

Supplementary Information (SI) for:

Graphene oxide as a recyclable phase transfer catalyst

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1. General

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References

1. General

All chemicals used in this study were obtained from commercial sources and used without further purification. The organocatalysts examined in this study were prepared according to the literature procedure. The chromatographic purification of the products was conducted by flash chromatography using Merck silica gel 60 (230–400 mesh). Thin-layer chromatography was conducted on Merck silica gel 60F plates.

1.1 Materials

Natural graphite (Bay Carbon, SP-1 graphite), sulphuric acid (95-97%), hydrogen peroxide (30 wt.%), potassium permanganate, sodium nitrate, potassium hydroxide, sodium hydroxide, and cesium hydroxide were obtained from commercial sources and used as received.

2. General Procedure for GO preparation

GO was prepared from natural graphite powder by the modified Hummers and Offenman's method using sulfuric acid, potassium permanganate, and sodium nitrate.¹

2.1 Characterization

Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). X-ray photoemission spectroscopy (XPS) measurements were made by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-K α X-ray source at 100 W.

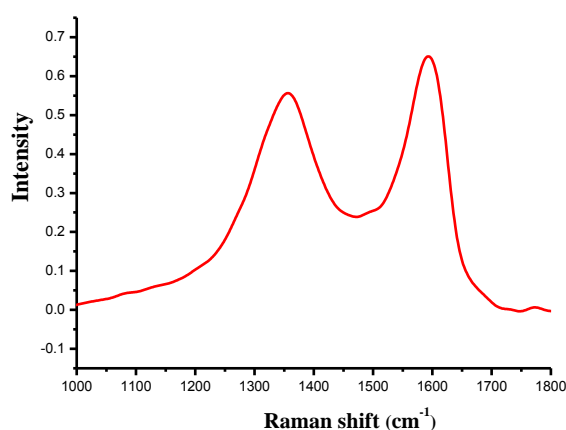


Figure S1. Raman spectra of GO.

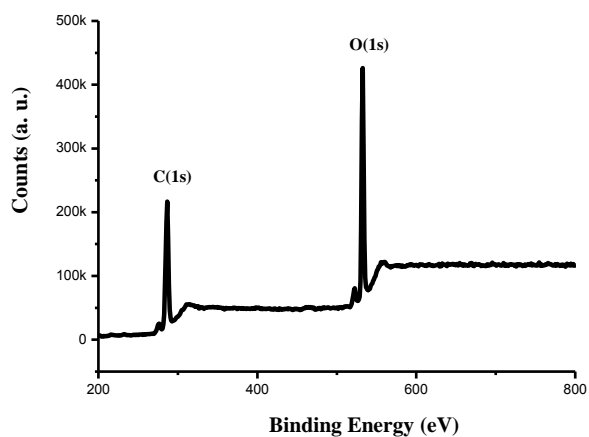


Figure S2. XPS of GO.

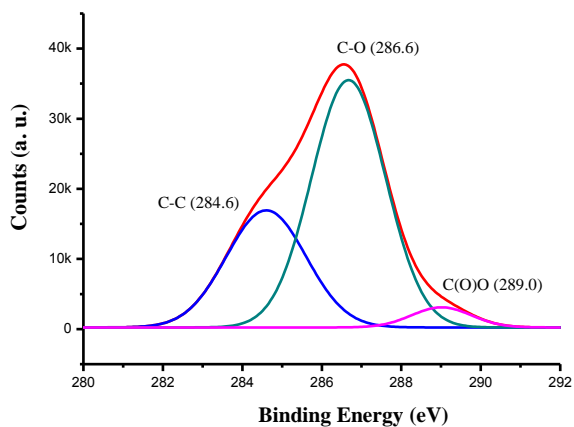


Figure S3. High-resolution C1s spectra of GO.

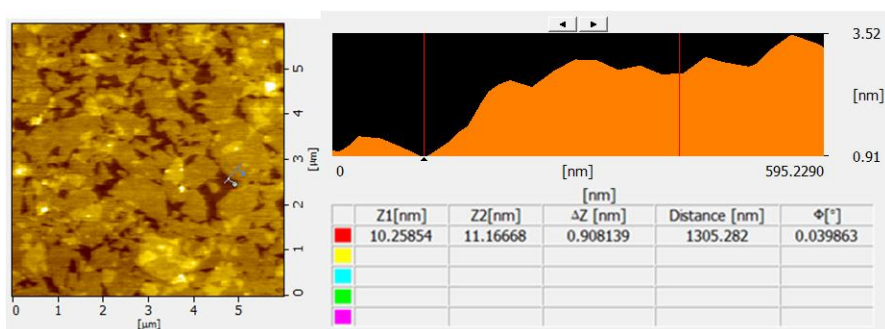


Figure S4. AFM image of GO.

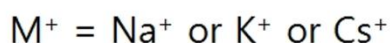
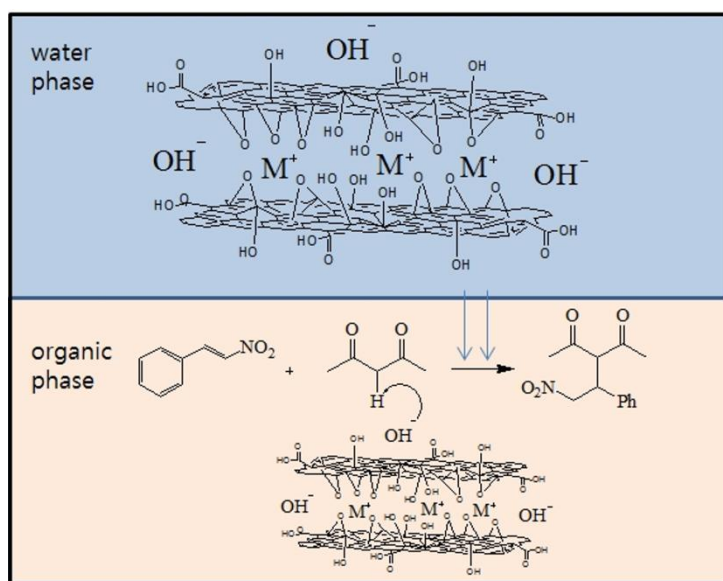


Figure S5. GO Phase-transfer catalyst in the Michael addition reaction.

Table S1 Recycling of graphene oxide as a Michael addition catalyst^a

Cycle	Yield [%]	Cycle	Yield [%]	Cycle	Yield [%]
1	83	4	82	7	77
2	81	5	80	8	78
3	80	6	79	9	76

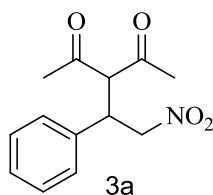
^a All cycles were carried out with **1a** (25 mg, 0.1676 mmol), **2** (1.5 equiv.), KOH (1.1 equiv.), and 0.5 mg ml⁻¹ GO aqueous (0.5 ml) in MC (1 ml).

3. General procedure for the Michael Addition

Graphene oxide was dispersed in DI water to make concentration of 0.5 mg/ml and potassium hydroxide (10.3 mg, 1.1 equiv.) as a base was added to 0.5 ml of this solution. And then was added to mixture of MC solution which included reactants, trans-β-nitrostyrene (**1a**, 25 mg, 0.1676 mmol, 1 equiv.), and 2,4-pentanedione (**2**, 0.03ml, 1.5 equiv.) in a 5 ml vial. The reaction mixture was vigorously stirred by using one magnetic bar at a stirring speed of 900 rpm at room temperature. After completion of the reaction, which was monitored by TLC, an

aqueous HCl solution (1 N, 1 mL) was added to quench the reaction and then extracted with CH₂Cl₂ (3 x 5 mL). The combined organic phase was washed with water and dried over anhydrous Na₂SO₄, and the solvent was concentrated. The obtained crude product was purified by column chromatography on silica gel to afford the Michael addition product **3a**. After the reaction was over the used GO was recovered by simple filtration and washing with MC using nylon membrane filter, 0.45µm pore size. The residual part was then dried by vacuum desiccator for several hours in order to recover GO.

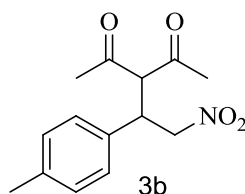
4. Product Characterization



Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3a** as a white solid (83% yield). Analytical data was matched with previously reported values.

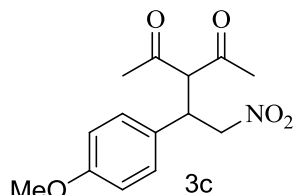
¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.26-7.19 (m, 3H), 7.12-7.10 (m, 2H), 4.58-4.55 (m, 2H), 4.30 (d, 1H, *J* = 10.5 Hz), 4.21-4.17 (m, 1H), 2.23 (s, 3H), 1.87 (s, 3H); HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0. mL/min, 220 nm): *t*_{major} = 10.5 min, *t*_{minor} = 14.1 min; ~7% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*R*) by comparison of the retention time of HPLC with the literature data.²



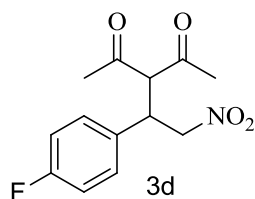
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3b** as a white solid (80% yield). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.20-6.97(m 4H), 4.54-4.52 (m, 2H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.17-4.11 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H)²



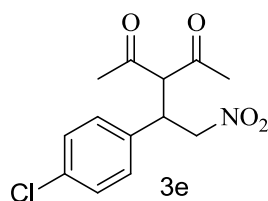
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3c** as a white solid (77% yield). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.03 (d, *J* = 8.7 Hz, 3H), 6.76 (d, *3J* = 8.7 Hz, 2H), 4.53-4.51 (m, 2H), 4.23 (d, *J* = 11.1 Hz, 1H), 4.16-4.08 (m, 1H), 3.69 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H)²



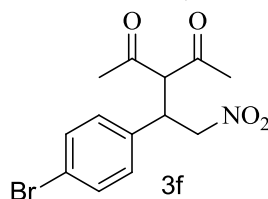
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3d** as a white solid (69% yield). Analytical data was matched with previously reported values.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , Me_4Si): δ 7.13 - 7.09 (m, 2H), 6.97-6.91 (m, 2H), 4.58-4.49 (m, 2H), 4.27 (d, $J = 10.8$, 1H), 4.21- 4.13 (m, 1H), 2.20 (s, 3H), 1.89 (s, 3H)²



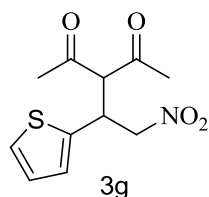
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3e** as a white solid (79% yield). Analytical data was matched with previously reported values.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , Me_4Si): δ 7.23 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.55 (d, $J = 6.3$ Hz, 2H), 4.14 (d, $J = 10.5$ Hz, 1H), 4.20-4.12 (m, 1H), 2.20 (s, 3H), 1.90 (s, 3H)²



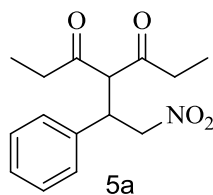
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3f** as a white solid (75% yield). Analytical data was matched with previously reported values.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , Me_4Si): δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 4.62 (d, $J = 6.3$ Hz, 2H), 4.25 (d, $J = 6.0$ Hz, 1H), 4.26-4.18 (m, 1H), 2.29 (s, 3H), 1.98 (s, 3H)²



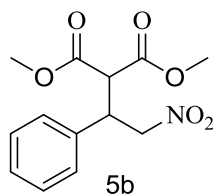
Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **3g** as a white solid (78% yield). Analytical data was matched with previously reported values.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , Me_4Si): δ 7.28-7.23 (m, 1H), 6.93-6.89 (m, 2H), 4.68-4.66 (m, 2H), 4.58-4.51 (m, 1H), 4.40 (d, $J = 9.9$ Hz, 1H), 2.29 (s, 3H), 2.07(s, 3H)²



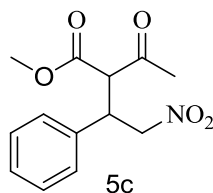
Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded **5a** as a white solid (80% yield). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.32-7.27 (m, 3H), 7.18-7.15 (m, 2H), 4.71-4.60 (m, 2H), 4.35-4.23 (m, 2H), 2.65-2.44 (m, 2H), 2.38-2.25 (m, 1H), 2.20-2.04 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H)²



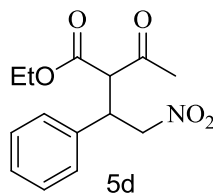
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5b** as a white solid (50% yield). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.33-7.21 (m, 5H), 4.96-4.83 (m, 2H), 4.24 (td, *J* = 8.8, 5.7 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H)²



Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5c** as a white solid (79% yield, 1 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

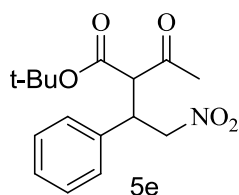
¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.33-7.25 (m, 3H), 7.21-7.18 (m, 2H), 4.83-4.81 (m, 1 H), 4.78-4.76 (m, 1 H), 4.29-4.17 (m, 1 H), 4.12 (d, *J* = 9.6 Hz, 0.5 H), 4.03 (d, *J* = 9.6 Hz, 0.5 H), 3.77-3.53 (s, 3H), 2.29-2.05 (s, 3H); dr = 1 : 1 (determined by integration of ¹H NMR)²



Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded **5d** as a white solid. Analytical data was matched with previously reported values (80% yield, 1.5:1 mixture of diastereomers).

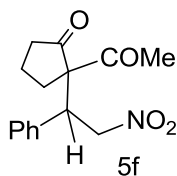
¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.32-7.27 (m, 3H), 7.22-7.19 (m, 2H), 4.89-4.76 (m, 2H), 4.26-4.18 (m, 2 H), 4.12 (d, *J* = 9.9 Hz, 0.6H) 4.03 (d, 0.4 H, *J* = 9.9 Hz), 3.96 (q, 1H, *J* = 7.2 Hz), 2.30-2.05 (s, 3H), 1.28-1.00 (t, *J* = 7.2 Hz, 4H); dr = 1.5 : 1 (determined by integration of ¹H

NMR)²



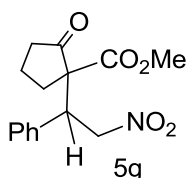
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5e** as a white solid (83% yield, 4.9 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.34-7.29 (m, 3H), 7.25-7.20 (m, 2H), 4.85-4.82 (m, 0.4H), 4.77-4.65 (m, 2H), 4.23-4.10 (m, 1H), 4.03 (d, J = 10.2 Hz, 0.83H), 3.92 (d, J = 10.2 Hz, 0.17H), 2.30-2.06 (s, 3H), 1.47 - 1.11 (s, 9H)²



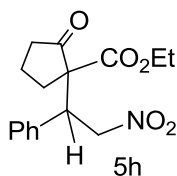
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5f** as a white solid (66% yield, 7.3 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.24-7.34(m, 5H), 5.01(dd, J = 11.1, 13.2 Hz, 0.12H) 4.86(dd, J = 11.4 Hz and J = 13.5 Hz, 0.88H), 4.60-4.51 (dd, J = 3.9 Hz and 13.2 Hz, 1H), 4.39-4.28 (dd, J = 3.9 and J = 11.1 Hz, 1H), 2.61-2.54 (m, 1H), 2.33 (s, 3H), 2.26-2.14(m, 1H), 2.03-1.93 (m, 1H), 1.80-1.65 (m, 3H); dr = 7.3 : 1 (determined by integration of ¹H NMR)²



Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **5g** as a colorless oil (82% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

¹H NMR (300 MHz, CDCl₃, Me₄Si): δ 7.31-7.23 (m, 5H), 5.17 (dd, J = 4.2 and 13.5 Hz, 1H), 5.01(dd, J = 10.8 Hz and J = 13.5Hz, 1H), 4.08 (dd, J = 3.9 Hz and 10.8 Hz, 1H), 3.75 (s, 3H), 2.40-2.32 (m, 2H), 2.05-1.82 (m, 4H) ; dr >99 : 1 (determined by integration of ¹H NMR)²

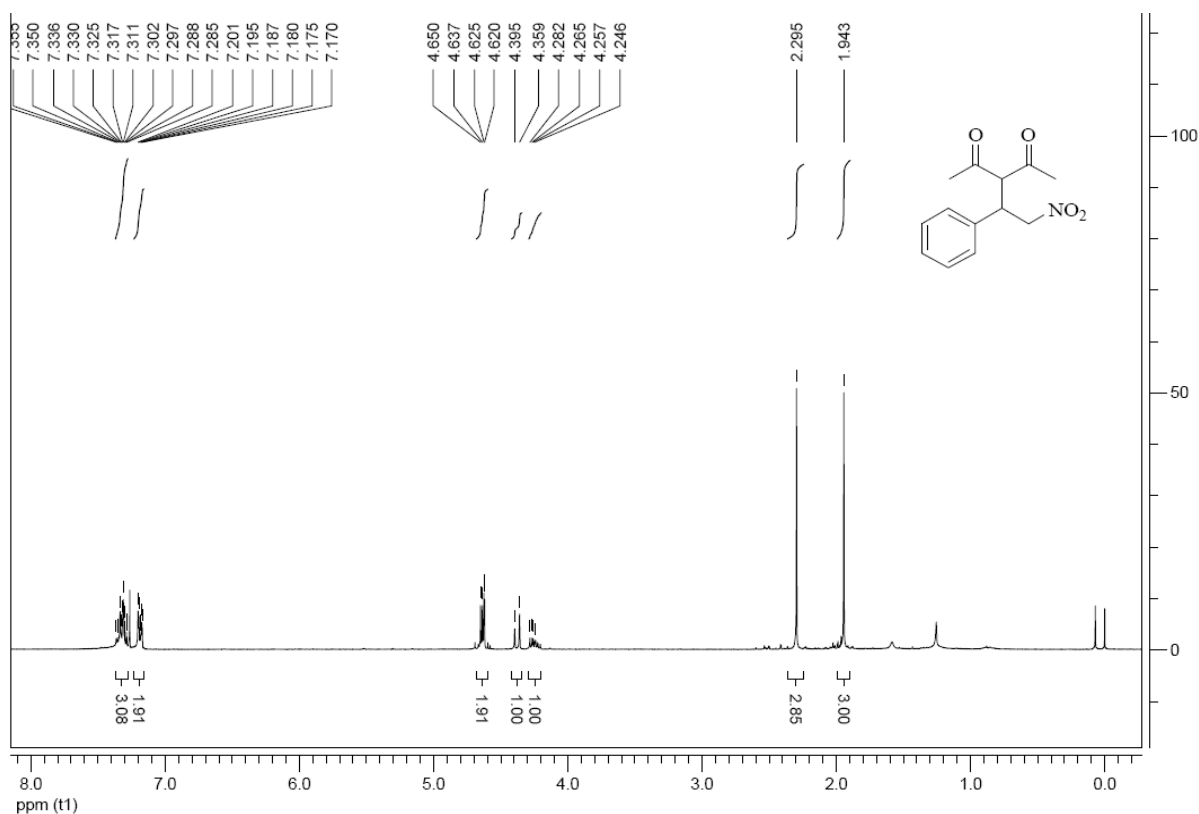


Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **5h** as a colorless oil (81% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

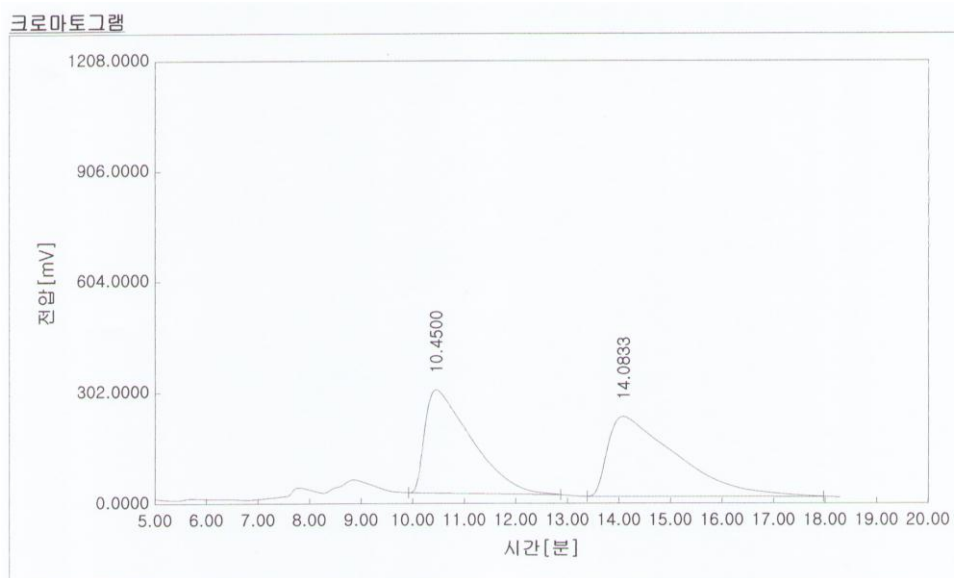
$^1\text{H NMR}$ (300 MHz, CDCl_3 , Me_4Si): δ 7.34-7.27 (m, 5H), 5.18 (dd, $J = 3.9$ and 13.6 Hz, 1H), 5.01 (dd, $J = 10.9$ and 13.5 Hz, 1H), 4.24-4.17 (m, 1H), 4.08 (dd, $J = 3.9$ and 10.9 Hz, 1H), 2.40-2.32 (m, 2H), 2.07-1.74 (m, 4H), 1.27 (t, $J = 7.1$ Hz, 1H); dr >99 : 1 (determined by integration of $^1\text{H NMR}$)²

5. $^1\text{H NMR}$ Spectra for Table 2

3a (Entry 1, Table 3)



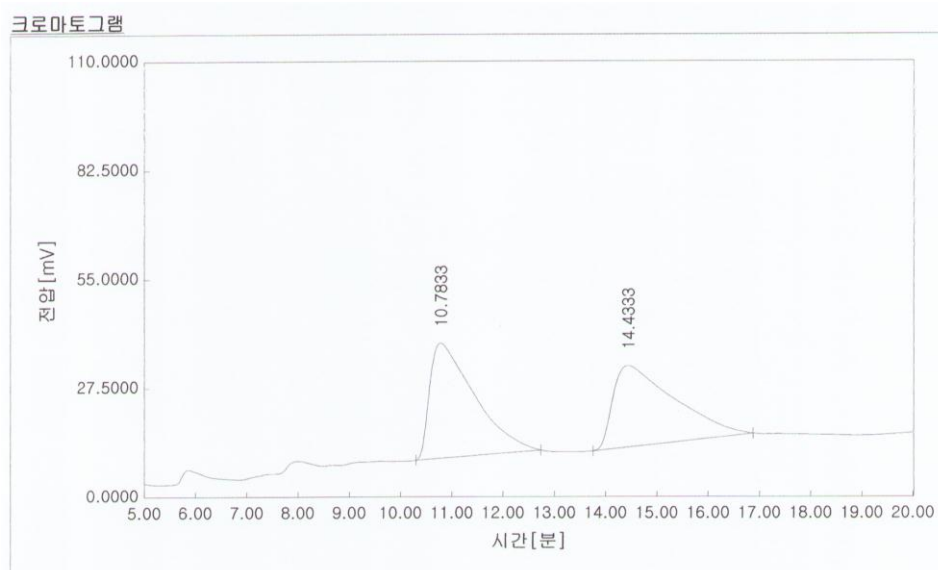
(a) Product by GO PTC



분석 결과

번호	RT[분]	면적[mAbs*s]	형태	폭[초]	면적%
1	10.4500	17680.5190	FF	177.0000	46.6870
2	14.0833	20189.7792	BB	275.0000	53.3130
합계		37870.2981			

(b) Product by CE and only base

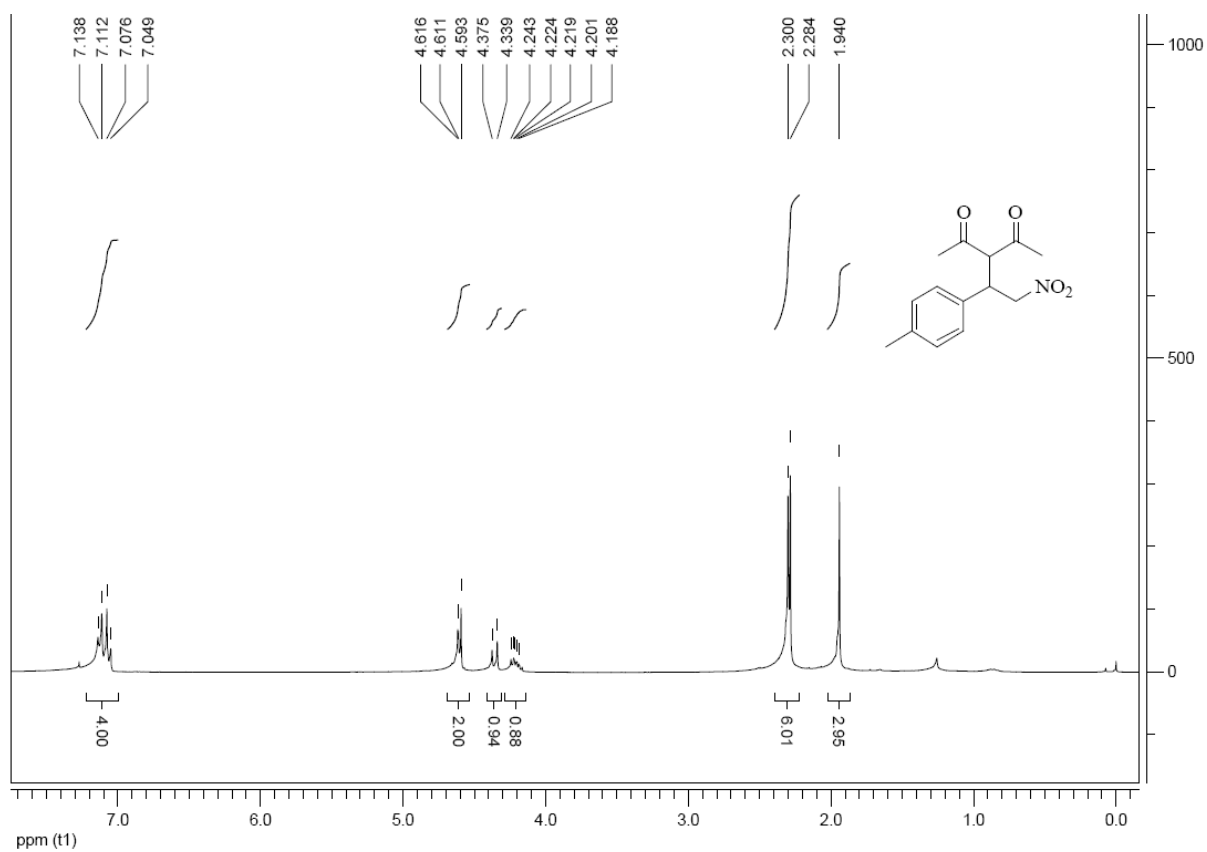


분석 결과

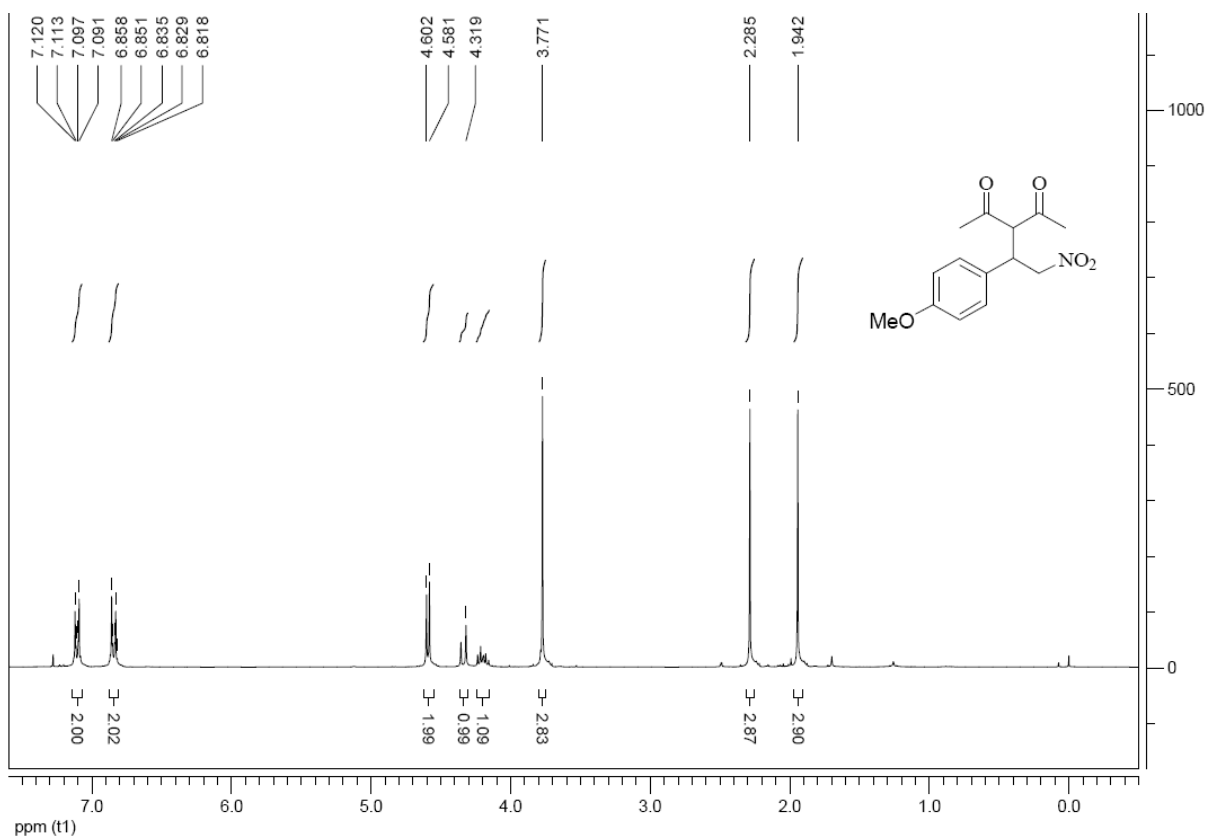
번호	RT[분]	면적[mAbs*s]	형태	폭[초]	면적%
1	10.7833	1754.6759	FF	146.0000	50.9374
2	14.4333	1690.0953	FF	187.0000	49.0626
합계		3444.7712			

(a) Enantiomeric selective property of **3a** product with the GO PTC and it showed ~7% enantiomeric excess. (b) The CE PTC product and only base treated product were racemic in comparison to GO PTC product. The 2D template structure of GO helps to get an enantiomerically selective product even though the ee value is not high. Now our current work is focused on improving the yield and enantiomeric selectivity of GO PTC product.

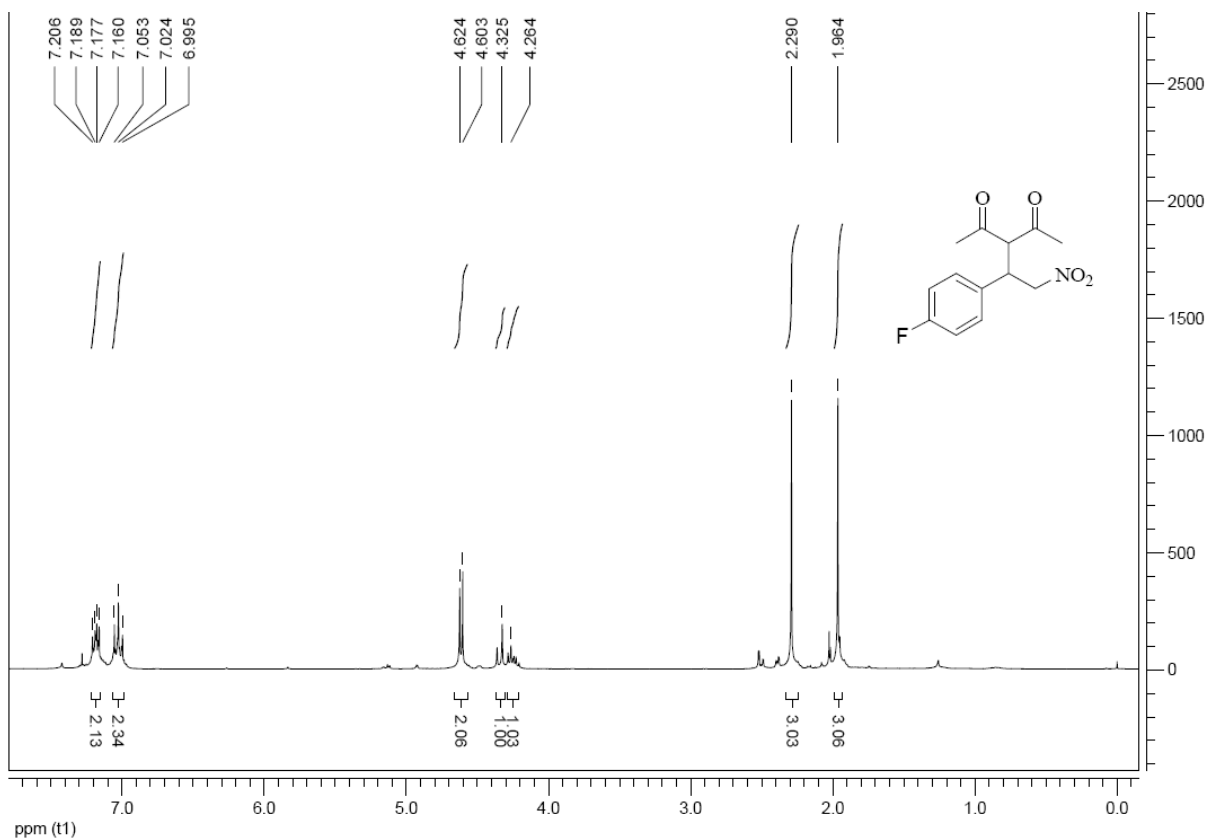
3b (Entry 2, Table 3)



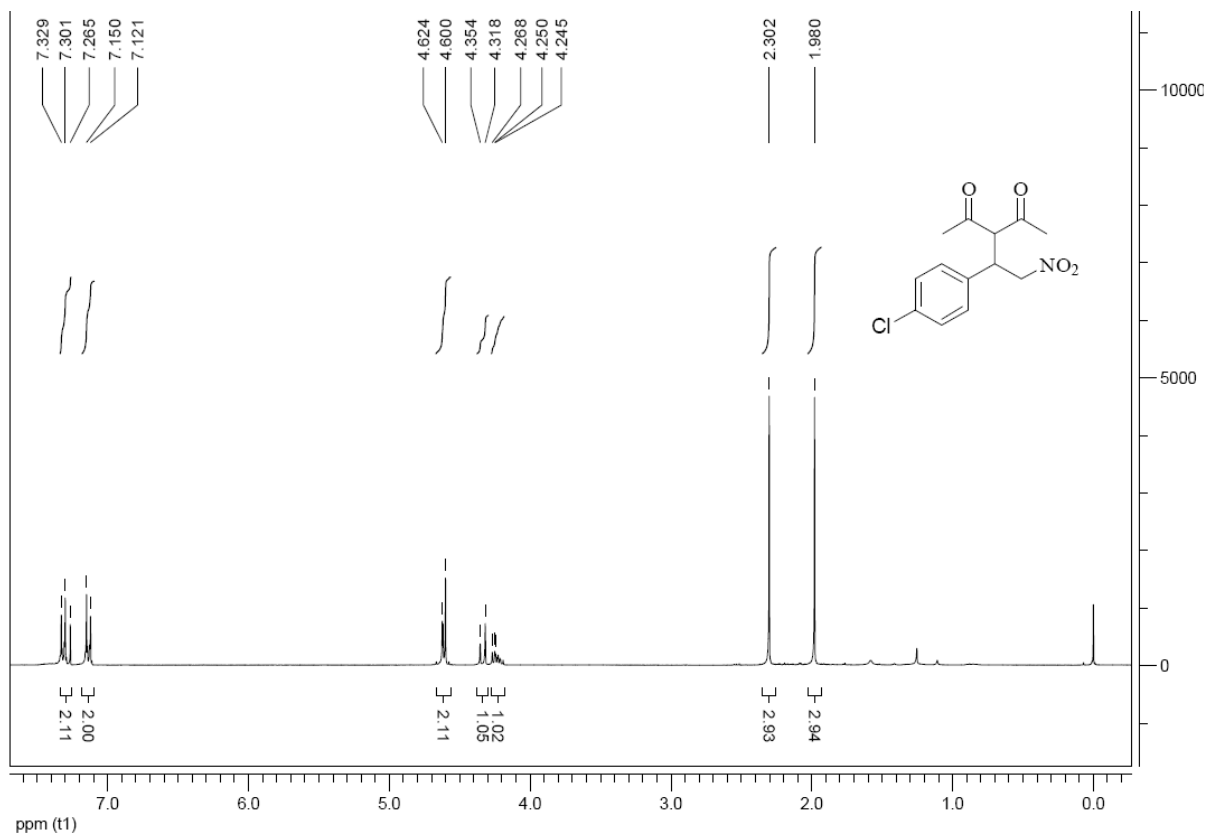
3c (Entry 3, Table 3)



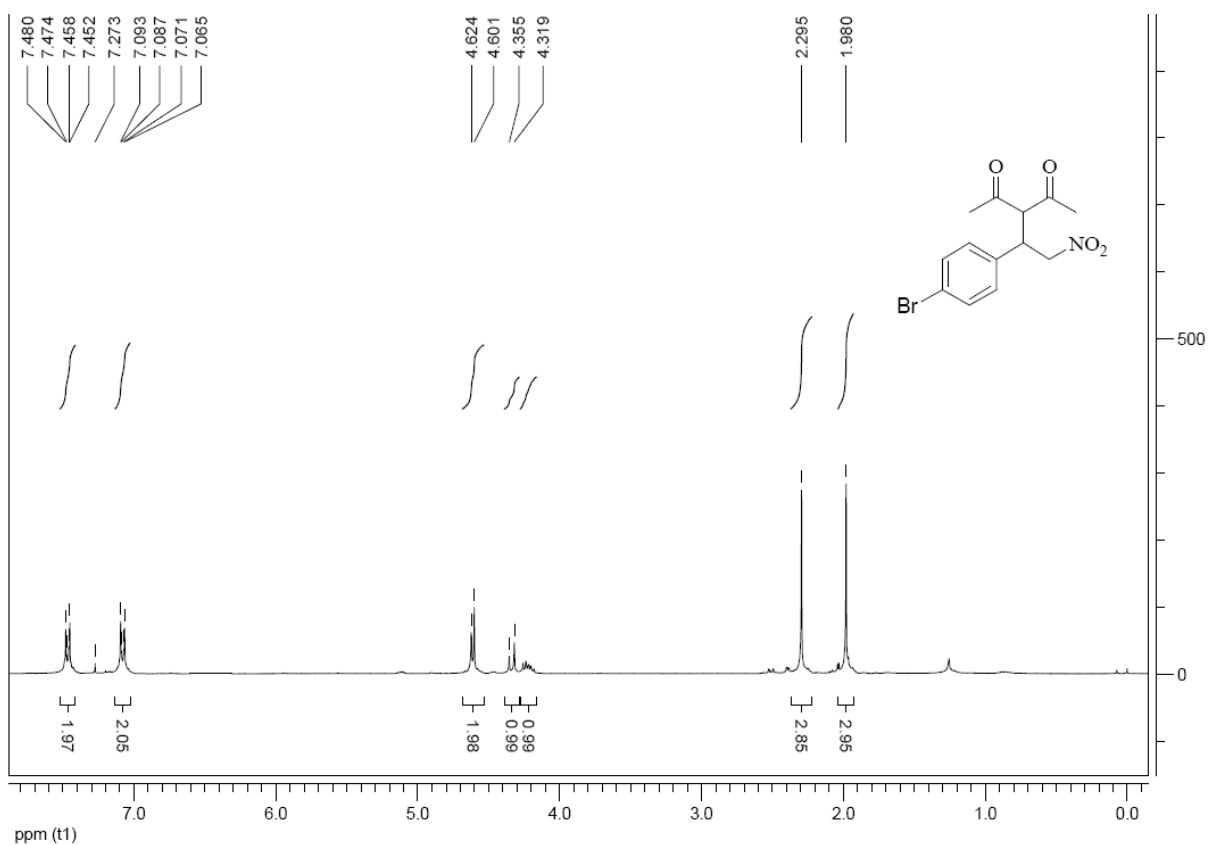
3d (Entry 4, Table 3)



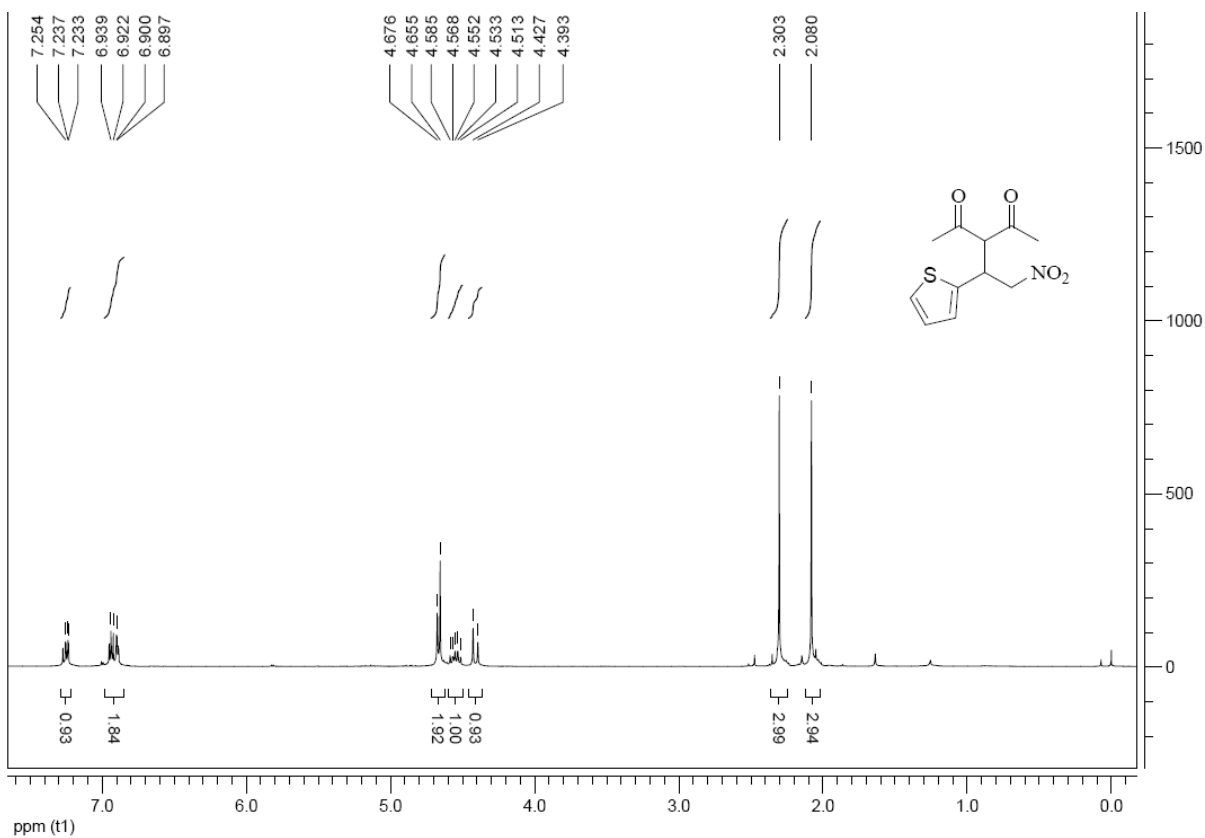
3e (Entry 5, Table 3)



3f (Entry 6, Table 3)

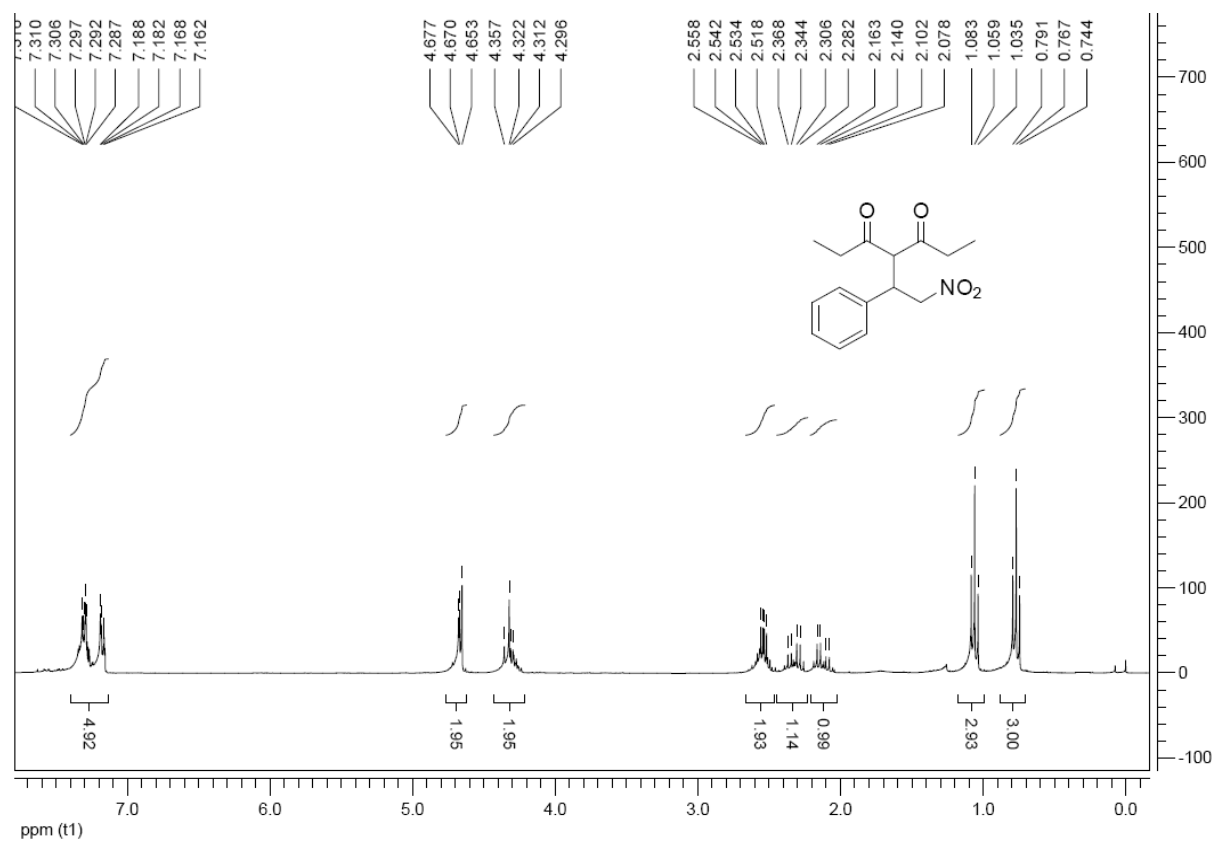


3g (Entry 7, Table 3)

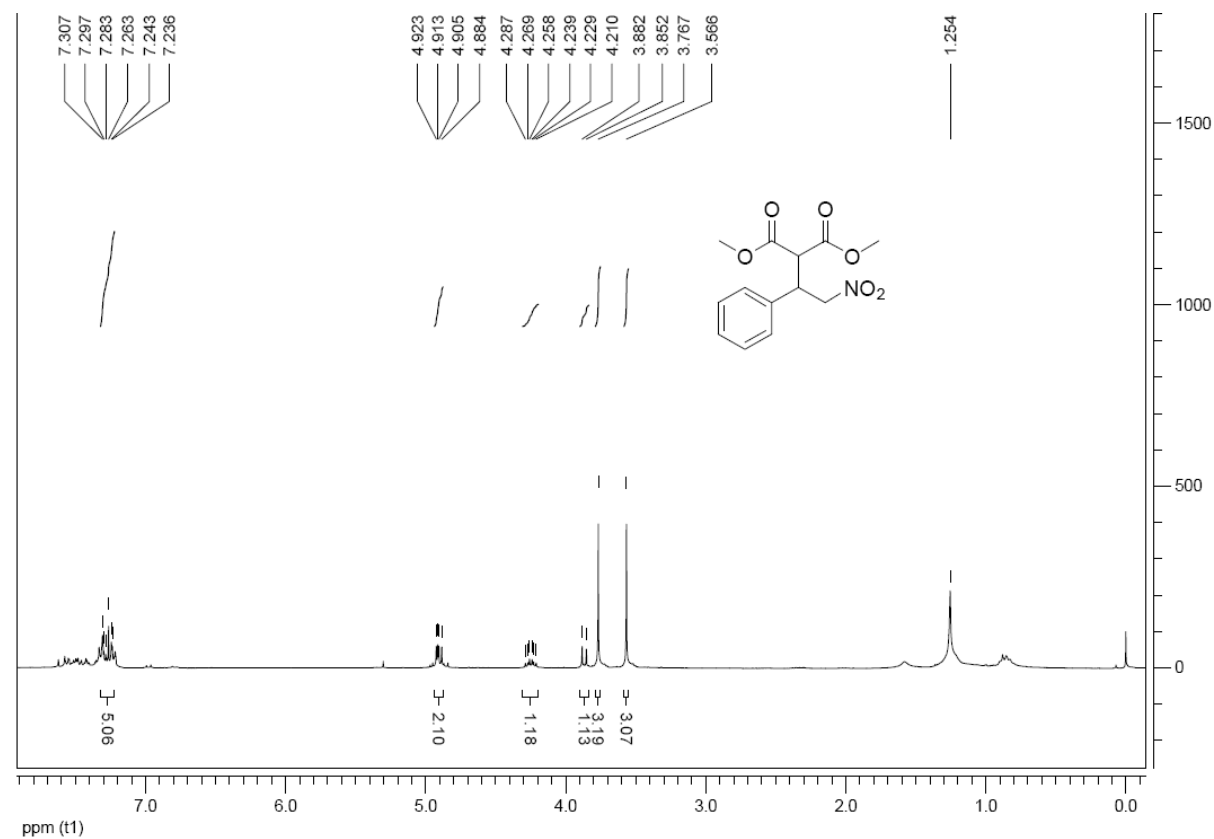


6. ¹H NMR Spectra for Table 4

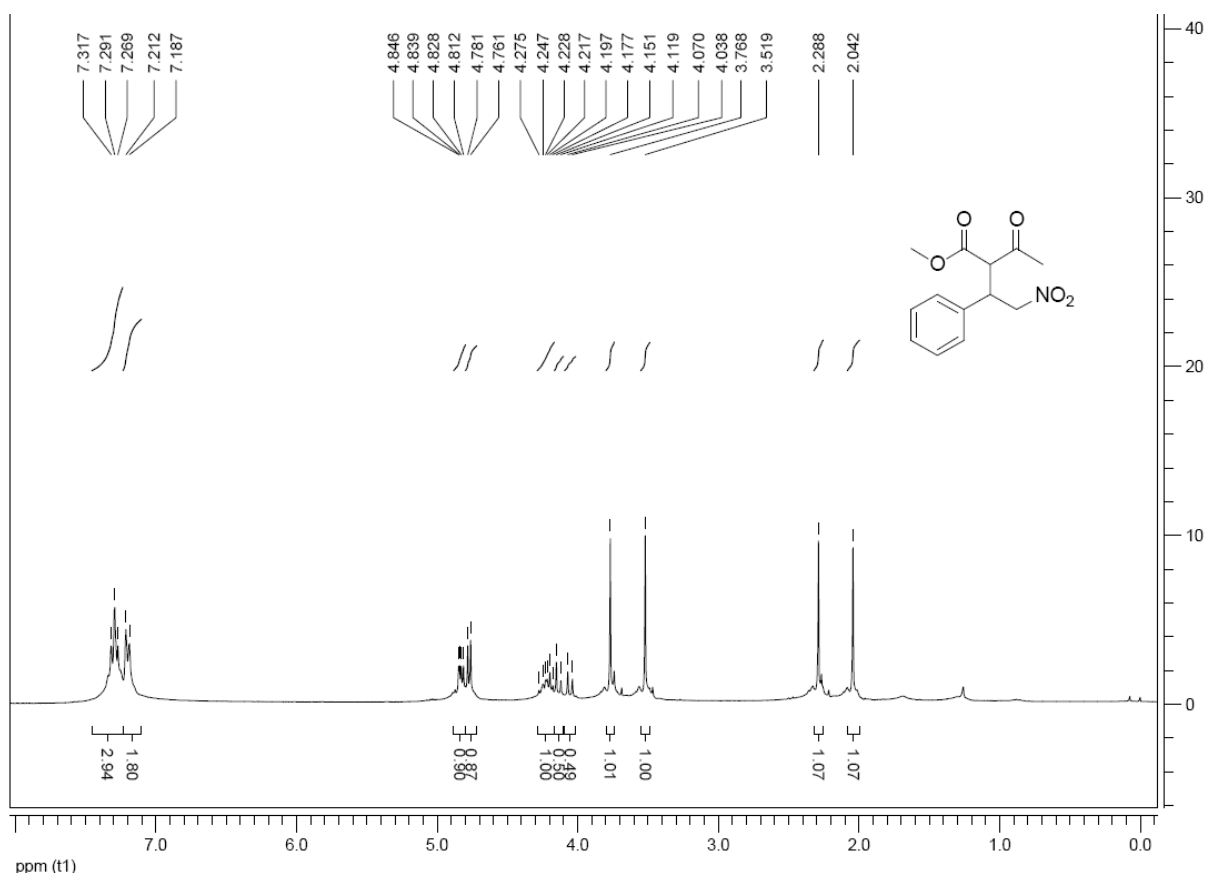
5a (Entry 1, Table 4)



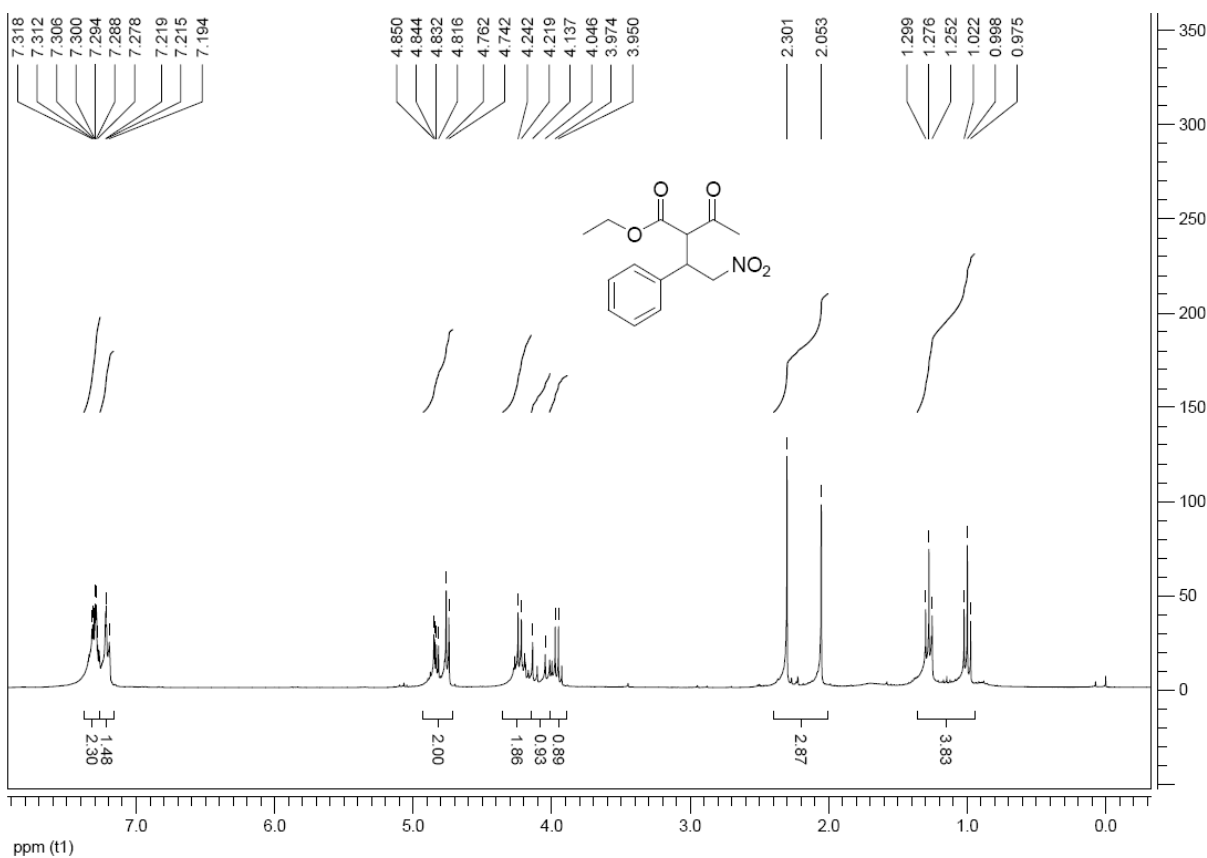
5b (Entry 2, Table 4)



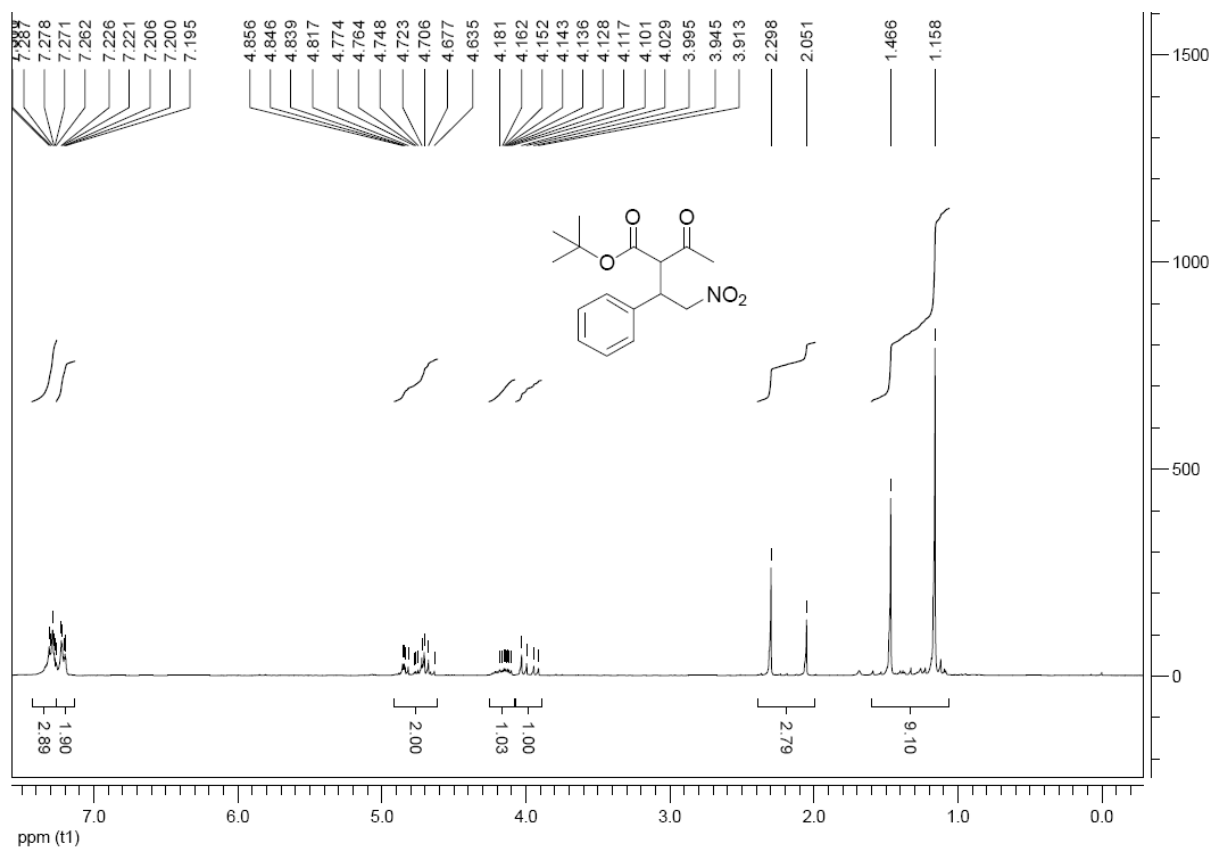
5c (Entry 3, Table 4)



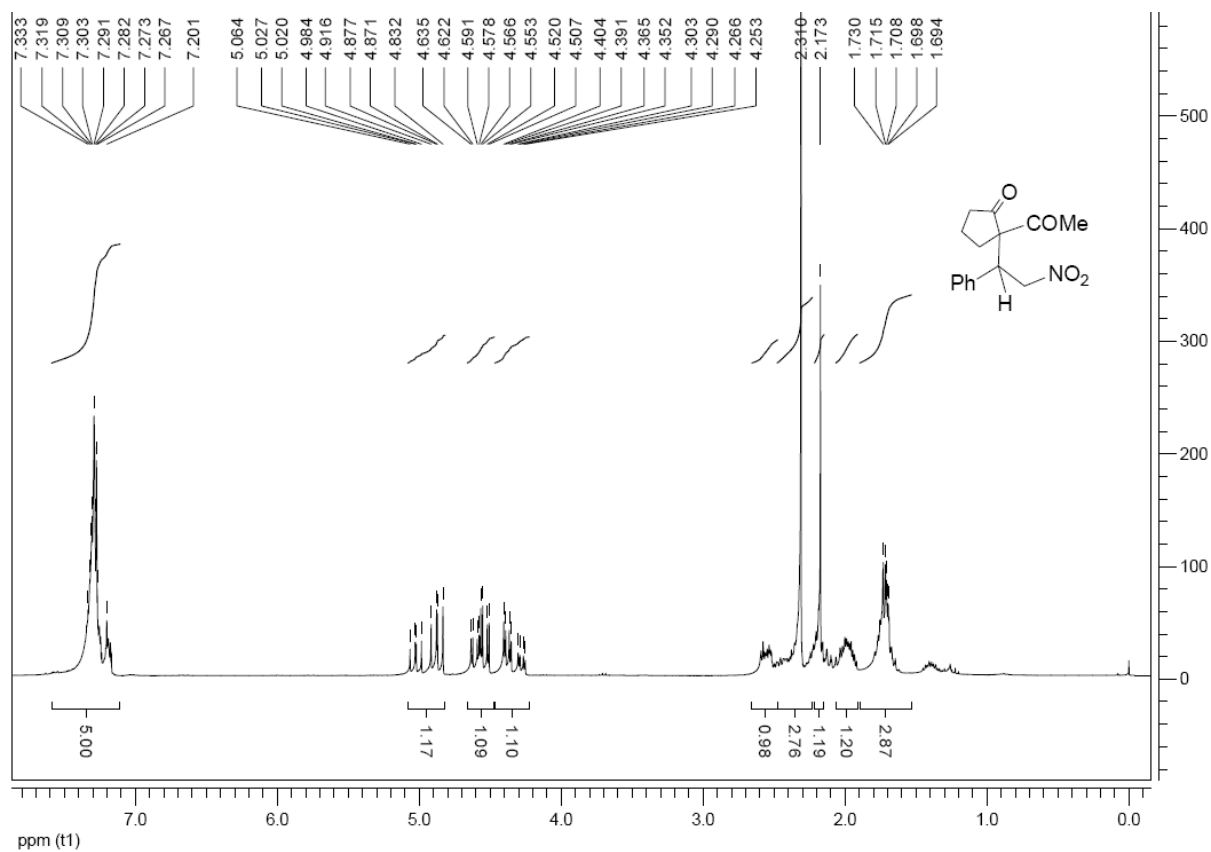
5d (Entry 4, Table 4)



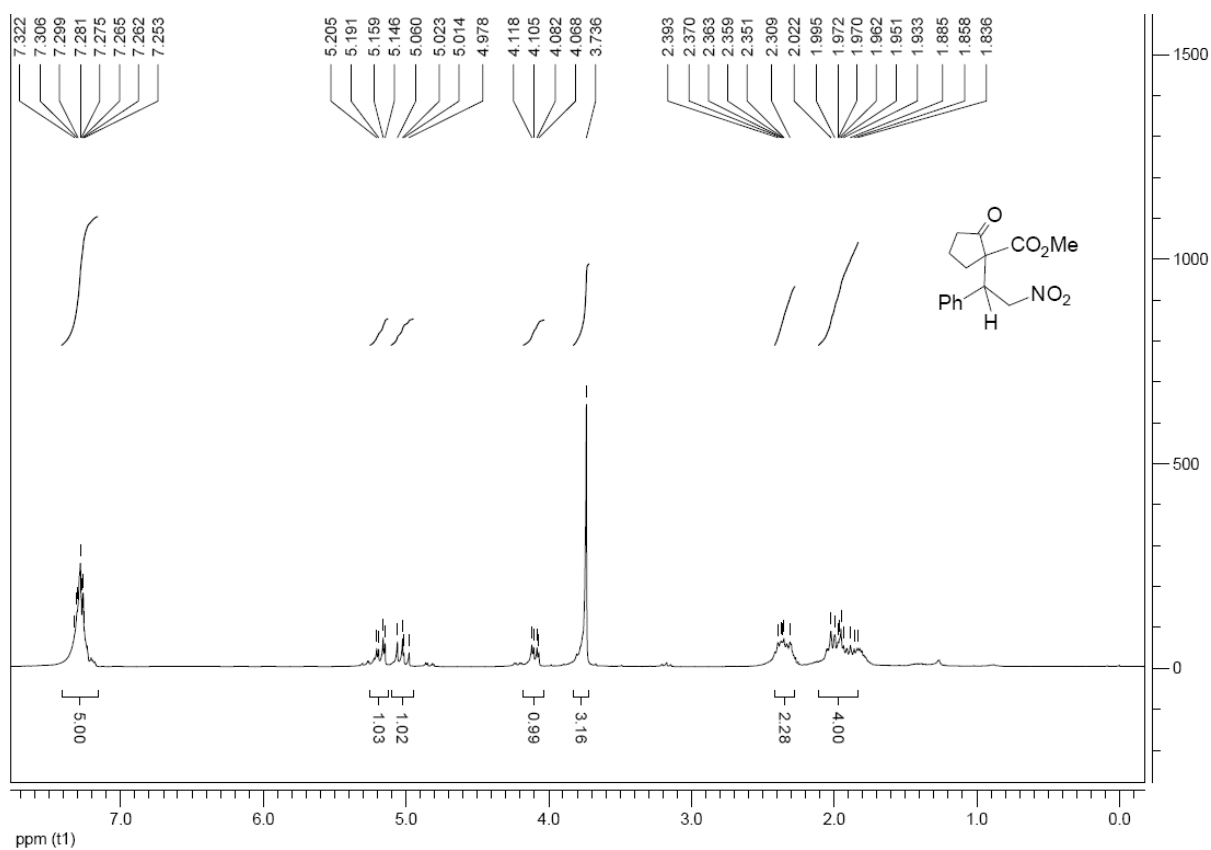
5e (Entry 5, Table 4)



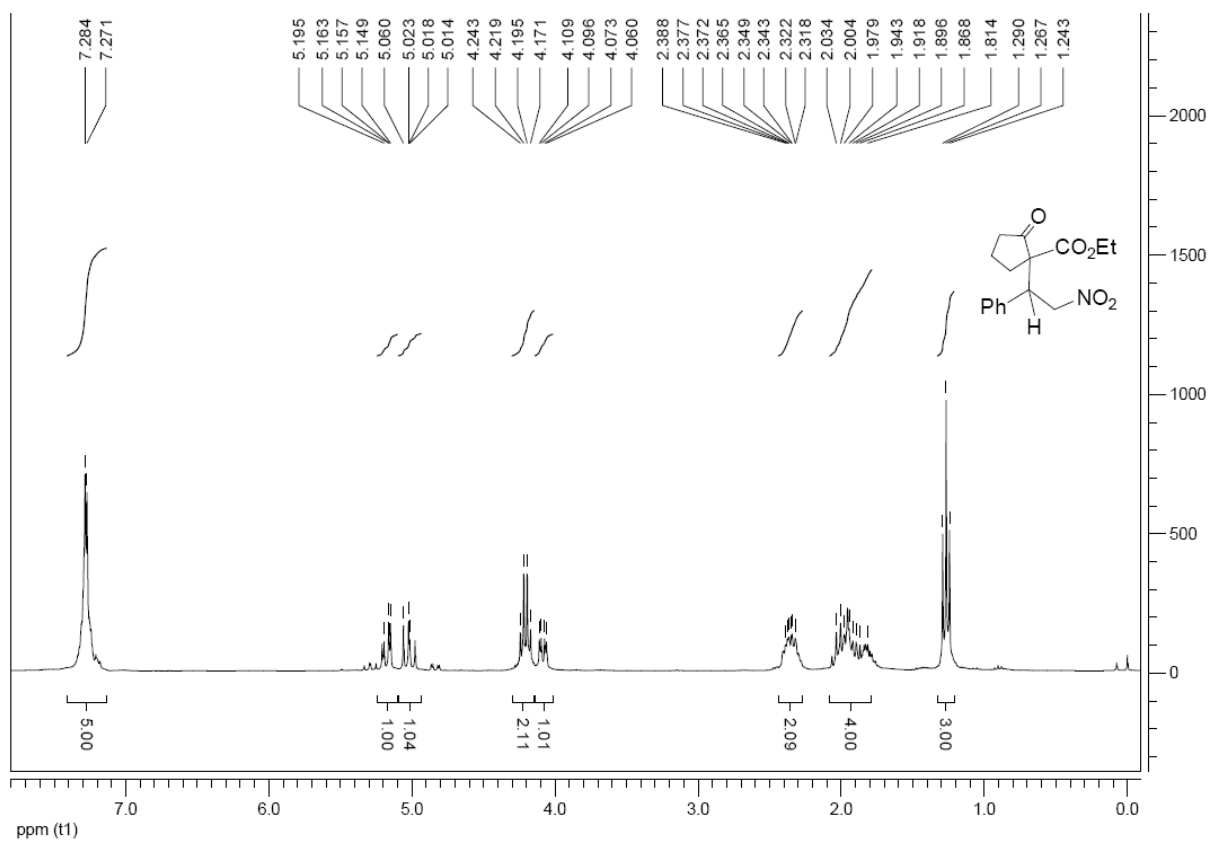
5f (Entry 6, Table 4)



5g (Entry 7, Table 4)



5h (Entry 8, Table 4)



Reference

1. I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.* **2010**, *1*, 73.
2. H. Y. Bae, S. Some, J. S. Oh, Y. S. Lee and C. E. Song, *Chem. Commun.* **2011**, *47*, 9621-9623.