

Supporting Information 1

Title: Remarkable catalytic activity of ultra small free-CeO₂ nanoparticles in selective carbon-carbon bond formation reactions in water at room temperature

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Reagents and solvents:

All the active methylene compounds, conjugated alkenes, Cerium nitrate and ammonium hydroxide were purchased from Sigma-Aldrich and were used as received. Ethyl acetate, ethanol and hexane were purchased from FisherSci used as received. DI water was used for reaction purpose. The NMR spectra were measured in chloroform-*d* (CDCl₃) solvent in a Varian 500 NMR instrument. FT-IR spectra were recorded in Perkin-Elmer instrument in neat conditions. The nanoparticles (NPs) were characterized by TEM, XRD and XPS studies.

ESI-1: Synthesis of dextran coated cerium oxide NPs:

A solution containing 5.0mL of 1.0 M cerium (III) nitrate and 10.0mL of 1.0 M dextran T-10 was added drop by drop to a 30.0 mL ammonium hydroxide solution (Sigma Aldrich, 30%) and stirred for 24 h at 25 °C. The color of the solution changed from light yellow to dark brown, indicating the formation of stabilized dextran-coated CeO₂ NPs. Afterwards, the solution was centrifuged for two 30 min cycles to settle any debris and large agglomerates. Finally, the centrifuged solution was purified from free dextran and concentrated using an Amicon cell (YM 30 K; Millipore Inc).

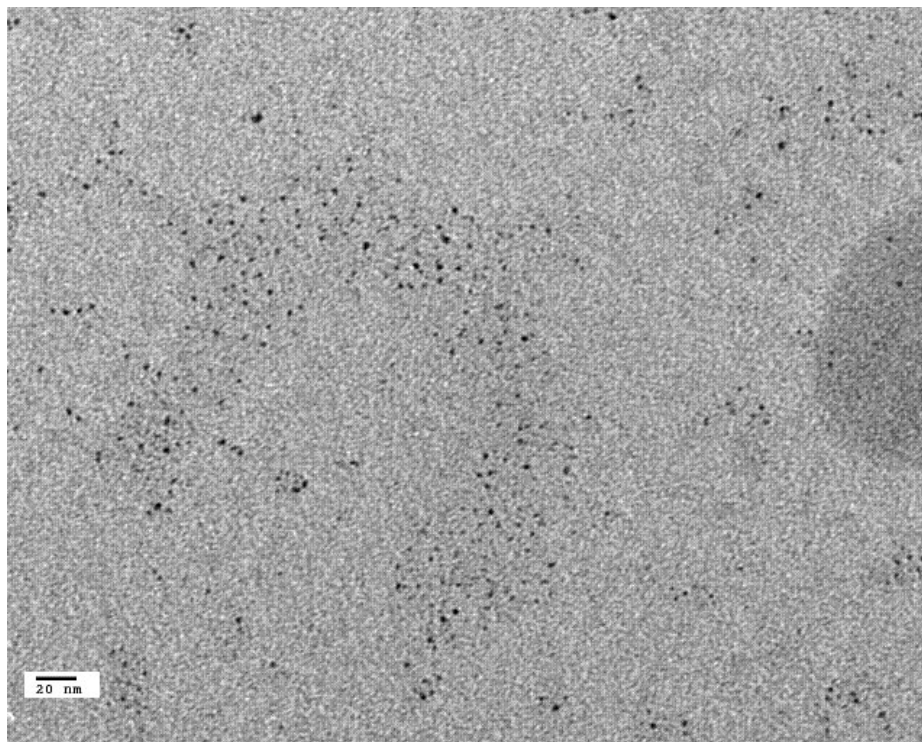


Fig. 1S TEM image of dextran coated CeO₂ NPs (DCNPs; size ~ 2-5 nm).

ESI-2: Synthesis and characterization of free-CeO₂ NPs:

(i) Synthesis of free-CeO₂ NPs:

A solution containing 5.0mL of 1.0 M cerium (III) nitrate was added drop by drop to a 30.0 mL ammonium hydroxide solution and stirred for 24 h at room temperature. The solution was centrifuged and washed with ethanol-water mixture to remove the excess reagents. Finally, the formation of crystalline nanoceria was confirmed by TEM, XRD and XPS analysis.

(ii) Autocatalytic Study:

To check the oxidation state of prepared CeO₂NPs, we have tested the by the treatment of hydrogen peroxide (H₂O₂) as an oxidizer. We observed a color change of form light yellow to red upon treatment with H₂O₂. The red color slowly faded way with time and back to its original light yellow color after ten days (**Fig. 2S**).

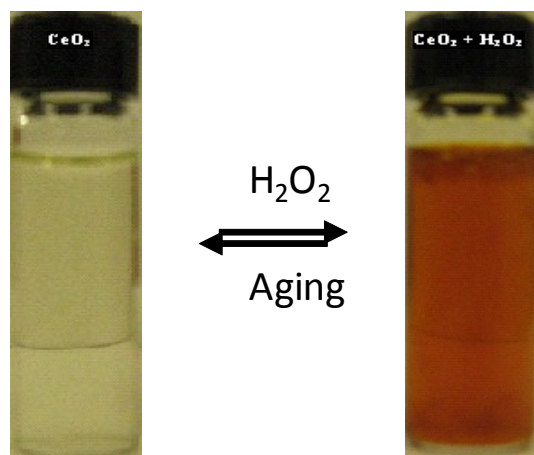


Fig. 2S The digital image of the aqueous solution of the CeO₂ NPs in absence and presence of H₂O₂ showing autocatalytic activity.

(iii) XPS Study:

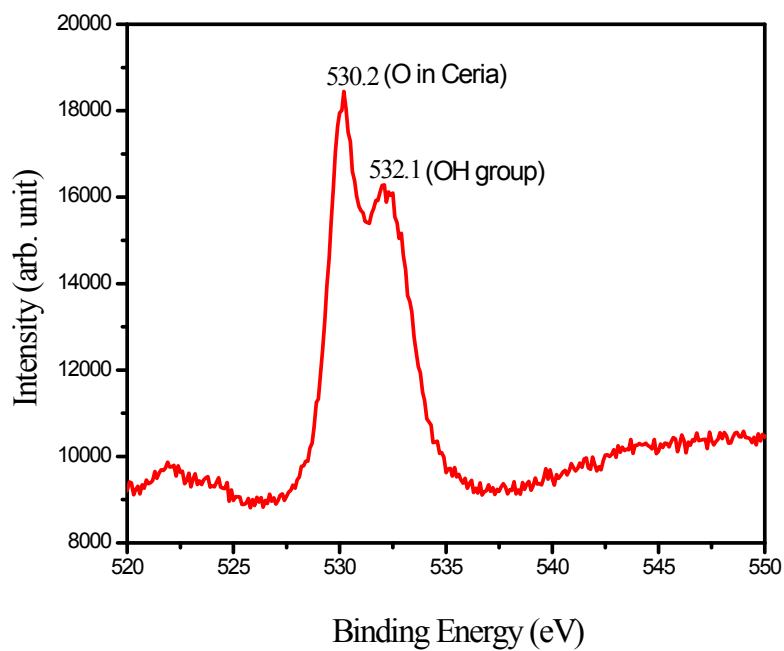
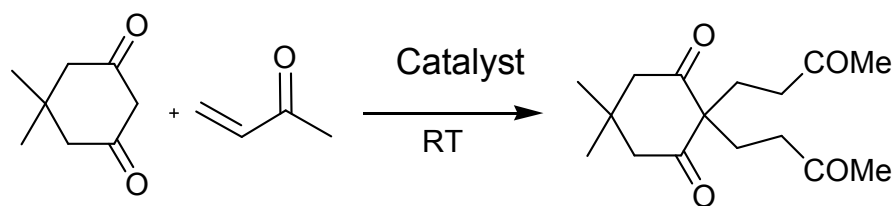


Fig. 3S High resolution XPS spectrum of O1s.

ESI 3:

(i) Optimization of reaction Conditions:

Table 1S Standardization of reaction conditions using the model reaction between dimedone and MVK

entry	reaction medium	catalyst (mol %)	time (h)	Yield (%) ^a
1	H ₂ O ^b	20 ^c	24	40
2	H ₂ O ^b	5 ^d	3	90
3	H ₂ O ^b	-	24	-
4	Neat	5 ^d	12	50
5	Ethanol	5 ^d	12	75
6	THF	5 ^d	12	35
7	Toluene	5 ^d	12	20
8	CH ₃ CN	5 ^d	12	45

^aIsolated yield. ^bReactions were carried out using 1 ml of DI H₂O. ^cReactions were carried out using dextran coated CeO₂ NPs. ^dReactions were carried out using free-CeO₂ NPs.

(ii) General experimental procedure for the free-CeO₂ NPs catalyzed Michael addition of active methylene compounds to conjugated alkenes:

Representative example for the Michael addition of 5,5-dimethyl-1,3-cyclohexadione to MVK (Entry 13, Table 1):

MVK (140.18 mg, 2 mmol) was added to a mixture of 5,5-dimethyl-1,3-cyclohexadione (140 mg, 1 mmol) and CeO₂ NP (~ 8.5 mg, 5 wt %) in water (0.5 mL) and stirred the mixture for 4 h until completion of reaction (TLC). The reaction mixture was centrifuged for 5 minutes and the aqueous part was extracted with ethyl acetate, dried over anhydrous Na₂SO₄ and evaporated the solvent to leave crude product, which was purified by short column chromatography over silica gel (ethyl acetate: hexane 1:9) to provide pure bis-Michael adduct, 5,5-Dimethyl-2,2-bis-(3-oxo-butyl)-cyclohexane-1,3-dione as white solid in excellent yield (252 mg, 90 %). The product was characterized by its IR and ¹H NMR and ¹³C NMR spectroscopic data and compared with reported one. The NPs were washed with ethanol and reused for subsequent runs. This procedure was followed for all the reactions listed in Table 1 in main manuscript.

Table 2S Comparative study of catalysts for bis-Michael addition reactions

Sl. No.	Catalyst	Time (h)	Yield (%)	Ref.
1	<i>Trans</i> -hydrido(<i>n'</i> - <i>o</i> -enolato)ruthenium(II) complex	46-96	60-89	18
2	SiO ₂ NPs	3-5	70-90	4(d)
3	[bmIm]OH	1-4	80-96	19
4	CeO₂ NPs	3-7	72-90	Present Study

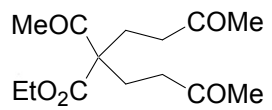
ESI-4: General experimental procedure for the free-CeO₂ NPs catalyzed allylation of active methylene compounds: Representative example for the allylation of malononitrile with allyl iodide (Entry 2, Table 2):

A mixture of allyl iodide (1 mmol), malonitrile (1 mmol) and CeO₂ NP was stirred for 10 h until completion of reaction (TLC). The reaction mixture was centrifuged for 5 minutes and the aqueous part was extracted with ethyl acetate, dried over anhydrous Na₂SO₄ and evaporated the solvent to leave crude product, which was purified by short column chromatography over silica gel (ethyl acetate: hexane 3:7) to provide pure 2-Allyl-malononitrile (84 mg, 80%) as a pale yellow liquid.

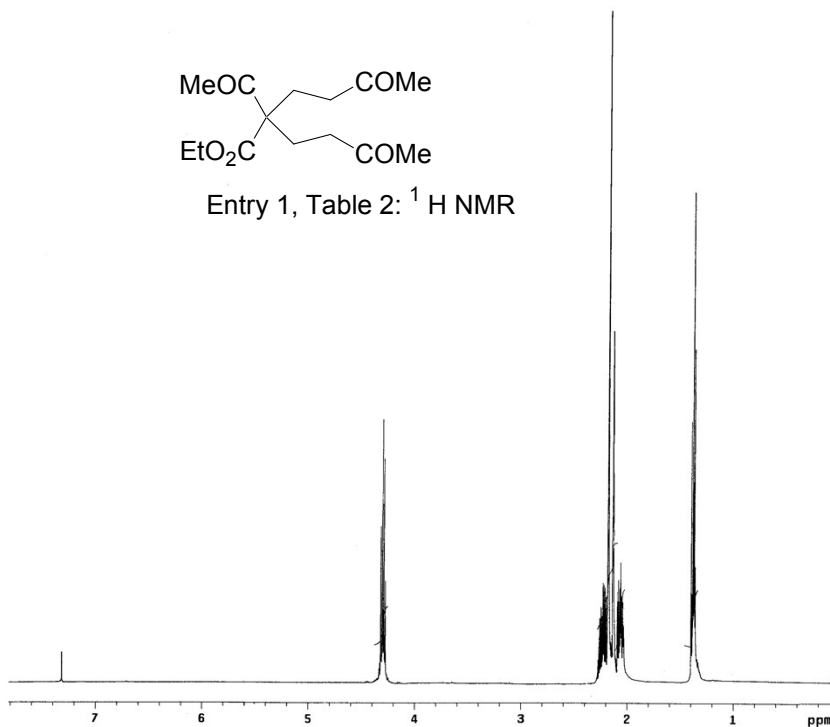
All the products listed in Table 2 and Table 3 are known and were characterized by spectroscopic data and compared these data with reported values¹⁻²

Copy of ¹H NMR spectra of all products listed in Table 1 and Table 2 were given below.

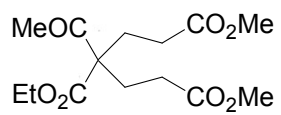
Supporting Information 7



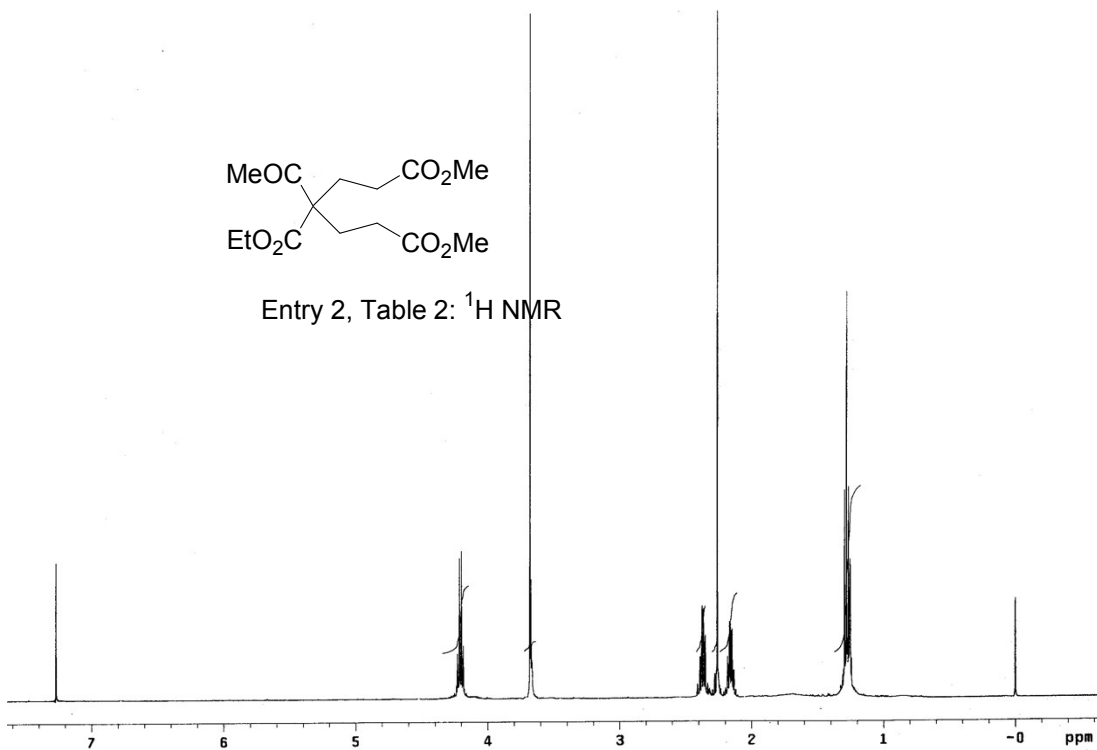
Entry 1, Table 2: ¹H NMR



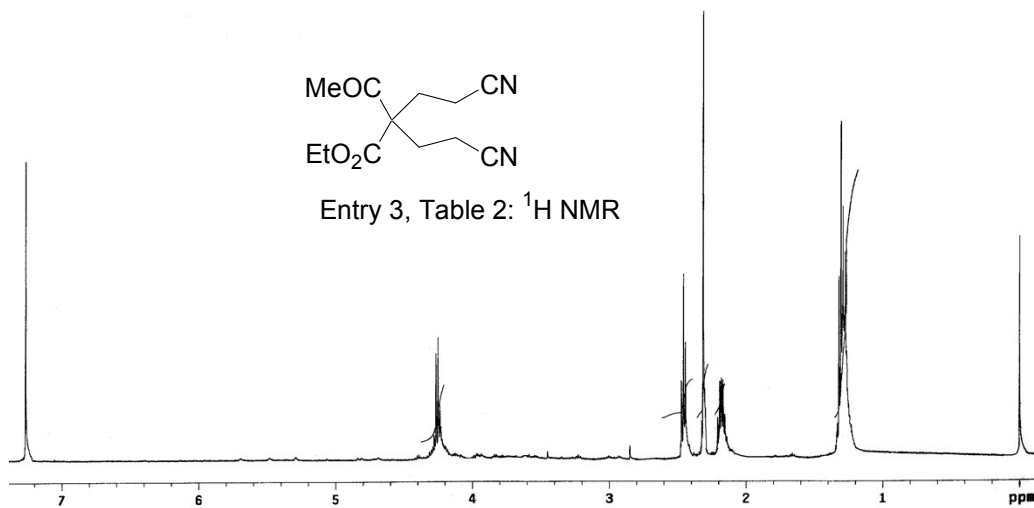
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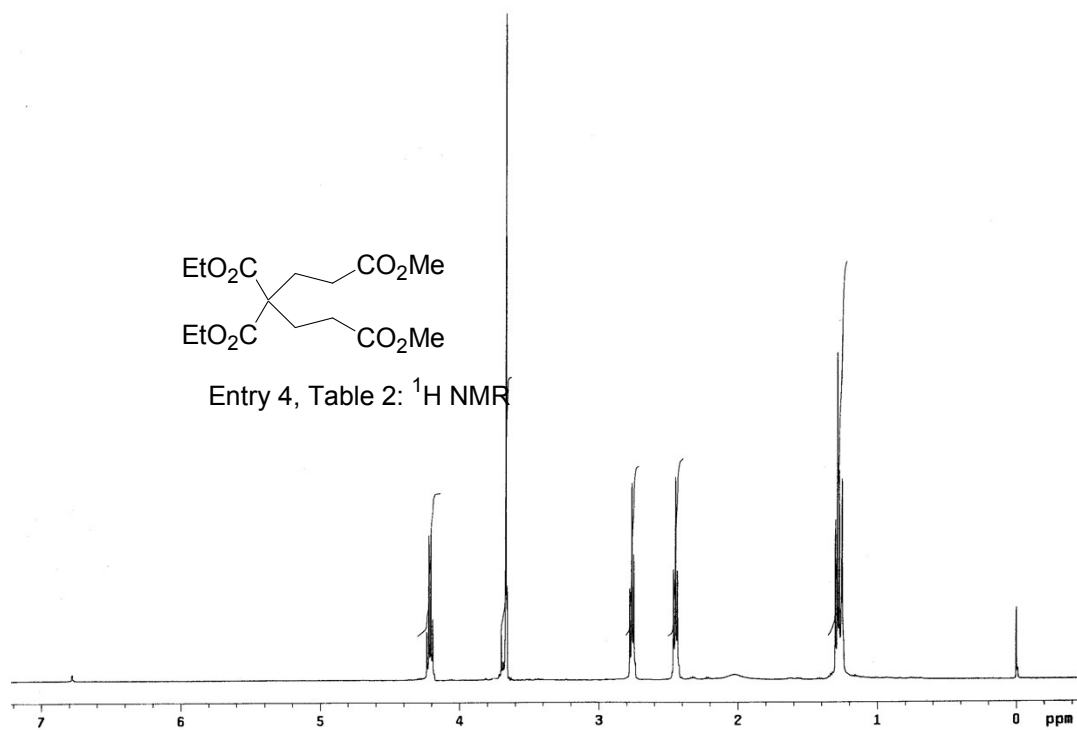
Entry 2, Table 2: ¹H NMR



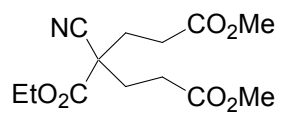
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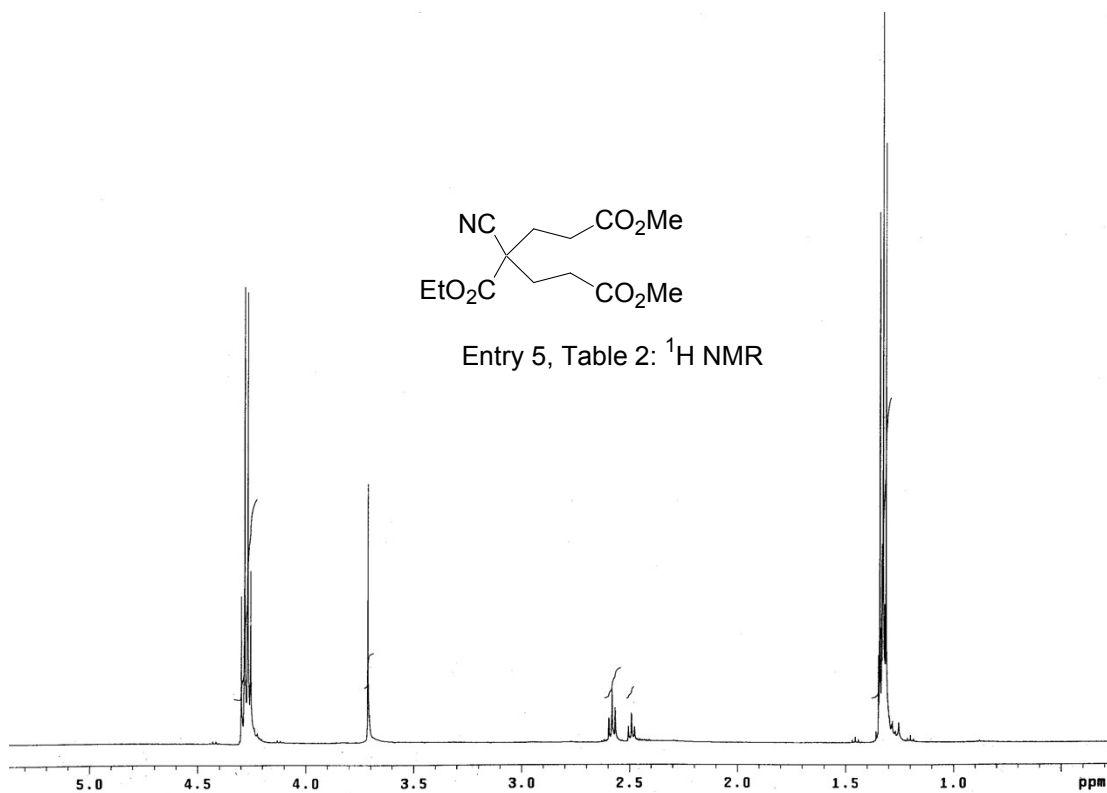
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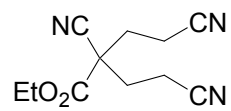
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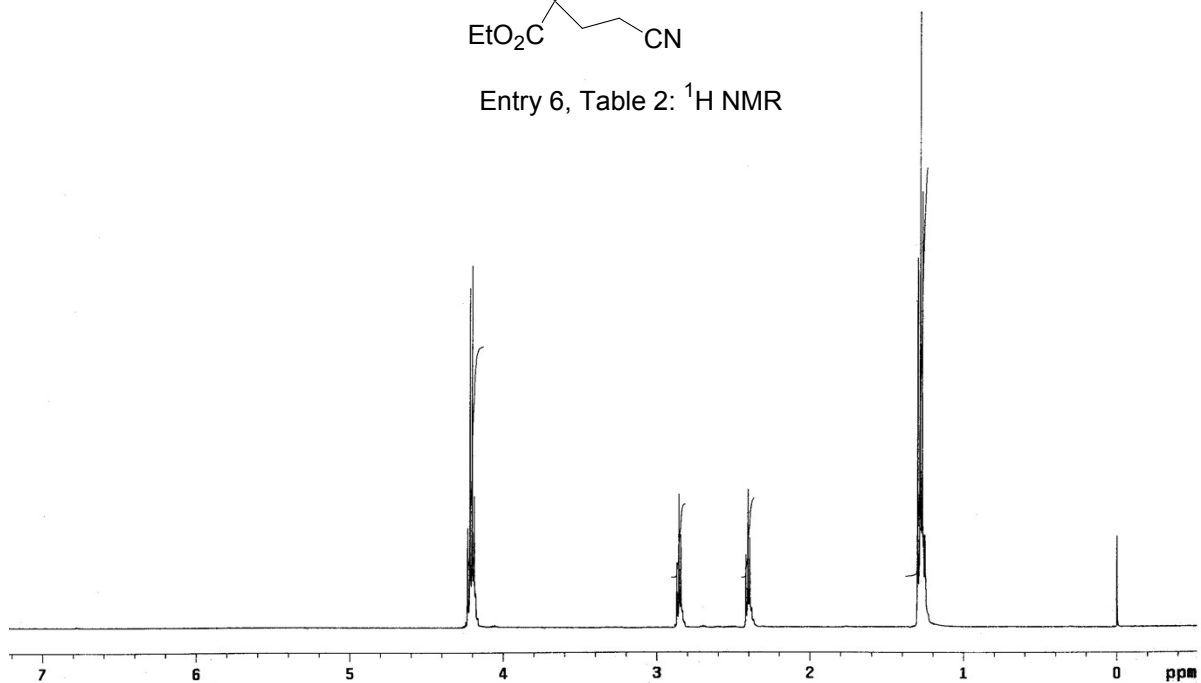
Entry 5, Table 2: ¹H NMR



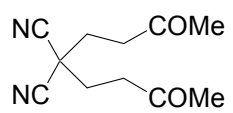
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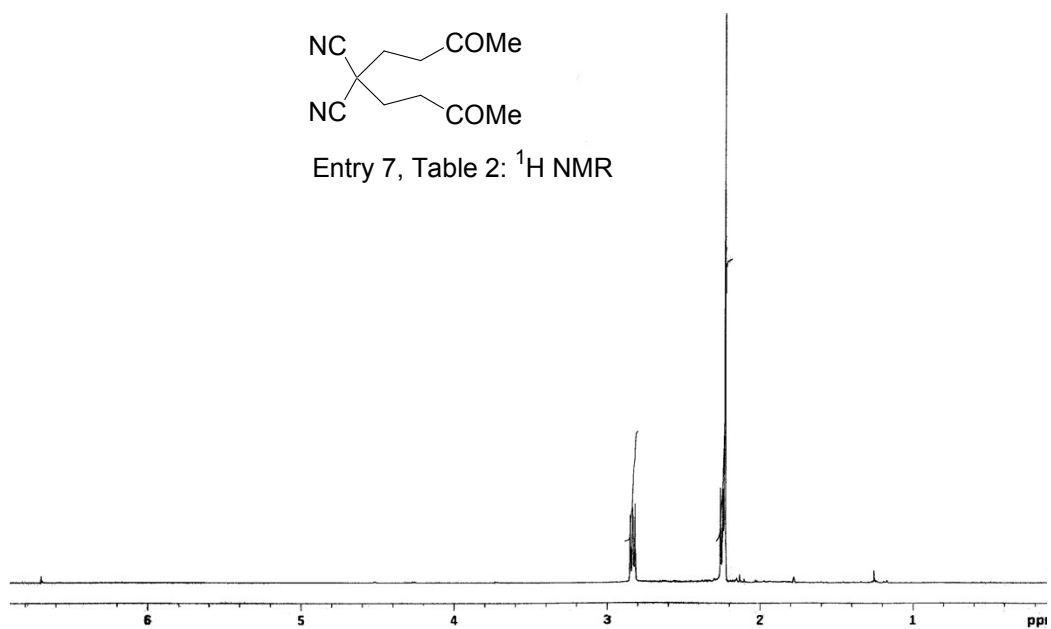
Entry 6, Table 2: ¹H NMR



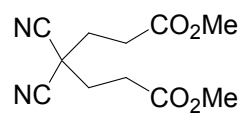
Supporting Information 13



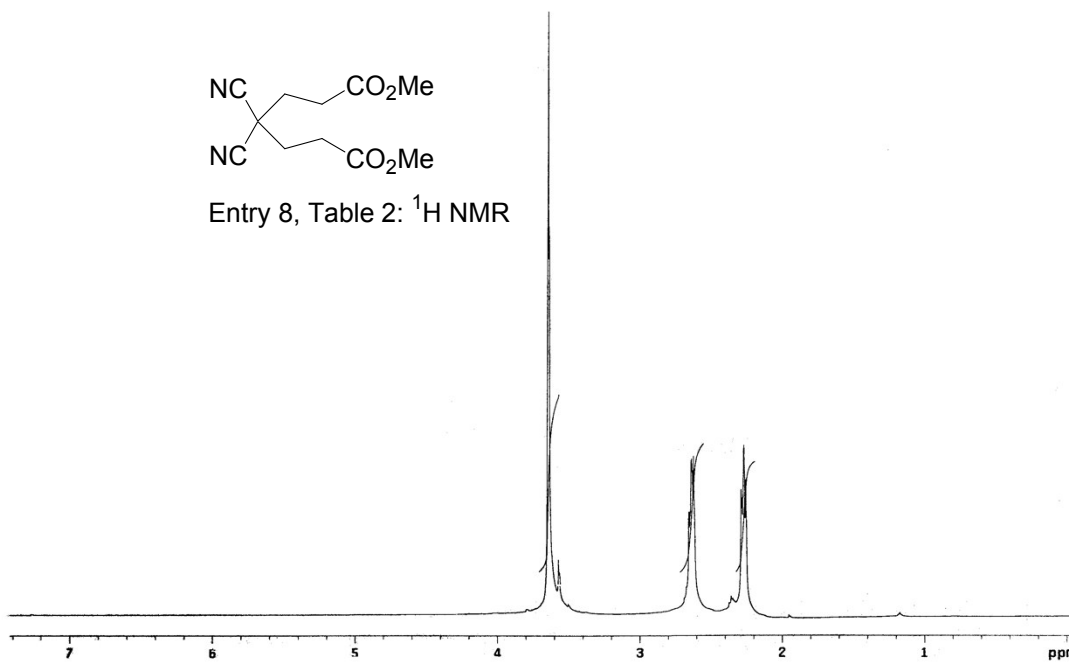
Entry 7, Table 2: ^1H NMR



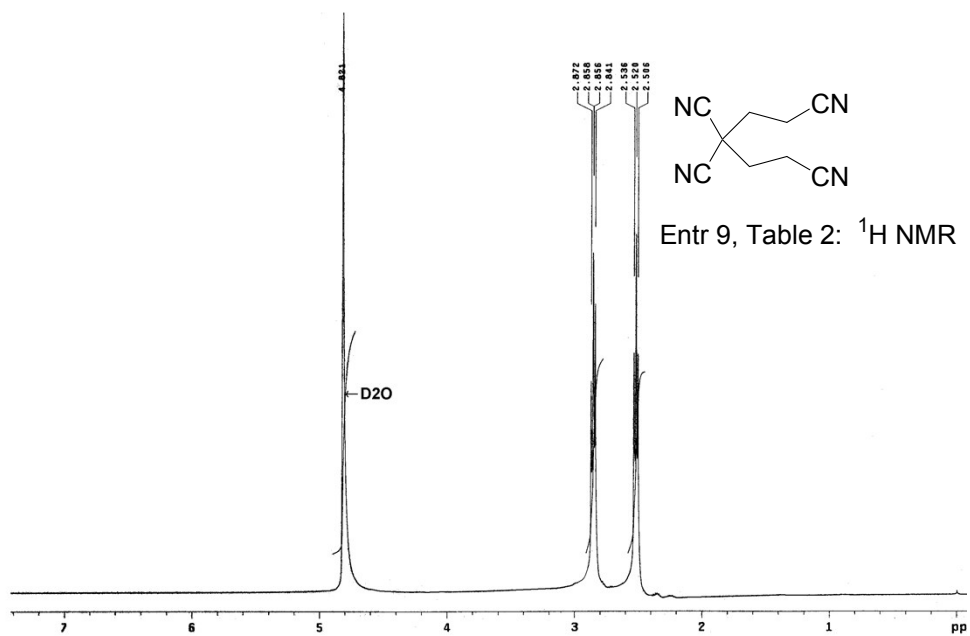
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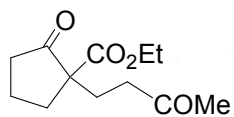
Entry 8, Table 2: ¹H NMR



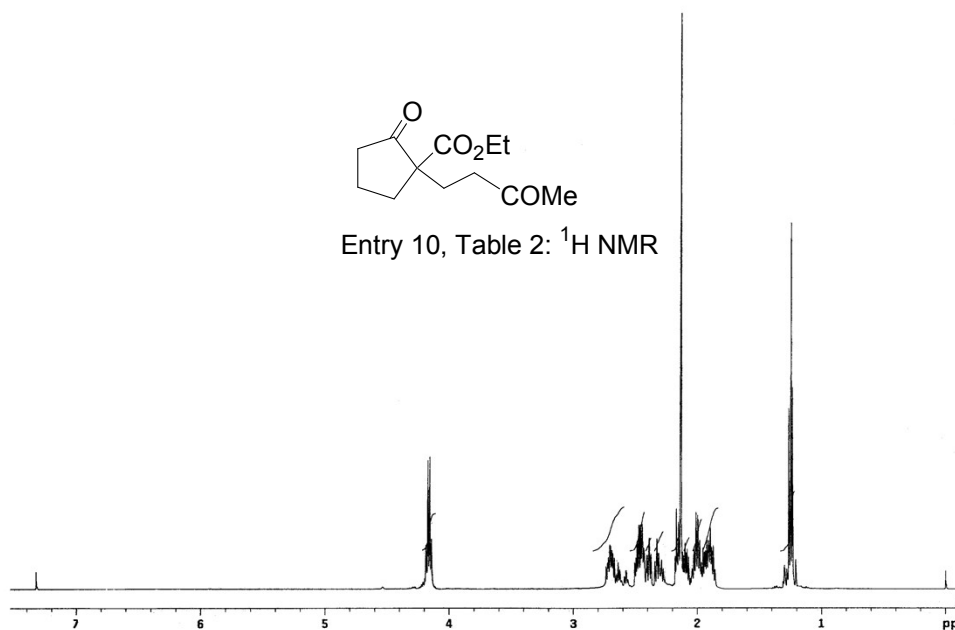
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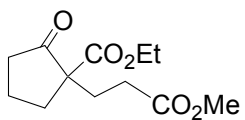
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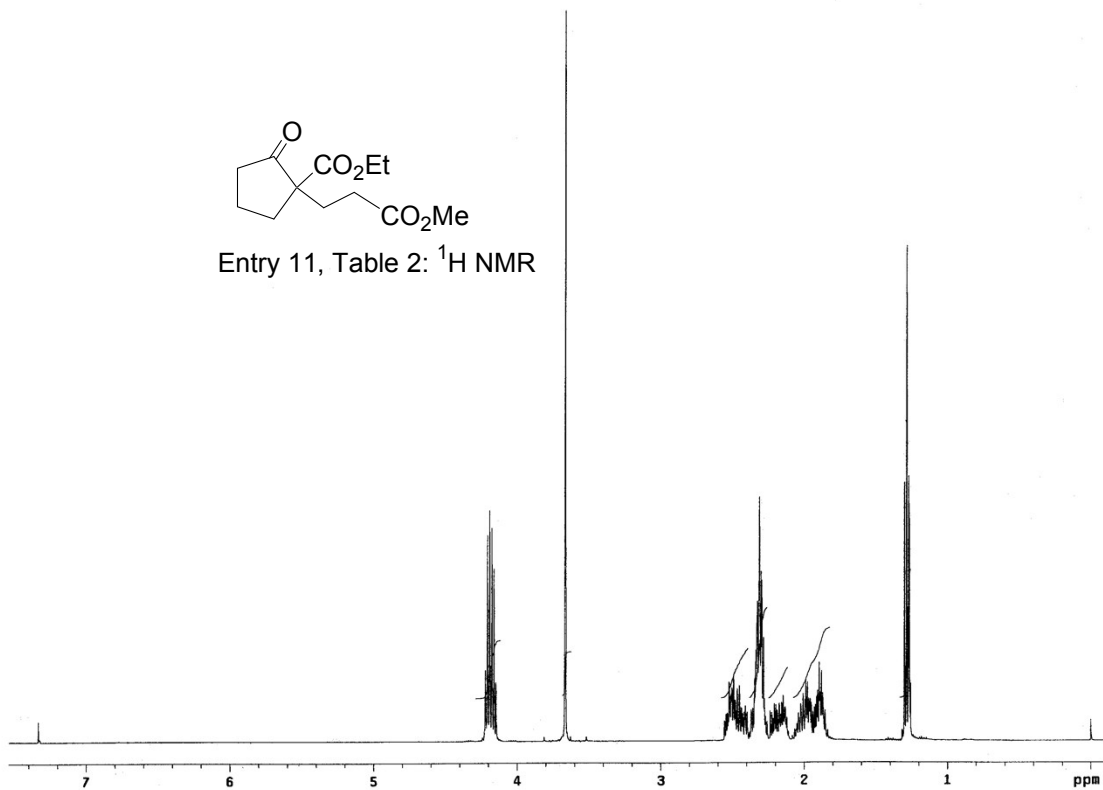
Entry 10, Table 2: ^1H NMR



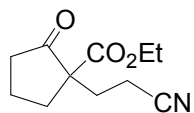
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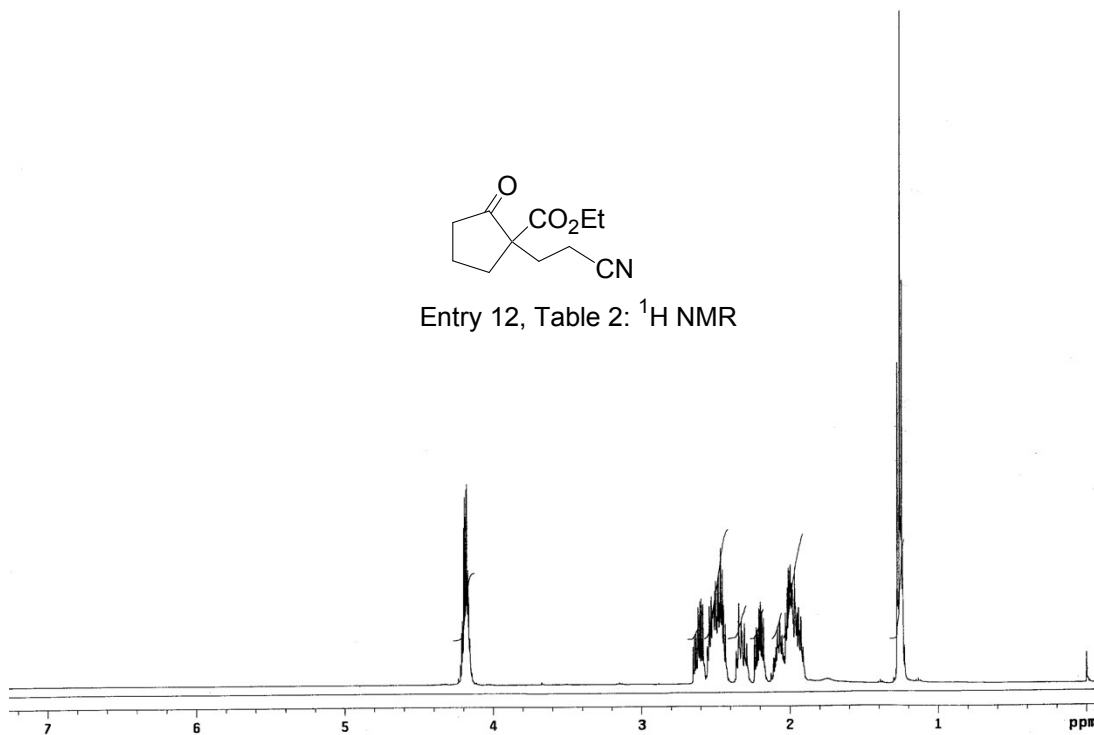
Entry 11, Table 2: ¹H NMR



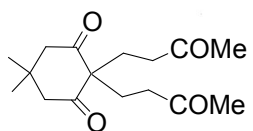
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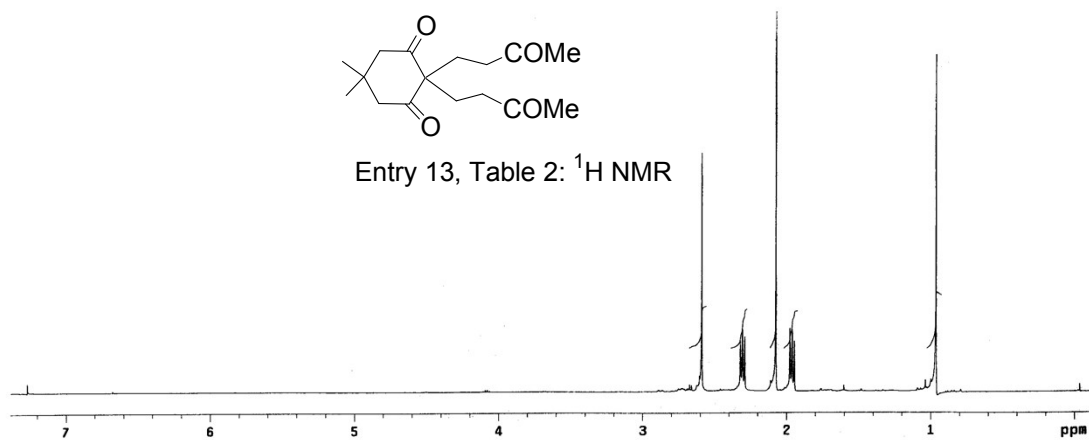
Entry 12, Table 2: ¹H NMR



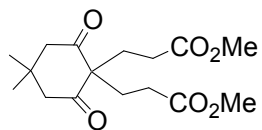
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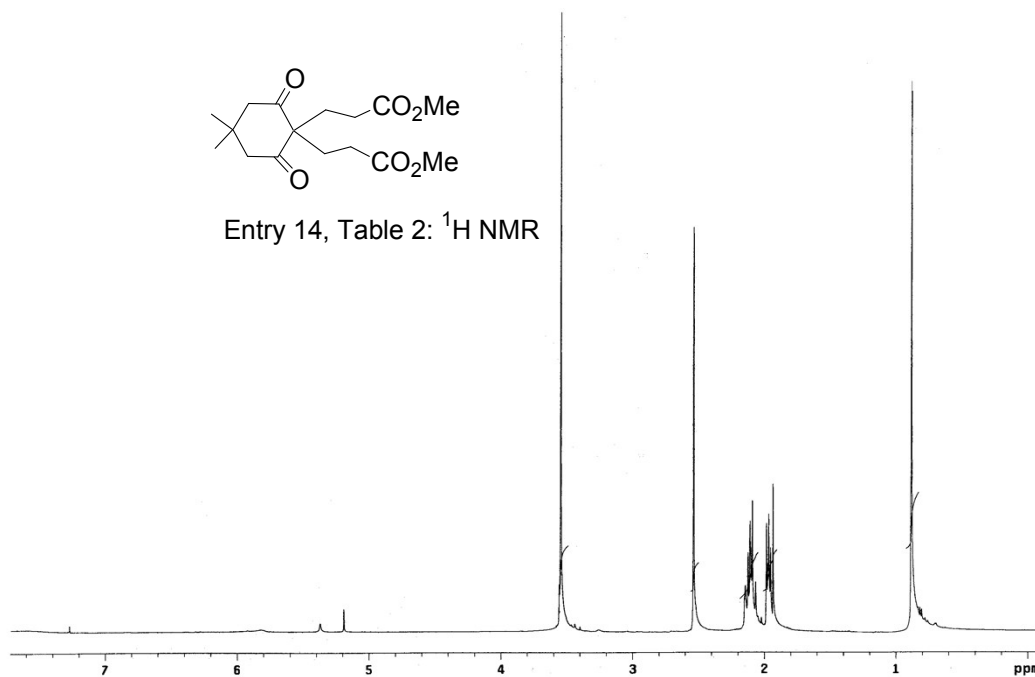
Entry 13, Table 2: ¹H NMR



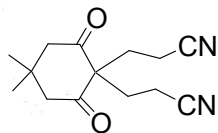
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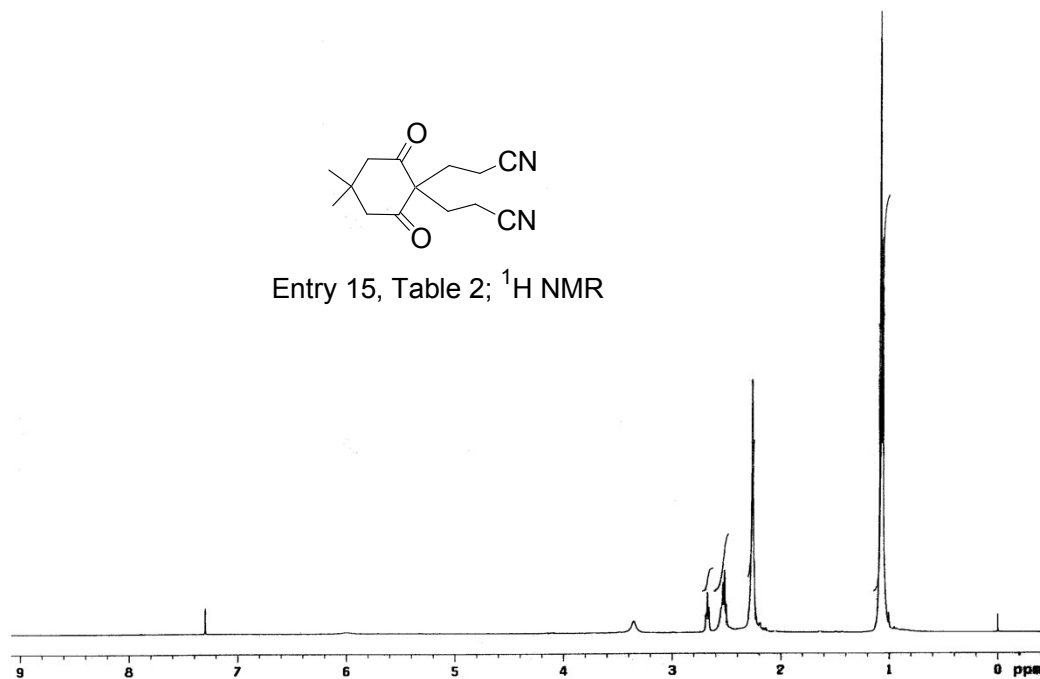
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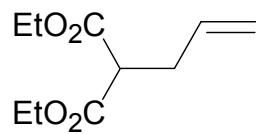
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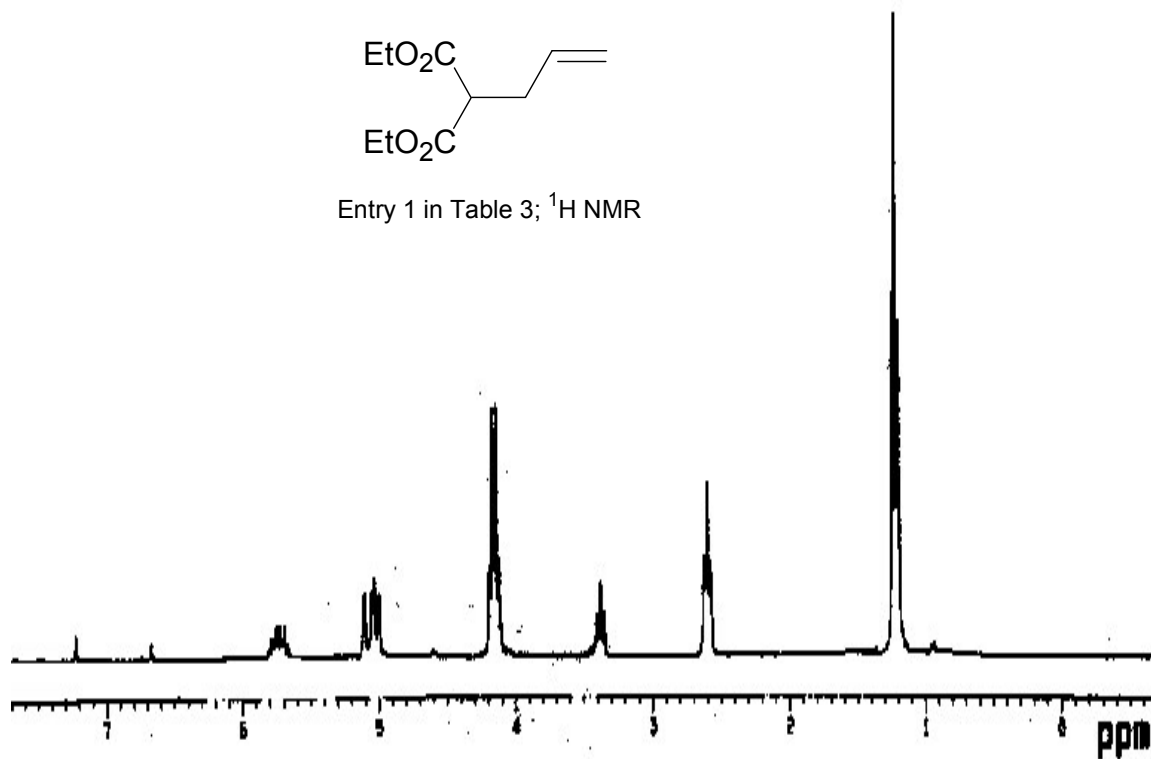
Entry 15, Table 2; ^1H NMR



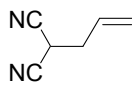
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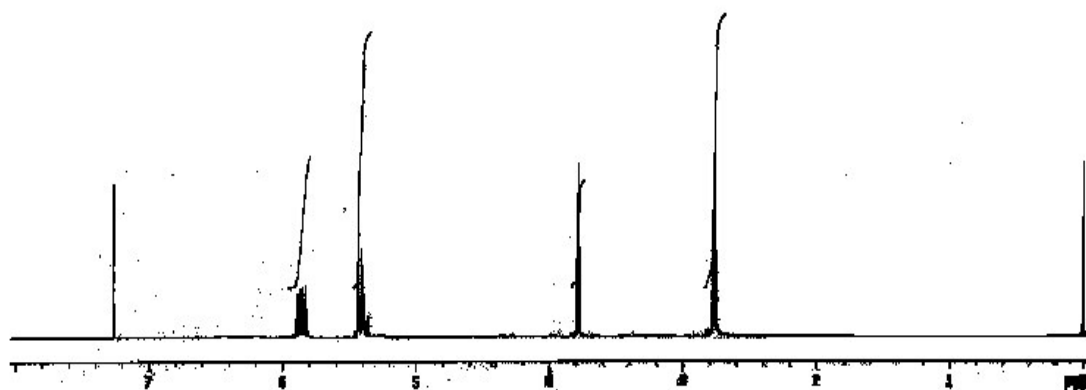
Entry 1 in Table 3; ¹H NMR



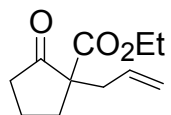
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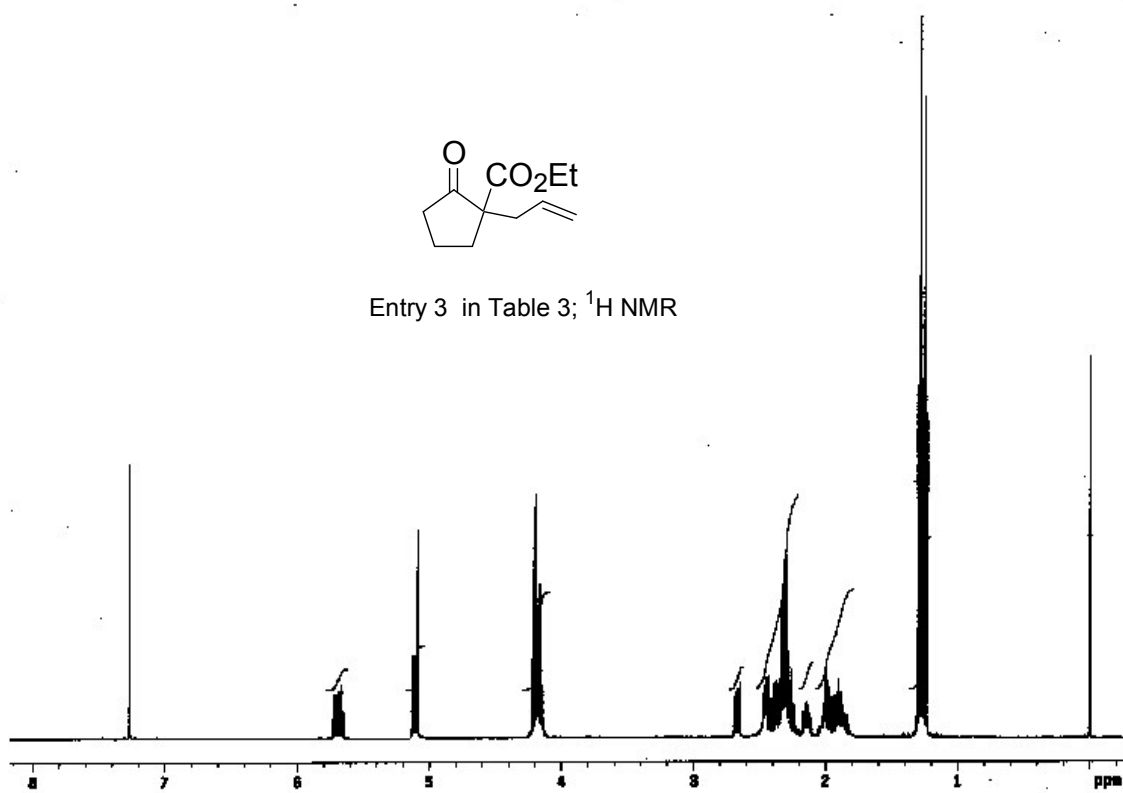
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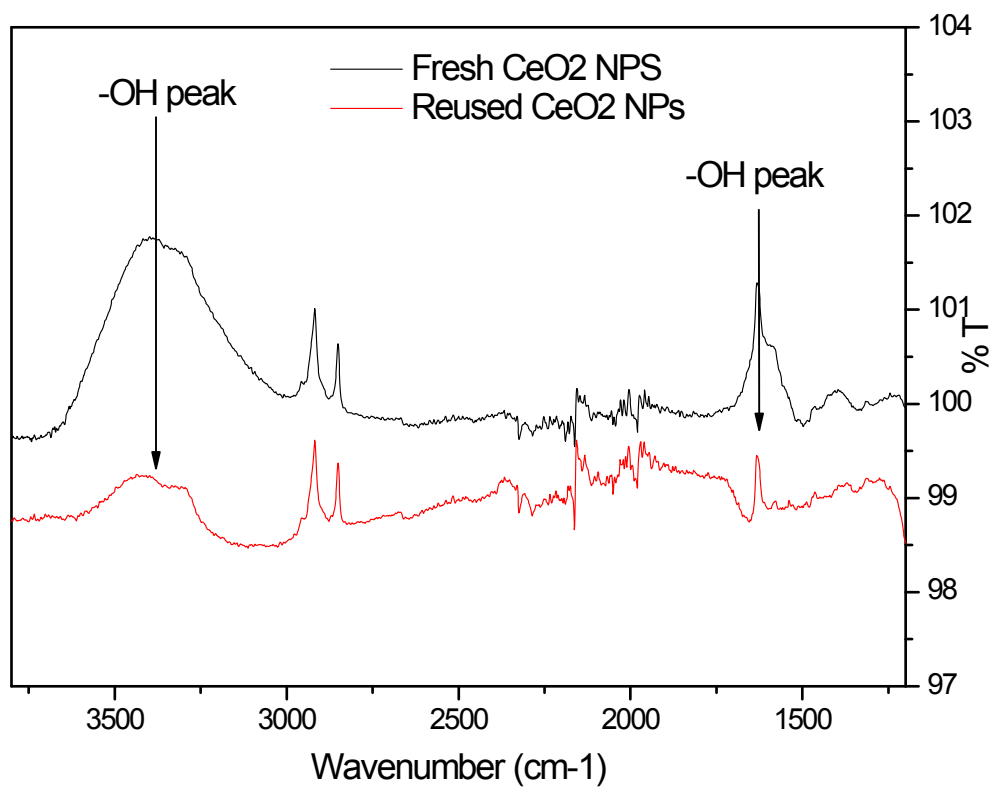


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Entry 3 in Table 3; ¹H NMR



FT-IR spectra of fresh and reused CeO₂ NPs

References:

1. S. Banerjee and S. Santra, *Tetrahedron Lett.*, 2009, **50**, 2037.
2. B. C. Ranu, K. C. Chattopadhyay and L. Adak, *Org. Lett.*, 2007, **9**, 4595.