CHEMISTRY
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Supporting Information

Product Control in Alkene Trifluoromethylation: Hydrotrifluoromethylation, Vinylic Trifluoromethylation, and Iodotrifluoromethylation using Togni Reagent

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1. General

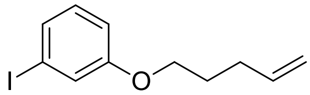
^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a JEOL JNM-ECS-400 spectrometer at 400, 100 and 376 MHz, respectively. Chemical shifts were reported downfield from TMS (= 0) or $CHCl_3$ for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$. For ^{19}F NMR, chemical shifts were reported in the scale relative to a $CFCl_3$ external standard (0 ppm). Infrared spectra were measured on a Thermo Nicolet iS5, and only diagnostic absorptions are listed below. FI-MS was taken on a JEOL JMS-T100GCV. ESI-MS was taken on Bruker micrOTOF-QII-$_{\mathrm{RSL}}$ and Varian QFT-7. Column chromatography was performed with silica gel N-60 (40-50 μm) purchased from Kanto Chemical Co., Inc. In some cases, purification was carried out using JIA recycling preparative HPLC system [LC-918R; column, JAIGEL-H; chloroform]. TLC analysis was performed on Silica gel 60 F_{254}-coated glass plates (Merck). Visualization was accomplished by means of ultraviolet (UV) irradiation at 254 nm or by spraying 12-molybdo (VI) phosphoric acid ethanol solution as the developing agent.

Dehydrated 1,4-dioxane and *N,N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc. Tetrabutylammonium iodide (TBAI), K_2CO_3 and KI were obtained from commercial sources and were used as received. Other reagents were purified by usual methods. Known alkenes[1] and Togni reagent[2] were prepared according to literature procedures. New alkenes were prepared with the reported methods,[3,4] their characterizations were described the following section 2.1.

2. Preparation of starting materials

2.1. Preparation of alkenes

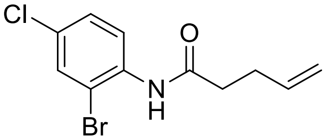
2.1.1. 3-(4-pentenyloxy)-iodobenzene (2b)



Compound **2b** was prepared from 2-iodophenol and 4-penten-1-ol by the Mitsunobu reaction, according to procedure reported in the literature[3] and was provided as colorless oil in 96% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.83-1.90 (m, 2H), 2.20-2.26 (m, 2H), 3.93 (t, J = 6.4 Hz, 2H), 4.99-5.09 (m, 2H), 5.79-5.89 (m, 1H), 6.85 (ddd, J = 0.9, 2.3, 8.3 Hz, 1H), 6.98 (dd, J = 8.3, 8.3 Hz, 1H), 7.24-7.28 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 28.4, 30.2, 67.4, 94.5, 114.4, 115.5, 123.7, 129.8, 130.9, 137.8, 159.8 ppm; IR (neat): 2939, 1640, 1225, 1059, 989, 912 cm^{-1}; HRMS (FI): Calcd. for [C$_{11}$H$_{13}$IO]$^+$: m/z = 288.0011, Found: 288.0006.

2.1.2. *N*-(2-bromo-4-chlorophenyl)-4-pentenamide (2c)

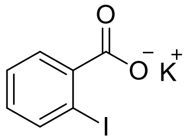


Compound **2c** was prepared from 4-pentenoyl chloride and 2-bromo-4-chloroaniline, according to procedure reported in the literature[4], and was provided as white solid in 90% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.47-2.56 (m, 4H), 5.08 (dtd, J = 1.4. 1.4, 10.1 Hz, 1H), 5.14 (dtd, J = 1.4, 1.4, 17.0 Hz, 1H), 5.84-5.94 (m, 1H), 7.29 (dd, J = 2.3, 8.7 Hz, 1H), 7.54 (d, J = 2.3 Hz, 1H), 7.55-7.60 (bs, 1H), 8.33 ppm (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 29.3, 37.2, 113.4, 116.4, 122.6, 128.6, 129.5, 131.8, 134.5, 136.4, 170.6 ppm; IR (neat): 3337, 1302, 1278, 1183, 915, 824 cm^{-1}; HRMS (ESI): Calcd. for [C$_{11}$H$_{11}$BrClNO+Na]$^+$: m/z = 309.9605, Found: 309.9613.

2.2. Synthesis of 2-iodo benzoate salts

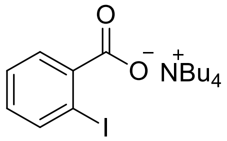
2.2.1 potassium 2-iodobenzoate [5]



To an acetone solution (10 mL) of 2-iodobenzoic acid (2.5 g, 1.1 equiv.) was added KOH (0.50 g, 1.0 equiv.) dissolved in a minimum of distilled water at 0 °C. After stirring for 30 min at room temperature, the reaction mixture was filtered. The residue was then washed several times with cold acetone and dried in vacuo. Potassium 2-iodobenzoate (1.0 g, 40%) was given as a white solid.

^{1}H NMR (400 MHz, CD_3OD): δ = 6.96 (ddd, J = 1.8, 7.4, 7.4 Hz, 1H), 7.31(ddd, J = 0.9, 7.4, 7.4 Hz, 1H), 7.34 (dd, J = 1.8, 7.4 Hz, 1H), 7.78 ppm (dd, J = 0.9, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ = 92.5, 128.3, 128.7, 129.9, 140.3, 148.9, 177.3 ppm; IR (neat): 1574, 1550, 1392, 1360, 746, 687 cm^{-1}

2.2.2 tetrabutylammonium 2-iodobenzoate[6]



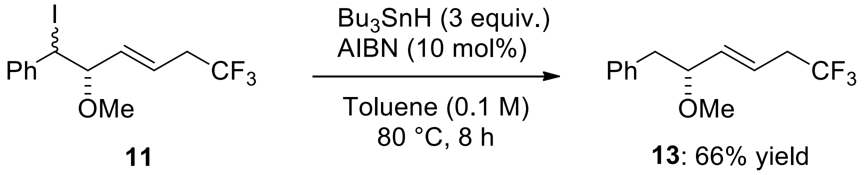
Tetrabutylammonium hydroxide (40% in water, 1.3 g, 1.0 equiv.) was added to MeOH (10 mL) solution of 2-iodobenzoic acid (0.50 g, 1.0 equiv.). After stirring for 30 min at room temperature, the reaction mixture was diluted with EtOH (2 mL) and concentrated under reduced pressure. To remove water completely, the reaction mixture was freeze-dried overnight. Then, the solid was washed several times with dehydrated Et_2O and dried in vacuo to provide Tetrabutylammonium 2-iodobenzoate (0.72 g, 73%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 12H), 1.44 (sextet, J = 7.4 Hz, 8H), 1.64-1.72 (m, 8H), 3.39-3.43 (m, 8H), 6.82 (ddd, J = 1.8, 7.4, 7.4 Hz, 1H), 7.22 (ddd, J = 0.9, 7.4, 7.4 Hz, 1H), 7.56 (dd, J = 1.8, 7.8 Hz, 1H), 7.73 ppm (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =13.8, 19.8, 24.2, 58.8, 93.3, 127.4, 127.7, 128.6, 138.9, 149.5, 172.9 ppm; IR (neat): 2959, 1601, 1457, 1348, 1009, 739 cm^{-1}

3. Structural determination of 11 and 12

3.1. Deiodination of (*E*)-(6,6,6-trifluoro-1-iodo-2-methoxy-3-hexyl)benzene (11)[6]

Iodo-trifluoromethylation product **11** was obtained as diastereomeric mixture from the radical cation clock substrate **10** (eq. 2). In order to confirm the structure of main chain of **11**, deiodination was carried out under the described conditions.



11

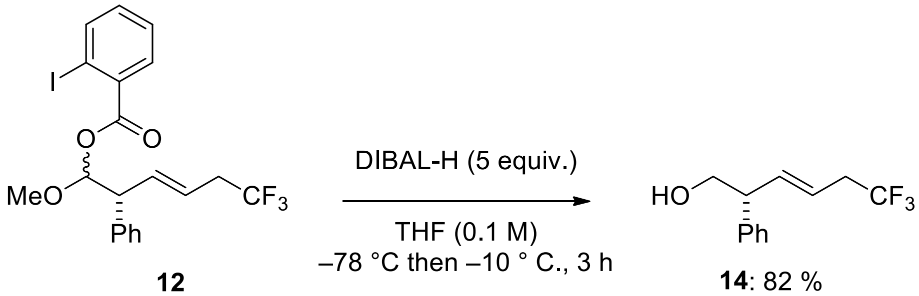
13: 66% yield

Tributyltin hydride (80 μL, 3 equiv.) was added to toluene (1 mL) solution of **11** (39.9 mg, 0.11 mmol) and AIBN (1.6 mg, 0.1 equiv.). After stirring for 8 h at 80 °C, the reaction mixture was diluted with EtOAc (5 mL), and distillated water was added. The mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure to provide **13** (17.5 mg, 66%).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.72-2.86 (m, 3H), 2.91-2.96 (m, 1H), 3.26 (s, 3H), 3.78 (dt, J = 6.9, 6.9 Hz, 1H), 5.45-5.53 (m, 1H), 5.57-5.63 (m, 1H), 7.16-7.23 (m, 3H), 7.26-7.30 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.1 (q, J = 29.9 Hz), 42.1, 56.6, 82.7, 121.1 (q, J = 2.9 Hz), 125.9 (q, J = 276.5 Hz), 126.4, 128.3, 129.7, 137.7, 137.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –66.3 ppm (t, J = 10.8 Hz); IR (neat): 2933, 1604, 1256, 1099, 974, 748 cm^{-1}; HRMS (FI): Calcd. for $[C_{13}H_{15}F_3O]^+$: m/z = 244.1075, Found: 244.1064

3.2. Reduction of (*E*)-6,6,6-trifluoro-1-methoxy-2-phenyl-3-hexenyl 2-iodobenzoate (12)

Diastereomixture of oxy-trifluoromethylation product **12** was obtained as byproduct in the iodo-trifluoromethylation reaction of radical cation clock substrate **10** (eq. 2). In order to confirm the structure of **12**, a reduction of **12** with DIBAL-H was conducted as follows.



12

14: 82 %

DIBAL-H (1 M, 810 μL, 5 equiv.) was added to a THF (1.6 mL) solution of **12** (79.6 mg, 0.16 mmol) at –78 °C. After stirring for 3 h at –10 °C, the reaction was quenched with MeOH (2 mL) and saturated potassium sodium tartrate (10 mL). The mixture was additionally stirred for 1 h. The organic layer was washed with distillated water. The mixture was extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silicagel to provide **14** (30.8 mg, 82%).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, J = 6.4 Hz, 1H), 2.80-2.89 (m, 2H), 3.57 (dt, J = 7.4, 7.4 Hz, 1H), 3.81-3.87 (m, 2H), 5.56 (dtd, J =1.4, 7.4, 15.6 Hz, 1H), 5.93 (dd, J = 7.4, 15.6 Hz, 1H), 7.21-7.29 (m, 3H), 7.33-7.38 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.6 (q, J = 29.9 Hz), 51.4, 66.3, 120.5 (q, J = 2.9 Hz), 125.9 (q, J = 276.5 Hz), 127.3, 128.0, 129.0, 137.8, 140.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –66.4 ppm (t, J = 10.8 Hz); IR (neat): 3362, 1494, 1251, 1131, 970, 757 cm^{-1}; HRMS (FI): Calcd. for $[C_{12}H_{13}F_3O]^+$: m/z = 230.0918, Found: 230.0910.

4. References

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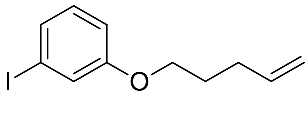
[4] J. -F. Cui, H. Huang, H. N. C. Wong, *Synlett,* **2011**, 1018.

[5] The compound was prepared according to the literature procedure. See, S. B. Litwin, W. F. Skogen, S. R. McCreadia, M. B. Laver, *J. Appl. Physiol.,* **1976**, *41*, 900.

[6] T. Yoshinari, K. Ohmori, M. G. Schrems, A. Pfaltz, K. Suzuki, *Angew. Chem. Int. Ed.,* **2010**, *49*, 881.

5. NMR spectra



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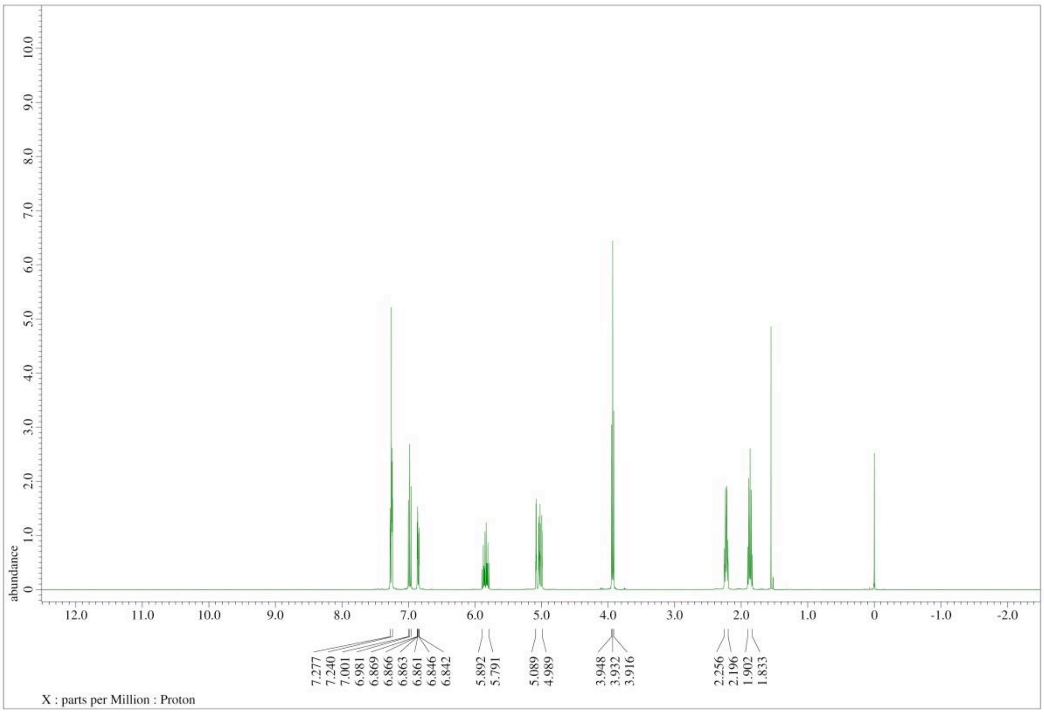

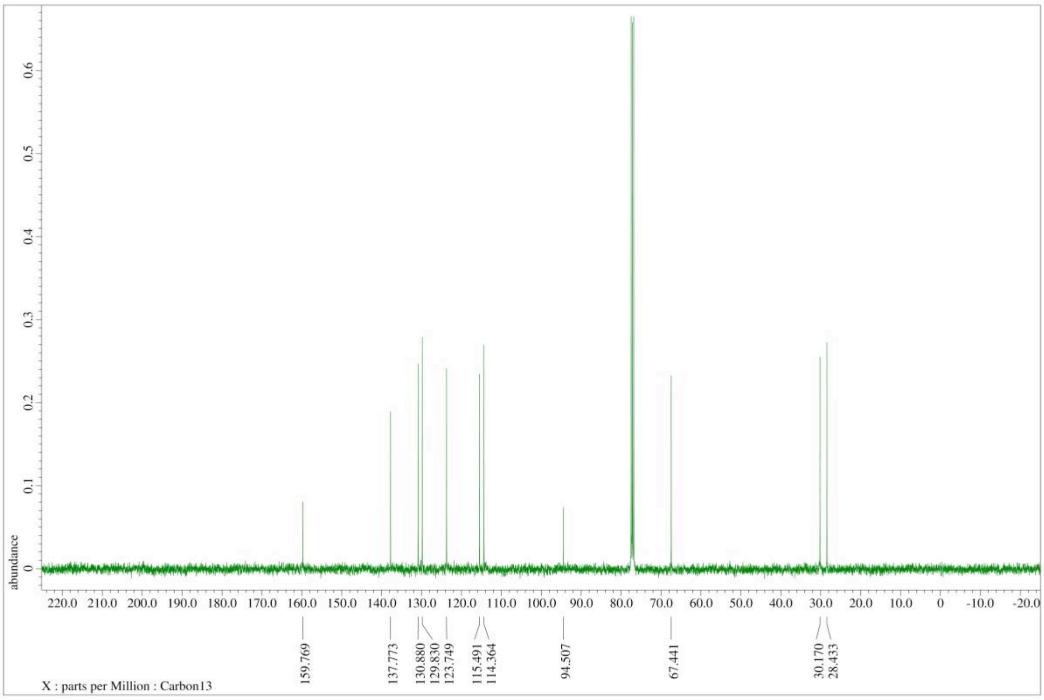

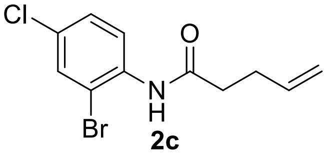
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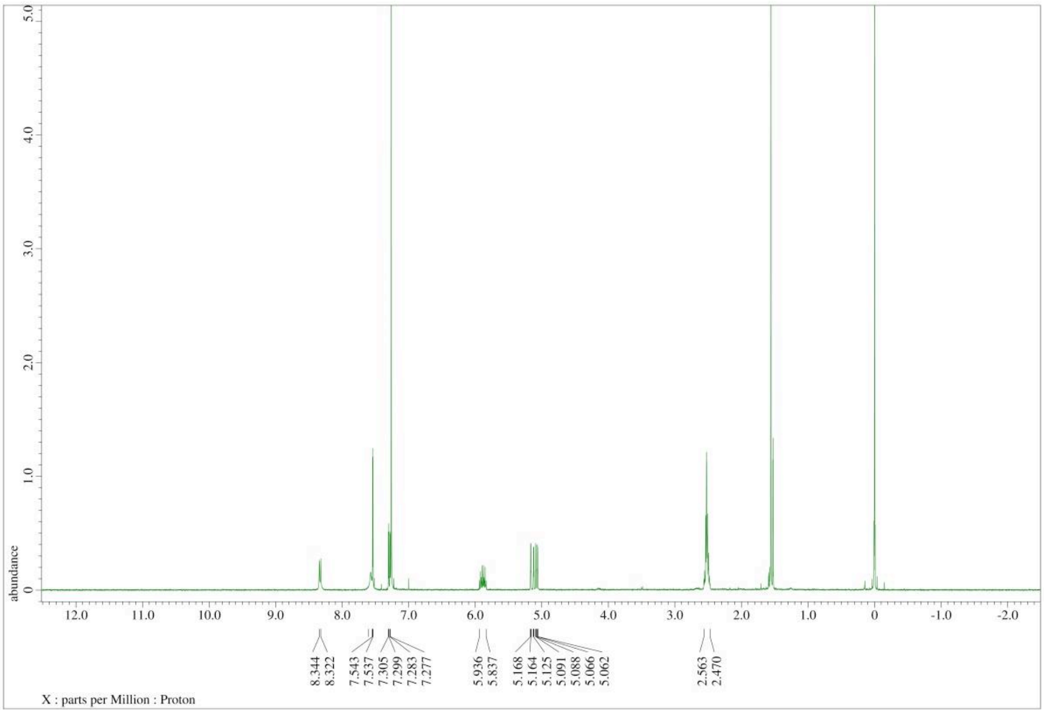
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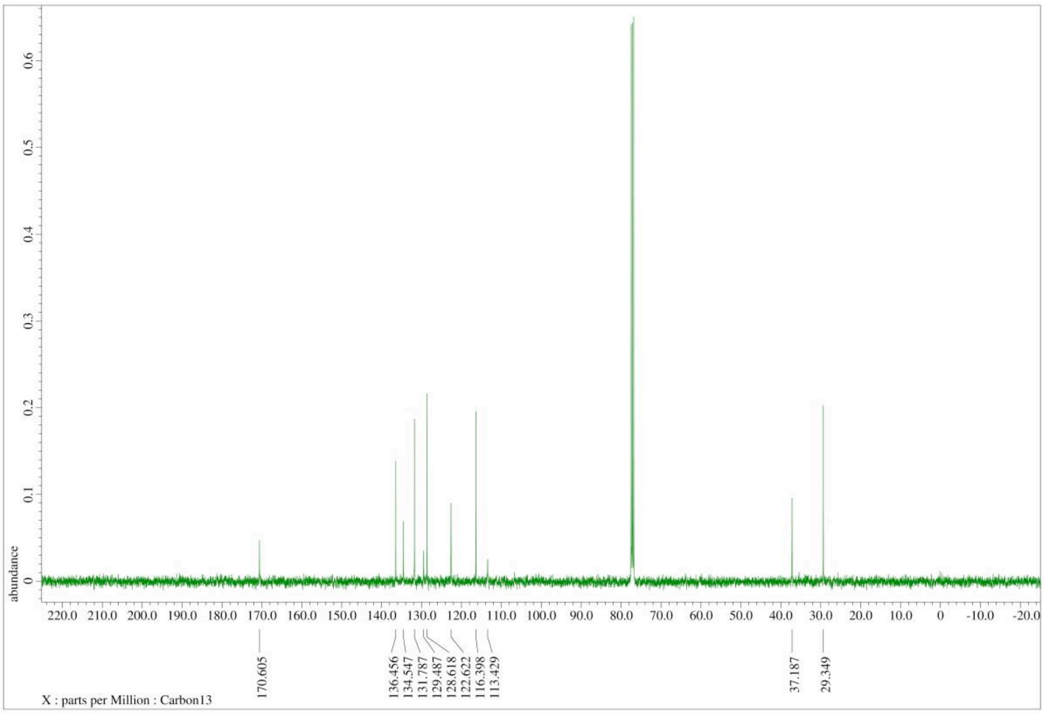
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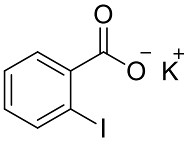
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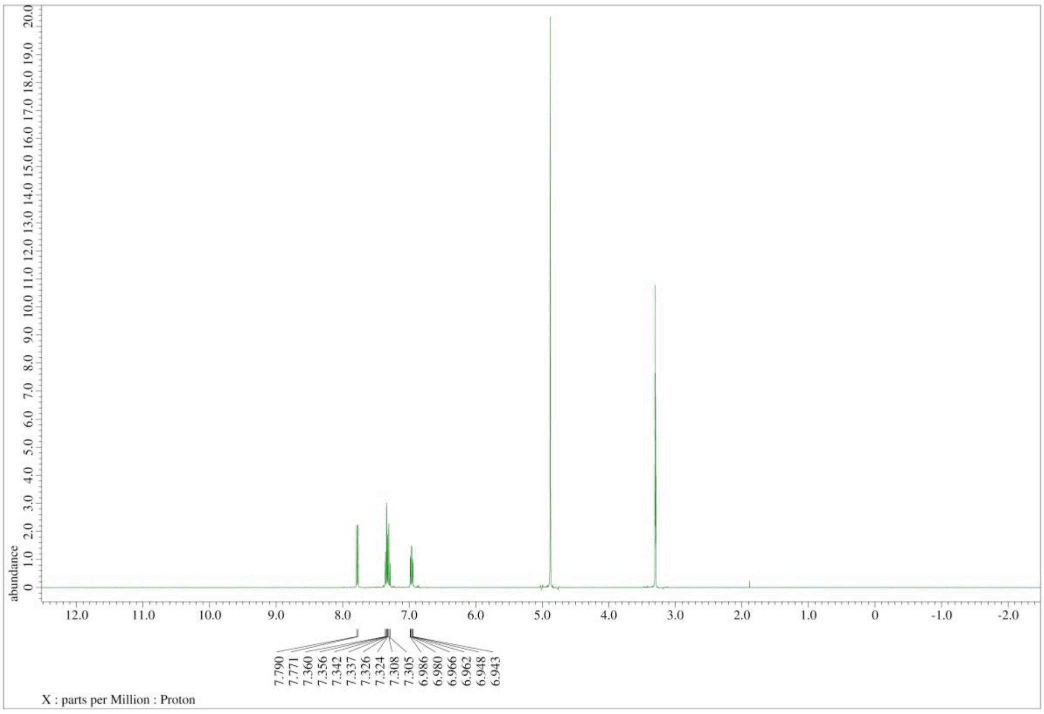
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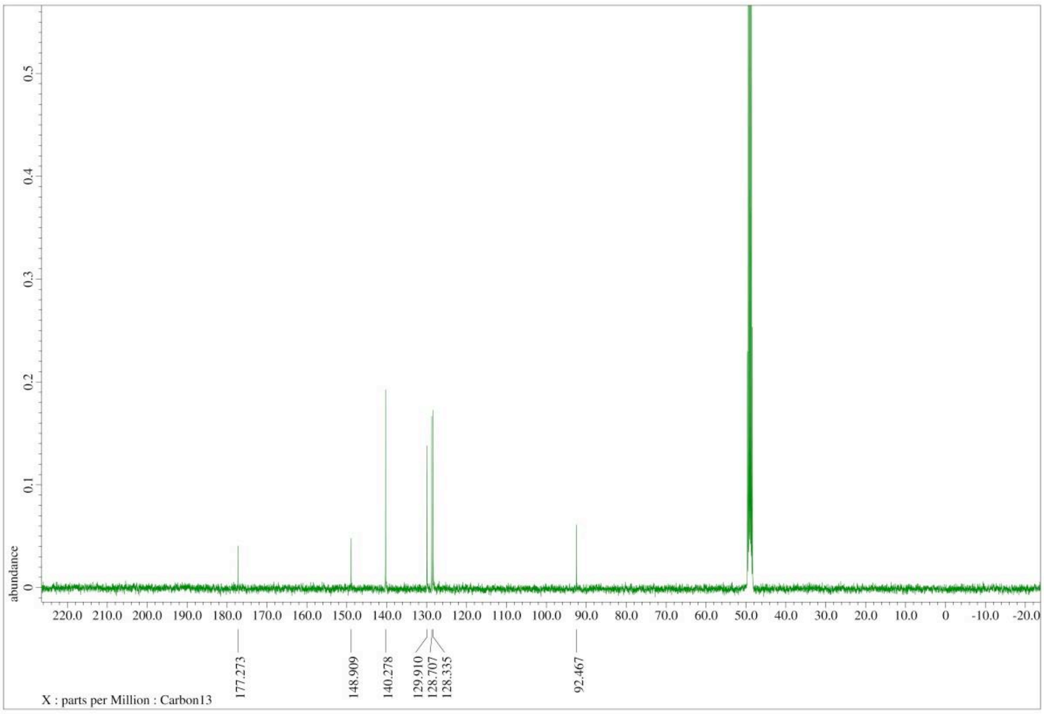
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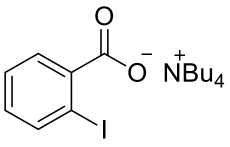
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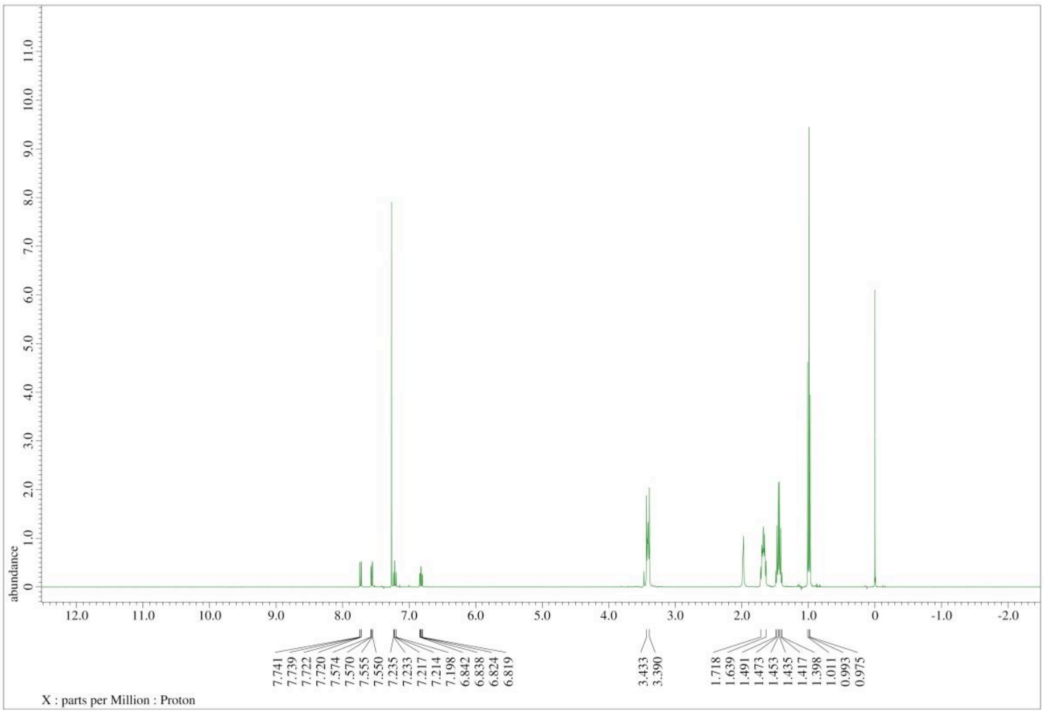
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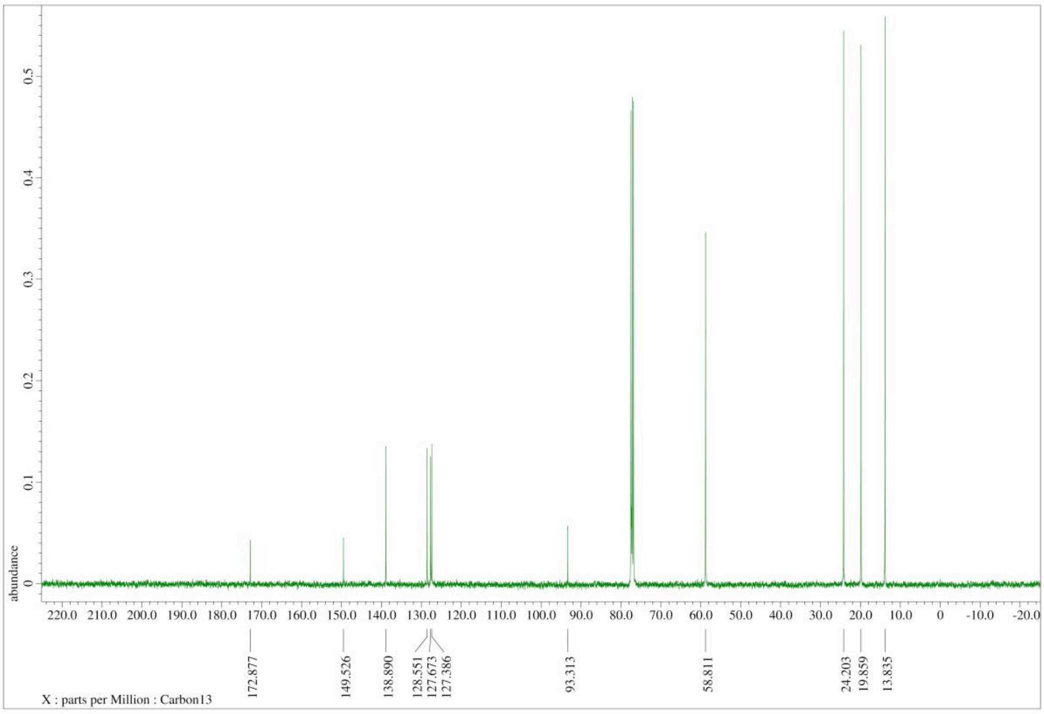
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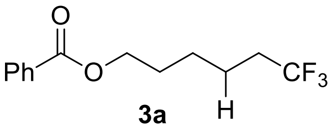
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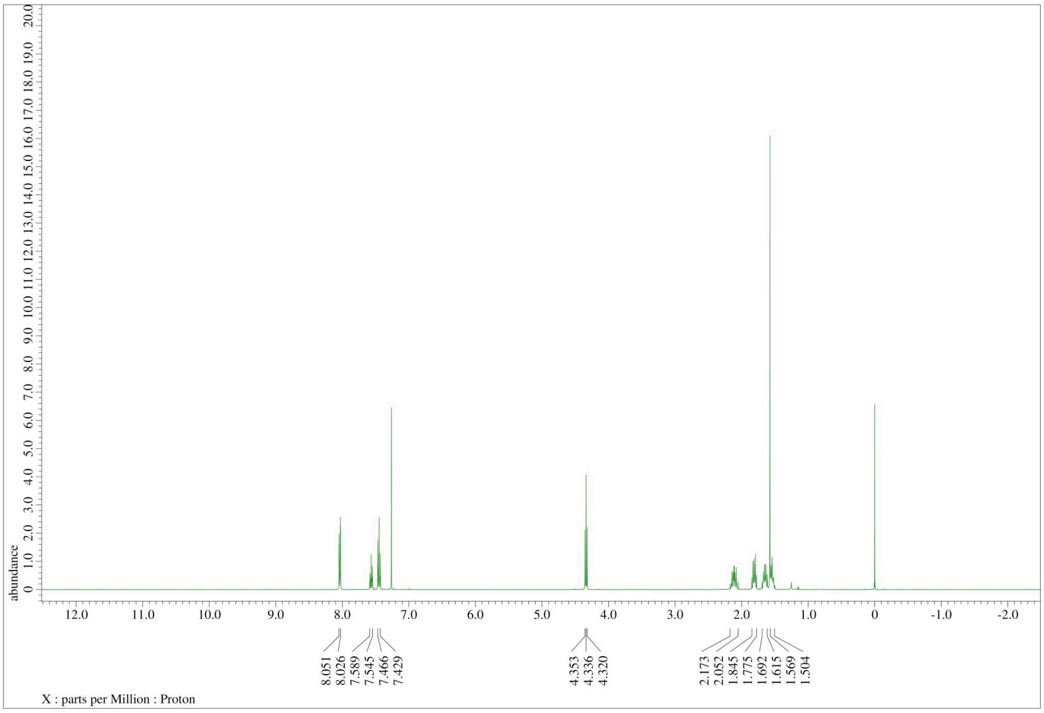
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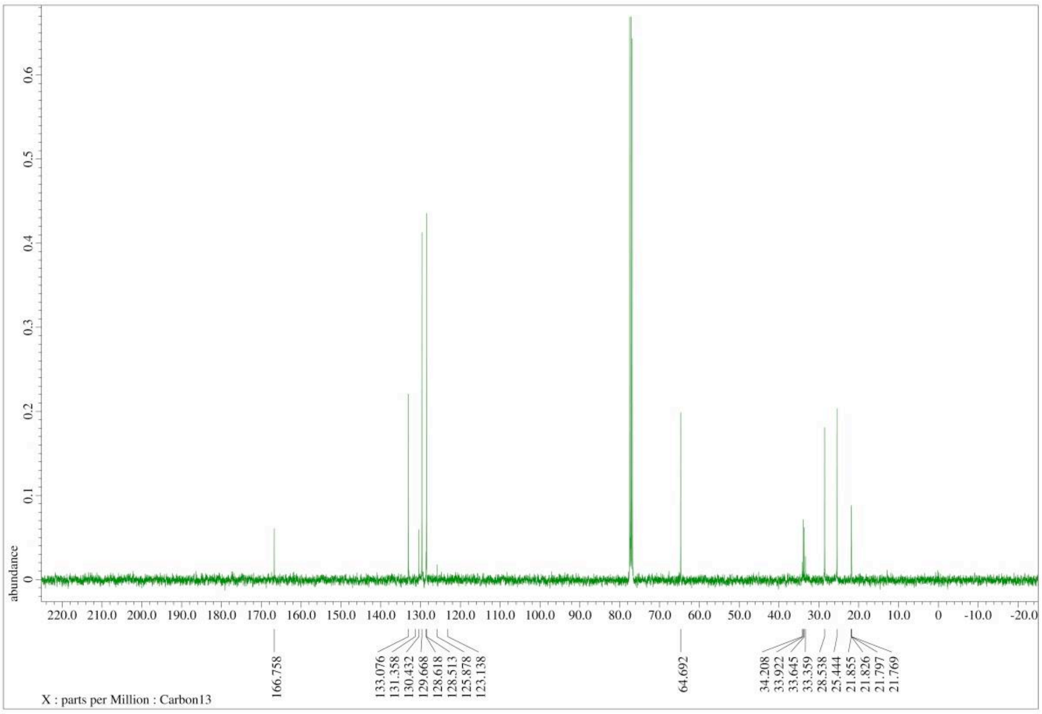
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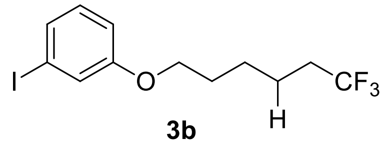
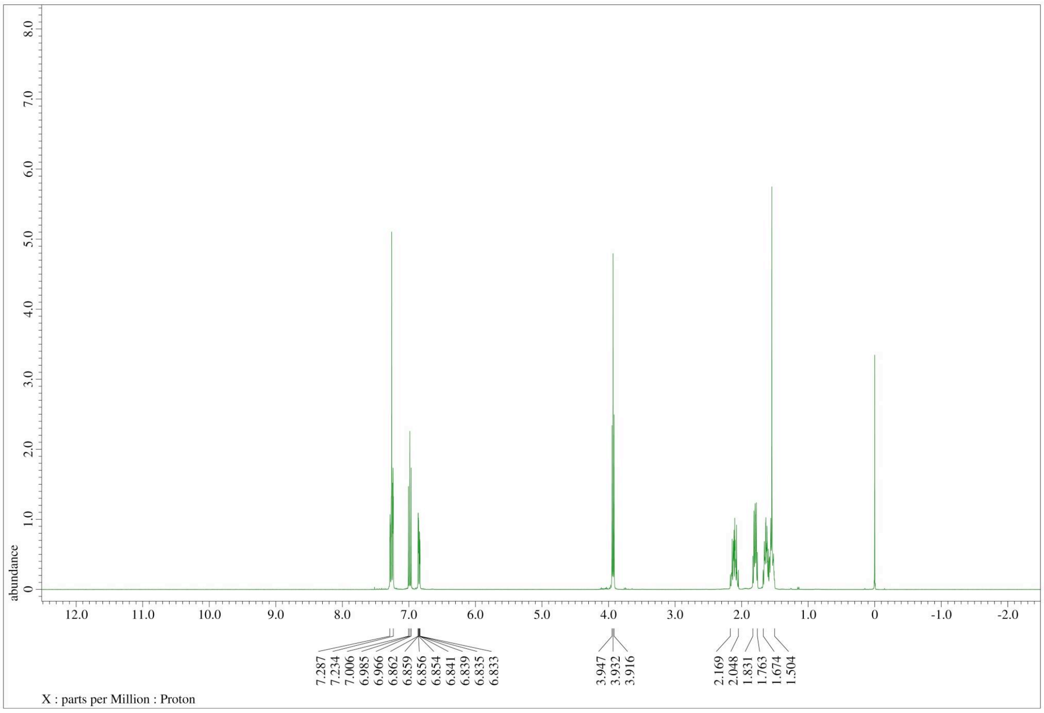
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.758
133.076
131.358
130.432
129.668
128.618
128.513
125.878
123.138
64.692
34.208
33.922
33.645
33.359
28.538
25.444
21.855
21.826
21.797
21.769
X : parts per Million : Carbon13


I
O
CF3
H

3b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1.0
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abundance
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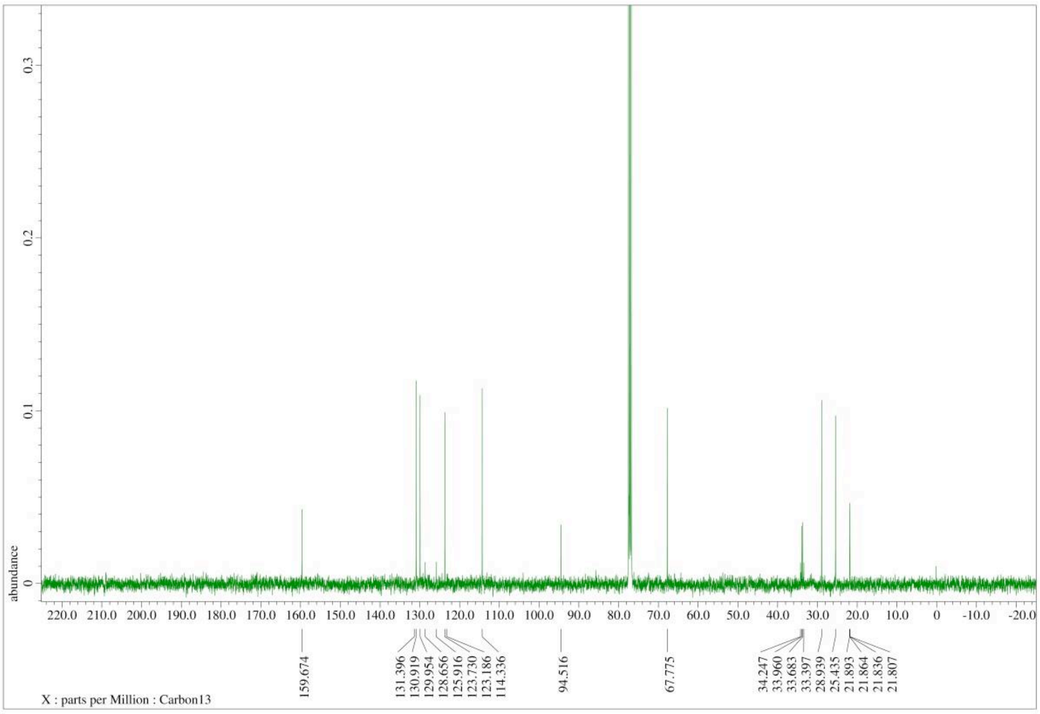
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.287
7.234
7.006
6.985
6.966
6.862
6.859
6.856
6.854
6.841
6.839
6.835
6.833
3.947
3.932
3.916
2.169
2.048
1.831
1.763
1.674
1.504
X : parts per Million : Proton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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
159.674
131.396
130.919
129.954
128.656
125.916
123.730
123.186
114.336
94.516
67.775
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33.397
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25.435
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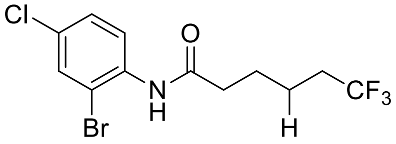
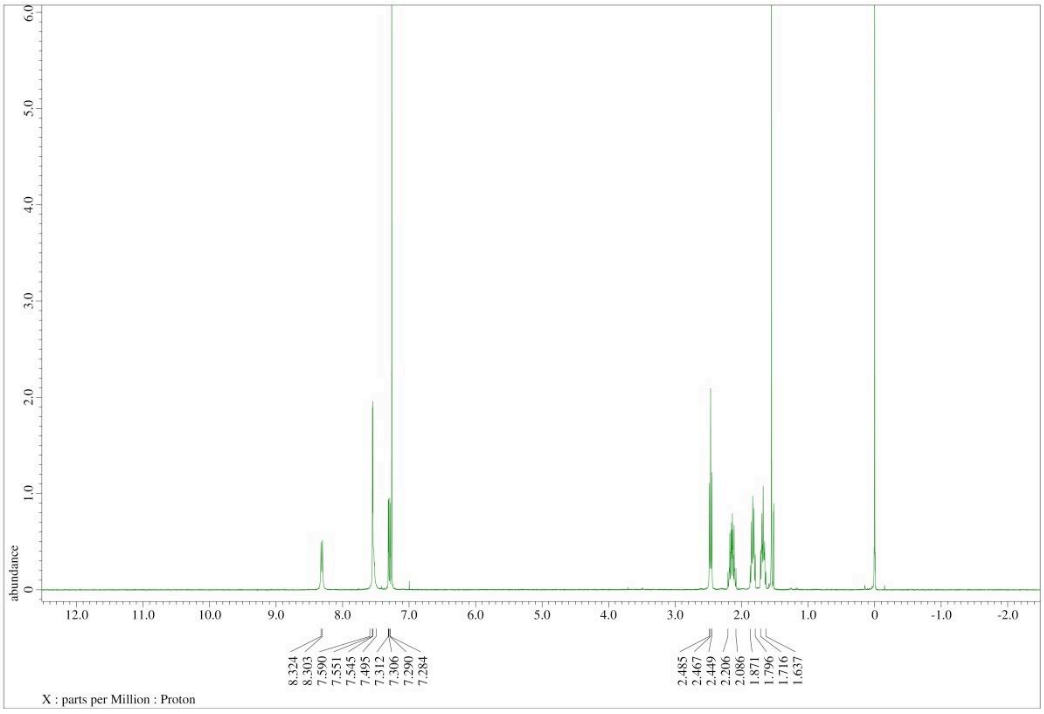
21.864
21.836
21.807
X : parts per Million : Carbon13


Cl
O
N
H
Br
H
CF3

3c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6.0
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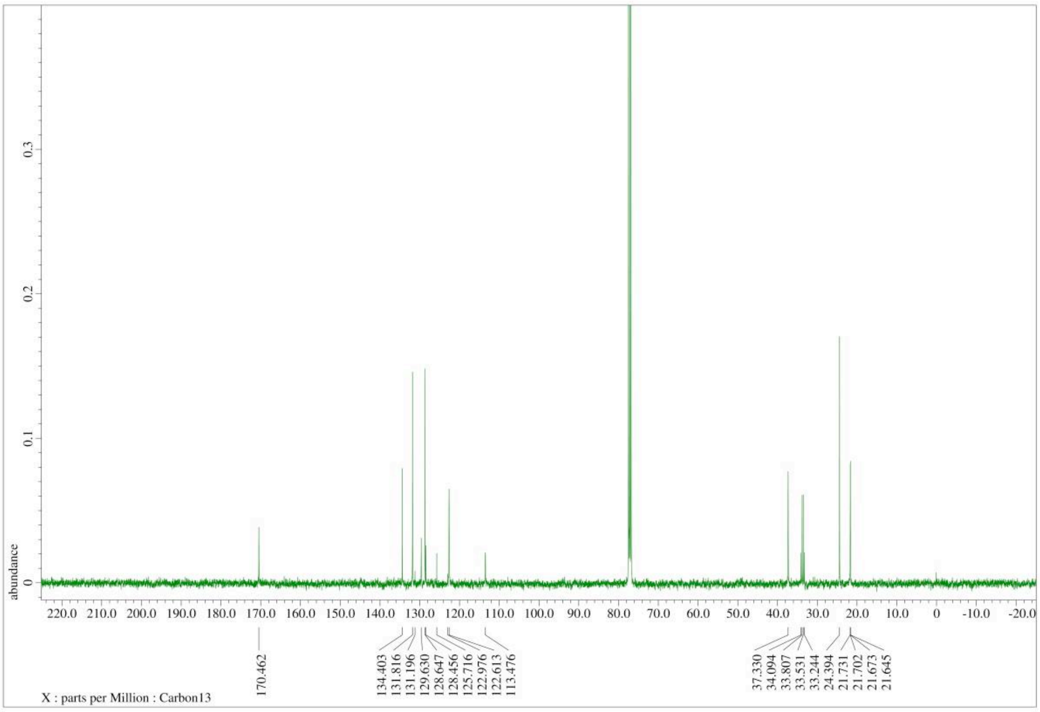
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.324
8.303
7.590
7.551
7.545
7.495
7.312
7.306
7.290
7.284
2.485
2.467
2.449
2.206
2.086
1.871
1.796
1.716
1.637
X : parts per Million : Proton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200.0
190.0
180.0
170.0
160.0
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
170.462
134.403
131.816
131.196
129.630
128.647
128.456
125.716
122.976
122.613
113.476
37.330
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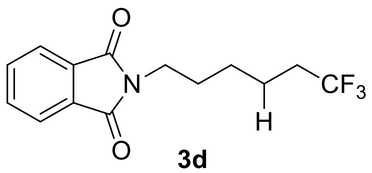
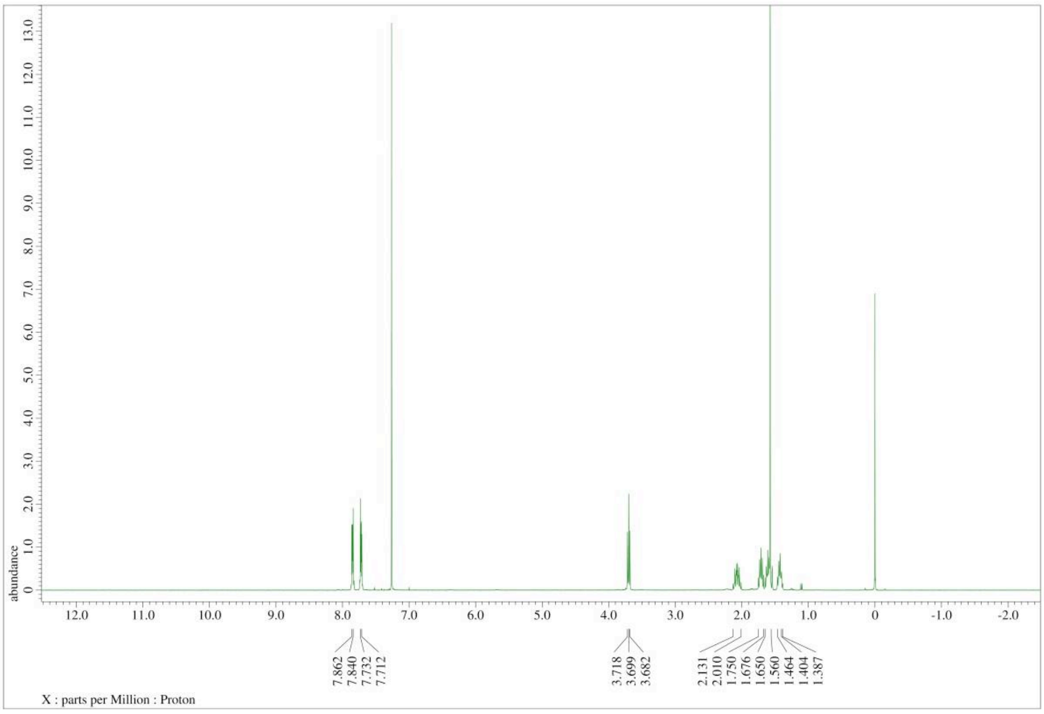
33.807
33.531
33.244
24.394
21.731
21.702
21.673
21.645
X : parts per Million : Carbon13


O
N
CF3
H
O

3d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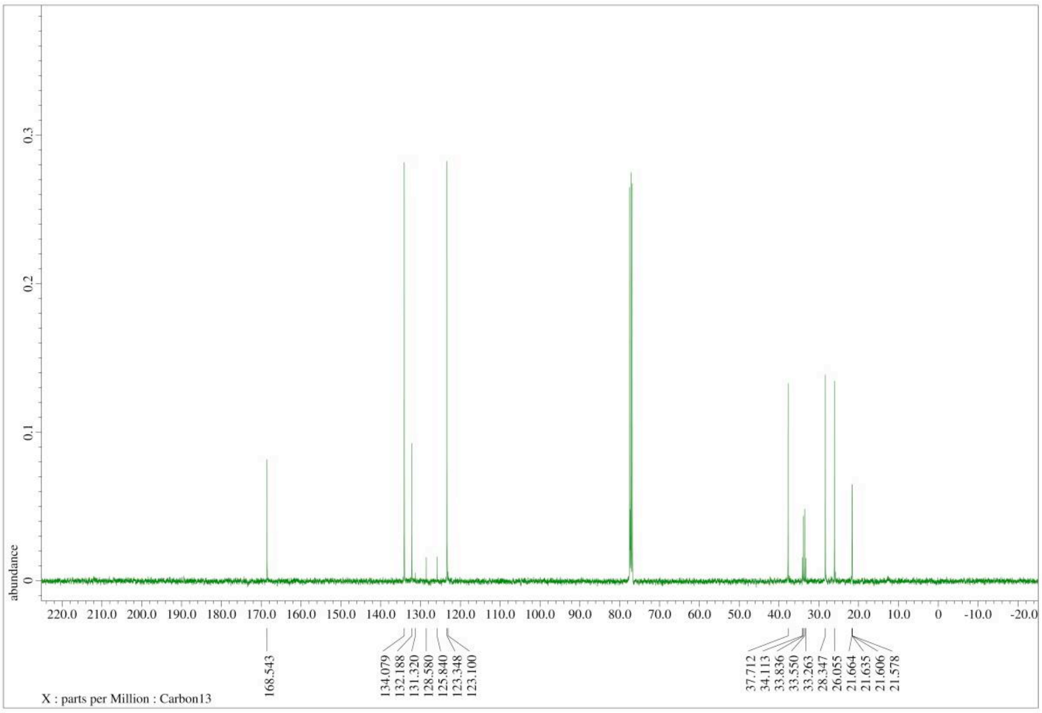
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.862
7.840
7.732
7.712
3.718
3.699
3.682
2.131
2.010
1.750
1.676
1.650
1.560
1.464
1.404
1.387
X : parts per Million : Proton


abundance
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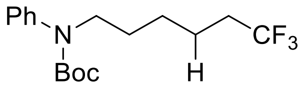
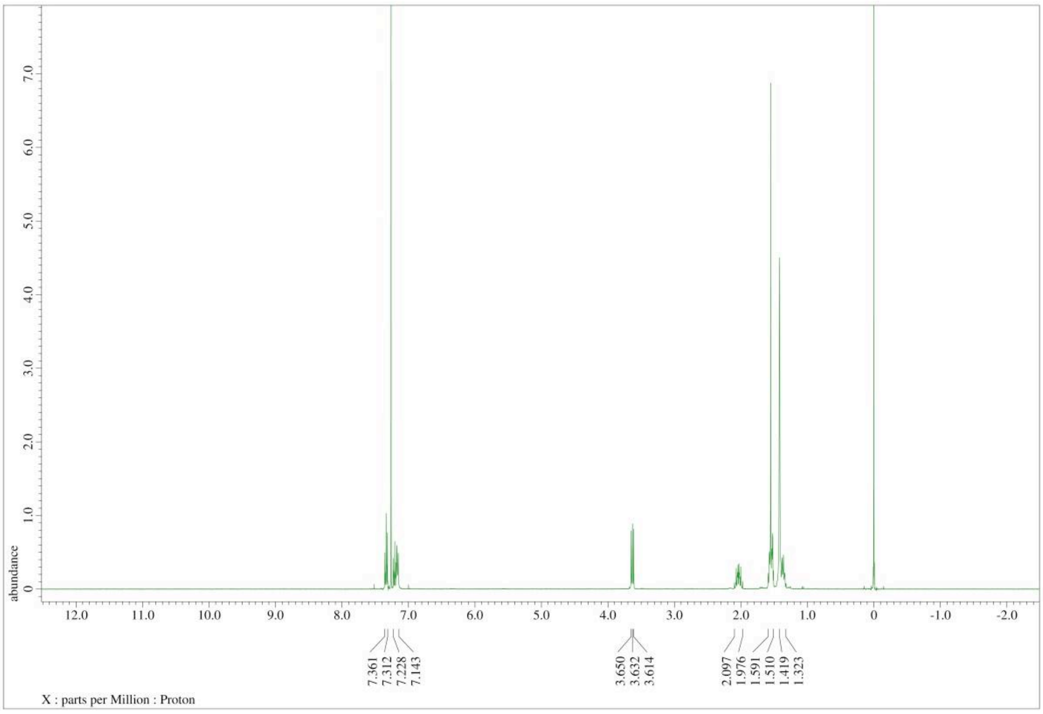
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
168.543
134.079
132.188
131.320
128.580
125.840
123.348
123.100
37.712
34.113
33.836
33.550
33.263
28.347
26.055
21.664
21.635
21.606
21.578
X : parts per Million : Carbon13


Ph
N
Boc
H
CF3

3e


abundance
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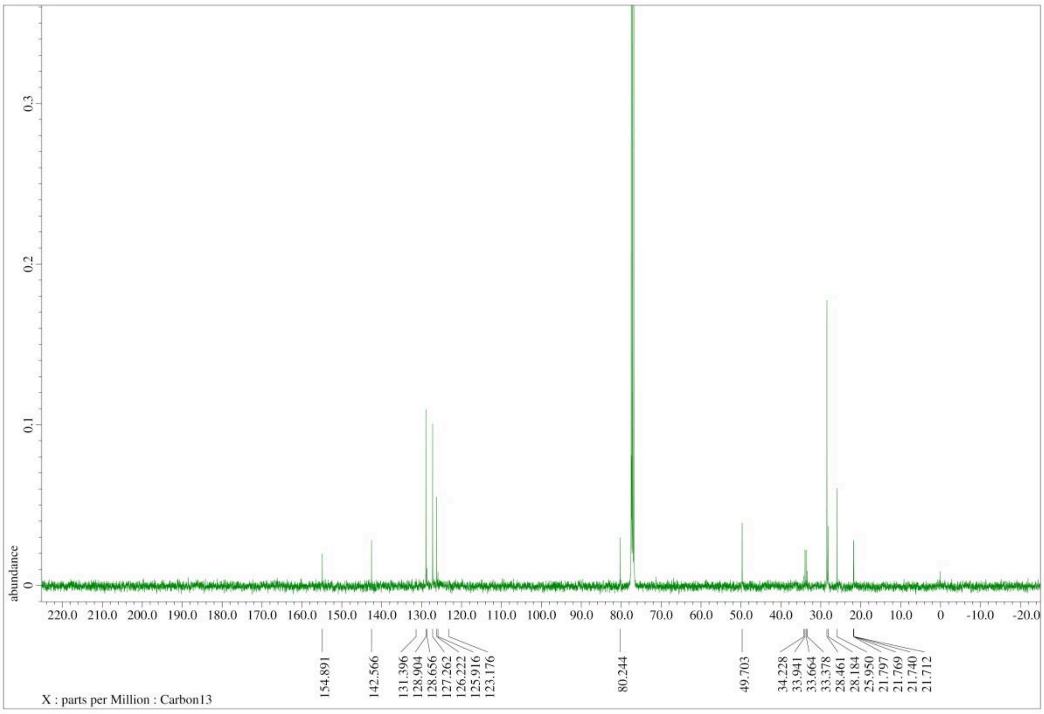
2.0
3.0
4.0
5.0
6.0
7.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.361
7.312
7.228
7.143
3.650
3.632
3.614
2.097
1.976
1.591
1.510
1.419
1.323
X : parts per Million : Proton


abundance
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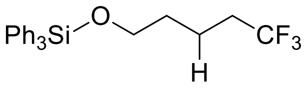
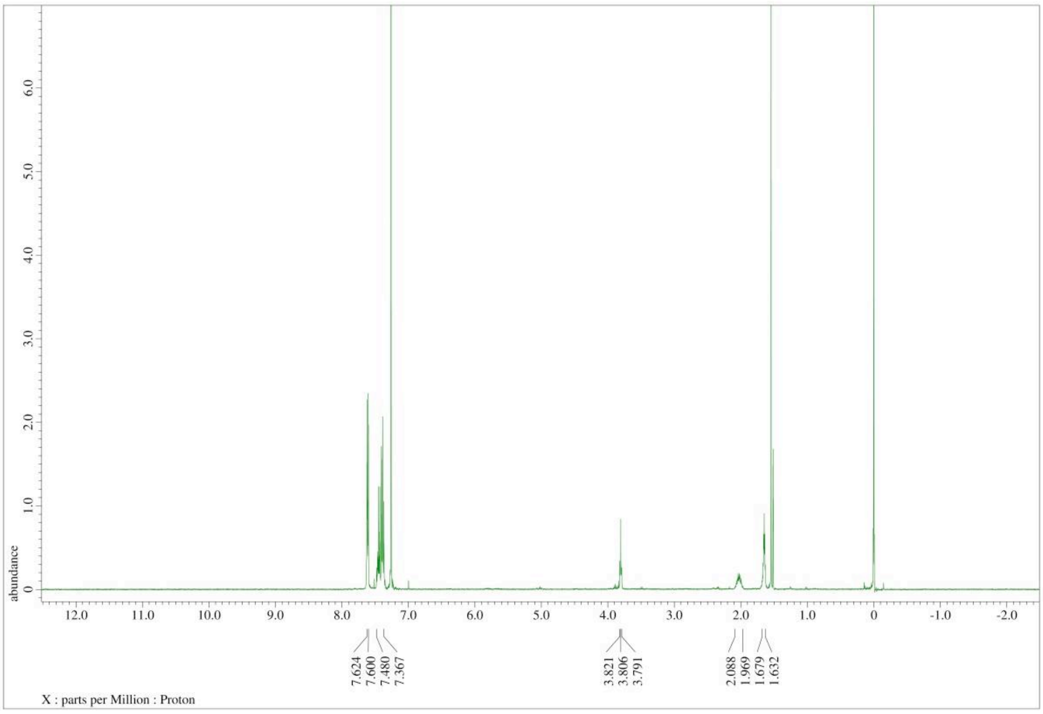
0.2
0.3
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
154.891
142.566
131.396
128.904
128.656
127.262
126.222
125.916
123.176
80.244
49.703
34.228
33.941
33.664
33.378
28.461
28.184
25.950
21.797
21.769
21.740
21.712
X : parts per Million : Carbon13


Ph3Si
O
H
CF3

3f


abundance
0
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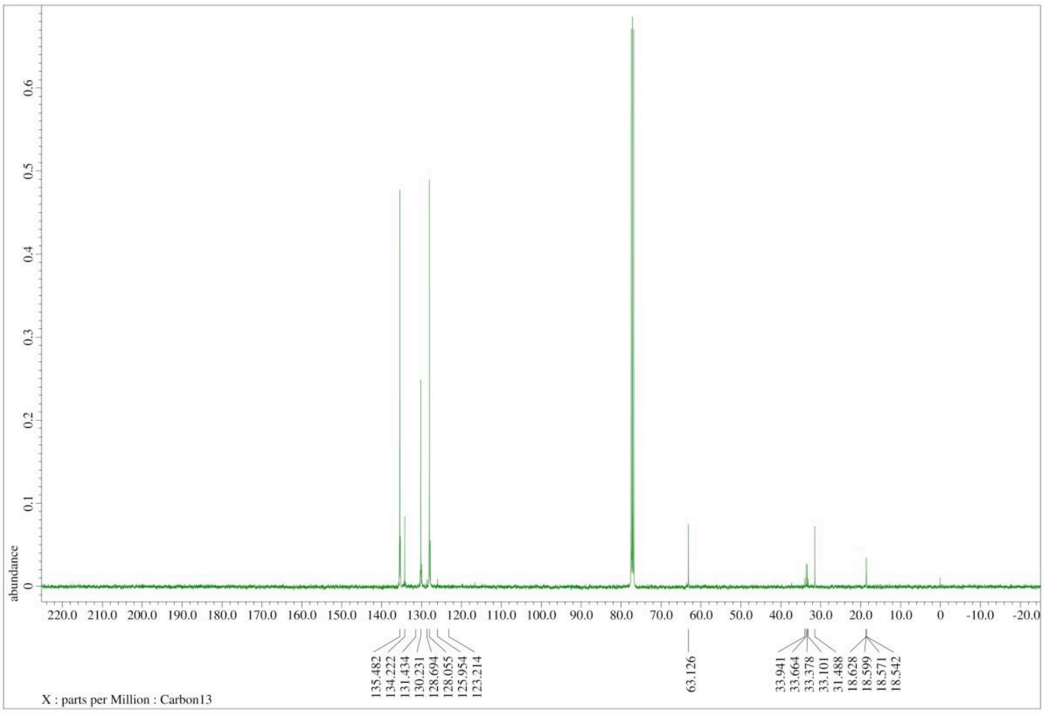
2.0
3.0
4.0
5.0
6.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.624
7.600
7.480
7.367
3.821
3.806
3.791
2.088
1.969
1.679
1.632
X : parts per Million : Proton


abundance
0
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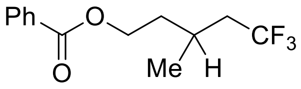
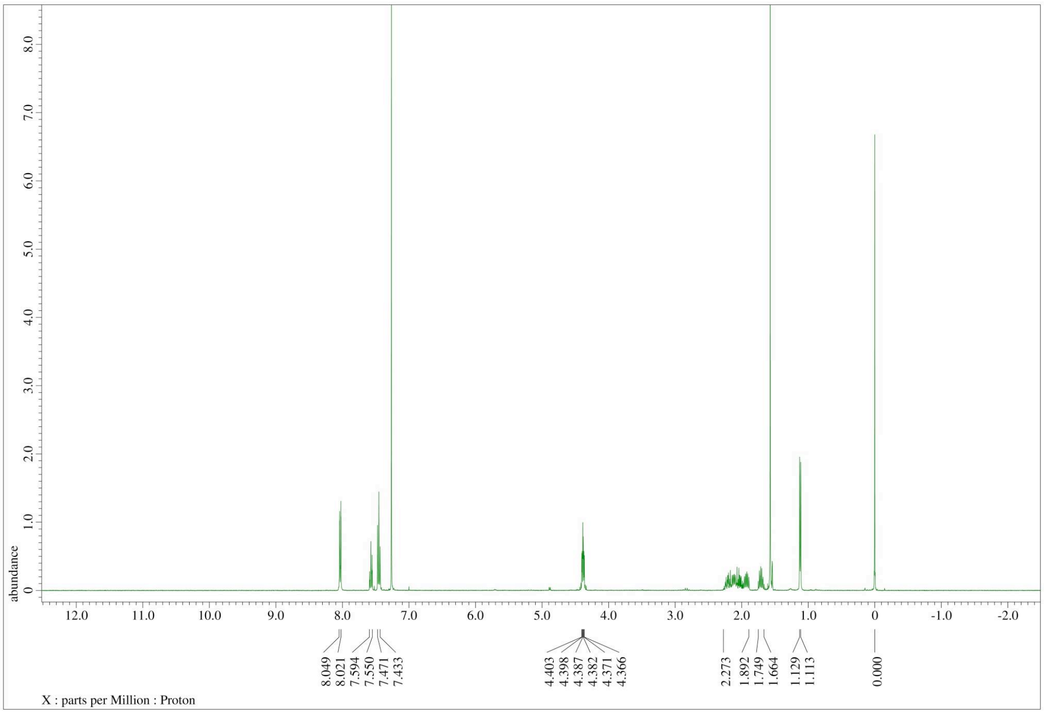
0.2
0.3
0.4
0.5
0.6
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
135.482
134.222
131.434
130.231
128.694
128.055
125.954
123.214
63.126
33.941
33.664
33.378
33.101
31.488
18.628
18.599
18.571
18.542
X : parts per Million : Carbon13


Ph
O
O
Me
H
CF3

3g


abundance
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4.0
5.0
6.0
7.0
8.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.049
8.021
7.594
7.550
7.471
7.433
4.403
4.398
4.387
4.382
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2.273
1.892
1.749
1.664
1.129
1.113
0.000
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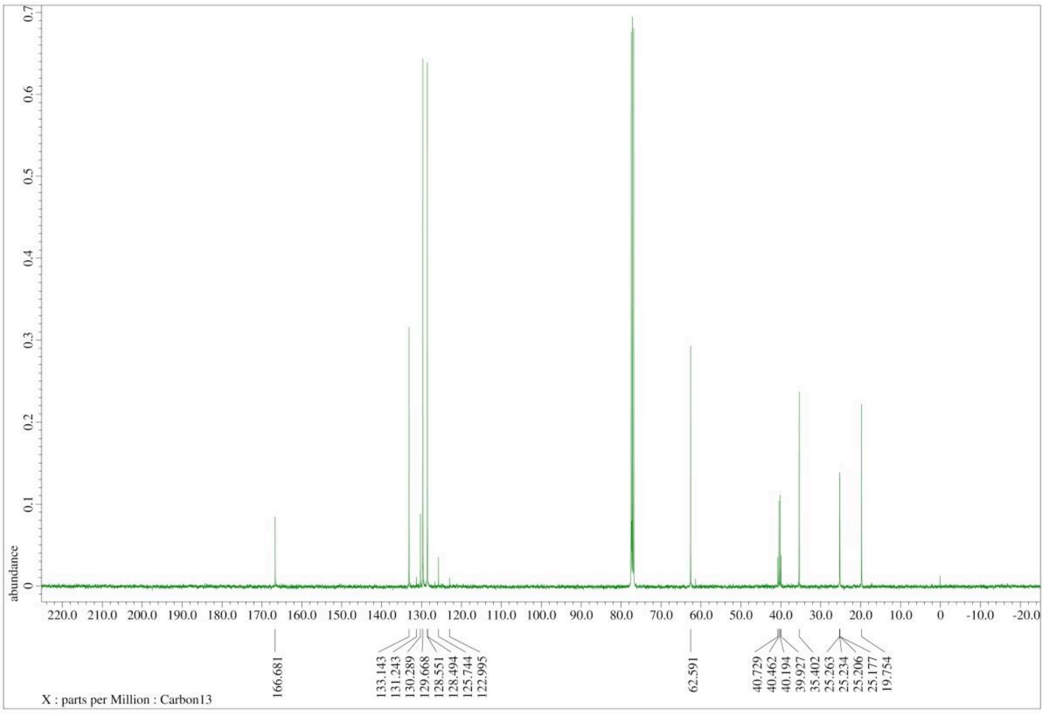
abundance
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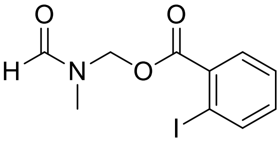
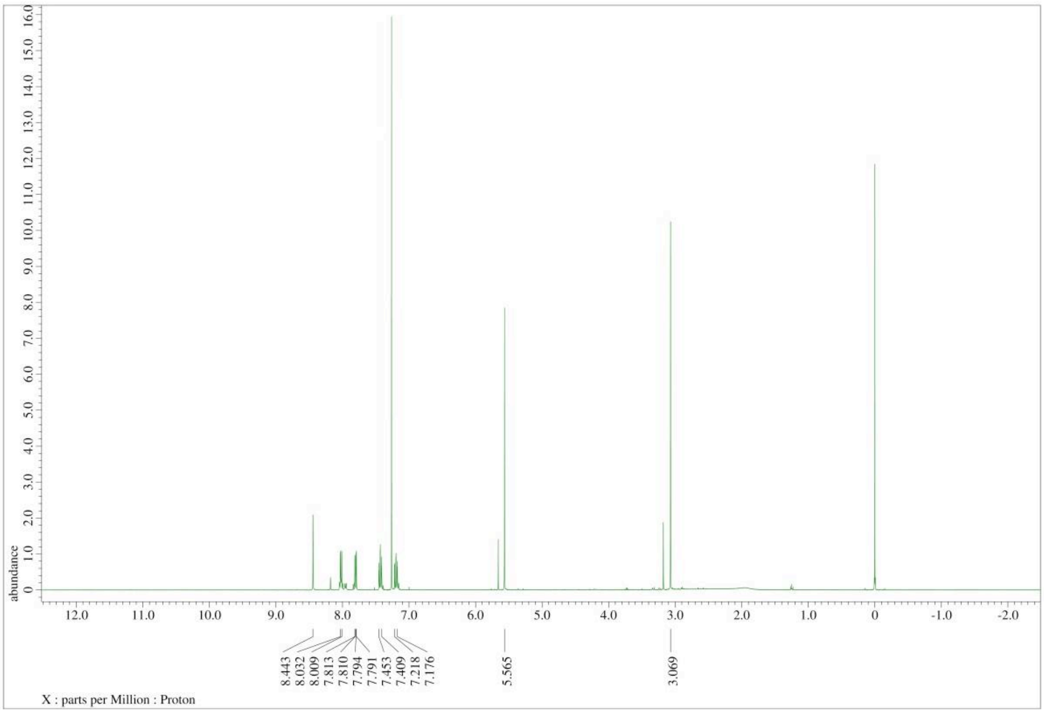
0.3
0.4
0.5
0.6
0.7
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.681
133.143
131.243
130.289
129.668
128.551
128.494
125.744
122.995
62.591
40.729
40.462
40.194
39.927
35.402
25.263
25.234
25.206
25.177
19.754
X : parts per Million : Carbon13


O
O
H
N
O
I

5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8.0
9.0
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16.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.443
8.032
8.009
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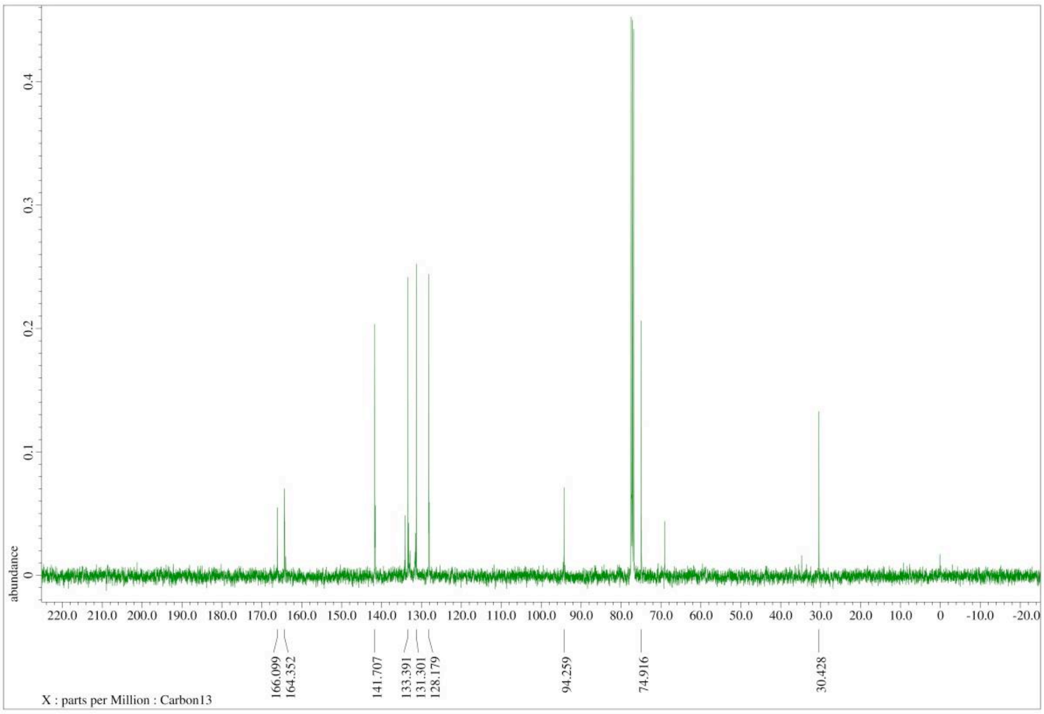
7.794
7.791
7.453
7.409
7.218
7.176
5.565
3.069
X : parts per Million : Proton


abundance
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0.2
0.3
0.4
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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
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141.707
133.391
131.301
128.179
94.259
74.916
30.428
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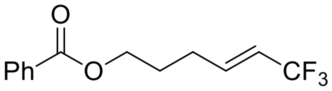
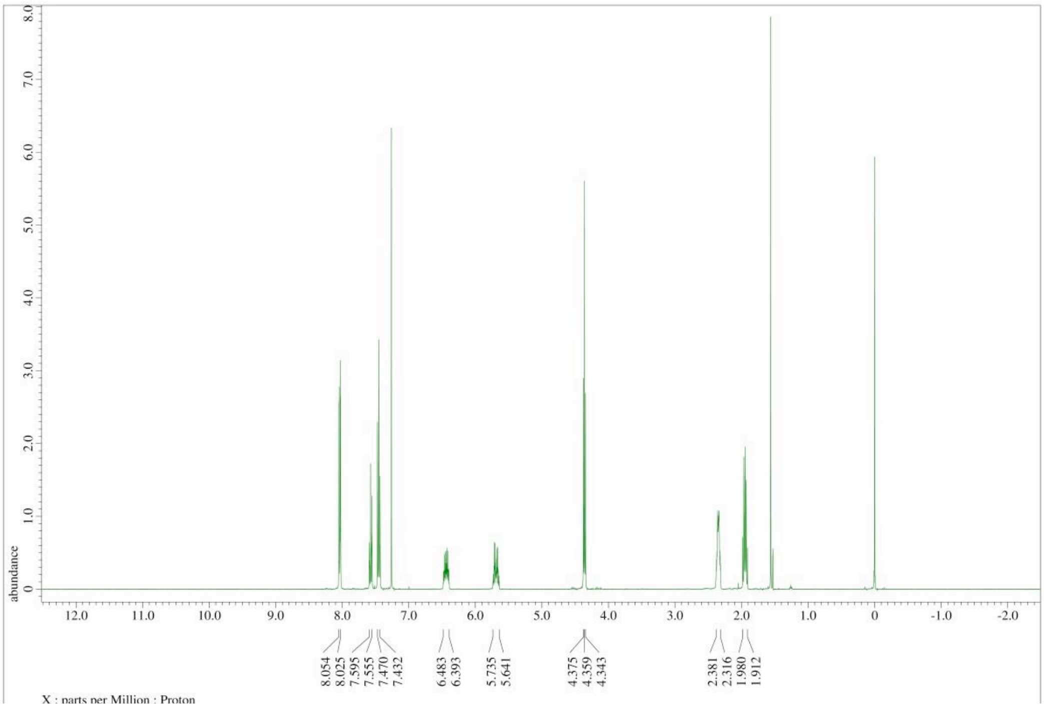


O
Ph
O
CF3

4a



abundance
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2.0
3.0
4.0
5.0
6.0
7.0
8.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.054
8.025
7.595
7.555
7.470
7.432
6.483
6.393
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2.316
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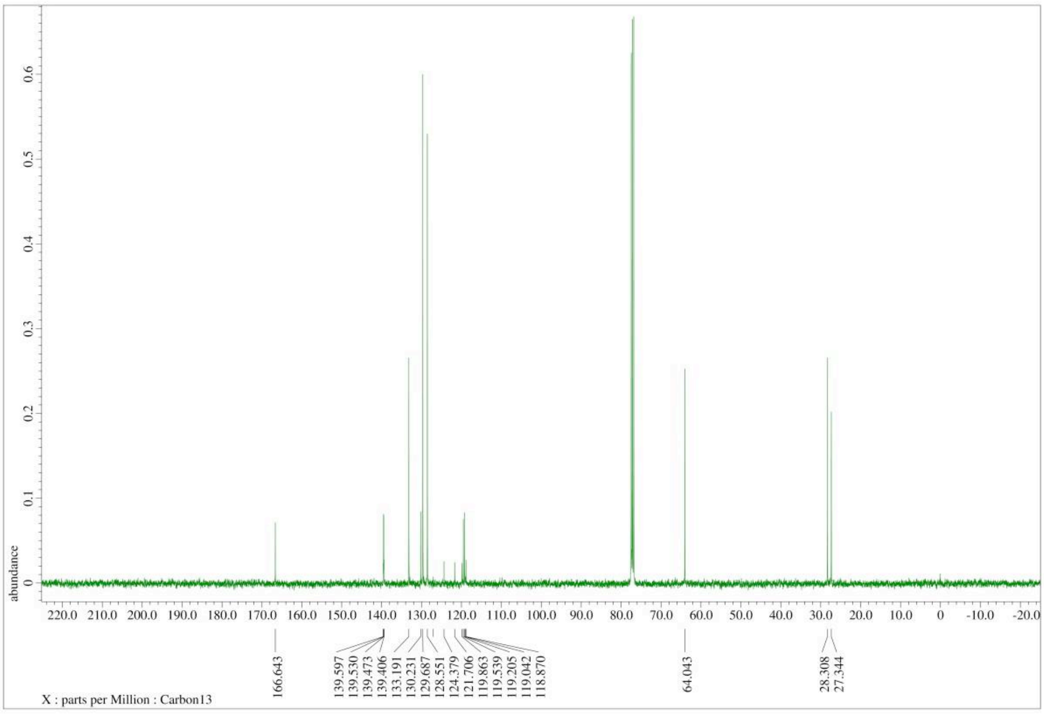

abundance
0
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0.2
0.3
0.4
0.5
0.6
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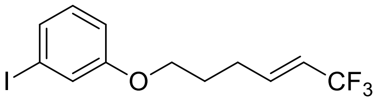
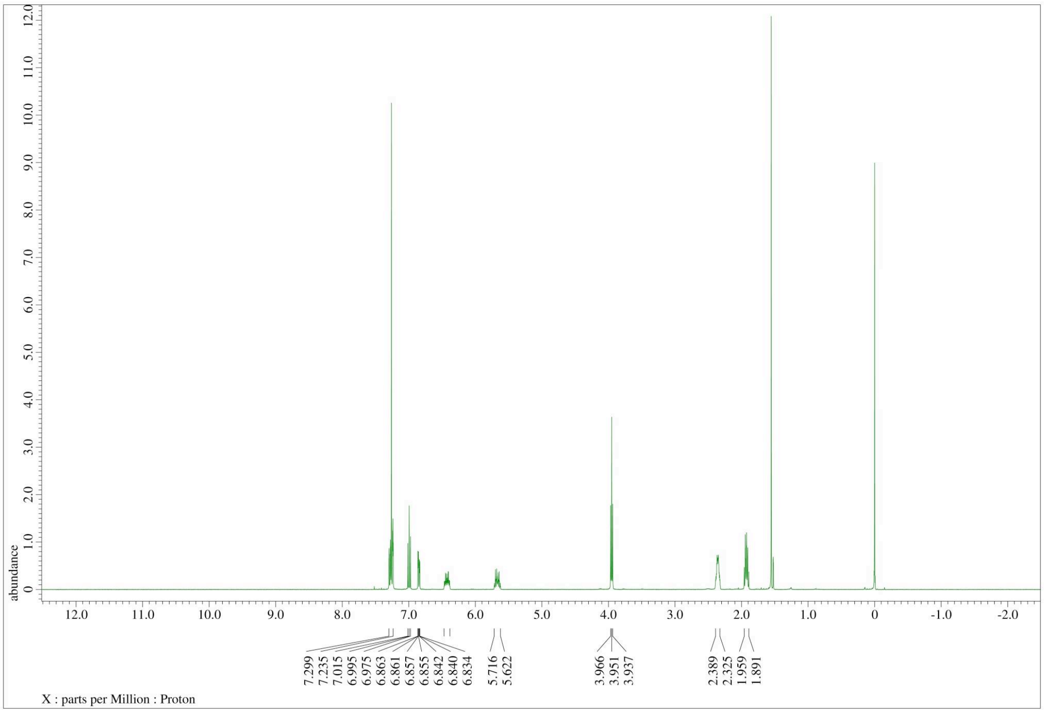
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.643
139.597
139.530
139.473
139.406
133.191
130.231
129.687
128.551
124.379
121.706
119.863
119.539
119.205
119.042
118.870
64.043
28.308
27.344
X : parts per Million : Carbon13


I
O
CF3

4b


abundance
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4.0
5.0
6.0
7.0
8.0
9.0
10.0
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12.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.299
7.235
7.015
6.995
6.975
6.863
6.861
6.857
6.855
6.842
6.840
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3.966
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3.937
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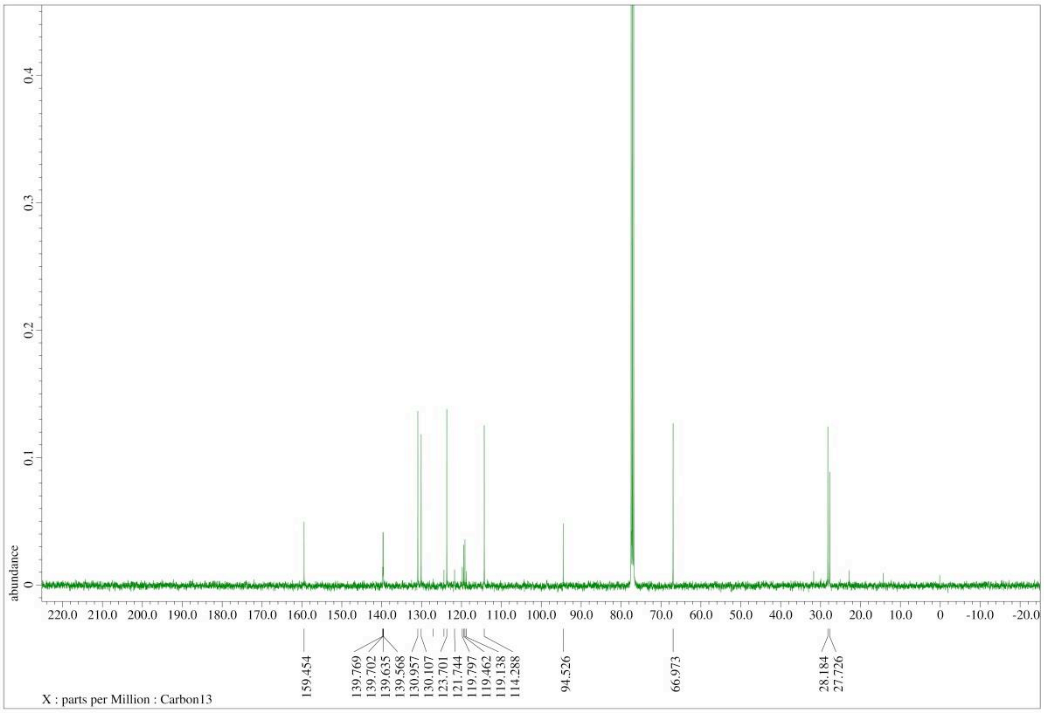
2.325
1.959
1.891
X : parts per Million : Proton


abundance
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0.2
0.3
0.4
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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
159.454
139.769
139.702
139.635
139.568
130.957
130.107
123.701
121.744
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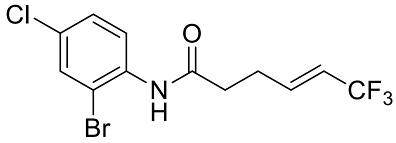
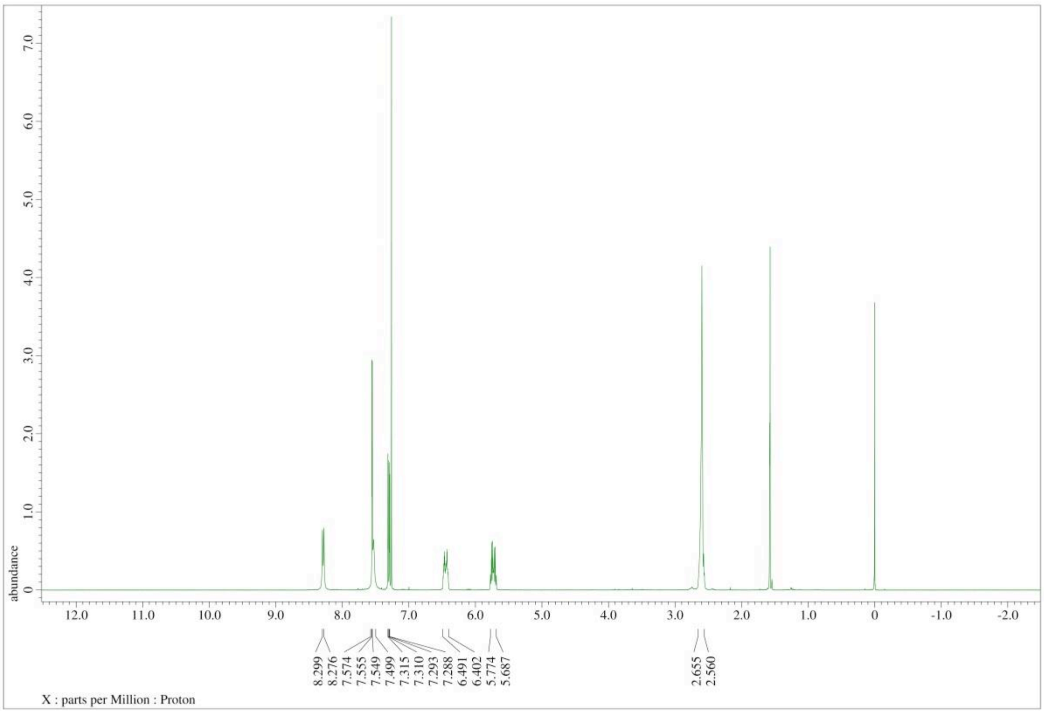
119.462
119.138
114.288
94.526
66.973
28.184
27.726
X : parts per Million : Carbon13


Cl
O
N
H
CF3
Br

4c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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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-2.0
8.299
8.276
7.574
7.555
7.549
7.499
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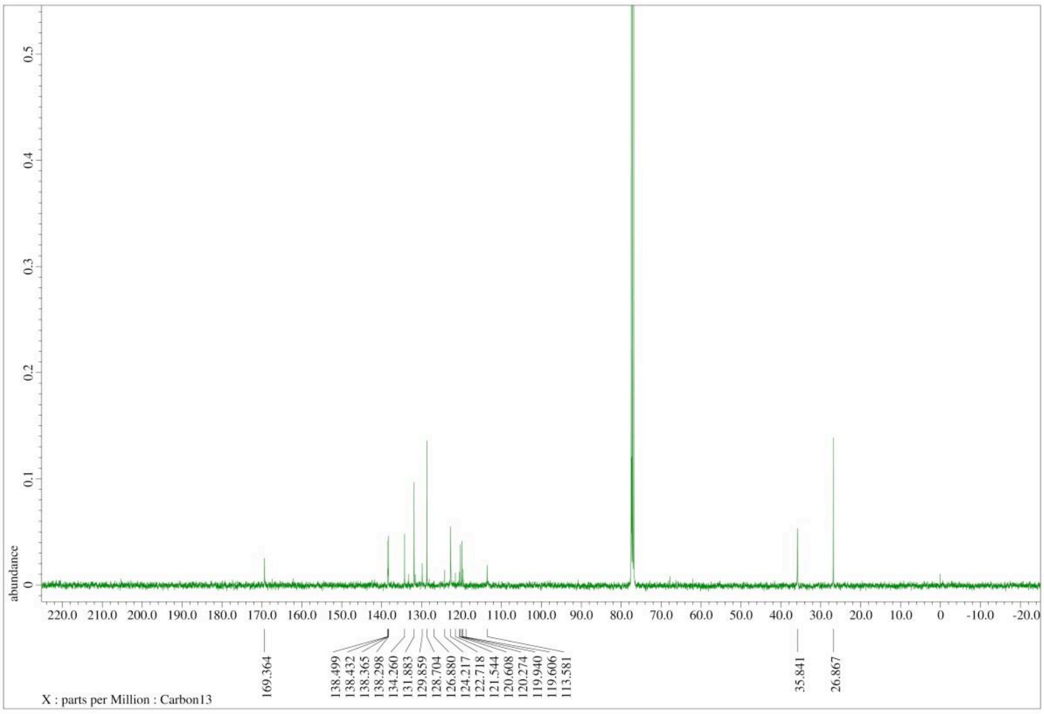
7.293
7.288
6.491
6.402
5.774
5.687
2.655
2.560
X : parts per Million : Proton


abundance
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0.3
0.4
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160.0
150.0
140.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
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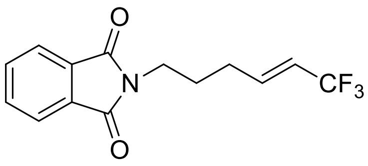
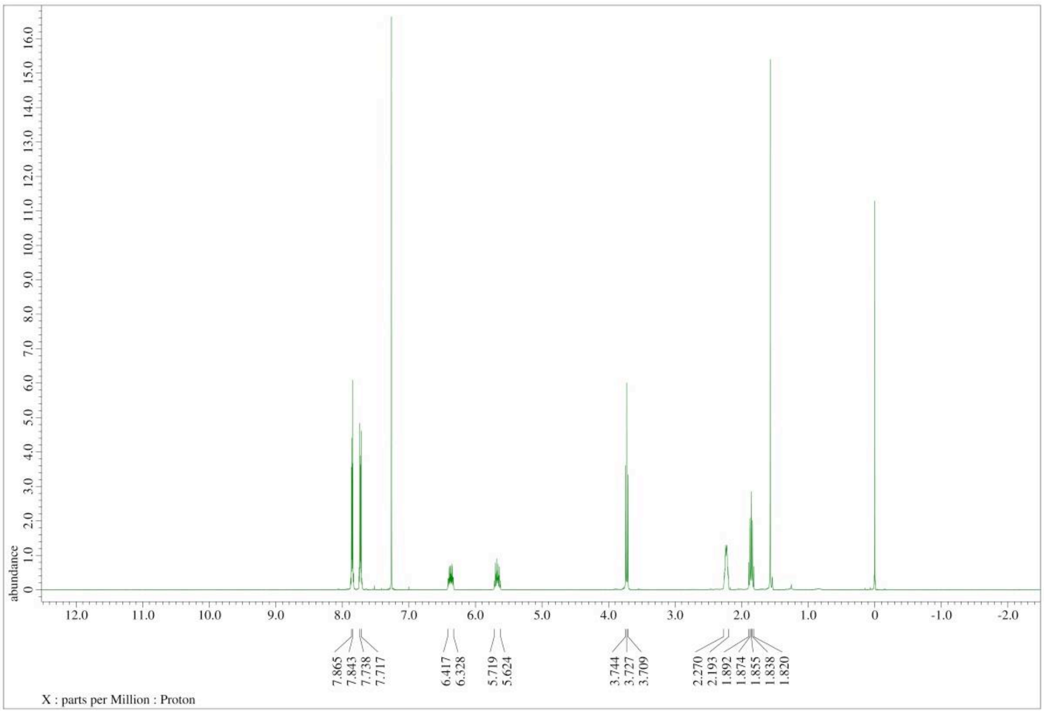
30.0
20.0
10.0
0
-10.0
-20.0
169.364
138.499
138.432
138.365
138.298
134.260
131.883
129.859
128.704
126.880
124.217
122.718
121.544
120.608
120.274
119.940
119.606
113.581
35.841
26.867
X : parts per Million : Carbon13


O
N
CF3
O

4d


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
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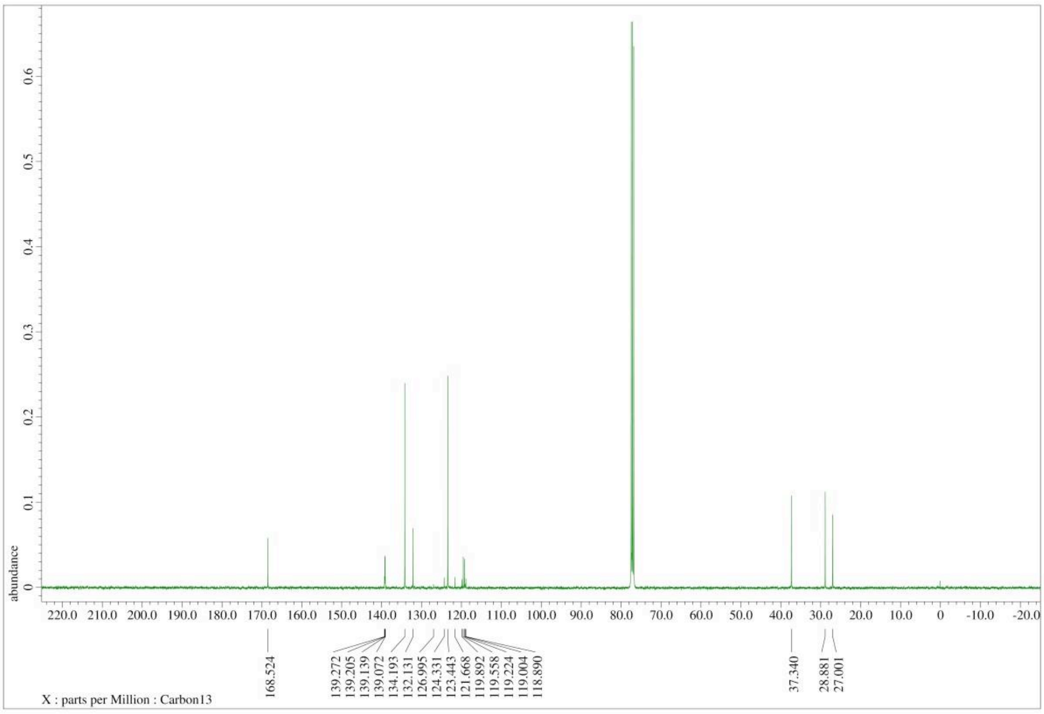
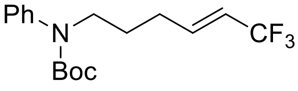
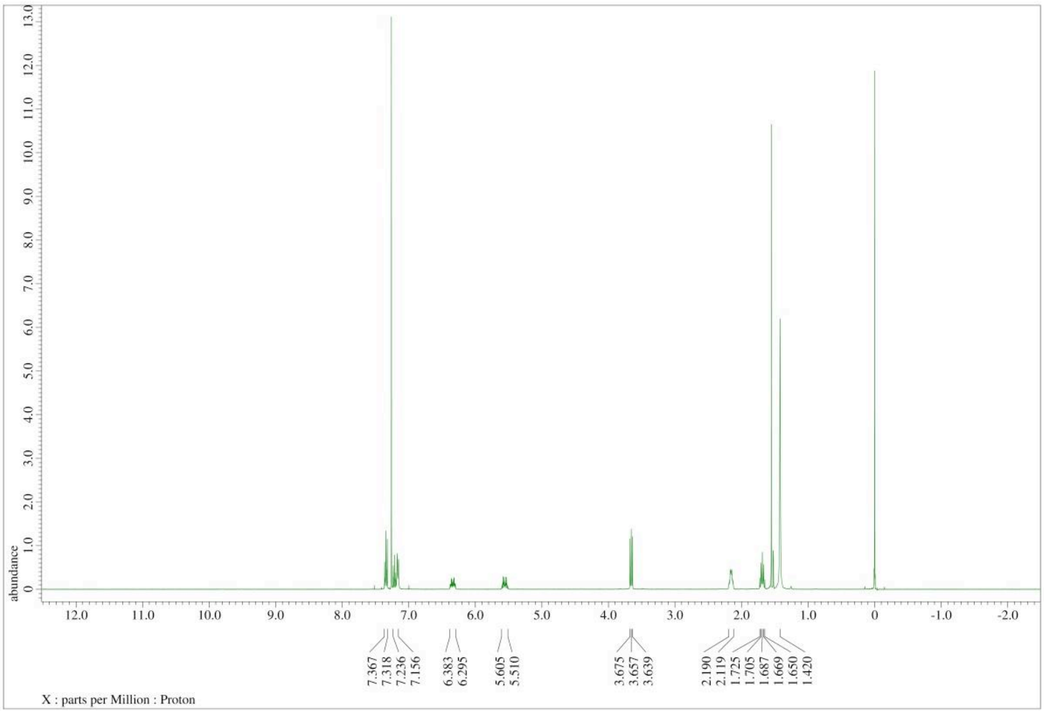
12.0
13.0
14.0
15.0
16.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.865
7.843
7.738
7.717
6.417
6.328
5.719
5.624
3.744
3.727
3.709
2.270
2.193
1.892
1.874
1.855
1.838
1.820
X : parts per Million : Proton

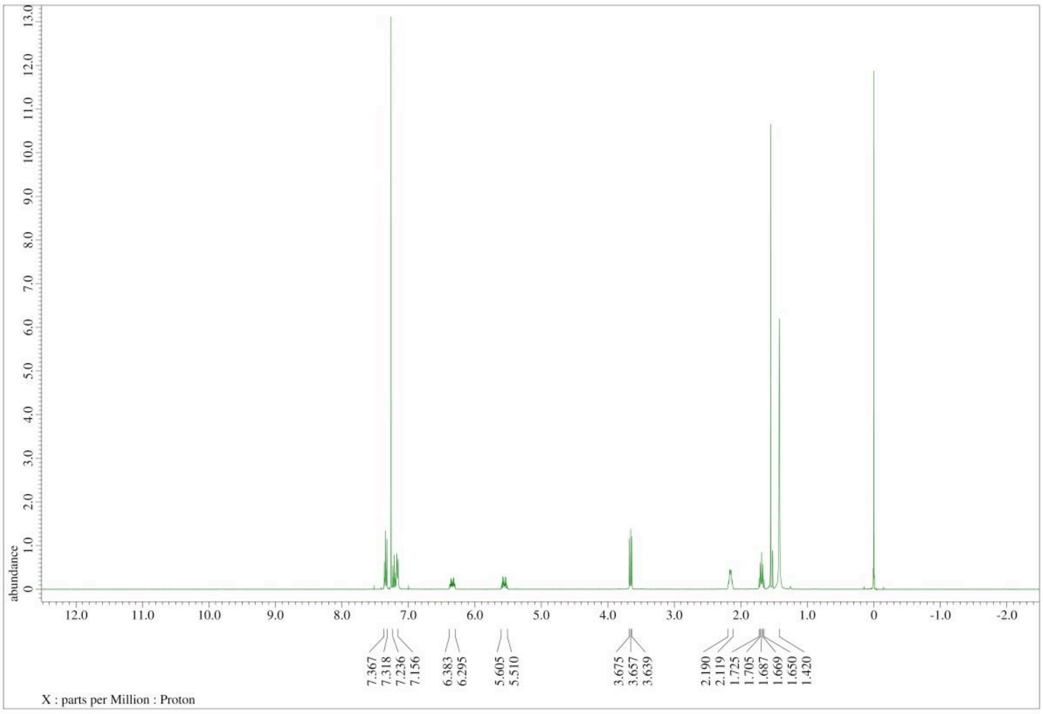

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
168.524
139.272
139.205
139.139
139.072
134.193
132.131
126.995
124.331
123.443
121.668
119.892
119.558
119.224
119.004
118.890
37.340
28.881
27.001
X : parts per Million : Carbon13



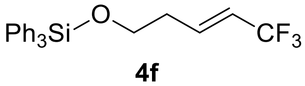
4e



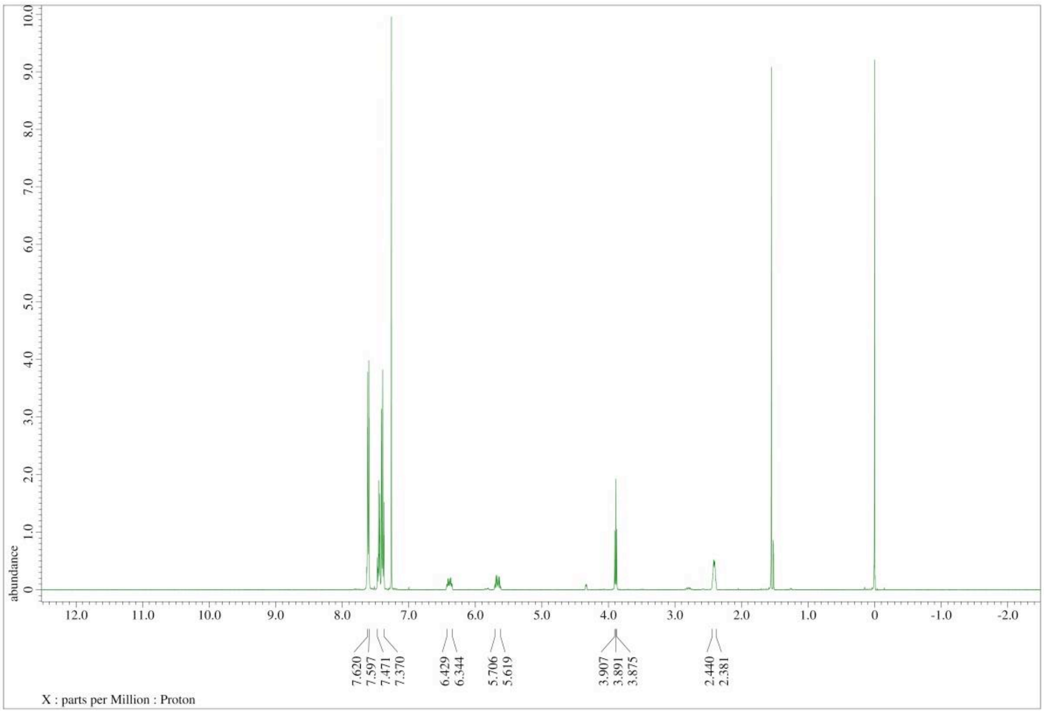
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.367
7.318
7.236
7.156
6.383
6.295
5.605
5.510
3.675
3.657
3.639
2.190
2.119
1.725
1.705
1.687
1.669
1.650
1.420
X : parts per Million : Proton

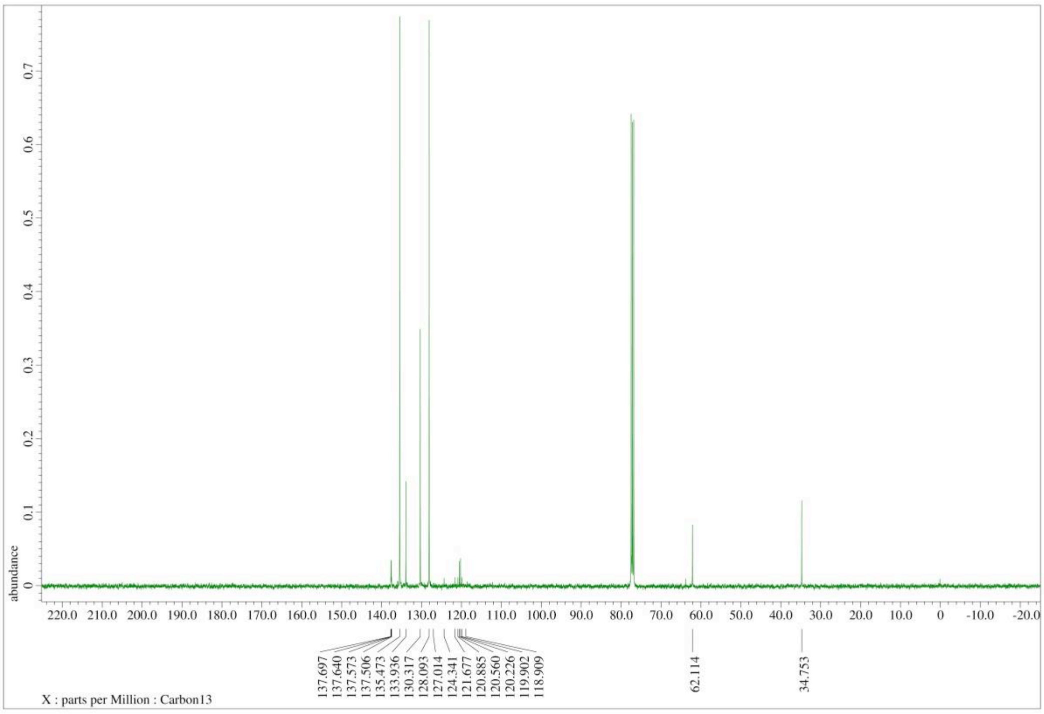


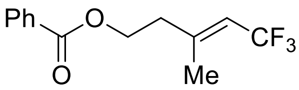
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.367
7.318
7.236
7.156
6.383
6.295
5.605
5.510
3.675
3.657
3.639
2.190
2.119
1.725
1.705
1.687
1.669
1.650
1.420
X : parts per Million : Proton


Ph3Si
O
CF3

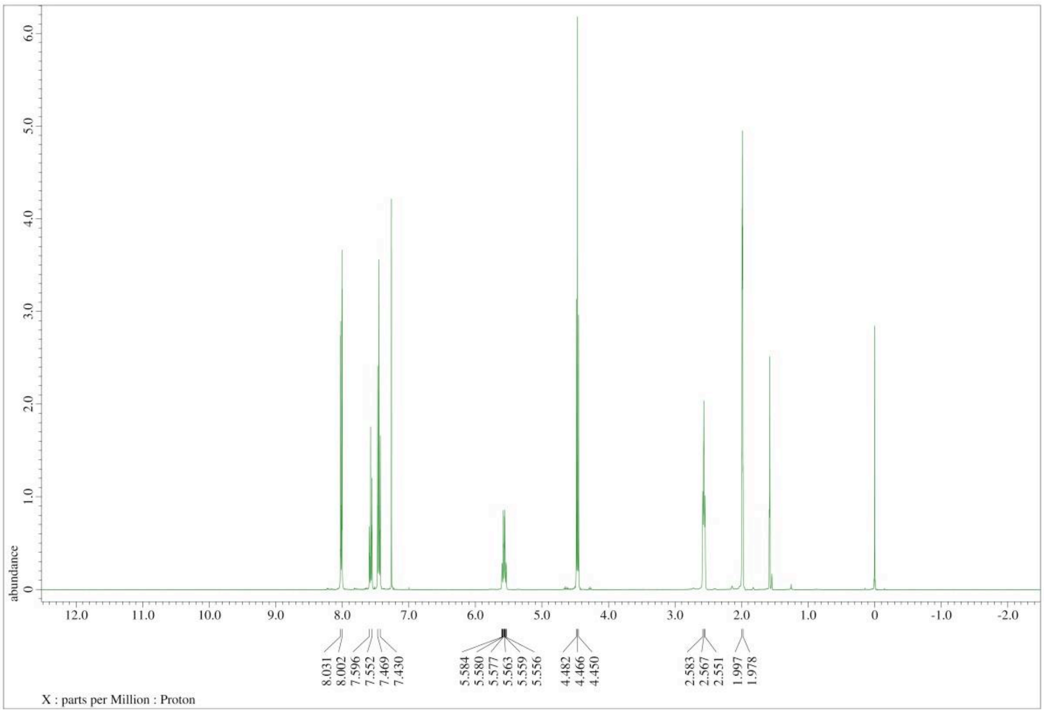
4f

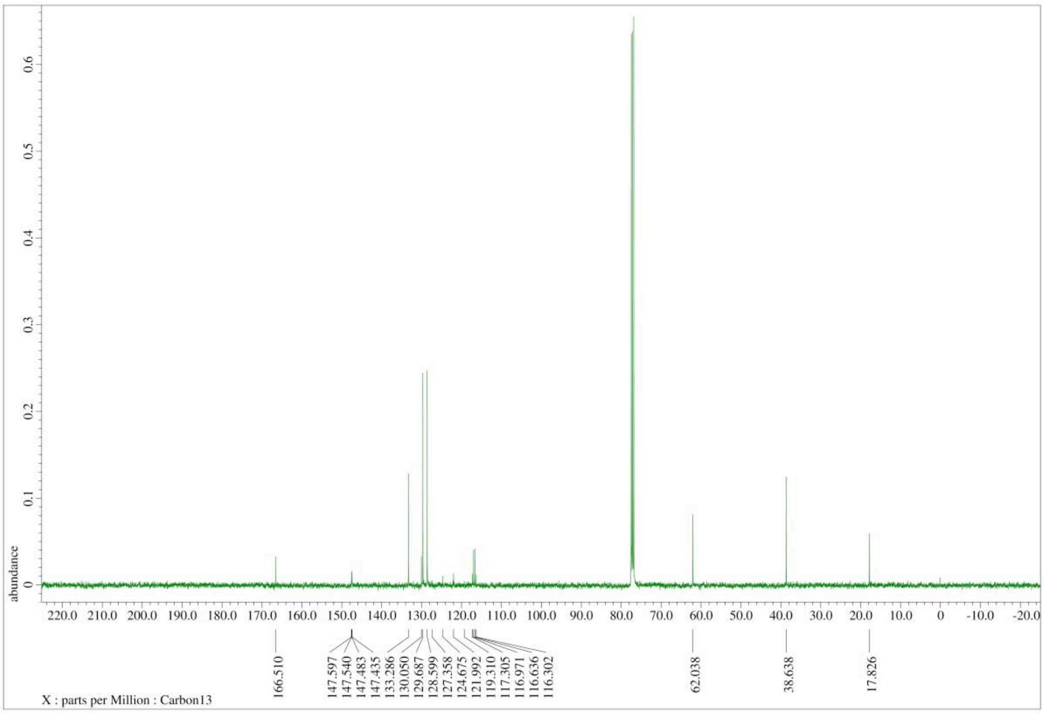

abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.620
7.597
7.471
7.370
6.429
6.344
5.706
5.619
3.907
3.891
3.875
2.440
2.381
X : parts per Million : Proton

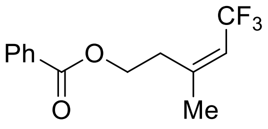

abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
137.697
137.640
137.573
137.506
135.473
133.936
130.317
128.093
127.014
124.341
121.677
120.885
120.560
120.226
119.902
118.909
62.114
34.753
X : parts per Million : Carbon13


Ph
O
O
CF3
Me

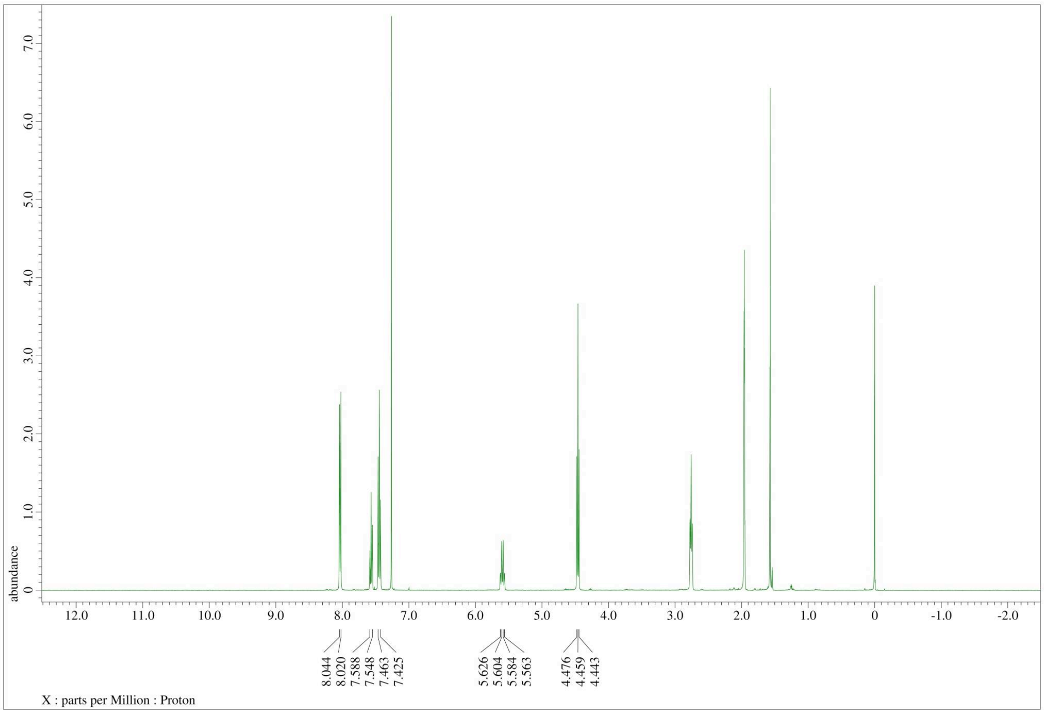
4g (*E*)


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.031
8.002
7.596
7.552
7.469
7.430
5.584
5.580
5.577
5.563
5.559
5.556
4.482
4.466
4.450
2.583
2.567
2.551
1.997
1.978
X : parts per Million : Proton


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.510
147.597
147.540
147.483
147.435
133.286
130.050
129.687
128.599
127.358
124.675
121.992
119.310
117.305
116.971
116.636
116.302
62.038
38.638
17.826
X : parts per Million : Carbon13


CF3
Ph
O
O
Me

4g (*Z*)


abundance
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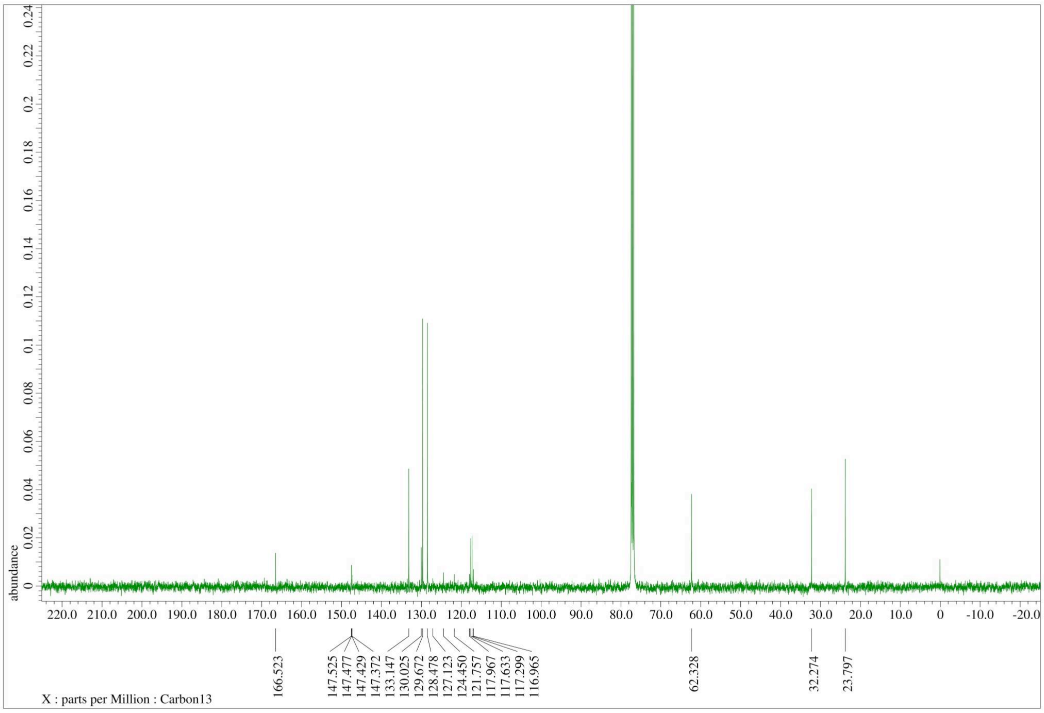
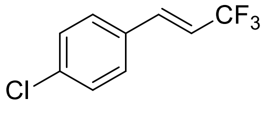
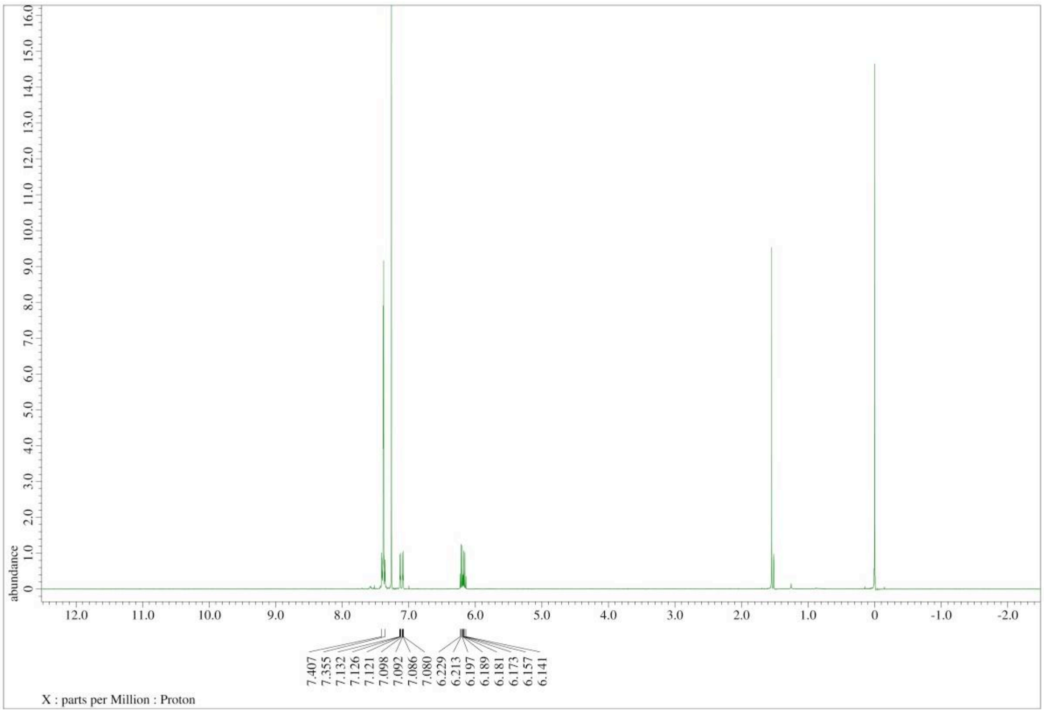
1.0
2.0
3.0
4.0
5.0
6.0
7.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.044
8.020
7.588
7.548
7.463
7.425
5.626
5.604
5.584
5.563
4.476
4.459
4.443
X : parts per Million : Proton


abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.523
147.525
147.477
147.429
147.372
133.147
130.025
129.672
128.478
127.123
124.450
121.757
117.967
117.633
117.299
116.965
62.328
32.274
23.797
X : parts per Million : Carbon13


CF3
Cl

8


abundance
0
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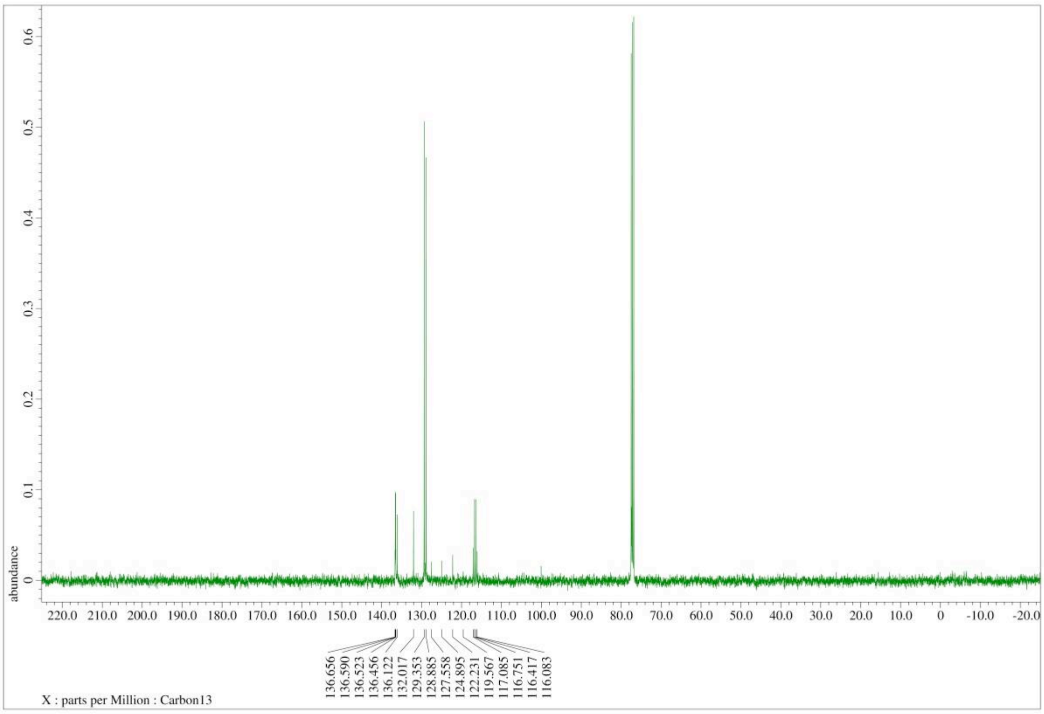
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.407
7.355
7.132
7.126
7.121
7.098
7.092
7.086
7.080
6.229
6.213
6.197
6.189
6.181
6.173
6.157
6.141
X : parts per Million : Proton


abundance
0
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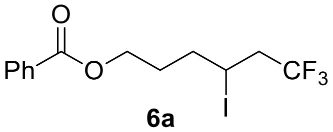
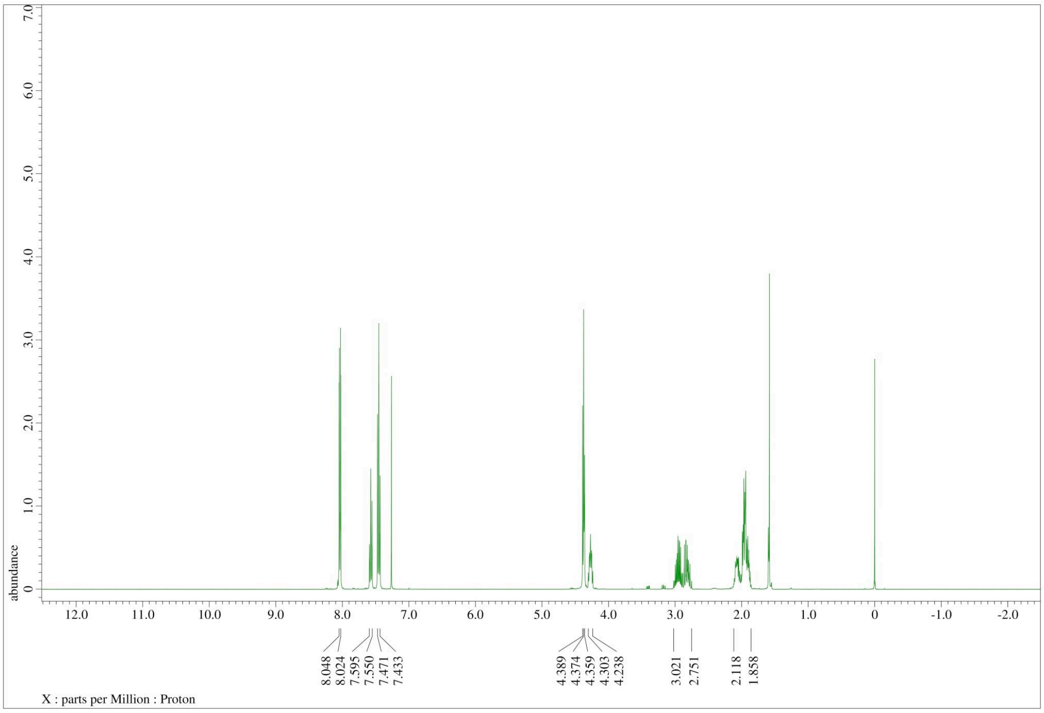
0.2
0.3
0.4
0.5
0.6
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
136.656
136.590
136.523
136.456
136.122
132.017
129.353
128.885
127.558
124.895
122.231
119.567
117.085
116.751
116.417
116.083
X : parts per Million : Carbon13


Ph
O
O
CF3
I

6a


abundance
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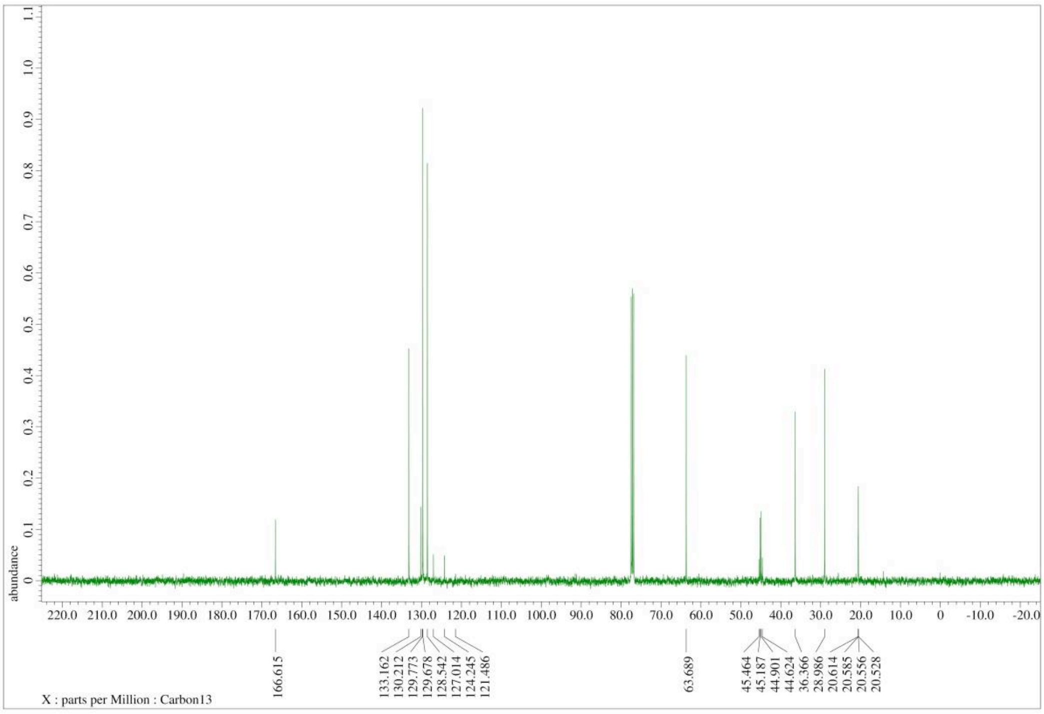
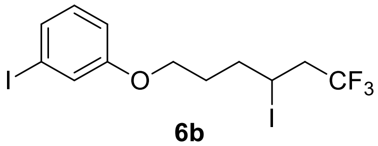
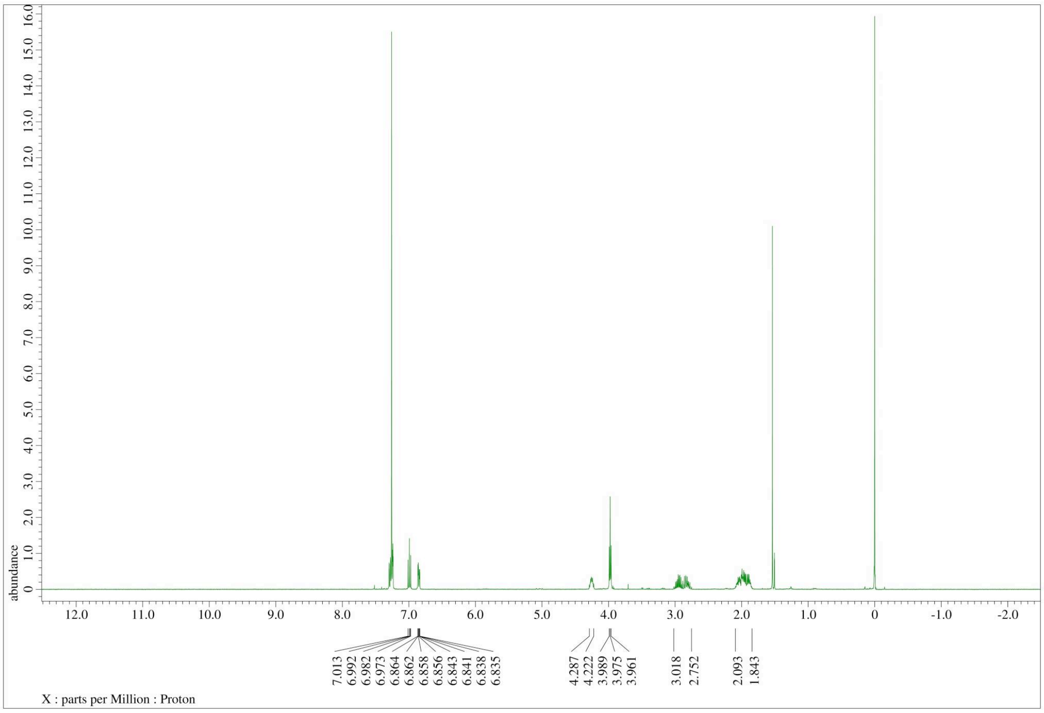
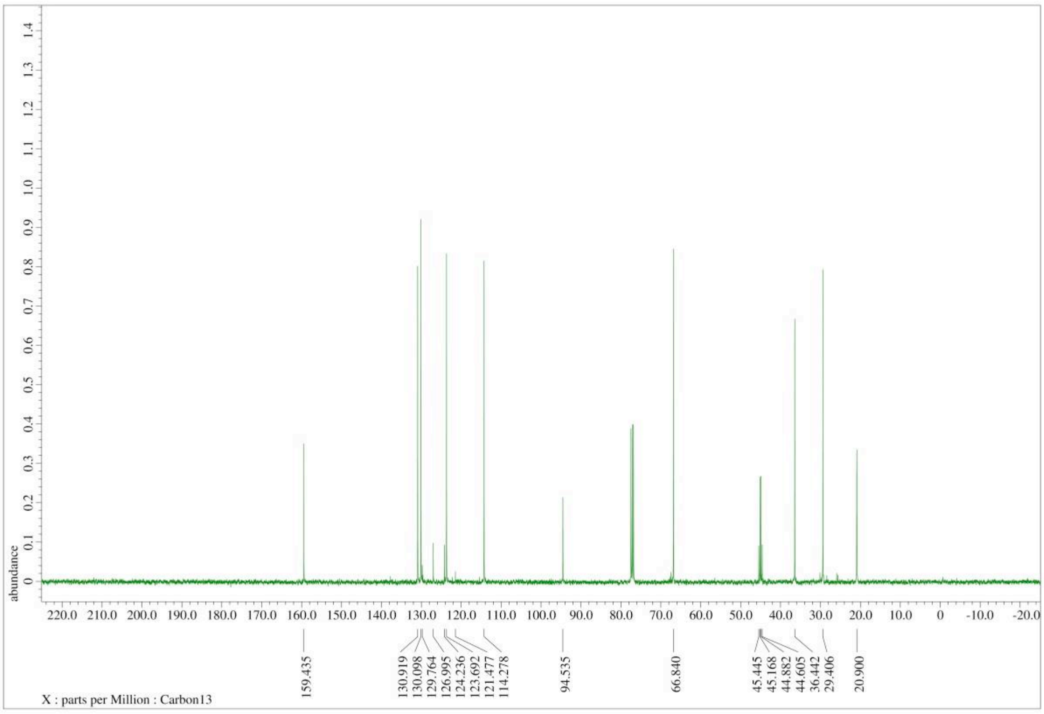
2.0
3.0
4.0
5.0
6.0
7.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.048
8.024
7.595
7.550
7.471
7.433
4.389
4.374
4.359
4.303
4.238
3.021
2.751
2.118
1.858
X : parts per Million : Proton

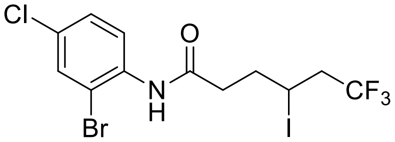

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.615
133.162
130.212
129.773
129.678
128.542
127.014
124.245
121.486
63.689
45.464
45.187
44.901
44.624
36.366
28.986
20.614
20.585
20.556
20.528
X : parts per Million : Carbon13


I
O
CF3
I

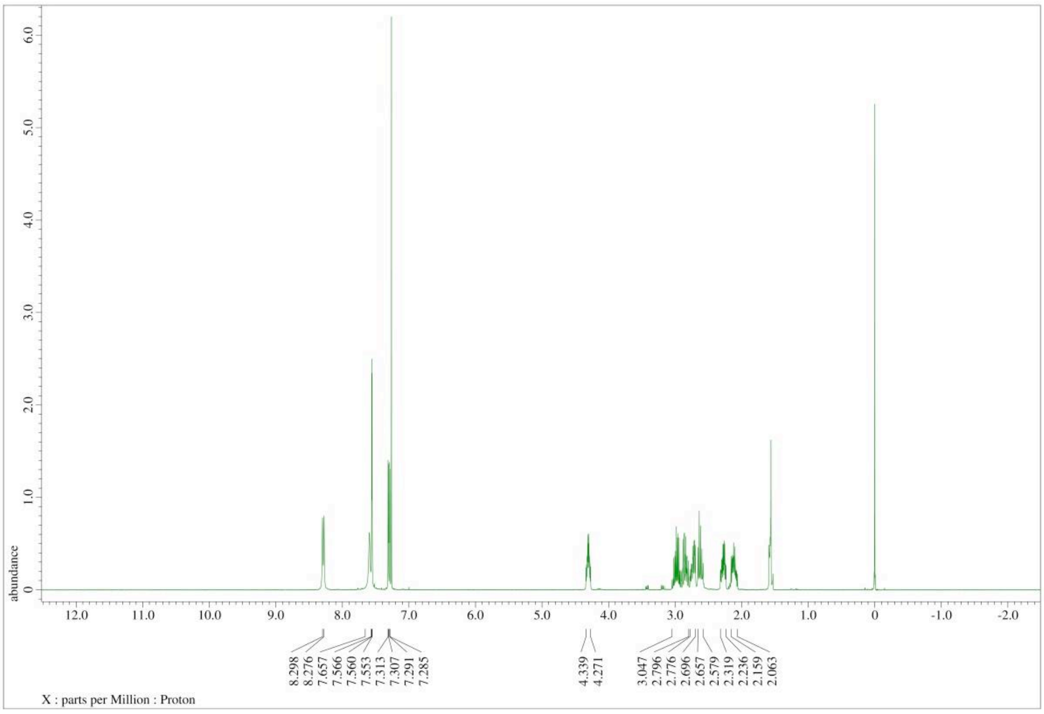
6b

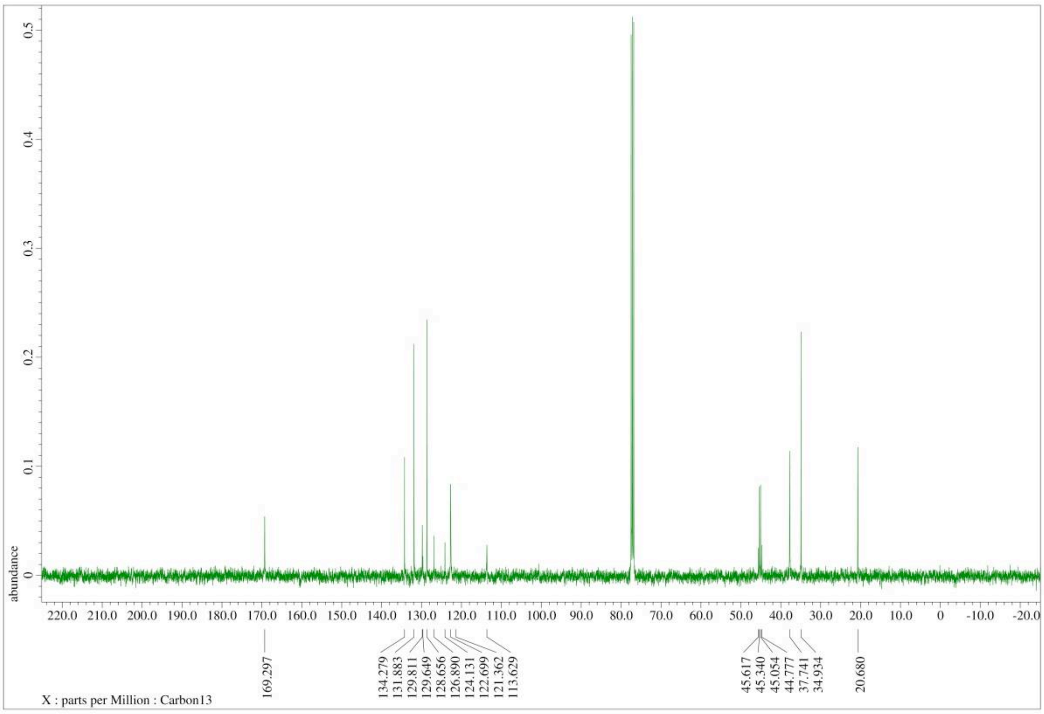

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.013
6.992
6.982
6.973
6.864
6.862
6.858
6.856
6.843
6.841
6.838
6.835
4.287
4.222
3.989
3.975
3.961
3.018
2.752
2.093
1.843
X : parts per Million : Proton

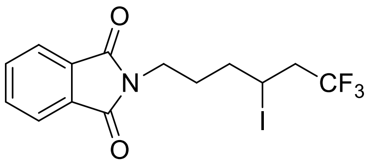

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
159.435
130.919
130.098
129.764
126.995
124.236
123.692
121.477
114.278
94.535
66.840
45.445
45.168
44.882
44.605
36.442
29.406
20.900
X : parts per Million : Carbon13


Cl
O
N
H
Br
I
CF3

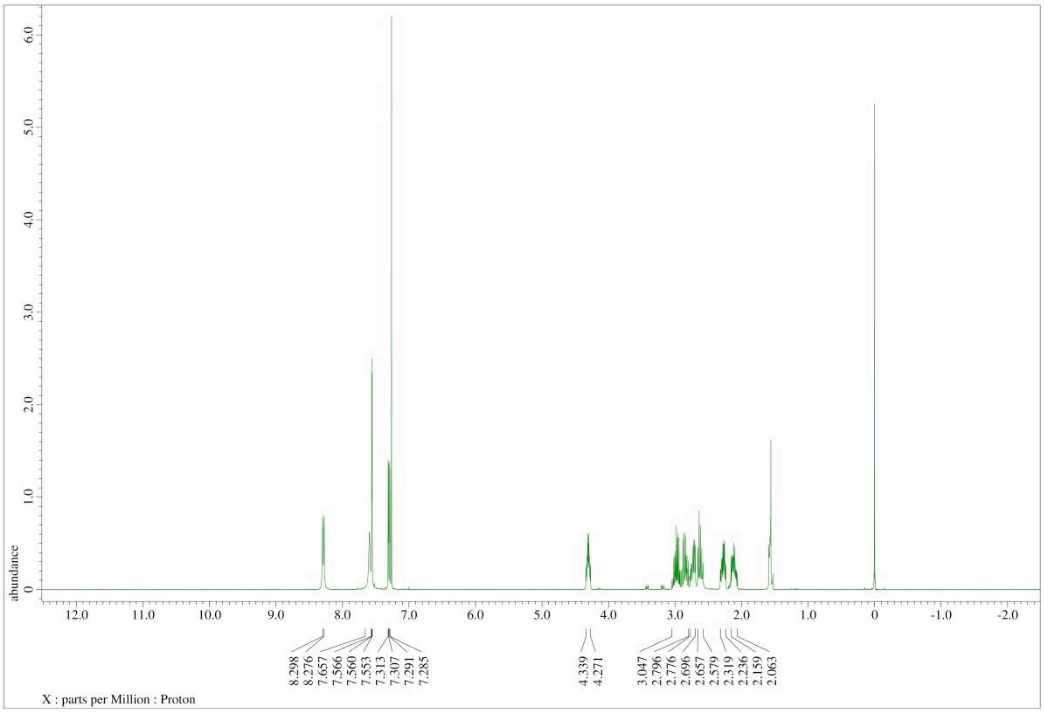
6c

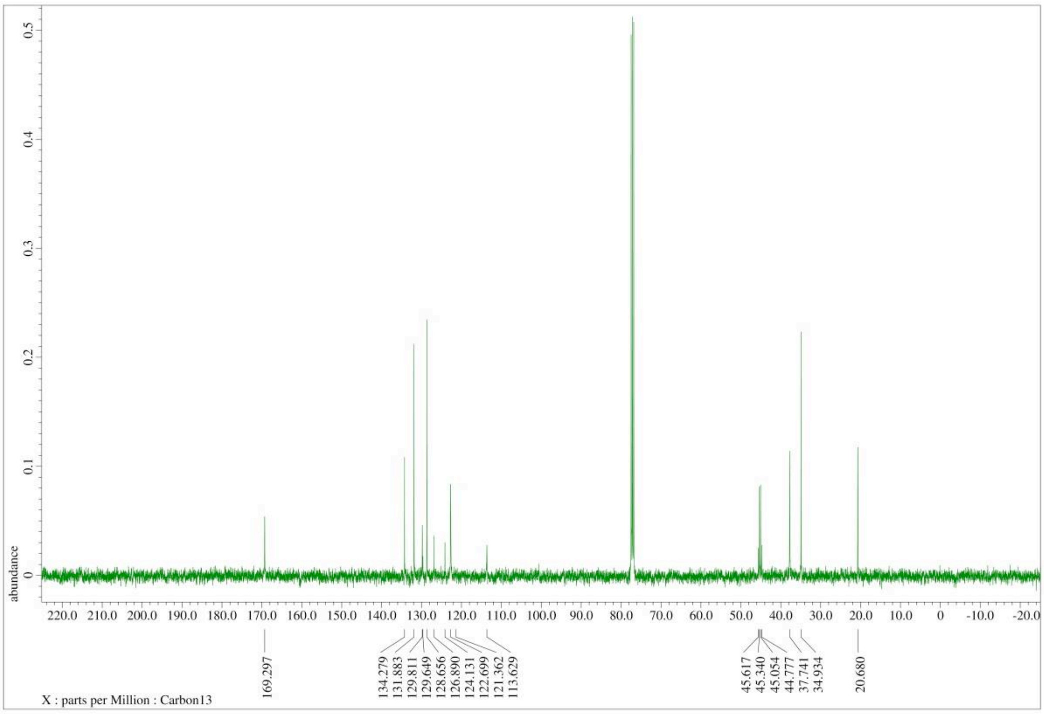

abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
8.298
8.276
7.657
7.566
7.560
7.553
7.313
7.307
7.291
7.285
4.339
4.271
3.047
2.796
2.776
2.696
2.657
2.579
2.319
2.236
2.159
2.063
X : parts per Million : Proton


abundance
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
169.297
134.279
131.883
129.811
129.649
128.656
126.890
124.131
122.699
121.362
113.629
45.617
45.340
45.054
44.777
37.741
34.934
20.680
X : parts per Million : Carbon13


O
N
O
CF3
I

6d


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.298
8.276
7.657
7.566
7.560
7.553
7.313
7.307
7.291
7.285
4.339
4.271
3.047
2.796
2.776
2.696
2.657
2.579
2.319
2.236
2.159
2.063
X : parts per Million : Proton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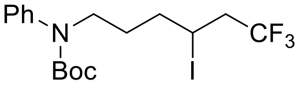
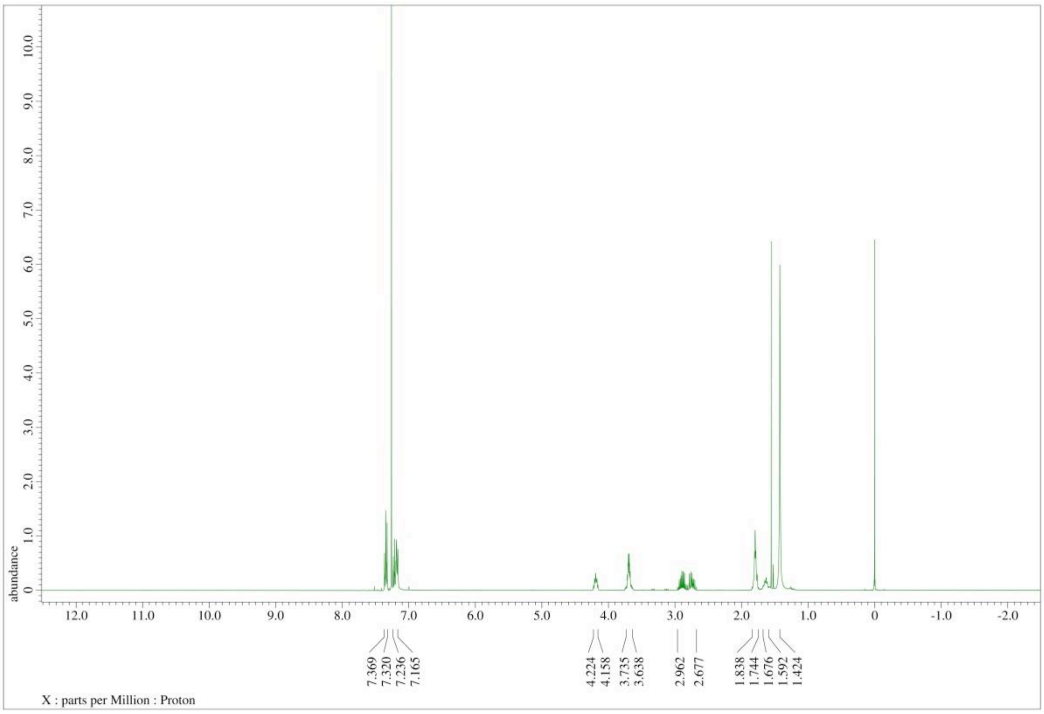
0.4
0.5
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
169.297
134.279
131.883
129.811
129.649
128.656
126.890
124.131
122.699
121.362
113.629
45.617
45.340
45.054
44.777
37.741
34.934
20.680
X : parts per Million : Carbon13


Ph
N
Boc
I
CF3

6e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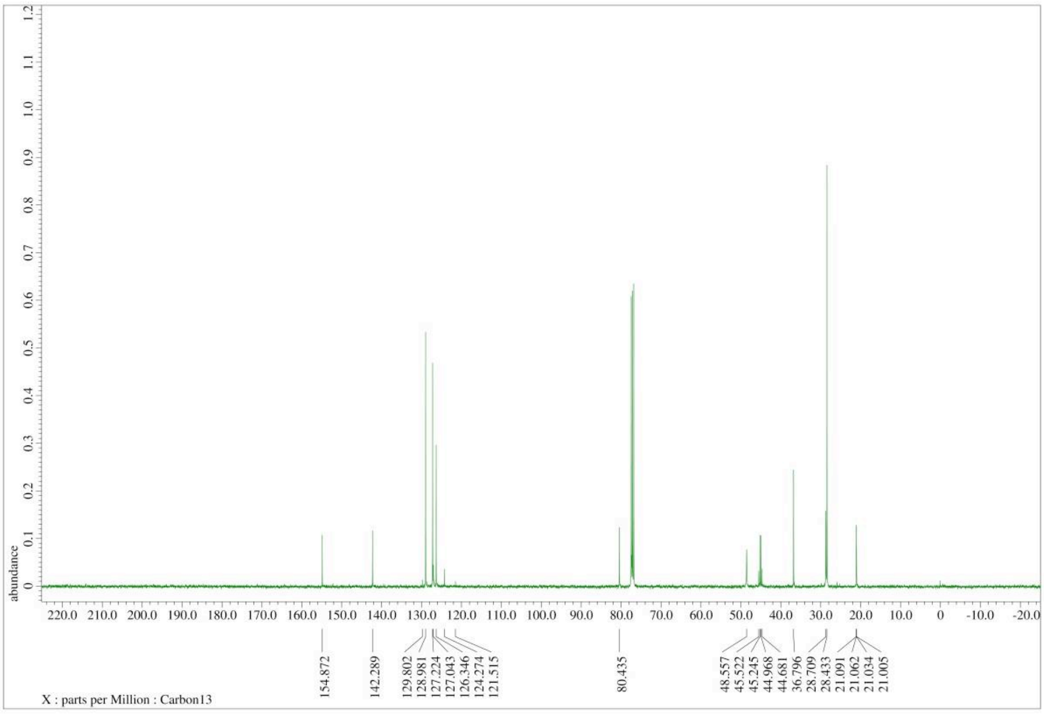
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.369
7.320
7.236
7.165
4.224
4.158
3.735
3.638
2.962
2.677
1.838
1.744
1.676
1.592
1.424
X : parts per Million : Proton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0.9
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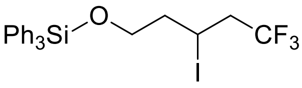
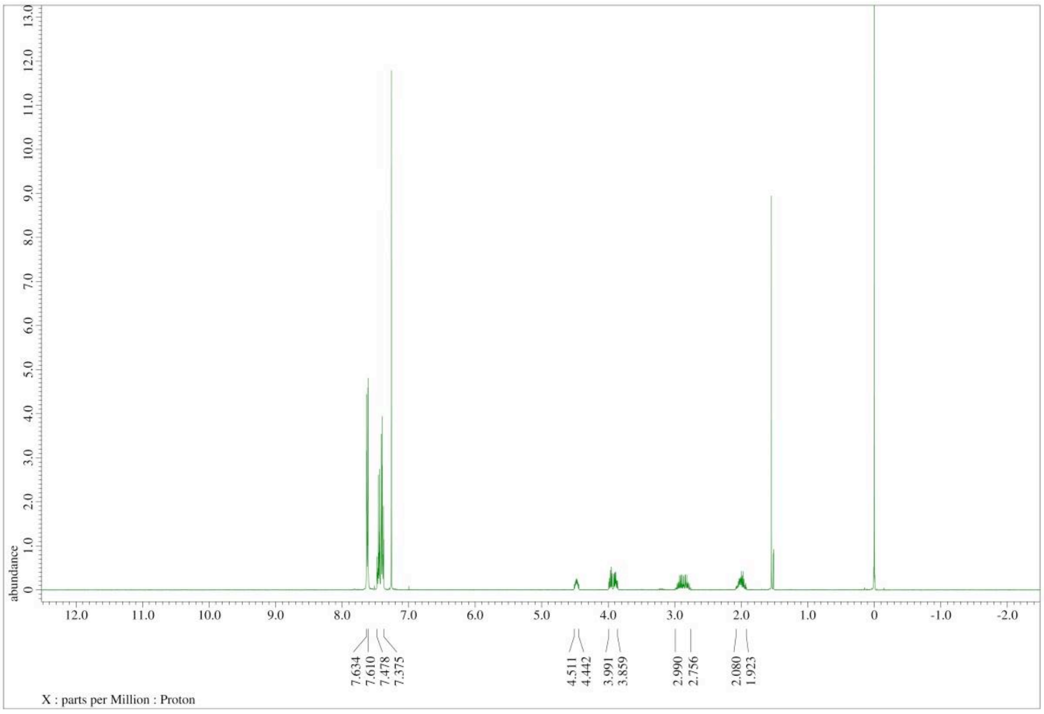
1.1
1.2
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
154.872
142.289
129.802
128.981
127.224
127.043
126.346
124.274
121.515
80.435
48.557
45.522
45.245
44.968
44.681
36.796
28.709
28.433
21.091
21.062
21.034
21.005
X : parts per Million : Carbon13


Ph3Si
O
CF3
I

6f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3.0
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9.0
10.0
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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.634
7.610
7.478
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4.442
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2.990
2.756
2.080
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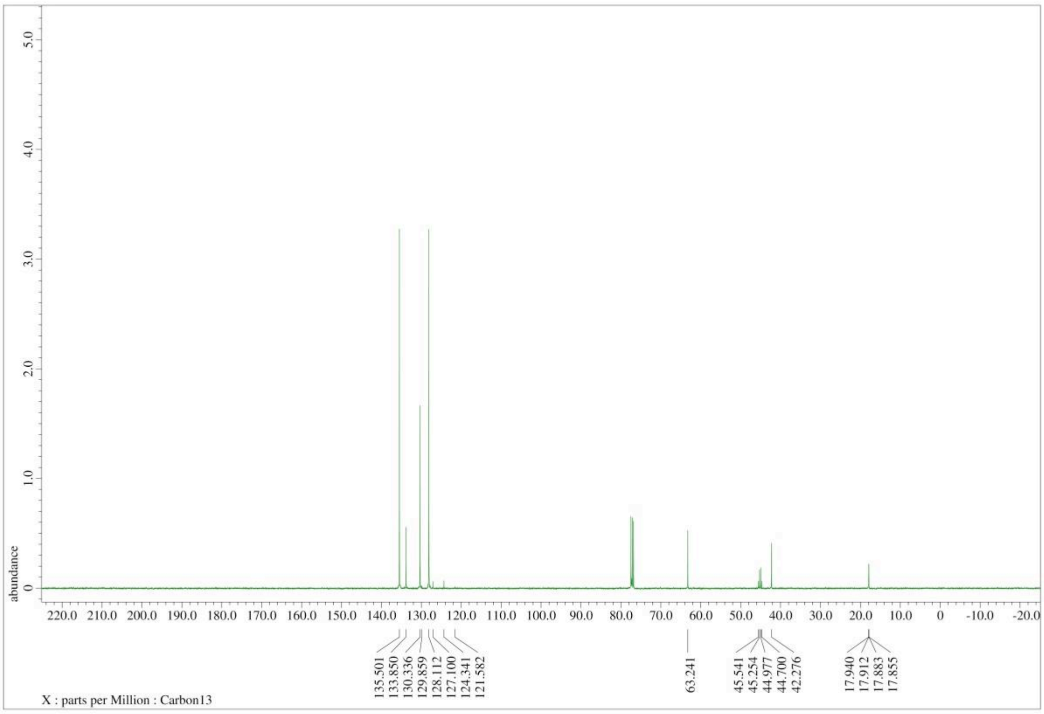
X : parts per Million : Proton


abundance
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190.0
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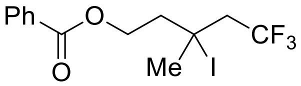
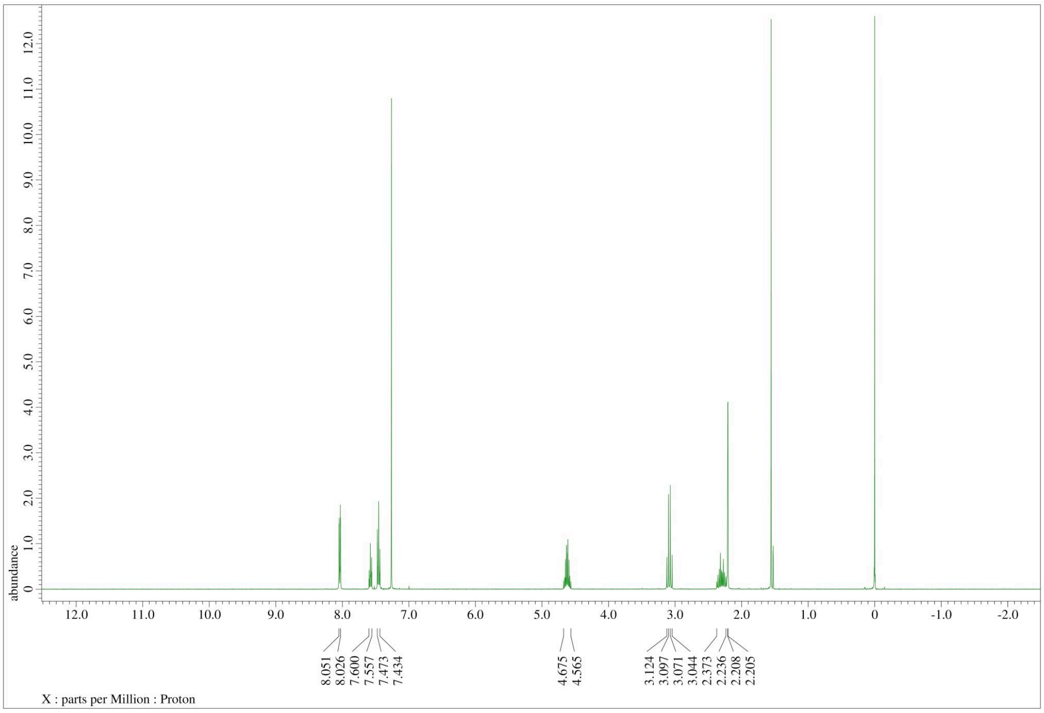
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
135.501
133.850
130.336
129.859
128.112
127.100
124.341
121.582
63.241
45.541
45.254
44.977
44.700
42.276
17.940
17.912
17.883
17.855
X : parts per Million : Carbon13


Ph
O
O
Me
I
CF3

6g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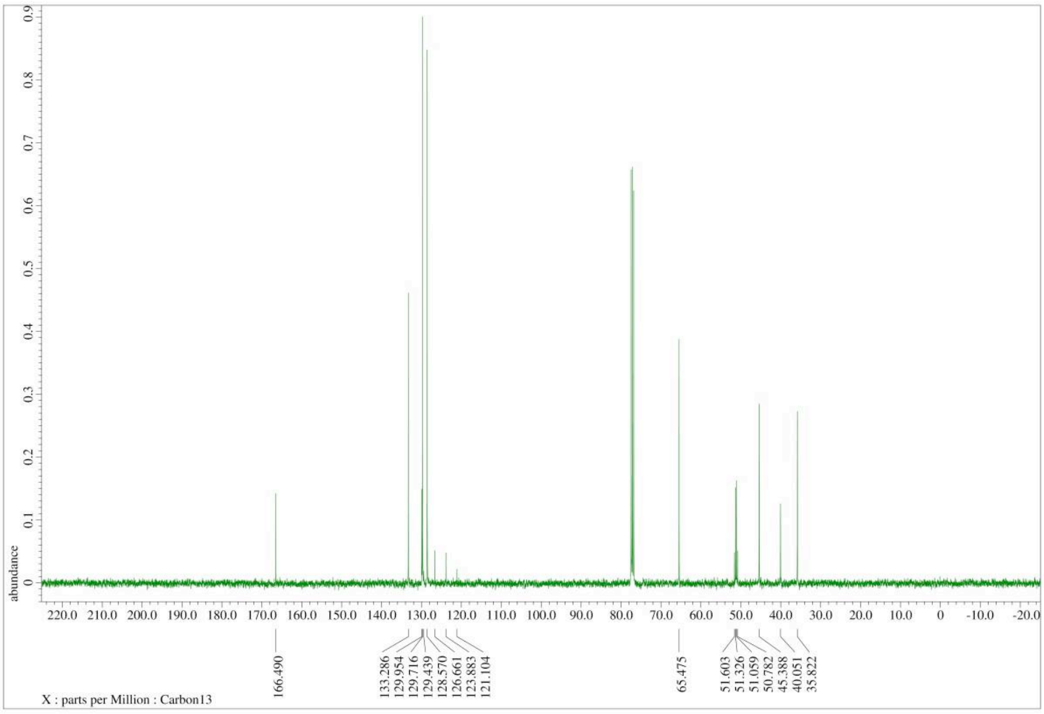
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
8.051
8.026
7.600
7.557
7.473
7.434
4.675
4.565
3.124
3.097
3.071
3.044
2.373
2.236
2.208
2.205
X : parts per Million : Proton


abundance
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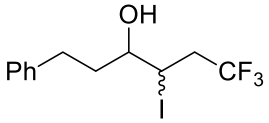
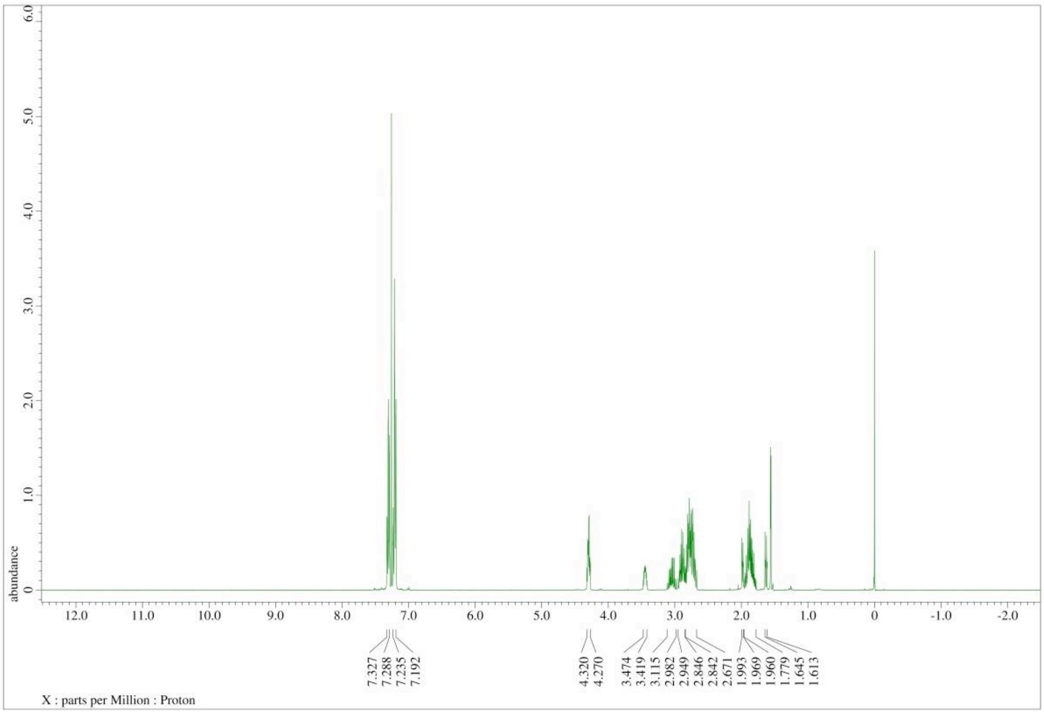
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.490
133.286
129.954
129.716
129.439
128.570
126.661
123.883
121.104
65.475
51.603
51.326
51.059
50.782
45.388
40.051
35.822
X : parts per Million : Carbon13


OH
Ph
CF3
I

6h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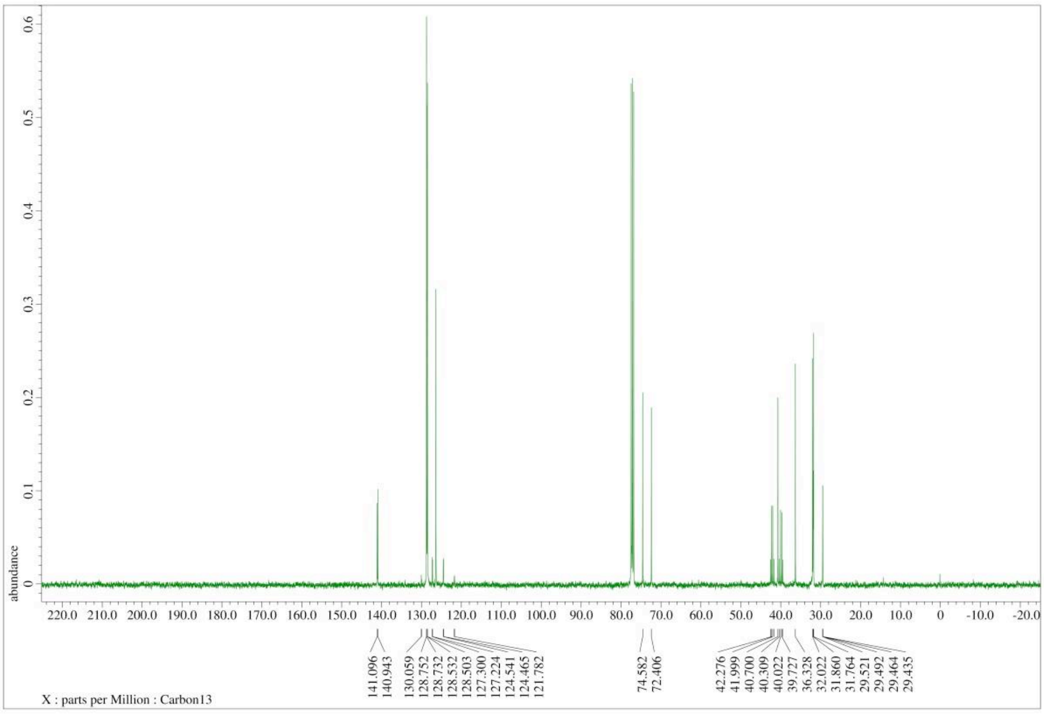
4.0
5.0
6.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.327
7.288
7.235
7.192
4.320
4.270
3.474
3.419
3.115
2.982
2.949
2.846
2.842
2.671
1.993
1.969
1.960
1.779
1.645
1.613
X : parts per Million : Proton


abundance
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0.4
0.5
0.6
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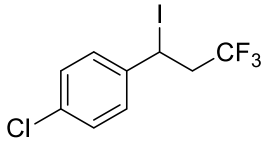
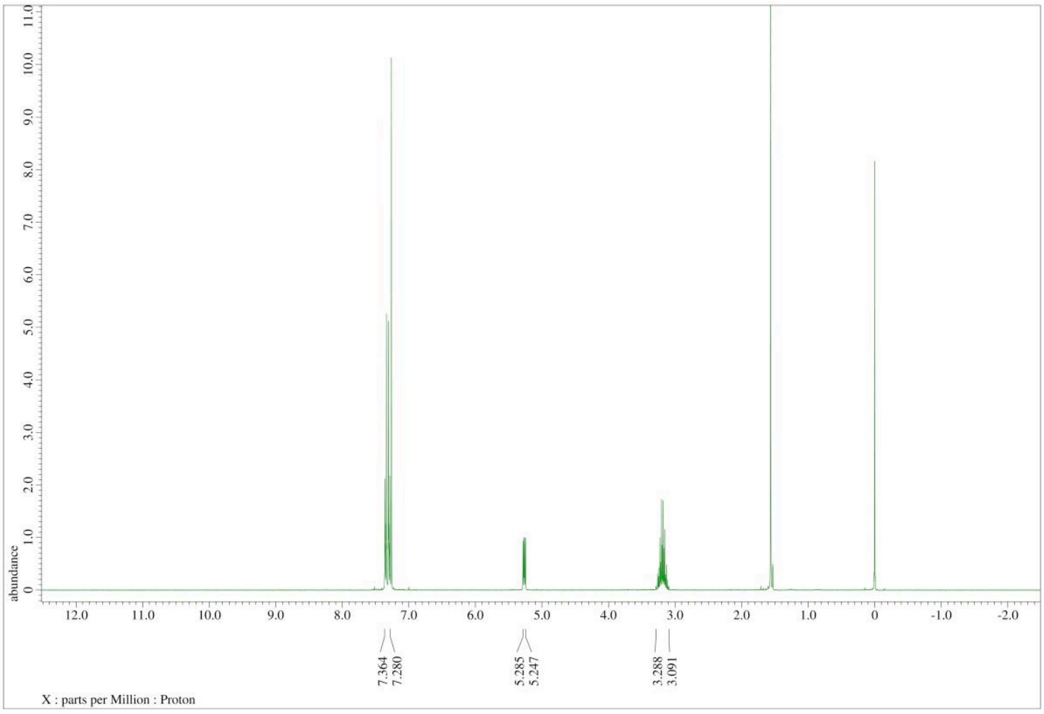
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
141.096
140.943
130.059
128.752
128.732
128.532
128.503
127.300
127.224
124.541
124.465
121.782
74.582
72.406
42.276
41.999
40.700
40.309
40.022
39.727
36.328
32.022
31.860
31.764
29.521
29.492
29.464
29.435
X : parts per Million : Carbon13


I
CF3
Cl

9


abundance
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4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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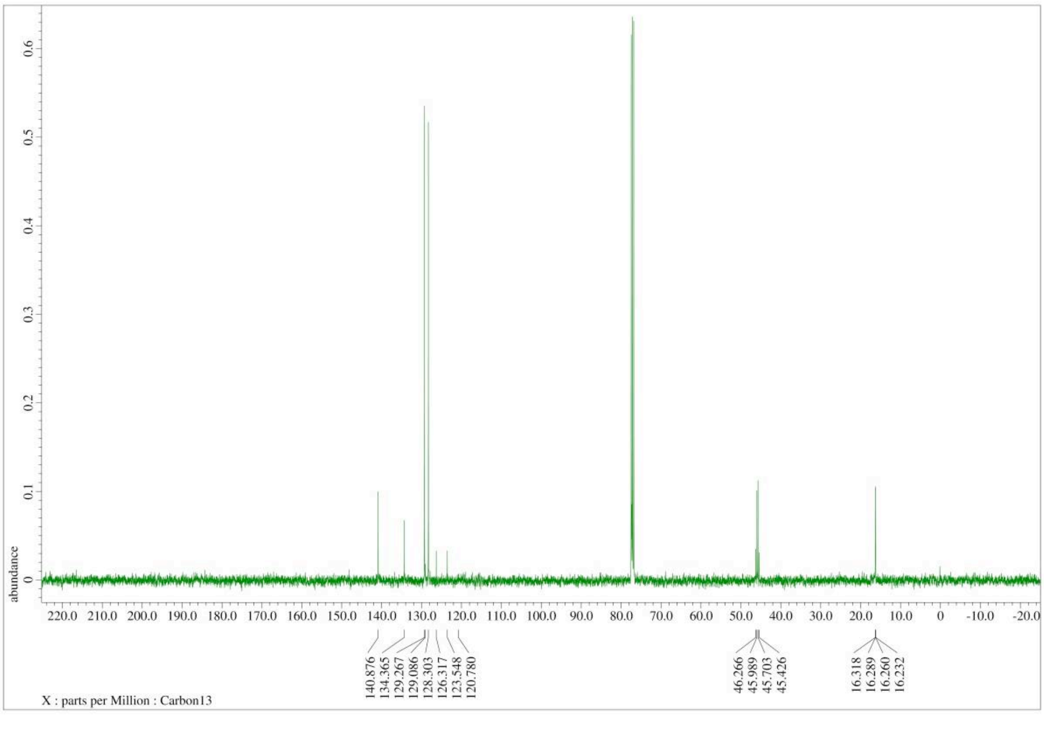
-2.0
7.364
7.280
5.285
5.247
3.288
3.091
X : parts per Million : Proton


abundance
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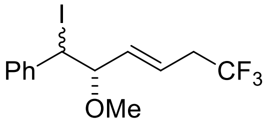
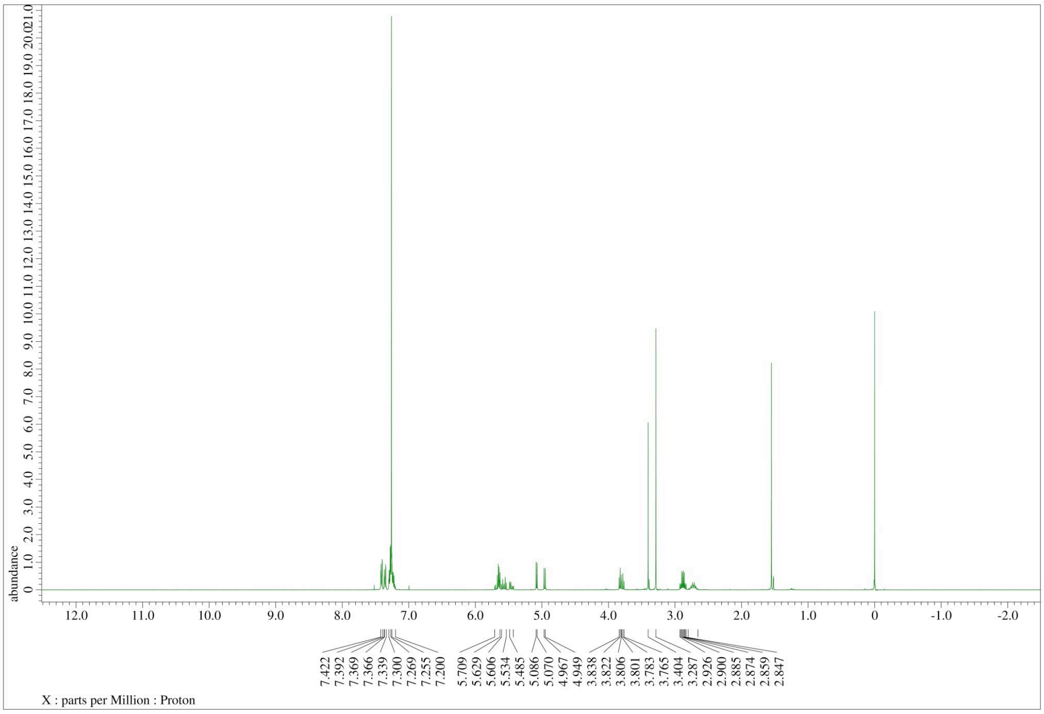
0.6
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
140.876
134.365
129.267
129.086
128.303
126.317
123.548
120.780
46.266
45.989
45.703
45.426
16.318
16.289
16.260
16.232
X : parts per Million : Carbon13


I
Ph
CF3
OMe

11


abundance
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3.0
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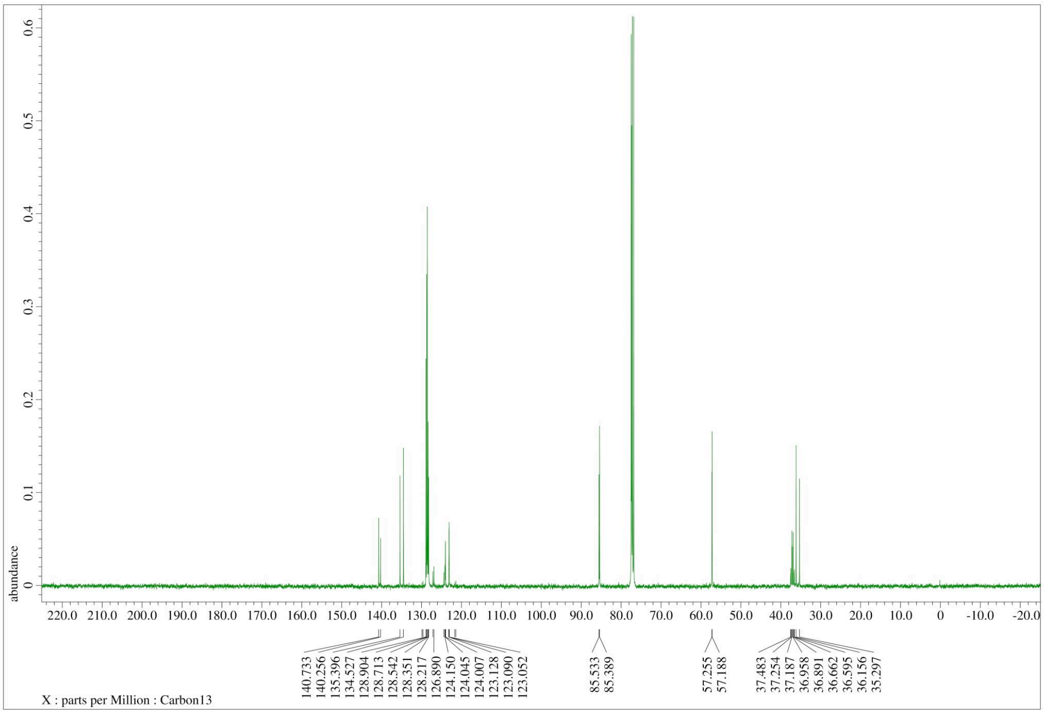
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.422
7.392
7.369
7.366
7.339
7.300
7.269
7.255
7.200
5.709
5.629
5.606
5.534
5.485
5.086
5.070
4.967
4.949
3.838
3.822
3.806
3.801
3.783
3.765
3.404
3.287
2.926
2.900
2.885
2.874
2.859
2.847
X : parts per Million : Proton


abundance
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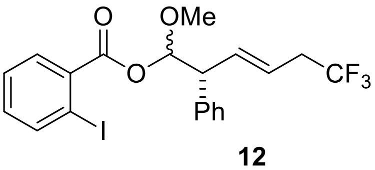
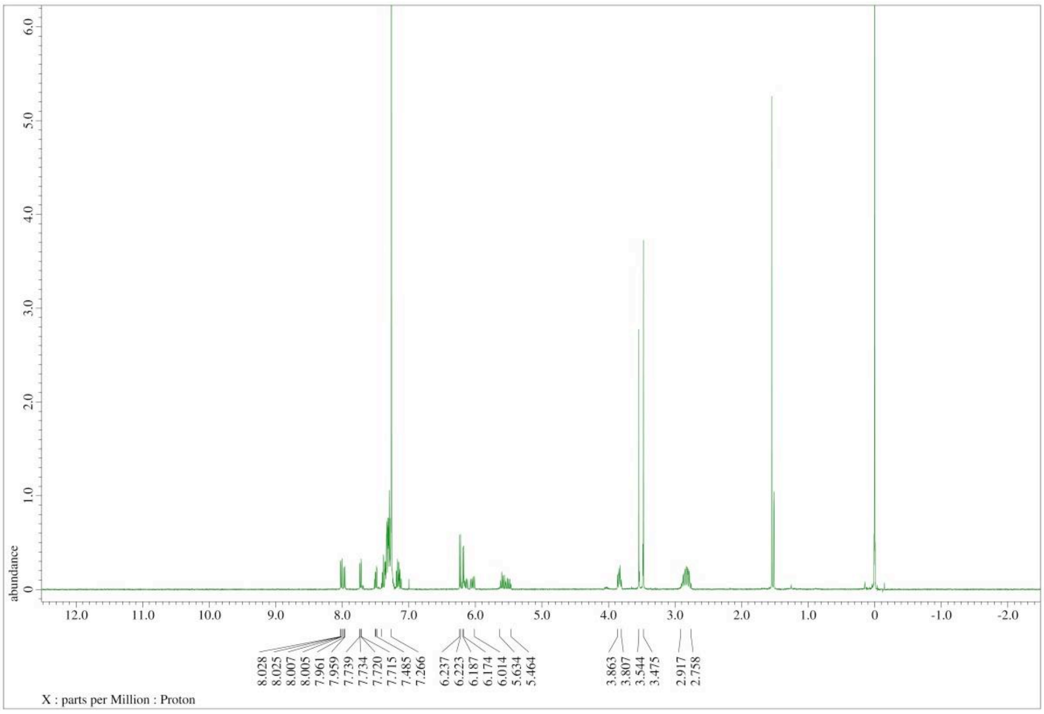
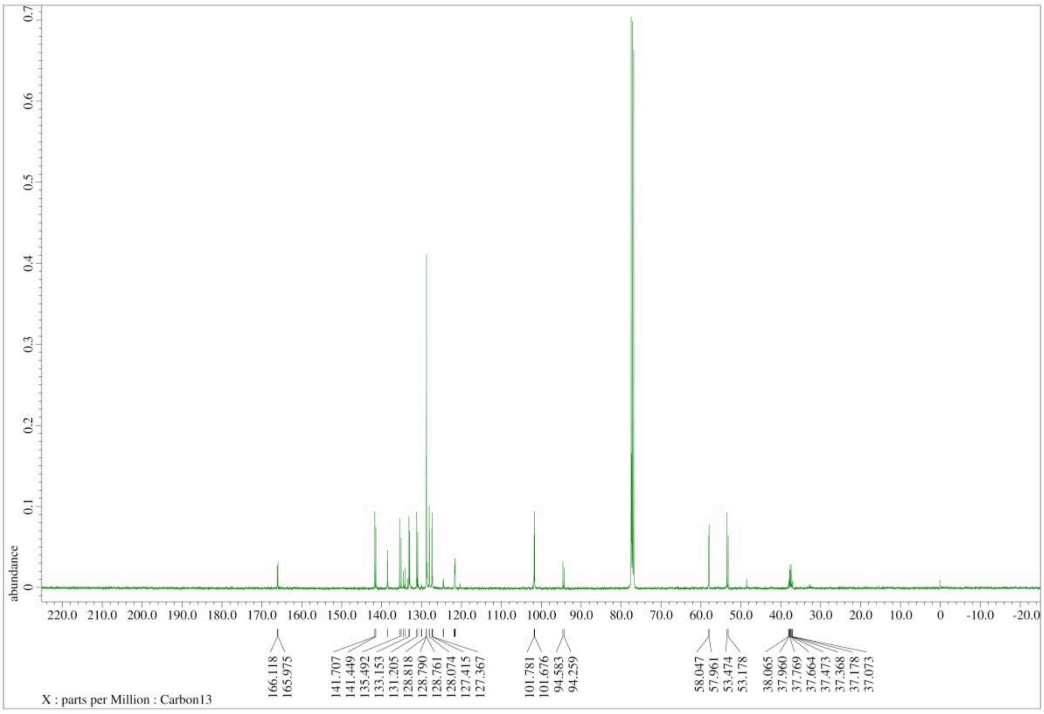
0.2
0.3
0.4
0.5
0.6
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
140.733
140.256
135.396
134.527
128.904
128.713
128.542
128.351
128.217
126.890
124.150
124.045
124.007
123.128
123.090
123.052
85.533
85.389
57.255
57.188
37.483
37.254
37.187
36.958
36.891
36.662
36.595
36.156
35.297
X : parts per Million : Carbon13


O
OMe
O
CF3
Ph
I

12


6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.028
8.025
8.007
8.005
7.961
7.959
7.739
7.734
7.720
7.715
7.485
7.266
6.237
6.223
6.187
6.174
6.014
5.634
5.464
3.863
3.807
3.544
3.475
2.917
2.758
X : parts per Million : Proton


0.7
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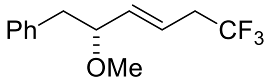
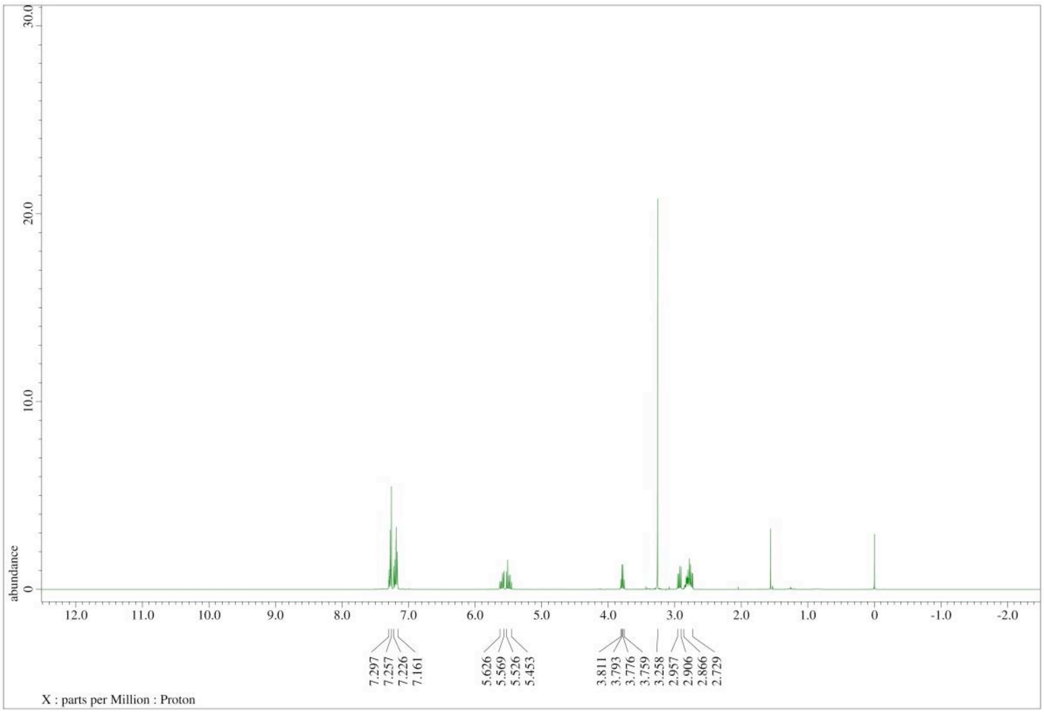
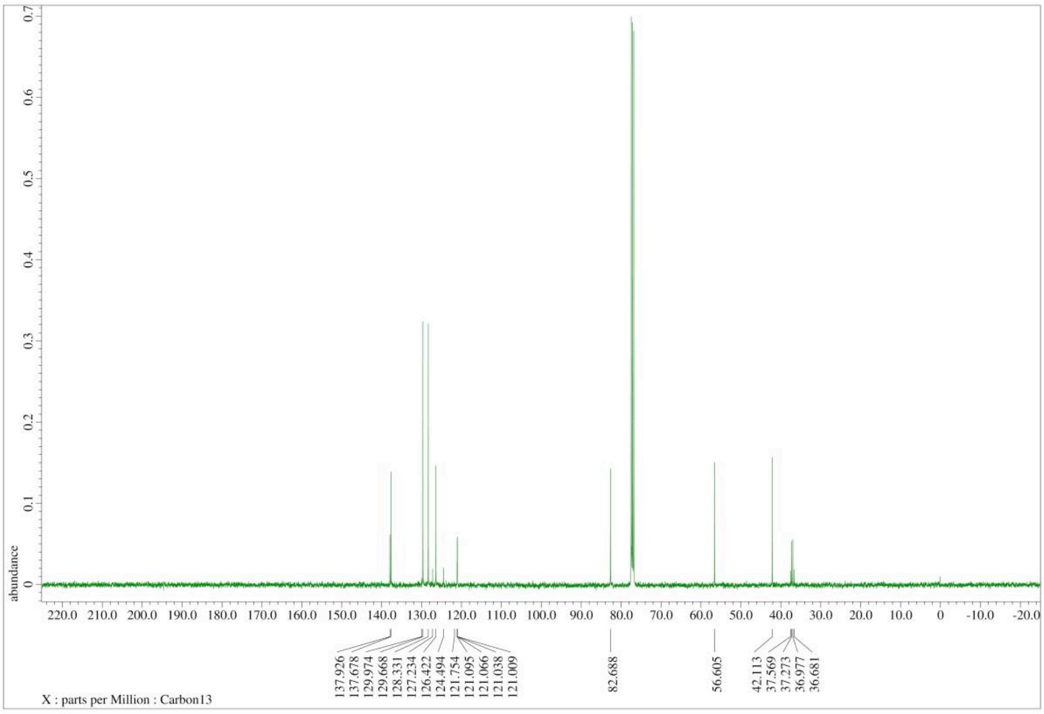
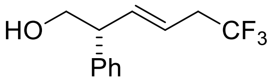
0.5
0.4
0.3
0.2
0.1
0
abundance
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.118
165.975
141.707
141.449
135.492
133.153
131.205
128.818
128.790
128.761
128.074
127.415
127.367
101.781
101.676
94.583
94.259
58.047
57.961
53.474
53.178
38.065
37.960
37.769
37.664
37.473
37.368
37.178
37.073
X : parts per Million : Carbon13


Ph
OMe
CF3

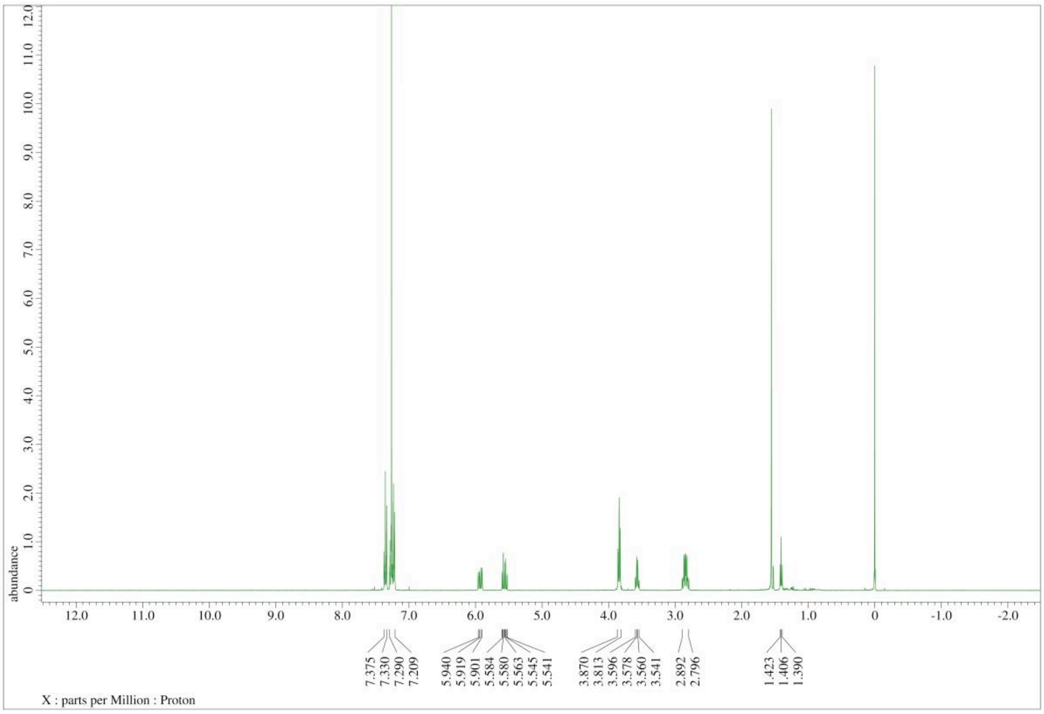
13

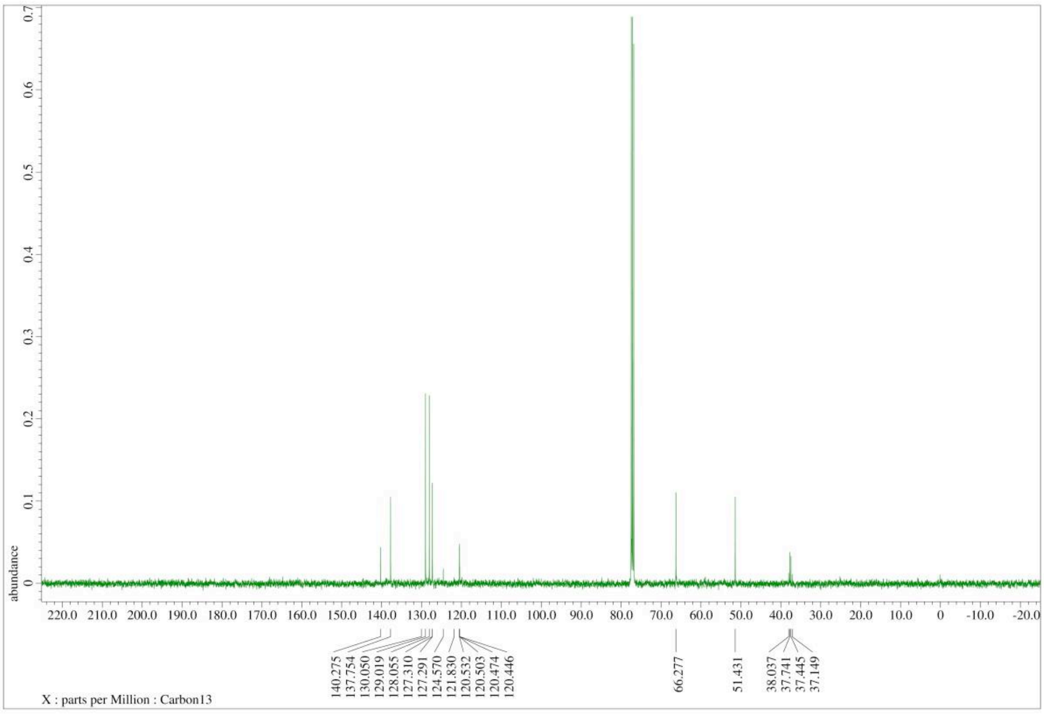

30.0
20.0
10.0
0
abundance
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.297
7.257
7.226
7.161
5.626
5.569
5.526
5.453
3.811
3.793
3.776
3.759
3.258
2.957
2.906
2.866
2.729
X : parts per Million : Proton


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.926
137.678
129.974
129.668
128.331
127.234
126.422
124.494
121.754
121.095
121.066
121.038
121.009
82.688
56.605
42.113
37.569
37.273
36.977
36.681
X : parts per Million : Carbon13


HO
CF3
Ph

14


abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.375
7.330
7.290
7.209
5.940
5.919
5.901
5.584
5.580
5.563
5.545
5.541
3.870
3.813
3.596
3.578
3.560
3.541
2.892
2.796
1.423
1.406
1.390
X : parts per Million : Proton


abundance
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0.4
0.3
0.2
0.1
0
220.0
210.0
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190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
140.275
137.754
130.050
129.019
128.055
127.310
127.291
124.570
121.830
120.532
120.503
120.474
120.446
66.277
51.431
38.037
37.741
37.445
37.149
X : parts per Million : Carbon13