Synthesis of Photoresponsive Polyethers

Felix Starck[a], Peter G. Jones[b], and Rainer Herges*[a]

Institut für Organische Chemie, Technische Universität Braunschweig[a],
Hagenring 30, D-38106 Braunschweig, Germany
Fax: (internat.) +49(0)531/391-8185
E-mail: r.herges@tu-bs.de

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig[b],
Hagenring 30, D-38106 Braunschweig, Germany

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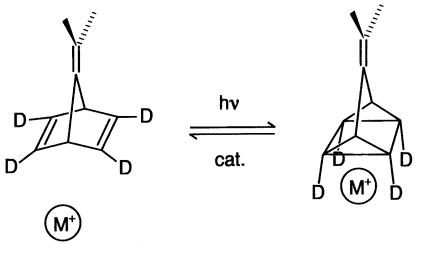
A Diels–Alder, retro Diels–Alder sequence provides access to 2,3,5-tri- and 2,3,5,6-tetraester-substituted norbornadienes. Attempts to reduce the norbornadiene esters with $LiAlH_4$ failed. The corresponding quadricyclanes, which are available by photoisomerization of the norbornadienes give the alcohols in 32 and 74% yield. The quadricyclane alcohols **2a–c** are converted with methyl iodide to compounds **3a–c** or with 2-methoxyethyl 4-toluenesulfonate to the "tentacle molecules" **4a–c**. A number of catalysts were tested to reisomerize the "tentacle" quadricyclanes to the norbornadienes. Neutral aluminum oxide proved to be most effective. In preliminary studies the tentacle quadricyclanes exhibit excellent complexing properties for Na^+ and K^+, whereas the norbornadiene isomers are less effective complexing agents.

Introduction

Most of the photoresponsive complexing ligands so far published, are based on the *cis*/*trans* isomerization of azobenzenes[1] or the [4+4]cycloaddition/reversion of anthracene derivatives.[2] Azobenzenes have been used as carriers in lipophilic membranes but to date none of these systems provides a light-driven transport of cations against a concentration gradient. Our approach starts from the norbornadiene/quadricyclane (nb/qc) system. According to simple model considerations and quantum chemical calculations, 2,3,5,6-tetrasubstituted norbornadienes upon irradiation and isomerization to the quadricyclanes perform a grab-like or pincer movement with the four ligands (Scheme 1).

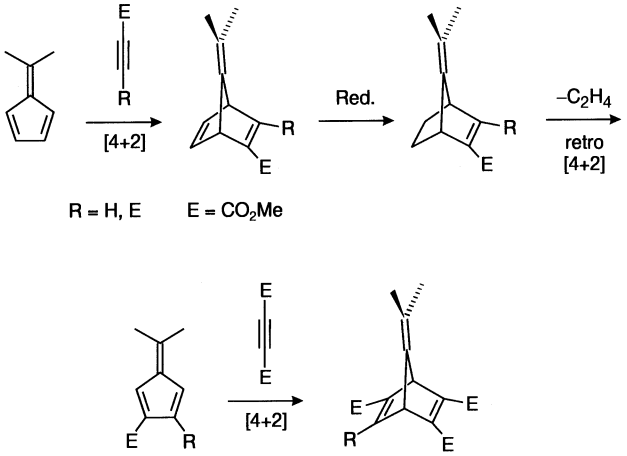
Scheme 1. "Pincer principle" of the photoresponsive norbornadiene/quadricyclane system (D = donor ligands)



2,3,5-Tri- and 2,3,5,6-tetraester-substituted norbornadienes can be prepared by a Diels−Alder/retro Diels−Alder sequence (Scheme 2).

We now report on the synthesis of tri- and tetrasubstituted norbornadienes and quadricyclanes by reduction of the quadricyclane esters and etherification of the alcohols. The polyether-substituted systems can be viewed as "tentacle molecules"[3][4] (Scheme 3) and are potential photoresponsive complexing agents.

Scheme 2. Synthesis of 2,3,5-tri- and 2,3,5,6-tetrasubstituted norbornadienes



Results and Discussion

Reduction of Quadricyclane Esters

Attempts to reduce the ester-substituted norbornadienes with $LiAlH_4$ or DIBAH failed and resulted in undefinable product mixtures. To avoid the problems that are common to α,β-unsatured esters[5] we photoisomerized the norbornadienes to the corresponding quadricyclanes. The quantum yield of the [2+2]cycloaddition, which is low because of the isopropylidene substitution[6] can be considerably im-

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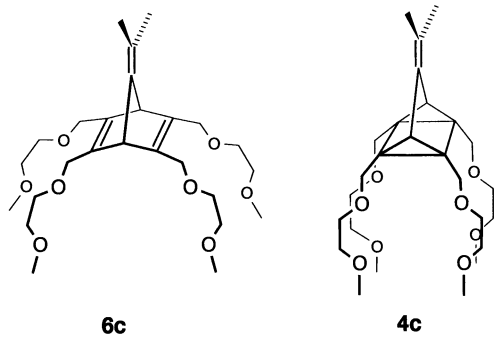
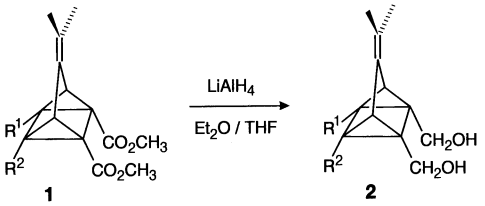
Scheme 3. "Tentacle" molecules **4c** and **6c** with four ether ligands based on the norbornadiene/quadricyclane system



6c **4c**

proved by Cu(I) catalysis (CuOTf × $Bz_{0.5}$).[7] The quadricyclane esters are reduced with $LiAlH_4$ in moderate to good yields.[8]

Table 1. Reduction of the quadricyclane esters **1a–c** to the corresponding alcohols **2a–c**



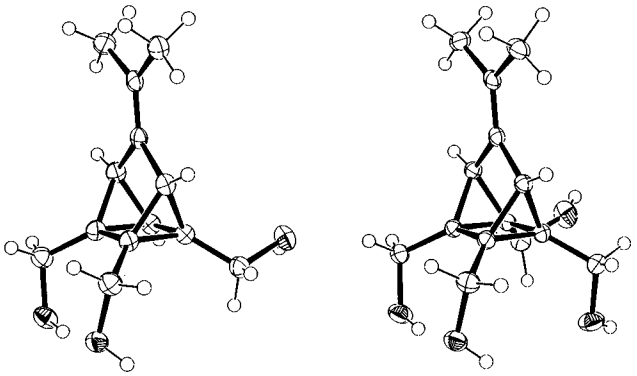
1 **2**

	R^1	R^2
1a	H	H
1b	CO_2CH_3	H
1c	CO_2CH_3	CO_2CH_3

	R^1	R^2	yield
2a	H	H	81%
2b	CH_2OH	H	32%
2c	CH_2OH	CH_2OH	74%

The alcohols are nicely crystalline and colorless compounds. We obtained X-ray structures for the tri- and tetraalcohol (Figure 1); the latter crystallizes as a hemihydrate.

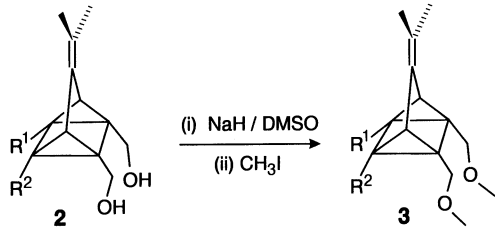
Figure 1. Crystal structure of **2b** (left) and **2c** (right)



Etherification of Quadricyclane Alcohols

DMSO and NaH in homogeneous solution were found to be suitable reaction conditions for the etherification of the alcohols **2a–c**. The methylsulfinyl anion[9], which is formed from DMSO and NaH even in large excess, does not lead to undesirable deprotonations of the quadricyclane framework. Attempts to prepare the methoxymethyl ethers using the phase-transfer-catalyzed alkylation with dimethyl sulfate[10] lead only to partially methylated products. The methoxy ethers **3a–c** are colorless or yellowish oils that polymerize under oxygen and acid catalysis at room temperature.

Table 2. Synthesis of the methoxymethyl ethers **3a–c**

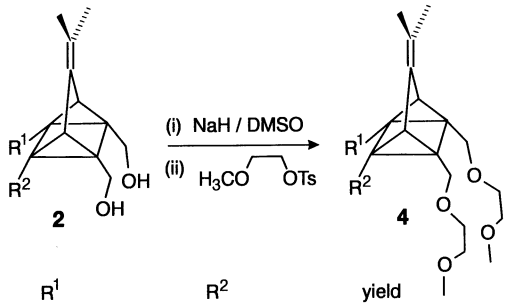


2 **3**

	R^1	R^2	yield
3a	H	H	91%
3b	CH_2OCH_3	H	72%
3c	CH_2OCH_3	CH_2OCH_3	85%

We expected quadricyclanes with longer tentacle-like polyether ligands to exhibit improved complexing properties. Reaction of the di-, tri- and tetraalcohols **2a–c** with 4-toluenesulfonic acid 2-methoxy ethyl ester[11] furnished the corresponding ethers **4a–c**.

Table 3. Synthesis of the tentacle quadricyclanes **4a–c**



2 **4**

	R^1	R^2	yield
4a	H	H	73%
4b	CH_2O OCH_3	H	85%
4c	CH_2O OCH_3	CH_2O OCH_3	62%

Reisomerization of the Quadricyclane Ethers

Norbornadiene ethers are not directly accessible by reduction of the corresponding esters but only via the quadricyclanes, reduction and reisomerization. The catalytic isomerization of quadricyclanes to norbornadienes has been thoroughly studied since the early sixties mainly because of potential applications for solar energy storage.[12] Most of the catalysts are transition-metal complexes or electron-transfer reagents.[13] However, in our hands the transition-metal complexes described in the literature (Co-porphy-

rins[14], [(NBD)ClRh]$_2$[15]) were not active for tetraester-substituted quadricyclanes.[16] This observation was confirmed by our investigations on tetraether-substituted quadricyclanes in the present study. We additionally tested a number of substituted porphyrins and porphyrin analoga[17] (Scheme 4) and found that quadricyclanes with fewer than four substitutents isomerize within periods of a minute to several days (Table 4). The fact that disubstituted quadricyclanes are more reactive than trisubstituted ones and that quadricyclanes with short ether ligands react faster than those with the extended ether chains suggests that sterical hindrance is the main reason for the lack of reactivity of the tetrasubstituted systems.

Scheme 4. Transition-metal catalysts which were tested for the quadricyclane-norbornadiene isomerization

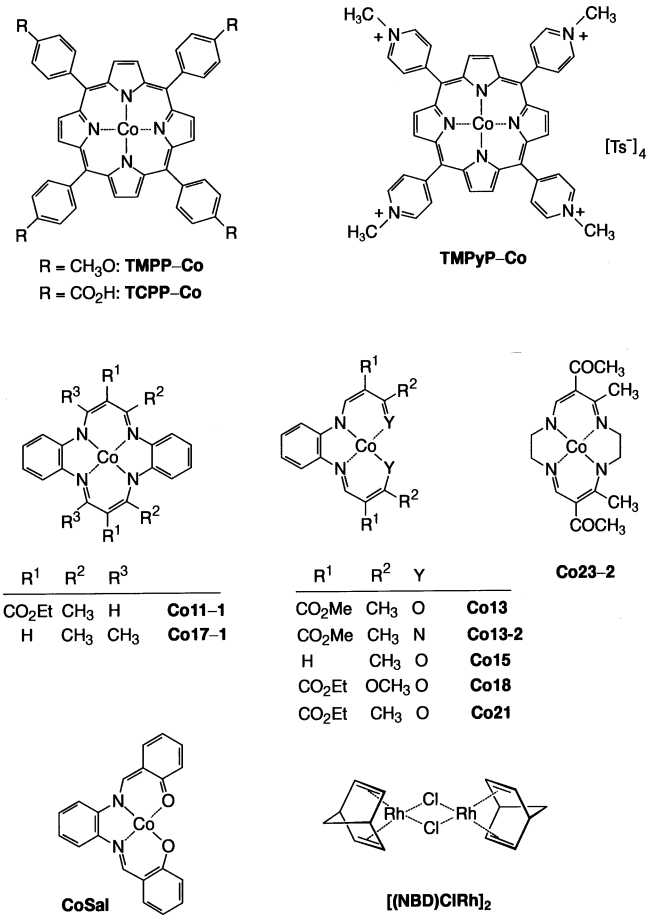


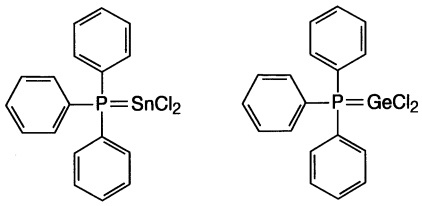
Table 4. Experimentally determined half-lifes in isomerization reactions of quadricyclanes with a selection of the most reactive catalysts

	TMPP-Co	Rh cat.	Co13	Co18	Co21
3a	15 min	7 h	< 30 s	< 30 s	< 30 s
4a	30 min	12 h	1 min	1 min	1 min
3b	30 min	> 24 h	1 min	2 min	2 min
4b	2 h	> 24 h	10 min	20 min	1 h
3c	[a]	[a]	[b]	[a]	[a]

[a] No reisomerization. – [b] Decomposition.

Stimulated by reports on the catalytic activity of base-stabilized stannylenes in the literature[18] we applied stannylene **7** and the analogous germylene compound **8**[19] as catalysts for the isomerization of our quadricyclanes. Indeed, both compounds **7** and **8** exhibit catalytic activity on tetrasubstituted **3c**.

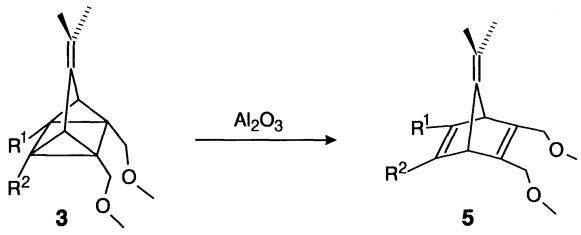
Scheme 5. Triphenylphosphane-dichlorostannylene **7** and -germylene **8**



With germylene **8** the isomerization to the norbornadiene proceeds at room temperature and stannylene reacts at 80°C. However, in both reactions side products are formed and almost equimolar amounts of stannylene and germylene are needed for a quantitative conversion.

The most efficient and applicable catalyst for the conversion of tetrasubstituted quadricyclanes to the corresponding norbornadienes was found by accident; later we noticed that a similar process was already described by Butler and Gupta.[20] During purification by chromatography on aluminum oxide the quadricyclanes **3c** and **4c** isomerized to some extent. We optimized the process by adsorption of the quadricyclane on aluminum oxide, removal of the solvent in a rotatory evaporator and elution of the norbornadiene with an appropriate mixture of ethyl acetate/hexane. The mechanism of the catalytic process is unknown. For other rearrangement reactions it has been proposed that synergetic effects of basic and acidic sites on the surface of aluminum oxide may play a role.[21]

Table 5. Reisomerization of quadricyclane ethers **3a–c** with aluminum oxide

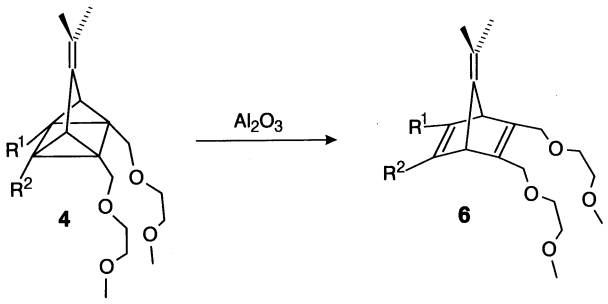


	R^1	R^2	yield
5a	H	H	58%
5b	CH_2OCH_3	H	47%
5c	CH_2OCH_3	CH_2OCH_3	77%

Complexing Properties

In preliminary experiments we investigated the complex formation of Na^+ and K^+ with the quadricyclanes **3a–c**

Table 6. Reisomerization of quadricyclane ethers **4a−c** with aluminum oxide



	R^1	R^2	yield
6a	H	H	44%
6b	CH_2O OCH_3	H	60%
6c	CH_2O OCH_3	CH_2O OCH_3	51%

and **4a−c** and the norbornadienes **5a−c** and **6a−c**. Simple extraction experiments show that only the tri- and tetrasubstituted quadricyclanes with longer ether ligands and six or eight oxygen donor atoms **4b** and **4c** are able to extract sodium and potassium picrate from an aqueous phase into chloroform. The corresponding norbornadienes **6b** and **6c** are much less effective. This is in agreement with our model considerations ("pincer principle") which predicts that the ligands in quadricyclanes are arranged in a convergent direction suitable for complexation, whereas in the norbornadienes the ligands point away from each other. No extraction was observed with the methoxy ethers either of quadricyclanes and norbornadienes. Four ether oxygen atoms obviously do not provide a complexing environment that could compete with water in the aqueous phase.

We are currently determining complex formation constants of **4b**, **4c**, **6b** and **6c** with Li^+, Na^+, K^+ and Cs^+ and investigating transport properties by using our host molecules as carriers in lipophilic membranes.

Conclusion

2,3,5,6-Tetraether-substituted norbornadienes undergo a grab or pincer-like movement with their ligands upon photoisomerization to the corresponding quadricyclanes. This leads to improved complexing properties with Na^+ and K^+. The quadricyclanes are isomerized back to the norbornadienes using neutral aluminum oxide as catalyst.

The systems **4b/6b** and **4c/6c** can be viewed as photochemically/catalytically switchable polypodants or tentacle molecules. The catalytical process has yet to be improved to obtain a sufficient reversibility for active transport in artificial membranes.

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Experimental Section

General: All solvents used for reactions and chromatography were distilled before use. Tetrahydrofuran (THF), diethyl ether and pentane were distilled from sodium/benzophenone, dimethyl sulfoxide from CaH_2. Commercially available chemicals were used as received. All operations were carried out under dry nitrogen. Flash chromatography[22]: Merck Kieselgel 60 (0.040−0.063 mm). − TLC: Merck DC-Fertigplatten Kieselgel 60, F_{254}. − Melting points, uncorrected: Laboratory Devices Mel-Temp II. − IR: Nicolet FT-IR spectrometer 320. − NMR: Bruker AM 400 (400 MHz and 100.6 MHz, for ^1H and ^{13}C, respectively). For ^1H NMR, $CDCl_3$ and [D_4]methanol were used as solvent, TMS as internal standard; for ^{13}C NMR, [D_4]methanol δ_C = 49.0. − MS: Finnigan MAT 8430. − Elemental analysis: Vario EL.

General Procedure for the Synthesis of the Quadricyclane Alcohols **2**: To a stirred suspension of $LiAlH_4$ (1.0 equiv. per ester group) in diethyl ether (100 ml) a solution of quadricyclane ester **1** (20 mmol) in THF (200 ml) was slowly added. The mixture was stirred at room temp. for 12 h and then 1 h under reflux. The excess of $LiAlH_4$ was hydrolyzed by adding water (200 ml). The gelatinous residue was sucked off and washed with diethyl ether. After the organic layer was separated, the aqueous layer was extracted with chloroform (5 × 100 ml). The combined organic solution was dried (Na_2SO_4) and evaporated. The crude product was recrystallized from acetone to give colorless crystals.

(3-Isopropylidenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1,5-diyl)dimethanol (**2a**): Yield: 4.0 g (81%). − M.p. 124°C. − ^1H NMR ([D_4]methanol): δ = 4.86 (s, 2 H, O*H*). 3.84, 3.74 (2 d, ^2J = 12.4 Hz, 4 H, CH_2), 1.96 (d, ^3J = 4.6 Hz, 2 H, 2,4-H), 1.85 [s, 6 H, C(CH_3)$_2$], 1.81 (d, ^3J = 4.7 Hz, 2 H, 6,7-H). − ^{13}C NMR ([D_4]methanol): δ = 140.01 (C-8), 119.25 (C-3), 61.59 (*C*H$_2$), 35.46 (C-1,5), 29.97 (C-2,4), 22.08 [C(*C*H$_3$)$_2$], 21.70 (C-6,7). − IR (KBr): $\tilde{\nu}$ = 3301 cm^{-1} (s), 3090, 3083, 3069 (w), 2973 (s), 2963 (w, sh), 2917, 2866, 2838 (s), 1446 (s), 1410 (m), 1376 (s), 1352, 1254 (w), 1237, 1197, 1149 (m), 1102 (w), 1096 (w, sh), 1012, 997 (ss), 987, 951, 884 (s), 865, 827 (m), 815 (s), 775 (w), 716 (m), 688 (s), 626 (m), 609 (w, sh), 545, 450 (w). − MS (EI, 70eV); *m/z* (%): 192 (29) [M^+], 174 (21), 159 (36), 143 (34), 131 (56), 128 (40), 115 (32), 105 (41), 91 (100), 79 (20), 77 (25), 43 (32). − $C_{12}H_{16}O_2$ (192.25): calcd. C 74.97, H 8.39; found C 74.66, H 8.38.

(3-Isopropylidenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1,5,6-triyl)trimethanol (**2b**): Yield: 1.5 g (32%). − M.p. 140°C. − ^1H NMR ([D_4]methanol): δ = 4.85 (s, 3 H, O*H*), 3.99, 3.82 (2 d, ^2J = 12.5 Hz, 2 H, CH_2), 3.84, 3.80 (2 d, ^2J = 12.3 Hz, 2 H, CH_2), 3.79 (s, 2 H, CH_2), 2.07 (d, ^3J = 4.9 Hz, 1 H, 7-H), 1.92 (d, *J* = 2.0 Hz, 1 H, 4-H), 1.90 (dd, ^3J = 4.9, *J* = 2.0 Hz, 1 H, 2-H), 1.84, 1.83 [2 s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ([D_4]methanol): δ = 139.42 (C-8), 119.35 (C-3), 61.43, 60.96, 59.82 (*C*H$_2$), 39.09, 36.7, 34.74 (C-1, C-5, C-6), 35.20 (C-4), 30.97 (C-2), 24.28 (C-7), 22.07, 21.94 (C(*C*H$_3$)$_2$). − IR (KBr): $\tilde{\nu}$ = 3252 cm^{-1} (s, sh), 3240 (s), 3216, 2981 (w), 2920, 2864, 2845, 1471 (m), 1373 (w), 1360 (m), 1238 (w), 1128 (m), 1053 (m), 1020 (ss), 1008, 1004 (s), 988 (m), 977, 944, 755, 678 (w). − MS (EI, 70eV); *m/z* (%): 222 (34) [M^+], 204 (56), 189 (38), 186 (29), 175 (36), 173 (74), 161 (35), 159 (39), 157 (40), 145 (79), 143 (85), 142 (34), 133 (33), 131 (61), 129 (58), 128 (72), 121 (45), 119 (40), 117 (44), 115 (55), 107 (42), 105 (89), 93 (27), 91 (100), 79 (30), 77 (44), 65 (21), 55 (19), 43 (24), 41 (32). − $C_{13}H_{18}O_3$ (222.28): calcd. C 70.24, H 8.16; found C 69.96, H 8.13.

(3-Isopropylidenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1,5,6,7-tetrayl)tetramethanol (**2c**): Yield: 3.7 g (74%). − M.p. 155°C. − ^1H NMR ([D_4]methanol): δ = 4.86 (s, 4 H, O*H*), 3.99, 3.87 (2 d, ^2J = 12.6 Hz, 8 H, CH_2), 2.01 (s, 2 H, 2,4-H), 1.82 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ([D_4]methanol): δ = 138.56 (C-8), 119.63 (C-3), 59.59 (*C*H$_2$), 38.99 (C-1,5,6,7), 36.15 (C-2,4), 21.96 [C(*C*H$_3$)$_2$]. − IR (KBr): $\tilde{\nu}$ = 3260 cm^{-1}, 3066 (w), 2977 (w), 2944, 2915, 2866, 2849, 1465 (w,

b), 1372 (w), 1241 (m), 1058 (w), 1040 (m), 1023 (ss), 1000 (s), 979, 777, 681 (w). − MS (EI, 70eV); *m/z* (%): 252 (20) [M^+], 234 (28), 216 (59), 203 (39), 187 (50), 173 (71), 159 (51), 157 (63), 145 (85), 129 (59), 119 (55), 115 (55), 105 (100), 91 (82), 77 (43), 43 (22). − $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.99; found C 66.40, H 8.00.

Table 7. Crystal and structure solution data for compounds **2b** and **2c**[25]

	2b	**2c** · 1/2 H_2O
formula	$C_{13}H_{18}O_3$	$C_{14}H_{21}O_{4.5}$
M [g mol^{-1}]	222.27	261.31
temperature [K]	173(2)	143(2)
diffractometer	Siemens $P4$	Stoe-STADI4
radiation	λ = 0.71073 Å (Mo-K_α)	
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pccn$
a [Å]	12.517(2)	10.511(2)
b [Å]	10.579(2)	28.022(6)
c [Å]	8.902(2)	9.040(2)
α [°]	90	90
β [°]	103.09(2)	90
γ [°]	90	90
V [Å^3]	1148.2(4)	2662.6(10)
$\rho_{calcd.}$ [g cm^{-1}]	1.286	1.304
Z	4	8
F(000)	480	1128
crystal size [mm]	0.40 × 0.25 × 0.10	0.90 × 0.40 × 0.40
scan range (2 θ) [°]	6.08/50	6.12/55.08
hkl range	−14/14, −1/12, −0/10	−13/3, 0/36, 0/11
collected reflections	2196	3985
unique reflections	2031	3068
observed reflections	1210	2363
refined parameters	150	201
$R1$ for observed	0.0429	0.0488
$R1$ for all	0.0803	0.0706
$wR2$ for all	0.1028	0.1247
goodness of fit	0.855	1.040

General Procedure for the Synthesis of the Quadricyclane Ethers **3 and 4**: NaH (50% dispersion in mineral oil) was washed twice with pentane (20 ml) to remove the mineral oil. DMSO (30 ml) was added and the suspension was stirred over night. To the homogenous solution quadricyclane alcohol dissolved in DMSO (150 ml) was added and the mixture was stirred for 3 h at room temperature. Then the alkylation agent was added and after stirring for additional 6 h at room temperature the reaction mixture was quenched with water (150 ml). The aqueous phase was extracted with diethyl ether (6 × 100 ml), the combined organic phases were washed with water and dried over Na_2SO_4. After concentration in vacuo the crude oil was further purified by flash chromatography.

3-Isopropylidene-1,5-bis(methoxymethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane (**3a**): According to the general procedure, reaction of **2a** (0.48 g, 2.5 mmol) with NaH dispersion (0.60 g, 12.5 mmol) and methyl iodide (0.78 ml, 12.5 mmol) gave the quadricyclane diether **3a** after flash chromatography as colorless oil. − Yield: 500 mg (91%). − R_f(TLC) = 0.37 (hexane/ethyl acetate, 2:1). − ^{1}H NMR ($CDCl_3$): δ = 3.56, 3.78 (2 d, ^2J = 11.2 Hz, 4 H, CH_2), 3.35 (s, 6 H, OCH_3), 1.99 (d, ^3J = 4.6 Hz, 2 H, 2,4-H), 1.88 [s, 6 H, C(CH_3)$_2$], 1.80 (d, ^3J = 4.6 Hz, 2 H, 6,7-H). − ^{13}C NMR ($CDCl_3$): δ = 138.00 (C-8), 119.66 (C-3), 71.23 (*C*H_2), 58.20 (O*C*H_3), 31.97 (C-1,5), 29.02 (C-2,4), 22.06 [C(*C*H_3)$_2$], 20.58 (C-6,7). − IR (neat): $\tilde{\nu}$ = 3064 cm^{-1} (w), 2979, 2922, 2890, 2872, 2855, 2816 (s), 1467 (m), 1448 (s), 1416, 1391 (w), 1374, 1360 (m), 1269 (w), 1192, 1169 (s), 1102 (ss), 1008, 967, 952, 944 (w), 916 (m), 849, 830, 819, 684, 655 (w). − MS (EI, 70eV); *m/z* (%): 220 (31) [M^+], 205 (12), 188 (37), 175 (58), 173 (86), 156 (42), 145 (47), 143 (100), 141 (63), 129 (66), 128 (90), 118 (33), 115 (48), 106 (55), 105 (39), 91 (89), 77 (24), 75 (27), 45 (66). − $C_{14}H_{20}O_2$: calcd. for [M^+] 220.1463; found 220.1463 ± 7 (HRMS).

3-Isopropylidene-1,5,6-tris(methoxymethyl)tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**3b**): According to the general procedure, reaction of **2b** (0.55 g, 2.5 mmol) with NaH dispersion (0.90 g, 18.8 mmol) and methyl iodide (1.18 ml, 18.8 mmol) gave the quadricyclane triether **3b** after flash chromatography as colorless oil. Yield: 476 mg (72%). − R_f(TLC) = 0.38 (hexane/ethyl acetate, 1:2). − ^{1}H NMR ($CDCl_3$): δ = 3.86, 3.64 (2 d, ^2J = 11.3 Hz, 2 H, CH_2), 3.79, 3.57 (2 d, ^2J = 11.4 Hz, 2 H, CH_2), 3.74, 3.59 (2 d, ^2J = 11.6 Hz, 2 H, CH_2), 3.35, 3.33, 3.32 (3 s, 9 H, OCH_3), 2.05 (d, ^3J = 4.9 Hz, 1 H, 7-H), 1.87 (dd, ^3J = 4.9 Hz, J = 2.0 Hz, 1 H, 2-H), 1.85, 1.84 [2 s, 6 H, C(CH_3)$_2$], 1.84 (d, J = 2.0 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 137.51 (C-8), 119.47 (C-3), 71.01, 70.18, 69.38 (*C*H_2), 58.21, 58.18, 58.12 (O*C*H_3), 35.64, 32.98, 31.23(C-1, C-5, C-6), 33.45 (C-4), 30.14 (C-2), 23.46 (C-7), 22.04, 21.98 [C(*C*H_3)$_2$]. − IR (neat): $\tilde{\nu}$ = 3061 cm^{-1} (w), 2979, 2922, 2872, 2855, 2818 (s), 1637 (w), 1468, 1449 (m), 1413 (w), 1374 1247 (m), 1194 (s), 155, 1135 (m), 1100 (ss), 1059, 951, 939, 910 (m), 682 (w). − MS (EI, 70eV); *m/z* (%): 264 (23) [M^+], 232 (71), 219 (63), 217 (45), 200 (44), 187 (100), 185 (45), 172 (32), 169 (27), 157 (51), 155 (41), 143 (35), 135 (29), 129 (36), 115 (26), 105 (17), 91 (31), 75 (58), 45 (75). − $C_{16}H_{24}O_3$: calcd. for [M^+]; 264.1725 found 264.1725 ± 8 (HRMS).

3-Isopropylidene-1,5,6,7-tetrakis(methoxymethyl)tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**3c**): According to the general procedure, reaction of **2c** (0.63 g, 2.5 mmol) with NaH dispersion (1.20 g, 25.0 mmol) and methyl iodide (1.56 ml, 25.0 mmol) gave the quadricyclane tetraether **3c** after flash chromatography as colorless oil. − Yield: 655 mg (85%). − R_f(TLC) = 0.29 (hexane/ethyl acetate, 1:2). − ^{1}H NMR ($CDCl_3$): δ = 3.86, 3.64 (2 d, ^2J = 11.4 Hz, 8 H, CH_2), 3.32 (s, 12 H, OCH_3), 1.90 (s, 2 H, 2,4-H), 1.83 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 136.84 (C-8), 119.38 (C-3), 69.24 (*C*H_2), 58.11 (O*C*H_3), 35.21 (C-1,5,6,7), 34.53 (C-2,4), 21.95 [C(*C*H_3)$_2$]. − IR (neat): $\tilde{\nu}$ = 2979 cm^{-1}, 2924, 2876, 2856, 2820 (s), 1722, 1630 (w), 1467 (sh, m), 1450, 1375 (s), 1243 (m), 1194(s), 1155 (m), 1105 (ss), 941, 908 (m). − MS (EI, 70eV); *m/z* (%): 308 (13) [M^+], 276 (56), 263 (14), 244 (100), 231 (66), 229 (32), 213 (21), 201 (33), 199 (53), 187 (24), 185 (26), 171 (20), 169 (29), 157 (18), 155 (19), 141 (18), 129 (17), 128 (17), 115 (17), 91 (15), 75 (59), 45 (37). − $C_{18}H_{28}O_4$: calcd. for [M^+] 308.1988; found 308.1988 ± 6 (HRMS).

3-Isopropylidene-1,5-bis(2-methoxyethoxymethyl)tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**4a**): According to the general procedure, reaction of **2a** (0.38 g, 2.0 mmol) with NaH dispersion (0.38 g, 8.0 mmol) and 2-methoxyethyl 4-toluenesulfonate (2.19 g, 9.5 mmol) gave the quadricyclane diether **4a** after flash chromatography as colorless oil. − Yield: 452 mg (73%). − R_f(TLC) = 0.40 (diethyl ether). − ^{1}H NMR ($CDCl_3$): δ = 3.91, 3.69 (2 d, ^2J = 11.8 Hz, 4 H, CH_2O), 3.66−3.52 (m, 8 H, CH_2CH_2), 3.38 (s, 6 H, OCH_3), 1.98 (d, ^3J = 4.6 Hz, 2 H, 2,4-H), 1.87 [s, 6 H, C(CH_3)$_2$], 1.79 (d, ^3J = 4.6 Hz, 2 H, 6,7-H). − ^{13}C NMR ($CDCl_3$): δ = 138.12 (C-8), 119.57 (C-3), 72.03 (*C*H_2O), 69.75, 69.29 (*C*H_2CH_2), 58.89 (O*C*H_3), 31.92 (C-1,5), 28.98 (C-2,4), 22.04 [C(*C*H_3)$_2$], 20.88 (C-6,7). − IR (neat): $\tilde{\nu}$ = 3064 cm^{-1} (w), 2979 (m), 2908, 2902, 2872, 2859 (s), 2730 (w), 1450, 1373, 1350 (m), 1269, 1244 (w), 1199, 1169 (m), 1133 (s), 1101 (ss), 1041 (m), 983, 852, 818 (w). − MS (EI, 70eV); *m/z* (%): 308 (4) [M^+], 232 (12), 219 (5), 217 (7), 173 (20), 159 (18), 157 (23), 156 (55), 145 (20), 143 (32), 141 (28), 131 (16), 129 (23), 128 (21), 117 (11),115 (17), 106 (23), 105 (15), 91 (32), 77 (9), 65 (6), 59 (100), 45 (15). − $C_{18}H_{28}O_4$: calcd. for [M^+] 308.1988; found 308.1988 ± 9 (HRMS).

3-Isopropylidene-1,5,6-tris(2-methoxyethoxymethyl)tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**4b**): According to the general procedure, reaction of **2b** (0.44 g, 2.0 mmol) with NaH dispersion (0.58 g, 12.0 mmol) and 2-methoxyethyl 4-toluenesulfonate (3.31 g, 14.4 mmol) gave the quadricyclane triether **4b** after flash chromatography as colorless oil. − Yield: 637 mg (85%). − R_f(TLC) = 0.50 (diethyl ether/ethanol, 20:1). − ^{1}H NMR ($CDCl_3$): δ = 3.99, 3.76 (2 d, ^2J = 11.6 Hz, 2 H, CH_2O), 3.86, 3.71 (2 d, ^2J = 11.8 Hz, 2 H, CH_2O), 3.82, 3.74 (2 d, ^2J = 12.1 Hz, 2 H, CH_2O), 3.67−3.50 (m, 12 H, CH_2CH_2), 3.38, 3.38, 3.37 (3 s, 9 H, OCH_3), 2.05 (d, ^3J = 4.6 Hz, 1 H, 7-H), 1.85−1.83 (2 H, 2,4-H), 1.85, 1.83 [2 s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 137.64 (C-8), 119.38 (C-3), 72.04, 72.01 (CH$_2$*C*H$_2$), 69.54, 68.68, 67.76 (*C*H$_2$O), 69.30, 69.19, 69.16 (*C*H$_2$CH$_2$), 58.89, 58.87, 58.85 (O*C*H$_3$), 35.71, 33.24, 31.19, (C-1, C-5, C-6), 33.30 (C-4), 30.10 (C-2), 23.76 (C-7), 21.97, 21.95 (C(*C*H$_3$)$_2$). − IR (neat): $\tilde{\nu}$ = 3059 cm^{-1} (w), 2979 (m), 2920, 2916, 2872, 2859 (s), 2731 (w), 1450, 1373, 1354 (m), 1285 (w), 1246 (m), 1199 (s), 1133, 1101 (ss), 1037, 982 (m), 951 (w), 852 (m). − MS (EI, 70eV): *m/z* (%): 396 (1) [M$^+$], 320 (9), 278 (5), 244 (15), 231 (9), 185 (13), 168 (12), 157 (11), 118 (7), 91 (6), 59 (100). − $C_{22}H_{36}O_6$: calcd. for [M$^+$] 396.2512; found 396.2512 ± 12 (HRMS).

3-Isopropylidene-1,5,6,7-tetrakis(2-methoxyethoxymethyl)-tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**4c**): According to the general procedure, reaction of **2c** (0.50 g, 2.0 mmol) with NaH dispersion (0.77 g, 16.0 mmol) and 2-methoxyethyl 4-toluenesulfonate (4.41 g, 19.2 mmol) gave the quadricyclane tetraether **4c** after flash chromatography as colorless oil. − Yield: 602 mg (62%). − R_f(TLC) = 0.46 (diethyl ether/ethanol, 10:1). − ^{1}H NMR ($CDCl_3$): δ = 3.95, 3.78 (2 d, ^2J = 11.8 Hz, 8 H, CH_2O), 3.50−3.63 (m, 16 H, CH_2CH_2), 3.37 (s, 12 H, OCH_3), 1.91 (s, 2 H, 2,4-H), 1.82 (s, 6 H, C(CH_3)$_2$). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 137.00 (C-8), 119.32 (C-3), 72.01, 69.17 (*C*H$_2$*C*H$_2$), 67.62 (*C*H$_2$O), 58.85 (O*C*H$_3$), 35.33 (C-1,5,6,7), 34.33 (C-2,4), 21.91 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 3039 cm^{-1} (w), 2979 (s), 2924, 2877, 2871 (ss), 2831 (s, sh), 2732, 1637, 1631 (w), 1451 (s), 1380 (m), 1356 (s), 1286 (m), 1244, 1199 (s), 1178 (m), 1132, 1098 (ss), 1034 (s, sh), 982 (m), 948, 924 (w), 850 (m), 681, 663 (w). − MS (EI, 70eV); *m/z* (%): 484 (0.5), 408 (5), 332 (11), 179 (9), 98 (16), 71 (11), 59 (37), 45 (100). − $C_{26}H_{44}O_8$: calcd. for [M$^+$] 484.3036; found 484.3036 ± 14 (HRMS).

Synthesis of the Norbornadiene Ethers by Reisomerization of the Quadricyclane Ethers on Aluminium Oxide. − General Procedure: To a suspension of 20 g of aluminum oxide (ICN, neutral) in 100 ml of methylene chloride was added 0.20 g of the respective quadricyclane ether. The solvent was removed in a rotatory evaporator and the norbornadiene washed off with a mixture of ethyl acetate/hexane. The solvent was evaporated and the crude oil purified by flash chromatography to give a yellowish oil.

7-Isopropylidene-2,3-bis(methoxymethyl)bicyclo[2.2.1]hepta-2,5-diene (**5a**): Yield: 116 mg (58%). − R_f(TLC) = 0.36 (hexane/ethyl acetate, 3:1). − ^{1}H NMR ($CDCl_3$): δ = 6.90 (t, ^3J = 2.0 Hz, 2 H, 5,6-H), 4.14, 4.06 (2 d, ^2J = 12.1 Hz, 4 H, CH_2O), 4.06 (t, ^3J = 2.0 Hz, 2 H, 1,4-H), 3.23 (s, 6 H, OCH_3), 1.46 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 162.57 (C-7), 149.06 (C-2,3), 142.07 (C-5,6), 95.56 (C-8), 67.70 (*C*H$_2$O), 57.58 (O*C*H$_3$), 52.32 (C-1,4), 18.28 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 3115 cm^{-1} , 3064 (w), 2879, 2922, 2878, 2855, 2817 (s), 2727, 1722, 1656, 1554 (w), 1149, 1372 (s), 1353, 1279, 1226 (m), 1193, 1146 (s), 1102, 1091 (ss), 1064 (s), 1043, 954 (w), 903 (m), 802, 793 (w), 693 (m), 660 (s). − MS (EI, 70eV); *m/z* (%): 220 (55) [M$^+$], 205 (23), 188 (26), 175 (52), 173 (100), 157 (41), 156 (39), 145 (52), 143 (64), 141 (48), 129 (56), 128 (58), 117 (28), 115 (42), 106 (83), 105 (33), 91 (77), 77 (23), 75 (29), 65 (14), 45 (44). − $C_{14}H_{20}O_2$: calcd. for [M$^+$] 220.1463; found 220.1463 ± 4 (HRMS).

7-Isopropylidene-2,3,5-tris(methoxymethyl)bicyclo[2.2.1]hepta-2,5-diene (**5b**): Yield: 94 mg (47%). − R_f(TLC) = 0.44 (hexane/ethyl acetate, 1:1). − ^{1}H NMR ($CDCl_3$): δ = 6.63 (m, 1 H, 6-H), 4.17−4.06 (m, 6 H, CH_2O), 4.03 (m, 1 H, 1-H), 3.96 (m, 1 H, 4-H), 3.28, 3.24, 3.23 (3s, 9 H, OCH_3), 1.47 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 161.28 (C-7), 154.20, 149.42, 148.61 (C-2, C-3, C-5), 137.12 (C-6), 96.08 (C-8), 70.73, 67.72, 67.58 (*C*H$_2$O), 57.81, 57.61, 57.56 (O*C*H$_3$), 53.63 (C-4), 52.18 (C-1), 18.29, 18.16 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 3064 cm^{-1} (w), 2980, 2923, 2893, 2877, 2855, 2818 (s), 2727, 1722, 1689, 1662, 1624 (w), 1466 (m, sh), 1450, 1372 (s), 1353 (m), 1280 (w), 1236, 1227 (m), 1193, 1146 (s), 1120, 1094 (ss), 1046 (m, sh), 1001 (w), 953 (m), 933 (w), 902, 817 (m). − MS (EI, 70eV); *m/z* (%): 264 (69) [M$^+$], 249 (19), 232 (56), 219 (48), 217 (49), 200 (41), 187 (100), 185 (64), 173 (44), 169 (45), 157 (75), 155 (58), 143 (50), 135 (52), 129 (50), 118 (41), 115 (52), 105 (31), 91 (77), 75 (66), 59 (97), 45 (90). − $C_{16}H_{24}O_3$: calcd. for [M$^+$] 264.1725; found 264.1725 ± 8 (HRMS).

7-Isopropylidene-2,3,5,6-tetrakis(methoxymethyl)bicyclo[2.2.1]-hepta-2,5-diene (**5c**): Yield: 155 mg (77%). − R_f(TLC) = 0.40 (hexane/ethyl acetate, 1:2). − ^{1}H NMR ($CDCl_3$): δ = 4.13, 4.09 (2 d, ^2J = 12.0 Hz, 8 H, CH_2O), 4.04 (s, 2 H, 1,4-H), 3.25 (s, 12 H, OCH_3), 1.49 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 159.58 (C-7), 148.68 (C-2,3,5,6), 96.78 (C-8), 67.58 (*C*H$_2$O), 57.58 (O*C*H$_3$), 54.43 (C-1,4), 18.18 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 2979 cm^{-1}, 2924, 2890, 2876, 2854, 2817 (s), 2727, 1724, 1649 (w), 1465 (m), 1450, 1372 (s), 1354 (m), 1281 (w), 1228 (m), 1193 (s), 1149 (m), 1122, 1110, 1093 (ss), 950 (m), 931 (w), 901 (s). − MS (EI, 70eV); *m/z* (%): 308 (33) [M$^+$], 276 (36), 261 (19), 244 (80), 231 (91), 229 (35), 213 (26), 201 (47), 199 (73), 197 (23), 187 (38), 185 (40),171 (32), 169 (51), 162 (56), 157 (27), 155 (32), 149 (23), 147 (21), 141 (30), 133 (28), 129 (29), 128 (31),119 (29), 115 (34), 105 (23), 91 (33), 77 (18), 75 (100), 45 (71). − $C_{18}H_{28}O_4$: calcd. for [M$^+$] 308.1988; found 308.1988 ± 6 (HRMS).

7-Isopropylidene-2,3-bis(2-methoxyethoxymethyl)bicyclo-[2.2.1]hepta-2,5-diene (**6a**): Yield: 88 mg (44%). − R_f(TLC) = 0.51 (hexane/ethyl acetate, 1:1). − ^{1}H NMR ($CDCl_3$): δ = 6.88 (m, 2 H, 5,6-H), 4.26, 4.16 (2 d, ^2J = 12.7 Hz, 4 H, CH_2O), 4.08 (m, 2 H, 1,4-H), 3.52 (m, 4 H, CH$_2$CH_2), 3.41−3.37 (m, 4 H, CH_2CH$_2$), 3.39 (s, 6 H, OCH_3), 1.45 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 162.41 (C-7), 149.03 (C-2,3), 141.96 (C-5,6), 95.58 (C-8), 71.92 (CH$_2$*C*H$_2$), 68.61 (*C*H$_2$CH$_2$), 66.33 (*C*H$_2$O), 58.99 (O*C*H$_3$), 52.23 (C-1,4), 18.24 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 3063 cm^{-1} (w), 2978 (s), 2916, 2864 (ss), 2825 (s, sh), 2729, 1722, 1553 (w), 1449, 1371, 1351 (s), 1285, 1226 (m), 1199 (s), 1132, 1096 (ss), 977, 851 (m), 789 (w), 693 (m), 658 (s). − MS (EI, 70eV); *m/z* (%): 308 (16) [M$^+$], 293 (3), 277 (2), 249 (3), 232 (54), 217 (42), 173 (37), 159 (34), 157 (38), 156 (60), 145 (35), 143 (45), 141 (42), 131 (27), 129 (34), 128 (36), 115 (27), 106 (60), 91 (48), 79 (19), 77 (20), 65 (9), 59 (100), 45 (25). − $C_{18}H_{28}O_4$: calcd. for [M$^+$] 308.1988; found 308.1988 ± 6 (HRMS).

7-Isopropylidene-2,3,5-tris(2-methoxyethoxymethyl)bicyclo-[2.2.1]hepta-2,5-diene (**6b**): Yield: 120 mg (60%). − R_f(TLC) = 0.48 (diethyl ether/ethanol, 20:1). − ^{1}H NMR ($CDCl_3$): δ = 6.61 (m, 1 H, 6-H), 4.30−4.13 (m, 6 H, CH_2O), 4.04 (m, 1 H, 1-H), 3.97 (m, 1 H, 4-H), 3.55−3.38 (m, 12 H, CH_2CH_2), 3.38 (2 s, 9 H, OCH_3), 1.45 [s, 6 H, C(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 161.22 (C-7), 153.98, 149.40, 148.39 (C-2, C-3, C-5), 137.03 (C-6), 95.96 (C-8), 71.95, 71.91 (*C*H$_2$*C*H$_2$), 69.39 (*C*H$_2$O), 69.09, 68.85, 68.63(*C*H$_2$*C*H$_2$), 66.33 (*C*H$_2$O), 58.96 (O*C*H$_3$), 53.60 (C-4), 52.05 (C-1), 18.25, 18.19 [C(*C*H$_3$)$_2$]. − IR (neat): $\tilde{\nu}$ = 3062 cm^{-1}, 3049 (w), 2979 (s), 2915 (s, b), 2874, 2859 (s), 2824 (s, sh), 2730, 1721, 1656, 1616 (w), 1450 (s), 1371 (m), 1351 (s), 1327, 1286, 1241 (m),

1199 (s), 1120, 1094 (ss), 1048 (s), 1012, 981 (m), 923, 882 (w), 851 (m), 816 (w). – MS (EI, 70eV); *m/z* (%): 396 (13) [M^+], 321 (24), 320 (98), 307 (14), 261 (33), 245 (51), 244 (100), 231 (59), 229 (31), 194 (29), 187 (39), 186 (51), 185 (76), 173 (40), 171 (56), 170 (45), 169 (68), 168 (47), 157 (75), 156 (38), 155 (53), 143 (44), 129 (36), 128 (31), 119 (29), 115 (27), 105 (25), 91 (35). – $C_{22}H_{36}O_6$: calcd. for [M^+] 396.2512; found 396.2512 ± 8 (HRMS).

7-Isopropylidene-2,3,5,6-tetrakis(2-methoxyethoxymethyl)bicyclo[2.2.1]hepta-2,5-diene (**6c**): Yield: 102 mg (51%). – R_f(TLC) = 0.42 (diethyl ether/ethanol, 20:1). – ^{1}H NMR ($CDCl_3$): δ = 4.24, 4.20 (2 d, ^2J = 12.6 Hz, 8 H, CH_2O), 4.05 (s, 2 H, 1,4-H), 3.52 (m, 8 H, CH_2CH_2), 3.50–3.40 (m, 8 H, CH_2CH_2), 3.37 (s, 12 H, OCH_3), 1.46 [s, 6 H, C(CH_3)$_2$]. – ^{13}C NMR ($CDCl_3$): δ = 159.63 (C-7), 148.49 (C-2,3,5,6), 96.57 (C-8), 71.93 (CH_2CH_2), 68.87 (CH_2CH_2), 66.33 (CH_2O), 58.93 (OCH_3), 54.40 (C-1,4), 18.14 [C(CH_3)$_2$]. – IR (neat): $\tilde{\nu}$ = 2978 cm^{-1} (m), 2920, 2916, 2878, 2859, 2824 (s), 2731, 1723, 1648 (w), 1451, 1371 (m), 1351 (s), 1287, 1271 (w), 1240 (m), 1199 (s), 1131, 1113, 1093 (ss), 1045, 1009, 981, 972 (m), 929, 882 (w), 851 (m).– MS (EI, 70eV); *m/z* (%): 484 (1) [M^+], 408 (15), 332 (45), 319 (21), 273 (13), 256 (17), 243 (15), 206 (14), 169 (14), 157 (10), 141 (7), 105 (6), 91 (7), 59 (100), 45 (7). – $C_{26}H_{44}O_8$: calcd. for [M^+] 484.3036; found 484.3036 ± 14 (HRMS).

Catalytical Reisomerization of the Quadricyclanes: The catalysts used for the reisomerization processes are summarized in Scheme 4. Cobalt porphyrins: TMPP-Co (Aldrich-Chemie), TCPP-Co (the ligand was synthesized according to ref.[24], the complex was synthesized according to ref.[25]), TMPyP-Co (the ligand was purchased from Aldrich-Chemie, the complex synthesized according to ref.[25]). – Cobalt porphyrin analoga were kindly provided by Prof. Jäger, Jena[17] – Di-μ-chlorobis[(2,5-norbornadiene)rhodium(I)] (Aldrich-Chemie).

Reisomerization Experiments: A solution of the catalyst (5 to 10 mol%) was added to a solution of the quadricyclane ethers **3** and **4.** The rate of isomerization was monitored by TLC and ^{1}H NMR. The catalyst was dissolved in CH_2Cl_2 except for TCPP-Co and TMPyP-Co which were dissolved in ethanol. TLC was carried out with hexane/ethylacetate, 1:1 (**3a**), 2:1 (**3b**), diethyl ether (**4a**) and diethyl ether/ethanol, 20:1 (**4b**). The solvents used for NMR experiments were [D_4]methanol for TCPP-Co and TMPyP-Co and $CDCl_3$ for all other catalysts.

Reisomerization of Quadricyclane Tetraether **3c** *with Stannylene* **7** *and Germylene* **8**: To a solution of different concentrations of the respective catalyst in dry $CDCl_3$ or [D_6]benzene the quadricyclane ether **3c** was added and the progress of the reisomerization monitored by ^{1}H NMR. Conversion was almost complete only when one equivalent of **7** or **8** was used. Purification by flash chromatography gave the norbornadiene tetraether **5c** in a yield of 14–21%.

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