Supporting Information

for

Sustainable carboxylation of diamines with hydrogen carbonate.

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1. Experimental

Preparation of TEAHC according to reported procedure.

Dry tetraethylammonium chloride was dissolved in methanol (~ 2 mmol/ml) and KOH (1.0 equivalent) was added. A white precipitate immediately forms. The reaction was allowed to stir for 2h at room temperature, then the precipitate was filtered off. CO_2 was slowly bubbled into the solution for 1h, and the solvent was evaporated under reduced pressure. The resulting TEAHC, as a white solid, was kept overnight under high vacuum.

Carboxylation scale-up with SpiroHC. Synthesis of dibutyl hexane-1,6-diyldicarbamate, 1.

SpiroHC (2.81 g, 15.0 mmol) was dissolved in 150 ml of acetonitrile, and hexamethylenediamine (0.58 g, 5.0 mmol, dissolved in 10 ml of acetonitrile) was added. The solution was allowed to stir at room temperature for 2h. Butyl chloride (2.1 ml, 20.0 mmol) was added, and the reaction mixture heated at 80 °C for 3h. The solvent was removed under reduced pressure, and the resulting residue was extracted with ethyl acetate (3 × 100 ml). The collected organic fractions were concentrated to dryness to afford 1.39 g of product (88% yield).

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

Off-white waxy solid, ≥ 83% yield (BuI), ≥ 85% yield (BuCl). ^{1}H 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.[a]

Yellowish oil, ≥ 92% yield (BuI), ≥ 87% yield (BuCl). ^{1}H 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.[b]

White solid, ≥ 85% yield (BuI), ≥ 82% yield (BuCl). ^{1}H 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.[c]

Yellowish solid, 10% yield. ^{1}H 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.[c]

White solid, 13% yield. ^{1}H 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).

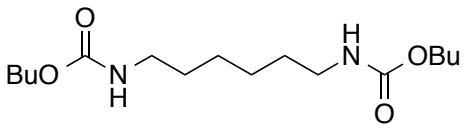
5-azoniaspiro[4.4]nonane chloride, 2.[d]

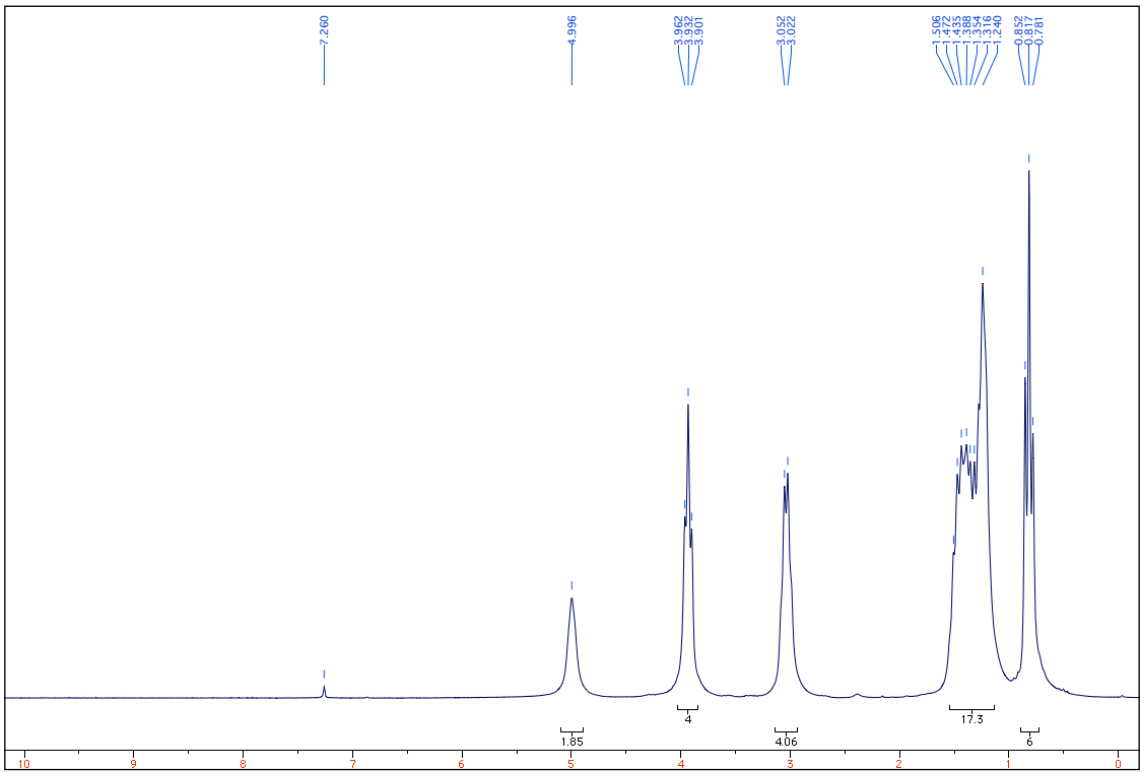
^{1}H NMR (200 MHz, $CDCl_3$) δ= 3.86 (bs, 8H), 2.28 (bs, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 62.7, 22.1.

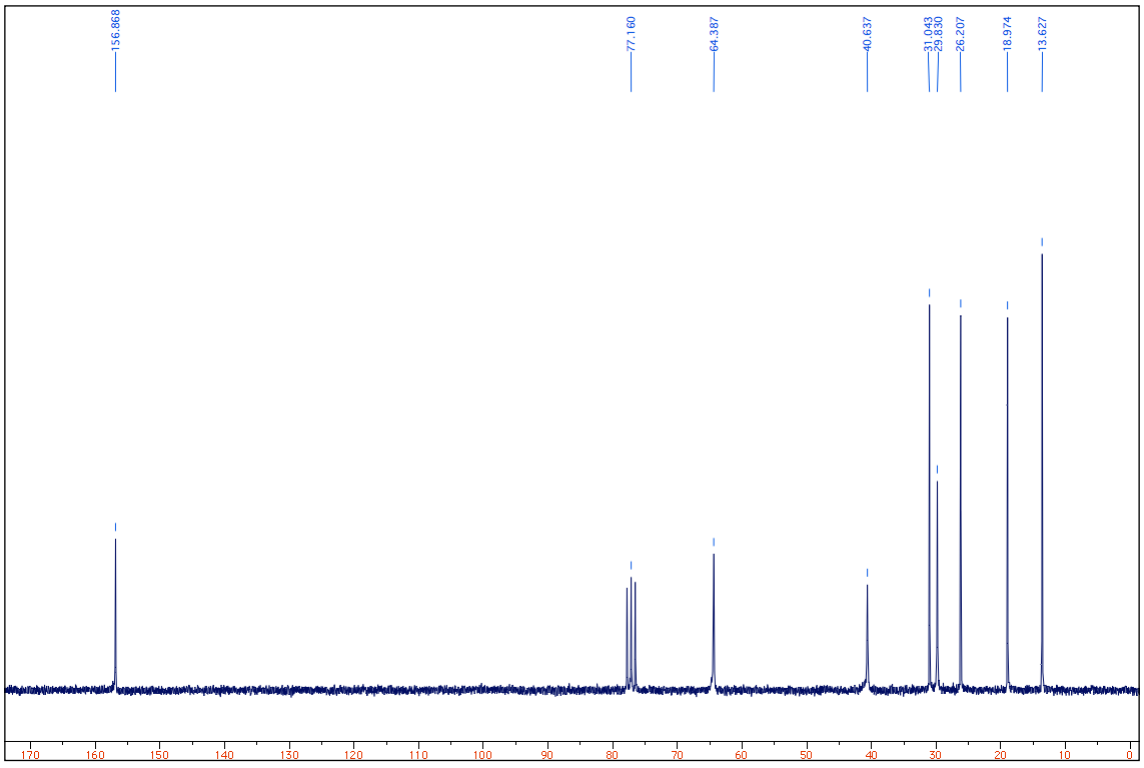
5-azoniaspiro[4.4]nonane hydrogen carbonate, SpiroHC.

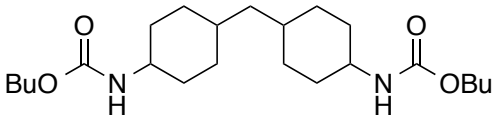
^{1}H NMR (200 MHz, $CDCl_3$) δ= 3.70 (m, 8H), 2.15 (bs, 8H); ^{13}C NMR (50 MHz, D_2O) δ= 160.5, 62.8, 62.7, 62.6, 21.6.

2. NMR Spectra.





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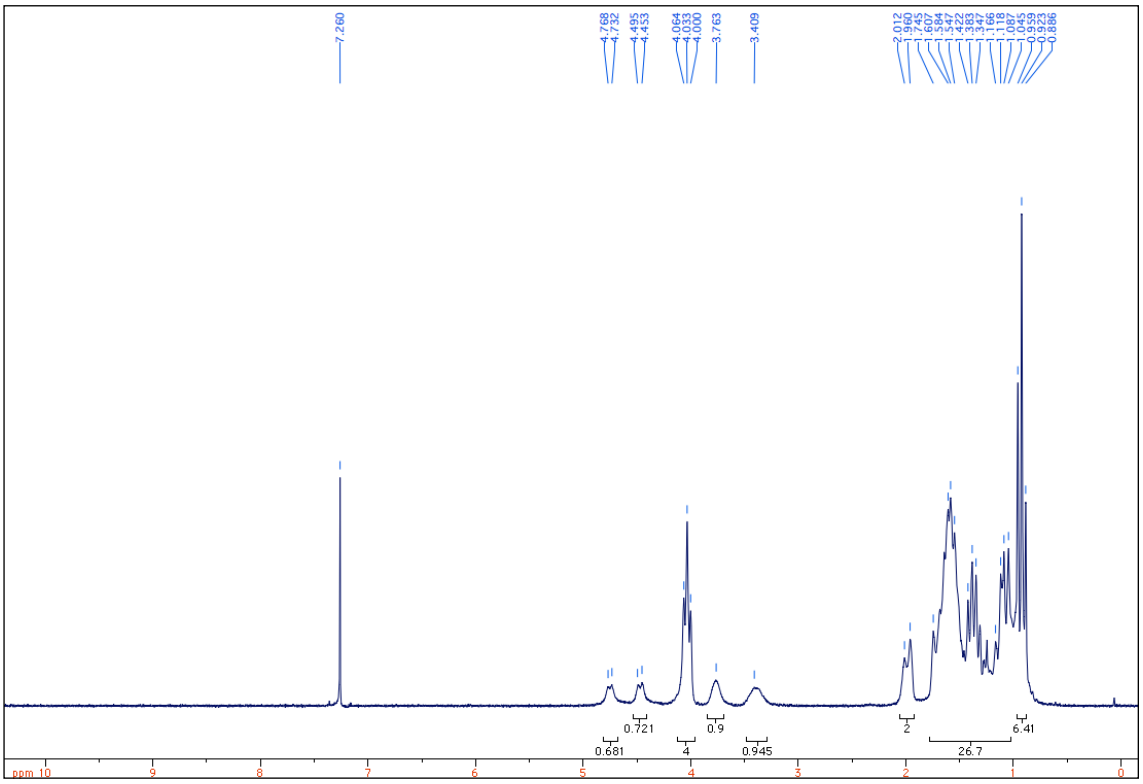
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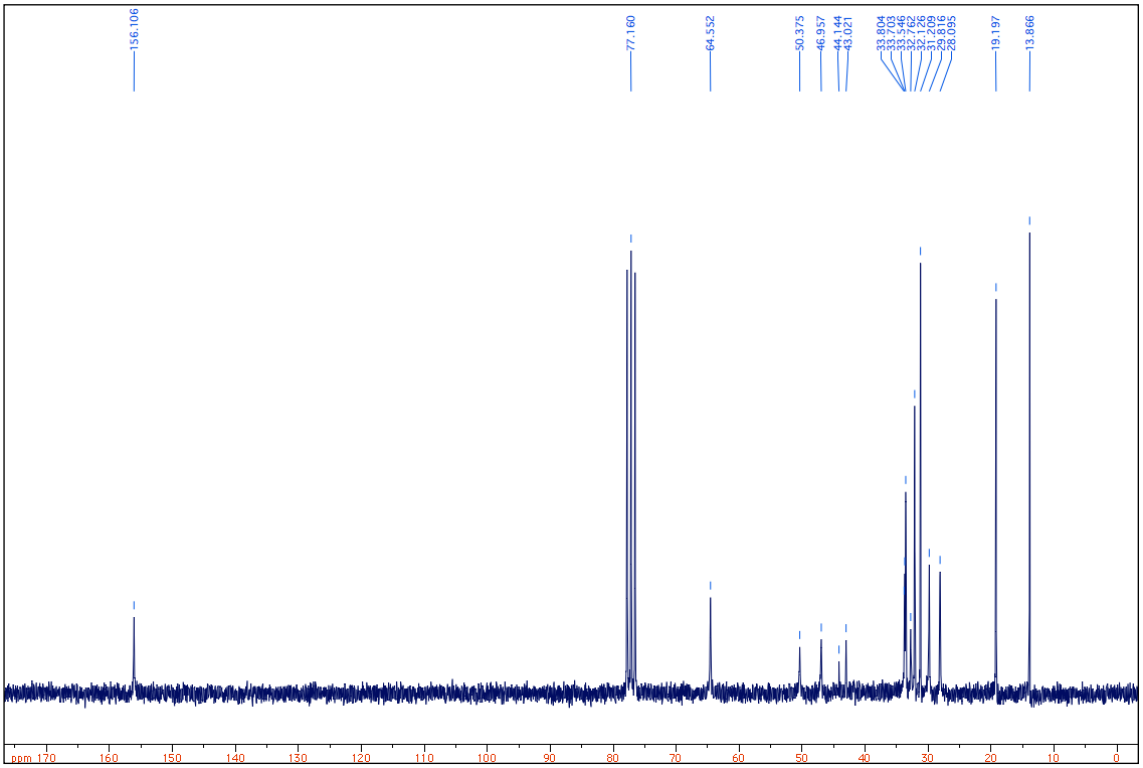
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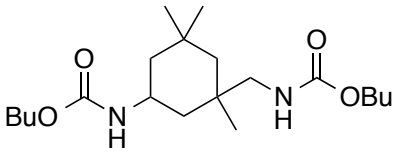
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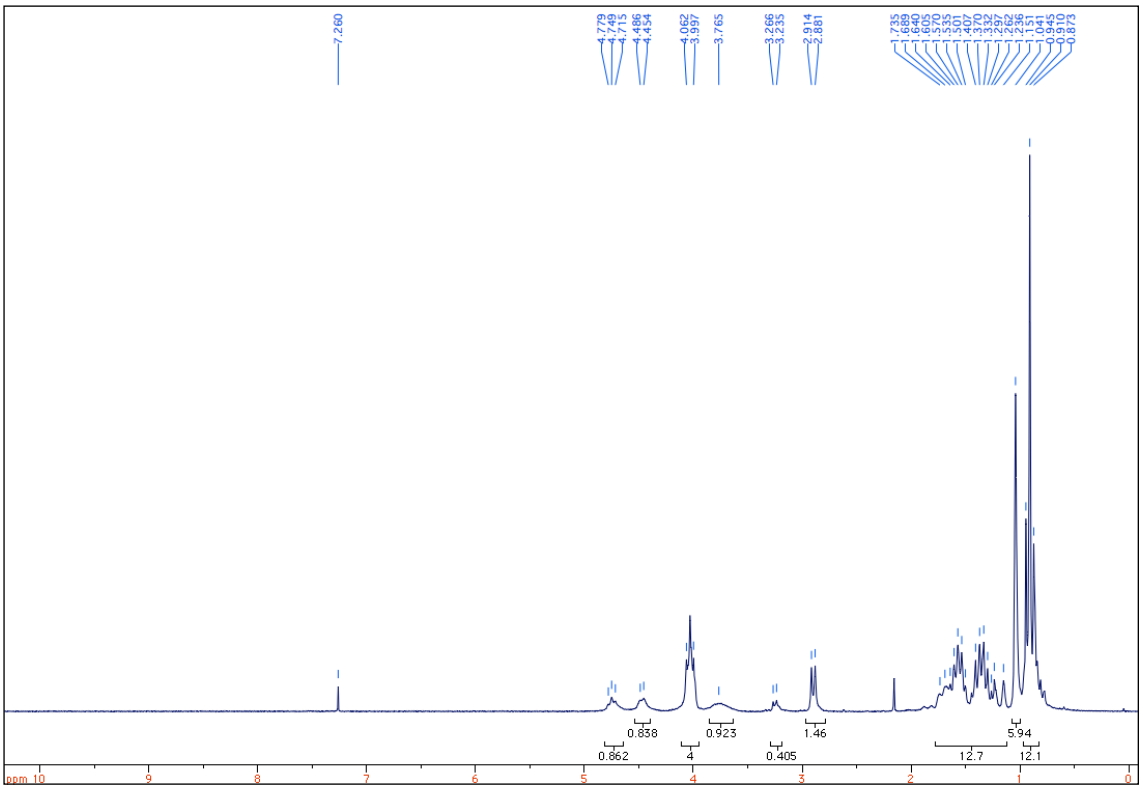
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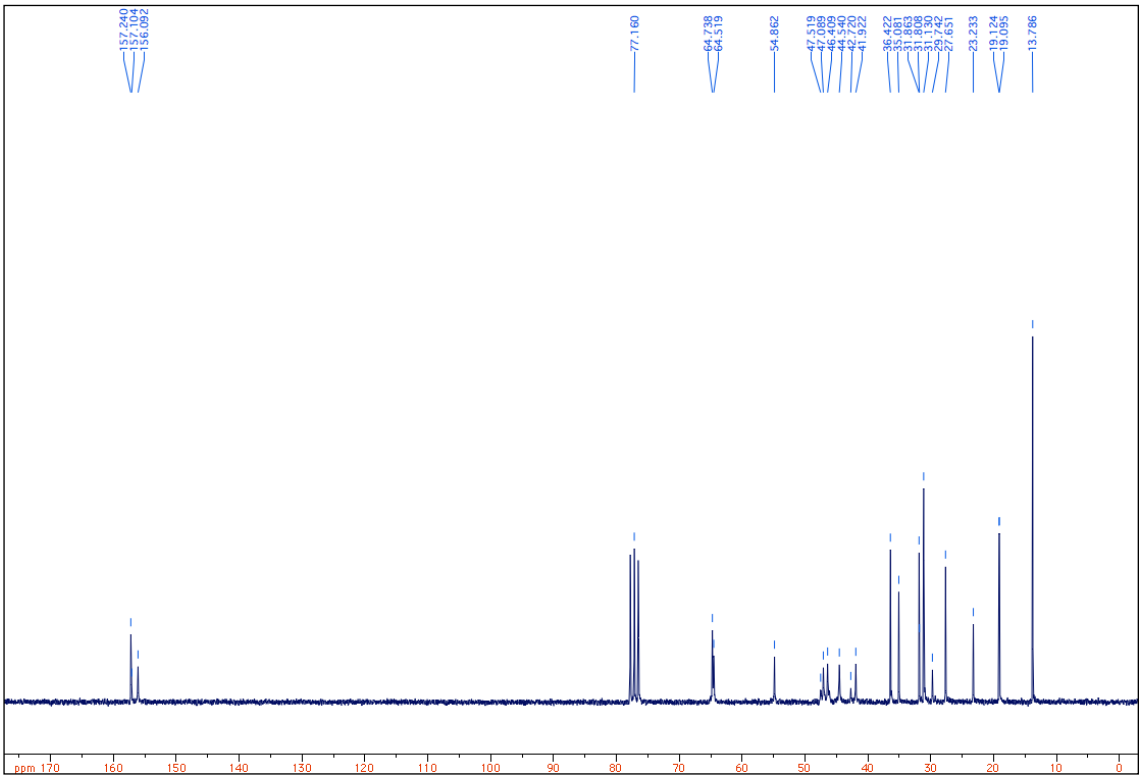
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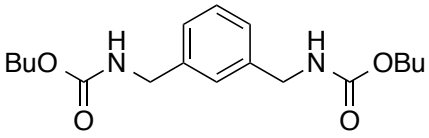
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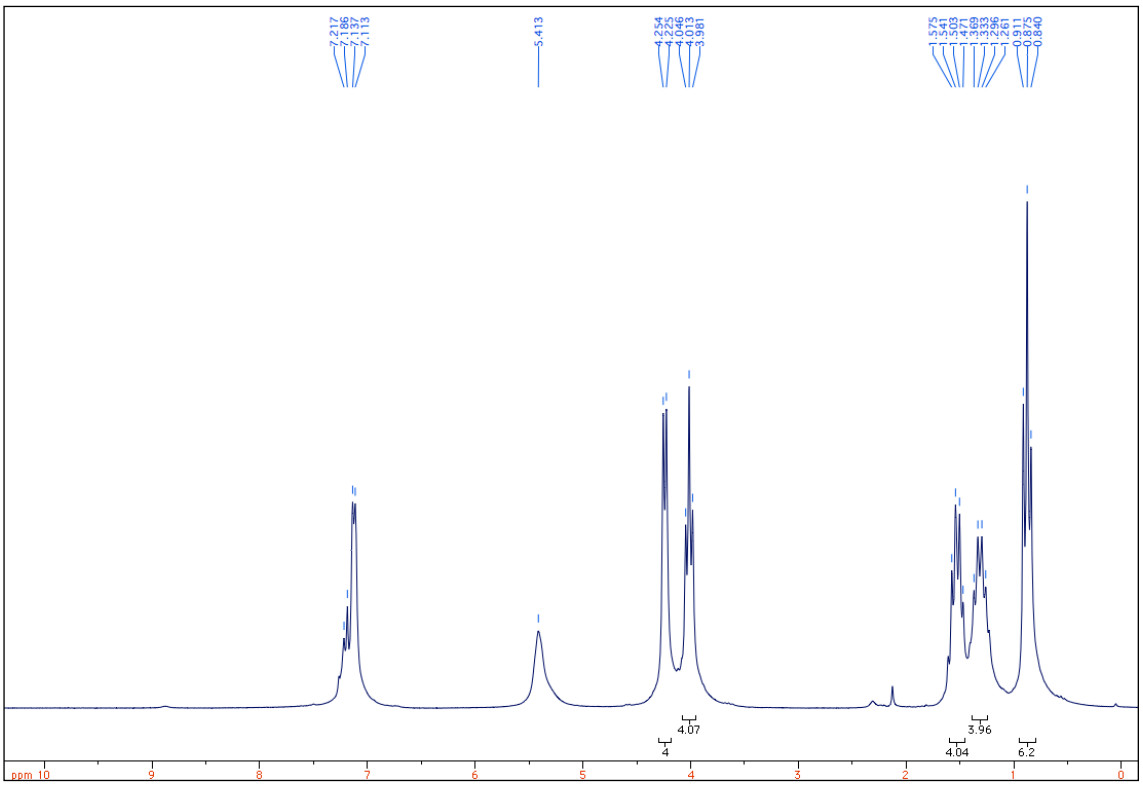
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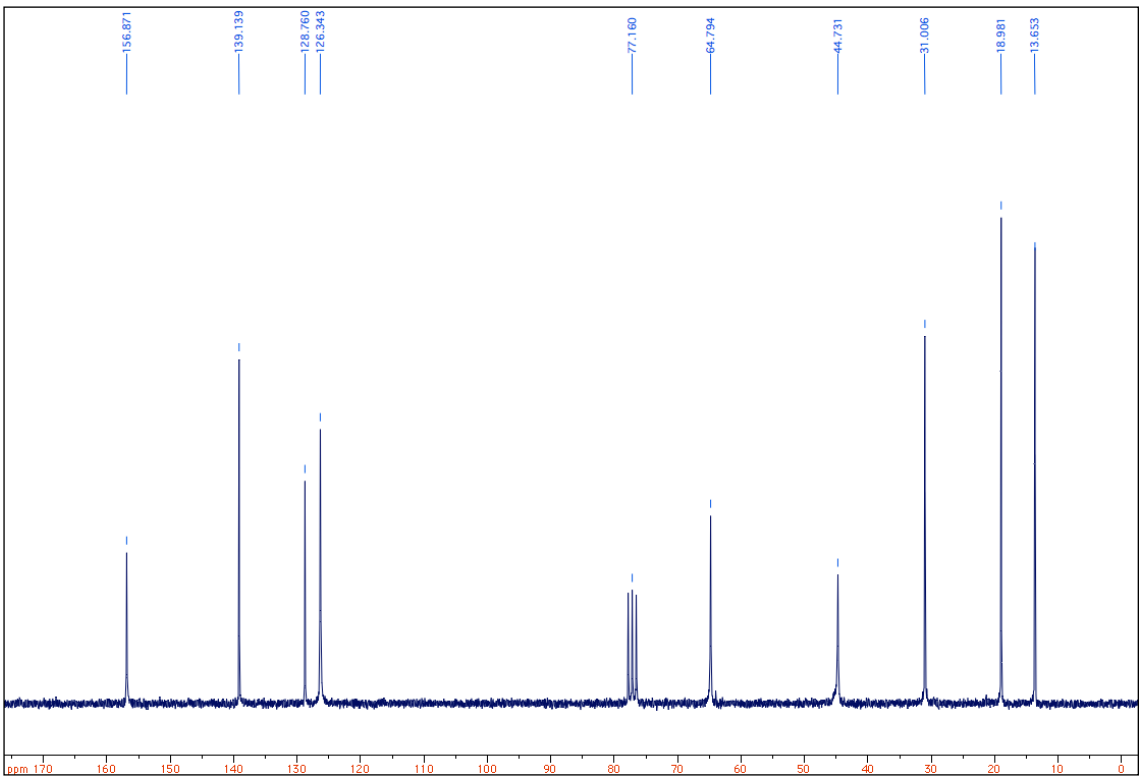
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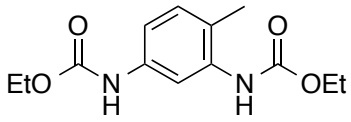
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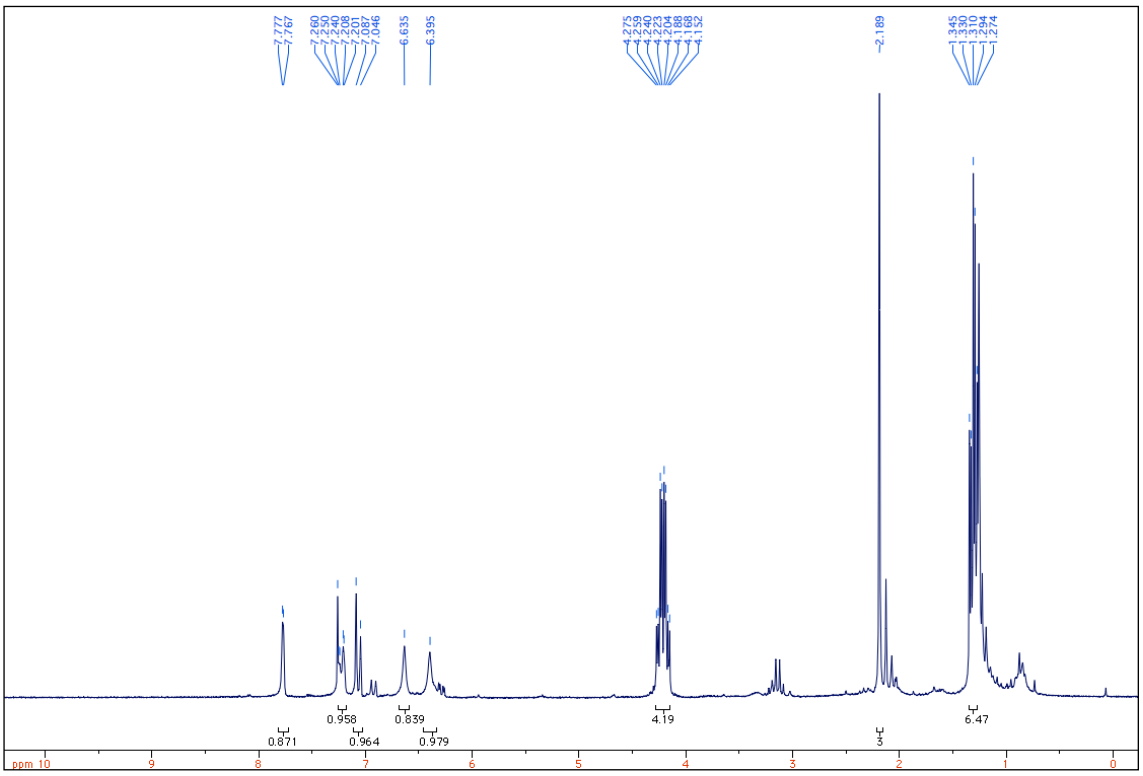
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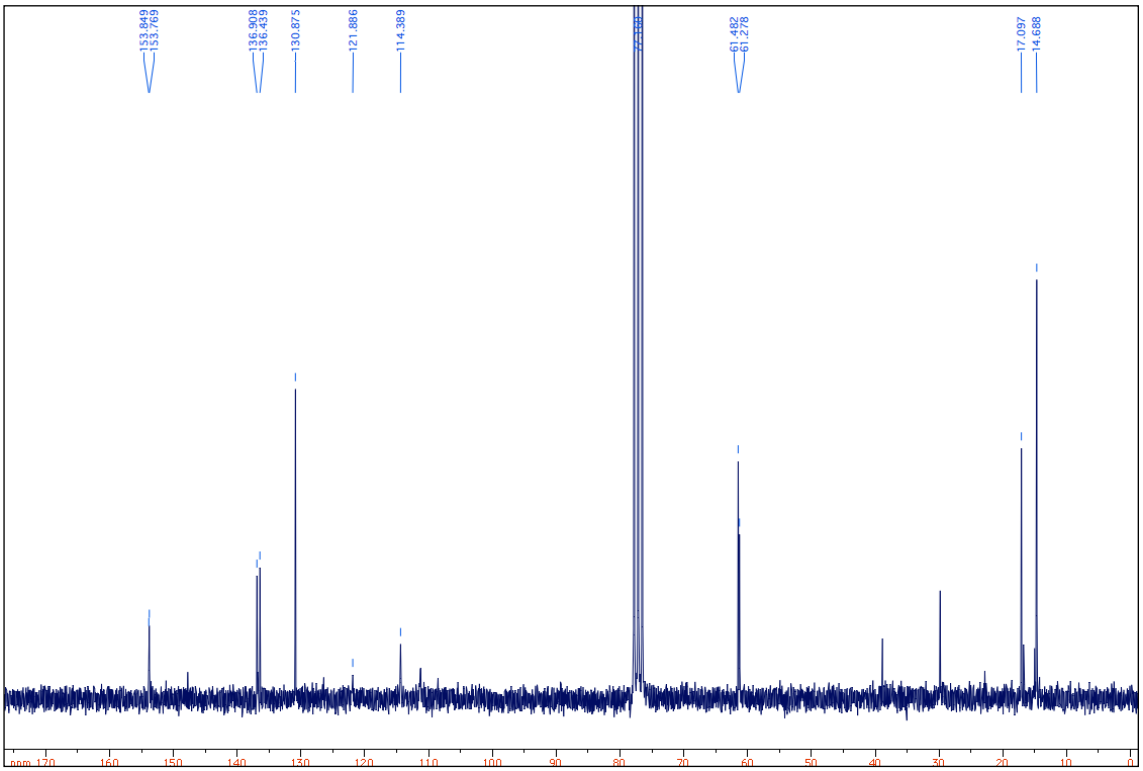
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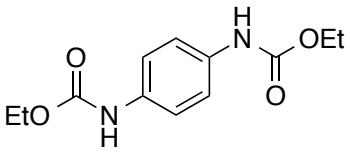
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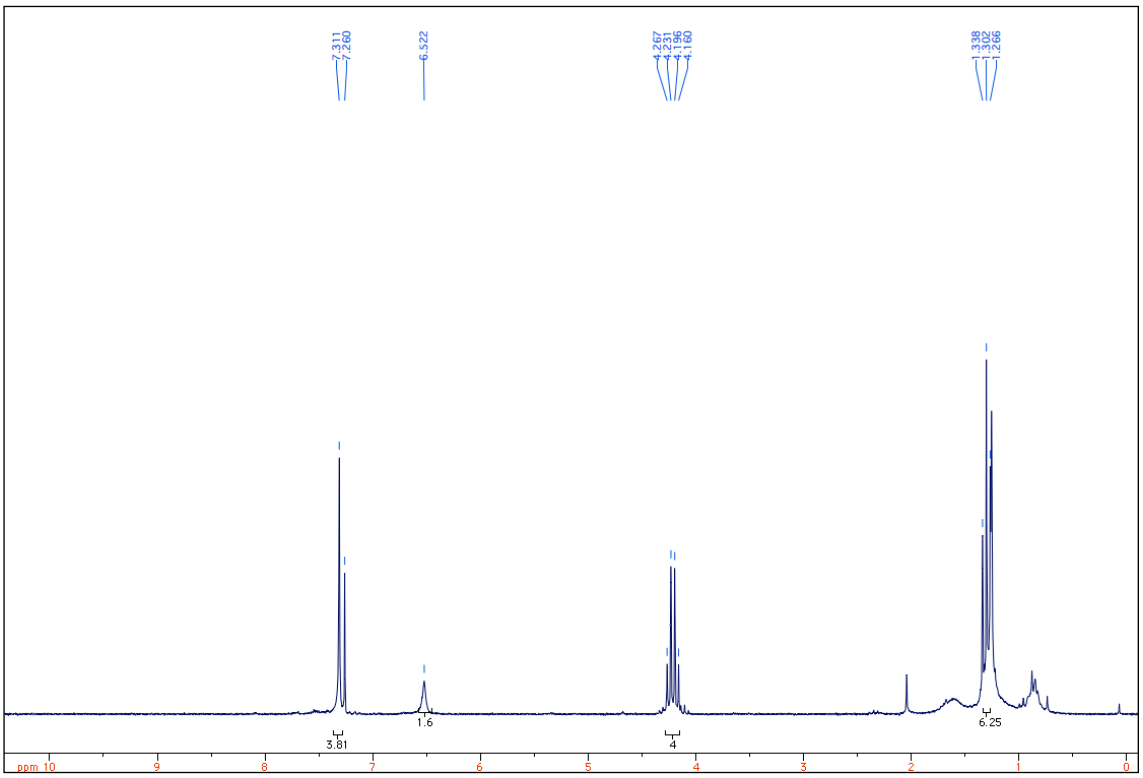
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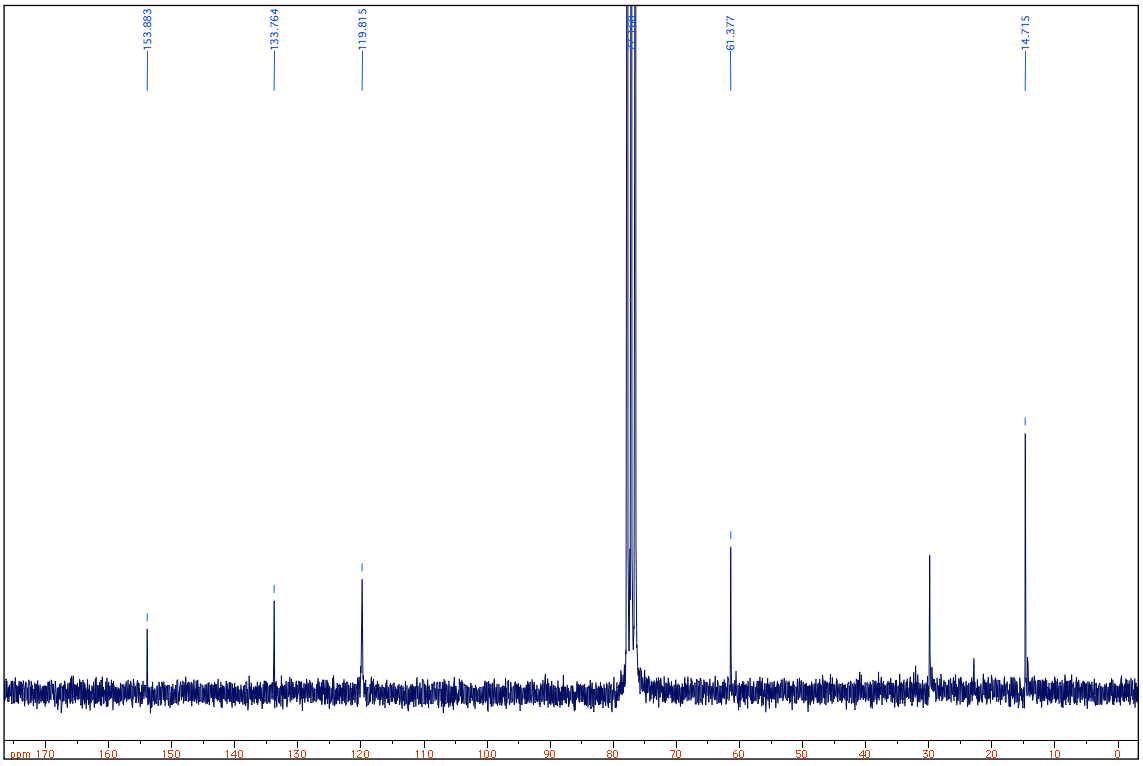
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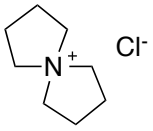
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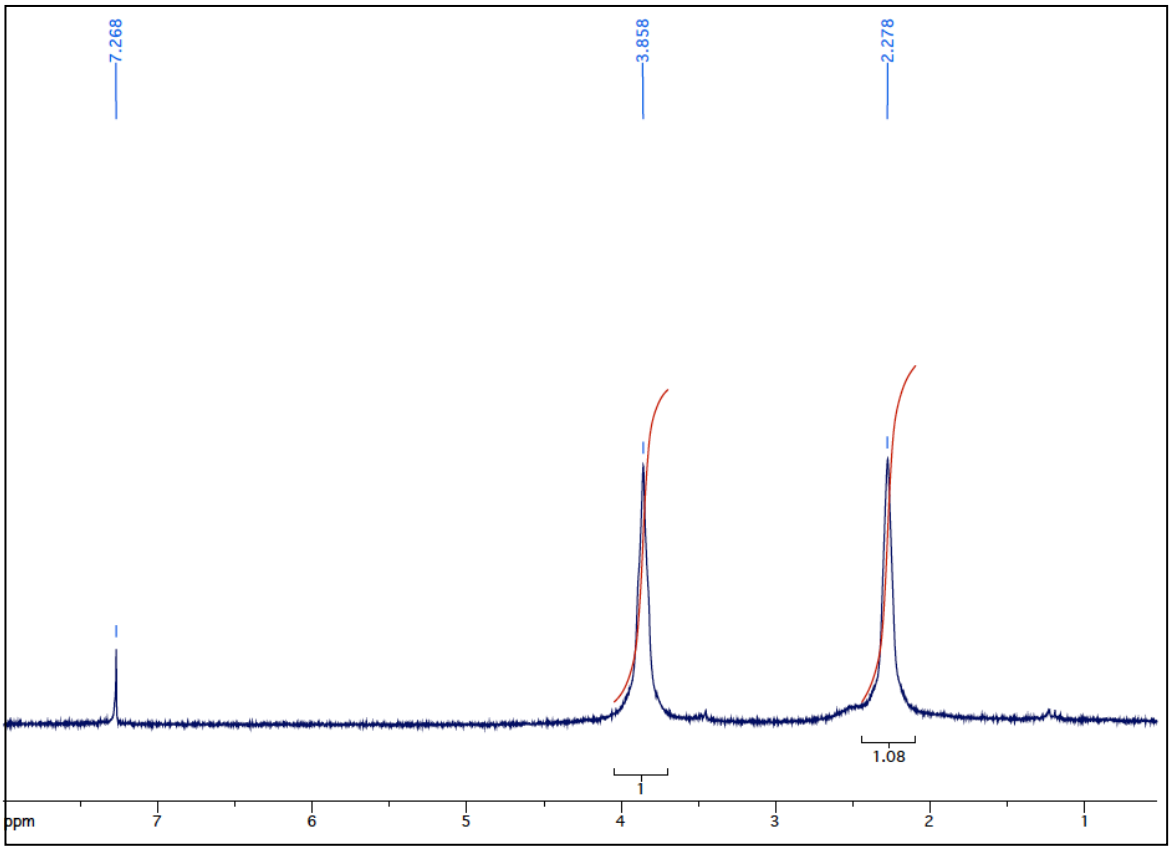
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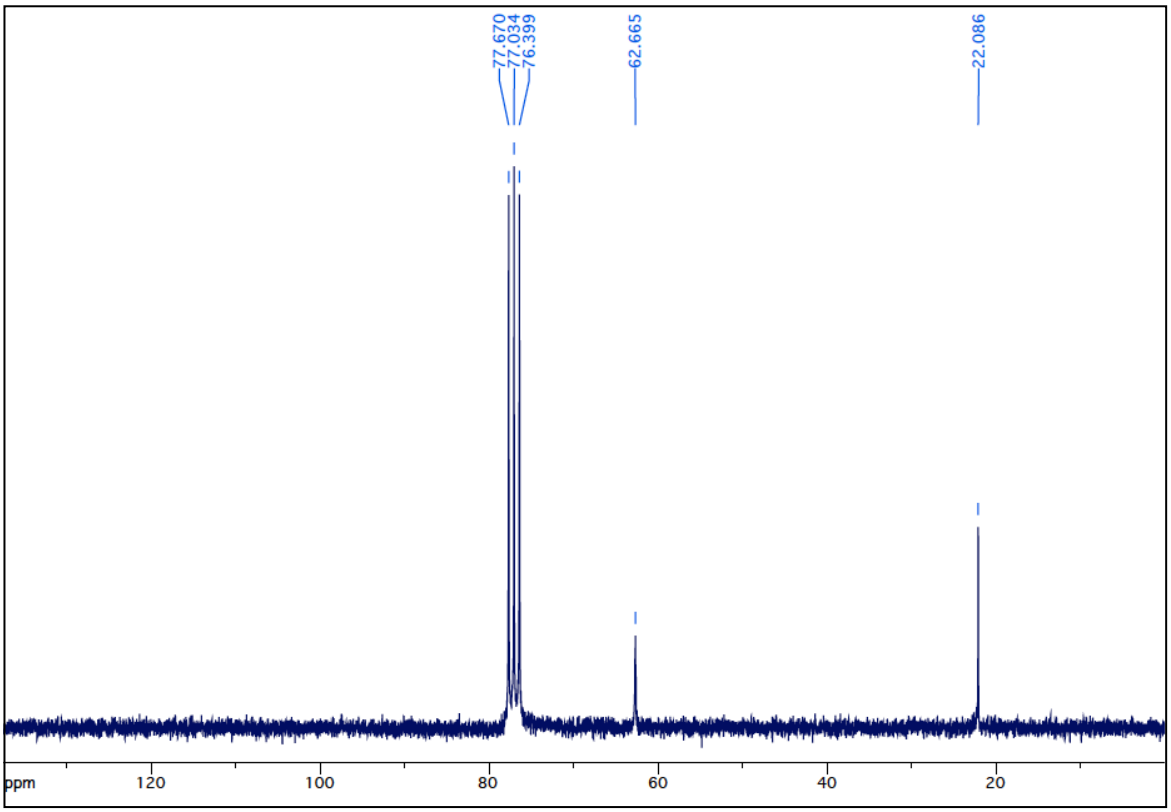
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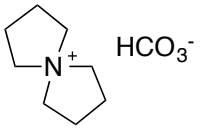
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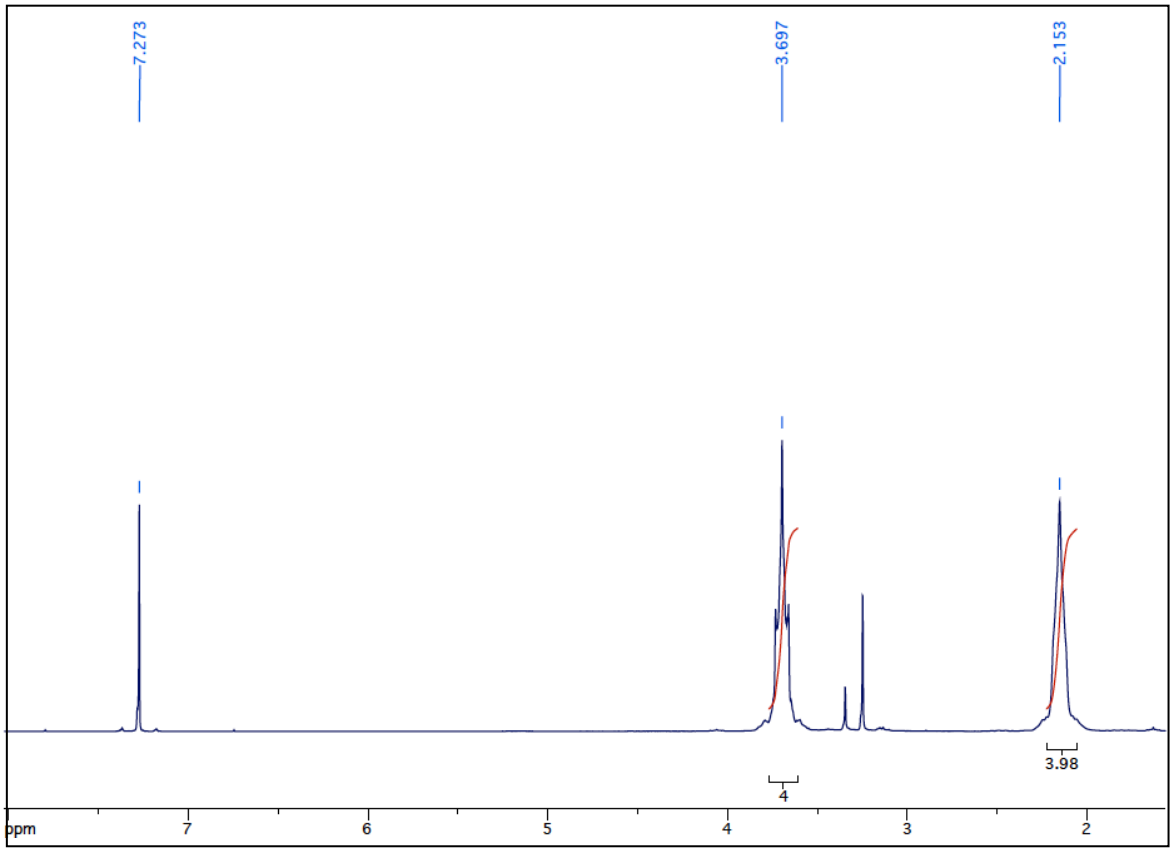
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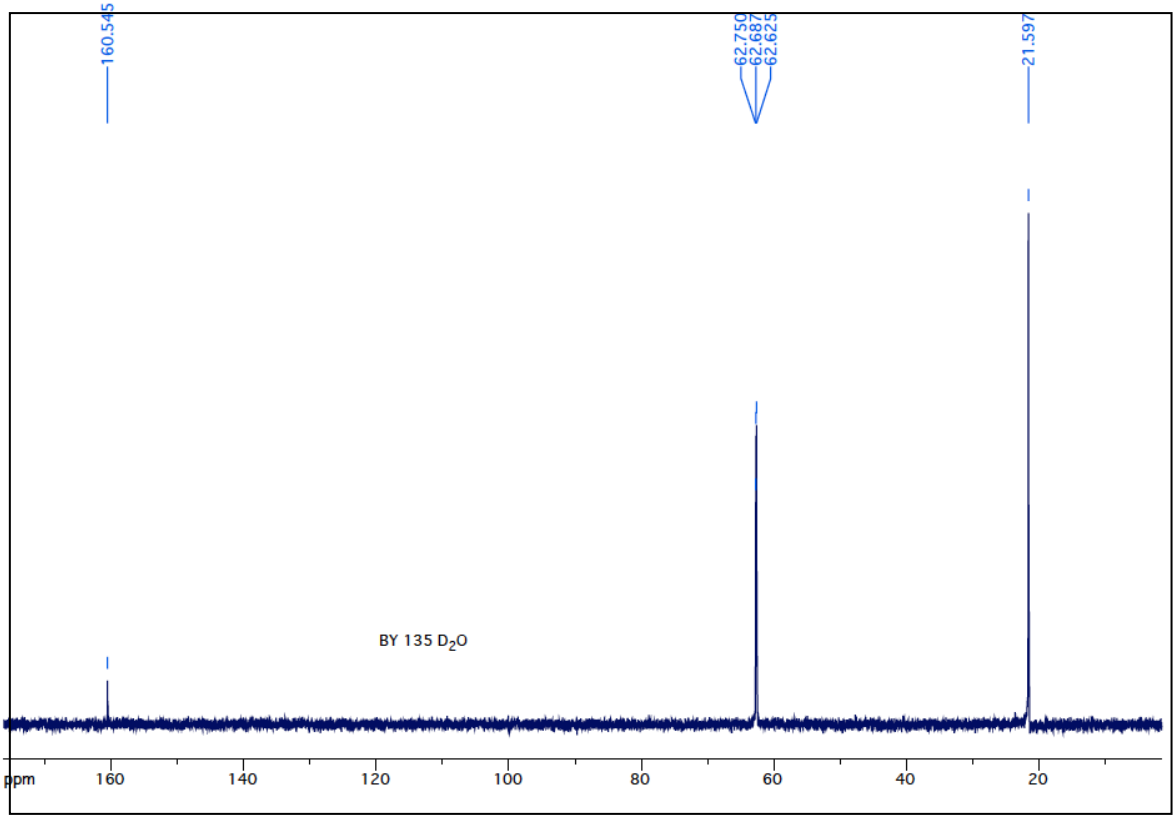
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120
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80
60
40
20

3. References.

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(b) K. Kojima, H. Tsukada, M. Takashina, C. Shimakawa and N. Kakinuma, Method for producing meta-xylylenediisocyanates. US20160145201 A1.

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(d) T. Sukizaki, S. Fukuda, T. Yamaguchi, K. Fujii, R. Kanzaki, K. Chiba, H. Yamamoto, Y. Umebayashi and S. Ishiguro; Raman Spectroscopic Study and DFT Calculations on the Conformation of 5-azonia-spiro[4.4]nonane cation in crystal and dimethyl carbonate solution. *Electrochemistry*, 2007, **75**, 628-634.