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Synthesis of Methylene-Bridge Polyarenes through Palladium-Catalyzed Activation of Benzylic Carbon-Hydrogen Bond

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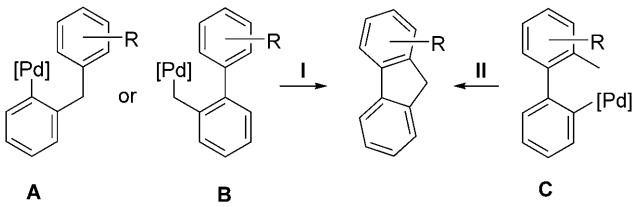
Abstract: In the presence of palladium(II) acetate [$Pd(OAc)_2$] and an N-heterocyclic carbene (NHC) ligand, fluorene derivatives can be generated in good to excellent yields from 2-halo-2′-methylbiaryls through the benzylic C–H bond activation (14 examples; 81–97% yields). The scope and limitations of this protocol have been examined. A wide range of functional groups, such as alkyl, alkoxy, ester, nitrile, and others, is able to tolerate the reaction conditions herein. The cyclization of an isotope-labelled biphenyl gave the corresponding product with a primary kinetic isotope effect ($k_H/k_D = 4.8:1$), which indicates that the rate-determining step of this reaction is the activation of the benzylic C–H bond. Moreover, indenofluorenes were also accessed in excellent results from terphenyls (3 examples; 91–92% yields). The cascade reaction of 2,6-dichloro-2′-methylbiphenyl with diphenylacetylene produced 8,9-diphenyl-4*H*-cyclopenta[*def*]phenanthrene in 60% yield through the activation of an aryl and a benzylic C–H bond.

Keywords: C–H bond activation; fluorenes; indenofluorenes; NHC ligands; palladium; polyarenes

Introduction

Methylene-bridge polyarenes are classified as non-alternant polycyclic aromatic hydrocarbons (PAHs) because the additional methylene carbon cannot present aromaticity associated with the Kekulé structure.[1] This structural characteristic causes them to have different chemical and physical properties from those of alternant benzenoid PAHs. Fluorene is the simplest example of this class of compounds, and it is an important building block of organic materials, including those used in optoelectronics,[2] semiconductors,[3] solar cells[4] and other applications. Several synthetic methods for preparing fluorenes have been developed, and the strategy of closing the central five-membered ring using a biphenyl reactant is generally employed.[5,6] Of these synthetic procedures, catalytic activation of a C–H bond with subsequent C–C bond formation is promising[7] because it has several advantages, such as simplicity, cleanliness and atom economy.[8,9] The formation of fluorene by metal-catalyzed C–H bond activation can be classified as either the aryl or the benzylic type (Scheme 1). For example, the Pd-catalyzed cyclization of 1-halo-2-(arylmethyl)-benzene[10] and *o*-aryl-substituted benzyl chloride[11] *via* intermediates **A** and **B**, respectively, proceeds by aryl C–H bond activation (Type **I**). These approaches have been extensively investigated, and were found to be non-regiospecific. The ratio of the regioisomers depends on the nature of the substituents. Alternatively, 2-methyl-2′-palladabiphenyl **C** can undergo cyclization through benzylic C–H bond activation (Type **II**). The crowded environment and the short distance between the palladium moiety and the methyl group cause this process to be efficient.[12] Hu et al. developed a simi-



Scheme 1. Synthesis of fluorene derivatives through the aryl (**I**) and benzylic (**II**) C–H activation.

lar reaction, but they focused on the tandem-type coupling reaction of 1,2-dihalobenzenes with 2,6-dimethylphenylmagnesium bromide[13] or 2-tolylboronic acid.[14] The scope and limitations of the arylation of the benzylic C–H bond have not been examined, and only the synthesis of fluorenes and indenofluorenes by this method has been described. Herein, 2-halo-2′-alkylbiphenyl (**1**) was selected as the prototype in an investigation of the benzylic C–H bond activation, which was adopted as a method for the preparation of some interesting methylene-bridge polyarenes.

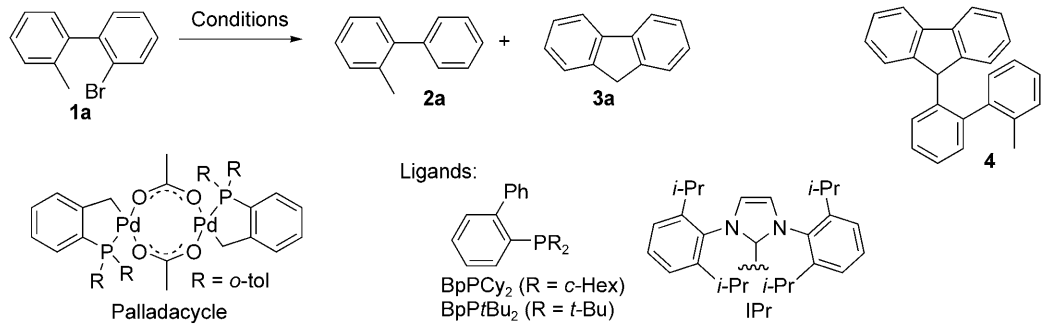
Results and Discussion

Heating 2-bromo-2′-methylbiphenyl (**1a**) in the presence of palladium catalysts yielded a mixture of 2-methylbiphenyl (**2a**) and fluorene (**3a**, Table 1).

Systematic studies of the reaction conditions revealed that the palladium catalyst, base, and solvent all have critical roles. The combination of $Pd(OAc)_2$ and PCy_3 or NHC ligand (IPr)[15] is more efficient than $PdCl_2(PCy_3)_2$, palladacycle or other catalytic systems that are shown in Table 1. Apparently, the use of K_2CO_3 or KOAc was determined to be superior to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and Cs_2CO_3 (entries 4–6 and 8 in Table 1). Additionally, Cs_2CO_3 furnished compound **4** by the cross coupling of **3a** with **1a**.[16] Generation of the debrominated byproduct **2a** was a serious problem in this reaction, and the amount formed was reduced by conducting the reaction in *N*-methylpyrrolidinone (NMP) rather than dimethylacetamide (DMAc). Under our optimal conditions, the desired **3a** was produced in 86% yield – slightly higher than that obtained by the Hu's catalytic system (entries 7 and 13 in Table 1).[17]

The reactivity of numerous biphenyls **1** was tested under optimal conditions and on most occasions, the desired products were produced in good to excellent yields (Table 2). Another advantage of this procedure is its compatibility with several functional groups, such as alkyl, alkoxy, ester, nitrile, and others. 2-Bromo-2′-methylbiphenyl (**1a**) provided a slightly lower yield than its chloro-substituted analogue **1b** (entries 1 and 2 in Table 2). Ethyl- and benzyl-substituted reactants **1c** and **1d**, respectively, did not give

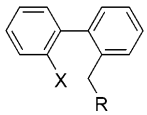
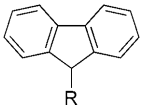
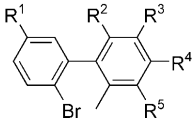
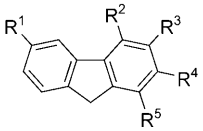
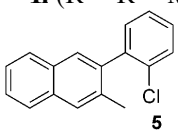
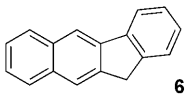
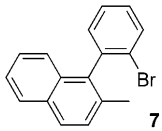
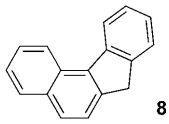
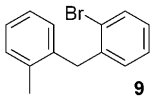
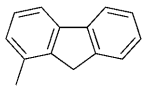
Table 1. Optimization of reaction conditions for the preparation of **3a**.[a]



Entry	Catalyst (mol%)	Ligand (mol%)	Base (equiv.)	Solvent	*t* [h]	*T* [°C]	**1a**:**2a**:**3a**[b]	Yield [%][c]
1	$PdCl_2(PCy_3)_2$ (5)	–	DBU (3)	DMAc	24	150	30:23:47	–
2	$PdCl_2(PCy_3)_2$ (5)	–	K_2CO_3 (3)	DMAc	24	150	17:83:0	–
3	Palladacycle (5)	–	K_2CO_3 (3)	DMAc	24	150	70:17:13	–
4	$Pd(OAc)_2$ (5)	PCy_3 (10)	DBU (3)	DMAc	24	150	95:2:3	–
5	$Pd(OAc)_2$ (5)	PCy_3 (10)	Cs_2CO_3 (3)	DMAc	24	150	0:40:12:(48)[d]	–
6	$Pd(OAc)_2$ (5)	PCy_3 (10)	K_2CO_3 (3)	DMAc	24	150	0:20:80	–
7	$Pd(OAc)_2$ (3)	PCy_3 (6)+Piv (100)	K_2CO_3 (6)	DMAc	5	150	0:3:97	84[e]
8	$Pd(OAc)_2$ (5)	PCy_3 (10)	KOAc (3)	DMAc	24	150	0:17:83	–
9	$Pd(OAc)_2$ (5)	$BpPCy_2$ (10)	K_2CO_3 (3)	DMAc	24	150	71:13:16	–
10	$Pd(OAc)_2$ (5)	$BpP(t\text{-}Bu)_2$ (10)	K_2CO_3 (3)	DMAc	24	150	90:10:0	–
11	$Pd(OAc)_2$ (5)	IPr·HCl (10)	K_2CO_3 (3)	DMAc	24	150	0:8:92	78
12	$Pd(OAc)_2$ (1)	IPr·HCl (2)	K_2CO_3 (3)	DMAc	24	150	66:10:24	–
13	$Pd(OAc)_2$ (2)	IPr·HCl (4)	K_2CO_3 (1)	NMP	12	130	0:4:96	86
14	$Pd(OAc)_2$ (2)	IPr·HCl (4)	KOAc (3)	NMP	12	130	0:9:91	–

[a] Reaction was performed with **1** (0.50 mmol) in a thick-walled sealed tube.
[b] Determination by GC MS.
[c] Isolated yield of **3a**.
[d] Amounts of **4** and its steric isomer (ratio 3:1) are shown in parentheses and they were isolated in 47% yield, see: ref.[16]
[e] Similar to ref.[14] Piv = pivalic acid.

Table 2. Preparation of fluorene derivatives and other arenes.[a]

Entry	Starting Material	Time [h]	Product	Isolated Yield [%]
				
1	**1a** (R = H, X = Br)	12	**3a**	86
2	**1b** (R = H, X = Cl)	24	**3a**	88[b]
3	**1c** (R = Me, X = Br)	12	**3c**	traces
4	**1d** (R = Ph, X = Br)	12	**3d**	traces
				
5	**1e** (R^1 = Me, R^2 = R^3 = R^4 = R^5 = H)	12	**3e**	97
6	**1f** (R^3 = F, R^1 = R^2 = R^4 = R^5 = H)	12	**3f**	90
7	**1g** (R^3 = CO_2Me, R^1 = R^2 = R^4 = R^5 = H)	4	**3g**	81
8	**1h** (R^3 = CN, R^1 = R^2 = R^4 = R^5 = H)	1	**3h**	91
9	**1i** (R^3 = OMe, R^1 = R^2 = R^4 = R^5 = H)	12	**3i**	86
10	**1j** (R^4 = *n*Bu, R^1 = R^2 = R^4 = R^5 = H)	12	**3j**	84
11	**1k** (R^5 = F, R^1 = R^2 = R^3 = R^4 = H)	12	**3k**	87
12	**1l** (R^2 = R^4 = Me, R^1 = R^3 = R^5 = H)	12	**3l**	90
13	 **5**	12	 **6**	91
14	 **7**	12	 **8**	89
15	 **9**	12	 **3m**	92

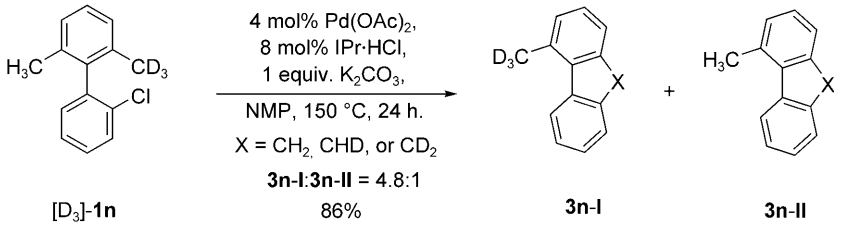
[a] Reaction was conducted with **1** (0.50 mmol), $Pd(OAc)_2$ (2 mol%), IPr·HCl (4 mol%), K_2CO_3 (0.50 mmol) and NMP (1.5 mL) in a thick-walled sealed tube that was heated at 130 °C.

[b] Reaction was conducted at 150 °C.

the corresponding fluorenes (entries 3 and 4 in Table 2), and most of **1c** (92%) remained unchanged, whereas **1d** completely converted to 2-benzylbiphenyl. These results were not improved by performing the reaction either at higher temperature (200 °C) or using with a stronger base, such as Cs_2CO_3 and *t*-BuOK. Steric effects should be responsible for the inefficiency of these two reactions because the benzylic proton in **1d** is more acidic than those in **1a** and **1c**.[18] Accordingly, the conditions herein can be applied only for reacting 2-halo-2′-methylbiphenyls.

The change in the acidity of the benzylic proton caused by the substituent in 2-bromo-2′-methylbiphenyls **1f**–**1j** did not strongly influence the cyclization, but a strong electron-withdrawing group, such as ester or nitrile, increases the reaction rate (entries 6–10 in Table 2). Sterically congested biphenyl **1l** and naphthyl-substituted biaryl **5** gave fluorene **3l** and benzo[*b*]fluorene (**6**), respectively, in good yields (entries 12 and 13 in Table 2). 2-Methyl-1-(2-bromophenyl)naphthalene (**7**) proceeded predominately (>99%) through the benzylic C–H bond activation to form benzo[*c*]fluorene (**8**) in 89% yield, whereas (2-bromophenyl)-2-tolylmethane (**9**) favored the furnishing of 1-methylfluorene (**3m**) rather than 9,10-dihydroanthracene (entries 14 and 15 in Table 2). Notably, heteroaryl-substituted reactants, such as 2-bromo-1-(2-methylthiophenyl)benzene, 2-bromo-1-(2-toyl)pyrrole and 3-methyl-2-(2-toyl)pyridine did not undergo the cyclization.

Compound [D_3]-**1n** was used to study the kinetic isotope effect on the cyclization because the proton at C-9, but not the methyl proton, in methylfluorene is exchangeable under the reaction conditions utilized herein (Scheme 2). The ratio of 4-methylfluorenes **3n-I** and **3n-II** formed through the C–H and C–D bond



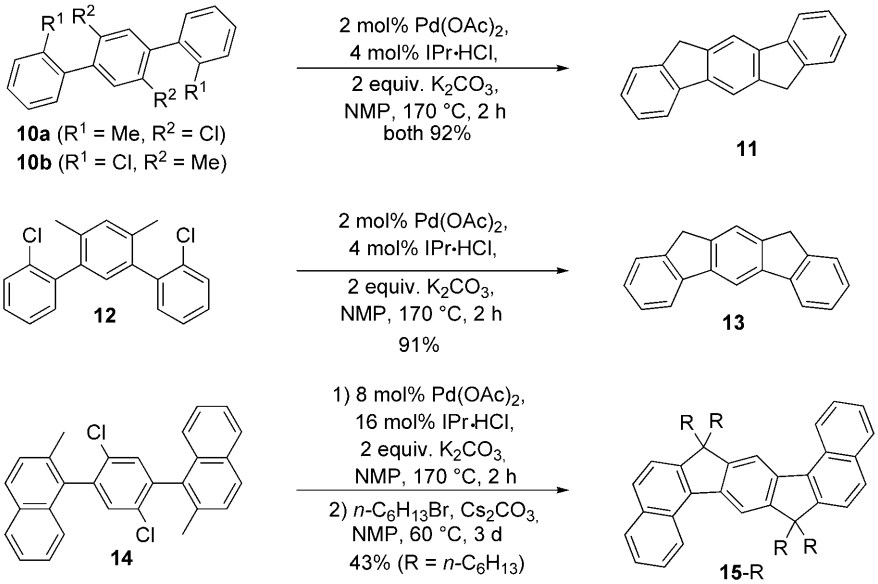
Scheme 2. The kinetic isotope effect on the cyclization.

activation, respectively, was determined by comparing the integrations of the methyl and aryl moieties, and the value was estimated to be $k_H/k_D = 4.8{:}1$. This primary isotope effect indicates that the rate-determining step of this reaction is the activation of the benzylic C–H bond.[19]

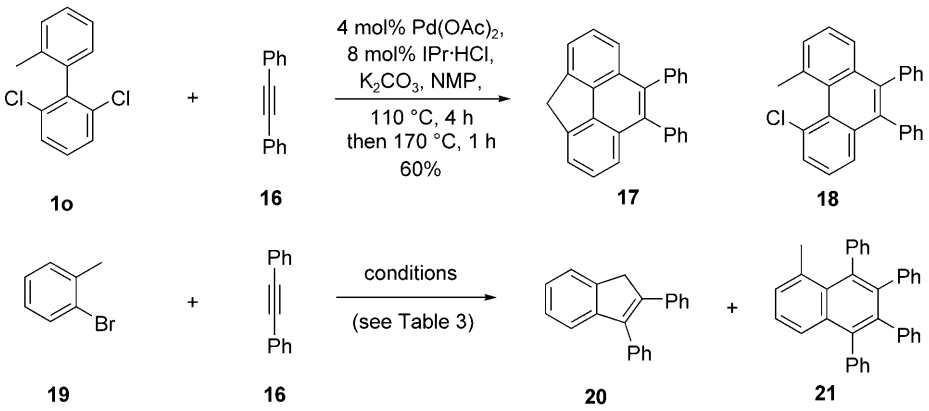
The protocol herein was employed to prepare 6,12-dihydroindeno[1,2-*b*]fluorene (**11**)[20] and 10,12-dihydroindeno[2,1-*b*]fluorene (**13**)[21] from terphenyls **10a**/**10b** and **12**, respectively (Scheme 3). These indenofluorenes **11** and **13** were obtained in high yields when the reaction was carried out at higher temperature (170 °C, 2 h) with little catalyst and ligand. However, the more extended derivative **15** was synthesized from **14**, but a higher catalyst loading was necessary. The low solubility of **15**-H in common organic solvents made the purification difficult and caused the further reaction to be inefficient. The low solubility of **15**-H was improved upon conversion into the tetra-*n*-hexyl-substituted analogue **15**-*n*Hex.

The cascade reaction of 2,6-dichloro-2′-methylbiphenyl (**1o**) with diphenylacetylene (**16**) gave cyclopenta[*def*]phenanthrene **17** in 60% yield, and phenanthrene **18** was observed as the key intermediate (Scheme 4). Reaction at 170 °C for a longer time decreased the yield of **17**. An attempt was made to synthesize indene **20**[22] by the cycloaddition of *o*-bromotoluene (**19**) with diphenylacetylene (**16**). The formation of indene **20** and naphthalene **21** was competitive, and the latter was observed as the major product when the reaction was conducted at low temperature (110 °C) or excess alkyne was used (Table 3). Although at 150 °C, the amount of **20** exceeded that of **21**, the former was isolated in only 25% yield. Significant debromination of *o*-bromotoluene under these conditions should be responsible for this poor result.

X-ray quality crystals of **11**, **15**-*n*Hex and **17** were obtained by slow evaporation of the CH_2Cl_2/MeOH solvent mixture at ambient temperature (Table 4).[23] In solids, none of these three compounds exhibits the π-π stacking, which is a typical intermolecular interaction in PAHs.[24] Notably, bond lengths and bond angles in **17** are significantly different from those in pyrene, as shown in Figure 1.[25] The five-membered ring in the former causes the phenanthrene moiety to deviate from the perfect geometry.



Scheme 3. Synthesis of methylene-bridge polyarenes **11**, **13** and **15**.



Scheme 4. Preparations of cycloadduct **17** and indene **20**.

Table 3. Preparation of indene **20**. For details, see Scheme 4.[a]

Entry	**16**:**19**	*T* [°C]	**20**:**21**
1	1.1:1	110	33:67
2	1.1:1	130	43:57
3	1.1:1	150	79:21[b]
4	2.1:1	150	19:21

[a] Reaction was conducted with **19** (0.50 mmol), $Pd(OAc)_2$ (2 mol%), IPr·HCl (4 mol%), K_2CO_3 (0.50 mmol) and NMP (1.5 mL) in a thick-walled sealed tube for 24 h. The ratio of products was determined by GC MS.

[b] **20** was isolated in 25% yield.

Conclusions

This investigation presents a simple and efficient procedure for generating fluorenes, indenofluorenes and other methylene-bridge polyarenes through the benzylic C–H bond activation. Extension of our protocol to the construction of methylene-bridge buckybowls, such as sumanene[26] and its derivatives, and studies of their physical properties are in progress.

Experimental Section

General Procedure for Cyclization of Biaryls (GP1)

A mixture of biaryl (0.50 mmol), $Pd(OAc)_2$ (2.25 mg, 10.0 μmol), IPr·HCl (8.50 mg, 20.0 μmol), K_2CO_3 (69.0 mg, 0.50 mmol) and NMP (1.5 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was then kept in an oil bath at 130 °C for 12 h. After cooling to room temperature, the solution was extracted with hexane or toluene (2×10 mL) and washed with water. The organic phase was dried over $MgSO_4$ and filtered. The solvents of the filtrate were removed under reduced pressure. The residue was subjected to chromatography on silica gel. A crystal could be obtained by crystallization from CH_2Cl_2/CH_3OH.

Table 4. Crystal structure data of cycloadducts **11**, **15**-*n*Hex and **17**.[23]

	11	**15**-*n*Hex	**17**
CCDC No.[a]	779934	784424	779935
Formula	$C_{20}H_{14}$	$C_{78}H_{99}$	$C_{27}H_{18}$
M.W.	254.31	1036.57	342.41
Temp. (K)	296(2)	100(2)	295(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P12_1/n1$	*P*-1	*P*-1
Z	2	2	2
Unit cell dimensions	$a=7.6904(10)$, $b=5.7749(7)$, $c=14.5229(17)$ Å, $\alpha=\gamma=90$, $\beta=91.622(7)°$	$a=11.4763(3)$, $b=16.7075(5)$, $c=18.9869(6)$ Å, $\alpha=66.5110(10))$, $\beta=80.0760(10)$, $\gamma=74.0020(10)°$	$a=8.6884(9)$, $b=9.9953(11)$, $c=11.1578(12)$ Å, $\alpha=81.570(2)$, $\beta=74.060(2)$, $\gamma=88.541(2)°$,
V (Å^3)	644.72(14)	3201.50(16)	921.54(17)

[a] CCDC 779934, CCCDC 784424, and CCDC 779935 contain the supplementary crystallographic data for compounds **11**, **15**-*n*Hex and **17**, respectively, of 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.

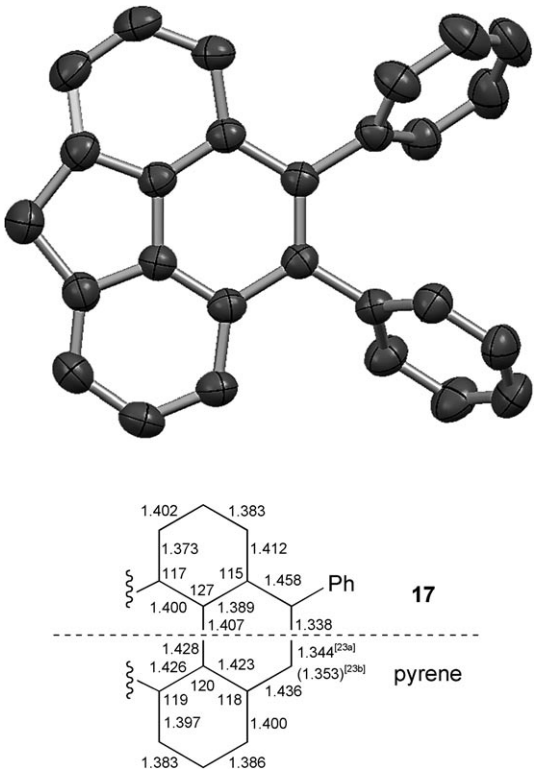


Figure 1. The molecular structure of **17** (*top*) and comparison of its bond lengths (Å) and bond angles (deg) with those of pyrene (*bottom*).

General Procedure for Cyclization of Terphenyls (GP2)

A mixture of terphenyl (1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 20.0 μmol), IPr·HCl (17.0 mg, 40.0 μmol), K_2CO_3 (276 mg, 2.00 mmol) and NMP (3 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was then kept in an oil bath at 170 °C for 2 h. After cooling to room temperature, the solution was extracted with toluene (3 × 25 mL) and washed with water. The solvents of the organic phase were removed under reduced pressure. The residue was subjected to chromatography on silica gel, eluting with hexane/CH_2Cl_2. Crystals could be obtained by crystallization from CH_2Cl_2/CH_3OH at room temperature. [***Note:*** *These compounds have very low solubility in common organic solvents. The extract should not be dried over* $MgSO_4$.]

Procedure for Preparation of 7,7,15,15-Tetra-*n*-butyl-7,15-dihydrobenzo[*g*]benz[6,7]indeno[1,2-*b*]fluorene (15-*n*Hex)

A mixture of **14** (107 mg, 0.25 mmol), $Pd(OAc)_2$ (4.5 mg, 20.0 μmol), IPr·HCl (17.0 mg, 40.0 μmol), K_2CO_3 (276 mg, 2.0 mmol) and NMP (1.5 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was then kept in an oil bath at 170 °C for 6 h. After cooling to room temperature and adding Cs_2CO_3 (652 mg, 2.00 mmol) and *n*-bromohexane (248 mg, 1.50 mmol), the suspension was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 60 °C for 3 d, and, then, was allowed to cool to room temperature. The reaction mixture was extracted with toluene (3 × 30 mL), and washed with hydrochloric acid (0.1 M, 2 × 20 mL) and water (20 mL). The solvents of the organic phase were removed under reduced pressure. The residue was subjected to chromatography on silica gel, eluting with hexane gave **15**-*n*Hex as a white solid; yield: 74.1 mg (43%). A colorless crystal (mp 129.8–130.4 °C) could be obtained by crystallization from CH_2Cl_2/CH_3OH at room temperature.

Procedure for Preparation of 8,9-Diphenyl-4*H*-cyclopenta[*def*]phenanthrene (17)

A mixture of biphenyl **1o** (119 mg, 0.50 mmol), diphenylacetylene (93.5 mg, 0.53 mmol), $Pd(OAc)_2$ (4.5 mg, 20.0 μmol), IPr·HCl (17.0 mg, 40.0 μmol) and NMP (1.5 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was then kept in an oil bath at 110 °C for 4 h and subsequently at 170 °C for 1 h. After cooling to room temperature, the solution was extracted with toluene (2 × 10 mL) and washed with water. The organic phase was dried over $MgSO_4$ and filtered. The solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel, eluting with hexane/CH_2Cl_2 (6:1) to afford **17** as a colorless solid; yield: 102 mg (60%). A suitable crystal of **17** [mp 219.6–220.6 °C (dec.)] for the X-ray diffraction analysis was grown from CH_2Cl_2/MeOH.

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References

[1] R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, New York, **1997**.

[2] For reviews, see: a) K. D. Belfield, S. Yao, M. V. Bondar, *Adv. Polym. Sci.* **2008**, *213*, 97; b) J. U. Wallace, S. H. Chen, *Adv. Polym. Sci.* **2008**, *212*, 145; c) A. C. Grimsdale, K. Müllen, *Macromol. Rapid Commun.* **2007**, *28*, 1676; d) G. Hughes, M. R. Bryce, *J. Mater. Chem.* **2005**, *15*, 94; e) U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477; f) M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737.

[3] a) Y. Ie, Y. Umemoto, M. Nitani, Y. Aso, *Pure Appl. Chem.* **2008**, *80*, 589; b) C. Gadermaier, L. Luer, A. Gambetta, T. Virgili, M. Zavelani-Rossi, G. Lanzani, in: *Semiconducting Polymers*, (Eds.: G. Hadziioannou, G. G. Malliaras), 2nd edn., Wiley-VCH, Weinheim, **2007**, pp 205.

[4] a) O. Inganas, F. Zhang, M. R. Andersson, *Acc. Chem. Res.* **2009**, *42*, 1731; b) D. Jones, *Org. Photovoltaics* **2008**, 57; c) G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, *21*, 1323.

[5] Fluorene, 2-halo- and 2,7-dihalo-substituted fluorenes are commercially available at reasonable prices. Gener-

ation of functional groups at other positions has to be processed with many steps, see: a) A. Tsuge, T. Yamasaki, T. Moriguchi, T. Matsuda, Y. Nagano, H. Nago, S. Mataka, S. Kajigaeshi, M. Tashiro, *Synthesis* **1993**, 205; b) S. Kajigaeshi, T. Kadowaki, A. Nishida, S Fujisaki, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 97; c) A. K. Sarkar, A. Chatterjee, B. Bandyopadhyay, *Tetrahedron* **1976**, *32*, 65. For a recent review for synthesis of fluorenes, see: d) S. Toyota, T. Iwanaga, in: *Science of Synthesis*, Georg Thieme Verlag, Stuttgart, Vol. 45b, p 818.

[6] For the synthesis of (heteroatom-substituted) fluorenes not through the metal-catalyzed C–H activation, see: a) M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.* **2008**, *130*, 15982; b) I. A. Kashulin, I. E. Nifant′ev, *J. Org. Chem.* **2004**, *69*, 5476; c) Y.-S. Song, S. D. Kong, S. A. Khan, B. R. Yoo, I. N. Jung, *Organometallics* **2001**, *20*, 5586; d) W. Kirmse, K. Kund, E. Ritzer, A. E. Dorigo, K. N. Houk, *J. Am. Chem. Soc.* **1986**, *108*, 6045; e) D. L. J. Clive, R. Sunasee, *Org. Lett.* **2007**, *9*, 2677; f) K. Boeckmann, F. Vögtle, *Chem. Ber.* **1981**, *114*, 1065.

[7] For reviews of aryl C–H bond activation, see: a) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318; b) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; c) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359; d) P. W. N. M. van Leeuwen, J. G. de Vries, in: *Handbook of C–H Transformations*, (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, p 203; e) Y. Fujiwara, C. Jia, *Pure Appl. Chem.* **2001**, *73*, 319; f) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; g) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; h) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826; i) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633. For reviews on C(sp^3)–H bond activation, see: j) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; k) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074.

[8] B. M. Trost, *Angew. Chem.* **1995**, *107*, 285; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259.

[9] Several protocols involving metal-catalyzed functionalization of the benzylic C–H bond with the subsequent C–C bond formation have been reported. Pd: a) T. Kesharwani, R. C. Larock, *Tetrahedron* **2008**, *64*, 6090; b) J.-I. Inoh, T. Satoh, S. Pivsa-Art, M. Miura, M. Nomura, *Tetrahedron Lett.* **1998**, *39*, 4673. Pt: c) S. Yang, Z. Li, X. Jian, C. He, *Angew. Chem.* **2009**, *121*, 4059; *Angew. Chem. Int. Ed.* **2009**, *48*, 3999. Pt and Ru: d) M. Tobisu, H. Nakai, N. Chatani, *J. Org. Chem.* **2009**, *74*, 5471. Cu: e) T. Matsumoto, K. Ohkubo, K. Honda, A. Yazawa, H. Furutachi, S. Fujinami, S. Fukuzumi, M. Suzuki, *J. Am. Chem. Soc.* **2009**, *131*, 9258. Fe: f) Y.-Z. Li, B.-J. Li, X.-Y. Lu, S. Lin, Z.-J. Shi, *Angew. Chem.* **2009**, *121*, 3875; *Angew. Chem. Int. Ed.* **2009**, *48*, 3817; g) C.-X. Song, G.-X. Cai, T. R. Farrell, Z.-P. Jiang, H. Li, L.-B. Gan, Z.-J. Shi, *Chem. Commun.* **2009**, 6002.

[10] a) F. Wang, W. Ueda, *Chem. Eur. J.* **2009**, *15*, 742; b) L.-C. Campeau, M. Parisien, A. Jean, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 581; c) M. Shimizu, K. Mochida, T. Hiyama, *Angew. Chem.* **2008**, *120*, 9906; *Angew. Chem. Int. Ed.* **2008**, *47*, 9760; d) K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* **2006**, *128*, 1434.

[11] S. J. Hwang, H. J. Kim, S. Chang *Org. Lett.* **2009**, *11*, 4588.

[12] In a crowded environment, the C–H bond in a methyl group can be activated, see: a) M. Chaumontet, R. Piccardi, N. Audic, J. Hitce, J.-L. Peglion, E. Clot, O. Baudoin, *J. Am. Chem. Soc.* **2008**, *130*, 15157; b) O. Baudoin, A. Herrbach, F. Guéritte, *Angew. Chem.* **2003**, *115*, 5914; *Angew. Chem. Int. Ed.* **2003**, *42*, 5736; c) W. A. Herrmann, C. Broßmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844; d) G. Dyker, *J. Org. Chem.* **1993**, *58*, 6426; e) G. Dyker, *Angew. Chem.* **1994**, *106*, 117; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 103; f) G. Dyker, *Angew. Chem.* **1992**, *104*, 1079; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1023.

[13] a) C.-G. Dong, Q.-S. Hu, *Tetrahedron* **2008**, *64*, 2537; b) C.-G. Dong, Q.-S. Hu, *Angew. Chem.* **2006**, *118*, 2347; *Angew. Chem. Int. Ed.* **2006**, *45*, 2289.

[14] T.-P. Liu, C.-H. Xing, Q.-S. Hu, *Angew. Chem.* **2010**, *122*, 2971; *Angew. Chem. Int. Ed.* **2010**, *49*, 2909. This procedure is not so efficient as they described. We repeated the coupling reaction of 1,2-dibromobenzene with 2-tolylboronic acid three times and fluorene (**3a**) was indeed observed in ca. 50% GC yield. 2-Methylbiphenyl (15–20%) and 1,2-bis(2-tolyl)benzene (15–30%) were obtained as the serious by-products. Replacing 1,2-dibromobenzene with 1-bromo-2-chlorobenzene or changing ligand PCy_3 to $PCy_3{\cdot}HBF_4$ could not improve unsatisfactory results. Our optimal condition is also inefficient for this tandem reaction.

[15] Reviews for NHC ligands: a) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612; b) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445; c) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677; d) *N-Heterocyclic Carbenes in Synthesis*, (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**.

[16] Compound **4** and its steroisomer were obtained as an inseparable mixture after the chromatography. Crystallization from CH_2Cl_2/MeOH gave pure fluorene **4**. Unfortunately, the accurate structure of the stereoisomer of **4** cannot be assigned based on ^{1}H- and ^{13}C NMR and mass spectra.

[17] This catalytic system has been used for other C(sp^3)-H activation, see: M. Lafrance, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 14570.

[18] Based on the pK_a values of toluene ($pK_a = 42$) and diphenylmethane ($pK_a = 32$), the benzylic proton in **1d** should be more acidic than those in **1a** and **1c**, see: a) F. G. Bordwell, D. Algrim, N. R. Vanier, *J. Org. Chem.* **1977**, *42*, 1817; b) F. G. Bordwell, W. S. Matthews, N. R. Vanier, *J. Am. Chem. Soc.* **1975**, *97*, 442.

[19] The formation of benzocyclobutenes through the C-(sp^3)–H activation gave a similar result, see: M. Chaumontet, R. Piccardi, N. Audic, J. Hitce, J.-L. Peglion, N. Audic, J. Hitce, J.-L. Peglion, E. Clot, O. Baudoin, *J. Am. Chem. Soc.* **2008**, *130*, 1515.

[20] For conventional protocols for synthesizing indenofluorene **11**, see: a) S. Merlet, M. Birau, Z. Y. Wang, *Org. Lett.* **2002**, *4*, 2157. Indenofluorene **11** and its derivatives have been applied as semiconductors and blue organic electroluminescent devices: b) T.-C. Lin, C.-S. Hsu, C.-L. Hu, Y.-F. Chen, W.-J. Huang, *Tetrahedron Lett.* **2009**, *50*, 182; c) C. Poriel, J. J. Liang, J. Rault-Berthelot, F. Barriere, N. Cocherel, A. M. Z. Slawin, D. Horhant, M. Virboul, G. Alcaraz, N. Audebrand, L. Vignau, N. Huby, G. Wantz, L. Hirsch, *Chem. Eur. J.* **2007**, *13*, 10055; d) K. Wong, L. Chi, S. Huang, Y. Liao, L. Y. Wang, *Org. Lett.* **2006**, *8*, 5029; e) T. Hadizad, J. Zhang, Z. Y. Wang, T. C. Gorjanc, C. Py, *Org. Lett.* **2005**, *7*, 795.

[21] A conventional protocol for synthesizing indenofluorene **13**, see: M. Shimizu, Y. Tomioka, I. Nagao, T. Hiyama, *Synlett* **2009**, 3147.

[22] Synthesis of indenes through metal-catalyzed coupling reactions of haloarenes with alkynes, see: a) D. A. Alonso, C. Nájera, M. C. Pacheco, *Adv. Synth. Catal.* **2002**, *344*, 172; b) D. K. Rayabarapu, C.-H. Cheng, *Chem. Commun.* **2002**, 942; c) C.-C. Liu, R. P. Korivi, C.-H. Cheng, *Chem. Eur. J.* **2008**, *14*, 9503; d) L. G. Quan, V. Gevorgyan, Y. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 3545; e) A. A. Pletnev, Q. Tian, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 9276; f) D. K. Rayabarapu, C.-H. Yang, C.-H. Cheng, *J. Org. Chem.* **2003**, *68*, 6726; g) K.-J. Chang, D. K. Rayabarapu, C.-H. Cheng, *Org. Lett.* **2003**, *5*, 3963; h) D. Zhang, E. K. Yum, Z. Liu, R. C. Larock, *Org. Lett.* **2005**, *7*, 4963; i) R. Deng, L. Sun, Z. Li, *Org. Lett.* **2007**, *9*, 5207.

[23] X-ray crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

[24] a) G. R. Desiraju, A. Gavezzotti, *J. Chem. Soc. Chem. Commun.* **1989**, 621; b) C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525; c) L. L. Miller, K. R. Mann, *Acc. Chem. Res.* **1996**, *29*, 417.

[25] a) C. S. Frampton, K. S. Knight, N. Shankland, K. Shankland, *J. Mol. Struct.* **2000**, *520*, 29; b) Y. Kai, F. Hama, N. Yasuoka, N. Kasai, *Acta Crystallogr. B:* **1978**, *34*, 1263.

[26] H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878.

