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Supporting Information

Imidazolium-based ionic liquids functionalized reduced graphene oxide supported palladium as a reusable catalyst for Suzuki-Miyaura reactions

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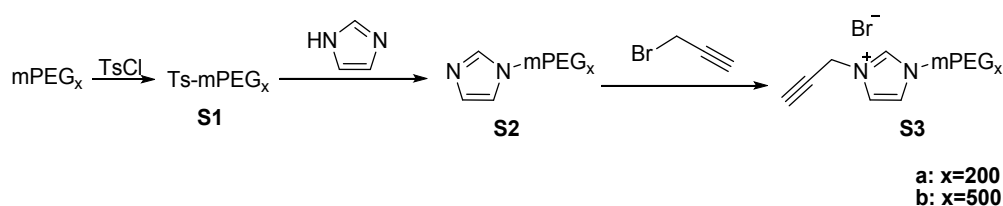
KEYWORDS: Palladium hybrid catalyst, supported ionic liquids, carbon material.

Jan 9 2018

1. General Considerations

All chemical reagents are obtained from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra are recorded on an AVANCE III Bruker spectrometer operating at 500 MHz and 125 MHz in CDCl_3 , respectively, and chemical shifts were reported in ppm relative to the center of the singlet at 7.27 ppm for CDCl_3 . GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: $30\text{ m} \times 320\ \mu\text{m} \times 0.25\ \mu\text{m}$, carrier gas: H_2 , FID detection. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120kv. Xray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al $K\alpha$ X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. Thermal gravitational analysis (TGA) was performed with a thermal analyzer (TGA/DSC2, METTLER TOLEDO) from 50 °C to 800 °C with a heating rate of 10 °C min^{-1} under N_2 atmosphere.

2. Synthesis of 1-mPEGx-3-propargyl-imidazolium bromide



2.1.1 Synthesis of the tosylation of poly(ethylene oxide) monomethyl ether, Ts-mPEG₂₀₀ (S1a).¹

Poly(ethylene oxide) monomethyl ether 200 (2 g, 10 mmol) and tosyl chloride (2.1 g, 11 mmol) were dissolved in THF. NaOH (2.5 equiv) was dissolved in water and added dropwise to mixture at 0 °C. The reaction was stirred for 30 min and left overnight to warm to room temperature. Then the product was extracted three times with CH_2Cl_2 and organic layer was dried over anhydrous Na_2SO_4 . After removing the drying agent by vacuum filtration, the solvents was evaporated under reduced pressure. A colorless liquid was obtained in 89% yield.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, $J = 7.9$ Hz, 2H), 7.35 (d, 2H), 4.16 (t, 2H), 3.77 – 3.46 (m, 14H), 3.36 (s, 3H), 2.45 (s, 3H).

2.1.2 Synthesis of the tosylation of poly(ethylene oxide) monomethyl ether, Ts-mPEG₅₀₀ (S1b).

Compound **S1b** was prepared according to the general procedure for the **S1a**. A colorless liquid was obtained in 86% yield.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, 2H), 7.35 (d, 2H), 4.14 (t, 2H), 3.75 – 3.53 (m, 42H), 3.38 (s, 4H), 2.45 (s, 3H).

2.2.1 Synthesis of the 1-mPEG₂₀₀-imidazole (S2a).¹

A mixture of **S1a** (3.5 g, 10 mmol), imidazole (0.68g, 10 mmol) and NaOH 50% (w/w) solution (0.96 g, 10 mmol) in THF (15 mL) was reflux for 1 day. After cooling to room temperature, removal of

solvents in a rotary evaporator, the product was extracted three times with CH₂Cl₂/H₂O and dried with anhydrous Na₂SO₄. After filtration, the solvent was removed in a rotary evaporator. A yellow liquid was obtained in 83% yield.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 6.82 (d, 2H), 3.93 (t, 2H), 3.67 – 3.30 (m, 14H), 3.18 (s, 3H).

2.2.2 Synthesis of the 1-mPEG₅₀₀-imidazole (S2b).

Compound **S2b** was prepared according to the general procedure for the **S2a**. A yellow liquid was obtained in 80% yield.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 (s, 1H), 6.87 (d, 2H), 3.91 (t, 2H), 3.64 – 3.28 (m, 42H), 3.18 (s, 3H).

2.3.1 Synthesis of the 1-mPEG₂₀₀-3-propargyl-imidazolium bromide (S3a).

A mixture of **S2a** (1.33 g, 5 mmol) and 3-bromopropyne (0.65 g, 5.5 mmol) in THF (10 mL) was reflux overnight. After cooling to room temperature, removal of solvents in a rotary evaporator and the product was washed with petroleum ether three times. Then the mixture was placed under vacuum to remove any remaining solvent. A viscous dark-brown liquid was obtained in 88% yields.

¹H NMR (500 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 7.89 – 7.82 (m, 1H), 7.66-7.61 (m, 1H), 5.50 – 5.32 (m, 2H), 4.56 (m, 2H), 3.89 (m, 2H), 3.82 – 3.45 (m, 12H), 3.34 (s, 3H), 2.78 (s, 1H).

2.3.1 Synthesis of the 1-mPEG₅₀₀-3-propargyl-imidazolium bromide (S3b).

Compound **S3b** was prepared according to the general procedure for the **S3a**. A dark-brown liquid was obtained in 83% yield.

¹H NMR (500 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 7.87 – 7.78 (m, 1H), 7.62 (t, 1H), 5.44 – 5.27 (m, 2H), 4.59 (m, 2H), 3.87 (t, 2H), 3.82 – 3.45 (m, 40H), 3.30 (s, 3H), 2.76 (s, 1H).

3. Preparation of RGO-IL-Pd catalyst

3.1 Preparation of reduced graphene oxide (RGO)

Graphene oxide powders were reduced by ascorbic acid to obtain reduced graphene oxide (RGO). 1 g of GO and 1 g of ascorbic acid were placed in a 250 mL flask and then 100 mL of water were added. Then the mixture was refluxed under agitation 24h after dispersed by ultrasonication. The product was filtered, washed with de-ionized water and dried at 50 °C for 24 h in an oven.

3.2 Preparation of RGO-IL

RGO (200 mg) and 2-chloroethyl isocyanate (1.06 g, 10 mmol) were added to DMF (50 mL) in a 100 mL round-bottom flask. The mixture was stirred at room temperature for 24 h under Ar. Then the product was filtered and washed several times with DCM (50 mL), and dried at 50 °C in an oven. After that, the powders (200 mg) were dispersed in DMSO (100 mL) in a 250 mL round-bottom flask. The mixture was stirred at 50 °C for 48 h after sodium azide (1.56 g, 24 mmol) added. The product was filtered and washed with water and DCM, and dried at 50 °C in an oven. Finally, the prepared powders (100 mg) was dispersed in a mixture of H₂O/EtOH (2:1, 3 mL) by ultrasonication. Sodium ascorbate (60 mg, 0.32 mmol), CuSO₄ (20 mg, 0.14 mmol) and **S3** (1 mmol) were added to

the solution. The mixture was stirred at room temperature for 3 days. The product was filtered and washed with water and DCM, and dried at 50 °C in an oven.

3.2 Preparation of RGO-IL-Pd

RGO-IL (100 mg), KO^tBu (0.7 mmol) and Pd(OAc)₂ (0.7 mmol) was added to a flask under Ar. A mixture of THF/DMF (1:1, 3 mL) was added. It was stirred at room temperature for 48 h after dispersed by ultrasonication. Then the mixture was filtered and washed by DMF, H₂O and EtOH and dried at 50 °C in an oven. (**1a**: 1.6 mmol/g Pd and **1b**: 0.75 mmol/g Pd by ICP-MS)

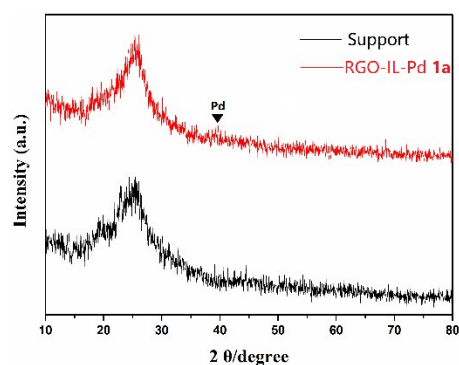
4. General procedure for RGO-IL-Pd catalyzed Suzuki-Miyaura reactions.

0.5 mmol aryl halide, 0.5 mol% catalyst (based on Pd), 0.65 mmol aryl boronic acid, 1 mmol K₂CO₃ and 2 mL solvent (EtOH:H₂O=1:1) were added into a tube with a magnetic bar. And the reaction mixture was stirred at room temperature in air. The product was extracted with addition of 3 mL *n*-hexane. The organic layer was dried with Na₂SO₄ and the solvent was then removed under reduced pressure after filtered. Pure products were obtained by column chromatography on silica using the *n*-hexane and ethyl acetate mixture as an eluent. All the products were characterized by ¹H NMR and ¹³C NMR.

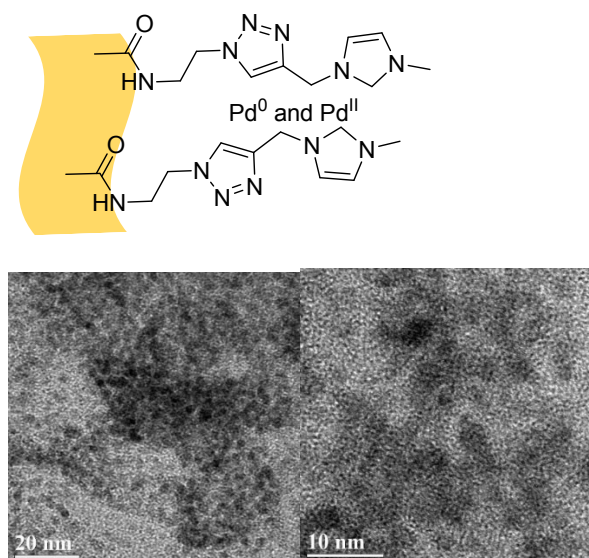
5. General procedure for the reusability test of RGO-IL-Pd catalyzed Suzuki-Miyaura reactions.

0.5 mmol aryl halide, 0.5 mol% catalyst (based on Pd), 0.65 mmol aryl boronic acid, 1 mmol K₂CO₃ and 2 mL solvent (EtOH:H₂O=1:1) were added into a tube with a magnetic bar. And the reaction mixture was stirred at room temperature in air. After completion of the reaction, the product was extracted with *n*-hexane and the aqueous phase containing the catalyst was loaded with the reactants, base and EtOH for the next run. The catalyst in water could be reused for 5 subsequent runs without loss of activity.

6. Figure S1. XRD patterns of support and RGO-IL-Pd 1a

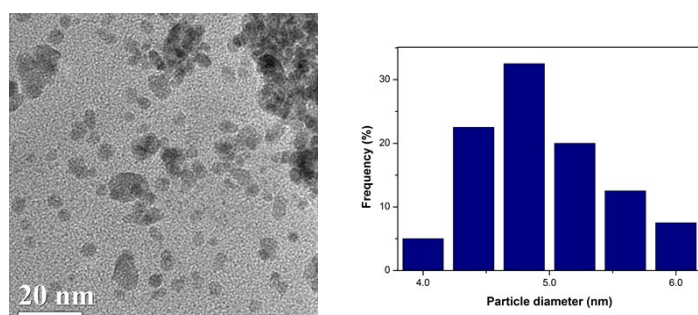


7. Figure S2. The structure and TEM images of RGO-IL-Pd 1c



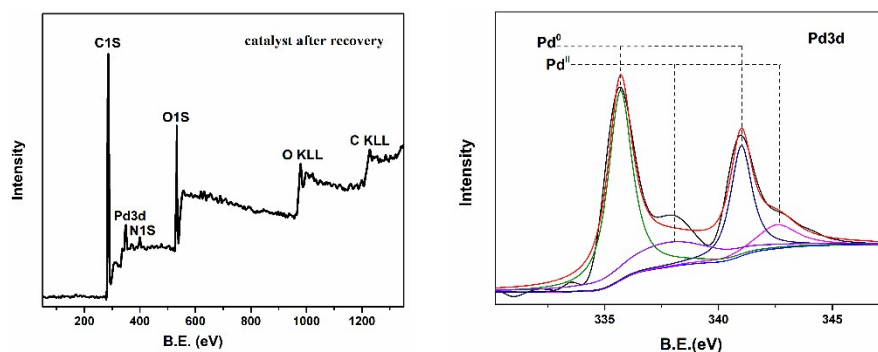
8. Table S1. Comparison of efficiency of various heterogeneous palladium catalysts in Suzuki reaction

9. Figure S3. TEM images and size distribution of RGO-IL-Pd 1a after the five runs

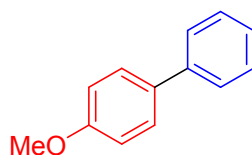


Catalyst	Conditions	Time (h)	Yield (%)	Ref.
RGO-IL-Pd 1a (0.5 mol%)	K ₂ CO ₃ , EtOH/H ₂ O (1:1), r.t.	3	82-98	This work
NHC-Pd/GO-IL (0.1-0.2 mol%)	K ₂ CO ₃ , EtOH/H ₂ O (1:1), 60-90 °C	2.5-12	42-98	23 (a)
GO-NHC-Pd ²⁺ (0.25 mol%)	K ₂ CO ₃ , EtOH/H ₂ O (1:1), 80-90 °C	3-24	83-96	23 (b)
GO-NHC-Pd (1 mol%)	Cs ₂ CO ₃ , DMF/H ₂ O (1:1), 50-80 °C	1	81-93	23 (c)
NHC-Pd/SBA-16-IL (0.01 mol%)	K ₃ PO ₄ , EtOH/H ₂ O (1:1), 50 °C	5-10	87-99	23 (d)

10. Figure S4. XPS spectrum of catalyst after recovery

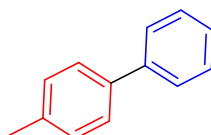


11. Characterization data of the products



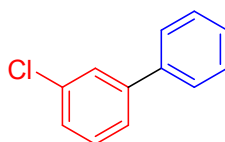
4-methoxybiphenyl

¹H NMR (500 MHz, Chloroform-*d*) δ 7.58 (ddd, $J = 11.4, 7.8, 1.6$ Hz, 4H), 7.45 (td, $J = 7.7, 1.6$ Hz, 2H), 7.34 (td, $J = 7.2, 1.4$ Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 3.87 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.4, 55.5.



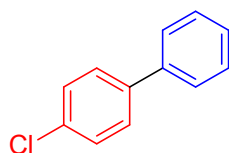
4-methylbiphenyl

¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.43 – 7.38 (m, 2H), 7.34 (t, $J = 7.8$ Hz, 2H), 7.24 (td, $J = 7.2, 1.3$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 140.2, 137.4, 136.1, 128.5, 127.8, 126.0, 20.2.



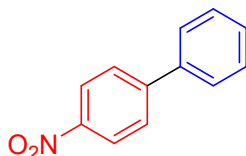
3-chlorobiphenyl

¹H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 3H), 7.49 (dtd, $J = 7.9, 6.1, 1.5$ Hz, 3H), 7.43 – 7.34 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.2, 138.9, 133.7, 129.1, 128.0, 126.9, 126.4, 126.2, 124.4.



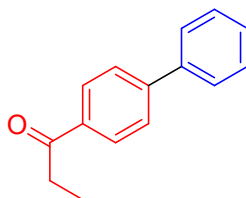
4-chlorobiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.52 – 7.39 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.1, 138.7, 132.5, 128.0, 127.5, 126.7, 126.1.



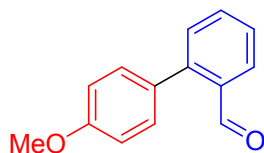
4-nitrobiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 8.34 – 8.26 (m, 2H), 7.77 – 7.71 (m, 2H), 7.67 – 7.60 (m, 2H), 7.53 – 7.42 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.7, 146.1, 137.8, 128.2, 128.0, 126.8, 126.4, 123.2.



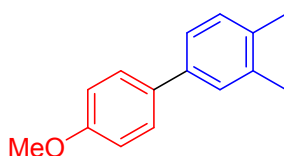
1-(biphenyl-4-yl)propan-1-one

^1H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 2H), 7.71 – 7.66 (m, 2H), 7.65 – 7.61 (m, 2H), 7.47 (dd, J = 8.4, 6.8 Hz, 2H), 7.43 – 7.38 (m, 1H), 3.04 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.4, 144.6, 139.0, 134.7, 128.0, 127.6, 127.2, 126.3, 126.2, 30.9, 7.4.



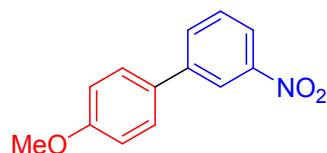
4'-methoxybiphenyl-2-carbaldehyde

^1H NMR (500 MHz, Chloroform-*d*) δ 9.99 (d, J = 0.8 Hz, 1H), 8.00 (dd, J = 7.7, 1.4 Hz, 1H), 7.62 (td, J = 7.6, 1.5 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.34 – 7.27 (m, 2H), 7.04 – 6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 192.8, 159.8, 145.8, 133.9, 133.6, 131.4, 130.9, 130.2, 127.7, 127.5, 114.1, 55.5.



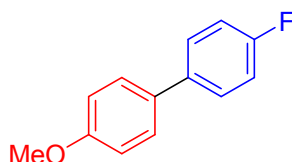
4'-methoxy-3,4-dimethylbiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 7.56 (dd, J = 8.6, 1.6 Hz, 2H), 7.39 (s, 1H), 7.34 (dd, J = 7.7, 1.8 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.01 (dd, J = 8.6, 1.6 Hz, 2H), 3.88 (d, J = 1.4 Hz, 3H), 2.36 (d, J = 13.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 138.6, 137.0, 135.2, 134.0, 130.2, 128.2, 128.1, 124.3, 114.3, 55.5, 20.1, 19.5.



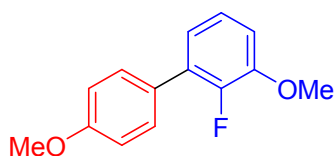
4'-methoxy-3-nitrobiphenyl

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.41 (t, $J = 2.1$ Hz, 1H), 8.14 (dt, $J = 8.2, 1.2$ Hz, 1H), 7.90 – 7.84 (m, 1H), 7.61 – 7.54 (m, 3H), 7.06 – 6.98 (m, 2H), 3.87 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.2, 148.9, 142.6, 132.6, 131.2, 129.7, 128.4, 121.5, 114.7, 55.5.



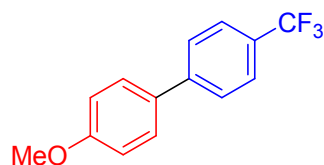
4-fluoro-4'-methoxybiphenyl

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 4H), 7.13 – 7.07 (m, 2H), 7.00 – 6.95 (m, 2H), 3.85 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 162.22 (d, $J = 245.0$ Hz), 159.25, 137.10, 132.97, 128.33 (d, $J = 8.0$ Hz), 128.15, 115.64 (d, $J = 21.3$ Hz), 114.38. $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ -116.7.



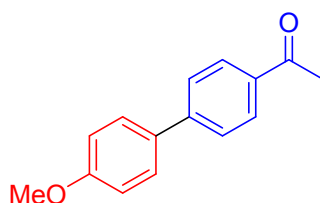
2-fluoro-3,4'-dimethoxybiphenyl

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.10 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.01 – 6.97 (m, 3H), 6.93 (dd, $J = 8.0, 1.6$ Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 159.40, 150.73, 148.60 (d, $J = 44.5$ Hz), 130.31, 129.63, 128.14, 123.92, 122.02, 114.03, 111.92, 56.51, 55.43.



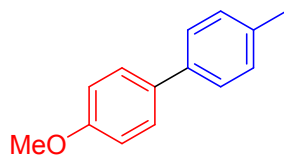
4-methoxy-4'-(trifluoromethyl)biphenyl

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 4H), 7.57 – 7.52 (m, 2H), 7.02 – 6.99 (m, 2H), 3.87 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.0, 144.4, 132.3, 128.5, 127.0, 125.8, 114.6, 55.5. $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ -141.4.



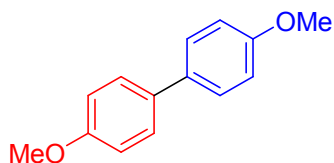
1-(4'-methoxybiphenyl-4-yl)ethanone

^1H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 7.97 (m, 2H), 7.67 – 7.62 (m, 2H), 7.61 – 7.55 (m, 2H), 7.03 – 6.98 (m, 2H), 3.86 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.8, 160.1, 145.5, 135.4, 132.4, 129.1, 128.5, 126.7, 114.5, 55.5, 26.7.



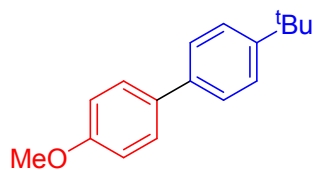
4-methoxy-4'-methylbiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.49 – 7.45 (m, 2H), 7.24 (d, $J = 7.6$ Hz, 2H), 7.01 – 6.96 (m, 2H), 3.86 (d, $J = 1.3$ Hz, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 138.1, 136.5, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.2.



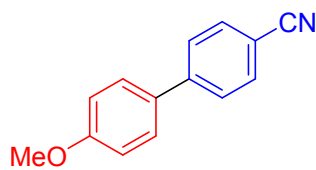
4,4'-dimethoxybiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 4H), 6.98 – 6.94 (m, 4H), 3.84 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.8, 133.6, 127.9, 114.3, 55.5.



4-*tert*-butyl-4'-methoxybiphenyl

^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 4H), 7.49 – 7.45 (m, 2H), 6.99 (dd, $J = 8.6, 1.9$ Hz, 2H), 3.86 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 149.7, 138.1, 133.8, 128.1, 126.5, 125.8, 114.3, 55.5, 34.6, 31.5.



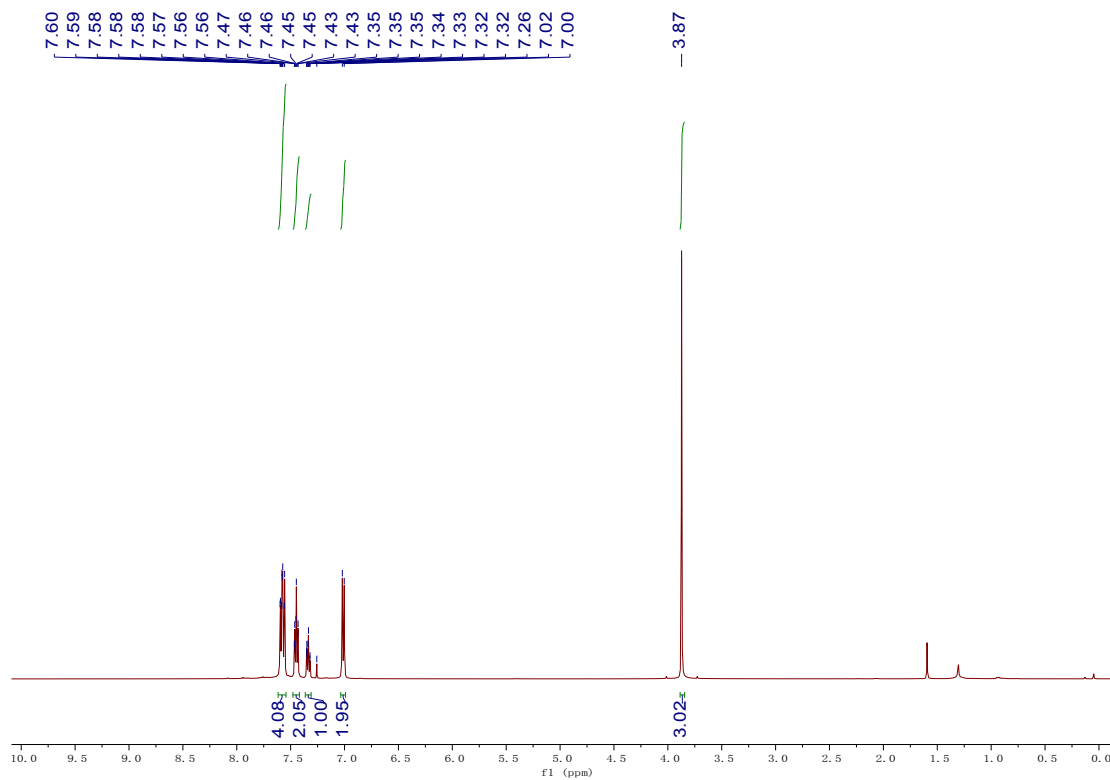
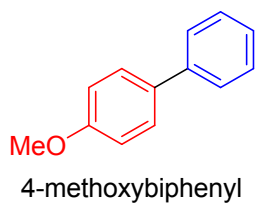
4'-methoxybiphenyl-4-carbonitrile

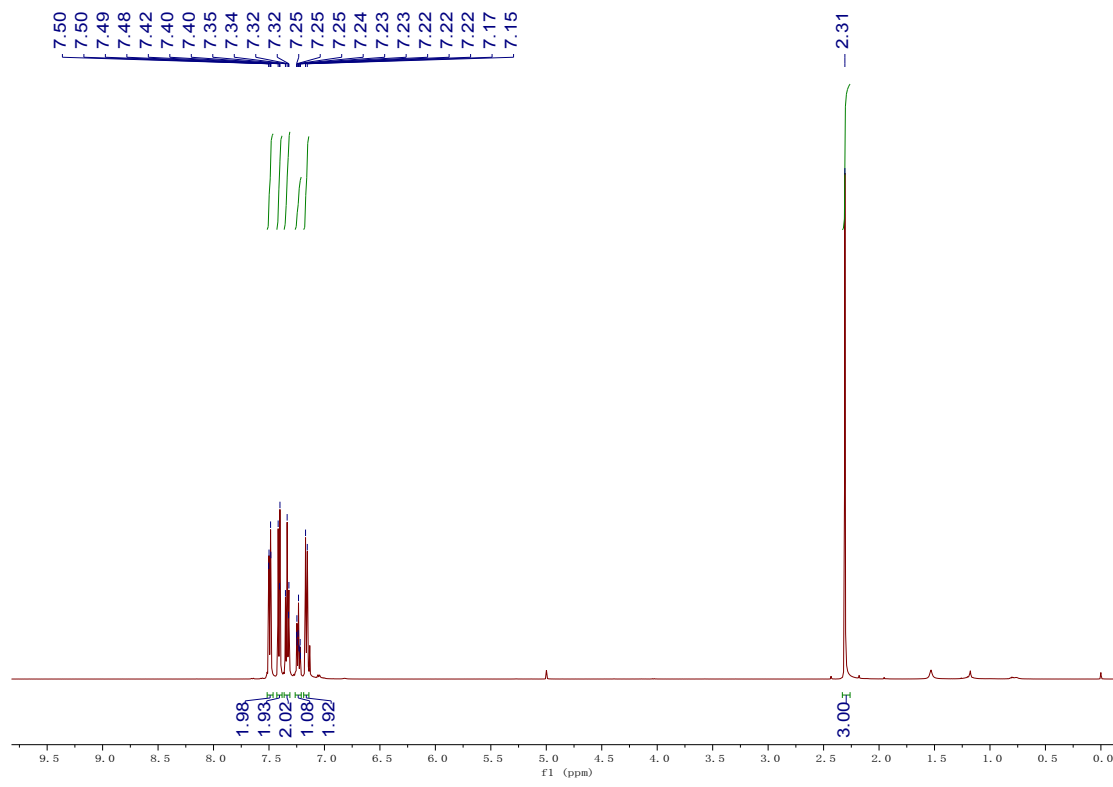
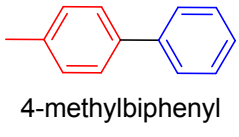
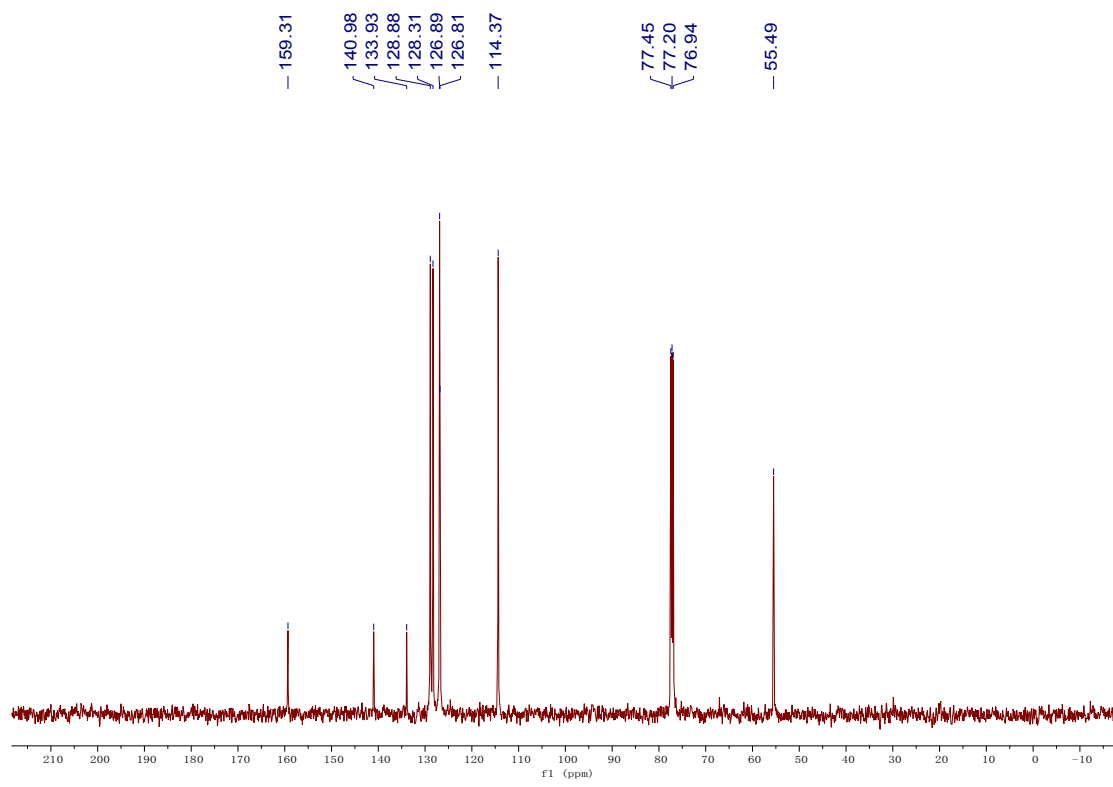
^1H NMR (500 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 4H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 160.3, 145.4, 132.7, 131.6, 128.5, 127.2, 119.2, 114.7, 110.2, 55.5.

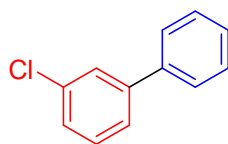
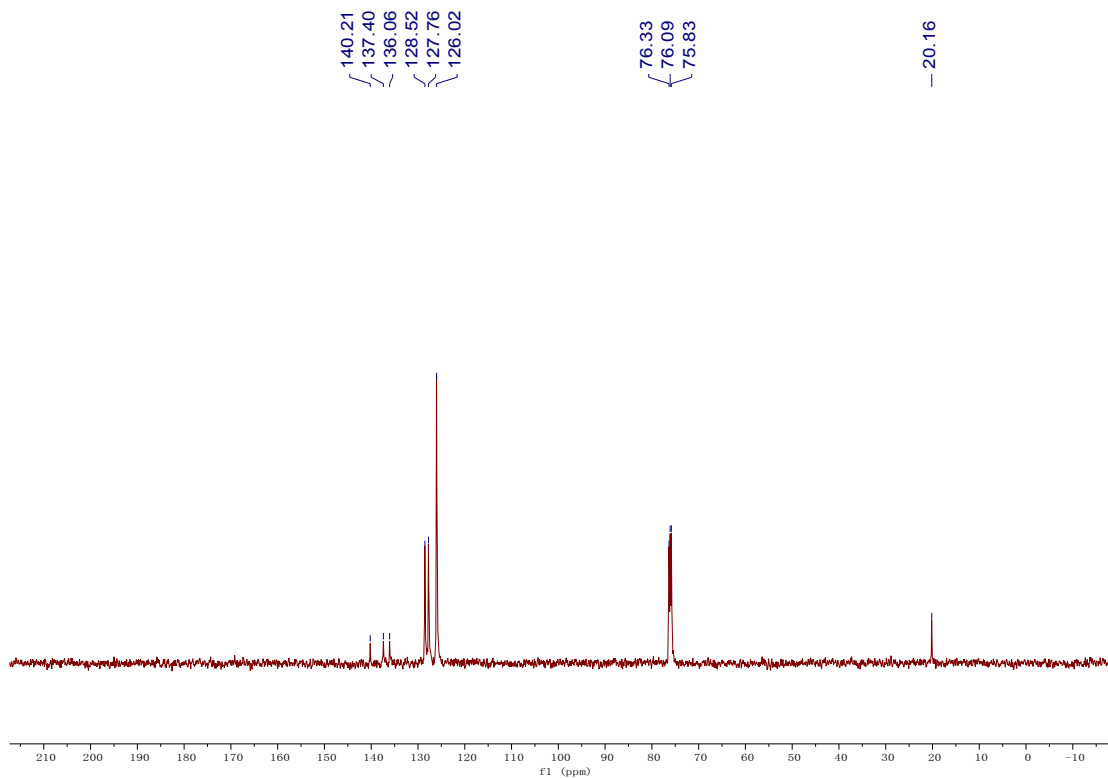
12. Reference

1. Z. Jia, W. Yuan, C. Sheng, H. Zhao, H. Hu and G. L. Baker, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1339-1350.

13. NMR spectra of the products

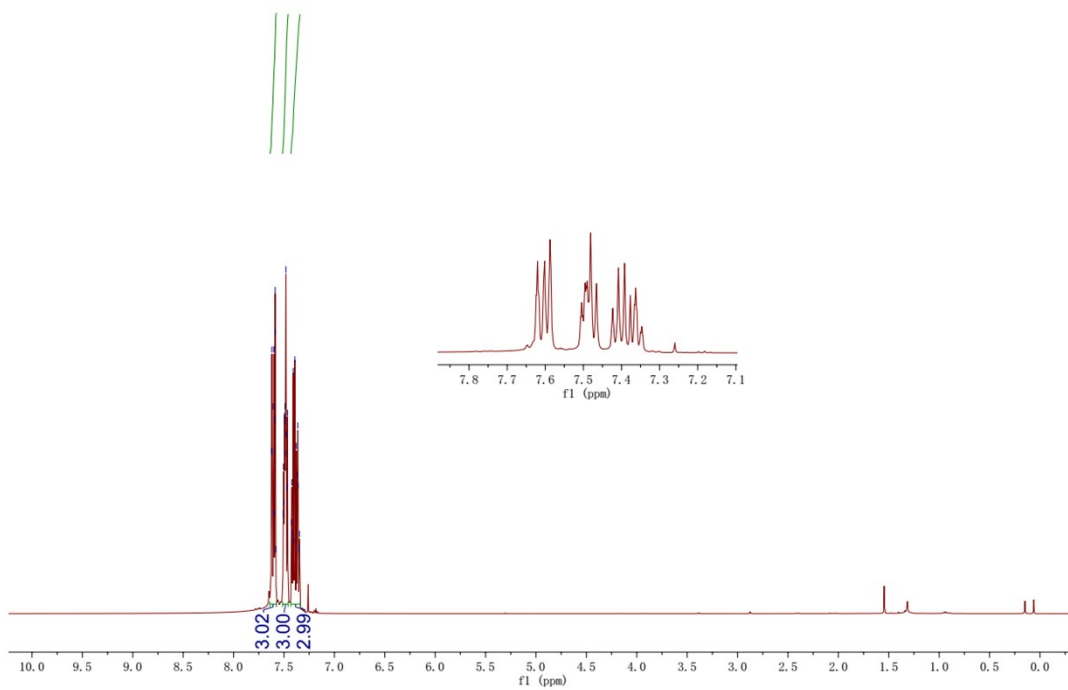


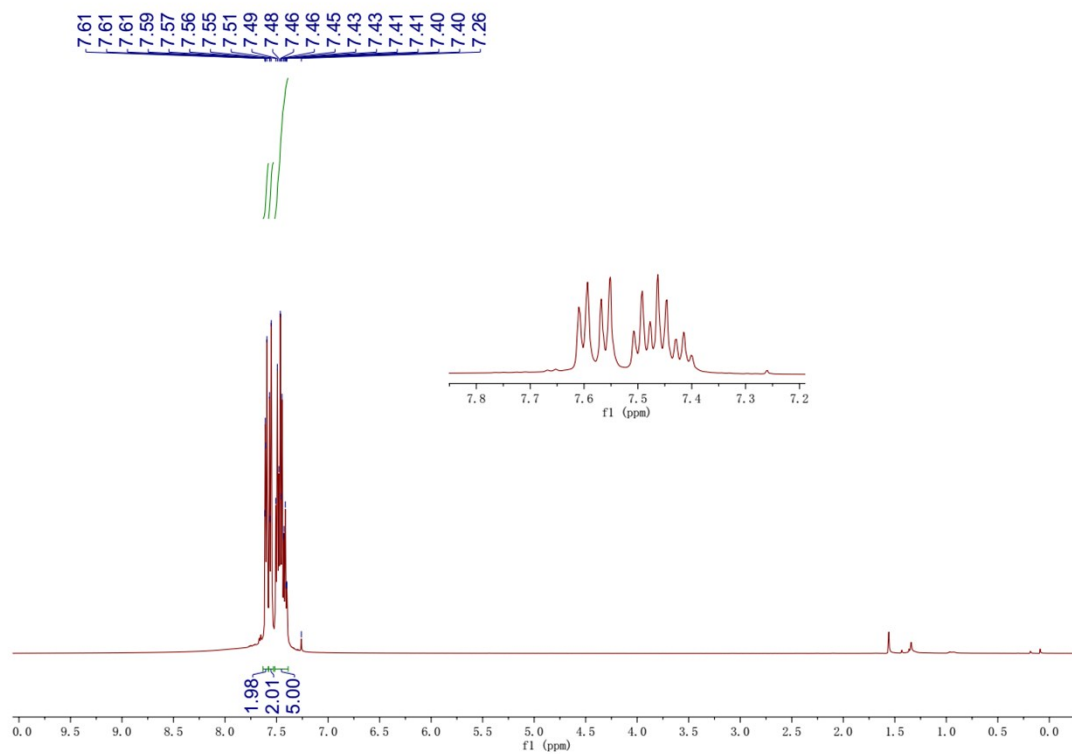
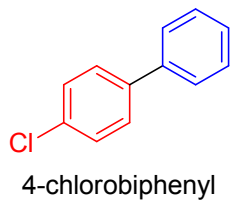
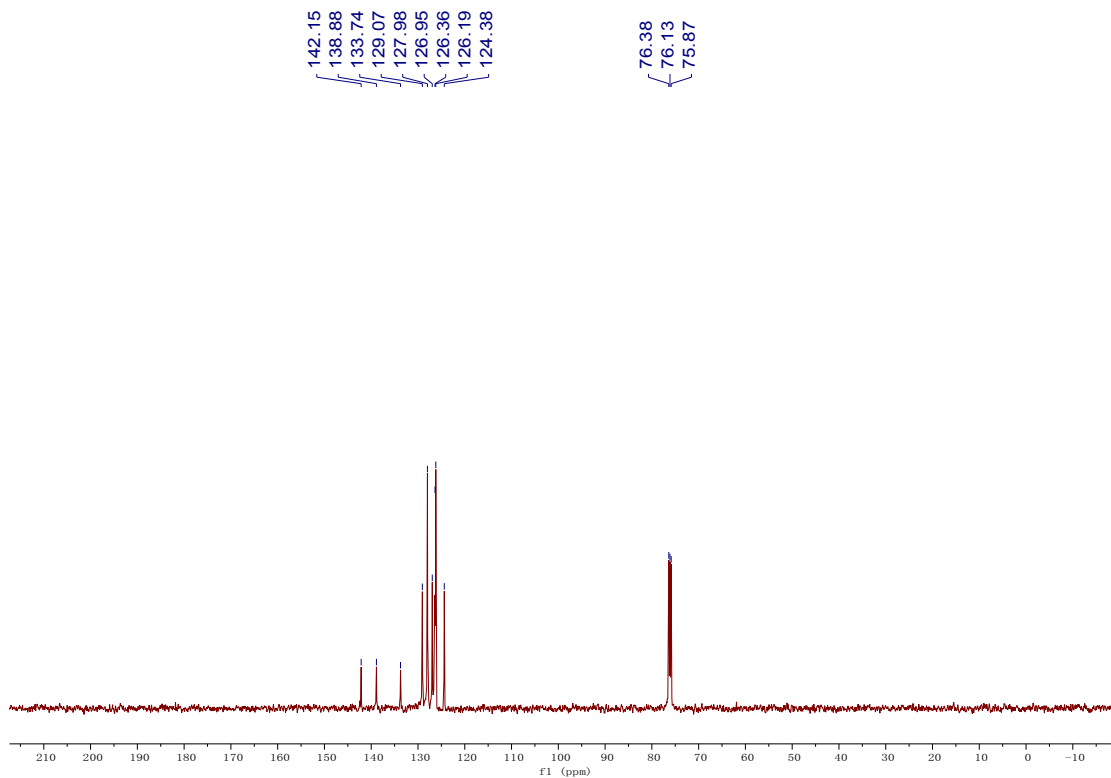


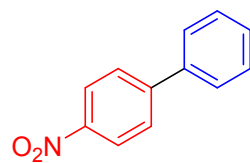
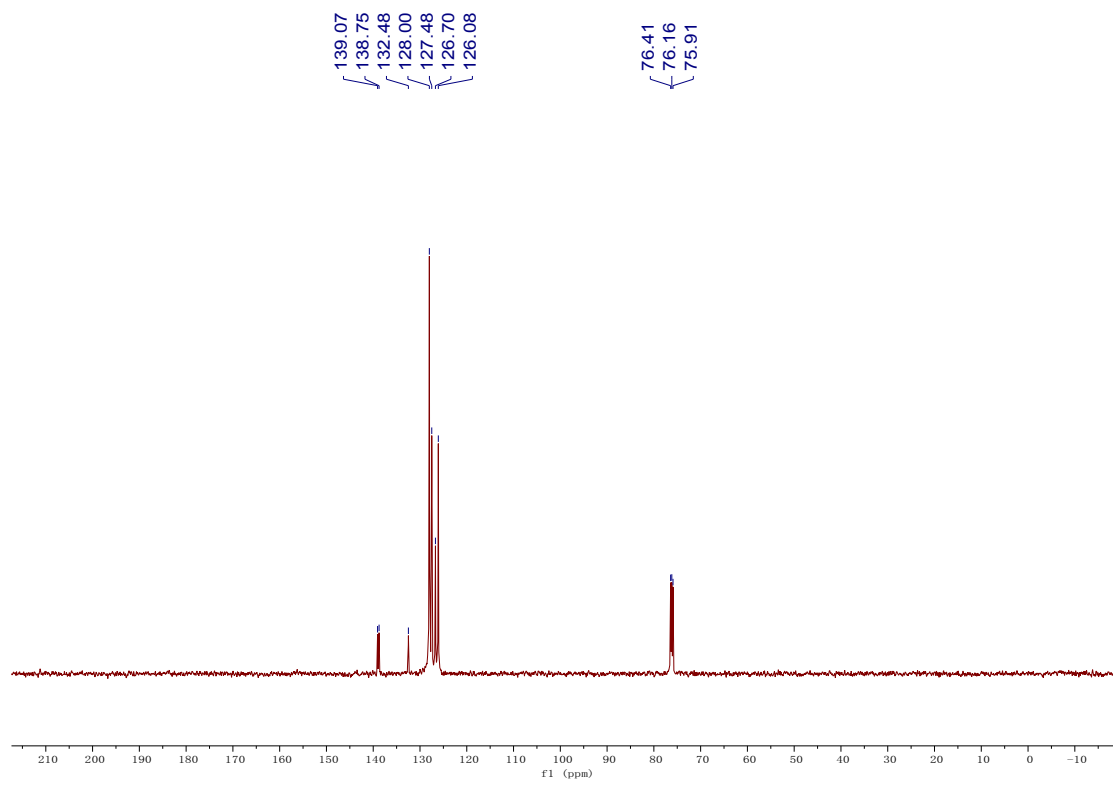


3-chlorobiphenyl

7.62
7.62
7.60
7.60
7.59
7.59
7.58
7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.35







4-nitrobiphenyl

