[Supporting Information]

Bipyridyl Palladium Embedded Porous Organic Polymer as Highly Efficient and Reusable Heterogeneous Catalyst for Suzuki-Miyaura Coupling Reaction

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A. General information

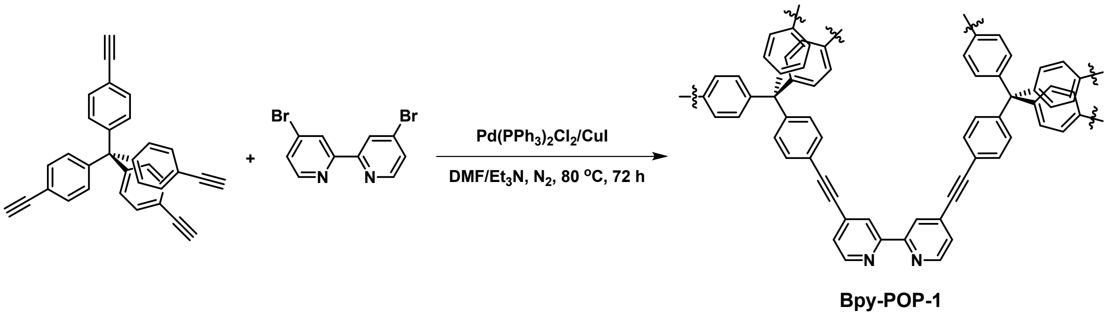
Chemicals and solvents were purchased from commercial suppliers and, if necessary, purified before use by standard techniques. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. The chemical shifts δ are given in ppm (parts per million) relative to tetramethylsilane (TMS) and the coupling constants J are given in Hz. All the spectra were recorded in $CDCl_3$ as solvent at room temperature. TMS served as the internal standard (δ = 0.00 ppm) for ^{1}H NMR, while $CDCl_3$ as the internal standard (δ = 77.0 ppm) for ^{13}C NMR. Elemental analysis was performed on an Elementar Analysensysteme GmbH VarioEL V3.00 elemental analyzer. FT-IR spectra were recorded on a Nicolet NEXUS 670 instrument. N_2 adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDPT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were collected with a Rigaku D/MAX-2400 X-ray diffractometer operated at 40 kV and 100 mA with Cu Kα radiation at a scan rate of 15°/min. X-ray photoelectron spectroscopy (XPS) date were obtained with an ESCALab220i-XL VG Scientific electron spectrometer using 300W Al Kα radiation. Transmission electron microscope (TEM) images were obtained by using a Tecnai G2 F20 instrument operated at 200 kV.

B. Materials and experimental procedures

Materials: All reagents were purchased from commercial sources. Et_3N and DMF were dried through the standard procedures. Tetra(4-ethynylphenyl)methane and 1,3,5-triethynylbenzene were prepared according to the literature procedure [1]. $Pd(PPh_3)_2Cl_2$, $PdCl_2$ and 4,4'-dibromo-2,2'-bipyridine were purchased from J&K. All catalytic reactions were performed in a 7 mL centrifuge tube.

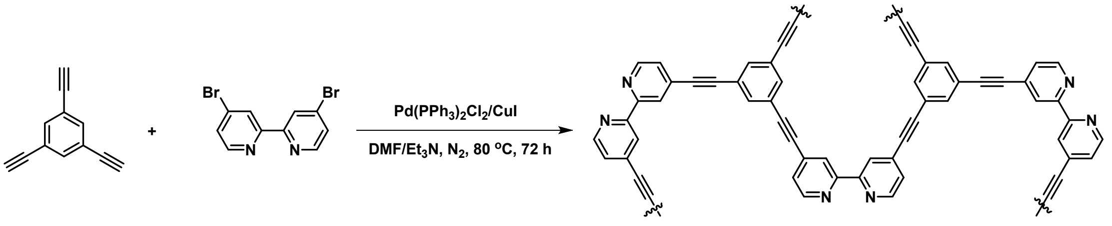
Experimental procedures:

(I) Synthesis of Bpy-POP-1[2]



4,4'-dibromo-2,2'-bipyridine (132 mg, 0.42 mmol), tetra(4-ethynylphenyl)methane (87 mg, 0.21 mmol), bis-(triphenylphosphine)palladium(II) dichloride (15 mg) , and copper (I) iodide (10 mg) were added into a dried round-bottom flask under nitrogen atmosphere. Anhydrous DMF (5.0 mL) and Et_3N (5.0 mL) were added to the mixture via a syringe. The resulting mixture was heated to 80 ^{o}C and stirred for 72 h under nitrogen atmosphere. After cooling to room temperature, the precipitate network polymer was filtered and washed four times (once each) with chloroform, water, methanol and acetone to remove any unreacted monomer or catalyst residures. Further purification of the polymer was carried out by soxhlet extraction with methanol for 48 h. The product was dried at 70 ^{o}C under vacuum for 6 h to give a brown powder. Yield: 148 mg (80%). The elemental analysis result of **Bpy-POP-1** found: C 73.67, N 6.59, H 3.47.

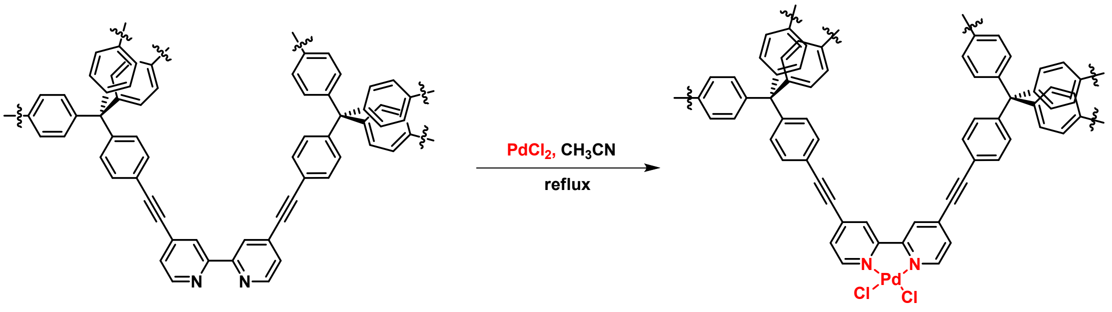
(II) Synthesis of Bpy-POP-2[2]



Bpy-POP-2

4,4'-dibromo-2,2'-bipyridine (157 mg, 0.50 mmol), 1,3,5-triethynylbenzene (50 mg, 0.33 mmol), bis-(triphenylphosphine)palladium(II) dichloride (15 mg) , and copper (I) iodide (10 mg) were added into a dried round-bottom flask under nitrogen atmosphere. Anhydrous DMF (5.0 mL) and Et_3N (5.0 mL) were added to the mixture via a syringe. The resulting mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. After cooling to room temperature, the precipitate network polymer was filtered and washed four times (once each) with chloroform, water, methanol and acetone to remove any unreacted monomer or catalyst residures. Further purification of the polymer was carried out by soxhlet extraction with methanol for 48 h. The product was dried at 70 °C under vacuum for 6 h to give a brown powder. Yield: 142 mg (85%). The elemental analysis result of **Bpy-POP-2** found: C 73.55, N 8.00, H 3.25.

(III) Synthesis of Bpy-Pd-POP-1[3]

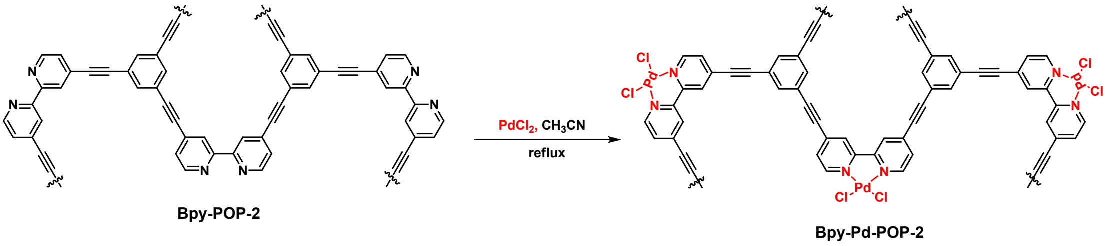


Bpy-POP-1

Bpy-Pd-POP-1

Palladium chloride (70.8 mg, 0.4 mmol) was dissolved in 10 mL of hot acetonitrile, and then **Bpy-POP-1** (100 mg, 2.35 mmol/g) was added. The mixture was kept refluxing for 6 h. The resulting solid was isolated by filtering and washed with acetonitrile using Soxhlet extraction for 24 h, then dried at 80 °C under vacuum for 12 h to yield **Bpy-Pd-POP-1** as a brown powder (126 mg). The Pd content in **Bpy-Pd-POP-1** was 15.05% as determined by ICP.

(IV) Synthesis of Bpy-Pd-POP-2[3]



Palladium chloride (70.8 mg, 0.4 mmol) was dissolved in 10 mL of hot acetonitrile, and then **Bpy-POP-2** (100 mg, 2.86 mmol/g) was added. The mixture was kept refluxing for 6 h. The resulting solid was isolated by filtering and washed with acetonitrile using Soxhlet extraction for 24 h, then dried at 80 °C under vacuum for 12 h to yield **Bpy-Pd-POP-2** as a brown powder (142 mg). The Pd content in **Bpy-Pd-POP-2** was 16.29% as determined by ICP.

C. TGA for Bpy-POP-1

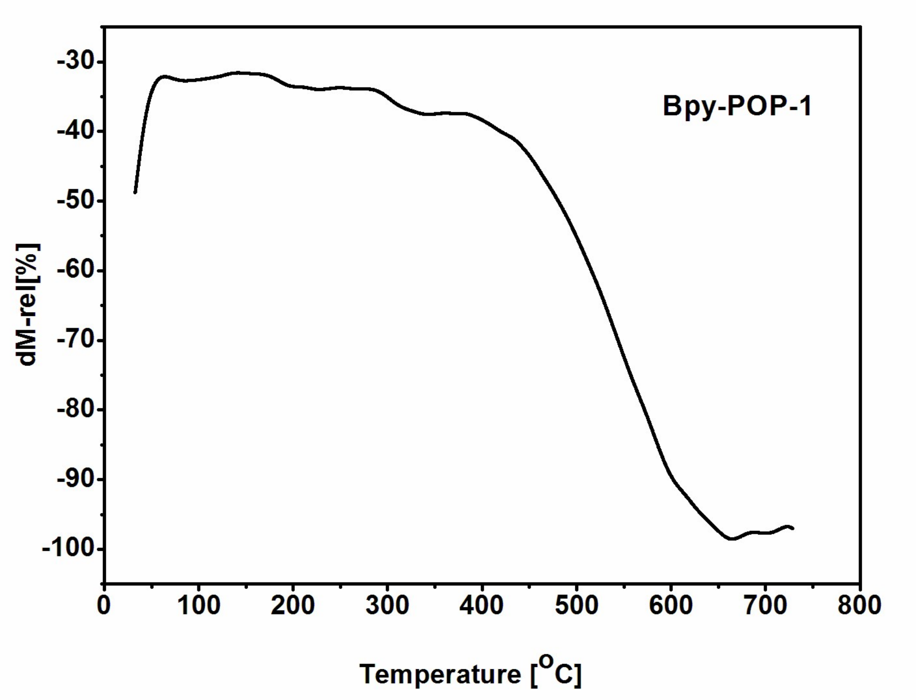


Figure S1. TGA for **Bpy-POP-1** under nitrogen atmosphere

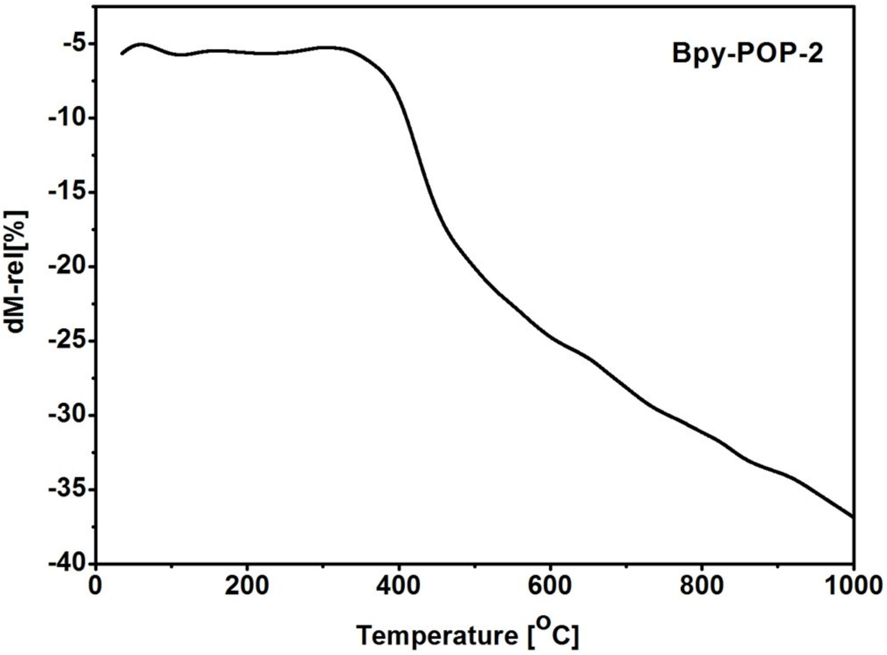


Figure S2. TGA for **Bpy-POP-2** under nitrogen atmosphere

D. Powder X-Ray diffraction of Bpy-POP-1

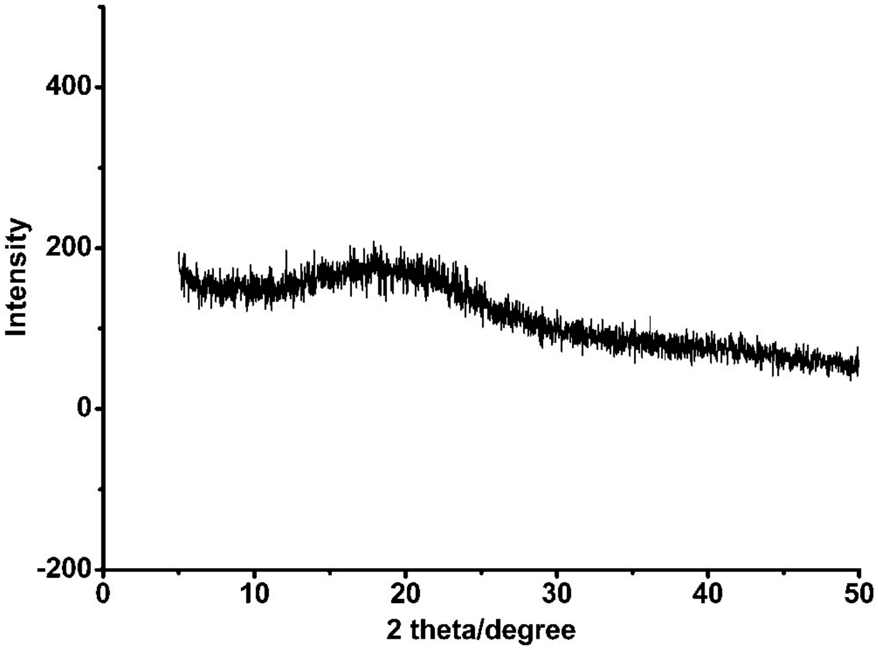


Figure S3. Power x-ray diffraction pattern of **Bpy-POP-1.** No intensive diffraction peaks were observable.

E. The permanent porosity of Bpy-POPs

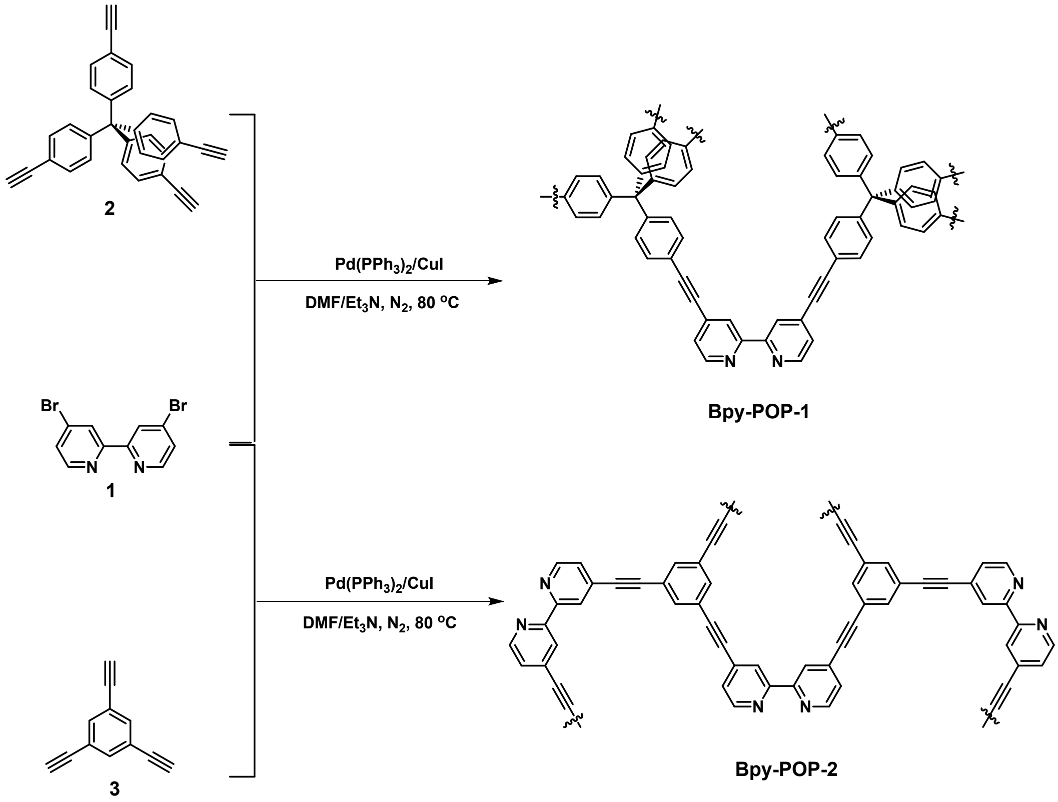


Table S1. The permanent porosity of **Bpy-POPs-1** and **Bpy-POPs-2**

Polymer	Building Blocks		Molar	S_{BET}	S_{micro}	V_{total}	V_{micro}
	Functional	Structural	Ratio	$(m^2g^{-1})^a$	$(m^2g^{-1})^b$	$(cm^3g^{-1})^c$	$(cm^3g^{-1})^b$
Bpy-POP-1	**1**	**2**	2:1	506	206	0.72	0.11
Bpy-POP-2	**1**	**3**	3:2	443	150	0.57	0.07

[a] surface area calculated from the N_2 adsorption isotherm using the BET method. [b] Micro surface area and micropore volume calculated using the t-plot method. [c] Total pore volume at $P/P_0 = 0.99$

F. BET surface area plot for Bpy-POP-1 and Bpy-POP-2 calculated from the isotherm

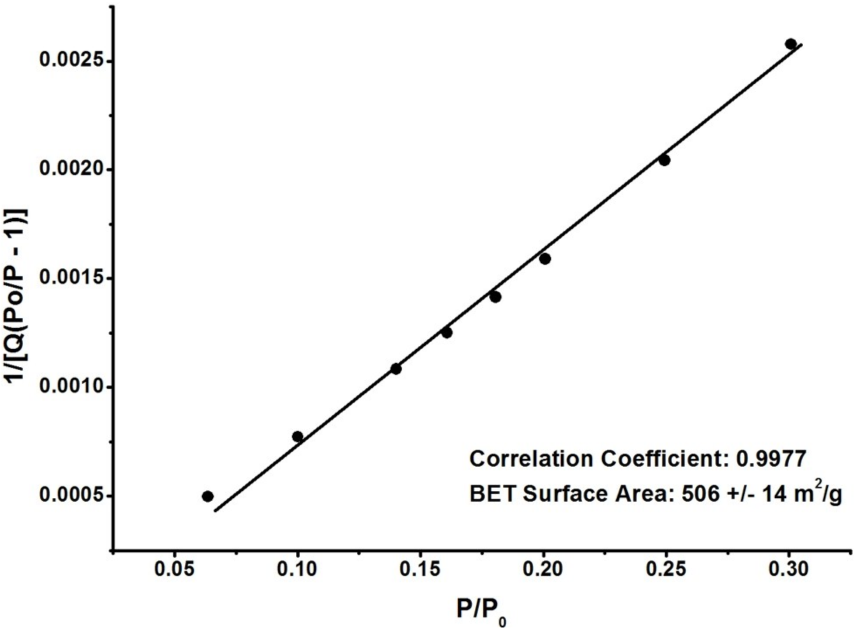


Figure S4. BET surface area plot for **Bpy-POP-1** calculated from the isotherm

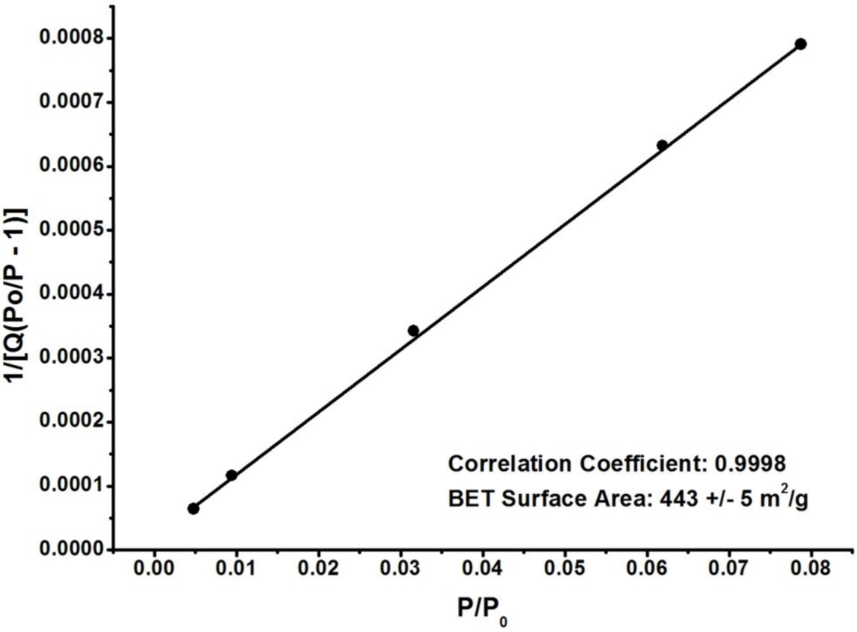


Figure S5. BET surface area plot for **Bpy-POP-2** calculated from the isotherm

G. ^{13}C CP/MAS NMR spectra of Bpy-POP-2

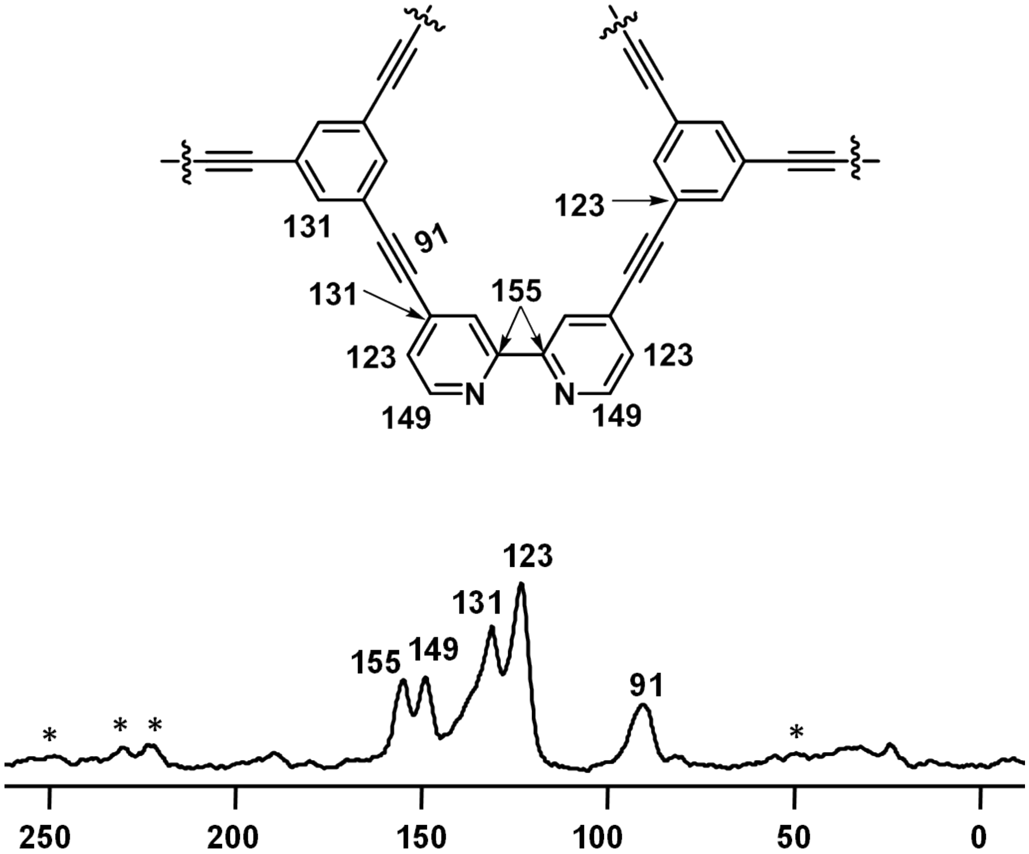


Figure S6. Solid-state ^{13}C CP/MAS NMR spectra of **Bpy-POP-2.**

The chemical composition of **Bpy-POP-2** were characterized by solid-state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy. Figure S5 shows the ^{13}C CP/MAS NMR spectra recorded for **Bpy-POP-2**. The signals at $\delta = 123$, 149 and 155 ppm confirmed that the bipyridyl monomer skeleton has well been embedded into the polymer networks, while the peak at approximately 91 ppm represent the alkynyl groups in the polymers. The peak at about 123 and 131 ppm also confirm that the 1,3,5-triethynylbenzene skeleton has been successful embedded into the frameworks.

H. FT-IR spectra for Bpy-POP and Bpy-Pd-POP

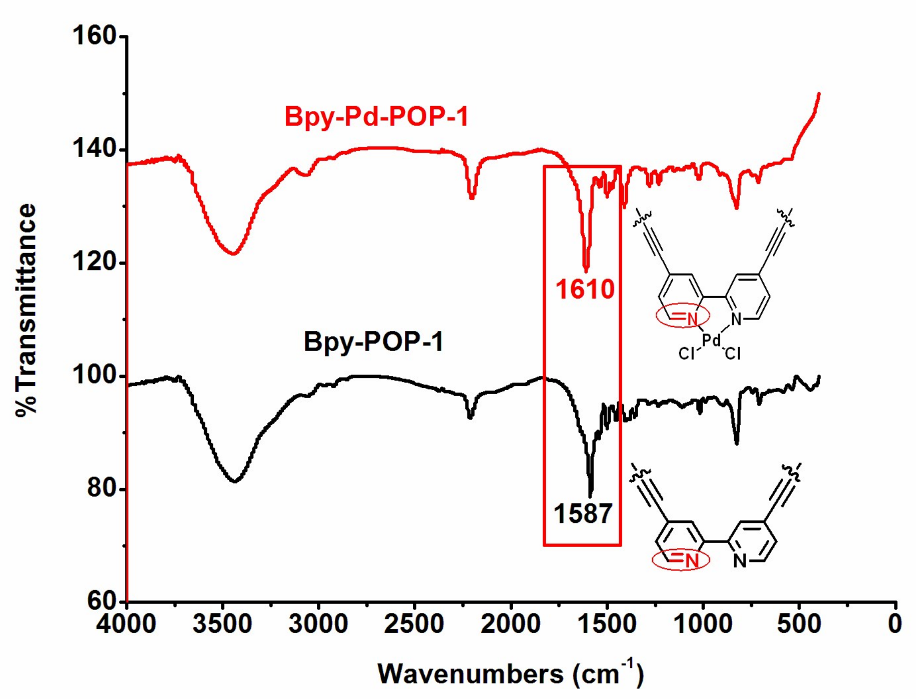


Figure S7. FT-IR spectra of **Bpy-POP-1** (in black) and **Bpy-Pd-POP-1** (in red). The slight difference in the FT-IR spectra of **Bpy-POP-1** and **Bpy-Pd-POP-1** could be attributed to the low concentration of the coordinated palladium chloride.

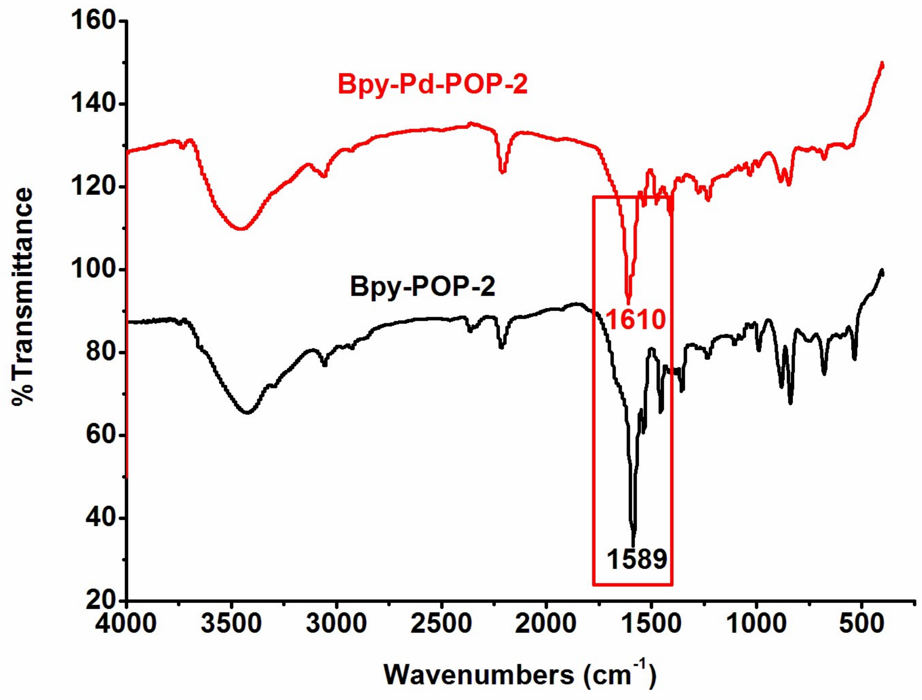


Figure S8. FT-IR spectra of **Bpy-POP-2** (in black) and **Bpy-Pd-POP-2** (in red).

I. XPS characterization of Bpy-Pd-POP-1 after catalytic runs

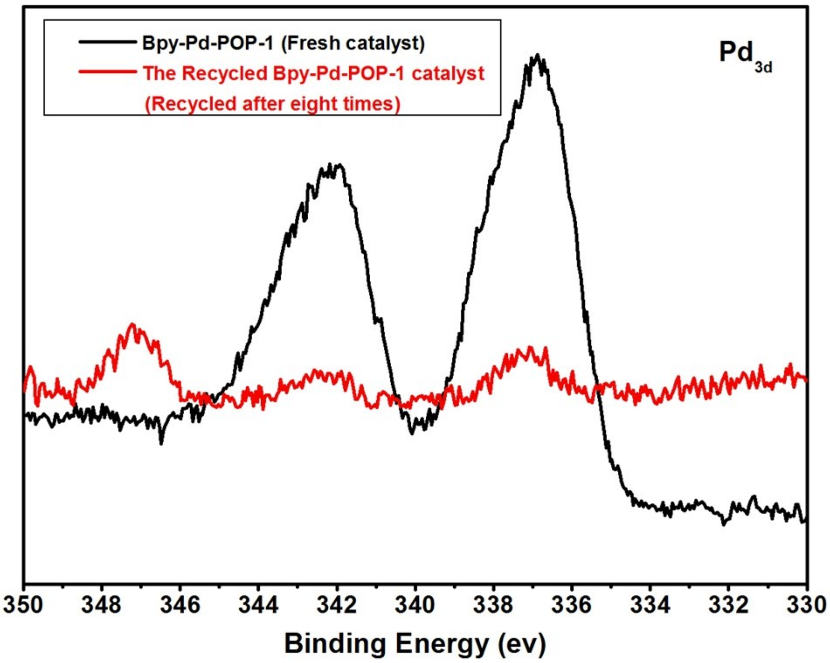
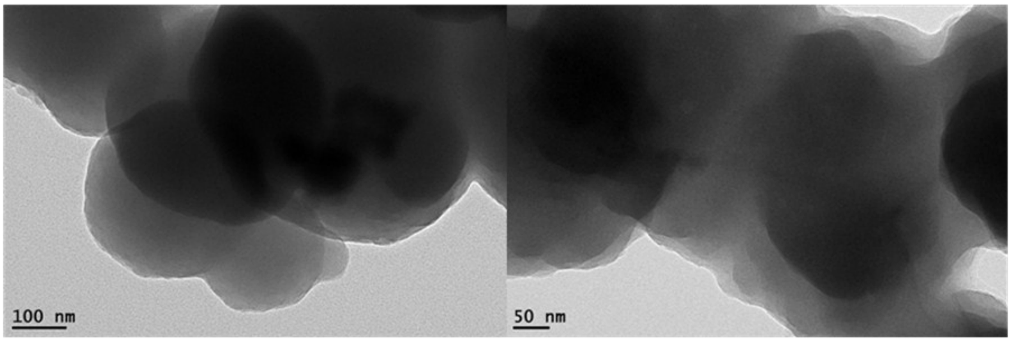


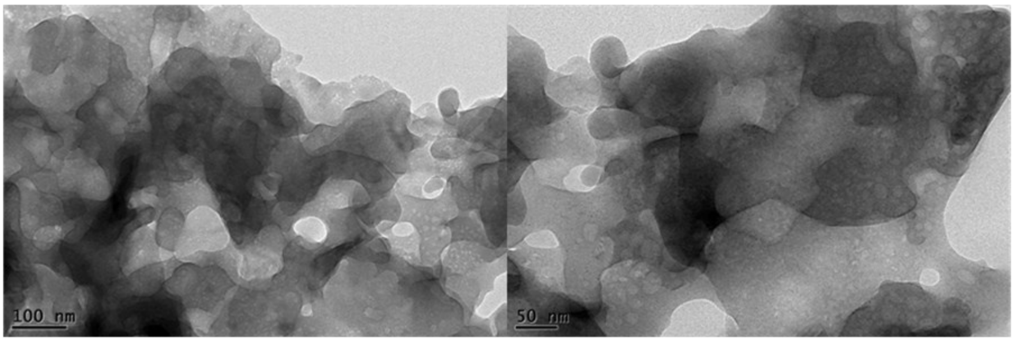
Figure S9. XPS characterization of **Bpy-Pd-POP-1** (in black) and **the recycled Bpy-Pd-POP-1 catalyst** (in red).

XPS characterization of **Bpy-Pd-POP-1** after catalytic runs showed the well-retained state of Bpy-Pd (II) catalytic species.

J. TEM images of fresh catalyst (Bpy-Pd-POP-1) and the recycled Bpy-Pd-POP-1catalyst



A:Fresh catalyst

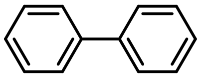


B: Recycled catalyst

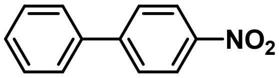
Figure S10. TEM images of fresh catalyst **(A:Bpy-Pd-POP-1)** and the recycled **Bpy-Pd-POP-1**catalyst (**B**)

K. General procedure for the Suzuki-Miyaura coupling reaction

In a typical run of catalytic activity test of **Bpy-Pd-POP-1,** aryl halide (0.5 mmol), phenylboronic acid (91.5 mg, 0.75 mmol, 1.5 eq), K_2CO_3 (138 mg, 1.0 mmol, 2.0 eq), and **Bpy-Pd-POP-1** (3.0 mg, 0.8 mol%) were added to 1.0 mL of 1.0/1.0 EtOH-H_2O (v/v) mixture. The reaction mixture was stirred at 80 °C under ambient atmosphere. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with EtOH (1 x 5 mL) and EtOAc (3 x 5 mL). The combined organic phase was washed with water to remove K_2CO_3 residue. After the evaporation of the solvent under vacuum, the residue was purified by flash column chromatography with petroleum ether or petroleum ether/EtOAc = 10:1 as the eluent.



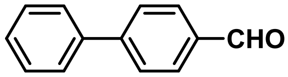
Prepared according to the typical procedure with bromobenzene (or iodobenzene) and phenylboronic acid. The product was collected as clear oil after silica gel chromatography with petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.58 (m, 4H), 7.46 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 128.7, 127.2, 127.1.



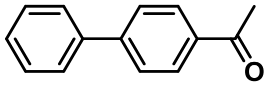
Prepared according to the typical procedure with *p*-nitrobromobenzene and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.54–7.37 (m, 3H).. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.1, 138.8, 129.1, 128.9, 127.4, 124.1.

Prepared according to the typical procedure with 4-bromobiphenyl and phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.63 (m, 8H), 7.48 (t, J = 7.6

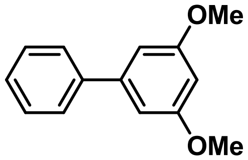
Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.



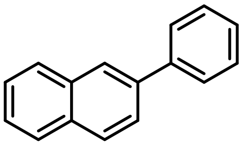
Prepared according to the typical procedure with 4-bromobenzaldehyde and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.08 (s, 1H), 8.01–7.92 (m, 2H), 7.81–7.74 (m, 2H), 7.69–7.62 (m, 2H), 7.53–7.46 (m, 2H), 7.45–7.41 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.9, 147.2, 139.7, 135.2, 130.2, 129.0, 128.5, 127.9, 127.3.



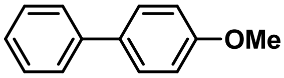
Prepared according to the typical procedure with *p*-bromoacetophenones and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.09–8.01 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67–7.61 (m, 2H), 7.49 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.45–7.38 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.7, 145.8, 139.9, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.



Prepared according to the typical procedure with 1-bromo-3,5-dimethoxybenzene and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.49–7.41 (m, 2H), 7.36 (dd, *J* = 15.4, 8.1 Hz, 1H), 6.76 (d, *J* = 2.2 Hz, 2H), 6.50 (t, *J* = 2.2 Hz, 1H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.1, 143.5, 141.2, 128.7, 127.5, 127.2, 105.5, 99.3, 55.4.



Prepared according to the typical procedure with 2-bromonaphthalene and phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (d, J = 1.1 Hz, 1H), 7.98–7.85 (m, 3H), 7.75 (tt, J = 3.1, 1.9 Hz, 3H), 7.56–7.45 (m, 4H), 7.43–7.34 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.1, 138.6, 133.7, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6.

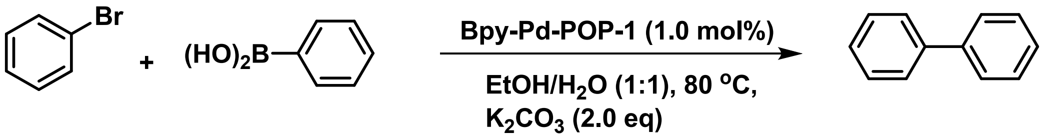


Prepared according to the typical procedure with 4-iodoanisole and phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.52 (m, 4H), 7.44 (dd, J = 10.4, 4.9 Hz, 2H), 7.37–7.28 (m, 1H), 7.06–6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

L. Recyclability of Bpy-Pd-POP-1 catalyst

The recycling experiment was performed by recovering the **Bpy-Pd-POP-1** catalyst using the centrifugation method. The recovered **Bpy-Pd-POP-1** catalyst was washed with EtOAc to remove the residual product and simply dried before resuse. We chose the suzuki-miyaura coupling reaction of bromobenzene to phenylboronic acid to investigate the recyclability of **Bpy-Pd-POP-1** catalyst, and the results are summarized in Table S2.

Table S2. Recycling of **Bpy-Pd-POP-1** catalyst for the Suzuki-Miyaura coupling reaction. [a]



Cycle	Time (h)	Yield (%) [b]	Cycle	Time (h)	Yield (%) [b]
1	0.5	99	9	20	97
2	1.5	99	10	20	98
3	12	98	11	28	98
4	12	98	12	28	97
5	12	98	13	28	98
6	12	99	14	36	98
7	20	99	15	36	98
8	20	99			

[a] General condition: phenylboronic acid (0.5 mmol), bromobenzene (1.0 mmol), K_2CO_3 (1.0 mmol), and **Bpy-Pd-POP-1** (0.005 mmol), EtOH/H_2O (1.0 mL), 80 °C.
[b] Isolated yield after silica gel column chromatography.

Note: In the recycling experiments, a progressive increase in reaction time is needed, which could be due to the partial blocking of the polymeric nanopores.

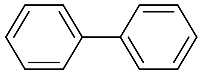
References

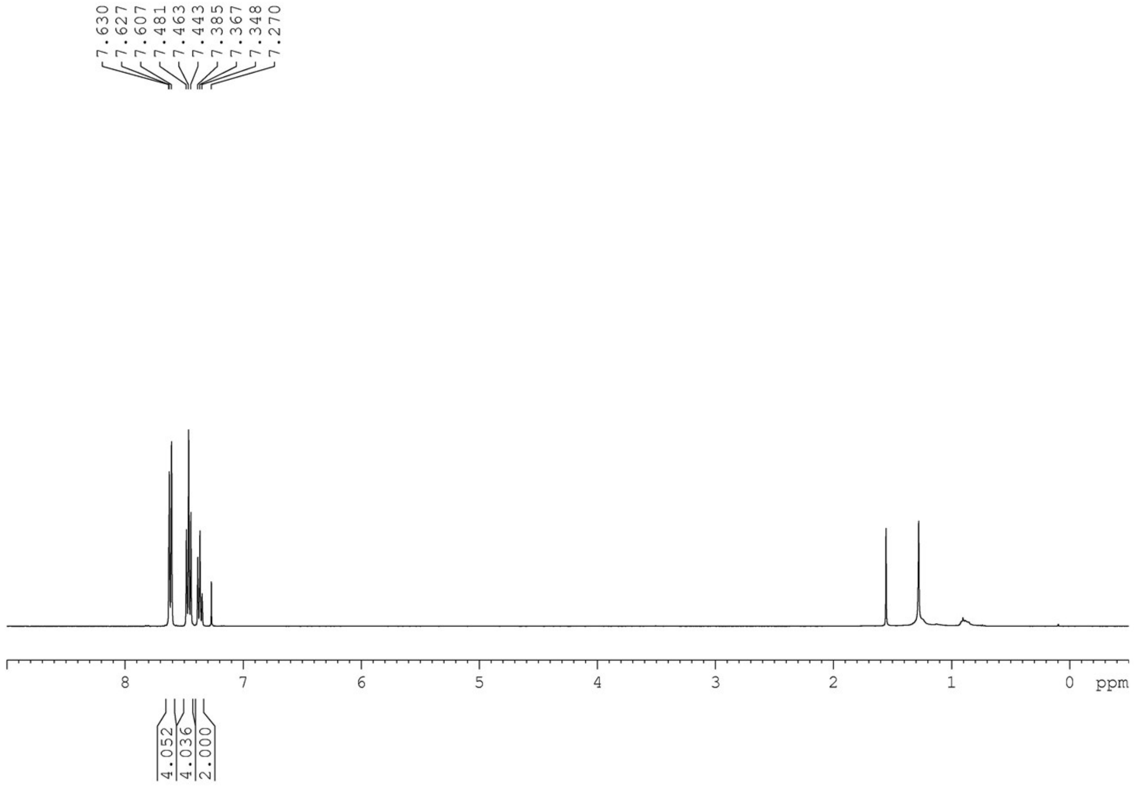
[1]. (a) S. Yuan, S. Kirklin, B. Dorney, J. -J. Liu and L. Yu, *Macromolecules,* 2009, **42**, 1554; (b) T. Kuroda, Y. Sakurai, Y. Suzuki, A. O. Nakamura, M. Kuwahara, H. Ozaki and H. Sawai, *Chem. Asina J.,* 2006, **1**, 575.

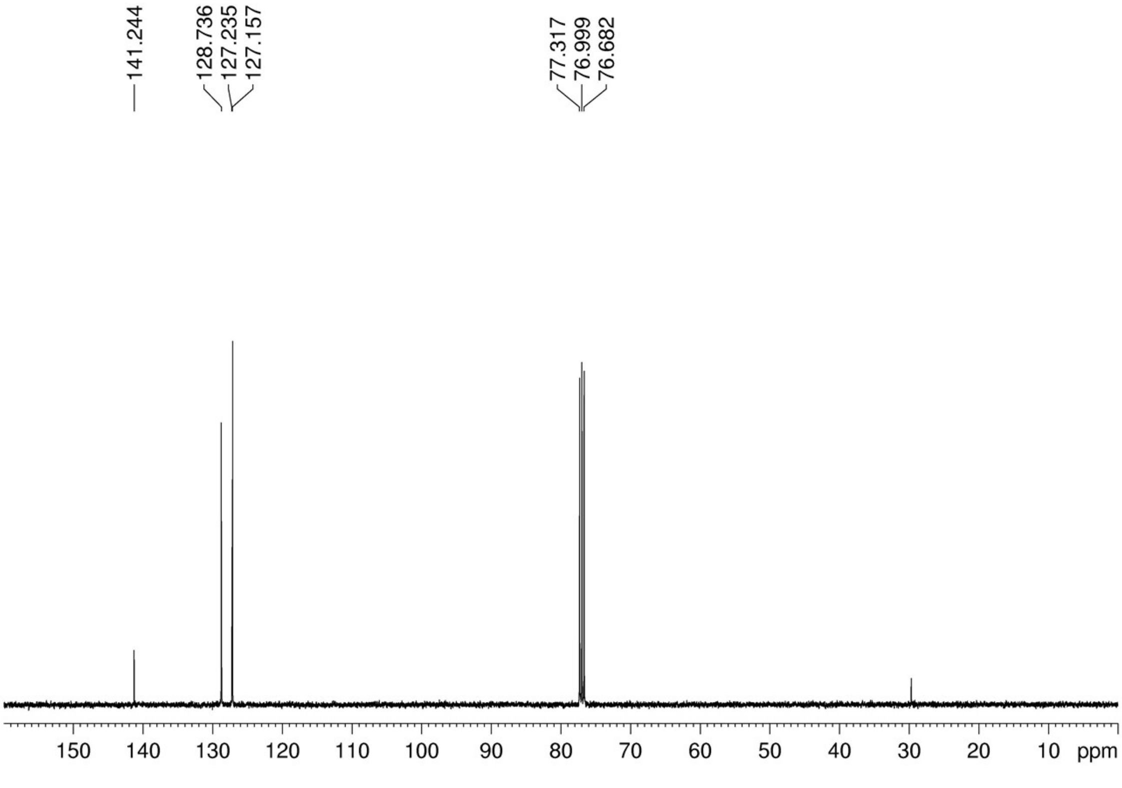
[2] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J. Am. Chem. Soc.,* 2008, **130**, 7710.

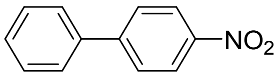
[3] N. B. Debata, D. Tripathy, V. Ramkumar and D. K. Chand, *Tetrahedron Lett.,* 2010, **51**, 4449.

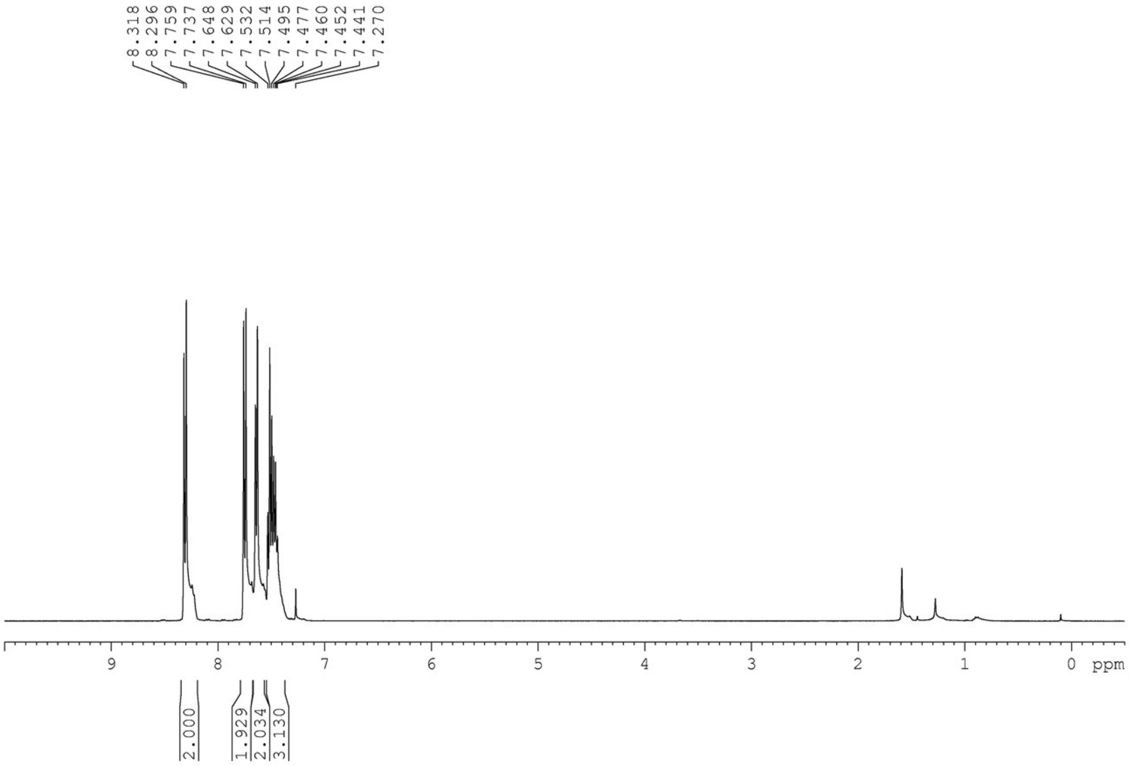
M. ^{1}H NMR and ^{13}C NMR spectra of the products








NO2


8.318
8.296
7.759
7.737
7.648
7.629
7.532
7.514
7.495
7.477
7.460
7.452
7.441
7.270
9
8
7
6
5
4
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2
1
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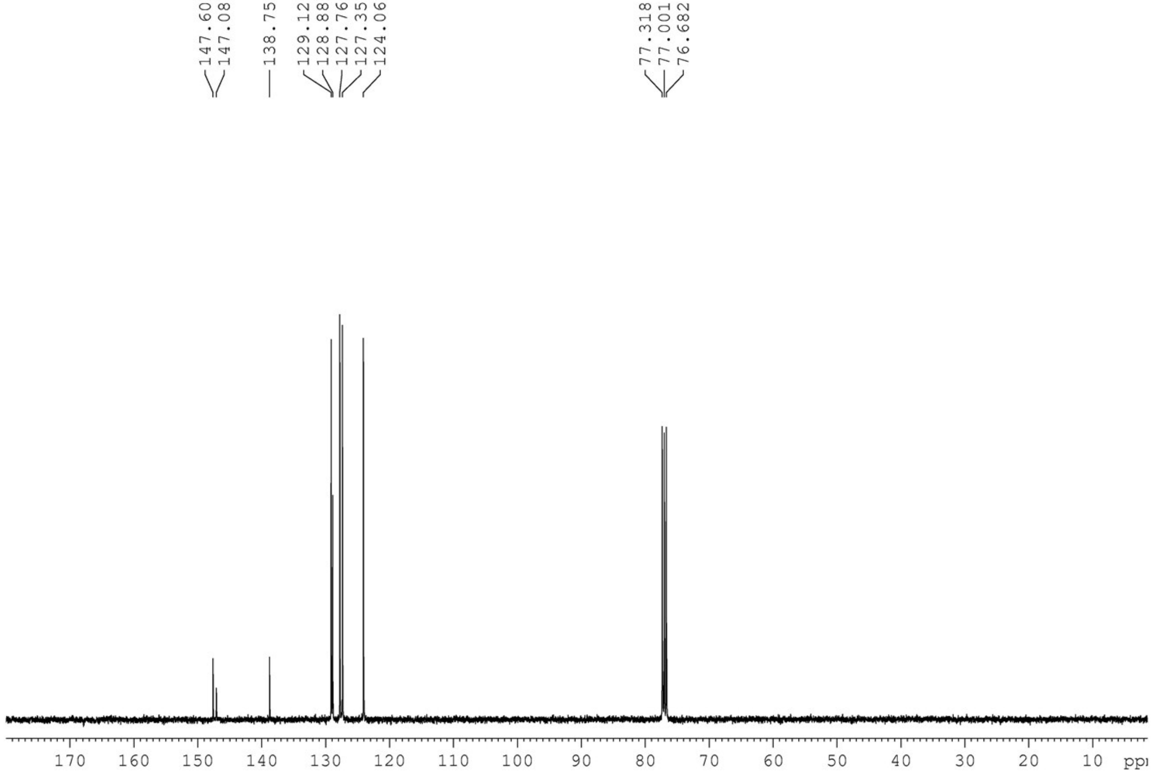
1.929
2.034
3.130


147.602
147.087
138.752
129.127
128.888
127.764
127.351
124.067
77.318
77.001
76.682
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150
140
130
120
110
100
90
80
70
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50
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30
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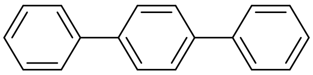
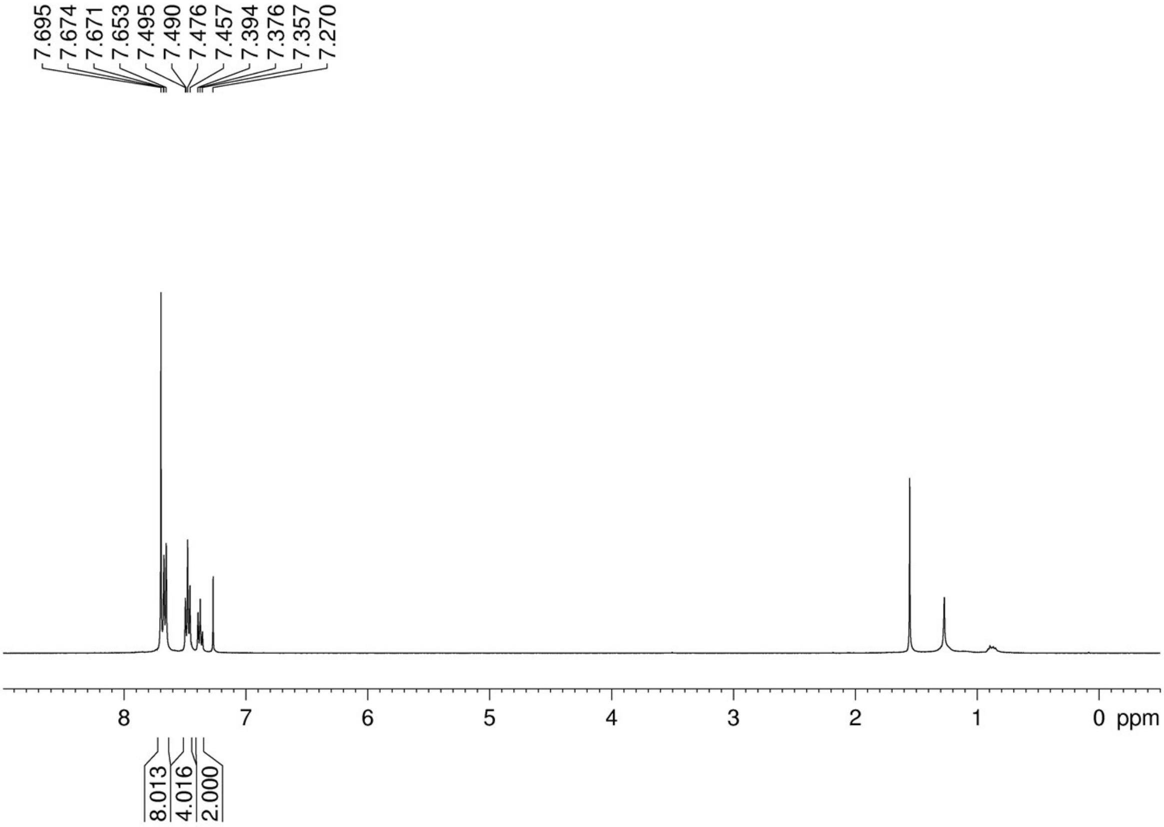
10
pp

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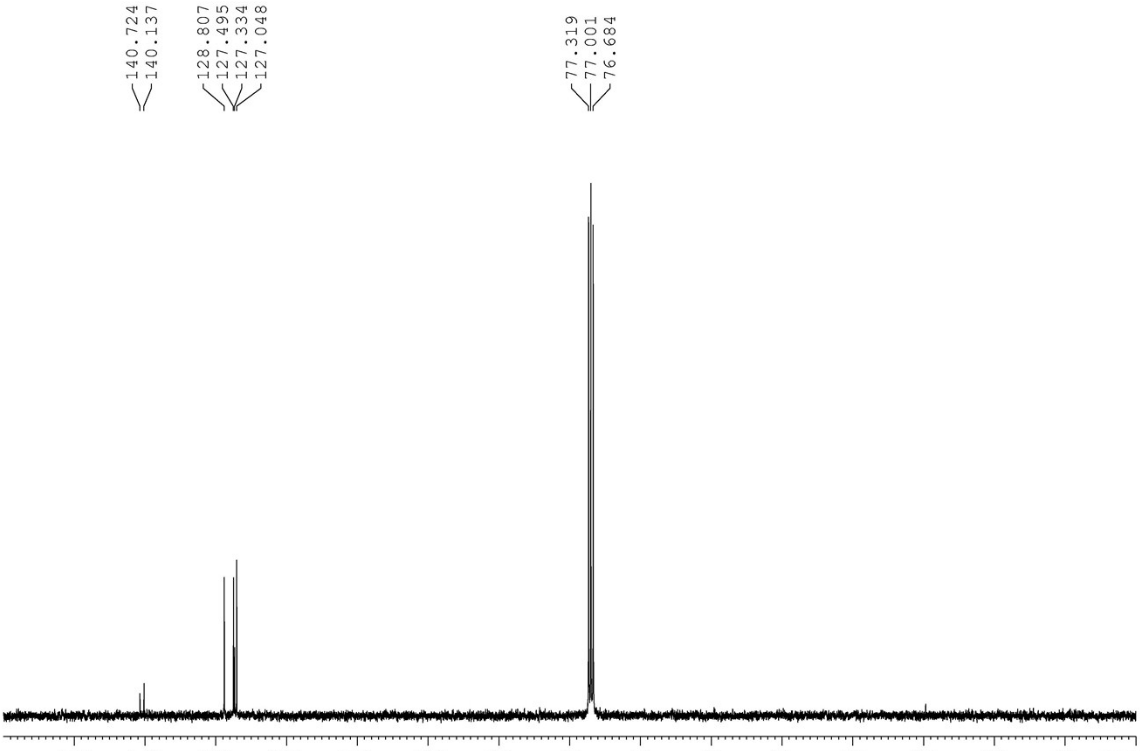
7.674
7.671
7.653
7.495
7.490
7.476
7.457
7.394
7.376
7.357
7.270
8
7
6
5
4
3
2
1
0 ppm
8.013
4.016
2.000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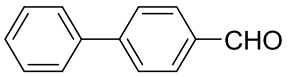
140.137
128.807
127.495
127.334
127.048
77.319
77.001
76.684
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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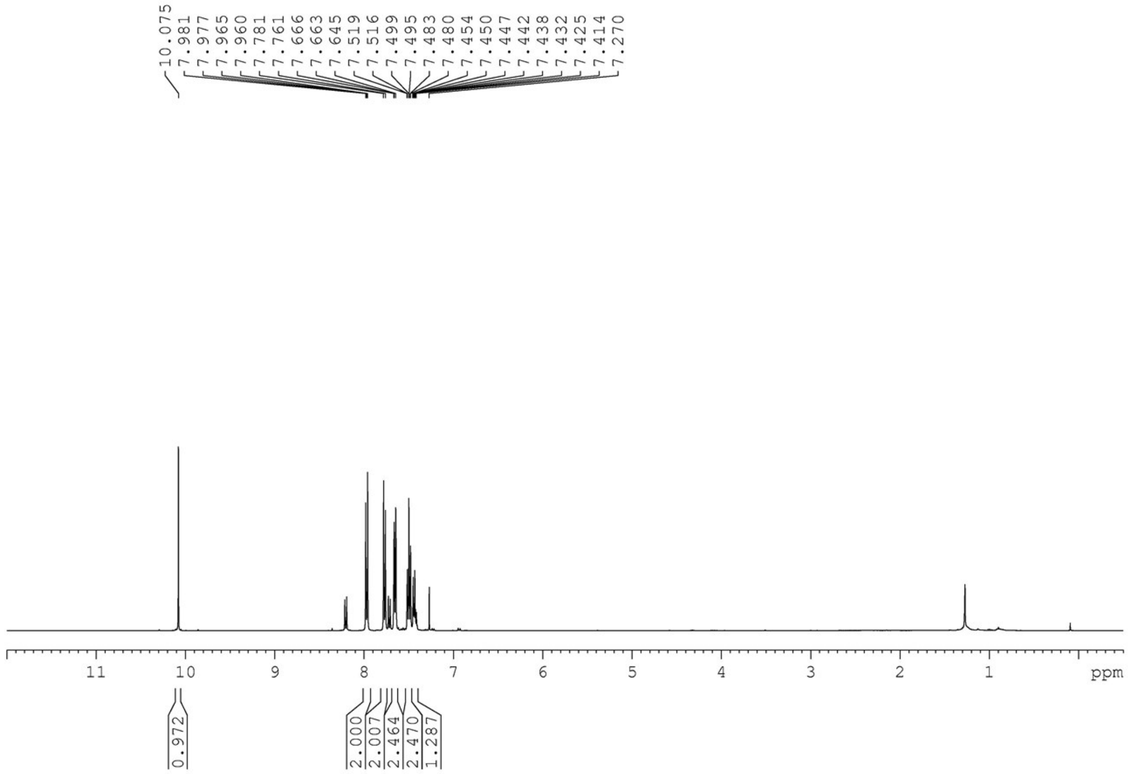
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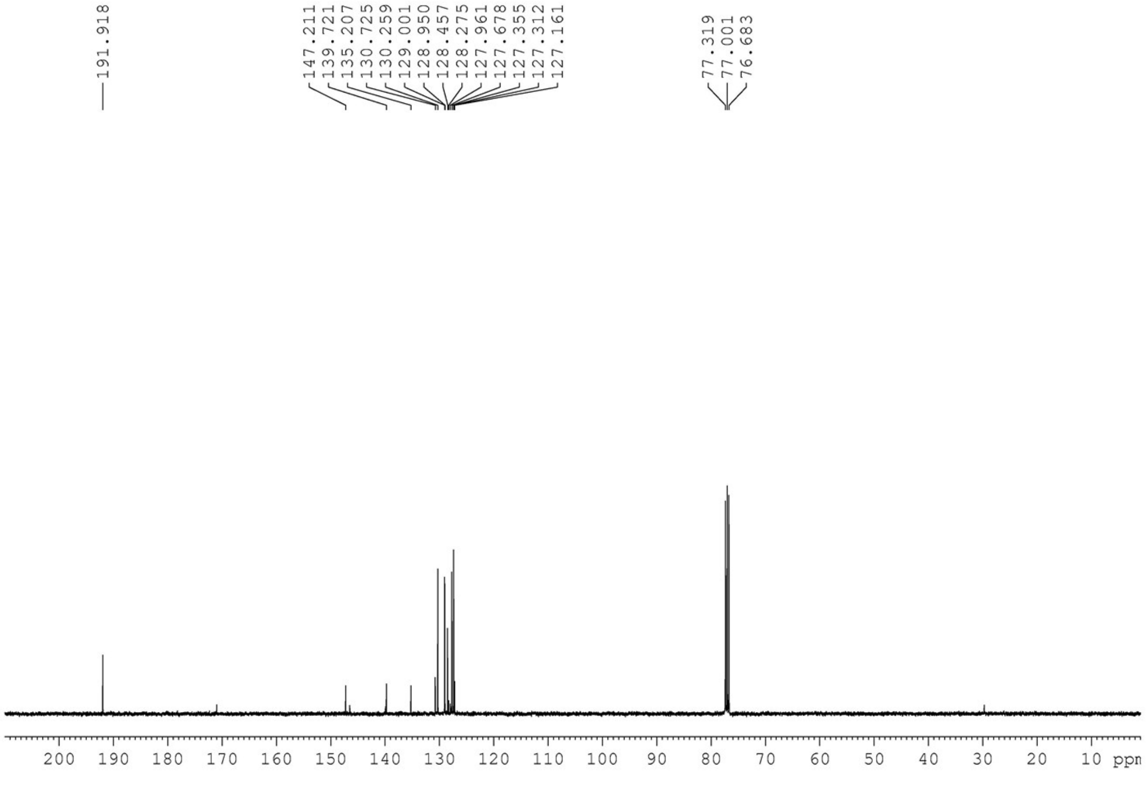
7.981
7.977
7.965
7.960
7.781
7.761
7.666
7.663
7.645
7.519
7.516
7.499
7.495
7.483
7.480
7.454
7.450
7.447
7.442
7.438
7.432
7.425
7.414
7.270
11
10
9
8
7
6
5
4
3
2
1
ppm
0.972
2.000
2.007
2.464
2.470
1.287


191.918
147.211
139.721
135.207
130.725
130.259
129.001
128.950
128.457
128.275
127.961
127.678
127.355
127.312
127.161
77.319
77.001
76.683
200
190
180
170
160
150
140
130
120
110
100
90
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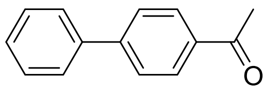
50
40
30
20
10
ppm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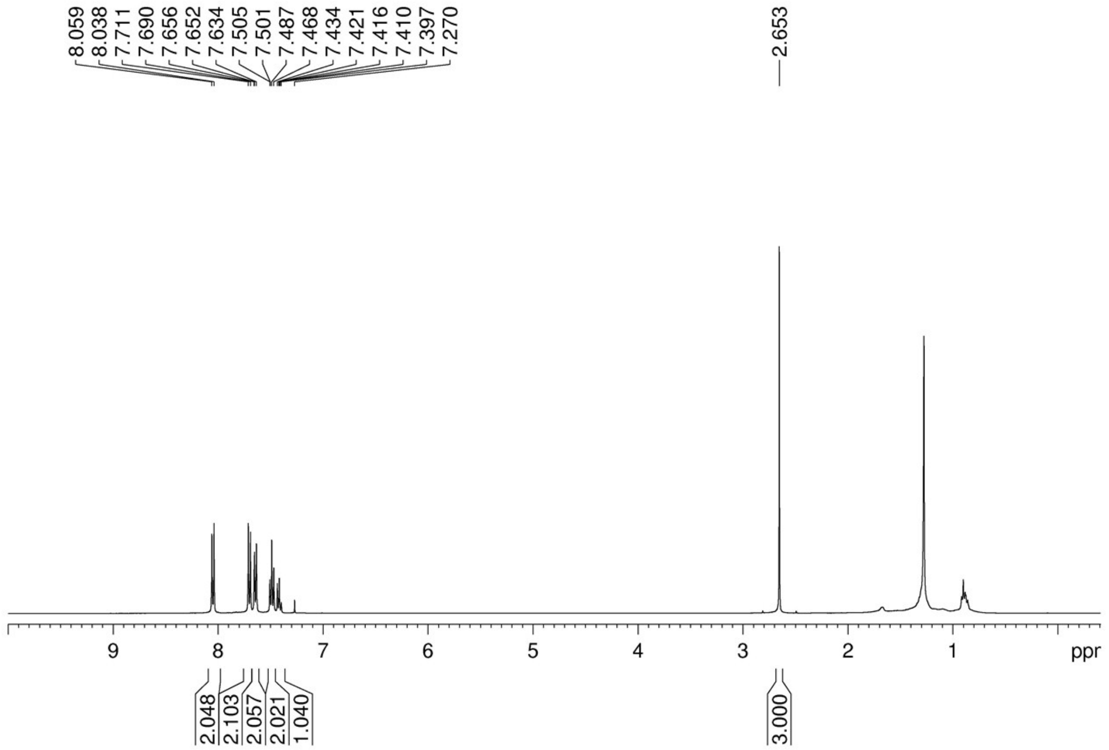
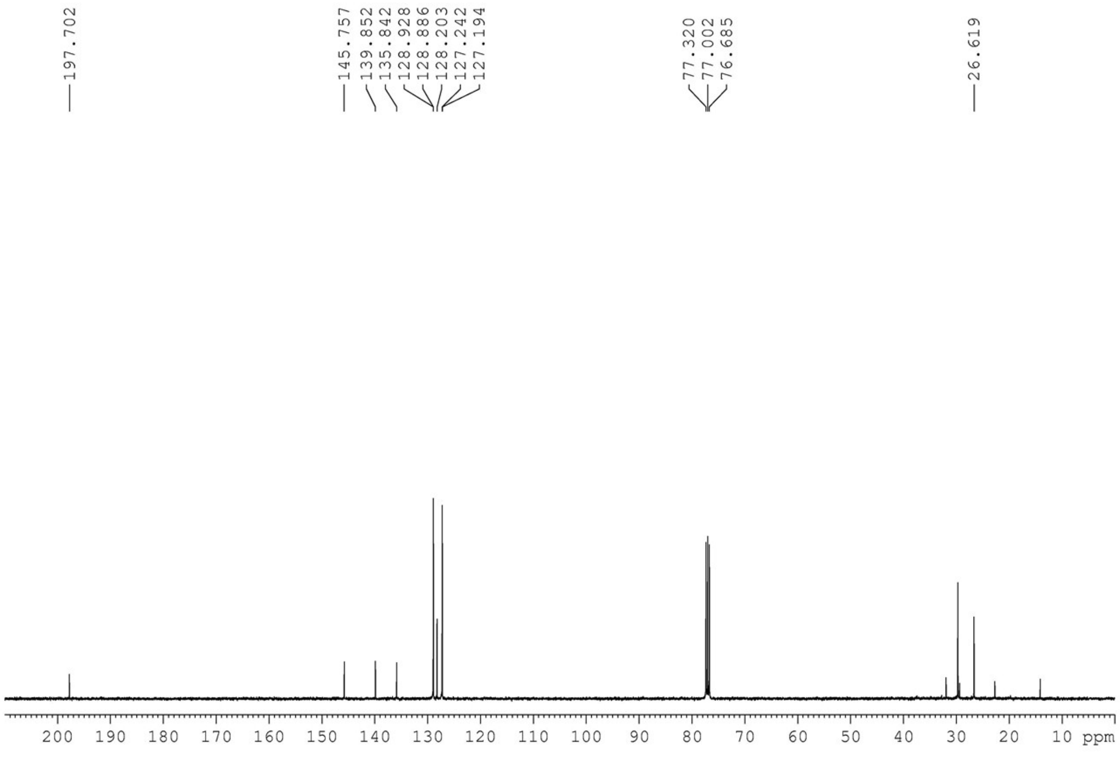
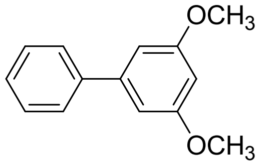
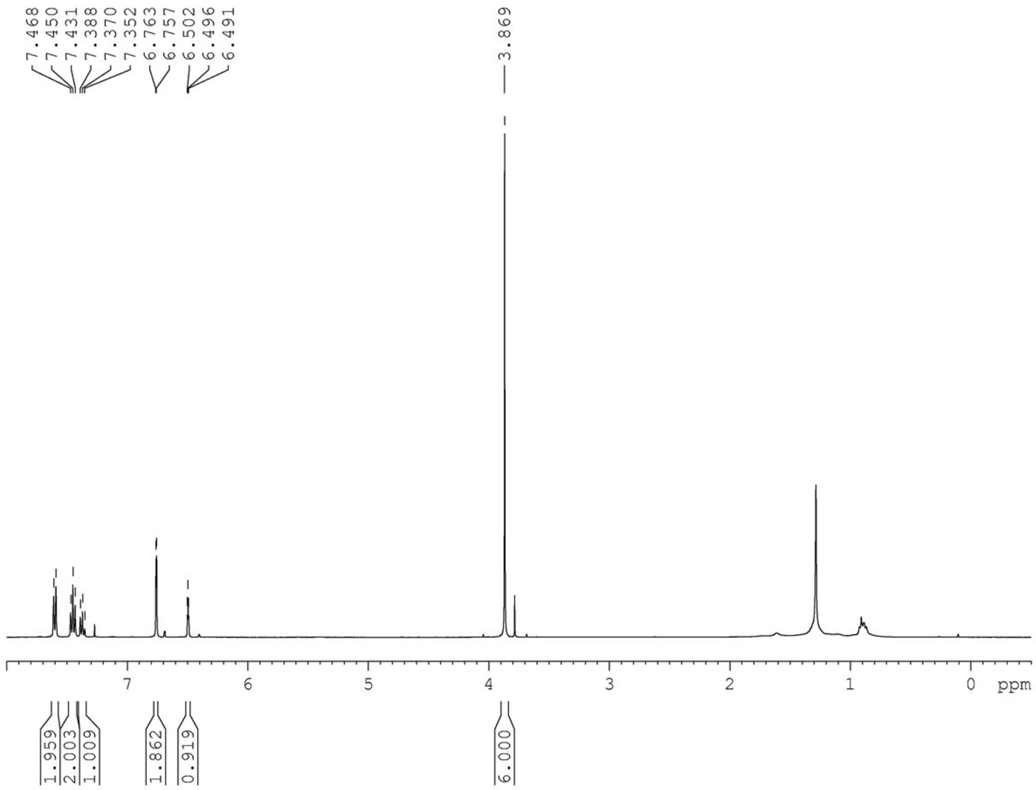
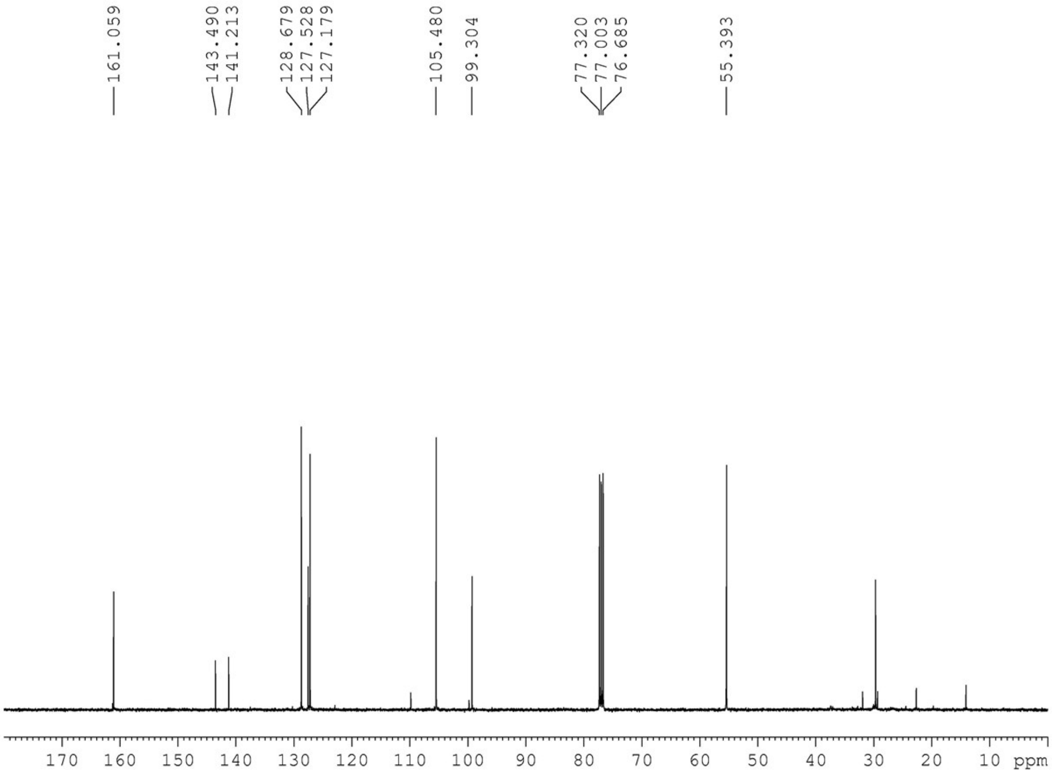
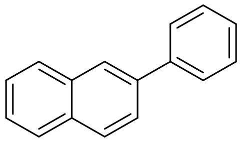

8.059
8.038
7.711
7.690
7.656
7.652
7.634
7.505
7.501
7.487
7.468
7.434
7.421
7.416
7.410
7.397
7.270
2.653
9
8
7
6
5
4
3
2
1
ppm
2.048
2.103
2.057
2.021
1.040
3.000

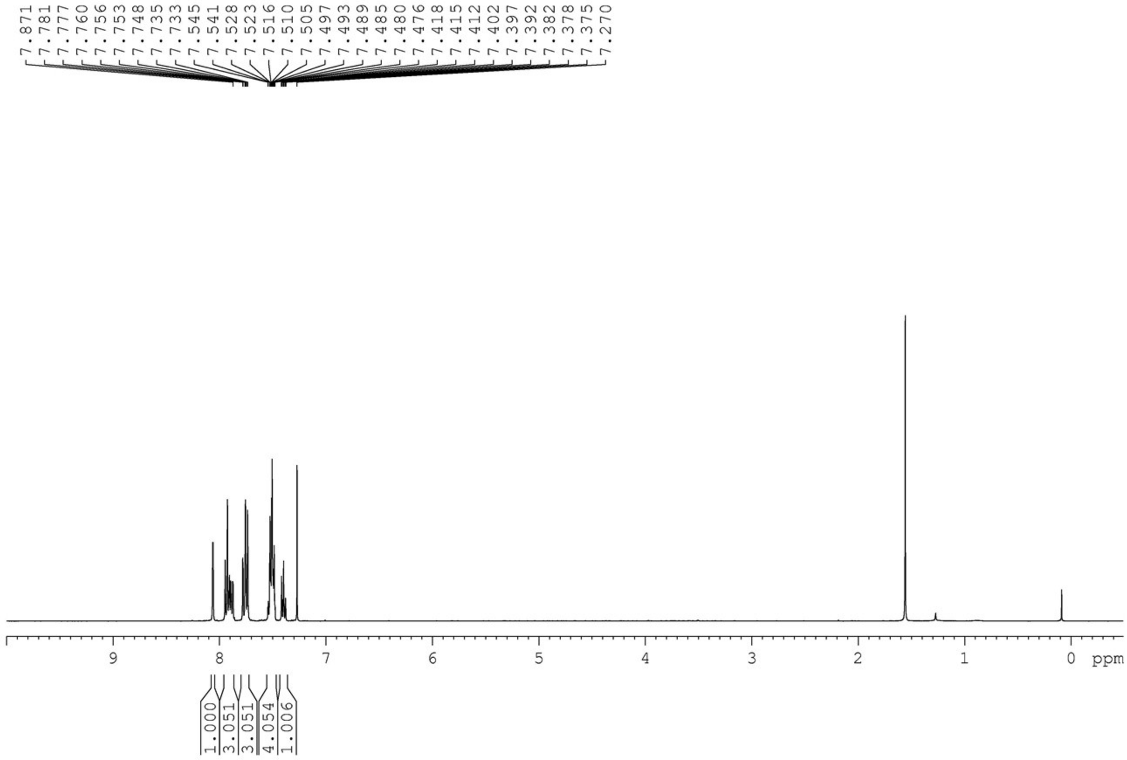

197.702
145.757
139.852
135.842
128.928
128.886
128.203
127.242
127.194
77.320
77.002
76.685
26.619
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

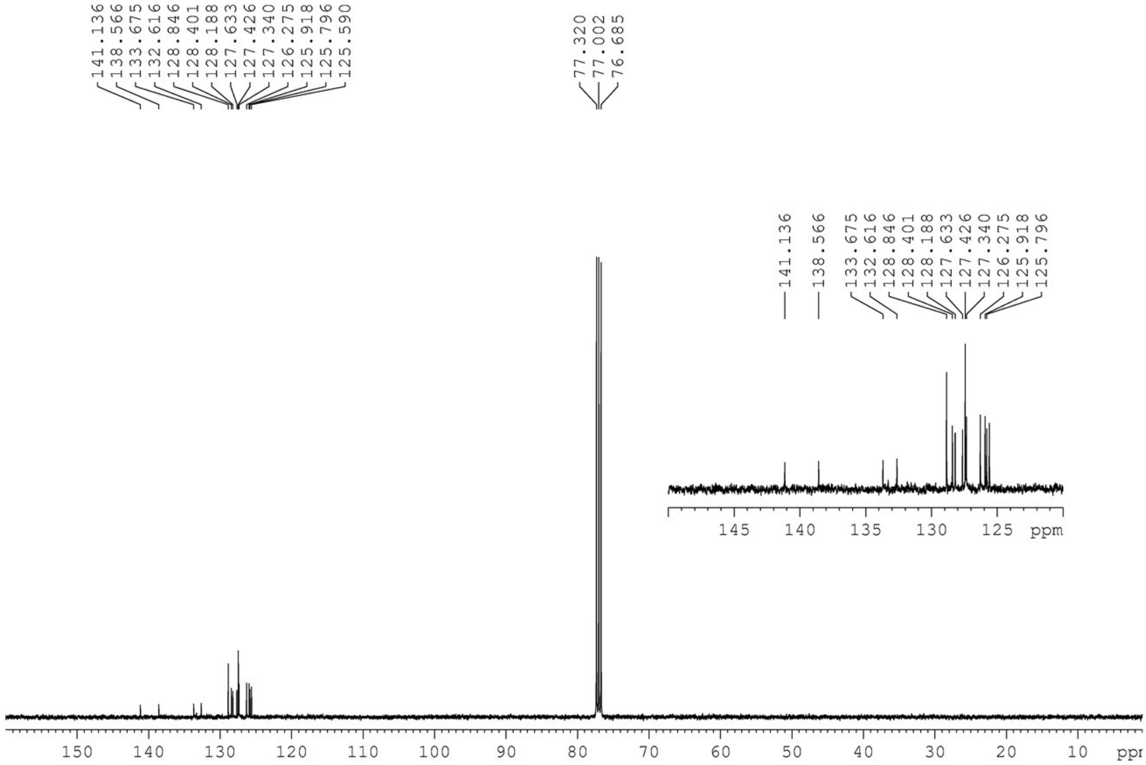

OCH3
OCH3

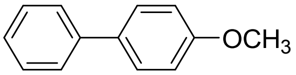

7.468
7.450
7.431
7.388
7.370
7.352
6.763
6.757
6.502
6.496
6.491
3.869
7
6
5
4
3
2
1
0 ppm
1.959
2.003
1.009
1.862
0.919
6.000

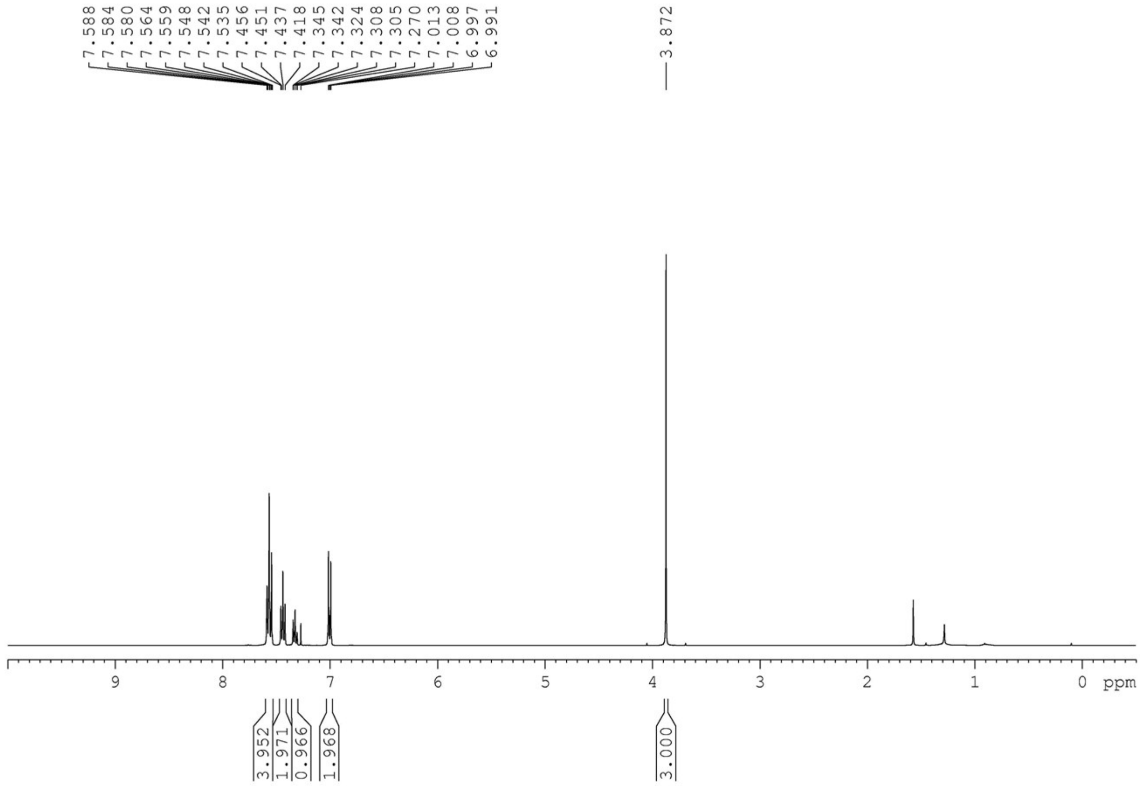

161.059
143.490
141.213
128.679
127.528
127.179
105.480
99.304
77.320
77.003
76.685
55.393
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

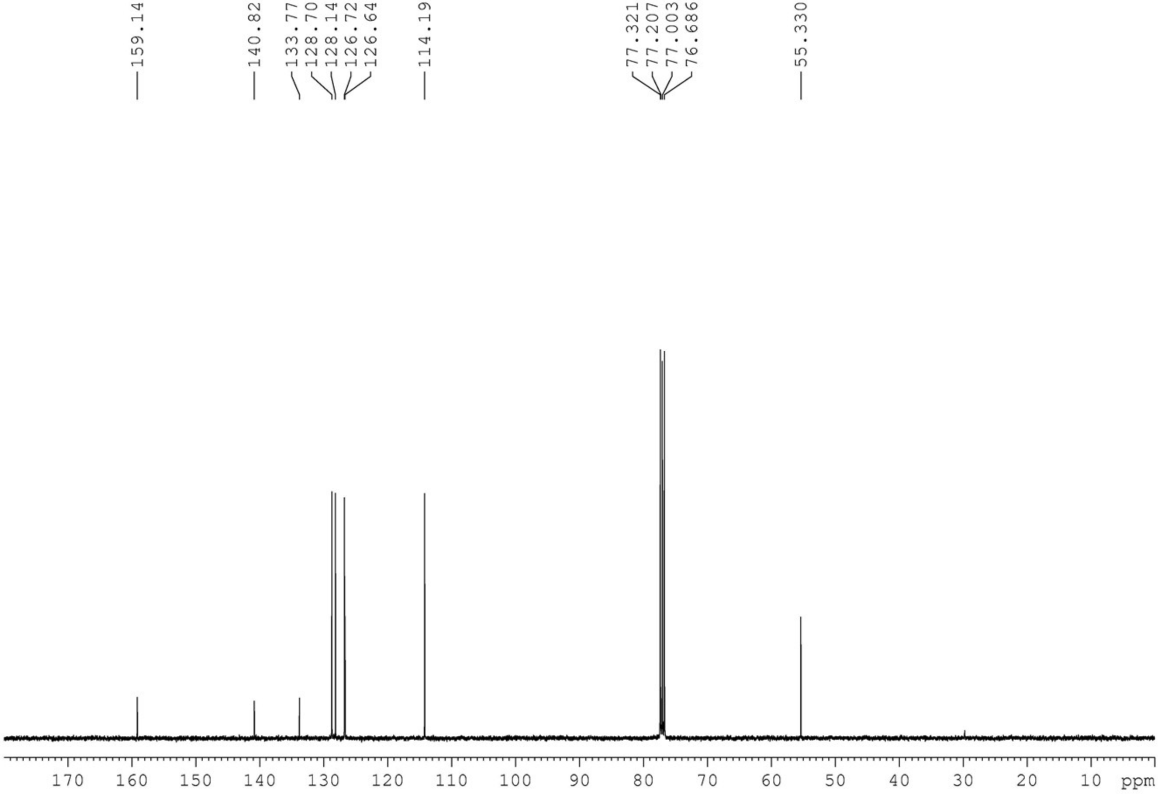



7.871
7.781
7.777
7.760
7.756
7.753
7.748
7.735
7.733
7.545
7.541
7.528
7.523
7.516
7.510
7.505
7.497
7.493
7.489
7.485
7.480
7.476
7.418
7.415
7.412
7.402
7.397
7.392
7.382
7.378
7.375
7.270
9
8
7
6
5
4
3
2
1
0 ppm
1.000
3.051
3.051
4.054
1.006


141.136
138.566
133.675
132.616
128.846
128.401
128.188
127.633
127.426
127.340
126.275
125.918
125.796
125.590
77.320
77.002
76.685
141.136
138.566
133.675
132.616
128.846
128.401
128.188
127.633
127.426
127.340
126.275
125.918
125.796
145
140
135
130
125 ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OCH3


7.588
7.584
7.580
7.564
7.559
7.548
7.542
7.535
7.456
7.451
7.437
7.418
7.345
7.342
7.324
7.308
7.305
7.270
7.013
7.008
6.997
6.991
3.872
9
8
7
6
5
4
3
2
1
0 ppm
3.952
1.971
0.966
1.968
3.000


159.142
140.823
133.779
128.703
128.141
126.726
126.640
114.193
77.321
77.207
77.003
76.686
55.330
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm