DOI: 10.1002/ejoc.200700999

Domino Heck–Diels–Alder Reactions of Monosubstituted Bicyclopropylidenes[‡]

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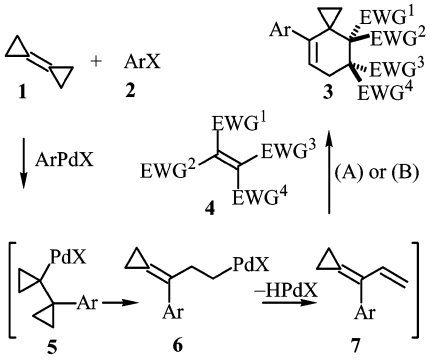
Keywords: Bicyclopropylidene / Deboropalladation / Domino reactions / Heck coupling / Multicomponent reaction

A three-component domino Heck–Diels–Alder reaction involving pinacol bicyclopropylideneboronate (**8b**), iodobenzene (**9**) and methyl acrylate (**12**) under Jeffery conditions [$Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN] produced a mixture of phenylspiro[2.5]octeneboronates *syn*/*anti*-(*E*)-**14b** and methyl phenylspirooctenecarboxylate **25** in 25 and 38% yield, respectively. The major product **25** was most probably formed via the homoallylpalladium complex **23b** undergoing deboropalladation rather than dehydropalladation. Similarly, reactions of tributylstannyl- and hydroxydimethylsilyl-substituted bicyclopropylidenes **8c–d** with **9** and *tert*-butyl acrylate gave the *tert*-butyl phenylspirooctenecarboxylate **26** via the diene **24** formed by demetallopalladation processes. The reaction of methyl 1,1′-bicyclopropylidene-2-carboxylate (**8e**) with iodobenzene (**9**) in the presence of *tert*-butyl acrylate (**13**) furnished a mixture of regioisomeric and diastereomeric spirooctenes *syn*/*anti*-(*E*)-**15e** and *syn*/*anti*-(*Z*)-**15e** in 69 and 6% yield, respectively. The structures of the major pair of diastereomers *syn*-(*E*)-**15e** and *anti*-(*E*)-**15e** were rigorously proved by X-ray crystal structure analyses.

Introduction

1,1′-Bicyclopropylidene (**1**) is a highly strained alkene which can undergo various chemical transformations with great facility.[1] Among other features, it is particularly remarkable that **1**, unlike most other tetrasubstituted alkenes, exhibits superior reactivity in Heck cross-coupling reactions.[2] Carbopalladation of **1** was found to proceed even faster than that of alkyl acrylates, which allows one to perform multicomponent sequential transformations involving **1** and an acrylate with a palladium precatalyst in the same pot.[2a–2c] Thus, a versatile three-component domino Heck–Diels–Alder reaction of **1** leads to differently substituted spiro[2.5]octene derivatives.[3] Under typical Heck [$Pd(OAc)_2$, PPh_3, Et_3N, DMF] or so-called Jeffery conditions[4] [$Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN] bicyclopropylidene firstly undergoes carbopalladation with an initially formed arylpalladium halide leading to an intermediate **5** containing a (cyclopropylmethyl)palladium halide moiety. Rapid rearrangement of the latter to a homoallylpalladium halide **6** and subsequent *β*-hydride elimination yields an allylidenecyclopropane derivative of type **7**, which immediately reacts with a dienophile **4** present in the reaction medium to afford a spiro[2.5]octene derivative **3** (Scheme 1).[3]



Scheme 1. Three-component domino Heck–Diels–Alder reaction involving bicyclopropylidene (**1**) an aryl halide **2** and a dienophile **4**. (A): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, Et_4NCl, K_2CO_3, Me_3CN, 80 °C, 48 h. (B): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, Et_3N, DMF, 80 °C, 48 h.

This chemistry based principally on carbopalladations of bicyclopropylidene with aryl- or alkenylpalladium halides was further developed by working in the presence of tris(2-furyl)phosphane (TFP) instead of triphenylphosphane and addition of a nucleophilic secondary amine to yield 8-(1′-aminoethyl)-substituted spiro[2.5]octenes.[5] Moreover, 4-oxaspiro[2.5]octene and 5-oxa-4-azaspiro[2.5]octene derivatives could be obtained by allowing allylidenecyclopropanes of type **7** to react with various hetero-dienophiles.[6]

In addition, the library of spiro[2.5]octenes was enlarged by employing substituted bicyclopropylidenes **8b–e** in the domino Heck–Diels–Alder process. Preliminary results

[‡] Cyclopropyl Building Blocks in Organic Synthesis, 147. Part 146: J. Revuelta, S. Cicchi, A. de Meijere, A. Brandi, *Eur. J. Org. Chem.*, in press. Part 145: I. Emme, C. Bruneau, P. H. Dixneuf, A. de Meijere, *Synthesis*, **2007**, 3574–3588.

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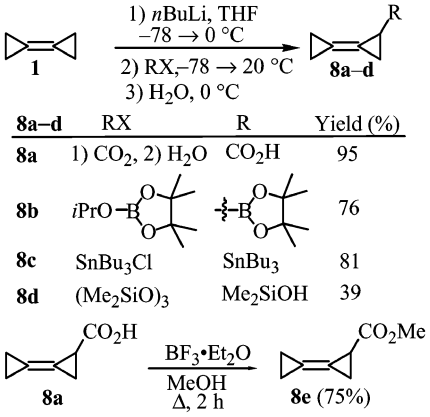
along this line have previously been reported,[7] and here we present the full scope of investigated domino Heck–Diels–Alder reactions with monosubstituted bicyclopropylidenes **8b**–**e**.

Results and Discussion

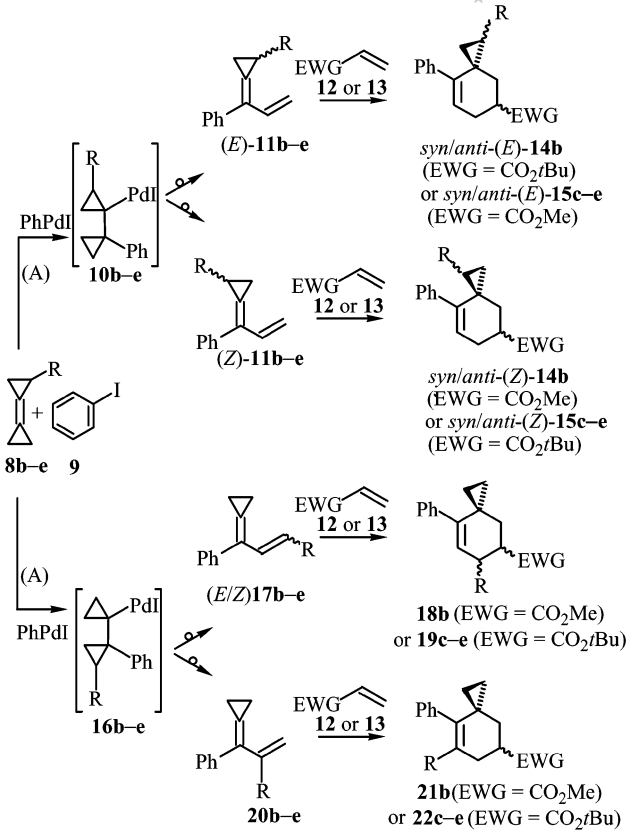
Substituted bicyclopropylidenes **8a**–**e** are easily available by lithiation of bicyclopropylidene (**1**) with *n*-butyllithium and subsequent trapping with electrophiles at low temperature according to established protocols (Scheme 2).[8] Except for bicyclopropylidenecarboxylic acid (**8a**), the bicyclopropylidene derivatives **8b**–**e** were directly utilized in the domino Heck–Diels–Alder process. The acid **8a** was converted into its methyl ester **8e** applying a protocol developed by Seebach et al.[9]



Scheme 2. Preparation of monosubstituted bicyclopropylidene derivatives **8a**–**e**.

The carbopalladation of a monosubstituted bicyclopropylidene with e.g. phenylpalladium iodide can produce two regioisomeric intermediates **10b**–**e** and **16b**–**e**. Each of these intermediates then can undergo cyclopropylcarbinyl- to homoallylpalladium iodide rearrangement in two modes possibly affording five different diastereomeric and regioisomeric (1′-arylallylidene)cyclopropanes [(*E*)- and (*Z*)-**11b**–**e**, as well as (*E*)- and (*Z*)-**17b**–**e**, **20b**–**e**]. Diels–Alder reactions of these allylidenecyclopropanes with an alkyl acrylate (methyl **12** or *tert*-butyl **13**) can produce up to seven different diastereomeric and regioisomeric spiro[2.5]octene derivatives (Scheme 3).[10]

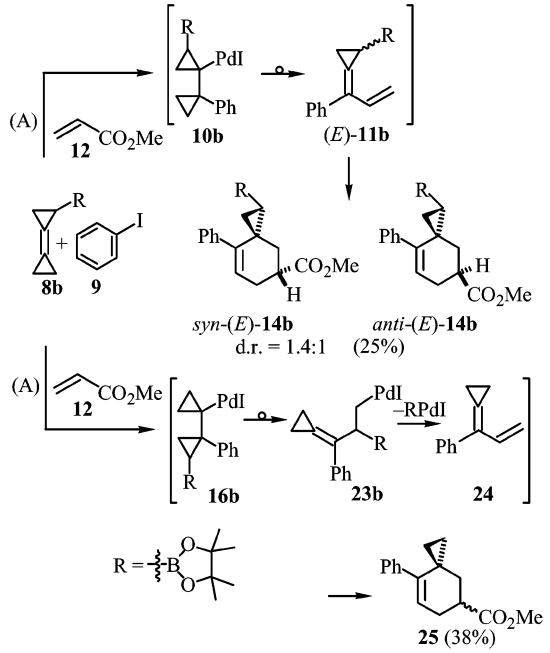
However, the one-pot reaction of pinacol bicyclopropylideneboronate (**8b**) with phenyl iodide (**9**) in the presence of methyl acrylate (**12**) under Jeffery conditions[4] gave a mixture of only two diastereomers, namely *syn*-(*E*)-**14b** and *anti*-(*E*)-**14b** (25%) along with the unsubstituted methyl 4-phenylspiro[2.5]oct-4-ene-7-carboxylate (**25**) (38% yield) (Scheme 4). In the ^{1}H NMR spectrum of the crude reaction mixture, none of the other conceivable isomers was detected. Compound **25** must arise from an initially formed carbopalladation intermediate **16b** which undergoes opening of the boron-substituted cyclopropane ring yielding the homoallylpalladium species **23b** that immediately undergoes β-deboropalladation rather than β-dehydropalladation. Heating of the spirooctenes *syn*-(*E*)-**14b** and *anti*-(*E*)-**14b** with the palladium precatalyst mixture [$Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN] at 80 °C for 24 h did not furnish any of the spirooctene **25**. The configuration of diastereomers *syn*-(*E*)-**14b** and *anti*-(*E*)-**14b** was proved by NOESY-NMR measurements as well as by an X-ray crystal structure analysis of the major diastereomer *syn*-(*E*)-**14b** (Figure 1).[11]



Scheme 3. Mechanistic rationalization of the possible formation of regioisomeric dienes [(*E*)- and (*Z*)-**11b**–**e**, as well as (*E*)- and (*Z*)-**17b**–**e**, **20b**–**e**] via carbopalladated intermediates **10b**–**e** and **16b**–**e** from monosubstituted bicyclopropylidenes **8b**–**e** and of possible subsequent regio- and diastereomeric spiro[2.5]octene derivatives. (A): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, 48 h. **12**: EWG = CO_2Me. **13**: EWG = CO_2tBu.

Similarly, reactions of the functionalized bicyclopropylidenes **8c** and **8d** with phenyl iodide (**9**) in the presence of *tert*-butyl acrylate (**13**) produced *tert*-butyl 4-phenylspiro[2.5]oct-4-ene-7-carboxylate (**26**) in 49 and 25% yield, respectively. Although, mixtures of the spirooctenes *syn*/*anti*-(*E*)-**15c**–**d** and/or *syn*/*anti*-(*Z*)-**15c**–**d** were observed in the ^{1}H NMR spectra of the crude products, these other compounds could not be isolated, and their exact configurations as well as their yields could not be determined (Scheme 5).

The anologous domino Heck–Diels–Alder reaction of methyl bicyclopropylidenecarboxylate (**8e**) gave completely regioselectively a mixture of the four diastereomers *syn*/*anti*-(*E*)-**15e** and *syn*/*anti*-(*Z*)-**15e** in 69 and 6% yield,



Scheme 4. Three-component domino Heck–Diels–Alder reaction involving pinacol bicyclopropylideneboronate (**8b**), iodobenzene (**9**) and methyl acrylate (**12**). (A): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, 48 h.

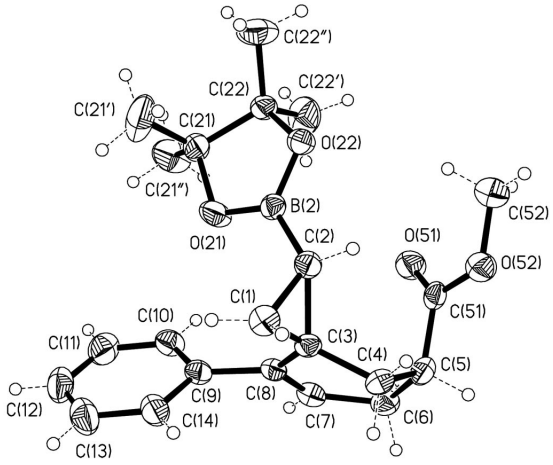
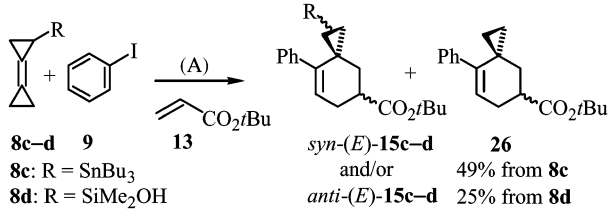
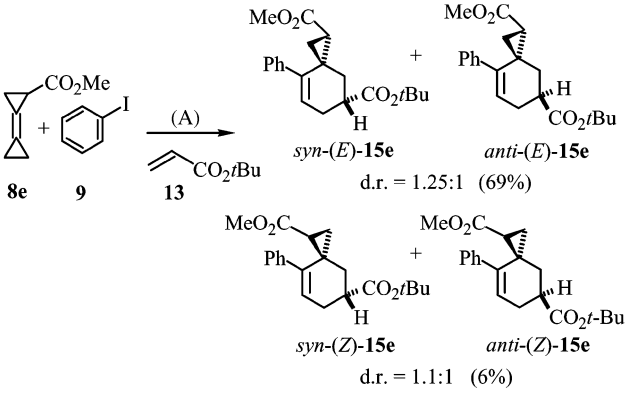


Figure 1. Structure of the 1-boron-substituted spiro[2.5]octene derivative *syn*-(*E*)-**14b** (major diastereomer) in the crystal.[11]

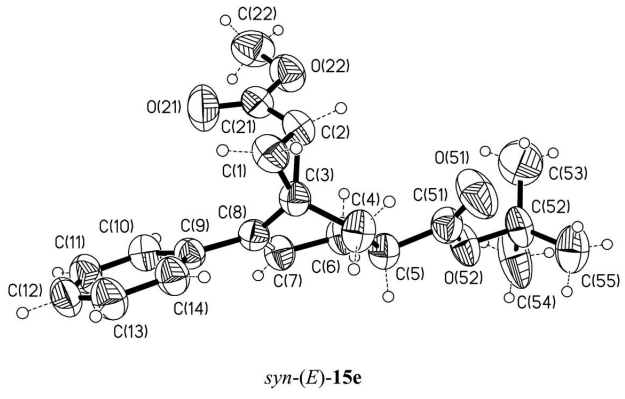


Scheme 5. Three-component domino Heck–Diels–Alder reactions involving monosubstituted bicyclopropylidenes **8c** and **8d**, iodobenzene (**9**) and *tert*-butyl acrylate (**13**). (A): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, 48 h.

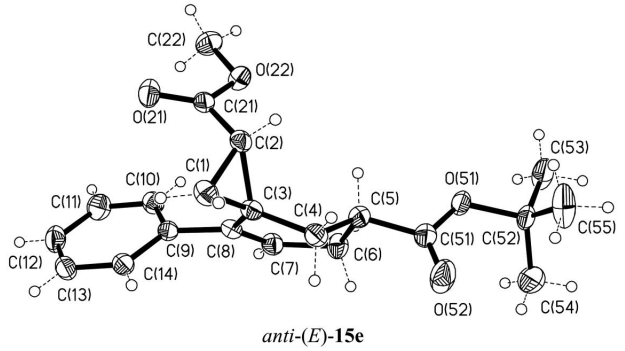
respectively (Scheme 6). Apparently, carbopalladation of **8e** proceeds regioselectively to give the intermediate **10e** and not **16e**, so that the opening of the unsubstituted cyclopropane ring in **10e** is the governing pathway. The most probable reason for the selective formation of **10e** is the possible chelation of phenylpalladium iodide with the methoxycarbonyl group on the cyclopropane ring during the carbopalladation process. The configurations of both diastereomers *syn*-(*E*)-**15e** and *anti*-(*E*)-**15e** (Figure 2) were rigorously proved by X-ray crystal structure analyses (Figure 1).[11] In



Scheme 6. Three-component domino Heck–Diels–Alder reaction involving methyl bicyclopropylidenecarboxylate (**8e**), iodobenzene (**9**) and *tert*-butyl acrylate (**13**). (A): 5 mol-% $Pd(OAc)_2$, 15 mol-% PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, 48 h.



syn-(*E*)-**15e**



anti-(*E*)-**15e**

Figure 2. Structures of the 1-methoxycarbonyl-substituted spirooctene derivatives *syn*-(*E*)-**15e** (major diastereomer) and *anti*-(*E*)-**15e** (minor diastereomer) in the crystals.[11]

both structures, the ester functionality on the cyclopropane ring is oriented towards the phenyl group which is perpendicular to the plane of the double bond in the spiro[2.5]-octene moiety due to steric interaction between its *ortho* hydrogen atoms and the cylopropane ring. Moreover, the configurations of diastereomers *syn*-(*Z*)-**15e** and *anti*-(*Z*)-**15e** were determined by NOESY and other twodimensional NMR measurements.

Conclusions

Certain monosubstituted bicyclopropylidenes like the pinacol bicyclopropylideneboronate (**8b**) and methyl 1,1′-bicyclopropylidene-2-carboxylate (**8e**) take part in the three-component reaction with iodoarenes and dienophiles previously discovered for 1,1′-bicyclopropylidene itself. They react with a moderate or high degree of regioselectivity such that the substituent ends up on the three-membered ring in the spiro[2.5]octene derivative. They thus enhance the diversity of the library of biaryl mimics obtained from **1**, iodoarenes and dienophiles. The boronate **8b** also reacts to a certain extent – and the stannyl- as well as the hydroxydimethylsilyl-substituted bicyclopropylidenes **8c**,**d** do that exclusively – with opening of the substituted three-membered ring and subsequent demetallopalladation to furnish the same spiro[2.5]octene derivative which is obtained from unsubstituted bicyclopropylidene (**1**).

Experimental Section

General Remarks: NMR spectra were recorded with Bruker AM 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR), Varian UNITY-300 (300 MHz for ^{1}H and 75.5 MHz for ^{13}C NMR) and Varian Inova 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C NMR) instruments. Chemical shifts δ are given in ppm relative to residual peaks of deuterated solvents and coupling constants, *J*, are reported in Hertz. The following abbreviations are used to describe spin multiplicities in ^{1}H NMR spectra: s = singlet; br. s = broad singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; ddd = doublet of doublets of doublets; dt = doublet of triplets; dq = doublet of quartets; m = multiplets. Multiplicities in ^{13}C NMR spectra were determined by DEPT (Distortionless Enhancement by Polarization Transfer): + = primary or tertiary (positive DEPT signal), – = secondary (negative DEPT Signal), C_{quat} = quaternary carbon atoms] or APT (Attached Proton Test) measurements. HMQC (Heteronuclear Multiple Quantum Coherence) spectra were also measured in certain cases. IR spectra were recorded on a Bruker IFS 66 spectrometer and measured as KBr pellets or as oils between KBr plates. Low resolution mass spectra (EI at 70 eV or DCI with NH_3) were obtained on a Finnigan MAT 95 spectrometer. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95 spectrometer by preselected-ion peak matching at $R \approx 10000$ to be within ±2 ppm of the exact masses. Elemental analyses were carried out by the Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen. Chromatographic separations were performed with Merck Silica 60 (200–400 or 70–230 mesh). The dimensions of the columns are given as "diameter × height of the silica gel column". TLC was performed with Macherey–Nagel TLC Alugram® Sil G/UV 254 plates, detection was under UV light at 254 nm and development with MOPS reagent (10% molybdophosphoric acid in ethanol). All reagents were used as purchased from commercial suppliers without further purification unless otherwise indicated. Acetonitrile was dried with P_2O_5, DMF and CH_2Cl_2 were distilled from CaH_2. Ether and THF were freshly distilled from sodium benzophenone ketyl. Solvents for column chromotography, ethyl acetate and light petroleum were distilled in a rotary evaporator. The following compounds were prepared according to known literature methods: 1,1′-bicyclopropylidene (**1**),[12] 2-(1,1′-bicyclopropylidene-2-yl)-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (**8b**),[8b,8c] 2-(tributylstannyl)-1,1′-bicyclopropylidene (**8c**),[8c] methyl 1,1′-bicyclopropylidene-2-carboxylate (**8e**).[8a]

2-(1,1′-Bicyclopropylidene-2′-yl)-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (8b): To a solution of *n*BuLi (16.1 mL of a 1.54 M solution in hexane) in 25 mL of anhydrous THF was added dropwise at –30 °C 1,1′-bicyclopropylidene (**1**) (2.0 g, 25.0 mmol) with a syringe. After stirring the mixture at 0 °C for 1 h, the formed bicyclopropylidenyllithium was quenched at –78 °C by slow addition of 2-isopropyloxy-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (6.97 g, 37.5 mmol), and the reaction mixture was stirred at 0 °C for 1 h and at room temperature for 24 h. After cooling to 0 °C, saturated solution of NH_4Cl (10 mL) was added and the mixture stirred for 10 min. The water phase was extracted with diethyl ether (3 × 20 mL), and the collected organic fractions were dried ($MgSO_4$) and concentrated in a rotary evaporator. The residue was subjected to column chromatography on silica gel (180 g, 3.5 × 50 cm, light petroleum/diethyl ether, 4:1, R_f = 0.64) to yield **8b** (3.91 g, 76%, yellowish oil). IR (film): $\tilde{\nu}$ = 3051, 2979, 2931, 1444, 1385, 1320, 951, 866, 687 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.78–0.97 (m, 2 H, cPr-H), 1.15–1.22 (m, 2 H, cPr-H), 1.23–1.30 (m, 14 H, cPr-H, CH_3), 1.39–1.44 (m, 1 H, cPr-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT)*: δ = 2.99 (–, cPr-C), 3.58 (–, cPr-C), 8.00 (–, cPr-C), 24.53 (+, 2 C, CH_3), 83.24 (C_{quat}), 108.24 (C_{quat}), 113.11 (C_{quat}) ppm. *Peaks of C-2 could not be observed because of ^{13}C-$^{10/11}$B coupling. MS (70 eV, EI): *m*/*z* (%) = 206 (27) [M^+], 191 (17) [$M^+ - CH_3$], 149 (14), 133 (26), 123 (19), 119 (16), [$C_6H_{15}O_2^+$], 107 (30), 105 (65), 91 (19), 83 (100) [$C_6H_{11}^+$], 79 [56] [$C_6H_7^+$], 57 (28), 55 (61), 41 (65) [$C_3H_5^+$]. $C_{22}H_{29}BO_2$ (206.1): calcd. 206.1478 (correct HRMS).

2-(Tributylstannyl)-1,1′-bicyclopropylidene (8c): To a solution of *n*BuLi (8.03 mL of a 1.54 M solution in hexane) in 20 mL of anhydrous THF was added dropwise at –30 °C **1** (1.0 g, 12.5 mmol) with a syringe. After stirring the mixture at 0 °C for 1 h, the formed bicyclopropylidenyllithium was quenched at –78 °C by slow addition (1 h) of tributyltin chloride (6.97 g, 37.5 mmol) in 10 mL of anhydrous THF, and the reaction mixture was stirred at 0 °C for 0.5 h and at room temperature for 2 h. After cooling to 0 °C, saturated solution of NH_4Cl (10 mL) was added and the resulting mixture was diluted with water (20 mL). The water phase was extracted with diethyl ether (3 × 20 mL), and the collected organic fractions were dried ($MgSO_4$) and concentrated in a rotary evaporator. The residue was subjected to column chromatography on silica gel (120 g, 2.5 × 40 cm, light petroleum/diethyl ether, 10:1, R_f = 0.88) to yield **8c** (3.73 g, 81%, yellowish oil). IR (film): $\tilde{\nu}$ = 3046, 2956, 2925, 2871, 1464, 1376, 952 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70–0.97 (m, 18 H, cPr-H, CH_2, CH_3), 1.10–1.22 (m, 4 H, cPr-H), 1.25–1.37 (m, 6 H, CH_2), 1.43–1.53 (m, 6 H, CH_2) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.17 (+, cPr-C), 3.06 (–, cPr-C), 3.16 (–, cPr-C), 6.70 (–, cPr-C), 9.21 (–, 3 C, CH_2), 13.70 (+, 3 C, CH_3), 27.30 (–, 3 C, CH_2), 29.02 (–, 3 C, CH_2), 105.98 (C_{quat}), 114.81 (C_{quat}) ppm. MS (70 eV, EI): *m*/*z* (%) = 369 (5) [$M^+ - H$], 317 (20), 313 (100) [$M^+ - C_4H_9$], 291 (45) [$M^+ - C_6H_6$], 257 (21) [$M^+ - C_4H_9 - C_4H_8$], 235 (60) [$M^+ - C_6H_6 - C_4H_9$], 177

(80) [$M^+ - C_6H_7 - C_4H_9 - C_4H_9$], 120 (45) [$M^+ - C_6H_7 - C_4H_9 - C_4H_9 - C_4H_9$], 91 (19), 55 (10), 41 (22) [$C_3H_5^+$]. $C_{18}H_{34}Sn$ (369.1): calcd. C 58.57, H 9.28; found C 58.26, H 9.16.

(1,1′-Bicyclopropyliden-2-yl)dimethylsilanol (8d): To a solution of *n*BuLi (5.25 mL of a 2.5 M solution in hexane) in 15 mL of anhydrous THF was added dropwise at –30 °C bicyclopropylidene (**66**) (1.0 g, 12.5 mmol) in 2 mL anhydrous THF with a syringe. After stirring the mixture at 0 °C for 1 h, the formed bicyclopropylidenyllithium was quenched at –78 °C by slow addition of hexamethylcyclotrisiloxane (0.92 g, 4.13 mmol) in 5 mL of anhydrous THF, and the reaction mixture was stirred at –78 °C for 1 h and at room temperature for 2 h. After cooling to –78 °C, 10% HCl (10 mL) was added, the mixture warmed to room temperature and finally poured into 100 mL of diethyl ether and extracted. The organic phase was dried ($MgSO_4$) and concentrated in a rotary evaporator. The residue was subjected to column chromatography on silica gel (100 g, 3 × 30 cm, light petroleum/ethyl acetate, 10:1) to yield **8d** (0.75 g, 39%, colorless oil). IR (film): ṽ = 3282, 3050, 2979, 2958, 1270, 1251, 1192, 1075, 998, 954, 904, 862, 840, 819, 777, 686 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 3 H, CH_3), 0.10 (s, 3 H, CH_3), 0.72–0.80 (m, 1 H, cPr-H), 1.22–1.09 (m, 5 H, cPr-H), 1.34–1.41 (m, 1 H, cPr-H), 2.03 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT): δ = –1.53 (+, CH_3), –1.07 (+, CH_3), 2.86 (–, cPr-C), 3.33 (–, cPr-C), 5.15 (+, cPr-C), 5.85 (–, cPr-C), 107.56 (C_{quat}), 112.43 (C_{quat}) ppm. MS (DCI): *m*/*z* (%) = 172.1 (100) [M + NH_4^+], 155 (37) [M + H^+], 109 (13).

General Procedure for Three-Component Domino Heck–Diels–Alder Reactions Involving a Monosubstituted 1,1′-Bicyclopropylidene Derivatives 8b–e, Phenyl Iodide (9) and a Dienophile (12 or 13). General Procedure 1 (GP-1): A screw-cap Pyrex bottle was charged with anhydrous acetonitrile (2 mL), K_2CO_3 (2 equiv.) and Et_4NCl (1 equiv.). Argon was bubbled through the mixture for 5 min, $Pd(OAc)_2$ (5 mol-%), and triphenylphosphane (15 mol-%) were added, and the mixture was stirred for 5 min with argon bubbling through, before phenyl iodide **9** (1 equiv.), the respective monosubstituted bicyclopropylidene derivative **8b–e** (2 equiv.) and the respective dienophile (2 equiv.) were added. The bottle was tightly closed, and the mixture was stirred for the given period of time at the stated temperature. After cooling to room temperature, the reaction mixture was taken up in 20 mL of diethyl ether. The solution was washed with water (2 × 20 mL), the aqueous phase was extracted with diethyl ether (2 × 20 mL), and the combined organic phases were dried ($MgSO_4$). After removal of the solvent in a rotary evaporator, the residue was subjected to chromatography on silica gel.

Domino Heck–Diels–Alder Reaction of 2-(1,1′-Bicyclopropyliden-2-yl)-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (8b): According to GP-1, $Pd(OAc)_2$ (19.3 mg, 85 μmol), triphenylphophane (67 mg, 254 μmol), K_2CO_3 (470 mg, 3.40 mmol), Et_4NCl (281.5 mg, 1.70 mmol), iodobenzene (**9**, 347 mg, 1.70 mmol), 2-(1,1′-bicyclopropyliden-2-yl)-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (**8b**, 700 mg, 3.40 mmol) and methyl acrylate (**12**, 293 mg, 3.40 mmol) were stirred in anhydrous MeCN (2 mL) at 80 °C for 48 h. After work-up and column chromatography on silica gel (100 g, 3 × 30 cm, light petroleum/ethyl acetate, 10:1) a mixture of *syn*- and *anti*-(*E*)-**14b** (156.5 mg, 25%, yellowish oil, ratio 1.4:1 according to NMR) and **methyl 8-phenylspiro[2.5]oct-7-ene-5-carboxylate*** (**25**, 156 mg, 38%, yellowish oil) were obtained. The diastereomer *syn*-(*E*)-**14b** could be crystallized by slow evaporation of the solvents from a solution in ethyl acetate/diethyl ether (1:1). *For the spectroscopic data of compound **25** see ref.[3].

Methyl 8-Phenyl-1-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)spiro[2.5]oct-7-ene-5-carboxylate [*syn*/*anti*-(*E*)-14b]

Major Diastereomer [*syn*-(*E*)-14b]: R_f = 0.18 (light petroleum/ethyl acetate, 10:1). IR (KBr): ṽ = 3075, 2979, 2924, 2882, 2827, 1737, 1632, 1599, 1492, 1421, 1389, 1379, 1381, 1359, 1334, 1261, 1233, 1190, 1171, 1142, 1073, 1045, 1001, 973, 959, 914, 903, 867, 844, 812, 757, 702 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 0.14 (dd, *J* = 7.7, 10.0 Hz, 1 H, cPr-H), 0.90 (s, 6 H, 2 × CH_3), 0.92 (s, 6 H, 2 × CH_3), 0.97 (dd, *J* = 4.1, 10.2 Hz, 1 H, cPr-H), 1.28 (dd, *J* = 3.8, 12.4 Hz, 1 H, 4-H), 1.52 (dd, *J* = 4.2, 7.6 Hz, 1 H, cPr-H), 2.31 (t, *J* = 12.2 Hz, 1 H, 4-H), 2.42–2.64 (m, 2 H, 6-H), 3.04–3.15 (m, 1 H, 5-H), 3.33 (s, 3 H, OCH_3), 5.62 (t, *J* = 3.8 Hz, 1 H, 7-H), 7.09–7.25 (m, 5 H, Ph) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT)*: δ = 18.44 (–, cPr-C), 24.35 (+, 2 × CH_3), 25.03 (+, 2 × CH_3), 26.96 (C_{quat}, cPr-C), 28.78 (–, C-6), 39.73 (+, C-5), 40.69 (–, C-4), 51.57 (+, OCH_3), 82.76 (2 × C_{quat}), 126.09 (+, Ph), 127.08 (+, 2 × Ph), 127.67 (+, C-7), 128.84 (+, 2 × Ph), 141.08 (C_{quat}), 142.24 (C_{quat}), 175.93 (C_{quat}, C=O) ppm. *Peaks of C-2 could not be observed because of ^{13}C-$^{10/11}B$ coupling. MS (70 eV, EI): *m*/*z* (%) = 368 (25) [M^+], 308 (10), 268 (26), 240 (60), 213 (21), 180 (100), 167 (38), 153 (19), 115 (16), 101 (30), 85 (65), 55 (18), 41 (22). $C_{21}H_{26}O_4$ (342.4): calcd. C 71.75, H 7.94; found C 71.46, H 7.68.

Minor Diastereomer [*anti*-(*E*)-14b]: R_f = 0.21 (light petroleum/ethyl acetate, 10:1). IR (Film): ṽ = 3079, 3054, 3026, 2998, 2977, 2929, 2857, 1738, 1599, 1492, 1437, 1407, 1373, 1330, 1256, 1230, 1196, 1171, 1143, 1115, 1016, 963, 907, 857, 760, 704 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.22–0.25 (m, 1 H, cPr-H), 0.96–0.99 (m, 1 H, cPr-H), 1.03 (s, 6 H, 2 × CH_3), 1.07 (s, 6 H, 2 × CH_3), 1.20 (dd, *J* = 3.9, 7.5 Hz, 1 H, cPr-H), 1.80 (dd, *J* = 5.8, 13.4 Hz, 1 H, 4-H), 2.17 (dd, *J* = 6.4, 12.9 Hz, 1 H, 4-H), 2.48–2.54 (m, 1 H, 6-H), 2.62–2.68 (m, 1 H, 6-H), 2.83–2.89 (m, 1 H, 5-H), 3.76 (s, 3 H, OCH_3), 5.80 (t, *J* = 4.4 Hz, 1 H, 7-H), 7.20–7.29 (m, 5 H, Ph) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT)*: δ = 16.66 (–, cPr-C), 24.42 (+, 2 × CH_3), 25.12 (+, 2 × CH_3), 25.84 (C_{quat}, cPr-C), 27.61 (–, C-6), 39.44 (+, C-5), 39.55 (–, C-4), 51.78 (+, OCH_3), 82.70 (2 × C_{quat}), 126.19 (+, Ph), 127.30 (+, 2 × Ph), 128.08 (+, C-7), 128.54 (+, 2 × Ph), 141.40 (C_{quat}), 143.58 (C_{quat}), 175.72 (C_{quat}, C=O) ppm. *Peaks of C-2 could not be observed because of ^{13}C-$^{10/11}B$ coupling. MS (70 eV, EI): *m*/*z* (%) = 368 (36) [M^+], 336 (10), 308 (12), 268 (35), 240 (64), 224 (27), 205 (39), 181 (100), 167 (43), 154 (20), 141 (17), 115 (18), 85 (72), 69 (29), 55 (44). $C_{22}H_{29}BO_4$ (368.29): calcd. 368.2159 (correct HRMS).

Domino Heck–Diels–Alder Reaction of 2-(Tributylstannyl)-1,1′-bicyclopropylidene (8c): According to GP-1, $Pd(OAc)_2$ (15.2 mg, 67μmol), triphenylphophane (53.2 mg, 202 μmol), K_2CO_3 (374.4 mg, 2.7 mmol), Et_4NCl (250 mg, 1.35 mmol), iodobenzene (**9**, 276 mg, 1.35 mmol), 2-(tributylstannyl)bicyclopropylidene (**8c**, 1.0 g, 2.7 mmol) and *tert*-butyl acrylate (**13**, 347 mg, 2.7 mmol) were stirred in anhydrous MeCN (2 mL) at 80 °C for 48 h. After work-up and column chromatography on silica gel (100 g, 3 × 30 cm, light petroleum/ethyl acetate, 14:1) a mixture of *syn*/*anti*-(*E*)-**15c** and/or *syn*/*anti*-(*Z*)-**15c*** along with some unidentified impurities (33 mg, yellowish oil) and ***tert*-butyl 8-phenylspiro[2.5]oct-7-ene-5-carboxylate*** (**26**) (187 mg. 49%, yellowish oil) were obtained. *These spirooctenes could not be isolated in pure form and their relative configurations could not be assigned. For the spectroscopic data of compound **26** see ref.[3].

Domino Heck–Diels–Alder Reaction of (1,1′-Bicyclopropyliden-2-yl)-dimethylsilanol (8d): According to GP-1, $Pd(OAc)_2$ (18.2 mg, 80 μmol), triphenylphophane (64 mg, 243 μmol), K_2CO_3 (448 mg, 3.24 mmol), Et_4NCl (300 mg, 1.62 mmol), iodobenzene (**9**, 330 mg, 1.62 mmol), **8d** (500 mg, 3.24 mmol) and *tert*-butyl acrylate (**13**, 415 mg, 3.24 mmol) were stirred in anhydrous MeCN (2 mL) at 80 °C for 48 h. After work-up and column chromatography on sil-

ica gel (100 g, 3 × 30 cm, light petroleum/ethyl acetate, 14:1), a mixture of *syn*/*anti*-(*E*)-**15d** and/or *syn*/*anti*-(*Z*)-**15d*** along with some unidentified impurities (214 mg, colorless oil) and ***tert*-butyl 8-phenylspiro[2.5]oct-7-ene-5-carboxylate*** (**26**) (116 mg, 25%, yellowish oil) was obtained. *These spirooctenes could not be isolated in pure form, and their relative configurations could not be assigned. For the spectroscopic data of compound **26** see ref.[3].

Domino Heck–Diels–Alder Reaction of Methyl 1,1′-Bicyclopropylidene-2-carboxylate (8e): According to GP-1, $Pd(OAc)_2$ (20.3 mg, 90 μmol), triphenylphophane (71.3 mg, 271 μmol), K_2CO_3 (500 mg, 3.62 mmol), Et_4NCl (300 mg, 1.81 mmol), iodobenzene (**9**, 369 mg, 1.81 mmol), methyl bicyclopropylidenecarboxylate (**8e**, 500 mg, 3.62 mmol) and *tert*-butyl acrylate (**13**, 464 mg, 3.62 mmol) were stirred in anhydrous MeCN (2 mL) at 80 °C for 48 h. After work-up and column chromatography on silica gel (100 g, 3 × 30 cm, light petroleum/ethyl acetate, 10:1) a mixture of *syn*- and *anti*-(*E*)-**15e** (ratio 1.25:1 according to NMR, 427.5 mg, 69%, colorless solid) as well as a mixture of *syn*- and *anti*-(*Z*)-**15e** (ratio 1.1:1 according to NMR, 37 mg, 6%, yellowish oil) were obtained. The diastereomers *syn*- and *anti*-(*E*)-**15e** were partially separated from each other as crystals by slow evaporation of solvents from an ethyl acetate/diethyl ether (1:1) solution of these compounds.

***tert*-Butyl 1-Methoxycarbonyl-8-phenylspiro[2.5]oct-7-ene-5-carboxylate [*syn*/*anti*-(*E*)-15e]**

Major Diastereomer [*syn*-(*E*)-15e]: R_f = 0.37 (light petroleum/ethyl acetate, 10:1). IR (KBr): $\tilde{\nu}$ = 3064, 3027, 2997, 2977, 2956, 2919, 2876, 1732, 1723, 1495, 1481, 1440, 1389, 1370, 1351, 1320, 1280, 1265, 1226, 1212, 1194, 1169, 1068, 1048, 946, 892, 846, 757, 696 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19 (dd, J = 5.2, 8.3 Hz, 1 H, cPr-H), 1.49 [s, 9 H, $C(CH_3)_3$], 1.58 (t, J = 5.6 Hz, 1 H, cPr-H), 1.74–2.13 (*AB system*, δ_A = 2.08, δ_B = 1.78, J_A = 7.9, 13.5, J_B = 5.3, 13.5 Hz, 2 H, 4-H or 6-H), 1.97–2.03 (m, 1 H, cPr-H), 2.47–2.53 (m, 2 H, 4-H or 6-H), 2.64–2.75 (m, 1 H, 5-H), 3.36 (s, 3 H, OCH_3), 5.94 (t, J = 4.7 Hz, 1 H, 7-H), 7.13–7.32 (m, 5 H, Ph) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 18.27 (–, cPr-C), 27.49 (–, C-4 or C-6), 28.07 [+, $C(CH_3)_3$], 29.39 (+, cPr-C), 29.62 (C_{quat}, cPr-C), 37.42 (–, C-4 or C-6), 40.03 (+, C-5), 51.25 (+, OCH_3), 80.50 [C_{quat}, $C(CH_3)_3$], 126.52 (+, Ph), 127.56 (+, 2 × Ph), 127.62 (+, 2 × Ph), 129.30 (+, C-7), 140.96 (C_{quat}), 141.70 (C_{quat}), 170.88 (C_{quat}, C=O), 174.53 (C_{quat}, C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 342 (11) [M^+], 327 (4) [$M^+ - CH_3$], 311 (6), 286 (26), 240 (48), 226 (46), 209 (17), 181 (100), 167 (22), 154 (11), 57 (26).

Minor Diastereomer [*anti*-(*E*)-15e]: R_f = 0.37 (light petroleum/ethyl acetate, 10:1). IR (KBr): $\tilde{\nu}$ = 3080, 3027, 2996, 2978, 2955, 2927, 2867, 1733, 1723, 1494, 1481, 1437, 1387, 1370, 1351, 1318, 1280, 1258, 1226, 1212, 1192, 1170, 1068, 947, 893, 846, 829, 756, 697 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.29–1.36 (m, 2 H, cPr-H, 4-H or 6-H), 1.46 [s, 9 H, $C(CH_3)_3$], 1.63–1.68 (m, 1 H, cPr-H), 1.76–1.81 (m, 1 H, cPr-H), 2.23 (t, J = 12.7 Hz, 1 H, 4-H or 6-H), 2.39–2.67 (m, 2 H, 4-H or 6-H), 2.89–3.03 (m, 1 H, 5-H), 3.34 (s, 3 H, OCH_3), 5.76 (t, J = 3.8 Hz, 1 H, 7-H), 7.06–7.10 (m, 2 H, Ph), 7.20–7.31 (m, 3 H, Ph) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 19.92 (–, *c*Pr-C), 28.06 [+, $C(CH_3)_3$], 29.0 (–, C-4 or C-6), 30.38 (C_{quat}, cPr-C), 30.50 (+, cPr-C), 38.80 (–, C-4 or C-6), 40.37 (+, C-5), 51.32 (+, OCH_3), 80.38 [C_{quat}, $C(CH_3)_3$], 126.39 (+, C-7), 127.40 (+, 2 × Ph), 128.07 (+, 2 × Ph), 130.16 (+, Ph), 138.97 (C_{quat}), 141.59 (C_{quat}), 170.90 (C_{quat}, C=O), 174.34 (C_{quat}, C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 342 (4) [M^+], 286 (22), 240 (42), 226 (44), 181 (100), 167 (24), 154 (16), 115 (9), 57 (82), 41 (39). $C_{21}H_{26}O_4$ (342.4): calcd. C 73.66, H 7.65; found C 73.56, H 7.43. The elemental analysis was carried out with the purified mixture of *syn*- and *anti*-diastereomers.

5-*tert*-Butyl 1-Methoxycarbonyl-8-phenylspiro[2.5]oct-7-ene-5-carboxylate [*syn*/*anti*-(*Z*)-15e]: R_f = 0.46 (light petroleum/ethyl acetate, 10:1). IR (Film): $\tilde{\nu}$ = 3079, 3056, 3003, 2977, 2951, 2931, 2846, 1729, 1492, 1479, 1441, 1392, 1368, 1335, 1316, 1258, 1212, 1192, 1170, 1152, 1070, 990, 904, 849, 829, 764, 705 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93–0.97 (m, 1 H, cPr-H), 1.13 (dd, J = 4.9, 8.1 Hz, 1 H, cPr-H), 1.19 (dd, J = 4.6, 6.0 Hz, 1 H, cPr-H), 1.28–1.32 (m, 1 H, cPr-H), 1.43 [s, 9 H, $C(CH_3)_3$], 1.44 [s, 9 H, $C(CH_3)_3$], 1.55–1.60 (m, 1 H, cPr-H), 1.75 (dd, J = 6.0, 8.3 Hz, 1 H, cPr-H), 1.89–2.19 (m, 4 H, 4-H or 6-H), 2.34–2.44 (m, 4 H, 4-H or 6-H), 2.48–2.60 (m, 1 H, 5-H), 2.68–2.78 (m, 1 H, 5-H), 3.65 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 5.59–5.64 (m, 2 H, 2 × 7-H), 6.99–7.04 (m, 4 H, Ph), 7.19–7.29 (m, 6 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, DEPT): δ = 17.80 (–, cPr-C), 18.59 (–, cPr-C), 24.65 (+, 2 × cPr-C), 28.03 [+, 2 × $C(CH_3)_3$], 28.32 (–, C-4 or C-6), 28.60 (–, C-4 or C-6), 29.25 (C_{quat}, cPr-C), 29.90 (–, C-4 or C-6), 30.06 (C_{quat}, cPr-C), 30.99 (–, C-4 or C-6), 40.24 (+, C-5), 40.43 (+, C-5), 51.68 (+, OCH_3), 51.72 (+, OCH_3), 80.09 [C_{quat}, $C(CH_3)_3$], 80.21 [C_{quat}, $C(CH_3)_3$], 126.48 (+, C-7), 126.81 (+, C-7), 126.94 (+, Ph), 126.99 (+, Ph), 127.71 (+, 2 × Ph), 127.77 (+, 2 × Ph), 129.34 (+, 2 × Ph), 129.42 (+, 2 × Ph), 139.07 (C_{quat}), 139.48 (C_{quat}), 140.66 (C_{quat}), 140.87 (C_{quat}), 171.87 (C_{quat}, C=O), 172.09 (C_{quat}, C=O), 174.25 (C_{quat}, C=O), 175.50 (C_{quat}, C=O) ppm. MS (DCI): *m*/*z* (%) = 702.7 (12) [2*M* + NH_4^+], 360 (100) [*M* + NH_4^+], 343 (14) [*M* + H^+] 304 (61). HRMS-ESI for $C_{21}H_{26}O_4$ (342.43): [*M* + H]$^+$ 343.19047, calcd. 343.19039; [*M* + Na]$^+$ 365.17244, calcd. 365.17233. *For all measurements the pure mixture of *syn*- and *anti*-diastereomers of (*Z*)-**15e** was used.

CCDC-664722 [for *syn*-(*E*)-**14b**], -664723 [for *syn*-(*E*)-**15e**] and -664724 [for *anti*-(*E*)-**15e**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Land Niedersachsen as well as BAYER, BASF and Degussa AG (gifts of chemicals). The authors are grateful to Reinhard Machinek for his technical support and suggestions in measuring NOESY and other two-dimensional NMR spectra.

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[11] Crystal structure analysis of *syn*-(*E*)-**14b** (Figure 1): $C_{22}H_{29}BO_4$ (390.42); crystal size: $1.00 \times 0.60 \times 0.40$ mm^3, monoclinic, a = 727.87(7), b = 1643.88(13), c = 1005.23(8) pm, α = 90°, β = 97.141(10)°, γ = 90°, V = 1.02293(16) nm^3; Z = 2, space group $P2(1)$, T = 200(2) K, ρ = 1.196 Mg/m^{-3}, absorption coefficient: 0.080 mm^{-1}, F_o = 396, θ range for data collection: 3.52 to 24.91°, reflection collected: 2344, R_{int} = 2209[0.0541], data/restraints/paramaters: 2209/1/249, Goof on F^2 = 1.064, final R indices [$I > 2\sigma(I)$] = R_1(0.0373), wR_2(0.0975), R indices (all data): R_1(0.0387), wR_2(0.0991), largest diff. peak and hole: 0.160 and –0.210 e Å^{-3}. Crystal structure analysis of *syn*-(*E*)-**15e** (Figure 2): $C_{21}H_{26}O_4$ (342.42); crystal size: $0.50 \times 0.50 \times 0.50$ mm^3, monoclinic, a = 1718.9(3), b = 637.12(13), c = 1748.3(4) pm, α = 90°, β = 94.58(3)°, γ = 90°, V = 1.9085(7) nm^3; Z = 4, space group $P2_1/n$, T = 200(2) K, ρ = 1.192 Mg/m^{-3}, absorption coefficient: 0.081 mm^{-1}, F_o = 736, θ range for data collection: 3.58 to 24.97°, reflection collected: 6956, R_{int} = 3342[0.0781], data/restraints/paramaters: 3342/0/231, Goof on F^2 = 1.043, final R indices [$I > 2\sigma(I)$] = R_1(0.0548), wR_2(0.1398), R indices (all data): R_1(0.0765), wR_2(0.1560), largest diff. peak and hole: 0.350 and –0.169 e Å^{-3}. Crystal structure analysis of *anti*-(*E*)-**15e** (Figure 2): $C_{21}H_{26}O_4$ (342.42); crystal size: $0.70 \times 0.20 \times 0.20$ mm^3, monoclinic, a = 628.33(13), b = 2413.4(5), c = 1274.9(3) pm, α = 90°, β = 99.42(3)°, γ = 90°, V = 1.9073(7) nm^3; Z = 4, space group Cc, T = 140(2) K, ρ = 1.192 Mg/m^{-3}, absorption coefficient: 0.081 mm^{-1}, F_o = 736, θ range for data collection: 1.69 to 24.77°, reflection collected: 5426, R_{int} = 3037[0.0498], data/restraints/paramaters: 3037/2/230, Goof on F^2 = 1.057, final R indices [$I > 2\sigma(I)$] = R_1(0.0375), wR_2(0.1052), R indices (all data): R_1(0.0383), wR_2(0.1062), largest diff. peak and hole: 0.156 and –0.131 e Å^{-3}.

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Received: October 22, 2007
Published Online: December 14, 2007

