Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Mono epoxidation of α,ω–dienes using NBS in a water-soluble cavitand

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General Information and experimental procedure

All commercially available chemicals were purchased from TCI, Alfa aesar, Energy chemicals, Macklin and used without further purification. Dry solvents directly purchased from Energy chemical and transferred *via* dry syringe. NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. ^{1}H NMR, and COSY NMR spectra were recorded at 600 MHz on a Bruker DRX-600 spectrometer at the reported temperatures. Chemical shifts are reported in ppm using the residual solvent peaks as reference: D_2O $\delta = 4.79$ ppm (^{1}H NMR); CD_3OD $\delta = 3.34$ ppm (^{1}H NMR). GC analyses were performed by SHIMADZU Nexis GC 2030 gas chromatography.

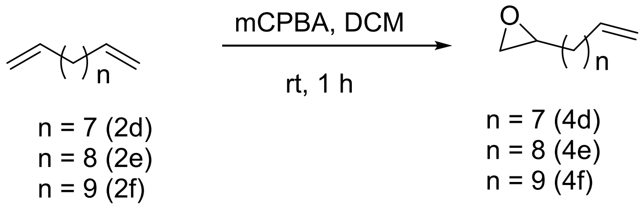
Experimental procedures: In a vial, a solution of the guest (50 mM in MeOH, 14 μL) was added and methanol was removed by reduced pressure. Cavitand **1** in D_2O (1.4 mM, 0.5 mL) was added to the vial in order to get a host-guest ratio 1:1. The final mixture was sonicated for 6 h and analyzed by ^{1}H NMR spectroscopy.

Δδ Calculation:

Δδ (ppm) = the chemical shift of bound (ppm)-the chemical shift of free (ppm)

Cavitand 1 was synthesized according to reported procedure in literature.[1-3]

Synthesis of monepoxides 4c-f



General experiment : To a stirred solution of dienes (**2d-f**, 6 mmol) in DCM (10 ml), was added *m*-chloroperbenzoic acid (*m*-CPBA) (3 mmol) and the resulting mixture stirred for 2 h. Then quenched with $NaHCO_{3(aq.)}$ (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resultant crude was further purified column chromotography (SiO_2, EtOAc/ hexane, 1:19) to give **4c-f** as a colourless oil.

2-(non-8-en-1-yl)oxirane (**4d**)[4]: ^1H NMR ($CDCl_3$, 600 MHz): δ 5.84-5.79 (m, 1H), 4.99 (d, *J* = 18 Hz, 1H), 4.93 (d, *J* = 6 Hz, 1H), 2.92-2.89 (m, 1H), 2.74 (t, *J* = 6 Hz, 1H), 2.46 (dd, *J* = 6 Hz, *J* = 6 Hz, 1H), 2.04 (m, 2H), 1.54-1.52 (m, 2H), 1.47-1.43 (m, 2H), 1.40-1.28 (m, 8H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 139.2, 114.2, 52.4, 47.1, 33.8, 32.5, 29.4, 29.0, 28.9, 25.9**.**

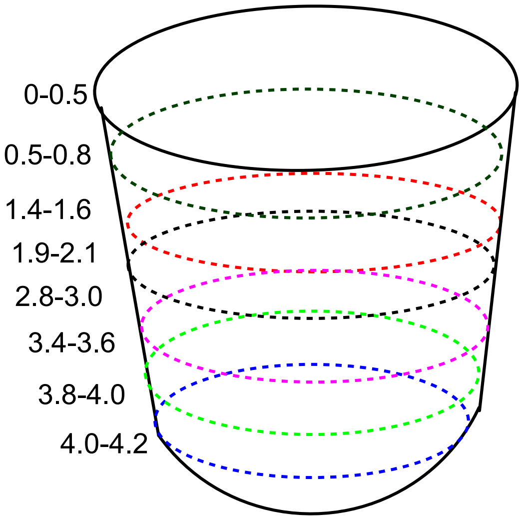
2-(dec-9-en-1-yl)oxirane (**4e**)[5, 6]: ^1H NMR ($CDCl_3$, 600 MHz): δ 5.83-5.78 (m, 1H), 4.99 (d, *J* = 18 Hz, 1H), 4.92 (d, *J* = 6 Hz, 1H), 2.91-2.88 (m, 1H), 2.74 (t, *J* = 6 Hz, 1H), 2.46-2.45 (m, 1H), 2.06-2.02 (m, 2H), 1.54-1.51 (m, 2H), 1.48-1.41 (m, 2H), 1.40-1.32 (m, 4H), 1.32-1.27 (m, 6H). ^{13}C NMR (CDCl3, 150 MHz): *δ* 139.2, 114.1, 52.4, 47.1, 33.8, 32.5, 29.5, 29.4, 29.3, 29.1, 28.9, 26.0.

2-(undec-10-en-1-yl)oxirane (**4f**): ^1H NMR ($CDCl_3$, 600 MHz): δ 5.86-5.76 (m, 1H), 4.99 (d, *J* = 24 Hz, 1H), 4.93 (d, *J* = 18 Hz, 1H), 2.92-2.89 (m, 1H), 2.75 (t, *J* = 6 Hz, 1H), 2.48-2.45 (m, 1H), 2.04 (m, 2H), 1.53-1.49 (m, 2H), 1.39-1.30 (m, 4 H), 1.28 (m, 8H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 139.3, 114.2, 52.5, 47.2, 33.9, 32.6, 29.6, 29.6, 29.5, 29.2, 29.0, 26.1.

Synthesis of Bromohydrin (C_{10}): 2-(oct-7-en-1-yl)oxirane (300 mg, 1.94 mmol) was added to a solution of LiBr (540 mg, 6.21 mmol), $CuBr_2$ (693 mg, 3.10 mmol) in dry THF (20 mL) at room temperature. The resultant mixture was stirred for 4 h at room temperature. Then quenched with $NH_4Cl_{(aq.)}$ (10 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic layer dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resultant crude was further purified by column chromatography (SiO_2, EtOAc/ hexane, 1:18) to provided bromohydrin as colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.83-5.78 (m, 1H), 4.99 (d, *J* = 18 Hz, 1H), 4.93 (d, *J* = 12 Hz, 1H), 3.78-3.77 (m, 1H), 2.10 (d, *J* = 6 Hz, 1H), 2.06-2.02 (m, 2H), 1.57-1.53 (m, 2H), 1.48-1.43 (m, 1H), 1.40-1.30 (m, 7H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 139.1, 114.3, 71.1, 40.7, 35.1, 33.7, 29.3, 28.9, 28.8, 25.6.

1,6-di(oxiran-2-yl)hexane (diepoxide)[7]: Synthesized by using reported procedure. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.91-2.88 (m, 1H), 2.73 (t, J = 6 Hz, 1H), 2.45 (dd, J = 3 Hz, J = 5 Hz, 1H), 1.64-1.27 (m, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): *δ* 52.3, 47.1, 32.4, 29.3, 25.9.

Approximate upfield shifts (–Δδ) experienced by nuclei in cavitands 1



1

Figure S1. Approximate upfield shifts (–Δδ) experienced by nuclei in cavitand **1**.

^{1}H and ^{13}C NMR spectra of authentic compounds

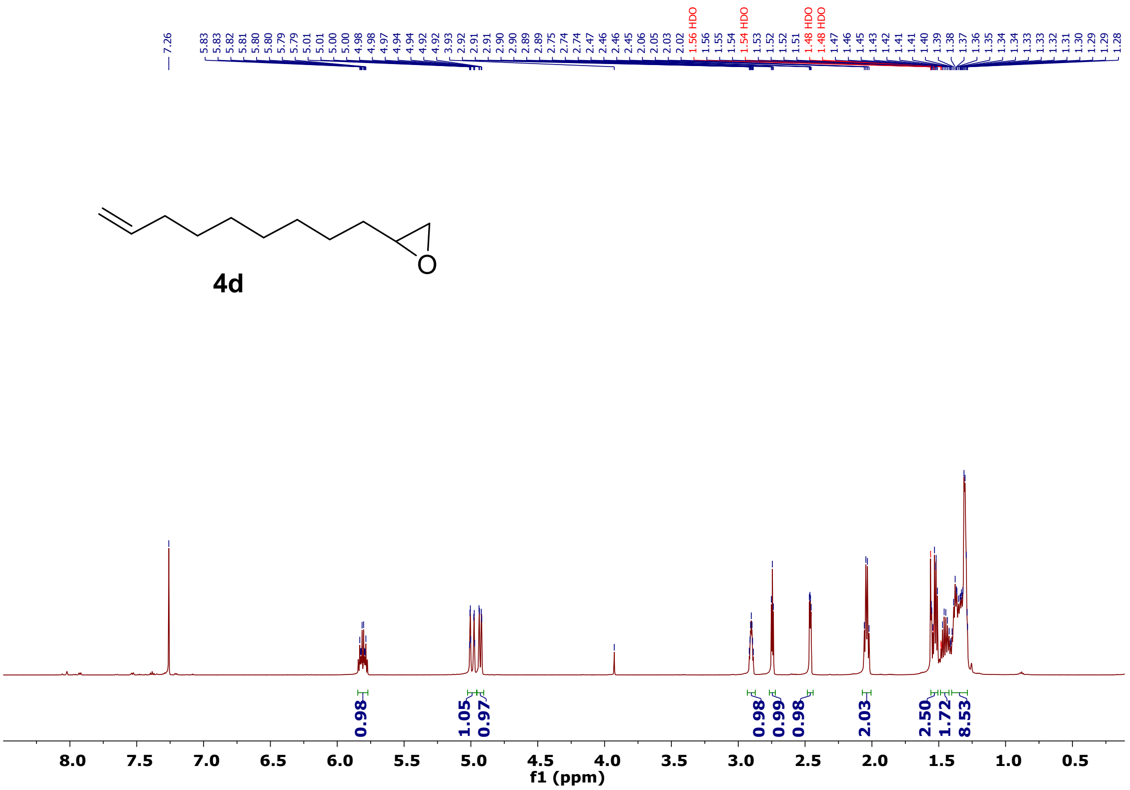


Figure S2. ^{1}H NMR of **4d** ($CDCl_3$, 600 MHz)

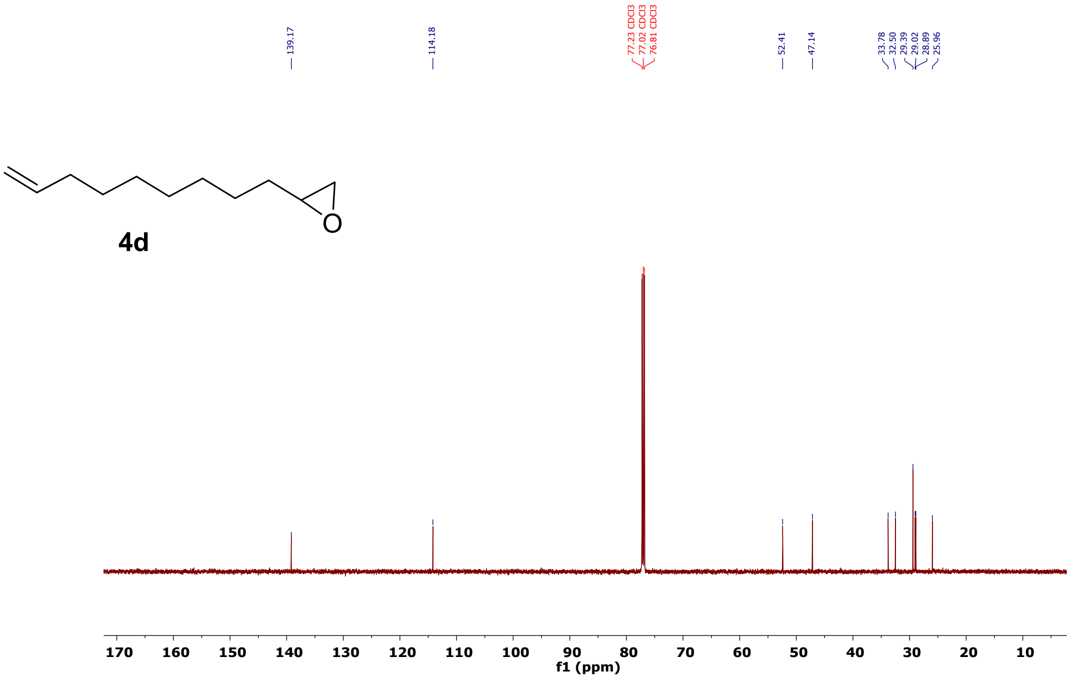


Figure S3. ^{13}C NMR of **4d** ($CDCl_3$, 150 MHz)

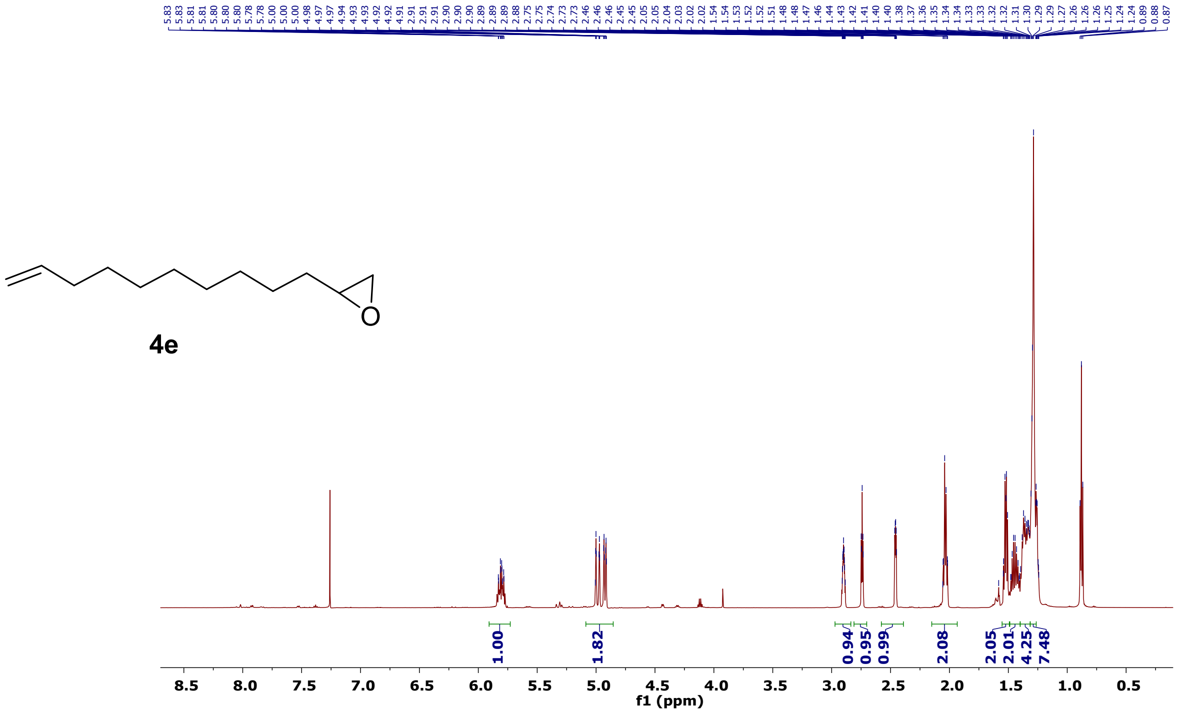


Figure S4. ^{1}H NMR of **4e** ($CDCl_3$, 600 MHz)

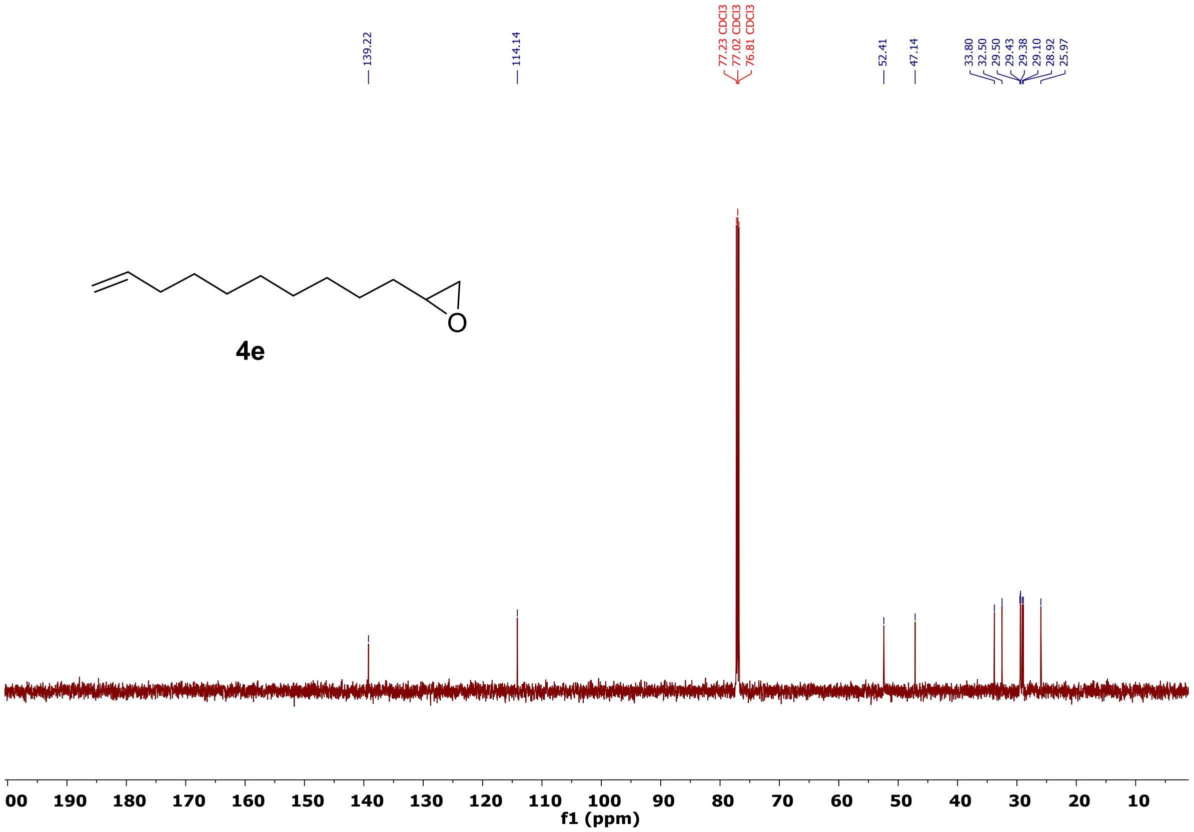


Figure S5. ^{13}C NMR of **4e** ($CDCl_3$, 150 MHz)

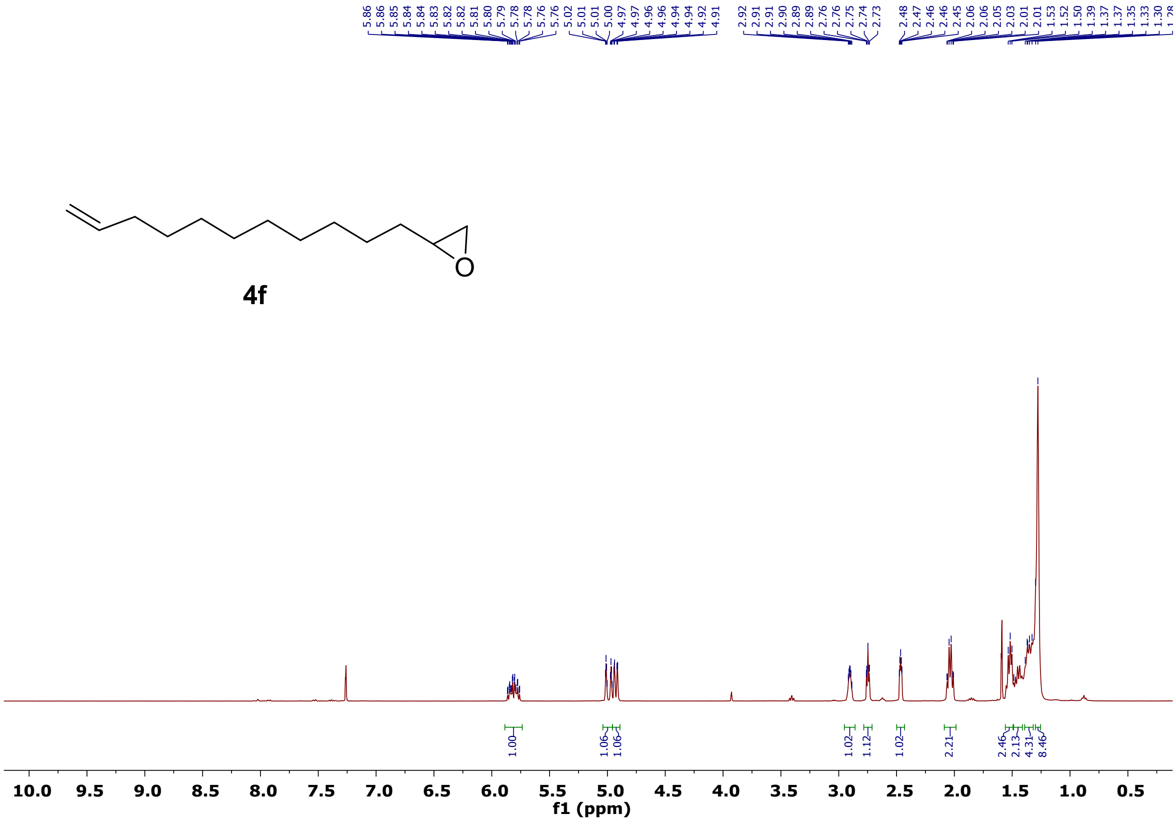


Figure S6. ^{1}H NMR of **4f** ($CDCl_3$, 600 MHz)

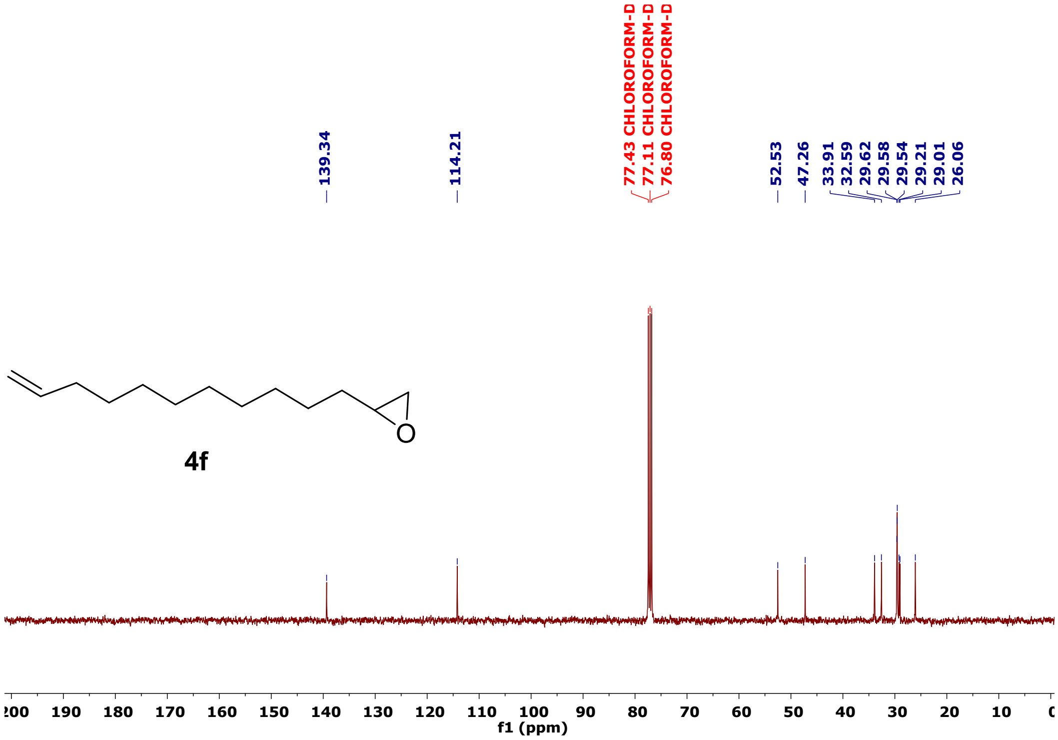


Figure S7. ^{13}C NMR of **4f** ($CDCl_3$, 150 MHz)

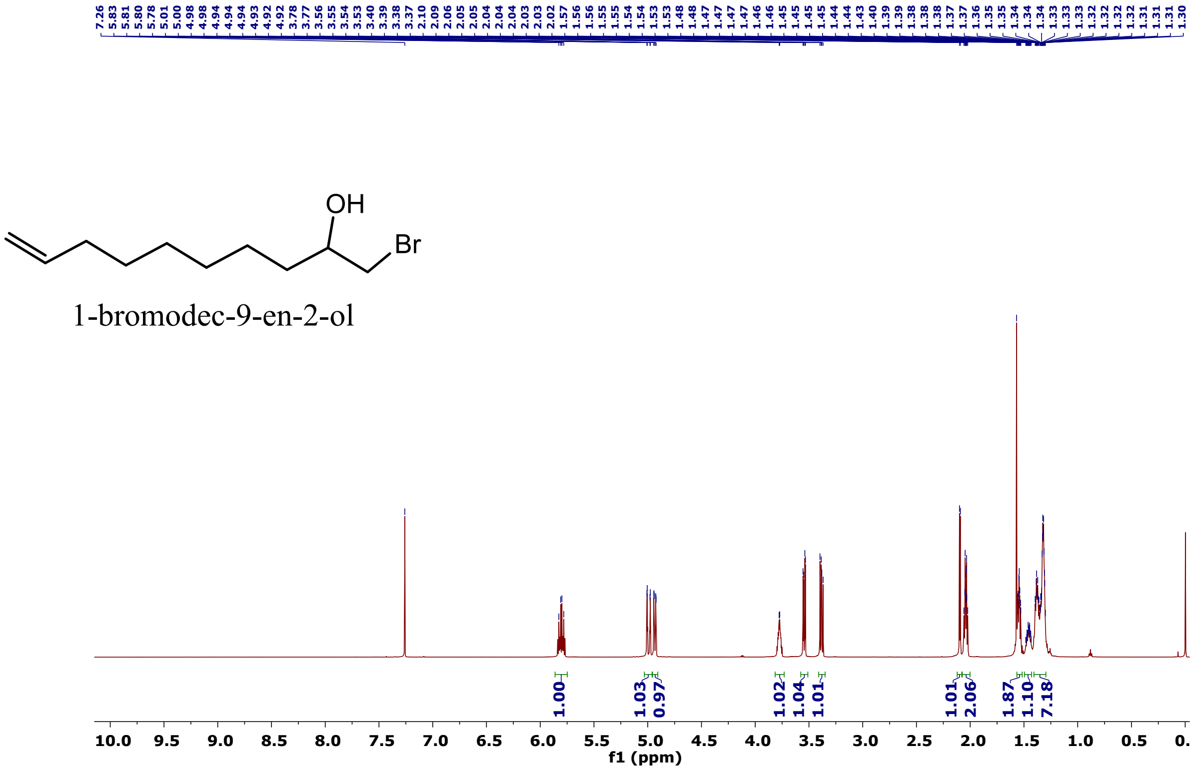


Figure S8. ^{1}H NMR of bromohydrin (C_{10}) ($CDCl_3$, 600 MHz

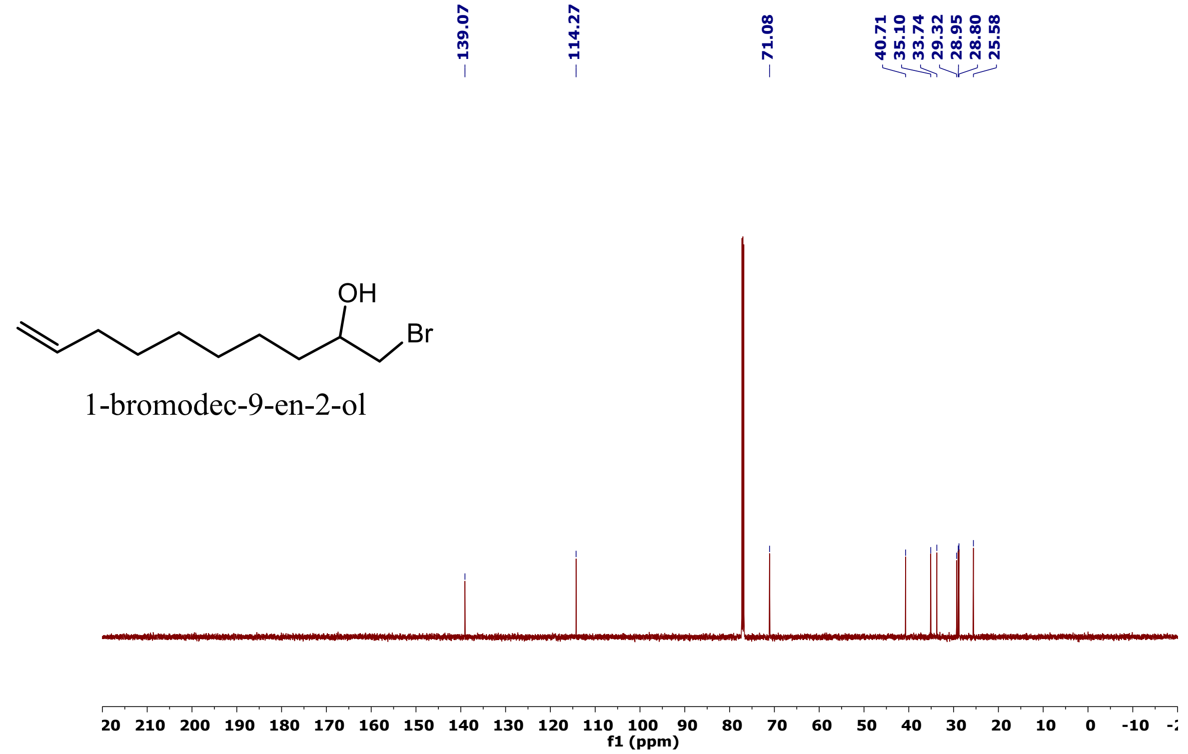


Figure S9. ^{13}C NMR of bromohydrin (C_{10}) ($CDCl_3$, 150 MHz)

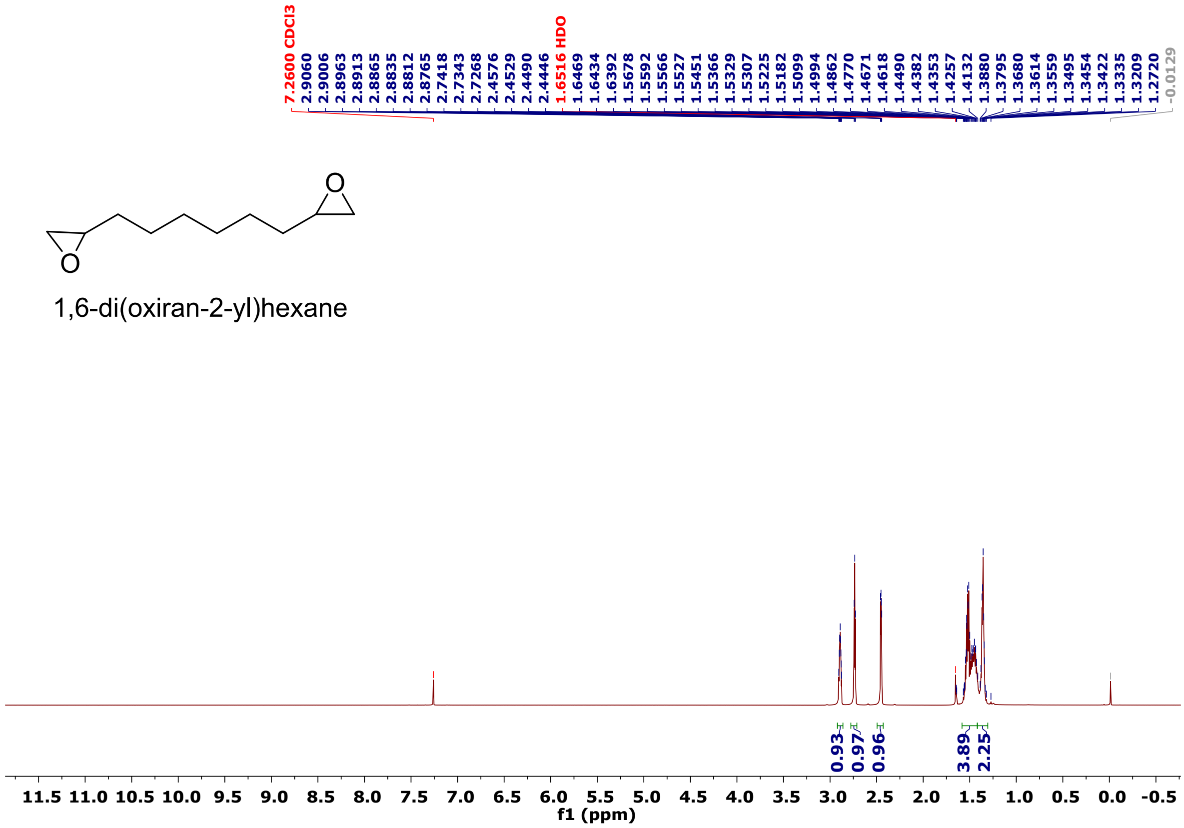


Figure S10. ^{1}H NMR of 1,6-di(oxiran-2-yl)hexane (diepoxide) ($CDCl_3$, 600 MHz)

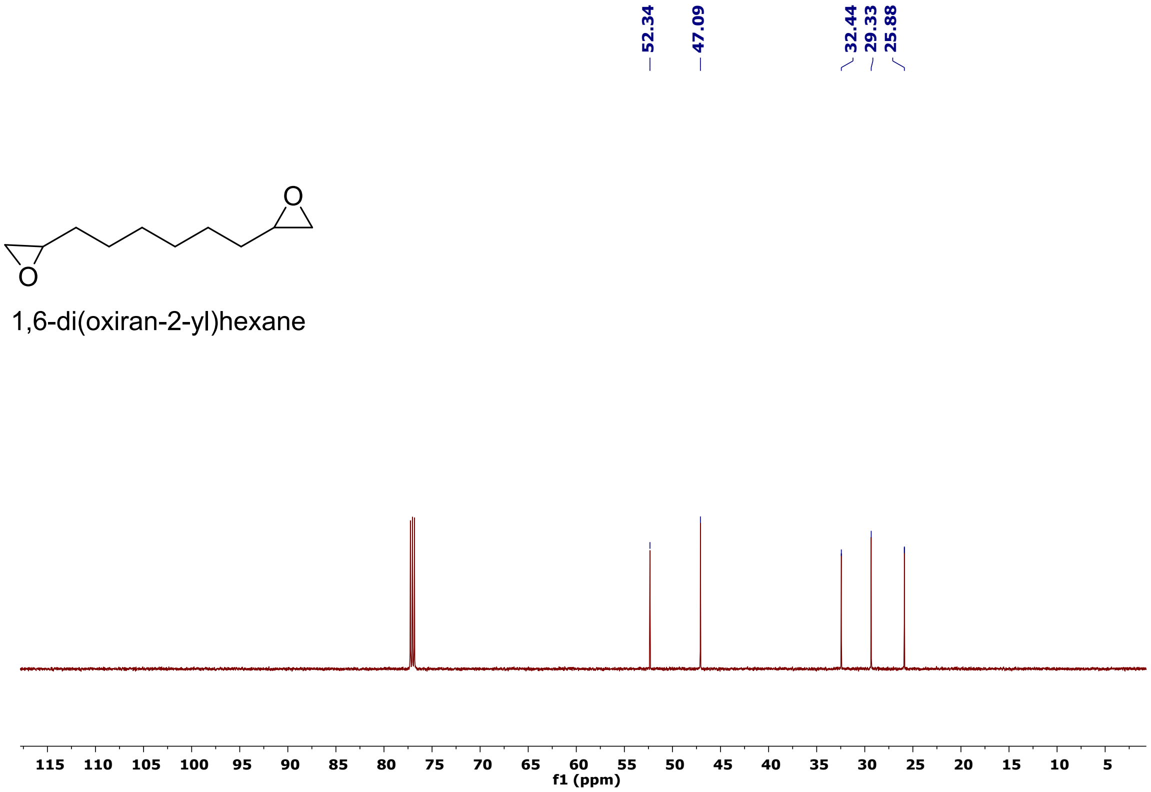


Figure S11. ^{13}C NMR of 1,6-di(oxiran-2-yl)hexane (diepoxide) ($CDCl_3$, 150 MHz)

Binding and conformation studies in cavitand 1

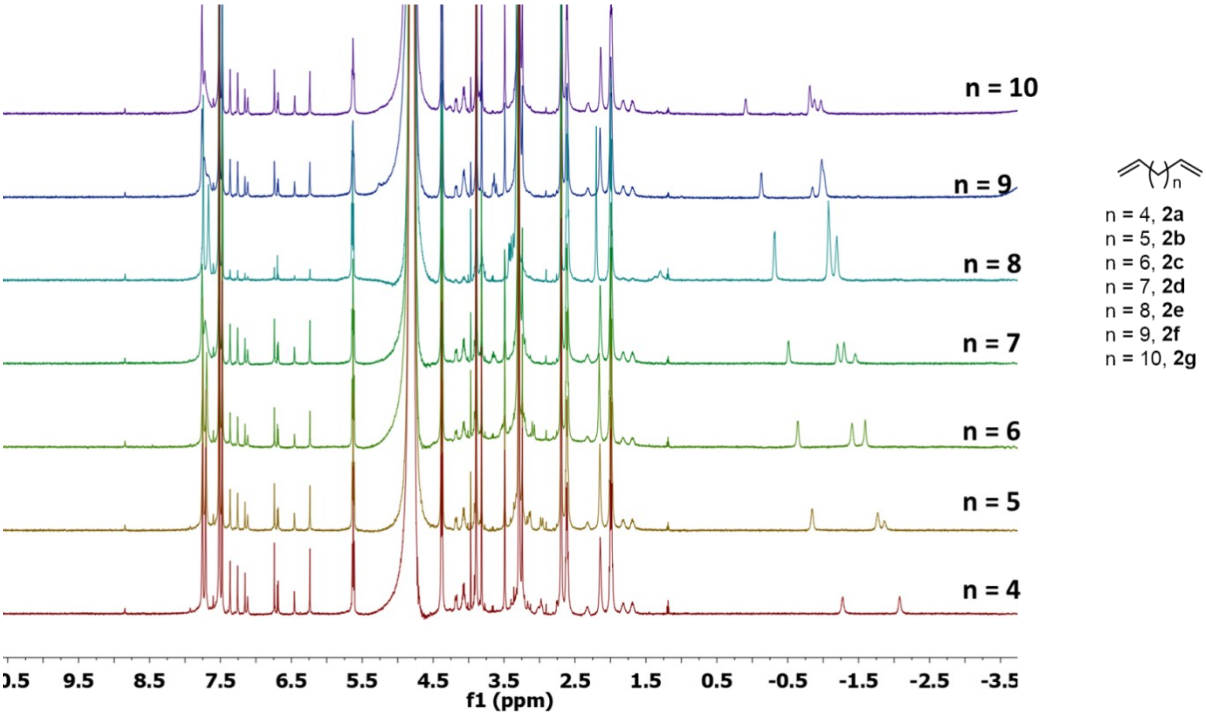


Figure S12. Stacked full ^{1}H NMR spectra of α,ω-dienes (**2a-g**) binding in cavitand **1**.

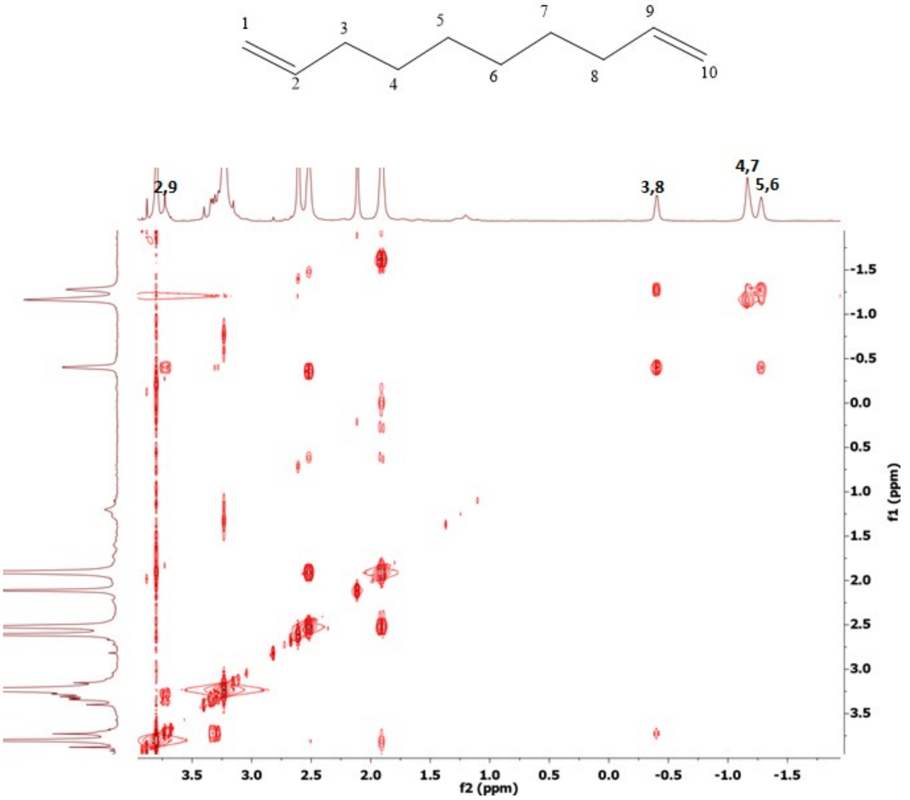
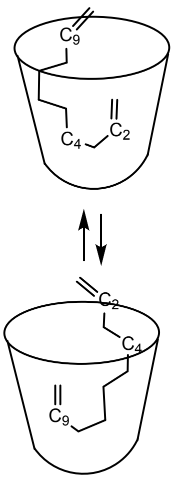
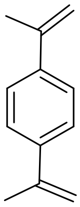


Figure S13. Partial COSY NMR spectrum of **2c** in **1**.



deca-1,9-diene (C_{10})			
	Free	Bound	Δδ
	(ppm)	(ppm)	(ppm)
2,9	5.73	3.82	-1.91
3,8	2.01	-0.32	-2.33
4,7	1.30	-1.08	-2.38
5,6	1.28	-1.19	2.47

Figure S14. Cartoon conformation and relative chemical shifts of **2c** in **1**. The average Δδ value for each methylene is recorded on the structure.



1,4-di(prop-1-en-2-yl)benzene (**3**)

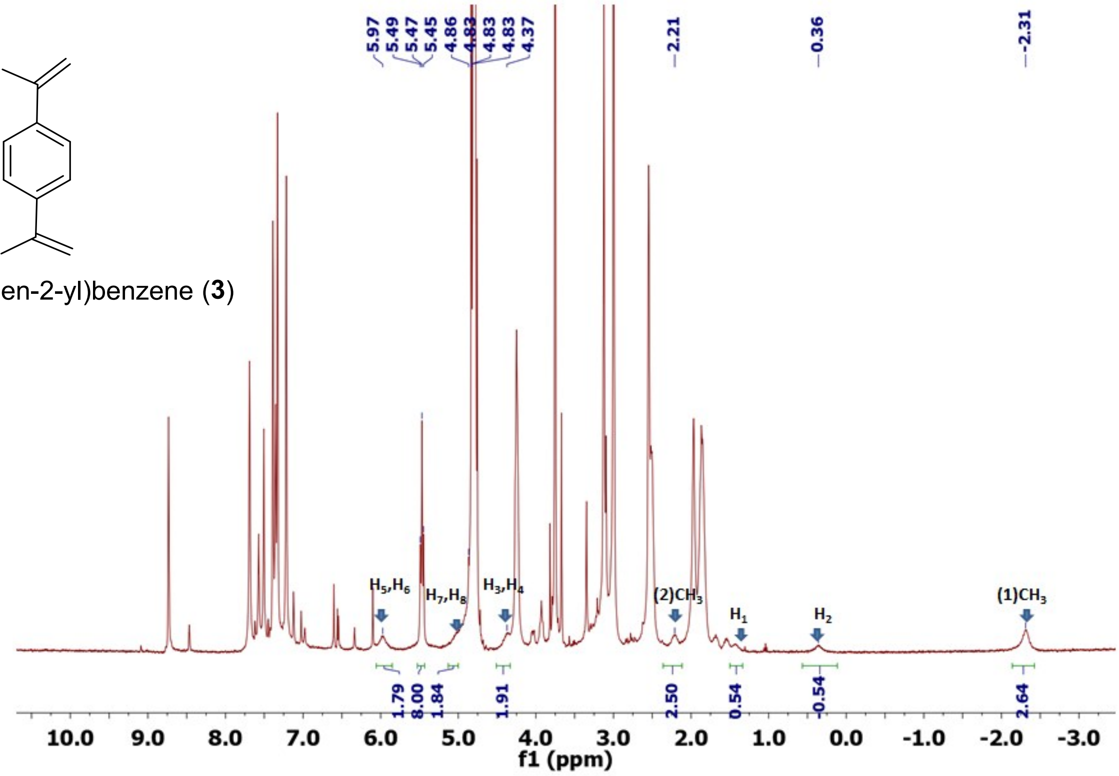
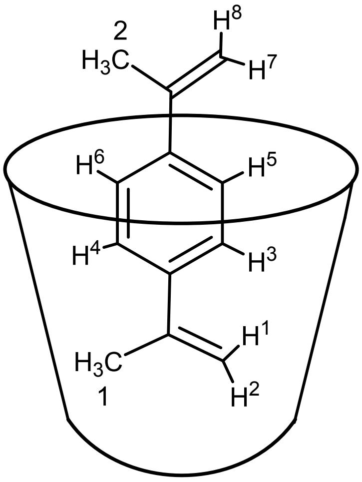


Figure S15. Full ^{1}H NMR spectrum of 1,4-di(prop-1-en-2-yl)benzene (**3**) in **1**.



1,4-di(prop-1-en-2-yl)benzene (3)			
	Free	**Bound**	**Δδ**
	(ppm)	**(ppm)**	**(ppm)**
$CH_3(2)$	2.21	2.2	0.01
H^8	5.09	5.01	0.08
H^7	5.4	5.01	0.39
H^5,H^6	7.45	5.97	1.48
H^4,H^3	7.45	5.01	2.44
H^1	5.4	1.39	-4.01
$CH_3(1)$	2.16	-2.31	-4.47
H^2	5.09	0.31	-4.78

Figure S16. Cartoon conformation and relative chemical shifts of **3** in **1**. The average ∆δ value for each methylene is recorded on the structure.

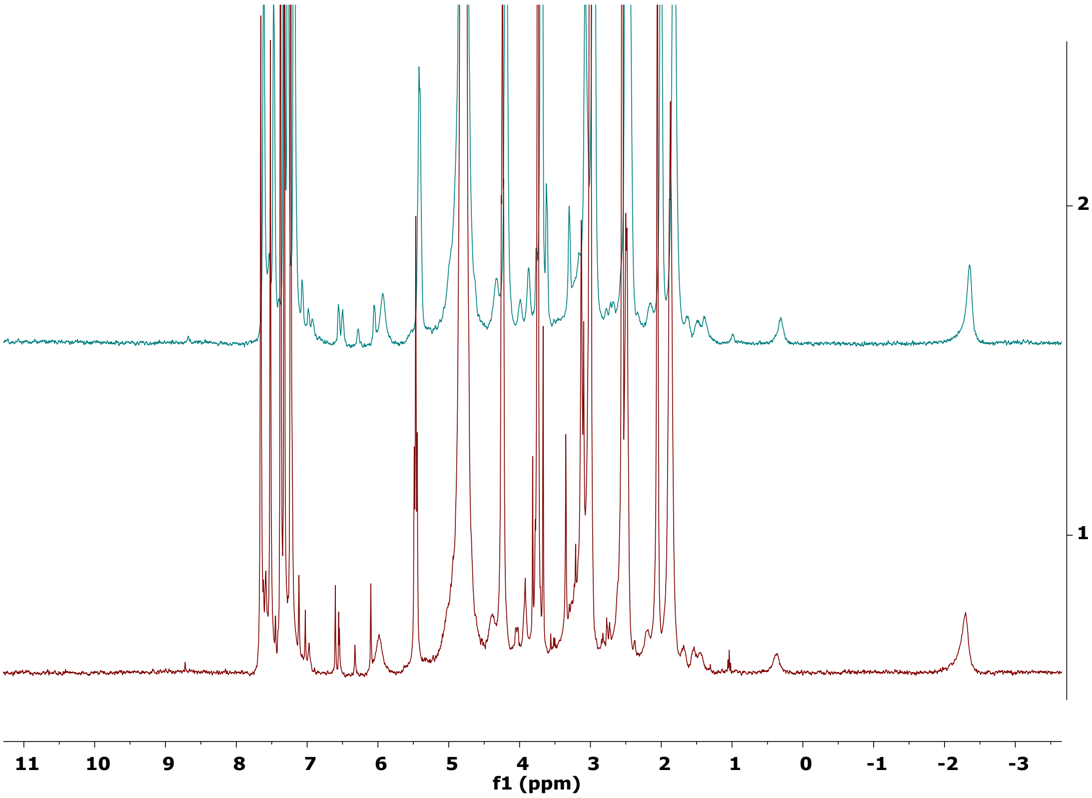


Figure S17. Full stacked spectra of **3** in **1** (400 MHz, D_2O) at low temperature (1) 10 ºC; (2) 5 ºC.

Mono functionalization reaction of α,ω-dienes 2c-g (C_{10}-C_{14}) and aromatic-1,4-substituted diene 3 by epoxidation with NBS

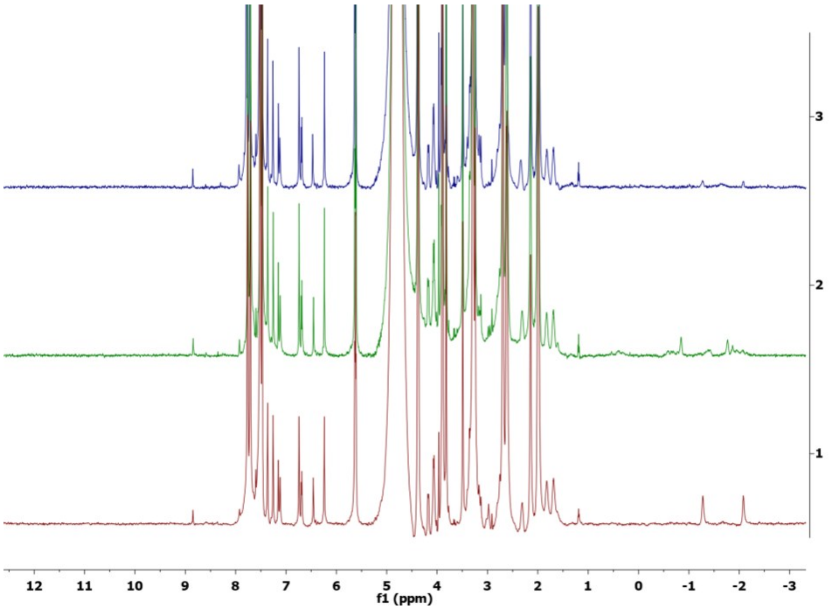


Figure S18. Stacked full ^{1}H NMR spectra **2a** in **1**. Reaction progress were recorded after addition of NBS (14 μL, 50 mM in DMSO-d_6) and stirred at 50 ºC : (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 μL, 50 mM in DMSO-d_6), 12 h; (3) sample 2, K_2CO_3 (7 μL in D_2O), 12 h. The product mon-epoxide (C_8) could be more soluble in water (hydrophilic), therefore most time product stay in water.

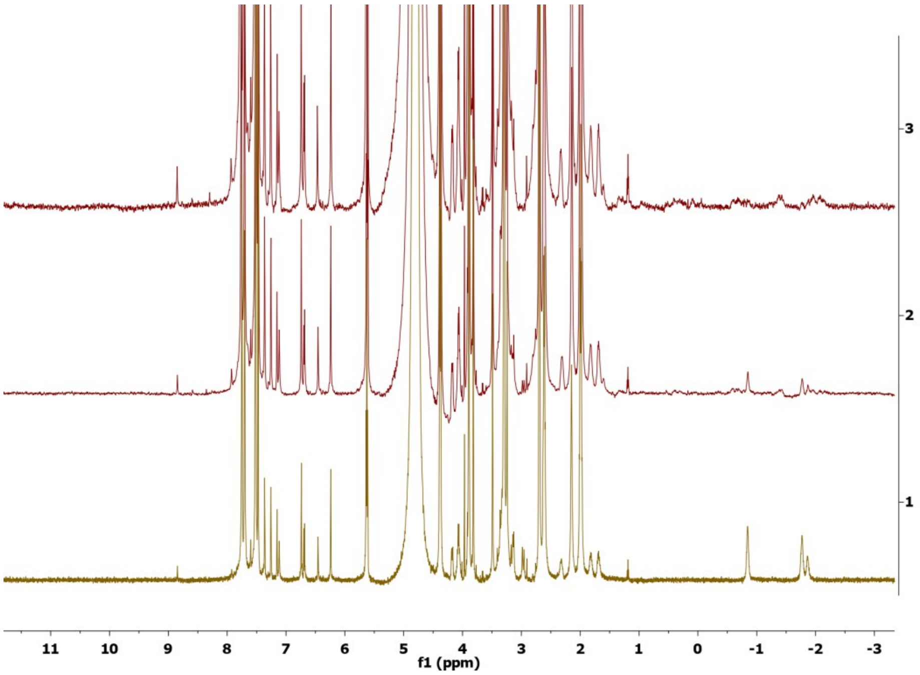


Figure S19. Stacked full ^{1}H NMR spectra **2b** in **1**. Reaction progress were recorded after addition of NBS (14 μL, 50 mM in DMSO-d_6) and stirred at 50 ºC : (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 μL, 50 mM in DMSO-d_6), 12 h; (3) sample 2, K_2CO_3 (7 μL in D_2O), 12 h. The product mon-epoxide (C_8) could be more soluble in water (hydrophilic), therefore most time product stay in water.

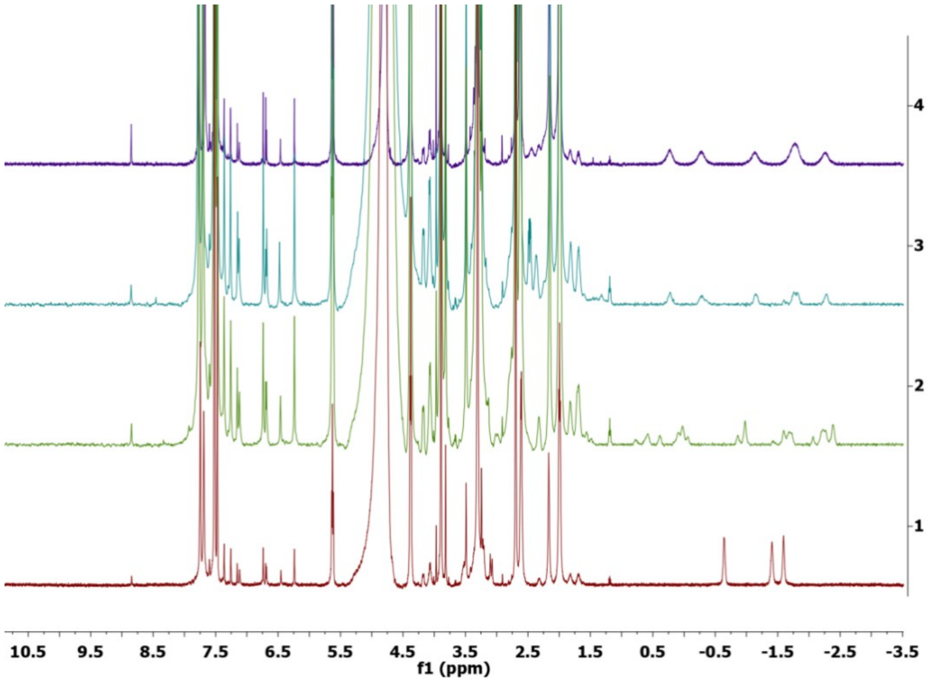


Figure S20. Stacked full ^{1}H NMR spectra **2c** in **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC : (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d_6), 12 h; (3) sample 2, K_2CO_3 (7 µL in D_2O), 12 h; (4) spectra of authentic C_{10} monoepoxide.

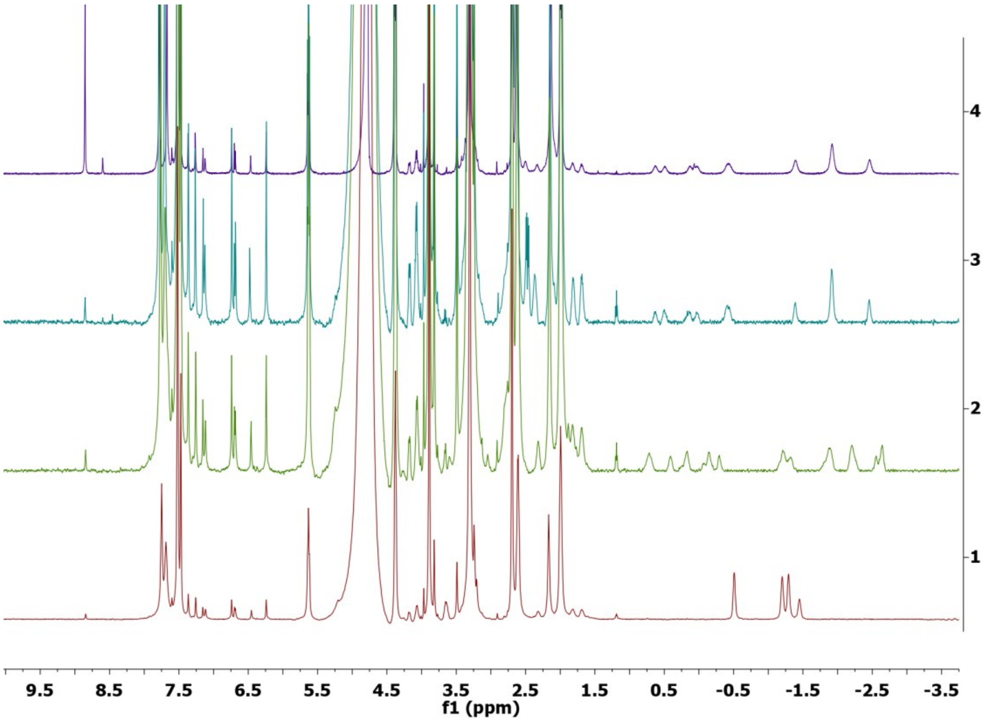


Figure S21. Stacked full ^{1}H NMR spectra **2d** in cavitand **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC: (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d6), 12 h; (3) sample 2, K_2CO_3 (7 µL in D_2O), 12 h; (4) spectra of authentic C_{11} monoepoxide.

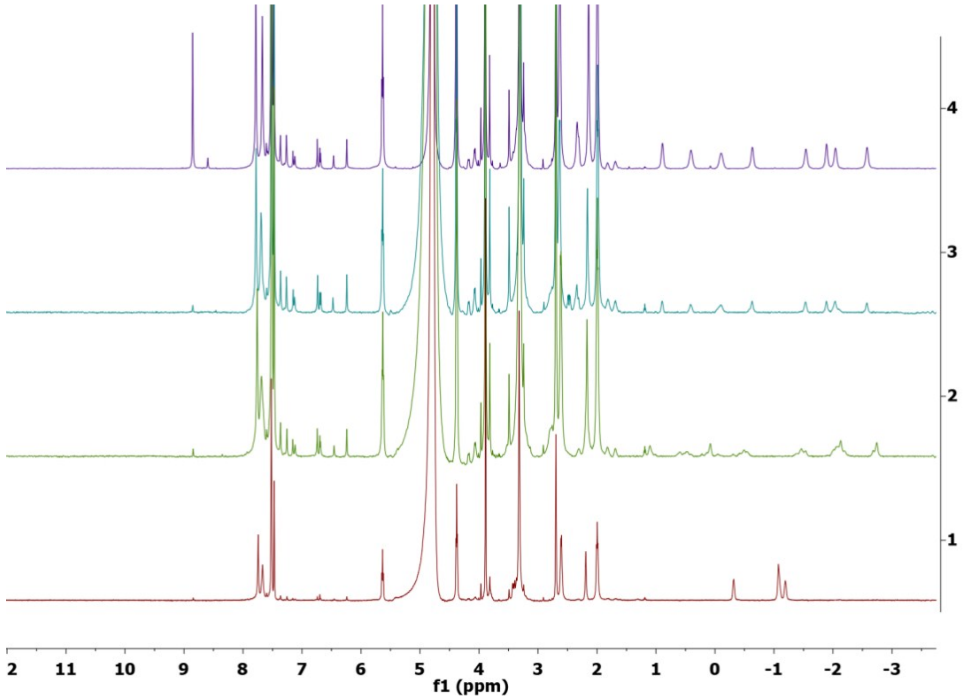


Figure S22. Stacked full ^{1}H NMR spectra **2e** in cavitand **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC: (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d_6), 12 h; (3) sample 2, K_2CO_3 (7 µL in D_2O), 12 h; (4) spectra of authentic C_{12} monoepoxide.

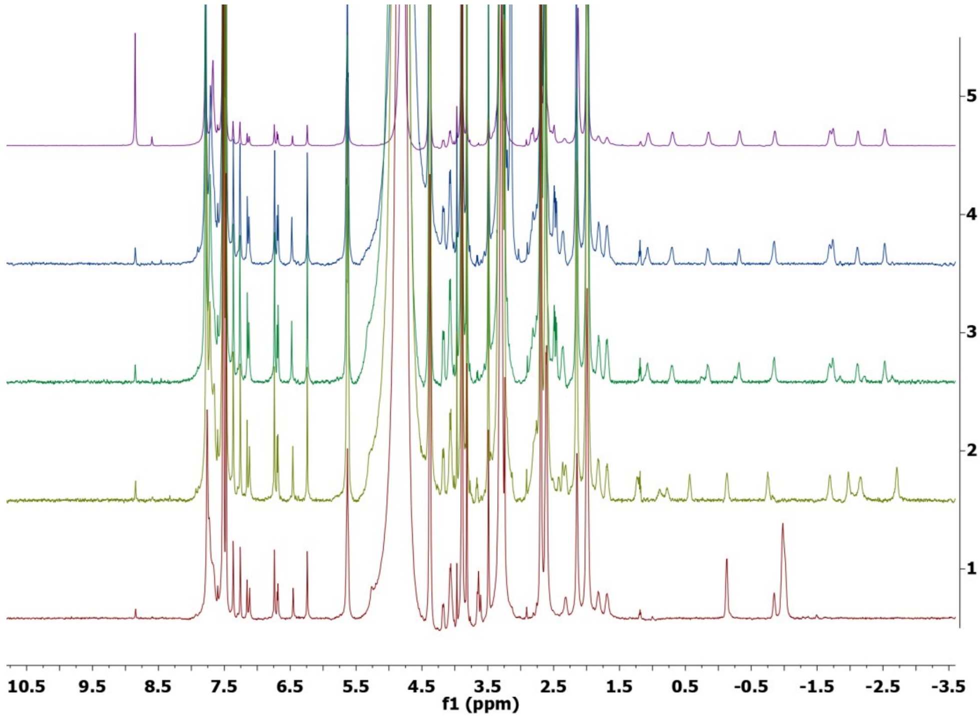


Figure S23. Stacked full ^{1}H NMR spectra **2f** in cavitand **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC: (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d_6), 2 h; (3) sample 2, 4h; (4) K_2CO_3 (7 µL in D_2O), 4 h; (4) spectra of authentic C_{13} monoepoxide.

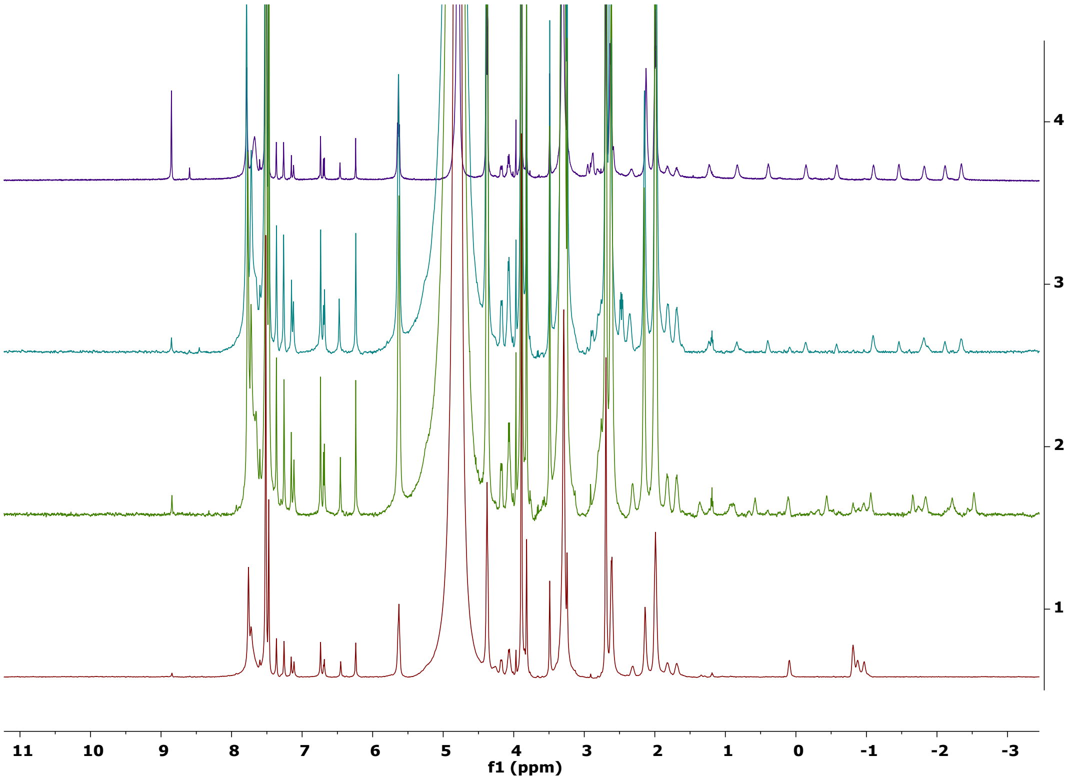
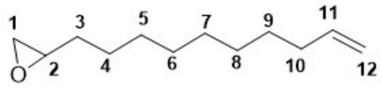


Figure S24. Stacked full ^{1}H NMR spectra **2g** in cavitand **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC: (1) after 3 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d_6), 2 h; (3) sample 2, 4h; (4) K_2CO_3 (7 µL in D_2O), 4 h; (4) spectra of authentic C_{14} monoepoxide.

Mono epoxide conformational study and stability



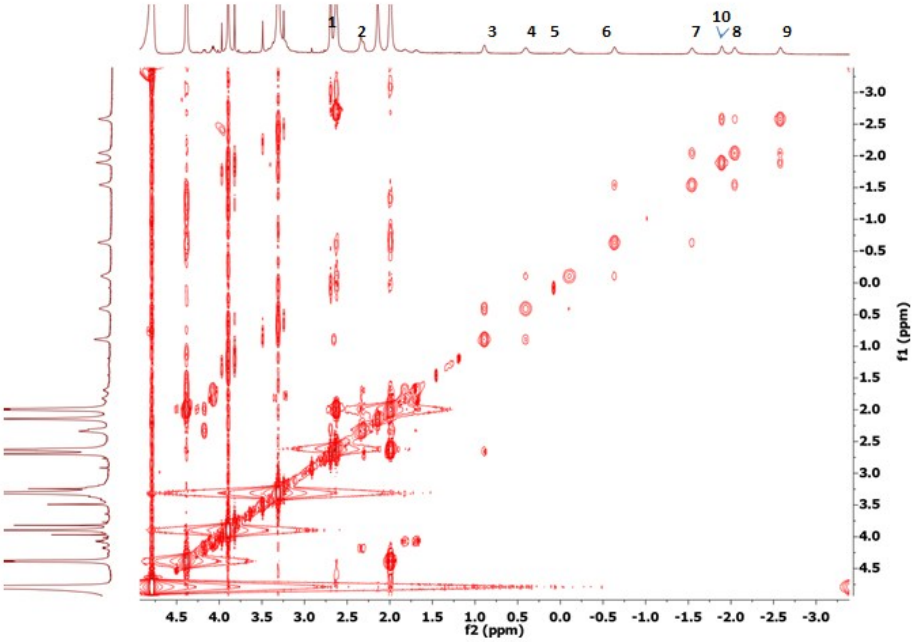


Figure S25. Partial COSY NMR spectrum of 2-(dec-9-en-1-yl)oxirane **4e** (C_{12}) in **1**.

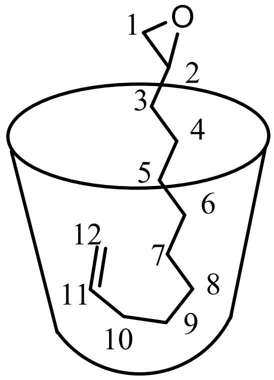
	**2-(dec-9-en-1-yl)oxirane** (C_{12})			
		Free (ppm)	Bound (ppm)	Δδ (ppm)
	1	2.61	2.61	0
	2	2.29	2.28	0.01
	3	1.48	0.89	-0.59
	4	1.38	0.41	-0.97
	5	1.30	0.11	-1.19
	6	1.30	-0.63	-1.93
	7	1.30	-1.54	-2.84
	8	1.30	-2.05	-3.35
	9	1.40	-2.57	-3.97
	10	2.02	-1.89	-3.91
	11	5.7		
	12	4.97		

Figure S26. Cartoon conformation and relative chemical shifts of 2-(dec-9-en-1-yl)oxirane **4e** (C_{12}) in **1**. The average Δδ value for each methylene is recorded on the structure.

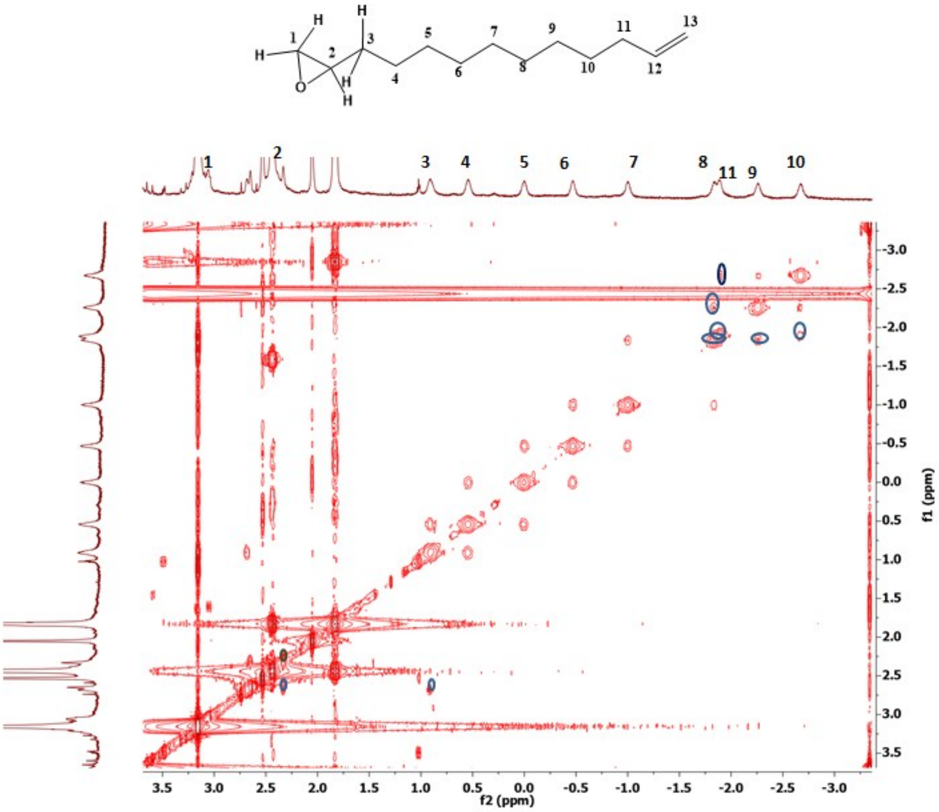


Figure S27. Partial COSY NMR spectrum of 2-(undec-10-en-1-yl)oxirane **4f** (C_{13})in cavitand **1**.

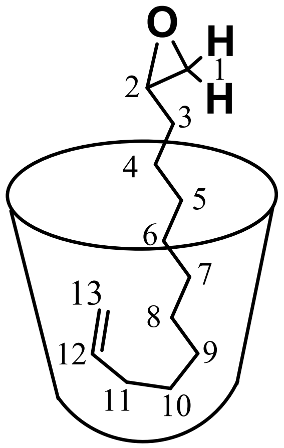
<table>
<tr><td rowspan="16">
</td><td colspan="4">2-(undec-10-en-1-yl)oxirane (C13)</td></tr>
<tr><td></td><td>Free</td><td>Bound</td><td>Δδ</td></tr>
<tr><td></td><td>(ppm)</td><td>(ppm)</td><td>(ppm)</td></tr>
<tr><td>1</td><td>2.79</td><td>2.79</td><td>0</td></tr>
<tr><td>2</td><td>2.74</td><td>2.70</td><td>-0.04</td></tr>
<tr><td>3</td><td>1.36</td><td>1.07</td><td>-0.29</td></tr>
<tr><td>4</td><td>1.27</td><td>0.72</td><td>-0.55</td></tr>
<tr><td>5</td><td>1.27</td><td>0.17</td><td>-1.10</td></tr>
<tr><td>6</td><td>1.27</td><td>-0.30</td><td>-1.57</td></tr>
<tr><td>7</td><td>1.27</td><td>-0.84</td><td>-2.11</td></tr>
<tr><td>8</td><td>1.27</td><td>-1.67</td><td>-2.94</td></tr>
<tr><td>9</td><td>1.44</td><td>-2.09</td><td>-3.53</td></tr>
<tr><td>10</td><td>1.51</td><td>-2.51</td><td>-4.02</td></tr>
<tr><td>11</td><td>2.04</td><td>-1.72</td><td>-3.76</td></tr>
<tr><td>12</td><td>5.81</td><td></td><td></td></tr>
<tr><td>13</td><td>4.9</td><td></td><td></td></tr>
</table>

Figure S28. Cartoon conformation and relative chemical shifts of 2-(undec-10-en-1-yl)oxirane **4f** (C_{13}) in cavitand **1**. The average Δδ value for each methylene is recorded on the structure.

Confirmation of bromohydrin intermediate formation in cavitand 1 with NBS

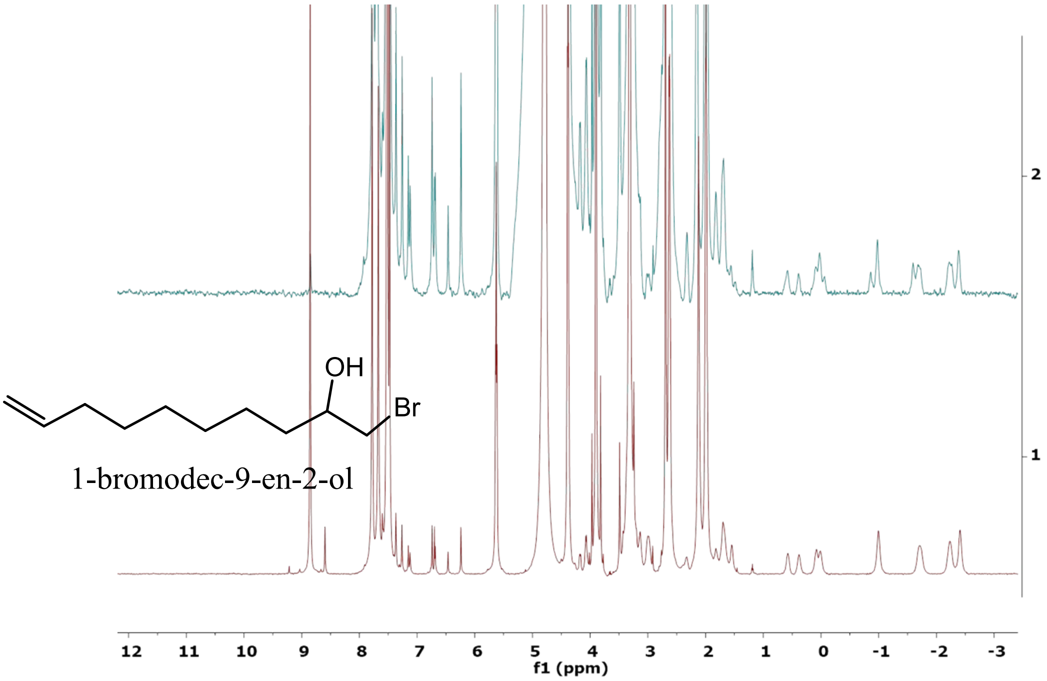


Figure S29. Stacked Full ^{1}H NMR spectrum to confirm bromohydrin intermediate; (1) authentic bromohydrin in cavitand **1**; (2) **2c** in cavitand **1**, after addition of NBS (1 equiv.) and stirred at 50 ºC for 12 h.

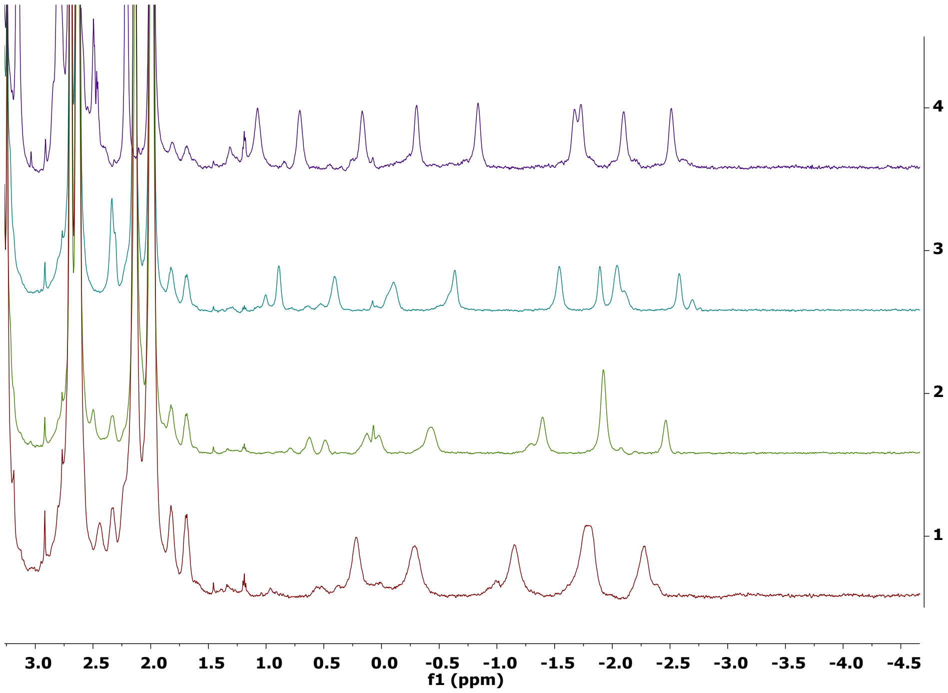


Figure S30. Partial ^{1}H NMR spectra of **2c-f**. Spectra recorded after reaction with 0.2 equiv. excess of NBS; Stirred for 6 hours. (1) C_{10} diene; (2) C_{11} diene; (3) C_{12} diene; (4) C_{13} diene

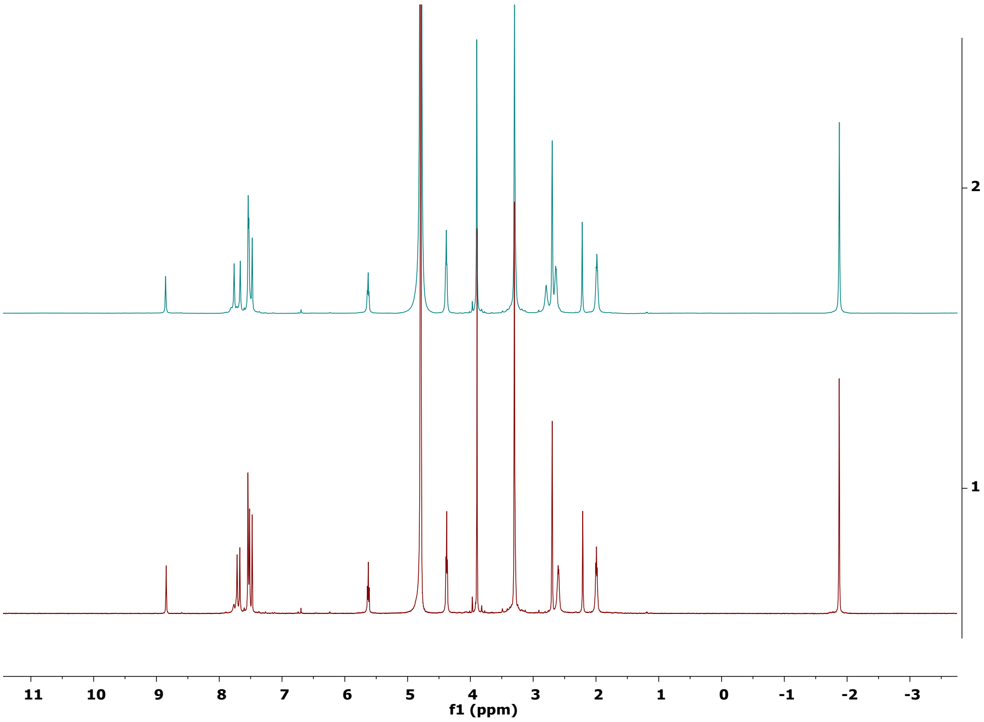


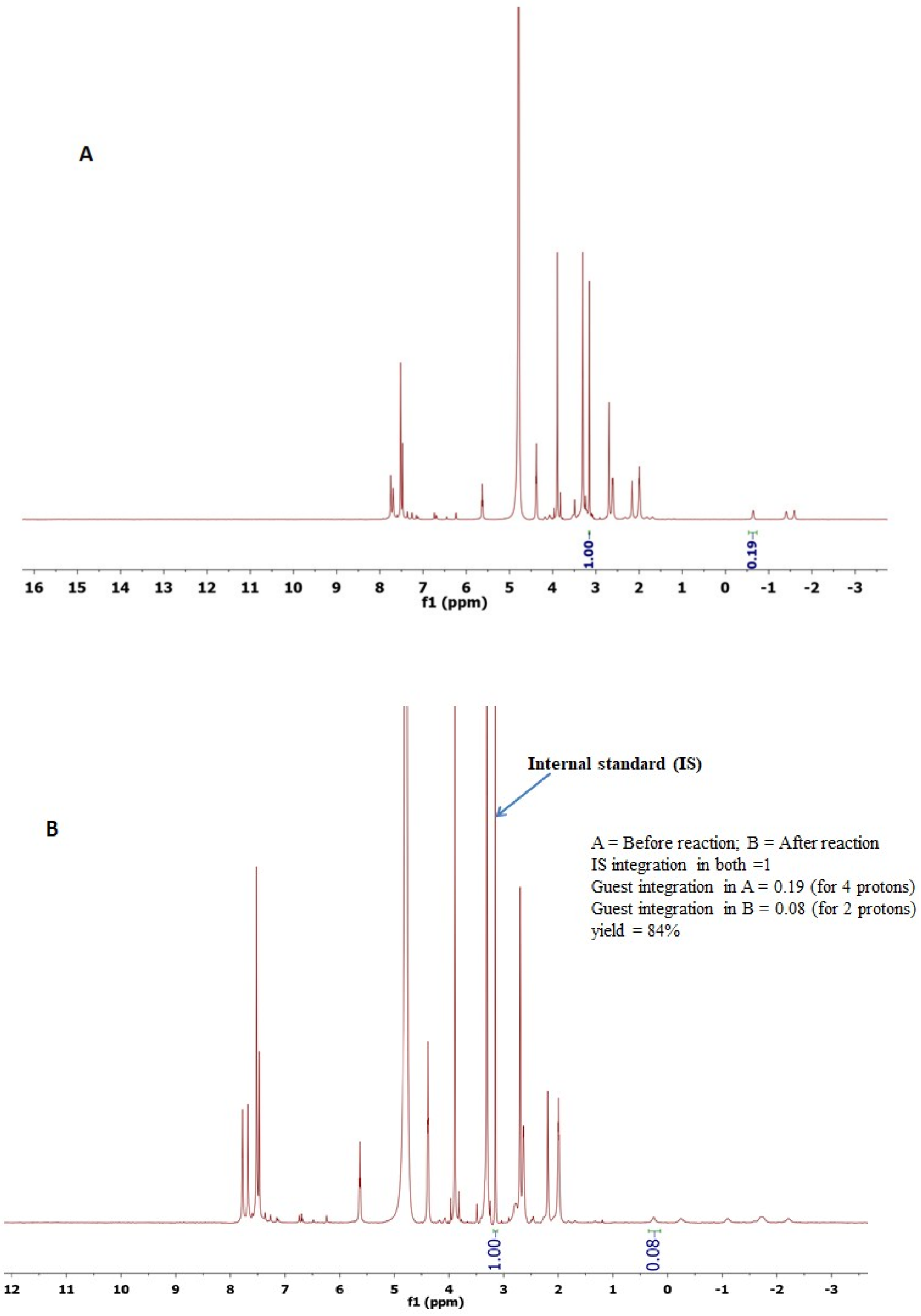
Figure S31. Stacked full spectrum of cavitand **1** with cycloheptane (1:1) host-guest ratio. (1) cavitand **1** with guest cycloheptane (1:1); (2) spectrum 1, with 1 eq. of NBS and stirred for 12 h at 50 ºC.

Relative yield calculations of mono epoxidation with α,ω-dienes

Dimethyl sulfone was used as water soluble internal standard (NMR chemical shift for six protons = 3.15 ppm). Concentration of the internal standard (IS) was always used 1.4 mM. The reaction substrates (**2c-f**) (1.4 mM), and cavitand **1** (1.4 mM) was added and sonicated for 3 h to ensure complete complexation. After complexation, internal standard (IS) was added and recorded the ^{1}H NMR spectroscopy. Integration of IS and bound guest peaks (**2c-f**) was checked before the reaction. Again, the integration of IS and product nuclei was checked after reaction with sequencial addition DMSO-d_6 at given temperature and time.

% of yield was calculated by following equation using selective known peak integration.

$$\%\ of\ yield\ = \frac{Integration\ number\ of\ after\ reaction\ for\ 2\ protons}{Integration\ number\ of\ before\ reaction\ for\ 2\ protons} \times 100$$

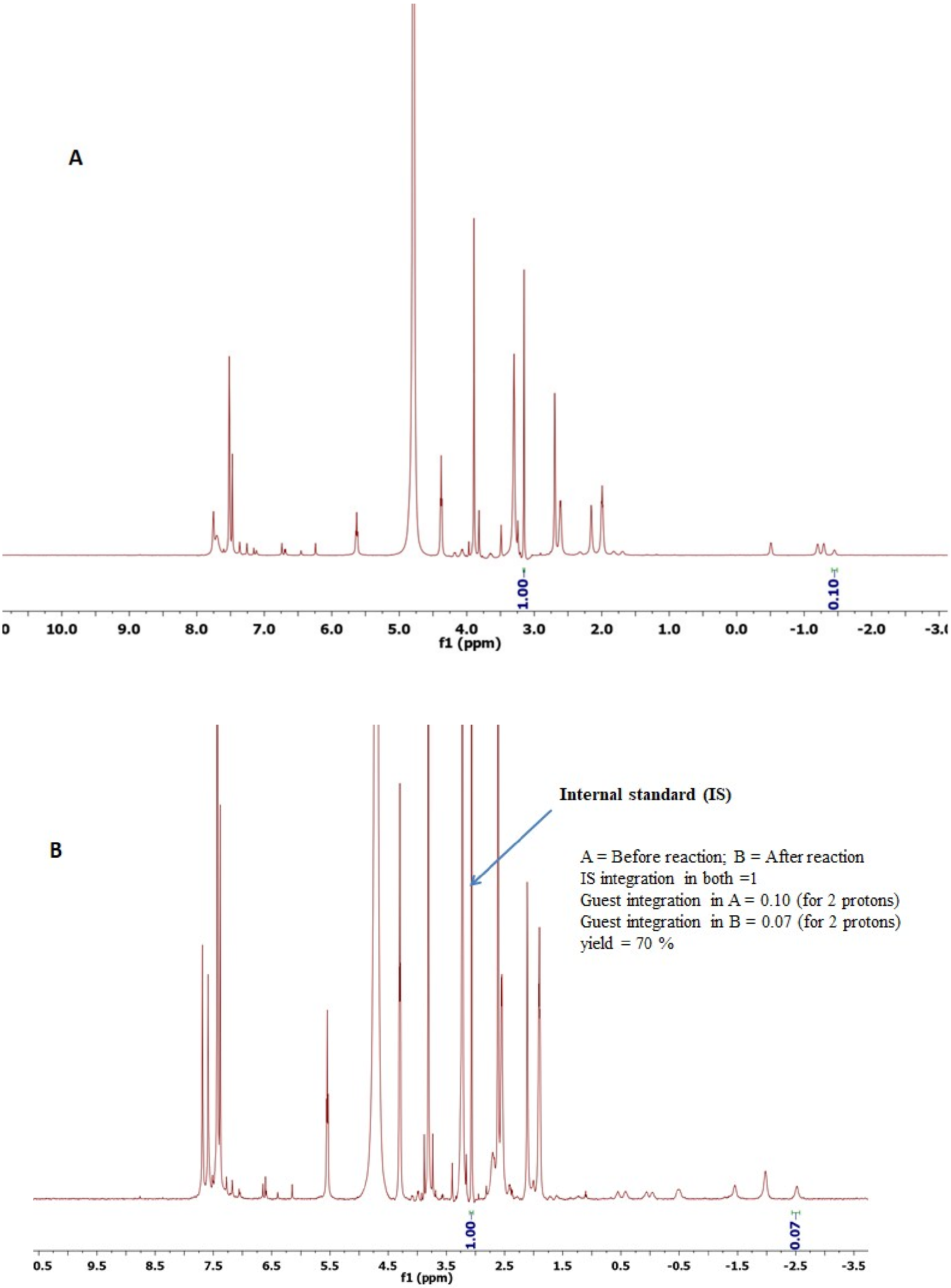


Internal standard (IS)

A = Before reaction; B = After reaction
IS integration in both =1
Guest integration in A = 0.19 (for 4 protons)
Guest integration in B = 0.08 (for 2 protons)
yield = 84%

Figure S32. Full ^{1}H NMR spectra of **4c** with internal standard for quantifying the yield.

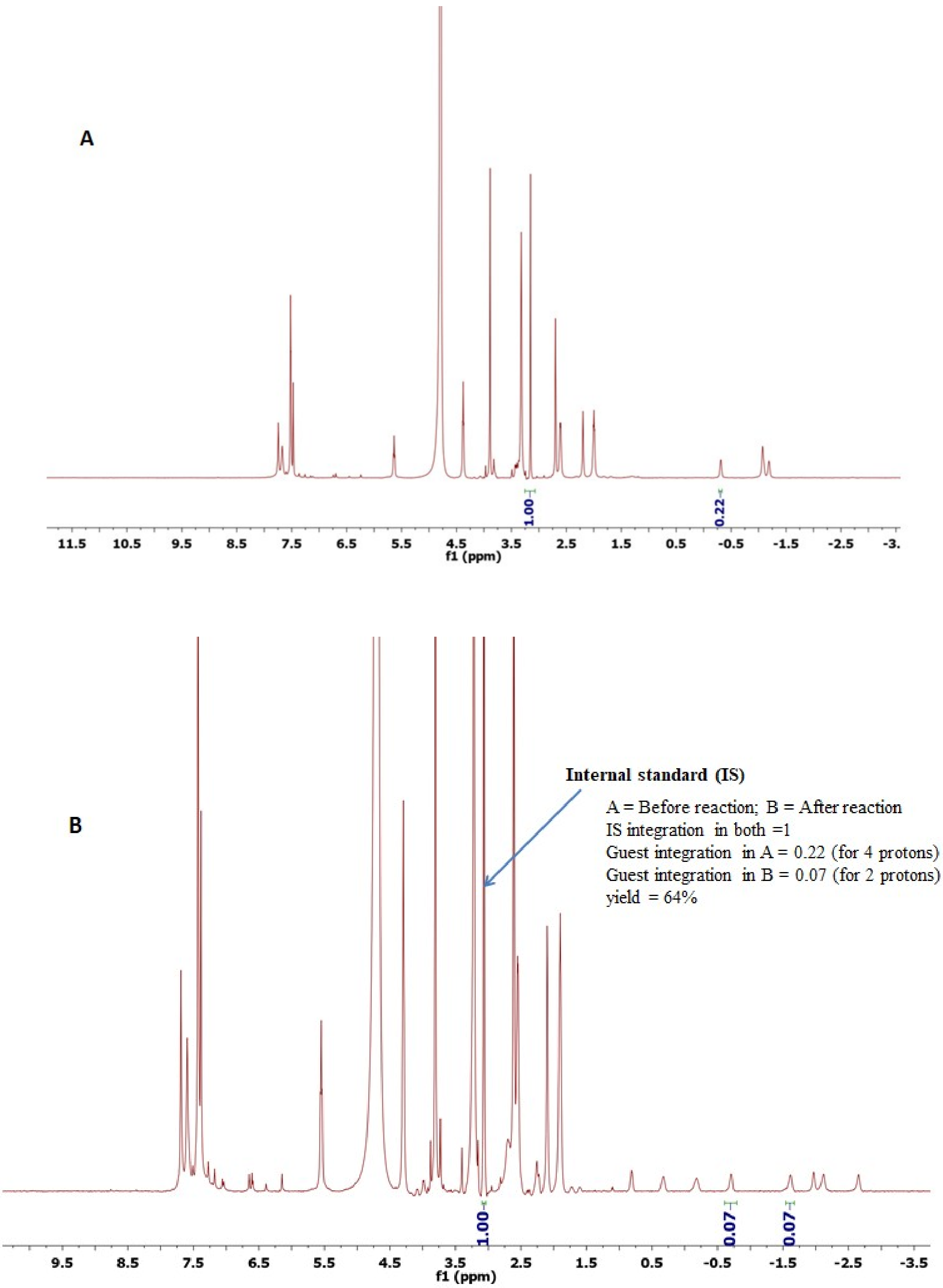
Spectrum A is before reaction; Spectrum B is after reaction.



Internal standard (IS)

A = Before reaction; B = After reaction
IS integration in both =1
Guest integration in A = 0.10 (for 2 protons)
Guest integration in B = 0.07 (for 2 protons)
yield = 70 %

Figure S33. Full ^{1}H NMR spectra of **4d** with internal standard for quantifying the yield. Spectrum A is before reaction; Spectrum B is after reaction.

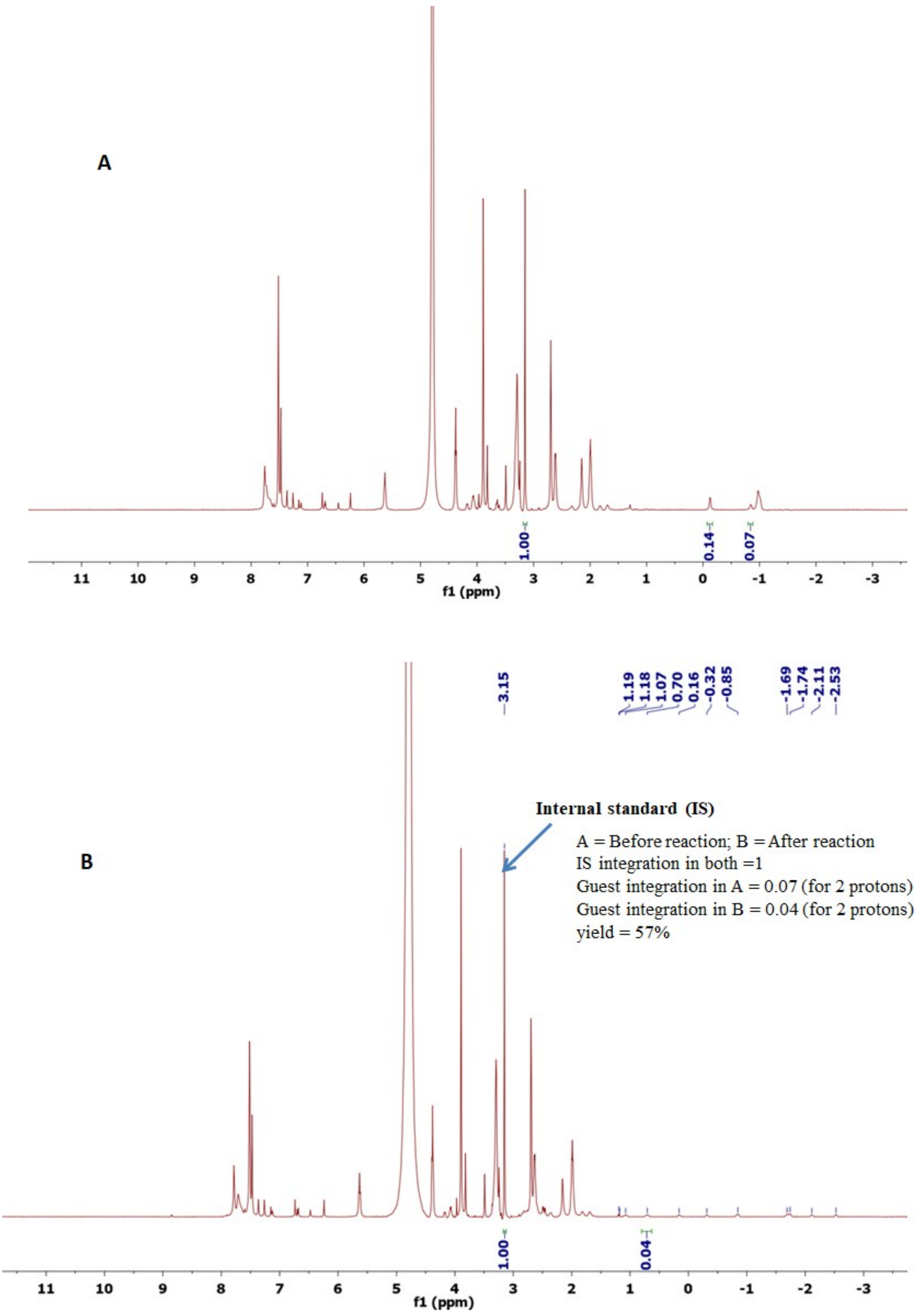


Internal standard (IS)

A = Before reaction; B = After reaction
IS integration in both =1
Guest integration in A = 0.22 (for 4 protons)
Guest integration in B = 0.07 (for 2 protons)
yield = 64%

Figure S34. Full ^{1}H NMR spectra of **4e** with internal standard for quantifying the yield.

Spectrum A is before reaction; Spectrum B is after reaction.



Internal standard (IS)

A = Before reaction; B = After reaction
IS integration in both =1
Guest integration in A = 0.07 (for 2 protons)
Guest integration in B = 0.04 (for 2 protons)
yield = 57%

Figure S35. Full ^{1}H NMR spectra of **4f** with internal standard for quantifying the yield.

Spectrum A is before reaction; Spectrum B is after reaction.

Reactivity of 1,4-disubstituted aromatic diene in 1 with NBS

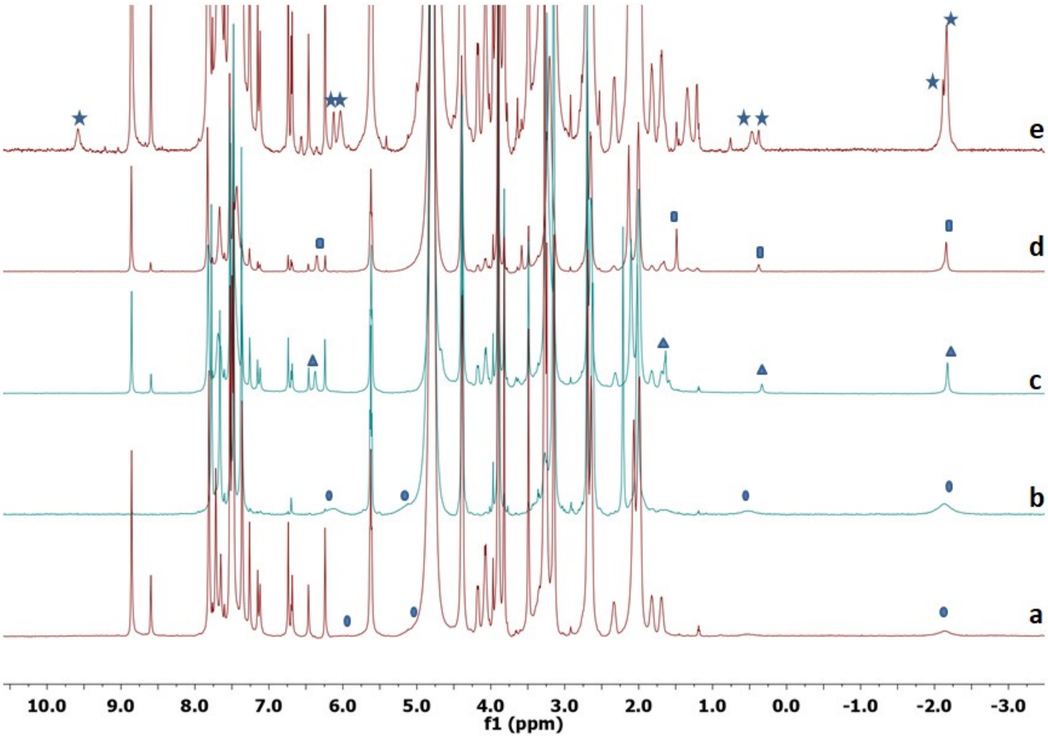


Figure S36. Stacked full ^{1}H NMR spectra **3** in cavitand **1**. Reaction progress were recorded after addition of NBS (14 µL, 50 mM in DMSO-d_6) and stirred at 50 ºC: (1) after 1 h under sonication at 25 ºC, DMSO-d_6 used as co-solvent; (2) sample 1, NBS (14 µL, 50 mM in DMSO-d_6), 2 h; (3) sample 2, 4h; (4) K_2CO_3 (7 µL in D_2O), 4 h; (4) spectra of authentic monoepoxide.

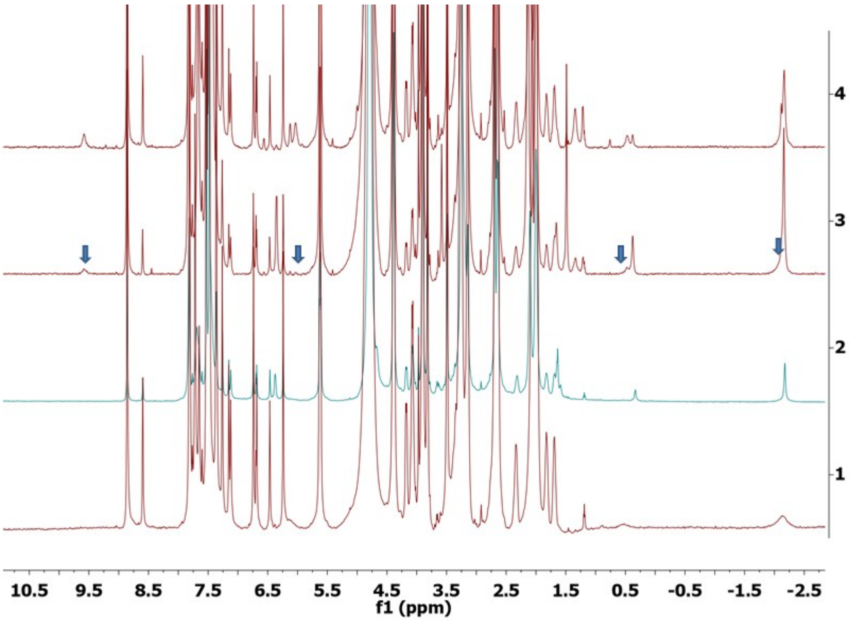
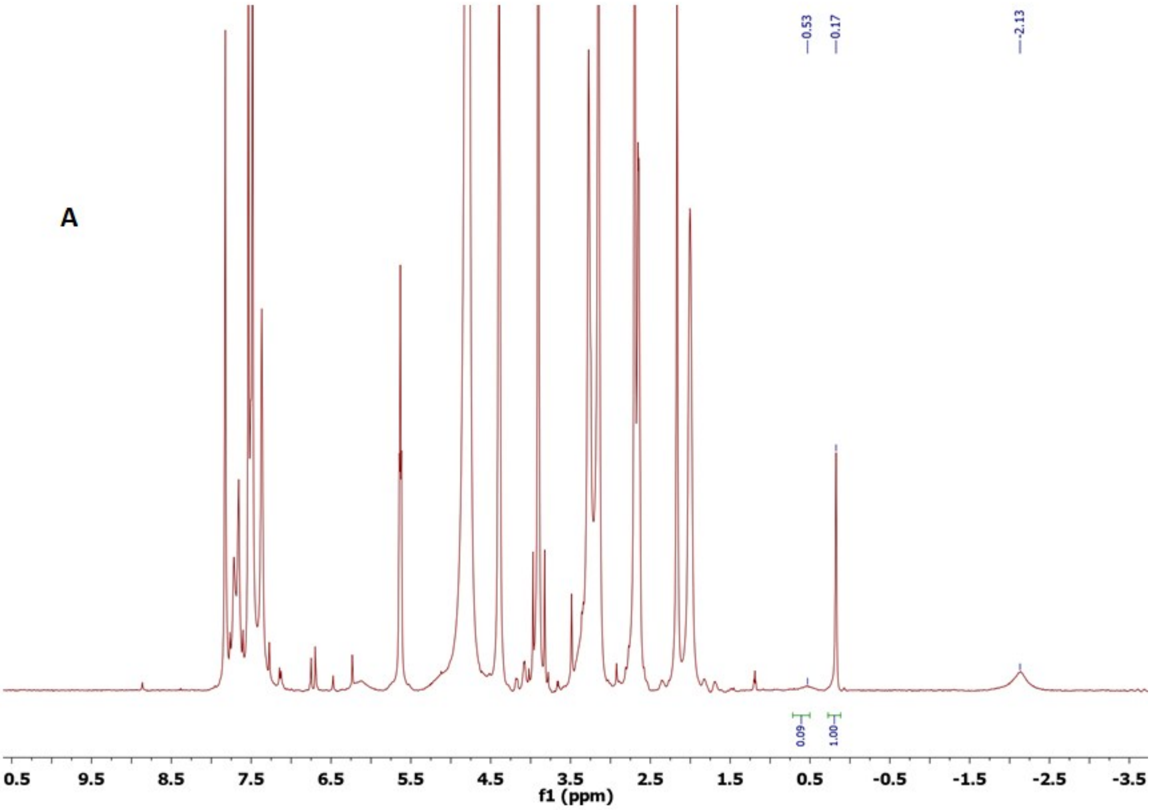
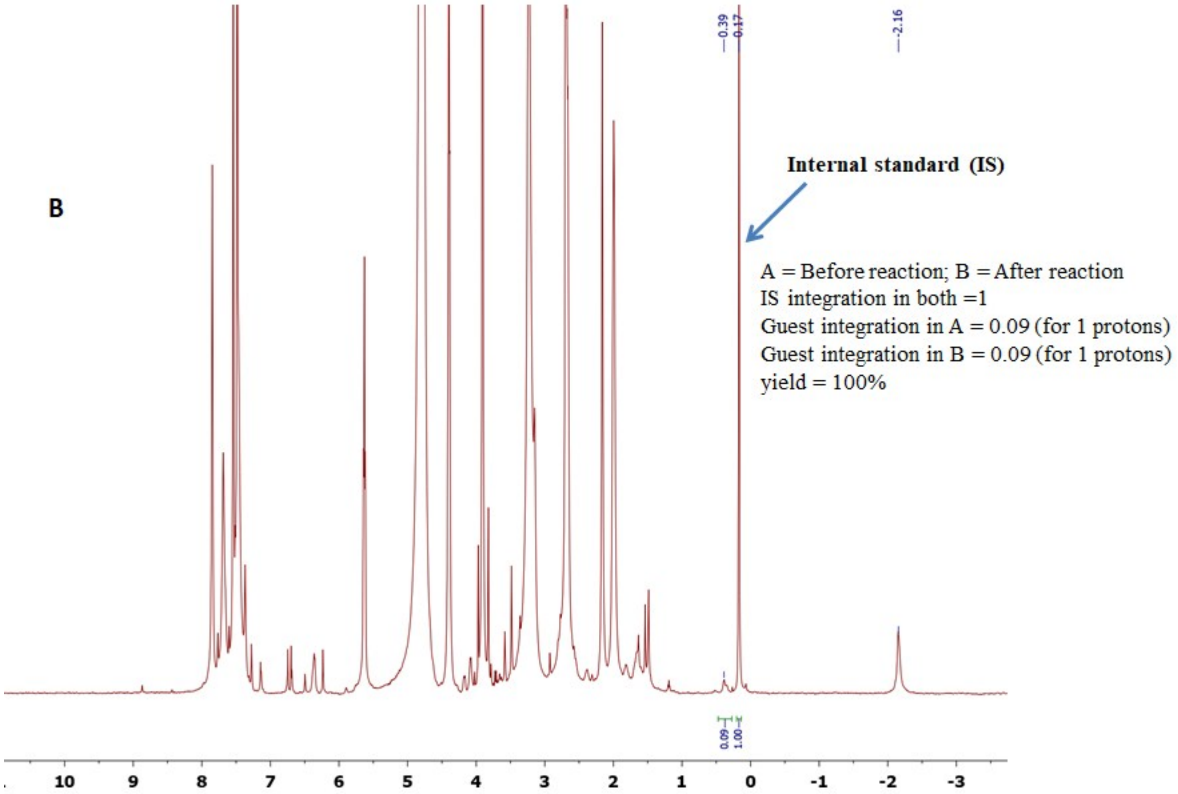


Figure S37. Full stacked ^{1}H NMR spectra of **3**. (1) binding of **3** in **1** (2:1); (2) after reaction with NBS (1 eq), K_2CO_3 (0.5 equiv). (3) sample 2, long time stirred at rt for 8 h; (4) authentic aldehyde **6**.

Relative yield calculations of mono-functionalization of aromatic-1,2-substituted diene (3)

Dimethyl sulfone was used as water soluble internal standard (NMR chemical shift for six protons = 3.15 ppm). Concentration of the internal standard (IS) was always used 1.4 mM. The reaction substrate **3** (1.4 mM), and cavitand **1** (2.8 mM) was added and sonicated for 3 h to ensure complete complexation. After complexation, internal standard (IS) was added and recorded the ^{1}H NMR spectroscopy. Integration of IS and bound guest peaks (**5**) was checked before the reaction. Again, the integration of IS and product nuclei was checked after reaction with sequencial addition DMSO-d_6 at given temperature and time.





Internal standard (IS)

A = Before reaction; B = After reaction
IS integration in both =1
Guest integration in A = 0.09 (for 1 protons)
Guest integration in B = 0.09 (for 1 protons)
yield = 100%

Figure S38. Full ^{1}H NMR spectra of **3** with internal standard for quantifying the yield. Spectrum A is before reaction; Spectrum B is after reaction.

Control experiments without cavitand 1 for α,ω-diene (C_{10})

General procedure: A solution of **2c** in DMSO (1.4 mM, 18 μL) was mixed with 0.5 mL of D_2O/acetonitrile mixture (25% of Acetonitrile-d_3, v/v) and stirred at 50 ºC. Reaction progress was monitored using NMR spectroscopy. The product distribution was checked by gas chromatography**.**

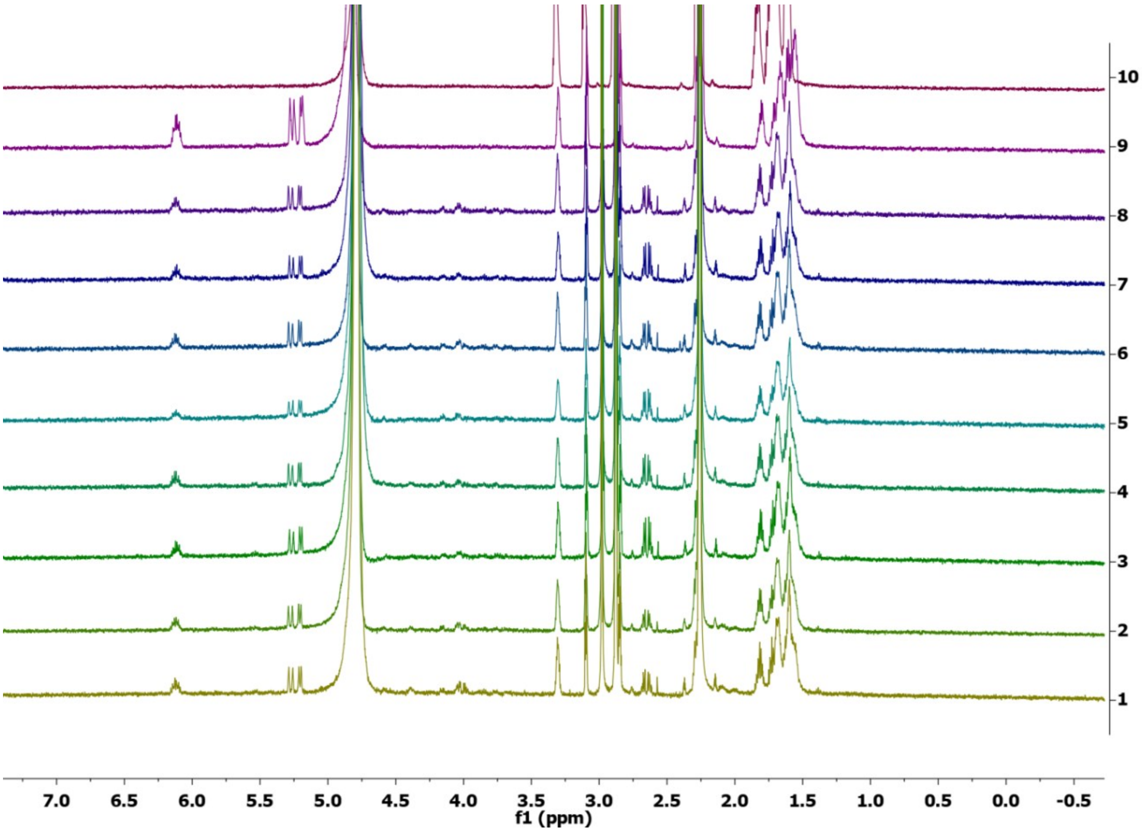


Figure S39. Stacked full ^{1}H NMR spectra of **2c** without cavitand **1**. (1) 1 h (2) 2 h; (3) 3 h; (4) 4 h; (5) 5 h; (6) 6 h; (7) 7 h; (h) 8 h; (8) 9 h (9) authentic mono epoxide 4c; (10) authetic diepoxide (C_{10}).

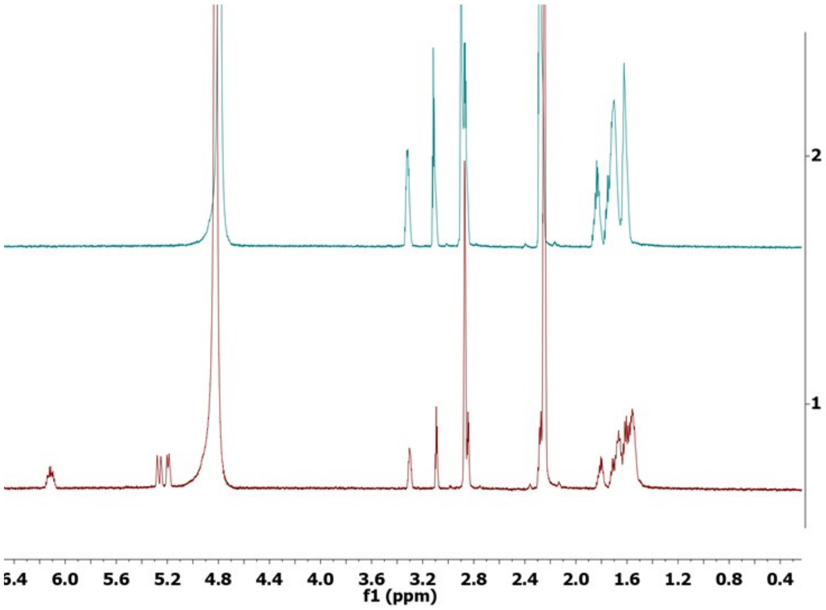
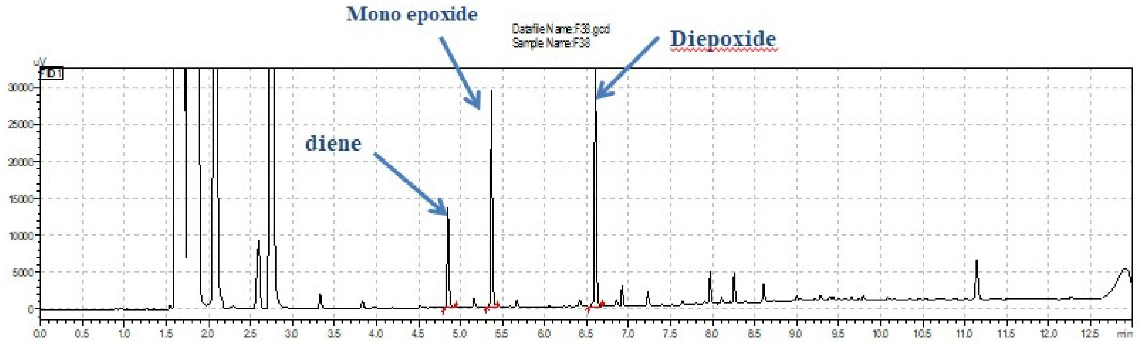
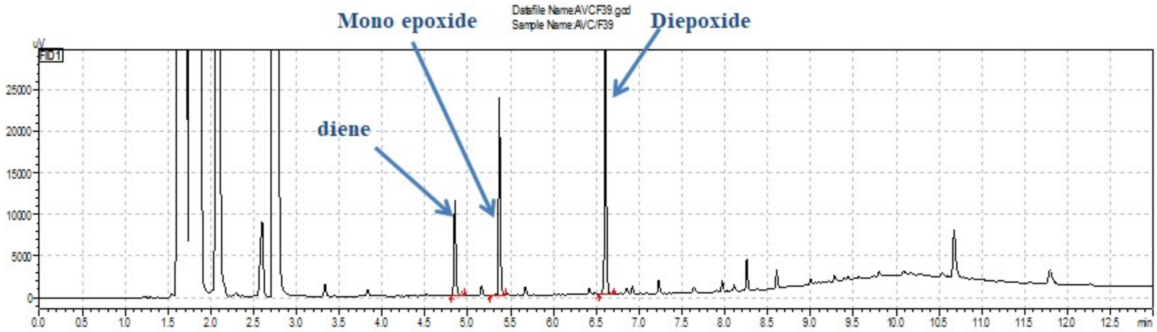


Figure S40. Full expanded ^{1}H NMR spectrum of **2c** without cavitand **1** after 2 h. (1) Monoepoxide; (2) Diepoxide (C_{10}). Can't differentiate mono, di-epoxide (C_{10}) and starting compound diene (C_{10}).



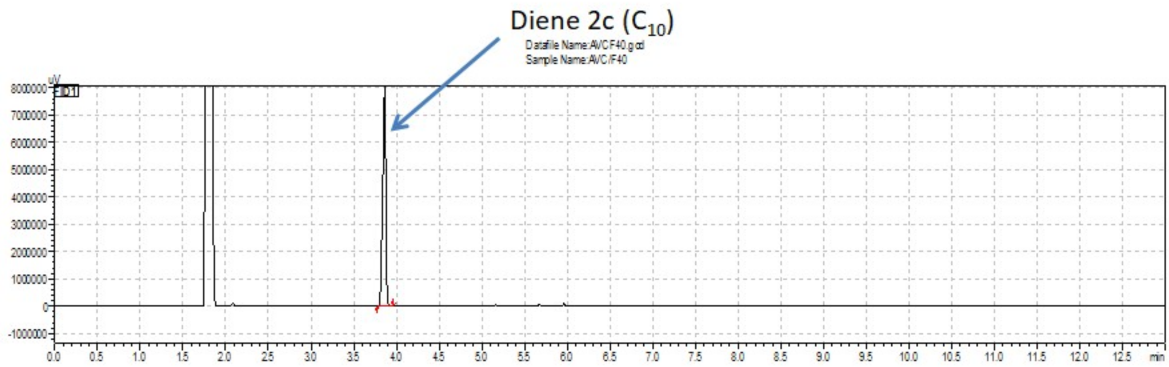
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.85	20544	13222	18.213	18.213
2	5.368	40970	28507	36.32	36.32
3	6.605	51287	36076	45.467	45.467
Total		112801	77806	100	100

Figure S41. GC spectrum of reaction mixture after 2 h.



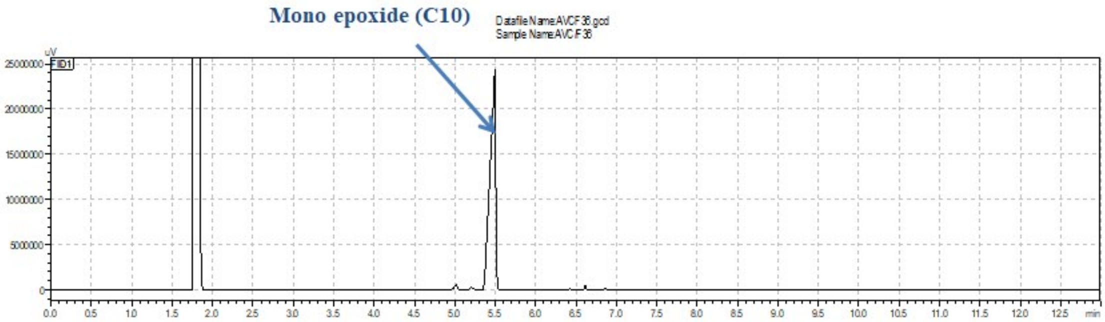
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.849	17901	11193	18.507	18.507
2	5.368	33878	23183	35.025	35.025
3	6.605	44948	31276	46.469	46.469
Total		96727	65651	100	100

Figure S42. GC spectrum of reaction mixture after 12 h.



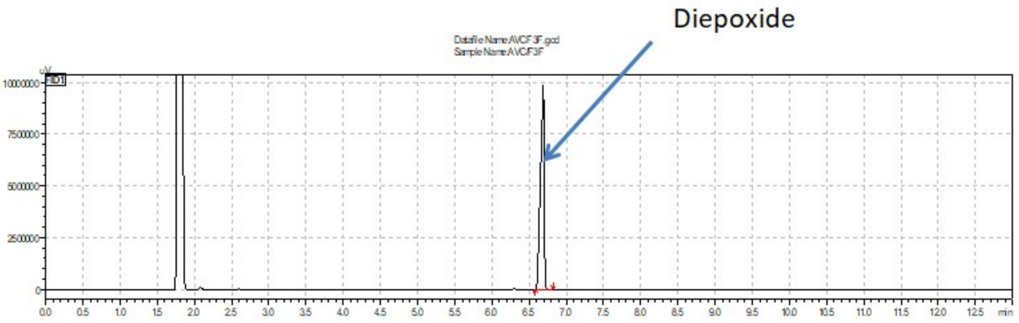
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	3.864	20529313	8348788	100	100
Total		20529313	8348788	100	100

Figure S43. GC spectrum of authentic α,ω-diene **2c** (C_{10}).



Peak#	Ret. Time	Height	Conc.	Area%
1	5.494	24230970	100	100
Total		24230970	100	100

Figure S44. GC spectrum of authentic mono-epoxide (C_{10}).



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.689	32703020	9776104	100	100
Total		32703020	9776104	100	100

Fugure S45. GC spectrum of authentic di-epoxide (C_{10}).

Control experiments for formation of epoxide and aldehyde in cavitand 1 with NBS using aromatic 1,4-disubstitued diene

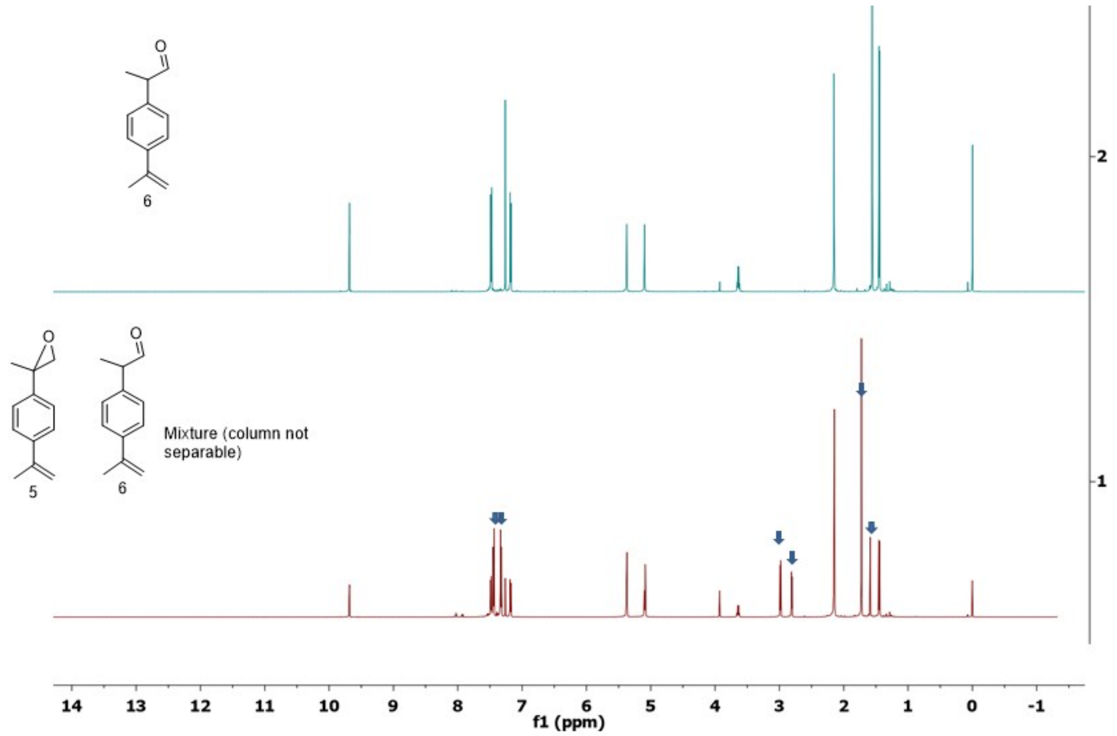
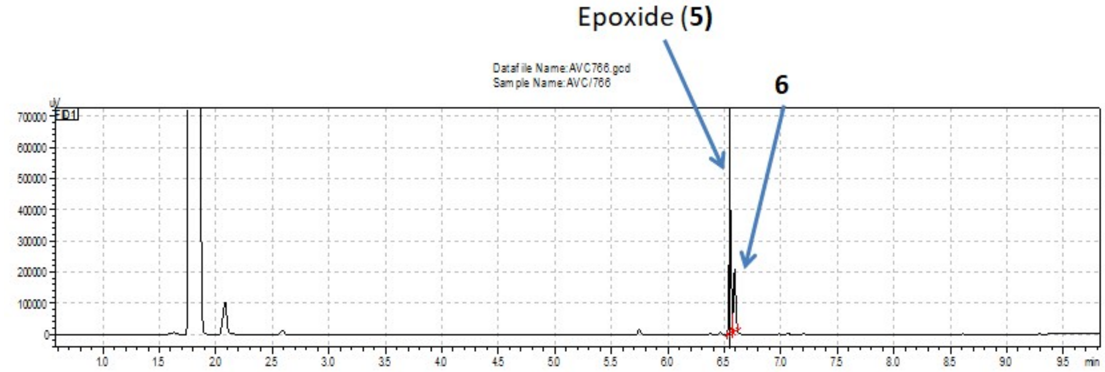


Figure S46. Stacked full ^{1}H NMR spectra. (1) Mixtures of epoxide **5** and aldehyde **6**. (2) Pure aldehyde **6**. Blue arrows indicates monoepoxide proton peaks.



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.51	549380	407003	67.659	67.659
2	6.591	262607	198359	32.341	32.341
Total		811987	605362	100	100

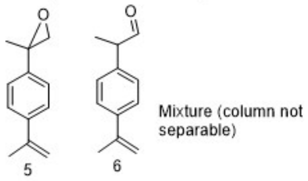
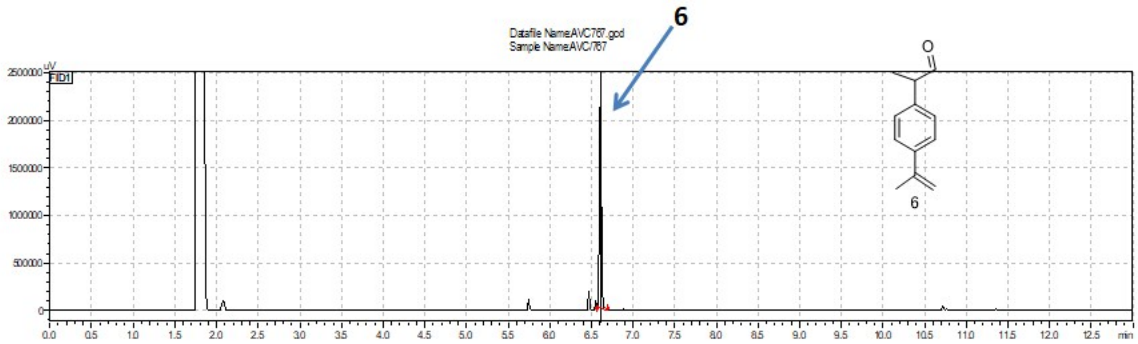
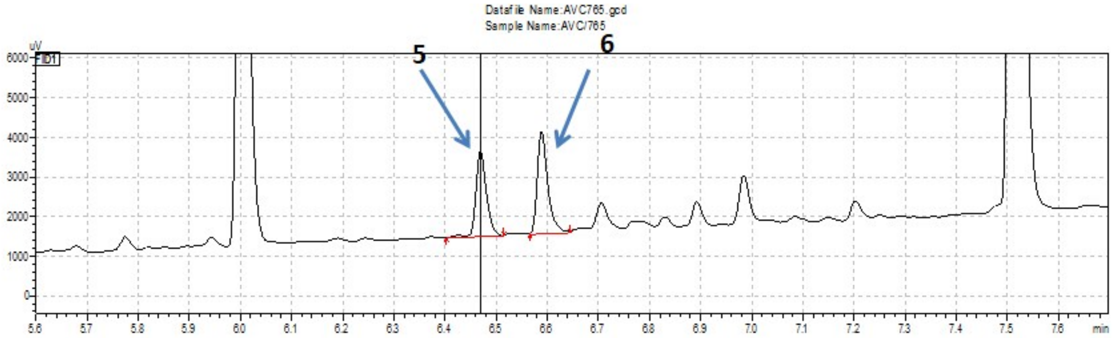


Figure S47. GC spectrum of of mixtures aldehyde **6** and epoxide **5**.



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.591	3712938	2306128	100	100
Total		3712938	2306128	100	100

Figure S48. GC spectrum of aldehyde **6**.

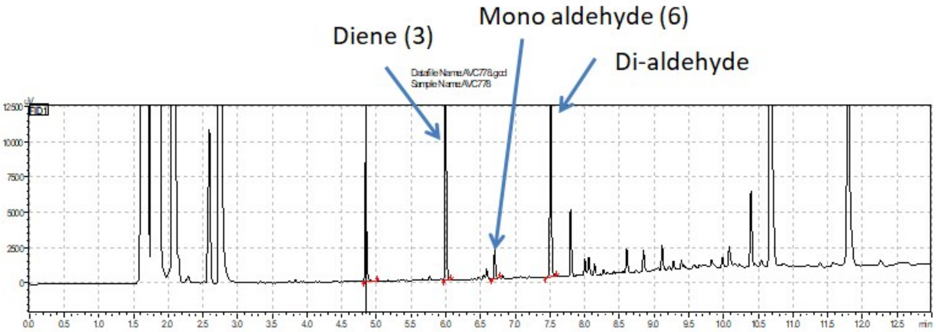


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.47	3090	2100	45.444	45.444
2	6.59	3710	2513	54.556	54.556
Total		6800	4613	100	100

Figure S49. GC spectrum of reaction mixture in cavitand 1 using **3**. After reaction the NMR tube solution was extracted with EtOAc and checked GC.

Control experiments without cavitand 1 for 1,4-disubsituted aroamtic diene (3)

General procedure: A solution of 3 in DMSO (1.4 mM, 18 µL) was mixed with 0.5 mL of D_2O/acetonitrile mixture (25% of Acetonitrile-d_3, v/v) and stirred at 50 ºC. Reaction progress was monitored using NMR spectroscopy. The product distribution was checked by gas chromatography.



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.845	13298	8806	19.878	19.878
2	5.995	24884	17907	37.196	37.196
3	6.704	2796	2099	4.18	4.18
4	7.506	25921	17858	38.746	38.746
Total		66899	46669	100	100

Figure S50. GC spectrum of **3** without cavitand 1. Reaction with NBS (1 Equiv.) , stirred for 12 h and the stirred with $K_2CO_{3(aq.)}$ for 12 h. Then, the reaction mixture was exracted with EtOAc and checked for GC to know the ratio.

References

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