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Direct Addition of Zr−C Bonds of Alkylzirconocenes to Activated Alkenes

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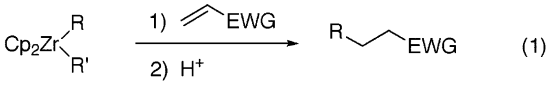
Direct addition of alkylzirconocenes to activated alkenes was found, for the first time. Octyl- and decylzirconocene chloride reacted with benzylidenemalononitrile to give the corresponding addition products after hydrolysis in 86% and 79% yield, respectively. Zirconacyclopentanes showed a similar reactivity toward activated alkenes with a two-electron-withdrawing group. On the other hand, treatment of the reaction mixture of zirconacyclopentanes and ylidenemalononitriles with iodine afforded six-membered cyclic compounds in high yields. The diastereoselectivity of the cyclized compound was remarkably high and the high selectivity originated from the Zr-promoted cyclization. The structures of cyclic compounds **10b** and the major diastereoisomer of **10d** were determined by X-ray analysis. Zirconacyclopentenes reacted with ylidenemalononitrile with high chemoselectivity in which the sp^3-carbon attached to zirconium reacted with ylidenemalononitrile.

Introduction

Direct addition of organometallic compounds to activated alkenes is one of the most useful carbon−carbon bond formation methods.[1] Recently, organozirconocene compounds have become readily and conveniently available from alkenes and/or alkynes.[2,3] Addition of organozirconocene to activated alkenes has been done only after transmetalation[4] of the organic moiety from zirconium to Cu,[5,6] Zn,[7] or Ni.[8] Herein we would like to report the first example of the direct addition of the Zr-sp^3 carbon bond of organozirconocenes to activated alkene (eq 1).[9,10]



(1)

Results and Discussion

Reaction of Alkylzirconocenes with Activated Alkenes. Our initial study was focused on the reaction of simple alkylzirconocene compounds such as $Cp_2Zr(Me)Cl$ (**1a**) and Cp_2ZrMe_2 (**1b**) with activated alkenes. It was found that the reaction of these compounds with alkenes bearing one electron-withdrawing group (EWG), namely, cinnamonitrile or cinnamyl acetate, did not give any

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(1) (a) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Tetrahedron Organic Chemistry Series, No. 9; Pergamon Press: Oxford, 1992. (b) Lee, V. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 4, Chapter 1.2. (c) Posner, G. H. *Org. React.* **1972**, *19*, 1. (d) Kozlowski, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 4, Chapter 1.4. (e) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

(2) For a recent review on zirconacyclopentanes, zirconacyclopentenes, and zirconacyclopentadienes, see: (a) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591−2602 and references therein. For a recent review on zirconium−alkene and −alkyne complexes, see: (b) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755−769 and references therein.

(3) For hydrozirconation of alkenes and alkynes, see: (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115−8116. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (c) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405. (d) Wailes, P. C.; Weigold, H.; Bell *J. Organomet. Chem.* **1971**, *27*, 373. (e) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679−680.

(4) For reviews on conjugate addition of organozirconium after transmetalation, see: (a) Wipf, P.; Jahn, H. *Tetrahedron* **1996**, *52*, 12853−12910. (b) Lipshutz, B. H.; Bhandari, A.; Lindsley, C.; Keil, R.; Wood, M. R. *Pure Appl. Chem.* **1994**, *66*, 1493−1500.

(5) Conjugate addition of alkenylzirconocene compounds after transmetalation to Cu, see: (a) Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303−1306. (b) Lipshutz, B. M.; Ellsworth, E. *J. Am. Chem. Soc.* **1990**, *112*, 7440−7441. (c) Lipshutz, B. M.; Wood, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 12625−12626. (d) Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, 679. (e) Lipshutz, B. H.; Wood, M. R. *Tetrahedron Lett.* **1994**, *35*, 6433−6436. (f) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**, *51*, 4407−4420.

(6) Conjugate addition of alkylzirconocene compounds after transmetalation to Cu, see: (a) Wipf, P.; Smitrovich, J. H. *J. Org. Chem.* **1991**, *56*, 6494−6496. (b) Wipf, P.; Smitrovich, J. H.; Lehman, R.; Venanzi, L. M. *Tetrahedron* **1994**, *50*, 1935−1954. (c) Wipf, P.; Smitrovich, J. H.; Moon, X.-W. *J. Org. Chem.* **1992**, *57*, 3178−3186. (d) Lipshutz, B. H.; Wood, M. R.; Tirado, R. *J. Am. Chem. Soc.* **1995**, *117*, 6126−6127.

(7) Conjugate addition of organozirconocene compounds after transmetalation to Zn, see: Lipshutz, B. H.; Wood, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 11689−11702.

(8) Ni-catalyzed conjugate addition of organozirconocenes, see: (a) Loots, M. J.; Schwarz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045−8046. (b) Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1978**, 4381−4382. See also: (c) Hauske, J. R.; Dorff, P.; Julin, S.; Martinelli, G.; Bussolari, J. *Tetrahedron Lett.* **1992**, *33*, 3715−3716. (d) Hauske, J. R.; Dorff, P.; Julin, S.; DiBrino, J.; Spencer, R.; Williams, R. *J. Med. Chem.* **1992**, *35*, 4284−4296. (e) Sun, R. C.; Okabe, M.; Coffen, D. L.; Schwartz, J. *Org. Synth.* **1993**, *71*, 83−88. (f) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333−1340. (g) Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3976−3978. (h) Dayrit, F. M.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4466−4473.

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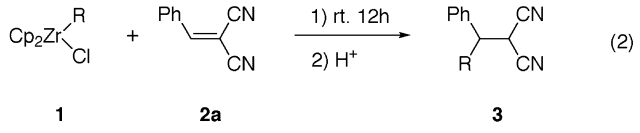
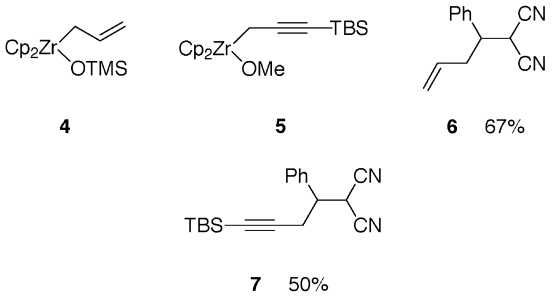
products. On the other hand, the use of alkenes with two EWG groups, for example, benzylidenemalononitrile **2a**, resulted in the formation of the desired addition product 2-(1-phenylethyl)propanedinitrile (**3a**), although it was obtained in low yields (20%). However, switching to $Cp_2Zr(n\text{-Oct})Cl$ (**1c**) and $Cp_2Zr(n\text{-Dec})Cl$ (**1d**) which were prepared in situ by hydrozirconation of 1-octene and 1-decene produced the corresponding **3b** and **3c** in 86% and 79% yields, respectively (eq 2).



1 **2a** **3**

1c R= *n*-C_8H_{17} **3b** (86%)
1d R= *n*-$C_{10}H_{21}$ **3c** (79%)

Other organozirconocene compounds such as allyl- (**4**) and propargylzirconocenes[11] (**5**) reacted with benzylidenemalononitrile (**2a**) to give conjugate addition products **6** (67%) and **7** (50%).

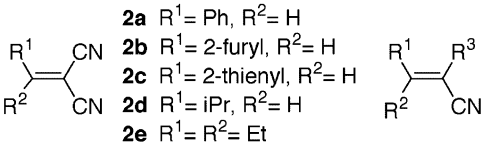


4 **5** **6** 67%

7 50%

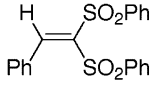
The above-mentioned results prompted us to study the reactions of zirconacycles such as zirconacyclopentanes and -pentenes as alkylzirconocene derivatives with the activated alkenes.

Reaction of Zirconacyclopentanes with Activated Alkenes. We chose zirconacyclopentane **8** to investigate the reactions with activated alkenes. The best results of the direct addition were obtained with alkenes **2a**−**k** activated by two electron-withdrawing groups such as CN, COOR, and SO_2Ph. In a typical reaction, addition



2a R^1= Ph, R^2= H
2b R^1= 2-furyl, R^2= H
2c R^1= 2-thienyl, R^2= H
2d R^1= iPr, R^2= H
2e R^1= R^2= Et

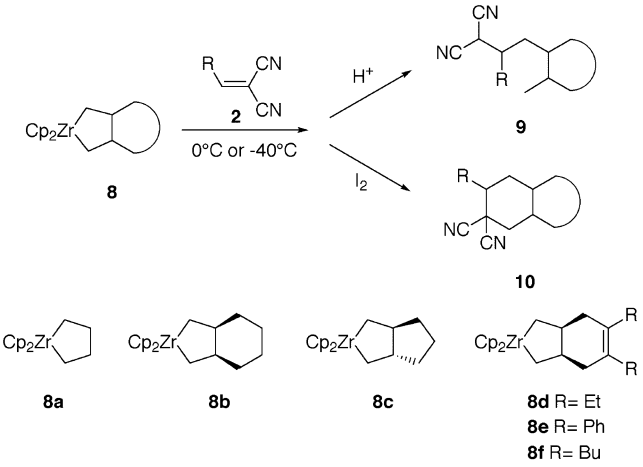
2f R^1= H, R^2= iPr, R^3 = COOEt
2g R^1= H, R^2= Ph, R^3 = SO_2Ph
2h R^1= H, R^2= Ph, R^3 = COOEt
2i R^1= R^2= Et, R^3 = CO_2Et
2j R^1= R^2= R^3= CN



2k

of ylidenemalononitrile (**2**, 1.2 equiv) to a THF solution of zirconacyclopentanes (**8**) at 0 °C or −40 °C prepared

SCHEME 1



from alkenes[12,13] by Cp_2ZrBu_2 (Negishi reagent)[13a] (1 equiv) resulted in an immediate color change from deep-yellow to light-yellow. After the mixture was stirred for an appropriate time at 0 or −40 °C, the desired product **9** was formed in up to 96% yield after acidic hydrolysis. To our surprise, when 2.5 equiv of I_2 was added to the reaction mixture instead of hydrolysis, iodinated products were not obtained, instead cyclized six-membered carbocycles **10** were formed cleanly (Scheme 1). This result is of potentially synthetic interest because the zirconacycles **8** can be converted into highly functionalized carbocycles in high yields in a one-pot procedure.

The results of the reaction with alkylidenepropanedinitriles are summarized in Table 1. In all cases, hydrolysis of the reaction mixture afforded alkylated propanedinitriles **9** as mixtures of diastereoisomers. Iodinolysis afforded the corresponding monocyclic or bicyclic carbocycles **10** as a mixture of diastereoisomers, which turned out to be easily separated by column chromatography. However, aliphatic ylidenemalononitriles **2d** and **2e** (entries 8 and 9) did not afford the desired cyclized products. It is noteworthy that the reaction of zirconabicyclononane **8b** (entry 2) with **2a** afforded **10b** as a single isomer after iodinolysis. Also, in the case of the products **10c**, **10d**, and **10e** (entries 3, 4, and 5) the ratio of the diastereoisomers was unexpectedly high (7:1, 10:1, and 8:1). X-ray analysis of **10b** and the major isomer of **10d** confirmed their structures as well as the relative stereochemistry of the substituents at the bicyclic systems. The influence of a phenyl group on diastereoselectivity of cyclization is noteworthy. On

(9) For reactions with CO: (a) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 4, Chapter 1.2. Insertion of aldehydes into the Zr−C bond: (b) Coperet, C.; Negishi, E.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* **1994**, *35*, 695−698.

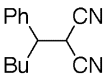
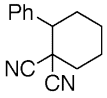
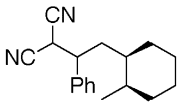
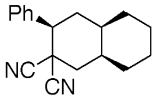
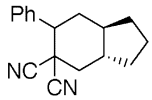
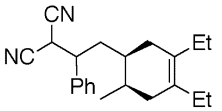
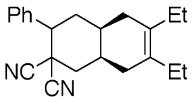
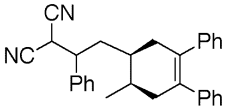
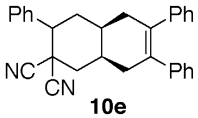
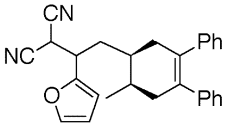
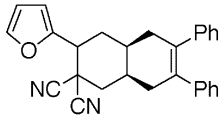
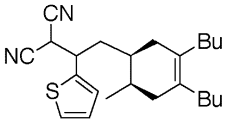
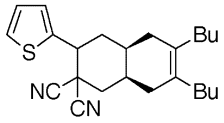
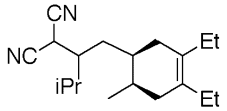
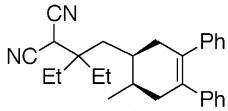
(10) Recently we have reported 1,1-cycloaddition of zirconacyclopentadienes to propynoates without transmetalation: Takahashi, T.; Sun, W.-H.; Xi, C.; Kotora, M. *Chem. Commun.* **1997**, 2069−2070. However, substituted propynoates did not react with zirconacyclopentadienes.

(11) Ito, H.; Nakamura, T.; Taguchi, T.; Hanzawa, Y. *Tetrahedron* **1995**, *51*, 4507−4518.

(12) (a) Takahashi, T.; Fischer, R.; Xi, Z.; Nakajima, K. *Chem. Lett.* **1996**, 357−358. (b) Xi, Z.; Hara, T.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444−4448.

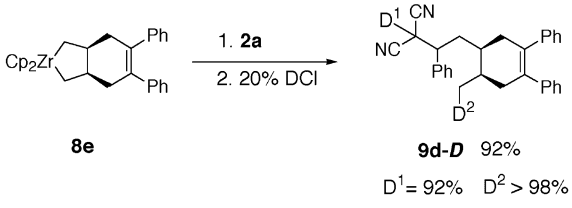
(13) (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105.

TABLE 1. Reaction of Zirconzcyclopentanes 8 with Ylidenemalononitriles 2

Entry	8	Alkenes	Products of hydrolysis	Yield (%)[a,b]	Products of iodinolysis	Yield (%)[a,b]
1	**8a**	**2a**	 **9a**	90 (73)	 **10a**	- (83)
2	**8b**	**2a**	 **9b**	84 (70)[c] 3.4:1	 **10b**	86 (73)
3	**8c**	**2a**	*f*		 **10c**	- (44) 7:1
4	**8d**	**2a**	 **9c**	95 (92) 3.7:1	 **10d**	84 (62) 10:1
5	**8e**	**2a**	 **9d**	96 (88) 2.8:1	 **10e**	- (69) 8:1
6	**8e**	**2b**	 **9e**	- (79)[d] 1.4:1	 **10f**	- (82) 2:1
7	**8f**	**2c**	 **9f**	92 (75)[d] 3.3:1	 **10g**	86 (70) 2.6:1
8	**8d**	**2d**	 **9g**	70 (58)[d] 2.8:1	*f*	
9	**8e**	**2e**	 **9h**	- (45)[e]	*f*	

[a] GC or ^{1}H NMR yields. Isolated yields are given in parentheses. Below the yields are given diastereomeric ratios. [b] Unless otherwise noted, all the reactions were carried out at 0 °C for 1 h for the addition reaction. Cyclization was done by treatment with 2.5 equiv of I_2, 20 °C, 3 h. [c] −20 °C, 3 h. [d] −40 °C, 3−9 h. [e] 0 °C, 9 h. [f] An inseparable mixture of products was obtained.

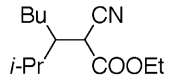
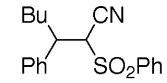
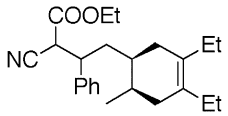
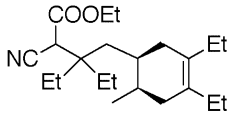
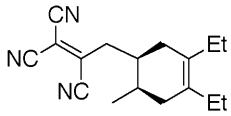
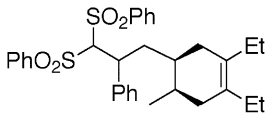
the other hand, the use of alkylidenepropanedinitriles **2b** and **2c** (entries 6 and 7) bearing thienyl and furyl groups afforded products in rather low diastereoisomeric ratios of 2:1 and 2.6:1, respectively. The reaction of zirconabicyclononene **8e** with **2a** followed by deuteriolysis with 20% DCl in D_2O afforded, after workup, dideuterated compound **9d-*D*** in 92% yield with high deuterium incorporation (D^1 = 92%, D^2 > 98%) (eq 3).



8e **9d-*D*** 92%
D^1 = 92% D^2 > 98% (3)

To investigate the scope of the reaction we tested a number of differently substituted activated alkenes **2f**−**k**. The results are summarized in Table 2. Simple

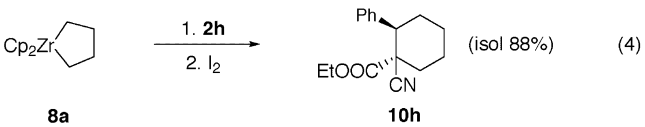
TABLE 2. Reaction of Zirconacyclopentanes 8 with Various Subtituted Alkenes 2

Entry	8	Alkenes	Conditions	Products of hydrolysis	Yield (%)[a]
1	**8a**	**2f**	-40°C, 12h	 **9i**	- 72 (61) 1.2:1
2	**8a**	**2g**	0°C, 3h	 **9j**	- (89) 1.8:1
3	**8d**	**2h**	0°C, 1h	 **9k**	97 (90) 3.7:3.7:1.4:1
4	**8d**	**2i**	0°C, 36h	 **9l**	51 (49) 1.4:1
5	**8d**	**2j**	-78°C, 3h	 **9m**	87 (65)
6	**8d**	**2k**	20°C, 12h	 **9n**	- (24) 2:1

[a] GC or ^{1}H NMR yields. Isolated yields are given in parentheses. Below the yields are given diastereomeric ratios.

zirconacyclopentane **8a** reacted with both **2f** and **2g** to give high yields of products **9i** and **9j** as a mixture of diastereoisomers in good yields (72 and 89%). Reaction of **8d** with **2h** afforded **9k** in almost quantitative yield (97%) as a mixture of four stereoisomers with a ratio of 3.7:3.7:1.4:1. Reaction proceeded even with tetrasubstituted **2i** to give **9l** in a reasonable yield of 51% as a 1.4:1 mixture of diastereoisomers. When tetracyanoethylene (**2j**) was used, substitution occurred to afford alkyltricyanoethylene derivative **9m** in high yield (87%). Presumably the addition and elimination took place. The reaction with **2k** afforded a low yield of **9n** (24%).

The reaction of **8a** with **2h** followed by iodinolysis afforded substituted cyclohexane **10h** as a single isomer



8a **10h**

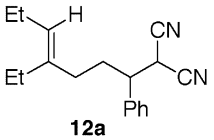
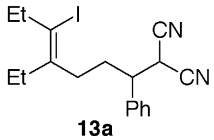
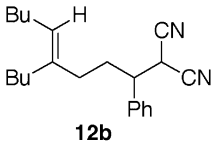
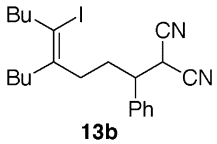
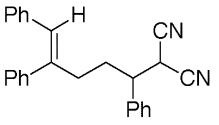
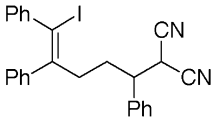
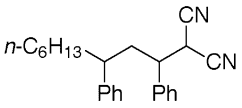
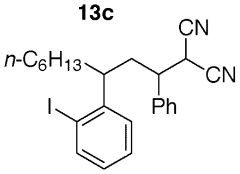
in high yield (88%).[14] Although speculative, it is reasonable to assume that the initial geometry of the double bond of **2h** was retained during the reaction with the ethoxycarbonyl group in a trans position to the phenyl group. It is also reasonable to assume that this configuration provides more stable isomer due to steric requirements.

Reaction of Zirconacyclopentenes with Activated Alkenes. Zirconacyclopentenes (**11**),[15] which have one Zr−sp^3 C bond, reacted with **2a** as well (Scheme 2). The results are summarized in Table 3. Hydrolysis of the reaction mixtures afforded substituted 2-(4-pentenyl)-propanedinitriles (**12**), and iodinolysis afforded substituted 2-(5-iodo-4-pentenyl)propanedinitriles (**13**). The reaction of **2a** proceeded also with zirconaindan **11d** (Table 3, entry 4) to give the products of hydrolysis and iodinolysis, **12d** and **13d**, in reasonable yields, respectively. As expected, the formation of cyclic products after iodinolysis was not detected. It is interesting to note that the sp^3 carbon attached to Zr selectively added to alkenes

(14) (a) Avenoza, A.; Cativiela, C.; Paris, M.; Peregrina, J. M. *Tetrahedron: Asymmetry* **1995**, *6*, 1409−1418. (b) Cativiela, C.; Avenoza, A.; Paris, M.; Peregrina, J. M. *J. Org. Chem.* **1994**, *59*, 7774−7778.

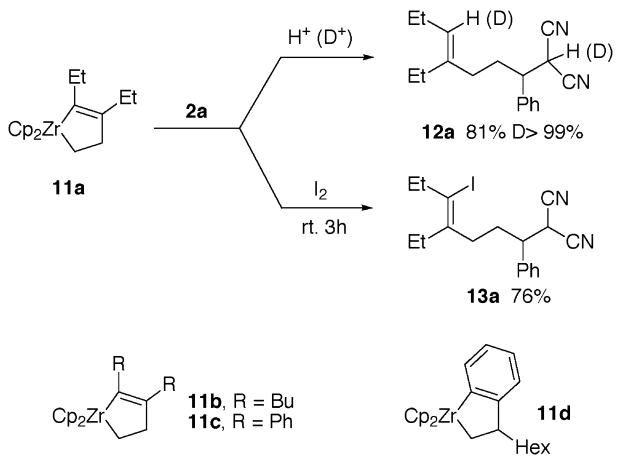
(15) (a) Reference 12b. (b) Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001−1004. (c) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara. R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687−690. (d) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802−6806.

TABLE 3. Direct Reaction of Zirconacyclopentenes 11 with Ylidenemalonitrile 2a

Entry	11	Product of hydrolysis	Yield (%)[a,b]	Product of iodinolysis	Yield (%)[a,b]
1	**11a**	 **12a**	81 (67)	 **13a**	76 (65)
2	**11b**	 **12b**	79 (60)	 **13b**	72 (61)
3	**11c**	 **12c**	77 (51)[c]	 **13c**	69 (65)[c]
4	**11d**	 **12d**	55 (43)[d]	 **13d**	- (41)[d]

[a] GC or ^{1}H NMR yields. Isolated yields are given in parentheses. [b] Unless otherwise noted, all the reactions were carried out from 0 to 20 °C, 3 h for the addition reaction. Iodination was done by treatment with 2.5 equiv of I_2, 0 °C, 3 h. [c] −20 °C, 1 h. [d] −78 to 30 °C.

SCHEME 2



in the case of zirconacyclopentenes. The chemoselectivity in this case is in sharp contrast to the copper-mediated Michael addition reactions of zirconacyclopentenes where the sp^2 carbon attached to Zr selectively added to alkenes as Lipshutz et al reported.[5i,16] The sp^2 carbon on Zr is more reactive toward transmetalation to Cu, since the π-bond can have strong interaction with Cu. On the other hand, the nucleophilicity of the sp^3 carbon is generally higher than that of the sp^2 carbon, and for the radical path, the sp^3 carbon−Zr bond is favorable for the homolytic cleavage over the sp^2 carbon−Zr bond. Therefore, the direct addition (without transmetalation) to the activated alkenes occurred on the sp^3 carbon selectively.

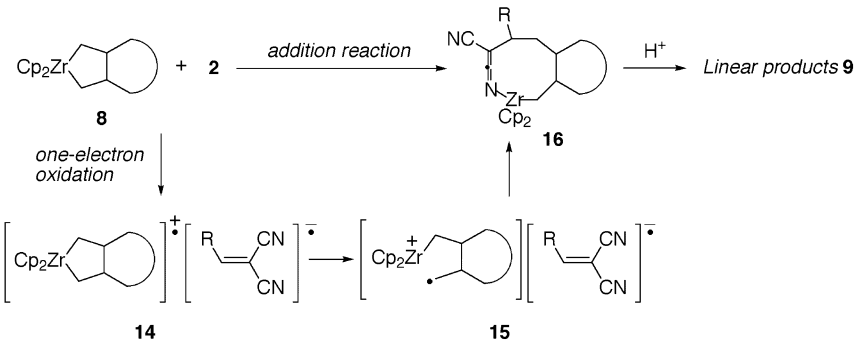
Reaction Mechanism. Generally, two reaction mechanisms for the conjugate addition of organometals can be considered: (i) single electron transfer (SET) and (ii) direct nucleophilic addition (Scheme 3). For the case of conjugate addition of transition metal compounds such as organocopper and -nickel compounds, evidence supporting both mechanisms has been presented; however, definitive conclusion remains open.[17] On the other hand, one-electron oxidation of d^0 organometallics was documented by using TTFC, Ag^+, TCNQ, or $[Cp_2Fe]^+$ as oxidant.[18] For example, Jordan and co-workers have reported that Cp_2ZrR_2 (R = CH_3, CH_2Ph) reacted with Ag^+ or $[Cp_2Fe]^+$ to produce the cationic complexes $Cp_2ZrR(L)^+$ along with the loss of alkyl radical.[18a] Thus a plausible mechanism in a SET pathway might involve the following: (i) electron transfer between **8** and **2** leading to a transient radical ion pair **14**, (ii) homolysis of the metal−carbon bond to form the radical-cation pair **15**, and (iii) addition of the radical to the reduced olefinic substrate followed by collapse of the pair to give the same intermediate **16** as in the pathway of nucleophilic addition. Hydrolysis of **16** afforded linear product **9**.

(16) Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 109−110.

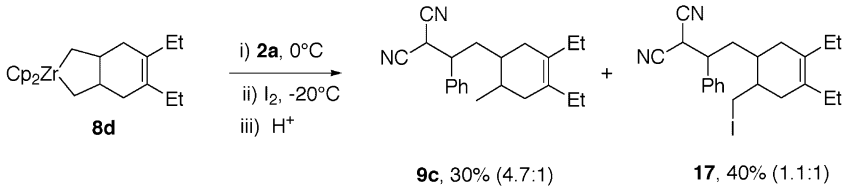
(17) Detailed discussion on the reaction mechanism of conjugate additions of organometals can be found in the following references: 1a, 8g, and 8h.

(18) (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, B. S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111−4113. (b) Burk, M. J.; Staley, D. L.; Tumas, W. *J. Chem. Soc., Chem. Commun.* **1990**, 809−810. (c) Burk, M. J.; Tumas, W.; Ward, M. D.; Wheelar, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133−6135 and references therein.

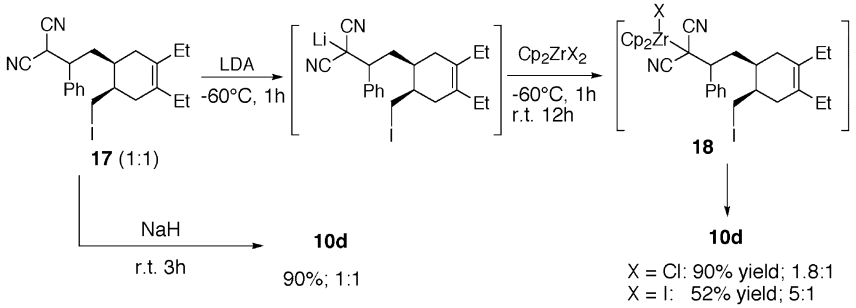
SCHEME 3



SCHEME 4



SCHEME 5



The other noteworthy observation was high diastereoselectivity of the cyclization of the addition products upon iodinolysis. In many cases, the diastereoselectivity of the cyclized products was enhanced compared with that of the corresponding hydrolysis products. To clarify the origin of this phenomenon it is important to find at which reaction step the diastereoselection took place. We conducted the reactions shown in Scheme 4 to find this origin.The reaction of **8d** with **2a** was carried out at 0 °C and was followed by the addition of iodine (2.5 equiv) at −20 °C (Scheme 4). Monoiodination product **17** was obtained as a mixture of two diastereoisomers in 40% yield along with the formation of **9c** in 30% yield. The formation of **17** at low temperature clearly indicates that the intermediate for the cyclization after addition of iodine is **18** (Scheme 5).

The intermediate **18** was in situ prepared by treatment of **17** with LDA at −60 °C for 1 h and by subsequent addition of zirconocene dihalides at the same temperature. When the intermediate **18** in solution was warmed to room temperature, the expected cyclization proceeded and the final product **10d** was obtained as shown in Scheme 5. Surprisingly, the diastereoselectivity was remarkably increased to 5:1 when **18** was prepared in situ with Cp_2ZrI_2. Control experiment with NaH afforded **10d** without change of the diaseteoselectivity. It is quite interesting to note that the zirconium-promoted cyclization controlled the diastereoselectivity of the cyclized product. This is the origin of the enhancement of the ratio of diastereoisomers of the cyclized product after addition of iodine.

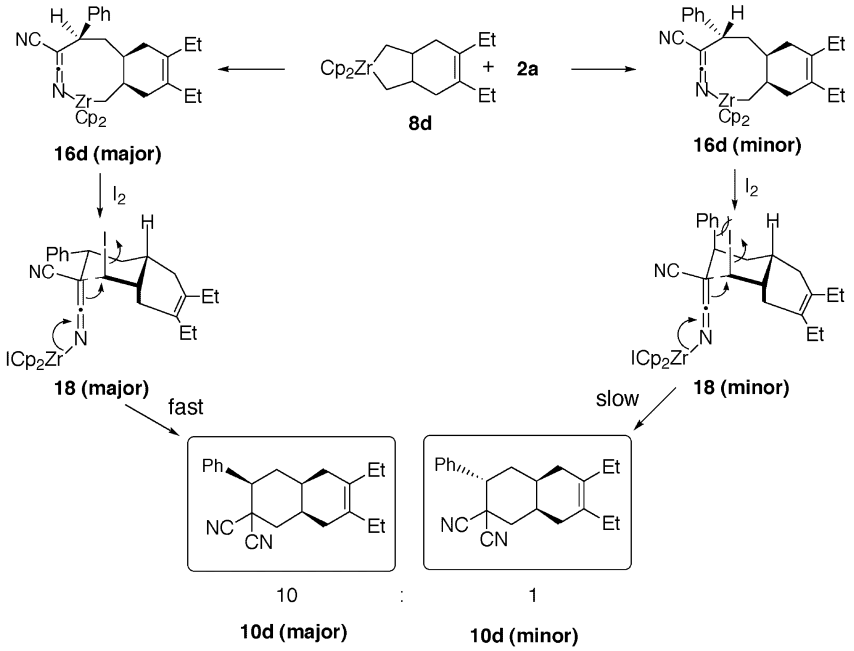
The overall reaction mechanism from **8d** to **10d** is shown in Scheme 6. It involves the direct addition of the sp^3 carbon attached to zirconium of **8d** to **2a** and iodination of the intermediate **16d** giving **18**. Cyclization of the major isomer of **18** is much faster than that of the minor isomer since the minor isomer has a sterical problem between the Ph group and the I group in its chair conformation.

Experimental Section

All reactions were carried out with the standard Schlenk technique under nitrogen. THF was distilled over sodium/benzophenone. All commercial reagents were used without further purification. Flash chromatography was performed with Merck silica gel 60 (40−60 μm). *n*-Butyllithium (1.6 M solution in hexane) was used as purchased. Zirconacyclopentanes **8a**,[12b] **8b**−**c**,[13b] and **8d**−**f**,[19] zirconacyclopentenes **11a**−**c**,[15c] zirconaindan (**11d**),[20] and allylic and propargylic zirconocene compounds **4** and **5**[11] were prepared according to the previously published procedures. Benzylidenemalononitrile (**2a**) and tetracyanoethylene (**2j**) were used as purchased.

(19) Takahashi, T.; Kotora, M.; Kasai, K. *J. Chem. Soc., Chem. Commun.* **1994**, 2693−2694. For the preparation of 1,4,7-trienes, see: Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685−5688.

SCHEME 6



Other ylidenemalononitriles **2b**−**i** were prepared by the condensation reaction of malononitrile with aldehydes or ketones.[21]

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (containing 1% TMS) solutions at 400 and 100 MHz, respectively. All melting points were determined by a micro melting point apparatus and are uncorrected. GC analysis was performed on a SHIMADZU GC-14A equipped with a fused silica capillary column SHIMADZU CBP1-M25-O25 and a SHIMADZU C-R6A-Chromatopac integrator. Single-crystal X-ray diffraction data were collected in Enraf-Nonius CAD4 diffractometers with molybdenum or copper cathodes. The characterization data of compounds **3c**, **9(d-*D*)**, **9f**, **9l**, **10a**, **10c**, **10g**, and **13b**, and structures of **10b** and **10d** are given in the Supporting Information.

General Procedure for the Reaction of Alkylzirconocene Compounds with Benzylidenemalononitrile (2a). To a suspension of Cp_2ZrHCl (0.26 g, 1 mmol) in THF (5 mL) was added 1-alkene (1 mmol) with stirring at room temperature for 1 h. Then benzylidenemalononitrile (0.23 g, 1.5 mmol) was added and the mixture stirred at room temperature for 12 h. The reaction mixture was extracted with Et_2O (3 × 10 mL) and the combined organic extracts were washed with water, aq $NaHCO_3$, and brine and dried ($MgSO_4$). Filtration and evaporation followed by column chromatography on silica gel (hexane/EtOAc) afforded the products.

2-(1-Phenylethyl)propanedinitrile (3a). This compound was formed by the reaction of **1a** or **1b** with **2a.** Its spectra were consistent with the published data.[22] GC yield 20%.

2-(1-Phenylnonyl)propanedinitrile (3b). GC yield 86%. Isolated yield 75%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.86 (t, J = 7.0 Hz, 3H), 1.22−1.29 (m, 12H), 1.94−2.00 (m, 2H), 3.17 (td, J = 7.0, 6.2 Hz, 1H), 3.88 (d, J = 6.2 Hz, 1H), 7.29−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.92, 22.46, 26.77, 28.96, 29.05, 30.07, 31.59, 31.94, 46.33, 111.97, 127.72, 128.64, 129.07, 136.78. HRMS calcd for $C_{18}H_{24}N_2$ 268.1938, found 268.1939.

Reaction of Allylzirconium (4) with Benzylidenemalononitrile. 2-(1-Phenyl-3-butenyl)propanedinitrile (6).[23] To a solution of allylzirconium compound **4** (prepared from 1.1 mmol of Cp_2ZrCl_2)[11] was added benzylidenemalononitrile (0.17 g, 1.1 mmol) at 0 °C with stirring for 3 h. The reaction mixture was qeunched with 3 N HCl and extracted with Et_2O. Column chromatography on silica gel (hexane/EtOAc) afforded the product. GC yield 67%. Isolated yield 60%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.69−2.80 (m, 2H), 3.25−3.31 (m, 1H), 4.00 (d, J = 5.7 Hz, 1H), 5.15−5.26 (m, 2H), 5.60−5.71 (m, 1H), 7.24−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 28.88, 36.36, 45.80, 111.49, 111.91, 119.76, 127.86, 128.90, 129.14, 132.95, 136.3. HRMS calcd for $C_{13}H_{12}N_2$ 196.1000, found 196.1002.

Reaction of Propargylic Zirconium 5 with Benzylidenemalononitrile. 2-(4-*tert*-Butyldimethylsilyl-1-phenyl-3-butynyl)propanedinitrile (7). To a solution of propargylzirconium compound **5** (prepared from 1.1 mmol of Cp_2ZrCl_2)[11] was added benzylidenemalononitrile (0.17 g, 1.1 mmol) at 0 °C. After being stirred at room temperature for 3 h, the reaction mixture was qeunched with 3 N HCl and extracted with Et_2O. Column chromatography on silica gel (hexane/EtOAc) afforded the product. Isolated yield 58%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.09 (s, 6H), 0.89 (s, 9H), 2.89 (t, J = 6.6 Hz, 2H), 3.40−3.45 (m, 1H), 4.36 (d, J = 6.2 Hz, 1H), 7.37−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −4.75, 16.36, 23.93, 25.93, 28.10, 45.23, 88.40, 101.27, 111.18, 111.77, 127.65, 129.14, 129.20, 135.58. HRMS calcd for $C_{19}H_{24}N_2Si$ 308.1707, found (M + 1) 309.1788.

General Procedure for the Preparation of 9. To a solution of zirconacyclopentane **8** (prepared from 1.1 mmol of Cp_2ZrCl_2)[12b,13b,19] was added ylidenemalononitrile **2** (1.2−2 mmol) at −40 °C or 0 °C with stirring for the appropriate time (see Table 1). The reaction mixture was quenched with 3 N HCl and extracted with ether. Combined organic extracts were washed with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concetrated in vacuo. Column chromatography on silica gel (hexane/EtOAc) afforded the products.

(20) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (c) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246. See also: (d) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411−7413.

(21) Allen, C. F. H.; Spangler, F. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. 3, pp 377−379.

(22) Chikashita, H.; Nishida, S.; Miyazaki, M.; Morita, Y.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 737.

(23) This compound was reported, but the NMR data were not available. Kazuhiko, M.; Munehiro, I.; Yoshio, O. *Chem. Lett.* **1988**, *9*, 1507.

2-(1-Phenylpentyl)propanedinitrile (9a).[24] GC yield 90%. Isolated yield 73%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, J = 7.2 Hz, 3H), 1.10−1.41 (m, 4H), 1.94−2.00 (m, 2H), 3.17−3.20 (m, 1H), 3.88 (d, J = 6.3 Hz, 1H), 7.29−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.56, 22.04, 28.85, 30.03, 31.63, 46.26, 111.98, 127.70, 128.61, 129.05, 136.78. HRMS calcd for $C_{14}H_{16}N_2$ 212.1313, found 212.1306.

2-[2-(*cis*-2-Methylcyclohexyl)-1-phenylethyl]propanedinitrile (9b). GC yield 84%. Isolated yield 70% (3.4:1 mixture of diastereoisomers). A colorless liquid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83 (d, J = 7.1 Hz, 3H), 1.09−1.64 (m, 9H), 1.76−1.93 (m, 3H), 3.22−3.28 (m, 1H), 3.85 (d, J = 6.1 Hz, 1H), 7.29−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.98, 21.21, 25.39, 28.19, 30.24, 30.39, 32.50, 35.06, 36.85, 43.88, 112.21, 127.91, 128.75, 129.19, 137.13. The minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (d, J = 7.0 Hz, 3H), other peaks were overlapped by the signals of the major diastereoisomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.14, 22.66, 23.73, 26.82, 30.64, 31.72, 32.88, 33.46, 36.38, 44.12, 112.18, 127.97, 136.89, other peaks were overlapped by the signals of the major diastereoisomer. HRMS calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1778.

2-[2-(*cis*-3,4-Diethyl-6-methylcyclohex-3-enyl)-1-phenylethyl]propanedinitrile (9c). GC yield 95%. Isolated yield 92% (3.7:1 mixture of diastereoisomers). A colorless liquid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.79−0.97 (m, 9H), 1.68−1.99 (m, 12H), 3.28−3.31 (m, 1H), 3.88 (d, J = 6.2 Hz, 1H), 7.30−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.91, 12.98, 13.03, 25.31, 25.41, 28.50, 30.20, 32.14, 34.25, 34.44, 36.23, 44.08, 111.97, 112.01, 121.71, 127.83, 128.62, 128.79, 129.07, 136.97. The monor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.85 (d, J = 6.1 Hz, 1H), other peaks were overlapped by the signals of the major diastereoisomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.20, 14.93, 25.45, 25.50, 30.61, 31.20, 31.40, 32.83, 34.00, 35.51, 44.29, 128.31, 128.65, 129.12, 136.61, other peaks were overlapped by the signals of the major diastereoisomer. Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.40; H, 8.91; N, 8.67.

2-[2-(*cis*-6-Methyl-3,4-diphenylcyclohex-3-enyl)-1-phenylethyl]propanedinitrile (9d). GC yield 96%. Isolated yield 88% (2.8:1 mixture of diastereoisomers). A colorless liquid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.00 (d, J = 6.9 Hz, 3H), 1.66−1.72 (m, 1H), 1.96−2.34 (m, 5H), 2.45−2.56 (m, 2H), 3.30−3.38 (m, 1H), 3.80 (d, J = 6.2 Hz, 1H), 6.84−7.41 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.00, 30.86, 31.38, 33.03, 34.10, 34.67, 38.72, 44.45, 111.82, 111.93, 125.85, 125.95, 127.61, 127.73, 127.91, 128.82, 128.86, 128.98, 129.37, 132.33, 133.74, 136.44, 143.08, 143.11. The minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.06 (d, J = 6.9 Hz, 3H), 1.77−1.81 (m, 1H), 3.83 (d, J = 6.3 Hz, 1H), other peaks were overlapped with the signals of the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.30, 28.70, 30.52, 34.27, 34.57, 35.29, 38.90, 44.37, 112.16, 112.23, 126.01, 127.78, 127.80, 127.93, 127.99, 129.08, 129.70, 132.71, 133.03, 136.79, 142.74, 143.12, other peaks were overlapped with the signals of the major isomer. HRMS calcd for $C_{30}H_{28}N_2$ 416.2251, found 416.2252.

2-[2-(*cis*-6-Methyl-3,4-diphenylcyclohex-3-enyl)-1-(2-furyl)ethyl]propanedinitrile (9e). Isolated yield 79% (1.4:1 mixture of diastereoisomers). A colorless liquid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.0 (d, J = 6.9 Hz, 3H), 1.78−2.41 (m, 6H), 2.41−2.62 (m, 2H), 3.46−3.54 (m, 1H), 3.91 (d, J = 5.9 Hz, 1H), 6.35−6.40 (m, 2H), 6.89−7.09 (m, 10H), 7.41 (dd, J = 8.4, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.93, 28.75, 28.80, 31.16, 34. 43, 34.67, 38.54, 39.38, 109.38, 110.63, 111.45, 111.51, 125.81, 125.87, 127.55, 128.77, 128.82, 132.70, 133.70, 142.99, 143.12, 143.17. The minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.94 (d, J = 6.0 Hz, 1H), other peaks were overlapped by the signals of the major diastereoisomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.12, 28.43, 31.85, 33.08, 34.80, 34.84, 38.40, 38.59, 109.21, 111.58, 125.78, 125.80, 127.65, 132.26, 133.05, 142.71, 143.10, other peaks were overlapped by the signals of the major diastereoisomer. HRMS calcd for $C_{28}H_{26}N_2O$ 406.2044, found 406.2032.

2-[2-(*cis*-3,4-Diethyl-6-methylcyclohex-3-enyl)-1-(1-methylethyl)ethyl]propanedinitrile (9g). GC yield 70%. Isolated yield 58% (2.8:1 mixture of diastereoisomers). A colorless liquid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.79 (d, J = 6.9 Hz, 3H), 0.90−1.11 (m, 13H), 1.39−1.44 (m, 1H), 1.52−1.64 (m, 1H), 1.68−1.80 (m, 2H), 1.80−2.21 (m, 9H), 3.79 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.96, 13.11, 13.24, 18.94, 19.37, 25.09, 25.46, 29.37, 30.06, 30.68, 32.05, 34.39, 36.16, 42.94, 112.55, 112.89, 128.80, 129.31. The minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.87 (d, J = 6.8 Hz, 3H), 3.82 (d, J = 4.3 Hz, 1H), other peaks were overlapped with the signals of the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.01, 13.17, 14.65, 18.54, 19.82, 25.09, 25.43, 29.17, 30.24, 30.68, 31.96, 34.60, 35.61, 43.15, 112.65, 112.80, 128.40, 129.88, other peaks were overlapped with the signals of the major isomer. HRMS calcd for $C_{19}H_{30}N_2$ 286.2407, found 286.2418.

2-[1,1-Diethyl-2-(*cis*-6-methyl-3,4-diphenylcyclohex-3-enyl)ethyl]propanedinitrile (9h). Isolated yield 45%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J = 7.4 Hz, 6H), 1.07 (d, J = 6.7 Hz, 3H), 1.51−1.73 (m, 6H), 2.07−2.36 (m, 4H), 2.50−2.55 (m, 1H), 2.69−2.75 (m, 1H), 3.67 (s, 1H), 6.95−7.11 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.05, 8.09, 13.80, 27.95, 28.39, 31.07, 32.22, 32.39, 36.99, 37.66, 39.36, 43.90, 112.24, 125.78, 125.85, 127.55, 127.64, 128.83, 133.12, 133.27, 142.90, 143.12. HRMS calcd for $C_{28}H_{32}N_2$ 396.2564, found 396.2580.

2-Cyano-3-isopropylheptanoic Acid Ethyl Ester (9i). GC yield 72%. Isolated yield 61% (1.2:1 mixture of diastereoisomers). A colorless liquid. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88−1.02 (m, 8H), 1.26−1.40 (m, 8H), 1.52−1.57 (m, 2H), 1.83−2.01 (m, 2H), 3.61 (d, J = 3.5 Hz, 1H), 4.24−4.30 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.77, 13.87, 19.05, 20.13, 22.74, 27.97, 29.57, 30.30, 39.62, 44.97, 62.58, 116.11, 166.93. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.62 (d, J = 5.57, 1H), other peaks were overlapped by the signals of the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.81, 13.86, 18.31, 21.55, 22.56, 29.35, 29.71, 29.97, 40.62, 44.87, 62.48, 115.95, 166.72. HRMS calcd for $C_{13}H_{23}NO_2$ 225.1729, found (M + 1) 226.1807.

3-Phenyl-2-phenylsulfonylheptanenitrile (9j). Isolated yield 89% (1.8:1 mixture of diastereoisomers). A colorless liquid. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83 (t, J = 7.6 Hz, 3H), 1.10−1.31 (m, 4H), 1.89−2.19 (m, 2H), 3.64 (ddd, J = 11.95, 11.91, 3.2 Hz, 1H), 4.04 (d, J = 2.9 Hz, 1H), 7.23−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.65, 22.07, 28.91, 30.94, 42.09, 63.45, 113.02, 127.43 (2C), 127.93, 129.01, 129.03, 129.47, 134.97, 136.69, 139.32. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J = 7.6 Hz, 3H), 1.10−1.31 (m, 4H), 1.89−2.19 (m, 2H), 3.56 (ddd, J = 9.69, 9.60, 5.6 Hz, 1H), 4.30 (d, J = 5.4 Hz, 1H), 7.23−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.63, 22.02, 28.85, 34.28, 43.25, 62.60, 113.43, 127.89, 128.44, 128.48, 129.15, 134.50, 136.45, 137.20, one peak was overlapped by the signals of the major isomer. HRMS calcd for $C_{19}H_{21}NO_2S$ 327.1293, found 327.1293.

2-Cyano-4-(*cis*-3,4-diethyl-6-methylcyclohex-3-enyl)-3-phenylbutyric Acid Ethyl Ester (9k). GC yield 97%. Isolated yield 90% (3.7:3.7:1.4:1 mixture of diastereoisomers). A colorless liquid. One of the major diastereoisomers: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.76−0.97 (m, 9H), 1.09 (t, J = 7.2 Hz, 3H), 1.42−1.99 (m, 12H), 3.41−3.45 (m, 1H), 3.62 (d, J = 6.4 Hz, 1H), 4.04−4.16 (m, 2H), 7.29−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.71, 13.49, 13.81, 13.85, 25.47, 25.58, 28.14, 32.50, 34.14, 34.71, 36.40, 43.52, 45.53, 62.70, 115.89, 128.22, 128.69, 128.85, 138.83, 139.33, 165.47. HRMS calcd for $C_{24}H_{33}NO_2$ 367.2511, found 367.2511.

2-[1-Cyano-2-(*cis*-3,4-diethyl-6-methylcyclohex-3-enyl)-ethylidene]propanedinitrile (9m). GC yield 87%. Isolated

(24) This compound was reported, but the NMR data were not available. Kazuhiko, M.; Kazuhisa, N.; Atsushi, T.; Yoshio, O. *J. Chem. Soc., Chem. Commun.* **1991**, *5*, 344−345.

yield 65%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92−0.99 (m, 9H), 1.69−2.21 (m, 10H), 2.66−2.68 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.00, 13.17, 15.46, 25.53, 30.91, 32.11, 35.17, 36.30, 38.09, 99.47, 109.68, 109.70, 113.52, 127.79, 130.44, 148.78. HRMS calcd for $C_{17}H_{21}N_3$ 267.1734, found 267.1852.

[2-(*cis*-3,4-Diethyl-6-methylcyclohex-3-enyl)-1-phenylethyl]bis(phenylsulfonyl)methane (9n). Isolated yield 24% (2.0:1 mixture of diastereoisomers). A colorless liquid. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.70 (d, J = 6.6 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.23−1.37 (m, 4H), 1.58−2.04 (m, 7H), 2.60 (td, J = 10.8, 3.1 Hz, 1H), 3.82−3.87 (m, 1H), 4.75 (d, J = 1.3 Hz, 1H), 7.21−7.99 9m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.08, 13.35, 13.85, 25.67, 25.83, 30.57, 30.82, 31.66, 34.98, 36.67, 42.80, 89.31, 127.33, 127.67, 128.60, 128.62, 128.83, 128.88, 129.25, 129.44, 129.92, 133.87, 134.59, 138.11, 140.17, 141.30. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.84−3.90 (m, 1H), 4.71 (d, J = 1.2 Hz, 1H), other peaks were overlapped by the signals of the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.71, 13.08, 13.15, 25.50, 25.62, 28.29, 30.62, 32.44, 37.00, 37.78, 42.77, 88.66, 127.28, 128.45, 128.60, 128.73, 128.83, 129.33, 129.48, 133.82, 133.88, 134.52, 134.62, 138.34, 140.39, 141.33. HRMS calcd for $C_{32}H_{38}O_4S_2$ 550.2211, found 520.2211.

General proCedure for the Preparation of 10. To a solution of zirconacyclopentane **8** (prepared from 1.1 mmol of Cp_2ZrCl_2)[12b,13b,19] was added ylidenemalononitrile (1.2−2 mmol) at −40 or 0 °C (Table 1) with stirring for the appropriate time (see Table 1). Then iodine (0.64 g, 2.5 mmol) was added and the reaction mixture was warmed to room temperature and stirred for an additional 1−3 h. The reaction mixture was quenched with 3 N HCl and extracted with Et_2O. Combined organic extracts were washed with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated in vacuo. Column chromatography on silica gel (hexane/EtOAc) afforded the products.

(3*R,4a*R**,8a*S**)-3-Phenyloctahydro-1*H*-naphthalene-2,2-dicarbonitrile (10b).** GC yield 86%. Isolated yield 73%. A colorless solid, mp 111−112 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.21 (ddddd, J = 12.8, 12.8, 12.8, 3.5, 3.5 Hz, 1H), 1.33−1.45 (m, 1H), 1.50−1.70 (m, 5H), 1.80−1.88 (m, 1H), 1.95−2.05 (m, 2H), 2.15 (dddd, J = 13.0, 13.0, 13.0, 3.5 Hz, 1H), 2.32 (dd, J = 14.2, 2.5 Hz, 1H), 2.45 (ddd, J = 13.3, 13.3, 12.9 Hz, 1H), 2.52 (dd, J = 14.2, 1.4 Hz, 1H), 3.00 (dd, J = 12.8, 2.9 Hz, 1H), 7.34−7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.90, 26.47, 26.88, 28.13, 31.70, 35.09, 36.26, 37.52, 41.76, 51.03, 116.00, 116.45, 128.53, 128.77, 128.80, 137.83. HRMS calcd for $C_{18}H_{20}N_2$ 264.1626, found 264.1617. Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 82.0; H, 7.81; N, 10.74.

(3*R,4a*S**,8a*S**)-6,7-Diethyl-3-phenyl-3,4,4a,5,8,8a-hexahydro-1*H*-naphthalene-2,2-dicarbonitrile (10d).** GC yield 84%. Isolated yield 62% (10:1 mixture of diastereoisomers). A white solid. The major isomer, mp 139−140 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93−1.02 (m, 6H), 1.55−2.50 (m, 12H), 2.63 (dd, J = 14.2, 1.5 Hz, 1H), 2.73−2.85 (m, 1H), 3.08 (dd, J = 12.8, 2.8 Hz, 1H), 7.25−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.19, 25.44, 25.54, 28.18, 29.15, 31.25, 34.80, 34.93, 37.31, 40.13, 50.91, 116.05, 116.52, 128.17, 128.55, 128.59, 128.66, 128.73, 137.62. HRMS $C_{22}H_{26}N_2$ 318.2095, found 318.2100. The minor isomer, mp 141−143 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94−1.01 (m, 6H), 1.76−2.40 (m, 14H), 3.26 (dd, J = 13.3, 3.4 Hz, 1H), 7.38−7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.17, 13.31, 25.45, 25.62, 28.24, 30.03, 30.66, 32.65, 33.96, 36.64, 41.03, 43.83, 114.35, 115.87, 128.34, 128.45, 128.59, 128.83, 128.85, 137.27. HRMS calcd for $C_{22}H_{26}N_2$ 318.2095, found 318.2097.

(3*R,4a*S**,8a*S**)-3,6,7-Triphenyl-3,4,4a,5,8,8a-hexahydro-1*H*-naphthalene-2,2-dicarbonitrile (10e).** Isolated yield 69%. A white solid. The major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.78−1.82 (m, 1H), 2.22−2.57 (m, 6H), 2.70 (d, J = 14.1 Hz, 1H), 2.96−3.02 (m, 1H), 3.15 (dd, J = 12.7, 2.8 Hz, 1H), 3.34−3.41 (m, 1H), 6.97−7.13 (m, 10H), 7.38−7.51 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.45, 31.16, 31.23, 34.77, 37.39, 37.93, 39.86, 50.91, 116.00, 116.30, 126.10, 126.16, 127.75, 127.77, 128.60, 128.78, 128.84, 128.89, 131.76, 132.22, 137.38, 142.30, 142.73. HRMS calcd for $C_{30}H_{26}N_2$ 414.2095, found 414.2099. The minor isomer, mp 228−230 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.95 (dd, J = 14.2, 3.2 Hz, 1H), 2.34−2.59 (m, 8H), 2.94−2.99 (m, 1H), 3.33 (dd, J = 13.2, 3.5 Hz, 1H), 6.96−7.48 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 30.08, 30.77, 31.38, 32.44, 36.80, 37.05, 41.07, 43.85, 114.23, 115.68, 126.31, 126.35, 127.87, 127.88, 128.57, 128.90, 128.98, 132.09, 132.33, 137.01, 142.34, 142.37. HRMS calcd for $C_{30}H_{26}N_2$ 414.2095, found 414.2080.

(3*S,4a*S**,8a*S**)-3-(2-Furyl)-6,7-diphenyl-3,4,4a,5,8,8a-hexahydro-1*H*-naphthalene-2,2-dicarbonitrile (10f).** Isolated yield 82% (2:1 mixture of diastereoisomers). A white solid. The major isomer, mp 135−138 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.92 (dt, J = 13.9, 2.9 Hz, 1H), 2.13−2.52 (m, 6H), 2.67 (dd, J = 14.3, 1.5 Hz, 1H), 2.90−3.02 (m, 1H), 3.22−3.34 (m, 1H), 3.36 (dd, J = 12.4, 3.0 Hz, 1H), 6.39−6.40 (m, 1H), 6.49 (d, J = 3.2 Hz, 1H), 6.95−7.12 (m, 10H), 7.45 (d, J = 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 28.16, 30.99 (2C), 33.95, 35.33, 37.67, 39.05, 44.62, 108.42, 110.54, 115.72, 116.35, 126.05, 126.10, 127.70, 128.71, 128.76, 131.60, 132.12, 142.20, 142.64, 142.88, 151.14. HRMS $C_{28}H_{24}N_2O$ 404.1887, found 404.1890. The minor isomer, mp 208−209 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.03 (dd, J = 14.5, 3.2 Hz, 1H), 2.29−2.49 (m, 8H), 2.92−2.96 (m, 1H), 3.53 (dd, J = 13.1, 3.5 Hz, 1H), 6.37−6.38 (m, 1H), 6.43 (d, J = 3.3 Hz, 1H), 6.95−7.21 (m, 10H), 7.41−7.43 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.85, 30.16, 31.20, 31.34, 35.91, 36.89, 37.99, 39.28, 108.40, 110.52, 113.83, 115.66, 126.24, 126.27, 127.80, 128.79, 128.87, 131.94, 132.11, 142.19, 142.27, 142.94, 151.13. HRMS $C_{28}H_{24}N_2O$ 404.1887, found 404.1877.

Ethyl (1*R,2*S**)-1-cyano-2-phenyl-1-cyclohexanecarboxylate (10h).** Isolated yield 88%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J = 7.2 Hz, 3H), 1.30−1.51 (m, 1H), 1.85−2.17 (m, 7H), 3.05 (dd, J = 12.9, 3.1 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 7.24−7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.81, 21.63, 25.23, 28.65, 34.51, 48.74, 52.93, 62.00, 117.91, 127.56, 127.85, 128.20, 139.64, 168.54. HRMS calcd for $C_{16}H_{19}NO_2$ 257.1416, found 257.1416. Methyl (1*R**,2*S**)-1-cyano-2-phenyl-1-cyclohexanecarboxylate was also prepared in 70% isolated yield to compare the NMR data of the known compound. The spectral data were consistent with published values.[25]

A Representative Procedure for the Reaction of Benzylidenemalononitrile (2a) with Zirconacyclopentenes. Synthesis of 12a and 13a. To a solution of diethylzirconacyclopentene **11** (prepared from 3.6 mmol of Cp_2ZrCl_2 and 7.2 mmol of EtMgBr) in THF (20 mL) was added benzylidenepropanedinitrile (6.6 mmol, 1.02 g) at 0 °C and the mixture was stirred for 3 h at room temperature. The reaction mixture was then quenched with 3 N HCl at room temperature or with iodine (6.6 mmol, 1.67 g) at 0 °C. The reaction mixture was extracted with Et_2O (3 × 30 mL), and combined organic extracts were washed with water, aq $NaHCO_3$, and brine and dried ($MgSO_4$). Filtration and evaporation followed by column chromatography on silica gel (hexane/EtOAc) afforded the products.

2-(4-Ethyl-1-phenyl-4*E*-heptenyl)propanedinitrile (12a). GC yield 81%. Isolated yield 67%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88−0.96 (m, 6H), 1.81−2.14 (m, 8H), 3.16−3.22 (m, 1H), 3.89 (d, J = 6.2 Hz, 1H), 5.01 (t, J = 7.2 Hz, 1H), 7.29−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.20, 14.63, 20.84, 22.64, 30.20, 30.24, 33.33, 45.82, 112.05, 127.95, 128.02, 128.85, 129.24, 136.69, 138.02. HRMS calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1788.

(25) (a) Avenoza, A.; Cativiela, C.; Paris, M.; Peregrina, J. M. *Tetrahedron: Asymmetry* **1995**, *6*, 1409−1418. (b) Cativiela, C.; Avenoza, A.; Paris, M.; Peregrina, J. M. *J. Org. Chem.* **1994**, *59*, 7774−7778.

2-(4-Ethyl-5-deuterio-1-phenyl-4*E*-heptenyl)-2-deuteriopropanedinitrile (12a-*D*). GC yield 81%. Isolated yield 68%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 7.6 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H), 1.80−2.11 (m, 8H), 3.15−3.21 (m, 1H), 3.89 (d, J = 6.3 Hz, 1H), 7.29−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.21, 14.62, 20.74, 22.62, 30.18, 30.23, 33.26, 45.75, 112.17, 127.54, 128.05, 128.82, 129.21, 136.76, 137.95. HRMS calcd for $C_{18}H_{20}D_2N_2$ 267.1845, found 267.1843.

2-(4-Butyl-1-phenyl-4*E*-nonenyl)propanedinitrile (12b). GC yield 79%. Isolated yield 60%. A pale yellow liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83−0.97 (m, 6H), 1.20−1.35 (m, 8H), 1.81−2.20 (m, 8H), 3.16−3.22 (m, 1H), 3.89 (d, J = 6.2 Hz, 1H), 5.03 (t, J = 7.1 Hz, 1H), 7.29−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.99, 14.01, 22.46, 22.72, 27.41, 29.34, 30.20, 30.27, 30.60, 32.21, 33.71, 45.82, 111.96, 126.98, 128.01, 128.88, 129.26, 136.67, 136.94. HRMS calcd for $C_{22}H_{30}N_2$ 322.2409, found 322.2397.

2-(1,4,5-Triphenyl-4*E*-pentenyl)propanedinitrile (12c). GC yield 77%. Isolated yield 51%. A pale yellow liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.01−2.13 (m, 2H), 2.31−2.38 (m, 1H), 2.47−2.54 (m, 1H), 3.22−3.07 (m, 1H), 3.76 (d, J = 6.2 Hz, 1H), 6.28 (s, 1H), 6.88−6.91 (m, 2H), 7.04−7.11 (m, 5H), 7.24−7.32 (m, 5H), 7.37−7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.93, 30.25, 37.34, 45.62, 111.73, 126.57, 127.43, 127.82, 127.92, 128.06, 128.47, 128.83, 128.99, 129.04, 129.35, 136.15, 136.70, 139.83, 140.15. Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.25; H, 6.34; N, 7.70.

2-(1,3-Diphenylnonyl)propanedinitrile (12d). GC yield 55%. Isolated yield 43%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, J = 7.1 Hz, 3H), 0.92−1.32 (m, 8H), 1.52−1.62 (m, 2H), 2.17 (ddd, J = 12.1, 12.1, 3.2 Hz, 1H), 2.20−3.30 (m, 1H), 2.37 (ddd, J = 12.2, 12.2, 2.4 Hz, 1H), 2.83 (ddd, J = 11.8, 6.3, 3.5 Hz, 1H), 3. 66 (d, J = 6.2 Hz, 1H), 6.96−7.46 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.01, 22.54, 27.28, 29.12, 30.51, 31.60, 37.60, 38.52, 53.05, 44.26, 111.84, 111.87, 126.81, 127.59, 128.12, 128.78, 128.92, 129.27, 136.28, 143.2. HRMS calcd for $C_{24}H_{28}N_2$ 344.2252, found 344.2265.

2-(4-Ethyl-5-iodo-1-phenyl-4*Z*-heptenyl)propanedinitrile (13a). GC yield 76%. Isolated yield 65%. A pale brown liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J = 7.5 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H), 2.06−2.18 (m, 6H), 2.51 (q, J = 7.4 Hz, 2H), 3.20−3.22 (m, 1H), 3.98 (d, J = 6.1 Hz, 1H), 7.36−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.47, 14.68, 24.58, 29.87, 30.11, 34.94, 39.62, 46.25, 107.93, 111.90, 111.96, 128.00, 128.92, 129.17, 136.28, 142.89. HRMS calcd for $C_{18}H_{21}IN_2$ 392.0749, found 392.0734.

2-(5-Iodo-1,4,5-triphenyl-4*E*-pentenyl)propanedinitrile (13c). GC yield 69%. Isolated yield 65%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.12 (q, J = 8.0 Hz, 2H), 2.67−2.78 (m, 2H), 3.18−3.23 (m, 1H), 3.85 (d, J = 6.1 Hz, 1H), 6.87−7.10 (m, 10H), 7.24−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.54, 30.21, 42.44, 45.95, 101.43, 111.63, 111.68, 127.13, 127.28, 127.65, 128.07, 128.17, 128.91, 129.03, 129.25, 129.74, 135.86, 138.83, 144.04, 146.81. HRMS calcd for $C_{26}H_{21}IN_2$ 488.0749, found 488.0732.

2-[3-(2-Iodophenyl)-1-phenylnonyl]propanedinitrile (13d). Isolated yield 41%. A pale brown liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83 (t, J = 6.6 Hz, 3H), 1.01−1.59 (m, 10H), 2.26−2.45 (m, 2H), 2.86−2.91 (m, 2H), 3.71 (d, J = 6.2 Hz, 1H), 6.91 (ddd, J = 7.7, 7.5,1.4 Hz, 1H), 7.11−7.47 (m, 7H), 7.78 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.02, 22.54, 26.66, 29.24, 30.58, 31.56, 37.51, 38.10, 44.25, 45.70, 103.01, 111.82, 111.86, 126.61, 128.25, 128.38, 128.96, 129.01, 129.41, 136.02, 139.91, 145.78. HRMS calcd for $C_{24}H_{27}IN_2$ 470.1219, found 470.1225.

2-[2-(*cis*-3,4-Diethyl-6-iodomethylcyclohex-3-enyl)-1-phenylethyl]propanedinitrile (17). The title compound was obtained by iodinolysis of the reaction mixture at −40 °C. Isolated yield 38% (1.5:1 mixture of diastereoisomers). A colorless liquid. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83−0.98 (m, 6H), 1.85−2.01 (m, 12H), 3.06−3.40 (m, 3H), 3.84 (d, J = 6.4 Hz, 1H), 7.33−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 9.57, 13.75, 13.85, 25.89, 25.94, 31.01, 31.28, 32.48, 33.59, 34.07, 41.22, 44.97, 111.71, 111.82, 128.29, 128.41, 128.54, 129.56, 129.71, 135.96. Minor isomer: ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.64, 13.56, 13.70, 25.74, 25.86, 30.75, 33.05, 33.50, 34.07, 35.22, 39.59, 45.20, 111.74, 111.84, 129.04, 129.18, 129.47, 129.79, 129.94, 136.71. HRMS calcd for $C_{22}H_{27}IN_2$ 446.1219, found 446.1219.

Cyclization of 17 to 10d under Controlled Reaction Conditions. To a THF solution of **17** (diastereomeric ratio is 1:1) was added 1 equiv of NaH at room temperature with stirring for 3 h; **10d** was formed in 90% GC yield with the same diastereomeric ratio. Addition of LDA (1 equiv) to the THF solution of **17** (diastereomeric ratio is 1:1) at −60 °C for 1 h was followed by the addition of Cp_2ZrX_2 (X= Cl or I, 1 equiv) at the same temperature with stirring for 1 h. The mixture was warmed to room temperature and stirred for 12 h. **10d** was formed with increased diastereomeric ratio (for X = Cl, the diastereomeric ratio is 1.8:1, 90% GC yield; for X = I, the diastereomeric ratio is 5:1, 52% GC yield).

Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **10b** and **10d** and 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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