

Supporting Informations

Reactivity of Carbon Dioxide in hydrofluoroethers:

Facile Access to Cyclic Carbonates

Marius Mamone, Thierry Milcent, Benoit Crousse*

Univ. Paris-Sud, BioCIS, CNRS, Faculté de Pharmacie, LabEx LERMIT
5 Street J. B. Clément, Châtenay-Malabry 92296, France

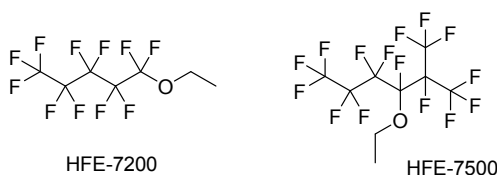
Experimental procedures

1. Reagents

Commercially available epoxides, solvents, were purchased from various commercial sources (Acros, Aldrich) and used without further purification. Carbon dioxide (purchased from carboxique carbopharm) was used without further purification or drying *prior to* its use.

TLC was performed on silica gel, 60F-250 (0.26mm thickness) plates. The plates were visualized with UV light (254 nm) or with a 3.5% solution of phosphomolybdic acid in ethanol or with a solution of KMnO_4 in water. Flash chromatography (FC) was performed on Merck 60 silica gel (230 – 400 mesh). Melting points were determined on a Kofler melting point apparatus. NMR spectra were measured on an Ultrafield AVANCE300 (^1H , 300 MHz; ^{13}C , 75 MHz) spectrometer. Unless otherwise stated, NMR data were obtained under ambient temperature conditions. Chemical shifts δ are in ppm, and the following abbreviations are used: singlet (s), doublet (d), doublet doublet (dd), triplet (t), quintuplet (quint), multiplet (m) and broad singlet (brs).

The hydrofluoroethers HFE-7200 and HFE-7500 were provided by 3M, and their formulas are as follows:



2. General procedure for the preparation of cyclic carbonates:

Under 1 atm of CO_2 : CO_2 from a gas balloon was allowed to react with epoxide (1 mmol), TBAI (5 mol%) in 2 mL of HFE-7500 according to the reported time in the Table 2, under vigorous stirring.

Under 5 bar: A 30 mL stainless steel autoclave was charged with the epoxide precursor (1 mmol), the catalyst TBAI (5mol%), and HFE-7500 (2 mL). The autoclave was placed under pressure of CO_2 (5 bar). The autoclave was sealed and heated according to the reported time in the Table 3.

Purification : After addition of 4 mL of methanol, HFE-7500 was separated of the organic phase.

The HFE-7500 could be also removed by simple distillation (bp: 129°C) from the carbonate.

In the case of solid products, a simple filtration was required to remove and recover the HFE-7500.

Then the products were purified by flash chromatography on silica gel (cyclohexane/EtOAc: 7/3).

4-Phenoxymethyl-1,3-dioxolan-2-one (2a)¹. White solid; mp 99–100°C (lit.¹ 98–100°C); ^1H NMR (CDCl_3 , 300 MHz): δ 7.31 (2H, t, $J = 7.6$ Hz, Ar-H), 7.02 (1H, t, $J = 7.2$ Hz, Ar-H), 6.91 (2H, d, $J = 8.0$ Hz, Ar-H), 5.00 (1H, m, OCH), 4.61 (1H, dd, $J = 8.4$ and 5.4 Hz, OCH_2),

4.54 (1H, dd, $J = 8.4$ and 8.4 Hz, OCH₂), 4.26-4.13 (2H, m, OCH₂). ¹³C NMR (CDCl₃, 75 MHz): δ 157.7, 154.7, 129.6, 121.8, 114.5, 74.2, 66.8, 66.0.

4-Bromomethyl-1,3-dioxolan-2-one (2b)²: colourless oil. ¹H NMR (300 MHz, CDCl₃): δ 4.94 (1H, m), 4.55 (1H, t, $J = 8.0$ Hz), 4.29 (1H, m), 3.63-3.51 (2H, m); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 154.2, 73.9, 68.0, 31.9.

4-Allyloxymethyl-1,3-dioxan-2-one (2c)¹. colourless oil. ¹H NMR (CDCl₃, 300 MHz): δ 5.80 (1H, m, CH=CH₂), 5.22 (1H, m, CH=CH₂), 5.15 (1H, m, CH=CH₂), 4.80 (1H, m, OCH), 4.46 (1H, t, $J = 8.3$ Hz, OCH₂), 4.33 (1H, dd, $J = 8.3$ and 6.0 Hz, OCH₂), 4.00 (2H, m, OCH₂), 3.65 (1H, dd, $J = 11.1$ and 3.5 Hz), 3.55 (1H, dd, $J = 11.1$ and 3.7 Hz). ¹³C NMR (CDCl₃, 75 MHz): δ 154.9, 133.6, 117.5, 75.0, 72.3, 68.7, 66.1.

4-Phenyl-1,3-dioxolan-2-one (2d)¹. White solid; mp : 66-67°C (lit.¹ 68-69°C); ¹H NMR (CDCl₃, 300 MHz): δ 7.44-7.41 (3H, m, Ar-H), 7.39-7.31 (2H, m, Ar-H), 5.65 (1H, t, $J = 8.0$ Hz, OCH), 4.8 (1H, t, $J = 8.4$ Hz, OCH₂), 4.30 (1H, t, $J = 8.2$ Hz, OCH₂). ¹³C NMR (CDCl₃, 75 MHz): δ 154.7, 135.7, 129.4, 129.0, 125.7, 77.8, 71.0.

4-Chloromethyl-1,3-dioxolan-2-one (2e)¹. colourless liquid. ¹H NMR (CDCl₃, 300 MHz): δ 4.97- 4.95 (1H, m, OCH), 4.58 (1H, dd, $J = 8.9$ and 8.6 Hz, OCH₂), 4.42 (1H, dd, $J = 5.7$ and 8.9 Hz, OCH₂), 3.81-3.68 (2H, m, ClCH₂). ¹³C NMR (CDCl₃, 75 MHz): δ 154.2, 74.3, 66.8, 43.8.

4-Naphthyl-1-oxymethyl-1,3-dioxolan-2-one (2f) : white solid; mp : 136-138°C; ¹H NMR (300 MHz, DMSO-d₆): δ 8.09 (1H, m), 7.89 (1H, m), 7.57-7.50 (3H, m), 7.43 (1H, t, $J = 7.8$ Hz), 7.00 (1H, d, $J = 7.6$ Hz), 5.30 (1H, m, CHO), 4.73 (1H, t, $J = 8.5$ Hz), 4.58 (1H, dd, $J = 8.5$ and 5.2 Hz), 4.48 (1H, dd, $J = 11.10$ and 2.3 Hz), 4.39 (1H, dd, $J = 11.10$ and 3.6 Hz). ¹³C NMR (75 MHz, DMSO-d₆): δ 155.0, 153.2, 133.9, 127.4, 126.5, 126.0, 125.5, 124.6, 121.0, 120.6, 105.4, 74.7, 67.7, 66.3. Elemental Analysis C₁₄H₁₂O₄ (244.24) : calculated :C, 68.85; H, 4.95; O, 26.20; found C, 68.90; H, 4.91; O, 26.05.

4-n-Nonyl-1,3-dioxolan-2-one (2g). colourless liquid. ¹H NMR (CDCl₃, 300 MHz): δ 4.68 (1H, m, OCH), 4.50 (1H, t, $J = 8.3$ Hz, OCH₂), 4.04 (1H, dd, $J = 8.3$ and 7.2 Hz, OCH₂), 1.85-1.6 (2H, m, CH₂), 1.50-1.16 (4H, m, CH₂CH₂), 0.86 (3H, t, $J = 7.0$ Hz, CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 154.9, 76.9, 69.1, 33.1, 26.1, 21.9, 13.4. Elemental Analysis: C₁₃H₂₄O₃ (228.17) : calculated C, 68.38; H, 10.59; O, 21.02; found C, 68.25; H, 10.62; O, 20.89.

4-Methyl-1,3-dioxolan-2-one (2h)²: pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 4.85-4.93 (1H, m), 1.50 (3H, d, $J = 6.4$ Hz), 4.54 (1H, t, $J = 8.0$ Hz), 4.03 (1H, t, $J = 8.0$ Hz); ¹³C NMR (75 MHz, CDCl₃): δ 154.9, 73.4, 70.4, 18.9.

4-n-Butyl-1,3-dioxolan-2-one (2i)¹: pale yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 4.60 (1H, m, OCH), 4.44 (1H, t, $J = 8.1$ Hz, OCH₂), 3.95 (1H, t, $J = 8.1$ Hz, OCH₂), 1.8-1.5 (2H, m, CH₂), 1.40-1.22 (4H, m, CH₂CH₂), 0.85 (3H, t, $J = 6.8$ Hz, CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 154.9, 76.9, 69.1, 33.1, 26.1, 21.9, 13.4.

References :

1. J. Qin, P. Wang, Q. Li, Y. Zhang, D. Yuan and Y. Yao *Chem. Commun.* **2014**, 50, 10952.

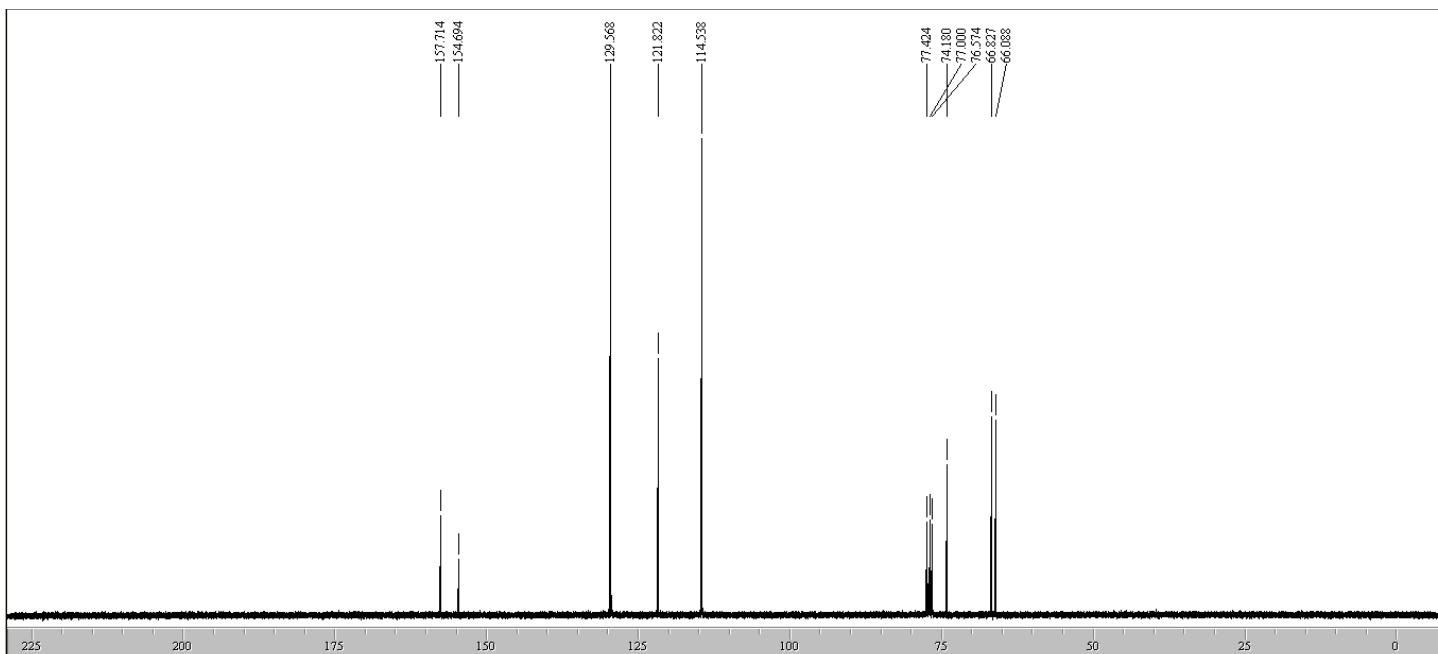
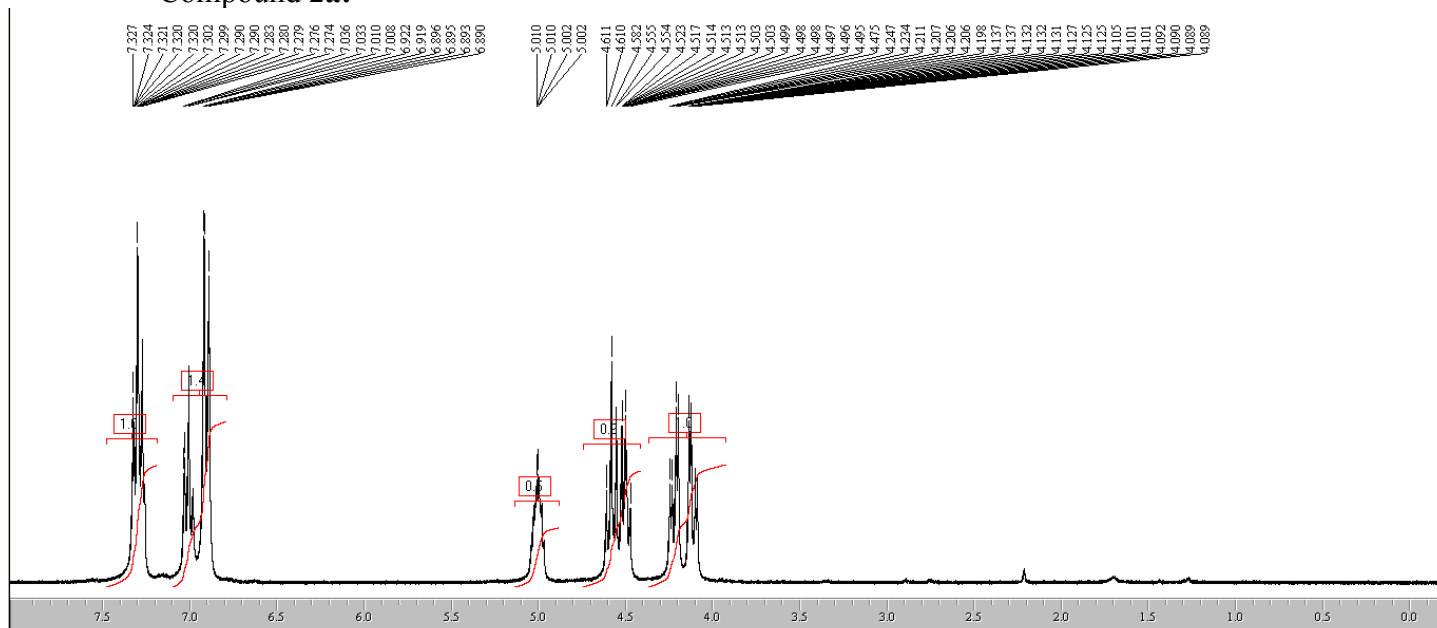
2. W. Chen, L.-x. Zhong, X.-w. Peng, R.-c. Sun, F.-c. Lu *ACS Sustainable Chem. Eng.*, **2015**, *3* (1), 147–152.

Table. Information describing qualitatively the appearance of the systems formed when 1 mM of epoxide and 5% of catalyst mixed with 2 mL of HFE 7500.

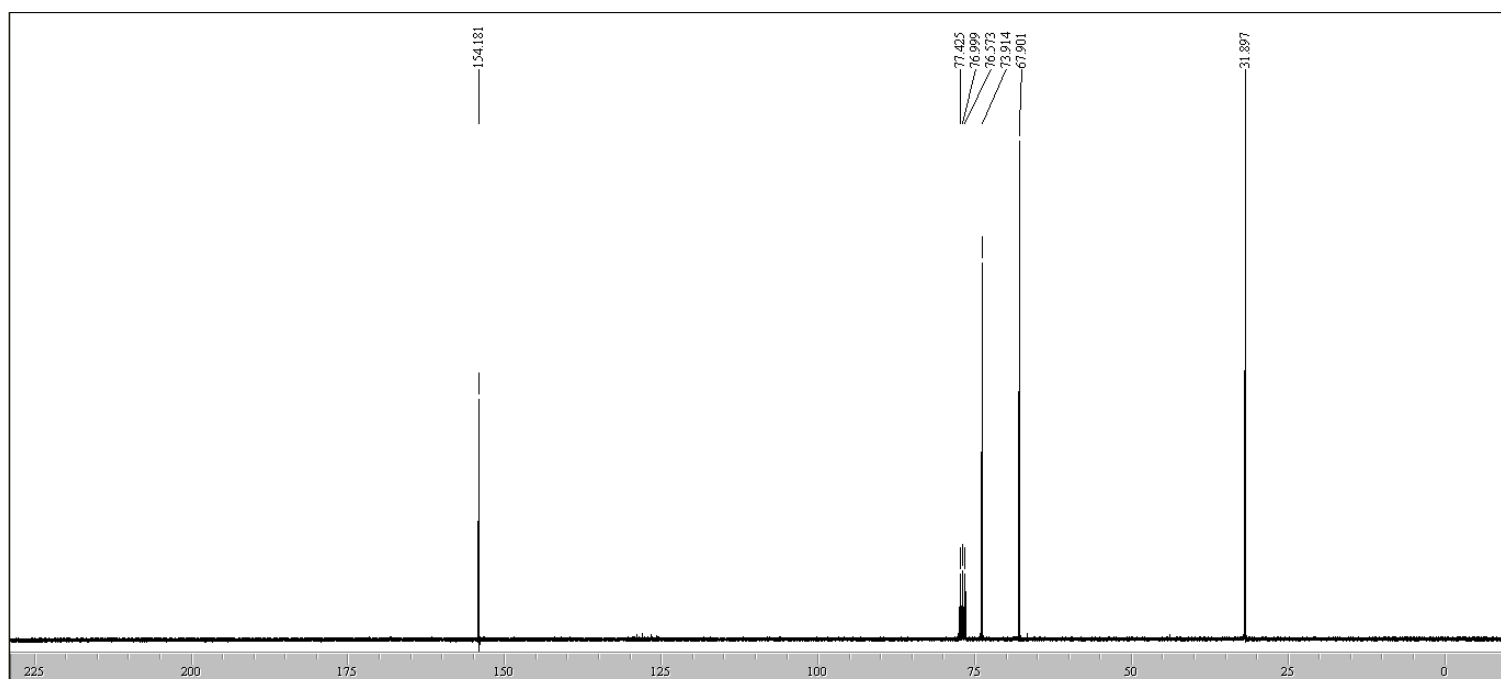
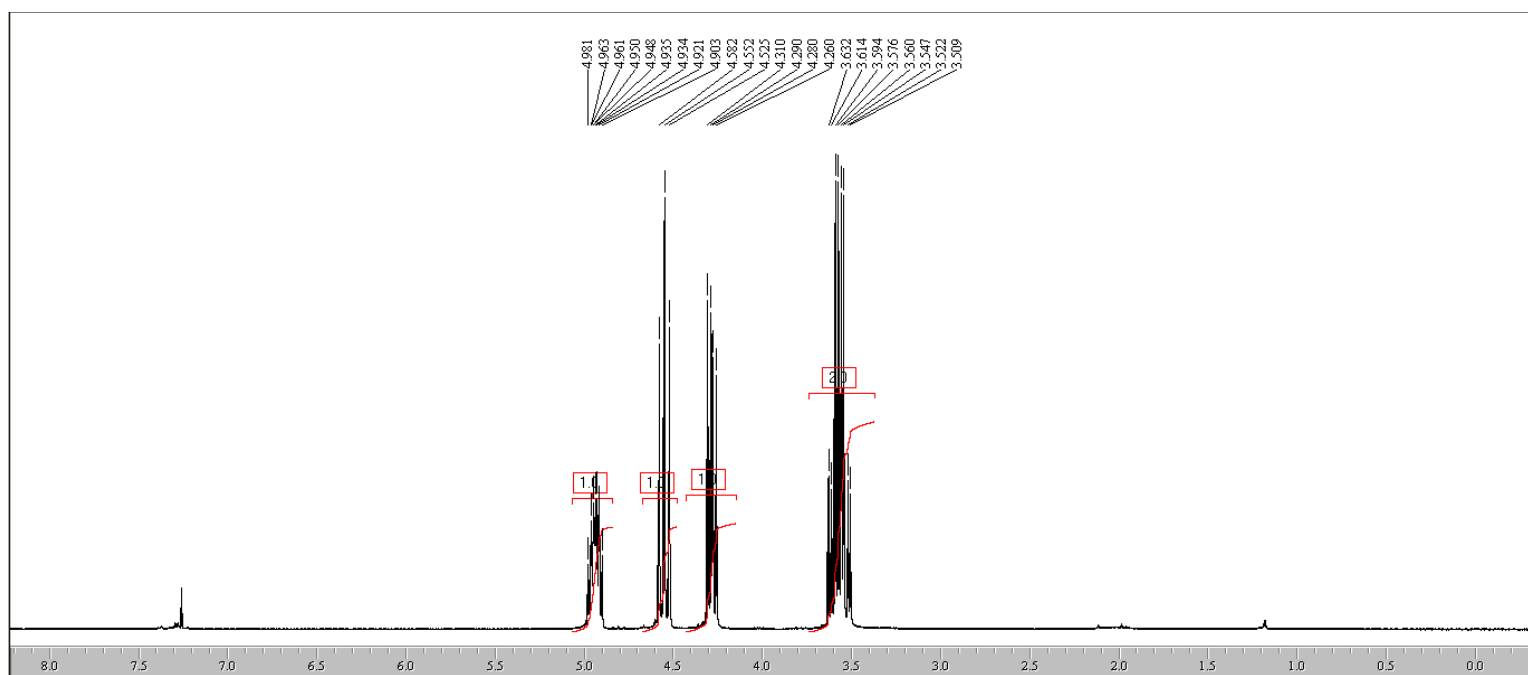
Epoxide	State of matter of 1a-i	System of 1mM epoxide/ 5% catalyst/2mL solvent	Temperature
1a	Liquid	two phase (L/L)	rt
1a	Liquid	two phase (L/L)	80°C
1b	Liquid	two phase (L/L)	rt
1b	Liquid	two phase (L/L)	80°C
1c	Liquid	two phase (L/L)	rt
1c	Liquid	two phase (L/L)	80°C
1d	Liquid	two phase (L/L)	rt
1d	Liquid	two phase (L/L)	80°C
1e	Liquid	two phase (L/L)	80°C
1f	Liquid	two phase (L/L)	80°C
1g	Liquid	two phase (L/L)	80°C
1h	Liquid	two phase (L/L)	80°C
1i	Liquid	two phase (L/L)	80°C

4. Copies of ^1H and ^{13}C NMR data for the Carbonate compounds :

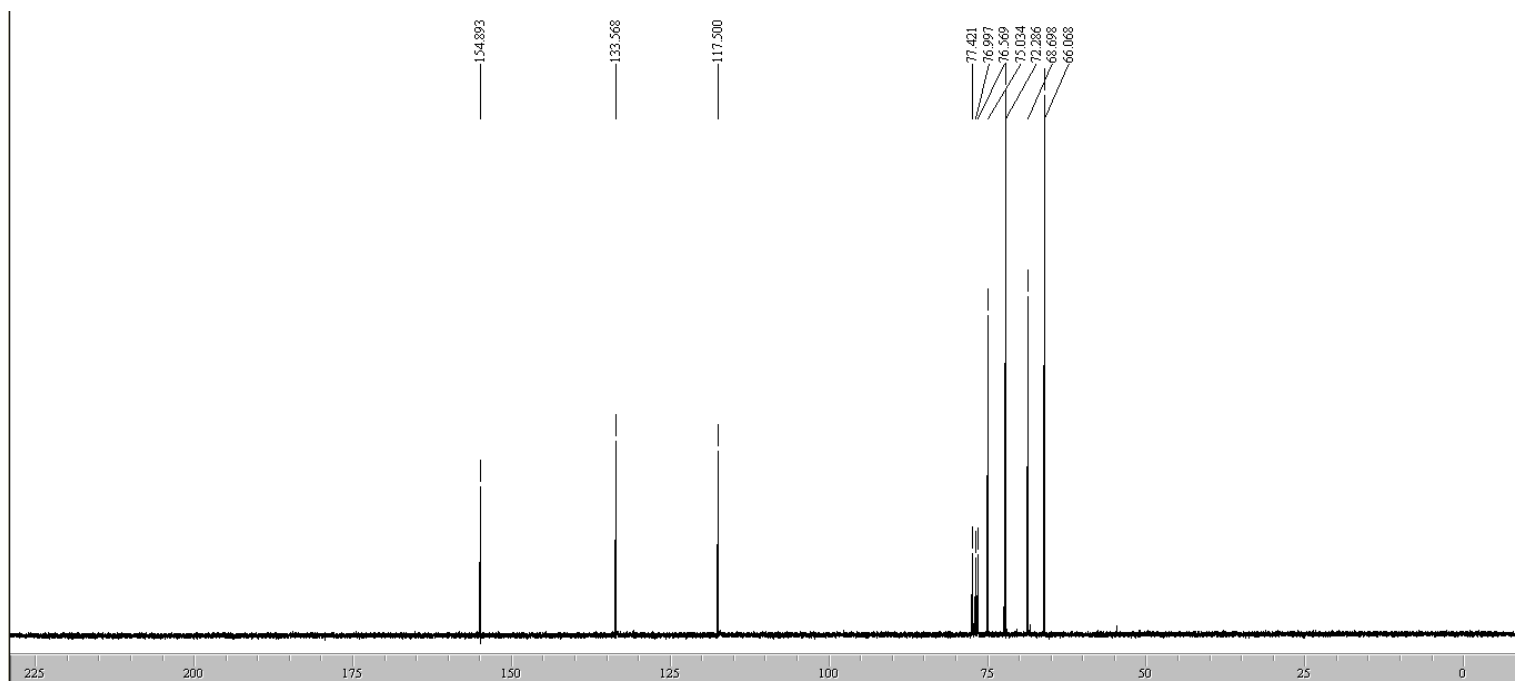
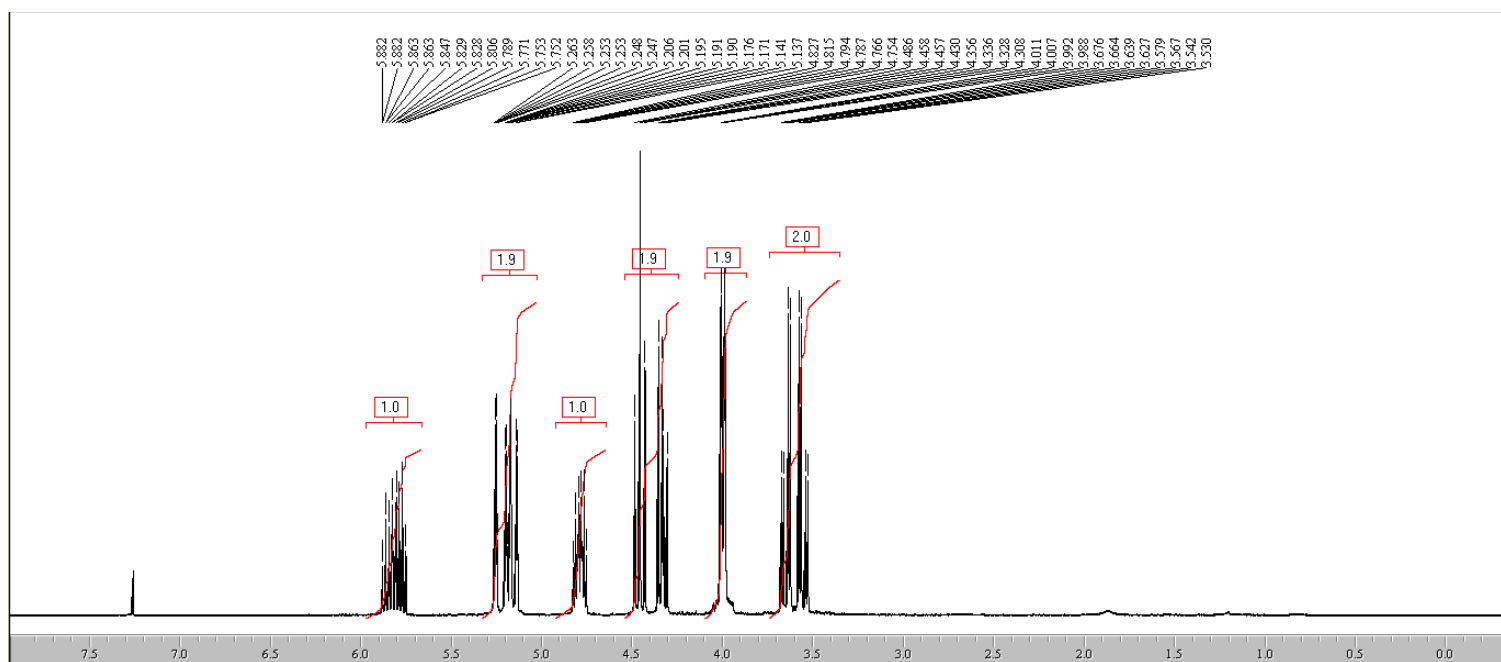
Compound 2a:



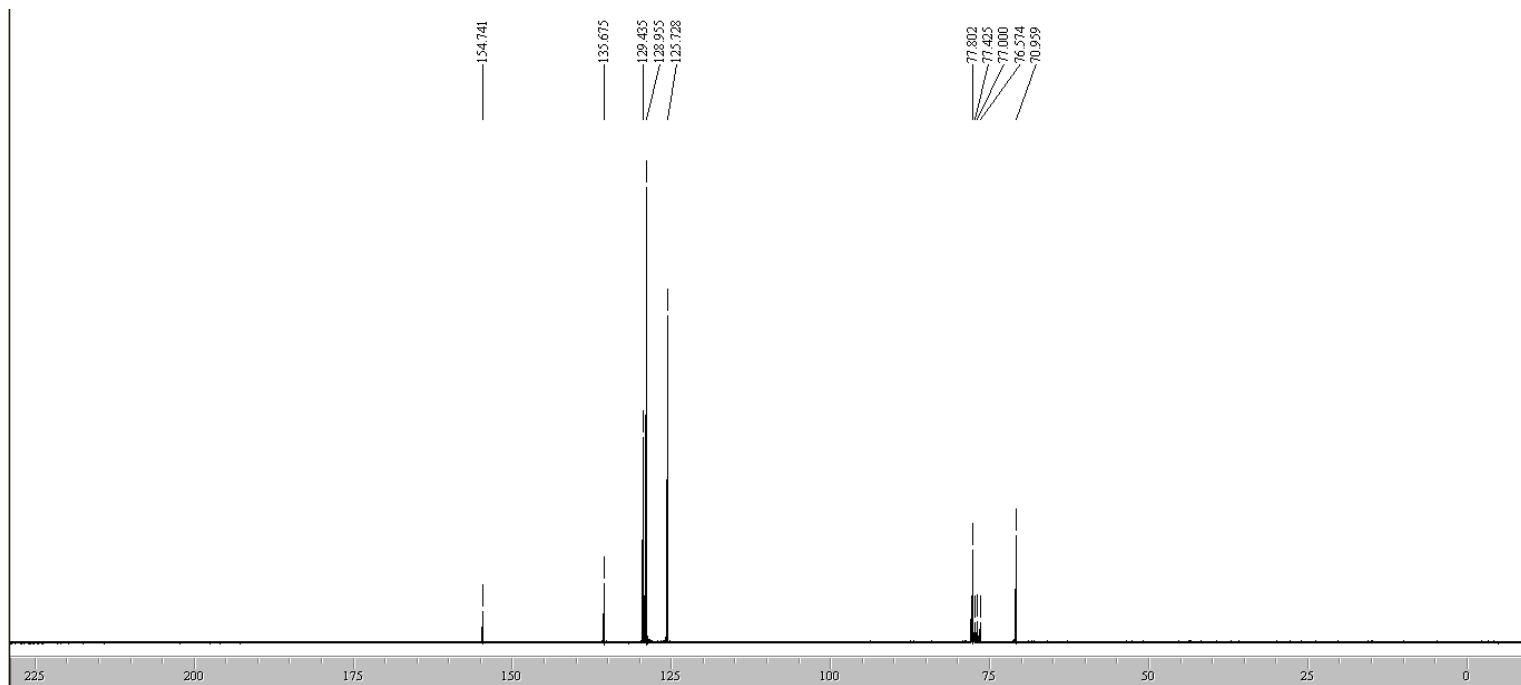
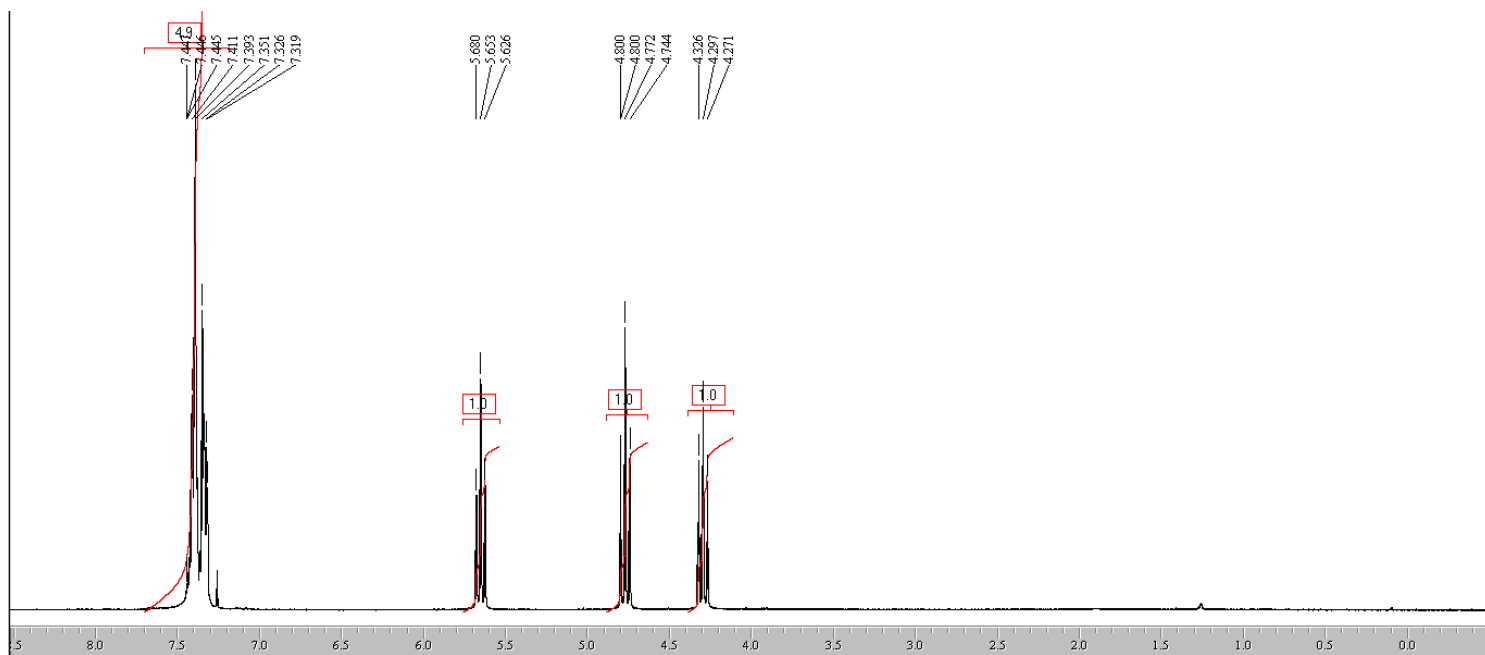
Compound **2b**:



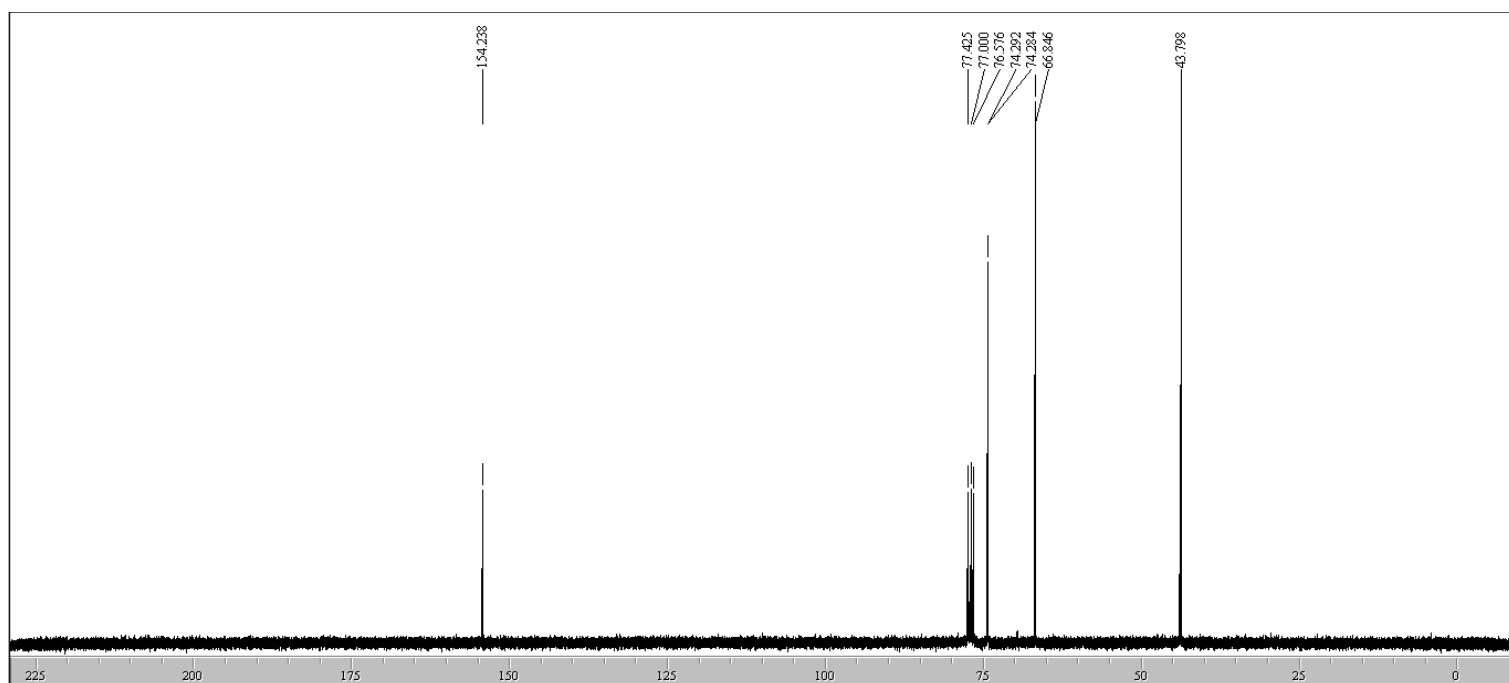
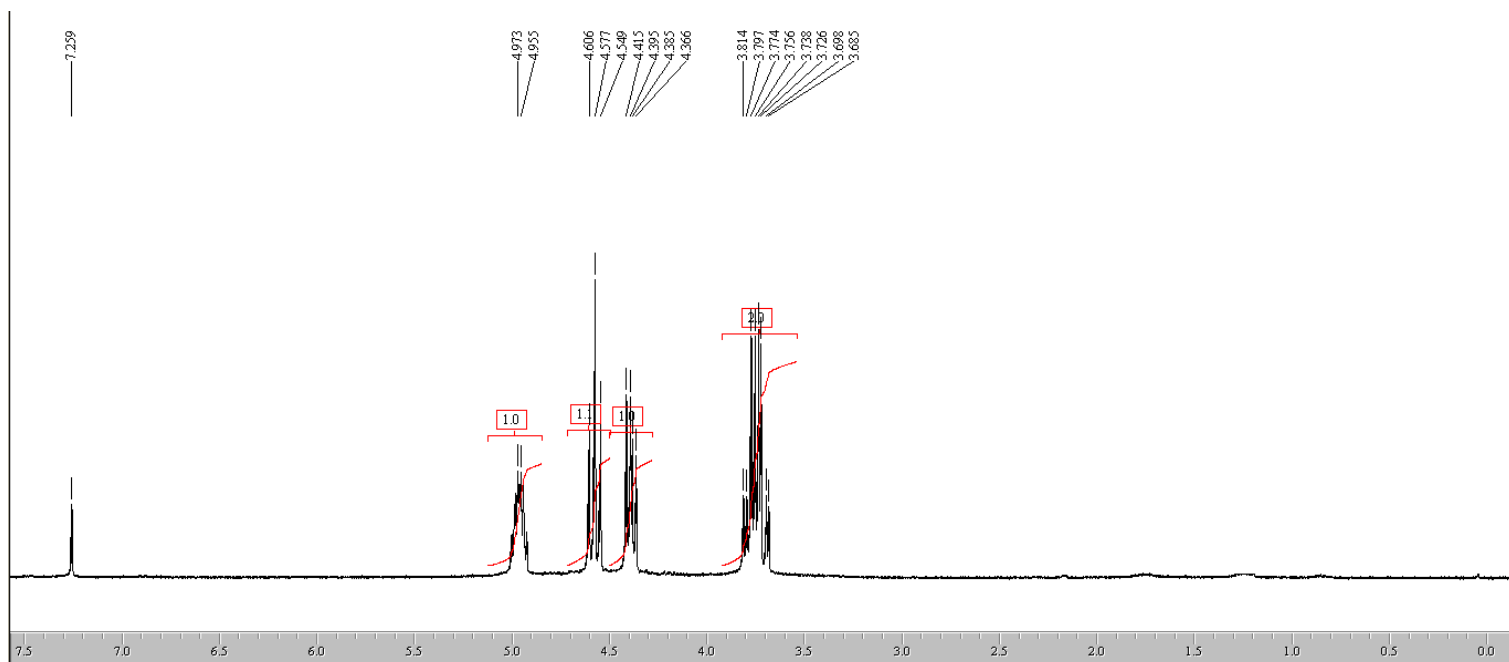
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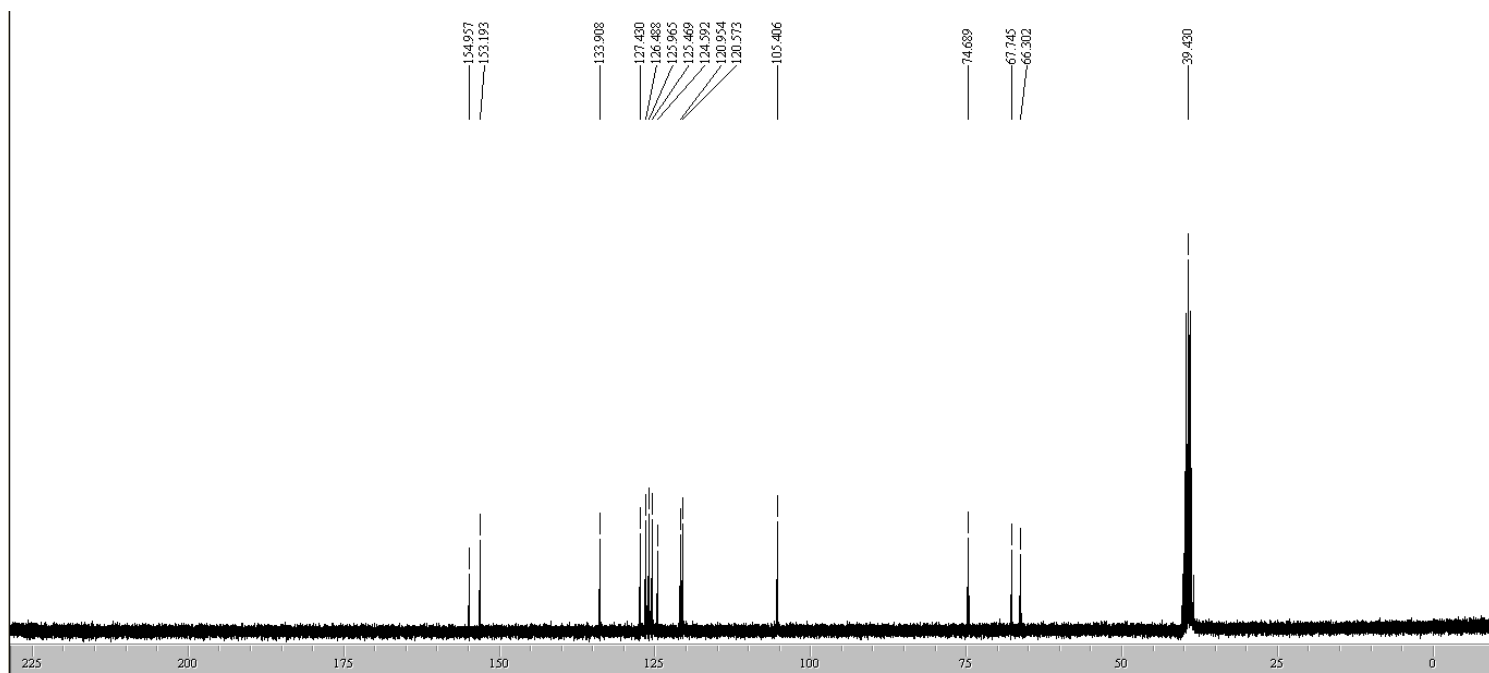
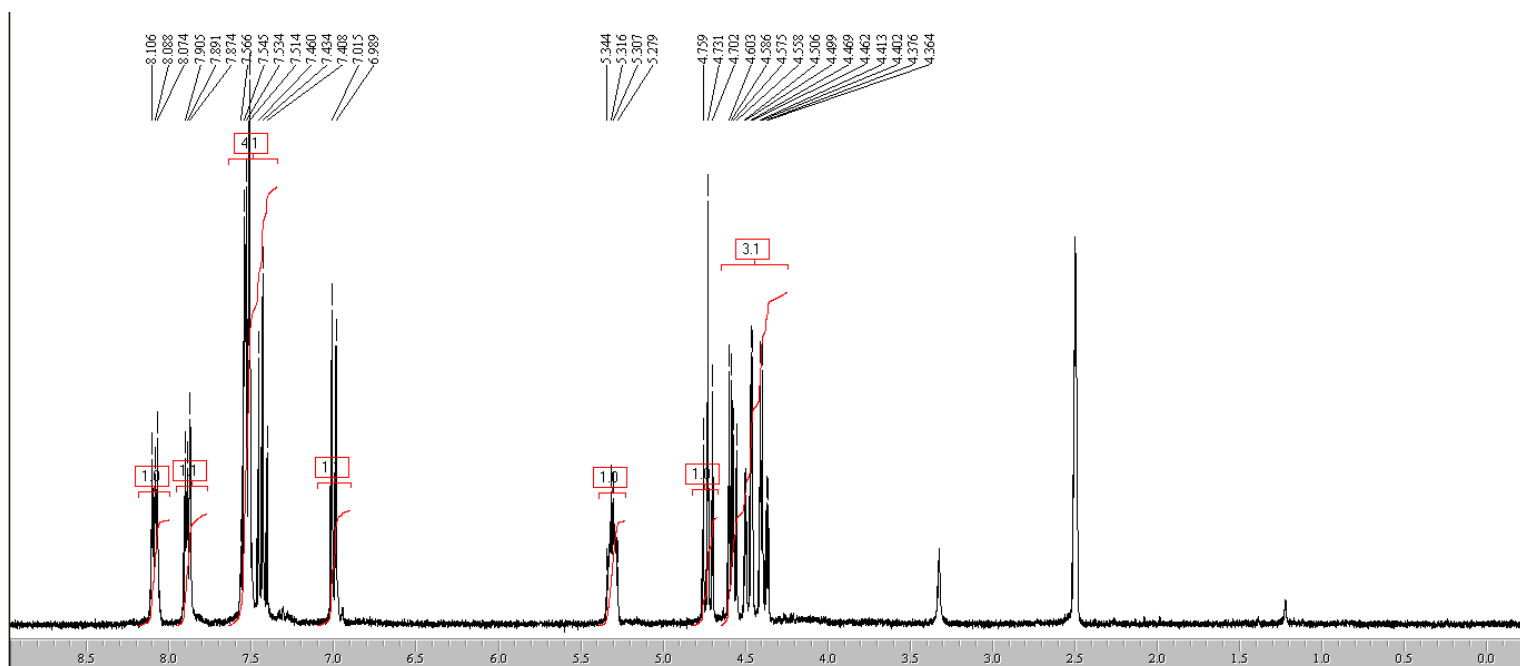
Compound 2d:



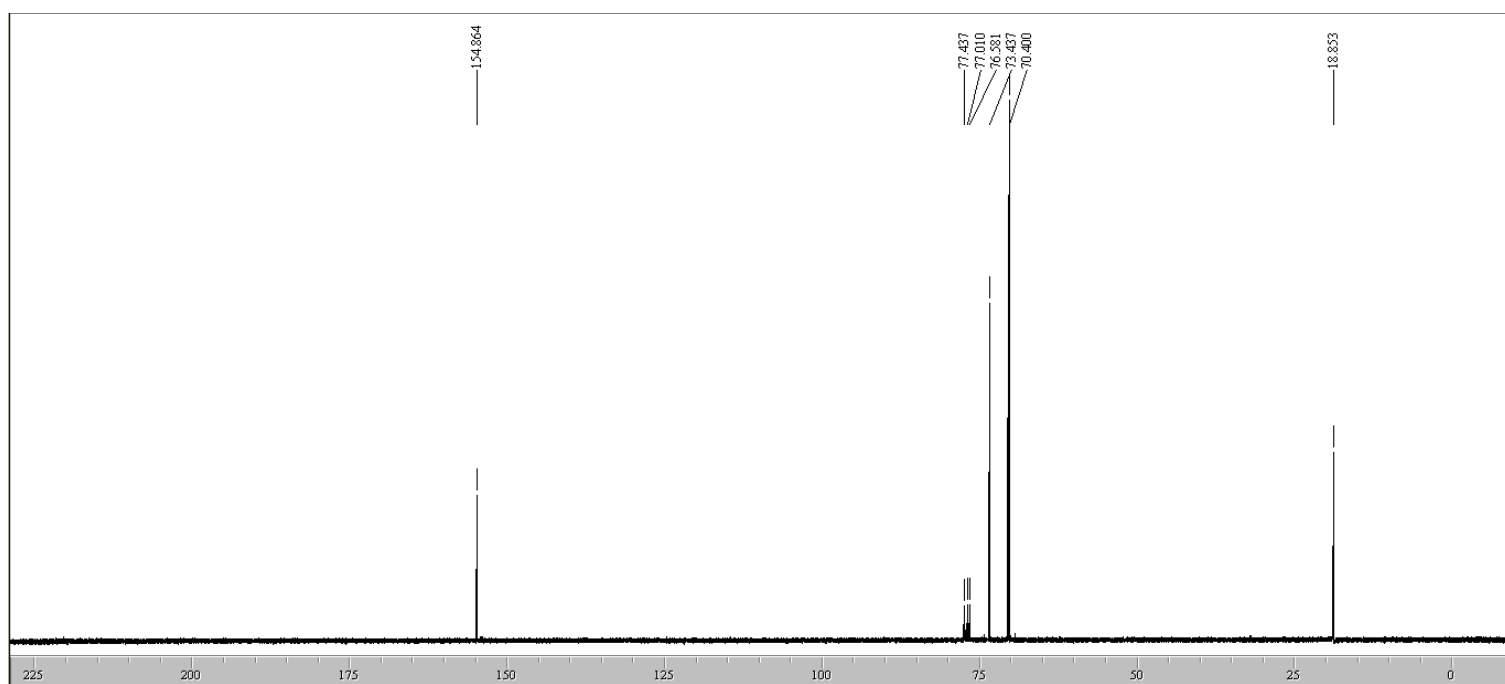
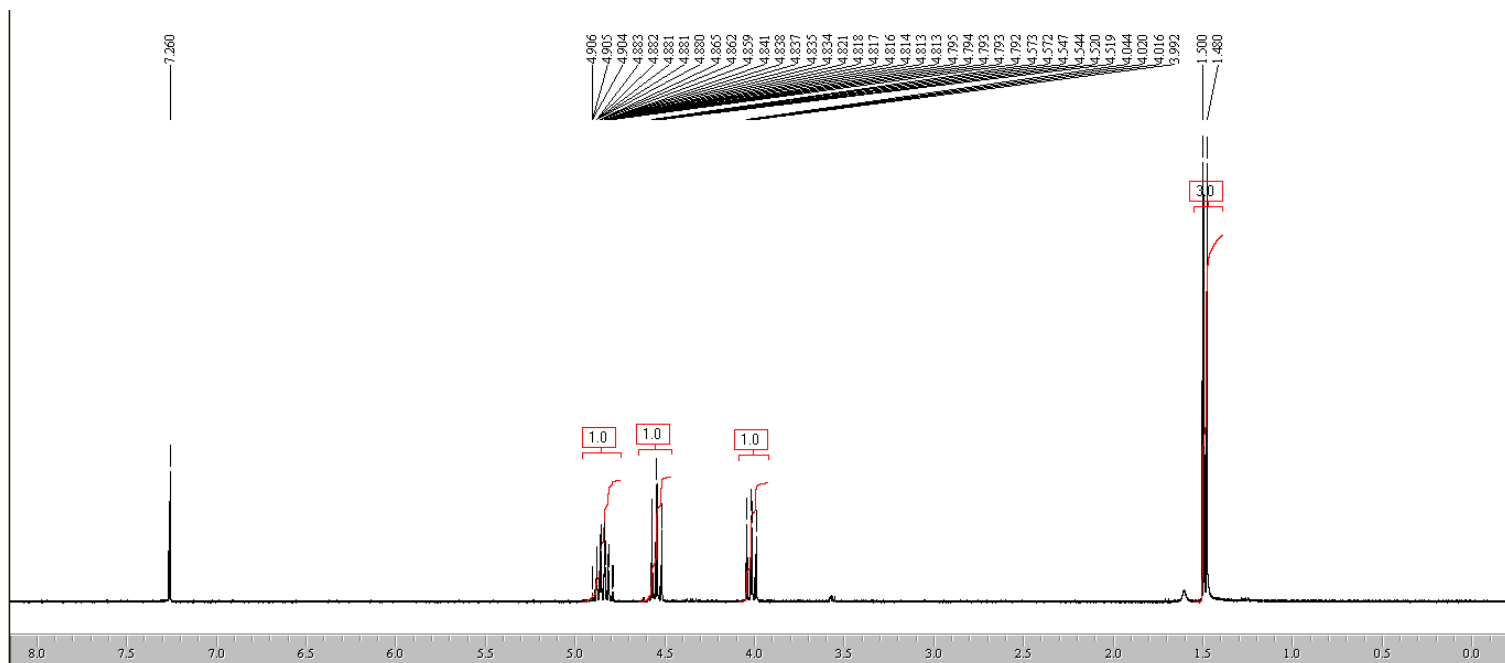
Compound 2e:



Compound 2f:



Compound **2h**:



Compound 2i:

