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Dimerization of Aromatic Compounds Using Palladium-Carbon-Catalyzed Suzuki–Miyaura Cross-Coupling by One-Pot Synthesis

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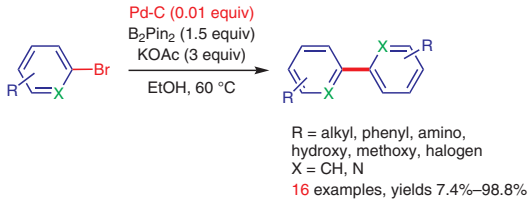

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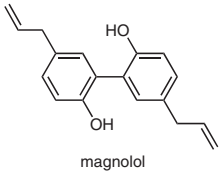
Abstract The aromatic dimers play a significant role in many aspects. Herein, we report a simple palladium-carbon catalyst that is highly effective for the dimerization of brominated aromatic compounds under mild conditions using abundant brominated aromatic compounds, bis(pinacolate)diboron and potassium acetate by a 'one-pot' method. This process, which we believe proceeds via a Suzuki–Miyaura cross-coupling reaction mechanism, allows access to a variety of aromatic compounds under mild reaction conditions and has a good functional group tolerance with moderate to high yields.

Key words self-coupling, Suzuki–Miyaura cross-coupling, palladium-carbon, catalysis, dimerization

Aromatic dimers are ubiquitous reagents in organic synthesis and play a significant role in many aspects, such as pharmaceutical and chemical industries. The antimicrobial agent, magnolol (Figure 1), extracted from *Magnolia officinalis* is a typical aromatic dimer.[1–3] In recent years, some theoretical studies have confirmed that dimers or oligomers are the main features of G-protein-coupled receptors, such as the opioid receptor.[4–6] Chung and his coworkers[7] discovered that biphenyl-type neolignan derivatives from the twigs of *Magnolia denudate* have anti-inflammatory activity. The dimers of small molecules have been used in the development of new drugs.[8,9]



magnolol

Figure 1 The structure of magnolol

The main features of aromatic compounds are as follows: solid molecular structure, high electron density, and symmetry,[10,11] which have important effect on the polymeric materials. Therefore, aromatic polymer materials are widely used in engineering plastics, polymeric membranes, etc.

As the aromatic polymers have become more and more functional, the research on their synthetic methods has attracted scientists' attention. The C–C bond-formation reactions involving name reactions include the Suzuki,[12] Heck,[13] and Sonogashira[14] cross-coupling reaction, etc. Certainly, the synthetic methods of biphenyl derivatives are mainly as follows:[15–18] the substituted halobenzene coupled with substituted phenyl boronic acid catalyzed by palladium catalysts with different ligands or supports such as $Pd(dba)_2$, [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II), palladium chloride, etc.

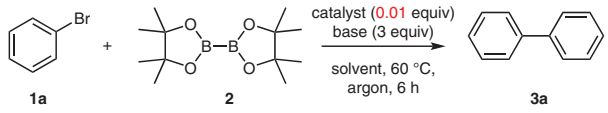
The byproducts of the Suzuki–Miyaura cross-coupling have been reported,[19] but no general method was proposed. Here, we disclose the development of conditions for the dimerization of substituted brominated aromatic compounds using the cheap and readily available catalyst of palladium-carbon. These reactions occur at mild temperature (60 °C), employ substituted brominated aromatic compounds and inexpensive catalysts, and afford high yields. These reactions likely proceed via a Suzuki–Miyaura coupling reaction pathway. Importantly, this process is general with respect to both the substituents and aromatic ring type. This wide scope allows the preparation of many substituted aromatic dimers. To our delight, some substituted brominated aromatic compounds showed a good functional group tolerance with moderate to high yields, and some coupling results can be preliminarily summarized which were advantageous for the preparation of self-coupling compounds.

The experimental procedures were conducted according to a literature report[20] with some modifications which were conducive to the formation of coupling products (Table 1). At first, we examined the reaction of bromobenzene in acetonitrile. Under basic conditions in the presence of a catalyst, only a small amount of the desired product bibenzene (**3a**) was obtained (Table 1, entry 1)

Attempts to optimize the molar ratio of bibenzene with bis(pinacolate)diboron were successful. This led to more promising results when the ratio increased to 1.5 (Table 1, entries 1–4). The reaction temperature was also an important factor and the coupling reaction cannot be carried out at room temperature (Table 1, entry 5). Different solvents including acetonitrile, dimethylsulfoxide, and ethanol were tested and a protic solvent was favored, with ethanol being the most effective in the screening reaction (Table 1, entries 6–8). Attempts to optimize the reaction through modification of the base proved unsuccessful, and the kind of bases had an important effect on the reaction, with potassium acetate proving to be optimal in terms of yield and ease of use. We replaced palladium-carbon with a palladium catalyst with different ligands which led to different results. With the use of $PdCl_2$(dppf) and $Pd(PPh_3)_4$, the desired self-coupling products were not observed and the main products were benzene borates (Table 1, entries 12 and 13). Under these optimized conditions, the desired bibenzene was isolated in 98.7% yield. The reaction enjoys wide substrate scope with respect to substituted brominated aromatic compounds (Table 2).

A range of functional groups on the substituted bromobenzene proved to be compatible, including phenyl, alkyl, methoxy, hydroxyl, and amino (**1b–j**, Table 2, entries 2–10). The ability of substituted bromobenzene to participate in the reaction opens the possibility for dimerization of heteroaromatic compounds. Bromopyridine and substituted bromopyridine can also be used in the reaction (**1k**,**l**, Table 2, entries 11 and 12). The use of brominated aromatic compounds bearing groups at different positions gave different yields. Brominated aromatic compounds substituted in the *para* position were prone to produce desired products of self-coupling. Moreover, brominated aromatic compounds substituted in the *para* position produced the desired products more easily than compounds substituted in the *meta* position. When the substituents were in the *meta* position, the coupling reaction was not prone to occur, and resulted in a 7.4% yield of **1j** (Table 2, entry 10). Nevertheless, when the substituent was a carboxyl group, the coupling products could not be observed and debromination occurred, such as **1o**,**p** (Table 2, entries 15 and 16). Surprisingly, the yields of debromination were above 90%. On the contrary, after the esterification of carboxyl groups, the desired self-coupling product was obtained (**1m**, Table 2, entry 13). A plausible explanation for this difference was the kinetic competition between the hydrogen source and the borate

Table 1 Identification of the Reaction Conditions



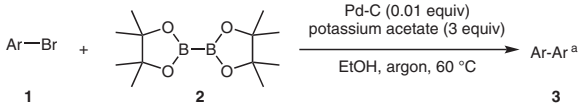
1a **2** **3a**

Entry	Molar Ratio (**1a:2**)	Solvent	Base	Catalyst	Temp (℃)	Yield (%)[a]
1	1:0.1	MeCN	MeCOOK	Pd-C	60	9.2
2	1:0.5	MeCN	MeCOOK	Pd-C	60	20.3
3	1:1	MeCN	MeCOOK	Pd-C	60	56.8
4	1:1.5	MeCN	MeCOOK	Pd-C	60	87.2
5[b]	1:1.5	MeCN	MeCOOK	Pd-C	AT[b]	–
6[c]	1:1.5	MeCN	MeCOOK	Pd-C	80	86.0
7	1:1.5	EtOH	MeCOOK	Pd-C	60	98.7
8	1:1.5	DMSO	MeCOOK	Pd-C	60	45.6
9	1:1.5	EtOH	Et_3N	Pd-C	60	60.3
10	1:1.5	EtOH	Na_2CO_3	Pd-C	60	70.0
11	1:1.5	EtOH	$NaHCO_3$	Pd-C	60	71.7
12[c]	1:1.5	EtOH	MeCOOK	$PdCl_2$(dppf)	60	–
13[c]	1:1.5	EtOH	MeCOOK	$Pd(PPh_3)_4$	60	–

[a]Isolated yield with column chromatography.
[b]AT = ambient temperature.
[c]Almost no reactions were observed by TLC.

ester undergoing transmetalation. The proton was not conducive to the formation of boronate ester intermediates, resulting in debromination. Additionally, the coupling activity of bromobenzyl (**1n**, Table 2, entry 14) was also very high and afforded 1,2-diphenylethane in 78% yield. The formation of benzylboronic acid pinacol ester (**3q**, Figure 2) proved that bromobenzyl underwent the same mechanism leading to 1,2-diphenylethane.

Table 2 Scope with Respect to Substituted Aromatic Compounds



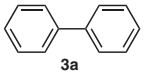
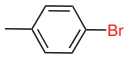
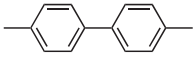
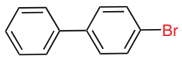
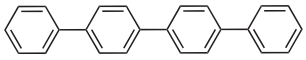
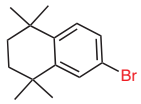
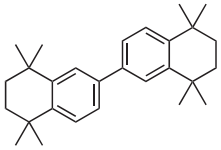
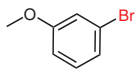
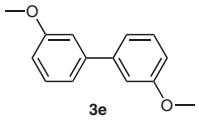
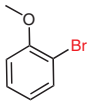
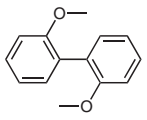
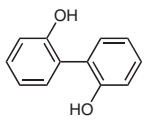
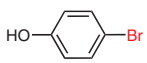
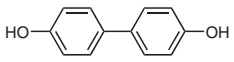
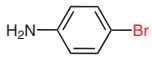
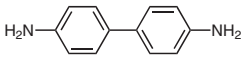
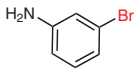
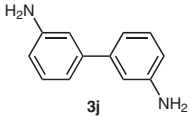
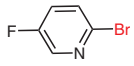
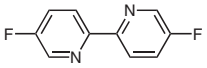
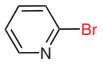
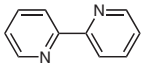
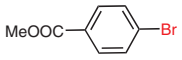
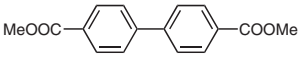
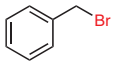
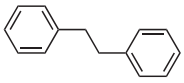
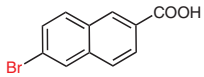
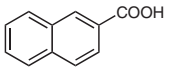
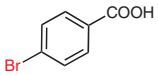
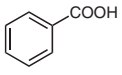
Entry	Substrate	Products	Time (h)	Yield (%)[b]
1	 **1a**	 **3a**	6	98.7
2	 **1b**	 **3b**	12	98.1
3	 **1c**	 **3c**	5	30.3
4	 **1d**	 **3d**	8	50.0
5	 **1e**	 **3e**	3	66.7
6	 **1f**	 **3f**	3	87.7
7	 **1g**	 **3g**	12	75.5
8	 **1h**	 **3h**	12	90.0
9	 **1i**	 **3i**	8	94.3

Table 2 (continued)

Entry	Substrate	Products	Time (h)	Yield (%)[b]
10	 1j	 3j	8	7.4
11	 1k	 3k	18	98.2
12	 1l	 3l	12	41.8
13	 1m	 3m	8	48.4
14	 1n	 3n	3	78.0
15[c]	 1o	 3o	6	98.8
16[c]	 1p	 3p	7	93.3

[a]Unless otherwise noted, the product was dimeric.
[b]Isolated yield with column chromatography.
[c]The self-coupling target products were not observed and debromination occurred.

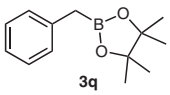
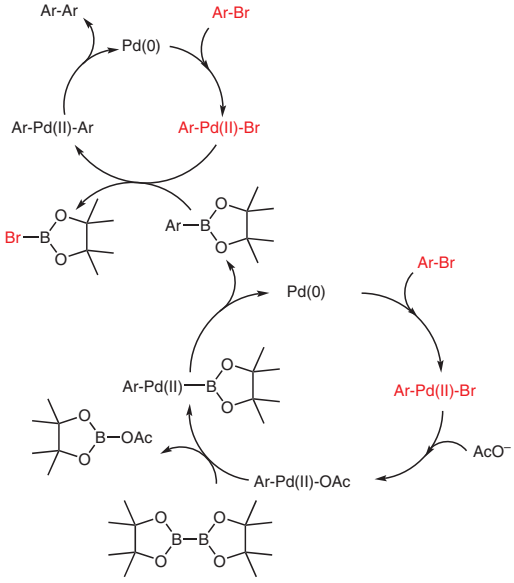

3q

Figure 2 The intermediate of benzylboronic acid pinacol ester

The mechanism of the self-coupling is analogous to the catalytic cycle for the other cross-coupling reactions and has four distinct steps:[12] 1) oxidative addition of an organic halide to the Pd(0) species to form Pd(II); 2) exchange of the anion attached to the palladium for the anion of the base (metathesis); 3) transmetalation between Pd(II) and the alkylborate complex; and 4) reductive elimination to form the C–C σ bond and regeneration of Pd(0). Certainly, the brominated aromatic compounds reacted with bis(pinacolate)diboron which underwent two cycles resulting in self-coupling products (Scheme 1). The main processes are as follows: a molecule of brominated aromatic compound coupled with bis(pinacolate)diboron and formed an arylborate complex. Then the intermediate coupled with another molecule of the aryl-palladium(II)–bromine complex resulting in the aromatic dimer.

In summary, we have developed a catalytic system for the dimerization of brominated aromatic compounds that utilizes readily available brominated aromatic compounds and related heteroaromatic compounds. This protocol proposes an inexpensive catalyst of palladium-carbon in C–C bond construction and provides some examples of dimerization of brominated aromatic compounds using readily available starting materials under mild reaction conditions. This reaction allows the conversion of simple starting materials into complex aromatic compounds, which are important synthetic intermediates in organic synthesis. The key to this discovery was the identification of a cheap catalyst of palladium-carbon that can be used to synthesize the aromatic dimer compounds by a 'one-pot' method. To our delight, some substituted brominated aromatic compounds



Scheme 1 The mechanism of the catalytic cycle

showed a good functional group tolerance with moderate to high yields. However, reactions with some special substrates such as aromatic carboxylic acids did not produce the target products of self-coupling, but resulted in debromination in very high yields. Efforts to apply our palladium-carbon system to other catalytic dimerization reactions and to expand the scope of the dimerization of aromatic compounds to other classes of aromatic compounds are currently under way in our laboratory.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591892.

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(22) **General Procedure**
To a solution of brominated aromatic compounds (1 equiv), bis(pinacolate)diboron (1.5 equiv), and anhydrous ethanol (15 mL) was added palladium-carbon (0.01 equiv), followed by potassium acetate (3 equiv) under argon. The mixture was heated to 60 °C with stirring for the indicated time. The reactor was cooled to room temperature, and the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was extracted with dichloromethane (3 × 20 mL), and the organic layer was washed with water (2 × 20 mL) and once with brine (25 mL), dried over magnesium sulfate and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether as eluent.
Biphenyl (3a)
Yield 0.97 g, 98.7%; pale solid; mp 69–71 °C (lit.[21a] mp 69–71 °C); R_f = 0.23 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (t, *J* = 1.24 Hz, 2 H), 7.44 (t, *J* = 7.20 Hz, 2 H), 7.34 (t, *J* = 7.36 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.2, 128.7, 127.2, 127.1. GC–MS: *m/z* = 154.2.
4,4′-Dimethyl-1,1′-biphenyl (3b)
Yield 0.52 g, 98.1%; white solid; mp 125 °C (lit.[21b] mp 125 °C);

R_f = 0.50 (PE). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.68 Hz, 2 H), 7.24 (d, J = 8.22 Hz, 2 H), 2.38 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.3, 136.7, 129.4, 126.8, 21.1. GC–MS: m/z = 182.2.

Benzerythrene (3c)

Yield 0.20 g, 30.3%; white solid; mp > 300 ℃ (lit.[21c] mp 315–318 °C); R_f = 0.57 (EtOAc/PE = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.37 (m, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.7, 140.3, 139.6, 128.8, 127.6, 127.5, 127.1. GC–MS: m/z = 306.2.

5,5,5′,5′,8,8,8′,8′-Octamethyl-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-binaphthalene (3d)

Yield 0.35 g, 50.0%; colorless oily liquid; R_f = 0.41 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 2 H), 7.48–7.32 (m, 4 H), 1.73 (s, 8 H), 1.35 (d, J = 5.08 Hz, 24 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.9, 143.5, 138.9, 126.7, 125.3, 124.5, 35.2, 35.1, 34.3, 34.1, 31.9, 31.8. GC–MS: m/z = 374.3.

3,3′-Dimethoxy-1,1′-biphenyl (3e)

Yield 0.38 g, 66.7%; colorless oily liquid (lit.[21d] mp 36 ℃); R_f = 0.57 (EtOAc/PE = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.86 Hz, 2 H), 7.17–7.15 (m, 2 H), 7.11 (t, J = 2.22 Hz, 2 H), 6.88–6.86 (m, 2 H), 3.81 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 142.6, 129.7, 119.7, 112.9, 112.8, 55.2. GC–MS: m/z = 214.2.

2,2′-Dimethoxy-1,1′-biphenyl (3f)

Yield 0.50 g, 87.7%; white solid; mp 154–155 °C (lit.[21e] mp154–155 ℃); R_f = 0.60 (EtOAc/PE = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 2 H), 7.26–7.02 (m, 2 H), 7.00 (q, J_1 = 7.44 Hz, J_2 = 6.60 Hz, 4 H), 3.77 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.0, 131.4, 128.6, 127.8, 120.3, 111.1, 55.7. ESI-MS: m/z [M + H]$^+$ = 215.1.

2,2′-Biphenol (3g)

Yield 0.41 g, 75.5%; colorless oily liquid (lit.[21f] mp 50 °C); R_f = 0.35 (EtOAc/PE = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.33 (m, 2 H), 7.30 (d, J = 1.36 Hz, 1 H), 7.10–7.05 (q, J_1 = 1.00 Hz, J_2 = 8.64 Hz, 4 H), 5.40 (br, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.0, 130.6, 129.2, 122.9, 120.9, 115.9. ESI-MS: m/z [M + H]$^+$ = 184.9.

4,4′-Biphenol (3h)

Yield 0.86 g, 90.0%; white solid; mp 283 ℃ (lit.[21g] mp 282–284 ℃); R_f = 0.50 (EtOAc/PE = 1:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.38 (s, 2 H), 7.37 (d, J = 8.52 Hz, 4 H), 6.79 (d, J = 8.52 Hz, 4 H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 155.7, 130.5, 126.3, 115.0. ESI-MS: m/z [M + H]$^+$ = 184.9.

4,4′-Bianiline (3i)

Yield 0.50 g, 94.3%; brown solid; mp 117–119 °C (lit.[21h] mp 80 ℃); R_f = 0.15 (EtOAc/PE = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.8 Hz, 4 H), 6.74 (d, J = 7.8 Hz, 4 H), 3.67 (s, 4 H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 146.2, 128.0, 125.4, 113.7. ESI-MS: m/z [M + H]$^+$ = 185.1.

3,3′-Diaminobiphenyl (3j)

Yield (40 mg, 7.4%); brown solid; mp 89–90 °C (lit.[21i] mp 93 ℃); R_f = 0.26 (EtOAc/PE = 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.16 (q, J_1 = 8.32 Hz, J_2 = 16.08 Hz, 2 H), 6.95 (d, J = 7.64 Hz, 2 H), 6.84 (s, 2 H), 6.64–6.62 (q, J_1 = 1.44 Hz, J_2 = 7.88 Hz, 2 H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 135.5, 133.7, 131.5, 115.4, 115.3, 112.7. ESI-MS: m/z [M+H]$^+$ = 185.1.

5,5′-Difluoro-2,2′-bipyridine (3k)

Yield 0.54 g, 98.2%; off-white solid; mp 153–154 °C (lit.[21j] mp 153–154 ℃); R_f = 0.87 (EtOAc/PE = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50 (d, J = 2.34 Hz, 2 H), 8.39 (dd, J_1 = 4.38 Hz, J_2 = 8.76 Hz, 2 H), 7.54–7.51 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.7, 159.0, 151.4, 151.42, 137.3, 137.1, 123.9, 123.8, 122.3, 122.2. GC-MS: m/z = 192.2.

2,2′-Bipyridine (3l)

Yield 0.41 g, 41.8%; white solid; mp 72 °C (lit.[21k] mp 71–72 ℃); R_f = 0.27 (EtOAc/PE = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 (d, J = 4.26 Hz, 2 H), 8.44 (d, J = 7.86 Hz, 2 H), 7.85 (t, J = 7.62 Hz, 2 H), 7.34 (t, J = 5.4 Hz, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.0, 149.1, 137.1, 123.8, 121.2. ESI-MS: m/z [M + H]$^+$ = 157.1.

4,4′-Bis(methoxycarbonyl)biphenyl (3m)

Yield 0.30 g, 48.4%); white solid; mp 224 °C (lit.[21l] mp 224 ℃); R_f = 0.56 (EtOAc/PE = 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.36 Hz, 4 H), 7.72 (q, J_1 = 8.40 Hz, J_2 = 1.60 Hz, 4 H), 3.97 (s, 6 H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 167.4, 143.7, 130.4, 129.1, 127.8, 52.7. GC–MS: m/z = 270.2.

1,2-Diphenylethane (3n)

Yield 0.83 g, 78.0%; white solid; mp 48–50 °C (lit.[21m] mp 48–50 ℃); R_f = 0.37 (EtOAc/PE = 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 5 H), 7.20 (m, 5 H), 2.92 (s, 4 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.3, 125.9, 37.9. GC–MS: m/z = 182.2.

2-Naphthoic Acid (3o)

Yield 0.68 g, 98.8%; white solid; mp 174–180 °C (lit.[21n] mp 180–183 ℃); R_f = 0.57 (EtOAc/PE/AcOH = 1:3:0.2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 8.15 (d, J = 8.52 Hz, 1 H), 8.02 (d, J = 8.16 Hz, 1 H), 7.93 (t, J = 9.18 Hz, 2 H), 7.66–7.58 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.9, 136.0, 132.4, 132.2, 129.6, 128.7, 128.4, 127.8, 126.8, 126.4, 125.4. ESI-MS: m/z [M – H]$^-$ = 170.9.

Benzoic Acid (3p)

Yield 0.47 g, 93.3%; white solid; mp 120–121 °C (lit.[21o] mp 119–121 ℃); R_f = 0.60 (EtOAc/PE = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.13 (dd, J_1 = 1.02 Hz, J_2 = 8.10 Hz, 2 H), 7.63–7.61 (m, 1 H), 7.49 (t, J = 7.68 Hz, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.4, 133.8, 130.2, 129.3, 128.5. ESI-MS: m/z [M – H]$^-$ = 120.9.