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Supporting Information

A Simple Access to β-Trifluoromethyl-Substituted Ketones via Copper-Catalyzed Ring-Opening Trifluoromethylation of Substituted Cyclopropanols

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I. General Methods and Starting Materials

Methanol (>99.6%, Laboratory Reagent grade, Sigma-Aldrich) was used as a solvent. Deuterated solvents were purchased from Armar Chemicals. Other solvents were purified by conventional methods. 3,3-Dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (**3**) and 1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (**4**) used in the optimization experiments were purchased from Sigma-Aldrich. Togni reagent **3** employed in the preparative runs was synthesized according to the published procedure.[1]

Purified "white" copper(I) chloride, free of copper(II) salts, was prepared by two methods: (A) commercial "olive-green" reagent was stirred with glacial acetic acid overnight, then filtered under argon and washed subsequently with glacial acetic acid, methanol, diethyl ether and dried; (B) CuCl prepared by the reduction of $CuCl_2$ with sodium sulfite in aqueous solution was then filtered under argon, washed with glacial acetic acid, methanol, diethyl ether and dried. Both samples of CuCl displayed equal efficiency in the trifluoromethylation reaction and were stored under argon. Copper(I) bromide was prepared from $CuBr_2$ according to the procedure (B). Other copper salts were used as obtained from commercial suppliers.

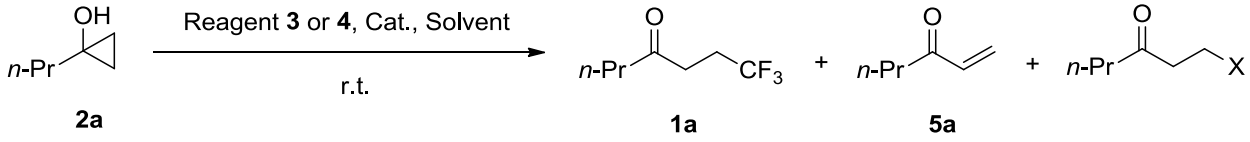
Cyclopropanols **2a-f**, **2h-m** were prepared by the Kulinkovich cyclopropanation of the corresponding carboxylic esters.[2] Cyclopropanol **2g** and *cis*-1,2-disubstituted cyclopropanols **2n**, **2o** were prepared according to the general procedure described in ref.[3] Enantiomerically enriched (66% *ee*) cyclopropanol (1*S*,2*S*)-**2n** was synthesized as described in ref.[4]

Silica gel 40 – 100 μm was used for column chromatography; silica gel 60 F_{254} plates were used for TLC. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (100.6 MHz) spectra were taken on a Bruker Avance III spectrometer. Chemical shifts were given in δ value with $CHCl_3$ (δ = 7.26) and $CDCl_3$ (δ = 77.16) as internal standards for ^{1}H NMR and ^{13}C NMR spectra, respectively. FT-IR spectra were recorded on a Bruker Tensor 27 FT spectrometer. HPLC determination of *ee* was done on an Agilent Technologies 1200 series chromatograph. Specific rotation was measured using an Anton Paar MCP 500 polarimeter. HRMS data was obtained on an Agilent HPLC/Q-TOF G6540A Mass Spectrometer using APPI or APCI methods in positive or negative ion detection modes. GC-MS analysis was performed on a Shimadzu GCMS-QP2010 instrument.

II. Optimization of Reaction Conditions

The following procedure was used for the optimization runs: 1-propylcyclopropanol (**2a**, 5.0 mg, 0.05 mmol), Togni Reagent **3** or **4** (0.05 mmol), a copper catalyst and an additive were combined together in 0.5 mL of the corresponding solvent in a 1.5 mL vial and stirred overnight (ca. 20 h). The reaction mixture was diluted with water (~ 1-2 mL), extracted with $CDCl_3$ (~2 × 0.5 mL) and the extract was transferred into a NMR tube through a thin layer of $MgSO_4$ placed in a Pasteur pipette. Experiments with 5-10% of the catalyst load were run in 0.1 mmol scale, and the lower loads (1-3%) of the catalyst were made in 0.5 mmol scale. A number of the optimization experiments were also performed/reproduced in deuterated solvents and monitored directly without any work-up procedures. Experiments in the entries 13-28 were carried out under argon. The composition of the reaction mixtures was determined by ^{1}H NMR spectroscopy using an internal standard (for this purpose, a minor inert impurity in cyclopropanol **2a** was used) and for the selected runs (Entries 13, 20, 27-29, Table S1) yields were also confirmed by ^{19}F NMR spectroscopy with 1,4-bis(trifluoromethyl)benzene as an internal standard. NMR spectra were acquired and processed using the parameters adequate for quantitative measurements. Typically 15-20 s interscan delays were used.

Table S1. Results of the optimization experiments



2a **1a** **5a**

Entry	Reagent	Catalyst	Solvent	Additive	Yields of products, %			
					1a	**5a**	X = Hal	X = OMe
1	**3**	-	CD_3OD	-	no reaction			
2	**4**	-	CD_3OD	-	no reaction			
3	**3**	100% $Zn(OTf)_2$	$CDCl_3$	-	0	mixture of unidentified ketone products		
4	**3**	20% CuCl[a]	CD_3OD	-	55	30	6	-
6	**4**	20% CuCl[a]	CD_3OD	-	23	60	4	-
7	**3**	20% $CuCl_2 \cdot 2H_2O$	CH_3OH	-	68	7	20	-
8	**4**	20% $CuCl_2 \cdot 2H_2O$	CH_3OH	-	12	40	10	-
9	**3**	20% $CuSO_4 \cdot 5H_2O$	CH_3OH	-	0	8	0	50
10	**3**	20% $Cu(OAc)_2 \cdot 2H_2O$	CH_3OH	-	0	10	0	45
11	**3**	20% $Cu(OTf)_2$	CH_3OH	-	n.d.[b]	0	-	25
12	**3**	100% $CuCl_2 \cdot 2H_2O$	CH_3OH	-	25	15	60	-
13	**3**	20% CuCl[d]	CD_3OD	-	80[c]	7	3	-
14	**3**	20% CuBr	CH_3OH	-	63[e]	8	7	-
15	**3**	20% CuI	CH_3OH	-	30[f]	5	-	-
16	**3**	20% CuCl[d]	CH_3OH	Xantphos	0	16	-	-
17	**3**	25% CuCl[d]	CH_3OH	1,10-Phen	35	30	-	-
18	**3**	20% CuCl[d]	CH_3OH	2 eq. LiCl	80	4	10	-
19	**3**	20% CuBr	CH_3OH	2 eq. LiBr	50	7	28	-

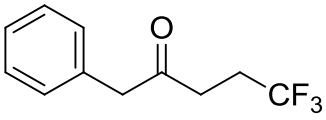
20	**3**	10% CuCl[d]	CD_3OD	1 eq. LiCl	80	4	7	-
21	**3**	10% CuCl[d]	CH_3OH	2 eq. LiCl	82	4	8	-
22	**3**	5% CuCl[d]	CH_3OH	1 eq. LiCl	83	4	5	-
23	**3**	10% CuCl[d]	$CDCl_3$	1 eq. LiCl	70	0	4	-
24	**3**	10% CuCl[d]	CD_3CN	1 eq. LiCl	60	6	20	-
25	**3**	1% CuCl[d]	CH_3OH	0.5 eq. LiCl	78	4	4	-
26	**3**	1% $CuCl_2 \cdot 2H_2O$	CD_3OD	0.5 eq. LiCl	74	3	2	-
27	**3**	100% CuCl[d]	CD_3OD	5 eq. LiCl	67	7	14	-
28[g]	**3**	3% CuCl[d]	CD_3OD	1 eq. LiCl	81	3	8	
29[g]	**3**	3% CuCl[d]	CD_3OD	1 eq. LiCl	47	13	8	

[a] Unpurified "olive-green" CuCl was used. [b] Not determined due to the signal overlap in ^{1}H NMR. [c] ^{19}F NMR spectrum of the reaction mixture also demonstrates the presence of some fluorine-containing impurities (~6%), δ = -64.9 (t, *J* = 10.6 Hz), -67.2 (d, *J* = 8.8 Hz). [d] Purified "white" CuCl was employed. [e] 20% of the starting material **2a** remained. [f] 50% of the starting material **2a** remained. [g] The reactions were performed with cyclopropanol **2h** as a substrate. The experiment in the entry 28 was carried out under argon, while entry 29 was carried out under air.

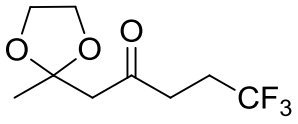
The reaction given in the entry 26 was performed employing 55 mg (0.55 mmol) of cyclopropanol **2a**, 200 mg (0.61 mmol) of the reagent **3**, 1.0 mg (1 mol.%) of $CuCl_2 \cdot 2H_2O$ and 13 mg (0.30 mmol) of LiCl in 2 mL of methanol as described above. Volatile 1,1,1-trifluoroheptan-4-on (**1a**) was isolated in 52% yield (48 mg) according to the following procedure: the reaction mixture was diluted with water (2 mL) and extracted with pentane (4 × 2 mL). After the solvent evaporation, the residue was subjected to silica gel column chromatography (eluent – pentane/diethyl ether, 20:1). A colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (m, 2H), 2.47–2.37 (m, 4H), 1.63 (hex, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.26, 127.12 (q, *J* = 275.7 Hz), 44.84, 35.02 (q, *J* = 2.5 Hz), 28.03 (q, *J* = 29.8 Hz), 17.37, 13.79. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.63 (t, *J* = 10.9 Hz). IR (film): ν = 2968, 1722, 1143. HRMS (APPI) calcd. for $C_7H_{12}F_3O$ $[M+H]^+$ 169.0835, found m/z 169.0834.

III. Synthesis and Characterization of β-Trifluoromethyl Ketones

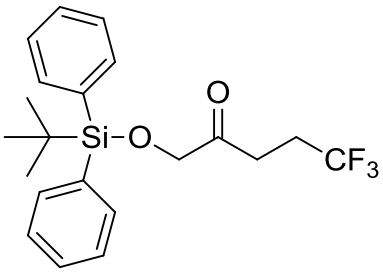
General procedure: A 25 mL round-bottomed flask was charged with CuCl (3 mg, 0.03 mmol, 3 mol.%), LiCl (42.5 mg, 1 mmol), closed with a rubber septum and flushed with argon. Methanol (1 mL) was added and the mixture was stirred for 10 min to produce a clear colourless solution. Then a solution of cyclopropanol **2** (1 mmol) and reagent **3** (363 mg, 1.1 mmol) in methanol (3 mL) was added via syringe. At this point the reaction mixture usually warms up and attains pale-blue color which disappears within 10-15 min. The solution was stirred until the reaction is completed (usually within 1 h; if necessary, the reaction mixture could be kept overnight without the change in yields) and then diluted with water (10 mL). The water phase was extracted with CH_2Cl_2 (4 × 5 mL), washed with brine and dried ($MgSO_4$). The solvent was evaporated and β-trifluoromethyl ketones **1** were isolated by silica gel column chromatography.



5,5,5-Trifluoro-1-phenylpentan-2-one (1b). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless solid. Yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 3H), 7.22–7.18 (m, 2H), 3.73 (s, 2H), 2.71 (m, 2H), 2.43–2.31 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.72, 133.61, 129.47, 129.07, 127.50, 127.00 (q, *J* = 275.7 Hz), 50.19, 34.33 (q, *J* = 2.6 Hz), 28.09 (q, *J* = 29.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.58 (t, *J* = 10.9 Hz). IR (neat): ν = 1721, 1257, 1143, 701. HRMS (APPI) calcd. for $C_{11}H_{10}F_3O$ $[M-H]^-$ 215.0689, found m/z 215.0685.

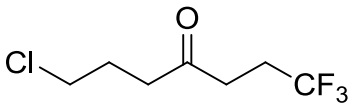


5,5,5-Trifluoro-1-(2-methyl-1,3-dioxolan-2-yl)pentan-2-one (1c). Column chromatography eluent – petroleum ether/ethyl acetate, 10:1. A colourless liquid. Yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02–3.94 (m, 4H), 2.82–2.78 (m, 4H), 2.46–2.34 (m, 2H), 1.40 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.07, 127.12 (q, *J* = 275.6 Hz), 107.88, 64.80, 51.92, 36.71 (q, *J* = 2.6 Hz), 27.95 (q, *J* = 29.8 Hz), 24.55. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.55 (t, *J* = 10.9 Hz). IR (neat): ν = 2988, 1719, 1259, 1141. HRMS (APCI) calcd. for $C_9H_{12}F_3O_3$ $[M-H]^-$ 225.0744, found m/z 225.0744.

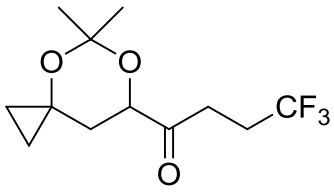


1-((*tert*-Butyldiphenylsilyl)oxy)-5,5,5-trifluoropentan-2-one (1d). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.62 (m, 4H), 7.48–7.38 (m, 6H), 4.20 (s, 2H), 2.83 (m, 2H), 2.44–2.32 (m, 2H), 1.11 (m, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.33, 135.64, 132.44, 130.28, 128.10, 127.08 (q, *J* = 275.7 Hz), 69.70, 31.51 (q, *J* = 2.8 Hz), 27.65 (q, *J* = 30.0 Hz), 26.88, 19.34. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.68 (t,

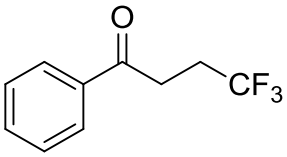
J = 10.8 Hz). IR (neat): ν = 1730, 1258, 1113, 703. HRMS (APCI) calcd. for $C_{21}H_{24}F_3O_2Si$ $[M-H]^-$ 393.1503, found m/z 393.1500.



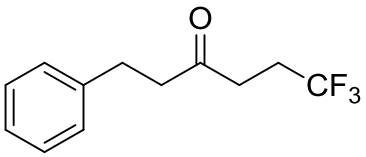
7-Chloro-1,1,1-trifluoroheptan-4-one (1e). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, J = 6.2 Hz, 2H), 2.71 (m, 2H), 2.66 (t, J = 7.0 Hz, 2H), 2.48–2.36 (m, 2H), 2.07 (quint, J = 6.8 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 205.93, 127.00 (q, J = 275.7 Hz), 44.35, 39.45, 35.22 (q, J = 2.6 Hz), 28.00 (q, J = 29.9 Hz), 26.24. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.65 (t, J = 10.9 Hz). IR (neat): ν = 1722, 1147. Anal. calcd. for $C_7H_{10}ClF_3O$: C 41.50, H 4.97%; found: C 41.19, H, 5.01%. GC-MS m/z 202 (M^+), 204 (M^+).



1-(5,5-Dimethyl-4,6-dioxaspiro[2.5]octan-7-yl)-4,4,4-trifluorobutan-1-one (1f). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless solid. Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.51 (dd, J = 12.0, 3.1 Hz, 1H), 2.98 (dt, J = 19.3, 7.8 Hz, 1H), 2.87 (dt, J = 19.3, 7.3 Hz, 1H), 2.47–2.33 (m, 2H), 2.15 (ddd, J = 13.5, 12.0, 1.7 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H), 1.27 (dd, J = 13.5, 3.1 Hz, 1H), 0.87 (dddd, J = 10.8, 6.5, 4.7, 1.7 Hz, 1H), 0.78 (ddd, J = 10.8, 6.5, 5.4 Hz, 1H), 0.66 (ddd, J = 10.4, 6.5, 4.7 Hz, 1H), 0.46 (ddd, J = 10.4, 6.5, 5.4 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.78, 127.16 (q, J = 275.7 Hz), 100.74, 74.25, 53.64, 33.47, 30.71 (q, J = 2.7 Hz), 29.77, 27.56 (q, J = 30.0 Hz), 21.10, 14.60, 10.18. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.54 (t, J = 10.9 Hz). IR (KBr): ν = 3095, 3013, 1725, 1199, 1155, 1122, 971. HRMS (APCI) calcd. for $C_{12}H_{16}F_3O_3$ $[M-H]^-$ 265.1057, found m/z 265.1066.

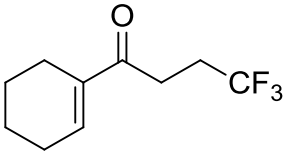


4,4,4-Trifluoro-1-phenylbutan-1-one (1g). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless solid. Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.95 (m, 2H), 7.63–7.58 (m, 1H), 7.51–7.47 (m, 2H), 3.26 (m, 2H), 2.66–2.54 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 196.46, 136.24, 133.75, 128.92, 128.15, 127.30 (q, J = 275.7 Hz), 31.37 (q, J = 2.7 Hz), 28.50 (q, J = 29.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.43 (t, J = 10.8 Hz). IR (KBr): ν = 1686, 1335, 1140, 750. HRMS (APPI) calcd. for $C_{10}H_8F_3O$ $[M-H]^-$ 201.0533, found m/z 201.0532.

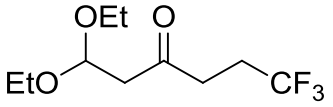


6,6,6-Trifluoro-1-phenylhexan-3-one (1h). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 2H), 7.22–7.16 (m, 3H), 2.92 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 2.64 (m,

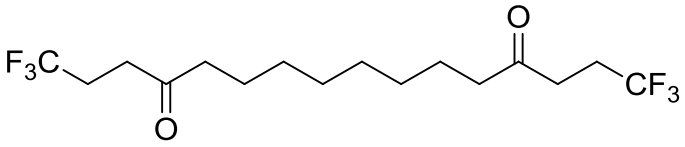
2H), 2.45–2.33 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 206.23, 140.68, 128.72, 128.40, 127.03 (q, *J* = 275.7 Hz), 126.44, 44.39, 35.31 (q, *J* = 2.6 Hz), 29.82, 27.99 (q, *J* = 29.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.63 (t, *J* = 10.9 Hz). IR (neat): ν = 1721, 1256, 1145, 701. HRMS (APPI) calcd. for $C_{12}H_{12}F_3O$ $[M-H]^-$ 229.0846, found m/z 229.0846.



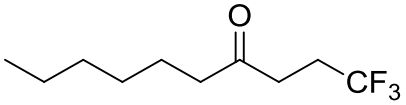
1-(Cyclohex-1-en-1-yl)-4,4,4-trifluorobutan-1-one (1i). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (m, 1H), 2.91 (m, 2H), 2.50–2.38 (m, 2H), 2.31–2.20 (m, 4H), 1.69–1.58 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.36, 140.90, 138.95, 127.40 (q, *J* = 275.7 Hz), 29.70 (q, *J* = 2.6 Hz), 28.67 (q, *J* = 29.5 Hz), 26.24, 23.25, 21.98, 21.62. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.51 (t, *J* = 11.0 Hz). IR (neat): ν = 2937, 1672, 1138. HRMS (APPI) calcd. for $C_{10}H_{14}F_3O$ $[M+H]^+$ 207.0991, found m/z 207.0992.



1,1-Diethoxy-6,6,6-trifluorohexan-3-one (1j). Column chromatography eluent – petroleum ether/acetone, 20:1. A colourless liquid. Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.87 (t, *J* = 5.6 Hz, 1H), 3.71–3.63 (m, 2H), 3.56–3.49 (m, 2H), 2.77–2.74 (m, 4H), 2.46–2.34 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.32, 127.05 (q, *J* = 275.6 Hz), 99.96, 62.64, 47.69, 36.47 (q, *J* = 2.6 Hz), 27.80 (q, *J* = 29.9 Hz), 15.31. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.65 (t, *J* = 10.9 Hz). IR (neat): ν = 2980, 1723, 1257, 1137, 1062. HRMS (APPI) calcd. for $C_{10}H_{16}F_3O_3$ $[M-H]^-$ 241.1057, found m/z 241.1051.

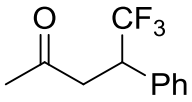


1,1,1,16,16,16-Hexafluorohexadecane-4,13-dione (1k). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless solid. Yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (m, 4H), 2.49–2.33 (m, 8H), 1.65–1.53 (m, 4H), 1.33–1.20 (m, 8H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.33, 127.12 (q, *J* = 275.7 Hz), 42.91, 35.01 (q, *J* = 2.6 Hz), 29.26, 29.17, 28.05 (q, *J* = 29.8 Hz), 23.81. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.63 (t, *J* = 10.8 Hz). IR (KBr): ν = 2933, 2852, 1706, 1327, 1250, 1152. HRMS (APCI) calcd. for $C_{16}H_{23}F_6O_2$ $[M-H]^-$ 361.1608, found m/z 361.1604.

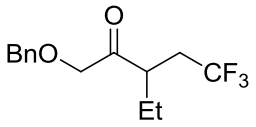


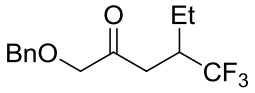
1,1,1-Trifluorodecan-4-one (1l). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (m, 2H), 2.46–2.35 (m, 4H), 1.66–1.53 (m, 2H), 1.37–1.23 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.41, 127.13 (q, *J* = 275.7 Hz), 42.99, 34.99 (q, *J* = 2.6 Hz), 31.68, 28.96, 28.06 (q, *J* = 29.7 Hz), 23.88, 22.61,

14.15. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.65 (t, *J* = 10.9 Hz). IR (neat): ν = 2933, 1723, 1144. HRMS (APPI) calcd. for $C_{10}H_{18}F_3O$ $[M+H]^+$ 211.1304, found m/z 211.1308.

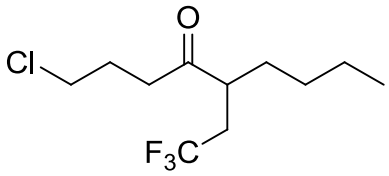


5,5,5-Trifluoro-4-phenylpentan-2-one (1m). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless solid. Yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.29 (m, 5H), 4.01 (m, 1H), 3.14–3.02 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 203.81, 134.54 (q, *J* = 1.8 Hz), 129.08, 128.86, 128.50, 126.83 (q, *J* = 279.4 Hz), 44.72 (q, *J* = 27.6 Hz), 43.13 (q, *J* = 1.8 Hz), 30.55. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -69.97 (d, *J* = 9.6 Hz). IR (film): ν = 1717, 1252, 1105, 701. HRMS (APPI) calcd. for $C_{11}H_{10}F_3O$ $[M-H]^-$ 215.0689, found m/z 215.0695.



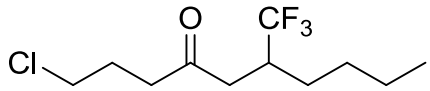


1-(Benzyloxy)-3-ethyl-5,5,5-trifluoropentan-2-one (1na) and 1-(benzyloxy)-4-(trifluoromethyl)hexan-2-one (1nb). The reaction was performed twice: with the racemic *cis*-**2n** and the enantiomerically enriched (66% ee) cyclopropanol (1*S*,2*S*)-**2n**. 1.35 equiv. of Togni reagent **3** was used to achieve full conversion of the starting material. The ratio of the products is **1na**:**1nb** = 55:45 according to ^{19}F and ^{1}H NMR spectroscopy. The mixture of ketones **1na**, **1nb** was isolated by column chromatography (eluent – petroleum ether/diethyl ether, 20:1). A colourless liquid. Yield 50%. The analysis of the enantiomeric composition was made by HPLC using Phenomenex Lux 3μ Amylose-2 column (95:5 *n*-hexane/2-propanol, flow rate 1.0 mL·min^{-1}, detection at 210 nm). $[\alpha]_D^{25}$ = −20.5 (*c* 0.57, hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5H), 4.64–4.57 (m, 2H), 4.14 (s, 1.1H), 4.07 (s, 0.9H), 2.99 (m, 0.55H), 2.86–2.52 (m, 1.9H), 2.11 (m, 0.55H), 1.75–1.65 (m, 1H), 1.57–1.37 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 1.3H), 0.90 (t, *J* = 7.5 Hz, 1.7H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.14, 205.72, 137.16, 137.03, 128.74, 128.69, 128.32, 128.22, 128.09, 128.03, 126.66 (q, *J* = 276.6 Hz), 75.15, 74.80, 73.66, 73.50, 42.28 (q, *J* = 2.3 Hz), 38.96 (q, *J* = 26.1 Hz), 37.30 (q, *J* = 2.3 Hz), 34.05 (q, *J* = 28.6 Hz), 25.13, 21.70, 21.67, 11.32, 11.09. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.92 (t, *J* = 11.0 Hz), -70.86 (d, *J* = 9.0 Hz). IR (neat): ν = 2971, 1734, 1264, 1122, 741. HRMS (APPI) calcd. for $C_{14}H_{16}F_3O_2$ $[M-H]^-$ 273.1108, found m/z 273.1103.



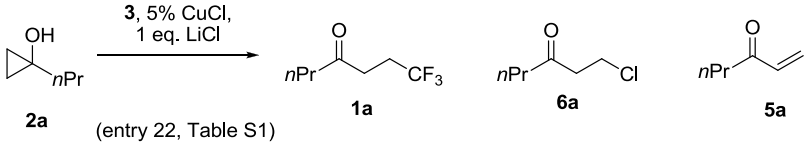
1-Chloro-5-(2,2,2-trifluoroethyl)nonan-4-one (1oa). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, *J* = 6.3 Hz, 2H), 2.88–2.58 (m, 4H), 2.16–2.02 (m, 3H), 1.68–1.59 (m, 1H), 1.49–1.37 (m, 1H), 1.32–1.17 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 210.51, 126.66 (q, *J* = 276.8 Hz), 45.25 (q, *J* = 2.2 Hz), 44.36, 39.54, 34.80 (q, *J* = 28.6 Hz), 32.03, 28.95, 26.14, 22.67, 13.92. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -65.00

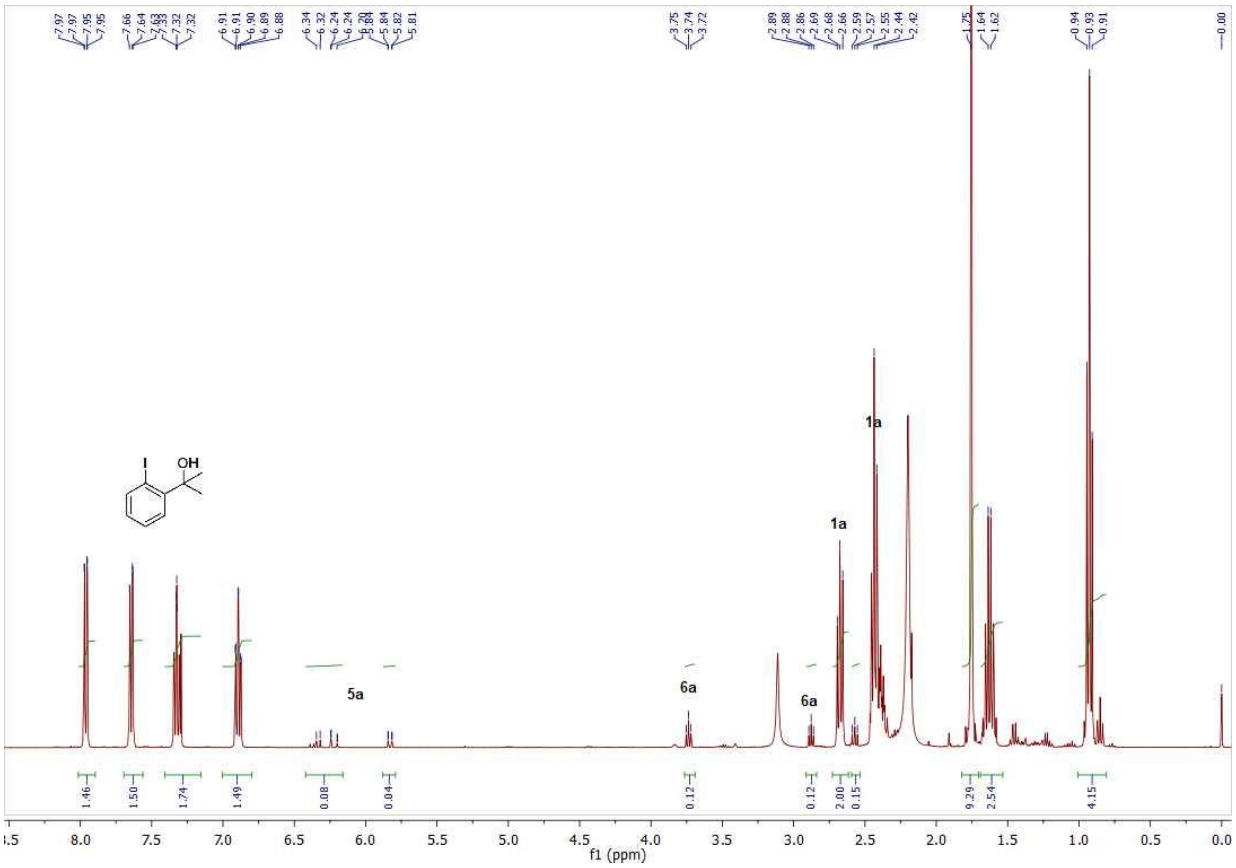
(t, *J* = 10.9 Hz). IR (neat): ν = 2961, 1719, 1257, 1155, 1131. HRMS (APPI) calcd. for $C_{11}H_{19}ClF_3O$ $[M+H]^+$ 259.1071, found m/z 259.1066.



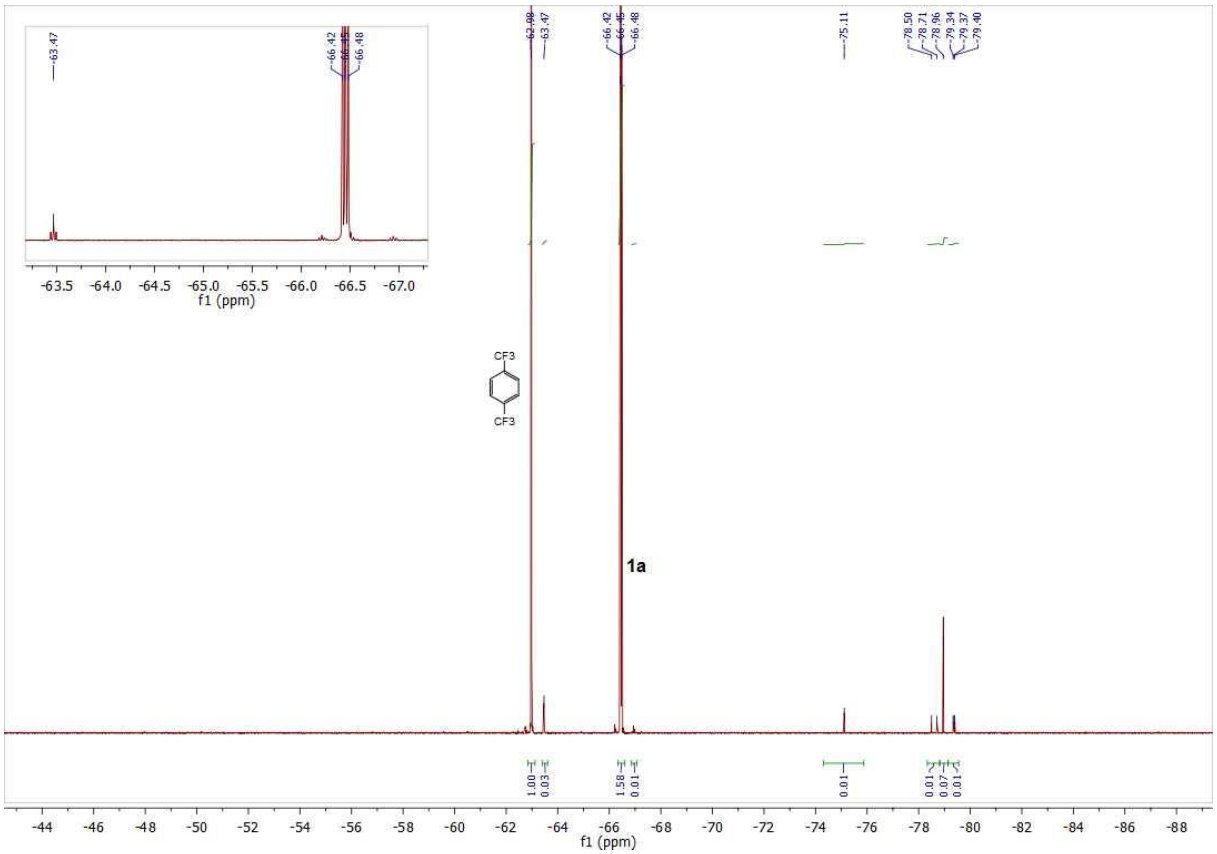
1-Chloro-6-(trifluoromethyl)decan-4-one (1ob). Column chromatography eluent – petroleum ether/diethyl ether, 20:1. A colourless liquid. Yield 12%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, *J* = 6.2 Hz, 2H), 2.84 (m, 1H), 2.73 (dd, *J* = 17.7, 5.4 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.47 (dd, *J* = 17.7, 6.7 Hz, 1H), 2.07 (m, 2H), 1.65 (m, 1H), 1.39–1.19 (m, 5H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 206.18, 128.22 (q, *J* = 279.6 Hz), 44.37, 41.45 (q, *J* = 2.3 Hz), 39.87, 38.09 (q, *J* = 26.1 Hz), 28.97, 28.37 (q, *J* = 2.1 Hz), 26.25, 22.73, 13.94. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -71.11 (d, *J* = 9.4 Hz). IR (neat): ν = 2960, 1722, 1260, 1167, 1131. HRMS (APPI) calcd. for $C_{11}H_{19}ClF_3O$ $[M+H]^+$ 259.1071, found m/z 259.1072.

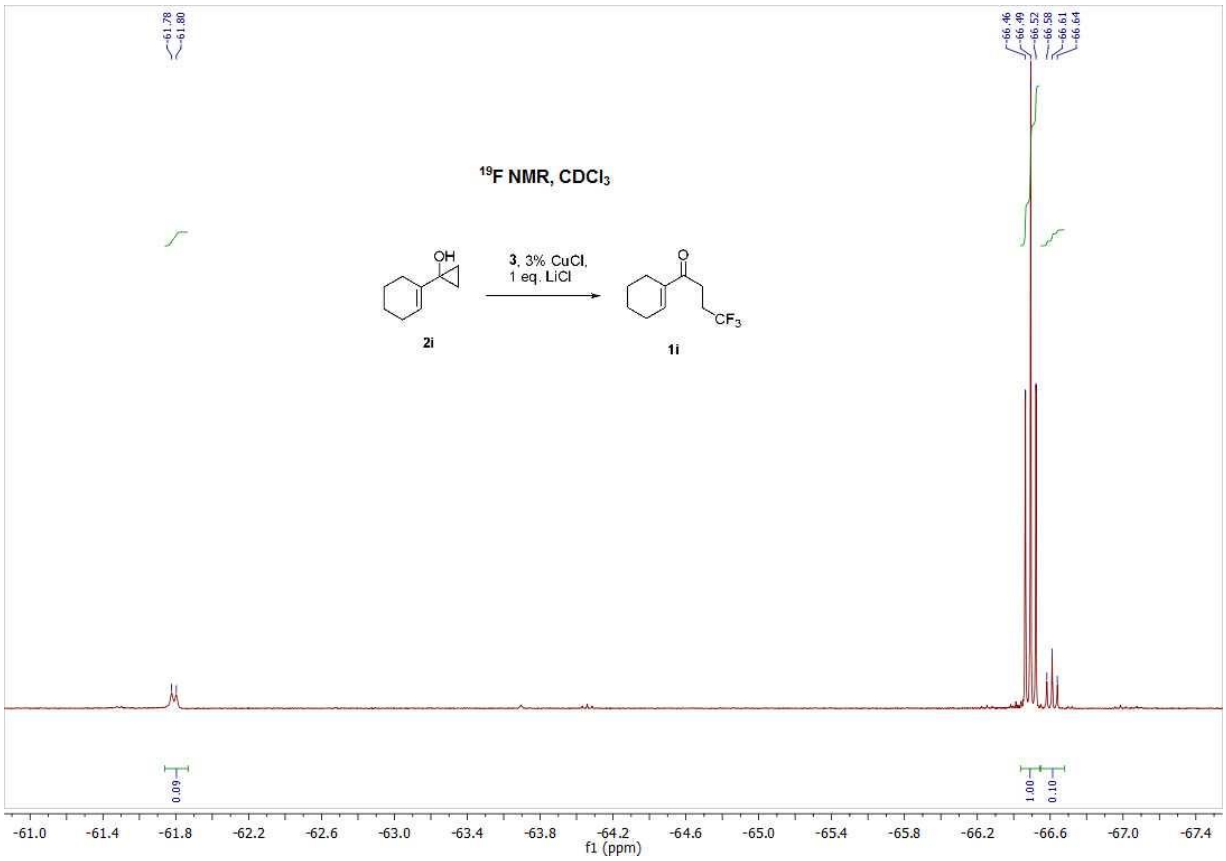
IV. Selected ^{1}H NMR and ^{19}F NMR Spectra of the Reaction Mixtures



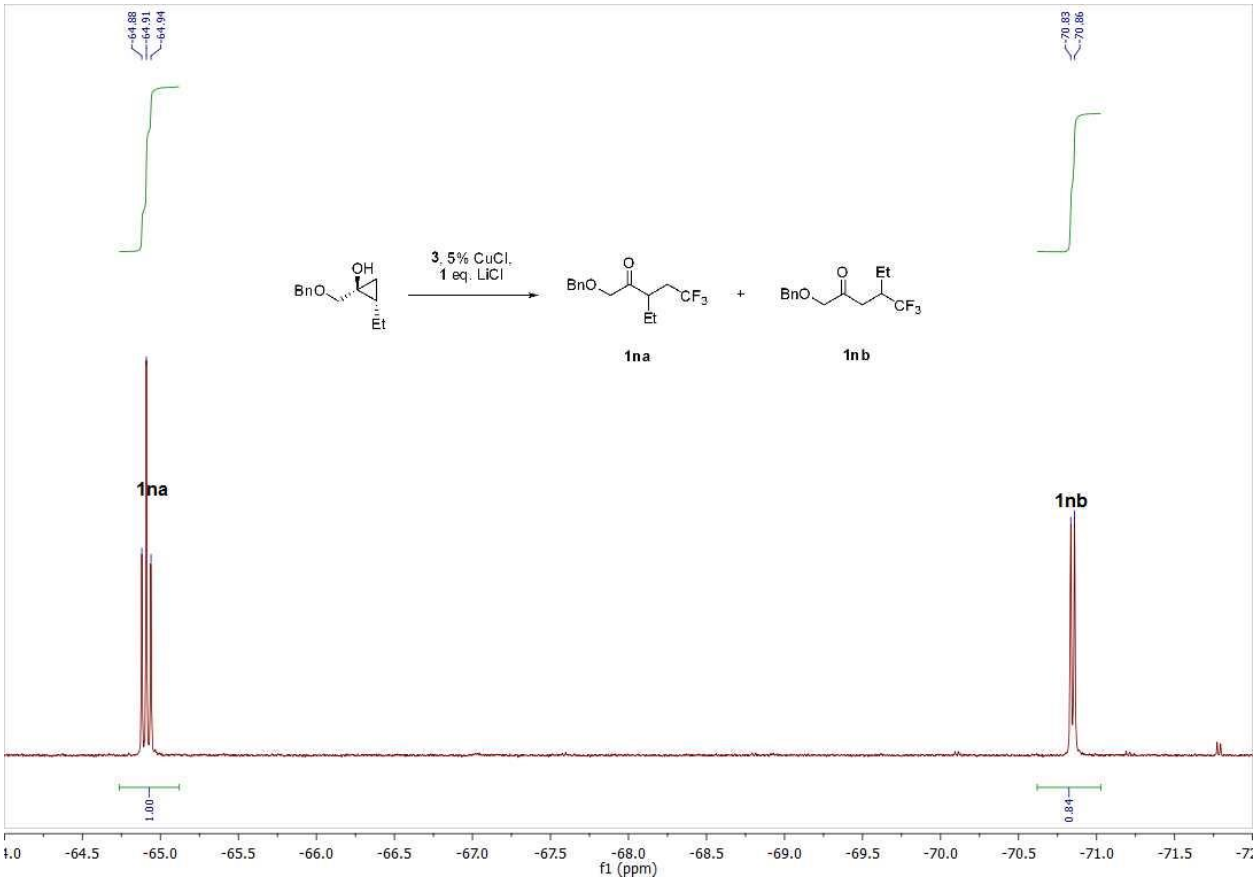


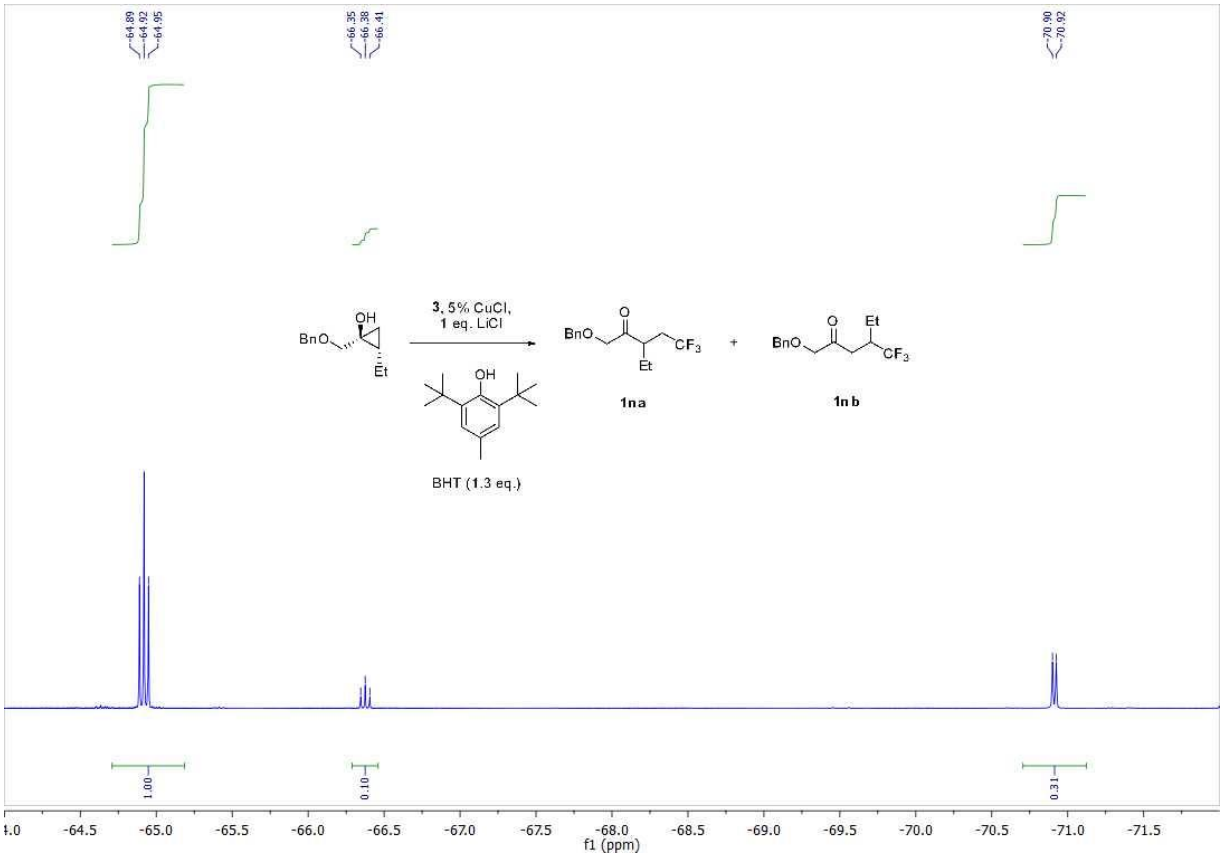
^{19}F NMR, entry 20, CD_3OD



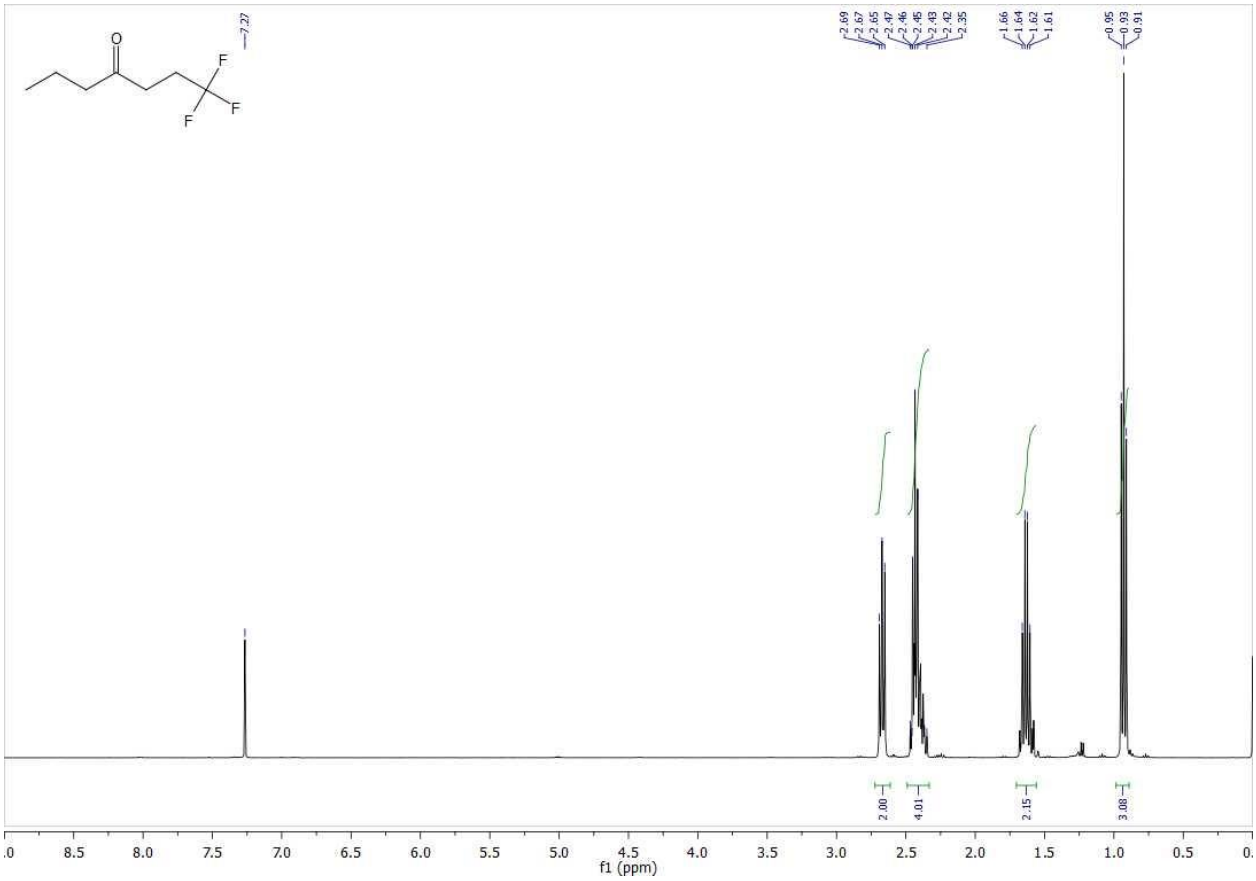


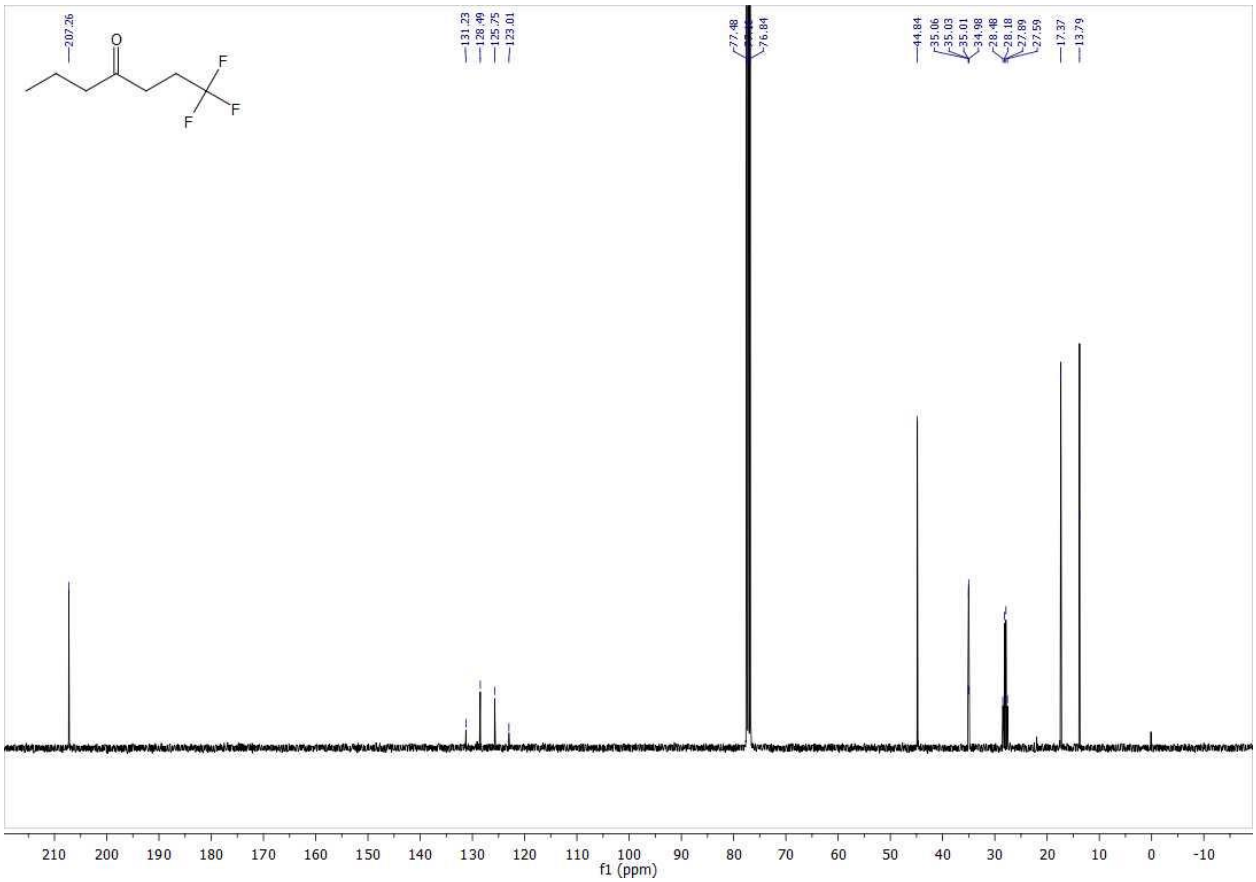
BHT inhibition experiments

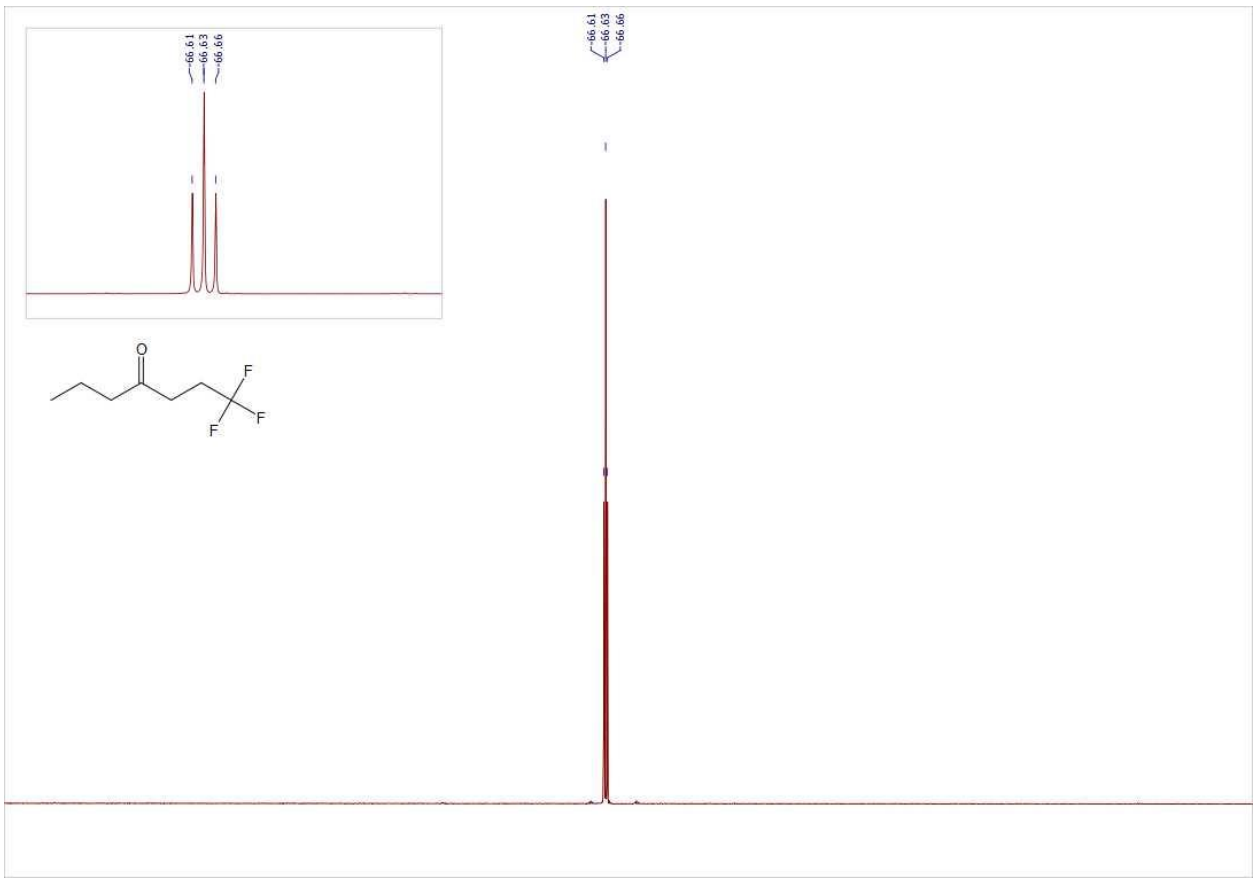


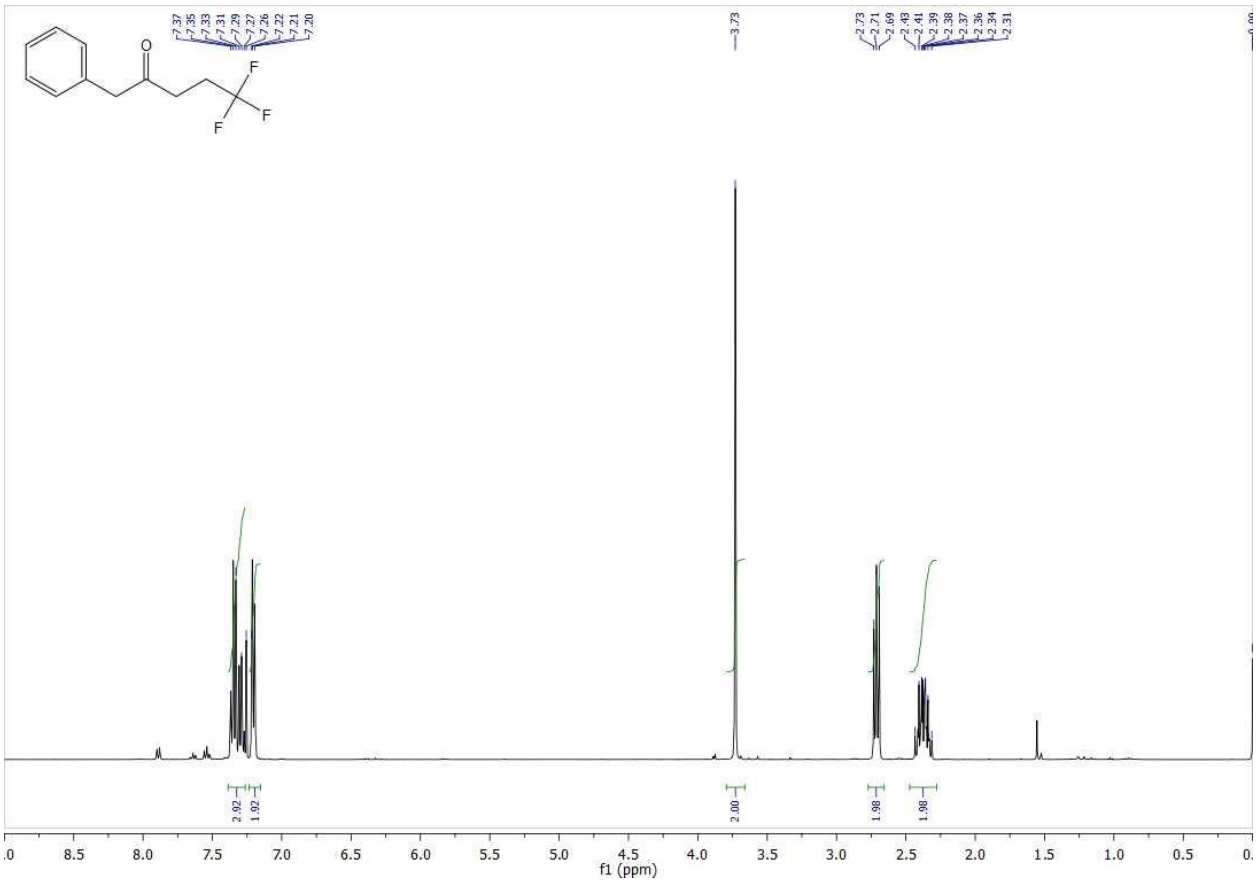


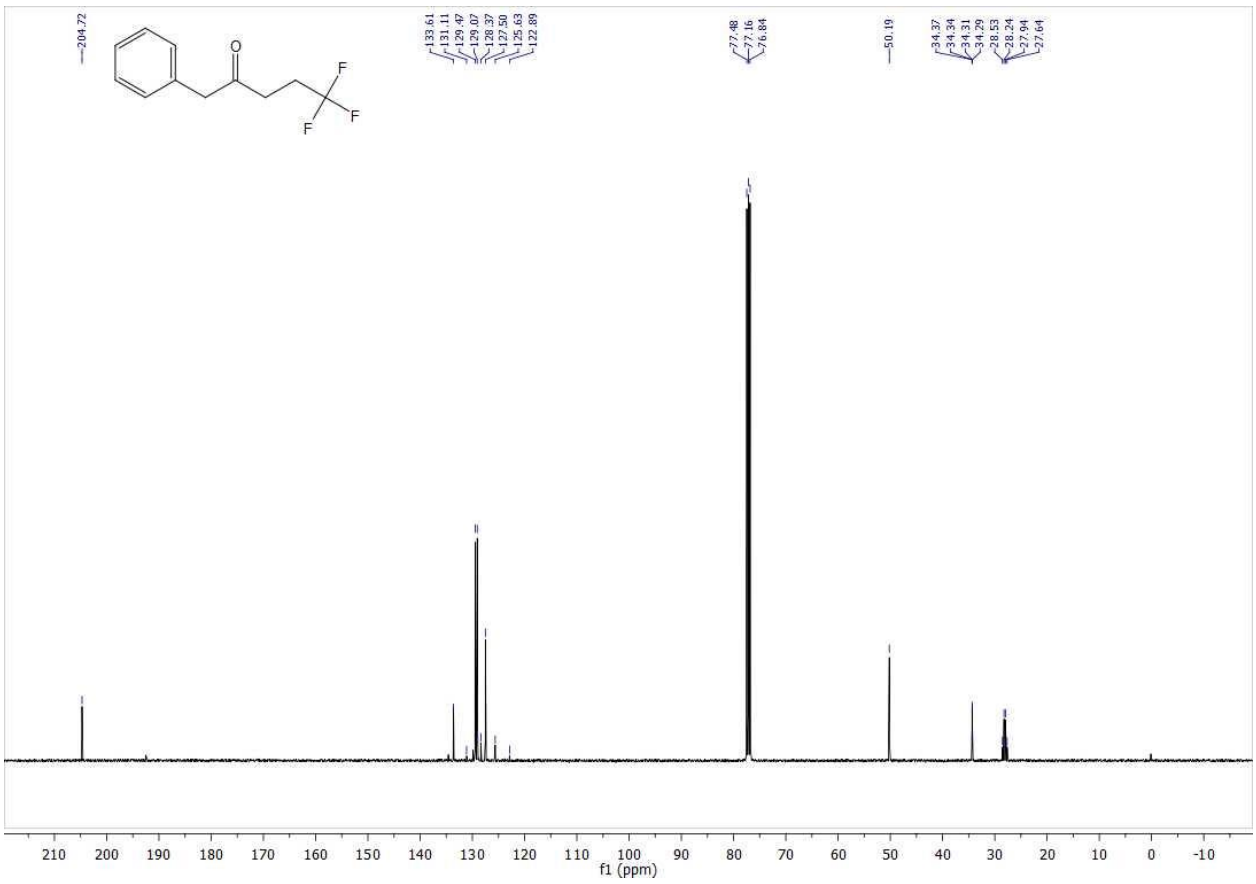
V. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra of β-Trifluoromethyl Ketones

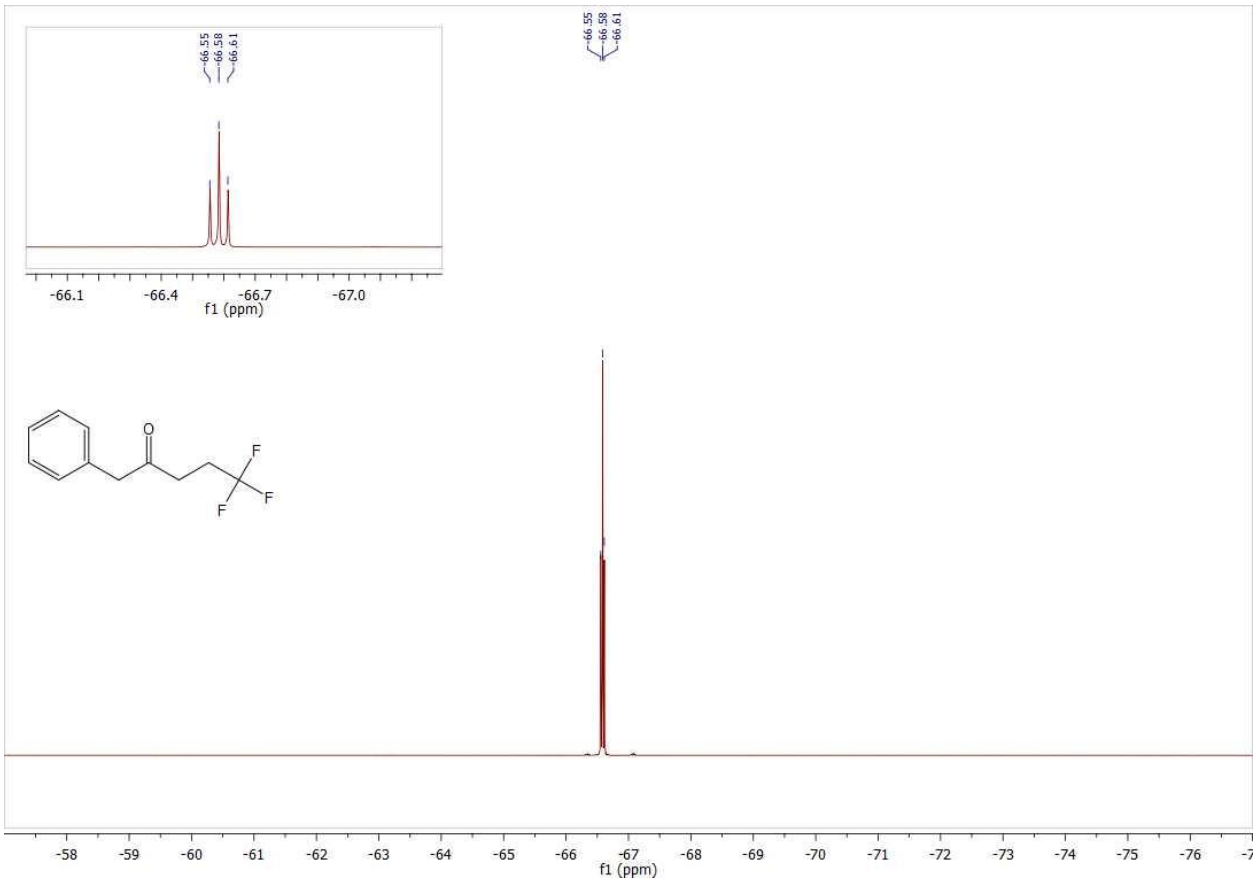





-66.61
-66.63
-66.66
O
F
F
F


7.37
7.35
7.33
7.31
7.29
7.27
7.26
7.22
7.21
7.20
3.73
2.73
2.71
2.69
2.43
2.41
2.39
2.38
2.37
2.36
2.34
2.31
O
F
F
F
2.92
1.92
2.00
1.98
1.98
f1 (ppm)


204.72
133.61
131.11
129.47
129.07
128.37
127.50
125.63
122.89
77.48
77.16
76.84
50.19
34.37
34.34
34.31
34.29
28.53
28.24
27.94
27.64
O
F
F
F
f1 (ppm)


66.55
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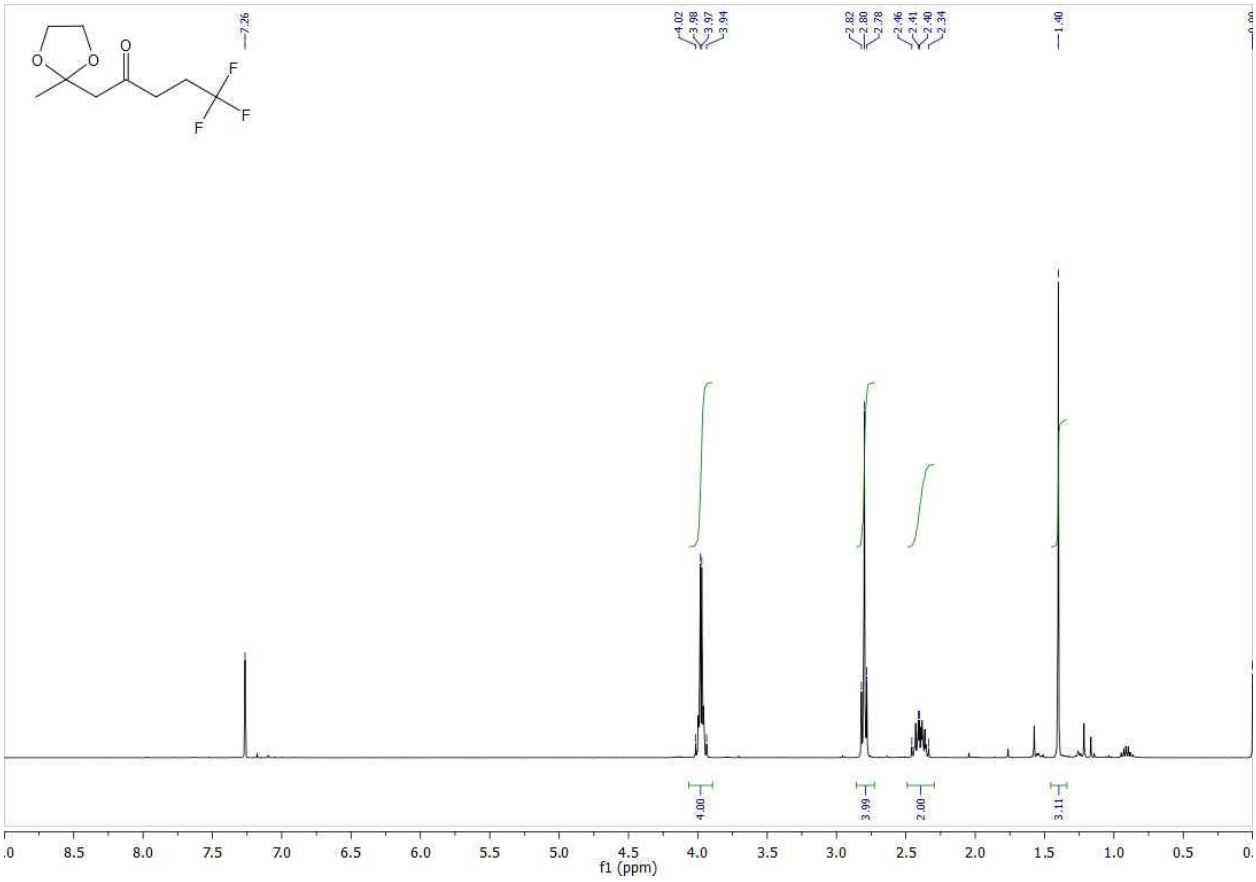
66.61
-66.1
-66.4
-66.7
-67.0
f1 (ppm)
O
F
F
F
f1 (ppm)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4.02
3.98
3.97
3.94
2.82
2.80
2.78
2.46
2.41
2.40
2.34
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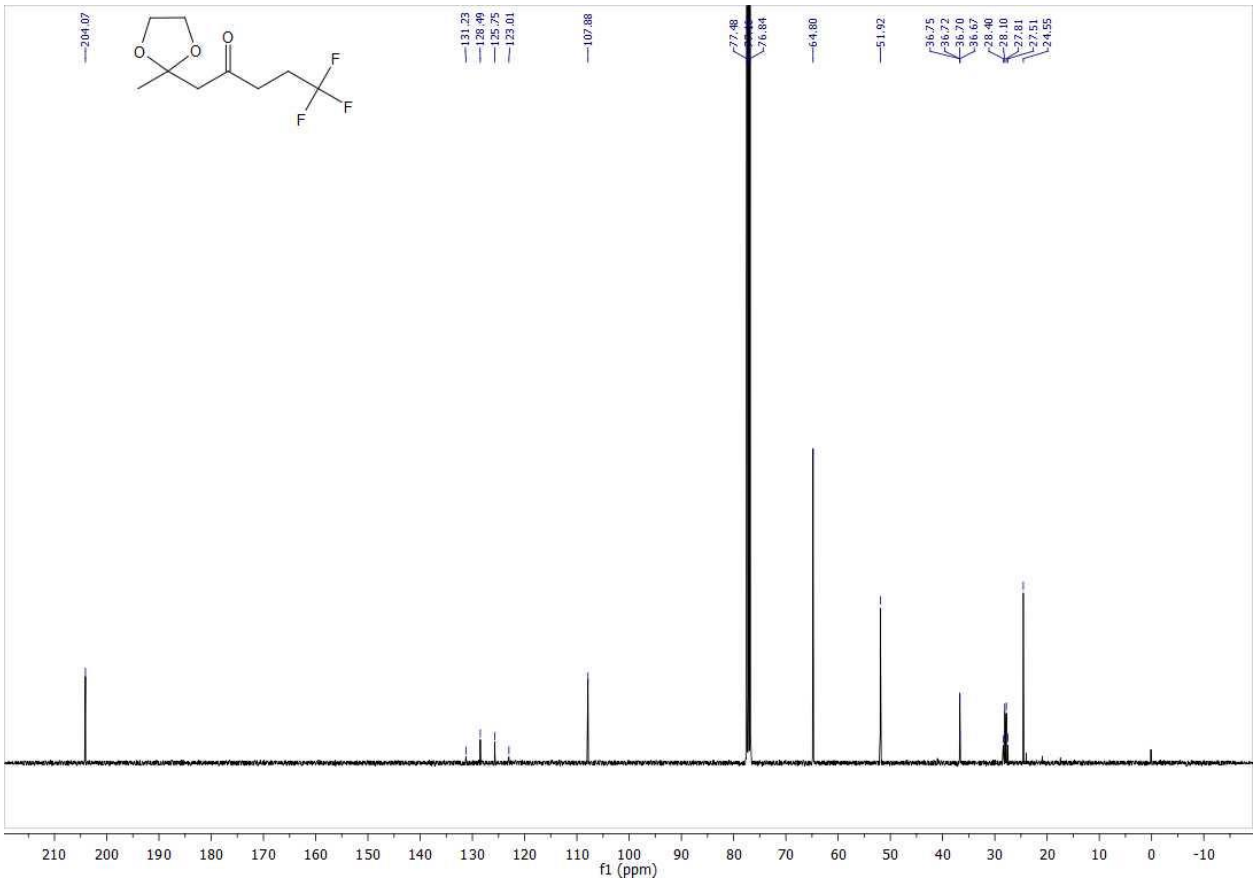
4.00
3.99
2.00
3.11
f1 (ppm)


204.07
131.23
128.49
125.75
123.01
107.88
77.48
76.84
64.80
51.92
36.75
36.72
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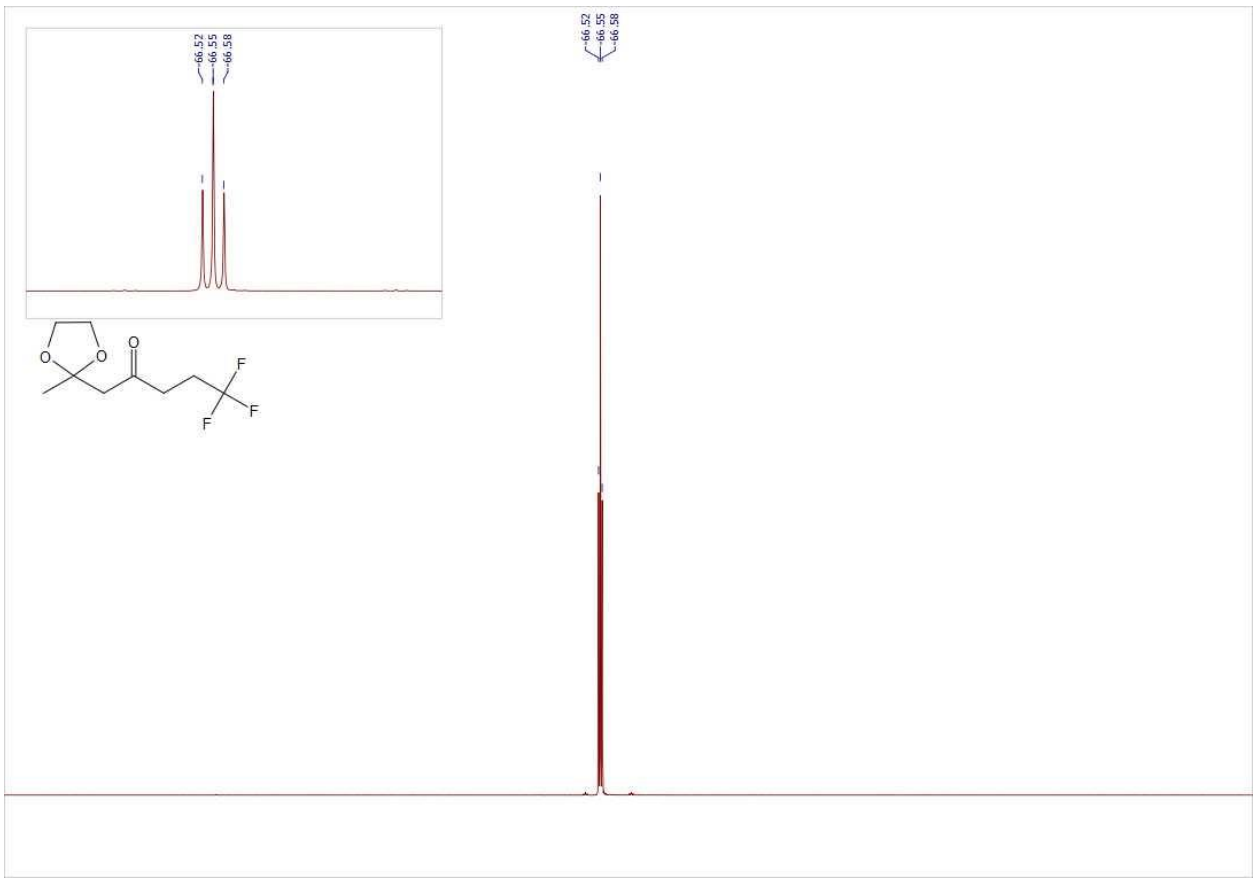
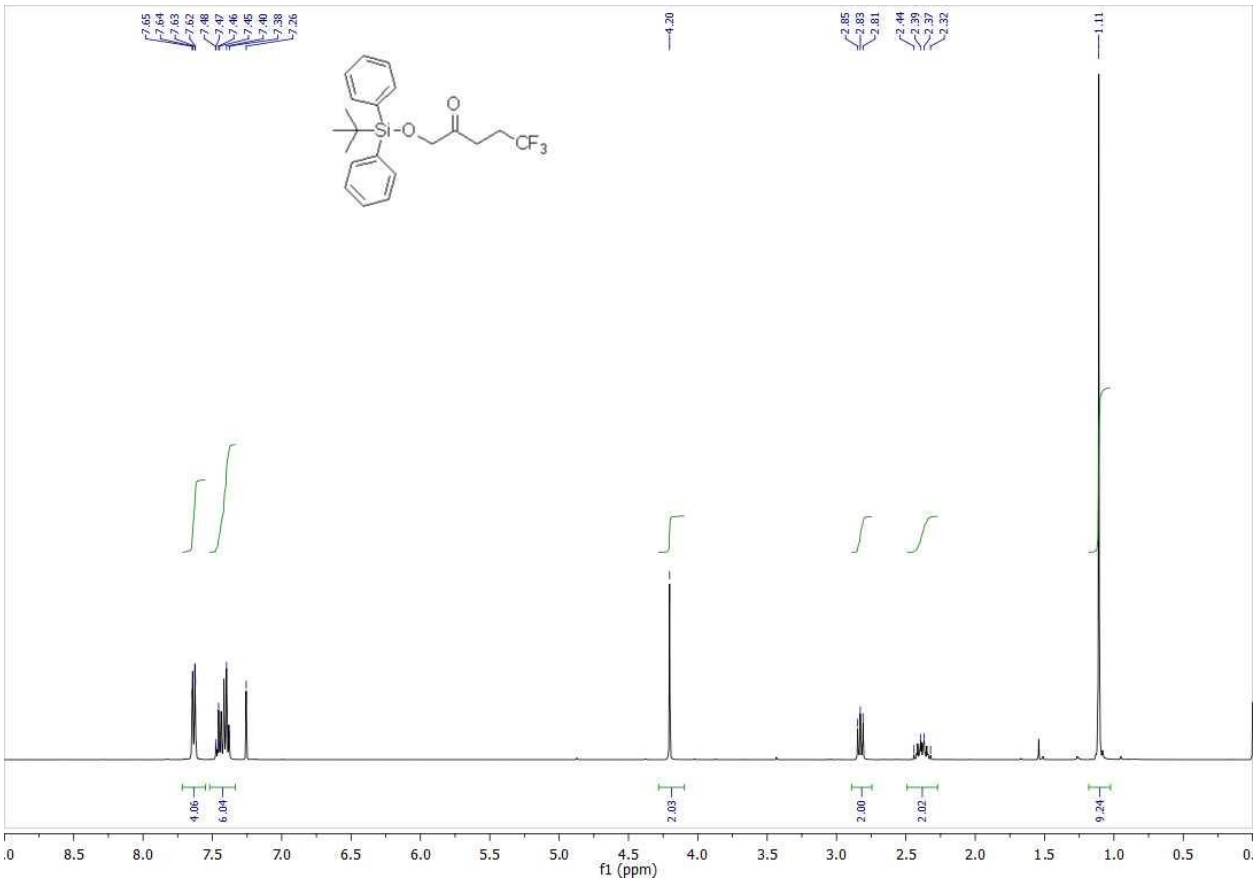
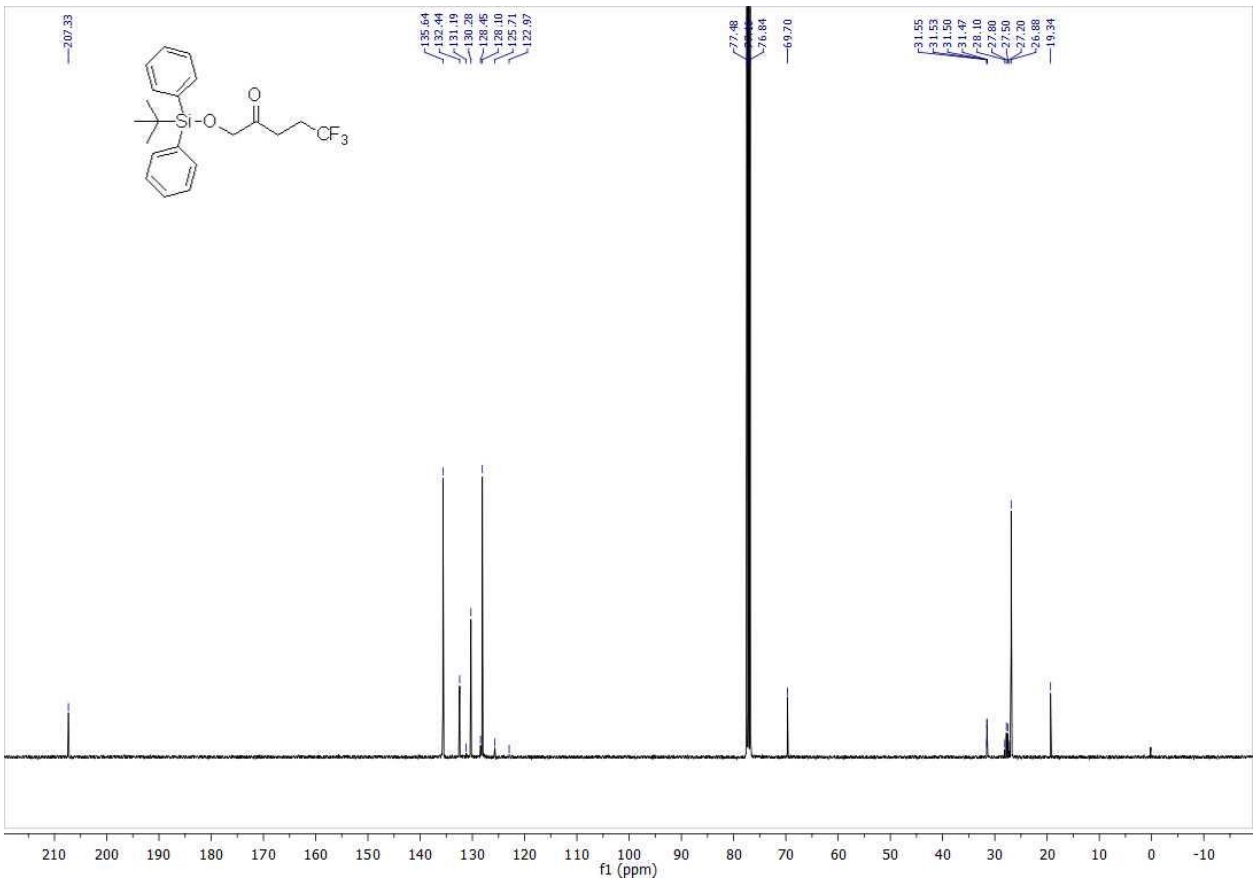
28.40
28.10
27.81
27.51
24.55
f1 (ppm)


-66.52
-66.55
-66.58
O
O
O
F
F
F


7.65
7.64
7.63
7.62
7.48
7.47
7.46
7.45
7.40
7.38
7.26
4.20
2.85
2.83
2.81
2.44
2.39
2.37
2.32
1.11
Si
O
O
CF3
4.06
6.04
2.03
2.00
2.02
9.24
f1 (ppm)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135.64
132.44
131.19
130.28
128.45
128.10
125.71
122.97
77.48
76.84
69.70
31.55
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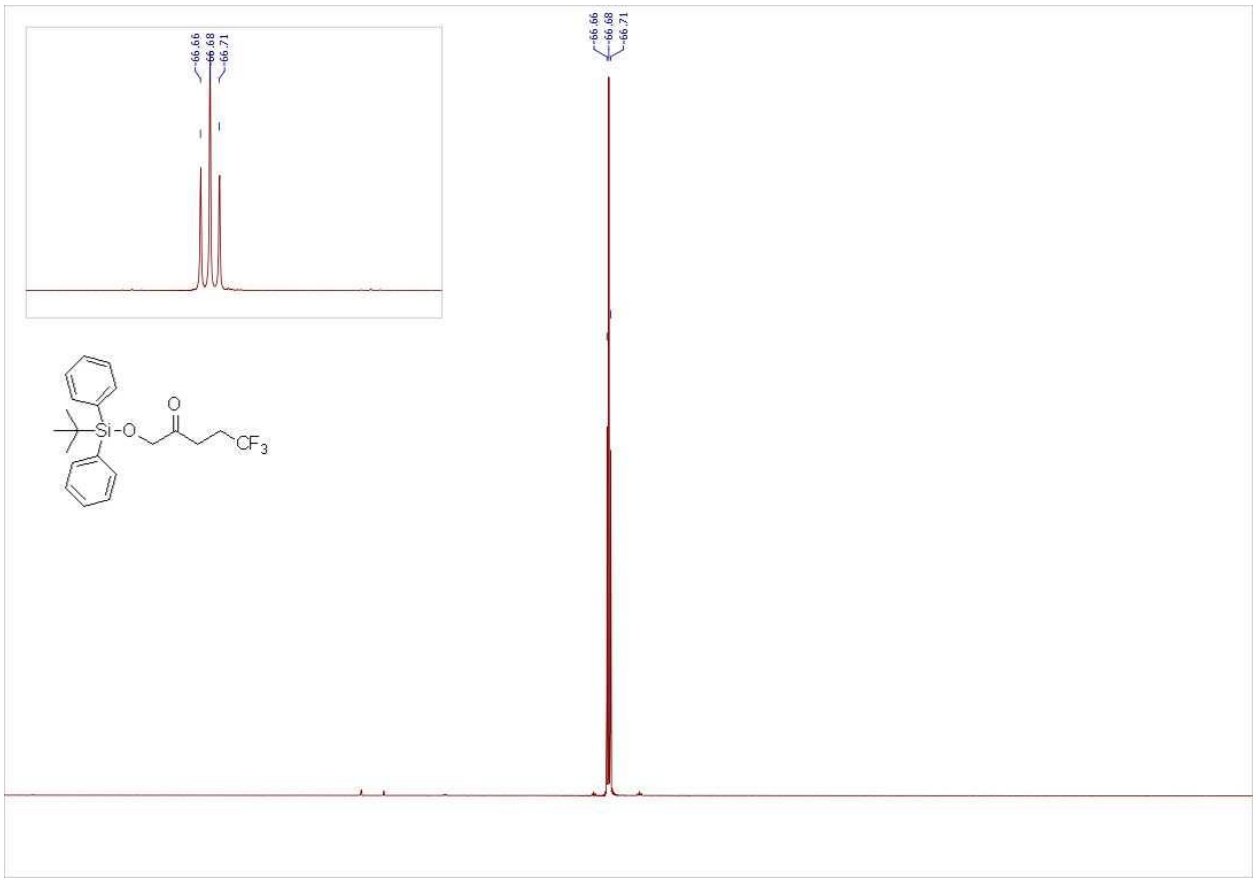
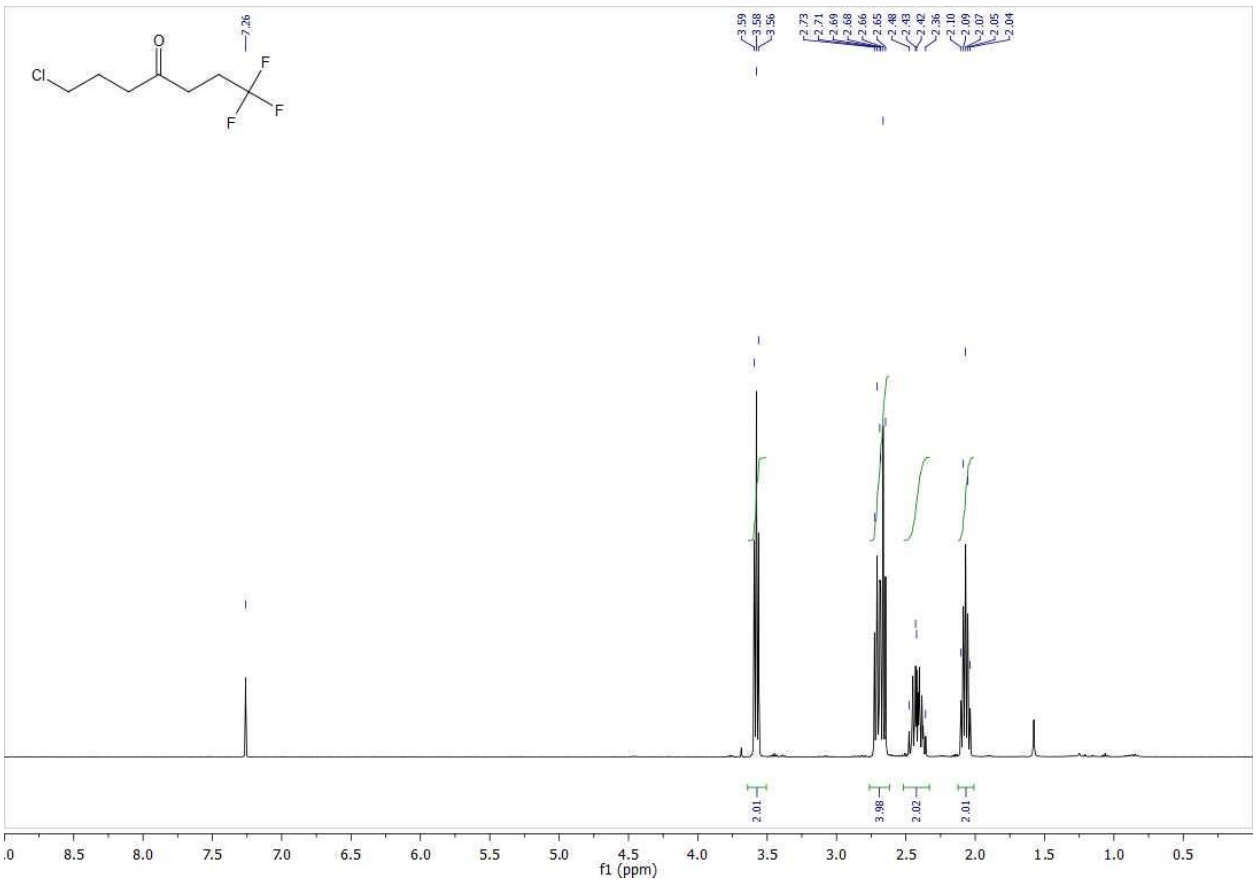
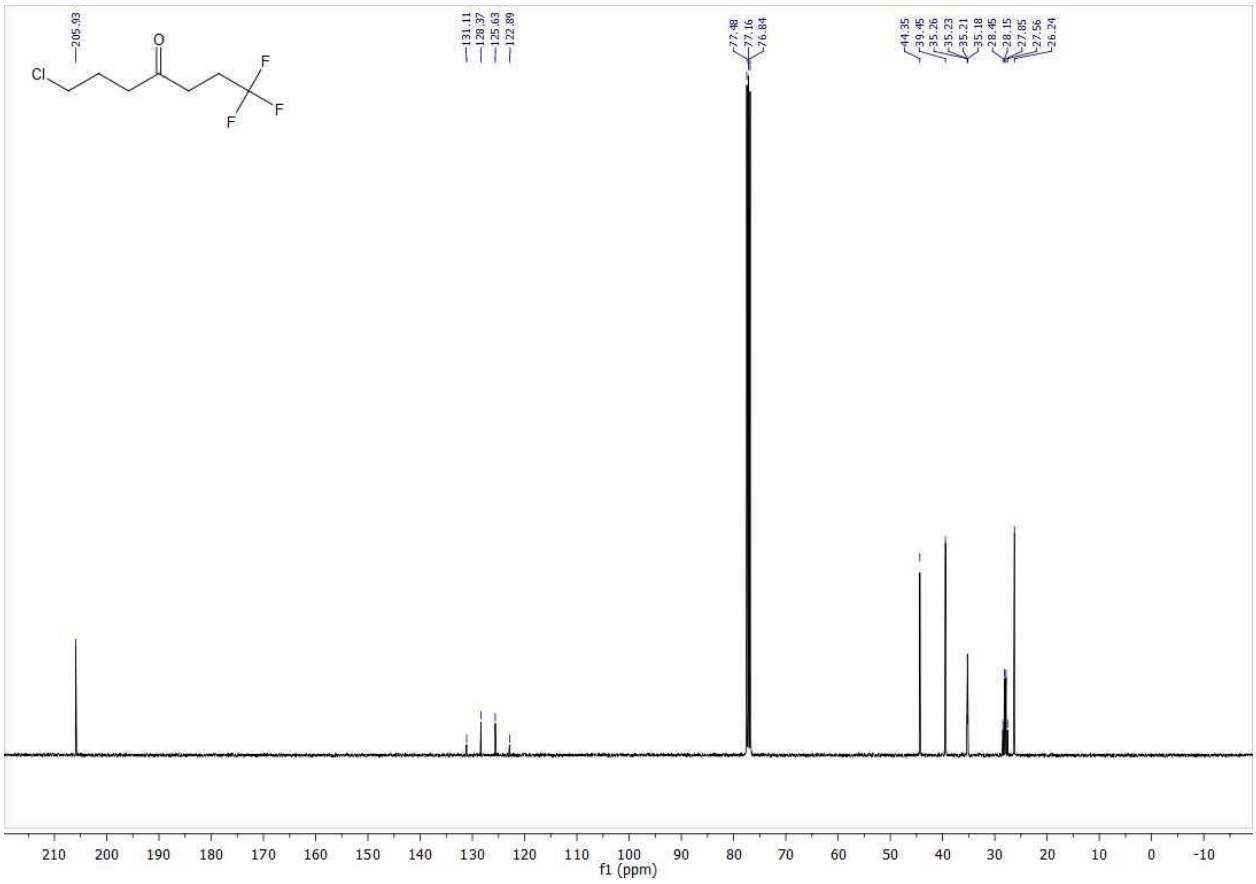
27.20
26.88
19.34
Si
O
CF3
f1 (ppm)


66.66
66.68
66.71
Si
O
CF3


7.26
3.59
3.58
3.56
2.73
2.71
2.69
2.68
2.66
2.65
2.48
2.43
2.42
2.36
2.10
2.09
2.07
2.05
2.04
Cl
O
F
F
F
2.01
3.98
2.02
2.01
f1 (ppm)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76.84
44.35
39.45
35.26
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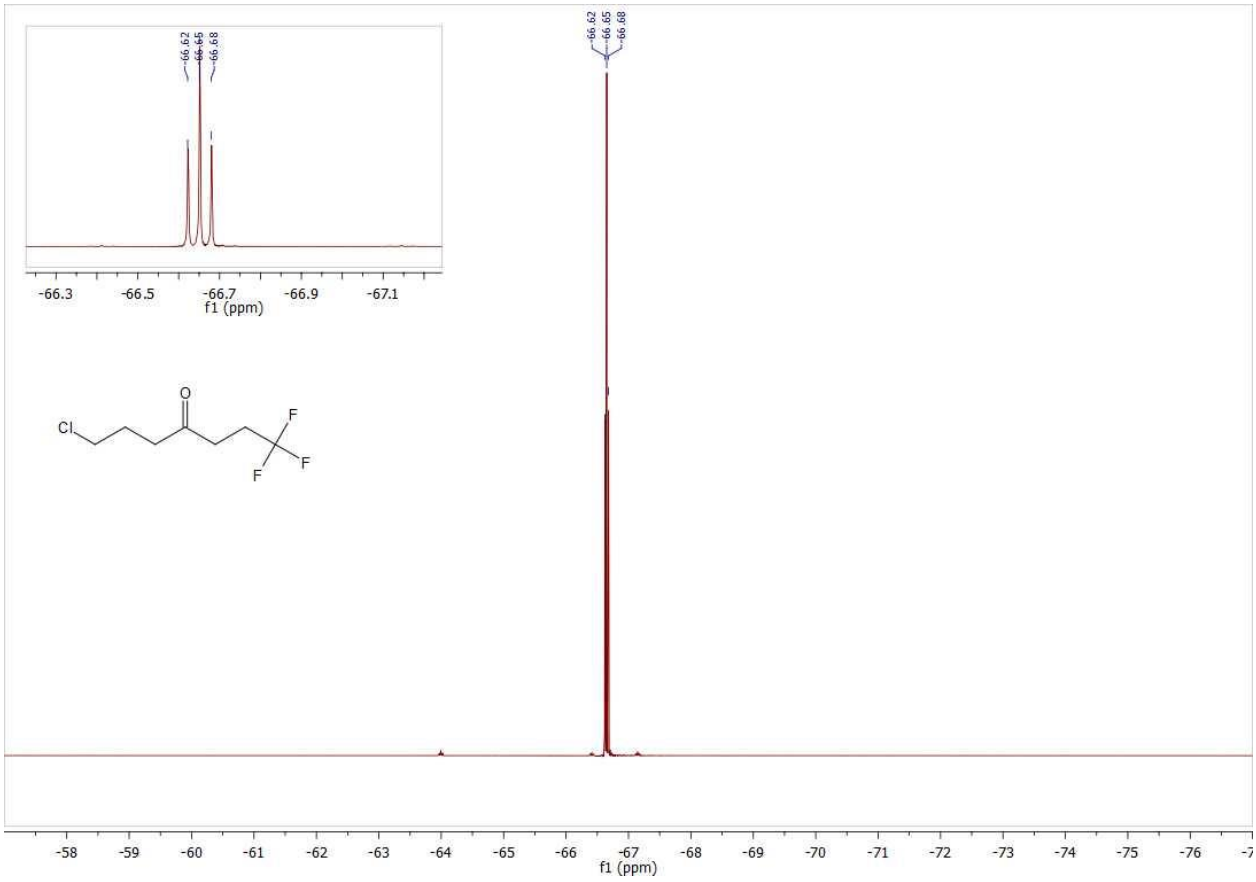
35.18
28.45
28.15
27.85
27.56
26.24
Cl
O
F
F
F
f1 (ppm)


-66.62
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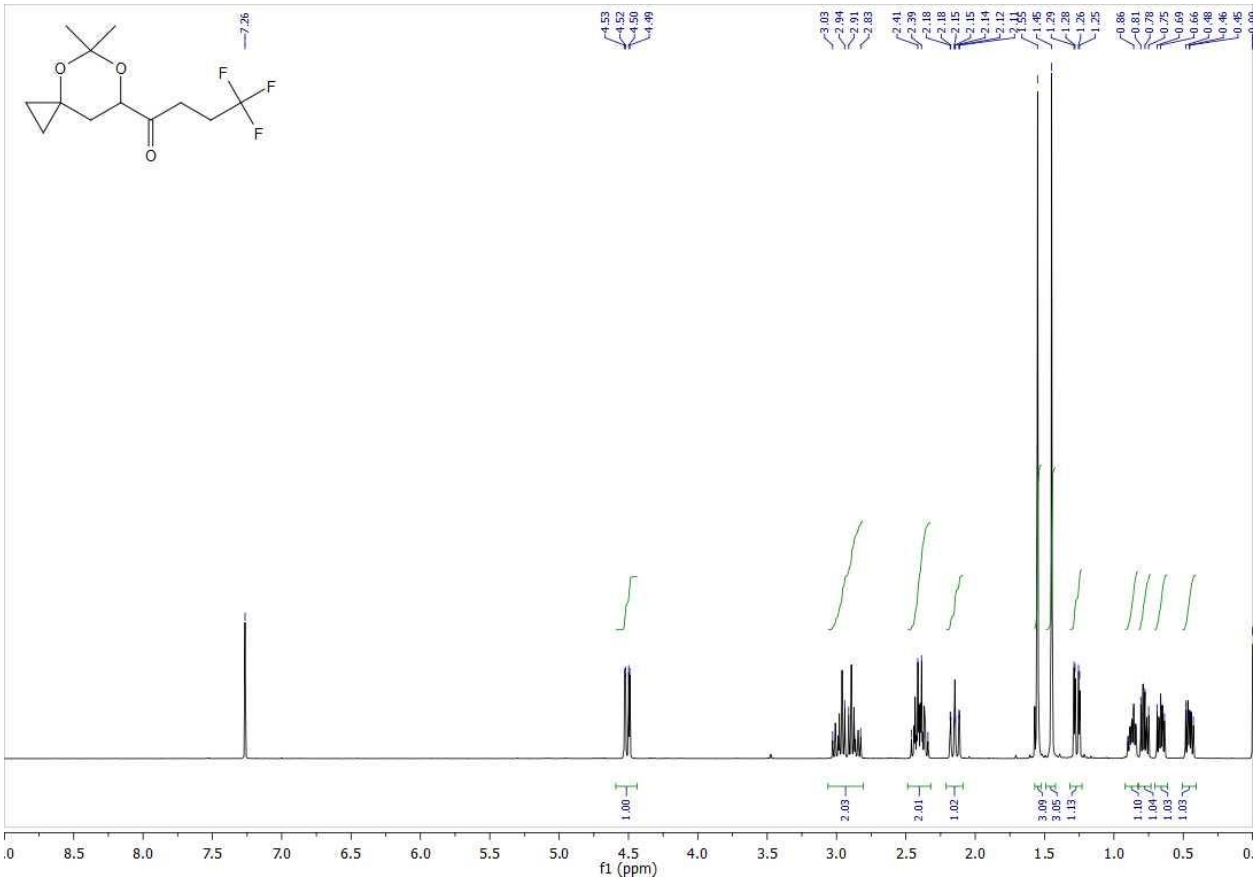
-66.7
-66.9
-67.1
f1 (ppm)
Cl
O
F
F
F
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
f1 (ppm)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O
O
F
F
F
O
4.53
4.52
4.50
4.49
3.03
2.94
2.91
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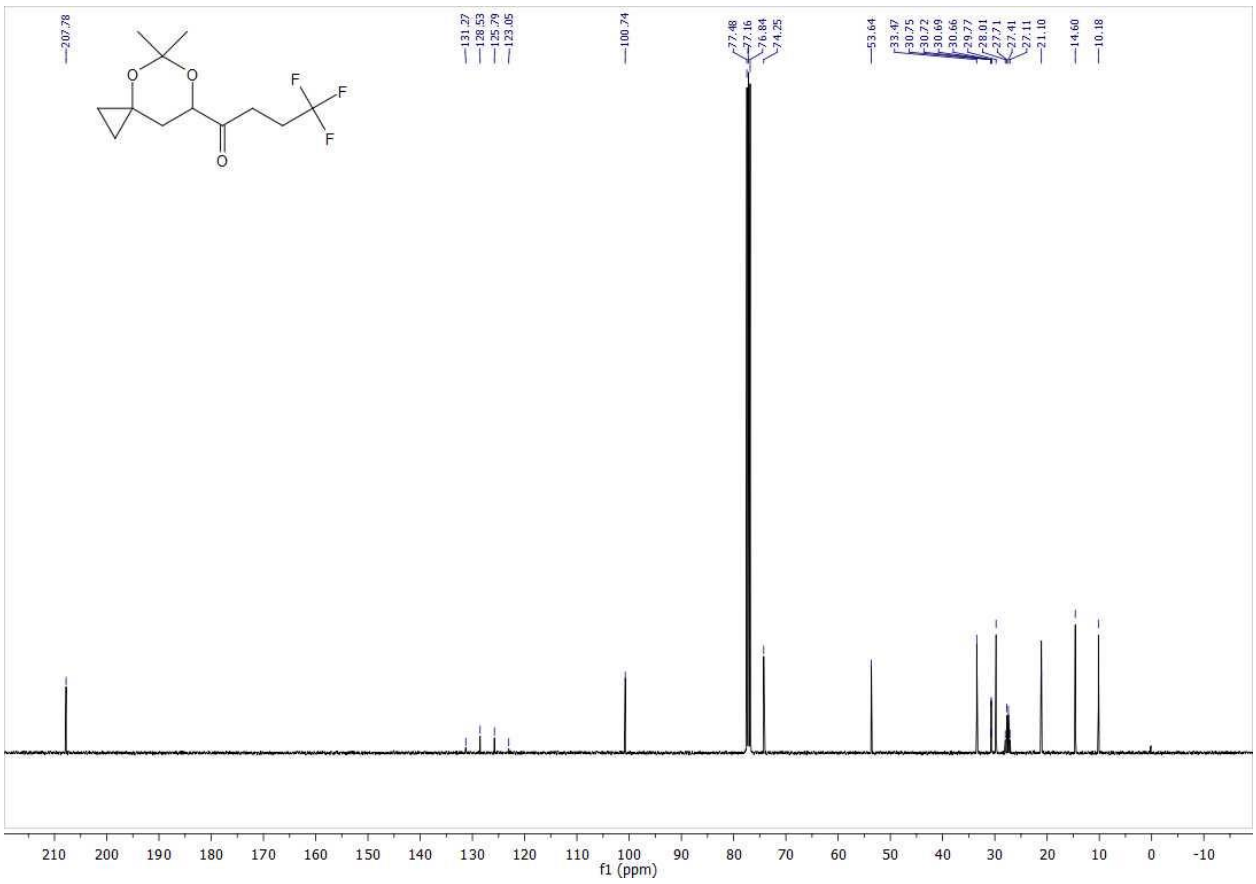
2.41
2.39
2.18
2.15
2.14
2.12
1.45
1.29
1.28
1.26
1.25
0.86
0.81
0.78
0.75
0.69
0.66
0.48
0.46
0.45
1.00
2.03
2.01
1.02
3.09
3.05
1.13
1.10
1.04
1.03
1.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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33.47
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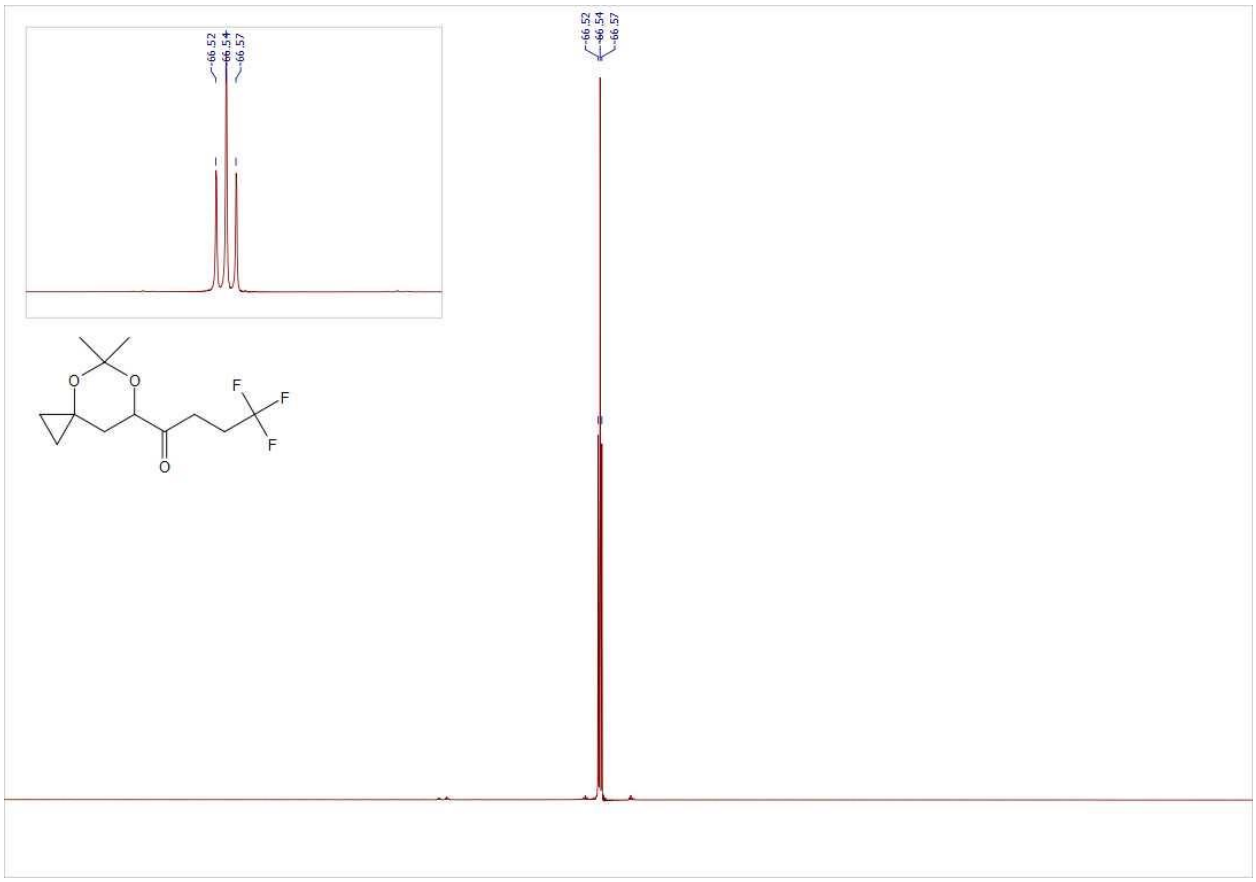
30.72
30.69
30.66
29.77
28.01
27.71
27.41
27.11
21.10
14.60
10.18
O
O
F
F
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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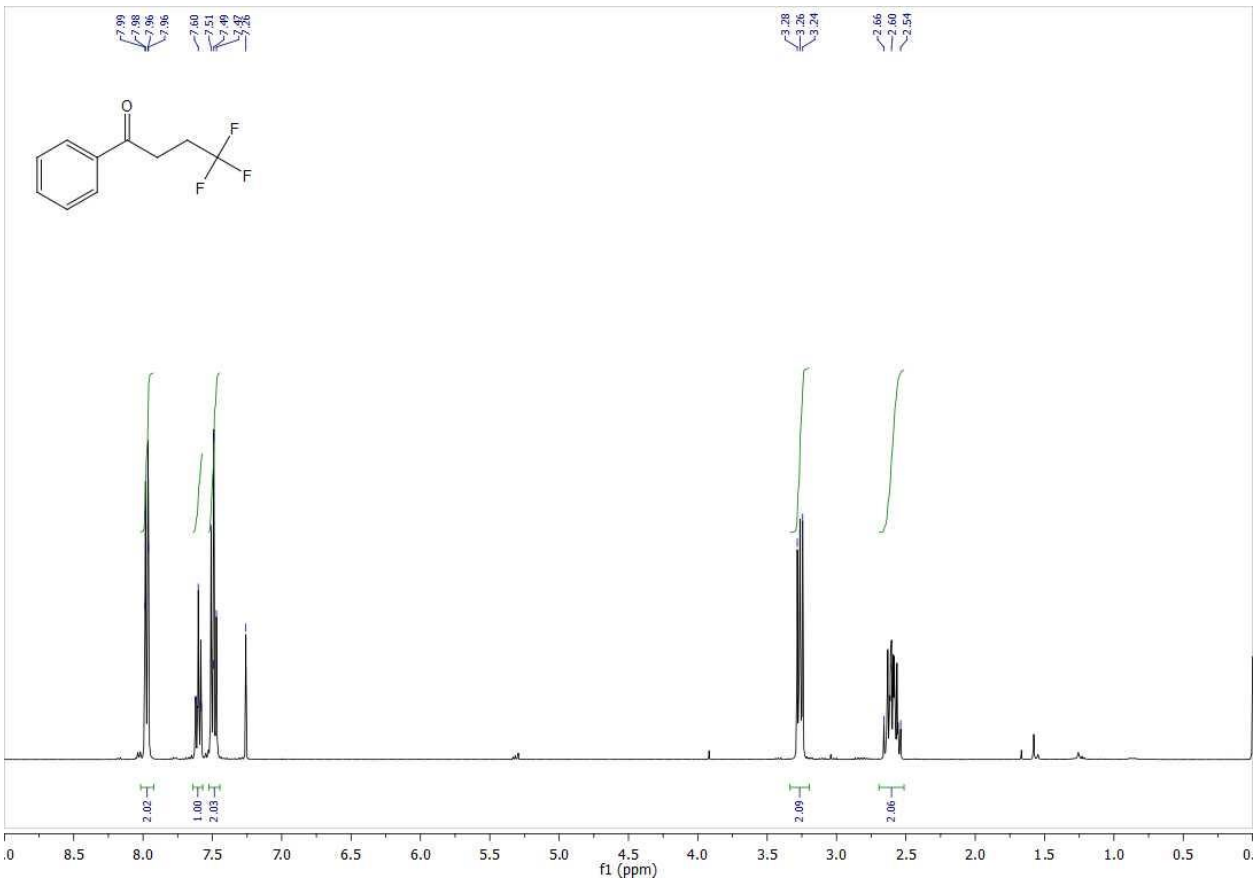
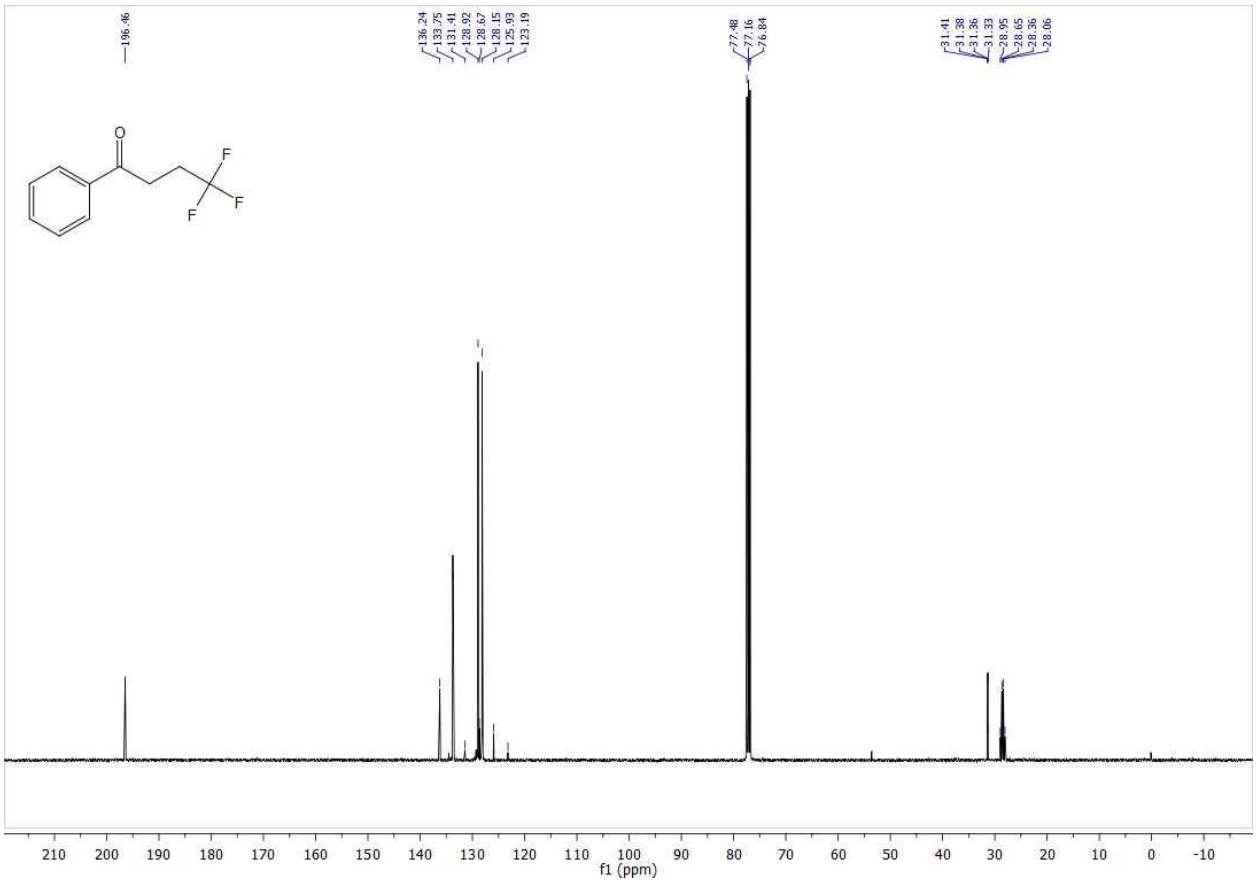
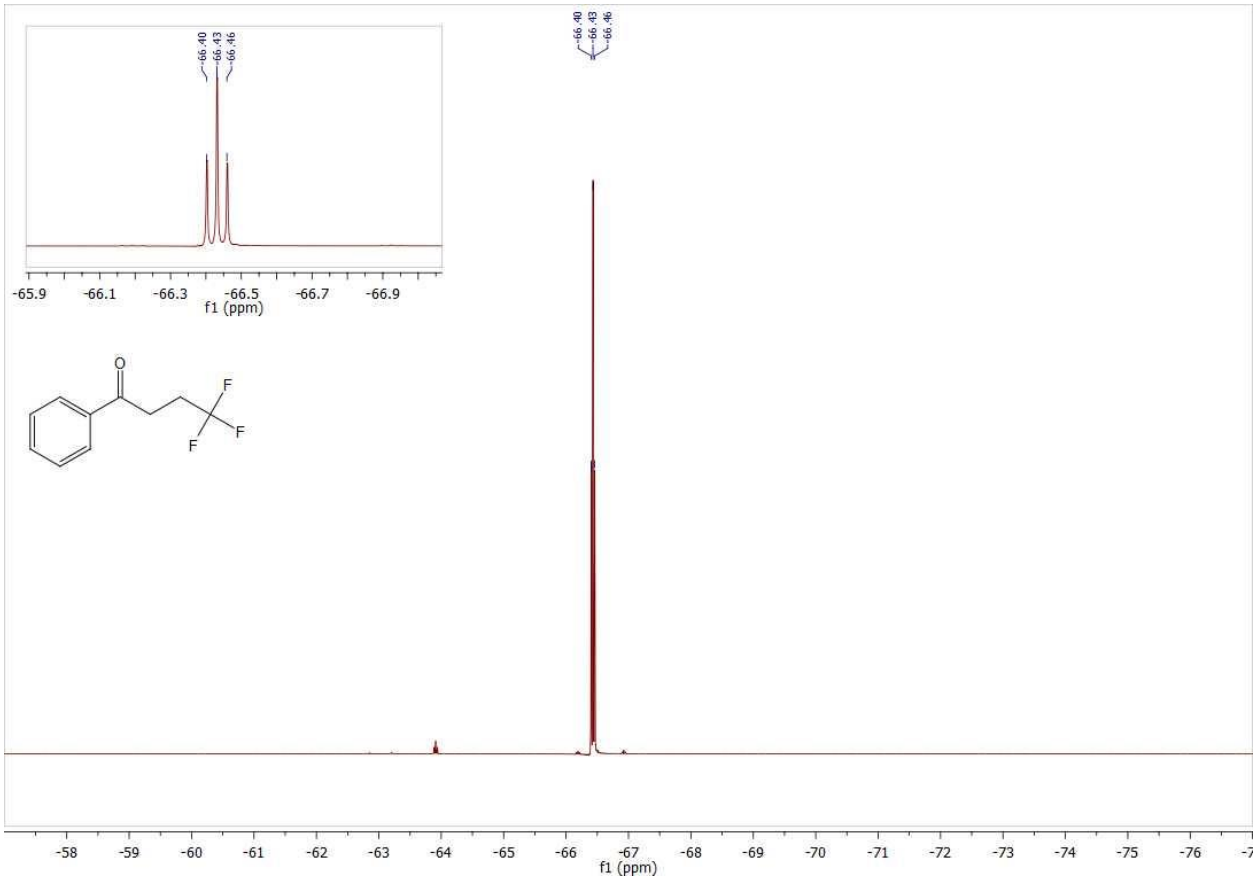
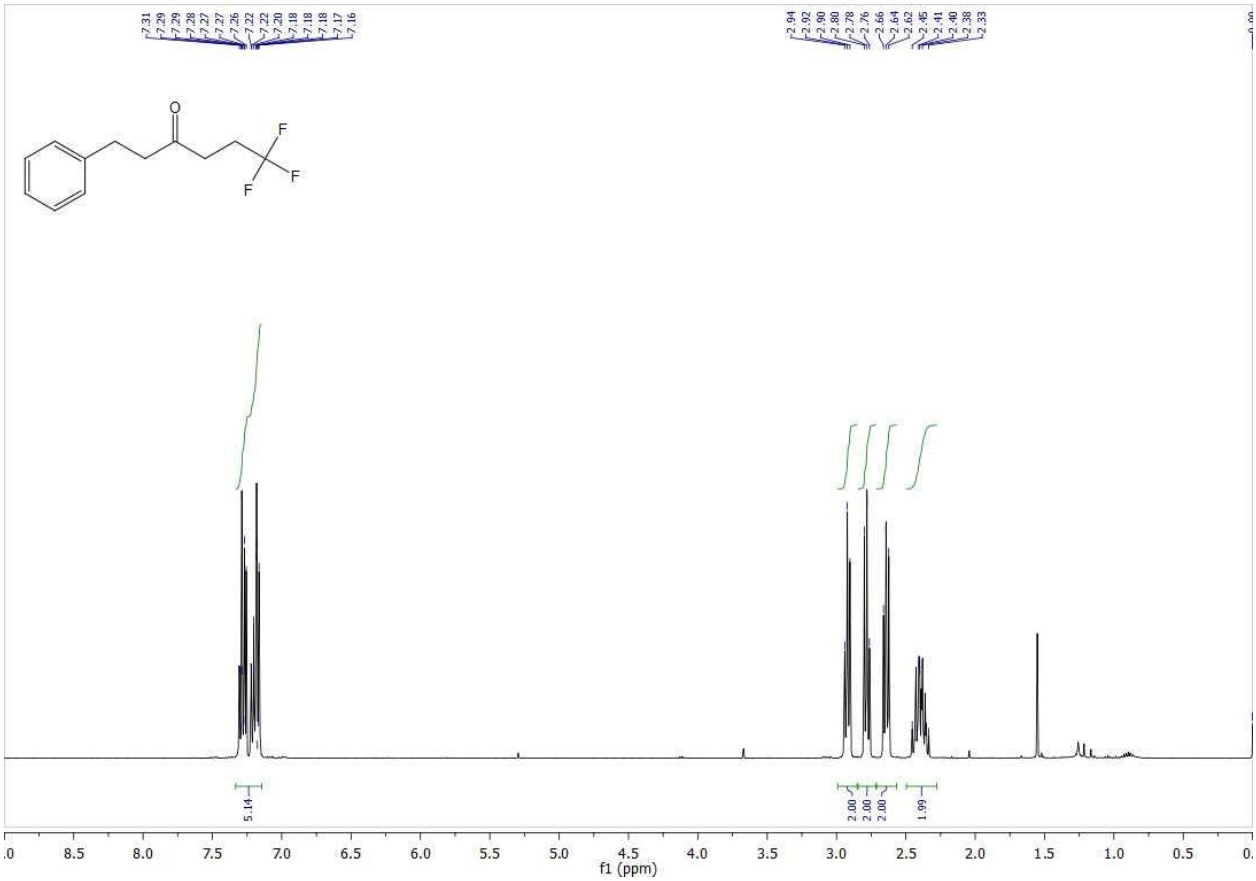
66.54
66.57
O
O
F
F
F
O


7.99
7.98
7.96
7.96
7.60
7.51
7.49
7.47
7.26
3.28
3.26
3.24
2.66
2.60
2.54
O
F
F
F
2.02
1.00
2.03
2.09
2.06
f1 (ppm)


196.46
136.24
133.75
131.41
128.92
128.67
128.15
125.93
123.19
77.48
77.16
76.84
31.41
31.38
31.36
31.33
28.95
28.65
28.36
28.06
O
F
F
F
f1 (ppm)


-66.40
-66.43
-66.46
-65.9
-66.1
-66.3
-66.5
-66.7
-66.9
f1 (ppm)
O
F
F
F
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
f1 (ppm)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7.29
7.29
7.28
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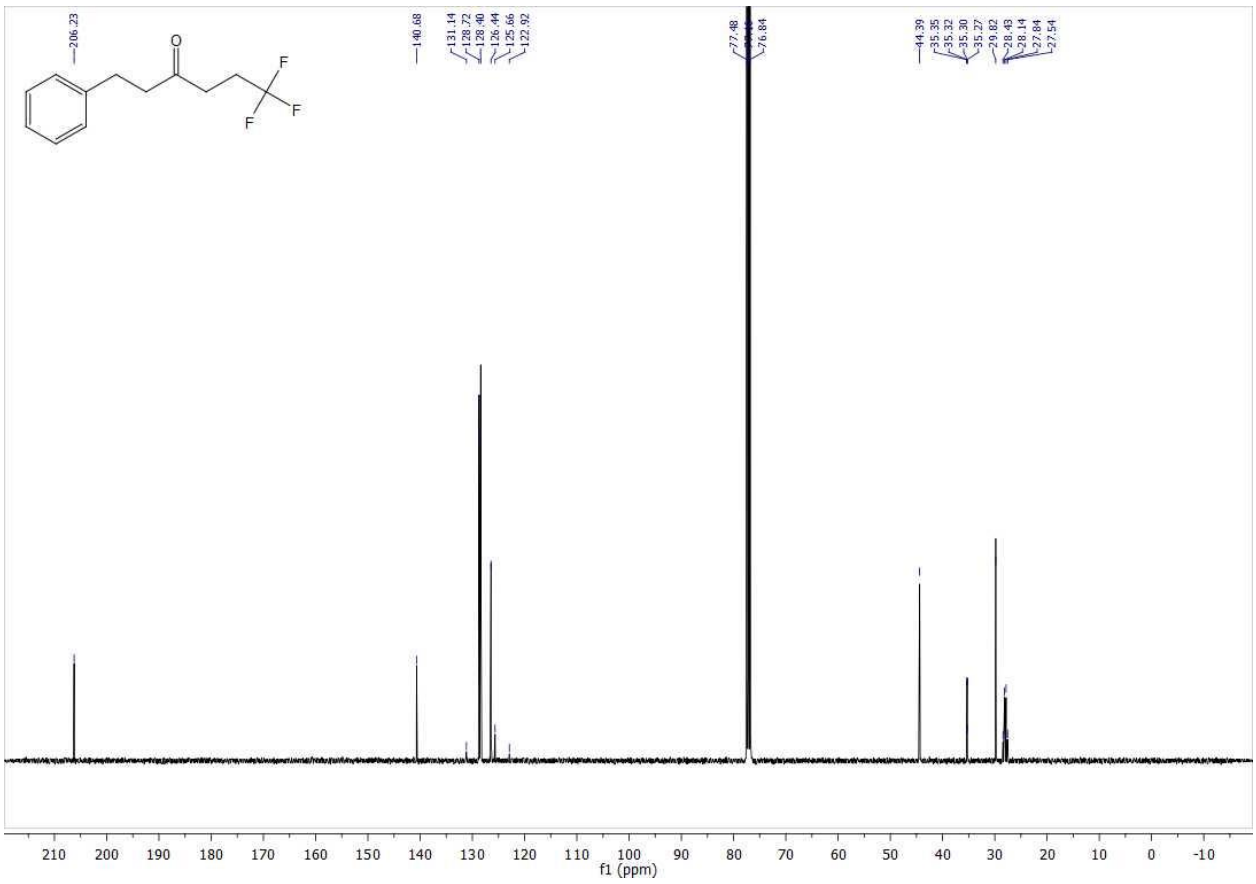
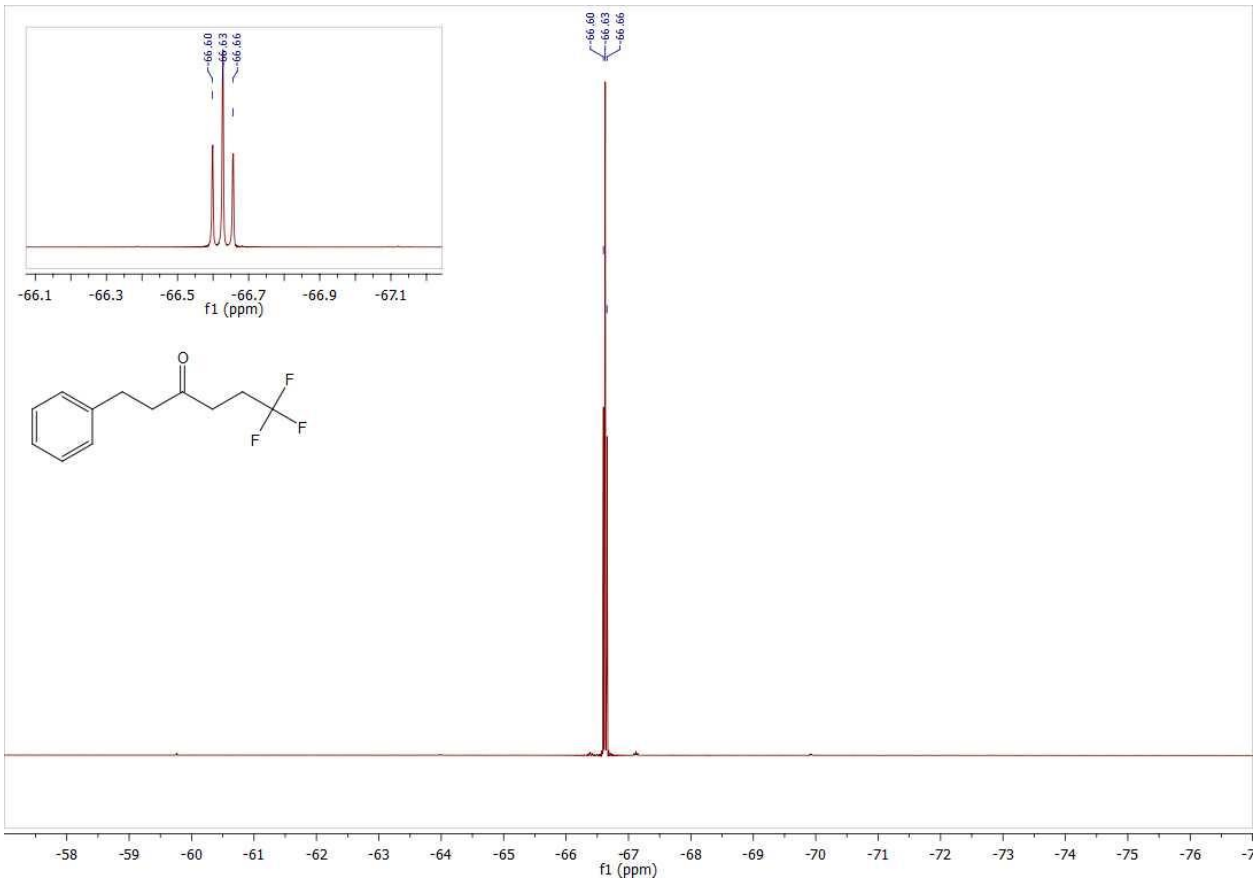
7.27
7.26
7.22
7.22
7.20
7.18
7.18
7.18
7.17
7.16
2.94
2.92
2.90
2.80
2.78
2.76
2.66
2.64
2.62
2.45
2.41
2.40
2.38
2.33
O
F
F
F
5.14
2.00
2.00
2.00
1.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


206.23
140.68
131.14
128.72
128.40
126.44
125.66
122.92
77.48
76.84
44.39
35.35
35.32
35.30
35.27
29.82
28.43
28.14
27.84
27.54
O
F
F
F
f1 (ppm)


66.60
66.63
66.66
-66.1
-66.3
-66.5
-66.7
-66.9
-67.1
f1 (ppm)
O
F
F
F
-58
-59
-60
-61
-62
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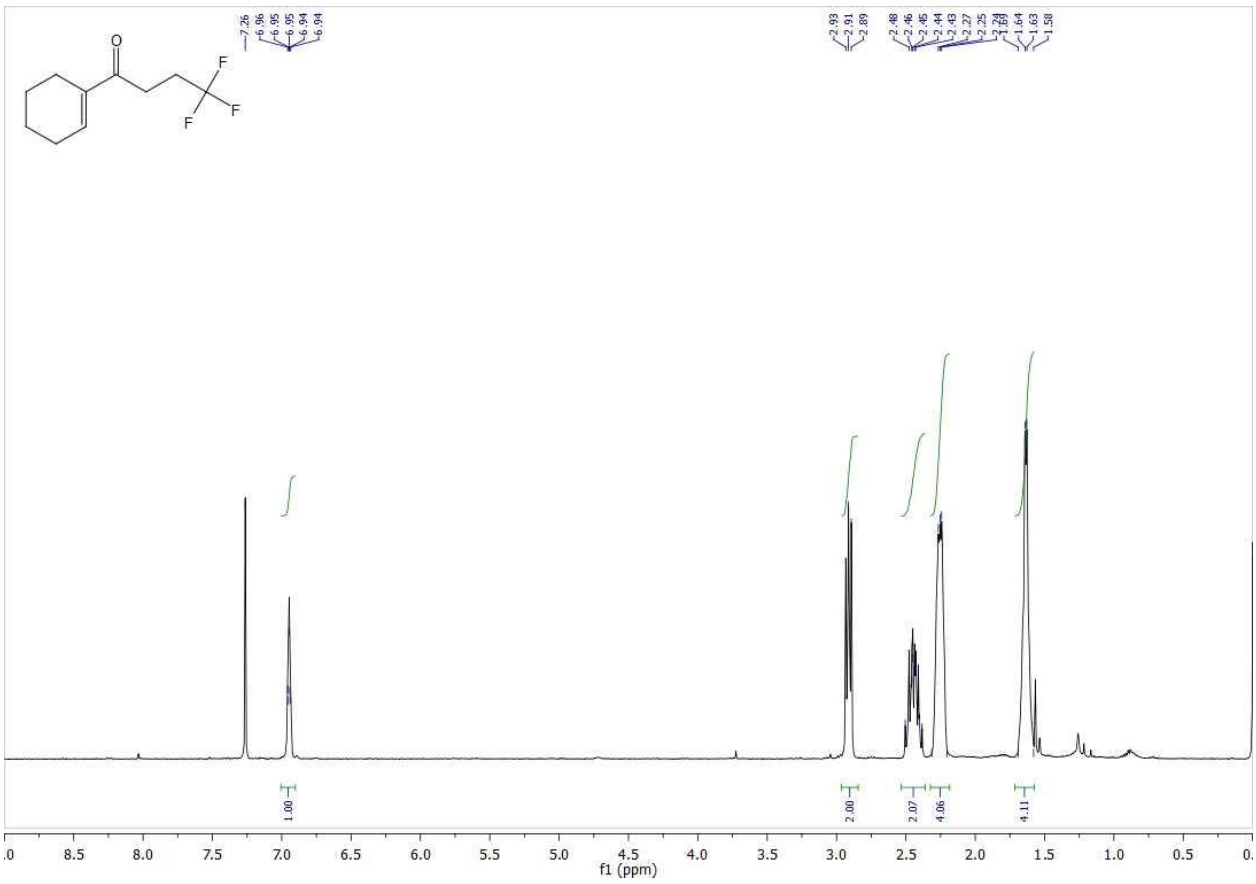
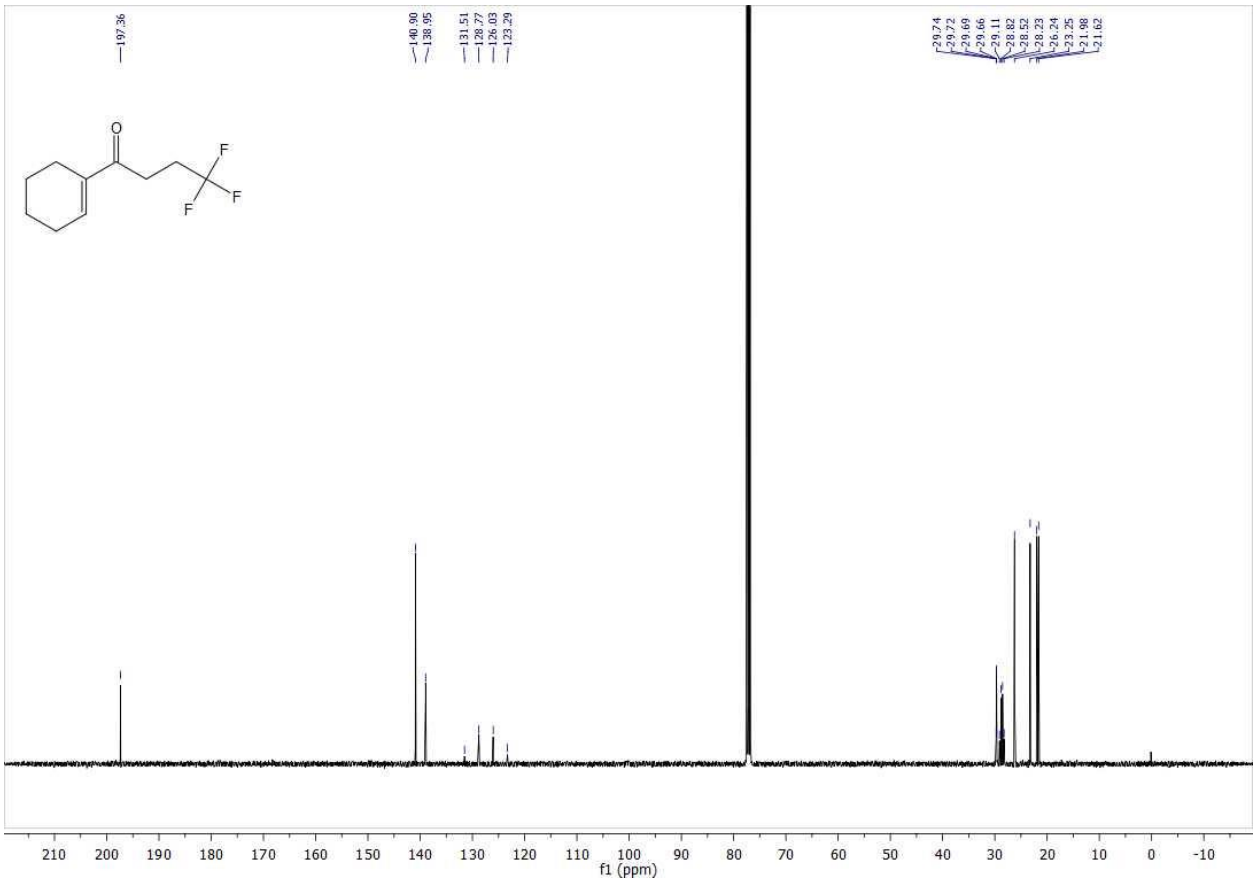
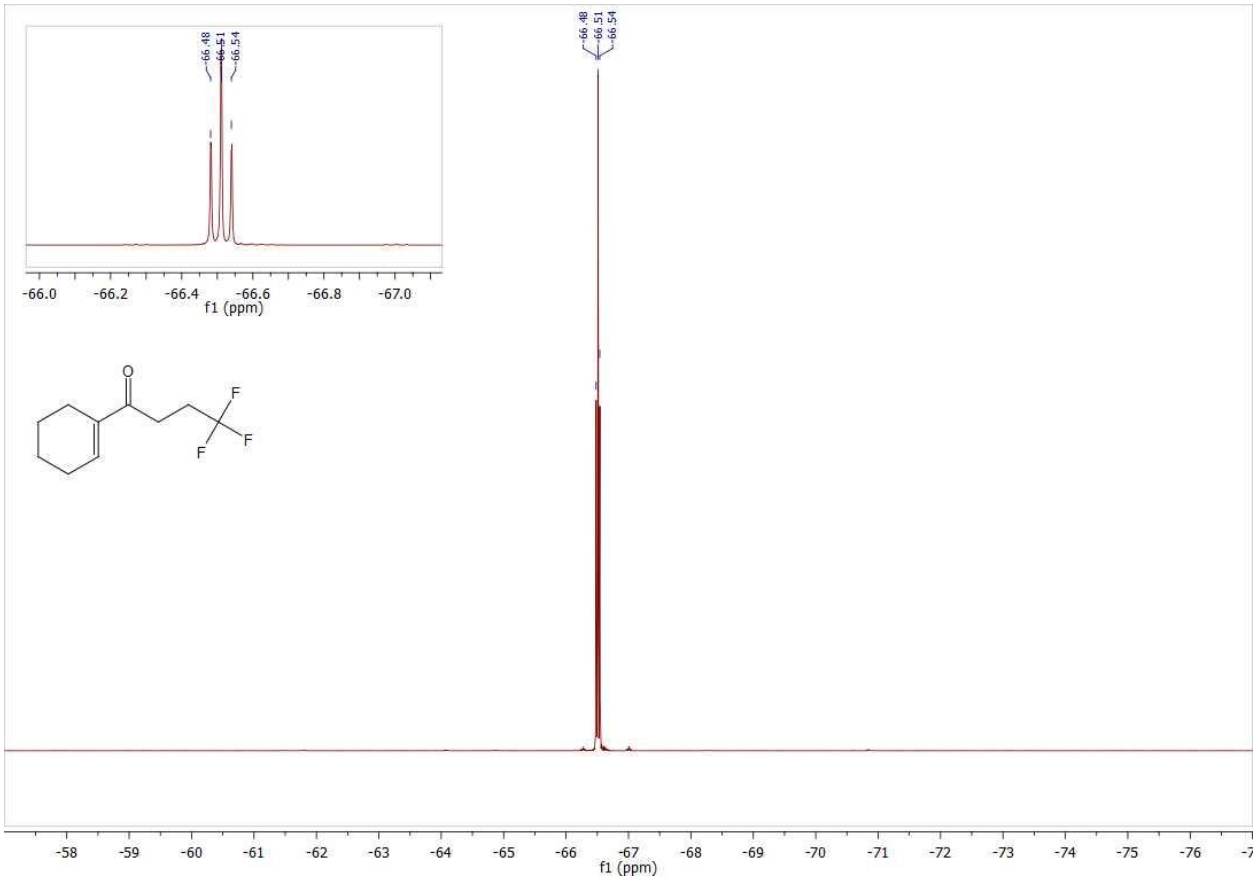
-72
-73
-74
-75
-76
f1 (ppm)


O
F
F
F
7.26
6.96
6.95
6.95
6.94
6.94
2.93
2.91
2.89
2.48
2.46
2.45
2.44
2.43
2.27
2.25
1.64
1.63
1.58
1.00
2.00
2.07
4.06
4.11
f1 (ppm)


O
F
F
F
197.36
140.90
138.95
131.51
128.77
126.03
123.29
29.74
29.72
29.69
29.66
29.11
28.82
28.52
28.23
26.24
23.25
21.98
21.62
f1 (ppm)


-66.48
-66.51
-66.54
-66.0
-66.2
-66.4
-66.6
-66.8
-67.0
f1 (ppm)
O
F
F
F
-58
-59
-60
-61
-62
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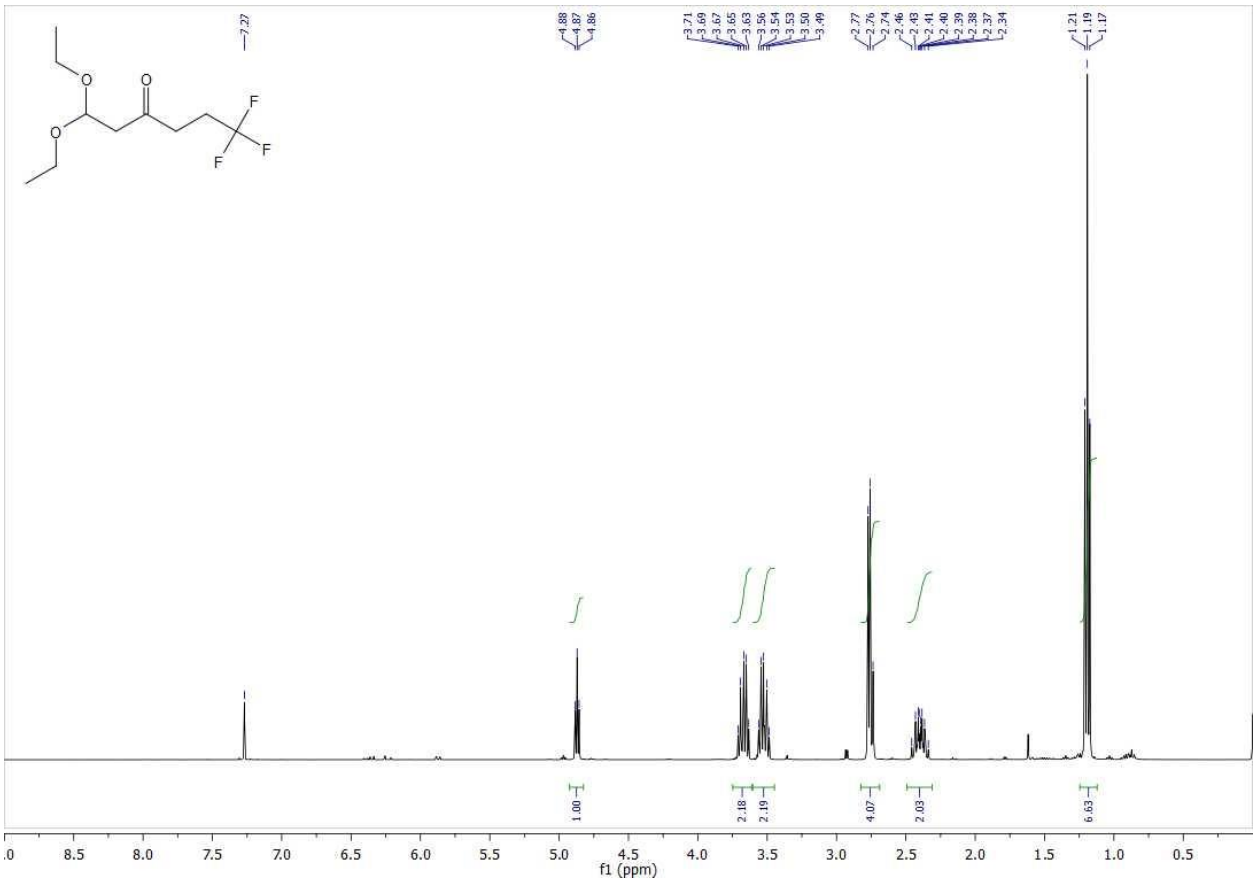
-72
-73
-74
-75
-76
f1 (ppm)


7.27
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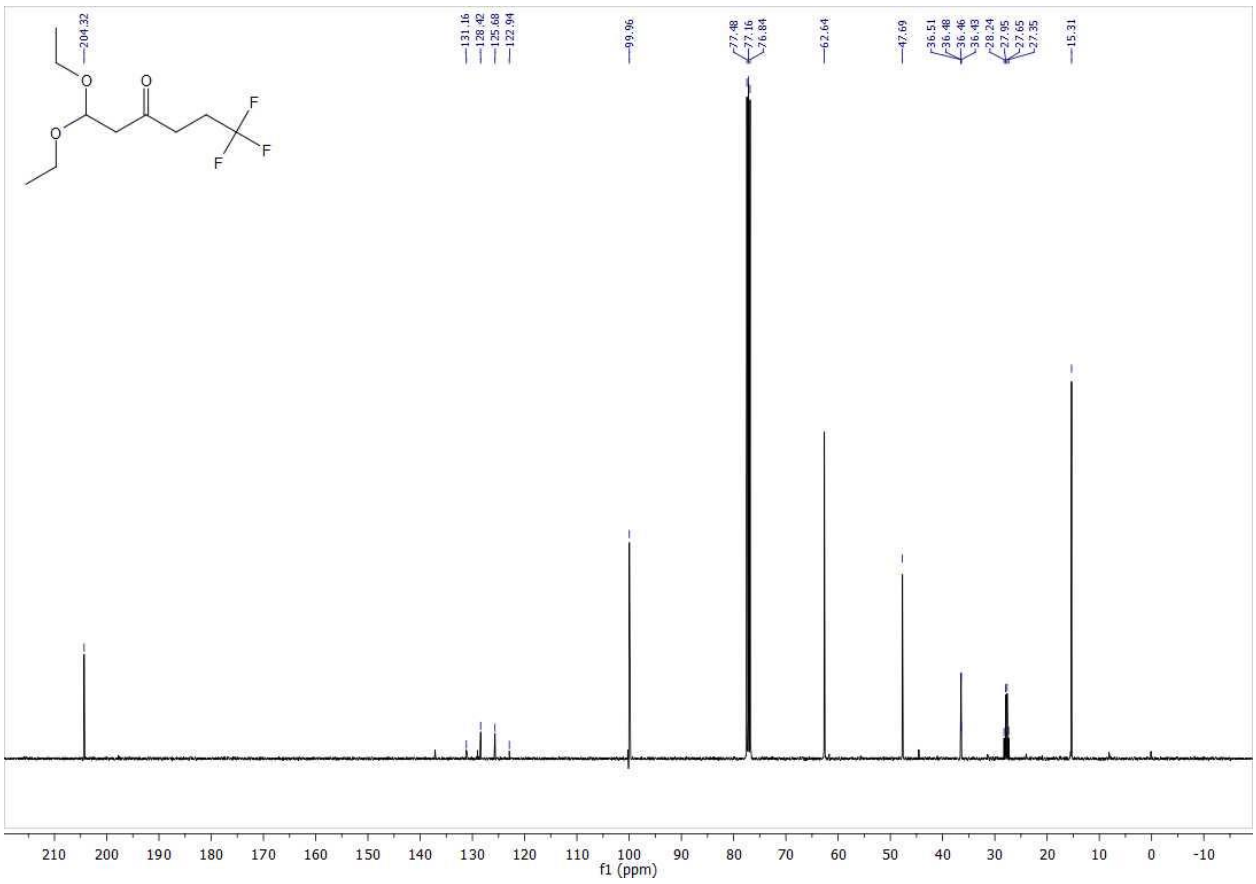
4.87
4.86
3.71
3.69
3.67
3.65
3.63
3.56
3.54
3.53
3.50
3.49
2.77
2.76
2.74
2.46
2.43
2.41
2.40
2.39
2.38
2.37
2.34
1.21
1.19
1.17
O
O
O
F
F
F
1.00
2.18
2.19
4.07
2.03
6.63
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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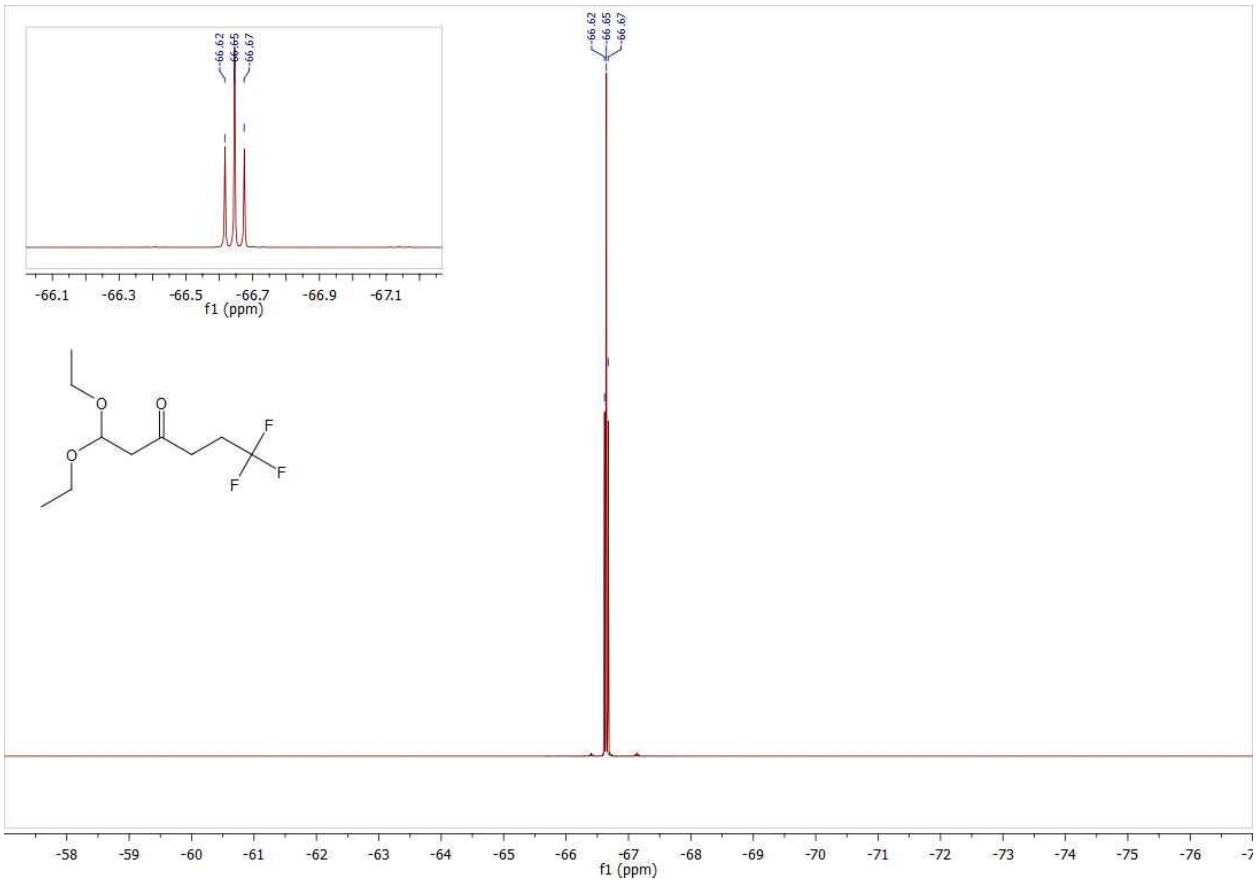
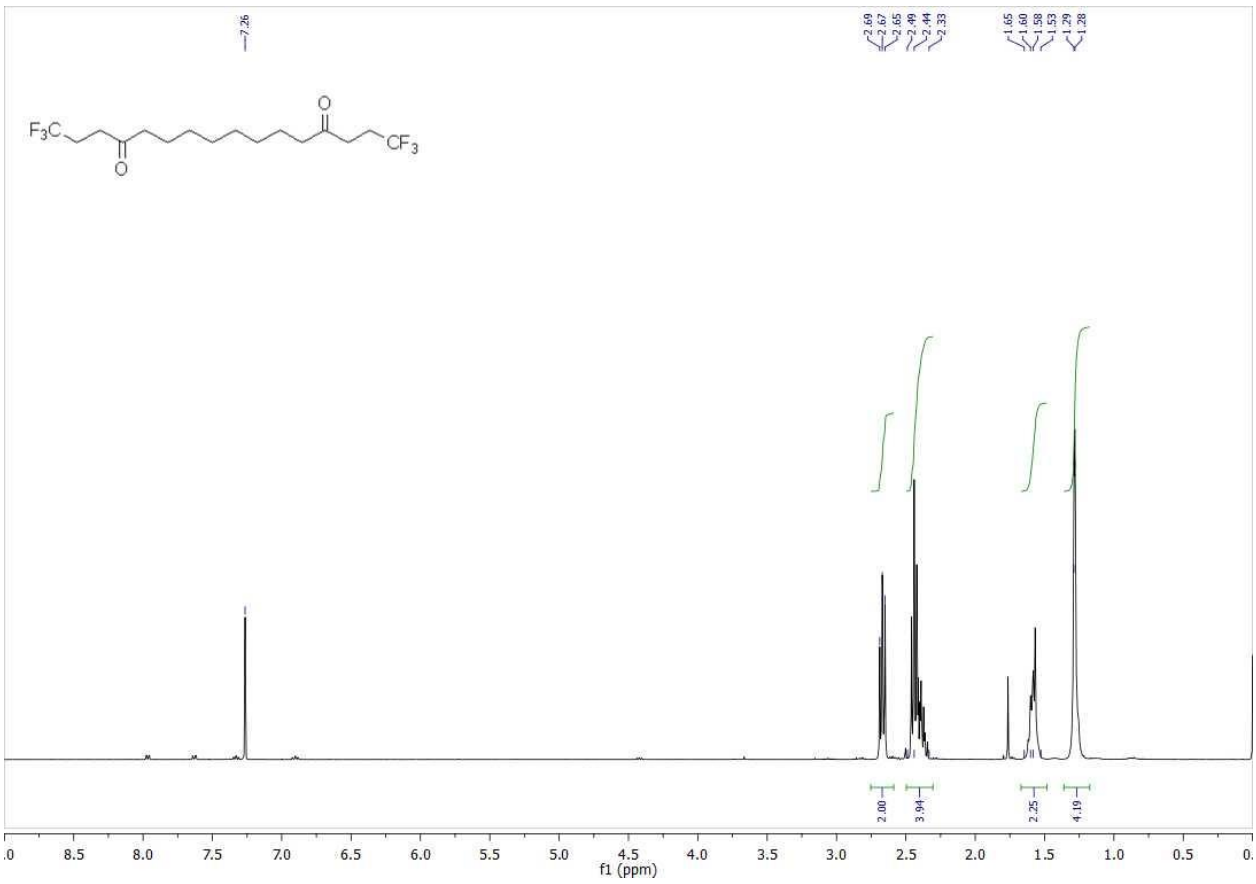
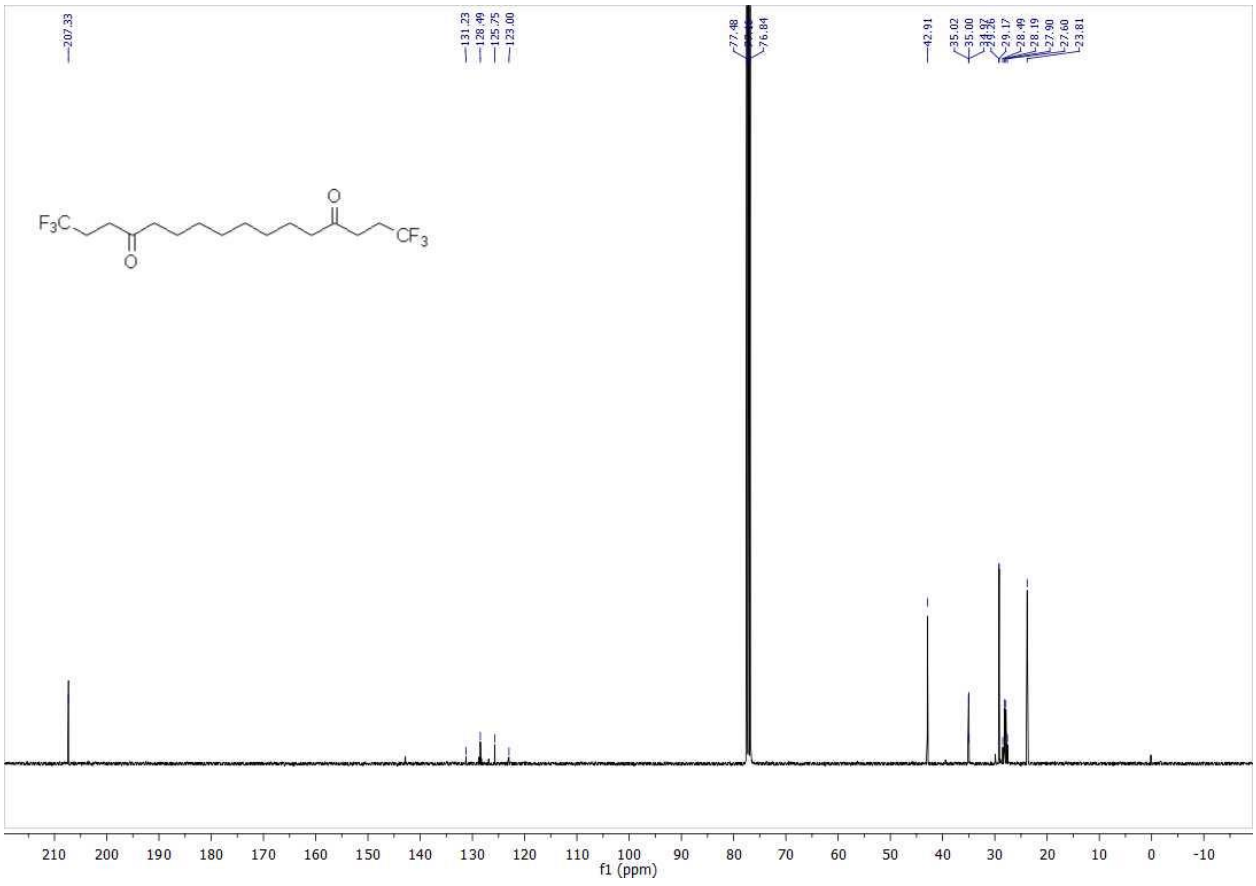
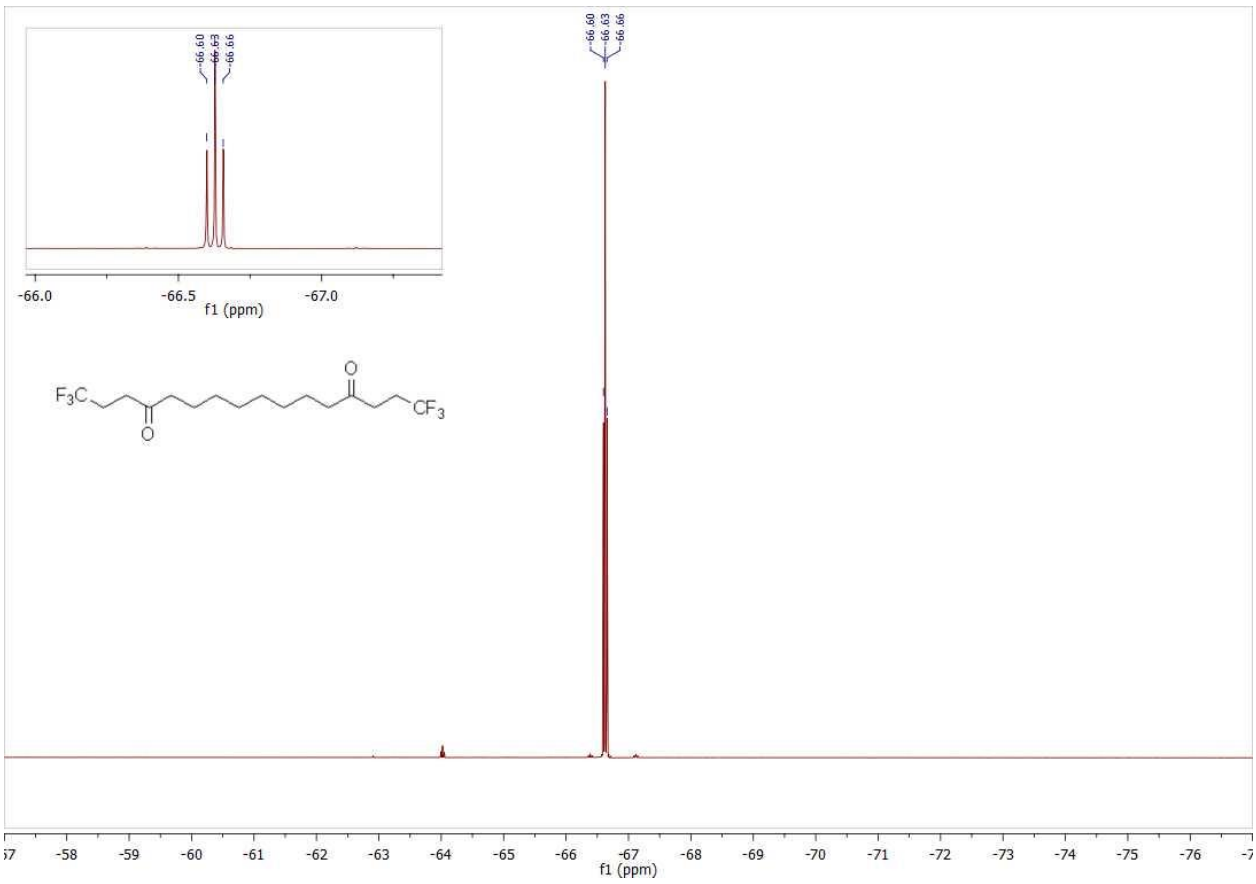
131.16
128.42
125.68
122.94
99.96
77.48
77.16
76.84
62.64
47.69
36.51
36.48
36.46
36.43
28.24
27.95
27.65
27.35
15.31
O
O
O
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


66.62
66.65
66.67
-66.1 -66.3 -66.5 -66.7 -66.9 -67.1
f1 (ppm)
O
O
O
F
F
F
-58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76
f1 (ppm)


7.26
2.69
2.67
2.65
2.49
2.44
2.33
1.65
1.60
1.58
1.55
1.29
1.28
F3C
CF3
O
O
2.00
3.94
2.25
4.19
f1 (ppm)


207.33
131.23
128.49
125.75
123.00
77.48
76.84
42.91
35.02
35.00
29.17
28.49
28.19
27.90
27.60
23.81
F3C
CF3
O
O
f1 (ppm)


-66.60
-66.63
-66.66
-66.0
-66.5
-67.0
f1 (ppm)
F3C
O
O
CF3
-66.60
-66.63
-66.66
-57
-58
-59
-60
-61
-62
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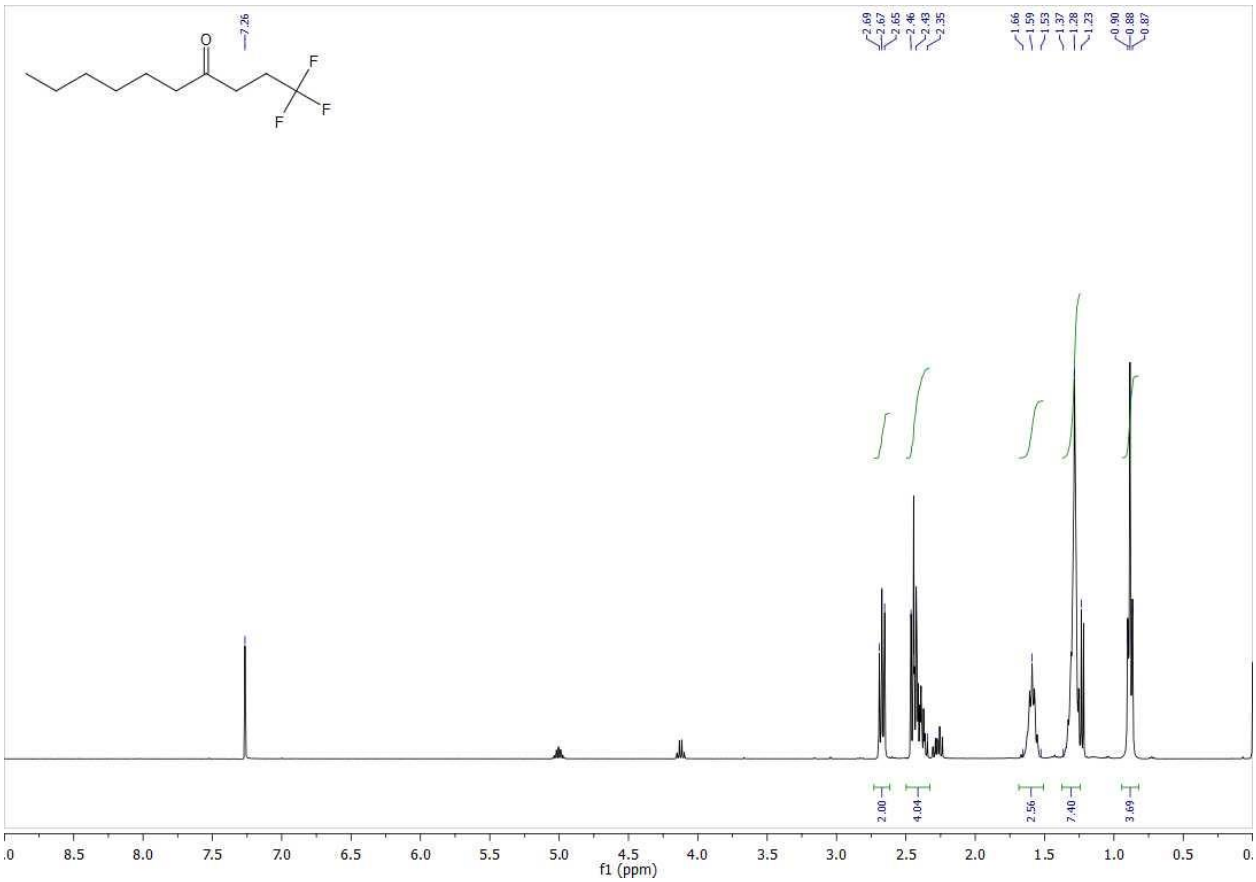
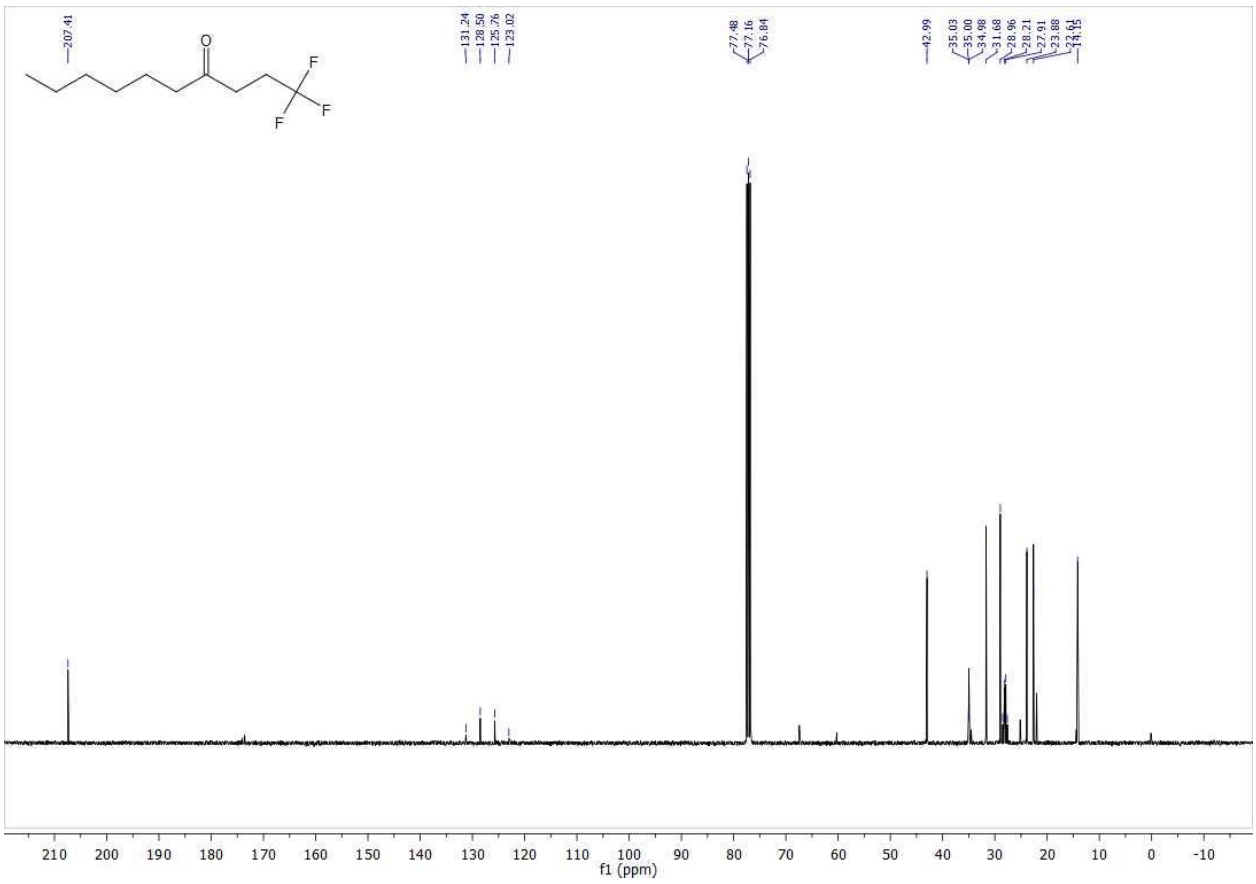
-72
-73
-74
-75
-76
f1 (ppm)


7.26
O
F
F
F
2.69
2.67
2.65
2.46
2.43
2.35
1.66
1.59
1.53
1.37
1.28
1.23
0.90
0.88
0.87
2.00
4.04
2.56
7.40
3.69
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
f1 (ppm)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128.50
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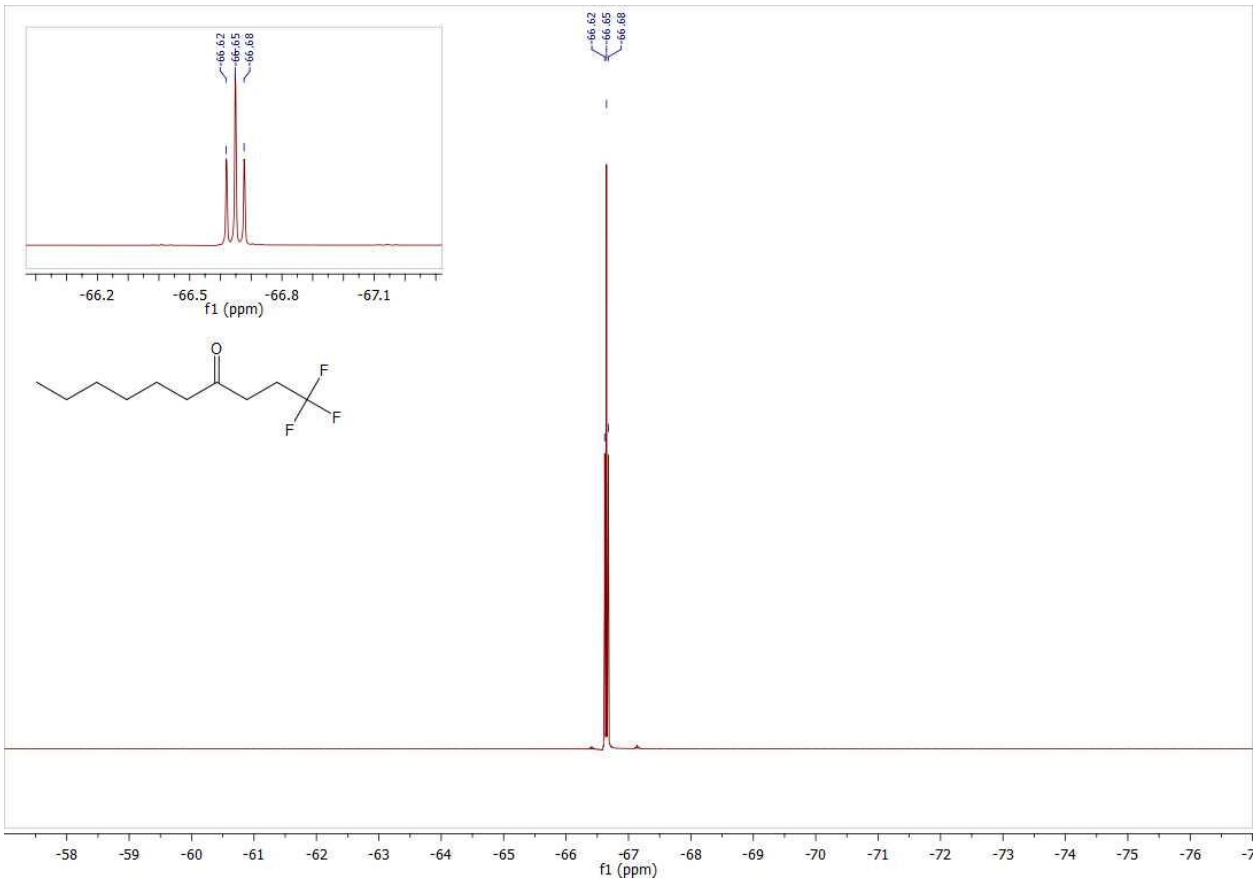
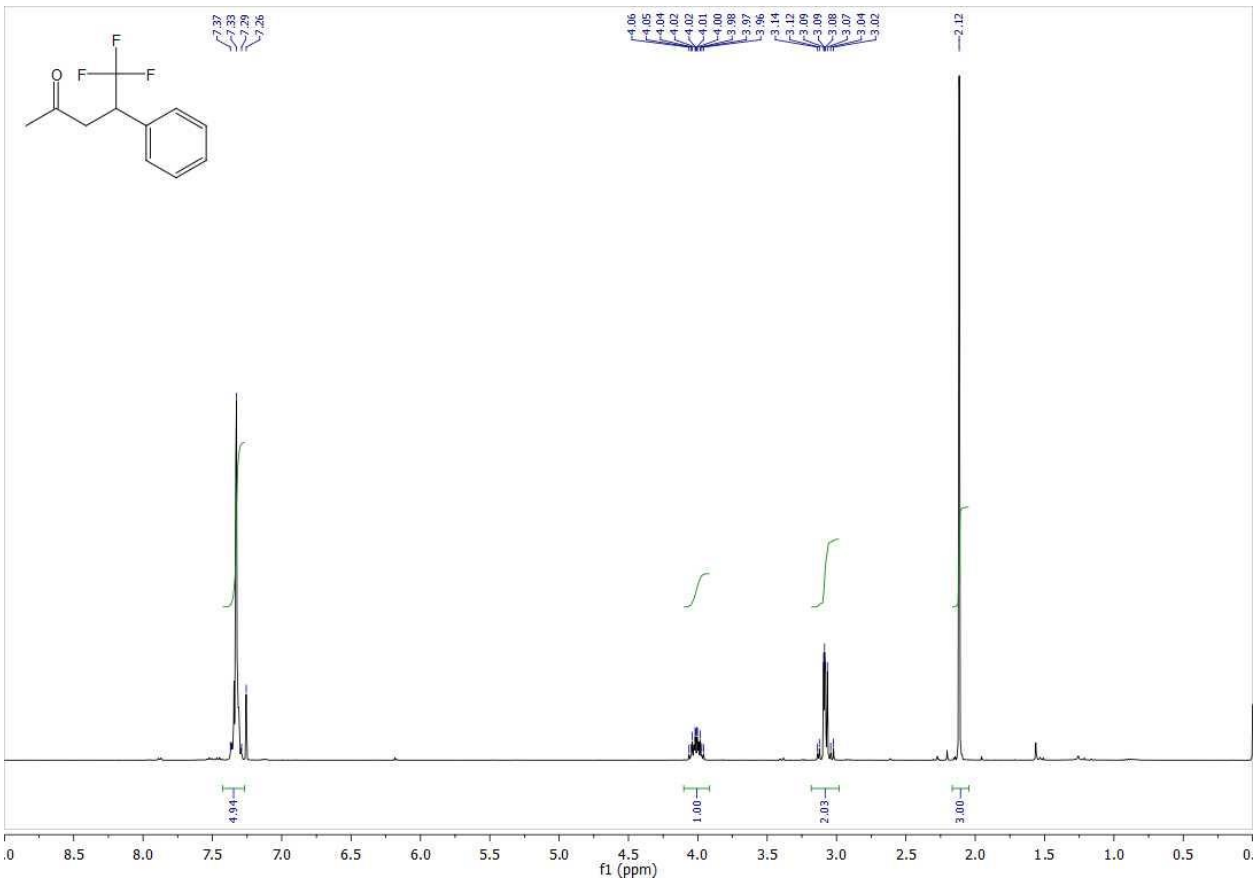
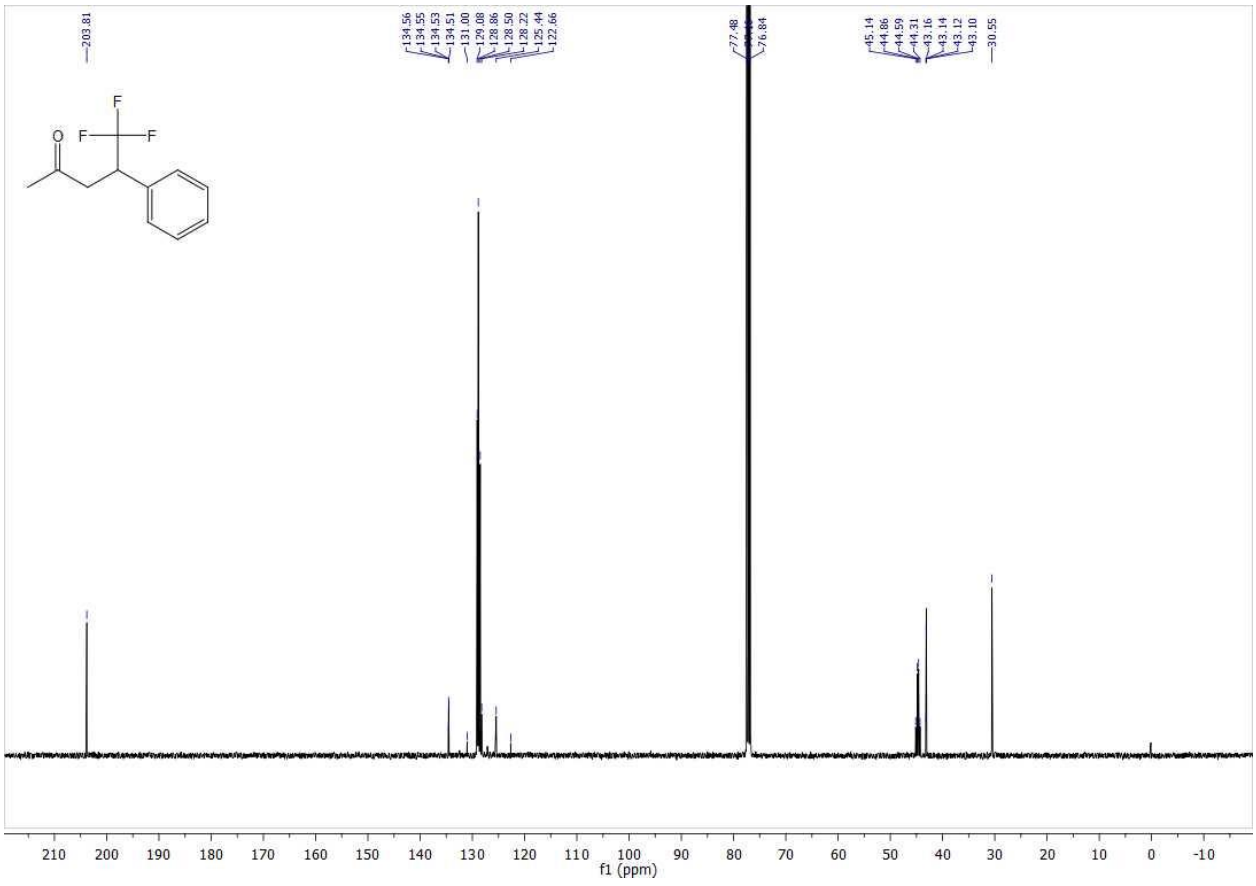
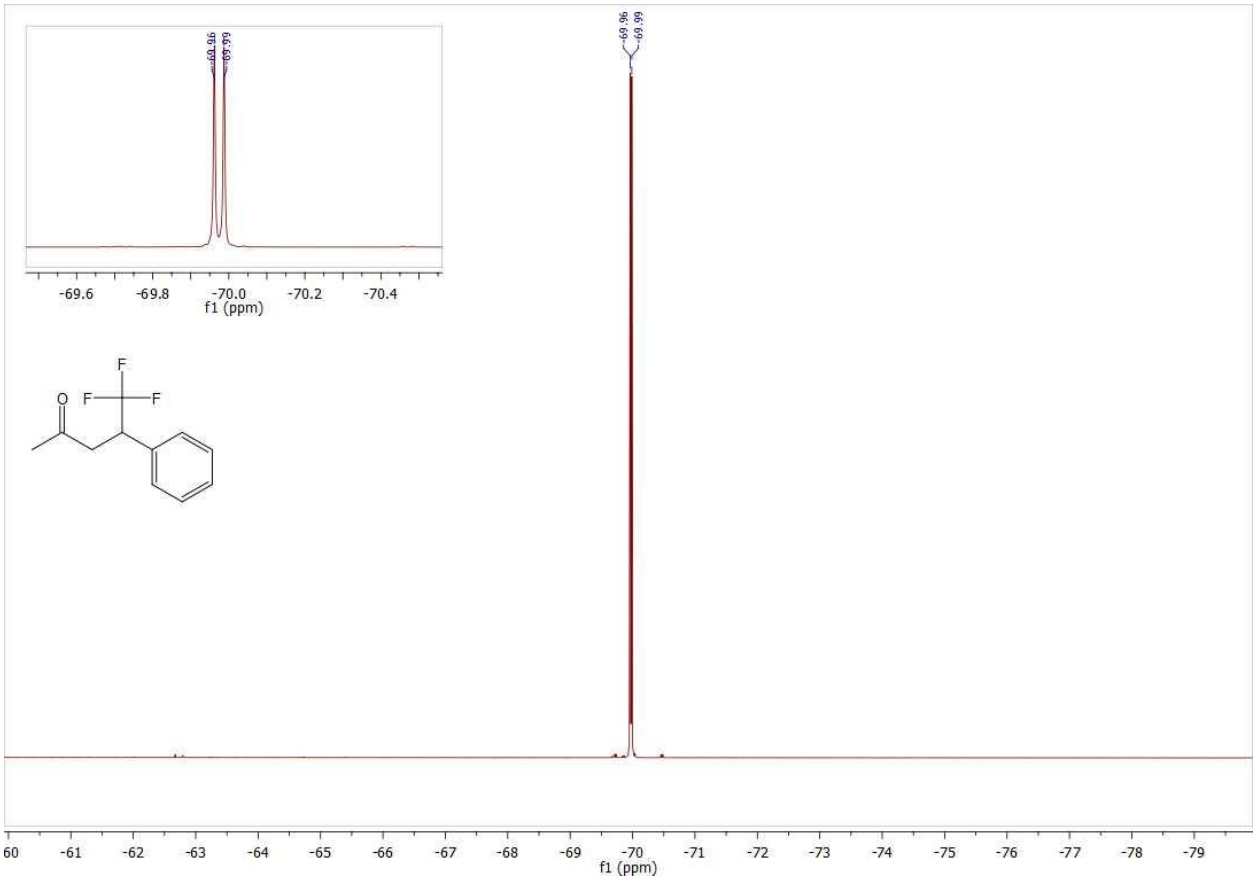
77.16
76.84
42.99
35.03
35.00
34.98
31.68
28.96
28.21
27.91
23.88
13.93
13.85
O
F
F
F
f1 (ppm)


66.62
66.65
66.68
-66.2
-66.5
-66.8
-67.1
f1 (ppm)
O
F
F
F
f1 (ppm)


F
O F F
7.37
7.33
7.29
7.26
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.98
3.97
3.96
3.14
3.12
3.09
3.09
3.08
3.07
3.04
3.02
2.12
4.94
1.00
2.03
3.00
f1 (ppm)


F
O F F
203.81
134.56
134.55
134.53
134.51
131.00
129.08
128.86
128.50
128.22
125.44
122.66
77.48
77.16
76.84
45.14
44.86
44.59
44.31
43.16
43.14
43.12
43.10
30.55
f1 (ppm)


-69.96
-69.99
-69.6
-69.8
-70.0
-70.2
-70.4
f1 (ppm)
F
O
F
F
60
-61
-62
-63
-64
-65
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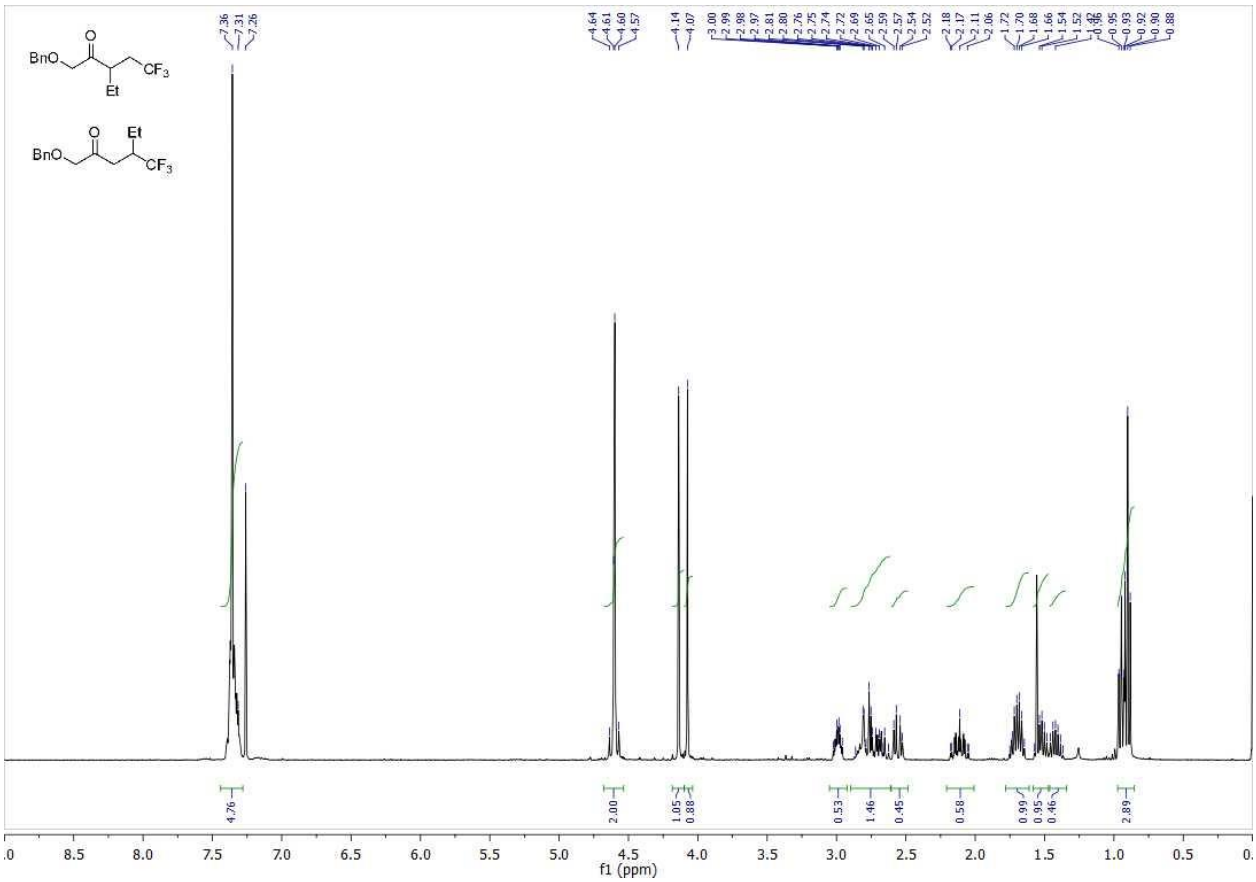
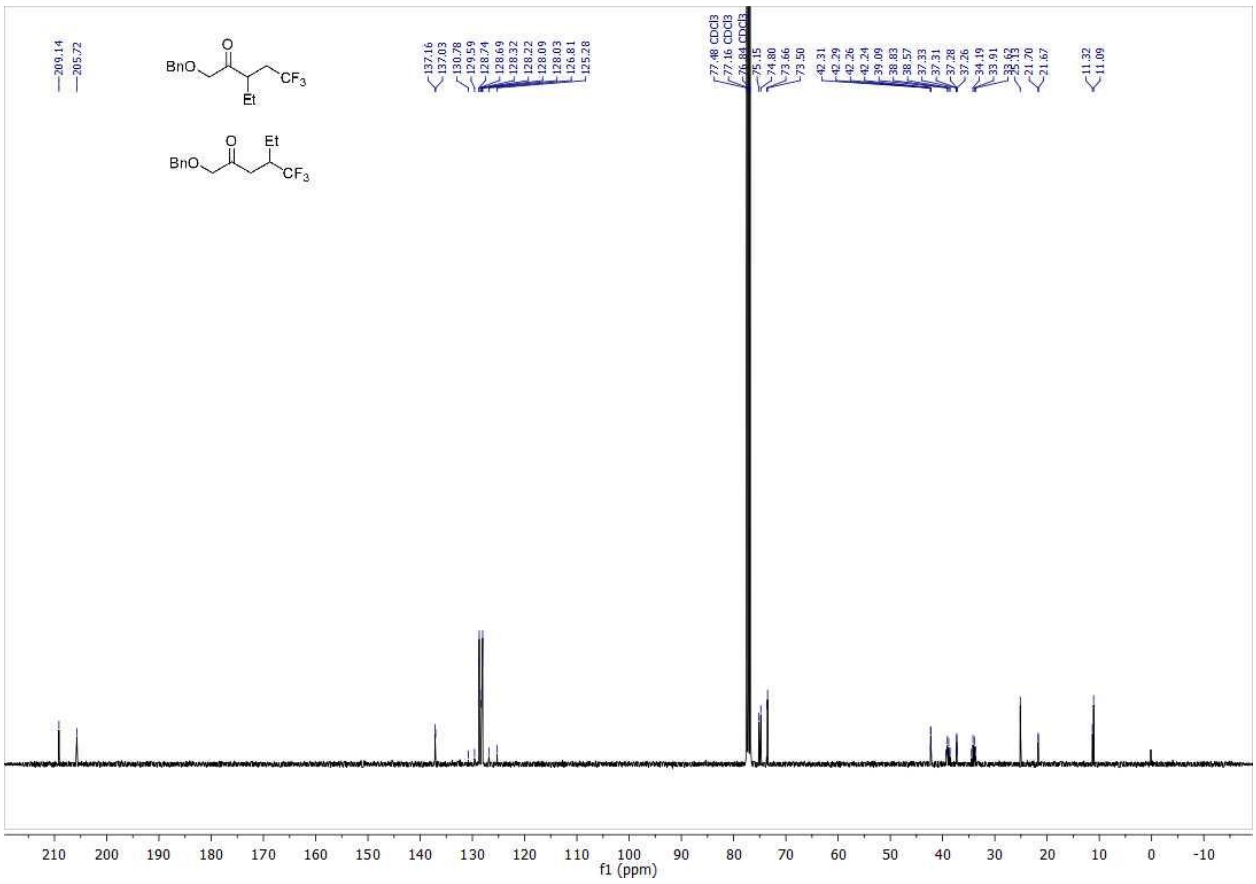
-75
-76
-77
-78
-79
f1 (ppm)


BnO
O
CF3
Et
BnO
O
Et
CF3
4.76
2.00
1.05
0.88
0.53
1.46
0.45
0.58
0.99
0.95
0.46
2.89
.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
f1 (ppm)


209.14
205.72
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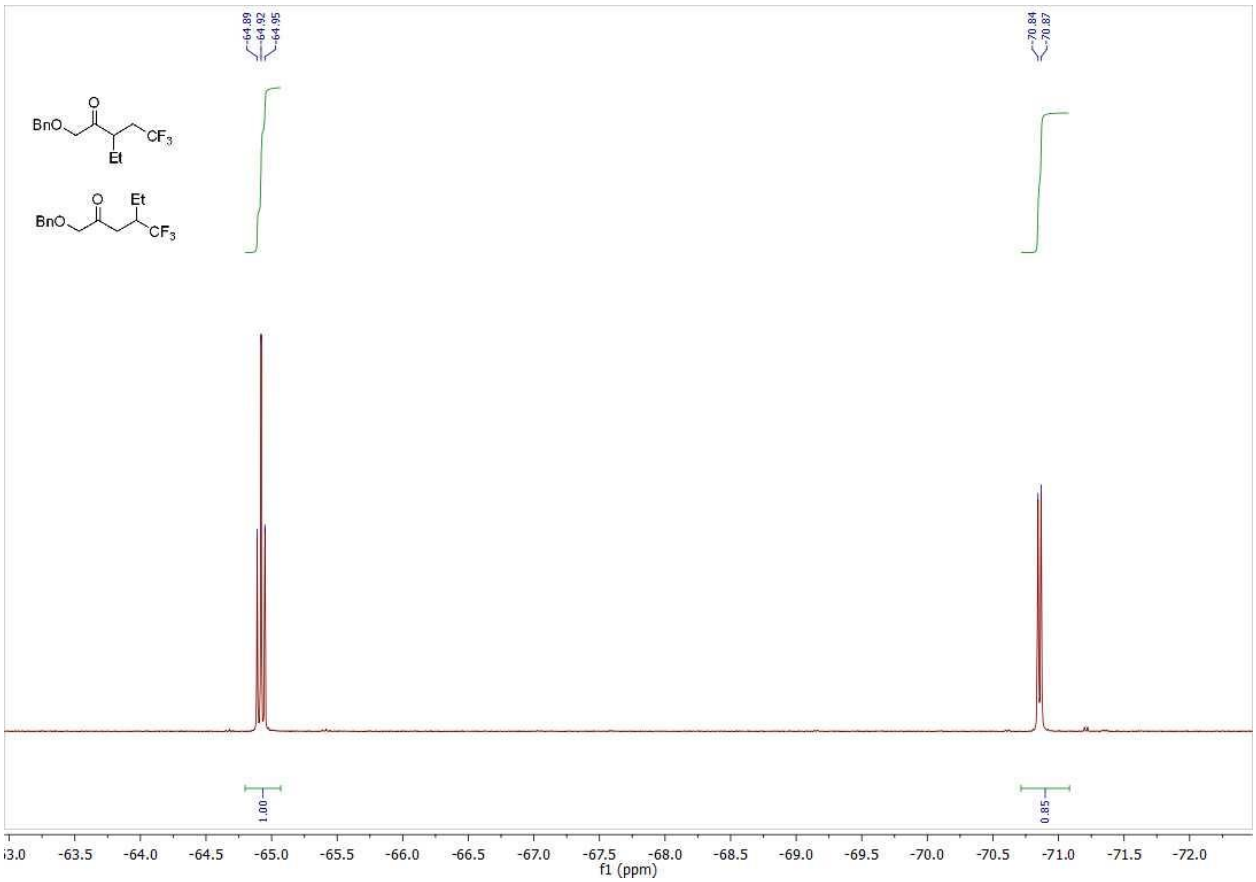
137.03
130.78
129.59
128.74
128.69
128.32
128.22
128.09
128.03
126.81
125.28
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.15
74.80
73.66
73.50
42.31
42.29
42.26
42.24
39.09
38.83
38.57
37.33
37.31
37.28
37.26
34.19
33.91
33.62
25.13
21.70
21.67
11.32
11.09
BnO
CF3
Et
f1 (ppm)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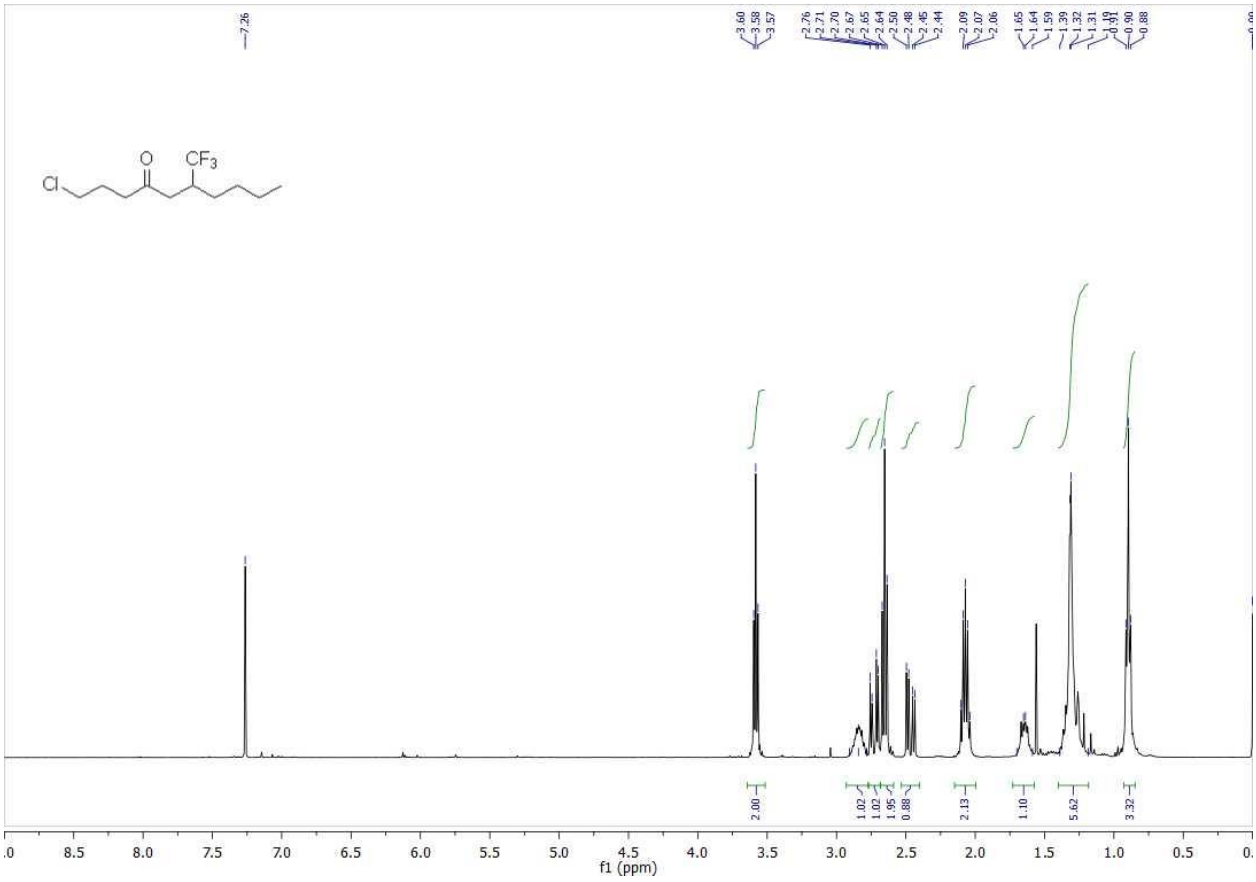
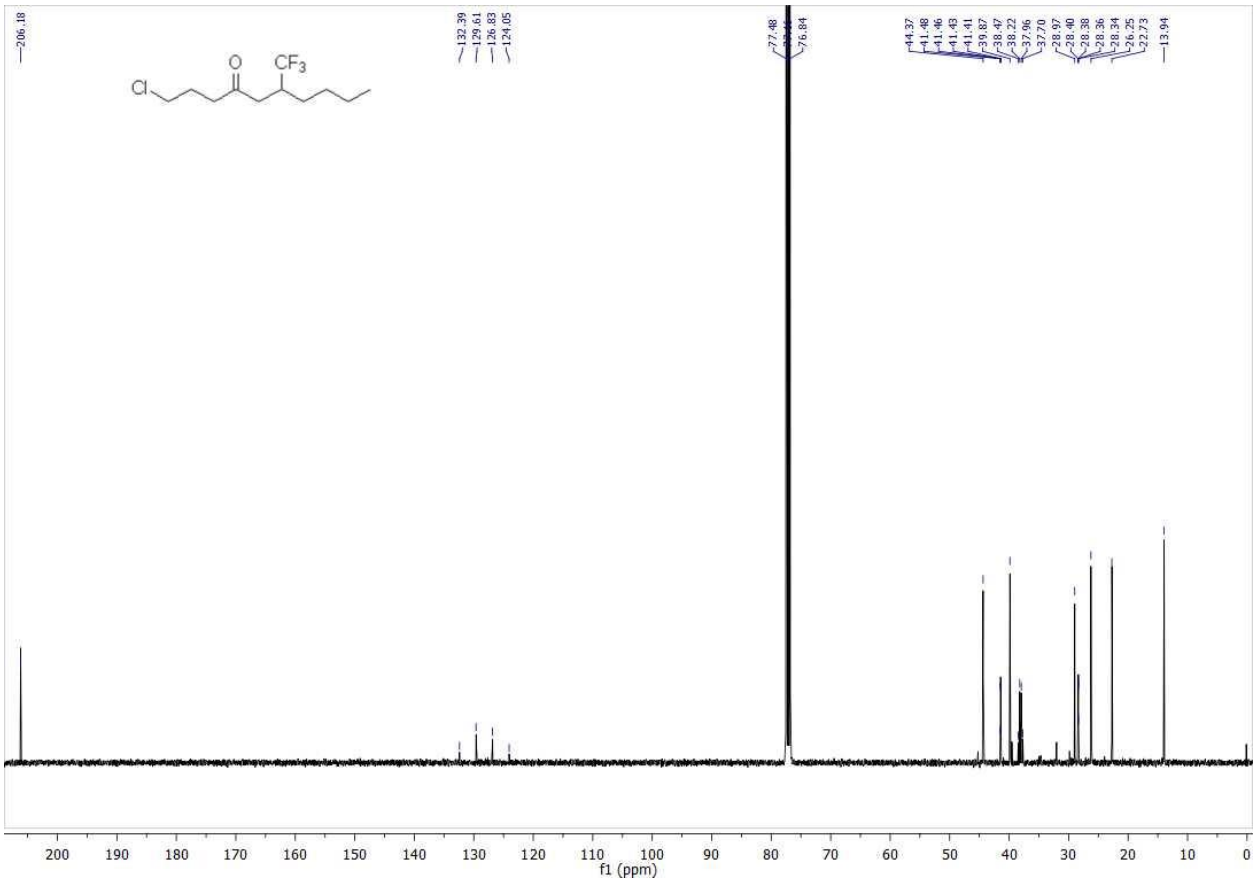
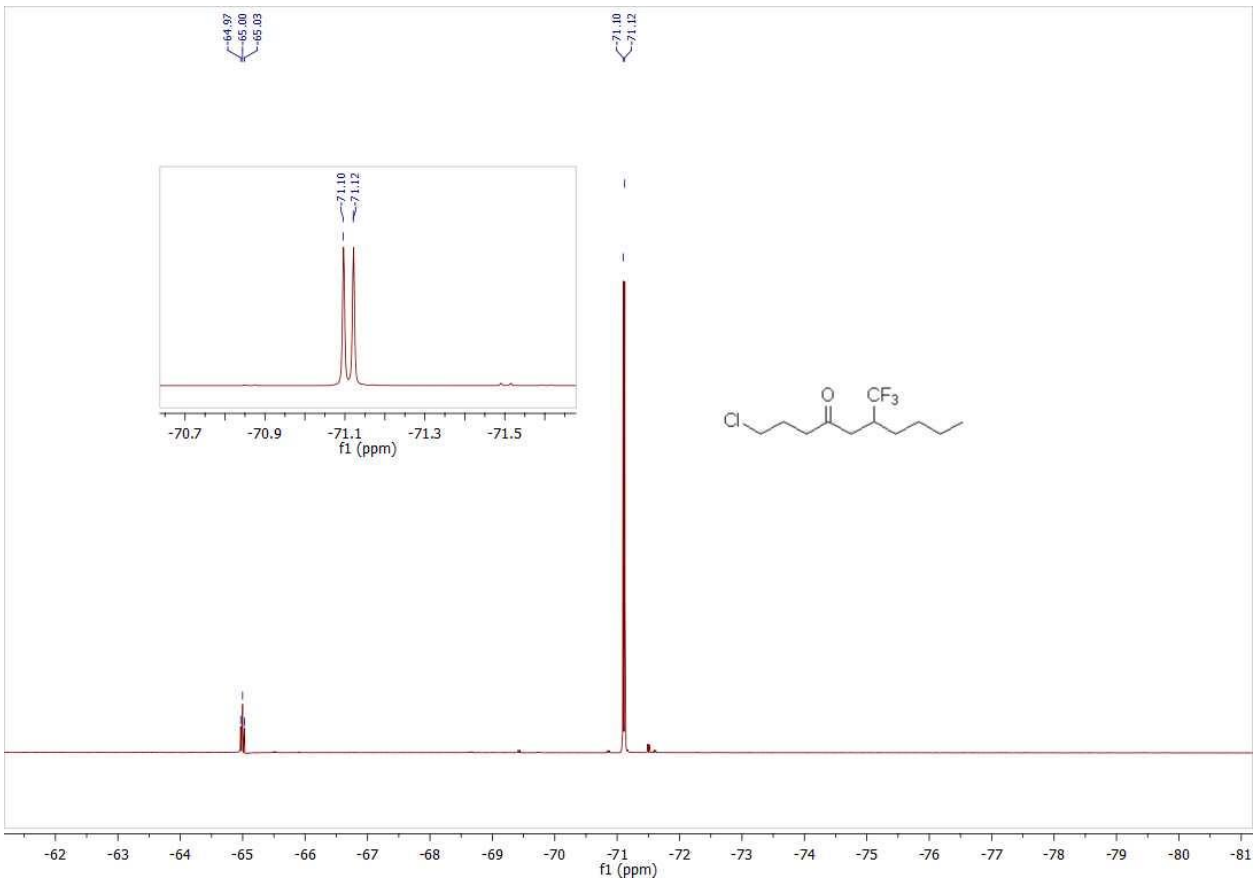
64.92
64.95
70.84
70.87
BnO
CF3
Et
1.00
0.85
f1 (ppm)


7.26
3.60
3.58
3.57
2.76
2.71
2.70
2.67
2.65
2.64
2.50
2.48
2.45
2.44
2.09
2.07
2.06
1.65
1.64
1.59
1.39
1.32
1.31
0.91
0.90
0.88
O
CF3
Cl
2.00
1.02
1.02
1.95
0.88
2.13
1.10
5.62
3.32
f1 (ppm)


206.18
132.39
129.61
126.83
124.05
77.48
76.84
44.37
41.48
41.46
41.43
41.41
39.87
38.47
38.22
37.96
37.70
28.97
28.40
28.38
28.36
28.34
26.25
22.73
13.94
O
CF3
Cl
f1 (ppm)


-64.97
-65.00
-65.03
-71.10
-71.12
-70.7
-70.9
-71.1
-71.3
-71.5
f1 (ppm)
O
CF3
Cl
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
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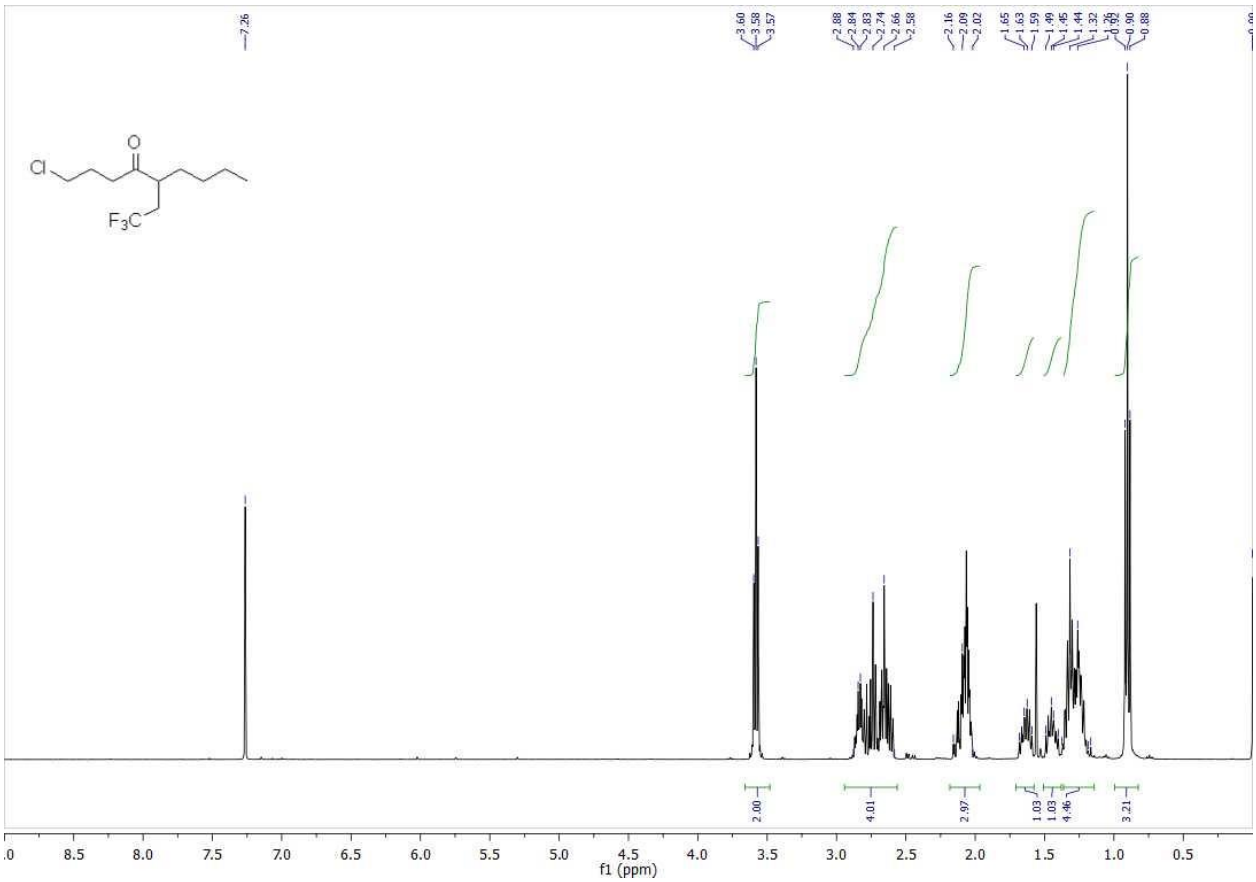
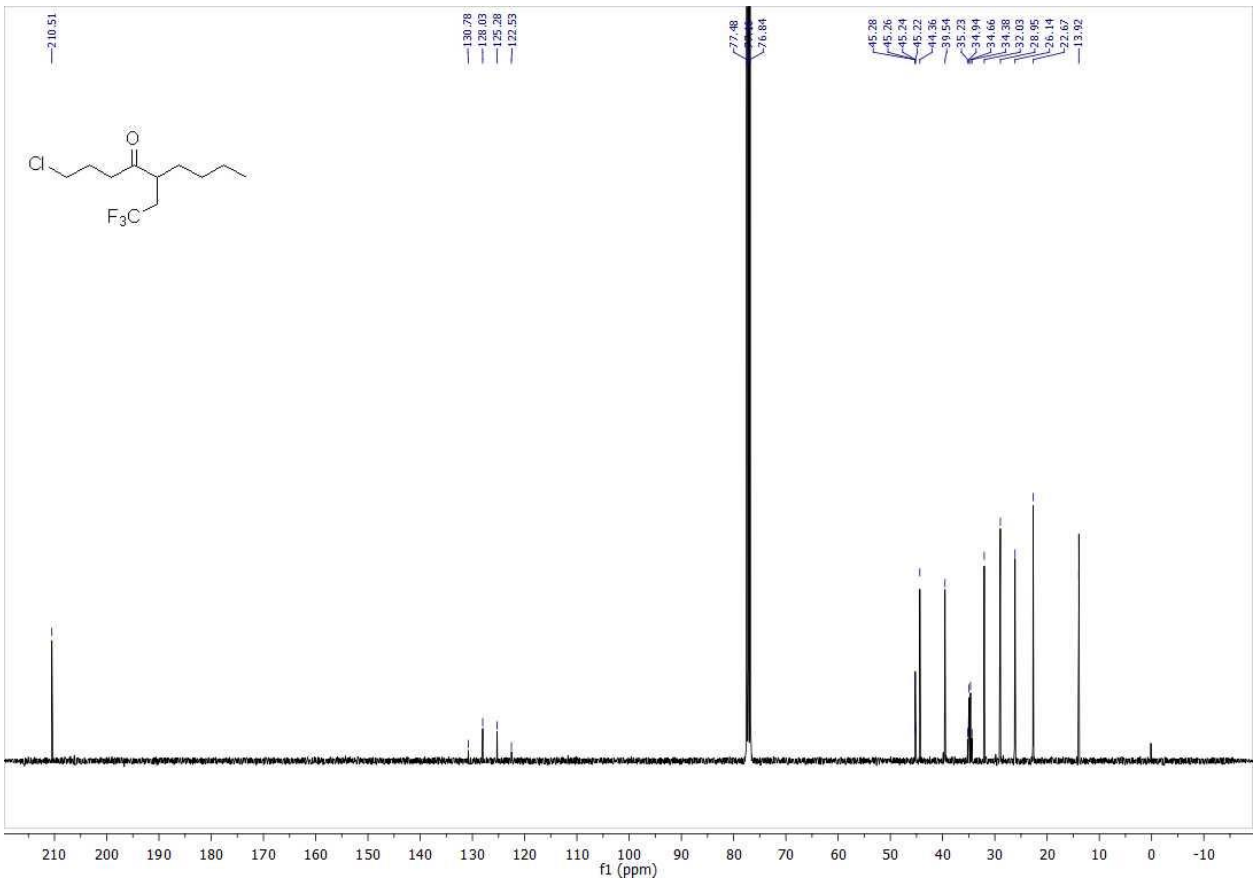
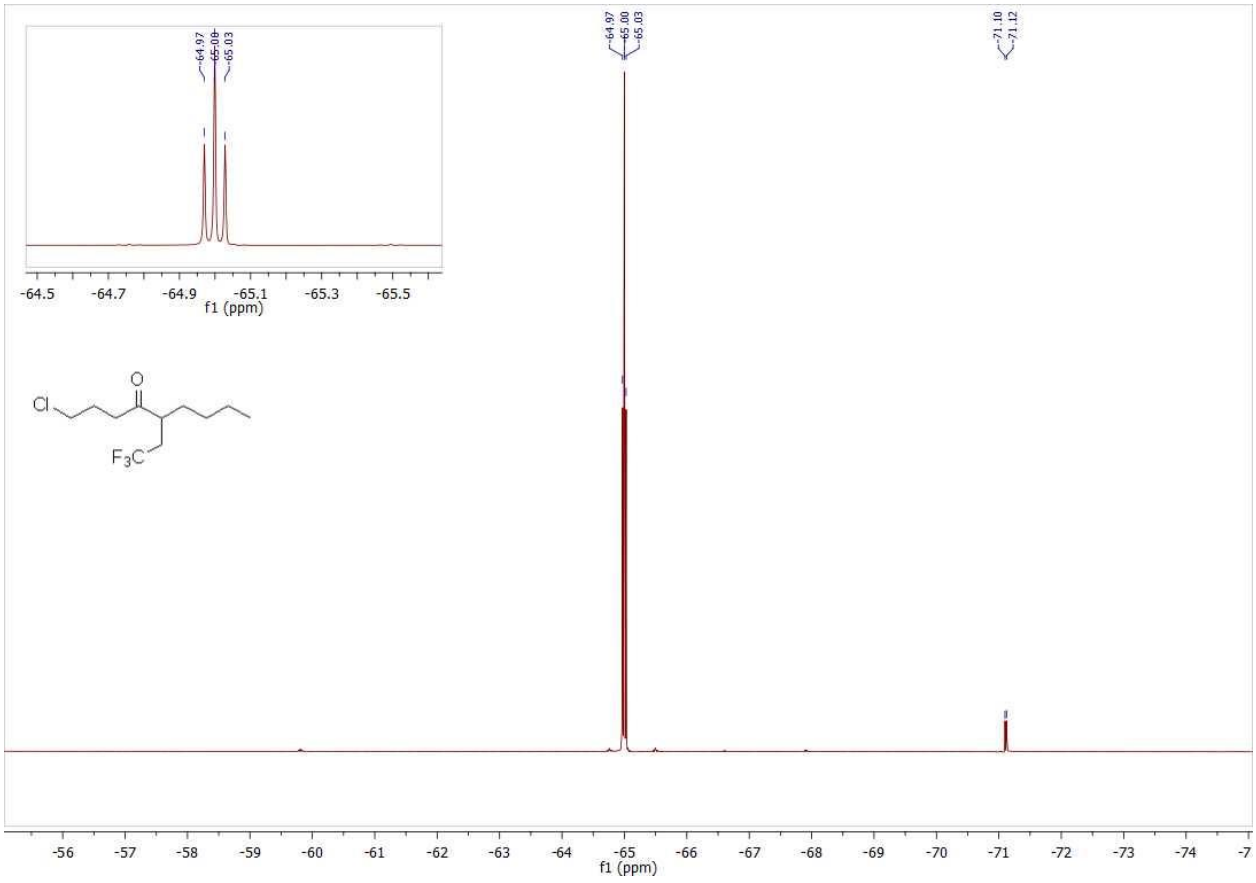
-77
-78
-79
-80
-81
f1 (ppm)


7.26
3.60
3.58
3.57
2.88
2.84
2.83
2.74
2.66
2.58
2.16
2.09
2.02
1.65
1.63
1.59
1.49
1.45
1.44
1.32
0.92
0.90
0.88
O
Cl
F3C
2.00
4.01
2.97
1.03
1.03
4.46
3.21
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
f1 (ppm)

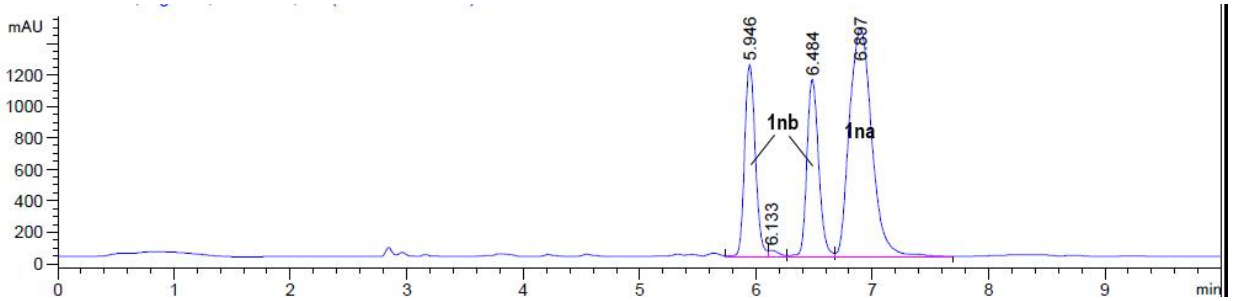

210.51
130.78
128.03
125.28
122.53
77.48
76.84
45.28
45.26
45.24
45.22
44.36
39.54
35.23
34.94
34.66
34.38
32.03
28.95
26.14
22.67
13.92
O
Cl
F3C
f1 (ppm)


64.97
65.00
65.03
71.10
71.12
-64.97
-65.00
-65.03
f1 (ppm)
O
Cl
F3C
f1 (ppm)

VI. HPLC Chromatograms of the Compound 1nb

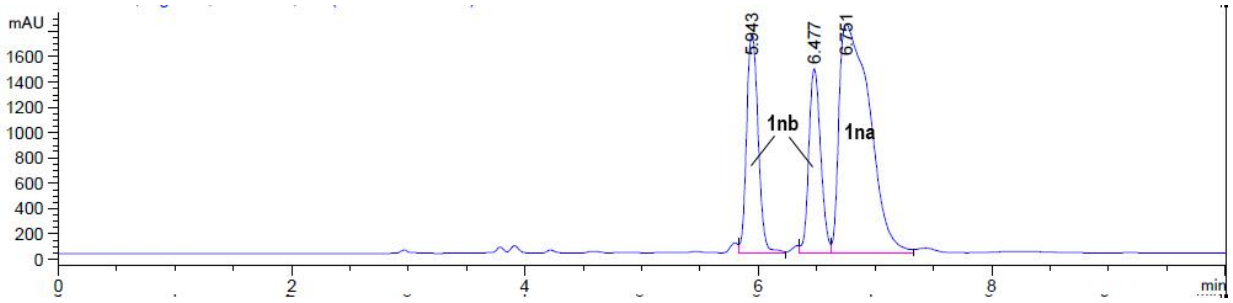
The analysis of the enantiomeric composition for the compound **1nb** was made by HPLC using Phenomenex Lux 3µ Amylose-2 column (95:5 *n*-hexane/2-propanol, flow rate 1.0 mL·min^{-1}, detection at 210 nm).

A) A mixture of **1na** and **1nb** prepared from the racemic **2n**.



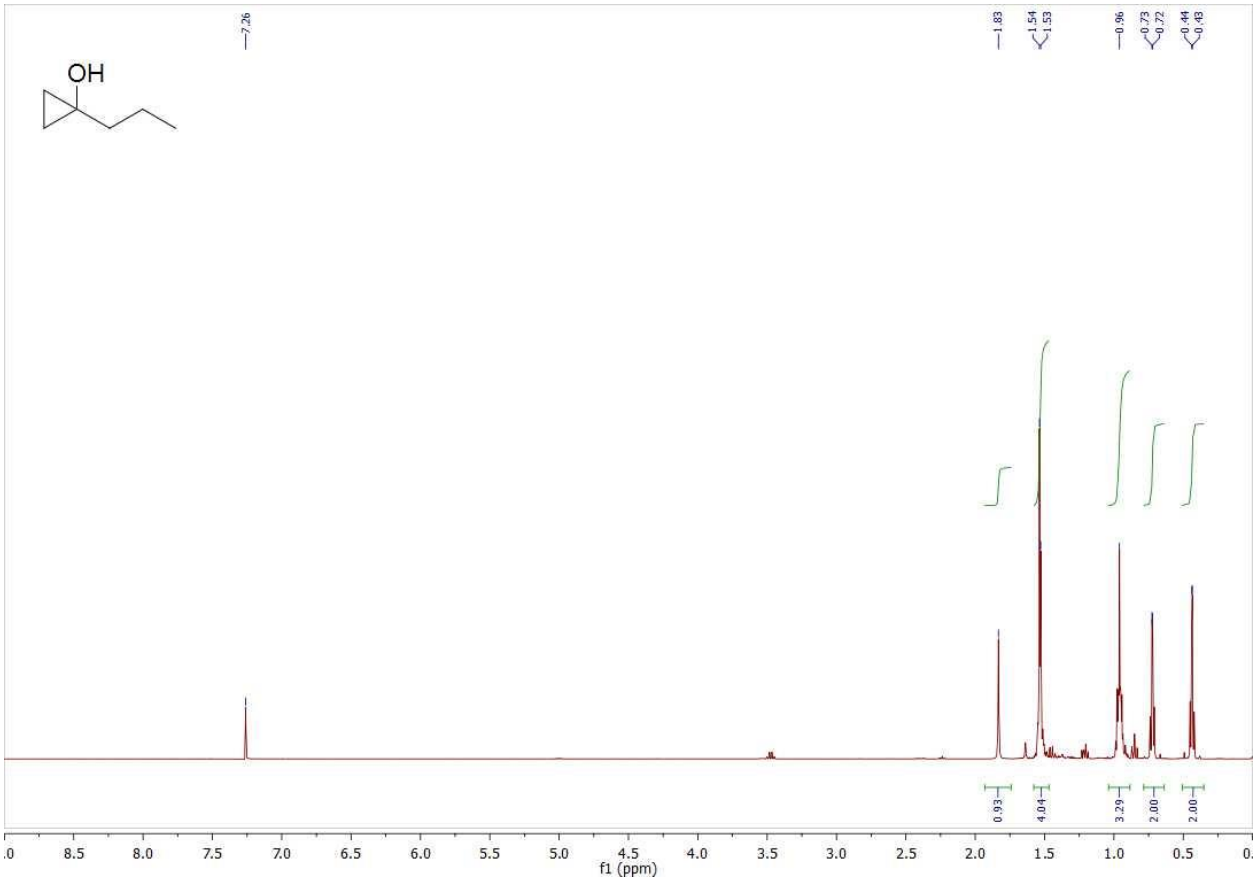
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.946	VV	0.1009	7832.01953	1219.17883	22.1124
2	6.133	VV	0.0935	248.68303	40.58344	0.7021
3	6.484	VV	0.1099	7895.52490	1124.61792	22.2917
4	6.897	VV	0.2162	1.94428e4	1451.92615	54.8937

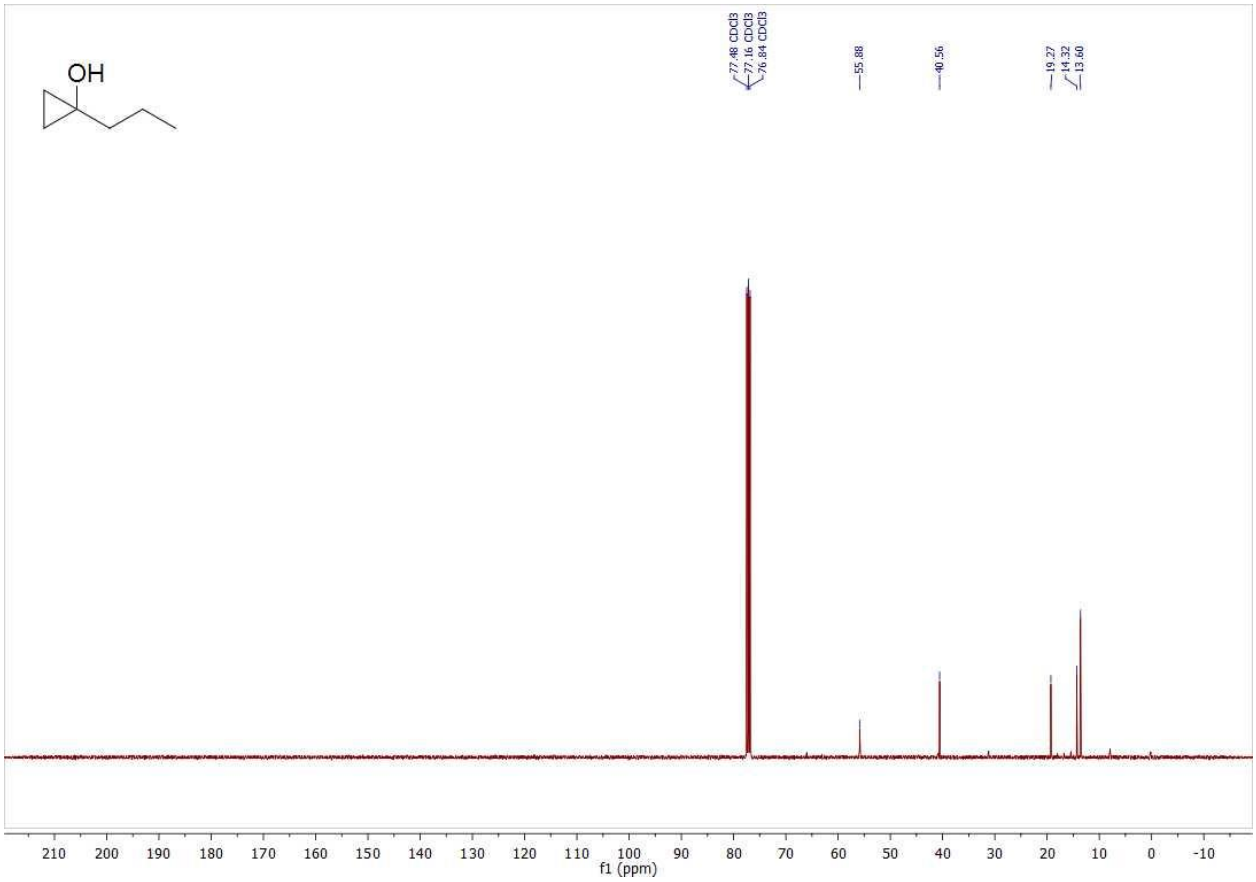
B) A mixture of **1na** and **1nb** prepared from the chiral sample of **2n**.

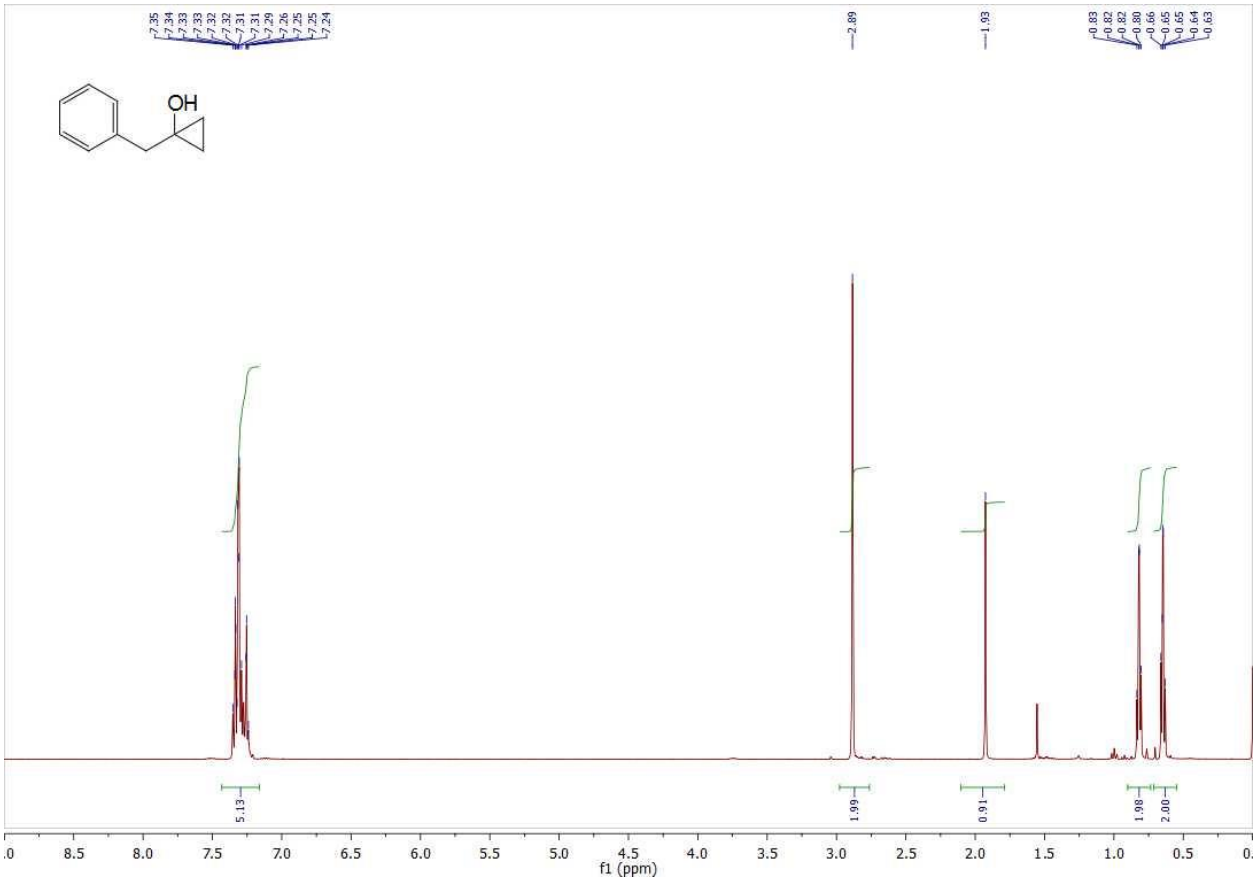


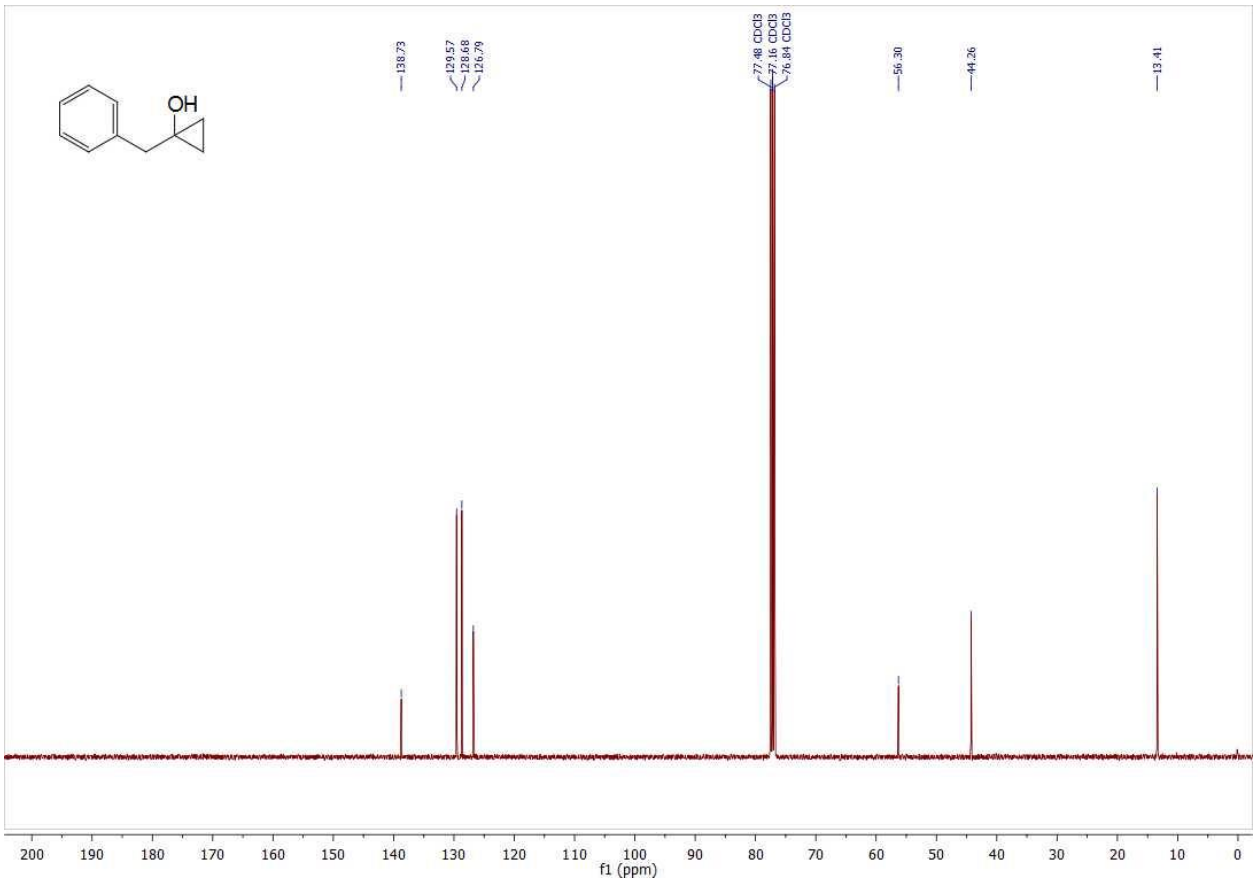
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.943	VV	0.1111	1.20311e4	1730.29114	21.7202
2	6.477	VV	0.1125	1.03235e4	1459.37549	18.6373
3	6.751	VV	0.2505	3.30367e4	1813.97522	59.6425

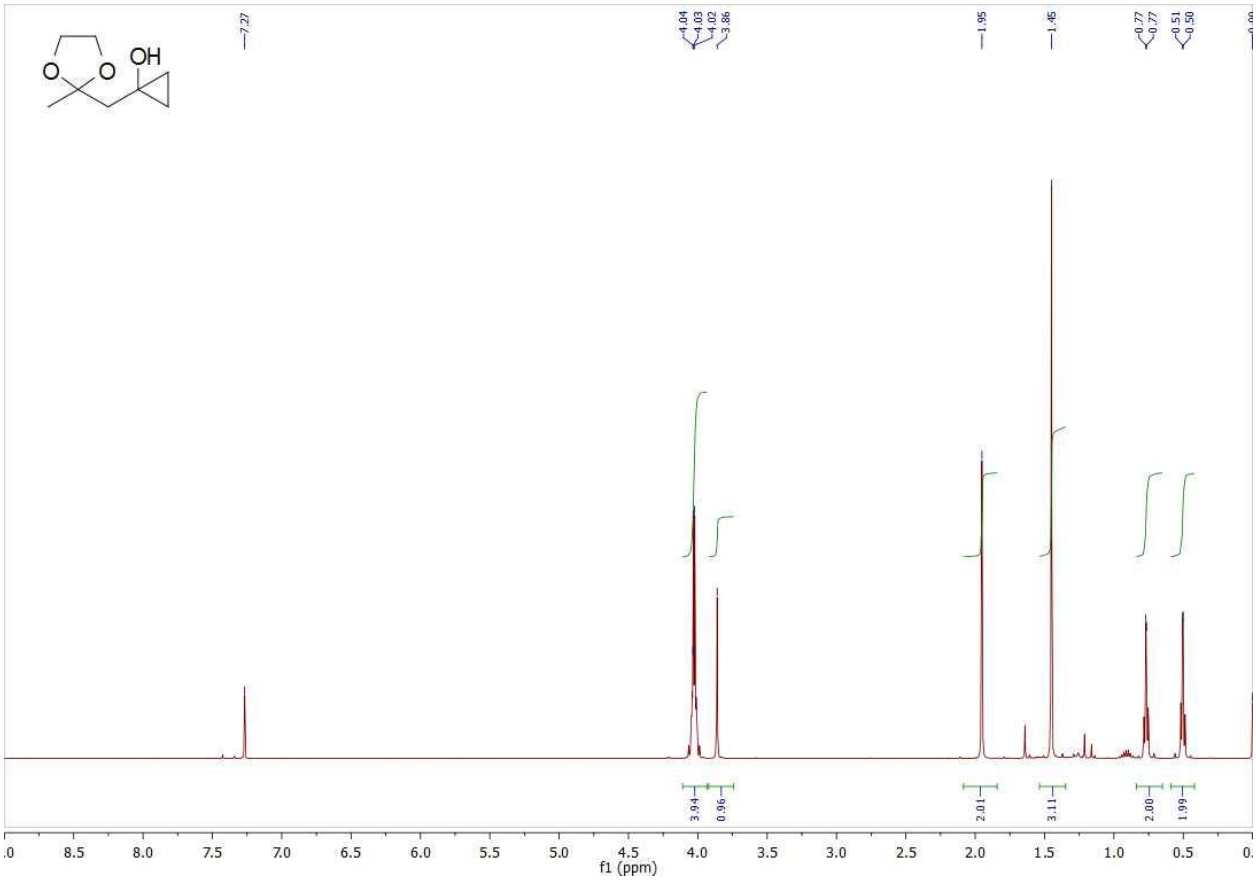
VII. Copies of ^{1}H and ^{13}C NMR Spectra of Cyclopropanols

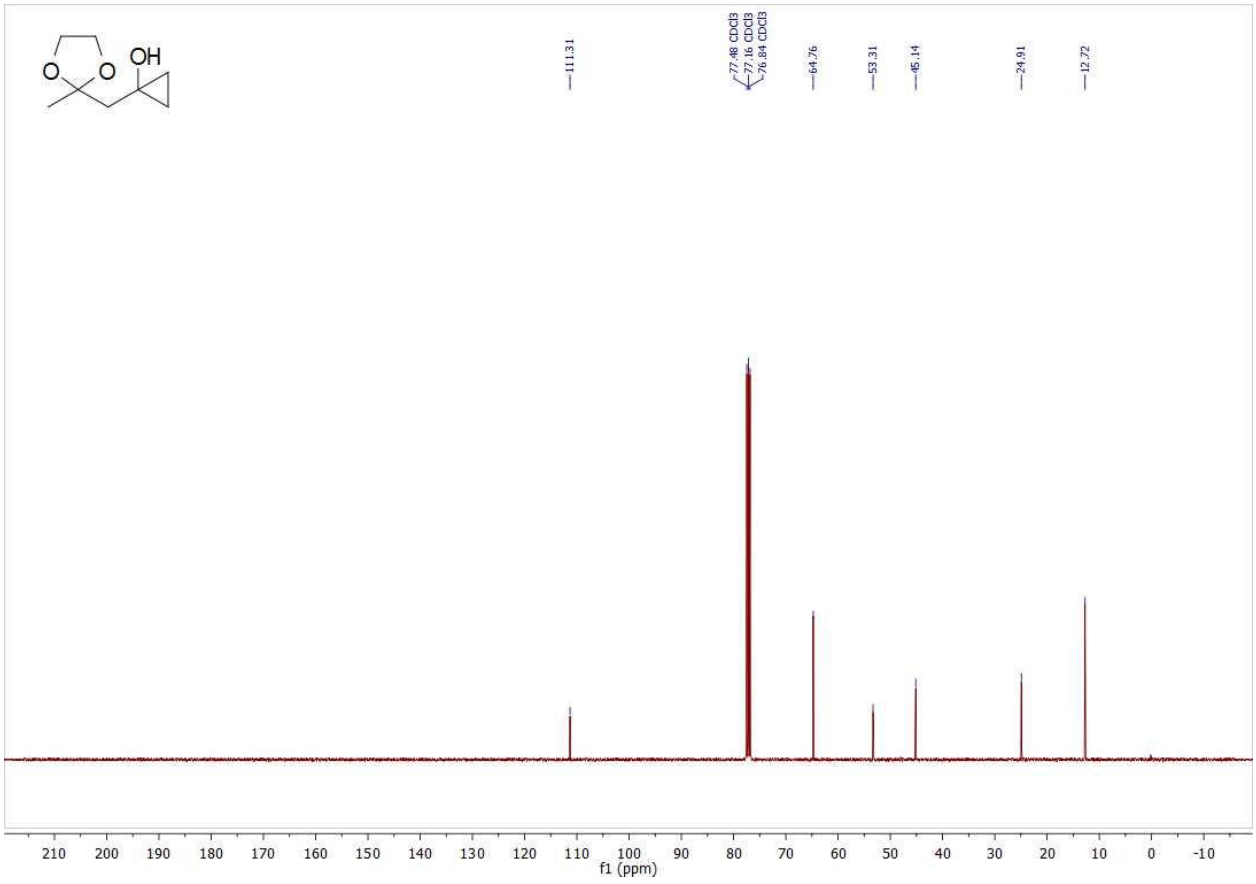


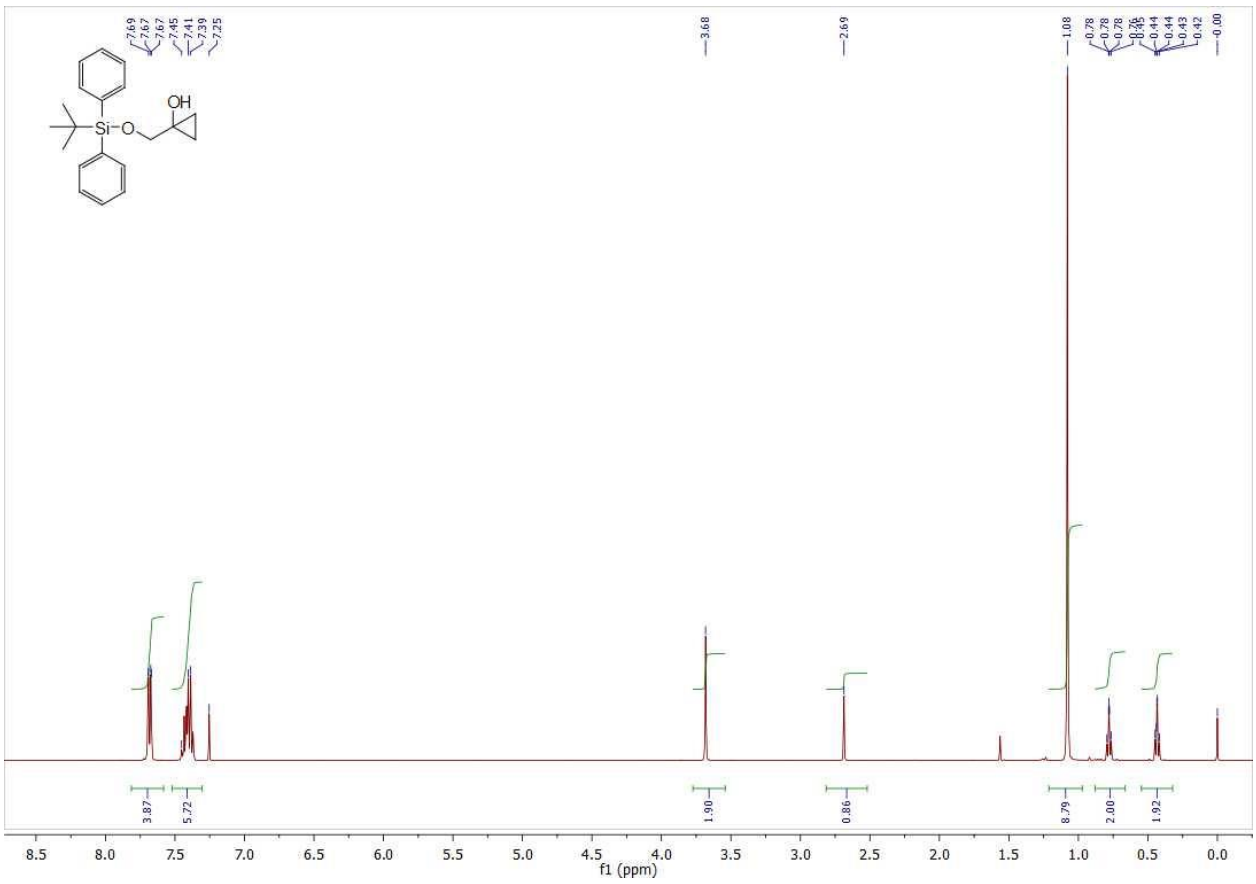


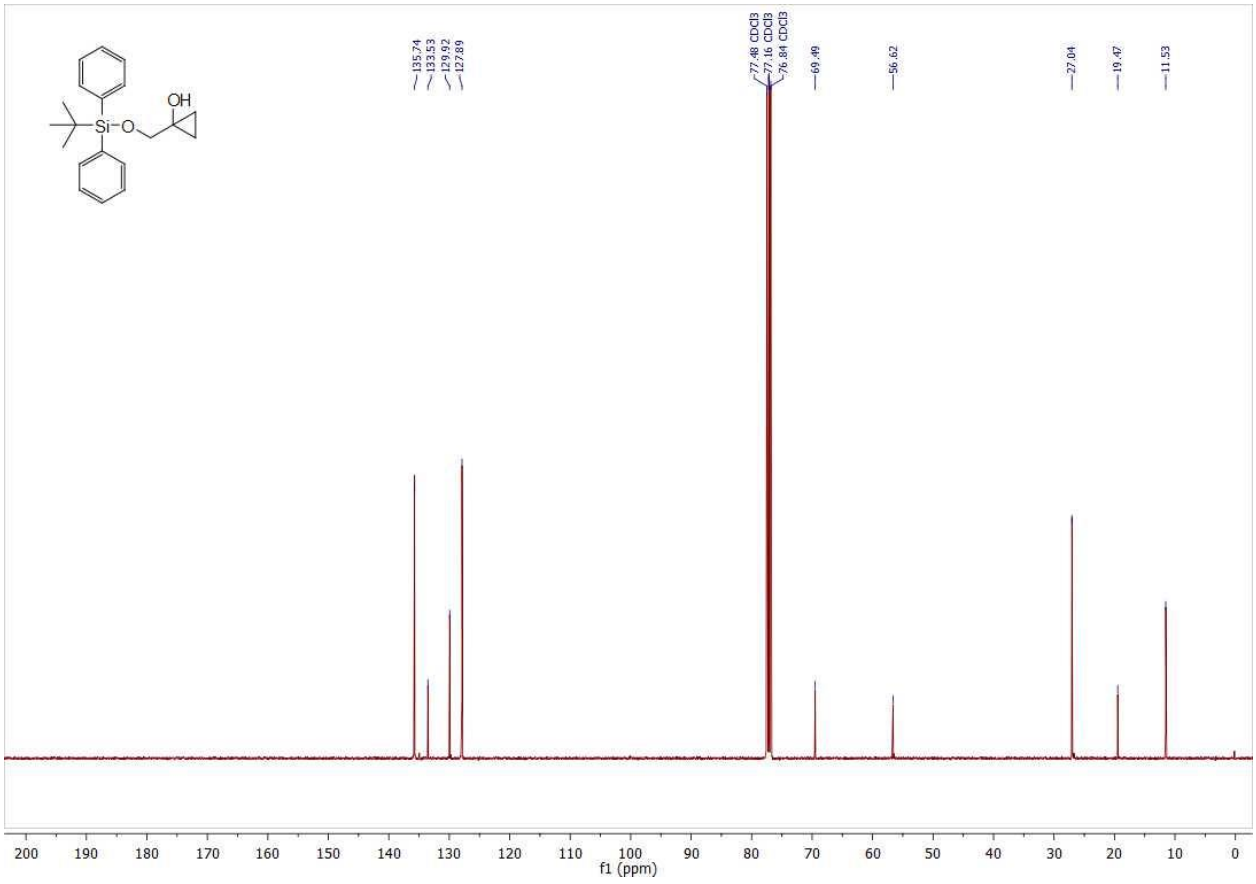

OH
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.29
7.26
7.25
7.25
7.24
2.89
1.93
0.83
0.82
0.82
0.80
0.66
0.65
0.65
0.64
0.63
5.13
1.99
0.91
1.98
2.00
f1 (ppm)

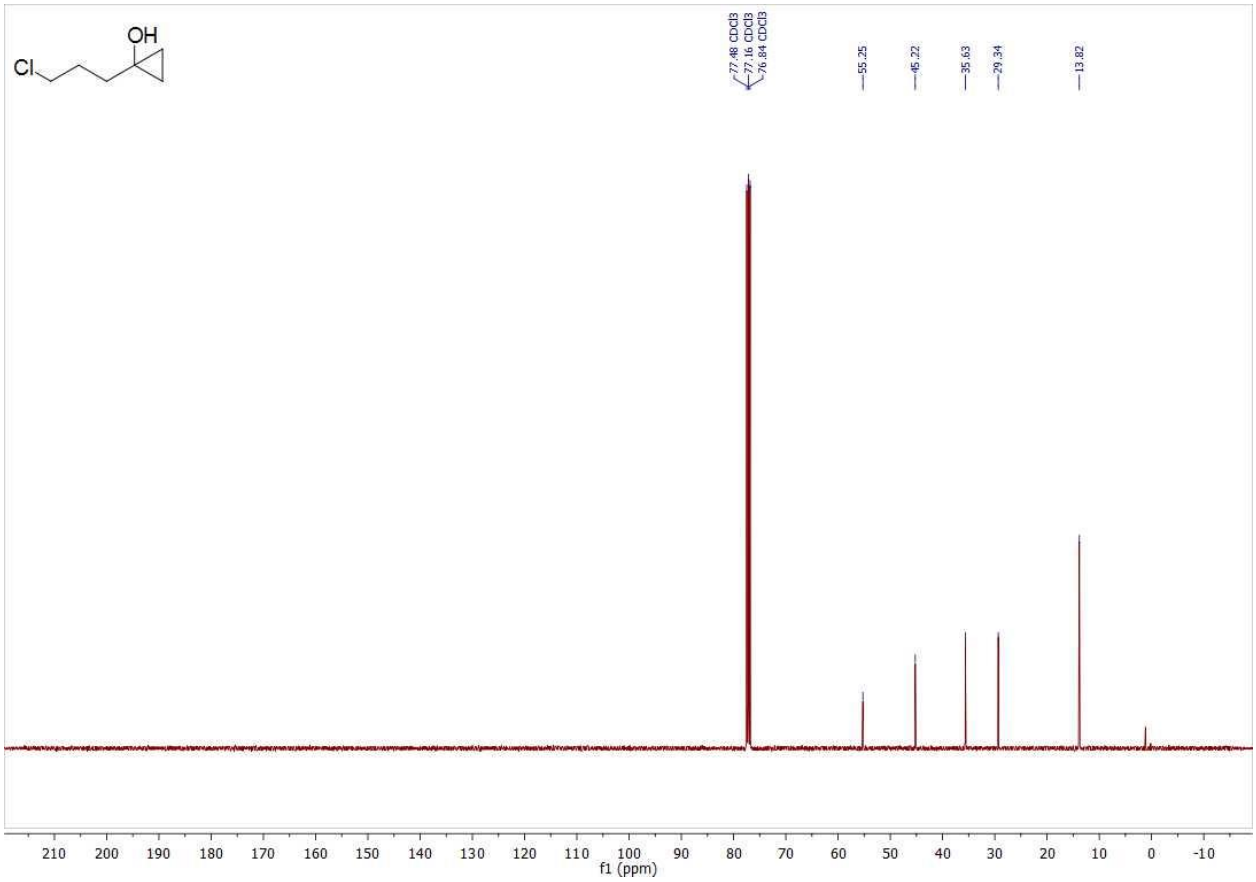

OH
138.73
129.57
128.68
126.79
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.30
44.26
13.41
f1 (ppm)

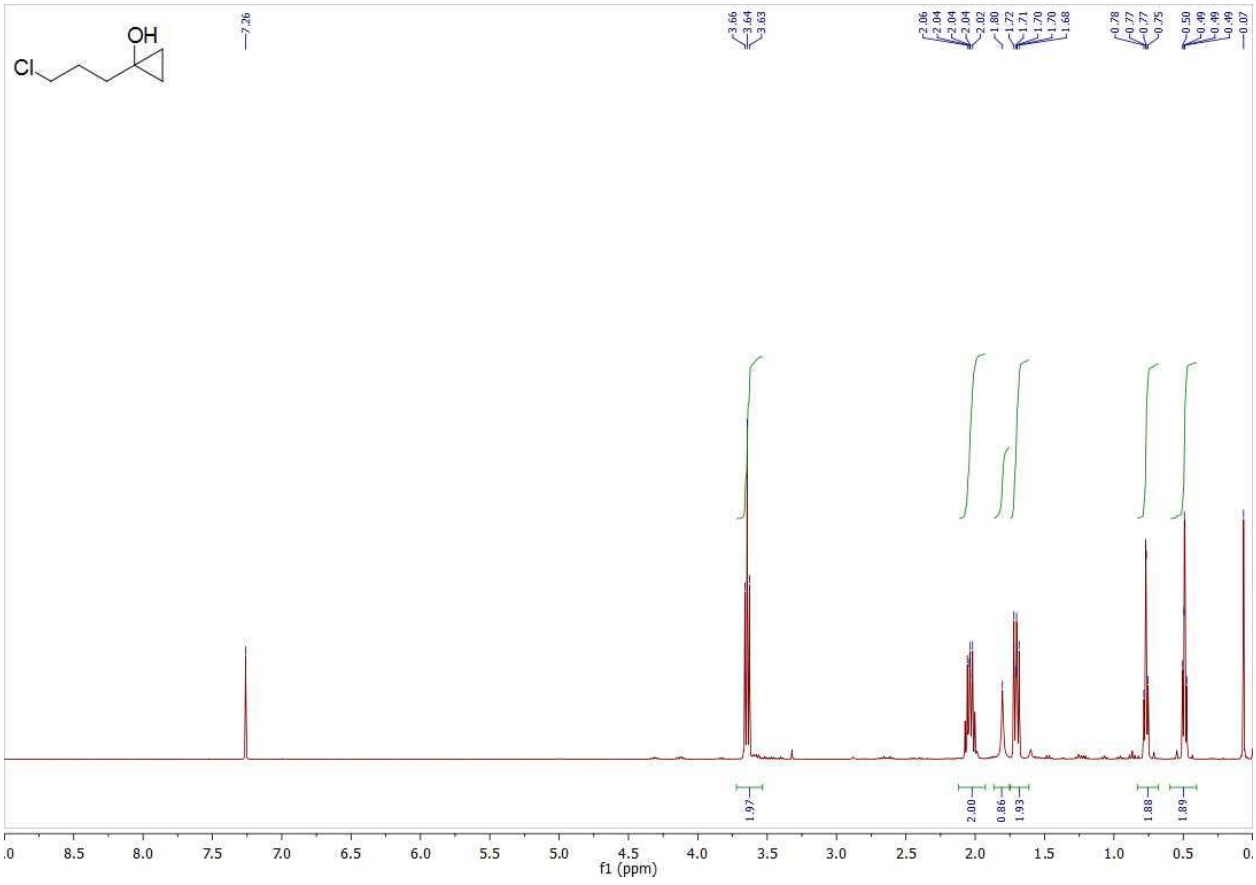

OH
7.27
4.04
4.03
4.02
3.86
1.95
1.45
0.77
0.77
0.51
0.50
3.94
0.96
2.01
3.11
2.00
1.99
f1 (ppm)

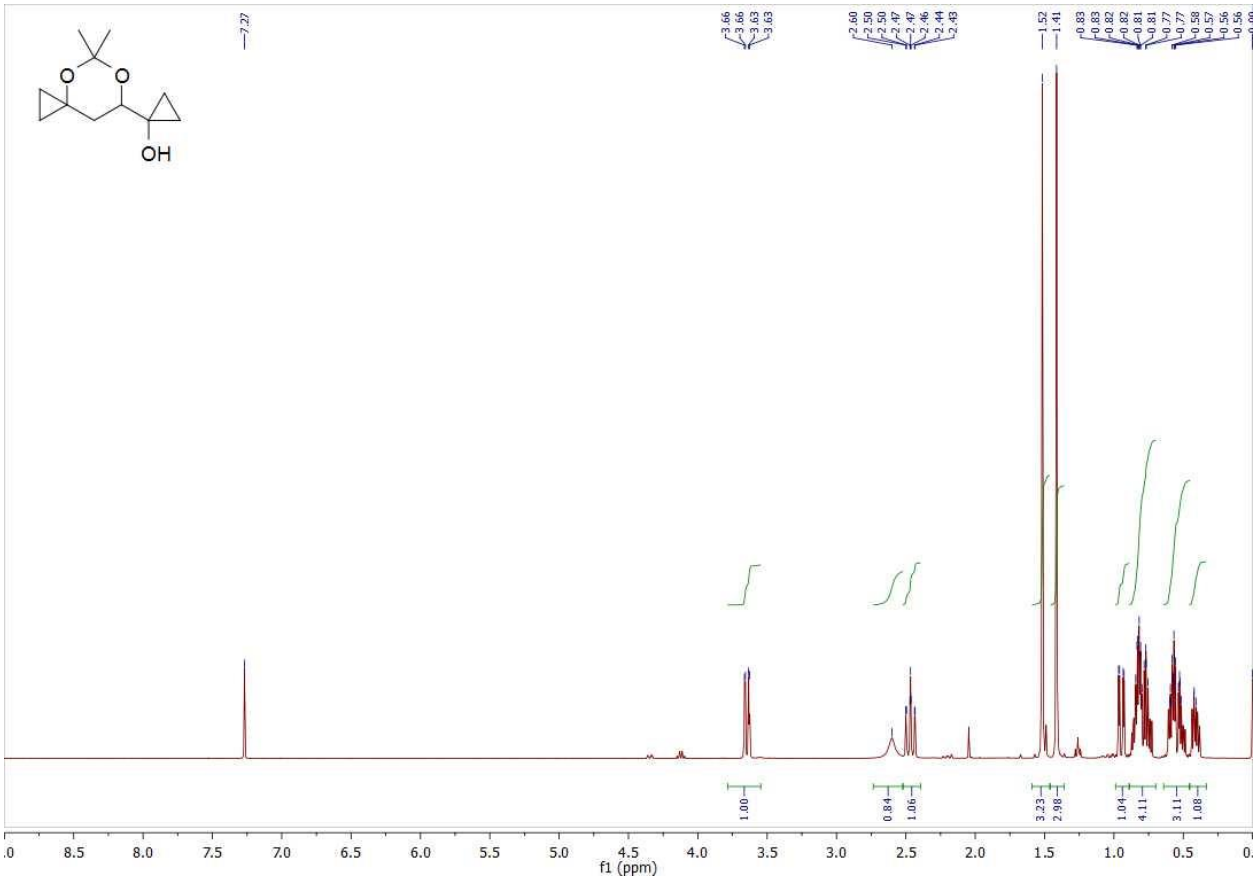

OH
111.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.76
53.31
45.14
24.91
12.72
f1 (ppm)

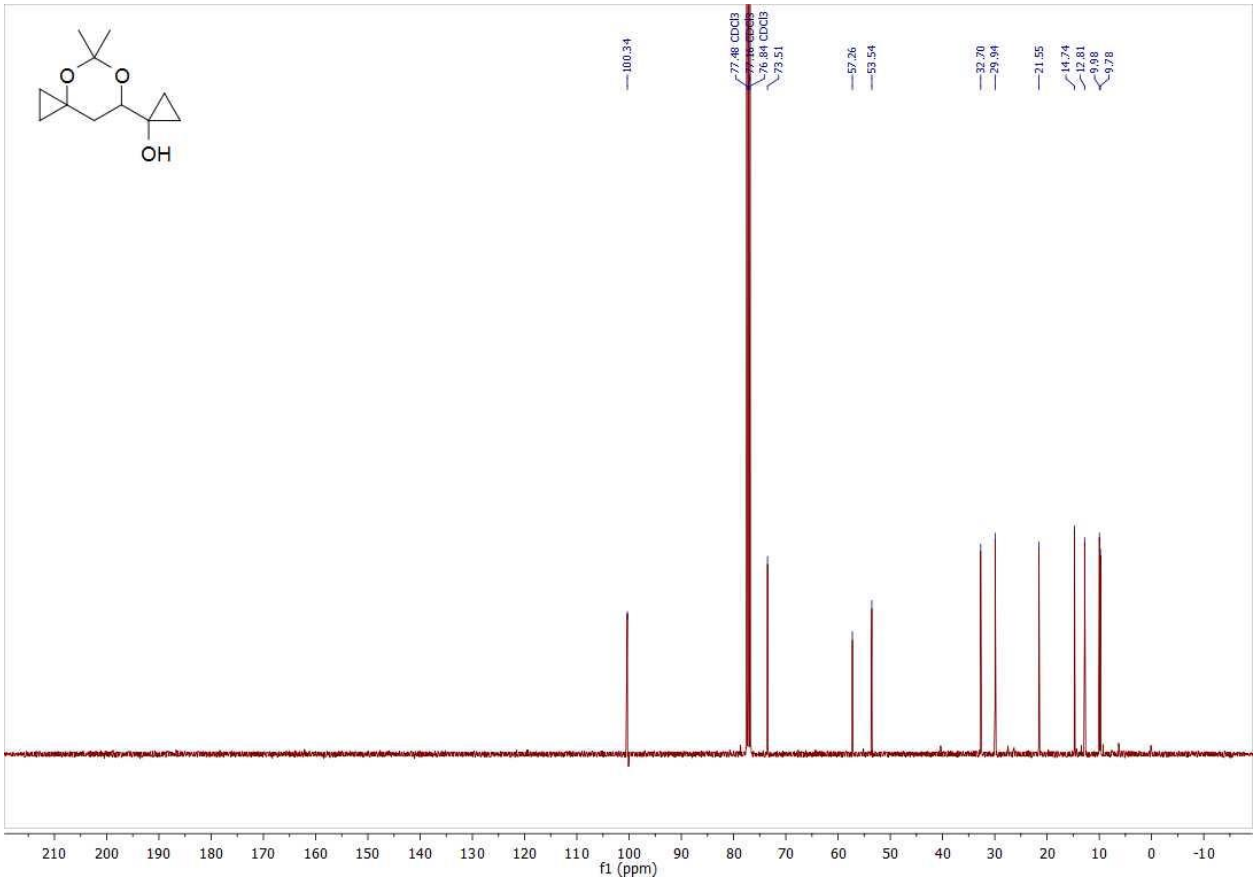

OH
Si
O
7.69
7.67
7.67
7.45
7.41
7.39
7.25
3.68
2.69
1.08
0.78
0.78
0.78
0.44
0.44
0.43
0.42
-0.00
3.87
5.72
1.90
0.86
8.79
2.00
1.92
f1 (ppm)

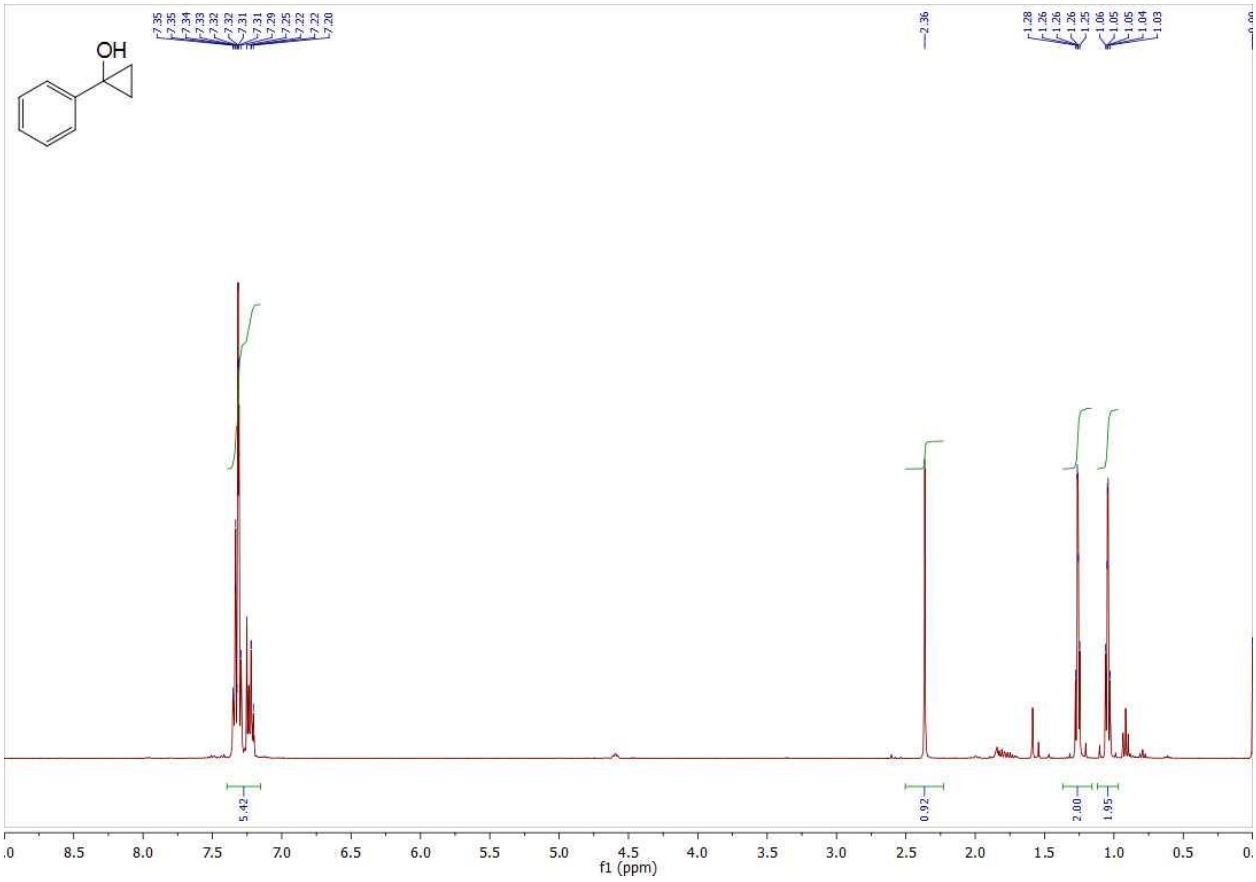

OH
Si
O
135.74
133.53
129.92
127.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.49
56.62
27.04
19.47
11.53
f1 (ppm)

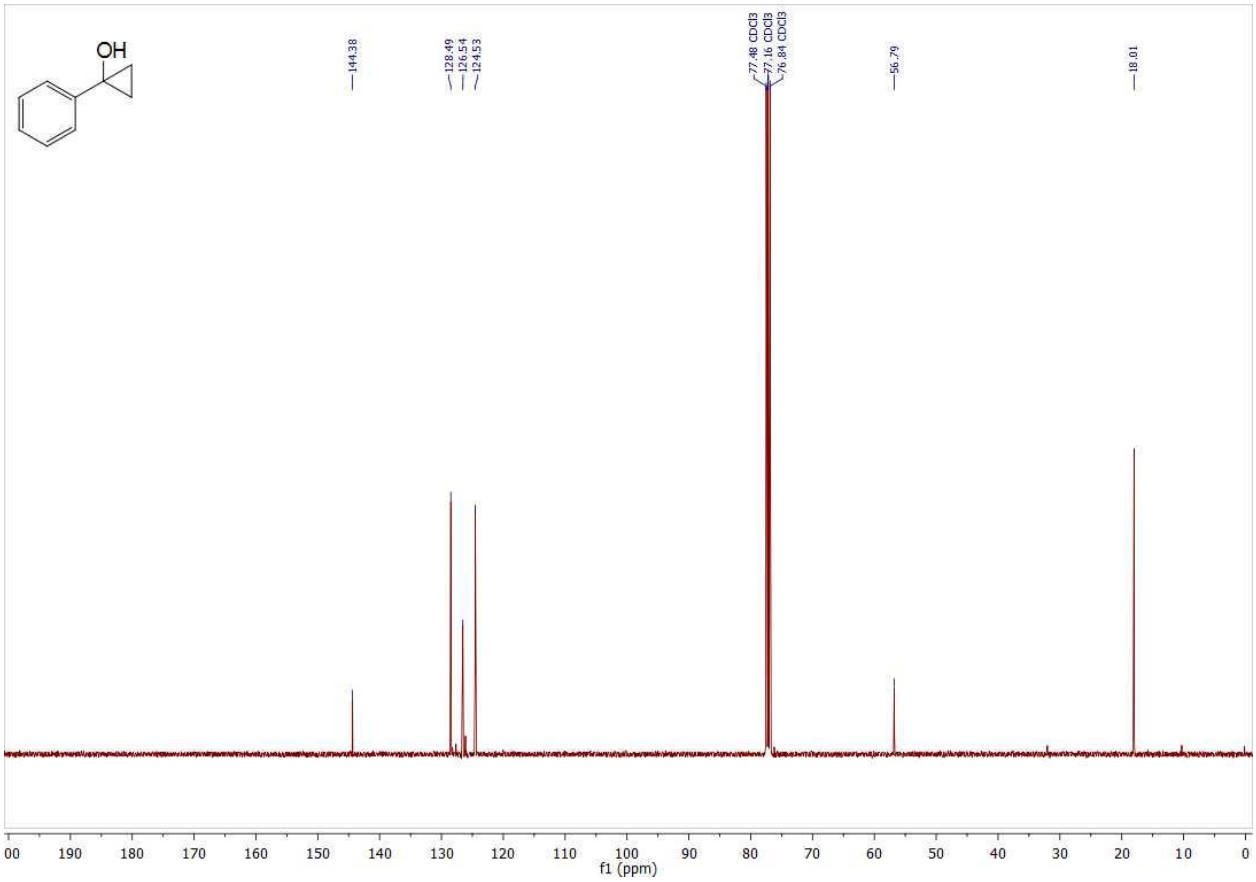

OH
Cl
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.25
45.22
35.63
29.34
13.82
f1 (ppm)

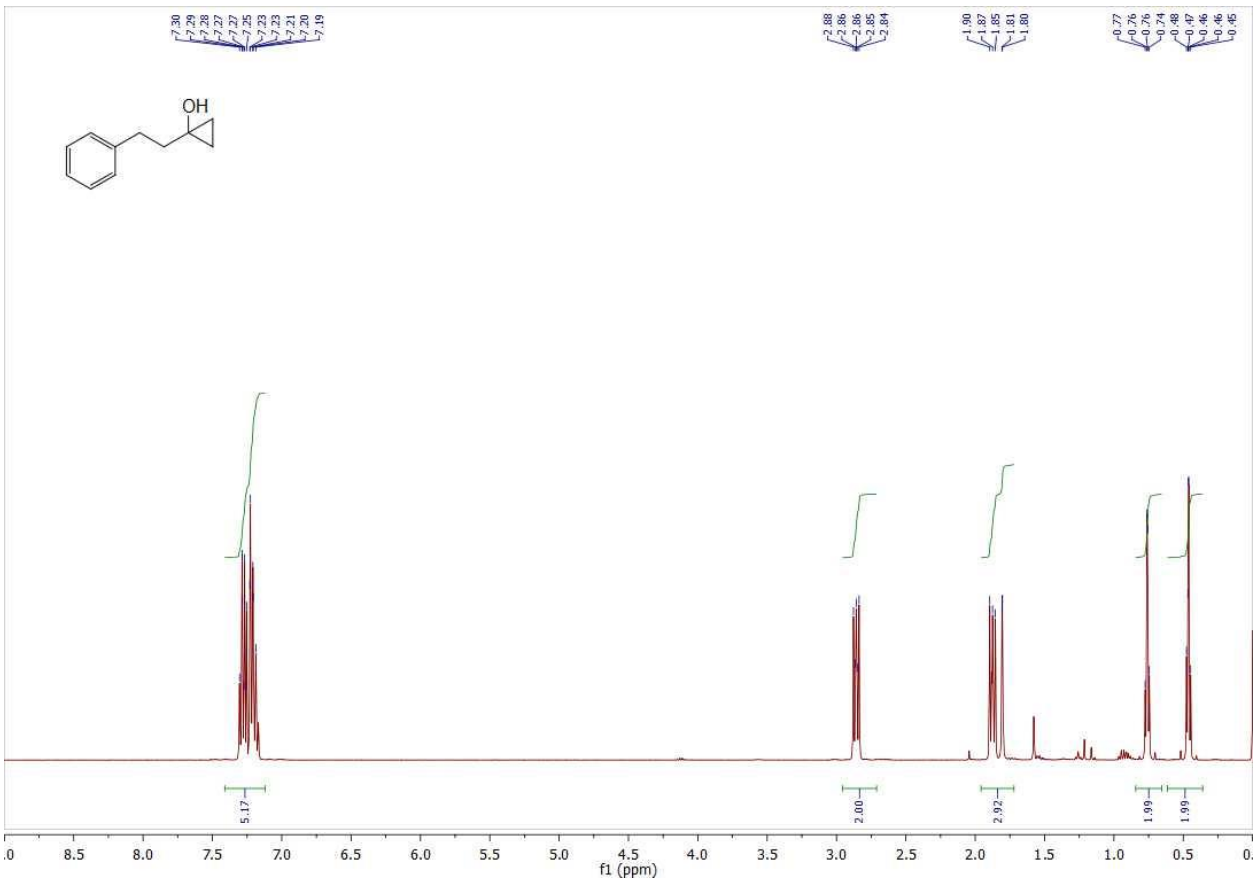

OH
Cl
7.26
3.66
3.64
3.63
2.06
2.04
2.04
2.04
2.02
1.80
1.72
1.71
1.70
1.70
1.68
0.78
0.77
0.77
0.75
0.50
0.49
0.49
0.49
0.07
1.97
2.00
0.86
1.93
1.88
1.89
f1 (ppm)

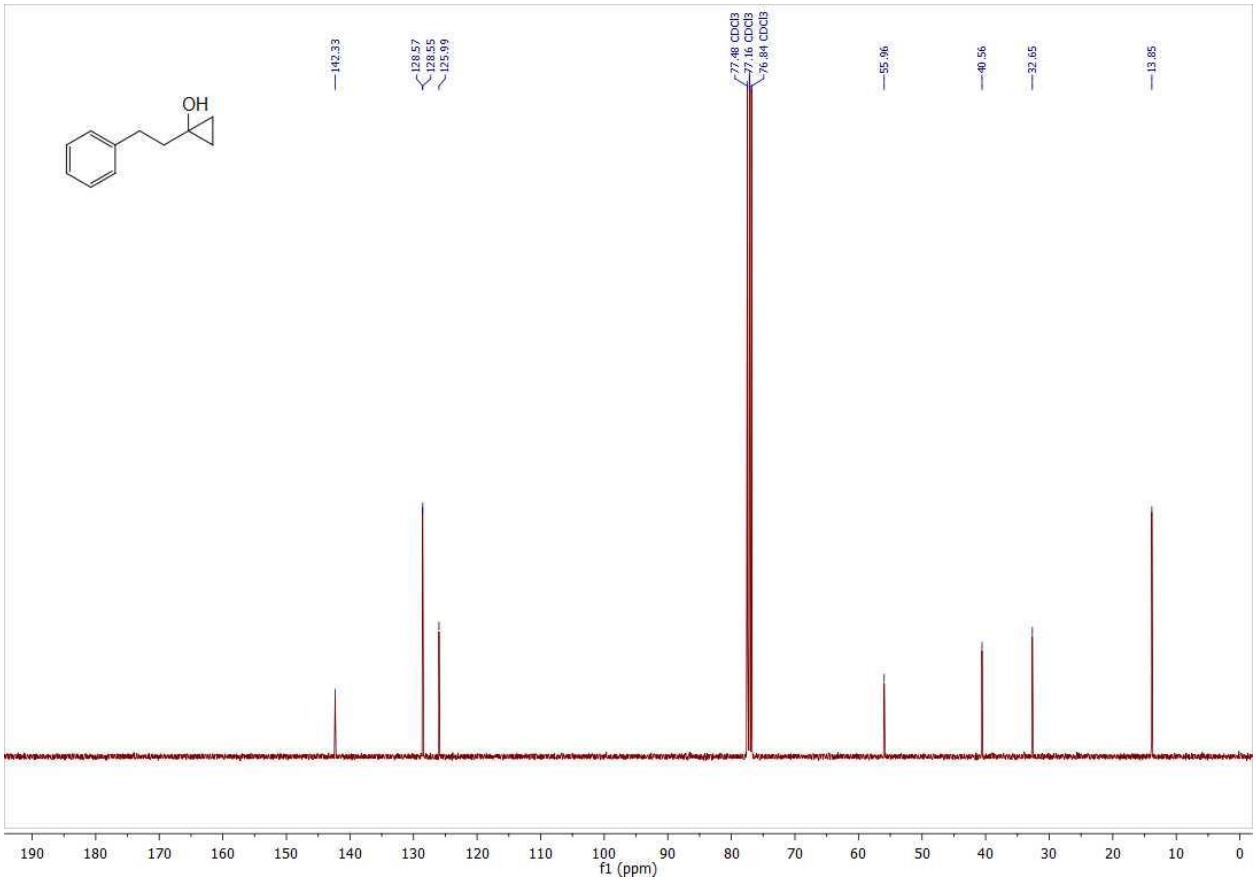

OH
7.27
3.66
3.63
2.60
2.50
2.47
2.46
2.44
2.43
1.52
1.41
0.83
0.82
0.81
0.77
0.58
0.57
0.56
1.00
0.84
1.06
3.23
2.98
1.04
4.11
3.11
1.08
f1 (ppm)

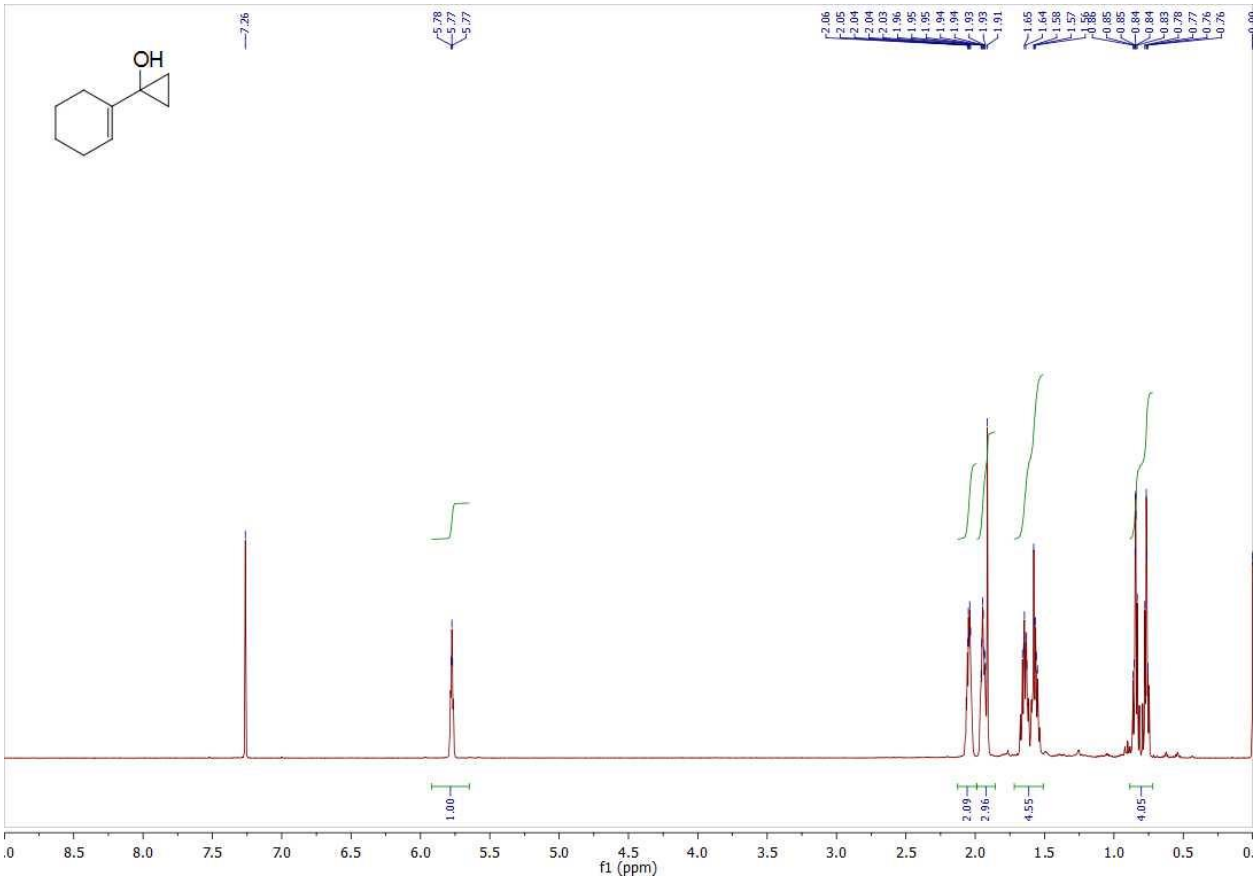

OH
100.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.51
57.26
53.54
32.70
29.94
21.55
14.24
12.81
9.98
9.78
f1 (ppm)

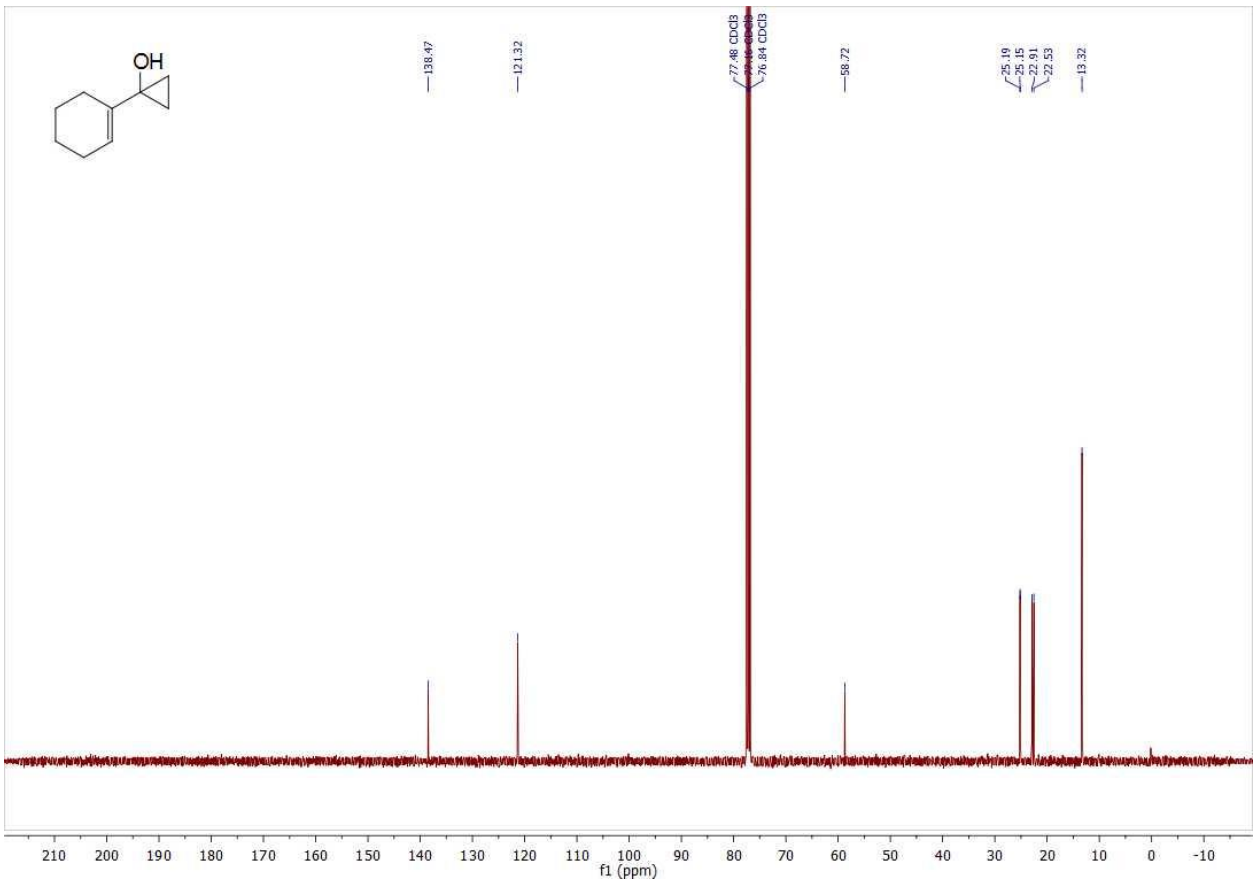

OH
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.29
7.25
7.22
7.20
2.36
1.28
1.26
1.26
1.26
1.25
1.06
1.05
1.05
1.04
1.03
5.42
0.92
2.00
1.95
f1 (ppm)

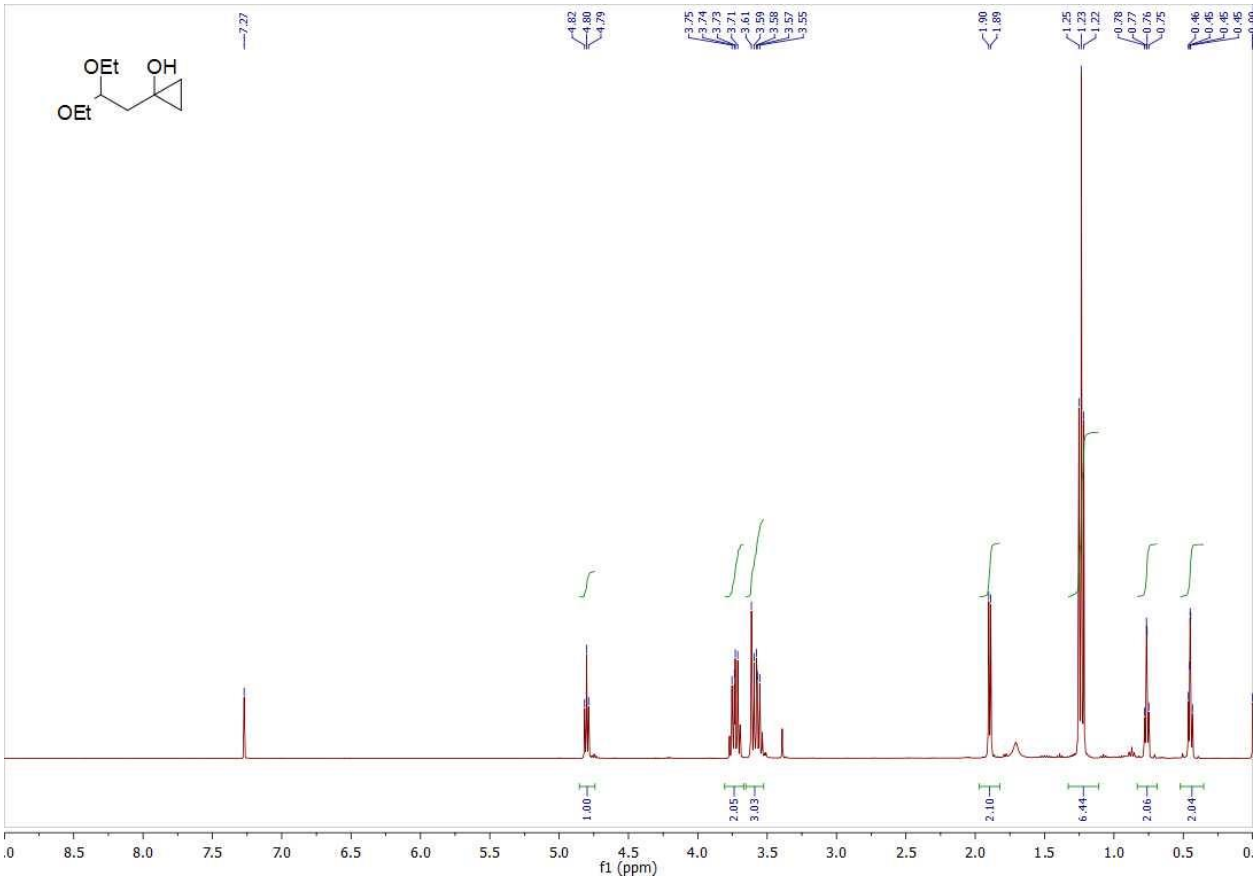

OH
144.38
128.49
126.54
124.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.79
18.01
f1 (ppm)

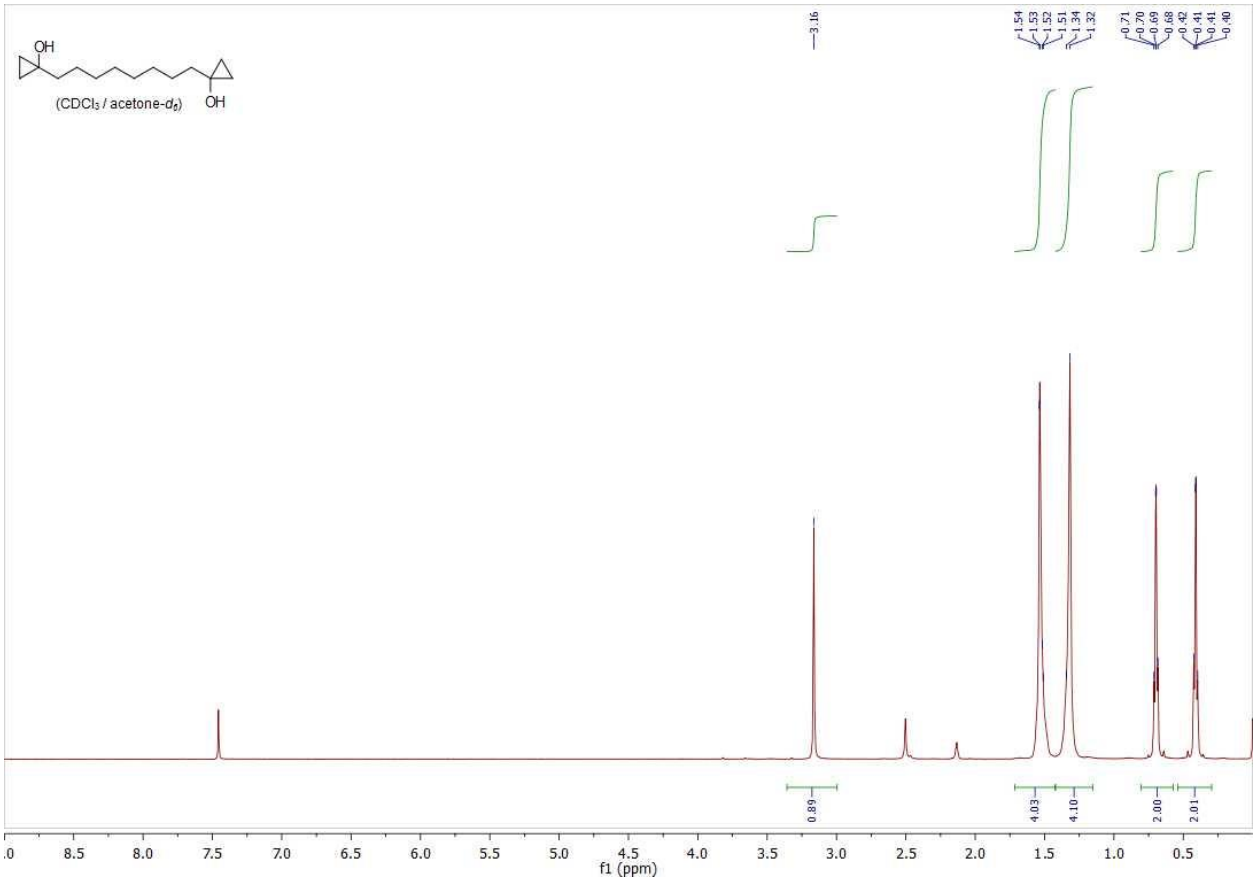

OH
7.30
7.29
7.28
7.27
7.27
7.25
7.23
7.23
7.21
7.20
7.19
2.88
2.86
2.86
2.85
2.84
1.90
1.87
1.85
1.81
1.80
0.77
0.76
0.76
0.74
0.48
0.47
0.46
0.46
0.45
5.17
2.00
2.92
1.99
1.99
f1 (ppm)

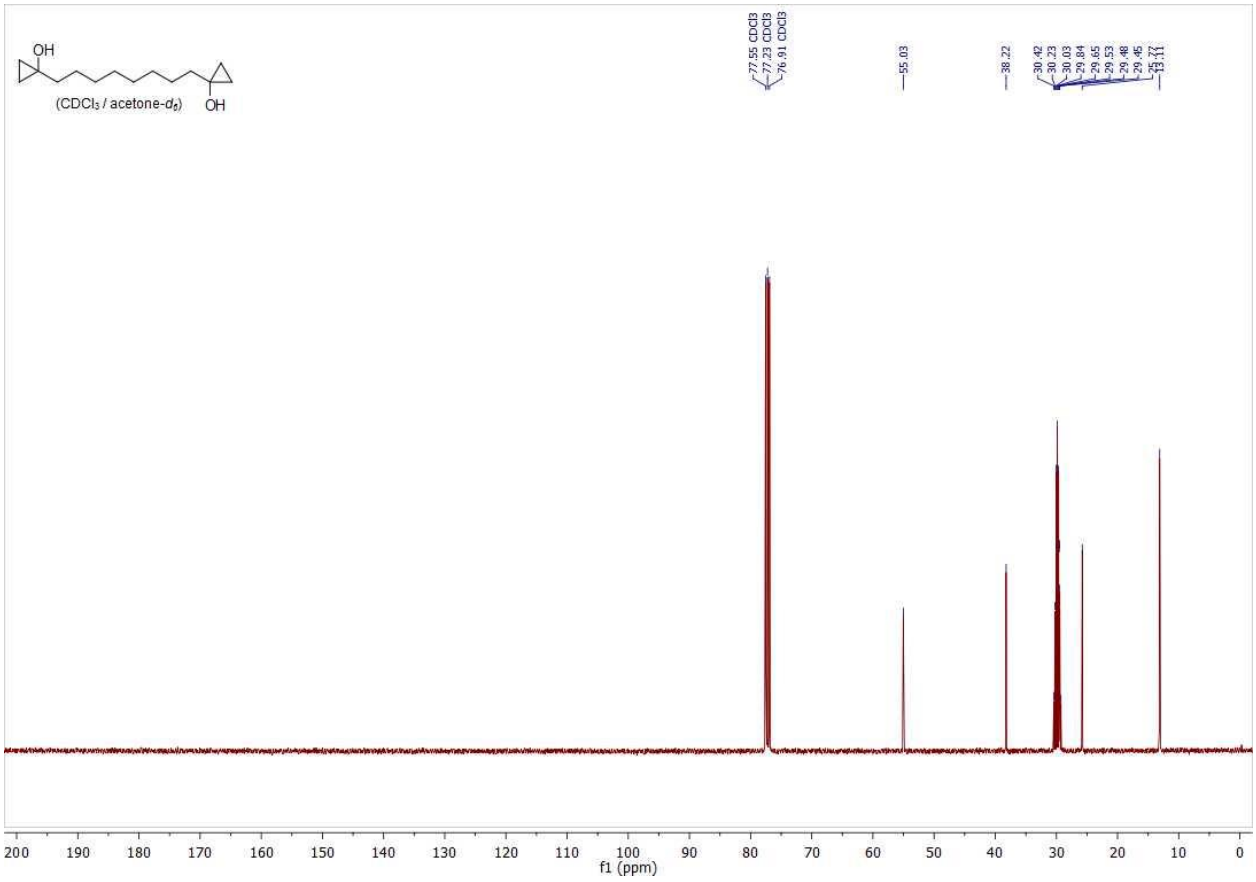

OH
142.33
128.57
128.55
125.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.96
40.56
32.65
13.85
f1 (ppm)

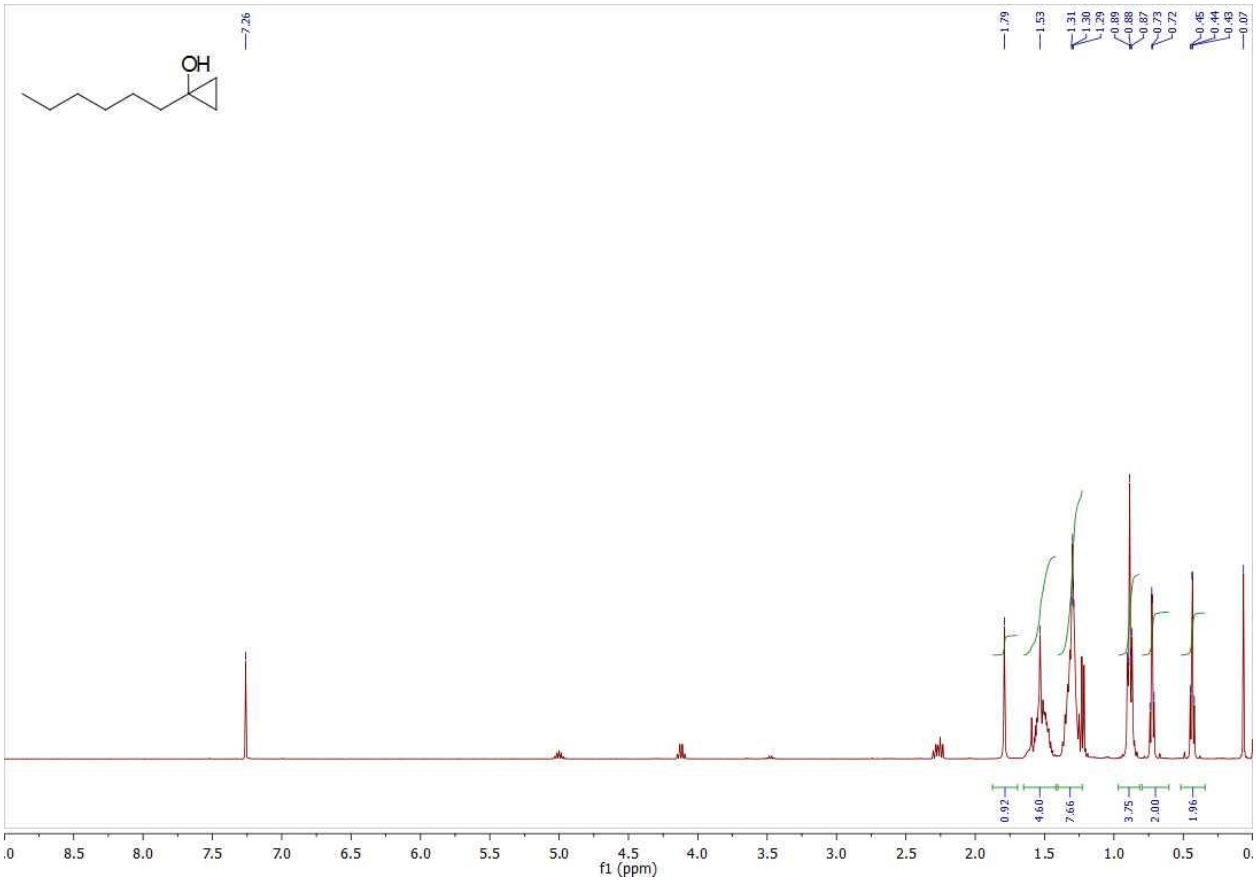

OH
7.26
5.78
5.77
5.77
2.06
2.05
2.04
2.04
2.03
1.96
1.95
1.95
1.94
1.94
1.93
1.93
1.91
1.65
1.64
1.58
1.57
0.88
0.85
0.85
0.84
0.84
0.83
0.78
0.77
0.76
0.76
1.00
2.09
2.96
4.55
4.05
f1 (ppm)

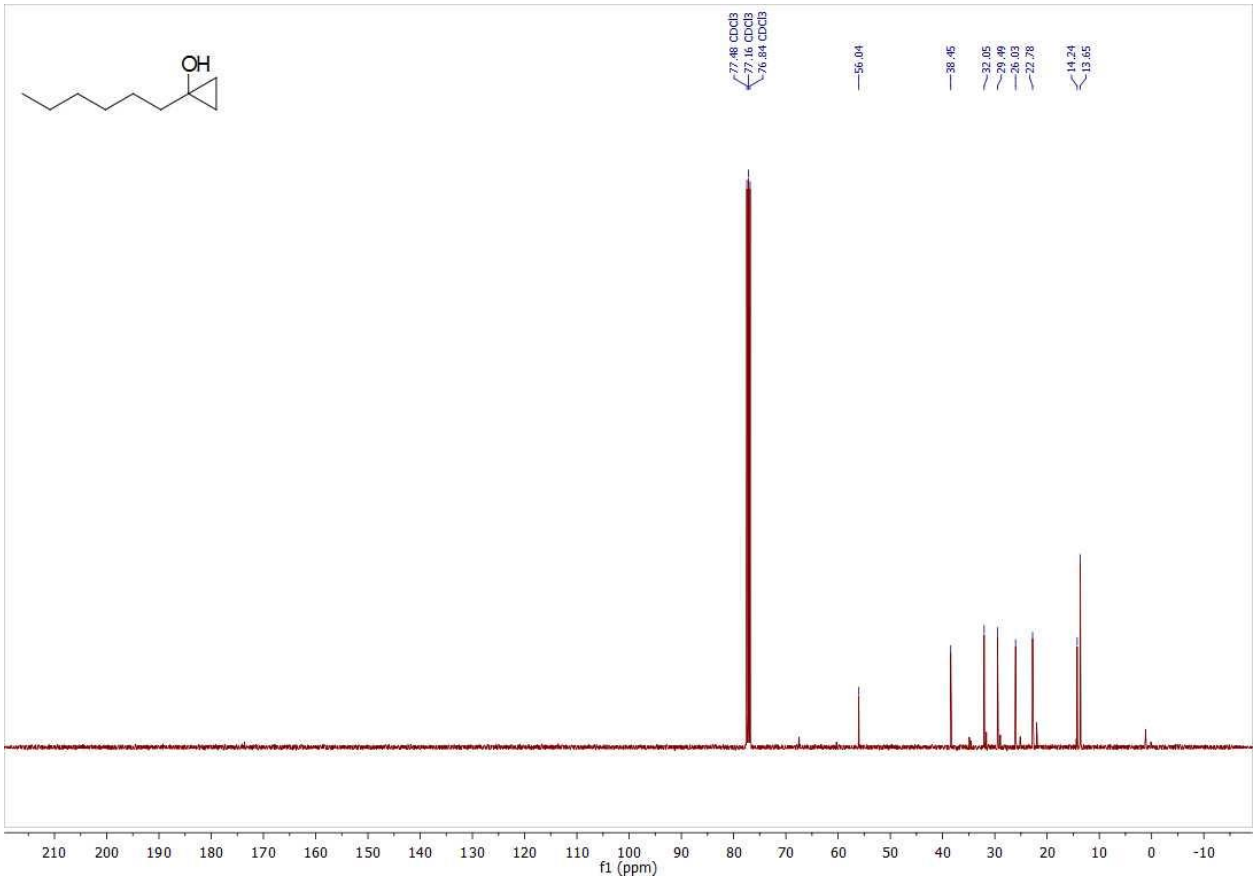

OH
138.47
121.32
77.48 CDCl3
76.84 CDCl3
58.72
25.19
25.15
22.91
22.53
13.32
f1 (ppm)

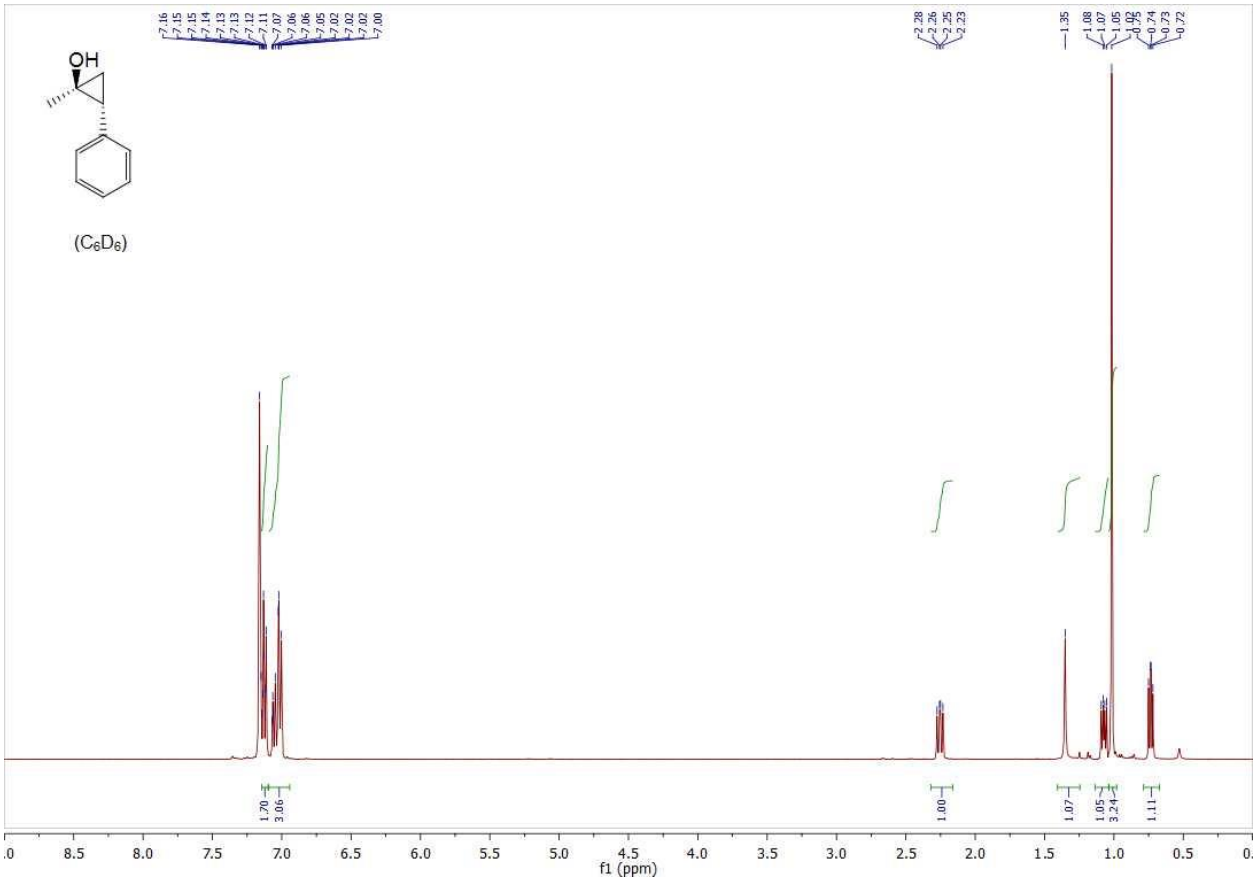

OEt
OH
OEt
7.27
4.82
4.80
4.79
3.75
3.74
3.73
3.71
3.61
3.59
3.58
3.57
3.55
1.90
1.89
1.25
1.23
1.22
0.78
0.77
0.76
0.75
0.46
0.45
0.45
1.00
2.05
3.03
2.10
6.44
2.06
2.04
f1 (ppm)

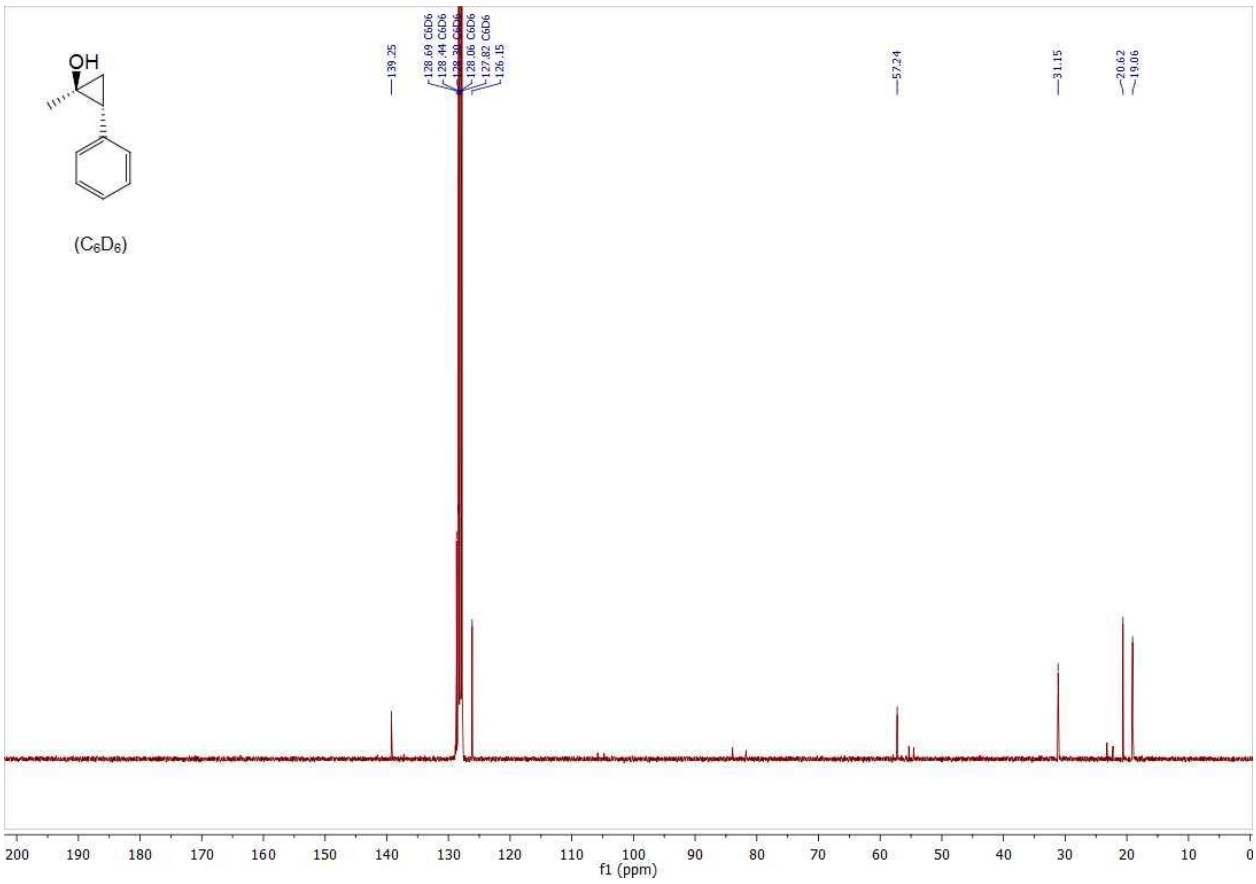

OH
(CDCl3 / acetone-d6)
OH
3.16
1.54
1.53
1.52
1.51
1.34
1.32
0.71
0.70
0.69
0.68
0.42
0.41
0.41
0.40
0.89
4.03
4.10
2.00
2.01
f1 (ppm)

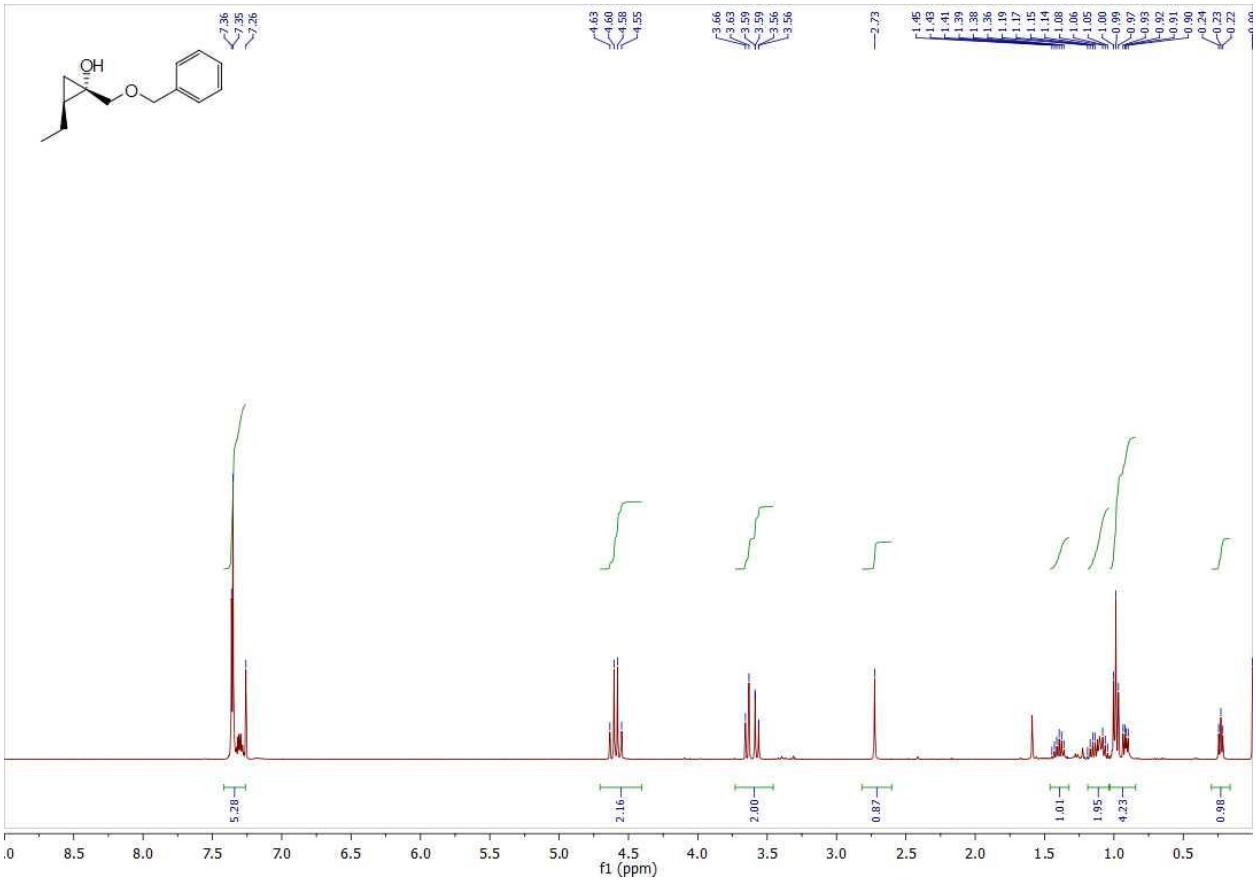

OH
(CDCl3 / acetone-d6)
OH
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
55.03
38.22
30.42
30.23
30.03
29.84
29.65
29.53
29.48
29.45
13.11
f1 (ppm)

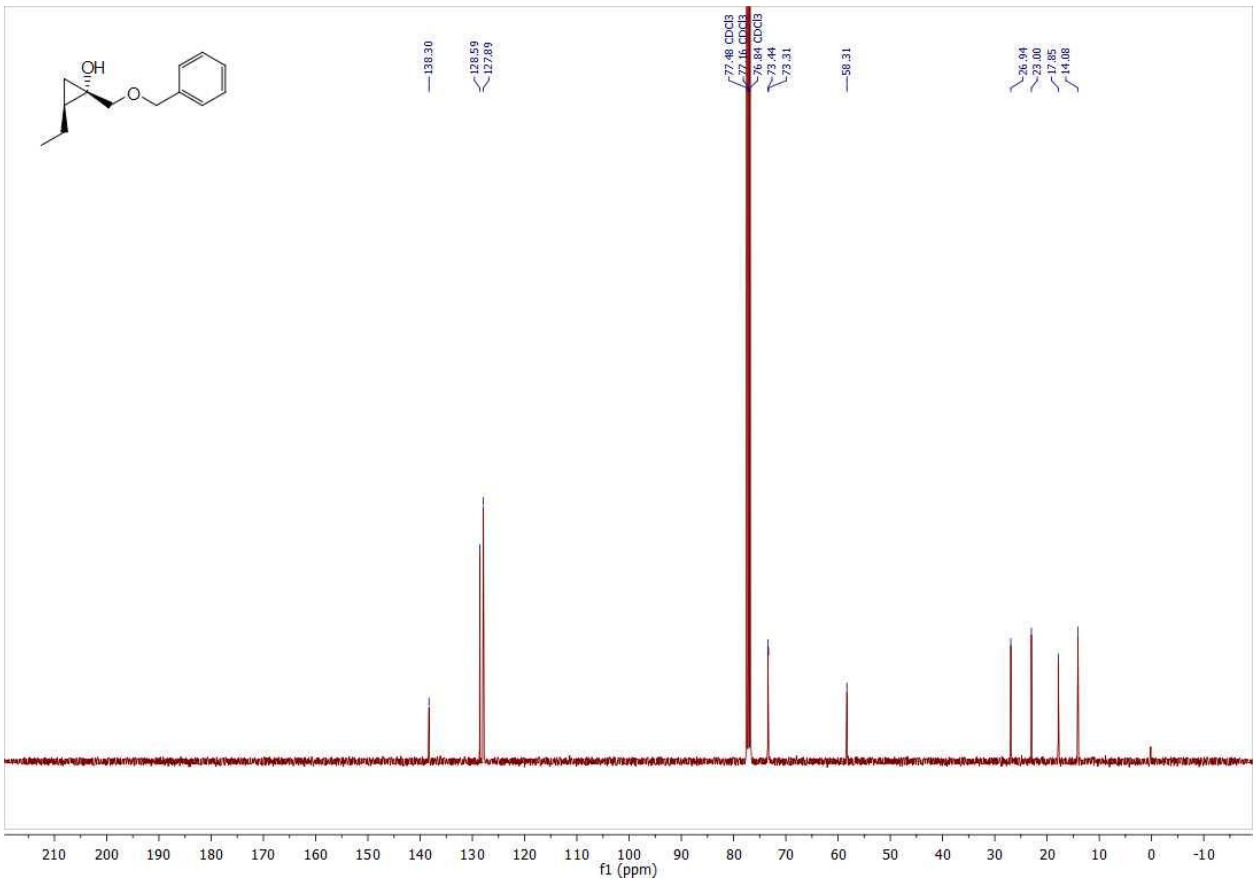

7.26
OH
1.79
1.53
1.31
1.30
1.29
0.89
0.88
0.87
0.73
0.72
0.45
0.44
0.43
0.07
0.92
4.60
7.66
3.75
2.00
1.96
f1 (ppm)

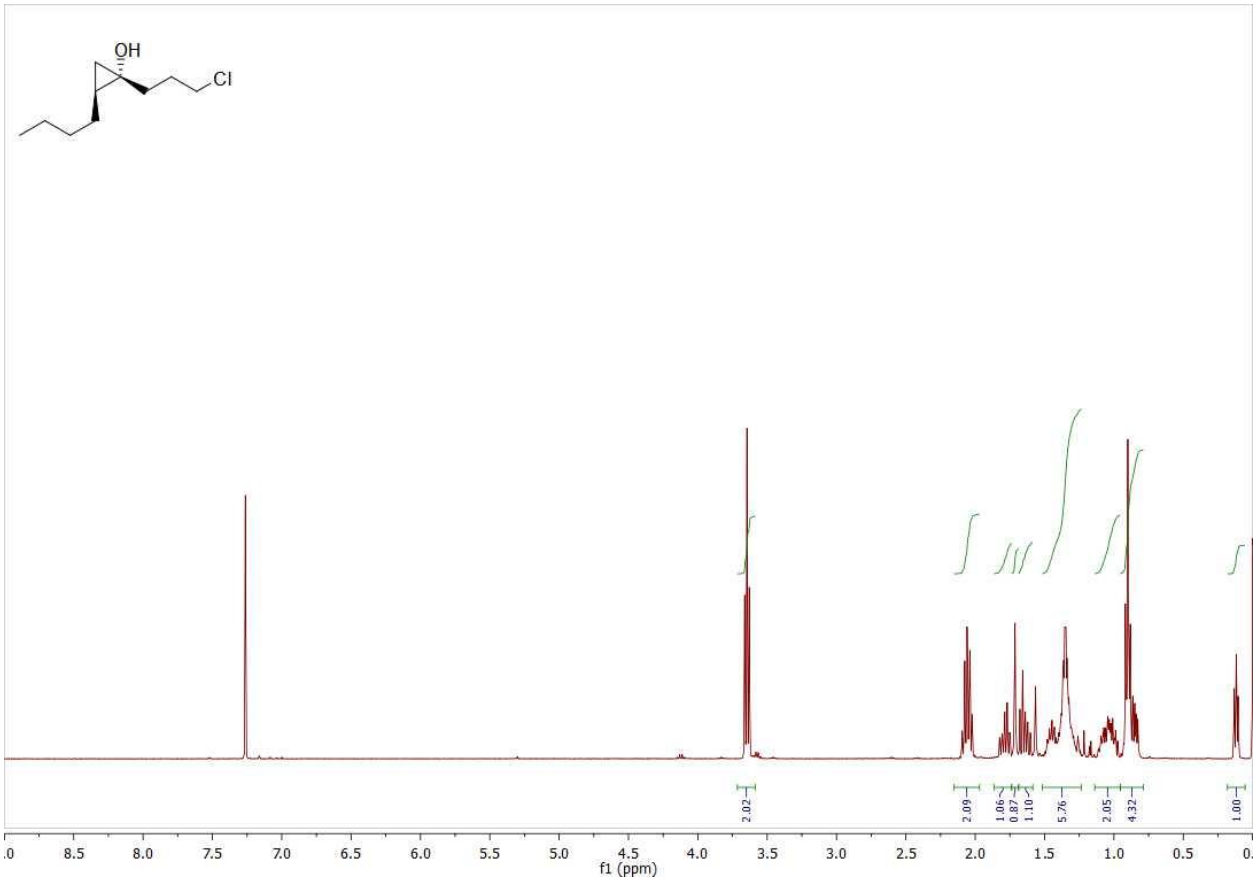

OH
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.04
38.45
32.05
29.49
26.03
22.78
14.24
13.65
f1 (ppm)

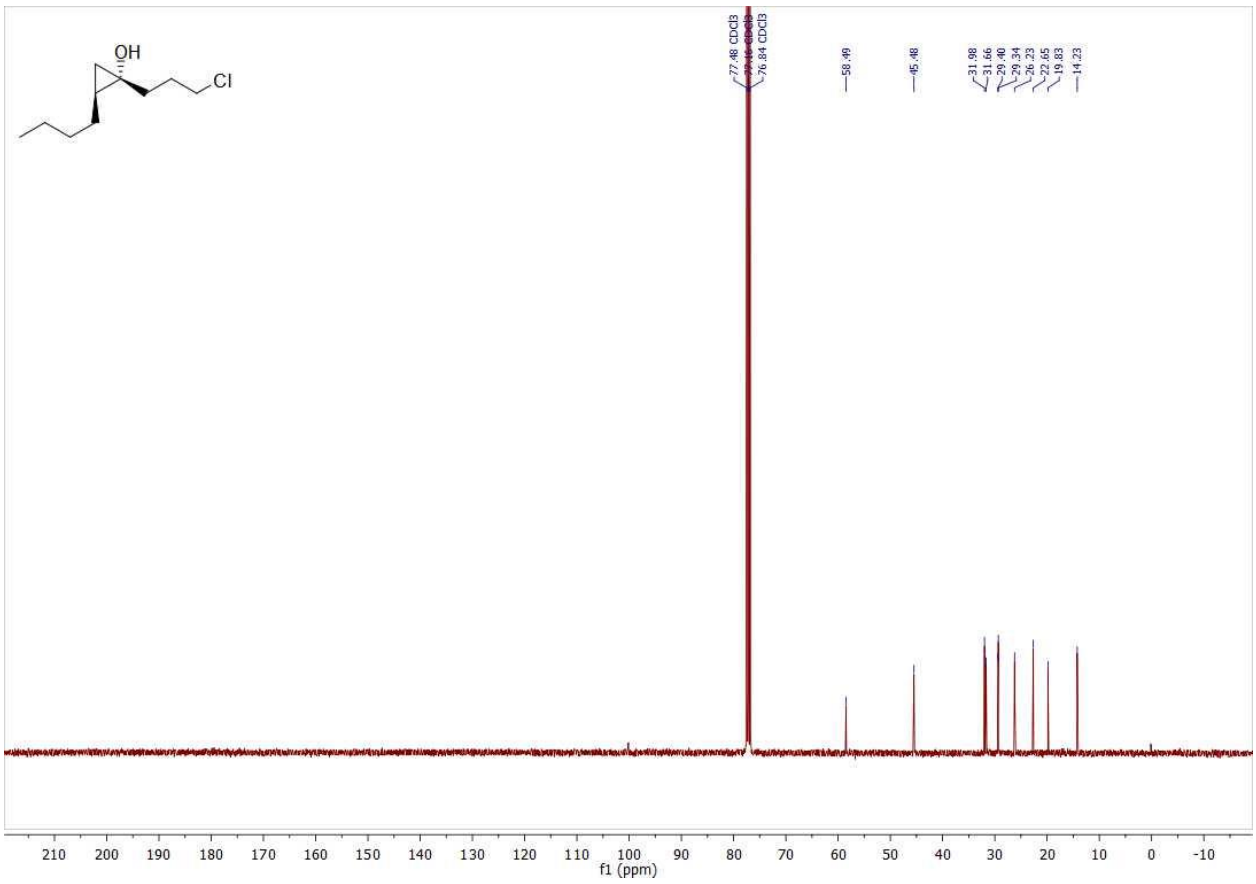

OH
(C6D6)
f1 (ppm)


OH
(C6D6)
139.25
128.69 C6D6
128.44 C6D6
128.20 C6D6
128.06 C6D6
127.82 C6D6
126.15
57.24
31.15
20.62
19.06
f1 (ppm)


OH
O
7.36
7.35
7.26
4.63
4.60
4.58
4.55
3.66
3.63
3.59
3.59
3.56
3.56
2.73
1.45
1.43
1.41
1.39
1.38
1.36
1.19
1.17
1.15
1.14
1.08
1.06
1.05
1.00
0.99
0.97
0.93
0.92
0.91
0.90
0.24
0.23
0.22
5.28
2.16
2.00
0.87
1.01
1.95
4.23
0.98
f1 (ppm)


OH
O
138.30
128.59
127.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.44
73.31
58.31
26.94
23.00
17.85
14.08
f1 (ppm)


OH
Cl
2.02
2.09
1.06
0.87
1.10
5.76
2.05
4.32
1.00
f1 (ppm)


OH
Cl
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
58.49
45.48
31.98
31.66
29.40
29.34
26.23
22.65
19.83
14.23
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)

VIII. References

1. V. Matoušek, E. Pietrasiak, R. Schwenk, A. Togni, *J. Org. Chem.* **2013**, *78*, 6763−6768.
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