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Supplementary Information

Preparation, characterization and application of a novel organic-inorganic hybrid magnetic nanomaterial as a highly efficient catalyst for the synthesis of bis-coumarins

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Chemicals and instruments

The used materials and solvents were purchased from Fluka or Merck Chemical Companies. To observe progress of the reactions, thin layer chromatography (TLC) (silica gel SIL G/UV 254 plates) was applied. To measure melting points, a Thermo Scientific 9200 apparatus was used. For recording the FT-IR spectra, a Thermo device (model AVATAR) was used. A Bruker Avance DPX, FT-NMR spectrometer was utilized for running the NMR spectra. Energy dispersive X-ray spectroscopy (EDX) and elemental mapping analysis were done by a SAMX-EDS instrument (France system). FE-SEM instrument TESCAN (model MIRA III) was utilized for determining sizes and morphologies of the particles. VSM analysis was performed using a MDK device (Meghnatis Daghigh Kavir, Iran) at room temperature. XRD analysis was carried out by a PHILIPS apparatus (Cu K α radiation, $\lambda=1.54056 \text{ \AA}$, model PW1730). TGA was done using TA apparatus (model Q600), at 25-600 °C, with temperature increase rate of 10 °C.min⁻¹ in argon atmosphere. Mass spectra were recorded by a Shimadzu GC-MS-QP 1100 Ex instrument.

Selected spectral data of the synthesized bis-coumarins

Product 4

¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 3.61 (s, 3H, CH₃O), 3.74 (s, 3H, CH₃O), 6.37 (s, 1H, methine CH), 6.73 (d, $J = 8.8 \text{ Hz}$, 1H, Ar), 6.80 (s, 1H, Ar), 6.86 (d, $J = 8.4 \text{ Hz}$, 1H, Ar), 7.34 (d, $J = 7.5 \text{ Hz}$, 2H, Ar), 7.41 (d, $J = 8.5 \text{ Hz}$, 2H, Ar), 7.62 (t, $J = 7.3 \text{ Hz}$, 3H, Ar), 7.67-7.90 (br., 2H, 2OH), 7.96 (d, $J = 7.7 \text{ Hz}$, 2H, Ar); ¹³C NMR (75 MHz, DMSO-*d*₆): δ (ppm) 36.1, 55.9, 56.1, 105.1, 111.8, 112.1, 116.6, 117.8, 119.4, 124.3, 124.4, 131.9, 132.6, 147.8, 149.1, 152.6, 165.0, 165.4.

Product 8

¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 6.37 (s, 1H, methine CH), 7.31 (d, $J = 7.5 \text{ Hz}$, 2H, Ar), 7.36 (d, $J = 8.7 \text{ Hz}$, 2H, Ar), 7.52 (d, $J = 8.4 \text{ Hz}$, 1H, Ar), 7.57-7.63 (m, 3H, Ar), 7.83 (s, 1H, Ar), 7.92 (d, $J = 7.8 \text{ Hz}$, 2H, Ar); ¹³C NMR (75 MHz, DMSO-*d*₆): δ (ppm) 36.5, 103.6,

116.4, 118.8, 122.2, 124.0, 124.2, 124.5, 131.4, 132.3, 133.0, 143.3, 148.1, 152.9, 164.8, 166.5;

Mass (EI, 70 eV): m/z 491 (M^+), 492 ($M^+ + 1$).

Product 11

^1H NMR (300 MHz, DMSO- d_6): δ (ppm) 6.37 (s, 1H, methine CH), 7.17 (d, $J = 7.8$ Hz, 2H, Ar), 7.33 (d, $J = 7.7$ Hz, 2H, Ar), 7.37-7.45 (m, 4H, Ar), 7.61 (t, $J = 8.0$ Hz, 2H, Ar), 7.95 (d, $J = 7.8$ Hz, 2H, Ar), 8.87 (br., 2H, 2OH); ^{13}C NMR (75 MHz, DMSO- d_6): δ (ppm) 36.2, 104.4, 116.5, 118.1, 119.2, 124.3, 124.4, 129.6, 131.4, 132.6, 139.9, 152.7, 165.2, 165.6.

Selected original spectrums of the synthesized bis-coumarins

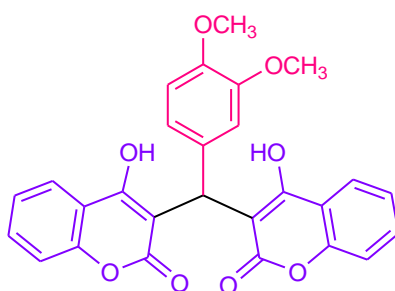
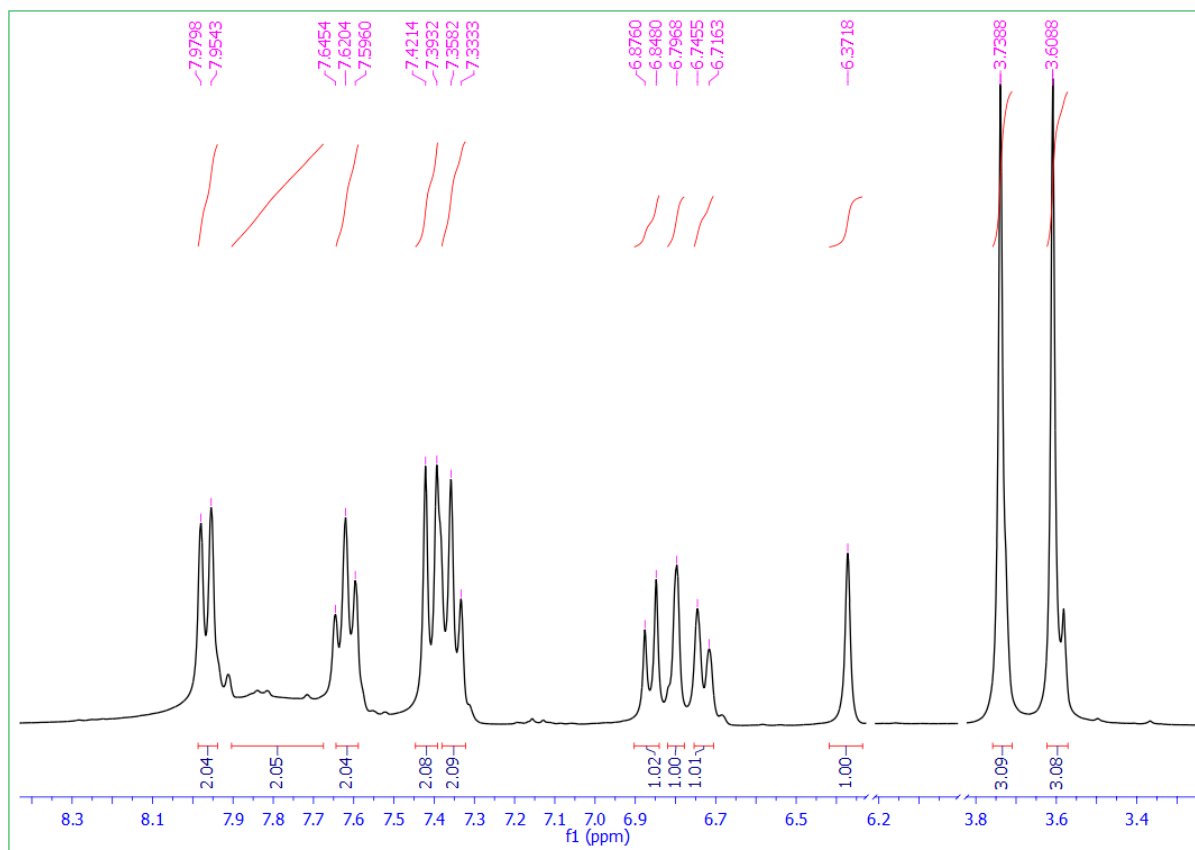


Fig. S1. The ^1H NMR spectrum of product **4**.

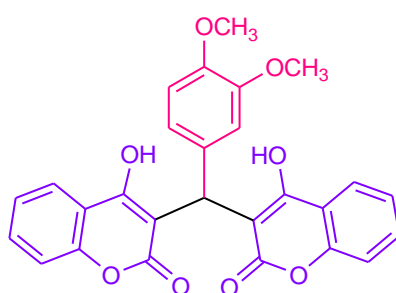
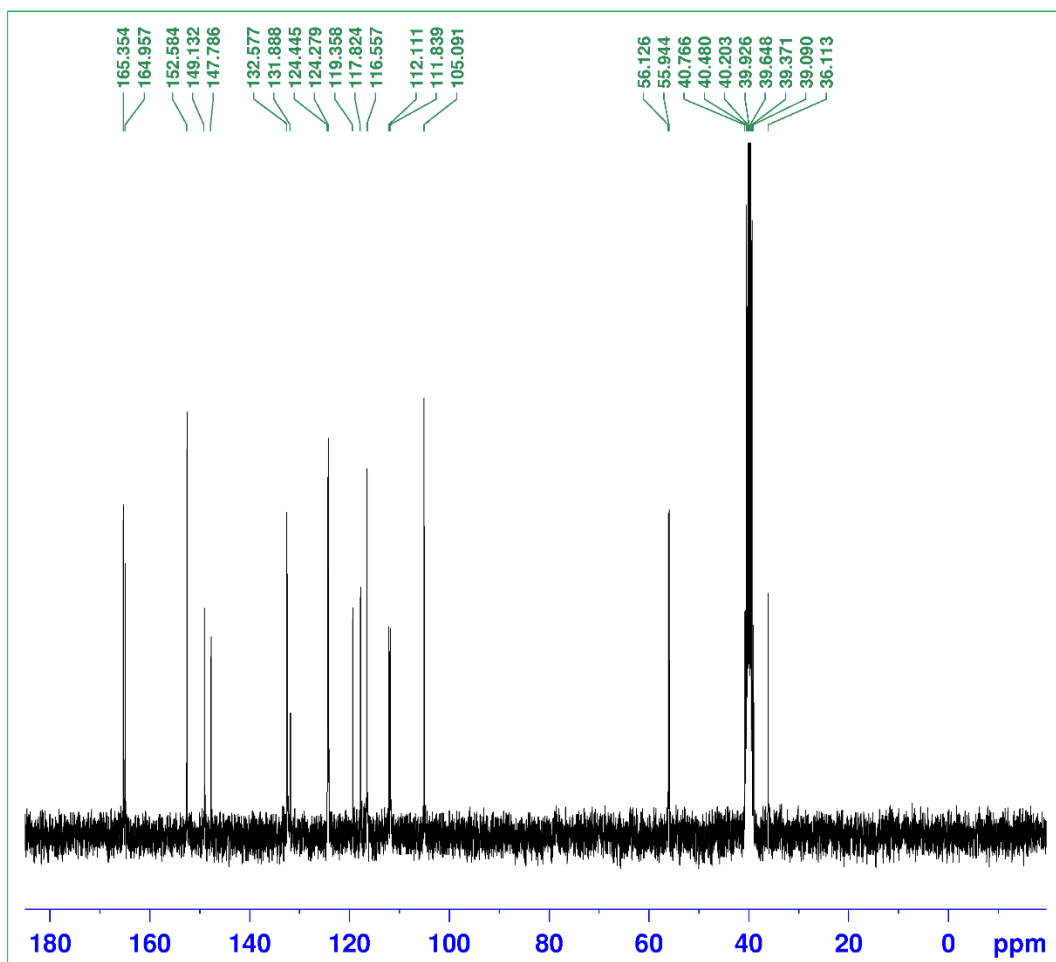


Fig. S2. The ^{13}C NMR spectrum of product 4.

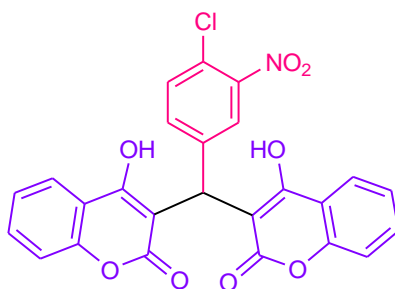
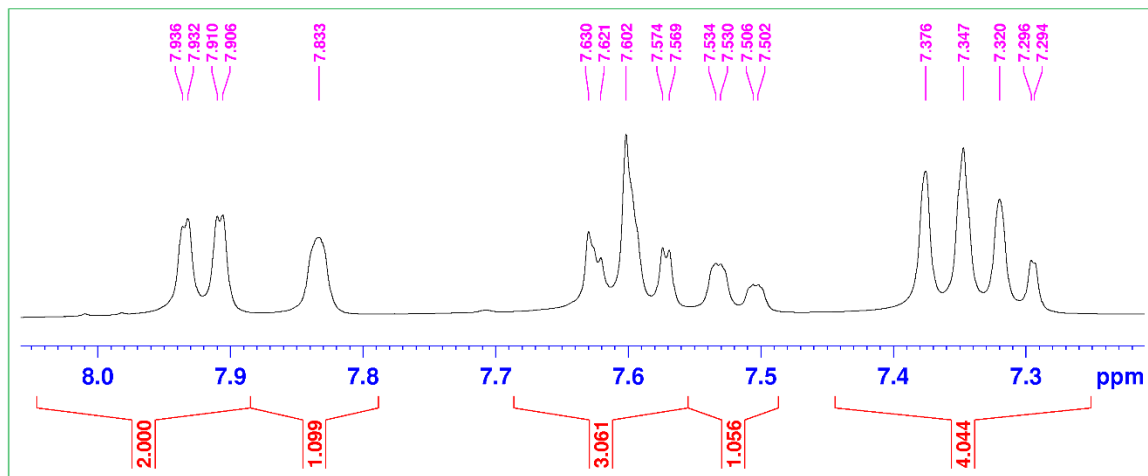
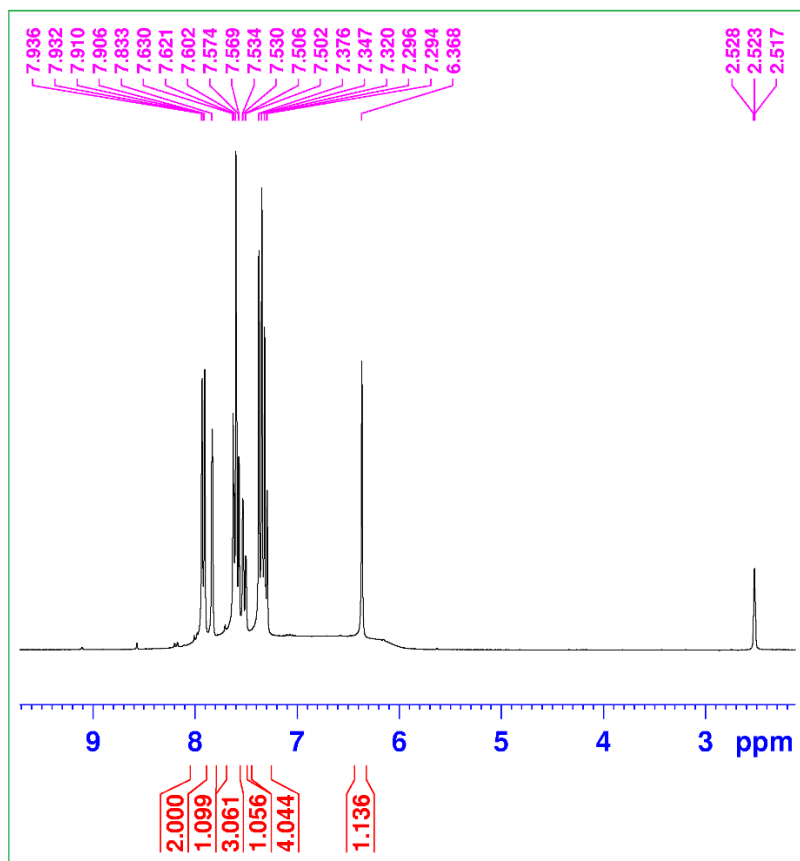


Fig. S3. The ¹H NMR spectrum (and expanded spectrum) of product **8**.

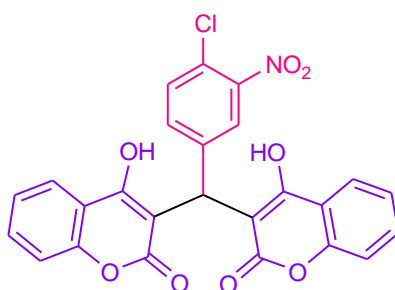
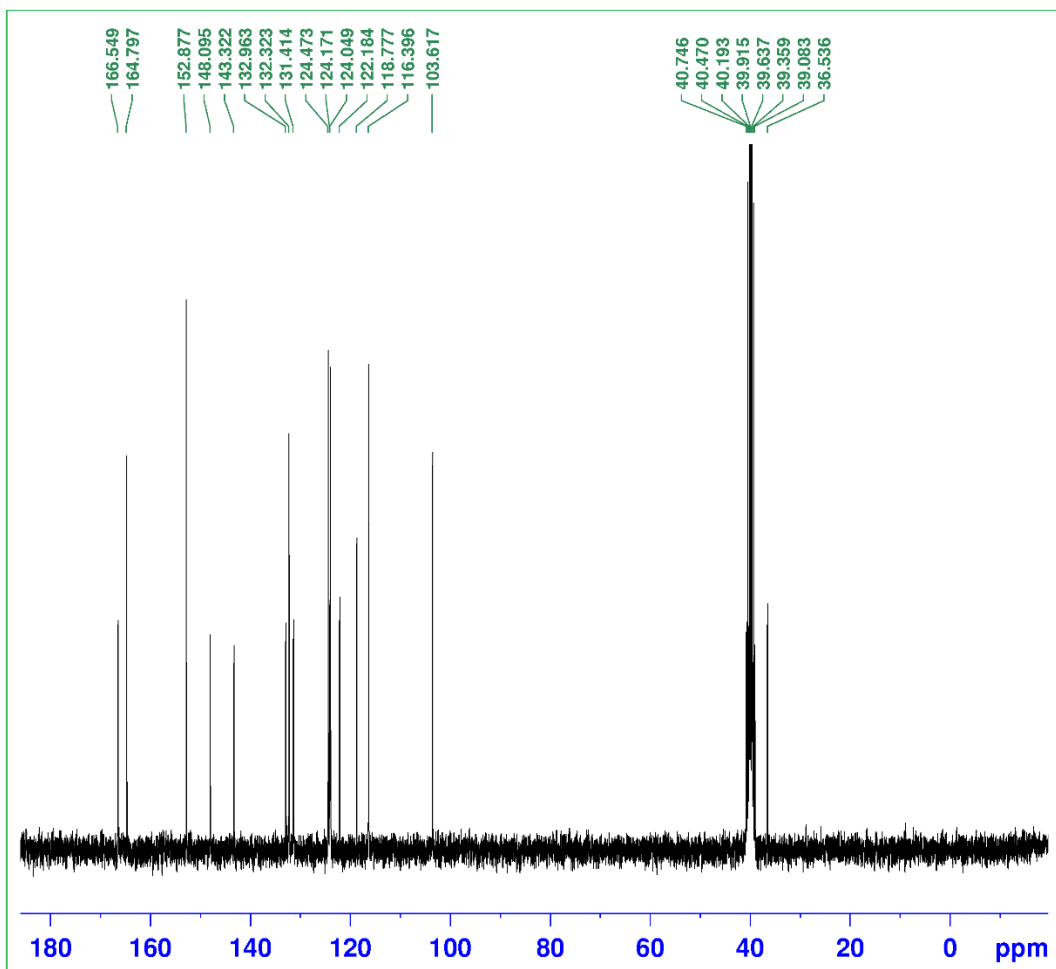


Fig. S4. The ^{13}C NMR spectrum of product **8**.

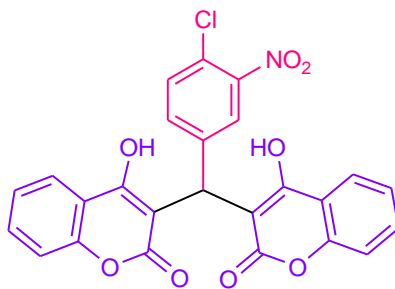
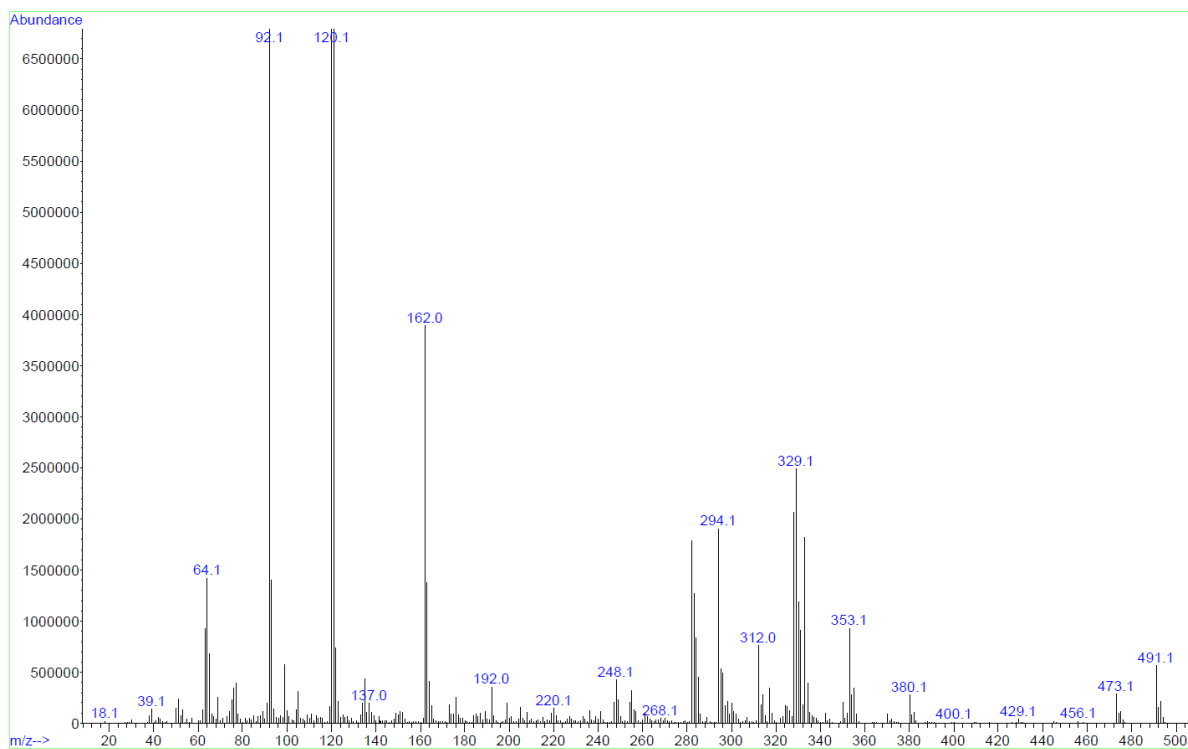


Fig. S5. The mass spectrum of product **8**.

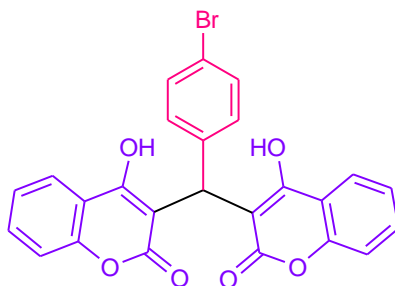
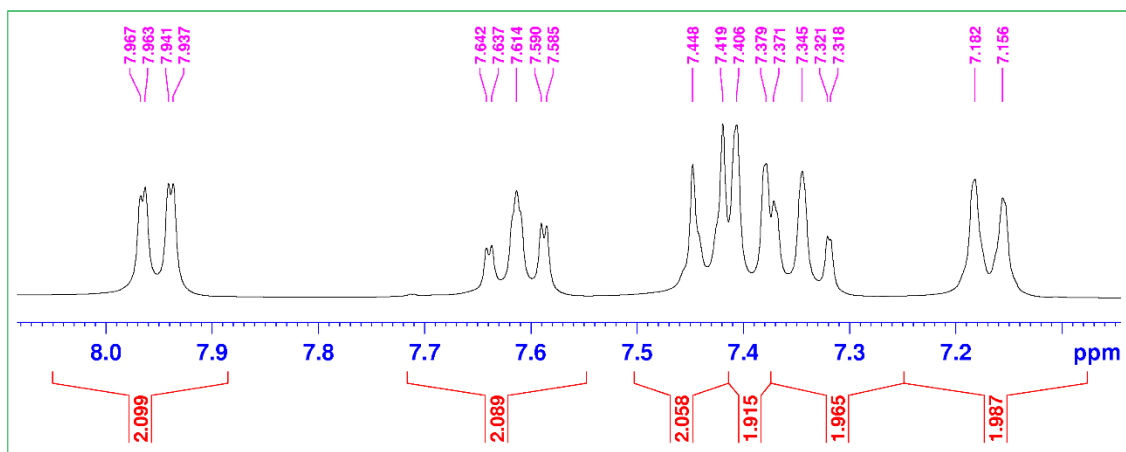
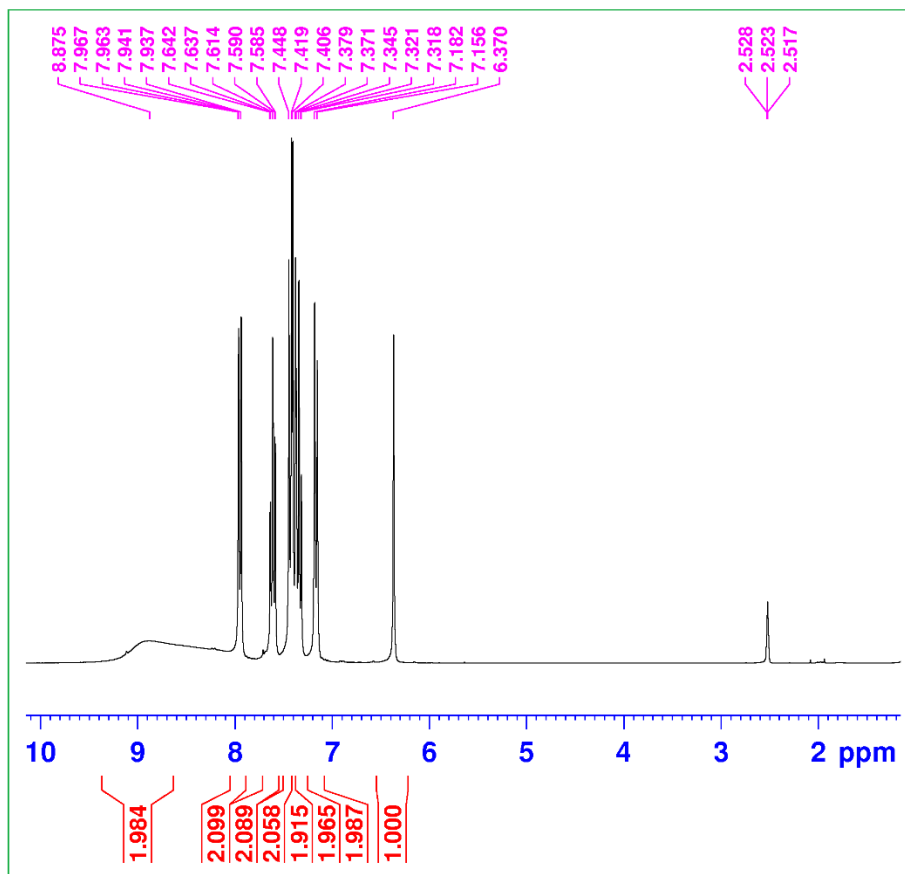


Fig. S6. The ^1H NMR spectrum (and expanded spectrum) of product **11**.

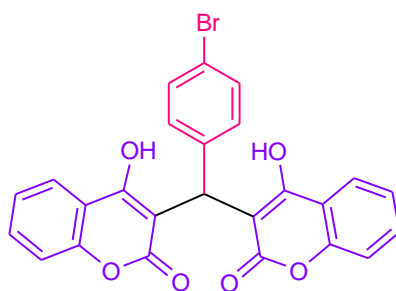
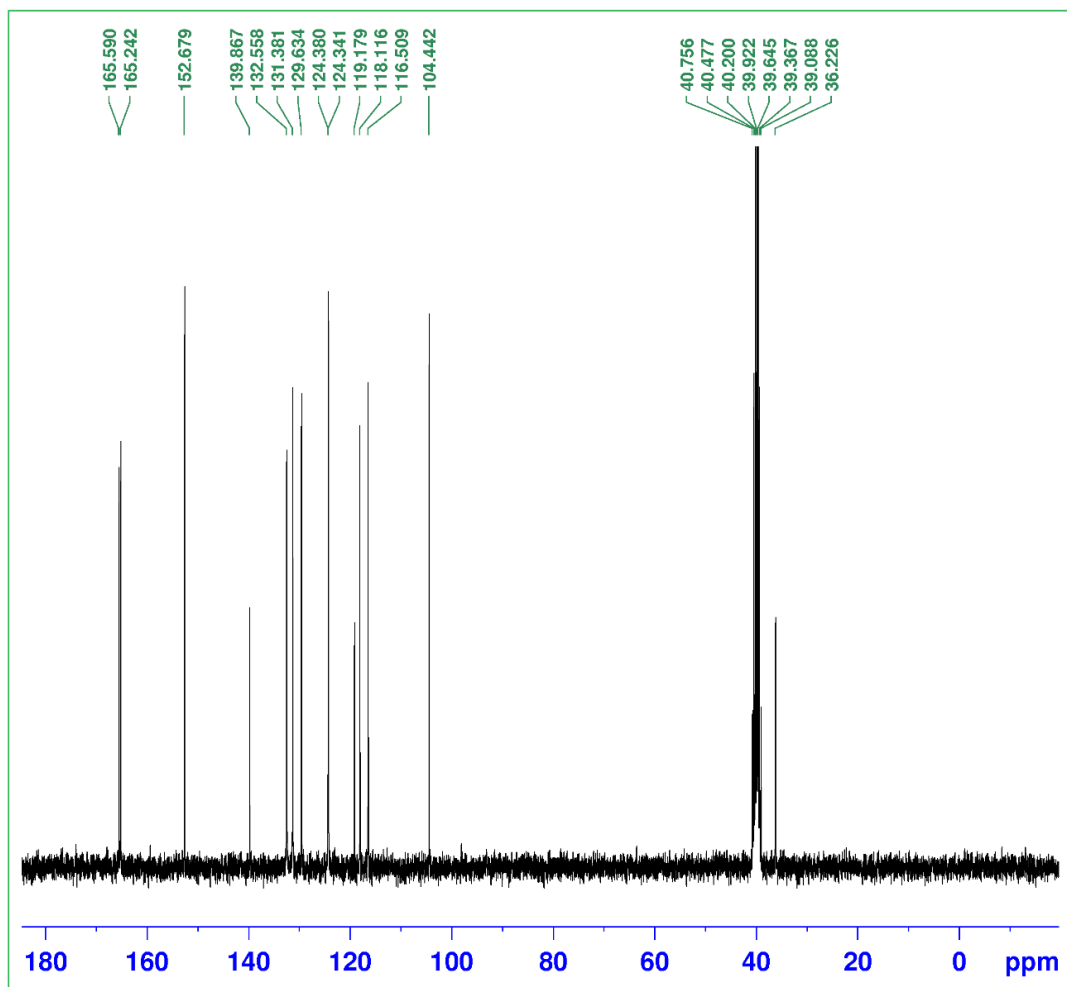


Fig. S7. The ^{13}C NMR spectrum of product 11.