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Supplementary Information

Finely dispersed CuO on nitrogen-doped carbon hollow nanospheres for selective oxidation of the C-H bond

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1. Experimental details

1.1 Materials

Tetraethyl orthosilicate (TEOS, 98%), Ammonia solution (25% in water), Sodium chloride (>99%), Sodium hydroxide pellets (>97%), Poly(diallyldimethylammonium chloride) solution (PDDA, 20 wt.% in water with average Mw 400,000 Da - 500,000 Da) and poly(sodium 4-styrenesulfonate) solution (PSS, 30 wt.% in water with average Mw ~200,000 Da) were purchased from Sigma-Aldrich. Cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.5%) was purchased from S.D. Fine-Chem Limited. L-Histidine (>99%) was purchased from Tokyo Chemical Industry. Ethyl benzene and various other substrates were purchased from Alfa Aesar. TLC Silica gel 60 F254 was purchased from Merck chemicals. *tert*-Butyl hydroperoxide solution (70 wt. % in water) and all the solvents were obtained from Avra Synthesis Private Limited. All chemicals were used as received without further purification.

1.2 Characterization methods

Powder X-ray diffraction patterns (XRD) of all the as-prepared catalysts were recorded in the range of 10-80 2θ value on Shimadzu XRD-6100 X-ray diffractometer ($\text{Cu K}\alpha \lambda = 1.5405 \text{ \AA}$) at a scan rate of 2° min^{-1} . Oxidation state of various elements in CuO/N-C-HNSs was studied by X-ray photoelectron spectroscopy (XPS) using Omicron ESCA⁺ (Oxford Instruments, Germany) spectrometer using Al $\text{K}\alpha$ radiations and equipped with Argus analyzer having a mean diameter of 124 mm. The binding energy was calibrated by C 1s peak at 284.6 eV. Percentage loading of copper in CuO/N-C-HNSs was estimated by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis. Surface morphology of the catalyst was analyzed by field emission gun-scanning electron microscope (FEG-SEM) using Tescan MIRA-3 model. Elemental analysis and mappings were obtained using energy dispersive X-ray spectroscopy (EDS) and High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) respectively on JEOL JEM-ARM 200F. High Resolution-Transmission Electron Microscopy (HR-TEM) was performed on a FEI Technai G² 20 electron microscope. The Brunauer-Emmett-Teller (BET) surface area measurement of the catalyst was done on Micromeritics ASAP 2020 instrument by measuring N₂ adsorption and desorption at -196°C . Thermo Gravimetric Analysis (TGA) was carried out on Perkin Elmer (STA 6000) thermogravimetric analyzer under continuous flow of N₂ gas (30 mL min^{-1}) with a heating rate of $20^\circ \text{C min}^{-1}$.

The identification of reaction products was done on a GC-MS (Shimadzu QP2010) fitted with Rtx-5MS capillary column. The products were confirmed by recording their ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectrum on 500 MHz and 126 MHz spectrometer respectively. Tetramethylsilane (TMS) was used as an internal standard and chemical shifts (δ) were reported in ppm relative to TMS.

1.3 Procedure for the synthesis of CuO/N-C-HNSs

The nanocomposite, CuO/N-C-HNSs was synthesized according to our previous protocol.¹ Initially, SiO_2 nanospheres with particle sizes in the range of 100-150 nm was prepared by a modified Stöber's method.² In a typical procedure, 6 mL of TEOS was transferred into a beaker containing 200 mL of ethanol under continuous stirring. To the resulting mixture, 12 mL of aqueous ammonia and 12 mL of distilled water was added and the reaction mixture was kept stirring for 5 h at room temperature. The colourless solution gradually turned into a turbid suspension indicating the formation of colloidal SiO_2 nanoparticles. The SiO_2 nanoparticles were isolated by centrifugation at 10000 rpm for 10 min and then washed with distilled water and ethanol mixture several times by centrifugation and redispersion. The obtained solid was dried at 80 °C for 12 h and finally grinded to obtain the SiO_2 nanospheres.

Next, the surface of the as-prepared SiO_2 nanospheres was functionalized with negative charges using poly(diallyldimethylammonium chloride) solution (PDDA) and poly(sodium 4-styrenesulfonate) solution (PSS) polymers. Specifically, the as-prepared SiO_2 nanospheres (1.2 g) were dispersed in 200 mL distilled water containing 6 g NaCl by ultra sonication for 30 min. To the resulting suspension, 2 g of PDDA solution was added, and the mixture was kept stirring for 1 h at room temperature. After that, the PDDA-modified SiO_2 nanospheres were isolated and washed with distilled water by centrifugation at 10000 rpm for 10 min. The PDDA coated SiO_2 nanospheres were redispersed in 200 mL distilled water and 2 g of PSS solution was added and the mixture was kept stirring for 1 h at room temperature. After that, the PDDA/PSS-modified SiO_2 nanospheres were isolated and washed with distilled water by centrifugation at 10000 rpm for 10 min. Following the similar procedure, the surface of the PDDA/PSS-modified SiO_2 nanospheres was further coated with the layers of PDDA and PSS successively to obtain the negatively charged PDDA/PSS/PDDA/PSS-modified SiO_2 nanospheres. Subsequently, 1 g of the PDDA/PSS/PDDA/PSS-modified SiO_2 nanospheres were dispersed by ultra sonication in 10 mL distilled water containing 100 mg of copper (II) nitrate trihydrate. To the above suspension, 400 mg of histidine was added and kept stirring

for 30 min at room temperature. The resulting mixture was vacuum-dried at 80 °C for 2h and then pyrolyzed in an alumina boat crucible under N₂ atmosphere at 800 °C for 3h with a heating rate of 2 °C min⁻¹. The SiO₂ template in the pyrolyzed material was removed by etching with 2M NaOH (100 mL) for 24h at room temperature and then washed with distilled water several times and dried for overnight at 100 °C to obtain the final product CuO/N-C-HNSs.

1.4 Procedure for the synthesis of CuO/C-HNSs

CuO/C-HNSs were synthesized as per the following procedure. Initially, SiO₂ nanospheres having particle sizes in the range of 100-150 nm was prepared by a modified Stöber's method. In a typical procedure, 6 mL of TEOS was transferred into a beaker containing 200 mL of ethanol under continuous stirring. To the resulting mixture, 12 mL of aqueous ammonia and 12 mL of distilled water was added and the reaction mixture was kept stirring for 5 h at room temperature. The colourless solution gradually turned into a turbid suspension indicating the formation of colloidal SiO₂ nanoparticles. The SiO₂ nanoparticles were isolated by centrifugation at 10000 rpm for 10 min and then washed with distilled water and ethanol mixture several times by centrifugation and redispersion. The obtained solid was dried at 80 °C for 12 h and finally grinded to obtain the SiO₂ nanospheres.

Next, the surface of the as-prepared SiO₂ nanospheres was coated with poly(sodium 4-styrenesulfonate) solution (PSS) polymer. Specifically, the as-prepared SiO₂ nanospheres (1.2 g) were dispersed in 200 mL distilled water containing 6 g NaCl by ultra sonication for 30 min. To the resulting suspension, 2 g of PSS solution was added, and the mixture was kept stirring for 1 h at room temperature. After that, the PSS-coated SiO₂ nanospheres were isolated and washed with distilled water by centrifugation at 10000 rpm for 10 min. Subsequently, 1 g of the PSS-coated SiO₂ nanospheres were redispersed by ultra sonication in 10 mL distilled water containing 100 mg of copper (II) nitrate trihydrate and kept stirring for 30 min at room temperature. The resulting mixture was vacuum-dried at 80 °C for 2h and then pyrolyzed in an alumina boat crucible under N₂ atmosphere at 800 °C for 3h with a heating rate of 2 °C min⁻¹. The SiO₂ template in the pyrolyzed material was removed by etching with 2M NaOH (100 mL) for 24h at room temperature and then washed with distilled water several times and dried for overnight at 100 °C to obtain the final product CuO/C-HNSs.

2. List of Figures

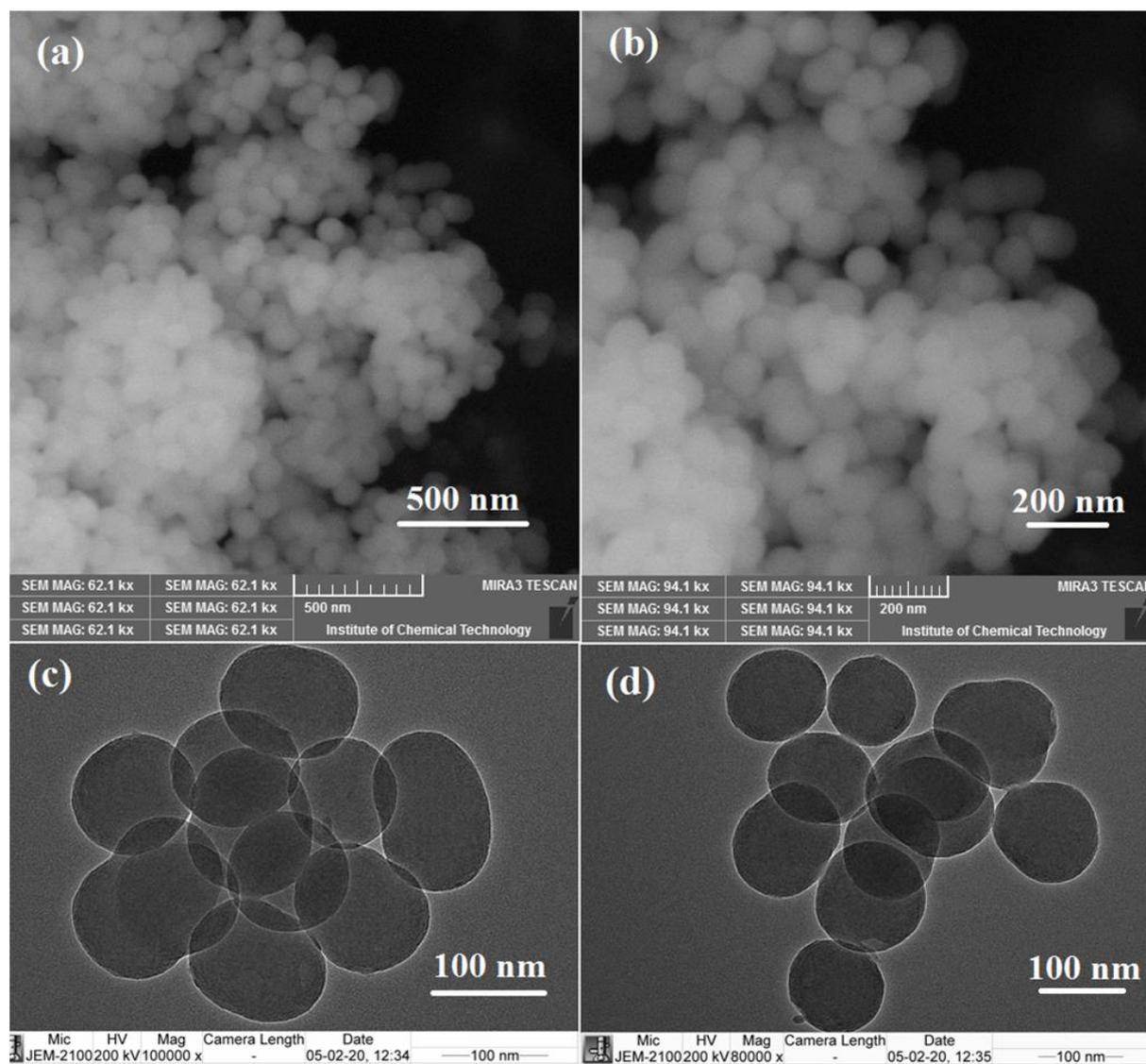


Fig. S1 FE-SEM images (a) and (b), TEM images (c) and (d) of as-prepared SiO₂ template.

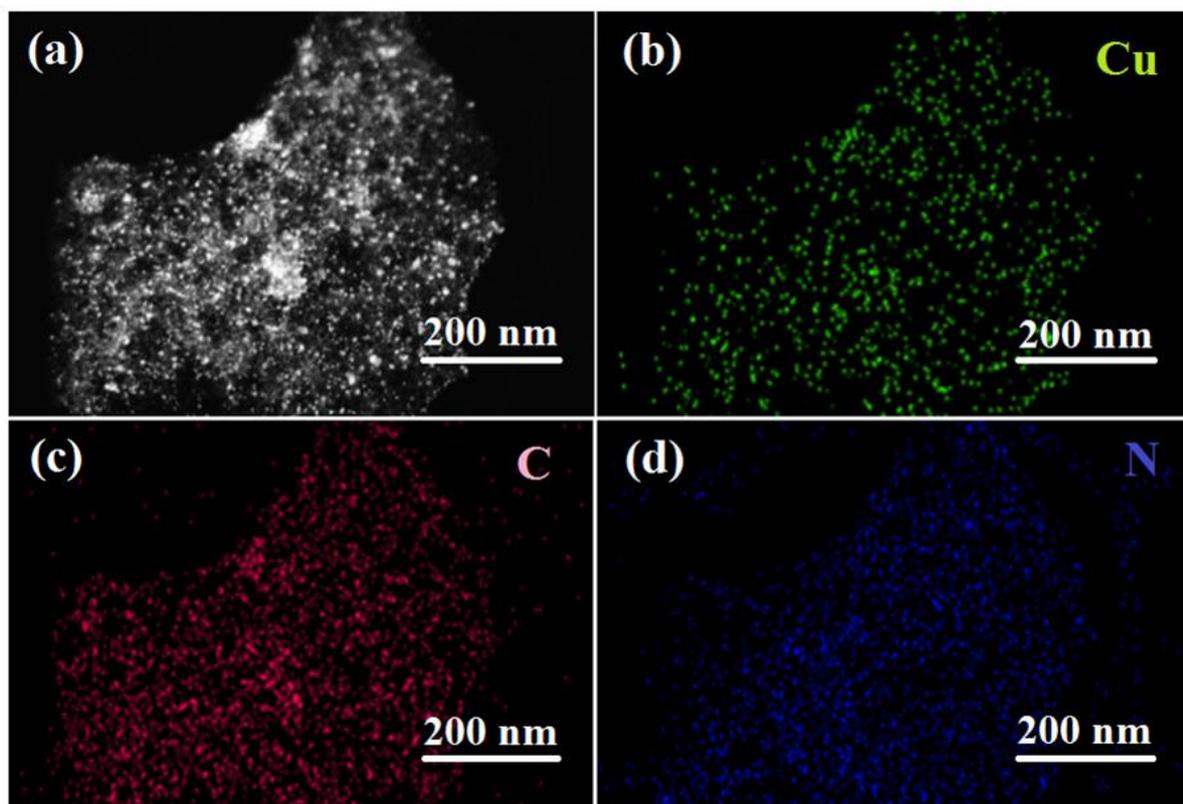


Fig. S2 HAADF-STEM images of CuO/N-C-HNSs (a) and the corresponding Cu (b), C (c) and N (d) elemental maps.

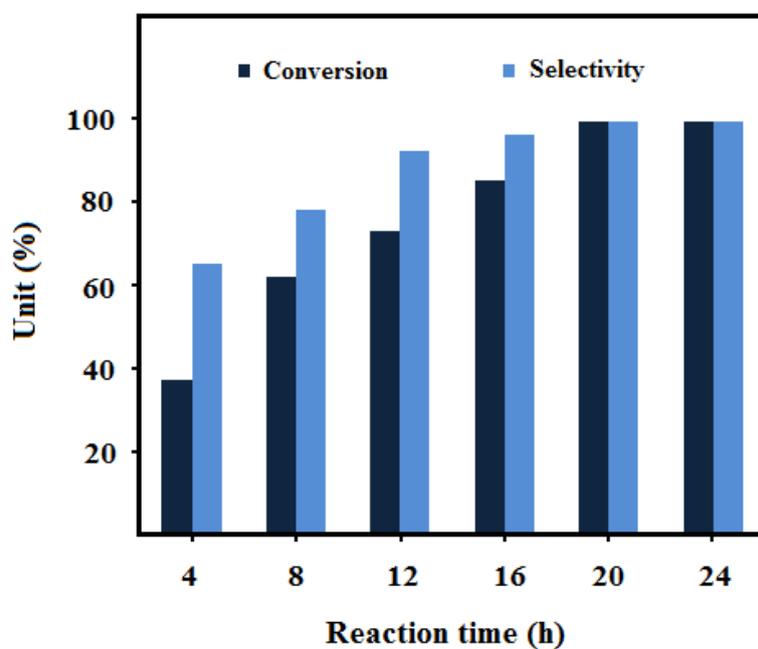


Fig. S3 Effect of reaction time on oxidation of ethyl benzene.

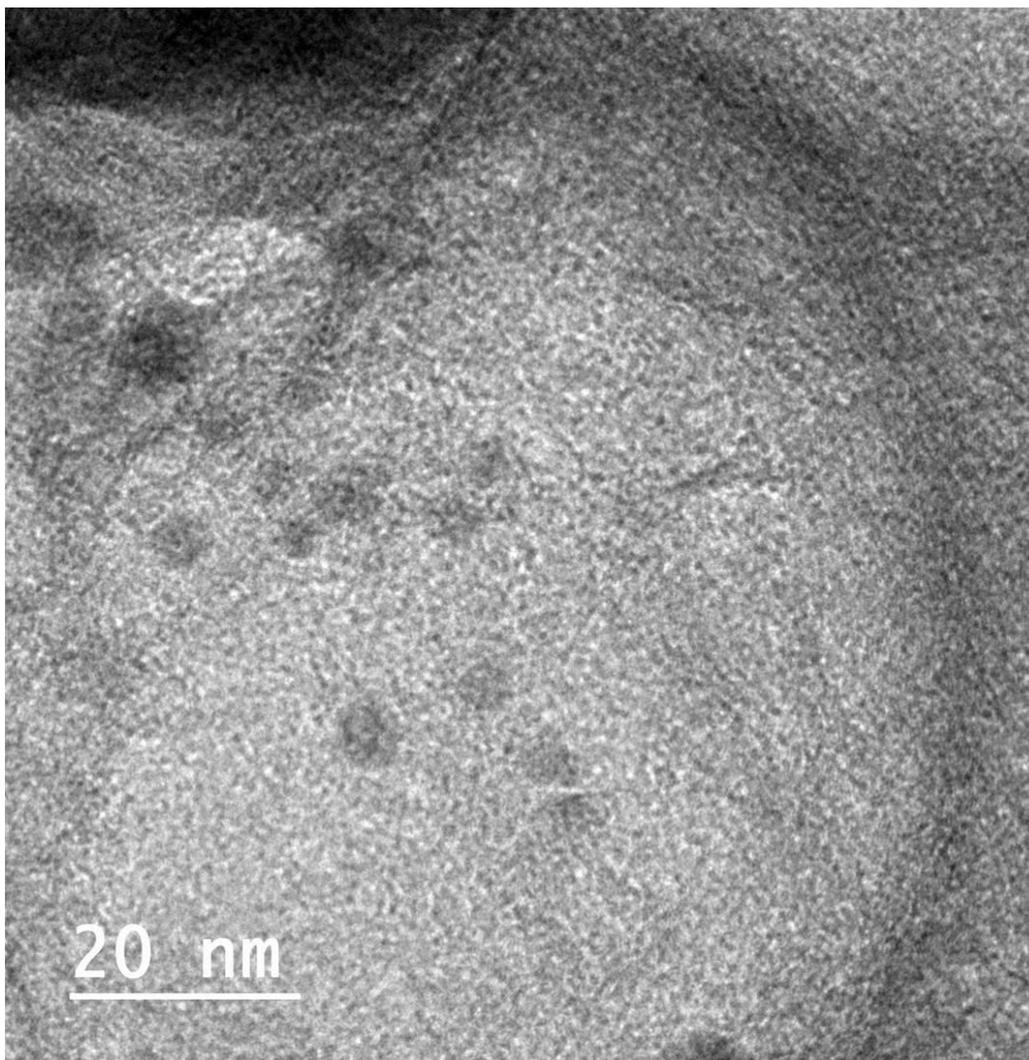


Fig. S4 HRTEM image of recycled CuO/N-C-HNSs.

3. ^1H NMR and ^{13}C NMR of products

Benzophenone (Colourless liquid, Isolated yield: 86%)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dt, $J = 8.4, 1.5$ Hz, 2H), m, 2H), 7.65 – 7.58 (m, 1H), 7.54 – 7.48 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.70, 137.59, 132.39, 130.03, 128.26.

phenyl(pyridin-4-yl)methanone (White solid, Isolated yield: 77%)

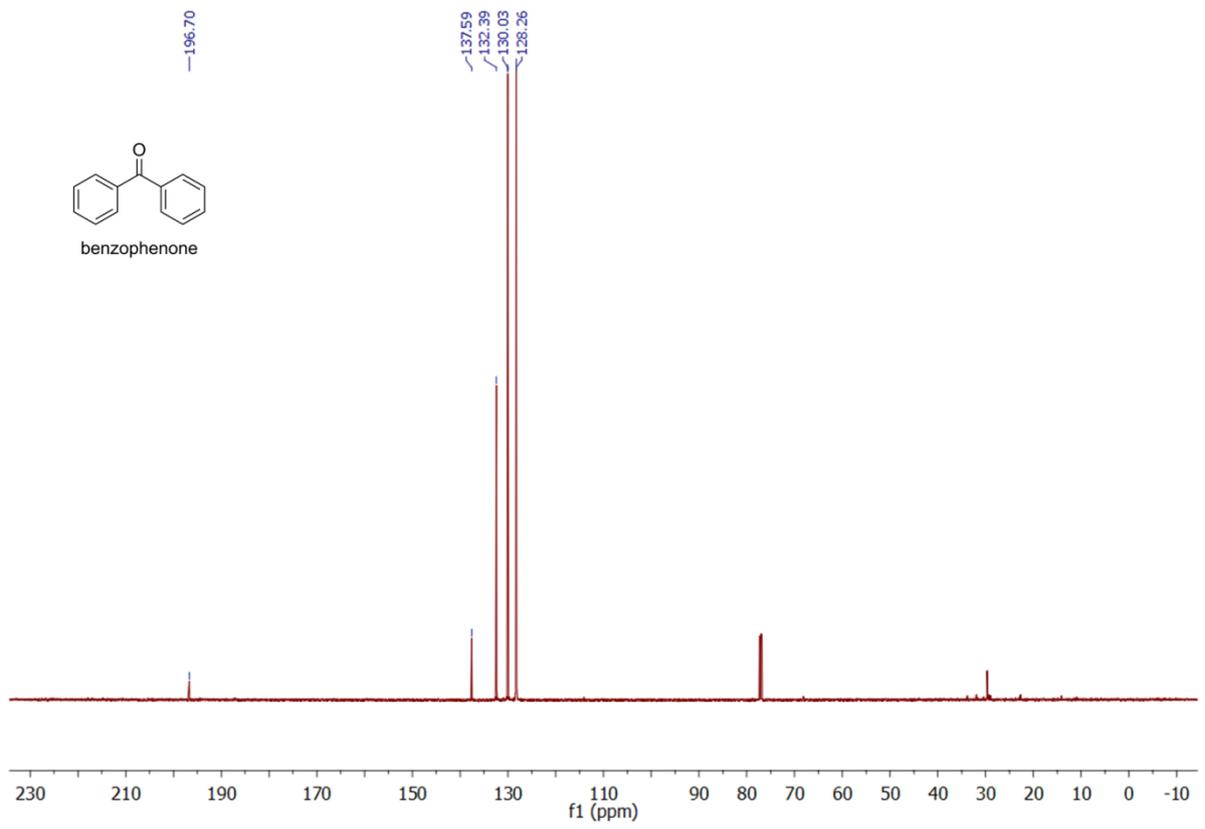
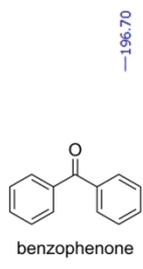
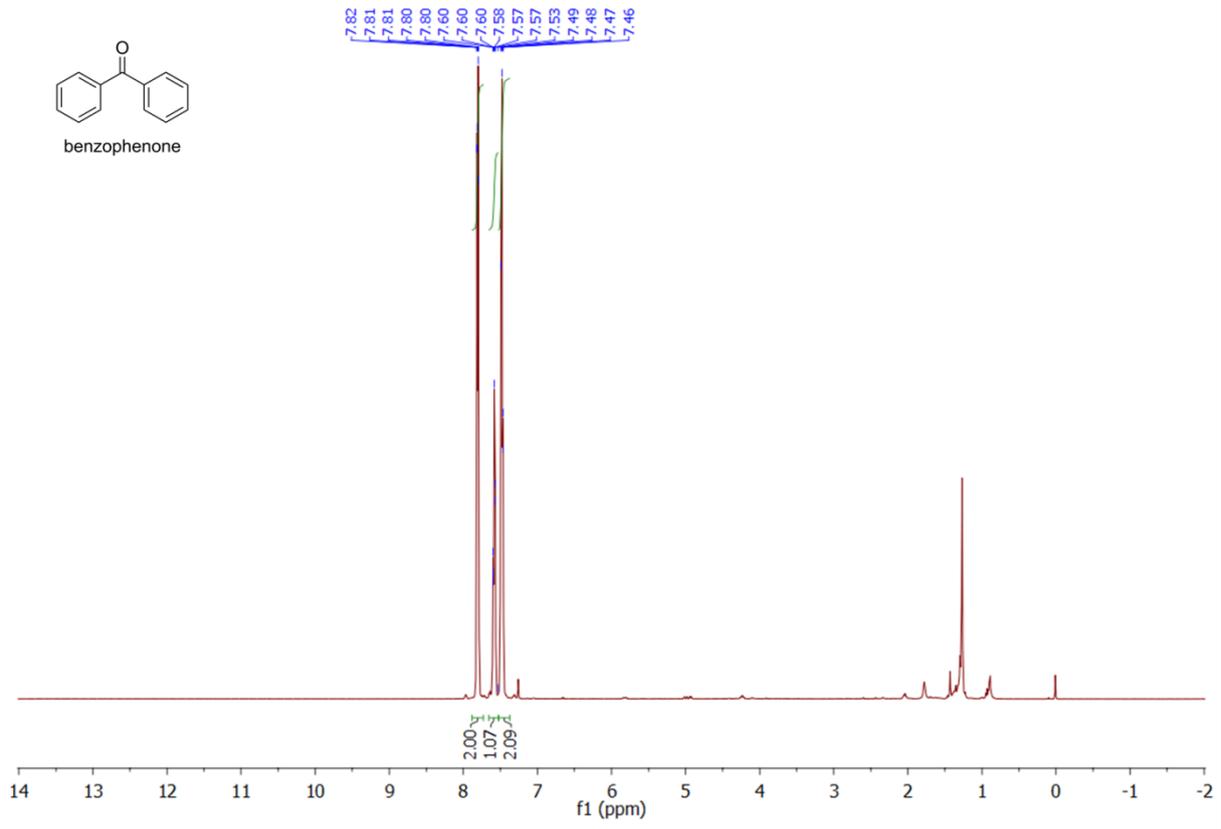
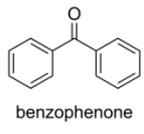
^1H NMR (500 MHz, Chloroform-*d*) δ 8.86 – 8.81 (m, 2H), 7.84 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.70 – 7.64 (m, 1H), 7.63 – 7.59 (m, 2H), 7.54 (t, $J = 7.8$ Hz, 2H).

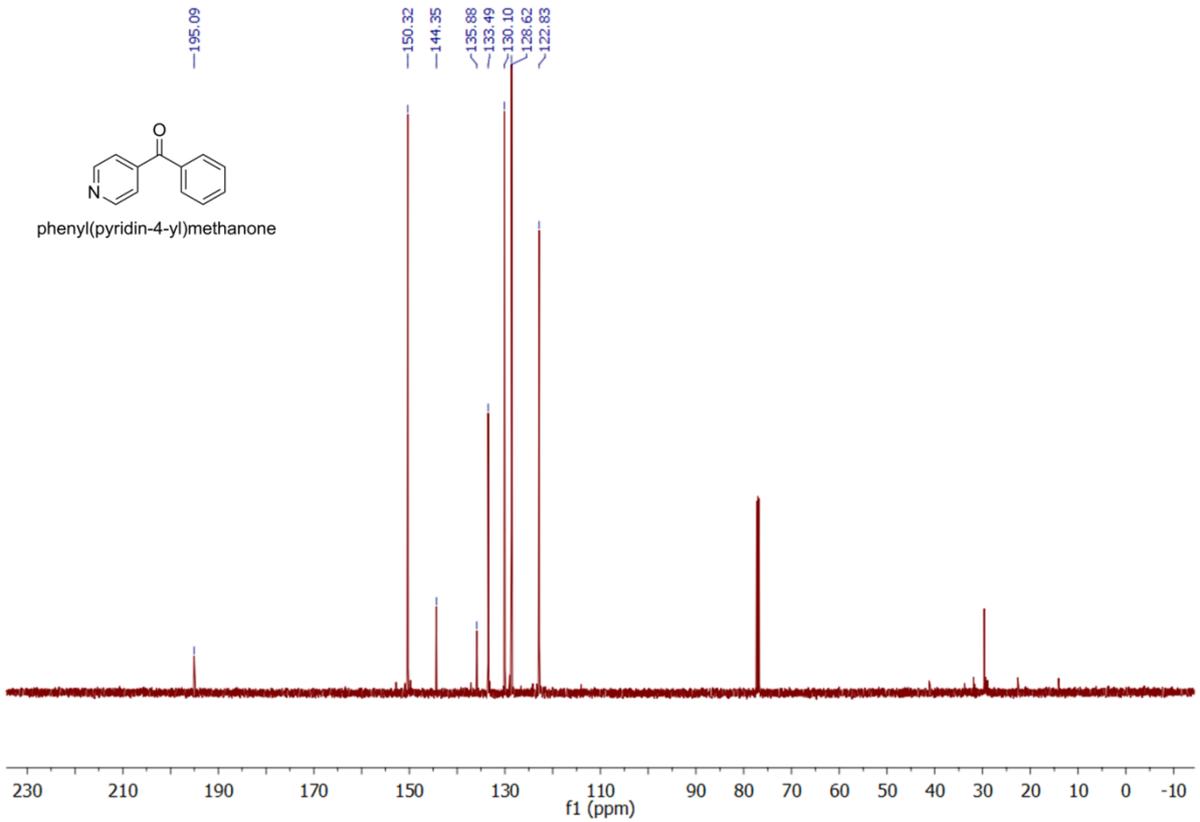
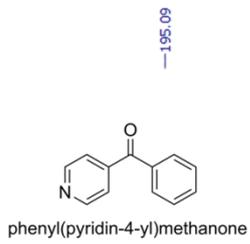
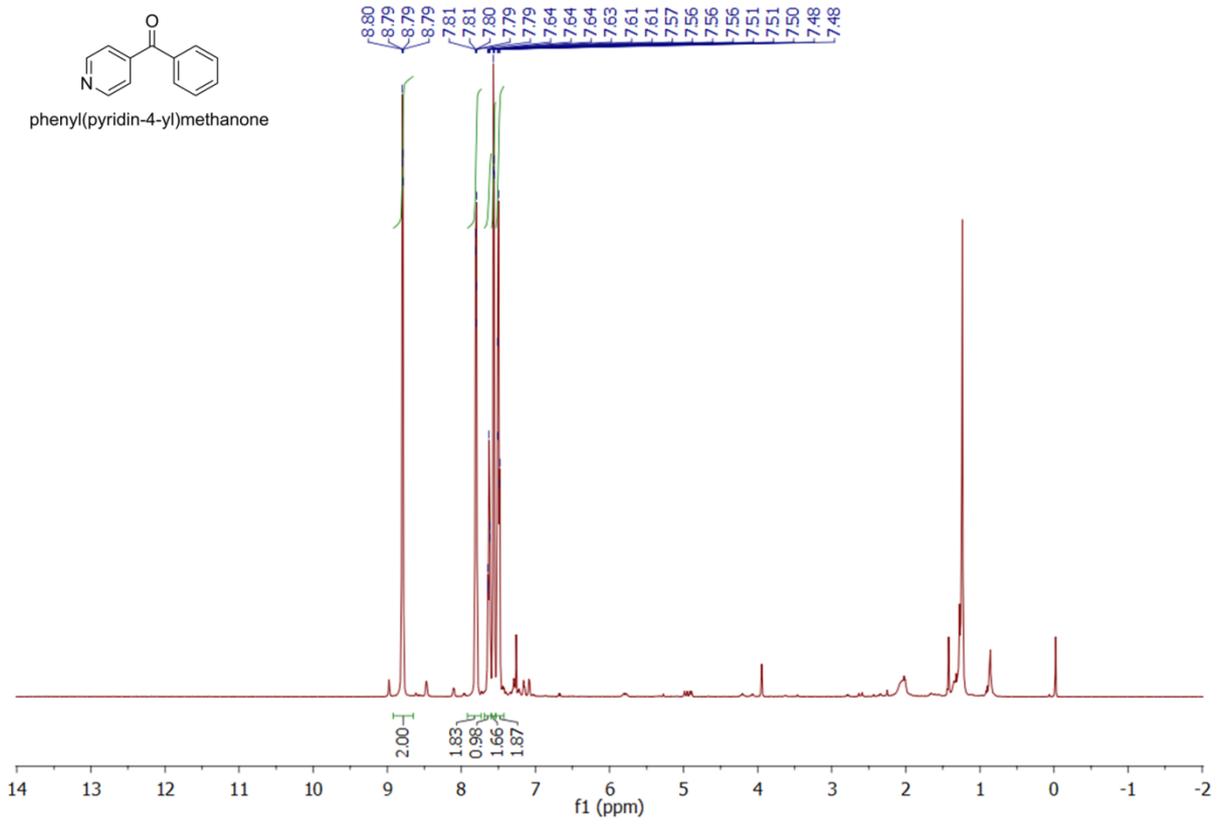
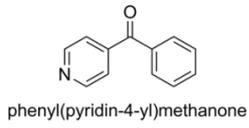
^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.09, 150.32, 144.35, 135.88, 133.49, 130.10, 128.62, 122.83.

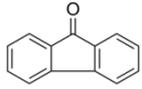
9H-fluoren-9-one (Yellow solid, Isolated yield: 83%)

¹H NMR (500 MHz, Chloroform-*d*) δ 7.64 d, $J = 7.4$ Hz, 2H, 7.50 – 7.44 (m, 4H), 7.30 – 7.25 (m, 2H).

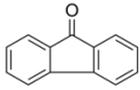
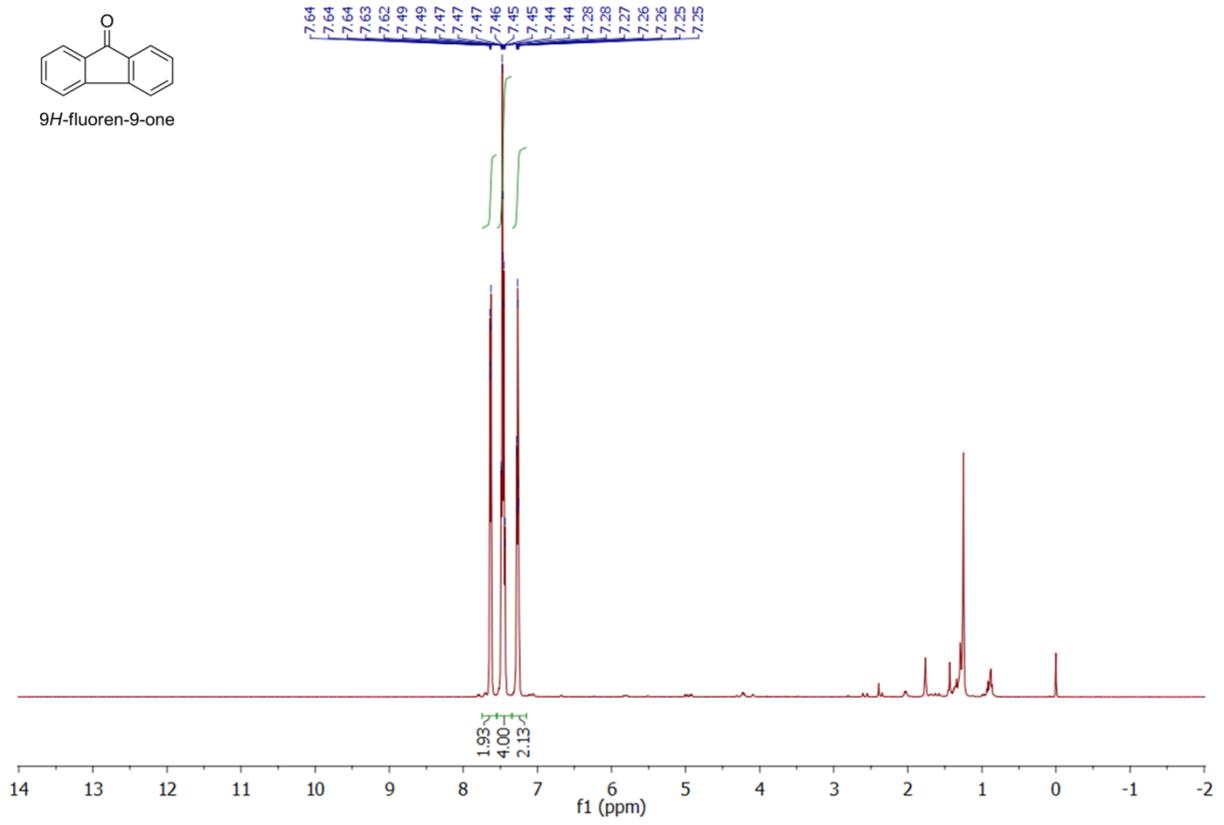
¹³C NMR (126 MHz, Chloroform-*d*) δ 193.84, 144.38, 134.64, 134.11, 129.03, 124.25, 120.27.



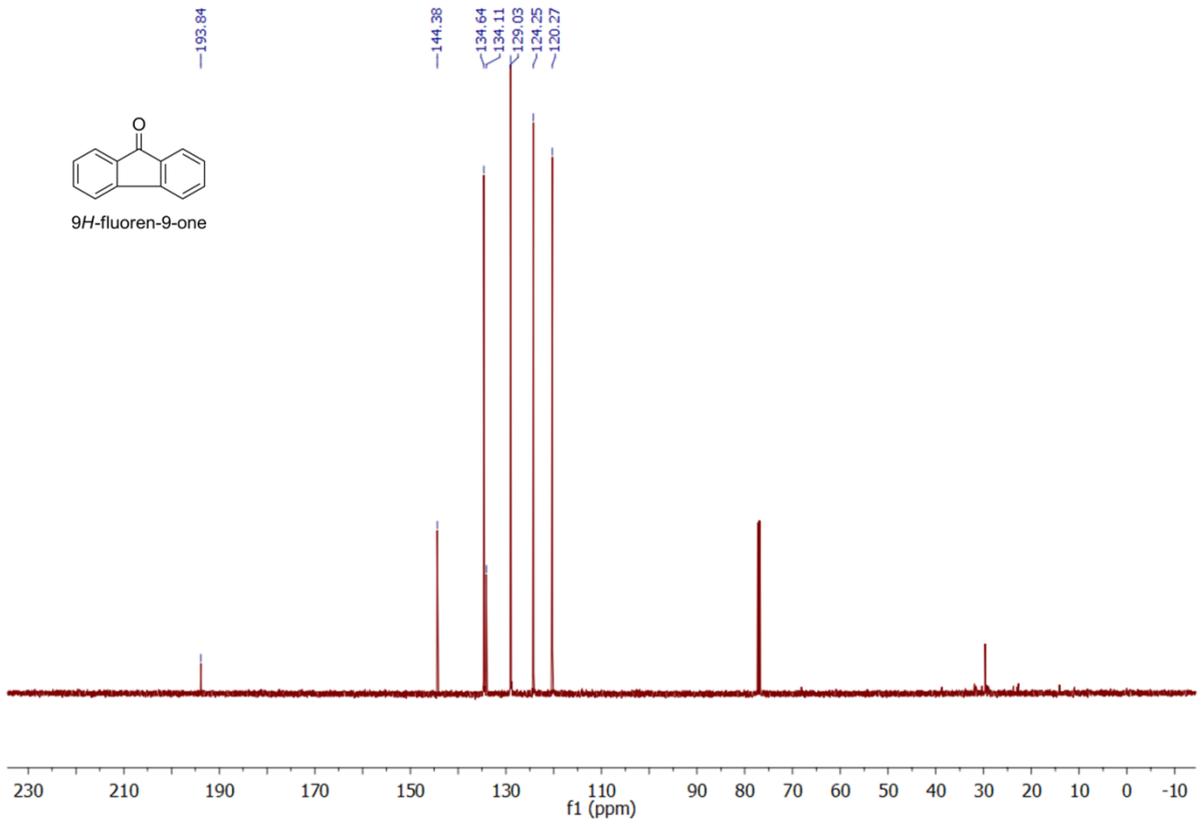




9H-fluoren-9-one



9H-fluoren-9-one



4. References

- 1 S. S. R. Gupta, A. Vinu and M. L. Kantam, *Chempluschem*, 2021, **86**, 259–269.
- 2 X. Qiu, T. Li, S. Deng, K. Cen, L. Xu and Y. Tang, *Chem. - A Eur. J.*, 2018, **24**, 1246–1252.