Supplementary Information for
**One-Pot Preparation of Arylalkynes by a Tandem Catalytic
Iodination of Arenes and Palladium-Catalyzed Coupling of
Iodoarenes with Terminal Alkynes**

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General: Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification.

Instrumentation:

- ¹H NMR spectra and ¹³C NMR spectra were recorded on a 400MHz NMR system in CDCl₃ solvent with TMS internal standard unless otherwise specified.
- TLC was run on 2cm×5cm silica plate. Column chromatography was run on silica gel (300-400 mesh).
- GC analysis was performed on a GC112A Gas-Chromatograph. The capillary column used is ALPHA-CoI (30QC3/AC1 0.25).
- Elemental analysis, EI-MS and HRMS were performed at the Shanghai Institute of Organic Chemistry, Chinese Academic of Science.
- Melting points were measured with Microscopic Melting-point Detector.

Iodination of Arenes: General procedure for oxidative iodination of arenes catalyzed by BNP-BiCl₃ in MeCN. Anisole (108.2 mg, 1.0 mmol), I₂ (126.9mg, 0.5 mmol), BNP (12.1 mg, 0.025 mmol, 2.5 mol %), BiCl₃ (7.8 mg, 0.025 mmol, 2.5 mol %), MeCN (1.0 mL) and a magnetic stir bar were placed in a dried flask. The mixture was stirred at room temperature for desired time or until complete consumption of starting material detected by TLC and GC analysis. Then the reaction mixture was desorbed by dichloromethane (3 × 10 mL). The organic extracts were successively washed with aq. Na₂S₂O₃ solution, dried over anhydrous MgSO₄ and then evaporated under reduced pressure. The crude product was purified by column chromatography over silica to furnish the pure iodides.

Table 1 Effects of catalysts^a

$2\text{MeO}-\text{C}_6\text{H}_4 + \text{I}_2 + 1/2\text{O}_2(\text{Air}) \xrightarrow[\text{MeCN, r.t.}]{\text{Cat.}} 2\text{MeO}-\text{C}_6\text{H}_4\text{I} + \text{H}_2\text{O}$				
Entry	Catalyst	Amount (mol%)	Time (h)	Yield (%) ^b
1	BNP	5	15	80
			26	92
			18	89 ^c
			26	99 ^c
2	BNP	2.5	24	60
3	Fe(NO ₃) ₃	5	24	51
			48	73
4	Cu(NO ₃) ₂	5	24	35
5	BiCl ₃	5	24	Trace
6	Bi ₂ O ₃	5	24	Trace
7	CuCl ₂	5	24	Trace
8	Cu(OAc) ₂	5	24	Trace
9	K ₂ S ₂ O ₈	5	24	Trace
10	KMnO ₄	5	24	Trace
11	BNP+ZnCl ₂	2.5/2.5	24	70
12	BNP+BiCl ₃	2.5/2.5	6	90
13	BNP+BiCl ₃	0.4/0.4	12	87
14	No catalyst		24	Trace
15	NaNO ₃	5	24	6

^a Conditions: anisole (1.0 mmol), iodine (0.5 mmol), catalyst (5.0 mol%), MeCN (1.0 mL), air, r.t. ^b GC yield. ^c 1.0 atm O₂.

Table 2 Effects of solvents^a

$2\text{MeO}-\text{C}_6\text{H}_4 + \text{I}_2 + 1/2\text{O}_2(\text{Air}) \xrightarrow[\text{Solvent, r.t.}]{\text{Cat.BNP-BiCl}_3} 2\text{MeO}-\text{C}_6\text{H}_4\text{I} + \text{H}_2\text{O}$			
Entry	Solvent	Time (h)	Yield (%) ^b
1	CH ₂ Cl ₂	6(24)	71(97)
2	CH ₂ ClCH ₂ Cl	6(30)	70(98)
3	HOAc	6(24)	82(99)
4	MeCN	6	90

^a Conditions: anisole (1.0 mmol), iodine (0.5 mmol), BNP (0.025 mmol), BiCl₃ (0.025 mmol), solvent (1.0 mL), air, 6h, r. t. ^b GC yield.

One-Pot Preparation of Arylalkynes by a Tandem Catalytic Iodination of Arenes and Palladium-Catalyzed Coupling of Iodoarenes with Terminal Alkynes:

For activated arenes: Anisole (108.2 mg, 1.0 mmol), I₂ (126.9mg, 0.5 mmol), BNP (12.1 mg, 0.025 mmol, 2.5 mol %), BiCl₃ (7.8 mg, 0.025 mmol, 2.5 mol %), MeCN (1.0 mL) and a magnetic stir bar were placed in a dried flask. The mixture was stirred at room temperature for desired time or until complete consumption of starting material detected by TLC and GC analysis. Then, piperidine (0.5 mL, 5 mmol), PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol, 2.5 mol %) and terminal acetylene (1.0 mmol) were added into the reaction flask. The reaction flask with stirring bar was sealed and heated in an oil bath pre-heated at 70°C until completion of the coupling reaction (3 h). After cooling to room temperature, water and dichloromethane (3 × 10 mL) were added to the mixture and the organic material was extracted and then it was washed with acid (15% v/v HCl) until the washings were neutral. The organic layer was washed with water (40 mL) again before being dried over MgSO₄. Finally, the dichloromethane was removed under reduced pressure to obtain the crude product, which was purified by column chromatography.

For benzene: Benzene (78.0 mg, 0.51 mmol), silver triflate (256.7 mg, 1.0 mmol), iodine (253.8 mg, 1.0 mmol), CH₂ClCH₂Cl (1.0 mL) and a magnetic stir bar in a darkened flask. The mixture was stirred at room temperature for 5 min until complete consumption of starting material detected by TLC and GC analysis. Then, piperidine (0.5 mL, 5 mmol), PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol, 2.5 mol %) and terminal acetylene (1.0 mmol) were added into the reaction flask. The reaction flask was sealed and heated in an oil bath pre-heated at 70°C until completion of the coupling reaction (3 h). After cooling to room temperature, water and dichloromethane (3 × 10 mL) were added to the mixture and the organic material was extracted and then it was washed with acid (15% v/v HCl) until the washings were neutral. The organic layer was washed with water (40 mL) again before being dried over MgSO₄. Finally, the dichloromethane was removed under reduced pressure to obtain the crude product, which was purified by column chromatography.

Characterization of the products:

4-iodo-1-methoxybenzene (2a)¹: white crystal. m.p.: 52-53°C.

¹H NMR (400 MHz) (CDCl₃): δ 3.78 (s, 3H), 6.68 (d, *J* = 9.2Hz, 2H), 7.56 (d, *J* = 9.2Hz, 2H).

1-butoxy-4-iodobenzene (2b): liquid

¹H NMR (400 MHz) (CDCl₃): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.47 (m, 2H), 1.75 (m, 2H), 3.91 (t, *J* = 6.2 Hz, 2H), 6.67 (d, *J* = 9.2Hz, 2H), 7.53 (d, *J* = 9.2Hz, 2H).

¹³C NMR (100 MHz) (CDCl₃): δ 14.1, 19.4, 31.4, 68.0, 82.6, 117.1, 138.3, 159.2.

EI-MS *m/z*: 275 (M⁺, 43.07), 220 (100).

HRMS: Calc. for C₁₀H₁₃OI: 276.0011. Found: 276.0015.

1-iodo-4-methoxynaphthalene (2c)¹: white crystal. m.p.: 52-53°C.

¹H NMR (400 MHz) (CDCl₃): δ 3.99 (s, 3H), 6.60 (d, *J* = 8 Hz, 1H), 7.52 (td, *J*₁ = 7.3 Hz, *J*₂ = 0.9 Hz, 1H), 7.58 (td, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H).

2-ethoxy-1-iodonaphthalene (2d): white crystal. m.p.: 76°C.

¹H NMR (400 MHz) (CDCl₃): δ 2.31 (t, *J* = 6.8 Hz, 3H), 4.26 (q, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.407 (td, *J*₁ = 8.6 Hz, *J*₂ = 0.9 Hz, 1H), 7.553 (td, *J*₁ = 8 Hz, *J*₂ = 0.9 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H).

¹³C NMR (100 MHz) (CDCl₃): δ 15.4, 66.3, 89.1, 114.7, 124.6, 128.2, 128.4, 130.2, 130.4, 131.6, 135.9, 156.4.

Anal. Calcd for C₁₂H₁₁OI: C, 48.35; H, 3.72. Found: C, 48.71; H, 3.99.

4-iodo-1-methoxy-2-methylbenzene (2e)²: white crystal. m.p.: 79-80°C.

¹H NMR (400 MHz) (CDCl₃): δ 2.16 (s, 3H), 3.80 (s, 3H), 6.58 (d, *J* = 8 Hz, 1H), 7.44 (m, 2H).

2-iodo-1-methoxy-4-methylbenzene (2f)³: liquid

¹H NMR (400 MHz) (CDCl₃): δ 2.26 (s, 3H), 3.85 (s, 3H), 6.72 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.2, 2.8 Hz, 1H), 7.61 (d, *J* = 2.8 Hz, 1H).

1-iodo-2,4-dimethylbenzene (2g)⁴: liquid.

¹H NMR (400 MHz) (CDCl₃): δ 2.26 (s, 3H), 2.38 (s, 3H), 6.69 (d, *J* = 8 Hz, 1H), 7.06 (s, 1H), 7.66 (d, *J* = 8 Hz, 1H).

2-iodo-1,3,5-trimethylbenzene (2h)⁵: white crystal. m.p.: 30-31°C.
¹H NMR (400 MHz) (CDCl₃): δ 2.24 (s, 3H), 2.43 (s, 6H), 6.89 (s, 2H).

3-iodo-1,2,4,5-tetramethylbenzene (2i)⁶: white crystal. m.p.: 80-81°C.
¹H NMR (400 MHz) (CDCl₃): δ 2.31 (s, 6H), 2.44 (s, 6H), 6.89 (s, 1H).

1-methoxy-4-(phenylethynyl)benzene (4a)⁷: white crystal. m.p.: 58-59°C.
¹H NMR (400 MHz) (CDCl₃): δ 3.84 (s, 3H), 6.88 (d, *J* = 9.2 Hz, 2H), 7.32-7.34 (m, 3H), 7.46-7.52 (m, 4H).

1,2-bis(4-methoxyphenyl)ethyne (4b)⁸: white crystal. m.p.: 147-148°C.
¹H NMR (400 MHz) (CDCl₃): δ 3.81 (s, 6H), 6.86 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.8 Hz, 4H);

1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene (4c): liquid
¹H NMR (400 MHz) (CDCl₃): δ 3.80 (s, 6H), 3.83 (s, 3H), 6.45 (t, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 2H), 6.88 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 2H), 7.47 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 2H);
¹³C NMR (100 MHz) (CDCl₃): δ 55.5, 55.6, 88.3, 89.2, 101.8, 109.4, 114.2, 115.4, 125.1, 133.3, 159.9, 160.7.
 EI-MS *m/z*: 268 (M⁺, 100), 253 (19).
 HRMS: Calc. for C₁₇H₁₆O₃: 268.1099. Found: 268.1093.

6-(4-methoxyphenyl)hex-5-yn-1-ol (4d): liquid.

^1H NMR (400 MHz) (CDCl_3): δ 1.71 (m, 4H), 2.44 (t, $J = 6.8$ Hz, 2H), 3.71 (t, $J = 6.4$ Hz, 2H), 3.79 (s, 3H), 6.81 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.4$ Hz, 2H), 7.32 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 2H);

^{13}C NMR (100 MHz) (CDCl_3): δ 19.4, 25.3, 32.1, 55.5, 62.7, 80.9, 88.4, 114.0, 116.2, 133.1, 159.2.

EI-MS m/z : 204 (M^+ , 19), 145 (63), 121 (100).

HRMS: Calc. for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150. Found: 204.1156.

1-methoxy-4-((4-pentylphenyl)ethynyl)benzene (4e): white crystal. m.p.: 44-45°C.

^1H NMR (400 MHz) (CDCl_3): δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.31 (m, 4H), 1.61 (m, 2H), 2.60 (t, $J = 7.6$ Hz, 2H), 3.83 (s, 3H), 6.92 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.5$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.42 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 2H), 7.46 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H);

^{13}C NMR (100 MHz) (CDCl_3): δ 14.3, 22.8, 31.2, 31.9, 36.1, 55.5, 88.4, 88.9, 114.2, 115.8, 120.9, 128.7, 131.6, 133.2, 143.3, 159.7.

EI-MS m/z : 278 (M^+ , 66), 221 (100).

HRMS: Calc. for $\text{C}_{20}\text{H}_{22}\text{O}$: 278.1671. Found: 278.1674.

4-((4-methoxyphenyl)ethynyl)-N,N-dimethylbenzenamine (4f): white crystal. m.p.: 135-136°C.

^1H NMR (400 MHz) (CDCl_3): δ 2.98 (s, 6H), 3.82 (s, 3H), 6.66 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H);

^{13}C NMR (100 MHz) (CDCl_3): δ 40.5, 55.5, 87.3, 89.3, 110.6, 112.1, 114.1, 116.5, 132.8, 132.9, 150.1, 159.3.

EI-MS m/z : 251 (M^+ , 100), 236 (58).

HRMS: Calc. for $\text{C}_{17}\text{H}_{17}\text{NO}$: 251.1310. Found: 251.1311.

1-methoxy-4-((oct-1-ynyl)benzene (4g)⁹: liquid.

^1H NMR (400 MHz) (CDCl_3): δ 0.90 (t, 3H), 1.29 (m, 6H), 1.44 (m, 2H), 2.38 (t, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 6.81 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 7.33 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H);

^{13}C NMR (100 MHz) (CDCl_3): δ 14.3, 19.7, 22.8, 28.9, 29.1, 31.6, 55.4, 80.4, 89.0, 114.0, 116.5, 133.1, 159.1.

1-methoxy-2-methyl-4-(phenylethynyl)benzene (4h): light yellow crystal. m.p.: 88-89°C.

^1H NMR (400 MHz) (CDCl_3): δ 2.21 (s, 3H), 3.85 (s, 3H), 6.79 (d, $J = 8.4$ Hz, 1H), 7.33 (m, 5H), 7.51 (d, $J = 8.4$ Hz, 2H);

^{13}C NMR (100 MHz) (CDCl_3): δ 16.4, 55.6, 88.0, 89.9, 110.0, 115.0, 123.9, 127.1, 128.1, 128.5, 130.8, 131.7, 134.1, 158.2.

EI-MS m/z : 222 (M^+ , 100), 207 (64), 178 (40).

HRMS: Calc. for $\text{C}_{16}\text{H}_{14}\text{O}$: 222.1045. Found: 222.1042.

1, 2-diphenylethyne (4i)¹⁰: white crystal. m.p.: 63-64°C.

^1H NMR(400 MHz) (CDCl_3): δ 7.33-7.37 (m, 6H), 7.53-7.55 (m, 4H).

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8.242
8.221

8.028
8.007
7.961
7.940

7.603
7.583
7.565
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