Electronic Supplementary Material (ESI) for Chemical Communications.

The reduction of graphene oxide with hydrazine: Elucidating its reductive capability based on a reaction-model approach

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Experimental

Materials

Natural graphite was obtained from Asbury Carbons, USA. Sulfuric acid (95–98 %), hydrochloric acid (37 %), sodium nitrate and 1,2,3,4-tetrahydro-1-naphthol were purchased from Sigma-Aldrich, Singapore. 1-tetralone, 2-tetralone, 2-naphthol, 2-acetonapthone, 2-naphthoic acid, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-1-naphthoic acid, hydrogen peroxide (30 %) and hydrazine monohydrate was obtained from Alfa Aesar, Singapore. 2-methoxynaphthalene was obtained from TCI. *N,N*-Dimethylformamide and diethyl ether were obtained from Tedia. Potassium permanganate was obtained from J. T. Baker. Milli-Q water (resistivity: 18.2 MΩ.cm) was used throughout the experiments.

Equipment

X-ray photoelectron spectroscopy was performed with Phoibos 100 spectrometer and Mg X-ray radiation source (SPECS, Germany). Both survey and high-resolution spectra for C1s were collected. Relative sensitivity factors were used for evaluation of atomic percentage from the XPS survey spectra measurements. XPS samples were prepared by coating a carbon tape with a uniform layer of the materials under study. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 500 MHz spectrometers.

Procedures

Preparation of graphite oxide. Graphite oxide was prepared by the modified Hummers method. Graphite (0.5 g) was stirred with 23.0 mL of sulfuric acid (95–98 %) for 20 min at 0 °C prior to the addition of $NaNO_3$ (0.5 g) in portions. The mixture was left to stir for 1 hr. $KMnO_4$ (3 g) was then added in portions at 0 °C. The mixture was subsequently heated to 35 °C for 1 hr. Water (40 mL) was then added into the mixture and resulted in the temperature of the mixture to rise up to 90 °C. The temperature was maintained at 90 °C for 30 min. Additional water (100 mL) was added into the mixture. This was followed by a slow addition of 30 % H_2O_2 (~10 mL). The warm solution was centrifuged and washed with warm water (100 mL). The solid was subsequently washed with a copious amount of water until a neutral pH was obtained. The material then was dried in vacuum oven at 30 °C for 5 days.

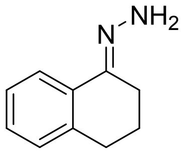
Preparation of hydrazine-reduced graphene oxide. Dry graphite oxide powder (80 mg) was dispersed in a mixture of DMF:water (9:1)to give a 1.0 mg/mL colloidal solution and ultrasonicated (150 W) for 2 h. Hydrazine hydrate (1.6 mL, 32.1 mmol) was added dropwise at 47 °C, and then, the reaction mixture was heated to 100 °C for 24 h. After cooling to room temperature, the mixture was filtered (PTFE membrane filter, 0.2 µm) and washed repeatedly with methanol and water. The material was dried in vacuum oven at 30 °C for 5 days.

Reactions models with conjugated aromatic compounds. The conjugated aromatic compounds (10 mmol) was added into a 10 mL mixture of DMF:water (9:1). Hydrazine monohydrate (30 mmol) was then added and the reaction mixture was left to stir at 100 °C for 24 hours. Control experiments were performed under similar procedures but in the absence of hydrazine monohydrate. The reaction mixture was subsequently extracted with diethyl ether and water. The organic phase was dried over K_2CO_3 (for **4**, **5**, **7**) or $MgSO_4$ (for **1**, **2**, **3**, **6**, **8**). The obtained yield was either measured from the obtained crude samples (for **4a** and **8a**) or estimated from the crude samples with 1,4-dinitrobenzene as internal standard (for **5a** and **7a**).

General Information on NMR spectra

Corresponding chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d (δ=7.26, singlet). Multiplicities were given as: s=singlet, d=doublet, t-triplet, m=multiplet and dd=doublet of doublet. Values of coupling constant are reported as *J* in Hz.

Compound 4a

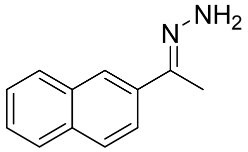


Compound **4a** was the dominant species based on the NMR of crude sample, shown below. The analytical data are in accordance with the literature.[1]

^{1}H NMR: (CDCl$_3$, 500 MHz): *δ* 7.96-7.94 (m, 1H); 7.19-7.18 (m, 2H); 7.12-7.10 (m, 1H); 5.30 (s, 2H); 2.75-2.73 (m, 2H); 2.51-2.48 (m, 2H); 1.97-1.92 (m, 2H)

^{13}C NMR: (CDCl$_3$, 125 MHz): *δ* 147.3, 138.5, 133.5, 128.2, 127.9, 126.5, 123.9, 29.7, 23.9, 21.6

Compound 5a



Compound **5a** was the dominant species based on the NMR of crude sample. Compounds **5a** was obtained as yellow powder after washing with cold ethanol.

^{1}H NMR: (CDCl$_3$, 500 MHz): *δ* 7.97-7.95 (m, 2H); 7.86-7.80 (m, 3H); 7.48-7.46 (m, 2H); 5.44 (s, 2H); 2.25 (s, 3H)

^{13}C NMR: (CDCl$_3$, 125 MHz): *δ* 147.10, 136.72, 133.29, 133.21, 128.33, 127.90, 127.61, 126.16, 126.10, 124.58, 123.53

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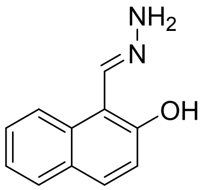
[1] T. Kleine, R. Fröhlich, B. Wibbeling, E.-U. Würthwein, *J. Org. Chem.* **2011**, *76*, 4591.

Compound 7a

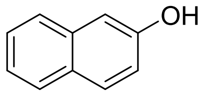


Compound **7a** was the dominant species based on the NMR of crude sample. Compounds **7a** was obtained as yellow powder after washing with cold hexane. The analytical data are in accordance with the literature.[2]

^{1}H NMR: (CDCl$_3$, 500 MHz): *δ* 12.31 (s, 1H); 8.79 (s, 1H); 7.98-7.97 (d, *J*=8.5 Hz, 1H); 7.78-7.76 (d, *J*=8.1 Hz, 1H); 7.73-7.71 (d, *J*=8.9 Hz, 1H); 7.50-7.47 (m, 1H); 7.35-7.32 (m, 1H), 7.20-7.19 (d, *J*=8.9 Hz, 1H), 5.53 (s, 2H)

^{13}C NMR: (CDCl$_3$, 125 MHz): *δ* 157.62, 143.74, 131.48, 131.25, 129.04, 128.16, 127.03, 123.14, 119.90, 119.07, 108.65

Compound 8a



Compound **8a** was the dominant species based on the NMR of crude sample. Compound **8a** was obtained as beige powder after acid-base extraction.

^{1}H NMR: (CDCl$_3$, 500 MHz): *δ* 7.79-7.76 (t, *J*=8.7 Hz, 2H); 7.70-7.68 (d, *J*=8.2 Hz, 1H); 7.46-7.43 (m, 1H); 7.36-7.33 (m, 1H); 7.16-7.15 (d, *J*=2.4 Hz, 1H); 7.12-7.10 (dd, *J*=2.5 Hz,1H); 5.01 (s, 1H)

^{13}C NMR: (CDCl$_3$, 125 MHz): *δ* 153.29, 134.60, 129.90, 128.99, 127.80, 126.57, 126.39, 123.68, 117.73, 109.53

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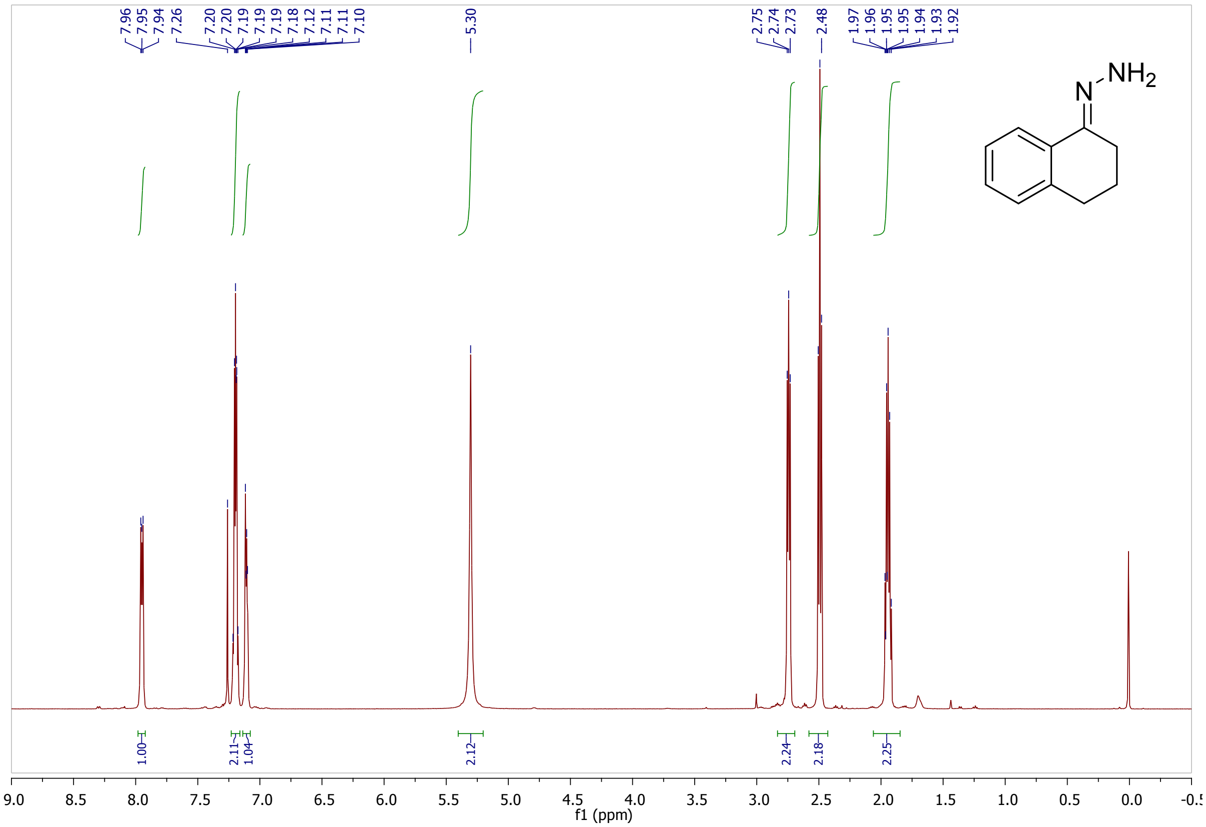
[2] C. Sousa, C. Freire, B. De Castro, *Molecules* **2003**, *8*, 894.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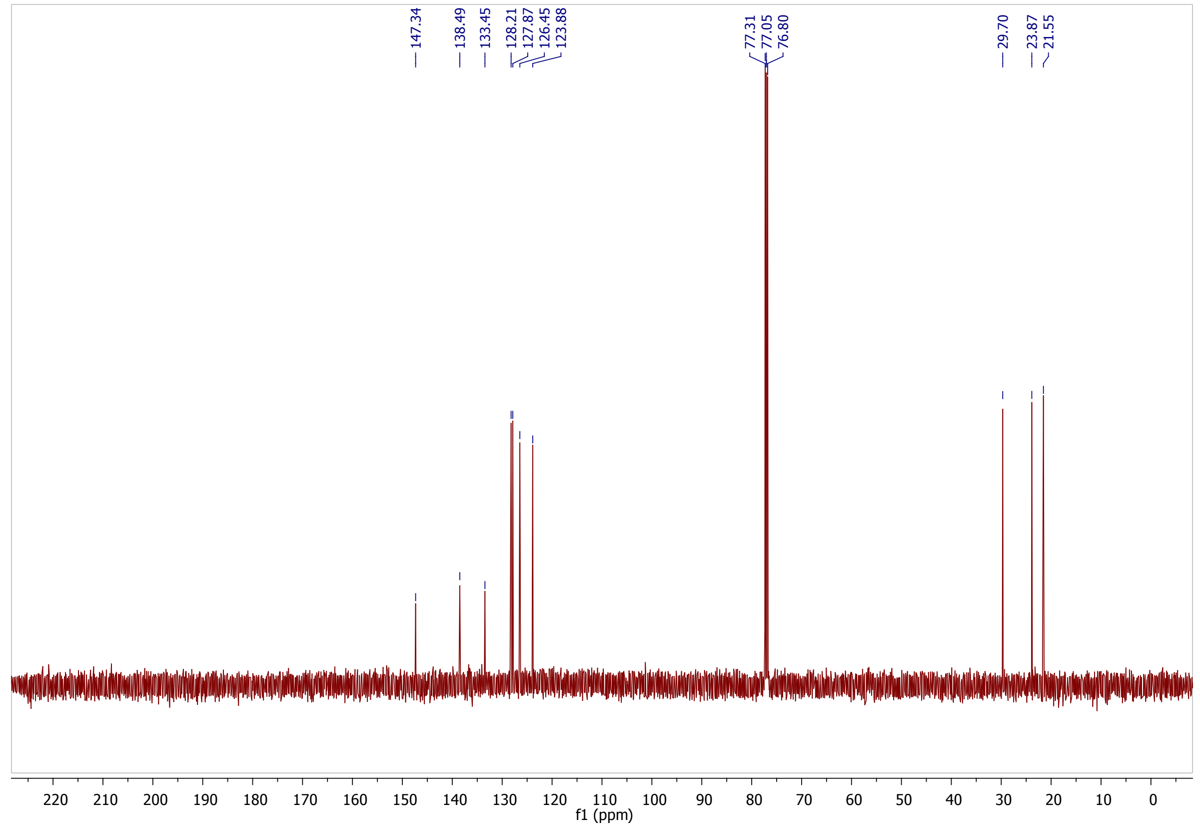
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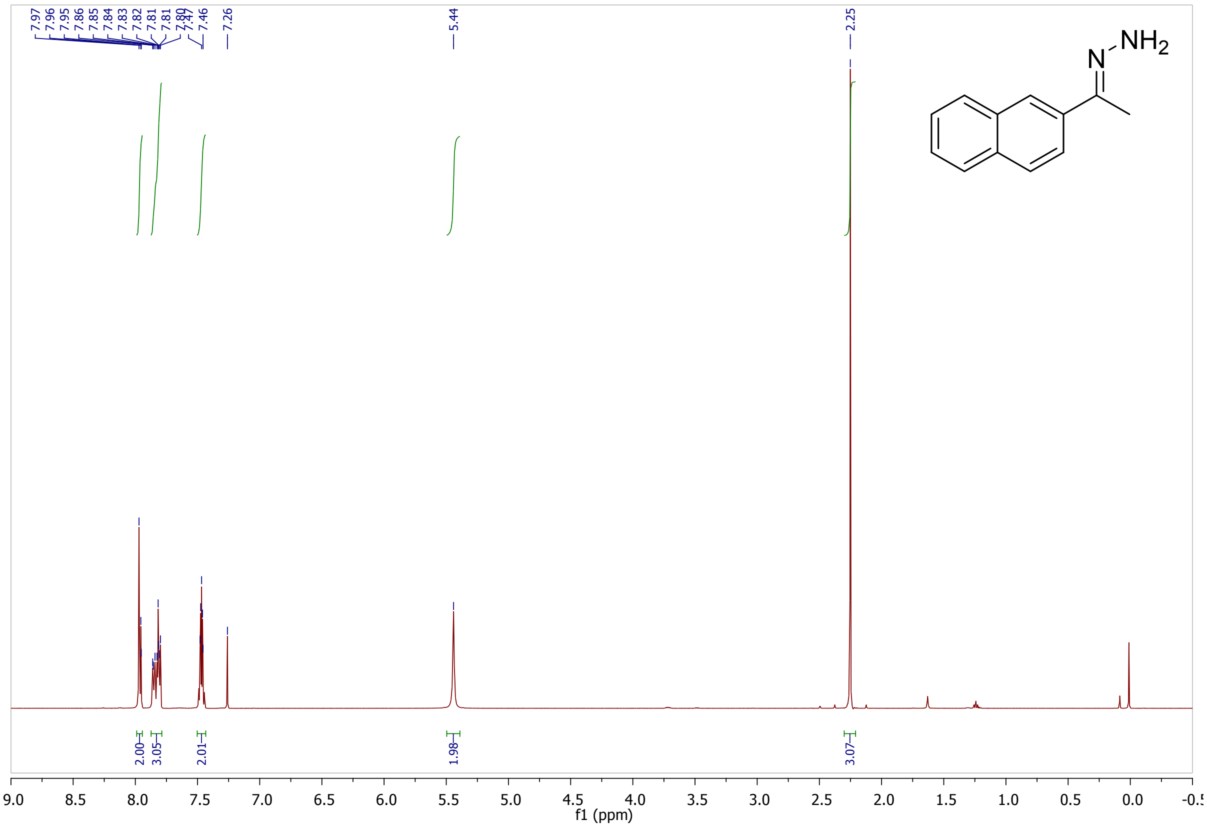
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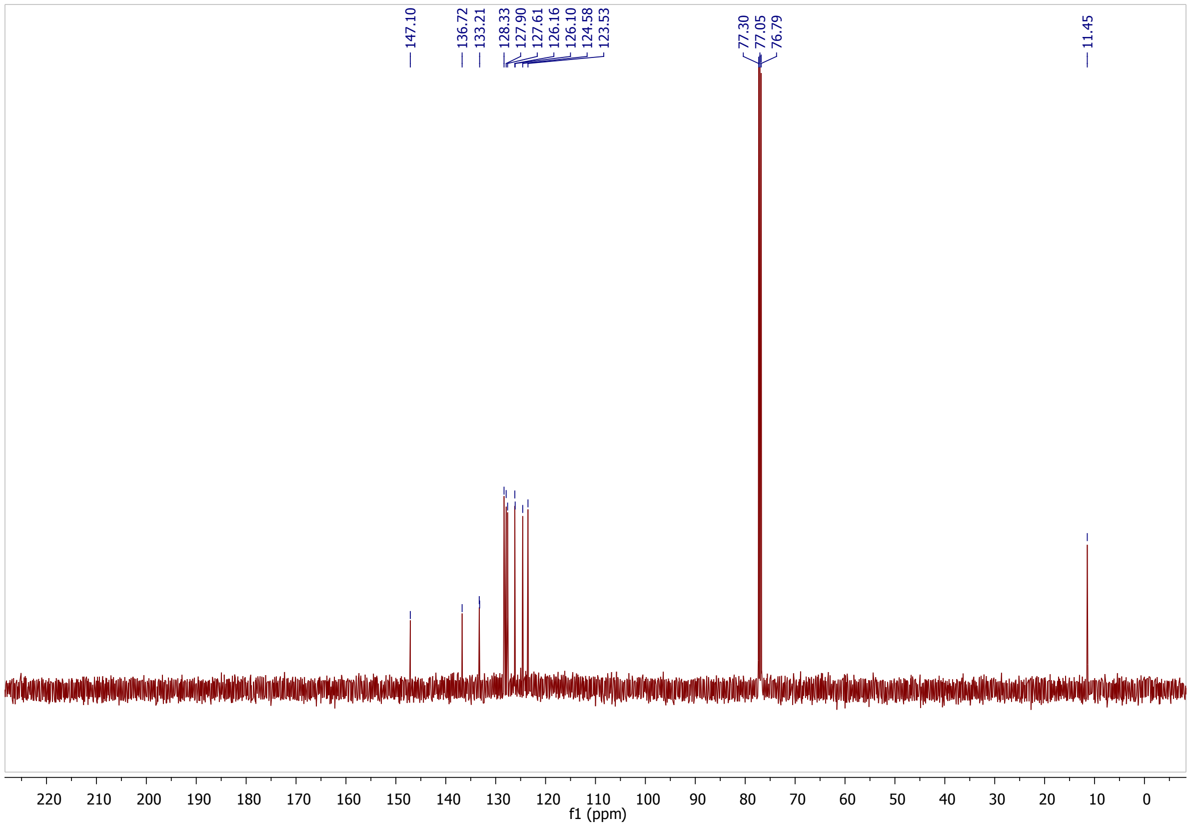
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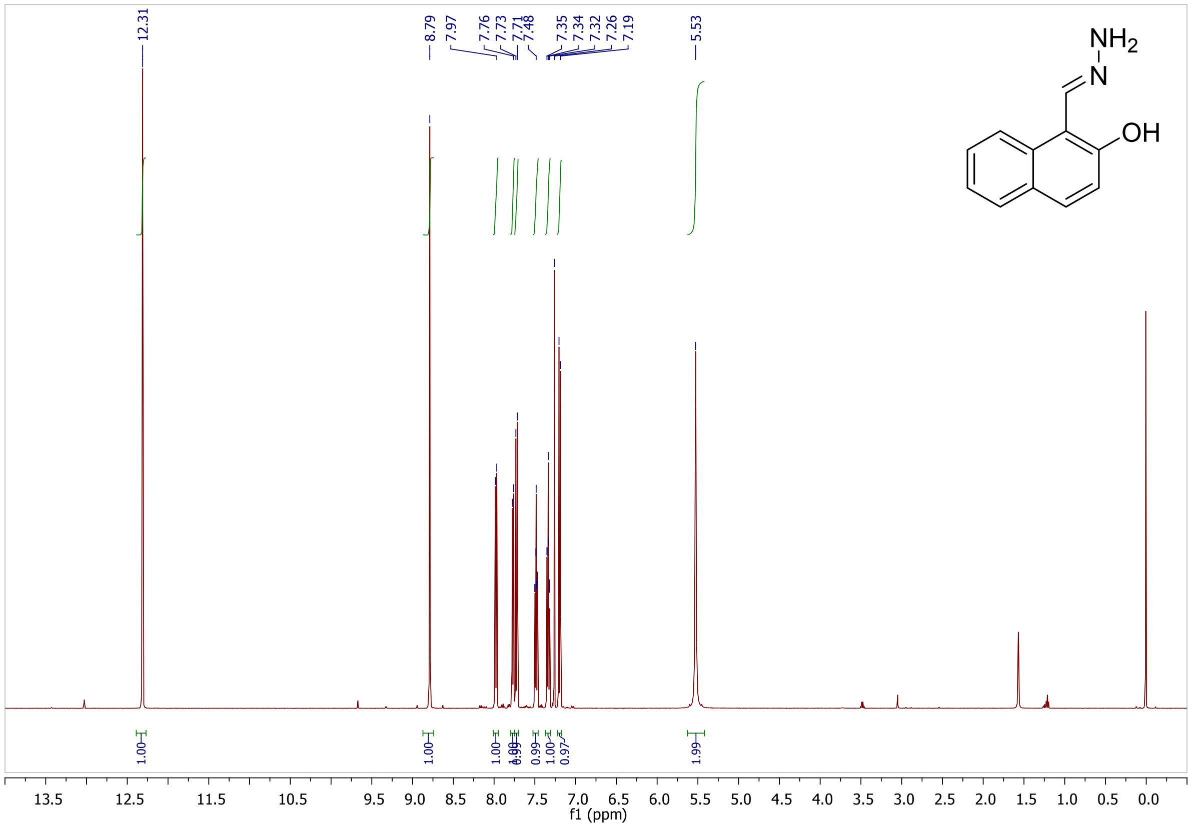
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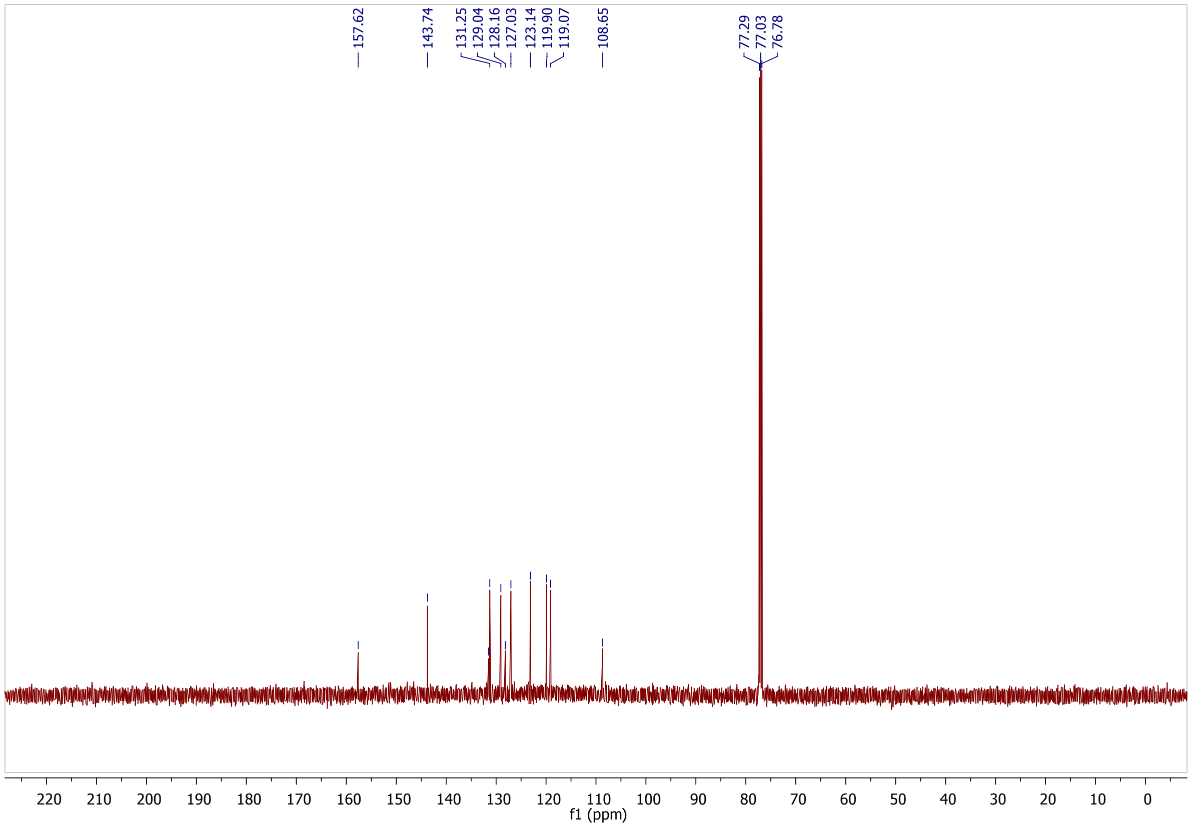
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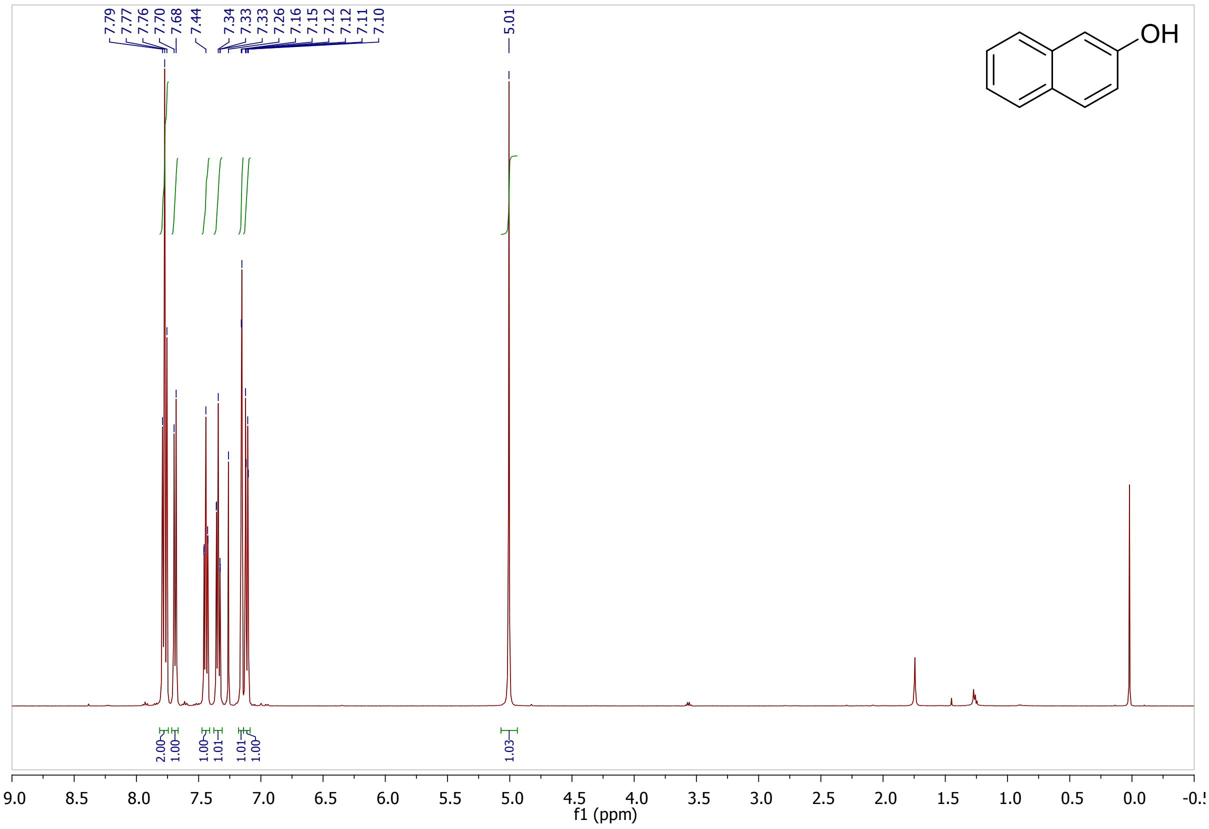
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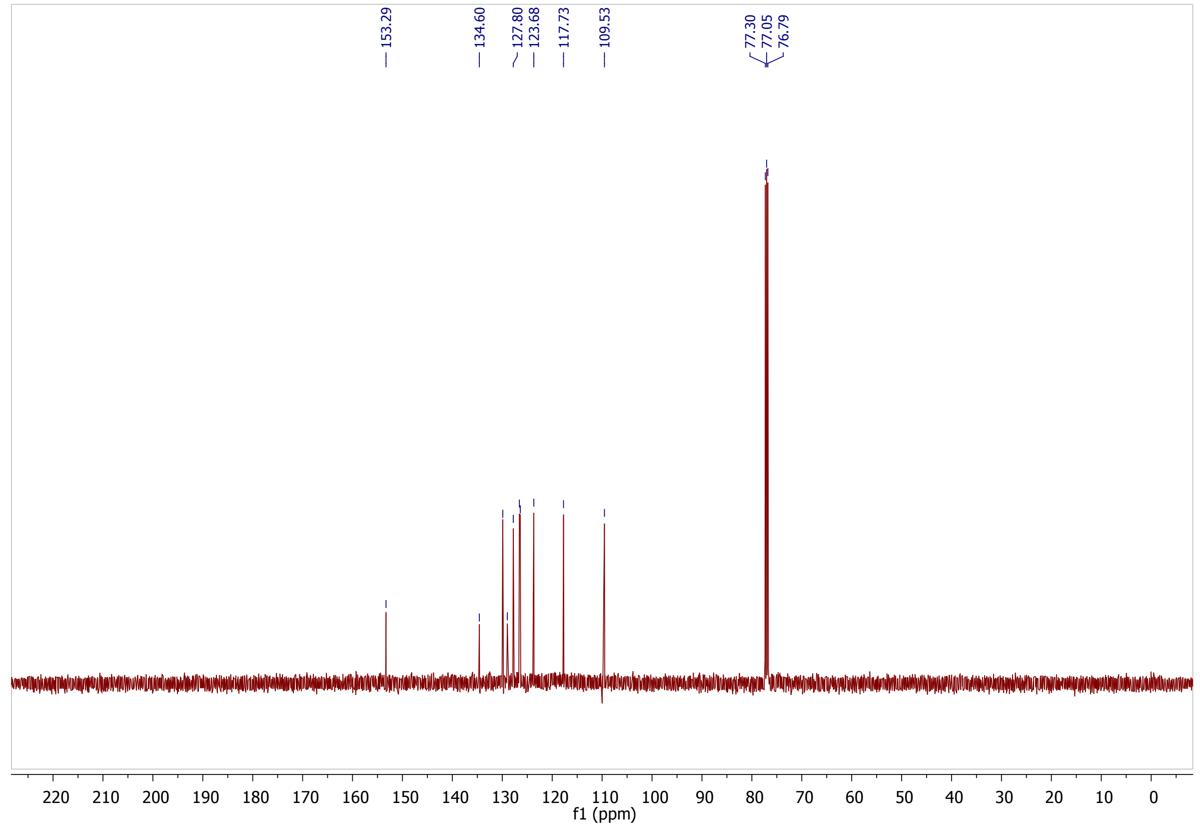
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