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Novel Synthetic Route to Octasubstituted Naphthalenes from Four Alkynes and One Olefin Unit via Zirconacyclopentadienes and 1,2-Diiodo-3,4,5,6-tetraalkylbenzene

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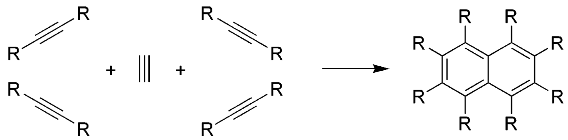
Abstract: 1,2,3,4-Tetrasubstituted benzene derivatives were prepared by the reaction of zirconacyclopentadienes with vinyl bromide in the presence of $NiCl_2(PPh_3)_2$. 1,2-Diiodo-3,4,5,6-tetraalkylbenzenes were formed by treatment of 1,2,3,4-tetraalkylbenzenes with iodine and periodic acid in the presence of a catalytic amount of sulfuric acid. Reaction of the 1,2-diiodo-3,4,5,6-tetraalkylbenzenes with zirconacyclopentadienes in the presence of a stoichiometric amount of CuCl gave sterically crowded octasubstituted naphthalenes in moderate yields.

Octasubstituted naphthalenes have attracted considerable interest in the field of synthetic organic chemistry,[1] because synthetic methodology of the octasubstituted naphthalenes is usually limited as a result of the steric repulsion caused by the eight substituents on the naphthalene ring.[2] The overcrowded naphthalene cores are twisted from planar to release the steric hindrance and form a twisted aromatic ring system that has unique structural characteristics and properties.[3]

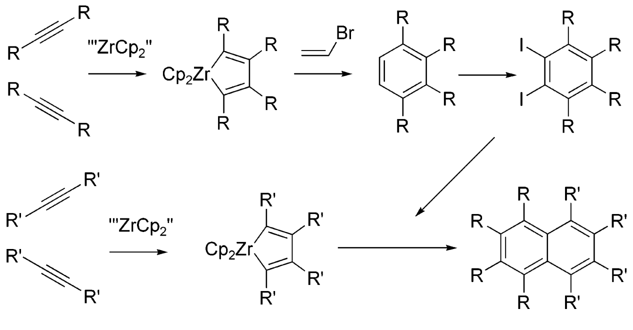
There are several precedented synthetic methods for the persubstituted naphthalenes, such as Diels–Alder reaction,[2a–f] nucleophilic substitution of perfluoronaphthalene,[2g–j] coupling reactions of the lithiated butadiene and dibromobenzene derivatives having a bicyclo[2.2.0] framework,[2i] and so on.[2k,l] However, in these methods it is difficult to prepare the naphthalenes with mixed substituents. The simplest way to prepare the octasubstituted naphthalene is the coupling of four internal alkynes and one acetylene as shown in Scheme 1. To realize this reaction, transition-metal-mediated coupling of internal alkynes is one attractive method.

Our group has developed zirconium-mediated highly selective coupling reactions of internal alkynes to construct a series of aromatic rings.[4] In this paper, we describe a zirconium-mediated method for the synthesis of octasubstituted naphthalenes by coupling of four alkynes and one vinyl bromide as shown in Scheme 2.

SCHEME 1



SCHEME 2



Methods for preparation of 1,2,3,4-tetrasubstituted benzene derivatives from alkynes are very limited. In this strategy, a novel synthetic method of 1,2,3,4-tetrasub-

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[†] Hokkaido University.

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(1) For reviews for substituted naphthalenes, see: (a) de Koning, C. B.; Rousseau A. L.; van Otterlo, W. A. L. *Tetrahedron* **2003**, *59*, 7. (b) Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567.

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(3) For studies on the structures of octasubstituted naphthalenes, see: (a) Simaan, S.; Marks, V.; Gottlieb, H. E.; Stanger, A.; Biali S. E. *J. Org. Chem.* **2003**, *68*, 637. (b) Christofi, A. M.; Garratt, P. J.; Hogarth, G.; Ibbett, A. J.; Ng, Y.-F.; Steed, J. W. *Tetrahedron* **2002**, *58*, 4543. (c) Pascal, R. A., Jr.; Barnett, L.; Qiao, X.; Ho, D. M. *J. Org. Chem.* **2000**, *65*, 7711. (d) Oiao, X.; Pelczer, I.; Pascal, R. A., Jr. *Chirality* **1998**, *10*, 154. (e) García, R.; Riera, J.; Carilla, J.; Juliá, L.; Sánchez-Baeza, F. J.; Molins, E. *Tetrahedron* **1995**, *51*, 3627. (f) Sim, G. A. *Acta Crystallogr.* **1982**, *B38*, 623. (g) Hart, H.; Teuerstein, A.; Jeffares, M.; Kung, W.-J. H.; Ward, D. L. *J. Org. Chem.* **1980**, *45*, 3731. (h) Ward, D. L. *Acta Crystallogr.* **1980**, *B36*, 963. (i) Gafner, G.; Herbstein, F. H. *Nature* **1963**, *200*, 130. (j) Donaldson, D. M.; Robertson, J. M. *J. Chem. Soc.* **1953**, 17. See also ref 2a,b,f–i.

(4) (a) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (b) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (c) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093. (d) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (e) Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 361. (f) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (g) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059. (h) Takahashi, T.; Tsai, F.-Y.; Kotora, M. *J. Am. Chem. Soc.* **2000**, *122*, 4994. (i) Xi, Z.-F.; Sato, K.; Gao, Y.; Lu, J.-M.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568.

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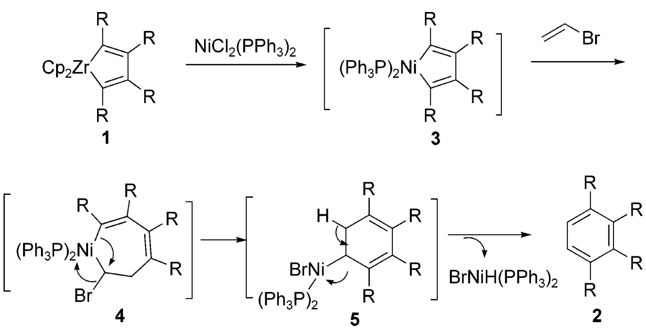
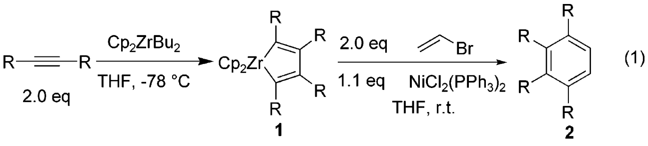
SCHEME 3



stituted benzenes had to be developed. To obtain the 1,2,3,4-tetrasubstituted benzene, acetylene or its equivalent is required as the third alkyne, since tetrasubstituted zirconacyclopentadienes as intermediates are readily available from two internal alkynes and Cp_2ZrBu_2 or Cp_2ZrEt_2. We used vinyl bromide as an acetylene equivalent. The thus-formed 1,2,3,4-tetrasubstituted benzenes were converted into diiodides, which in turn reacted with the second zirconacyclopenadienes to give octasubstituted naphthalenes as shown in Scheme 2.

It is known that 1,2,3,4-tetraalkylbenzene formation from alkynes is very limited. Usually, coupling reaction of alkynes gives a mixture of regioisomers of alkyl-substituted benzenes. Although rearrangement of the alkyl substituents on the benzene rings has been reported as the Jacobsen reaction, only 1,2,3,4-tetramethyl- or -tetraethylbenzene has been synthesized by this method.[5]

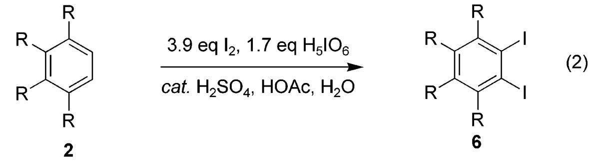
We have already reported selective formation of benzene derivatives from alkynes via zirconacyclopentadienes.[4d,e] Here we developed a novel preparative method of 1,2,3,4-tetraalkylbenzene derivatives by the reaction of zirconacyclopentadienes and vinyl bromide. As shown in eq 1, zirconacyclopentadiene **1** reacted with vinyl bromide (2.0 equiv) in the presence $NiCl_2(PPh_3)_2$ (1.1 equiv) to afford the corresponding 1,2,3,4-tetrasubstituted benzenes **2** in good yields. In this reaction, vinyl bromide acted as an acetylene equivalent.



2b: R = Et, 48%
2c: R = Pr, 52%
2d: R = Bu, 55%

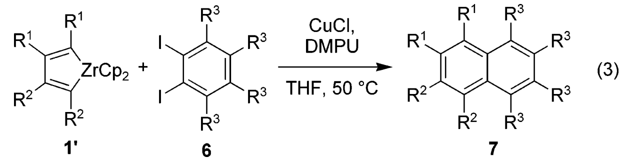
The proposed reaction mechanism is shown in Scheme 3. First, transmetalation from Zr to Ni proceeds to give a nickelacycle **3** as we reported.[4c] Then insertion of vinyl bromide followed by migration of an sp^2 carbon and β-H elimination seem reasonable to afford the final product.

Iodination of the tetraalkylbenzenes **2b**−**d** with iodine (3.9 equiv) and periodic acid (1.7 equiv) in the presence of a catalytic amount of sulfuric acid proceeds smoothly to give the corresponding diiodobenzenes **6b**−**d** in good yields (eq 2).[6]



6b: R = Et, 81%
6c: R = Pr, 55%
6d: R = Bu, 69%

Finally, the desired octasubstituted naphthalenes **7** were produced via a coupling reaction between 1,2-diiodobenzene **6** with a second zirconacyclopentadiene **1′** (eq 3), which could be either the same or different from the first zirconacyclopentadiene **1**.[4a,b] The coupling reaction proceeded smoothly in the presence of CuCl at 50 °C, and after 3 h of stirring, the corresponding octasubstituted naphthalenes **7a**−**g** were obtained in good yields. All results are summarized in Table 1. The best yield was achieved when tetraphenylzirconacycle **1d** was used, probably as a result of the smaller steric hindrance of **7d** at the *peri*-position compared to that of the peralkylated derivatives.



These results clearly show the advantage of this zirconocene-mediated method. That is, zirconacyclopentadienes could be efficiently used for the naphthalene cores. Different substitutents could be introduced in the naphthalene by changing the zirconacyclopentadines. For example, when tetraethylzirconacyclopentadiene **1a** prepared from 3-hexyne and Cp_2ZrBu_2 coupled with 1,2-diiodo-3,4,5,6-tetramethylbenzene (**6a**), mixed methyl- and ethyl-substituted naphthalenes **7a** could be obtained in good yield. In a similar way, ethyl- and phenyl-substituted naphthalene **7d** was also obtained in high yield. With the bicyclic zirconacycle **1e**, which was prepared from 3,9-dodecadiyne, the corresponding tetrahydroanthracene **7e** was formed. Furthermore, unsymmetrical zirconacycles can be easily prepared by a selective cyclization of two different alkynes with zirconocene as we reported previously.[7] So unsymmetrical zirconacycles **1f** and **1g** were used in this reaction to afford the naphthalene (**7f** and **7g**, respectively) with three different substituents. To the best of our knowledge, these persubstituted naphthalenes are unprecedented even though they have simple substitution patterns.

Figure 1 shows the result of X-ray crystallographical analysis of naphthalene **7d**. The naphthalene ring was twisted to release the steric repulsion as reported.[3] The

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[5] (a) Smith, L. I.; Guss, C. O. *J. Am. Chem. Soc.* **1940**, *62*, 2631−2635: (b) Marvell, E. N.; Webb, D. *J. Org. Chem.* **1962**, *27*, 4408−4412

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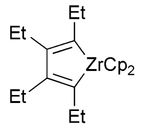
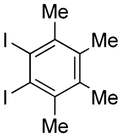
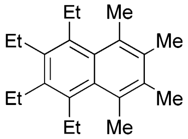
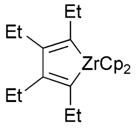
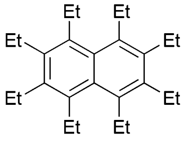
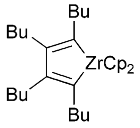
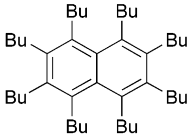
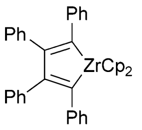
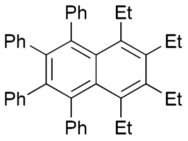
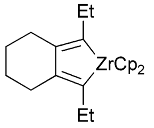
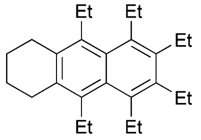
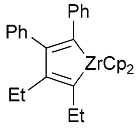
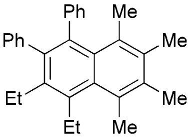
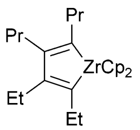
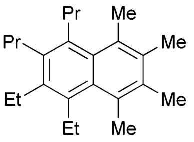
[7] (a) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444. (b) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687. See also ref 4c−e.

TABLE 1. Formation of Octasubstituted Naphthalenes

zirconacyclopentadienes[a]	diiodide	product	yield / %
 **1a**	 **6a**[b]	 **7a**	62
 **1a**	**6b**	 **7b**	40
 **1c**	**6d**	 **7c**	40
 **1d**[c]	**6b**	 **7d**	75
 **1e**	**6b**	 **7e**	29
 **1f**	**6a**	 **7f**	53
 **1g**	**6a**	 **7g**	41

[a] Used in 2.0 equiv to **6** unless otherwise noted. [b] Prepared from the iodination of 1,2,3,4-tetramethylbenzene. [c] Used in 4.0 equiv to **6b**.

end-to-end twist angle of **7d** was 27°, which is in the range of the usual twist angle (20−30°) of octasubstituted naphthalenes.

In summary, we have reported an effective method to synthesize octasubstituted naphthalenes from four alkynes and a vinyl halide via zirconacyclopentadienes.

Experimental Section

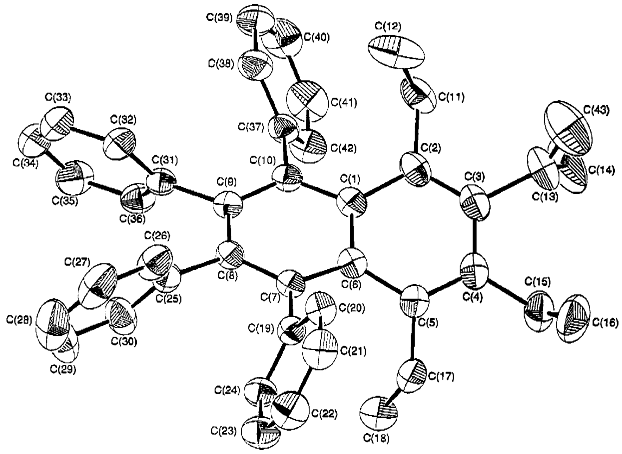


FIGURE 1. Perspective view of naphthalene **7d**. C(14) of an ethyl group is disordered.

Typical Procedure for Preparation of 1,2,3,4-Tetrasubstituted Benzene Derivatives. 1,2,3,4-Tetraethylbenzene (2b). To a THF (5 mL) solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) was added *n*-BuLi (1.59 M hexane solution, 1.26 mL, 2.0 mmol) at −78 °C, and the mixture was stirred for 1 h. 3-Hexyne (0.22 mL, 2.0 mmol) was added, and the mixture was warmed to room temperature. After 3 h, vinyl bromide (0.14 mL, 2.0 mmol) and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol), which was prepared from $NiCl_2(H_2O)_6$ and PPh_3,[8] were added to the resulting reaction mixture at room temperature. After stirring for 1 h, the mixture was quenched with 3 N HCl and extracted with hexane. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane as eluent) to afford the title compound as a colorless oil (91 mg, 48% isolated yield). NMR yield, 53%. All spectral data are consistent with the literature.[4i]

1,2,3,4-Tetrapropylbenzene (2c). 4-Octyne (40.0 mmol) was used as starting material. Colorless oil (2.54 g, 52% isolated yield). All spectral data are consistent with the literature.[4i]

1,2,3,4-Tetrabutylbenzene (2d). 5-Decyne (20.0 mmol) was used as starting material in this case. Colorless oil (1.55 g, isolated yield 55%). ^1H NMR ($CDCl_3$, Me_4Si): δ 1.00 (t, $J = 7.5$ Hz, 6H), 1.03 (t, $J = 6.9$ Hz, 6H), 1.40−1.66 (m, 16H), 2.58−2.66 (m, 8H), 6.98 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.0, 23.1, 23.5, 28.8, 32.8, 33.6, 33.9, 126.7, 138.4, 138.6. HRMS: calcd for $C_{22}H_{38}$ 302.2973, found 302.2964.

Typical Reaction Procedure for Iodination of 1,2,3,4-Tetraalkylbenzenes.[6] Preparation of 5,6-Diiodo-1,2,3,4-tetraethylbenzene (6b). 1,2,3,4-Tetraethylbenzene **2b** (1.90 g, 10.0 mmol) was dissolved in 80% acetic acid (50 mL) and added with 10 mL of concentrated sulfuric acid, iodine (10.0 g, 39.0 mmol), and periodic acid (3.89 g, 17.0 mmol). The mixture was rapidly stirred and heated at 70−80 °C for 1 h. Saturated aqueous solution of sodium hydrogensulfite was added to remove an excess of iodine. The white precipitate was collected by filtration and purified by recrystallization from ethanol to afford the title compound as a colorless solid (3.80 g, 81% isolated yield). All data are consistent with the literature.[6]

1,2-Diiodo-3,4,5,6-tetrapropylbenzene (6c). 1,2,3,4-Tetrapropylbenzene **2c** (5.0 mmol) was used as starting material. Recrystallization from ethanol gave the title compound as a colorless solid (1.37 g, 55% isolated yield). ^1H NMR ($CDCl_3$, Me_4Si): δ 1.03 (t, $J = 7.3$ Hz, 6H), 1.04 (t, $J = 7.3$ Hz, 6H), 1.45−1.58 (m, 8H), 2.54−2.58 (m, 4H), 2.93−3.00 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.50, 15.0, 23.1, 24.6, 33.4, 45.1, 116.1, 140.1, 144.4. HRMS calcd for $C_{18}H_{28}I_2$ 498.0269, found 498.0281. Anal. Calcd for $C_{18}H_{28}I_2$: C, 43.39; H, 5.66; I, 50.94. Found: C, 43.58; H, 5.64; I, 50.77.

1,2-Diiodo-3,4,5,6-Tetrabutylbenzene (6d). 1,2,3,4-Tetrabutylbenzene **2d** (3.0 mmol) was used as starting material.

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[8] (a) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719. (b) Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 501. (c) Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, *83*, 344.

Recrystallization from ethanol gave the title compound as a colorless solid (1.15 g, 69%). ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.98 (t, J = 6.9 Hz, 12H), 1.45−1.57 (m, 16H), 2.59 (t, J = 7.9 Hz, 4H), 2.98 (t, J = 8.0 Hz, 4H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 13.8, 13.9, 23.1, 23.4, 30.8, 31.8, 33.3, 42.7, 116.0, 140.1, 144.4. HRMS calcd for $C_{22}H_{36}I_2$ 554.0906, found 554.0885. Anal. Calcd for $C_{22}H_{36}I_2$: C, 47.67; H, 6.55; I, 45.79. Found: C, 47.45; H, 6.32; I, 45.84.

Representative Procedure for Coupling Reaction of Zirconacyclopentadienes 1′ and 1,2,3,4-Tetraalkyl-5,6-diiodobenzenes 6. Synthesis of 1,2,3,4-tetraethyl-5,6,7,8-tetraphenylnaphthalene (7d). To a solution of Cp$_2$ZrCl$_2$ (584 mg, 2.0 mmol) in THF (10 mL) was added *n*-butyllithium (1.59 M in hexane solution, 2.5 mL, 4.0 mmol) at −78 °C. After the mixture stirred for 1 h at the same temperature, diphenylacetylene (712 mg, 4.0 mmol) was added, and the reaction mixture was warmed to room temperature for 3 h. Then copper(I) chloride (416 mg, 4.2 mmol), DMPU (0.73 mL, 6.0 mmol), and 1,2,3,4-tetraethyl-5,6-diiodobenzene (**6b**) (221 mg, 0.5 mmol) were added and stirred at 50 °C for 3 h. After usual workup, the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 99/1) to afford the title compound (203 mg, 75% isolated yield) as a colorless solid. Single crystals suitable for X-ray structural analysis were prepared by crystallization from AcOEt/hexane. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.68 (t, J = 7.3 Hz, 6H), 1.20 (t, J = 7.4 Hz, 6H), 2.33 (q, J = 7.3 Hz, 4H), 2.74 (q, J = 7.4 Hz, 4H), 6.59−6.62 (m, 4H), 6.77−6.79 (m, 6H), 6.99−7.04 (m, 10H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 15.9, 16.3, 22.7, 23.1, 124.6, 125.6, 126.2, 126.9, 131.4, 131.5, 132.7, 136.4, 136.7, 137.4, 139.2, 141.2, 143.6. HRMS calcd for $C_{42}H_{40}$ 544.3130, found 544.3132. Anal. Calcd for $C_{42}H_{40}$: C, 92.60; H, 7.40. Found: C, 92.74; H, 7.31.

5,6,7,8-Tetraethyl-1,2,3,4-tetramethylnaphthalene (7a). Zirconacycle **1a** was prepared from Cp$_2$ZrCl$_2$ (584 mg, 2.0 mmol), 3-hexyne (454.4 μL, 4.0 mmol), and *n*-BuLi (1.59 M in hexane solution, 2.5 mL, 4.0 mmol). 1,2-Diiodo-3,4,5,6-tetramethylbenzene (**6a**) (386 mg, 1.0 mmol) was used as the starting material. Isolated yield 62%, GC yield 70%, white solid. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 1.15 (t, J = 7.5 Hz, 6H), 1.20 (t, J = 7.5 Hz, 6H), 2.32 (s, 6H), 2.53 (s, 6H), 2.81 (q, J = 7.5 Hz, 4H), 2.97 (q, J = 7.5 Hz, 4H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 15.9, 16.8, 17.0, 21.5, 22.2, 24.5, 128.4, 132.0, 134.5, 134.7, 137.2. HRMS calcd for $C_{22}H_{32}$ 296.2504, found 296.2506

1,2,3,4,5,6,7,8-Octaethylnaphthlene (7b). Zirconacycle **1a** was prepared from Cp$_2$ZrCl$_2$ (584 mg, 2.0 mmol), 3-hexyne (454.4 μL, 4.0 mmol), and *n*-BuLi (1.59 M in hexane solution, 2.5 mL, 4.0 mmol). 1,2-Diiodo-3,4,5,6-tetraethylbenzene (**6b**) (442 mg, 1.0 mmol) was used as starting material. Isolated yield 52%, white solid. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 1.14 (t, J = 7.3 Hz, 12H), 1.17 (t, J = 7.3 Hz, 12H), 2.78 (q, J = 7.3 Hz, 8H), 2.96 (q, J = 7.3 Hz, 8H). ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 15.9, 16.5, 22.3, 24.3, 134.1, 134.8, 136.5. HRMS calcd for $C_{26}H_{40}$ 352.3130, found 352.3131. Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.41; H, 11.58.

1,2,3,4,5,6,7,8-Octabutylnaphthalene (7c). Zirconacycle **1c** was prepared from Cp$_2$ZrCl$_2$ (584 mg, 2.0 mmol), 5-Decyne (718 μL, 4.0 mmol), and *n*-BuLi (1.59 M in hexane, 2.5 mL, 4.0 mmol). 1,2-Diiodo-3,4,5,6-tetrabutylbenzene **6d** (554 mg, 1.0 mmol) was used as the coupling partner. Isolated yield 40%, GC yield 52%, colorless oil. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.81 (t, J = 7.2 Hz, 12H), 0.99 (t, J = 6.9 Hz, 12H), 1.11−1.23 (m, 8H), 1.26−1.36 (m, 8H), 1.41−1.57 (m, 16H), 2.66 (t, J = 7.5 Hz, 8H), 2.89 (t, J = 7.5 Hz, 8H). ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14.0, 23.1, 23.5, 29.5, 31.4, 33.9, 34.0, 133.3, 133.7, 135.0. HRMS calcd for $C_{42}H_{72}$ 576.5634, found 576.5641.

1,2,3,4,9,10-Hexaethyl-6,7,8,9-tetrahydroanthracene (7e). Zirconacycle **1e** was prepared from Cp$_2$ZrCl$_2$ (584 mg, 2.0 mmol), 3,9-dodecadiyne (391 μL, 2.0 mmol), and *n*-BuLi (1.59 M in hexane, 2.5 mL, 4.0 mmol). 1,2-Diiodo-3,4,5,6-tetraethylbenzene (**6b**) (442 mg, 1.0 mmol) was used as the coupling partner. Isolated yield 30%, GC yield 50%, white solid. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 1.07 (t, J = 7.5 Hz, 6H), 1.15 (t, J = 7.2 Hz, 6H), 1.16 (t, J = 7.5 Hz, 6H), 1.74, (br, 4H), 2.73 (q, J = 7.5 Hz, 4H), 2.77-(br, 4H), 2.83(q, J = 6.9 Hz, 4H), 2.85(q, J = 7.5 Hz, 4H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 14.9, 15.8, 16.8, 22.2, 23.4, 24.3, 24.5, 27.4, 132.7, 134.1, 134.3, 134.6, 136.9. HRMS calcd for $C_{26}H_{38}$ 350.2973, found 350.2964.

5,6-Diethyl-1,2,3,4-tetramethyl-7,8-diphenylnaphthalene (7f). To a solution of Cp$_2$ZrCl$_2$ (643.1 mg, 2.2 mmol) in THF (10 mL) was added ethylmagnesium bromide (4.4 mmol, 0.89 M in THF solution, 4.94 mL) at −78 °C. After 1 h of stirring at the same temperature, diphenylacetylene (356.5 mg, 2.0 mmol) was added, and the reaction mixture was stirred at 0 °C for 3 h. Then 3-hexyne (0.227 mL, 2.0 mmol) was added, and the mixture was heated at 50 °C for 1 h. Copper(I) chloride (416 mg, 4.2 mmol), DMPU (0.73 mL, 6.0 mmol), and 1,2-diiodo-3,4,5,6-tetramethylbenzene **6a** (386 mg, 1.0 mmol) were added at room temperature. The mixture was stirred at 50 °C for 3 h. After usual workup, the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 99/1) to afford the title compound (208 mg, 53% isolated yield) as a white solid. GC yield 60%. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.97 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.70 (s, 3H), 2.22 (s, 3H), 2.39 (s, 3H), 2.64 (q, J = 7.5 Hz, 2H), 2.68 (s, 3H), 3.20 (q, J = 7.2 Hz, 2H), 6.87−7.14 (m, 10H). ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 15.77, 16.70, 17.05, 17.37, 20.83, 21.95, 23.73, 24.81, 125.06, 125.49, 126.70, 126.80, 128.19, 130.44, 131.02, 131.76, 132.20, 133.32, 133.83, 134.91, 135.70, 136.50, 137.13, 138.94, 141.73, 144.05. HRMS calcd for $C_{30}H_{32}$ 392.2504, found 392.2509.

5,6-Diethyl-1,2,3,4-tetramethyl-7,8-dipropylnaphthalene (7g). This reaction was carried out in the same way described above for **7f** using 4-octyne instead of diphenylacetylene. Isolated yield 41%, GC yield 59%, colorless oil. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.91 (t, J = 7.5 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.5 Hz, 3H), 1.19 (t, J = 7.5 Hz, 3H), 1.44−1.55 (m, 4H), 2.31 (s, 6H), 2.51 (s, 3H), 2.52 (s, 3H), 2.67−2.73 (m, 2H), 2.79 (q, J = 7.5 Hz, 2H), 2.86−2.91 (m, 2H), 2.96(q, J = 7.5 Hz, 2H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 14.90, 14.97, 15.85, 16.72, 16.94, 21.26, 21.49, 22.34, 24.45, 25.07, 25.43, 31.94, 34.28, 128.35, 128.37, 131.83, 131.88, 133.66, 134.51, 134.55, 135.95, 137.30. HRMS calcd for $C_{24}H_{36}$ 324.2817, found 324.2791

Supporting Information Available: X-ray crystallographic data of naphthalene **7d** and and NMR spectra for **2d**, **7a**, **7c**, **7e**, **7f**, and **7g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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