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PAPER

Cycloisomerization of dienes and enynes catalysed by a modified ruthenium carbene species†

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Cycloisomerization is a totally atom economic procedure which converts dienes and enynes into cyclic molecules. Modification of Grubbs' 2nd generation catalysts by reaction with dimethylformamide provides a new species able to catalyse this transformation. Selection of suitable conditions allowed high yields and selectivity. Studies performed in order to identify the catalytic species point to a non-carbenic ruthenium complex that has lost the phosphine. No hydride signals appeared. In addition, the reaction works with enynes and the new species catalyses efficiently crossed cyclotrimerizations of alkynes with diynes.

Introduction

Non-metathetic transformations[1] are side reactions observed frequently when developing metathesis reactions catalysed by ruthenium alkylidene catalysts.[2] However, these alternative reactions, if optimized, may be useful transformations. Examples include oxidations, hydrosilylations of alkynes, hydrogenation of olefins, cyclopropanations, cycloaddition reactions and olefin isomerizations. We have shown recently the ability of second generation Grubbs' catalyst to mediate in a concurrent tandem catalysed triple process including RCM-isomerization and cyclopropanation.[3] This transformation is achieved by heating the reaction after the completion of the RCM. Upon heating, the catalyst is presumably transformed into another species, possibly a ruthenium hydride able to produce a shift of the double bond formed in the RCM and to mediate in the final cyclopropanation step with ethyl diazoacetate. Many times the key issue in directing a particular process either to a metathesis or to a different transformation is to modify the ruthenium species before or during the reaction. Thus, various groups have reported on thermal transformations of **[Ru]-I** and **[Ru]-II** leading to species able to produce olefin isomerization.[4] In addition, ruthenium hydrides can be obtained from **[Ru]-II** by reaction with methoxide or other additives. These hydrides mediate in double bond shifts,[5] reductions[6] and hydrovinylations.[7] During our studies devoted to identify the catalytic species and the mechanism of the tandem RCM-isomerization-cyclopropanation transformation, we have found that when heated in dimethylformamide (DMF), **[Ru]-II** can be transformed into a new species that produces cycloisomerization of dienes. Recently, Arisawa and Nishida developed the selective cycloisomerization of dienes by a combination of **[Ru]-II** and vinyloxytrimethylsilane. They identified hydride **A** as the catalytic species and applied this methodology to the synthesis of indoles (Fig. 1).[8]

Cycloisomerizations can be catalyzed by various transition metals, such as palladium, nickel, rhodium and some ruthenium complexes[9] like $[RuCl_2(p\text{-cymene})]_2$[10] or $[Ru(cod)Cl_2]_2$.[11] Development of convenient selective methodologies based on efficient and easy to handle catalysts for the cycloisomerization of dienes is highly desirable and herein we present our results in

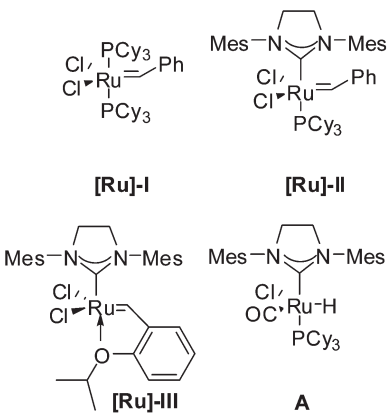

Fig. 1 Catalytic ruthenium species.

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the use of ruthenium species obtained by reaction of Grubb's catalysts and DMF in cycloisomerization reactions.

Results and discussion

Our initial aim was exploring different reaction conditions with diene **1a** (Table 1). Searching for RCM-isomerization products we explored the use of DMF as solvent. When performing a reaction at r.t., the metathesis product **3a** was isolated in 89% yield as the only reaction product detectable in the ^{1}H NMR spectrum (entry 1). Heating the reaction to 120 °C, after mixing all the components, provided a mixture of **3a**, its isomer **4a** and the cycloisomerization product **2a** (entry 2). In view of this result we decided to heat **[Ru]-II** for a short period of time and then add the diene continuing the reaction for 3 additional hours. Under these conditions (entry 3) conversion was low, but the major product was **2a** albeit in low yield (17%) jointly with 5% of **3a**. The finding of optimum conditions to obtain **2a** was achieved with a subtle combination of time for the modification of the catalyst, catalyst loading and concentration. Finally, the best conditions were those of entry 6, with 10 mol% of catalyst, 10 min. for the modification of the complex and a concentration of 0.27 mM. Under these conditions total conversion was achieved and a 72% of cycloisomerization product **2a** was isolated along with 7% of RCM product **3a**. A slight variation of these conditions (entry 7) allowed total selectivity towards **2a** (62% isolated yield) and a lower catalyst loading although without total conversion.

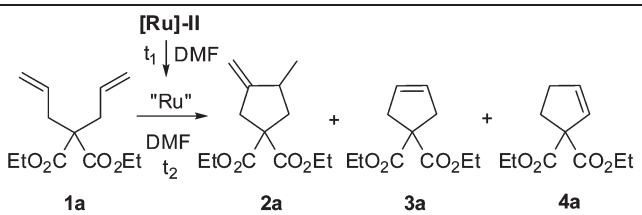
The ability of **[Ru]-I** and **[Ru]-III** to catalyse this reaction was checked next. As expected, due to its thermal instability **[Ru]-I** did not produce any identifiable product but an extensive decomposition of starting material (entry 10). On the other hand, **[Ru]-III** gave a mixture of RCM and RCM-isomerization products along with a small amount of cycloisomerization (entry 11). In an attempt to improve further the yields of this reaction avoiding the presumable decomposition of starting materials due to the high temperatures and with the aim to decrease the amount of DMF needed, we studied the possibility of carrying out the second part of the reaction in toluene. Thus, after modifying the complex in DMF (5 mL per mmol) a solution of the diene in toluene was added, reaching the optimized concentration, and reacted at reflux temperature (entry 12). To our delight the yield of **2a** became excellent under these conditions (91%) and the reaction was completed after 30 min.

Once the feasibility of performing a selective cyloisomerization was proved, we studied the scope of the reaction with different 1,5-dienes using the conditions of entry 12 in Table 1. Results are summarized in Table 2.

The reaction gave excellent results with dienes **1b–d** (entries 1–3). Protected amino groups were tolerated, giving tosyl derivative **1e** good yields of cycloisomerization product **2e** with a small amount of its thermodynamically stable isomer **2e′** (90% yield jointly, entry 4). However, the parent BOC derivative **1f** produced only 36% yield of **2f**, and a double bond isomerization reaction was the major process and a (7 : 3) mixture of **5f** + **5f′** was isolated in 40% yield (entry 5). The cycloisomerization of amide **1g** gave a mixture of the two possible lactams **2g** and **2g′** in good global yield (57%, entry 6). On the other hand, a double bond shift was the only process observed with sulfone **1h** (entry 7).

The extension of the reaction to larger rings seem to be precluded as compound **6** gave only a 38% of a isomerization–cycloisomerization 5 membered-ring product **9**. In addition, we

Table 1 Study of the cycloisomerization conditions[a]



Entry	Cat. (mol%)	Conc **1a** (mM)	t_1 (min)	t_2 (h)	Conv.	Yield[b] (%) **2a**	**3a**	**4a**
1	5 **[Ru]-II**	0.10	3 h at r.t.		100	n.d.	89	n.d.
2	10 **[Ru]-II**	0.10	3 h at 120 °C		100	10	50	16
3	5 **[Ru]-II**	0.10	3	3	15	17	5	n.d.
4	5 **[Ru]-II**	0.27	30	3	37	26	n.d.	n.d.
5	10 **[Ru]-II**	0.15	5	3	100	40	15	32
6	10 **[Ru]-II**	0.27	10	3	100	72	7	n.d.
7	7.5 **[Ru]-II**	0.27	5	3	85	62	n.d.	n.d.
8	10 **[Ru]-II**	0.44	5	3	95	59	7	n.d.
9	10 **[Ru]-II**	0.36	7.5	3	100	57	15	6
10	10 **[Ru]-I**	0.27	7.5	3	100	n.d.	n.d.	n.d.
11	10 **[Ru]-III**	0.27	7.5	3	100	4	47	44
12	10 **[Ru]-II**	0.27	12	0.5(tol)	100	91	6	n.d.

[a] Reactions were carried out in anhydrous DMF (except entry 12, see text) at 120 °C except otherwise indicated and under inert atmosphere. [b] Yields in pure products. n.d. = not detected.

Table 2 Cycloisomerization reactions of dienes **1b–h**, **6** and enynes **10a–b**[a]

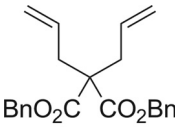
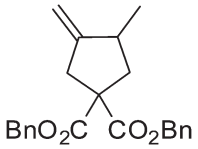
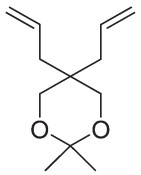
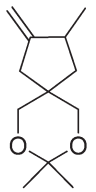
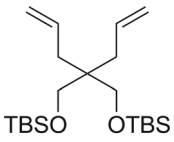
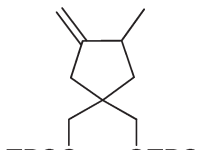
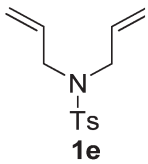
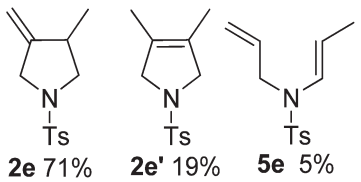
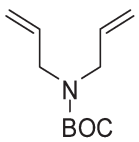
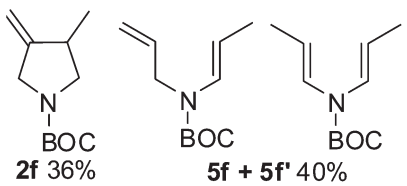
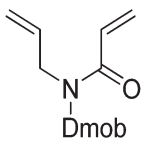
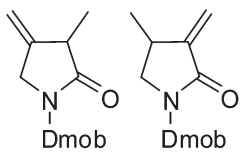
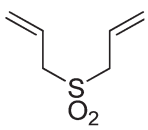
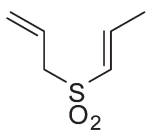
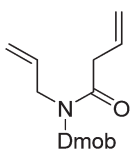
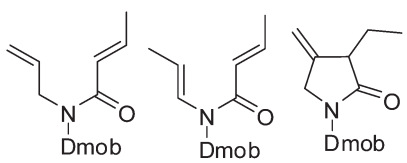
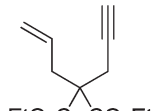
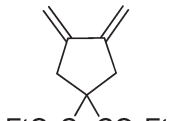
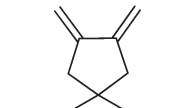
No.	Reagents	t_2	Products and yields[b] (%)
1	 **1b**	16 h	 **2b** 93%
2	 **1c**	25 min	 **2c** 66%
3	 **1d**	45 min	 **2d** 88%
4	 **1e**	20 min	 **2e** 71% **2e'** 19% **5e** 5%
5	 **1f**	1 h	 **2f** 36% **5f + 5f'** 40%
6	 **1g**	16 h	 **2g** 45% **2g'** 12%
7	 **1h**	3 h	 **5h** 90%
8	 **6**	16 h	 **7** 15% **8** 35% **9** 38%

Table 2 *(Contd.)*

No.	Reagents	t_2	Products and yields[b] (%)
9	 **10a**	20 min	 **11a** 80%
10	 **10b**	20 min	 **11b** 63%

[a] Reaction conditions: **Ru-[II]** (10 mol%) in DMF at 120 °C for 12 min then a solution of the substrate in toluene was added and refluxed. [b] Yields in pure products. Bn = benzyl; Dmob = 2,4-dimethoxybenzyl.

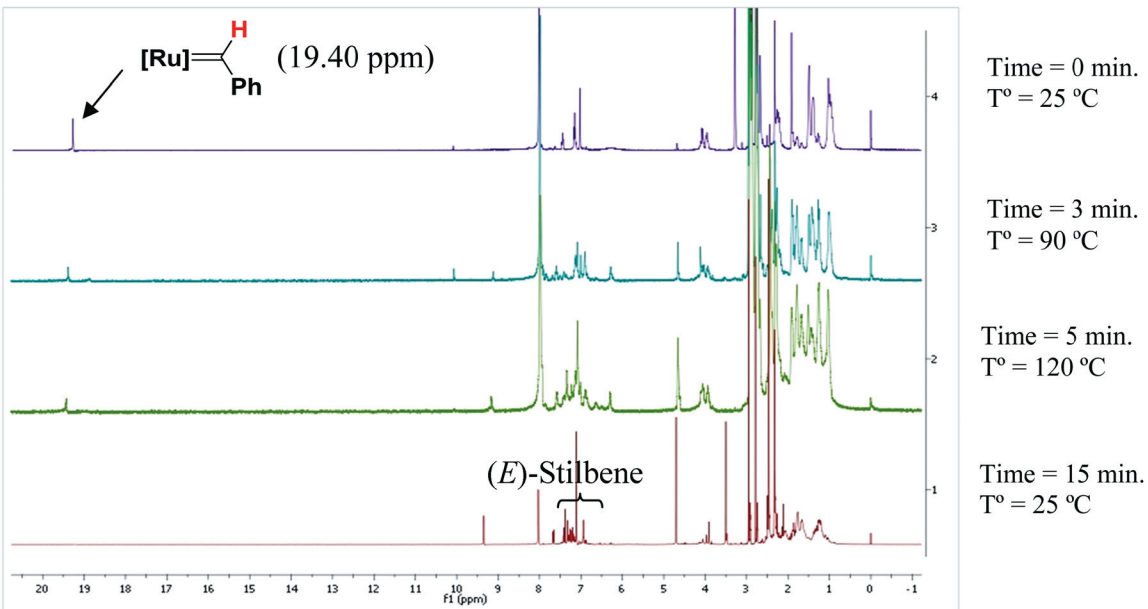


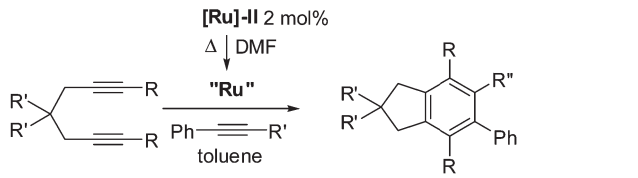
Fig. 2 ^{1}H NMR spectra of the reaction of **[Ru]-II** in DMF-d_7.[14]

obtained mixtures of two isomers of the starting material, **7** and **8**, that were separated and are formed upon one or two double bond shifts respectively. On the other hand, we studied the behavior of enynes **10a–b** under the same reaction conditions. Interestingly, these substrates were transformed into **11a–b** as the only reaction products (80 and 63% respectively).[12]

Next we dedicated our efforts to try to identify the catalytic species formed upon the reaction of **[Ru]-II** with DMF. Thus, we performed ^{31}P, ^{1}H and ^{13}C NMR spectra of the ruthenium species before and after reaction with DMF and we also followed the transformation of the complex by ^{1}H NMR (Fig. 2).[13] From these spectra,[14] we observed the disappearance of the carbenic signal at 19.4 ppm as well as the signals corresponding to the phenyl group. At the same time (*E*)-stilbene appeared in the spectrum. After 15 min a new broad singlet at 9.18 ppm appeared corresponding to an imidazolinium salt. No ruthenium hydride species were detected. NMR measurements were conducted down to −35 ppm to check the possible presence of ruthenium hydrides which were not detected. In addition, the ^{31}P spectra showed the loss of the ^{31}P signal at 30 ppm while a signal at 50 ppm corresponding to $P(O)Cy_3$ appeared (see ESI†). From these data it can be presumed that the catalyst suffers successive loss of the phosphine and the benzylidene moieties. It is possible that the vacancies left are occupied by DMF molecules creating complexes similar to those described in the literature.[15] At the end of the process the species is totally decomposed and the only product isolated is an imidazolinium salt (9.18 ppm),[16] produced from the NHC ligand. The catalytic species could be an unstable complex formed along the process. Upon extraction of aliquots after 7 and 15 min of the catalyst modification

process we recorded sluggish ^{1}H- and ^{13}C-NMR spectra (see Fig. 2 and ESI†) and the IR spectra showed absorptions around 1630 cm^{-1} plus one absorption at 1947 cm^{-1} which may correspond to a CO ligand bonded to ruthenium[15] which would come from thermal decomposition of DMF into CO and dimethylamine. MS spectra at 7 min showed a peak at 1002 which suggests a dimeric nature of an intermediate complex. This hypothetical structure could be similar to the ones described by Grubbs in the studies on the thermal decomposition of **[Ru]-II** and other ruthenium-based carbenic catalysts.[17] If the mixture is analysed after 15 min it becomes more complex and we can see peaks at 1298, 1669 and 1882. Unfortunately, we were not able to isolate a pure sample of the active species. Attempts to separate it from imidazolinium salts phosphine oxides and other subproducts led to extensive decomposition. The inability of the new species to catalyse metathesis whereas it is capable to produce both cycloisomerization and double bond shifts means a transformation into one or more active catalysts possibly with a short life. The preference for each process seems to be related mainly to the structure of the substrate.

Following our recent results in the use of ruthenium carbenes in cyclotrimerization reactions of alkynes,[18] we checked the ability of the new species to promote this transformation. In Scheme 1 three crossed-cyclotrimerization reactions are shown between diynes **12a–b** and phenylacetylene or 1-phenylpropyne. The reaction was highly efficient even when constructing sterically crowded products as **13c**. As the cyclotrimerization reaction catalysed by ruthenium complexes is presumed to proceed through a cascade metathesis mechanism, this result opens the possibility of a different reaction pathway with this complex, possibly related with that observed with other metal complexes used in cyclotrimerization reactions.



Scheme 1 Crossed-ciclotrimerization reactions of **12a–b** catalysed by the modified ruthenium species.

Conclusions

In summary, second generation Grubb's catalyst has been modified by reaction with DMF. We have shown the ability of the new species to catalyse several isomerization reactions with dienes, enynes and diynes. Extension of this methodology to more substrates and further studies on this topic are currently underway. Funding of this project by Spanish MEC (No. CTQ2009-07738/BQU) is acknowledged. A.M. and S.M. thank FUSP-CEU for a pre-doctoral fellowship.

Experimental section

General procedures

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were acquired on Bruker AM-300, Bruker AV400 and Bruker AVIII 700 spectometers. Chemical shifts(TM) are in parts per million relative to tetramethylsilane at 0.00 ppm. IR spectra were determined by a FT-IR Perkin-Elmer 2000 spectrometer. TLC analyses were performed on commercial aluminium sheets bearing 0.25 mm layer of Silica gel. Silica gel 0.035–0.070 mm, 60 Å was used for column chromatography. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased and used without further purification. Hexane and toluene were refluxed over calcium hydride. All reactions were conducted under argon atmosphere.

Preparation of starting materials

Products **1a**,[19] **1b**,[19] **1c**,[20] **1d**,[20] **1e**,[21] **1f**,[21] **1g**,[3] **1h**,[22] **6**,[3] **10a**,[23] and **12a**[24] were prepared according to the reported procedures. Compounds **3a**,[25] **4a**,[26] **5e**[27] have already been described and matched with the bibliography data.

Preparation of 6-allyl-2,2,3,3,9,9,10,10-octamethyl-6-(prop-2-ynyl)-4,8-dioxa-3,9-disilaundecane (10b). 2-Allyl-2-(prop-2-ynyl)propane-1,3-diol[28] (400.0 mg, 2.6 mmol), TBSCl (1.70 g, 10.4 mmol) and imidazol (884.0 mg, 13.0 mmol) were dissolved in anhydrous DMF (13 mL) and the reaction was conducted under argon for 2 h at r.t. A mixture of water–ice (30 mL) and diethyl ether (30 mL) was added and the organic layer was extracted, washed with water (5 × 10 mL), brine (3 × 10 mL), dried with $MgSO_4$ and the solvent was evaporated. The resulting oil was purified by performing a silica gel chromatography (hexane, R_f = 0.88 in hexane) obtaining **10b** (862 mg, 2.25 mmol, 87%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.60 (m, 1H, *CH*=CH_2), 5.08–5.01 (m, 2H, CH=*CH*$_2$), 3.41–3.34 (m, 4H, 2 × CH_2O), 2.08–2.06 (m, 4H, 2 × CH_2), 1.89 (t, J = 2.6 Hz, 1H, C≡*CH*), 0.85 (s, 18H, 2 × $C(CH_3)_3$), 0.00 (s, 12H, 2 × $(CH_3)_2Si$)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 117.8, 81.7, 69.8, 63.6, 43.3, 35.1, 25.9, 21.0, 18.3, −5.6; IR (neat) 3077, 2955, 2930, 2858, 1640 cm^{-1}; Anal. Calcd for $C_{21}H_{42}O_2Si_2$: C, 65.90; H, 11.06. Found: C, 66.04; H, 11.18.

Preparation of dibenzyl 2,2-di(but-2-ynyl)malonate (12b). Over a suspension of NaH (288.2 mg, 12.0 mmol) in anhydrous THF (20 mL) at 0 °C and under argon, a solution of dibenzyl malonate[29] (1.36 g, 4.80 mmol) in anhydrous THF (5 mL) was added and the mixture was heated to r.t. and stirred for 30 min. 1-Bromobut-2-yne (1.40 g, 10.6 mmol, 0.95 mL) was added and the reaction was stirred at r.t. until no more starting material was observed (TLC). Water (20 mL) was slowly added and the crude was extracted with DCM (3 × 40 mL). The organic layers were dried with $MgSO_4$, organic solvents were evaporated and the resulting oil was purified by performing a silica gel chromatography (Hex–AcOEt 9 : 1, R_f = 0.57 in Hex–AcOEt 4 : 1) obtaining **12b** (1.27 g, 3.26 mmol, 68%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.25 (m, 10H, 2 × Ar), 5.13 (s, 4H, 2 × Ar–CH_2O), 2.94 (d, J = 2.5 Hz, 4H, 2 × *CH*$_2$C≡CCH$_3$), 1.67 (t, J = 2.5 Hz, 6H, 2 × CH_2C≡C*CH*$_3$); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 169.0, 135.4, 128.5, 128.2, 128.1, 79.2, 73.1, 67.3, 57.3, 23.0, 3.5; IR (neat) 3034, 2957, 2921, 1740, 1607, 1587, 1498 cm^{-1}; Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77,13; H, 6.16.

General procedure for cycloisomerization reaction

Catalyst **[Ru]-II** (36 mg, 0.042 mmol) was placed in a flame-dried two-necked flask equipped with a condenser, and two cycles of vacuum-argon were performed. Anhydrous DMF (0.2 mL) was added and the suspension was heated at 120 °C for 12 min. The dark solution was cooled to r.t., anhydrous toluene (0.9 mL) was added followed by the addition of diene (0.42 mmol) in anhydrous toluene (1 mL). The mixture was gently refluxed until no more starting material was detected (TLC), cooled to r.t., filtered through Celite and solvents were removed under reduced pressure. The resulting dark-brown oil was purified by flash chromatography.

Diethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2a).[29] Following general procedure for cycloisomerization, starting with **1a** (100 mg, 0.416 mmol) after 25 min **2a** was obtained after silica gel chromatography (Hex–AcOEt 49 : 1, R_f = 0.63 in Hex–AcOEt 9 : 1) as a colorless oil (91 mg, 0.38 mmol, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (d, J = 2.0 Hz, 1H, C=CHa), 4.80 (d, J = 2.1 Hz, 1H, C=CHb), 4.19 (q, J = 7.2 Hz, 2H, CO_2CH_2CH3), 4.18 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 3.08–2.90 (m, 2H, $CO_2CCH_2C{=}CH_2$), 2.57–2.51 (m, 2H, CO_2CCH_2CH), 1.80–1.70 (m, 1H, CO_2CCH_2-*CH*), 1.25 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 1.24 (t, J = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.11 (d, J = 6.1 Hz, 3H, CCH_3); Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.14; H, 8.47.

Dibenzyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2b). Following general procedure for cycloisomerization, starting with **1b** (100 mg, 0.27 mmol) after 16 h **2b** was obtained after silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.53 in Hex–AcOEt 9 : 1) as a colorless oil (93 mg, 0.25 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 10H, Ar), 5.11 (s, 2H, Ar–CH_2O), 5.11 (s, 2H, Ar–CH_2O), 4.90 (d, J = 2.1 Hz, 1H, C=CHa), 4.79 (d, J = 2.2 Hz, 1H, C=CHb), 3.11–2.93 (m, 2H, $CO_2CCH_2C{=}CH_2$), 2.63–2.53 (m, 2H, CO_2CCH_2CH), 1.83–1.74 (m, 1H, CO_2CCH_2CH), 1.09 (d, J = 6.3 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 171.9, 153.5, 135.9, 128.9, 128.6, 128.3, 106.1, 67.6, 67.5, 58.8, 42.5, 41.0, 37.6, 18.4; IR (neat) 3067, 3034, 2961, 2932, 2873, 1733, 1659 cm^{-1}; Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.72; H, 6.54.

2,8,8-Trimethyl-3-methylidene-7,9-dioxaspiro[4.5]decane (2c).[20] Following general procedure for cycloisomerization, starting with **1c** (100 mg, 0.509 mmol) after 25 min **2c** was obtained after silica gel chromatography (Hex–AcOEt 49 : 1, R_f = 0.45 in Hex–AcOEt 9 : 1) as a colorless oil (66 mg, 0.33 mmol, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.86 (s, 1H, C=CH_2), 4.78 (s, 1H, C=CH_2), 3.64–3.55 (m, 4H, 2 × CH_2O), 2.54–2.46 (m, 1H, $CHCH_3$), 2.42–2.17 (m, 2H, $CH_2C{=}CH_2$), 1.99 (dd, 1H, J_1 = 13.0 Hz, J_2 = 8.2 Hz, CH_2CHCH_3), 1.43 (s, 3H, CH_3C), 1.42 (s, 3H, CH_3C), 1.08 (d, J = 6.7 Hz, 3H, CH_3CH), 1.03 (dd, J_1 = 12.8 Hz, J_2 = 10.5 Hz, 1H, CH_2CHCH_3); Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.61; H, 10.12.

(3-Methyl-4-methylenecyclopentane-1,1-diyl)bis(methylene)bis-(oxy)bis(*tert*-butyldimethylsilane) (2d).[20] Following general procedure for cycloisomerization, starting with **1d** (100 mg, 0.26 mmol) after 45 min **2d** was obtained after silica gel chromatography (hexane, R_f = 0.50 in hexane) as a colorless oil (88 mg, 0.23 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (s, 1H, C=CH_2), 4.69 (s, 1H, C=CH_2), 3.41–3.33 (m, 4H, 2 × CH_2O), 2.49–2.45 (m, 1H, $CHCH_3$), 2.14 (s, 2H, $CH_2C{=}CH_2$), 1.79 (dd, 1H, J_1 = 12.9 Hz, J_2 = 8.3 Hz, CH_2CHCH_3), 1.08 (d, J = 6.7 Hz, 3H, CH_3CH), 0.97 (dd, J_1 = 12.8 Hz, J_2 = 10.5 Hz, 1H, CH_2CHCH_3), 0.86 (s, 18H, 2 × $C(CH_3)_3$), 0.00 (s, 12H, 2 × $(CH_3)_2Si$)); Anal. Calcd for $C_{21}H_{44}O_2Si_2$: C, 65.56; H, 11.53. Found: C, 65.69; H, 11.64.

3-Methyl-4-methylene-1-[(4-methylphenyl)sulfonyl]pyrrolidine (2e).[30] Following general procedure for cycloisomerization, starting with **1e** (100 mg, 0.398 mmol) after 20 min and purification through silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.29 for **2e** and R_f = 0.24 for **2e′**, both in Hex–AcOEt 9 : 1) **2e** (71 mg, 0.282 mmol, 71%) was obtained as a white solid (Mp: 60–63 °C) and **2e′** (19 mg, 0.075 mmol, 19%) as a white solid (Mp: 152–156 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H, Ar), 7.34 (d, J = 8.3 Hz, 2H, Ar), 4.91 (d, J = 1.5 Hz, 1H, C=CHa), 4.85 (d, J = 1.9 Hz, 1H, C=CHb), 3.96 (d, J = 13.7 Hz, 1H, $NCHaC{=}CH_2$), 3.73 (d, J = 14.2 Hz, 1H, $NCHbC{=}CH_2$), 3.58 (m, 1H, NCH_2CH), 2.72–2.67 (m, 2H, NCH_2CH), 2.44 (s, 3H, CH_3–Ar), 1.04 (d, J = 5.9 Hz, 3H, CH_3); Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.00; H, 6.93; N, 5.41.

3,4-Dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (2e′).[31] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 3.97 (s, 4H, 2 × NCH_2C), 2.42 (s, 3H, CH_3–Ar), 1.54 (s, 6H, 2 × CH_3); Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.03; H, 6.65; N, 5.44.

***tert*-Butyl 3-methyl-4-methylenepyrrolidine-1-carboxylate (2f)**[21]**.** Following general procedure for cycloisomerization, starting with **1f** (100 mg, 0.398 mmol) after 1 h and purification through silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.36 for **2f** and R_f = 0.67 for **5f** + **5f′**, both in Hex–AcOEt 4 : 1) **2f** (36 mg, 0.18 mmol, 36%) and **5f** + **5f′** (70 : 30, 40 mg, 0.202 mmol, 40%) were obtained as colorless oils. Data for **2f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.95 (bs, 1H, C=CH*a*), 4.89 (q, 1H, J = 2.3 Hz, C=CHb), 3.98 (q, J = 9.6 Hz, 2H, $NCH_2C{=}CH_2$), 3.78–3.61 (m, 1H, NCH_2CH), 2.91 (t, J = 9.2 Hz, 1H, $NCHaCH$), 2.79–2.63 (m, 1H, $NCHbCH$), 1.47 (s, 9H, 3 × CH_3), 1.12 (d, J = 6.7 Hz, 3H, $CHCH_3$); Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 67.05; H, 9.58; N, 7.01.

Data for (*E*)-*tert*-butyl allyl(prop-1-enyl)carbamate, (5f) and *tert*-butyl di(*E*)-prop-1-enylcarbamate, (5f′). ^{1}H NMR (300 MHz, $CDCl_3$) δ: **5f**, 6.70 (d, J = 13.6 Hz, 1H, $CH{=}CHCH_3$), 5.75–5.62 (m, 1H, $CH_2CH{=}CH_2$), 5.06–4.99 (m, 2H, $CH_2CH{=}CH_2$), 4.83–4.69 (m, 1H, $CH{=}CHCH_3$), 4.00 (bs, 2H, $CH_2CH{=}CH_2$), 1.63 (dd, J_1 = 6.7 Hz, J_2 = 1.6 Hz, 3H,

CH═CHCH_3), 1.41 (s, 9H, C(CH_3)$_3$); **5f′**, 6.22 (d, J = 14.1 Hz, 2H, 2 × CH═CHCH_3), 5.31–5.19 (m, 2H, 2 × CH═CHCH$_3$), 1.60 (d, J = 6.6 Hz, 6H, 2 × CH═CHCH_3), 1.41 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 133.1, 127.8, 127.0, 115.7, 115.2, 103.6, 81.0, 80.8, 46.5, 28.3, 15.4, 15.2.

1-(2,4-Dimethoxybenzyl)-3-methyl-4-methylidenepyrrolidin-2-one (2g). Following general procedure for cycloisomerization, starting with **1g** (100 mg, 0.383 mmol) after 16 h and purification through silica gel chromatography (Hex–AcOEt 4 : 1, R_f = 0.60 for **2g** and R_f = 0.55 for **2g′**, both in Hex–AcOEt 1 : 1) **2g** (45 mg, 0.17 mmol, 45%) and **2g′** (12 mg, 0.045 mmol, 12%) were obtained as pale yellow oils. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, J = 8.8 Hz, 1H, Ar), 6.46–6.44 (m, 2H, Ar), 5.03–5.00 (m, 2H, C═CH_2), 4.48 (s, 2H, CH_2Ar), 3.90–3.77 (m, 2H, NCH_2C═CH_2), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.05 (q, J = 7.3 Hz, 1H, CHCH$_3$), 1.32 (d, J = 7.3 Hz, 3H, CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 160.8, 159.0, 144.6, 131.2, 117.1, 108.0, 104.5, 98.7, 55.7, 55.7, 51.6, 41.8, 40.7, 15.8; IR (neat) 2924, 2851, 1711, 1649, 1615, 1589 cm^{-1}; Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.03; H, 7.24; N, 5.33.

1-(2,4-Dimethoxybenzyl)-4-methyl-3-methylidenepyrrolidin-2-one (2g′). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 8.8 Hz, 1H, Ar), 6.47–6.43 (m, 2H, Ar), 6.00 (d, J = 2.4 Hz, 1H, C═CHa), 5.27 (d, J = 2.4 Hz, 1H, C═CHb), 4.56 (d, J = 14.6 Hz, 1H, CHaAr), 4.48 (d, J = 14.6 Hz, 1H, CHbAr), 3.81 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.45 (t, J = 7.8 Hz, 1H, NCHaC═CH_2), 2.92–2.80 (m, 2H, NCHbC═CH_2 & NCH_2CH), 1.18 (d, J = 6.4 Hz, 3H, CHCH_3); IR (neat) 2921, 2858, 1645, 1589, 1507 cm^{-1}; Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.79; H, 7.40; N, 5.25.

(1*E*)-1-(prop-2-en-1-ylsulfonyl)prop-1-ene (5h).[32] Following general procedure for cycloisomerization, starting with **1h** (100 mg, 0.68 mmol) after 3 h was obtained after silica gel chromatography (Hex–AcOEt 4 : 1, R_f = 0.43 in Hex–AcOEt 2 : 1) **5h** (90 mg, 0.61 mmol, 90%) was obtained as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96–6.82 (m, 1H, CHCH$_3$), 6.30 (apparent dd, J_1 = 15.1 Hz, J_2 = 1.6 Hz, 1H, SO_2CH═CH), 5.94–5.88 (m, 1H, CH_2CH═CH_2), 5.51 (d, J = 10.2 Hz, 1H, CH_2CH═CH_2), 5.44 (d, J = 17.0 Hz, 1H, CH_2CH═CH_2), 3.71 (*AB system*, 2H, CH_2CH═CH_2), 1.97 (dd, J_1 = 6.7 Hz, J_2 = 1.6 Hz, 3H, CH═CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 128.6, 124.9, 124.4, 59.4, 17.4. IR (neat) 2975, 2922, 1640 cm^{-1}; Anal. Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89. Found: C, 49.38; H, 6.80.

1-(2,4-Dimethoxybenzyl)-3-ethyl-4-methylenepyrrolidin-2-one (9). Following general procedure for cycloisomerization, starting with **6** (100 mg, 0.68 mmol) after 16 h **9** was obtained after silica gel chromatography (Hex–AcOEt 6 : 1 to 2 : 1, R_f = 0.23 in Hex–AcOEt 2 : 1) (38 mg, 0.25 mmol, 38%) as a brown oil and 55 mg of a mixture of **7** + **8** which was separated by column chromatography (Hex–AcOEt 6 : 1) to give 15 mg of **7** (15%) and 35 mg of **8** (35%) as colorless oils. Data for **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J = 9.1 Hz, 1H, Ar), 6.46–6.42 (m, 2H, Ar), 5.05–5.01 (m, 2H, C═CH_2), 4.57 (d, J = 14.5 Hz, 1H, CHaAr), 4.39 (d, J = 14.6 Hz, 1H, CHbAr), 3.82–3.67 (m, 2H, NCH_2C═CH_2), 3.80 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.03 (bs, 1H, COCH), 1.93–1.72 (m, 2H, CHCH_2CH$_3$), 0.89 (t, J = 7.3 Hz, 3H, CHCH$_2$$CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 160.6, 158.7, 142.1, 130.9, 116.9, 108.3, 104.3, 98.4, 55.4 (2 × C), 51.6, 47.7, 40.4, 24.0, 9.7; IR (neat) 2962, 2930, 2854, 1693, 1663, 1613, 1589 cm^{-1}; Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.89; H, 7.72; N, 5.03.

Data for (*E*)-*N*-allyl-*N*-(2,4-dimethoxybenzyl)but-2-enamide, (7). ^{1}H NMR (300 MHz, DMSO-d_6, 80 °C) δ 6.99 (d, J = 8.4 Hz, 1H, Ar), 6.75–6.65 (m, 1H, CH═CHCH$_3$), 6.56 (d, J = 2.3 Hz, 1H, Ar), 6.49 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H, Ar), 6.36 (dd, J_1 = 14.9 Hz, J_2 = 1.5 Hz, 1H, CH═CHCH$_3$), 5.78–5.71 (m, 1H, CH_2CH═CH_2), 5.11–5.04 (m, 2H, CH_2CH═CH_2) 4.44 (s, 2H, ArCH_2N), 3.92 (*AB system*, 2H, CH_2CH═CH_2), 3.79 (s, 3H, OMe), 3.76 (s, 3H, OMe), 1.83 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 2 conformers δ 167.1, 160.4, 160.2, 158.0, 141.8, 141.8, 133.5, 133.4, 130.6, 127.9, 122.1, 117.5, 117.0, 116.3, 104.3, 103.9, 98.6, 98.3, 55.4, 55.2, 49.6, 48.2, 45.4, 43.2, 18.2;

Data for (*E*)-*N*-(2,4-dimethoxybenzyl)-*N*-((*E*)-prop-1-enyl)but-2-enamide, (8). ^{1}H NMR (300 MHz, DMSO-d_6, 80 °C) δ 6.96 (d, J = 13.6 Hz, 1H, NCH═CHCH$_3$), 6.83–6.75 (m, 1H, CH═CHCH$_3$), 6.77 (d, J = 10.9 Hz, 1H, CH═CHCH$_3$), 6.57 (d, J = 2.4 Hz, 1H, Ar), 6.47 (d, J = 8.4 Hz, 1H, Ar), 6.49 (dd, J_1 = 8.4 Hz, J_2 = 2.5 Hz, 1H, Ar), 5.01–4.90 (m, 1H, NCH═CHCH$_3$), 4.68 (s, 2H, ArCH_2N), 3.82 (s, 3H, OMe), 3.75 (s, 3H, OMe), 1.85 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 3H, CH$_3$), 1.62 (dd, J_1 = 6.6 Hz, J_2 = 1.6 Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 2 conformers δ 169.8, 157.7, 157.3, 143.3, 129.3, 127.2, 126.8, 122.2, 117.7, 116.8, 110.6, 107.1, 104.1, 98.4, 55.4, 55.3, 44.2, 18.3, 15.5.

Diethyl 3,4-dimethylenecyclopentane-1,1-dicarboxylate (11a)[33]**.** Following general procedure for cycloisomerization, starting with **10a** (100 mg, 0.42 mmol) after 20 min **11a** (80 mg, 0.34 mmol, 80%) was obtained after silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.42 in Hex–AcOEt 6 : 1) as pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (s, 2H, 2 × C═CHa), 4.95 (s, 2H, 2 × C═CHb), 4.19 (q, J = 7.2 Hz, 4H, 2 × OCH_2CH$_3$), 3.03 (s, 4H, 2 × CCH$_2$C), 1.24 (t, J = 7.0 Hz, 6H, 2 × OCH$_2$$CH_3$); Anal. Calcd for $C_{13}H_{18}NO_4$: C, 65.53; H, 7.61. Found: C, 65.42; H, 7.53.

(3,4-Dimethylenecyclopentane-1,1-diyl)bis(methylene)bis(oxy)-bis(*tert*-butyldimethylsilane) (11b). Following general procedure for cycloisomerization, starting with **10b** (100 mg, 0.26 mmol) after 20 min **11b** (63 mg, 0.16 mmol, 63%) was obtained after silica gel chromatography (hexane, R_f = 0.62 in hexane) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (s, 2H, C═CH_2), 4.83 (s, 2H, C═CH_2), 3.39 (s, 4H, 2 × CH_2O), 2.26 (s, 4H, 2 × CH_2), 0.87 (s, 18H, 2 × C(CH_3)$_3$), 0.00 (s, 12H, 2 × (CH_3)$_2$Si)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 104.6, 64.7, 47.0, 38.6, 25.9, 18.3, −5.5; IR (neat) 2955, 2930, 2857, 1676 cm^{-1}; Anal. Calcd for $C_{21}H_{42}O_2Si_2$: C, 65.90; H, 11.06. Found: C, 65.73; H, 11.19.

General procedure for cyclotrimerization reaction

Catalyst **[Ru]-II** (7.2 mg, 0.008 mmol) was placed in a flame-dried two-necked flask equipped with a condenser, and two cycles of vacuum-argon were performed. Anhydrous DMF (0.2 mL) was added and the suspension was heated at 120 °C for 12 min. The dark solution was cooled to r.t., anhydrous toluene (0.9 mL) was added followed by the addition of a mixture of diyne (0.42 mmol) and monoyne (1.27 mmol) in anhydrous toluene (1.5 mL). The reaction was gently refluxed until no more starting material was detected (TLC), cooled to r.t., filtered through Celite and solvents were removed under reduced pressure. The resulting dark-brown oil was purified by flash chromatography.

Diethyl 5-phenyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (13a)[34]. Following general procedure for cyclotrimerization, starting with **12a** (100 mg, 0.42 mmol) after 24 h **13a** (124.5 mg, 0.37 mmol, 87%) was obtained after silica gel chromatography (Hex–AcOEt 49 : 1 to 20 : 1, R_f = 0.37 in Hex–AcOEt 9 : 1) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H, Ar), 7.42–7.37 (m, 4H, Ar), 7.33–7.23 (m, 2H, Ar), 4.21 (q, J = 7.1 Hz, 4H, 2 × OCH_2CH$_3$), 3.64 (s, 2H, H-3), 3.63 (s, 2H, H-1), 1.26 (t, J = 7.1 Hz, 6H, 2 × OCH$_2$$CH_3$); Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.37; H, 6.63.

Dibenzyl 4,7-dimethyl-5-phenyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (13b). Following general procedure for cyclotrimerization, starting with **12b** (100 mg, 0.259 mmol) after 24 h **13b** was obtained after silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.38 in Hex–AcOEt 9 : 1) (105.4 mg, 0.21 mmol, 83%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 16H, Ar), 5.15 (s, 4H, 2 × ArCH$_2$O), 3.61 (s, 4H, H-1 & H-3), 2.22 (s, 3H, CH$_3$–C4), 2.10 (s, 3H, CH$_3$–C7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 142.0, 141.1, 139.3, 137.5, 135.5, 130.6, 130.0, 129.4, 128.6, 128.3, 128.0, 126.6, 67.4, 59.9, 40.3, 39.7, 18.6, 16.7; IR (neat) 3033, 2950, 2920, 1733, 1600 cm^{-1}; Anal. Calcd for $C_{33}H_{30}O_4$: C, 80.79; H, 6.16. Found: C, 80.6 3; H, 6.39.

Dibenzyl 4,5,7-trimethyl-6-phenyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (13c). Following general procedure for cyclotrimerization, starting with **12b** (100 mg, 0.259 mmol) after 24 h **13c** was obtained after silica gel chromatography (Hex–AcOEt 20 : 1, R_f = 0.44 in Hex–AcOEt 9 : 1) (92.3 mg, 0.18 mmol, 71%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2H, Ar), 7.33–7.22 (m, 11H, Ar), 7.10–7.07 (m, 2H, Ar), 5.14 (s, 4H, 4H, 2 × ArCH$_2$O), 3.66 (s, 2H, H-3), 3.60 (s, 3H, H-1), 2.17 (s, 3H, CH$_3$), 1.90 (s, 3H, CH$_3$), 1.85 (s, 3H, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 142.0, 141.2, 137.4, 135.8, 135.5, 133.5, 129.5, 129.4, 128.9, 128.5, 128.3, 128.3, 128.0, 126.4, 67.4, 59.6, 40.4, 40.2, 17.4, 17.3, 16.4; IR (neat) 3063, 3033, 2924, 1733, 1601 cm^{-1}; Anal. Calcd for $C_{34}H_{32}O_4$: C, 80.93; H, 6.39. Found: C, 80.78; H, 6.37.

Notes and references

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