Supporting Information:

Self-assembled benzophenone *bis*-urea macrocycles facilitate selective oxidations by singlet oxygen.

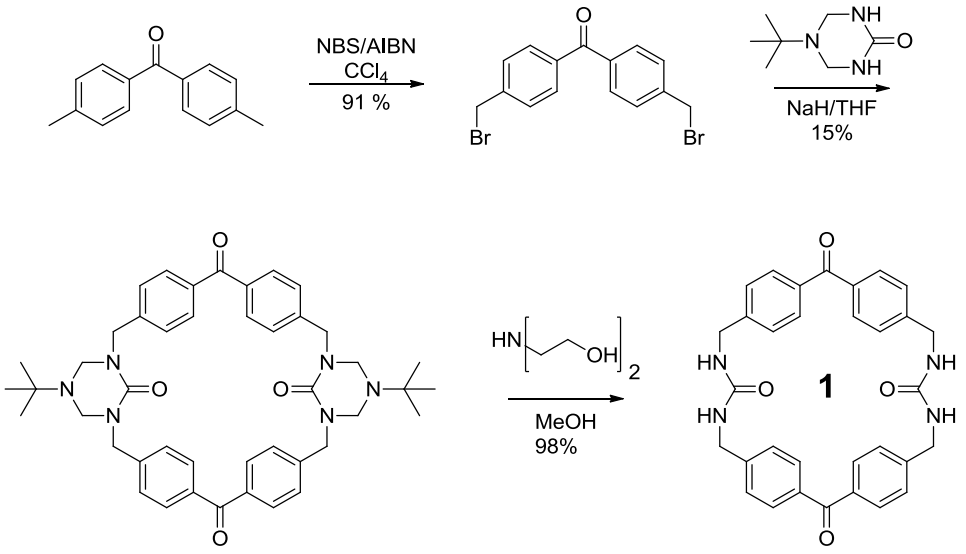
Michael F. Geer,[a] *Michael D. Walla,*[a] *Kyril Solntsev,*[b] *Christian A. Strassert,*[c] *Linda Shimizu**[a].

[a] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208.

[b] School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Dr., Atlanta, Georgia 30332-0400.

[c] Physikalisches Institut and Center for Nanotechnology (CeNTech), Universitat Münster, Heisenbergstrasse 11 48149 Münster, Germany.

List of Figures, Tables, and Schemes:



Scheme S1. Synthesis of the *bis*-urea benzophenone macrocycle (host **1**). Reagents and Conditions: 4,4-dimethylbenzophenone was reacted with N-bromosuccinimide (NBS) and 2,2'-azo*bis*(isobutyronitrile) (AIBN) in CCl_4 to produce 4,4'-*bis*(bromomethyl) benzophenone. This was then reacted with triazinanone and NaH in refluxing THF to give the cyclized product. The protected macrocycle was deprotected in an acidic diethanol amine aqueous/methanol mixture to yield the desired *bis*-urea benzophenone macrocycle (**1).**

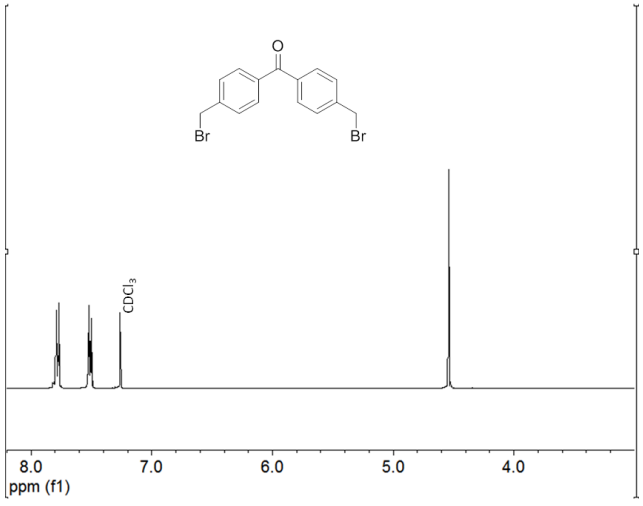


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) of 4,4'-*bis*(bromomethyl) benzophenone.

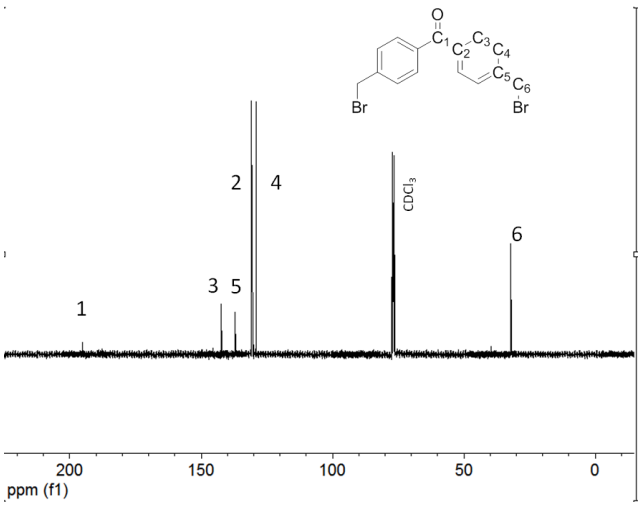


Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$) of 4,4'-*bis*(bromomethyl) benzophenone.

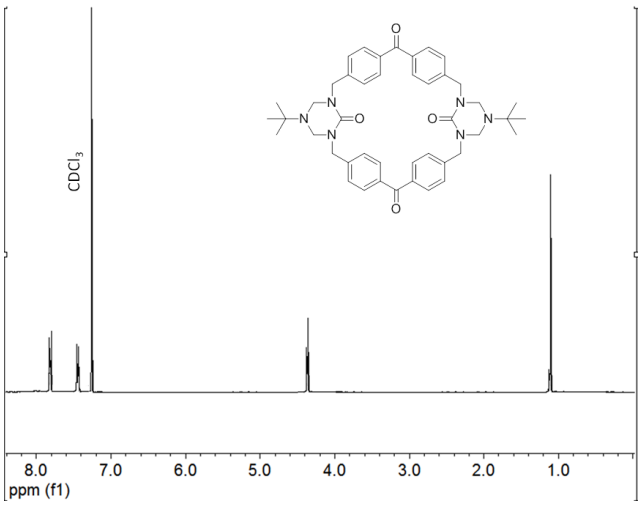


Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) of protected *bis*-urea macrocycle.

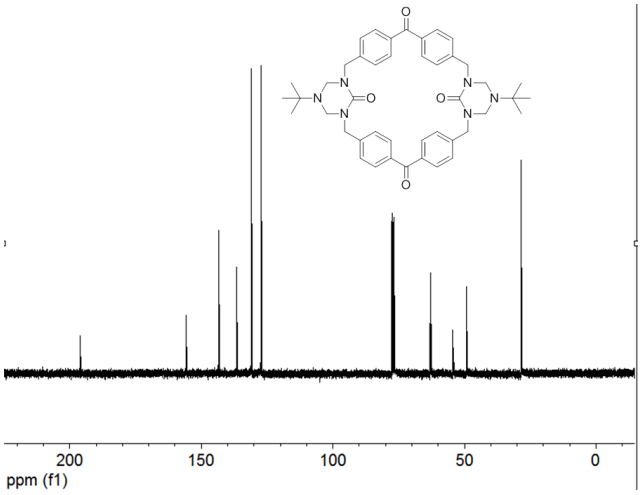


Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$) of protected *bis*-urea macrocycle.

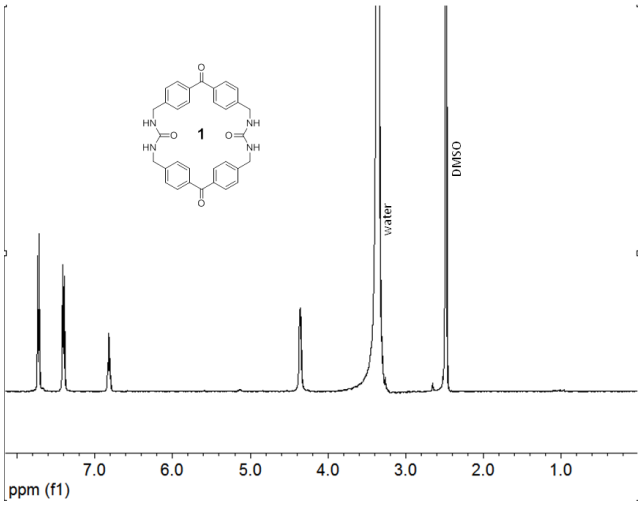


Figure S5. ^{1}H NMR (300 MHz, δ_6-DMSO) of benzophenone *bis*-urea macrocycle (host **1**).

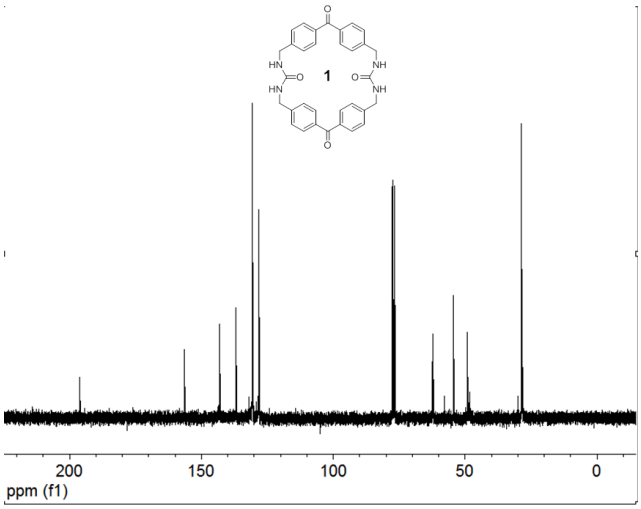


Figure S6. ^{13}C-NMR (75 MHz, δ_6-DMSO) of benzophenone *bis*-urea macrocycle (host **1**).

Phosphorescence study of Host 1

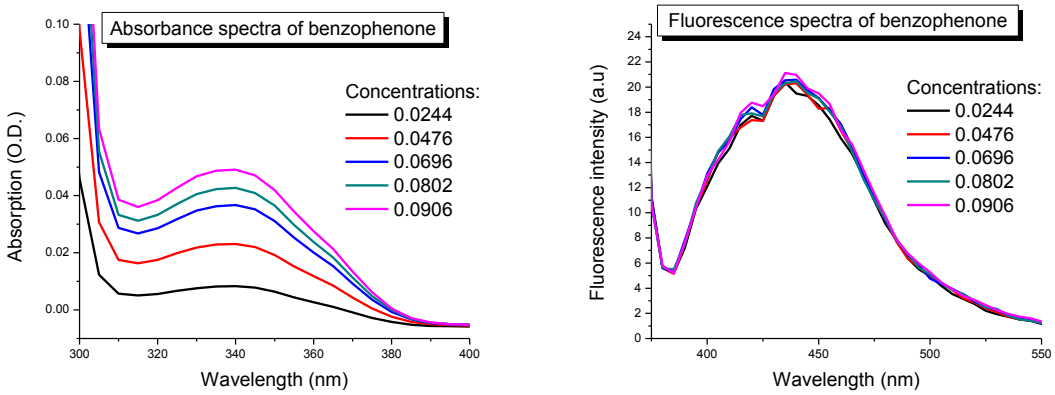


Figure S7. Absorption and emission spectra of benzophenone (DMSO).

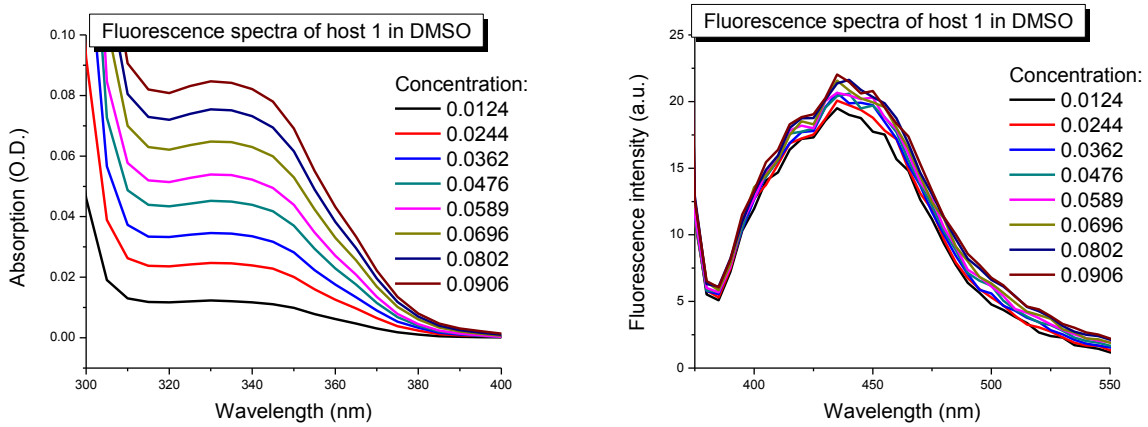


Figure S8. Absorption and emission spectra of macrocycle **1** (DMSO).

Quantum yield solid-state study:

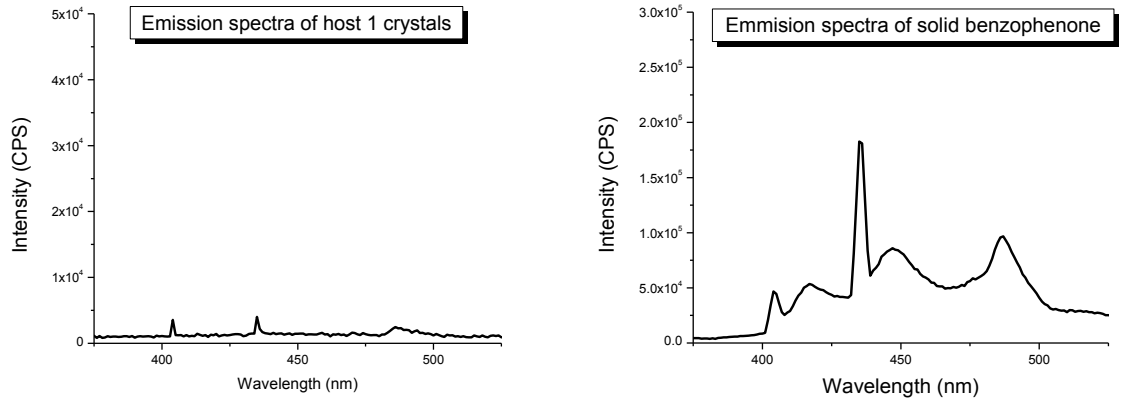


Figure S9. Emission spectra of host **1** and benzophenone powder samples taken in the Quata-φ integrating sphere.

Lifetime studies:

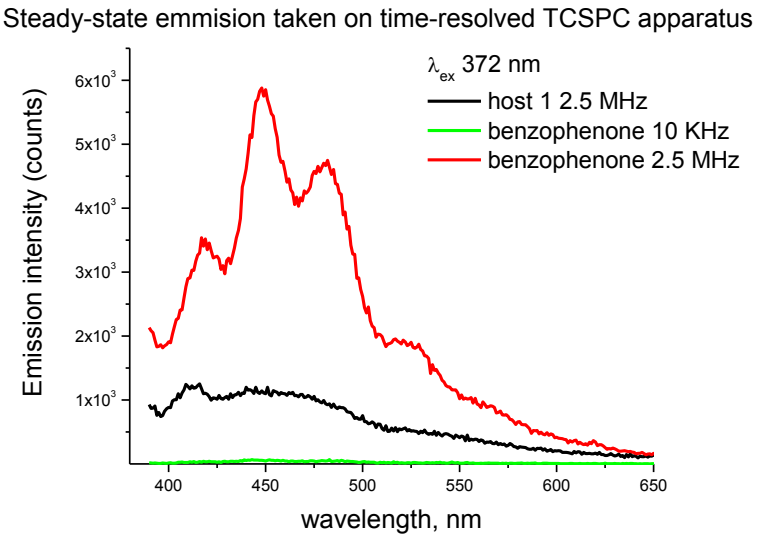


Figure S10. Comparison of the steady-state emission spectra of benzophenone and host **1** (TCSPC).

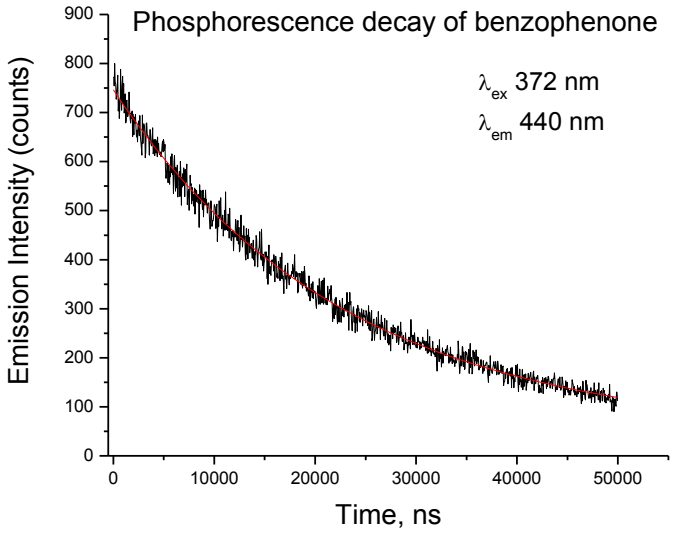


Figure S11. Phosphorescence decay of benzophenone.

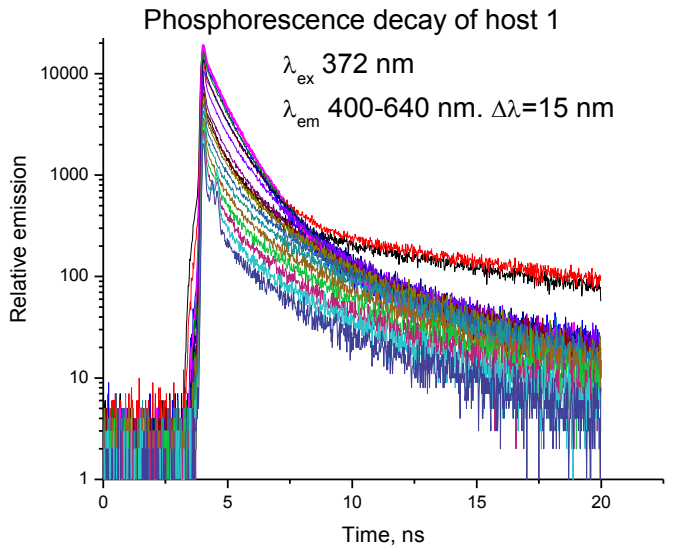


Figure 12. Phosphorescence decay of host **1** (400-640 nm).

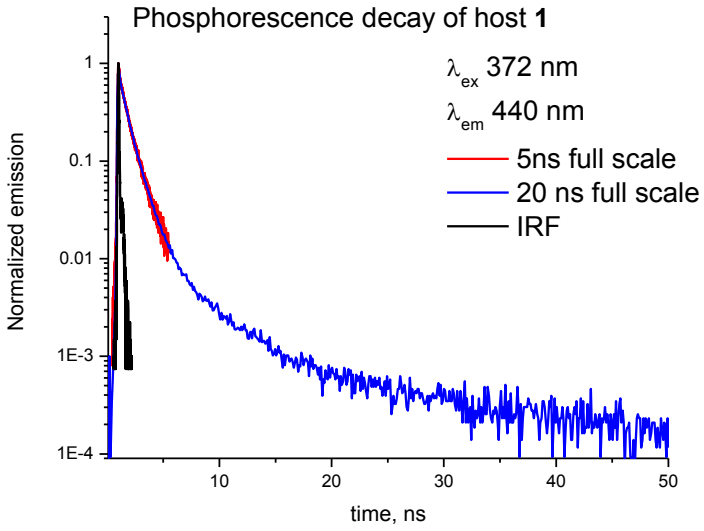


Figure S13. Phosphorescence decay of host **1** (5 ns and 20 ns scale).

Table S1. Values of the time constants (τ_i) and normalized (to 1) pre-exponential factors (A_i) of the multi-exponential function fitting the emission transients of solid-state host **1** at room temperature. The excitation wavelength was 372 nm.

Timescale	τ_1, ns[1]	A_1[2]	τ_2, ns	A_2	τ_3, ns	A_3	τ_4, ns	A_4	τ_{av}, ns
20 ns	0.036	0.64	0.33	0.14	1.0	0.21	4.3	0.01	0.32
5ns	0.11	0.56	0.62	0.27	1.31	0.17			0.46

[1]The fit quality was inspected using the weighted residuals, and the values of χ^2 which in all cases was < 1.1.

[2]All amplitudes are normalized in a following way: $\sum_{i=1}^{n} A_i = 1$

Singlet oxygen photoluminescence study:

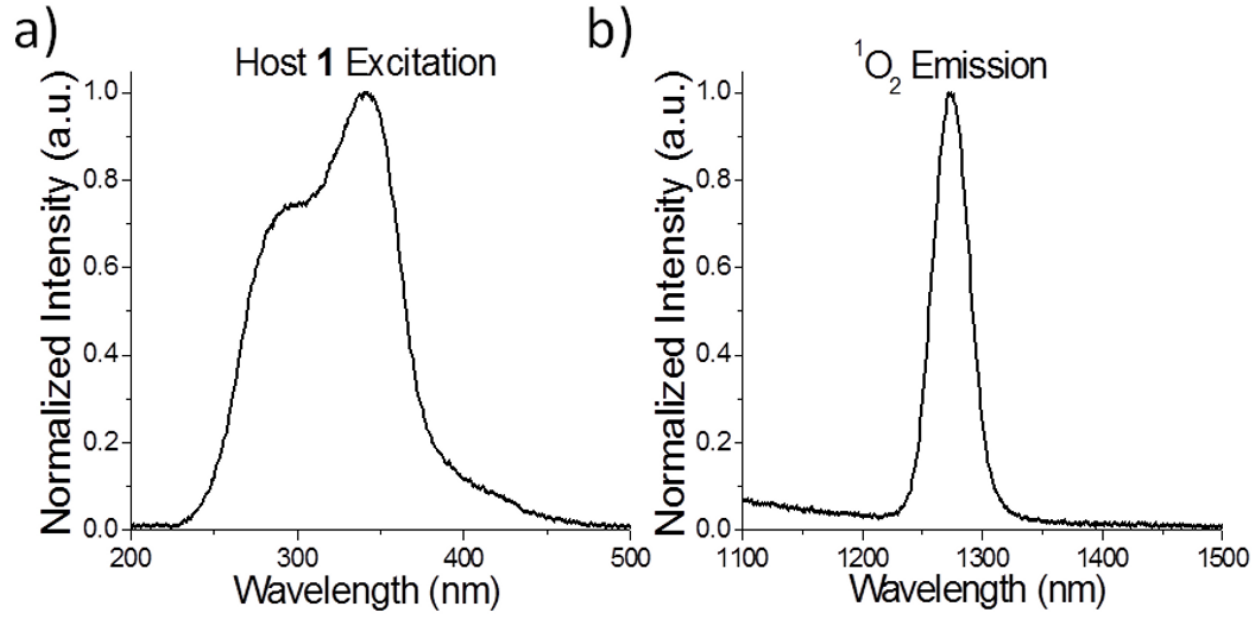


Figure S14. a) The absorption spectra of host **1** crystal suspension showing a λ_{max} of 345 nm. b) The near IR emission spectra of singlet oxygen produced from the excitation of the host **1** crystals at λ_{max}.

Determination of guest loading:

Thermogravimetric analysis (TGA):

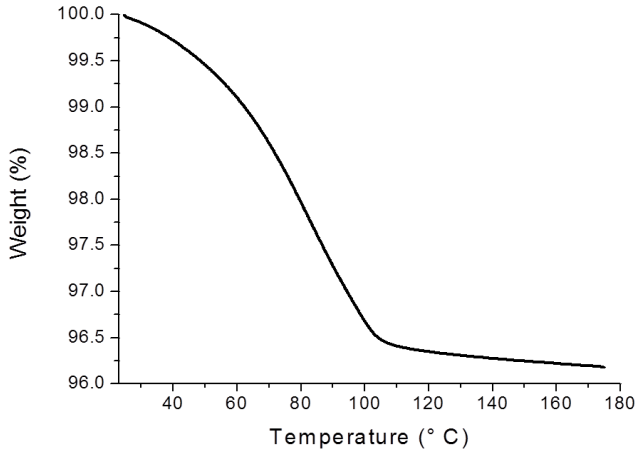


Figure S15. TGA desorption of 2-methyl-2-butene.

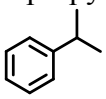
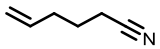
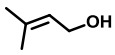
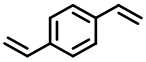
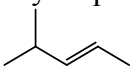
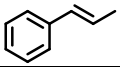
The host **1**:guest ratios were calculated using the following formula:

$$\textbf{Molar ratio host 1: guest} = \frac{\textbf{moles guest}}{\textbf{moles host 1}}$$

$$\textbf{Moles host 1} = \frac{\textbf{final mass}}{\textbf{molecular weight of host 1}}$$

$$\textbf{Moles guest} = \frac{\boldsymbol{\Delta}\textbf{ mass}}{\textbf{Moelcular weight guest}}$$

Table S2: Absorption of guests by host **1** as determined by TGA experiments.

Alkene	Loading (host:guest)[a]	Guest	Loading (host:guest)[a]
2-methyl-2-butene 	3.0:1	cumene (isopropyl benzene) 	5.6:1
2,3-dimethyl-2-butene 	4.0:1	hex-5-enenitrile 	5:1
3-methyl-2-buten-1-ol 	4.0:1	cyclohexadiene 	2:1
2-methyl-2-pentene 	5.0:1	Divinyl benzene 	3.5:1
trans-2-pentene 	2.7:1	α-methyl styrene 	3:1
4-methyl-2-pentene 	6.5:1	β-methyl styrene 	2.5:1

[a] all host:guest ratios are an average of at least 3 separate loading experiments.

NMR :

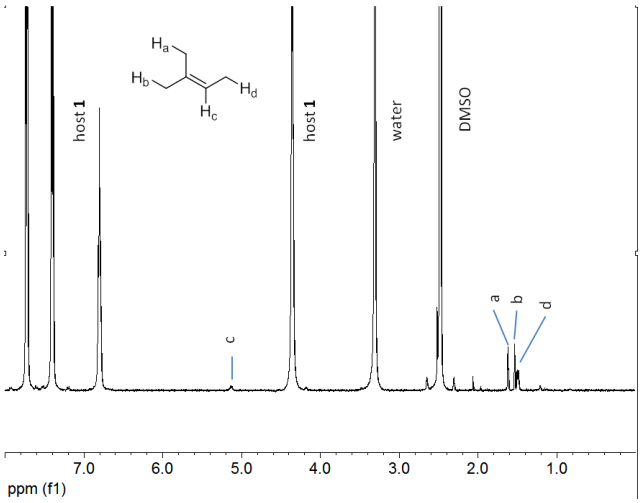


Figure S16. ^{1}H-NMR (400 MHz, δ_6-DMSO) of host **1**•2-2methyl-2-butene complex.

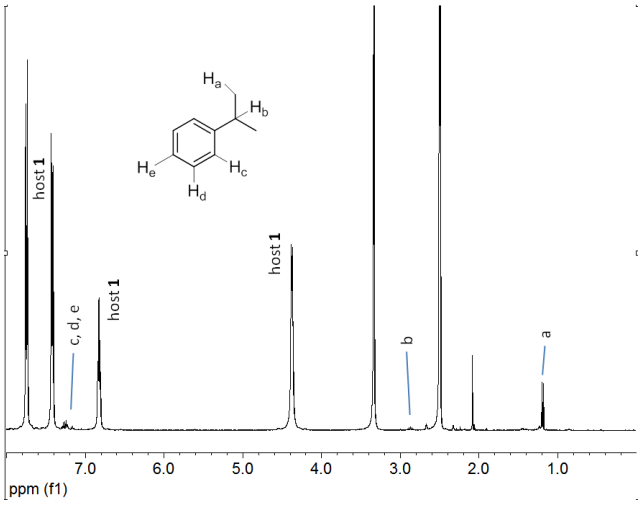


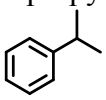
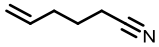
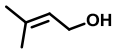
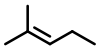
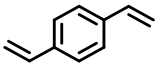
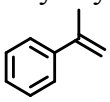
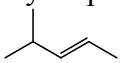
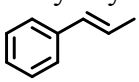
Figure S17. ^{1}H-NMR (400 MHz, δ_6-DMSO) of host **1**•cumene complex.

The host 1:guest ratios were calculated using the following formulas:

$$\textbf{Integration per H} = \frac{\textbf{peak intergal}}{\textbf{number H}}$$

$$\textbf{molar ration host 1:guest} = \frac{\textbf{ave integral per H guest}}{\textbf{average integral per H host 1}}$$

Table S3: Molar ratios of host **1**:guest by NMR

Alkene	Loading (host:guest)[a]	Guest	Loading (host:guest)[a]
2-methyl-2-butene 	3.0:1	cumene (isopropyl benzene) 	5.6:1
2,3-dimethyl-2-butene 	4.5:1	hex-5-enenitrile 	5.8:1
3-methyl-2-buten-1-ol 	4.0:1	cyclohexadiene 	2.2:1
2-methyl-2-pentene 	5.2:1	Divinyl benzene 	3.9:1
trans-2-pentene 	2.7:1	α-methyl styrene 	3.6:1
4-methyl-2-pentene 	6.8:1	β-methyl styrene 	2.8:1

[a] all host:guest ratios are an average of at least 3 separate loading experiments.

PXRD of Host 1 and inclusion complex:

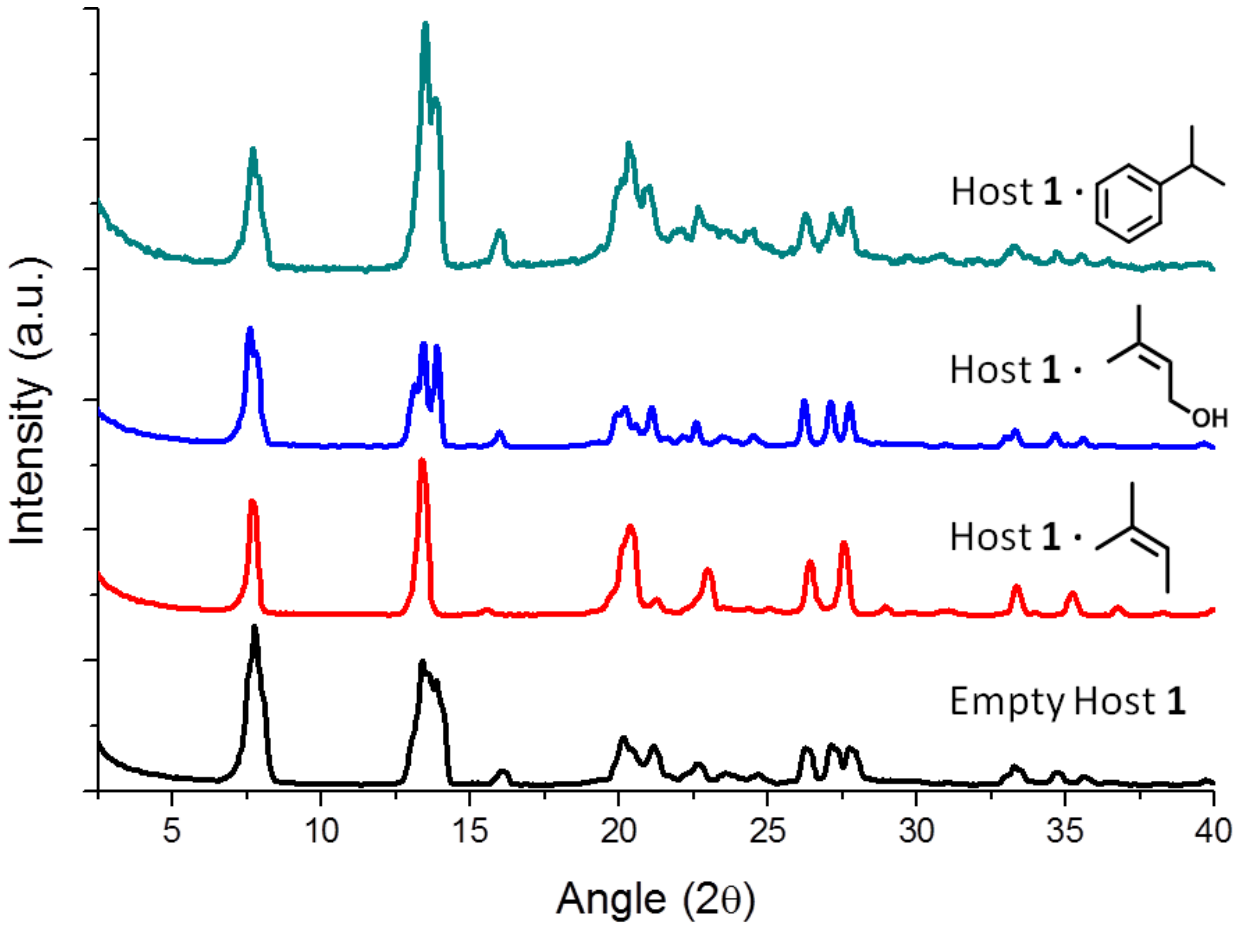


Figure S18. Comparison of PXRD patterns of host **1**, host **1**•2-methyl-2-butene, host **1**•3-methyl-2-butene-1-ol, and host **1**•cumene.

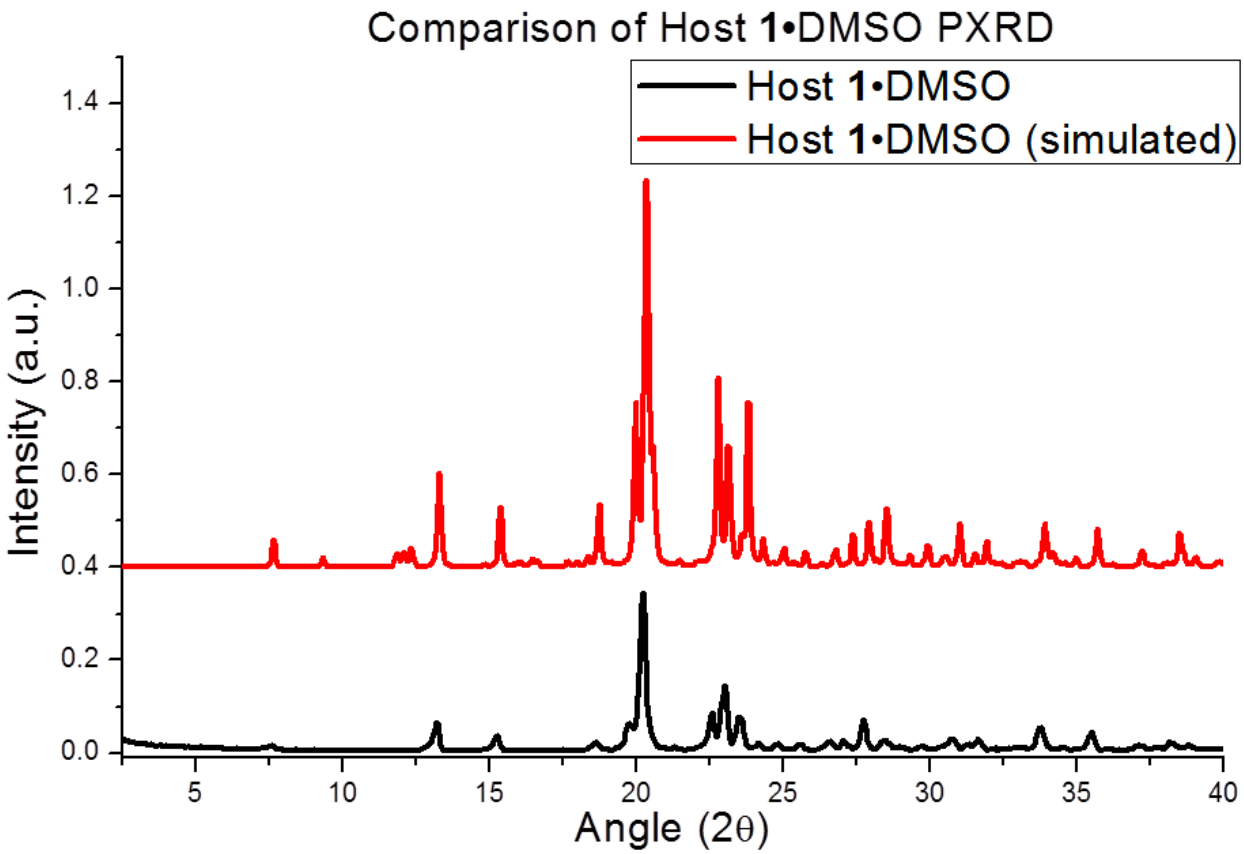


Figure S19. Comparison of simulated and experimental host **1**•DMSO PXRD patterns.

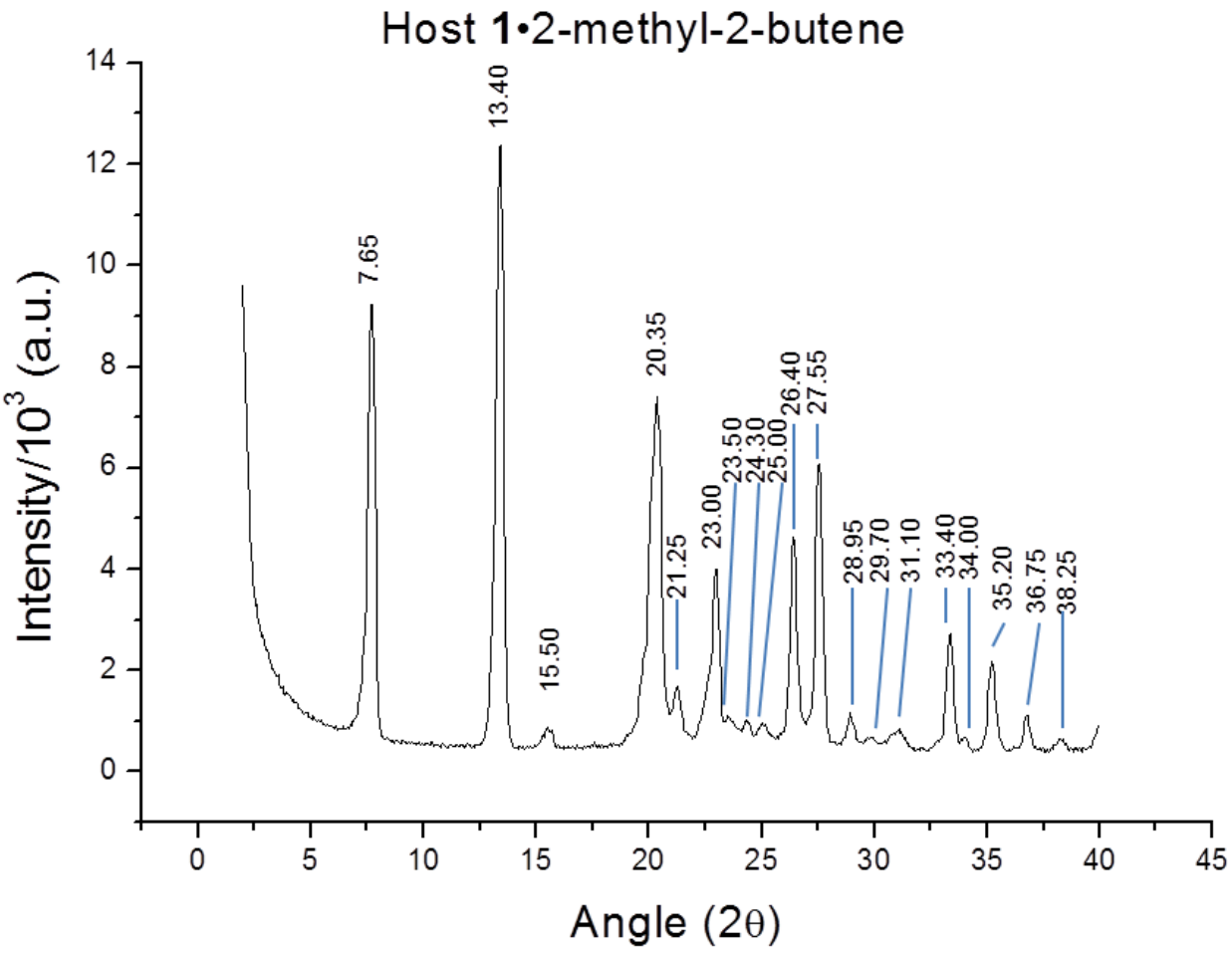


Figure S20. PXRD pattern of host **1**•2-methyl-2-butene.

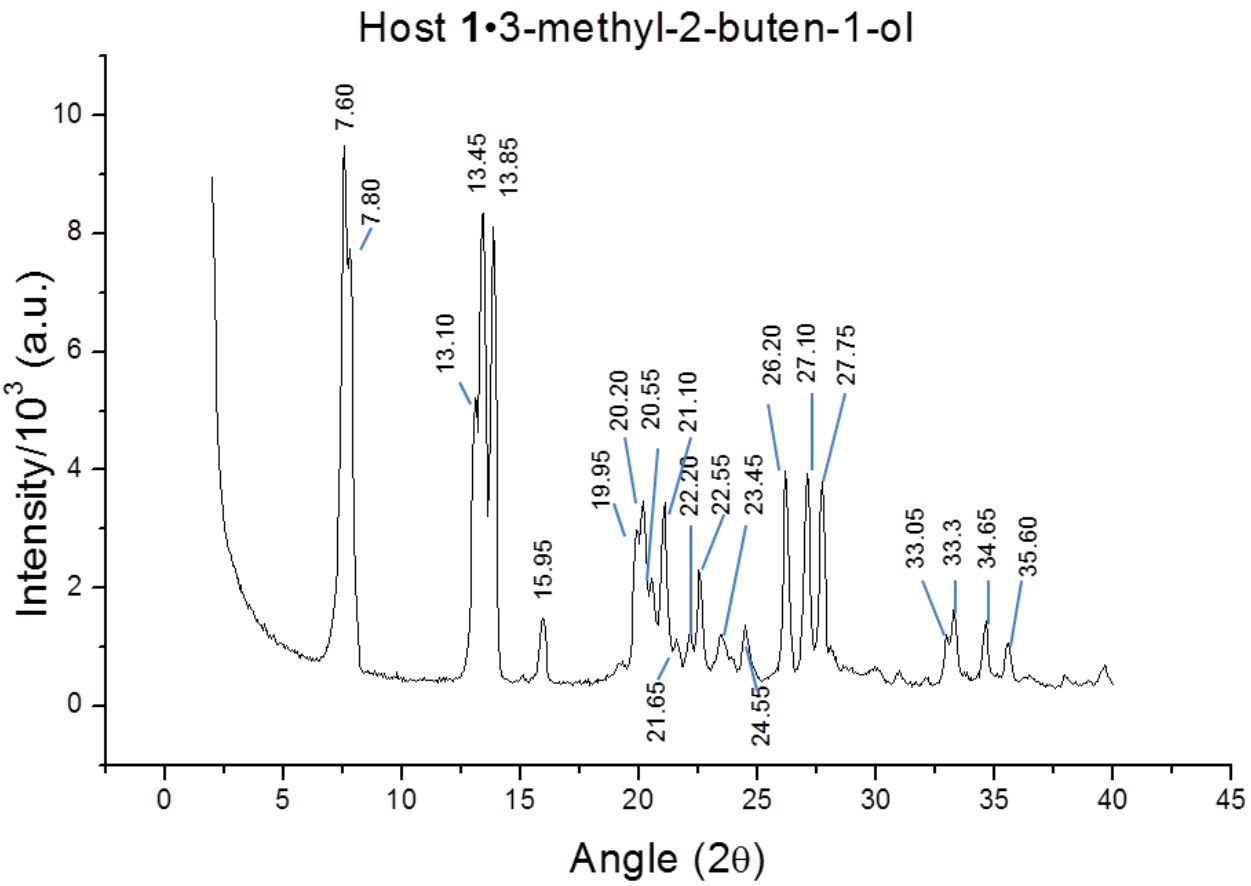


Figure S21. PXRD pattern of host **1**•3-methyl-2-buten-1-ol.

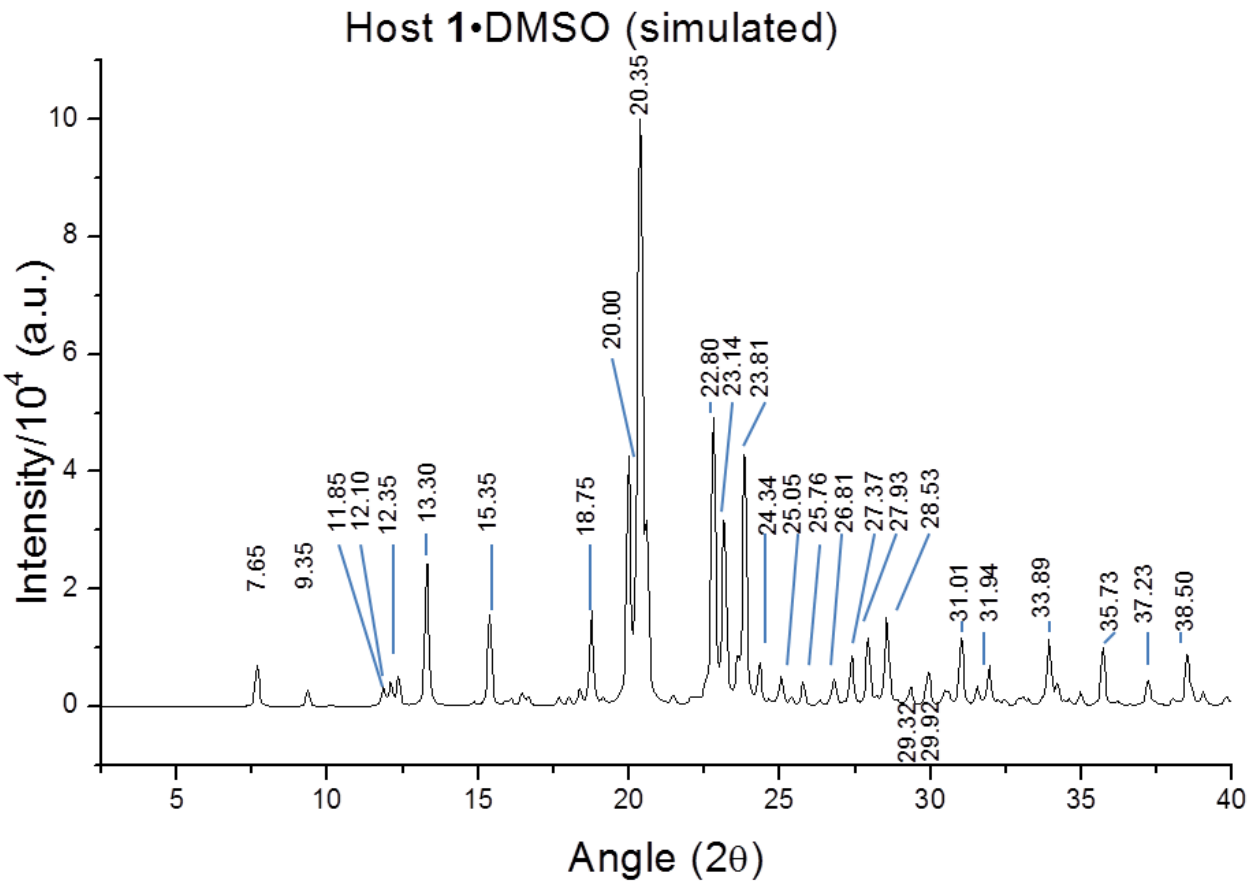


Figure 22. PXRD pattern of host **1**•DMSO (simulated).

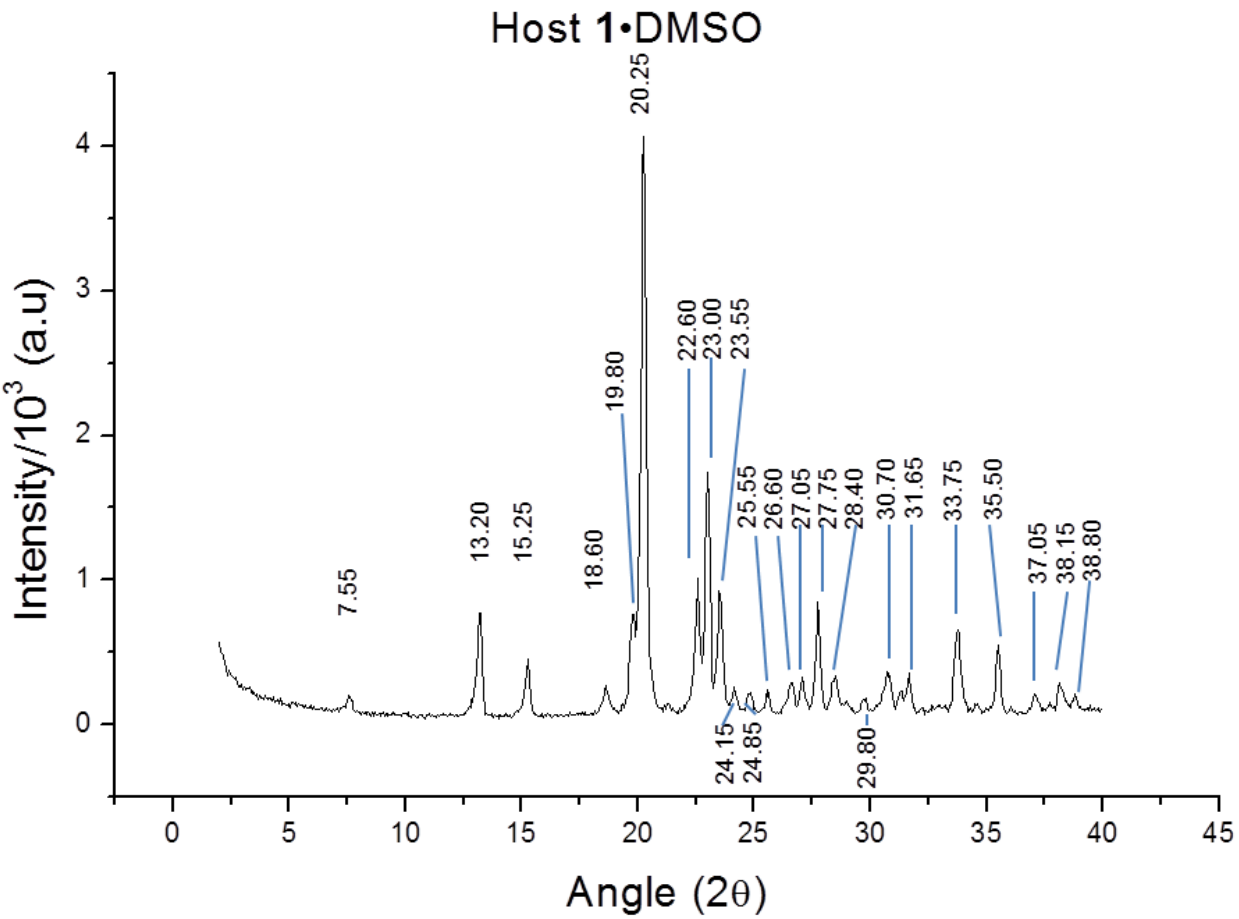


Figure S23. PXRD pattern of host **1**•DMSO (experimental).

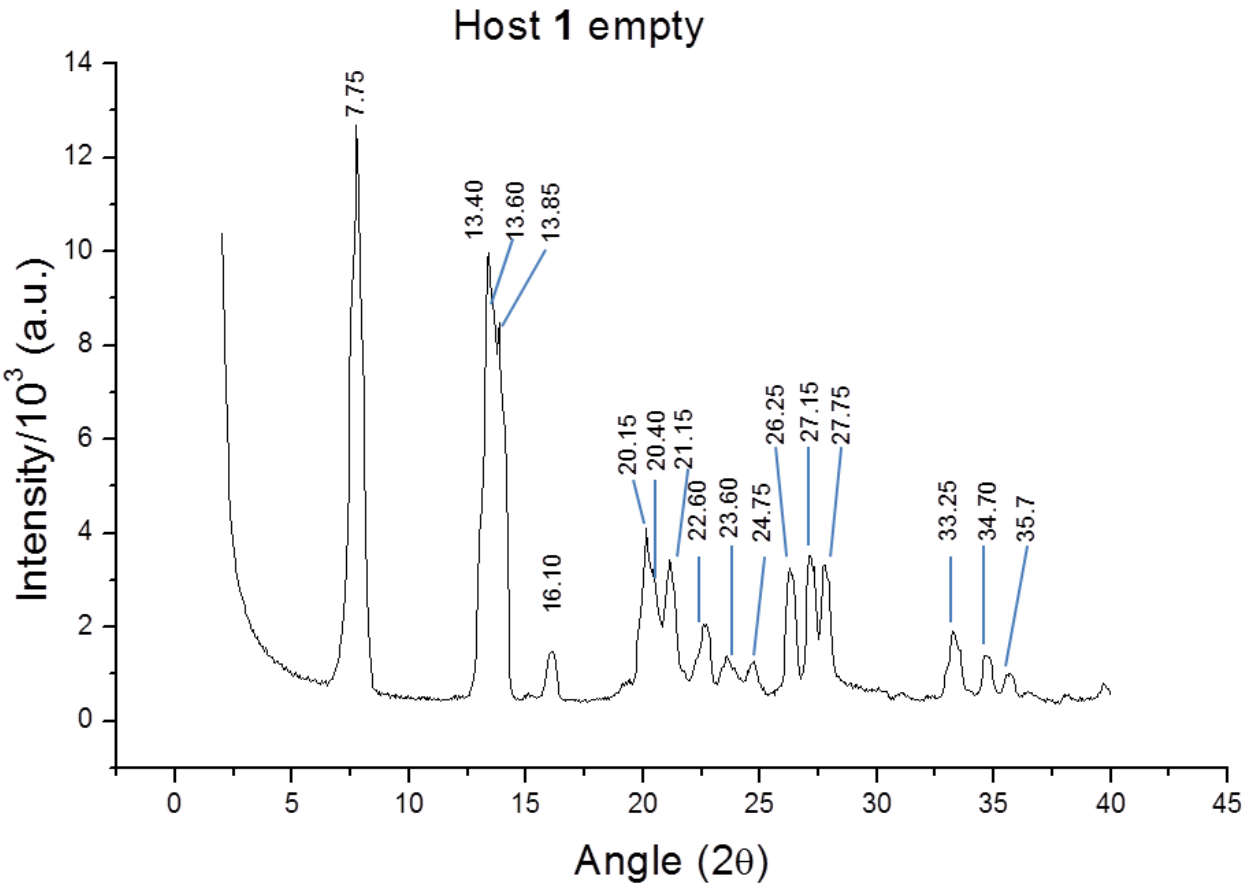


Figure S24. PXRD pattern of empty host **1**.

Scanning electrom microscopy (SEM): SEM was taken as previously reported.[1] Freshly recrystallized assembled host **1** was loaded onto a silicon wafer The image was recorded on a Quanta 200 SEM with accelerating voltage of 30 kV.

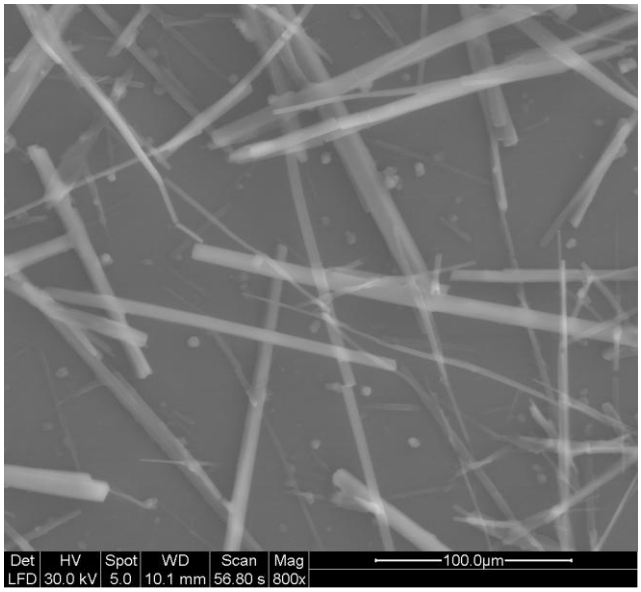


Figure S25. SEM image of the host **1** crystals.

Oxidation General

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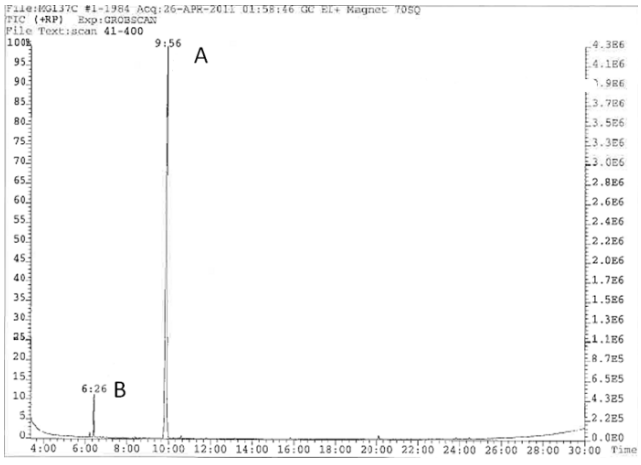

Figure S26. GC trace of oxidation products of 2-methyl-2-butene isolated from host **1**.

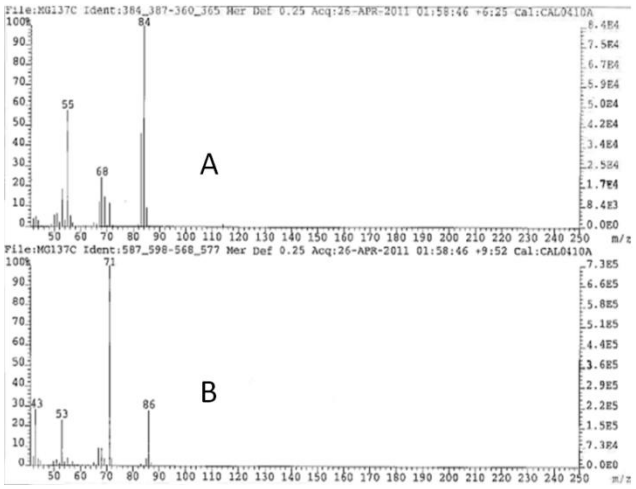

Figure S27. Mass spectra of oxidation products of 2-methyl-2-butene isolated from host **1**.

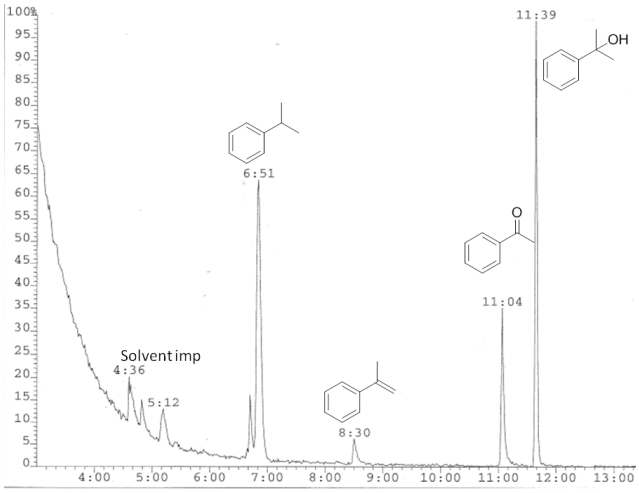

Figure S28. GC trace of oxidation products of cumene isolated from host **1**.

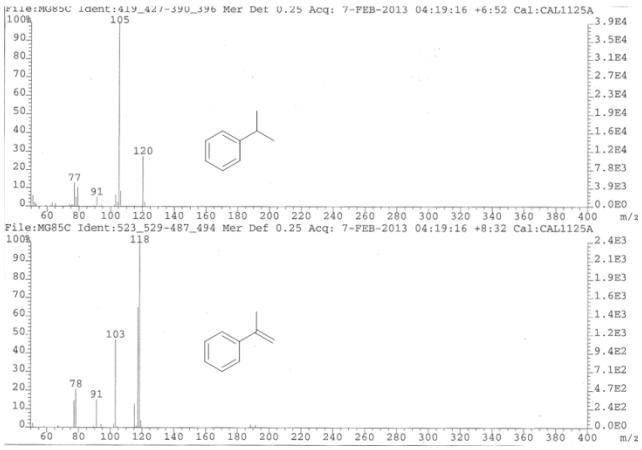

Figure S29. Mass spectra of oxidation products of cumene isolated from host **1**

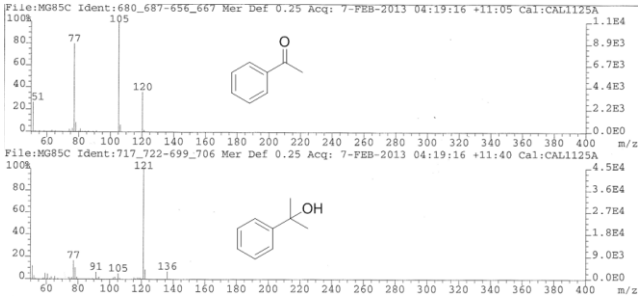

Figure S30. Mass spectra of oxidation products of cumene isolated from host **1**

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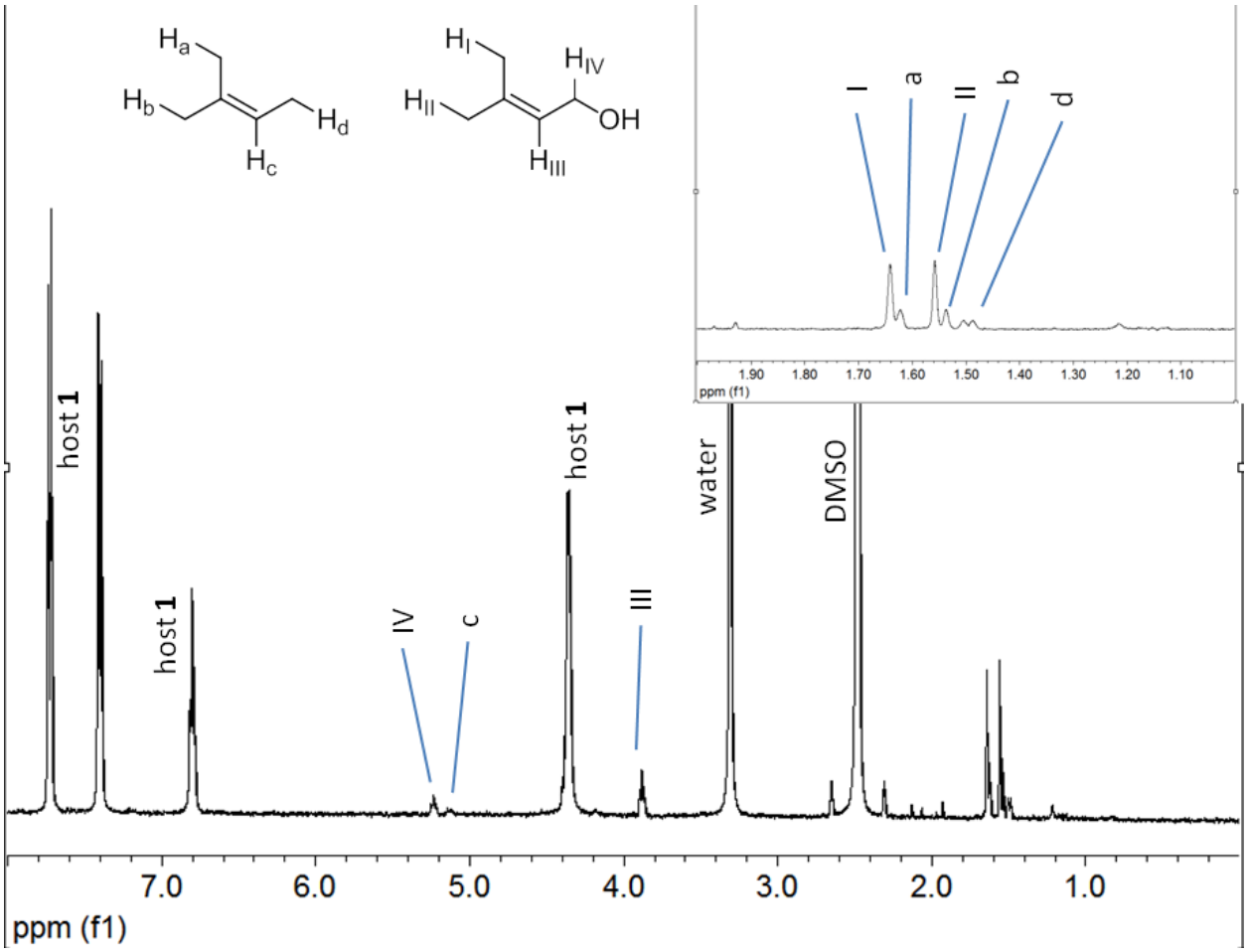

Figure S31. ^{1}H-NMR (400 MHz, δ_6-DMSO) of host **1**•oxidation products from 2-methyl-2-butene.

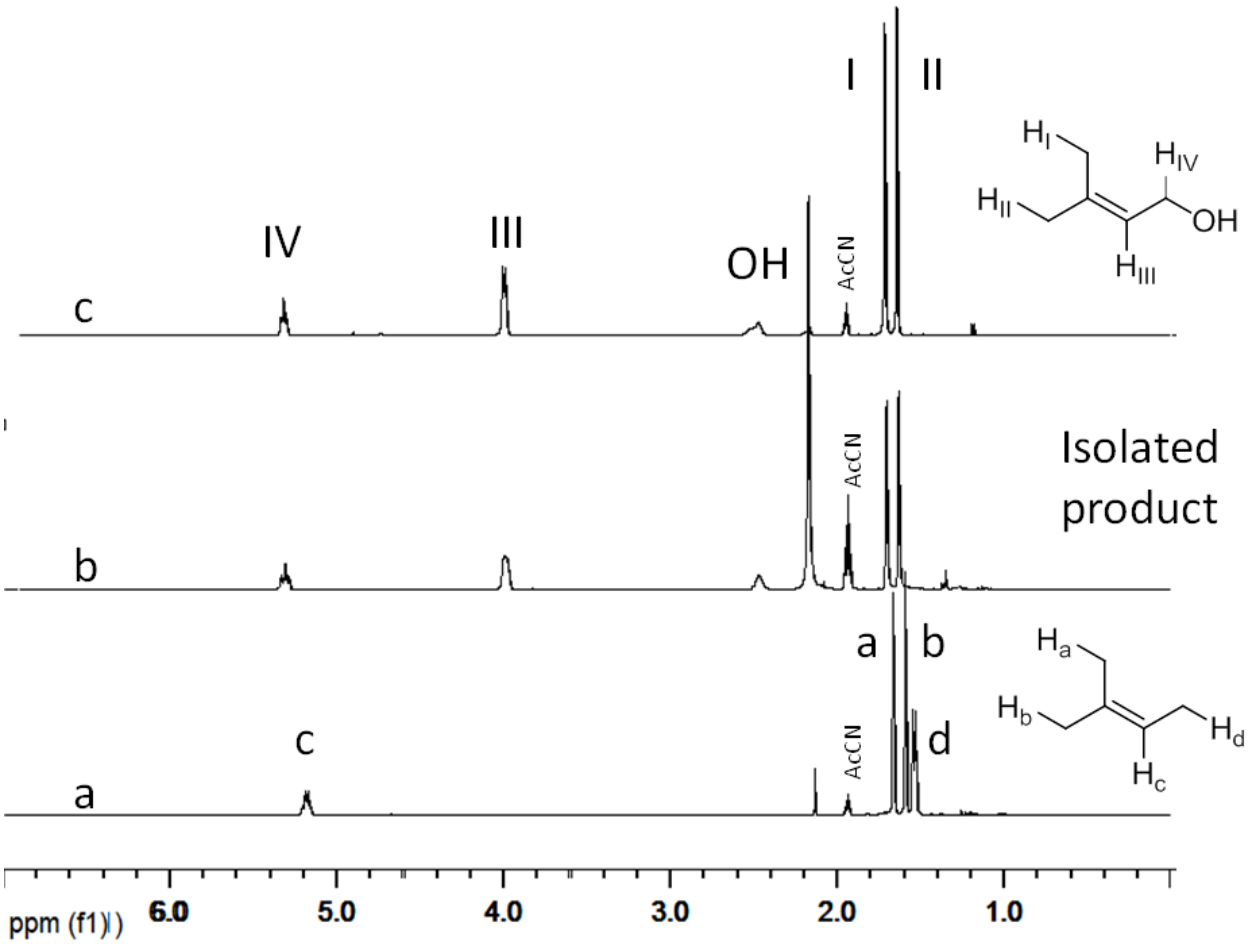

Figure S32. Comparison of ^{1}H-NMR (300 MHz, δ_3-AcCN) of oxidation products of 2-methy-2-butene at 0, 30, 60, 120, and 180 min.

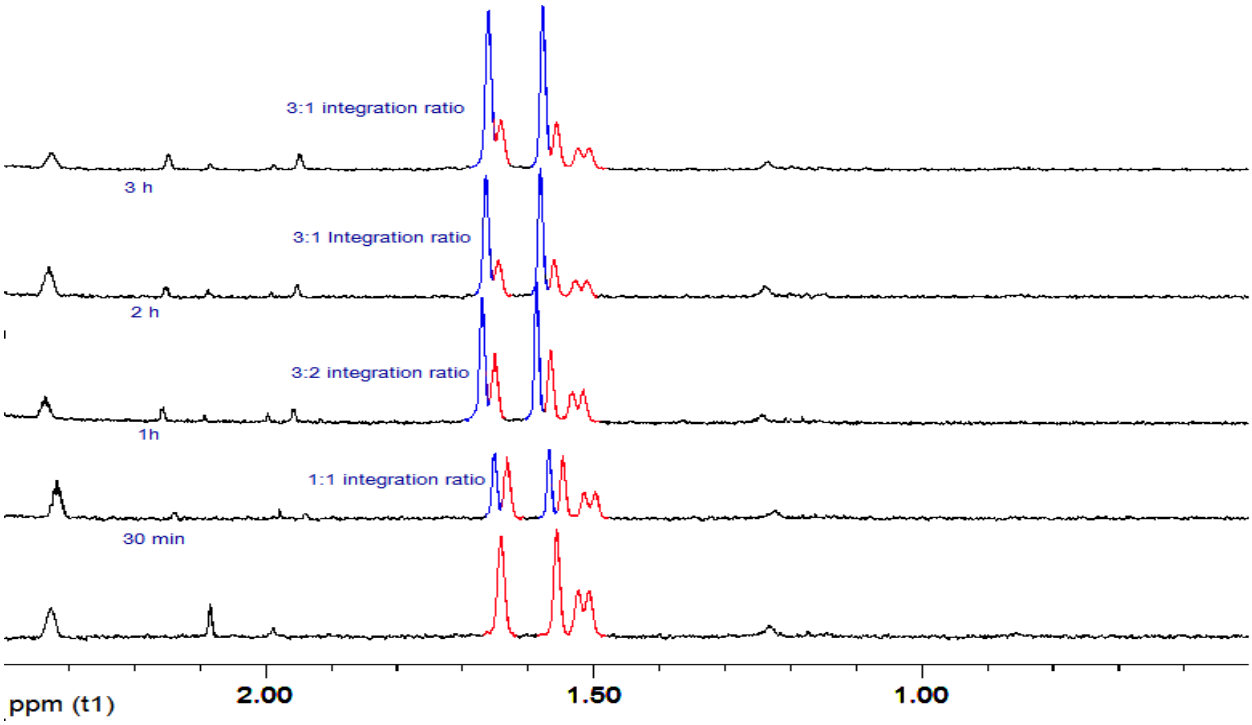

Figure S33. Comparison of ^{1}H-NMR (300 MHz, δ_3-AcCN) of oxidation products of 2-methy-2-butene at 0, 30, 60, 120, and 180 min. The % conversion were determined by the following equations:

$$\%\ conversion = \frac{Ave\ integration\ of\ product\ H}{Ave.int.of\ starting\ material + Ave.int.of\ product}$$

Table S4. % conversion of oxidation of 2-methyl-2-butene as determined by ^{1}H-NMR

Run time	Integration of peak H_c	Integration of peak H_d	Integration of peak H_{III}	Integration of peak H_{IV}	Ave integration of 3-methyl-2-butene-1-ol	Ave peak integration of 2-methyl-2-butene	% conversion
2 h	0.29	1.12	1.02	2.44	1.12	0.33	77.2
1 h	0.56	1.62	1.99	.96	0.99	0.67	59.6
30 min	0.88	3.35	1.00	2.26	1.07	1.00	51.8

Catalytic study:

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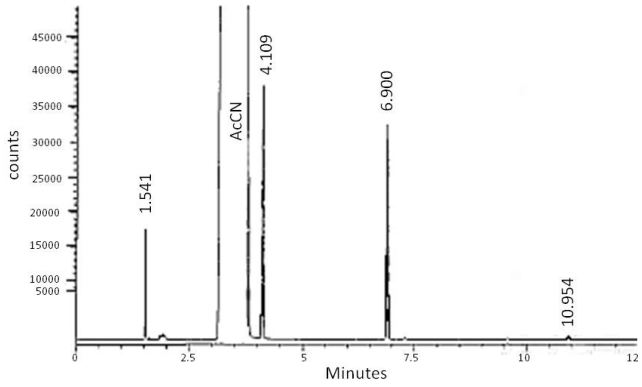

Figure S34. Comparison of GC of oxidation products from suspension of host **1** in acetonitrile.

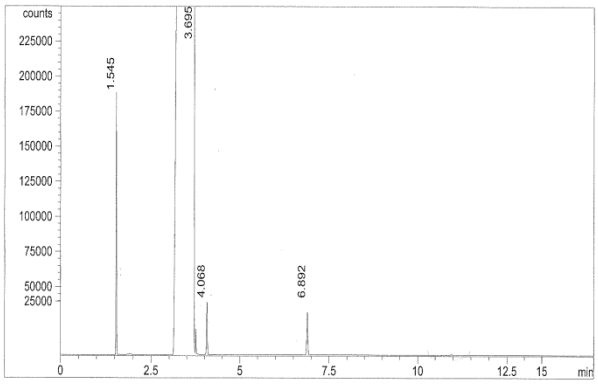

Figure S35. Comparison of GC of oxidation products from suspension of host **1** in acetonitrile/water mixtures.

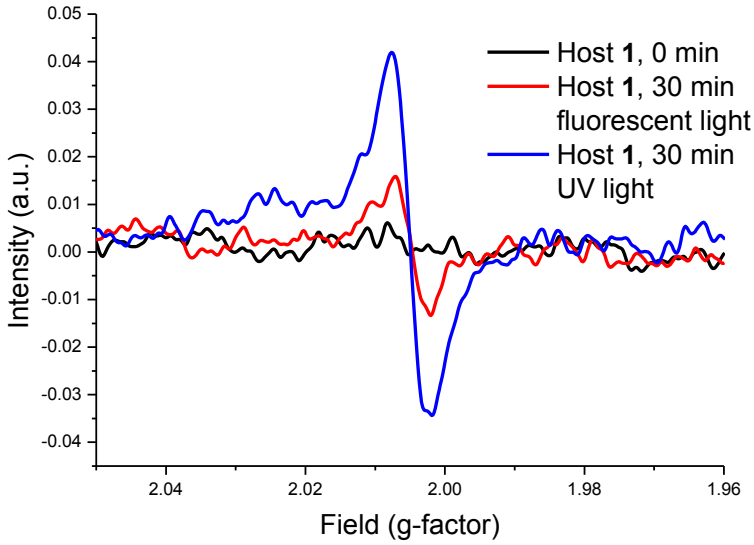

Figure S36. Comparison of EPR spectra of host **1**, host **1** after exposure to fluorescent light, host **1** after exposure to UV light.

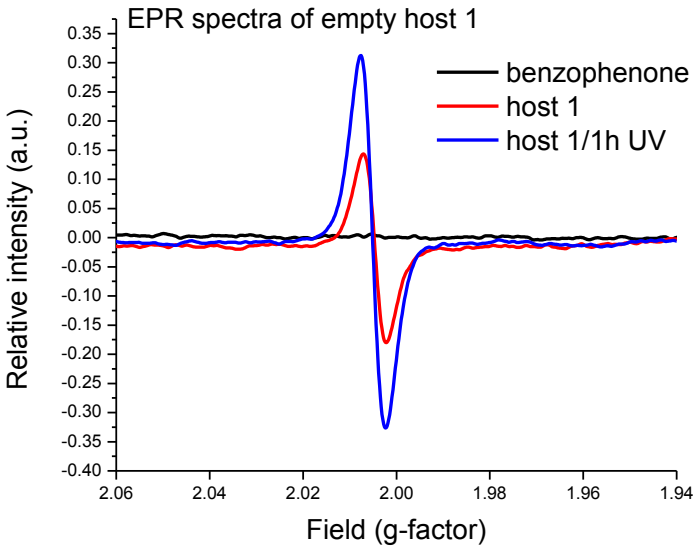

Figure S37. Comparison of EPR spectra of benzophenone, host **1** (ambient conditions), and host **1** (1 h UV exposure).

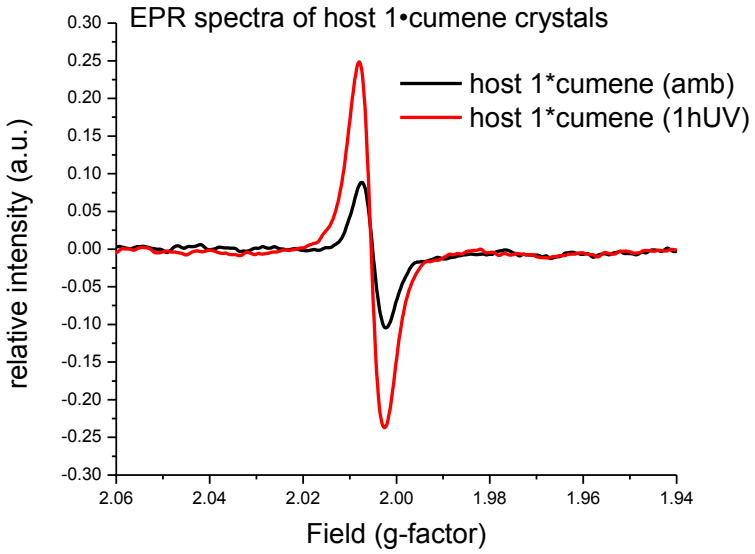

Figure S38. EPR spectra of host **1**•cumene before and after UV irradiation.

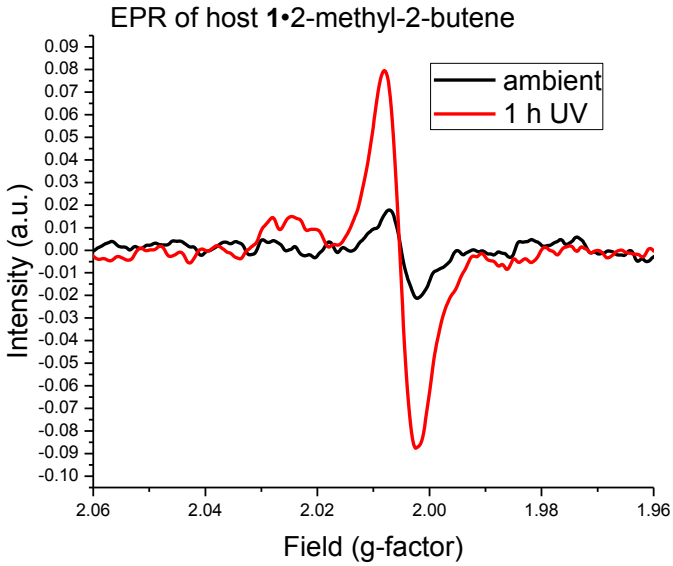

Figure S39. EPR spectra of host **1**•2-methyl-2-butene before and after UV irradiation.

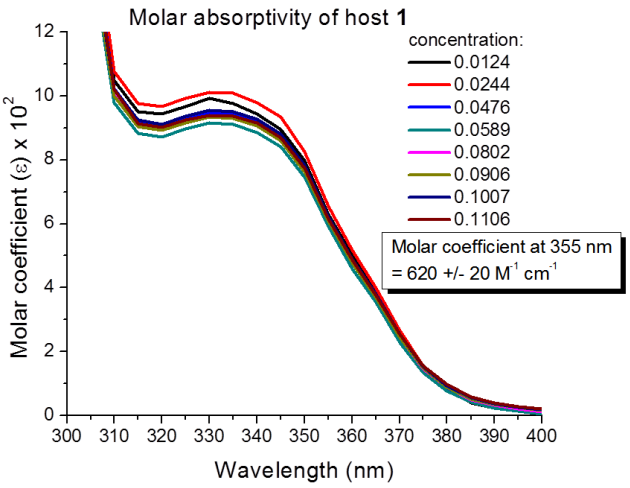

Figure S40. Molar absorptivity of host **1** in DMSO

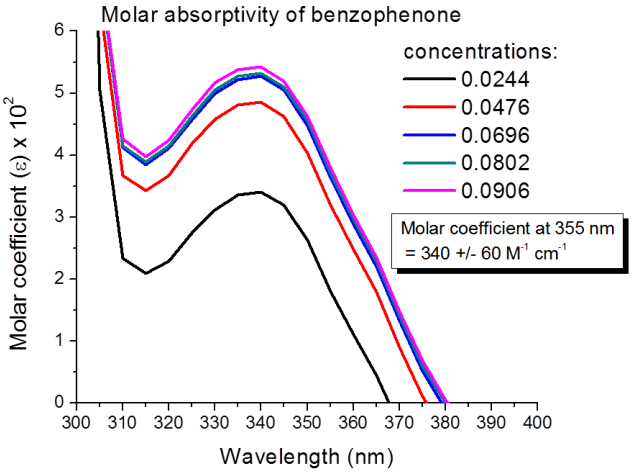

Figure S41. Molar absorptivity of benzophenone in DMSO.

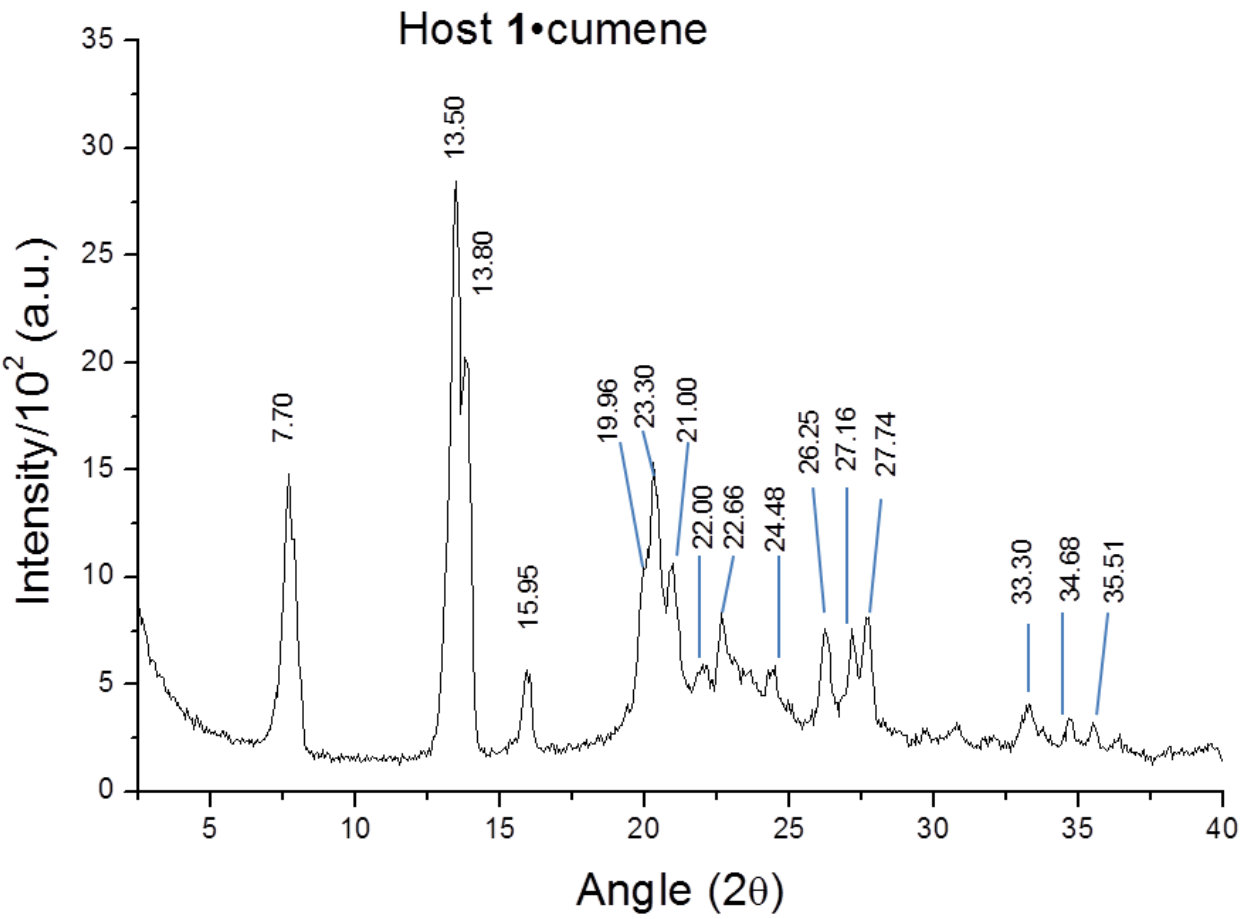

Figure S42. PXRD pattern of host **1**•cumene.

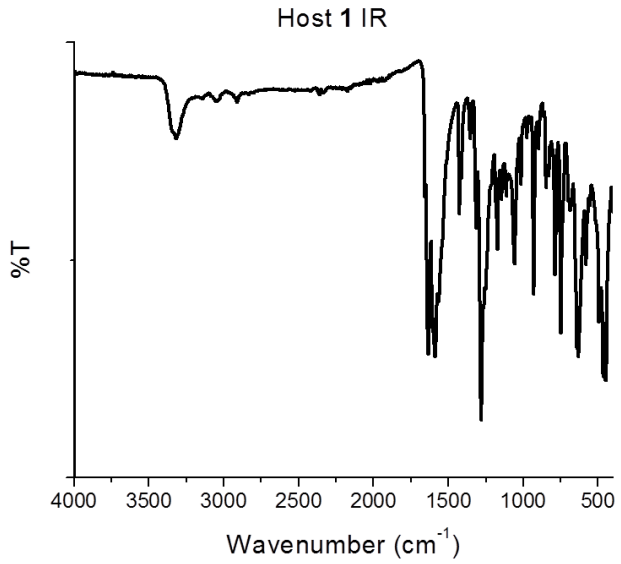

Figure S43. IR spectra of host **1**.

Table S5. List of major peaks in the IR spectra before and after UV irradiation.

Host **1** (cm^{-1})	Host **1** 1 h UV irradiation (cm^{-1})
3317	3314
1634	1635
1588	1589
1426	1427
1314	1314
1281	1282
1172	1172
1058	1058
931	931
787	787
749	749
634	634
493	793
465	465
448	448

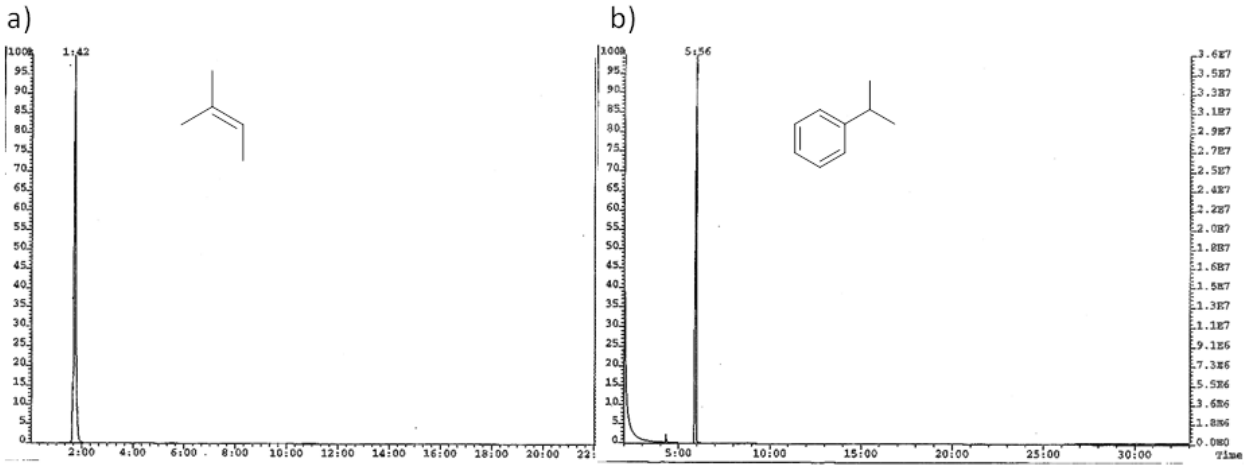

Figure S44. a) GC trace of isolated products from host **1**•2-methyl-2-butene after irradiation under argon. b) GC trace of isolated products from host **1**•cumene after irradiation under argon.

References:

1. Mitchell, A. R.; Pagoria, P. F.; Coon, C. L.; Jessop, E. S.; Poco, J. F.; Tarver, C. M.; Breithaupt, R. D.; Moody, G. L., Nitroureas .1. Synthesis, Scale-up and Characterization of K-6. *Propell Explos Pyrot* 1994, *19* (5), 232-239.

2. Dewal, M. B.; Xu, Y. W.; Yang, J.; Mohammed, F.; Smith, M. D.; Shimizu, L. S., Manipulating the cavity of a porous material changes the photoreactivity of included guests. *Chem Commun* 2008, (33), 3909-3911.