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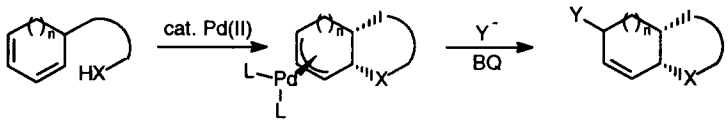
Palladium(II)-Catalyzed Carbocyclization: Vinylpalladium in 1,4-Oxidation of Conjugated Dienes

Ylva I. M. Nilsson, Roberto G. P. Gatti, Pher G. Andersson and Jan-E. Bäckvall*
Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21
Uppsala, Sweden

Abstract: Palladium-catalyzed 1,4-oxidation of conjugated dienes involving carbon-carbon bond formation has been realized. The reaction is performed with both acyclic and cyclic dienes with a carbon chain containing a terminal or internal triple bond. A vinylpalladium species formed by chloropalladation of the alkyne inserts one of the double bonds of the diene in a Heck-type reaction. The addition of palladium and chloride over the triple bond is non-stereoselective while the overall 1,4-addition by carbon and chloride over the diene is highly stereoselective and occurs anti. The stereoselectivity of the chloropalladation is dependent on the chloride concentration and varies with the substrate. Copyright © 1996 Elsevier Science Ltd

Introduction

We have recently developed a number of intramolecular palladium(II)-catalyzed 1,4-oxidations of conjugated dienes.[1] In these reactions halide, oxygen or nitrogen nucleophiles are added across the diene (Scheme 1). A synthetically interesting extension in the series would be to let one of the nucleophiles be a carbon nucleophile. Carbon nucleophiles have had limited synthetic use in Pd(II)-catalyzed reactions due to their ability to be oxidized under the reaction conditions. Thus, in Pd(II)-catalyzed oxidations where Pd(0) is reoxidized by an oxidant, carbon nucleophiles are expected to be more readily oxidized than the metal.[2,3]

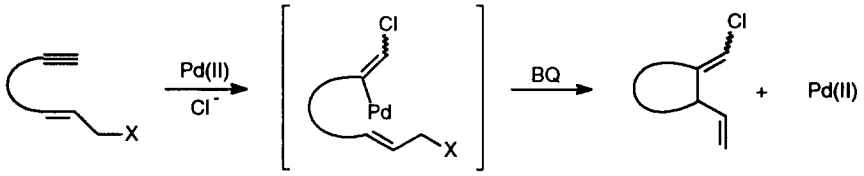


n = 1, 2
X = O, NTs, NCOR,CO_2
Y = OAc, Cl, OR
BQ = 1,4-benzoquinone

Scheme 1.

One way of circumventing these problems would be to use an in situ-generated vinyl-palladium species compatible with the reaction conditions. It has been shown that one class of these reactive intermediates formed by chloropalladation of acetylenes, can react in a Heck-type reaction with allylic halides in either intra-

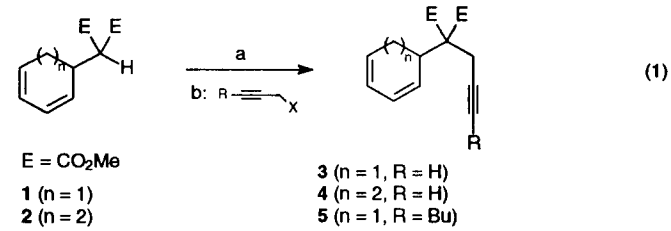
or intermolecular reactions in the presence of palladium(II) salts (Scheme 2).[4] In this paper we wish to report on the full account of the use of in situ generated vinyl palladium species in the 1,4-oxidation of conjugated dienes.[5]



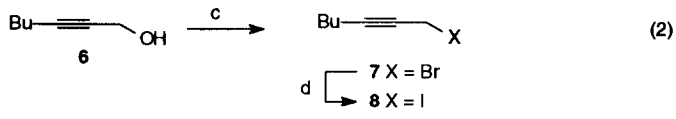
Scheme 2.

Results and Discussion

Preparation of Starting Materials. Dienynes **3** and **4** were prepared from the reaction of propargyl bromide with the sodium salts of dimethyl (2,4-cyclohexadien-1-yl) malonate (**1**)[1c,1e,6] and dimethyl (2,4-cycloheptadiene-1-yl) malonate (**2**)[1c,6] in 77 and 76% yield, respectively (eq 1). Dienyne **5** was synthesized in 80% yield by reaction of the sodium anion of dimethyl (2,4-cyclohexadien-1-yl) malonate (**1**) with iodide **8**, obtained from the corresponding bromide **7** (eq 2).



(1)



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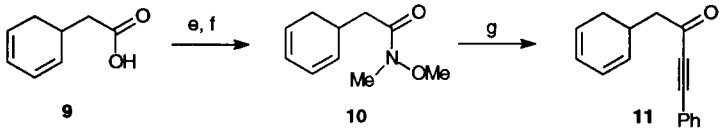

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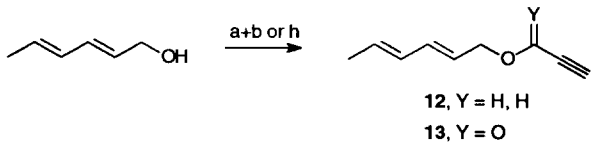
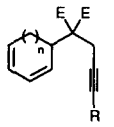
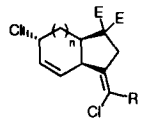
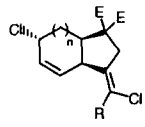
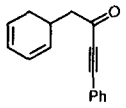
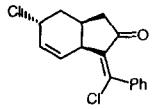
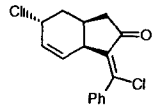
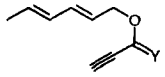
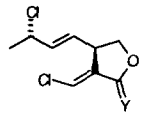
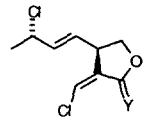


(4)

Reaction conditions: a. NaH, THF; b. $HC{\equiv}CCH_2Br$: **3** (77%), **4** (76%), **12** (75%), $BuC{\equiv}CCH_2I$: **5** (80%); c. MsCl, 2,4,6-collidine, LiBr, DMF, 0° to 20° (90%); d. NaI, acetone (56%); e. $(COCl)_2$; f. HN(Me)OMeHCl, pyridine; g. $PhC{\equiv}CLi$ (69%, 3 steps); h. $HC{\equiv}CCOOH$, DCC, DMAP (51%)

Table 1. Palladium-catalyzed carbochlorination of dienes.

entry	substrate	method[a]	products		ratio[b]	yield[c]
			cis chloro-palladation	trans chloro-palladation		
						
1	**3** (n = 1, R=H)	A	*Z*-**14**	*E*-**14**	1.5:1	65
2	**4** (n = 2, R=H)	B	*Z*-**15**	*E*-**15**	15:1	26[d]
3	**5** (n = 1, R=Bu)	B	*Z*-**16**	*E*-**16**	4:1	25
						
4	**11**	B	*E*-**17**	*Z*-**17**	1:9[e]	51
						
5	**12** (Y=H,H)	C	*E*-**18**	*Z*-**18**	3:1	53
6	**13** (Y=O)	B[f]	*E*-**19**	*Z*-**19**	1:9[e]	46

a) In all reactions $Pd(OAc)_2$ (10 mol%), benzoquinone (2 equiv.) and acetone:acetic acid was used. Method A: 4 equiv. LiCl, $[Cl^-]$ = 3.3 M, [substrate] = 0.83 M. The dienyne was added during 2 h and the reaction stirred another 3 h. Method B: 2.4-3 equiv. LiCl, $[Cl^-]$ = 0.48-0.6 M, [substrate] = 0.2 M. The dienyne was added during 12 h and the reaction stirred another 3-5 h. C; 2.5 equiv. LiCl in a two phase system pentane-acetic acid (10:1). $[Cl^-]$ = 0.3 M, [substrate] = 0.11 M. The dienyne dissolved in acetone (3 M) was added during 14 h to the slowly stirred mixture and the reaction mixture was stirred 36 h. b) Ratio refers to cis chloropalladation / trans chloropalladation. c) Combined yields (%) after flash chromatography. d) Contaminated with 19% of the isomers from *syn*-addition of chloride and carbon over the diene (*E*-**15**- and *Z*-**15**-*syn*). e) Note that the *Z*-isomer comes from a trans chloropalladation in this reaction. f) The dienyne was added during 8 h and the reaction was stirred for another 30 h.

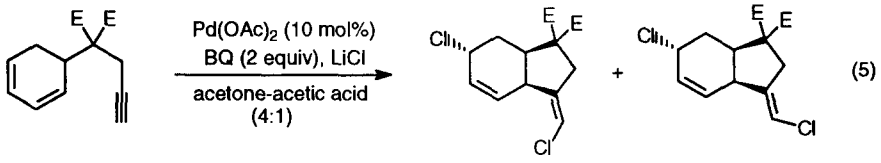
Compound **7** was prepared from the corresponding alcohol (**6**), which was obtained according to a literature procedure.[7] Dienyne **11** was prepared from diene acid **9**[1c,8] in three steps. Transformation into methoxyamide **10** followed by reaction with the appropriate lithium acetylide[9] afforded **11** in 69% yield from **8** (eq 3). Acyclic dienynes **12** and **13** were prepared from commercially available (*E,E*)-2,4-hexadien-1-ol. By treatment with NaH and propargyl bromide, **12** was isolated in 75% yield. Esterification of (*E,E*)-2,4-hexadienol with propiolic acid in the presence of DCC and DMAP gave **13** in 51% yield (eq 4).

Palladium(II)-Catalyzed Carbochlorinations of Conjugated Dienes. Dienynes **3**, **4**, **5**, **11**, **12** and **13** were allowed to react with LiCl and 1,4-benzoquinone (BQ, 2 equiv.) in acetone-acetic acid (4:1) in the presence of $Pd(OAc)_2$ (10 mol%) as catalyst. The dienes were added slowly to avoid Diels-Alder reaction

between the diene and BQ. In addition the acetylene concentration should be kept low to avoid oligomerization. The reaction was continued until judged complete according to TLC. With all substrates a highly stereoselective 1,4-carbochlorination took place but the formation of the vinylic carbon-chloro bond was less stereoselective and led to mixtures of the *E* and *Z* products (Table 1). The configuration was assigned by NOE experiments.

The yields reported in Table 1 are modest but in light of the stereoselective 1,4-functionalization of the diene involving carbon-carbon bond formation the results should be of interest. In the reactions of **3**, **4**, **5**, and **12** the product arising from cis chloropalladation of the triple bond predominates (entries 1-3 and 5). With substrates **11** and **13** where the acetylene is situated α to a carbonyl, the relative amount of product from trans chloropalladation was high (entries 4 and 6).Cyclization of dienyne **3** was performed under concentrated reaction conditions. A faster chloropalladation of the triple bond prevents oligomerization of the acetylene. In this reaction the diastereoselectivity was low and a 1.5:1 ratio between cis and trans chloropalladation products was obtained (entry 1). The structure of (*Z*)-**14** has also been confirmed by X-ray determination.[5] An increased concentration of the reactants resulted in lower yields with some of the other dienynes due to side reactions. For example, the reaction of **4** led to an increased formation of the 1,4-syn-addition product at high concentrations due to the lability of the allylic chloride in **15** which epimerizes by Cl^- attack.

During our studies of these reactions we noticed a variation in the cis:trans chloropalladation ratio with the Cl^- concentration. In all cases the amount of product arising from a trans chloropalladation increased at a higher Cl^- concentration. Some experiments with dienyne **3** at different chloride ion and substrate concentrations are presented in Figure 1. The effect of dilution of the reaction, thus lowering both the Cl^- and substrate concentration, is clear. Upon dilution the relative amount of *Z*-product increases (entries 1-4). Also when the concentration of Cl^- was lowered at a constant volume the *Z*:*E* ratio increased (entries 3, 5 and 6; entries 4 and 7 in Figure 1).

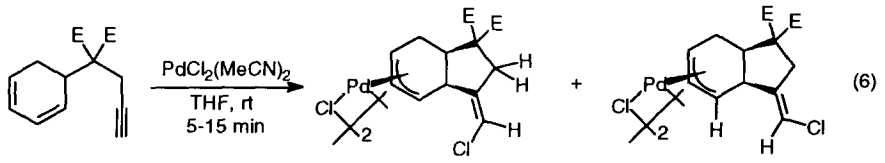


3 **Z-14** **E-14**

Entry	[3]	[Cl^-]		
1	0.83	3.3	1.5	1
2	0.42	1.67	2.2	1
3	0.2	0.81	3.0	1
4	0.07	0.27	4.5	1
5	0.2	0.6	3.3	1
6	0.2	0.48	3.4	1
7	0.07	0.6	3.8	1

Figure 1. The effect on product distribution of dilution and chloride concentration in the palladium(II)-catalyzed oxidation of dienyne **3**.

A similar investigation on the formation of the (π-allyl)palladium intermediate was performed. In a 0.26 M solution of **3** with a stoichiometric amount of $PdCl_2(MeCN)_2$ the product distribution between π-allyl complexes (*Z*)-**20** : (*E*)-**20** was found to be 1:1.3. At 0.026 M this ratio was 1.8:1 (Fig. 2). The *Z*:*E* ratios were determined by transferring the dimeric (π-allyl)palladium intermediates **20** to the monomeric **20'** by treating the mixture of (*Z*)-**20** and (*E*)-**20** with $Ag(CF_3SO_3)$ in CD_3OD. The NMR spectra of the monomeric π-allyl complexes were simplified compared to those of the dimeric species (*Z*)-**20** and (*E*)-**20**, which in each case consists of two diastereomers.[10] The results from the reaction of **3** with $PdCl_2(MeCN)_2$ again shows the concentration dependency of the chloropalladation and that the amount of *E*-isomer decreases on dilution.



3 *Z*-**20** *E*-**20**

[3]	[Cl⁻]		
0.26	0.52	1	1.3
0.08	0.16	1.3	1
0.026	0.052	1.8	1

Figure 2. The effect on product distribution of dilution in the formation of π-allyl **20**.

The results from these investigations show that the trans and cis chloropalladations are formed through different mechanisms. The cis chloropalladation is a unimolecular reaction while the trans chloropalladation is a bimolecular reaction. This is in line with a cis-migration from metal to carbon for the former reaction and with an external attack for the latter process.[11]

To investigate the effect of solvent, four experiments with dienyne **3** were performed with different acetone-acetic acid compositions (Table 2). The relative amount of *Z*-**14** decreased with a decreased acetone:acetic acid ratio. Acetic acid-rich solutions gave a faster consumption of starting material, but on the other hand lower yields were obtained.

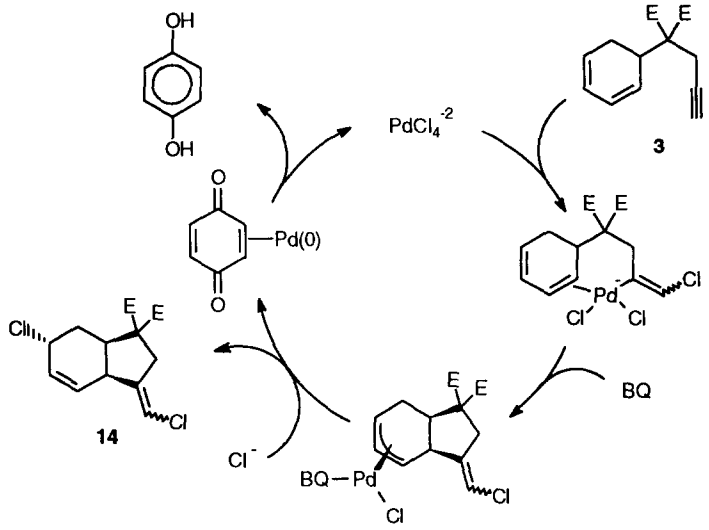
These stereodefined allylic chlorides are useful synthetic intermediates since the chloro group can be stereospecifically substituted with either retention or inversion by a number of nucleophiles.[1,12] For further synthetic transformations, the mixture of *Z* and *E* vinylic chlorides is not a problem, since the vinylic chloride can be transformed to an aldehyde/ketone or be reduced to a C-H bond.

Mechanism. The catalytic reaction starts with a chloropalladation of the triple bond to form a vinylpalladium species (Scheme 3). On the basis of previous reports on chloropalladation of acetylenes, chloride is expected to preferentially attack the C-2 carbon of the terminal acetylene.[4a] With our substrates this regioisomer can not react further but presumably the two regioisomers are in equilibrium with starting material. The small amount of isomer where palladium occupies the internal position is the reactive species. Syn insertion of the diene into the vinyl palladium bond in a Heck-type reaction gives a (π-allyl)palladium complex. Benzoquinone(BQ)-induced, external attack by Cl^- yields the product.[1,12] Finally the catalytic cycle is closed with the oxidation of Pd(0) by BQ to regenerate the active Pd(II)-catalyst.

Table 2. The effect of solvent on the product distribution in the oxidation of dienes with carbon nucleophiles.

entry	solvent (acetone-acetic acid)	products (*Z*-**14**:*E*-**14**)	yield
1	9:1	3.9:1	51%
2	4:1	3.9:1	44%
3	1:1	2.9:1	36%
4	1:4	1.8:1	32%

Dienyne **3** was treated with $Pd(OAc)_2$ (10%), BQ (2 equiv) and LiCl (4 equiv.) in a mixture of acetone-acetic acid ([Cl] = 0.6 M, [substrate] = 0.2 M).



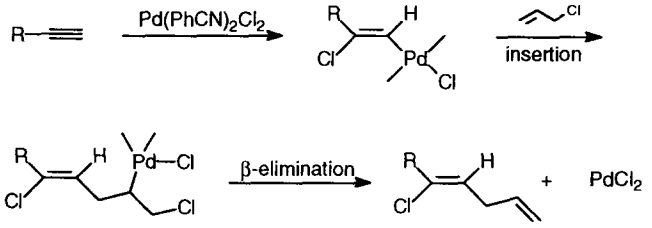
Scheme 3. Catalytic cycle for the Pd-catalyzed 1,4-oxidation of dienes with carbon and chloride as nucleophiles (BQ = 1,4-benzoquinone).

The chloropalladation of the triple bond is not stereoselective and both *Z*- and *E*-isomers were obtained. On the other hand, the 1,4-addition across the diene is stereoselective (1,4-anti),[13] as also required by the mechanism.

To confirm the proposed mechanism stoichiometric reactions under conditions similar to the catalytic reaction were performed in an NMR tube and the intermediate (π-allyl)palladium chloro dimer was studied (cf. eq 6). To the diene **3** in acetic acid-d_4-acetone-d_6 (4:1) or alternatively THF-d_8, was added 1 equiv. of a $Pd(OAc)_2$ and 3-6 equiv. of LiCl. From the NMR study it was clear that the triple bond reacted before the diene in the chloropalladation. The acetylenic proton had disappeared completely within 5 min after the addition of the palladium(II) salt. Two different π-allyls were detected and it was clear that they are the result from a non-stereoselective chloropalladation of the acetylene followed by insertion of one of the double bonds

of the diene. The π-allyl-protons had different shifts and pattern compared to those of the (π-allyl)palladium complex obtained from 1,3-cyclohexadiene, palladium(II) and LiCl in a control experiment. In the latter control experiment it was found that chloropalladation of 1,3-cyclohexadiene is reversible and slow. After 15 min a 1:1 mixture of the (π-allyl)palladium-complex and 1,3-cyclohexadiene was obtained, and the ratio did not change upon prolonged reaction time. From these experiments we conclude that the triple bond reacts prior to the diene in the chloropalladation of **3**. The results from these experiments eliminate an alternative pathway for formation of cyclized products by chloropalladation of the diene and subsequent insertion of acetylene into the allylpalladium bond.[14]

Stereoselectivity in Chloropalladation of Acetylenes. The chloropalladation of different substituted acetylenes was studied by Kaneda *et al.* in 1979.[4a] They observed only product from syn attack and these results were recently confirmed by Kosugi *et al.*[15] In both these investigations the reaction was performed in neat allyl chloride. The allyl chloride reacts with the vinyl palladium in an insertion reaction which after β-chloride elimination regenerates the active palladium catalyst (Scheme 4). The presence of both *Z* and *E* chlorovinyl groups in the products obtained in Table 1 suggests that a non-stereoselective chloropalladation of the triple bond occurs. Results obtained by Ma and Lu[4b,16] in similar reactions were also best explained by involvement of both cis and trans chloropalladation of acetylenes.



Scheme 4. Chloropalladation of acetylenes in the presence of allyl chloride.

We recently studied the chloropalladation of acetylenes under conditions similar to those used in Table 1.[17] Indeed we observed that the chloropalladation of acetylenes can occur both cis and trans. Thus, at a low chloride concentration cis chloropalladation predominates whereas at a high chloride concentration there is a preference for trans chloropalladation. This is in accordance with the results shown in Figures 1 and 2.

Concluding Remarks

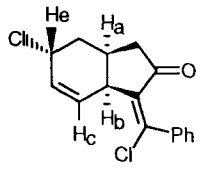
Palladium-catalyzed carbocyclization in the 1,4-oxidation of dienes has been realized. An intermediate vinylpalladium species inserts one of the double bonds in the conjugated diene, in a Heck-type reaction. The addition of carbon and chloride over the diene is highly stereoselective and occurs anti. However, the chloropalladation of the acetylene is non-stereoselective and results in the formation of both *E* and *Z* chlorovinyl groups. At higher Cl^- concentration more of the isomer requiring trans chloropalladation is obtained. The cis chloropalladation is unimolecular, while the trans chloropalladation is bimolecular. The allylic chloride obtained in all reactions is stable under the reaction conditions and is not affected by the Pd(II) catalyst.[18]

Experimental Section

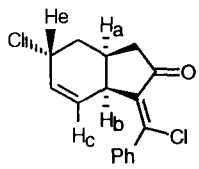
NMR spectra were recorded for $CDCl_3$ solutions with a Varian 400 or 300 spectrometer, ^1H at 400 or at 300 MHz and ^{13}C at 100.5 or at 75.4 MHz using chloroform-d_1 (7.26 ppm, ^1H, 77.0 ppm, ^{13}C) as internal standard. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using a 0.1 mm KBr cell on neat samples or with $CDCl_3$ as the solvent. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument in the electron impact mode using a potential of 70 eV volt. Slow addition was performed by the use of a Sage Instruments Model 355 syringe pump. 1,4-Benzoquinone (BQ) was recrystallized from ethanol. Lithium chloride (99%), (*E,E*-2,4-hexadien-1-ol (97%), propiolic acid (98%), propargyl bromide (80% in toluene), phenylacetylene (98%), *N,O*-dimethylhydroxylamin hydrochloride (98%) were purchased from Aldrich. Oxalylchloride (98%) was purchased from Merck. $Pd(OAc)_2$ was bought from Engelhard. 2-Heptyn-1-ol (**6**) was prepared according to ref. 7. $PdCl_2$ was obtained from Johnson Matthey. $PdCl_2(PhCN)_2$ was prepared according to literature procedures.[19] Merck silica gel 60 (240-400 mesh) was used for flash chromatography.

NOE measurements.

For assignment of compound **14** see reference 5. Compound **17** was assigned as follows. (*E*)-**17**: H_b gave no NOE to any aromatic proton. (*Z*)-17: H_b gave NOE to the aromatic protons. Since NOE was observed between H_a and H_b in both isomers the cis ring junction was established. In neither case did H_e give any detectable NOE to H_a.

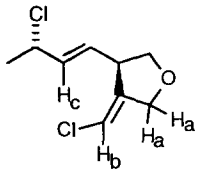


(*E*)-**17**

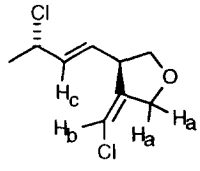


(*Z*)-**17**

Compound **18** was assigned as follows. (*E*)-**18**: H_b gave no NOE to H_c. H_b gave NOE to H_a. (*Z*)-**18**: H_b gave no NOE to H_a. The shifts of protons H_b and H_c were too close to allow a measurement of NOE.

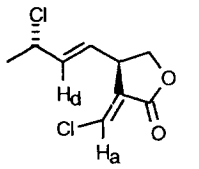


(*E*)-**18**

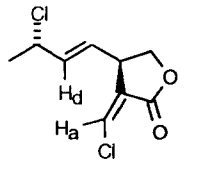


(*Z*)-**18**

Compound **19** was assigned as follows. (*E*)-**19**: H_a gave no NOE to H_d. (*Z*)-**17**: H_a gave NOE to H_d.



(*E*)-**19**



(*Z*)-**19**

For assignment of compound **20** see the text (Fig. 2, ref. 10).

Dimethyl (2,4-cyclohexadien-1-yl)malonate 1 was prepared according to ref. 1e.

Dimethyl (2,4-cycloheptadien-1-yl)malonate 2 was prepared according to ref. 1c.

Dimethyl (2,4-cyclohexadien-1-yl)(2-propyn-1-yl)malonate 3. To NaH (60%, 0.285 g, 7.12 mmol) washed with ether in THF (55 mL) was added dimethyl (2,4-cyclohexadien-1-yl)malonate **1** (1.15 g, 5.48 mmol). The mixture was stirred until no more hydrogen gas was evolved (30 min). The solution was cooled to 0 °C and propargyl bromide (80% in toluene, 1.22 g, 8.22 mmol) was added dropwise. The reaction was continued until the disappearance of the starting material (TLC). The reaction was poured into water (40 mL) and extracted with ether (4 x 15 mL). The combined organic layers were washed with brine (15 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by flash chromatography (pentane-ether). Dienyne **3** was isolated in 77% yield, 1.04 g as a colorless viscous oil which solidified upon cooling. ^{1}H NMR (400 MHz) δ 5.97 (m, 1 H, olefinic), 5.86 (m 1 H, olefinic), 5.79-5.71 (m 2 H, C*H*=CHCH=C*H*), 3.75 (s, 3 H, CH_3), 3.73 (s, 3 H, CH_3), 3.35 (m, 1 H, CH_2CH), 2.91 (dd, *J* = 17.2, 2.6 Hz, 1 H, C*H*H), 2.84 (dd, *J* = 17.2, 2.6 Hz, 1 H, CH*H*), 2.41 (dddd, 17.5, 9.3, 4.7, 1.8 Hz, 1 H, C*H*HCH), 2.33 (dddd, 17.5, 11.8, 4.0, 2.0 Hz, 1 H, CH*H*CH), 2.02 (t, *J* = 2.6 Hz, 1 H, H-acetylenic); ^{13}C NMR (100.5 MHz) δ 170.0, 126.2, 125.7, 125.2, 123.5, 79.0, 71.4, 59.4, 52.7, 52.6, 35.6, 23.4, 22.6.

Dimethyl (2,4-cycloheptadiene-1-yl)(2-propyn-1-yl)malonate (4) was prepared from dimethyl (2,4-cycloheptadiene-1-yl)malonate **2** as described for **3** in 76% yield. ^{1}H NMR (400 MHz) δ 5.80-5.60 (m, 4 H, 4 x olefinic), 3.64 (s, 3 H, CH_3), 3.63 (s, 3 H, CH_3), 3.05 (brd, *J* = 9 Hz, 1 H, C=CCH), 2.79 (d, *J* = 2.6 Hz, 2 H, CH_2), 2.32 (m, 2 H, C=CCH_2), 2.03 (m, 1 H, CH_2CHHCH), 1.95 (t, *J* = 2.6 Hz, 1 H, H-acetylenic), 1.49 (m, 1H, CH_2CH*H*CH); ^{13}C NMR (100.5 MHz) δ 169.8, 169.7, 134.2, 131.9, 124.8, 124.3, 78.9, 71.3, 60.0, 52.23, 52.18, 43.8, 31.5, 29.6, 23.1; IR ν (neat) 3308, 2954, 2254, 1740, 1436, 1329, 1305, 1274, 1215, 918, 748.

Dimethyl (2,4-cyclohexadien-1-yl)(2-heptyn-1-yl)malonate (5) was prepared from **7** and **1** as described for **3** in 80% yield. ^{1}H NMR (400 MHz) δ 5.96 (qq, *J* = 5.0 ,1.1 Hz, 1 H), 5.88-5.83 (m, 1 H), 5.79 (ddt, *J* = 9.9, 4.0, 0.9 Hz, 1 H), 5.76-5.70 (m, 1 H), 3.72 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.37-3.27 (m, 1 H), 2.86 (dt, *J* = 17.1, 2.4 Hz, 1 H), 2.78 (dt, *J* = 17.1, 2.4 Hz, 1 H), 2.45-2.27 (m, 2 H), 2.13-2.08 (m, 2 H), 1.47-1.32 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz) δ 170.35, 170.32, 126.2, 125.8, 125.3, 123.5, 83.6, 74.3, 59.7, 52.5, 52.4, 36.4, 30.9, 24.3, 23.0, 21.8, 18.3, 13.6; IR (neat) 3040, 2955, 2933, 2872, 1736, 1434, 1268, 1223, 1065, 1051.

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.01; H, 7.95. Found: C, 70.90; H, 8.02.

1-Bromo-2-heptyne (7).[20] To a stirred solution of alcohol **6** (1.500 g, 13.38 mmol), LiBr (1.407 g, 16.20 mmol) and 2,4,6-Collidine (12.117 g, 100.29 mmol) in DMF (24 mL) at 0 °C. Methanesulfonyl chloride (MsCl) (1.524 mL, 21.87 mmol) was added slowly (20 minutes). The temperature was allowed to increase to room temperature and the reaction was judged complete by TLC after 2 h. After dilution with diethyl ether (300 mL) and addition of water (30 mL) the layers were shaken and separated. Washing with water (30 mL), 10 % water solution of $Cu(NO_3)_2$ (2 × 50 mL), water (30 mL), brine (30 mL) followed by drying ($MgSO_4$) and bulb-bulb distillation afforded 2.11 (90 %) of the title compound **7**. ^{1}H NMR (300 MHz) δ 4.14 (t, *J* = 2.4 Hz, 2 H, CH_2Br), 2.23 (tt, *J* = 6.9, 2.4 Hz, 2 H, $CH_2C{\equiv}C$), 1.54-1.33 (m, 4 H, $CH_2CH_2CH_3$), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (74.5 MHz) δ 87.7, 74.8, 31.3, 30.4, 21.9, 18.5, 13.5; IR (neat) 2958, 2931, 2872, 2235, 1610, 1571, 1459, 1410, 1263.

1-Iodo-2-heptyne (8).[7] Bromide **7** (700 mg, 4.00 mmol) was stirred with NaI (1.12 g, 7.47 mmol) in acetone (15 mL) at room temperature for 2 h. After 2 h the reaction mixture was diluted with diethyl ether:*n*-pentane (40:60) and filtered. Evaporation and flash chromatography (diethyl ether:*n*-pentane, 40:60) gave 497 mg (56 % yield) of the title compound. ^{1}H NMR (300 MHz) δ 3.71 (t, J = 2.4 Hz, 1 H, CH_2I), 2.19 (tt, J = 6.9, 2.4, 2 H, $CH_2C{\equiv}C$), 1.52-1.33 (m, 4 H, $CH_2CH_2CH_3$), 0.90 (t, 7.2 Hz, 3 H, CH_3); ^{13}C NMR (74.5 MHz) δ 86.8, 76.9, 30.4, 21.9, 18.8, 13.6, -16.6; IR (neat) 2958, 2932, 2871, 2231, 1465, 1430, 1379, 1262, 1172, 1144.

2-(2,4-cyclohexadien-1-yl)acetic acid (9) was prepared as described in ref. 8.

***N*-methoxy-*N*-methyl-2-(2,4-cyclohexadien-1-yl)acetic amide (10).** ^{1}H NMR (300 MHz) δ 5.94-5.85 (m, 2 H, olefinic), 5.79-5.71 (m, 2 H, olefinic), 3.67 (s, 3 H, OCH_3), 3.18 (s, 3 H, CH_3), 2.90-2.77 (m, 1 H, CH-bridge), 2.50 (app d, J = 7.5 Hz, 2 H, $C{=}CCH_2$), 2.39 (dddd, J = 17.4, 8.7, 4.2, 1.5 Hz, 1 H, C*H*HCO), 2.02 (dddd, J = 17.4, 9.4, 4.2, 1.5 Hz, 1 H, CH*H*CO); ^{13}C NMR (74.5 MHz) δ 175.8, 130.2, 125.3, 124.1, 123.8, 61.2, 38.0, 35.5, 28.9, 28.2; IR (neat) 3036, 2936, 1728, 1666, 1461, 1414, 1383, 1177, 1113, 997.

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.26; H, 8.34. Found: C, 66.02; H, 8.27.

(2,4-cyclohexadien-1-yl)methyl (phenylethynyl) ketone (11). ^{1}H NMR (400 MHz) δ 7.61-7.32 (m, 5 H, Ph), 5.99-5.91 (m, 2 H, olefinic), 5.83-5.75 (m, 2 H, olefinic), 3.05-2.96 (m, 1 H, CH), 2.78 (m, 2 H, $C{=}CCH_2$), 2.43 (dddd, J = 17.2, 8.4, 4.0, 1.6 Hz, 1 H, C*H*HCO), 2.09 (m, 1 H, CH*H*CO); ^{13}C NMR (100.5 MHz) δ 186.9, 133.1, 130.7, 129.2, 128.6, 125.3, 124.6, 124.0, 119.9, 90.8, 87.9, 49.4, 29.1, 28.1; IR ($CDCl_3$-solution) 3038, 2927, 2203, 1664, 1597, 1490, 762.

((*E*,*E*)-2,4-hexadien-1-yl) 2-propyn-1-yl ether (12).[21] To a slurry of NaH (10 mmol) in THF (10 mL) at -30 °C (*E*,*E*)-2,4-hexadien-1-ol (10 mmol) was added dropwise. When no more gas was evolved (10 min) propargyl bromide (12 mmol) was added and the reaction mixture was stirred over night at room temperature and worked up when ready according to TLC. The reaction was poured onto water (50 mL) and extracted with ether (3 x 30 mL). The combined organic layers were washed with brine (30 mL) and dried ($MgSO_4$). After evaporation of the solvent by rotary evaporation the crude was purified by flash chromatography (pentane-ether, 95:5). Ether **12** was isolated in 75% yield. ^{1}H NMR (300 MHz) δ 6.23 (dd, J = 15.0, 11.3 Hz, 1 H), 6.06, (ddq, J = 15.0, 11.3, 1.7 Hz, 1 H), 5.72 (dq, J = 15.0, 6.7 Hz, 1 H), 5.60 (dt, J = 15.0, 6.3 Hz, 1 H), 4.13 (d, J = 2.4 Hz, 2 H), 4.07 (d, J = 6.3 Hz, 2 H), 2.42 (t, J = 2.4 Hz, 1 H), 1.75 (brd, J = 6.5 Hz, 3 H); ^{13}C NMR (74.5 MHz) δ 134.2, 130.6, 130.5, 125.5, 79.7, 74.3, 69.9, 56.7, 18.1.

((*E*,*E*)-2,4-hexadien-1-yl) propiolate (13).[22] To a solution of propiolic acid (1.0 g, 14.3 mmol) and (*E*,*E*)-2,4-hexadien-1-ol (1.4 g, 14.3 mmol) in ether (5 mL) was added at -20 °C dropwise a solution of DCC (3.04 g, 14.6 mmol) and DMAP (0.052 g, 0.43 mmol) in ether (18 mL) with stirring. The reaction was stirred for 22 h at room temperature. After the reaction was complete, the white solid was filtered off and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (pentane-ether, 98:2). The ester **13** was isolated as a colorless oil in 51% yield. ^{1}H NMR (400 MHz) δ 6.29 (ddm, J = 15, 10.3 Hz, 1 H), 6.05 (ddqd, J = 15, 10.3, 1.7, 0.8 Hz, 1 H), 5.79 (dq, J = 15, 6.7 Hz, 1 H), 5.62 (dtq, J = 15, 6.8, 0.8 Hz, 1 H), 4.68 (brd, J = 6.8 Hz, 2 H), 2.87 (s, 1 H), 1.77 (dm, J = 6.7 Hz, 3 H); ^{13}C NMR (100.5 MHz) δ 152.5, 136.2, 132.1, 130.1, 122.0, 74.6, 66.7, 18.1.

General procedure for palladium(II)-catalyzed oxidation of dienynes. To a stirred solution of $Pd(OAc)_2$ (0.011 g; 0.05 mmol), LiCl (0.085 g; 2.0 mmol) and 1,4-benzoquinone (0.108 g; 1.0 mmol) in acetone (0.30 mL) and acetic acid (0.12 mL) was added dienyne (0.124 g; 0.5 mmol) in acetone (0.18 mL)

during 2 h. After additional 3 h stirring of the reaction water (3 mL) and ether (3 mL) was added. The water layer was extracted with ether (3 x 3 mL). The combined organic layers were washed with NaOH (2 M) until the water layer was colorless and with brine (5 mL). The water layers were back-extracted with ether. The combined organic layers were dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the crude product was purified by flash chromatography with pentane ether as the eluent.

(*Z*)-14. ^{1}H NMR (400 MHz) δ 6.45 (dd, *J* = 9.8, 4.3 Hz, 1 H, CHClCH=C*H*), 6.01-5.94 (m, 2 H, olefinic), 4.61-4.57 (m, 1 H, C*H*ClCH=CH), 3.77 (s, 3 H, CH_3), 3.76 (s, 3 H, CH_3), 3.69-3.62 (m, 1 H, ClC=CCH), 3.52-3.44 (m, 1 H, CH_2CH), 3.18 (dt, *J* = 16.2, 2.8 Hz, 1 H, C*H*HC=CHCl), 2.86 (dt, *J* = 16.2, 1.0 Hz, 1 H, CH*H*C=CHCl), 1.81-1.75 (m, 1 H, C*H*HCH), 1.72-1.64 (m, 1 H, CH*H*CH); ^{13}C NMR (74.5 MHz) δ 170.8, 140.9, 128.6, 126.6, 112.1, 62.5, 53.1, 52.90, 52.86, 52.0, 41.3, 38.4, 37.4, 30.7.

Anal. Calcd for $C_{14}H_{16}O_4Cl_2$: C, 52.68; H, 5.05. Found: C, 52.60; H, 4.97.

(*E*)-14. ^{1}H NMR (400 MHz) δ 6.01-5.91 (m, 2 H, olefinic), 5.77 (q, *J* = 2.8 Hz, 1 H, C=CHCl), 4.58-4.54 (m, 1 H, C*H*ClCH=CH), 3.78 (s, 3 H, CH_3), 3.76 (s, 3 H, CH_3), 3.51-3.44 (m, 1 H, CH_2CH), 3.37 (dt, *J* = 19.0, 2.8 Hz, 1 H, C*H*HC=CHCl), 2.99 (dm, *J* = 2.99 Hz, 1 H, CH*H*C=CHCl), 1.75-1.69 (m, 1 H, C*H*HCH), 1.67-1.59 (m, 1 H, CH*H*CH).; ^{13}C NMR (74.5 MHz) δ 171.5, 169.4, 143.5, 128.6, 127.2, 112.6, 61.3, 53.1, 52.9, 52.4, 42.6, 38.6, 36.6, 29.9.

Anal. Calcd for $C_{14}H_{16}O_4Cl_2$: C, 52.68; H, 5.05. Found: C, 52.85; H, 5.08.

(*Z*)-15-*anti*. ^{1}H NMR (400 MHz) δ 6.02 (td, *J* = 2.2, 2.0 Hz, 1 H), 5.59 (dddd, *J* = 11.3, 5.2, 2.8, 1.4 Hz, 1 H), 5.48 (ddd, *J* = 11.3, 3.8, 0.7 Hz, 1 H), 4.50 (m, 1 H), 4.05 (m, 1 H), 3.72 (s, 3 H, CO_2CH_3), 3.67 (s, 3 H, CO_2CH_3), 3.24 (dt *J* = 16.6, 1.6 Hz, 1 H), 3.07 (ddd, *J* = 18.2, 11.5, 9.3 Hz, 1 H), 2.62 (ddd, 16.6, 2.5, 1 Hz, 1 H), 2.38 (m, 1 H), 2.16 (m, 1 H), 1.99 (dt, *J* = 14, 11 Hz, 1 H), 1.32 (dtd, *J* = 14, 11, 0.7 Hz, 1 H); ^{13}C NMR (100.5 MHz) δ 171.1, 170.5, 144.5, 131.6, 127.2, 111.5, 62.0, 58.5, 52.7, 52.3, 49.6, 42.1, 40.1, 33.3, 32.3.

(*E*)-15-*anti*. ^{1}H NMR (300 MHz) δ significant peak 4.59 (m, 1 H).

(*Z*)-15-*syn*. ^{1}H NMR (400 MHz) δ 6.00 (app q, *J* = 2.1 Hz, 1 H), 5.55 (dm, *J* = 11 Hz, 1 H), 5.46 (dm, *J* = 11 Hz, 1 H), 4.94 (m, 1 H), 3.88 (m, 1 H), 3.73 (s, 6 H, 2 x CO_2CH_3), 3.20 (dt *J* = 16.5, 1.6 Hz, 1 H), 3.07 (m, 1 H), 2.63 (dd, 16.3, 2 Hz, 1 H), 2.21 (m, 1 H), 2.07 (m, 1 H), 1.86 (m, 2 H).

(*E*)-15-*syn*. ^{1}H NMR (300 MHz) significant peak 5.20 (md, *J* = 8.3 Hz, 1 H).

(*Z*)-16. ^{1}H NMR (400 MHz) δ 6.01-5.93 (m, 2 H, olefinic), 4.59-4.55 (m, 1 H, CHCl), 3.77 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.60-3.56 (m, 1 H, CHC=CCl), 3.45-3.38 (m, 1 H, CH_2CHCH_2), 3.20 (dm, *J* = 17.6 Hz, 1 H, ClC=CC*H*H), 3.09 (dm, *J* = 17.6 Hz, ClC=CCH*H*), 2.40-2.26 (m, 2 H, C=C$ClCH_2$), 1.77-1.73 (m, 2 H, $CHClCH_2$), 1.66-1.23 (m, 4 H, $CH_2CH_2CH_3$), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100.5 MHz) δ 171.3, 169.4, 134.3, 130.4, 129.8, , 127.3, 61.7, 53.0, 52.8, 52.1, 41.1, 39.1, 38.6, 35.9, 30.7, 29.8, 22.0, 13.9.

(*E*)-16. ^{1}H NMR (400 MHz) δ 6.49 (dd, *J* = 9.8, 4.4 Hz, 1 H, C*H*=CHCHCl), 5.95 (dddd, *J* = 9.2, 5.6, 2.6, 0.9, 1 H, CH=C*H*CHCl), 4.60-4.56 (m, 1 H, CHCl), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.65-3.60 (m, 1 H, C=CHC*H*CHC=), 3.49-3.41 (m, 1 H, CH_2CHCH_2), 3.06 (dm, *J* = 16.2 Hz, 1 H, C*H*HC=CCl), 2.94 (dd, *J* = 16.2, 1.1 Hz, 1 H, CH*H*C=CCl), 2.39-2.22 (m, 2 H, CH_2CCl=), 1.80-1.64 (m, 2 H, CH_2CHCl), 1.52-1.44 (m, 2 H, $CH_2CH_2CH_3$), 1.30-1.21 (m, 2 H, CH_2CH_3), 0.90 (t, *J* = 7.3 Hz, 3 H, CH_3); ^{13}C NMR (100.5 MHz) δ 170.9, 169.4, 133.7, 129.8, 129.4, 126.3, 62.5, 53.0, 52.8, 52.3, 42.0, 37.3, 37.2, 36.8, 30.8, 29.4, 21.6, 14.0; IR ($CDCl_3$-solution) 2958, 2930, 2859, 1731, 1614, 1454, 1446, 1272, 1241.

(*Z*)-17. ^{1}H NMR (400 MHz) δ 7.46-7.36 (m, 5 H, Ph), 5.72 (ddd, *J* = 10.1, 5.0, 3.7 Hz, 1 H, C=C*H*CH), 5.21 (ddd, 3,7, 5.0, 10.1 Hz, 1 H, =C*H*-CHCl) 4.55-4.50 (m, 1 H, C*H*Cl), 3.70-3.66 (m, 1 H, C=CHC*H*), 2.75-2.66 (m, 1 H, CH_2CHCH_2), 2.62 (dd, *J* = 17.4, 8.1 Hz, 1 H, C*H*HCO), 2.30 (dd, *J* = 17.4, 6.4 Hz, 1 H, CH*H*CO), 2.17-2.06 (m, 1 H, CHClC*H*H), 1.99 (ddd, *J* = 14.2, 6.7, 3.8 Hz, 1 H, CHClCH*H*); ^{13}C NMR (100.5 MHz) δ 202.0, 138.6, 138.5, 134.1, 129.9, 129.1, 128.8, 128.5, 127.9, 51.9, 42.8, 42.1, 34.1, 31.6, 29.2, 22.7.

(*E*)-18. ^{1}H NMR (400 MHz) δ 6.05 (q, *J* = 2.3 Hz, 1 H), 5.76 (ddd, *J* = 15, 7.0, 0.9 Hz, 1 H), 5.64 (ddd, *J* = 15, 7.0, 0.9 Hz, 1 H), 4.54 (m, *J* = 6.8 Hz, 1 H, CH_3CH), 4.38 (m, 1 H CH_3CH), 4.29 (m, 1 H CH_3CH), 4.00 (dd, *J* = 9.0, 6.5 Hz, 1 H CH_3CH), 3.58 (dd, *J* = 8.5, 3.7 Hz, 1 H CH_3CH), 3.59 (m, 1 H CH_3CH), 1.60, (d, *J* = 6.7 Hz, 3 H, CH_3); ^{13}C NMR (100.5 MHz) δ 143.4, 134.3, 128.4, 110.8, 73.7, 70.3, 57.6, 45.7, 25.3.

(*Z*)-18. ^{1}H NMR (400 MHz) δ 5.81 (q, *J* = 2.5 Hz, 1 H), 5.75 (ddd, *J* = 15, 7.5, 0.8 Hz, 1 H), 5.54 (ddd, *J* = 15, 8.5, 1 Hz, 1 H), 4.53 (m, *J* = 6.5 Hz, 1 H, CH_3CH), 4.50 (m, 1 H), 4.42 (m, 1 H), 4.13 (dd, *J* = 8.5, 7.2 Hz, 1 H), 3.58 (t, *J* = 8.5 Hz, 1 H), 3.39 (qm, *J* = 8.5 Hz, 1 H), 1.61, (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (100.5 MHz) δ 144.6, 135.6, 128.4, 110.7, 74.0, 70.5, 56.9, 47.1, 25.2.

(*Z*)-α-(Chloromethylene)-β-((*E*)-3-chlorobut-1-en-1-yl)-γ-butyrolactone ((*Z*)-19). ^{1}H NMR (400 MHz) δ 6.55 (d, *J* = 2.5 Hz, 1 H, C=CHCl), 5.86 (dd, *J* = 15, 7.3 Hz, 1 H, CHClC*H*=CH), 5.62 (dd, *J* = 15, 7.9 Hz, 1 H, CH=C*H*), 4.55 (m, *J* = 6.8 Hz, 1 H, CH_3CHCl), 4.50 (t, *J* = 8.75 Hz, 1 H, C*H*H), 4.01 (dd, *J* = 8.75, 7.3 Hz, 1 H, CH*H*), 3.82 (qd, *J* = 8.2, 2.5 Hz, 1 H, C*H*C=CHCl), 1.63 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (100.5 MHz) δ 153.4, 137.5, 129.3, 127.1, 116.1, 69.4, 56.0, 43.9, 25.0.

(*E*)-α-(Chloromethylene) β-((*E*)-3-chlorobut-1-en-1-yl)-γ-butyrolactone ((*E*)-19). ^{1}H NMR (400 MHz) δ significant peaks: 6.86 (1 H), 5.44 (1 H), 4.40 (1 H), 4.33 (1 H), 3.45 (1 H), 1.77 (3 H).

(*Z*)-20' (monomer of **(*Z*)-20**).[10] ^{1}H NMR (400 MHz) δ 6.23 (app. t, *J* = 2.8 Hz, 1H), 5.77 (dt, *J* = 6.4, 0.8 Hz, 1H), 5.55 (app. t, *J* = 6.4 Hz, 1H), 5.03 (app. t, *J* = 6.4 Hz, 1H), 3.65 (s, 3 H, CH_3), 3.62 (s, 3 H, CH_3), 3.29-3.24 (m, 1H), 3.03-2.99 (m, 1H), 2.8 (td, *J* = 15.6, 1.6 Hz, 1H), 2.58 (mq, *J* = 8.4 Hz, 1H), 2.04-1.97 (m, 1H), 1.40 (app. q, *J* = 10.0 Hz, 1H,).

(*E*)-20' (monomer of **(*Z*)-20**).[10] ^{1}H NMR (400 MHz) δ 6.19 (td, *J* = 6.8, 6.4 Hz, 1H), 5.85 (dt, *J* = 6.4, 0.6 Hz, 1H), 5.20 (app. t, *J* = 6.4 Hz, 1H), 5.01 (app. t, *J* = 6.4 Hz, 1H), 3.65 (s, 3 H, CH_3), 3.63 (s, 3 H, CH_3), 3.23-3.19 (m, 1H), 2.98-2.97 (m, 1H), 2.97-2.92 (m, 1H), 2.44 (td, *J* = 7.2, 10.8 Hz, 1H), 1.96-1.88 (m, 1H), 1.26-1.16 (m, 1H).

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