Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

In situ formation of Well-dispersed Pd Nanoparticles Immobilized in Imidazolium-based Organic Ionic Polymers

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Content

Experimental details.

General Information: All chemicals were commercially available and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III NMR spectrometer at 400 and 100 MHz, respectively, using tetramethylsilane (TMS) as an internal standard. Solid-state ^{13}C CP/MAS NMR was performed on a Bruker SB Avance III 500 MHz spectrometer with a 4-mm double-resonance MAS probe, a sample spinning rate of 7.0 kHz, a contact time of 2 ms and pulse delay of 5 s. Thermogravimetric-mass spectrometric(TG-MS) analysis was carried out on NETZSCH STA 449 C coupled with NETZSCH QMS 403 C by heating samples from 40 to 1000 ^oC in a dynamic nitrogen atmosphere with a heating rate of 10 $°C·min^{-1}$. IR spectra were recorded with KBr pellets using Perkin-Elmer Instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250XI spectrometer, using non-monochromatic Al Kα x-rays as the excitation source and choosing C 1s (284.8 eV) as the reference line. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 system. The samples were degassed at 80 ^oC for 10 h before the measurements. Specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Field-emission scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F operated at an accelerating voltage of 3.0 kV. Transmission electron microscope (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained with TECNAI G^2 F20 instrument. Powered X-ray diffraction (PXRD) patterns were recorded in the range of $2\theta = 5\text{-}90^o$ on a desktop X-ray diffractometer (RIGAKU-Miniflex II) with Cu Kα radiation (λ = 1.5406 Å). Inductively coupled plasma (ICP) analysis was measured on Jobin Yvon Ultima2. Gas chromatography (GC) was performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector.

Synthesis of 1,3-bis(4-bromophenyl)imidazolium bromide: The complex was synthesized according to a modified procedure.[1] 4-Bromoaniline (3.44 g, 20 mmol) in toluene (100 mL) was added dropwise into a suspension of paraformaldehyde (150 mg, 10 mmol) in toluene (100 mL), the mixture was stirred at 100 ^{o}C until the solid was totally dissolved. After cooling to 40 ^{o}C, glyoxal (40 wt% in water, 1.2 mL, 10 mmol) was dropwise added to the solution. After stirring for 10 min, 3 mol L^{-1} HBr in 1,4-dioxane (3.3 mL, 10 mmol) was added, and the mixture was allowed to warm up to 100 ^{o}C and stirred overnight. The resultant brown precipitate was filtrated, washed with dichloromethane and dried in vacuo. Yield: 2.87 g (62%); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 10.43 (s, 1H), 8.60 (s, 2H), 7.93 (dd, J_1=8.76, J_2=22.44 Hz, 8H); ^{13}C NMR (100 MHz, [D$_6$] DMSO): δ 135.5, 134.4, 133.5, 124.6, 123.6, 122.4.

Synthesis of 1,3,5-tri(4-pinacholatoborolanephenyl)benzene: The complex was synthesized according to a modified procedure.[2] A mixture of 1,3,5-tri(4-iodinephenyl)benzene (1.09 g, 2 mmol), bis(pinacolato)diboron (3.05 g, 12 mmol), Pd(II)[1,1′-bis(diphenylphosfino)-ferrocene] dichloride (0.29 g, 0.4 mmol) and potassium acetate (2.94 g, 30 mmol) in 1,4-dioxane (50 mL) was degassed through three freeze-pump-thaw cycles using liquid nitrogen and purged with nitrogen. The above mixture was stirred at 80 ^{o}C under inert atmosphere for 8 h and then allowed to cool down to room temperature. After removal of solvent, the crude product was dissolved in dichloromethane, washed with water and then dried under vacuum. The product was purified by column chromatography using petroleum ether and ethyl acetate as eluent. Yield: 1.20 g (88%); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 (d, J=8.08 Hz, 6H), 7.86 (s, 3H), 7.75 (d, J=8.08, 6H), 1.41(s, 12H); ^{13}C NMR (100 MHz,CDCl$_3$): δ 143.7, 142.3, 135.4, 126.7, 125.6, 83.9, 24.9.

Synthesis of Pd@OIP-1: A mixture of 1,3-bis(4-bromophenyl)imidazolium bromide (0.55 g, 1.2 mmol), 1,3,5-tri(4-pinacholatoborolanephenyl)benzene (0.55 g, 0.8 mmol) and

$Pd(PPh_3)_4$ (0.14 g, 0.12 mmol) in 1,4-dioxane (120 mL) was degassed through three freeze-pump-thaw cycles using liquid nitrogen and purged with nitrogen. An aqueous solution of K_2CO_3 (10 mL, 2 M) was added to the above mixture, the resultant mixture was further degassed through three freeze-pump-thaw cycles and purged with nitrogen. The reaction mixture was stirred at 110 ^{o}C for 48 h. The precipitate was filtrated and washed with excess water, DMF and methanol, respectively. The resultant reddish brown product was further Soxhlet extracted with dichloromethane and then dried in vacuo at 80 ^{o}C to give the target product. IR (KBr cm^{-1}): 2362 (w), 2328 (w), 1595 (s), 1498 (s), 1437 (w), 1387 (w), 1290 (w), 1184 (m), 1108 (m), 817 (s), 694 (m), 621 (w), 530 (m).

Synthesis of Pd@OIP-2: The same synthetic procedure as that of Pd@OIP-1 was used except that 1,4-dioxane was replaced by DMF. IR (KBr cm^{-1}): 2362 (w), 2328 (w), 1595 (s), 1498 (s), 1437 (w), 1387 (w), 1290 (w), 1184 (m), 1108 (m), 817 (s), 694 (m), 621 (w), 530 (m).

General procedures for reduction of nitroarenes: $NaBH_4$ (94.6 mg, 2.5 mmol) was added in one portion to a stirring mixture of nitroarenes (0.5 mmol) and Pd@OIP-2 (1 mol%) in H_2O/THF (2.5 mL, 9:1 v/v) at 25 ^{o}C. After 1.5 h, the resultant mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layer was analyzed by using GC, and concentrated under reduced pressure. The crude products were further purified by flash column chromatography on silica gel to afford the desired products. The identity of the products was confirmed by comparison with literature spectroscopic data.

General procedures for recyclability test of Pd@OIP-2: $NaBH_4$ (94.6 mg, 2.5 mmol) was added in one portion to a stirring aqueous solution (2.5 mL) of nitrobenzene (0.5 mmol) and Pd@OIP-2 (1 mol%) at room temperature for 15 min. After the reaction was finished, the resultant mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layer was determined by GC analysis. The residual solid in aqueous solution was separated by centrifugation, washed with water thoroughly, and then used for the next run with recharge of fresh substrates.

Characterization data.

1,3-bis(4-bromophenyl)imidazolium bromide. ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 10.43 (s, 1H), 8.60 (s, 2H), 7.93 (dd, J_1=8.76, J_2=22.44 Hz, 8H); ^{13}C NMR (100 MHz, [D$_6$] DMSO): δ 135.5, 134.4, 133.5, 124.6, 123.6, 122.4.

1,3,5-tri(4-pinacholatoborolanephenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J=8.08 Hz, 6H), 7.86 (s, 3H), 7.75 (d, J=8.08 Hz, 6H), 1.41(s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.3, 135.4, 126.7, 125.6, 83.9, 24.9.

***p*-Anisidine.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, J=8.8 Hz, 2H), 6.67 (d, J=8.84 Hz, 2H), 3.77 (s, 3H), 3.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 140.0, 116.4, 114.8, 55.8.

***p*-Toluidine.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, J=8.12 Hz, 2H), 6.63 (d, J=8.24 Hz, 2H), 3.55 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 129.7, 127.8, 115.2, 20.4.

***o*-Toluidine.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (t, J=7.48 Hz, 2H), 6.78-6.71 (m, 2H), 3.61 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, [D$_1$]$CDCl_3$): δ 144.6, 130.5, 127.0, 122.3, 118.7, 115.0, 17.3.

4-*tert*-Butylaniline. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J=8.28 Hz, 2H), 6.69 (d, J=8.28 Hz, 2H), 3.51 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 141.4, 126.1, 115.0, 33.9, 31.6.

4-Aminophenol. ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 8.33 (s, 1H), 6.46 (dd, J_1=8.76, J_2=24.78 Hz, 4H), 4.37 (s, 2H). ^{13}C NMR (100 MHz, [D$_6$] DMSO): δ 148.7, 141.1, 116.0, 115.7.

***p*-Phenylenediamine.** ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 6.37 (s,4H), 4.18 (s, 4H). ^{13}C NMR (100 MHz, [D$_6$] DMSO): δ 139.4, 115.9.

1-(4-aminophenyl)ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J=8.32 Hz, 2H), 6.64 (d, J=8.32 Hz, 2H), 4.76 (q, J=6.44 Hz, 1H), 3.24 (s, 2H), 1.45 (d, J=6.48 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 136.1, 126.6, 115.2, 70.0, 24.8.

***m*-Phenylenediamine.** ^{1}H NMR (400 MHz,$CDCl_3$): δ 6.97 (t, J=7.84 Hz, 1H), 6.14 (dd, J_1=1.92, J_2=7.84 Hz, 2H), 6.03 (s, 1H), 3.60 (s, 2H). (100 MHz, $CDCl_3$): δ 147.6, 130.2, 106.0, 102.0.

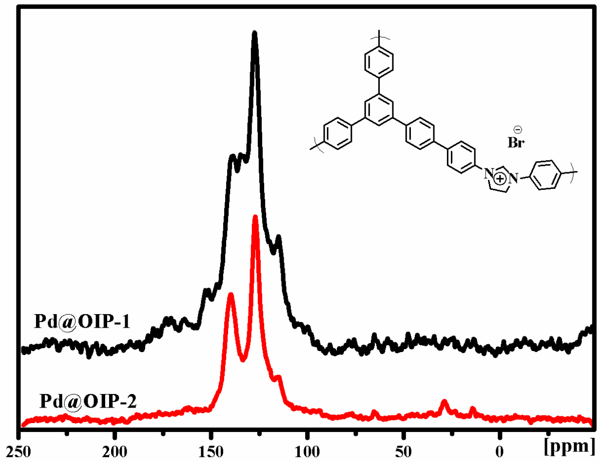


Fig. S1 Solid-state ^{13}C NMR spectra of Pd@OIP-1 and Pd@OIP-2.

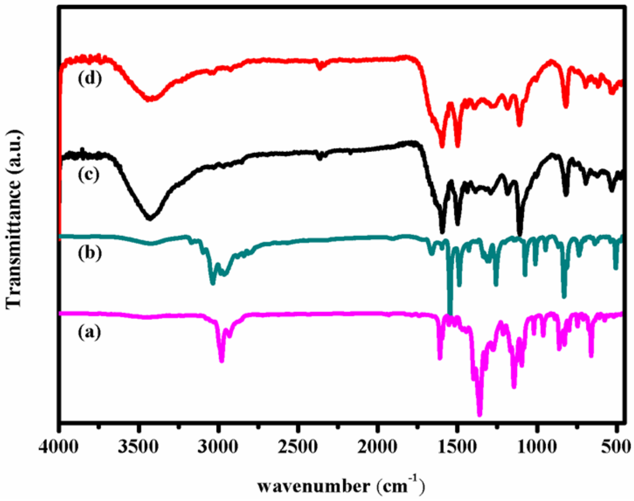


Fig. S2 FTIR spectra of (a) boric acid ester, (b) imidazolium-based aryl bromides, (c)Pd@OIP-1 and (d) Pd@OIP-2.

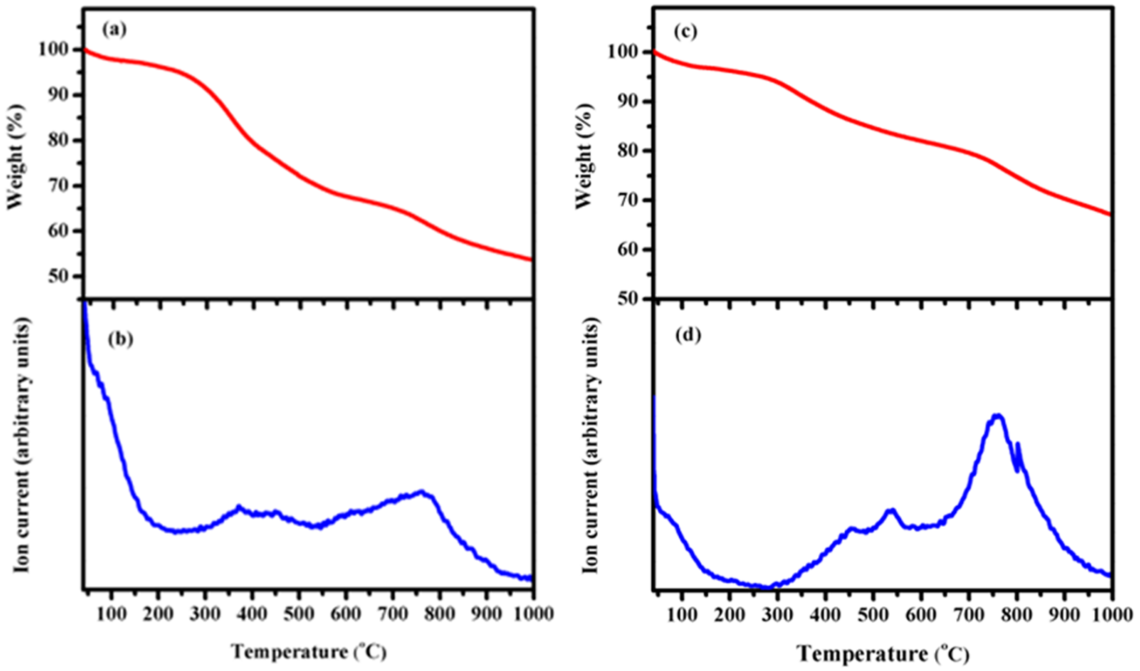


Fig. S3 TGA/MS curves of Pd@OIP-1 and Pd@OIP-2: (a) TGA curve of Pd@OIP-1; (b) MS curve of Pd@OIP-1 with the ion current of H_2O at m/z=18; (c) TGA curve of Pd@OIP-2; (d) MS curve of Pd@OIP-2 with the ion current of H_2O at m/z=18.

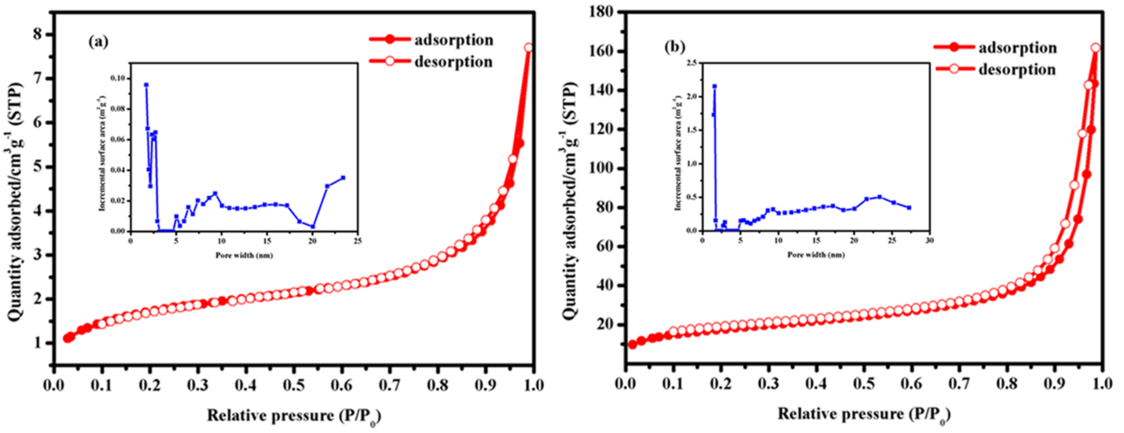


Fig. S4 N_2 adsorption (solid symbols)/desorption (open symbols) isotherms and pore size distributions (inset) of (a) Pd@OIP-1 and (b) Pd@OIP-2 measured at 77K.

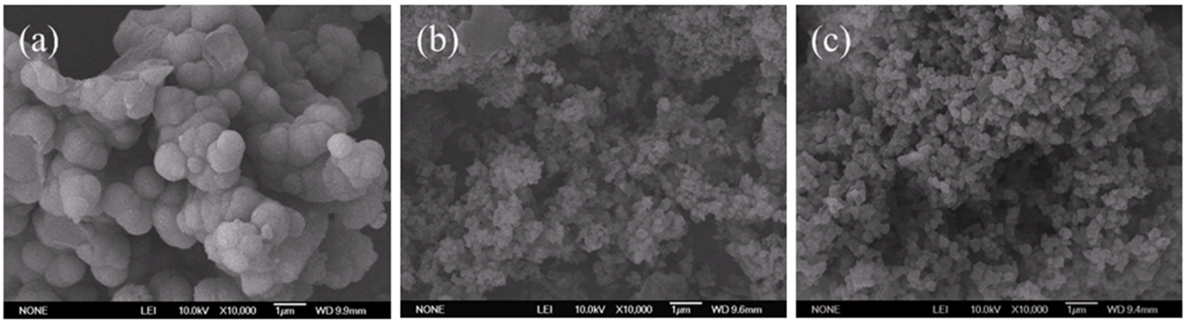


Fig. S5 SEM images of (a) Pd@OIP-1, (b) Pd@OIP-2 and (c) Pd@OIP-2 after consecutive six runs.

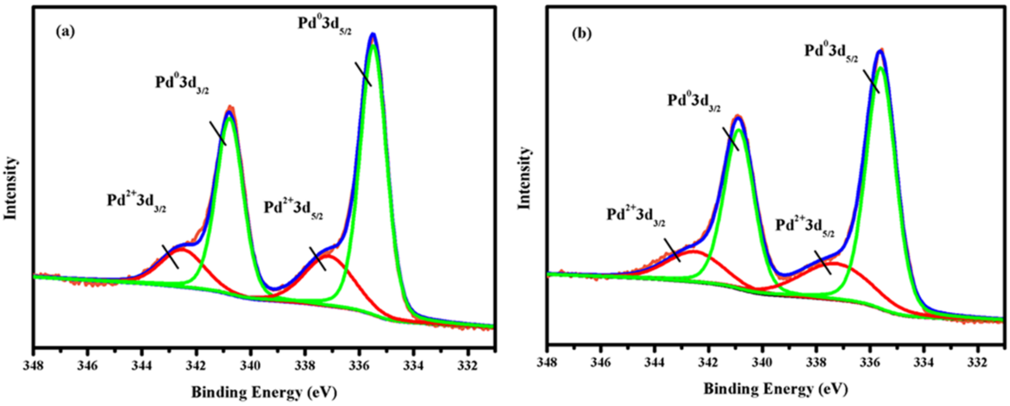


Fig. S6 Pd 3d spectra for (a) Pd@OIP-1 and (b) Pd@OIP-2.

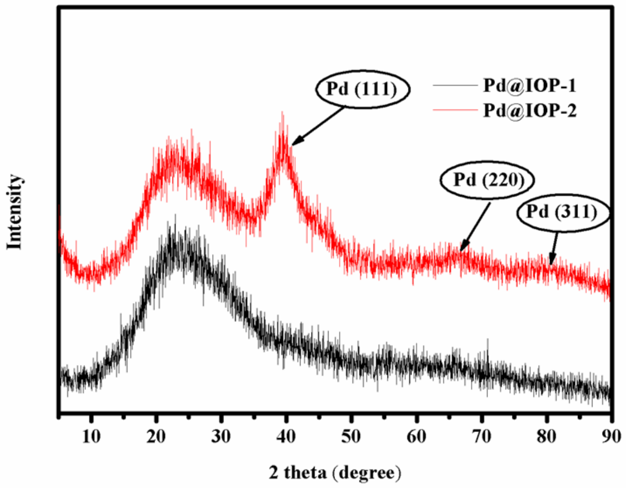


Fig. S7 PXRD patterns of Pd@OIP-1 and Pd@OIP-2.

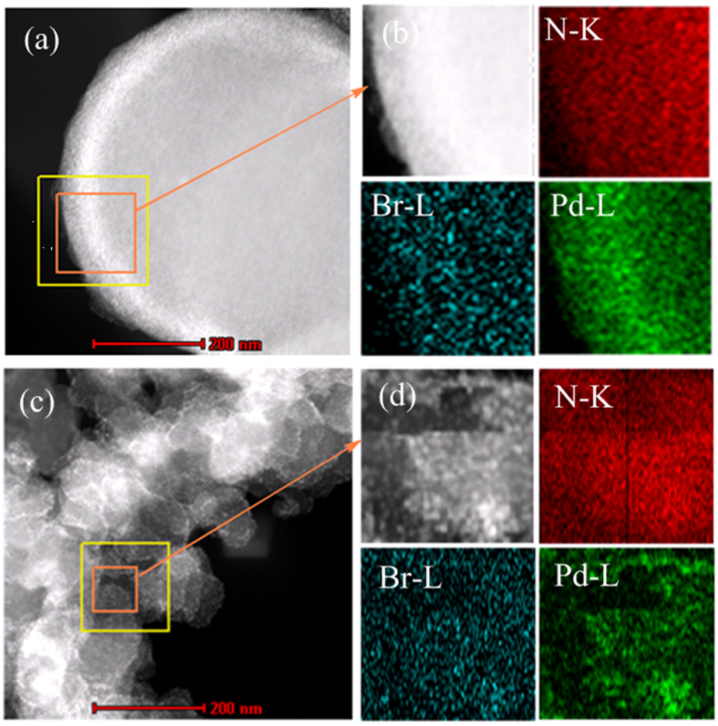


Fig. S8 (a) HAADF-STEM image of Pd@OIP-1; (b) EDX elemental mapping images of Pd@OIP-1; (c) HAADF-STEM image of Pd@OIP-2; (d) EDX elemental mapping images of Pd@OIP-2.

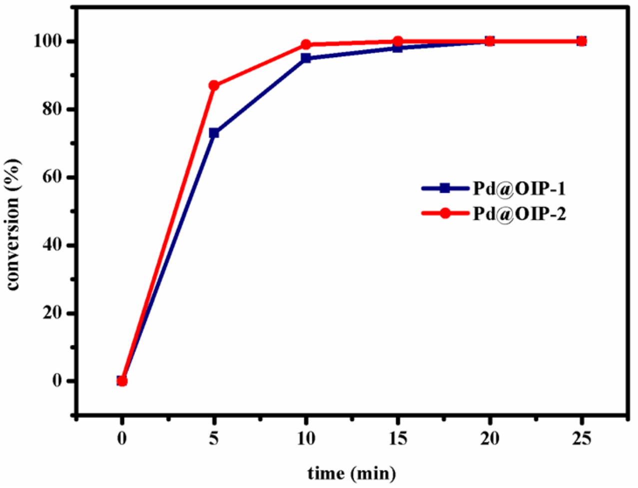
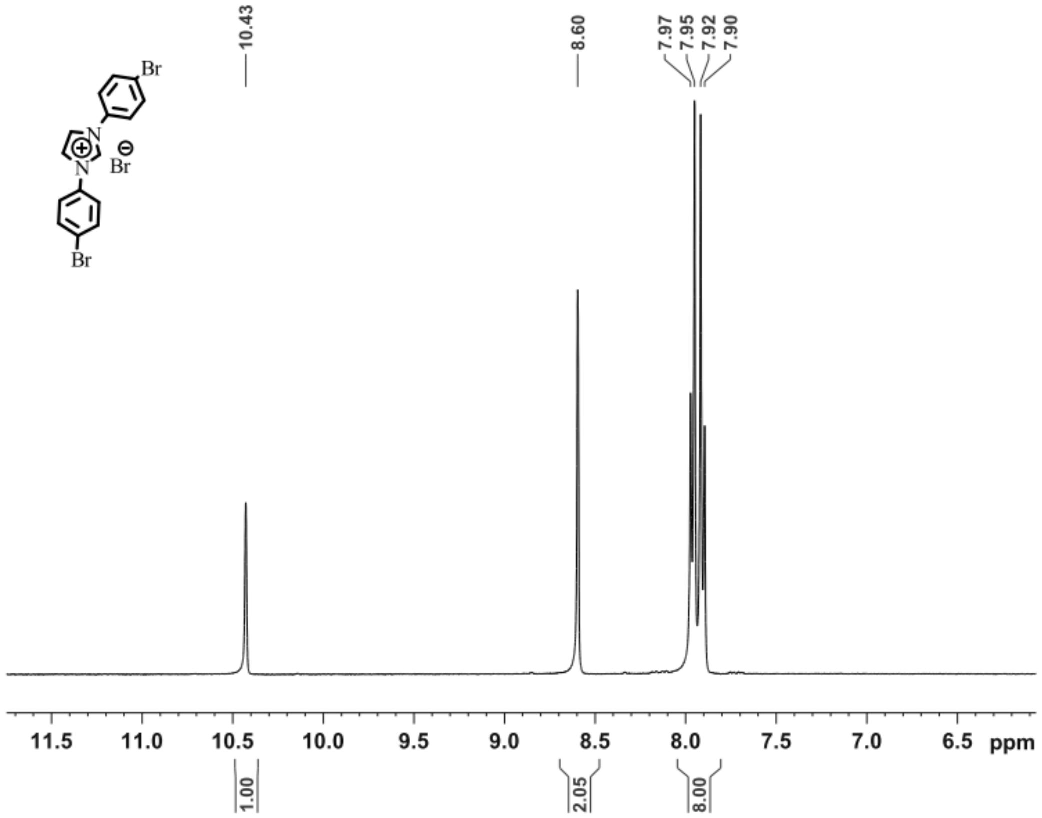


Fig. S9 Conversion of nitrobenzene to aniline as a function of time in hydrogenation reaction. Reaction conditions: nitrobenzene (0.2 mmol), $NaBH_4$ (1 mmol), [Pd] (1 mol%), H_2O (1 mL).

NMR spectra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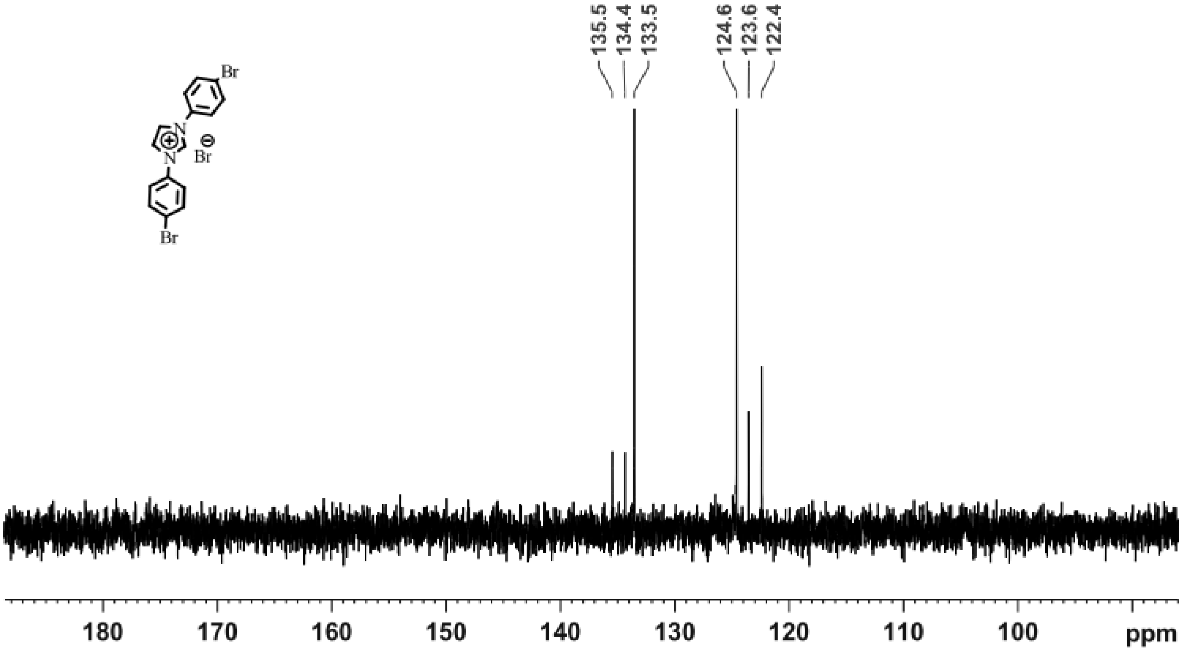
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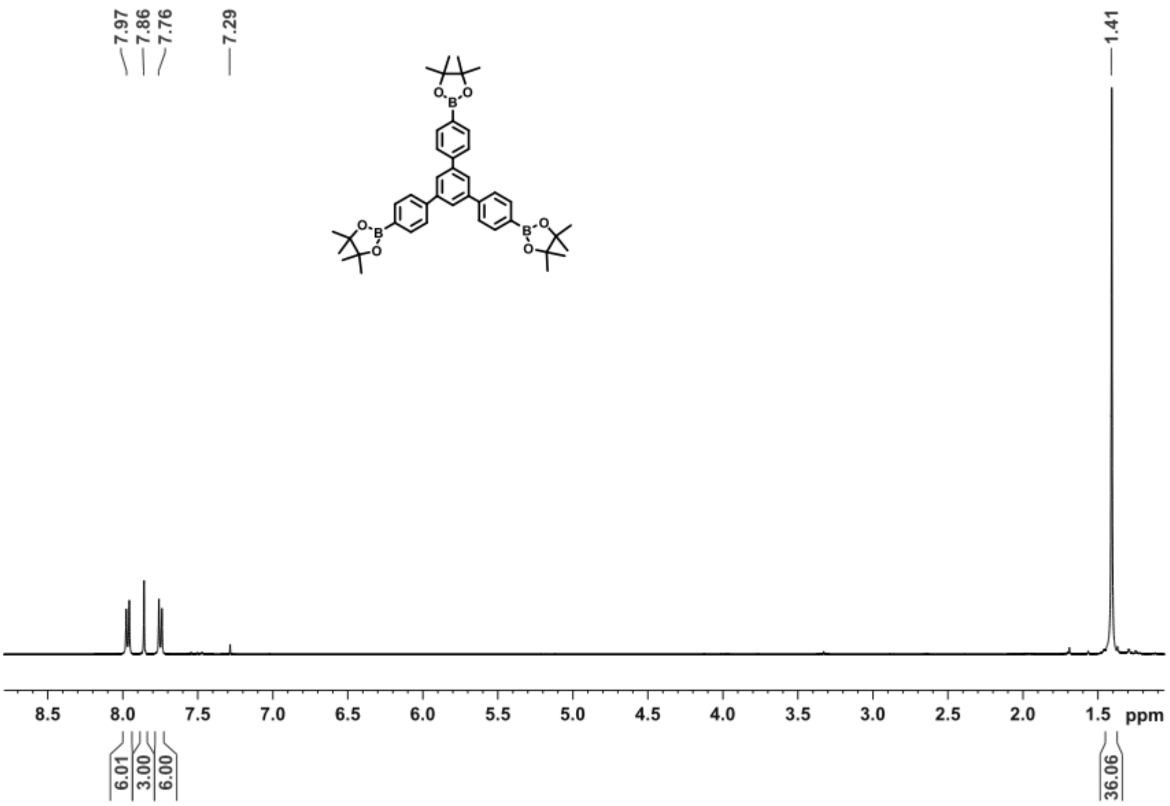
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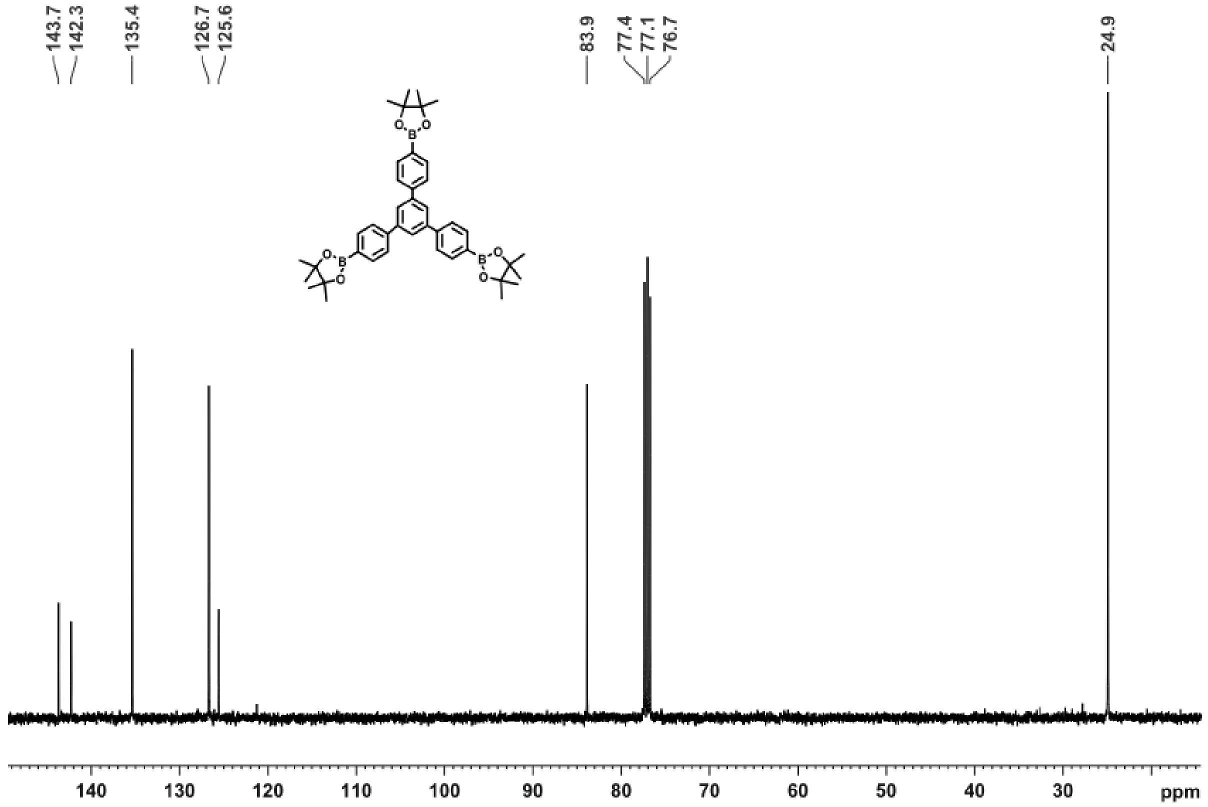
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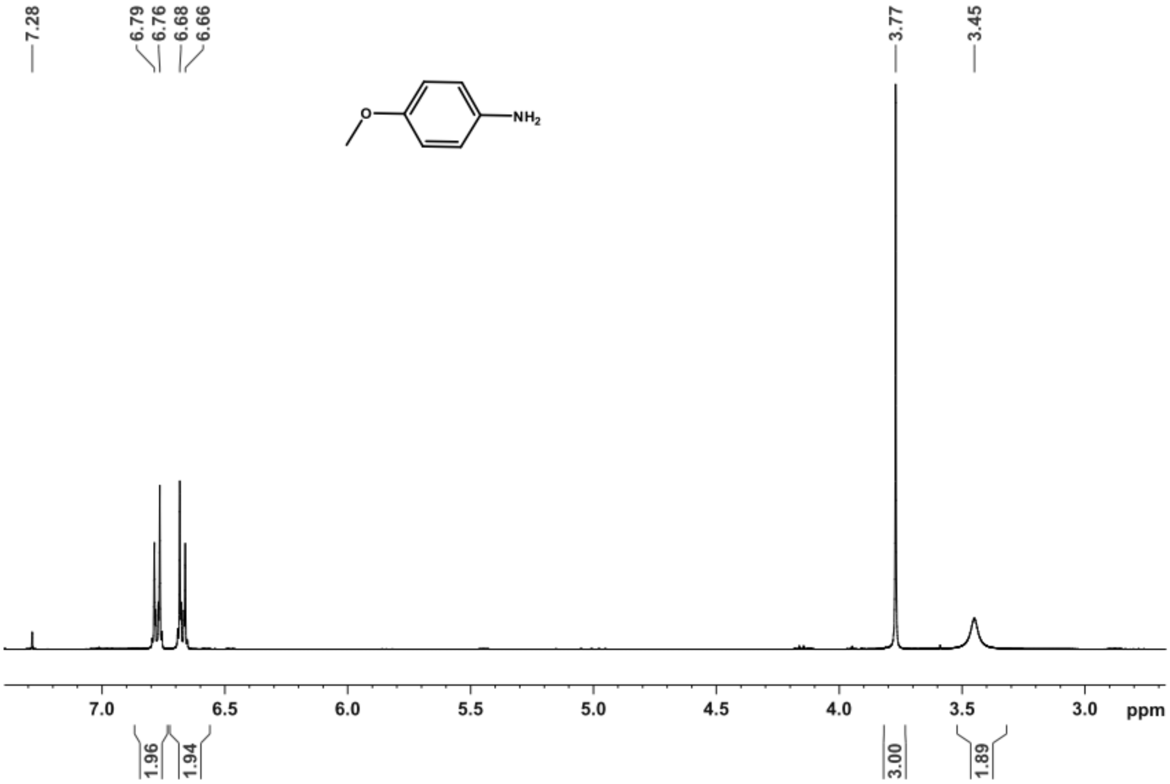
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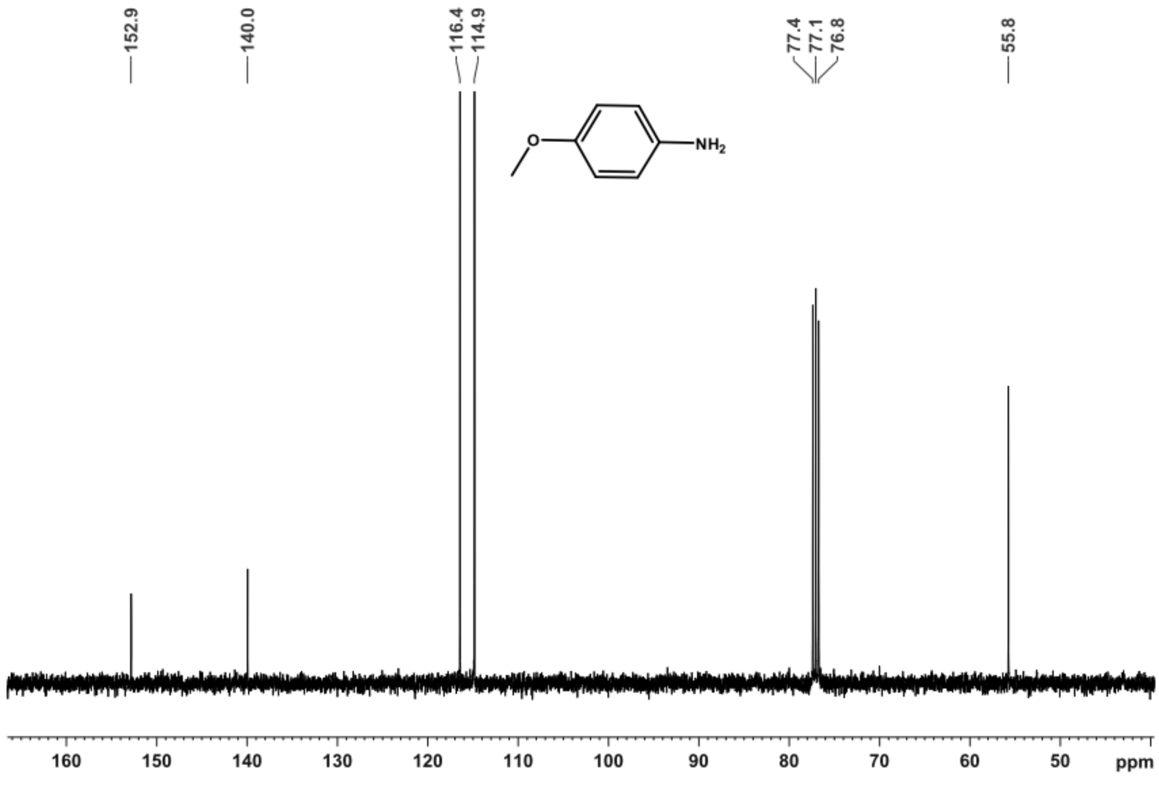
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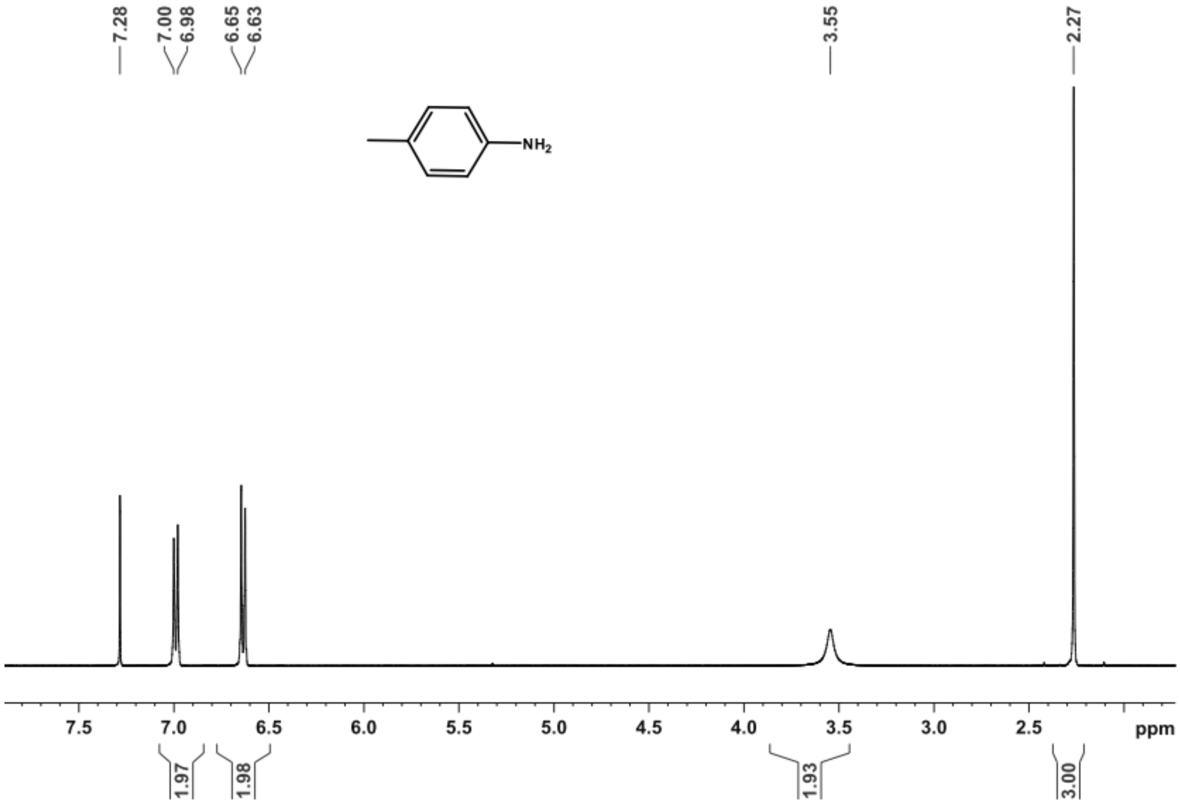
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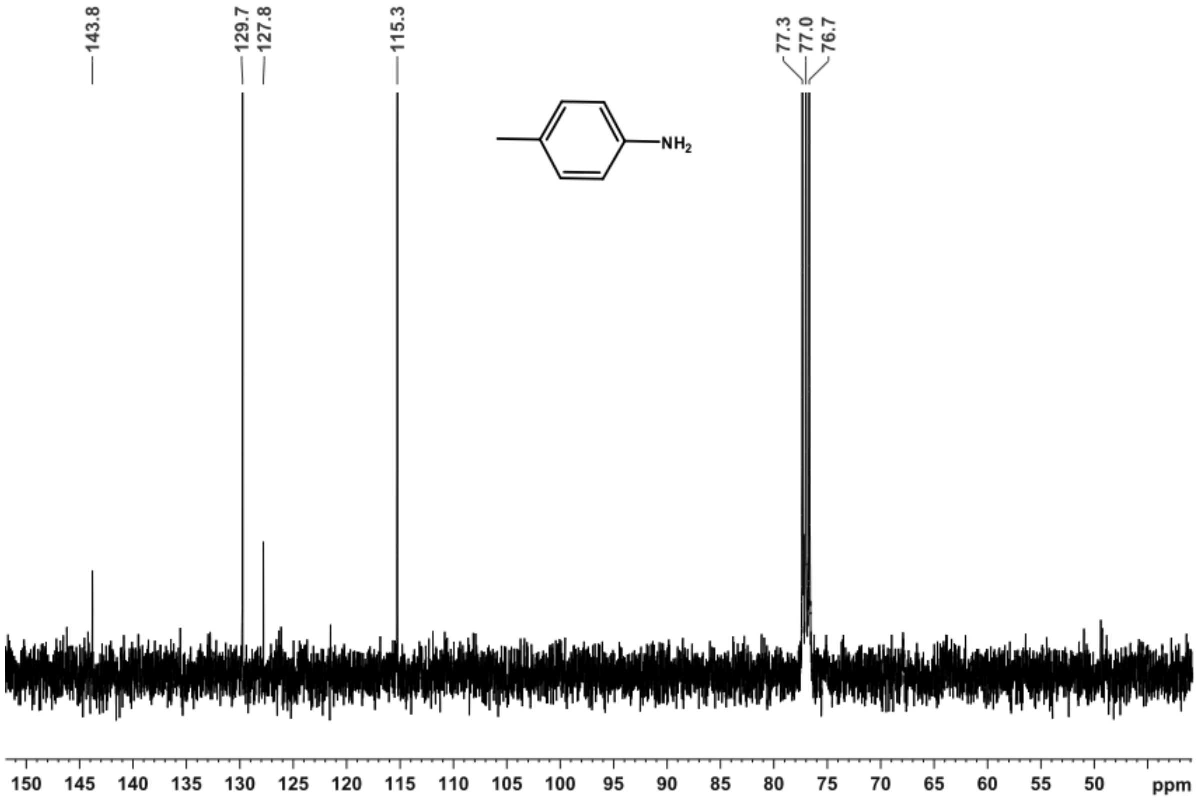
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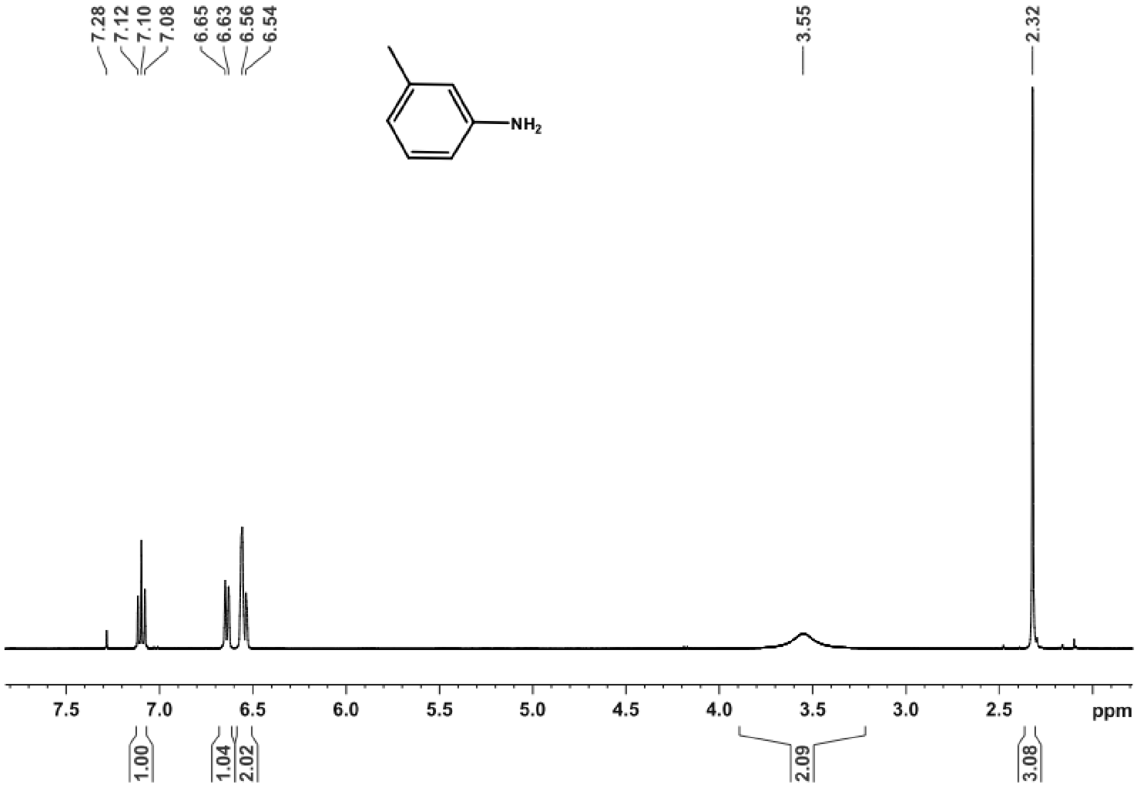
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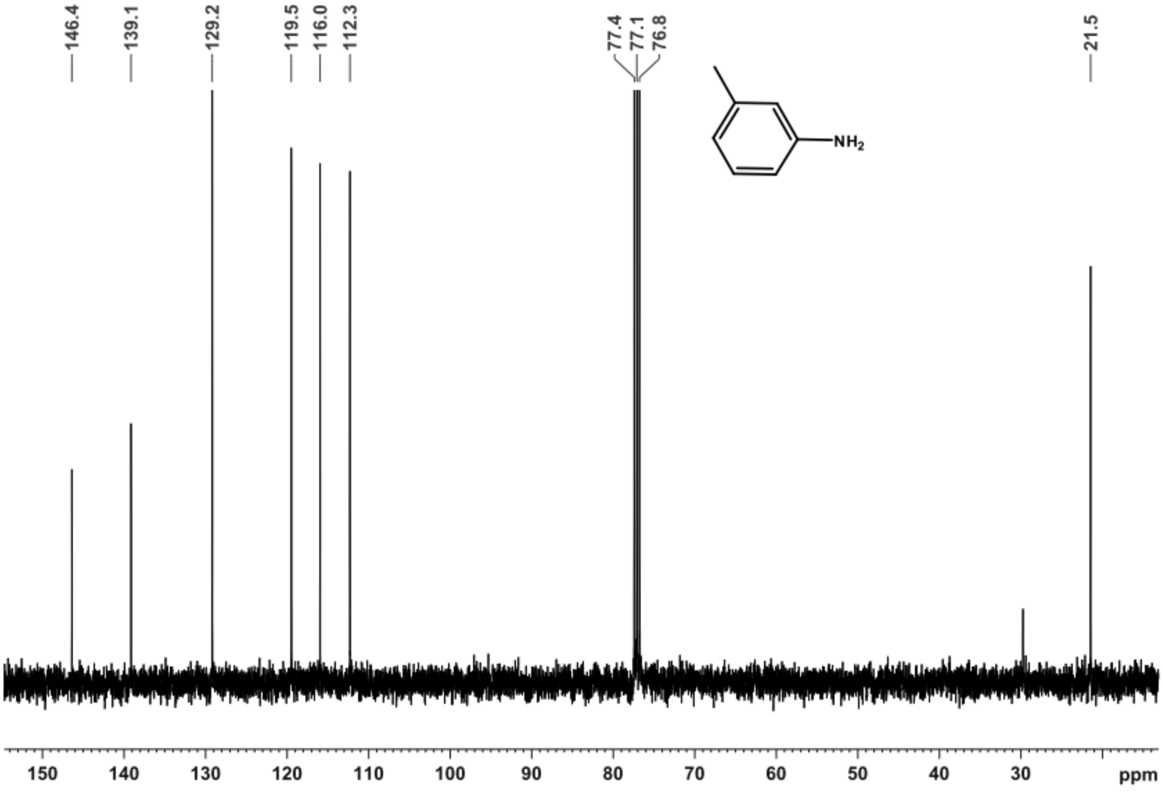
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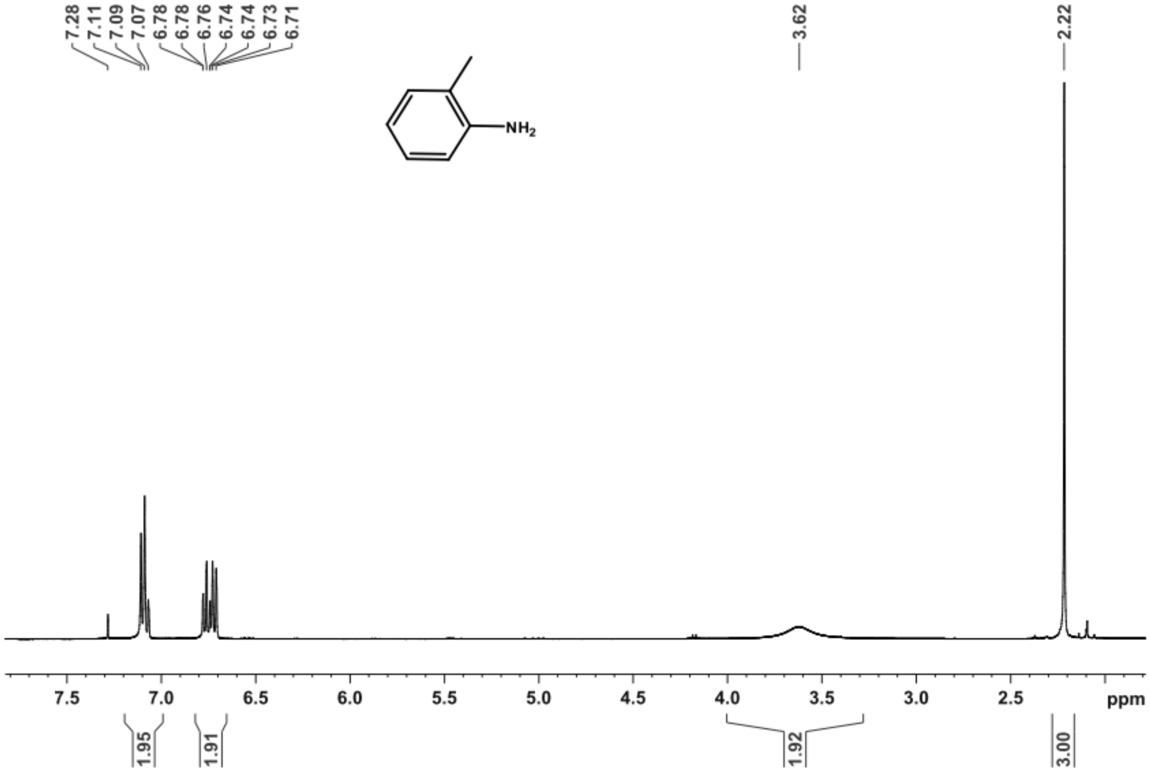
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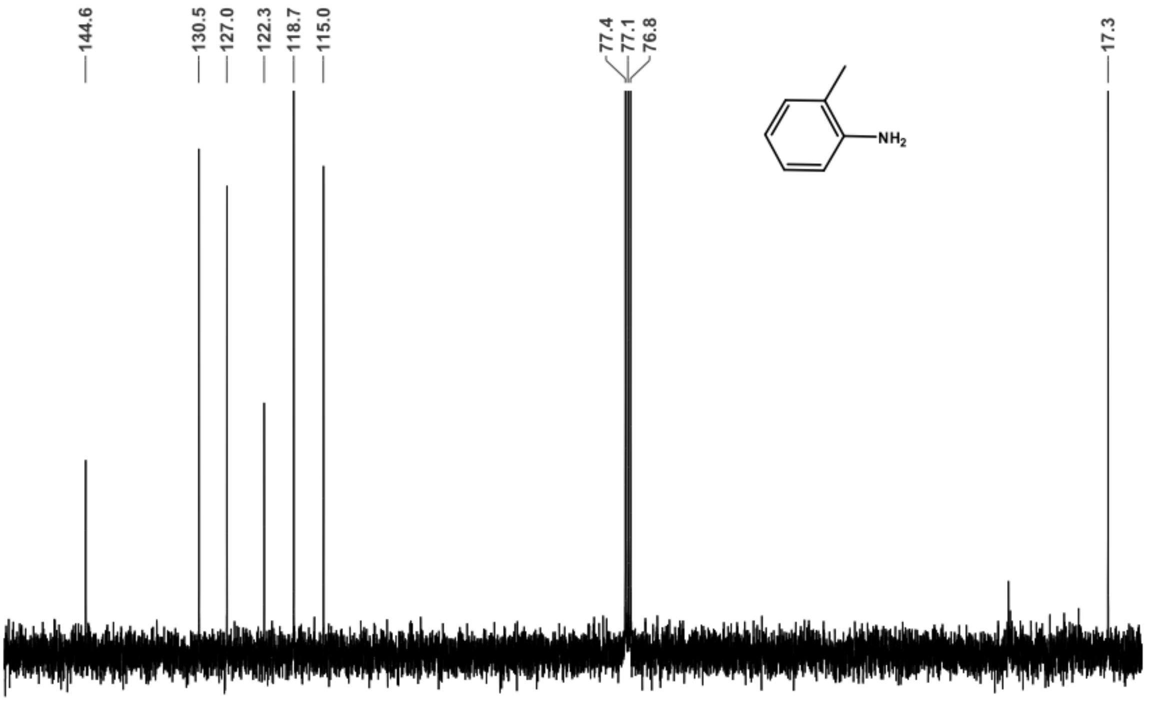
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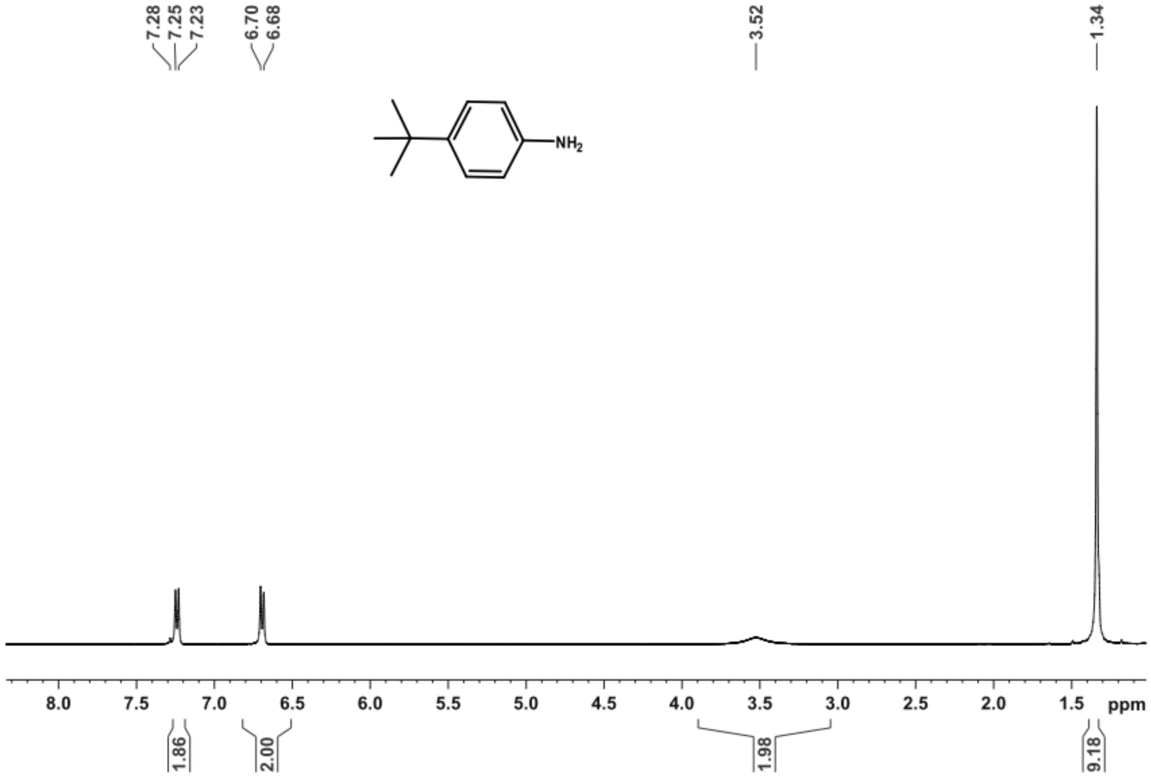
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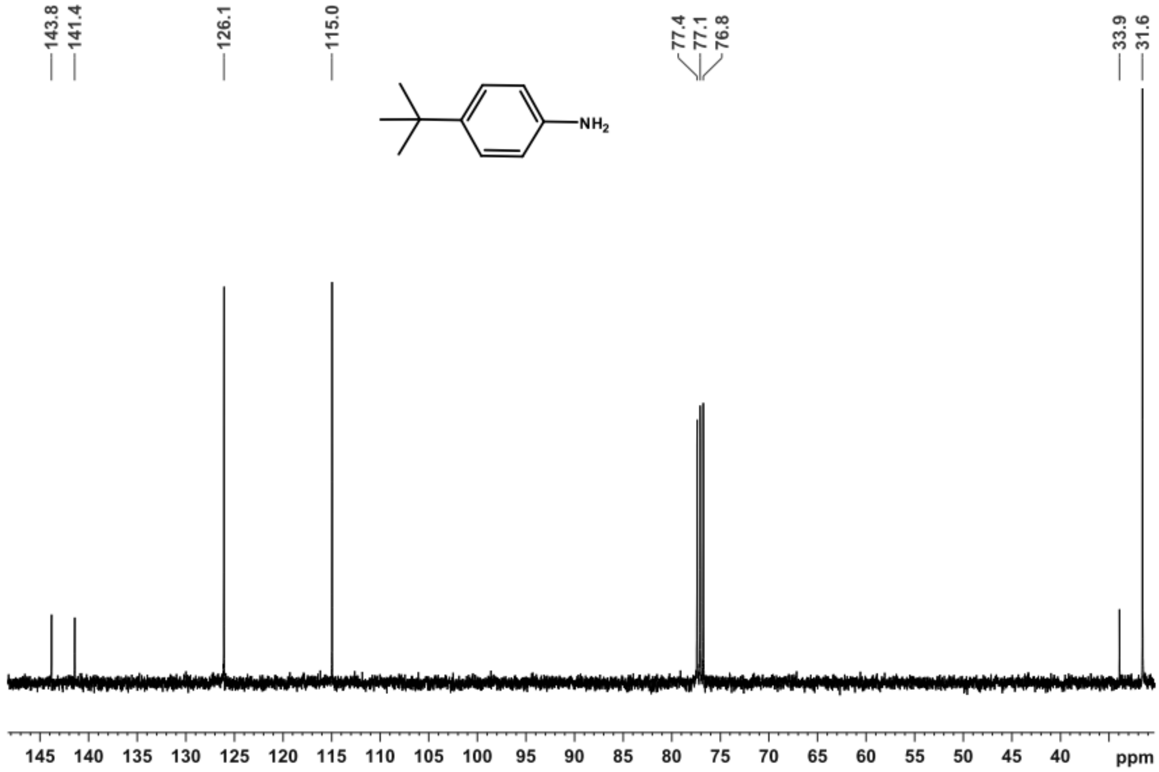
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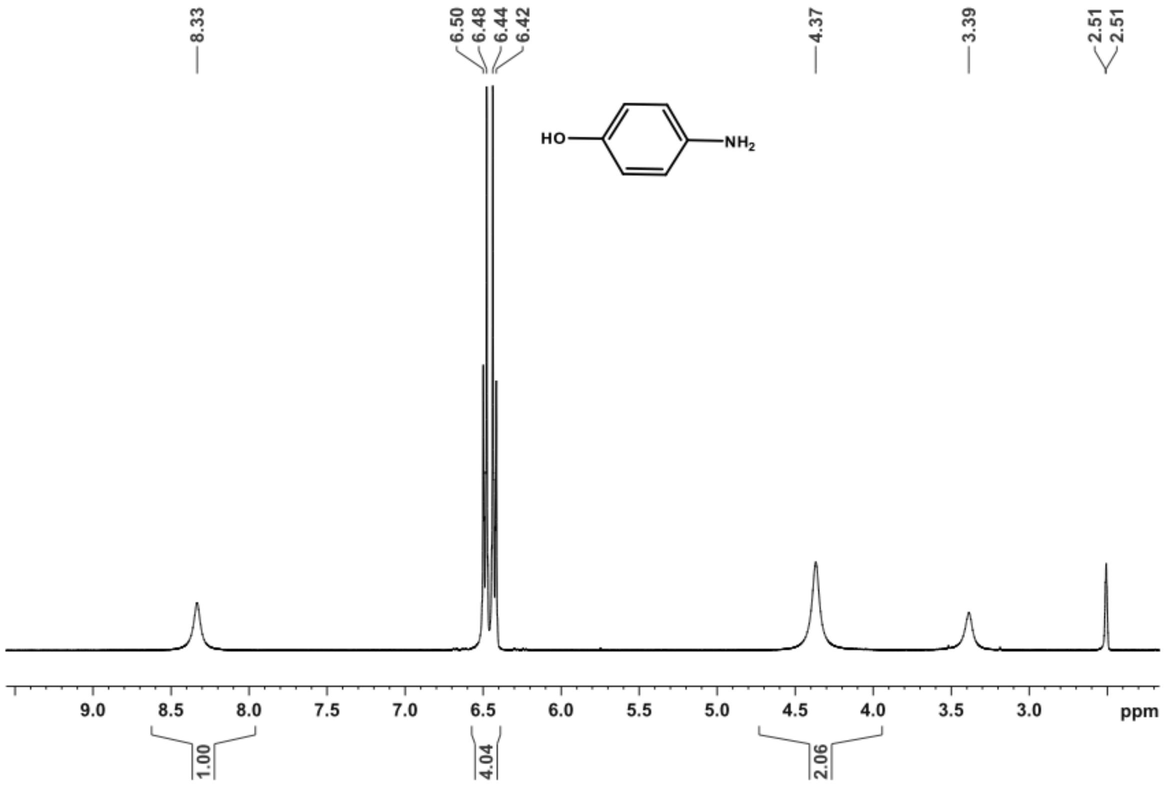
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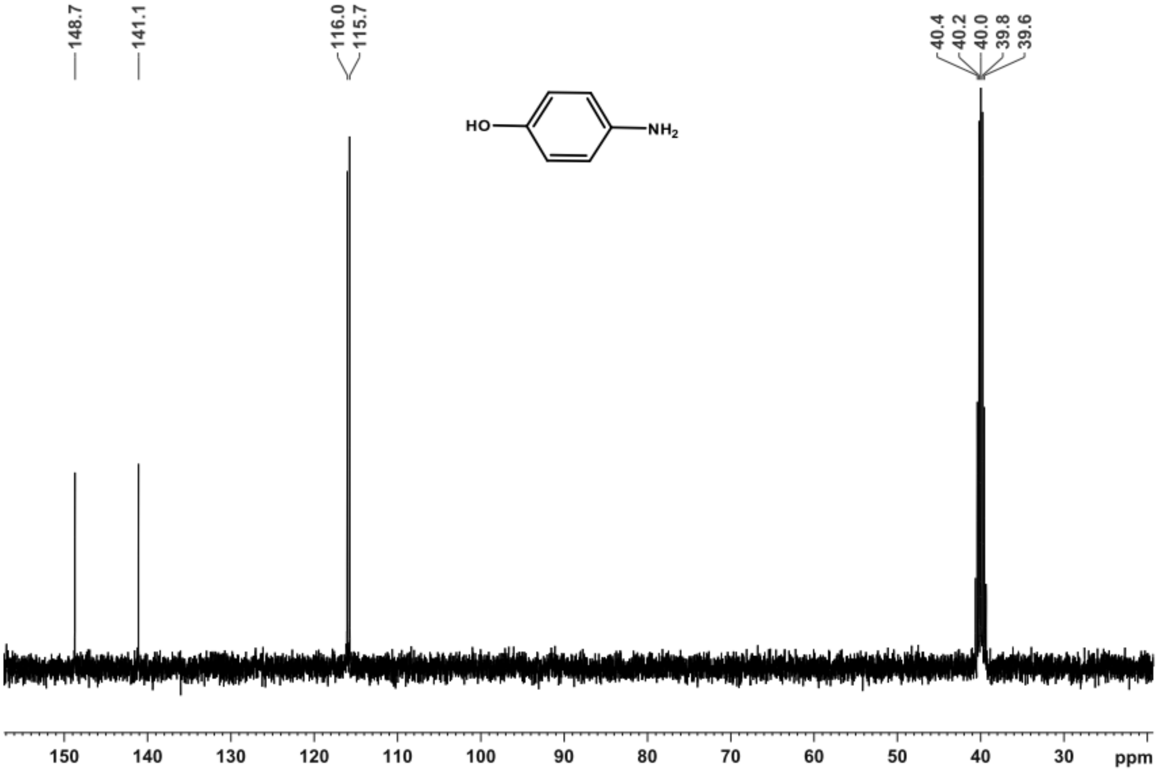
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140
130
120
110
100
90
80
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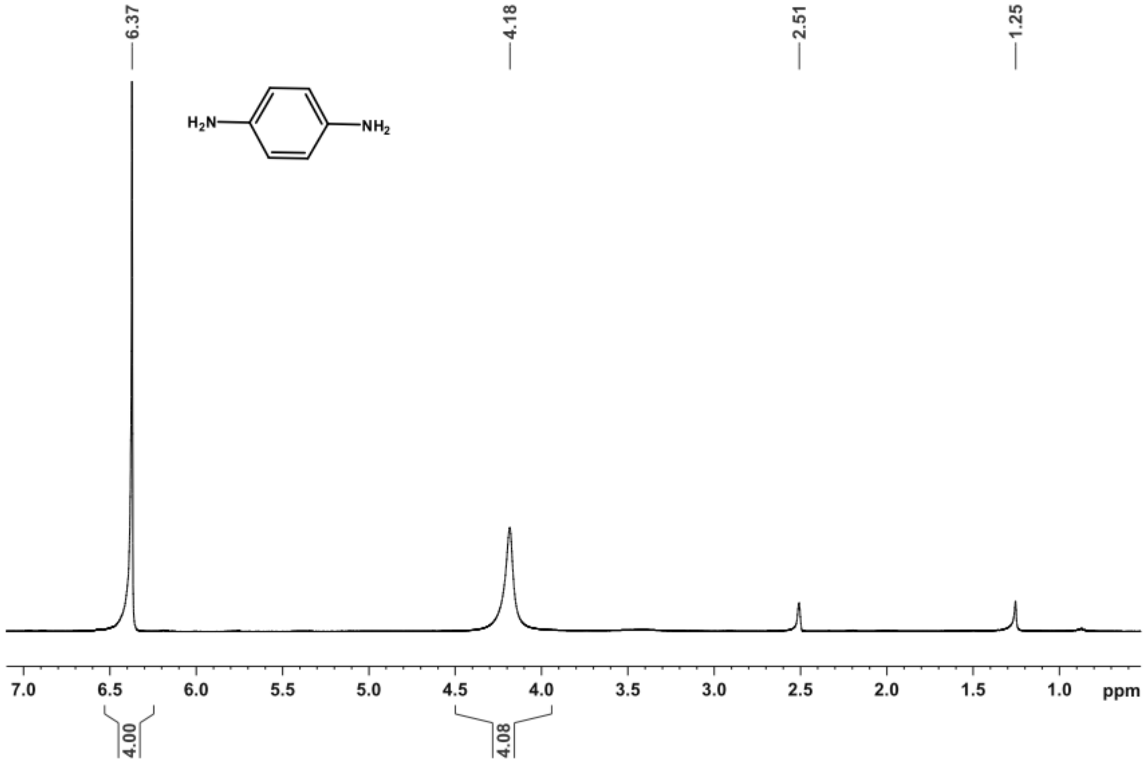
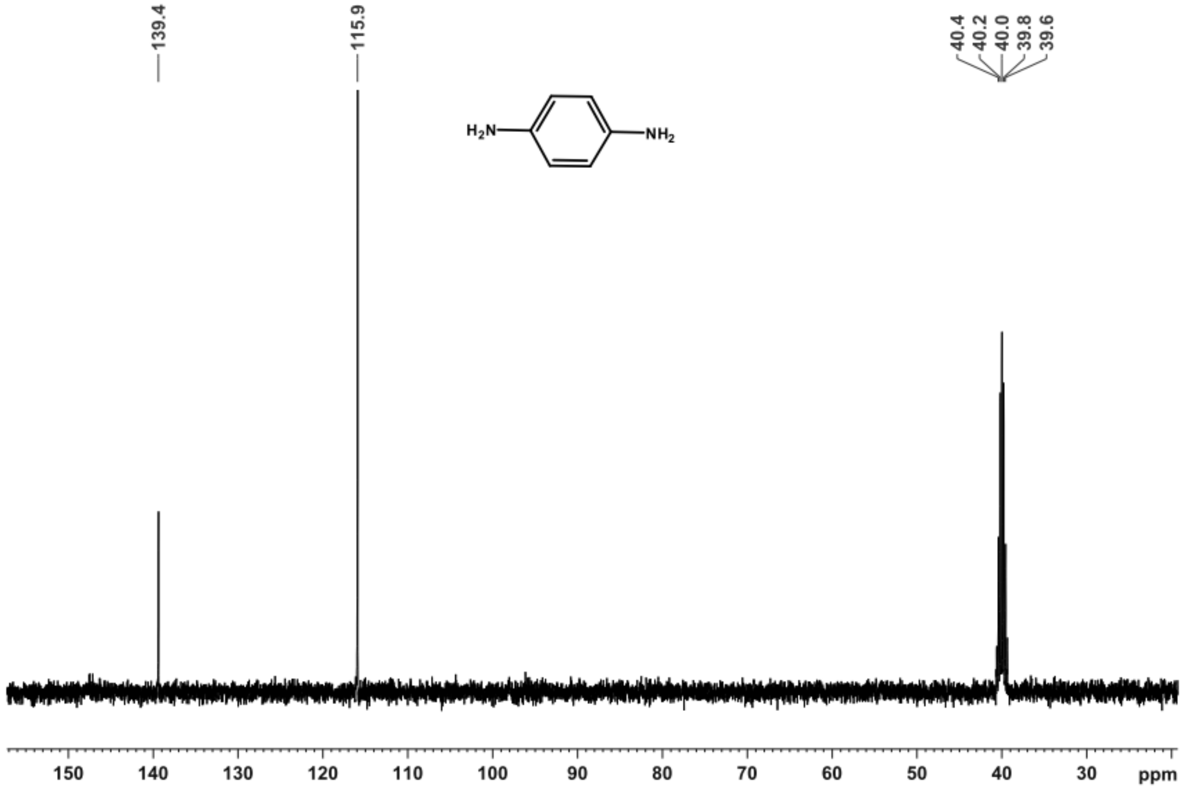
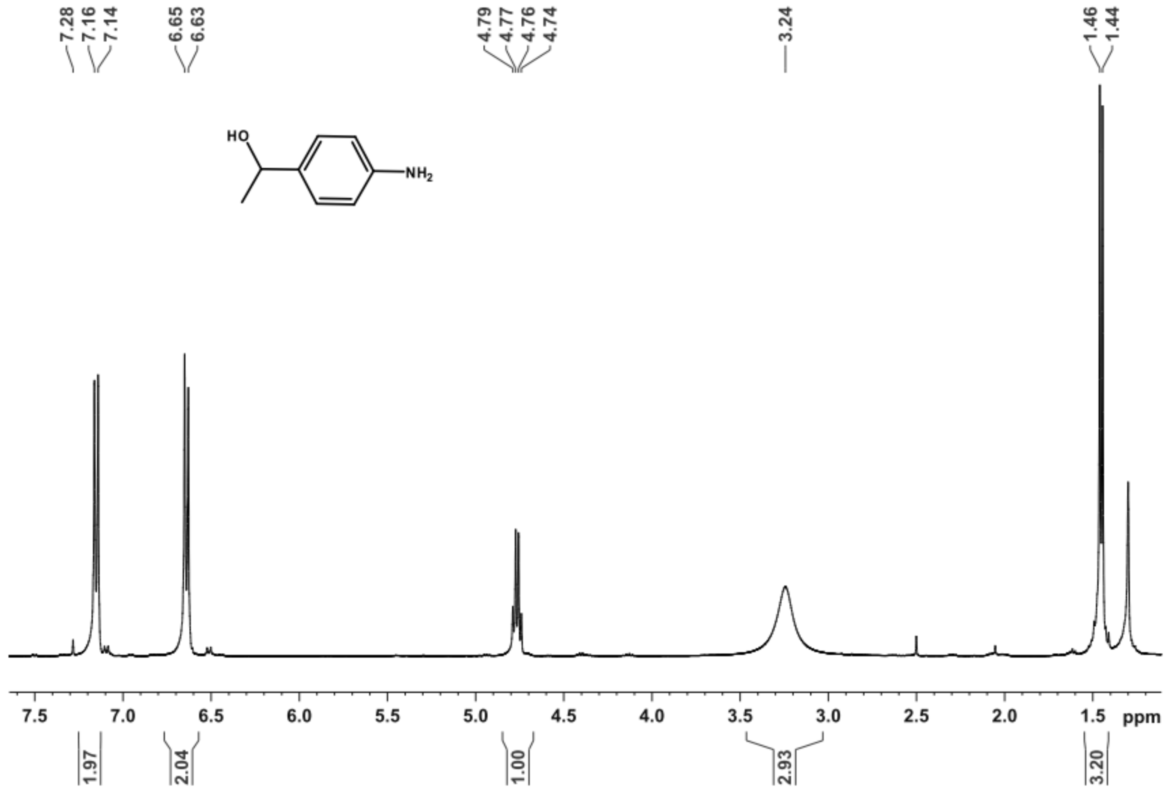
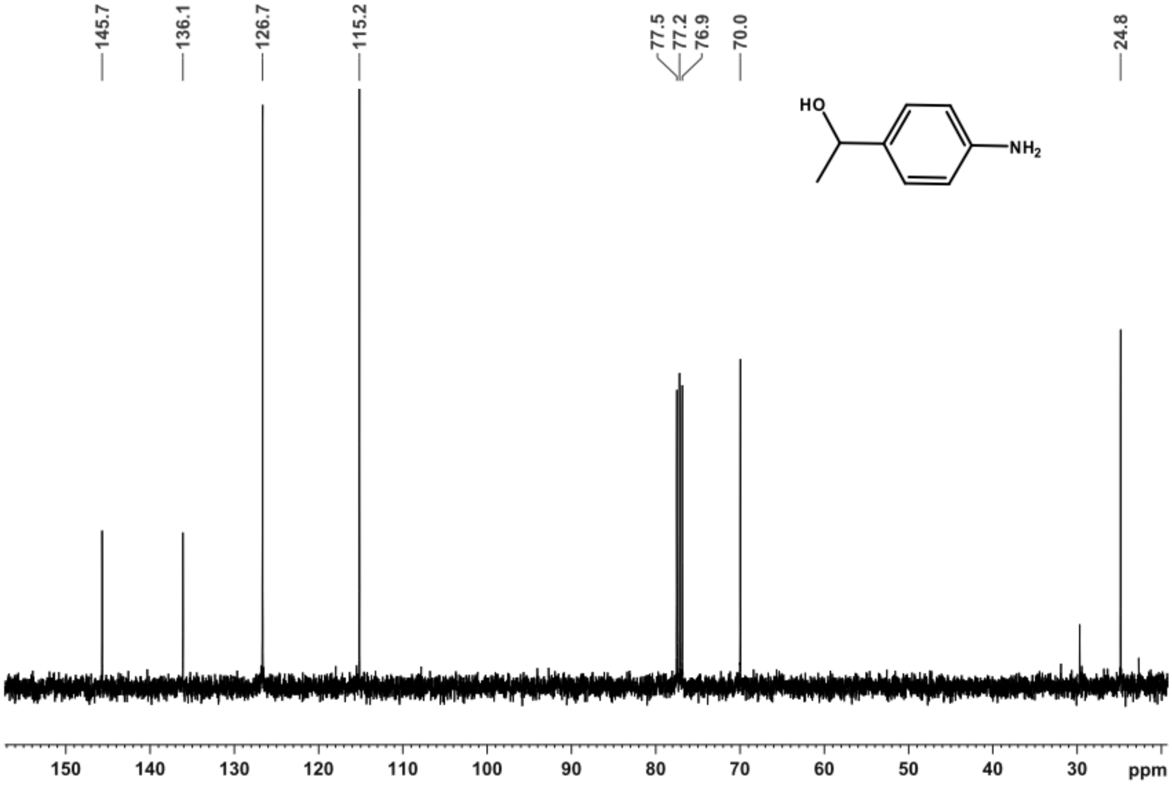
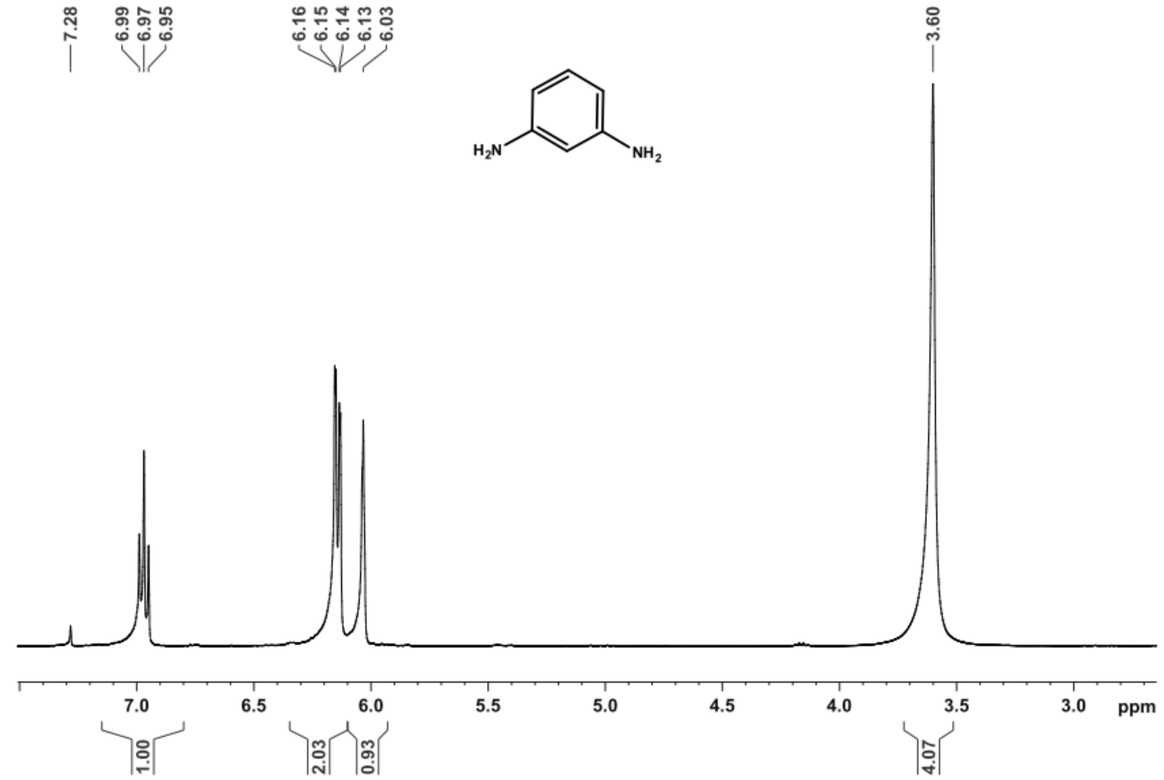
50
40
30
ppm

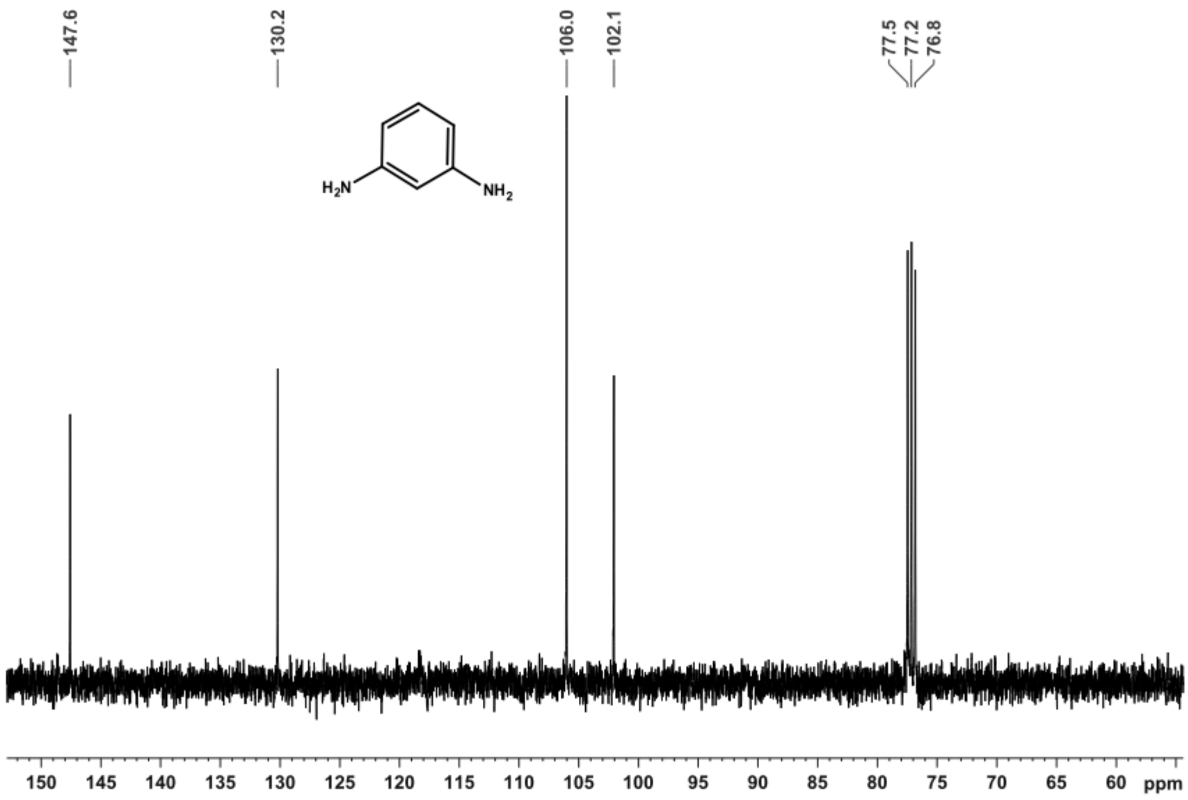

6.37
4.18
2.51
1.25
H$_2$N
NH$_2$
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.00
4.08


139.4
115.9
40.4
40.2
40.0
39.8
39.6
H$_2$N
NH$_2$
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.28
7.16
7.14
6.65
6.63
4.79
4.77
4.76
4.74
3.24
1.46
1.44
HO
NH2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.97
2.04
1.00
2.93
3.20


145.7
136.1
126.7
115.2
77.5
77.2
76.9
70.0
24.8
HO
NH2
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.28
6.99
6.97
6.95
6.16
6.15
6.14
6.13
6.03
3.60
H2N
NH2
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
2.03
0.93
4.07


147.6
130.2
106.0
102.1
77.5
77.2
76.8
H2N
NH2
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
ppm

References.

1 S. Leuthauber, D. Schwarz and H. Plenio, *Chem. Eur. J.*, 2007, **13**, 7195-7203.

2 N. S. Kushakova, A. V. Shapovalov, D. A. Rud, A. G. Vitukhnovskiy, A.V. Krotov, G. I. Timofeeva and I. A. Khotina, *Polym. Sci. Ser. B.*, 2009, **51**, 409-415.