Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information

Dimethylacetamide-stabilized ruthenium nanoparticles for catalysing α-alkylations of amides with alcohols

Honami Iguchi,[a] Nobuki Katayama,[a] Takeyuki Suzuki,[b] Tetsuaki Fujihara,[c] Yuan Jing,[d] Takashi Toyao,[d] Zen Maeno,[e] Ken-ichi Shimizu,[d] Yasushi Obora*[a]

[a] Department of Chemistry and Material Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

[b] Comprehensive Analysis Centre, SANKEN, Osaka University, Ibaraki, Osaka 567-0047, Japan

[c] Department of Energy and Hydrocarbon Chemistry Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

[d] Institute for Catalysis, Hokkaido University, Sapporo, Hokkaido 001-0021, Japan

[e] School of Advanced Engineering, Kogakuin University, Hachioji, Tokyo 192-0015, Japan

* obora@kansai-u.ac.jp

Table of Contents

1. General information

Gas chromatography (GC) was performed using a GC-2025 system (Shimadzu Co., Kyoto, Japan) with an incorporated flame ionization detector and equipped with a 0.22 mm × 25 m capillary column (BP-5). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired at 400 and 100 MHz, respectively, in $CDCl_3$ with TMS as an internal standard (JNM-ECZ-400S, Japan Electron Optics Laboratory Co., Tokyo, Japan). All starting materials were commercially available and used without purification. Compounds **3a**,[1] **3b**,[1] **3c**,[1] **3d**,[1] **3e**,[2] **3f**,[1] **3g**,[3] **3h**,[1] **3j**,[1] **3k**,[4] **3l**,[1] **3m**,[4] **3n**,[4] **3o**,[5] **3p**,[1] **3q**,[6] **4a**,[1] **6a**,[1] and **7a**[7] were reported previously. The products were characterized by ^{1}H NMR and ^{13}C NMR spectroscopies, and GC-mass spectrometry (GC-MS, electron ionization). Compound **3i** was also examined by infrared (IR) spectroscopy and high-resolution MS (micrOTOF with APCI II source, Bruker Inc., MA, USA). GC-MS spectra were recorded with a GCMS-QP2010 SE instrument (Shimadzu Co.) IR spectroscopy was performed with a Fourier-transform (FT)-IR spectrometer (Shimadzu IRAffinity-1, Shimadzu Co.) X-ray single-crystal structural analysis of **4a** was performed at Kyoto University (VariMax instrument with a Saturn 724+CCD detector, Rigaku Co., Tokyo, Japan). The product yields were estimated from the peak areas in gas chromatograms by using the internal standard technique. X-ray photoelectron spectroscopy (XPS) data were acquired with a PHI5000 VersaProbe instrument (ULVAC-PHI, Inc., Kanagawa, Japan) with an Al Kα X-ray source. Scanning transmission electron microscopy images were obtained with a JEM-ARM200F instrument (Japan Electron Optics Laboratory Co.) at an accelerating voltage of 200 kV. Ultraviolet (UV)-visible spectra were obtained with a UV-visible spectrophotometer (UV-1900i, Shimadzu Co., Kyoto, Japan). The measurement range was 300–800 nm. Photoluminescence (PL) spectra were recorded with a spectrofluorometer (RF-6000, Shimadzu Co.) The excitation wavelength for the fluorescence measurements was 350 nm. Fluorescence spectra were recorded with a data interval of 0.5 nm and a fluorescence wavelength range of 360–600 nm at a scanning rate of 6000 nm/min. IR spectra were obtained by the liquid-film method on a NaCl plate (IRAffinity-1 FT-IR spectrometer, Shimadzu Co.) X-ray diffraction patterns were recorded with a MiniFlex600-C instrument (Rigaku). Ru K-edge X-ray absorption spectroscopy (XAS) was performed in transmittance mode at the BL14B2 beamline (operated at 8 GeV) of SPring-8 (Hyogo, Japan) with a Si(311) double-crystal monochromator (proposal 2021A1615). Athena software ver. 0.9.25, included in the Demeter package, was used for data analysis.[8] The Fourier transformation of the k^3-weighted extended X-ray absorption fine structure (EXAFS) weas performed over a k range 3-12 $Å^{-1}$.

2. Experimental procedures

Typical Ru-NP-catalysed α-alkylation procedure: reaction of 1a with 2a (Table 1, entry 1)

A mixture of benzyl alcohol (**1a**; 108 mg, 1 mmol), *N*,*N*-dimethylacetamide (**2a**; 1 mL), Ru NPs (0.001 mmol), and KO^{t}Bu (224 mg, 2 mmol) was stirred at 130 °C (bath temperature) for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). The product yield was determined from the GC peak areas by using the internal standard method with *N*,*N*-dimethylbenzamide as the internal standard. The reaction was quenched by adding diethyl ether (10 mL). The base was removed from the reaction mixture by paper filtration.

The product was isolated by vacuum distillation with a Kugelrohr apparatus (0.25 h at 80 °C, 0.5 h at 130 °C, vacuum 0.3 mmHg). The product was isolated in 84% yield (148.9 mg) as a colourless oil.

Synthesis of Ru nanoparticles

All the synthetic operations carried out under open air atmosphere. A 0.1 M $RuCl_3$ solution was prepared by dissolving $RuCl_3 \cdot nH_2O$ (0.1 mmol) in HCl aq (1 M, 1 mL). The solution was left in the dark overnight.
Then DMAc (50 mL) was added to a 300 mL three-necked flask, which was then preheated at 160 °C for 5 min. The $RuCl_3$ solution (500 μL) was added at once to the preheated DMAc using micropipette and refluxed at 160 °C for 8 h under air atmosphere. After reaction, the resulting ruthenium nanoparticles (Ru NPs) solution was cooled at room temperature. The resulting solution was used as 1 mM Ru NPs (DMAc) solution for catalytic reactions.

Preparation of samples for scanning tunnelling electron microscopy

Solvents were removed from a Ru NPs suspension (1 mL, 1 mM) under vacuum with an evaporator and the NPs were redispersed in ethanol (2 mL). After the reaction, the Ru NPs were extracted by using a separating funnel (three times with water). The diethyl ether layer, from which bases had been completely removed, was collected and the solvent was replaced with ethanol.

Preparation of samples for PL and UV-visible spectroscopies

Samples (2 mL) of 1.0 and 0.1 mM Ru NPs were prepared in DMAc.

Preparation of samples for X-ray photoelectron spectroscopy, X-ray diffraction, and thermogravimetry

The DMAc in the Ru NP suspension was distilled off by using an evaporator. The samples were heated to 100 °C in a desiccator and depressurized for 4 h with a diaphragm pump, and for 1 h with a turbomolecular pump. For the XPS measurements, metallic Ru powder samples were prepared by sandwiching metallic Ru powder between layers of indium, and adhering the powder to the indium layers. The Ru NP samples were prepared by placing the NPs on an Ag plate of dimensions 5 mm × 5 mm. The XPS measurement of Ru NPs after reaction was

performed by the same manner using the recovered Ru NPs (see page S9 for the synthesis of the recovered Ru NPs). For XRD measurements, the dried and solidified NPs were sealed in an airtight cell in an Ar-filled bag.

Preparation of samples for XAS

Standard samples were obtained from the SPring-8 beamline. DMAc was removed from the Ru NPs with an evaporator, and the final liquid samples were prepared by adding DMAc to obtain the required concentration of 35 mM. Spectra were recorded at ambient temperature.

Single crystal X-ray diffraction

Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **4a** in cyclohexane. Intensity data were collected at 143 K on a Rigaku Saturn723+ with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). The structure was solved by direct methods (SIR92) and refined by the full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The crystal data are as follows: $C_{15}H_{22}N_2O_2$; FW = 262.35, orthorhombic, *P*bca, a = 7.960(4) Å, b = 11.510(6) Å, c = 32.253(18) Å, V = 2955(1) Å^3, Z = 8, Dc = 1.179 g cm^{-3}, R1 = 0.098 ($I > 2\ \sigma(I)$), wR2 = 0.279 (all data), GOF = 1.106. CCDC 2184335. CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results of PL and UV-visible spectroscopic analyses

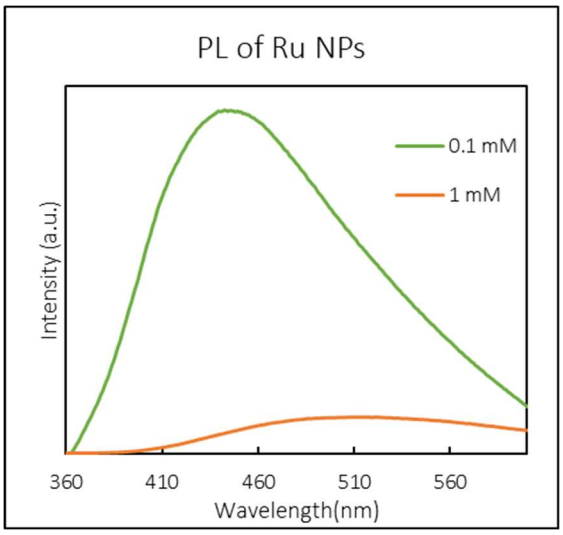


Fig. S1. PL spectra of Ru NPs under irradiation with 350 nm excitation light. The decrease in fluorescence intensity at 1 mM is caused by concentration quenching.

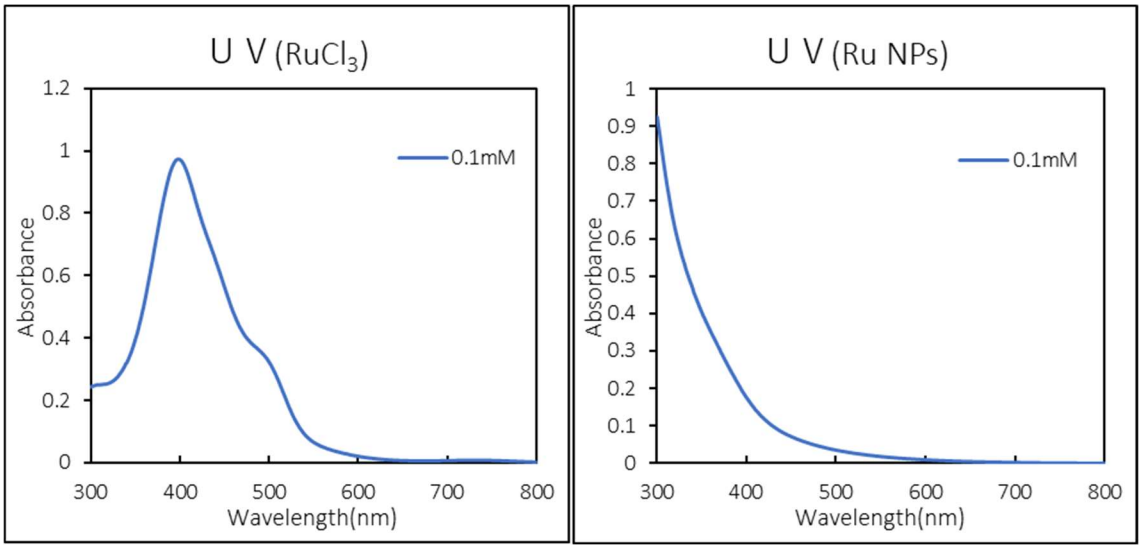


Fig. S2. UV-visible spectra of precursor (left, $RuCl_3 \cdot nH_2O$) and Ru NPs (right). The decrease in fluorescence intensity at 1 mM is caused by concentration quenching. No precursor peaks are present in the NP spectrum, which suggests that all the Ru species are nanoparticulated.

4. Results of XPS analysis

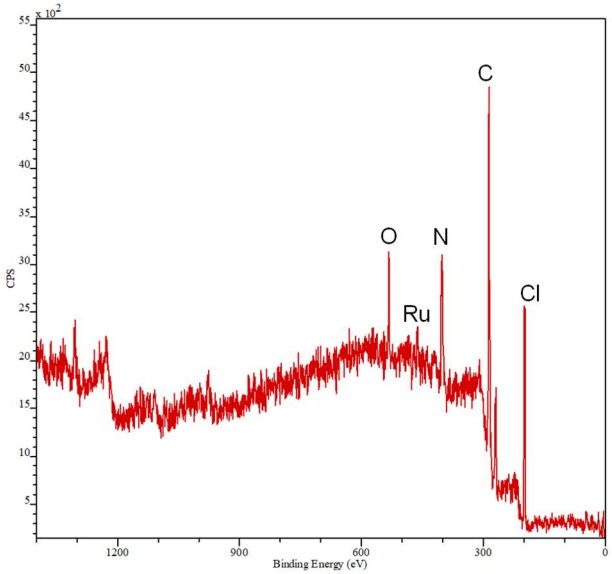


Fig. S3. Wide-scan XPS spectrum of Ru NPs before reaction.

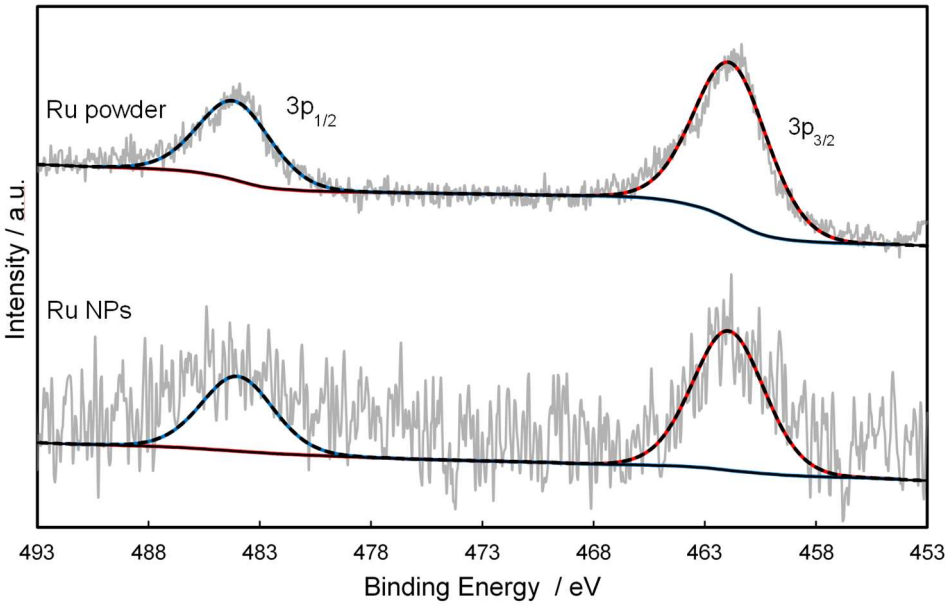


Fig. S4. Narrow-scan XPS spectrum of Ru NPs before reaction.

Table S1. XPS peak positions and full-width at half-maximum (FWHM) values[9]

Sample		Binding Energy (eV)	FWHM
Ru Powder	Ru $3p_{3/2}$	461.8	3.8
	Ru $3p_{1/2}$	484.1	3.8
Ru NPs before reaction	Ru $3p_{3/2}$	461.9	3.8
	Ru $3p_{1/2}$	484.0	3.8

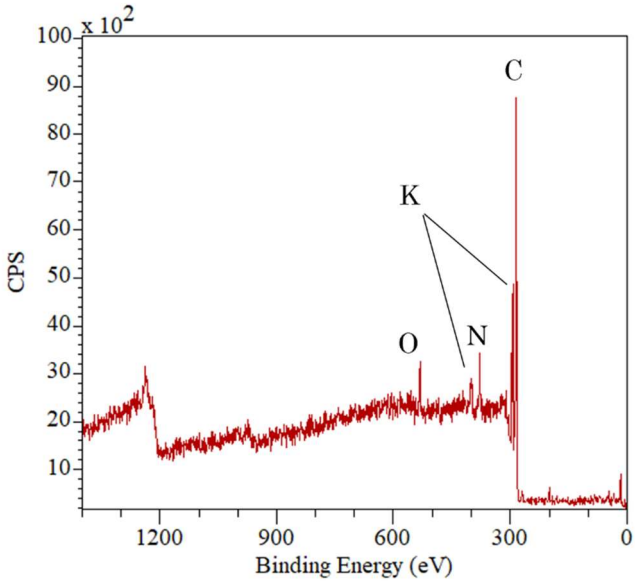


Fig. S5. Wide-scan XPS spectrum of Ru NPs after reaction. The sample was prepared by following the same procedure as the XAS measurement. The base (potassium-containing compound) on the surface of the Ru NPs sample could not be completely removed, which indicates unanalysable spectra in the Ru 3p peak area.

5. Results of XAS analysis

Table S2. Curve-fitting analysis for Ru K-edge extended X-ray absorption fine structures of Ru NPs before and after reaction

Sample	Shell	CN [a]	*R* (Å) [b]	σ^2 (Å^2) [c]	R_f (%) [d]
Ru NPs before reaction	Ru–Cl	5.6	2.37	0.005	2.1
	Ru–Ru	6.7	2.65	0.014	
Ru NPs after reaction	Ru–O	3.5	2.14	0.006	1.5
	Ru–Ru	3.3	2.66	0.015	

[a]Coordination number. [b]Bond distance. [c]Debye–Waller factor. [d]Residual factor.

6. Recycling experiment procedure

The reaction of **1a** with **2a** was performed under the conditions in Table 1, entry 1. After the reaction, diethyl ether (10 mL) was added to the reaction mixture and the reaction solution was separated into solid and liquid phase (A) using a centrifuge (6000 rpm, 5 min). DMF (10 mL) was added to the obtained solid and the solution was separated into solid and liquid phase (B) using centrifuge (6000 rpm, 5 min). The solution (B) was evaporated (80 °C, 30 hPa) and dissolved in water (10 mL) (solution C). The solutions (A) and (C) were mixed and extracted with water (10 mL x 2) to recover the Ru NPs. The water layer was evaporated (80 °C, 30 hPa), and the residue (recovered Ru NPs) was used as catalyst for the recycling experiment as follows. A mixture of benzyl alcohol (**1a**; 108 mg, 1 mmol), *N*,*N*-dimethylacetamide (**2a**; 1 mL) and KO^{t}Bu (224 mg, 2 mmol) was added to the recovered Ru NPs and stirred at 130 °C (bath temperature) for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). The product (**3a**) was obtained in 68% yield determined from the GC peak areas by using the internal standard method with *N*,*N*-dimethylbenzamide as the internal standard.

7. Other information

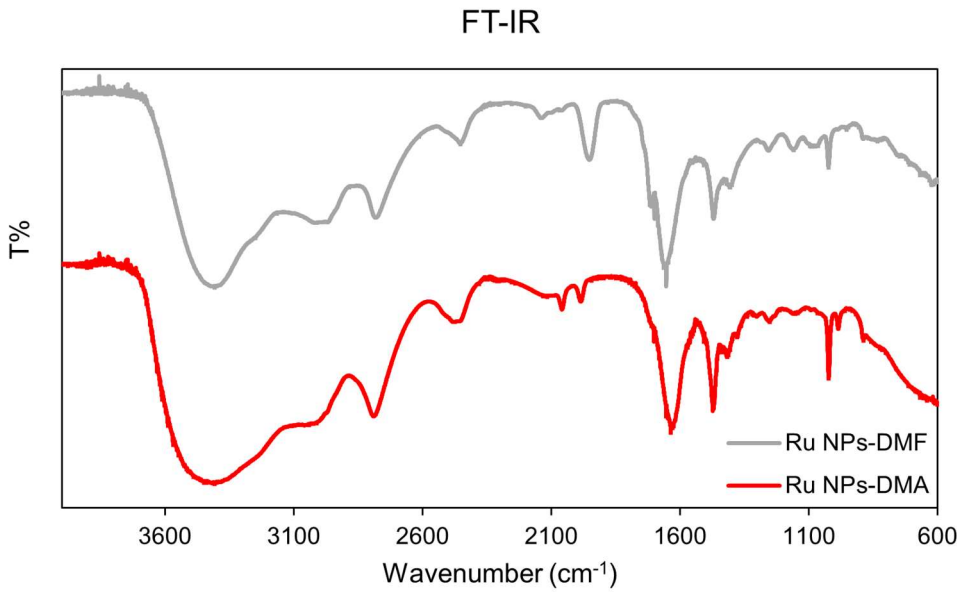


Fig. S6. FT-IR spectra of DMF-stabilized Ru NPs (gray) and DMAc-stabilized Ru NPs (red).

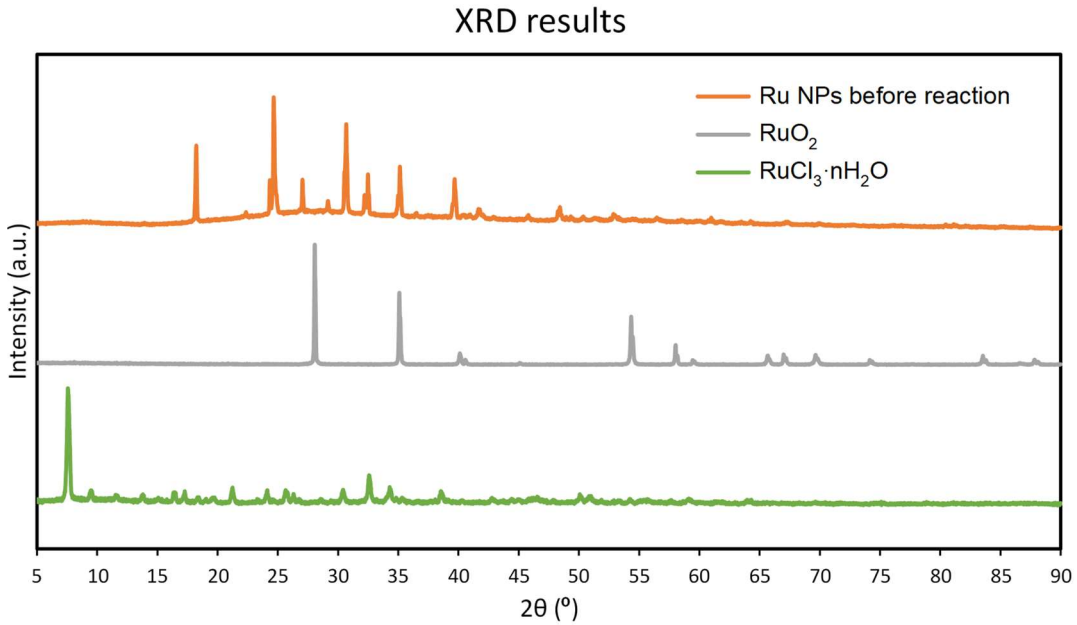


Fig. S7. XRD pattern of Ru NPs before reaction (orange line).

No peaks corresponding to ruthenium oxide (grey line) or ruthenium chloride (green line) are present.

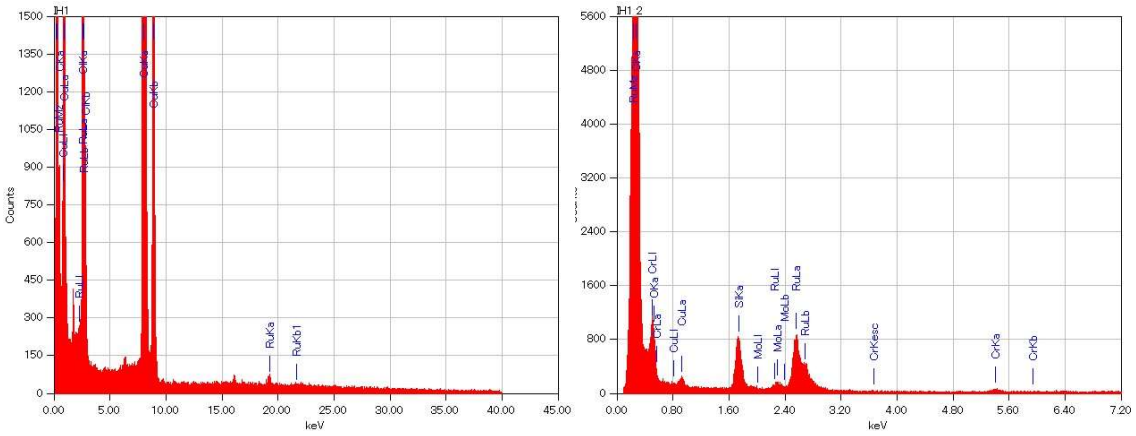


Fig. S8. Energy-dispersive X-ray spectroscopic analysis of Ru peaks

(left: before reaction; right: after reaction).

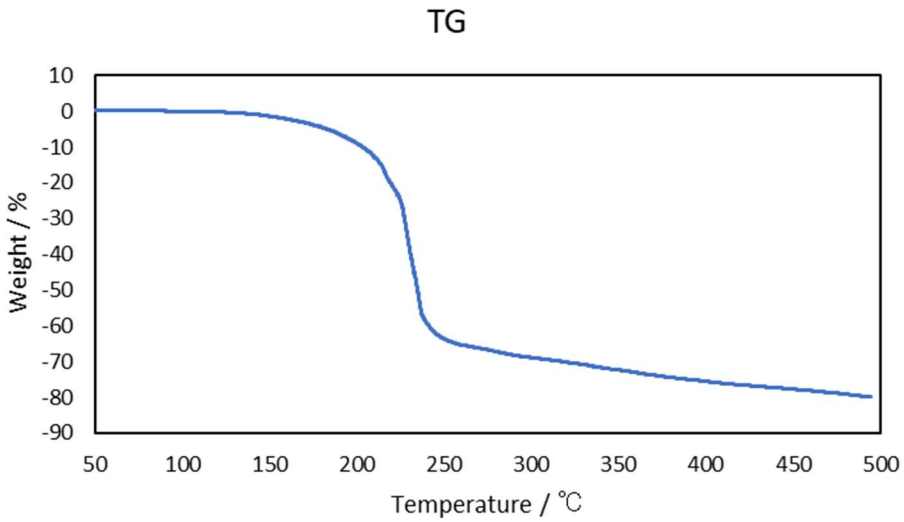
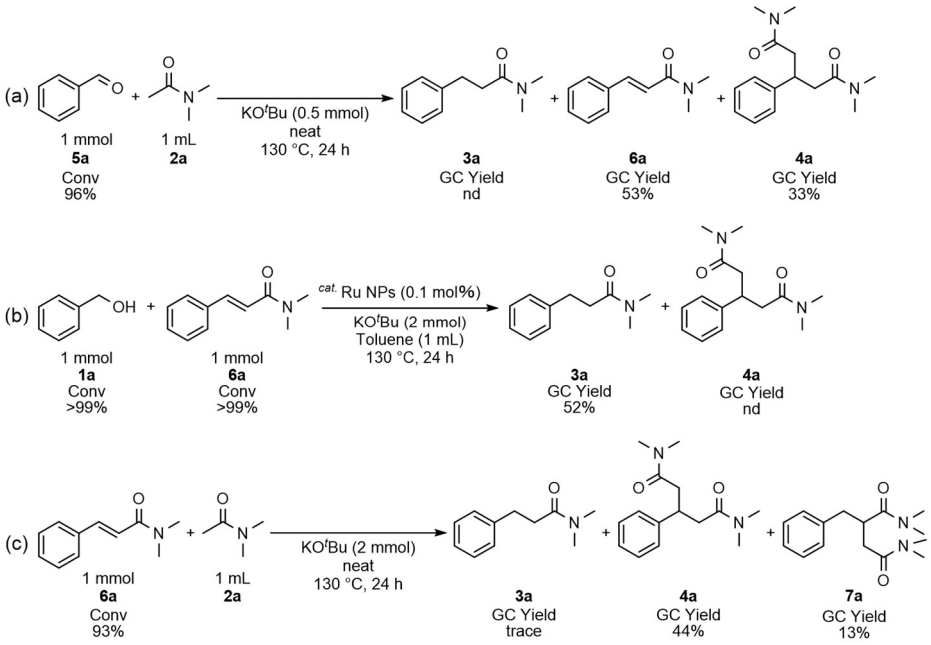


Fig. S9. Thermogravimetric analysis of Ru NPs;

Td_5: 183 °C.



Scheme S1. Control experiments

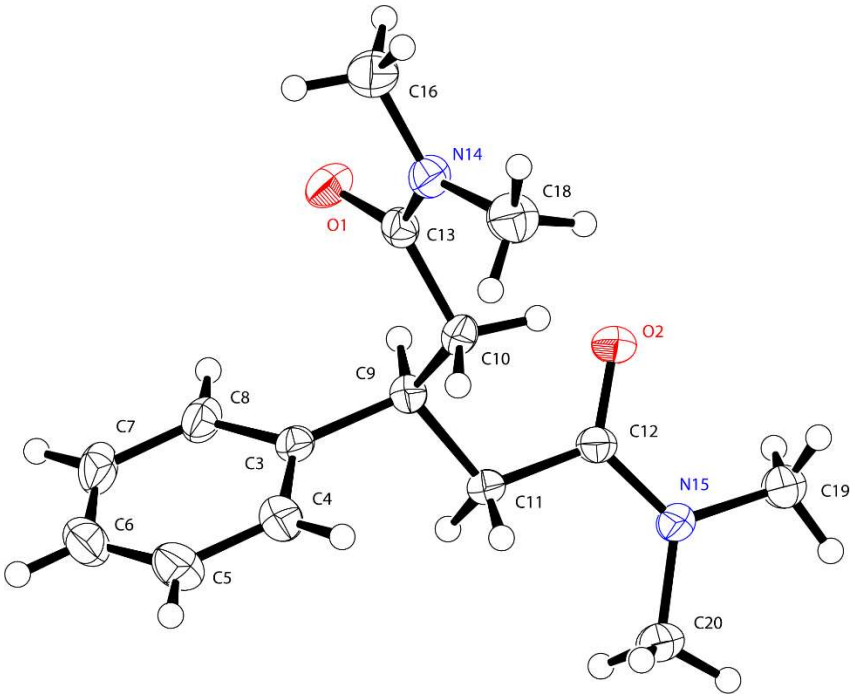


Fig. S10. Crystal structure of **4a** obtained by X-ray single-crystal structural analysis.

8. Screening information

Table S3. Effect of base

Entry	Base	Yield (GC)	
		3a	**4a**
1	KO^{t}Bu	93%	7%
2	KOH	11%	nd
3	K_2CO_3	nd	nd
4	Cs_2CO_3	7%	nd
5	LiO^{t}Bu	26%	11%
6	NaO^{t}Bu	22%	nd

Reaction conditions: benzyl alcohol (1 mmol), *N*,*N*-dimethylacetamide (1 mL), Ru NPs (0.001 mmol, 0.1 mol%), base (2 mmol), pressure tube, 130 °C oil bath, 24 h reaction time; nd: not detected.

Table S4. Effect of amount of base

Entry	Base amount	Yield (GC)	
		3a	**4a**
1	1.0 mmol	31%	nd
2	1.2 mmol	52%	nd
3	1.5 mmol	72%	4%
4	2.0 mmol	93%	7%

Reaction conditions: benzyl alcohol (1 mmol), *N*,*N*-dimethylacetamide (1 mL), Ru NPs (0.001 mmol, 0.1 mol%), KO^{t}Bu (*X* mmol), pressure tube, 130 °C oil bath, 24 h reaction time; nd: not detected.

Table S5. Effect of substrate ratio

Entry	*N*,*N*-dimethylacetamide amount	Yield (GC)	
		3a	**4a**
1[a]	1 mmol	25%	nd
2[a]	3 mmol	66%	nd
3	5 mmol	41%	18%
4	1 mL (11 mmol)	93%	7%

Reaction conditions: benzyl alcohol (1 mmol), *N*,*N*-dimethylacetamide (***X*** mmol), Ru NPs (0.001 mmol, 0.1 mol%), KO^{t}Bu (2 mmol), pressure tube, 130 °C oil bath, 24 h reaction time; nd: not detected.

[a]Toluene (1 mL) was added as solvent.

Table S6. Effect of solvent

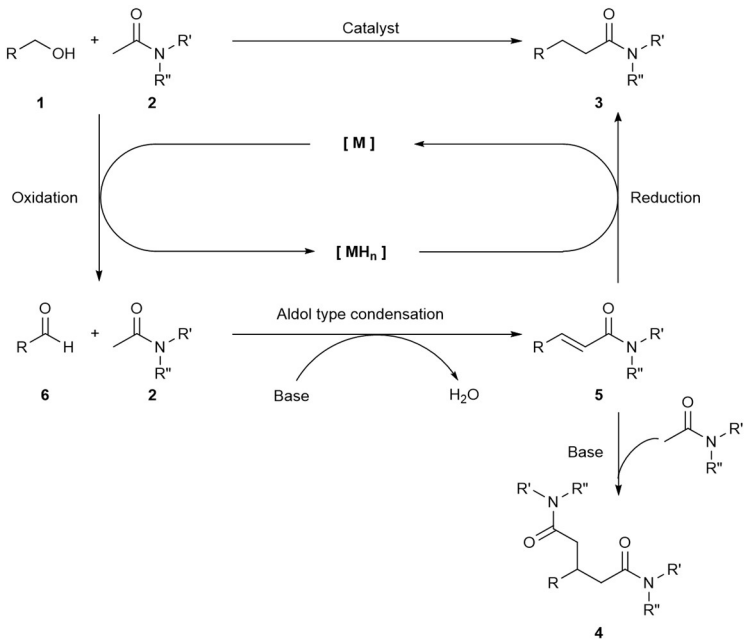
Entry	Solvent	Yield (GC)	
		3a	**4a**
1	Toluene	66%	nd
2	1,4-Dioxane	53%	8%
3	^{t}BuOH	nd	nd
4	DMF	45%	25%
5[a]	DMAc	93%	7%

Reaction conditions: benzyl alcohol (1 mmol), *N*,*N*-dimethylacetamide (3 mmol), Ru NPs (0.001 mmol, 0.1 mol%), KO^{t}Bu (2 mmol), solvent (1 mL), pressure tube, 130 °C oil bath, 24 h reaction time; nd: not detected. [a] *N*,*N*-dimethylacetamide (1 mL) was added as a substrate and solvent.

Table S7. Effect of temperature

Entry	Reaction temperature	Yield (GC)	
		3a	**4a**
1	80 °C	34%	nd
2	110 °C	74%	6%
3	130 °C	93%	7%

Reaction conditions: benzyl alcohol (1 mmol), *N*,*N*-dimethylacetamide (1 mL), Ru NPs (0.001 mmol, 0.1 mol%), KO^{t}Bu (2 mmol), pressure tube, *X* °C oil bath, 24 h reaction time; nd: not detected.



Scheme S2. A plausible reaction mechanism

9. Characterization data

3a : *N*,*N*-dimethyl-3-phenylpropanamide

The desired product was purified by distillation with a Kugelrohr apparatus (0.25 h at 80 °C, 0.5 h at 130 °C, vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 84% (148.9 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.30-7.18 (m, 5H), 2.99-2.92 (m, 8H, overlapping signals of NMe_2, and CH_2), 2.63-2.59 (m, 2H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.2 (C), 141.5 (C), 128.5 (CH), 128.4 (CH), 126.1 (CH), 37.1 (CH_2), 35.4 (CH_2), 35.3 (CH_3), 31.4 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 177(100) $[M]^+$, 72(59), 91(54), 105(31), 45(23).

The spectroscopic data correspond to those reported in the literature.[1]

3b : *N*,*N*-dimethyl-3-(*o*-tolyl)propanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 130 °C,0.25 h at 140 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 69% (132.0 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.16-7.10 (m, 4H), 2.98-2.93 (m, 8H), 2.58-2.54 (m, 2H), 2.33 (s, 3H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.2 (C), 139.5 (C), 135.9 (C), 130.2 (CH), 128.7 (CH), 126.2 (CH), 126.0 (CH), 37.0 (CH_3), 35.3 (CH_3), 33.8 (CH_2), 28.6 (CH_2), 19.2 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 191(88) $[M]^+$, 105(100), 118(82) ,72(53).

The spectroscopic data correspond to those reported in the literature.[1]

3c : *N*,*N*-dimethyl-3-(*m*-tolyl)propanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 140 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 79% (151.1 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.20-7.16 (t, 1H), 7.04-7.01 (m, 3H), 2.99-2.87 (m, 8H), 2.62-2.58 (m, 2H), 2.33 (s, 3H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.2 (C), 141.4 (C), 138.0 (C), 129.2 (CH), 128.4 (CH), 126.8 (CH), 125.4 (CH), 37.2 (CH_3), 35.4 (CH_3), 35.4 (CH_2), 31.3 (CH_2), 21.4 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 191(100) $[M]^+$, 105(93), 118(76) ,119(47).

The spectroscopic data correspond to those reported in the literature.[1]

3d : *N*,*N*-dimethyl-3-(*p*-tolyl)propanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 150 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 76% (145.4 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.26-6.96 (m, 4H), 2.96.-2.87 (m, 8H), 2.70-2.57 (m, 2H), 2.31 (s, 3H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.3 (C), 138.4 (C), 135.6 (C), 129.1 (CH), 128.3 (CH), 37.2 (CH_3), 35.5 (CH_3), 35.4 (CH_2), 31.0 (CH_2), 21.0 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 191(100) $[M]^+$, 105(92), 118(74) ,119(48).

The spectroscopic data correspond to those reported in the literature.[1]

3e : *N*,*N*-dimethyloctadecanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 130 °C,0.5 h at 230 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 65% (202.5 mg), white solid, m.p. 46 °C.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 3.00 (s, 3H), 2.94 (s, 3H), 2.30 (t. 2H, J = 7.7 Hz), 1.66-1.59 (m, 2H), 1.30-1.21 (br, 28H), 0.88 (t, 3H J = 6.7 Hz) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 173.3 (C), 37.3 (CH_3), 35.4 (CH_3), 33.5 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 25.2 (CH_2), 22.7 (CH_2) 14.1 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 227(78) $[M]^+$, 154(100), 141(64), 155(63), 72(35).

The spectroscopic data correspond to those reported in the literature.[2]

3f : 3-(4-methoxyphenyl)-*N*,*N*-dimethylpropanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 160 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 71% (147.16 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.27-7.13 (m, 2H), 6.84-6.82 (m, 2H), 3.79 (s, 3H), 2.95-2.89 (m, 8H), 2.60-2.56 (s, 2H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.3 (C), 157.9 (C), 133.5 (C), 129.4 (CH), 113.8 (CH), 55.3 (CH_3), 37.2 (CH_3), 35.6 (CH_3), 35.4 (CH_2), 30.5 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 207(9) $[M]^+$, 121(100), 134(97), 135(30).

The spectroscopic data correspond to those reported in the literature.[1]

3g : 3-(4-(tert-butyl)phenyl)-*N*,*N*-dimethylpropanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.25 h at 110 °C,0.5 h at 180 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 70% (163.3 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.33-7.31 (m, 2H), 7.31.-7.15 (m, 2H), 2.95-2.92 (m, 8H), 2.63-2.59 (m, 2H) 1.31 (s, 9H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.3 (C), 148.9 (C), 138.4 (C), 128.1 (CH), 125.3 (CH), 37.2 (CH_3), 35.4 (CH_3), 35.3 (CH_2), 34.4 (C), 31.4 (CH_3), 30.8 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 233(94) $[M]^+$, 145(100), 46(71), 218(69), 117(40).

The spectroscopic data correspond to those reported in the literature.[3]

3h : 4-chloro-*N*,*N*-dimethylbenzenepropanamide

The desired product was purified by column chromatography (silica gel, hexane/ethyl acetate, 3:2) after removing

the base by paper filtration. Isolated yield 28% (59.2 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.25 (2H, d, *J* = 8.5 Hz), 7.16 (2H, d, *J* = 8.6 Hz), 2.94 (8H, t, *J* = 7.8 Hz), 2.59 (2H, t, *J* = 7.8 Hz) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 171.7 (C), 139.9 (C), 131.7 (C), 129.8 (CH), 128.4 (CH), 37.1 (CH_3), 35.4 (CH_3), 34.9 (CH_2), 30.5 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity) 211 (95) $[M]^+$, 45 (100), 211 (95), 72 (76), 125 (68).

The spectroscopic data correspond to those reported in the literature.[4]

3l : *N*,*N*-dimethyl-3-(naphthalen-1-yl)propanamide

The desired product was purified by preparative GPC (3cycles, $CHCl_3$) after removing the base by paper filtration. Isolated yield 33% (75.0 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 8.04 (d, 1H, *J* = 8.3 Hz), 7.83 (d, 1H, *J* = 7.8 Hz), 7.70 (d, 1H, *J* = 7.4 Hz), 7.52-7.43 (m, 2H), 7.40-7.34 (m, 2H) 3.43 (t, 2H, *J* = 8.0 Hz), 2.93 (s, 3H), 2.79 (s, 3H), 2.70 (t, 2H, *J* = 8.0 Hz) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.1 (C), 137.4 (C), 133.7 (C), 131.5 (C), 128.7 (CH), 126.8 (CH), 126.0 (CH), 125.9 (CH), 125.5 (CH), 125.4 (CH), 123.4 (CH), 36.9 (CH_3), 35.3 (CH_3), 34.3 (CH_2), 28.3 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 227(91) $[M]^+$, 141(100), 154(96), 155(50), 153(47).

The spectroscopic data correspond to those reported in the literature.[1]

3m : *N*,*N*-dimethyl-3-(naphthalen-2-yl)propanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 150 °C,0.5 h at 200 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 52% (118.2 mg), colorless oil.

IR (neat): 3049, 2934, 2360, 1653, 1507, 1420, 1268, 1142, 820, 748, 668 cm^{-1}.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.78 (3H, t, *J* = 9.2 Hz), 7.66 (s, 1H,), 7.46-7.35 (m, 3H), 3.13 (2H, t, *J* = 7.9 Hz), 2.95 (s, 3H,), 2.92 (s, 3H,) 2.69 (2H, t, *J* = 7.9 Hz) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.1 (C), 139.0 (C), 133.6 (C), 132.1 (C), 128.0 (CH), 127.6 (CH), 127.4 (CH), 127.2 (CH), 126.5 (CH), 126.0 (CH), 125.3 (CH), 37.2 (CH_3), 35.5 (CH_3), 35.2 (CH_2), 31.5 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 227(78) $[M]^+$, 154(100), 141(64), 155(63), 72(35).

HR-MS (ESI) *m/z* calcd for $C_{15}H_{17}NO$ $[M]^+$: 228.1383, found 228.1385.

3n : *N*,*N*-dimethyl-3-(pyridin-3-yl)propanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.25 h at 100 °C,0.5 h at 150 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 54% (96.2 mg), colorless oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 8.49-8.46 (m, 2H), 7.59-7.57 (m, 1H), 7.23-7.21 (m, 1H), 3.01-2.96 (m, 8H), 2.63 (t, 2H, *J* = 7.7 Hz,) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 171.4 (C), 149.9 (CH), 147.6 (CH), 136.8 (CH), 136.2 (CH), 123.4 (CH), 37.1 (CH_3), 35.4 (CH_3), 34.7 (CH_2), 28.3 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 178(1) $[M]^+$, 135(100), 134(67), 106(43), 72(22).

The spectroscopic data correspond to those reported in the literature.[1]

3q : *N*-methyl-3-phenylpropanamide

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 110 °C,0.5 h at 150 °C, Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 67% (109.4 mg), white solid, m.p. 56-58 °C.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.36-7.18 (m, 5H), 5.59 (br, s, 1H), 2.96 (t, J = 7.8 Hz, 2H), 2.76 (d, J = 4.8 Hz, 3H), 2.46 (t, J = 7.8 Hz, 2H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 172.8 (C), 140.9 (C), 128.5 (CH), 128.3 (CH), 126.2 (CH), 38.4 (CH_2), 31.7 (CH_2), 26.3 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 163(100) $[M]^+$, 91(94), 105(72), 104(50), 58(34).

The spectroscopic data correspond to those reported in the literature.[5]

3r : *N*,*N*-diethyl-3-phenylpropanamide

The desired product was purified by column chromatography (silica gel, hexane/ethyl acetate, 1:1.5) after removing the base by paper filtration. Isolated yield 50% (102.7 mg), yellow oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.30-7.17 (m, 5H), 3.38 (q, J = 7.1 Hz, 2H), 3.22 (q, J = 7.2 Hz, 2H), 3.00.-2.96 (m, 2H), 2.61-2.57 (m, 2H), 1.13-1.08 (m, 6H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 17 (C), 141.6 (C), 128.5 (CH), 128.5 (CH), 126.1 (CH), 41.9 (CH_2), 40.2 (CH_2), 35.1 (CH_2), 31.7 (CH_2), 14.3 (CH_3), 13.1 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 205(61) $[M]^+$, 58(100), 91(46), 72(38), 105(33).

The spectroscopic data correspond to those reported in the literature.[5]

3s : 3-phenyl-1-(piperidin-1-yl)propan-1-one

The desired product was purified by preparative GPC (3cycles, $CHCl_3$) after removing the base by paper filtration. Isolated yield 38% (82.6 mg), yellow oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.30-7.17 (m, 5H), 3.55 (t, J = 5.5 Hz, 2H), 3.33 (t, J = 5.5 Hz, 2H), 2.98-2.94 (m, 2H), 2.62-2.60 (m, 2H), 1.63-1.42 (m, 6H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ:170.4 (C), 141.5 (C), 128.5 (CH), 128.4 (CH), 126.1 (CH), 46.6 (CH_2), 42.7 (CH_2), 35.2 (CH_2), 31.6 (CH_2), 26.4 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 217(47) $[M]^+$, 126(100), 84(39), 91(29), 85(13).

The spectroscopic data correspond to those reported in the literature.[6]

3t : 1-morpholino-3-phenylpropan-1-one

The desired product was purified by distillation with Kugelrohr apparatus (0.5 h at 120 °C,0.5 h at 230 °C,

Vacuum 0.3 mmHg) after removing the base by paper filtration. Isolated yield 51% (111.8 mg), yellow oil.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.30-7.19 (m, 5H), 3.62-3.34 (m, 8H), 3.00-2.96 (m, 2H), 2.63-2.59 (m, 2H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 170.9 (C), 141.1 (C), 128.6 (CH), 128.5 (CH), 126.3 (CH), 66.9 (CH_2), 66.5 (CH_2), 46.0 (CH_2), 41.9 (CH_2), 34.8 (CH_2), 31.5 (CH_2) ppm.

GC-MS (EI) *m/z* (relative intensity), 219(100) $[M]^+$, 91(88), 105(61), 57(58), 86(53).

The spectroscopic data correspond to those reported in the literature.[1]

4a : N^1,N^1,N^5,N^5-tetramethyl-3-phenylpentanediamide

Synthesis conditions: benzaldehyde (1 mmol), *N*,*N*-dimethylacetamide (3 mmol), KOH (2 mmol), pressure tube, 130 °C oil bath, 24 h reaction time. The desired product was purified by distillation with an evaporator after removing the base by paper filtration. The solid was further purified by freeze-drying with benzene. Isolated yield 68% (178.4 mg), white solid, m.p. 61–62 °C.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.67 (d, J = 15.4 Hz, 1H), 7.54-7.34 (m, 5H), 6.89 (d, J = 15.6 Hz, 1H), 3.17-3.07 (m, 6H) ppm.

^{13}C-NMR (100 MHz; $CDCl_3$) δ: 166.7 (C), 142.3 (CH), 135.4 (C), 129.5 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 117.4 (CH), 37.4 (CH_3), 35.9 (CH_3) ppm.

GC-MS (EI) *m/z* (relative intensity), 175(42) $[M]^+$, 131(100), 103(65), 77(30), 174(16).

The spectroscopic data correspond to those reported in the literature.[1]

7a : N^1,N^1,N^4,N^4-tetramethyl-2-(phenylmethyl)butanediamine

Separation of **7a** from **4a** was difficult, therefore the NMR spectrum of the mixture was recorded.

^{1}H-NMR (400 MHz; $CDCl_3$) δ: 7.31-7.17 (m, 5H), 3.57-3.50 (m, 1H), 3.04-2.68 (m, 15H) 2.31 (dd, J = 16.4, 3.7 Hz, 1H) ppm.

GC-MS (EI) *m/z* (relative intensity), 262(7) $[M]^+$, 72(100), 176(73), 145(19), 46(16), 173(14), 91(13).

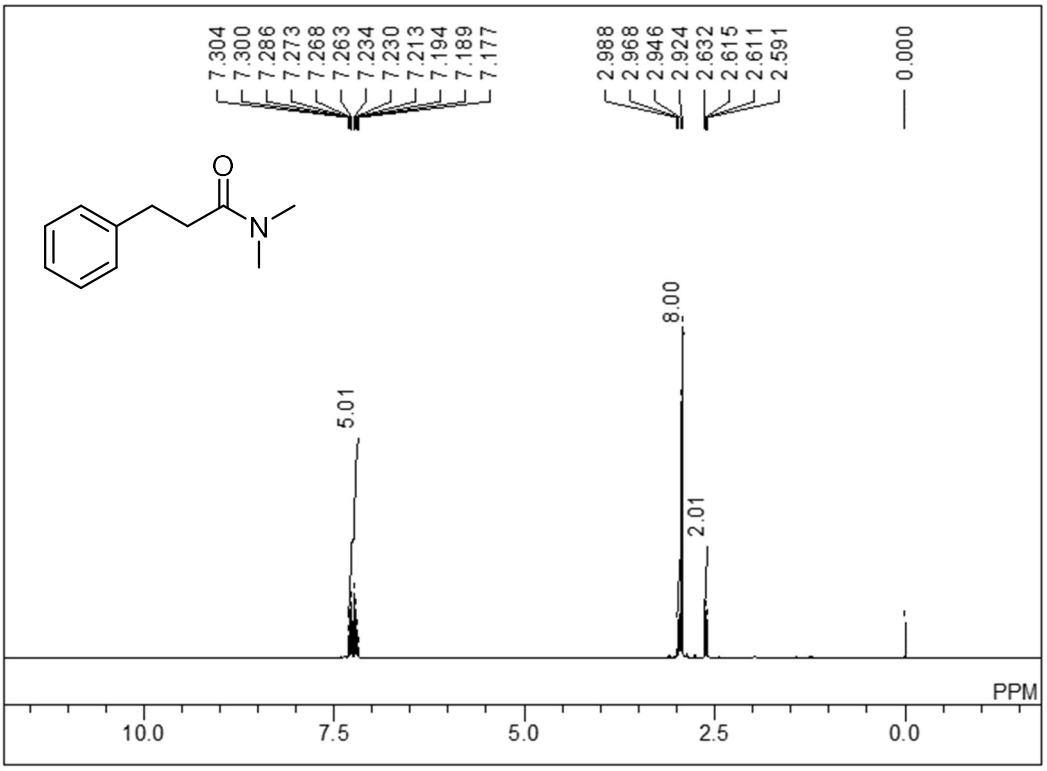
The spectroscopic data correspond to those reported in the literature.[7]

N,*N*-Dimethyl-3-[4-(trifluoromethyl)phenyl]-2-propenamide[8]

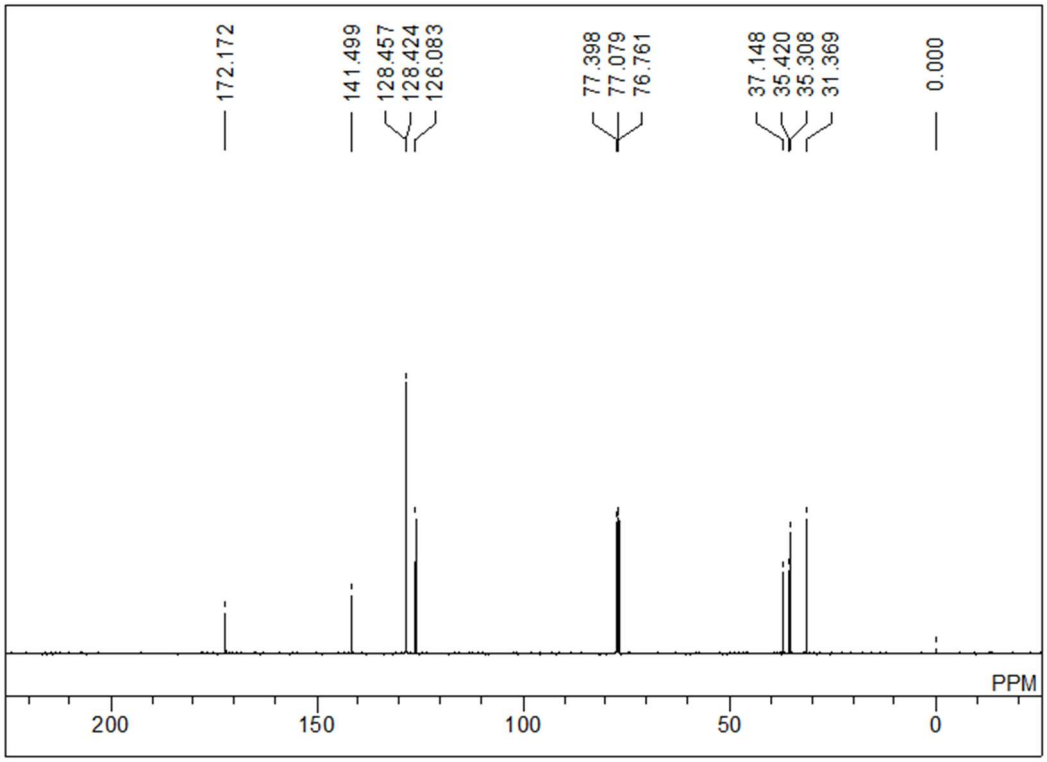
GC-MS (EI) *m/z* (relative intensity) 243 (48) $[M]^+$, 199 (100), 151 (52), 171 (50), 98 (29).

10. NMR-Spectra

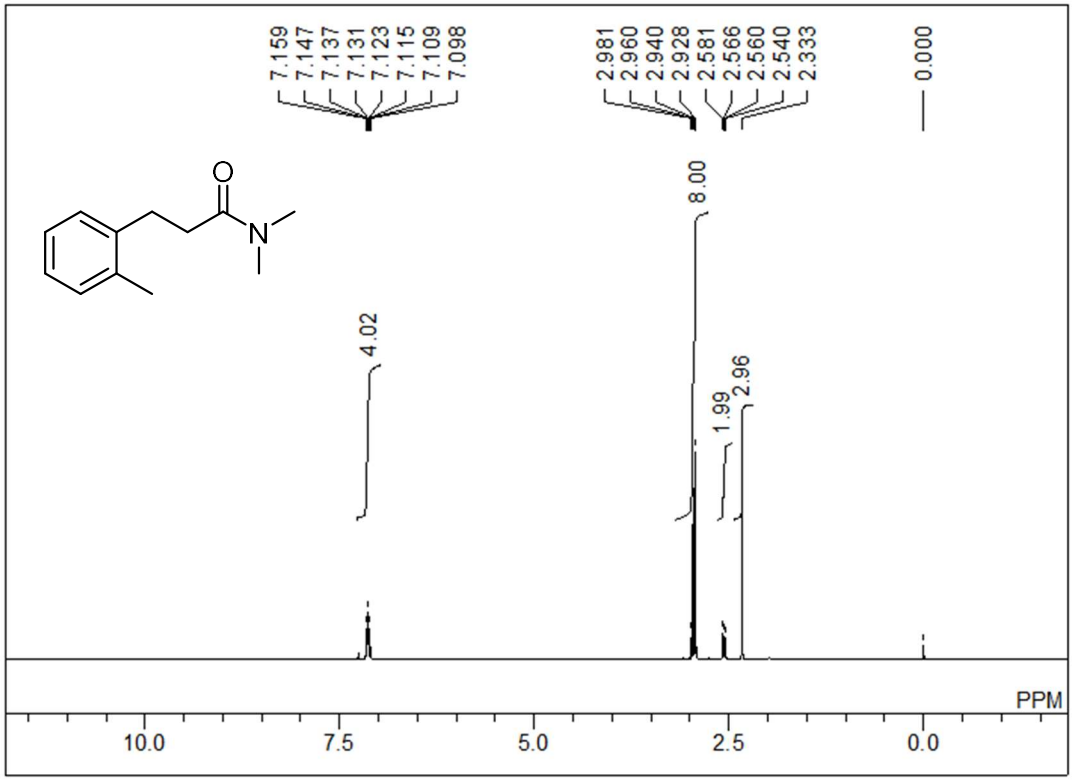
3a ^{1}H-NMR



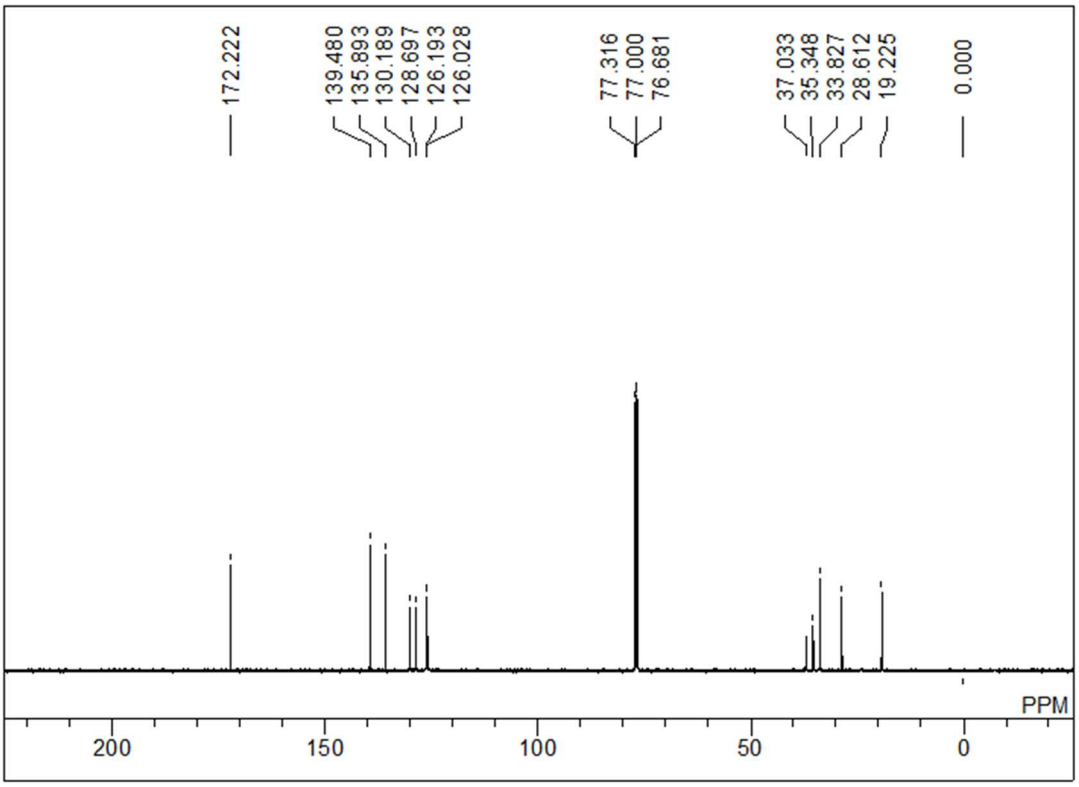
^{13}C-NMR



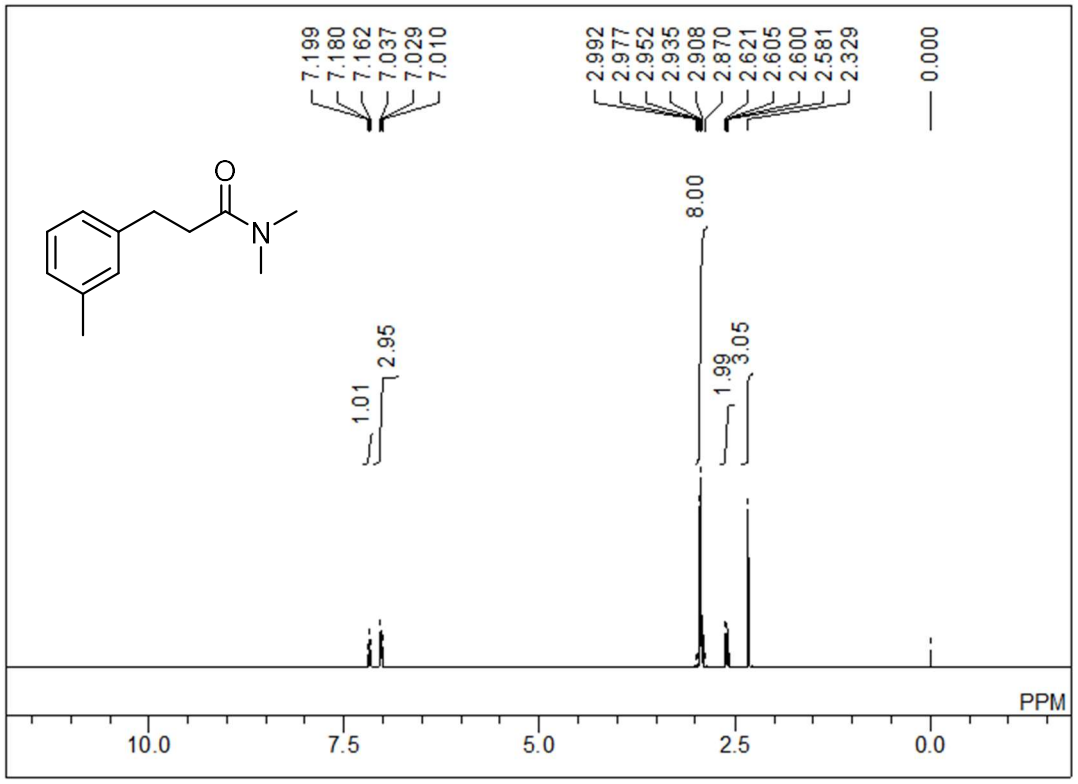
3b ^{1}H-NMR



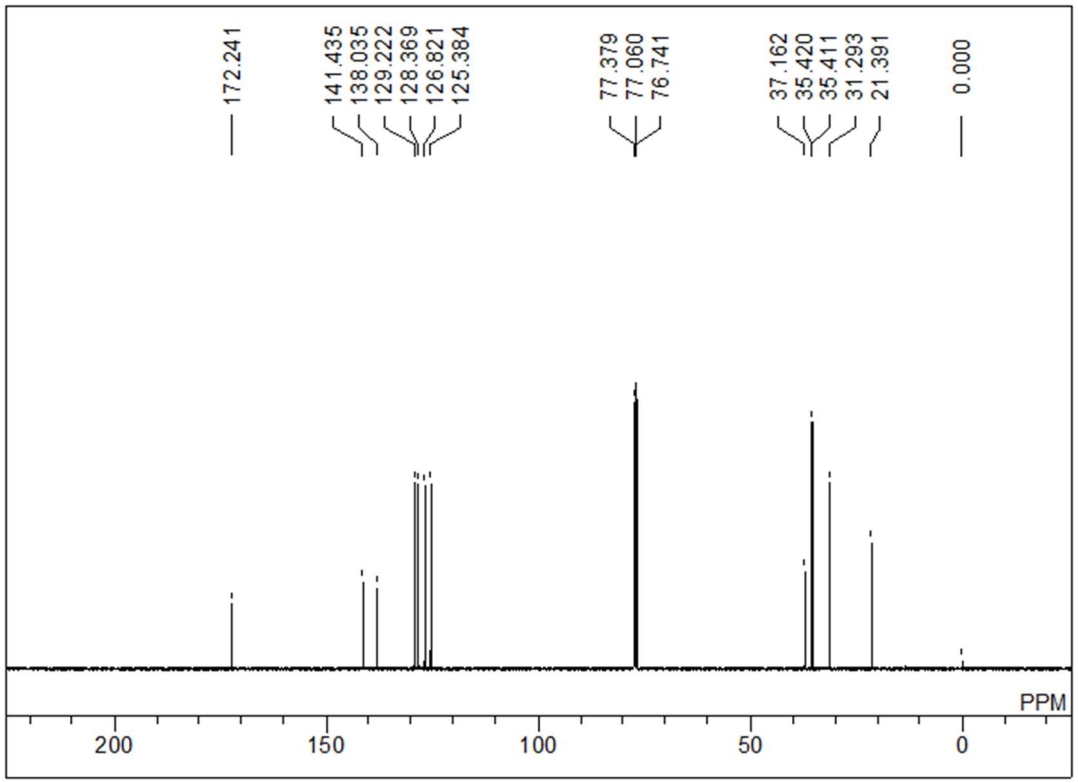
^{13}C-NMR



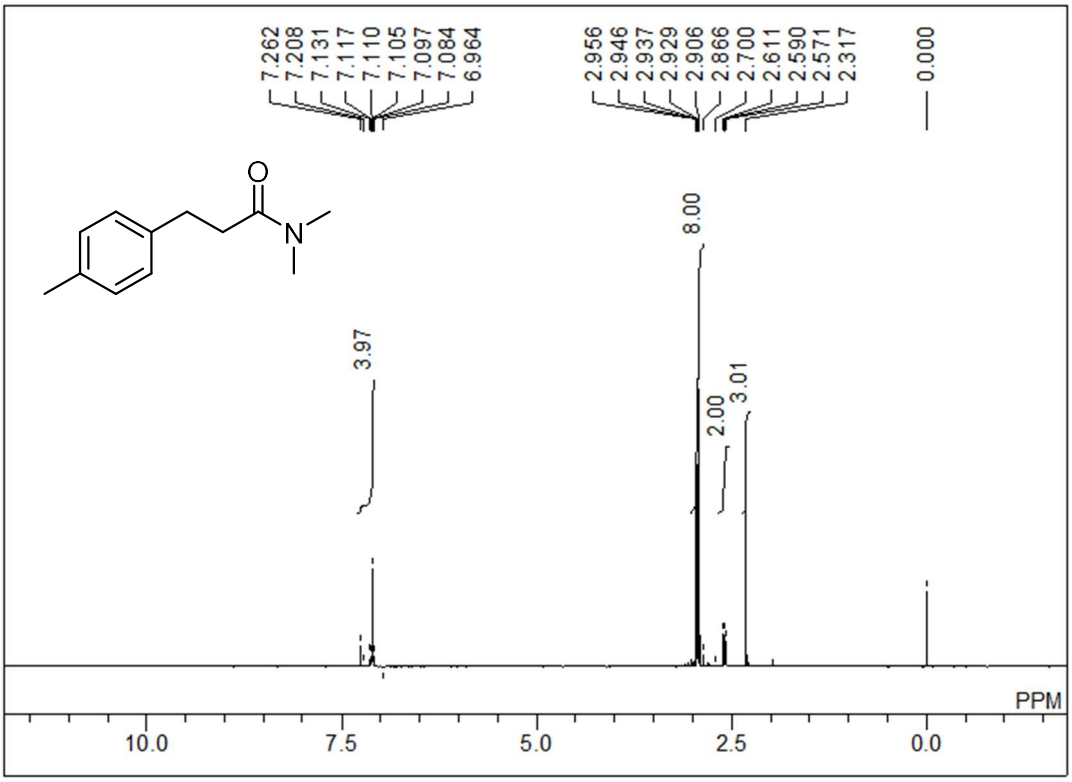
3c ^{1}H-NMR



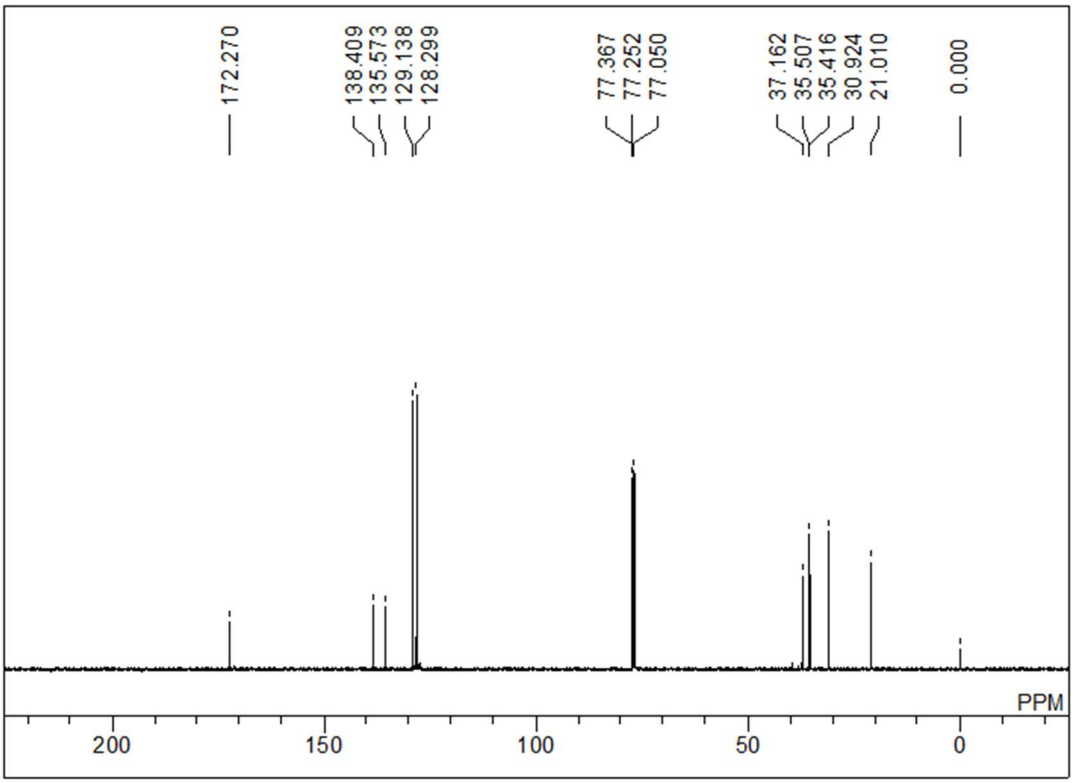
^{13}C-NMR



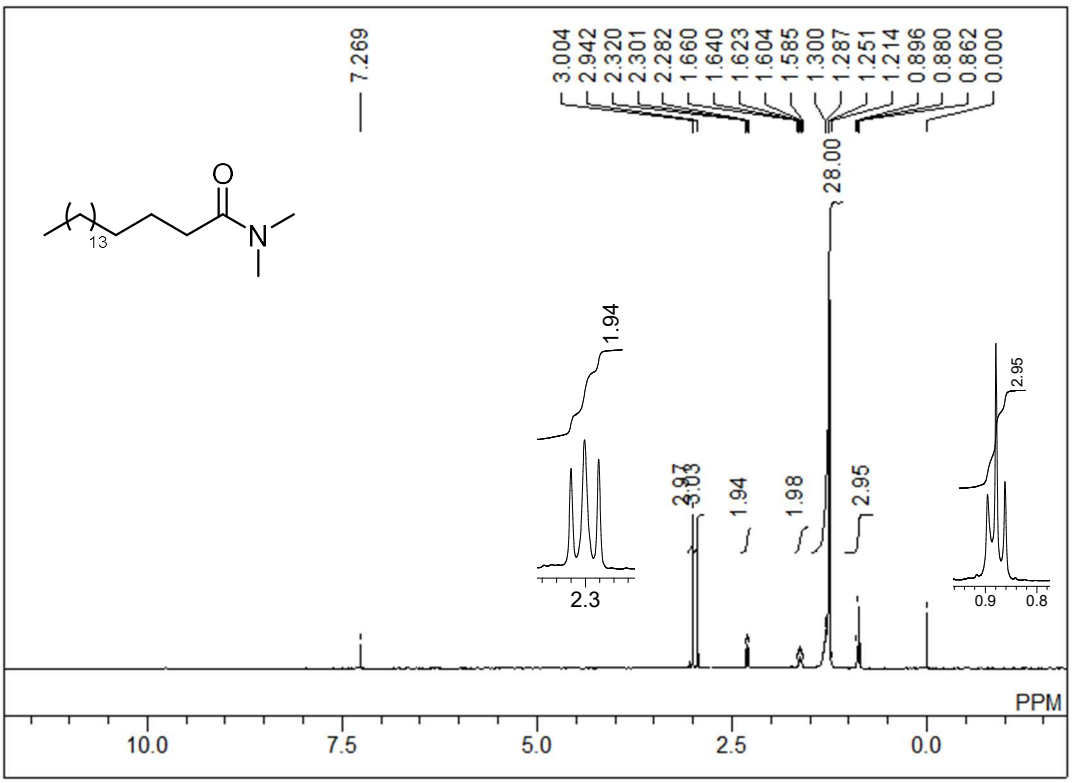
3d ^{1}H-NMR



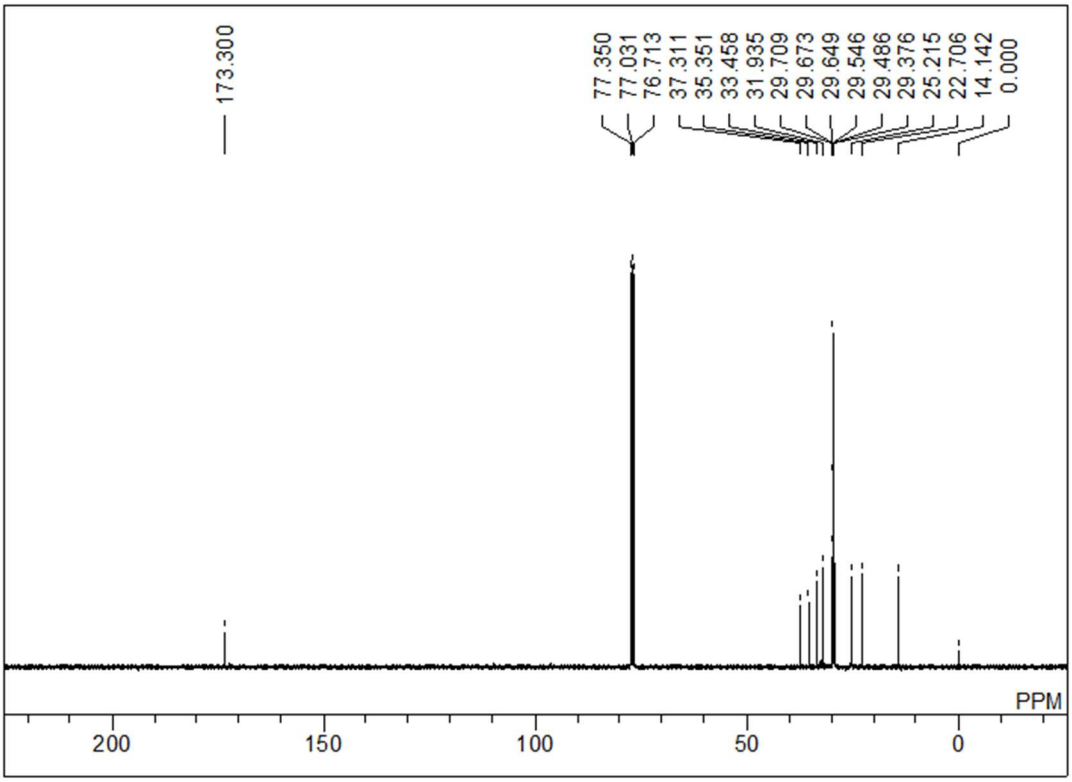
^{13}C-NMR



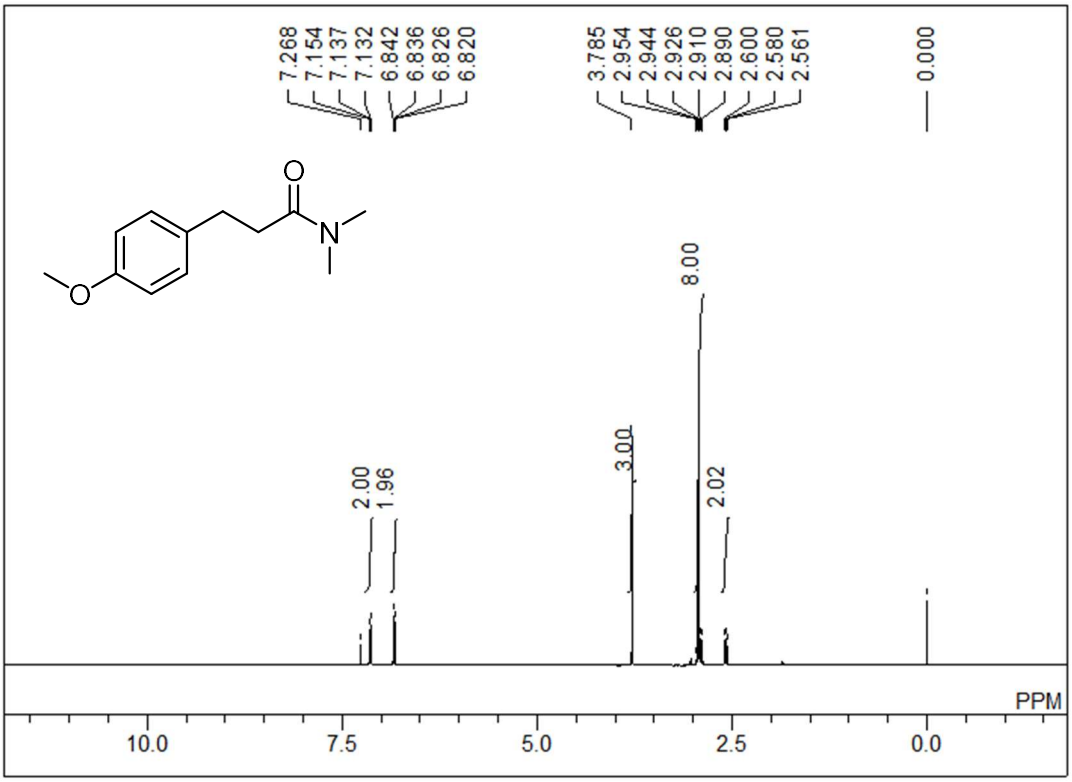
3e ^{1}H-NMR



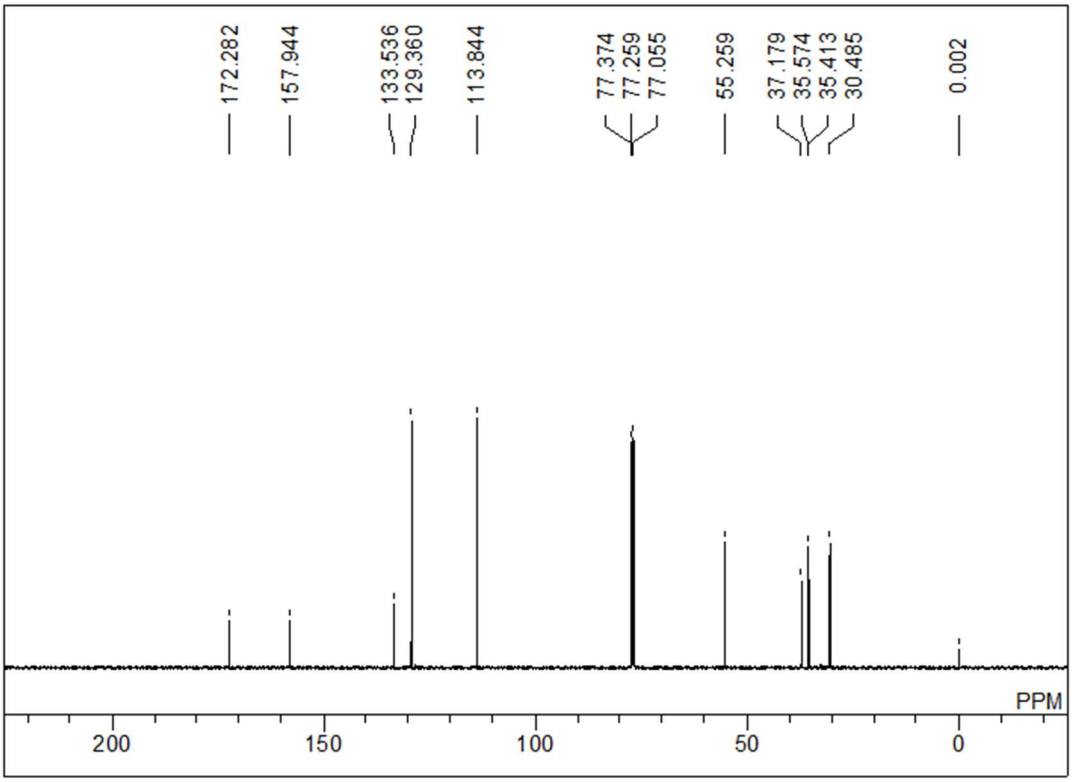
^{13}C-NMR



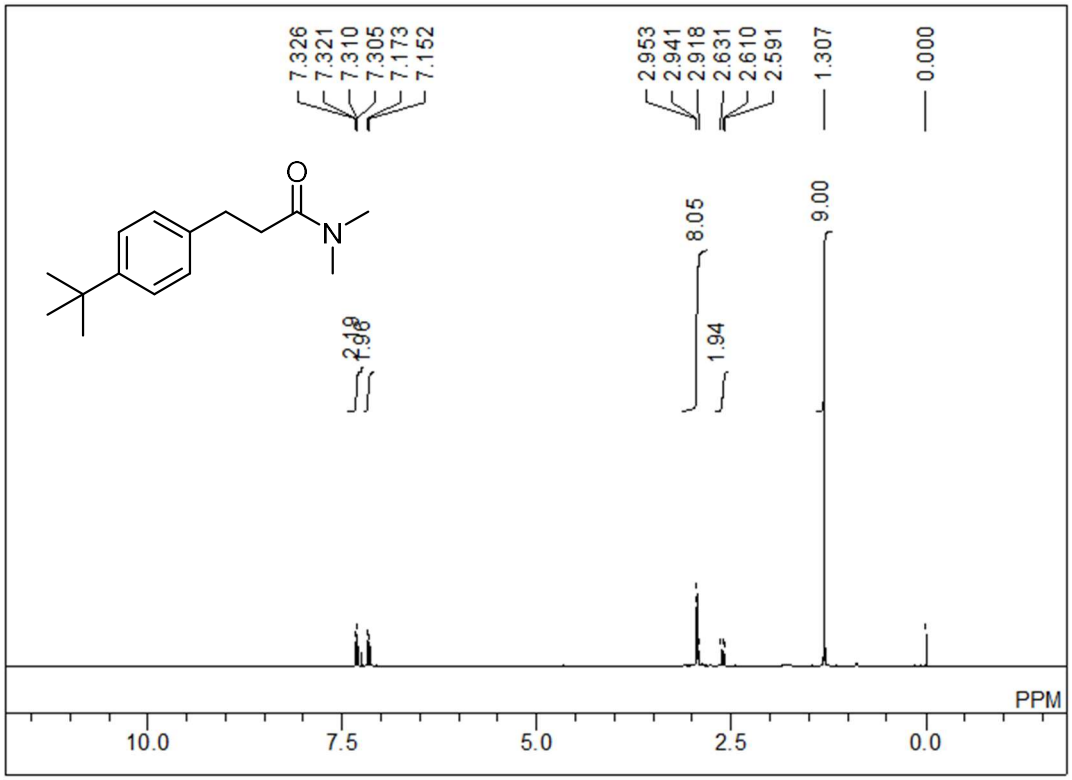
3f ^{1}H-NMR



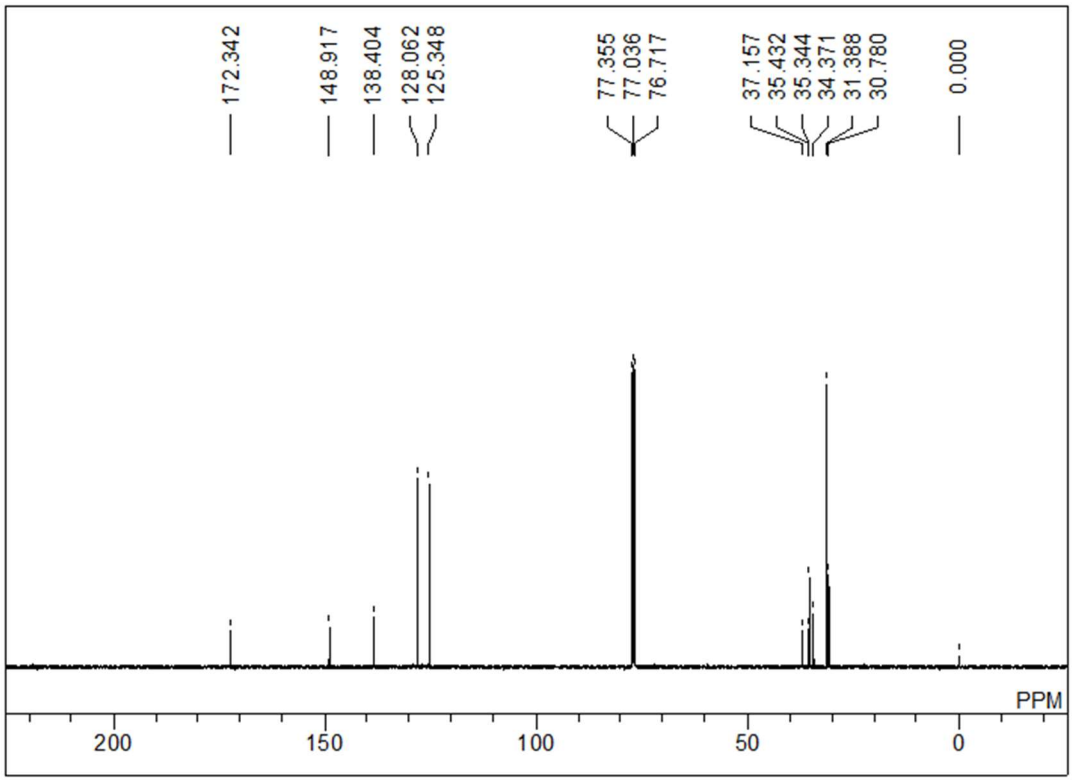
^{13}C-NMR



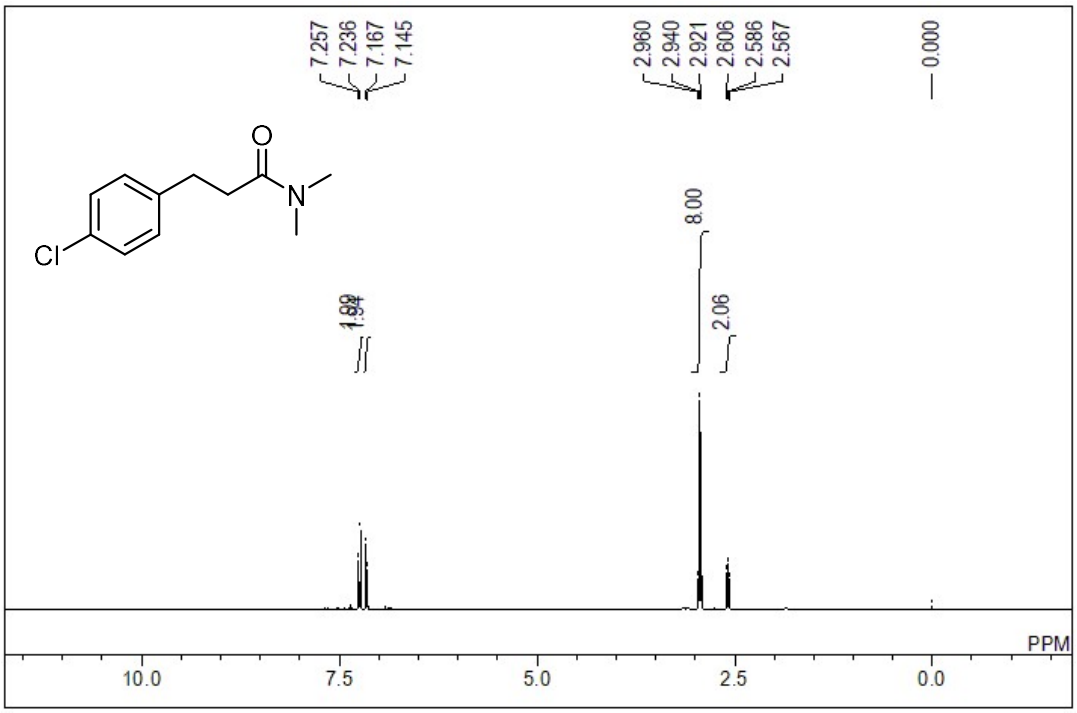
3g ^{1}H-NMR



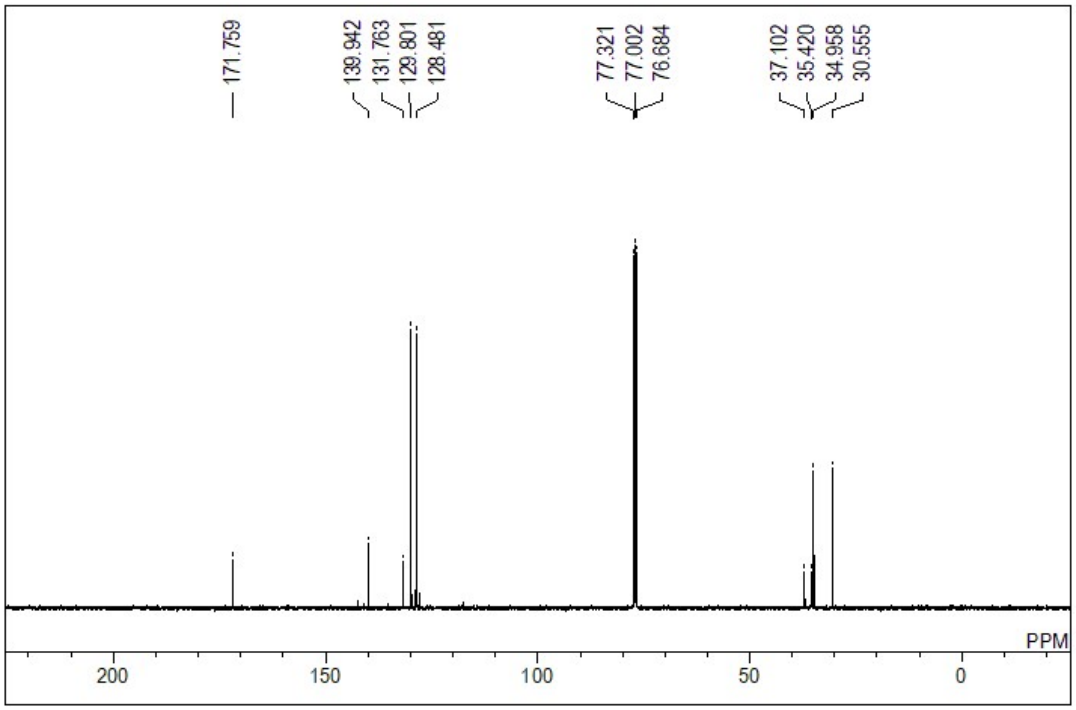
^{13}C-NMR



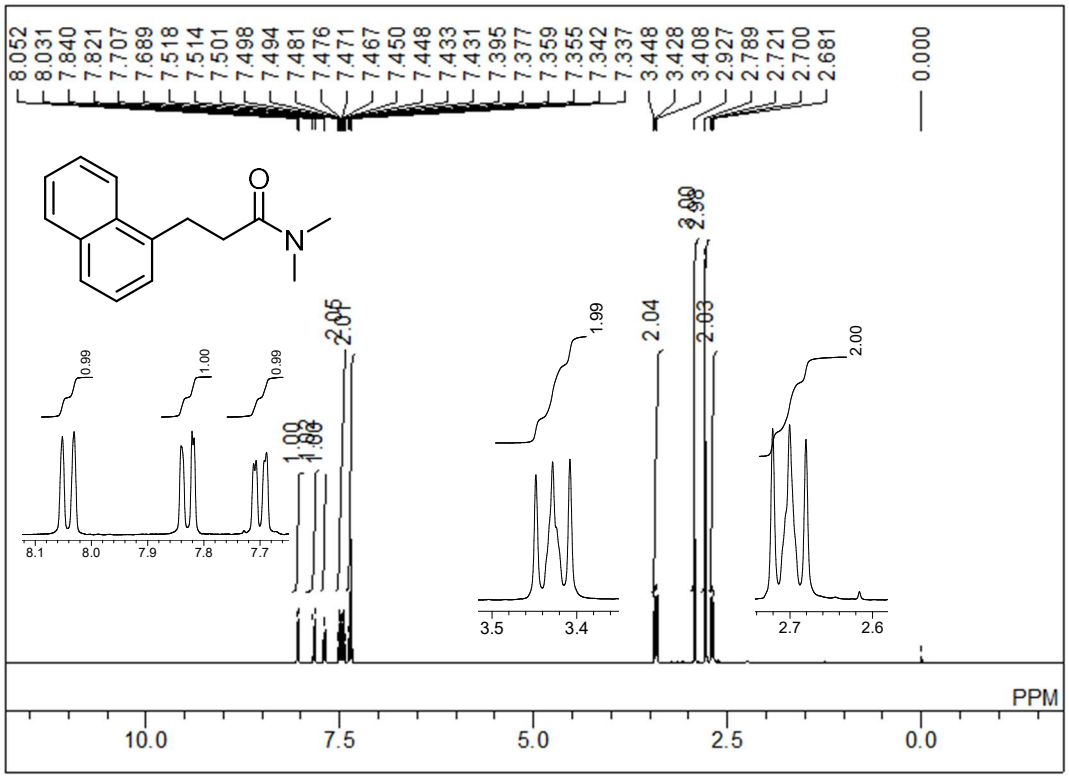
3h ^{1}H-NMR



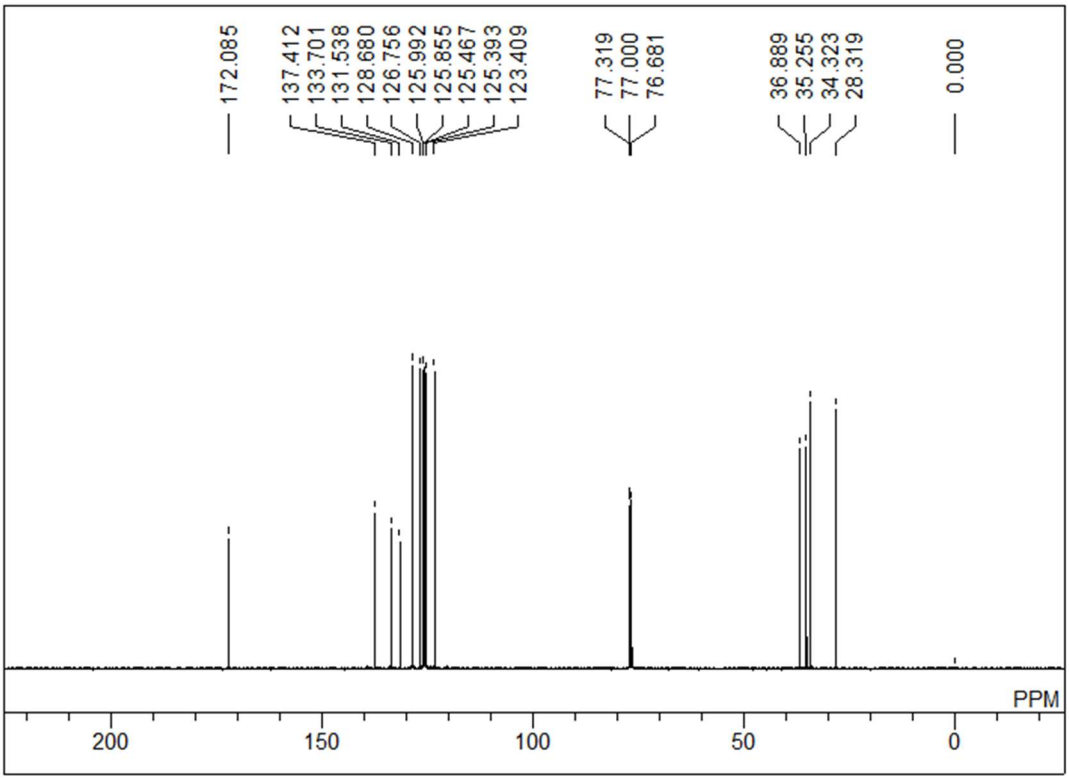
^{13}C-NMR



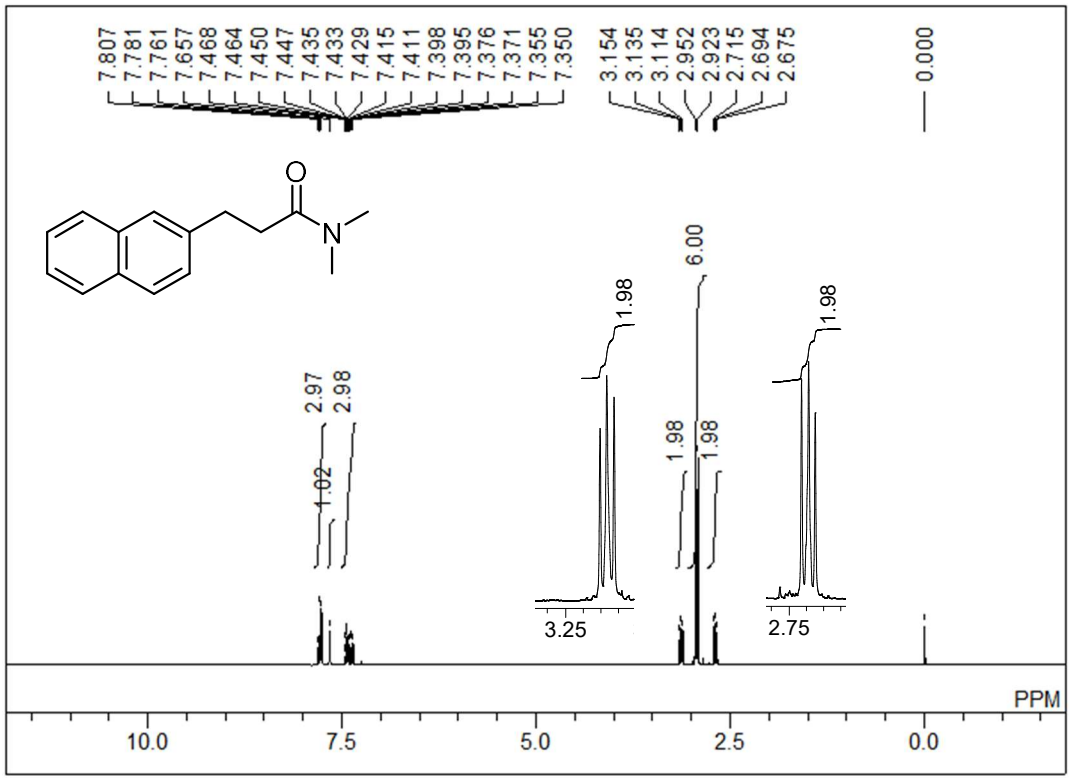
3l ^{1}H-NMR



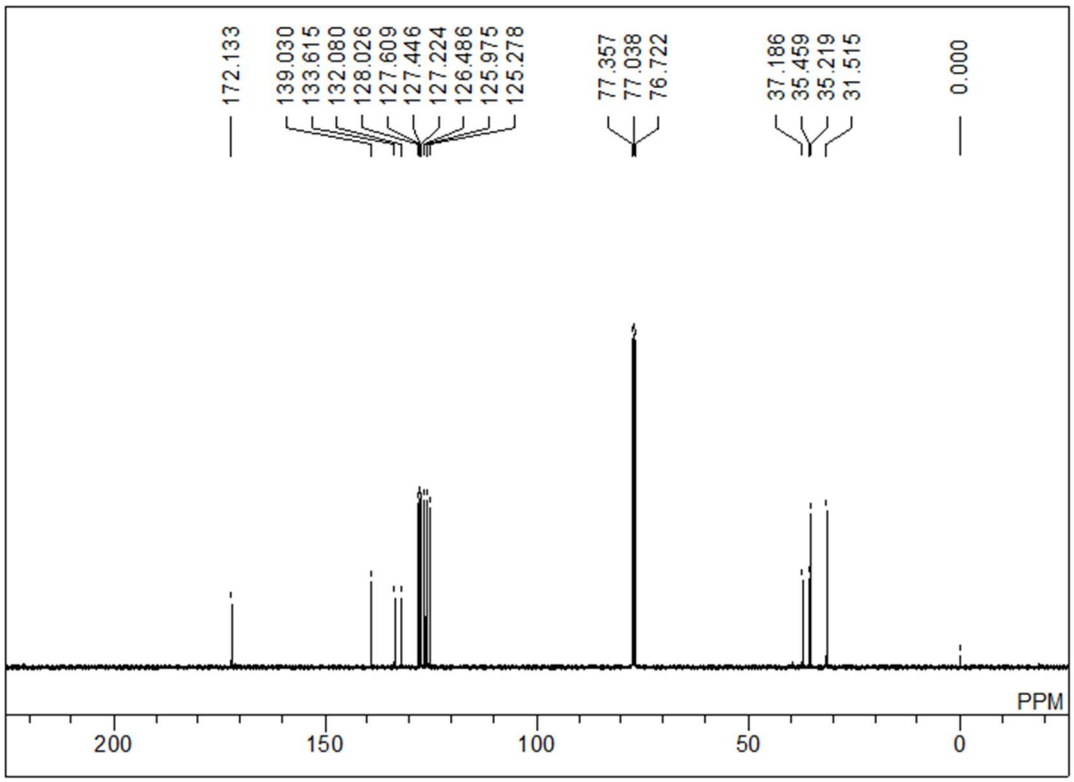
^{13}C-NMR



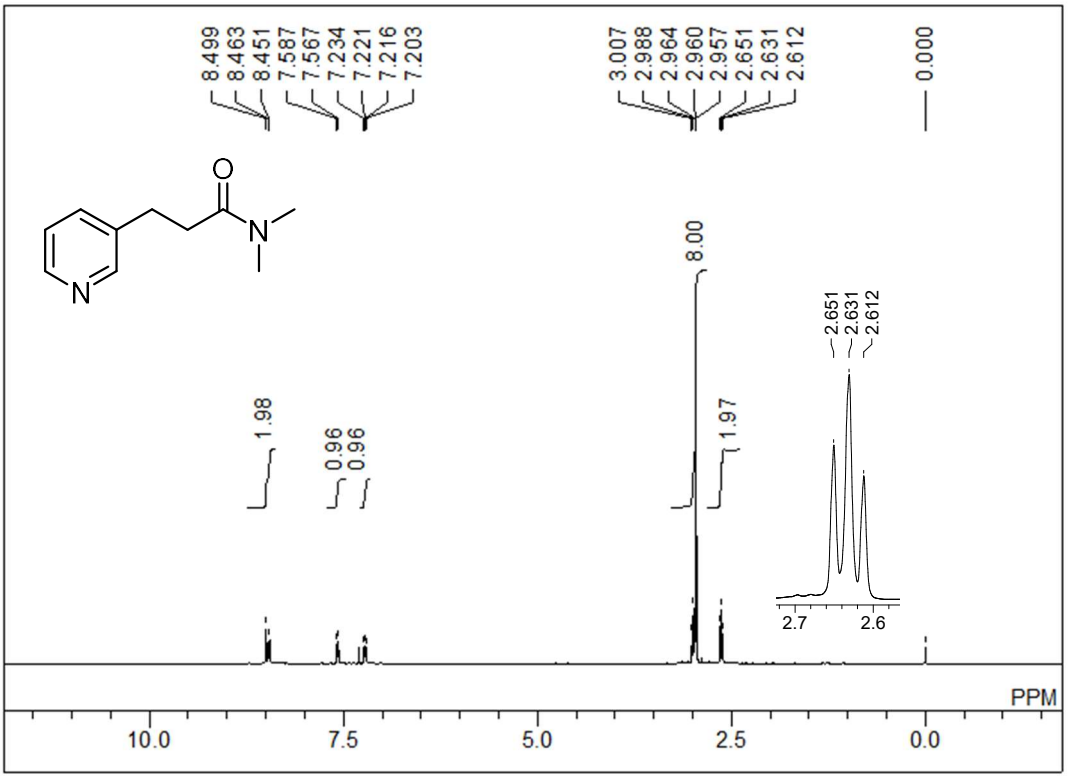
3m ^{1}H-NMR



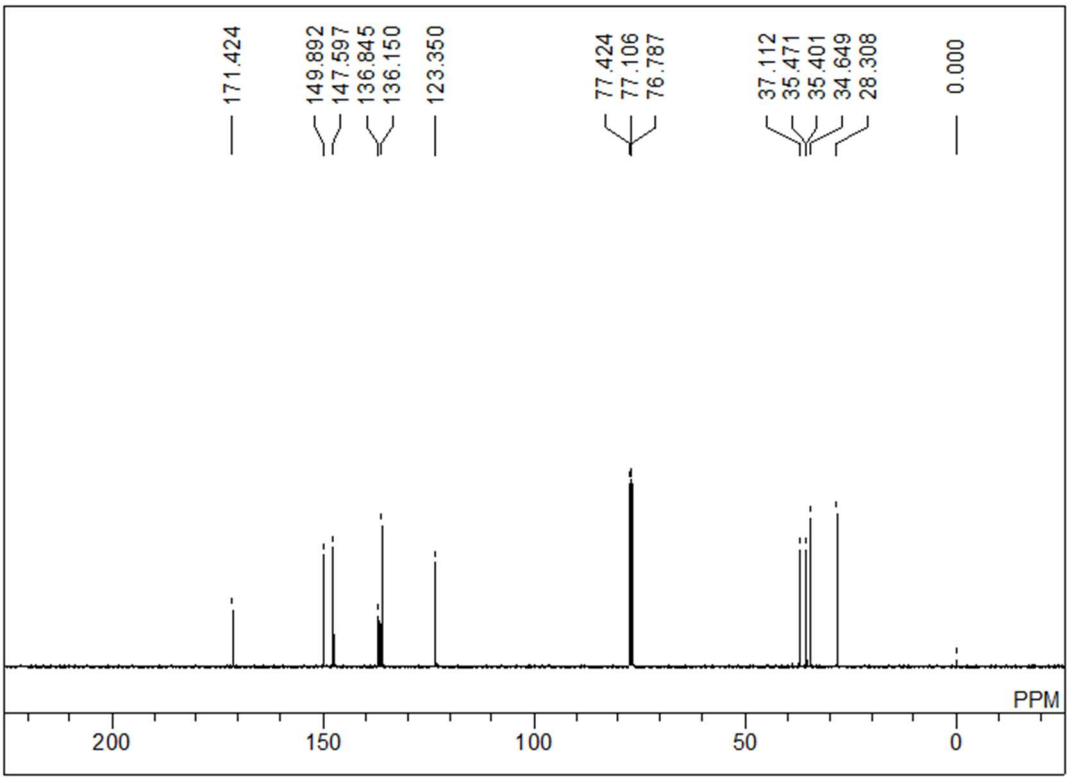
^{13}C-NMR



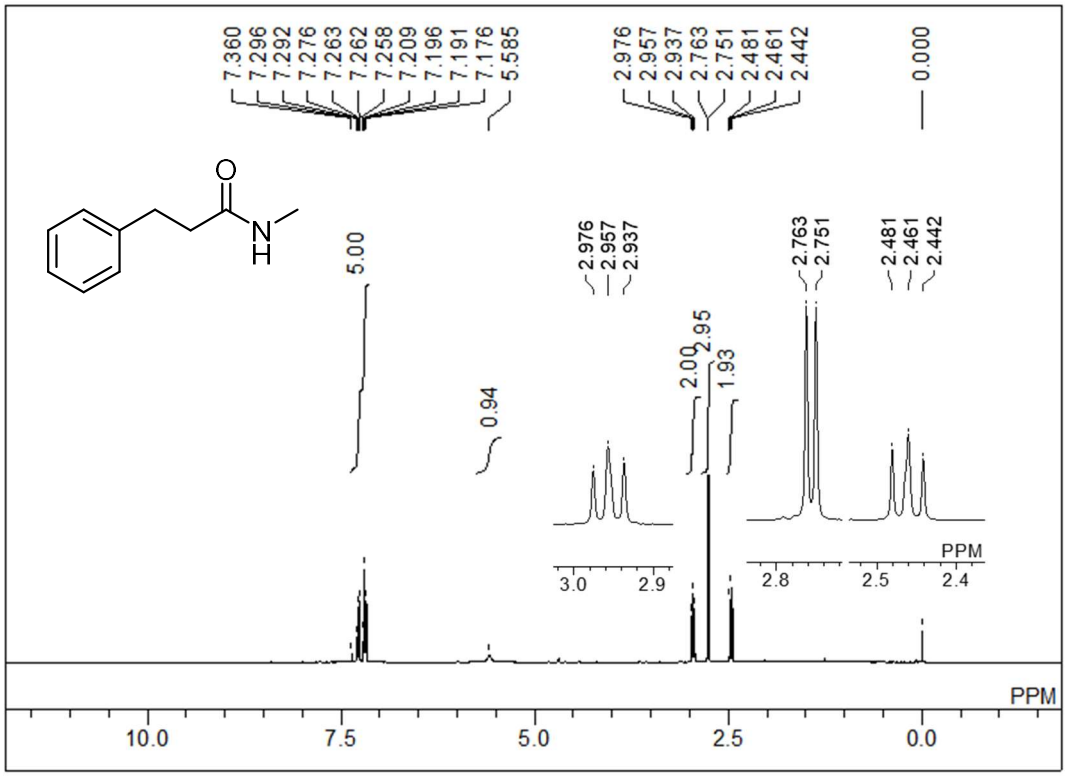
3n ^{1}H-NMR



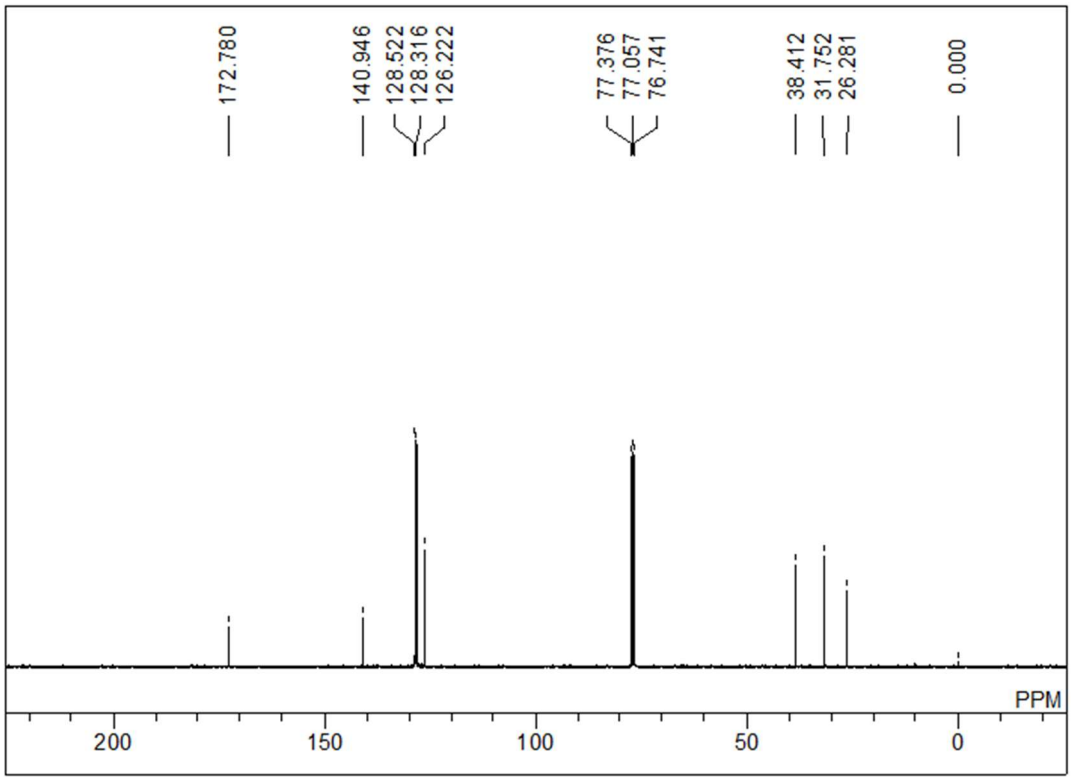
^{13}C-NMR



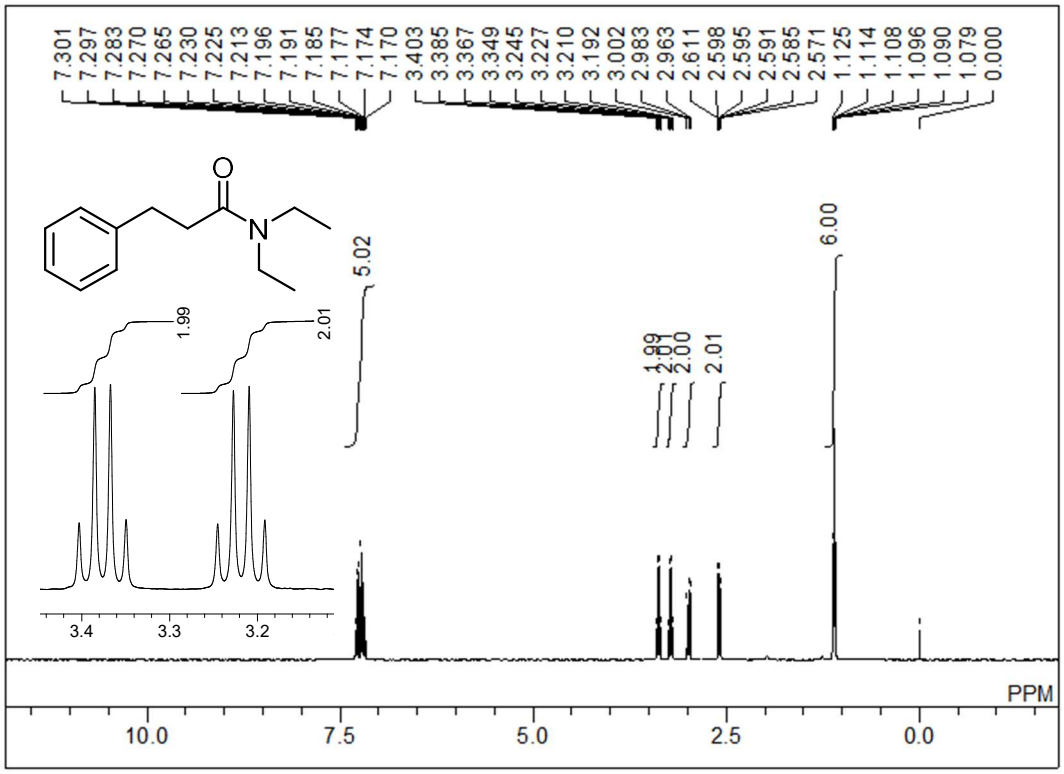
3q ^{1}H-NMR



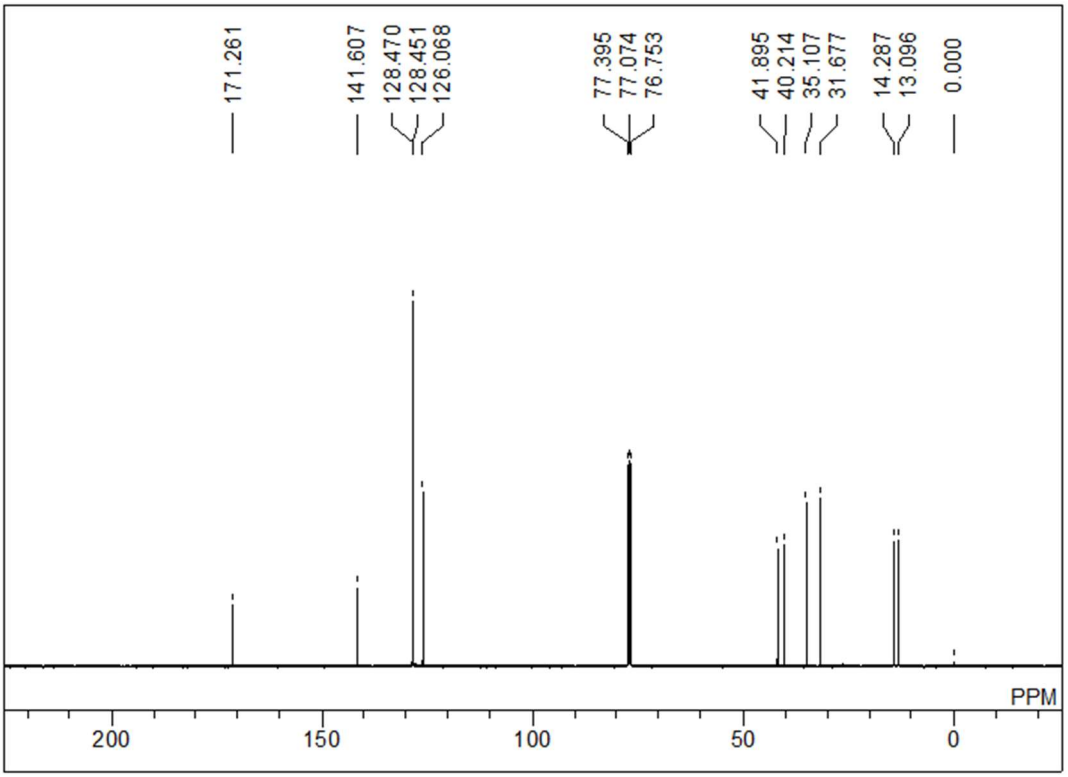
^{13}C-NMR



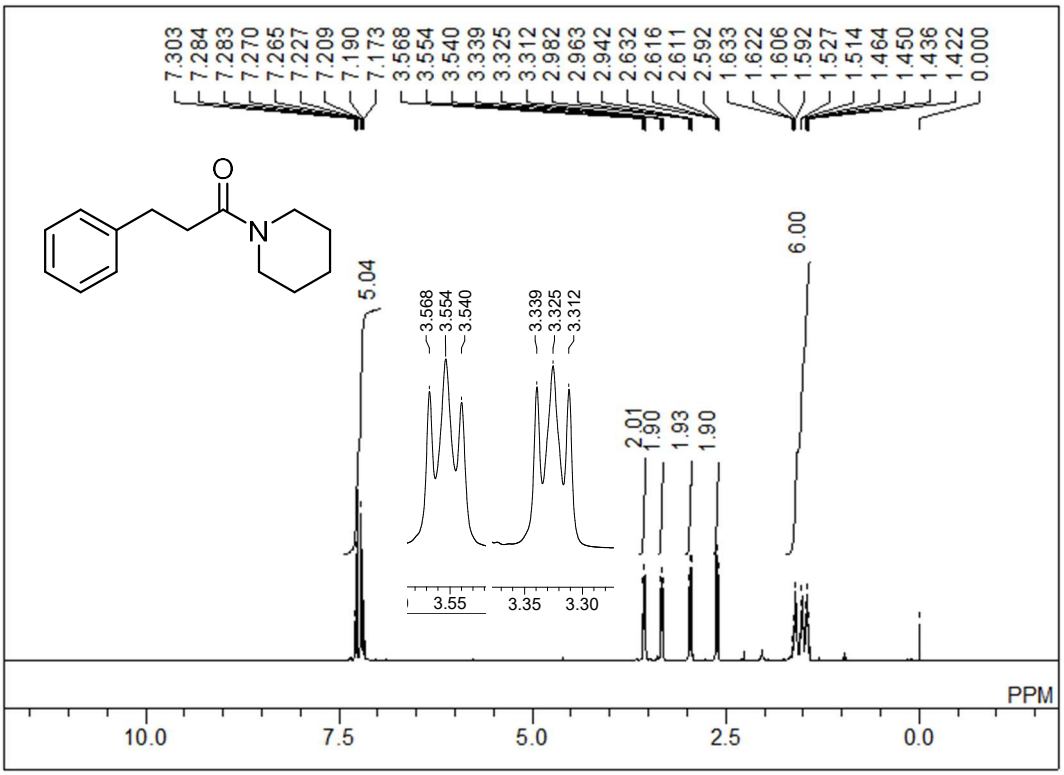
3r ^{1}H-NMR



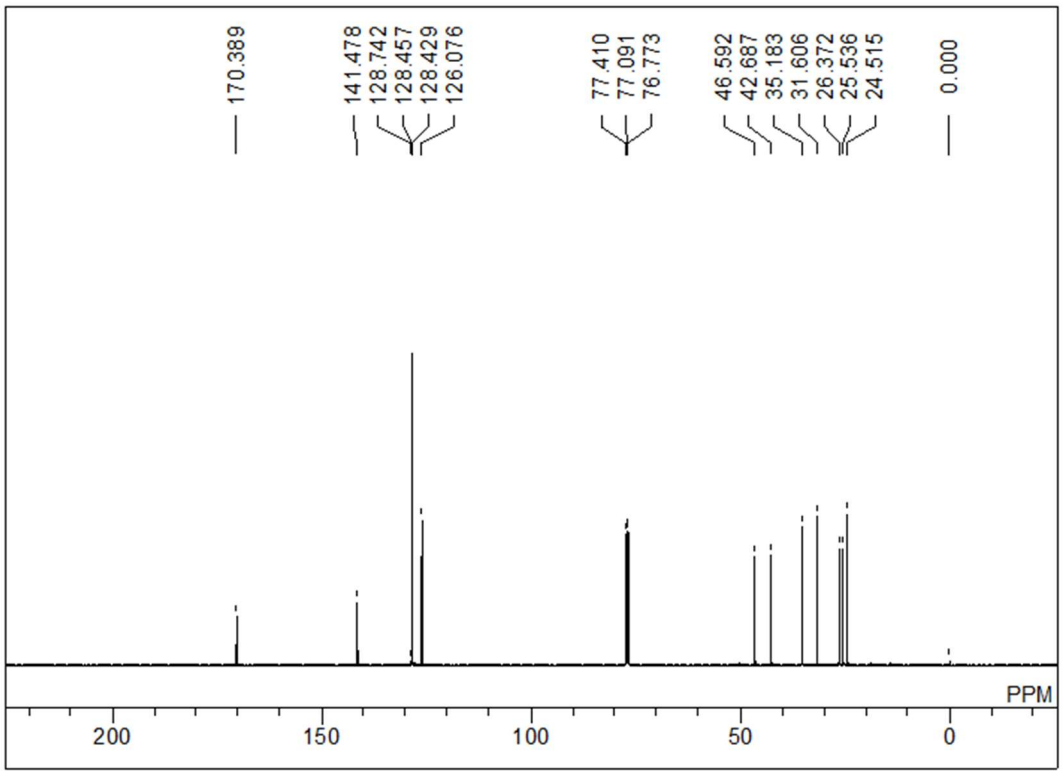
^{13}C-NMR



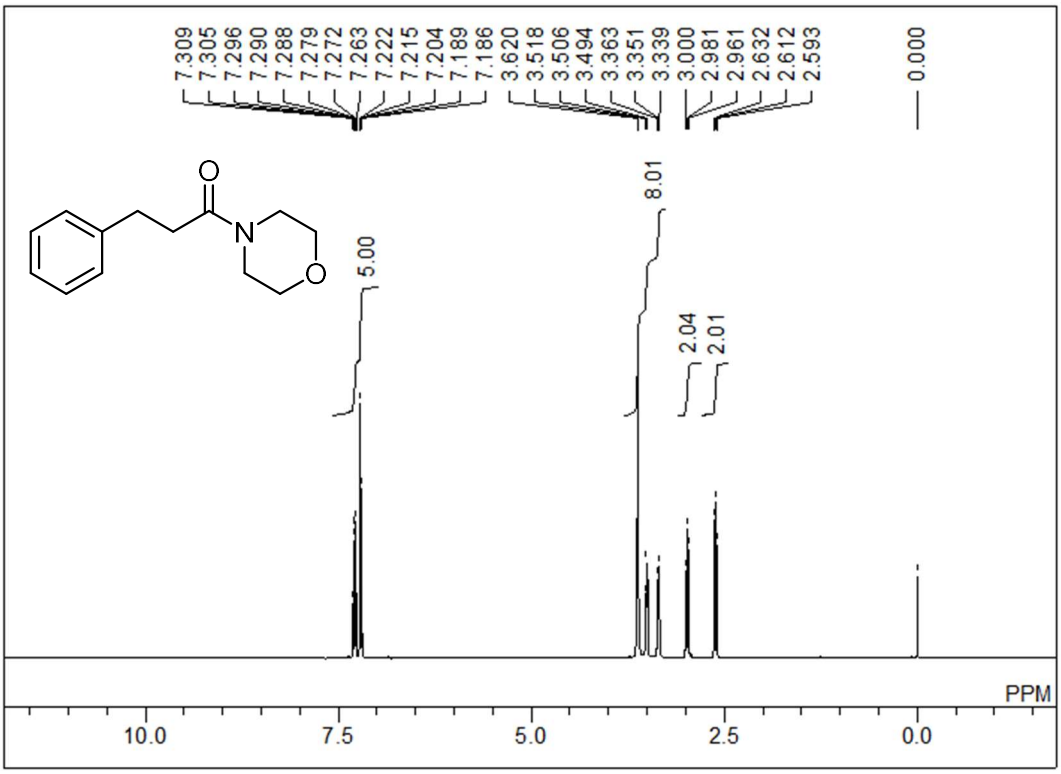
3s ^{1}H-NMR



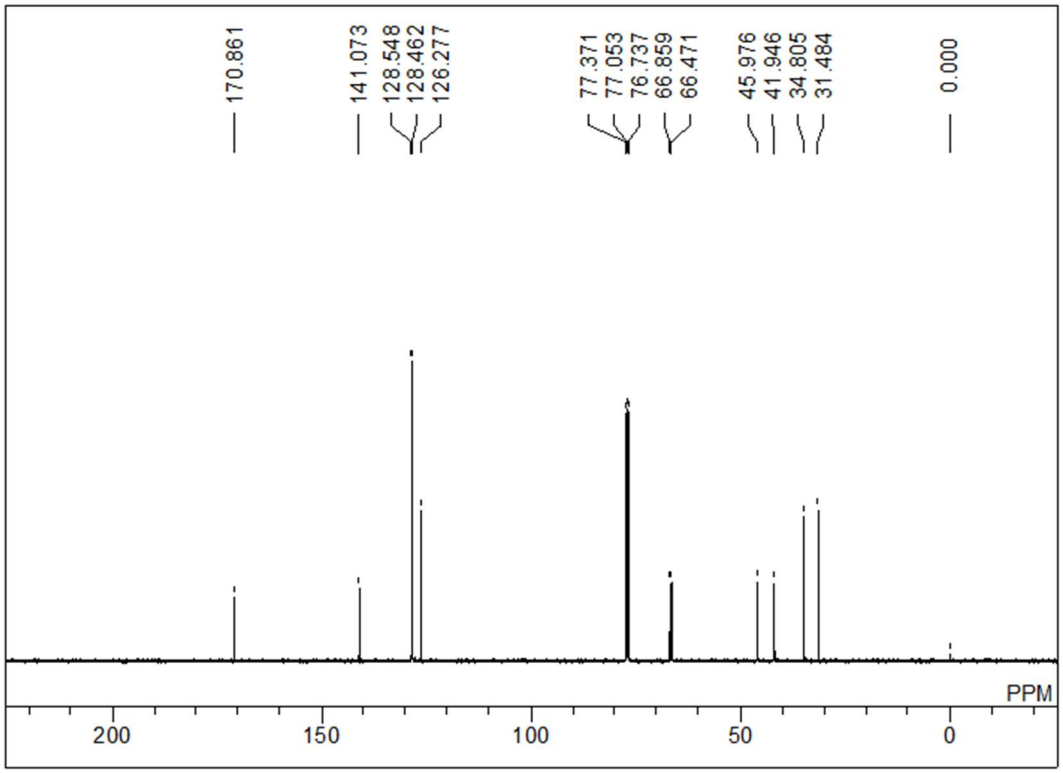
^{13}C-NMR



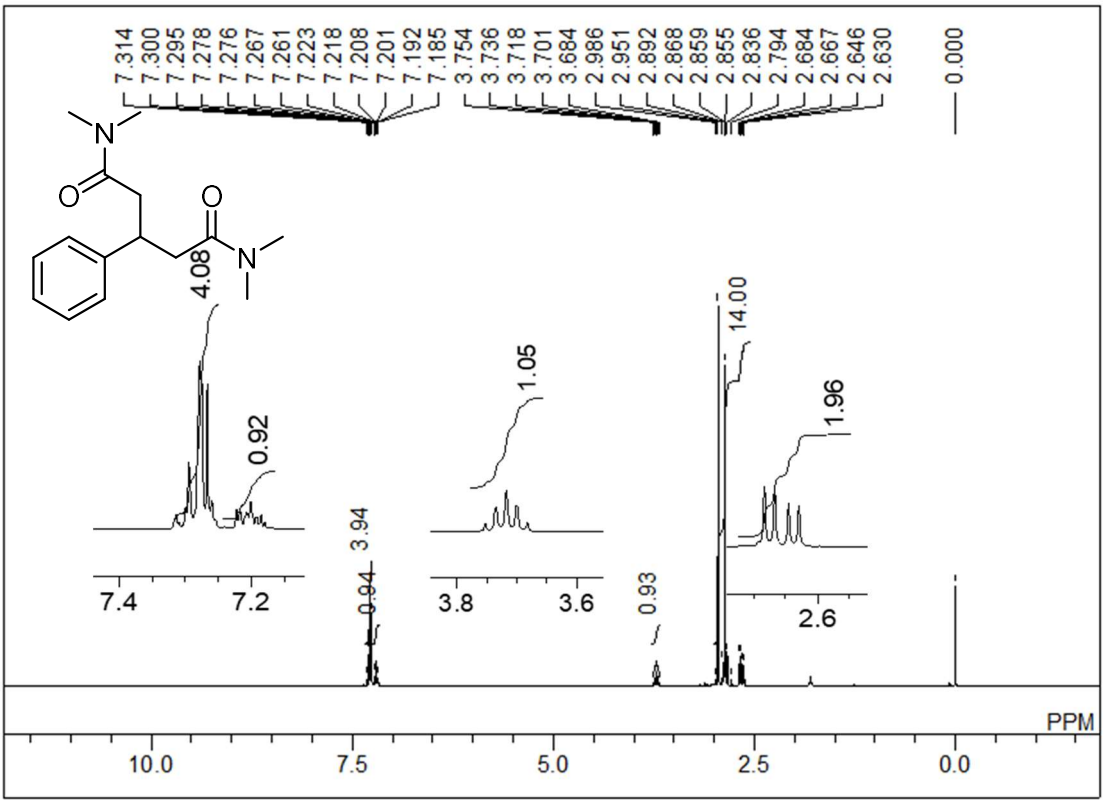
3t ^{1}H-NMR



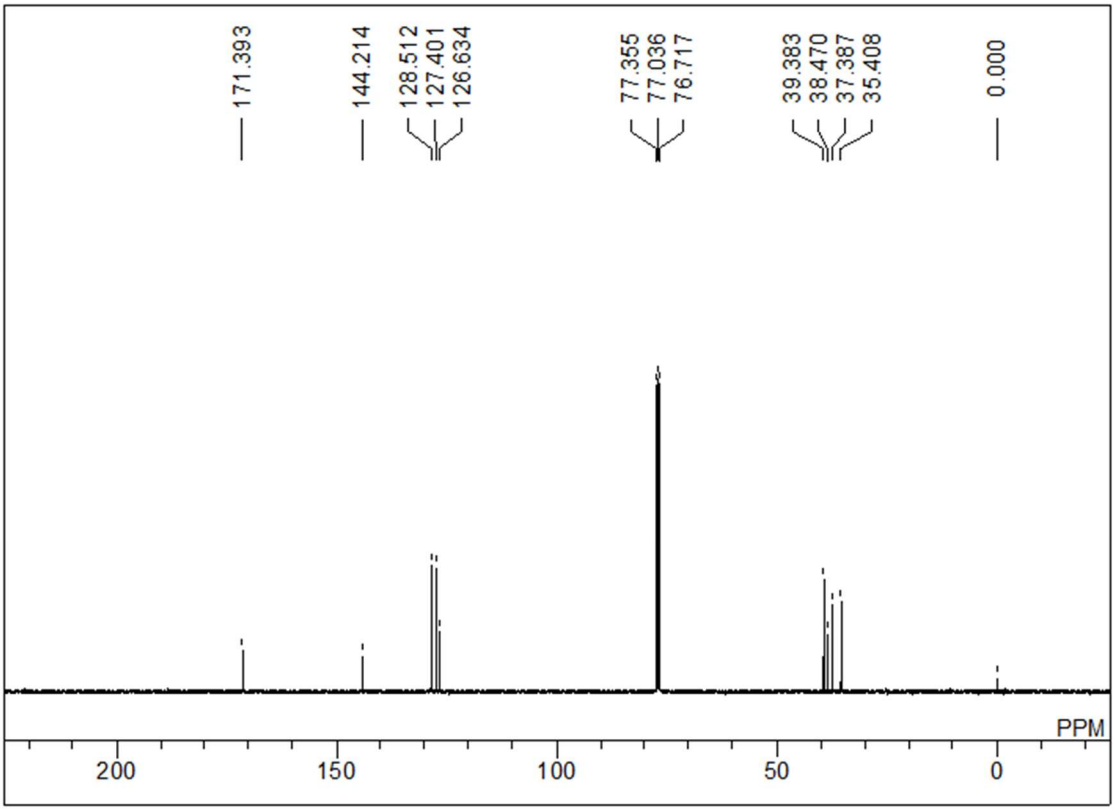
^{13}C-NMR



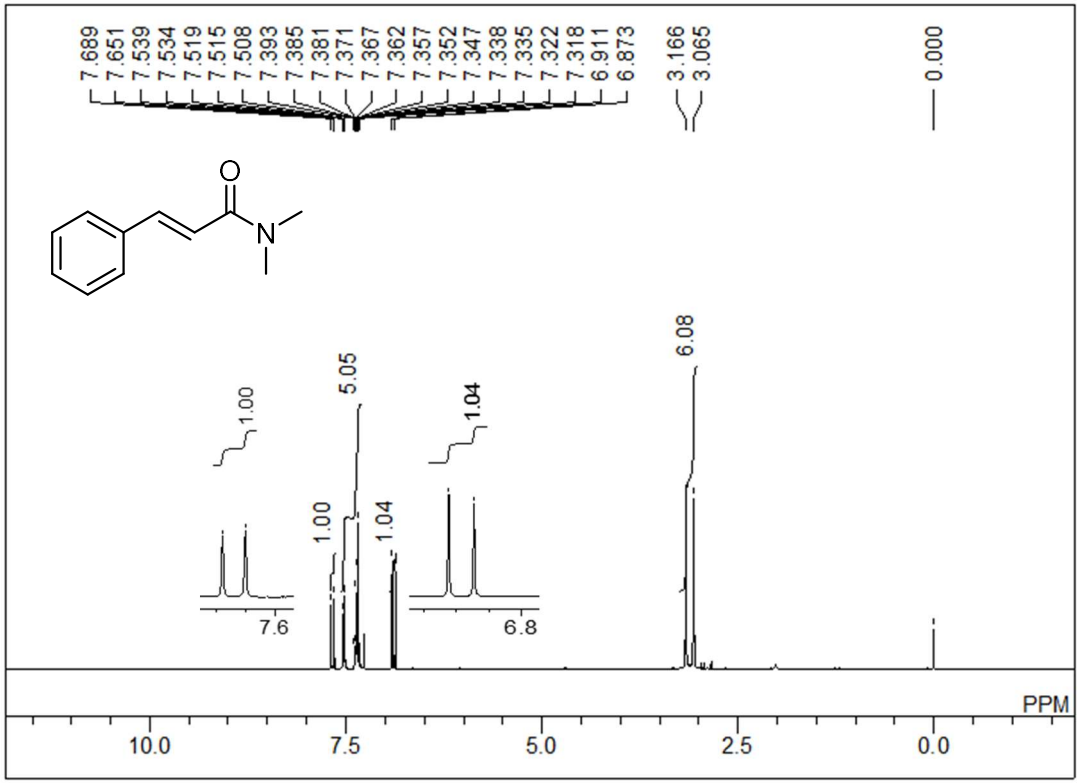
4a ^{1}H-NMR



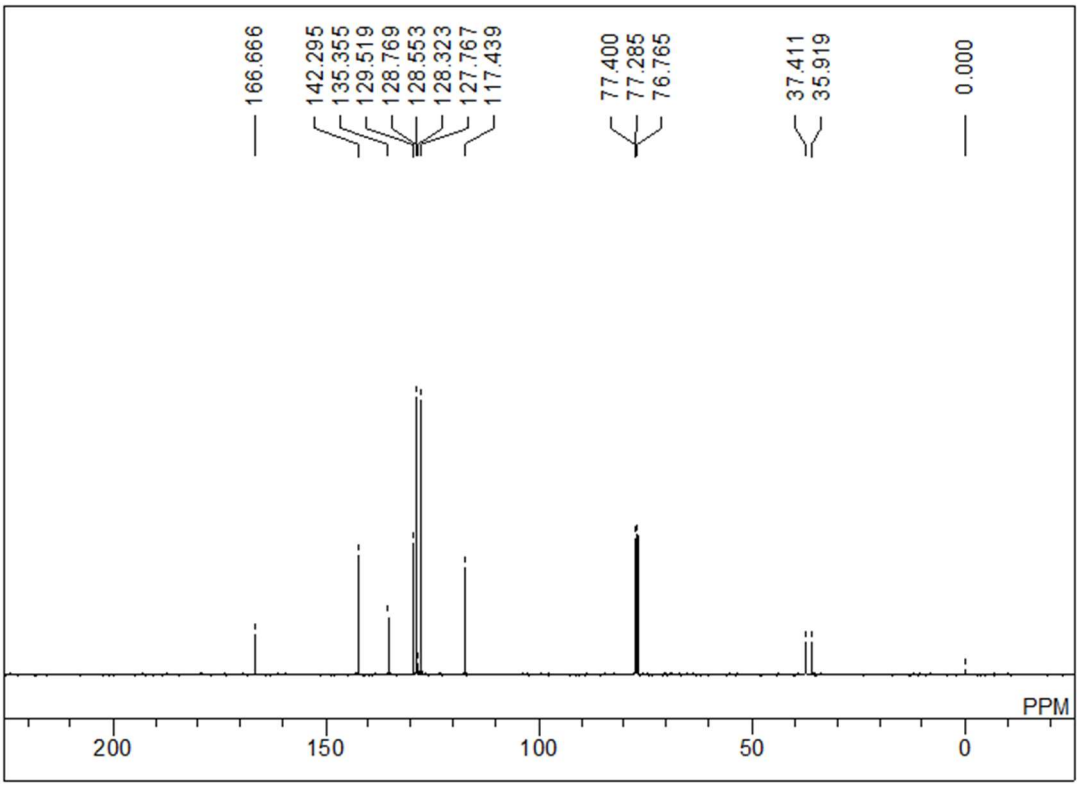
^{13}C-NMR



6a ^{1}H-NMR



^{13}C-NMR



11. References

1. N. Deibl and R. Kempe, *J. Am. Chem. Soc.*, 2016, **138**, 10786–10789.
2. K. Kurata, J. Ono and A. Dobashi, *J. Chromatogr. A*, 2005, **1080**, 140–147.
3. T. Kuwahara and T. Fukuyama, I. Ryu, *RSC Adv*., 2013, **3**, 13702.
4. D. Gong, B. Hu, W. Yang and D. Chen, *ChemCatChem*, 2019, **11**, 4841–4847.
5. Y. K. Jang, T. Krückel, M. Rueping and O. El-Sepelgy, *Org. Lett.*, 2018, **20**, 7779–7783.
6. M. B. Chaudhari, G. S. Bisht, P. Kumari and B. Gnanaprakasam, *Org. Biomol. Chem.*, 2016, **14**, 9215–9220.
7. S. A. Dandekar, S. N. Greenwood, T. D. Greenwood, S. Mabic, J. S. Merola, J. M. Tanko, and J. F. Wolfe, *J. Org. Chem.*, 1999, **64**, 1543-1553.
8. M. Lai, Z. Wu, F. Su, Y. Yu, Y. Jing, J. Kong, Z. Wang, S. Wang and M. Zhao, *Eur. J. Org. Chem*., 2020, **2020**, 198–208.