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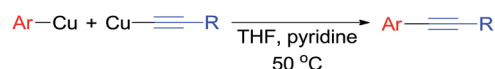
External oxidant-free cross-coupling of arylcopper and alkynylcopper reagents leading to arylalkyne†

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External oxidant-free oxidative cross-coupling between arylcopper and alkynylcopper has been performed, which provides a new way for the formation of arylalkyne with high selectivity.

Introduction

Arylalkynes are useful building blocks in organic synthesis as well as basic functional groups in various bioactive compounds and natural products.¹ The most common approach to arylalkynes is transition-metal-catalyzed cross-coupling reaction such as Sonogashira reaction² or Stille reaction³ between arylhalides and terminal alkynes or alkynyltin compounds. Recently, the oxidative cross-coupling reaction has been considered as a convenient method to synthesize arylalkynes under mild conditions utilizing various transition metals as catalysts in the presence of oxidants.⁴ Although this reaction provides a straightforward strategy for the synthesis of the unsymmetrical alkynes, realizing oxidative cross-coupling between arylmetal and alkylmetal in high efficiency with oxidants is still difficult since potential side reactions such as homo-coupling of the arylmetals or the alkylmetals as well as direct reaction between organometallic reagents and oxidants. During the course of our study on the carbon-carbon bond formation utilizing alkynylcoppers,⁵ we found a direct cross-coupling of alkynylcopper and arylcopper reagents to afford arylalkynes with excellent selectivity without external oxidant, which possibly underwent disproportionation mechanism and was worthy of investigation (Scheme 1).



Scheme 1 Direct coupling reaction of organocoppers.

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Results and discussion

Initially, we used phenylcopper **2a** generated from phenyl magnesium **1a** with CuCl·2LiCl salts⁶ and (phenylethynyl) copper **3a** as starting materials. Reaction of **2a** and **3a** in the THF solvent at room temperature for 12 h afforded **4aa** in 5% yield (Table 1, entry 1). During the reaction, we noticed the reaction mixture was a slurry. Therefore, we tried to add some additives such as hexamethyl-phosphoramide (HMPA), tetramethylethylenediamine (TMEDA), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), 4-dimethylaminopyridine (DMAP) and pyridine, respectively in the vessel to improve the solubility of

Table 1 Initial optimization studies^a

Entry	Temp (°C)	Additive	Yield [%] of 4aa ^b
1	rt	—	5
2	rt	HMPA	Trace
3	rt	TMEDA	Trace
4	rt	DBU	Trace
5	rt	DMAP	Trace
6	rt	Pyridine	18
7	50	Pyridine	85 (75)
8	67	Pyridine	72
9	80	Pyridine	70
10 ^c	50	Pyridine/DDQ	Trace
11 ^c	50	Pyridine/DCE	9
12 ^c	50	Pyridine/DBE	6

^a Reaction conditions: phenylcopper **2a** prepared *in situ* from the corresponding phenylmagnesium bromide **1a** (0.50 mmol, 1.0 M in THF, 1.0 mL) with the 0.6 mL 1 M CuCl·2LiCl in THF-solution; (phenylethynyl)copper **3a** (0.5 mmol, 82 mg), N₂, 12 h. ^b GC yield, yield based on n-dodecane, isolated yield was given in parenthesis. ^c Diphenyl was obtained around in 60% GC yield.



Table 2 Coupling of arylcopper **2b**^a with various alkynylcopper reagents

Entry	Alkynylcopper reagent	Alkyne	Yield ^b (%)
1			73
2			62
3			72
4			63
5			75
6			66
7			58
8			42

^a The (3-methoxyphenyl)copper **2b** was prepared *in situ* from (3-methoxyphenyl)magnesium bromide **1a** (0.50 mmol, 1.0 M in THF, 1.0 mL) with the 0.6 mL 1 M CuCl·2LiCl in THF-solution. ^b Isolated yields.

organometallic reagents (entries 2–6). Only pyridine was found to enhance the yield to 18% (entry 6). The reaction was screened in different temperature (entries 6–9) and we found that when the reaction was treated at 50 °C, the product **4aa** was formed in 75% isolated yield (entry 7). In the above reactions, the homo-coupling products have not been obtained and copper mirror on the wall of the reaction vessel was observed.

Theoretically, oxidative coupling of two organometallic reagents forming C–C bond, the oxidants are definitely necessary to take away two redundant electrons from organometallics. Therefore, dichloroethane (DCE), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and dibromoethane (DBE) were examined as the oxidants under the same reaction conditions. In each case, trace product **4aa** and homo-coupling product diphenyl was detected in GC-MS (entries 10–12). Compared with oxidative cross-coupling reaction in the presence of external oxidant, our reaction may take place through an intermolecular disproportionation of arylcopper and alkynylcopper. The formation of copper mirror on the wall of the reaction vessel further confirmed the intermolecular disproportionation.

Table 3 Oxidative coupling of various arylcopper **2**^a with alkynylcopper reagent **3**

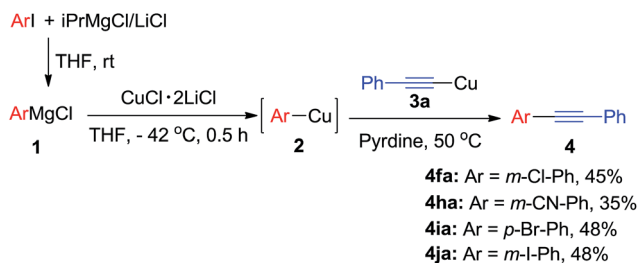
Entry	Grignard reagent	Alkyne	Yield ^b (%)
1			66
2			70
3			78
4			45
5			44
6			35

^a The arylcopper reagent **2** was prepared *in situ* from the corresponding arylmagnesium halide **1** (0.50 mmol) with the CuCl·2LiCl in THF-solution. ^b Isolated yields.

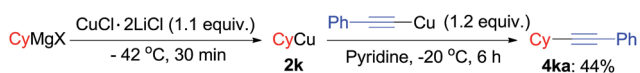
Under the optimized conditions, the experiments about functional-group compatibility were carried out. Firstly, aryl substituted alkynylcoppers **3** including phenyl, 4-chlorophenyl, 4-fluorophenyl, 4-methylphenyl, and thiophen-3-yl groups were used to react with (3-methoxyphenyl)copper **2b** and a range of alkynes **4** were obtained in good yields (entries 1–5). Then, we tried (cyclohex-1-en-1-ylethynyl)copper **3f** and desired product **4bf** was obtained in 66% yield. Furthermore, employment of hex-1-yn-1-ylcopper **3g** and (5-chloropent-1-yn-1-yl)copper **3h** also afforded product **4bg** and **4bh** in 58% and 42% yields, respectively.

To establish the full scope of the reaction, compatibility of various arylcoppers in cross coupling reaction was studied. The

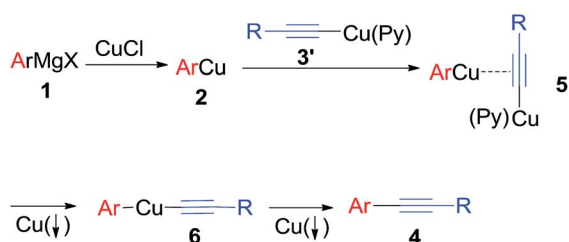




Scheme 2 Use of PhMgCl prepared by I/Mg exchange with iPrMgCl.



Scheme 3 Cross-coupling between alkylcopper and alkynylcopper.



Scheme 4 Plausible reaction mechanism.

representative results are summarized in Table 3. The reaction generally lead to satisfactory yields with electron-rich arylcoppers (entries 1–3). While arylcoppers bearing electron-poor groups such as Cl, CO₂Me, and CN afforded the corresponding alkyne in diminished yields (entries 4–6) as well as formation of undesired self-coupling product from arylcoppers. Notably, the reaction seemed no sensitive to steric hindrance and the results as shown in Table 2 (entry 1) and Table 3 (entries 2–3).

Arylmagnesium reagents are sensitive, which can be generated from aryl halides *in situ*. From practical point of view, aryl halides could be converted into the corresponding arylmagnesium reagents (**1f**, **1h**, **1i**, and **1j**) by iodine/magnesium exchange from iodoarenes and iPrMgCl·LiCl.⁷ It was then transmetalated with CuCl·2LiCl (in THF solution) to give the corresponding arylcopper reagents, which was treated subsequently with the compound **3a** to generate the alkyne (**4fa**, **4ha**, **4ia**, and **4ja**) (Scheme 2), respectively.

We also tried to use alkylcopper reagents in the reaction. As an example, reaction of cyclohexylcopper with alkynylcopper in the presence of pyridine at –20 °C for 6 h and product **4ka** was isolated in 44% (Scheme 3) as well as bicyclohexane was detected in GC-MS.

Based on the above results, a possible mechanism for the oxidative cross-coupling of an arylmagnesium and an alkynylcopper is proposed in Scheme 4. First, transmetalation of arylmagnesium compound **1** with CuCl yields arylcopper **2**. An alkynylcopper **3'** in the presence of pyridine coordinates to the

copper of the arylcopper **2** to form intermediate **5**, which undergoes disproportionation reaction leading to intermediate **6** and formation of copper powder. Finally, reductive elimination yields the desired cross-coupling product **4** with concomitant precipitation of another molecular copper powder from the reaction mixture.

Conclusions

We have reported a new oxidative coupling of the arylcopper and alkynylcopper, which provides a complementary way for formation of arylalkyne. It is the first procedure for oxidative cross-coupling of two different organocopper reagents without external oxidant.

Experimental section

General procedure for preparation of alkynylcopper reagents

Alkynylcopper reagents were prepared according to literature reported.⁸ To round-bottom flask equipped with a magnetic stirrer were added CuSO₄·5H₂O (2.5 g, 10 mmol), 100 mL H₂O, 10 mL 28% aqueous ammonia and 1.4 g NH₂OH·HCl (1.4 g, 20 mmol), and the solution was cooled to 0 °C. Then terminal alkyne (10 mmol) dissolved in 60 mL EtOH was added. Yellow precipitation appeared immediately and the mixture was stirred vigorously for 5 min, followed by filtration. The solid was washed with H₂O (15 mL × 2), EtOH (15 mL × 2) and Et₂O (15 mL × 3) and dried in vacuum.

Preparation of CuCl·2LiCl (1 M in THF)

1 M CuCl·2LiCl solution was prepared according to literature reported.⁶ To nitrogen-flushed 50 mL Schlenk-tube containing a magnetic stirrer was added LiCl (0.95 g, 20 mmol) and was heated to 130 °C for 1 h in high vacuum. Then Schlenk-tube was cooled to room temperature and charged with CuCl (0.98 g, 10 mmol, 99.999% metal basis) under nitrogen flow. The Schlenk-tube was heated to 130 °C for 5 h in high vacuum. After cooling to room temperature, 10 mL fresh-distilled THF was added and the mixture was stirred vigorously overnight under nitrogen atmosphere protecting from light with aluminium foil. Colorless solution was obtained and stored away from light.

Typical procedure to generate arylcopper reagents

Procedure 1. Nitrogen-flushed Schlenk-tube equipped with a magnetic stirrer was charged with Grignard reagents (0.5 mmol). 2 mL Fresh-distilled THF was added. Then, the mixture was cooled to –42 °C and charged with 0.6 mL CuCl·2LiCl (1 M in THF, 0.6 mmol). After 0.5 h, arylcopper reagents were obtained.

Procedure 2. Nitrogen-flushed Schlenk-tube equipped with a magnetic stirrer was charged with aryl iodide (0.5 mmol). 2 mL fresh-distilled THF was added and the solution was cooled to 0 °C. 0.5 mL iPrMgCl·LiCl (1.2 M in THF, 0.6 mmol) was added dropwise. The solution was stirred vigorously for 0.5 h. Then the mixture was cooled to –42 °C and charged with 0.6 mL



CuCl₂·2LiCl (1 M in THF, 0.6 mmol). After 0.5 h, arylcopper reagents were obtained.

General procedure of cross coupling between arylcopper reagents and alkynylcopper reagents

To a solution of arylcopper reagents (0.5 mmol) was added alkynylcopper reagents (0.6 mmol). 2 mL pyridine (extra dry) was added and the mixture was heated to 50 °C for 12 h. To quench the reaction, 5 mL HCl (1 M) was added, extracted with EtOAc (5 mL × 3). The combined organic layer was washed with saturated NaCl solution, dried by Na₂SO₄, evaporated and purified by flash chromatography.

1,2-Diphenylethyne⁹ (4aa). 67 mg, 75% yield, white solid, mp: 60–62 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.59–7.54 (m, 4H), 7.40–7.34 (m, 6H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 131.7, 128.5, 128.4, 123.4, 89.5. GC-MS: 178.

1-Methoxy-3-(phenylethynyl)benzene⁹ (4ba). 76 mg, 73% yield, yellow solid, mp: 63–64 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.55–7.51 (m, 2H), 7.34 (d, *J* = 5.1 Hz, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 6.92–6.86 (m, 1H), 3.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.3, 131.6, 129.4, 128.3, 128.3, 124.2, 124.1, 123.1, 116.3, 114.9, 89.3, 89.2, 55.2. GC-MS: 208.

1-((4-Chlorophenyl)ethynyl)-3-methoxybenzene (4bb). 75 mg, yield: 62%, yellow solid, mp: 95–97 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.34–7.30 (m, 2H), 7.26–7.22 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.06–7.03 (m, 1H), 6.92–6.88 (m, 1H), 3.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.3, 134.3, 132.8, 129.5, 128.7, 124.1, 123.9, 121.7, 116.3, 115.1, 90.2, 88.0, 55.1. GC-MS: 242.

1-((4-Fluorophenyl)ethynyl)-3-methoxybenzene (4bc). 81 mg, 72% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.53–7.48 (m, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.13–7.10 (m, 1H), 7.06–7.01 (m, 3H), 6.91–6.87 (m, 1H), 3.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 162.5 (d, *J* = 249.5 Hz), 159.3, 133.5 (d, *J* = 8.2 Hz), 129.4, 124.1, 124.0, 119.2 (d, *J* = 3.4 Hz), 116.3, 115.6 (d, *J* = 22.1 Hz), 114.9, 88.9, 88.1, 55.2. GC-MS: 226.

1-Methoxy-3-(*p*-tolylethynyl)benzene¹⁰ (4bd). 70 mg, 63% yield, yellow solid, mp: 63–64 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 11.1, 7.9 Hz, 3H), 7.05 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 2H), 2.36 (s, 2H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.3, 138.4, 131.5, 129.3, 129.1, 124.4, 124.1, 120.0, 116.2, 114.8, 89.4, 88.6, 55.2, 21.5. GC-MS: 222.

3-((3-Methoxyphenyl)ethynyl)thiophene (4be). 80 mg, 75% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.53–7.50 (m, 1H), 7.28 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.25–7.19 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 2.4, 1.4 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.3, 129.8, 129.4, 128.7, 125.4, 124.1, 124.0, 122.2, 116.2, 114.9, 88.8, 84.3, 55.2. GC-MS: 214.

1-(Cyclohex-1-en-1-ylethynyl)-3-methoxybenzene¹¹ (4bf). 70 mg, 66% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.20 (t, *J* = 8.0 Hz, 1H), 7.04–7.01 (m, 1H), 6.97–6.94 (m, 1H), 6.86–6.82 (m, 1H), 6.22 (dt, *J* = 4.1, 2.2 Hz, 1H), 3.79 (s, 3H), 2.25–2.21 (m, 2H), 2.15 (dq, *J* = 6.0, 3.7 Hz, 2H), 1.65 (dddd, *J* = 20.4, 9.0,

5.4, 3.3 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.4, 135.5, 129.4, 124.9, 124.1, 120.8, 116.3, 114.6, 91.2, 86.8, 55.3, 29.3, 25.9, 22.5, 21.6. GC-MS: 212.

1-(Hex-1-yn-1-yl)-3-methoxybenzene¹² (4bg). 55 mg, 58% yield, yellow solid, mp: 48–50 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.18 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.94–6.91 (m, 1H), 6.84–6.80 (m, 1H), 3.79 (s, 3H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.63–1.55 (m, 2H), 1.53–1.43 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.2, 129.2, 125.1, 124.1, 116.4, 114.1, 90.3, 80.4, 55.2, 30.8, 22.0, 19.1, 13.6. GC-MS: 188.

1-(5-Chlorohex-1-yn-1-yl)-3-methoxybenzene (4bh). 44 mg, 42% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.01–6.97 (m, 1H), 6.94–6.90 (m, 1H), 6.86–6.82 (m, 1H), 3.79 (s, 3H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.06 (p, *J* = 6.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.4, 129.4, 124.7, 124.3, 116.6, 114.5, 88.1, 81.6, 55.4, 43.9, 31.6, 17.0. GC-MS: 208.

3-(*o*-Tolylethynyl)thiophene¹³ (4ce). 65 mg, 66% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.51 (dt, *J* = 3.0, 1.0 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.31–7.29 (m, 1H), 7.24–7.13 (m, 4H), 2.50 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 140.2, 131.9, 130.0, 129.6, 128.4, 128.4, 125.7, 125.5, 123.1, 122.6, 88.4, 87.9, 20.9. GC-MS: 198.

1-Methoxy-2-(phenylethynyl)benzene¹⁴ (4da). 73 mg, 70% yield, yellow oil. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.61–7.55 (m, 2H), 7.52 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.37–7.29 (m, 4H), 6.98–6.89 (m, 2H), 3.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 160.1, 133.7, 131.8, 129.9, 128.4, 128.2, 123.7, 120.6, 112.6, 110.8, 85.9, 56.0. GC-MS: 208.

1-Methoxy-4-(phenylethynyl)benzene¹⁴ (4ea). 81 mg, 78% yield, yellow solid, mp: 57–59 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.56–7.51 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.38–7.29 (m, 3H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 159.7, 133.2, 131.6, 128.4, 128.1, 123.7, 115.5, 114.1, 89.5, 88.20, 55.4. GC-MS: 208.

1-Chloro-3-(phenylethynyl)benzene¹⁵ (4fa). 48 mg, 45% yield, white solid, mp: 30–32 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.54–7.50 (m, 3H), 7.42–7.39 (m, 1H), 7.37–7.34 (m, 3H), 7.32–7.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 134.1, 131.7, 131.4, 129.7, 129.5, 128.6, 128.5, 128.4, 125.0, 122.7, 90.5, 87.9. GC-MS: 212.

Methyl 3-((4-fluorophenyl)ethynyl)benzoate (4gc). 56 mg, 44% yield, white solid, mp: 73–75 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 8.20 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.55–7.50 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 8.6 Hz, 2H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 166.5, 162.8 (d, *J* = 250.0 Hz), 135.8, 133.7 (d, *J* = 8.5 Hz), 132.8, 130.6, 129.4, 128.7, 123.7, 119.1 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 22.1 Hz), 89.3, 88.1, 52.4. GC-MS: 254.

3-(Phenylethynyl)benzonitrile¹⁴ (4ha). 36 mg, 35% yield, yellow solid, mp: 68–70 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.79 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.38–7.35 (m, 3H). ¹³C NMR (101 MHz, CDCl₃-*d*) δ 135.6, 134.9, 131.7, 131.3, 129.2, 129.0, 128.5, 124.9, 122.2, 118.1, 112.8, 91.8, 86.9. GC-MS: 203.

1-Bromo-4-(phenylethynyl)benzene¹⁶ (4ia). 62 mg, 48% yield, white solid, mp: 82–83 °C. ¹H NMR (400 MHz, CDCl₃-*d*) δ 7.55–



7.45 (m, 4H), 7.4–7.31 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3 -*d*) δ 133.0, 131.6, 128.5, 128.4, 122.9, 122.4, 122.2, 90.5, 88.3. GC-MS: 256.

1-Iodo-3-(phenylethynyl)benzene¹⁷ (4ja). 73 mg, 48% yield, white solid, mp: 83–85 °C. ^1H NMR (400 MHz, CDCl_3 -*d*) δ 7.90 (t, $J = 1.6$ Hz, 1H), 7.68–7.65 (m, 1H), 7.54–7.48 (m, 3H), 7.37–7.34 (m, 3H), 7.08 (t, $J = 7.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 -*d*) δ 140.1, 137.2, 131.6, 130.7, 129.8, 128.6, 128.4, 125.3, 122.7, 93.79, 90.7, 87.6. GC-MS: 304.

(Cyclohexylethynyl)benzene¹⁸ (4ka). 40 mg, 44 yield, yellow oil. ^1H NMR (400 MHz, CDCl_3 -*d*) δ 7.42–7.36 (m, 2H), 7.31–7.24 (m, 3H), 2.61–2.55 (m, 1H), 1.91–1.85 (m, 2H), 1.77–1.74 (m, 2H), 1.58–1.51 (m, 3H), 1.38–1.31 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3 -*d*) δ 131.7, 128.2, 127.5, 124.2, 94.6, 80.6, 32.8, 29.8, 26.0, 25.0. GC-MS: 184.

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