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CuX_2-mediated [4+2] benzannulation as a new synthetic tool for stereoselective construction of haloaromatic compounds

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ABSTRACT

The CuX_2-mediated reaction of enynal units, including *ortho*-alkynylbenzaldehydes, with alkynes gives a variety of haloaromatic compounds stereoselectively in good to high yields. 2,2′-Binaphthyl skeletons are also readily prepared by the reaction of *ortho*-alkynylbenzaldehydes and diynes. The method was applied to the synthesis of poly-substituted tetracene derivatives.

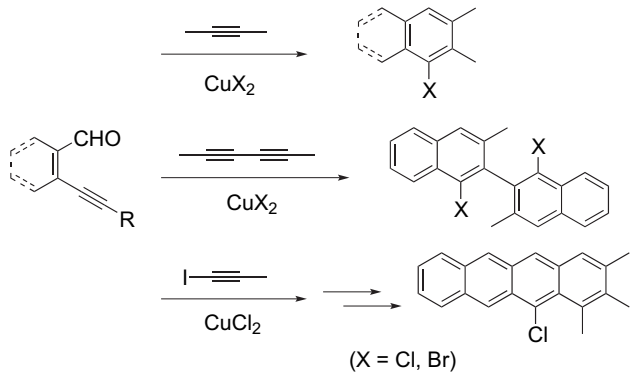
1. Introduction

Haloaromatic compounds are extremely valuable not only as precursors of aryl-metals but also as substrates for transition metal-catalyzed cross coupling reactions.[1] They are also important structural motifs in a wide variety of natural products and functional materials.[2] Direct electrophilic halogenations of aromatic compounds and halogenation of aryldiazonium salts have been widely used for preparation of those useful compounds.[3,4] However, a drawback of these methods is often the difficulty in controlling chemo- and regioselectivity. While functional group-directed *ortho*-metalation followed by nucleophilic halogenation as well as transition metal-catalyzed halogenation through C–H activation are regioselective, suitable functional groups are essential for these protocols.[5,6] Herein, we report the CuX_2-mediated benzannulation reaction of enynal units, including *ortho*-alkynylbenzaldehydes, with alkynes, leading to regioselective formation of chloro-, and bromo aromatic compounds through the cleavage of a triple bond of enynal units in good to high yields.[7] Furthermore, we applied the current transformation to the synthesis of halogenated 2,2′-binaphthyls and tetracene derivatives (Scheme 1).

2. Results and discussion

2.1. Synthesis of 1-halonaphthalenes

We have reported that Lewis acid-catalyzed benzannulations between enynal units and alkynes gave a wide range of aromatic compounds.[8] While exploring the scope of these unprecedented reactions, we found that a chlorinated naphthalene was formed in the reaction of *ortho*-alkynylbenzaldehyde **1a** with phenylacetylene **2a** in the presence of $CuCl_2$. This result prompted us to investigate the reaction and the results are summarized in Table 1. When the reaction of **1a** with **2a** was carried out in the presence of 1.2 equiv of $CuCl_2$ in $(CH_2Cl)_2$ at 70 °C for 8 h, **3a** was obtained in 51% yield (entry 1). The chemical yield was increased to 78% by using 2 equiv of $CuCl_2$ (entry 2). Besides $(CH_2Cl)_2$, CH_3CN and CH_3NO_2 are suitable solvents (entries 3–4). The reaction of **1b**, having a butyl group at the terminus of the alkynyl part, also gave **3a** in 67% yield (entry 5). As for alkynes **2**, not only aromatic alkynes but also aliphatic alkynes are applicable for the present benzannulation. For instance, the reaction with 1-hexyne gave **3d** in 78% yield (entry 8). Even with sterically bulky 3,3-dimethylbut-1-yne



Scheme 1. CuX_2-mediated [4+2] benzannulation.

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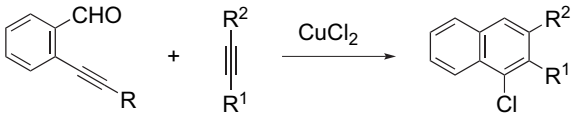
Table 1
$CuCl_2$-mediated benzannulation between **1** and alkynes **2**[a]



1a: R = Ph
1b: R = C_4H_9 **2** **3**

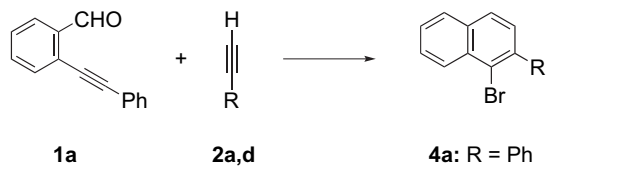
Entry	1	2	R^1	R^2	Solvent	Condition	Yield[b] 3 (%)	
1[c]	**1a**	**2a**	Ph	H	$(CH_2Cl)_2$	70 °C, 8 h	**3a**	51
2	**1a**	**2a**	Ph	H	$(CH_2Cl)_2$	70 °C, 6 h	**3a**	78
3	**1a**	**2a**	Ph	H	CH_3CN	70 °C, 3 h	**3a**	66
4	**1a**	**2a**	Ph	H	CH_3NO_2	80 °C, 4 h	**3a**	85
5	**1b**	**2a**	Ph	H	CH_3CN	70 °C, 3 h	**3a**	67
6	**1a**	**2b**	*p*-$CF_3C_6H_4$	H	$(CH_2Cl)_2$	70 °C, 5.5 h	**3b**	80
7	**1a**	**2c**	*p*-$MeOC_6H_4$	H	$(CH_2Cl)_2$	70 °C, 4 h	**3c**	70
8	**1a**	**2d**	C_4H_9	H	CH_3NO_2	80 °C, 3 h	**3d**	78
9[d]	**1a**	**2e**	*t*-Bu	H	CH_3NO_2	80 °C, 2 h	**3e**	51
10[d]	**1a**	**2f**	TMS	H	CH_3NO_2	80 °C, 2 h	**3f**	25[e]
11	**1a**	**2g**	Ph	Me	$(CH_2Cl)_2$	70 °C, 3.5 h	**3g**	74
12	**1a**	**2h**	C_3H_7	C_3H_7	$(CH_2Cl)_2$	70 °C, 16 h	**3h**	50
13[f]	**1a**	**2i**	1-*c*C_6H_9	H	$(CH_2Cl)_2$	70 °C, 4 h	**3i**	60
14[g]	**1a**	**2j**	PhCH=CH	Br	$(CH_2Cl)_2$	70 °C, 17 h	**3j**	70

[a] Reactions were conducted using **1** (1 equiv), **2** (1.2 equiv), and $CuCl_2$ (2 equiv) unless otherwise mentioned.
[b] Isolated yield.
[c] 1.2 equiv of $CuCl_2$ was used.
[d] 5 equiv of **2** was used.
[e] **3f′** was obtained in 40% yield.
[f] 1-*c*C_6H_9=1-cyclohexenyl.
[g] 2 equiv of **2j** was used.

2e, the reaction proceeded to give **3e** although the chemical yield was low (22%), probably due to its low boiling point. Indeed, the chemical yield was increased up to 51% by using an excess amount of **2e** (entry 9). On the other hand, in the case of trimethylsilylacetylene **2f**, the reversal of the selectivity was observed, and the regioisomer of **3f** (**3f′**: R^1=H, R^2=TMS) was obtained predominantly (**3f**:**3f′**=1:1.6). The similar reversal has been observed previously in the gold-catalyzed benzannulation.[8] With the present method, 2,3-disubstituted chloronaphthalenes can be prepared by use of internal alkynes (entries 11–12). In comparison with prop-1-ynylbenzene **2g**, oct-4-yne **2h** is less reactive, probably due to the steric effect of two propyl groups of **2h**. It is worth mentioning that one more halogen can be introduced on the acene skeletons regioselectively with 1-halo-alkynes. For example, the reaction with (4-bromobut-1-en-3-ynyl)benzene **2j** gave 3-bromo-1-chloro-2-styrylnaphthalene **3j** in 70% yield (entry 14).

$CuBr_2$, as well as $CuCl_2$, promoted the reaction to give bromo-substituted naphthalenes although the chemical yields of products were slightly lower than those of chloro-substituted analogs (Scheme 2). We also found that addition of LiBr to the $CuCl_2$-mediated reaction was an alternative method for formation of **4**. For example, the reaction of **1a** with **2a** in the presence of a 1:2 mixture of $CuCl_2$ and LiBr afforded **4a** in 59% yield along with a small amount of **3a** (5%). Barluenga and Larock independently have reported the iodonium ion-mediated benzannulations between *ortho*-alkynylbenzaldehydes and alkynes to produce 1-iodonaphthalene products effectively.[9] The present method can be used as a complementary approach for preparation of a wide range of halonaphthalene compounds.

Previously, we have reported the $Cu(OTf)_2$-catalyzed benzannulation of enynal units with alkynes, leading to aromatic compounds through the cleavage of a triple bond of enynal units.[8] Probably, products **3** and **4** might be produced similarly by the dissociation of the alkynyl part of **1**. We then conducted the $CuCl_2$-mediated reaction of **1b** with **2a** in $CDCl_3$ to investigate the reaction mechanism with NMR experiments. After completion of the reaction, ^1H NMR spectrum of the reaction mixture indicated the generation of **3a** in 68% yield together with pentanoyl chloride **5a** in the same yield as shown in Scheme 3.

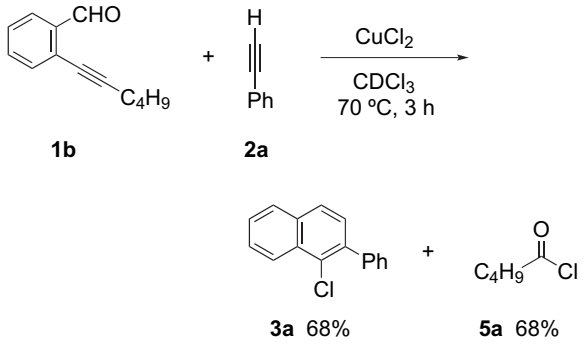


1a **2a,d**

4a: R = Ph
4b: R = C_4H_9

$CuBr_2/CH_3NO_2$, 60 °C, 2 h — **4a:** 62%
$CuBr_2/CH_3NO_2$, 60 °C, 2 h — **4b:** 50%
$CuCl_2$-2LiBr/CH_3CN, 80 °C, 5 h — **4a:** 59% **3a:** 5%

Scheme 2. Construction of bromo-substituted naphthalenes.

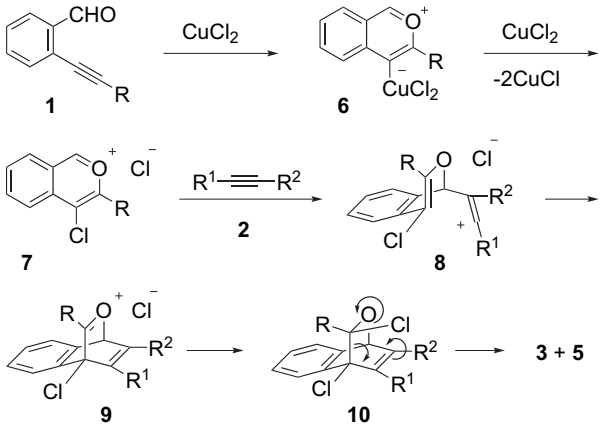


1b **2a**

3a 68% **5a** 68%

Scheme 3. Detection of **5a** with ^1H NMR experiments.

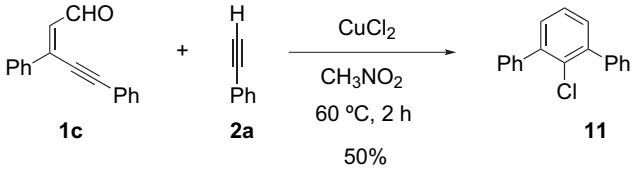
On the basis of these results, we proposed a reaction mechanism as shown in Scheme 4. The coordination of the triple bond of **1** to $CuCl_2$ enhances the electrophilicity of the alkyne, and the subsequent nucleophilic attack of the carbonyl oxygen to the electron deficient alkyne forms the ate complex **6**, which is converted to the intermediate **7** by chlorination. Then, addition of alkyne **2** to **7** occurs to form the bicyclic intermediate **9** through the formation of **8**. The regioselectivities observed in Table 1 are accounted for by intervention of **8**. When R^1 are aryl or alkyl groups, the intermediate **8** would be stabilized by resonance or inductive effects of R^1. On the other hand, the predominant formation of **3f′** in the reaction of trimethylsilylacetylene **2f** is ascribed to the well-known β-silyl effect: a carbocation β to trimethylsilyl group is stabilized significantly.[10] Then, the attack of Cl^- to the carbon of RCO of **9** occurs and the resulting intermediate **10** undergoes retro Diels–Alder reaction to produce **3** and **5**.[8,9] It is well known that NCS is a chlorinating agent in organic synthesis. However, no reaction took place between **1a** and **2a** in the presence of 2 equiv of NCS, instead of $CuCl_2$, in CH_3NO_2 even under 80 °C for 18 h. This result clearly suggested that $CuCl_2$ exhibits dual roles in the current reaction; it acts as an alkynophilic Lewis acid and as a chlorinating agent.



Scheme 4. Plausible reaction mechanism.

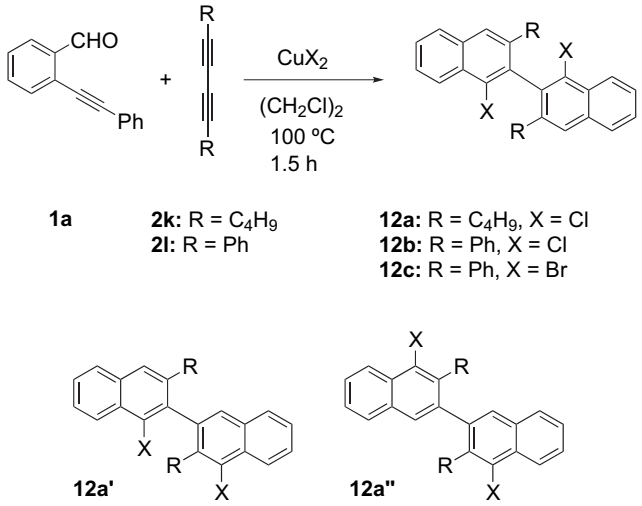
2.2. Synthesis of halogenated aromatic compounds

Since halogenated naphthalene derivatives were produced unexpectedly easily from benzaldehyde derivatives **1a**–**b**, we applied the present method to the construction of other aromatic skeletons. The reaction of conjugated enynal **1c** with **2a** proceeded smoothly and the corresponding 2′-chloro-[1,1′;3′,1″]terphenyl **11** was obtained in 50% yield (Scheme 5).



Scheme 5. Construction of benzene frameworks.

Next, we examined the reaction of **1a** with conjugated diyne **2k** instead of simple alkynes. We expected that the double benzannulation might occur in this system because the first benzannulation product, derived from **1a** and **2k**, would have an alkynyl group on the naphthalene skeleton, which might be available for the second benzannulation. As we expected, when **1a** (2.5 equiv) was treated with diyne **2k** (1 equiv) in the presence of $CuCl_2$ in CH_3NO_2 at 100 °C, 2,2′-binaphthyl **12a** was obtained in 70% yield (Scheme 6). It is worth mentioning that the reaction proceeded in a highly stereoselective manner because **12a** is one of the three possible isomers (**12a′** and **12a″**). The reactions of **1a** with **2l** also proceeded with $CuCl_2$ or $CuBr_2$ smoothly to give **12b** and **12c** in 65% and 45% yields, respectively. Although aryl–aryl bond formation has been studied well as the most common synthetic route for biaryl compounds,[11] the present method can be used as an alternative approach. The structure of **12a** was confirmed by X-ray crystallographic analysis as shown in Figure 1.



Scheme 6. Construction of 2,2′-biphenyl skeletons.

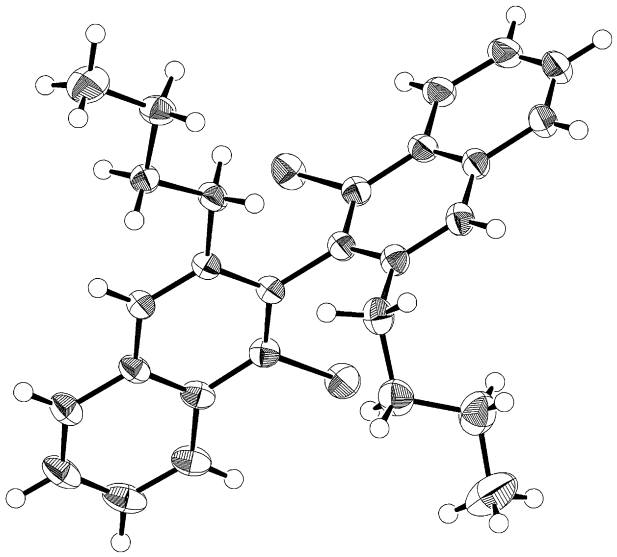
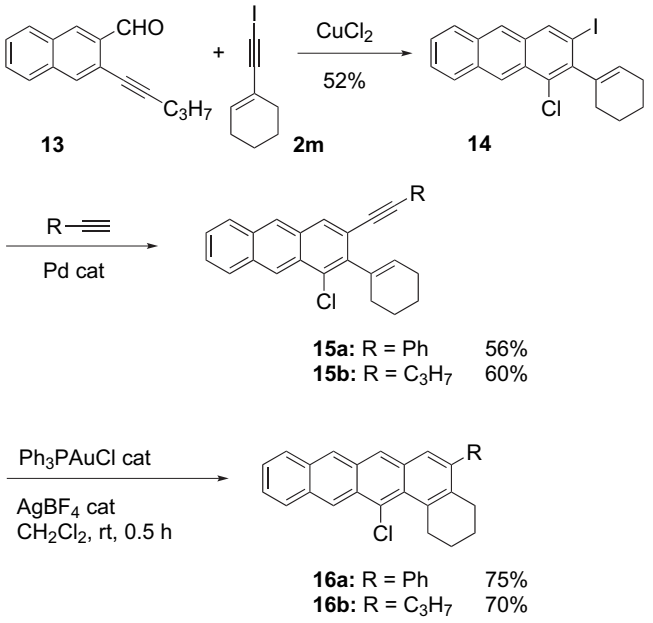


Figure 1. X-ray structure of **12a**.

Finally, the method was applied to the synthesis of a tetracene framework, which has been widely studied as the semiconducting layers in field effect transistors.[12–14] The copper-mediated benzannulation of naphthaldehyde derivative **13** with iodo-substituted conjugated enyne **2m** proceeded smoothly and the corresponding iodo-substituted anthracene product **14** was obtained in 52% yield. Sonogashira coupling between **14** and phenylacetylene gave **15a** in 56% yield, which was aromatized with the gold catalyst to afford

chloro-substituted tetracene derivative **16a** in 75% yield.[15] The propyl-substituted product **16b** was also prepared in the similar way in good yield (Scheme 7).



Scheme 7. Preparation of chloro-substituted tetracene derivatives.

3. Conclusions

A novel and highly efficient synthetic method of chloro- and bromo-substituted aromatic compounds has been developed. CuX_2 (X=Cl, Br) acts not only as a Lewis acid for promotion of the benzannulation but also as a halogenating agent. The present method allows us to provide various kinds of stereo-defined halogenated aromatic compounds. The synthetic utility of the method is enhanced by its ability to prepare 2,2′-binaphthyl skeletons and poly-substituted tetracene derivatives.

4. Experimental

4.1. General

NMR spectra were measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C by JEOL JNM-AL 400 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane with reference to internal residual $CHCl_3$ (δ=7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ=77.0) in $CDCl_3$. GC–MS analysis was performed with an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m×0.25 mm capillary column, HP-5MS). High-resolution mass spectra (HRMS) were performed on Bruker Daltonics Apex III spectrometer. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (Kieselgel 60 F254, 0.2 mm) were used. The products were purified by flash column chromatography on silica gel 60 N (KANTO, 40–50 μm). All manipulations were carried out under argon atmosphere using standard Schlenk techniques.

4.2. (*Z*)-3,5-Diphenylpent-2-en-4-ynal (1c)

To a solution of (*Z*)-3-bromo-3-phenylacrylaldehyde[16] (4.8 g, 23 mmol) in CH_3CN (70 mL) and Et_3N (18 mL) were added $PdCl_2$ (204 mg, 1.15 mmol), PPh_3 (603 mg, 2.3 mmol), CuI (438 mg, 2.3 mmol), and phenylacetylene (3.8 mL, 34.6 mmol) successively at room temperature and the mixture was stirred for 1 h at 50 °C. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and ether as eluent to give **1c** (4.1 g, 17.9 mmol) in 78% yield as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.41 (d, *J*=8.0 Hz, 1H), 7.86 (dd, *J*=2.0, 7.4 Hz, 1H), 7.61 (d, *J*=2.0, 7.6 Hz, 1H), 7.49–7.42 (m, 6H), 6.81 (d, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.0, 142.4, 135.5, 131.9, 131.0, 130.9, 129.8, 128.8, 128.6, 127.1, 121.5; IR (KBr) 2204, 1661, 1556, 1489, 1448, 1348, 1138, 1074, 827, 758 cm^{-1}; GC–MS (EI) *m*/*z* (%) 231 ([M$^+$−1], 53), 203 (100); HRMS (ESI) calcd for ([$C_{17}H_{12}O$+Na])$^+$ 255.0780, found 255.0781; mp 42–44 °C.

4.3. (*E*)-(4-Bromobut-1-en-3-ynyl)benzene (2j)

To a solution of (*E*)-(2-bromovinyl)benzene (7.7 mL, 60 mmol) in THF (150 mL) and Et_3N (40 mL) were added $PdCl_2$ (532 mg, 3.0 mmol), PPh_3 (1.57 g, 6.0 mmol), CuI (1.14 g, 6.0 mmol), and trimethylsilylacetylene (17 mL, 120 mmol) successively at room temperature and the mixture was stirred for 12 h at 60 °C. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and CH_2Cl_2 as eluent to give (*E*)-trimethyl(4-phenylbut-3-en-1-ynyl)silane (7.3 g, 36.4 mmol) in 61% yield. To a solution of 85% KOH (666 mg, 10.0 mmol) in MeOH (45 mL) was added (*E*)-trimethyl(4-phenylbut-3-en-1-ynyl)silane (3.65 g, 18.2 mmol) at 0 °C and the mixture was stirred for 1.5 h at room temperature. A saturated aqueous solution of NH_4Cl was added at 0 °C, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and CH_2Cl_2 as eluent to give (*E*)-but-1-en-3-ynylbenzene (2.1 g, 16.4 mmol) in 90% yield. To a mixture of NBS (3.52 g, 19.2 mmol) and $AgNO_3$ (272 mg, 1.6 mmol) in acetone (50 mL) was added (*E*)-but-1-en-3-ynylbenzene (2.05 g, 16 mmol) and the mixture was stirred for 1.5 h at room temperature and cooled to 0 °C. Water was added and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using hexane as eluent to give **2j** (3.1 g, 15.0 mmol) in 94% yield. Spectral data of (*E*)-trimethyl(4-phenylbut-3-en-1-ynyl)silane, (*E*)-but-1-en-3-ynylbenzene, and **2j** were identical to those reported in the literature.[17,18]

Aldehydes **1a**,[19] **1b**,[19] and alkyne **2m**[20] were prepared according to the literature.

4.4. General procedure for the synthesis of 1-halonaphthalenes

To a suspension of $CuCl_2$ (135 mg, 1 mmol) in CH_3NO_2 (2 mL) were added **1** (0.5 mmol) and **2** (0.6 mmol) successively at room temperature under an Ar atmosphere. The mixture was stirred at 80 °C for 4 h and then cooled to room temperature. The resulting mixture was transferred to a silica gel column, and the product was isolated using a mixture of hexane and CH_2Cl_2 as eluent.

*4.4.1. 1-Chloro-2-phenylnaphthalene (**3a**).* White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, *J*=8.5 Hz, 1H), 7.89 (d, *J*=8.0 Hz, 1H), 7.82 (d, *J*=8.5 Hz, 1H), 7.65–7.44 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.2, 137.8, 133.5, 131.2, 129.7, 129.4, 128.4, 128.00, 127.97, 127.5,

127.3, 126.7, 126.5, 125.0; IR (KBr) 1491, 1443, 1331, 1242, 1069, 1024, 970, 866, 818, 748, 700 cm^{-1}; GC–MS (EI) *m/z* (%) 234 (M^+, 100); Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.65, found: C, 80.41; H, 4.70; mp 85 °C.

*4.4.2. 1-Chloro-2-(4-(trifluoromethyl)phenyl)naphthalene (**3b**).* White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, *J*=8.5 Hz, 1H), 7.91 (d, *J*=7.8 Hz, 1H), 7.85 (d, *J*=8.3 Hz, 1H), 7.74 (d, *J*=8.3 Hz, 2H), 7.69–7.58 (m, 4H), 7.43 (d, *J*=8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.7, 136.4, 133.8, 131.1, 130.1, 129.64 (q, *J*=33.0 Hz), 129.57, 128.1, 127.8, 127.6, 127.1, 126.9, 125.03, 124.99, 124.2 (q, *J*=270.0 Hz); IR (KBr) 1655, 1614, 1560, 1499, 1406, 1327, 1167, 1123, 1082, 1063, 816 cm^{-1}; GC–MS (EI) *m/z* (%) 306 (M^+, 100); Anal. Calcd for $C_{17}H_{10}ClF_3$: C, 66.57; H, 3.29, found: C, 66.58; H, 3.46; mp 121–122 °C.

*4.4.3. 1-Chloro-2-(4-methoxyphenyl)naphthalene (**3c**).* White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.40 (d, *J*=8.5 Hz, 1H), 7.88 (d, *J*=9.3 Hz, 1H), 7.80 (d, *J*=8.3 Hz, 1H), 7.63 (dd, *J*=8.0, 8.0 Hz, 1H), 7.55 (dd, *J*=7.6, 7.6 Hz, 1H), 7.46–7.44 (m, 3H), 7.01 (d, *J*=2.4 Hz, 2H), 3.89 (t, *J*=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 137.4, 133.4, 132.5, 131.2, 130.9, 129.4, 128.6, 127.9, 127.3, 126.7, 126.3, 124.9, 113.5, 55.3; IR (KBr) 1607, 1514, 1495, 1460, 1439, 1286, 1252, 1177, 1024, 972, 821 cm^{-1}; GC–MS (EI) *m/z* (%) 268 (M^+, 100); Anal. Calcd for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88. Found: C, 75.99; H, 5.13; mp 103–104 °C.

*4.4.4. 2-Butyl-1-chloronaphthalene (**3d**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J*=8.3 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 7.69 (d, *J*=8.3 Hz, 1H), 7.57 (tt, *J*=1.5, 8.0 Hz, 1H), 7.48 (tt, *J*=1.2, 8.0 Hz, 1H), 7.34 (d, *J*=8.5 Hz, 1H), 2.95 (t, *J*=7.8 Hz, 2H), 1.69 (quint, *J*=7.8 Hz, 2H), 1.44 (sext, *J*=7.3 Hz, 2H), 0.97 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.8, 133.0, 131.2, 130.1, 128.0, 127.8, 126.8, 126.5, 125.6, 124.3, 34.2, 32.2, 22.7, 14.1; IR (neat) 3053, 2957, 2930, 2862, 1560, 1504, 1466, 1377, 1354, 1339, 1259, 1225, 988, 812 cm^{-1}; GC–MS (EI) *m/z* (%) 218 (M^+, 43), 175 (100); Anal. Calcd for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91, found: C, 76.86; H, 7.08.

*4.4.5. 2-tert-Butyl-1-chloronaphthalene (**3e**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.45 (d, *J*=8.5 Hz, 1H), 7.80 (d, *J*=8.0 Hz, 1H), 7.40 (d, *J*=8.8 Hz, 1H), 7.63 (d, *J*=9.0 Hz, 1H), 7.57 (tt, *J*=1.5, 8.5 Hz, 1H), 7.49 (tt, *J*=1.2, 8.0 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.7, 132.9, 132.2, 130.7, 127.5, 126.8, 126.5, 125.8, 125.3, 124.6, 36.7, 30.2; IR (neat) 2961, 2924, 1483, 1364, 1335, 1240, 976, 812 cm^{-1}; GC–MS (EI) *m/z* (%) 218 (M^+, 59), 218 (100); HRMS (EI) calcd for $C_{14}H_{15}Cl$ (M^+) 218.0862, found 218.0862.

*4.4.6. (4-Chloronaphthalen-2-yl)trimethylsilane (**3f**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J*=8.3 Hz, 1H), 7.83 (d, *J*=7.8 Hz, 1H), 7.74 (d, *J*=8.3 Hz, 1H), 7.50–7.61 (m, 3H), 0.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3, 135.9, 135.0, 130.9, 130.7, 127.9, 126.9, 126.8, 126.0, 124.4, −0.4; IR (neat) 2953, 1304, 1247, 973, 866, 835, 810 cm^{-1}; MS (EI) *m/z* (%) 234 (M^+, 18), 183 (100); HRMS (EI) calcd for $C_{13}H_{15}ClSi$ (M^+) 234.0632, found 234.0631.

*4.4.7. (1-Chloronaphthalen-2-yl)trimethylsilane (**3f'**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J*=8.3 Hz, 1H), 7.90 (s, 1H), 7.86 (d, *J*=8.1 Hz, 1H), 7.65 (s, 1H), 7.60 (dd, *J*=6.8, 7.1 Hz, 1H), 7.54 (ddd, *J*=1.0, 6.8, 7.8 Hz, 1H), 0.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.7, 134.2, 132.7, 131.5, 130.8, 129.8, 128.2, 127.3, 126.6, 124.2, −1.09; IR (neat) 2954, 1249, 1096, 974, 819, 746 cm^{-1}; MS (EI) *m/z* (%) 234 (M^+, 26), 219 (100); HRMS (EI) calcd for $C_{13}H_{15}ClSi$ (M^+) 234.0632, found 234.0630.

*4.4.8. 1-Chloro-3-methyl-2-phenylnaphthalene (**3g**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.29 (d, *J*=7.6 Hz, 1H), 7.81 (d, *J*=7.3 Hz, 1H), 7.79 (s, 1H), 7.67–7.41 (m, 5H), 7.25 (m, 2H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.5, 139.2, 135.3, 133.6, 130.5, 129.5, 129.1, 128.3, 127.3, 127.2, 126.7, 126.5, 126.3, 124.8, 21.9; IR (neat) 3057, 1489, 1445, 1258, 920, 880, 847, 750 cm^{-1}; GC–MS (EI) *m/z* (%) 252 (M^+, 100); Anal. Calcd for $C_{17}H_{13}Cl$: C, 80.79; H, 5.18, found: C, 80.63; H, 5.38.

*4.4.9. 1-Chloro-2,3-dipropylnaphthalene (**3h**).* White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J*=8.5 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.54 (s, 1H), 7.52–7.42 (m, 2H), 2.98–2.93 (m, 2H), 2.80–2.76 (m, 2H), 1.77–1.60 (m, 4H), 1.10–1.03 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6, 137.4, 132.7, 131.1, 129.9, 127.3, 126.2, 126.0, 125.6, 124.3, 35.9, 32.7, 24.3, 23.0, 14.6, 14.2; IR (KBr) 2960, 1489, 1450, 1251, 935, 894, 748 cm^{-1}; GC–MS (EI) *m/z* (%) 246 (M^+, 100); Anal. Calcd for $C_{16}H_{19}Cl$: C, 77.87; H, 7.76, found: C, 77.88; H, 7.74; mp 32–33 °C.

*4.4.10. 1-Chloro-2-cyclohexenylnaphthalene (**3i**).* White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, *J*=7.8 Hz, 1H), 7.82 (d, *J*=8.0 Hz, 1H), 7.71 (d, *J*=8.3 Hz, 1H), 7.58 (tt, *J*=1.5, 8.3 Hz, 1H), 7.49 (tt, *J*=1.2, 7.1 Hz, 1H), 7.29 (d, *J*=8.5 Hz, 1H), 5.74 (sept, *J*=1.9 Hz, 1H), 2.37 (m, 2H), 2.44 (m, 2H), 1.83 (m, 2H), 1.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.7, 138.1, 133.2, 131.1, 128.9, 127.83, 127.75, 127.4, 126.9, 126.5, 125.9, 124.6, 29.3, 25.5, 23.0, 22.1; IR (KBr) 1497, 1435, 1325, 978, 918, 860, 810, 772 cm^{-1}; GC–MS (EI) *m/z* (%) 242 (M^+, 92), 179 (100); Anal. Calcd for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23, found: C, 78.95; H, 7.74; mp 49–50 °C.

*4.4.11. 3-Bromo-1-chloro-2-styrylnaphthalene (**3j**).* White crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J*=8.0 Hz, 1H), 8.11 (s, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.64–7.52 (m, 4H), 7.42 (t, *J*=7.2 Hz, 2H), 7.33 (t, *J*=7.2 Hz, 1H), 7.28–7.24 (m, 1H), 7.08 (d, *J*=16 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.2, 136.6, 133.7, 133.5, 131.2, 130.5, 130.3, 128.7, 128.2, 127.5, 127.3, 127.0, 126.7, 125.5, 125.2, 121.3; IR (KBr) 1767, 1553, 1487, 1450, 1250, 1184, 964, 847, 779, 764, 737 cm^{-1}; GC–MS (EI) *m/z* (%) 344 (M^+, 18), 228 (100); Anal. Calcd for $C_{18}H_{12}BrCl$: C, 62.91; H, 3.52, found: C, 62.60; H, 3.84; mp 108–109 °C.

*4.4.12. 1-Bromo-2-phenylnaphthalene (**4a**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, *J*=7.8 Hz, 1H), 7.87–7.66 (m, 2H), 7.65 (tt, *J*=8.0, 1.2 Hz, 1H), 7.57 (tt, *J*=6.8, 1.2 Hz, 1H), 7.54–7.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 140.7, 133.5, 132.4, 129.6, 128.4, 128.0, 127.91, 127.88, 127.6, 127.5, 127.4, 126.5, 122.5; IR (neat) 1491, 1441, 1323, 1240, 1024, 955, 864, 816, 758 cm^{-1}; GC–MS (EI) *m/z* (%) 282 (M^+, 100); HRMS (EI) calcd for $C_{16}H_{11}Br$ (M^+) 282.0044, found 282.0040.

*4.4.13. 1-Bromo-2-butylnaphthalene (**4b**).* Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, *J*=8.5 Hz, 1H), 7.79 (d, *J*=8.0 Hz, 1H), 7.72 (d, *J*=8.5 Hz, 1H), 7.58 (tt, *J*=1.2, 6.8 Hz, 1H), 7.47 (tt, *J*=1.2, 8.0 Hz, 1H), 7.34 (d, *J*=4.1 Hz, 1H), 2.99 (t, *J*=7.8 Hz, 2H), 1.69 (quint, *J*=5.9 Hz, 2H), 1.51 (sext, *J*=7.3 Hz, 2H), 0.98 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 133.0, 132.6, 128.1, 127.9, 127.3, 127.2, 127.1, 125.6, 123.5, 37.2, 32.4, 22.7, 14.1; IR (neat) 3057, 1488, 1445, 1352, 1258, 920, 880, 847, 775 cm^{-1}; GC–MS (EI) *m/z* (%) 262 (M^+, 58), 219 (100); Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74, found: C, 63.84, H, 5.74.

4.5. 1-Chloro-2,6-diphenylbenzene (11)

To a suspension of $CuCl_2$ (135 mg, 1 mmol) in CH_3NO_2 (2 mL) were added **1c** (116 mg, 0.5 mmol) and **2a** (0.07 mL, 0.6 mmol) successively at room temperature under an Ar atmosphere. The mixture was stirred at 60 °C for 2 h and then cooled to room temperature. The resulting mixture was transferred to a silica gel column, and the product was isolated using hexane as eluent; **10**

was obtained as a white solid (66 mg, 0.25 mmol) in 50% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49–7.43 (m, 8H), 7.43–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.5, 140.0, 130.9, 130.3, 129.5, 127.9, 127.4, 126.3; IR (KBr) 3055, 1495, 1456, 1439, 1398, 1049, 1030, 802, 762, 700 cm^{-1}; MS (EI) *m*/*z* (%) 264 (M^+ 100); Anal. Calcd for $C_{18}H_{13}Cl$: C, 81.66; H, 4.95, found: C, 81.65; H, 5.02; mp 90 °C.

4.6. General procedure for the synthesis of 2,2′-binaphthyls

To a suspension of CuX_2 (1 mmol) in $(CH_2Cl)_2$ (2 mL) were added **1a** (0.5 mmol) and **2** (0.2 mmol) successively at room temperature under an Ar atmosphere. The mixture was stirred at 100 °C for 1.5 h and then cooled to room temperature. The resulting mixture was transferred to a silica gel column, and the product was isolated using a mixture of hexane and CH_2Cl_2 as eluent.

*4.6.1. 3,3′-Dibutyl-1,1′-dichloro-2,2′-binaphthyl (**12a**).* White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (dd, *J*=4.8, 4.8 Hz, 1H), 7.87 (dd, *J*=4.8, 4.8 Hz, 1H), 7.76 (s, 1H), 7.59–7.56 (m, 2H), 2.37 (t, *J*=7.5 Hz, 2H), 1.56–1.52 (m, 2H), 1.21 (sext, *J*=7.3 Hz, 2H), 0.78 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.5, 136.0, 133.9, 131.1, 129.5, 127.6, 126.7, 126.3, 125.8, 124.8, 33.4, 31.4, 22.5, 13.9; IR (KBr) 2957, 2870, 1487, 1464, 1319, 1259, 878, 849, 748 cm^{-1}; GC–MS (EI) *m*/*z* (%) 434 (M^+, 100); Anal. Calcd for $C_{28}H_{28}Cl_2$: C, 77.23; H, 6.48, found: C, 77.32; H, 6.43; mp 101–103 °C.

*4.6.2. 1,1′-Dichloro-3,3′-diphenyl-2,2′-binaphthyl (**12b**).* White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, *J*=8.3 Hz, 1H), 7.82 (d, *J*=7.5 Hz, 1H), 7.65 (m, 2H), 7.57 (tt, *J*=1.2, 7.6 Hz, 1H), 7.08 (dd, *J*=7.6, 7.6 Hz, 1H), 6.98 (dd, *J*=7.6, 7.6 Hz, 2H), 6.71 (d, *J*=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 139.9, 134.8, 133.6, 133.3, 129.8, 129.2, 128.2, 128.0, 127.2, 127.1, 127.0, 126.7, 125.0; IR (KBr) 1591, 1556, 1485, 1447, 1325, 1265, 976, 918, 893, 849, 750 cm^{-1}; GC–MS (EI) *m*/*z* (%) 474 (M^+, 100); Anal. Calcd for $C_{32}H_{20}Cl_2$: C, 80.84; H, 4.24, found: C, 81.62; H, 4.41; mp 206–208 °C.

*4.6.3. 1,1′-Dibromo-3,3′-diphenyl-2,2′-binaphthyl (**12c**).* White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, *J*=8.7 Hz, 1H), 7.80 (d, *J*=8.1 Hz, 1H), 7.64 (m, 2H), 7.56 (tt, *J*=1.2, 7.4 Hz, 1H), 7.08 (dd, *J*=7.4, 7.4 Hz, 1H), 6.98 (dd, *J*=7.6, 7.6 Hz, 2H), 6.74 (d, *J*=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 139.9, 139.2, 133.6, 131.2, 129.4, 129.0, 128.2, 127.9, 127.5, 127.4, 127.2, 127.0, 126.8; IR (KBr) 1653, 1576, 1553, 1522, 1508, 1481, 1458, 1321, 1250, 893, 750 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{20}Br_2$ (M^+) 561.9932, found 561.9930; mp 229 °C.

4.7. 3-(Phenylethynyl)-2-naphthaldehyde (13)

4.7.1. Preparation of (3-(pent-1-ynyl)naphthalen-2-yl)methanol. To a solution of (3-iodonaphthalen-2-yl)methanol[21] (5.2 g, 18.4 mmol) in Et_3N (40 mL) were added $PdCl_2$ (65.3 mg, 0.37 mmol), PPh_3 (193 mg, 0.74 mmol), CuI (294 mg, 1.54 mmol), and pentyne (2.17 mL, 22 mmol) successively at room temperature and the mixture was stirred for 3 h at 60 °C. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and AcOEt as eluent to give (3-(pent-1-ynyl)naphthalen-2-yl)methanol (3.67 g, 16.4 mmol) in 89% yield as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (s, 1H), 7.81 (s, 1H), 7.74–7.80 (m, 2H), 7.43–7.49 (m, 2H), 4.95 (d, *J*=6.1 Hz, 2H), 2.44–2.53 (m, 3H), 1.69 (ddd, *J*=7.3, 14.4, 14.4 Hz, 2H), 1.11 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.8, 132.5, 132.3, 132.0, 127.7, 127.2, 126.5, 126.2, 125.6, 119.9, 94.9, 78.5, 64.4, 22.3, 21.6, 13.7; IR (neat) 3304, 2927, 1600, 1492, 1341, 1108, 1035, 876, 742 cm^{-1}; GC–MS (EI) *m*/*z* 224 (M^+, 100); HRMS (ESI) calcd for $C_{16}H_{16}ONa$ ($[M+Na]$)$^+$ 247.1093, found 247.1092; mp 70.5 °C.

*4.7.2. Preparation of **13**.* To a solution of $(COCl)_2$ (2.3 mL, 26.8 mmol) in CH_2Cl_2 (40 mL) was added dropwise a solution of DMSO (2.8 mL, 39.4 mmol) in CH_2Cl_2 (8 mL) at −78 °C over 10 min. After the mixture was stirred for 15 min at −78 °C, a solution of (3-(pent-1-ynyl)naphthalen-2-yl)methanol (2.8 g, 12.5 mmol) in CH_2Cl_2 (15 mL) was added dropwise over 10 min and the reaction temperature rised to −45 °C. After the mixture was stirred for 1 h at −45 °C, Et_3N (12.3 mL, 88 mmol) was added. The mixture was allowed to warm to 0 °C and it was stirred for 20 min. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and AcOEt as eluent to give **13** (2.0 g, 9.2 mmol) in 73% yield as a yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.68 (s, 1H), 8.43 (s, 1H), 8.00 (s, 1H), 7.95 (d, *J*=8.1 Hz, 1H), 7.81 (d, *J*=8.3 Hz, 1H), 7.59 (dd, *J*=6.8, 8.1 Hz, 1H), 7.53 (dd, *J*=7.1, 7.8 Hz, 1H), 2.52 (t, *J*=6.8 Hz, 2H), 1.71 (dt, *J*=7.1, 21.5 Hz, 2H), 1.12 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.3, 135.5, 133.1, 132.4, 131.5, 129.9, 129.2, 129.1, 127.3, 127.2, 122.1, 96.9, 76.9, 22.2, 21.7, 13.8; IR (neat) 2962, 2228, 1693, 1620, 1494, 1397, 1247, 1041, 810, 636 cm^{-1}; GC–MS (EI) *m*/*z* 222 (M^+, 17), 165 (100); HRMS (ESI) calcd for $C_{16}H_{14}ONa$ ($[M+Na]^+$) 245.0937, found 245.0935.

4.8. 1-Chloro-2-cyclohexenyl-3-iodoanthracene (14)

To a suspension of $CuCl_2$ (270 mg, 2 mmol) in $(CH_2Cl)_2$ (1 mL) were added a solution of **13** (222 mg, 1.0 mmol) in $(CH_2Cl)_2$ (1.5 mL) and a solution of 1-(iodoethynyl)cyclohex-1-ene **2m** (464 mg, 2.0 mmol) in $(CH_2Cl)_2$ (1.5 mL) successively at room temperature. The mixture was stirred at 40 °C for 1 h and then cooled to room temperature. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and CH_2Cl_2 as eluent to give **14** (217 mg, 0.52 mmol) in 52% yield as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (s, 1H), 8.52 (s, 1H), 8.24 (s, 1H), 8.02–8.08 (m, 1H), 7.95–8.01 (m, 1H), 7.47–7.55 (m, 2H), 6.66 (dd, *J*=2.0, 3.7 Hz, 1H), 2.22–2.38 (m, 4H), 1.89–1.96 (m, 2H), 1.75–1.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.51, 141.49, 140.8, 137.3, 132.3, 132.2, 131.8, 128.6, 128.54, 128.51, 127.8, 126.3, 126.2, 125.4, 124.1, 97.2, 28.4, 25.3, 22.8, 21.9; IR (neat) 3854, 2928, 1603, 1445, 1122, 916, 872, 781, 710 cm^{-1}; GC–MS (EI) *m*/*z* 418 (M^+, 100); HRMS (EI) calcd for $C_{20}H_{16}ClI$ (M^+) 417.9985, found 417.9982; mp 125.5 °C.

4.9. General procedure for the synthesis of anthracene derivatives

To a solution of **14** (418 mg, 1.0 mmol) in THF (5 mL) and Et_3N (0.5 mL) were added $PdCl_2$ (3.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (15.2 mg, 0.08 mmol), and alkyne (2 mmol) successively at room temperature and the mixture was stirred for 4 h at 60 °C. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with ether three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and CH_2Cl_2 as eluent to give **15**.

*4.9.1. 1-Chloro-2-cyclohexenyl-3-(phenylethynyl)anthracene (**15a**).* Yellow crystal; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.84 (s, 1H), 8.37 (s, 1H), 8.17 (s, 1H), 8.03–8.10 (m, 1H), 7.96–8.02 (m, 1H), 7.47–7.59

(m, 4H), 7.33–7.42 (m, 3H), 5.80 (dd, J=1.7, 3.4 Hz, 1H), 2.37–2.48 (m, 2H), 2.26–2.36 (m, 2H), 1.76–1.97 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 136.4, 132.6, 131.9, 131.5, 131.2, 130.5, 129.4, 128.7, 128.7, 128.4, 128.3, 127.9, 127.6, 126.5, 126.19, 126.16, 123.9, 123.4, 121.1, 92.5, 88.9, 28.7, 25.6, 23.2, 22.3; IR (neat) 2360, 2341, 1739, 1365, 1217, 904, 882, 739, 687 cm^{-1}; Anal. Calcd for $C_{28}H_{21}Cl$: C, 85.59; H, 5.39; Cl, 9.02; found C, 85.54; H, 5.50; Cl, 9.11; mp 145.5 °C.

*4.9.2. 1-Chloro-2-cyclohexenyl-3-(pent-1-ynyl)anthracene (**15b**).* Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (s, 1H), 8.31 (s, 1H), 8.03–8.05 (m, 1H), 8.02 (s, 1H), 7.94–8.00 (m, 1H), 7.46–7.53 (m, 2H), 5.71 (dt, J=1.9, 3.7 Hz, 1H), 2.46 (t, J=7.1 Hz, 2H), 2.31–2.38 (m, 2H), 2.23–2.30 (m, 2H), 1.73–1.92 (m, 4H), 1.67 (dt, J=7.3, 14.4 Hz, 2H), 1.09 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.7, 136.6, 132.4, 131.8, 130.8, 130.6, 129.2, 128.6, 128.5, 127.8, 127.2, 126.1, 126.0, 125.9, 123.8, 121.9, 93.5, 79.9, 28.6, 25.5, 23.1, 22.4, 22.2, 21.8, 13.7; IR (neat) 2921, 2361, 1738, 1365, 1217, 895, 881, 797, 736, 676, 631 cm^{-1}; GC–MS (EI) m/z 358 (M^+, 61), 265 (100); HRMS (EI) calcd for $C_{25}H_{23}Cl$ (M^+) 358.1488, found 358.1485; mp 131.5 °C.

4.10. General procedure for the synthesis of tetracene derivatives

To a mixture of Ph_3PAuCl (4.5 mg, 0.009 mmol) and $AgBF_4$ (2.1 mg, 0.01 mmol) in CH_2Cl_2 (1 mL) was added a solution of **15** (0.18 mmol) in CH_2Cl_2 at room temperature and the mixture was stirred for 30 min at the same temperature. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with CH_2Cl_2 three times. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated to leave the crude product, which was purified by silica gel column chromatography using a mixture of hexane and CH_2Cl_2 as eluent to give **16**.

*4.10.1. 14-Chloro-5-phenyl-1,2,3,4-tetrahydrobenzo[a]tetracene (**16a**).* Red solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.21 (s, 1H), 8.58 (s, 1H), 8.46 (s, 1H), 8.08 (dd, J=3.3, 5.5 Hz, 1H), 7.98 (dd, J=3.3, 5.5 Hz, 1H), 7.61 (s, 1H), 7.35–7.50 (m, 7H), 3.73–3.82 (m, 2H), 2.65–2.72 (m, 2H), 1.76–1.88 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ141.4, 140.6, 135.3, 133.0, 132.2, 131.6, 131.3, 129.7, 129.4, 129.1, 129.1, 129.0, 128.0, 127.6, 127.4, 127.1, 127.0, 126.9, 126.1, 125.7, 125.5, 124.3, 33.0, 30.9, 23.7, 22.5; IR (neat) 2358, 2339, 1737, 1364, 1217, 904, 873, 732, 702, 627, 609 cm^{-1}; HRMS (EI) calcd for $C_{28}H_{21}Cl$ (M^+) 392.1332, found 392.1330; mp 223 °C.

*4.10.2. 14-Chloro-5-propyl-1,2,3,4-tetrahydrobenzo[a]tetracene (**16b**).* Red crystal; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.22 (s, 1H), 8.55 (s, 1H), 8.42 (s, 1H), 8.03–8.10 (m, 1H), 7.94–8.00 (m, 1H), 7.53 (s, 1H), 7.38–7.45 (m, 2H), 3.74 (t, J=6.3 Hz, 2H), 2.89 (t, J=6.3 Hz, 2H), 2.68 (t, J=7.3 Hz, 2H), 1.90–1.98 (m, 2H), 1.68–1.84 (m, 4H), 1.08 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 139.0, 136.3, 132.7, 132.2, 132.0, 131.3, 129.7, 129.2, 129.1, 129.0, 127.7, 126.9, 125.9, 125.8, 125.6, 125.4, 125.3, 124.2, 35.0, 33.1, 28.3, 23.6, 23.0, 22.6, 14.3; IR (neat) 3734, 2943, 2361, 2341, 1734, 1540, 1458, 1362, 1265, 1116, 901, 884, 867, 830, 819, 729, 671 cm^{-1}; Anal. Calcd for $C_{25}H_{23}Cl$: C, 83.66; H, 6.46; Cl, 9.88, found C, 83.59; H, 6.41; Cl, 9.40; mp 136 °C.

4.11. X-ray crystallographic analysis

*4.11.1. X-ray crystallographic analysis of **12a**.* X-ray data of **12a** were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71070 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.[22,23]

*4.11.2. Crystal data of 3,3′-Dibutyl-1,1′-dichloro-2,2′-binaphthyl (**12a**).* $C_{28}H_{28}Cl_2$, M_w=435.43, colorless prism, 0.20×0.20 ×0.20 mm, triclinic, space group P-1 (no. 2), a=8.156(6) Å, b=9.859(7) Å, c=14.837(11) Å, α=96.633(13)°, β=100.974(14)°, γ=98.632(14)°, V=1145.0(14) Å^3, T=173 K, Z=2, μ(Mo Kα)=2.957 cm^{-1}, 16,635 reflections measured, 5187 unique (R_{int}=0.017). The final $R1$ and $wR2$ were 0.0461 ($I>2.00\sigma(I)$) and 0.1316 (for all data), respectively. Crystallographic data (excluding structure factors) for the structure of **12a** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 727312. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: t44 (0)1223 336033 or e-mail:deposit@ccdc.cam.ac.uk).

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