Cycloadditions of Bifunctional Vinyl Ethers with Electrophilic Alkenes through Tetramethylene Zwitterion Intermediates

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Dedicated to Professor *Rolf Huisgen* on the happy occasion of his 85th birthday

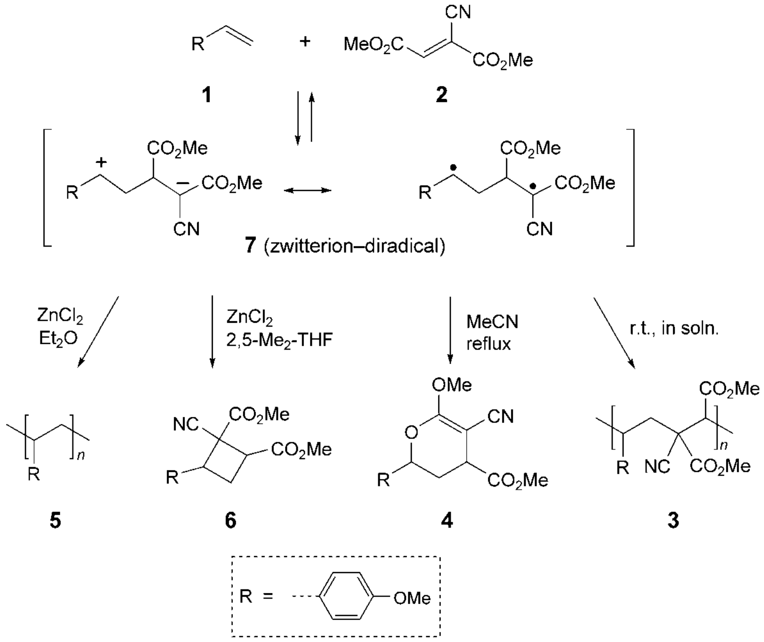
Bifunctional vinyl ethers react with electron-poor alkenes to cyclobutanes in good yields. The second C=C bond reacted with neither the cyclobutane nor its zwitterion intermediate, even on heating. Cyclobutanes formed from 'tetracyanoethylene' (**8**) were transformed into tetrahydropyridines by reaction of the corresponding zwitterion with MeCN as the solvent. In contrast, cyclobutanes formed from dimethyl (dicyanomethylidene)propanedioate (**9**) did not react with MeCN, which is ascribed to diminished stabilization of the zwitterion intermediate, and increased steric effects. These results extend the classical studies of *Huisgen* and his co-workers.

Introduction. – The competition of both [2+2] and [2+4] cycloadditions with spontaneous polymerizations in reactions of electron-rich alkenes with electron-poor alkenes has long been of interest in our laboratory [1–3]. The reaction pathway is dependent on the disparity in the energy levels of the participating HOMO–LUMO orbitals, and also on the reaction conditions [4]. A case in point (*Scheme 1*) is the reaction of '*p*-methoxystyrene' (**1**) with dimethyl 'cyanofumarate' (**2**). When the reaction is performed at high concentration, the monomers form the alternating co-polymer **3**, and the kinetics of this free-radical co-polymerization was studied in great detail [5]. When the same components at lower concentration are heated in MeCN, dihydropyran **4** is formed by an inverse-electron-demand [2+4] *Diels–Alder* cyclo-addition. When **2** and **3** are combined with *Lewis* acids ($LiClO_4$ or $ZnCl_2$) in Et_2O, homopolymer **5** is obtained. And, finally, when the reaction is performed with $ZnCl_2$ in 2,5-dimethyltetrahydrofuran, [2+2]-cycloadducts **6** are formed exclusively, providing a good route to substituted cyclobutanes [3].

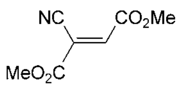
During the spontaneous cycloadditions and polymerizations ('charge-transfer polymerizations') that occur upon mixing electron-rich olefins with electron-poor vinyl monomers, colored charge-transfer complexes were involved in neither the initiation nor propagation step [4–8]. The key initiator was the tetramethylene zwitterion–diradical **7** originally proposed by *Huisgen* for [2+2] cycloaddition reactions [9][10]. We proposed that **7** initiates polymerization, *i.e.*, *cationic* homo-polymerization if it is a zwitterion, and *radical* co-polymerization if it is a diradical. The larger the energy difference between the two olefins, the greater is the zwitterionic character of the intermediate.

This paper describes a study of the cycloadditions between the electron-poor alkenes **2**, **8**, **9**, or **10**, and the electron-rich bifunctional vinyl ethers **11a**–**16a**. This

Scheme 1. *Reactions of a Styrene* (**1**) *with Dimethyl (2*E*)-2-Cyanobut-2-ene-1,4-dioate* (**2**)



Electron-deficient alkenes:



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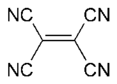

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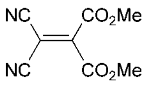

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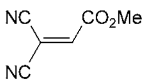

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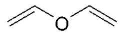
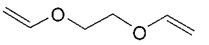
Electron-rich bifunctional vinyl ethers:

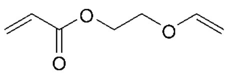
11a



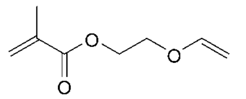
12a



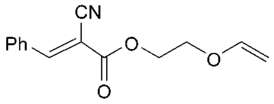
13a



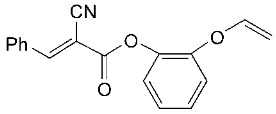
14a



15a



16a

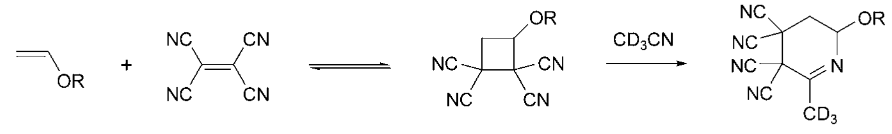


approach creates the possibility of additional reactions after the first cycloaddition. The second C=C bond varied from another electron-rich vinyl ether moiety to highly substituted acrylate functionalities.

Results. – The selected vinyl ethers **11a**–**16a** were reacted with an equimolar amount of an electron-poor alkene in CD_3CN. A small amount of radical inhibitor was added to prevent spontaneous co-polymerization. The reactions were run at low temperature (−42°, then −22°), after which NMR spectra were recorded. Each sample was then exposed to higher temperatures to check for further reactions.

Cyclobutanes **11b**–**16b** were obtained as the major products from the reaction of **8** with each of the vinyl ethers **11a**–**16a** (*Scheme 2*). These cycloadducts were easily identified by the ^{1}H-NMR absorptions of the cyclobutane H-atoms at δ(H) 3.1–3.4 (*dd*, $J = 12-16$ and 7–9 Hz), 3.4–3.6 (*dd*, $J = 12-16$ and 7–9 Hz), and 4.9–5.5 (*t*, $J = 7-9$ Hz). The adduct **11b** was isolated in 55% yield by column chromatography, and further characterized by ^{13}C-NMR and IR spectroscopy. Yields in the other cases were calculated from the ^{1}H-NMR spectra.

Scheme 2



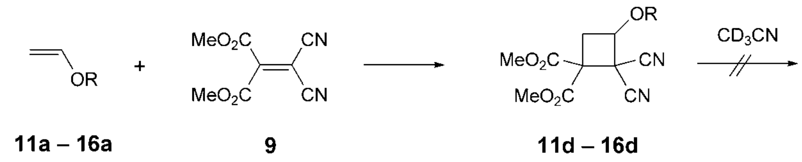
11a – 16a **8** **11b – 16b** **11c – 16c**

In CD_3CN, compounds **11b**–**16b** were converted, slowly at room temperature, or more rapidly on heating to 45°, into the tetrahydropyridines **11c**–**16c**, showing that these cyclobutanes were re-opening to the intermediate zwitterions. The latter were adding to CD_3CN (solvent) in a type of insertion reaction first described by *Huisgen* [9]. In no case was a product from the reaction of the zwitterion with the second C=C bond from the electron-rich alkenes **11a**–**16a** observed. The FAB mass spectrum of **13c** showed the expected $[M+1]^+$ peak at m/z 315. The H-atoms on the tetrahydropyridine rings of **11c**–**16c** absorbed at δ(H) 2.3–2.7 (*dd*, $J = 14-15$ and 7–9 Hz), 2.9–3.1 (*dd*, $J = 14-15$ and 5 Hz), and 5.2–5.8 (*dd*, $J = 7-9$ and 5 Hz). The formation of tetrahydropyridines could be avoided completely, increasing the cyclobutane yields, by using toluene rather than MeCN as the solvent.

The adducts **11d**–**16d** of compound **9** were formed analogously to adducts **11b**–**16b**, but did not react further to tetrahydropyridines on prolonged exposure to MeCN (*Scheme 3*). The cyclobutane-ring NMR absorptions for **11d**–**16d** were at δ(H) 2.7–3.1 (*dd*, $J = 12-14$ and 8–9 Hz), 2.9–3.1 (*dd*, $J = 12-14$ and 8 Hz), and 4.8–5.4 (*dd*, $J = 8$ and 8–9 Hz), and the MeO absorptions were at δ(H) 3.8–3.9. The adduct **11d** was purified for ^{13}C-NMR and IR characterization.

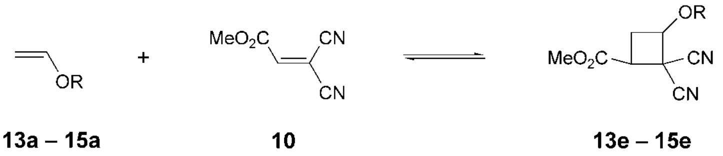
Reaction between olefin **10** and vinyl ethers **13a**–**15a** gave cyclobutanes **13e**–**15e** in 40–70% yield after 2–3 d at room temperature in MeCN or toluene (*Scheme 4*). The cyclobutane H-atoms geminal to the O-atoms gave *triplets* of *doublets* at δ(H) 4.6–4.8 ($J = 8, 1$ Hz), with long-range coupling across the cyclobutane ring. Attempted

Scheme 3



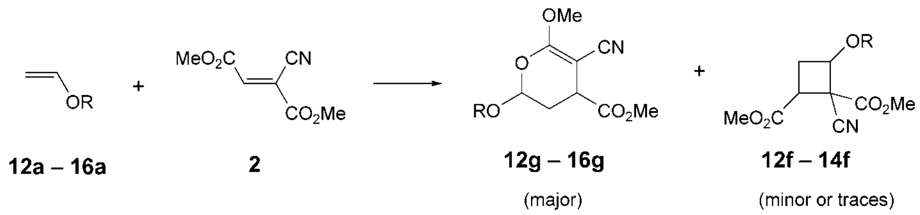
reactions of electron-rich dienes **11a** and **11b** with **10** resulted in anionic homopolymerization of the latter.

Scheme 4

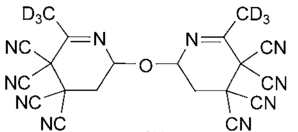


Dimethyl cyanofumarate (**2**) reacted with the electron-rich alkenes **12a**–**16a** to the dihydropyrans **12g**–**16g** by inverse-electron-demand *Diels*–*Alder* reaction. Only small amounts (1–10%) of the cyclobutanes **12f**–**14f** were observed according to the NMR spectra, detected especially by the *triplet* ($J = 8$ Hz) at δ(H) 4.3–4.7 (*Scheme 5*).

Scheme 5



The two alkenes **11a** and **12a** were different from **13a**–**16a** in that they contained *two* electron-rich alkene moieties, and, thus, could potentially give bis-adducts. A small amount (5%) of the bis-adduct **17** (mixture of *rac*- and *meso*-forms) was observed when equimolar amounts of **11a** and **8** were used; the yield of **17** increased to 27%, when the ratio **8**/**11a** was increased to 2 : 1. The bis-adduct **18** was found in 10% yield for a ratio **9**/**11a** of 2 : 1, but was not observed for a 1 : 1 ratio. Bis-adducts analogous to **17** and **18** were not observed with alkene **12a**, probably because the reaction was not conducted with an excess of electrophilic alkene.



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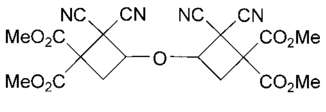


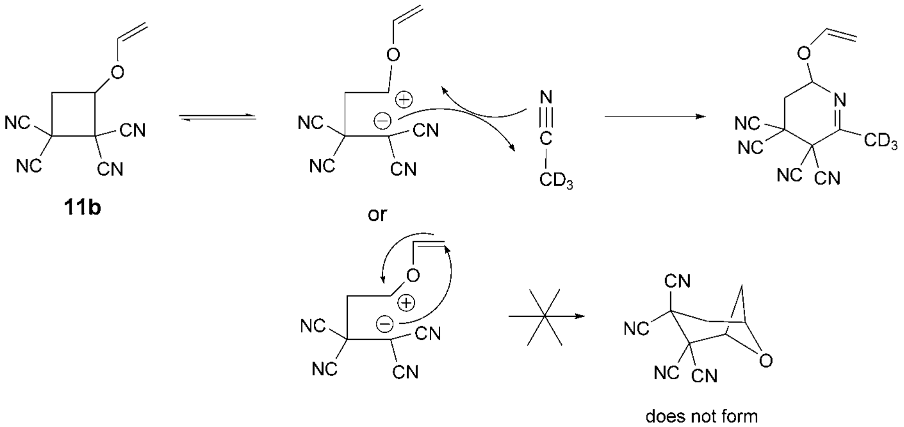
18

We were unsuccessful in observing significant amounts of cycloaddition products with the following electron-poor alkenes: *N*-phenylmaleimide, maleic anhydride, dimethyl maleate, acrylonitrile, and fumaronitrile. These alkenes lack the strong stabilization of the anionic end of the zwitterion provided by two CN substituents, or a CN group and a MeOOC group.

Discussion. – This study was undertaken to test the ability of a zwitterionic intermediate to react with an internal C=C bond. Olefins containing a second electron-rich vinyl ether C=C bond, or a more-neutral C=C bond, were allowed to react with electrophilic alkenes.

In the case of 'tetracyanoethylene' (**8**), its reaction of the vinyl ether moiety proceeded exactly as had been shown 30 years ago by *Huisgen* [9] [10]. The cyclobutane adduct is formed and isolated. In a polar solvent, the cyclobutane is in equilibrium with the zwitterionic intermediate. This zwitterion does not react with the other C=C bond in the vinyl ether molecule, but does react with the solvent MeCN (*Scheme 6*). In the case of divinyl ether (**11a**), the intramolecular reaction would have led to a [3.1.1]bicyclic adduct, while with **12a** it would have been a [4.3.1]bicyclic adduct, neither one of which is highly strained. This indicates that, under these reaction conditions, the anionic end of the zwitterions of type **7** reacts faster than the cationic end, as shown in *Scheme 6*, and, consequently, that the anionic end is less-stabilized than the cationic one. We have, in the past, demonstrated initiation of cationic homopolymerization of vinyl ethers in the presence of electrophilic olefins, which, in principle, is the same reaction as the formation of the putative bicyclic compound in this case [11]. The double inductive stabilization of the two CN substituents is not as strong as the resonance stabilization of the cationic site by the neighboring ether functionality.

Scheme 6. *Possible Reactions of the Cyclobutane Adduct* **11b**



In the reactions of **9** with the vinyl ethers, only cyclobutane adducts are obtained. In these adducts, the two CN groups are in α-position to the alkoxy substituents, because they offer better stabilization than the two ester functions. These cyclobutanes do not react with MeCN, *i.e.*, no insertion takes place. The stabilization of the two zwitterion termini is the same as for the reactions of **8**, but the two ester substituents in β-positions provide less stabilization to the anionic charge, and they stabilize the cyclobutane structure by the so-called 'gem-dimethyl' effect. The other electron-poor alkenes in this study did not provide enough stabilization to allow the reversible reaction from the cyclobutane adduct to the zwitterion. Also, olefins such as dimethyl cyanofumarate, which have an ester functionality at the more-negative end, do not form cyclobutane adducts, but undergo *Diels–Alder* reactions to dihydropyrans. If the concerted reaction is possible, it will be the preferred pathway.

Experimental Part

General. '*Divinyl ether*' (=*1,1′-oxybisethene* (**11a**), containing 0.01% of '*N*-phenyl-α-naphthylamine') was commercially available from *Merck AG*. '*Ethylene glycol divinyl ether*' (=*1,1′-[ethane-1,2-diylbis(oxy)]diethylidene*; **12a**) was prepared by *t*-BuOK induced elimination of HCl from ethylene glycol bis(2-chloroethyl)ether according to [12]. '*Vinyloxyethyl acrylate*' (=*2-(ethenyloxy)ethyl prop-2-enoate*; **13a**) was prepared by acylation of 'vinylethylene glycol' with acroyl chloride. '*Vinyloxyethyl methacrylate*' (=*2-(ethenyloxy)ethyl 2-methylprop-2-enoate*; **14a**) was prepared using the method of *Bauer* and *Neher* [13]. *2-(Ethenyloxy)ethyl (2*E*)-2-cyano-3-phenylprop-2-enoate* (**15a**) was prepared by DCC (dicyclohexylcarbodiimide) coupling of 'vinylethylene glycol' with (*E*)-2-cyano-3-phenylprop-2-enoic acid according to [14]. *2-(Ethenyloxy)phenyl (2*E*)-2-cyano-3-phenylprop-2-enoate* (**16a**) was prepared by DCC coupling of 'vinylcatechol' with (*E*)-2-cyano-3-phenylprop-2-enoic acid according to [15]. IR Spectra: in cm^{-1}. NMR Spectra: at 250 (^{1}H) or 62.9 MHz (^{13}C) on a *Bruker 250* spectrometer; chemical shifts δ in ppm, coupling constants *J* in Hz.

Representative Procedure. To a stirred 1M soln. of the electron-poor alkene (1 equiv.) in CD_3CN at −42° under Ar atmosphere, a 1M soln. of the electron-rich olefin (1 equiv.) in CD_3CN was added dropwise over 5 min. The reactants were maintained at −42° for an additional 30 min, then kept in a freezer at −22°. Some samples were kept for several days at r.t. (25°), some at 45°, and some at 60° to encourage the reactions to proceed further. Reactions were monitored by TLC and ^{1}H-NMR analysis. All yields refer to NMR integrations, except for **11b** and **11d** (isolated yields).

Data of **11b**. Reaction for 5 d at r.t., followed by column chromatography (CC) (SiO_2; 20% AcOEt in hexanes). Yield: 55%. IR (film): 3059, 2976, 2350, 2261, 1631, 1372, 1327, 1199, 1164, 1154, 951, 934, 850, 661, 628. ^{1}H-NMR (CD_3CN): 3.30 (*dd*, *J* = 14.1, 7.7); 3.58 (*dd*, *J* = 14.1, 7.9); 4.47 (*dd*, *J* = 6.8, 3.4); 4.54 (*dd*, *J* = 14.1, 3.5); 5.33 (*dd*, *J* = 7.9, 7.7); 6.50 (*dd*, *J* = 14.1, 6.9). ^{13}C-NMR (CD_3CN): 33.1; 45.3; 73.5; 94.2; 108.9; 111.0; 111.9; 112.1; 148.9.

Data of **11c**. Reaction for 5 d at r.t. Yield: 40%. ^{1}H-NMR (CD_3CN): 2.56 (*dd*, *J* = 15, 7.5); 3.13 (*dd*, *J* = 15, 5); 4.27 (*dd*, *J* = 6.5, 2); 4.52 (*dd*, *J* = 14, 2); 5.51 (*dd*, *J* = 7.5, 5); 6.61 (*dd*, *J* = 14, 6.5).

Data of **11d**. Reaction for 2 d at r.t. Yield: 80%. An anal. sample was purified by CC (SiO_2; 15% AcOEt in hexanes). IR (film): 3120, 3080, 2850, 2359, 2251, 1758, 1755, 1645, 1629, 1437, 1373, 1359, 1327, 1279, 1197, 1162, 1152, 1132, 1100, 1079, 1073, 1049, 1000, 963, 945, 883, 849. ^{1}H-NMR (CD_3CN): 2.91 (*dd*, *J* = 13, 9.5); 3.05 (*dd*, *J* = 13, 8); 3.85 (*s*); 4.42 (*dd*, *J* = 7, 3); 4.55 (*dd*, *J* = 14, 3); 5.17 (*dd*, *J* = 9.5, 8); 6.50 (*dd*, *J* = 14, 7). ^{13}C-NMR (CD_3CN): 35.4; 42.2; 54.1; 54.7; 55.3; 72.0; 93.6; 111.4; 112.9; 149.2; 166.6; 167.3.

Data of **12b**. Reaction for 3 d at r.t. Yield: 50%. ^{1}H-NMR ($CDCl_3$): 3.15 (*dd*, *J* = 12, 8); 3.9–4.2 (*m*); 4.28 (*dd*, *J* = 14, 2.5); 4.32 (*dd*, *J* = 12, 9); 4.90 (*t*, *J* = 8.5); 6.58 (*dd*, *J* = 14, 7).

Data of **12c**. Reaction for 3 d at r.t. Yield: 35%. ^{1}H-NMR ($CDCl_3$): 2.35 (*dd*, *J* = 15, 8.5); 2.99 (*dd*, *J* = 15, 5); 5.18 (*dd*, *J* = 8.5, 5); the other signals were obscured.

Data of **12d**. Reaction for 3 d at r.t. Yield: 80%. ^{1}H-NMR ($CDCl_3$): 2.93 (*dd*, *J* = 13, 9); 3.05 (*dd*, *J* = 13, 8); 3.90 (*s*); 3.93 (*s*); 4.09 (*dd*, *J* = 7, 2.5); 4.23 (*dd*, *J* = 14.5, 2.5); 4.78 (*dd*, *J* = 9, 8); 6.55 (*dd*, *J* = 14.5, 7).

Data of **12g**. Reaction for 3 d at r.t. Yield: 35%. ^{1}H-NMR ($CDCl_3$): 2.05 (*m*); 2.59 (*dt*, *J* = 14.5, 3); 3.25 (*dd*, *J* = 7, 3); 3.69 (*s*); 3.83 (*s*); 4.05 (*dd*, *J* = 7, 2); 4.18 (*dd*, *J* = 14.5, 2); 5.45 (*t*, *J* = 2.5); 6.44 (*dd*, *J* = 14.5, 7).

Data of **13b**. Reaction for 2 d at r.t. Yield: 75% (80% in toluene after 1 d at 45°). ^{1}H-NMR ($CDCl_3$): 3.17 (*dd*, *J* = 13.5, 8.5); 3.44 (*dd*, *J* = 13.5, 7.5); 4.01 (*t*); 4.38 (*m*); 4.91 (*dd*, *J* = 8.5, 7.5); 5.92 (*dd*, *J* = 10.5, 1.5); 6.20 (*dd*, *J* = 17.5, 10.5); 6.48 (*dd*, *J* = 17.5, 1.5).

Data of **13c**. Reaction for 4 d at 45°. Yield: 95%. ^{1}H-NMR ($CDCl_3$): 2.34 (*dd*, *J* = 14.5, 9); 2.94 (*dd*, *J* = 14.5, 5); 4.00 (*m*); 4.28 (*m*); 4.36 (*m*); 4.47 (*m*); 5.16 (*dd*, *J* = 9, 5); 5.89 (*dd*, *J* = 10.5, 1.5); 6.16 (*dd*, *J* = 17.5, 10.5); 6.46 (*dd*, *J* = 17.5, 1.5).

Data of **13d**. Reaction for 3 d at r.t. Yield: 95%. ^{1}H-NMR ($CDCl_3$): 2.75 (*dd*, $J = 13, 9$); 2.93 (*dd*, $J = 13, 8$); 3.81 (*s*); 3.90 (*m*); 4.26 (*m*); 4.80 (*dd*, $J = 9, 8$); 5.86 (*dd*, $J = 10.5, 1.5$); 6.14 (*dd*, $J = 17.5, 10.5$); 6.37 (*dd*, $J = 17.5, 1.5$).

Data of **13e**. Reaction for 2 d at r.t. Yield: 70% (also after 3 d at r.t. in toluene). ^{1}H-NMR ($CDCl_3$): 2.60 (*ddd*, $J = 12, 10, 4$); 2.75 (*ddd*, $J = 12, 8, 4$); 3.49 (*ddd*, $J = 10, 4, 1$); 3.80–3.90 (*m*); 3.83 (*s*); 4.37 (*m*); 4.67 (*td*, $J = 8, 1$); 5.86 (*dd*, $J = 10.5, 1.5$); 6.18 (*dd*, $J = 17.5, 10.5$); 6.47 (*dd*, $J = 17.5, 1.5$).

Data of **13f**. Yield: 10% (byproduct of **13g**). ^{1}H-NMR ($CDCl_3$): 4.69 (*dt*, $J = 8, 1$).

Data of **13g**. Reaction for 3 d at r.t. Yield: 80%. ^{1}H-NMR ($CDCl_3$): 2.03 (*m*); 2.37 (*dt*, $J = 14.5, 3$); 3.23 (*dd*, $J = 7, 3$); 3.57 (*s*); 3.77 (*s*); 3.78 (*m*); 4.15 (*m*); 5.43 (*t*, $J = 3$); 5.87 (*dd*, $J = 10.5, 1.5$); 6.12 (*dd*, $J = 17.5, 10.5$); 6.36 (*dd*, $J = 17.5, 1.5$).

Data of **14b**. Reaction for 1 h at r.t. Yield: 75%. ^{1}H-NMR ($CDCl_3$): 1.97 (*t*, $J = 1.5$); 3.17 (*dd*, $J = 13, 8.5$); 3.43 (*dd*, $J = 13, 7.5$); 3.98–4.02 (*m*); 4.38 (*m*); 4.90 (*t*, $J = 7.5$); 5.65 (br. *s*); 6.18 (br. *s*).

Data of **14c**. Reaction for 4 d at 45°. Yield: 90%. ^{1}H-NMR ($CDCl_3$): 1.96 (br. *s*); 2.34 (*dd*, $J = 14.5, 8.5$); 2.94 (*dd*, $J = 14.5, 5$); 4.02 (*m*); 4.30 (*m*); 4.44 (*m*); 5.16 (*dd*, $J = 8.5, 5$); 5.62 (br. *s*); 6.14 (br. *s*).

Data of **14d**. Reaction for 2 d at r.t. Yield: 80%. ^{1}H-NMR ($CDCl_3$): 1.96 (br. *s*); 2.88 (*dd*, $J = 13.5, 9$); 2.91 (*dd*, $J = 13.5, 8$); 3.89 (*m*); 3.90 (*s*); 3.91 (*s*); 4.00 (*m*); 4.33–4.38 (*m*); 4.78 (*dd*, $J = 9, 8$); 5.62 (br. *s*); 6.18 (br. *s*).

Data of **14e**. Reaction for 2 d at r.t. Yield: 60%. ^{1}H-NMR ($CDCl_3$): 1.96 (br. *s*); 2.66 (*m*); 2.81 (*ddd*, $J = 13, 8, 4$); 3.62 (*m*); 3.85 (*s*); 4.35 (*m*); 4.73 (*td*, $J = 8, 1$); 5.62 (*d*, $J = 1.5$); 6.18 (br. *s*).

Data of **14g**. Reaction for 2 d at r.t. Yield: 70%. ^{1}H-NMR ($CDCl_3$): 2.06 (*ddd*, $J = 14.5, 7, 3$); 2.62 (*dt*, $J = 14.5, 3$); 3.27 (*dd*, $J = 7, 3$); 4.25 (*m*); 5.43 (*t*, $J = 3$); 3.68 (*s*); 3.82 (*s*).

Data of **15b**. Reaction for 1 h at r.t. Yield: 80%. ^{1}H-NMR ($CDCl_3$): 3.20 (*dd*, $J = 16, 8.5$); 3.53 (*dd*, $J = 16, 7.5$); 4.05 (*m*); 4.15 (*m*); 4.50 (*m*); 4.59 (*m*); 5.00 (*t*, $J = 8$); 7.50–7.63 (*m*); 8.02 (*dd*, $J = 8, 2$); 8.32 (*s*).

Data of **15c**. Reaction for 2 d at r.t. Yield: 30%. ^{1}H-NMR ($CDCl_3$): 2.38 (*dd*, $J = 14.5, 8.5$); 3.01 (*dd*, $J = 14.5, 5$); 4.0–4.6 (*m*); 5.21 (*dd*, $J = 8.5, 5$); 7.50–7.63 (*m*); 8.02 (*dd*, $J = 8, 2$); 8.29 (*s*).

Data of **15d**. Reaction for 2 d at r.t. Yield: 100%. ^{1}H-NMR ($CDCl_3$): 2.90 (*dd*, $J = 12.5, 9$); 2.98 (*dd*, $J = 12.5, 8$); 3.90 (*s*); 3.91 (*s*); 4.00 (*m*); 4.10 (*m*); 4.52 (*m*); 4.83 (*t*, $J = 8$); 7.49–7.60 (*m*); 8.01 (*dd*, $J = 8, 2$); 8.31 (*s*).

Data of **15e**. Reaction for 2 d at r.t. Yield: 40%. ^{1}H-NMR ($CDCl_3$): 2.68 (*m*); 2.86 (*ddd*, $J = 11.5, 8, 4$); 3.63 (*m*); 3.85 (*s*), 4.55 (*m*); 4.78 (*td*, $J = 8, 1$); 8.34 (*s*).

Data of **15g**. Reaction for 2 d at r.t. Yield: 70%. ^{1}H-NMR ($CDCl_3$): 2.06 (*ddd*, $J = 14.5, 7, 3$); 2.62 (*dt*, $J = 14.5, 3$); 3.27 (*dd*, $J = 7, 3$); 3.71 (*s*); 3.85 (*s*); 3.92 (*m*); 4.05 (*m*); 4.42 (*m*); 5.49 (*t*, $J = 3$); 7.53–7.61 (*m*); 8.06 (*dd*, $J = 8, 2$); 8.33 (*s*).

Data of **16b**. Reaction for 2 d at 45°. Yield: 10%. ^{1}H-NMR ($CDCl_3$): 3.38 (*dd*, $J = 13.5, 8$); 3.64 (*dd*, $J = 13.5, 7.5$); 5.49 (*t*, $J = 8$); other signals masked by resonances of starting material.

Data of **16c**. Reaction for 2 d at 45°. Yield: 10%. ^{1}H-NMR ($CDCl_3$): 2.66 (*dd*, $J = 15, 8$); 3.15 (*dd*, $J = 15, 5$); 5.84 (*dd*, $J = 8, 5$); other signals masked by resonances of starting material.

Data of **16d**. Reaction for 2 d at 60°. Yield: 55%. ^{1}H-NMR ($CDCl_3$): 3.09 (*dd*, $J = 13, 8$); 3.12 (*dd*, $J = 13, 8$); 5.36 (*t*, $J = 8$); 8.31 (*s*); other signals masked by resonances of starting material.

Data of **16g**. Reaction for 2 d at 60°. Yield: 60%. ^{1}H-NMR ($CDCl_3$): 2.15 (*ddd*, $J = 14.5, 8, 3$); 2.83 (*dt*, $J = 14.5, 3$); 3.31 (*dd*, $J = 8, 3$); 3.73 (*s*); 3.78 (*s*); 5.95 (*t*, $J = 3$); other signals masked by resonances of starting material.

Data of **17**. Reaction for 14 d at r.t. with 2 equiv. of **8** afforded 10 and 5% of the major and minor stereoisomers of **17**, resp. ^{1}H-NMR (CD_3CN; major isomer): 2.48 (*dd*, $J = 15, 7.5$); 3.11 (*dd*, $J = 15, 5$); 5.84 (*dd*, $J = 7.5, 5$). ^{1}H-NMR (CD_3CN; minor isomer): 2.65 (*dd*, $J = 15, 7.5$); 3.12 (*dd*, $J = 15, 5$); 5.67 (*dd*, $J = 7.5, 5$).

Data of **18**. Reaction for 2 d at r.t. with 2 equiv. of **9**. Yield: 10%. ^{1}H-NMR ($CDCl_3$): 5.24 (*t*, $J = 7.5$); 3.88 (*s*).

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