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2-(diphenylphosphino)pyridine platinum (I) and palladium (I) complex as an efficient binuclear catalyst for Suzuki-Miyaura coupling reaction in water under mild reaction conditions

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Binuclear complex of platinum (I) and palladium (I) showed superior activity in Suzuki-Miyaura coupling reaction of aryl halides with arylboronic acids compared to the sole palladium or platinum species. The catalyst showed good tolerance in water and coupling reactions were performed in water as a green solvent. Aryl iodides were reacted at room temperature and the reactions of aryl bromides were performed at 60 °C.

1. Introduction

Palladium has found such wide utility because it affects an extraordinary number of very different reactions, including many carbon–carbon bond-forming reactions [1–5]. Among the different types of palladium catalyzed reactions, Suzuki-Miyaura coupling reaction, which is the reaction of organic electrophiles, such as aryl or alkenyl halides and triflates with organoboron compounds in the presence of a base, is one of the important organic reactions [6–14]. Despite numerous reports on development of Suzuki-Miyaura coupling reaction, efforts to improve the conditions of the reaction are still in progress. Along this line, improving the low reactivity of aryl bromides and chlorides, introducing of new efficient catalysts, using recyclable heterogeneous catalysts, shortening of the reaction times and conducting reactions in eco-friendly solvents such as water are challenging subjects for investigation [6–23].

In recent years bimetallic catalysts have attracted great attention in the field of catalysts [24,25]. In fact, synergistic combination of two metals enhances their catalytic performance, activity, selectivity, and stability compared to corresponding monometallic catalysts. Along this line, catalytic activity of palladium catalysts in the presence of other transition metals in coupling reactions were investigated. $NiFe_2O_4$-dopamine-Pd composite has been found as a magnetically separable and efficient catalyst for Heck C–C coupling reactions [26].

Recently, Pd/Cu bimetallic composite nanoparticles exhibited high catalytic activity in the Sonogashira cross-coupling reaction between aryl iodide and terminal alkynes [27]. Also, bimetallic Au/Pd alloy nanoclusters showed excellent reactivity for Ullmann coupling of chloroarenes in aqueous media at low temperature [28,29]. Recently, we have demonstrated synergistic effect between palladium and copper species using copper ferrite supported palladium nanoparticles in cyanation reaction of aryl halides [30]. Most recently, we have also reported assemblies of copper ferrite and palladium nanoparticles on silica spheres as a bimetallic catalyst for Sonogashira coupling reaction [31]. However, among the different types of bimetallic catalysts, platinum based bimetallic catalysts are most commonly used in catalytic and electro

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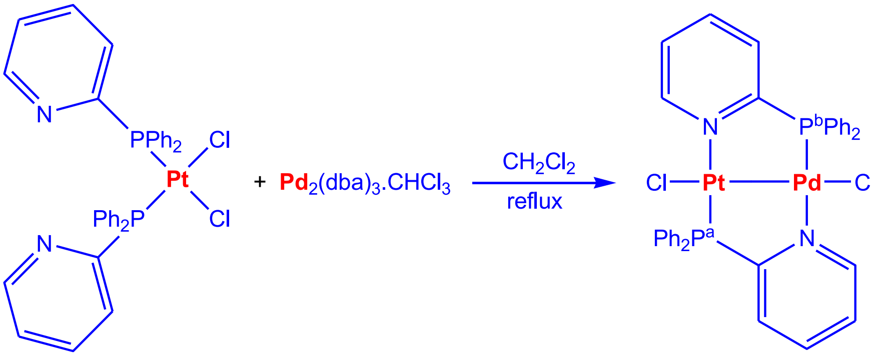


Scheme 1. Synthesis of binuclear complexes of platinum (I) and palladium (I) involving 2-(diphenylphosphino)pyridine as a bridging ligand.

catalytic applications [32]. Literature search reveals that there is only one report on using platinum catalyzed Suzuki-Miyaura coupling reaction and platinum based catalysts are not potent catalysts for coupling reactions [33]. However, combination of second metal such as palladium with platinum can increase catalytic activity of new bimetallic catalyst [32].

Very recently, synergistic effect of a conjugated organometallic platinum moiety with palladium was applied in Suzuki and Heck coupling reactions of aryl bromides under mild reaction conditions [34,35]. Now in this article, we have introduced binuclear complex of platinum (I) and palladium (I) catalyst involving 2-(diphenylphosphino)pyridine ligand (Scheme 1) as a highly efficient catalyst in Suzuki-Miyaura coupling reactions in neat water under mild reaction conditions.

The catalyst successfully was prepared according to the reported method by Balch and coworker [36] using $Pd_2(dba)_3.CHCl_3$ and $Pt(Ph_2Ppy)_2Cl_2$ in CH_2Cl_2 (Scheme 1) and was characterized using ^1H (see supporting information) and $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR of the catalyst in $CDCl_3$ shows two different signals for phosphorus atoms (Fig. 1). The P_a atom bonded to the platinum center is appeared at $\delta = -7.6$ ppm with a large platinum coupling constant $^1J_{PtP} = 4047$ Hz, whereas the P_b atom bonded to the palladium atom is observed at $\delta = 7.0$ ppm with a much smaller platinum coupling constant $^2J_{PtP}$ value of 111 Hz. It is interesting to note, due to P_aP_b coupling, the two non-equivalent phosphorus atoms in this catalyst are coupled to each other through the Pt–Pd metal bond and so each resonance appears as a doublet with $^3J^{ab}_{PP} = 14$ Hz.

The thermogravimetric analysis (TGA) curve of catalyst has been shown in Fig. 2. According to this curve, the prepared catalyst has high thermal stability and negligible ligand leaching up to 200 °C.

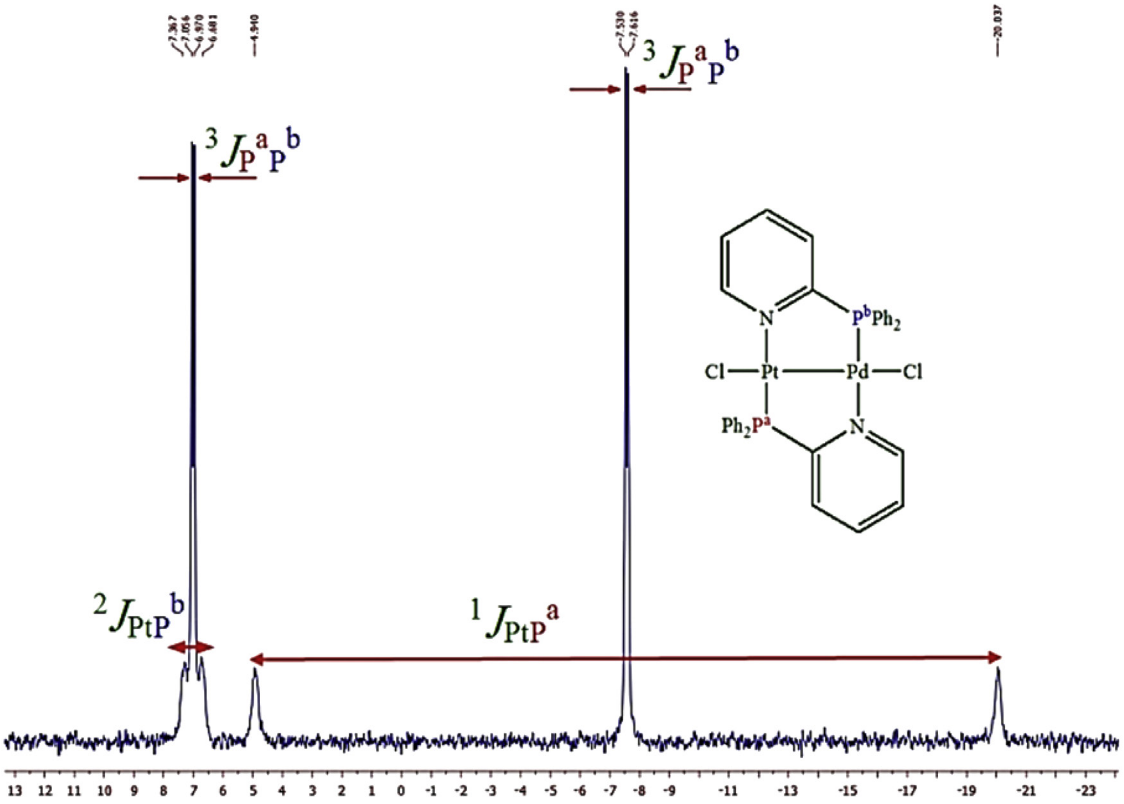


Fig. 1. $^{31}P\{^1H\}$ NMR of catalyst in $CDCl_3$.

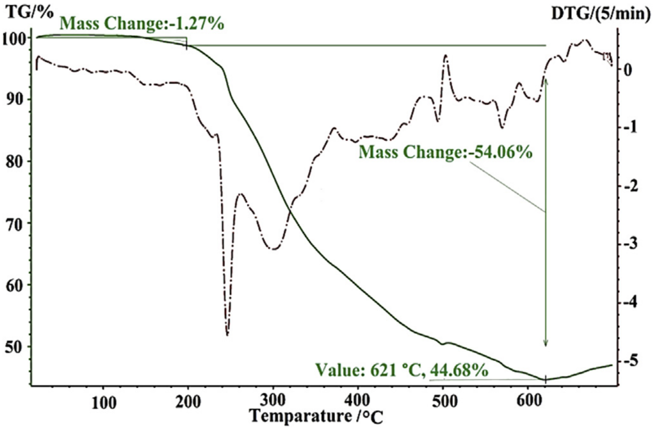
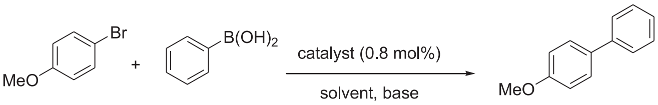


Fig. 2. Thermogravimetric diagram of the catalyst.

Table 1

Screening of different reaction conditions for the reaction of 4-bromoanisole with phenylboronic acid in the presence of catalyst.



Entry	Solvent	Base	Temp. (° C)	Yield(%)[a]
1	CH_3CN	K_3PO_4	60	5
2	Toluene	K_3PO_4	60	19
3	THF	K_3PO_4	60	7
4	DMF	K_3PO_4	60	21
5	H_2O	K_3PO_4	60	86
6	H_2O–EtOH	K_3PO_4	60	73
7	H_2O–EtOH	K_3PO_4	50	35
8	H_2O	*t*-BuOK	50	51
9	H_2O	DABCO	50	52
10	H_2O	K_2CO_3	50	60
11	H_2O–EtOH	K_2CO_3	60	10
12	H_2O–EtOH	*t*-BuOK	60	16
13	H_2O–EtOH	DABCO	60	56
14	H_2O–EtOH	Et_3N	60	54
15	DMF	DABCO	60	4

[a] GC yields.

2. Results and discussion

The catalytic activity of prepared catalyst were assessed in Suzuki-Miyaura coupling reaction. In initial experiments, reaction of less reactive 4-bromoanisole with phenylboronic acid was selected as a model reaction and effect of different reaction conditions such base, solvent and temperature was studied (Table 1).

The results of Table 1 indicated that using K_3PO_4 as a base and H_2O as a solvent at 60 °C in the presence of the catalyst are the most effective reaction conditions for the reaction of 4-bromoanisole with phenylboronic acid. The scope of the reaction was further expanded for the reactions of structurally varied aryl halides under optimized reaction conditions (Table 2). Due to more reactivity of aryl iodides than aryl bromides and chlorides, we decided to perform reactions of aryl iodides in both 60 °C and room temperature under optimized reaction conditions (Table 2, entries 1–10). The results of Table 2 indicated that reactions of aryl iodides with arylboronic acids proceeded well at room temperature and desired biphenyl products were obtained in excellent yields (Table 2, entries 2,3, and 5–10). However, reactions of aryl iodides at 60 °C afforded excellent yields in shorter reaction times. In addition, aryl bromides reacted efficiently with arylboronic acids and gave coupling products in high to excellent yields (Table 2, entries 11–22). Reactions of aryl chlorides under optimized reaction conditions were sluggish. Therefore, we increased reaction temperature to 80 °C. Under this condition, desired coupling products were obtained in 47–56% isolated yields (Table 2, entries 23–24). Also, results of Table 2 indicated that heterocyclic aryl halides such as 2-iodothiophene and 5-bromopyrimidine were reacted efficiently and produced coupling products in 80–97% yields (Table 2, entries 9 and 18–19).

The catalyst is not soluble in the reaction medium and reactions proceeded under heterogeneous reaction conditions. However, in order to confirm the heterogeneity of catalyst, we have studied hot filtration test for the reaction of 4-bromoanisol and phenylboronic acid. The reaction mixture was filtered after 8 h at the reaction temperature and GC analysis showed 46% GC yield. Then, filtrate allowed reacting for 24 h. GC analysis of reaction after 24 h showed 57% yield.

In addition, we have also studied poisoning test using poly(4-vinylpyridine) with ratio of 400: 1 with respect to the catalyst for the reaction of 4-bromoanisol and phenylboronic acid under optimized reaction conditions. GC analysis of the reaction showed 69% conversion to desired coupling product while, similar reaction in the absence of poisoning was produced 86% GC yield. This result also confirmed that reaction proceeded mostly under heterogeneous conditions [40].

Furthermore, leaching of the catalyst into the reaction mixture after 24 h was determined by atomic absorption spectroscopy to be 3.5%. Therefore, we assume that the catalyst predominantly have a heterogeneous nature at the reaction conditions.

In order to confirm the synergistic effect between Pd and Pt species in the catalyst, we have performed reaction of 4-bromoanisole with phenylboronic acid in the presence of sole Pd and Pt species under optimized reaction conditions (Scheme 2). However, results indicated that in the presence of corresponding monometallic catalysts, low isolated yields of products were obtained.

It is worth mentioning that it is difficult to recognize how the electronic and chemical properties of bimetallic systems affected property of them, compared to individual metals [24,25]. The observed superior activity in the presented platinum (I) and palladium (I) catalyst may related to electron exchange between palladium and platinum which cause the modifications of the chemical and catalytic property of the catalyst.

3. Conclusions

In conclusion, we have described application of binuclear complex of platinum (I) and palladium (I) as an efficient catalyst for Suzuki-Miyaura coupling reaction of aryl halides in aqueous media. Using this catalyst, aryl iodides and bromides were reacted effectively at 25–60 °C and high to excellent isolated yields were obtained. Reactions of aryl chlorides were sluggish and moderate isolated yields were obtained.

4. Experimental

4.1. General

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^1H (400 MHz, TMS), ^{13}C (100 MHz, TMS) and ^{31}P (162 MHz, 85% H_3PO_4). The chemical shifts and coupling constants are in ppm and

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Table 2
Reactions of structurally different aryl halides with arylboronic acids in the presence of the catalyst.[a]

$$Ar_1X + Ar_2X \xrightarrow[\substack{K_3PO_4,\ H_2O \\ 25\text{-}80\ °C}]{\text{Catalyst (0.8 mol\%)}} Ar_1\text{-}Ar_2$$

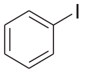
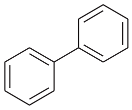
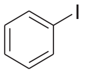
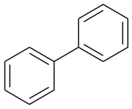
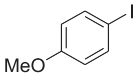
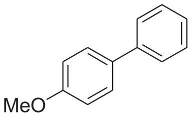
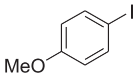
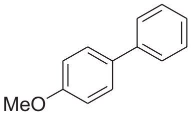
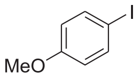
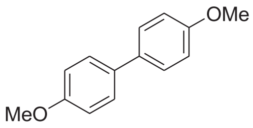
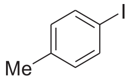
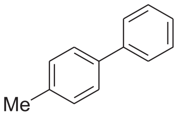
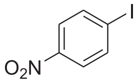
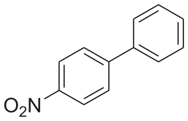
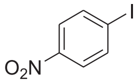
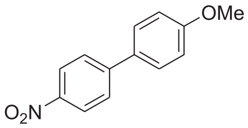
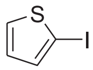
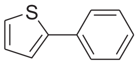
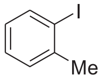
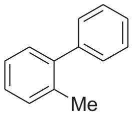
Entry	Ar_1X	Temp. (°C)	Ar_2	Time	Product	Isolated yield(%)
1		60	Ph	0.5	 **1a**	99
2		25	Ph	15	 **1a**	83
3		25	Ph	15	 **2a**	98
4		60	Ph	2	 **2a**	95
5		25	4-$MeOC_6H_4$-	15	 **3a**	96
6		25	Ph	15	 **4a**	94
7		25	Ph	3	 **5a**	75
8		25	4-$MeOC_6H_4$-	3	 **6a**	80
9		25	Ph	5	 **7a**	97
10		25	Ph	24	 **8a**	72

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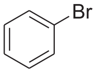
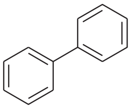
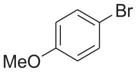
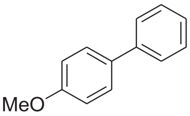
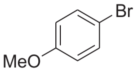
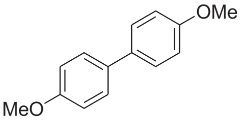
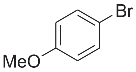
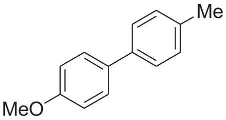
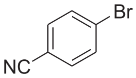
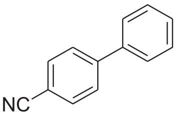
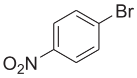
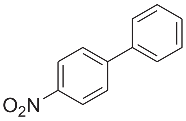
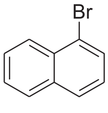
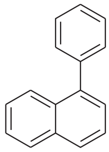
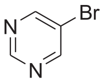
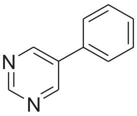
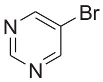
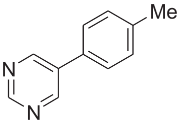
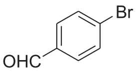
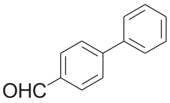
Table 2 (*continued*)

Entry	Ar_1X	Temp. (°C)	Ar_2	Time	Product	Isolated yield(%)
11		60	Ph	24	 **1a**	86
12		60	Ph	24	 **2a**	81
13		60	4-$MeOC_6H_4$-	24	 **3a**	91
14		60	4-MeC_6H_4-	24	 **9a**	87
15		60	Ph	2	 **10a**	90
16		60	Ph	10	 **5a**	92
17		60	Ph	24	 **11a**	86
18		60	Ph	20	 **12a**	80
19		60	4-MeC_6H_4-	24	 **13a**	83
20		60	Ph	24	 **14a**	75

(*continued on next page*)

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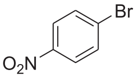
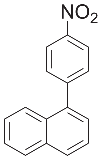
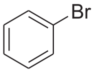
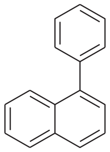
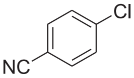
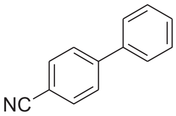
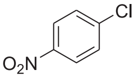
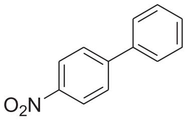
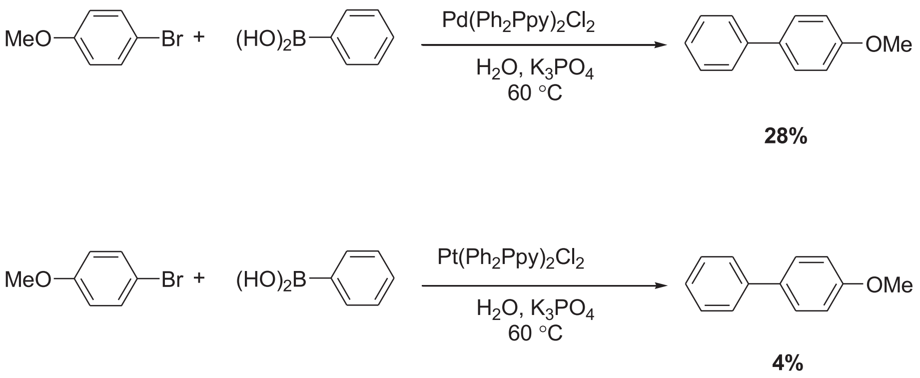
Table 2 (*continued*)

Entry	Ar_1X	Temp. (°C)	Ar_2	Time	Product	Isolated yield(%)
21		60	1-naphthyl	10	 **15a**	96
22		60	1-naphthyl	24	 **11a**	76
23		80	Ph	24	 **10a**	56
24		80	Ph	24	 **5a**	47

[a] Reaction conditions: ArX (1 mmol), $ArB(OH)_2$ (1.5 mmol), K_3PO_4 (1.5 mmol), H_2O (2 mL), and catalyst 0.8 mol%.



Scheme 2. Reaction of 4-bromoanisole with phenylboronic acid in the presence of sole Pd and Pt species.

Hz, respectively. The microanalyses were performed using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. The progress of the reactions was followed with TLC using silica gel SILG/UV 254 plates or by GC Varian CP 3800 instrument. $Pt(Ph_2Ppy)_2Cl_2$ [37], $Pd(Ph_2Ppy)_2Cl_2$ [38] and $Pd_2(dba)_3.CHCl_3$ [39] were prepared according to literature methods.

4.2. General procedure for the preparation of catalyst

The catalyst was prepared according to the reported procedure in the literature [36], which briefly will explain here. A solution containing $Pd_2(dba)_3.CHCl_3$ (0.149 g, 0.15 mmol) and $Pt(Ph_2Ppy)_2Cl_2$ (0.237 g, 0.30 mmol) in 50 mL of dichloromethane was heated in reflux condition for 2 h under nitrogen atmosphere. Then the solution was cooled to room temperature, and diethyl ether was added slowly to precipitate a greenish brown solid. The precipitate was collected by filtration and dried by vacuum. Yield 0.085 g, 73%. $C_{34}H_{28}Cl_2N_2P_2PdPt$ (MW = 898.95): calcd. C 45.43, H 3.14, N, 3.12. Found: C 45.21, H 3.13, N 3.48. ^1H NMR in $CDCl_3$: δ 9.61–9.50 (m, 2H), 7.75–7.32 (m, 24H), 6.78–6.67 (m, 2H). ^{31}P NMR in $CDCl_3$: δ −7.6 (d, $^3J_{PP}^{ab} = 14$ Hz, $^1J_{PtP} = 4047$ Hz, 1 P, P^a bonded to the Pt), 32.4 (d, $^3J_{PP}^{ab} = 14$ Hz, $^1J_{PtP} = 111$ Hz, 1 P, P^b bonded to the Pd) ppm.

4.3. General procedure for the Suzuki–Miyaura reaction

Aryl halide (1 mmol), arylboronic acid (1.5 mmol), catalyst (0.8 mol%), K_3PO_4 (1.5 mmol) and distilled water (2 mL) were added to a 5 mL flask. The mixture was stirred for appropriate reaction time at 25 °C for aryl iodides, 60 °C for aryl bromides and 80 °C for aryl chlorides. The progress of the reaction was monitored by GC.

After completion of the reaction, the aqueous layer was extracted with ethyl acetate or hexane (5 × 1 mL) and further purified by column chromatography using hexane and ethyl acetate as an eluant.

1a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.61 (d, J = 7.7, 2H), 7.45 (t, J = 7.6, 2H), 7.36 (t, J = 7.3, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 141.4, 128.9, 127.4, 127.3.

2a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.55 (t, J = 8.2, 4H), 7.42 (t, J = 7.6, 2H), 7.31 (t, J = 7.3, 1H), 6.98 (d, J = 8.7, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.3, 141.0, 134.0, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.

3a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.48 (d, J = 8.6, 2H), 6.96 (d, J = 8.7, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 158.8, 133.6, 127.9, 114.3, 55.46.

4a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.70 (d, J = 7.1, 2H), 7.62 (d, J = 8.1, 2H), 7.54 (t, J = 7.6, 2H), 7.44 (t, J = 7.4, 1H), 7.36 (d, J = 7.9, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 141.3, 138.5, 137.1, 129.6, 128.8, 127.1, 127.0, 21.2.

5a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.30 (d, J = 8.8, 2H), 7.74 (d, J = 8.8, 2H), 7.63 (d, J = 7.7, 2H), 7.48 (m, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 147.8, 147.2, 138.9, 129.3, 129.1, 128.0, 127.5, 124.3.

6a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.26 (d, J = 8.8, 2H), 7.68 (d, J = 8.8, 2H), 7.58 (d, J = 8.7, 2H), 7.02 (d, J = 8.7, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 160.5, 147.3, 146.6, 131.1, 128.7, 127.1, 124.2, 114.7, 55.51.

7a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.62 (d, J = 7.3, 2H), 7.38 (t, J = 7.6, 2H), 7.32–7.28 (m, 3H), 7.08 (dd, J = 5.0, 3.6, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 144.7, 134.6, 129.1, 128.2, 127.7, 126.2, 125.1, 123.3.

8a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.50 (t, J = 7.3, 2H), 7.43 (t, J = 7.1, 3H), 7.3–7.33 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 142.1, 135.5, 130.4, 129.9, 129.3, 128.9, 128.2, 127.4, 126.9, 125.9, 20.6.

9a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.57 (d, J = 8.7, 2H), 7.51 (d, J = 8.0, 2H), 7.28 (d, J = 8.0, 2H), 7.02 (d, J = 8.7, 2H), 3.89 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.0, 138.1, 136.4, 133.8, 129.6, 128.1, 126.7, 114.3, 55.4, 21.2.

10a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.73–7.67 (m, 4H), 7.60 (d, J = 7.2, 2H), 7.49 (t, J = 7.1, 2H), 7.46–7.39 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 145.7, 139.2, 132.7, 129.2, 128.8, 127.8, 127.3, 119.0, 111.0.

11a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.91 (dd, J = 8.1, 1.5, 2H), 7.87 (d, J = 8.2, 1H), 7.56–7.41 (m, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 140.9, 140.4, 133.9, 131.7, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 125.9, 125.5.

12a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.22 (s, 1H), 8.98 (s, 2H), 7.62–7.56 (m, 2H), 7.56–7.51 (m, 2H), 7.50–7.46 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 157.3, 155.0, 134.2, 129.6, 129.3, 127.2.

13a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.23 (s, 1H), 9.02 (s, 2H), 7.48 (d, J = 8.0, 2H), 7.33 (d, J = 7.8, 2H), 2.43 (s, 3H).

14a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 10.06 (s, 1H), 7.96 (d, J = 8.3, 2H), 7.76 (d, J = 8.2, 2H), 7.66–7.61 (m, 2H), 7.49 (t, J = 7.4, 2H), 7.42 (dd, J = 8.4, 6.2, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 192.1, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

15a. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.37 (d, J = 8.5, 2H), 7.95 (dd, J = 7.9, 2.9, 2H), 7.79 (d, J = 8.4, 1H), 7.68 (d, J = 8.6, 2H), 7.57–7.43 (m, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 147.8, 147.3, 137.9, 133.9, 131.7, 131.1, 129.1, 128.7, 128.5, 128.4, 127.3, 126.9, 126.4, 125.5, 125.3, 123.7.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.05.047.

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