Intramolecular Diels Alder reactions in highly organized imidazolium salts-based ionic liquid crystals

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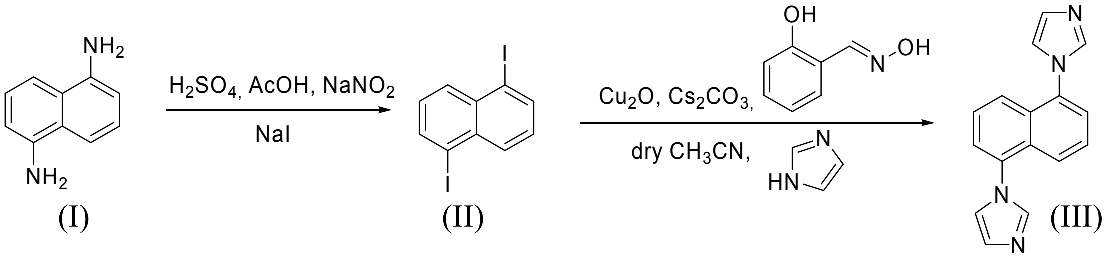
General methods. All chemicals were purchased from Aldrich Chemicals in their highest purity and used without further purification. CD_3OD or $CDCl_3$ were also purchased from Aldrich Chemicals. All solvents were purchased from EDM and liquid reagents were degassed by bubbling nitrogen for 15 min before each use. NMR experiments were recorded Bruker Avance 400 RG at 400 MHz. All NMR experiments were obtained by the use of the sequence commercially available on Brucker spectrometer. Coupling constants are given in Hertz (Hz) and chemical shifts are given in ppm (δ) measured relative to residual solvent. Data are reported as follows : chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, m = multiplet). Mass spectral data were obtained by the Université de Montréal Mass Spectrometry Facility and were recorded on a Mass spectrometer LC-LCQ Advantage (Ion trap) Thermo Scientific with ESI ionization source.

Analytical methods. Differential scanning calorimetry (DSC) analyses were carried out on a Q2000 TA instruments, with argon as protection gas. Experimental data were displayed such a way that exothermic peaks occur at negative heat flow and endothermic peaks occur at positive heat flow. DSC heating rate and cooling rate runs at $5^oC\ min^{-1}$. X-ray diffraction studies were carried out on a Bruker D8 Discover, equipped with a Hi-Star detector. XRD data were collected using GADDS 4.1.1.4 software and EVA 8.0.0.2 software was used for data analysis. A custom made XYZ stage with a temperature control chamber and a Cu source (Ka energy of 8.04 keV and $\lambda = 1.541838$ Ǻ were used. Polarizing optical microscopy (POM) studies were carried out with a Zeiss Axioskop 40Pol miscrocope coupled with a Linkam Scientific Instrument THMS600 hot stage and a TMS94 temperature controller.

Synthesis



1,5-diiodonaphthalene

To a solution of sodium nitrite (3g, 0.044 moles) in concentrated sulfuric acid (25 ml) at 0°C was added drop wise a solution of 1,5-diaminonaphthalene (3g, 0.019 moles) in glacial acetic acid (25 ml). The mixture was stirred for 15 minutes and poured onto ice (50 g) and urea (0.25 g), and then an aqueous solution of potassium iodide (30 g, 0.18 moles) (100 ml) was added and the mixture was stirred overnight. The solid was filtered, dried and extracted with dichloromethane. The combined extracts were refluxed with charcoal and purified by silica gel column chromatography (hexane/dichloromethane = 4/1) to give 1,5-diaminonaphthalene as pale-yellow needles (5.17 g, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 8.13 (d, 4H, J = 7.6 Hz), 7.26 (t, 2H, J = 7.6 Hz).

1,5-di(1H-imidazol-1-yl)naphthalene

Under nitrogen atmosphere, 1,5-diiodonaphthalene (2g, 5.89 mmol, 1 eq.), imidazole (1.26 g, 18 mmol), salicylaldoxime (247 mg, 1.8 mmol), Cu_2O (72 mg, 0,45 mmol) and Cs2CO3 (6.19 g, 19 mmol) were dissolved in dry acetonitrile. The mixture was refluxed overnight. The combined extracts were evaporated under reduced pressure, then purified by silicagel column chromatography (hexane/dichloromethane/methanol/ammonium hydroxide = 44/150/5/1) to give the desired product as white solid (800mg, 51%). ^{1}H NMR (CD_3CN, 400 MHz) : δ(ppm) 7.82 (s, 1H), 7.62-7.77 (m, 3H), 7.42 (s, 1H), 7.43 (s, 1H), 7.26 (s, 1H). HRMS m/z found : 261.1147 ($[M+H]^+$), calc. : 261.1135

General procedure for the synthesis of dialkyl(1,5-naphthalene)diimidazolium salts

To a solution of 1,5-di(*1H*-imidazol-1-yl)naphthalene (1 eq.) in acetonitrile was added the appropriate alkyl bromide (10 eq). The solution was refluxed and stirred for 24h and then filtered. The residual solid was washed with 20 mL of hexane and diethyl ether, then dried under high reduced pressure for 24h, giving the diimidazolium bromide salt as an off-white solid (92-95% yield).

To a solution of diimidazolium bromide salts in methanol was added either lithium bis(trifluoromethylsulfonyl)imidate, lithium tetraborophosphate, ammonium triflate, or postassium hexafluorophosphate (2.2 eq) and the solution was refluxed for 12h. After evaporation of the solvent, the residual solid was washed with 20 mL water and the subsequent salts was filtered and dried under high vacuum. The absence of HBr in the final solid was confirmed by the absence of halide in the washing aqueous phases by testing with $AgNO_3$.

1,1'-didodecyl-3,3'-(1,5-naphthalene)diimidazolium bis[bis(trifluoromethanesulfonyl)imide]

^{1}H NMR (CD_3OD, 400 MHz): δ(ppm) 7.75-8.12 (m, 5H), 4.46 (d, J = 7.4 Hz, 4H), 2.10 (quint, J = 7.4 Hz, 1H), 1.27-1.53 (m, 36H), 0.92 (t, J = 6.0 Hz, 6H). ^{13}C NMR (CD_3OD, 100 MHz): δ(ppm) 131.9, 129.1, 127.9, 126.4, 124.8, 124.6, 123.1, 121.1, 118.5, 50.2, 31.7, 29.5, 29.1 (multiple peaks), 28.7, 26.0, 22.3, 13.0. HRMS *m/z* found : 229.7514 ([M - NTf_2 + H]$^{2+}$), calc. : 229.7521; found : 597.4891 [M*]$^+$, calc. 597.4892

1,1'-dihexdecyl-3,3'-(1,5-naphthalene)diimidazolium bis[bis(trifluoromethanesulfonyl)imide]

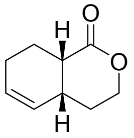
^{1}H NMR (CD_3OD, 400 MHz) : δ(ppm) 7.81-8.12 (m, 5H), 4.47 (d, J = 7.4 Hz, 4H), 2.12 (quint, J = 7.4 Hz, 1H), 1.27-1.54 (m, 52H), 0.92 (t, J = 6.0 Hz, 6H). ^{13}C NMR (CD_3OD, 100 MHz): δ(ppm) 132.0, 129.1, 127.9, 126.4, 124.8, 124.6, 123.1, 124.6, 50.2, 31.7, 29.6, 29.3 (multiple peaks), 28.7, 26.0, 22.3. 13.0. HRMS *m/z* found : 355.8152 ([M - NTf_2 + H]$^{2+}$), calc. : 355.8147; found : 710.6218 [M*]$^+$, calc. 710.6221.

General procedure for Intramolecular Diels Alder reaction in ionic solvents

Mixtures of ester tethered 1,3,9-tridecatriene compounds were prepared by dissolving the 1,3,9-tridecatriene ester (1 eq.) and the ionic solvent in dichloromethane, evaporating the volatile solvent under reduced pressure, and pumping on the residue under high vacuum for 1-2 h, which gave a solid mixture. The solid mixture was heated to 130°C with constant agitation, and kept under stirring at this temperature for 5 minutes. The reaction mixture was then cooled to 90°C, temperature at which the Diels Alder reactions were carried out for 15 h. The crude residue was extracted with diethyl ether. The combined organic layers were concentrated under reduced pressure and purified by column chromatography (hexane/isopropanol = 95/5) on silica gel.

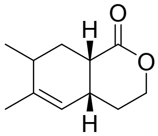
The ionic liquid was reused as it in a subsequent Diels-Alder reaction, without any further purification.

4a,8a-cis-3,4,4a,7,8,8a-Hexahydro-1H-isochromen-1-one



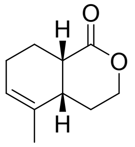
^{1}H NMR ($CDCl_3$, 400 MHz) : δ(ppm) 5.84 (d, J = 8.0, 1H), 5.52 (d, J = 7.4 Hz, 1H), 4.27 (t, J = 7.4 Hz, 2H), 2.72-2.78 (m, 2H), 2.00-2.06 (m, 4H), 1.70-1.74 (m, 2H).). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) 173.5, 129.6, 127.8, 67.2, 39.3, 31.7, 28.1, 23.4, 22.3. HRMS *m/z* found : 152.0840 ([M*]$^+$), calc. : 152.0837.

4a,8a-cis-6,7-dimethyl-3,4,4a,7,8,8a-Hexahydro-1H-isochromen-1-one



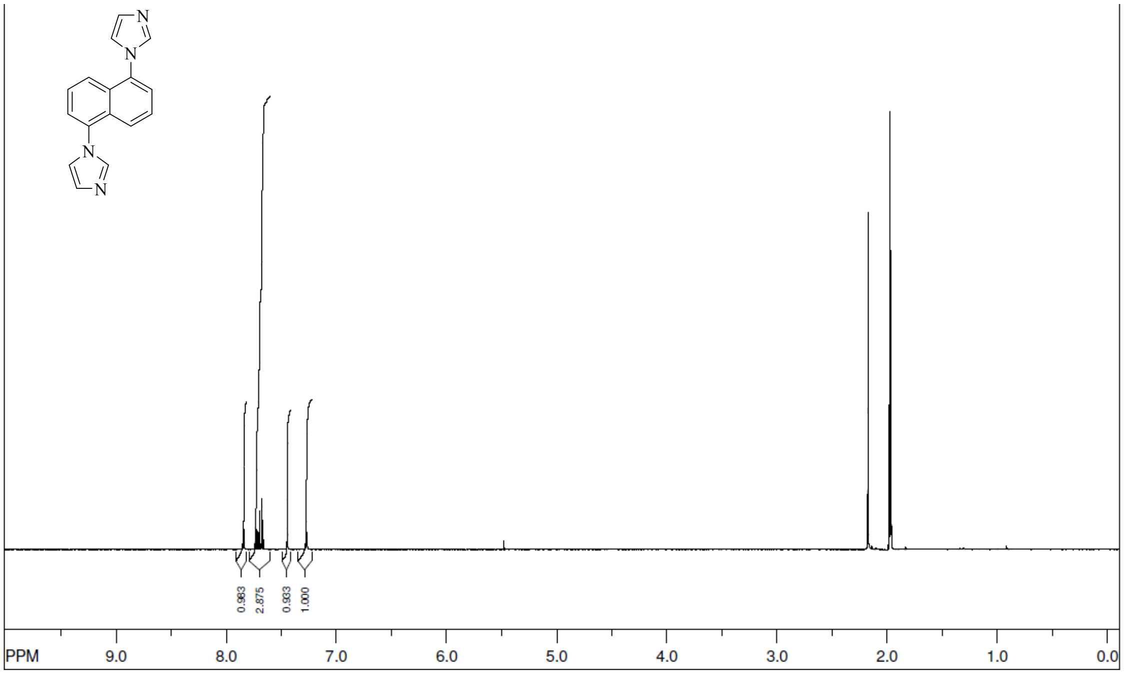
^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 5.34 (s, 1H), 4.48 (m, 1H), 4.28 (m, 1H), 2.78-2.85 (m, 1H), 2.55 (s, 1H), 2,26 (s, 1H), 2.09-2.19 (m, 1H). 1.85-1.89 (m, 1H), 1.60-1.79 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) 171.9, 135.7, 124.2, 70.5, 46.5, 44.9, 33.0, 28.0, 20.9, 19.0. HRMS *m/z* found : 180.1152 ([M+H]$^+$), calc. : 180.1145.

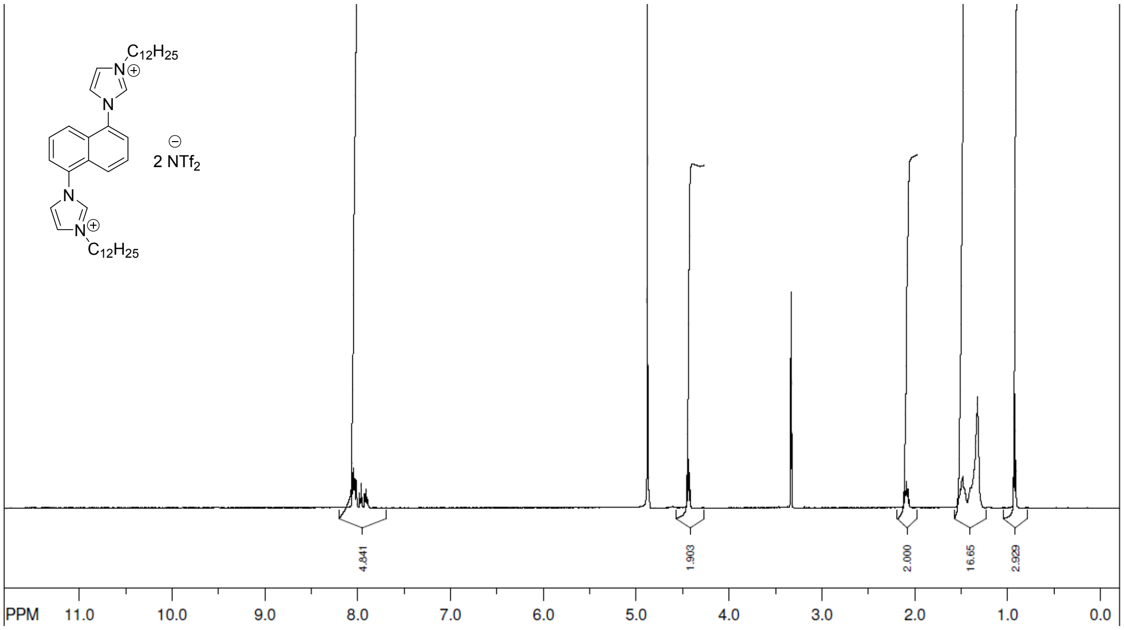
4a,8a-cis-5-methyl-3,4,4a,7,8,8a-Hexahydro-1H-isochromen-1-one



^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.60 (s, 1H), 5.70 (s, 1H), 4.26-4.33 (m, 2H),2.78-2.85 (m, 1H), 2.80 (s, 1H), 2.50 (s, 1H), 2.00-2.06 (m, 4H). 1.80-1.84 (m, 2H), 1.68 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 174.0, 132.8, 124.4, 68.0, 40.4, 36.2, 25.9, 23.5, 21.1. HRMS *m/z* found : 167.10673 ([M+H]$^+$), calc. : 180.10666, found 189.0887 ([M+Na]), calc. 189.0886.

Characterization of the compounds

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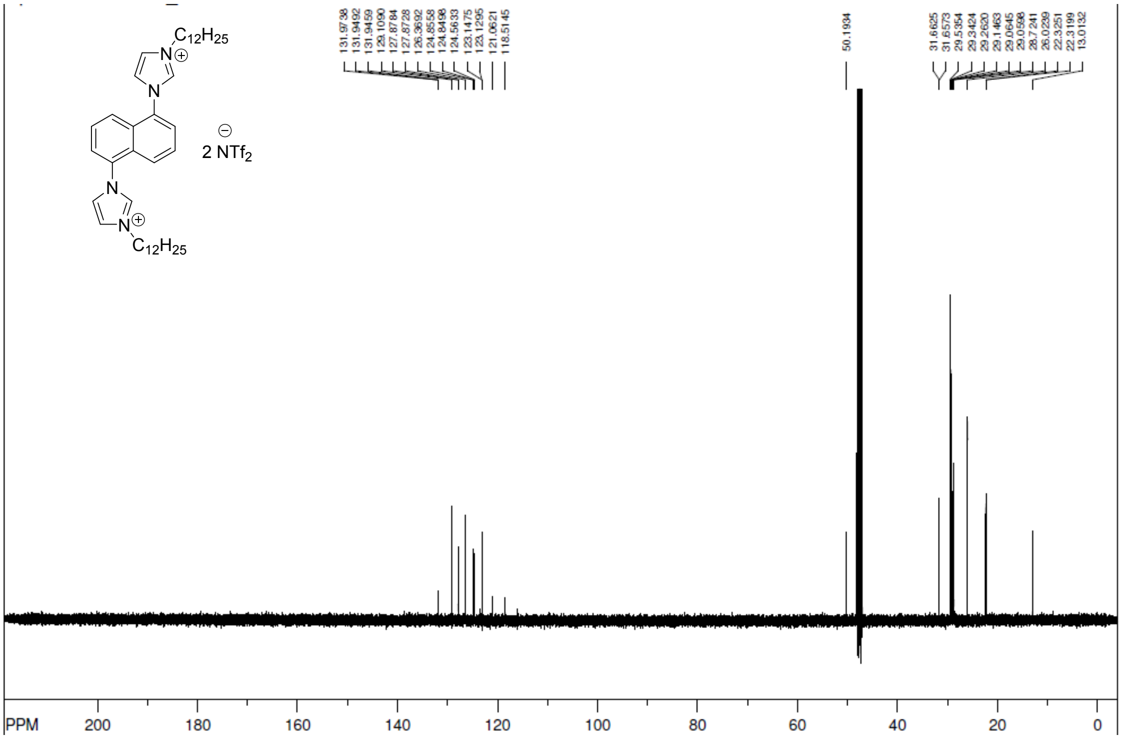
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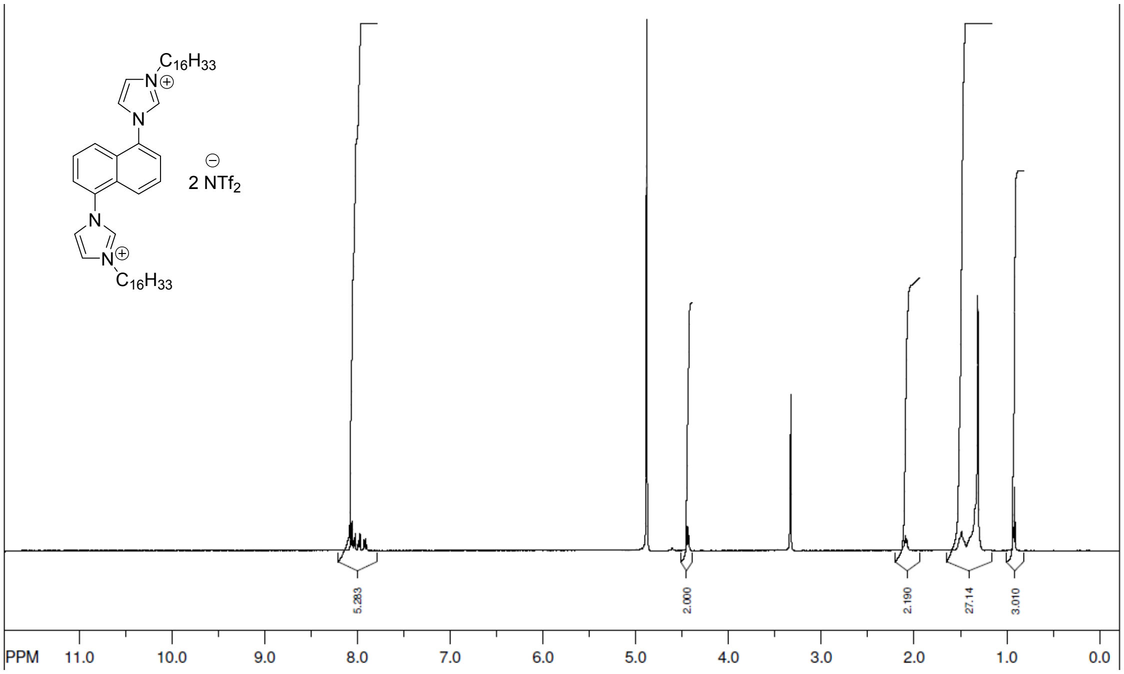
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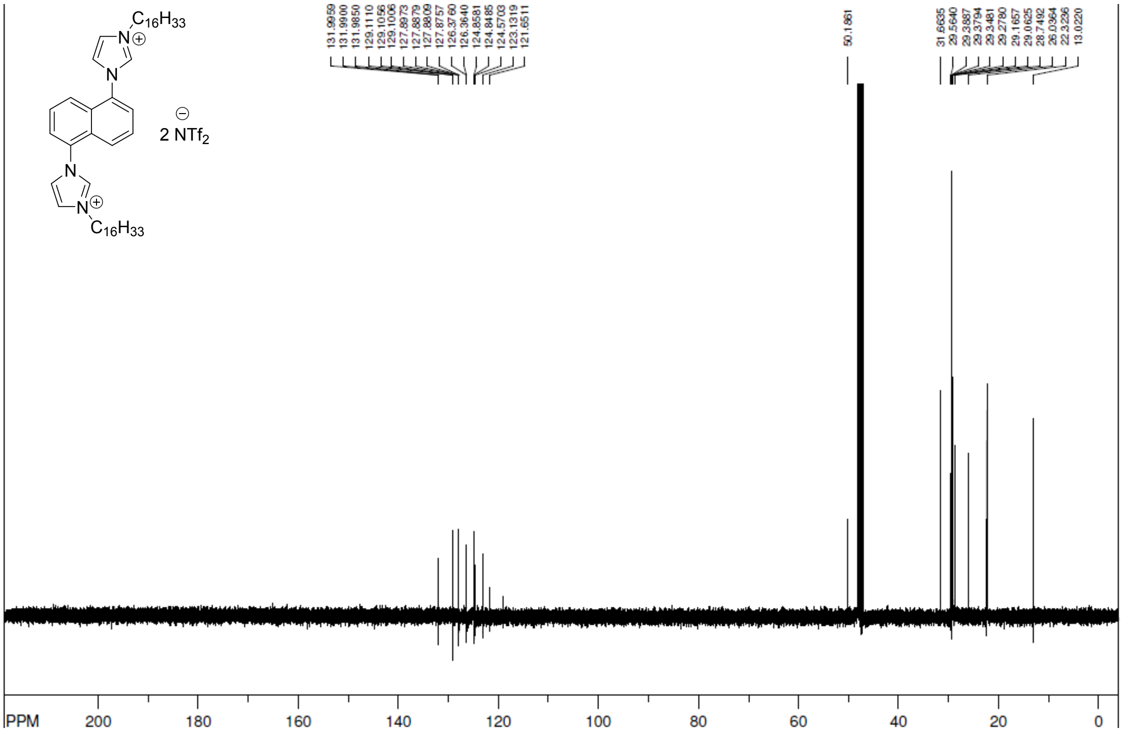
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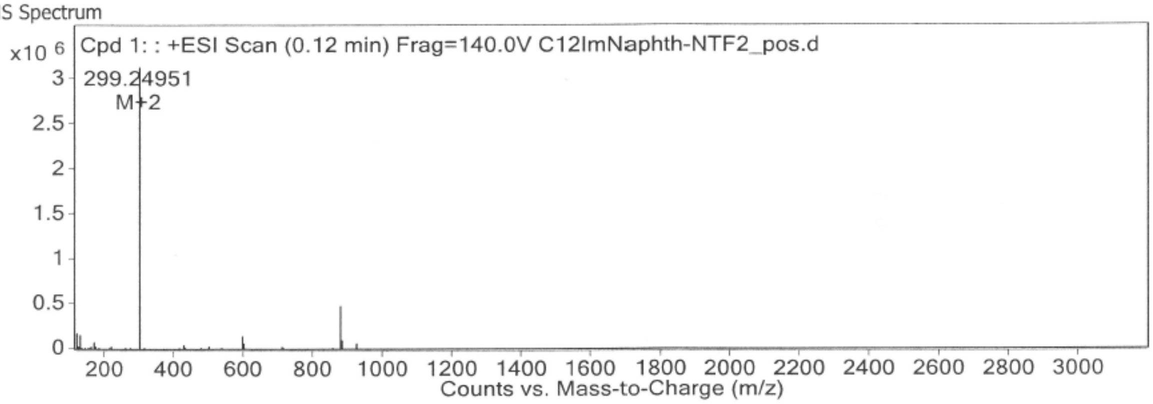
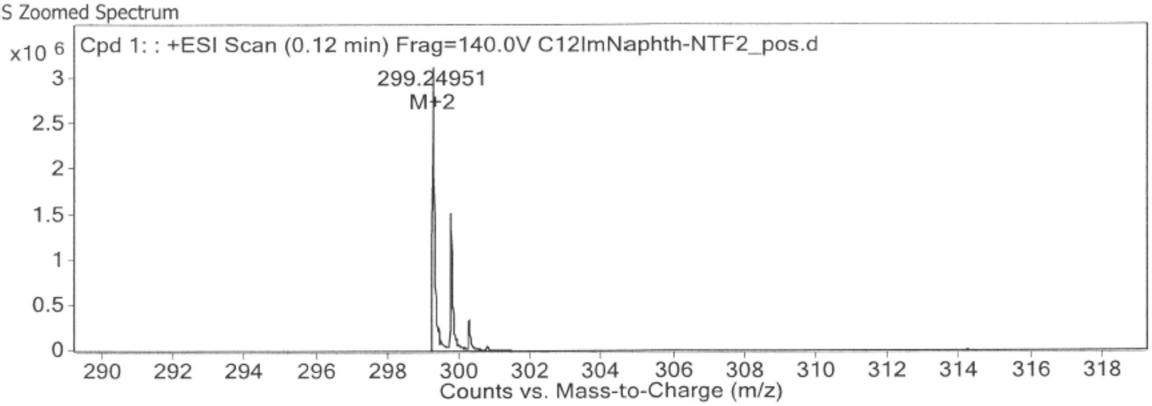
MS Spectrum



MS Zoomed Spectrum



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Data File	C12ImNaphth-NTF2-neg.d	**Sample Name**	C12ImNaphth-NTF2-neg
Sample Type	Sample	**Position**	P1-D8
Analysis Date	11/5/2014 10:23:43 AM	**User Name**	Karine
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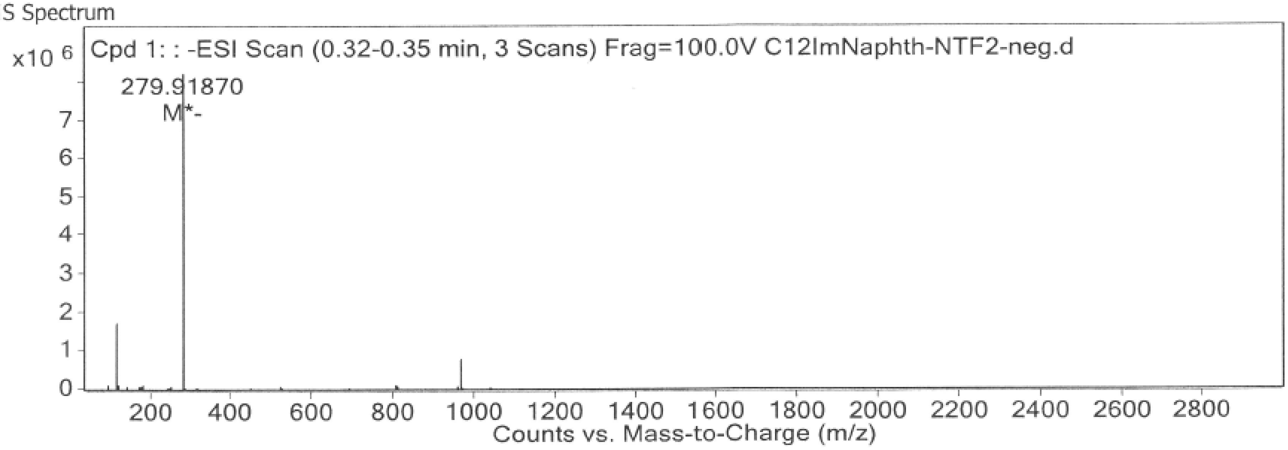
Comment			

MS Spectrum



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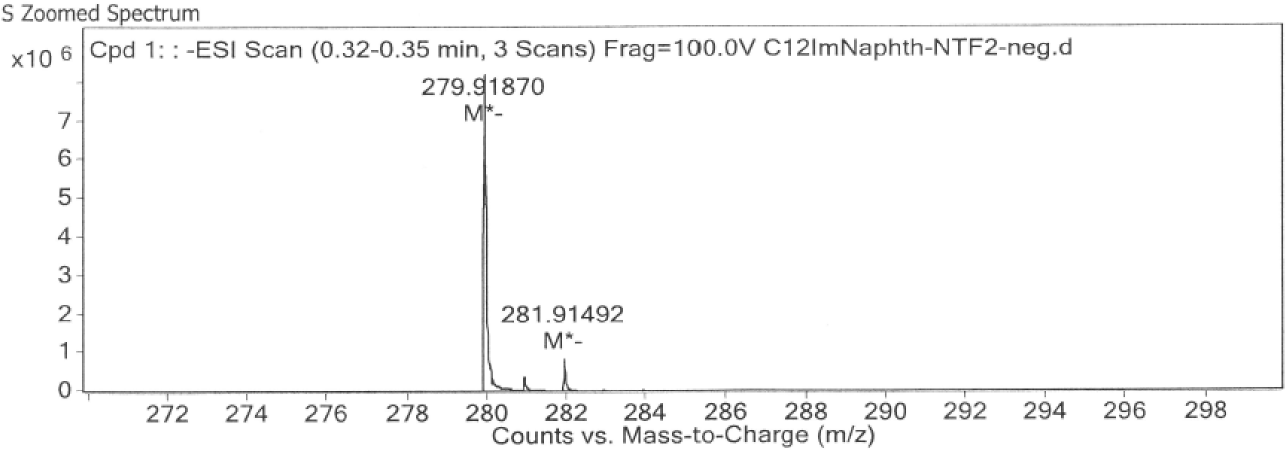

MS Spectrum Peak List

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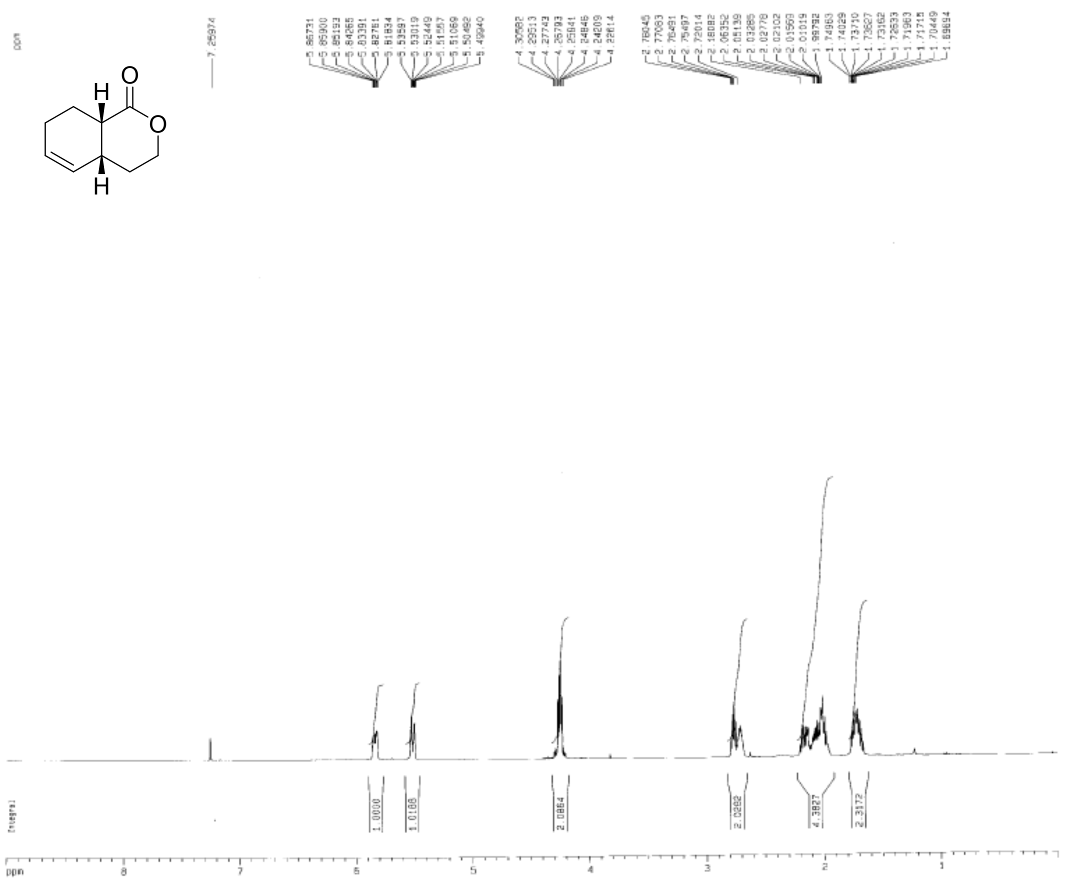
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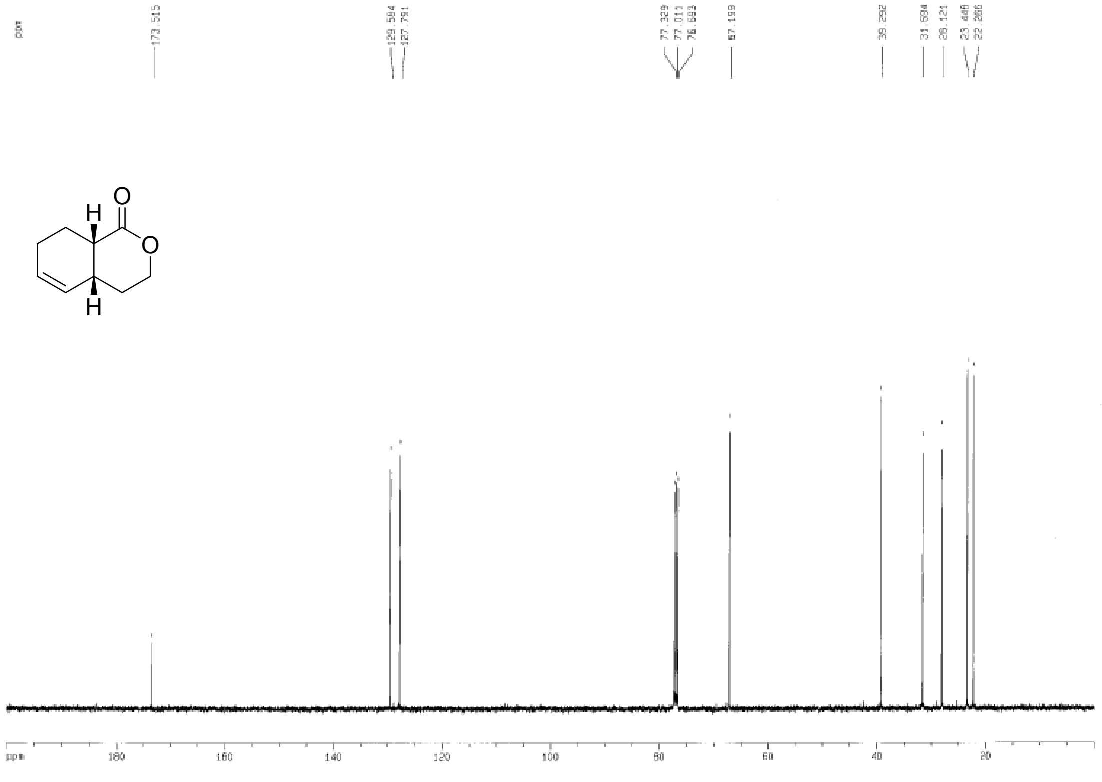
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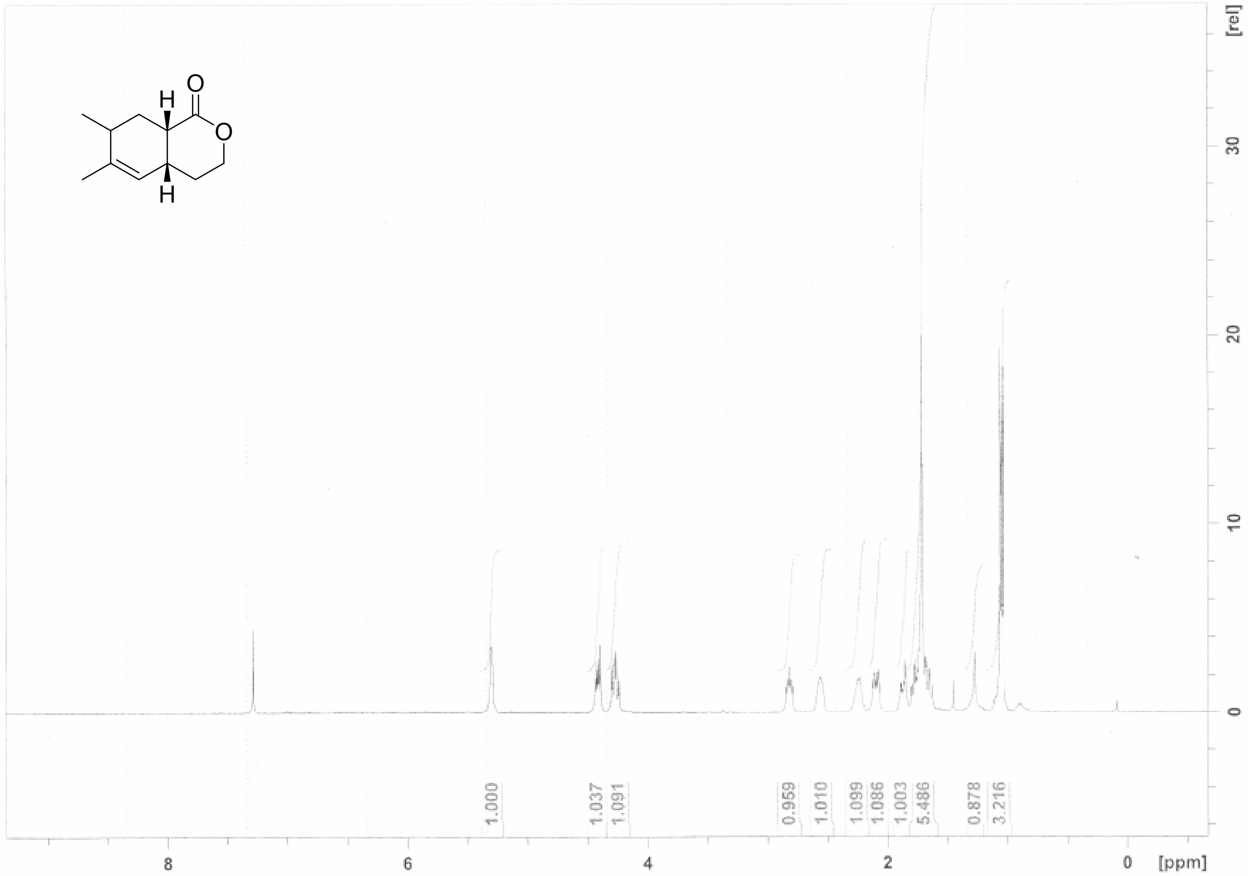
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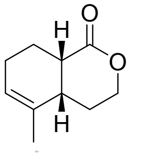
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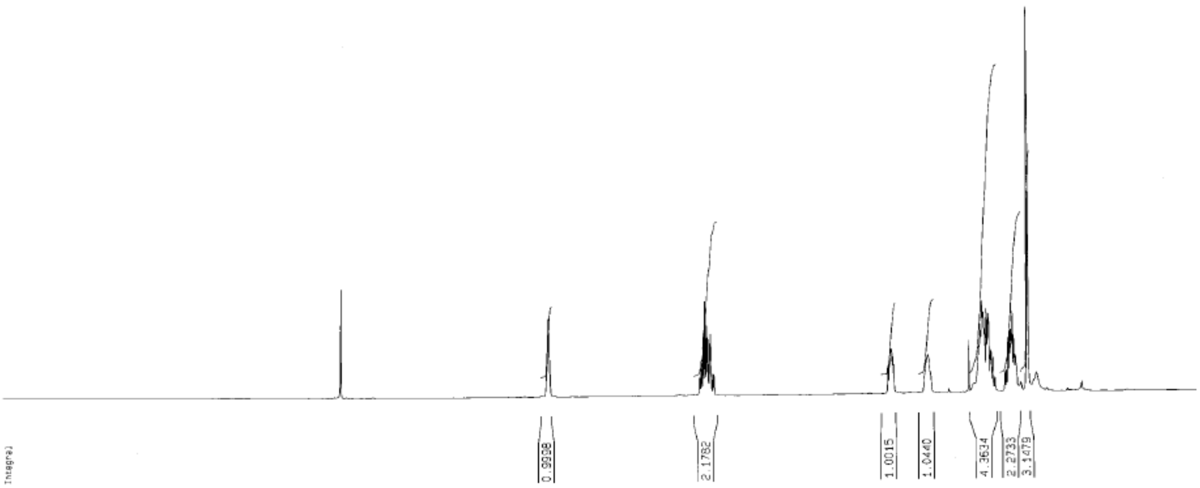
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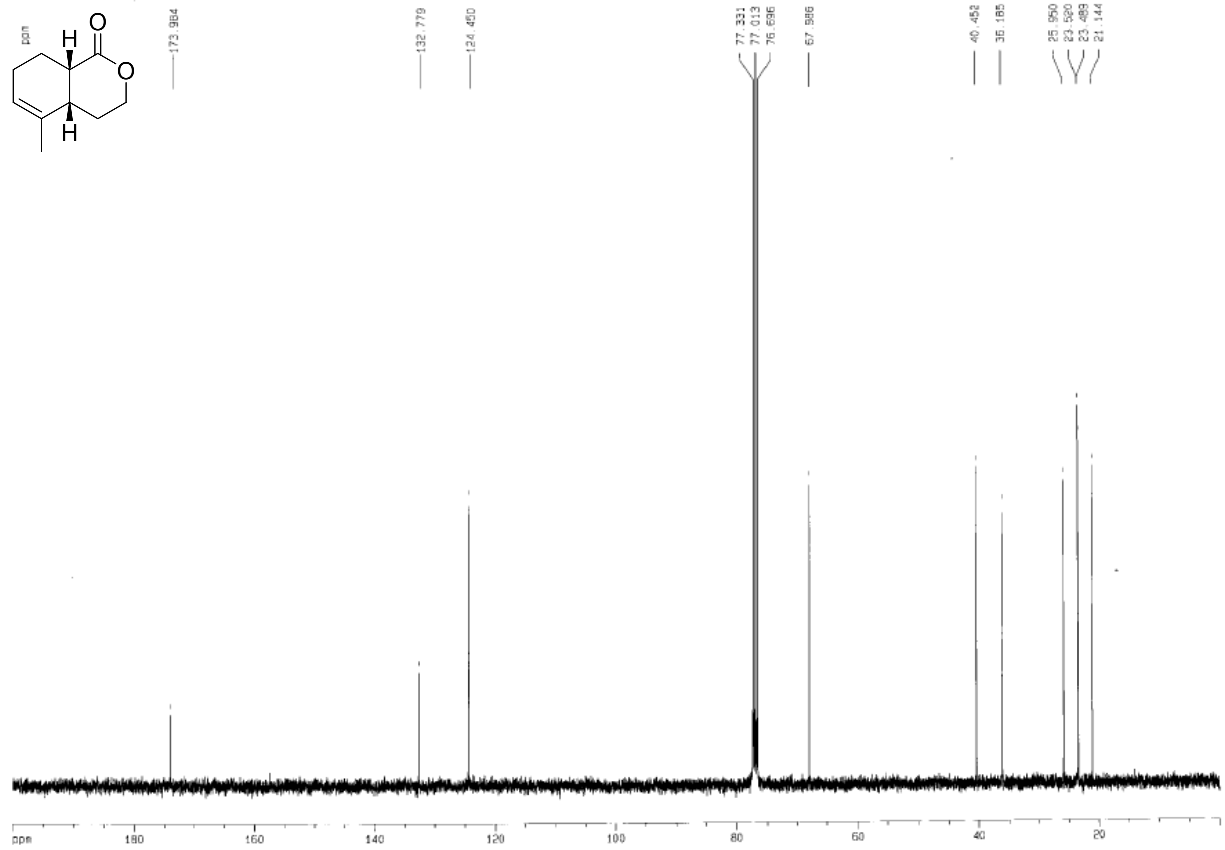
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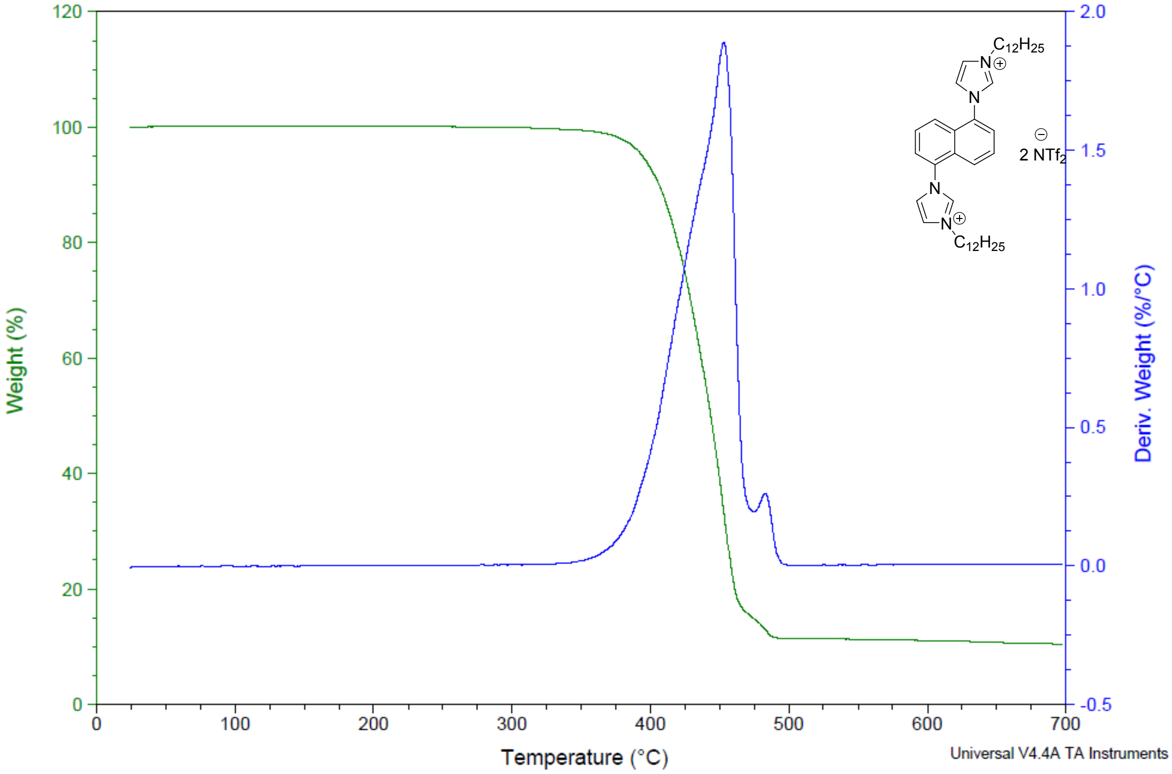
TGA of compound **1e**



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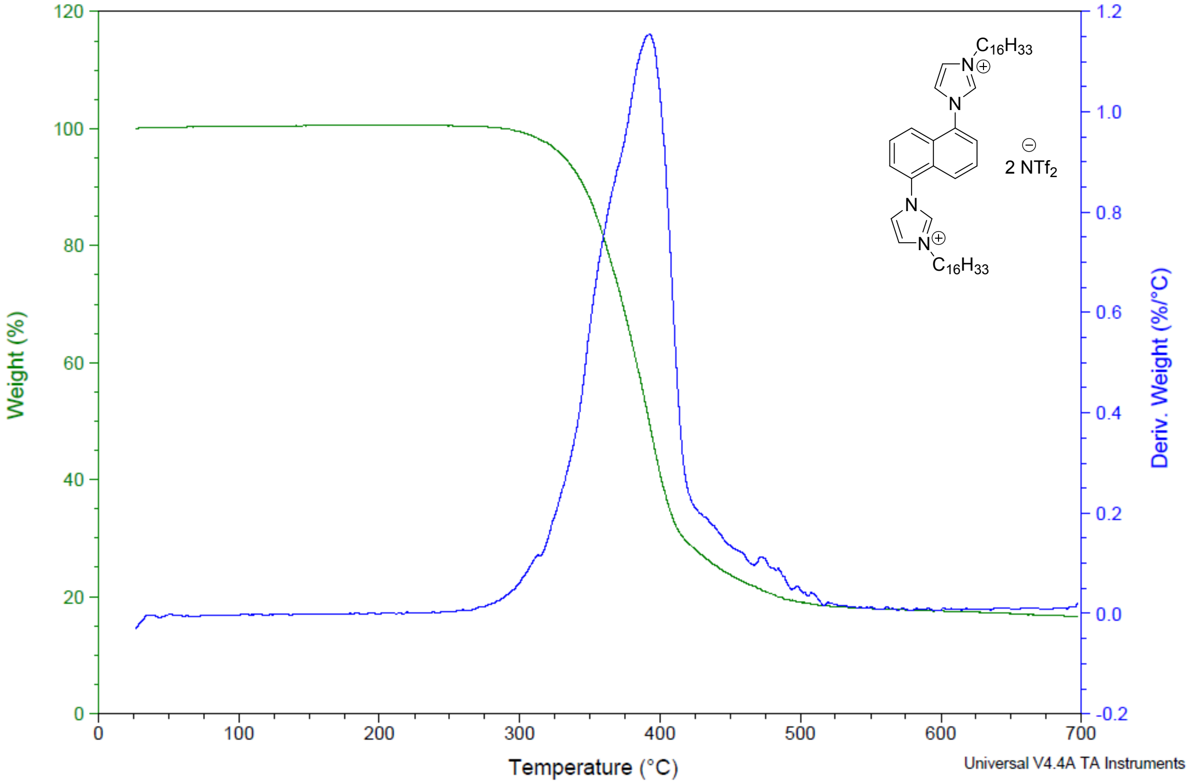

Molecular modelling

The 3D structures of the molecules were built with Hyperchem software (version 7.5). All calculations were performed using Gaussian 98. The geometry optimizations were carried out by the B3LYP method emplying the 6-31G(d) basis set, with no initial symmetry restrictions.