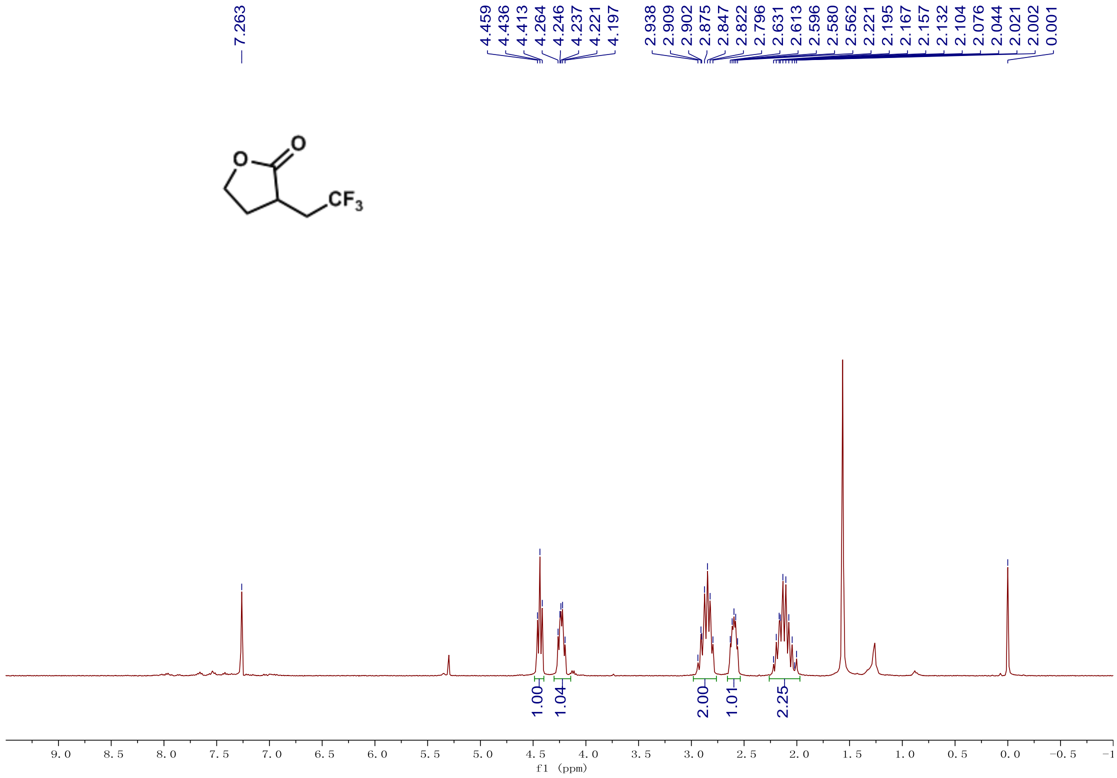
7.263
4.095
2.750
2.718
2.685
2.087
2.070
2.059
2.042
2.030
2.014
2.002
1.986
1.884
1.875
1.867
1.858
1.847
1.838
1.830
1.820
1.813
1.804
1.793
1.783
1.749
1.739
1.455
1.295
1.267
1.256
1.254
1.236
1.225
1.206
1.195
1.175
1.164
-0.000
CF3
N
Boc
1.84
1.92
2.06
2.97
9.00
2.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

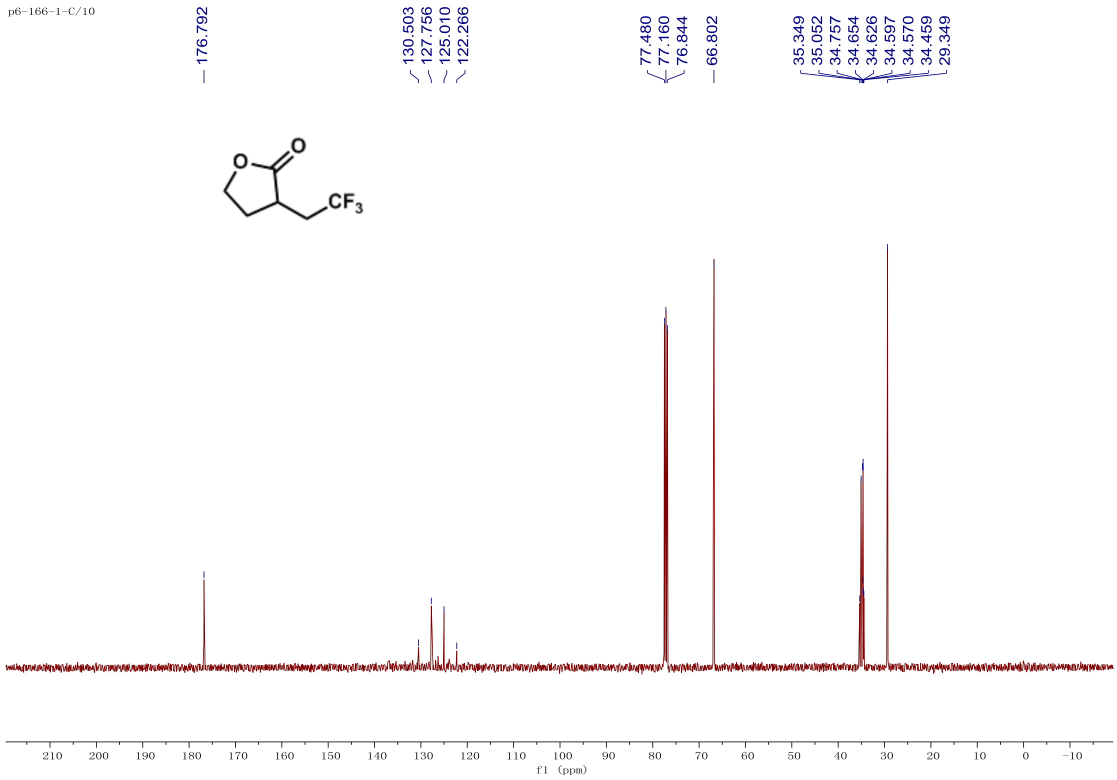


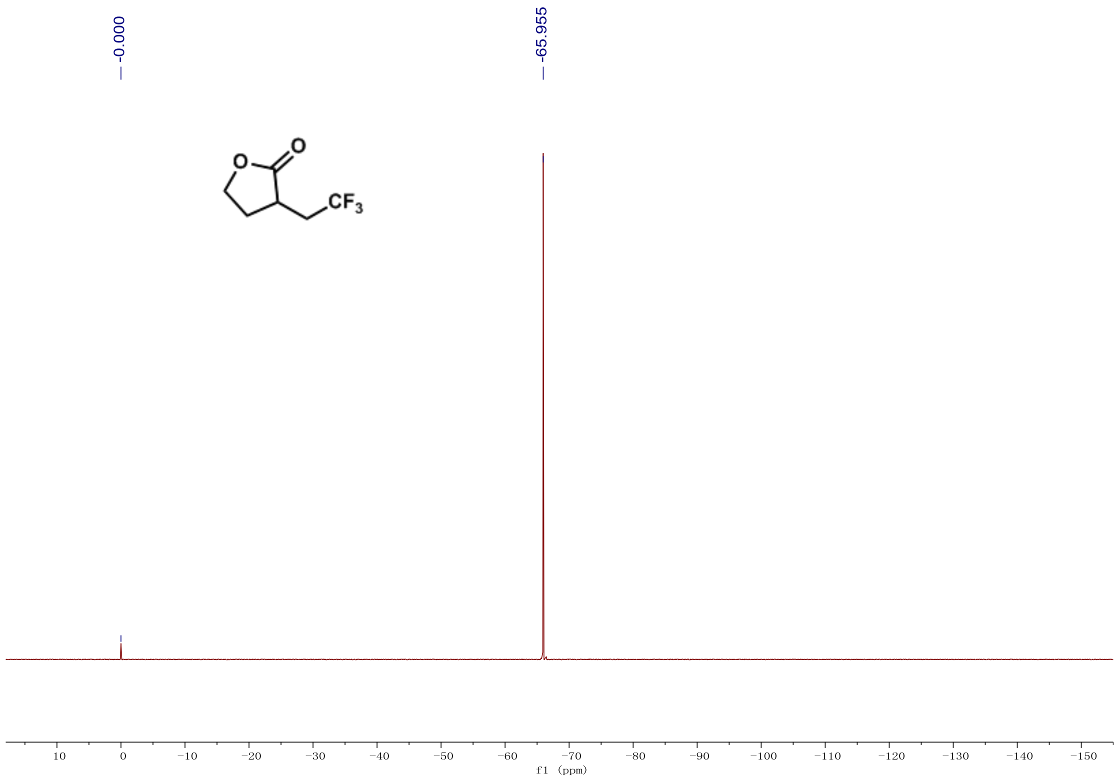
154.796
131.031
128.276
125.520
122.765
79.560
77.480
77.160
76.842
43.626
40.546
40.272
40.000
39.729
31.994
30.704
30.676
30.653
30.626
28.494
CF3
N
Boc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-63.811
CF3
N
Boc
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

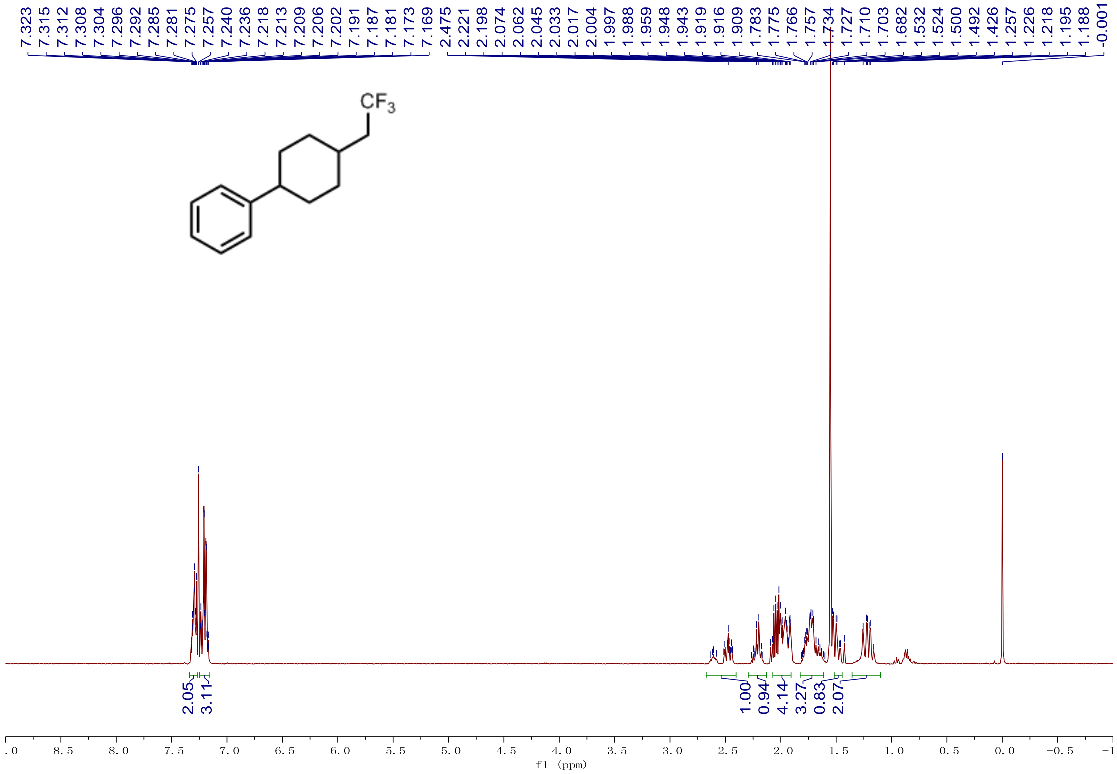
2-46

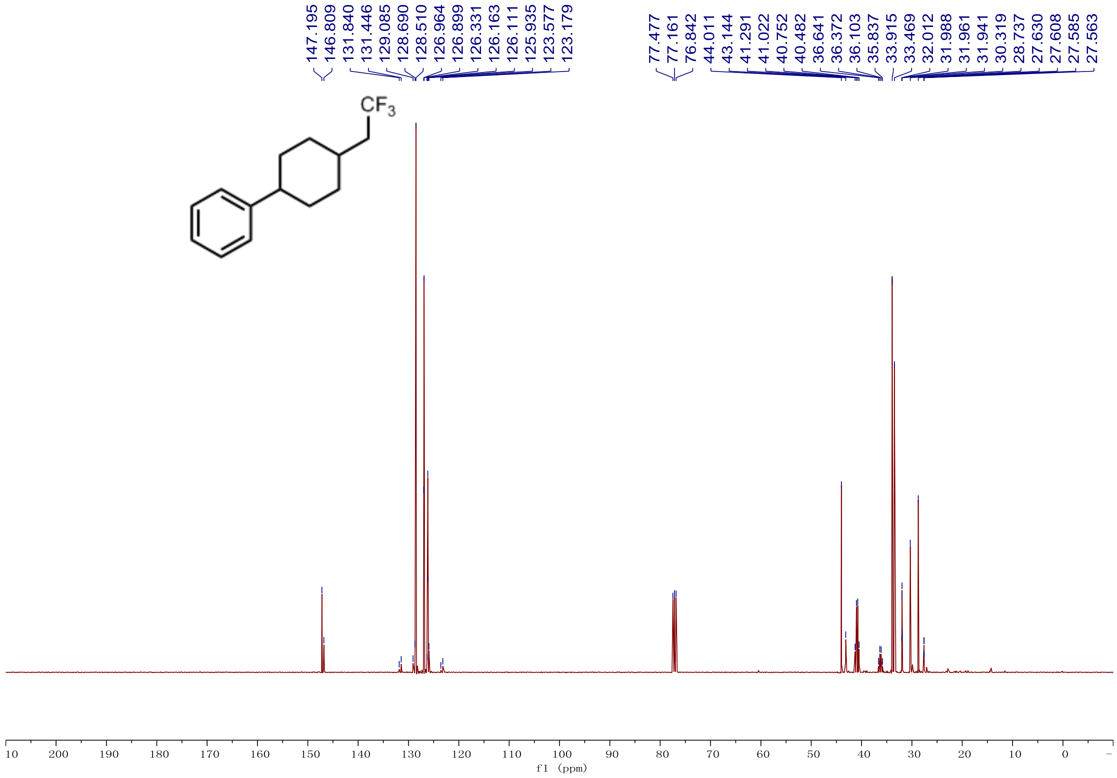

7.263
4.459
4.436
4.413
4.264
4.246
4.237
4.221
4.197
2.938
2.909
2.902
2.875
2.847
2.822
2.796
2.631
2.613
2.596
2.580
2.562
2.221
2.195
2.167
2.157
2.132
2.104
2.076
2.044
2.021
2.002
0.001
O
O
CF3
1.00
1.04
2.00
1.01
2.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

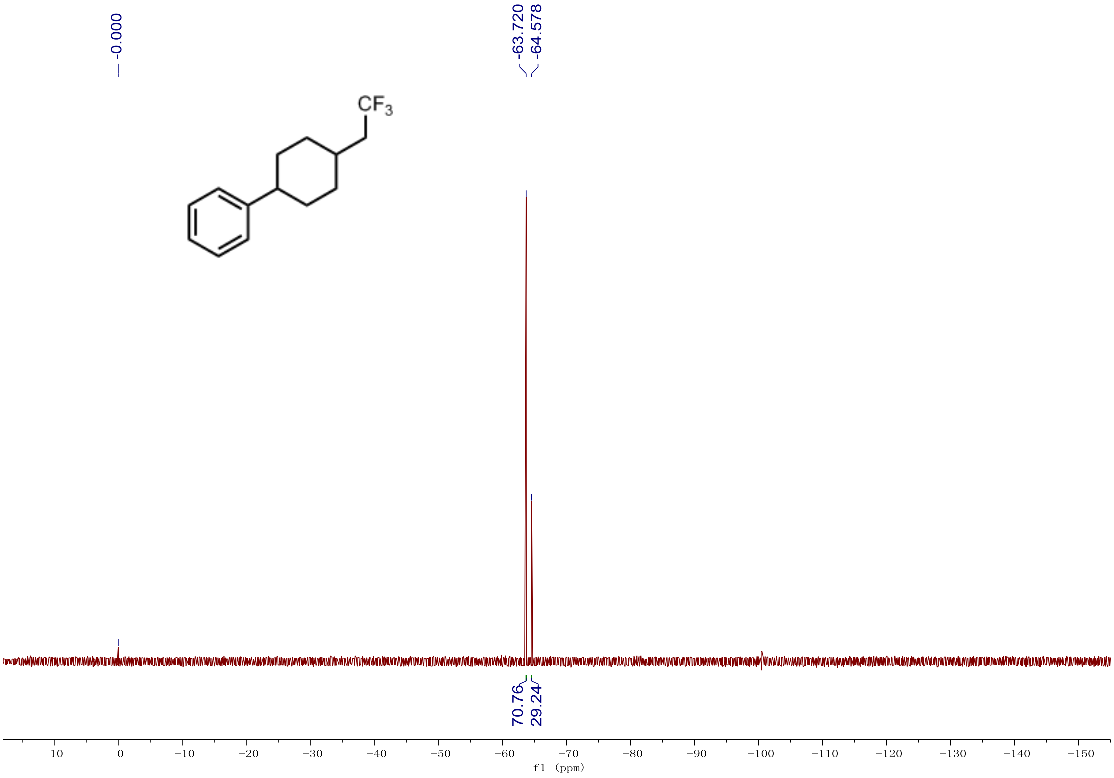

p6-166-1-C/10
176.792
130.503
127.756
125.010
122.266
77.480
77.160
76.844
66.802
35.349
35.052
34.757
34.654
34.626
34.597
34.570
34.459
29.349
O
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-0.000
-65.955
O
O
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

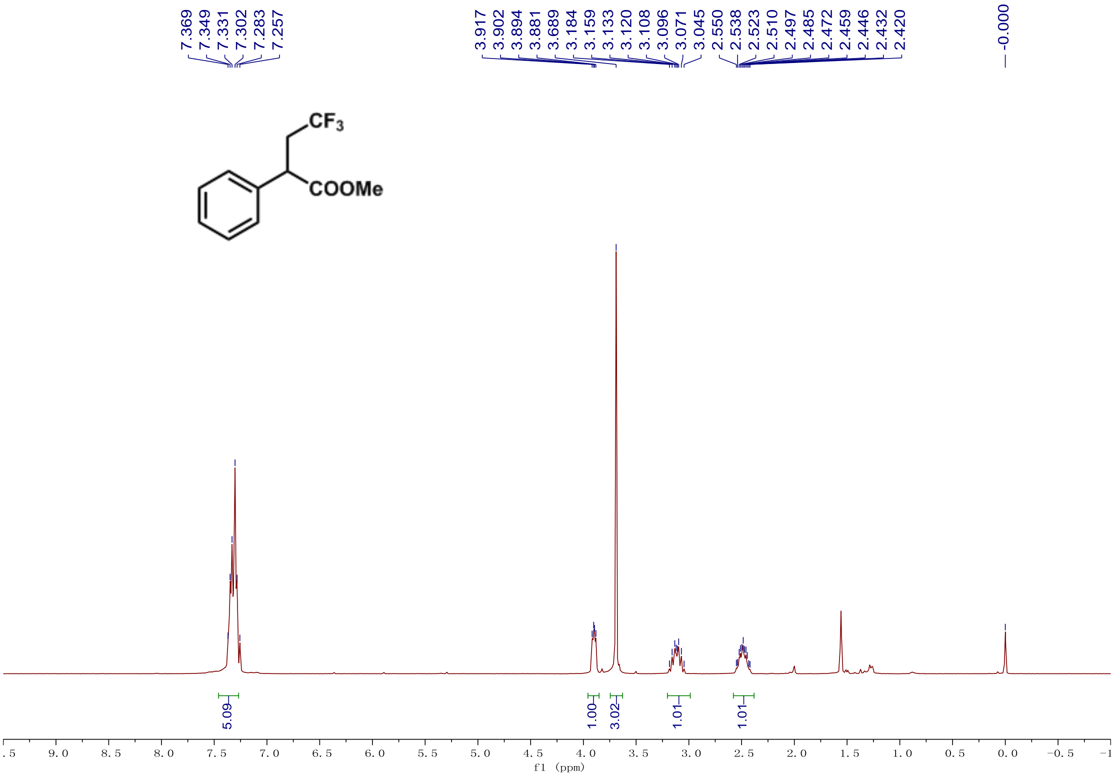
2-47

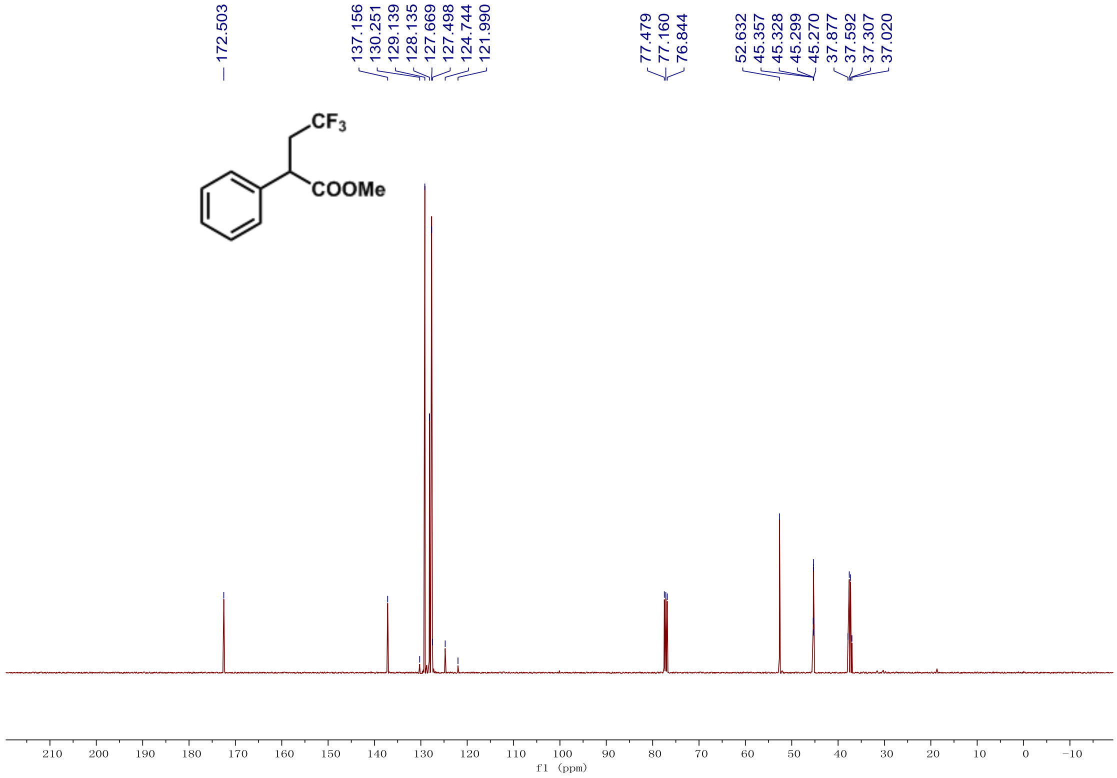

7.323
7.315
7.312
7.308
7.304
7.296
7.292
7.285
7.281
7.275
7.257
7.240
7.236
7.218
7.213
7.209
7.206
7.202
7.191
7.187
7.181
7.173
7.169
2.475
2.221
2.198
2.074
2.062
2.045
2.033
2.017
2.004
1.997
1.988
1.959
1.948
1.943
1.919
1.916
1.909
1.783
1.775
1.766
1.757
1.734
1.727
1.710
1.703
1.682
1.532
1.524
1.500
1.492
1.426
1.257
1.226
1.218
1.195
1.188
-0.001
CF3
2.05
3.11
1.00
0.94
4.14
3.27
0.83
2.07
.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
-1
f1 (ppm)

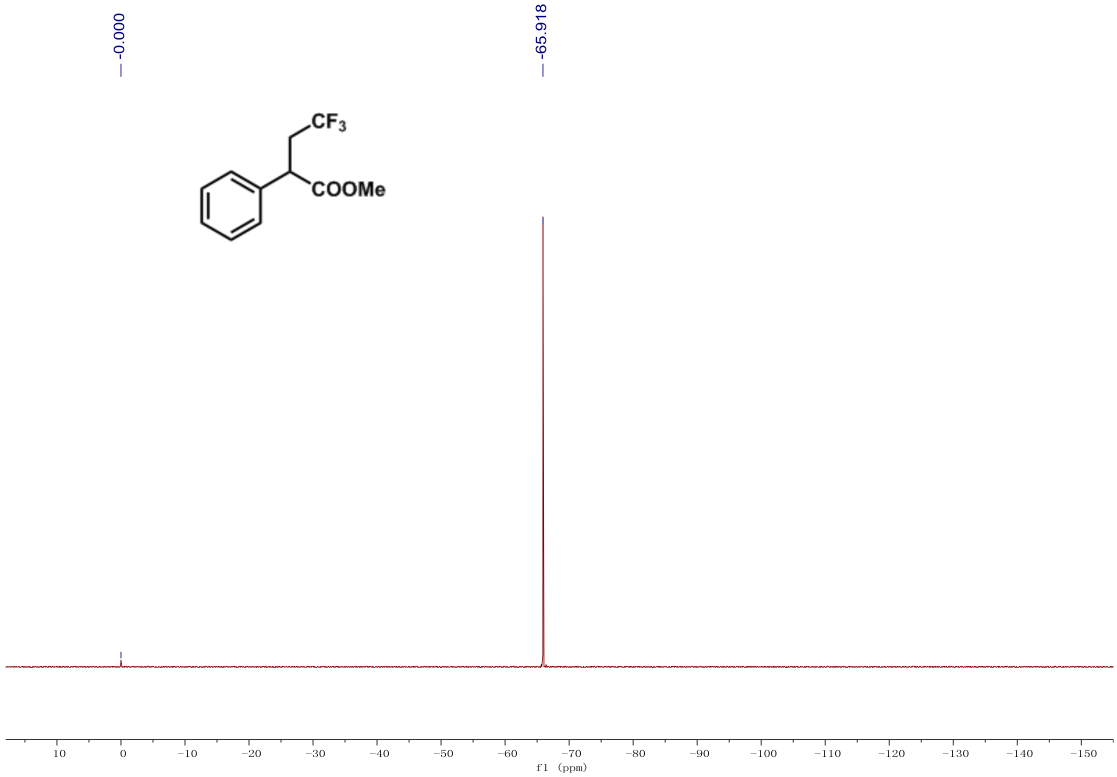

147.195
146.809
131.840
131.446
129.085
128.690
128.510
126.964
126.899
126.331
126.163
126.111
125.935
123.577
123.179
77.477
77.161
76.842
44.011
43.144
41.291
41.022
40.752
40.482
36.641
36.372
36.103
35.837
33.915
33.469
32.012
31.988
31.961
31.941
30.319
28.737
27.630
27.608
27.585
27.563
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)


-0.000
-63.720
-64.578
CF3
70.76
29.24
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

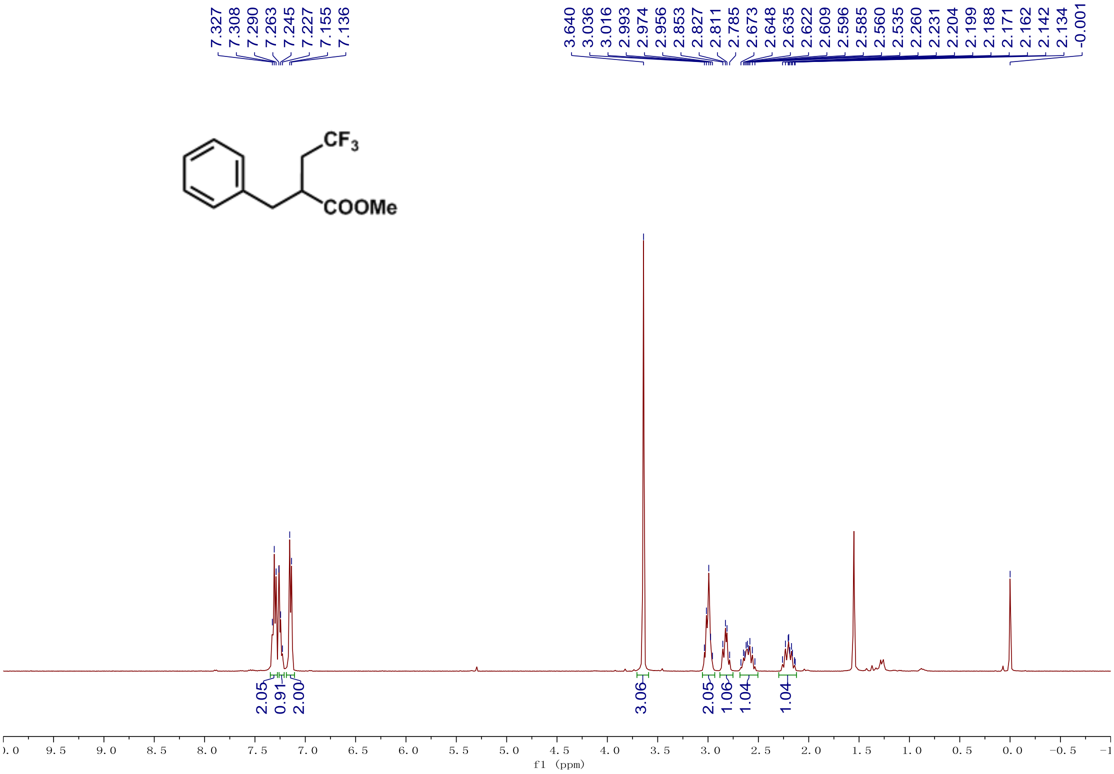
2-48

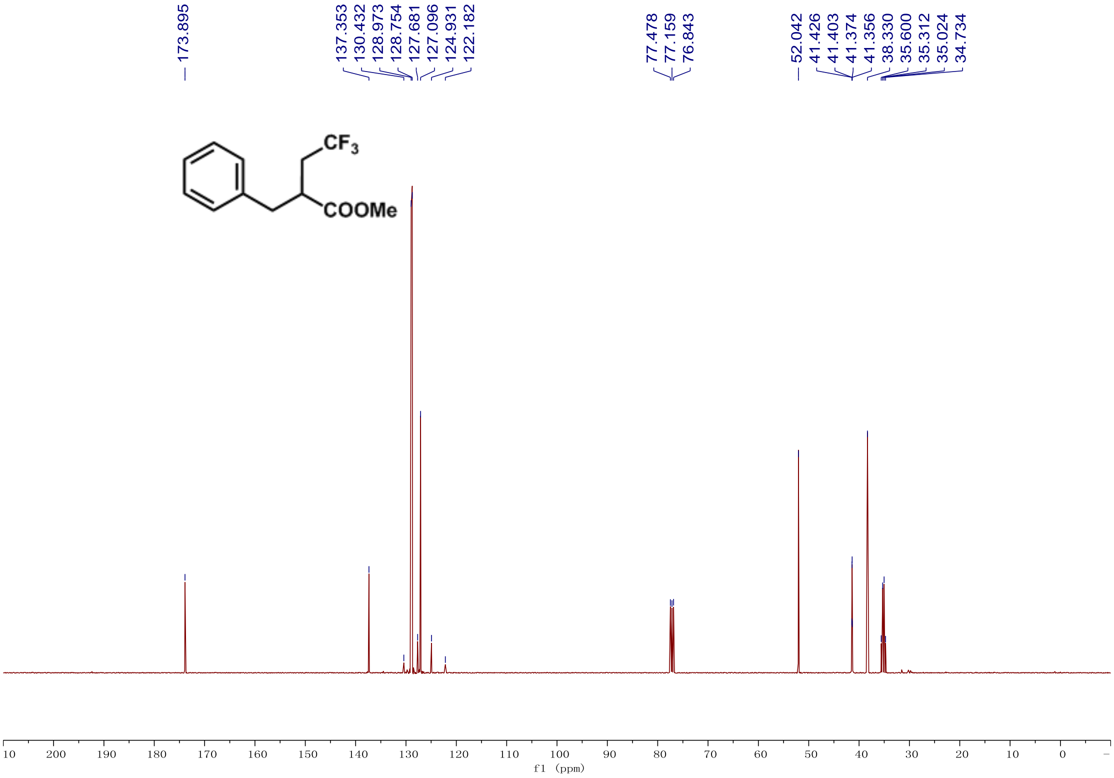

7.369
7.349
7.331
7.302
7.283
7.257
3.917
3.902
3.894
3.881
3.689
3.184
3.159
3.133
3.120
3.108
3.096
3.071
3.045
2.550
2.538
2.523
2.510
2.497
2.485
2.472
2.459
2.446
2.432
2.420
-0.000
CF3
COOMe
5.09
1.00
3.02
1.01
1.01
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

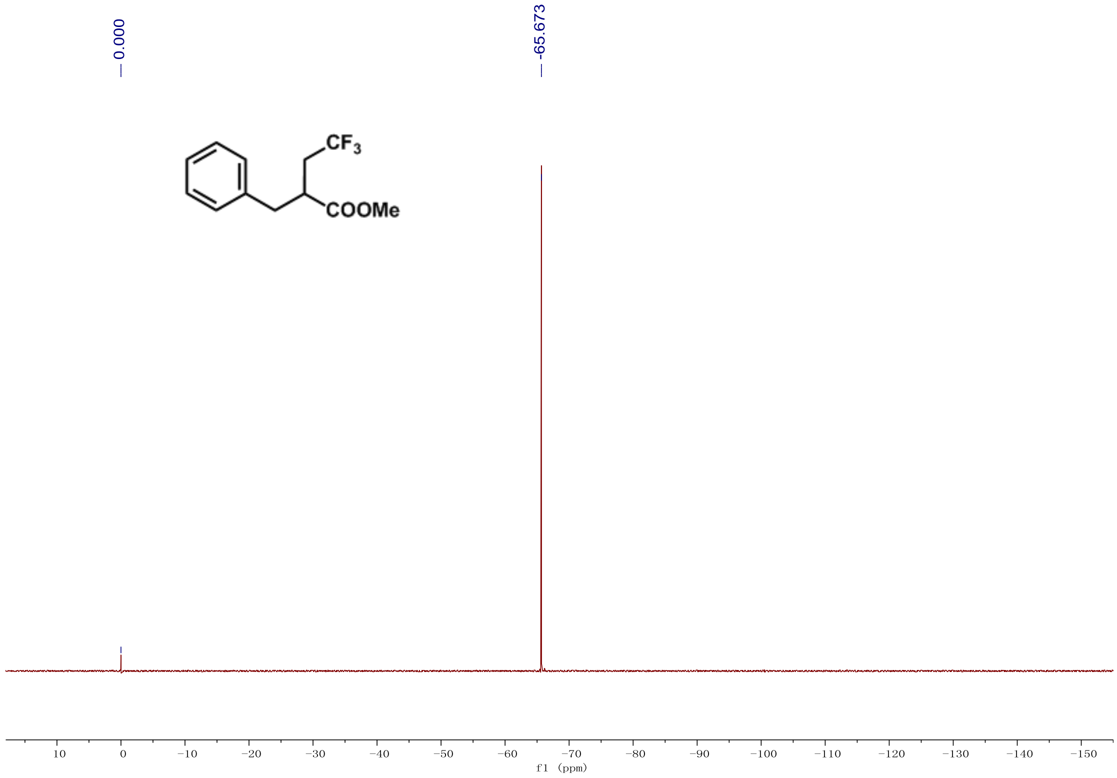

172.503
137.156
130.251
129.139
128.135
127.669
127.498
124.744
121.990
77.479
77.160
76.844
52.632
45.357
45.328
45.299
45.270
37.877
37.592
37.307
37.020
CF3
COOMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-0.000
-65.918
CF3
COOMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

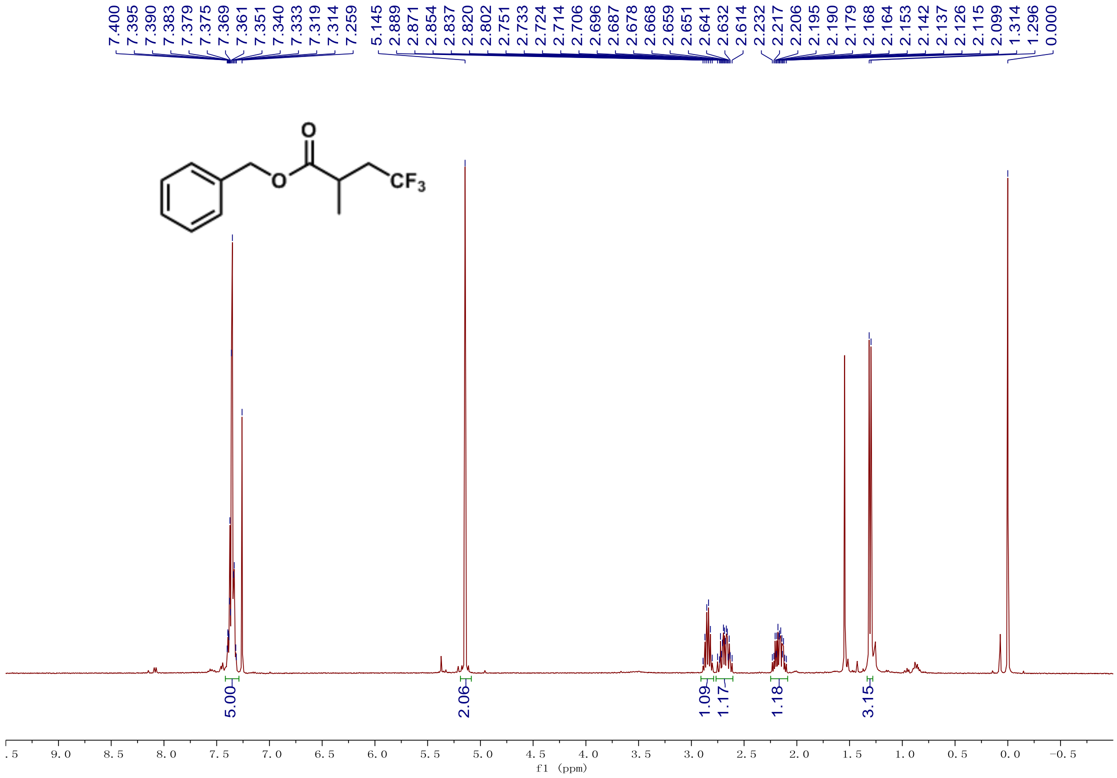
2-49

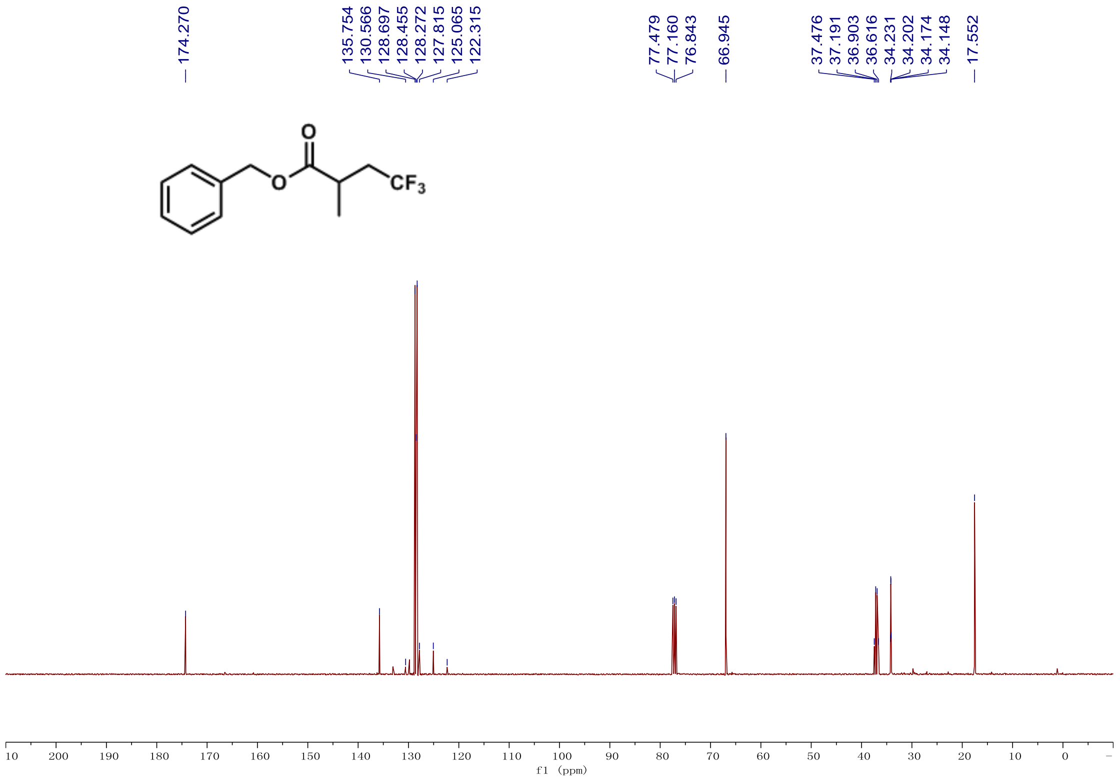

7.327
7.308
7.290
7.263
7.245
7.227
7.155
7.136
3.640
3.036
3.016
2.993
2.974
2.956
2.853
2.827
2.811
2.785
2.673
2.648
2.635
2.622
2.609
2.596
2.585
2.560
2.535
2.260
2.231
2.204
2.199
2.188
2.171
2.162
2.142
2.134
-0.001
CF3
COOMe
2.05
0.91
2.00
3.06
2.05
1.06
1.04
1.04
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

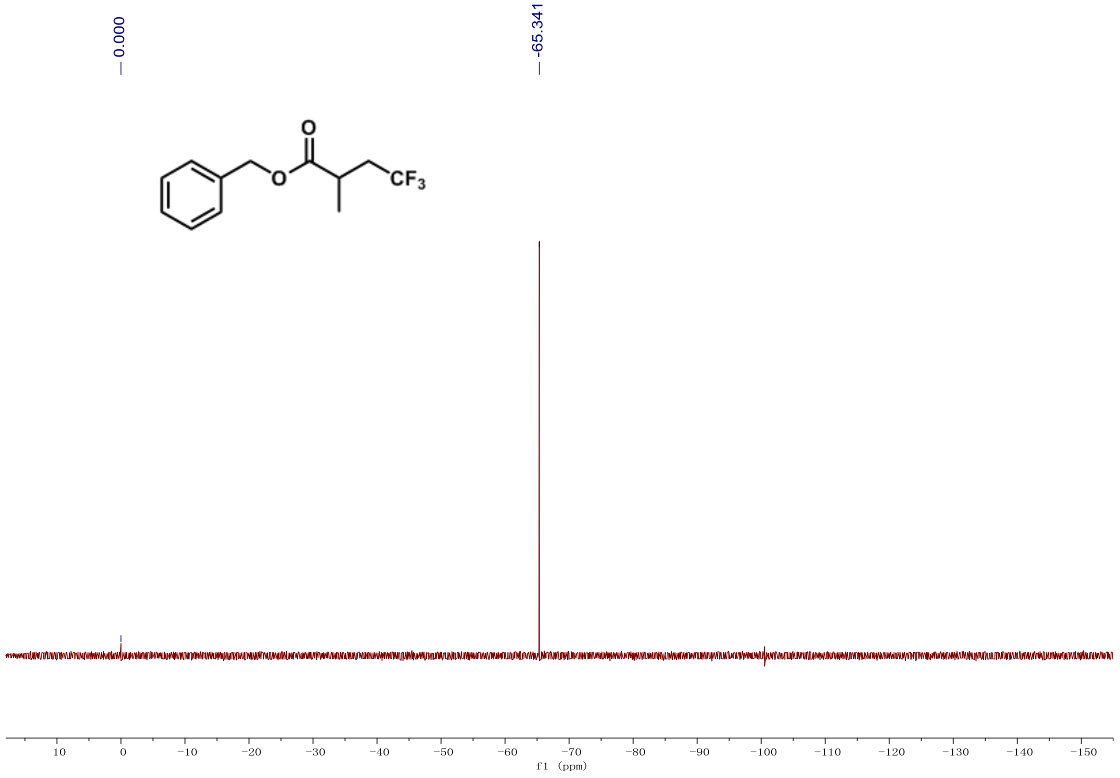

173.895
137.353
130.432
128.973
128.754
127.681
127.096
124.931
122.182
77.478
77.159
76.843
52.042
41.426
41.403
41.374
41.356
38.330
35.600
35.312
35.024
34.734
CF3
COOMe
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-65.673
CF3
COOMe
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

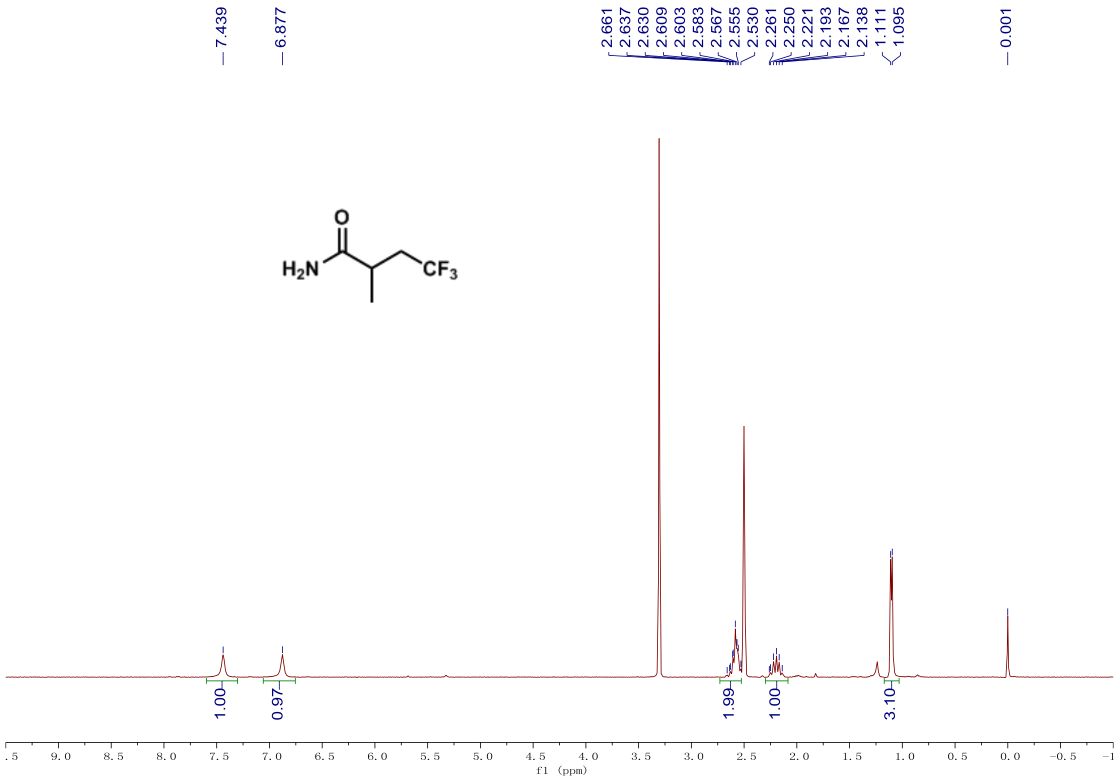
2-50

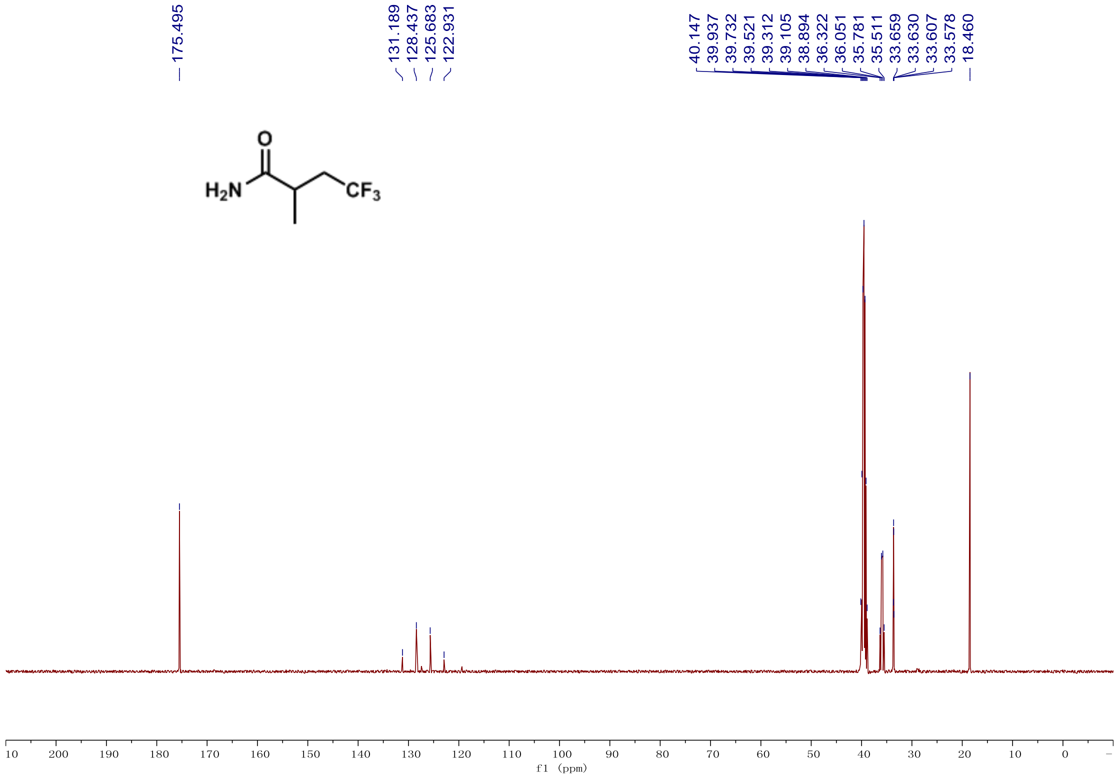

7.400
7.395
7.390
7.383
7.379
7.375
7.369
7.361
7.351
7.340
7.333
7.319
7.314
7.259
5.145
2.889
2.871
2.854
2.837
2.820
2.802
2.751
2.733
2.724
2.714
2.706
2.696
2.687
2.678
2.668
2.659
2.651
2.641
2.632
2.614
2.232
2.217
2.206
2.195
2.190
2.179
2.168
2.164
2.153
2.142
2.137
2.126
2.115
2.099
1.314
1.296
0.000
O
O
CF3
5.00
2.06
1.09
1.17
1.18
3.15
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

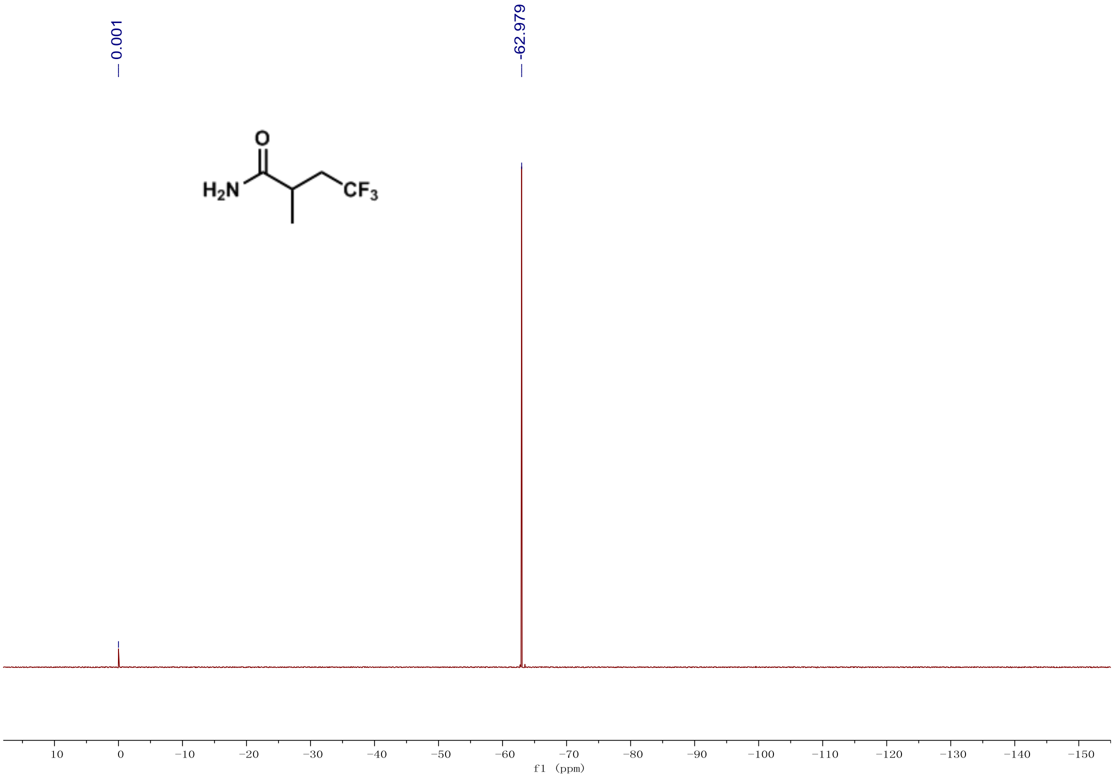

174.270
135.754
130.566
128.697
128.455
128.272
127.815
125.065
122.315
77.479
77.160
76.843
66.945
37.476
37.191
36.903
36.616
34.231
34.202
34.174
34.148
17.552
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.000
-65.341
O
O
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

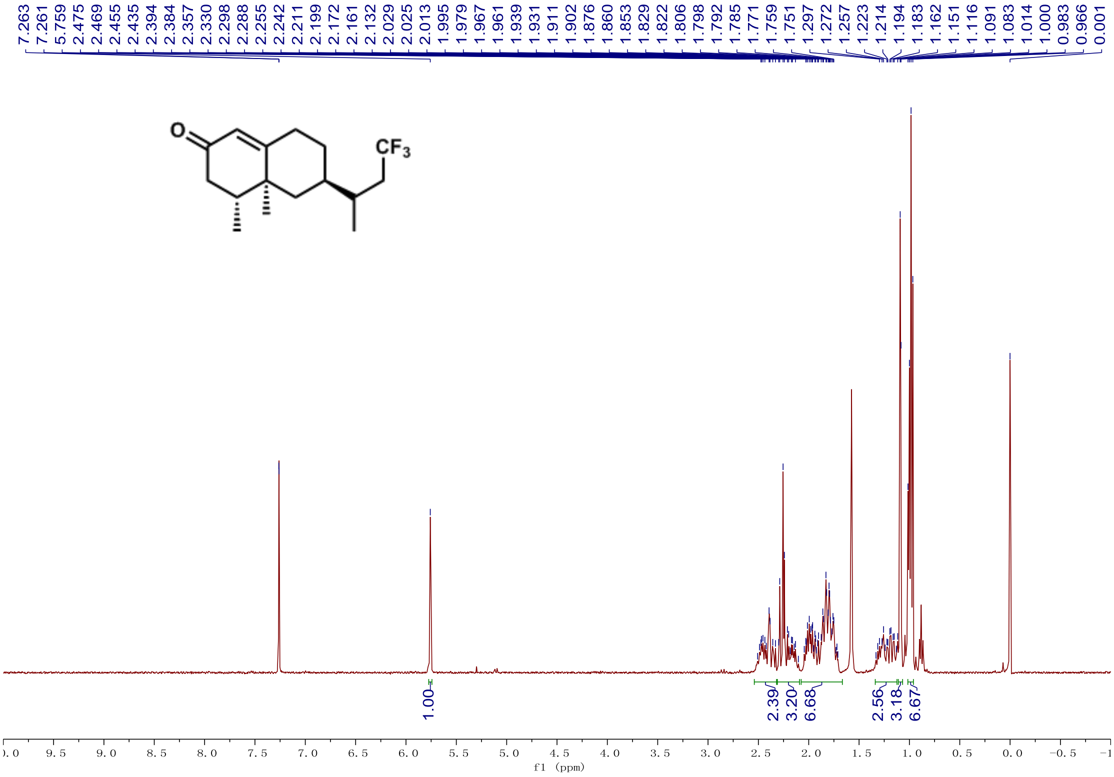
2-51

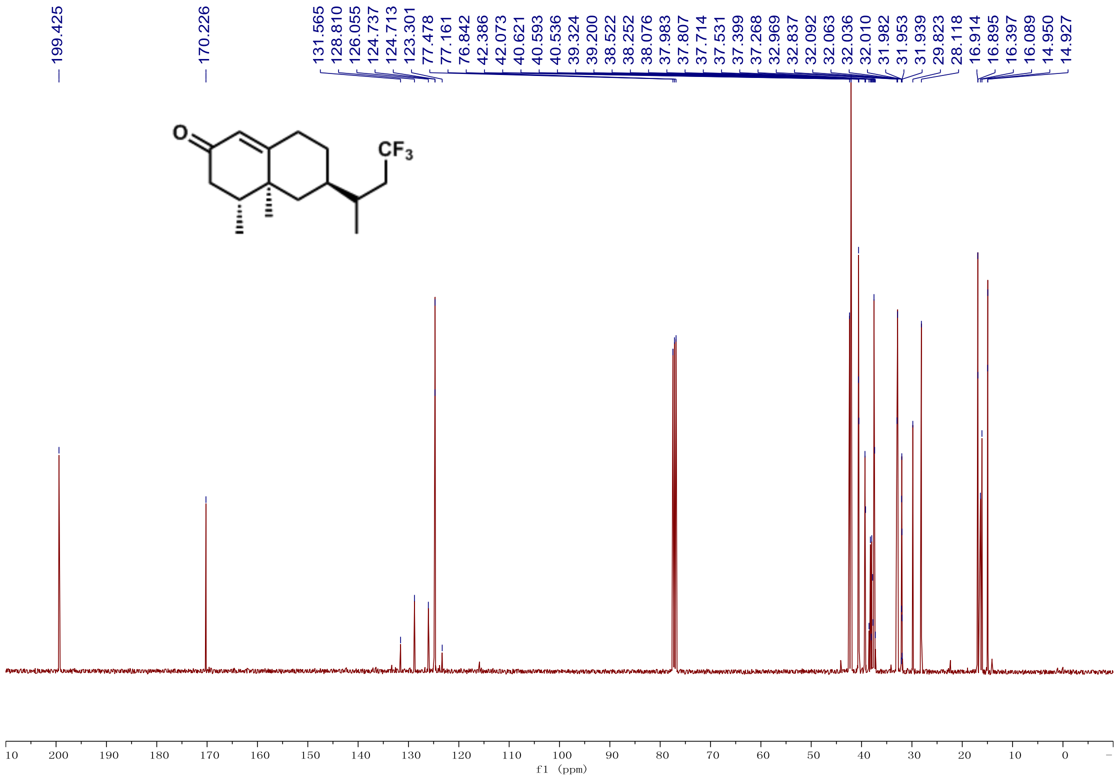

7.439
6.877
2.661
2.637
2.630
2.609
2.603
2.583
2.567
2.555
2.530
2.261
2.250
2.221
2.193
2.167
2.138
1.111
1.095
0.001
O
H_2N
CF_3
1.00
0.97
1.99
1.00
3.10
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

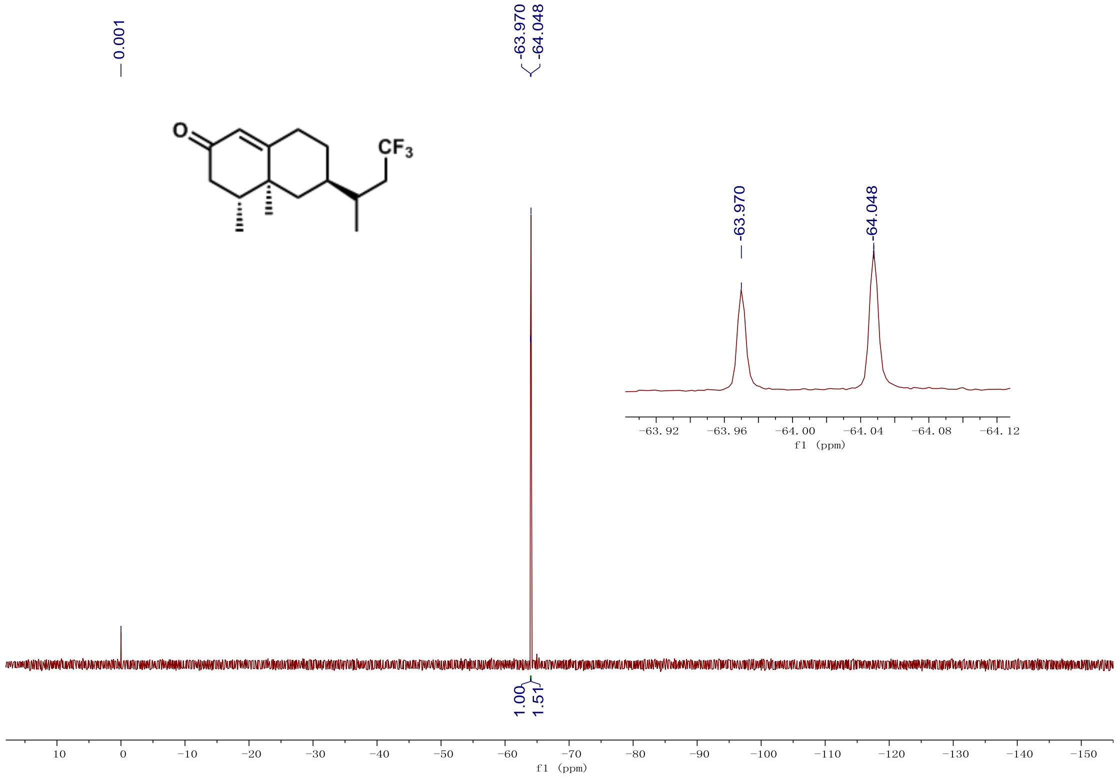

175.495
131.189
128.437
125.683
122.931
40.147
39.937
39.732
39.521
39.312
39.105
38.894
36.322
36.051
35.781
35.511
33.659
33.630
33.607
33.578
18.460
O
H_2N
CF_3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −
f1 (ppm)


0.001
-62.979
O
H$_2$N
CF$_3$
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

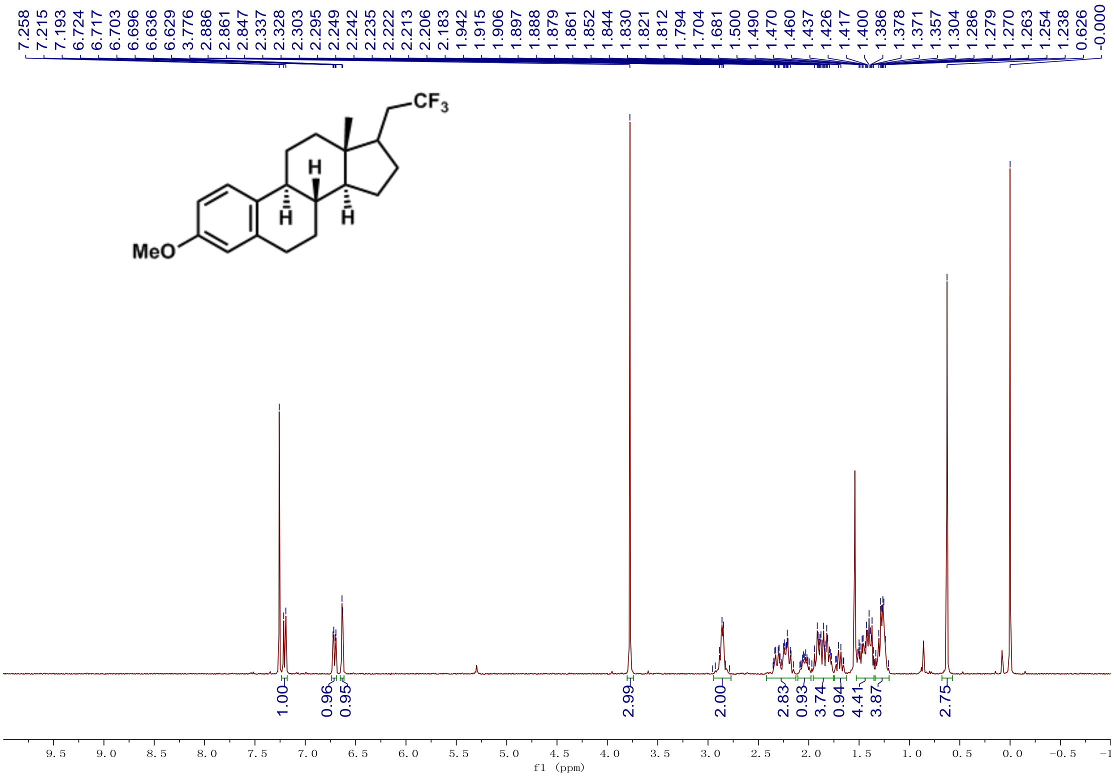
2-52

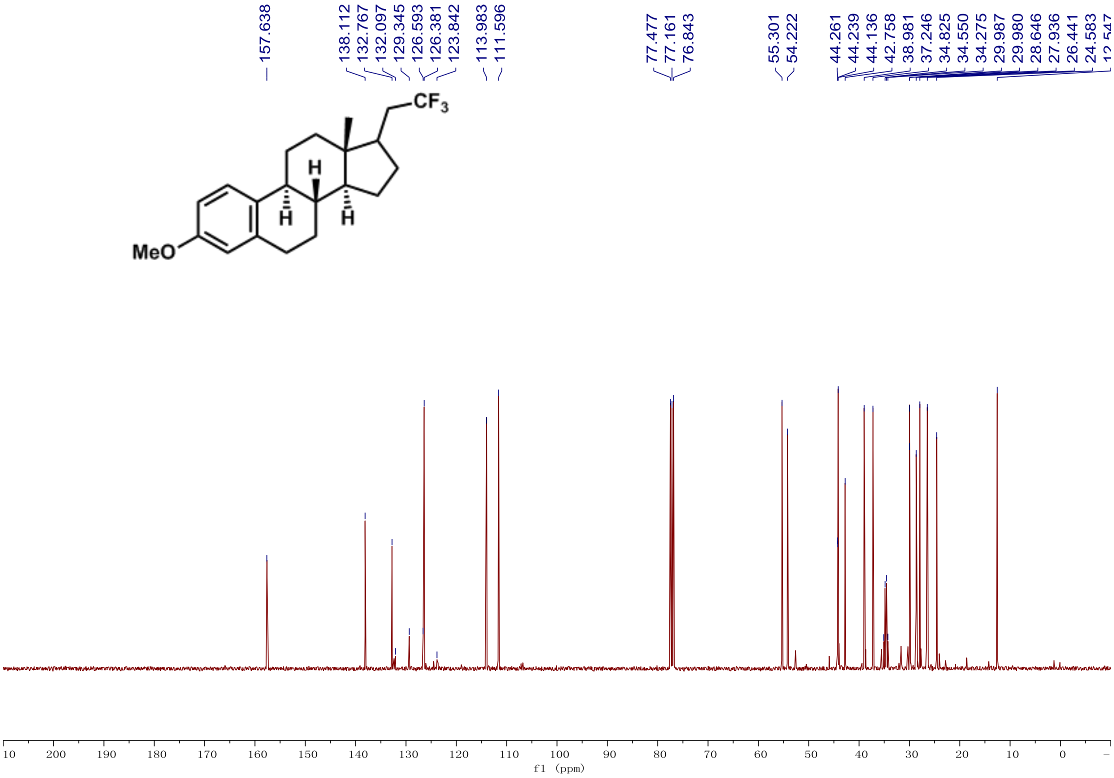

7.263
7.261
5.759
2.475
2.469
2.455
2.435
2.394
2.384
2.357
2.330
2.298
2.288
2.255
2.242
2.211
2.199
2.172
2.161
2.132
2.029
2.025
2.013
1.995
1.979
1.967
1.961
1.939
1.931
1.911
1.902
1.876
1.860
1.853
1.829
1.822
1.806
1.798
1.792
1.785
1.771
1.759
1.751
1.297
1.272
1.257
1.223
1.214
1.194
1.183
1.162
1.151
1.116
1.091
1.083
1.014
1.000
0.983
0.966
0.001
O
CF$_3$
1.00
2.39
3.20
6.68
2.56
3.18
6.67
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

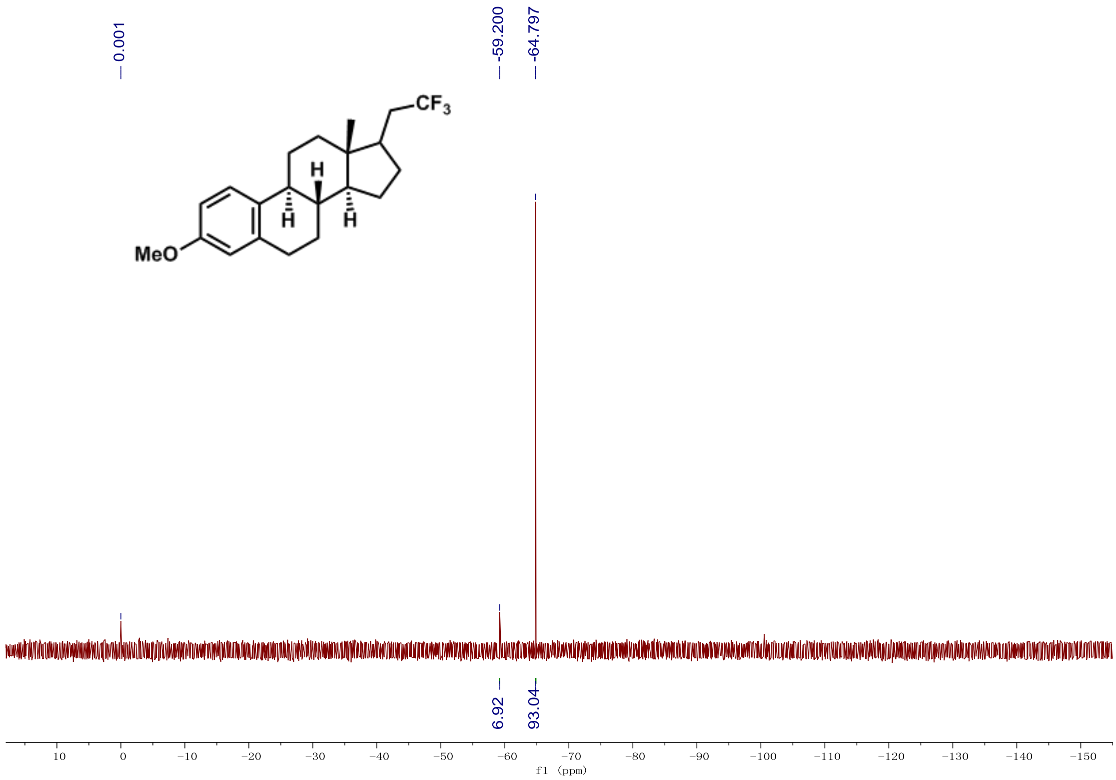

199.425
170.226
131.565
128.810
126.055
124.737
124.713
123.301
77.478
77.161
76.842
42.386
42.073
40.621
40.593
40.536
39.324
39.200
38.522
38.252
38.076
37.983
37.807
37.714
37.531
37.399
37.268
32.969
32.837
32.092
32.063
32.036
32.010
31.982
31.953
31.939
29.823
28.118
16.914
16.895
16.397
16.089
14.950
14.927
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-63.970
-64.048
O
CF3
-63.970
-64.048
-63.92
-63.96
-64.00
-64.04
-64.08
-64.12
f1 (ppm)
1.00
1.51
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

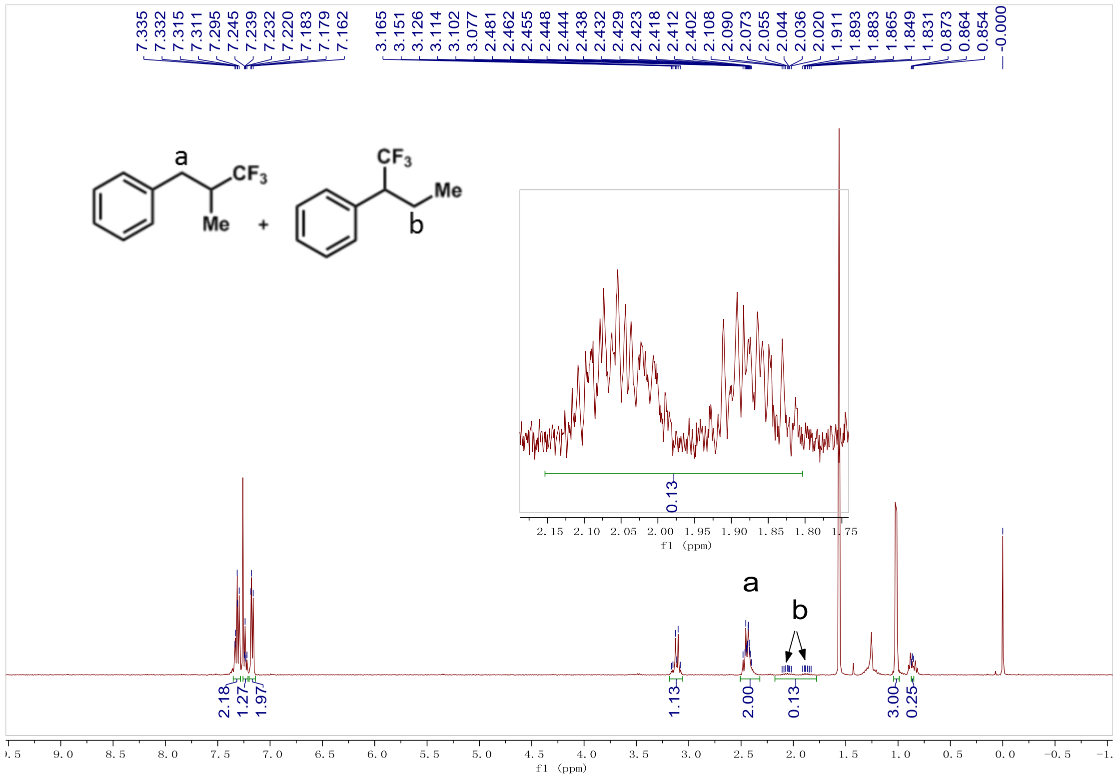
2-53

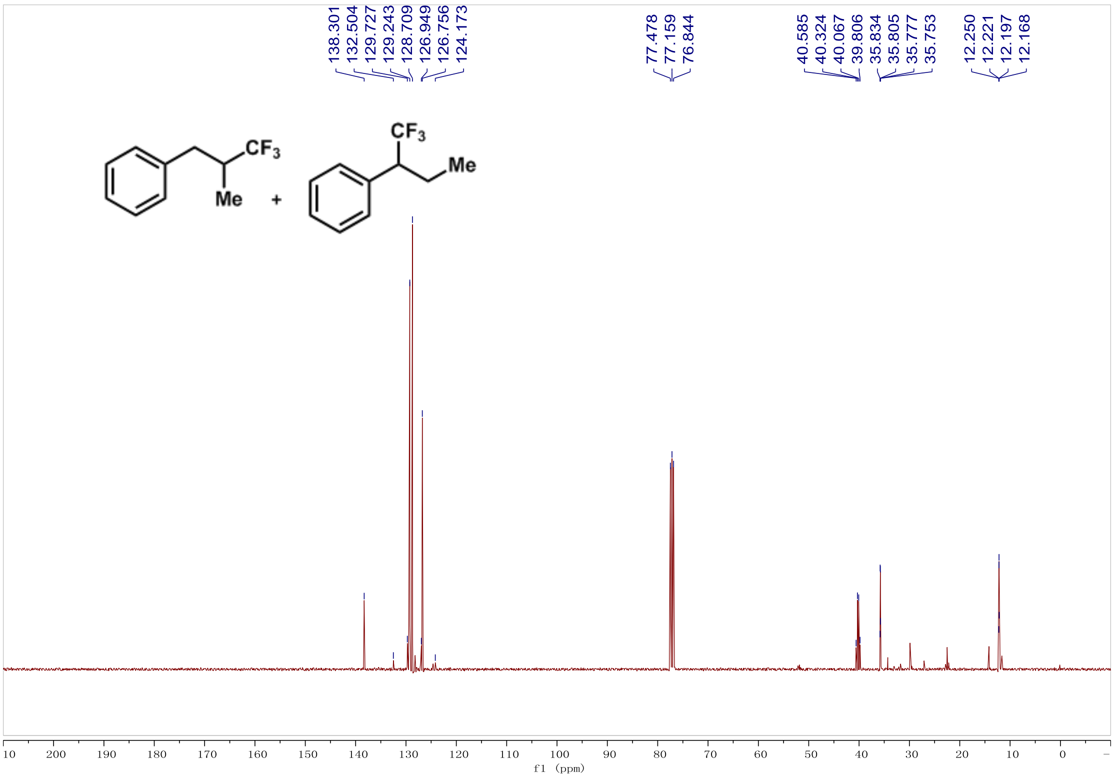

7.258
7.215
7.193
6.724
6.717
6.703
6.696
6.636
6.629
3.776
2.886
2.861
2.847
2.337
2.328
2.303
2.295
2.249
2.242
2.235
2.222
2.213
2.206
2.183
1.942
1.915
1.906
1.897
1.888
1.879
1.861
1.852
1.844
1.830
1.821
1.812
1.794
1.704
1.681
1.500
1.490
1.470
1.460
1.437
1.426
1.417
1.400
1.386
1.378
1.371
1.357
1.304
1.286
1.279
1.270
1.263
1.254
1.238
0.626
-0.000
CF3
H
H
H
MeO
1.00
0.96
0.95
2.99
2.00
2.83
0.93
3.74
0.94
4.41
3.87
2.75
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

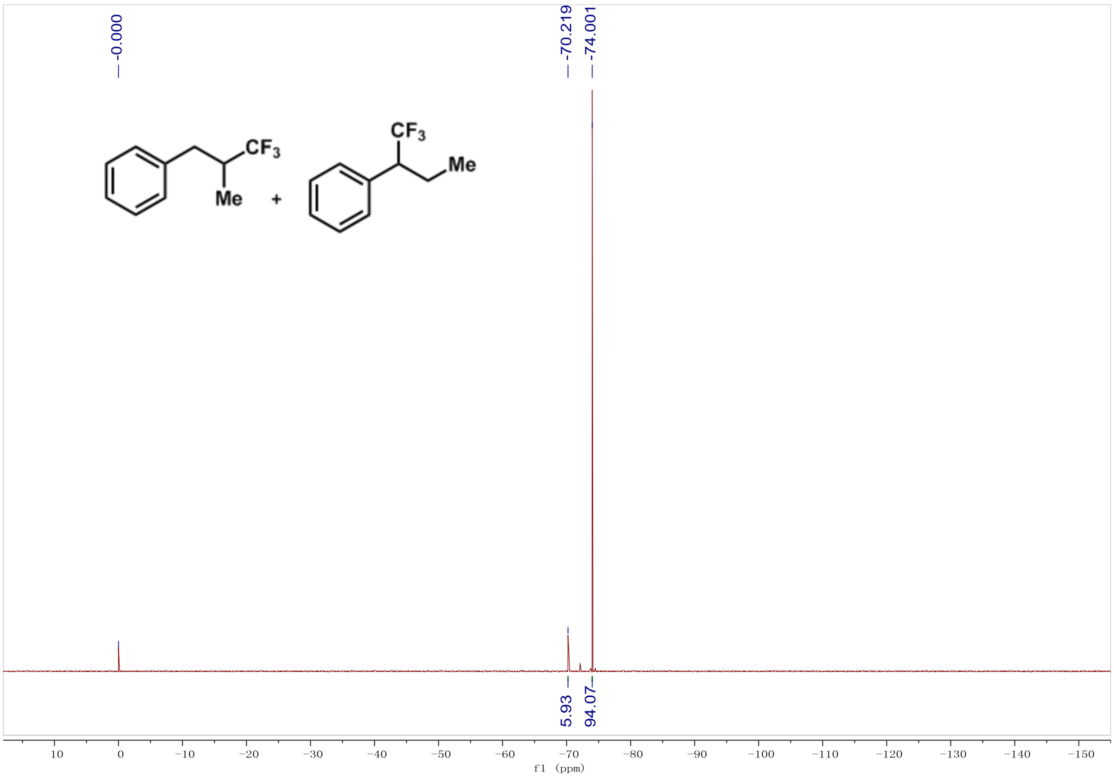

157.638
138.112
132.767
132.097
129.345
126.593
126.381
123.842
113.983
111.596
77.477
77.161
76.843
55.301
54.222
44.261
44.239
44.136
42.758
38.981
37.246
34.825
34.550
34.275
29.987
29.980
28.646
27.936
26.441
24.583
CF3
H
H
H
MeO
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-59.200
-64.797
CF3
H
H
H
MeO
6.92
93.04
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

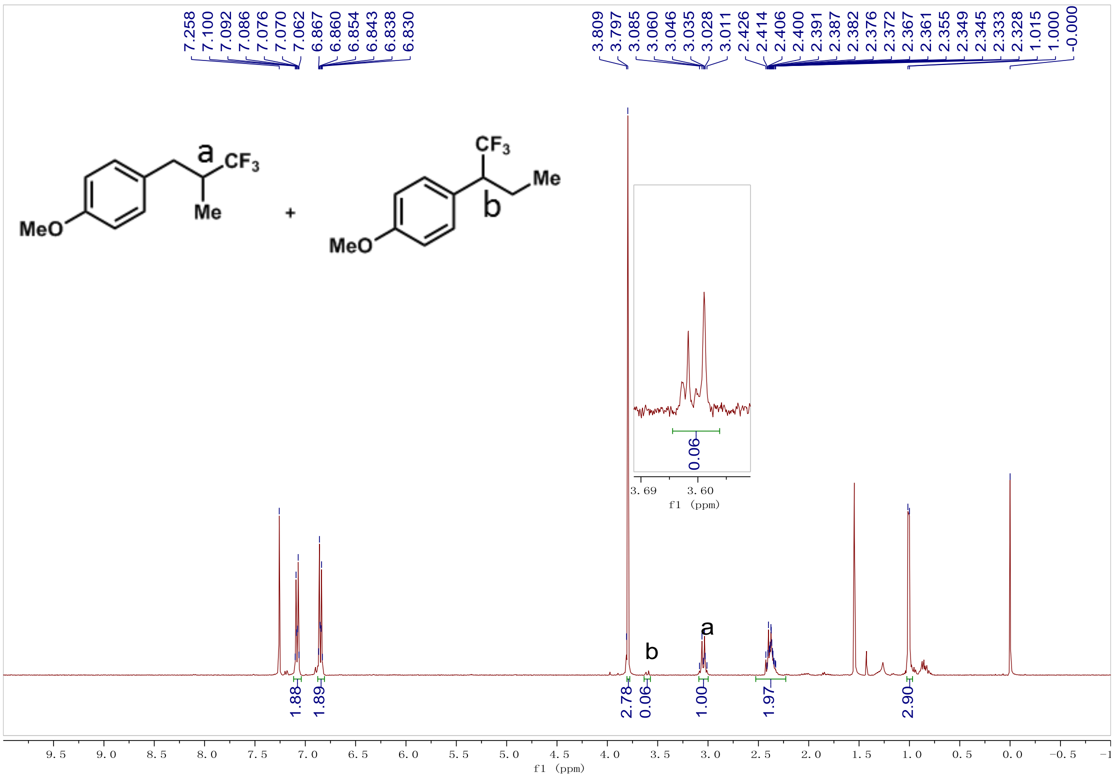
2-54

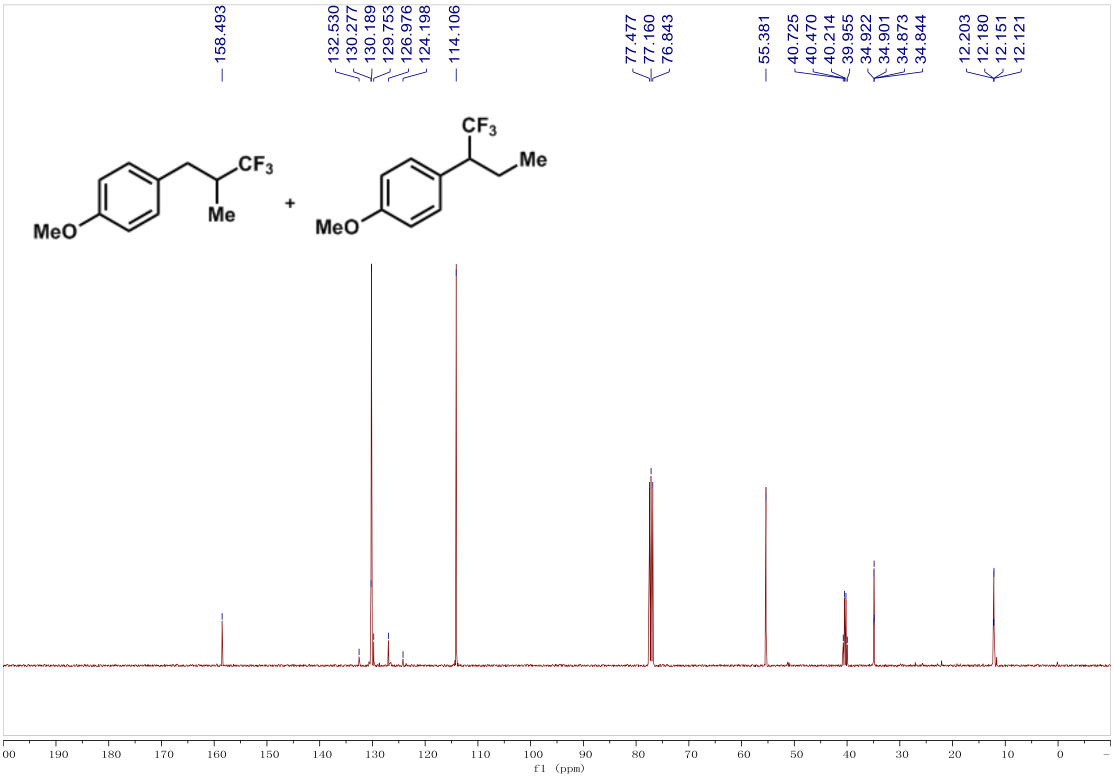

7.335
7.332
7.315
7.311
7.295
7.245
7.239
7.232
7.220
7.183
7.179
7.162
3.165
3.151
3.126
3.114
3.102
3.077
2.481
2.462
2.455
2.448
2.444
2.438
2.432
2.429
2.423
2.418
2.412
2.402
2.108
2.090
2.073
2.055
2.044
2.036
2.020
1.911
1.893
1.883
1.865
1.849
1.831
0.873
0.864
0.854
-0.000
a
CF3
Me
+
CF3
Me
b
0.13
2.15
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
f1 (ppm)
a
b
2.18
1.27
1.97
1.13
2.00
0.13
3.00
0.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
f1 (ppm)

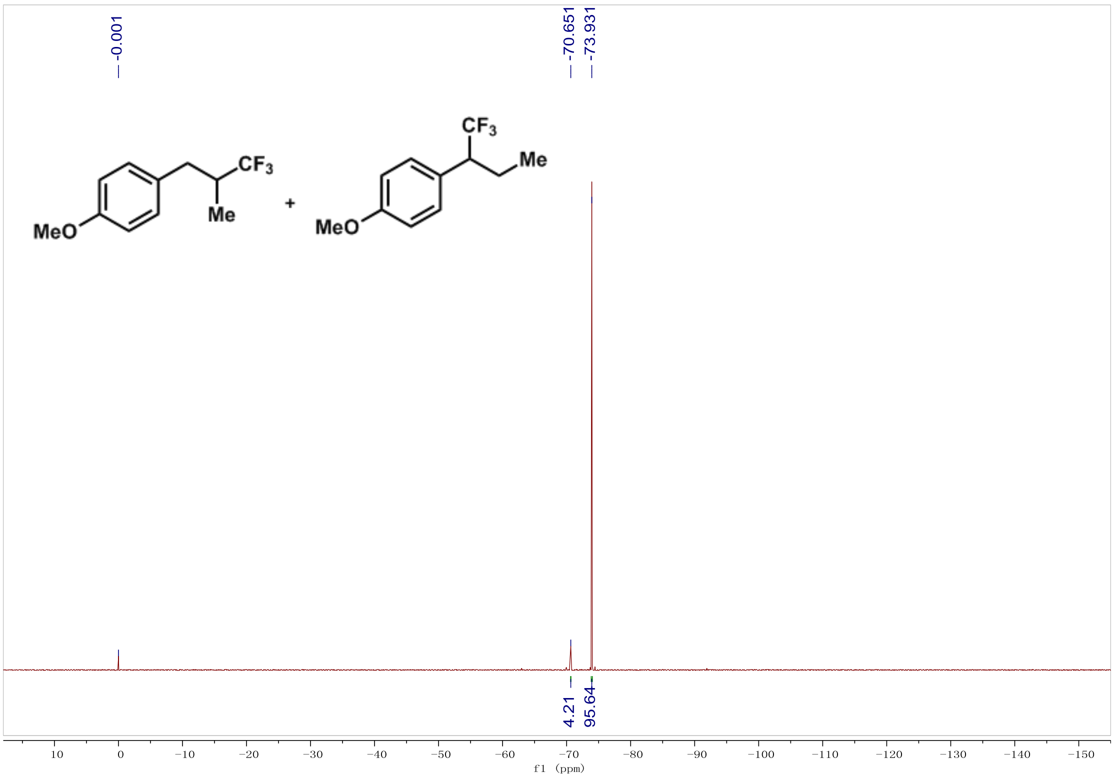

138.301
132.504
129.727
129.243
128.709
126.949
126.756
124.173
77.478
77.159
76.844
40.585
40.324
40.067
39.806
35.834
35.805
35.777
35.753
12.250
12.221
12.197
12.168
CF3
Me
+
CF3
Me
f1 (ppm)


-0.000
-70.219
-74.001
CF3
Me
+
CF3
Me
5.93
94.07
f1 (ppm)

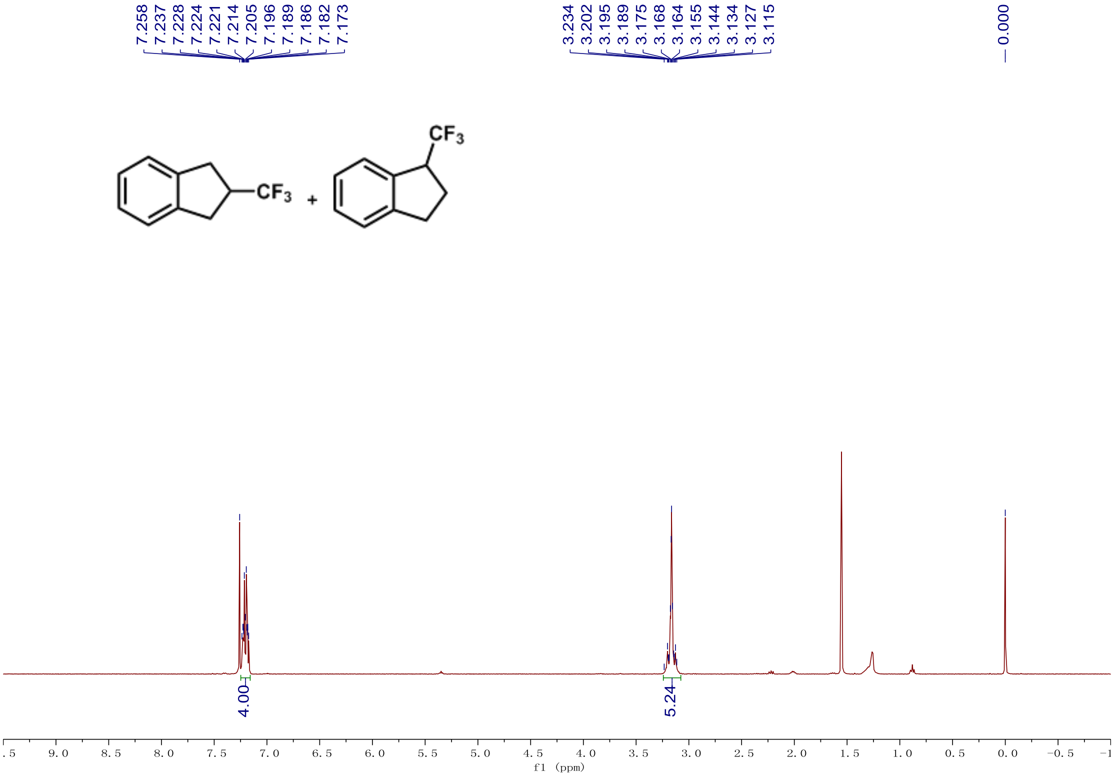
2-55

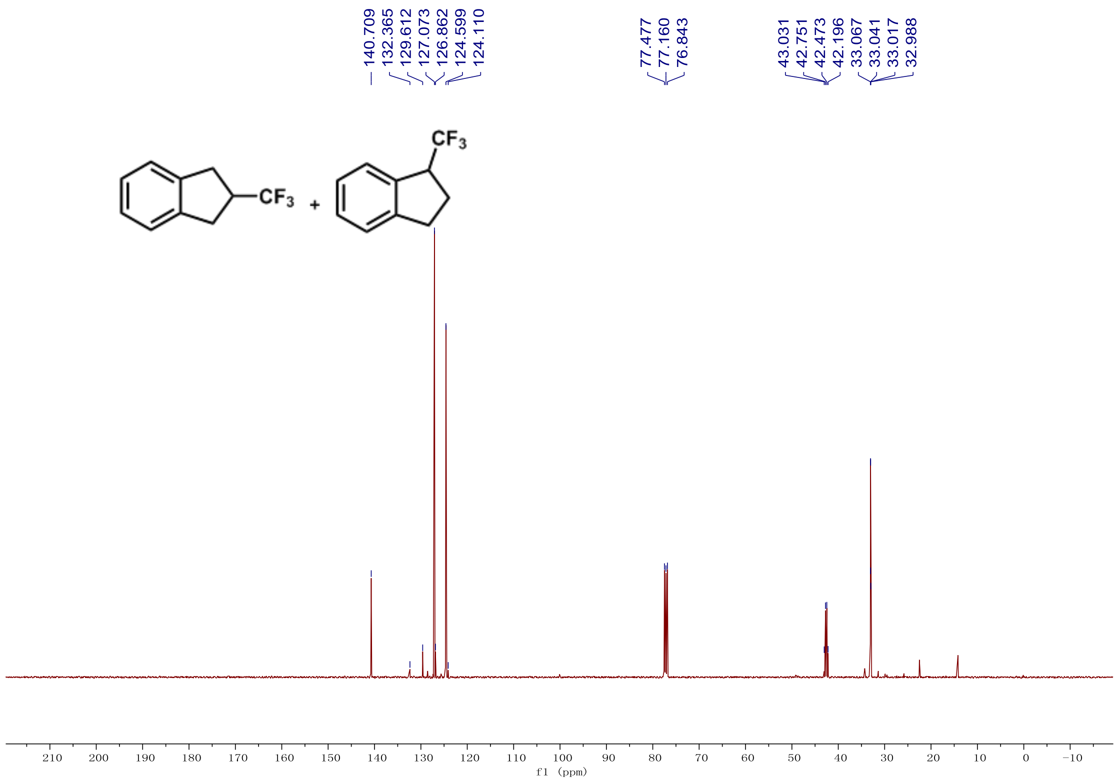

7.258
7.100
7.092
7.086
7.076
7.070
7.062
6.867
6.860
6.854
6.843
6.838
6.830
3.809
3.797
3.085
3.060
3.046
3.035
3.028
3.011
2.426
2.414
2.406
2.400
2.391
2.387
2.382
2.376
2.372
2.367
2.361
2.355
2.349
2.345
2.333
2.328
1.015
1.000
-0.000
a
CF3
Me
MeO
+
CF3
Me
b
MeO
0.06
3.69
3.60
f1 (ppm)
b
a
1.88
1.89
2.78
0.06
1.00
1.97
2.90
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

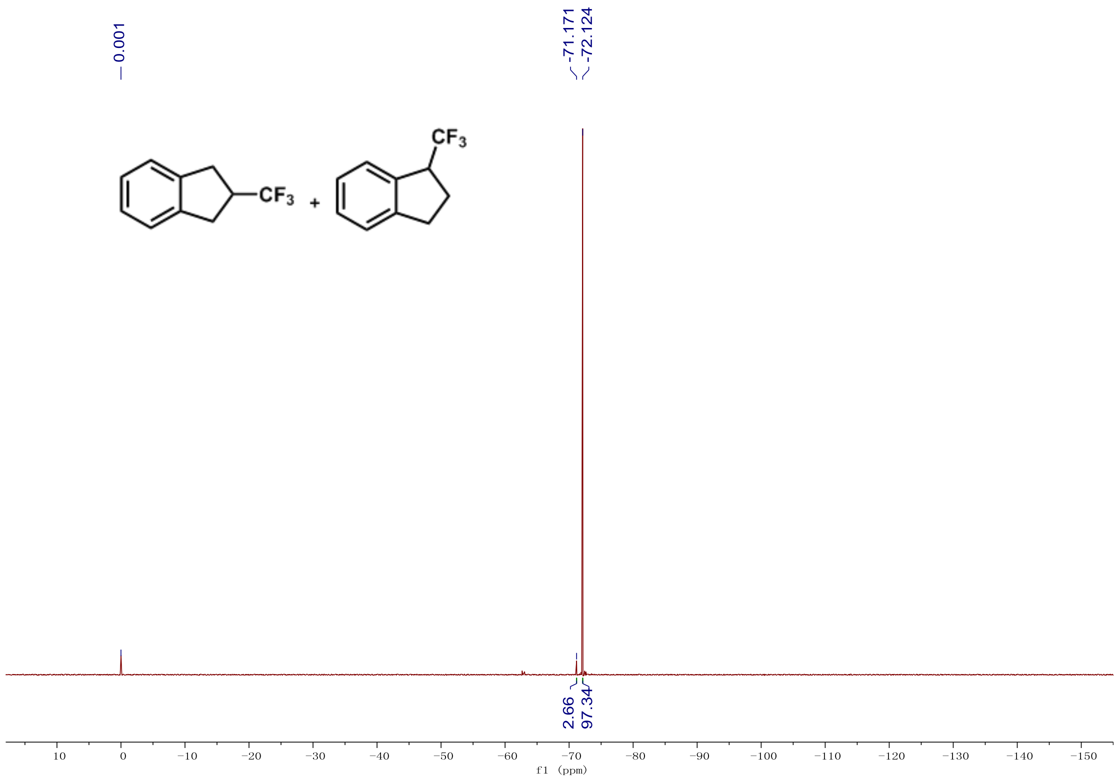

158.493
132.530
130.277
130.189
129.753
126.976
124.198
114.106
77.477
77.160
76.843
55.381
40.725
40.470
40.214
39.955
34.922
34.901
34.873
34.844
12.203
12.180
12.151
12.121
CF3
Me
MeO
+
CF3
Me
MeO
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.001
-70.651
-73.931
CF3
MeO
Me
+
CF3
Me
MeO
4.21
95.64
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

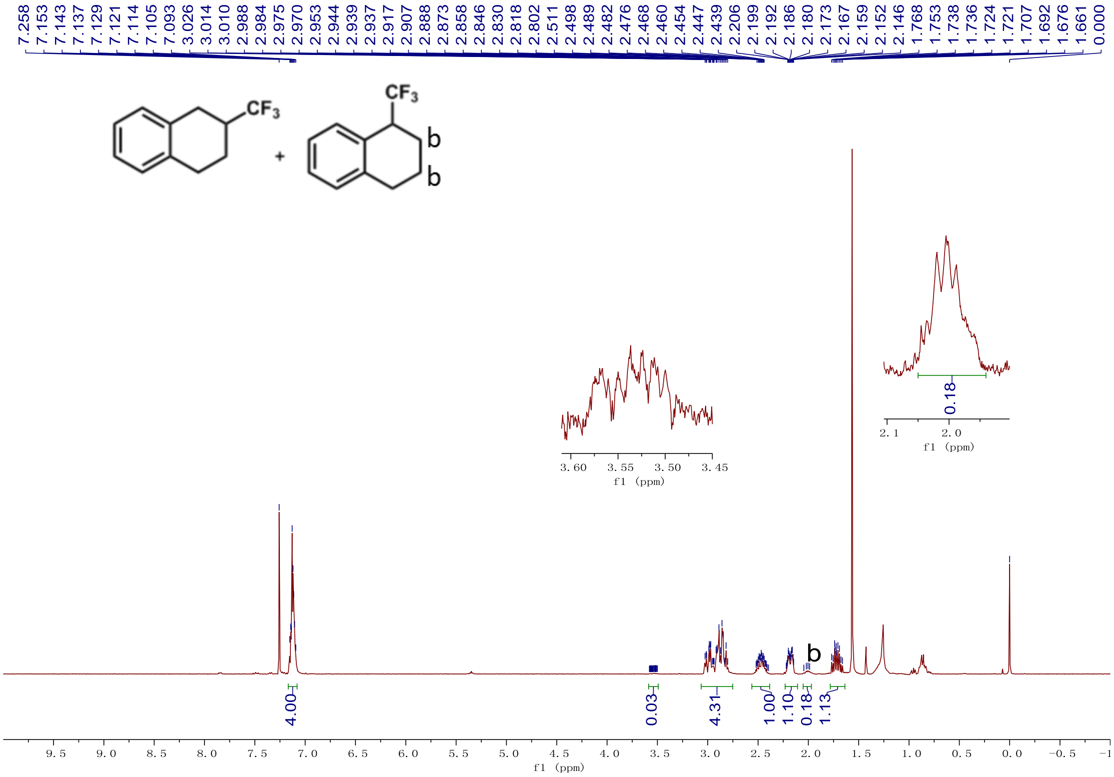
2-56


7.258
7.237
7.228
7.224
7.221
7.214
7.205
7.196
7.189
7.186
7.182
7.173
3.234
3.202
3.195
3.189
3.175
3.168
3.164
3.155
3.144
3.134
3.127
3.115
0.000
CF3
+
CF3
4.00
5.24
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


140.709
132.365
129.612
127.073
126.862
124.599
124.110
77.477
77.160
76.843
43.031
42.751
42.473
42.196
33.067
33.041
33.017
32.988
CF3
+
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


0.001
-71.171
-72.124
CF3
+
CF3
2.66
97.34
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

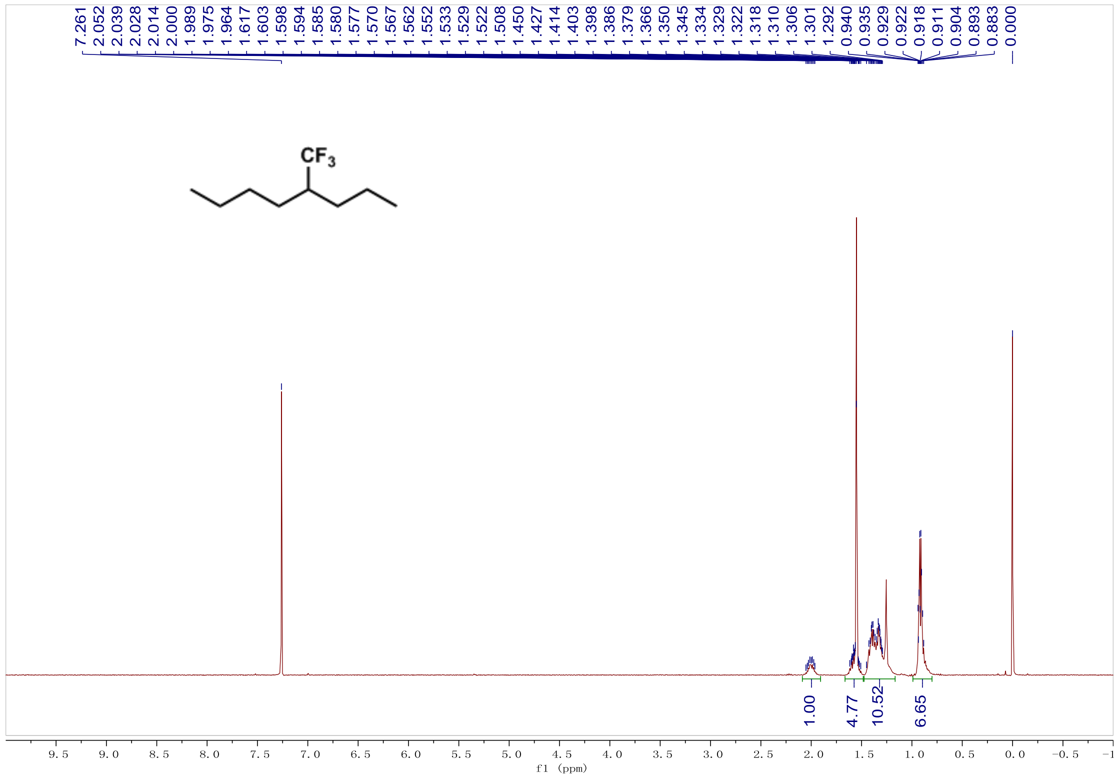
2-57

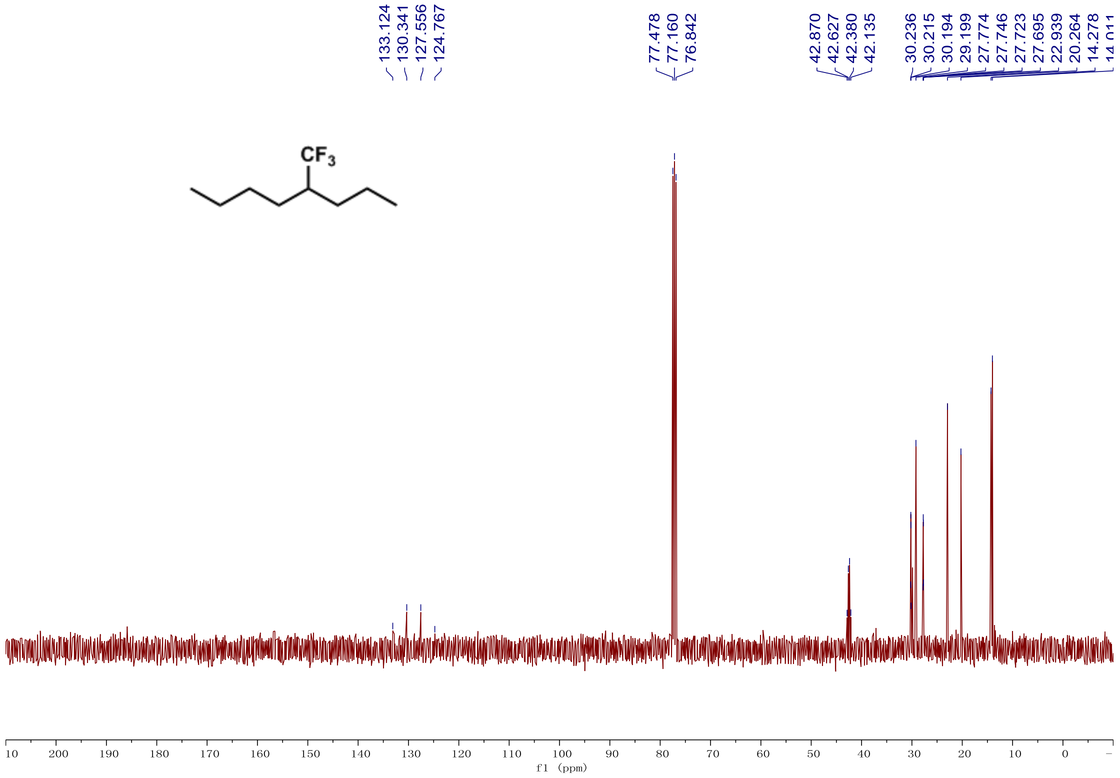

7.258
7.153
7.143
7.137
7.129
7.121
7.114
7.105
7.093
3.026
3.014
3.010
2.988
2.984
2.975
2.970
2.953
2.944
2.939
2.937
2.917
2.907
2.888
2.873
2.858
2.846
2.830
2.818
2.802
2.511
2.498
2.489
2.482
2.476
2.468
2.460
2.454
2.447
2.439
2.206
2.199
2.192
2.186
2.180
2.173
2.167
2.159
2.152
2.146
1.768
1.753
1.738
1.736
1.724
1.721
1.707
1.692
1.676
1.661
0.000
CF3
+
CF3
b
b
0.18
2.1
2.0
f1 (ppm)
3.60
3.55
3.50
3.45
f1 (ppm)
b
4.00
0.03
4.31
1.00
1.10
0.18
1.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

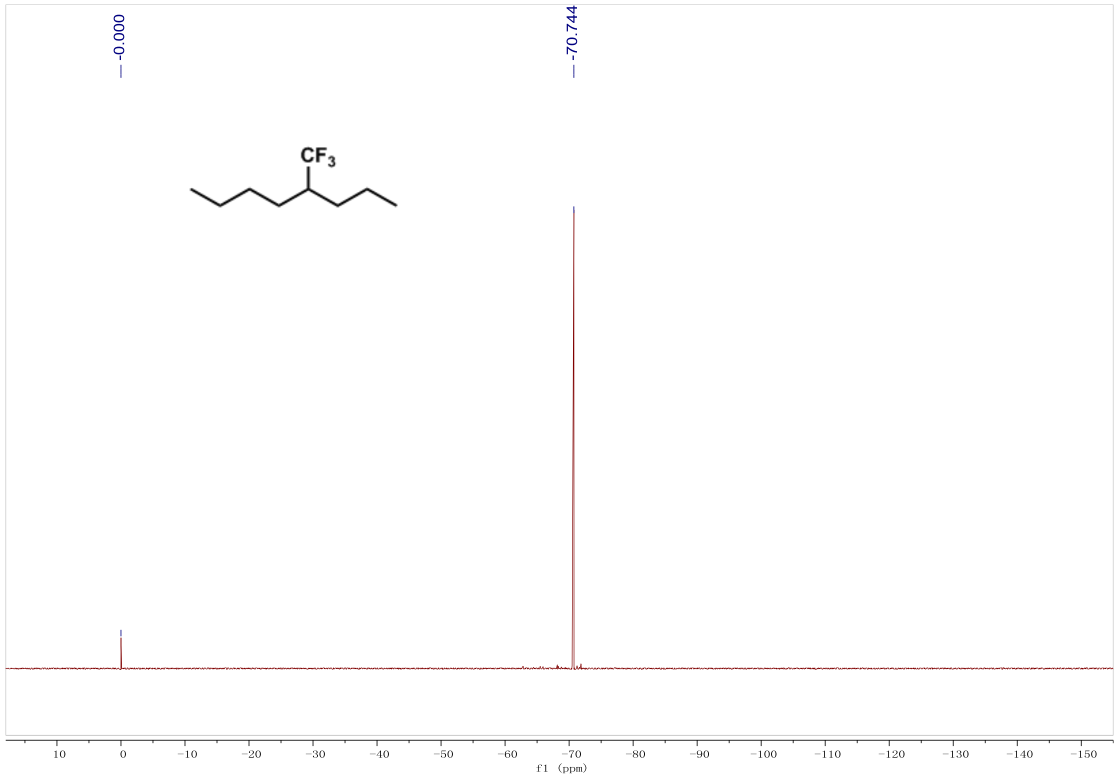

135.578
133.742
132.138
129.372
129.295
128.976
126.605
126.393
126.232
123.840
77.478
77.160
76.842
39.826
39.557
39.287
39.017
28.344
28.321
28.292
28.263
22.335
22.306
22.278
22.250
CF3
+
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-68.235
-74.197
CF3
+
CF3
3.64
96.30
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

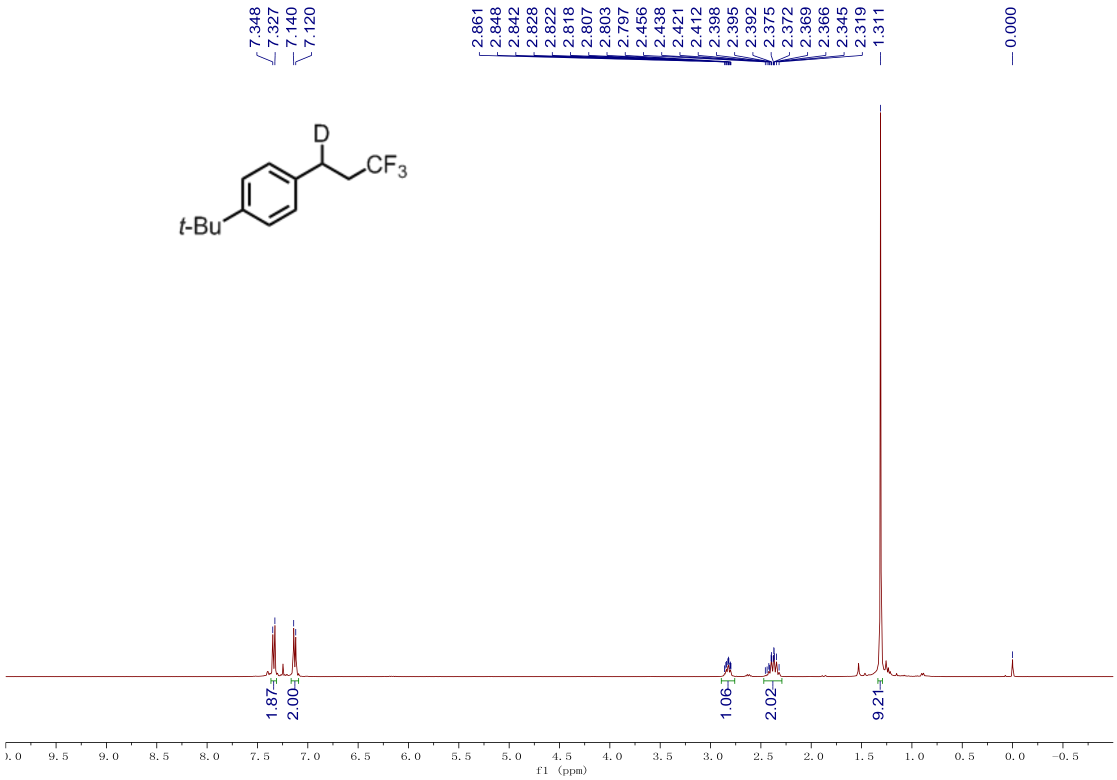
2-58

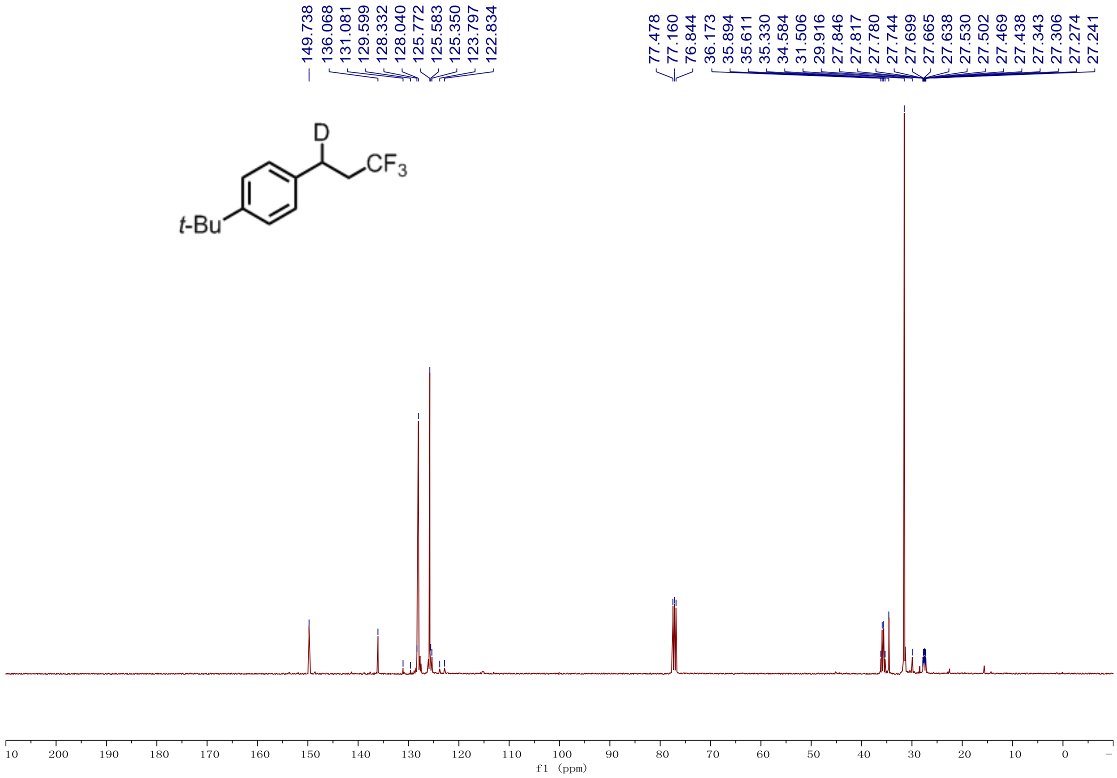

7.261
2.052
2.039
2.028
2.014
2.000
1.989
1.975
1.964
1.617
1.603
1.598
1.594
1.585
1.580
1.577
1.570
1.567
1.562
1.552
1.533
1.529
1.522
1.508
1.450
1.427
1.414
1.403
1.398
1.386
1.379
1.366
1.350
1.345
1.334
1.329
1.322
1.318
1.310
1.306
1.301
1.292
0.940
0.935
0.929
0.922
0.918
0.911
0.904
0.893
0.000
CF3
1.00
4.77
10.52
6.65
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

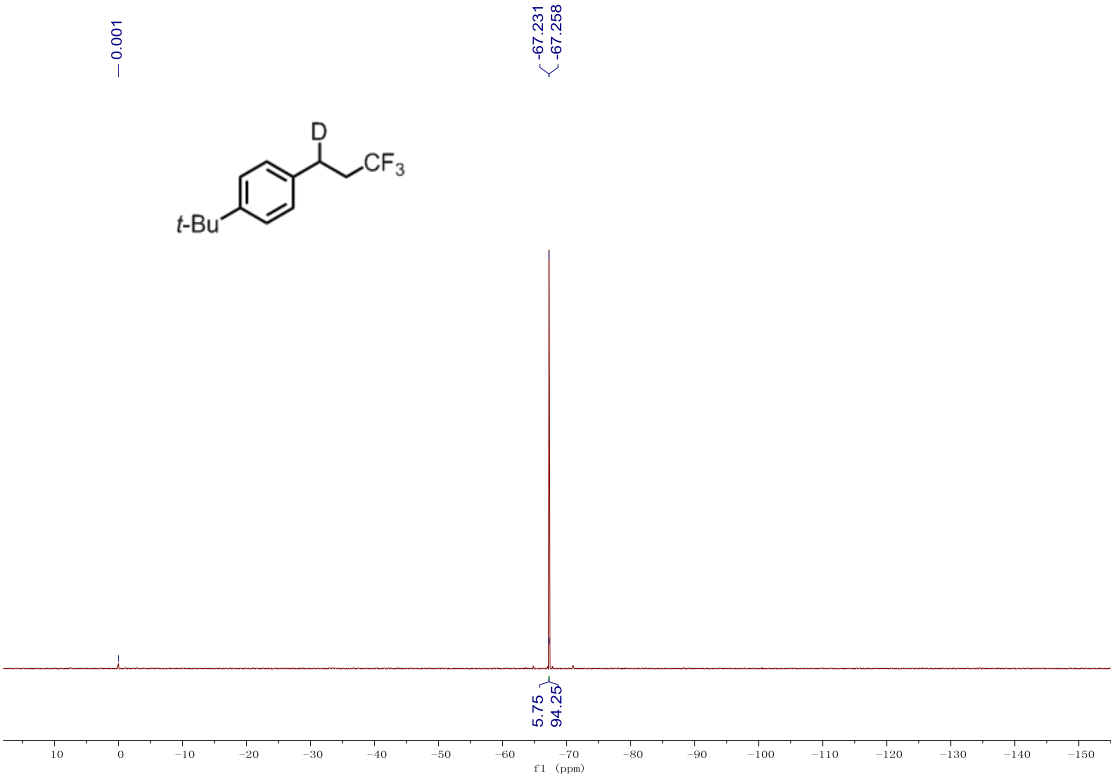

133.124
130.341
127.556
124.767
77.478
77.160
76.842
42.870
42.627
42.380
42.135
30.236
30.215
30.194
29.199
27.774
27.746
27.723
27.695
22.939
20.264
14.278
14.011
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.000
-70.744
CF3
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

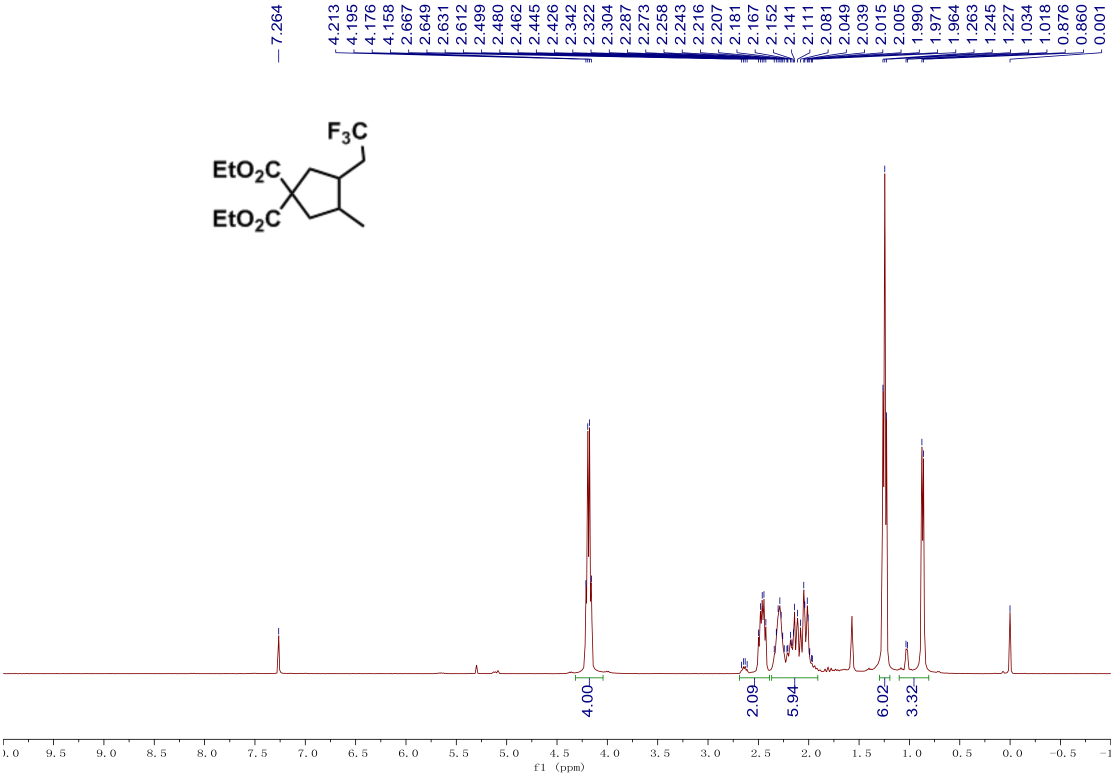
2-6D

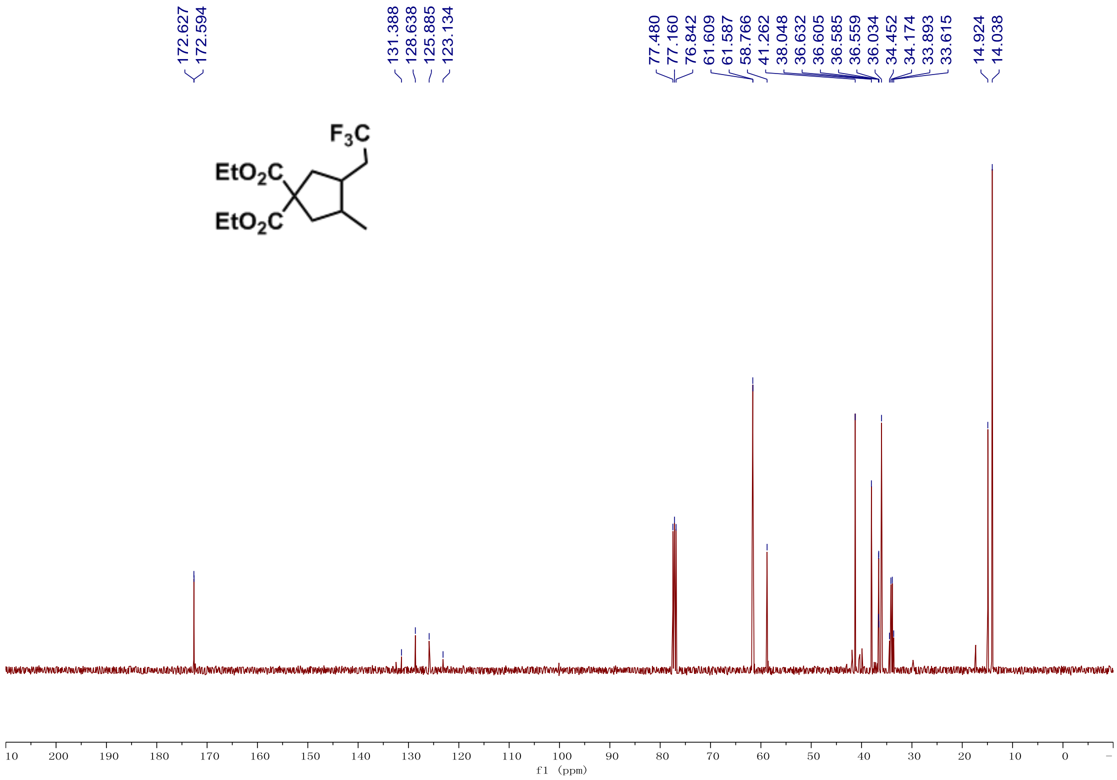

7.348
7.327
7.140
7.120
2.861
2.848
2.842
2.828
2.822
2.818
2.807
2.803
2.797
2.456
2.438
2.421
2.412
2.398
2.395
2.392
2.375
2.372
2.369
2.366
2.345
2.319
1.311
0.000
D
CF3
t-Bu
1.87
2.00
1.06
2.02
9.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

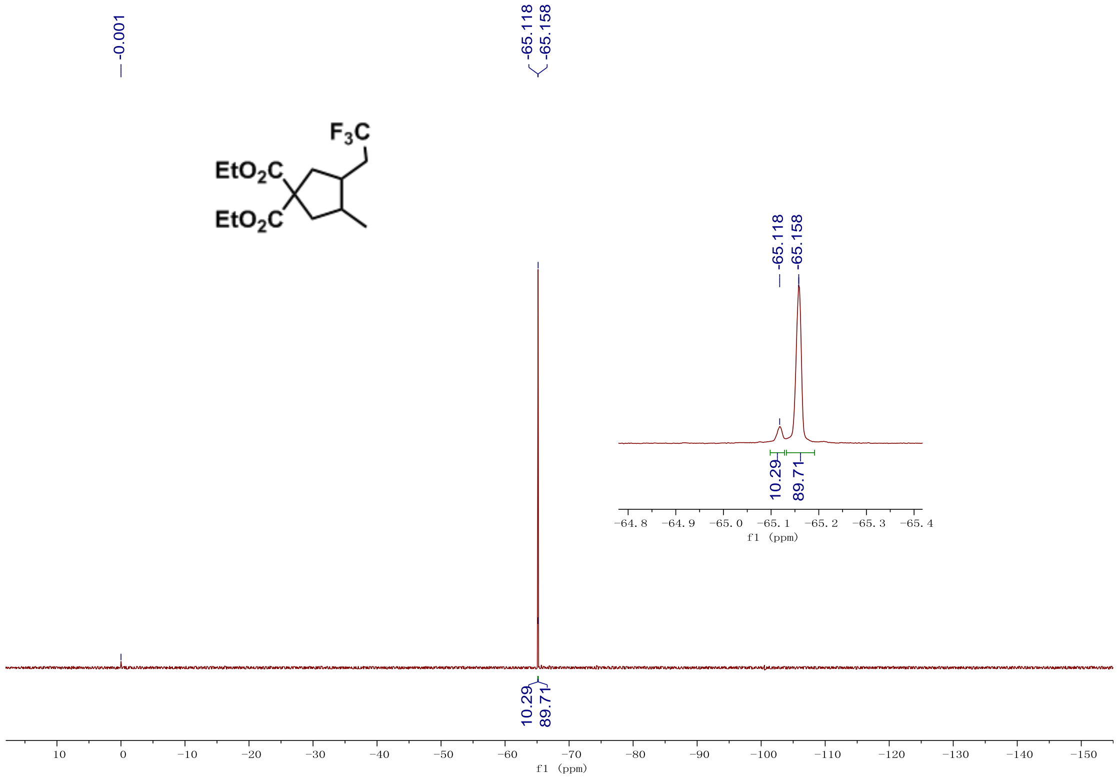

149.738
136.068
131.081
129.599
128.332
128.040
125.772
125.583
125.350
123.797
122.834
77.478
77.160
76.844
36.173
35.894
35.611
35.330
34.584
31.506
29.916
27.846
27.817
27.780
27.744
27.699
27.665
27.638
27.530
27.502
27.469
27.438
27.343
27.306
27.274
27.241
D
CF3
t-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0.001
-67.231
-67.258
D
CF3
t-Bu
5.75
94.25
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

4


7.264
4.213
4.195
4.176
4.158
2.667
2.649
2.631
2.612
2.499
2.480
2.462
2.445
2.426
2.342
2.322
2.304
2.287
2.273
2.258
2.243
2.216
2.207
2.181
2.167
2.152
2.141
2.111
2.081
2.049
2.039
2.015
2.005
1.990
1.971
1.964
1.263
1.245
1.227
1.034
1.018
0.876
0.860
0.001
F3C
EtO2C
EtO2C
4.00
2.09
5.94
6.02
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


172.627
172.594
131.388
128.638
125.885
123.134
77.480
77.160
76.842
61.609
61.587
58.766
41.262
38.048
36.632
36.605
36.585
36.559
36.034
34.452
34.174
33.893
33.615
14.924
14.038
F3C
EtO2C
EtO2C
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-0.001
-65.118
-65.158
F3C
EtO2C
EtO2C
-65.118
-65.158
10.29
89.71
-64.8
-64.9
-65.0
-65.1
-65.2
-65.3
-65.4
f1 (ppm)
10.29
89.71
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

CF_3ZnBr•2MeCN