

Supporting Information

Highly Active PdCu/Graphene Catalyst for Efficient Suzuki Cross-coupling Reaction

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General Remarks: Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. 2.3 Characterization. The PdCu bimetallic nanocubics @3D graphene catalysts were characterized by transmission electron microscopy (TEM) (JEOL JEM-1200EX), Field emission scanning electron microscopy (FeSEM, Quanta 250), X-ray photoelectron spectroscopy (XPS) spectra (Thermo ESCALAB 250Xi). X-ray diffraction (XRD) measurement was carried out using a Bruker D8 X-ray diffractometer at 40 KV and 20 mA, with Cu K α radiation source ($\lambda=1.5418$ Å). ¹HNMR and ¹³CNMR were recorded at ambient temperature in CDCl₃ (7.27 ppm). DMSO (2.5 ppm) Chemical shift values are expressed as parts per million (ppm) and J values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet or combination, br. s broad singlet or m: multiplet.

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1. Synthesis of graphene oxide (GO).

The GO used in this work was prepared by oxidation of crystalline flake graphite according to a modified method described by Hummers. The concrete steps of synthesis are as follows. Concentrated H_2SO_4 (120 mL) and graphite powder (5 g) were added to an appropriate container and continuously stirred in the ice bath. KMnO_4 (15 g) was added slowly in stages, and the mixture was kept at a temperature not exceeding 20°C for 30 minutes. Then the reaction was heated to 35°C and stirred for 2 h. Next, 230 mL ultra-pure water is added to the reaction. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (700 mL) and 30% H_2O_2 solution (12 mL). At this point the mixture turns a bright yellow. The mixture was centrifuged in a 1:10 HCl solution (1.25 L) to remove the metal ions. Then the mixture is centrifuged in ultrapure water until neutral. After ultrasonic for 6h, the mixture was centrifuged at low speed to retain the filtrate.

References:

- (1) C. Hu, X. Zhai, Y. Zhao, K. Bian, J. Zhang, L. Qu, H. Zhang and H. Luo. Small-sized PdCu nanocapsules on 3D graphene for high-performance ethanol oxidation. *Nanoscale*, 2014, **6**, 2768-2775.
- (2) N. Kovtyukhova, P. Ollivier, B. Martin, T. Mallouk, S. Chizhik, E. Buzaneva and A. Gorchinskiy, Layer-by-Layer Assembly of Ultrathin Composite Films from Micron-Sized Graphite Oxide Sheets and Polycations. *Chem. Mater.*, 1999, **11**, 771-778.
- (3) L. Cote, F. Kim and J. Huang, Langmuir–Blodgett Assembly of Graphite Oxide Single Layers. *J. Am. Chem. Soc.*, 2009, **131**, 1043-1049.
- (4) J. J. Lv, Z. J. Wang, J. J. Feng, R. H. Qiu and A. J. Wang, Facile synthesis of highly active Pd-Cu nanowires catalyst through a simple wet-chemical strategy for ligand-free Suzuki cross coupling reaction. *Appl. Catal. A: Gen.*, 2016, **522**, 188-193.

2. Synthesis of Pd-Cu nanocubics anchored on 3D graphene without addition of 10 wt% KOH/ ethylene glycol solution (Pd-Cu/G-2).

The ethylene glycol solution of palladium chloride (6.7 mg/mL, 2 mL), GO (10 mg/L, 3 mL), 20 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50 mg of sodium glutamate were mixed together in 30 mL of ethylene glycol solution to form a homogeneous mixing suspension. After this, the suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave followed by thermal treatment at 160°C for 6 h. After cooling down to room temperature, 3D graphene loaded with Pd and Cu nanoparticles were obtained. The product was washed with deionized water several times, and we applied lyophilization to prevent the aggregation of graphene sheets during the drying process. The sample thus obtained was denoted as Pd-Cu/G-2. The TEM images of Pd-Cu/G-2 was provided as **Fig. S1**. In comparison with the Pd-Cu/G synthesized with the addition of KOH as shown in the maintext, it can be seen that as for the Pd-Cu/G-2 composite, the distribution of Cu and Pd nanoparticles is non uniform, which might be inferior to the catalytic activity.

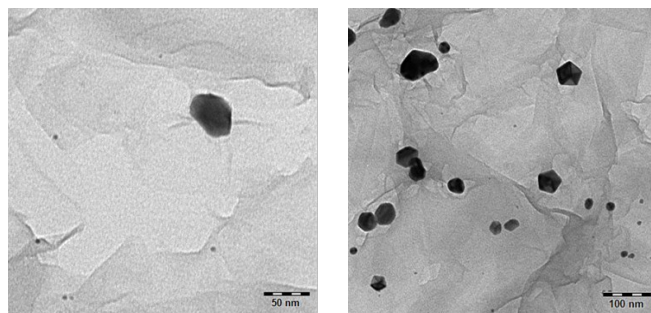


Fig. S1 TEM images of Pd-Cu/G-2

Synthesis of Pd-Cu nanocubics anchored on 3D graphene with various Pd/Cu ratio.

To better analysis the influence of Pd/Cu ratio on the catalytic activity, the Pd-Cu/G composite with different Pd/Cu ratio was fabricated as well. As for Pd-Cu/G-3 with the Pd/Cu ratio of 1:3, the fabrication process is similar to the Pd-Cu/G composite, except that the amount of PdCl_2 (6.7 mg/mL) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were adjusted to be 1 ml and 30 mg, respectively. The TEM images of Pd-Cu/G-3 were provided as **Fig. S2**. It can be seen that almost no Pd nanoparticles appeared on the nanosheet, with only Cu nanoparticles being clearly observed. Furthermore, the Pd-Cu/G-4 with the Pd/Cu ratio of 3:1 was synthesized as well via the above same method, except that 3 ml PdCl_2 (6.7 mg/mL) and 10 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were added as the metal sources. As can be seen from the TEM images of Pd-Cu/G-4 as shown in Fig. S3, uniform Pd nanoparticles were clearly observed across the whole graphene nanosheet. While as for Cu nanoparticles, the concentration is quite low with nearly no Cu particles being observed.

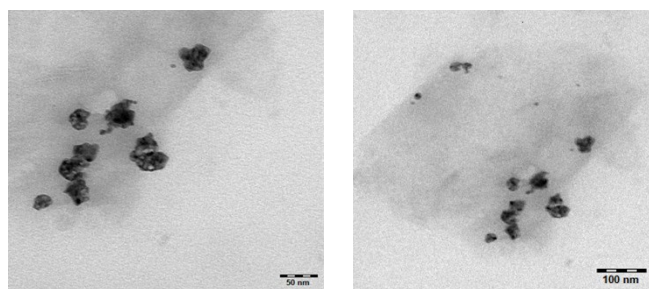


Fig. S2 TEM images of Pd-Cu/G-3 with a different radio (Pd:Cu=1:3)

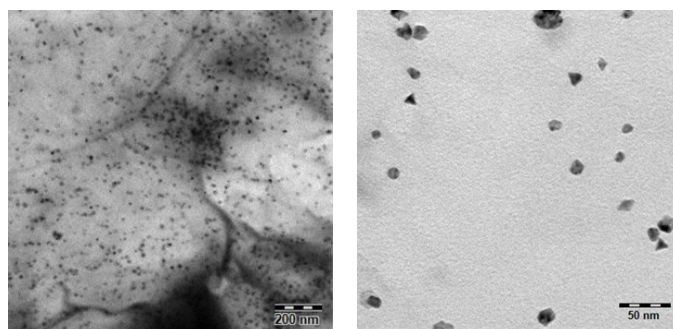


Fig. S3 TEM images of Pd-Cu/G-4 with a different ratio (Pd:Cu=3:1)

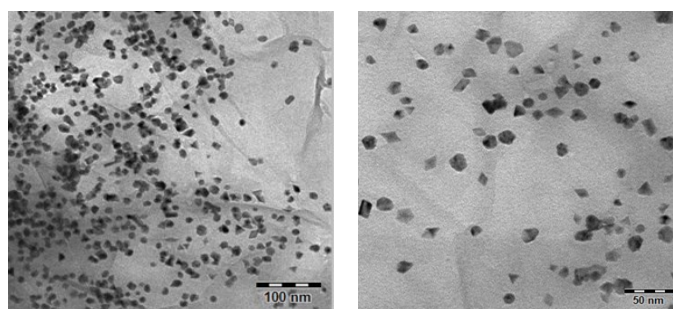


Fig. S4 TEM images of Pd/G.

Synthesis of Pd NPs or Cu NPs on grapheme nanosheet (Pd/G and Cu/G).

Pure Cu/G was prepared by a similar procedure as the method for the fabrication of Pd-Cu/G, except that no PdCl_2 was added in the reaction solution. The Pd/G was also fabricated via this similar method with only PdCl_2 , GO and sodium glutamate were mixed in ethylene glycol solution.

In addition, we synthesized catalyst without KOH/ ethylene glycol solution during synthesis and catalyst with different ratio of Pd and Cu. To distinguish the materials, we named them Pd-Cu/G-2 (without KOH/ ethylene glycol solution during synthesis), Pd-Cu/G-3 (Pd:Cu=1:3), Pd-Cu/G-4 (Pd:Cu=3:1) and Pd/G(without Cu). TEM tests were carried out on the samples. Related TEM images were provided in Fig.S1, Fig.S2, Fig.S3 and Fig.S4 respectively. It can draw a conclusion that the morphology was optimum with KOH/ ethylene glycol solution during synthesis and the Pd/Cu ratio of 1:1.

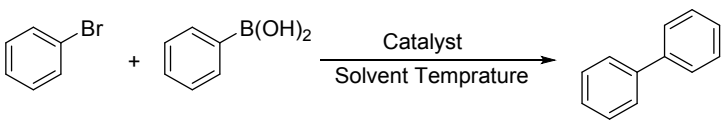
3. Analysis of the result of the Suzuki coupling reactions

The catalytic activity of Pd-Cu/G based catalysts for the Suzuki coupling reaction was further analyzed, with bromobenzene and benzene boric acid being adopted as substrates. The experimental result was provided in Table S1, from which it can be seen that the Pd-Cu/G (with Pd/Cu ratio of 1:1) exhibited the best performance, with the efficiency being >99.9% (entry 2). Thus might be owing to the fact that the proper metal ratio lead to the best synergistic effect between Pd and Cu. Meanwhile, it is noteworthy that as for the Pd-Cu/G-2 that was synthesized without the addition of KOH exhibited relatively inferior activity, which might be due to the non

uniform distribution of Cu and Pd nanoparticles.

4. Optimization of the reaction

Table S1. The yield of different conditions of Suzuki coupling reactions^a



Entry	Catalyst	Base	T/°C	Solvent	Yield/ %
1	Pd-Cu/G	K ₂ CO ₃	50	EtOH :H ₂ O=1:1	68.3
2	Cu/G	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	-
3	Pd/G	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	70.3
4	Pd-Cu/G	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	>99.9
5	Pd-Cu/G	Na ₂ CO ₃	80	EtOH :H ₂ O=1:1	88.5
6	Pd/C(10%)	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	78.6
7	Pd-Cu/G	K ₂ CO ₃	80	EtOH	60.8
8	Pd-Cu/G-2	K ₂ CO ₃	50	EtOH :H ₂ O=1:1	56.2
9	Pd-Cu/G-2	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	74.5
10	Pd-Cu/G-4	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	56.3
11	Pd-Cu/G-3	K ₂ CO ₃	80	EtOH :H ₂ O=1:1	30.5
12	Pd-Cu/G-2	K ₂ CO ₃	80	EtOH	50.8
13	Pd-Cu/G-2	Na ₂ CO ₃	80	EtOH :H ₂ O=1:1	67.2

^aReaction conditions: phenylboronic acid (66.5 mg, 0.55 mmol, 1.1 equiv.), bromobenzene (78 mg, 0.5 mmol, 1 equiv.), Base (1 mmol, 2 equiv.), catalyst (1 mg, 1.3% equiv.), 4 mL ethanol: H₂O= 2 mL: 2 mL, 80 °C, 10 h.

Table S2. The yield of catalyst after five cycles.

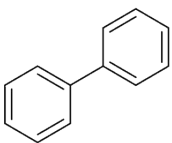
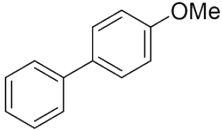
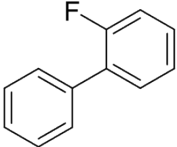
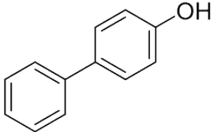
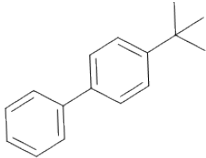
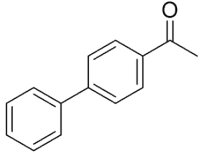
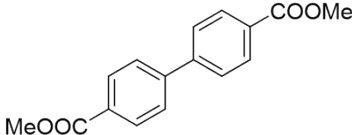
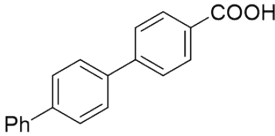
Entry	Catalyst	Base	Cycle	Yield/%	TON	TOF/h ⁻¹
1	Pd-Cu/G	K ₂ CO ₃	1	>99.9	1785	178.5
2	Pd-Cu/G	K ₂ CO ₃	2	>99.9	1785	178.5
3	Pd-Cu/G	K ₂ CO ₃	3	99.7	1780	178.0
4	Pd-Cu/G	K ₂ CO ₃	4	99.4	1776	177.6
5	Pd-Cu/G	K ₂ CO ₃	5	99.1	1769	176.9

^aReaction conditions: phenylboronic acid (66.5 mg, 0.55 mmol, 1.1 equiv.), bromobenzene (78 mg, 0.5 mmol, 1 equiv.), Base (1 mmol, 2 equiv.), catalyst (1 mg, 1.3% equiv.), 4 mL ethanol: H₂O= 2 mL: 2 mL, 80 °C, 10 h.

The stability is also an important character of an advanced catalyst. As for the heterogeneous catalyst, it can be easily recycled, which provides an ideal material platform for the sustainable industrial application. The stability of Pd-Cu/G catalyst was analysed as shown in Fig. 4. It can be seen that after five reaction cycle, the yield of this coupling reaction remains at more than 95%. Meanwhile, the TEM image of the catalyst that had been recycled five times was also provided as Fig. 4b, from which no obvious morphology changes was observed, confirming the high stability of the catalyst. Turnover number (TON) or turnover frequency (TOF) play an important role in the

catalytic performance comparison of catalysts. Inductively coupled plasma (ICP) was used the ratio of Pd and Cu in the Pd-Cu/G and Pd/C, and the results shown the amount of Pd and Cu in the catalyst of Pd-Cu/G was 1.4 % and 1.6 %, respectively. Through data processing, TON and TOF of Pd-Cu/G were shown in the table S3. The catalyst showed excellent catalytic activity after 5 cycles, indicating high stability of the catalyst. The remarkable stability of Pd-Cu/G can be ascribed to the unique and stable meso-pores nanostructure of the 3D graphene.

Table S3 TON and TOF of different products

Entry	Product	Yield/%	TON	TOF/h ⁻¹
1		99.9	1784	178.4
2		98.5	1758	175.8
3		99.7	1780	178.0
4		96.4	1721	172.1
5		99.5	1776	177.6
6		98.2	1753	175.3
7		97.3	1737	173.7
8		95.3	1702	170.2

A proposed mechanism was presented as Figure N1. Firstly, PhBr and Pd(0)-Cu(0)/G reacted by oxidative addition reaction transferring to intermediate **I** [Pd(II)-Cu(0)]. By the oxidative

additive process, the bond of PhBr was excited. Next, intermediate **I** with K_2CO_3 occurred a neutralization reaction to intermediate **II**. And then, The activated phenylboronic acid intermediate **IV** reacted with intermediate **II** to the key intermediate **III** [Pd(II)-Cu(II)] which connected the two benzene rings in the chemical bond and realized the spatial approach. The intermediate **IV** reacted the reductive elimination, getting the target biphenyl product.

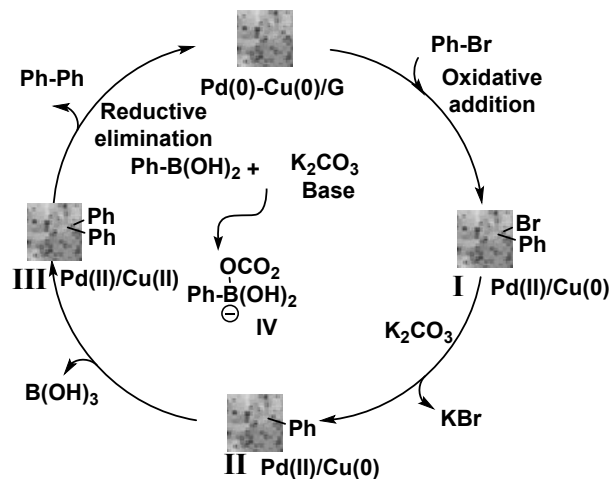
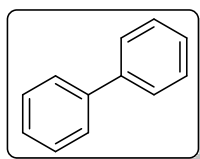


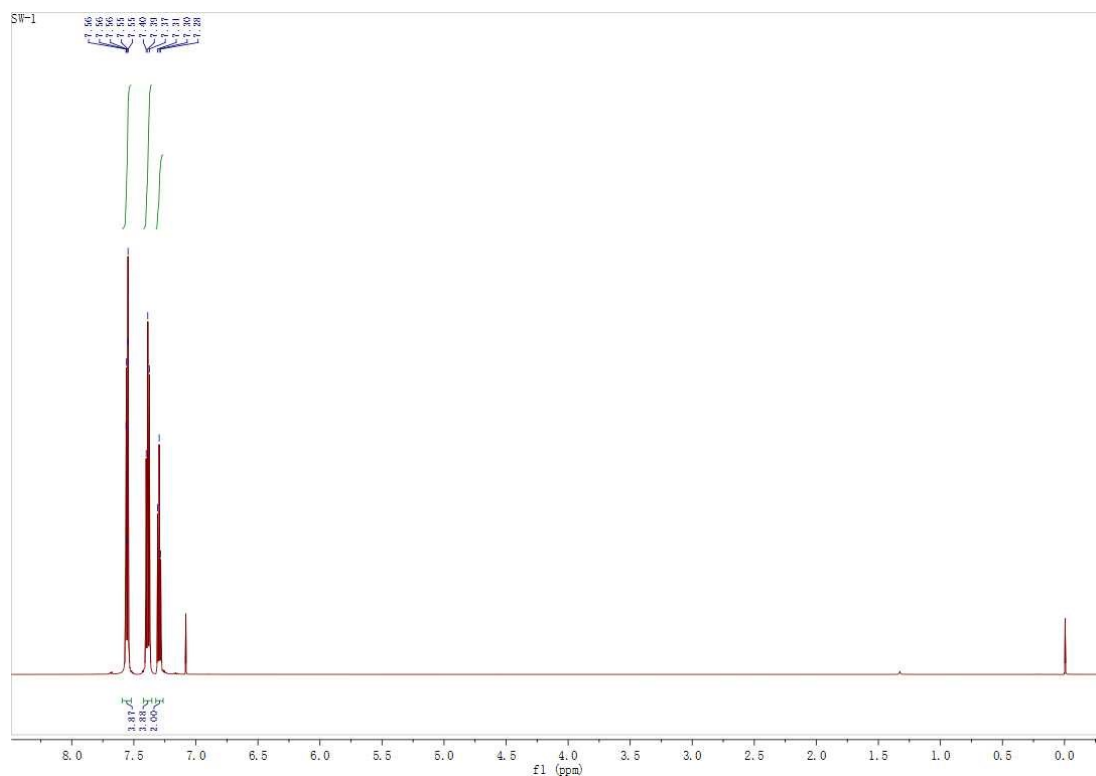
Figure N2. Proposed mechanism of the Pd-Cu/Graphene catalyzed Suzuki cross coupling reaction

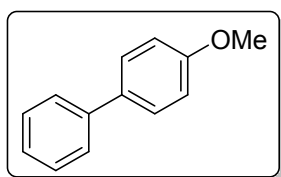
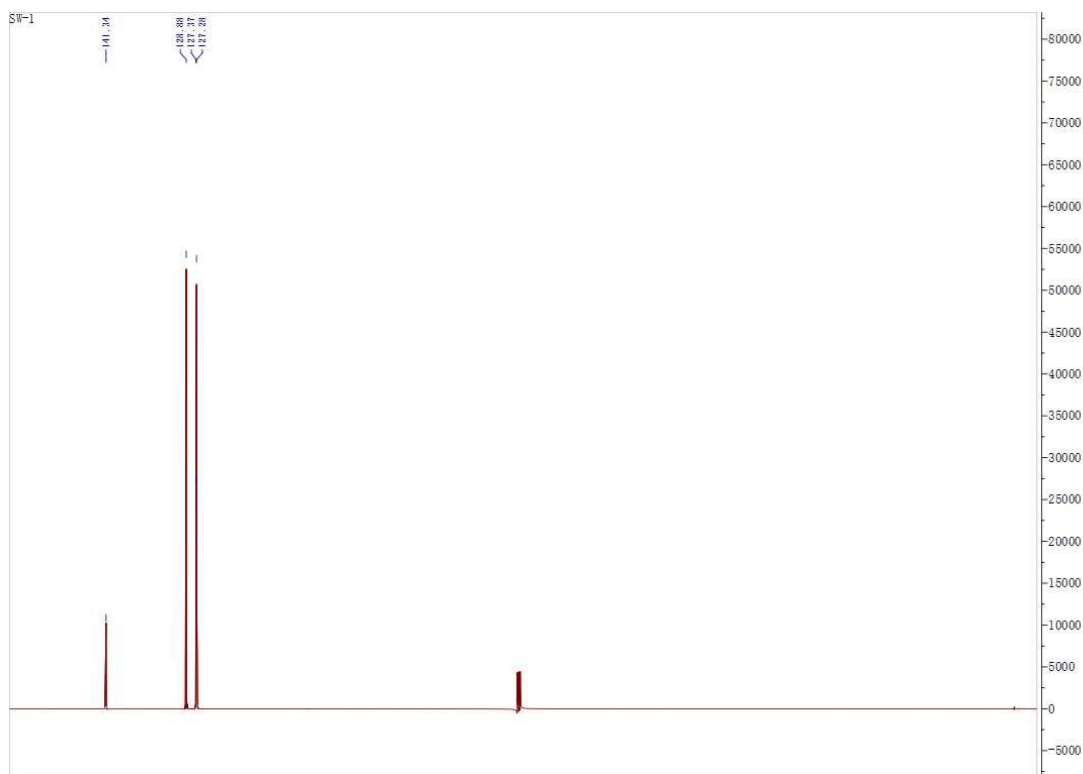
5. NMR Spectra of all compounds



3aa 1,1'-biphenyl¹

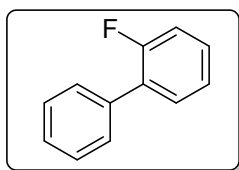
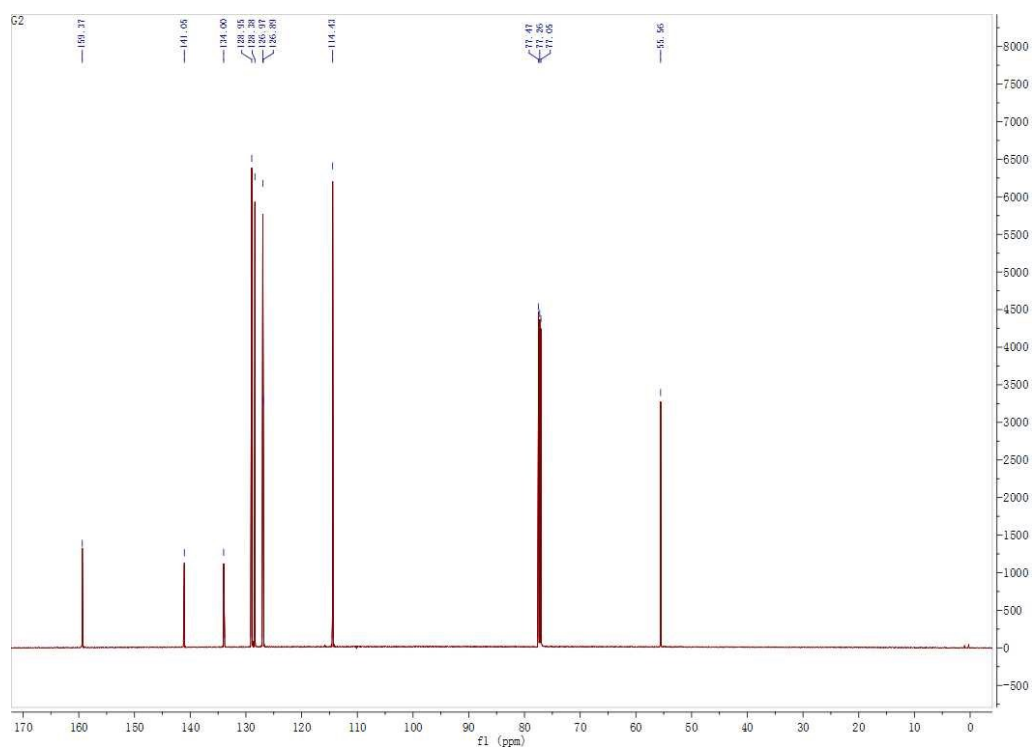
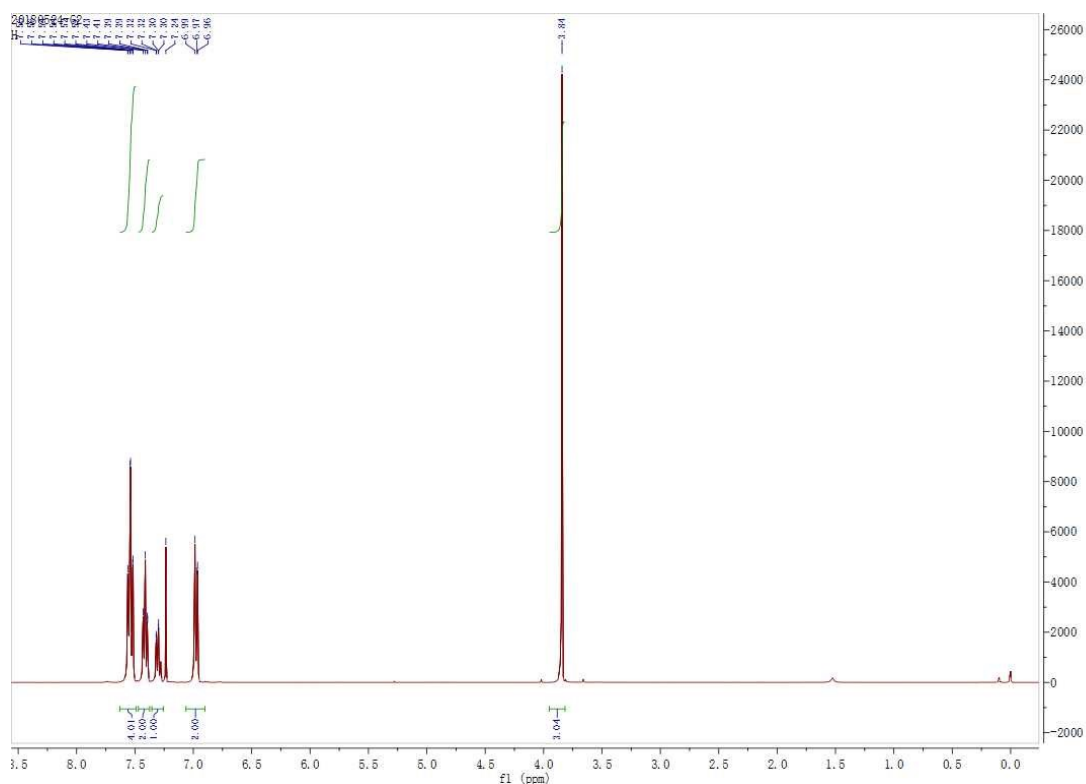
Bromobenzene (0.5 mmol, 78.5 mg), phenylboronic acid (0.55mmol, 67.2 mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1mmol, 138mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 10) getting a light white solid (76 mg, yield of 99.9%). ¹H NMR (600 MHz, CDCl₃) δ 7.56 (t, *J*=1.2 Hz, 4H), 7.40 (t, *J*=1.2 Hz, 4H), 7.30 (tt, *J*=4.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.4, 128.9, 127.4, 127.3.





3ab 4-methoxy-1,1'-biphenyl²

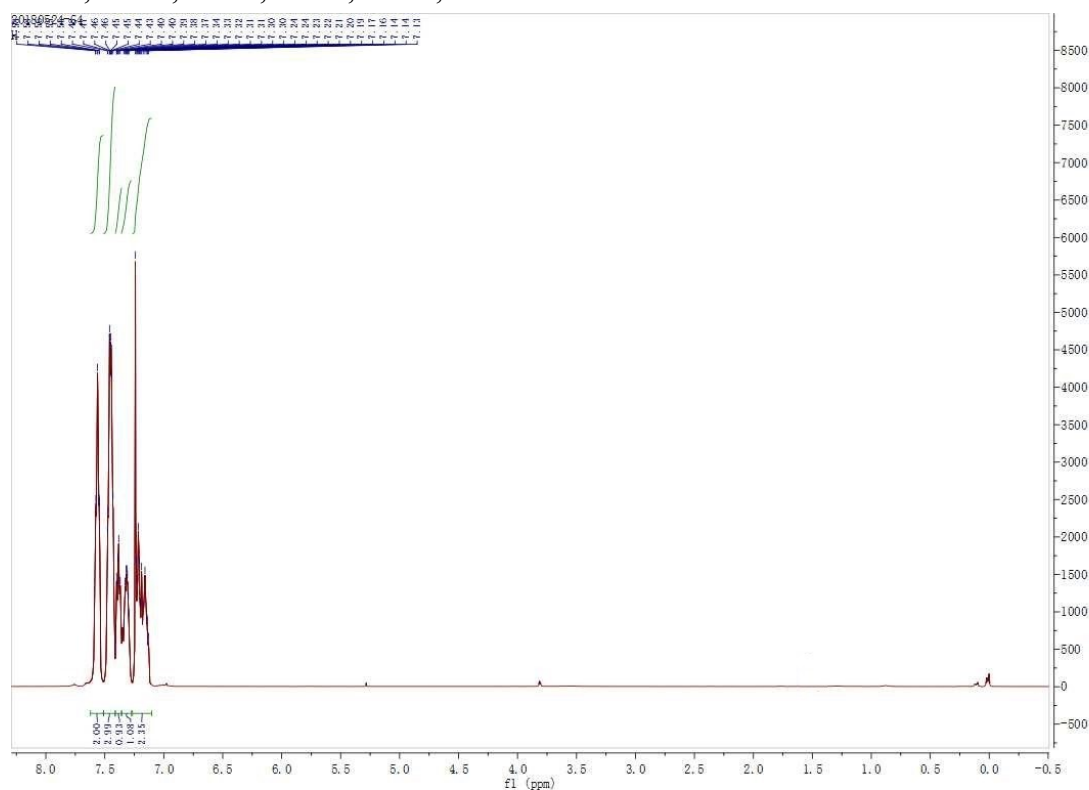
Bromobenzene (0.5 mmol, 78.5 mg), (4-methoxyphenyl)boronic acid (0.55 mmol, 76.1 mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 10) getting a light white solid (91.0 mg, yield of 98.5%). ¹HNMR (400 MHz, CDCl₃) δ=7.54 (t, *J*=9 Hz, 4H), 7.41 (t, *J*=7.6 Hz, 2H), 7.31 (d, *J*=7.3 Hz, 1H), 7.01 (d, *J*=8.4 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ=159.3, 141.0, 134.0, 128.9, 128.3, 126.9, 126.8, 114.4, 55.5.

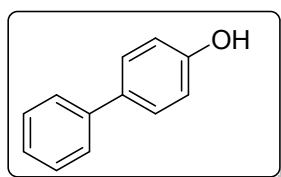
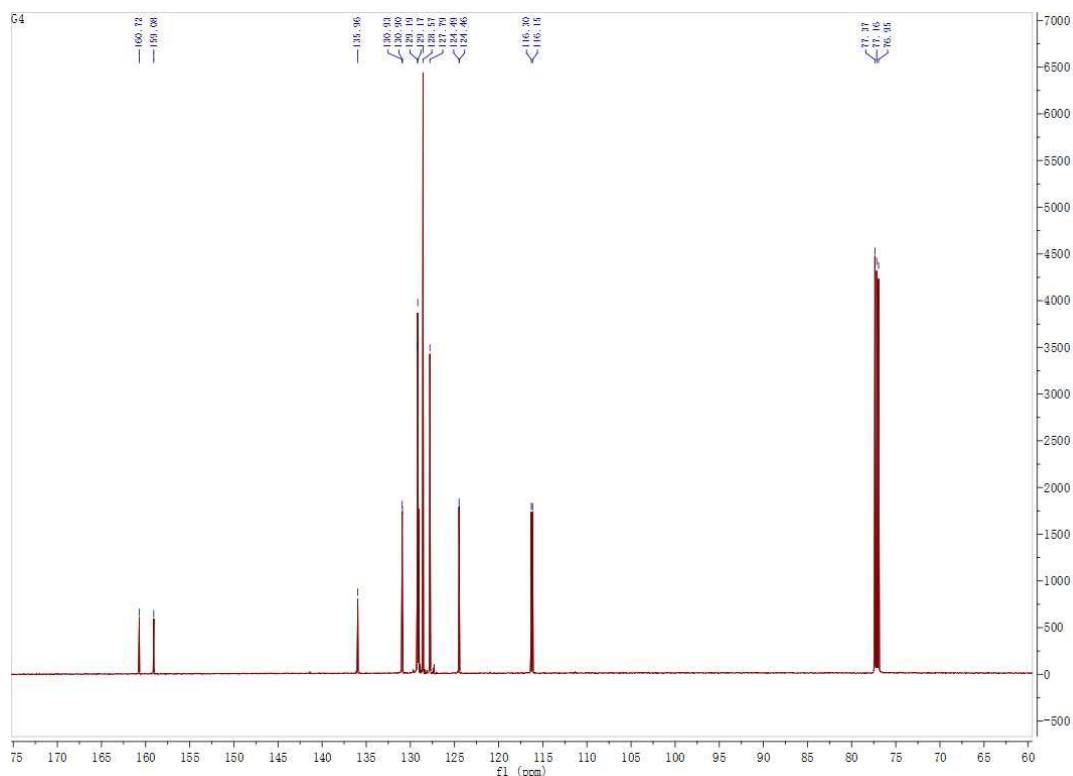


3ac 2-fluoro-1,1'-biphenyl³

bromobenzene (0.5 mmol, 78.5 mg), (2-fluorophenyl)boronic acid (0.55 mmol, 70.5

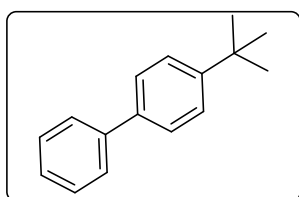
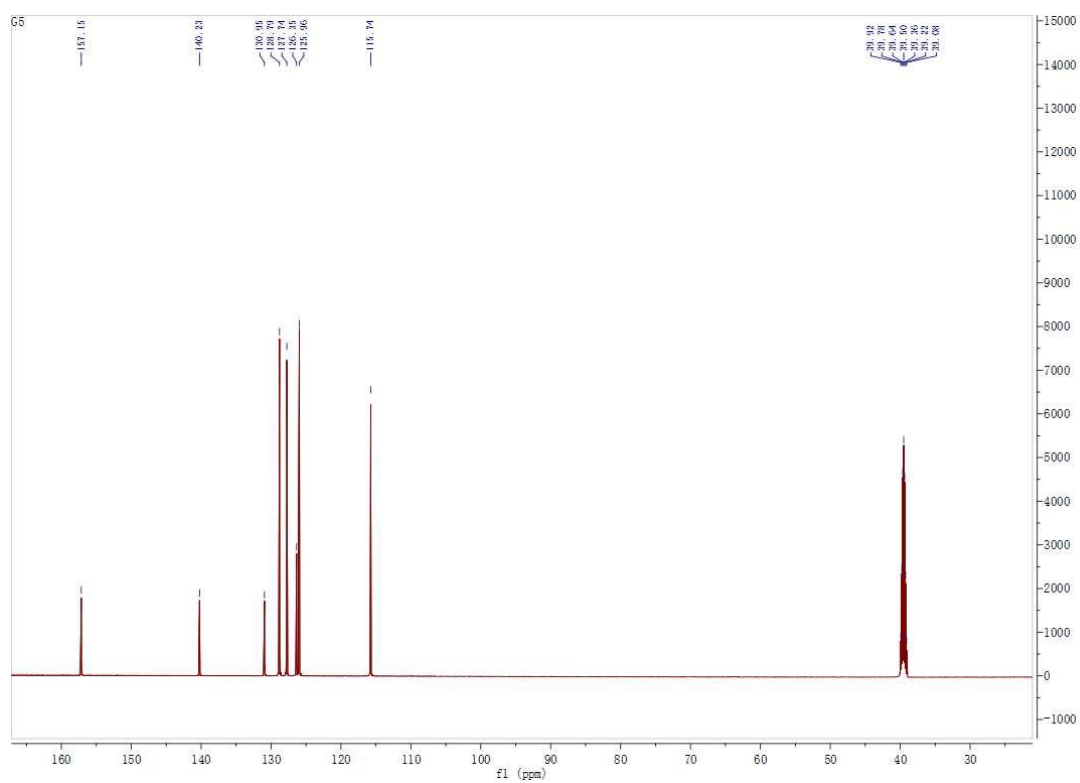
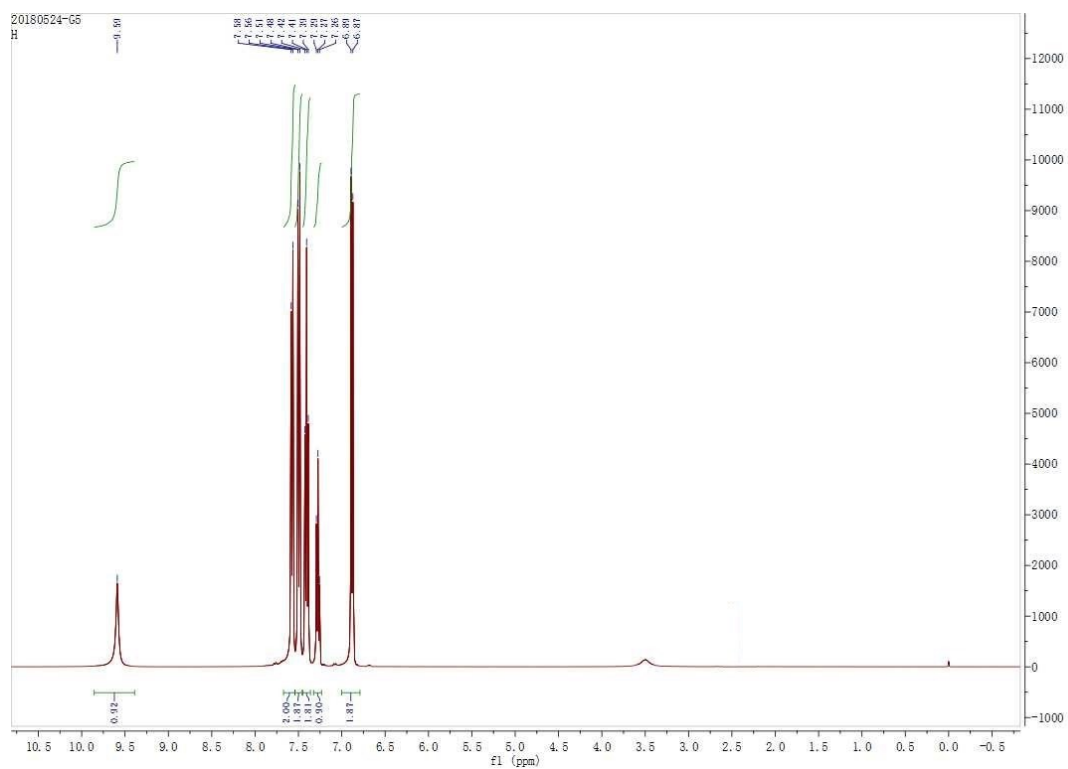
mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1: 10) getting a light white solid (99.4 mg, yield of 99.7%). ¹H NMR (400 MHz, CDCl₃): δ=7.62-7.51 (d, 2H), 7.50-7.41 (m, 3H), 7.35 (m, *J*=8.0 Hz, 1 H), 7.26-7.18 (m, 1 H). ¹³C NMR (101 MHz, CDCl₃) δ=160.7, 159.0, 136.0, 130.9, 130.9, 129.2, 129.2, 128.6, 127.8, 124.5, 116.3, 116.1.





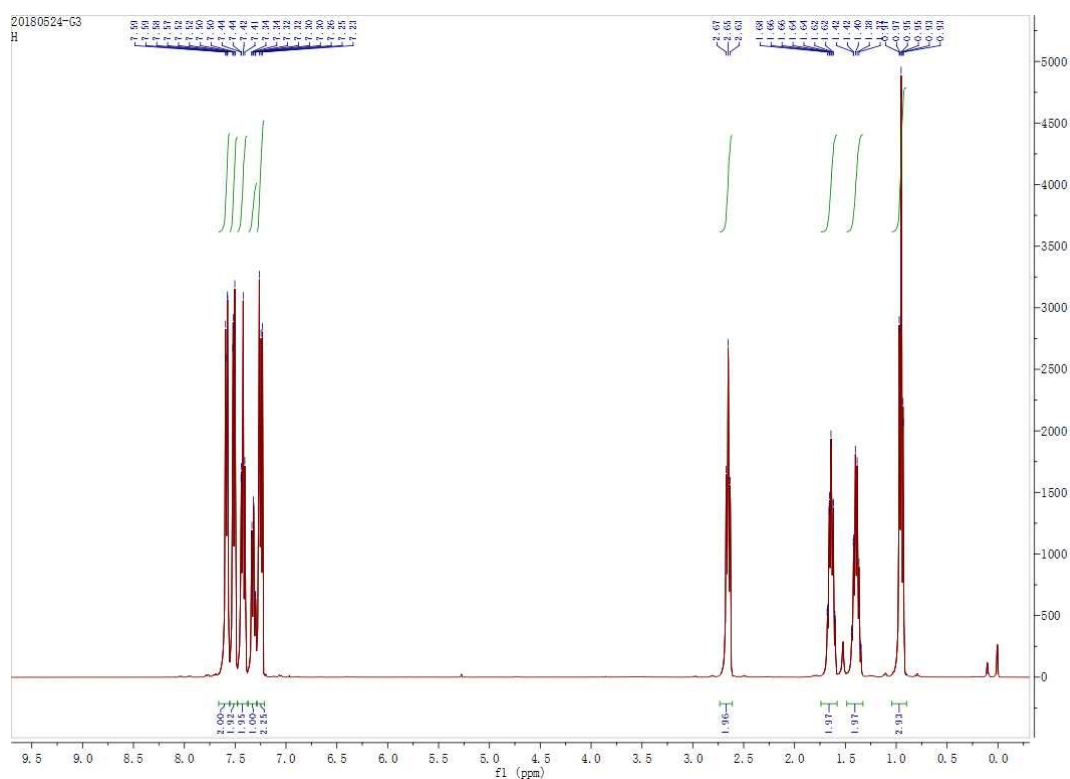
3ad [1,1'-biphenyl]-4-ol⁴

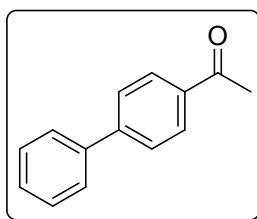
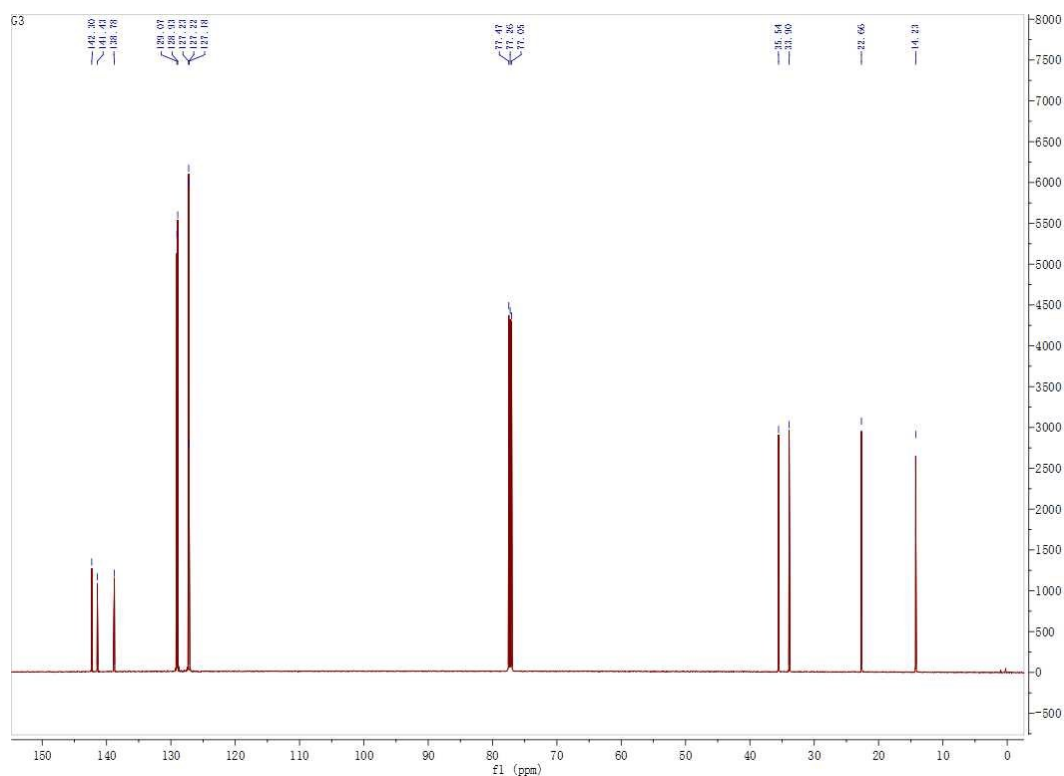
Bromobenzene (0.5 mmol, 78.5 mg), (4-hydroxyphenyl)boronic acid (0.58 mmol, 80.5 mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1 : 5) getting a light white solid (81.8 mg, yield of 96.4%). [1,1'-biphenyl]-4-ol ¹H NMR (400 MHz, DCCl₃) δ=9.59 (s, 1H), 7.57 (d, *J*=5.4 Hz, 2H), 7.49 (d, *J*=6.6 Hz, 2H), 7.42 (d, *J*=6.0 Hz, 2H), 7.27 (t, 1H), 6.92 (d, *J*=6.3 Hz, 2H). ¹³C NMR (101 MHz, DMSO) δ=157.2, 140.2, 131.0, 128.8, 127.7, 126.3, 126.0, 115.7,



3ae 4-(tert-butyl)-1,1'-biphenyl⁵

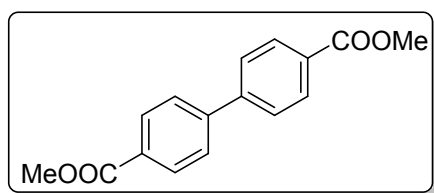
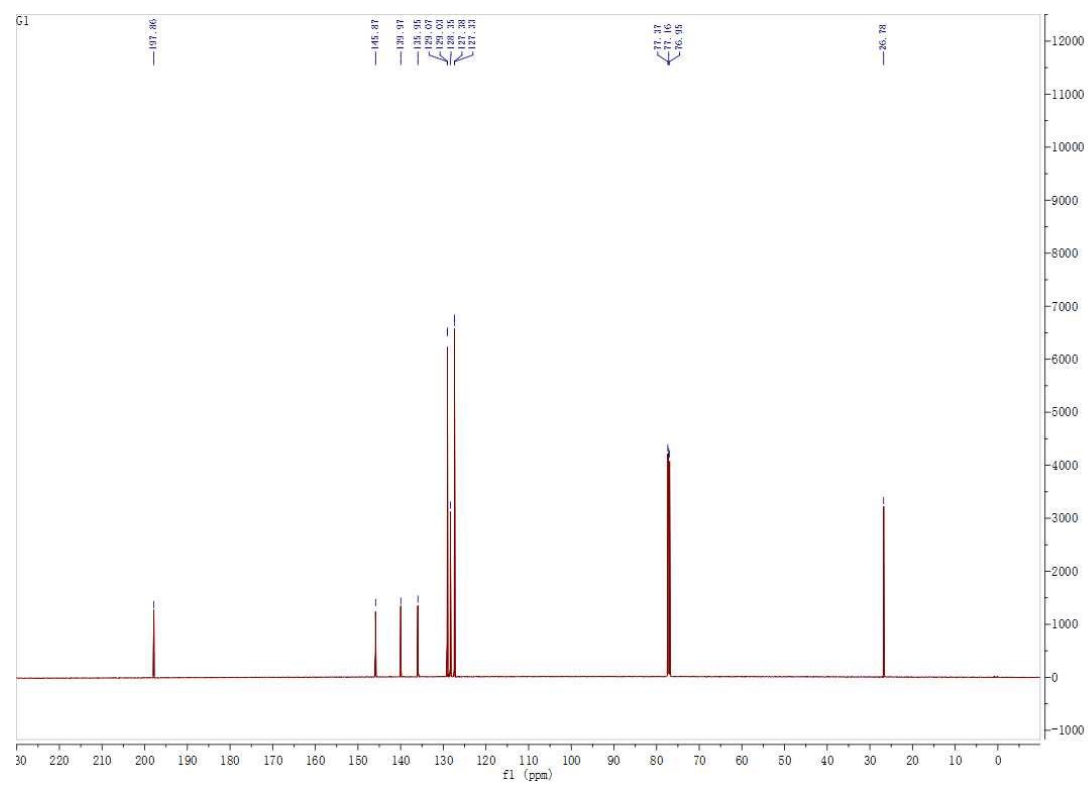
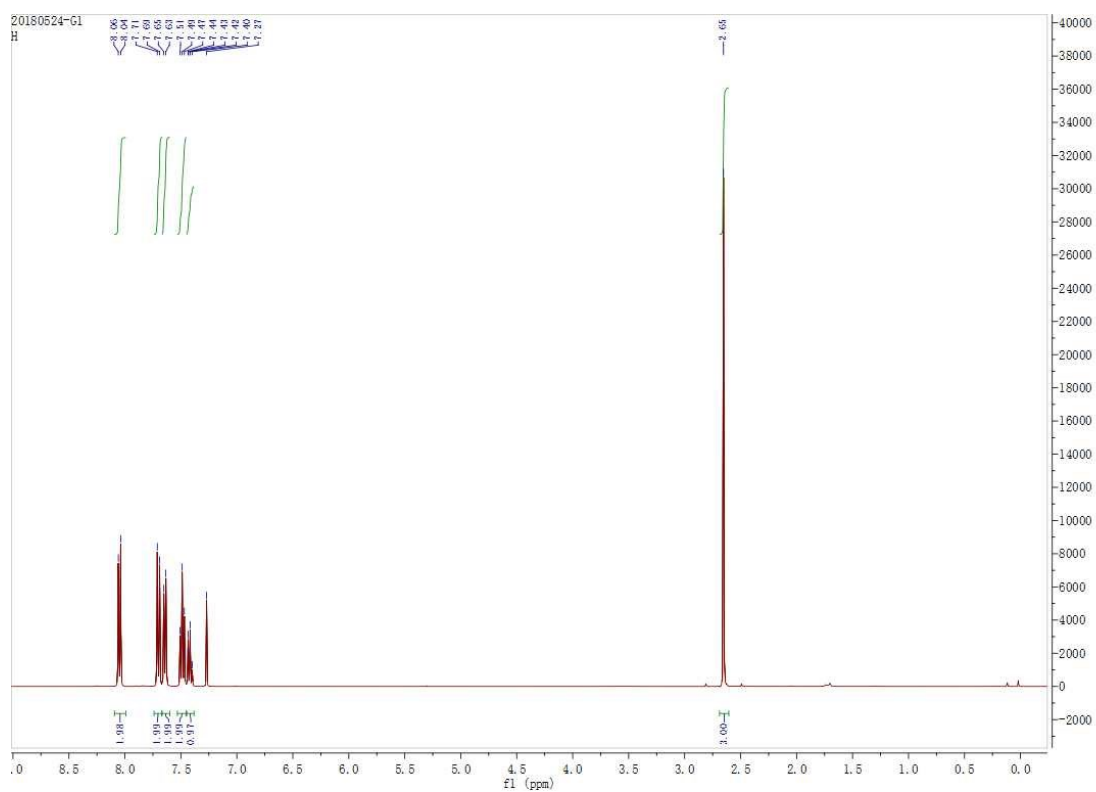
Bromobenzene (0.5 mmol, 78.5 mg), (4-(*tert*-butyl)phenyl)boronic acid (0.55 mmol, 80.5 mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1 : 10) getting a light white solid a light white solid (99.4 mg, yield of 99.5%).
¹H NMR (400 MHz, CDCl₃) δ=7.59 (d, *J*=7.3 Hz, 2H), 7.39-7.40 (m, 4H), 7.24 (t, *J*=7.2 Hz, 1H), 6.71 (d, *J*=8.0, 2H), 2.65 (t, *J*=7.6 Hz, 4H), 1.80-1.57 (m, 4H), 1.57-1.31 (m, 5H), 0.95 (td, *J*=7.3, Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ=142.3, 141.4, 138.7, 129.0, 128.9, 127.2, 127.2, 127.1, 35.5, 33.9, 22.6, 14.2.





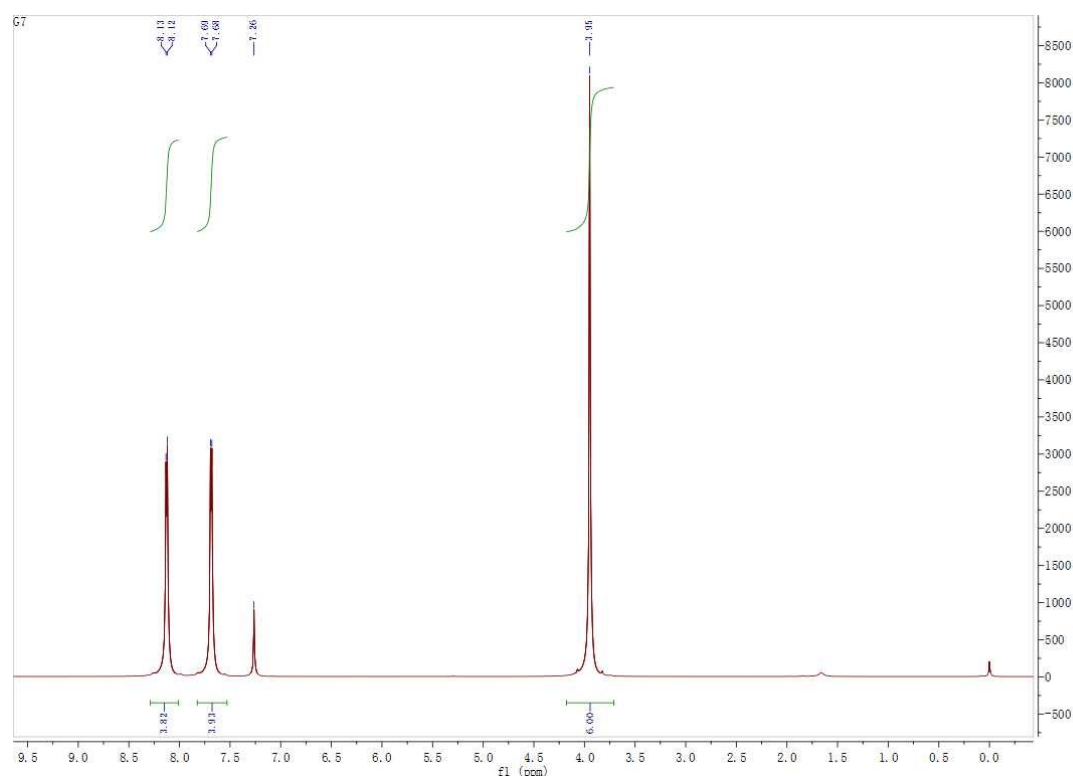
3af 1-([1,1'-biphenyl]-4-yl)ethan-1-one⁶

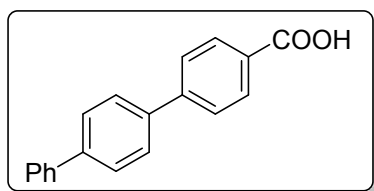
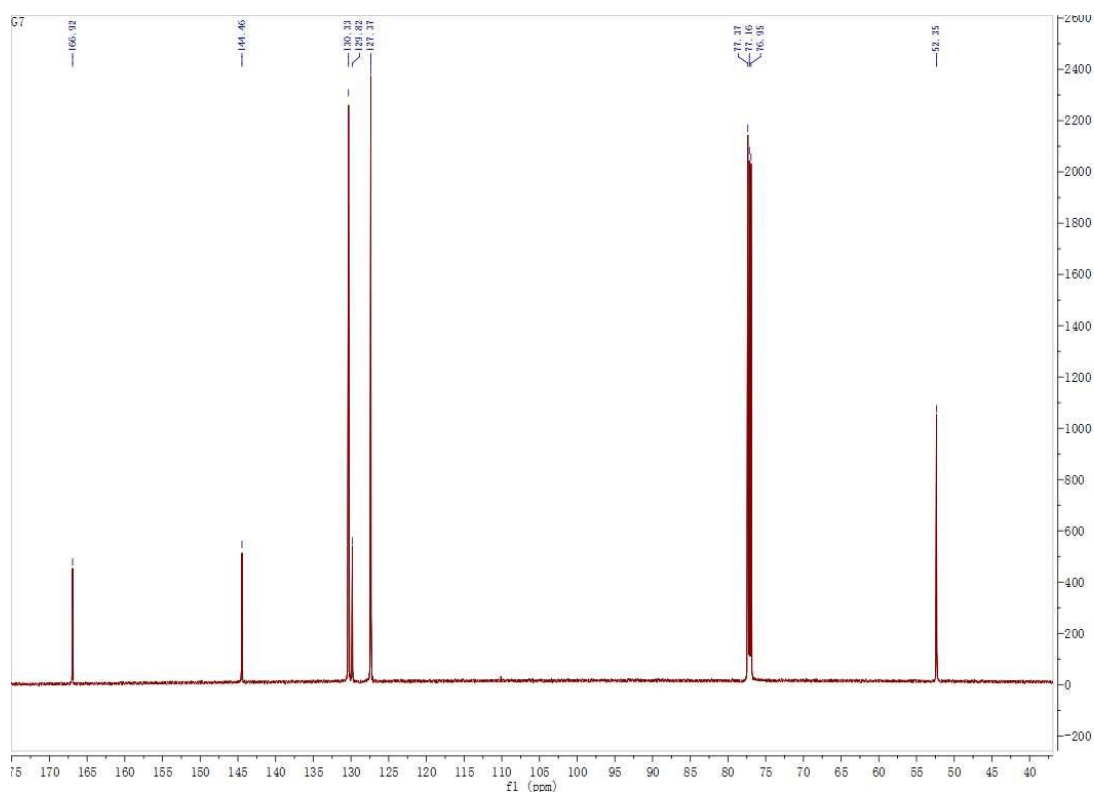
Bromobenzene (0.5 mmol, 78.5 mg), (4-acetylphenyl)boronic acid (0.55 mmol, 90.5 mg) and EtOH (2 mL), water (2 mL), K₂CO₃ (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 15 mL) and then the combined organic extracts were washed with brine for three times (3 × 5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1 : 10) getting a light yellow oil (96.2 mg, yield of 98.2%). ¹H NMR (400 MHz, CDCl₃) δ=8.05 (d, *J*=0.6 Hz, 2H), 7.70 (d, *J*=0.6 Hz, 2H), 7.65 (d, *J*=0.6 Hz, 2H), 7.49 (t, *J*=0.6 Hz, 2H), 7.42 ((t, *J*=0.6 Hz, 2H), 2.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ=197.9, 145.9, 140.0, 136.0, 129.1, 129.1, 128.4, 127.4, 127.4, 26.8.



3bg dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate⁷

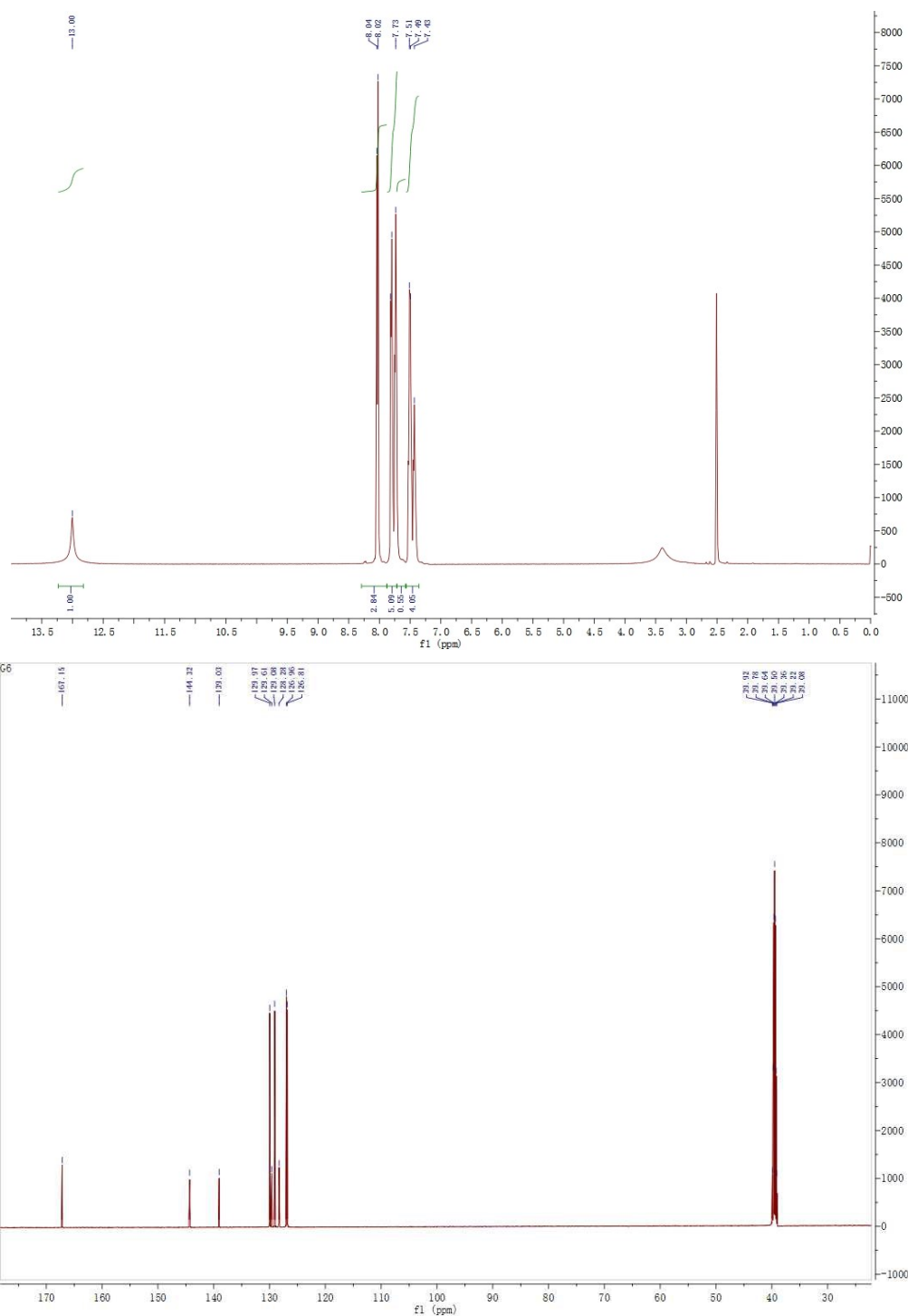
Methyl 4-bromobenzoate (0.5 mmol, 107 mg), (4-(methoxycarbonyl)phenyl)boronic acid (0.55 mmol, 90.1 mg) and EtOH (2 mL), water (2 mL), K_2CO_3 (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2×15 mL) and then the combined organic extracts were washed with brine for three times (3×5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1 : 5) getting a light white solid (131 mg, yield of 97.3%). 1H NMR (600 MHz, $CDCl_3$): δ =8.13 (d, J = 8.0 Hz, 4H), 7.69 (d, J = 8.0 Hz, 4H), 3.95 (s, 6H). ^{13}C NMR (101 MHz, d-DMSO): δ =166.9, 144.5, 130.3, 129.8, 127.4, 52.4.





3ch [1,1':4',1''-terphenyl]-4-carboxylic acid

4-bromo-1,1'-biphenyl (0.5 mmol, 116 mg), 4-boronobenzoic acid (0.55 mmol, 91.3 mg) and EtOH (2 mL), water (2 mL), K_2CO_3 (1 mmol, 138 mg) were added in a round-bottom flask (25 mL), 10 h. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2×15 mL) and then the combined organic extracts were washed with brine for three times (3×5 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether = 1 : 5) getting a light white solid (130 mg, yield of 95.1%). 1H NMR (400 MHz, DMSO) δ =13.00 (s, 1H), 8.07 (d, J =7.7 Hz, 3H), 7.81 (d, J =8.6 Hz, 5H), 7.71 (s, J =7.7 Hz, 1H), 7.47 (t, J =7.3 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ =167.1, 144.3, 139.0, 130.0, 129.6, 129.1, 128.3, 127.0, 126.8.



Notes and references

- 1) Altan, O.; Serindağ, O.; Sayın, K.; Karakaş, D. J. P., Sulfur; Silicon; Elements, t. R., Pd (II) complexes of novel phosphine ligands: Synthesis, characterization, and catalytic activities on Heck reaction. Phosphorus, Sulfur, and Silicon and the Related Elements. 2016, **191** (7), 993-999.
- 2) Bao, G.; Fan, X.; Xu, T.; Li, C.; Bai, J. J. A. O. C., Preparing Pd catalysts based on urea ligand via electrospinning for Suzuki - Miyaura cross - coupling reactions. Applied Organometallic Chemistry. 2020, **34** (10), e5877.
- 3) Xu, W.; Liu, C.; Xiang, D.; Luo, Q.; Shu, Y.; Lin, H.; Hu, Y.; Zhang, Z.; Ouyang, Y. J. R. a., Palladium catalyst immobilized on functionalized microporous organic polymers for C-C

coupling reactions. RSC advances .2019, **9** (59), 34595-34600

4) Marset, X.; Saavedra, B.; Gonzalez-Gallardo, N.; Beaton, A.; Leon, M. M.; Luna, R.; Ramon, D. J.; Guillena, G., Palladium Mesoionic Carbene Pre-catalyst for General Cross-Coupling Transformations in Deep Eutectic Solvents. *Frontiers in Chemistry*, 2019, **7**, 700.

5) Paul, S.; Pradhan, K.; Ghosh, S.; De, S. K.; Das, A. R.; Magnetically Retrievable Nano Crystalline Nickel Ferrite-Catalyzed Aerobic, Ligand-Free C-N, C-O, and C-C Cross-Coupling Reactions for the Synthesis of a Diversified Library of Heterocyclic Molecules. *Adv. Synth. Catal.* 2014, **356**, 1301–1316.

6) Gabriel Flores-Rojas, G.; Gonzalez-Sebastian, L.; Reyes-Martinez, R.; Aguilar-Castillo, B. A.; Hernandez-Ortega, S.; Morales-Morales, D., Synthesis and characterization of Pd(II) complexes bearing NS, CS, SNS and SCS ligands. Evaluation of their microwave assisted catalytic activity in C-C coupling reactions. *Polyhedron* 2020, **185**, 114601.

7) Bao, F.; Liu, Z.; Bai, H.; Zhang, H.; Liu, P.; Zhang, Q.; Chai, G., Palladium/Sensory Component-Catalyzed Homocoupling Reactions of Aryl Halides. *Syn. Lett.* 2020, **31** (15), 1501-1506.