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An Extremely Simple Dibenzopentalene Synthesis from 2-Bromo-1-ethynylbenzenes Using Nickel(0) Complexes: Construction of Its Derivatives with Various Functionalities

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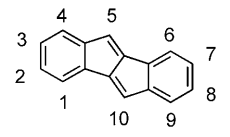
Abstract: An extremely simple dibenzopentalene synthesis from readily available 2-bromo-1-ethynylbenzenes using a nickel(0) complex is described. Although the yields are moderate, the formation of three C–C bonds in a single process and the high availability of the starting materials are important advantages of this reaction. The corresponding aryl–nickel(II) complex as an important intermediate was isolated as relatively stable crystals, and the structure was confirmed by X-ray crystallographic analysis. The high stability of this complex should play a key role in this reaction. The reaction is applicable to the preparation of dibenzopentalenes bearing various functional groups. Their electronic properties are consistent with theoretical calculations. The cyclic voltammograms of these compounds reveal highly amphoteric redox properties. In particular, the electron-donating property of a tetramethoxy derivative is greater than that of oligothiophenes and dibenzodithiophenes and almost comparable to that of pentacene.

Keywords: alkynes · aromatic compounds · electrochemistry · organometallic compounds · theoretical chemistry

Introduction

Dibenzopentalene **1** is a fairly stable compound with a planar structure, despite possessing a 4$n\pi$-electron periphery.[1] The antiaromatic character provides corresponding stable dianion and dication species.[2] Therefore, dibenzopentalenes with appropriate functionalities would be promising for application as functional dyes with highly amphoteric redox properties. Since the first synthesis of dibenzopentalenes by Brand in 1912,[3a] various dibenzopentalenes bearing functional groups at positions 5 and 10 have been prepared.[3] The derivatives functionalized at the aromatic rings are rarely prepared probably because of the limitation of the known synthetic methods. From the viewpoint of materials science, the potential of the π-system has not been well explored.



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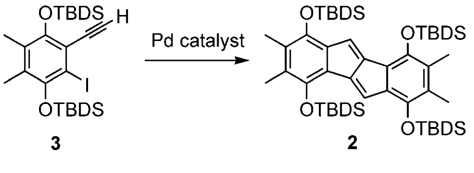
In 1999, Youngs and co-workers reported the formation of dibenzopentalene derivative **2** from 2-iodo-1-ethynylbenzene **3** under the usual conditions for Sonogashira coupling (Scheme 1).[4] This reaction, however, seems to be an exceptional case because the reaction of 2-iodo-1-ethynylbenzenes



Scheme 1. Youngs' dibenzopentalene synthesis. TBDS = *tert*-butyldimethylsilyl.

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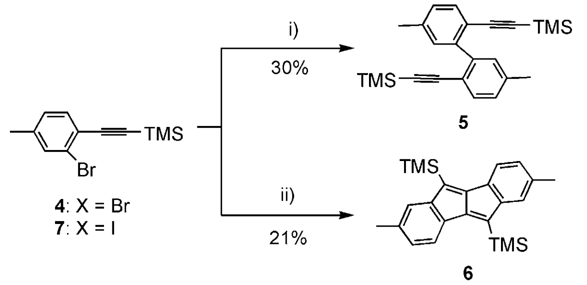
commonly afforded phenyleneethynylene macrocycles.[5] The dibenzopentalene synthesis starting from 2-halo-1-ethynylbenzenes is quite attractive from the viewpoint of synthetic chemistry because of the high availability of the starting materials and the formation of three C–C bonds in one process. It has been known that nickel(0) complexes effectively catalyze the Ullman-type coupling of aryl halides.[6] On the other hand, we found a nickel(0)-mediated reaction that yields dibenzopentalenes from 2-bromo-1-ethynylbenzenes in place of the corresponding biaryls. Although the yields were not so high, the reaction is applicable to the preparation of dibenzopentalenes bearing various functional groups. Herein, we discuss the preparation and the properties of the newly obtained dibenzopentalene derivatives.



Scheme 2. A nickel(0)-mediated reaction of **4**. Regents and conditions: 1) [$NiCl_2(PPh_3)_2$] (0.2 equiv), Zn (1.5 equiv), Et_4NI (1.0 equiv), THF (0.04 M), 50 °C, 24 h; 2) [$NiCl_2(PPh_3)_2$] (0.2 equiv), Zn (1.5 equiv), THF (0.04 M), 50 °C, 24 h. TMS = trimethylsilyl.

Results and Discussion

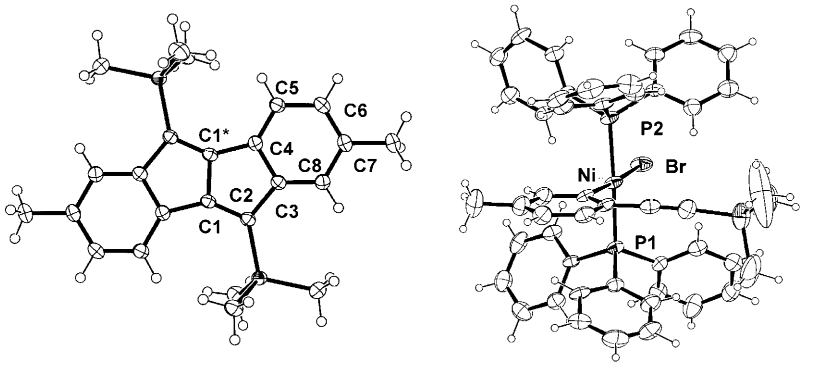


Figure 1. ORTEP drawings of **6** (left) and **8** (right) (50 % probability). Selected bond lengths [Å] for **6**: C1–C2 1.364(2), C2–C3 1.503(2), C3–C4 1.425(2), C4–C5 1.383(2), C5–C6 1.404(2), C6–C7 1.385(3), C7–C8 1.409(2), C8–C3 1.383(2), C1–C1* 1.471(3), C4–C1* 1.471(2); **8**: Br–Ni 2.372(1), Ni–P1 2.218(3), Ni–P2 2.219(3), Ni–C 1.875(7).

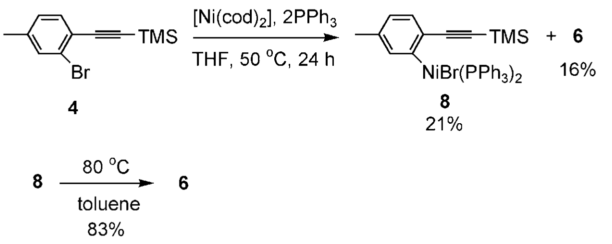
Table 1. Reaction of **4** with [$NiCl_2(PPh_3)_2$] under various conditions.

Entry	Conditions					Yield [%]		
	equiv of **4**	solvent	t [h]	T [°C]	additive	**4**	**5**	**6**
1[a]	0.2	THF (0.04 M)	24	50	Et_4NI (1.0 equiv)	20	30	–
2[b]	0.05	THF (0.04 M)	24	50	PPh_3 (0.4 equiv)	70	14	–
3[b]	0.05	DMF (0.04 M)	24	50	PPh_3 (0.4 equiv)	75	–	–
4[a]	0.2	THF (0.04 M)	24	50	none	53	–	21
5[a]	0.2	THF (0.04 M)	48	50	none	37	–	24
6[a]	1.3	THF (0.04 M)	100	50	none	27	–	22
7[a,c]	0.2	THF (0.04 M)	24	50	none	11	trace	15
8[a,d]	0.2	THF (0.04 M)	24	50	none	6	48	21
9[a]	0.5	toluene (0.2 M)	24	110	none	–	–	27
10[a]	1.0	toluene (0.2 M)	24	110	none	–	–	35
11[a]	1.0	toluene (0.2 M)	24	110	COD (1.0 equiv)	–	–	39
12[a]	1.0	toluene/DME (4:1, 0.2 M)	24	80	none	–	–	41
13[a]	1.0	DME (0.2 M)	24	80	none	–	–	20

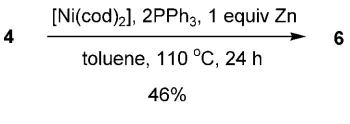
[a] 1.5 equivalents of Zn were added. [b] 1.0 equivalents of Zn were added. [c] Iodide **7** was employed. [d] [$NiCl_2(dppp)$] was employed.

The treatment of 2-bromo-4-methyl-1-(2-trimethylsilylethynyl)benzene (**4**) with a Ni^0 complex, generated from the reduction of [$NiCl_2(PPh_3)_2$] with zinc dust in THF in the presence of Et_4NI,[6c] furnished the corresponding biaryl **5** in 30 % yield. Surprisingly, the reaction was carried out in the absence of Et_4NI to produce **6** in approximately 20 % with high reproducibility (Scheme 2). The structure of **6** was estimated from spectral data and finally confirmed by X-ray crystallographic analysis (Figure 1, left).[7] We investigated the reaction under various conditions, and the results are summarized in Table 1. It has been known that the presence of an excess amount of PPh_3 or I^- ions effectively promotes biaryl coupling.[6] Inversely, the presence of these additives hampered the formation of **6** (Table 1, entries 1–3). Convincingly, the reaction using 2-iodo-4-methyl-1-(2- trimethylsilylethynyl)benzene (**7**) deceased the yield of **6** (Table 1, entry 6) because iodide ions were formed during the reaction. When 0.2 equivalents of the nickel complex ([$NiCl_2(PPh_3)_2$] or [$NiCl_2(dppp)$]; dppp = l,3-bis(diphenylphosphine)propane) were employed, a considerable amount of **4** was recovered (Table 1, entries 3 and 7). A prolonged reaction time and an increase in the nickel complex resulted in decreased recovery, but the yield of **6** did not increase (Table 1, entries 4 and 5). Actually, **6** is relatively labile under the reaction conditions. Upon two days of exposure to the reaction conditions, only 36 % of **6** was recovered, as a considerable amount of **6** changed into insoluble material. Although the mechanistic details have not been clarified yet, the Ni^0 complex generated under these under conditions may have led both to the formation and decomposition of dibenzopentalene. The fact that yields of **6** do not exceed approximately 20 % show the counterbalance between both processes.

The reactions using [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) were examined to investigate the reaction mechanism because [Ni(PPh$_3$)$_2$] as an active Ni^0 reagent forms cleanly under mild conditions. A solution of **4**, [Ni(cod)$_2$], and PPh$_3$ in a 1:1:2 stoichiometry in THF was heated at 50 °C to afford an aryl–nickel(II) complex **8** (21 % yield) together with **3** (16 % yield; Scheme 3). Complex **8** can be purified by column chromatography on silica gel and was obtained as air-stable pale yellow crystals. The structure was established by X-ray crystallographic studies (Figure 1, right).[7] The oxidative addition of [Ni(PPh$_3$)$_2$] to **4** produced **8**. This type of aryl–nickel(II) complex has been known as an intermediate of nickel-mediated homo-coupling reactions, and ordinarily as a thermally labile and air-sensitive compound. However, some derivatives bearing bulky ligands are stable enough to be isolable.[8] The molecular structure of **8** reveals that the C–Ni bond is effectively submerged by a bulky trimethylsilyethynyl group and two triphenylphosphine ligands. On the other hand, complex **8** is relatively thermally labile; furthermore, heating a solution of **8** in toluene to over 80 °C led to **6** being obtained in high yield (Scheme 3). The formation of **6** obviously indicates that **8** is an important intermediate of the dibenzopentalene synthesis. According to the results, the highest yield was obtained (i.e., 46 %) when a solution of **4** in toluene (0.2 M) was heated at 110 °C in the presence of [Ni(cod)$_2$], PPh$_3$, and zinc dust in a 1:2:1 stoichiometry (Scheme 4). Dilute conditions (0.04 M) or the absence of zinc dust resulted in a drastic decrease in the yield of **6**.



Scheme 3. Preparation and thermal reaction of aryl–nickel(II) complex **8**.

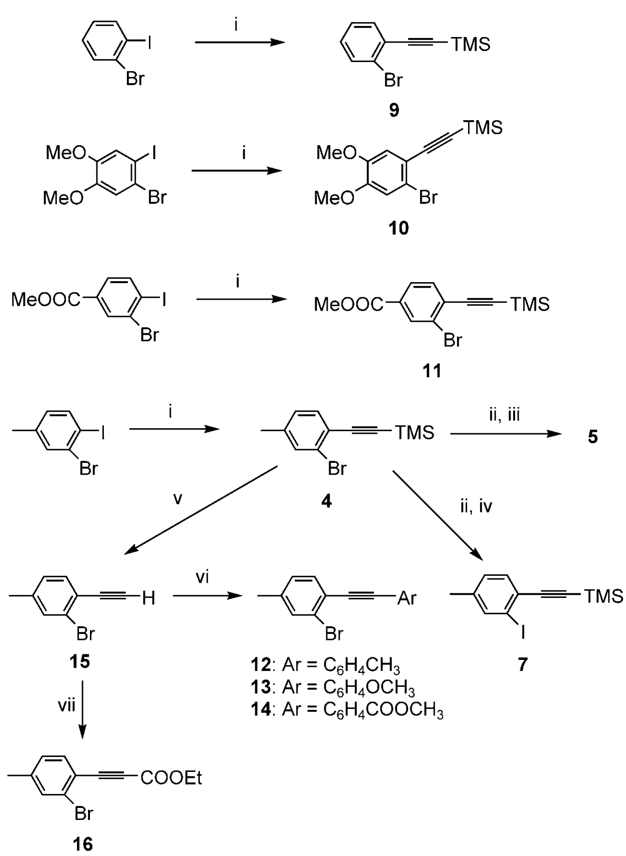


Scheme 4. Synthesis of dibenzopentalene **6** using [Ni(cod)$_2$].

Given these results, we investigated the conditions using [NiCl$_2$(PPh$_3$)$_2$] as a reagent for convenience. When one equivalent of the complex and toluene as a solvent were employed, **6** was obtained in 35–39 % yield (Table 1, entries 10 and 11). The presence of a small amount of 1,2-dimethoxyethane (DME; toluene/DME = 4:1) accelerated the reaction rate, and the yield of **6** went up to 41 % yield (Table 1, entry 12). However, the reaction in DME alone decreased the yield to 20 % (Table 1, entry 13). The reactions carried out in low-polarity solvent systems provided better yields. These conditions would hamper the decomposition of **6**.

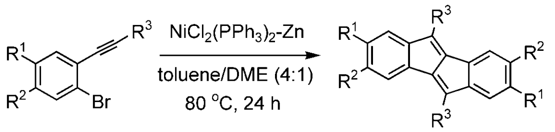
A simple radical coupling mechanism cannot be adopted because the oxidative coupling of 2-lithio-4-methyl-1-(2-trimethylsilylethynyl)benzene, generated from **4** using CuCl$_2$, afforded **5** in high yield. The thermal reaction of **8** led to **6** through the formation of three C–C bonds involving a dimerization reaction. The insertion reaction of the C–Ni bond to alkyne is known in several nickel-mediated reactions.[9] Although plausible reaction mechanisms cannot be concluded at this stage, the high thermal stability of **8** presumably plays a key role in this reaction. Further mechanistic studies will be reported in due course.

2-Bromoarylacetylenes **9**–**16** with various functionalities were prepared (Scheme 5) and subjected to this reaction under the conditions of entry 12 in Table 1 to give dibenzopentalenes **17**–**22** in acceptable yields (Scheme 6). Unfortu-



Scheme 5. Synthesis of *ortho*-haloethynylbenzenes. Reagents and conditions: i) [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N/THF (1:1), TMS-C≡C-H, RT, 12 h; ii) *n*BuLi, THF, −70 °C; iii) CuCl$_2$; iv) I$_2$; v) K$_2$CO$_3$, MeOH, RT, 12 h; vi) [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_3$N/THF (1:1), ArI, RT, 12 h; vii) LDA, THF, −70 °C, then ClCOOEt. LDA = lithium diisopropylamide.

nately, the reaction of bromophenylacetylenes **15** or **16** afforded complex mixtures. However, taking into account that three C$-$C bonds form in one reaction, the yields are not so poor.



17: R^1, R^2 = H, R^3 = TMS 35%
18: R^1, R^2 = OMe, R^3 = TMS 13%
19: R^1 = COOMe, R^2 = H, R^3 = TMS 24%
20: R^1 = Me, R^2 = H, R^3 = C$_6$H$_4$Me 16%
21: R^1 = Me, R^2 = H, R^3 = C$_6$H$_4$OMe 13%
22: R^1 = Me, R^2 = H, R^3 = C$_6$H$_4$COOMe 13%

Scheme 6. Synthesis of dibenzopentalenes bearing various functionalities.

Consistent with the reported molecular structures of dibenzopentalenes,[3g] **6** also has large and small bond alternations in the five- and six-membered rings, respectively. Although the large bond alternation greatly suppresses the antiaromatic character of the pentalene moieties, the geometry of the benzene rings might be affected by the 8π-electron system. The large bond length of the C3$-$C4 bond would reflect a propensity to dislike unfavorable effects from the 4*n*π-cyclic conjugation of the pentalene moiety, whereas the aromatic character of the benzene rings appears to be adequately operative according to the small bond alternation of the other bonds in the benzene rings. The nucleus-independent chemical shift (NICS) calculation[10] supports this consideration. The NICS(1) values of unsubstituted dibenzopentalene calculated at the GIAO-RB3LYP/6–31G**//RB3LYP/6–31G** level were +5.88 and −6.23 for the five- and six-membered rings, respectively. The pentalene moiety possesses much less paratropicity than pentalene itself (+18.42), whereas the benzene rings retain almost more than half of diatropicity of benzene itself (−11.31).

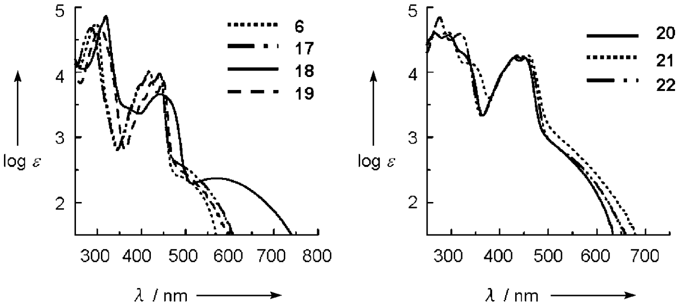


Figure 2. Absorption spectra of **6** and **17–19** (left) and **20–22** (right) in CH$_2$Cl$_2$.

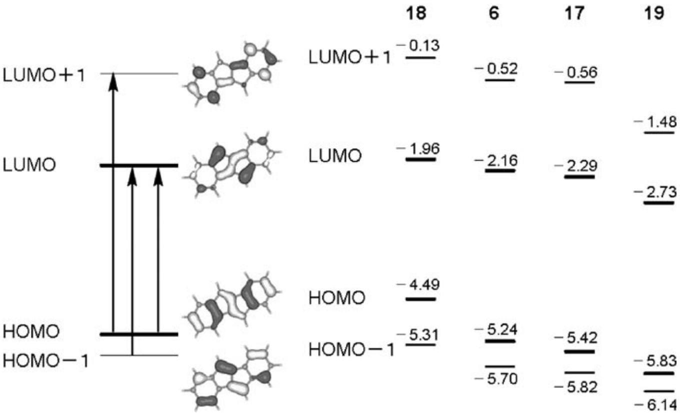


Figure 3. The molecular orbitals of unsubstituted dibenzopentalene calculated with the RB3LYP/6–31G** method. Energy diagram (eV) of dibenzopentalene derivatives **6** and **17–19** evaluated by the TD-DFT (RB3LYP/6–31G**) calculation.

Table 2. Absorption wavelengths and oscillator strengths of dibenzopentalene evaluated by the TD-DFT (RB3LYP/6–31G**) calculation.

Compd	Absorption [nm] (oscillator strength)	Assignments (%)
6	544 (0.00)	HOMO→LUMO (45)
	393 (0.18)	HOMO−1→LUMO (36)
		HOMO→LUMO−1 (8)
17	538 (0.00)	HOMO→LUMO (45)
	394 (0.19)	HOMO−1→LUMO (37)
		HOMO→LUMO−1 (7)
18	696 (0.00)	HOMO→LUMO (45)
	433 (0.13)	HOMO−1→LUMO (40)
		HOMO→LUMO−1 (3)
19	539 (0.00)	HOMO→LUMO (45)
	409 (0.17)	HOMO−1→LUMO (36)
		HOMO−1→LUMO (8)

The electronic spectra of the dibenzopentalenes exhibit three characteristic absorption bands: the longest, but relatively weak, absorption band (450–700 nm); the second longest absorption band (350–450 nm); the third longest, and most intense, absorption band (250–350 nm; Figure 2). According to calculations at the TD-DFT(RB3LYP/6–31G**) level of theory (Figure 3 and Table 2),[11] the longest absorption bands ($S_0 \rightarrow S_1$ bands) are attributable to HOMO→LUMO transitions, which are symmetry forbidden and typical of 4*n*π-electron systems. Actually, the observed longest absorption bands are relatively weak ($\log\varepsilon = 2.5 \approx 3.0$). The second and third longest absorption bands are also assignable to the HOMO−1→LUMO and HOMO→LUMO+1 transitions, respectively. The 2,3,7,8-tetramethoxy derivative **18** shows a considerably large bathochromic shift in the HOMO→LUMO transition, though others exhibit quite similar absorption curves. The anomaly in the absorption bands of **18** is completely supported by the time-dependent density functional theory (TD-DFT) calculations. The DFT results suggest that the small HOMO–LUMO gap of **18** relative to **6**, **17**, and **19** would stem from a large positive shift in energy of the HOMO, which is consistent with electrochemical results (see below). On the other hand, substitution of aryl groups at positions 5 and 10 causes bathochromic shifts of approximately $\Delta\lambda = 50$ nm in the first and second absorption bands of **20–22**. Substitution at the *para* position of the aryl groups provides relatively small variations (Figure 2, right).

The redox properties of the dibenzopentalenes were examined by cyclic voltammetry (the redox potentials are summarized in Table 3). These dibenzopentalenes basically possess four-stage redox properties as expected and the redox potentials vary with the electronic properties of the substituents. In particular, the cyclic voltammogram of **18** exhibits reversible first oxidation (${}^{ox}E_1$) and pseudoreversible second oxidation waves (Figure 4). The oxidation potentials for **18** indicate a high electron-donating property and the ${}^{ox}E_1$ value is higher than for oligothiophenes[12] and dibenzodithiophenes[13] and almost comparable to pentacene ($E_{ox}=0.22$ V, $E_{red}=-1.87$ V, ferrocene/ferrocenium (Fc/Fc$^+$) $=0$ V in $C_6H_4Cl_2$).[14] Combined with the relatively long-wavelength absorption, the HOMO of **18** was elevated to a considerably higher energy level. On the other hand, methoxycarbonyl derivatives **19** and **22** possess higher electron affinities than the others. In particular, **22** shows two readily reversible reduction waves, thus indicating the formation of a stable dianion species. Because the dibenzopentalene dianion has the highest electron density at positions 5 and 10,[2] methoxycarbonylphenyl groups at these positions effectively stabilize the formed dianion. These redox properties are almost comparable to those of perfluoropentacene ($E_{ox}=0.79$ V, $E_{red}=-1.13$ V, Fc/Fc$^+=0$ V in $C_6H_4Cl_2$).[14b]

Table 3. Redox potentials of **6** and **17**–**22** in DMF.[a]

Compound	${}^{ox}E_{2,1/2}$ [V]	${}^{ox}E_{1,1/2}$ [V]	${}^{red}E_{1,1/2}$ [V]	${}^{red}E_{2,1/2}$ [V]
6	1.06[b]	0.87[b]	−1.60	−2.17[b]
17	1.16[b]	0.97[b]	−1.53	−2.17[b]
18	0.72[b]	0.35	−1.63	−2.21[b]
19	–[c]	–[c]	−1.23	−1.85[b]
20	0.98[b]	0.87[b]	−1.62	−2.18[b]
21	1.13[b]	0.81[b]	−1.66	−2.24[b]
22	1.05[b]	0.94[b]	−1.38	−1.74

[a] V versus Ag/Ag$^+$ in 0.1 M nBu$_4$NClO$_4$/DMF; scan rate: 100 mV s^{-1}; +25 °C; Fc/Fc$^+=+0.05$ V. [b] Half-wave potentials. [c] Not detected.

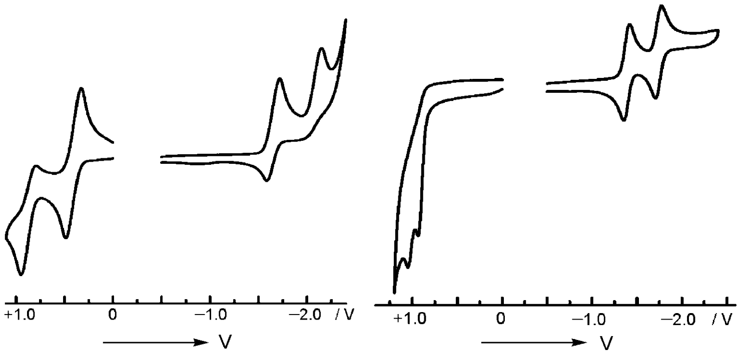


Figure 4. Cycic voltammograms of **18** (left) in CH_2Cl_2 and **22** (right) in DMF at 25 °C.

Conclusion

A nickel(0)-mediated reaction of 2-bromoethynylbenzene derivatives afforded dibenzopentalene derivatives. Although the yields are low to moderate, the formation of three C−C bonds in a single process and the high availability of the starting materials are highly advantageous for this reaction. This process could be widely applicable to bromoalkynes with various functionalities and π flames, such as polycyclic and heteroaromatic compounds, to produce a variety of novel π-conjugated systems with pentalene skeletons. The electronic properties of the functionalized dibenzopentalenes are consistent with theoretical calculations and the dibenzopentalenes have highly amphoteric redox properties. Particularly, the tetramethoxy derivative possesses considerably strong electron-donating properties that are almost comparable to those of pentacene. Further studies are now in progress.

Experimental Section

General: All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred by syringe. Analytical thin-layer chromatography was performed using glass plates precoated with Merck art. 7730 Kieselgel 60 GF-254. The TLC plates were visualized by exposure to UV light. Solutions in organic solvents were concentrated by rotary evaporation at approximately 15 Torr using a diaphragm pump. Column chromatography was performed on Merck Kiesel gel 60 and Merck art. 1097 aluminum oxide 90 (Aktivitatss fufe II-III).

All the reagents were purchased from Tokyo Kasei Co., Nakarai Tesc., Wako Co., and other commercial suppliers and were used as supplied, unless otherwise stated. Solutions of butyllithium in hexane were purchased from Mitsuwa Pure Chemicals, Inc. Anhydrous diethyl ether and toluene were purchased from Kanto Chemical Co. and dried as necessary by using standard procedures. THF and DME were purchased from Wako Chemical Co. and distilled from sodium/benzophenone at 760 Torr in a nitrogen atmosphere before used. Trimethylsilylacetylene was purchased from Shin-Etsu Chemical Co., Ltd. Compounds **9**[15] and **16**,[16] 3-bromo-4-iodotoluene,[17] 4-bromo-5-iodo-1,2-dimethoxybenzene,[18] and methyl 3-bromo-4-iodobenzoate[19] were prepared according to previously reported procedures.

Melting points were recorded on a Yanaco MP 500D apparatus and uncorrected. FAB and EI mass spectra were measured on a JEOL JMS-SX 102 instrument and Shimadzu GCMS-QP5050 A. ^{1}H NMR spectra (tetramethylsilane (TMS) as an internal standard ($\delta=0$ ppm)) and ^{13}C NMR spectra ($CDCl_3$; as an internal standard ($\delta=77.0$ ppm)) were recorded on JEOL lambda-500, JEOL JNM-GSX-400, and JEOL EX-270 apparatus. The chemical shifts are given in ppm. IR spectra were recorded on a JASCO FT-IR-460 K2 spectrometer. Electronic (UV/Vis) spectra were recorded on a Jasco V-570 spectrophotometer.

2-Bromo-4-methyl-1-(2-trimethylsilylethynyl)benzene (4): A solution of 2-bromo-1-iodo-4-methylbenzene (15.4 g, 51.9 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.666 g, 0.95 mmol), and copper(I) iodide (0.119 g, 0.62 mmol) in triethylamine (100 mL), THF (100 mL), and trimethylsilylacetylene (12 mL, 84.3 mmol) was stirred for 12 h under N$_2$. The reaction mixture was diluted with n-hexane (50 mL), washed with hydrochloric acid (6 mol L^{-1}), water, and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated, and the residue was purified by distillation (102.0–104.0 °C, 1.5 mmHg) to give **4** as a yellow oil (7.98 g, 58 %). B.p. 102.0?104.0 °C; ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta=0.27$ (s, 9H), 2.32 (br s, 3H), 7.04 (m, 1H), 7.34 (d, $J=7.7$ Hz, 1H), 7.40 ppm (m, 1H);

^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = 0.41$, 21.63, 99.11, 103.75, 122.77, 126.04, 128.31, 133.39, 133.80, 140.70 ppm; IR (neat): $\tilde{\nu} = 2960$ (m), 2922 (w), 2898 (w), 2163 (m), 1602 (w), 1485 (m), 1447 (w), 1391 (w), 1251 (m), 1227 (m), 1045 (m), 877 (m), 843 (bm), 820 (m), 776 (w), 760 (m), 700 (w), 675 (w), 633 (w), 562 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 268 ($[M+2]^+$, 23), 266 ($[M]^+$, 21), 253 (65), 251 (66), 149 (100); elemental analysis (%) calcd for $C_{12}H_{15}BrSi$: C 53.93, H 5.66, Br 29.90, Si 10.51; found: C 53.97, H 5.76.

2-Iodo-4-methyl-1-(2-trimethylsilylethynyl)benzene (7): nBuLi (1.6 mol L^{-1}, 3.8 mL, 6.1 mmol) was added to a solution of **4** (1.35 g, 5.04 mmol) in THF (30 mL) at −70 °C under N$_2$. The reaction mixture was stirred at this temperature for 15 min and then I$_2$ (2.20 g, 8.68 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and diluted with n-hexane (50 mL). The solution was washed with saturated aqueous NaS$_2$O$_3$, water, and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated, and the residue was purified by distillation (ca. 120 °C, 1.5 mmHg) to give **7** as a colorless oil (1.21 g, 76 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 0.28$ (s, 9 H), 2.29 (br s, 3 H), 7.08 (br d, $J = 8.1$ Hz, 1 H), 7.34 (d, $J = 8.1$ Hz, 1 H), 7.6 ppm (s, 1 H); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = -0.15$, 20.89, 97.79, 101.16, 106.66, 126.70, 128.61, 132.36, 139.21, 140.07 ppm; IR (neat): $\tilde{\nu} = 3056$ (w), 3028 (w), 2959 (m), 2920 (w), 2898 (w), 2161 (m), 1906 (w), 1595 (w), 1549 (w), 1477 (m), 1446 (w), 1408 (w), 1387 (w), 1332 (w), 1251 (m), 1225 (w), 1140 (w), 1038 (m), 995 (w), 872 (s), 844 (s), 820 (m), 760 (m), 700 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 314 ($[M]^+$, 34), 299 (73), 149 (95), 105 (100); elemental analysis (%) calcd for $C_{12}H_{15}ISi$: C 45.87, H 4.81, I 40.38, Si 8.94; found: C 46.21, H 4.74.

2-Bromo-1-(2-trimethylsilylethynyl)benzene (9): A solution of 2-bromo-1-iodobenzene (5.32 g, 18.8 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.256 g, 0.36 mmol), copper(I) iodide (0.037 g, 0.19 mmol), triethylamine (100 mL), and trimethylsilylacetylene (3.2 mL, 22.4 mmol) was stirred for 12 h under N$_2$. The reaction mixture was diluted with n-hexane (50 mL) and washed with hydrochloric acid (6 mol L^{-1}), water, and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated, and the residue was purified by distillation ($\approx$100 °C, 1.5 mmHg) to give **9** as a yellow oil (2.86 g, 60 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 0.28$ (s, 9 H), 7.15 (m, $J = 7.6$, 1.9 Hz, 1 H), 7.23 (m, $J = 7.6$, 1.4 Hz, 1 H), 7.49 (m, $J = 7.6$, 1.6 Hz, 1 H), 7.57 ppm (m, $J = 7.8$, 1.4 Hz, 1 H).

1-Bromo-3,4-dimethoxy-5-(2-trimethylsilylethynyl)benzene (10): A solution of 1-bromo-2-iodo-4,5-dimethoxybenzene (2.17 g, 6.32 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.094 g, 0.13 mmol), copper(I) iodide (0.044 g, 0.26 mmol), triethylamine (15 mL), and trimethylsilylacetylene (2.2 mL, 15.4 mmol) was stirred at 50 °C for 12 h under N$_2$. The reaction mixture was diluted with n-hexane/ethyl acetate (2:1, 50 mL) and washed with hydrochloric acid (6 mol L^{-}), water, and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated and the residue was purified by distillation (140?160 °C, 1.5 mmHg) to give **10** as a yellow solid (1.17 g, 59 %). M.p. 88.9–89.3 °C; ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 0.27$ (s, 9 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 6.96 (s, 1 H), 7.01 ppm (s, 1 H); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = -0.08$, 56.09, 56.16, 97.63, 103.81, 115.09, 115.41, 117.06, 117.16, 147.96, 149.97 ppm; IR (neat): $\tilde{\nu} = 3004$ (w), 2960 (w), 2898 (w), 2844 (w), 2156 (m), 1599 (m), 1564 (w), 1508 (s), 1482 (w), 1442 (m), 1383 (w), 1332 (w), 1265 (s), 1248 (s), 1218 (s), 1200 (m), 1171 (m), 1047 (w), 1030 (w), 974 (m), 953 (w), 864 (s), 842 (s), 802 (m), 762 (m), 706 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 314 ($[M+2]^+$, 85), 312 ($[M]^+$, 83), 299 (97), 297 (100); elemental analysis (%) calcd for $C_{13}H_{17}BrO_2Si$: C 49.84, H 5.47, Br 25.51, O 10.21, Si 8.97; found: C 50.21, H 5.44.

Methyl 3-bromo-4-[(trimethylsilyl)ethynyl]benzoate (11): A solution of methyl 3-bromo-4-iodobenzoate (8.59 g, 25.2 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.72 g, 1.02 mmol), copper(I) iodide (0.103 g, 0.54 mmol), triethylamine (100 mL), and trimethylsilylacetylene (11 mL, 77.3 mmol) was stirred at 50 °C for 12 h under N$_2$. The reaction mixture was diluted with n-hexane/ethyl acetate (2:1, 50 mL) and washed with hydrochloric acid (6 mol L^{-1}), water, and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated, and the residue was purified by distillation (130–140 °C, 1.5 mmHg) to give **11** as a yellow oil (2.33 g, 30 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 0.28$ (s, 9 H), 7.52 (d, $J = 8.1$ Hz, 1 H), 7.88 (dd, $J = 1.9$, 8.1 Hz, 1 H), 8.22 ppm (d, $J = 1.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta = -0.22$, 52.45, 102.28, 103.24, 125.55, 127.74, 129.27, 129.51, 130.78, 133.23, 165.13 ppm; IR (neat): $\tilde{\nu} = 3069$ (w), 2956 (s), 2899 (w), 2844 (w), 2163 (m), 2068 (w), 1944 (w), 1730 (s), 1597 (s), 1548 (w), 1489 (w), 1436 (m), 1385 (m), 1287 (s), 1251 (s), 1111 (s), 1044 (m), 972 (w), 871 (s), 845 (s), 803 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 312 ($[M+2]^+$, 23), 310 ($[M]^+$, 23), 297 (100), 295 (99); HRMS (EI): m/z calcd for $C_{13}H_{15}BrO_2Si$: 310.0025; found: 310.0001.

2-Bromo-1-ethynyl-4-methylbenzene (15): K$_2$CO$_3$ (16.1 g) was added to a solution of 2-bromo-4-methyl-1-(2-trimethylethynyl)benzene (**4**) in THF (20 mL) and methanol (80 mL) under N$_2$. The suspension was stirred for 12 h at ambient temperature and quenched with water (100 mL). The reaction mixture was extracted with n-hexane (2 × 100 mL). The combined organic layers were washed with water and brine and dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (40 g). From a hexane fraction, **15** was obtained as a pale-yellow oil (2.51 g, 75 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 2.33$ (s, 3 H), 3.31 (s, 1 H), 7.06 (d, $J = 7.8$ Hz, 1 H), 7.40 (d, $J = 7.9$ Hz, 1 H), 7.42 ppm (s, 1 H); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = 21.09$, 80.94, 82.01, 121.23, 125.28, 127.91, 132.95, 133.75, 140.66 ppm; IR (neat): $\tilde{\nu} = 3293$ (s), 3030 (w), 2921 (w), 2864 (w), 2110 (w), 1908 (w), 1602 (m), 1484 (s), 1043 (m), 862 (m), 820 (s) 710 (w), 677 cm^{-1} (m); MS (EI, 70 eV): m/z (rel. intensity): 196 ($[M+2]^+$, 64), 194 ($[M]^+$, 65), 115 (100); elemental analysis (%) calcd for C_9H_7Br: C 53.42, H 3.62, Br 40.96; found: C 55.69, H 3.70.

Ethyl 3-(2-bromo-4-methylphenyl)propiolate (16): A solution of 2-bromo-1-ethynyl-4-methylbenzene **15** (0.789 g, 4.78 mmol) in THF (5 mL) was added to a solution of LDA, which was generated from diisopropylamine (1.25 mL) and nBuLi (1.6 M, 5.5 mL, 8.8 mmol) in THF (10 mL), at −70 °C under N$_2$. The reaction mixture was stirred at this temperature for 20 min and then ethyl chloroformate (1.6 mL, 16.7 mmol) was added. The mixture was allowed to warm to ambient temperature, quenched with aqueous ammonium chloride, and extracted with n-hexane/ethyl acetate. The organic layer was washed with water and brine and dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (10 g, toluene/n-hexane = 3:1) to give **16** as a pale-yellow oil (0.766 g, 60 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 1.35$ (t, $J = 7.3$ Hz, 3 H), 2.35 (s, 3 H), 4.30 (q, $J = 7.0$ Hz, 2 H), 7.08–7.12 (m, 1 H), 7.44–7.45 (m, 1 H), 7.47 ppm (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = 14.10$, 21.28, 62.08, 84.01, 84.30, 119.38, 126.37, 128.13, 133.38, 134.57, 142.69, 153.89 ppm; IR (neat): $\tilde{\nu} = 2982$ (w), 2212 (w), 1422 (m), 1709 (s), 1601 (w), 1488 (w), 1446 (w), 1390 (w), 1366 (w), 1297 (m), 1259 (m), 1194 (m), 1142 (w), 1095 (w), 1050 (w), 1021 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 268 ($[M+2]^+$, 29), 266 ($[M]^+$, 30), 223 (71), 221 (78), 196 (93), 194 (100); HRMS(ESI): m/z calcd for $C_{12}H_{12}O_2Br$ $[M+H]^+$: 267.0015; found: 267.0000.

1-(2-Bromo-4-methylphenyl)-2-(4-methylphenyl)ethyne (12): A solution of **15** (0.68 g, 3.48 mmol), *para*-iodotoluene (0.70 g, 3.21 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.062 g, 0.09 mmol), copper(I) iodide (0.025 g, 0.13 mmol), and triethylamine (30 mL) was stirred for 12 h at ambient temperature under N$_2$. The reaction mixture was diluted with n-hexane (50 mL); washed with hydrochloric acid (6 mol mL^{-1}), water, and brine; and dried over anhydrous Na$_2$SO$_4$. The filtrate was evaporated and the residue was purified by distillation under reduced pressure (220–250 °C, 2 mmHg) to give **12** as a colorless solid (0.78 g, 85 %). M.p. 81.5–82.2 °C; ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C): $\delta = 2.34$ (s, 3 H), 2.37 (s, 3 H), 7.08 (m, 1 H), 7.16 (d, $J = 8.6$ Hz, 1 H), 7.17 (m, 1 H), 7.42 (2 H, AA′XX′), 7.46 ppm (2 H, AA′XX′); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = 21.10$, 21.52, 87.53, 93.37, 120.08, 122.57, 125.32, 127.93, 129.11, 131.52, 132.82, 132.95, 138.61, 139.79 ppm; IR (KBr): $\tilde{\nu} = 3025$ (w), 2916 (w), 2215 (w), 1909 (w), 1597 (w), 1557 (w), 1511 (s), 1480 (m), 1260 (w), 1208 (w), 1179 (w), 1105 (w), 1040 (m), 1018 (w), 957 (w), 945 (w), 876 (w), 817 (s), 762 (w), 708 cm^{-1} (w); MS (EI, 70 eV): m/z (rel. intensity): 286 ($[M+2]^+$, 93), 284 ($[M]^+$, 100), 205 (38), 189 (48); elemental analysis (%) calcd for $C_{16}H_{13}Br$: C 67.39, H 4.59, Br 28.02; found: C 67.09, H 4.55.

1-(2-Bromo-4-methylphenyl)-2-(4-methoxyphenyl)ethyne (13): A solution of **15** (0.78 g, 4.14 mmol), *para*-iodoanisole (0.85 g, 3.62 mmol), $[PdCl_2(PPh_3)_2]$ (0.058 g, 0.083 mmol), and copper(I) iodide (0.014 g, 0.074 mmol) in triethylamine (20 mL) and THF (10 mL) was stirred for 12 h at ambient temperature under N_2. The reaction mixture was diluted with *n*-hexane/ethyl acetate (50 mL); washed with hydrochloric acid (6 mol mL^{-1}), water, and brine; and dried over anhydrous Na_2SO_4. The filtrate was evaporated, and the residue was purified by distillation under reduced pressure (220–250 °C, 2 mmHg) to give **13** as a pale yellow solid (1.04 g, 95 %). M.p. 79.4–79.8 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.34 (s, 3H), 3.83 (s, 3H), 6.88 (2H, AA′XX′), 7.08 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.43 (m, 1H), 7.50 ppm (2H, AA′XX′); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 21.09, 55.31, 86.93, 93.24, 114.02, 115.27, 122.68, 125.21, 127.93, 132.70, 132.92, 133.10, 139.62, 159.83 ppm; IR (KBr): $\tilde{\nu}$ = 2960 (w), 2932 (w), 2835 (w), 2218 (m), 1604 (s), 1512 (s), 1289 (m), 1248 (s), 1173 (m), 1149 (m), 1107 (w), 1025 (s), 955(w), 878 (w), 837 (s), 813 (s), 760 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 302 ([*M*+2]$^+$, 98), 300 ([*M*]$^+$, 100); elemental analysis (%) calcd for $C_{16}H_{13}BrO$: C 63.81, H 4.35, Br 26.53, O 5.31; found: C 63.92, H 4.32.

1-(2-Bromo-4-methylphenyl)-2-(4-methoxycarbonylphenyl)ethyne (14): A solution of **15** (0.78 g, 4.00 mmol), methyl *para*-iodobenzoate (1.16 g, 4.41 mmol), $[PdCl_2(PPh_3)_2]$ (0.068 g, 0.096 mmol), and copper(I) iodide (0.011 g, 0.057 mmol) in triethylamine (20 mL) and THF (10 mL) was stirred for 12 h at ambient temperature under N_2. The reaction mixture was diluted with *n*-hexane/ethyl acetate (50 mL); washed with hydrochloric acid (2 mol mL^{-1}), water, and brine; and dried over anhydrous Na_2SO_4. The filtrate was evaporated, and the residue was purified by distillation under reduced pressure (220–250 °C, 2 mmHg) to give **14** as a colorless solid (0.75 g, 57 %). M.p. 107.2–107.9 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.36 (s, 3H), 3.93 (s, 3H), 7.11 (m, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.46 (m, 1H), 7.62 (2H, AA′XX′), 8.02 ppm (2H, AA′XX′); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 21.17, 52.20, 91.01, 92.26, 121.84, 125.54, 127.82, 128.03, 129.49, 129.65, 131.49, 133.07, 140.63, 166.51 ppm; IR (KBr): $\tilde{\nu}$ = 3065 (w), 2950 (w), 2360 (w), 2218 (w), 1721 (s, C=O), 1599 (m), 1558 (w), 1513 (w), 1483 (w), 1458 (w), 1435 (m), 1405 (m), 1308 (m), 1281 (s), 1176 (m), 1108 (m), 1043 (w), 1015 (w), 960 (w), 892 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 330 ([*M*+2]$^+$, 99), 328 ([*M*]$^+$, 100), 287 (44), 285 (45), 259 (14), 257 (14); elemental analysis (%) calcd for $C_{17}H_{13}BrO_2$: C 62.03, H 3.98, Br 24.27, O 9.72; found: C 62.17, H 3.97.

2,2′-Bis(2-trimethylsilylethynyl)-5,5′-dimethylbiphenyl (5): A solution of *n*-butyllithium in hexane (1.6 M, 0.75 mL, 1.2 mmol) was added by syringe to a solution of **4** (0.268 g, 1.00 mmol) in THF (15 mL) at −70 °C under N_2. The reaction mixture was stirred at this temperature for 45 min and then $CuBr_2$ (0.38 g, 1.7 mmol) was added. The reaction mixture was allowed to warm to ambient temperature. The mixture was passed over a column of alumina with hexane as the eluent to remove insoluble copper salts. The crude product was purified by column chromatography on silica gel (40 g, hexane) to give **5** as a pale yellow oil (0.095 g, 51 %). B.p. 110.0?115.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.05 (s, 18H), 2.36 (s, 6H), 7.08 (m, 2H), 7.25 (m, 2H), 7.43 ppm (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = −0.25, 21.39, 96.23, 104.92, 119.46, 127.75, 130.98, 132.21, 137.59, 143.30 ppm; IR (neat): $\tilde{\nu}$ = 33025 (w), 2959 (w), 2923 (w), 2898 (w), 2157 (m), 1604 (w), 1473 (w), 1408 (w), 1250 (m), 1217 (w), 1135 (w), 1043 (w), 864 (m), 842 (m), 819 (m), 759 (w), 699 (w), 634 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 374 ([*M*]$^+$, 100]; elemental analysis (%) calcd for $C_{24}H_{30}Si_2$: C 76.94, H 8.07, Br 14.99; found: C 76.70, H 8.09.

***trans*-[Bromo(5-methyl-2-trimethylsilylethynylphenyl)bis(triphenylphosphine)nickel(II)] (8)**: A suspension of **4** (0.269 g, 1 mmol), $[Ni(cod)_2]$ (0.277 g, 1.0 mmol), and PPh_3 (0.524 g, 2.0 mmol) in THF (15 mL) was heated at 50 °C for 24 h under argon. The dark-red reaction mixture was passed over a column chromatography on alumina using hexane/CH_2Cl_2 as the eluent to remove insoluble materials. The crude products were subjected to column chromatography on silica gel to give **4** (0.036 g, 13 %) and **6** (0.036 g, 16 %) from hexane elutions and **8** as a yellow solid from a CH_2Cl_2 elution (0.187 g, 21%). Pure **8** was obtained as yellowish plates after recrystallization from hexane/CH_2Cl_2. **8**: M.p. 179.7–180.1 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.45 (s, 9H), 1.76 (s, 3H), 5.96 (d, *J* = 7.7 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 6.70 (s, 1H), 7.31–7.68 ppm (m, 30H); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (2.98), 316 (4.15), 286 (4.43), 259 (4.66), 232 nm (4.92); IR (KBr): $\tilde{\nu}$ = 3902 (w), 3802 (w), 3725 (w), 3650 (w), 3052 (w), 2958 (w), 2141 (m), 1653 (w) 1482 (m), 1435 (s), 1251 (m), 1095 (s), 1029 (w), 870 (s), 840 (s), 755 (m), 692 (s), 634 (w), 522 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (rel. intensity): 374 (8), 262 (100), 183 (77); MS (ESI) *m*/*z*: 849.2000, 587.1183, 410.9997.

The preparation of dibenzopentalene 6 from Ni^{II} complex (8): A solution of **8** (0.015 g, 0.018 mmol) in toulene (6 mL) was heated with dryer at 80 °C for a few minutes. The solution changed from pale yellow to yellow–orange. The crude product was subjected to column chromatography on silica gel to give **6** (0.0033 g, 83 %).

General procedure for the preparation of dibenzopentalenes: A suspension of 2-bromo-1-ethynylbenzenes (**4** and **9**–**14**; 1 mmol), Zn powder (1.5 mmol, 0.098 g), and $[NiCl_2(PPh_3)_2]$ (1.0 mmol, 0.654 g) in toluene (4 mL) and DME (1 mL) was heated at 80 °C for 24 h under N_2. The dark red reaction mixture was subjected to column chromatography on alumina with hexane and or hexane/CH_2Cl_2 as the eluent to remove insoluble materials. The crude product was purified by column chromatography on silica gel.

2,7-Dimethyl-5,10-ditrimethylsilylindeno[2,1-a]indene (6): The reaction was carried out using **4** (0.267 g, 1.00 mmol) to give **6** as red–brown needles after recrystallization from *n*-hexane (0.077 g, 41 %). M.p. 209.6–210.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.38 (s, 18H), 2.19 (s, 6H), 6.61 (m, 2H), 6.84 (m, 1H), 7.03 ppm (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 0.24, 21.52, 123.33, 125.46, 126.43, 132.98, 137.80, 140.11, 155.69, 158.83 ppm; UV/Vis λ_{max} (log ε) = 442 (3.96), 417 (4.01), 397 (3.79), 299 (4.75), 292 (4.72), 236 nm (4.33); IR (KBr): $\tilde{\nu}$ = 3675 (w), 3649 (w), 3628 (w), 3567 (w), 3067 (w), 2959 (m), 2908 (w), 2361 (w) 1869 (w), 1595 (w), 1438 (m), 1250 (m), 1240 (m), 1159 (w), 866 (m), 843 (s), 809 (s), 755 (m), 74 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 374 ([*M*]$^+$, 100), 359 (23), 343 (17), 301 (48); elemental analysis (%) calcd for $C_{24}H_{30}Si_2$: C 76.94 H 8.07, Si 14.99; found: C 77.12, H 8.10.

5,10-Bis(trimethylsilyl)indeno[2,1-a]indene (17): The reaction was carried out using **9** (0.253 g, 1.00 mmol) to give **17** as red–brown needles (0.053 g, 31 %). Red–brown prisms were obtained from recrystallization from hexane/EtOH. M.p. 145.8–146.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.43 (s, 18H), 6.82–6.85 (m, 4H), 7.03–7.05 (m, 2H), 7.15–7.17 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.35, 123.51, 124.33, 126.37, 127.88, 135.77, 141.56, 155.06, 158.32 ppm; UV/Vis λ_{max} (log ε) = 441.0 (3.98), 416 (4.02), 398 (3.81), 286 (4.68), 232 nm (4.31); IR (KBr): $\tilde{\nu}$ = 3084 (w), 2967 (w), 1422 (w), 1331 (w), 1262 (w), 1247 (m), 1100 (w), 967 (m), 843 (s), 741 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (rel. intensity): 346 ([*M*]$^+$, 100); elemental analysis (%) calcd for $C_{22}H_{26}Si_2$: C 76.23, H 7.56, Si 16.21; found: C 75.92, H 7.43.

2,3,7,8-Tetramethoxy-5,10-bis(trimethylsilyl)indeno[2,1-a]indene (18): The reaction was carried out using **10** (0.316 g, 1.00 mmol) to give **18** as green–yellow leaflets (0.030 g, 13 %). Green–yellow leaflets were obtained after recrystallization from *n*-hexane/CH_2Cl_2. M.p. 215.7–216.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.40 (s, 18H), 3.79 (s, 6H), 3.80 (s, 6H), 6.56 (s, 2H), 6.70 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.26, 56.15, 56.23, 108.99, 109.67, 129.33, 139.56, 147.18, 148.19, 148.69, 158.32 ppm; UV/Vis λ_{max} (log ε) = 571 (2.40), 442 (3.66), 319 (4.86), 239 nm (4.25); IR (KBr): $\tilde{\nu}$ = 2939 (w), 2899 (w), 1586 (m), 1462 (s), 1436 (s), 1404 (w), 1286 (s), 1245 (m), 1219 (m), 1162 (w), 1122 (w), 1020 (m), 875 (m), 855 (s), 745 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (rel. intensity): 466 ([*M*]$^+$, 100); elemental analysis (%) calcd for $C_{26}H_{34}O_4Si_2$: C 66.91, H 7.34, O 13.71, Si 12.04; found: C 66.74, H 7.07.

Dimethyl 5,10-bis(trimethylsilyl)indeno[2,1-a]indene-2,7-dicarboxylate (19): The reaction was carried out using **14** (0.321 g, 1.03 mmol) and zinc powder (1.6 mmol, 0.104 g) with toluene (5 mL) as a solvent to give **13** as red–brown prisms (0.058 g, 24 %). Red–brown prisms were obtained after recrystallization from *n*-hexane/CH_2Cl_2. M.p. 264.3–265.2 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.46 (s, 18H), 3.89 (s, 6H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.60 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.74 ppm (d, *J* = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.26, 52.10, 123.02, 125.28, 129.06, 129.52, 140.11, 144.70, 154.74, 157.62, 166.70 ppm; UV/Vis λ_{max} (log ε) =

449 (3.88), 423 (3.86), 310 (4.63), 304 (4.63), 228 nm (4.30); IR (KBr): $\tilde{\nu}$ = 2951 (w), 1712 (s), 1543 (w), 1431 (m), 1340 (m), 1295 (s), 1256 (s), 1199 (m), 1102 (m), 846 (s), 759 (s), 628 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 462 ([*M*]$^+$, 100), 447 (33), 431 (8), 389 (37); elemental analysis (%) calcd for $C_{26}H_{30}O_4Si_2$: C 67.49, H 6.54, O 13.83, Si 12.14; found: C 67.39, H 6.44.

2,7-Dimethyl-5,10-di-*para*-tolylindeno[2,1-a]indene (20): The reaction was carried out using **12** (0.286 g, 1.00 mmol) to give **20** as red–brown leaflets (0.032 g, 16 %). Red–brown leaflets were obtained after recrystallization from CH_2Cl_2/*n*-hexane. M.p. 285.7–286.6 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.18 (s, 6H), 2.45 (s, 6H), 6.62 (m, 2H), 6.82 (s, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.31 (4H, AA′XX′), 7.55 ppm (4H, AA′XX′); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 21.49, 21.51, 121.59, 123.37, 127.35, 128.47, 129.31, 131.26, 132.50, 137.51, 138.51, 139.41, 143.19, 150.16 ppm; UV/Vis $\lambda_{\max}$ ($\log\varepsilon$) = 452 (4.23), 429 (4.23), 406 (4.02), 325 (4.30), 294 (4.57), 267 nm (4.61); IR (KBr): $\tilde{\nu}$ = 1596 (w), 1508 (m), 1440 (s), 1295 (w), 1169 (w), 838 (w), 813 (s), 736 (w), 536 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (rel. intensity): 410 ([*M*]$^+$, 100), 205 (18); elemental analysis (%) calcd for $C_{32}H_{26}$: C 93.62 H 6.38; found: C 93.30, H 6.41

5,10-Bis(4-methoxyphenyl)-2,7-dimethylindeno[2,1-a]indene (21): The reaction was carried out using **13** (0.301 g, 1.00 mmol) to give **21** as red–brown needles (0.029 g, 13 %). Red–brown needles were obtained after recrystallization from CH_2Cl_2/*n*-hexane. M.p. 254.8–255.7 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.19 (s, 6H), 3.89 (s, 6H), 6.63 (m, 2H), 6.83 (m, 2H), 7.04 (4H, AA′XX′), 7.09 (d, J = 7.3 Hz, 2H), 7.60 ppm (4H, AA′XX′); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.58, 55.35, 114.00, 121.34, 123.21, 126.51, 127.24, 129.87, 132.49, 137.25, 138.79, 142.63, 149.99, 159.71 ppm; UV/Vis $\lambda_{\max}$ ($\log\varepsilon$) = 457 (4.28), 436 (4.28), 339 (4.17), 293 (4.63), 273 nm (4.58); IR (KBr): $\tilde{\nu}$ = 3006 (w), 2952 (w), 2833 (w), 1601 (m), 1567 (w), 1508 (s), 1459 (w), 1449 (m), 1312 (w), 1300 (m), 1249 (s), 1168 (m), 1109 (w), 1033 (m), 846 (w), 805 (w), 790 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 442 ([*M*]$^+$, 100), 427 (13), 221 (28); elemental analysis (%) calcd for $C_{32}H_{26}O_2$: C 86.85 H 5.92, O 7.23; found: C 86.58, H 5.86.

5,10-Bis(4-methoxycarbonylphenyl)-2,7-dimethylindeno[2,1-a]indene (22): The reaction was carried out using **14** (0.326 g, 1.00 mmol) to give **22** as red–brown needles (0.031 g, 13 %), which were obtained after recrystallization from CH_2Cl_2/*n*-hexane. M.p. 296.3–297.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.19 (s, 6H), 3.97 (s, 6H), 6.63 (d, J = 7.6 Hz, 2H), 6.77 (s, 2H), 7.02 (d, J = 7.4 Hz, 2H), 7.71 (4H, AA′XX′), 8.19 ppm (4H, AA′XX′); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.60, 52.26, 121.84, 123.37, 127.76, 128.41, 129.90, 130.09, 131.74, 138.31, 138.61, 138.86, 144.42, 149.65, 166.57 ppm; UV/Vis $\lambda_{\max}$ ($\log\varepsilon$) = 455 (4.23), 434 (4.25), 317 (4.59), 276 (4.85), 230 nm (4.49); IR (KBr): $\tilde{\nu}$ = 2952 (w), 1717 (s), 1599 (m), 1559 (w), 1434 (m), 1405 (w), 1285 (s), 1180 (w), 1113 (m), 1017 (w), 967 (w), 870 (w), 805 (w), 780 (w), 741 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (rel. intensity): 498 ([*M*]$^+$, 100), 363 (7), 249 (8); elemental analysis (%) calcd for $C_{34}H_{26}O_4$: C 81.91 H 5.26, O 12.84; found: C 81.75, H 5.26.

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[7] a) Crystal data of **6**: $C_{48}H_{60}Si_4$, M_r = 749.34, 0.30 × 0.20 × 0.20 mm^3, crystal system = monoclinic, a = 7.282(3), b = 15.076(6), c = 10.496(4) Å, β = 109.695(4)°, V = 1084.8(7) Å^3, space group $P2_1/n$ (no. 14), Z = 1, $\mu(Mo_{K\alpha})$ = 1.68 cm^{-1}, T = 150 K, $R1(F^2 > 2\sigma(F^2))$ = 0.041, $wR2$(all data) = 0.118, S = 1.92, reflections/parameters = 2052/178. b) Crystal data of **8:** $C_{48}H_{45}BrNiP_2Si$, M_r = 850.52, 0.20 × 0.10 × 0.10 mm^3, crystal system = monoclinic, a = 41.777(3), b = 10.7641(8), c = 21.290(2) Å, β = 115.760(2)°, V = 8622(1) Å^3, space group $C2/c$ (no. 15), Z = 8, $\mu(Mo_{K\alpha})$ = 15.13 cm^{-1}, T = 296 K, $R1(F^2 > 2\sigma(F^2))$ = 0.095, $wR2$(all data) = 0.247, S = 1.00, reflections/parameters = 4559/478. CCDC-702714 (**6**) and CCDC-702715 (**8**) contain 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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