Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

for

Towards a sustainable electrochemical activation for recycling CO_2: synthesis of bis-*O*-alkylcarbamates from aliphatic and benzyl diamines.

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1. Description of electrochemical cells.

a - Divided Electrochemical Cell

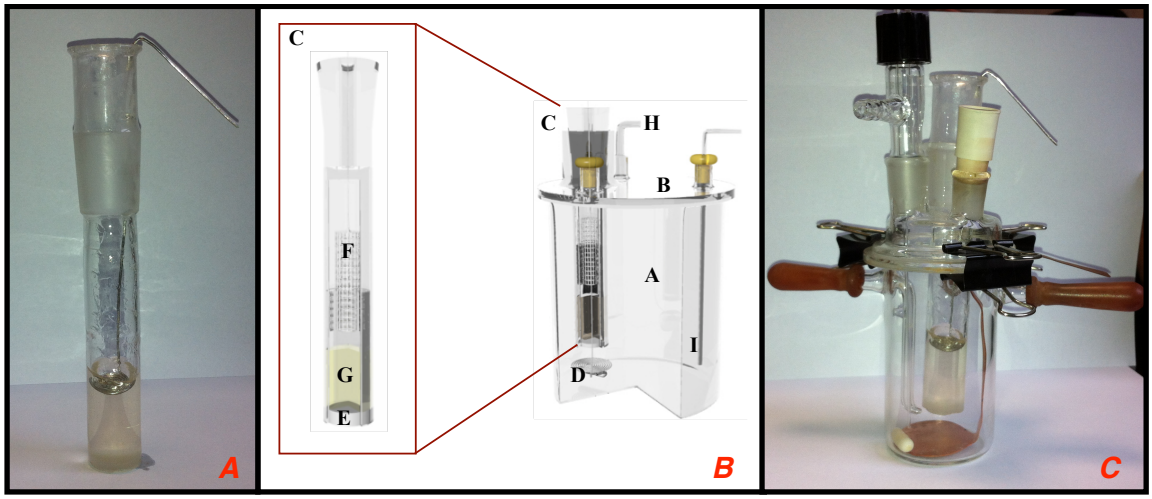


Figure S1. The cell (*panel B*) is composed of a beaker (A, *panel C*), which contains the copper cathode (D, $A \simeq 10$ cm^2), covered with a three-necked lid (B). A glass tube (C, *panel B*), endowed with a glass frit (E), is filled with methylcellulose gel (G) and contains the platinum anode (F, 99.9%, apparent area: $A \simeq 1$ cm^2). The gas inlet is provided by a pipette (I) which dips into the solution, while the gas outlet is ensured by a side-necked plug (H).

b - Undivided Electrochemical Cell

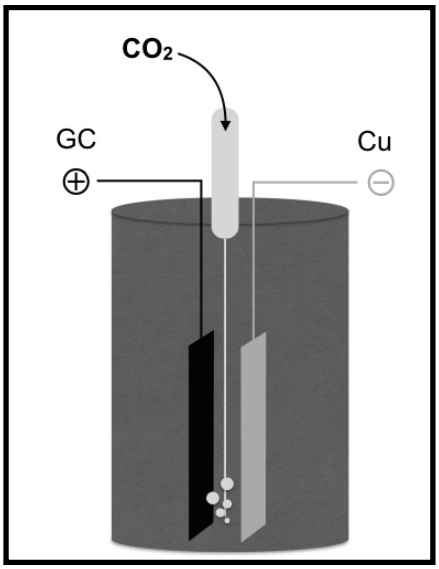


Figure S2. The cell is composed of a beaker which contains the copper cathode (Cu) and the glassy carbon anode (GC). The CO_2 inlet is provided by a glass pipette which dips into the solution.

c - H-shaped Electrochemical Cell

Figure S3. The cell (*panel A and B*) is an H-type open glass tube endowed with a glass frit (porosity: 3; *panel C*). Each of the two compartments ($\phi \simeq 1.4$ cm) contains one electrode: a copper foil (Cu, cathode) and a glassy carbon plate (GC, anode). The area of the electrodes is in the range 3-4 cm^2, depending on the amount of solvent used. The gas inlet is provided by glass pipettes close to the cathode surface.

2. Experimental procedures.

a - Materials and methods.

Electrolyses under galvanostatic control were carried out with an Amel 552 potentiostat equipped with an Amel 721 integrator. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC 200 spectrometer using $CDCl_3$ as internal standard.

Cu electrodes were custom made from a copper foil (99.98%, thickness 0.25 mm, Sigma-Aldrich). Prior to each experiments, the electrode was cleaned in 10% HNO_3 until uniform color, rinsed with deionized water, and oven-dried.

HPLC grade acetonitrile (≥ 99.9%, Sigma-Aldrich) was used in all the experiments. Tetraethylammonium chloride and tetrafluoroborate (≥ 99.9%, Sigma-Aldrich) were stored in a desiccator. All other reagents were used as received.

Each experiment described was repeated at least three times, and the yields (reported as average values in the manuscript) are calculated on the amount of product isolated after purification.

*b - General protocol to alkyl dicarbamate esters (**divided cell setup**).*

In a two-compartment electrochemical cell (see Fig. S1) typically 20 to 30 mL of 0.1 M of tetraethylammonium tetrafluoroborate ($TEABF_4$) in CH_3CN were added to the cathodic compartment and gaseous CO_2 was bubbled in. A 25 mA current was applied (I = 25 $mA \cdot cm^{-2}$) until the consumption of 300 C (3.0 Faradays per mole of amino-group). The current was stopped, the anodic compartment was removed and the solution was flushed with a nitrogen stream for 10'. The amine (0.5 mmol) was added to the catholyte and the solution was kept under nitrogen atmosphere while stirring. After 1 hour, the cathode was removed and the alkylating agent (5.0 mmol) was added. The solution was allowed to stand overnight under constant stirring at room temperature. The crude reaction was purified by flash column chromatography (silica gel, AcOEt:*n*-hexane) to afford the pure dicarbamate esters.

Methylcellulose gel. Prepared with 1M solution of tetraethylammonium chloride in DMF (7g methylcellulose/100 mL solution).

*c - General protocol to alkyl dicarbamate esters (**undivided cell setup**).*

Gaseous CO_2 was bubbled in a single-compartment electrochemical cell (see Fig. S2) typically containing 20 to 30 mL of 0.1 M of tetraethylammonium tetrafluoroborate

($TEABF_4$) in CH_3CN. A 25 mA current was applied (I = 25 mA·cm^{-2}) until the consumption of 300 C (3.0 Faradays per mole of amino-group). The current was stopped, the electrodes removed, and the solution was flushed with a nitrogen stream for 10'. The amine (0.5 mmol) was added and the solution kept under nitrogen atmosphere while stirring. After 1 hour, the alkylating agent (5.0 mmol) was added. The solution was allowed to stand overnight under constant stirring at room temperature. The crude reaction was analyzed by NMR spectroscopy.

*d - General protocol to alkyl dicarbamate esters (**H-cell setup**).*

In an H-shaped electrochemical cell (see Fig. S3) typically 10 mL of 0.1 M of tetraethylammonium chloride (TEAC) in CH_3CN were added to both compartments and gaseous CO_2 was bubbled into the cathodic side. A 50 mA current was applied (electrode apparent surface area ≃ 3 cm, I ≃ 15 mA·cm^{-2}) until the consumption of 300 C (3.0 Faradays per mole of amino group).

The current was stopped, the electrodes removed and the solution in the cathodic compartment was placed in a round-bottom flask containing the diamine (0.5 mmol). The solution was stirred for 1 hour and then the alkylating agent (2.0 mmol) was added. When butyl iodide was used, the solution was allowed to stand overnight at room temperature under constant stirring while, in the case of butyl chloride, the reaction mixture was heated at 80 °C for 3 hours before the workup. The solvent was evaporated under reduced pressure and the remaining solid was extracted with ethyl acetate (3 times). The organic layers were combined and evaporated in vacuo. The crude reaction mixture was purified by flash column chromatography (silica gel, AcOEt:*n*-hexane) to afford the pure dicarbamate esters.

***Diethyl hexane-1,6-diyldicarbamate, 7**.[a]*

White powder, > 90%. ^{1}H NMR (200 MHz, $CDCl_3$) δ= 4.78 (bs, 2H), 4.06 (q, J = 7.2 Hz, 4H), 3.11 (app. q, 4H), 1.49-1.42 (m, 4H), 1.32-1.27 (m, 4H), 1.20 (t, J = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 156.8, 60.7, 40.8, 30.00, 26.3, 14.7. Rf = 0.3 (*n*-hexane: ethyl acetate 8:2).

***Dibutyl hexane-1,6-diyldicarbamate, 8**.[a]*

White powder, ≥ 82% yield (BuI), ≥ 82% yield (BuCl). ^{1}H NMR (200 MHz, $CDCl_3$) δ= 5.00 (bs, 2H), 3.93 (t, J = 6.0 Hz, 4H), 3.04 (app. q, 4H), 1.51-1.24 (m, 16H, overlapped with

H_2O signal), 0.82 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 156.9, 64.4, 40.6, 31.0, 29.8, 26.2, 19.0, 13.6. R*f* = 0.3 (*n*-hexane: ethyl acetate 7:3).

Dibutyl (methylene-bis(cyclohexane-4,1,diyl))dicarbamate, 9.[a]

Off-white waxy solid, ≥ 83% yield (BuI), ≥ 85% yield (BuCl). ^1H NMR (200 MHz, $CDCl_3$) δ= 4.77-4.73 (m, 1H), 4.50-4.45 (m, 1H), 4.03 (t, *J* = 6.2 Hz, 4H), 3.76 (bs, 1H), 3.41 (bs, 1H), 2.01-1.96 (m, 2H), 1.75-1.05 (m, 26H, overlapped with H_2O signal), 0.92 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 156.1, 64.6, 50.4, 47.0, 44.1, 43.0, 33.8, 33.7, 33.5, 32.8, 32.1, 31.2, 29.8, 28.1, 19.2, 13.9. R*f* = 0.3 (*n*-hexane: ethyl acetate 8:2).

Butyl ((5-((butoxycarbonyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate, 10.[a]

Yellowish oil, ≥ 92% yield (BuI), ≥ 87% yield (BuCl). ^1H NMR (200 MHz, $CDCl_3$) δ= 4.78-4.72 (m, 1H), 4.49-4.54 (m, 1H), 4.06-4.00 (m, 4H), 3.77 (bs, 1H), 3.25 (d, *J* = 6.2 Hz, 0.4H), 2.90 (d, *J* = 6.6 Hz, 1.5H), 1.74-1.15 (m, 11H, overlapped with H_2O signal), 1.04 (s, 6H), 0.95-0.87 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 157.2, 157.1*,156.1, 64.7, 64.5, 54.9, 47.5*, 47.1, 46.4, 44.5, 42.7*, 41.9, 36.4, 35.1, 31.9, 31.8*, 31.1, 29.7, 27.7, 23.2, 19.12, 19.09, 13.8. R*f* = 0.3 and 0.2 - pair of diastereomers - (*n*-hexane: ethyl acetate 8:2).

* *minor diastereomers*.

Dibutyl (1,3-phenylenebis(methylene))dicarbamate, 11.[b]

White solid, ≥ 85% yield (BuI), ≥ 82% yield (BuCl). ^1H NMR (200 MHz, $CDCl_3$) δ= 7.22-7.11 (m, 4H), 5.41 (bs, 2H), 4.24 (d, *J* = 5.8 Hz, 4H), 4.01 (t, *J* = 6.5 Hz, 4H), 1.58-1.47 (m, 4H), 1.37-1.26 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 156.9, 139.1, 128.8, 126.3, 64.8, 44.7, 31.0, 19.0, 13.7. R*f* = 0.1 (*n*-hexane: ethyl acetate 8:2).

Diethyl (4-methyl-1,3-phenylene)dicarbamate, 12.[c]

Yellowish solid, 10% yield. ^1H NMR (200 MHz, $CDCl_3$) δ= 7.77 (d, J_m = 1.8 Hz, 1H), 7.22 (dd, J_o = 8.2 Hz, J_m = 1.8 Hz, 1H), 7.09 (d, J_o = 8.2 Hz, 1H), 6.64 (s, 1H), 6.40 (s, 1H), 4.28-4.15 (m, 4H), 2.19 (s, 3H), 1.35-1.27 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 153.9, 153.8, 136.9, 136.4, 130.9, 121.9, 114.4, 61.5, 61.3, 17.1, 14.7. R*f* = 0.2 (*n*-hexane: ethyl acetate 8:2).

Diethyl 1,4-phenylenedicarbamate, 13.[c]

White solid, 13% yield. ^1H NMR (200 MHz, $CDCl_3$) δ= 7.31 (s, 4H), 6.52 (bs, 2H), 4.21 (q, *J* = 7.2 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 153.9, 133.8, 119.8, 61.4, 14.7. R*f* = 0.2 (*n*-hexane: ethyl acetate 8:2).

Butyl benzylcarbamate.[d]

White solid, 63% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ= 7.35-7.28 (m, 5H, overlapped with $CDCl_3$ signal), 4.94 (bs, 1H), 4.37 (d, *J* = 6.0 Hz, 4H), 4.10 (t, *J* = 6.6 Hz, 2H), 1.68-1.54 (m, 2H), 1.43-1.32 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

*e - Preparation of **8** with butyl chloride at room temperature (under the use of ammonium iodides).*

- *TBAI in catalytic amount (H-cell setup).* In an H-shaped electrochemical cell (see Fig. S3) typically 10 mL of 0.1 M of TEAC in CH_3CN were added to both compartments and gaseous CO_2 was bubbled into the cathodic side. A 50 mA current was applied (electrode apparent surface area ≃ 3 cm, $I \simeq 15$ mA·cm^{-2}) until the consumption of 300 C (3.0 Faradays per mole of amino group). The current was stopped and the electrodes removed. The solution in the cathodic compartment was placed in a round-bottom flask containing hexamethylenediamine (0.5 mmol) and stirred for 1 hour. Butyl chloride (5.0 mmol) was added, followed by tetrabutylammonium iodide (TBAI, 1-5 mol%), and the solution was allowed to stand overnight at room temperature under constant stirring. The solvent was evaporated under reduced pressure and the remaining solid was extracted with ethyl acetate (3 times). The organic layers were combined and evaporated in vacuo. The crude reaction mixture was purified by flash column chromatography (silica gel, AcOEt:*n*-hexane) to afford the pure dicarbamate ester.
- *TEAI as Supporting Electrolyte.* In an H-shaped electrochemical cell (see Fig. S3) typically 10 mL of 0.1 M of tetraethylammonium iodide (TEAI) in CH_3CN were added to both compartments and gaseous CO_2 was bubbled into the cathodic side. A 50 mA current was applied (electrode apparent surface area ≃ 3 cm, $I \simeq 15$ mA·cm^{-2}) until the consumption of 300 C (3.0 Faradays per mole of amino group). The current was stopped, the electrodes removed and the solution in the cathodic compartment was placed in a round-bottom flask containing hexamethylenediamine (0.5 mmol). The solution was stirred for 1 hour and then butyl chloride (2.0 mmol) was added. The solution was allowed to stand overnight at room temperature under constant stirring. The solvent was evaporated under reduced pressure and the remaining solid was extracted with ethyl acetate (3 times). The organic layers were combined and

evaporated in vacuo. The crude reaction mixture was purified by flash column chromatography (silica gel, AcOEt:*n*-hexane) to afford the pure dicarbamate ester.

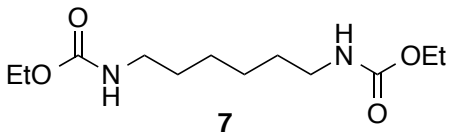
f - Selective carboxylation of benzylamine.

In an H-shaped electrochemical cell (see Fig. S3) typically 10 mL of 0.1 M of TEAC in CH_3CN were added to both compartments and gaseous CO_2 was bubbled into the cathodic side. A 50 mA current was applied (electrode apparent surface area ≃ 3 cm, I ≃ 15 $mA \cdot cm^{-2}$) until the consumption of 150 C.

The current was stopped, the electrodes removed and the solution in the cathodic compartment was placed in a round-bottom flask containing benzylamine (0.5 mmol) and *p*-toluidine (0.5 mmol). The solution was stirred for 1 hour and then butyl chloride (1.0 mmol) was added. The reaction mixture was heated at 80 °C for 3 hours before the workup.

The solvent was evaporated under reduced pressure and the remaining solid was extracted with ethyl acetate (3 times). The organic layers were combined and evaporated in vacuo. The crude reaction mixture was purified by flash column chromatography (silica gel, AcOEt:*n*-hexane) to afford butyl benzylcarbamate in 63% yield and butyl *p*-tolylcarbamate in less than 2%. NMR spectra of the isolated products are consistent with those reported in the literature.

3. NMR Spectra.



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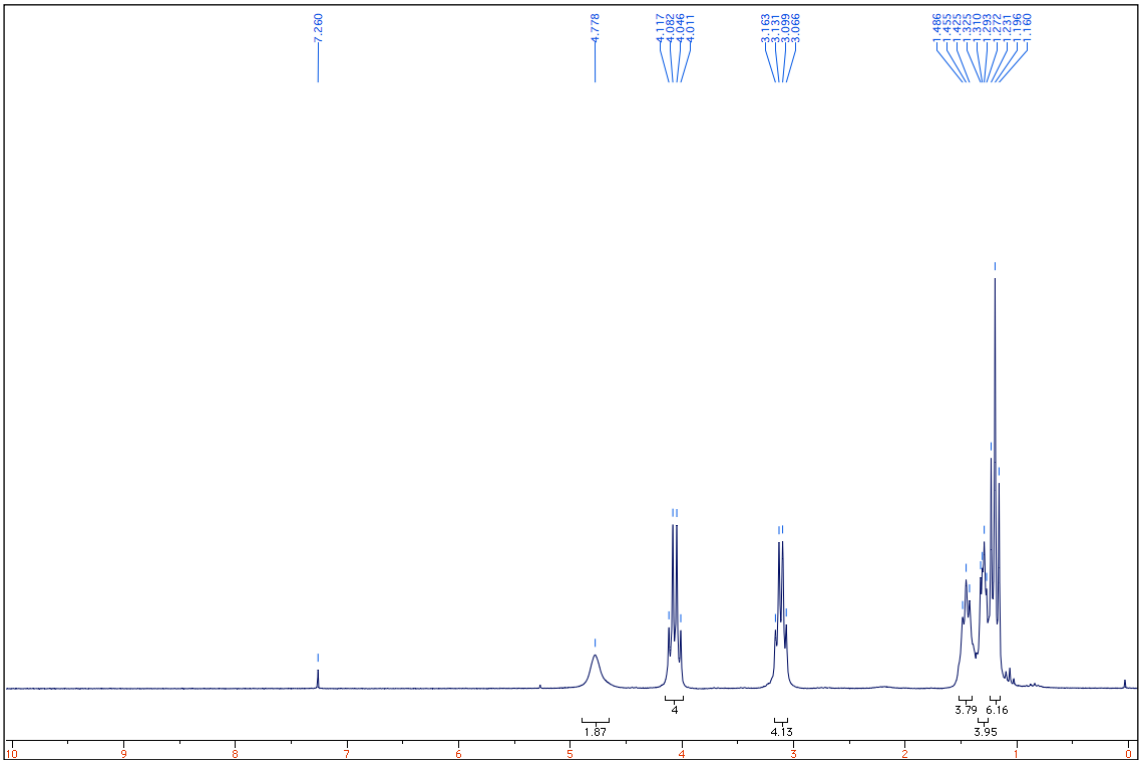

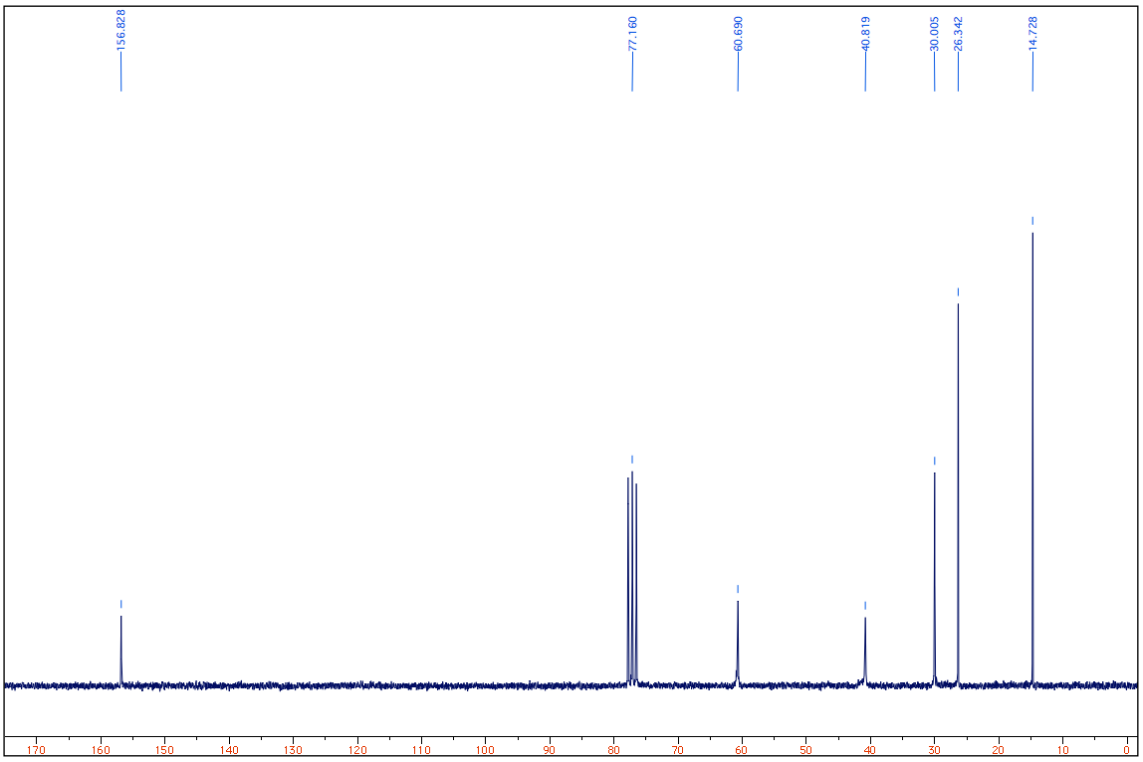

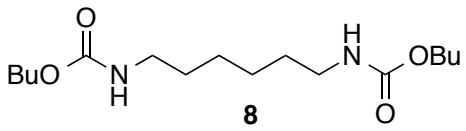
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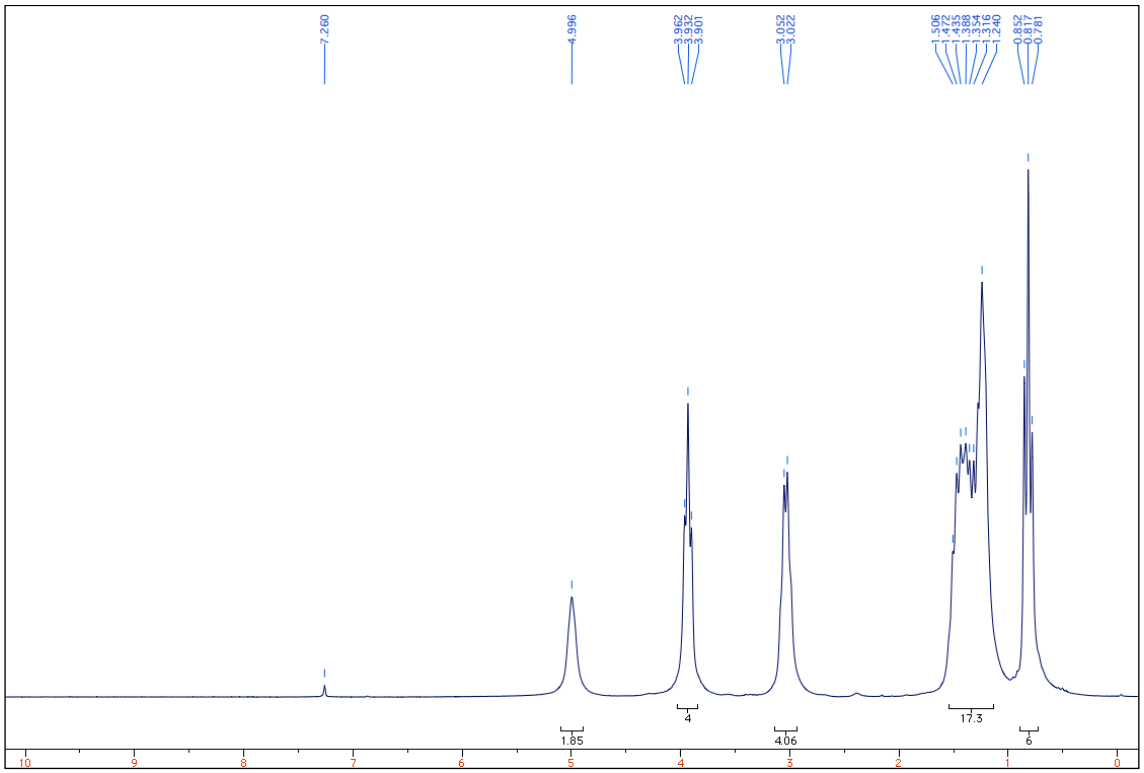
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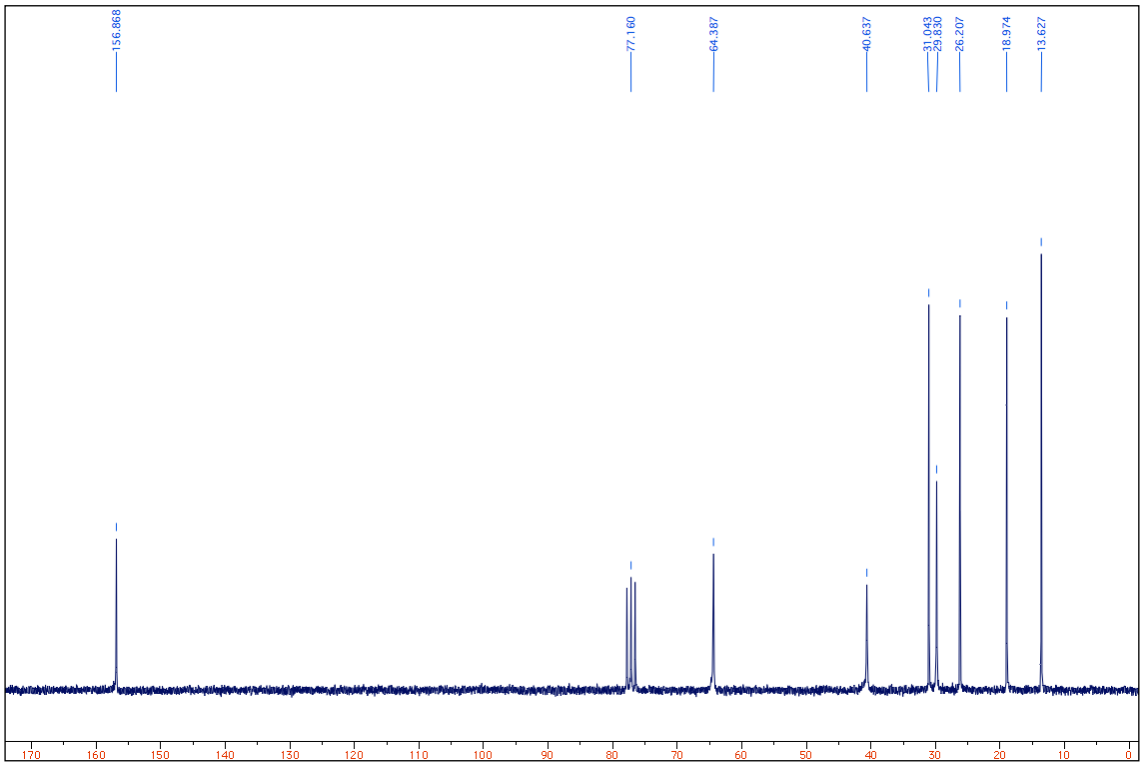
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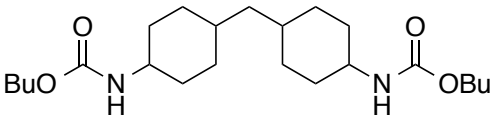
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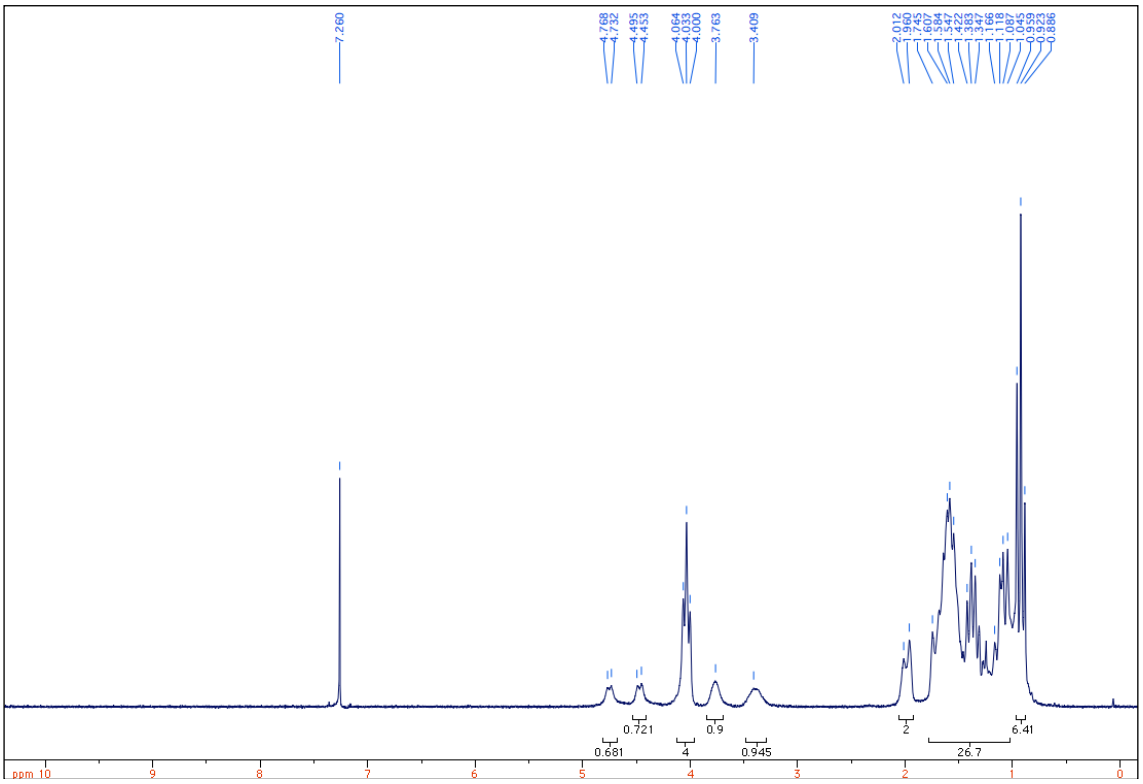
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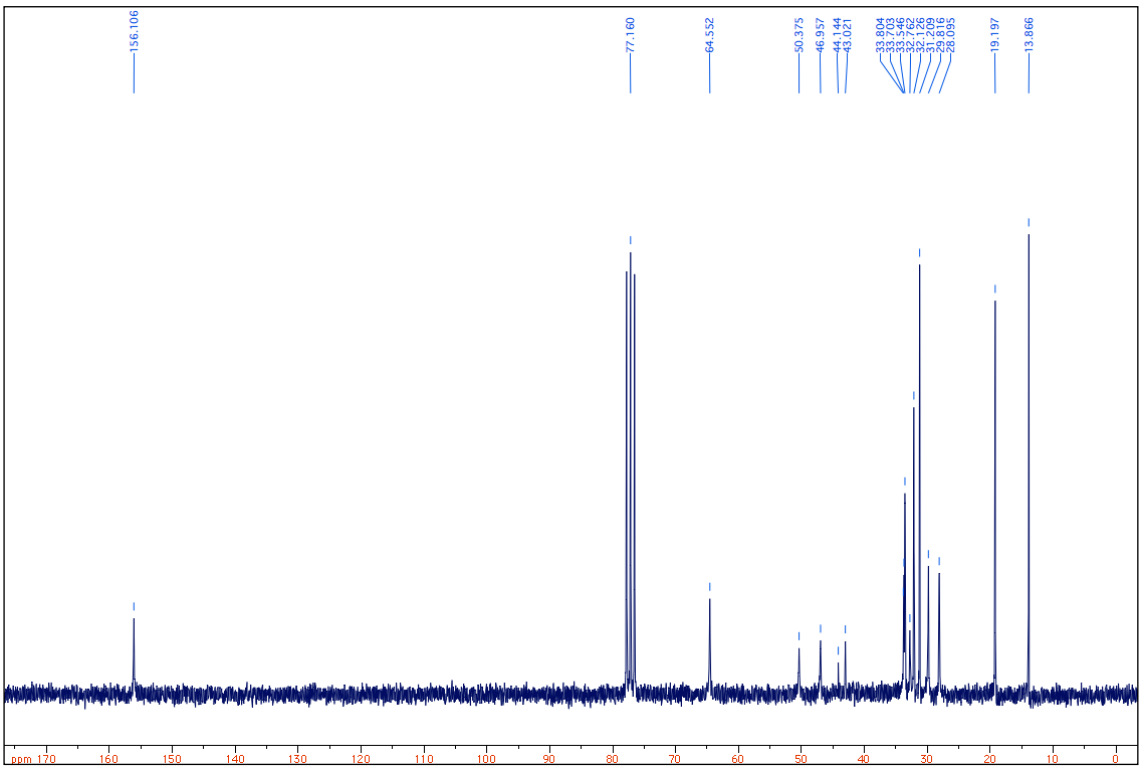
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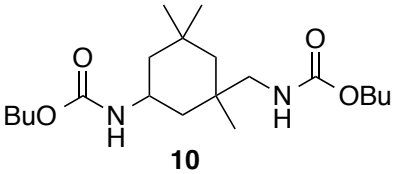
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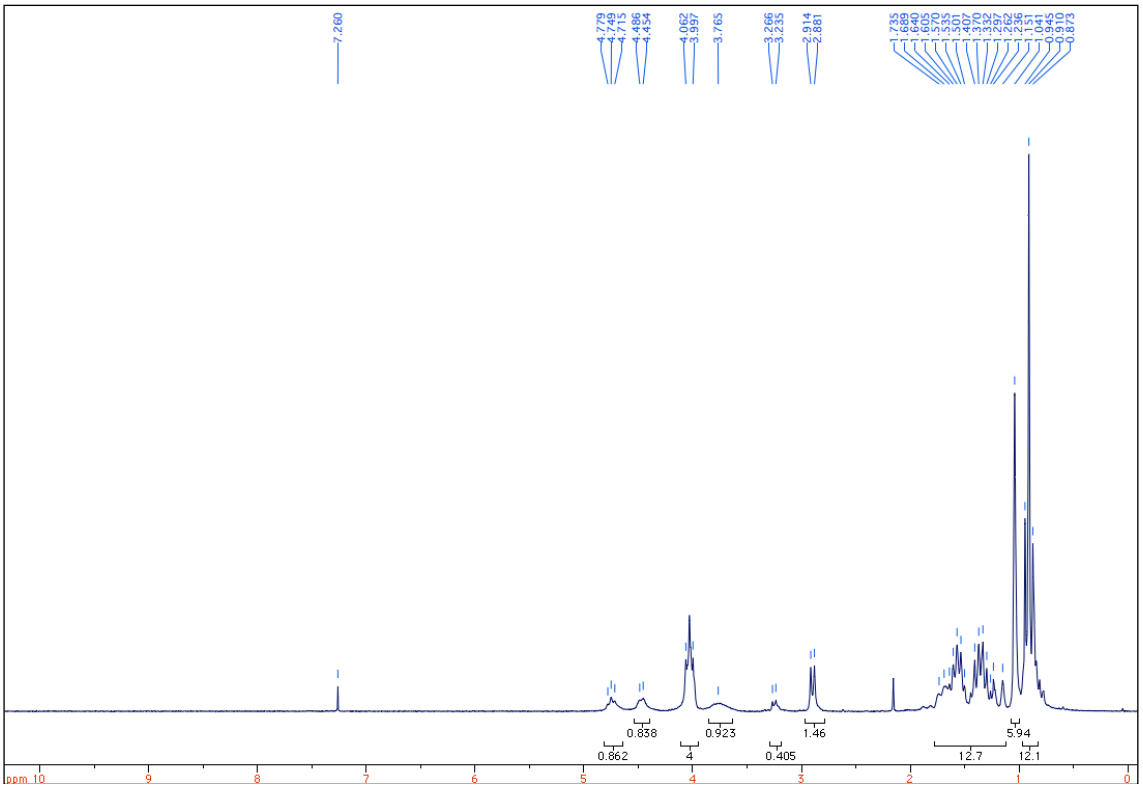
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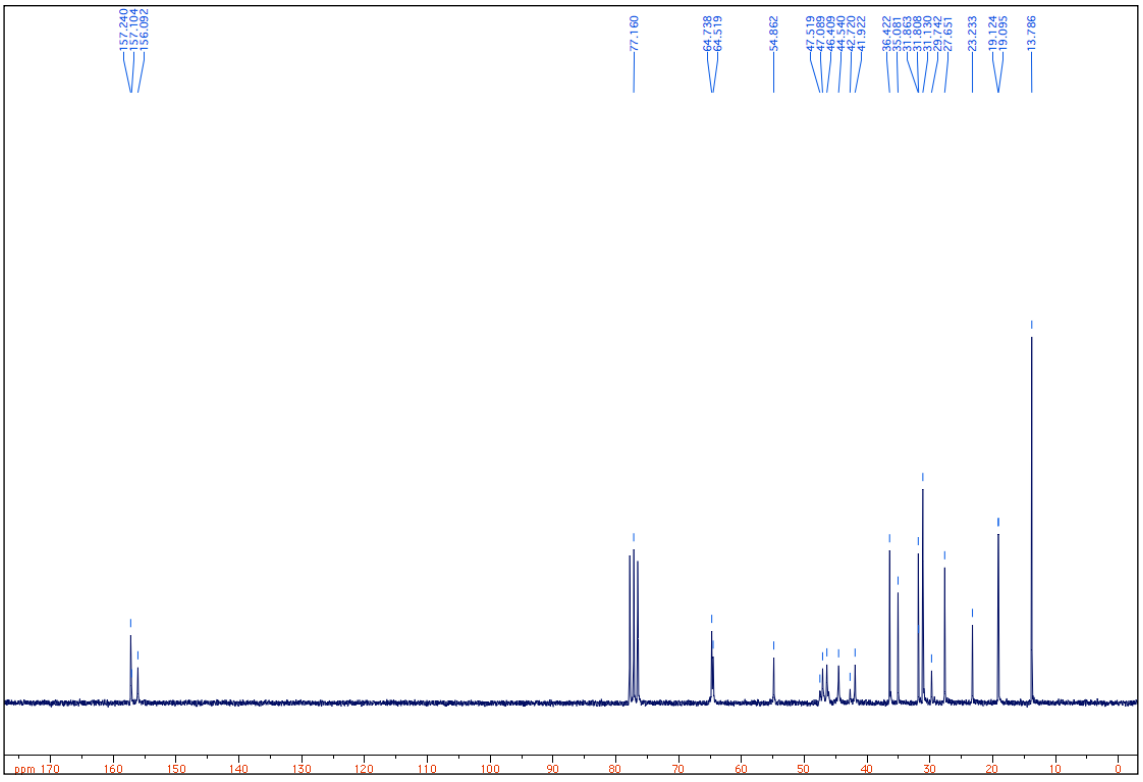
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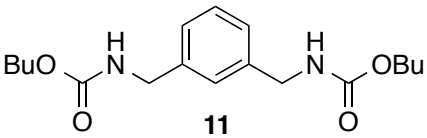
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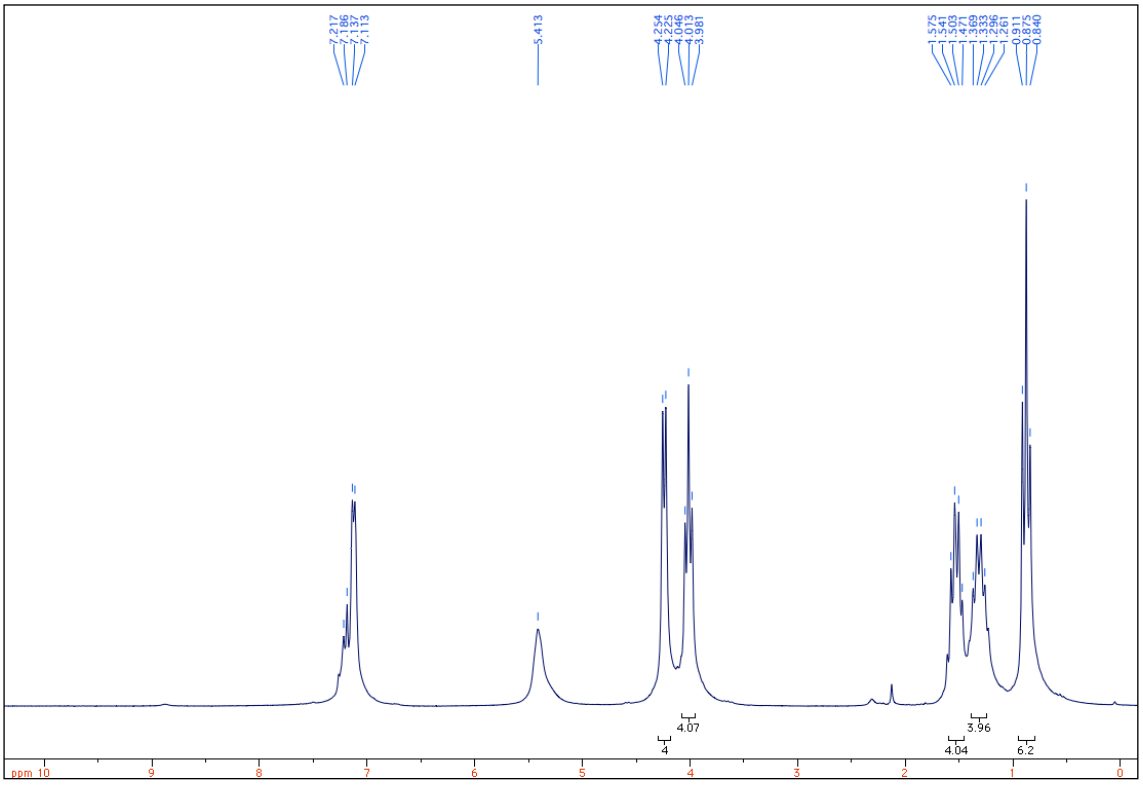
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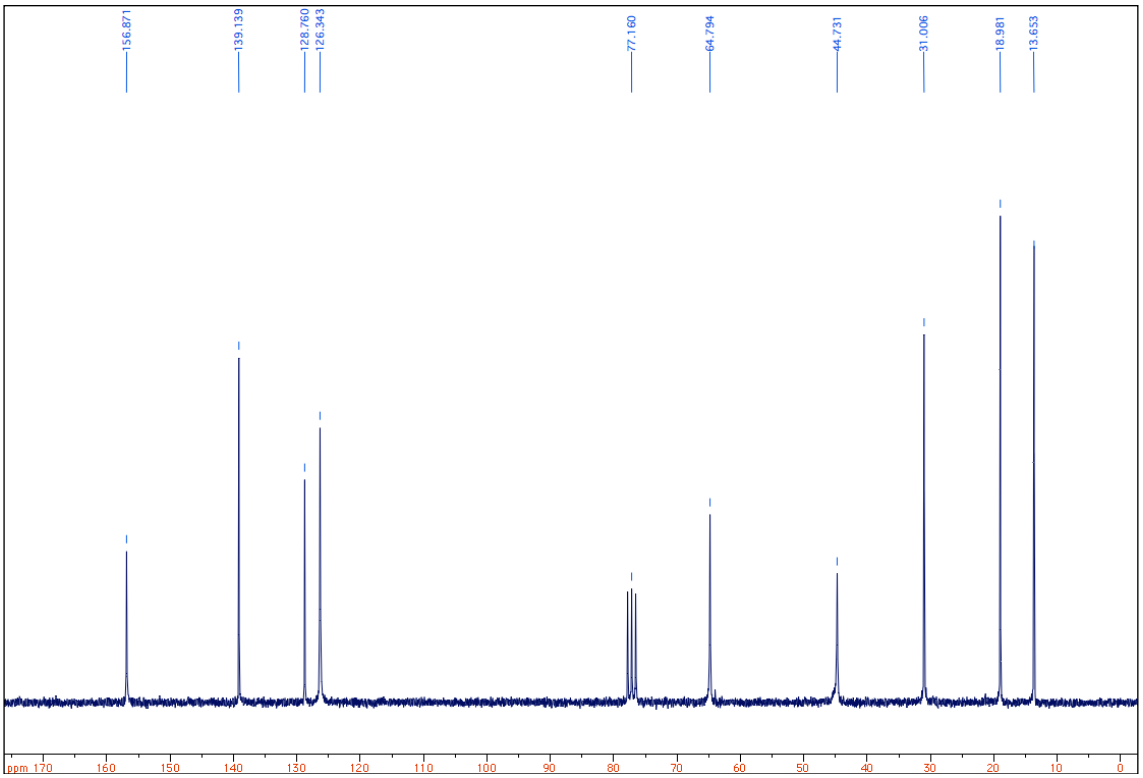
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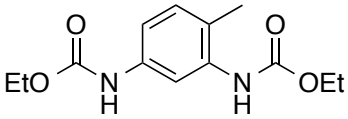
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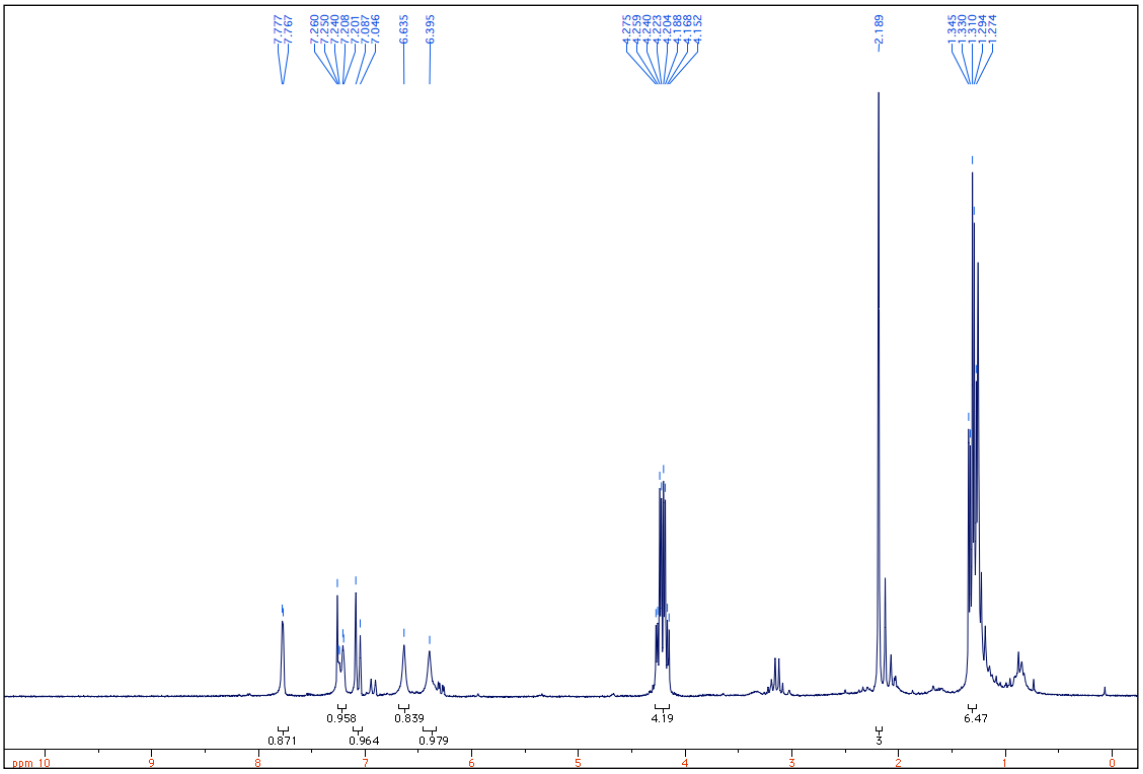
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7.767
7.260
7.250
7.240
7.208
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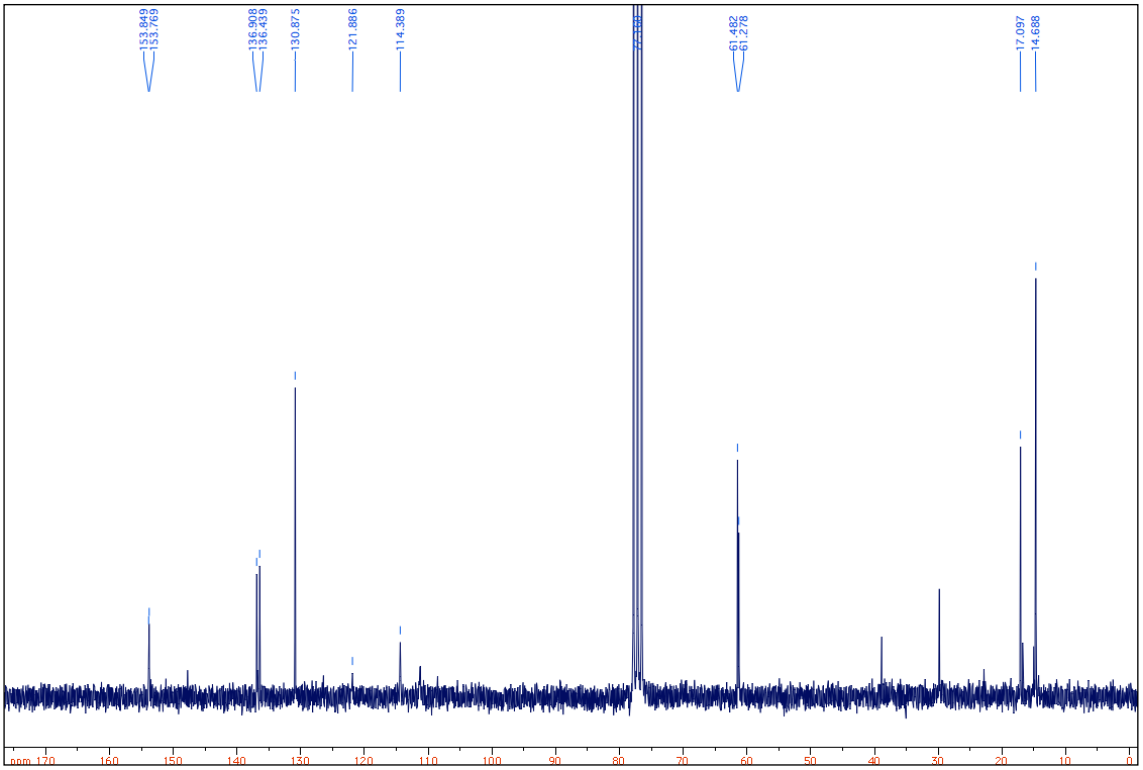
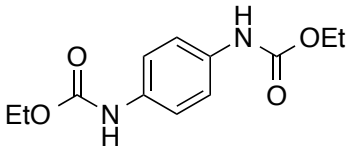
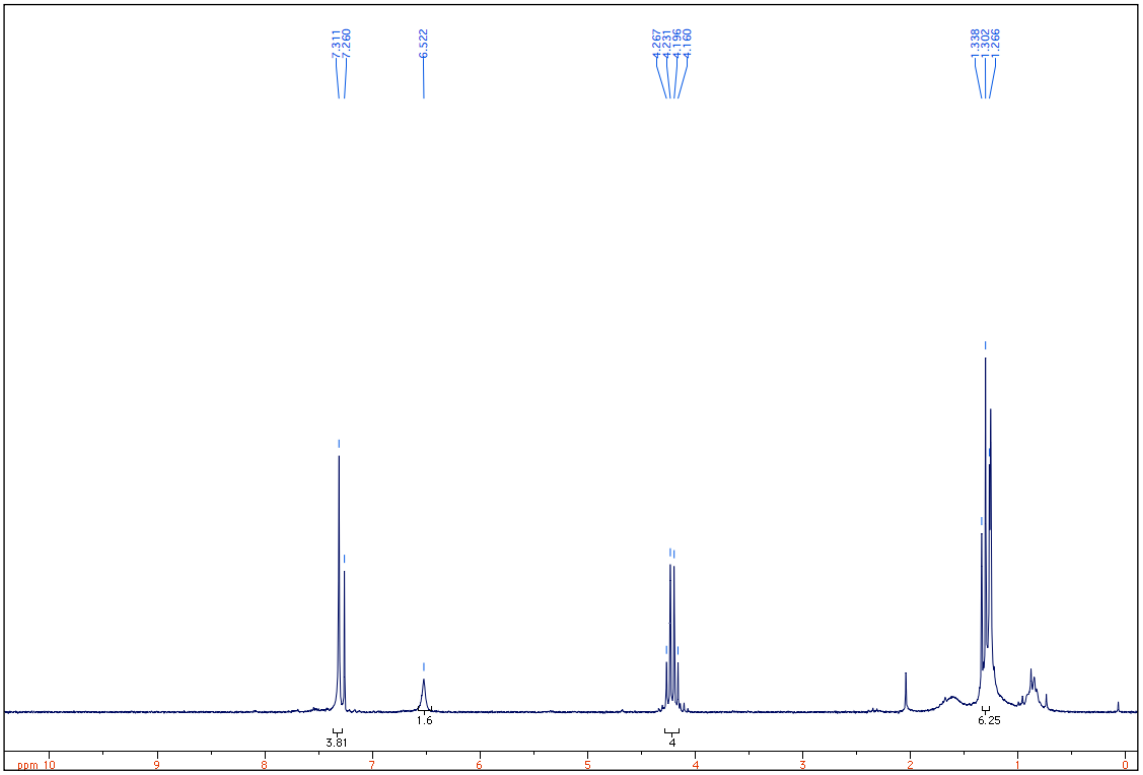
7.087
7.046
6.635
6.395
4.275
4.259
4.240
4.223
4.204
4.188
4.168
4.152
2.189
1.345
1.330
1.310
1.294
1.274
0.871
0.958
0.964
0.839
0.979
4.19
3
6.47
ppm 10
9
8
7
6
5
4
3
2
1
0


153.849
153.769
136.908
136.439
130.875
121.886
114.389
77.318
61.482
61.278
17.097
14.688
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


H
N
OEt
O
O
EtO
N
H

13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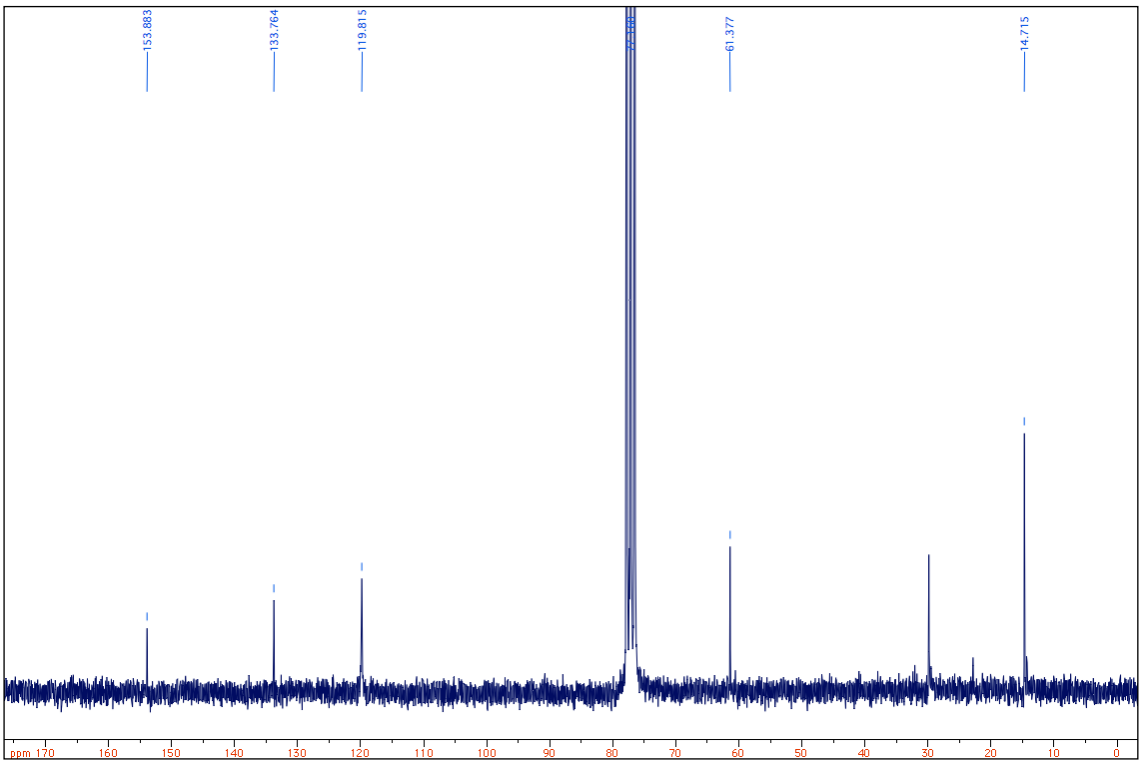
7.260
6.522
4.267
4.231
4.196
4.160
1.338
1.302
1.266
3.81
1.6
4
6.25
ppm 10
9
8
7
6
5
4
3
2
1
0


153.883
133.764
119.815
77.380
61.377
14.715
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
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20
10
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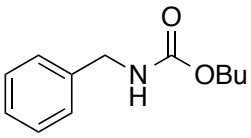
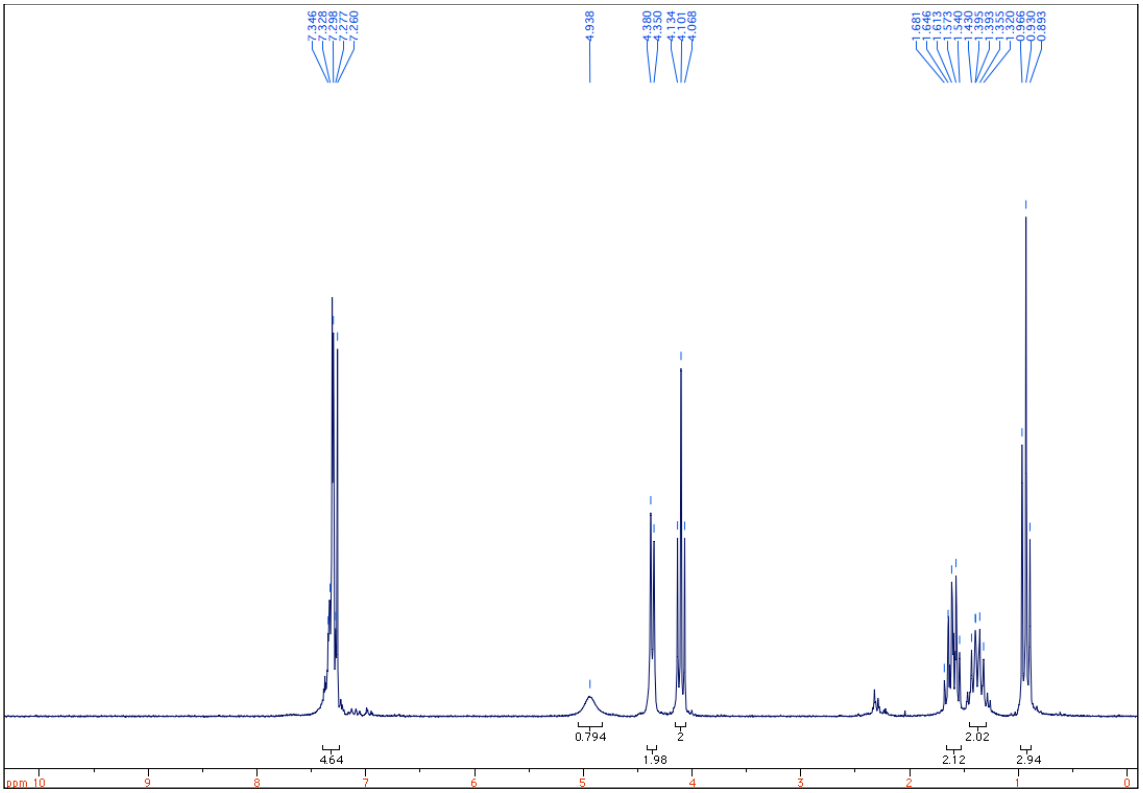

O
N
H
OBu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7.328
7.298
7.277
7.260
4.938
4.380
4.350
4.134
4.101
4.068
1.681
1.646
1.613
1.573
1.540
1.430
1.395
1.393
1.355
1.320
0.966
0.930
0.893
0.794
2
2.02
4.64
1.98
2.12
2.94
ppm 10
9
8
7
6
5
4
3
2
1
0

4. References.

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