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1,2,3,4-Tetrasubstituted Cyclopentadienes and Their Applications for Metallocenes: Efficient Synthesis through Zirconocene- and CuCl-Mediated Intermolecular Coupling of Two Alkynes and One Diiodomethane

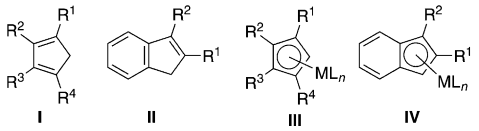
Weizhi Geng,[a] Chao Wang,[a] Jie Guang,[a] Wei Hao,[a] Wen-Xiong Zhang,[a] and Zhenfeng Xi*[a, b]

Abstract: 1,2,3,4-Tetrasubstituted cyclopentadienes and indene derivatives with identical or different substituents were obtained in good to excellent isolated yields through a zirconocene- and CuCl-mediated intermolecular coupling process. This synthetic procedure involved three organic partners, including one CH_2I_2, and two different or identical alkynes. Two alkynes or one diyne undergo Cp_2Zr^{II}-mediated ($Cp = \eta^5$-C_5H_5) pair-selective reductive coupling to afford the corresponding zirconacyclopentadiene derivatives, which react, in the presence of CuCl and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), with CH_2I_2 through intermolecular followed by intramolecular coupling to afford the cyclopentadiene derivatives. An application of the prepared tetrasubstituted cyclopentadiene derivatives was demonstrated by the facile synthesis of the corresponding zirconocene complexes [($^{4R}Cp)_2ZrCl_2$] and [($^{4R}Cp)_2ZrR'_2$] (R′ = Me, Et, or *n*Bu). The unique 1,2,3,4-tetrasubstituted cyclopentadiene ligands and the corresponding metallocenes are expected to have further applications in organometallic chemistry and organic synthesis.

Keywords: cyclopentadienyl ligands · metallocenes · pair-selective coupling · transmetallation · zirconium

Introduction

It is well known that the reactivity of metallocenes is significantly influenced by the substitution pattern on the cyclopentadienyl ligands.[1–4] For example, Chirik and co-workers investigated cyclopentadienyl-substituent effects in zirconocenes and realized the homogeneous transformation of dinitrogen into ammonia with a zirconocene containing η^5-C_5Me_4H ligands.[4] As a consequence, synthetic methods for multiply-substituted cyclopentadiene derivatives, which are mostly used as precursors for metallocene complexes, have always been in great demand.[5–9] Among the multiply-substituted cyclopentadienes,[5] 1,2,3,4-tetrasubstitution (**I**, Scheme 1) is unique, not only because this substitution pattern would increase the solubility and stability of the corresponding metallocenes,[6] but also because the remaining C–H bond could be functionalized more easily to give new ligands.[7] However, in contrast to the many reports in the literature for the synthesis of cyclopentadiene derivatives with other substitution patterns, reports on the synthesis of 1,2,3,4-tetrasubstituted compounds are rare.[8] The well-known tetrasubstituted cyclopentadiene is 1,2,3,4-tetramethylcyclopentadiene, which is synthesized from tetramethyl-2-cyclopenten-1-one by following the conventional reduction and dehydrogenation procedure.[9] As a consequence, knowledge of the properties and applications of metallocenes with 1,2,3,4-tetrasubstituted cyclopentadienyl ligands (**III**, Scheme 1) is very limited.[4,10]



I II III IV

Scheme 1. 1,2,3,4-Tetrasubstituted cyclopentadienes (**I**), related indene derivatives (**II**), and the corresponding metallocene complexes (**III** and **IV**; L = ligand).

In this article, we report an efficient one-pot synthesis of 1,2,3,4-tetrasubstituted cyclopentadiene derivatives through zirconocene- and CuCl-mediated three-component coupling of two identical or different alkynes with one CH_2I_2. Similarly, indene derivatives (**II**, Scheme 1) and tetrahydroindene derivatives could also be prepared in excellent yields after isolation from the corresponding benzyne or diyne with CH_2I_2. An application of the prepared 1,2,3,4-tetrasubstituted cyclopentadiene derivatives was demonstrated by the

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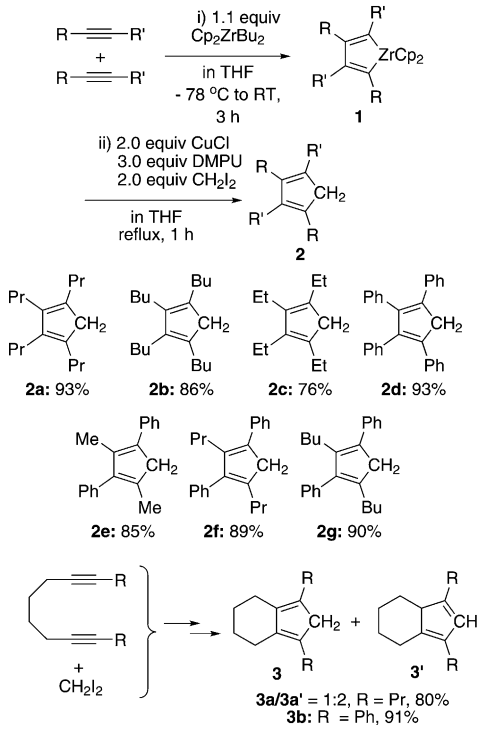
facile synthesis of the corresponding zirconocene complexes $[(^{4R}Cp)_2ZrCl_2]$. The corresponding dialkyl zirconocene complex could also be obtained efficiently.

Results and Discussion

One-pot synthesis of tetrasubstituted cyclopentadienes: Zirconacyclopentadienes **1** (Scheme 2) could be readily formed

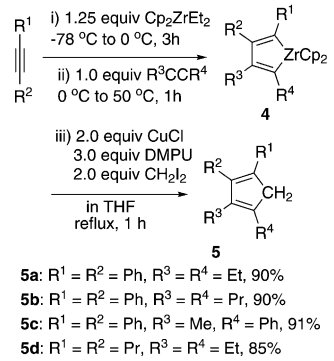


Scheme 2. One-pot synthesis of tetrasubstituted cyclopentadienes **2** and tetrahydroindenes **3** or **3′** from Cp_2Zr^{II}- and CuCl-mediated coupling of CH_2I_2 with two identical alkynes or one diyne. Cp = η^5-C_5H_5; THF = tetrahydrofuran; DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone.

in excellent yields through Cp_2Zr^{II}-mediated pair-selective coupling of two identical or two different alkynes, as reported by the groups of Takahashi, Negishi, and others.[11] Copper-mediated synthetic applications of zirconacylopentadienes **1** have been extensively studied by Takahashi and coworkers[12] and by others.[13] Addition of two equivalents of CuCl to the solution of **1** in THF that was formed in situ caused the gradual formation of an insoluble yellow precipitate. When three equivalents of DMPU were added to the mixture, the yellow powder dissolved to form a dark-brown solution. Two equivalents of CH_2I_2 were then added, and the solution was heated to 70 °C. The reaction was complete when the color of the solution changed to light yellow. After cooling of the mixture to room temperature, a normal workup afforded products **2** in excellent yields after isolation (Scheme 2).

Both tetraalkyl-substituted cyclopentadienes (**2a–c)** and the tetraphenyl-substituted product **2d** could be synthesized in excellent yields after isolation. If unsymmetric alkynes such as 1-phenyl-1-propyne, 1-phenyl-1-pentyne, and 1-phenyl-1-hexyne were used, the corresponding cyclopentadienes **2e–g** were obtained as the sole double-bond-positional isomers. Tetrahydroindene derivative **3a** and the double-bond-positional isomer **3a′** were obtained in 1:2 molar ratio in 80% combined yield after isolation from the diyne and CH_2I_2. However, the phenyl-substituted tetrahydroindene **3b** was obtained as a single isomer in 91% yield after isolation.

To investigate the scope of the reaction, we used two different alkynes, such as one diphenylacetylene and one alkyl-substituted alkyne. As shown in Scheme 3, under the same

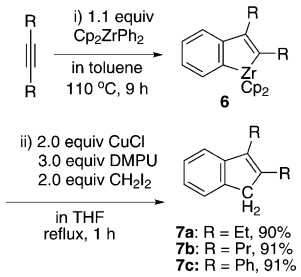


Scheme 3. One-pot synthesis of 1,2,3,4-tetrasubstituted cyclopentadienes **5** from Cp_2Zr^{II}- and CuCl-mediated coupling of CH_2I_2 with two different alkynes.

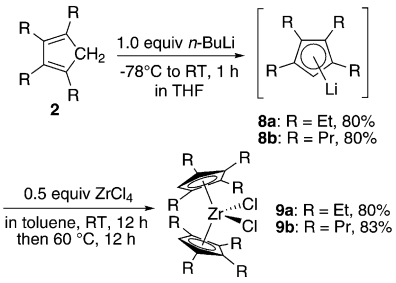
conditions as those described above, unsymmetric cyclopentadienes **5a** and **5b** were both obtained in 90% yield after isolation. When 1-phenyl-1-propyne was used, the corresponding cyclopentadiene **5c** was formed selectively in 91% yield after isolation. The cyclopentadiene derivative **5d**, formed from two aliphatic alkynes, was isolated in 85% yield. It should be pointed out that such unsymmetrically substituted cyclopentadienes are not available by other methods.

One-pot synthesis of substituted indene derivatives: The development of useful methods for the synthesis of substituted indenes has attracted much attention.[5a–c,g] After the successful development of the above one-pot preparation of cyclopentadiene derivatives, we applied this strategy to the preparation of substituted indenes. As illustrated in Scheme 4, treatment of $[Cp_2ZrPh_2]$ with one alkyne afforded zirconaindene **6** after the mixture had been stirred for 9 h at 110 °C in toluene.[14] The toluene was evaporated, and the solvent was changed to THF. After that, CuCl, DMPU, and CH_2I_2 were successively added into the reaction mixture. After the reaction mixture had been kept at 70 °C for 1 h, substituted indene derivatives **7a–c** were obtained.

Mechanistic aspects: As mentioned above, a relatively high temperature (70 °C) was required for the reaction between



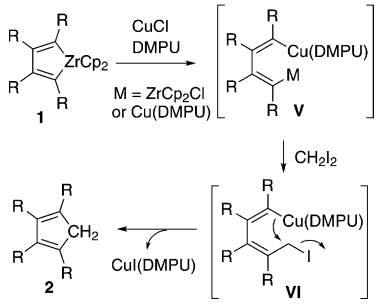
Scheme 4. One-pot synthesis of indene derivatives **7** from Cp_2Zr^{II}- and CuCl-mediated coupling of CH_2I_2 with one alkyne and one benzyne.



Scheme 6. Synthesis of zirconocene complexes **9** via Cp′Li compounds **8**.

1a and CH_2I_2. By contrast, if CH_2ICl was used in the reaction with **1a**, room temperature was enough to afford **2a** in 90% isolated yield, probably because of the higher reactivity of the C–I bond in CH_2ICl (48.8 kcal mol^{-1}) than that in CH_2I_2 (50.6 kcal mol^{-1}).[15]

Based on all of the above observations and related references,[12,13] a proposed reaction mechanism is given in Scheme 5. If a zirconacyclopentadiene **1** is treated with



Scheme 5. Proposed reaction mechanism.

CuCl, transmetalation of the diene moiety from zirconium to copper could proceed to form intermediate **V**. The effect of DMPU is remarkable: in addition to stabilizing intermediate **V**, DMPU could also obstruct the homocoupling of **V**. The high reactivity of the C–I bond is essential for the intermolecular coupling to generate the intermediate **VI** and for reducing the possibility of the homocoupling reaction. Finally, intramolecular coupling affords the products **2**.

Application of 1,2,3,4-tetrasubstituted cyclopentadienes for the synthesis of metallocenes: To demonstrate the synthetic utility of these 1,2,3,4-tetrasubstituted cyclopentadienes as ligands for the corresponding metallocenes and to learn the properties of such metallocenes, multiply-substituted zirconocene complexes **9** were synthesized from metal-exchange process via cyclopentadienyl lithium intermediates **8** (Scheme 6).[16] Thus, the cyclopentadienyl lithium reagents **8a**,**b** were firstly prepared in 80% yield from the reaction of compounds **2** and *n*BuLi. The formation of **8a**,**b** was confirmed by NMR spectroscopy. The chemical shifts of the cyclopentadienyl ring protons of **8a** ($\delta = 4.86$ ppm) and **8b** ($\delta = 5.17$ ppm) are shifted upfield compared with those for CpLi ($\delta = 5.64$ ppm) due to the electron-donating effect of the alkyl substituents. The signals for the Cp-ring carbon atoms connected to protons ($\delta = 96.7$ ppm in **8a**, $\delta =$ 98.7 ppm in **8b**) in the ^{13}C NMR spectra are also shifted upfield compared with those for CpLi ($\delta = 103.5$ ppm). The reaction of these lithio reagents with $ZrCl_4$ proceeded cleanly to afford the corresponding zirconocenes **9**. The structures of **9a** and **9b** were determined by single-crystal X-ray structural analysis (Figure 1 and Table 1).

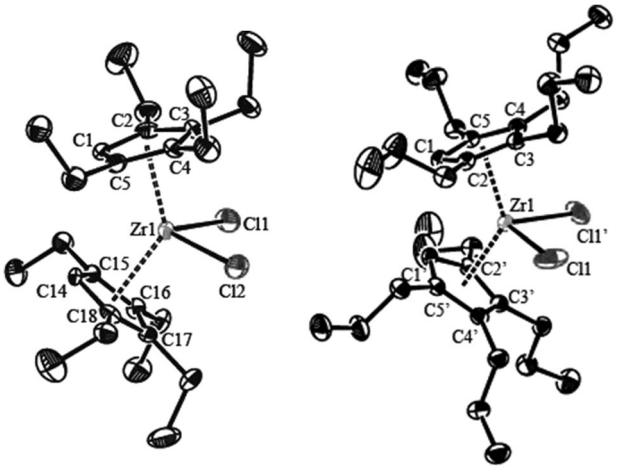


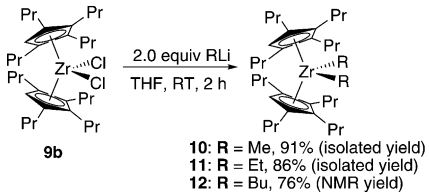
Figure 1. ORTEP drawings of **9a** (left) and **9b** (right) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Bond lengths and angles for **9a**,**b** and similar reported zirconocene compounds.

	$[Cp_2ZrCl_2]$	$[(C_5Me_4H)_2ZrCl_2]$	$[(C_5Et_4H)_2ZrCl_2]$ (**9a**)	$[(C_5Pr_4H)_2ZrCl_2]$ (**9b**)
Zr–Cl1 [Å]	2.437(2)	2.434(3)	2.4239(14)	2.4345(11)
Zr–Cl2(Cl1′) [Å]	2.433(18)	2.434(3)	2.437(12)	2.4345(11)
Zr–Cp(Cent) [Å]	2.194(7)	2.225(3)	2.234(4)	2.240(3)
Zr–Cp(av) [Å]	2.488(7)	2.531(6)	2.536(4)	2.546(3)
⧖ Cl1-Zr-Cl2(Cl1′) [°]	96.70(7)	97.61(9)	95.27(5)	96.41(8)
⧖ Cp(Cent)-Zr-Cp(Cent) [°]	129.20(17)	133.1(1)	131.46(16)	131.54(19)
⧖ Cp-Cp [°]	53.26(17)	53.7(4)	54.45(16)	55.31(19)

The molecular structures of **9a** and **9b** are shown in Figure 1. Both structures take a least-repulsion state. Selected bond lengths and angles are given in Table 1. The Cl-Zr-Cl angle is 95.27(5)° for **9a** and 96.41(8)° for **9b**, values that are similar to those for $[Cp_2ZrCl_2]$ and $[(C_5Me_4H)_2ZrCl_2]$.[17a,e] The Cent-Zr-Cent angle (Cent is the centroid of the Cp ring) of 131.5(2)° for **9a** and **9b** is smaller than the value of 133.1(1)° for $[(C_5Me_4H)_2ZrCl_2]$. However, the dihedral angle between the two Cp planes becomes larger as the size of the substituents on the Cp ring increases (H < Me < Et < Pr), which could be attributed to the steric effect of the substitutions. The Zr–Cl bond lengths of complexes **9** (2.431(3) Å for **9a** and 2.435(1) Å for **9b**) are in a normal range for zirconocene dichlorides. The distances from the Zr atom to the centriods of the cyclopentadienyl rings (2.234(4) Å for **9a** and 2.240(3) Å for **9b**) are larger than those (2.215–2.225 Å) found in analogous zirconocene compounds.[17]

Substituted dimethylzirconocene complexes $[Cp'_2ZrMe_2]$ have been proved to be useful as catalysts for olefin polymerization.[18,19] The zirconocene dichlorides **9** were further applied for the synthesis of the corresponding dimethylzirconocenes. As illustrated in Scheme 7, treatment of the zirconocene dichloride **9b** with two equivalents of MeLi generated the dimethylzirconocene complex **10** as a white solid in 91% yield after isolation. The structure was determined by single-crystal X-ray structural analysis (Figure 2). The Me-Zr-Me angle is 93.2(2)° and the Me–Zr bond length is 2.243(2) Å, values that are similar to those of dimethylzirconocenes.[18]



Scheme 7. Synthesis of dialkyl zirconocene complexes **10**–**12**.

It is known that dialkyl zirconocene complexes with β-hydrogen atoms, such as $[Cp_2ZrBu_2]$ and $[Cp_2ZrEt_2]$, are not stable. β-Hydride abstraction and reductive elimination readily take place to generate low-valent Cp_2Zr^{II} species,[20] which have been demonstrated to undergo an oxidative cyclization process with alkynes to afford zirconacyclopentadienes, such as the above-mentioned zirconacyclopentadienes **1**, **4**, and **6**.[11–13] However, if complex **9b**, instead of $[Cp_2ZrCl_2]$, was applied to the reaction process for the preparation of zirconacyclopentadienes **1**, **4**, and **6**, the corresponding zirconacyclopentadiene derivatives could not be formed, even at higher temperatures and with prolonged reaction times. NMR studies indicated that the corresponding diethylzirconocene complex **11** and dibutylzirconocene complex **12** (Scheme 7) did not undergo the commonly observed β-hydride abstraction and reductive elimination process.[21]

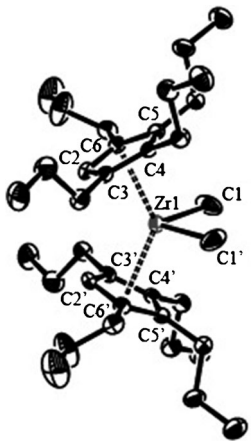


Figure 2. ORTEP drawings of **10** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths: Zr1–C1 2.242(3), Zr1–C1′ 2.242(2), Zr1–Cp(Cent) 2.255(2), C2–C3 1.410(3), C2–C6 1.402(3) Å; selected angles: C1-Zr1-C1′ 93.2(2), C3-C2-C6 109.6 (2), Cp(Cent)-Zr1-Cp(Cent) 133.10(17)°.

Obviously, the 1,2,3,4-tetrasubstitution pattern played a key role for the reactivity of the dialkyl zirconocene complexes.

Conclusion

An efficient one-pot synthesis of 1,2,3,4-tetrasubstituted cyclopentadienes was realized through zirconocene- and CuCl-mediated intermolecular coupling of two alkynes and diiodomethane. These 1,2,3,4-tetrasubstituted cyclopentadienes were successfully applied for the synthesis of the corresponding zirconocene derivatives. The unique 1,2,3,4-tetrasubstituted cyclopentadiene ligands and the corresponding metallocenes are expected to have further applications in organometallic chemistry and organic synthesis.

Experimental Section

General methods: All reactions were conducted under a slightly positive pressure of dry nitrogen by using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure that both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 solvent purification system and dried over fresh Na chips in the glovebox. *n*BuLi was obtained from Acros. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by using J. Young valve NMR tubes (Wilmad 528-JY). ^1H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) or a JEOL-AL300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer by using ESI (electrospray ionization). Microelemental analyses were performed on an Elemental Analyzer vario EL apparatus.

One-pot synthesis of tetrasubstituted cyclopentadienes from two alkynes and one CH_2I_2: *A typical procedure for the preparation of 1,2,3,4-tetrapropylcyclopentadiene (**2a**)*: *n*BuLi (4.8 mmol, 1.6 M, 3.0 mL) was added dropwise with a syringe to a THF (10 mL) solution of $[Cp_2ZrCl_2]$ (2.4 mmol, 700 mg) at −78 °C (dry ice/acetone) in a 20 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then, 4-octyne (4.0 mmol, 440 mg) was added, and the reaction mixture was warmed to 25 °C and stirred at this temperature for 3 h. The mixture was cooled to −78 °C, and CuCl (396 mg, 4.0 mmol), DMPU (768 mg, 6.0 mmol), and CH_2I_2 (1.072 g, 4.0 mmol) were added. The solution was heated to 70 °C and kept at this temperature for 1 h. The reaction mixture was then cooled down to room temperature and quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with diethyl ether three times, then washed with water and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was subjected to a SiO_2 chromatography column with hexane as the eluent.

*1,2,3,4-Tetrapropylcyclopentadiene (**2a**)*: Yellow oil; 93% yield after isolation (436 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87–0.97 (m, 12H, CH_3), 1.33–1.52 (m, 8H, CH_2), 2.14–2.28 (m, 8H, CH_2), 2.74 ppm (s, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.37 (2CH_3), 14.52 (2CH_3), 23.74 (4CH_2), 28.10 (2CH_2), 30.63 (2CH_2), 43.62 (CH_2), 138.14 (2 quat C), 140.20 ppm (2 quat C); HRMS: calcd for $C_{17}H_{31}$ $[M+H]^+$: 235.2420; found: 235.2422.

*1,2,3,4-Tetrabutylcyclopentadiene (**2b**)*: Yellow oil; 86% yield after isolation (499 mg); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.88–0.94 (m, 12H, CH_3), 1.25–1.51 (m, 16H, CH_2), 2.29–2.35 (m, 8H, CH_2), 2.71 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, C_6D_6): δ = 14.31 (2CH_3), 14.36 (2CH_3), 23.29 (2CH_2), 23.43 (2CH_2), 26.14 (2CH_2), 28.62 (2CH_2), 33.31 (2CH_2), 33.32 (2CH_2), 43.96 (CH_2), 137.98 (2 quat C), 140.51 ppm (2 quat C); HRMS: calcd for $C_{21}H_{39}$ $[M+H]^+$: 291.3046; found: 291.3048.

*1,2,3,4-Tetraethylcyclopentadiene (**2c**)*: Yellow oil; 76% yield after isolation (271 mg); the NMR spectra were consistent with the reported data.[8e]

*1,2,3,4-Tetraphenylcyclopentadiene (**2d**)*: White solid; 93% yield after isolation (688 mg); the NMR spectra are consistent with the reported data.[6c]

*1,3-Dimethyl-2,4-diphenylcyclopentadiene (**2e**)*: Yellow oil; 85% yield (418 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.40 (s, 2H, CH_2), 7.20–7.43 ppm (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.23 (CH_3), 14.40 (CH_3), 47.16 (CH_2), 125.56 (CH), 126.50 (CH), 127.52 (2CH), 128.01 (2CH), 128.21 (2CH), 129.40 (2CH), 136.52 (quat C), 136.64 (quat C), 137.80 (quat C), 138.17 (quat C), 138.31 (quat C), 143.96 ppm (quat C); HRMS: calcd for $C_{19}H_{19}$ $[M+H]^+$: 247.1481; found: 247.1486.

*1,3-Dipropyl-2,4-diphenylcyclopentadiene (**2f**)*: Yellow oil; 89% yield (554 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (t, J = 7.2 Hz, 3H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3), 1.14–1.24 (m, 2H, CH_2), 1.45–1.55 (m, 2H, CH_2), 2.28 (t, J = 8.0 Hz, 2H, CH_2), 2.38 (t, J = 8.0 Hz, 2H, CH_2), 3.37 (s, 2H, CH_2), 7.18–7.40 ppm (m, 10H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 (CH_3), 14.21 (CH_3), 22.36 (CH_2), 23.67 (CH_2), 29.02 (CH_2), 30.79 (CH_2), 45.13 (CH_2), 125.70 (CH), 126.47 (CH), 127.62 (2CH), 127.97 (2CH), 128.27 (2CH), 129.32 (2CH), 136.70 (quat C), 137.37 (quat C), 138.17 (quat C), 143.07 (quat C), 143.40 (quat C), 143.78 ppm (quat C); HRMS: calcd for $C_{23}H_{27}$ $[M+H]^+$: 303.2107; found: 303.2113.

*1,3-Dibutyl-2,4-diphenylcyclopentadiene (**2g**)*: Yellow oil; 90% yield (596 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (t, J = 7.2 Hz, 3H, CH_3), 0.85 (t, J = 7.2 Hz, 3H, CH_3), 1.03–1.06 (m, 2H, CH_2), 1.14–1.24 (m, 2H, CH_2), 1.45–1.67 (m, 4H, CH_2), 2.27 (t, J = 7.6 Hz, 2H, CH_2), 2.38 (t, J = 7.6 Hz, 2H, CH_2), 3.37 (s, 2H, CH), 7.18–7.40 ppm (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.56 (CH_3), 13.96 (CH_3), 22.55 (CH_2), 22.61 (CH_2), 26.39 (CH_2), 28.34 (CH_2), 31.02 (CH_2), 32.70 (CH_2), 45.00 (CH_2), 125.60 (CH), 126.40 (CH), 127.50 (2CH), 127.89 (2CH), 128.20 (2CH), 129.25 (2CH), 136.38 (quat C), 137.21 (quat C), 138.02 (quat C), 143.10 (quat C), 143.47 (quat C), 143.56 ppm (quat C); HRMS: calcd for $C_{25}H_{31}$ $[M+H]^+$: 331.2420; found: 331.2424.

One-pot synthesis of substituted tetrahydroindenes from one diyne and one CH_2I_2: *A typical procedure for the preparation of 1,3-dipropyl-4,5,6,7-tetrahydro-1H-indene (**3a**)*: The procedure was the same as that for the preparation of **2a** but instead of 4-octyne (4.0 mmol, 440 mg), tetradeca-4,10-diyne (2.0 mmol, 380 mg) was used.

*1,3-Dipropyl-4,5,6,7-tetrahydro-1H-indene (**3a**)*: Yellow oil; 2:1 mixture of positional double-bond isomers; 80% combined yield (327 mg); ^{1}H NMR of the mixture (300 MHz, C_6D_6): δ = 0.83–0.93 (m, 6H, CH_3), 1.04–2.63 (m, 17H, CH_2), 5.16–5.40 ppm (m, 1H, CH); ^{13}C NMR of the major isomer (75 MHz, C_6D_6): δ = 14.65 (CH_3), 14.83 (CH_3), 20.67 (CH_2), 22.42 (CH_2), 22.92 (CH_2), 22.98 (CH_2), 23.57 (CH_2), 25.22 (CH_2), 33.46 (CH), 36.55 (CH_2), 45.85(CH_2), 115.76 (CH), 136.08 (quat C), 146.06 (quat C), 146.39 ppm (quat C); HRMS: calcd for $C_{15}H_{25}$ $[M+H]^+$: 205.1951; found: 205.1949.

*1,3-Diphenyl-4,5,6,7-tetrahydro-2H-indene (**3b**)*: Yellow solid; 90% yield (490 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71–1.75 (m, 4H, CH_2), 2.79–2.81 (t, J = 3.0 Hz, 4H, CH_2), 3.74 (s, 2H, CH_2), 7.19–7.49 ppm (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.41 (2CH_2), 27.29 (2CH_2), 43.78 (CH_2), 125.71 (2CH), 126.97 (4CH), 128.36 (4CH), 136.39 (2 quat C), 137.21 (2 quat C), 141.23 ppm (2 quat C); HRMS: calcd for $C_{21}H_{21}$ $[M+H]^+$: 273.1638; found: 273.1640.

One-pot synthesis of unsymmetric tetrasubstituted cyclopentadienes from two different alkynes and one CH_2I_2: *A typical procedure for the preparation of 1,2-diethyl-3,4-diphenyl cyclopentadiene (**5a**)*: EtMgBr (4.8 mmol, 1.6 M, 3.0 mL) was added dropwise with a syringe to a THF (10 mL) solution of $[Cp_2ZrCl_2]$ (2.4 mmol, 700 mg) at −78 °C (dry ice/acetone) in a 20 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then, 1,2-diphenylethyne (2.0 mmol, 356 mg) was added, and the reaction mixture was warmed to 0 °C and stirred at this temperature for 3 h. 3-Hexyne (2.0 mmol, 164 mg) was added, and the reaction mixture was warmed to 25 °C and stirred at this temperature for 1 h. The mixture was then cooled to −78 °C, and CuCl (396 mg, 4.0 mmol), DMPU (768 mg, 6.0 mmol), and CH_2I_2 (1.072 g, 4.0 mmol) were added. The solution was heated to 70 °C and kept at this temperature for 1 h. The reaction mixture was then cooled down to room temperature and quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with diethyl ether three times, then washed with water and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was subjected to a SiO_2 chromatography column with hexane as the eluent.

*1,2-Diethyl-3,4-diphenylcyclopentadiene (**5a**)*: Yellow oil; 90% yield after isolation (493 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (t, J = 7.5 Hz, 3H, CH_3), 1.18 (t, J = 7.5 Hz, 3H, CH_3), 2.19 (q, J = 7.5 Hz, 2H, CH_2), 2.46 (q, J = 7.5 Hz, 2H, CH_2), 3.40 (s, 2H, CH_2), 7.99–7.54 ppm (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.52 (CH_3), 15.05 (CH_3), 18.77 (CH_2), 21.45 (CH_2), 44.12 (CH_2), 125.50 (CH), 126.71 (CH), 127.24 (2CH), 127.94 (2CH), 128.50 (2CH), 129.23 (2CH), 137.00 (quat C), 137.50 (quat C), 138.34 (quat C), 141.93 (quat C), 142.83 (quat C), 144.35 ppm (quat C); HRMS: calcd for $C_{21}H_{23}$ $[M+H]^+$: 275.1794; found: 275.1799.

*1,2-Dipropyl-3,4-diphenylcyclopentadiene (**5b**)*: Yellow oil; 90% yield after isolation (544 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (t, J = 7.3 Hz, 3H, CH_3), 0.86 (t, J = 7.5 Hz, 3H, CH_3), 1.14–1.24 (m, 2H, CH_2), 1.45–1.55 (m, 2H, CH_2), 2.28 (t, J = 7.7 Hz, 2H, CH_2), 2.38 (t, J = 8.0 Hz, 2H, CH_2), 3.37 (s, 2H, CH_2), 7.18–7.40 ppm (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.13 (CH_3), 14.39 (CH_3), 22.87 (CH_2), 23.70 (CH_2), 27.78 (CH_2), 30.69 (CH_2), 44.51 (CH_2), 125.46 (CH), 126.66 (CH), 127.20 (2CH), 127.93 (2CH), 128.45 (2CH), 129.17 (2CH), 136.94 (quat C), 137.35 (quat C), 138.36 (quat C), 141.02 (quat C), 141.73 (quat C), 144.41 ppm (quat C); HRMS: calcd for $C_{23}H_{27}$ $[M+H]^+$: 303.2107; found: 303.2113.

*2-Methyl-1,3,4-triphenylcyclopentadiene (**5c**)*: Yellow solid; 91% yield after isolation (560 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3H, CH_3), 3.85 (d, J = 1.4 Hz, 2H, CH_2), 7.08–7.48 ppm (m, 15H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.96 (CH_3), 45.17 (CH_2), 126.12 (2CH), 127.04 (CH), 127.47 (2CH), 127.73 (2CH), 128.10 (2CH), 128.38 (CH), 128.63 (2CH), 129.44 (2CH), 131.59 (CH), 136.49 (quat C), 137.48 (quat C), 137.54 (quat C), 138.69 (quat C), 139.36 (quat C), 139.48 (quat

C), 145.56 ppm (quat C); HRMS: calcd for $C_{24}H_{21}$ $[M+H]^+$: 309.1638; found: 309.1633.

*1,2-Diethyl-3,4-tripropylcyclopentadiene (**5d**)*: Yellow oil; 85% yield after isolation (350 mg); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.89$–1.10 (m, 12H, CH_3), 1.37–1.52 (m, 4H, CH_2), 2.16–2.37 (m, 8H, CH_2), 2.76 ppm (s, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.37$ (CH_3), 14.48 (CH_3), 15.12 (2CH_3), 18.76 (CH_2), 21.23 (CH_2), 23.78 (2CH_2), 28.05 (CH_2), 30.64 (CH_2), 43.11 (CH_2), 138.20 (quat C), 139.13 (quat C) 140.03 (quat C), 141.17 ppm (quat C); HRMS: calcd for $C_{15}H_{27}$ $[M+H]^+$: 207.2107; found: 207.2110.

One-pot synthesis of substituted indene derivatives from one alkyne and one CH_2I_2: *A typical procedure for the preparation of 2,3-diethyl-1H-indene (**7a**)*: PhLi (2.0 mmol, 2.0 M, 2.0 mL) was added dropwise with a syringe to a toluene (10 mL) solution of $[Cp_2ZrCl_2]$ (2.0 mmol, 584 mg) at −78 °C (dry ice/acetone) in a 20 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at 25 °C for 2 h. 3-Hexyne (2.0 mmol, 164 mg) was added, and the reaction mixture was warmed to 110 °C and stirred at this temperature for 9 h. The mixture was cooled to room temperature, and the solvent was changed to THF. This solution was cooled to −78 °C, and CuCl (396 mg, 4.0 mmol), DMPU (768 mg, 6.0 mmol), and CH_2I_2 (1.072 g, 4.0 mmol) were added. The solution was heated to 70 °C and kept at this temperature for 1 h. The reaction mixture was then cooled to room temperature and quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with diethyl ether three times, then washed with water and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was subjected to a SiO_2 chromatography column with hexane as the eluent.

*2,3-Diethyl-1H-indene (**7a**)*: Yellow oil; 90% yield after isolation (310 mg); the NMR spectra are consistent with the reported data.[5h]

*2,3-Dipropyl-1H-indene (**7b**)*: Yellow oil; 91% yield after isolation (362 mg); the NMR spectra are consistent with the reported data.[5h]

*2,3-Diphenyl-1H-indene (**7c**)*: Yellow solid; 91% yield after isolation (488 mg); the NMR spectra are consistent with the reported data.[5h]

Synthesis of tetrasubstituted cyclopentadienyl lithium: *A typical procedure for the preparation of 1,2,3,4-tetraethylcyclopentadienyl lithium (**8a**)*: *n*BuLi (10.0 mmol, 1.6 M, 6.25 mL) was added dropwise with a syringe to a THF (20 mL) solution of **2c** (10.0 mmol, 1.78 g) at −78 °C (dry ice/acetone) in a 50 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h, then warmed to 25 °C and stirred at this temperature for 3 h. THF was removed under vacuum, and hexane was added. The produced lithium salt was isolated by filtration to give **8a** as a white precipitate.

*1,2,3,4-Tetraethylcyclopentadienyl lithium (**8a**)*: White solid; 80% yield after isolation (1.47 g); ^{1}H NMR (400 MHz, C_4D_8O): $\delta=0.85$ (t, $J=$ 7.4 Hz, 6H, CH_3), 0.97 (t, $J=7.4$ Hz, 6H, CH_3), 2.14–2.24 (m, 8H, CH_2), 4.86 ppm (s, 1H, CH); ^{13}C NMR (100 MHz, C_4D_8O): $\delta=16.72$ (2CH_3), 18.45 (2CH_3), 19.65 (2CH_2), 21.24 (2CH_2), 96.71 (CH), 114.14 (2 quat C), 114.49 ppm (2 quat C); elemental analysis: calcd (%) for $C_{13}H_{21}Li$: C 84.74, H 11.49; found: C 84.59, H 11.62.

*1,2,3,4-Tetrapropylcyclopentadienyl lithium (**8b**)*: White solid; 80% yield after isolation (1.93 g); ^{1}H NMR (300 MHz, C_4D_8O): $\delta=0.87$–0.93 (m, 12H, CH_3), 1.31–1.55 (m, 8H, CH_2), 2.30–2.36 (m, 8H, CH_2), 5.17 ppm (s, 1H, CH); ^{13}C NMR (75 MHz, C_4D_8O): $\delta=15.11$ (2CH_3), 15.14 (2CH_3), 26.28 (2CH_2), 27.75 (2CH_2), 30.05 (2CH_2), 31.66 (2CH_2), 98.71 (CH), 113.39 (2 quat C), 113.79 ppm (2 quat C); elemental analysis: calcd (%) for $C_{17}H_{29}Li$: C 84.95, H 12.16; found: C 84.77, H 12.31.

Synthesis of tetrasubstituted zirconocene complexes: *A typical procedure for the preparation of bis(1,2,3,4-tetraethylcyclopentadienyl) zirconium dichloride (**9a**)*: $ZrCl_4$ (4.0 mmol, 924 mg) was added to a toluene (20 mL) solution of **8a** (8.0 mmol, 1.47 g) at room temperature in a 50 mL Schlenk tube under an N_2 atmosphere. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h, then warmed to 60 °C and stirred at this temperature for 12 h. The LiCl salt was removed by filtration, and the filtrate was dried out under vacuum to give product **9a** as a white solid.

*Bis(1,2,3,4-tetraethylcyclopentadienyl) zirconium dichloride (**9a**)*: White solid; 85% yield after isolation (1.48 g); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.07–1.15 (m, 24H, CH_3), 2.35–2.57 (m, 16H, CH_2), 5.68 ppm (s, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=15.26$ (4CH_3), 16.18 (4CH_3), 20.23 (4CH_2), 21.89 (4CH_2), 107.14 (2CH), 129.13 (4 quat C), 132.84 ppm (4 quat C); elemental analysis: calcd (%) for $C_{26}H_{42}Cl_2Zr$: C 60.43, H 8.19; found: C 60.55, H 8.08.

*Bis(1,2,3,4-tetrapropylcyclopentadienyl) zirconium dichloride (**9b**)*: White solid; 80% yield after isolation (2.0 g); ^{1}H NMR (300 MHz, C_4D_8O): $\delta=$ 0.93–1.02 (m, 24H, CH_3), 1.41–1.54 (m, 16H, CH_2), 2.19–2.43 (m, 16H, CH_2), 5.85 ppm (s, 2H, CH); ^{13}C NMR (75 MHz, C_4D_8O): $\delta=14.50$ (4CH_3), 15.24 (4CH_3), 25.33 (4CH_2), 26.09 (4CH_2), 30.77 (4CH_2), 31.60 (4CH_2), 109.29 (2CH), 127.45 (4 quat C), 132.62 ppm (4 quat C); elemental analysis: calcd (%) for $C_{34}H_{58}Cl_2Zr$: C 64.93, H 9.29; found: C 64.81, H 9.18.

A typical procedure for dimethylzirconocene complex 10: MeLi (1.0 mmol, 1.0 M, 1.0 mL) was added with a syringe to a THF (10 mL) solution of **9b** (0.5 mmol, 313 mg) at room temperature in a 20 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h, and the solvent was removed under vacuum. The residue was extracted with hexane, and the LiCl salt was removed by filtration. The filtrate was dried out under vacuum to give product **10** as a white solid. Similarly, diethylzirconocene **11** and dibutylzirconocene **12** were prepared from EtLi and *n*BuLi, respectively.

*Dimethyl bis(1,2,3,4-tetrapropylcyclopentadienyl) zirconium (**10**)*: White solid; 91% yield after isolation (267 mg); ^{1}H NMR (300 MHz, C_4D_8O): $\delta=-0.94$ (s, 6H, CH_3), 0.94 (t, $J=7.2$ Hz, 12H, CH_3), 1.02 (t, $J=7.2$ Hz, 12H, CH_3), 1.40–1.60 (m, 16H, CH_2), 1.89–1.99 (m, 4H, CH_2), 2.20–2.38 (m, 12H, CH_2), 5.00 ppm (s, 2H, CH); ^{13}C NMR (75 MHz, C_4D_8O): $\delta=$ 14.66 (4CH_3), 15.33 (4CH_3), 26.02 (4CH_2), 26.16 (4CH_2), 30.54 (4CH_2), 31.02 (4CH_2), 35.23 (2CH_3), 104.55 (2CH), 122.59 (4 quat C), 125.09 ppm (4 quat C); elemental analysis: calcd (%) for $C_{36}H_{64}Zr$: C 73.52, H 10.97; found: C 73.37, H 10.77.

*Diethyl bis(1,2,3,4-tetrapropylcyclopentadienyl) zirconium (**11**)*: Yellow solid; 86% yield after isolation (106 mg, 0.2 mmol scale); ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.87$–1.00 (m, 30H, CH_3), 1.54–1.62 (m, 20H, CH_2), 2.07–2.14 (m, 2H, CH_2), 2.18–2.23 (m, 2H, CH_2), 2.37–2.50 (m, 4H, CH_2), 2.60–2.78 (m, 8H, CH_2), 5.51 ppm (s, 2H, CH); ^{13}C NMR (100 MHz, C_6D_6): $\delta=14.34$ (4CH_3), 15.10 (4CH_3), 18.60 (2CH_3), 25.26 (4CH_2), 25.79 (4CH_2), 29.58 (4CH_2), 30.55 (4CH_2), 46.56 (2CH_2), 107.08 (2CH), 123.43 (4 quat C), 124.24 ppm (4 quat C).

*Dibutyl bis(1,2,3,4-tetrapropylcyclopentadienyl) zirconium (**12**)*: Yellow oil; NMR yield: 76%; ^{1}H NMR (400 MHz, C_4D_8O): $\delta=1.05$–1.13 (m, 30H, CH_3), 1.41–1.63 (m, 24H, CH_2), 2.10–2.52 (m, 20H, CH_2), 5.60 ppm (s, 2H, CH); ^{13}C NMR (100 MHz, C_4D_8O): $\delta=14.10$ (2CH_3), 14.45 (4CH_3), 15.20 (4CH_3), 25.11 (2CH_3), 26.38 (4CH_2), 29.99 (2CH_2), 30.76 (4CH_2), 31.59 (4CH_2), 36.54 (2CH_2), 54.44 (2CH_2), 107.75 (2CH), 123.98 (4 quat C), 128.47 ppm (4 quat C).

X-ray crystallographic studies: Single crystals of **9a**, **9b**, and **10** suitable for X-ray analysis were grown. The crystals were manipulated under a nitrogen atmosphere and were sealed in a thin-walled glass capillary. Data collections were performed at 25 °C on a Rigaku Raxis Rapid IP diffractometer by using graphite-monochromated Mo Kα radiation ($l=$ 0.71073 Å). The determination of crystal class and unit cell parameters was carried out with the Rapid-Auto (Rigaku 2000) program package. The raw frame data were processed by using the Crystal Structure (Rigaku/MSC 2000) software to yield the reflection data file. The structures were solved by use of the SHELXTL program.[19] Refinement was performed on *F*2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and processing parameters for compounds **9a**, **9b** and **10** are summarized in the Supporting Information. CCDC 921086 (**9a**), 921085 (**9b**), and 921084 (**10**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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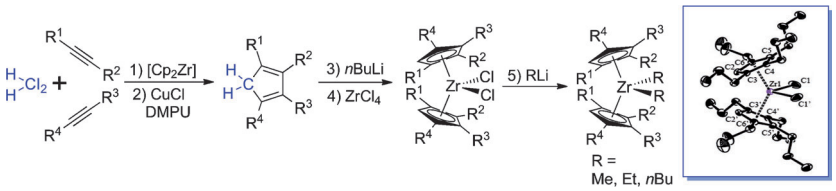

Ringing in the changes: A one-pot synthesis of 1,2,3,4-tetrasubstituted cyclopentadienes by zirconocene- and CuCl-mediated intermolecular coupling of two alkynes and diiodomethane (see scheme; Cp = η^5-C_5H_5; DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) gave products that were successfully applied for the synthesis of corresponding zirconocene derivatives.

Synthetic Methods

*W. Geng, C. Wang, J. Guang, W. Hao, W.-X. Zhang, Z. Xi** ..... ▮▮▮▮–▮▮▮▮

1,2,3,4-Tetrasubstituted Cyclopentadienes and Their Applications for Metallocenes: Efficient Synthesis through Zirconocene- and CuCl-Mediated Intermolecular Coupling of Two Alkynes and One Diiodomethane