Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Expedient and Efficient One Pot Synthesis of Trifluoroethyl Ethers From Metal Free 2,4,6-tris-(2,2,2-Trifluoro-Ethoxy)-[1,3,5] Triazene

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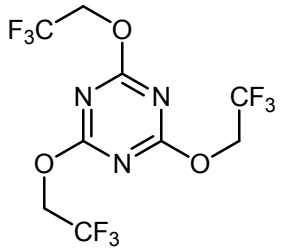
1. General Methods
2. Experimental procedure and characterization data
3. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra and Mass spectra

1. General Methods

Nuclear magnetic resonance (^{1}H NMR (400MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (400MHz)) spectra were determined on a JEOL JNM-ECS 400 spectrometer. Tetramethylsilane was used as the internal standard for proton NMR and δ scale used for chemical shift values for ^{1}H NMR. Chemical shifts for ^{13}C NMR were reported in ppm relative to deuterated chloroform ($CDCl_3$, 77 ppm) and TMS is used as internal standard. Analytical thin layer chromatography (TLC) was performed on MERCK precoated analytical plates, 0.25 mm thick, silica gel 60 F_{254}. All the chemicals used in synthesis were of analytical grade and purchased from Sigma-Aldrich, USA. All moisture sensitive reactions were carried out under an anhydrous argon atmosphere in dry and freshly distilled solvents under anhydrous conditions.

2. Experimental procedure and characterization data f

2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine (TriTFET)



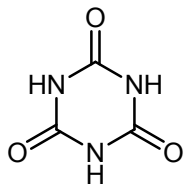
Trifluoroethanol (0.6 ml, 8 mmol) and NaOH (120 mg, 3 mmol) were added to a suspension of cyanuric chloride (184 mg, 1mmol) in acetone (3 ml) at 0 °C. The solution was heated to 50 °C and stirred for additional 2 hrs. The reaction was then allowed to cool to room temperature. The precipitate was filtered, washed with acetone and dried to afford the product TriTFET (90% yield) as white crystalline solid.

^{1}H NMR ($CDCl_3$); δ 4.84-4.80 (q, *J*=8Hz, 6H); ^{13}C NMR ($CDCl_3$); δ 172.34, 126.56-118.19 (q, *J*=282 Hz, -**C**F_3), 64.7-63.65 (m, *J*= 37 Hz, -CH_2-); ^{19}F NMR ($CDCl_3$); δ -73.65. HRMS Calculated $C_9H_6F_9N_3O_3$ = 375.0261; Found (M+H)= 376.0331

General procedure for etherification of alcohols

To a solution of alcohol (5 mmol), TriTFET (975 mg, 0.6 equiv) in acetonitrile (15ml) was added PTSA (172 mg, 0.2 equiv) at room temperature. The reaction mixture was stirred until the reaction was complete. The residue was dissolved with EtOAc (100ml) and washed with saturated $NaHCO_3$, water and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to get TFE protected alcohols in good yield.

Identification of isocynuric acid

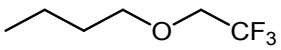


The solid sample which was insoluble in organic solvents was collected by simple filteration and characterized by NMR.

1H NMR (DMSO-d_6): δ11.14 (br s, 3H); ^{13}C NMR (DMSO-d_6): δ 149.93.

Characterization of TFE protected alcohols:

(1a) 1-(2,2,2-trifluoroethoxy)butane

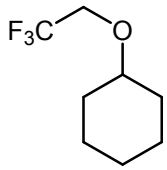


^{1}H NMR ($CDCl_3$): δ 4.7 (m, 2H), 4.4 (t, *J*=6.5 Hz, 2H), 1.7 (m, 2H), 1.4 (m, 2H), 0.94 (t, *J*=6.2 Hz, 3H);

^{13}C NMR ($CDCl_3$): δ 126.0-120.1 (q, *J*=201 Hz); 68.8-68.69 (m, *J*=36.5 Hz); 61.69; 39.95; 29.67; 14.49.

^{19}F NMR ($CDCl_3$): δ -73.47.

(2a) (2,2,2-trifluoroethoxy)cyclohexane

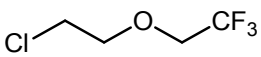


^{1}H NMR ($CDCl_3$): δ 4.8 (q, 2H); 3.5 (m, 1H); 2.02-1.2 (m, 10H)

^{13}C NMR ($CDCl_3$): δ 128-121 (q, *J*=242 Hz); 69.29; 64-63 (m); 30.8; 30.4; 29.6; 18.9; 13.6.

^{19}F NMR ($CDCl_3$): δ -73.6

(3a) 2-(2-chloroethoxy)-1,1,1-trifluoroethane

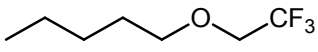


^{1}H NMR ($CDCl_3$): δ 4.3 (m, 2H); 3.6 (t, *J*= 5.2 Hz, 2H); 3.1 (t, *J*= 5.1 Hz, 2H)

^{13}C NMR ($CDCl_3$): δ 117.2-109.2 (q, *J*=222 Hz); 67.8; 61.1 (m); 39.8.

^{19}F NMR ($CDCl_3$): δ -73.5

(4a) 1-(2,2,2-trifluoroethoxy)pentane

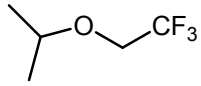


^{1}H NMR ($CDCl_3$): δ 4.7 (m, 2H); 3.4 (t, *J*=6.4 Hz, 2H); 1.5 (m, 4H); 1.2 (m, 2H); 0.8 (t, *J*=4.1 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 126-118 (q, *J*= 218 Hz); 64 (m); 53.5; 30.8; 29.7; 29.16; 13.8.

^{19}F NMR ($CDCl_3$): δ -73.4

(5a) 2-(2,2,2-trifluoroethoxy)propane

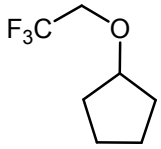


^{1}H NMR ($CDCl_3$): δ 3.9 (m, 1H); 3.8 (m, 2H); 1.13 (d, *J*=1.6 Hz, 6H).

^{13}C NMR ($CDCl_3$): δ 128-120 (q, *J*= 210 Hz); 64.9; 60-59 (m), 24.7

^{19}F NMR ($CDCl_3$): δ -74.5

(6a) (2,2,2-trifluoroethoxy)cyclopentane

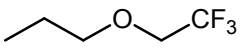


^{1}H NMR ($CDCl_3$): δ 4.8 (m, 2H); 3.5 (m, 1H); 2.1-1.8 (m, 4H); 1.2 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 128.5-120.9 (q); 69.2; 63.6 (m), 30.4; 29.6; 18.6; 13.6.

^{19}F NMR ($CDCl_3$): δ 73.7

(7a) 1-(2,2,2-trifluoroethoxy)propane

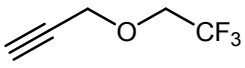


^{1}H NMR ($CDCl_3$): δ 4.5 (m, 2H); 3.9 (t, *J*= 8 Hz, 2H); 1.3 (m, 2H); 0.9 (t, *J*= 4.8 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 128.4-120.0 (q, *J*= 280 Hz); 61.1-60.1 (m); 50.4; 22.98; 14.9.

^{19}F NMR ($CDCl_3$): δ -73.11.

(8a) 3-(2,2,2-trifluoroethoxy)prop-1-yne

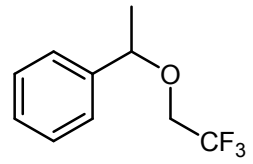


^{1}H NMR ($CDCl_3$): δ 4.8 (m, 2H); 4.2 (d, *J*= 2.4 Hz, 2H); 2.4 (t, *J*= 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$): δ 128-120 (q, J= 280 Hz); 81.3; 73.9; 61.1-60.1 (m); 50.4.

^{19}F NMR ($CDCl_3$): δ 73.9

(9a) {1-(2,2,2-trifluoroethoxy)ethyl} benzene

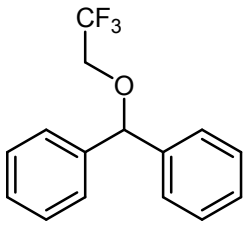


^{1}H NMR ($CDCl_3$): δ 7.2 (m, 5H); 5.03 (q, 1H); 4.6 (m, 2H); 1.5 (d, *J*= 4Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 134.19; 129.3; 128.5; 127.0; 125.3; 127.0-124.1 (q, *J*=228 Hz); 83.4; 63.4 (m); 22.6.

^{19}F NMR ($CDCl_3$): δ -73.38

(10a) {(2,2,2-trifluoroethoxy)methylene} dibenzene

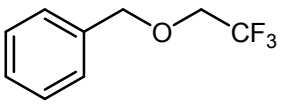


^{1}H NMR ($CDCl_3$): δ 7.78 (d, *J*=8Hz, 2H); 7.4 (t, *J*=12 Hz, 2H); 7.4 (m, 4H); 7.3 (m, 2H); 6.8 (s, 1H); 4.6 (m, 2H)

^{13}C NMR ($CDCl_3$): δ 128.4; 125.9-120.0 (q, *J*=238 Hz); 125.6; 122.8; 121.6; 108.6; 61.7 (m).

^{19}F NMR ($CDCl_3$): δ -72.8

(11a) {(2,2,2-trifluoroethoxy)methyl}benzene

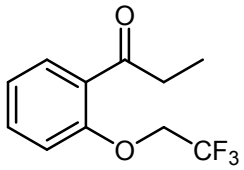


^{1}H NMR ($CDCl_3$): δ 7.2 (m, 5H); 4.7 (s, 2H); 4.6 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 133.9; 129.3; 128.5; 127.4; 127.2-122.8 (q, *J*=272 Hz); 82.4; 63.4 (m)

^{19}F NMR ($CDCl_3$): δ 74.4.

(12a) 1-{2-(2,2,2-trifluoroethoxy)phenyl}propan-1-one

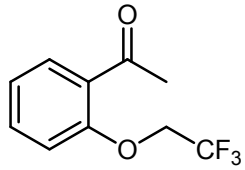


^{1}H NMR ($CDCl_3$): δ 7.7 (d, *J*=8 Hz, 1H); 7.4 (d, J=7.6 Hz, 1H); 6.9 (dd, *JJ*=14Hz, 1H); 6.8 (d, *J*=12Hz, 1H); 4.8 (m, 2H); 3.8 (q, *J*=9.6Hz, 2H); 1.2 (t, *J*=8Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 207.5; 162.08, 136.2; 129.8; 128.4;-119.4 (q, *J*=276 Hz); 119.01; 118.3; 61.5; 60.8 (m), 31.92; 8.1.

^{19}F NMR ($CDCl_3$): δ -73.92

(13a) 1-{2-(2,2,2-trifluoroethoxy)phenyl} ethanone

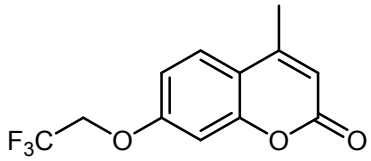


^{1}H NMR ($CDCl_3$): δ 7.7 (d, *J*= 8Hz, 1H); 7.4 (t, *J*= 12Hz, 1H); 6.9 (d, *J*=12Hz, 1H); 6.5 (t, 9.5 Hz, 1H); 4.5 (m, 2H); 2.3 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 207.4; 162.1; 136.3; 129.7; 128-119 (q 280 Hz); 119.03; 118.3; 61.5 (m); 31.8.

^{19}F NMR ($CDCl_3$): δ -74.04

(14a) 4-methyl-7-(2,2,2-trifluoroethoxy)-2H-chromen-2-one

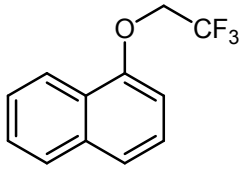


^{1}H NMR ($CDCl_3$): δ 7.4 (d, *J*=12 Hz, 1H); 6.8 (s, 1H); 6.8 (d, *J*= 8Hz, 1H); 6.1 (s, 1H); 3.9 (m, 2H); 2.3 (s,3H).

^{13}C NMR ($CDCl_3$): δ 161.7; 155.2; 151.9; 136.4; 128-122 (q, *J*=262 Hz); 112.8; 101.1; 87.8 (m); 20.9.

^{19}F NMR ($CDCl_3$): δ -73.3

(15a) 1-(2,2,2-trifluoroethoxy)naphthalene

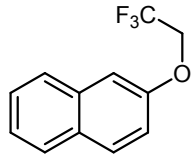


^{1}H NMR ($CDCl_3$): δ 8.3 (d, *J*=6.8 Hz, 1H); 8.0 (t, *J*= 8.8 Hz, 1H); 7.8 (d, *J*= 8.2 Hz, 1H); 7.3 (m, 2H); 6.8 (t, *J*= 5.8 Hz, 1H); 6.4 (d, *J*= 12 Hz, 1H); 4.5 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 172.7; 155.4; 150.54; 142.4; 139.27; 136.4; 130.3; 129.9; 128.9-122.8 (q, *J*=242 Hz); 63.6 (m).

^{19}F NMR ($CDCl_3$): δ -73.37

(16a) 2-(2,2,2-trifluoroethoxy)naphthalene

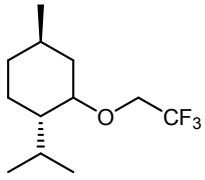


^{1}H NMR ($CDCl_3$): δ 8.3 (d, *J*=10 Hz, 1H); 8.1 (d, *J*= 8.8 Hz, 1H); 7.7 (t, *J*=6Hz, 1H); 7.4 (t, J= 6.8 Hz, 1H); 6.9-6.8 (t, *J*=6.6 Hz, 2H); 4.5 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 167.6; 149.1; 147.2; 142.1; 133.9; 130.2; 129.3-123.1 (q, *J*= 246 Hz); 119.0; 61.5 (m).

^{19}F NMR ($CDCl_3$): δ -73.9

(17a) (1S,4R)-1-isopropyl-4-methyl-2-(2,2,2-trifluoroethoxy)cyclohexane

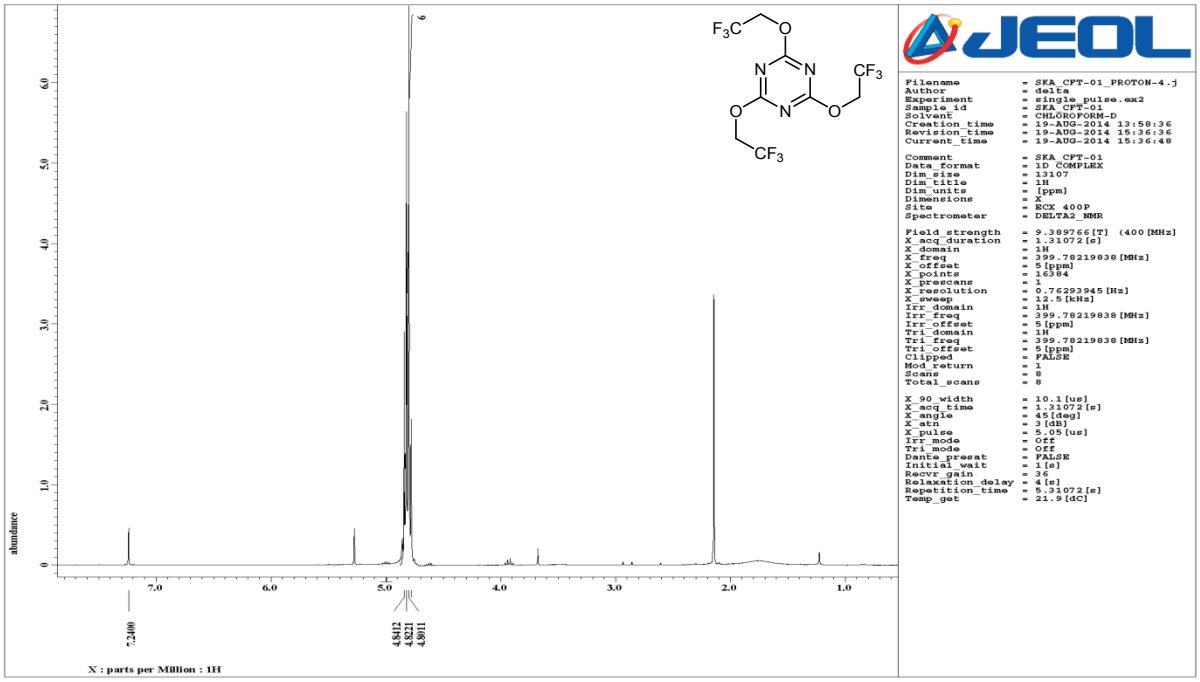


^{1}H NMR ($CDCl_3$): δ 4.6 (q, 2H); 3.4 (m, 1H); 2.2-1.9 (m, 2H); 1.5 (m, 2H); 1.4-1.2 (m, 2H); 0.9-0.8 (m, 12H).

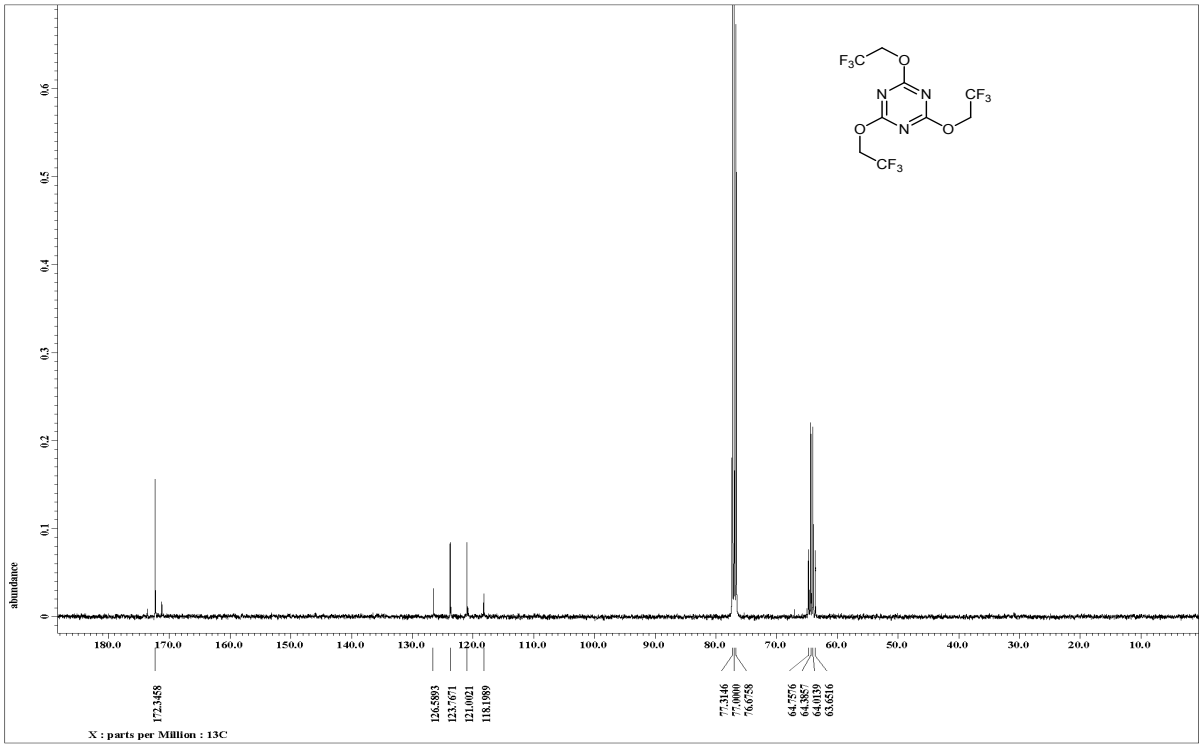
^{13}C NMR ($CDCl_3$): δ 126-119 (q, *J*=276 Hz); 72.5; 67 (m); 49.65; 44.36; 34.34; 31.63; 25.75; 23.02; 22.09; 20.9; 15.9.

^{19}F NMR ($CDCl_3$): δ -74.25

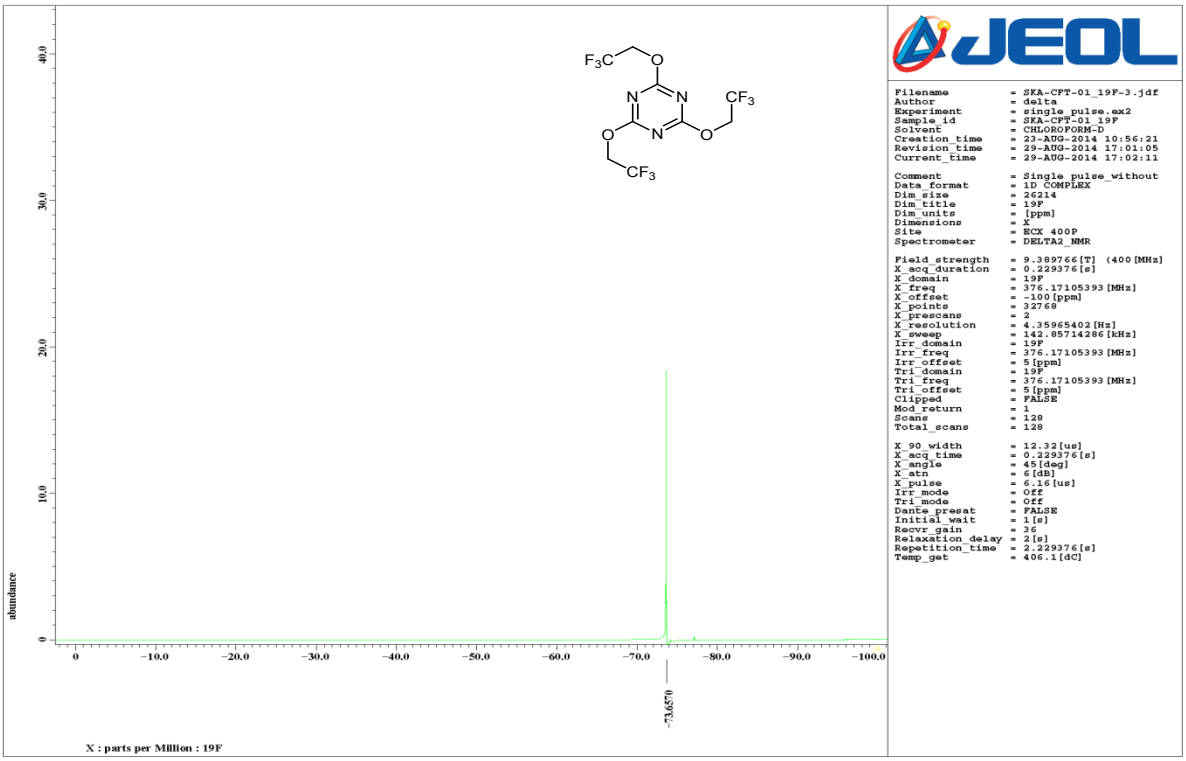
^{1}H NMR spectra of TriTFET



^{13}C NMR specta of TriTFET



^{19}F NMR of Tri TFET



Mass spectra of TriTFET

Qualitative Compound Report

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Sample Type	Sample	**Position**	P1E2
Instrument Name	Instrument 1	**User Name**	lcmsdu-PC\admin
Acq Method	29.10.2014.m	**Acquired Time**	10-03-2015 14:49:05
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Info.

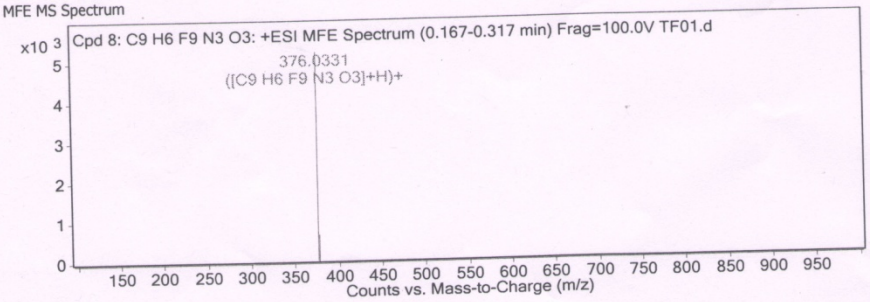
Sample Group	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

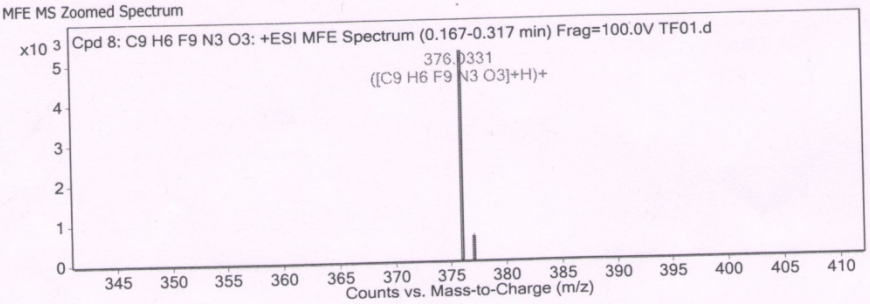
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 8: C9 H6 F9 N3 O3	0.212	375.026	C9 H6 F9 N3 O3	C9 H6 F9 N3 O3	1.46	C9 H6 F9 N3 O3

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 8: C9 H6 F9 N3 O3	376.0331	0.212	Find by Molecular Feature	375.026

MFE MS Spectrum



MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
376.0331	1	5249.36	C9 H6 F9 N3 O3	(M+H)+
377.0372	1	678.56	C9 H6 F9 N3 O3	(M+H)+

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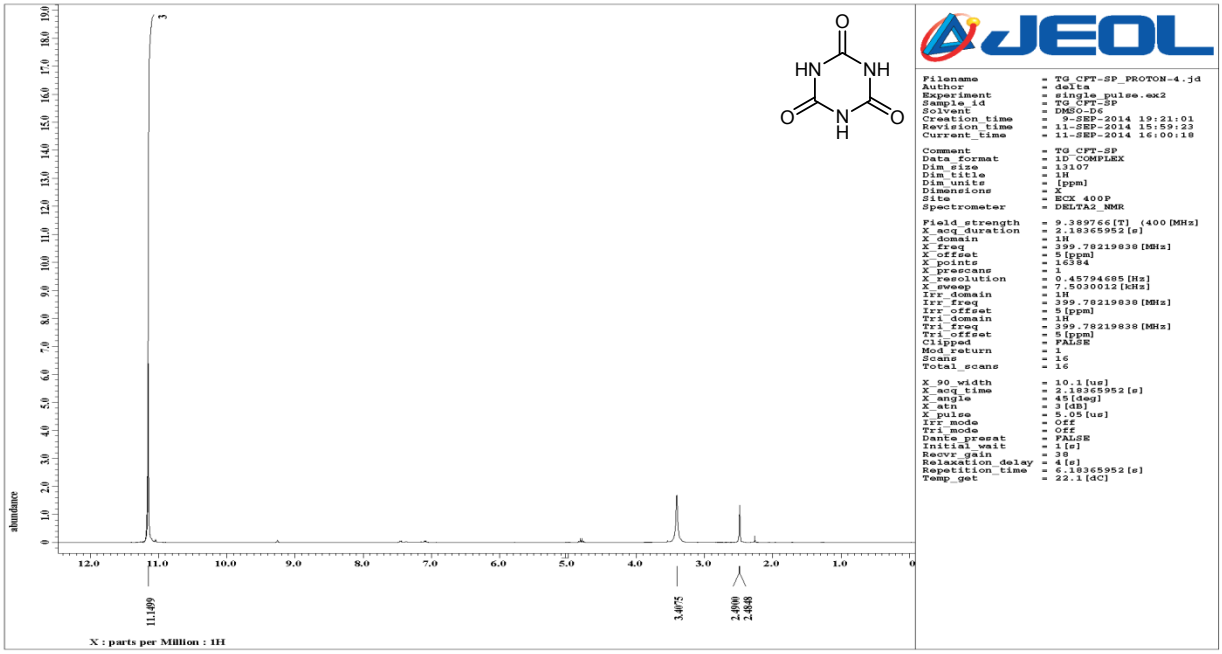
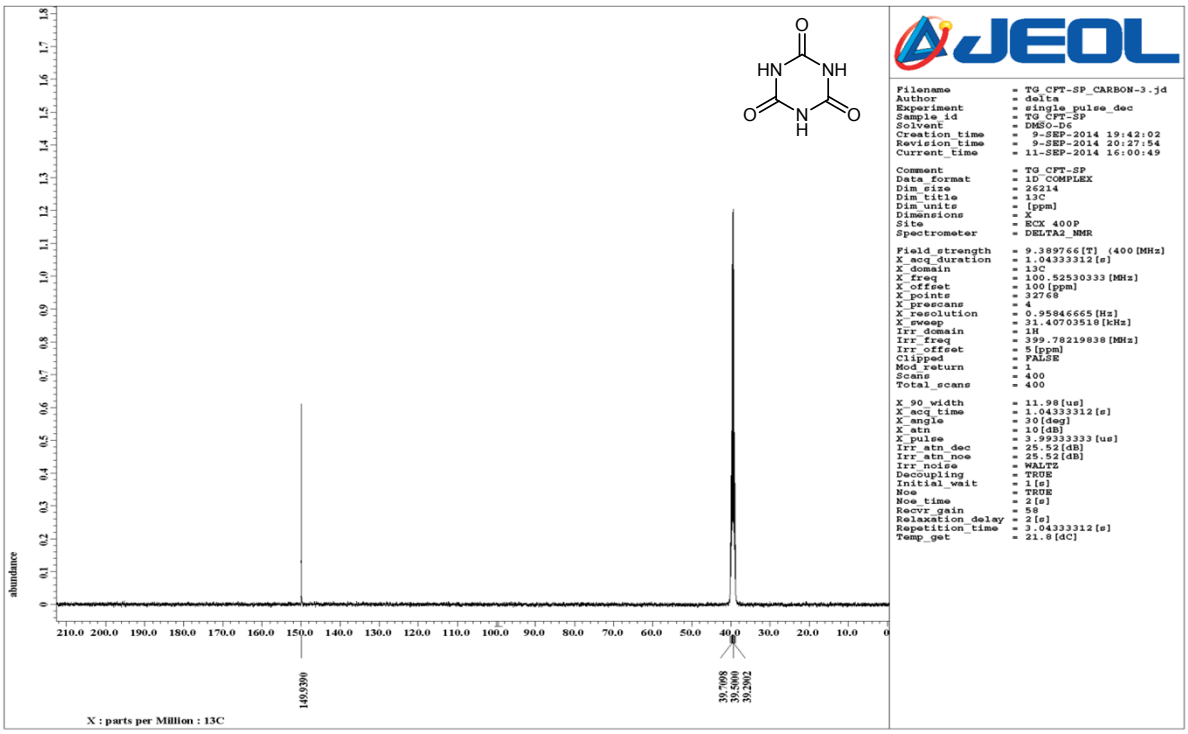
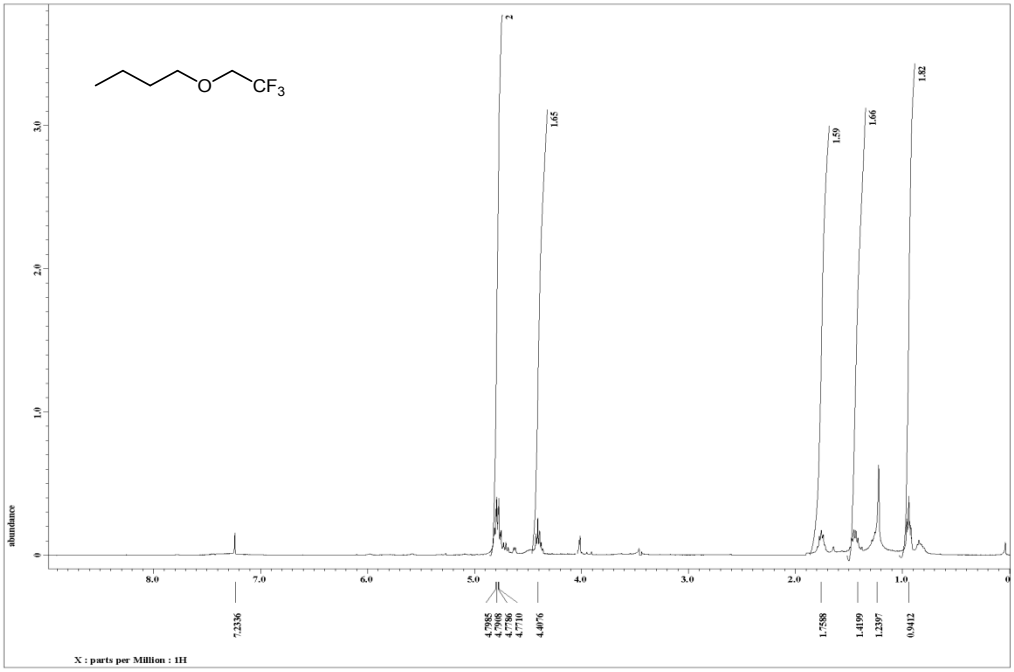
^{1}H NMR spectra of isocynuric acid



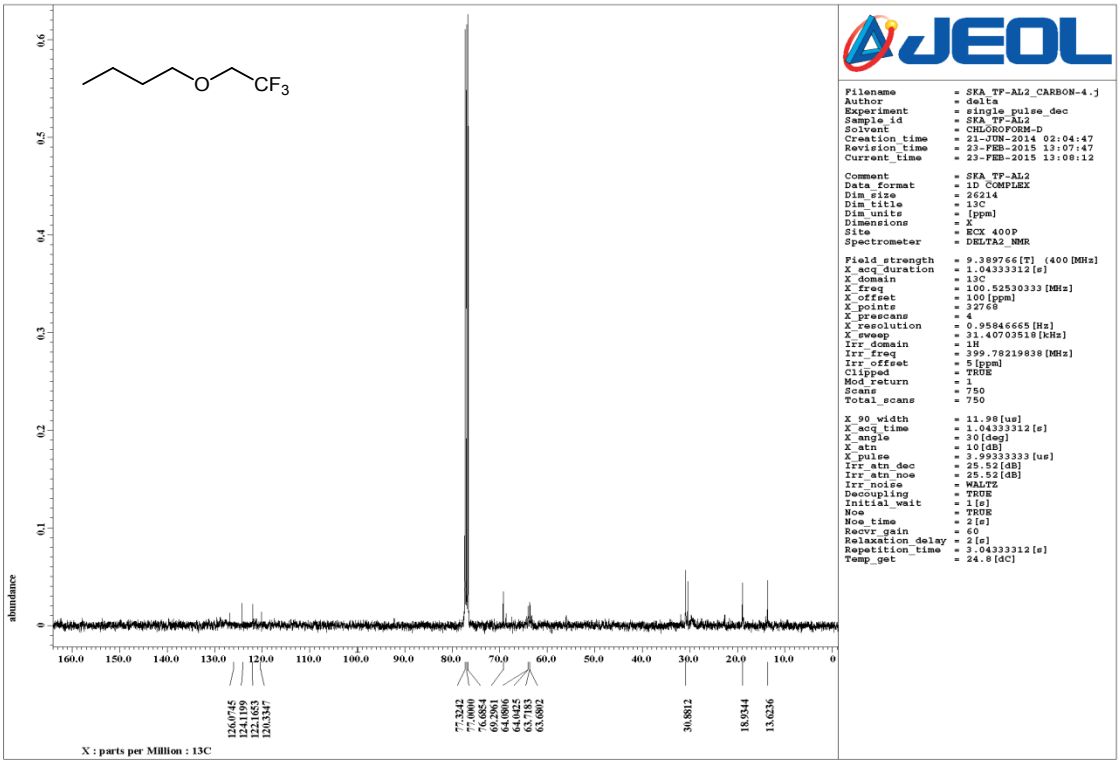
^{13}C NMR spectra of isocynuric acid



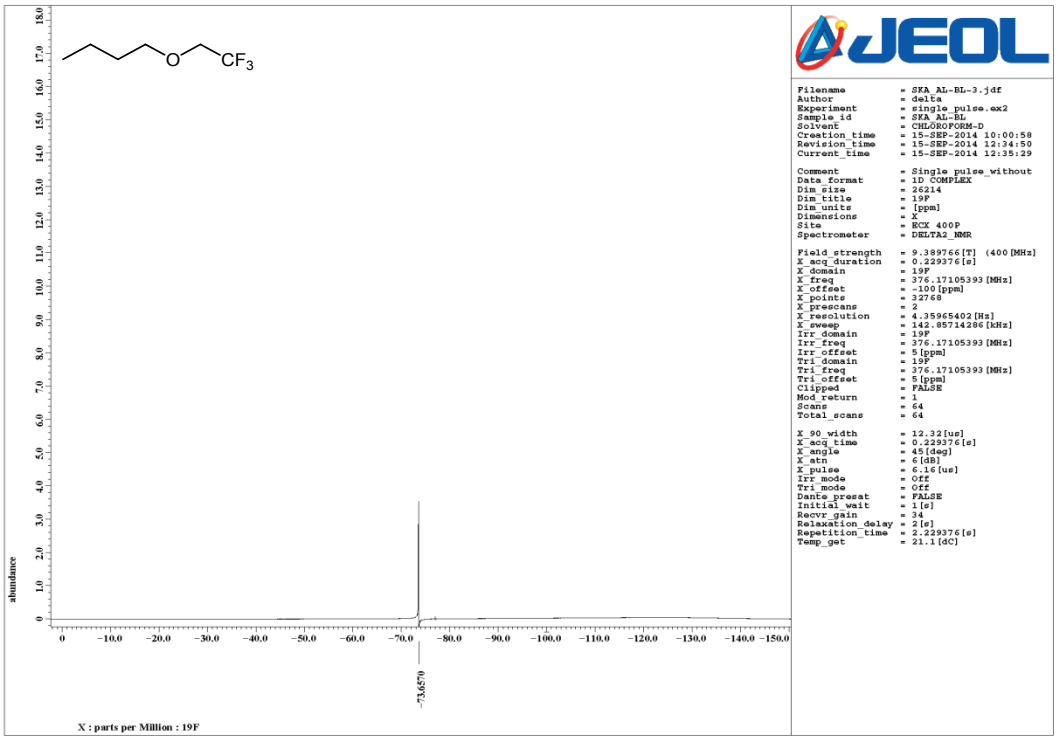
^{1}H NMR spectra of product 1a:



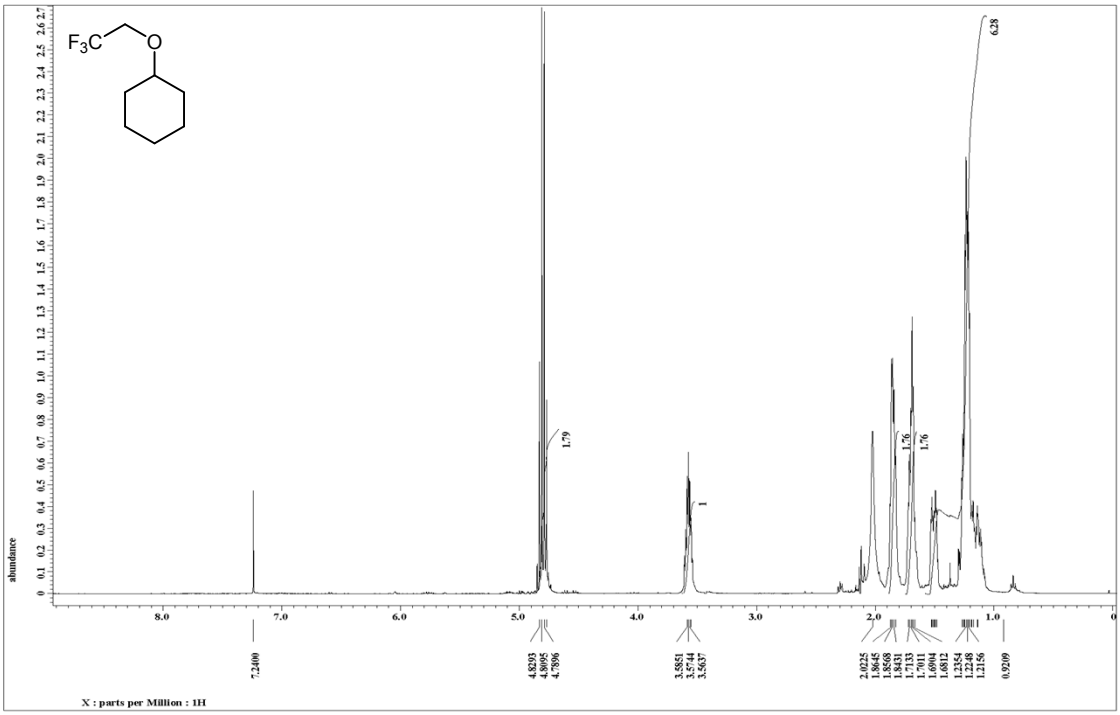
^{13}C NMR of product 1a:



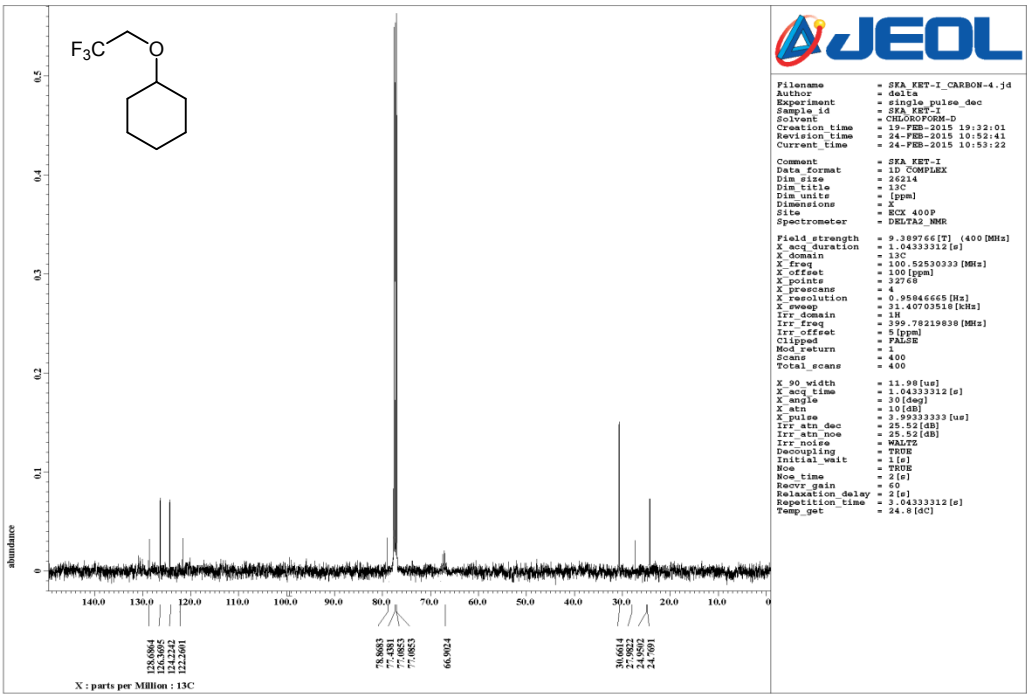
^{19}F NMR of product 1a:



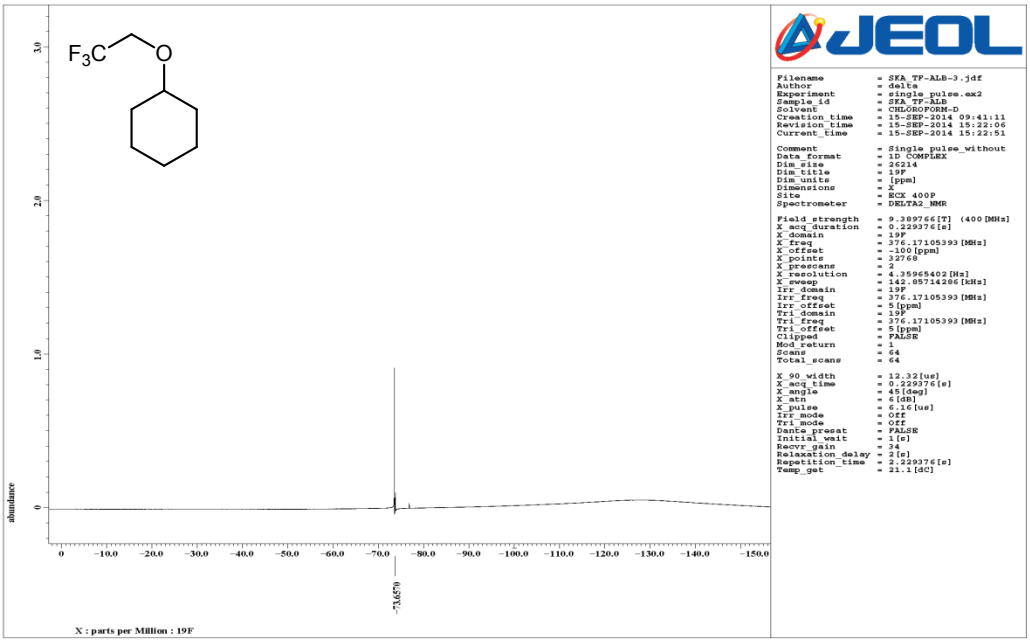
^{1}H NMR of product 2a:



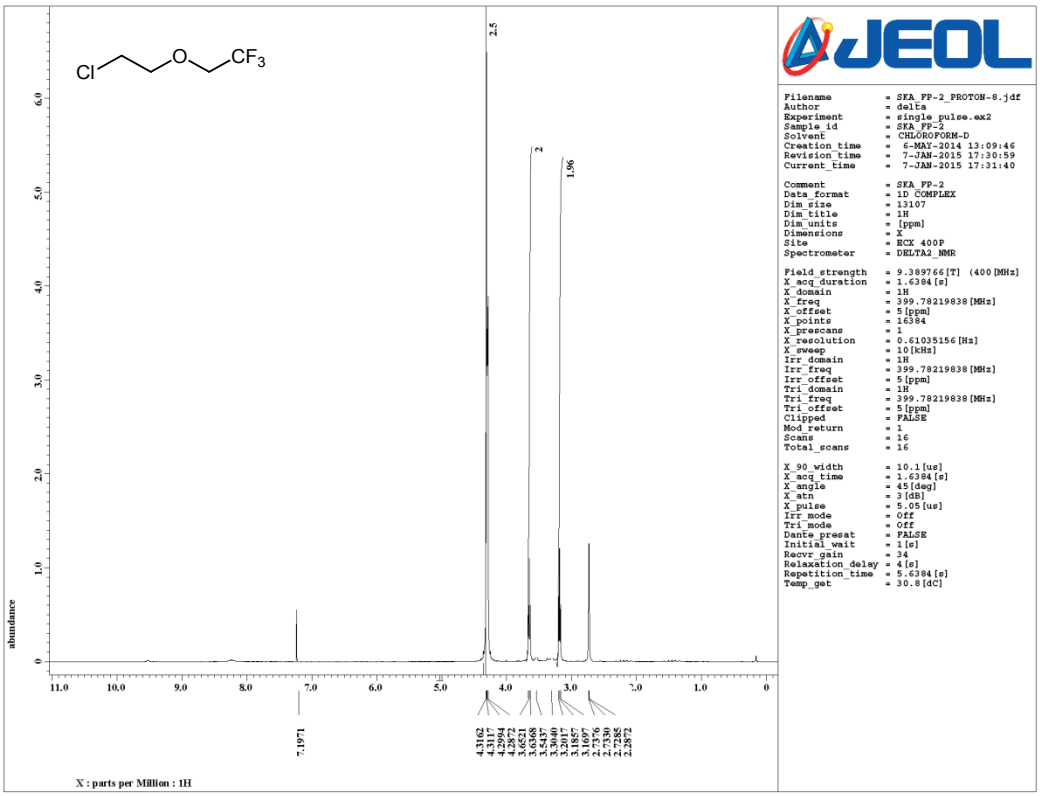
^{13}C NMR of product 2a:



^{19}F NMR of product 2a:



1H NMR of product 3a:



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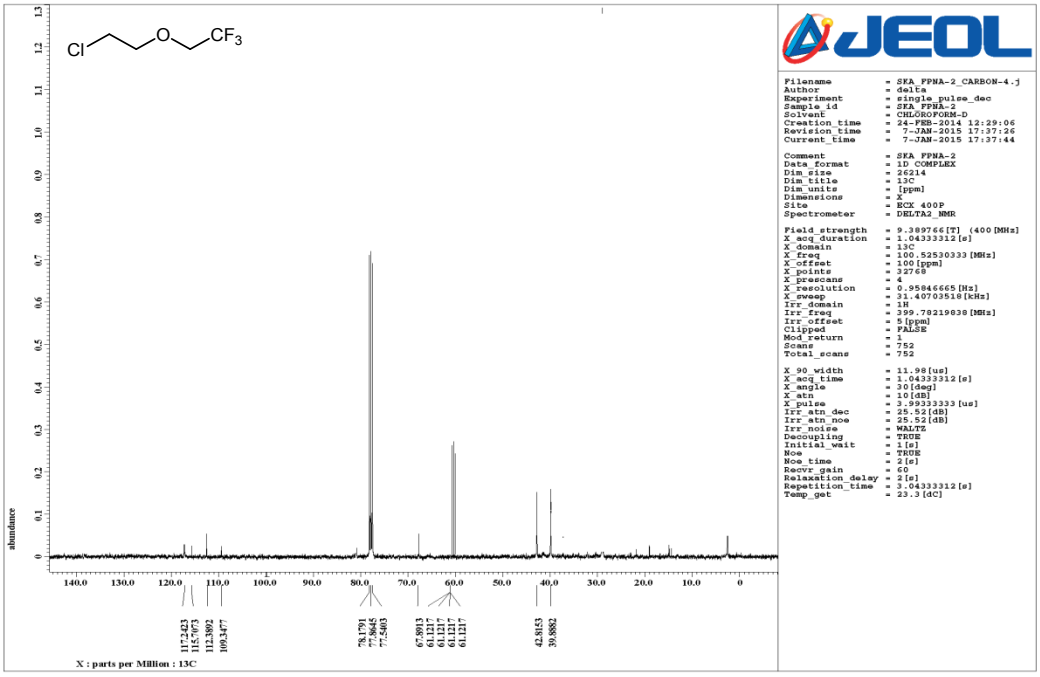

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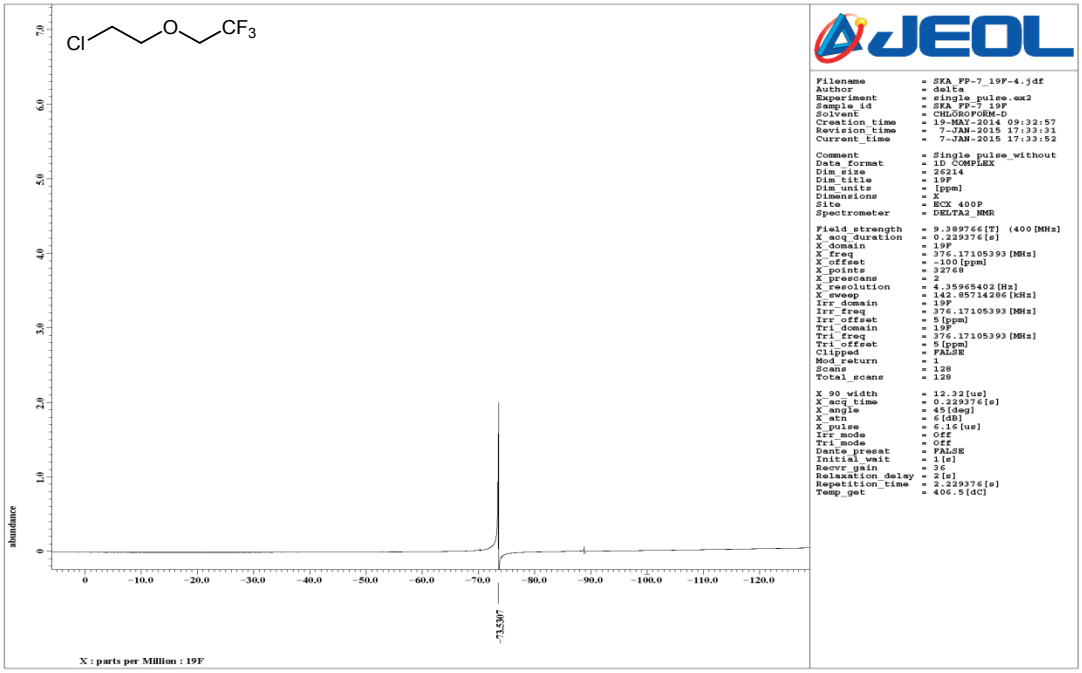
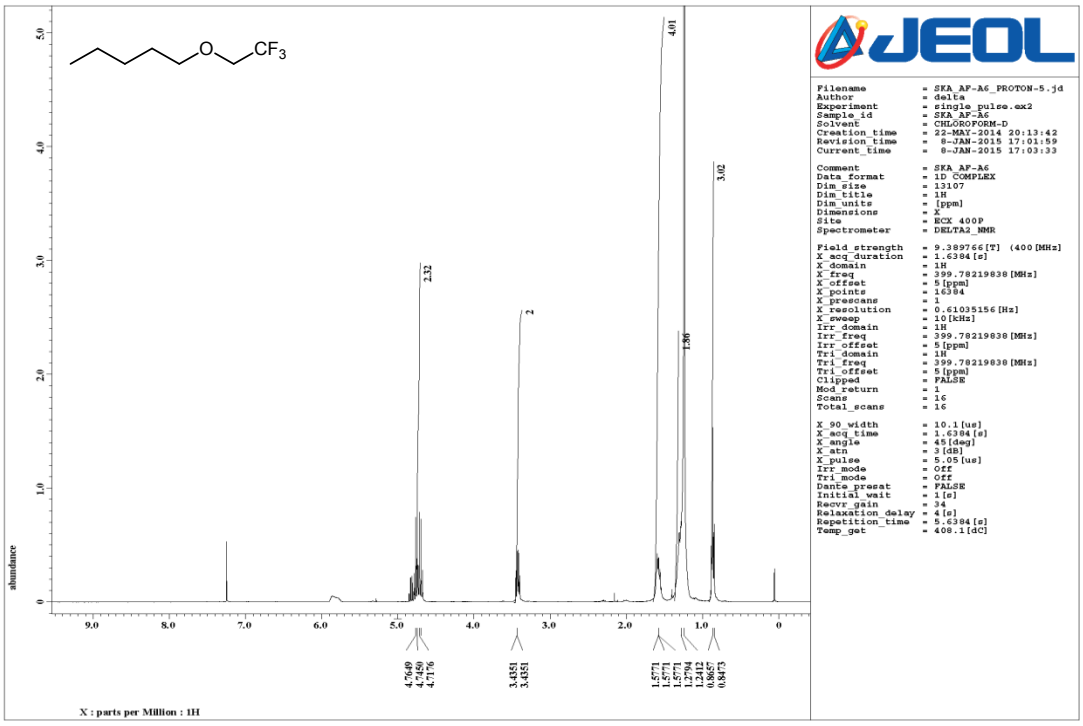
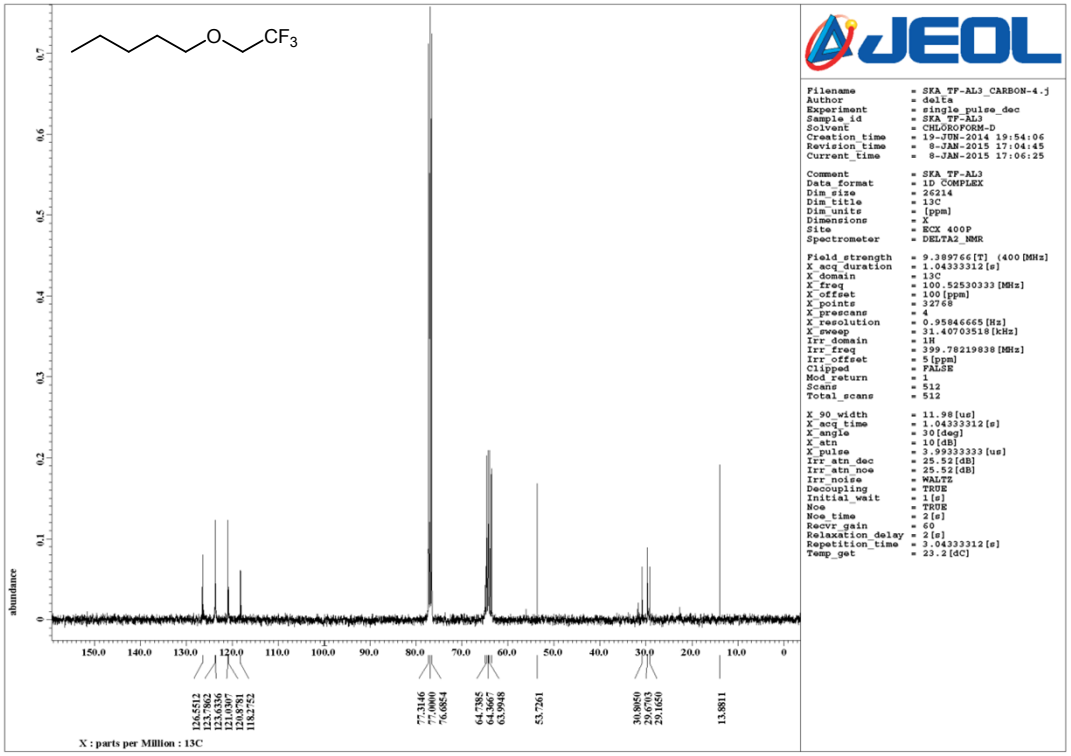


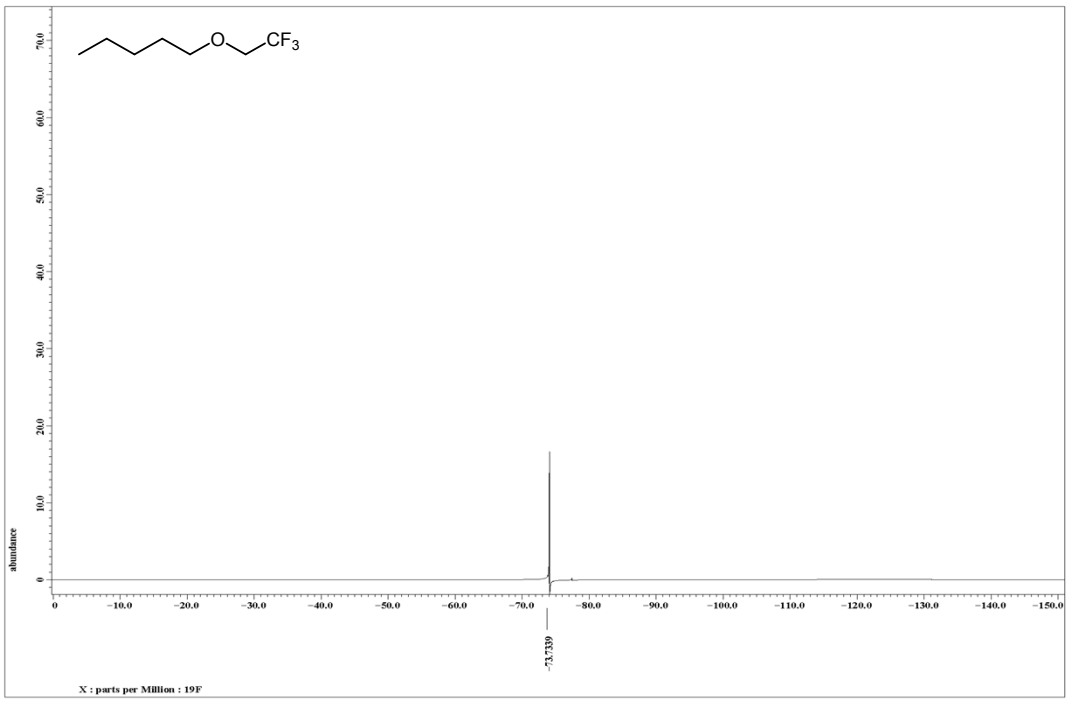
^{1}H NMR of product 4a:



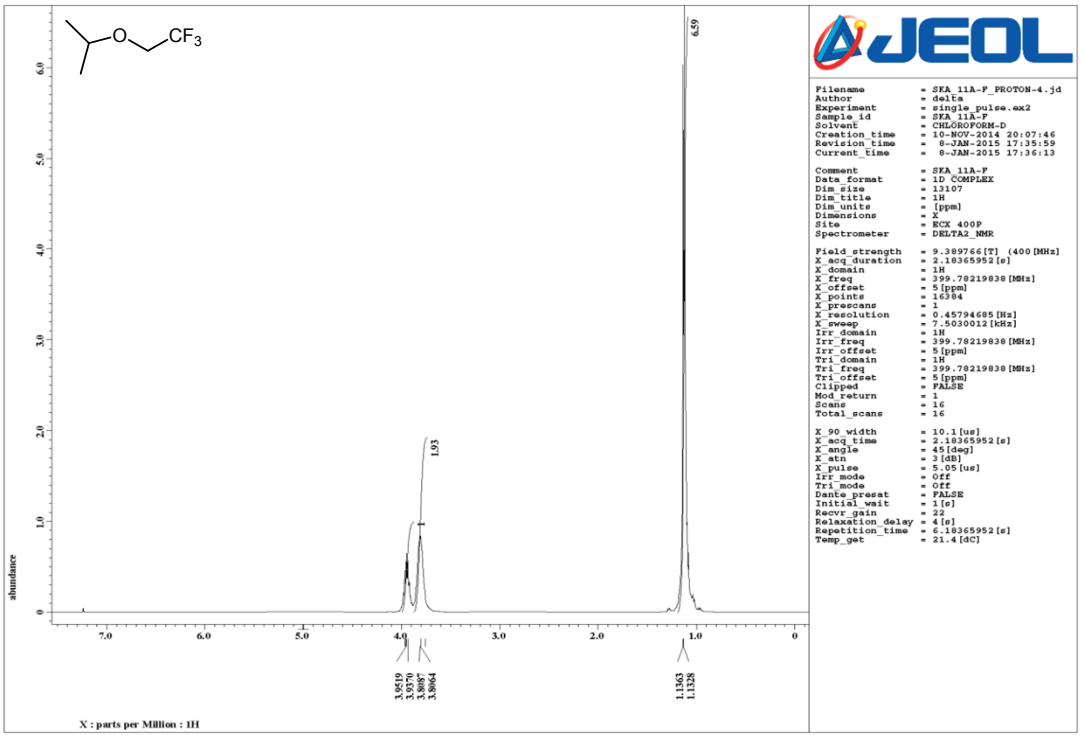
^{13}C NMR of product 4a:



^{19}F NMR of product 4a:



^{1}H NMR of product 5a:



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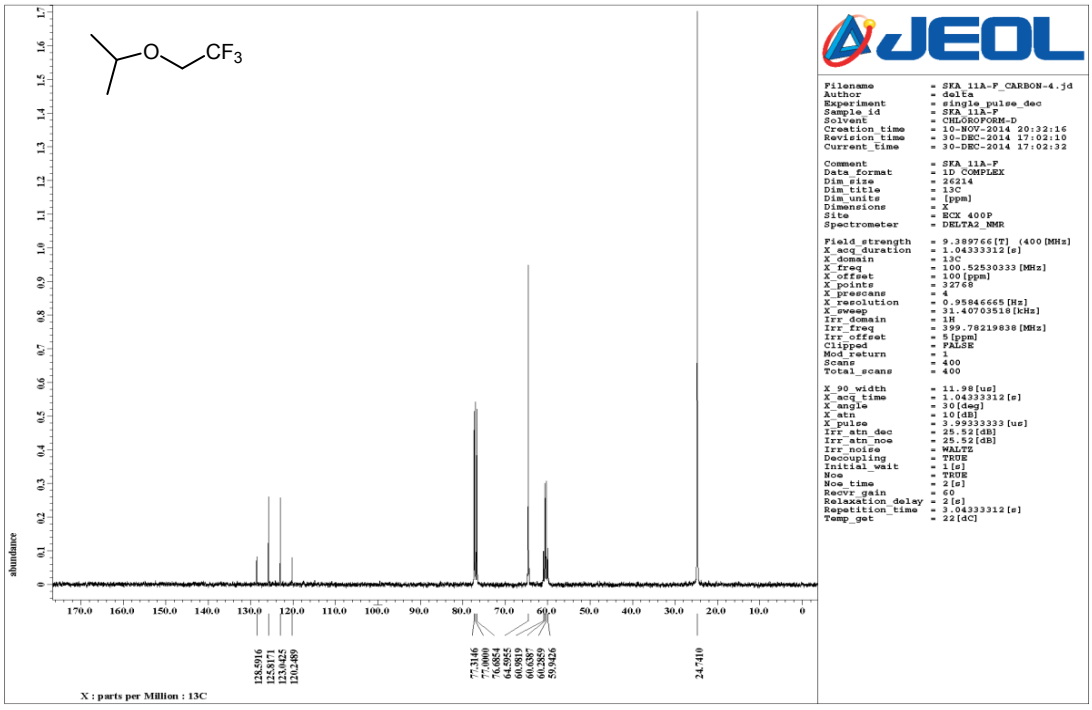

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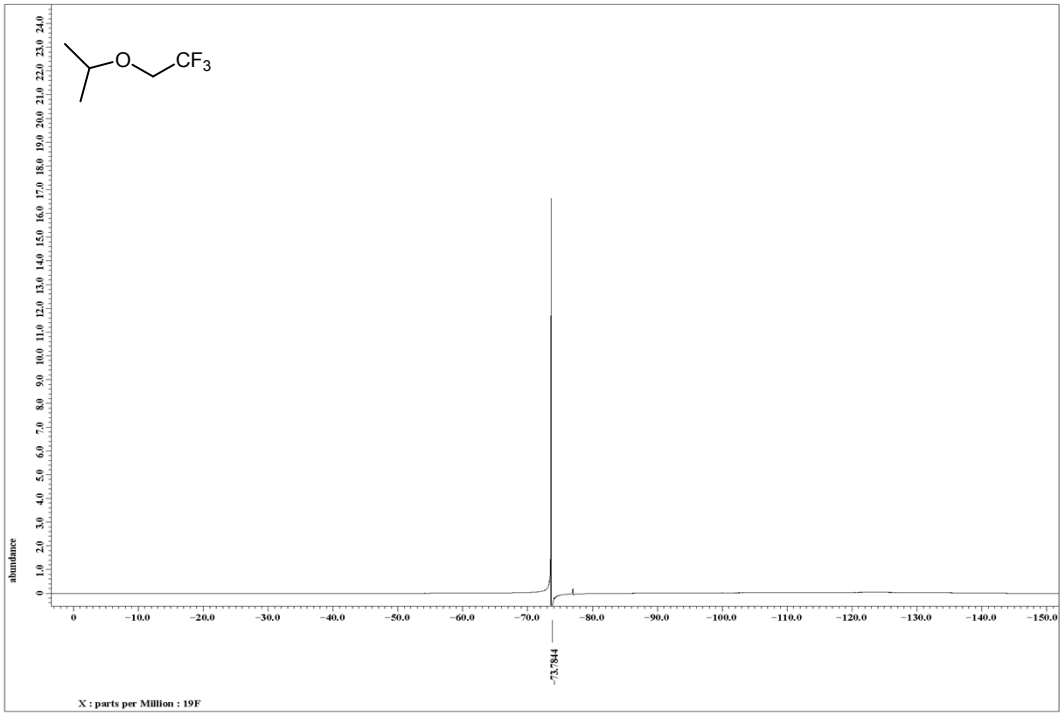

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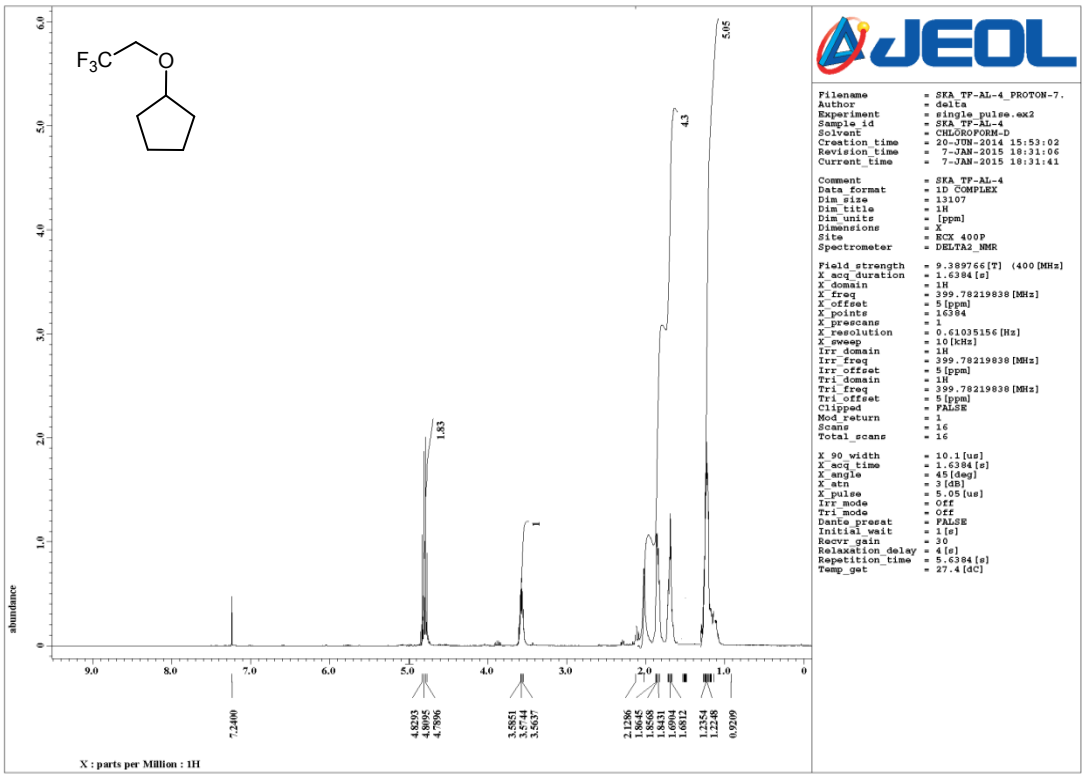

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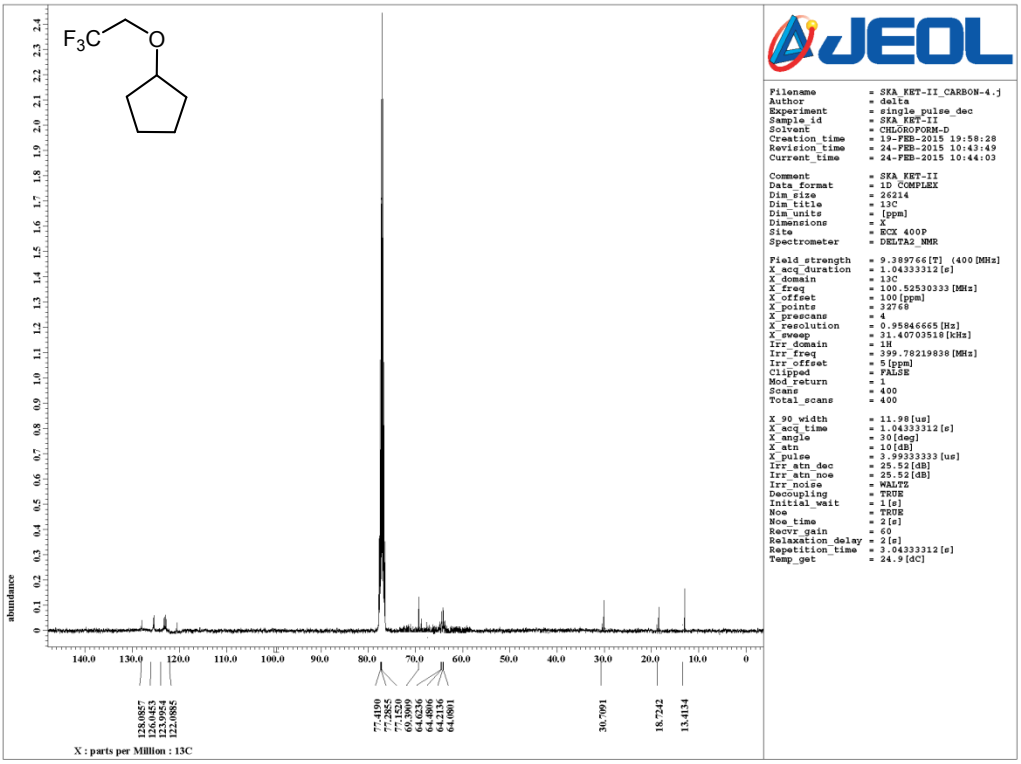

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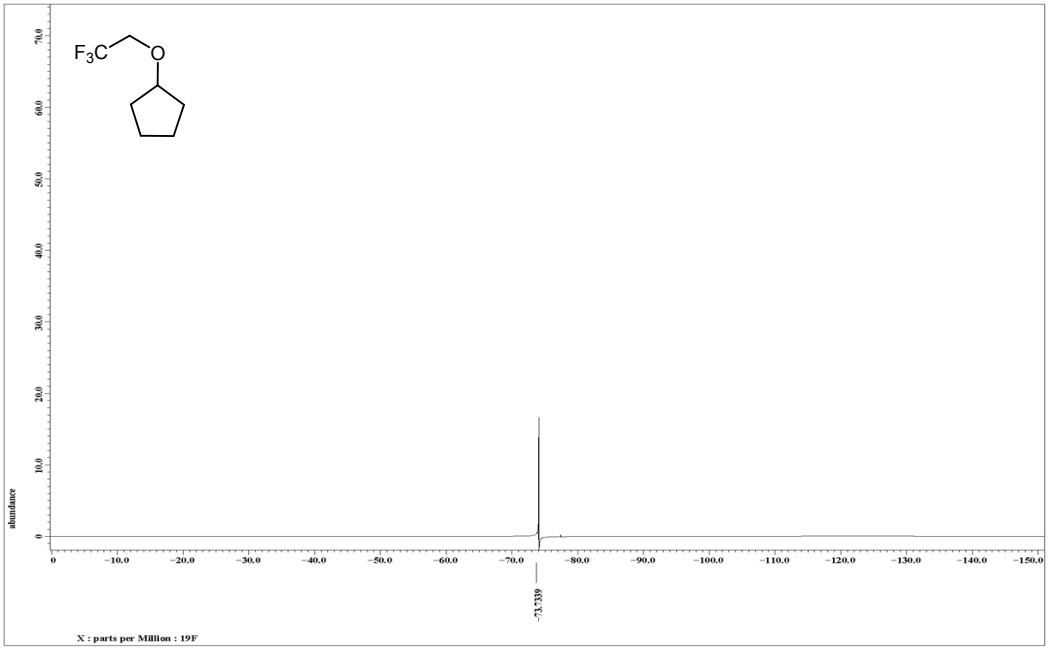
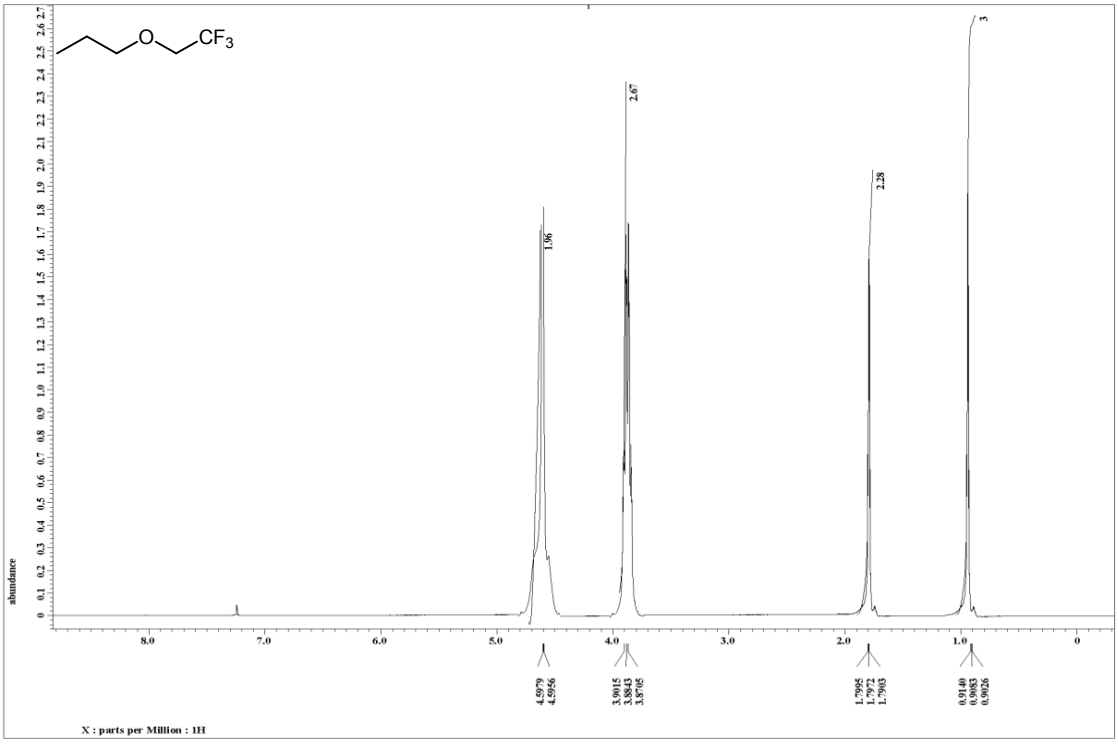


^{1}H NMR of product 7a:



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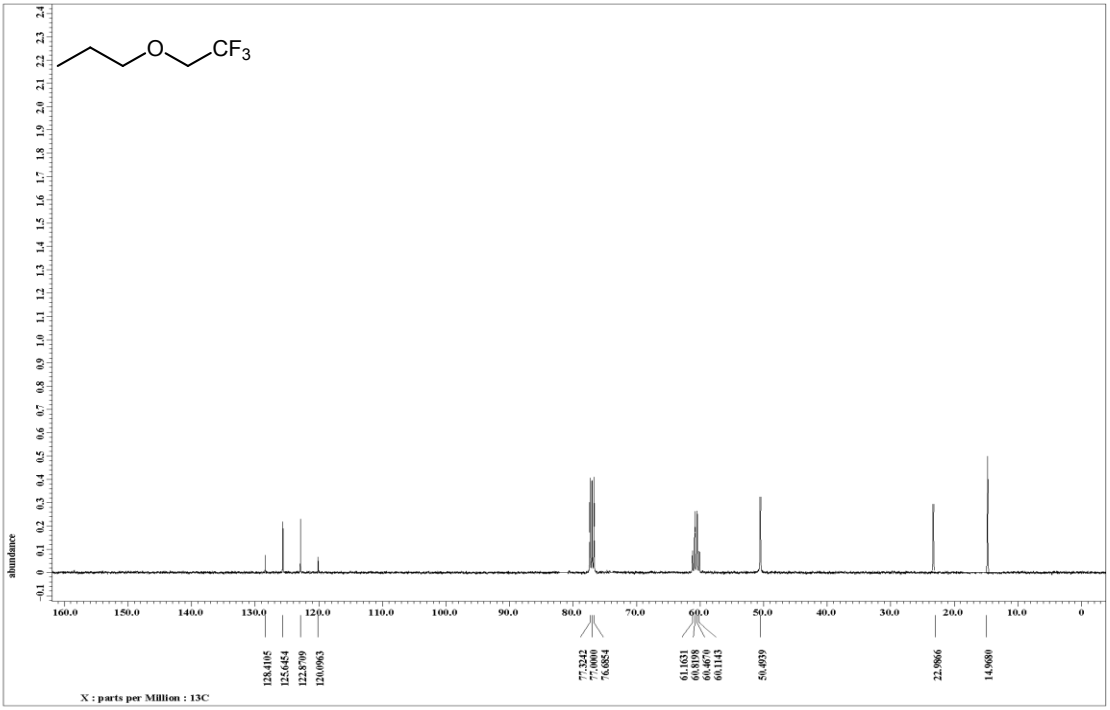
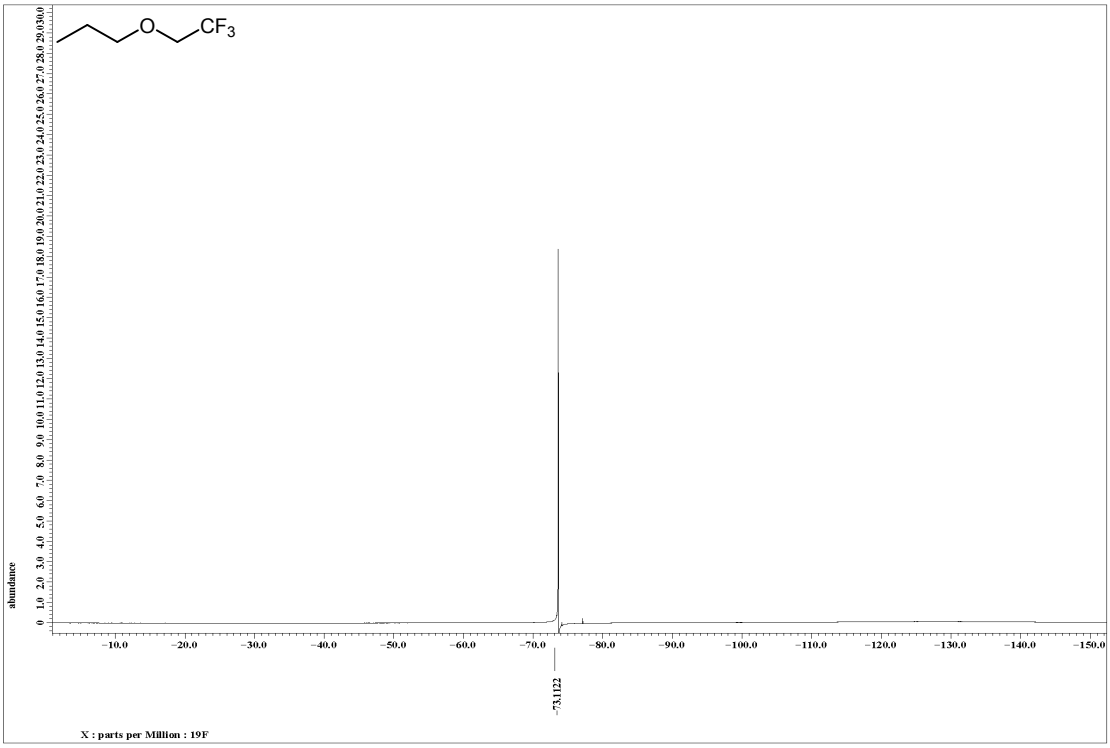
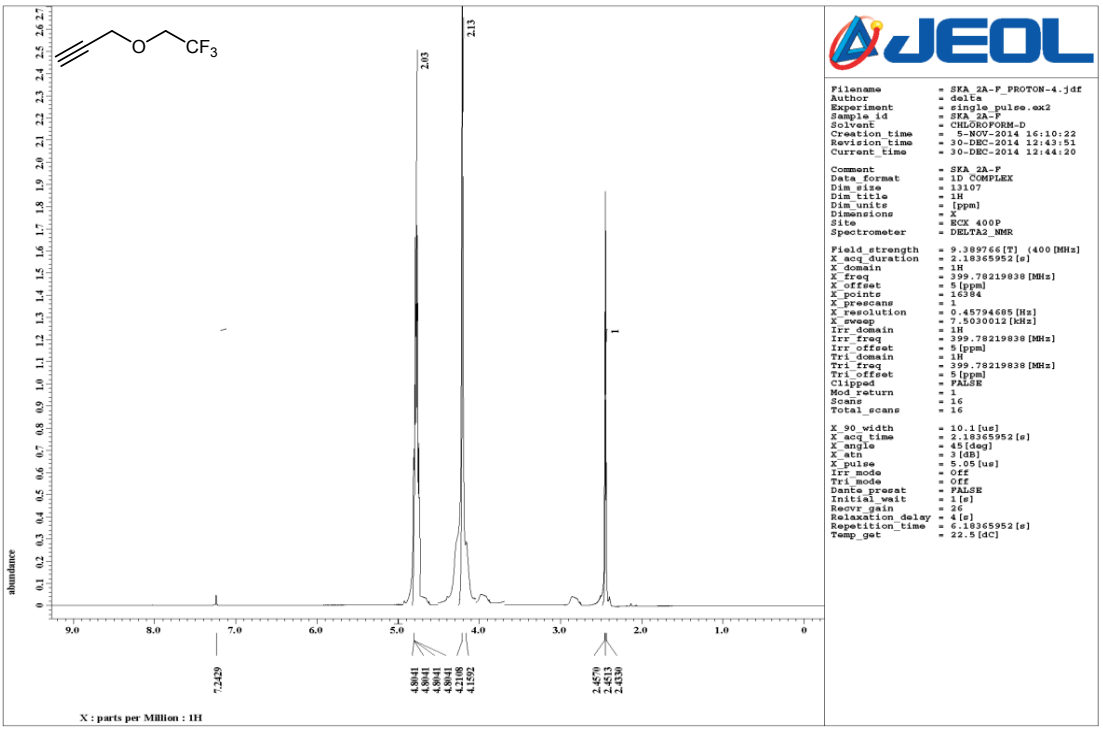


^{19}F NMR of product 7a:



^{1}H NMR of product 8a:



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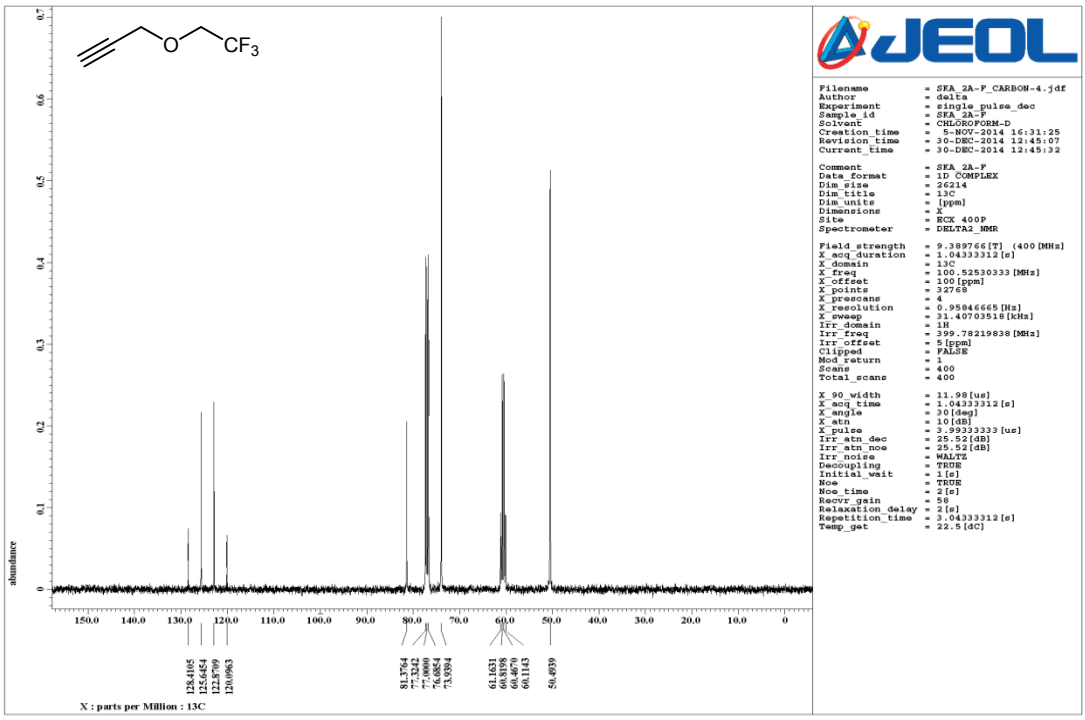

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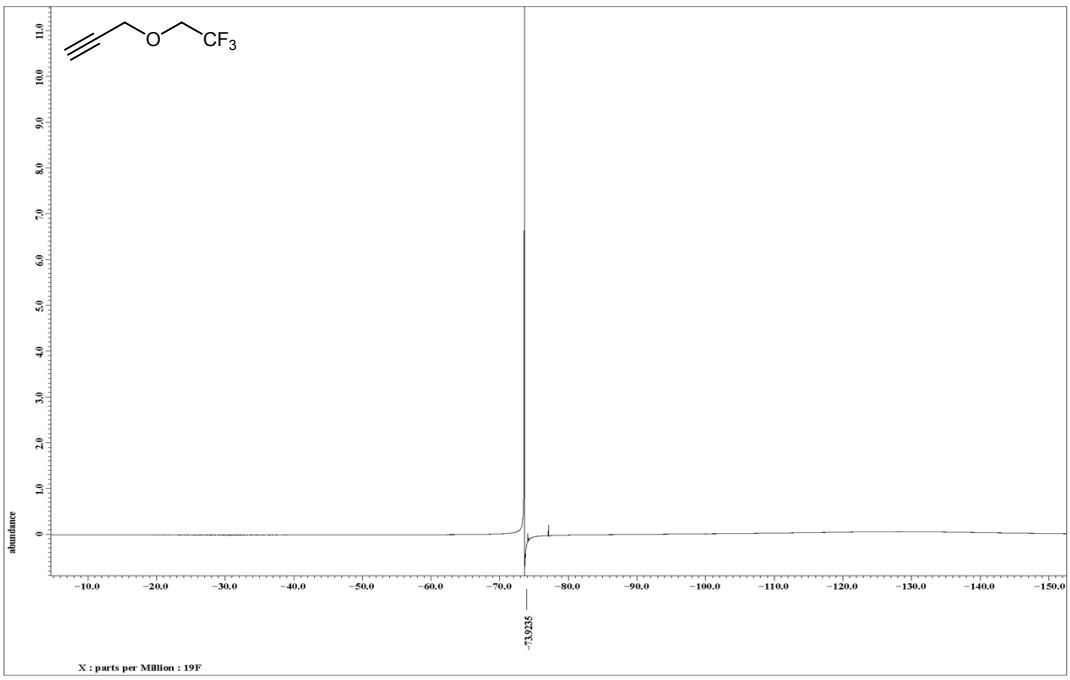
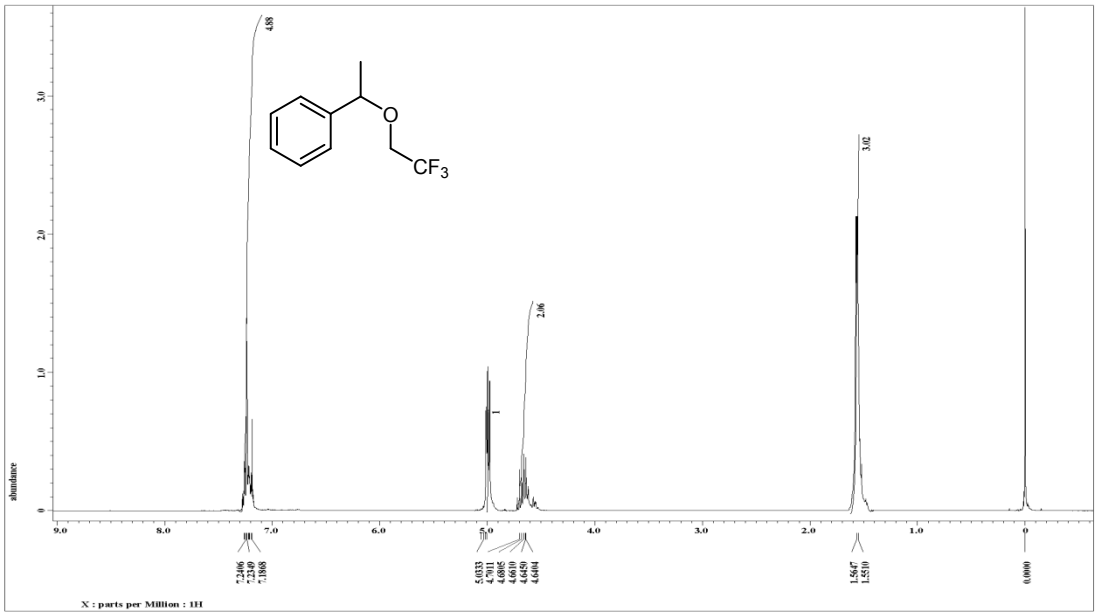
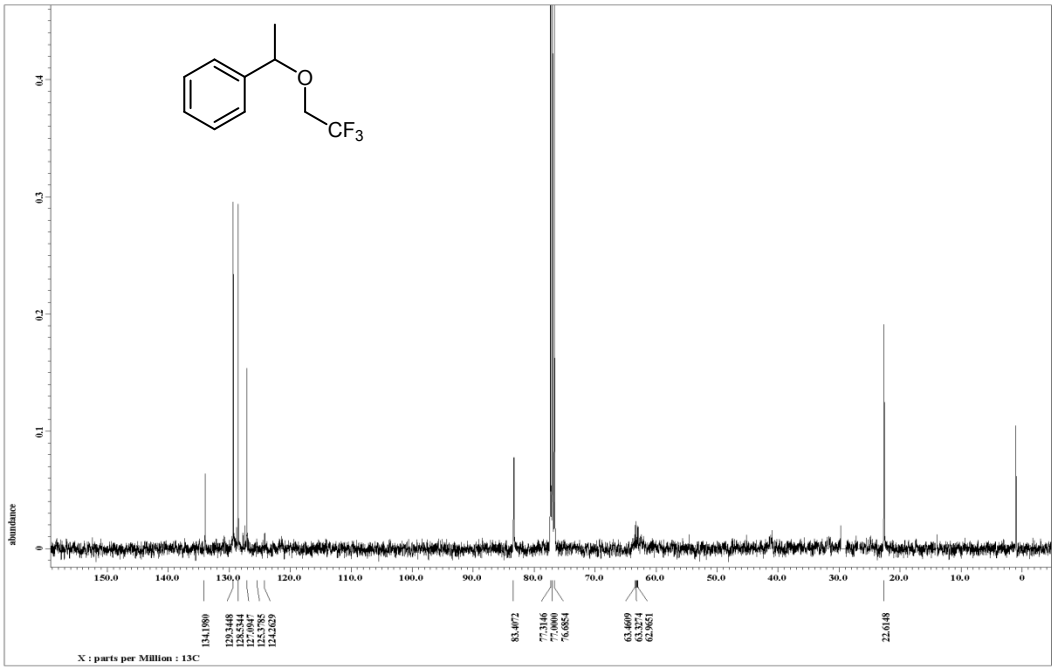


^{1}H NMR of product 9a:



^{13}C NMR of product 9a:



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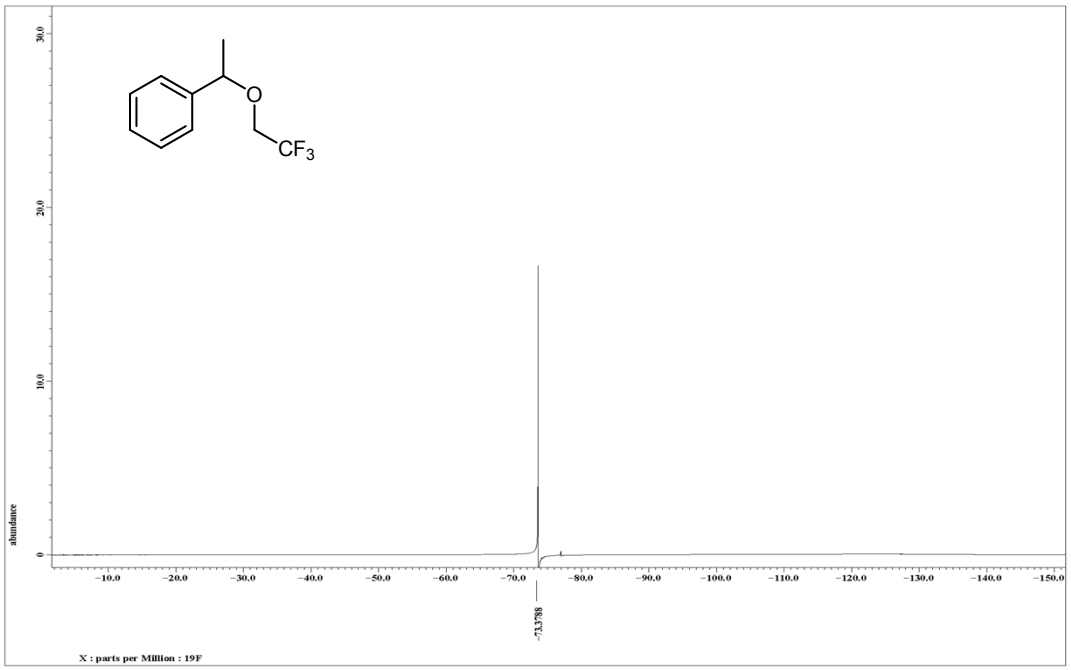

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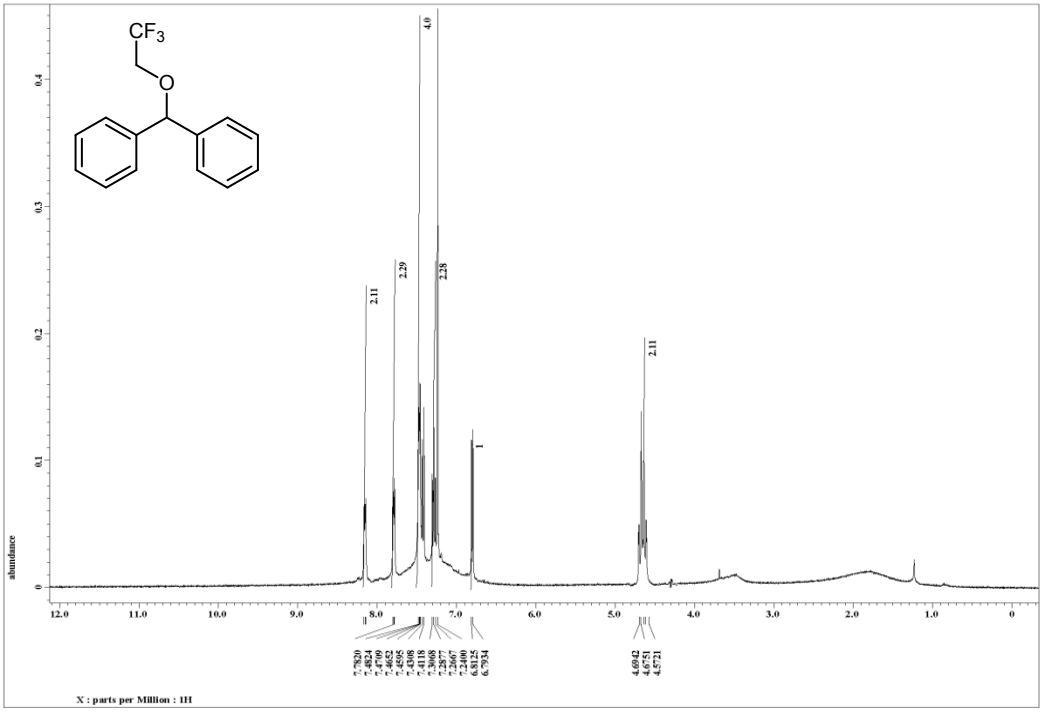

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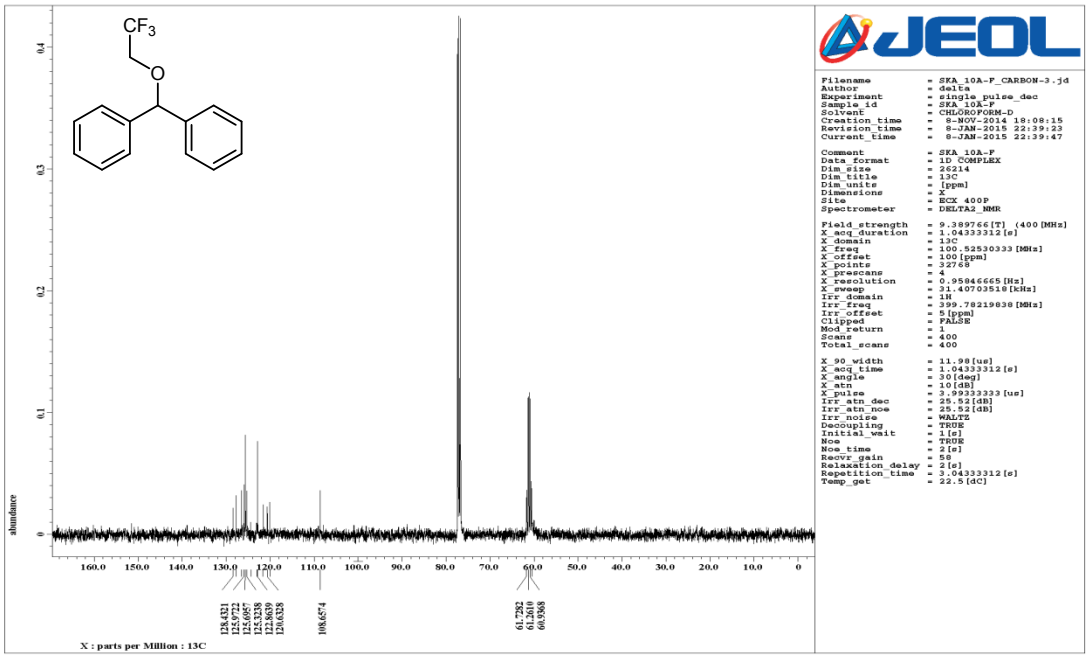

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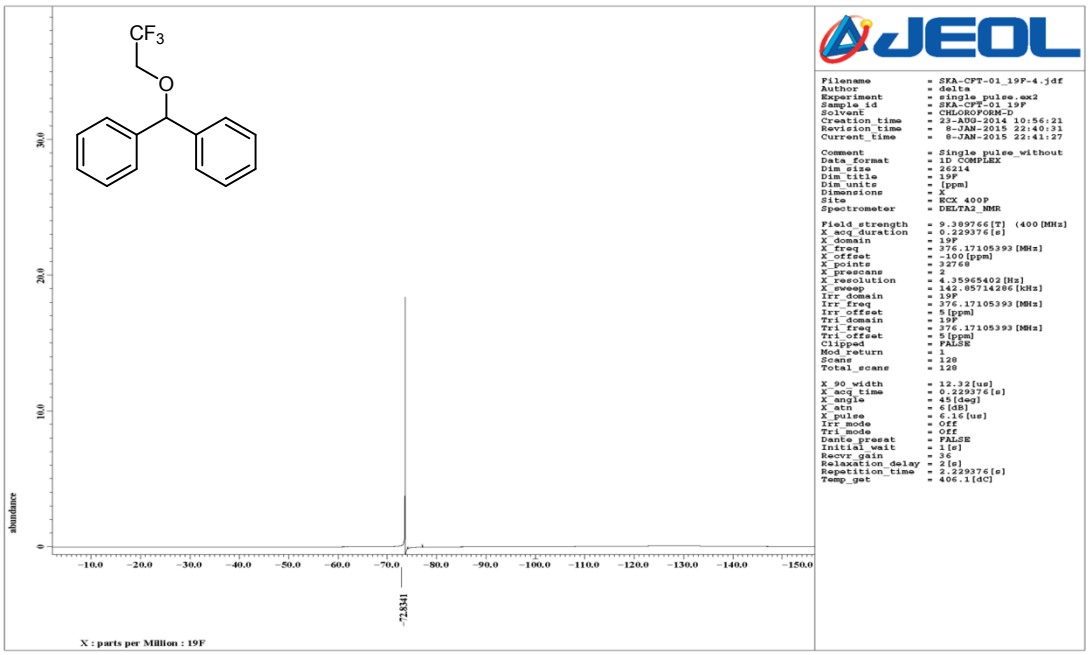
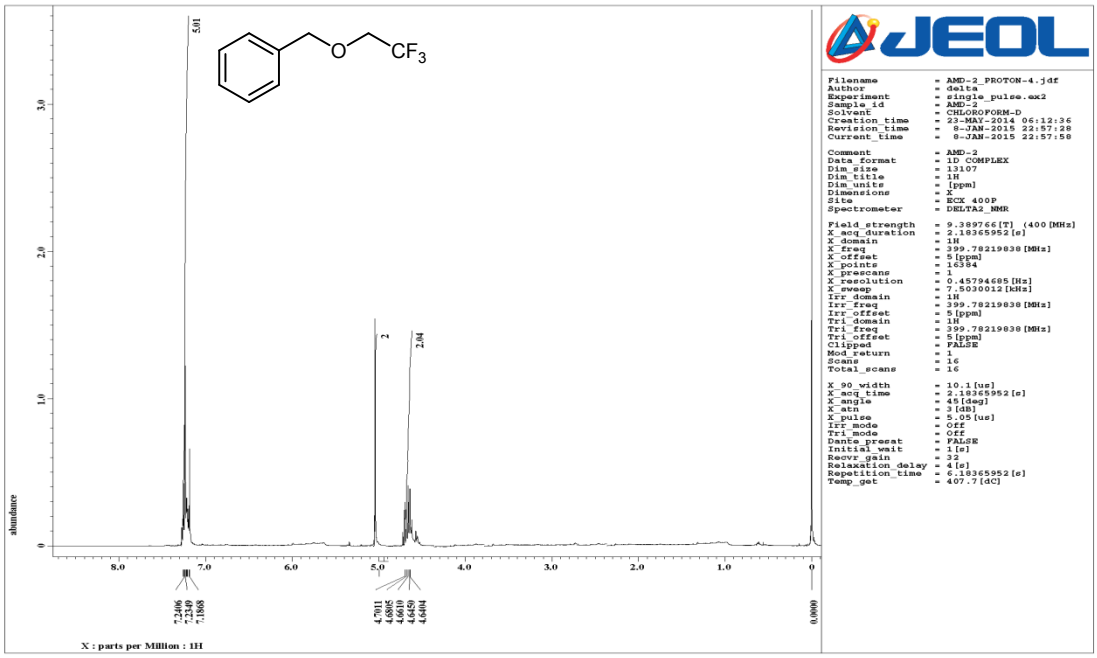


^{1}H NMR of product 11a:



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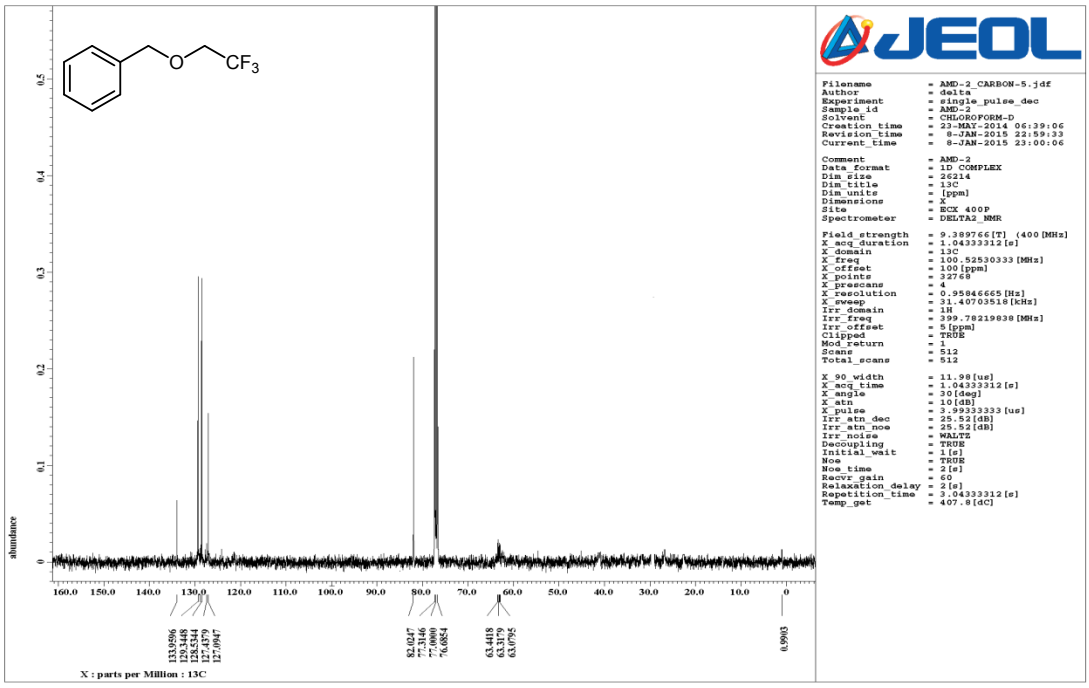

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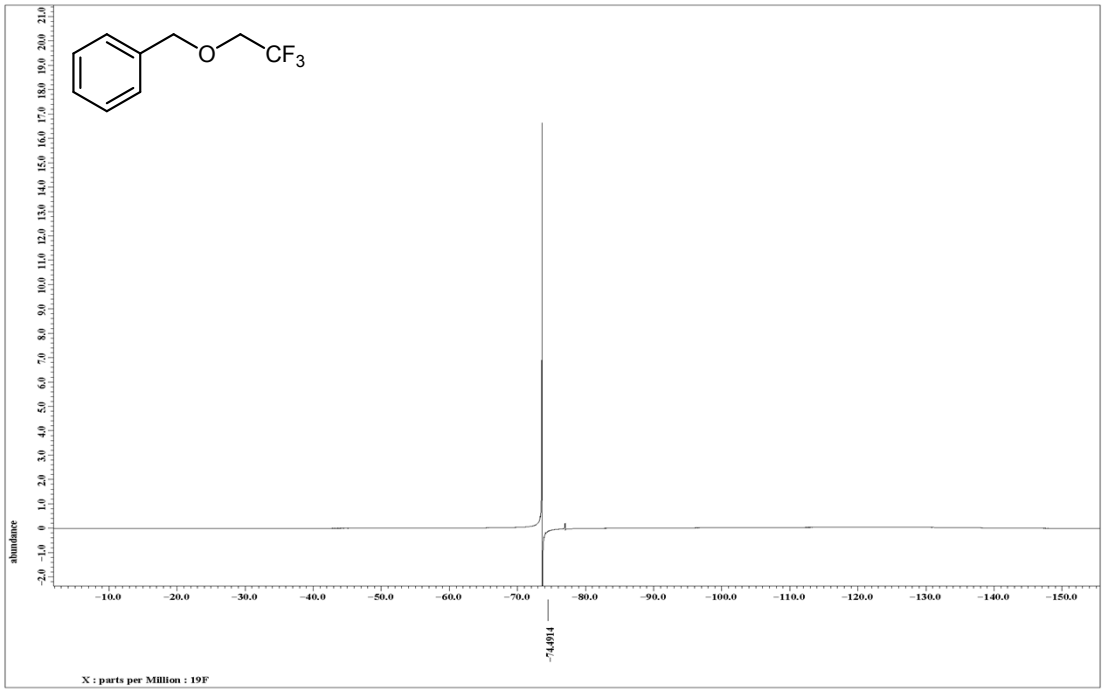

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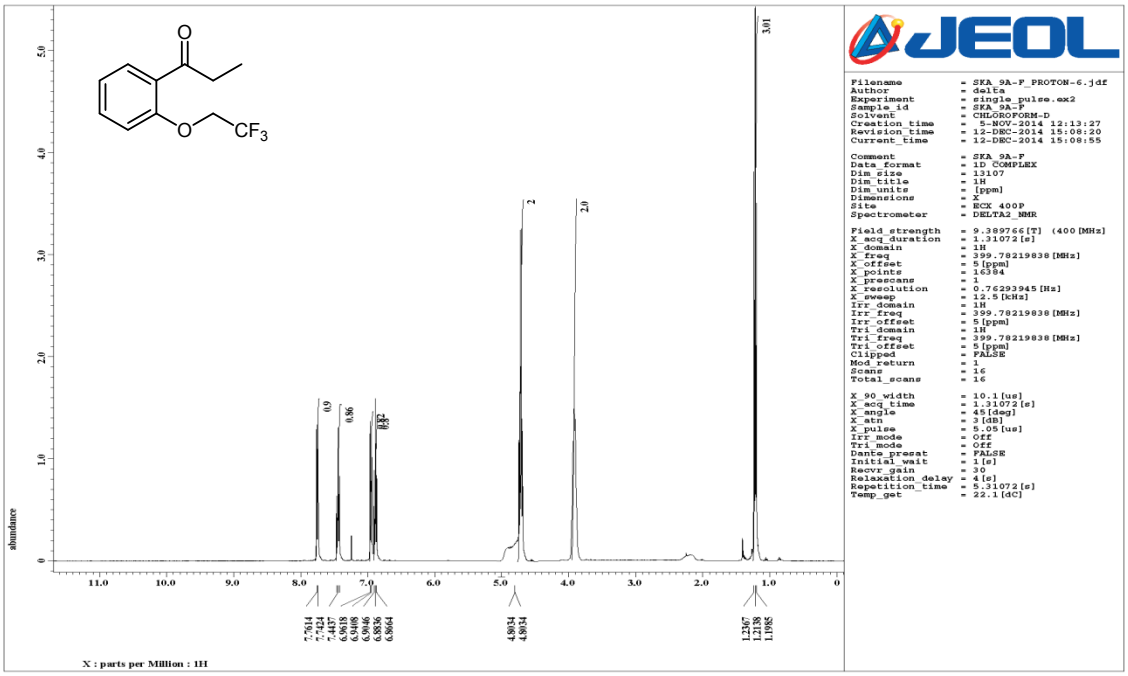

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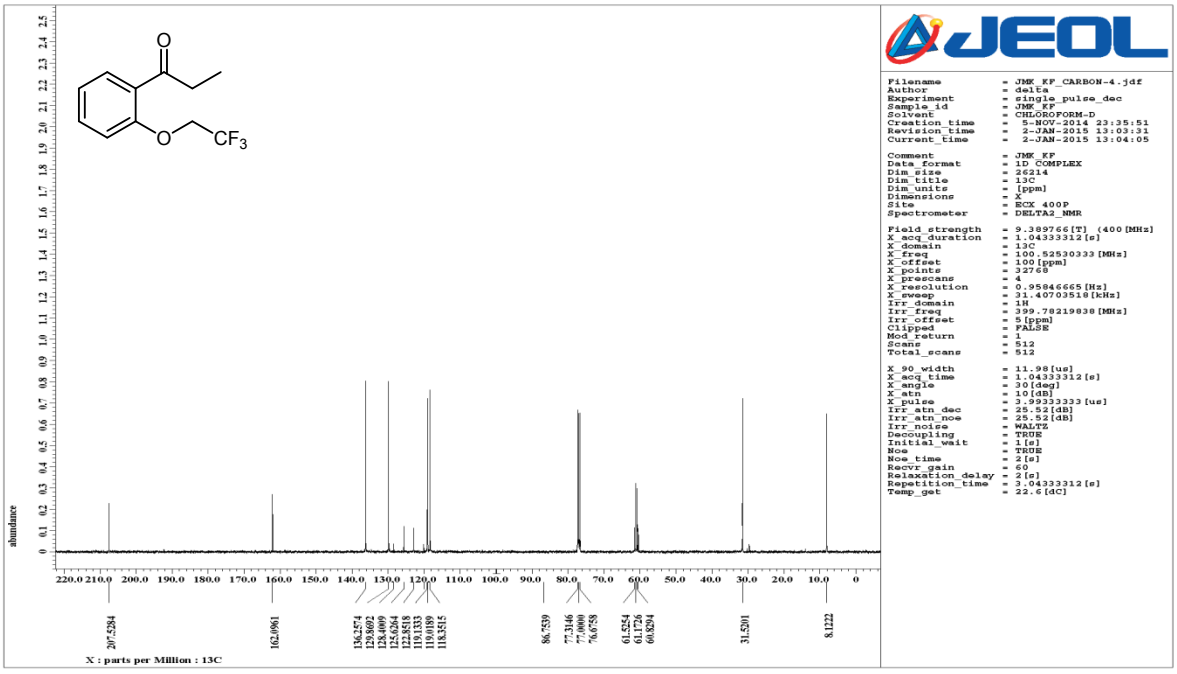

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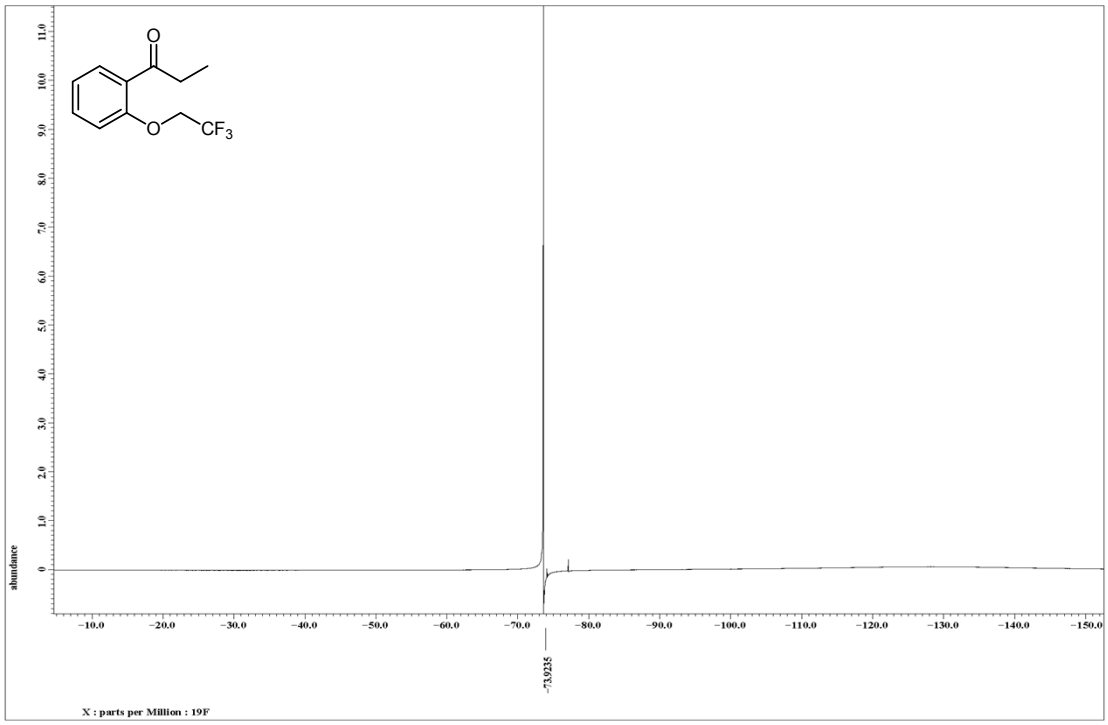
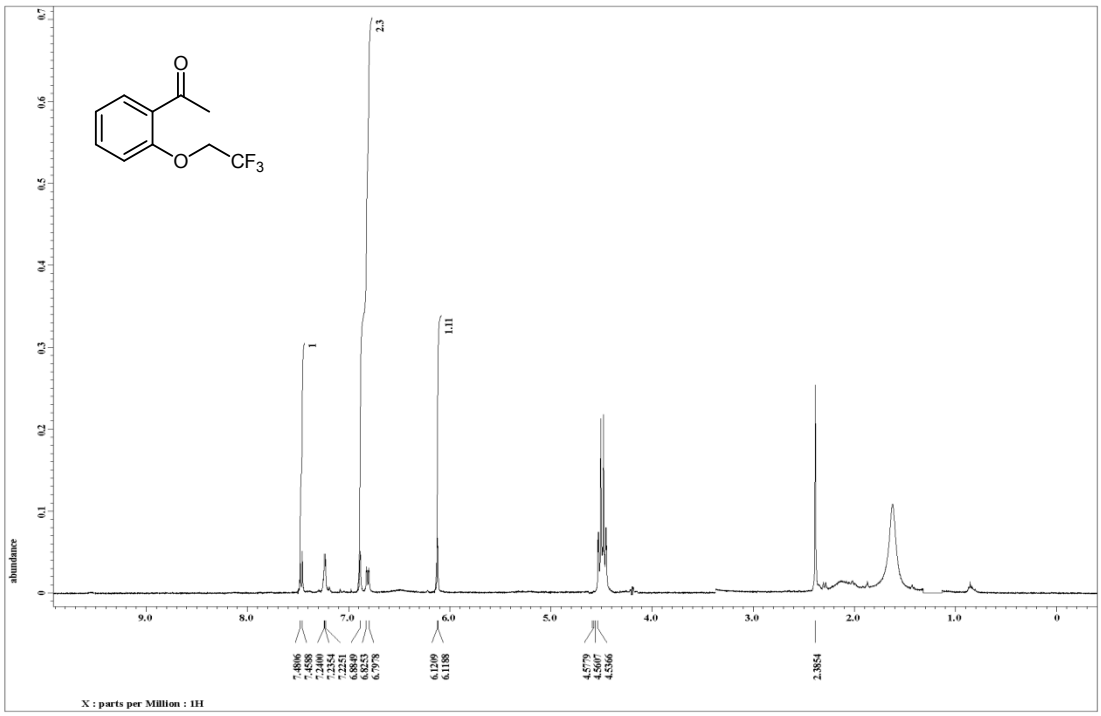


^{1}H NMR of product 13a:



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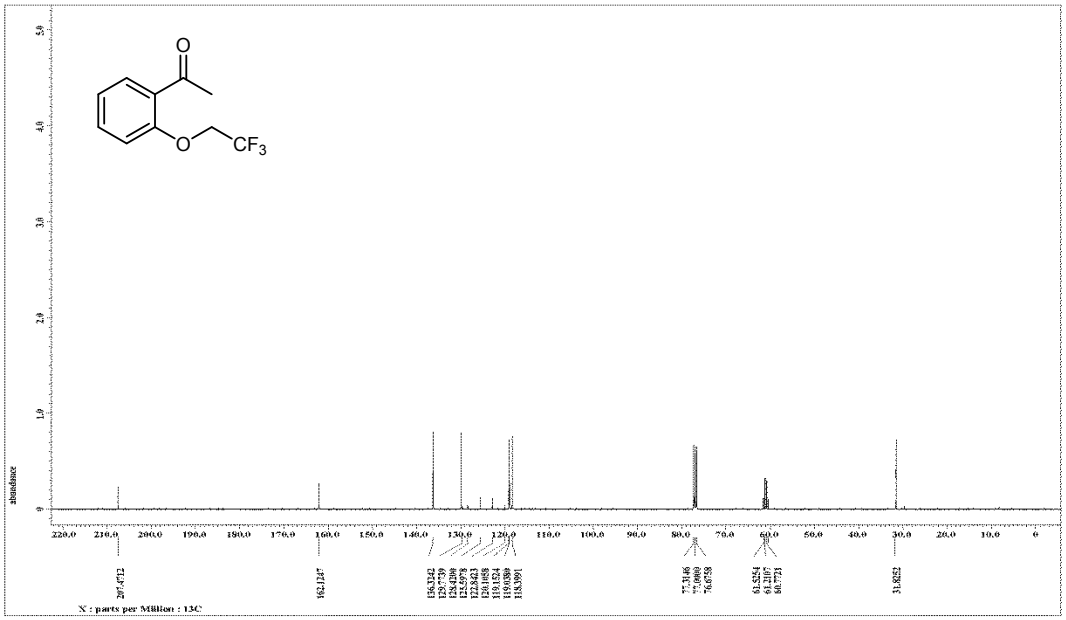

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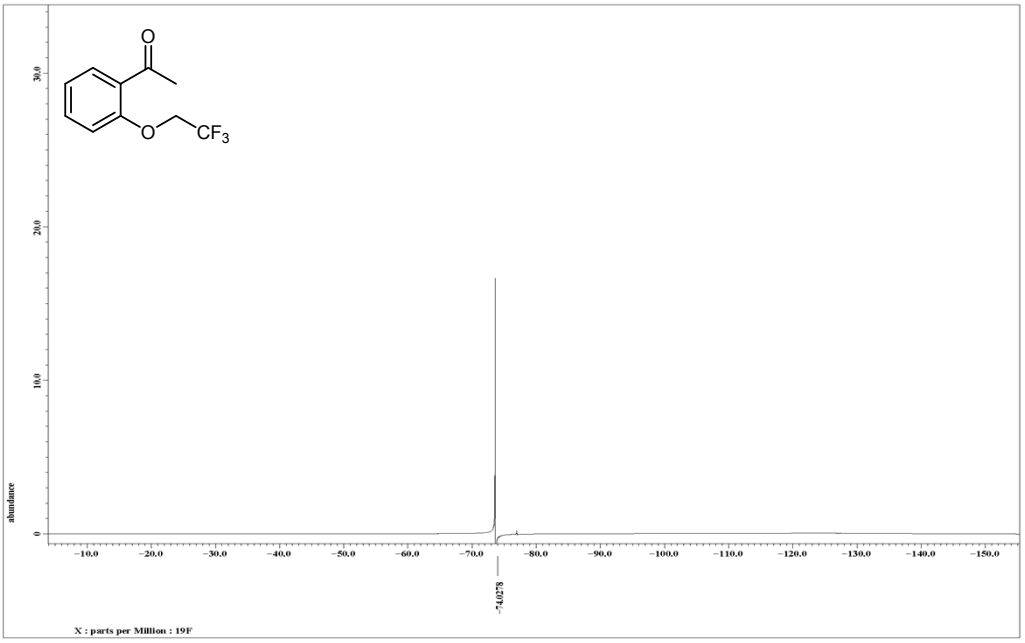
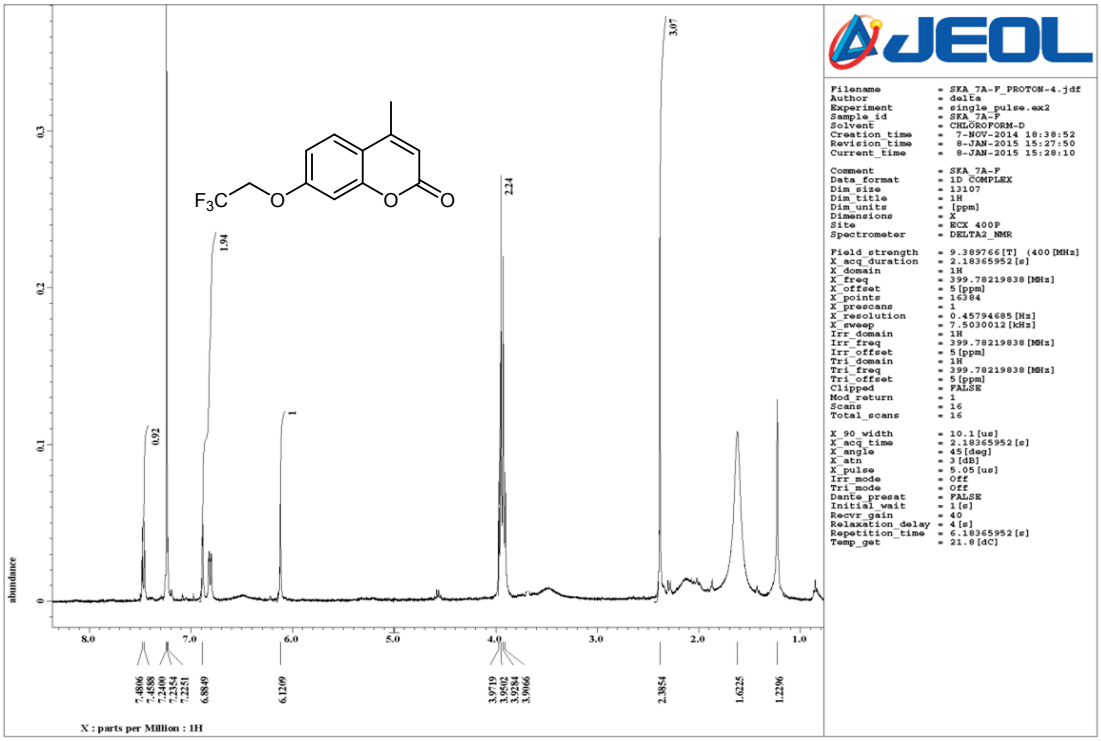


^{1}H NMR of product 14a:



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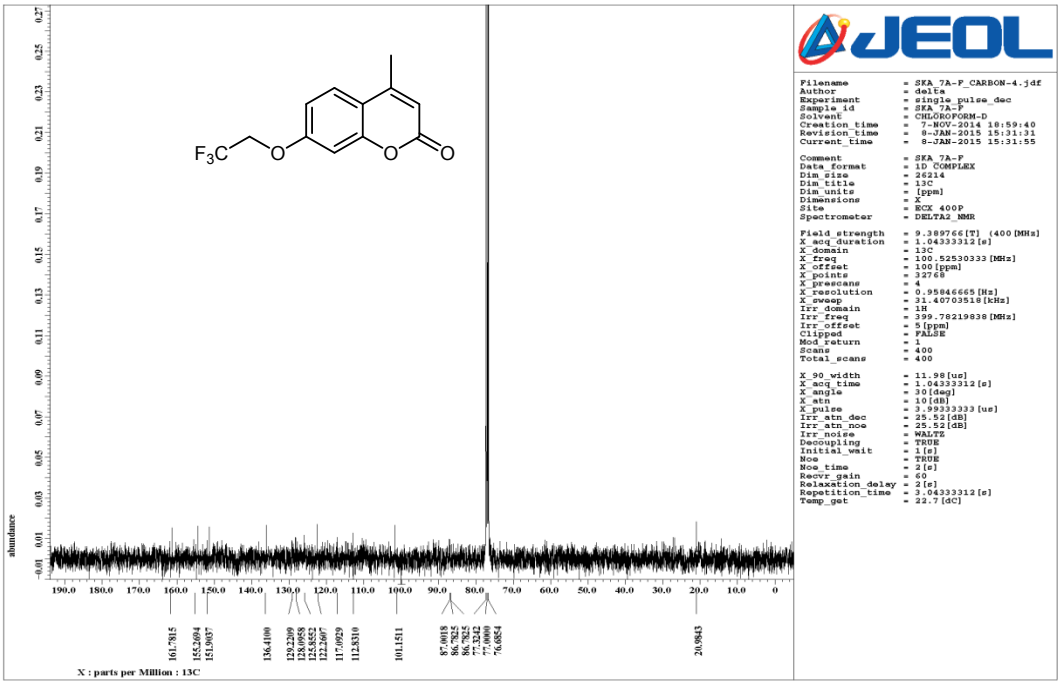
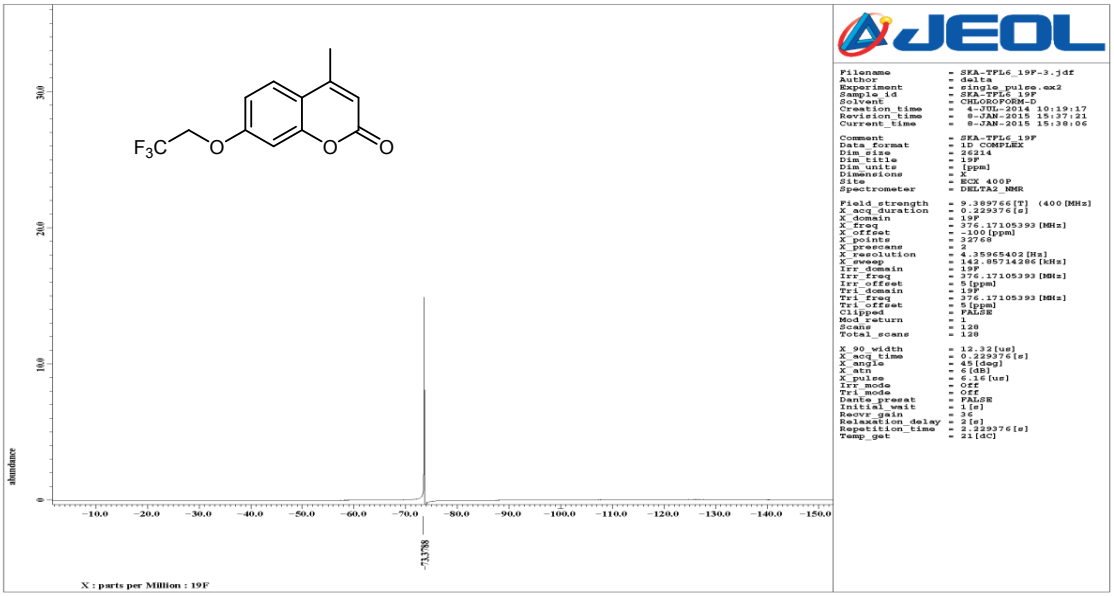
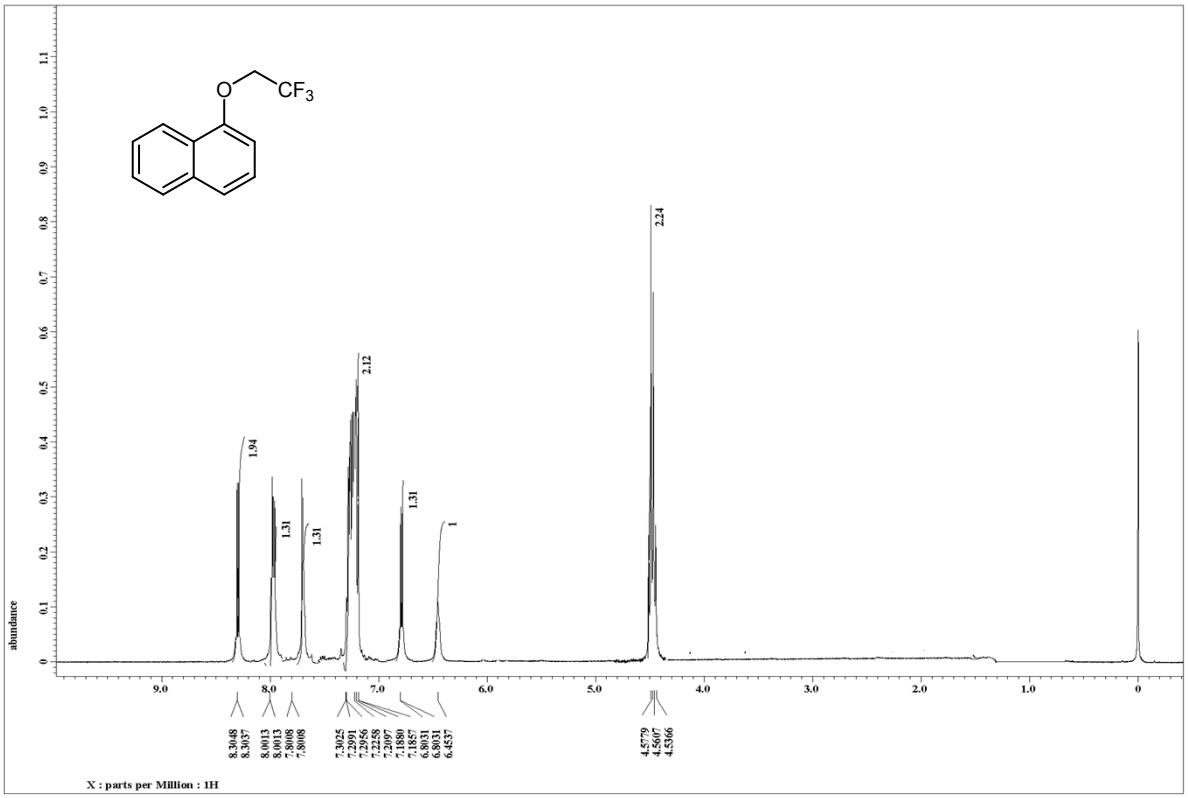


^{19}F NMR of product 14a:



^{1}H NMR of product 15a:



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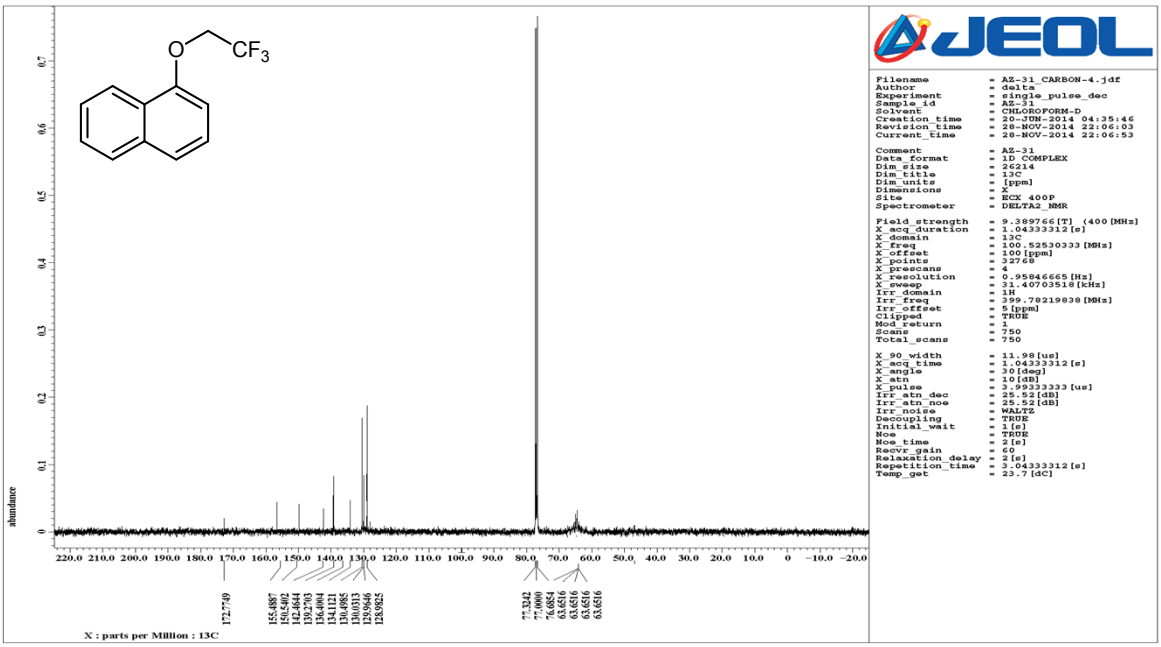

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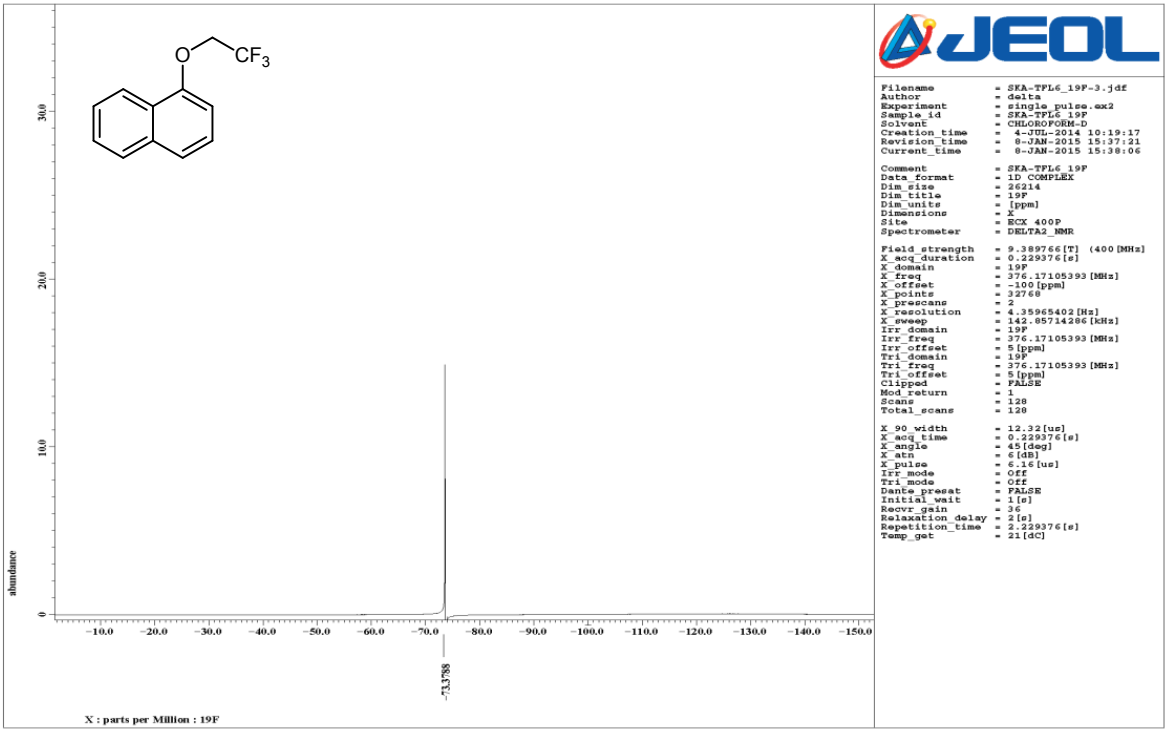
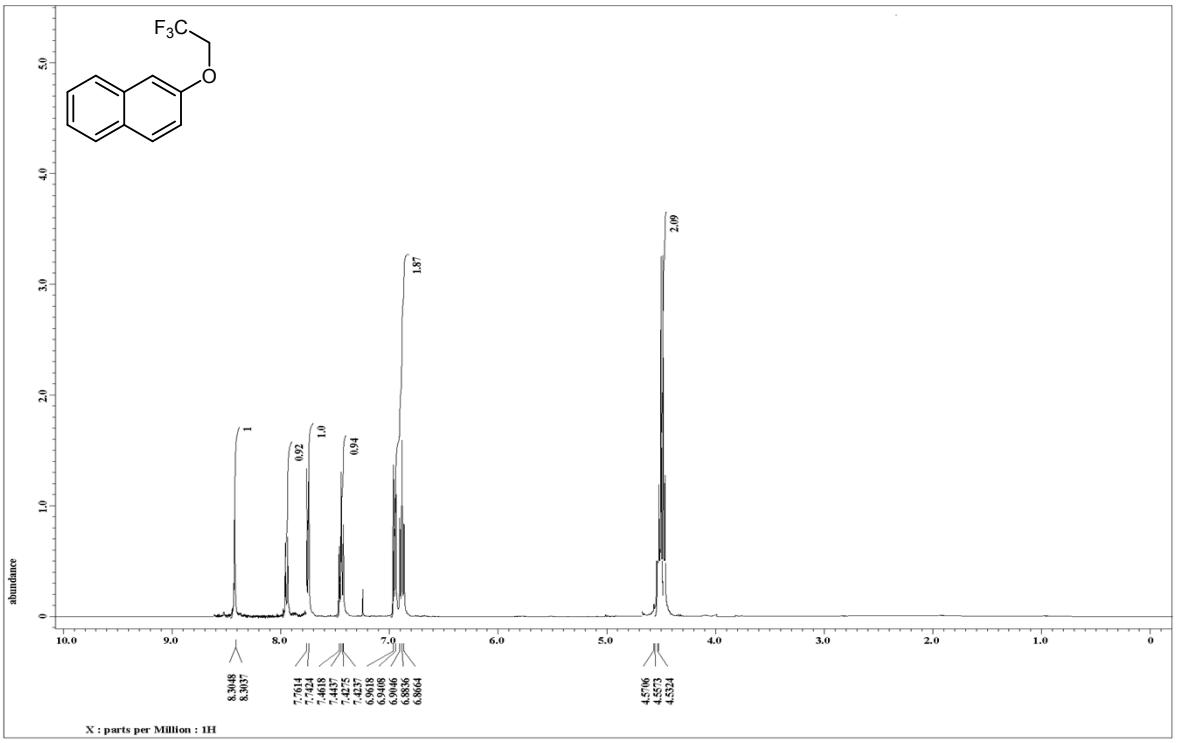


^{1}H NMR of product 16a:



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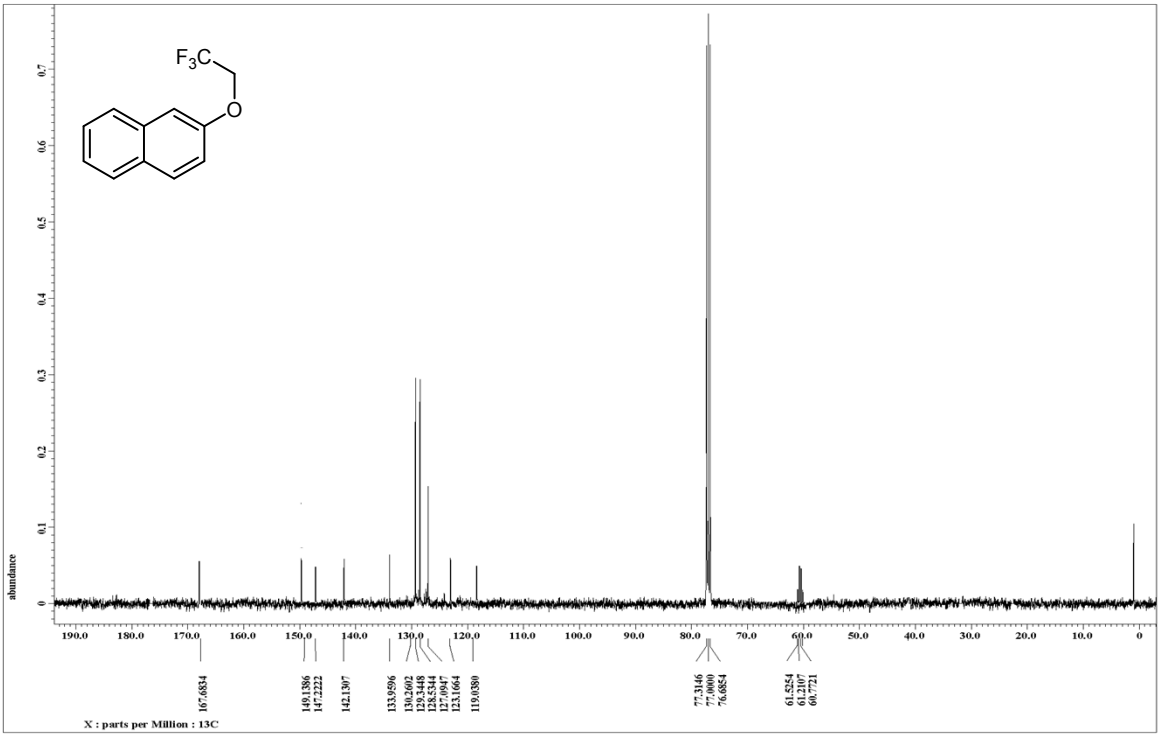

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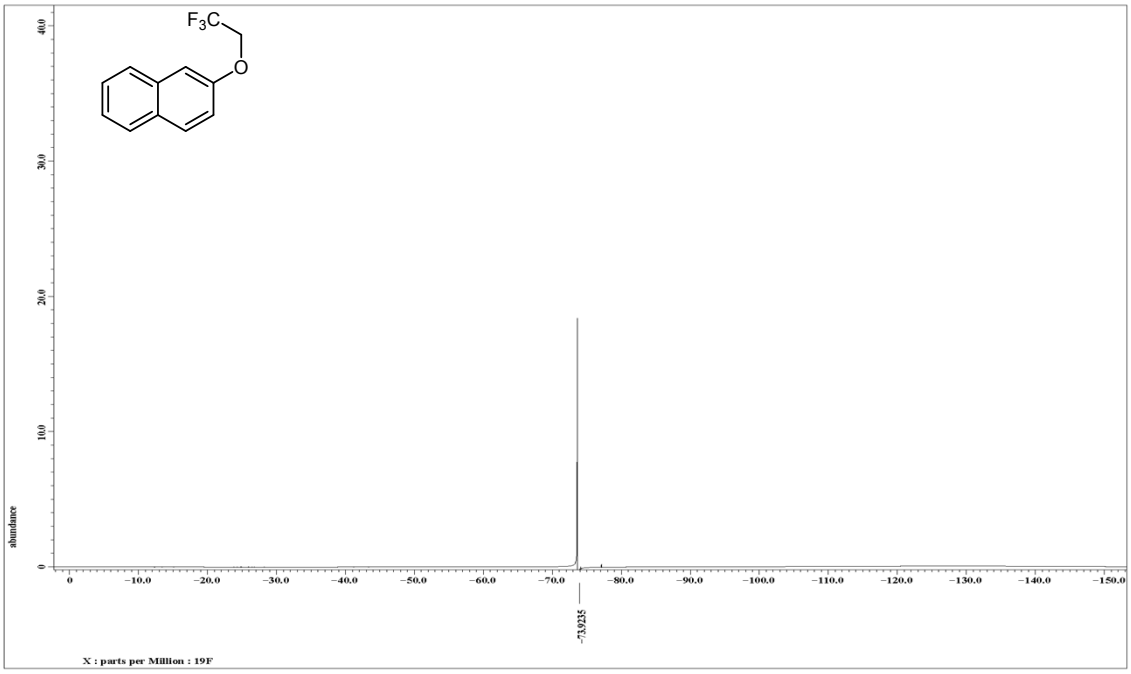

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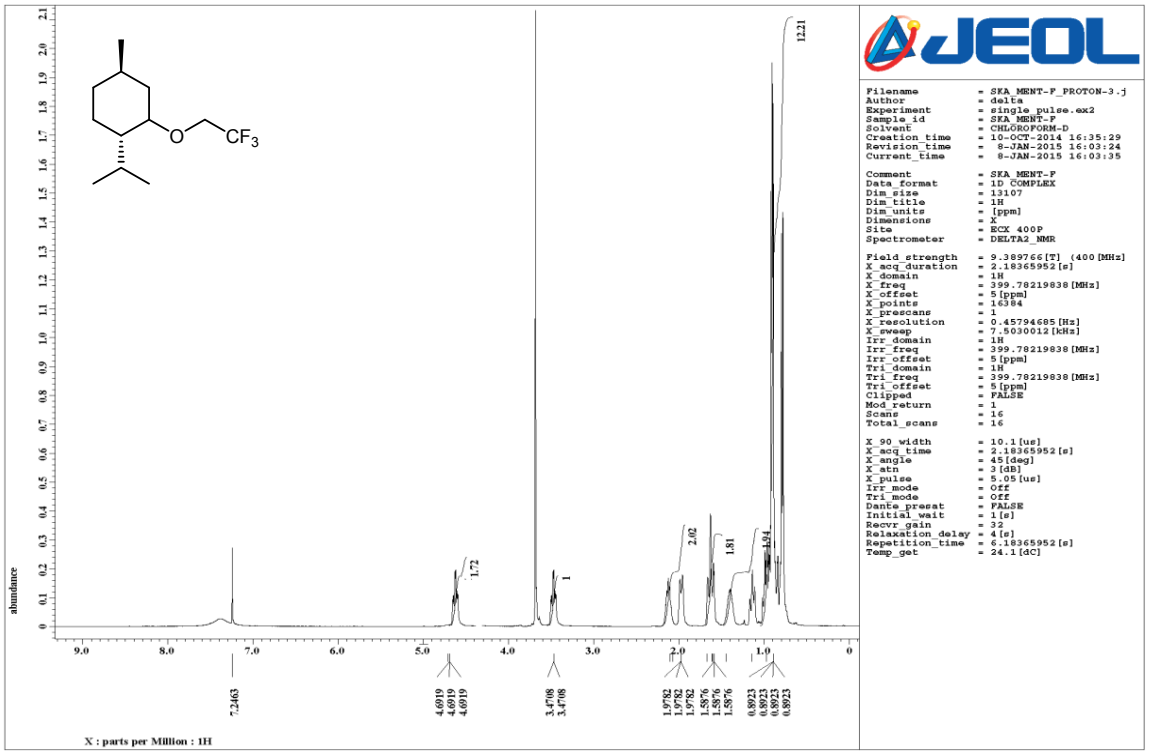

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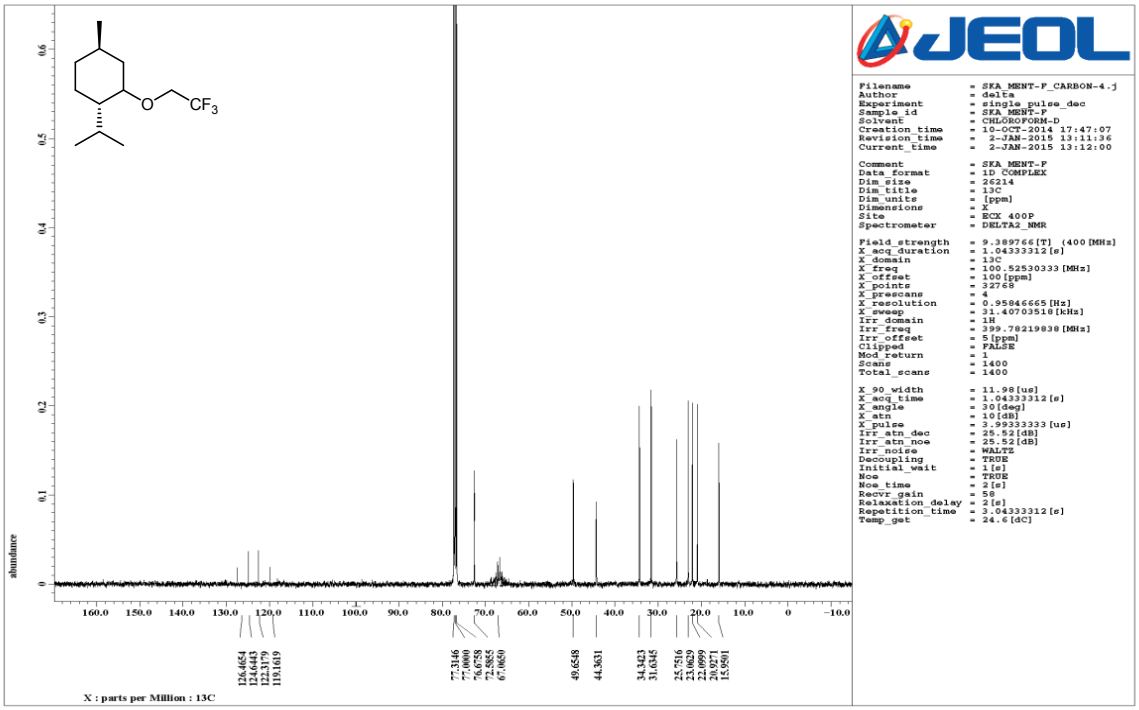

^{19}F NMR of product 17a: