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Electronic Supplementary Information

Visible-light-mediated dehydrogenative cross-coupling between terminal alkynes and aldehydes by employing supramolecular polymeric ensemble of PBI derivative

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GENERAL EXPERIMENTAL SECTION

Materials and reagents: All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone as an indicator. UV-vis studies were performed in THF and distilled water .

Instrumentation: UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25°C. The fluorescence spectra were recorded with a SHIMADZU- 5301 PC spectrofluorometer. UV-vis spectra were recorded on Shimadzu UV-2450PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25°C. The scanning electron microscope (SEM) images were obtained with a field-emission scanning electron microscope (SEM CARL ZEISS SUPRA 55). The TEM mages was recorded from Transmission Electron Microscope (TEM) - JEOL 2100F.. The dynamic light scattering (DLS) data were recorded with MALVERN Instruments (Nano-ZS). Elemental analysis was done using a Flash EA 1112 CHNS/O analyser from Thermo Electron Corporation. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-AVANCE-II FT-NMR-AL 500 MHz spectrophotometer using $CDCl_3$, DMSO-d_6 as solvent and tetramethylsilane, SiMe4 as internal standards. Data are reported as follows: chemical shifts in ppm, multiplicity (s = singlet, br = broad signal, d = doublet, t = triplet, m = multiplet), coupling constants J (Hz), integration and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography.

UV-vis and Fluorescence Titrations. A 10^{-3} (M) stock solution of derivative **3** was prepared by dissolving 13.43 mg of derivative **3** in 10.0 ml of dry THF. 30 µl of this stock solution was further diluted with 2970 µl water/THF to prepare 3.0 ml solution of derivative 3 (10 µM) and this solution was used for each UV-vis experiment.

Synthesis of PBI derivative 3

To a solution of **1** (0.5 g, 0.5656 mmol) and **2** (0.438 g, 1.24 mmol) in 20.0 mL 1,4 dioxane were added potassium carbonate (1.2 g, 4.52 mmol) and distilled water (2.0 mL).The reaction mixture was charged with [Pd(PPh_3)$_2$$Cl_2$] as catalyst (0.326 g, 0.28 mmol) under an N_2 atmosphere and it was refluxed at 90°C. After 24h it was cooled to RT. The 1,4-dioxane was then removed under vacuum, treated with water (25 mL) and extracted with chloroform (3 × 20 mL). The combined organic layer was then washed with water, dried over anhydrous Na_2SO_4 and removed under reduced pressure to give a solid residue. This residue so obtained was purified by column chromatography using chloroform/methanol mixture (98:2) which gave derivative 3 in 60 % yield a dark red solid, melting point: 235°C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 8.83 (s, 4H), 8.76 (d, J = 8 Hz, 4H), 8.72 (d, J = 8 Hz, 4H), 8.68 (s, 2H), 8.22 (d, J = 8 Hz, 4H), 8.07 (d, J = 8 Hz, 2H), 7.94 (d, J = 8 Hz, 4H), 7.89-7.91 (m, 2H), 7.74 (d, J = 8 Hz, 4H), 7.39-7.37 (m, 4H), 4.19 (t, J = 4 Hz, 4H), 1.72 (s, 4H), 1.24 (s, 36H), 0.86 (t, J = 6 Hz, 6H). The ^{13}C NMR (CDCl3, 125 MHz, ppm) 163.5, 156.2, 149.2, 142.8, 140.3, 138.9, 137.0, 135.2, 134.7, 132.7,130.4, 129.8, 129.2, 127.8, 124.0, 122.4, 122.1, 121.4, 118.9, 31.9, 29.7, 29.6, 29.5, 29.4, 27.2, 22.7, 14.1. The mass spectrum of derivative **3** showed a parent ion peak at m/z = 1341.6642 [M] (Fig. S17-19, ESI†); Elemental analysis: calcd for C90H84N8O4: C, 80.57; H, 6.31; N, 8.35; O, 4.77. Found: C, 80.56; H, 6.32; N, 8.33; O, 4.79.

Preparation of the supramolecular polymer 4:ZnO NPs

A solution of derivative **3** (10 µM, 3 mL) in (H_2O/THF ,1:1) and Zn(ClO_4)$_2$ in THF (0.1 M) was stirred for 14 h at RT After continuous stirring the colour of the mixture changed from red to light yellow green demonstrating the formation of the supramolecular polymer 4:ZnO NPs. The resulting solution was sonicated to obtain a homogeneous mixture and 500 µl of this solution (4 µmol) was used as such in each photocatalytic experiment

Table S1: Comparison of method for the preparation of supramolecular polymer **4**: ZnO NPs in this manuscript with other reported methods in the literature for the preparation of ZnO NPs.

Entry	**Method of preparation of NPs**	**NPs**	**Reducing agent/Oxidizing agent**	**Special additive or surfactant**	**Temp. (°C)**	**Time**	**Shape of NPs**	**Size (nm)**	**Application of NPs**	**Journals**
1	**Wet Chemical method**	**Supramolecular polymer 4:ZnO NPs**	**No**	**No**	**RT**	**14 h**	**Spherical**	**3-5**	**Photocatalytic Dehydrogenative coupling reaction**	**Present manuscript**
2	Sol-gel	ZnO	Yes	Yes	RT	-	Thorn	50	Nano-antibiotics	*Scientific Reports* 6:27689 DOI: 10.1038/srep27689
3	Chemical method	ZnO	Yes	No	60 °C	3 h	Nanosheet-Nanorod	50-80	NO_2 Sensor	*ACS Appl. Mater. Interfaces* 2016, 8, 8600−8607
4	Ball milling methodology	ZnO	Yes	No	600 °C	3 h	Hexagonal and flower like	3-5	Photocatalytically	*Green Chem.*, 2014, 16, 2876–2885 | 2877
5	Coprecipitation method	ZnO	Yes	Yes	60 ^{0}C	24 h	Nanofake-like	38	Antibacterial	*J. Mater. Chem.* B, 2013, 1, 5950–5962
6	Microfuidic system	ZnO	Yes	No	60 ^{0}C	-	Irregular morphology	3-5	Photovoltaic application	*Nanoscale,* 2014, 6, 2840
7	Chemical method	ZnO	Yes	-	-	-	Irregular morphology	20	Photocatalytic oxidation of methane	*Natu.Commun.* 7:12273 DOI: 10.1038/ncomms12273
8	Wet chemical method	ZnO	No	No	RT	3 h	Spherical shape	10-20	One-pot multicomponent synthesis of tetrahydropyridines	*Chem. Commun.,* 2015, 51, 1483
9	Cryogenic ball-milling	ZnO	Yes	No	600 ^{0}C	3 h	Quasi-spherical	60	antibacterial	*J. Mater. Chem.* B, 2014, 2, 3065
10	wet chemical method	ZnO	Yes	No	500-800 ^{0}C	-	Nanocubes.	~4–5	Photocatalyst	*Green Chem.*, 2012, 14, 2790
11	Chemical method	ZnO	Yes	No	60 ^{0}C	3 h	Speherical	5	Thin-Film Transistors	*Chem. Mater.* 2012, 24, 3517−3524

Table S2: Comparison of catalytic efficiency of supramolecular ensemble **4**: ZnO NPs for the photocatalytic dehydrogenative coupling with other reported photocatalysts in literature.

Serial.No	**Catalyst**	**Time**	**Temparature (˚C)**	**Publication**
1	**Supramolecular polymer 4:ZnO NPs**	**24 h**	**RT**	**This manuscript**
2	$CuBr_2$	12 h	60	*ACS Catal*. 2016, 6, 1263−1267
3	$Zn(OTf)_2$	27 h	80	*Angew. Chem. Int. Ed*. 2015, 54, 15850 –15853
4	$AuCl_3$	10 h	40	*J. Am. Chem. Soc.* 2014, 136, 12233−12236
5	copper nanoparticle	24 h	40	*Green Chem.,* 2013, 15, 2356–2360
6	Pd catalyst	1 h	110	*J. Org. Chem*, *Vol. 69*, *No. 5*, *2004*
7	iodine reagents	3 h	120	*z*
8	Ir (III)- and Rh (III)-catalyzed,	20 h	RT	*Org. Lett*. 2015, 17, 920−923
9	$Cu(OTf)_2$	14 h	60	*Org. Lett*., Vol. 15, No. 17, 2013
10	$ZnBr_2$	24 h	100	*J. Am. Chem.Soc*. 2012, 134, 2504−2507

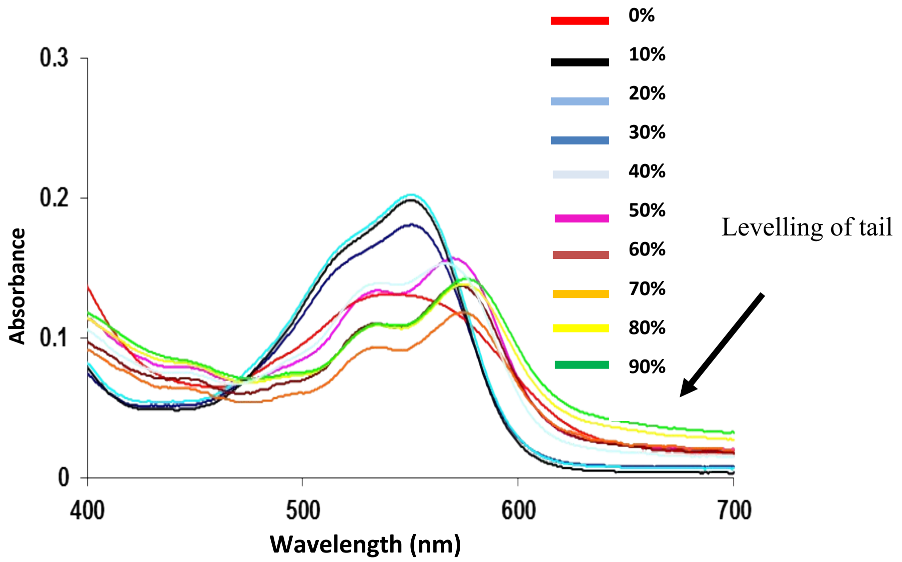


Fig. S1 UV-vis spectra showing variation of absorption intensity of derivative **3** in different H_2O/THF mixtures.

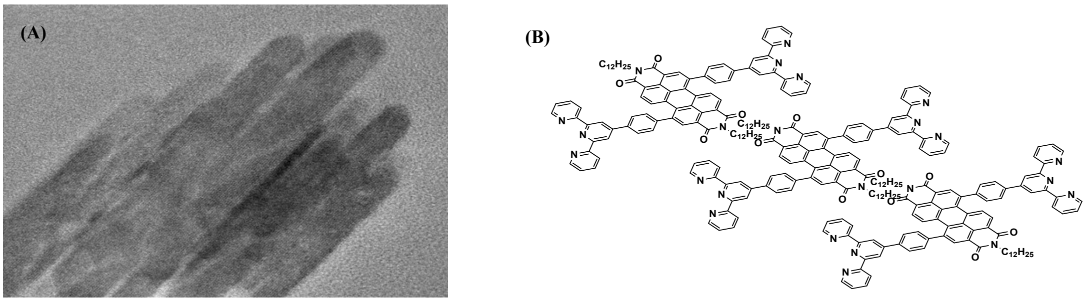


Fig. S2 (A) TEM image of aggregates of derivative **3** in H_2O/THF (1:1); (B) Schematic diagram showing formation of *J*-aggregates of derivative **3** in H_2O/THF (1:1) solvent mixture.

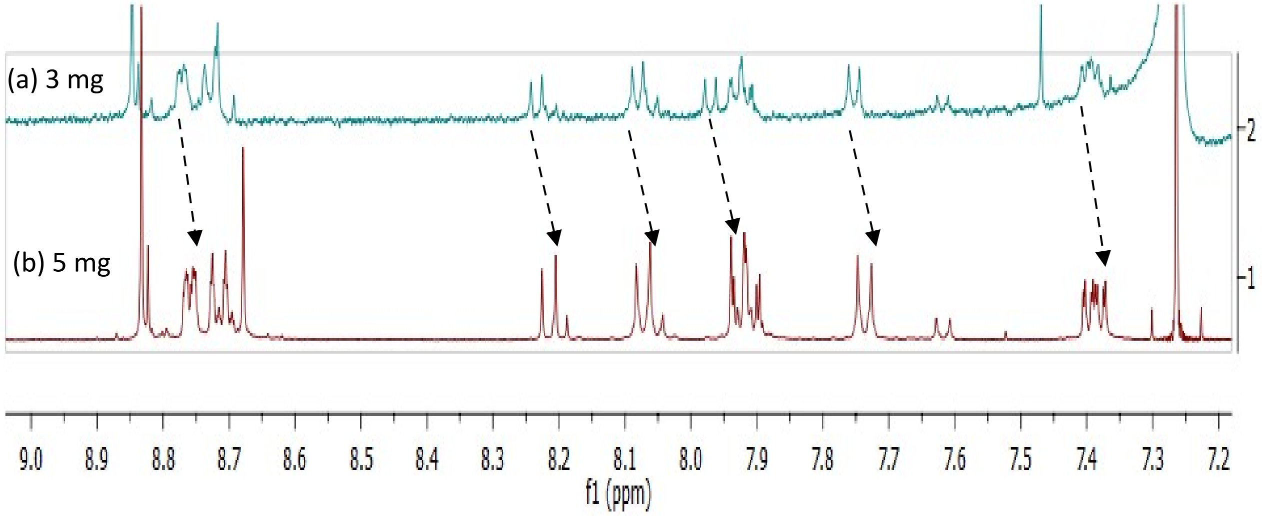


Fig. S3 Concentration dependent ^{1}H NMR spectrum of derivative **3**: (a) 3 mg and (b) 5 mg each in 0.6 ml $CDCl_3$. NMR frequency 500 MHz.

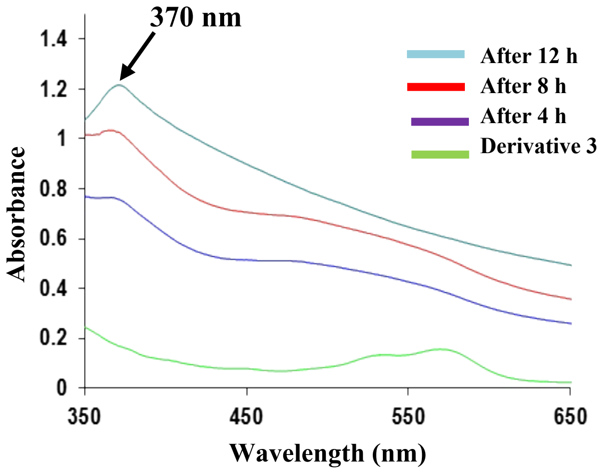


Fig. S4 UV-vis spectra of derivative **3** in presence of Zn^{2+} ions (200 equiv.) recorded at different time intervals. UV-vis band at 370 nm corresponds to ZnO nanoparticles.

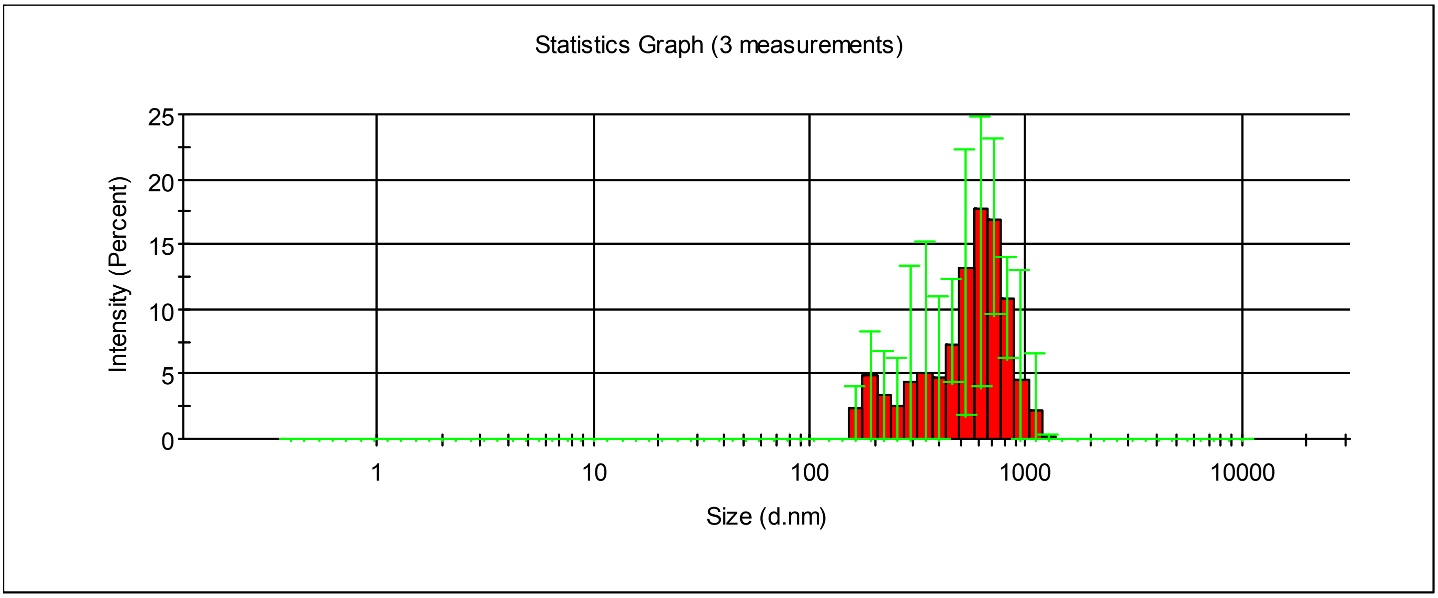


Fig. 5 The DLS studies of solution of derivative **3** in presence of zinc ions showed the presence of aggregates having average size of 600 nm.

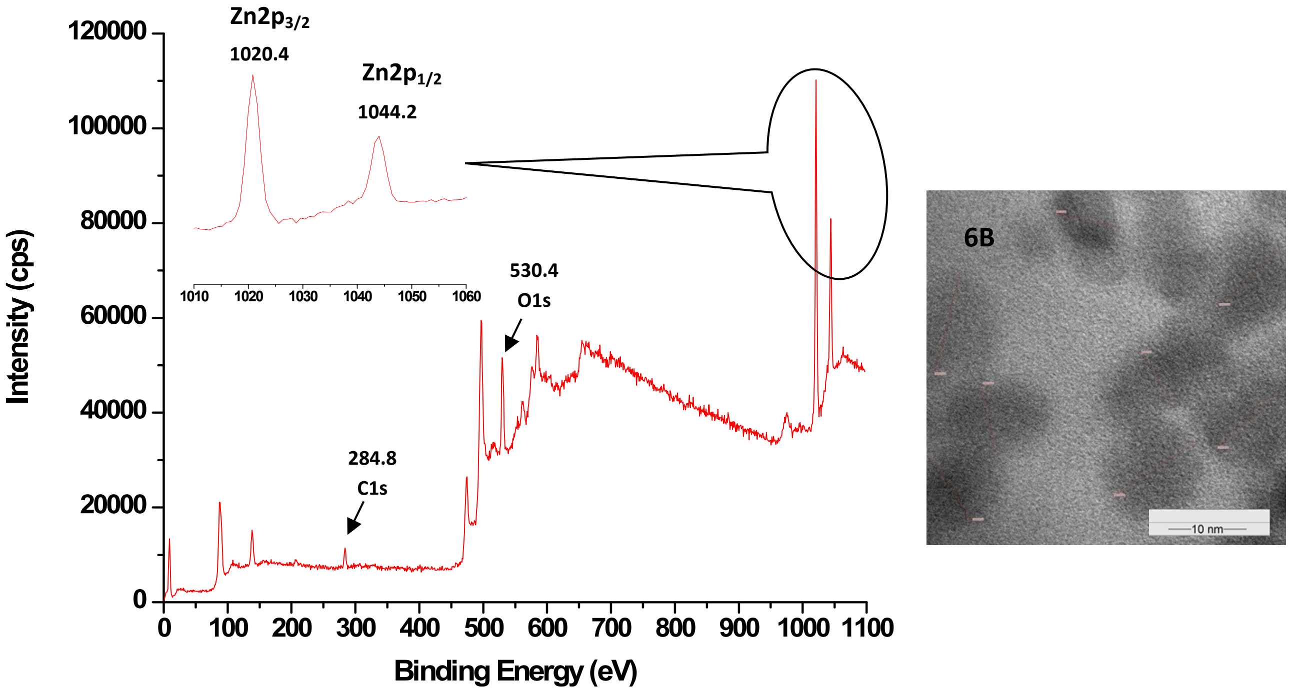


Fig. S6A XPS analysis of supramolecular polymer **4**:ZnO NPs and **6B :** TEM image of ZnO NPs.

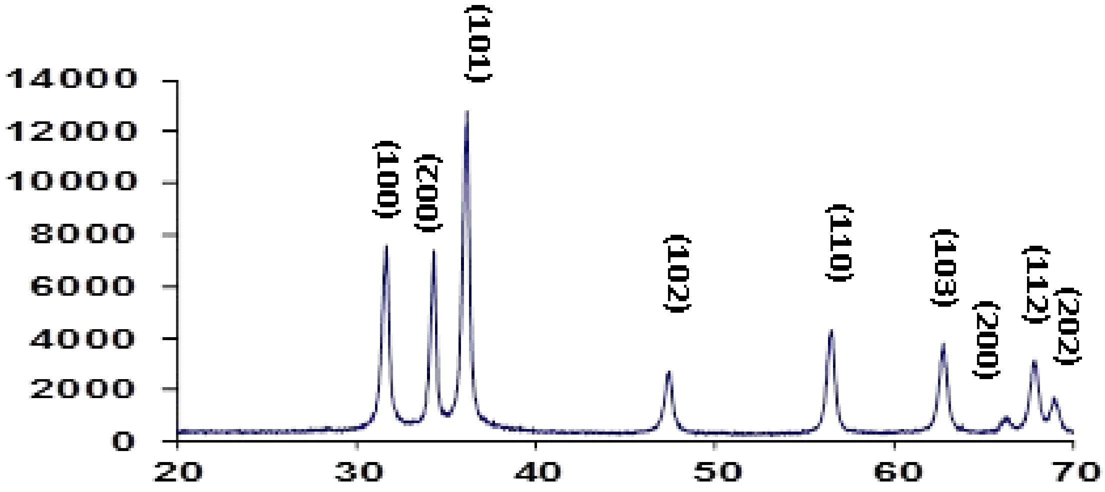


Fig. S7 X-Ray Diffraction (XRD) pattern of ZnO NPs.

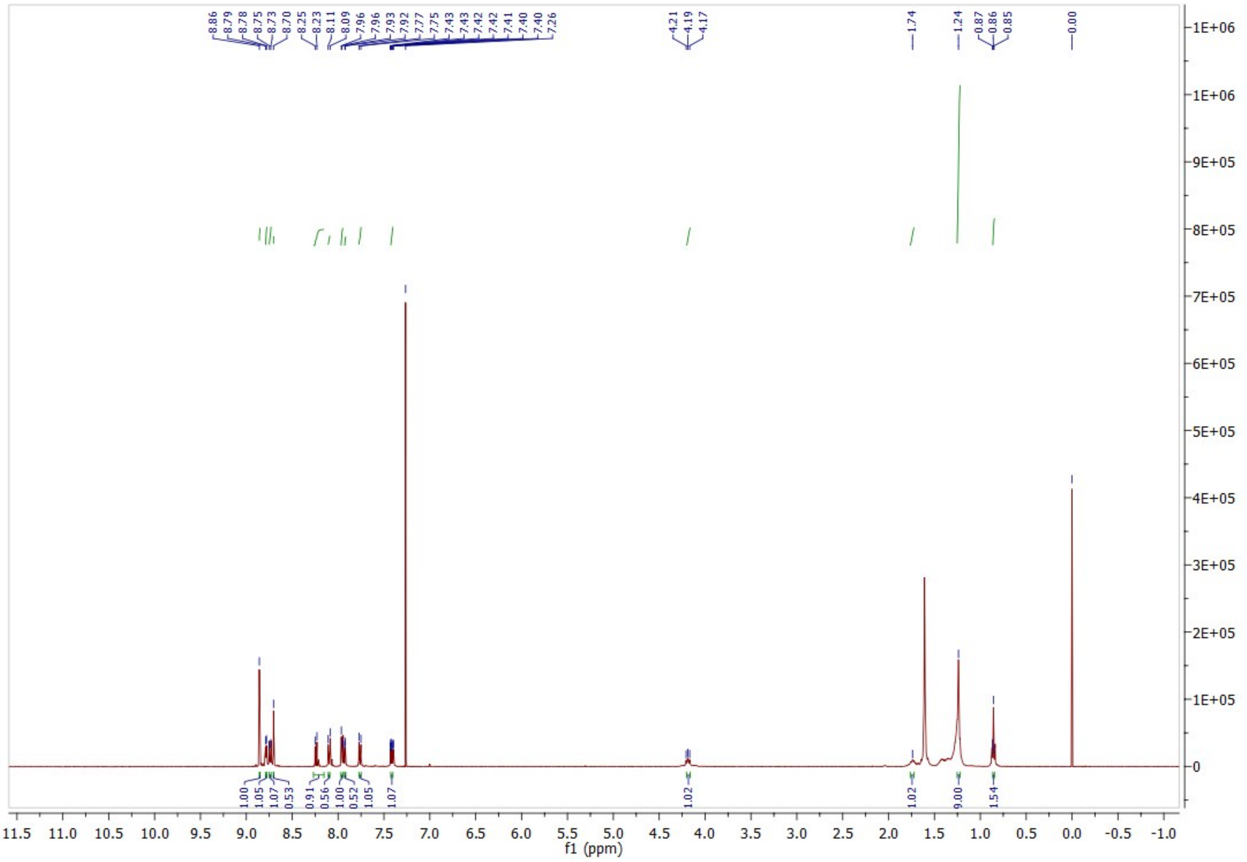


Fig. S8 The ^{1}H NMR spectrum of Derivative **4** in $CDCl_3$.

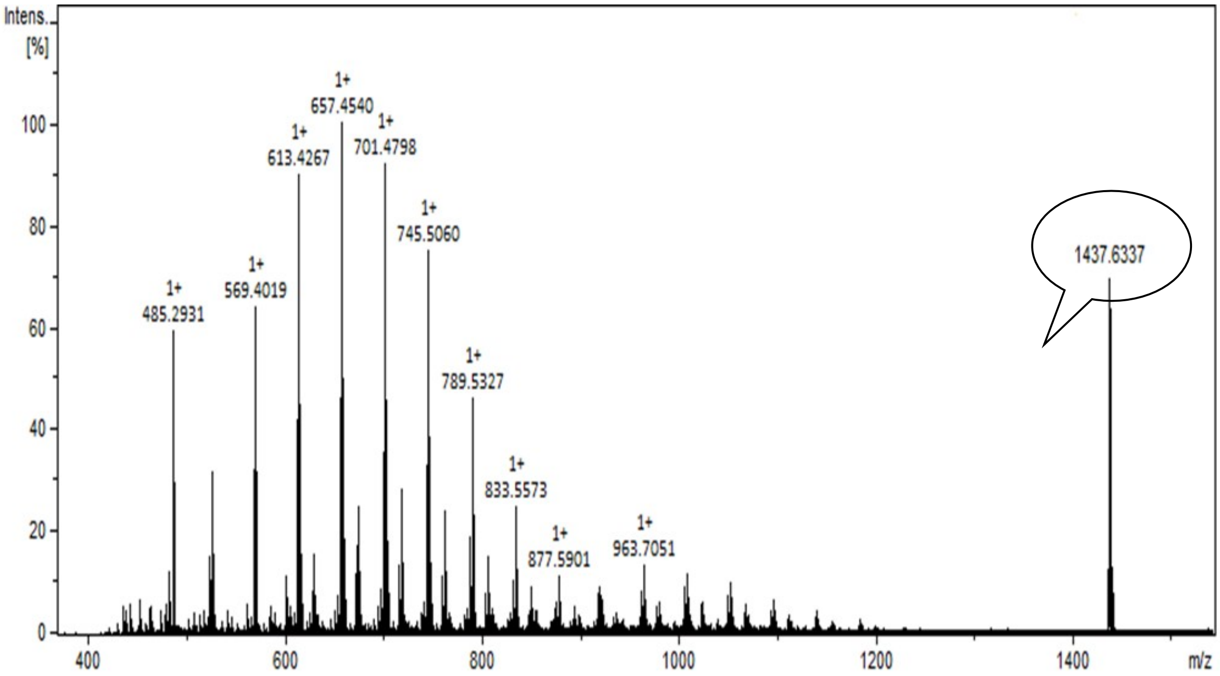


Fig 9. The mass spectrum of derivative **4** .

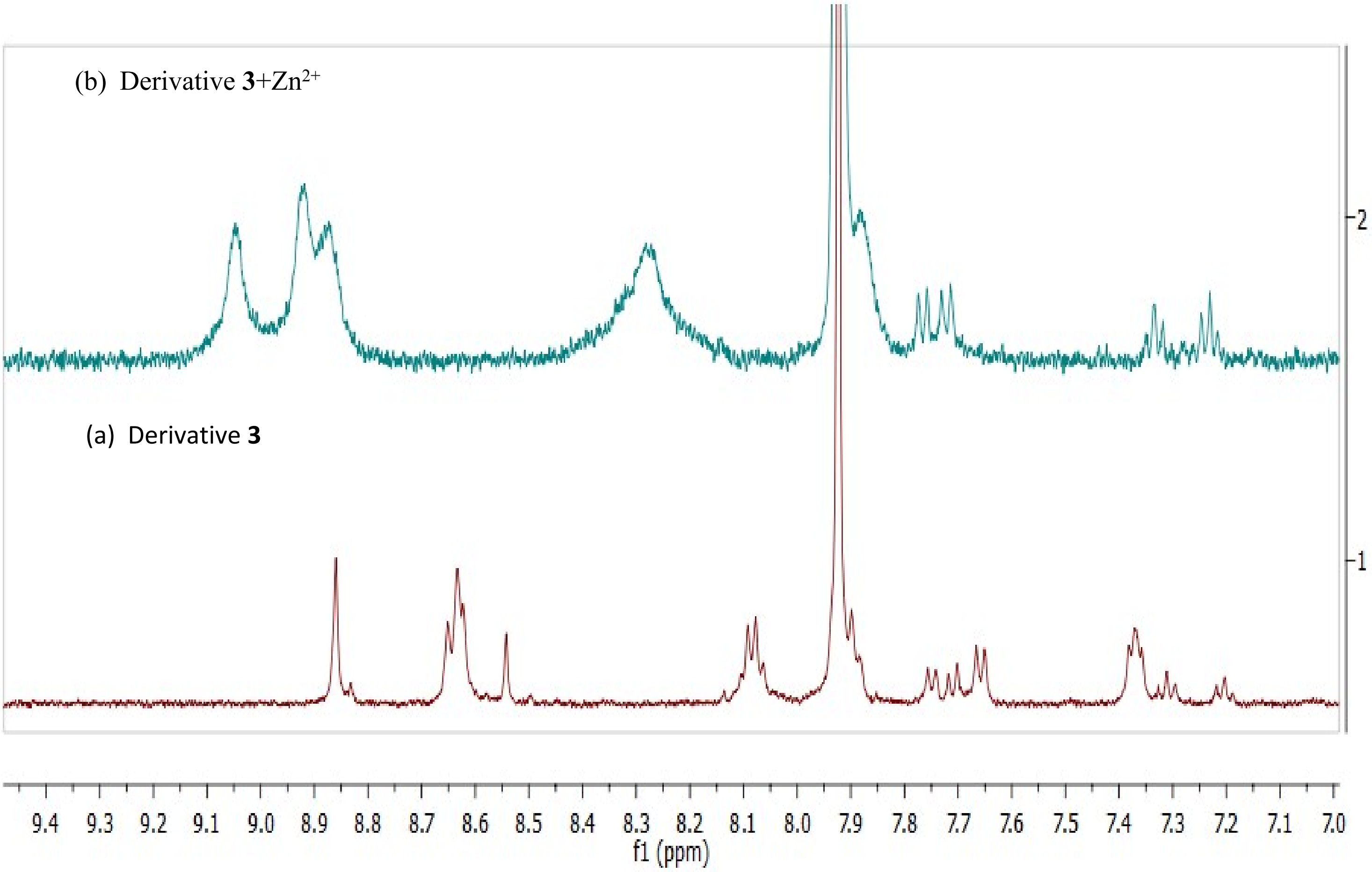


Fig. 10 (a) ^{1}H NMR spectra of derivative **3** and (b) derivative **3** +Zn^{2+} ions in (D_2O:THF(d_8),(1:1, v:v) solvent mixture.

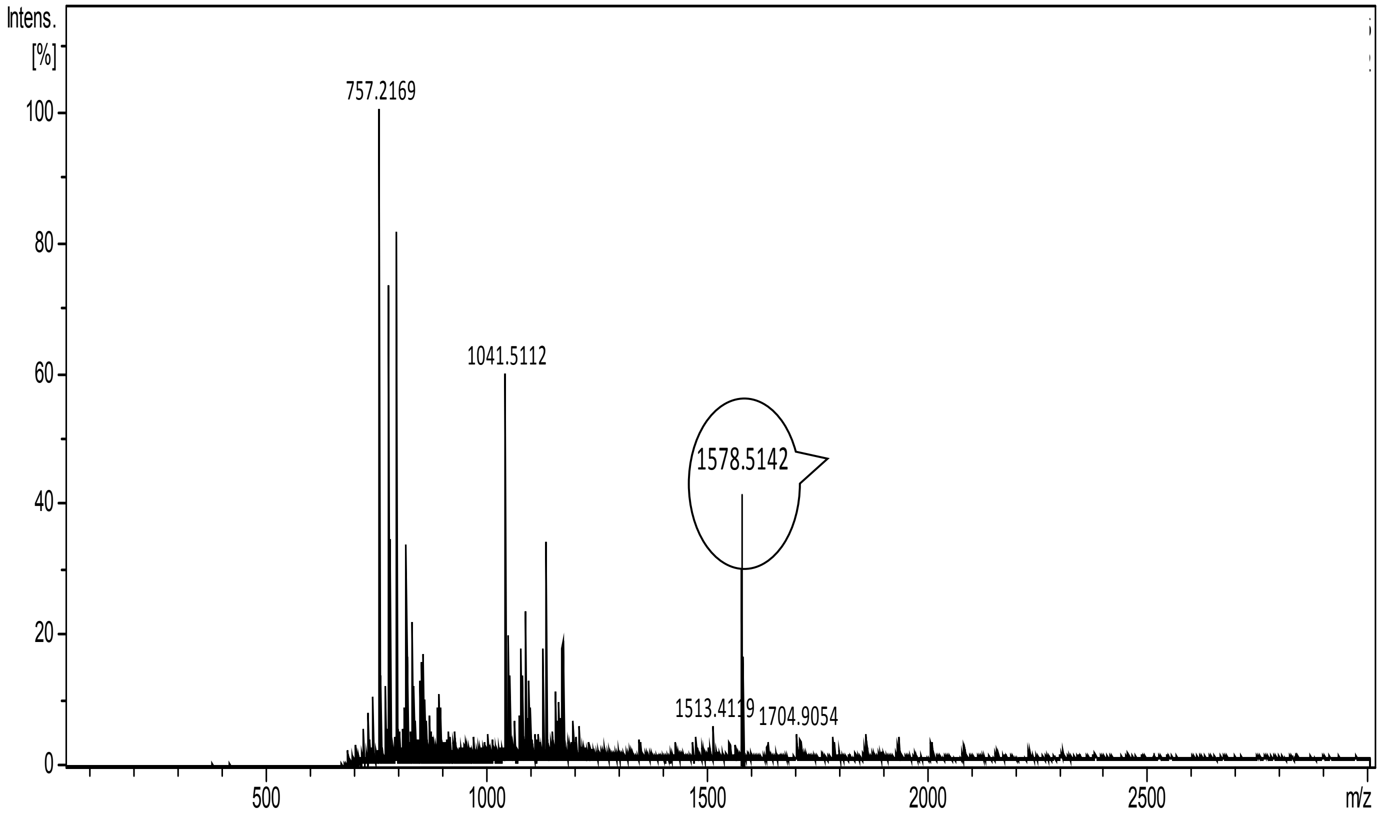


Fig. S11 The mass spectrum of Polymeric species.

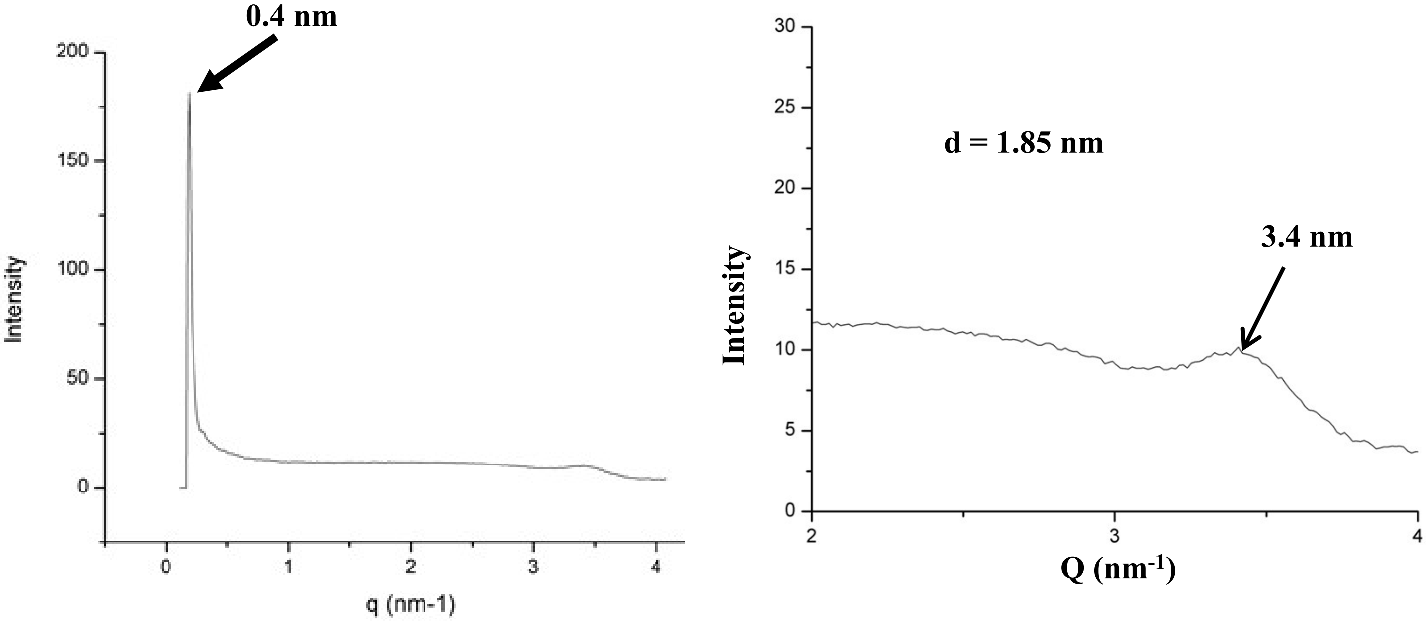


Fig. S12 The small-angle X-ray scattering (SAXS) measurements of the derivative **3** in the presence of Zn^{2+} ions H_2O/THF (1:1) showed a peak at 0.4 nm (Q). Further, the peak is observed at 3.4 nm (Q).

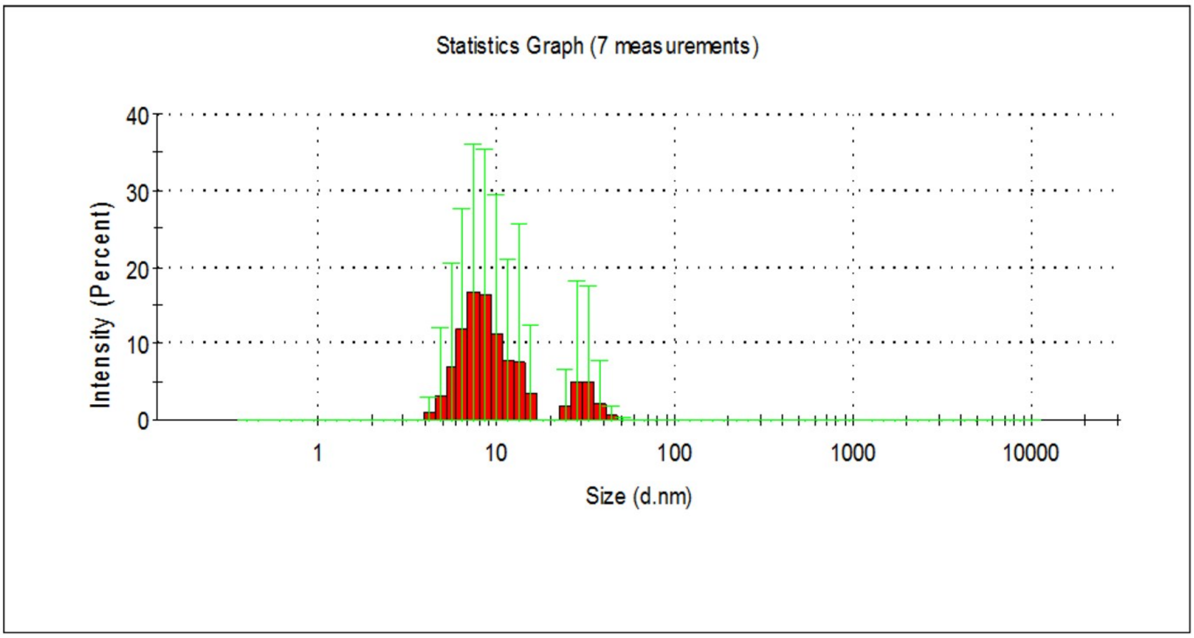
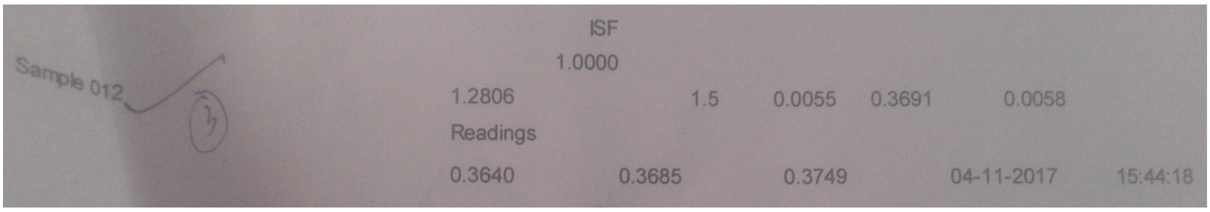


Fig. S13a DLS of ZnO NPs prepared by reported method.



Sample 012

ISF
1.0000
1.2806 1.5 0.0055 0.3691 0.0058
Readings
0.3640 0.3685 0.3749 04-11-2017 15:44:18

Fig. S13b AAS data to calaculate amount of zinc deposited on the catalyst.

The solution was 1000 times diluted for AAS studies. Thus, the toatal amount of Zinc deposited on the catalyst= 1.280*1000= 1280ppm

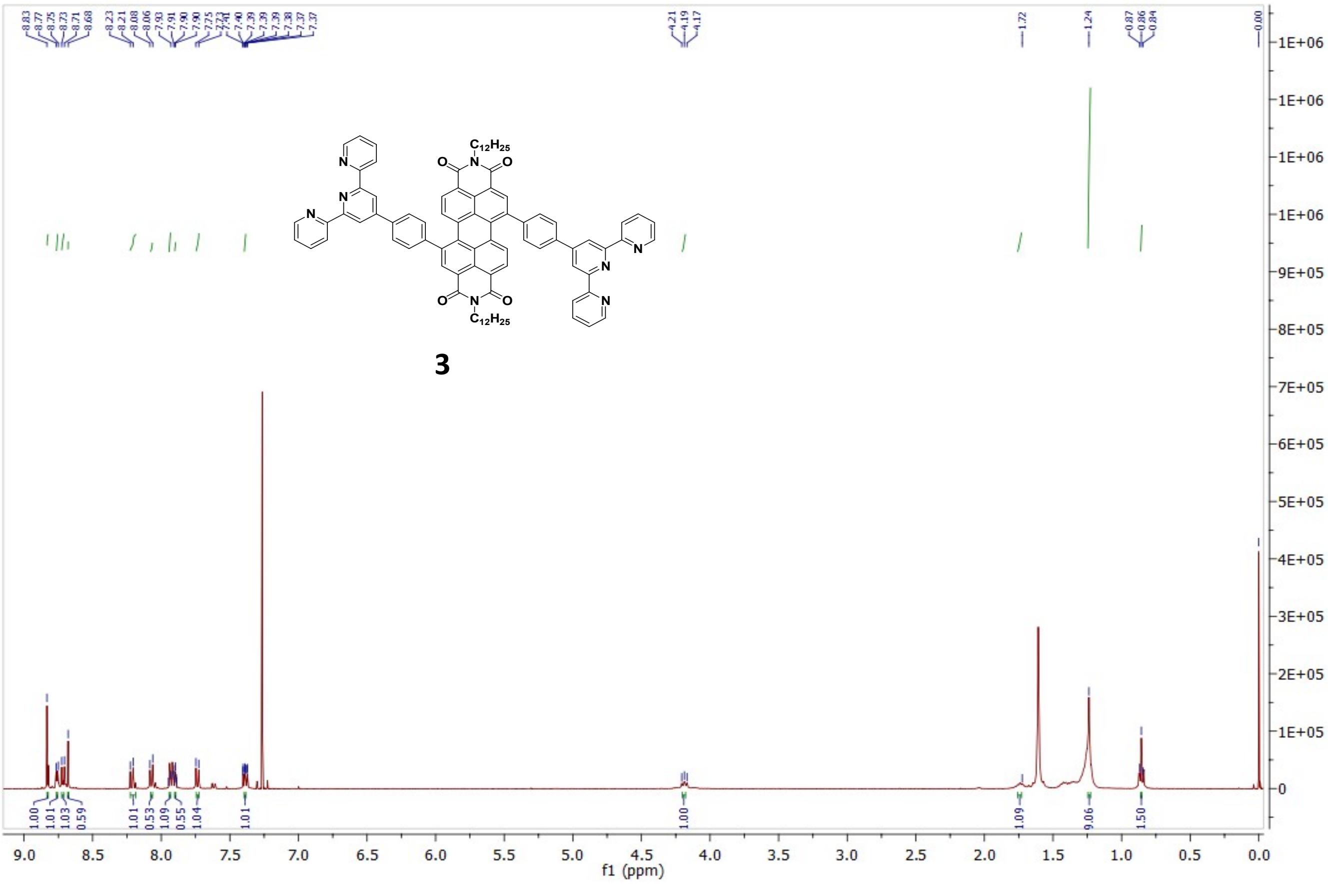


Fig. S14 The ^{1}H NMR spectrum of Derivative **3** in $CDCl_3$.

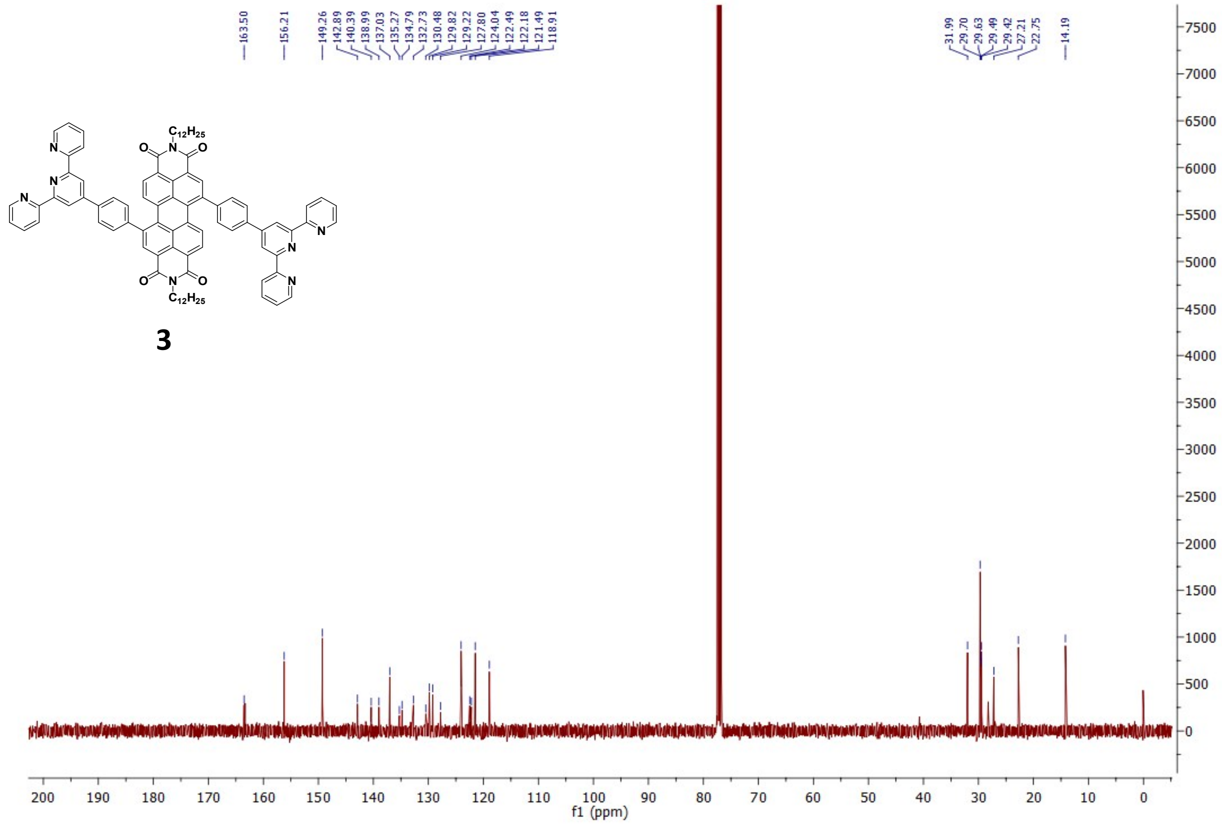


Fig. S15 The ^{13}C NMR spectrum of Derivative **3** in $CDCl_3$.

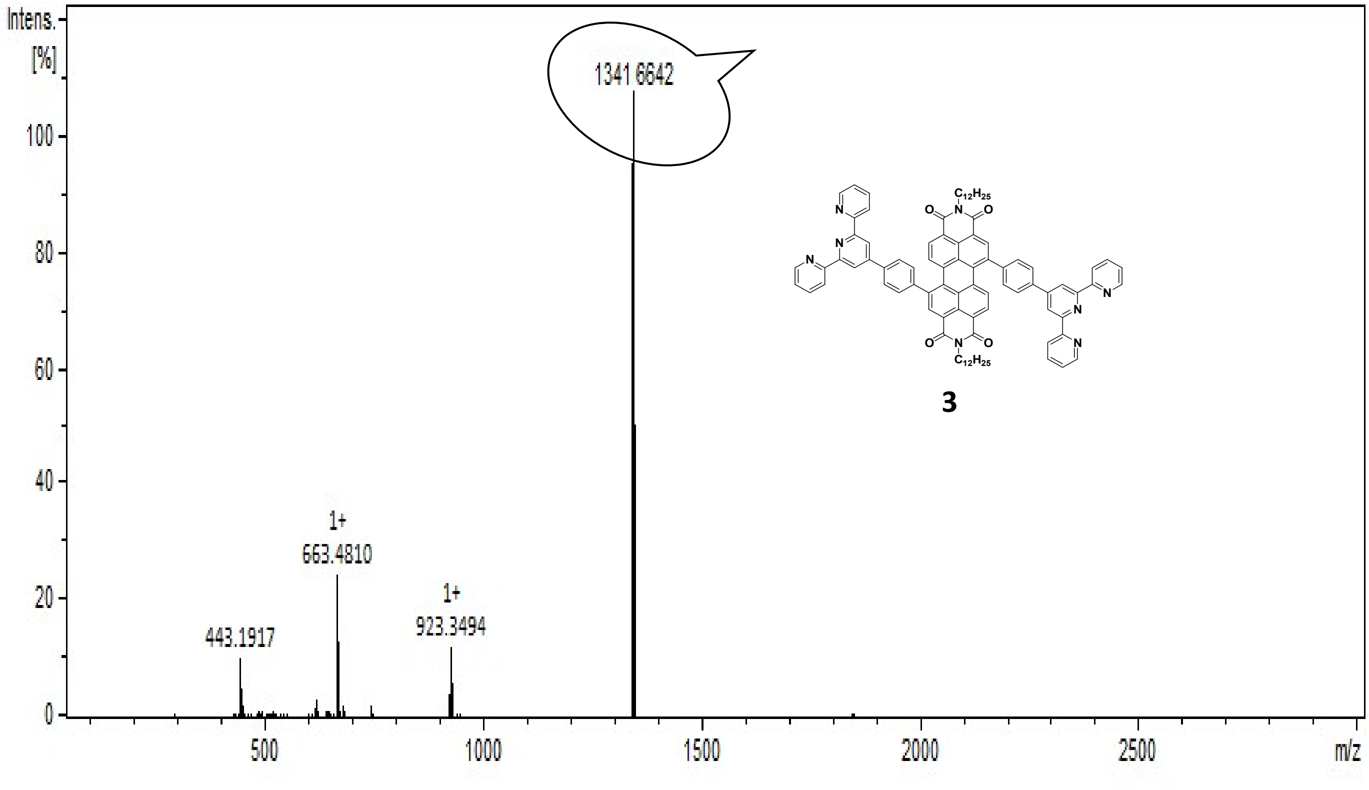


Fig. S16 The mass spectrum of derivative **3** .

Characterization of compounds

[1] **Compound 7a.** (Yellow solid) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (2H, d, *J*= 5 Hz), 7.68 (2H, d, *J*= 10 Hz), 7.62 (1H, t, *J*= 7.5 Hz), 7.51 (2H, t, *J*= 7.5 Hz), 7.47 (1H, d, *J*= 10 Hz), 7.41 (2H, t, *J*= 7.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) 178.3, 137.0, 133.8, 132.4, 129.8, 128.5, 127.8, 122.1, 96.9, 79.7

[2] **Compound 7b**. (Yellow solid) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (2H, d, *J*= 10 Hz), 7.68 (2H, d, *J*= 10 Hz), 7.48 (1H, t, *J*= 7.5 Hz), 7.42 (2H, t, *J*= 5 Hz), 7.31 (2H, d, *J*= 10 Hz), 2.45 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) 177.7, 145.3, 134.6, 133.0, 130.7, 129.7, 129.4, 128.7, 120.3, 92.6, 87.0, 21.9.

[2] **Compound 7c**. (Yellow solid) ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.20 (2H, d, *J*= 6 Hz), 7.68 (2H, d, *J*= 6 Hz), 7.48- 7.39(3H, m), 6.99 (2H, d, *J*= 9 Hz), 3.93 (3H, s, OMe). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) 176.7, 164.5, 133.0, 132.3, 132.0, 130.6, 130.3, 128.7, 113.9, 92.3, 86.9, 55.6.

[3] **Compound 7d**. (yellow solid) ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.66 (2H, d, *J*= 9 Hz), 7.50 (2H,s), 7.47-7.40 (3H, m), 3.96 (9H,s, OMe). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) 177.0, 153.2, 143.7, 133.1, 132.3, 130.9, 128.9, 120.2, 107.0, 93.0, 86.9, 68.1, 61.2, 56.4.

[2] **Compound 7e**. (Yellow solid) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.38 (4 H, s), 7.71 (2H, d, *J*= 5 Hz), 7. 54 (1H, t, *J*= 7.5 Hz), 7.46 (2H, t, *J*= 7.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) 175.9, 150.9, 141.0, 133.3, 131.5, 130.4, 128.9, 123.9, 119.4, 95.4, 86.5.

[2] **Compound 7f**. (Yellow solid) ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.09 (2H, d, J= 6 Hz), 7.87-7.80 (2H, m), 7.67-7.64 (2H, m), 7.49-7.42 (3H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) 189.2, 174.7, 146.6, 141.5, 132.5, 131.2, 129.1, 128.9, 128.7, 121.2, 118.0, 116.0, 96.8, 85.0.

[2] **Compound 7g**. (Yellow oil) ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.01 (1H, d, J= 5Hz), 7.73 (1H, d, J= 5Hz), 7.66 (2H, d, J= 10Hz), 7.48 (1H, t, J = 7.5 Hz), 7.42 (1H, t, J = 7.5 Hz), 7.19 (1H, t, J = 5Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) 169.8, 145.0, 135.2, 135.1, 133.0, 130.9, 128.7, 128.3, 120.0, 91.8, 86.5.

[1] **Compound 7h**. (Yellow solid) ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.24 (1H, d, J= 10Hz), 8.65 (1H, d, J= 10Hz), 8.11 (1H, d, J= 5Hz), 7.92 (1H, d, J= 10Hz),7.69 (3H, t, J= 10Hz), 7.63-7.57 (2H, m),7.49 (1H, t, J= 7.5Hz), 7.43 (2H, t, J= 7.5Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) 179.8, 135.1, 134.5, 133.9, 133.0, 133.0, 130.8, 130.6, 129.0, 128.7, 128.6, 126.8, 126.0, 124.5, 120.4, 91.7, 88.5.

[2] **Compound 8b**. (Colourless liquid) ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.15 (2H, d, J = 5Hz) 7.62 (1H, t, J = 7.5 Hz), 7.49 (2H, t, J = 7.5 Hz), 0.32 (9H, s, TMS). ^{13}C NMR (CDCl$_3$ 125 MHz, ppm) 174.7, 135.0, 134.5, 129.0, 128.8, 120.3, 80.0, 3.8

[6] **Compound 8c**. (Colourless liquid) ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.12 (2H, d, J = 6.0 Hz), 7.58 (1H, t, J = 7.5 Hz), 7.46 (2H, t, J = 7.5 Hz), 2.49 (2H, t, J = 7.5 Hz), 1.69-1.60 (2H m), 1.55-1.45 (2H, m), 0.94 (3H, t, J = 7.5 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) 178.3, 137.0, 133.8, 129.5, 128.5, 96.9, 79.7, 29.9, 22.1, 18.9, 13.5.

Compound 8d. (Light yellow solid) ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.22 (2 H, d, J = 9.0 Hz) 7.67-7.61 (3H m), 7.52 (2H, t, J = 7.5 Hz), 6.94 (2H,t, J = 9.0 Hz), 3.87 (3H, s). ^{13}C NMR (CDCl$_3$ 125 MHz, ppm) 178.2, 141.7, 137.1, 134.1, 133.2, 129.7, 129.6. 128.7, 117.1, 94.0, 86.9, 21.9.

Compound 8e. (Dark yellow solid) ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.22 (2 H, d, J = 10.0Hz) 7.62 (1H, t, J = 10 Hz), 7.58 (2H, d, J = 5.0 Hz), 7.51 (2 H, t, J = 7.5Hz), 7.23 (2H, d, J = 10 Hz), 2.40 (3H, s). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) 178.2, 161.8, 137.1, 135.3, 134.0, 129.6, 128.7, 114.5, 112.0, 94.4, 87.0, 55.5.

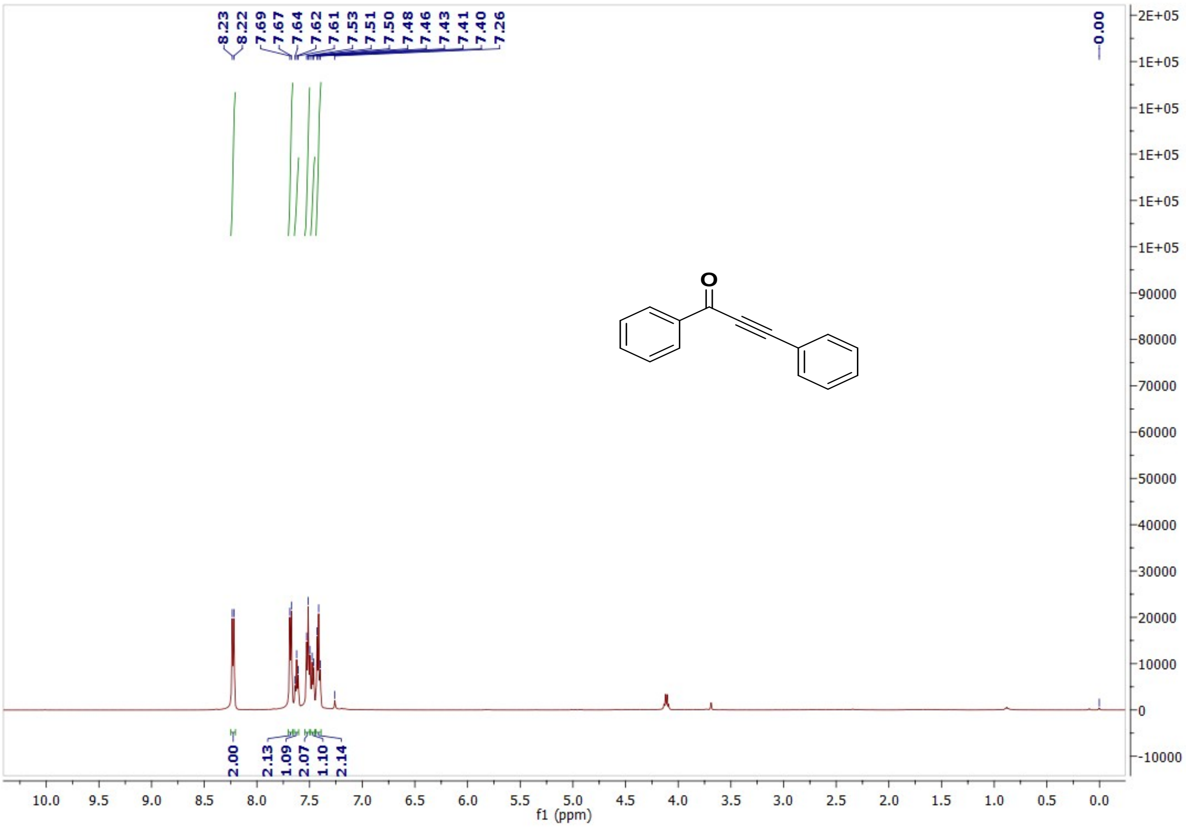


Fig. S17a The ^{1}H NMR spectrum of compound **7a** in $CDCl_3$**.**

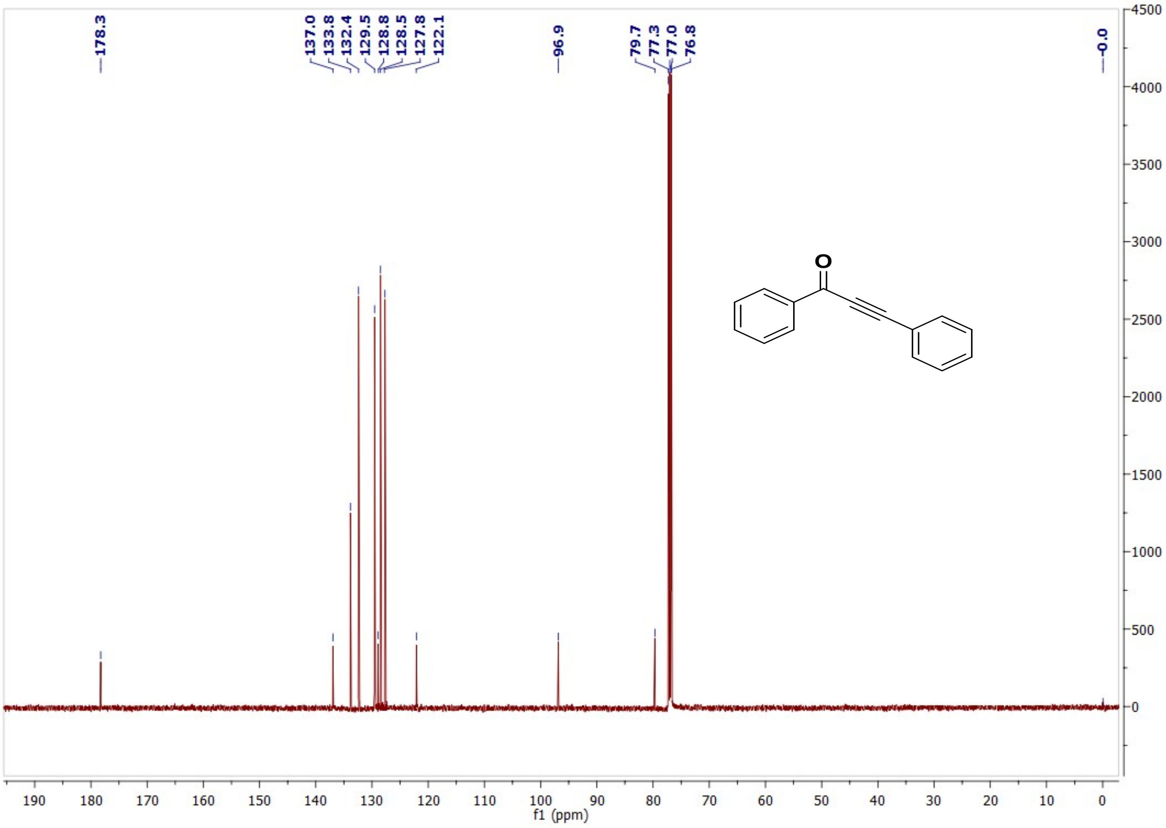


Fig. S17b The ^{13}C NMR spectrum of compound **7a** in $CDCl_3$**.**

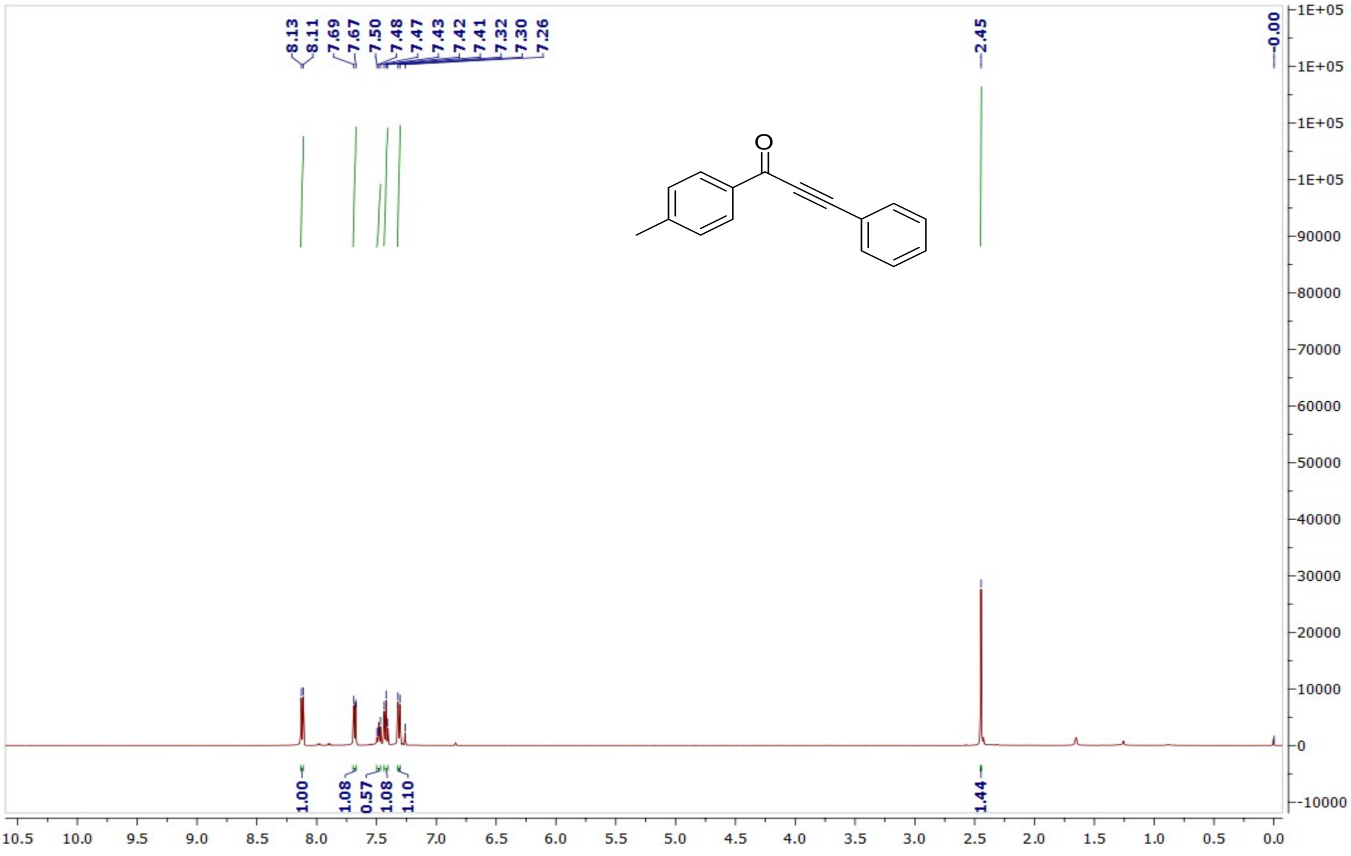


Fig. S18a The ^{1}H NMR spectrum of compound **7b** in $CDCl_3$.

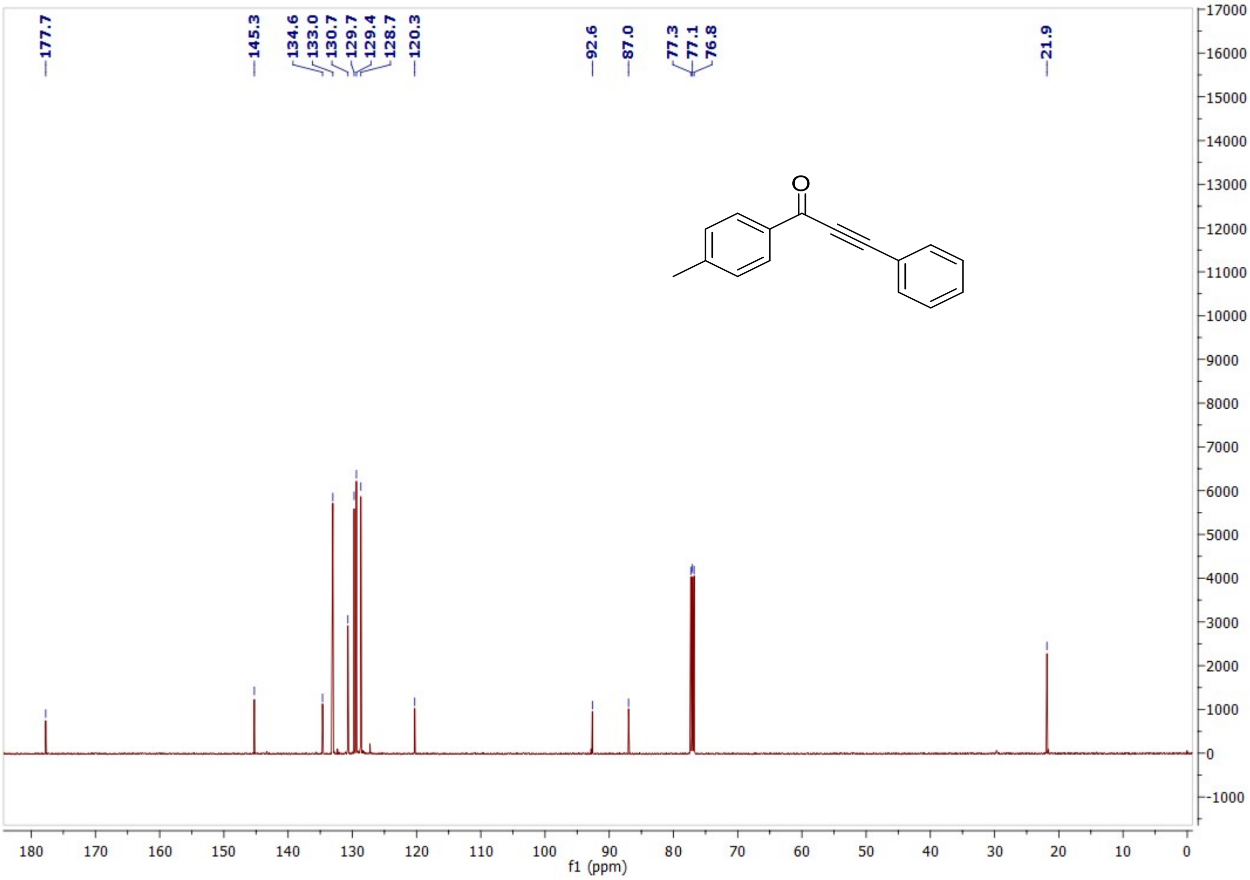


Fig. S18b The ^{13}C NMR spectrum of compound **7b** in $CDCl_3$.

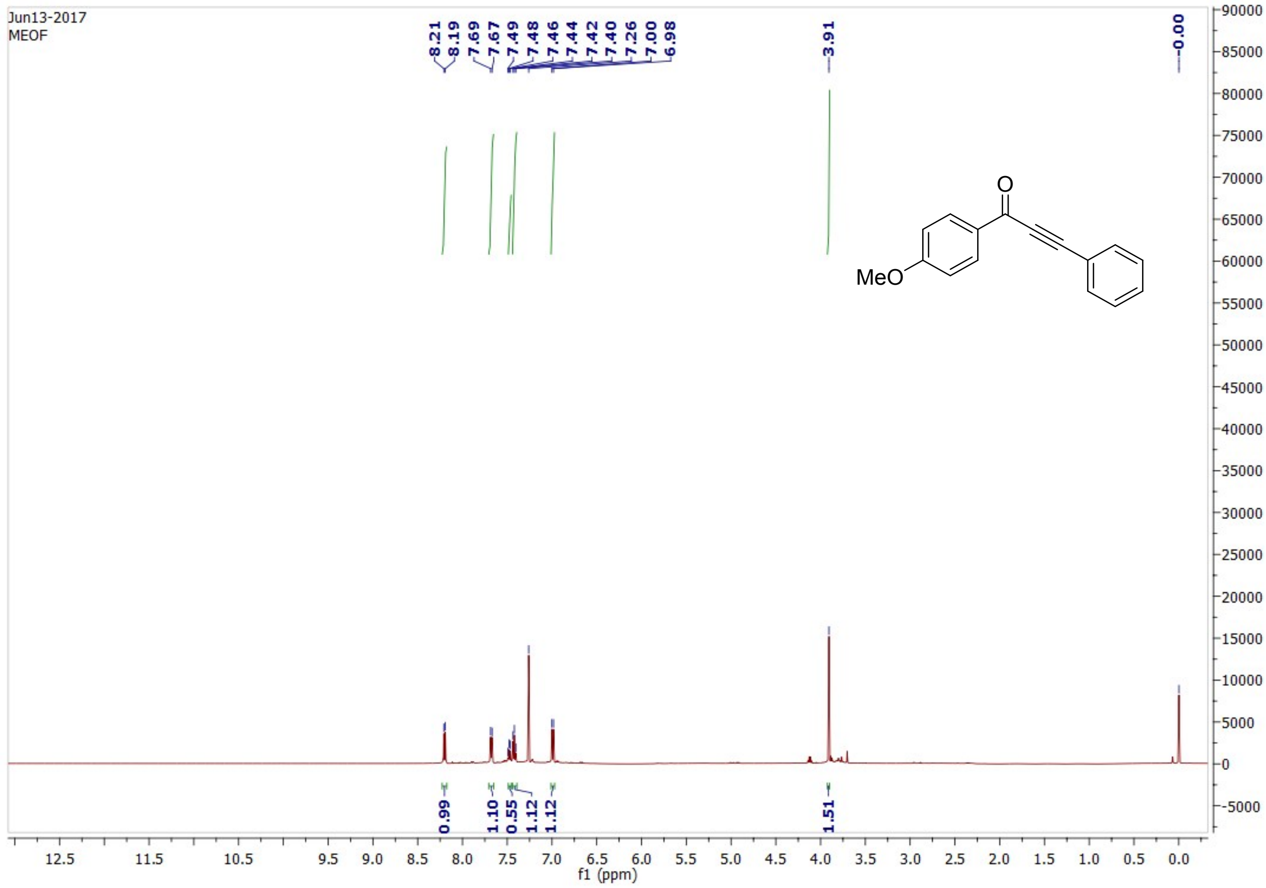


Fig. S19a The ^{1}H NMR spectrum of compound **7c** in CDCl$_3$.

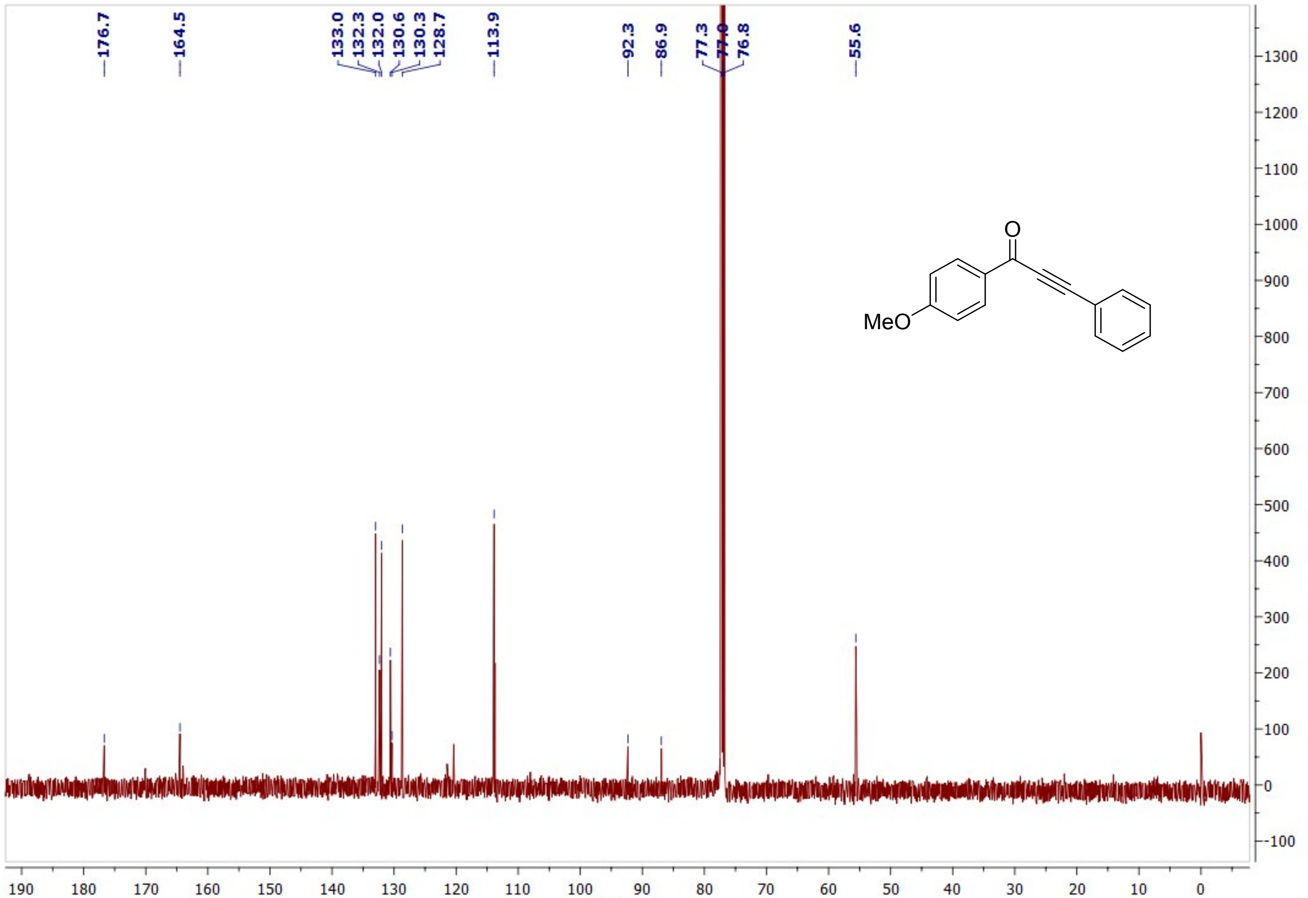


Fig. S19b The ^{13}C NMR spectrum of compound **7c** in CDCl$_3$.

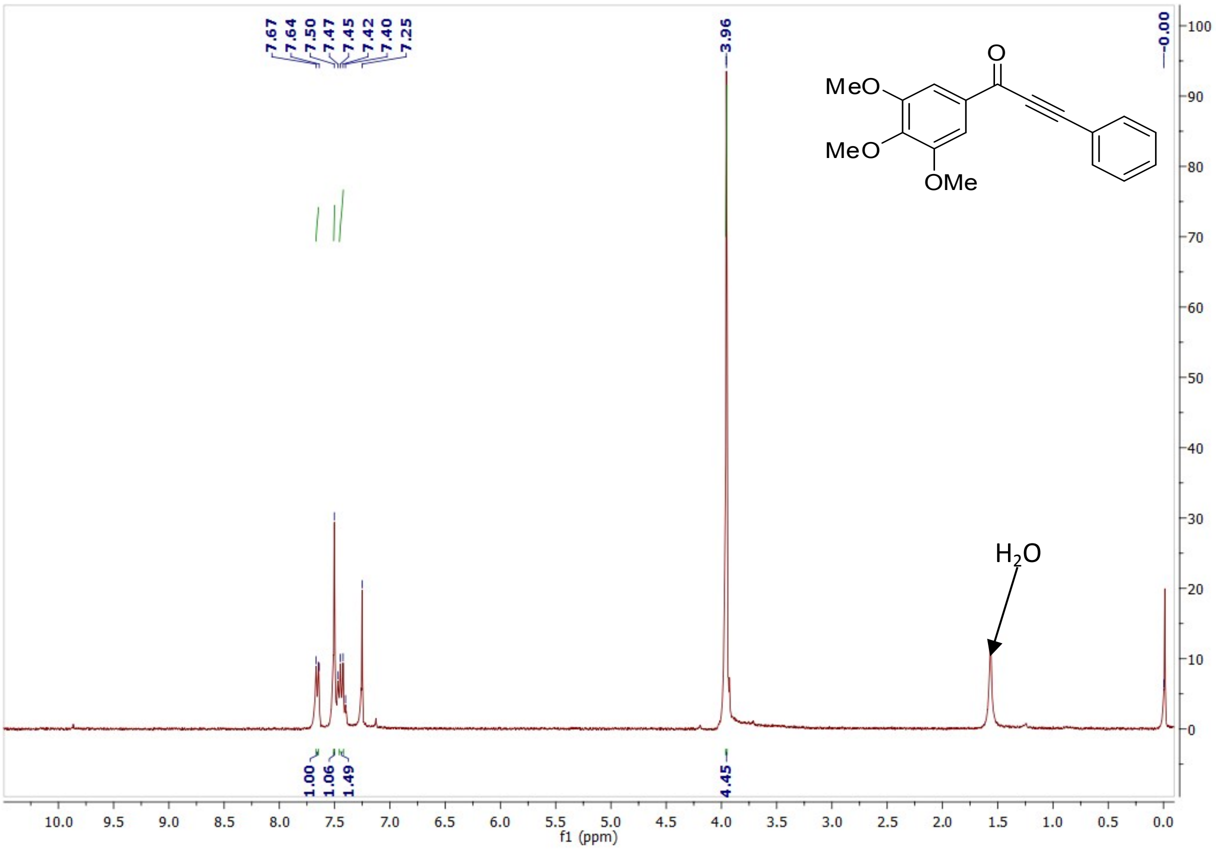


Fig. S20a The ^{1}H NMR spectrum of compound **7d** in $CDCl_3$**.**

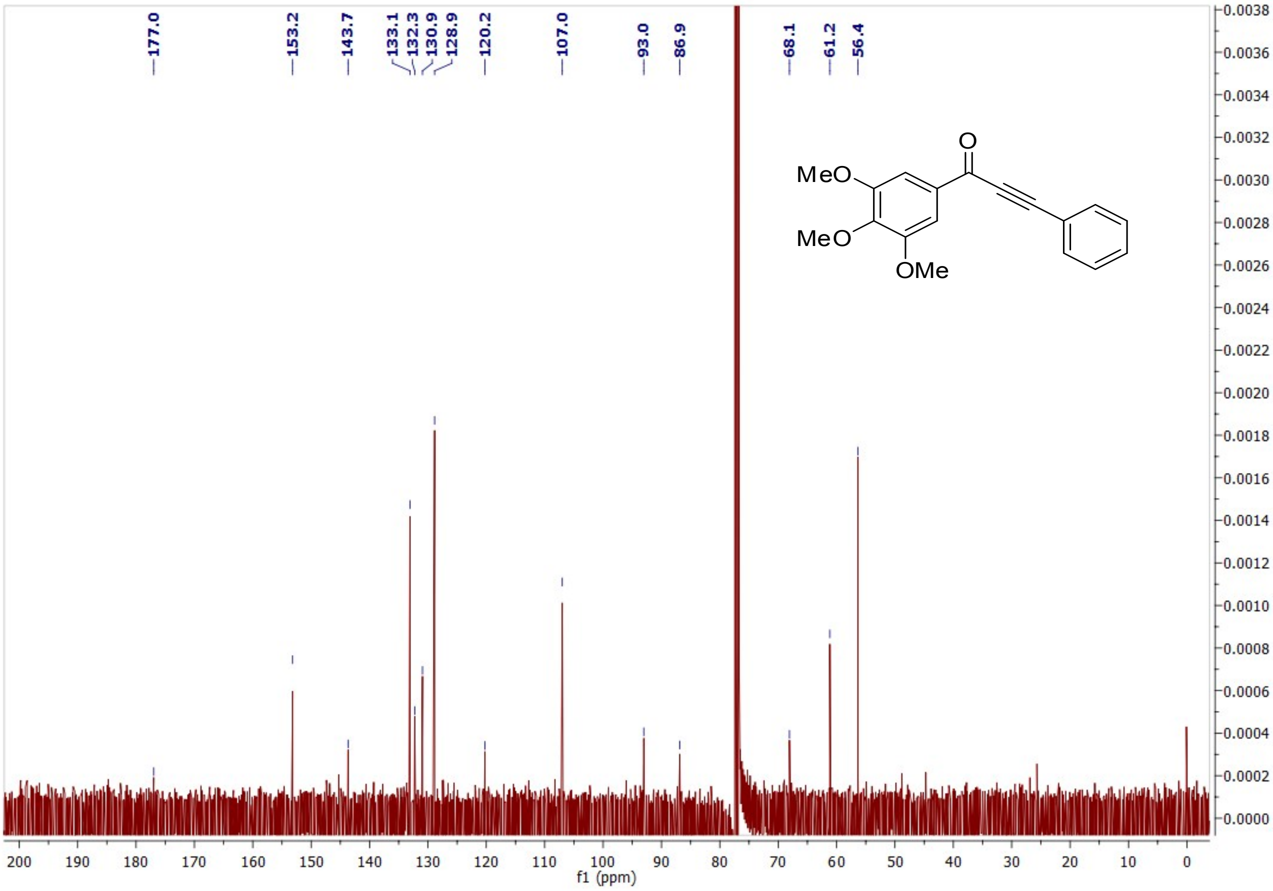


Fig. S20b The ^{1}H NMR spectrum of compound **7d** in $CDCl_3$**.**

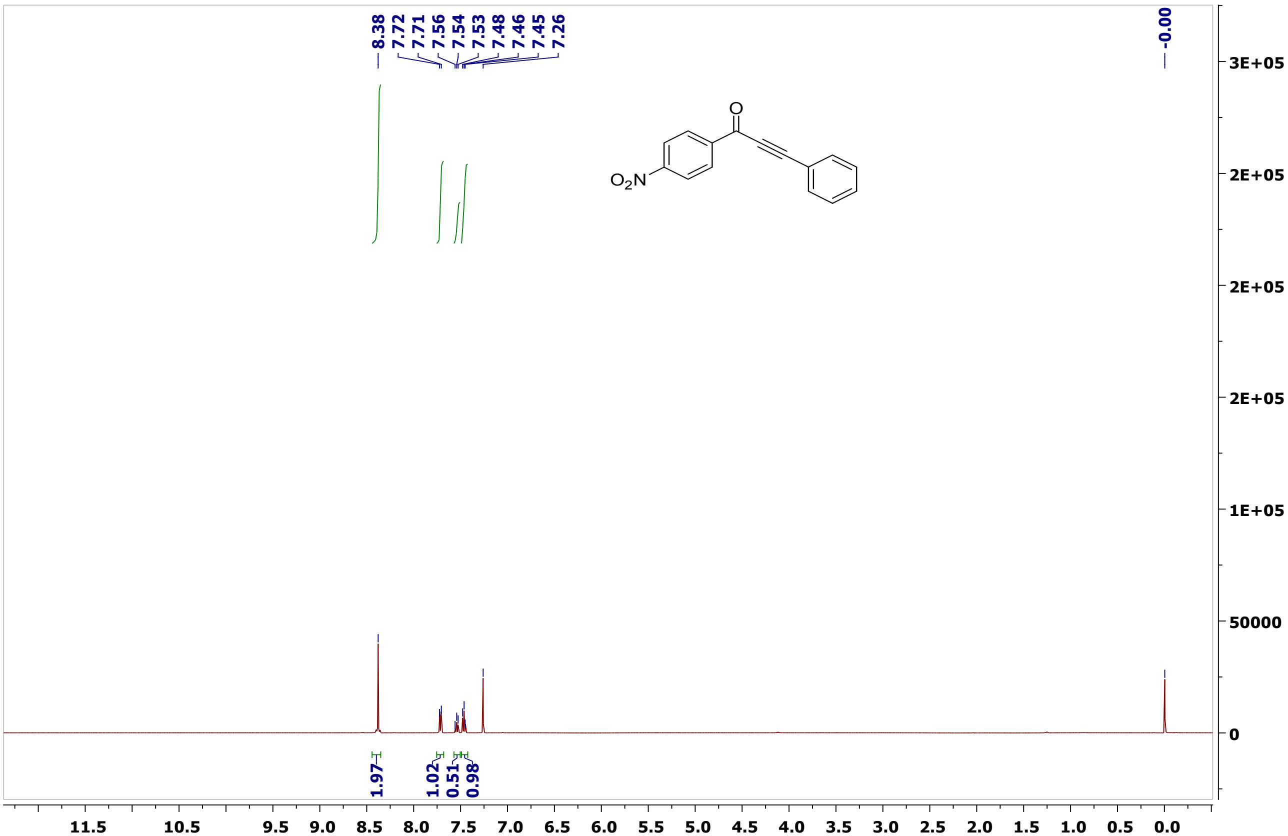


Fig. S21a The ^{1}H NMR spectrum of compound **7e** in CDCl$_3$**.**

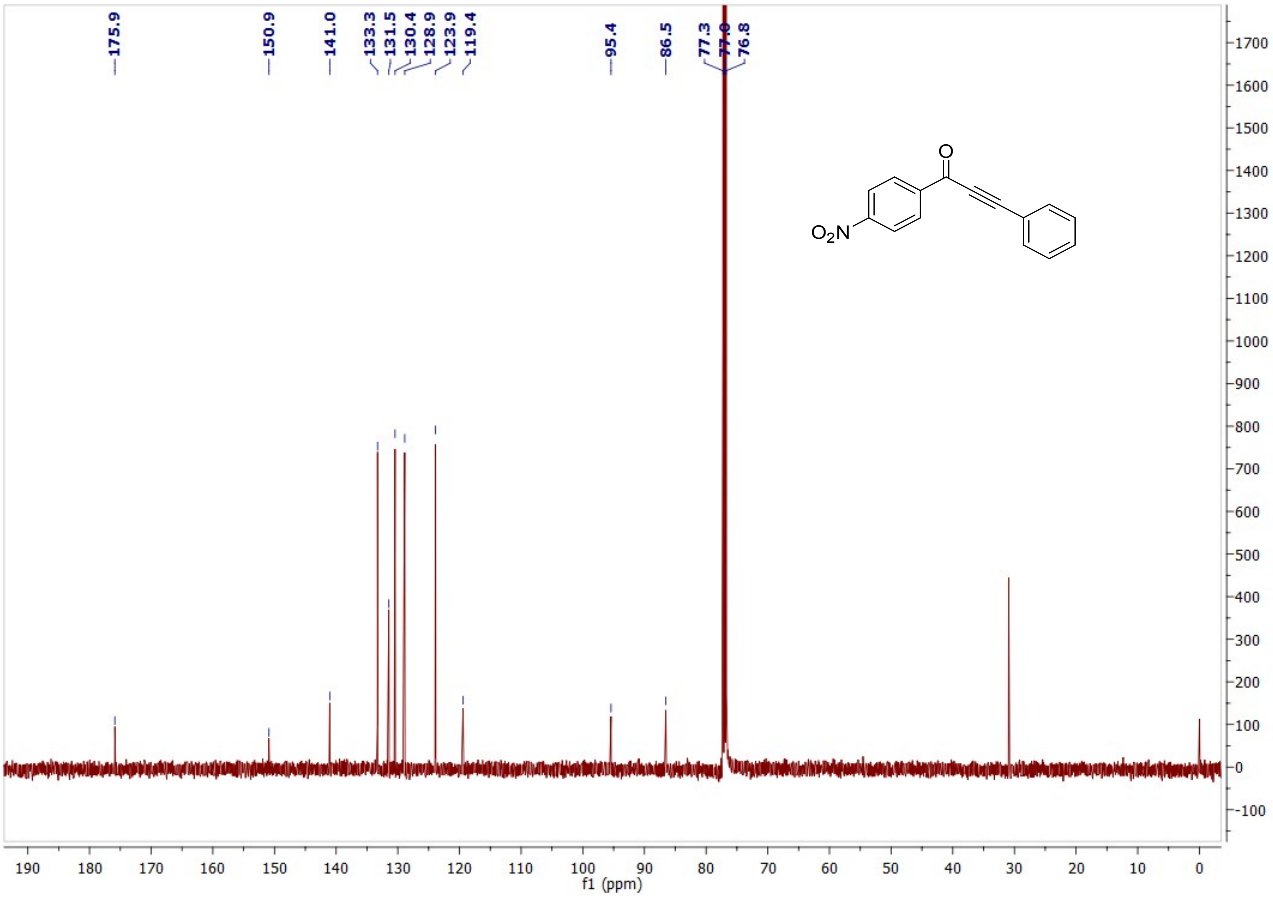


Fig. S21b The ^{1}H NMR spectrum of compound **7e** in CDCl$_3$

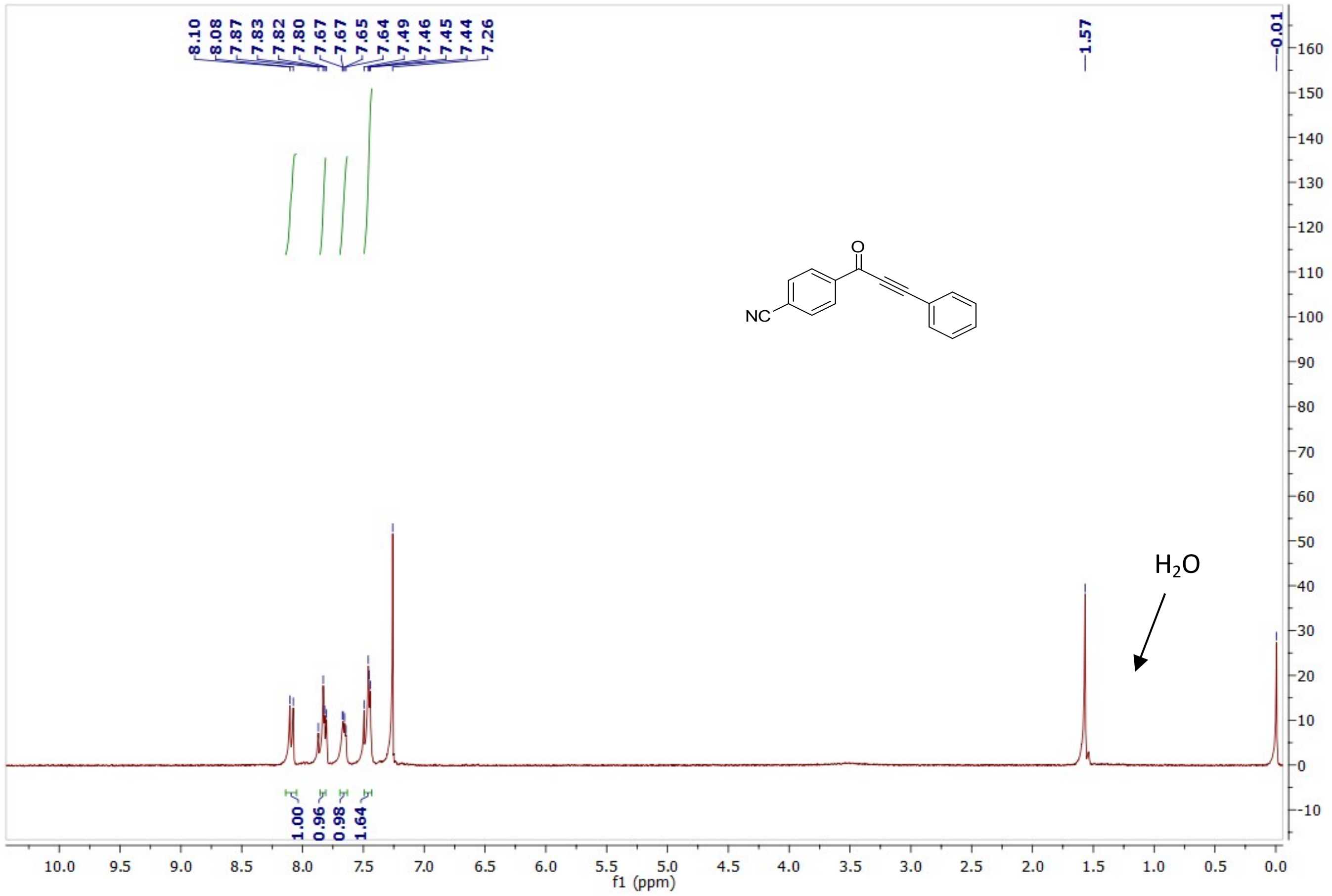


Fig. S22a The ^{1}H NMR spectrum of compound **7f** in $CDCl_3$.

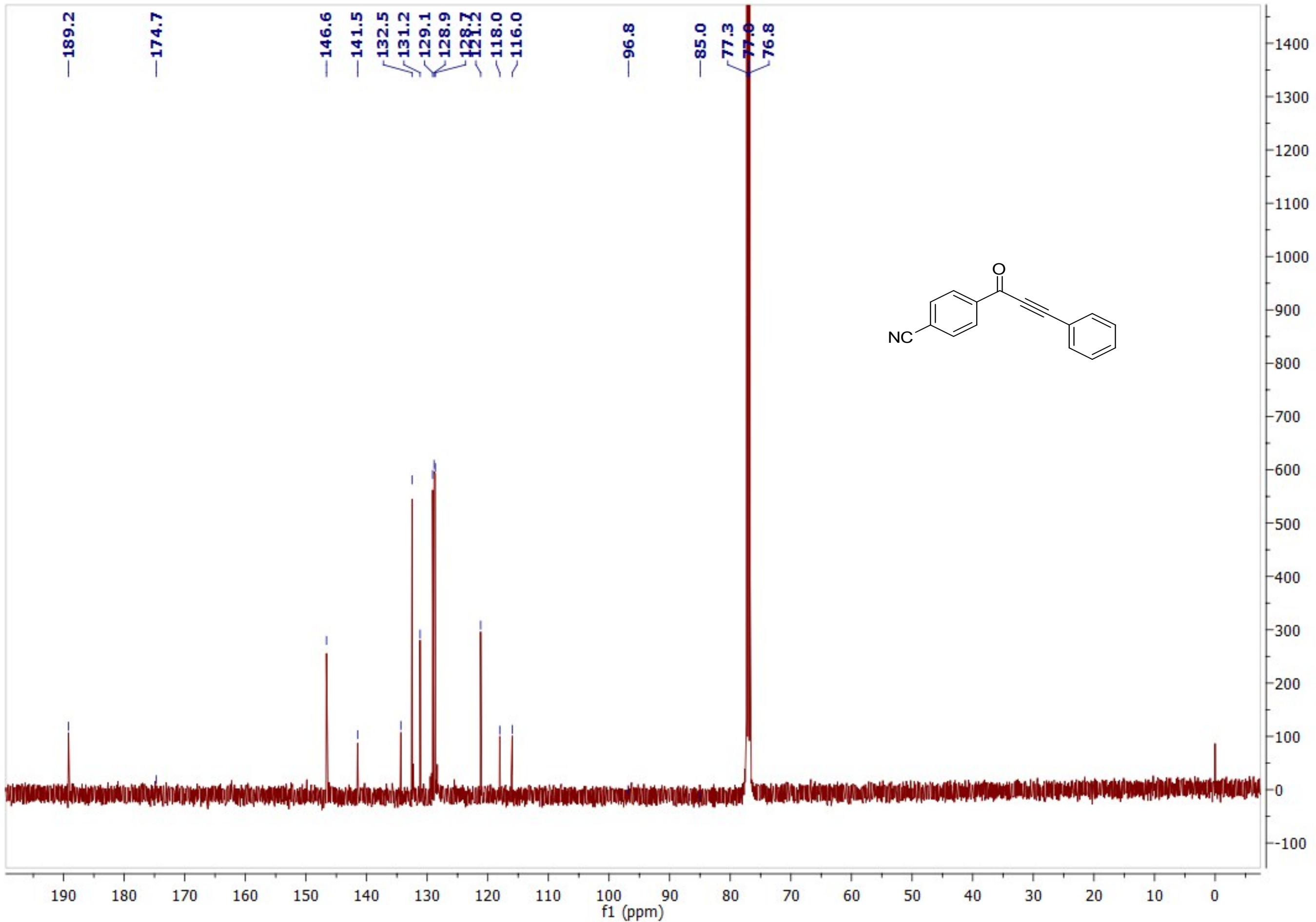


Fig. S22b The ^{13}C NMR spectrum of compound **7f** in $CDCl_3$.

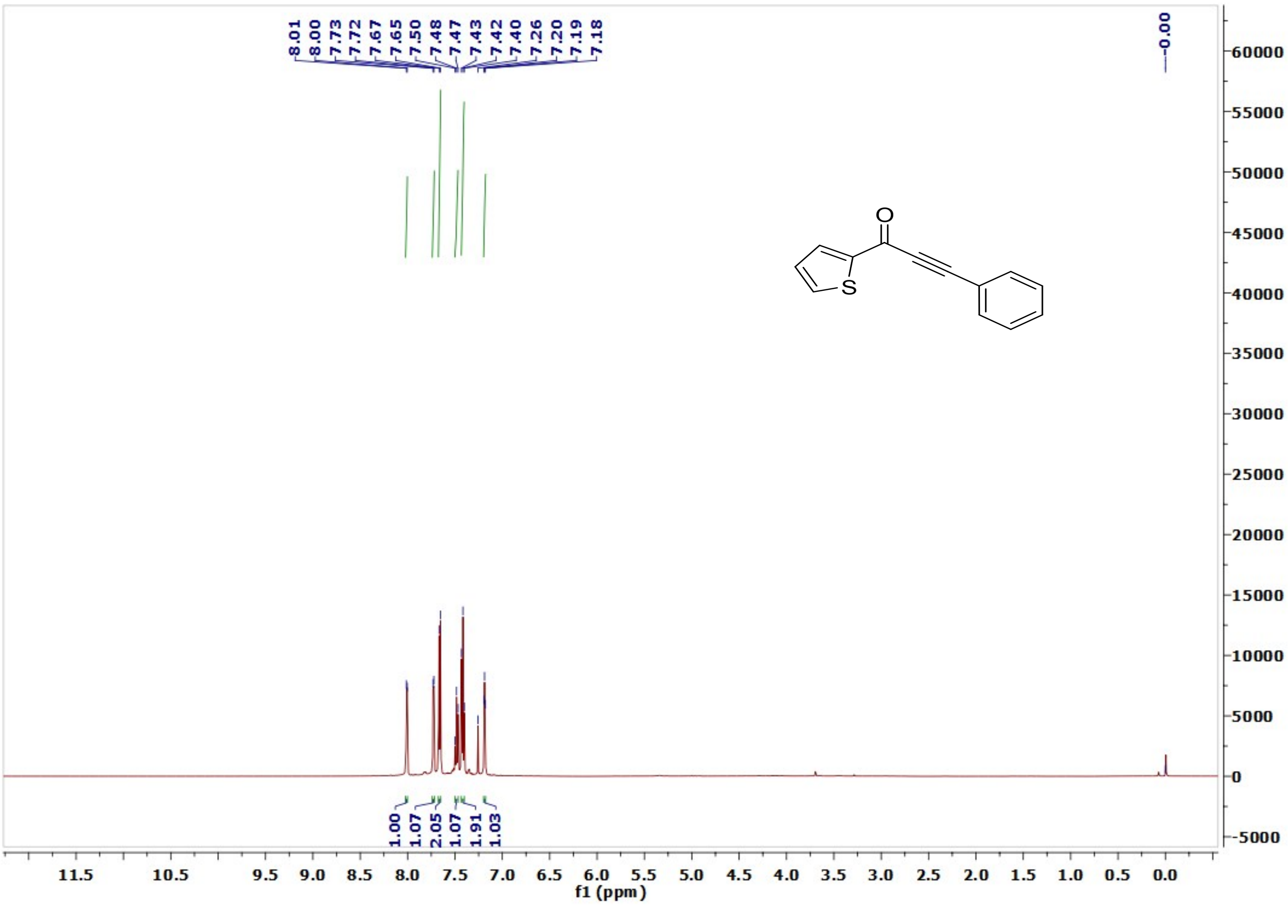


Fig. S23a The ^{1}H NMR spectrum of compound **7g** in $CDCl_3$.

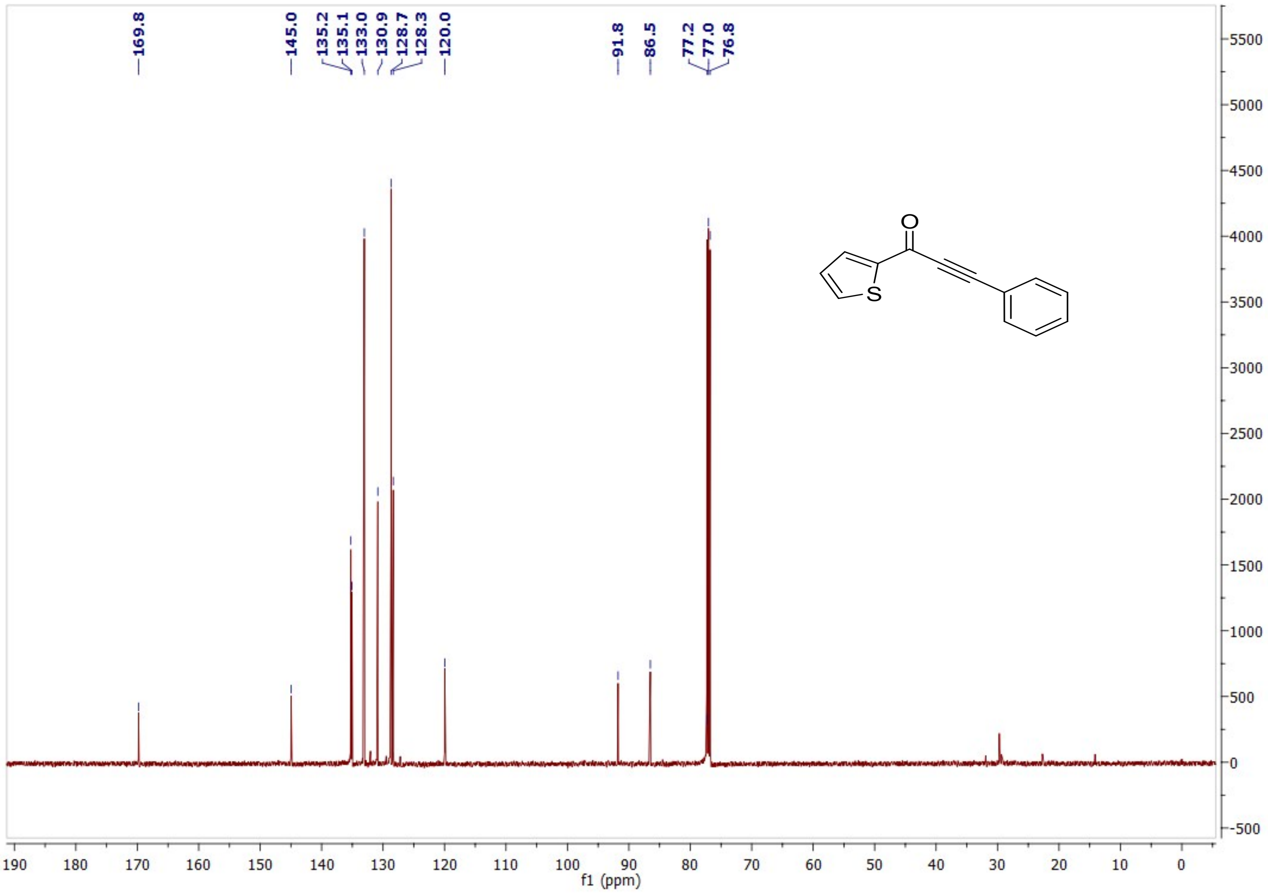


Fig. S23b The ^{13}C NMR spectrum of compound **7g** in $CDCl_3$.

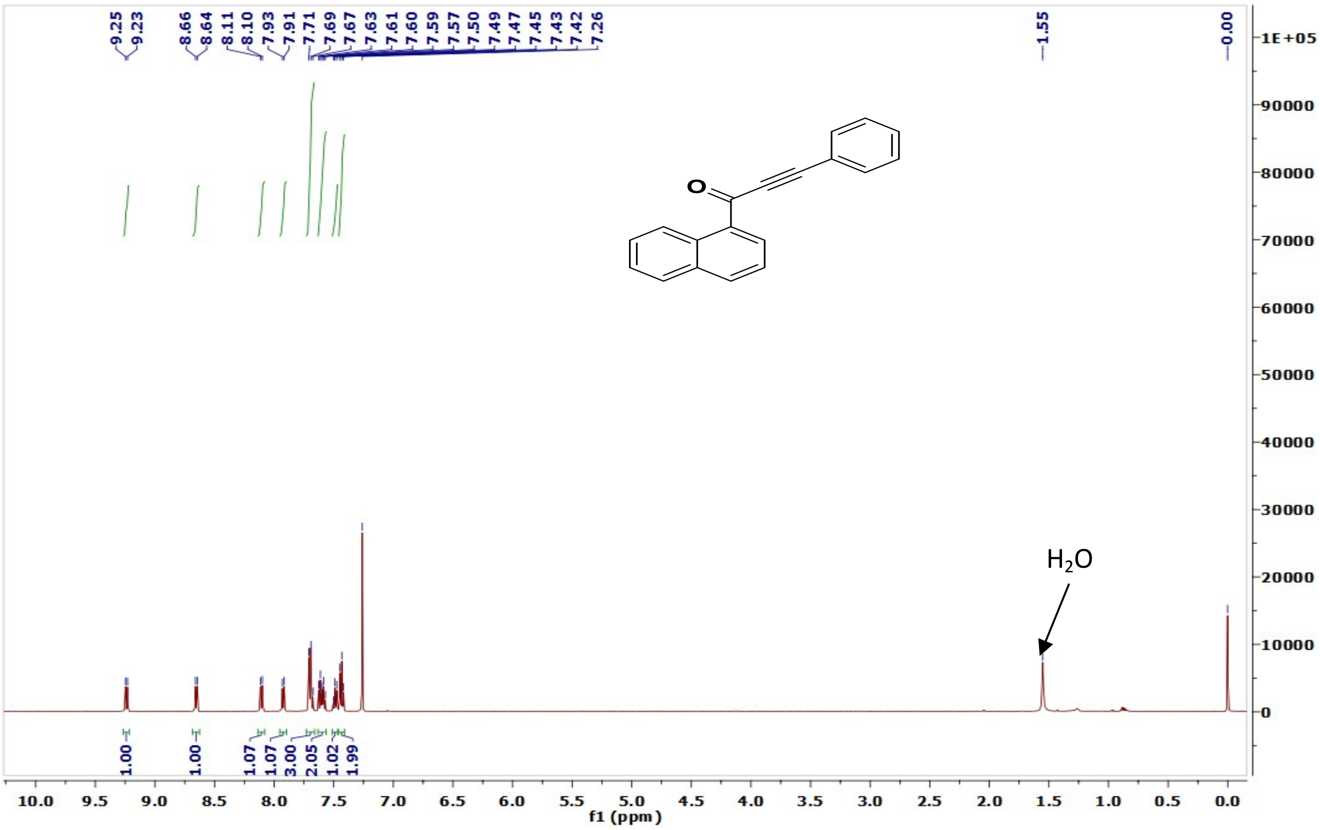


Fig. S24a The ^{1}H NMR spectrum of compound **7h** in $CDCl_3$**.**

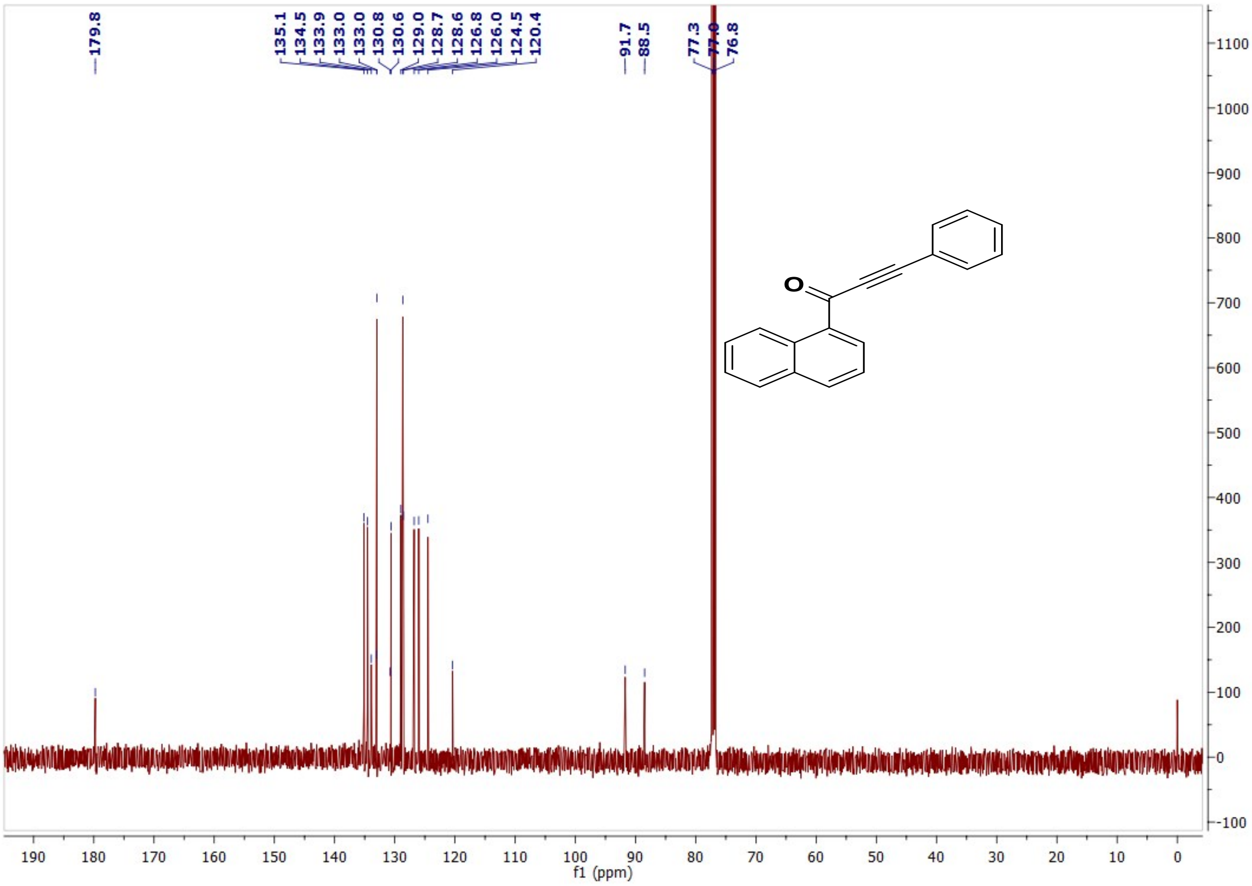


Fig. S24b The ^{1}H NMR spectrum of compound **7h** in $CDCl_3$**.**

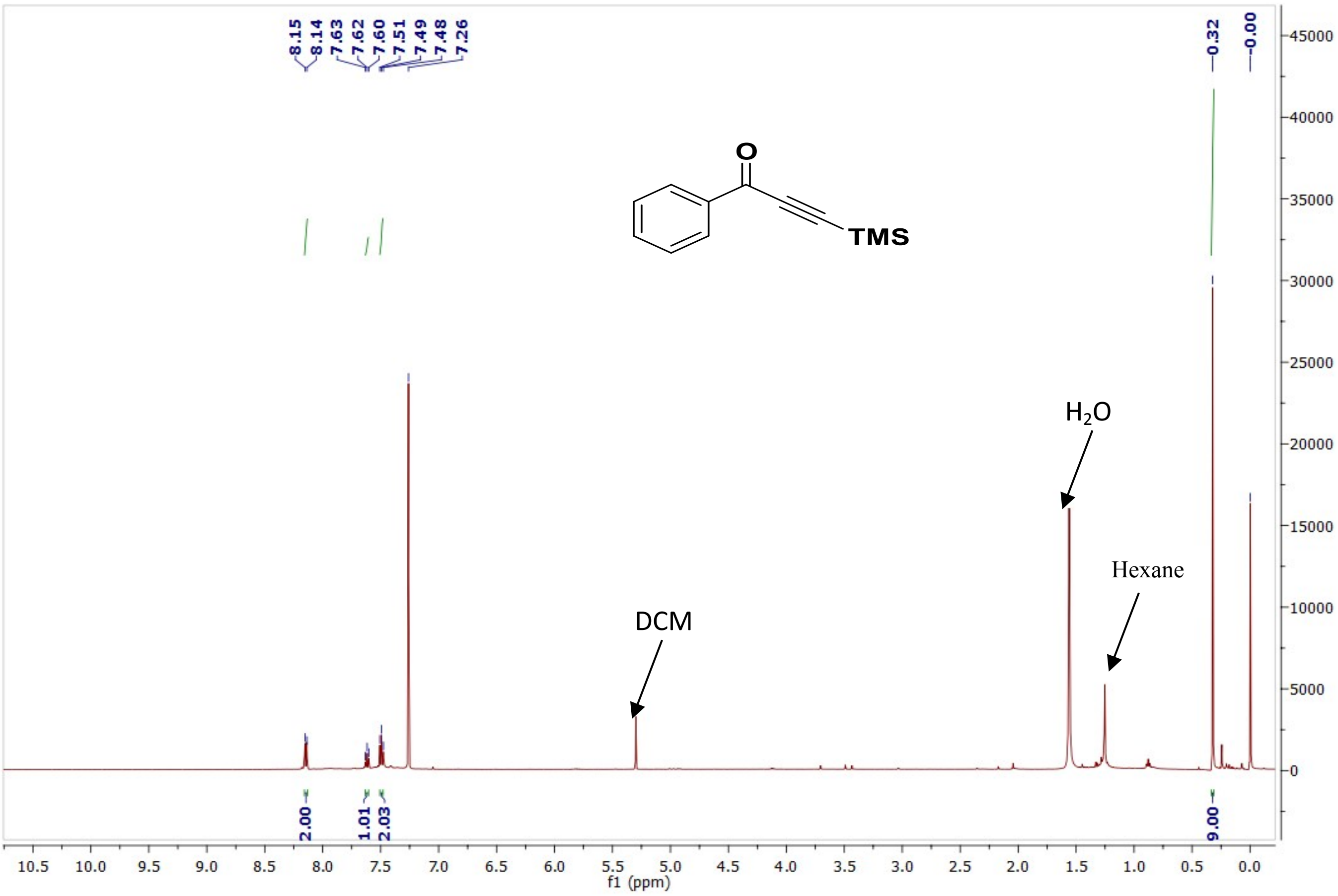


Fig. S25a The ^{1}H NMR spectrum of compound **8b** in $CDCl_3$**.**

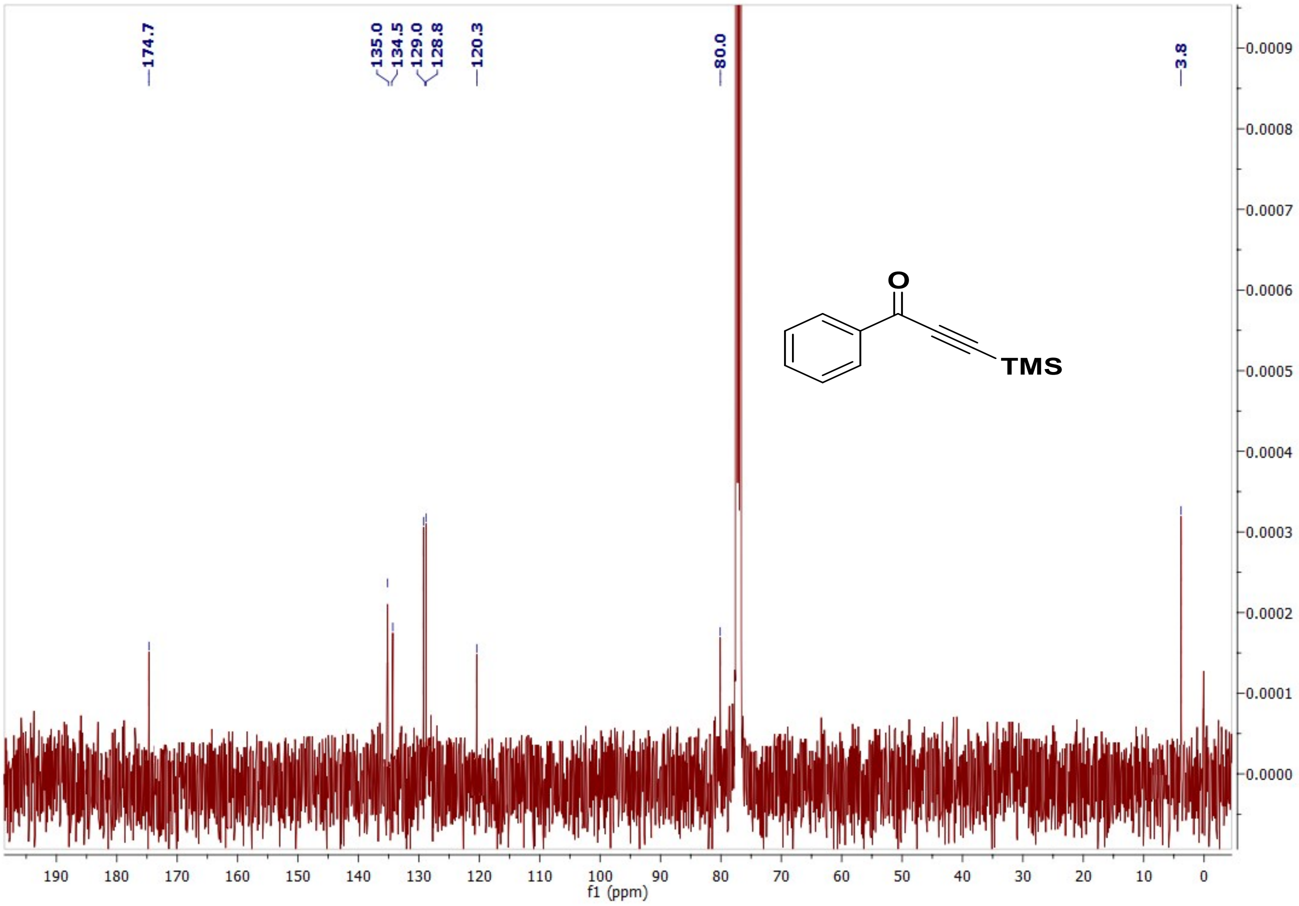


Fig. S25b The ^{1}H NMR spectrum of compound **8b** in $CDCl_3$**.**

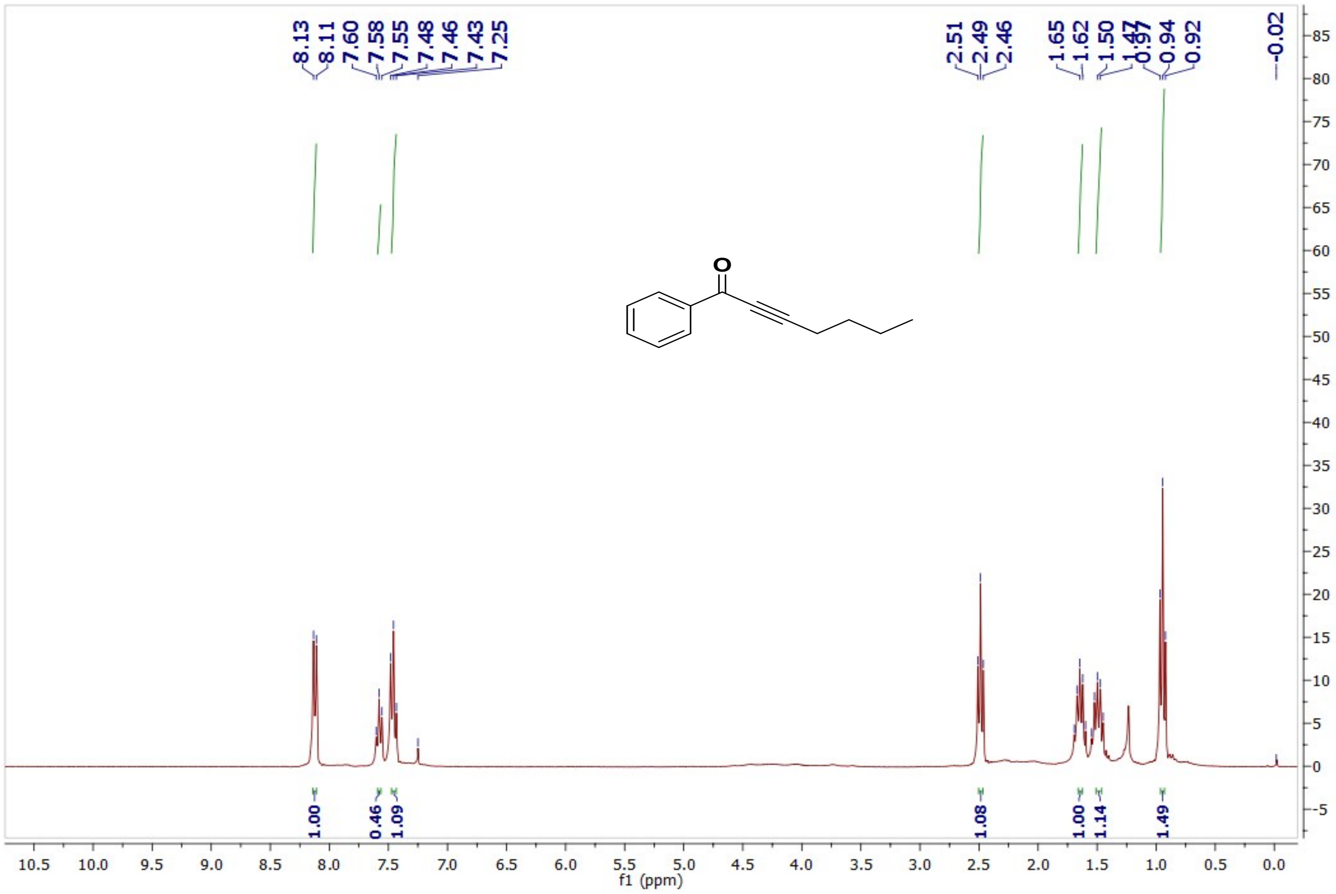


Fig. S26a The ^{1}H NMR spectrum of compound **8c** in CDCl$_3$.

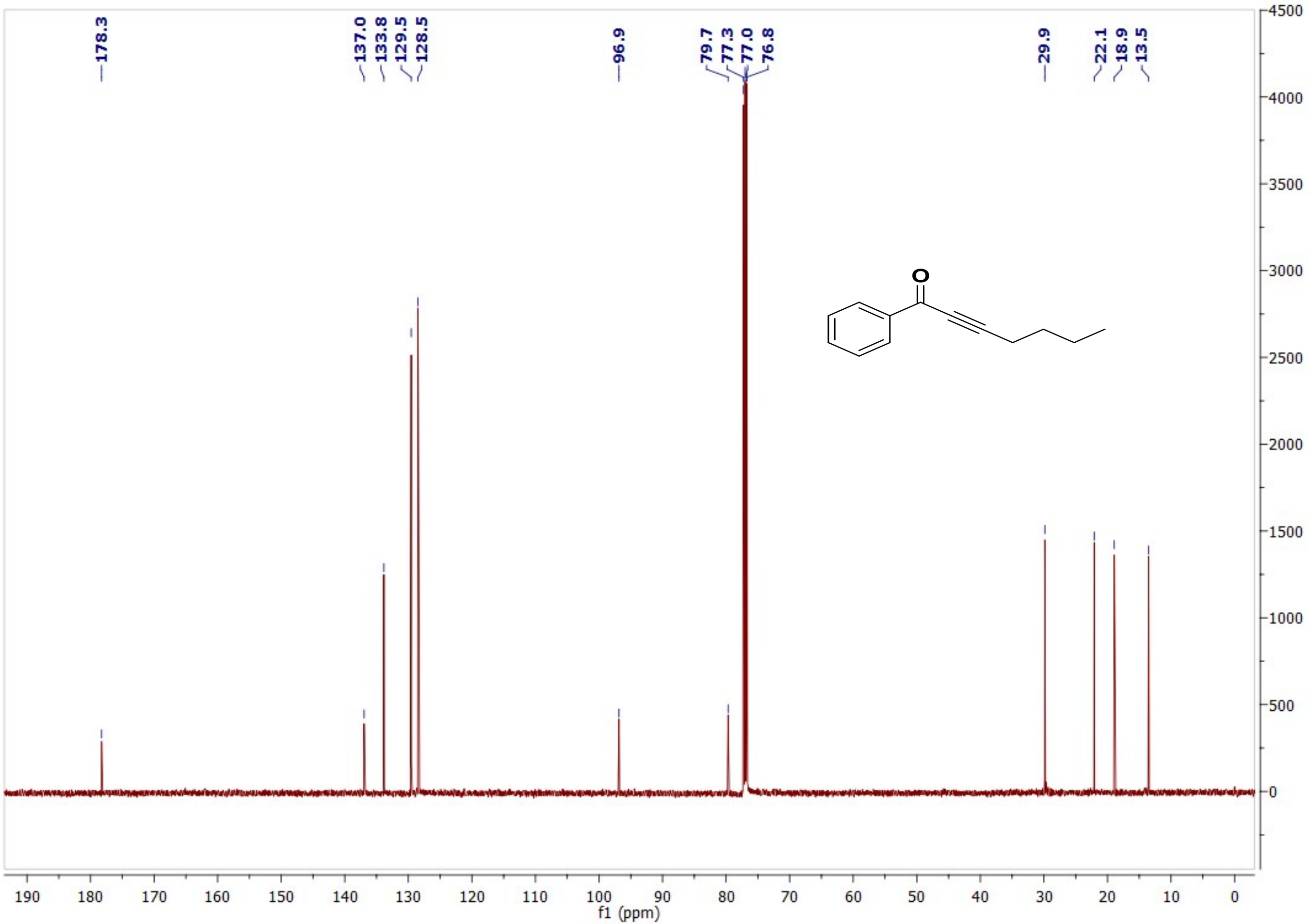


Fig. S26b The ^{1}H NMR spectrum of compound **8c** in CDCl$_3$.

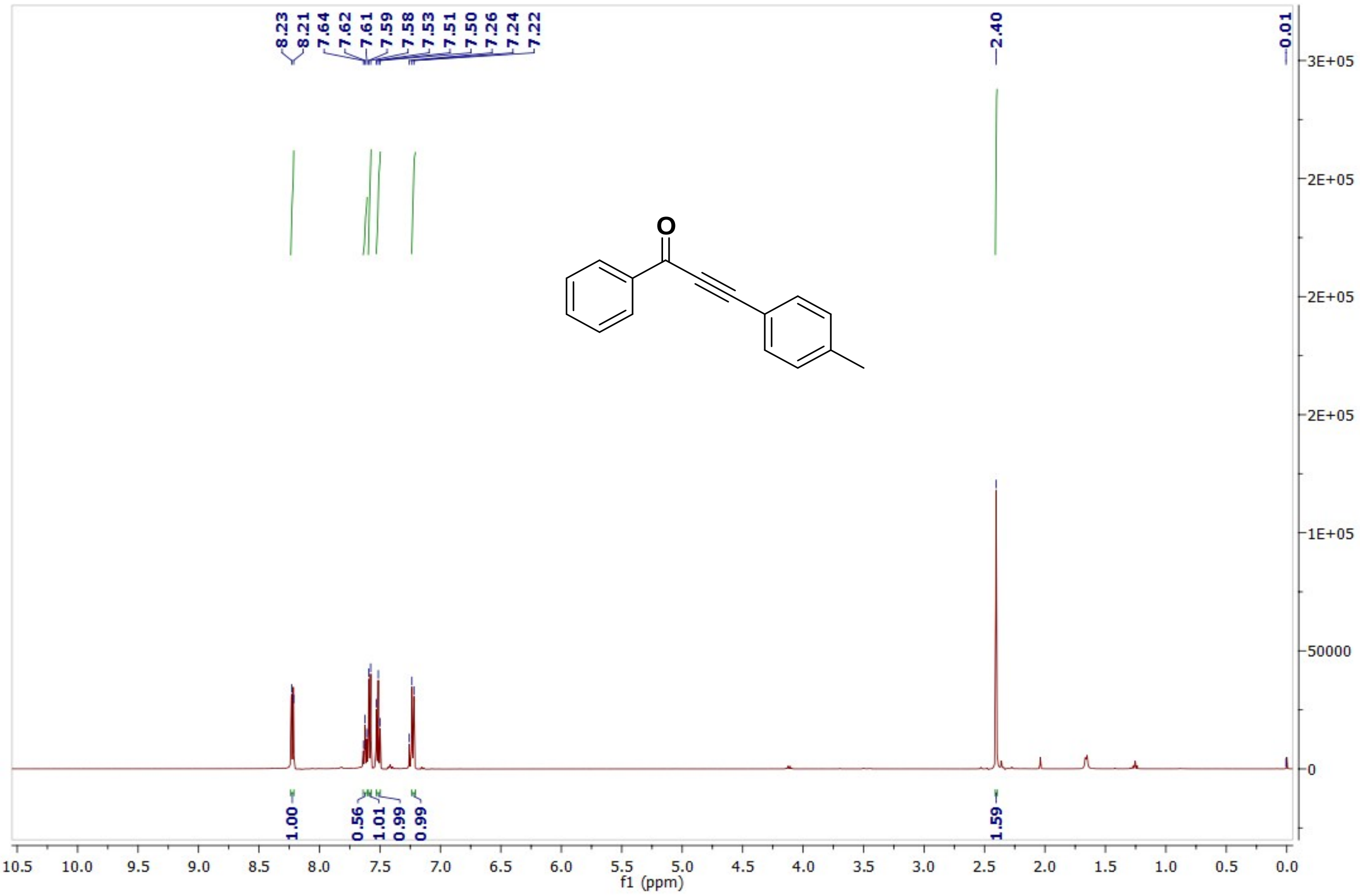


Fig. S27a The ^{1}H NMR spectrum of compound **8d** in CDCl$_3$**.**

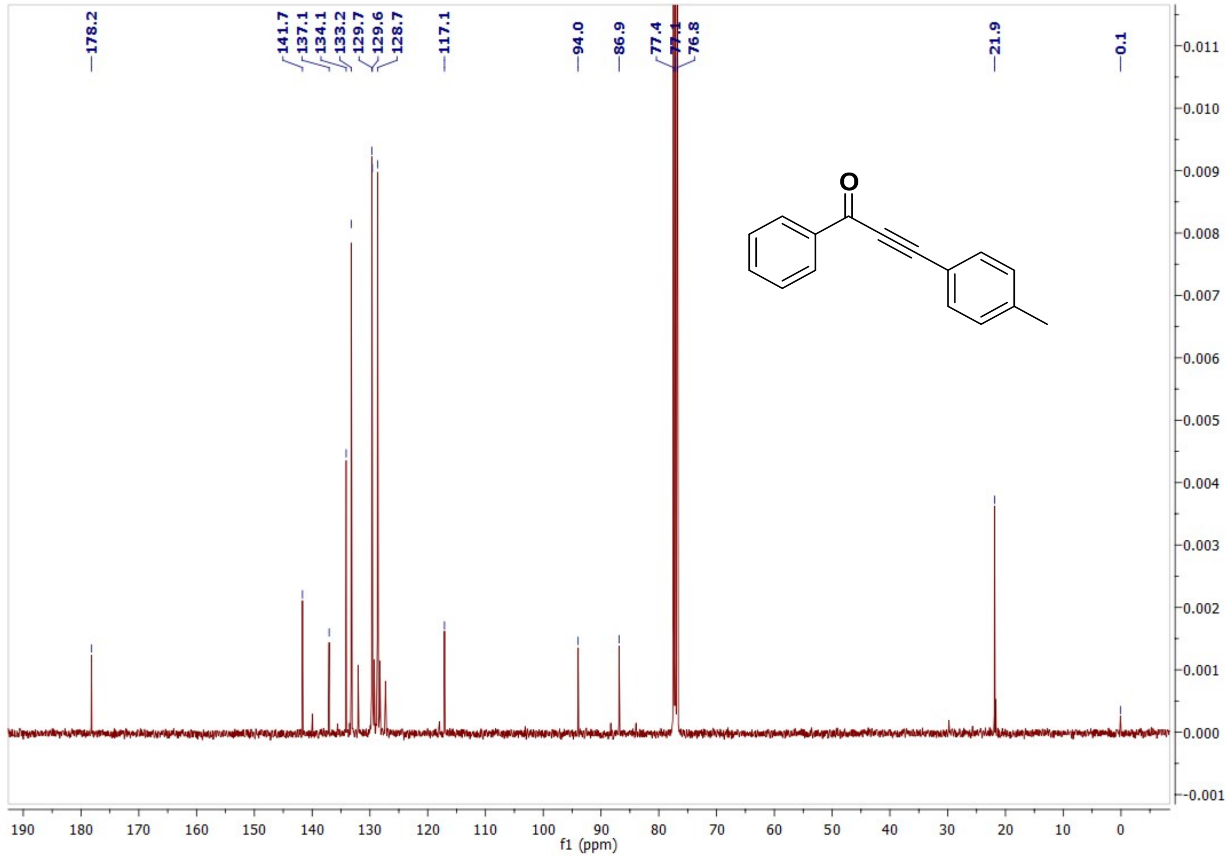


Fig. S27b The ^{1}H NMR spectrum of compound **8d** in CDCl$_3$**.**

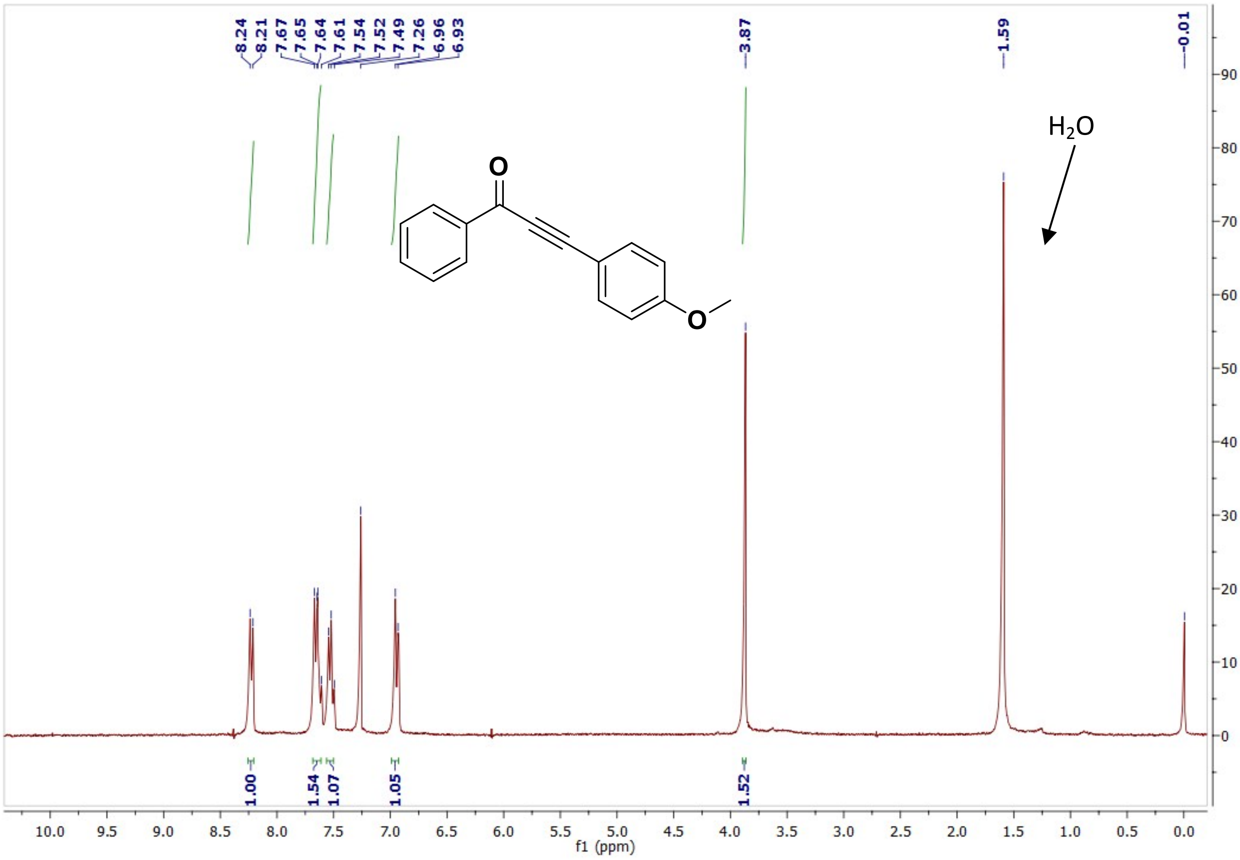


Fig. S28a The ^1H NMR spectrum of compound **8e** in $CDCl_3$.

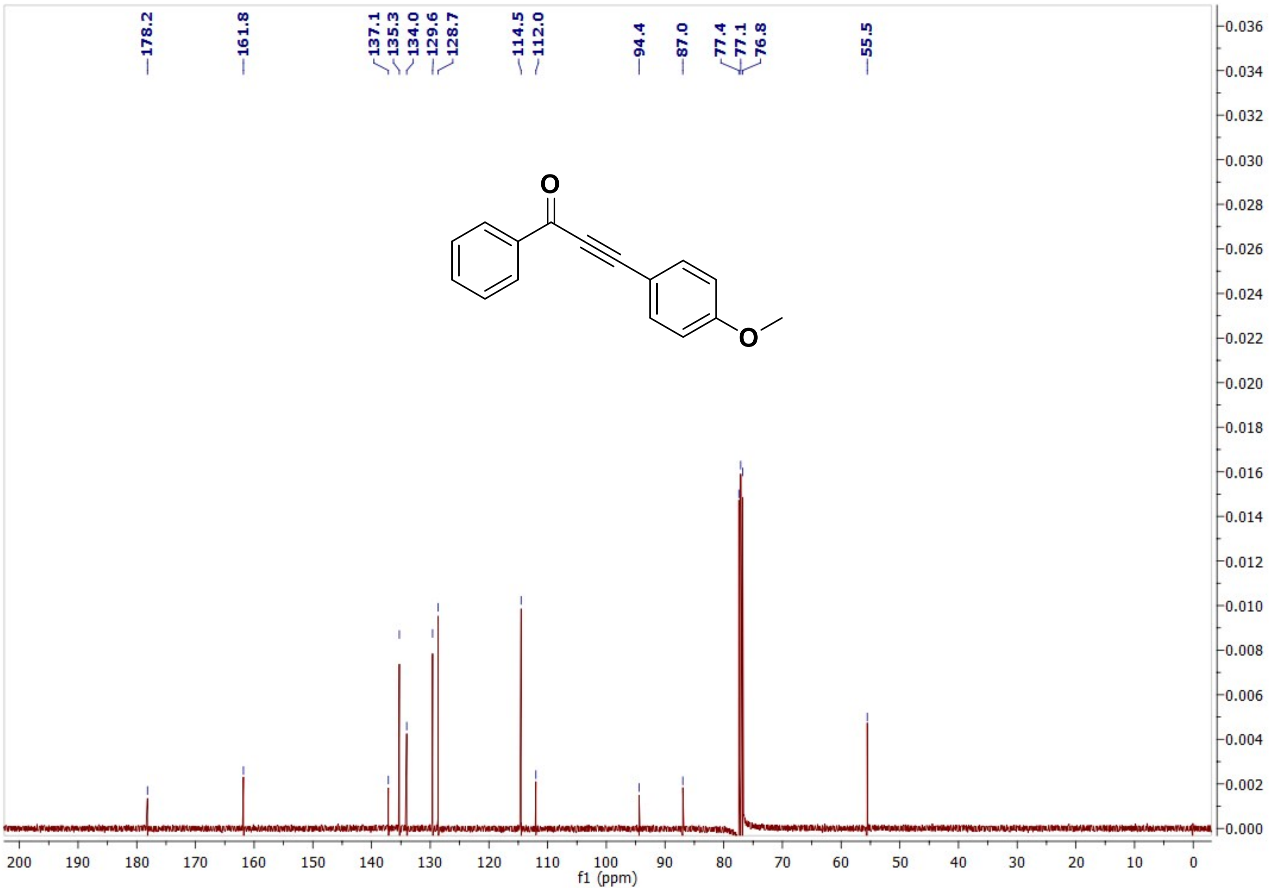


Fig. S28b The ^1H NMR spectrum of compound **8e** in $CDCl_3$.

Table S3: Catalytic efficiency of supramolecular polymer **4:**ZnO NPs for photocatalytic for dehydrogenative coupling reaction of benzaldehyde and phenylacetylene.

Entry	**Catalyst loading**	**Time (h)**	**Yield (%)**
1	4 μmol	24	78
2	2μmol	28	74
3	1μmol	30	72

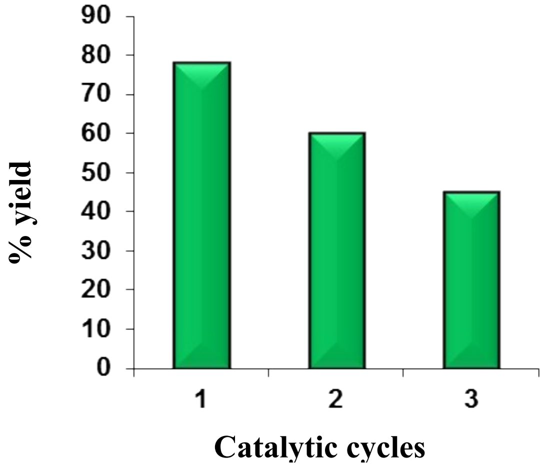
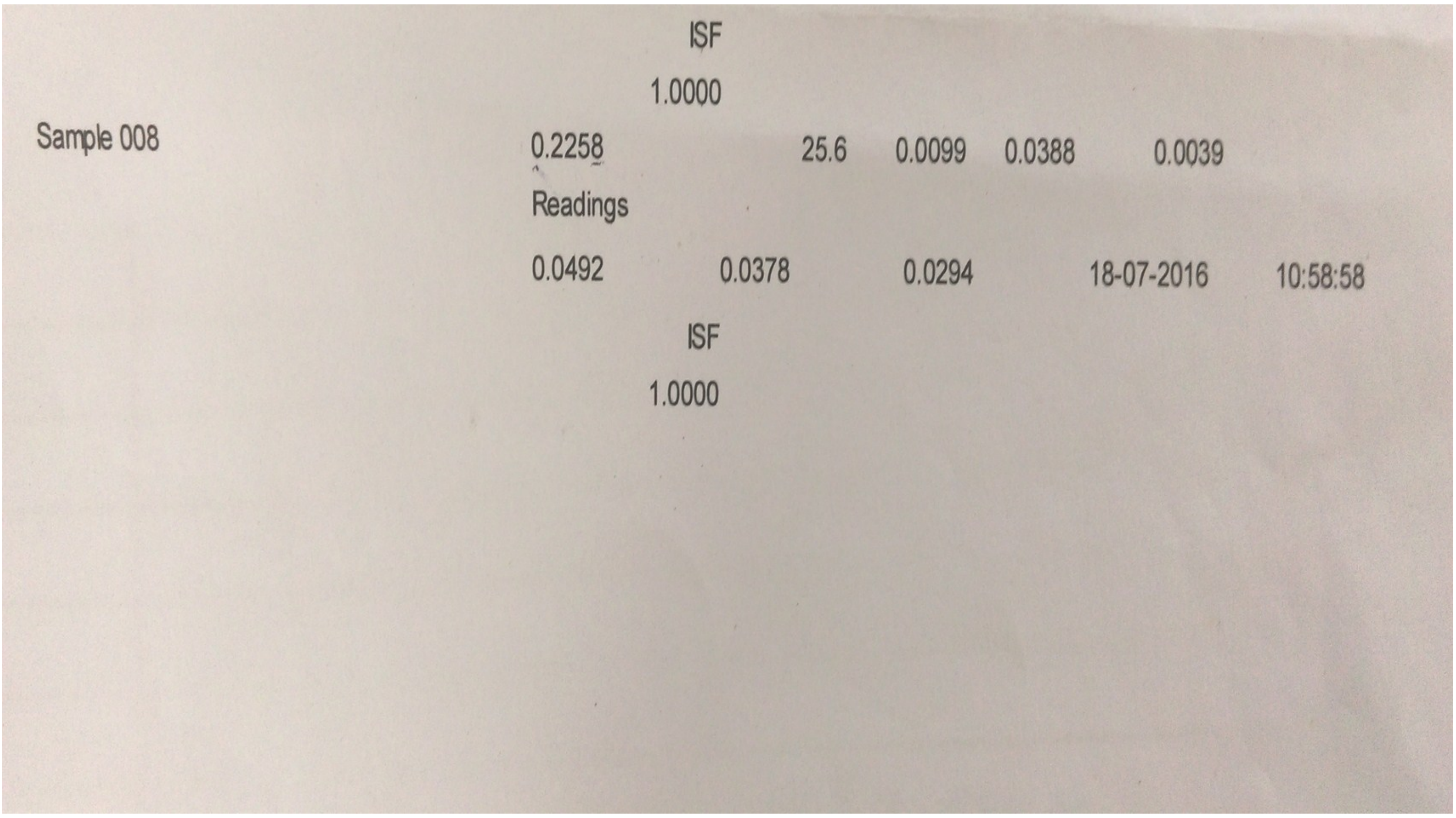


Fig. S29 Recyclability of supramolecular polymer **4**:ZnO NPs catalyst for dehydrogenative coupling reaction.



```
                                ISF
                              1.0000
Sample 008                0.2258              25.6    0.0099   0.0388      0.0039
                          Readings
                          0.0492       0.0378        0.0294       18-07-2016     10:58:58
                                ISF
                              1.0000
```

Fig. S30 Atomic absorption Studies (AAS) of the residual liquid left after the after the recycling of the catalyst and found that only 0.2258 mg/lit = 0.2258 ppm of zinc leached into the solution.

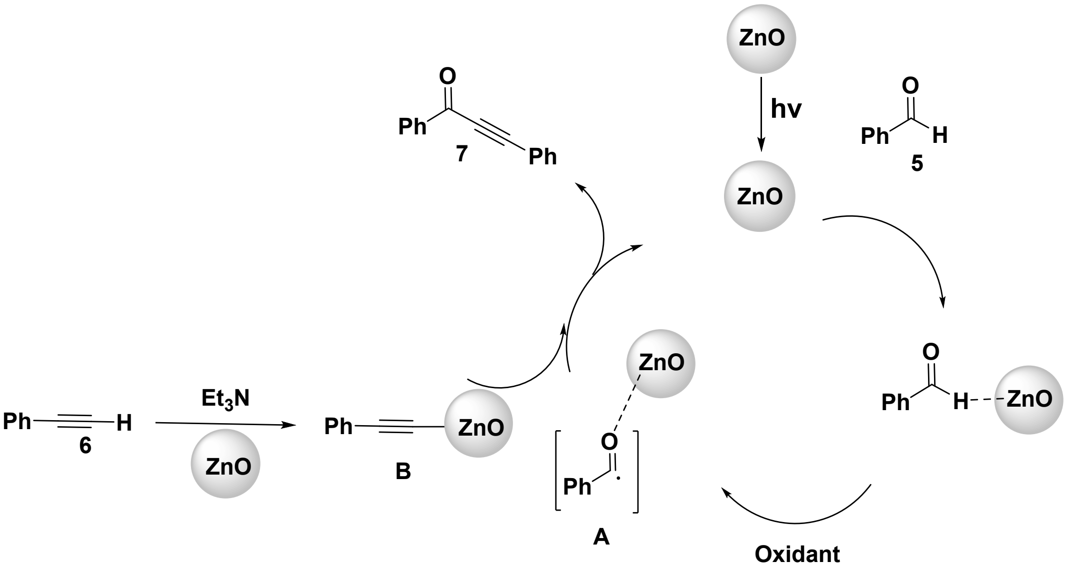


Fig. S31 A plausible reaction mechanism for ZnO NPs catalyzed dehydrogenative coupling.

Catalytic NMR References

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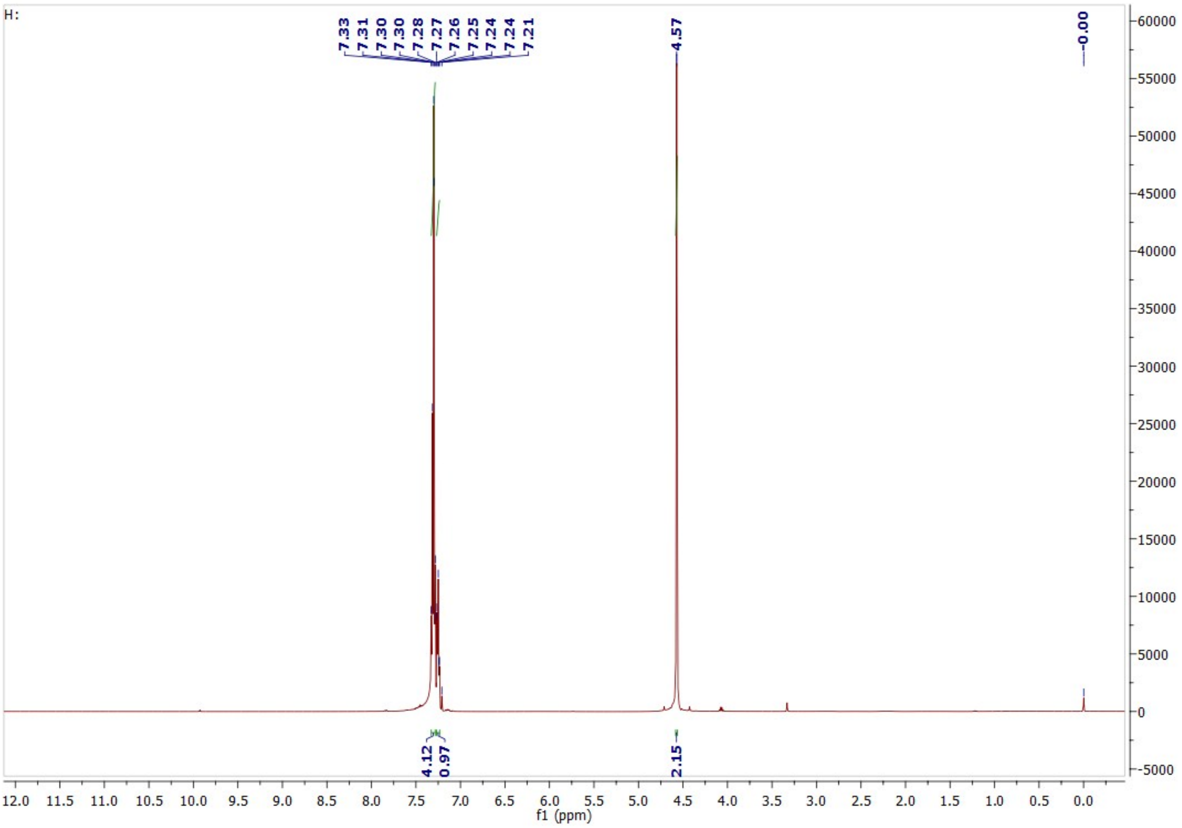

Fig S32a: ^{1}H NMR of phenyl methanol.

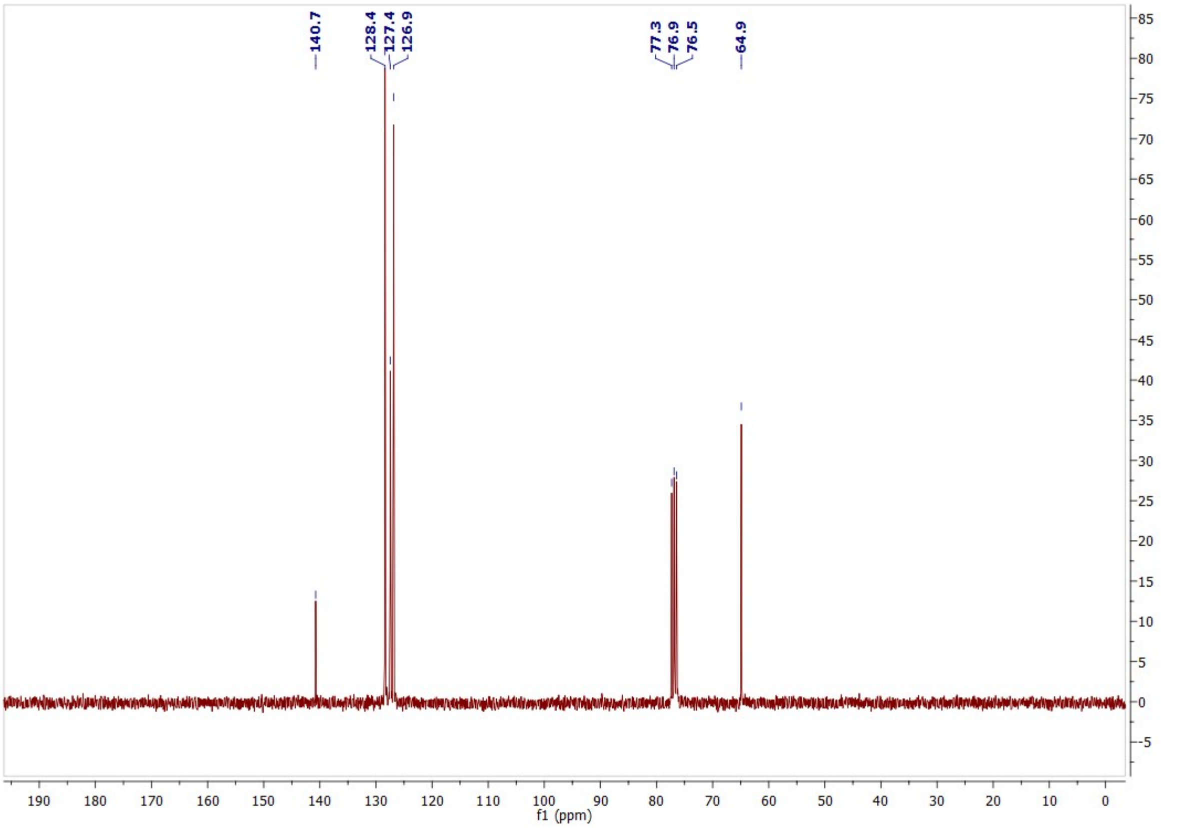

Fig S32b: ^{13}C NMR of phenyl methanol.