Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPLEMENTARY INFORMATION

A Practical Protocol for the Synthesis of Bibenzyls *via* C(SP^3)-H Activation of Methyl Arenes under Metal-free Conditions

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1. General information

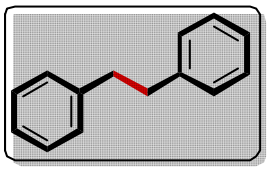
All the reagents and solvents were purchased from Sigma-Aldrich or Merck chemical Co. and were used directly without any further purification. The reactions were monitored by thin layer chromatography (TLC) using Merck Kieselgel 60 GF_{254} plates (thickness 0.25 mm). Visualization of TLC was performed using UV light; products purification was done using Merck silica gel (100-200 mess) column chromatography. ^{1}H NMR spectra were recorded at 500 MHz using JEOL AL-500 spectrometer and are reported in parts per million (ppm) on the δ scale relative to TMS as an internal standard. Coupling constants (*J*) reported in Hz. ^{13}C NMR spectra were recorded at 125 MHz.

2. General procedure for the synthesis of Bisbenzyles

Methylarene (1.0 mmol), $K_2S_2O_8$ (2.0 mmol), CH_3CN/H_2O (1:1) (2ml) were placed in a vial (10 mL) containing a magnetic stirring bar. The vial was capped and the mixture was stirred at 80 °C for 10 h. After the reaction was completed (TLC), the mixture was cooled to room temperature. The work up of the reaction mixture was performed using the ethyl acetate (30 mL) and water (50 mL x 3). The organic phase was dried over anhyd Na_2SO_4, filtered, evaporated under reduced pressure and purified by column chromatography.

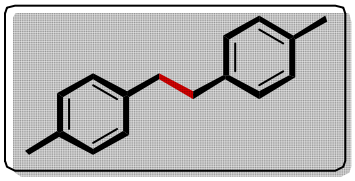
3. Characterization Data of the Products

(2a) 1,2-diphenylethane[1]



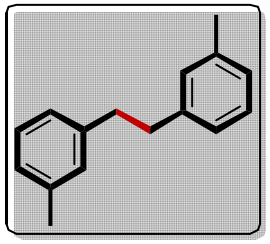
Physical state: Colourless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.20-7.14 (m, 4H), 7.10-7.06 (m, 6H), 2.83 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 141.8, 128.4, 128.3, 125.9, 37.9.

(2b) 1,2-di-p-tolylethane[1]



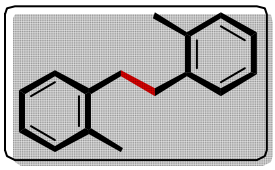
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.05-6.96 (m, 8H), 2.77 (s, 4H), 2.23 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 138.8, 135.2, 129.0, 128.3, 37.6, 21.0.

(2c) 1,2-di-m-tolylethane[6]



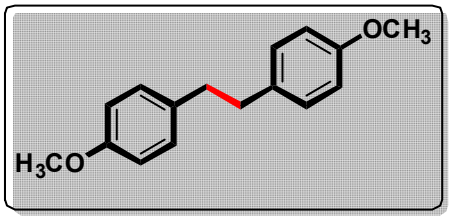
Physical state: Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.12-7.09 (m, 2H), 6.95-6.91 (m, 6H), 2.78 (s, 4H), 2.25 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 141.9, 137.9, 129.2, 128.2, 126.6, 125.4, 38.0, 21.4.

(2d) 1,2-di-o-tolylethane[1]



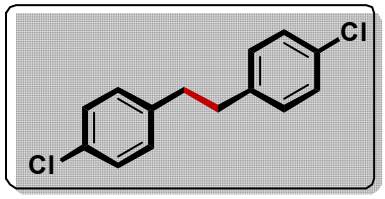
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.15-7.12 (m, 8H), 2.85 (s, 4H), 2.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 140.2, 135.9, 130.2, 128.8, 126.1, 126.0, 34.1, 19.3.

(2f) 1,2-bis(4-methoxyphenyl)ethane[2]



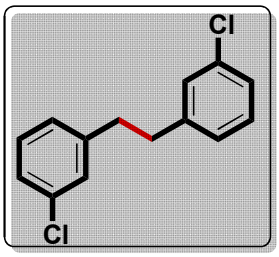
Physical state: colourless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.28 (d, J = 8.5 Hz, 4H), 6.87 (d, J = 5.0 Hz, 4H), 3.84 (s, 6H), 2.90 (s, 4H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 157.8, 134.0, 129.4, 113.7, 55.3, 37.3.

(2g) 1,2-bis(4-chlorophenyl)ethane[5]



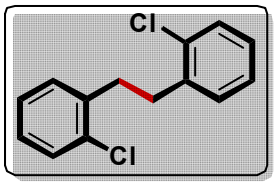
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.75 (d, J = 8.5 Hz, 4H), 6.96 (d, J = 7.5 Hz, 4H), 2.76 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 139.6, 131.8, 129.8, 128.4, 36.9.

(2h) 1,2-bis(3-chlorophenyl)ethane[6]



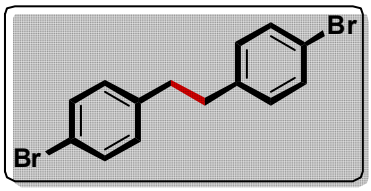
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.25-7.20 (m, 6H), 7.06 (d, J = 8.5 Hz, 2H), 2.91 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 143.2, 134.2, 129.6, 128.5, 126.6, 126.3, 37.2.

(2i) 1,2-bis(2-chlorophenyl)ethane[5]



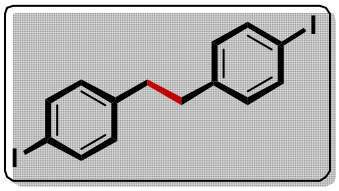
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.43-7.40 (m, 2H), 7.23-7.18 (m, 6H), 3.13 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 138.9, 134.0, 130.6, 129.4, 127.5, 126.7, 33.8.

(2j) 1,2-bis(4-bromophenyl)ethane[1]



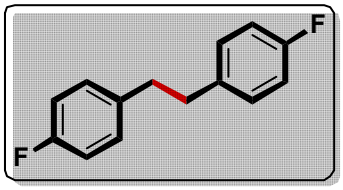
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.29 (d, J = 8.5 Hz, 4H), 6.90 (d, J = 8.5 Hz, 4H), 2.75(s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 140.2, 131.5, 130.1, 120.0, 37.1.

(2k) 1,2-bis(4-iodophenyl)ethane[7]



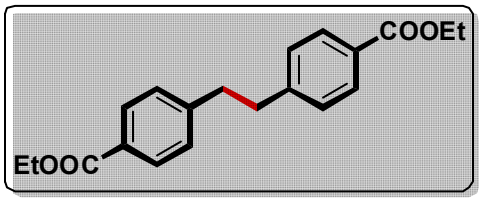
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.58 (d, J = 8.5 Hz, 4H), 6.88 (d, J = 8.5 Hz, 4H), 2.82 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 140.7, 137.4, 130.6, 91.2, 37.0.

(2l) 1,2-bis(4-fluorophenyl)ethane[1]



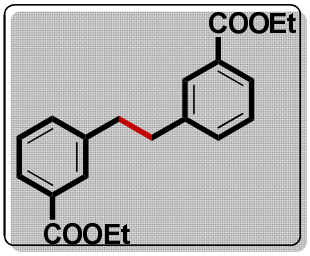
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.06-7.05 (m, 4H), 7.03-6.90 (m, 4H), 2.84 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 163.0, 161.1, 137.6, 130.5, 130.4, 115.8,115.7, 37.8.

(2m) diethyl 4,4'-(ethane-1,2-diyl)dibenzoate[3]



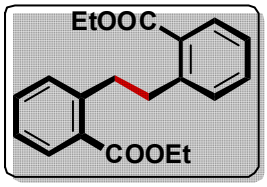
Physical state: Colourless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.95 (d, J = 8.5 Hz, 4H), 7.20 (d, J = 7.5 Hz, 4H), 4.38 (q, J = 6.5 Hz, 4H), 2.99 (s, 4H), 1.40 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 166.7, 146.5, 129.9, 129.8, 128.5, 60.9, 37.5, 14.4.

(2n) diethyl 3,3'-(ethane-1,2-diyl)dibenzoate[8]



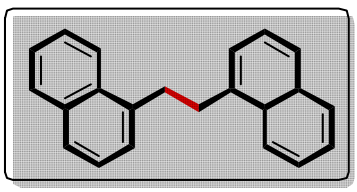
Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.91-7.86 (m, 4H), 7.36-7.33 (m, 4H), 4.39 (q, J = 7.5 Hz, 4H), 2.99 (s, 4H), 1.42(t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 166.8, 141.6, 133.1, 130.7, 129.6, 128.5, 127.4, 122.4, 61.0, 37.6, 14.4.

(2o) diethyl 2,2'-(ethane-1,2-diyl)dibenzoate[9]



Physical state: Colourless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.91 (d, J = 9.0 Hz, 2H), 7.43 (t, = 9.0 Hz, 2H), 7.23-7.25 (m, 4H), 4.42 (q, J = 7.0 Hz, 4H), 3.30 (s, 4H), 1.43 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 167.9, 143.8, 132.0,131.5, 130.7, 130.1, 126.1, 61.0, 36.4, 14.6.

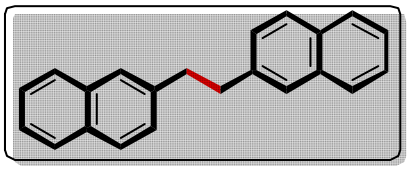
(2p) 1,2-di(naphthalen-1-yl)ethane[2]



Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.04 (d, J = 7.5 Hz, 2H), 7.80 (d, J = 6.8 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.44-7.39 (m, 4H), 7.32 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 16.0 Hz, 2H), 3.43 (s, 4H);

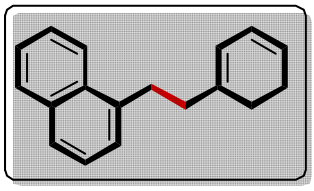
^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 138.0, 133.9, 131.8, 128.8, 126.8, 125.9, 125.7, 125.6, 125.5, 123.6, 34.1.

(2q) 1,2-di(naphthalen-2-yl)ethane[2]



Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.84-7.78 (m, 6H), 7.68 (s, 2H), 7.49-7.43 (m, 4H), 7.40 (d, *J* = 8.5 Hz , 2H), 3.21 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 139.4, 133.7, 132.2, 128.0, 127.7, 127.6, 127.4, 126.6, 126.0, 125.3, 38.1.

(3a) 1-phenethylnaphthalene[4]



Physical state: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.11 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.74(d, *J* = 8.5 Hz 1H), 7.53-7.49 (m, 2H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.32 (d, *J* = 3.5 Hz, 2H), 7.30-7.23 (m, 4H), 3.40 (t, *J* = 8.5 Hz, 2H), 3.08 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c: 142.1, 137.9, 134.0, 131.8, 128.9, 128.5, 127.4, 126.8, 126.1, 125.9, 125.6, 125.5, 124.3, 123.7, 37.2, 35.2.

References:

(1) K. Sato, Y. Inoue, T. Mori, A. Sakaue, A. Tarui, M. Omote, I. Kumadaki and A. Ando, *Org. Lett*., 2014, **16**, 3756.

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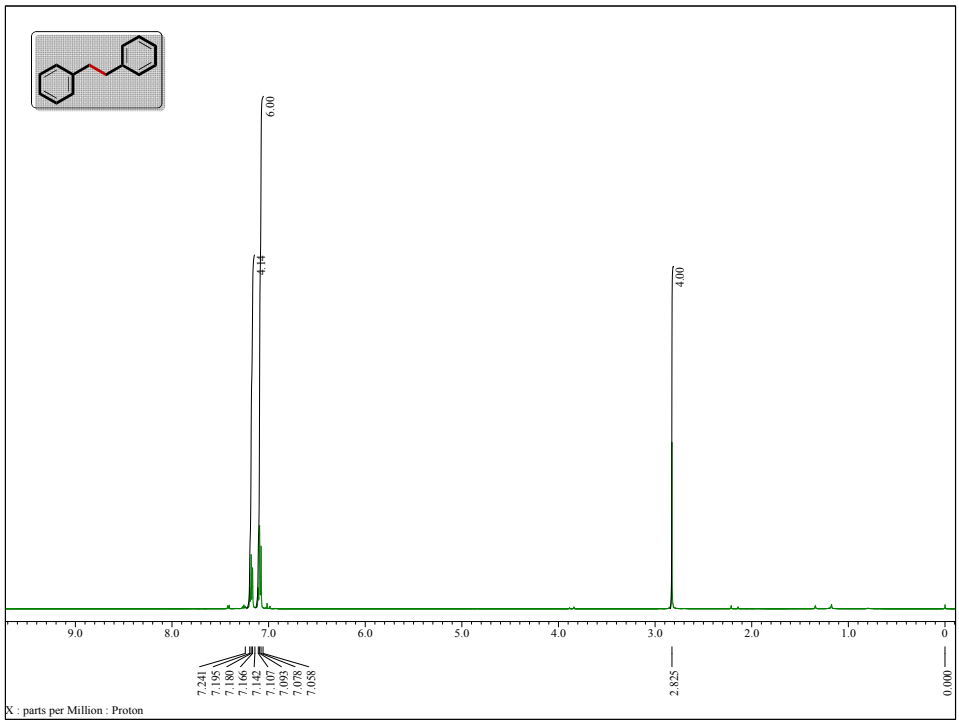
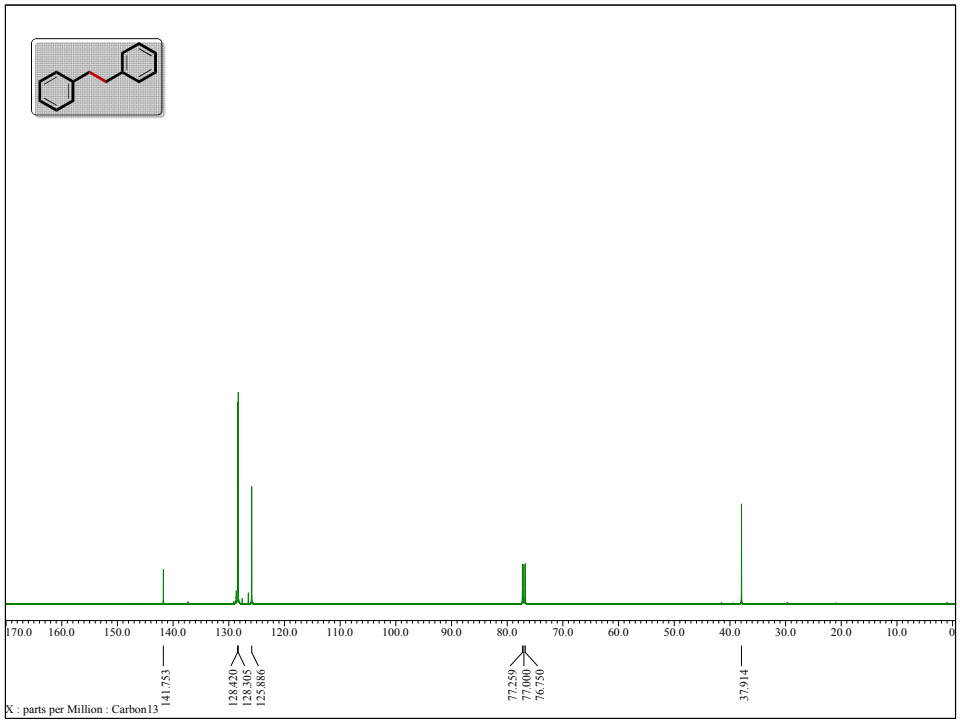
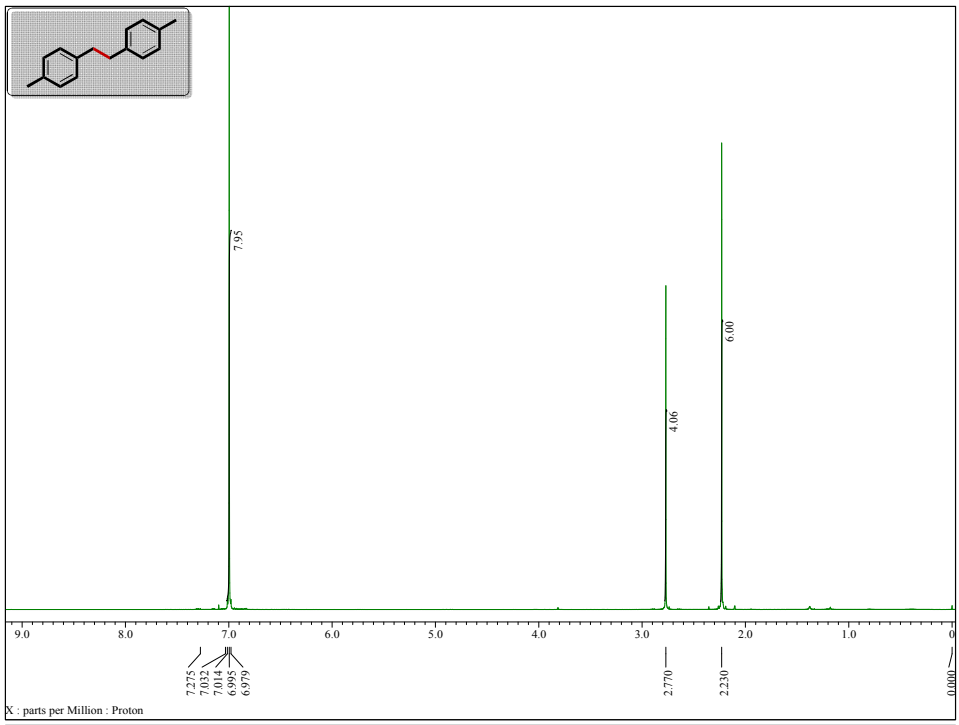
5. COPIES OF ^{1}H-&^{13}C-NMR SPECTRA OF THE PRODUCTS



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9.0
8.0
7.0
6.0
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3.0
2.0
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6.979
2.770
2.230
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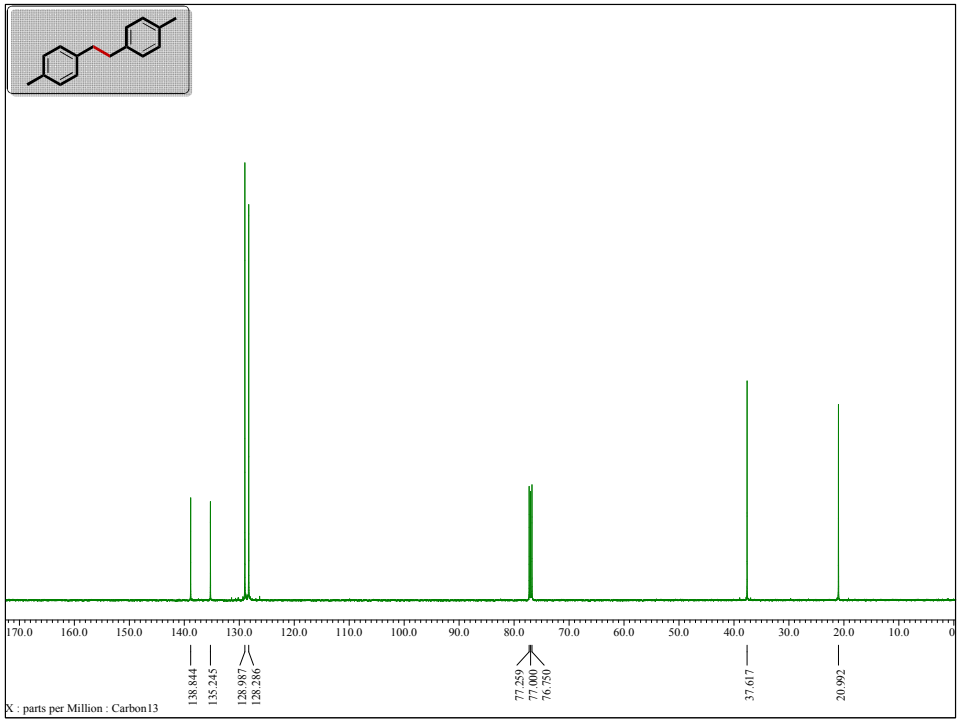
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20.0
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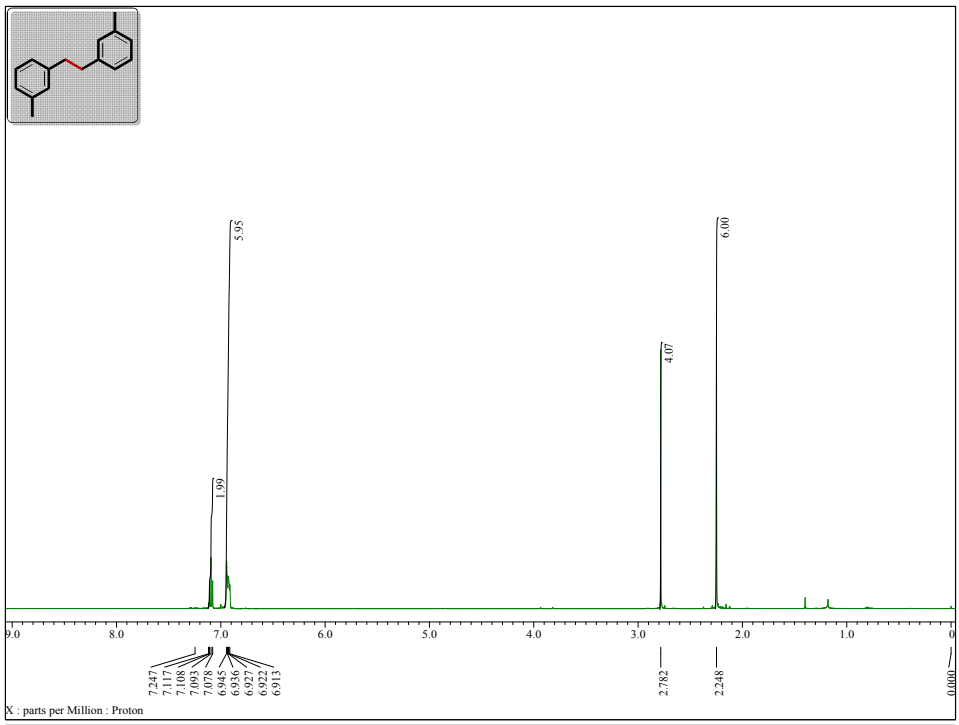
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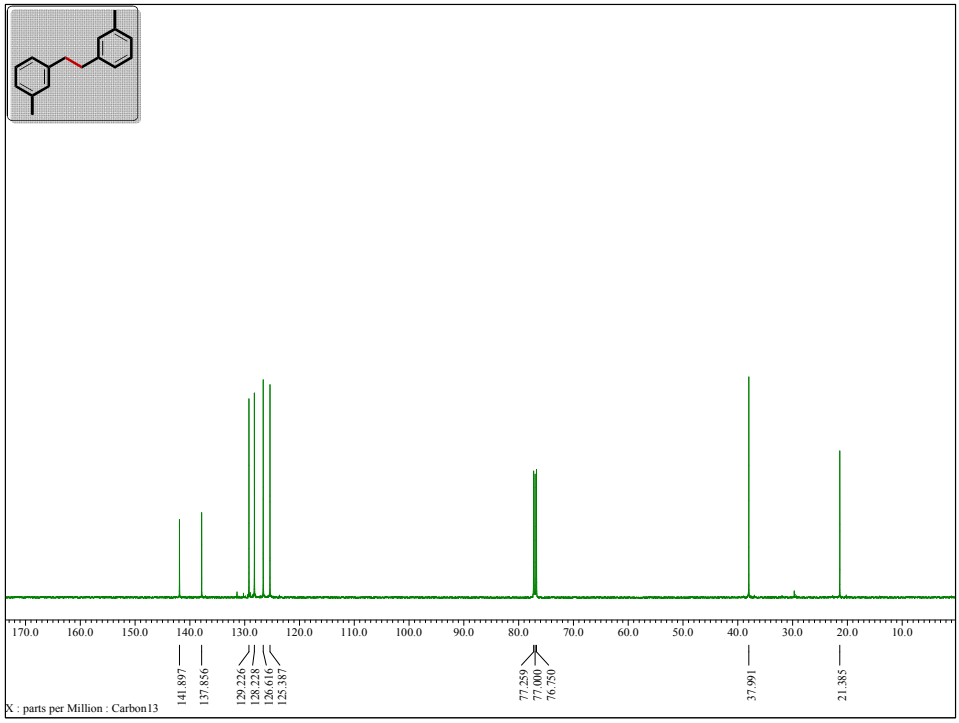
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30.0
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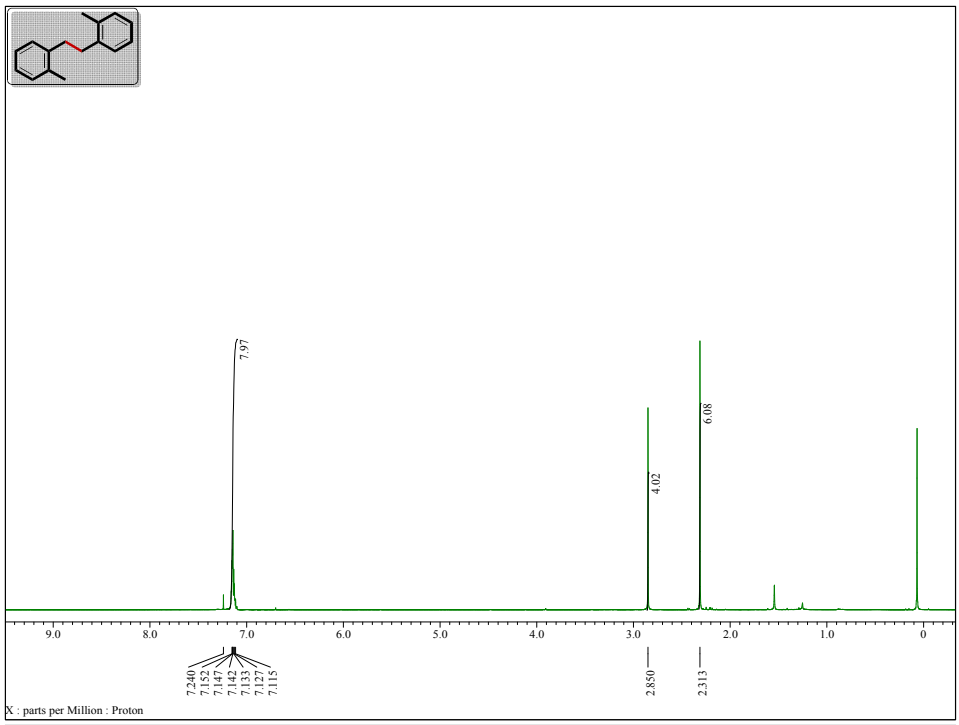
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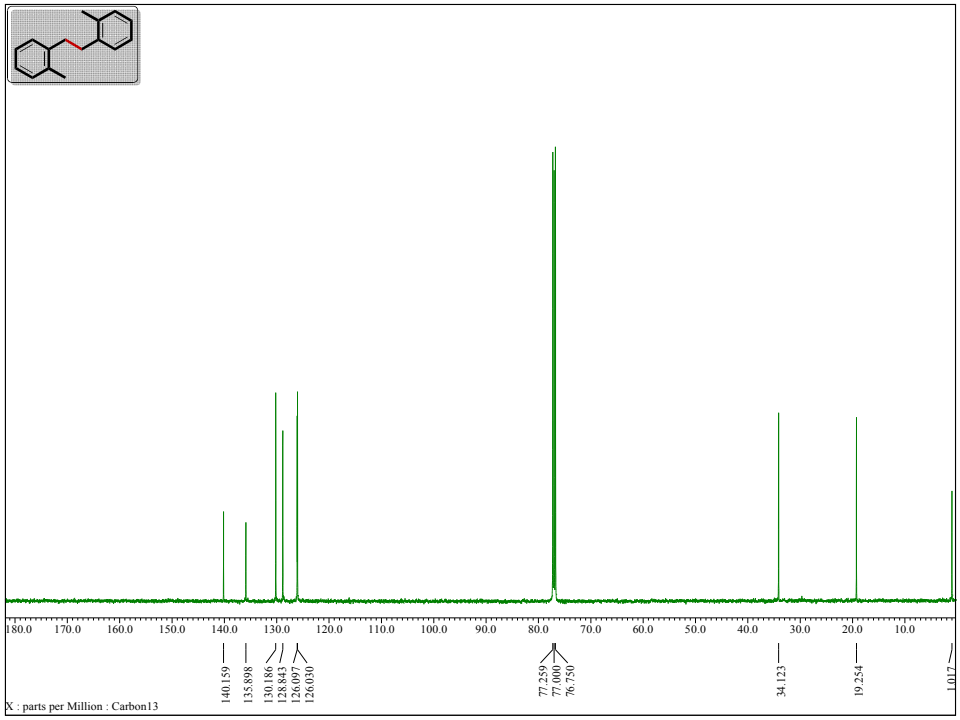
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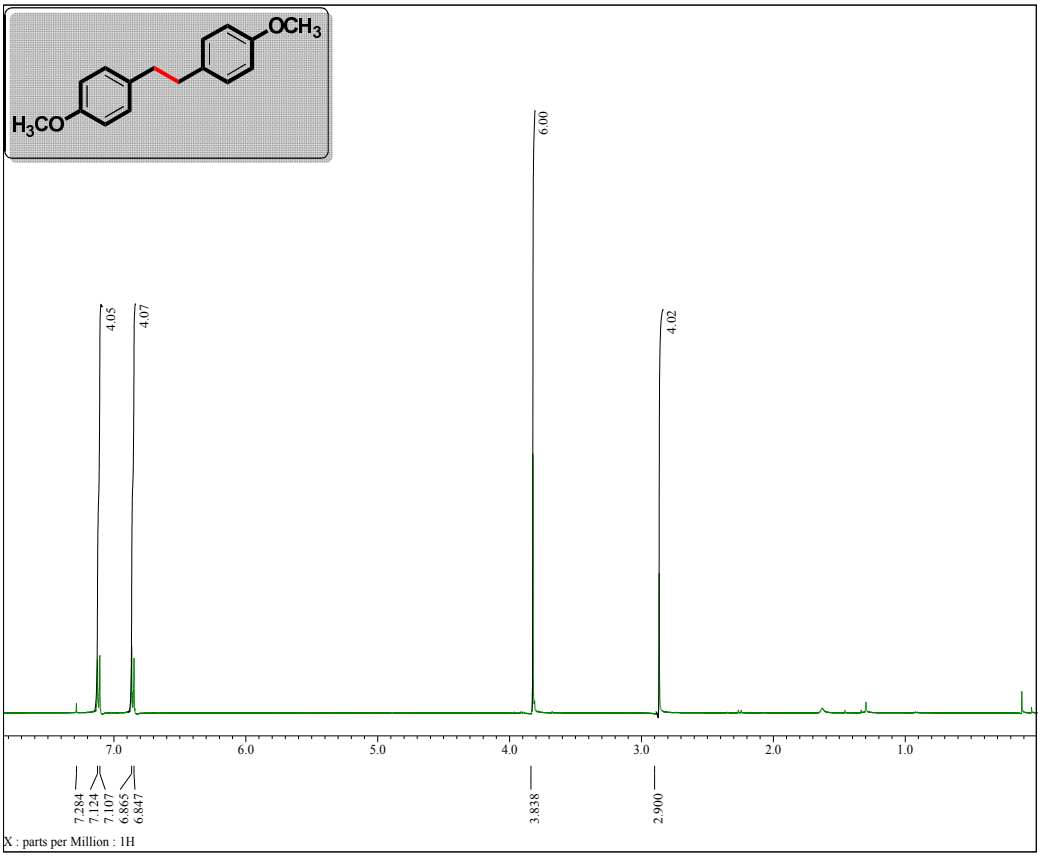
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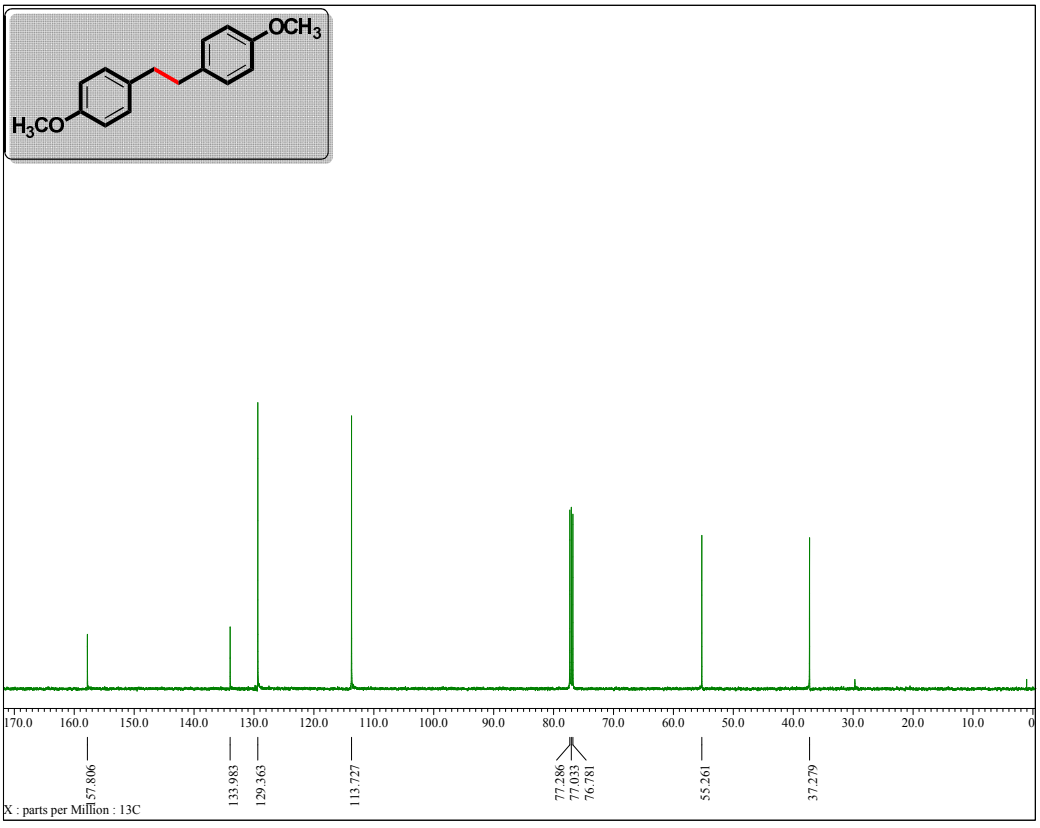
X : parts per Million : 1H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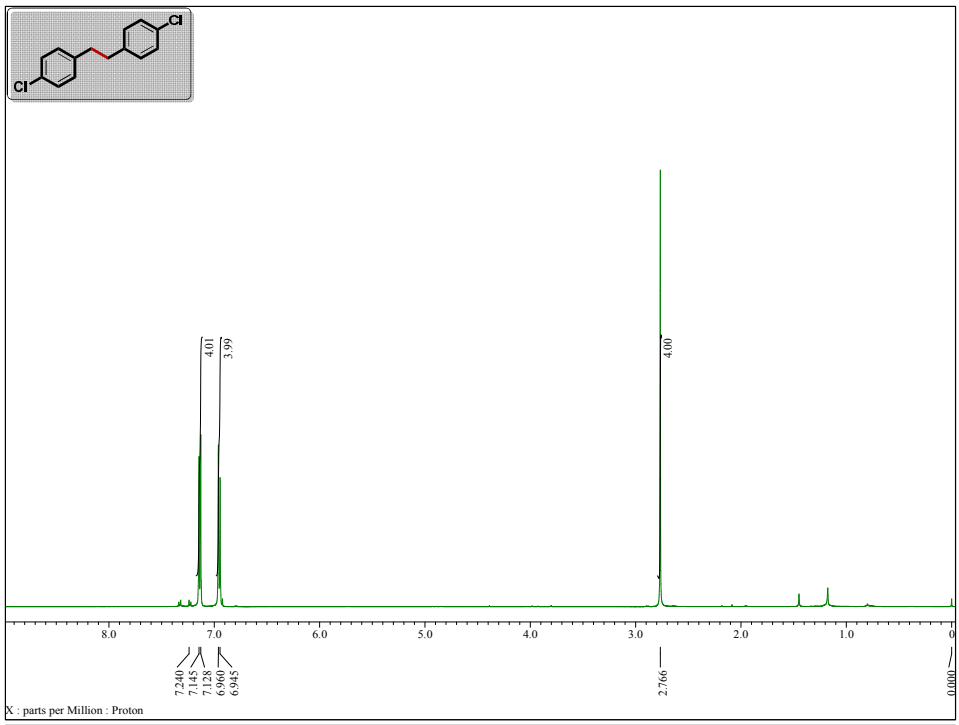
60.0
50.0
40.0
30.0
20.0
10.0
0
57.806
133.983
129.363
113.727
77.286
77.033
76.781
55.261
37.279
X : parts per Million : 13C


Cl
Cl
4.01
3.99
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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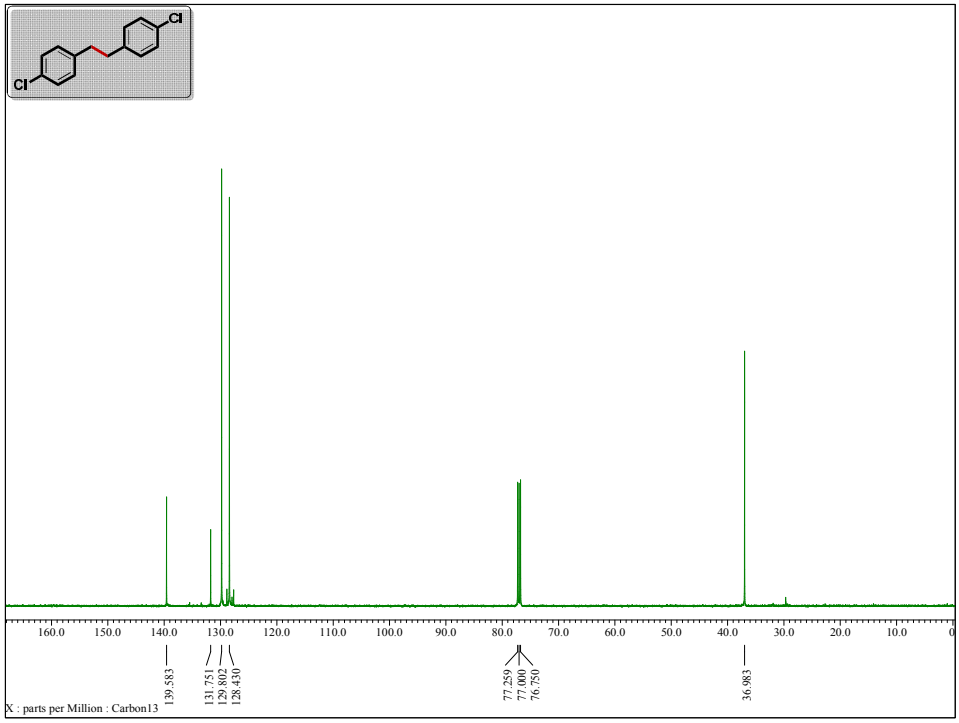
0
7.240
7.145
7.128
6.960
6.945
2.766
0.000
X : parts per Million : Proton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Cl
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100.0
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
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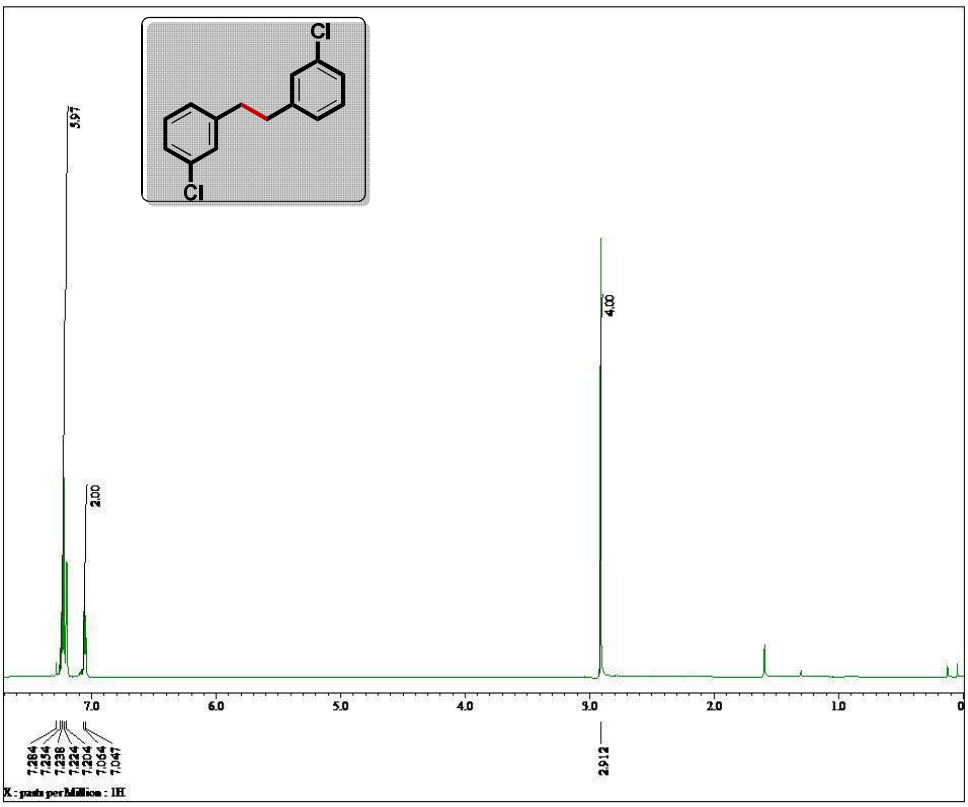
131.751
129.802
128.430
77.259
77.000
76.750
36.983
X : parts per Million : Carbon13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Cl
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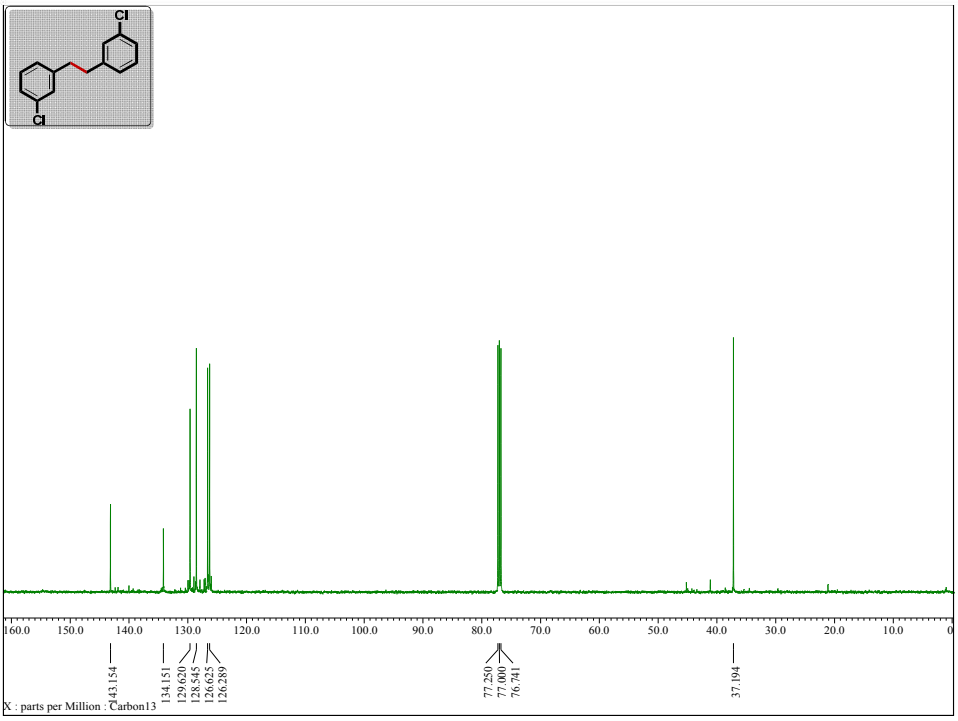
4.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.284
7.254
7.238
7.224
7.204
7.054
7.047
2.912
X : parts per Million : 1H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Cl
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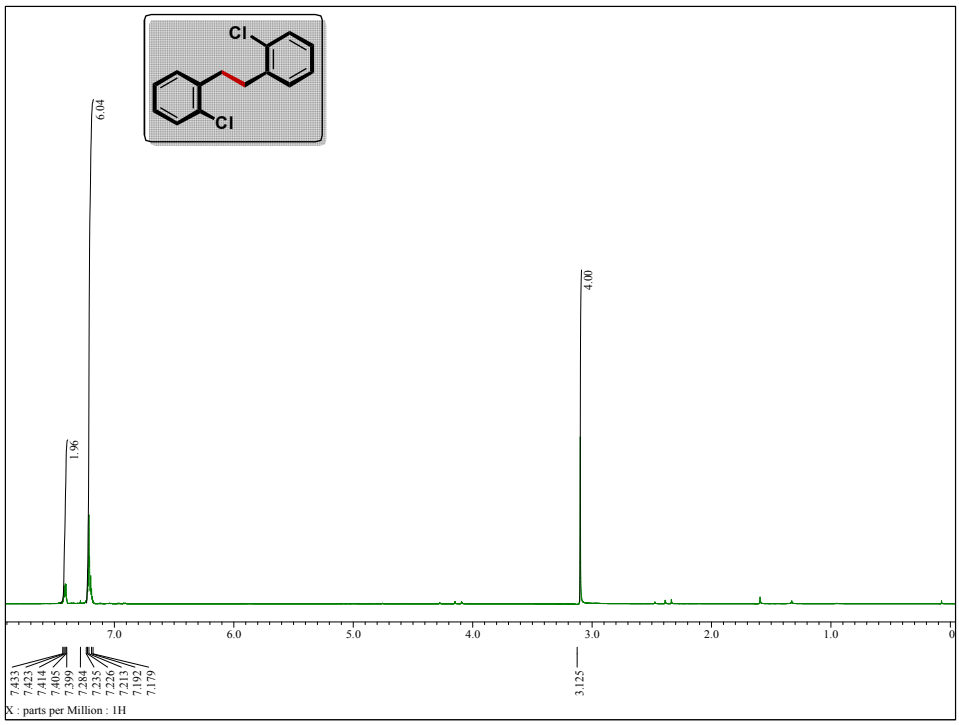
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.154
134.151
129.620
128.545
126.625
126.289
77.250
77.000
76.741
37.194
X : parts per Million : Carbon13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Cl
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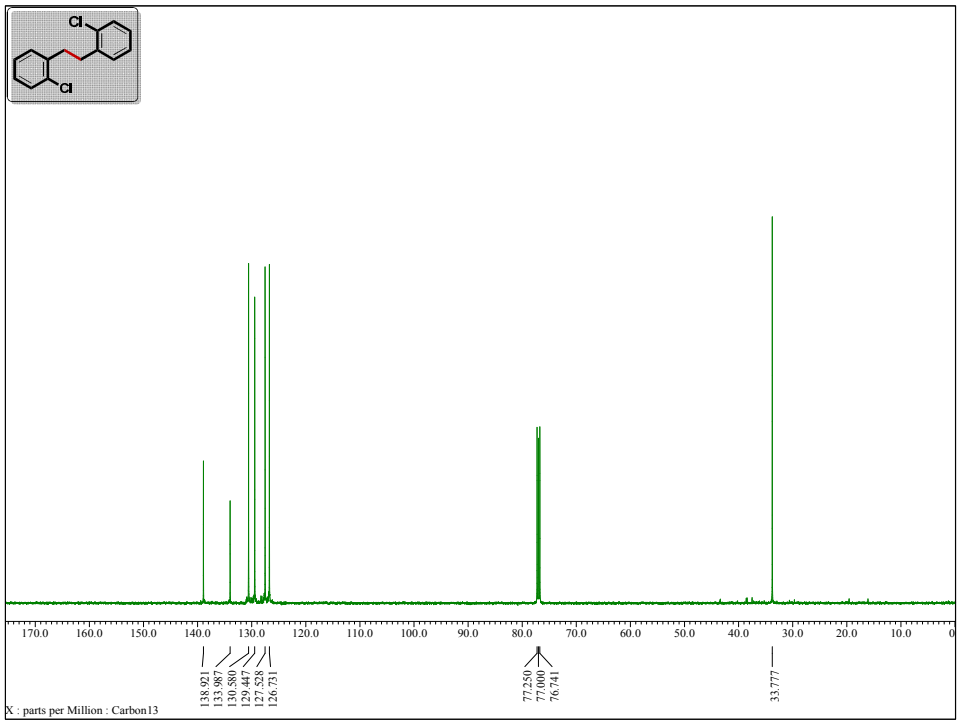
4.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.433
7.423
7.414
7.405
7.399
7.284
7.235
7.226
7.213
7.192
7.179
3.125
X : parts per Million : 1H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Cl
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.921
133.987
130.580
129.447
127.528
126.731
77.250
77.000
76.741
33.777
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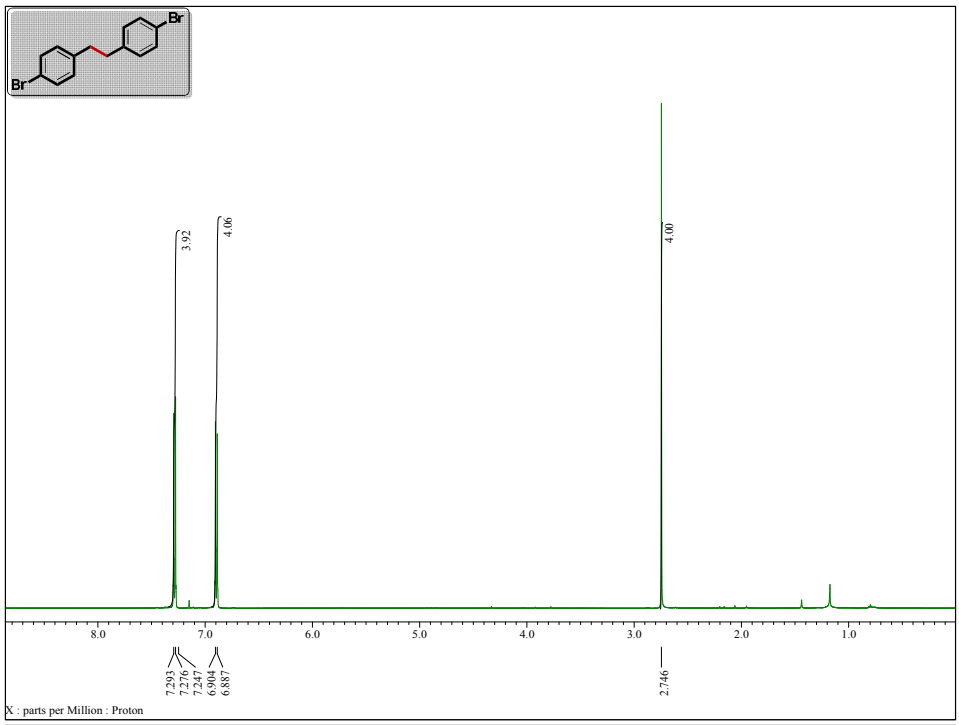
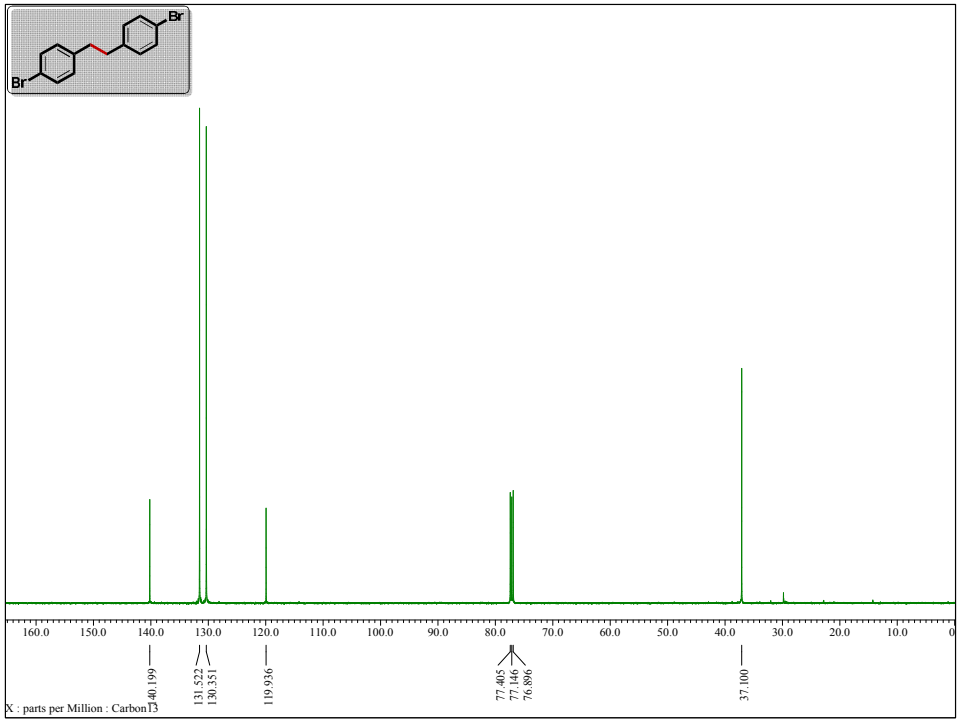

Br
Br
3.92
4.06
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.293
7.276
7.247
6.904
6.887
2.746
X : parts per Million : Proton


Br
Br
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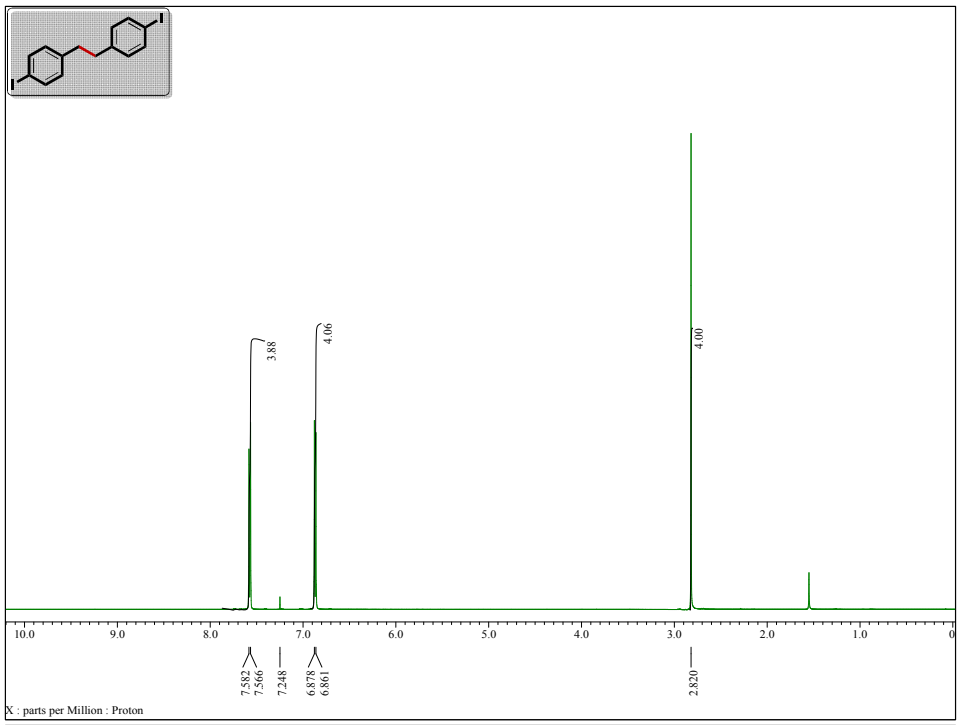
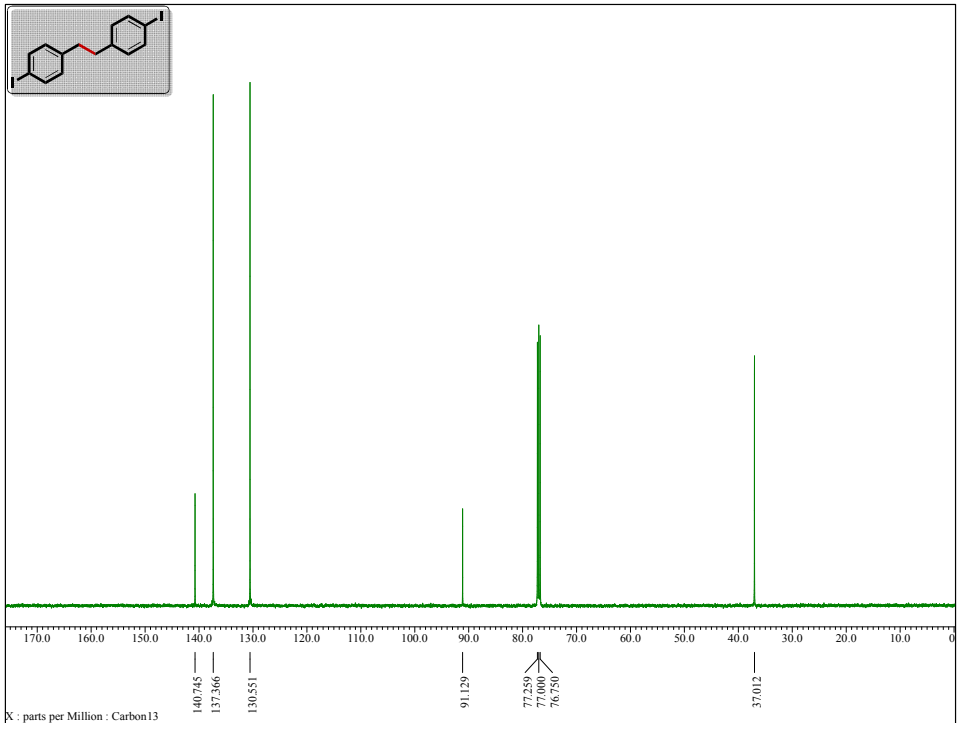
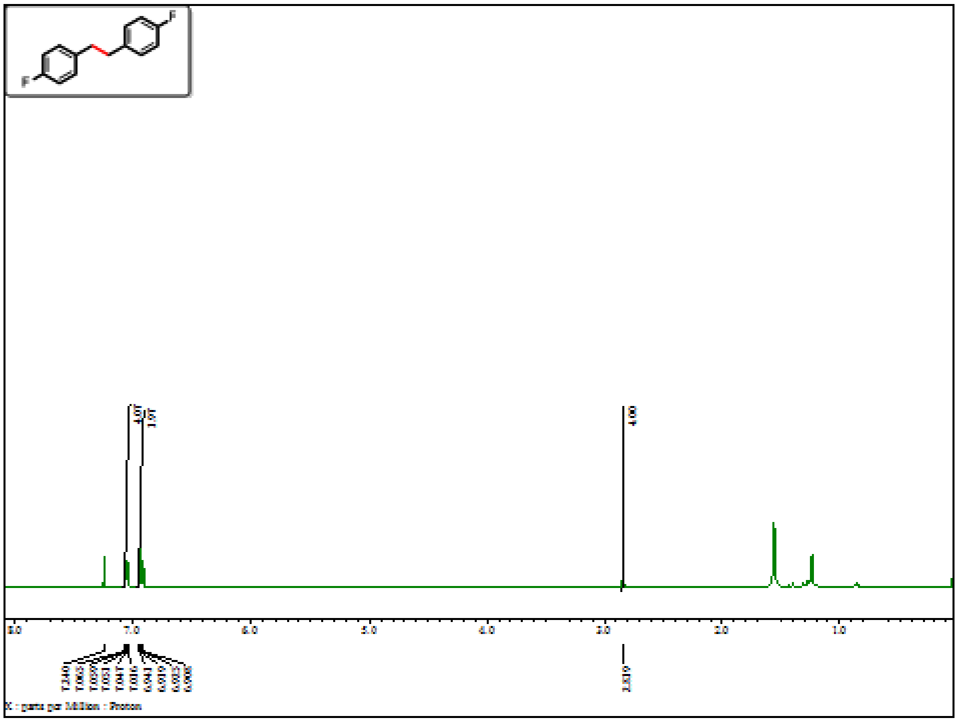
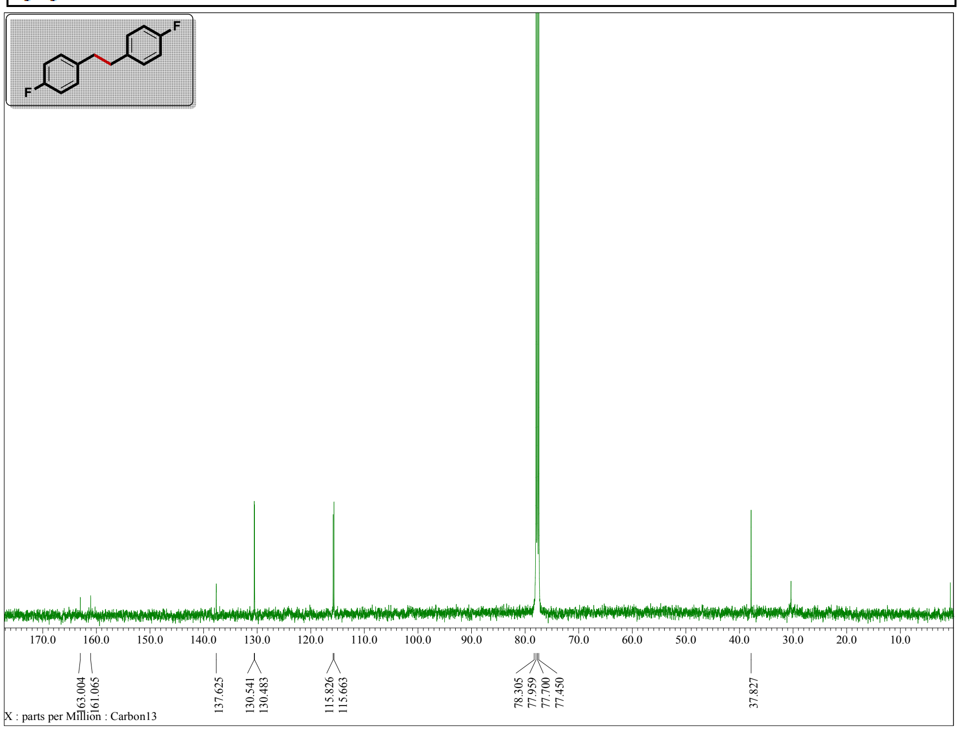
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
140.199
131.522
130.351
119.936
77.405
77.146
76.896
37.100
X : parts per Million : Carbon13


3.88
4.06
4.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.582
7.566
7.248
6.878
6.861
2.820
X : parts per Million : Proton


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
140.745
137.366
130.551
91.129
77.259
77.000
76.750
37.012
X : parts per Million : Carbon13


F
F
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton


F
F
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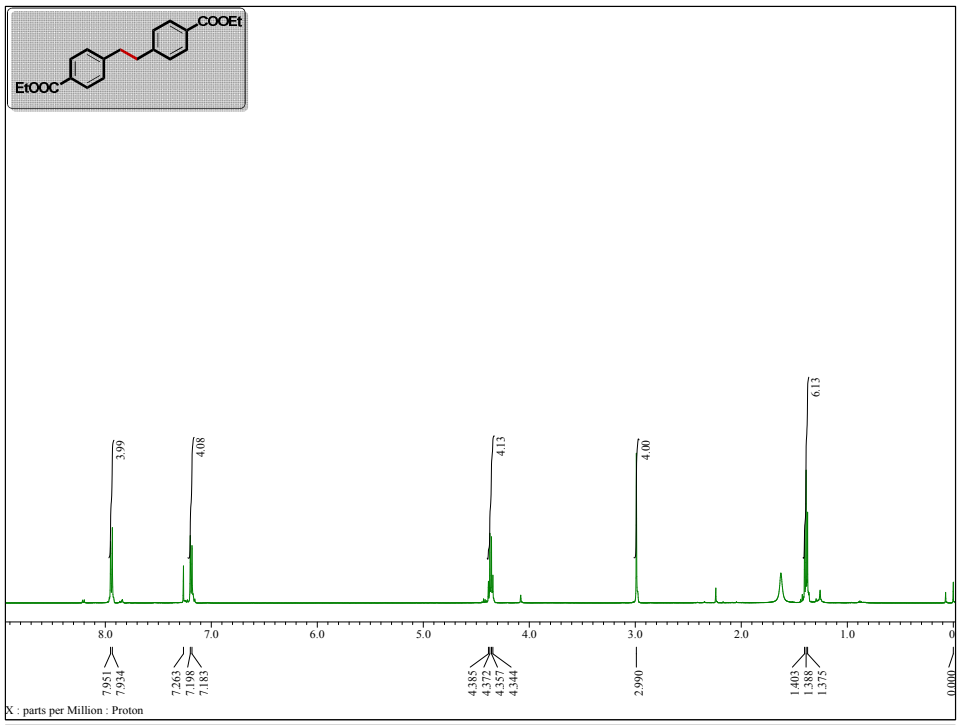
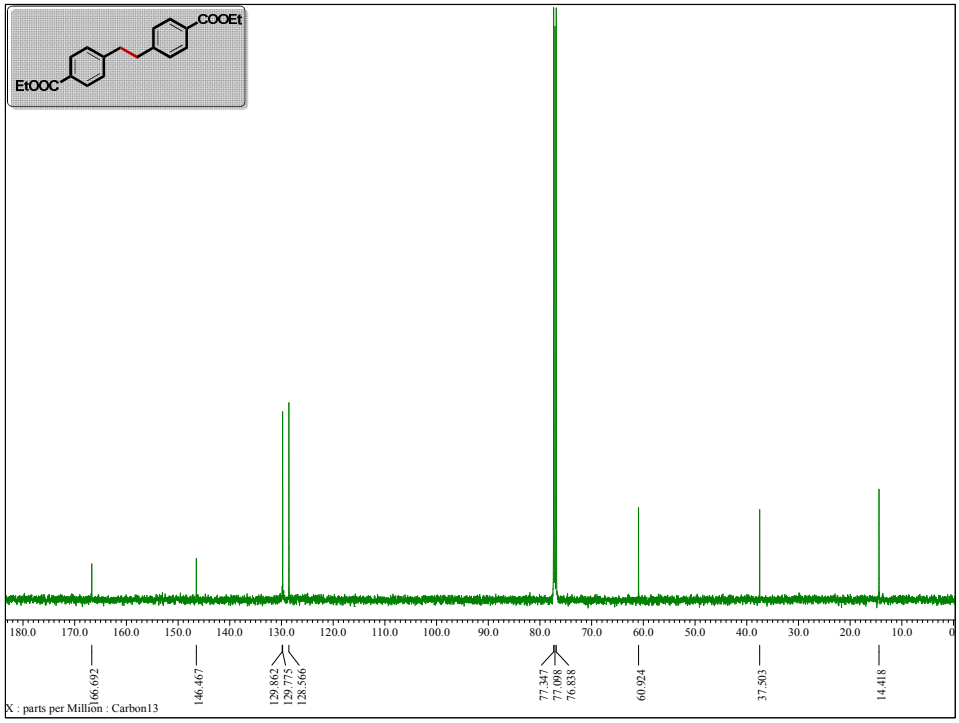
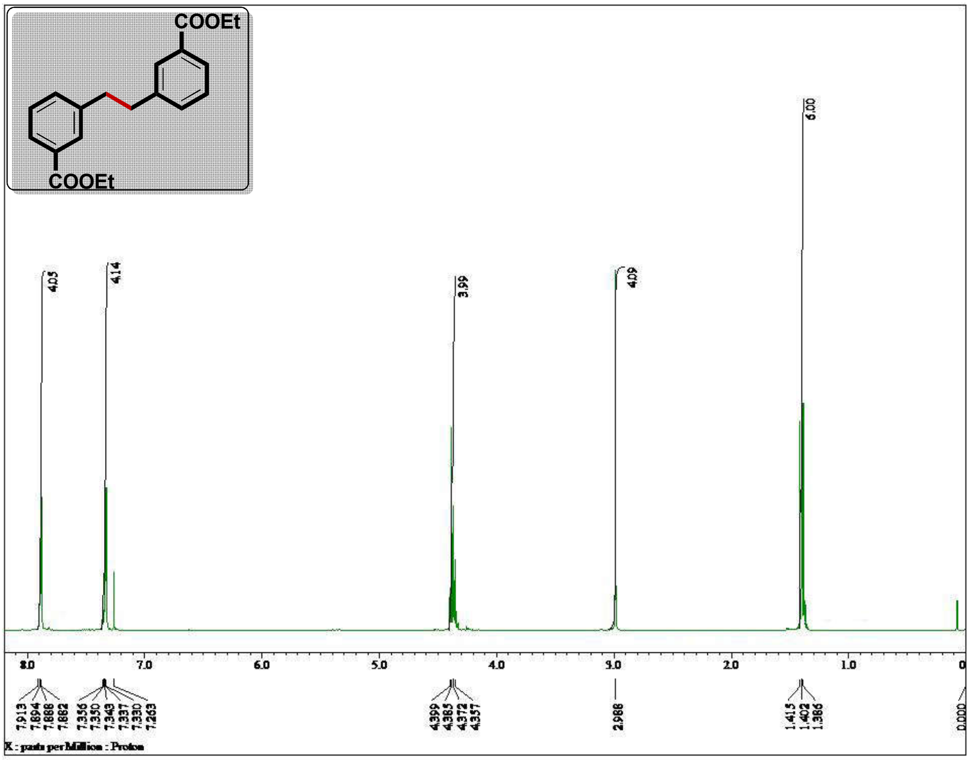
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
163.004
161.065
137.625
130.541
130.483
115.826
115.663
78.305
77.959
77.700
77.450
37.827
X : parts per Million : Carbon13


COOEt
EtOOC
3.99
4.08
4.13
4.00
6.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.951
7.934
7.263
7.198
7.183
4.385
4.372
4.357
4.344
2.990
1.403
1.388
1.375
0.000
X : parts per Million : Proton


COOEt
EtOOC
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
166.692
146.467
129.862
129.775
128.566
77.347
77.098
76.838
60.924
37.503
14.418
X : parts per Million : Carbon13


COOEt
COOEt
4.05
4.14
3.99
4.09
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.913
7.894
7.888
7.882
7.356
7.350
7.343
7.337
7.330
7.263
4.399
4.385
4.372
4.357
2.988
1.415
1.402
1.386
0.000
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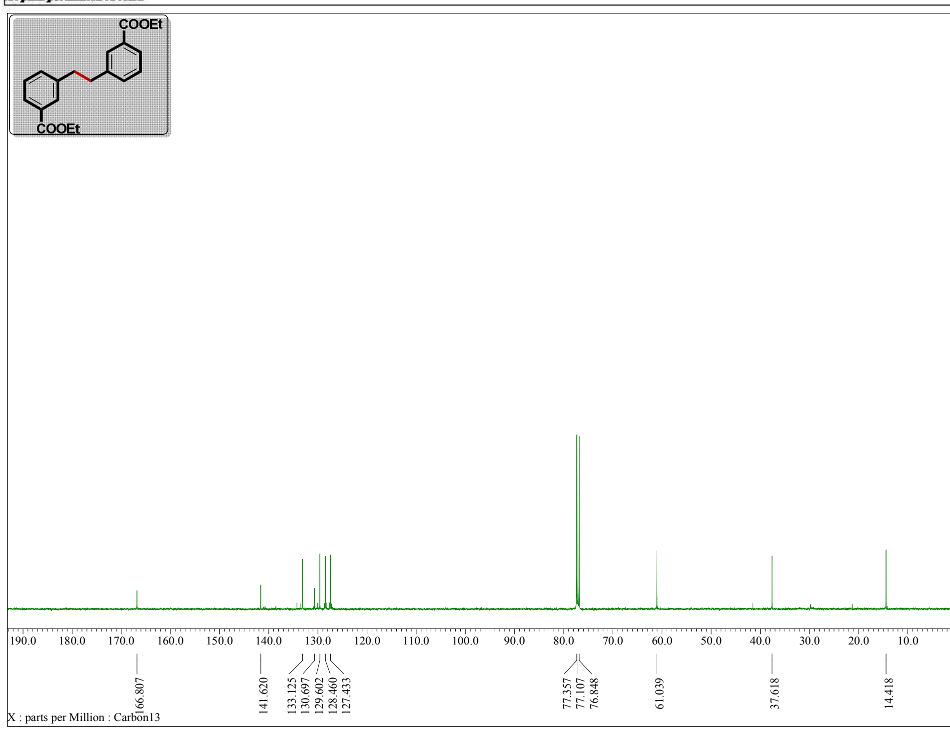
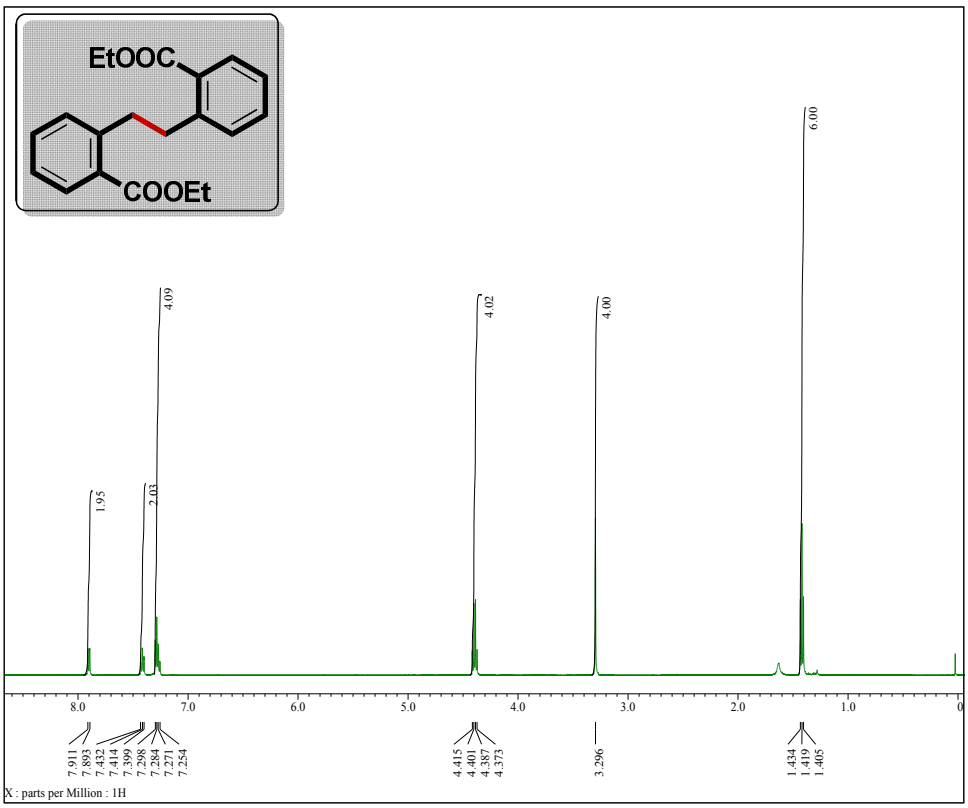
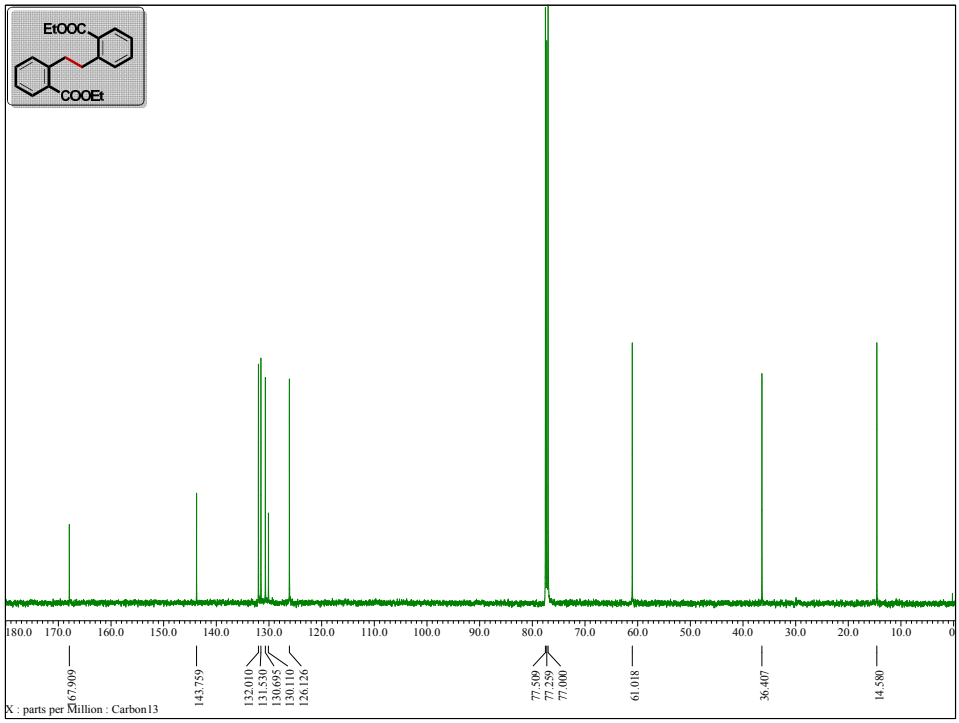
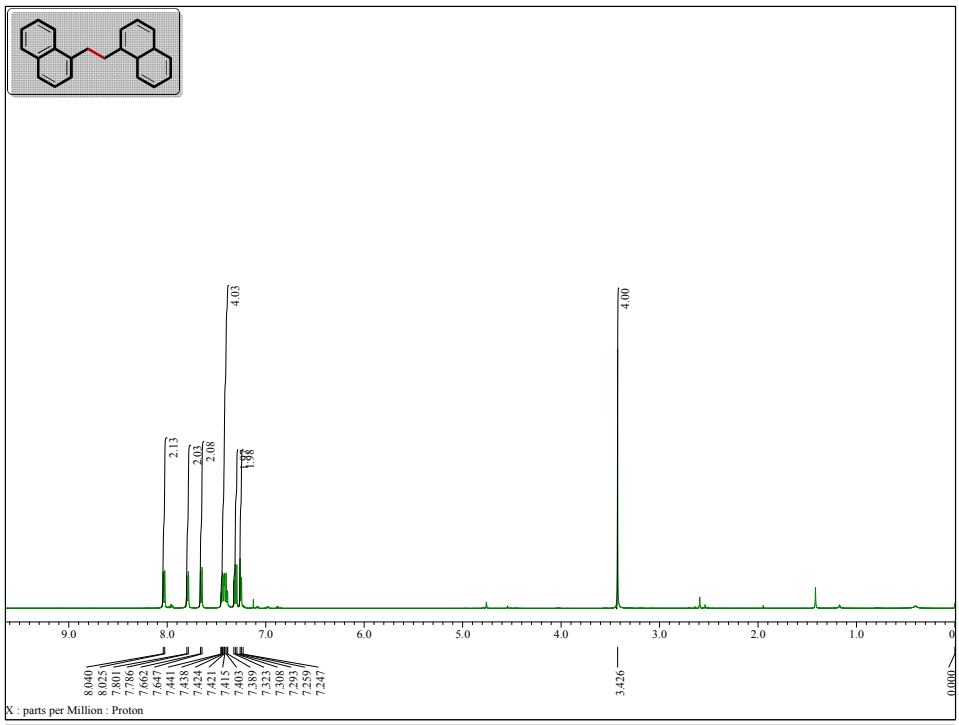
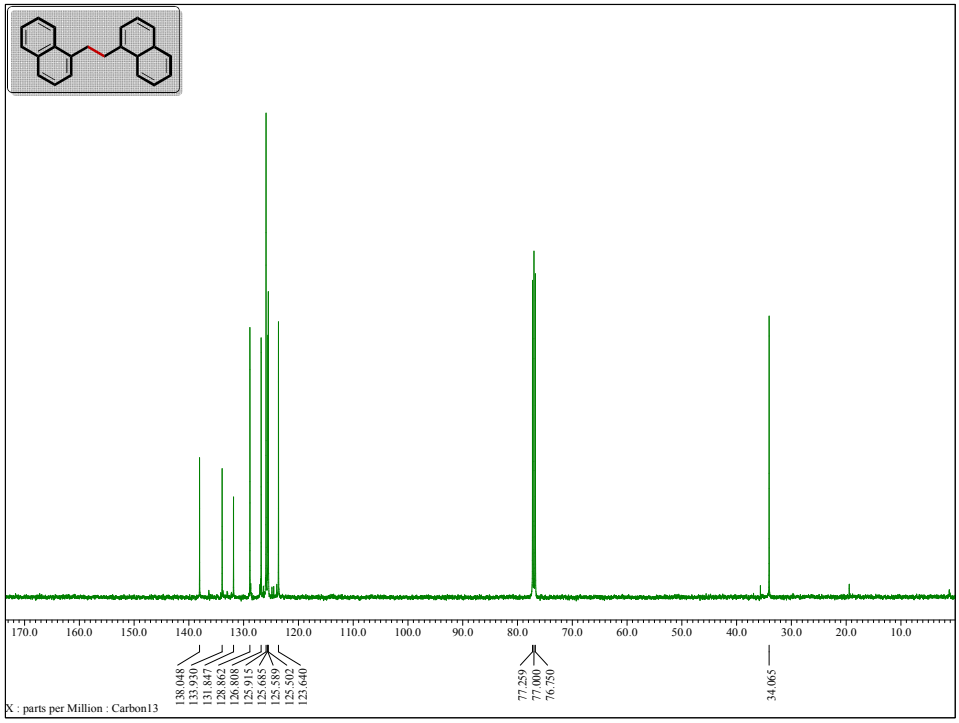

COOEt
COOEt
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
166.807
141.620
133.125
130.697
129.602
128.460
127.433
77.357
77.107
76.848
61.039
37.618
14.418
X : parts per Million : Carbon13


EtOOC
COOEt
6.00
4.09
4.02
4.00
2.03
1.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.911
7.893
7.432
7.414
7.399
7.298
7.284
7.271
7.254
4.415
4.401
4.387
4.373
3.296
1.434
1.419
1.405
X : parts per Million : 1H


EtOOC
COOEt
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
167.909
143.759
132.010
131.530
130.695
130.110
126.126
77.509
77.299
77.000
61.018
36.407
14.580
X : parts per Million : Carbon13


4.03
4.00
2.13
2.03
2.08
1.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.040
8.025
8.001
7.986
7.662
7.647
7.441
7.438
7.424
7.421
7.415
7.403
7.389
7.323
7.308
7.293
7.259
7.247
3.426
0.000
X : parts per Million : Proton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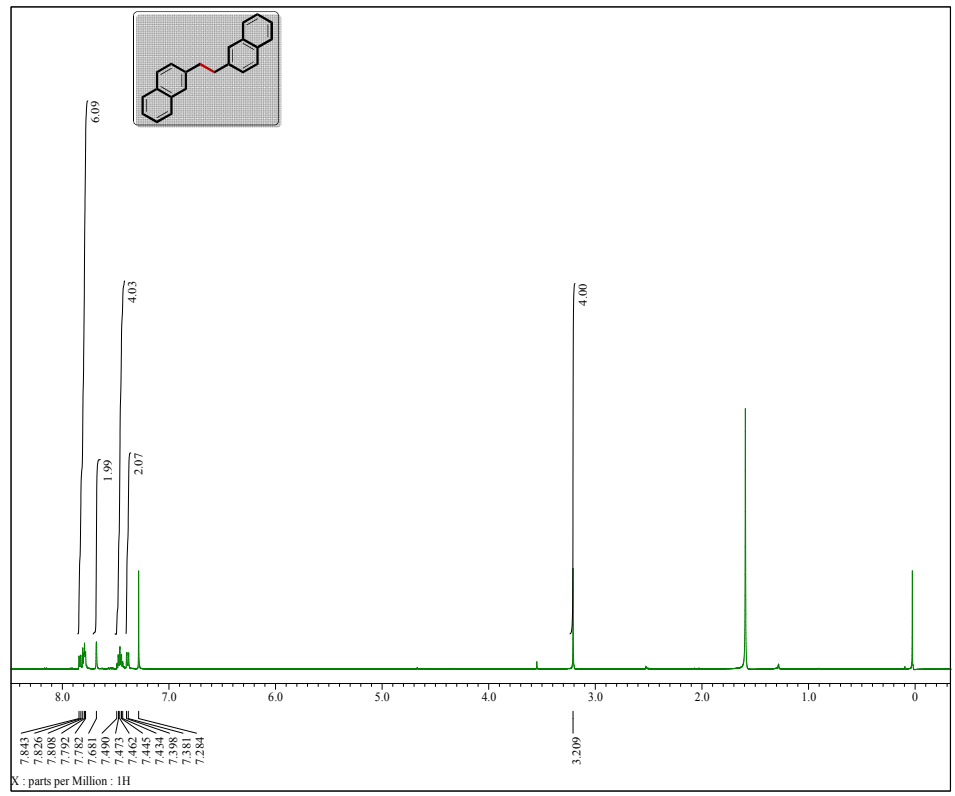
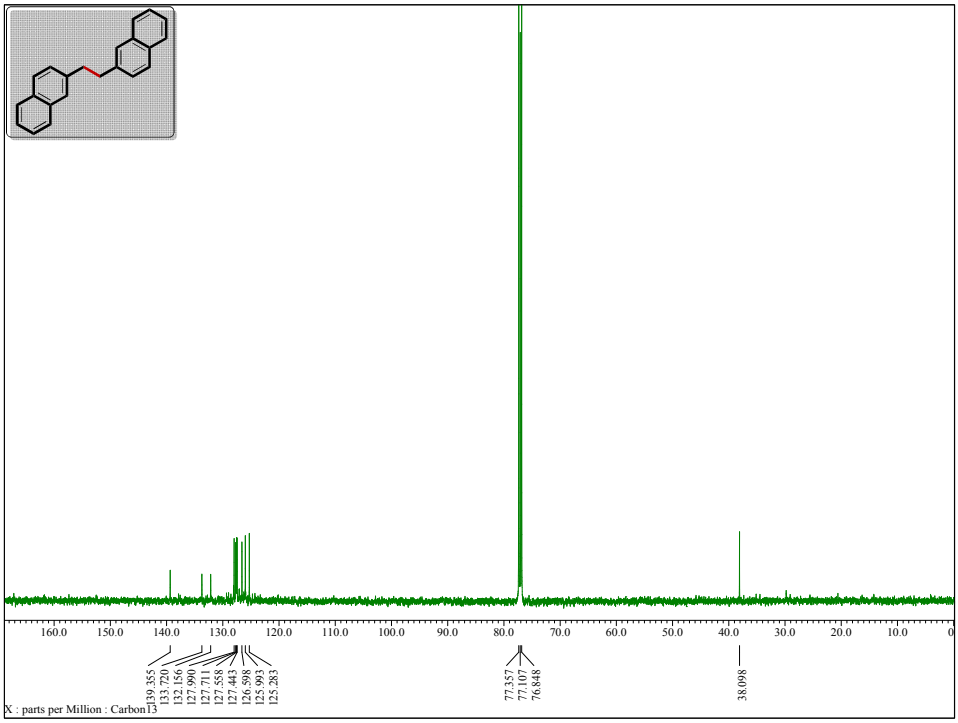
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
138.048
133.930
131.847
128.862
126.808
125.915
125.685
125.589
125.502
123.640
77.259
77.000
76.750
34.065
X : parts per Million : Carbon13


6.09
1.99
4.03
2.07
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.843
7.826
7.808
7.792
7.782
7.681
7.490
7.473
7.462
7.445
7.434
7.398
7.381
7.284
3.209
X : parts per Million : 1H


160.0
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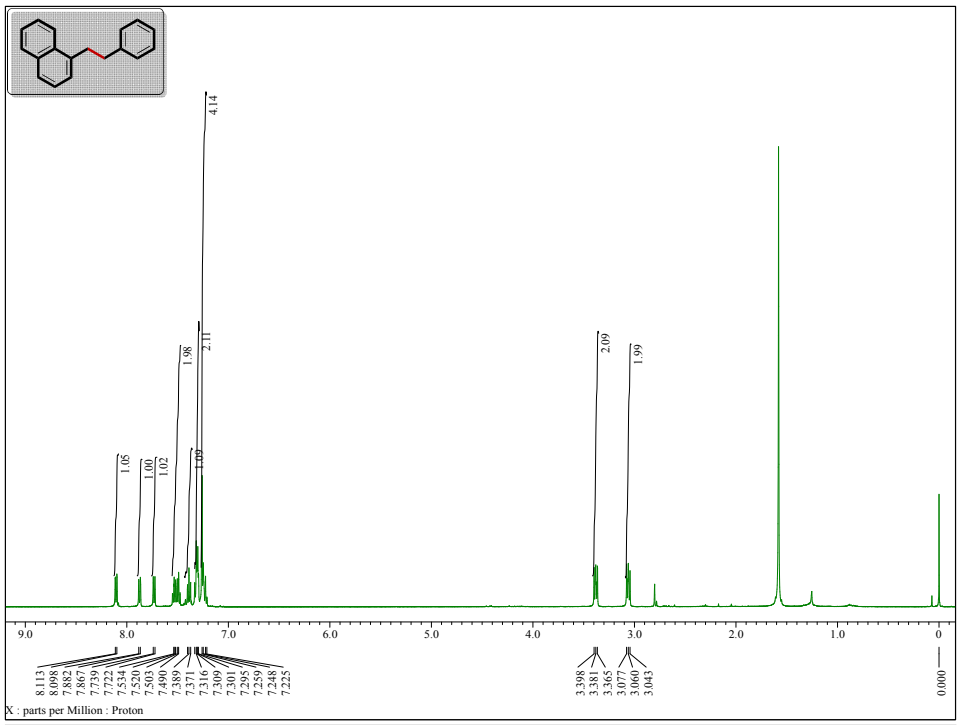
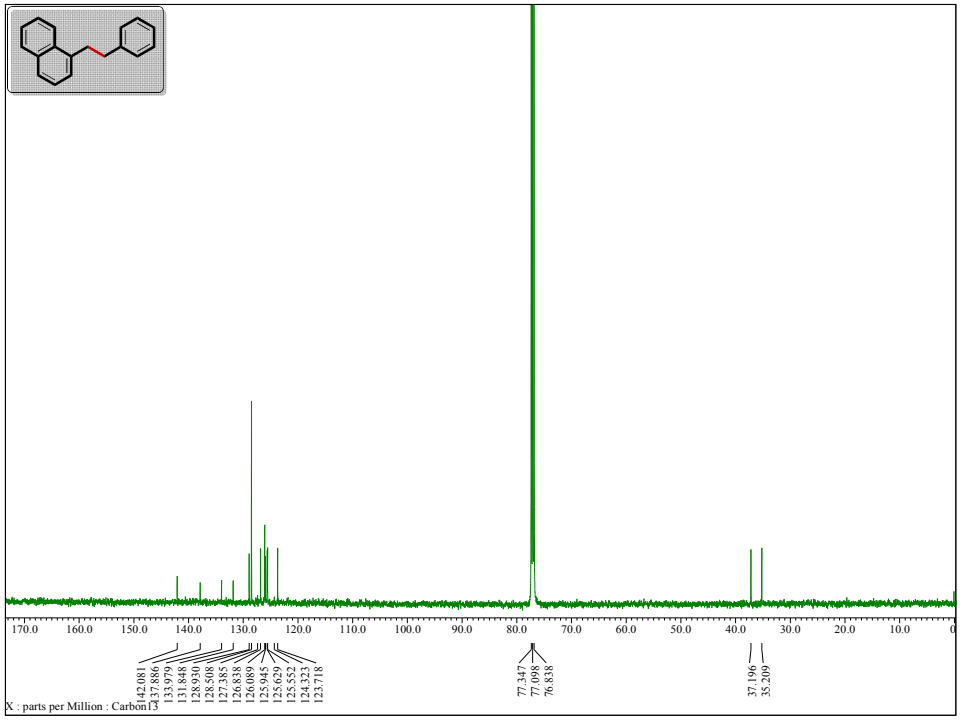
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.355
133.720
132.156
127.990
127.711
127.558
127.443
126.598
125.993
125.283
77.357
77.107
76.848
38.098
X : parts per Million : Carbon13


4.14
2.11
1.98
2.09
1.99
1.05
1.00
1.02
1.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.113
8.098
7.882
7.867
7.739
7.722
7.534
7.520
7.503
7.490
7.389
7.371
7.316
7.309
7.301
7.295
7.259
7.248
7.225
3.398
3.381
3.365
3.077
3.060
3.043
0.000
X : parts per Million : Proton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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
142.081
137.886
133.979
131.848
128.930
128.508
127.385
126.838
126.089
125.945
125.629
125.552
124.323
123.718
77.347
77.098
76.838
37.196
35.209
X : parts per Million : Carbon13