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Coupling Reaction of Zirconacyclopentadienes with Dihalonaphthalenes and Dihalopyridines: A New Procedure for the Preparation of Substituted Anthracenes, Quinolines, and Isoquinolines

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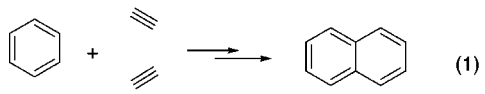
Abstract: Reactions of tetraiodobenzene with zirconacyclopentadienes, which were conveniently prepared from two alkynes (or diynes) and zirconocene complexes, afforded 1,2,3,4-tetrasubstituted diiodonaphthalene derivatives in good isolated yields. These 1,2,3,4-tetrasubstituted diiodonaphthalene derivatives could be converted to 1,2,3,4,5,6,7,8-octasubstituted anthracene derivatives by reaction with a second zirconacyclopentadiene. When the two zirconacyclopentadienes were different, unsymmetrical anthracenes such as 1,2,3,4-tetraethyl-5,6,7,8-tetraphenylanthracene (68% isolated yield) were obtained. On the other hand, treatment of a 2,3-dihalopyridine such as 2-bromo-3-iodopyridine with zirconacyclopentadienes gave 5,6,7,8-tetrasubstituted quinoline derivatives in good to high yields. 3,4-Dihalopyridines such as 4-chloro-3-iodopyridine reacted with zirconacyclopentadienes to afford 5,6,7,8-tetrasubstituted isoquinoline derivatives in good to high yields.

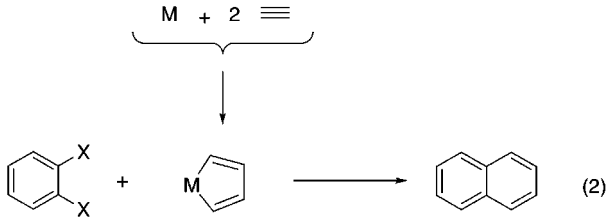
Introduction

Fused aromatic ring extension is an attractive and useful method for the construction of new polycyclic aromatic compounds in organic synthesis.[1,2] The most direct and simplest ideal method is the intermolecular cycloaddition of two alkynes to an arene as shown in eq 1.



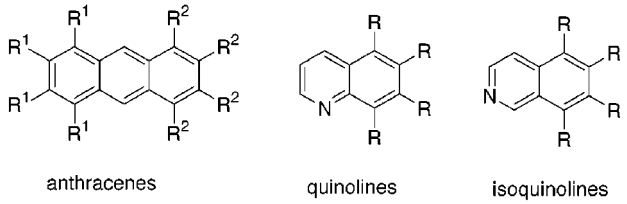
(1)

To perform this type of direct aromatic ring extension, we have investigated the coupling reaction of dihaloarenes and metalacyclopentadienes, which can be conveniently prepared from two alkynes and transition metals as shown in eq 2.[3,4]



(2)

In this paper, we report the details of our method for the coupling of dihaloarenes with zirconacyclopentadienes[5] and its application to the synthesis of substituted anthracenes,[6] substituted quinolines,[7] and isoquinolines.[8]



By this method, the substituents can be conveniently introduced into extended aromatic rings. For example, the benzo rings of quinolines and isoquinolines were highly substituted.

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‡ Aichi University of Education.

(1) For a review on aromatic ring formation, see (a) Watson, M. D.; Fethtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (b) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

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(3) Preliminary result was reported: see Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154−5155.

(4) Naphthalene formation from aryl halide or arylmetal compounds and two alkynes by use of transition metals, see (a) Wu, G.; Rheingold, A. L.; Feib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (b) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922. (c) Sakakibara, T.; Tanaka, Y.; Yamasaki, T.-I. *Chem. Lett.* **1986**, 797. (d) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1979**, *92*, 5625. (e) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203.

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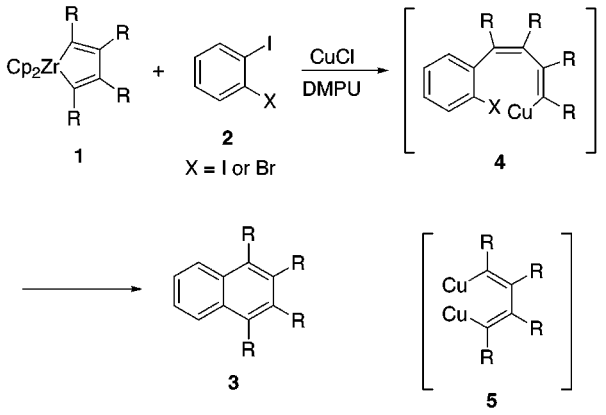
Scheme 1



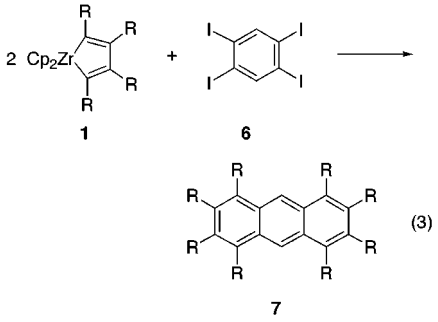
1 2 3 4 5

Results and Discussion

Reaction of Dihalobenzene with Zirconacyclopentadienes (Scheme 1). When diiodobenzene (**2**) was treated with zirconacyclopentadienes (**1**)[5] in the presence of CuCl[9] together with 3 equiv of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), the coupling reaction proceeded to give 1,2,3,4-tetrasubstituted naphthalene derivatives (**3**) as we preliminarily reported.[3] The rate-determining step of the coupling reaction is the first intermolecular coupling step. Once the first coupling step proceeds, the second coupling of the intermediate **4** is, in turn, an intramolecular coupling and is fast. Therefore, we did not observe the formation of *o*-dienylhalobenzene derivatives. Furthermore, at least one halogen should be iodine for the intermolecular coupling. Dibromobenzene did not react at all. The second halogen can be bromine because of the intramolecular coupling.[3]

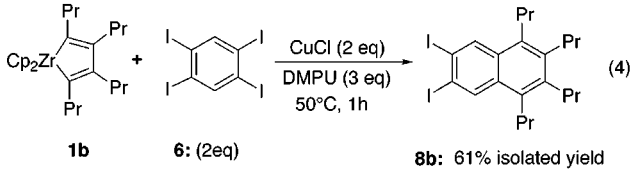
When the reaction was carried out without DMPU, naphthalenes were formed only in low yields (up to 20%), and moreover, they were accompanied by a number of other unidentified products. Our study showed that a gradual precipitation of a yellow powder from the reaction mixture was observed on addition of 2 equiv of CuCl to zirconacyclopentadienes without DMPU. Although the yellow powder could not be characterized because of its unstability, an organocopper intermediate such as **5** or its polymer was assumed to be formed since quantitative formation of zirconocene dichloride was observed by the ^{1}H NMR study. Addition of 3 equiv of DMPU dissolved the yellow powder to give a dark-brown solution that readily reacted with 1,2-diiodobenzene **2** to give naphthalenes **3**. It is reasonable to assume that DMPU breaks up the polymeric structure of the organocopper compound by coordinating the copper atoms and also increases the solubility in THF. Both CuCl and DMPU were added to the reaction mixture in all reactions described below.

Preparation of Dihalonaphthalene Derivatives. When tetraiodobenzene **6**[10] was used, the ring extension occurred on both sides of the tetraiodobenzene to give octahomosubstituted anthracenes **7**, as shown in eq 3.[3] Extension of two aromatic



1 6 7 (3)

rings occurs stepwise and the coupling of the tetraiodobenzene with the first zirconacyclopentadiene is faster than that of the second zirconacyclopentadiene. The reaction of the second zirconacyclopentadiene is relatively slow. Therefore, the diiodonaphthalene **8** could be selectively prepared. As shown in eq 4,



1b **6:** (2eq) **8b:** 61% isolated yield (4)

reaction of zirconacyclopentadiene **1b** with 1,2,4,5-tetraiodobenzene **6** gave diiodonaphthalene derivative **8b**. The structure of **8b** was confirmed by X-ray analysis.

Results are shown in Table 1. The optimal yields were obtained in the reaction of 1 equiv of zirconacyclopentadienes

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(6) For substituted anthracenes or fused aromatic compounds, see (a) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1531. (b) Benkhoff, J.; Boese, R.; Klärner, F. G. *Liebigs Ann. Recl.* **1997**, 501−516. (c) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660−4665. (d) Matsuura, A.; Nishinaga, T.; Komatsu, K. *Tetrahedron Lett.* **1997**, *38*, 3427.

(7) For substituted quinolines, see (a) Suginome, M.; Fukuda, T.; Ito, Y. *Org. Lett*. **1999**, *1*, 1977. (b) Beller, M.; Thiel, O. R.; Trauthwein, H.; Hartung, C. G. *Chem. Eur. J*. **2000**, *6*, 2513. (c) Ubeda, J. I.; Villacampa, M.; Avendano, C. *Synlett* **1997**, 285. (d) Larock, R. C.; Kuo, M.-Y. *Tetrahedron Lett.* **1991**, *32*, 569−572.

(8) For substituted isoquinolines, see (a) Roesch, K. R.; Larock, R. C. *Org. Lett*. **1999**, *1*, 553. (b) Lorsbach, B. A.; Bagdanoff, J. T.; Miller, R. B.; Kurth, M. J. *J. Org. Chem*. **1998**, *63*, 2244. (c) Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 5306−5307. (d) Beugelmans, R.; Chastanet, J.; Roussi, G. *Tetrahedron* **1984**, *40*, 311−314. (e) Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3221−3223.

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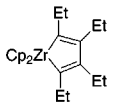
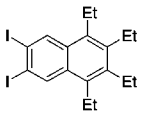
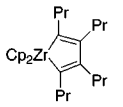
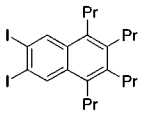
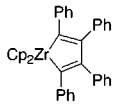
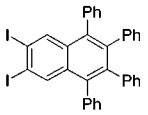
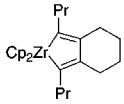
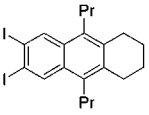
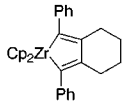
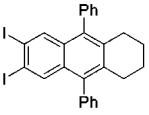
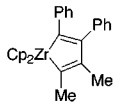
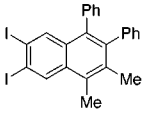
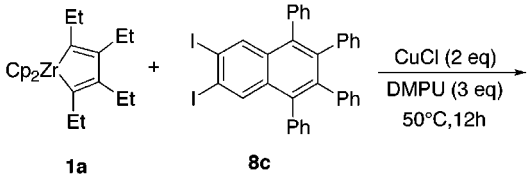
Table 1. Formation of Linear Diiodonaphthalene Derivatives by Reaction of Zirconacyclopentadienes with 1,2,4,5-Tetraiodobenzene **6**

Zirconacyclopentadiene		Reaction time (h)[a]	Diiodonaphthalene		Isolated yields (%)
	**1a**	1		(**8a**)	54
	**1b**	1		(**8b**)	61
	**1c**	1		(**8c**)	77
	**1d**	1		(**8d**)	57
	**1e**	3		(**8e**)	75
	**1f**	3		(**8f**)	54

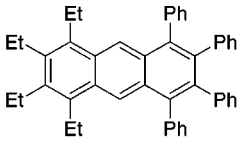
[a] At 50 °C.

with 2 equiv of **6**. Thus, the reaction of both of alkyl and aryl homosubstituted zirconacyclopentadienes gave good yields of diiodonaphthalenes **8a**−**c**. Unsymmetrically alkyl−aryl substituted zirconacyclopentadiene **1f** afforded the corresponding diiodonaphthalene **8f** in good yield as well. The use of bicyclic zirconacyclopentadienes allowed the introduction of two rings in one step and furnished diiodotetrahydroanthracenes **8d** and **8e**.

Formation of Substituted Anthracenes. The diiodonaphthalene derivatives **8** were used for further coupling reactions with zirconacyclopentadienes **1** to give unsymmetrically substituted anthracene derivatives **9**, as shown in eq 5.



1a **8c**

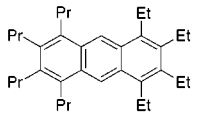
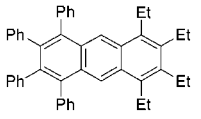
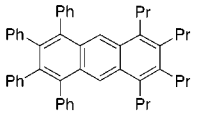
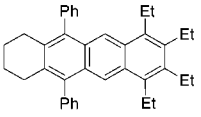
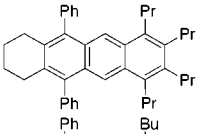
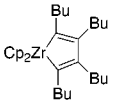
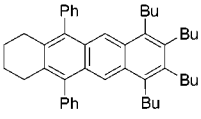
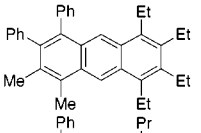
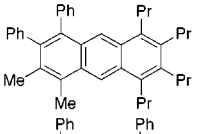
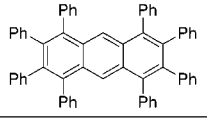


(5)

9b: 68% isolated yield

Some results are shown in Table 2. The reaction of tetraethylzirconacyclopentadiene **1a** and tetrapropylzirconacyclopentadiene **1b** with **8b** and **8c** in the presence of 2 equiv of CuCl and 3 equiv of DMPU gave unsymmetrically substituted anthracenes **9a**, **9b**, and **9c**, respectively, at 50 °C for 12 h. The

Table 2. Formation of Substituted Anthracenes **9** by the Reaction of Zirconacyclopentadienes with Diiodoarenes **8**

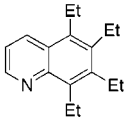
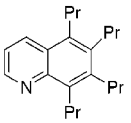
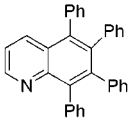
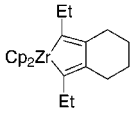
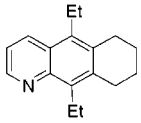
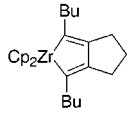
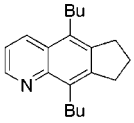
Zirconacyclopentadiene	8	Anthracenes		Isolated yields (%)
1a	**8b**		(**9a**)	57
1a	**8c**		(**9b**)	68
1b	**8c**		(**9c**)	58
1a	**8e**		(**9d**)	53
1b	**8e**		(**9e**)	50
 **1g**	**8e**		(**9f**)	46
1a	**8f**		(**9g**)	54
1b	**8f**		(**9h**)	56
1c	**8c**		(**9i**)	59

[a] Reaction temperature, 50 °C; reaction time, 12 h.

reaction with diiodonaphthalene required a longer reaction time, compared with the reaction with diiodobenzene or tetraiodobenzene. The structure of **9a** was confirmed by X-ray analysis. The use of **8e** in the reactions with tetraethyl- (**1a**), tetrapropyl- (**1b**), and tetrabutylzirconacyclopentadiene (**1g**) gave the corresponding alkyl/phenyl-substituted anthracenes **9d**−**f**. This methodology was also suitable for the preparation of unsymmetrically substituted anthracenes such as **9g** and **9h**.

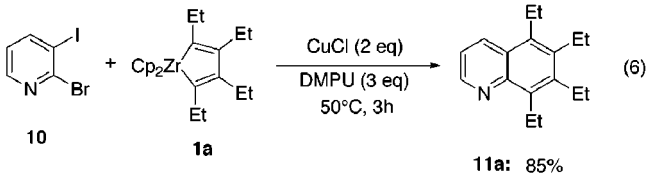
Formation of Substituted Quinoline Derivatives. 2,3-Dibromopyridine did not react with zirconacyclopentadienes as observed in the case of dibromobenzene even in the presence of CuCl and DMPU. 2-Bromo-3-iodopyridine **10** could be selectively prepared as a crystalline compound by the reaction of 2,3-dibromopyridine with *n*-BuLi followed by iodination. The thus-prepared 2-bromo-3-iodopyridine **10** reacted with **1a** in the presence of 2 equiv of CuCl and 3 equiv of DMPU at 50 °C to give the corresponding quinoline **11a** in 85% yield as shown in eq 6. The results are shown in Table 3. Tetrapropyl-substituted zirconacyclopentadiene **1b** afforded the corresponding quinoline **11b** in 63% yield in 3 h. On the other hand, the reaction of tetraphenylzirconacyclopentadiene with **10** required prolonged

Table 3. Quinoline-Forming Reaction of Zirconacyclopentadienes with 2-Bromo-3-iodopyridine **10**

Zirconacyclopentadiene	Reaction time (h)[a]	Quinoline	Yield (%)[b]
1a	3	 (**11a**)	85(81)
1b	3	 (**11b**)	67(63)
1c	18	 (**11c**)	- (35)
 **1h**	18	 (**11d**)	71(65)
 **1i**	18	 (**11e**)	58(31)

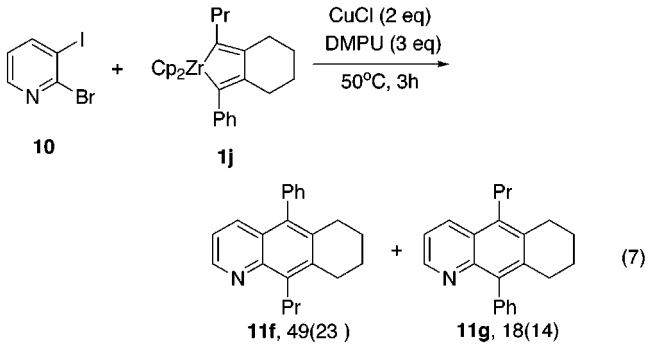
[a] At 50 °C. [b] GC yields. Isolated yields are given in parentheses.

reaction time (18 h) to obtain only a rather modest yield (35%) of 5,6,7,8-tetraphenylquinoline (**11c**). Similarly, tricyclic quinoline derivatives **11d** and **11e** were obtained from reaction of bicyclic zirconacyclopentadienes **1h** and **1i** with **10** after 18 h, respectively.



(6)

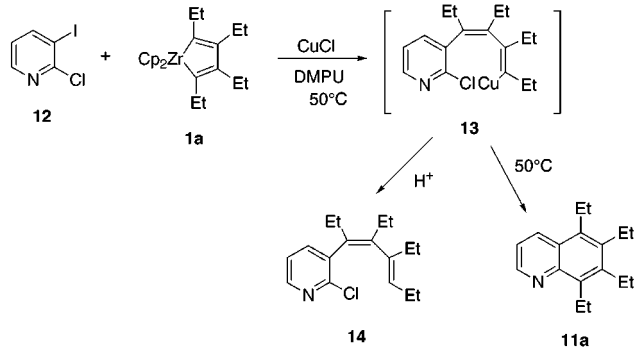
The reaction of **10** with unsymmetrically substituted zirconacyclopentadiene provided a mixture of **11f** and **11g** in a 2.7:1 ratio, as shown in eq 7. Fortunately, both isomers were readily separated by column chromatography and the structure of **11f** was determined by X-ray structural analysis.



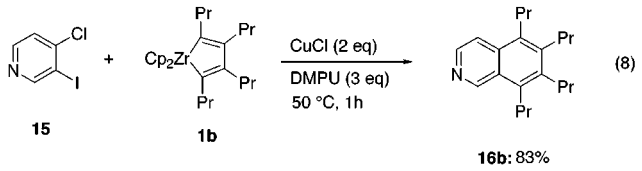
(7)

It is interesting to note that when **1a** was treated with 2-chloro-3-iodopyridine (**12**) instead of **10**, chlorodienylpyridine (**14**) was obtained in 10% yield along with the formation of the desired product **11a** (78%). This result clearly indicates that the first carbon−carbon bond formation proceeded at the iodopyridine moiety and the second carbon−carbon bond formation occurred on the chloropyridine moiety as shown in Scheme 2.

Scheme 2

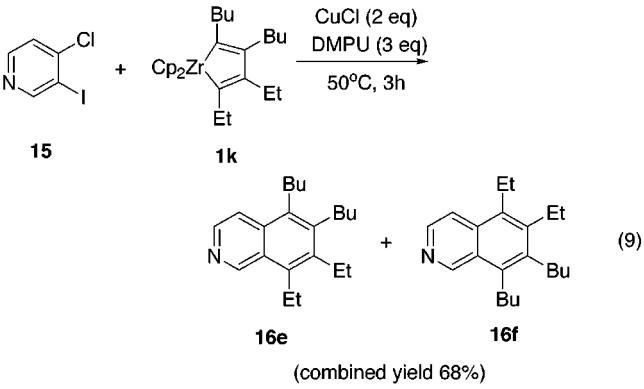


Formation of Substituted Isoquinolines. The above-mentioned strategy was also conveniently applied to the synthesis of isoquinolines. In this case, **1** reacted with 4-chloro-3-iodopyridine **15** under the above-mentioned conditions to yield substituted isoquinolines in good yields, as shown in eq 8. The



(8)

results are shown in Table 4. The reactions of tetraalkyl-substituted zirconacyclopentadienes with **15** furnished the corresponding isoquinolines **16a**−**c** in good to high yields in 1 h at 50 °C. However, the reaction of phenyl-substituted bicyclic zirconacyclopentadiene **1e** gave rise to isoquinoline **16d** with a side ring in only moderate yield. Reactions of **15** with unsymmetrically substituted zirconacyclopentadienes, such as 2,3-dibutyl-4,5-diethylzirconacyclopentadiene **1k**, gave a 1:1 mixture of regioisomers of **16e** and **16f** (eq 9).

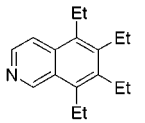
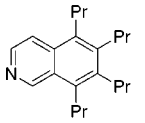
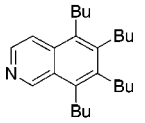
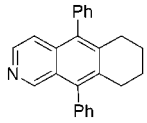


(9)

Experimental Section

General Information. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. THF was distilled over sodium and benzophenone. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU; Aldrich, 98%) was

Table 4. Isoquinoline-Forming Reaction of **1** with **15**[b]

Zirconacyclopentadiene	Isoquinoline	Yield (%)[a]
1a	 (**16a**)	- (65)
1b	 (**16b**)	83(70)
1g	 (**16c**)	- (74)
1e	 (**16d**)	- (42)

[a] GC yields. Isolated yields are given in parentheses. [b] Reaction temperature, 50 °C; reaction time, 1 h.

dried over calcium hydride and distilled under reduced pressure. Zirconocene dichloride (Nichia Chemical Industries, Ltd.), ethylmagnesium chloride (solution in THF, Kanto), and copper chloride (Wako Pure Chemical Industries, Ltd., 99.9%) were used as received. All other materials were of reagent-grade quality and were used as obtained from Tokyo Kasei Kogyo Co., Ltd., Aldrich Chemical Co., Inc., and Kanto Chemical Co., Inc.

^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ or C_6D_6 (containing 1% TMS) solutions on a Bruker-400 or Jeol JNM-AL300 NMR spectrometer. GC analysis was performed on a Shimadzu GC-14A instrument equipped with a fused silica capillary column (Shimadzu CBP1-M25-O25) and a Shimadzu C-R6A-Chromatopac integrator.

Formation of Diiodonaphthalenes 8 by the Reaction of Zirconacyclopentadienes with 1,2,4,5-Tetraiodobenzene 6: Typical Experimental Procedure. To a solution of a corresponding zirconacyclopentadiene **1**, prepared in situ from Cp_2ZrCl_2 (292 mg, 1 mmol), *n*-BuLi (2 mmol), and an alkyne (2 mmol) in THF (10 mL), were added DMPU (0.36 mL, 3.0 mmol), CuCl (200 mg, 2.0 mmol), and tetraiodobenzene **6** (1.16 g, 2.0 mmol), and the mixture was heated to 50 °C. The reaction mixture was quenched by addition of 3 N HCl and extracted with Et_2O (3 × 30 mL). The organic layer was separated, dried with magnesium sulfate, and concentrated in vacuo, leaving a dark oily residue. Column chromatography on silica gel (hexane) afforded the corresponding product **8**.

1,2,3,4-Tetraethyl-6,7-diiodonaphthalene (8a). A colorless solid (54%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.22 (t, J = 7.4 Hz, 6H), 1.27 (t, J = 7.5 Hz, 6H), 2.80 (q, J = 7.5 Hz, 4H), 2.99 (q, J = 7.5 Hz, 4H), 8.52 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.57, 15.64, 21.44, 22.85, 102.64, 131.95, 134.45, 135.46, 139.59; IR (KBr) 2967, 2928, 2901, 2868, 1555, 1443, 1057, 911, 876 cm^{-1}; HRMS calcd for $C_{18}H_{22}I_2$ 491.9811, found 491.9819.

6,7-Diiodo-1,2,3,4-tetrapropylnaphthalene (8b). A pale yellow solid (61%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.09 (t, J = 7.3 Hz, 6H), 1.09 (t, J = 7.3 Hz, 6H), 1.51−1.65 (m, 8H), 2.68 (t, J = 8.4 Hz, 4H), 2.88 (t, J = 8.3 Hz, 4H), 8.47 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.80, 15.02, 24.53, 24.72, 30.78, 32.57, 102.56, 132.10, 133.16, 135.51, 138.60; IR (KBr) 2957, 2926, 2870, 1555, 1464, 1455, 1377, 1115, 1086, 990, 966, 882, 875, 818 cm^{-1}; HRMS calcd for $C_{22}H_{30}I_2$ 548.0438, found 548.0449. Anal. Calcd for $C_{22}H_{30}I_2$: C, 48.19; H, 5.52; I, 46.29. Found: C, 48.02; H, 5.52; I, 46.42.

6,7-Diiodo-1,2,3,4-tetraphenylnaphthalene (8c). A light yellow solid (77%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.77−6.82 (m, 10H), 7.13−7.24 (m, 10H), 8.14 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 104.87, 125.59, 126.65, 126.90, 127.77, 130.98, 131.08, 132.72, 137.44, 137.65, 138.19, 139.87, 140.36; IR (KBr) 3056, 1599, 1547, 1493, 1438, 1441, 1074, 1026, 1001, 924, 897, 747, 698 cm^{-1}; HRMS calcd for $C_{34}H_{22}I_2$ 683.9811, found 683.9837.

1,2,3,4-Tetrahydro-6,7-diiodo-9,10-dipropylanthracene (8d). A colorless solid (57%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.07 (t, J = 7.4 Hz, 6H), 1.51−1.63 (m, 4H), 1.79−1.83 (m, 4H), 2.83−2.89 (m, 8H), 8.47 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.68, 22.80, 23.36, 27.81, 29.86, 102.38, 131.58, 132.88, 135.16, 135.29; IR (KBr) 2951, 2867, 2930, 2916, 1553, 1476, 1451, 1111, 926, 893, 870, 820 cm^{-1}; HRMS calcd for $C_{20}H_{24}I_2$ 517.9968, found 517.9963.

1,2,3,4-Tetrahydro-6,7-diiodo-9,10-diphenylanthracene (8e). A colorless solid (75%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.56−1.61 (m, 4H), 2.44−2.49 (m, 4H), 7.13−7.17 (m, 4H), 7.33−7.46 (m, 6H) 7.75 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.67, 28.40, 102.26, 126.39, 127.73, 128.95, 130.86, 134.48, 135.62, 135.72, 137.67; IR (KBr) 2940, 2934, 2924, 2859, 1601, 1493, 1441, 1073, 924, 911, 885, 750, 700 cm^{-1}; HRMS calcd for $C_{26}H_{20}I_2$ 585.9655, found 585.9668.

6,7-Diiodo-1,2-dimethyl-3,4-diphenylnaphthalene (8f). A colorless solid (54%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.17 (s, 3H), 2.64 (s, 3H), 6.94−7.01 (m, 5H), 7.10−7.25 (m, 5H) 7.96 (s, 1H), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.27, 19.02, 103.13, 104.45, 126.24, 126.62, 127.53, 127.59, 129.93, 130.21, 130.98, 131.98, 132.76, 133.97, 134.90, 135.81, 138.04, 138.44, 140.91, 141.50; IR (KBr) 3056, 3021, 1601, 1493, 1451, 1030, 785, 758, 698 cm^{-1}; HRMS calcd for $C_{24}H_{18}I_2$ 559.9498, found 559.9520.

Reaction of Zirconacyclopentadienes with Diiodoarenes 8. The reactions were conducted under the same conditions as for the preparation of **8**. Column chromatography on silica gel (99/1 hexane/AcOEt) afforded the corresponding products **9**.

1,2,3,4-Tetraethyl-5,6,7,8-tetrapropylanthracene (9a). A light green solid (57%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.12 (t, J = 7.2 Hz, 6H), 1.19 (t, J = 7.4 Hz, 6H), 1.28 (t, J = 7.5 Hz, 6H), 1.42 (t, J = 7.4 Hz, 6H), 1.57−1.68 (m, 4H), 1.74−1.84 (m, 4H), 2.78 (t, J = 8.3 Hz, 4H), 2.87 (q, J = 7.5 Hz, 4H), 3.18 (t, J = 8.3 Hz, 4H), 3.25 (q, J = 7.5 Hz, 4H), 8.70 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.02, 15.09, 15.38, 15.92, 22.06, 22.98, 24.56, 25.02, 31.65, 32.84, 119.37, 128.73, 129.04, 133.51, 134.68, 135.81, 136.62; IR (KBr) 2960, 2928, 2868, 1478, 1468, 1453, 1090, 1061, 887, 879, 868, 735 cm^{-1}; Anal. Calcd for $C_{34}H_{50}$: C, 89.01; H, 10.99. Found: C, 88.69; H, 11.15.

1,2,3,4-Tetraethyl-5,6,7,8-tetraphenylanthracene (9b). A colorless solid (68%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.12 (t, J = 7.3 Hz, 6H), 1.21 (t, J = 7.4 Hz, 6H), 2.77−2.93 (m, 8H), 6.81−6.92 (m, 10H), 7.21−7.29 (m, 10H), 8.32 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.06, 15.81, 21.87, 22.94, 122.69, 125.22, 126.36, 126.53, 127.44, 129.61, 129.86, 131.45, 135.01, 137.49, 137.64, 138.10, 139.95, 140.85; IR (KBr) 3054, 3025, 2971, 2961, 2870, 1601, 1493, 1443, 1071, 1061, 1028, 885, 754, 698 cm^{-1}; HRMS calcd for $C_{46}H_{42}$ 594.3287, found 594.3259.

1,2,3,4-Tetraphenyl-5,6,7,8-tetrapropylanthracene (9c). A colorless solid (58%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.82 (t, J = 7.3 Hz, 6H), 1.06 (t, J = 7.3 Hz, 6H), 1.47−1.59 (m, 8H), 2.66−2.71 (m, 4H), 2.74−2.80 (m, 4H), 6.83−6.93 (m, 10H), 7.20−7.29 (m, 10H), 8.24 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.55, 14.99, 24.22, 24.91, 31.60, 32.71, 122.73, 125.22, 126.30, 126.54, 127.53, 129.81, 129.83, 131.36, 131.44, 133.77, 136.59, 137.52, 138.11, 139.99, 140.83; IR (KBr) 3058, 3023, 2957, 2930, 2870, 1603, 1491, 1368, 1090, 1073, 1028, 891, 806, 747, 698 cm^{-1}; HRMS calcd for $C_{50}H_{50}$ 650.3913, found 650.3924.

7,8,9,10-Tetraethyl-1,2,3,4-tetrahydro-5,12-diphenylnaphthacene (9d). A colorless solid (53%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.07 (t, J = 7.4 Hz, 6H), 1.18 (t, J = 7.4 Hz, 6H), 1.72−1.77 (m, 4H),

2.70−2.87 (m, 12H), 7.37−7.58 (m, 10H), 8.00 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.93, 15.82, 21.83, 22.86, 23.09, 29.36, 121.38, 126.86, 128.37, 128.82, 129.61, 130.41, 132.59, 134.81, 136.77, 136.97, 140.52; IR (KBr) 3054, 3027, 2973, 2963, 2932, 2872, 1591, 1493, 1462, 1451, 1441, 1262, 1071, 1057, 1030, 878, 802, 745, 702 cm^{-1}; HRMS calcd for $C_{38}H_{40}$ 496.3130, found 496.3143.

1,2,3,4-Tetrahydro-5,12-diphenyl-7,8,9,10-tetrapropylnaphthacene (9e). A colorless solid (50%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J = 7.3 Hz, 6H), 1.04 (t, J = 7.3 Hz, 6H), 1.39−1.55 (m, 8H), 1.72−1.77 (m, 4H), 2.62−2.75 (m, 12H), 7.35−7.57 (m, 10H), 7.93 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.54, 14.98, 23.10, 24.08, 24.91, 29.36, 31.57, 32.65, 121.42, 126.79, 128.45, 129.04, 129.56, 130.34, 132.46, 133.56, 135.86, 136.97, 140.55; IR (KBr) 2955, 2930, 2868, 1591, 1468, 1455, 1441, 1090, 1071, 1028, 889, 750, 702 cm^{-1}; HRMS calcd for $C_{42}H_{48}$ 552.3756, found 552.3766.

7,8,9,10-Tetrabutyl-1,2,3,4-tetrahydro-5,12-diphenylnaphthacene (9f). A colorless solid (46%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, J = 7.3 Hz, 6H), 0.96 (t, J = 7.4 Hz, 6H), 1.14−1.26 (m, 4H), 1.36−1.50 (m, 12H), 1.70−1.77 (m, 4H), 2.64−2.78 (m, 12H), 7.36−7.57 (m, 10H), 7.94 (s, 2H), ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.90, 13.95, 23.10, 23.33, 23.50, 29.08, 29.36, 29.98, 33.07, 33.73, 121.38, 126.81, 128.43, 129.07, 129.53, 130.30, 132.48, 133.59, 135.86, 136.98, 140.63; IR (KBr) 3058, 3025, 2957, 2932, 2859, 1591, 1493, 1462, 1441, 1103, 1071, 1030, 884, 750, 702 cm^{-1}; HRMS calcd for $C_{46}H_{56}$ 608.4382, found 608.4401.

1,2,3,4-Tetraethyl-5,6-dimethyl-7,8-diphenylanthracene (9g). A colorless solid (54%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.06 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.4 Hz, 3H), 1.28 (t, J = 7.5 Hz, 3H), 1.45 (t, J = 7.4 Hz, 3H), 2.26 (s, 3H), 2.77−2.92 (m, 9H), 3.27−3.35 (m, 2H), 7.07−7.25 (m, 10H), 8.16 (s, 1H), 8.81 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.98, 15.40, 15.53, 15.84, 18.99, 21.82, 22.05, 22.90, 23.01, 118.37, 123.35, 125.89, 126.10, 127.27, 127.40, 128.96, 129.29, 129.50, 129.86, 130.23, 130.41, 130.84, 131.31, 134.79, 135.05, 136.66, 136.85, 137.38, 138.92, 140.22, 141.89; IR (KBr) 3056, 2968, 2928, 2872, 1601, 1595, 1491, 1485, 1443, 1090, 1061, 1028, 874, 802, 748, 700 cm^{-1}; HRMS calcd for $C_{36}H_{38}$ 470.2973, found 470.2973.

5,6-Dimethyl-7,8-diphenyl-1,2,3,4-tetrapropylanthracene (9h). A colorless solid (56%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.79 (t, J = 7.2 Hz, 3H), 1.06−1.15 (m, 6H), 1.23 (t, J = 7.2 Hz, 3H), 1.43−1.67 (m, 6H), 1.81−1.89 (m, 2H), 2.27 (s, 3H), 2.68−2.80 (m, 6H), 2.86 (s, 3H), 3.20−3.25 (m, 2H), 7.09−7.26 (m, 10H), 8.10 (s, 1H), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.50, 15.00, 15.07, 15.10, 15.42, 18.98, 24.16, 24.39, 24.94, 31.57, 32.70, 32.84, 118.38, 123.44, 125.90, 126.05, 127.37, 127.41, 129.19, 129.25, 129.77, 130.15, 130.41, 130.80, 131.24, 133.58, 133.81, 135.96, 136.57, 136.67, 138.84, 140.27, 141.88; IR (KBr) 2957, 2951, 2926, 2868, 1595, 1482, 1468, 1453, 1441, 1414, 1377, 1084, 1071, 1032, 1007, 889, 860, 768, 752, 698 cm^{-1}; HRMS calcd for $C_{40}H_{46}$ 526.3600, found 526.3584.

1,2,3,4,5,6,7,8-Octaphenylanthracene (9i). A pale yellow powder (59%); the solubility of this compound is very low. ^{1}H NMR (C_6D_6, Me_4Si, 70 °C) δ 6.79−7.26 (m, 40H), 8.34 (s, 2H); IR (KBr) 3081, 3025, 1601, 1493, 1443, 1073, 1030, 764, 752, 698 cm^{-1}; HRMS calcd for $C_{62}H_{42}$ 786.3287, found 786.3293.

2-Bromo-3-iodopyridine (10). 2,3-Dibromopyridine (2.36 g, 10 mmol) was dissolved in diethyl ether (50 mL); the solution was cooled to −78 °C, and *n*-BuLi (6.7 mL 1.57 M, 10.5 mmol) was slowly added. After the mixture was stirred for 15 min at −78 °C, a solution of iodine (2.67 g, 10.5 mmol) in diethyl ether (50 mL) was added; the mixture was stirred for a further 5 min at −78 °C and then allowed to warm to room temperature within 30 min. After quenching by addition of saturated aqueous sodium hydrogen carbonate solution, usual workup afforded a crude product, which was crystallized from hot methanol to give 2-bromo-3-iodopyridine as an off-white crystalline solid: Yield 1.66 g (59%); mp 101−101.5 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 7.00 (dd, J = 4.6 and 7.9 Hz, 1H), 8.11 (dd, J = 1.7 and 7.9 Hz, 1H), 8.35 (dd, J = 1.6 and 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 99.45, 123.40, 148.11, 148.39, 148.77; IR (KBr) 1551, 1381, 1125, 1005, 795, 716 cm^{-1}; EI-MS *m*/*z* (relative abundance, %) 285 (82), 283 (84) ($M^{+\bullet}$), 204 (100, $[M - Br]^+$); HRMS calcd for C_5H_3BrNI 282.8493, found 282.8500. Anal. Calcd for C_5H_3BrNI: C, 21.15; H, 1.07; N, 4.93. Found: C, 21.29; H, 1.08; N, 4.87.

General Procedure for Preparation of Quinolines (11). To a solution of the corresponding zirconacyclopentadiene **1**, prepared in situ from Cp_2ZrCl_2 (292 mg, 1 mmol), *n*-BuLi (2 mmol), and an alkyne (2 mmol) in THF (10 mL) were added DMPU (0.36 mL, 3.0 mmol), CuCl (200 mg, 2.0 mmol), and 2-bromo-3-iodopyridine **10** (284 mg, 1.0 mmol), and the mixture was heated to 50 °C. The reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate solution. The organic layer was separated, dried with magnesium sulfate, and evaporated in vacuo, leaving a dark oily residue. Column chromatography on silica gel (4/1 hexane/Et_2O) afforded the corresponding products **11**. For **11c**, 3/1 hexane/Et_2O was used.

5,6,7,8-Tetraethylquinoline (11a). A yellowish waxy solid (81%, GC yield 85%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.21−1.30 (m, 9H), 1.32 (t, J = 7.4 Hz, 3H), 2.86 (q, J = 7.5 Hz, 2H), 2.90 (q, J = 7.6 Hz, 2H), 3.06 (q, J = 7.6 Hz, 2H), 3.35 (q, J = 7.4 Hz, 2H), 7.29 (dd, J = 8.4 and 4.1 Hz, 1H), 8.03 (dd, J = 8.4 and 1.5 Hz, 1H), 8.85 (dd, J = 4.1 and 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.74, 15.76, 15.81, 15.84, 20.93, 21.24, 22.66, 22.96, 119.71, 125.53, 132.15, 135.02, 138.32, 138.51, 141.53, 146.22, 147.86; IR (KBr) 2971, 2932, 2870, 1595, 1584, 1566, 1491, 1478, 1462, 1453, 1061, 789 cm^{-1}; HRMS calcd for $C_{17}H_{23}N$ 241.1830, found 241.1828.

5,6,7,8-Tetrapropylquinoline (11b). A colorless viscous oil (63%, GC yield 67%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.05−1.12 (m, 12H), 1.51−1.73 (m, 8H), 2.71−2.81 (m, 4H), 2.93−2.99 (m, 2H), 3.22−3.29 (m, 2H), 7.27 (dd, J = 4.0 and 8.6 Hz, 1H), 8.24 (dd, J = 8.6 and 1.7 Hz, 1H), 8.82 (dd, J = 4.0 and 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.76, 14.94, 15.01, 15.05, 24.67, 24.83, 24.92, 24.98, 30.09, 30.70, 32.43, 32.73, 119.59, 125.69, 132.18, 133.71, 137.16, 137.63, 140.62, 146.34, 147.76; IR (neat) 3069, 2959, 2932, 2870, 1595, 1584, 1564, 1489, 1466, 1377, 1360, 1086, 909, 884, 783, 735 cm^{-1}; HRMS calcd for $C_{21}H_{30}N$ ($[M - H]^+$) 296.2378, found 296.2383.

5,6,7,8-Tetraphenylquinoline (11c). An off-white solid (35%): mp 225−7 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.78−6.90 (m, 10H), 7.11−7.28 (m, 11H), 7.95 (dd, J = 8.5 and 1.8 Hz, 1H), 8.89 (dd, J = 4.2 and 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 120.79, 125.54, 125.58, 126.30, 126.66, 126.69, 126.77, 127.10, 127.14, 127.67, 131.20, 131.57, 134.90, 138.44, 138.85, 139.47, 139.69, 139.95, 140.10, 142.43, 146.28, 150.16; IR (KBr) 3029, 1601, 1495, 1472, 1441, 1074, 1024, 1001, 802, 741, 696 cm^{-1}; HRMS calcd for $C_{33}H_{22}N$ ($[M - H]^+$) 432.1752, found 432.1772.

5,10-Diethyl-6,7,8,9-tetrahydrobenzo[*g*]quinoline (11d). A colorless waxy solid (65%, GC yield 71%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.18 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.4 Hz, 3H), 1.84 (q, J = 3.3 Hz, 4H), 2.88−2.94 (m, 2H), 2.95−3.04 (m, 4H), 3.32 (q, J = 7.5 Hz, 2H), 7.27 (dd, J = 8.6 and 4.0 Hz, 1H), 8.26 (dd, J = 8.6 and 1.4 Hz, 1H), 8.85 (dd, J = 1.4 and 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.35, 14.45, 20.10, 20.52, 22.96, 23.06, 27.44, 27.67, 119.62, 124.87, 131.81, 133.64, 134.65, 136.75, 137.84, 145.39, 147.94; IR (KBr) 2961, 2896, 2865, 1593, 1582, 1563, 1489, 1453, 1427, 1063, 1040, 781, 752 cm^{-1}; HRMS calcd for $C_{17}H_{21}N$ 239.1674, found 239.1674.

5,9-Dibutyl-6,7-dihydro-1*H*-cyclopenta[*g*]quinoline (11e). A colorless wax (31%, GC yield 58%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.96 (q, J = 7.6 Hz, 6H), 1.42−1.52 (m, 4H), 1.54−1.69 (m, 4H), 2.16 (q, J = 7.5 Hz, 2H), 2.92−2.99 (m, 2H), 3.06 (t, J = 7.5 Hz, 2H), 3.10 (t, J = 7.5 Hz, 2H), 3.17−3.23 (m, 2H), 7.31 (dd, J = 8.5 and 4.1 Hz, 1H), 8.28 (dd, J = 8.5 and 1.6 Hz, 1H), 8.85 (dd, J = 4.1 and 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.05, 14.21, 23.13, 23.24, 25.02, 28.59, 29.10, 31.79, 32.09, 32.57, 32.76, 119.22, 126.06, 130.68, 131.88, 133.85, 141.22, 144.34, 146.89, 147.55; IR (KBr) 2951, 2934, 2867, 2855, 1615, 1595, 1578, 1495, 1464, 1451, 1103, 1088, 783 cm^{-1}; HRMS calcd for $C_{20}H_{27}N$ 281.2143, found 281.2147.

5-Phenyl-10-propyl-6,7,8,9-tetrahydrobenzo[*g*]quinoline (11f) and 10-phenyl-5-propyl-6,7,8,9-tetrahydrobenzo[*g*]quinoline (11g). For **11f**, a white solid (23%, GC yield 49%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.13 (t, J = 7.3 Hz, 3H), 1.65−1.77 (m, 4H), 1.81−1.90 (m, 2H), 2.58 (t, J = 6.5 Hz, 2H), 3.05 (t, J = 6.5 Hz, 2H), 3.30−3.38 (m, 2H), 7.12 (dd, J = 8.6 and 4.1 Hz, 1H), 7.18−7.23 (m, 2H), 7.37−7.50 (m, 3H), 7.60 (dd, J = 8.6 and 1.7 Hz, 1H), 8.82 (dd, J = 4.1 and 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.89, 22.78, 23.00, 23.42, 27.60, 29.18, 29.42, 119.70, 126.08, 127.09, 128.49, 130.29, 134.20, 134.45, 135.77, 136.94, 138.04, 139.25, 145.14, 148.19; IR (neat) 3058, 3025, 2955,. 2934, 2870, 1595, 1574, 1563, 1499, 1487, 1474, 1453, 1443, 1117, 1073, 785, 756, 700 cm^{-1}; HRMS calcd for $C_{22}H_{23}N$ 301.1830, found 301.1841. For **11g**, a white wax (14%, GC yield 18%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.13 (t, J = 7.3 Hz, 3H), 1.61−1.75 (m, 4H), 1.81−1.90 (m, 2H), 2.62 (t, J = 6.5 Hz, 2H), 3.00 (t, J = 6.5 Hz, 2H), 3.02−3.09 (m, 2H), 7.23−7.51 (m, 6H), 8.33 (dd, J = 8.6 and 1.6 Hz, 1H), 8.75 (dd, J = 4.1 and 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.73, 22.70, 23.02, 23.67, 27.43, 29.86, 29.93, 119.62, 125.22, 126.66, 128.13, 130.28, 131.72, 134.04, 135.39, 137.83, 138.05, 140.02, 145.91, 148.87; IR (KBr) 3056, 2957, 2940, 2867, 1597, 1578, 1572, 1563, 1497, 1482, 1460, 1449, 1429, 1381, 1354, 1325, 1107, 1071, 926, 916, 791, 764, 708 cm^{-1}; HRMS calcd for $C_{22}H_{22}N$ ([M − H]$^+$) 300.1742, found 300.1752.

The identification of **11f** was done by single-crystal X-ray structural analysis.

2-Chloro-3-iodopyridine (12). 3-Amino-2-chloropyridine (10 mmol) and 5 mL of concentrated HCl were put in a 200-mL flask with 3 g of ice. An aqueous solution of $NaNO_2$ (11 mmol of $NaNO_2$ dissolved in 20 mL of H_2O) was added dropwise to the flask, and the solution was kept at 0 °C for 15 min. Then 34 mmol of KI aqueous solution was slowly added and kept standing for 12 h at room temperature. Usual workup gave the desired product as a slightly yellow solid: Yield 90%; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.90−6.99 (m, 1H), 8.10−8.20 (m, 1H), 8.30−8.40 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 94.91, 123.16, 148.67, 148.77, 154.29; IR (KBr) 1557, 1389, 1136, 1059, 1015, 797, 721 cm^{-1}; HRMS calcd for C_5H_3ClNI 238.8999, found 238.8991.

2-Chloro-3-{3-(4,5-diethyl-3*Z*,5*E*-octa-3,5-dienyl)}pyridine (14). Yellow liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.55 (t, J = 7.6 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.6 Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H), 1.76 (dq, J = 7.5 and 7.4 Hz, 2H), 1.80−1.90 (m, 1H), 1.91−2.09 (m, 1H), 2.11−2.40 (m, 3H), 2.50−2.65 (m, 1H), 5.02 (t, J = 7.4 Hz, 1H), 7.09 (dd, J = 7.5 and 4.7 Hz, 1H), 7.30 (dd, J = 7.2 and 2.0 Hz, 1H), 8.20 (dd, J = 4.6 and 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.86, 12.91, 13.36, 13.84, 20.79, 22.44, 23.36, 24.98, 121.36, 131.66, 131.70, 133.27, 138.93, 140.35, 144.56, 146.79, 150.95; IR (neat) 2967, 2932, 2872, 1574, 1557, 1454, 1389, 1198, 1123, 1115, 1065, 866, 800, 754 cm^{-1}; HRMS calcd for $C_{17}H_{24}ClN$ 277.1597, found 277.1595.

4-Chloro-3-iodopyridine (15). 4-Chloropyridine (10 mmol) was dissolved in THF (50 mL), the solution was cooled to −78 °C, and LDA (10 mmol) was slowly added. After the mixture was stirred for 1 h at −78 °C, iodine (10 mmol) was added. The mixture was warmed to room temperature and stirred for 3 h. Then it was quenched by water. Usual workup and column chromatography on silica gel (5/1 hexane/Et_2O) afford **15** as a slightly yellow solid: Yield 56%; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 7.37 (d, J = 5.1 Hz, 1H), 8.38 (d, J = 5.1 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 97.88, 124.78, 147.80, 149.46, 158.24; IR (KBr) 1549, 1455, 1387, 1264, 1115, 1071, 1009, 820, 731, 677 cm^{-1}; HRMS calcd for C_5H_3ClNI 238.8999, found 238.8980.

General Procedure for Preparation of Isoquinolines (16). To a solution of the corresponding zirconacyclopentadiene **1**, prepared in situ from Cp_2ZrCl_2 (292 mg, 1 mmol), *n*-BuLi (2 mmol), and an alkyne (2 mmol) in THF (10 mL), were added DMPU (0.36 mL, 3.0 mmol), CuCl (200 mg, 2.0 mmol), and 3-iodo-4-chloropyridine **15** (239 mg, 1.0 mmol), and the mixture was heated to 50 °C. The reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate solution and extracted with Et_2O (3 × 30 mL). The organic layer was separated, dried with magnesium sulfate, and concentrated in vacuo, leaving a dark oily residue. Column chromatography on silica gel (hexane/EtOAc) afforded the corresponding product **16**. For **16a** (9/1), **16b** (13/1), **16c** (25/1), and **16d** (5/1) the indicated mixtures were used.

5,6,7,8-Tetraethylisoquinoline (16a). A yellow solid (65%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.1−1.25 (m, 9H), 1.31 (t, J = 7.5 Hz, 3H), 2.7−2.9 (m, 4H), 2.96 (q, J = 7.2 Hz, 2H), 3.13 (t, J = 7.5 Hz, 2H), 7.73 (d, J = 6.0 Hz, 1H), 8.74 (d, J = 6.0 Hz, 1H), 9.83 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.34, 15.53, 15.70, 16.37, 21.10, 21.25, 22.44, 23.03, 117.87, 126.20, 133.96, 134.39, 137.35, 139.69, 142.28, 143.77, 151.57; IR (KBr) 2969, 2932, 2872, 1611, 1489, 1464, 1383, 1055, 828, 756 cm^{-1}; HRMS calcd for $C_{17}H_{23}N$ 241.1831, found 241.1850.

5,6,7,8-Tetrapropylisoquinoline (16b). A yellow solid (70%, GC 83%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.06−1.16 (m, 12H), 1.5−1.8 (m, 8H), 2.7−2.8 (m, 4H), 2.96 (t, J = 8.0 Hz, 2H), 3.11(t, J = 8.3 Hz, 2H), 7.77 (d, J = 5.1 Hz, 1H), 8.80 (br s, 1H), 9.90 (br s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.78, 15.01 (2C), 15.05, 24.48, 24.75, 24.92, 25.47, 30.54, 30.69, 32.22, 32.80, 117.92, 126.42, 133.22, 134.12, 136.24, 138.80, 142.32, 142.73, 151.65; IR (KBr) 2957, 2930, 2872, 1611, 1485, 1466, 1455, 1377, 1265, 1240, 1213, 1086, 1059, 822, 734 cm^{-1}; HRMS calcd for $C_{21}H_{31}N$ 297.2457, found 297.2449.

5,6,7,8-Tetrabutylisoquinoline (16c). A yellow liquid (74%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J = 7.2 Hz, 3H), 0.96−1.1 (m, 9H), 1.45−1.8 (m, 16H), 2.7−2.9 (m, 4H), 2.98 (t, J = 6.4 Hz, 2H), 3.13 (t, J = 6.4 Hz, 2H), 7.80 (br s, 1H), 8.82 (br s, 1H), 9.89 (br s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.85, 13.93, 14.03, 23.36, 23.48, 23.53, 23.56, 28.07, 28.17, 29.54, 30.14, 33.29, 33.43, 33.63, 34.22, 117.79, 126.53, 133.19, 134.01, 136.25, 138.71, 142.21, 142.63, 151.50; IR ($CHCl_3$ solution) 2959, 2930, 2872, 2861, 1613, 1462, 1379, 1105, 1061, 727, 666 cm^{-1} HRMS calcd for $C_{25}H_{39}N$ 353.3083, found 353.3089.

5,10-Diphenyl-6,7,8,9-tetrahydrobenzo[*g*]isoquinoline (16d). A yellow solid (42%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.6−1.9 (m, 4H), 2.5−2.8 (m, 4H), 7.2−7.8 (m, 11H), 8.28 (br s, 1H), 8.75 (br s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.61, 22.66, 28.98, 29.55, 118.25, 126.39, 127.41, 127.51, 128.60, 128.69, 130.00, 130.05, 133.47, 135.35, 136.56, 137.99, 138.18, 138.50, 138.70, 141.83, 150.99; IR (KBr) 3058, 2940, 1599, 1495, 1441, 1379, 1030, 750, 704 cm^{-1}; HRMS calcd for $C_{25}H_{21}N$ 335.1674, found 335.1671.

5,6-Dibutyl-7,8-diethylisoquinoline (16e) and 7,8-Dibutyl-5,6-diethylisoquinoline (16f). Column chromatography on silica gel (15/1 hexane/EtOAc) afforded an inseparable mixture of **16e** and **16f** (68%) as a yellow solid. Major to minor isomer ratio was 2:1. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.01 (t, J = 6.4 Hz, 6H), 1.24 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.4 Hz, 3H), 1.44−1.65 (m, 8H), 2.7−2.9 (m, 4H), 2.95−3.3 (m, 4H), 7.8 (br s, 1H), 8.83 (br s, 1H), 9.92 (br s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.84, 14.02, 15.34, 15.51, 21.26, 23.13, 23.45, 23.57, 28.06, 29.43, 33.66, 34.19, 117.69, 126.41, 133.83, 134.21, 136.35, 138.55, 142.24, 143.67, 151.65; HRMS calcd for $C_{21}H_{31}N$ 297.2456, found 297.2450. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, J = 7.2 Hz, 6H), 1.24 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.4 Hz, 3H), 1.35−1.8 (m, 8H), 2.9−3.3 (m, 8H), 7.81 (br s, 1H), 8.83 (br s, 1H), 9.92 (br s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.84, 13.91, 15.68, 16.34, 21.11, 22.55, 23.34, 23.50, 28.14, 30.03, 33.24, 33.48, 118.00, 126.51, 133.31, 134.12, 137.23, 139.71, 142.29, 142.61, 151.43; HRMS calcd for $C_{21}H_{31}N$ 297.2456, found 297.2450.

Supporting Information Available: Crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for **8b**, **9a**, and **11f** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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