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Synthesis of Benzofulvenes by Palladium-Catalyzed Cyclization of 1,2-Dialkynylbenzenes

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A palladium-catalyzed cyclization of enediynes for the synthesis of benzofulvenes **2** in yields of 59–76% was accomplished by treatment of dialkynylbenzenes **1** with 5 mol-% of PdX_2 and 3 equiv. of CuX_2 in acetonitrile at 60 °C for 2 h.

Introduction

The Bergman cyclization of enediynes to generate 1,4-dehydrobenzene biradicals has attracted much attention during the past two decades[1] because biradical intermediates are reported to be the key species of enediyne antibiotics that cause DNA damage.[2] More recently, the Bergman cyclization was applied to prepare a variety of π-conjugated materials.[3] In addition to the well-known thermally induced cyclization reaction of enediynes, several nonclassical Bergman-type cyclization reactions of enediynes initiated by either electrophiles,[4] nucleophiles,[5] radicals,[6] or organometallics[7] have been reported. The palladium-catalyzed reactions provide many unique organic transformations, especially for alkenes and alkynes.[8] To date, no report has mentioned the palladium-catalyzed cyclization reaction of enediynes; thus, we report herein the first examples of this reaction to afford benzofulvenes.

Result and Discussion

The PdX_2 and CuX_2 catalyst system was successfully employed in the carbonylation[9] and cyclotrimerization[10] of alkynes. We therefore treated 1,2-bis(2-phenylethynyl)benzene (**1a**) with 5 mol-% of $PdCl_2$ and 3 equiv. of $CuCl_2$ in acetonitrile at 60 °C for 2 h. Indene **2a** was obtained in 75% yield as a 4:1 mixture of (*E*/*Z*) isomers along with 21% yield of product **3a**.[11] The X-ray crystal structures of the major isomer of **2a** and compound **3a** are shown in Figures 1 and 2, respectively.[12] Upon treatment of **1a** with $PdBr_2$ and $CuBr_2$ under the same reaction conditions, compound **4a** was obtained in 95% yield. The spectroscopic data of **4a** are identical to those reported in the literature[13] and elemental analysis confirmed the structure formula. Because there is a report suggesting that compounds such as **2a** may be useful for the synthesis of fullerenes,[13] we explored this reaction as a general method for the preparation of benzofulvenes. Thus, extension of this palladium-catalyzed cyclization reaction to 1,2-dialkynylbenzenes **1b** and **1c** was carried out. Treatment of **1b** with $PdCl_2$ and $CuCl_2$ gave **2b** in 56% yield as a 4:1 mixture of stereoisomers and **3b** in 23% yield. Reaction of **1b** with $PdBr_2$ and $CuBr_2$ produced **4b** in 83% yield as a 5:1 mixture of stereoisomers and **3b** in 12% yield. Similar results were obtained by the reaction of **1c** with either $PdCl_2$ or $PdBr_2$ under the same reaction conditions to produce **2c** and **3c** in 42% and 87% yields, respectively, along with **3b** in 13% and 11% yields, respectively (Table 1). From the above results, we can conclude that the use of 5 mol-% of $PdBr_2$ and 3 equiv. of

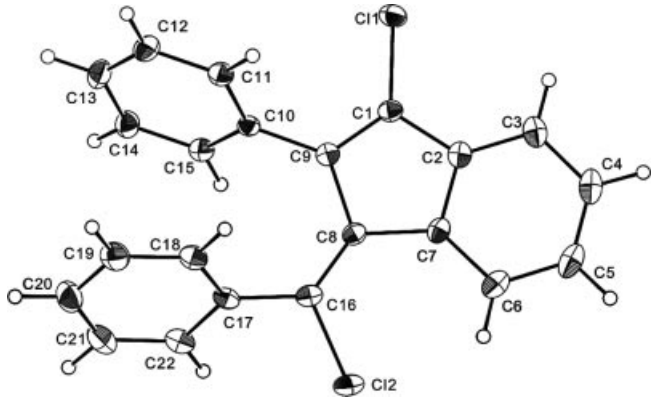

Figure 1. ORTEP plots for X-ray crystal structure of **2a**.

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$CuBr_2$ gives the benzofulvenes in better yields and higher stereoselectivities; additionally, indenone **3b** always appear as a byproduct in these reactions.

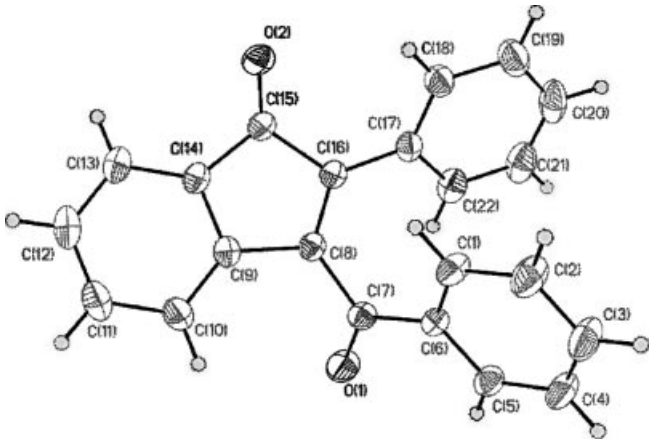
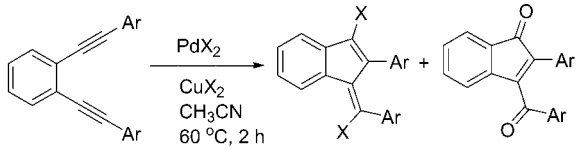


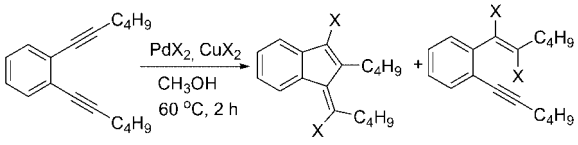
Figure 2. ORTEP plots for X-ray crystal structure of **3a**.

Table 1. Reaction of **1a**–**c** with PdX_2 and CuX_2 catalysts.



		Product yields [%]	
1a, Ar = Ph	X = Cl	**2a** (75)	**3a** (21)
	X = Br	**4a** (95)	
1b, Ar = 4-$CH_3OC_6H_4$	X = Cl	**2b** (56)	**3b** (23)
	X = Br	**4b** (42)	**3b** (13)
1c, Ar = 4-$CF_3C_6H_4$	X = Cl	**2c** (83)	**3c** (14)
	X = Br	**4c** (87)	**3c** (11)

1,2-Bis(1-hexynyl)benzene (**1d**) bearing an alkyl group on the alkyne terminus was examined in the cyclization reaction. Treatment of **1d** with $PdCl_2$ and $CuCl_2$ under the described reaction conditions gave **2d** in 59% yield as a 6:1 mixture of stereoisomers. Surprisingly, when the reaction of **1d** with $PdBr_2$ and $CuBr_2$ was carried out, fulvene **4d** was obtained in only 27% yield. The major product was obtained in 45% yield and the structure was assigned as compound **5d** [Equation (1)]. The less electron-stabilizing substituent, that is the alkyl group, may slow down the cyclization step; thus, the bromine addition adduct turns out to be the major product.



X = Cl **2d**, 59%

X = Br **4d**, 27% **5d**, 45% (1)

When compound **1a** was treated with $PdCl_2$ and $CuCl_2$ under the same reaction conditions except with the use of methanol as the solvent, three products were obtained. The major product obtained in 53% yield was assigned as compound **6a** as a 4:1 mixture of (*E*/*Z*) isomers. Fractional crystallization gave crystals of (*E*)-**6a**[12] (Figure 3). Compounds **2a** and **3a** were isolated in 8% and 15% yields, respectively. The reaction was also performed with ethanol as the solvent and compounds **6b**, **2a**, and **3a** were obtained in 45, 15, and 16% yields, respectively. This reaction can also be carried out by using CH_3CN as the solvent containing 10 equiv. of methanol, which affords compound **6a** in 75% yield as a 3:1 mixture of (*E*/*Z*) isomers. Instead of methanol, ethanol and 2-propanol were added into the reaction mixture, respectively. The yield of compound **2a** increased as the nucleophilicity of the additive decreased (Table 2). We also introduced other nucleophilic additives into the reaction mixture, such as HOAc, PhOH, and NaCN. However, only compound **2a** was obtained without

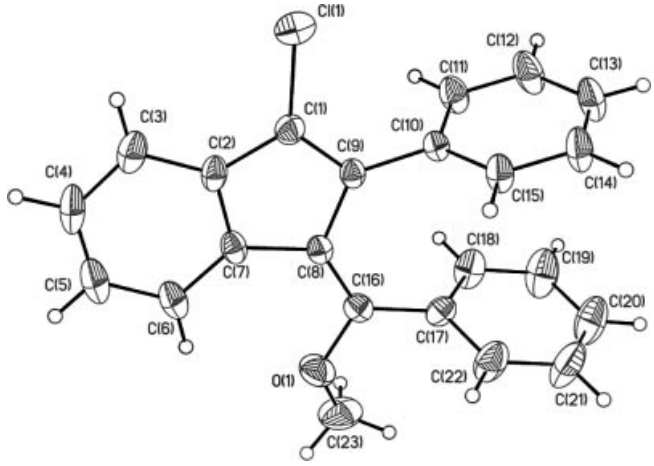
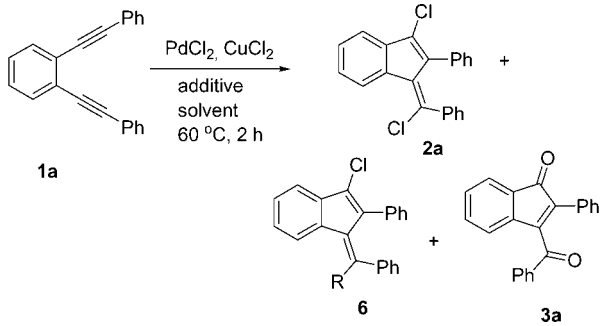


Figure 3. ORTEP plots for X-ray crystal structure of **6a**.

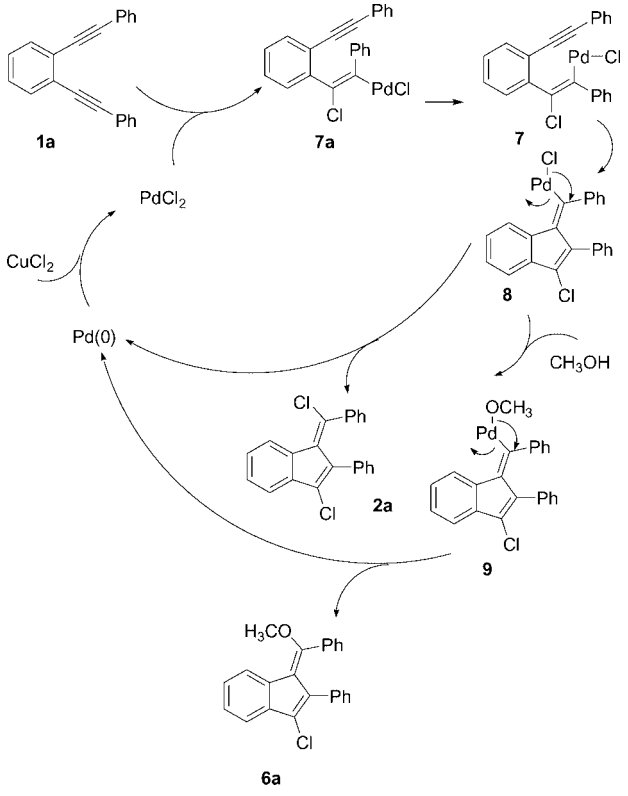
Table 2. Nucleophile effect on the synthesis of 1-chloro-3-[(chloro)(phenyl)methylene]-2-phenylindene (**2a**).



Solvent	Additive				
CH_3OH	none	**2a** (5)	R = OCH_3	**6a** (53)	**3a** (12)
EtOH	none	**2a** (15)	R = OEt	**6b** (45)	**3a** (16)
CH_3CN	CH_3OH (10 equiv.)	**2a** (8)	R = OCH_3	**6a** (75)	**3a** (15)
CH_3CN	EtOH (10 equiv.)	**2a** (28)	R = OEt	**6b** (44)	**3a** (23)
CH_3CN	*i*PrOH (10 equiv.)	**2a** (22)	R = O*i*Pr	**6c** (50)	**3a** (18)
CH_3CN	H_2O (10 equiv.)	**2a** (61)			**3a** (33)

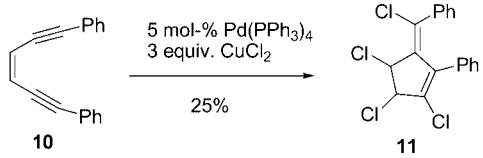
nucleophile-cooperated product **6**. The introduction of 10 equiv. of H_2O into the reaction mixture gave **2a** in 61% yield and **3a** in 33% yield.

A plausible mechanism for the formation of compounds **2a** and **6a** is proposed in Scheme 1. First, $PdCl_2$ undergoes addition to the alkyne to give intermediate **7a**, followed by vinylpalladium isomerization to give **7**. Intermediate **7** can then undergo 5-*exo*-dig cyclization to form **8**. Intermediate **8** then undergoes reductive elimination to give **2a** and palladium(0), which could be oxidized by $CuCl_2$ to regenerate $PdCl_2$. In the presence of methanol, the chloride ligand of **8** can be replaced to give **9**, which then undergoes reductive elimination to form compound **6a**.

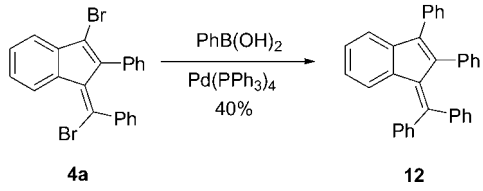


Scheme 1.

(*Z*)-1,6-Diphenyl-3-hexen-1,5-diyne (**10**) was also used in this reaction. Treatment of **10** with 5 mol-% of $Pd(PPh_3)_4$ and 3 equiv. of $CuCl_2$ under the described reaction conditions gave compound **11** in only 25% yield [Equation (2)]. This reaction is not very clean, and compound **11** is the product obtained after further reaction of the initially formed dichlorofulvene with $CuCl_2$. To explore the synthetic utility of these intermediary fulvene products, compound **4a** was treated with phenylboronic acid under Suzuki coupling reaction conditions to give **12** in 40% yield [Equation (3)].



(2)



(3)

Conclusions

We developed a general method for the synthesis of dihalobenzofulvenes. These products can be converted to a variety of substituted benzofulvenes. We also found that palladium-catalyzed cyclization of enediynes proceeds in the *exo–endo* mode to give the fulvenes instead of Bergman cyclization to give a benzene ring.

Experimental Section

General Procedure for the Cyclization of 1,2-Dialkynylbenzenes: To a stirred solution of 1,2-dialkynylbenzene (1 mmol) in 10 mL of CH_3CN was added $PdCl_2$ (0.05 mmol) and $CuCl_2$ (2 mmol), the solution was heated to 60 °C and stirred for 4 h. After cooling to room temperature, a saturated aqueous solution of NaCl was added into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried with anhydrous $MgSO_4$(s). After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

(*E*)-1-Chloro-3-[(chloro)(phenyl)methylene]-2-phenylindene (2a): Obtained as a yellow solid, m.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J = 7.6 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.48–7.40 (m, 2 H), 7.13 (dt, J = 8.0, 1.2 Hz, 2 H), 7.03–6.90 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 139.1, 138.4, 136.1, 134.9, 134.8, 134.3, 133.7, 130.4 (2 C), 130.1 (2 C), 128.9, 128.7, 128.6, 127.4, 127.2 (3 C), 125.1, 119.2 ppm. $C_{22}H_{14}C_{l2}$ (349.2526): calcd. C 75.66, H 4.04; found C 75.53, H 4.00.

(*E*)-1-Chloro-3-[(chloro)(4-methoxyphenyl)methylene]-2-(4-methoxyphenyl)indene (2b): Obtained as a yellow solid, m.p. 147–148 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 7.6 Hz, 1 H), 7.49–7.36 (m, 3 H), 7.04 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 6.51 (d, J = 8.8 Hz, 2 H), 6.43 (d, J = 8.8 Hz, 2 H), 3.69 (d, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 157.9, 139.5, 139.2, 135.8, 134.9, 134.3, 133.2 132.1 (2 C), 131.3 (2 C), 130.8, 128.3, 127.1, 126.2, 124.8, 118.9, 112.9 (2 C), 112.7 (2 C), 55.2, 55.1 ppm. $C_{24}H_{18}C_{l2}O_2$ (409.3045): calcd. C 70.43, H 4.43; found C 70.25, H 4.43.

(*Z*)-1-Chloro-3-[(chloro)(4-methoxyphenyl)methylene]-2-(4-methoxyphenyl)indene (2b): Obtained as a yellow solid, m.p. 137–138 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 5 H), 7.24 (t, J = 7.6 Hz, 1 H), 7.00–6.97 (m, 4 H), 6.94 (t, J = 7.6 Hz, 1 H), 6.42 (d, J = 8.0 Hz, 1 H), 3.89 (d, J = 11.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 159.1, 138.7, 137.8, 136.5, 135.5, 134.6, 134.4 132.2, 131.1 (2 C), 130.9 (2 C), 127.6, 127.3, 126.3, 122.7, 118.8, 114.3 (2 C), 113.5 (2 C), 55.4, 55.2 ppm.

$C_{24}H_{18}C_{l2}O_2$ (409.3045): calcd. C 70.43, H 4.43; found C 70.44, H 4.54.

(*E*)-1-Chloro-3-[(chloro)(4-trifluoromethylphenyl)methylene]-2-(4-trifluoromethylphenyl)indene (2c): Obtained as a yellow solid, m.p. 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 8.0 Hz, 1 H), 7.53–7.43 (m, 4 H), 7.27–7.17 (m, 5 H), 7.00 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 139.3, 137.3, 136.1, 134.5, 134.0, 131.8, 130.6 (3 C), 130.4 (3 C), 129.5, 129.3, 128.1, 127.2, 125.3, 124.3 (2 C), 124.2 (3 C), 119.7 ppm. $C_{24}H_{12}C_{l2}F_2$ (485.2486): calcd. C 59.40, H 2.49; found C 59.44, H 2.63.

(*Z*)-1-Chloro-3-[(chloro)(4-trifluoromethylphenyl)methylene]-2-(4-trifluoromethylphenyl)indene (2c): Obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 8.0 Hz, 1 H), 7.53–7.43 (m, 4 H), 7.27–7.17 (m, 5 H), 7.00 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 138.8, 138.7, 137.7, 135.3, 135.0, 131.8, 130.4 (2 C), 129.5 (3 C), 128.4, 127.2, 126.3, 126.2 (2 C), 126.1, 125.2, 125.1 (2 C), 125.0, 122.7, 119.5ppm.

(*E*)-2-Butyl-1-chloro-3-[(chloro)(butyl)methylene]indene (2d): Obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.6 Hz, 1 H), 7.38–7.22 (m, 3 H), 3.09 (t, J = 8.0 Hz, 2 H), 1.88–1.80 (m, 2 H), 1.64–1.44 (m, 6 H), 1.07–0.98 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 139.4, 137.5, 133.8, 133.6, 133.1, 127.4, 125.9, 122.6, 118.4, 40.4, 31.5, 29.8, 27.6, 22.8, 22.5, 13.9, 13.8 ppm. HRMS (EI): calcd. for $C_{18}H_{22}Cl_2$ 308.1099; found 308.1092.

3-Benzoyl-2-phenylindenone (3a): Obtained as an orange solid, m.p. 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 7.2 Hz, 1 H), 7.51 (d, J = 7.6 Hz, 1 H), 7.49–7.20 (m, 9 H), 7.04 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 194.6, 150.4, 144.0, 135.1, 134.4, 134.3, 129.6, 129.5, 129.3 (6 C), 128.9, 128.8 (2 C), 128.3 (2 C), 123.9, 121.7 ppm. $C_{22}H_{14}O_2$ (310.3454): calcd. C 85.14, H 4.55; found C 85.04, H 4.59.

3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)indenone (3b): Obtained as an orange solid, m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.2 Hz, 2 H), 7.57 (d, J = 6.8 Hz, 1 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 6.96 (d, J = 7.2 Hz, 1 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.77 (d, J = 8.8 Hz, 2 H), 3.81 (s, 3 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 194.6, 150.4, 144.0, 135.1, 134.4, 134.3, 129.6, 129.5, 129.3 (6 C), 128.9, 128.8 (2 C), 128.3 (2 C), 123.9, 121.7 ppm. $C_{24}H_{18}O_4$ (370.3973): calcd. C 80.11, H 4.97; found C 79.22, H 4.97.

3-(4-Trifloromethylbenzyl)-2-(4-trifluoromethylphenyl)indenone (3c): Obtained as a orange solid, m.p. 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.0 Hz, 2 H), 7.68–7.63 (m, 3 H), 7.50 (s, 4 H), 7.45–7.35 (m, 2 H), 7.0.7 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 193.2, 151.0, 143.2, 134.7, 132.8, 130.2, 129.6 (6 C), 129.2, 126.1 (2 C), 126.0, 125.9, 125.4 (2 C), 125.3 (2 C), 124.4, 122.2 ppm. $C_{24}H_{12}F_6O_2$ (446.3413): calcd. C 64.29, H 3.15; found C 63.99, H 3.01.

(*E*)-1-Bromo-3-[(bromo)(phenyl)methylene]-2-phenylindene (4a): Obtained as a yellow solid, m.p. 141–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.83 (d, J = 7.8 Hz, 1 H), 7.54–7.39 (m, 3 H), 7.14–7.01 (m, 2 H), 6.99–6.88 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.1, 140.7, 139.8, 138.1, 135.6, 134.9, 130.4 (2 C), 130.1 (2 C), 128.9, 128.7, 127.2 (3 C), 127.1 (3 C), 127.0, 126.5, 124.5, 120.7 ppm. $C_{22}H_{14}Br_2$ (438.1546): calcd. C 60.31, H 3.22; found C 60.33, H 3.14.

(*E*)-1-Bromo-3-[(bromo)(4-methoxyphenyl)methylene]-2-(4-methoxyphenyl)indene (4b): Obtained as a yellow solid, m.p. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 7.6 Hz, 1 H), 7.46–7.31 (m, 3 H), 7.03–6.99 (m, 2 H), 6.81 (td, J = 8.8, 2.4 Hz, 2 H), 6.50 (dd, J = 8.4, 2.0 Hz, 2 H), 6.41 (dd, J = 8.4, 3.2 Hz, 2 H), 3.71 (s, 3 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 157.9, 141.1, 139.5, 137.5, 135.7, 134.9, 133.3 132.2 (2 C), 131.3, 131.2, 131.1, 130.7, 128.6, 127.4, 126.7, 124.4, 122.7, 120.6, 112.8, 112.6 55.2, 55.1 ppm. $C_{24}H_{18}Br_2O_2$ (498.2065): calcd. C 57.86, H 3.64; found C 57.85, H 3.59.

(*Z*)-1-Bromo-3-[(bromo)(4-methoxyphenyl)methylene]-2-(4-methoxyphenyl)indene (4b): Obtained as a yellow solid, m.p. 157–158 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.18 (m, 6 H), 7.03–6.87 (m, 5 H), 6.27 (d, J = 7.6 Hz, 1 H), 3.88 (d, J = 4.6 Hz, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.7, 159.3, 140.9, 140.5, 139.8, 137.7, 135.0, 134.6 131.4 (2 C), 130.6 (2 C), 130.3, 129.3, 128.2, 127.4, 126.5, 122.8, 121.1, 119.9, 114.3, 113.6, 55.4, 55.2 ppm.

(*E*)-1-Bromo-3-[(bromo)(4-trifluorophenyl)methylene]-2-(4-trifluoromethylphenyl)indene (4c): Obtained as a yellow solid, m.p. 177–178 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.74 (dt, J = 6.8, 1.4 Hz, 1 H), 7.64 (s, 1 H), 7.52–7.42 (m, 3 H), 7.24–7.16 (m, 5 H), 7.06 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 140.9, 139.1, 138.6, 137.8, 135.2, 132.5, 131.7, 130.5 (6 C), 129.5 (2 C), 127.8, 124.8, 124.3 (2 C), 124.2 (3 C), 121.2 ppm. $C_{24}H_{12}Br_2F_6$ (574.1505): calcd. C 50.21, H 2.11; found C 50.17, H 2.36.

(*Z*)-1-Bromo-3-[(bromo)(4-trifluorophenyl)methylene]-2-(4-trifluoromethylphenyl)indene (4c): Obtained as a yellow solid, m.p. 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.71 (m, 4 H), 7.58–7.53 (m, 4 H), 7.39 (dt, J = 7.6, 0.8 Hz, 1 H), 7.29 (t, J = 7.6 Hz, 1 H), 6.94 (td, J = 7.6, 0.8 Hz, 1 H), 6.08 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3, 145.2, 139.8, 139.7, 139.0, 138.4, 134.3, 130.7 (2 C), 129.1 (2 C), 128.5, 127.3, 126.3, 126.2 (2 C), 126.1, 125.9, 125.3, 125.2 (2 C), 125.1, 122.8, 120.7 ppm.

(*E*)-1-Bromo-3-[(bromo)(butyl)methylene]-2-butylindene (4d): Obtained as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.6 Hz, 1 H), 7.34–7.17 (m, 3 H), 3.29 (t, J = 8.0 Hz, 2 H), 2.98 (t, J = 8.0 Hz, 2 H), 1.88–1.81 (m, 2 H), 1.79–1.40 (m, 6 H), 1.07–0.95 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.8, 140.4, 136.6, 134.8, 134.4, 127.6, 126.1, 125.7, 122.8, 119.4, 43.4, 31.6, 30.1, 29.1, 22.9, 22.4, 13.9, 13.8 ppm. HRMS (EI): calcd. for $C_{18}H_{22}Br_2$ 396.0088; found 396.0081.

1-[(*E*)-1,2-Dibromohexen-1-yl]-2-(hexyn-1-yl)benzene (5d): Obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.2 Hz, 1 H), 7.33–7.19 (m, 3 H), 2.98–2.74 (m, 2 H), 2.42 (t, J = 6.6 Hz, 2 H), 1.76–1.41 (m, 8 H), 1.28–0.93 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.9, 132.3, 128.7, 128.3, 127.6, 125.1, 123.1, 115.1, 94.9, 78.2, 39.9, 30.6, 29.7, 21.9, 21.7, 19.3, 14.0, 13.6 ppm. HRMS (EI): calcd. for $C_{18}H_{22}Br_2$ 396.0088; found 396.0091.

1-Chloro-3-[(methoxy)(phenyl)methylene]-2-phenylindene (6a): Obtained as a yellow solid and a 4:1 mixture of (*E*) and (*Z*) isomers, m.p. 111–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, J = 6.8 Hz, 0.8 H), 7.53–7.33 (m, 7 H), 7.05–6.86 (m, 12 H), 6.19 (d, J = 7.8 Hz, 0.2 H), 3.62 (s, 2.4 H), 3.11 (s, 0.6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) for (*E*) isomer: δ = 162.4, 137.8, 135.6, 134.5, 131.7, 130.5, 129.8, 129.5, 129.2, 129.1, 127.5 (3 C), 127.4, 126.9 (3 C), 26.3, 126.1, 123.9, 118.5, 57.4 ppm. HRMS (EI): calcd. for $C_{23}H_{17}ClO$ 344.0968; found 344.0965. $C_{23}H_{17}ClO$ (344.8335): calcd. C 80.11, H 4.97; found C 79.22, H 4.97.

1-Chloro-3-[(ethoxy)(phenyl)methylene]-2-phenylindene (6b): Obtained as a yellow solid and a 3:1 mixture of (*E*) and (*Z*) isomers,

m.p. 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 6.4 Hz, 0.7 H), 7.58–7.36 (m, 7 H), 7.19 (t, J = 7.2 Hz, 0.5 H), 7.08–7.05 (m, 3 H), 6.98–6.86 (m, 7 H), 6.16 (d, J = 7.8 Hz, 0.3 H), 3.88 (q, J = 7.6 Hz, 1.5 H), 3.40 (q, J = 7.6 Hz, 0.5 H), 1.39 (t, J = 7.6 Hz, 2.25 H), 0.65 (t, J = 7.6 Hz, 0.75 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) for (*E*) isomer: δ = 161.8, 137.8, 135.6, 134.6, 134.5, 132.1, 130.4 (2 C), 130.1 (2 C), 129.6, 129.1 (2 C), 127.4 (2 C), 126.9 (2 C), 126.4, 126.2, 123.9, 121.1, 118.4, 66.1, 15.5 ppm. $C_{24}H_{19}ClO$ (358.8601): calcd. C 80.33, H 5.34; found C 80.07, H 5.30.

1-Chloro-3-[(isopropoxy)(phenyl)methylene]-2-phenylindene (6c): Obtained as a yellow solid and a 9:1 mixture of (*E*) and (*Z*) isomers, m.p. 186–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 5.6 Hz, 0.9 H), 7.53–7.39 (m, 1 H), 7.37–7.34 (m, 2 H), 7.08–7.05 (m, 3 H), 6.97–6.87 (m, 7 H), 6.10 (d, J = 7.8 Hz, 0.1 H), 4.23 (sept, J = 6.4 Hz, 1 H), 3.89 (sept, J = 6.4 Hz, 0.1 H), 1.32 (d, J = 6.0 Hz, 5.4 H), 0.71 (d, J = 6.0 Hz, 0.6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) for (*E*) isomer: δ = 161.2, 137.9, 135.7, 134.8, 132.5, 130.4 (2 C), 130.1 (2 C), 129.7, 128.9, 127.4 (2 C), 127.2, 126.9 (2 C), 126.4, 126.2, 125.9, 124.0, 121.7, 118.4, 72.7, 27.6 (2 C) ppm. $C_{25}H_{21}ClO$ (372.8866): calcd. C 80.53, H 5.60; found C 80.43, H 5.71.

(*Z*)-[Chloro(3,4,5-trichloro-2-phenylcyclopent-2-enylidene)methyl]-benzene (11): Obtained as a pale yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52–7.28 (m, 4 H), 7.04–6.82 (m, 6 H), 5.34 (s, 1 H), 4.93 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.2, 136.8, 136.4, 135.8, 134.3, 131.4, 129.3, 128.9, 128.3, 128.1, 127.5, 127.2, 68.6, 64.1 ppm. HRMS (EI): calcd. for $C_{18}H_{12}Cl_4$ 367.9693; found 367.9695.

1-Benzhydrylidene-2,3-diphenylindene (12): Obtained as a yellow solid, m.p. 233–234 °C (ref.[14] 232 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.40 (m, 4 H), 7.28–7.11 (m, 8 H), 6.91–6.75 (m, 11 H), 6.42 (dt, J = 7.6, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 143.6, 143.5, 142.9, 141.2, 138.9, 138.1, 137.5, 136.4, 135.2, 132.1, 130.9, 130.7, 129.8, 128.6 (2 C), 127.8, 127.6, 126.8 (2 C), 125.2, 125.0, 123.4, 119.7 ppm. MS(EI): *m*/*z* (%) = 432 (100) $[M]^+$. $C_{34}H_{24}$ (432.5544): calcd. C 94.41, H 5.59; found C 93.82, H 5.56.

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[12] For **2a**: CCDC-623067 [cell parameters: a = 8.7380(2), b = 9.1320(2), c = 12.1690(3)]; for **3a**: CCDC-623068 [cell parameters: a = 8.4997(11), b = 10.0925(13), c = 19.635(3)]; for **6a**: CCDC-623069 [cell parameters: a = 9.4463(9), b = 12.0564(11), c = 17.1862(16)] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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