

Electronic Supplementary Information

Polystyrene supported [PdCl-(SeCSe)] complex: A novel, reusable and robust heterogeneous catalyst for the Sonogashira synthesis of 1,2-disubstituted alkynes and 1,3-enynes

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1. Experimental Procedure

1.1. General remarks

All materials were commercial grade and purchased from Merck, Aldrich, and Fluka. Chloromethylated polystyrene resin cross-linked with 2% DVB (200-400 mesh, 2.8-3.2 mmol/g of Cl) was a product of Acros chemicals. The NBP test procedure was applied according to the literature [1]. FTIR spectra were recorded using an ABB Bomem model FTLA 2000 spectrophotometer. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra of the final Sonogashira products were recorded on Bruker AQS-300 Avance spectrometer. The metal content of the catalyst was determined with Varian Vista-MPX inductively coupled plasma (ICP) instrument. Thermogravimetry analysis and differential thermogravimetry analysis were carried out using a thermal gravimetric analysis instrument (NETZSCH STA 409 PC/PG) under nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was performed with Physical Electronics PHI-5400. The surface morphology of the polystyrene supported species was analyzed by scanning electron microscope (Vega, TESCAN-Model) equipped with energy dispersive X-ray (EDX) facility.

1.2. Experimental procedure and spectroscopic data for compounds 1b-e

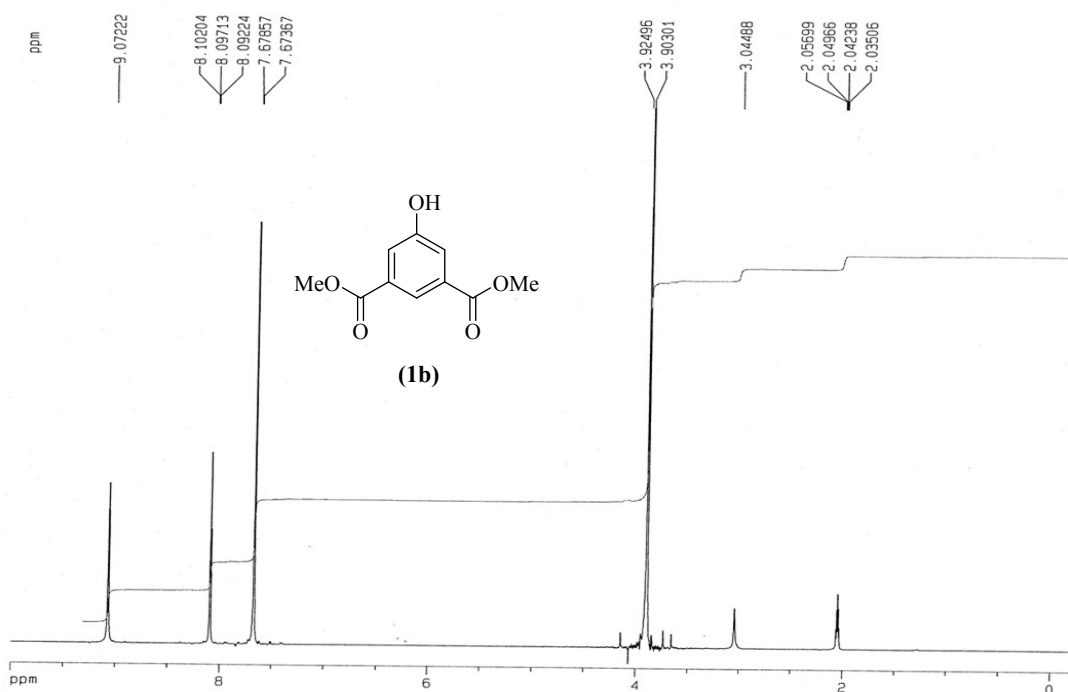
Dimethyl 5-hydroxyisophthalate (1b)

5-hydroxyisophthalic acid (**1a**) (3.5 g, 19 mmol) and concentrated H_2SO_4 (1 mL) was dissolved in MeOH (35 mL). The solution was warmed to 65 °C and refluxed for 24 h; then, 20 mL of water was added to the solution at room temperature and the resulting white solid was filtered off and washed with water. The final product was air dried and obtained as a white solid (3.8 g, 97%), m.p.: 160-162 °C (lit. m.p.: 165 °C [2]). ^1H NMR (300 MHz, d_6 -acetone): δ (ppm): 9.1 (s, 1H), 8.097 (s, 1H), 7.58 (s, 2H), 3.91 (s, 6H).

3,5-Di(hydroxymethyl)phenol (1c)

To a suspension of LiAlH_4 (1.357 g, 36 mmol) in dry THF (50 mL) at 0 °C, dimethyl 5-hydroxyisophthalate (3 g, 14 mmol) (**1b**) was slowly added. The mixture was gently heated to 50 °C and stirred overnight under argon atmosphere. The suspension was cooled to room temperature and THF was evaporated. The resulting paste was cooled down to 0 °C and 20% aq (v/v) H_2SO_4 (10 mL) was added dropwise to neutralize unreacted metal hydride; then the residue was partitioned between EtOAc (50 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (4 $\times$ 20 mL) and the combined organic layers were dried with MgSO_4 . The solvent evaporated under reduced pressure and the resulting viscose yellow oil was subjected to column chromatography (SiO_2 , eluent: *n*-hexane : EtOAc = 1:4) to afford (**1c**) as colorless viscose oil in 72% yield (1.55 g) [3].

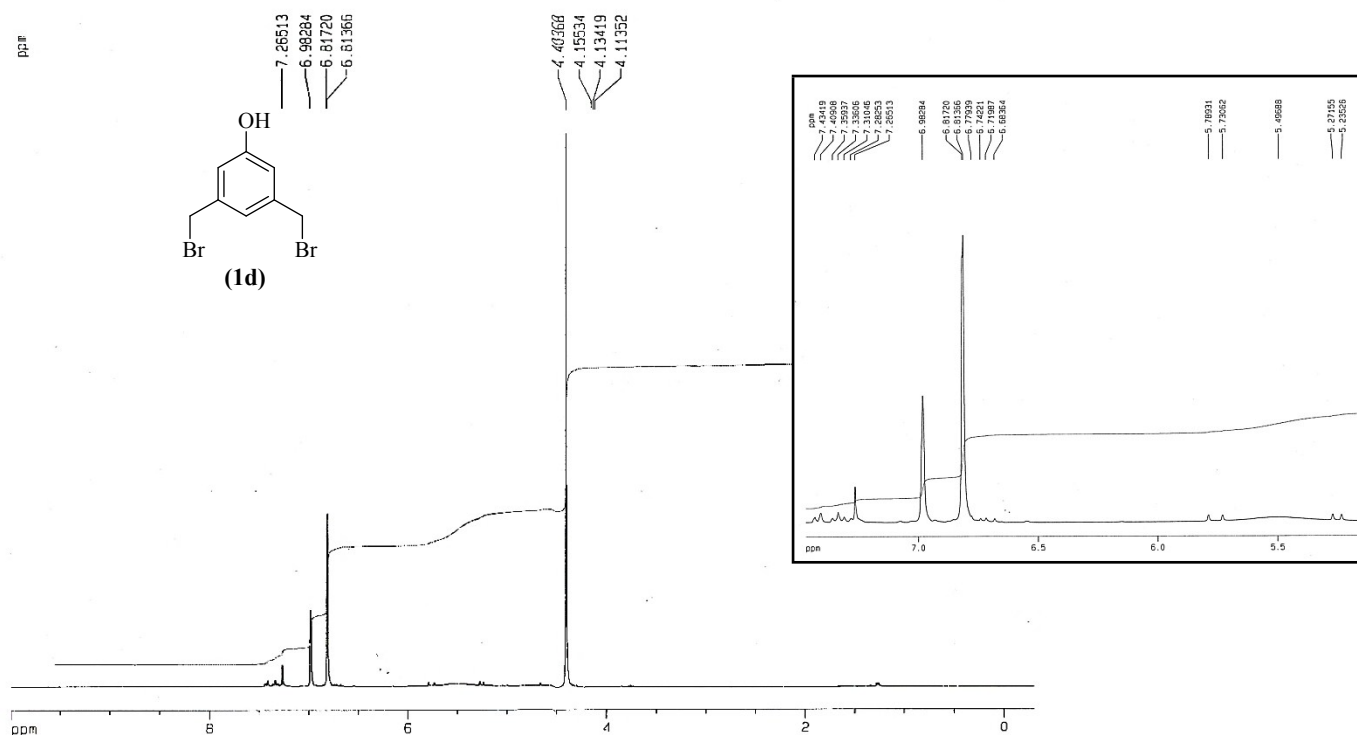
^1H NMR (d_6 -acetone, 300 MHz)



3,5-Di(bromomethyl)phenol (**1d**)

In a 100mL round-bottom flask, 3,5-di(hydroxymethyl)phenol (1.540 g, 10 mmol) was dissolved in dry THF (35 mL) and the solution cooled to 0 °C. The solution of phosphorus tribromide (3 mL, 30 mmol) in dry THF (5 mL) was slowly added over 30 min; then, the mixture was stirred for 72 h at 40 °C under argon atmosphere. After cooling to room temperature, the mixture was washed with saturated aq solution of NaHCO_3 and extracted with EtOAc (3×15 mL). The combined organic layers were dried over MgSO_4 and concentrated over reduced pressure. The crude mixture was purified by column chromatography (SiO_2 , eluent: *n*-hexane : EtOAc = 4:1) to give (**1d**) in pure form (2.2 g, yield = 78%). White solid; m.p.: 79-81 °C (lit. m.p.: 80-83 °C [4]). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 6.98 (s, 1H), 6.81 (s, 2H), 4.40 (s, 4H), 5.50 (s, br, 1H).

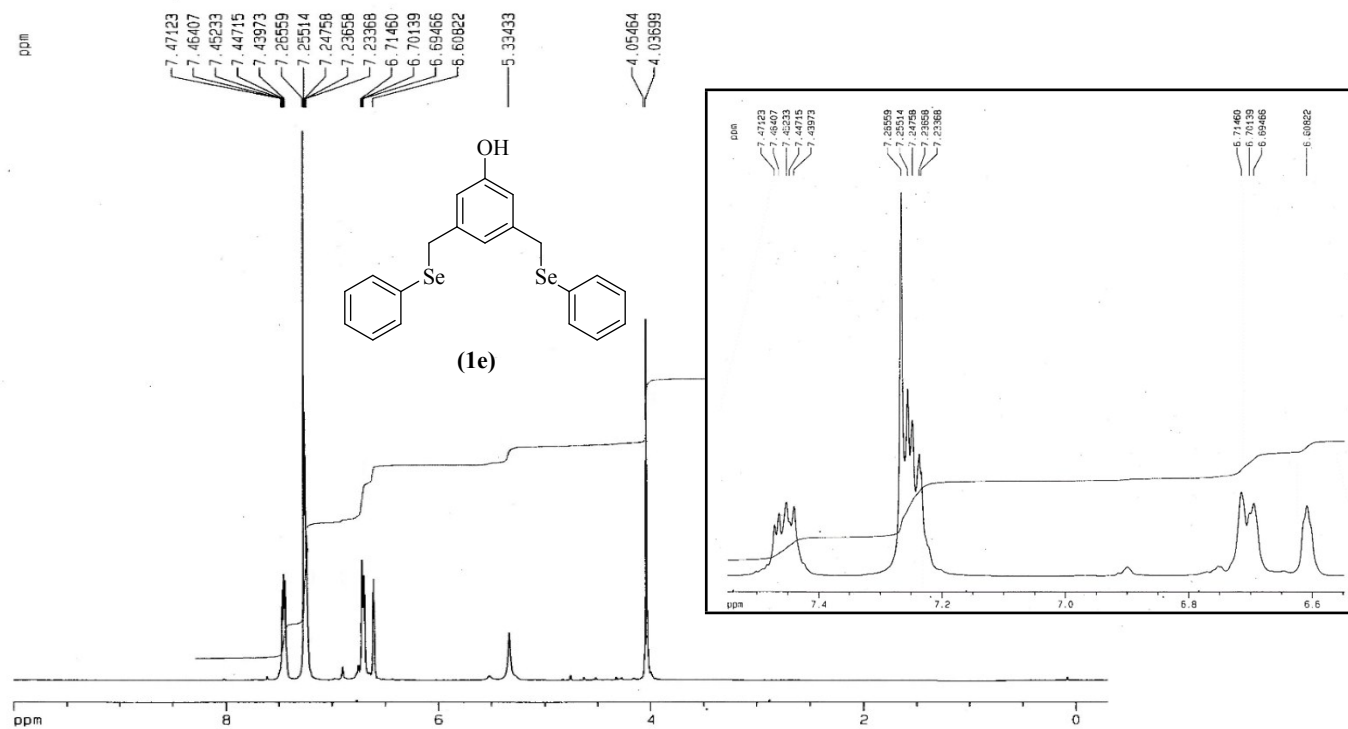
^1H NMR (CDCl_3 , 300 MHz)



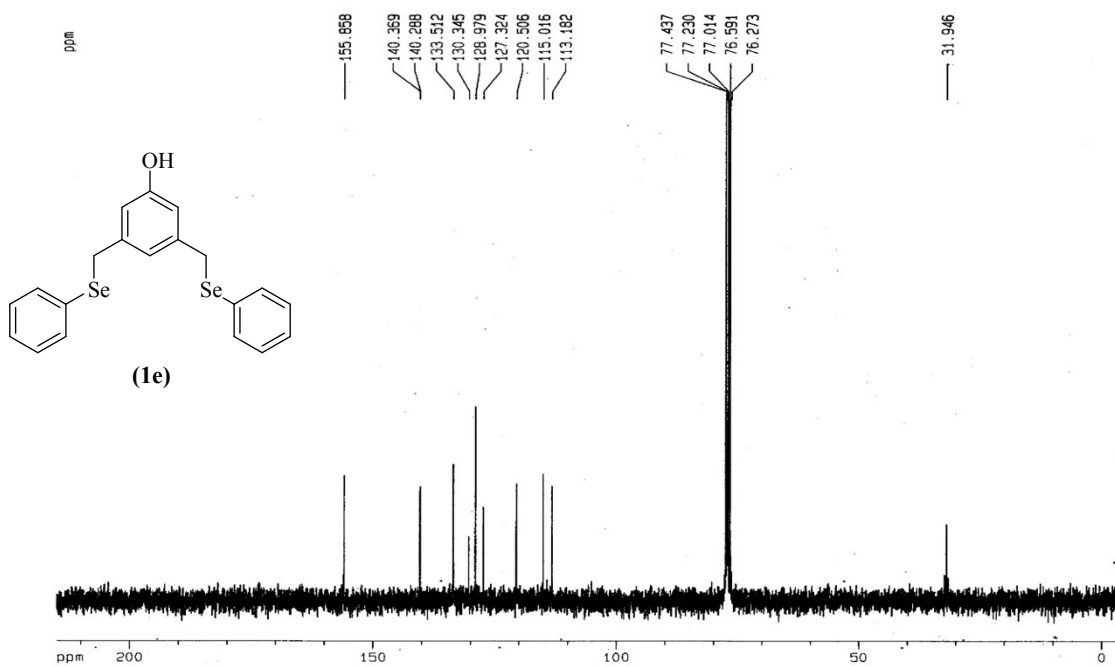
3,5-Bis((phenylselanyl)methyl)phenol (**1e**)

Diphenyl diselenide (2.7 g, 8.6 mmol) was dissolved in EtOH (70 mL); then a solution of NaBH_4 (0.654 g, 17.2 mmol) in aq 20% NaOH (5 mL) was added to the above solution and stirred under argon atmosphere for 10 min. During this period, the yellow color of solution turned to colorless, indicating the reduction of Ph_2Se_2 . Then, **(1d)** (2 g, 7.2 mmol) was dissolved in EtOH (30 mL) and then 20% aq NaOH (20 mL) was added to this solution, and the formation of the corresponding phenolate salt was monitored by thin layer chromatography, TLC. Next, this mixture was transferred to the PhSeNa solution and stirred at 40 °C for 15 h under Ar atmosphere, after which the EtOH was evaporated and EtOAc (15 mL) was added to the crude mixture. Then, the mixture treated with 20% aq H_2SO_4 (20 mL) and extracted with EtOAc (2 $\times$ 15 mL). Organic layers were collected and dried over MgSO_4 . For purification of the resulting mixture, silica gel column chromatography was applied (*n*-hexane : EtOAc = 4:1), which gave the **(1e)** in 52% yield as yellow oil (1.62 g). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.47-7.43 (m, 2H), 7.25-7.23 (m, 7H), 6.71-6.69 (m, 3H), 6.61 (s, 1H), 5.33 (s, 1H), 4.04 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm): 155.8, 140.3, 133.5, 130.4, 128.9, 127.3, 120.5, 115.0, 113.2, 31.9. EI-MS: 432.3 (8), 277 (24), 156 (24), 121 (100), 91 (57), 51 (8). Elemental analysis: calcd (%) for $\text{C}_{20}\text{H}_{18}\text{OSe}_2$: C 55.30, H 4.37, N 0; found: C 55.37, H 4.37, N 0.025.

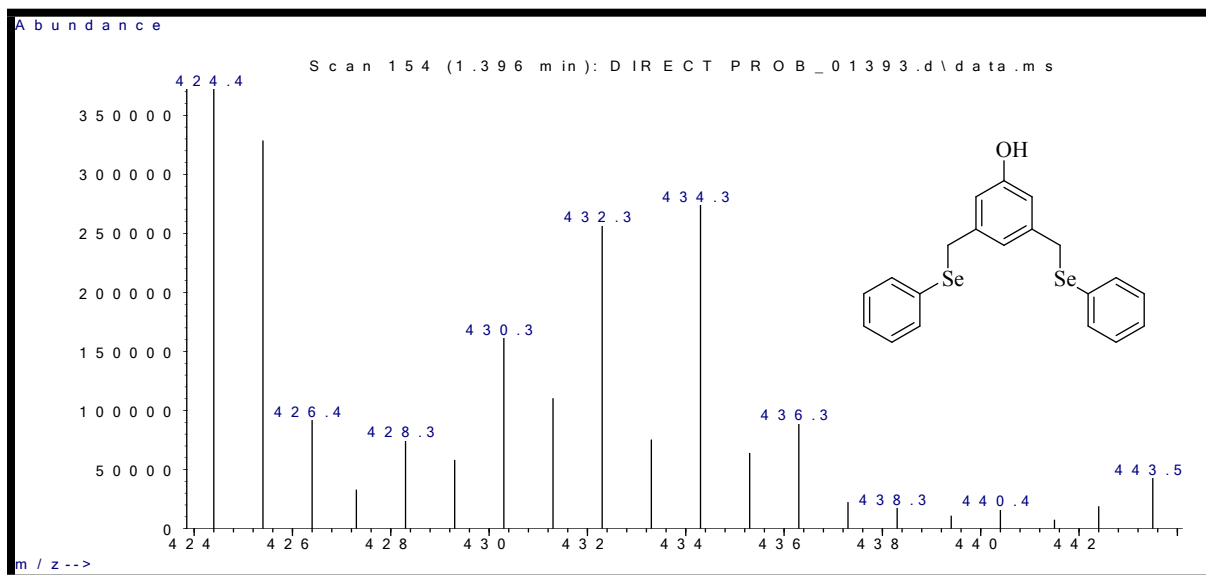
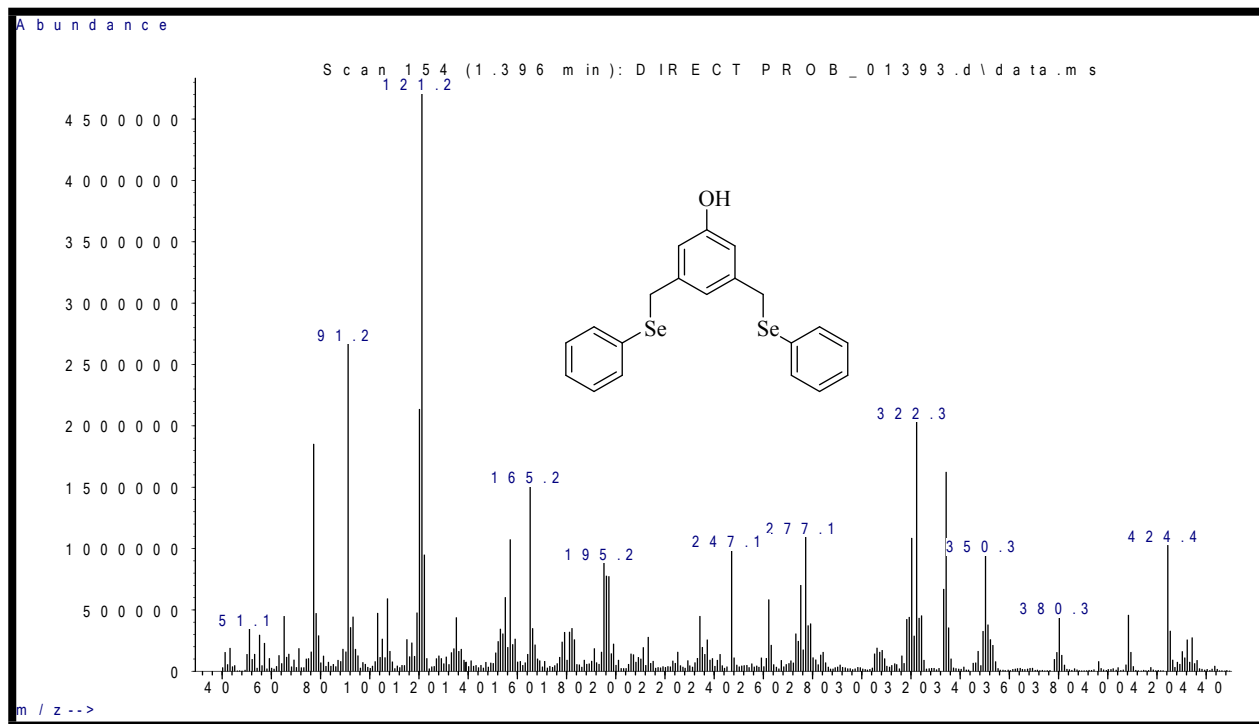
^1H NMR (CDCl_3 , 300 MHz)



^{13}C NMR (CDCl_3 , 75 MHz)



Mass Spectrum of (1e)



1.3. Preparation and characterization of polymer anchored SeCSe (1f) and [PdCl-(SeCSe)] (1g)

Synthesis of polystyrene supported-SeCSe pincer ligand (1f)

In a 50 mL round-bottom flask, chloromethylated polystyrene resin (0.6 g, ~ 1.8 mmol Cl) was allowed to swell in DMSO (15 mL) for 24 h at room temperature. Then, to the above flask was added successively 3,5-bis((phenylselanyl)methyl)phenol (1.5 g, 3.5 mmol), K_2CO_3 (1.5 g, 11 mmol), and tetra-*n*-butylammonium iodide (TBAI) (0.133 g, 0.36 mmol). The mixture was stirred at 60 °C under argon atmosphere. After 72 h, the functionalized polymer beads were filtered and washed with DMSO (10 mL), H_2O (20 mL), and MeOH (20 mL) and dried in an oven at 80 °C for 2 h (1.052 g of 1f was recovered).

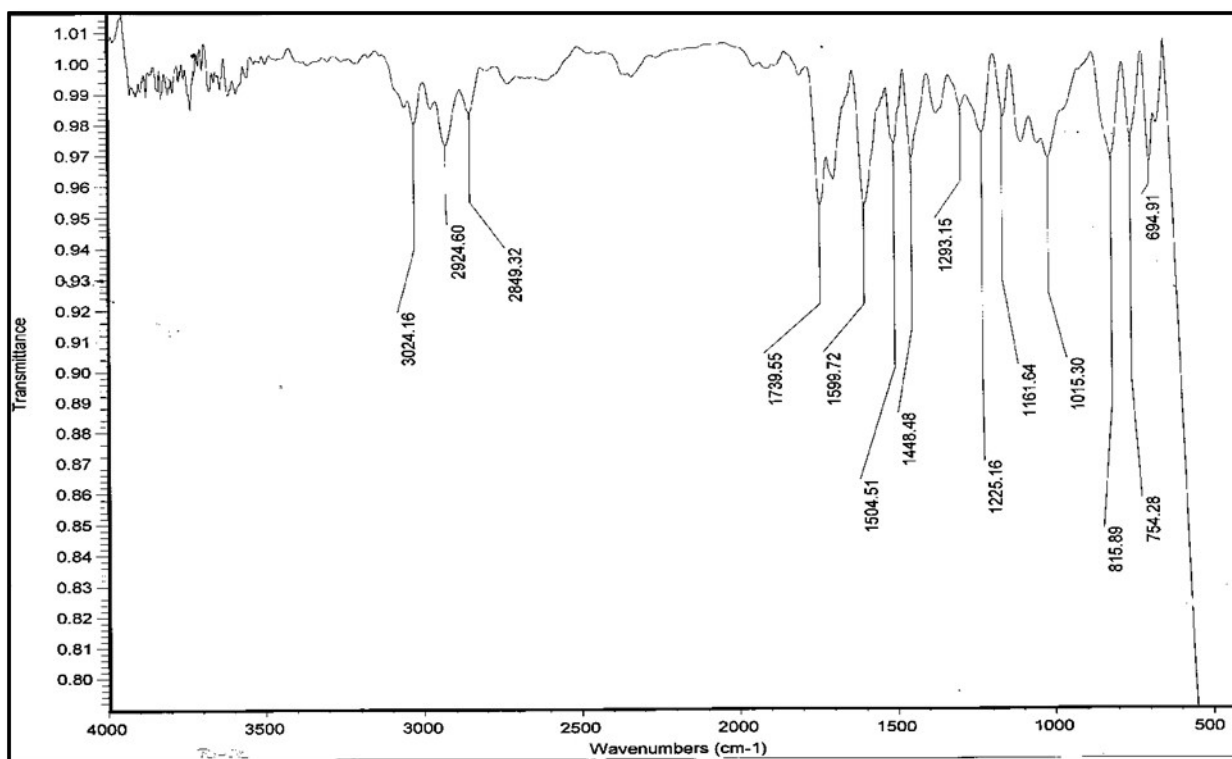


Figure S1. IR spectra of PS-SeCSe (1f)

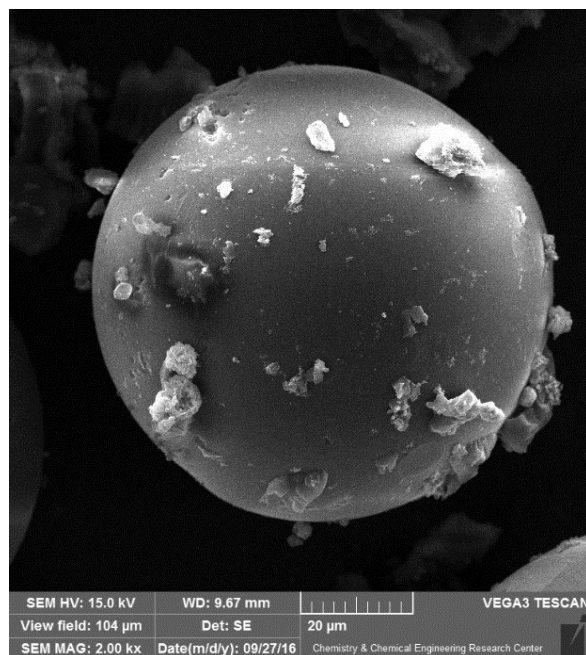


Figure S2. SEM image of PS-SeCSe (1f)

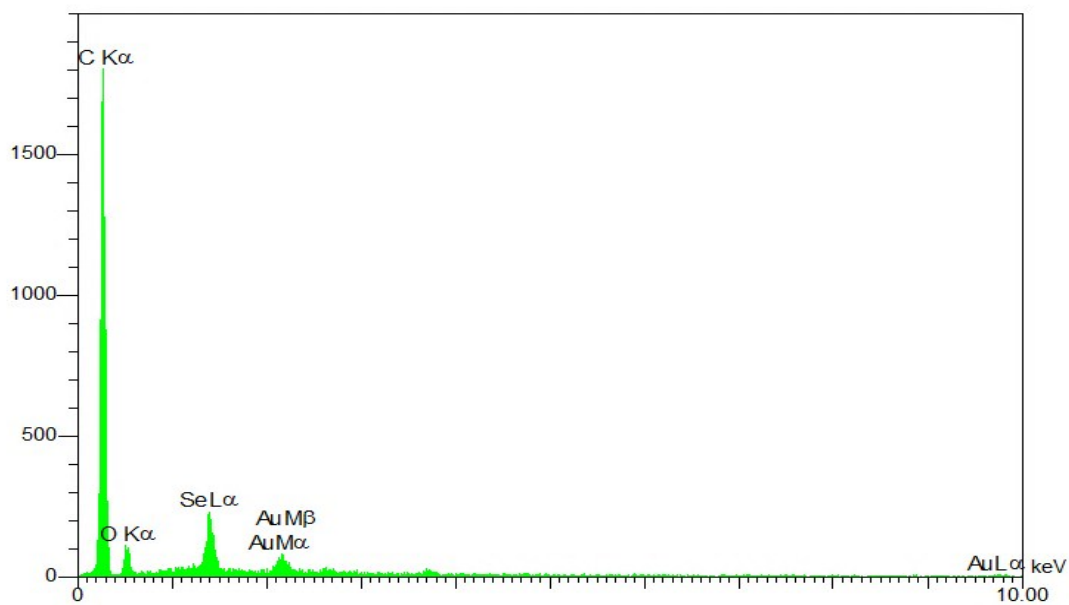


Figure S3. EDX spectra of PS-SeCSe (1f)

Synthesis of PS-[PdCl-(SeCSe)] pincer ligand (**1g**)

The PS-SeCSe resin beads (0.88 g) were swelled for 1 h in dry THF (25 mL); then PdCl₂ (0.177 g, 1 mmol) and Et₃N (0.3 mL, 2 mmol) were added to the suspension and stirred for 15 h at 50 °C. The resulting polymeric [PdCl-(SeCSe)] was filtered off and the filtrate was washed with THF (10 mL), CH₃CN (10 mL), and MeOH (10 mL) and dried in an oven at 70 °C for 2 h (0.933 g of **1g** was obtained).

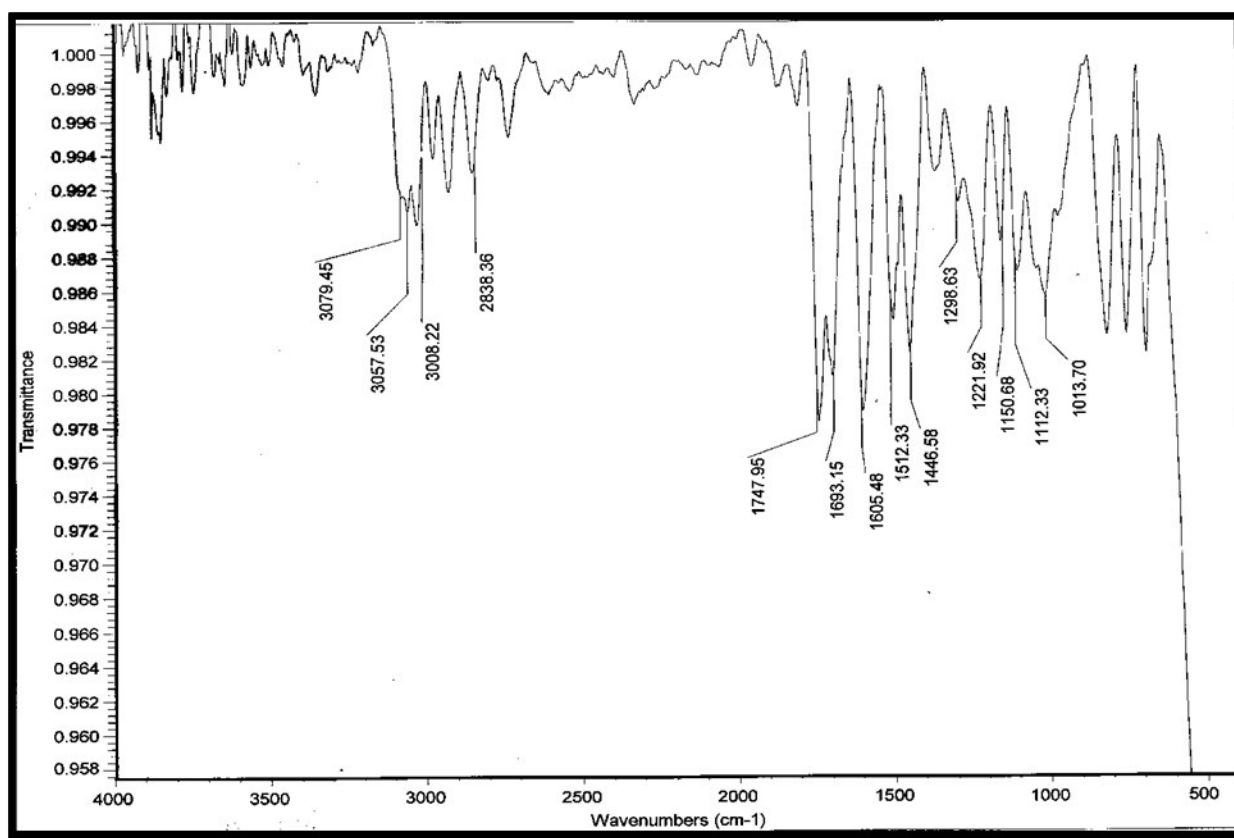


Figure S4. IR spectra of PS-[PdCl-(SeCSe)] (**1g**)

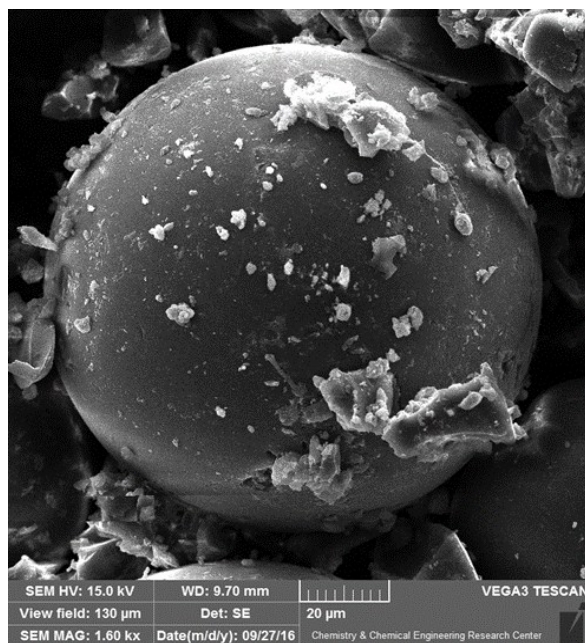


Figure S5. SEM image of PS-[PdCl-(SeCSe)] (1g)

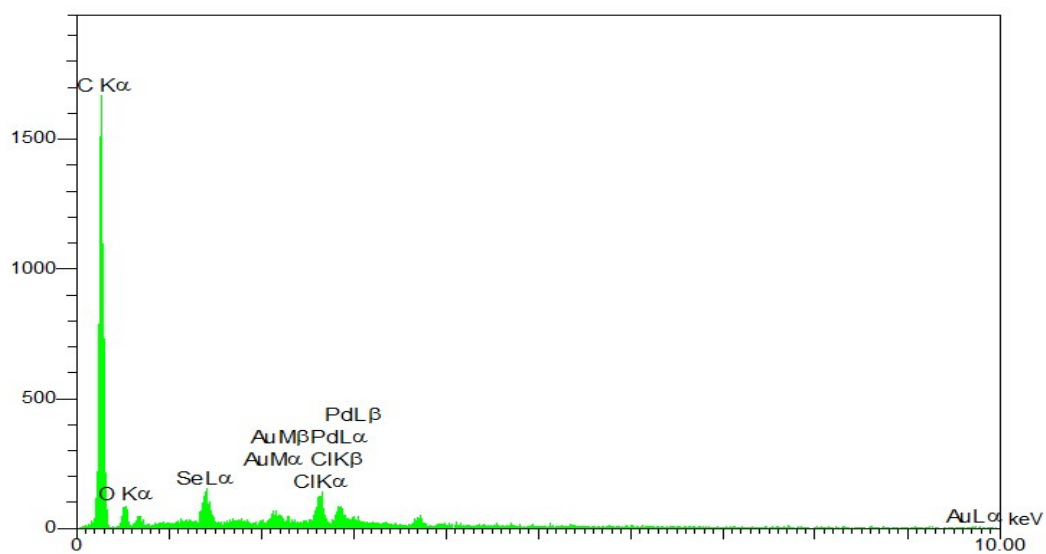


Figure S6. EDX spectra of PS-[PdCl-(SeCSe)] (1g)

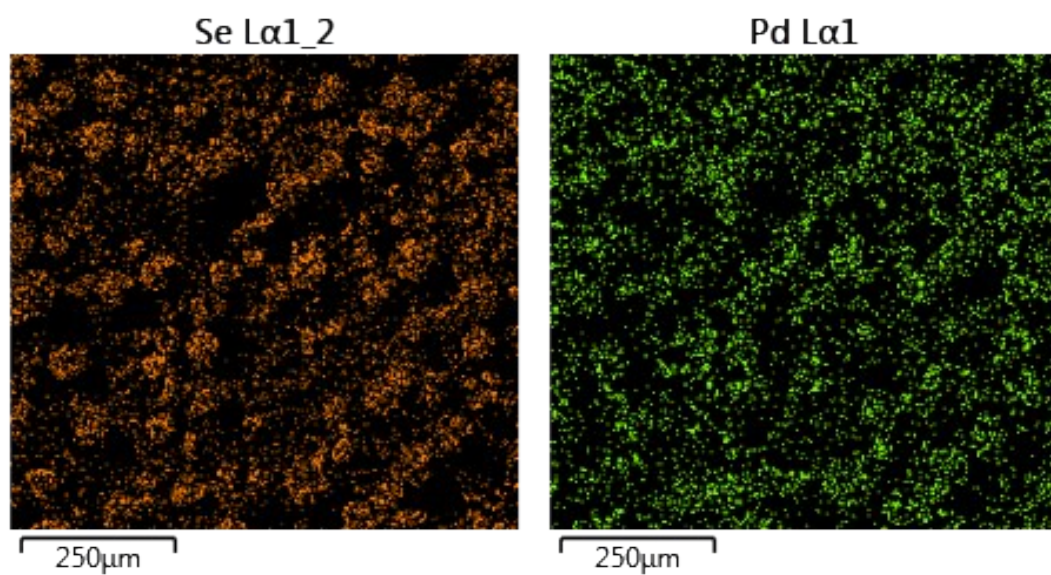


Figure S7. Elemental mapping images of PS-[PdCl-(SeCSe)] (1g)

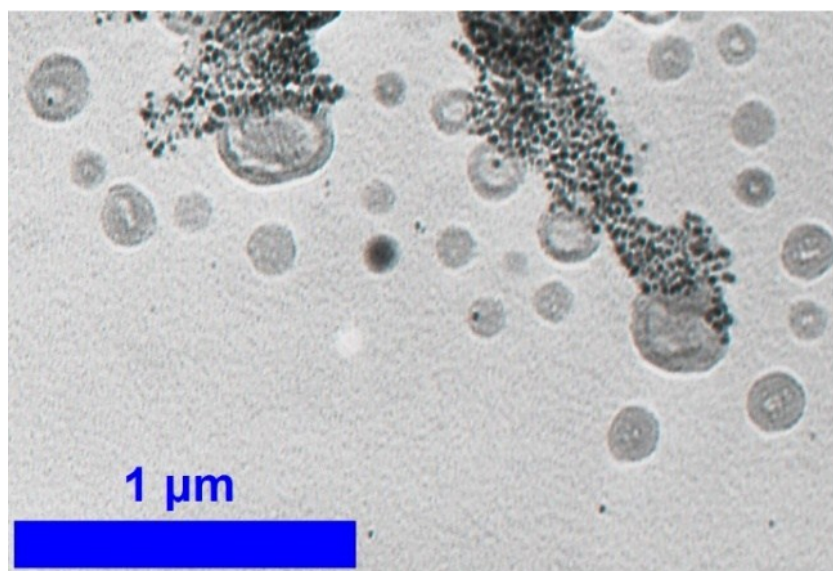


Figure S8. TEM image of PS-[PdCl-(SeCSe)] (1g)

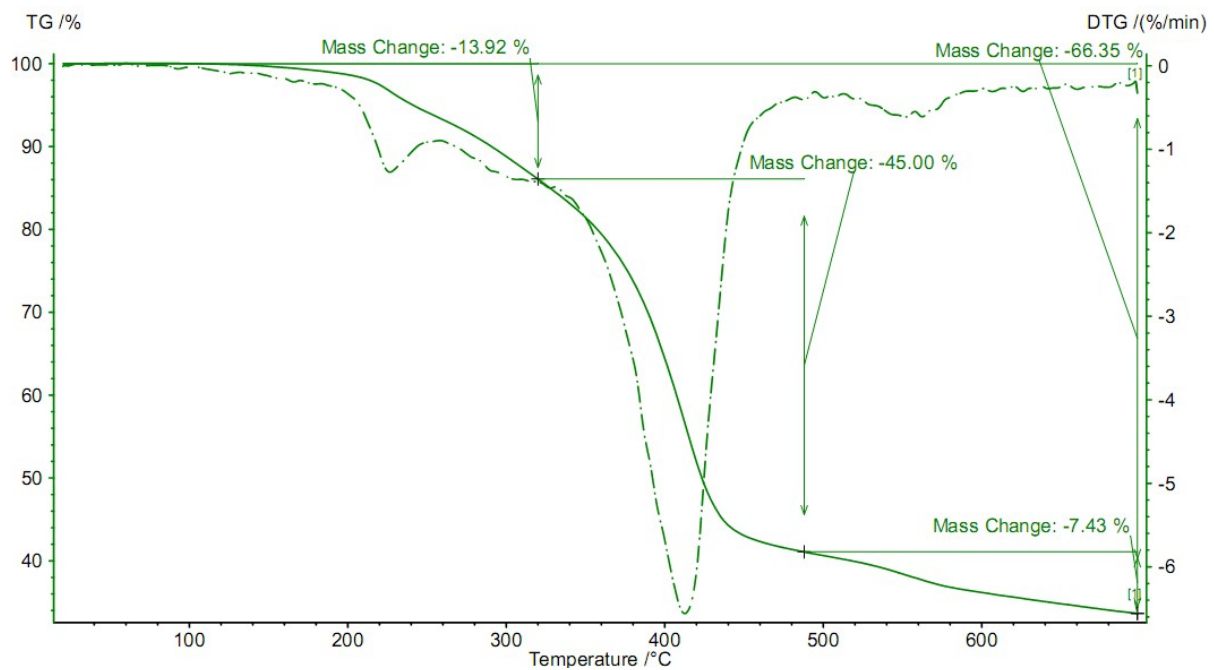


Figure S9. TG/DTG curve of PS-[PdCl-(SeCSe)] (1g)

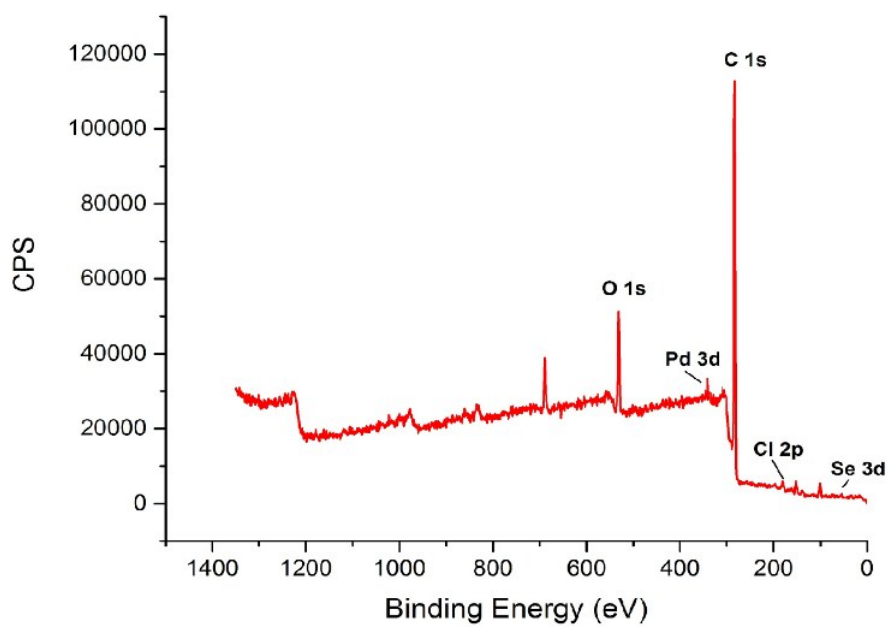


Figure S10. Full-range XPS spectra of PS-[PdCl-(SeCSe)] (1g)

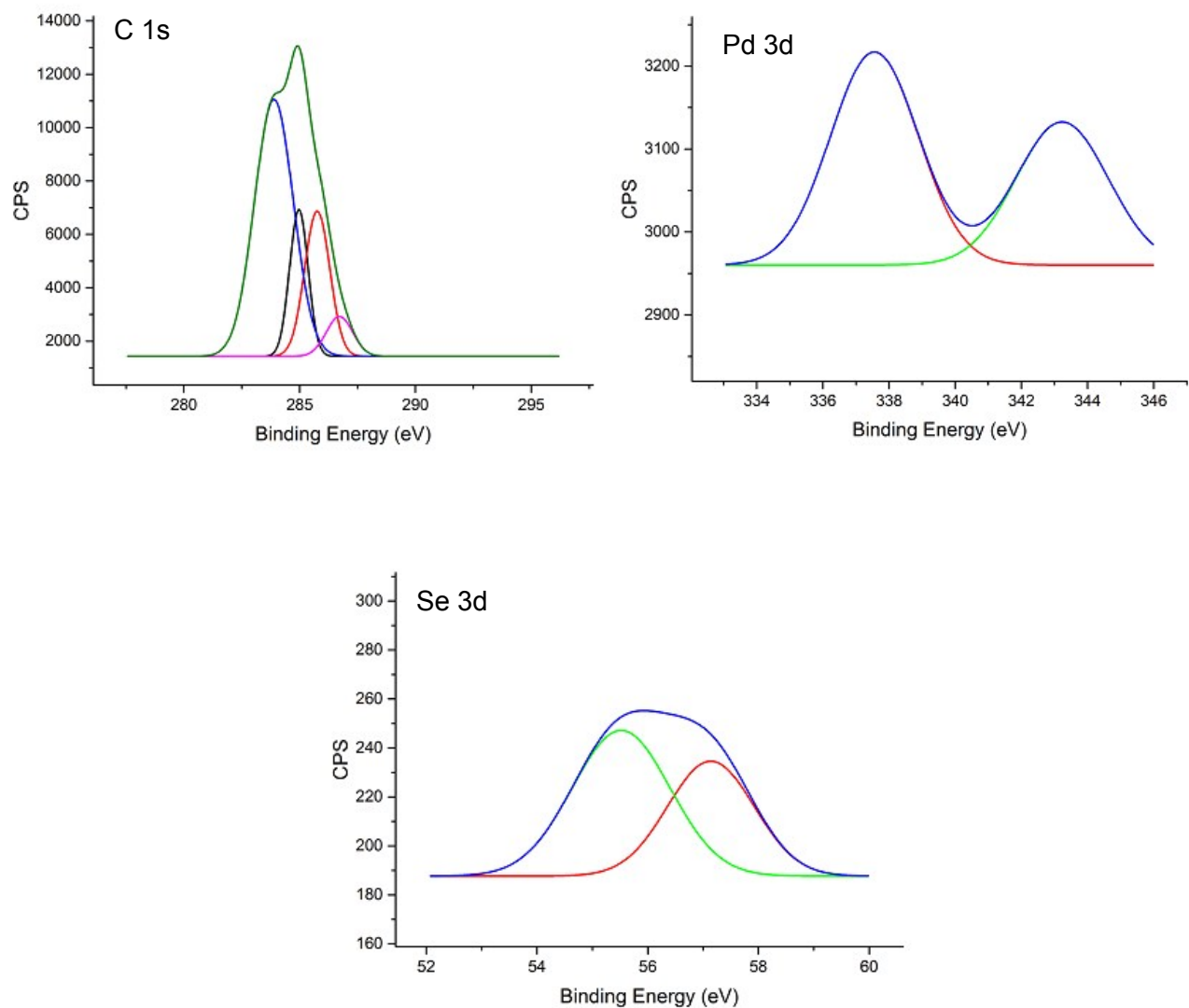


Figure S11. C 1s, Pd 3d, and Se 3d XPS spectrum of PS-[PdCl-(SeCSe)] (1g)

Table S1. Quantitative analysis of XPS data.

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	Atomic %
C1s	303.48	284.62	274.68	11633.03	3.25	39730.84	557.06	88.32
Cl2p	210.48	198.49	190.68	110.58	0.53	619.64	3	0.48
O1s	545.48	532.35	522.68	3053.19	3.37	11362.45	66.19	10.49
Pd3d	349.48	337.54	327.68	234.64	1.87	1756.77	1.32	0.21
Se3d	65.48	56.15	47.68	110.47	2.02	434	3.13	0.5

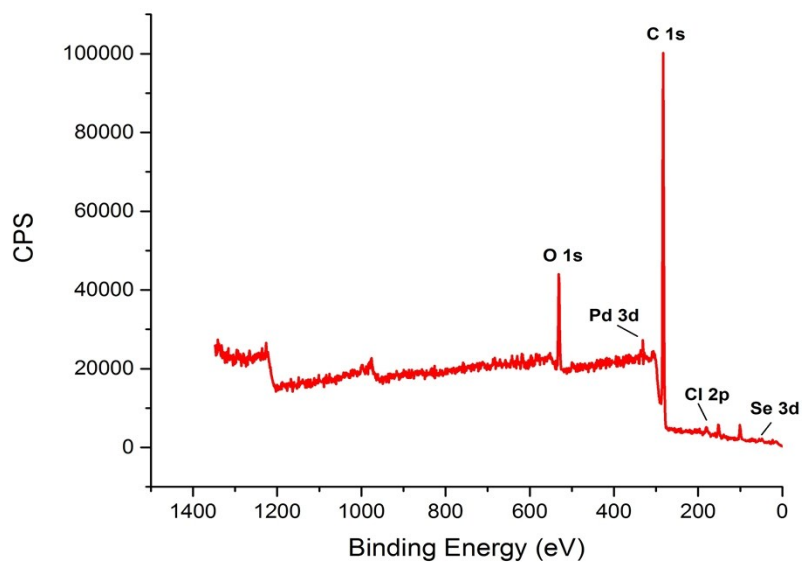


Figure S12. Full-range XPS spectra of PS-[PdCl-(SeCSe)] (1g) after 1st cycle

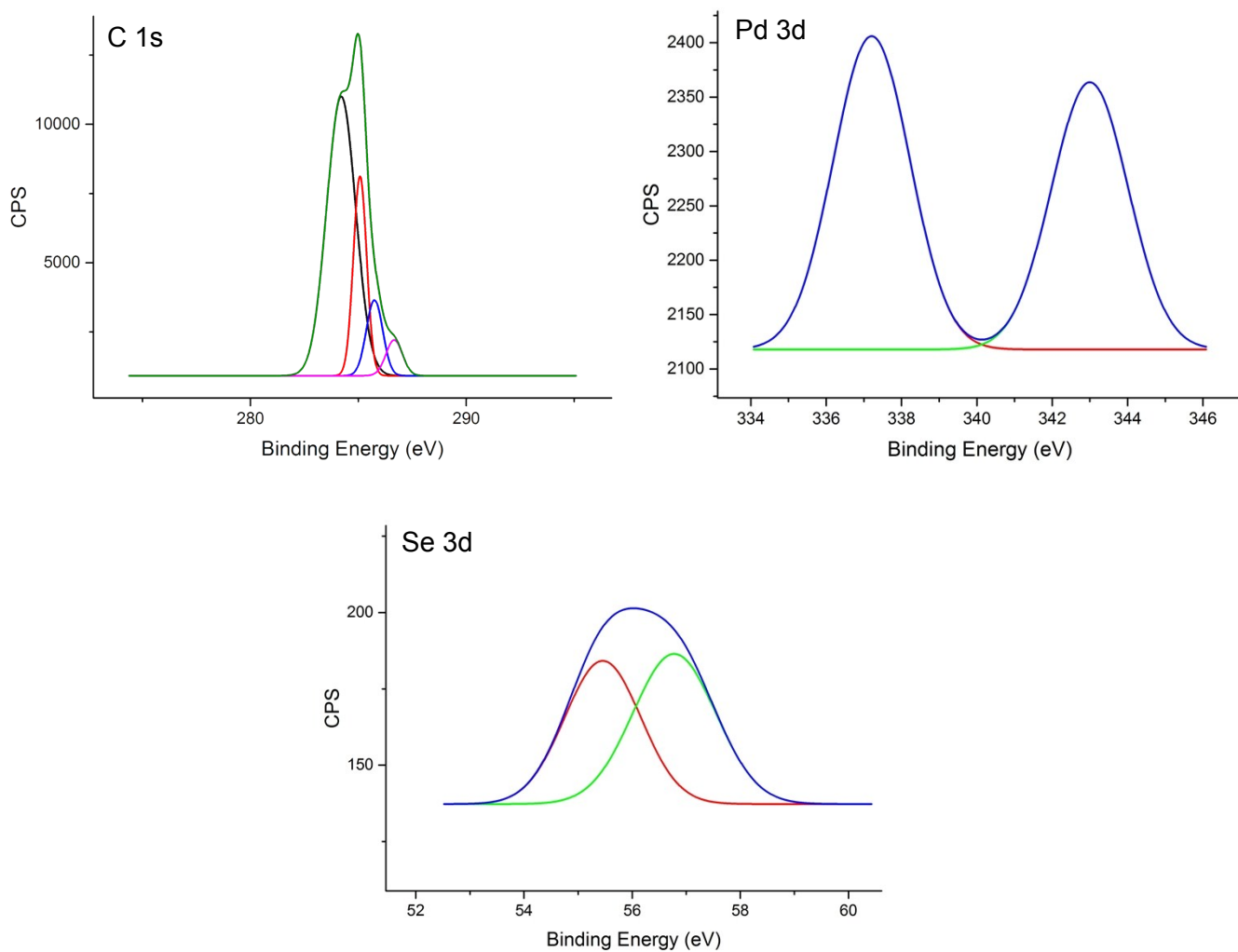


Figure S13. C 1s, Pd 3d, and Se 3d XPS spectrum of recovered PS-[PdCl-(SeCSe)] (1g)

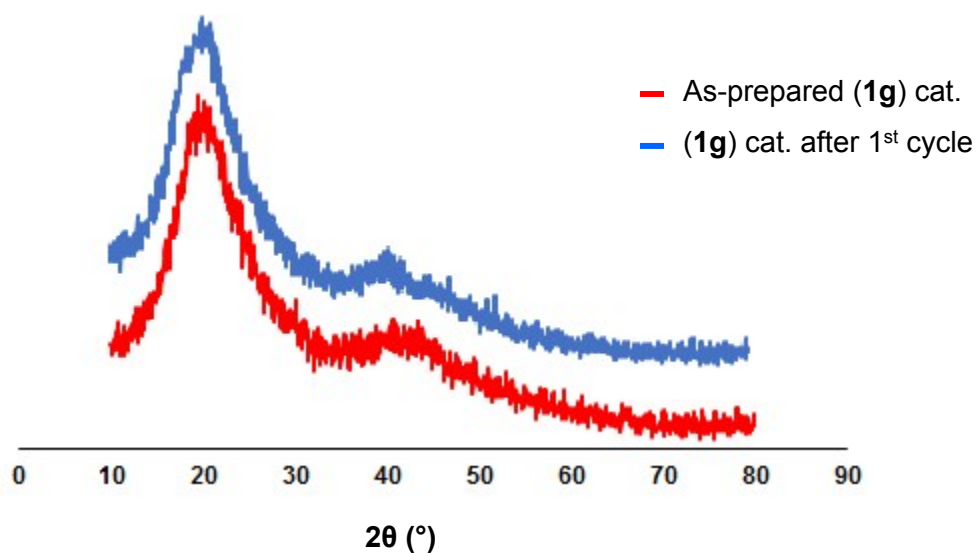


Figure S14. X-ray diffraction pattern of PS-[PdCl-(SeCSe)] (1g)

1.4. General procedure for the Sonogashira coupling of aryl halides or β -bromostyrene with terminal alkynes

A test tube was charged with aryl halide or β -bromostyrene (1 equiv.) and TBAF (2 equiv) and PS-[PdCl-(SeCSe)] (0.3 mol%) and NMP (1 mL). To the above mixture was added alkyne (1.5 equiv.) and heated to 70 °C under aerobic conditions. The progress of the reaction was monitored by TLC. Upon completion of the reaction, catalyst was filtered off and water was added (5 mL) and the residue was extracted with EtOAc (2×5 mL) and washed with H₂O (2×5 mL). The combined organic layers were dried, using MgSO₄ and concentrated under reduce pressure. The crude mixture was then purified by preparative thin layer chromatography (SiO₂, eluent: *n*-hexane).

1.5. Spectral data of compounds in Table 2 and Table 3

1,2-Diphenylethyne (Table 2, Entry 1)

White solid; m.p. = 59-60 °C (lit. 59-61 °C [5]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.56-7.60 (m, 4H), 7.36-7.42 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 132.5, 131.7, 128.4, 128.3, 123.1, 89.4.

1-Methoxy-4-(phenylethynyl)benzene (Table 2, Entries 2, 8, 11, 14, 18)

White solid; m.p. = 56-58 °C (lit. 56-58 °C [5]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.53 (dd, *J* = 7.4, 2.4 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.30-7.38 (m, 3H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 159.6, 133.1, 131.5, 128.3, 128.0, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

1-Nitro-4-(phenylethynyl)benzene (Table 2, Entries 4, 12, 16)

Yellow solid; m.p. = 119-121 °C (lit. 121-122 °C [6]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.23 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.55-7.59 (m, 2H), 7.39-7.41 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 146.9, 132.3, 131.8, 130.3, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5.

1-Methoxy-4-(p-tolylethynyl)benzene (Table 2, Entry 7)

Yellow solid; m.p. = 123-126 °C (lit. 118-120 °C [6]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.48 (d, *J* = 8.6 Hz, 2H); 7.43 (d, *J* = 7.9 Hz, 2H); 7.16 (d, *J* = 7.7 Hz, 2H); 6.89 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 159.4, 138.0, 132.9, 131.3, 129.1, 120.5, 115.6, 113.9, 88.6, 88.2, 55.3, 21.5.

1-(4-(Phenylethynyl)phenyl)ethan-1-one (Table 2, Entry 13)

White solid; m.p. = 94-97 °C (lit. 95-97 °C [6]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.94 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.54-7.58 (m, 2H), 7.37-7.39 (m, 3H), 2.61 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 197.3, 136.2, 131.8, 131.7, 128.8, 128.5, 128.3, 128.2, 122.6, 92.7, 88.6, 26.6.

4-(Phenylethynyl)benzonitrile (Table 2, Entry 17)

Yellow solid; m.p. = 105-107 °C (lit. 107-108 °C [6]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.60-7.66 (m, 4H), 7.54-7.57 (m, 2H), 7.38-7.40 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 132.1, 132.0, 131.7, 129.1, 128.5, 128.2, 122.2, 118.5, 111.4, 93.8, 87.3.

(E)-But-1-en-3-yn-1,4-diyl dibenzene (Table 3, Entry 1)

Pale yellow solid; m.p. = 84-86 °C (lit. 96-97 °C [7]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.44-7.50 (m, 4H), 7.31-7.41 (m, 6H), 7.07 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 141.3, 136.3, 131.5, 128.7, 128.6, 128.3, 128.1, 126.3, 123.4, 108.2, 91.7, 88.9.

(E)-1-Methyl-4-(4-phenylbut-3-en-1-yn-1-yl)benzene (Table 3, Entry 2)

Yellow solid; m.p. = 92-95 °C (lit. 75-76 °C [7]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.29-7.45 (m, 7H), 7.15 (d, *J* = 7.8 Hz, 2H); 7.04 (d, *J* = 16.2 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 140.8, 138.3, 136.4, 131.4, 129.1, 128.7, 128.5, 126.3, 120.3, 108.3, 91.9, 88.3, 21.5.

(E)-1-Methoxy-4-(4-phenylbut-3-en-1-yn-1-yl)benzene (Table 3, Entry 3)

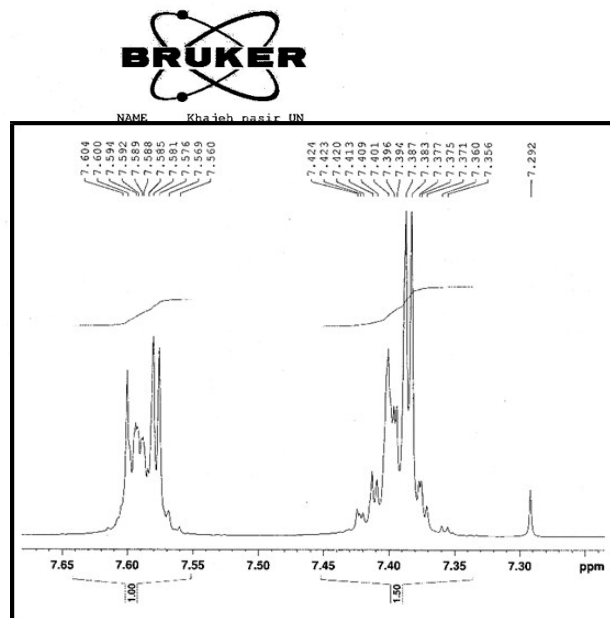
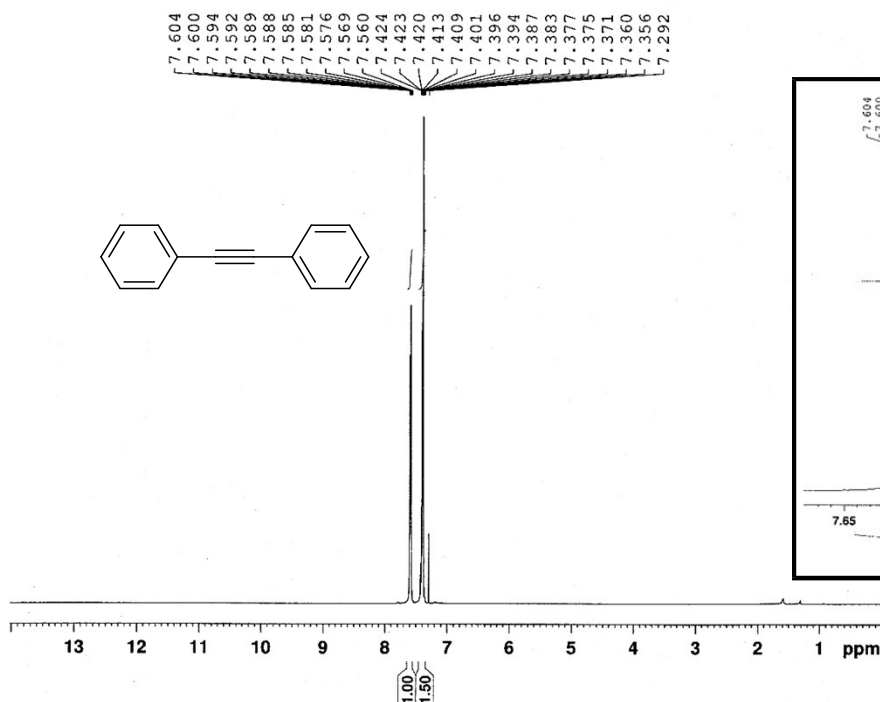
Yellow solid; m.p. = 86-88 °C (lit. [7]); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.43-7.46 (m, 4H), 7.27-7.38 (m, 3H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 16.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 159.6, 140.4, 136.5, 133.0, 128.7, 128.4, 126.2, 115.5, 114.0, 108.4, 91.9, 87.7, 55.3.

(E)-Dec-1-en-3-yn-1-ylbenzene (Table 3, Entry 4)

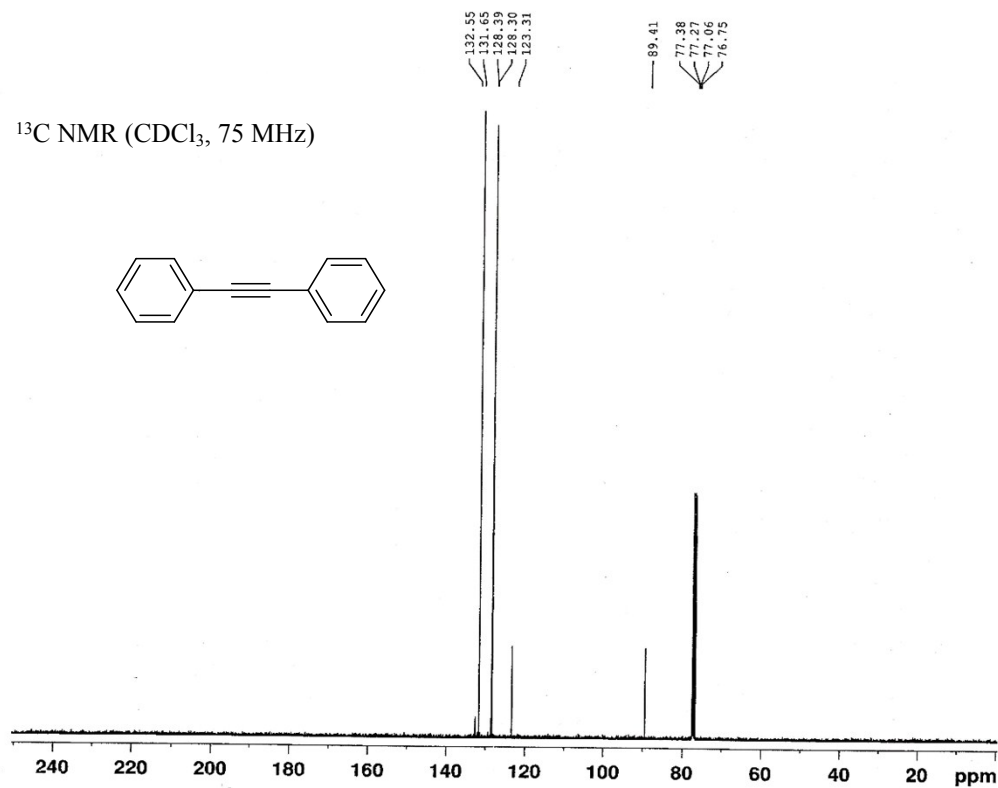
Orange oil; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.23-7.39 (m, 5H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.17 (dt, *J* = 16.2, 2.1 Hz, 1H), 2.38 (td, *J* = 7.0, 2.1 Hz, 2H), 1.57 (quint, *J* = 6.9 Hz, 2H), 1.41-1.48 (m, 2H), 1.27-1.39 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 139.9, 136.6, 128.6, 128.1, 126.0, 108.9, 93.1, 79.7, 31.4, 28.8, 28.6, 22.5, 19.6, 14.1.

1.6. ^1H and ^{13}C NMR of compounds in Table 2 and Table 3

^1H NMR (CDCl_3 , 300 MHz)



^{13}C NMR (CDCl_3 , 75 MHz)



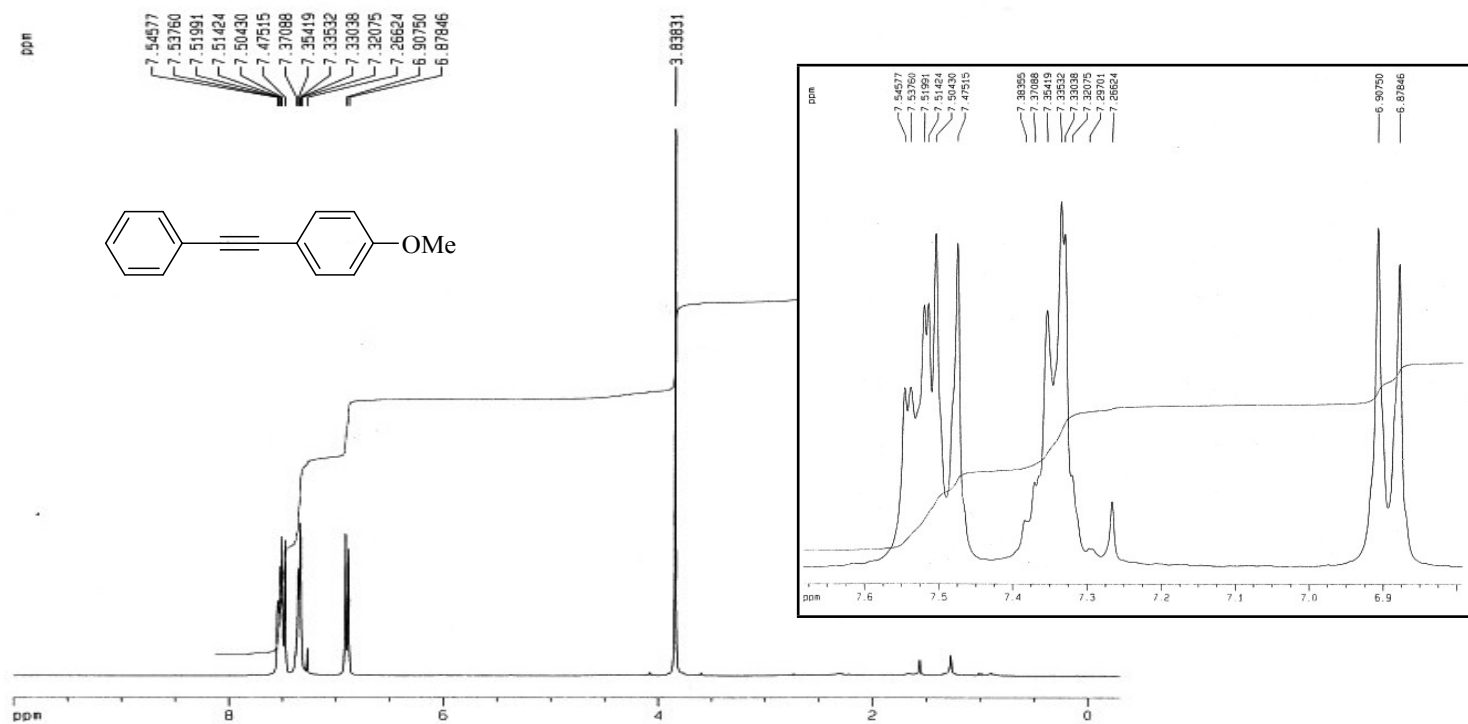
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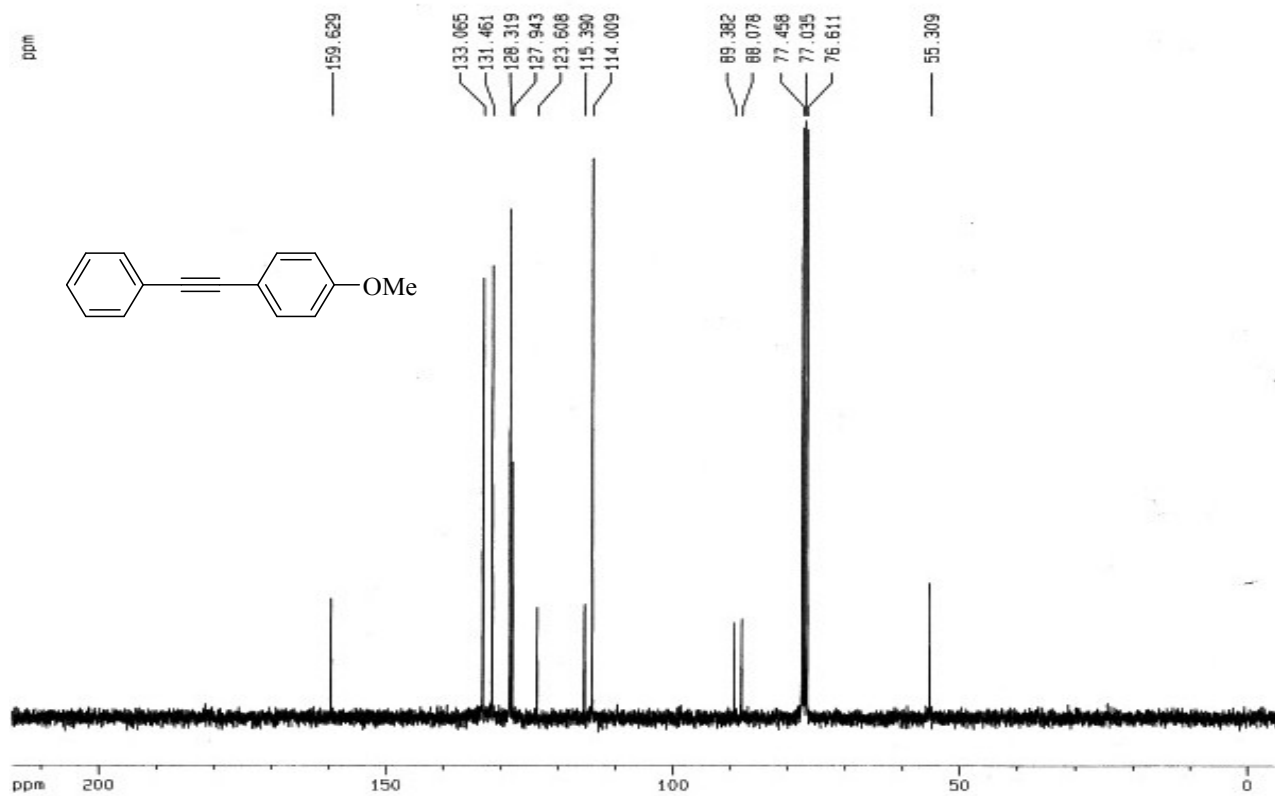
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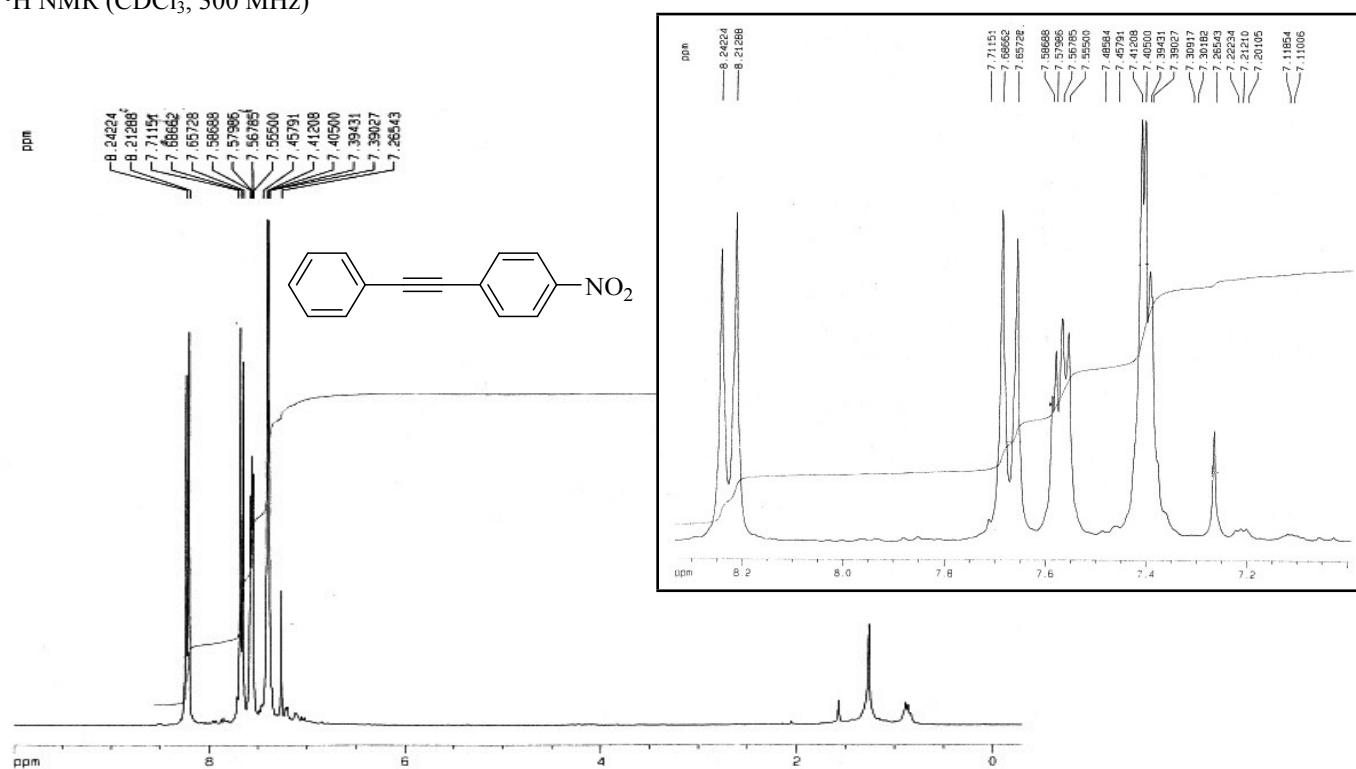
Chemical structure of 4-methoxy-1-phenyl-1,3-butadiene (1) is shown below the list of peaks. The structure consists of a phenyl ring connected to a 1,3-butadiene chain, with a methoxy group (OMe) attached to the 4-position of the phenyl ring.



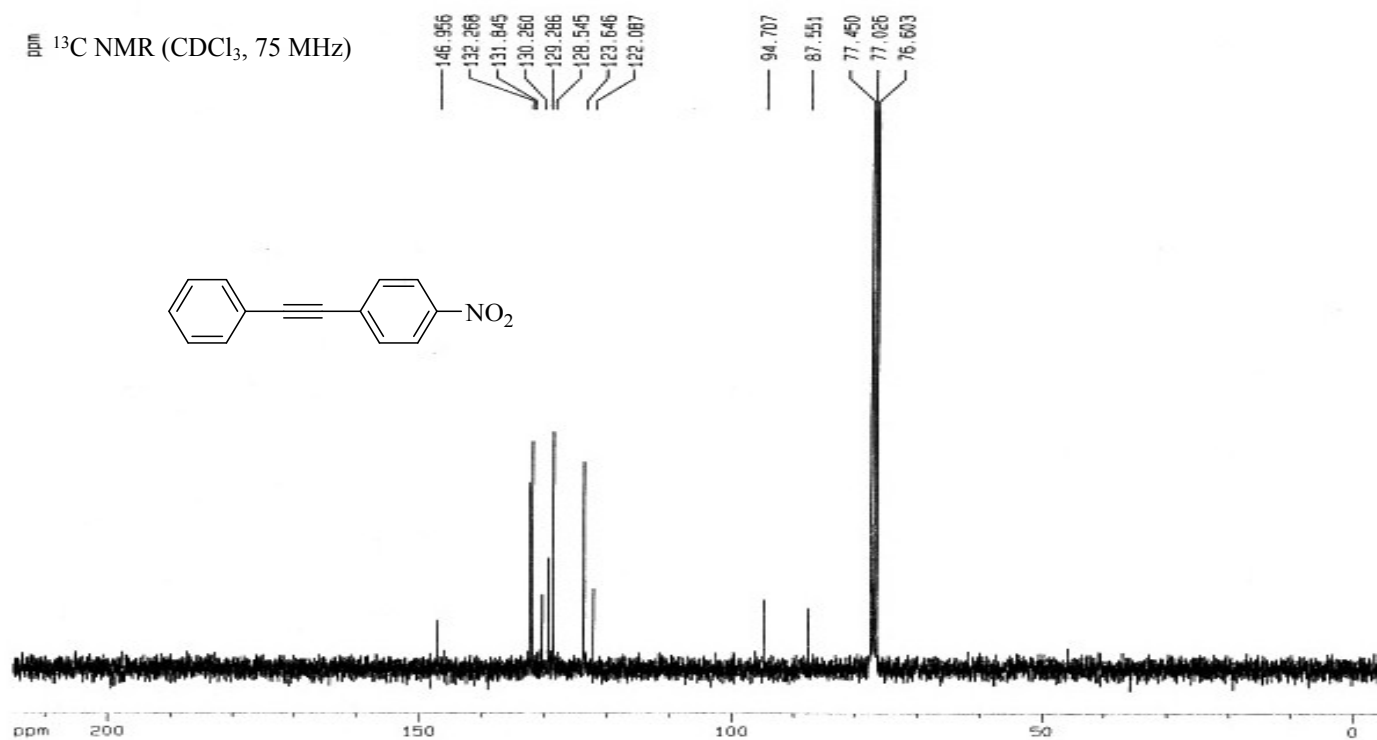
Chemical structure of 4-methoxy-1-phenyl-1,3-butadiene (10) is shown, with a chemical shift of $\delta = 159.629$ ppm.



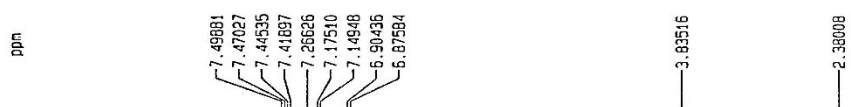
^1H NMR (CDCl_3 , 300 MHz)

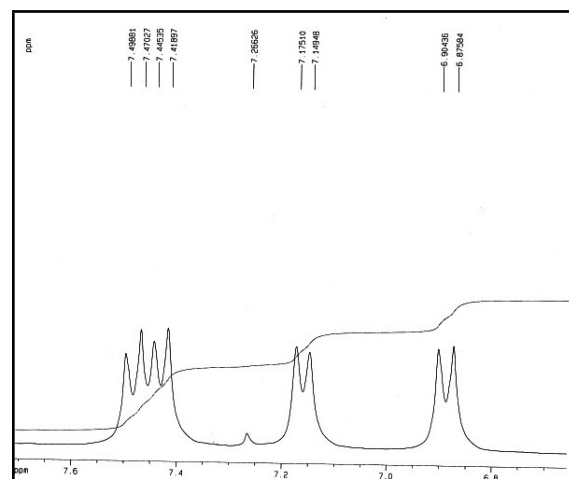
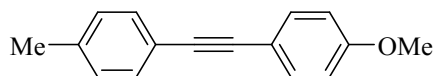


^{13}C NMR (CDCl_3 , 75 MHz)

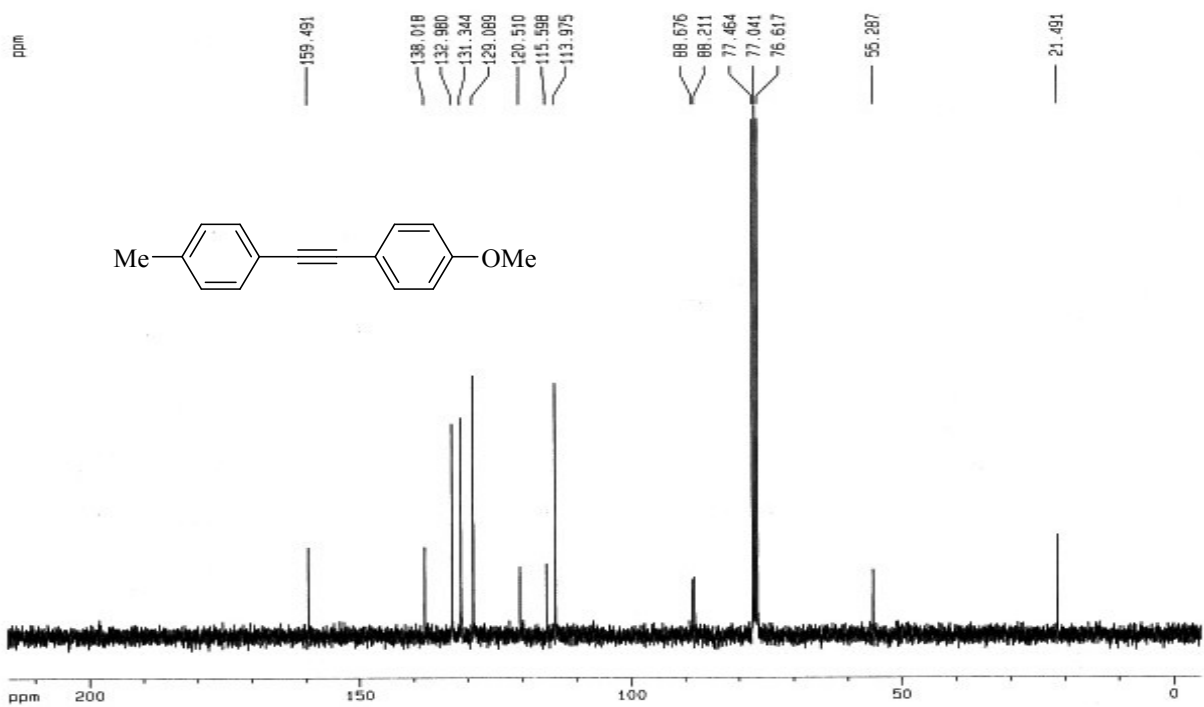


^1H NMR (CDCl_3 , 300 MHz)



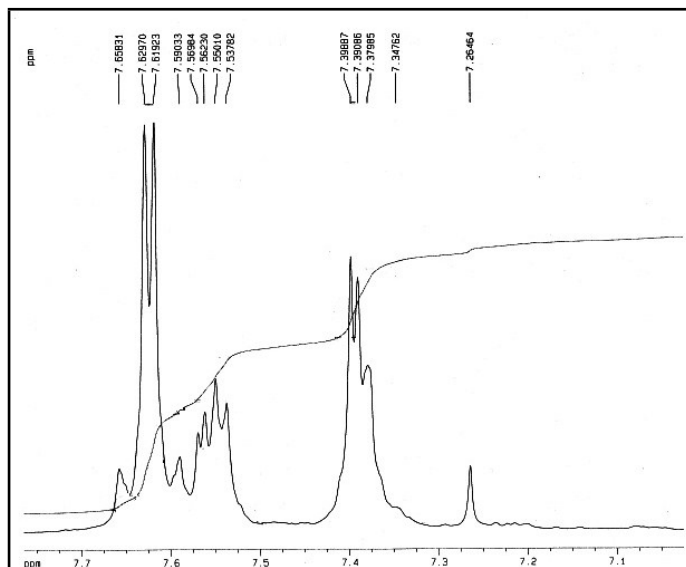
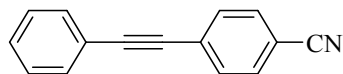


¹³C NMR (CDCl₃, 75 MHz)

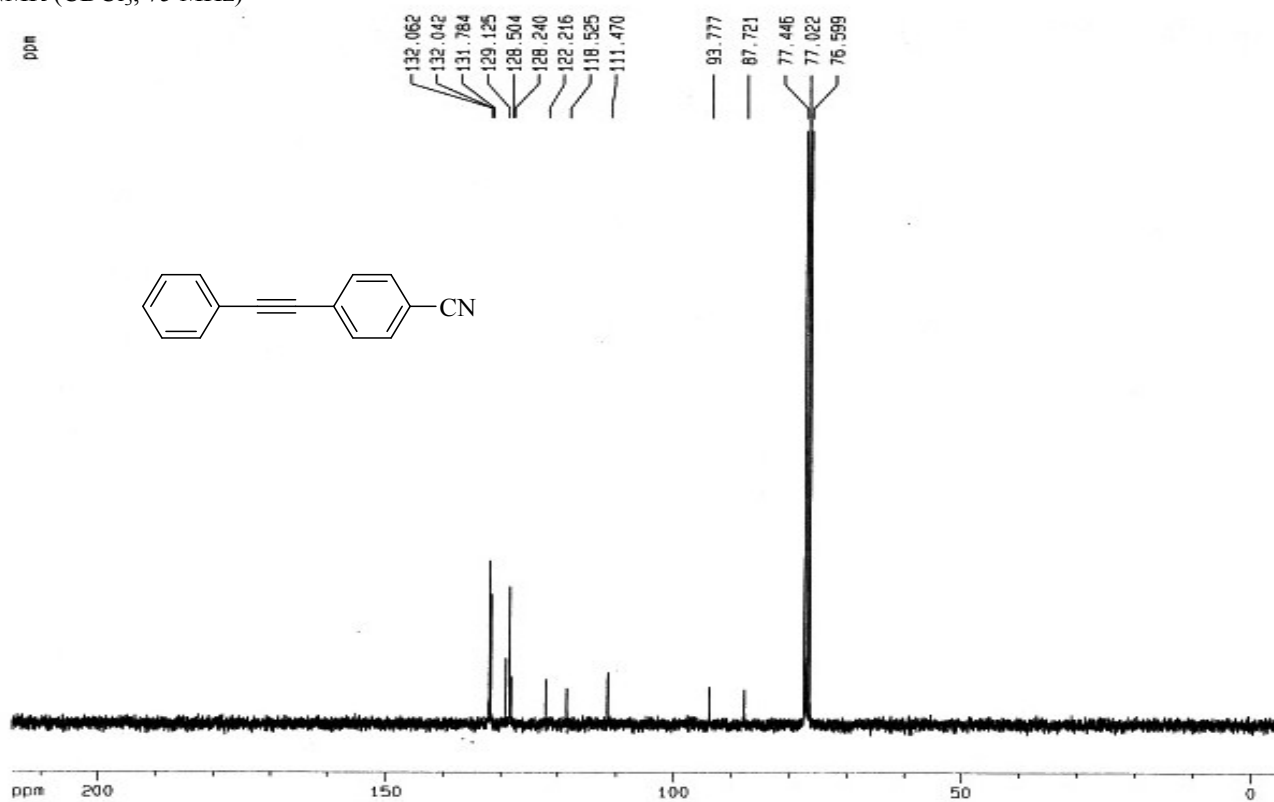


¹H NMR (CDCl₃, 300 MHz)

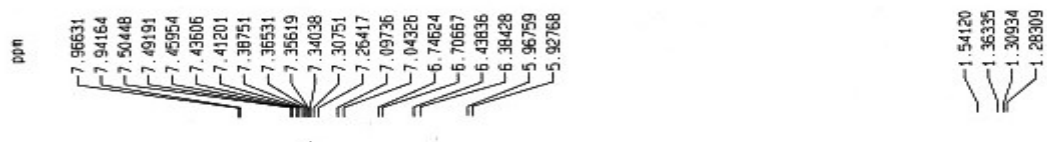


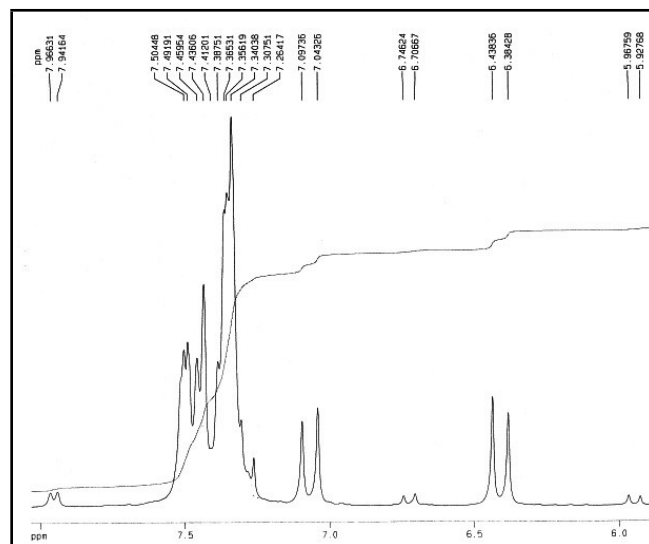
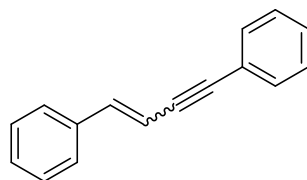


¹³C NMR (CDCl₃, 75 MHz)

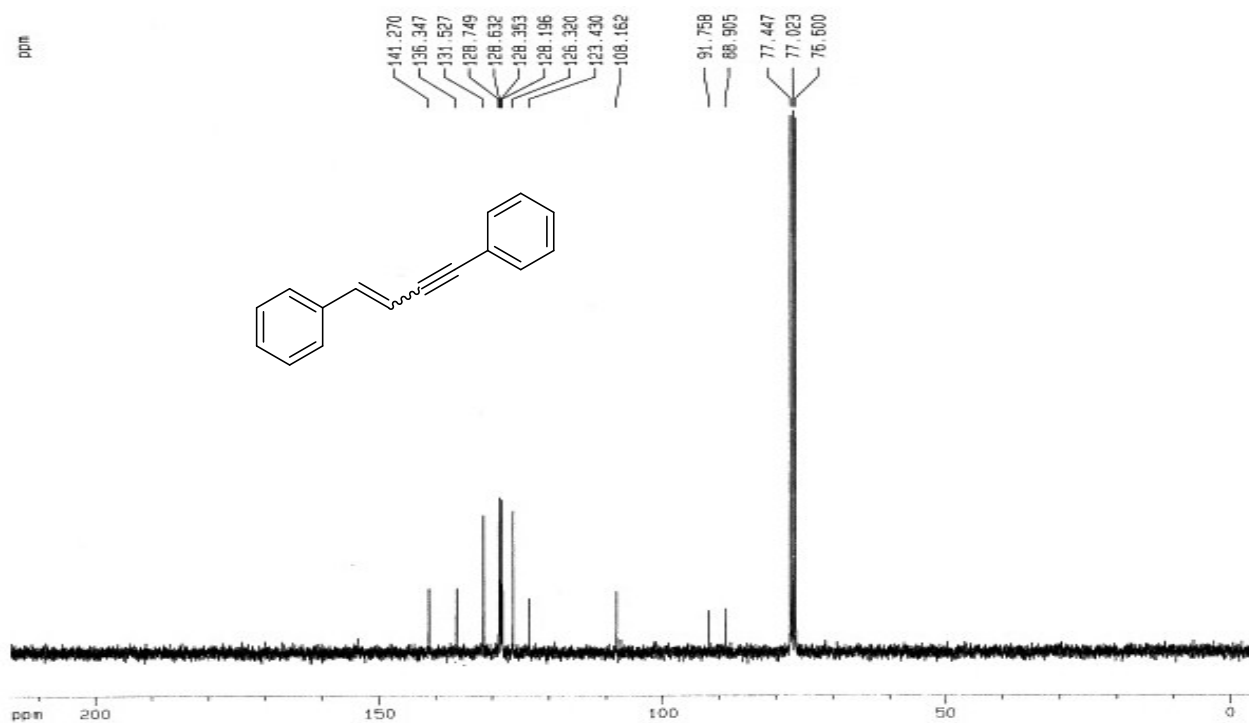


¹H NMR (CDCl₃, 300 MHz)

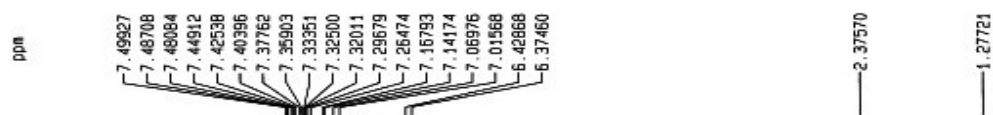


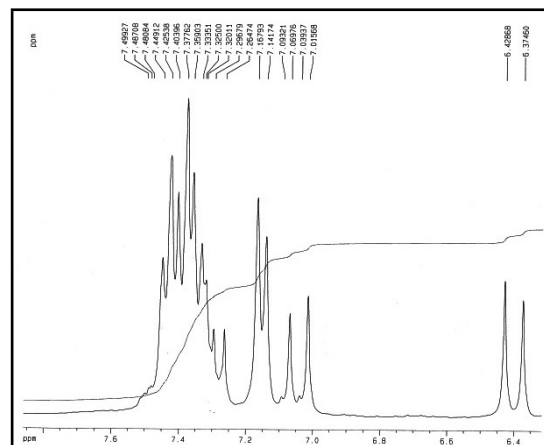
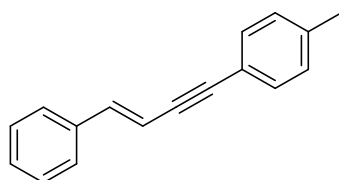


¹³C NMR (CDCl₃, 75 MHz)

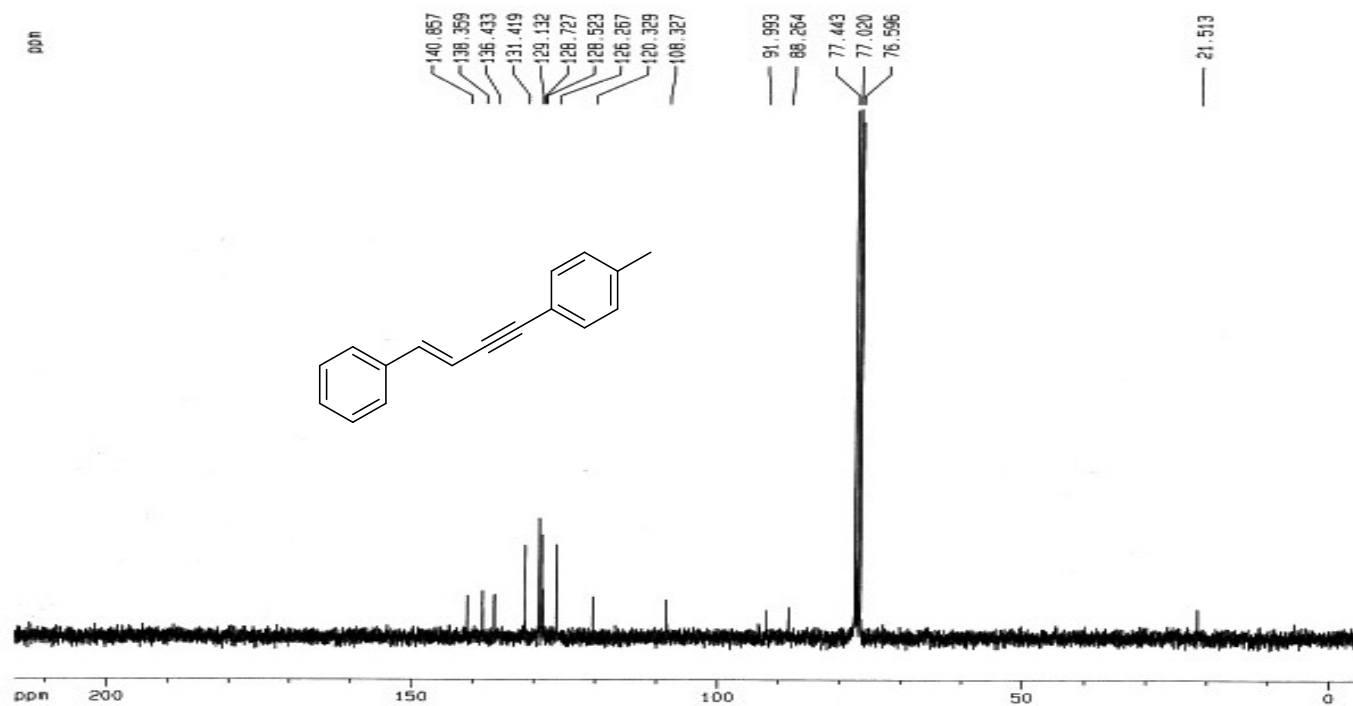


¹H NMR (CDCl₃, 300 MHz)

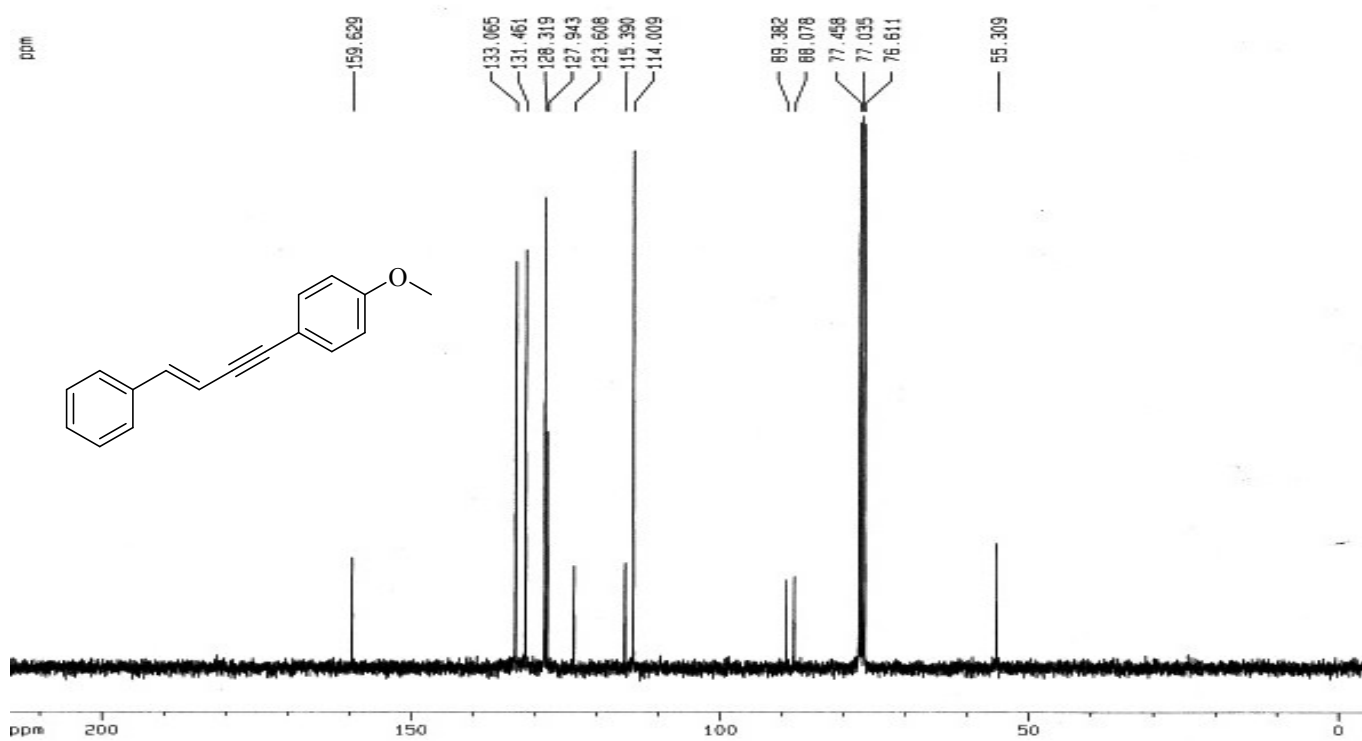
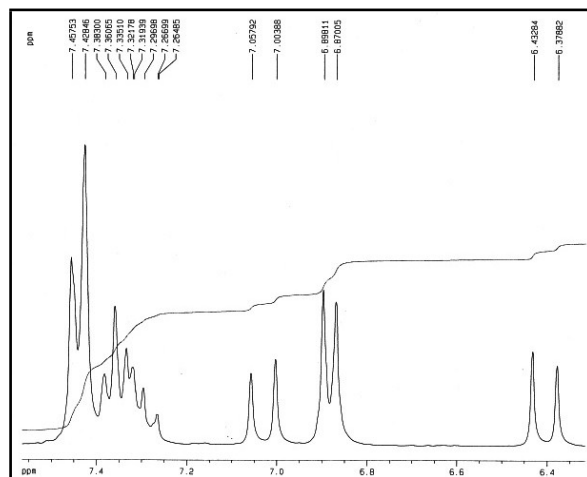
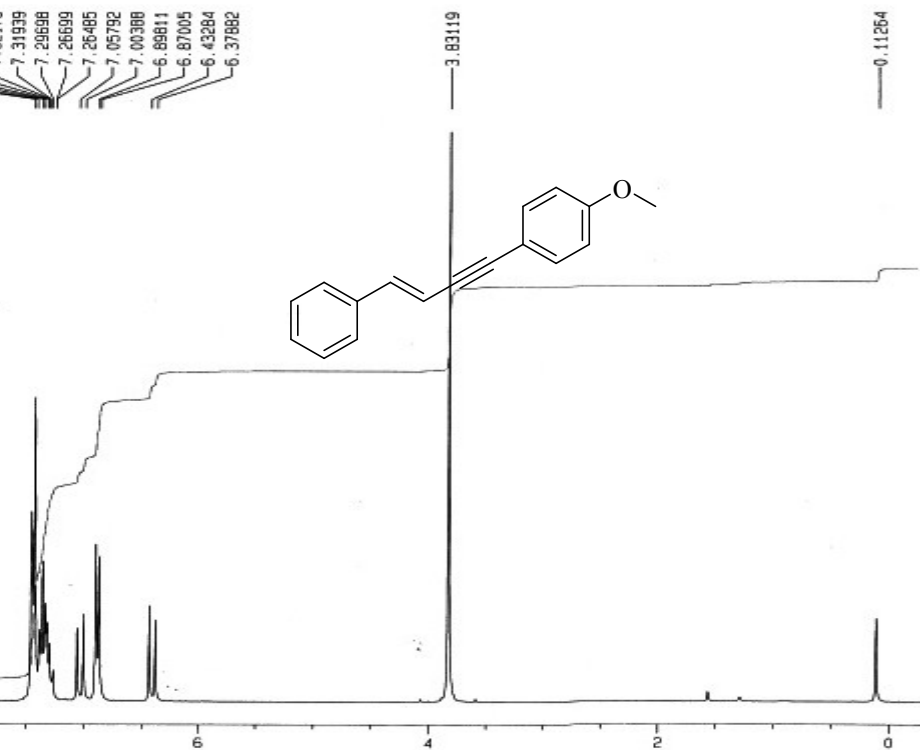




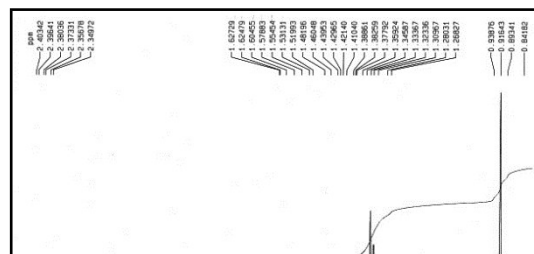
¹³C NMR (CDCl₃, 75 MHz)

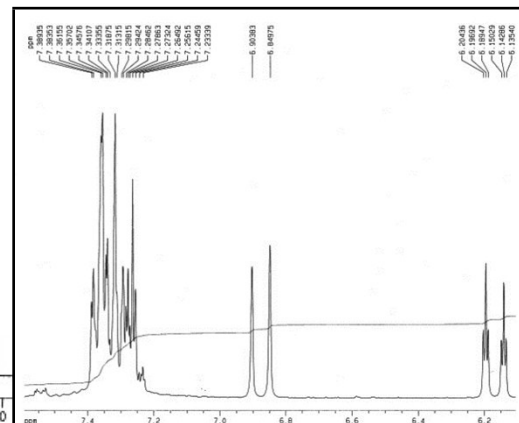


¹H NMR (CDCl₃, 300 MHz)



¹H NMR (CDCl₃, 300 MHz)





ppm

139.922
136.597
128.617
128.171
126.021

108.919

93.074

79.703
77.426
77.003
76.590

31.371
28.763
28.623
22.556
19.654
14.096

ppm

200
150
100
50
0

c1ccccc1/C=C/C#CCCCC

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