Domino Heck–Diels–Alder Reactions of Differently Substituted Cyclopropylallenes[‡]

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Several substituted cyclopropylallenes were coupled under Heck conditions with aryl iodides and aryl bromides, respectively, and the 1,3,5-hexatrienes resulting with ring-opening of the cyclopropyl group, were captured in situ by a number of reactive dienophiles to yield oligosubstituted cyclohexene derivatives (8–86 %, 33 examples) with diastereomeric ratios ranging from 1.4:1 to 4.9:1. The influences of the number, the nature and the pattern of substituents have been elaborated. The [4+2] cycloaddition most probably proceeds in two steps through a mesomerically well stabilized 1,6-zwitterionic intermediate.

Introduction

Efficiency has gained more and more importance during the ongoing search for new synthetic methods.[1] Domino processes are important tools in modern preparative synthesis because they increase efficiency by combining several operational steps without isolation of intermediates or changes of the conditions.[2] This principle, therefore, is highly efficient in terms of time as well as resources.[3] Allenes have already been used for several types of domino processes,[4] especially palladium-catalyzed cross-coupling reactions.[5] Research in our group has been focussed on domino reactions of building blocks containing small rings.[6] In this series we already presented the domino Heck–Diels–Alder reactions of bicyclopropylidene[7] and 1,3-dicyclopropyl-1,2-propadiene.[8] Herein we report the broader scope of this principle with respect to differently substituted cyclopropylallenes. When a cyclopropylallene is employed in a Heck reaction, the first formed carbopalladation product can undergo a cyclopropylcarbinyl to homoallyl rearrangement[9] with subsequent β-dehydropalladation to give a substituted 1,3,5-hexatriene which can react with various dienophiles in a Diels–Alder reaction. Because the allene is more reactive than the dienophile towards carbopalladation by, e.g., an arylpalladium halide, both reactions can be combined in a one-pot domino process.

Results and Discussion

Addition of the arylpalladium halide **2** to a cyclopropylallene **1** will give a π-allylpalladium species **3** which equilibrates with the two regioisomeric σ-allyl complexes **4a** and **4b** (Scheme 1). While **4b** will give undesired products through the addition to another cyclopropylallene, **4a** will undergo the very fast cyclopropylcarbinyl to homoallyl rearrangement to give **5**.[10] After β-dehydropalladation, the formed 1,3,5-hexatriene **6** is trapped by an appropriate dienophile to give the oligosubstituted cyclohexene derivatives **8**.

Surprisingly, the [4+2] cycloaddition was found to proceed in a non-concerted fashion. Thus, dimethyl maleate gave a mixture of *trans,trans*- and *cis,trans*-**8** with a preference for the thermodynamically more stable *trans,trans* isomer which cannot be formed in a concerted Diels–Alder reaction (Scheme 1). An analogous mixture of diastereomers was obtained with diethyl fumarate. This lack of stereocontrol can only be rationalized in terms of a stepwise reaction through the mesomerically well stabilized 1,6-zwitterionic intermediate **7** (Scheme 1).

Non-concerted [4+2] cycloadditions have been discussed previously.[11] According to density functional theory computations, the activation energy for the [4+2] cycloaddition of butadiene to ethylene is only a few kcal/mol higher than for the concerted one.[12] For the combination of highly donor-substituted dienes and acceptor-substituted dienophiles, the two-step addition can even be the preferred one.[13,14]

As mentioned before, the most important step is the selective formation of the regioisomer **4a** instead of **4b**. In order to determine how the regioselectivity can be influenced by substituents, the symmetric 1,3-dicyclopropyl-1,2-propadiene (**1a**)[15] was used initially. Its reaction with

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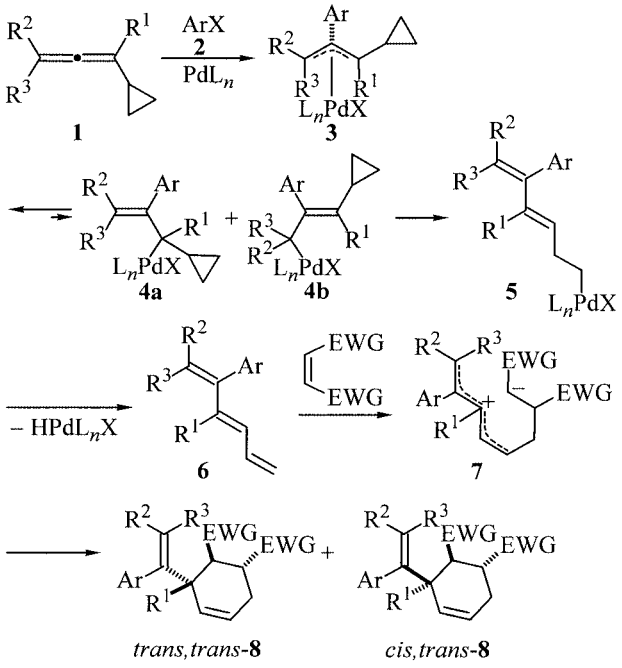


Scheme 1. Mechanistic rationalization of the domino Heck–Diels–Alder reactions with cyclopropylallenes.

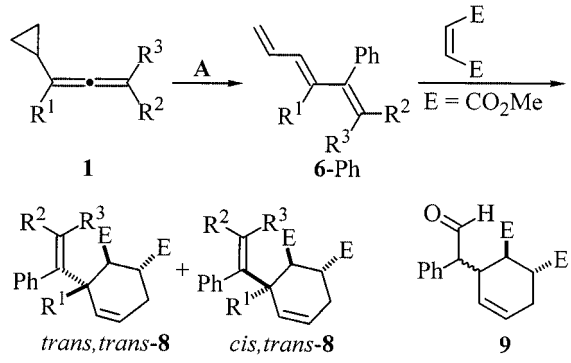
phenyl iodide in the presence of dimethyl maleate under palladium catalysis furnished the cross-coupling cycloadduct **8a**-Ph in 86% yield (Table 1, Entry 1). Although the (monocyclopropyl)allene[16] **1b** in principle should be able to react in the same way and give an analogous coupling cycloadduct, none of the expected **8b**-Ph could be isolated (Entry 2). With a methyl group in the 3-position, 1-cyclopropyl-1,2-butadiene (**1c**)[17] afforded the coupling cycloadduct **8c**-Ph in 16% isolated yield (Entry 3). With 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**),[18] which contains an additional methyl group, the corresponding product was obtained in 60% yield (Entry 4). This indicates that the regioselectivity of the addition might be controlled by attaching bulky groups. With 1-cyclopropyl-4,4-dimethyl-1,2-pentadiene (**1e**), containing a *tert*-butyl group, the yield was 35% (Entry 5), just between that from **1c** and **1d**.

After all, a substituent in the 3-position of the cyclopropylallene is not essential, as 1,1-dicyclopropyl-1,2-propadiene (**1f**)[19] and 3-cyclopropyl-1,2-butadiene (**1g**)[20] gave the corresponding coupling cycloadducts **8f**-Ph and **8g**-Ph in 43 and 47% yield, respectively (Entries 6, 7). Cyclopropylallenes with electron-withdrawing substituents like methyl cyclopropylallenecarboxylate (**1h**)[21] and cyanocyclopropyldimethylallene (**1i**)[22] did not react under the employed conditions (Entries 8, 9). The donor-substituted cyclopropylallenyl ether **1j**[23] did provide the coupling cycloadduct, albeit in poor yield (10%), when the reaction was carried out in two steps, but without work-up after the Heck coupling reaction (Entry 10). During the reaction, the enol ether was cleaved to some extent so that a mixture of the coupling product **8j**-Ph and the corresponding aldehyde **9** was isolated.

Table 1. Domino Heck–Diels–Alder reaction with substituted cyclopropylallenes (see Scheme 2).

Entry	Allene	R^1	R^2	R^3	Product	Yield (%)	*dr*[a]
1	**1a**	H	Cpr	H	**8a**-Ph	86	4.0:1
2	**1b**	H	H	H	**8b**-Ph	–	–
3	**1c**	H	Me	H	**8c**-Ph	16	1.9:1
4	**1d**	H	Me	Me	**8d**-Ph	60	3.9:1
5	**1e**	H	*t*Bu	H	**8e**-Ph	35	3.7:1
6	**1f**	Cpr	H	H	**8f**-Ph	43	2.0:1
7	**1g**	Me	H	H	**8g**-Ph	47	3.0:1
8	**1h**	CO_2Me	H	H	**8h**-Ph	–	–
9	**1i**	CN	Me	Me	**8i**-Ph	–	–
10	**1j**	H	OMe	H	**8j**-Ph[b]	10[c]	–[d]

[a] Ratio of the *trans,trans*- and *cis,trans*-diastereomer as determined according to NMR spectra. [b] Mixture of the enol ether and the corresponding aldehyde **9**. [c] The dienophile was added after 5 h. [d] Ratio was not determined.



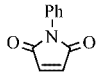
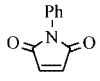
Scheme 2. Domino Heck–Diels–Alder reactions with substituted cyclopropylallenes. For details see Table 1. **A**: $Pd(OAc)_2$ (5 mol%), Ph_3P (15 mol%), PhI (1.3 equiv.), NEt_3 (2 equiv.), DMF, 100 °C, 18–24 h.

The reaction is not only influenced by the type and pattern of substituents on the cyclopropylallene, but also by the type of aryl halide and of the dienophile. While the reaction of **1a** with phenyl iodide and dimethyl maleate gave **8a**-Ph in 86% yield, that with 2-iodopyridine furnished **8a**-Py in lower yield (61%), but with a higher predominance (4.9:1) of the favored diastereomer (Table 2, Entry 1). Aryl bromides gave consistently lower yields, e.g. 46% for bromobenzene (Entry 2). Yet some aryl bromides like 1-bromo-3-nitrobenzene (Entry 3) and 1-bromo-4-nitrobenzene (Entry 4) are commercially available, whereas the corresponding iodides are not.

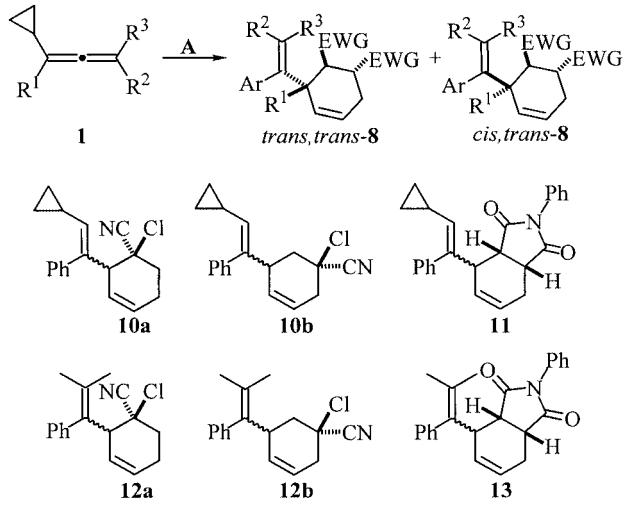
The reaction with phenyl iodide in the presence of 2-chloroacrylonitrile (Entry 5) gave the two separable regioisomers **10a** and **10b** (58%) with the domination of the "*ortho*" product (4.3:1). *N*-Phenylmaleimide gave a single isomer, albeit in 35% yield (Entry 6).

Analogous reactions with 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) showed the same tendency. With the sterically more congested 2-iodotoluene the yield decreased from 60 to 33% (Table 2, Entry 7) and with 4-iodotoluene the corresponding product was isolated in 22% yield (Entry 8). 4-Iodoanisole containing the electron-donating methoxy substituent gave a poor yield of 8% (Entry 9). The use of

Table 2. Domino Heck–Diels–Alder coupling cycloadducts from cyclopropylallenes, aryl halides and dienophiles (see Scheme 3).

Entry	Allene	Aryl Halide	Dienophile[a]	Product	Yield (%)	d.r.[b]
1	**1a**	2-Py-I		**8a**-Py	61	4.9:1
2	**1a**	PhBr		**8a**-Ph	46	3.4:1
3	**1a**	3-O_2N-C_6H_4Br		**8a**-3-O_2N-C_6H_4	44	3.2:1
4	**1a**	4-O_2N-C_6H_4Br		**8a**-4-O_2N-C_6H_4	36	2.2:1
5	**1a**	PhI		**10a**, **10b**	58	4.3:1[c]
6	**1a**	PhI		**11**	35	–[d]
7	**1d**	2-Me-C_6H_4I		**8d**-2-Me-C_6H_4	33	1.9:1
8	**1d**	4-Me-C_6H_4I		**8d**-4-Me-C_6H_4	22	2.4:1
9	**1d**	4-MeO-C_6H_4I		**8d**-4-MeO-C_6H_4	8	2.8:1
10	**1d**	4-MeO_2C-C_6H_4I		**8d**-4-MeO_2C-C_6H_4	13	1.8:1
11	**1d**	4-MeCO-C_6H_4I		**8d**-4-MeCO-C_6H_4	55	3.2:1
12	**1d**	4-F-C_6H_4I		**8d**-4-F-C_6H_4	28	2.8:1
13	**1d**	4-O_2N-C_6H_4Br		**8d**-4-O_2N-C_6H_4	23	4.0:1
14	**1d**	PhI		**12a**, **12b**	26	1.4:1[c]
15	**1d**	PhI		**13**	11	2.3:1
16	**1e**	2-Me-C_6H_4I		**8e**-2-Me-C_6H_4	23	2.9:1
17	**1e**	4-O_2N-C_6H_4Br		**8e**-4-O_2N-C_6H_4	32	1.9:1
18	**1e**	3-CHO-C_6H_4Br		**8e**-3-CHO-C_6H_4	13	3.5:1
19	**1f**	4-Me-C_6H_4I		**8f**-4-Me-C_6H_4	27	2.0:1
20	**1f**	4-MeO_2C-C_6H_4I		**8f**-4-MeO_2C-C_6H_4	35	1.9:1
21	**1f**	4-MeCO-C_6H_4I		**8f**-4-MeCO-C_6H_4	24	1.6:1
22	**1f**	4-O_2N-C_6H_4Br		**8f**-4-O_2N-C_6H_4	29	1.8:1
23	**1f**	4-O_2N-C_6H_4Br		**8f**-4-O_2N-C_6H_4	21	2.0:1[e]
24	**1f**	4-O_2N-C_6H_4Br		**8f**-4-O_2N-C_6H_4	11	1.9:1[f]
25	**1f**	4-MeO-C_6H_4I		**8f**-4-MeO-C_6H_4	11	1.8:1
26	**1g**	4-Me-C_6H_4I		**8g**-4-Me-C_6H_4	37	3.0:1
27	**1g**	4-MeCO-C_6H_4I		**8g**-4-MeCO-C_6H_4	59	3.2:1
28	**1g**	4-CF_3-C_6H_4Br		**8g**-4-CF_3-C_6H_4	32	2.8:1
29	**1g**	2-O_2N-C_6H_4Br		**8g**-2-O_2N-C_6H_4	13	2.1:1
30	**1g**	2-Br-4-Cl-Py		**8g**-4-Cl-Py	19	1.8:1

[a] E = CO_2Me. [b] Ratio of the *trans,trans*- and *cis,trans*-diastereomer as determined according to NMR spectra. [c] Ratio of the two separable regioisomers. The ratio of the diastereomers was not detected. [d] Only one diastereomer. [e] Reaction was carried out with $Pd_2dba_3{\cdot}CHCl_3$ and tBu_3P as a catalyst. [f] An excess of ArX (3.0 equiv.) was used.



Scheme 3. Domino Heck–Diels–Alder coupling cycloadducts from cyclopropylallenes, aryl halides and dienophiles. For details see Table 2. **A:** $Pd(OAc)_2$ (5 mol%), Ph_3P (15 mol%), ArX (1.3 equiv.), NEt_3 (2 equiv.), dienophile (2 equiv.), DMF, 100 °C, 18–24 h.

methyl 4-iodobenzoate in the sequential reaction gave a yield of only 13% (Entry 10). With the more prominantly acceptor-substituted 4-iodoacetophenone the yield was 55% (Entry 11) and the thermodynamically more stable *trans,trans* isomer again more predominant (3.2:1). 4-Iodofluorobenzene gave a yield of 28% (Entry 12). 1-Bromo-4-nitrobenzene gave the coupling cycloadduct in just 23% isolated yield (Entry 13). Other dienophiles like 2-chloroacrylonitrile (Entry 14) and *N*-phenylmaleimide (Entry 15) provided rather poor yields compared to those obtained with 1,3-dicyclopropyl-1,2-propadiene (Entries 5 and 6), probably due to the steric influence of the two methyl groups attached to the intermediate 1,3,5-hexatriene. This would also explain the lower predominance of the "*ortho*" product (1.4:1).

The results with 1-cyclopropyl-4,4-dimethyl-1,2-butadiene (**1e**) also fit in the picture. While the reaction with phenyl iodide gave a yield of 35% (Table 1, Entry 5), with 2-iodotoluene just 23% of the product was isolated (Table 2, Entry 16). 1-Bromo-4-nitrobenzene (32%, Entry 17) was comparable to phenyl iodide, but with 3-bromobenzaldehyde the yield was just 13% (Entry 18).

In the case of 1,1-dicyclopropyl-1,2-propadiene (**1f**), the differences between several aryl halides are less remarkable. A variation from 24% for 4-iodoacetophenone to 35% for methyl 4-iodobenzoate was found (Entries 19–22). An exception is the donor-substituted 4-iodoanisole which gave the corresponding coupling cycloadduct in just 11% isolated yield (Entry 25). We also observed, that other catalysts like $Pd_2dba_3{\cdot}CHCl_3$ in combination with tBu_3P give slightly poorer but comparable yields than $Pd(OAc)_2$ with PPh_3 (Entry 23). An excess of aryl halide usually did not improve the yield (Entry 24). With 3-cyclopropyl-1,2-butadiene (**1g**) the yield with 4-iodotoluene (37%, Entry 26) is much better than with 2-bromonitrobenzene (13%, Entry 29) or 2-bromo-4-chloropyridine (19%, Entry 30), but similar to the

result with bromobenzo trifluoride (32%, Entry 28). The best result was obtained with 4-iodoacetophenone (59%, Entry 27).

Conclusions

The sequential Heck and Diels–Alder reaction has been found to be a useful access to 4,5-disubstituted 3-alkenylcyclohexenes starting from easily prepared cyclopropylallenes and commercially available aryl halides and dienophiles. Best results are generally obtained with 1,3-dicyclopropyl-1,2-propadiene (**1a**) and 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) combined with electron-acceptor substituted aryl iodides and dimethyl maleate as a reactive dienophile.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded at 250, 300 or 600 MHz (^{1}H) and 62.9 or 75.5 MHz [^{13}C, DEPT (Distortionless Enhancement by Polarization Transfer)] with a Bruker AM 250, Varian Mercury 300 or Varian Inova 600 spectrometer, respectively, in $CDCl_3$ with Me_4Si as a standard. Mass spectra (EI and CI): Finnigan MAT 95. IR: Bruker IFS 66 FT-IR, measured as KBr pellets or as oils between KBr plates. Elemental analyses were performed by the Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen. R_f values refer to TLC on 0.25 mm precoated silica gel plates (Macherey–Nagel, Alugram Sil G/UV$_{254}$) with the same eluent as used for the purification of the compound by flash column chromatography employing silica gel 60 (Merck, 0.040–0.063 mm, 200–400 mesh). Melting points (m.p.): Büchi 510 melting point apparatus, values are uncorrected. DMF and other chemicals were used as commercially available.

General Procedure (GP) for the Domino Heck–Diels–Alder Reaction: A solution of palladium(II) acetate (11.2 mg, 50.0 μmol, 5 mol%) and triphenylphosphane (39.3 mg, 150 μmol, 15 mol%) in DMF (1 mL) was flushed with nitrogen for 10 min. The allene (1 mmol), the aryl halide (1.3 mmol), triethylamine (202 mg, 2.00 mmol) and the dienophile (2 mmol) were added, and the mixture was stirred at 100 °C for 18–24 h. The reaction was quenched with water (10 mL), and the mixture diluted with diethyl ether (4 × 10 mL). The combined organic layers were washed with water (3 × 25 mL) and brine (25 mL). The organic solution was dried ($MgSO_4$), the solvent removed, and the residue purified by flash column chromatography on silica gel.

Dimethyl 3-[(2′-Cyclopropyl-1′-phenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8a-Py): Prepared within 24 h from 1,3-dicyclopropyl-1,2-propadiene (**1a**) (121 mg, 1.00 mmol), phenyl iodide (245 mg, 1.20 mmol) and dimethyl maleate (288 mg, 2.00 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 10:1) **8a**-Ph (293 mg, 86%, *dr* = 4.0:1) was obtained as a colorless oil, R_f = 0.10. IR (film): $\tilde{\nu}$ = 2982, 2873 cm^{-1}, 1746, 1492, 1383, 1249, 1125, 1077, 953, 845, 763, 702. **Major Isomer:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.21–0.27 (m, 2 H, Cpr-H), 0.56 (ddd, ^3J = 8.2, 2.4, ^2J = 0.6 Hz, 2 H, Cpr-H), 1.17 (m, 1 H, Cpr-H), 2.10 (m, 1 H, 6-H), 2.27 (m, 1 H, 6-H), 2.69 (dd, ^3J = 10.9, 10.1 Hz, 1 H, 2-H), 2.94 (dt, ^3J = 10.9, 5.4 Hz, 1 H, 1-H), 3.37 (ddd, ^3J = 10.1, 3.9, ^4J = 2.0 Hz, 1 H, 3-H), 3.57 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 4.81 (s, 1 H, 2′-H), 5.64 (m, 2 H, 4-H, 5-H), 7.14–7.32 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.3 (CH_2, 2 C, Cpr-C), 11.1 (CH, Cpr-C), 27.2 (CH_2, C-6), 42.1 (CH, C-1), 46.6 (CH, C-2), 48.5 (CH, C-3), 51.5 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 124.6 (CH, C-5), 126.7 (CH, 2 C, Ph-C), 127.8 (CH, 2 C, Ph-C), 129.6 (CH, C-4), 129.7 (CH, Ph-C), 135.2 (CH, C-2′), 138.6 (C, Ph-C), 139.2 (C, C-1′), 174.4 (C, COO), 175.1 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 340 (38) [M$^+$], 309 (20), 280 (100), 249 (39), 221 (61), 205 (33), 193 (28), 167 (29), 143 (70), 128 (34), 115 (24), 91 (43), 77 (8), 59 (12), 41 (4). $C_{21}H_{24}O_4$ (340.42): calcd. C 74.09, H 7.11; found C 74.34, H 6.94.

Dimethyl 3-[(2′-Cyclopropyl-1′-pyrid-2′′-yl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8a-Py): Prepared within 24 h from 1,3-dicyclopropyl-1,2-propadiene (**1a**) (123 mg, 1.03 mmol), 2-iodopyridine (249 mg, 1.21 mmol) and dimethyl maleate (288 mg, 2.00 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8a**-Py (209 mg, 61%, *dr* = 4.9:1) was obtained as a colorless oil, R_f = 0.12. IR (film): $\tilde{\nu}$ = 3002, 2951 cm^{-1}, 1734, 1559, 1437, 1248, 1198, 1173, 1024, 948, 886, 751, 668. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.47 (m, 2 H, Cpr-H), 0.84 (m, 2 H, Cpr-H), 1.74 (m, 1 H, Cpr-H), 2.23 (m, 1 H, 6-H), 2.47 (m, 1 H, 6-H), 3.11 (dd, ^3J = 10.6, 9.4 Hz, 1 H, 2-H), 3.26 (dd, ^3J = 9.4, 5.4 Hz, 1 H, 1-H), 3.39 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 4.18 (dd, ^3J = 10.6, 4.0 Hz, 1 H, 3-H), 5.54 (s, 1 H, 2′-H), 5.73 (m, 2 H, 4-H, 5-H), 7.01 (dt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Aryl-H), 7.27 (dd, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Aryl-H), 7.51 (dt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Aryl-H), 8.45 (dd, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Aryl-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.1 (CH_2, 2 C, Cpr-C), 10.9 (CH, Cpr-C), 27.7 (CH_2, C-6), 40.1 (CH, C-1), 42.5 (CH, C-2), 45.9 (CH, C-3), 51.4 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 120.7 (CH, Aryl-C), 121.1 (CH, Aryl-C), 123.5 (CH, C-5), 131.8 (CH, C-4), 135.9 (CH, Aryl-C), 137.2 (C, Aryl-C), 140.0 (CH, C-2′), 148.4 (CH, Aryl-C), 159.1 (C, C-1′), 174.7 (C, COO), 175.0 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 341 (97) [M$^+$], 310 (34), 282 (100), 222 (18), 197 (57), 182 (46), 168 (61), 144 (18), 93 (4), 59 (3). $C_{20}H_{23}NO_4$ (341.41): calcd. C 70.36, H 6.79, N 4.10; found C 70.00, H 6.48, N 4.15.

Dimethyl 3-{[2′-Cyclopropyl-1′-(3′′-nitrophenyl)]ethenyl}cyclohex-4-ene-1,2-dicarboxylate (8a-3-O_2N-C_6H_4): Prepared within 24 h from 1,3-dicyclopropyl-1,2-propadiene (**1a**) (142 mg, 1.18 mmol), 3-bromonitrobenzene (276 mg, 1.36 mmol) and dimethyl maleate (339 mg, 2.35 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8a**-3-O_2N-C_6H_4 (198 mg, 44%, *dr* = 3.2:1) was obtained as a yellow oil, R_f = 0.10. IR (film): $\tilde{\nu}$ = 3027, 3003 cm^{-1}, 2952, 2847, 1737, 1529, 1436, 1349, 1250, 1199, 1165, 1023, 906, 809, 740, 695. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.35–0.41 (m, 2 H, Cpr-H), 0.61–0.69 (m, 2 H, Cpr-H), 1.20–1.27 (m, 1 H, Cpr-H), 2.02–2.16 (m, 1 H, 6-H), 2.29–2.44 (m, 1 H, 6-H), 2.70–2.82 (m, 1 H, 2-H), 2.87–3.01 (m, 1 H, 1-H), 3.30–3.42 (m, 1 H, 3-H), 3.60 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 4.95 (s, 1 H, 2′-H), 5.69–5.78 (m, 2 H, 4-H, 5-H), 7.38–7.67 (m, 3 H, Ph-H), 8.08–8.14 (m, 1 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.6 (CH_2, 2 C, Cpr-C), 11.0 (CH, Cpr-C), 27.1 (CH_2, C-6), 41.6 (CH, C-3), 46.2 (CH, C-1), 48.3 (CH, C-2), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 121.7 (CH, Ph-C), 124.4 (CH, C-5), 125.9 (CH, Ph-C), 127.6 (CH, Ph-C), 129.6 (CH, C-4), 132.5 (CH, Ph-C), 135.4 (C, Ph-C), 138.6 (C, Ph-C), 140.6 (CH, C-2′), 147.7 (C, C-1′), 174.1 (C, COO), 174.5 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 385 (71) [M$^+$], 354 (46), 325 (91), 266 (87), 248 (55), 199 (100), 165 (54), 115 (42), 91 (40), 59 (70), 41 (24). $C_{21}H_{23}NO_6$ (385.42): calcd. C 65.44, H 6.02, N 3.63; found C 65.08, H 5.93, N 3.65.

Dimethyl 3-{[2′-Cyclopropyl-1′-(4′′-nitrophenyl)]ethenyl}cyclohex-4-ene-1,2-dicarboxylate (8a-4-O_2N-C_6H_4): Prepared within 24 h from

1,3-dicyclopropyl-1,2-propadiene (**1a**) (177 mg, 1.47 mmol), 4-bromonitrobenzene (391 mg, 1.94 mmol) and dimethyl maleate (453 mg, 3.15 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8a**-4-O_2N-C_6H_4 (205 mg, 36%, *dr* = 2.2:1) was obtained as a red oil, R_f = 0.07. IR (film): $\tilde{\nu}$ = 3020, 1734 cm^{-1}, 1520, 1347, 1216, 909, 734, 669, 651. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.37–0.49 (m, 2 H, Cpr-H), 0.63–0.71 (m, 2 H, Cpr-H), 1.21–1.28 (m, 1 H, Cpr-H), 2.01–2.17 (m, 1 H, 6-H), 2.30–2.45 (m, 1 H, 6-H), 2.68–2.84 (m, 1 H, 2-H), 2.89–3.02 (m, 1 H, 1-H), 3.38–3.55 (m, 1 H, 3-H), 3.65 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 4.96 (s, 1 H, 2′-H), 5.69–5.75 (m, 2 H, 4-H, 5-H), 7.37–7.53 (m, 2 H, Ph-H), 8.16–8.25 (m, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.8 (CH_2, 2 C, Cpr-C), 10.8 (CH, Cpr-C), 22.3 (CH_2, C-6), 42.1 (CH, C-3), 45.4 (CH, C-1), 46.5 (CH, C-2), 51.6 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 122.8 (CH, 2 C, Ph-C), 124.0 (CH, C-5), 125.8 (CH, 2 C, Ph-C), 129.5 (CH, C-4), 136.7 (C, Ph-C), 137.3 (C, Ph-C), 140.6 (CH, C-2′), 146.4 (C, C-1′), 174.4 (C, COO), 174.6 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 385 (22) [M^+], 353 (26), 325 (100), 294 (65), 266 (83), 199 (93), 165 (42), 152 (36), 113 (27), 91 (28), 59 (55), 41 (23). $C_{21}H_{23}NO_6$ (385.42): calcd. C 65.44, H 6.02, N 3.63; found C 65.62, H 6.20, N 3.59.

Dimethyl 3-(1′-Phenylprop-1′-enyl)cyclohex-4-ene-1,2-dicarboxylate (8c-Ph): Prepared within 24 h from 1-cyclopropyl-1,2-butadiene (**1c**) (90 mg, 0.96 mmol), phenyl iodide (250 mg, 1.23 mmol) and dimethyl maleate (282 mg, 1.96 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8c**-Ph (49 mg, 16%, *dr* = 1.9:1) was obtained as a colorless oil, R_f = 0.19. IR (film): $\tilde{\nu}$ = 3057, 3026 cm^{-1}, 2952, 1736, 1626, 1599, 1576, 1494, 1436, 1357, 1266, 1198, 1171, 1075, 1026, 888, 758, 737, 701. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.43–1.58 (m, 3 H, 3′-H), 2.25–3.31 (m, 4 H, 6-H, 1-H, 2-H), 3.42–3.51 (m, 1 H, 3-H), 3.68 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.95–5.17 (m, 1 H, 2′-H), 5.76–6.09 (m, 2 H, 4-H, 5-H), 7.16–7.43 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3, C-3′), 27.3 (CH_2, C-6), 40.7 (CH, C-1), 43.9 (CH, C-2), 46.8 (CH, C-3), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 116.7 (CH, C-4), 125.8 (CH, Ph-C), 126.5 (CH, Ph-C), 127.4 (CH, Ph-C), 128.1 (CH, Ph-C), 128.6 (C, Ph-C), 128.8 (CH, Ph-C), 130.4 (CH, C-5), 132.8 (CH, C-2′), 140.8 (C, C-1′), 174.1 (C, COO), 174.5 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 314 (23) [M^+], 299 (51), 271 (43), 254 (100), 223 (42), 195 (94), 165 (50), 155 (39), 128 (28), 115 (51), 91 (67), 77 (30), 59 (31). $C_{19}H_{22}O_4$ (314.38): calcd. C 72.59, H 7.05; found C 72.24, H 6.61.

Dimethyl 3-[(2′-Methyl-1′-phenylprop-1′-enyl]cyclohex-4-ene-1,2-dicarboxylate (8d-Ph): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (132 mg, 1.22 mmol), phenyl iodide (400 mg, 1.96 mmol) and dimethyl maleate (304 mg, 2.11 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8d**-Ph (241 mg, 60%, *dr* 3.9:1) was obtained as a colorless oil, R_f = 0.21. IR (film): $\tilde{\nu}$ = 3025, 2952 cm^{-1}, 1734, 1700, 1696, 1662, 1646, 1576, 1559, 1540, 1472, 1457, 1388, 1357, 1252, 1198, 1166, 1025, 913, 756, 703, 668. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 2.25–2.46 (m, 2 H, 6-H), 2.78 (dd, ^3J = 10.4, 9.4 Hz, 1 H, 2-H), 3.05–3.16 (m, 1 H, 1-H), 3.22–3.34 (m, 1 H, 3-H), 3.65 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 4.99–5.14 (m, 2 H, 4-H, 5-H), 6.96–7.42 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3), 20.7 (CH_3), 33.2 (CH_2, C-6), 41.6 (CH, C-1), 47.7 (CH, C-2), 48.8 (CH, C-3), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 116.9 (C, C-2′), 126.0 (CH, C-4), 126.7 (CH, 2 C, Ph-C), 127.6 (CH, Ph-C), 129.0 (CH, 2 C, Ph-C), 131.0 (CH, C-5), 133.6 (C, Ph-C), 141.1 (C, C-1′), 174.5 (C, COO), 174.9 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 328 (43) [M^+], 297 (19), 268 (100), 237 (82), 209 (99), 193 (29), 181 (25), 167 (36), 152 (12), 131 (18), 91 (38), 77 (12), 59 (24), 41 (7). $C_{20}H_{24}O_4$ (328.41): calcd. C 73.15, H 7.37; found C 73.47, H 7.00.

Dimethyl 3-[2′-Methyl-1′-(2′′-methylphenyl)prop-1′-enyl]cyclohex-4-ene-1,2-dicarboxylate (8d-2-Me-C_6H_4): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (90 mg, 0.83 mmol), 2-iodotoluene (230 mg, 1.06 mmol) and dimethyl maleate (263 mg, 1.83 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8d**-2-Me-C_6H_4 (93 mg, 33%, *dr* = 1.9:1) was obtained as a yellow oil, R_f = 0.16. IR (film): $\tilde{\nu}$ = 3057, 2952 cm^{-1}, 2855, 1735, 1487, 1436, 1378, 1266, 1198, 1168, 1023, 966, 895. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28–1.41 (m, 6 H, CH_3), 2.06–2.11 (m, 3 H, CH_3), 2.37–2.48 (m, 2 H, 6-H), 2.72–2.85 (m, 1 H, 2-H), 2.90–3.00 (m, 1 H, 1-H), 3.06–3.19 (m, 1 H, 3-H), 3.64 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 4.99–5.06 (m, 2 H, 4-H, 5-H), 6.99–7.28 (m, 4 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3), 19.5 (CH_3), 20.4 (CH_3), 33.3 (CH_2, C-6), 42.1 (CH, C-1), 45.7 (CH, C-2), 48.8 (CH, C-3), 51.5 (CH_3, OCH_3), 52.0 (CH_3, OCH_3), 123.2 (CH, C-4), 125.3 (CH, Ph-C), 126.0 (CH, Ph-C), 127.2 (CH, Ph-C), 128.5 (CH, Ph-C), 129.3 (CH, C-5), 130.7 (C, Ph-C), 133.5 (C, Ph-C), 139.9 (C, C-2′), 165.7 (C, C-1′), 174.3 (C, COO), 174.9 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 343 (48) [M + H^+], 311 (39), 283 (44), 251 (26), 199 (100), 145 (22), 105 (20), 59 (6), 41 (5). $C_{21}H_{26}O_4$ (342.42): calcd. C 73.66, H 7.65; found C 73.20, H 6.77.

Dimethyl 3-[2′-Methyl-1′-(4′′-methoxycarbonylphenyl)prop-1′-enyl]-cyclohex-4-ene-1,2-dicarboxylate (8d-4-MeO_2C-C_6H_4): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (125 mg, 1.16 mmol), methyl 4-iodobenzoate (398 mg, 1.52 mmol) and dimethyl maleate (302 mg, 2.10 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8d**-4-MeO_2C-C_6H_4 (56 mg, 13%, *dr* = 1.8:1) was obtained as a colorless oil, R_f = 0.11. IR (film): $\tilde{\nu}$ = 2993, 2952 cm^{-1}, 2847, 1734, 1606, 1559, 1436, 1375, 1276, 1196, 1176, 1113, 1020, 966, 862, 776, 743, 712. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.29–2.54 (m, 2 H, 6-H), 2.74 (dd, ^3J = 10.4, 9.2 Hz, 1 H, 2-H), 3.02–3.13 (m, 1 H, 1-H), 3.20–3.32 (m, 1 H, 3-H), 3.62 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 4.86–5.13 (m, 2 H, 4-H, 5-H), 7.03–7.17 (m, 2 H, Ph-H), 7.91–8.04 (m, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3), 20.6 (CH_3), 33.2 (CH_2, C-6), 41.5 (CH, C-1), 47.4 (CH, C-2), 48.7 (CH, C-3), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 125.0 (CH, C-4), 128.3 (CH, Ph-C), 128.6 (CH, Ph-C), 129.0 (CH, Ph-C), 129.2 (CH, Ph-C), 131.0 (CH, C-5), 132.8 (C, Ph-C), 133.1 (C, Ph-C), 146.3 (C, C-2′), 146.5 (C, C-1′), 167.2 (C, Ph-COO), 174.3 (C, COO), 174.8 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 386 (34) [M^+], 355 (44), 327 (79), 295 (100), 267 (75), 235 (11), 207 (16), 179 (13), 165 (15), 115 (10), 59 (25). $C_{22}H_{26}O_6$ (386.44): calcd. C 68.38, H 6.78; found C 68.12, H 6.45.

Dimethyl 3-[1′-(4′′-Acetylphenyl)-2′-methylprop-1′-enyl]cyclohex-4-ene-1,2-dicarboxylate (8d-4-MeCO-C_6H_4): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (117 mg, 1.08 mmol), 4-iodoacetophenone (317 mg, 1.29 mmol) and dimethyl maleate (280 mg, 1.94 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8d**-4-MeCO-C_6H_4 (220 mg, 55%, *dr* = 3.2:1) was obtained as a yellow oil, R_f = 0.22. IR (film): $\tilde{\nu}$ = 3030, 2997 cm^{-1}, 2951, 2919, 2855, 1734, 1684, 1603, 1559, 1436, 1400, 1358, 1268, 1199, 1180, 1112, 1076, 1015, 959, 836, 819, 735, 703. **Major Isomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.29–2.46 (m, 2 H, 6-H), 2.55 (s, 3 H, $COCH_3$), 2.74 (dd, ^3J = 10.4, 9.2 Hz, 1 H,

2-H), 3.03–3.12 (m, 1 H, 1-H), 3.23–3.34 (m, 1 H, 3-H), 3.62 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 4.91–5.07 (m, 2 H, 4-H, 5-H), 7.05 (dd, ^3J = 8.2, ^4J = 1.8 Hz, 2 H, Ph-H), 7.84 (dd, ^3J = 8.2, ^4J = 1.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3), 20.6 (CH_3), 26.4 (CH_3, $COCH_3$), 33.1 (CH_2, C-6), 41.4 (CH, C-1), 47.3 (CH, C-2), 48.7 (CH, C-3), 51.6 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 127.2 (CH, 2 C, Ph-C), 127.8 (CH, C-4), 128.2 (C, Ph-C), 129.6 (CH, 2 C, Ph-C), 130.2 (CH, C-5), 132.8 (C, Ph-C), 134.9 (C, C-2′), 146.5 (C, C-1′), 174.2 (C, COO), 174.5 (C, COO), 197.7 (C, CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 370 (16) [M$^+$], 338 (12), 311 (78), 279 (62), 251 (39), 235 (11), 207 (22), 179 (10), 113 (19), 83 (27), 59 (11), 43 (100). $C_{22}H_{26}O_5$ (370.45): calcd. C 71.33, H 7.07; found C 71.09, H 6.77.

Dimethyl 3-[2′-Methyl-1′-(4′′-nitrophenyl)prop-1′-enyl]cyclohex-4-ene-1,2-dicarboxylate (8d-4-O_2N-C_6H_4): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (79 mg, 0.73 mmol), 4-bromonitrobenzene (187 mg, 0.93 mmol) and dimethyl maleate (234 mg, 1.63 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8d**-4-O_2N-C_6H_4 (62 mg, 23%, *dr* = 4.0:1) was obtained as a red oil, R_f = 0.25. IR (film): $\tilde{\nu}$ = 2952, 1734 cm^{-1}, 1596, 1517, 1437, 1346, 1265, 1198, 1166, 1109, 1015, 967, 913, 852, 734, 703. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 2.35–2.50 (m, 2 H, 6-H), 2.79 (dd, ^3J = 10.4, 10.1 Hz, 1 H, 2-H), 3.04–3.14 (m, 1 H, 1-H), 3.26–3.37 (m, 1 H, 3-H), 3.65 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 4.89–4.98 (m, 1 H, 4-H), 5.05–5.16 (m, 1 H, 5-H), 7.15 (dd, ^3J = 8.9, ^4J = 1.8 Hz, 2 H, Ph-H), 8.13 (dd, ^3J = 8.9, ^4J = 1.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.5 (CH_3), 20.6 (CH_3), 33.1 (CH_2, C-6), 41.3 (CH, C-1), 47.2 (CH, C-2), 48.6 (CH, C-3), 51.7 (CH_3, OCH_3), 52.0 (CH_3, OCH_3), 123.1 (CH, 2 C, Ph-C), 128.8 (CH, C-4), 129.8 (CH, 2 C, Ph-C), 130.0 (C, Ph-C), 130.3 (CH, C-5), 132.0 (C, Ph-C), 146.2 (C, C-2′), 148.6 (C, C-1′), 174.0 (C, COO), 174.4 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 373 (7) [M$^+$], 341 (22), 314 (100), 282 (68), 254 (59), 208 (22), 179 (25), 165 (24), 152 (13), 115 (15), 59 (55). $C_{20}H_{23}NO_6$ (373.41): calcd. C 64.33, H 6.21, N 3.75; found C 64.18, H 6.04, N 3.69.

Dimethyl 3-(3′,3′-Dimethyl-1′-phenylbut-1′-enyl)cyclohex-4-ene-1,2-dicarboxylate (8e-Ph): Prepared within 24 h from 1-cyclopropyl-4,4-dimethyl-1,2-pentadiene (**1e**) (141 mg, 1.04 mmol), phenyl iodide (261 mg, 1.28 mmol) and dimethyl maleate (295 mg, 2.05 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8e**-Ph (130 mg, 35%, *dr* = 3.7:1) was obtained as a yellow oil, R_f = 0.19. IR (film): $\tilde{\nu}$ = 3056, 3028 cm^{-1}, 2953, 2903, 2868, 1738, 1559, 1495, 1436, 1360, 1311, 1249, 1200, 1166, 1075, 1026, 896, 738, 704. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.79 [s, 9 H, $C(CH_3)_3$], 1.85–1.99 (m, 1 H, 6-H), 2.23–2.35 (m, 1 H, 6-H), 2.71 (dd, ^3J = 11.3, 11.0 Hz, 1 H, 2-H), 2.90–3.03 (m, 1 H, 1-H), 3.21–3.28 (m, 1 H, 3-H), 3.64 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 5.48 (s, 2 H, 4-H, 5-H), 5.52–5.60 (m, 1 H, 2′-H), 7.17–7.30 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.3 (CH_2, C-6), 31.1 [CH_3, 3 C, $C(CH_3)_3$], 33.4 [C, $C(CH_3)_3$], 42.0 (CH, C-1), 45.8 (CH, C-2), 51.5 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 52.9 (CH, C-3), 124.7 (CH, 2 C, Ph-C), 126.6 (CH, C-4), 127.1 (CH, 2 C, Ph-C), 127.1 (C, Ph-C), 128.7 (CH, C-5), 130.4 (CH, Ph-C), 138.3 (C, C-1′), 141.2 (CH, C-2′), 174.6 (C, COO), 175.3 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 356 (14) [M$^+$], 240 (16), 220 (61), 205 (51), 183 (42), 161 (100), 115 (48), 102 (74), 91 (68), 77 (29), 59 (90), 57 (65), 41 (31). $C_{22}H_{28}O_4$ (356.46): calcd. C 74.13, H 7.93; found C 73.79, H 7.54.

Dimethyl 3-[3′,3′-Dimethyl-1′-(2′′-methylphenyl)but-1-enyl]cyclohex-4-ene-1,2-dicarboxylate (8e-2-Me-C_6H_4): Prepared within 24 h from 1-cyclopropyl-4,4-dimethyl-1,2-pentadiene (**1e**) (118 mg, 0.87 mmol), 2-iodotoluene (211 mg, 0.97 mmol) and dimethyl maleate (189 mg, 1.31 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8e**-2-Me-C_6H_4 (74 mg, 23%, *dr* = 2.9:1) was obtained as a yellow oil, R_f = 0.22. IR (film): $\tilde{\nu}$ = 2952, 2867 cm^{-1}, 1738, 1636, 1436, 1348, 1250, 1200, 1167, 1116, 1024, 913, 805, 736, 693. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.78 [s, 9 H, $C(CH_3)_3$], 2.02–2.16 (m, 1 H, 6-H), 2.26 (s, 3 H, CH_3), 2.29–2.42 (m, 1 H, 6-H), 2.82–2.85 (m, 1 H, 2-H), 2.93–3.02 (m, 1 H, 1-H), 3.16–3.31 (m, 1 H, 3-H), 3.67 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 5.48–5.54 (m, 2 H, 4-H, 5-H), 5.64–5.76 (m, 1 H, 2′-H), 7.01–7.28 (m, 4 H, Ph-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6 (CH_3), 27.8 (CH_2, C-6), 30.4 [CH_3, 3 C, $C(CH_3)_3$], 33.8 [C, $C(CH_3)_3$], 42.9 (CH, C-1), 46.1 (CH, C-2), 50.2 (CH, C-3), 52.0 (CH_3, OCH_3), 52.6 (CH_3, OCH_3), 124.6 (CH, Ph-C), 126.0 (CH, C-4), 126.9 (CH, Ph-C), 127.9 (CH, Ph-C), 129.3 (CH, C-5), 129.9 (CH, Ph-C), 135.0 (C, Ph-C), 136.1 (C, Ph-C), 140.1 (CH, C-2′), 148.2 (C, C-1′), 174.7 (C, COO), 175.2 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 370 (91) [M$^+$], 339 (15), 314 (40), 295 (26), 255 (39), 223 (32), 203 (24), 174 (100), 131 (30), 115 (82), 91 (28), 77 (20), 59 (58), 57 (90), 41 (28). $C_{23}H_{30}O_4$ (370.49): calcd. C 74.56, H 8.16; found C 75.15, H 8.09.

Dimethyl 3-[3′,3′-Dimethyl-1′-(4′′-nitrophenyl)but-1′-enyl]cyclohex-4-ene-1,2-dicarboxylate (8e-4-O_2N-C_6H_4): Prepared within 24 h from 1-cyclopropyl-4,4-dimethyl-1,2-pentadiene (**1e**) (130 mg, 0.96 mmol), 4-bromonitrobenzene (268 mg, 1.33 mmol) and dimethyl maleate (246 mg, 1.71 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8e**-4-O_2N-C_6H_4 (124 mg, 32%, *dr* = 1.9:1) was obtained as a red oil, R_f = 0.10. IR (film): $\tilde{\nu}$ = 2956, 2869 cm^{-1}, 1737, 1598, 1520, 1436, 1346, 1259, 1201, 1166, 1109, 1067, 914, 856, 802, 734. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 [s, 9 H, $C(CH_3)_3$], 1.79–1.92 (m, 1 H, 6-H), 2.25–2.35 (m, 1 H, 6-H), 2.54 (t, ^3J = 11.2 Hz, 1 H, 2-H), 2.93 (dt, ^3J = 11.2, 5.2 Hz, 1 H, 1-H), 3.24–3.30 (m, 1 H, 3-H), 3.62 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 5.53 (br. s, 1 H, 2′-H), 5.59 (br. s, 2 H, 4-H, 5-H), 7.29–7.56 (m, 2 H, Ph-H), 8.05–8.19 (m, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.2 (CH_2, C-6), 30.9 [C, $C(CH_3)_3$], 33.6 [CH_3, 3 C, $C(CH_3)_3$], 41.7 (CH, C-2), 45.7 (CH, C-1), 51.3 (CH_3, OCH_3), 51.6 (CH, C-3), 51.9 (CH_3, OCH_3), 122.3 (CH, 2 C, Ph-C), 125.8 (CH, C-4), 128.0 (CH, C-5), 131.3 (CH, 2 C, Ph-C), 135.0 (C, Ph-C), 142.6 (CH, C-2′), 145.8 (C, Ph-C), 146.6 (C, C-1′), 174.2 (C, COO), 174.7 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 401 (51) [M$^+$], 370 (33), 345 (69), 341 (43), 313 (88), 285 (100), 266 (36), 254 (42), 226 (18), 165 (19), 143 (14), 79 (11), 59 (25), 57 (55), 41 (18). $C_{22}H_{27}NO_6$ (401.46): calcd. C 65.82, H 6.78, N 3.49; found C 65.64, H 6.62, N 3.40.

Dimethyl 3-[1′-(3′′-Formylphenyl)-3′,3′-dimethylbut-1′-enyl]cyclohex-4-en-dicarboxylate (8e-3-CHO-C_6H_4): Prepared within 24 h from 1-cyclopropyl-4,4-dimethyl-1,2-pentadiene (**1e**) (139 mg, 1.02 mmol), 3-bromobenzaldehyde (286 mg, 1.55 mmol) and dimethyl maleate (316 mg, 2.19 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8e**-3-CHO-C_6H_4 (52 mg, 13%, *dr* = 3.5:1) was obtained as a yellow oil, R_f = 0.08. IR (film): $\tilde{\nu}$ = 2954, 2869 cm^{-1}, 1735, 1700, 1597, 1577, 1436, 1364, 1249, 1201, 1166, 1036, 803, 747, 698. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77 [s, 9 H, $C(CH_3)_3$], 1.82–2.04 (m, 1 H, 6-H), 2.25–2.37 (m, 1 H, 6-H), 2.59 (t, ^3J = 11.3 Hz, 1 H, 2-H), 2.89–3.02 (m, 1 H, 1-H), 3.19–3.34 (m, 1 H, 3-H), 3.63 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 5.55 (s, 1 H, 2′-H), 5.60–5.67 (m, 2 H, 4-H, 5-H), 7.38–7.79 (m, 4 H, Ph-H), 10.0 (s, 1 H, CHO) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.3 (CH_2, C-6), 31.2 [CH_3, 3 C, $C(CH_3)_3$], 33.5 [C, $C(CH_3)_3$], 41.9 (CH, C-2), 45.8 (CH, C-1), 51.4 (CH, C-3), 51.6 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 125.5 (CH,

C-4), 127.9 (CH, C-5), 128.0 (CH, Ph-C), 128.5 (CH, Ph-C), 129.7 (CH, Ph-C), 131.7 (C, Ph-C), 135.4 (CH, Ph-C), 136.6 (C, Ph-C), 139.4 (C, C-1′), 142.4 (CH, C-2′), 174.4 (C, COO), 175.0 (C, COO), 192.5 (CH, CHO) ppm. MS (EI, 70 eV): *m/z* (%) = 384 (48) [M$^+$], 353 (19), 328 (23), 297 (33), 268 (35), 264 (25), 237 (90), 209 (61), 195 (25), 159 (23), 128 (24), 117 (36), 91 (38), 79 (31), 59 (36), 57 (100), 41 (59). $C_{23}H_{28}O_5$ (384.47): calcd. C 71.85, H 7.34; found C 72.06, H 7.50.

Dimethyl 3-Cyclopropyl-3-(1′-phenylethenyl)cyclohex-4-ene-1,2-dicarboxylate (8f-Ph): Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (144 mg, 1.20 mmol), phenyl iodide (320 mg, 1.57 mmol) and dimethyl maleate (298 mg, 2.07 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-Ph (177 mg, 43%, *dr* = 2.0:1) was obtained as a colorless oil, R_f = 0.18. IR (film): $\tilde{\nu}$ = 3057, 3001 cm^{-1}, 2952, 2844, 1734, 1628, 1598, 1576, 1559, 1492, 1436, 1356, 1262, 1197, 1168, 1073, 1027, 965, 921. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.42–0.46 (m, 2 H, Cpr-H), 0.93–1.06 (m, 2 H, Cpr-H), 1.23–1.41 (m, 1 H, Cpr-H), 2.42–2.83 (m, 2 H, 6-H), 2.99–3.09 (m, 2 H, 2-H, 1-H), 3.66 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 5.08–5.21 (m, 2 H, 2′-H), 5.36–5.90 (m, 2 H, 4-H, 5-H), 7.22–7.46 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.1 (CH_2, Cpr-C), 6.5 (CH_2, Cpr-C), 13.9 (CH, Cpr-C), 37.1 (CH_2, C-6), 40.7 (CH, C-1), 44.9 (CH, C-2), 48.0 (C, C-3), 51.5 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 116.8 (CH, Ph-C), 118.6 (CH_2, C-2′), 126.6 (CH, C-4), 127.3 (CH, C-5), 128.0 (CH, Ph-C), 128.1 (CH, Ph-C), 128.3 (CH, Ph-C), 129.7 (CH, Ph-C), 133.1 (C, Ph-C), 148.9 (C, C-1′), 173.5 (C, COO), 175.7 (C, COO) ppm. MS (EI, 70 eV): *m/z* (%) = 340 (25) [M$^+$], 308 (21), 280 (100), 265 (45), 249 (26), 221 (97), 197 (58), 165 (47), 115 (31), 91 (91), 77 (20), 59 (26), 41 (15). $C_{21}H_{24}O_4$ (340.42): calcd. C 74.09, H 7.11; found C 73.89, H 6.90.

Dimethyl 3-Cyclopropyl-3-[1′-(4′′-methylphenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8f-4-Me-C_6H_4): Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (132 mg, 1.10 mmol), 4-iodotoluene (292 mg, 1.34 mmol) and dimethyl maleate (296 mg, 2.06 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-4-Me-C_6H_4 (104 mg, 27%, *dr* = 2.0:1) was obtained as a colourless oil, R_f = 0.26. IR (film): $\tilde{\nu}$ = 3054, 2954 cm^{-1}, 1734, 1635, 1511, 1437, 1354, 1265, 1198, 1171, 1020, 923, 896, 821. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.38–0.49 (m, 2 H, Cpr-H), 1.04–1.13 (m, 2 H, Cpr-H), 1.27–1.35 (m, 1 H, Cpr-H), 2.48 (s, 3 H, CH_3), 2.72–3.02 (m, 2 H, 6-H), 3.11–3.20 (m, 1 H, 2-H), 3.23–3.37 (m, 1 H, 1-H), 3.72 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 5.13–5.32 (m, 2 H, 2′-H), 5.44–5.90 (m, 2 H, 4-H, 5-H), 7.19–7.38 (m, 4 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.2 (CH_2. Cpr-C), 6.6 (CH_2, Cpr-C), 14.0 (CH, Cpr-C), 21.1 (CH_3), 35.3 (CH_2, C-6), 40.7 (CH, C-1), 43.4 (CH, C-2), 46.7 (C, C-3), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 117.2 (CH_2, C-2′), 127.2 (CH, C-4), 127.6 (C, Ph-C), 128.3 (CH, C-5), 128.6 (CH, Ph-C), 129.0 (CH, Ph-C), 129.7 (C, Ph-C), 131.2 (CH, Ph-C), 137.2 (CH, Ph-C), 149.8 (C, C-1′), 173.6 (C, COO), 175.5 (C, COO) ppm. MS (EI, 70 eV): *m/z* (%) = 354 (7) [M$^+$], 294 (35), 235 (33), 179 (14), 143 (11), 105 (19), 91 (14), 59 (100), 41 (17). $C_{22}H_{26}O_4$ (354.45): calcd. C 74.55, H 7.39; found C 74.30, H 7.25.

Dimethyl 3-Cyclopropyl-3-[1′-(4′′-methoxycarbonylphenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8f-4-MeO_2C-C_6H_4): Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (128 mg, 1.07 mmol), methyl 4-iodobenzoate (372 mg, 1.42 mmol) and dimethyl maleate (291 mg, 2.02 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-4-MeO_2C-C_6H_4 (149 mg, 35%, *dr* = 1.9:1) was obtained as a colorless oil, R_f = 0.12. IR (film): $\tilde{\nu}$ = 3001, 2952 cm^{-1}, 2844, 1734, 1607, 1559, 1436, 1354, 1278, 1196, 1113, 1019, 966, 924, 860, 824, 777, 736, 710. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07–0.23 (m, 2 H, Cpr-H), 0.33–0.43 (m, 2 H, Cpr-H), 1.17–1.30 (m, 1 H, Cpr-H), 2.37–2.46 (m, 1 H, 6-H), 2.56–2.82 (m, 1 H, 6-H), 2.93–3.00 (m, 2 H, 1-H, 2-H), 3.60 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 5.01–5.18 (m, 2 H, 2′-H), 5.51–5.76 (m, 2 H, 4-H, 5-H), 7.24 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 2 H, Ph-H), 7.92 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.4 (CH_2, Cpr-C), 6.9 (CH_2, Cpr-C), 14.0 (CH, Cpr-C), 34.7 (CH_2, C-6), 41.1 (CH, C-1), 46.0 (CH, C-2), 48.0 (C, C-3), 51.7 (CH_3, OCH_3), 52.0 (CH_3, OCH_3), 52.6 (CH_3, OCH_3), 118.9 (CH_2, C-2′), 126.7 (CH, C-4), 127.3 (CH, C-5), 128.3 (CH, Ph-C), 128.7 (CH, Ph-C), 132.4 (C, Ph-C), 133.6 (C, Ph-C), 136.5 (CH, Ph-C), 138.1 (CH, Ph-C), 147.2 (C, C-1′), 166.9 (C, COO), 174.1 (C, COO), 174.5 (C, COO) ppm. MS (EI, 70 eV): *m/z* (%) = 398 (14) [M$^+$], 367 (15), 338 (52), 307 (36), 278 (75), 247 (100), 219 (78), 189 (22), 179 (39), 129 (27), 101 (17), 91 (10), 59 (46). $C_{23}H_{26}O_6$ (398.46): calcd. C 69.33, H 6.58; found C 69.61, H 6.33.

Dimethyl 3-[1′-(4′′-Acetylphenyl)ethenyl]-3-(cyclopropyl)cyclohex-4-ene-1,2-dicarboxylate (8f-4-MeCO-C_6H_4): Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (167 mg, 1.39 mmol), 4-iodoacetophenone (417 mg, 1.70 mmol) and dimethyl maleate (360 mg, 2.50 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8f**-4-MeCO-C_6H_4 (128 mg, 24%, *dr* = 1.6:1) was obtained as a yellow oil, R_f = 0.17. IR (film): $\tilde{\nu}$ = 3002, 2952 cm^{-1}, 1734, 1684, 1603, 1559, 1436, 1403, 1358, 1267, 1166, 1015, 958, 923, 836, 736, 702, 668. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08–0.25 (m, 2 H, Cpr-H), 0.35–0.42 (m, 2 H, Cpr-H), 1.17–1.34 (m, 1 H, Cpr-H), 2.27–2.43 (m, 1 H, 6-H), 2.51–2.52 (m, 4 H, $COCH_3$, 6-H), 2.77 (d, ^3J = 10.1 Hz, 1 H, 2-H), 2.92–3.06 (m, 1 H, 1-H), 3.60 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 5.02–5.19 (m, 2 H, 2′-H), 5.50–5.19 (m, 2 H, 4-H, 5-H), 7.27 (dd, ^3J = 8.5, ^4J = 1.4 Hz, 2 H, Ph-H), 7.85 (dd, ^3J = 8.5, ^4J = 1.4 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.4 (CH_2, Cpr-C), 6.9 (CH_2, Cpr-C), 14.2 (CH, Cpr-C), 26.5 (CH_3, $COCH_3$), 34.7 (CH_2, C-6), 41.1 (CH, C-1), 43.4 (C, C-3), 46.0 (CH, C-2), 51.7 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 118.0 (CH_2, C-2′), 128.0 (CH, C-4), 128.2 (CH, C-5), 128.7 (CH, Ph-C), 128.9 (CH, Ph-C), 132.3 (C, Ph-C), 133.8 (C, Ph-C), 135.3 (CH, Ph-C), 138.1 (CH, Ph-C), 147.5 (C, C-1′), 173.0 (C, COO), 175.6 (C, COO), 197.7 (C, $COCH_3$) ppm. MS (EI, 70 eV): *m/z* (%) = 382 (41) [M$^+$], 350 (27), 322 (83), 291 (31), 179 (15), 165 (18), 115 (6), 59 (15), 43 (100). $C_{23}H_{26}O_5$ (382.46): calcd. C 72.23, H 6.85; found C 72.51, H 6.62.

Dimethyl 3-Cyclopropyl-3-[1′-(4′′-nitrophenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8f-4-O_2N-C_6H_4): Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (136 mg, 1.13 mmol), 4-bromonitrobenzene (289 mg, 1.43 mmol) and dimethyl maleate (325 mg, 2.26 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-4-O_2N-C_6H_4 (125 mg, 29%, *dr* = 1.8:1) was obtained as a yellow oil, R_f = 0.09. IR (film): $\tilde{\nu}$ = 2952, 1734 cm^{-1}, 1595, 1517, 1437, 1347, 1261, 1200, 1167, 1108, 1027, 924, 855, 750, 706, 688. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15–0.32 (m, 2 H, Cpr-H), 0.39–0.52 (m, 2 H, Cpr-H), 1.21–1.30 (m, 1 H, Cpr-H), 2.32–2.50 (m, 1 H, 6-H), 2.58–2.67 (m, 1 H, 6-H), 2.84 (d, ^3J = 9.8 Hz, 1 H, 2-H), 2.97–3.11 (m, 1 H, 1-H), 3.64 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 5.05–5.19 (m, 2 H, 2′-H), 5.54–5.75 (m, 2 H, 4-H, 5-H), 7.39 (dd, ^3J = 8.9, ^4J = 2.1 Hz, 2 H, Ph-H). 8.15 (dd, ^3J = 8.9, ^4J = 2.1 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.5 (CH_2, Cpr-C), 7.0 (CH_2, Cpr-C), 13.9 (CH, Cpr-C), 34.4 (CH_2, C-6), 41.2 (CH, C-1), 46.6 (CH, C-2), 48.6 (C, C-3), 51.7 (CH_3,

OCH_3), 52.0 (CH_3, OCH_3), 118.9 (CH_2, C-2′), 123.0 (CH, Ph-C), 123.3 (CH, Ph-C), 129.3 (CH, C-4), 129.5 (CH, C-5), 131.3 (C, Ph-C), 135.0 (CH, Ph-C), 136.9 (CH, Ph-C), 146.3 (C, Ph-C), 149.2 (C, C-1′), 172.7 (C, COO), 175.3 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 385 (25) [M+], 353 (26), 326 (100), 294 (44), 266 (90), 191 (15), 165 (25), 115 (11), 91 (15), 59 (62), 41 (35). $C_{21}H_{23}NO_6$ (385.42): calcd. C 65.44, H 6.01, N 3.63; found C 65.24, H 6.08, N 3.58.

Variation A: Prepared within 24 h from $Pd_2dba_3{\cdot}CHCl_3$ (26 mg, 25 μmol), tBu$_3$P (150 μL, 150 μmol, 0.2 g/mol in dioxane), 1,1-dicyclopropyl-1,2-propadiene (**1f**) (112 mg, 0.93 mmol), 4-bromonitrobenzene (323 mg, 1.60 mmol) and dimethyl maleate (304 mg, 2.11 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-4-O_2N-C_6H_4 (76 mg, 21%, *dr* = 2.0:1) was obtained as a yellow oil, R_f = 0.09.

Variation B: Prepared within 24 h from 1,1-dicyclopropyl-1,2-propadiene (**1f**) (146 mg, 1.22 mmol), 4-bromonitrobenzene (751 mg, 3.72 mmol) and dimethyl maleate (463 mg, 3.22 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8f**-4-O_2N-C_6H_4 (52 mg, 11%, *dr* = 1.9:1) was obtained as a yellow oil.

Dimethyl 3-Methyl-3-(1′-phenylethenyl)cyclohex-4-ene-1,2-dicarboxylate (8g-Ph): Prepared within 24 h from 3-cyclopropyl-1,2-butadiene (**1g**) (176 mg, 1.87 mmol), phenyl iodide (497 mg, 2.44 mmol) and dimethyl maleate (502 mg, 3.49 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8g**-Ph (274 mg, 47%, *dr* = 3.0:1) was obtained as a colorless oil, R_f = 0.20. IR (film): $\tilde{\nu}$ = 2952, 2845 cm^{-1}, 1737, 1626, 1577, 1493, 1435, 1357, 1169, 1072, 1026, 1004, 922, 888, 835, 774, 737, 703. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 (s, 3 H, CH_3), 2.33–2.72 (m, 2 H, 6-H), 3.02–3.19 (m, 2 H, 2-H, 1-H), 3.66 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 5.08–5.19 (m, 2 H, 2′-H), 5.54–5.72 (m, 2 H, 4-H, 5-H), 7.10–7.38 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.6 (CH_3), 34.9 (CH_2, C-6), 37.3 (CH, C-1), 45.6 (C, C-3), 46.6 (CH, C-2), 51.2 (CH_3, OCH_3), 51.5 (CH_3, OCH_3), 118.2 (CH_2, C-2′), 126.4 (CH, C-4), 127.9 (CH, 2 C, Ph-C), 128.4 (CH, 2 C, Ph-C), 129.6 (CH, C-5), 131.7 (C, Ph-C), 136.0 (CH, Ph-C), 141.9 (C, C-1′), 173.2 (C, COO), 175.3 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 314 (14) [M+], 283 (13), 255 (85), 223 (71), 195 (100), 179 (25), 165 (30), 161 (34), 158 (66), 115 (31), 102 (22), 91 (33), 85, (37), 83 (63), 77 (16), 59 (43), 41 (6). $C_{19}H_{22}O_4$ (314.38): calcd. C 72.59, H 7.05; found C 72.33, H 6.94.

Dimethyl 3-Methyl-3-[1′-(4′′-methylphenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8g-4-Me-C_6H_4): Prepared within 24 h from 3-cyclopropyl-1,2-butadiene (**1g**) (146 mg, 1.55 mmol), 4-iodotoluene (425 mg, 1.94 mmol) and dimethyl maleate (432 mg, 3.00 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **8g**-4-Me-C_6H_4 (187 mg, 37%, *dr* = 3.0:1) was obtained as a colorless oil, R_f = 0.22. IR (film): $\tilde{\nu}$ = 3079, 3021 cm^{-1}, 2993, 2951, 2846, 1738, 1634, 1512, 1436, 1381, 1355, 1326, 1258, 1196, 1163, 1063, 1019, 994, 922, 821, 737. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.59–2.70 (m, 2 H, 6-H), 3.00–3.18 (m, 2 H, 2-H, 1-H), 3.66 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 5.07–5.18 (m, 2 H, 2′-H), 5.54–5.71 (m, 2 H, 4-H, 5-H), 7.02 (dd, ^3J = 7.9, ^4J = 1.8 Hz, 2 H, Ph-H), 7.13 (dd, ^3J = 7.9, ^4J = 1.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.9 (CH_3), 21.0 (CH_3), 35.1 (CH_2, C-6), 37.6 (CH, C-1), 45.8 (C, C-3), 46.5 (CH, C-2), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 118.3 (CH_2, C-2′), 128.0 (CH, 2 C, Ph-C), 128.2 (CH, C-4), 128.6 (C, Ph-C), 128.8 (CH, 2 C, Ph-C), 131.6 (CH, C-5), 136.1 (C, Ph-C), 139.1 (C, C-1′), 173.3 (C, COO), 175.7 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 328 (34) [M+], 297 (14), 268 (82), 237 (70), 209 (100), 179 (27), 165 (21), 125 (40), 115 (20), 91 (23), 77 (14), 59 (43). $C_{20}H_{24}O_4$ (328.41): calcd. C 73.15, H 7.37; found C 73.45, H 7.09.

Dimethyl 3-[1′-(4′′-Acetylphenyl)ethenyl]-3-methylcyclohex-4-ene-1,2-dicarboxylate (8g-4-MeCO-C_6H_4): Prepared within 24 h from 3-cyclopropyl-1,2-butadiene (**1g**) (76 mg, 0.81 mmol), 4-iodoacetophenone (264 mg, 1.07 mmol) and dimethyl maleate (279 mg, 1.94 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8g**-4-MeCO-C_6H_4 (169 mg, 59%, *dr* = 3.2:1) was obtained as a colorless oil, R_f = 0.18. IR (film): $\tilde{\nu}$ = 3000, 2952 cm^{-1}, 2846, 1738, 1684, 1604, 1559, 1436, 1402, 1358, 1326, 1268, 1197, 1164, 1095, 1015, 993, 958, 923, 839, 839, 736. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.56 (s, 3 H, CH_3), 2.61 (s, 3 H, $COCH_3$), 2.66–2.82 (m, 2 H, 6-H), 3.04–3.20 (m, 2 H, 2-H, 1-H), 3.68 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 5.10–5.21 (m, 2 H, 2′-H), 5.58–5.68 (m, 2 H, 4-H, 5-H), 7.23 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 2 H, Ph-H), 7.92 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.9 (CH_3), 26.4 (CH_3, CO*C*H_3), 34.5 (CH_2, C-6), 37.3 (CH, C-1), 45.7 (C, C-3), 46.7 (CH, C-2), 51.5 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 118.6 (CH_2, C-2′), 128.2 (CH, C-4), 128.5 (CH, 2 C, Ph-C), 128.9 (CH, 2 C, Ph-C), 130.9 (C, Ph-C), 135.3 (C, Ph-C), 135.7 (CH, C-5), 147.1 (C, C-1′), 172.9 (C, COO), 175.3 (C, COO), 197.5 (C, *C*OCH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 356 (11) [M+], 325 (13), 297 (93), 296 (61), 281 (22), 265 (60), 237 (58), 223 (44), 193 (15), 165 (18), 113 (20), 83 (58), 75 (21), 59 (26), 43 (100). $C_{21}H_{24}O_5$ (356.42): calcd. C 70.77, H 6.79; found C 70.55, H 6.68.

Dimethyl 3-Methyl-3-[1′-(2′′-nitrophenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8g-2-O_2N-C_6H_4): Prepared within 24 h from 3-cyclopropyl-1,2-butadiene (**1g**) (112 mg, 1.19 mmol), 2-bromonitrobenzene (362 mg, 1.79 mmol) and dimethyl maleate (306 mg, 2.13 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8g**-2-O_2N-C_6H_4 (54 mg, 13%, *dr* = 2.1:1) was obtained as a yellow oil, R_f = 0.14. IR (film): $\tilde{\nu}$ = 2952, 2848 cm^{-1}, 1737, 1608, 1571, 1526, 1437, 1353, 1259, 1198, 1165, 1098, 1063, 1020, 993, 923, 853, 789, 749, 706. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 2.55–2.72 (m, 2 H, 6-H), 3.07–3.26 (m, 2 H, 2-H, 1-H), 3.68 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 5.00–5.18 (m, 2 H, 2′-H), 5.54–5.71 (m, 2 H, 4-H, 5-H), 7.21 (dt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Ph-H), 7.39–7.47 (m, 1 H, Ph-H), 7.59 (dt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Ph-H), 8.00 (dd, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.8 (CH_3), 34.5 (CH_2, C-6), 37.1 (CH, C-1), 46.0 (C, C-3), 46.5 (CH, C-2), 51.7 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 119.2 (CH_2, C-2′), 124.6 (CH, Ph-C), 128.1 (CH, C-4), 128.7 (C, Ph-C), 129.7 (CH, Ph-C), 130.5 (CH, Ph-C), 130.9 (CH, Ph-C), 133.4 (CH, C-5), 137.2 (C, Ph-C), 165.7 (C, C-1′), 173.0 (C, COO), 175.7 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 359 (8) [M+], 328 (18), 282 (26), 268 (19), 240 (18), 222 (38), 206 (38), 194 (33), 178 (40), 165 (46), 160 (33), 152 (26), 128 (18), 115 (30), 113 (55), 91 (34), 77 (39), 59 (100), 43 (54). $C_{19}H_{21}NO_6$ (359.38): calcd. C 63.50, H 5.89, N 3.90; found C 63.46, H 6.04, N 3.90.

Dimethyl 3-[1′-(4′′-Chloropyrid-2′′-yl)ethenyl]-3-methylcyclohex-4-ene-1,2-dicarboxylate (8g-4-Cl-Py): Prepared within 24 h from 3-cyclopropyl-1,2-butadiene (**1g**) (96 mg, 1.02 mmol), 2-bromo-4-chloropyridine (248 mg, 1.29 mmol) and dimethyl maleate (278 mg, 1.93 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **8g**-4-Cl-Py (68 mg, 19%, *dr* = 1.8:1) was obtained as a yellow solid, m.p. 84 °C, R_f = 0.18. IR (KBr): $\tilde{\nu}$ = 2998, 2951 cm^{-1}, 2917, 2848, 1739, 1635, 1574, 1552, 1463, 1437, 1356, 1328, 1263, 1197, 1164, 1111, 1065, 1012, 994, 923, 842, 736. **Major Isomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.61 (s, 3 H, CH_3),

2.34–2.49 (m, 1 H, 6-H), 2.79–2.91 (m, 1 H, 6-H), 2.99–3.16 (m, 2 H, 2-H, 1-H), 3.64 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 5.05–5.14 (m, 2 H, 2′-H), 5.50–5.67 (m, 2 H, 4-H, 5-H), 7.11 (d, ^3J = 8.2 Hz, 1 H, Ar-H), 7.60 (dd, ^3J = 8.2, ^4J = 1.8 Hz, 1 H, Ar-H), 8.51 (d, ^4J = 1.8 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.9 (CH_3), 33.1 (CH_2, C-6), 37.3 (CH, C-1), 45.7 (C, C-3), 50.1 (CH, C-2), 51.7 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 118.9 (CH_2, C-2′), 124.5 (CH, C-4), 129.9 (C, Ar-C), 130.5 (C, Ar-C), 132.1 (CH, Ar-C), 135.7 (CH, C-5), 138.1 (CH, Ar-C), 148.1 (CH, Ar-C), 157.8 (C, C-1′), 173.0 (C, COO), 175.4 (C, COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 349 (83) [M$^+$], 318 (22), 290 (97), 258 (25), 230 (100), 204 (43), 190 (11), 178 (6), 59 (6). $C_{18}H_{20}ClNO_4$ (349.81): calcd. C 61.80, H 5.76, N 4.00; found C 61.76, H 5.87, N 4.07.

Dimethyl 3-[(2′-Methoxy-1′-phenyl)ethenyl]cyclohex-4-ene-1,2-dicarboxylate (8j-Ph) and Dimethyl 3-(2′-Oxo-1′-phenylethyl)cyclohex-4-ene-1,2-dicarboxylate (9): A solution of palladium(II) acetate (11.2 mg, 50.0 μmol, 5 mol%) and triphenylphosphane (39.3 mg, 150 μmol, 15 mol%) in DMF (1 mL) was flushed with nitrogen for 10 min. 1-Cyclopropyl-3-methoxy-1,2-propadiene (117 mg, 1.06 mmol), phenyl iodide (338 mg, 1.66 mmol), and triethylamine (218 mg, 2.16 mmol) were added and the mixture stirred at 80 °C for 5 h. Dimethyl maleate (304 mg, 2.11 mmol) was added and the solution was stirred at 100 °C for additional 18 h. The reaction was quenched with water (10 mL), and the mixture diluted with diethyl ether (4 × 10 mL). The combined organic layers were washed with water (3 × 25 mL) and brine (25 mL). The organic solution was dried ($MgSO_4$), the solvent removed, and the residue purified by flash column chromatography on silica gel (pentane/diethyl ether, 1:1). A mixture of **8j**-Ph and **9** (33 mg, ratio 3:1, 10%) was obtained.

1-Chloro-1-cyano-2-[(2′-cyclopropyl-1′-phenyl)ethenyl]cyclohex-3-ene (10a) and 1-Chloro-1-cyano-3-[(2′-cyclopropyl-1′-phenyl)ethenyl]cyclohex-4-ene (10b): Prepared within 24 h from 1,3-dicyclopropyl-1,2-propadiene (**1a**) (116 mg, 0.96 mmol), phenyl iodide (243 mg, 1.19 mmol) and 2-chloroacrylonitrile (175 mg, 2.00 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 50:1) **10a** (130 mg, 47%) and **10b** (31 mg, 11%) were obtained as colorless oils.

10a: R_f = 0.09. IR (KBr): $\tilde{\nu}$ = 3003, 2935 cm^{-1}, 2872, 2199, 1722, 1621, 1493, 1444, 1380, 1262, 1174, 1075, 1027, 952, 767. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62 (m, 2 H, Cpr-H), 0.81 (m, 2 H, Cpr-H), 1.62−1.72 (m, 1 H, Cpr-H), 1.77 (dd, ^3J = 6.7, ^4J = 1.5 Hz, 1 H, 2-H), 2.22−2.29 (m, 2 H, 5-H), 2.48 (m, 2 H, 6-H), 5.47 (d, ^3J = 10.1 Hz, 1 H, 2′-H), 5.75 (dt, ^3J = 9.8, 1.8 Hz, 1 H, 4-H), 5.96−6.07 (m, 1 H, 3-H), 7.28–7.36 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.9 (CH_2, 2 C, Cpr-C), 12.0 (CH, Cpr-C), 18.3 (CH, C-2), 21.7 (CH_2, C-5), 24.9 (CH_2, C-6), 68.1 (C, C-1), 120.1 (C, CN), 126.4 (CH, C-4), 127.4 (CH, Ph-C), 128.2 (CH, 2 C, Ph-C), 129.8 (CH, 2 C, Ph-C), 131.9 (CH, C-3), 136.0 (C, Ph-C), 137.3 (C, C-1′), 139.4 (CH, C-2′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 283 (31) [M$^+$], 247 (100), 246 (67), 232 (43), 218 (24), 165 (22), 115 (23), 91 (19), 77 (12), 41 (5). HRMS: 283.1128 ($C_{18}H_{18}NCl$, calcd. 283.1128).

10b: R_f = 0.20. IR (film): $\tilde{\nu}$ = 3031, 2933 cm^{-1}, 2240, 1677, 1494, 1443, 1380, 1259, 1115, 1078, 1027, 971, 759, 703. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.48 (m, 2 H, Cpr-H), 0.67−0.85 (m, 2 H, Cpr-H), 1.42 (m, 1 H, Cpr-H), 2.15 (m, 2 H, 2-H), 2.26 (m, 1 H, 3-H), 3.28 (t, ^3J = 2.8 Hz, 1 H, 6-H), 3.67 (t, ^3J = 2.8 Hz, 1 H, 6-H), 5.12 (s, 1 H, 2′-H), 5.70 (m, 1 H, 5-H), 5.90 (m, 1 H, 4-H), 7.25–7.40 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.6 (CH_2, Cpr-C), 8.0 (CH_2, Cpr-C), 11.5 (CH, Cpr-C), 22.6 (CH_2, C-2), 34.8 (CH_2, C-6), 54.3 (CH, C-3), 60.1 (C, C-1), 118.1 (C, CN), 125.3 (CH, C-5), 126.6 (CH, Ph-C), 128.0 (CH, 2 C, Ph-C), 128.7 (CH, C-4), 129.7 (CH, 2 C, Ph-C), 132.9 (C, Ph-C), 135.8 (C, C-1′), 139.6 (CH, C-2′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 283 (26) [M$^+$], 248 (12), 196 (18), 181 (28), 154 (100), 143 (49), 115 (27), 91 (22), 77 (17), 41 (7). HRMS: 283.1128 ($C_{18}H_{18}ClN$, calcd. 283.1128).

3-[(2′-Cyclopropyl-1′-phenyl)ethenyl]-*N*-phenyl-1,2,3,6-tetrahydrophthalimide (11): Prepared within 24 h from 1,3-dicyclopropyl-1,2-propadiene (**1a**) (122 mg, 1.02 mmol), phenyl iodide (204 mg, 1.00 mmol) and *N*-phenylmaleimide (298 mg, 1.72 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 5:1) **11** (130 mg, 35%) was obtained as a colorless solid, R_f = 0.06; m.p. 80 °C. IR (KBr): $\tilde{\nu}$ = 2923, 1717 cm^{-1}, 1696, 1653, 1496, 1387, 1177, 1028, 805, 756, 700. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.35−0.48 (m, 2 H, Cpr-H), 0.59−0.72 (m, 2 H, Cpr-H), 1.34–1.39 (m, 1 H, Cpr-H), 2.03–2.10 (m, 1 H, 6-H), 2.22−2.30 (m, 1 H, 6-H), 3.17 (m, 2 H, 1-H, 2-H), 3.38 (m, 1 H, 3-H), 4.96 (dd, ^3J = 9.7, ^4J = 1.2 Hz, 1 H, 2′-H), 6.05−6.12 (m, 1 H, 5-H), 6.28−6.34 (m, 1 H, 4-H), 7.18−7.54 (m, 10 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.2 (CH_2, Cpr-C), 7.6 (CH_2, Cpr-C), 11.5 (CH Cpr-C), 24.5 (CH_2, C-6), 40.1 (CH, C-1), 42.4 (CH, C-2), 42.6 (CH, C-3), 126.4 (CH, 2 C, Ph-C), 126.7 (CH, 2 C, Ph-C), 127.7 (CH, C-5), 128.1 (CH, 2 C, Ph-C), 128.3 (CH, 2 C, Ph-C), 128.9 (CH, Ph-C), 129.4 (CH, Ph-C), 130.0 (CH, C-4), 133.4 (CH, C-2′), 135.0 (C, Ph-C), 140.6 (C, C-1′), 141.0 (C, Ph-C), 175.5 (C, CO), 178.7 (C, CO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 369 (82) [M$^+$], 340 (8), 227 (14), 222 (10), 195 (34), 165 (24), 143 (100), 128 (27), 91 (31), 77 (24), 43 (12), 41 (7). $C_{25}H_{23}NO_2$ (369.46): calcd. C 81.27, H 6.27, N 3.79; found. C 80.97, H 6.55, N 3.77.

1-Chloro-1-cyano-2-[(2′-methyl-1′-phenyl)prop-1′-enyl]cyclohex-3-ene (12a) and 1-Chloro-1-cyano-3-[(2′-methyl-1′-phenyl)prop-1′-enyl]cyclohex-4-ene (12b): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (97 mg, 0.90 mmol), phenyl iodide (252 mg, 1.24 mmol) and 2-chloroacrylonitrile (237 mg, 2.71 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 20:1) **12a** (37 mg, 15%) and **12b** (26 mg, 11%) were obtained as colorless oils.

12a: R_f = 0.45. IR (film): $\tilde{\nu}$ = 3021, 2966 cm^{-1}, 2916, 2856, 2214, 1734, 1717, 1700, 1653, 1559, 1457, 1442, 1374, 1260, 1208, 1073, 1052, 1025, 964, 915, 829, 768, 736. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.56 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.96–2.01 (m, 1 H, 2-H), 2.26–2.42 (m, 4 H, 5-H, 6-H), 5.30–5.39 (m, 1 H, 3-H), 5.48–5.59 (m, 1 H, 4-H), 7.22–7.34 (m, 5 H, Ph-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.9 (CH_3), 20.2 (CH_3), 27.4 (CH_2, C-5), 30.9 (CH_2, C-6), 54.8 (CH, C-2), 59.3 (C, C-1), 119.0 (C, CN), 126.6 (CH, C-3), 127.2 (CH, Ph-C), 128.0 (CH, 2 C, Ph-C), 128.9 (CH, 2 C, Ph-C), 129.1 (C, Ph-C), 133.2 (CH, C-4), 137.4 (C, C-2′), 141.1 (C, C-1′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 273/271 (12/46) [M$^+$], 236 (6), 197/195 (6/19), 184 (63), 169 (73), 159 (16), 144 (29), 108 (23), 93 (100), 91 (54), 77 (42), 51 (16), 41 (28). HRMS: 271.1128 ($C_{17}H_{18}ClN$, calcd. 271.1128).

12b: R_f = 0.26. IR (film): $\tilde{\nu}$ = 3081, 2967 cm^{-1}, 2929, 2856, 2213, 2197, 1734, 1717, 1700, 1653, 1599, 1572, 1491, 1417, 1373, 1261, 1073, 1024, 964, 913, 870, 807, 735. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.56 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 1.83–1.90 (m, 1 H, 3-H), 2.28–2.47 (m, 2 H, 2-H), 3.07–3.18 (m, 1 H, 6-H), 3.36–3.50 (m, 1 H, 6-H), 5.27–5.50 (m, 1 H, 5-H), 5.82–5.95 (m, 1 H, 4-H), 6.98–7.44 (m, 5 H, Ph-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.6 (CH_3), 19.5 (CH_3), 25.0 (CH_2, C-2), 29.3 (CH_2, C-6), 45.6 (C, C-1), 61.2 (CH, C-3), 123.7 (C, CN), 126.8 (CH, C-5), 127.4 (CH, Ph-C), 128.0 (CH, Ph-C), 129.1 (CH, Ph-C), 129.8 (C, Ph-C), 130.0 (CH, C-4), 130.2 (CH, Ph-C), 137.4 (CH, Ph-C), 138.5

(C, C-2′), 139.4 (C, C-1′) ppm. MS (EI, 70 eV): *m/z* (%) = 273/271 (12/38) [M^+], 236 (26), 235 (100), 220 (69), 204 (34), 184 (53), 169 (40), 144 (17), 115 (10), 91 (15), 77 (10). HRMS: 271.1128 ($C_{17}H_{18}ClN$, calcd. 271.1128).

3-[(2′-Methyl-1′-phenyl)-*N*-(phenyl)prop-1′-enyl]-1,2,3,6-tetrahydrophthalimide (13): Prepared within 24 h from 1-cyclopropyl-3-methyl-1,2-butadiene (**1d**) (91 mg, 0.84 mmol), phenyl iodide (375 mg, 1.84 mmol) and *N*-phenylmaleimide (315 mg, 1.82 mmol) according to the GP. After column chromatography (pentane/diethyl ether, 2:1) **13** (33 mg, 11%) was obtained as a colorless oil; R_f = 0.26. IR (film): $\tilde{\nu}$ = 2973, 2928 cm^{-1}, 1712, 1598, 1498, 1447, 1381, 1264, 1176, 1073, 1027, 971, 759, 737, 703. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.47 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 2.11–2.17 (m, 2 H, 6-H), 2.67–2.76 (m, 1 H, 2-H), 3.10–3.26 (m, 1 H, 1-H), 3.29–3.42 (m, 1 H, 3-H), 5.89–5.98 (m, 1 H, 4-H), 6.08–6.14 (m, 1 H, 5-H), 7.13–7.51 (m, 10 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (CH_3), 22.6 (CH_2, C-6), 23.3 (CH_3), 40.0 (CH, C-3), 40.8 (CH, C-2), 41.5 (CH, C-1), 126.0 (CH, 2 C, Ph-C), 126.2 (CH, Ph-C), 126.4 (CH, C-4), 127.5 (CH, 2 C, Ph-C), 127.9 (CH, Ph-C), 128.3 (C, Ph-C), 128.6 (CH, 2 C, Ph-C), 128.7 (CH, 2 C, Ph-C), 129.0 (CH, C-5), 131.5 (C, Ph-C), 142.9 (C, C-2′), 157.0 (C, C-1′), 176.3 (C, CO), 178.7 (C, CO) ppm. MS (DCI, NH_3): *m/z* (%) = 732 (18) [2 M + NH_4^+], 375 (100) [M + NH_4^+], 358 (13) [M + H^+], 299 (44), 277 (11), 234 (9), 173 (4). HRMS: 357.1729 ($C_{24}H_{23}NO_2$, calcd. 357.1729).

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