Zirconium-Mediated Cross-Coupling of Terminal Alkynes and Vinyl Bromides: Selective Synthesis of Cyclobutene and 1,3-Diene Derivatives

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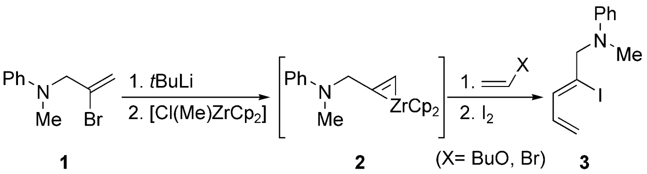
Abstract: A diastereoselective synthesis of 1,3-butadiene or cyclobutene derivatives by a zirconium-mediated reaction of alkenyllithium compounds and vinyl bromides is reported. The key steps involve the generation of zirconocene–alkyne complexes from haloalkenes and subsequent coupling with alkenyl bromides. Thus, formally the process supposes the cross-coupling reaction between a terminal alkyne and an alkenyl bromide. Moreover, the use of butyl vinyl ether instead of vinyl bromide as the unsaturated system allows an alternative access to different 1,3-butadiene regioisomers.

Keywords: dienes · C–C coupling · cross-coupling · cyclobutenes · zirconium

Introduction

Low-valent metals from the two ends of the transition series have been widely used for the reductive coupling of unsaturated molecules.[1] Usually, this process occurs through a metallacycle intermediate which can be easily transformed into a variety of interesting products.[2] In the last few years, the development of new synthetic methodologies mediated by organozirconium compounds has provided a variety of possibilities for the efficient preparation of a multitude of organic molecules.[3] Particularly interesting is the functionalization of unactivated alkynes through the formation of zirconacycles from a zirconocene–alkyne complex.[4] The Negishi system,[5] which is used for the generation of these zirconocene–alkyne complexes, has become a powerful tool in organic synthesis. This reagent has been successfully used in the key step in the synthesis of several natural products.[6] However, a major restriction of this system is that substrates containing terminal alkynes cannot be used, presumably due to the ready oxidative addition of the electron-rich metallocene to the acidic acetylene hydrogen atom.[7] An alternative method for the formation of zirconocene–alkyne complexes involves a β-hydrogen activation process.[8] By using this approach we reported the first zirconium-mediated intramolecular coupling of terminal alkynes.[9] Moreover, back in 1995 we published for the first time zirconium-mediated coupling reactions with electron-rich olefins to obtain functionalized 1,3-butadienes (Scheme 1).[10]



Scheme 1. Zirconium-mediated cross-coupling reaction of alkenyl bromides and enol ethers or vinyl bromide. Cp = cyclopentadiene.

Herein we report a more detailed study of this reaction. Thus, we have used different vinyl lithium derivatives as synthetic equivalents of terminal alkynes in zirconium-mediated coupling reactions with vinyl bromides and vinyl ethers. These reactions allowed us to access different 1,3-butadiene regioisomers by just varying the nature of the olefin used.

Results and Discussion

Zirconium-mediated cross-coupling of *N*-methyl-*N*-propargyl aniline and vinyl bromides: As shown in Scheme 1, treatment of *N*-(2-bromoallyl)-*N*-methylaniline (**1**) with *tert*-butyllithium at −78 °C followed by reaction with zirconocene methyl chloride at temperatures ranging between −78 and 20 °C affords the zirconacyclopropene **2**. As reported in our previous communication, [10a] complex **2** reacts with vinyl bromide **4a** (R = H) to form dienes **3** (57 % yield) or **6** (59 %

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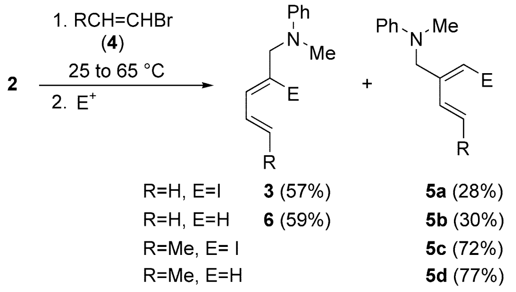
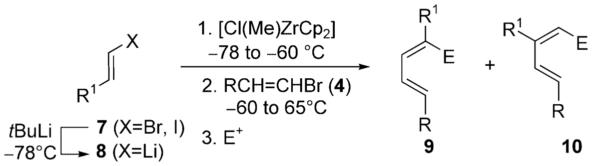
DOI: 10.1002/chem.200305337

yield) depending on the electrophile used in last step of the reaction (iodine or aqueous hydrochloric acid, respectively; Scheme 2). However, in a careful study of this reaction we have also observed the formation of dienes **5a** (28% yield) and **5b** (30% yield) as minor products of the reaction. Note that dienes **5a** and **5b** are regioisomers of **3** and **6**, respectively. When we tried to extend the reaction to other vinyl bromides such as 1-bromo-1-propene (**4b**; R = Me), surprisingly, only dienes **5c**,**d** were obtained in high yield and the expected diene regioisomers analogous to **3** or **6** were not observed (Scheme 2).



Scheme 2. Zirconium-mediated cross-coupling reaction with alkenyl bromides **4**.

Zirconium-mediated coupling reactions of alkenyllithium derivatives and vinyl bromides: Taking into account the results described above for the propargyl aniline–zirconocene complex **2**, we decided to investigate the behavior of other vinyl lithium derivatives as synthetic equivalents of terminal alkynes in zirconium-mediated coupling reactions with vinyl bromides. Thus, the reaction of organolithium compounds **8**, easily obtained from the corresponding vinyl bromides **7** and *tert*-butyllithium at −78 °C, with zirconocene methyl chloride in tetrahydrofuran at temperatures ranging between −78 and −60 °C, followed by addition of different vinyl bromides **4** and warming to 65 °C, led after reaction with the appropriate electrophile to dienes **9** or **10** in different ratios depending on the structure of the starting organolithium compound and the structure of the vinyl bromide used (Scheme 3 and Table 1).



Scheme 3. 1,3-butadienes **9** and/or **10** from the zirconium-mediated cross-coupling reaction of organolithium derivatives **8** and alkenyl bromides **4**.

From the analysis of the results summarized in Table 1 some trends can be inferred. The use of vinyl bromide **4a** led to mixtures of dienes **9** and **10** when the R^1 group of the alkenyllithium **8** was an alkyl chain (Table 1, entries 1,2). However, the major products of the reactions were the dienes **10**, which were easily separated from the minor products **9**. To our surprise, when the reactions were carried out with organolithium compounds **8c**,**d**, where R^1 is an aromatic group, we obtained exclusively the'extended' dienes **9** and the corresponding'branched' dienes **10** were not observed in the crude mixtures of the reactions (Table 1, entries 3,4). When the phenyl-substituted vinyl bromide *trans*-**4c** was used in the reaction with alkyl-substituted organolithium derivatives **8a**,**b**, the reaction also afforded mixtures of the dienes **9** and **10**, with the former being the major regioisomer (Table 1, entries 5,6). Interestingly, all experiments carried out with alkyl-substituted vinyl bromides **4b**,**d** led, independently of the structure of the starting organolithium

Table 1. 1,3-butadienes **9** and/or **10** from organolithium derivatives **8** and alkenyl bromides **4**.

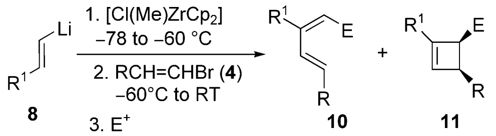
Entry	R^1	**8**	R	**4**	E^+ (E)	Product	Yield [%][a]
1	$PhCH_2$	**8a**	H	**4a**	H_2O (H)	**9a**/**10a**	22/60
2	$Ph(CH_2)_3$	**8b**	H	**4a**	H_2O (H)	**9b**/**10b**	24/62
3	Ph	**8c**	H	**4a**	H_2O (H)	**9c**	69
4	4-MeC_6H_4	**8d**	H	**4a**	H_2O (H)	**9d**	72
5	$PhCH_2$	**8a**	Ph	*trans*-**4c**	H_2O (H)	**9e**/**10c**	54/32
6	$Ph(CH_2)_3$	**8b**	Ph	*trans*-**4c**	H_2O (H)	**9f**/**10d**	55/35
7	$PhCH_2$	**8a**	Me	**4b**[b]	H_2O (H)	**10e**	88
8	$PhCH_2$	**8a**	Me	**4b**[b]	D_2O (D)	**10f**	83
9	$PhCH_2$	**8a**	Me	*cis*-**4b**	D_2O (D)	**10f**	77
10	$PhCH_2$	**8a**	Me	*trans*-**4b**	D_2O (D)	**10f**	80
11	$Ph(CH_2)_2$	**8e**	Me	**4b**[b]	H_2O (H)	**10g**	70
12	$Ph(CH_2)_3$	**8b**	Me	**4b**[b]	H_2O (H)	**10h**	71
13	Ph	**8c**	Me	**4b**[b]	I_2 (I)	**10i**	65
14	4-MeC_6H_4	**8d**	Me	**4b**[b]	I_2 (I)	**10j**	71
15	*t*Bu	**8f**	Me	**4b**[b]	I_2 (I)	**10k**	69
16	$PhCH_2$	**8a**	Hex	*trans*-**4d**	H_2O (H)	**10l**	81
17	$Ph(CH_2)_3$	**8b**	Hex	*trans*-**4d**	H_2O (H)	**10m**	77

[a] Isolated yield based on starting alkenyl halides **7**. [b] 1:1 *cis*/*trans* mixture.

Abstract in Spanish: *Se describe una síntesis diastereoselectiva de 1,3-butadienos o ciclobutenos a través de una reacción entre compuestos alquenillitio y bromuros de alquenilo promovida por complejos de zirconio. Los pasos claves de este proceso son la generación de un complejo alquino-zirconoceno a partir de un haloalqueno y la posterior reacción de acoplamiento con bromuros de alquenilo. Así, formalmente el proceso supone el acoplamiento entre un alquino terminal y un bromuro de alquenilo. Además, el uso de viniléteres como sistema insaturado en lugar de bromuro de vinilo permite acceder alternativamente a los 1,3-butadienos regioisómeros.*

compound **8**, to the exclusive isolation of the corresponding branched dienes **10e–m**, while extended dienes **9** were not observed in the crude mixtures of any of these reactions (Table 1, entries 7–17). Highly remarkable are the results from the zirconium-promoted coupling reaction of **8a** and 1-bromo-1-propene (**4b**; *cis*, *trans*, or a mixture of both stereoisomers), in which, independently of the stereochemistry of **4b**, the same stereoisomer of diene **10f** is formed when deuterium oxide was used as the electrophile (Table 1, entries 8–10).

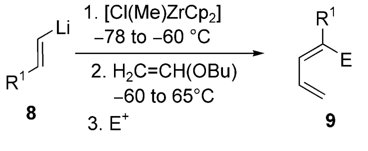
Preparation of cyclobutene derivatives: To gain some insight into the mechanism of the reaction we performed a set of experiments with several organolithium compounds **8** and vinyl bromides **4** while varying the temperature of the reaction. Also, with these experiments we wanted to study the influence of the temperature on the ratio of dienes **9**/**10** in those cases where mixtures of both were obtained. The reactions were carried out as described above but the temperature was maintained at 25 °C for 18 h. Under these conditions formation of the expected dienes **10** was not observed and instead cyclobutenes **11** were isolated (Scheme 4 and Table 2). The structure of cyclobutenes **11** was determined by NMR spectroscopy experiments.



Scheme 4. Cyclobutene derivatives **11** from the zirconium-mediated cross-coupling reaction of organolithium derivatives **8** and alkenyl bromides **4**.

Analysis of Table 2 showed us several interesting features. For example, when vinyl bromide **4a** was used, variable amounts of dienes **9** were obtained together with major products **11** (Table 2, entries 1,2). It should be noted that in these cases the amount of **9** is similar to that obtained when the reaction was carried out at 65 °C (see Scheme 3 and Table 1, entries 1,2). More interesting results were obtained from several experiments performed with organolithium compound **8a** and 1-bromo-1-propene (**4b**). As mentioned before, at 25 °C the reaction gave exclusively cyclobutenes **11c,d** depending only on the electrophile used in last step of the reaction (Table 2, entries 3,4). However, when the reaction was warmed to 40 °C for 2 h, a mixture of diene **10f** and cyclobutene **11d** was obtained (Table 2, entry 5). At this point it should be remembered that the reaction at 65 °C led exclusively to diene **10f** (see Scheme 3 and Table 1, entry 8). Moreover, when this reaction was slowly warmed from 25 to 65 °C and followed by thin-layer chromatography (TLC), formation of cyclobutene **11** could be observed at first and then the spot corresponding to this product slowly vanished and a new spot corresponding to diene **10** appeared; finally, after 1 h at 65 °C only the spot corresponding to the latter compound was observed. Even more surprising results were obtained when the reaction was carried out with *cis*-**4b**, *trans*-**4b**, or the mixture of both stereoisomers (Table 2, entries 4,6,7). All these experiments led to the same diastereoisomer of the cyclobutene **11d**, as unequivocally determined by NMR spectroscopy experiments.

Zirconium-mediated coupling reactions of alkenyllithium derivatives and butyl vinyl ether: As shown in Scheme 3 and Table 1 (entries 1,2), the reaction of zirconocene–alkyne complexes derived from an alkyl-substituted organolithium compound **8a,b** with vinyl bromide **4a** led to separable mixtures of dienes **9** and **10**, with the branched diene **10** being the major product of the reaction. Intrigued by the possibility of obtaining diene **9** as the main product of the reaction and taking into account our previously reported results on the reaction of zirconocene–alkyne complexes with vinyl ethers,[10a] we decided to carry out a set of experiments with different organolithium compounds **8** and butyl vinyl ether (Scheme 5 and Table 3). If this succeeded, we would be able to obtain either diene **9** or **10** only by choosing between vinyl bromide or butyl vinyl ether as the counterpart in the zirconium-mediated coupling reaction of organolithium derivatives **8**.



Scheme 5. 1,3-butadienes **9** from the zirconium-mediated cross-coupling reaction of organolithium derivatives **8** and butyl vinyl ether.

Table 2. Cyclobutenes **11** from organolithium derivatives **8** and alkenyl bromides **4**.

Entry	R^1	**8**	R	**4**	T [°C]	E$^+$ (E)	Product	Yield [%][a]
1	$PhCH_2$	**8a**	H	**4a**	25	H_2O (H)	**11a**[b]	56
2	$Ph(CH_2)_2$	**8e**	H	**4a**	25	H_2O (H)	**11b**[c]	61
3	$PhCH_2$	**8a**	Me	**4b**[d]	25	H_2O (H)	**11c**	72
4	$PhCH_2$	**8a**	Me	**4b**[d]	25	D_2O (D)	**11d**	75
5	$PhCH_2$	**8a**	Me	**4b**[d]	40	D_2O (D)	**10f/11d**	35/44
6	$PhCH_2$	**8a**	Me	*cis*-**4b**	25	D_2O (D)	**11d**	68
7	$PhCH_2$	**8a**	Me	*trans*-**4b**	25	D_2O (D)	**11d**	72
8	$Ph(CH_2)_2$	**8e**	Me	**4b**[d]	25	H_2O (H)	**11e**	70
9	$Ph(CH_2)_3$	**8b**	Me	**4b**[d]	25	H_2O (H)	**11f**	66

[a] Isolated yield based on starting alkenyl halides **7**. [b] 24 % of **9a** was also isolated. [c] 21 % of **9b** was also isolated. [d] 1:1 *cis*/*trans* mixture.

The reaction was performed following a procedure similar to the one before described. Thus, after addition of the butyl vinyl ether at −60 °C the solution was allowed to warm first to room temperature and then to 65 °C for one hour. After addition of the corresponding electrophile the reaction was worked up to obtain extended dienes **9** (Scheme 5 and

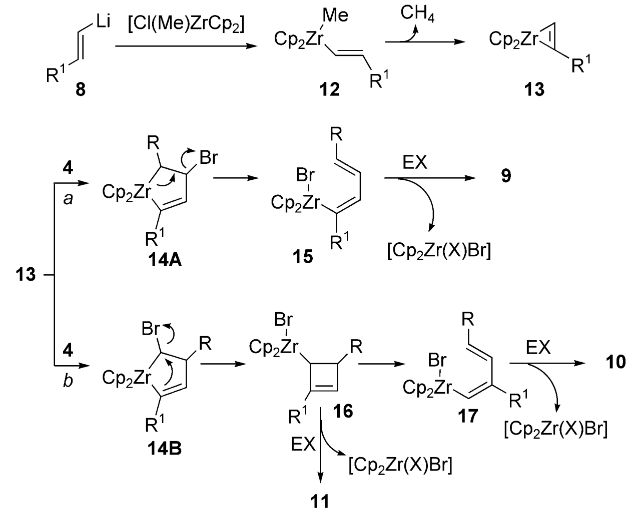
Table 3. 1,3-butadienes **9** from organolithium derivatives **8** and butyl vinyl ether.

Entry	R^1	**8**	E^+ (E)	Product	Yield [%][a]
1	$PhCH_2$	**8a**	I_2 (I)	**9g**	82
2	$Ph(CH_2)_2$	**8e**	H_2O (H)	**9h**	85
3	$Ph(CH_2)_3$	**8b**	H_2O (H)	**9b**	86
4	Ph	**8c**	H_2O (H)	**9c**	78
5	$4\text{-}MeC_6H_4$	**8d**	H_2O (H)	**9d**	80

[a] Isolated yield based on starting alkenyl halides **7**.

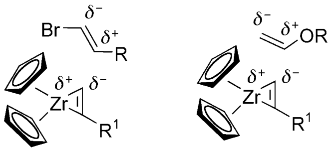
Table 3). No traces of regioisomer dienes **10** were observed in any case in the crude mixtures of the reactions. Maybe, the most interesting results were obtained from the reaction with alkyl-substituted organolithium compounds **8a,b,e** (Table 3, entries 1–3). These results can be considered complementary to those obtained from the reaction with vinyl bromide **4a** (see Scheme 3 and Table 1, entries 1,2). On the other hand, the reactions with aromatic-substituted organolithium derivatives **8c,d** led to extended dienes **9c,d** with either vinyl bromide (Table 1, entries 3,4) or butyl vinyl ether (Table 3, entries 4,5).

Mechanisms of the reactions: A plausible mechanism that explains the formation of dienes **9** or **10** and cyclobutene **11** is outlined in Scheme 6. First, addition of organolithium compound **8** to zirconocene methyl chloride gives the methyl(vinyl)zirconocene complex **12**. A cyclometalation reaction and subsequent elimination of methane leads to zirconocene–alkyne derivative **13**. The insertion of the double bond of the vinyl bromide takes place regioselectively at the less hindered zirconium–carbon bond of **13**. However, depending on the orientation of the vinyl bromide during the insertion step, two different zirconacyclopentene derivatives, **14A** or **14B**, can be obtained. Intermediate **14A** can undergo *β* elimination of bromine to give butadiene zirconocene derivative **15**, which gives diene **9** after reaction with an electrophile (path *a* in Scheme 6). Reaction with butyl vinyl ether also follows this mechanism to give diene **9** in all cases. On the other hand, formation of diene **10** and cyclobutene **11** can be understood from intermediate **14B** through an intramolecular migratory insertion process to afford cyclobutene–zirconocene complex **16**.[11] Quenching of this intermediate with the electrophile leads to cyclobutene derivative **11**. Moreover, thermal cleavage of cyclobutene complex **16** affords the new diene–zirconocene complex **17**, which gives diene **10** after reaction with the electrophile. Formation of diene **10** and cyclobutene **11** from the same intermediate **16** seems undoubted from analysis of the results summarized in Tables 1 and 2 (compare entries 4 and 5 of Table 2 with entry 8 of Table 1). Thus, the experiments carried out at room temperature led to cyclobutene **11**, whereas at higher temperatures the ring-opening process is favored to give **17** and finally diene **10**.



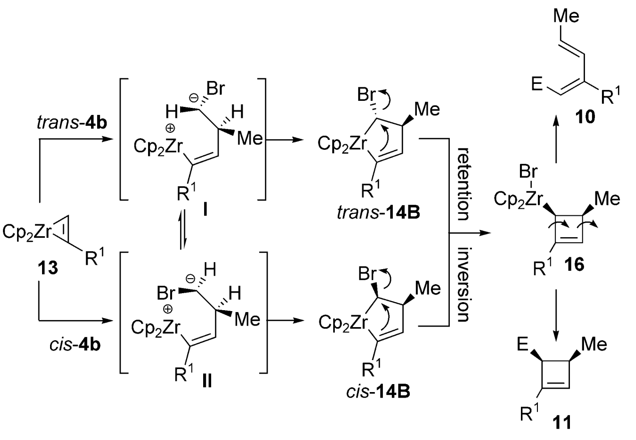
Scheme 6. Proposed mechanism for the formation of dienes **9** and **10** and cyclobutenes **11**.

The different outcome of the reaction leading to dienes **9** or **10** when vinyl bromides **4a–d** are used can be explained by a combination of electronic and steric effects. As represented in Scheme 6 formation of one or the other diene only depends on the orientation of the vinyl bromide in the insertion process to afford **14A** or **14B**. The electronic effects favor the orientation depicted in Scheme 7 to give regioisomer **14B** and finally diene **10**.[12] However, steric hindrance between the Cp ligands of the zirconocene moiety and the bromide or the R group also has to be taken into account. Thus, when vinyl bromide **4a** (R=H) is used, the electronic effects favor formation of **14B** but the steric factors favor the regioisomer **14A**. These two opposite effects would explain the formation of mixtures of dienes **9** and **10** in certain cases. When the vinyl bromide has an alkyl substituent (**4b** or **4d**) there is a comparative hindrance between the Cp ligands and the bromine atom or R group. In these cases the electronic effects dominate and formation of **14B** and finally diene **10** is preferred. The formation of mixtures of dienes **9** and **10** when *β*-bromostyrene (**4c**) is used could presumably be attributed to the comparative steric and electronic effects between the bromine and the phenyl group. Thus, both orientations are possible in the insertion reaction of **4c** into **13** and mixtures of **9** and **10** are obtained. Finally, in the insertion reaction of vinyl ethers, both the electronic and steric effects favor the formation of diene **9** from an intermediate analogous to **14A**, as depicted in Scheme 7 (see also Scheme 6).[12]



Scheme 7. Orientation of alkenyl bromides and enol ethers during the insertion process. Electronic and steric effects.

Probably, the most surprising and intriguing results described in this work are those that refer to the formation of the same diastereoisomer of cyclobutadiene **11d** independently



Scheme 8. Proposed mechanism for the formation of the same diastereiosomer of **10** or **11** from *trans*-**4b** or *cis*-**4b**.

of the *cis* or *trans* geometry of the vinyl bromide **4b**. Although more detailed studies must be done, we tentatively propose the mechanism depicted in Scheme 8 to explain these facts. Thus, we think that the insertion of vinyl bromide **4b** into the zirconium–carbon bond is a nonsynchronous process, which formally generates intermediates **I** or **II** from *trans*-**4b** or *cis*-**4b**, respectively.[13] Rotation around the σ bond would allow the conversion of one intermediate into the other. Formation of compounds **10** and **11** could be explained both from *trans*-**14B** and from *cis*-**14B**. From *trans*-**14B**, a migratory insertion reaction with retention of configuration would lead to **16**. Alternatively, a migratory insertion reaction with inversion of configuration on *cis*-**14B** would also lead to compound **16**. Finally, a conrotatory cleavage of intermediate **16** affords diene **17** (precursor of diene **10**), or reaction of **16** with the corresponding electrophile gives cyclobutene **11** where the Me and E groups are in a *cis* arrangement.

Conclusion

We have reported a diastereoselective synthesis of 1,3-butadiene or cyclobutene derivatives by a zirconium-mediated reaction of alkenyllithium compounds and vinyl bromides. The reaction is proposed to proceed through the formation of an alkyne–zirconocene intermediate and thus, formally, this process supposes the cross-coupling reaction between a terminal alkyne and an alkenyl bromide. Remarkably, the insertion reaction occurs with complete regioselectivity with respect to the zirconium complex and also with respect to the alkenyl bromide in those cases where this is alkyl-substituted. Moreover, the use of butyl vinyl ether instead of vinyl bromide as the unsaturated system allowed an alternative access to different 1,3-butadiene regioisomers.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 with oven-dried glassware and syringes. Tetrahydrofuran (THF), hexane, and Et_2O were distilled over sodium benzophenone ketyl under N_2 immediately prior to use, and CH_2Cl_2 was distilled over P_2O_5. The solvents used in column chromatography, hexane and EtOAc, were distilled before use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230–240 mesh. ^{1}H NMR (200, 300, 400 MHz) and ^{13}C NMR (50.5, 75.5, 100 MHz) spectra were measured at room temperature on Bruker AC-200, AC-300, and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$ ppm, ^{1}H NMR) or $CDCl_3$ ($\delta = 77.00$ ppm, ^{13}C NMR) as the internal standard. Carbon multiplicities were assigned by DEPT techniques. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on a Perkin–Elmer 2400 microanalyzer.

General procedure for the preparation of dienes 3, 5, 6, 9, and 10: *tert*-Butyllithium (2 mmol) was added to a stirred solution of the required alkenyl bromide (or iodide) **1** or **7** (1 mmol) in dry THF (10 mL) at −78 °C. After being stirred at this temperature for 30 min, the solution was added dropwise through a cannula to a stirred solution of bis(cyclopentadienyl)zirconium methyl chloride (1.2 mmol) in dry THF (10 mL) at −78 °C. After 30 min at this temperature, an excess of the appropriate alkenyl bromide **4** (3–10 mmol; 10 mmol of butyl vinyl ether can also be used, see Table 3) was added. The mixture was allowed to warm to room temperature and then heated to reflux for 3 h. The reaction was cooled to room temperature and the required electrophile was added (an excess of water, deuterium oxide, or iodine (2 mmol)). After 1 hour, the reaction was worked up by addition of water (20 mL) or a saturated solution of sodium thiosulphate (20 mL, when iodine was used as electrophile) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated, and the residue was purified by column chromatography to give compounds **3**, **5**, **6**, **9**, or **10**.

***N*-[(*Z*)-2-Iodo-2,4-pentadienyl]-*N*-methylaniline (3) and *N*-{2-[(*E*)-2-iodomethylene]-3-butenyl}-*N*-methylaniline (5a)**: Alkenyl bromide **1** (0.23 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 (4:1)). **3**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$–7.21, 6.82–6.71 (2 × m, 5 H; ArH), 6.90 (dt, $J = 16.6$, 9.8 Hz, 1 H; C*H*=CH_2), 6.72 (d, $J = 9.8$ Hz, 1 H; CI=CH), 5.81–5.63 (m, 2 H; CH=CH_2), 4.60 (s, 2 H; NCH_2), 3.42 (s, 3 H; NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.4$, 138.0, 132.2, 129.1, 121.0, 117.0, 111.9, 107.2, 65.2, 38.3 ppm; HRMS (EI): calcd for $C_{12}H_{14}IN$: 299.0170; found: 299.0164; elemental analysis: calcd (%) for $C_{12}H_{14}IN$: C 48.18, H 4.72, N 4.68; found: C 48.35, H 4.63, N 4.51. **5a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$–7.28, 6.92–6.72 (2 × m, 6 H; ArH and $CH_2\delta$=C*H*), 6.39 (s, 1 H; CHI), 5.53 (d, $J = 17.8$ Hz, 1 H; C*H*H=CH), 5.46 (d, $J = 11.4$ Hz, 1 H; CH*H*=CH), 4.20 (s, 2 H; NCH_2), 3.05 (s, 3 H; NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.9$, 139.9, 136.8, 129.0, 117,4, 116.6, 111.8, 81.9, 56.0, 38.3 ppm; HRMS (EI): calcd for $C_{12}H_{14}IN$: 299.0170; found: 299.0166; elemental analysis: calcd (%) for $C_{12}H_{14}IN$: C 48.18, H 4.72, N 4.68; found: C 48.28, H 4.63, N 4.56.

***N*-[(*E*)-2,4-Pentadienyl]-*N*-methylaniline (6) and *N*-methyl-*N*-(2-methylene-3-butenyl)aniline (5b)**: Alkenyl bromide **1** (0.23 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 (4:1)). **6**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$–7.22, 6.81–6.71 (2 × m, 5 H; ArH), 6.50–6.10 (m, 2 H; C*H*=C*H*=CH_2), 5.75 (dt, $J = 14.7$, 5.5 Hz, 1 H; NCH_2C*H*=CH), 5.20–5.00 (m, 2 H; CH=CH_2), 4.0 (d, $J = 5.5$ Hz, 2 H; NCH_2), 3.00 (s, 3 H; NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 140.4$, 136.3, 132.0, 129.8, 129.0, 116.5, 116.4, 112.4, 54.2, 37.9 ppm; HRMS (EI): calcd for $C_{12}H_{15}N$: 173.1204; found: 173.1204; elemental analysis: calcd (%) for $C_{12}H_{15}N$: C 83.19, H 8.73, N 8.08; found: C 83.30, H 8.58, N 8.11. **5b**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$–7.21, 6.78–6.67 (2 × m, 5 H; ArH), 6.53 (dd, $J = 17.9$, 11.2 Hz, 1 H; CH_2=C*H*), 5.27 (d, $J = 17.9$ Hz, 1 H; C*H*H=CH), 5.17 (s, 1 H; C=C*H*H), 5.16 (d, $J = 11.2$ Hz, 1 H; CH*H*=CH), 5.06 (s, 1 H; C=CH*H*), 4.12 (s, 2 H; NCH_2), 3.05 (s, 3 H; NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.4$, 140.5, 137.4, 129.0, 116.0, 115.6, 113.4, 111.7, 53.7, 38.3 ppm; HRMS (EI): calcd for $C_{12}H_{15}N$: 173.1204; found: 173.1205; elemental analysis: calcd (%) for $C_{12}H_{15}N$: C 83.19, H 8.73, N 8.08; found: C 83.29, H 8.64, N 8.01.

***N*-{2-[(*E*)-Iodomethylene]-3-pentenyl}-*N*-methylaniline (5c)**: Alkenyl bromide **1** (0.23 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 (4:1)). **5c**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.40$–7.10, 6.85–6.60 (2×m, 5H; ArH), 6.50 (d, $J=16.1$ Hz, 1H; $CH_3CH{=}C\mathit{H}$), 6.18–5.85 (m, 2H; $CH_3C\mathit{H}$ and CHI), 4.10 (s, 2H; NCH_2), 2.98 (s, 3H; NCH_3), 1.89 (d, $J=6.7$ Hz, 3H; $C\mathit{H}_3CH$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=140.3$, 134.3, 131.5, 129.6, 129.0, 116.6, 112.4, 111.8, 78.5, 56.5, 38.3, 18.8 ppm; HRMS (EI): calcd for $C_{13}H_{16}IN$: 313.0327; found: 313.0324; elemental analysis: calcd (%) for $C_{13}H_{16}IN$: C 49.86, H 5.15, N 4.47; found: C 49.94, H 5.06, N 4.33.

***N*-Methyl-*N*-(2-methylene-3-pentenyl)aniline (5d)**: Alkenyl bromide **1** (0.23 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 (4:1)). **5d**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.29$–7.15, 6.80–6.60 (2×m, 5H; ArH), 6.21 (d, $J=16.1$ Hz, 1H; $CH_3CH{=}C\mathit{H}$), 6.76 (dq, $J=16.1$, 6.7 Hz, 1H; $CH_3C\mathit{H}$), 5.06 (s, 1H; $C{=}C\mathit{H}H$), 4.88 (s, 1H; $C{=}CH\mathit{H}$), 4.06 (s, 2H; NCH_2), 2.98 (s, 3H; NCH_3), 1.83 (d, $J=6.7$ Hz, 3 H; $C\mathit{H}_3CH$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.4$, 140.3, 131.7, 128.9, 124.9, 115.9, 112.8, 111.6, 54.2, 38.2, 18.5 ppm; HRMS (EI): calcd for $C_{13}H_{17}N$: 187.1361; found: 187.1360; elemental analysis: calcd (%) for $C_{12}H_{15}N$: C 83.37, H 9.15, N 7.48; found: C 83.45, H 9.13, N 7.37.

(*E*)-5-Phenyl-1,3-pentadiene (9a) and 2-benzyl-1,3-butadiene (10a): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9a**[14] and **10a**[15] were in complete accordance with literature values.

(*E*)-7-Phenyl-1,3-heptadiene (9b) and 2-(3-phenylpropyl)-1,3-butadiene (10b): Alkenyl iodide **7b** (0.27 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol) or butyl vinyl ether (1.29 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9b**[16] were in complete accordance with literature values. **10b**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.38$–7.20 (m, 5H; ArH), 6.41 (dd, $J=17.7$, 10.7 Hz, 1H; $C\mathit{H}{=}CH_2$), 5.32 (s, 1H; $C{=}C\mathit{H}H$), 5.23 (d, $J=17.7$ Hz, 1H; $CH{=}C\mathit{H}H$), 5.09 (d, $J=10.7$ Hz, 1H; $CH{=}CH\mathit{H}$), 5.07 (s, 1H; $C{=}CH\mathit{H}$), 2.70 (t, $J=7.5$ Hz, 2H; $PhCH_2$), 2.30 (t, $J=7.5$ Hz, 2H; $Ph(CH_2)_2C\mathit{H}_2$), 1.95–1.70 (m, 2H; $PhCH_2C\mathit{H}_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=146.0$, 142.3, 138.8, 128.3, 128.2, 125.6, 115.7, 113.1, 35.6, 30.8, 29.7 ppm; elemental analysis: calcd (%) for $C_{13}H_{16}$: C 90.64, H 9.36; found: C 90.73, H 9.26.

(*E*)-1-Phenyl-1,3-butadiene (9c): Alkenyl bromide **7c** (0.13 mL, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol) or butyl vinyl ether (1.29 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9c**[14] were in complete accordance with literature values.

(*E*)-1-(4-Tolyl)-1,3-butadiene (9d): Alkenyl iodide **7d** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol) or butyl vinyl ether (1.29 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9d**[17] were in complete accordance with literature values.

(*E*)-1,5-Diphenyl-1,3-pentadiene (9e) and (*E*)-3-benzyl-1-phenyl-1,3-butadiene (10c): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide *trans*-**4c** (0.40 mL, 3 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9e**[18] were in complete accordance with literature values. **10c**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.50$–7.12 (m, 10H; ArH), 6.90 (d, $J=16.4$ Hz, 1H; $PhC\mathit{H}{=}CH$), 6.62 (d, $J=16.4$ Hz, 1H; $PhCH{=}C\mathit{H}$), 5.33 (s, 1H; $C{=}C\mathit{H}H$), 5.01 (s, 1H; $C{=}CH\mathit{H}$), 3.71 (s, 2H; $PhCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=144.8$, 139.2, 137.1, 130.5, 128.9, 128.7, 128.4, 128.2, 127.4, 126.3, 126.0, 118.6, 38.5 ppm; elemental analysis: calcd (%) for $C_{17}H_{16}$: C 92.68, H 7.32; found: C 92.79, H 7.19.

(*E,E*)-1,7-Diphenyl-1,3-heptadiene (9f) and (*E*)-1-phenyl-3-(3-phenylpropyl)-1,3-butadiene (10d): Alkenyl iodide **7b** (0.27 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide *trans*-**4c** (0.40 mL, 3 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **9f**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.52$–7.14 (m, 10H; ArH), 6.85 (dd, $J=15.6$, 10.4 Hz, 1H; $PhCH{=}C\mathit{H}$), 6.51 (d, $J=15.6$ Hz, 1H; $PhC\mathit{H}{=}CH$), 6.29 (dd, $J=15.0$, 10.4 Hz, 1H; $PhCH{=}CH{=}C\mathit{H}$), 5.91 (dt, $J=15.0$, 7.0 Hz, 1H; $C{=}C\mathit{H}CH_2$), 2.73 (t, $J=7.5$ Hz, 2H; $PhCH_2$), 2.26 (td, $J=7.5$, 7.0 Hz, 2H; $Ph(CH_2)_2C\mathit{H}_2$), 1.84 (quintuplet, $J=7.5$ Hz, 2H; $PhCH_2C\mathit{H}_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=142.2$, 137.5, 135.1, 130.8, 130.0, 129.2, 128.4, 128.2, 127.0, 126.0, 125.6, 35.2, 32.2, 30.8 ppm; elemental analysis: calcd (%) for $C_{19}H_{20}$: C 91.88, H 8.12; found: C 91.85, H 8.10. **10d**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.48$–7.18 (m, 10H; ArH), 6.85 (d, $J=16.4$ Hz, 1H; $PhC\mathit{H}{=}CH$), 6.53 (d, $J=16.4$ Hz, 1H; $PhCH{=}C\mathit{H}$), 5.20 (s, 1H; $C{=}C\mathit{H}H$), 5.12 (s, 1H; $C{=}CH\mathit{H}$), 2.74 (t, $J=7.6$ Hz, 2 H, $PhCH_2$), 2.41 (t, $J=7.7$ Hz, 2H; $Ph(CH_2)_2C\mathit{H}_2$), 1.98–1.87 (m, 2H; $PhCH_2C\mathit{H}_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=145.7$, 142.2, 137.2, 130.8, 128.4, 128.2, 127.9, 127.3, 126.3, 125.7, 116.3, 35.6, 31.4, 29.9 ppm; elemental analysis: calcd (%) for $C_{19}H_{20}$: C 91.88, H 8.12; found: C 92.04, H 7.93.

(*E*)-2-Benzyl-1,3-pentadiene (10e): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10e**: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.42$–7.19 (m, 5H; ArH), 6.17 (dq, $J=15.7$, 1.5 Hz, 1H; $CH_3CH{=}C\mathit{H}$), 5.77 (dq, $J=15.7$, 6.7 Hz, 1H; $CH_3C\mathit{H}$), 5.07 (s, 1H; (Z)$C{=}C\mathit{H}H$), 4.80 (s, 1H; (E)$C{=}CH\mathit{H}$), 3.56 (s, 2H; $PhCH_2$), 1.77 (dd, $J=6.7$, 1.5 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=145.0$, 139.7, 132.8, 128.7, 128.1, 125.9, 125.8, 115.4, 38.7, 18.2 ppm; elemental analysis: calcd (%) for $C_{12}H_{14}$: C 91.08, H 8.92; found: C 91.17, H 8.82.

(1*Z*,3*E*)-2-Benzyl-1-deuterio-1,3-pentadiene (10f): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (or *cis*-**4b** or *trans*-**4b**; 0.86 mL, 10 mmol). After addition of D_2O (1 mL) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10f**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.40$–7.17 (m, 5H; ArH), 6.17 (dq, $J=15.7$, 1.5 Hz, 1H; $CH_3CH{=}C\mathit{H}$), 5.77 (dq, $J=15.7$, 6.7 Hz, 1H; $CH_3C\mathit{H}$), 4.79 (s, 1H; $C{=}CHD$), 3.56 (s, 2H; $PhCH_2$), 1.77 (dd, $J=6.7$, 1.5 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=144.8$, 139.7, 132.8, 128.7, 128.2, 125.9, 125.8, 115.1 (t, $J=14$ Hz), 38.7, 18.2 ppm.

(*E*)-2-(2-Phenylethyl)-1,3-pentadiene (10g): Alkenyl iodide **7e** (0.26 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10g**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.41$–7.10 (m, 5H; ArH), 6.15 (d, $J=15.9$ Hz, 1H; $CH_3CH{=}C\mathit{H}$), 5.73 (dq, $J=15.9$, 6.7 Hz, 1H; $CH_3C\mathit{H}$), 4.94 (s, 1H; $C{=}C\mathit{H}H$), 4.90 (s, 1H; $C{=}CH\mathit{H}$), 2.84 (t, $J=7.8$ Hz, 2H; $PhCH_2$), 2.49 (t, $J=7.8$ Hz, 2H; $PhCH_2C\mathit{H}_2$), 1.83 (d, $J=6.7$ Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=145.4$, 141.6, 133.1, 128.3, 128.1, 125.6, 124.6, 113.1, 34.6, 34.0, 18.1 ppm; elemental analysis: calcd (%) for $C_{13}H_{16}$: C 90.64, H 9.36; found: C 90.73, H 9.25.

(*E*)-2-(3-Phenylpropyl)-1,3-pentadiene (10h): Alkenyl iodide **7b** (0.27 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [$Cp_2Zr(Me)Cl$] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10h**:

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.18 (m, 5H; ArH), 6.13 (d, J = 15.8 Hz, 1H; $CH_3CH{=}CH$), 5.73 (dq, J = 15.8, 6.7 Hz, 1H; CH_3CH), 4.95 (s, 1H; C=C*H*H), 4.91 (s, 1H; C=CH*H*), 2.70 (t, J = 7.8 Hz, 2H; $PhCH_2$), 2.29 (t, J = 7.9 Hz, 2H; $Ph(CH_2)_2CH_2$), 1.95–1.80 (m with d, J = 6.7 Hz, 5 H; $PhCH_2CH_2$ and CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 142.3, 133.2, 128.3, 128.1, 125.6, 124.6, 112.9, 35.6, 31.7, 29.8, 18.1 ppm; elemental analysis: calcd (%) for $C_{14}H_{18}$: C 90.26, H 9.74; found: C 90.38, H 9.61.

(*E,E*)-1-Iodo-2-phenyl-1,3-pentadiene (10i): Alkenyl bromide **7c** (0.13 mL, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10i**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.39–7.18 (m, 5H; ArH), 6.61 (d, J = 15.4 Hz, 1H; $CH_3CH{=}CH$), 6.17 (s, 1H; CHI), 5.71 (dq, J = 15.4, 6.7 Hz, 1H; CH_3CH), 1.85 (d, J = 6.7 Hz, 3H; CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 140.3, 134.8, 132.9, 128.6, 128.0, 127.6, 78.3, 18.5 ppm; elemental analysis: calcd (%) for $C_{11}H_{11}I$: C 48.91, H 4.10; found: C 48.80, H 4.01.

(*E,E*)-1-Iodo-2-(4-tolyl)-1,3-pentadiene (10j): Alkenyl iodide **7d** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10j**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16, 7.11 (2×d, J = 8.2 Hz, 4H; ArH), 6.60 (d, J = 15.4 Hz, 1H; $CH_3CH{=}CH$), 6.14 (s, 1H; CHI), 5.72 (dq, J = 15.4, 6.8 Hz, 1H; CH_3CH), 2.37 (s, 3H, $CH_3C_6H_4$), 1.84 (d, J = 6.8 Hz, 3H; CH_3CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 137.5, 137.4, 134.6, 133.0, 128.7, 128.4, 78.0, 21.1, 18.4 ppm; elemental analysis: calcd (%) for $C_{12}H_{13}I$: C 50.73, H 4.61; found: C 50.77, H 4.53.

(*E,E*)-2-*tert*-Butyl-1-Iodo-1,3-pentadiene (10k): Alkenyl iodide **7f** (0.21 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.16 (s, 1H; CHI), 5.86 (d, J = 15.9 Hz, 1H; $CH_3CH{=}CH$), 5.74 (dq, J = 15.9, 5.1 Hz, 1H; CH_3CH), 1.85 (d, J = 5.1 Hz, 3H; CH_3CH), 1.08 (s, 9H; 3×CCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 132.0, 129.9, 74.6, 38.7, 29.3, 18.3 ppm; elemental analysis: calcd (%) for $C_9H_{15}I$: C 43.22, H 6.04; found: C 43.30, H 5.94.

(*E*)-2-Benzyl-1,3-decadiene (10l): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide *trans*-**4d** (0.57 g, 3 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10l**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.15 (m, 5H; ArH), 6.19 (d, J = 15.9 Hz, 1H; $CH_2CH{=}CH$), 5.80 (dq, J = 15.9, 6.9 Hz, 1H; $CH_2CH{=}CH$), 5.12 (s, 1H; C=C*H*H), 4.85 (s, 1H; C=CH*H*), 3.61 (s, 2H; $PhCH_2$), 2.18–2.02 (m, 2H; $CH_2CH{=}CH$), 1.45–1.20 (m, 8H; $CH_3(CH_2)_4$), 0.92 (t, J = 7.0 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.0, 139.7, 131.5, 131.4, 128.7, 128.1, 125.8, 115.4, 38.8, 32.7, 31.6, 29.2, 28.7, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{17}H_{24}$: C 89.41, H 10.59; found: C 89.52, H 10.45.

(*E*)-2-(3-Phenylpropyl)-1,3-decadiene (10m): Alkenyl iodide **7b** (0.27 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide *trans*-**4d** (0.57 g, 3 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **10m**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.14 (m, 5H; ArH), 6.05 (d, J = 15.6 Hz, 1H; $CH_2CH{=}CH$), 5.63 (dq, J = 15.6, 6.7 Hz, 1H; $CH_2CH{=}CH$), 4.90 (s, 1H; C=C*H*H), 4.86 (s, 1H; C=CH*H*), 2.64 (t, J = 7.7 Hz, 2H; $PhCH_2$), 2.24 (t, J = 7.8 Hz, 2H; $Ph(CH_2)_2CH_2$), 2.10–1.92, 1.90–1.70, 1.42–1.20 (3×m, 12H; $CH_3(CH_2)_5$ and $PhCH_2CH_2$), 0.89 (t, J = 7.0 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 142.4, 131.7, 130.3, 128.3, 128.1, 125.6, 113.0, 35.6, 32.7, 31.6, 29.9, 29.3, 28.8, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{19}H_{28}$: C 88.99, H 11.01; found: C 89.08, H 10.89.

(*Z*)-4-Iodo-5-phenyl-1,3-pentadiene (9g): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of butyl vinyl ether (1.29 mL, 10 mmol). After addition of iodine (0.52 g, 2 mmol) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **9g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.12 (m, 5H; ArH), 6.49 (dt, J = 16.9, 9.7 Hz, 1H; $CH_2{=}CH$), 6.25 (d, J = 9.7 Hz, CI=CH), 5.44 (d, J = 16.9 Hz, 1H; CH=C*H*H), 5.33 (d, J = 9.7 Hz, 1H; CH=CH*H*), 3.94 (s, 2H; $PhCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 138.1, 135.1, 129.0, 128.4, 126.8, 120.5, 108.4, 51.7 ppm; elemental analysis: calcd (%) for $C_{11}H_{11}I$: C 48.91, H 4.10; found: C 45.05, H 4.02.

(*E*)-6-Phenyl-1,3-hexadiene (9h): Alkenyl iodide **7c** (0.26 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of butyl vinyl ether (1.29 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). Spectral data for **9h**[19] were in complete accordance with literature values.

General procedure for the preparation of cyclobutenes 11: *tert*-Butyllithium (2 mmol) was added to a stirred solution of the appropriate alkenyl bromide (or iodide) **1** or **7** (1 mmol) in dry THF (10 mL) at −78 °C. After stirring at this temperature for 30 min, the solution was added dropwise through a cannula to a stirred solution of bis(cyclopentadienyl)-zirconium methyl chloride (1.2 mmol) in dry THF (10 mL) at −78 °C. After 30 min at this temperature, an excess of the required alkenyl bromide **4** (3–10 mmol) was added. The mixture was allowed to warm to room temperature and the stirring continued for 18 h. An excess of water or deuterium oxide was added and then the mixture was extracted with diethyl ether (3×10 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated, and the residue was purified by column chromatography to give compounds **11**.

1-Benzylcyclobutene (11a): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.20 (m, 5H; ArH), 5.69–5.68 (m, 1H; C=CH), 3.37 (s, 2H; $PhCH_2$), 2.48–2.43 and 2.38–2.36 (2×m, 4H; 2×CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 148.5, 138.8, 128.7, 128.5, 128.2, 125.9, 38.1, 31.0, 26.5 ppm; elemental analysis: calcd (%) for $C_{11}H_{12}$: C 91.61, H 8.39; found: C 91.70, H 8.28.

1-(2-Phenylethyl)cyclobutene (11b): Alkenyl iodide **7e** (0.26 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4a** (0.35 mL, 5 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.21 (m, 5H; ArH), 5.79–5.68 (m, 1H; C=CH), 2.80 (t, J = 7.5 Hz, 2H; $PhCH_2$), 2.60–2.30 (m, 6H; 3×CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 142.1, 128.2, 127.2, 125.6, 33.0, 32.8, 31.1, 26.5 ppm; elemental analysis: calcd (%) for $C_{12}H_{14}$: C 91.08, H 8.92; found: C 91.16, H 8.82.

1-Benzyl-3-methylcyclobutene (11c): Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of vinyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.23 (m, 5H; ArH), 5.77 (s, 1H; C=CH), 3.38 (s, 2H; $PhCH_2$), 2.76–2.73 (m, 1H; CH_3CH), 2.62 (dd, J = 12.9, 4.1 Hz, 1H; CHC*H*H), 1.93 (d, J = 12.9 Hz, 1H; CHCH*H*), 1.15 (d, J = 6.8 Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 138.7, 134.0, 128.7, 128.2, 125.8, 38.5, 37.9, 34.0, 19.8 ppm; elemental analysis: calcd (%) for $C_{12}H_{14}$: C 91.08, H 8.92; found: C 91.19, H 8.79.

***cis*-1-Benzyl-4-deuterio-3-methylcyclobutene (11d)**: Alkenyl iodide **7a** (0.24 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and $[Cp_2Zr(Me)Cl]$ (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (or *cis*-**4b** or *trans*-**4b**; 0.86 mL, 10 mmol). After addition of D_2O (1 mL) and the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.20 (m, 5H; ArH), 5.77 (s, 1H; C=CH), 3.38 (s, 2H; $PhCH_2$), 2.76–2.70 (m, 1H; CH_3CH), 2.60 (s, 1H;

CHC*H*D), 1.93 (d, $J=12.9$ Hz, 1H; CHCH*H*), 1.13 (d, $J=6.8$ Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=146.3$, 138.8, 134.1, 128.7, 128.2, 125.8, 38.5, 37.9 (t, $J=20$ Hz), 33.9, 19.8 ppm.

3-Methyl-1-(2-phenylethyl)cyclobutene (11e): Alkenyl iodide **7e** (0.26 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [Cp_2Zr(Me)Cl] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11e**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.39$–7.20 (m, 5H; ArH), 5.84 (s, 1H; C=CH), 2.85–2.75 (m, 3H; $PhCH_2$ and CH_3C*H*), 2.65 (dd, $J=12.8$, 4.2 Hz, 1H; CHC*H*H), 2.38 (t, $J=7.6$ Hz, 2H; $PhCH_2CH_2$) 1.96 (dd, $J=12.8$, 1.2 Hz, 1H; CHCH*H*), 1.18 (d, $J=6.8$ Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=147.5$, 142.1, 132.9, 128.3, 128.2, 125.6, 38.6, 34.1, 33.1, 32.7, 19.8 ppm; elemental analysis: calcd (%) for $C_{13}H_{16}$: C 90.64, H 9.36; found: C 90.72, H 9.25.

3-Methyl-1-(3-phenylpropyl)cyclobutene (11f): Alkenyl iodide **7b** (0.27 g, 1 mmol) was treated with *t*BuLi (1.2 mL, 2 mmol) and [Cp_2Zr(Me)Cl] (0.34 g, 1.2 mmol). This was followed by addition of alkenyl bromide **4b** (0.86 mL, 10 mmol). After the extractive work-up, the resulting crude product was purified by silica gel column chromatography (hexane). **11f**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.31$–7.21 (m, 5H; ArH), 5.77 (s, 1H; C=CH), 2.75–2.60 (m, 3H; $PhCH_2$ and CH_3C*H*), 2.57 (dd, $J=12.9$, 4.1 Hz, 1H; CHC*H*H), 2.03 (t, $J=7.3$ Hz, 2H; $Ph(CH_2)_2CH_2$) 1.96 (d, $J=12.9$ Hz, 1H; CHCH*H*), 1.76 (quintuplet, $J=7.6$ Hz, 2H; $PhCH_2CH_2$), 1.18 (d, $J=6.7$ Hz, 3H; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=147.9$, 142.4, 132.7, 128.4, 128.1, 125.5, 38.5, 35.5, 34.0, 30.4, 28.5, 20.0 ppm; elemental analysis: calcd (%) for $C_{14}H_{18}$: C 90.26, H 9.74; found: C 90.37, H 9.61.

Acknowledgements

Financial support for this work was provided by the Dirección General de Investigación Científica y Técnica (DGICYT) of Spain (BQU-2001–3853) and the Ministerio de Educación y Cultura of Spain (grant to L.A.-R.). F.R. thanks the MCYT (Programa Ramón y Cajal) for funding.

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[1] L. S. Hegedus, in *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, CA, **1994**, p. 115.

[2] a) E. Negishi, in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, UK, **1991**, p. 1163; b) R. D. Broene, in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, UK, **1995**, p. 323. See also: c) K. Tamao, K. Kobayachi, Y. Ito, *Synlett* **1992**, 539; d) E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, *111*, 3336; e) S. C. Berk, R. B. Grossman, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 8593.

[3] E. Negishi, S. Huo, in *Titanium and Zirconium in Organic Synthesis* (Ed.: I. Marek), Wiley-VCH, Weinheim, Germany, **2002**, p. 1.

[4] For reviews, see: a) U. Rosenthal, P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, *Acc. Chem. Res.* **2000**, *33*, 119; b) A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burlakov, U. Rosenthal, *Synlett* **1996**, 111. For some selected examples, see: c) L. L. Schafer, J. R. Nitsche, S. S. H. Mao, F.-Q. Liu, G. Harder, M. Haufe, T. D. Tilley, *Chem. Eur. J.* **2002**, *8*, 74; d) A. A. Quntar, A. Melman, M. Srebnik, *J. Org. Chem.* **2002**, *67*, 3769; e) T. Takahashi, C. Xi, Y. Ura, K. Nakajima, *J. Am. Chem. Soc.* **2000**, *122*, 3228, and references therein. For zirconocene-stabilized aryne complexes, see, for example: f) M. Frid, D. Pérez, A. J. Peat, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9469, and references therein.

[5] E. Negishi, F. E. Cederbraum, T. Takahashi, *Tetrahedron Lett.* **1986**, *27*, 2829.

[6] a) C. Meyer, I. Marek, J. F. Normant, *Tetrahedron Lett.* **1996**, *37*, 857; b) P. A. Wender, F. E. McDonald, *Tetrahedron Lett.* **1990**, *31*, 3691; c) G. Agnel, Z. Owczarczyk, E. Negishi, *Tetrahedron Lett.* **1992**, *33*, 1543; d) G. Agnel, E. Negishi, *J. Am. Chem. Soc.* **1991**, *113*, 7424; e) E. Negishi, D. R. Swanson, F. E. Cederbraum, T. Takahashi, *Tetrahedron Lett.* **1986**, *27*, 2829.

[7] W. A. Nugent, D. L. Thorn, R. L. Harlow, *J. Am. Chem. Soc.* **1987**, *109*, 2788.

[8] a) J. Yin, J. Klosin, K. A. Abboud, W. M. Jones, *Tetrahedron Lett.* **1995**, *36*, 3107; b) M. C. J. Harris, R. J. Whitby, J. Blagg, *Synlett* **1993**, 705; c) S. L. Buchwald, R. T. Lum, R. A. Fisher, W. M. Davis, *J. Am. Chem. Soc.* **1989**, *111*, 9113; d) S. L. Buchwald, R. B. Nielsen, *J. Am. Chem. Soc.* **1989**, *111*, 2870; e) S. L. Buchwald, B. T. Watson, *J. Am. Chem. Soc.* **1987**, *109*, 2544; f) S. L. Buchwald, R. T. Lum, J. C. Dewan, *J. Am. Chem. Soc.* **1986**, *108*, 7441. For the synthesis of zirconocene-stabilized aryne complexes following this strategy, see: g) J. H. Tidwell, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11797, and references therein.

[9] J. Barluenga, R. Sanz, F. J. Fañanás, *Chem. Eur. J.* **1997**, *3*, 1324.

[10] a) J. Barluenga, R. Sanz, F. J. Fañanás, *Z. Naturforsch.* **1995**, *B50*, 312. After this paper appeared, other authors published the same process with internal alkynes: b) T. Takahashi, Z. Xi, R. Fischer, S. Huo, C. Xi, K. Nakajima, *J. Am. Chem. Soc.* **1997**, *119*, 4561; c) T. Takahashi, D. Y. Kondakov, Z. Xi, N. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 5871.

[11] Migratory insertion processes involving related metal carbenoids have been reported: a) G. J. Gordon, T. Luker, M. W. Tuckett, R. J. Whitby, *Tetrahedron* **2000**, *56*, 2113; b) A. Kasatkin, R. J. Whitby, *J. Am. Chem. Soc.* **1999**, *121*, 7039; c) M. W. Tuckett, W. J. Watkins, R. J. Whitby, *Tetrahedron Lett.* **1998**, *39*, 123; d) S. F. Fillery, G. J. Gordon, T. Luker, R. J. Whitby, *Pure Appl. Chem.* **1997**, *69*, 633; e) G. J. Gordon, R. J. Whitby, *Chem. Commun.* **1997**, 1321; f) G. J. Gordon, R. J. Whitby, *Chem. Commun.* **1997**, 1045; g) E. Negishi, K. Akiyoshi, B. O'Connor, K. Takagi, G. Wu, *J. Am. Chem. Soc.* **1989**, *111*, 3089.

[12] The same electronic effects have been invoked to explain the results of the hydroboration reaction of vinyl halides and enol ethers: E. Negishi, in *Organometallics in Organic Synthesis*, John Wiley & Sons, New York, **1980**, p. 297.

[13] Nonconcerted pathways for the insertion reactions of alkenes with zirconocene complexes have been reported: E. Negishi, D. Choueiry, T. B. Nguyen, D. R. Swanson, N. Suzuki, T. Takahashi, *J. Am. Chem. Soc.* **1994**, *116*, 9751.

[14] E. Roversi, F. Monnat, P. Vogel, K. Schenk, P. Roversi, *Helv. Chim. Acta* **2002**, *85*, 733.

[15] C. Nájera, J. M. Sansano, *Tetrahedron* **1994**, *50*, 5829.

[16] H. J. Reich, E. K. Eisenhart, W. L. Whipple, M. J. Kelly, *J. Am. Chem. Soc.* **1988**, *110*, 6432.

[17] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* **1999**, *18*, 2043.

[18] T. L. Underiner, H. L. Goering, *J. Org. Chem.* **1991**, *56*, 2563.

[19] J. Uenishi, R. Kawahama, O. Yonemitsu, J. Tsuji, *J. Org. Chem.* **1996**, *61*, 5716.

Received: July 15, 2003
Revised: September 3, 2003 [F5337]