CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200600361

# Diels–Alder Reactions of Novel (1′-Arylallylidene)cyclopropanes with Heterodienophiles**

**Ligang Zhao, Baris Yucel, René Peter Scheurich, Daniel Frank, and Armin de Meijere*[a]**

**Abstract:** Palladium-catalyzed cross-coupling of various aryl iodides with bicyclopropylidene provided isolable (1′-arylallylidene)cyclopropanes, which reacted with a number of carbonyl compounds in the presence of $Eu(fod)_3$ under high pressure to furnish oxaspiro[2.5]octene derivatives in moderate to good yields (22–69%). The reactions of the allylidenecyclopropanes with two azo compounds as dienophiles afforded diazaspiro[2.5]octenes in high yields (82 and 99%) even at ambient pressure. When treated with nitrosobenzene, two of the allylidenecyclopropanes gave the Diels–Alder adducts in up to 83 and 40% yield. 2,5-Diiodo-*p*-xylene coupled twice with bicyclopropylidene, and the product underwent a twofold Diels–Alder reaction with nitrosobenzene to produce the bis(spirocyclopropaneoxazine) derivative in 88% yield. This overall transformation can be brought about in a one-pot, two-step operation by addition of the nitrosoarene to the reaction mixture immediately after formation of the allylidenecyclopropanes to furnish various 5-oxa-4-azaspiro[2.5]oct-7-ene derivatives in 22–77% yield. The coupling of methyl bicyclopropylidenecarboxylate with 2,6-dimethylphenyl iodide produced a mixture of very stable regioisomeric allylidenecyclopropane derivatives in 90% yield. The reaction of this mixture with *N*-phenyltriazolinedione gave a corresponding mixture of the spirocyclopropanated heterobicycles in 61% yield.

**Keywords:** allylic compounds · bicyclopropylidene · cycloaddition · sequential reactions · spiro compounds

## Introduction

Over the last decade, multistep sequential transformations, including domino or cascade reactions, have emerged as a major advance toward higher efficiency in organic synthesis. Increasing needs for more elegant approaches to complex frameworks from readily accessible starting materials by simple synthetic operations have attracted considerable attention to this area.[1] Particularly impressive developments with respect to this concept have been realized with the assistance of transition-metal complexes by taking advantage of their unique reactivity patterns.[2]

For a number of years, we have been engaged in developing new palladium-catalyzed cascade reactions involving inter- or intramolecular Heck couplings and a subsequent pericyclic or cycloaddition reaction.[3] In all of these sequences, the carbopalladation of reactive multiple bonds in simple substrates is the first C–C bond-forming step. In Heck-type reactions with the uniquely reactive tetrasubstituted alkene bicyclopropylidene (**1**),[4] such carbopalladations by a wide range of aryl- and alkenylpalladium halides lead to cyclopropylcarbinylpalladium halide intermediates, which, after rearrangement and β dehydropalladation, afford allylidenecyclopropane derivatives **5** that readily undergo Diels–Alder reactions with a range of dienophiles (Scheme 1).[5]

As the carbopalladation of **1** is faster than that of many acceptor-substituted alkenes, including acrylates, the coupling of **1** with ensuing rearrangement and subsequent cycloaddition can be performed as a domino reaction, with the dienophile present in the reaction mixture from the beginning, to furnish spiro[2.5]octenes **7** in good to very good yields[3c,5] (Scheme 1). However, when the coupling of **1** was carried out in the presence of a heterodienophile such as diethyl azodicarboxylate (DEAD), the yields were much

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[**] Part 138 in the series "Cyclopropyl Building Blocks for Organic Synthesis". For Part 137, see: M. Ahmar, M. Knoke, A. de Meijere, B. Cazes, *Synthesis* **2007**, in press. Part 136: A. Osipova, D. S. Yufit, A. de Meijere, *Synthesis* **2007**, in press.

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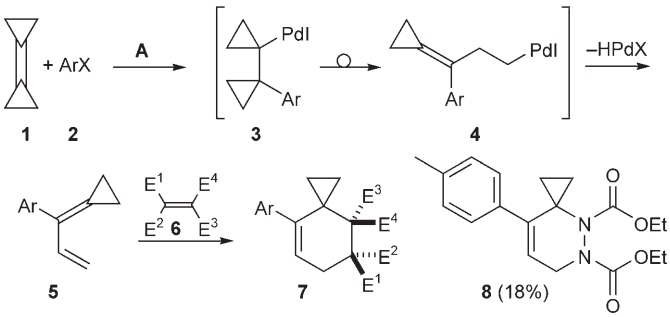



Scheme 1. Heck reactions of bicyclopropylidene (**1**) with aryl halides **2** to yield (1′-arylallylidene)cyclopropanes **5**, and their subsequent Diels–Alder reactions with dienophiles **6** to form spiro[2.5]octenes **7**. A = $Pd(OAc)_2$, $PPh_3$, $K_2CO_3$, $Et_4NCl$, MeCN, 80 °C, 12–24 h.

poorer; for example, the cross-coupling–cycloaddition product **8** from **1**, *p*-iodotoluene (**2b**), and DEAD was obtained in only 18% yield (Scheme 1).[6]

To check out other possibilities of achieving better yields of such heterobiaryl mimics, we turned our attention to the preparation of kinetically more stable allylidenecyclopropanes, which were then isolated and subsequently subjected to cycloadditions with various heterodienophiles.

## Results and Discussion

Most of the previously isolated allylidenecyclopropanes such as **5a**,**b** (from iodobenzene and *p*-iodotoluene, respectively) are prone to undergo rapid polymerization.[3c] As steric encumbrance by *ortho* substituents on the aryl group should kinetically stabilize **5**, Heck coupling of **1** with various aryl iodides **2c**–**g** containing *ortho* substituents were carried out under conditions similar to that of the Jeffery protocol ($Pd(OAc)_2$, $PPh_3$, $K_2CO_3$, $Et_4NCl$, MeCN, 80 °C, 24 h).[7] Among the (1′-arylallylidene)cyclopropanes **5c**–**g** obtained in good to moderate yields (Table 1), the 2-methylphenyl- and 2,6-dimethylphenyl-substituted compounds **5c** and **5d** were quite stable and could be kept at room temperature for several days without significant changes in their qualities.

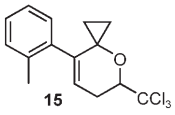
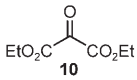
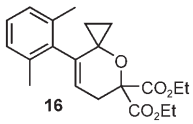
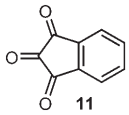
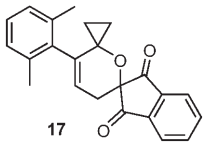
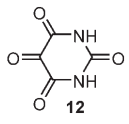
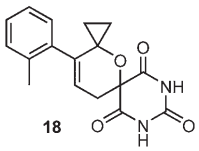
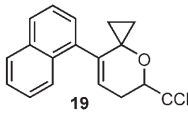
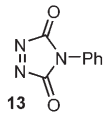
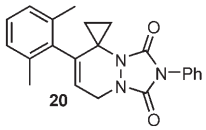
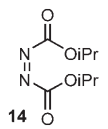
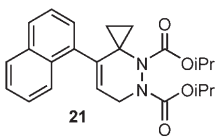
The isolated new (1′-arylallylidene)cyclopropanes **5c**–**e** were treated with some activated carbonyl and azo compounds that are known to be good heterodienophiles. As trichloroacetaldehyde (**9**) and acetaldehyde itself did not react with **5c**,**d** at temperatures up to 50 °C, not even in the presence of Lewis acids such as $BF_3{\cdot}OEt_2$, $LiClO_4$, or $Eu(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione), high pressure was employed.[8] Indeed, under a pressure of 10 kbar, dienes **5c** and **5d** in the presence of $Eu(fod)_3$ did react with trichloroacetaldehyde (**9**), diethyl mesoxalate (**10**), and indane-1,2,3-trione (**11**) at ambient temperature to furnish 4-oxaspiro[2.5]oct-7-ene derivatives **15**–**18** and **19** in moderate to good yields (22–69%; Table 2, entries 1–3 and 5).[9] The mild Lewis acid $Eu(fod)_3$ was essential for the success of this cycloaddition;[10] the presence of other Lewis acids such as $Sc(OTf)_3$ and $Yb(OTf)_3$ did not lead to the formation of the dihydropyrane products. Pyrimidine-2,4,5,6-tetrone (**12**) under a pressure of 10 kbar did not require the $Eu(fod)_3$ catalyst to undergo cycloaddition with **5c** at room temperature, and it yielded **18** (35%;

Table 1. Synthesis of (1′-arylallylidene)cyclopropanes **5a**,**c**–**g** by Heck coupling of bicyclopropylidene (**1**) with aryl iodides **2a**,**c**–**g**.[a]

| Entry | ArI (**2**) | Product | Yield [%][b] |
|---|---|---|---|
| 1 | PhI (**2a**) | **5a**[c] | 75 |
| 2 | 2-$MeC_6H_4I$ (**2c**) | **5c** | 90 |
| 3 | 2,6-$Me_2C_6H_3I$ (**2d**) | **5d** | 99 |
| 4 | 1-Naphth-I (**2e**) | **5e** | 62 |
| 5 | 9-Anthr-I (**2f**) | **5f** | 52 |
| 6 | 9-Phenanth-I (**2g**) | **5g** | 47 |

[a] Reaction conditions: ArI (1 equiv), **1** (2 equiv), $Pd(OAc)_2$ (5 mol%), $PPh_3$ (15 mol%), $K_2CO_3$, $Et_4NCl$, MeCN, 80 °C, 24 h. [b] Yield of isolated product. [c] An oil prone to polymerization.

Table 2. Diels–Alder reactions of (1′-arylallylidene)cyclopropanes **5c**–**e** with carbonyl and azo dienophiles (see Scheme 1).

| Entry | Diene | Dienophile | Conditions[a] | Product | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | **5c** |  **9** | A |  **15** | 54 |
| 2 | **5d** |  **10** | A |  **16** | 69 |
| 3 | **5d** |  **11** | A |  **17** | 22 |
| 4 | **5c** |  **12** | B |  **18** | 35 |
| 5 | **5e** |  **9** | A |  **19** | 30[c] |
| 6 | **5d** |  **13** | C |  **20** | 82 |
| 7 | **5e** |  **14** | D |  **21** | 99[c] |

[a] A = $Eu(fod)_3$ (10 mol%), 10 kbar, 23 °C; B = 10 kbar, 23 °C; C = 23 °C, 2 h, ambient pressure; D = 50 °C, 3 h, ambient pressure. [b] Yield of isolated product. [c] Mixture of two diastereomers (atropisomers), the ratio of which (2:3 for **19** and 2.6:1 for **21**) was determined by integration of relevant $^1H$ NMR signals in the spectra of the crude products.

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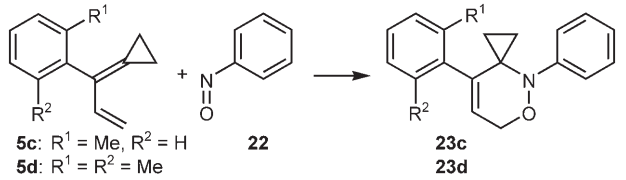
Table 2, entry 4). *N*-Phenyltriazolinedione (PTAD; **13**) and diisopropyl azodicarboxylate (DIAD; **14**) neither required a Lewis acid catalyst nor high pressure. Whereas **13** reacted with **5d** at ambient temperature to give the cycloadduct **20** in 82% yield, **14** required heating at 50°C for 3 h to furnish **21** virtually quantitatively (Table 2, entries 6 and 7).

Oxygen-containing medium-sized heterocycles, particularly 5,6-dihydropyran derivatives, are important structural units commonly found in various biologically active compounds.[8] Interestingly, however, these units have rarely been incorporated with other carbo- or heterocycles in spirocyclic frameworks.[9]

As nitrosoarenes[11] are known to be rather reactive heterodienophiles,[12] the reasonably reactive (1′-arylallylidene)cyclopropanes **5c**,**d** were also treated with nitrosobenzene (**22**) under various conditions to optimize the yields of the resulting 5-oxa-4-azaspiro[2.5]oct-7-ene derivatives **23** (Table 3). The reaction of **5c** with 1.1 equivalents of **22** in

Table 3. Diels–Alder reactions of (1′-arylallylidene)cyclopropanes **5c**,**d** with nitrosobenzene (**22**).




| Entry | Diene | **22** [equiv] | Solvent | *T* [°C] | *t* [h] | Product, yield [%][a] |
|---|---|---|---|---|---|---|
| 1 | **5c** | 1.1 | MeCN | 20 | 18 | **23c**, 83 |
| 2 | **5c** | 1.1 | toluene | 80 | 1 | **23c**, 62 |
| 3 | **5c** | 1.5 | MeCN | 20 | 18 | **23c**, 86 |
| 4 | **5c** | 1.5 | MeCN | 20[b] | 18 | **23c**, 66[b] |
| 5 | **5d** | 1.1 | toluene | 80 | 2 | **23d**, 32 |
| 6 | **5d** | 1.1 | MeCN | 20 | 30 | **23d**, 23 |
| 7 | **5d** | 1.5 | MeCN | 80 | 2 | **23d**, 40 |

[a] Yield of isolated product. [b] The reaction was carried out under a pressure of 10 kbar.

acetonitrile at room temperature after 18 h gave the oxazaspirooctene **23c** in 83% yield (Table 3, entry 1). The same reaction in toluene at 80°C after 1 h furnished a poorer yield (62%; Table 3, entry 2). The yield of **23c** from **5c** and **22** in acetonitrile could be slightly improved by employing 1.5 instead of 1.1 equivalents of the dienophile **22**. Surprisingly, application of high pressure (10 kbar) to a mixture of **5c** and **22** in acetonitrile led to a decrease in yield (66%; Table 3, entry 4). The sterically more encumbered 1′-(2,6-dimethylphenyl)allylidenecyclopropane (**5d**), however, gave under all of the tested conditions the oxazaspirooctene **23d** at best in 40% yield (Table 3, entry 7). Notably though, the reaction of both dienes **5c** and **5d** with **22** afforded only 5-oxa-4-azaspiro[2.5]octenes **23** with complete regioselectivity, as assigned on the basis of their NMR spectra (HMBC, HMQC, and $^1$H-$^1$H NOESY) and an X-ray crystal-structure analysis of **23c** (Figure 1).

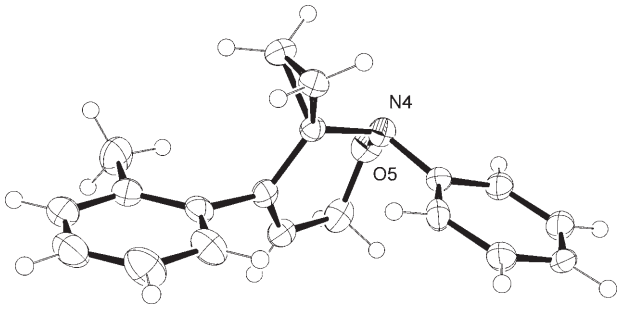
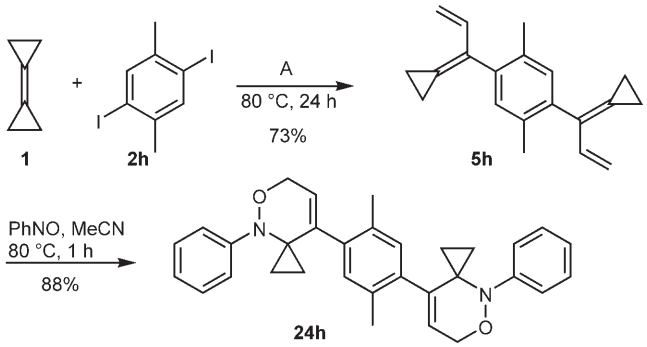



Figure 1. Structure of 8-(2-methylphenyl)-4-phenyl-5-oxa-4-azaspiro-[2.5]oct-7-ene (**23c**) in the crystal.[13] Thermal ellipsoids are drawn at the 50% probability level.

Remarkably, the twofold Heck coupling of **1** with 1,4-diiodo-2,5-dimethylbenzene (**2h**) to give the bisallylidenecyclopropane derivative **5h** proceeded in 73% yield, and the Diels–Alder reaction of **5h** with **22** in acetonitrile at 80°C for 1 h afforded the twofold cycloadduct **24h** in 88% yield (Scheme 2). The product **24h** was easily isolated by simple filtration of the reaction mixture, as upon addition of **22** to the solution of **5h**, the product **24h** immediately started to precipitate.

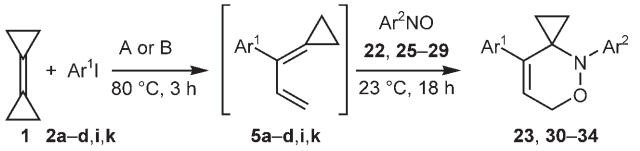



Scheme 2. Twofold Heck coupling of bicyclopropylidene (**1**) with 1,4-diiodo-2,5-dimethylbenzene (**2h**) and twofold Diels–Alder reaction of the resulting 1,4-bis-(1-cyclopropylideneallyl)-2,5-dimethylbenzene (**5h**) with nitrosobenzene (**22**). A = $Pd(OAc)_2$ (10 mol%), $PPh_3$ (30 mol%), $K_2CO_3$, $Et_4NCl$, MeCN.

The cross-coupling of **1** with aryl iodides **2** and subsequent cycloaddition of nitrosoarenes **22** and **25**–**29** to the initially formed (1′-arylallylidene)cyclopropanes **5** can also be performed in one pot without isolation of **5**, but not with the nitroso compound present from the beginning (Table 4).[14] Among the different conditions tested for the model reaction involving **1**, **2c**, and **22**, the best yield (77%) of the adduct **23c** was achieved when the first step was carried out under Jeffery-type conditions[7] at 80°C for 3 h, with subsequent addition of 1.5 equivalents of **22** and further stirring at ambient temperature for 18 h (Table 4, compare entries 1–3 and 4). When the cross-coupling step was performed under typical Heck conditions (i.e., $Pd(OAc)_2$, $Ph_3P$,

Table 4. One-pot, two-step sequential reaction involving cross-coupling of bicyclopropylidene (**1**) with aryl iodides **2a-d,i,k** and subsequent cycloaddition of nitrosoarenes.[a]

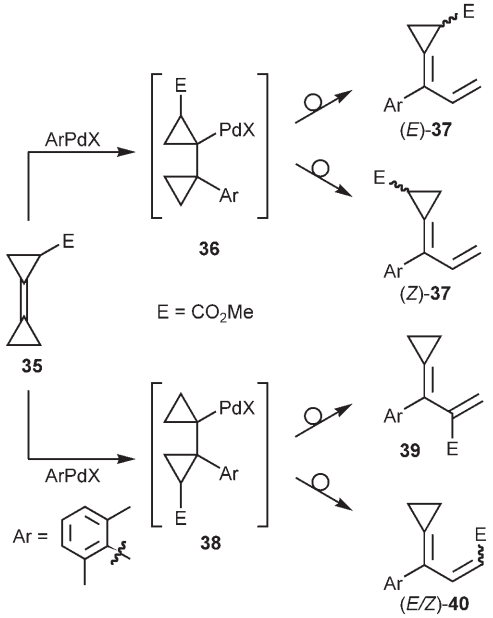



1 2a–d,i,k 5a–d,i,k 23, 30–34

| Entry | $Ar^1$ | $Ar^2$ | Product | Yield [%] |
|---|---|---|---|---|
| 1 | 2-$MeC_6H_4$ (**2c**) | Ph (**22**) | **23c** | 25[b] |
| 2 | 2-$MeC_6H_4$ (**2c**) | Ph (**22**) | **23c** | 64[c] |
| 3 | 2-$MeC_6H_4$ (**2c**) | Ph (**22**) | **23c** | 62[d] |
| 4 | 2-$MeC_6H_4$ (**2c**) | Ph (**22**) | **23c** | 77 |
| 5 | 2,6-$Me_2C_6H_3$ (**2d**) | Ph (**22**) | **23d** | 40[c] |
| 6 | Ph (**2a**) | Ph (**22**) | **23a** | 70 |
| 7 | 4-$MeC_6H_4$ (**2b**) | Ph (**22**) | **23b** | 60 |
| 8 | 4-$MeCOC_6H_4$ (**2i**) | Ph (**22**) | **23i** | 51 |
| 9 | 3-Py (**2k**) | Ph (**22**) | **23k** | 59 |
| 10 | 2-$MeC_6H_4$ (**2c**) | 4-Cl-$C_6H_4$ (**25**) | **30c** | 71 |
| 11 | 2-$MeC_6H_4$ (**2c**) | 4-Br-$C_6H_4$ (**26**) | **31c** | 75 |
| 12 | 2-$MeC_6H_4$ (**2c**) | 4-$MeO_2CC_6H_4$ (**27**) | **32c** | 76 |
| 13 | 2-$MeC_6H_4$ (**2c**) | 4-$MeC_6H_4$ (**28**) | **33c** | 71 |
| 14 | 2-$MeC_6H_4$ (**2c**) | 4-$MeOC_6H_4$ (**29**) | **34c** | 22 |

[a] Reaction conditions, except for entry 1, for the first step: A = $Pd(OAc)_2$, $PPh_3$, $K_2CO_3$, $Et_4NCl$, MeCN, 80 °C, 3 h; for the second step: 1.5 equivalents of $Ar^2NO$, ambient temperature, 18 h. [b] Reaction conditions for the first step: B = $Pd(OAc)_2$, $PPh_3$, $Et_3N$, DMF, 80 °C, 3 h; for the second step: same as in [a]. [c] Same conditions as A for the first step; 80 °C, 2 h for the second step. [d] Same conditions as A for the first step, but only 1.1 equivalents of **22** was added for the second step.

ent diastereomeric and regioisomeric (1′-arylallylidene)cyclopropanes (*E*)- and (*Z*)-**37**, **39**, as well as (*E*)- and (*Z*)-**40** can be formed (Scheme 3).




Scheme 3. The possible routes to five stereo- or regioisomeric 1′-arylallylidenecyclopropane derivatives (*E/Z*)-**37**, **39**, **40** from methyl bicyclopropylidenecarboxylate (**35**) via two regioisomeric carbopalladation intermediates **36** and **38**.

$Et_3N$, DMF), the overall yield was particularly low (25%; Table 4, entry 1).

The scope and limitations of this one-pot, two-step protocol was examined by employing a variety of other aryl iodides **2a–d,i,k** and nitrosoarenes **22** and **25–29** (Table 4, entries 5–14). This protocol for the reaction of **1** with **2d** and **22** produced the same overall yield (40%; Table 4, entry 5) as the cycloaddition of **22** to the isolated **5d** (Table 3, entry 7). The reaction sequence involving 3-iodopyridine (**2k**) furnished the oxazaspirooctene **23k** in 59% overall yield (Table 4, entry 9), although the intermediately formed 1′-pyridylallylidenecyclopropane **5k** turned out to be particularly unstable when it was isolated. Most of the 4-substituted nitrosobenzene derivatives **25–29** employed in the cycloaddition with 1′-(*o*-tolyl)allylidenecyclopropane obtained from **1** and **2c** gave the oxazaspirooctene derivatives **30c–34c** in good yields; only 4-methoxynitrosobenzene (**29**) gave the corresponding oxazaspiro[2.5]octene **34c** only in 22% yield.

The scope of this sequential reaction was further extended by employing methyl bicyclopropylidenecarboxylate (**35**), which is easily available from **1** in two steps,[15] in the cross-coupling step. The carbopalladation of **35** can lead to two regioisomeric intermediates **36** and **38**, each of which have two modes of cyclopropylcarbinyl- to homoallylpalladium halide rearrangement available. Thus, a total of five differ-

In practice though, the reaction of **35** with **2d** under Jeffery conditions[7] ($Pd(OAc)_2$, $PPh_3$, $K_2CO_3$, $Et_4NCl$, MeCN, 70 °C, 24 h) gave a mixture of only three stable (1′-arylallylidene)cyclopropanes, (*E*)-**37**, (*Z*)-**37**, and **39** (ratio 67:23:10), in very good yield (Scheme 4).[2e] The two diastereomeric major regioisomers (90% total) (*E*)-**37** and (*Z*)-**37** clearly arise by opening of the unsubstituted cyclopropane ring in **35**, that is, via the regioselectively formed carbopalladation intermediate **36**. The reason for this selectivity is most probably chelation of the arylpalladium halide approaching the double bond by the methoxycarbonyl group on the cyclopropane ring in **35**.[16] The mixture of (*E*)-**37**, (*Z*)-**37**, and **39**, upon reaction with *N*-phenyltriazolinedione (**13**) in a mixture of $CH_2Cl_2$ and MeCN at room temperature, gave a mixture of the three cycloadducts (*E*)-**41**, (*Z*)-**41**, and **42** in a 75:10:15 ratio (Scheme 4). The configurations of the diastereomeric oxazaspirooctene derivatives (*E*)-**41** and (*Z*)-**41** were confirmed by NMR NOESY experiments. The strong correlation of the cyclopropyl proton adjacent to the ester functionality with one of the methyl groups on the phenyl ring in the NOESY spectrum of (*Z*)-**41** and the correspondingly strong correlation of one of the cyclopropyl methylene protons in the spectrum of (*E*)-**41** with the same phenylmethyl protons were taken as proof of these configurations.

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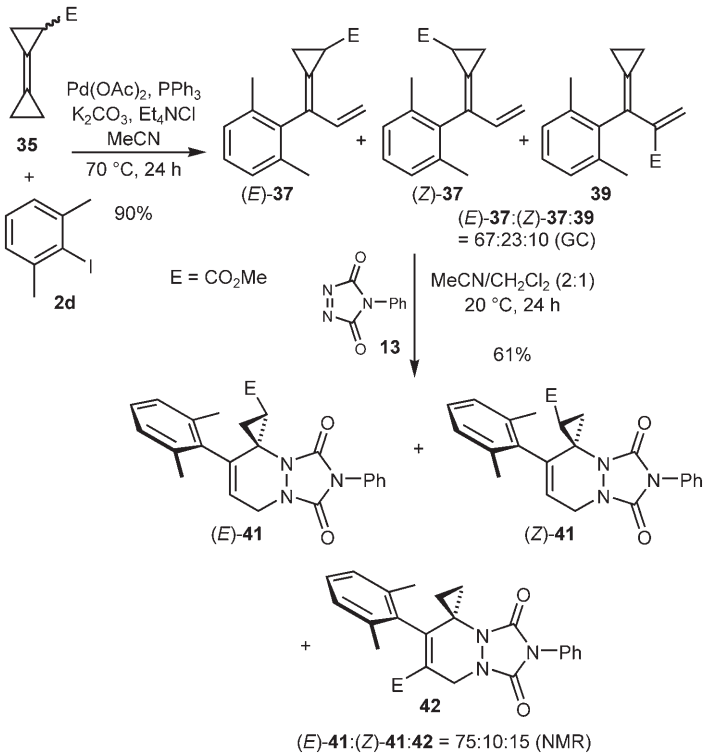


Scheme 4. Cross-coupling of methyl bicyclopropylidenecarboxylate (**35**) with 2,6-dimethyliodobenzene (**2d**) and subsequent cycloaddition of the thus formed (1′-arylallylidene)cyclopropanes (*E*)-**37**, (*Z*)-**37**, **39** with *N*-phenyltriazolinedione (**13**).

## Conclusions

*ortho*-Substituted aryl iodides, upon palladium-catalyzed cross-coupling with bicyclopropylidene (**1**), yield stable (1′-arylallylidene)cyclopropanes **5**, which, after isolation or in the same flask, react with various carbonyl, azo, and nitroso heterodienophiles to furnish heteroanalogues of the corresponding aryl-substituted spiro[2.5]octene derivatives in moderate to very good yields. Whereas carbonyl compounds have to be activated to react and mostly require a mild Lewis acid catalyst, azo compounds and nitrosoarenes undergo cycloadditions at ambient temperature and pressure. The variety of the thus available spirocyclopropanated heterocycles can be enhanced by the use of acceptor-substituted bicyclopropylidenes such as methyl bicyclopropylidenecarboxylate (**35**) in the cross-coupling step.

## Experimental Section

*General*

NMR spectra were recorded with a Varian Mercury 200 (200 MHz for $^1$H and 50.3 MHz for $^{13}$C), a Bruker AM 250 (250 MHz for $^1$H and 62.9 MHz for $^{13}$C NMR), a Varian UNITY-300 (300 MHz for $^1$H and 75.5 MHz for $^{13}$C NMR), or a Varian Inova 600 (600 MHz for $^1$H and 151 MHz for $^{13}$C NMR) instrument. Chemical shifts $\delta$ are given in ppm relative to residual peaks of deuterated solvents, and coupling constants $J$ are given in Hertz. Multiplicities 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) experiments. HMQC (heteronuclear multiple quantum coherence) spectra were also measured whenever necessary. IR spectra were recorded on a Bruker IFS 66 spectrometer as KBr pellets or 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 $R \approx 10\,000$ to be within $\pm 2$ ppm of the exact masses. Elemental analysis was 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 done under UV light at 254 nm, and development with MOPS reagent (10% molybdophosphoric acid in ethanol). Melting points were obtained with a Büchi apparatus according to Dr. Tottoli; values are uncorrected. All reagents were used as purchased from commercial suppliers without further purification. Acetonitrile was dried over $P_2O_5$, *N*,*N*-dimethylformamide (DMF) and $CH_2Cl_2$ were distilled from $CaH_2$. Ether and THF were freshly distilled from sodium/benzophenone ketyl. Solvents for column chromatography, ethyl acetate and light petroleum, were distilled in a rotatory evaporator. Nitrosoarenes[17] and **1**[6] were prepared according to published procedures.

*Syntheses*

General procedure for the synthesis of **5b–h** by Heck coupling of **1** with **2b–h**, Jeffery conditions (GP 1): A 50-mL screw-cap pyrex bottle containing anhydrous MeCN (25 mL) was charged under $N_2$ with palladium(II) acetate (56.0 mg, 0.25 mmol, 5.0 mol%), triphenylphosphine (198.0 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.0 mmol), and $Et_4NCl$ (830 mg, 5.00 mmol). Nitrogen was bubbled through the mixture for 5 min, and the mixture was treated with 5.00 mmol of the respective aryl iodide and **1** (800 mg, 10.00 mmol). After the mixture was stirred at 80 °C for 24 h, the bottle was cooled to ambient temperature. The reaction mixture was taken up in diethyl ether (50 mL). The solution was washed with water (5 × 25 mL), and the organic phase was dried with anhydrous $MgSO_4$. After removal of the solvent in a rotatory evaporator, the residue was subjected to chromatography on silica gel.

General procedure for Diels–Alder reaction of **5c–e** with **9–12** under high pressure (GP 2): A sealable teflon tube with anhydrous $CHCl_3$ (1.5 mL) was charged under argon with the respective (1′-arylallylidene)-cyclopropane (1.0 equiv), $Eu(fod)_3$ (10 mol%), and the respective dienophile (2.0 equiv). The mixture was pressurized at 10 kbar and heated at the stated temperature for the given time. After having reached ambient pressure and temperature again, the crude mixture was filtered, and the solids on the filter were washed with $Et_2O$ (10 mL). After removal of the solvent in a rotatory evaporator, the residue was subjected to chromatography on silica gel.

General procedure for Diels–Alder reaction of **5c–h** with **13**, **14**, **22**, **23c**, and **23d** (GP 3): The respective heterodienophile was added to a solution of **5** (1.00 mmol) in anhydrous solvent (2.0 mL) under a nitrogen atmosphere, then the mixture was stirred at the stated temperature for the stated time (Tables 2 and 3). After removal of the solvent in a rotatory evaporator under reduced pressure at room temperature, the residue was subjected to chromatography on silica gel with pentane/diethyl ether (10:1) as eluent.

General procedure for the one-pot, two-step reactions involving **1**, **2a–d**,**i**,**k,** and **22**, **25–29** (GP 4): A dry 20-mL pyrex bottle containing anhydrous MeCN (4 mL) was charged under $N_2$ with palladium(II) acetate (22.4 mg, 0.10 mmol, 5.0 mol%), triphenylphosphine (76.6 mg, 0.30 mmol, 15.0 mol%), $K_2CO_3$ (552 mg, 4.00 mmol), and $Et_4NCl$ (332 mg, 2.00 mmol). Nitrogen was bubbled through the mixture for 5 min, and the mixture was treated with 2.00 mmol of the respective aryl iodide (2.00 mmol) and **1** (320 mg, 4 mmol). After the reaction mixture was stirred at 80 °C for 3 h, it was cooled to ambient temperature, then

  

the respective nitrosoarene was added, and the mixture was stirred for 18 h at room temperature. The reaction was quenched by the addition of water (10 mL), then the mixture was extracted with diethyl ether (5× 25 mL), and the organic extracts were dried over anhydrous $MgSO_4$. After removal of the solvent in a rotatory evaporator, the residue was subjected to chromatography on silica gel.

**5c**: According to GP 1, $Pd(OAc)_2$ (56.0 mg 0.25 mmol, 5.0 mol%), $PPh_3$ (198 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.00 mmol), $Et_4NCl$ (830 mg, 5.00 mmol), **1** (800 mg, 10.0 mmol), and **2c** (1.09 g, 5.00 mmol) in MeCN (25.0 mL) at 80 °C for 24 h, after workup and purification (2× 30 cm column, $R_f$ = 0.60 (pentane)), yielded **5c** (765 mg, 4.50 mmol, 90%) as a colorless oil, which solidified at −20 °C. IR (film): $\tilde{\nu}$ = 3045, 3017, 2973, 1773, 1684, 1605, 1489, 1457, 991, 904, 758, 730, 579 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.08–1.13 (m, 2H, Cpr-H), 1.28–1.34 (m, 2H, Cpr-H), 2.16 (s, 3H, $CH_3$), 4.74 (d, $^3J$ = 17.5 Hz, 1H, 3-H), 5.07 (d, $^3J$ = 10.5 Hz, 1H, 3-H), 6.78 (dd, $^3J$ = 17.5, 10.5 Hz, 1H, 2-H), 7.09–7.26 ppm (m, 4H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT): $\delta$ = 2.8 (−, Cpr-C), 3.0 (−, Cpr-C), 19.6 (+, $CH_3$), 113.9 (−, C3), 125.4 (+, Ar-C), 127.0 (+, Ar-C), 127.3 (−, Cpr-C), 129.7 (+, Ar-C), 129.8 (+, Ar-C), 130.1 (−, $C_{quat}$, Ar-C), 136.5 (−, $C_{quat}$, Ar-C), 137.7 (+, C2), 138.8 ppm (−, C1); MS (70 eV, EI), *m/z* (%) = 171/170 (3/20) $[M+H]^+$, 170 (20) $[M]^+$, 169 (4) $[M-H]^+$, 155 (40), 144 (36), 129 (100), 115 (32), 91 (8), 77(4); HRMS: *m/z* calcd for $C_{13}H_{14}$: 170.1096 (correct HRMS).

**5d**: According to GP 1, $Pd(OAc)_2$ (56.0 mg 0.25 mmol, 5.0 mol%), $PPh_3$ (198 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.00 mmol), $Et_4NCl$ (830 mg, 5.00 mmol), **1** (800 mg, 10.0 mmol), and **2d** (1.16 g, 5.00 mmol) in MeCN (25.0 mL) at 80 °C for 24 h, after workup and purification (2× 30 cm column, $R_f$ = 0.68 (pentane)), yielded **5d** (911 mg, 4.95 mmol, 99%) as a colorless oil, which solidified at −20 °C. IR (film): $\tilde{\nu}$ = 3004, 2974, 2921, 1606, 1463, 1077, 1009, 904, 768, 603, 560 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.01–1.06 (m, 2H, Cpr-H), 1.27–1.34 (m, 2H, Cpr-H), 2.11 (s, 6H, 2 $CH_3$), 4.63 (d, $^3J$ = 17.5 Hz, 1H, 3-H), 4.98 (d, $^3J$ = 10.5 Hz, 1H, 3-H), 6.76 (dd, $^3J$ = 17.5, 10.5 Hz, 1H, 2-H), 7.04–7.26 ppm (m, 3H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT): $\delta$ = 2.7 (−, Cpr-C), 2.9 (−, Cpr-C), 19.7 (+, 2×$CH_3$), 113.1 (−, C3), 126.7 (+, Ar-C), 126.8 (−, Cpr-C), 127.0 (+, 2×Ar-C), 129.1 (−, $C_{quat}$, Ar-C), 136.7 (−, $C_{quat}$, 2×Ar-C), 136.9 (+, C2), 138.1 ppm (−, C1); MS (70 eV, EI): *m/z* (%) = 185/184 (8/35) $[M]^+$, 169 (90), 154 (44), 143 (100), 128 (60), 115 (36), 91 (16), 77 (17); HRMS: *m/z* calcd for $C_{14}H_{16}$: 184.1252 (correct HRMS).

**5e**: According to GP 1, $Pd(OAc)_2$ (56.0 mg 0.25 mmol, 5.0 mol%), $PPh_3$ (198 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.00 mmol), $Et_4NCl$ (830 mg, 5.00 mmol), **1** (800 mg, 10.0 mmol), and **2e** (1.27 g, 5.00 mmol) in MeCN (25.0 mL) at 80 °C for 24 h, after workup and purification (2× 20 cm column, $R_f$ = 0.52 (pentane)), yielded **5e** (639 mg, 3.10 mmol, 62%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3087, 3043, 3004, 2972, 1775, 1718, 1684, 1624, 1608, 1591, 1507, 1405, 1396, 1336, 1301, 1249, 1194, 1113, 1063, 990, 937, 903, 802, 775, 736 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.15 (m, 2H, Cpr-H), 1.45 (m, 2H, Cpr-H), 4.70 (dd, $^3J$ = 17.5, $^2J$ = 1.4 Hz, 1H, 3-H), 5.13 (dd, $^3J$ = 10.6, $^2J$ = 1.4 Hz, 1H, 3-H), 7.00 (dd, $^3J$ = 17.5, 10.6 Hz, 1H, 2-H), 7.38–7.57 (m, 4H, Ar-H), 7.80–7.93 ppm (m, 3H, Ar-H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta$ = 3.2 (−, Cpr-C), 3.2 (−, Cpr-C), 114.7 (−, C3), 125.4 (+, Ar-C), 125.5 (+, Ar-C), 126.3 (+, Ar-C), 127.0 (+, Ar-C), 127.3 (+, Ar-C), 128.2 (+, Ar-C), 128.8 (+, Ar-C), 129.0 ($C_{quat}$, Cpr-C), 132.0 ($C_{quat}$, Ar-C), 133.7 ($C_{quat}$, Ar-C), 137.2 ($C_{quat}$, C1), 138.2 (+, C2), 157.6 ppm ($C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%) = 207/206 (6/44) $[M]^+$, 205 (100) $[M-H]^+$, 191 (27), 178 (62), 179 (34), 165 (56), 152 (14), 139 (4), 115 (3), 101 (7), 89 (12), 76 (3); HRMS: *m/z* calcd for $C_{16}H_{14}$: 206.1096 (correct HRMS).

**5f**: According to GP 1, $Pd(OAc)_2$ (56.0 mg 0.25 mmol, 5.0 mol%), $PPh_3$ (198 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.00 mmol), $Et_4NCl$ (830 mg, 5.00 mmol), **1** (800 mg, 10.0 mmol), and **2f** (1.52 g, 5.00 mmol) stirred in MeCN (25.0 mL) at 80 °C for 24 h, after workup and purification (2×30 cm column, $R_f$ = 0.30 (pentane)), yielded **5f** (666 mg, 2.60 mmol, 52%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3020, 1700, 1653, 1599, 1506, 1457, 1216, 909, 771, 669 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.03 (m, 2H, Cpr-H), 1.57 (m, 2H, Cpr-H), 4.52 (dd, $^3J$ = 17.4, $^2J$ = 0.5 Hz, 1H, 3-H), 5.09 (dd, $^3J$ = 10.8, $^2J$ = 0.5 Hz, 1H, 3-H), 7.11 (dd, $^3J$ = 17.4, 10.8 Hz, 1H, 2-H), 7.47 (m, 4H, Ar-H), 8.03 (m, 4H, Ar-H), 8.48 ppm (s, 1H, Ar-H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta$ = 3.1 (−, Cpr-C), 3.3 (−, Cpr-C), 115.2 (−, C3), 125.0 (+, Ar-C), 125.2 (+, Ar-C), 126.2 (+, Ar-C), 126.6 (+, Ar-C), 127.1 ($C_{quat}$, Ar-C), 128.5 (+, Ar-C), 129.9 ($C_{quat}$, Cpr-C), 130.7 ($C_{quat}$, Ar-C), 131.5 ($C_{quat}$, Ar-C), 134.2 ($C_{quat}$, C1), 138.1 ppm (+, C2); MS (70 eV, EI): *m/z* (%) = 257/256 (17/92) $[M]^+$, 255 (100) $[M-H]^+$, 241 (15) $[M-CH_3]^+$, 229 (24) $[M+H-C_2H_4]^+$, 228 (62) $[M-C_2H_4]^+$, 215 (33) $[M+H-C_3H_6]^+$, 202 (10), 176 (3), 126 (6), 119 (13), 101 (5); HRMS: *m/z* calcd for $C_{20}H_{16}$: 256.1252 (correct HRMS).

**5g**: According to GP 1, $Pd(OAc)_2$ (56.0 mg 0.25 mmol, 5.0 mol%), $PPh_3$ (198 mg, 0.75 mmol, 15.0 mol%), $K_2CO_3$ (1.38 g, 10.00 mmol), $Et_4NCl$ (830 mg, 5.00 mmol), **1** (800 mg, 10.0 mmol), and **2g** (1.52 g, 5.00 mmol) in MeCN (25.0 mL) at 80 °C for 24 h, after workup and purification (2× 30 cm column, $R_f$ = 0.33 (pentane)), yielded **5g** (602 mg, 2.35 mmol, 47%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3056, 3019, 1772, 1693, 1639, 1598, 1528, 1494, 1451, 1217, 1050, 909, 752, 669 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.16 (m, 2H, Cpr-H), 1.54 (m, 2H, Cpr-H), 4.81 (d, $^3J$ = 21.5 Hz, 1H, 3-H), 5.12 (d, $^3J$ = 11.3 Hz, 1H, 3-H), 7.02 (dd, $^3J$ = 21.5, 11.3 Hz, 1H, 2-H), 7.50–7.80 (m, 5H, Ar-H), 7.91 (m, 2H, Ar-H), 8.77 ppm (m, 2H, Ar-H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta$ = 3.1 (−, Cpr-C), 3.2 (−, Cpr-C), 114.8 (−, C3), 122.5 (+, Ar-C), 122.7 (+, Ar-C), 126.2 (+, Ar-C), 126.3 (+, Ar-C), 126.3 (+, Ar-C), 126.6 (+, Ar-C), 127.0 (+, Ar-C), 127.5 (+, Ar-C), 128.4 (+, Ar-C), 129.0 ($C_{quat}$, Ar-C), 129.1 ($C_{quat}$, Ar-C), 130.0 ($C_{quat}$, Cpr-C), 130.4 ($C_{quat}$, Ar-C), 131.2 ($C_{quat}$, Ar-C), 131.8 ($C_{quat}$, Ar-C), 135.9 ($C_{quat}$, C1), 138.1 ppm (+, C2); MS (70 eV, EI): *m/z* (%) = 256 (97) $[M]^+$, 255 (100) $[M-H]^+$, 241 (25) $[M-CH_3]^+$, 239(37), 228 (42) $[M-C_2H_4]^+$, 215 (46) $[M+H-C_3H_6]^+$, 202 (13) $[M-C_2H_4-C_2H_2]^+$, 189 (4), 126 (5), 120 (9), 114 (12); HRMS: *m/z* calcd for $C_{20}H_{16}$: 256.1252 (correct HRMS).

**15**: According to GP 2, **5c** (130 mg, 0.763 mmol), $Eu(fod)_3$ (77.2 mg, 0.074 mmol), and **9** (0.15 mL, 1.50 mmol) in $CHCl_3$ (1.5 mL) at room temperature and 10 kbar for 24 h, after chromatography on silica gel (1× 20 cm column, $R_f$ = 0.15 (pentane/diethyl ether = 1:1)), gave **15** (131 mg, 54%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3059 (C−H), 3015, 2913, 2871, 2843, 1700, 1651 (C=C), 1600, 1487, 1406, 1368, 1266 (C−O), 1251, 1104, 1037 (C−Cl), 957, 910, 876, 800, 780, 729, 693, 617 $cm^{-1}$; $^1H$ NMR (300 MHz, $C_2D_4Cl_2$, 323 K, COSY): $\delta$ = 0.30–0.70 (m, 2H, Cpr-H), 0.76–0.90 (m, 1H, Cpr-H), 1.10 (m, 1H, Cpr-H), 2.22 (s, 3H, $CH_3$), 2.46 (ddd, $^2J$ = 10.1, $^3J$ = 5.8, 2.9 Hz, 2H, 6-H), 4.26 (dd, $^3J$ = 5.8, 2.9 Hz, 1H, 5-H), 5.58 (t, $^3J$ = 2.9 Hz, 1H, 7-H), 7.09–7.26 ppm (m, 4H, Ar-H); $^{13}C$ NMR (75 MHz, $C_2D_4Cl_2$, APT, HMQC): $\delta$ = 12.3 (−, Cpr-C), 12.6 (−, Cpr-C), 20.2 (+, $CH_3$), 27.6 (−, C6), 62.6 (−, C3), 84.1 (+, C5), 99.8 (−, $CCl_3$), 121.2 (+, C7), 125.1 (+, Ar-C), 127.7 (+, Ar-C), 129.7 (+, Ar-C), 129.7 (+, Ar-C), 136.7 (−, C8), 141.2 (−, Ar-C), 147.0 ppm ($C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%) = 322/320/318/316 (3/30/91/97) $[M]^+$, 307/305/303/301 (2/23/70/71) $[M-CH_3]^+$, 281 (13) $[M(^{35}Cl_3)-^{35}Cl]^+$, 225 (4) $[M-(^{35}Cl_3)-C_7H_7]^+$, 199 (17) $[M-CCl_3]^+$, 171 (87) $[M-CCl_3-CO]^+$, 157 (59) $[M-CCl_3-CO-CH_2]^+$, 143 (63) $[M-CCl_3-CO-C_2H_4]^+$, 129 (62) $[M-CCl_3-CO-C_3H_6]^+$, 115 (98) $[M-CCl_3-CO-C_4H_8]^+$, 91 (46) $[C_7H_7]^+$, 57 (100) $[C_3H_5O]^+$; elemental analysis: calcd (%) for $C_{15}H_{15}Cl_3O$ (317.64): C 56.72, H 4.76, Cl 33.48; found: C 56.48, H 4.58, Cl 33.31.

**16**: According to GP 2, **5d** (114 mg, 0.618 mmol), $Eu(fod)_3$ (64.3 mg, 0.062 mmol), and **10** (216 mg, 1.24 mmol) in $CHCl_3$ (1.5 mL) were pressurized at 10 kbar and room temperature for 24 h. Chromatography on silica gel (2×18 cm column, $R_f$ = 0.44 (pentane/diethyl = ether 4:1)) gave **16** (154 mg, 69%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2983, 1741 (C=O), 1456, 1369, 1273 (C−O), 1212, 1197, 1084, 912, 734, 650 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$, COSY): $\delta$ = 0.44 (m, AA′ part of an AA′BB′ system, 2H, Cpr-H), 1.14 (m, BB′ part of an AA′BB′ system, 2H, Cpr-H), 1.31 (t, $^3J$ = 7.2 Hz, 6H, $CO_2CH_2CH_3$), 2.21 (s, 6H, $ArCH_3$), 2.87 (d, $^3J$ = 4.0 Hz, 2H, 6-H), 4.29 (q, $^3J$ = 7.2 Hz, 4H, $CO_2CH_2CH_3$), 5.64 (t, $^3J$ = 4.0 Hz, 1H, 7-H), 7.00 ppm (m, 3H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, DEPT, HMQC, HMBC): $\delta$ = 12.8 (−, Cpr-C), 14.0 (+, $CO_2CH_2CH_3$), 20.0 (+, $ArCH_3$), 25.6 ($C_{quat}$, C3), 29.7 (−, C6), 61.8 (−, $CO_2CH_2CH_3$), 80.2 ($C_{quat}$, C5), 120.4 (+, C7), 127.2 (+, Ar-C), 127.2 (+, Ar-C), 136.2 ($C_{quat}$, Ar-C), 137.0 ($C_{quat}$, Ar-C), 137.9 ($C_{quat}$, C8), 168.4 ppm ($C_{quat}$, CO); MS (70 eV, EI): *m/z* (%) = 358 (2) $[M]^+$, 285 (2) $[M-CO_2CH_2CH_3]^+$, 211 (7) $[M-H-2\times CO_2CH_2CH_3]^+$, 200 (75), 172 (15), 169 (20) $[C_{13}H_{13}]^+$, 154

  

(100) $[M-H-2\times CO_2CH_2CH_3-C_2H_5-CO]^+$, 126 (66) $[C_{10}H_6]^+$, 83 (87), 57 (39); HRMS: *m/z* calcd for $C_{21}H_{26}O_5$: 358.1780 (correct HRMS).

**17**: According to GP 2, **5d** (52.9 mg, 0.287 mmol), Eu(fod)$_3$ (30.0 mg, 0.029 mmol), and a suspension of anhydrous **11**, obtained by stirring of ninhydrin monohydrate (104 mg, 0.584 mmol) in toluene (2.0 mL) with 4-Å molecular sieves for 18 h, was pressurized at 10 kbar and room temperature for 48 h. After purification of the crude product by chromatography on silica gel (1×10 cm column, $R_f$=0.32 (pentane/diethyl ether=5:1)), **17** (22.1 mg, 22%) was obtained as a yellowish solid. IR (film): $\tilde{\nu}$=2963, 2916, 1942, 1748 (C=O), 1714 (C=O), 1596, 1261 (C–O), 1048, 1033, 957, 878, 796, 695 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, COSY): $\delta$=0.58 (m, AA′ part of an AA′BB′ system, 2H, Cpr-H), 0.91 (m, BB′ part of an AA′BB′ system, 2H, Cpr-H), 2.43 (s, 6H, $ArCH_3$), 2.62 (d, $^3J$=4.0 Hz, 2H, 10-H), 5.72 (t, $^3J$=4.0 Hz, 1H, 11-H), 7.06 (m, 3H, Ar-H), 7.91 (m, 2H, Ar-H), 8.04 ppm (m, 2H, Ar-H); $^{13}$C NMR (50.3 MHz, $CDCl_3$, DEPT, HMQC, HMBC): $\delta$=13.6 (–, Cpr-C), 20.2 (+, Ar-$CH_3$), 26.7 (–, C10), 60.2 ($C_{quat}$, C3), 75.1 ($C_{quat}$, C5), 118.6 (+, C11), 124.0 (+, Ar-C), 127.2 (+, Ar-C), 127.3 (+, Ar-C), 136.4 (+, Ar-C), 136.9 ($C_{quat}$, Ar-C), 137.4 ($C_{quat}$, Ar-C), 139.2 ($C_{quat}$, Ar-C), 140.4 ($C_{quat}$, Ar-C), 197.4 ppm ($C_{quat}$, CO); MS (70 eV, EI): *m/z* (%)=345/344 (17/64) $[M]^+$, 329 (59) $[M-CH_3]^+$, 326 (100) $[M-H_2O]^+$, 311 (35) $[M-H_2O-CH_3]^+$, 287 (47) $[M-C_4H_9]^+$, 269 (13) $[M-H_2O-C_4H_9]^+$, 239 (10) $[M-C_8H_9]^+$, 199 (16), 183 (28) $[C_{14}H_{15}]^+$, 171 (60), 159 (40), 145 (25), 140 (23), 129 (54), 115 (43), 105 (28) $[C_8H_9]^+$, 91 (14) $[C_7H_7]^+$, 77 (23) $[C_6H_5]^+$, 57 (52); HRMS: *m/z* calcd for $C_{23}H_{20}O_3$: 344.1412 (correct HRMS).

**18**: According to GP 2, **5c** (222 mg, 1.30 mmol) and a suspension of anhydrous alloxane, obtained by stirring of alloxane monohydrate (341 mg, 2.13 mmol) in ethyleneglycol dimethyl ether (4.0 mL) with 4-Å molecular sieves for 12 h, was pressurized at 10 kbar and room temperature for 4 days. After purification of the crude product by chromatography on silica gel (3.5×28 cm column, $R_f$=0.37 (pentane/diethyl ether=1:1)), **18** (144 mg, 35%) was obtained as colorless crystals. M.p.: 224 °C; IR (KBr): $\tilde{\nu}$=3223, 3110, 2044, 1922, 1768 (C=O), 1732 (C=O), 1702 (C=O), 1524, 1486, 1441, 1372, 1277 (C–O), 1139, 1031, 946, 807, 752 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, COSY): $\delta$=0.40 (m, 1H, Cpr-H), 0.65 (m, 1H, Cpr-H), 0.95 (m, 2H, Cpr-H), 2.28 (s, 3H, $ArCH_3$), 2.70–3.00 (m, 2H, 11-H), 4.87 (s, 2H, 7-H, 9-H), 5.68 (t, $^3J$=4.0 Hz, 1H, 12-H), 6.90–7.18 ppm (m, 4H, Ar-H); $^{13}$C NMR (50.3 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=12.0 (–, Cpr-C), 15.5 (–, Cpr-C), 19.8 (+, $CH_3$), 26.5 (–, C11), 61.2 (–, C3), 75.2 (–, C5), 121.4 (+, C12), 126.0 (+, Ar-C), 128.7 (+, Ar-C), 130.8 (+, Ar-C), 131.0 (+, Ar-C), 138.1 (–, Ar-C), 138.8 (–, C13), 139.4 (–, Ar-C), 151.8 (–, CO), 169.9 ppm (–, CO); MS (70 eV, EI): *m/z* (%)=313/312 (10/56) $[M]^+$, 297 (6) $[M-CH_3]^+$, 295/294 (7/26) $[M-H_2O]^+$, 279 (8) $[M-H_2O-CH_3]^+$, 255 (26) $[M-C_2H_5-CO]^+$, 208 (10), 184 (26), 172 (36), 159 (46), 141 (48), 129 (54), 115 (100), 98 (26) $[C_3H_3N_2O_3-NH_3]^+$, 91 (14) $[C_7H_7]^+$; elemental analysis: calcd (%) for $C_{17}H_{16}N_2O_4$ (312.3): C 65.38, H 5.17, N 8.97; found: C 65.40, H 5.28, N 8.89.

**19**: According to GP 2, **5e** (268 mg, 1.30 mmol), Eu(fod)$_3$ (135 mg, 0.130 mmol), and **9** (0.26 mL, 2.83 mmol) in $CHCl_3$ (1.5 mL) were pressurized at 10 kbar and room temperature for 48 h. After purification of the crude product by chromatography on silica gel (2×23 cm column, $R_f$=0.83 (pentane/diethyl ether=2:1)), **19** (137 mg, 30%) was obtained as a colorless oil as a mixture of two diastereomers (atropisomers) (3:2 according to the $^1$H NMR spectrum). IR (film): $\tilde{\nu}$=3017, 2913, 2875, 1773, 1699, 1647 (C=C), 1624 (C=C), 1591, 1507, 1397, 1266 (C–O), 1216, 1036 (C–Cl), 952, 879, 766, 659, 509 cm$^{-1}$; Isomer I (major): $^1$H NMR (300 MHz, $CDCl_3$, COSY): $\delta$=0.34 (m, 1H, Cpr-H), 0.69 (m, 1H, Cpr-H), 0.93 (m, 1H, Cpr-H), 1.25 (m, 1H, Cpr-H), 2.82 (m, 2H, 6-H), 4.48 (dd, $^3J$=9.6, 4.6 Hz, 1H, 5-H), 5.85 (dd, $^3J$=5.2, 4.6 Hz, 1H, 7-H), 7.14 (m, 1H, Ar-H), 7.31–7.55 (m, 2H, Ar-H), 7.82 (m, 2H, Ar-H), 8.04 ppm (m, 2H, Ar-H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, APT, HMQC): $\delta$=13.3 (–, Cpr-C), 13.8 (–, Cpr-C), 27.8 (–, C6), 63.3 (–, C3), 84.2 (+, C5), 99.8 (–, $CCl_3$), 122.5 (+, C7), 124.9 (+, Ar-C), 125.5 (+, Ar-C), 125.9 (+, Ar-C), 126.1 (+, Ar-C), 126.5 (+, Ar-C), 128.0 (+, Ar-C), 128.1 (+, Ar-C), 132.4 (–, Ar-C), 133.2 (–, Ar-C), 135.4 (–, Ar-C), 140.3 ppm (–, C8); Isomer II (minor): $^1$H NMR (300 MHz, $CDCl_3$, COSY): $\delta$=0.43 (m, 1H, Cpr-H), 0.81 (m, 1H, Cpr-H), 0.93 (m, 1H, Cpr-H), 1.25 (m, 1H, Cpr-H), 2.82 (m, 2H, 6-H), 4.55 (dd, $^3J$=8.7, 5.3 Hz, 1H, 5-H), 5.85 (dd, $^3J$=5.3, 4.6 Hz, 1H, 7-H), 7.14 (m, 1H, Ar-H), 7.31–7.55 (m, 2H, Ar-H), 7.82 (m, 2H, Ar-H), 8.04 ppm (m, 2H, Ar-H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, APT, HMQC): $\delta$=13.4 (–, Cpr-C), 13.6 (–, Cpr-C), 27.9 (–, C6), 63.8 (–, C3), 84.2 (+, C5), 99.7 (–, $CCl_3$), 122.9 (+, C7), 124.9 (+, Ar-C), 125.3 (+, Ar-C), 125.7 (+, Ar-C), 126.4 (+, Ar-C), 127.4 (+, Ar-C), 127.8 (+, Ar-C), 128.2 (+, Ar-C), 132.6 (–, Ar-C), 133.5 (–, Ar-C), 134.9 (–, Ar-C), 138.5 ppm (–, C8); MS (70 eV, EI): *m/z* (%)=358/356/354/352 (5/31/98/100) $[M]^+$, 343/341/339/337/(2/14/47/49) $[M-CH_3]^+$, 321/319/317 (3/19/32) $[M-Cl]^+$, 235 (28) $[M-CCl_3]^+$, 222 (50), 207 (23) $[M-CCl_3-CO]^+$, 189 (54), 179 (56), 165 (85), 152 (98) $[C_{12}H_8]^+$, 141 (14), 129 (9), 109 (23) $[M+H-C_{10}H_7-CCl_3]^+$, 101 (10), 77 (4), 55 (11); HRMS: *m/z* calcd for $C_{18}H_{15}Cl_3O$: 352.0188 (correct HRMS).

**20**: *N*-bromosuccinimide (NBS; 1.78 g, 10.0 mmol) was added in portions to a solution of 4-phenylurazol (971 mg, 5.48 mmol) in $CH_2Cl_2$ (50 mL) at 0 °C. After complete addition, the solution was stirred for 20 min, then it was extracted with water (3×50 mL). The combined organic phases were dried and concentrated under reduced pressure. The remaining red solid was dissolved in $CH_2Cl_2$ (10 mL), and the solution was added slowly to a solution of **5d** (222 mg, 1.20 mmol) in $CHCl_3$ (5 mL). After the mixture had been stirred at room temperature for 2 h, the solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel (1×20 cm column, $R_f$=0.50 (pentane/diethyl ether=2:1)) to yield **20** (358 mg, 82%) as colorless crystals. M.p.: 203 °C ($CHCl_3$); IR (KBr): $\tilde{\nu}$=3442, 3016, 2918, 2860, 1766 (C=O), 1706 (C=O), 1492, 1419, 1356, 1312, 1135, 1072, 994, 913, 804, 752 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$, COSY): $\delta$=0.74 (m, AA′ part of an AA′BB′ system, 2H, Cpr-H), 2.05 (m, BB′ part of an AA′BB′ system, 2H, Cpr-H), 2.28 (s, 6H, $ArCH_3$), 4.41 (d, $^3J$=3.4 Hz, 2H, 6-H), 5.72 (t, $^3J$=3.4 Hz, 1H, 7-H), 7.11 (m, 3H, Ar-H), 7.47 ppm (m, 5H, Ar-H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, DEPT, HMQC): $\delta$=11.0 (–, Cpr-C), 20.1 (+, $ArCH_3$), 42.6 ($C_{quat}$, C3), 44.4 (–, C6), 118.6 (+, C7), 125.6 (+, Ar-C), 127.5 (+, Ar-C), 127.9 (+, Ar-C), 128.1 (+, Ar-C), 129.0 (+, Ar-C), 131.0 ($C_{quat}$, Ar-C), 134.4 ($C_{quat}$, Ar-C), 136.9 ($C_{quat}$, Ar-C), 137.8 ($C_{quat}$, C8), 150.2 ($C_{quat}$, CO), 152.8 ($C_{quat}$, CO); MS (70 eV, EI): *m/z* (%)=360/359 (22/100) $[M]^+$, 345/344 (14/65) $[M-CH_3]^+$, 330 (13) $[M-C_2H_5]^+$, 225 (17) $[M-C_2H_5-C_8H_9]^+$, 197 (6), 182 (15), 169 (12), 154 (9), 144 (9), 120 (10), 119 (11), 93 (13); elemental analysis: calcd (%) for $C_{22}H_{21}N_3O_2$ (359.42): C 73.51, H 5.90, N 11.69; found: C 73.28, H 5.72, N 11.58.

**21**: According to GP 3, **5e** (62.8 mg, 0.304 mmol) and **14** (123 mg, 0.61 mmol) in $CHCl_3$ (1.5 mL), after 3 h at 50 °C and purification of the residue by chromatography on silica gel (2×20 cm column, $R_f$=0.45 (pentane/diethyl ether=2:1)), gave **21** (123 mg, 99%) as a colorless oil as a mixture of two diastereomers (atropisomers) (2.6:1 according to $^1$H NMR spectroscopy). IR (film): $\tilde{\nu}$=3044, 2981, 2937, 2049, 1934, 1708 (C=O), 1598, 1507, 1259 (C–O), 1175, 1100, 1021, 917, 801, 655 cm$^{-1}$; Isomer I (major): $^1$H NMR (250 MHz, $CDCl_3$, COSY): $\delta$=0.52 (m, 1H, Cpr-H), 0.76 (m, 1H, Cpr-H), 1.14 (m, 1H, Cpr-H), 1.25 (d, $^3J$=6.3 Hz, 6H, $CO_2CH(CH_3)_2$), 1.41 (d, $^3J$=6.3 Hz, 6H, $CO_2CH(CH_3)_2$), 1.71 (m, 1H, Cpr-H), 4.15 (dd, $^2J$=18.0, $^3J$=2.0 Hz, 1H, 6-H), 4.64 (dd, $^2J$=18.0, $^3J$=4.2 Hz, 1H, 6-H), 4.99 (sept, $^3J$=6.3 Hz, 2H, $CO_2CH(CH_3)_2$), 5.68 (dd, $^3J$=4.2, 2.0 Hz, 1H, 7-H), 7.11 (m, 1H, Ar-H), 7.42 (m, 3H, Ar-H), 8.03 ppm (m, 3H, Ar-H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, DEPT, HMQC, HMBC): $\delta$=13.0 (–, Cpr-C), 15.8 (–, Cpr-C), 22.0 (+, $CO_2CH(CH_3)_2$), 22.1 (+, $CO_2CH(CH_3)_2$), 42.5 (–, C6), 44.4 ($C_{quat}$, C3), 69.3 (+, $CO_2CH(CH_3)_2$), 70.2 (+, $CO_2CH(CH_3)_2$), 121.9 (+, C7), 125.0 (+, Ar-C), 125.9 (+, Ar-C), 126.0 (+, Ar-C), 126.5 (+, Ar-C), 126.9 (+, Ar-C), 127.7 (+, Ar-C), 128.5 (+, Ar-C), 132.4 ($C_{quat}$, Ar-C), 133.1 ($C_{quat}$, Ar-C), 134.7 ($C_{quat}$, Ar-C), 141.3 ($C_{quat}$, C8), 155.1 ($C_{quat}$, CO), 156.50 ppm ($C_{quat}$, CO); Isomer II (minor): $^1$H NMR (250 MHz, $CDCl_3$, COSY): $\delta$=0.52 (m, 1H, Cpr-H), 0.76 (m, 1H, Cpr-H), 1.14 (m, 1H, Cpr-H), 1.26 (d, $^3J$=6.3 Hz, 6H, $CO_2CH(CH_3)_2$), 1.44 (d, $^3J$=6.3 Hz, 6H, $CO_2CH(CH_3)_2$), 1.74 (m, 1H, Cpr-H), 4.27 (dd, $^2J$=17.9, $^3J$=2.0 Hz, 1H, 6-H), 4.49 (dd, $^2J$=17.9, $^3J$=4.2 Hz, 1H, 6-H), 5.01 (sept, $^3J$=6.3 Hz, 2H, $CO_2CH(CH_3)_2$), 5.64 (dd, $^3J$=4.2, $^3J$=2.0 Hz, 1H, 7-H), 7.11 (m, 1H, Ar-H), 7.42 (m, 3H, Ar-H), 8.03 ppm (m, 3H, Ar-H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, DEPT, HMQC, HMBC): $\delta$=13.3 (–, Cpr-C), 16.0 (–, Cpr-C), 22.2 (+, $CO_2CH(CH_3)_2$), 22.3 (+, $CO_2CH(CH_3)_2$), 42.4 (–, C6), 43.4 ($C_{quat}$, C3), 69.6 (+, $CO_2CH(CH_3)_2$), 70.7 (+, $CO_2CH(CH_3)_2$), 122.8 (+, C7), 124.8 (+, Ar-

  

C), 125.3 (+, Ar-C), 125.7 (+, Ar-C), 126.1 (+, Ar-C), 127.0 (+, Ar-C), 127.9 (+, Ar-C), 128.1 (+, Ar-C), 133.6 ($C_{quat}$, Ar-C), 132.2 ($C_{quat}$, Ar-C), 134.3 ($C_{quat}$, Ar-C), 141.7 ($C_{quat}$, C8), 154.6 ($C_{quat}$, CO), 157.0 ppm ($C_{quat}$, CO); MS (200 eV, CI, $NH_3$): *m/z* (%) = 834 (28) $[2M+NH_4]^+$, 817 (5) $[2M+H]^+$, 656 (4), 426 $[M+NH_4]^+$, 409 (42) $[M+H]^+$, 322 (5) $[M+H-CO_2CH(CH_3)_2]^+$, 248 (10); HRMS: *m/z* calcd for $C_{24}H_{28}N_2O_4$: 408.20491 (correct HRMS).

**23d**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2d** (464 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 3 h. Compound **22** (321 mg, 3.00 mmol) was added at 80 °C, and the mixture was stirred for a further 2 h. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether = 5:1) to yield **23d** (233 mg, 40 %) as a colorless solid. M.p.: 94–95 °C; $R_f$ = 0.35 (pentane/diethyl ether = 20:1), IR (KBr): $\tilde{\nu}$ = 3102, 2837, 1596, 1480, 1338, 1293, 1050, 808, 774, 738 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 0.84–0.88 (m, 2H, Cpr-H), 1.18–1.19 (m, 2H, Cpr-H), 2.45 (s, 6H, $CH_3$), 4.48 (brs, 2H, 6-H), 5.61 (t, *J* = 2.15 Hz, 1H, 7-H), 6.90–7.14 (m, 4H, Ar-H), 7.31–7.40 ppm (m, 4H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$ = 14.0 (–, 2×Cpr-C), 20.8 (+, 2×$CH_3$), 41.6 (–, $C_{quat}$, C3), 63.3 (–, C6), 118.5 (–, 2×Ar-C), 122.2 (+, Ar-C), 122.9 (+, C7), 127.4 (+, 2×Ar-C), 127.5 (+, 2×Ar-C), 128.6 (+, Ar-C), 136.1 (–, $C_{quat}$, 2×Ar-C), 136.7 (–, $C_{quat}$, Ar-C), 137.0 (–, $C_{quat}$, C8), 146.8 ppm (–, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%) = 291 (4) $[M]^+$, 273 (14), 258 (6), 198 (32), 169 (16), 141 (16), 115 (8), 105 (10), 91 (30), 77 (100), 65 (24), 51 (32); elemental analysis: calcd (%) for $C_{20}H_{21}NO$ (291.39): C 82.44, H 7.26; found: C 82.36, H 7.11.

**5h**: Compound **2h** was prepared from *p*-xylene according to the published procedure.[20] According to GP 1, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 10 mol %), $PPh_3$ (76.6 mg, 0.30 mmol, 30.0 mol %), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.0 mmol), **1** (320 mg, 4.0 mmol), and **2h** (358 mg, 1.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 24 h. Chromatography on silica gel (2×30 cm column, $R_f$ = 0.50 (pentane)) yielded **5h** (190 mg, 0.73 mmol, 73 %) as a colorless solid. The sample slowly decomposed at room temperature, but could be kept at −20 °C for several weeks without obvious changes. M.p.: 101–102 °C; IR (film): $\tilde{\nu}$ = 3084, 3042, 2976, 2966, 2919, 1603, 1497, 1090, 989, 913, 894 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.13–1.18 (m, 4H, Cpr-H), 1.28–1.33 (m, 4H, Cpr-H), 2.11 (s, 6H, 2 $CH_3$), 4.80 (d, *J* = 17.5 Hz, 2H, vinyl H), 5.07 (d, *J* = 10.5 Hz, 2H, vinyl H), 6.82 (dd, *J* = 17.5, 10.5 Hz, 2H, vinyl H), 6.93 ppm (s, 2H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT): $\delta$ = 2.7 (–, 2×Cpr-C), 3.2 (–, 2×Cpr-C), 19.2 (+, 2×$CH_3$), 113.9 (–, 2×C3), 127.0 (–, $C_{quat}$, 2×Cpr-C), 130.1 (–, $C_{quat}$, 2×C1), 131.0 (+, 2×C2), 133.1 (–, $C_{quat}$, 2×Ar-C), 137.2 (–, $C_{quat}$, 2×Ar-C), 137.9 ppm (+, 2×Ar-C); MS (70 eV, EI): *m/z* (%) = 263/262 (4/16) $[M]^+$, 247 (60), 232 (20), 217 (28), 203 (24), 183 (100), 168 (30), 165 (24), 153 (20), 141 (8), 115 (6), 77 (8); HRMS: *m/z* calcd for $C_{20}H_{22}$: 262.1721 (correct HRMS).

**24h**: According to GP 3, **22** (62 mg, 0.58 mmol) in anhydrous MeCN (1.0 mL) was added to **5h** (50 mg, 0.19 mmol) in anhydrous MeCN (1.0 mL) at room temperature, and the mixture was stirred at 80 °C for 1 h. The precipitate formed was filtered off at room temperature and dried to afford **24h** (80 mg, 88 %) as a yellow solid. M.p.: 228–230 °C; IR (film): $\tilde{\nu}$ = 3090, 3003, 2924, 2852, 1597, 1488, 1341, 1293, 1053, 895, 771, 701 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 0.86 (brs, 2H, Cpr-H), 1.25 (brs, 6H, Cpr-H), 2.35 (s, 6H, $CH_3$), 4.39 (br, 4H, 6-H), 5.54 (t, *J* = 2.75 Hz, 2H, 7-H), 6.84 (s, 2H, Ar-H), 6.96–7.07 (m, 2H, Ar-H), 7.31–7.40 ppm (m, 8H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$ = 14.0 (–, 4×Cpr-C), 19.6 (+, 2×$CH_3$), 40.9 (–, $C_{quat}$, 2×C3), 62.7 (–, 2×C6), 118.4 (+, 4×Ar-C), 122.4 (+, 2×Ar-C), 122.8 (+, 2×C7), 128.8 (+, 4×Ar-C), 131.6 (+, 2×Ar-C), 133.1 (–, $C_{quat}$, 2×Ar-C), 136.0 (–, $C_{quat}$, 2×Ar-C), 136.9 (br, –, $C_{quat}$, 2×C8), 146.9 ppm (–, $C_{quat}$, 2×Ar-C); MS (70 eV, EI): *m/z* (%) = 476 (80) $[M]^+$, 461 (40), 447 (20), 384 (24), 354 (28), 312 (20), 260 (16), 220 (16), 207 (20), 178 (20), 165 (30), 130 (48), 106 (60), 77 (100); HRMS: *m/z* calcd for $C_{32}H_{32}N_2O_2$: 476.2464 (correct HRMS).

**23a**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2b** (408 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 3 h. Compound **22** (321 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether = 5:1) to yield **23a** (368 mg, 70 %) as a colorless solid. M.p.: 83–84 °C; $R_f$ = 0.65 (pentane/diethyl ether = 5:1); IR (KBr): $\tilde{\nu}$ = 3060, 3009, 2926, 2890, 2840, 1590, 1486, 1350, 1289, 1057, 810, 776, 702 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.24 (brs, 4H, Cpr-H), 4.39 (brs, 2H, H-6), 5.60 (t, *J* = 2.15 Hz, 1H, H-7), 7.03–7.08 (m, 1H, Ar-H), 7.22–7.26 (m, 2H, Ar-H), 7.30–7.40 ppm (m, 7H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$ = 14.4 (–, 2×Cpr-C), 40.4 (–, $C_{quat}$, C3), 63.0 (–, C6), 118.5 (+, 2×Ar-C), 122.5 (+, C7), 122.6 (+, Ar-C), 127.5 (+, Ar-C), 128.2 (+, 2×Ar-C), 128.5 (+, 2×Ar-C), 128.8 (+, 2×Ar-C), 138.1 (–, $C_{quat}$, Ar-C), 138.8 (–, $C_{quat}$, C8), 147.0 ppm (–, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%) = 263 (20) $[M]^+$, 262 (32) $[M-1]^+$, 246 (16), 235 (28), 206 (24), 186 (6), 171 (16), 156 (20), 141 (32), 130 (33), 115 (44), 103 (60), 91 (46), 77 (100), 51 (40); elemental analysis: calcd (%) for $C_{18}H_{17}NO$ (263.33): C 82.10, H 6.51; found: C 82.03, H 6.63.

**23b**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2b** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 3 h. Compound **22** (321 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether = 5:1) to yield **23b** (332 mg, 60 %) as a sticky oil. $R_f$ = 0.60 (pentane/diethyl ether = 5:1); IR (film): $\tilde{\nu}$ = 3023, 2920, 2876, 2832, 1598, 1490, 1346, 1292, 1056, 885, 763 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 0.83 (brs, 1H, Cpr-H), 1.26 (brs, 3H, Cpr-H), 2.37 (s, 3H, $CH_3$), 4.38 (brs, 2H, 6-H), 5.57 (t, *J* = 2.75 Hz, 1H, 7-H), 7.05–7.20 (m, 4H, Ar-H), 7.30–7.37 ppm (m, 5H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$ = 14.4 (–, 2×Cpr-C), 21.1 (+, $CH_3$), 40.4 (–, $C_{quat}$, C3), 63.1 (–, C6), 118.5 (+, 2×Ar-C), 122.3 (+, Ar-C), 122.5 (+, C7), 128.4 (+, 2×Ar-C), 128.7 (+, 2×Ar-C), 128.8 (+, 2×Ar-C), 135.2 (–, $C_{quat}$, Ar-C), 137.2 (–, $C_{quat}$, C8), 138.6 (–, $C_{quat}$, Ar-C), 147.0 ppm (–, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%) = 278/277 (4/36) $[M]^+$, 276 (20) $[M-1]^+$, 260 (20), 249 (40), 248 (34), 234 (20), 185 (24), 173 (20), 155 (22), 144 (20), 130 (32), 117 (80), 115 (84), 105 (36), 91 (60), 77 (100), 51 (38); elemental analysis: calcd (%) for $C_{19}H_{19}NO$ (277.36): C 82.28, H 6.90; found: C 82.22, H 6.99.

**23i**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2i** (246 mg, 1.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 3 h. Compound **22** (321 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether = 5:1) to yield **23i** (155 mg, 51 %) as a sticky oil. $R_f$ = 0.35 (pentane/diethyl ether = 5:1); IR (film): $\tilde{\nu}$ = 3056, 2919, 2877, 2830, 1694, 1608, 1559, 1491, 1344, 1246, 1053, 885, 773 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.07 (brs, 1H, Cpr-H), 1.26 (brs, 3H, Cpr-H), 2.62 (s, 3H, $CH_3$), 4.39 (brs, 2H, 6-H), 5.64 (t, *J* = 2.75 Hz, 1H, 7-H), 7.02–7.08 (m, 1H, Ar-H), 7.27–7.41 (m, 6H, Ar-H), 7.94–8.02 ppm (m, 2H, Ar-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$ = 14.5 (–, 2×Cpr-C), 26.5 (+, $CH_3$), 40.1 (–, $C_{quat}$, C3), 62.7 (–, C6), 118.3 (+, 2×Ar-C), 122.5 (+, Ar-C), 123.5 (+, C7), 128.2 (+, 2×Ar-C), 128.6 (+, 2×Ar-C), 128.7 (+, 2×Ar-C), 136.1 (–, $C_{quat}$, Ar-C), 138.1 (–, $C_{quat}$, Ar-C), 142.9 (–, $C_{quat}$, C8), 146.6 (–, $C_{quat}$, Ar-C), 197.4 ppm (–, $C_{quat}$, C=O); MS (70 eV, EI): *m/z* (%) = 306 (16) $[M-1]^+$, 305 (40) $[M]^+$, 304 (100) $[M-1]^+$, 288 (24), 276 (60), 232 (58), 218 (28), 204 (24), 153 (20), 128 (38), 115 (44), 91 (22), 77 (38), 43 (72); elemental analysis: calcd (%) for $C_{20}H_{19}NO_2$ (305.37): C 78.66, H 6.27; found: C 78.42, H 6.56.

**23k**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2i** (410 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80 °C for 3 h. Compound **22** (321 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel

  

(50 g, 2×20 cm column, pentane/diethyl ether=3:1) to yield **23k** (311 mg, 59%) as a sticky oil. $R_f$=0.10 (pentane/diethyl ether=5:1); IR (film): $\tilde{\nu}$=3024, 2926, 2878, 2835, 1595, 1560, 1488, 1410, 1347, 1290, 1060, 1027, 993, 885, 746, 693 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=1.08 (brs, 1H, Cpr-H), 1.26 (brs, 3H, Cpr-H), 4.38 (brs, 2H, 6-H), 5.66 (t, $J$=2.5 Hz, 1H, 7-H), 7.01–7.08 (m, 1H, Ar-H), 7.25–7.38 (m, 5H, Ar-H), 7.38–7.58 (m, 1H, Ar-H), 8.50 (d, $J$=1.5 Hz, 1H, Ar-H), 8.56 ppm (m, 1H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=14.2 (−, 2×Cpr-C), 40.2 (−, $C_{quat}$, C3), 62.8 (−, C6), 118.3 (+, 2×Ar-C), 122.7 (+, C7), 122.9 (+, Ar-C), 124.6 (+, Ar-C), 128.8 (+, 2×Ar-C), 133.6 (−, $C_{quat}$, Ar-C), 135.6 (−, $C_{quat}$, C8), 135.6 (+, Ar-C), 146.6 (−, $C_{quat}$, C8), 148.9 (+, Ar-C), 149.2 ppm (+, Ar-C); MS (70 eV, EI): *m/z* (%): 264 (28) $[M]^+$, 263 (100) $[M-1]^+$, 247 (20), 236 (44), 235 (60), 219 (30), 207 (32), 172 (24), 160 (24), 156 (46), 130 (72), 117 (40), 104 (64), 91 (40), 77 (68), 51 (50); elemental analysis: calcd (%) for $C_{17}H_{16}N_2O$ (264.32): C 77.25, H 6.10; found: C 77.00, H 6.35.

**30c**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2c** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80°C for 3 h. Compound **25** (426 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether=10:1) to yield **30c** (442 mg, 71%) as a sticky oil. $R_f$=0.55 (pentane/diethyl ether=10:1); IR (film): $\tilde{\nu}$=3017, 2935, 2883, 2840, 1593, 1487, 1412, 1255, 1056, 829, 770 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=0.83 (brs, 1H, Cpr-H), 1.21 (brs, 3H, Cpr-H), 2.36 (s, 3H, $CH_3$), 4.39 (brs, 2H, 6-H), 5.54 (t, $J$=2.15 Hz, 1H, 7-H), 7.10–7.33 ppm (m, 8H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=13.9 (−, 2×Cpr-C), 19.9 (+, $CH_3$), 41.0 (−, $C_{quat}$, C3), 62.7 (−, C6), 119.6 (+, 2×Ar-C), 122.6 (+, C7), 125.2 (+, Ar-C), 127.3 (−, $C_{quat}$, Ar-C), 127.6 (+, Ar-C), 128.8 (+, 2×Ar-C), 129.8 (+, Ar-C), 130.3 (+, Ar-C), 136.3 (−, $C_{quat}$, Ar-C), 136.4 (−, $C_{quat}$, C8), 136.9 (br, −, $C_{quat}$, Ar-C), 145.6 ppm (−, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%)=311 (4) $[M]^+$, 282 (4), 254 (2), 217 (2), 204 (2), 185 (4), 157 (4), 141 (4), 129 (12), 115 (20), 84 (100), 75 (10), 47 (32); elemental analysis: calcd (%) for $C_{19}H_{18}ClNO$ (311.81): C 73.19, H 5.82; found: C 72.90, H 5.65.

**31c**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2c** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80°C for 3 h. Compound **26** (534 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether=10:1) to yield **31c** (534 mg, 75%) as a colorless solid. M.p.: 100–101°C; $R_f$=0.55 (pentane/diethyl ether=10:1); IR (KBr): $\tilde{\nu}$=3022, 2952, 2927, 2893, 2846, 1585, 1489, 1436, 1283, 1251, 1062, 822, 764 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=0.88 (brs, 1H, Cpr-H), 1.13 (brs, 3H, Cpr-H), 2.35 (s, 3H, $CH_3$), 4.39 (brs, 2H, 6-H), 5.54 (t, $J$=2.15 Hz, 1H, 7-H), 7.10–7.25 (m, 6H, Ar-H), 7.42–7.47 ppm (m, 2H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=143.0 (−, 2×Cpr-C), 19.9 (+, $CH_3$), 41.0 (−, $C_{quat}$, C3), 62.8 (−, C6), 114.9 (−, $C_{quat}$, Ar-C), 119.9 (+, 2×Ar-C), 122.6 (+, C7), 125.2 (+, Ar-C), 127.6 (+, Ar-C), 129.8 (+, Ar-C), 130.4 (+, Ar-C), 131.7 (+, 2×Ar-C), 136.3 (−, $C_{quat}$, Ar-C), 136.4 (−, $C_{quat}$, C8), 137.0 (br, −, $C_{quat}$, Ar-C), 146.2 ppm (−, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%)=357 (8) $[M(^{81}Br)]^+$, 356 (6) $[M]^+$, 355 (12) $[M-(^{79}Br)]^+$, 326 (10), 311 (20), 282 (12), 246 (8), 232 (12), 204 (8), 185 (30), 155 (24), 129 (64), 115 (100), 91 (28), 75 (24); elemental analysis: calcd (%) for $C_{19}H_{18}BrNO$ (356.26): C 64.06, H 5.09; found: C 63.82, H 5.02.

**32c**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2c** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80°C for 3 h. Compound **27** (495 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether=5:1) to yield **32c** (510 mg, 76%) as a colorless solid. M.p.: 129–130°C; $R_f$=0.35 (pentane/diethyl ether=10:1); IR (KBr): $\tilde{\nu}$=3017, 2949, 2881, 2838, 1715, 1608, 1504, 1430, 1255, 1125, 853, 773 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=0.88 (br, 1H, Cpr-H), 1.24 (br, 3H, Cpr-H), 2.35 (s, 3H, $CH_3$), 3.90 (s, 3H, $CH_3$), 4.45 (brs, 2H, 6-H), 5.52 (t, $J$=2.75 Hz, 1H, 7-H), 7.17–7.21 (m, 4H, Ar-H), 7.34 (dd, $J$=1.75, 7.0 Hz, 2H, Ar-H), 8.02 ppm (dd, $J$=1.75, 7.0 Hz, 2H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=14.1 (−, 2×Cpr-C), 19.8 (+, $CH_3$), 41.1 (−, $C_{quat}$, C3), 51.8 (+, $CH_3$), 63.5 (−, C6), 116.6 (+, Ar-C), 122.2 (+, C7), 123.2 (−, $C_{quat}$, Ar-C), 125.2 (+, 2×Ar-C), 127.7 (+, Ar-C), 129.7 (+, Ar-C), 130.3 (+, Ar-C), 130.7 (+, 2×Ar-C), 136.2 (−, $C_{quat}$, 2×Ar-C), 137.3 (br, −, $C_{quat}$, C8), 151.3 (−, $C_{quat}$, Ar-C), 166.8 (−, $C_{quat}$, CO); MS (70 eV, EI): *m/z* (%)=336/335 (12/60) $[M]^+$, 306 (45), 304 (55), 276 (65), 246 (30), 232 (35), 186 (50), 169 (30), 155 (40), 129 (90), 115 (100), 91 (30), 77 (25); elemental analysis: calcd (%) for $C_{21}H_{21}NO_3$ (335.40): C 75.20, H 6.31; found: C 74.95, H 6.05.

**33c**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2c** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80°C for 3 h. Compound **28** (363 mg, 3.00 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether=5:1) to yield **33c** (415 mg, 71%) as a sticky yellow oil. $R_f$=0.55 (pentane/diethyl ether=10:1); IR (film): =3092, 3014, 2965, 2855, 1610, 1505, 1289, 1054, 1020, 812, 757 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=0.87 (brs, 1H, Cpr-H), 1.12 (brs, 3H, Cpr-H), 2.34 (s, 3H, $CH_3$), 2.38 (s, 3H, $CH_3$), 4.38 (brs, 2H, 6-H), 5.55 (t, $J$=2.15 Hz, 1H, 7-H), 7.15–7.31 (m, 8H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT, HMQC, HMBC): $\delta$=13.9 (−, 2×Cpr-C), 19.9 (+, $CH_3$), 20.6 (+, $CH_3$), 41.0 (−, $C_{quat}$, C3), 62.4 (−, C6), 118.6 (−, $C_{quat}$, 2×Ar-C), 122.7 (+, C7), 125.1 (+, Ar-C), 127.4 (+, Ar-C), 129.3 (+, 2×Ar-C), 129.9 (+, Ar-C), 130.3 (+, Ar-C), 131.9 (+, Ar-C), 136.3 (−, $C_{quat}$, Ar-C), 136.8 (−, $C_{quat}$, Ar-C), 137.0 (br, −, $C_{quat}$, C8), 144.4 ppm (−, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%)=291 (76) $[M]^+$, 276 (100), 262 (40), 248 (42), 232 (20), 218 (16), 185 (28), 172 (20), 155 (24), 144 (26), 129 (70), 115 (96), 105 (80), 91 (84), 65 (44); elemental analysis calcd (%) for $C_{20}H_{21}NO$ (291.39): C 82.44, H 7.26; found: C 82.29, H 7.03.

**34c**: According to GP 4, a mixture of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), $PPh_3$ (76.6 mg, 0.3 mmol), $K_2CO_3$ (552 mg, 4.00 mmol), $Et_4NCl$ (332 mg, 2.00 mmol), **2c** (436 mg, 2.00 mmol), and **1** (320 mg, 4.00 mmol) in MeCN (4.0 mL) was stirred at 80°C for 3 h. Compound **29** (411 mg, 3 mmol) was added at room temperature, and the mixture was stirred overnight. After workup, the residue was subjected to chromatography on silica gel (50 g, 2×20 cm column, pentane/diethyl ether=5:1) to yield **34c** (135 mg, 22%) as an oil, which contained traces of an inseparable impurity. $R_f$=0.40 (pentane/diethyl ether=10:1); IR (film): $\tilde{\nu}$=3014, 2948, 2883, 1592, 1515, 1345, 1242, 1112, 1026, 831, 762 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=0.78 (br, 1H, Cpr-H), 1.12 (br, 3H, Cpr-H), 2.37 (s, 3H, $CH_3$), 3.81 (s, 3H, $CH_3$), 4.31 (d, $J$=2.75 Hz, 2H, 6-H), 5.57 (t, $J$=2.75 Hz, 1H, 7-H), 6.76–6.98 (m, 3H, Ar-H), 7.15–7.31 ppm (m, 5H, Ar-H); $^{13}$C NMR (75 MHz, $CDCl_3$, APT): $\delta$=13.7 (−, 2×Cpr-C), 19.9 (+, $CH_3$), 41.2 (−, $C_{quat}$, C3), 55.4 (+, $OCH_3$), 62.2 (−, C6), 113.9 (+, 2×Ar-C), 120.6 (+, 2×Ar-C), 125.1 (+, C7), 125.9 (+, Ar-C), 127.5 (+, Ar-C), 129.9 (+, Ar-C), 130.3 (+, Ar-C), 136.4 (−, $C_{quat}$, Ar-C), 136.9 (−, $C_{quat}$, C8), 140.1 (−, $C_{quat}$, Ar-C), 155.5 (−, $C_{quat}$, Ar-C), 164.5 ppm (−, $C_{quat}$, Ar-C); MS (70 eV, EI): *m/z* (%)=307 (24) $[M]^+$, 292 (20), 263 (10), 248 (12), 202 (6), 185 (8), 171 (16), 134 (28), 129 (40), 121 (100), 115 (80), 107 (18), 92 (32), 77 (56); HRMS: *m/z* calcd for $C_{20}H_{21}NO_2$: 307 $[M+1]^+$; found: 308.16505 (correct HRMS).

(*E*)/(*Z*)-**37** and **39**: According to GP 1, a mixture of $Pd(OAc)_2$ (55 mg, 245 μmol), $PPh_3$ (200 mg, 762 μmol), $K_2CO_3$ (1382 mg, 10.0 mmol), $Et_4NCl$ (828 mg, 5.0 mmol), **2d**, (1160 mg, 5.00 mmol), and **35** (1382 mg, 10.0 mmol) in MeCN (6 mL) was stirred at 70°C for 24 h. After cooling to room temperature, the mixture was taken up in diethyl ether (60 mL). The solution was washed with water (2×40 mL), the aqueous phase was extracted with diethyl ether (2×40 mL), and the combined organic phases were dried ($MgSO_4$). After removal of the solvent in a rotatory evaporator, the residue was subjected to chromatography on silica gel (250 g, 5×40 cm column, light petroleum/ethyl acetate=12:1) to yield

  

1090 mg (90%) of a mixture of (*E*)-**37**, (*Z*)-**37**, and **39** (67:23:10 according to GC analysis) as a yellowish oil. The relative configurations of (*E*)- and (*Z*)-**37** were assigned on the basis of their NMR data and those of their cycloadducts with **13** (see below). For all spectroscopic measurements, a pure mixture of these isomers was used. In the $^1$H and $^{13}$C NMR spectra of the mixture, individual data for every single structure are labeled by the respective numbers [(*E*)-**37**, (*Z*)-**37**, or **39**] wherever possible. B.p.: 112 °C (0.1 Torr); $R_f$ = 0.26 (light petroleum/ethyl acetate = 12:1); IR (film): $\tilde{\nu}$ = 3088, 3005, 2951, 2921, 2857, 1734, 1608, 1582, 1464, 1436, 1412, 1378, 1346, 1291, 1261, 1233, 1195, 1169, 1138, 1112, 1079, 1049, 1030, 988, 970, 944, 911, 863, 812, 771, 736, 668 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.96–1.00 (m, 2H, Cpr-H) [**39**], 1.30–1.33 (m, 2H, Cpr-H) [**39**], 1.61–1.63 (m, 2H, Cpr-H) [(*E*)-**37**], 1.75 (dd, *J* = 4.0, 9.8 Hz, 1H, Cpr-H) [(*E*)-**37**], 2.00–2.03 (m, 2H, Cpr-H) [(*Z*)-**37**], 2.04 (s, 3H, Ar-$CH_3$) [(*Z*)-**37**], 2.05 (s, 3H, Ar-$CH_3$) [(*Z*)-**37**], 2.09 (s, 3H, Ar-$CH_3$) [(*E*)-**37**], 2.12 (s, 6H, 2 × Ar-$CH_3$) [**39**], 2.15 (s, 3H, Ar-$CH_3$) [(*E*)-**37**], 2.52 (d, *J* = 4.0 Hz, 1H, Cpr-H) [(*Z*)-**37**], 2.54 (d, *J* = 4.1 Hz, 1H, Cpr-H) [(*E*)-**37**], 3.52 (s, 3H, $OCH_3$) [(*Z*)-**37**], 3.72 (s, 3H, $OCH_3$) [(*E*)-**37**], 3.82 (s, 3H, $OCH_3$) [**39**], 4.71 (d, *J* = 17.3 Hz, 1H, vinyl H) [(*E*)-**37**], 4.73 (d, *J* = 17.3 Hz, 1H, vinyl H) [(*Z*)-**37**], 4.90 (s, 1H, vinyl H) [**39**], 5.05 (d, *J* = 10.4 Hz, 1H, vinyl H) [(*E*)-**37**], 5.09 (d, *J* = 10.6 Hz, 1H, vinyl H) [(*Z*)-**37**], 5.53 (s, 1H, vinyl H) [**39**], 6.60 (dd, *J* = 10.3, 17.3 Hz, 1H, vinyl H) [(*Z*)-**37**], 6.72 (dd, *J* = 10.4, 17.3 Hz, 1H, vinyl H) [(*E*)-**37**], 6.98–7.14 ppm (m, 9H, Ar) [(*E*)-**37**, (*Z*)-**37**, **39**]; $^{13}$C NMR (50.3 MHz, $CDCl_3$, DEPT): $\delta$ = 2.4 (–, Cpr-C) [**39**], 5.0 (–, Cpr-C) [**39**], 11.6 (–, Cpr-C) [(*Z*)-**37**], 11.7 (–, Cpr-C) [(*E*)-**37**], 17.7 (–, Cpr-C) [(*Z*)-**37**], 17.8 (–, Cpr-C) [(*E*)-**37**], 19.1 (+, 2 × Ar-$CH_3$) [**39**], 19.3 (+, 2 × Ar-$CH_3$) [(*Z*)-**37**], 19.6 (+, 2 × Ar-$CH_3$) [(*E*)-**37**], 51.5 (+, $OCH_3$) [(*Z*)-**37**], 51.7 (+, $OCH_3$) [**39**], 51.8 (+, $OCH_3$) [(*E*)-**37**], 115.5 (–, vinyl C) [(*E*)-**37**], 115.8 (–, vinyl C) [(*Z*)-**37**], 118.5 (–, vinyl C) [**39**], 124.5 ($C_{quat}$) [(*Z*)-**37**], 125.0 ($C_{quat}$) [**39**], 125.1 ($C_{quat}$) [(*E*)-**37**], 126.9 (+, 3 × Ar-C), 127.0 (+, Ar-C), 127.0 (+, 2 × Ar-C), 127.1 (+, Ar-C), 127.2 (+, 2 × Ar-C), 127.4 ($C_{quat}$) [**39**], 128.4 (2 × $C_{quat}$) [**39**], 130.2 ($C_{quat}$) [(*E*)-**37**], 130.6 ($C_{quat}$) [(*Z*)-**37**], 135.4 (+, vinyl C) [(*E*)-**37**], 135.7 (+, vinyl C) [(*Z*)-**37**], 135.9 ($C_{quat}$) [(*Z*)-**37**], 136.2 ($C_{quat}$) [(*E*)-**37**], 136.4 ($C_{quat}$) [(*Z*)-**37**], 136.48 ($C_{quat}$) [(*E*)-**37**], 136.65 ($C_{quat}$) [(*Z*)-**37**], 137.0 ($C_{quat}$) [(*E*)-**37**], 138.2 ($C_{quat}$) [**39**], 141.5 ($C_{quat}$) [**39**], 169.2 ($C_{quat}$, C=O) [**39**], 171.7 ($C_{quat}$, C=O) [(*Z*)-**37**], 172.3 ppm ($C_{quat}$, C=O) [(*E*)-**37**]; MS (70 eV, EI): *m/z* (%) = 242 (80) $[M]^+$, 227 (20), $[M-CH_3]^+$, 210 (22), 195 (20), 183 (85), 167 (100), 153 (33), 128 (14), 115 (8); elemental analysis: calcd (%) for $C_{16}H_{18}O_2$ (242.3): C 79.31, H 7.49; found: C 79.24, H 7.37.

(*E*)/(*Z*)-**41** and **42**: A mixture of (*E*)-**37**, (*Z*)-**37**, or **39** (242 mg, 1.00 mmol) and **13** (350 mg, 2.00 mmol) in anhydrous MeCN (2 mL) and $CH_2Cl_2$ (1 mL) was stirred at 20 °C for 24 h. The reaction mixture was then taken up in $CH_2Cl_2$ (50 mL). 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 rotatory evaporator, the residue was subjected to chromatography on silica gel (100 g, 3 × 30 cm column, light petroleum/ethyl acetate = 1:1) to yield 255 mg (61%) of a mixture of (*E*)-**41**, (*Z*)-**41**, ($R_f$ = 0.72 (light petroleum/ethyl acetate = 1:1)), and **42** ($R_f$ = 0.61 (light petroleum/ethyl acetate = 1:1)) (75:10:15 according to the $^1$H NMR spectrum of the crude product) as a yellowish oily solid.

(*E*)-**41***: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.70 (dd, *J* = 6.9, 8.7 Hz, 1H, Cpr-H), 2.12 (s, 3H, Ar-$CH_3$), 2.31 (s, 3H, Ar-$CH_3$), 2.41 (t, *J* = 9.23 Hz, 1H, Cpr-H), 3.21 (dd, *J* = 6.9, 9.8 Hz, 1H, Cpr-H), 3.53 (s, 3H, $OCH_3$), 4.31–4.63 (AB system, $\delta_A$ = 4.60, $\delta_B$ = 4.35, $^2J_{AB}$ = 17.3 Hz, $^2J$ = 3.4 Hz, 2H, 8′-H), 5.89 (t, $^3J$ = 3.4 Hz, 1H, 7′-H), 7.02–7.16 (m, 3H, Ar), 7.34–7.48 ppm (m, 5H, Ph); $^{13}$C NMR (75.5 MHz, $CDCl_3$, DEPT): $\delta$ = 16.7 (–, Cpr-C), 20.6 (+, Ar-$CH_3$), 20.8 (+, Ar-$CH_3$), 30.1 (+, Cpr-C), 44.8 (–, C8′), 48.3 ($C_{quat}$, Cpr-C), 52.1 (+, $OCH_3$), 124.7 (+, C7′), 125.5 (+), 127.5 (+), 127.7 (+), 127.9 (+), 128.3 (+), 129.1 (+), 130.8 ($C_{quat}$), 135.3 ($C_{quat}$), 135.7 ($C_{quat}$), 136.8 (2 × $C_{quat}$), 149.4 ($C_{quat}$, C=O), 152.4 ($C_{quat}$, C=O), 168.1 ($C_{quat}$, C=O).

(*Z*)-**41***: IR (KBr): $\tilde{\nu}$ = 3116, 3065, 2994, 2951, 2923, 2853, 1768, 1736, 1703, 1494, 1453, 1423, 1376, 1356, 1294, 1260, 1201, 1181, 1166, 1143, 805, 768, 754, 711, 692 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.25–1.28 (m, 1H, Cpr-H), 1.82 (dd, *J* = 7.5, 10.0 Hz, 1H, Cpr-H), 2.25 (s, 3H, Ar-$CH_3$), 2.33 (s, 3H, Ar-$CH_3$), 3.39 (t, *J* = 7.14 Hz, 1H, Cpr-H), 3.66 (s, 3H, $OCH_3$), 4.23–4.60 (AB system, $\delta_A$ = 4.56, $\delta_B$ = 4.27, $^2J_{AB}$ = 16.8 Hz, $^3J_{A-7'H}$ = 4.4 Hz, $^3J_{B-7'H}$ = 2.4 Hz, 2H, 8′-H), 5.77 (dd, *J* = 2.6, 3.9 Hz, 1H, 7′-H), 7.01–7.17 (m, 3H, Ar), 7.33–7.58 ppm (m, 5H, Ph); $^{13}$C NMR (75.5 MHz, $CDCl_3$, DEPT): $\delta$ = 17.1 (–, Cpr-C), 19.9 (+, Ar-$CH_3$), 20.3 (+, Ar-$CH_3$), 25.4 (+, Cpr-C), 46.9 (–, C8′), 46.3 ($C_{quat}$, Cpr-C), 52.2 (+, $OCH_3$), 121.4 (+, C7′), 126.2 (+), 127.6 (+), 128.1 (+), 128.3 (+), 129.1 (2 × +), 131.2 (+), 133.3 ($C_{quat}$), 136.2 ($C_{quat}$), 136.8 ($C_{quat}$), 137.6 ($C_{quat}$), 149.9 ($C_{quat}$, C=O), 154.9 ($C_{quat}$, C=O), 170.0 ppm ($C_{quat}$, C=O); MS (70 eV, EI): *m/z* (%) = 417 (100) $[M]^+$, 402 (12), $[M-CH_3]^+$, 385 (18), 370 (5), 357 (6), 342 (10), 330 (25), 240 (16), 211 (26), 181 (11), 167 (25), 154 (18), 128 (25), 91 (17), 55 (14); elemental analysis: calcd (%) for $C_{24}H_{23}N_3O_4$ (417.5): C 69.05, H 5.55, N 10.07; found: C 68.83, H 5.79, N 9.89.

* IR, EI MS, and elemental analysis were carried out with the mixture of diastereomers (*E*)/(*Z*)-**41**.

**42**: IR (KBr): $\tilde{\nu}$ = 3066, 3020, 2951, 2923, 2851, 1779, 1734, 1711, 1634, 1621, 1597, 1564, 1507, 1415, 1344, 1276, 1230, 1166, 1028, 765, 712, 688 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 50 °C): $\delta$ = 0.86–0.90 (m, 2H, Cpr-H), 2.08–2.13 (m, 2H, Cpr-H), 2.18 (s, 6H, 2 × Ar-$CH_3$), 3.51 (s, 3H, $OCH_3$), 4.62 (s, 2H, 8′-H), 7.00–7.52 ppm (m, 8H, Ar, Ph); $^{13}$C NMR (50.2 MHz, $CDCl_3$, DEPT): $\delta$ = 12.5 (–, 2 × Cpr-C), 19.9 (+, 2 × Ar-$CH_3$), 43.3 ($C_{quat}$, Cpr-C), 45.1 (–, C8′), 51.8 (+, $OCH_3$), 120.9 ($C_{quat}$), 122.1 ($C_{quat}$), 125.7 (+), 127.4 (+), 128.2 (+), 128.3 (+), 129.1 (+), 129.2 (+), 131.2 ($C_{quat}$), 132.9 ($C_{quat}$), 135.8 ($C_{quat}$), 148.4 ($C_{quat}$), 150.4 ($C_{quat}$, C=O), 153.1 ($C_{quat}$, C=O), 164.2 ppm ($C_{quat}$, C=O); MS (70 eV, EI): *m/z* (%) = 417 (38) $[M]^+$, 402 (18), $[M-CH_3]^+$, 358 (5), 269 (5), 212 (16), 181 (14), 167 (19), 128 (17), 119 (18), 93 (100), 77 (19), 65 (12); HRMS (ESI): *m/z* calcd for $C_{24}H_{23}N_3O_4$: 418.17613 $[M+H]^+$; found: 418.17619.

## Acknowledgements

L.Z. is indebted to the Alexander von Humboldt foundation for a research fellowship. The authors are particularly grateful to Dr. M. Noltemeyer, Universität Göttingen, for the X-ray crystal-structure analysis of compound **23c** and to Dr. B. Knieriem for his careful proof-reading of the final manuscript.

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Received: October 26, 2006
Published online: December 18, 2006

  