

Supporting Information

A Non-metal Catalyst for Molecular Hydrogen Activation with Comparable Catalytic Hydrogenation Capability to Noble Metal Catalyst

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Experimental Section

Reagents: C₇₀ was purchased from Henan yongxin chemical limited company, C₆₀ were purchased from Yongxin, Aldrich, Alfa-Aesar and TCI respectively, nitro compounds were purchased from Alfa-Aesar, other common reagents were purchased from Nanjing chemical limited company.

Preparation of C₆₀ and C₇₀ mono anion catalysts: Preparation of C₆₀ mono anion follows our previous work:^[1,2] C₆₀ (36mg, 0.05mmol), Ni-Al alloy (130mg) and NaOH (400mg, 10mmol) were put into a flask, evacuated to exclude oxygen and filled with N₂ for three times, and then fresh-distilled tetrahydrofuran (THF, 20ml) was added in it with vigorous stirring. After adding as-distilled water (5ml), the reduction reaction took place rapidly and a red cloud-like C₆₀ mono anion product diffused into the THF layer whose color turned to dark red-purple very quickly. After 10 minutes, the dark red-purple THF solution of C₆₀ mono anion was separated from the aqueous solution. The fresh prepared THF solution of C₆₀ mono anion was used as catalyst for the hydrogenation of various substrates. C₇₀ monoanion was prepared by similar procedures. In the case of C₆₀²⁻, DMSO replaced THF as solvent. In order to inspect if the metal contaminants were introduced by the preparation procedures of fullerene anions or not, a blank solution was prepared by the similar procedure with that of fullerene anion except for absence of C₆₀. The hydrogenation reaction of nitrobenzene in the blank solution was completed. No products of the hydrogenation reaction were observed, the result was listed in Table S2 (entry 9).

Hydrogenation under light irradiation condition: Hydrogenation of various substrates was carried out in a cylinder quartz reactor. For each reaction, substrate (1.000g), catalyst (0.036g, 0.050mmol) and THF (250ml) were added into the reactor and bubbled with N₂ for 2h to get rid of air, then bubbled H₂ for 0.5h to saturate H₂. The hydrogenation reaction was performed with bubbled H₂ and stirring under light irradiation (high pressure mercury lamp, 300W or Xe lamp, 350W) for 4h. The reaction temperature is controlled at ~25°C by cycling cold water. The products and intermediates were identified on a GCMS-QP2010 (SHIMADZU) spectrometer equipped with a DB-ms capillary column comparing with authentic samples.

Preparation of yield-time curves in Figure 1: Substrate (1.000g), catalyst (0.036g, 0.050mmol) and THF (250ml) were added into the cylinder quartz reactor and bubbled with nitrogen for 2h to get rid of air, then bubbled H₂ for 0.5h to saturate H₂. The hydrogenation reaction was performed under UV irradiation (high pressure mercury lamp, 300W) with stirring and bubbled H₂ at ~25°C. The samples were acquired every 10 minutes for GCMS analysis. The conversion and selectivity are a little bit lower than that in Table 1 because the light irradiation and stirring were stopped during acquisitions of samples, which disturbed the reaction.

Hydrogenation under dark condition: The hydrogenation of various substrates was carried out in a 100ml stainless steel autoclave. For each reaction, substrate (1.000g), catalyst (0.036g, 0.050mmol) and THF (40ml) were added into the autoclave. The autoclave was flushed with hydrogen for three times to get rid of air. The hydrogenation reaction was performed under hydrogen atmosphere (5.0MPa) at 140°C and stirring at 900 r.p.m. for 3h. Then, the autoclave was cooled to the ambient temperature and flushed twice with nitrogen. The catalyst was separated by centrifugation at 12,000 r.p.m., washed with THF (3×5ml) for characterization. The identification of products and intermediates was done on a GCMS-QP2010 (SHIMADZU) spectrometer equipped with a DB-ms capillary column by comparing with authentic samples.

Inductively Coupled Plasma (ICP) Emission Spectrometer analysis of fullerene: Fullerene (100.0 mg) from various companies were put in the crucible and heated in a muffle furnace at 500°C under air to oxide all samples, then several drops of 6M HCl aqueous solution was added in the crucible to make a clear transparent solution, which was transferred into a 10ml of volumetric flask for ICP measurements.

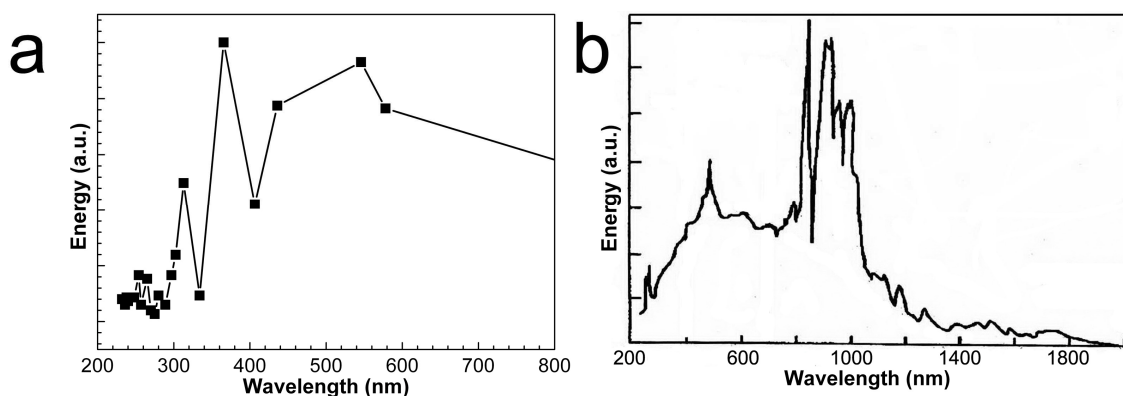


Figure S1 The energy distribution of high pressure mercury lamp (300 W) (a) and Xe lamp (350 W) (b)

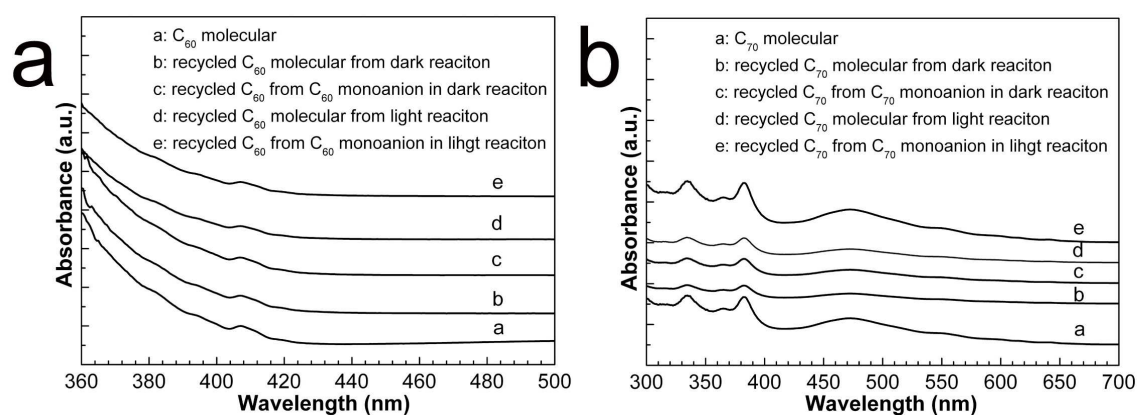


Figure S2 The UV-Vis spectrum of recycled C_{60} (a) and C_{70} (b) catalysts in toluene solution. C_{60}^- and C_{70}^- are very sensitive to air and forms neutral C_{60} and C_{70} with a few oxides when recovering from reaction solution in open air.

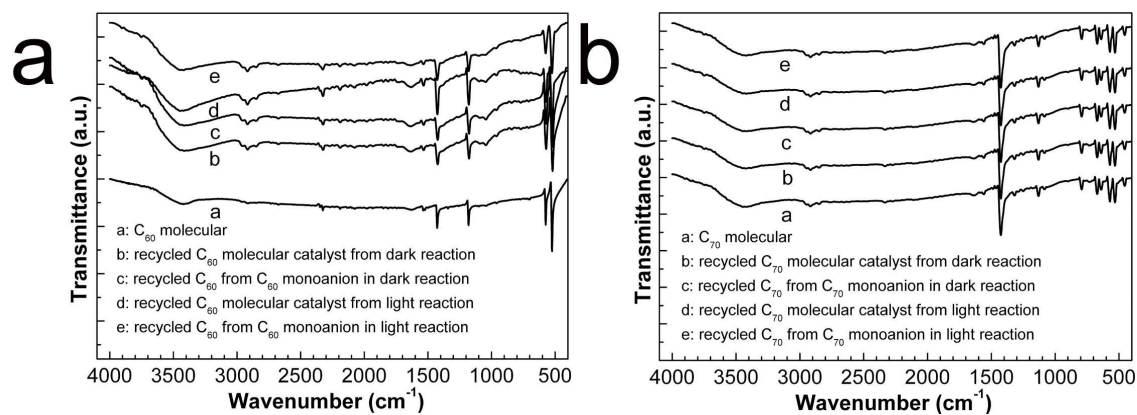


Figure S3 The IR spectrum of recycled C_{60} (a) and C_{70} (b) catalysts from dark and light reactions. C_{60}^- and C_{70}^- are very sensitive to air and forms neutral C_{60} and C_{70} with a few oxides when recovering from reaction solution in open air.

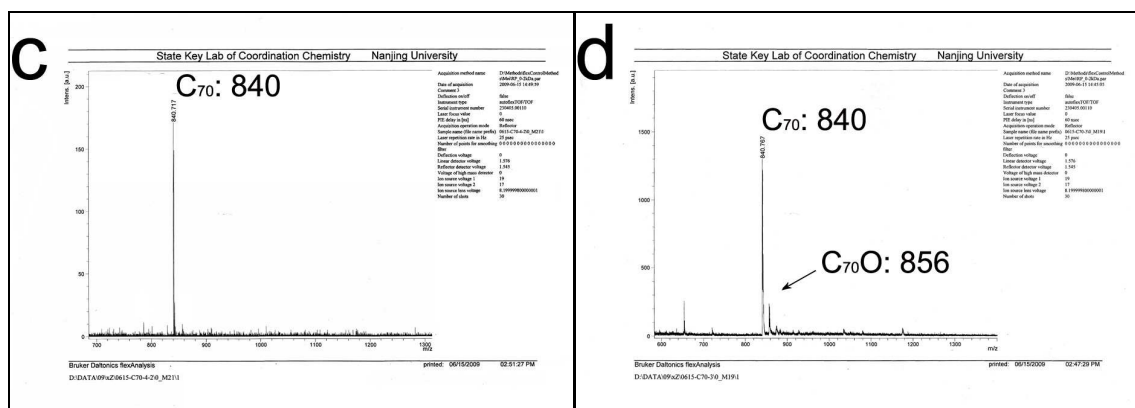


Figure S5 The MALDI-TOF of recycled C_{70} from C_{70} catalyst in dark (a) and light (c) reaction and from C_{70}^- catalyst in dark (b) and light (d) reaction. C_{70}^- is very sensitive to air and forms neutral C_{70} with a few oxides when recovering from reaction solution in open air.

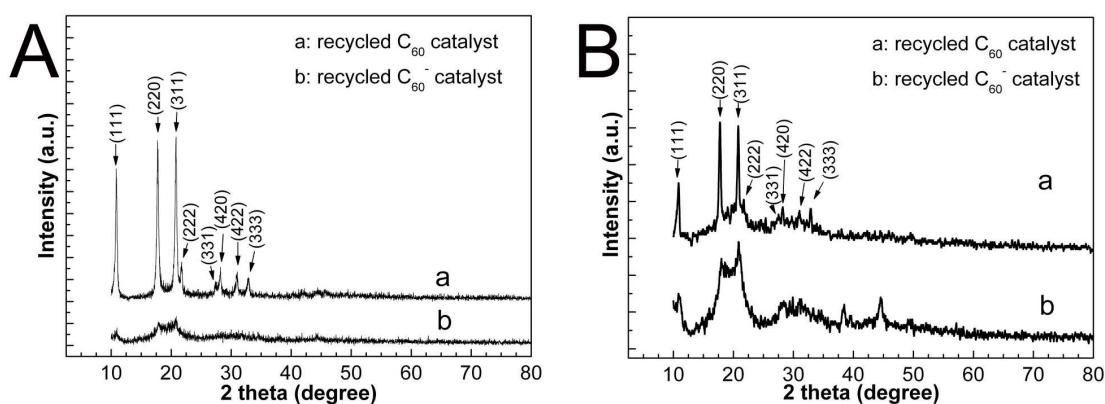


Figure S6 The XRD pattern of recycled C_{60} (curve a) and C_{60}^- (curve b) catalysts from dark (A) and light irradiation (B) reactions. C_{60}^- is very sensitive to air and forms neutral C_{60} with a few oxides when recovering from reaction solution. The sample recovered is directly used for XRD without recrystallisation. The crystallinity of recovered sample depends on the recovering conditions.

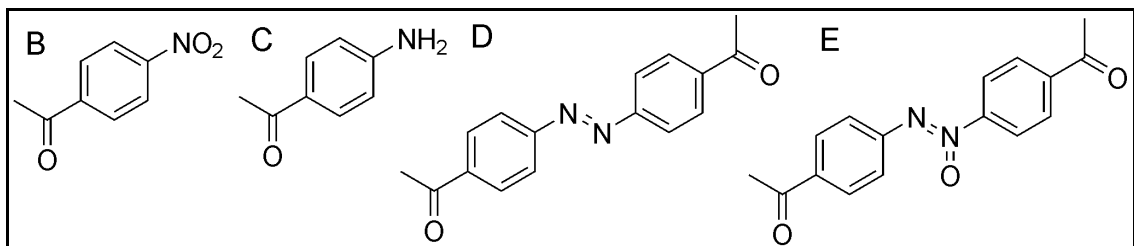
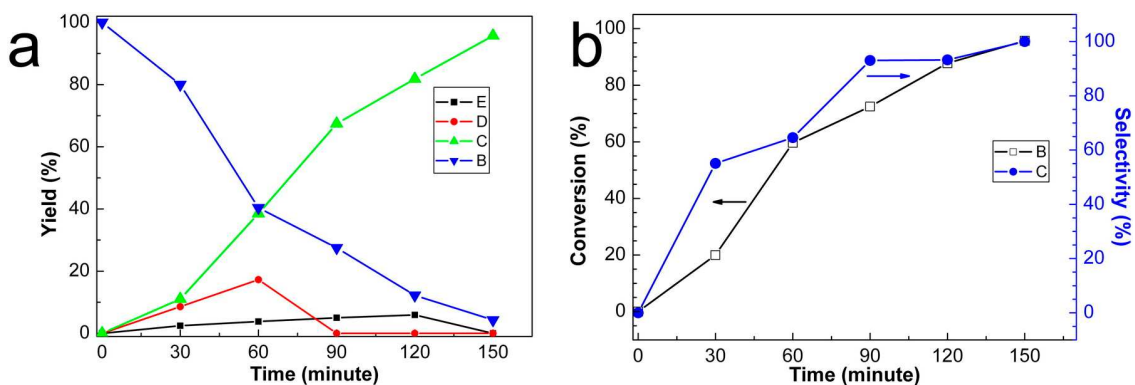


Figure S7 The plot of product distribution (a) and conversion and selectivity (b) vs. time in hydrogenation of 4-nitroacetophenone with C_{60} catalyst excited by ultraviolet radiation, Reaction conditions: 1.0 g substrate, 0.036 g catalyst and 250 mL THF solvent.

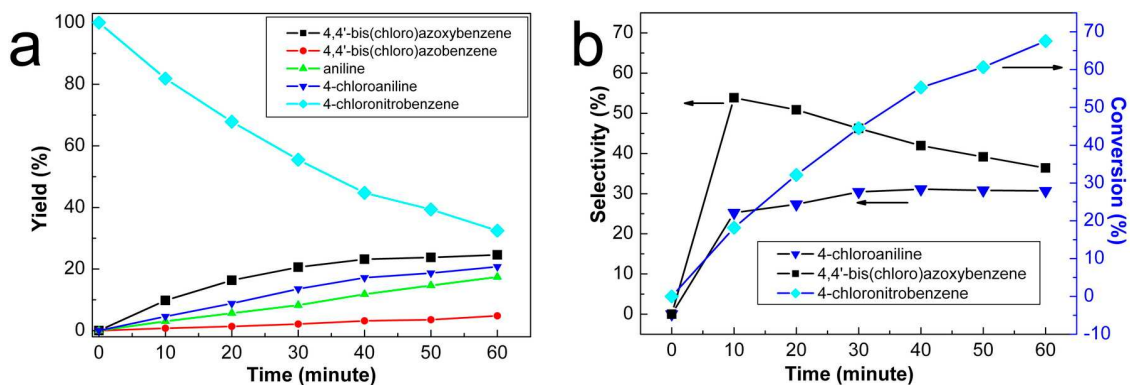


Figure S8 The plot of product distribution (a) and conversion and selectivity (b) vs. time in hydrogenation of 4-chloronitrobenzene with C_{60} catalyst excited by ultraviolet radiation, Reaction conditions: 1.0 g substrate, 0.036 g catalyst and 250 mL THF solvent.

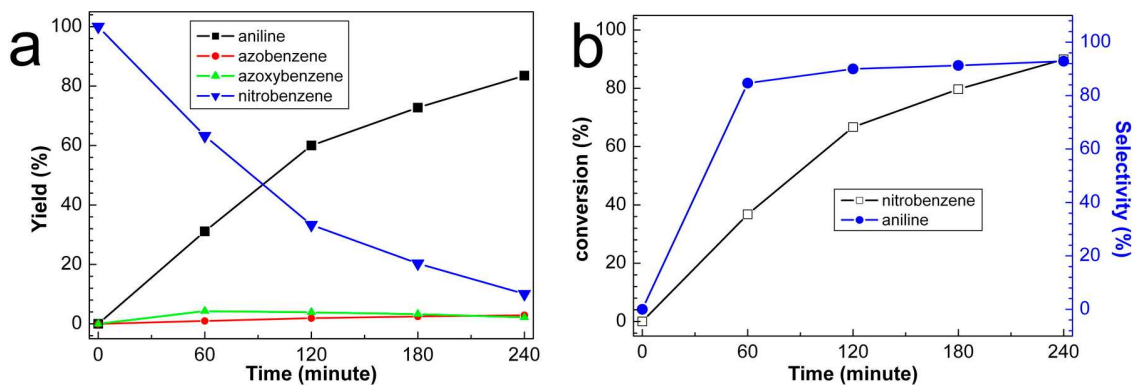


Figure S9 The plot of product distribution (a) and conversion and selectivity (b) vs. time in hydrogenation of nitrobenzene with C_{70} catalyst excited by ultraviolet radiation, Reaction conditions: 1.0 g substrate, 0.036 g catalyst and 250 mL THF solvent.

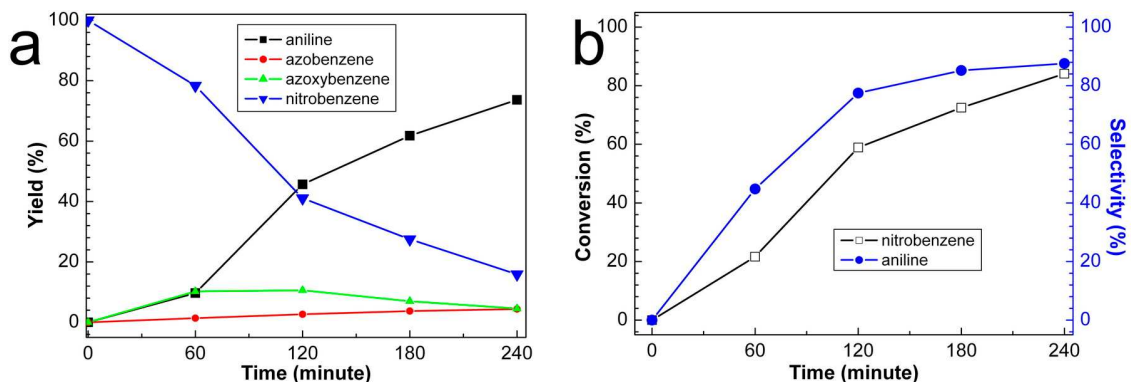


Figure S10 The plot of product distribution (a) and conversion and selectivity (b) vs. time in hydrogenation of nitrobenzene with C_{70} catalyst excited by ultraviolet radiation, Reaction conditions: 1.0 g substrate, 0.036 g catalyst and 250 mL THF solvent.

Table S1. The hydrogenation of nitrobenzene to aniline under light irradiation with various fullerene catalysts^[a].

Entry	Catalyst	Light Radiation	t (h)	Conv. (%)	Select. (%)
1	C ₆₀ (Aldrich)	UV	1.0	85.7	75.2
2	C ₆₀ (Aldrich)	UV	4.0	94.7	86.7
3	C ₆₀ (Alfa-Aesar)	UV	1.0	84.9	74.1
4	C ₆₀ (Alfa-Aesar)	UV	4.0	96.1	88.5
5	C ₆₀ (TCI)	UV	1.0	85.1	74.8
6	C ₆₀ (TCI)	UV	4.0	97.4	88.2
7 ^[b]	Fe ³⁺ (Fe(NO ₃) ₃)	UV	1.0	0	~
8 ^[b]	Co ²⁺ (Co(NO ₃) ₂)	UV	1.0	0	~
9 ^[b]	Cr ³⁺ (Cr(NO ₃) ₃)	UV	1.0	0	~
10 ^[b]	Cu ²⁺ (Cu(NO ₃) ₂)	UV	1.0	0	~
11 ^[b]	Ag ⁺ (AgNO ₃)	UV	1.0	0	~

[a] Reaction conditions: 1.0g substrate, 0.036g catalyst and 250ml THF solvent under 1 atmospheric pressure of H₂ and light irradiation (300W high pressure Hg lamps) in a cylinder quartz reactor. [b] 100 ppm of metal ion (25×10³μg) in reaction mixture (250ml) respectively and the amount of metal ions added is ~10⁴ times higher than that of 0.036g C₆₀ in 250ml THF in order to see their catalytic behavior clearly.

Table S2. The hydrogenation of nitrobenzene to aniline with various C₆₀ catalysts under dark condition^[a].

Entry	Catalyst	H ₂ (MPa)	T (°C)	Conv. (%)	Select. (%)
1	C ₆₀ ⁻ (Aldrich)	5.0	140	95.6	71.9
2	C ₆₀ ⁻ (Alfa-Aesar)	5.0	140	93.1	73.4
3	C ₆₀ ⁻ (TCI)	5.0	140	96.6	72.8
4 ^[b]	Fe ³⁺ (Fe(NO ₃) ₃)	5.0	140	0	~
5 ^[b]	Co ²⁺ (Co(NO ₃) ₂)	5.0	140	0	~
6 ^[b]	Cr ³⁺ (Cr(NO ₃) ₃)	5.0	140	0	~
7 ^[b]	Cu ²⁺ (Cu(NO ₃) ₂)	5.0	140	0	~
8 ^[b]	Ag ⁺ (AgNO ₃)	5.0	140	0	~
9 ^[c]	Blank solution	5.0	140	0	~

[a] Reaction conditions: 1.0g substrate, 0.036g catalyst and 40ml THF solvent for 4.0h. [b] 0.1 ppm of metal ion (4.1 μg) in reaction mixture (41 ml), which is ~10² times higher than that of 0.036g C₆₀ in 41ml THF. [c] blank solution was prepared by the similar procedure with that of C₆₀⁻ except for absence of C₆₀.

Table S3. ICP results of for metal contaminants contained in C₆₀ from various companies^[a] (μg/g).

Engtry	Catalyst	Co/ppm	Cr/ppm	Cu/ppm	Fe/ppm	Ag/ppm	Pd/ppm	Pt/ppm	Ni/ppm
1	C ₆₀ (Yongxin)	~ ^[b]	2.7	2.4	63.8	3.8	~ ^[b]	~ ^[b]	~ ^[b]
2	C ₆₀ (Aldrich)	0.1	0.6	2.3	36.1	0.3	~ ^[b]	~ ^[b]	~ ^[b]
3	C ₆₀ (Alfa-Aesar)	0.2	1.1	8.9	67.4	0.6	~ ^[b]	~ ^[b]	~ ^[b]
4	TCI	~ ^[b]	0.8	3.0	17.6	0.1	~ ^[b]	~ ^[b]	~ ^[b]

[a] experimental conditions were listed in experimental section. [b] below the detecting limit.

References

- (1) (a) Wu, M.; Wei, X.; Qi, L.; Xu, Z. *Tetrahedron Lett.* **1996**, 37, 7409-7412. (b) Wei, X.; Wu, M.; Qi, L.; Xu, Z. *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1389-1393.