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A Controllable Synthesis of Homoallyl Ketones and Multiply Substituted Cyclopentadienes by Direct Insertion of Aroyl Cyanides to Zirconacyclopentenes

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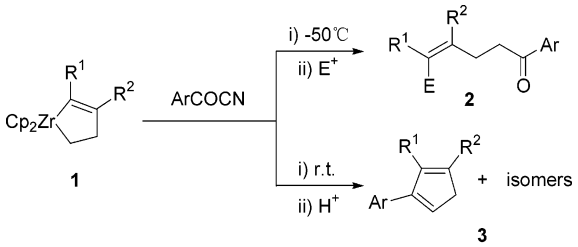
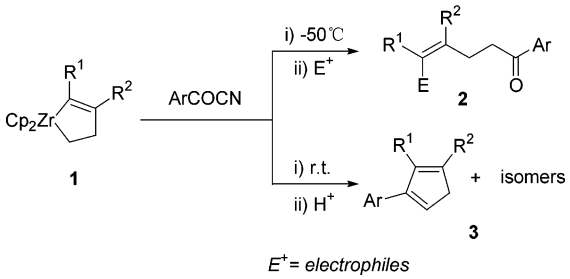


The direct reaction of aroyl cyanides with zirconacyclopentenes was achieved cleanly under controlled reaction conditions. This methodology provided an extremely efficient, one-pot, and high-yield route for the synthesis of homoallyl ketones when the reaction was carried out at −50 °C. Trapping of the zirconium intermediate by a variety of electrophiles afforded functionalized homoallyl ketones. Remarkably, the insertion reaction occurred with complete chemoselectivity, that means, the Zr−sp^3 carbon bond reacted preferentially, which is different from Cu-mediated elaboration of zirconacycles. Surprisingly, when the reaction was done at room temperature, 1,2,3-trisubstituted cyclopentadiene derivatives were readily formed in high yields. The direct insertion reaction of zirconacyclopentanes with acyl cyanides was also described. When bicyclic zirconacyclopentanes were used, cyclopentanol derivatives were obtained with high stereoselectivity.

Introduction

Over the past 20 years, synthetic organic transformations based on a wide variety of metallacycles have been extensively developed.[1] In this regard, zirconacycles, including zirconacyclopentadienes, -pentenes, and -pentanes, which are easily prepared by reductive coupling of unsaturated compounds such as alkynes and alkenes on a zirconocene equivalent, have been proved as efficient precursors for the selective transformation reactions.[2] The polarization of the carbon−zirconium bond is comparable to that of Grignard reagents; however, it is generally not reactive toward carbon electrophiles, possibly due to the steric hindrance caused by the bulky cyclopentadienyl ligands and the occupied coordination sites around the metal.[3] Much of the development of the chemistry of zirconacycles has therefore focused on indirect reaction pathways, i.e., through transmetalation

SCHEME 1



(1) For reviews, see: (a) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, p 741. (b) Cámpora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *193−195*, 207. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. (d) Mashima, K. *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 171. (e) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds; Pergamon Press Ltd.: Oxford, UK, 1991, Vol. 5, p 1129.

(2) For reviews, see: (a) Takahashi, T.; Xi, Z.; Hara, R. *Trends Organomet. Chem.* **1997**, *2*, 117. (b) Buchwald, S. L. *Science* **1993**, 261. (c) Kotora, M.; Xi, Z.; Takahashi, T. *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 958. (d) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755. (e) Takahashi, T.; Xi, Z.; Kotora, M. *Pure Appl. Chem.* **1998**, *2*, 515. (f) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591.

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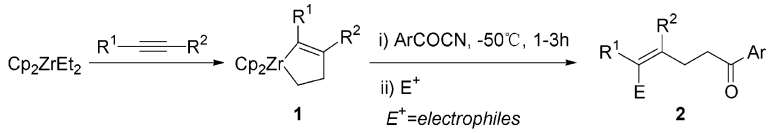
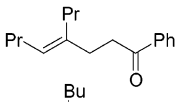
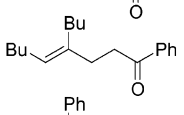
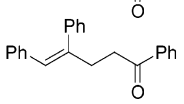
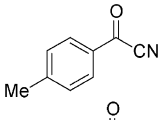
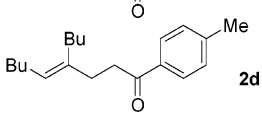
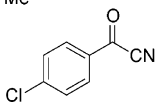
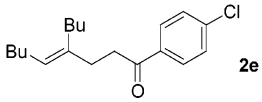
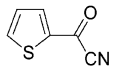
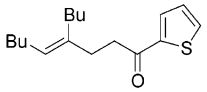
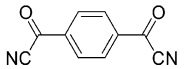
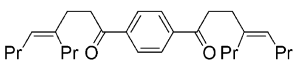
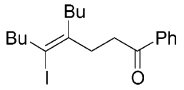
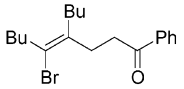
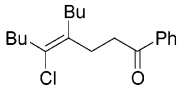
TABLE 1. Formation of Homoallyl Ketones by Direct Reaction of Acyl Cyanides with Zirconacyclopentenes



Alkyne	ArCOCN	Electrophile	Product		Yield[a]
Pr—≡—Pr	PhCOCN	HCl		**2a**[b]	81(74)
Bu—≡—Bu	PhCOCN	HCl		**2b**[b]	80(74)
Ph—≡—Ph	PhCOCN	HCl		**2c**	85(64)
Bu—≡—Bu		HCl		**2d**	90(84)
Bu—≡—Bu		HCl		**2e**	81(72)
Bu—≡—Bu		HCl		**2f**	75(67)
Pr—≡—Pr		HCl		**2g**	(49)
Bu—≡—Bu	PhCOCN	I_2		**2h**	96(68)[c]
Bu—≡—Bu	PhCOCN	Br_2		**2i**	95(86)[c]
Bu—≡—Bu	PhCOCN	NCS		**2j**	80(72)[c,d]

[a] GC yields, Isolated yields are given in parentheses. [b] Reference 5b,c. [c] 1.5 equiv of electrophile and 1 equiv of CuCl were used. [d] EtMgCl was used to prepare Cp_2ZrEt_2.

of the zirconium−carbon bond to other metal−carbon bonds such as Cu, Zn, Li, and Ni to increase the reactivity and achieve high yields.[3a,4] There were only a few reports of the direct reaction of zirconacycles with carbon electrophiles. Examples included the reaction with aldehydes,[5] 1,1-cycloaddition to propynoates,[6] and direct Michael addition to activated alkenes.[7] Nonetheless, these successful reactions indicated that the direct reaction with a suitable substrate might eventually be possible. In this paper, we describe the direct insertion of aroyl cyanides to zirconacycles followed by elimination of a cyano group. This reaction provides an efficient, controllable, and one-step preparation of homoallyl ketones and 1,2,3-trisubstituted cyclopentadiene derivatives in high yields (Scheme 1).

Results and Discussion

Formation of Homoallyl Ketones from the Reaction of Zirconacyclopentenes with Aroyl Cyanides.

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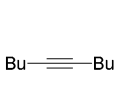
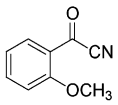
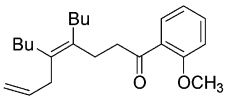
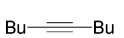
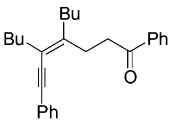
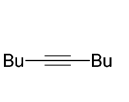
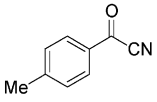
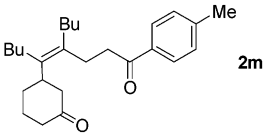
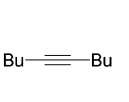
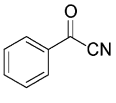
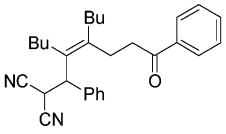
(4) For Cu, see: (a) Liu, Y.; Xi, C.; Hara, R.; Nakajima, K.; Yamazaki, A.; Kotora M.; Takahashi, T. *J. Org. Chem.* **2000**, *65*, 6951. (b) Lipshutz, B. M.; Wood, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 12625. (c) Liu, Y.; Shen, B.; Kotora, M.; Takahashi, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 949. (d) Lipshutz, B. H.; Wood, M. R.; Tirado, R. *J. Am. Chem. Soc.* **1995**, *117*, 6126. For Zn, see: (e) Lipshutz, B. H.; Wood, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 11689. (f) Duan, Z.; Nakajima, K.; Takahashi, T. *Chem. Commun.* **2001**, 1672. For Ni, see: (g) Hauske, J. R.; Dorff, P.; Julin, S.; Martinelli, G.; Bussolari, J. *Tetrahedron Lett.* **1992**, *33*, 3715. (h) Takahashi, T.; Tsai, F.; Li, Y.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059. For Li: see: (i) Seki, T.; Noguchi, Y.; Duan, Z.; Sun, W.; Takahashi, T. *Tetrahedron Lett.* **2004**, *45*, 9041. (j) Takahashi, T.; Huo, S.; Hara, R.; Noguchi, Y.; Nakajima, K.; Sun, W. *J. Am. Chem. Soc.* **1999**, *121*, 1094.

(5) (a) Copéret, C.; Negishi, E.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* **1994**, *35*, 695. (b) Zhao, C.; Yu, T.; Xi, Z. *Chem. Commun.* **2002**, 142. (c) Zhao, C.; Yan, J.; Xi, Z. *J. Org. Chem.* **2003**, *68*, 4355.

(6) Takahashi, T.; Sun, W.; Xi, C.; Kotora, M. *Chem. Commun.* **1997**, 2069.

(7) Liu, Y.; Shen, B.; Kotora, M.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2002**, *67*, 7019.

TABLE 2. Formation of Functionalized Homoallyl Ketones

Alkyne	ArCOCN	Electrophile	Product		Yield[a]
				**2k**	90(70)[b]
	PhCOCN			**2l**	90 (78)[c]
				**2m**	(52)[c]
				**2n**	(63)[c]

[a] GC yields. Isolated yields are given in parentheses. [b] 1 equiv of CuCl and 2 equiv of LiCl were used. [c] 1 equiv of CuCl was used.

It is known that zirconacyclopentene **1** is prepared by the reaction of an alkyne and $Cp_2Zr(CH_2{=}CH_2)$,[8] which is generated from Cp_2ZrCl_2 and 2 equiv of EtMgBr with high yields. Initially, acyl chlorides were chosen for the reaction with **1**. However, only a complicated reaction mixture was observed. Acyl cyanides are known to be more reactive acylating reagents than acid chlorides, since the adjacent cyano group enhances the reactivity of the carbonyl group.[9] It is also a safer and commercially available reagent. As we expected, acyl cyanides reacted smoothly with zirconacycle **1** to afford homoallyl ketones **2** in high yields after hydrolysis. Trapping of the zirconium intermediate by several electrophiles would provide functionalized homoallyl ketones. The reaction of **1a** (R^1 = Pr, R^2 = Pr) with 1.3 equiv of benzoyl cyanide at −50 °C for 1−3 h followed by treatment with 3 N HCl at the same temperature afforded 1-phenyl-4-propyl-oct-4-en-1-one (**2a**)[5b,c] in 81% yield. This result indicated that the reaction proceeded selectively at the Zr−sp^3 carbon bond. Double acylation product was not obtained even in the presence of an excess amount of ArCOCN. Chemoselectivity in this case is different from that of copper-mediated reactions of zirconacyclopentenes, where the Zr−sp^2 carbon bond was transmetalated with copper and reacted with electrophiles preferentially.[10] Recently, Xi et al. reported a novel synthesis of homoallyl ketones from zirconacyclopentenes and aldehydes via Oppenauer-type oxidation;[5b,c] in their work, an excess amount of aldehydes and Lewis acid was required. In our reaction, acyl cyanide reacted with zirconacycles directly and no additive was needed. The representative results are shown in Table 1. Functionalized acyl cyanides bearing a chlorine (81%) and a methyl (90%) or a heterocyclic group (75%) reacted with various zirconacycles, leading to the products **2d**−**f** in good to high yields. The reaction has also been accomplished starting from 1,4-disubstituted benzoyl cyanide, furnishing the phenyl-bridged product **2g** in 49% yield. Iodination of the reaction mixture of 2,3-dibutylzirconacyclopent-2-ene (**1b**) with benzoyl cyanide, using 1 equiv of iodine, gave iodinated product **2h** in 96% yield. Bromination or chlorination was also cleanly achieved by the reaction with Br_2 (95%) or NCS (80%).

To further investigate the reactivity of the zirconium intermediate we tested various carbon electrophiles to pursue C−C bond formation reactions under the optimized reaction conditions. As shown in Table 2, when employing allyl bromide or alkynyl bromide as a substrate, the reactions proceeded smoothly in the presence of 1 equiv of CuCl or CuCl/LiCl to afford the corresponding products **2k** and **2*l*** in 90% yields, respectively. The use of α,β-unsaturated compounds such as cyclohexenone or ylidenemalononitrile resulted in the formation of addition products **2m** and **2n** in moderate yields.

Formation of Cyclopentadiene Derivatives. The development of synthetic approaches to cyclopentadiene derivatives has attracted considerable attention due to their ability to function as important ligands for organometallic complexes.[11] Here we found that simply warming up the reaction mixture of zirconacycle **1** and acyl cyanide to room temperature, 1,2,3-trisubstituted cyclopentadienes **3**[10b] were formed immediately in high yields. The representative results are shown in Table 3. In most cases, the products **3** were obtained as a mixture of

(8) (a) Binger, P.; Mller, P.; Rufinsker, A.; Gabor, B.; Krger, C.; Betz, P. *Chem. Ber*. **1989**, *122*, 1035. (b) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett*. **1989**, 761. (c) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579.

(9) (a) Duplais, C.; Bures, F.; Sapountzis, L.; Korn, T. J.; Cahiez, G.; Knochel, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2968. (b) Hünig, R.; Schaller, *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 36.

(10) (a) Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 109. (b) Takahashi, T.; Xi, Z.; Kotora, M.; Xi, C. *Tetrahedron Lett.* **1996**, *37*, 7521.

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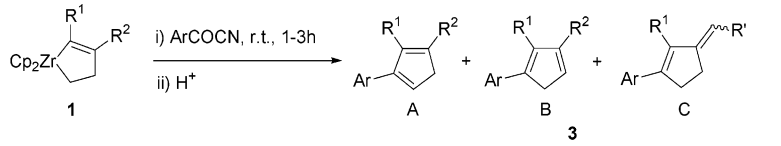
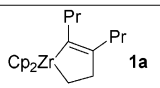
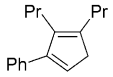
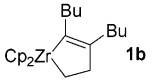
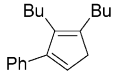
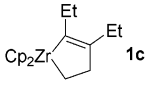
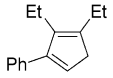
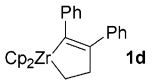
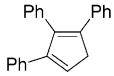
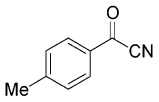
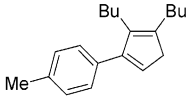
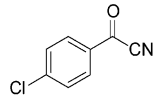
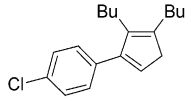
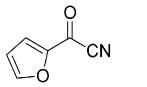
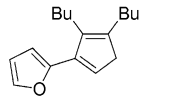
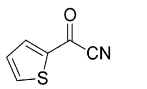
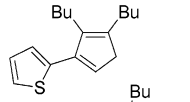
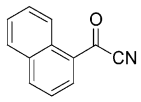
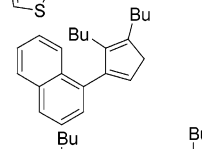
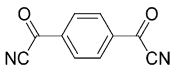
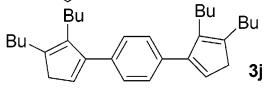
TABLE 3. Formation of Cyclopentadienes by Direct Reaction of Acyl Cyanides with Zirconacyclopentenes



Zirconacyclopentenes	ArCOCN	Product[a]	Ratio of isomers[b]	Yield[c]
 **1a**	PhCOCN	 **3a**	1:8:14	97(65)
 **1b**	PhCOCN	 **3b**	1:9:10	80(64)
 **1c**	PhCOCN	 **3c**	1:10:30	90(70)
 **1d**	PhCOCN	 **3d**	–	97(76)[d]
1b		 **3e**	1:6:34	89(61)
1b		 **3f**	1:7:7	80(58)
1b		 **3g**	0:1:10	74(57)
1b		 **3h**	0:1:3	98(72)
1b		 **3i**	1:3:2	(65)
1b		 **3j**	1:6:9	(56)

[a] Only cyclopentadiene was shown in the table. [b] The ratio is A:B:C or B:A:C, which was determined by NMR. [c] Combined GC yields. Isolated yields are given in parentheses. All the reactions were carried out at room temperature for 3h. [d] Only one isomer.

positional isomers of double bonds, whereas 1,2,3-triphenyl-substituted cyclopentadiene **3d** exists as a single isomer. It should be noted that one of the two double bonds in the ring isomerized to an exocyclic double bond in major isomers. This was confirmed by COSY NMR experiments and 2D heteronuclear multiple bond coherence (HMBC) technique of **3g**. The heterocycle groups were easily introduced to the cyclopentadienyl ring by employing heteroaromatic acyl cyanides. Interestingly, the 1,1′-bridged cyclopentadiene was readily prepared by this method, affording **3j** in 56% yield. This procedure represents a general, one-step and preparative route to multiply substituted cyclopentadienes from unactivated alkynes.

Reaction of Zirconacyclopentanes with Acyl Cyanides. To extend the scope of the title reaction, we also investigated the reaction of zirconacyclopentanes with acyl cyanides. Zirconacycle **4a** and **4b** were prepared by "pair"-selective ethyl−alkene coupling reactions of zirconocene−alkene complexes.[12] As shown in Figure 1, cyclopentene derivative **5** was obtained as a mixture of two isomers in 75% combined yield. When **4b** was treated

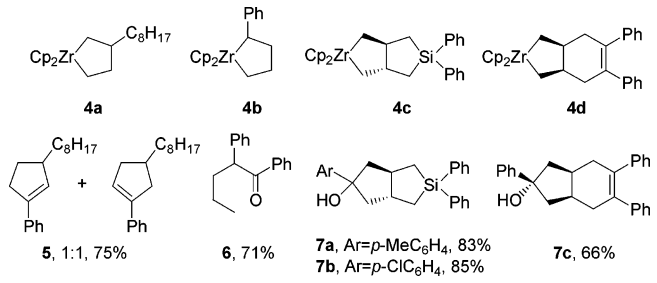
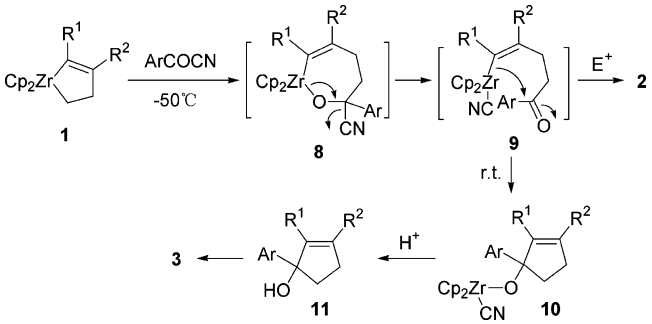


FIGURE 1. Direct reaction of acyl cyanides with zirconacyclopentanes.

(12) (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M. *J. Am. Chem. Soc.* **1991**, *113*, 6266. (b) Takahashi, T.; Kotora, M.; Kasai, K. *J. Chem. Soc., Chem. Commun.* **1994**, 2693.

SCHEME 2



with benzoyl cyanide, the sequential cyclization did not proceed due to steric factors. The acylation selectively occurred at the carbon that has a phenyl substituent, furnishing **6** in 71% yield. When bicyclic zirconacycle **4c** or **4d** reacted with acyl cyanide, cyclopentanols **7a**−**c** were formed and only one diastereoisomer were obtained in all cases. The stereochemistry of **7c** was deterimined by X-ray analysis and shown in the Supporting Informatiom.

Mechanistic Aspects. On the basis of the results obtained above, a plausible reaction mechanism is shown in Scheme 2. In the first step, insertion of acyl cyanide to **1** selectively occurred at the Zr−sp^3 carbon bond of zirconacycle to give **8**; this result is consistent with that reported for direct insertion of an aldehyde.[5] Complex **8** underwent β-elimination of a cyano group followed by nucleophilic attack of the zirconium compound to the carbonyl group at higher temperature to afford cyclopentadiene derivative **3** after hydrolysis. β-Elimination of the leaving group (halide or alkoxy group) from zirconacycles has been reported, which resulted in the carbozirconation products such as allylzirconation,[13] alkynylzirconation,[14] and vinylzirconation.[15] It should be noted that here the cyclization occurred without the use of any transmetalation reagents.

Conclusions

In summary, we have succeeded in developing an efficient, general, and one-pot procedure to synthesize homoallyl ketones and cyclopentadienes through direct insertion of acyl cyanide to zirconacycles. Remarkably, the insertion reaction occurs with complete chemoselectivity with respect to zirconacyclopentenes, which is different with Cu-mediated elaboration of zirconacycles. We are currently exploring the new synthetic potential of direct insertion reactions.

Experimental Section

A Typical Procedure for the Preparation of Homoallyl Ketone Product 2a. To a solution of Cp_2ZrCl_2 (0.365 g, 1.25 mmol) in THF (5 mL) was added EtMgBr (1.0 M THF solution, 2.5 mmol) at −50 °C. After the solution was stirred for 1 h at the same temperature, 4-octyne (0.11 g, 1.0 mmol) was added and the reaction mixture was warmed to 0 °C and stirred for 3 h. Benzoyl cyanide (0.17 g, 1.3 mmol) was added to the mixture at −50 °C and stirred at the same temperature for 2 h. The reaction mixture was quenched with 3 N HCl and extracted with diethyl ether. (**Caution**! Quench with HCl would generate HCN. All the work should be done in the hood.) The extract was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (ethyl acetate/petroleum ether: 1/30). A light-yellow liquid of homoallyl ketone **2a** (180 mg, 74%) was obtained.

The characterization data for products **2a** and **2b** were consistent with the published data.[5b,c]

(4*Z*)-1,4,5-Triphenylpent-4-en-1-one (2c): GC yield 85%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:30) afforded 200 mg (64%) of product as a white solid. Mp 83−84 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.91−2.96 (m, 2H), 2.99−3.05 (m, 2H), 6.51 (s, 1H), 6.90−6.94 (m, 2H), 7.00−7.05 (m, 3H), 7.15−7.19 (m, 2H), 7.22−7.29 (m, 3H), 7.32−7.37 (m, 2H), 7.43−7.48 (m, 1H), 7.83−7.86 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 34.9, 36.9, 126.2, 126.9, 127.0, 127.7, 127.7, 127.8, 128.4, 128.4, 128.5, 128.5, 128.9, 132.8, 136.6, 136.9, 140.2, 141.5, 199.3. IR (neat) 1687, 1597, 1447, 1204, 691 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{23}H_{20}O$ 312.1514, found 313.1592 [M + H]$^+$.

(4*E*)-4-Butyl-1-(*p*-tolyl)non-4-en-1-one (2d): GC yield 90%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:30) afforded 240 mg (84%) of product as a light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 6.6 Hz, 6H), 1.26−1.40 (m, 8H), 1.97−2.08 (m, 4H), 2.39 (s, 3H), 2.39−2.43 (m, 2H), 2.99−3.04 (m, 2H), 5.16 (t, J = 6.9 Hz, 1H), 7.23 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.9, 21.4, 22.3, 22.7, 27.3, 29.9, 30.6, 31.2, 32.1, 37.4, 125.2, 128.0, 129.0, 134.4, 137.9, 143.4, 199.6. HRMS (MALDI/DHB) calcd for $C_{20}H_{30}O$ 286.2297, found 287.2381 [M + H]$^+$.

(4*E*)-4-Butyl-1-(2-thienyl)non-4-en-1-one (2f): GC yield 75%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:30) afforded 186 mg (67%) of product as a light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.86−0.93 (m, 6H), 1.26−1.39 (m, 8H), 1.96−2.07 (m, 4H), 2.42 (t, J = 7.8 Hz, 2H), 2.95−3.01 (m, 2H), 5.16 (t, J = 7.2 Hz, 1H), 7.11 (dd, J = 3.9, 4.2 Hz, 1H), 7.61 (d, J = 4.8 Hz, 1H), 7.71 (d, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9, 13.9, 22.2, 22.6, 27.3, 29.8, 30.5, 31.5, 32.0, 38.3, 125.5, 127.9, 131.5, 133.2, 137.7, 144.3, 192.9. HRMS (MALDI/DHB) calcd for $C_{17}H_{26}OS$ 278.1704, found 279.1786 [M + H]$^+$.

(4*E*)-4-Propyl-1-[4-(4′*E*-4′-propyloct-4′-enoyl)phenyl]-oct-4-en-1-one (2g): Column chromatography on silica gel (ethyl acetate/petroleum ether 1:30) afforded 100 mg (49%) of product as a light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 6H), 0.91 (t, J = 7.2 Hz, 6H), 1.26−1.48 (m, 8H), 1.94−2.07 (m, 8H), 2.42 (t, J = 7.8 Hz, 4H), 3.07−3.12 (m, 4H), 5.17 (t, J = 7.2 Hz, 2H), 8.03 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 21.6, 23.1, 29.8, 31.0, 32.3, 38.0, 125.8, 128.2, 137.7, 140.0, 199.8. HRMS (MALDI/DHB) calcd for $C_{28}H_{42}O$ 410.3185, found 411.3265 [M + H]$^+$.

Functionalized Homoallyl Ketones Formation by Trapping of the Zirconium Intermediate with Electrophiles. To the reaction mixture described above in THF were added electrophiles such as I_2, Br_2, NCS, allyl bromide, alkynyl bromide, cyclohexenone, or benzalmalononitrile at −50 °C in the presence of 1 equiv of CuCl or 1 equiv of CuCl and 2 equiv of LiCl (in the case of allyl bromide). The mixture was warmed to room temperature over 2 h and stirred at the same temperature for 12 h. After the reaction mixture was quenched with 3 N HCl, it was extracted with ether. Combined organic extracts were washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated in a vacuum. Column chromatography on silica gel afforded the corresponding products.

(4*Z*)-4-Butyl-5-iodo-1-phenylnon-4-en-1-one (2h): GC yield 96%. Column chromatography on silica gel (ethyl acetate/

(13) Suzuki, N.; Kondakov, D. Y.; Kageyama, M.; Kotora, M.; Hara, R.; Takahashi, T. *Tetrahedron* **1995**, *51*, 4519−4540.
(14) Liu, Y.; Zhong, Z.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2002**, *67*, 7451.
(15) Takahashi, T.; Kondakov, D. Y.; Xi, Z.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 5871.

petroleum ether 1:30) afforded 270 mg (68%) of product as a light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.26−1.43 (m, 6H), 1.45−1.57 (m, 2H), 2.17−2.22 (m, 2H), 2.52 (t, J = 7.5 Hz, 2H), 2.60−2.66 (m, 2H), 3.06 (d, J = 8.4 Hz, 1H), 3.09 (d, J = 9.6 Hz, 1H), 7.41−7.46 (m, 2H), 7.51−7.56 (m, 1H), 7.97−8.00 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9, 21.5, 22.5, 30.8, 31.5, 31.8, 36.3, 36.9, 40.8, 105.9, 127.9, 128.3, 132.8, 136.5, 142.6, 199.0. HRMS (MALDI/DHB) calcd for $C_{19}H_{27}IO$ 398.1107, found 399.1181 $[M + H]^+$.

(4*Z*)-4,5-Dibutyl-1,7-diphenylhept-4-en-6-yn-1-one (2*l*): GC yield 90%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) afforded 290 mg (78%) of product as a light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J = 6.9 Hz, 3H), 0.95 (t, J = 6.9 Hz, 3H), 1.35−1.44 (m, 6H), 1.54−1.61 (m, 2H), 2.17−2.27 (m, 4H), 2.81 (t, J = 7.2 Hz, 2H), 3.14 (t, J = 7.5 Hz, 2H), 7.22−7.24 (m, 3H), 7.30−7.35 (m, 4H), 7.44−7.49 (m, 1H), 7.97−7.99 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 22.3, 22.8, 30.4, 30.7, 31.1, 31.3, 31.5, 37.7, 89.9, 92.3, 119.1, 123.8, 127.5, 128.0, 128.1, 128.4, 131.1, 132.7, 136.7, 147.0, 199.9. IR (neat) 2956, 2934, 1712, 1683, 1459, 1181 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{27}H_{32}O$ 372.2453, found 373.2541 $[M + H]^+$.

2-[(2*Z*)-2-Butyl-3-(3′-oxo-3′-phenylpropyl)-1-phenylhept-2-enyl]malononitrile (2n): Column chromatography on silica gel (ethyl acetate/petroleum ether 15:100) afforded 270 mg (63%) of product as a white solid. Mp 95−96°C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.60−0.69 (m, 1H), 0.74 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 6.9 Hz, 3H), 1.03−1.19 (m, 3H), 1.26−1.47 (m, 4H), 1.73−1.83 (m, 1H), 1.94−2.12 (m, 3H), 2.75−2.81 (m, 2H), 3.08−3.19 (m, 1H), 3.21−3.30 (m, 1H), 4.34 (d, J = 11.1 Hz, 1H), 4.79 (d, J = 11.1 Hz, 1H), 7.20−7.60 (m, 8H), 7.99 (d, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.5, 13.9, 23.0, 23.2, 25.5, 25.7, 27.9, 30.5, 31.7, 32.5, 37.7, 47.6, 112.4, 112.5, 127.2, 127.9, 128.0, 128.7, 128.9, 130.4, 133.2, 136.2, 136.7, 141.0, 199.3. HRMS (MALDI/DHB) calcd for $C_{29}H_{34}N_2O$ 426.2671, found 427.2759 $[M + H]^+$.

A Typical Procedure for the Preparation of Cyclopentadiene Product 3a. To a solution of zirconacyclopentene **1a** prepared as described above was added benzoyl cyanide (0.17 g, 1.3 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 3 h, it was quenched with 3 N HCl and extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (petroleum ether). A light-yellow liquid of cyclopentadiene derivative **3a** (147 mg, 65%) was obtained as a mixture of three isomers in the ratio of 14:8:1.

3a: GC yield 97%. NMR data of the major two isomers: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.5 Hz, 3H), 1.47−1.68 (m), 2.08−2.57 (m), 2.75−2.79 (m), 3.23 (br s), 5.32−5.34 (m, 1H), 6.04 (br s, 1H), 6.15 (br s, 1H), 7.17−7.36 (m); ^{13}C NMR ($CDCl_3$) δ 14.3, 14.3, 14.5, 14.6, 21.6, 22.3, 22.6, 23.2, 26.0, 27.8, 28.7, 30.4, 34.4, 42.6, 119.4, 124.9, 125.8, 126.5, 127.4, 127.6, 127.6, 128.1, 128.3, 138.2, 138.8, 140.0, 140.2, 142.4, 142.9, 147.2, 149.1. IR (neat) 2960, 1717, 1599, 1456, 759, 697 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{17}H_{22}$ 226.1721, found 227.1794 $[M + H]^+$.

3f: GC yield 80%. Column chromatography on silica gel (petroleum ether) afforded 167 mg (58%) of product as a mixture of isomers in the ratio of 7:7:1. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.86−1.00 (m), 1.28−1.64 (m), 2.08 (q, J = 7.5 Hz), 2.25−2.74 (m), 3.17 (br s), 5.34−5.39 (m, 1H), 6.04 (br s, 1H), 6.29 (br s, 1H), 7.20−7.31 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 13.8, 13.8, 14.0, 14.1, 22.6, 22.9, 23.0, 23.1, 25.3, 26.1, 26.2, 27.8, 30.7, 31.1, 31.5, 31.9, 34.2, 42.5, 118.2, 125.1, 128.2, 128.4, 128.7, 129.0, 131.5, 132.2, 136.6, 137.2, 138.7, 140.8, 140.9, 143.7, 147.5, 149.3. IR (neat) 2958, 1490, 1466, 1093, 826, 740 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{19}H_{25}Cl$ 288.1645, found 289.1716 $[M + H]^+$.

3g: GC yield 74%. Column chromatography on silica gel (petroleum ether) afforded 139 mg (57%) of product as a mixture of isomers in the ratio of 10:1. ^{1}H NMR ($CDCl_3$, Me_4Si) of the major isomer: δ 0.91−0.97 (m, 6H), 1.38−1.52 (m, 6H), 2.05−2.13 (m, 2H), 2.52−2.54 (m, 4H), 2.69−2.73 (m, 2H), 5.37 (t, J = 7.5 Hz, 1H), 6.27 (d, J = 3.6 Hz, 1H), 6.40 (dd, J = 3.3, 2.1 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) of the major isomer: δ 13.9, 14.0, 22.9, 25.4, 26.1, 30.8, 30.9, 31.6, 107.6, 111.0, 117.9, 130.3, 139.7, 141.5, 147.6, 153.4. ^{1}H NMR ($CDCl_3$, Me_4Si) of the minor isomer: δ 2.22−2.30 (m), 3.23 (s), 5.95 (s), 6.22 (d, J = 3.6 Hz), 7.38 (s), other peaks were overlapped with those of the major isomers. ^{13}C NMR ($CDCl_3$) of the minor isomer: δ 14.0, 22.7, 23.1, 26.6, 27.7, 30.7, 31.4, 40.0, 104.6, 111.1, 124.3, 129.6, 140.3, 143.1, 149.1, 153.2. HRMS (MALDI/DHB) calcd for $C_{17}H_{24}O$ 244.1827, found 245.1900 $[M + H]^+$.

3h: GC yield 98%. Column chromatography on silica gel (petroleum ether) afforded 187 mg (72%) of product as a mixture of isomers in the ratio of 3:1. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91−0.99 (m), 1.39−1.60 (m), 2.08 (q, J = 7.5 Hz), 2.25−2.82 (m), 3.27 (br s), 5.34 (t, J = 7.5 Hz, 1H), 5.92 (br s, 1H), 6.96−7.24 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 14.1, 22.7, 22.9, 23.2, 23.3, 25.8, 26.1, 26.8, 27.7, 30.2, 30.6, 31.1, 31.6, 33.6, 42.4, 118.0, 122.7, 122.8, 124.0, 124.5, 124.6, 126.8, 126.9, 133.3, 134.5, 139.8, 140.7, 143.0, 147.7, 149.3. HRMS (MALDI/DHB) calcd for $C_{17}H_{24}S$ 260.1599, found 261.1672 $[M + H]^+$.

A Typical Procedure for the Direct Reaction of Acyl Cyanide with Zirconacyclopentane. To a solution of zirconacyclopentane **4c** was added *p*-methylbenzoyl cyanide (0.19 g, 1.3 mmol) with stirring at room temperature for 3 h. The reaction mixture was quenched with 3 N HCl and extracted with diethyl ether. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (ethyl acetate/petroleum ether: 1:20). A white solid of **7a** (200 mg, 59%) was obtained.

7a: GC yield 83%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) afforded 200 mg (59%) of product as a white solid. Mp 91−92 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (p, J = 13.5 Hz, 2H), 1.48 (t, J = 5.4 Hz, 1H), 1.52 (t, J = 5.1 Hz, 1H), 1.65−1.79 (m, 2H), 1.83 (br s, 1H), 1.86−2.00 (m, 1H), 2.14−2.29 (m, 2H), 2.32 (s, 3H), 2.53 (dd, J = 13.2, 7.5 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.34−7.39 (m, 6H), 7.54−7.58 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 15.9, 16.8, 20.9, 49.5, 51.0, 51.5, 52.0, 85.6, 124.2, 127.9, 128.8, 129.3, 134.5, 135.8, 136.6, 146.7. IR (neat) 3302, 2942, 1427, 1112, 796, 698 cm^{-1}. HRMS (MALDI/DHB) calcd for $C_{26}H_{28}OSi$ 384.1909, found 407.1802 $[M + Na]^+$.

7b: GC yield 85%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) afforded 220 mg (60%) of product as a white solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (p, J = 13.5 Hz, 2H), 1.48 (t, J = 5.4 Hz, 1H), 1.53 (t, J = 5.1 Hz, 1H), 1.60−1.78 (m, 2H), 1.86 (br s, 1H), 1.87−1.98 (m, 1H), 2.13−2.30 (m, 2H), 2.49 (dd, J = 13.4, 7.2 Hz, 1H), 7.22−7.59 (m, 14H). ^{13}C NMR ($CDCl_3$) δ 15.9, 16.8, 49.6, 51.3, 51.7, 52.2, 85.5, 125.8, 128.0, 128.2, 129.5, 132.1, 134.6, 136.5, 148.2. HRMS (MALDI/DHB) calcd for $C_{25}H_{25}ClOSi$ 404.1363, found 427.1255 $[M + Na]^+$.

7c: GC yield 66%. Column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) afforded 187 mg (51%) of product as a white solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.84 (s, 1H), 1.84−1.90 (m, 2H), 2.15−2.22 (m, 2H), 2.39−2.48 (m, 2H), 2.65 (dd, J = 14.4, 5.7 Hz, 2H), 2.89−2.95 (m, 2H), 6.93−7.49 (m, 15H). ^{13}C NMR ($CDCl_3$) δ 35.4, 35.9, 47.7, 82.9, 119.2, 124.9, 125.8, 126.9, 127.8, 128.2, 128.8, 136.6, 136.7, 142.0, 145.9, 198.7. HRMS (MALDI/DHB) calcd for $C_{27}H_{26}O$ 366.1984, found 389.1876 $[M + Na]^+$.

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Supporting Information Available: Experimental details and characterization data for compounds **2e**, **2i**, **2j**, **2k**, **2m**, **3b**, **3c**, **3d**, **3e**, **3i**, **3j**, **5**, and **6** and crystallographic data for **7c** and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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