Supporting Information File

Light-Stabilised Dynamic Materials

Hannes A. Houck,[†,‡,§] Eva Blasco,[§,*] Filip E. Du Prez[†,*] and Christopher Barner-Kowollik[‡,§,*]

[†] Polymer Chemistry Research Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4-bis, 9000 Gent, Belgium

[‡] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George St, Brisbane, QLD 4000, Australia

[§] Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76131 Karlsruhe, Germany

* eva.blasco@kit.edu, filip.duprez@ugent.be, christopher.barnerkowollik@qut.edu.au

Table of contents

Supplementary Figures and Tables

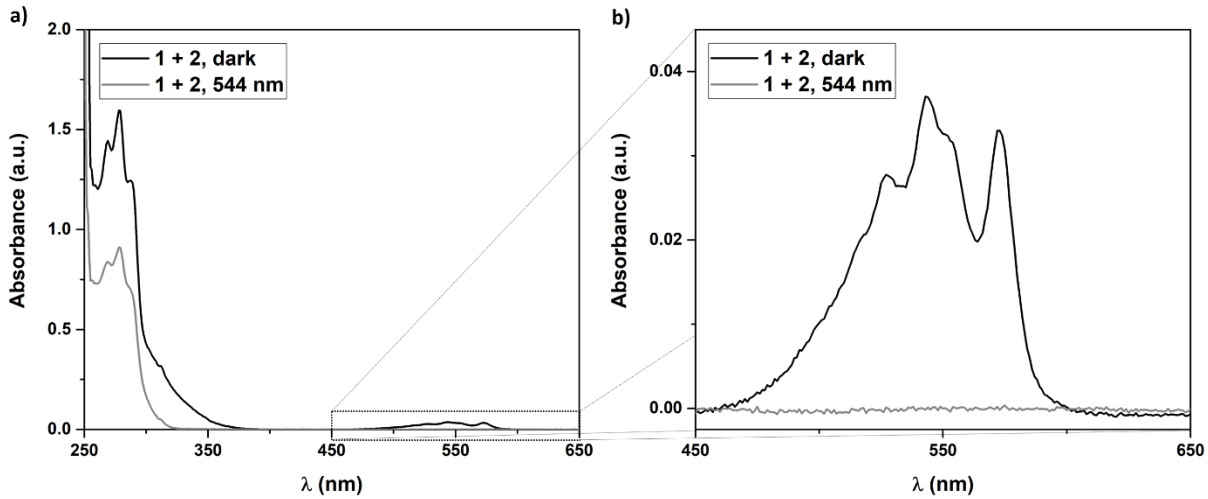


Figure S1. a) UV/vis absorption spectra (CCl_4) recorded before (black line) and after (grey line) green light irradiation (λ = 544 nm, 100 Hz, 2 mJ) of a 4-n-butyl-TAD **1** solution (15 mM in CCl_4) in the presence of naphthalene **2a** (1.2 eq.). b) Zoom in the visible region of the spectrum, indicating the complete disappearance of the purple coloured **1** upon visible light irradiation.

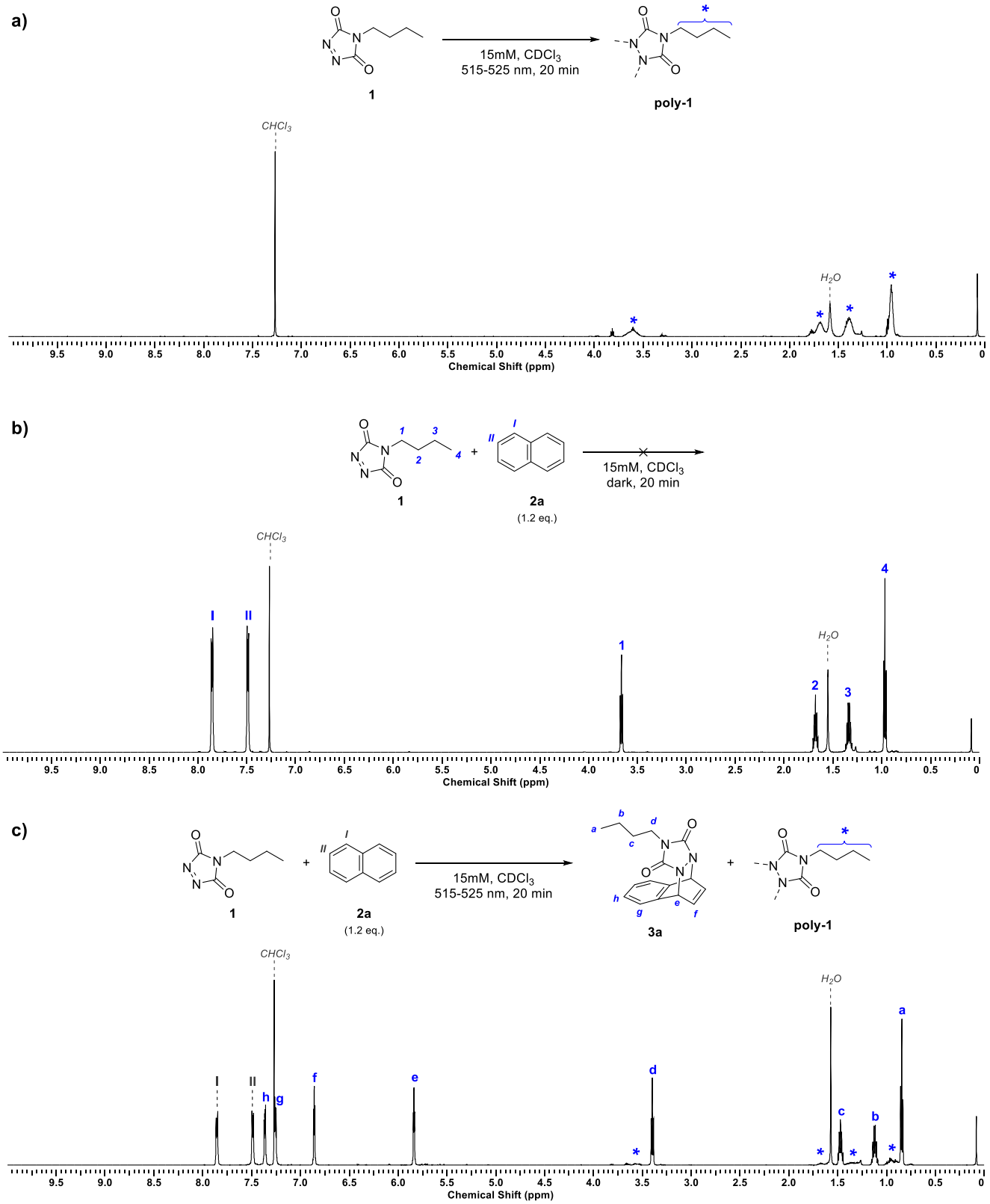


Figure S2. Assessment of competitive TAD-based photopolymerisation during cycloaddition upon visible light impact of **1** (15 mM in $CDCl_3$). a) Reference ^{1}H-NMR spectrum of the TAD-photopolymer, obtained after green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs, 20 min) of a blank 4-*n*-butyl-TAD solution in the absence of naphthalene. b) Less than 1 % of TAD-naphthalene cycloadduct **3a** is observed in a reference experiment whereby **1** and **2a** (1.2 eq.) are kept in the dark, thus indicating the true light-induced nature of the TAD-naphthalene cycloaddition. c) Shining green light (λ = 515 – 525 nm, 3 x 3 W LEDs, 20 min) on **1** in the presence of naphthalene **2a** (1.2 eq.) almost quantitatively gives the cycloadduct **3a**, although traces (i.e. < 2 %) of the TAD-photopolymer are also detected.

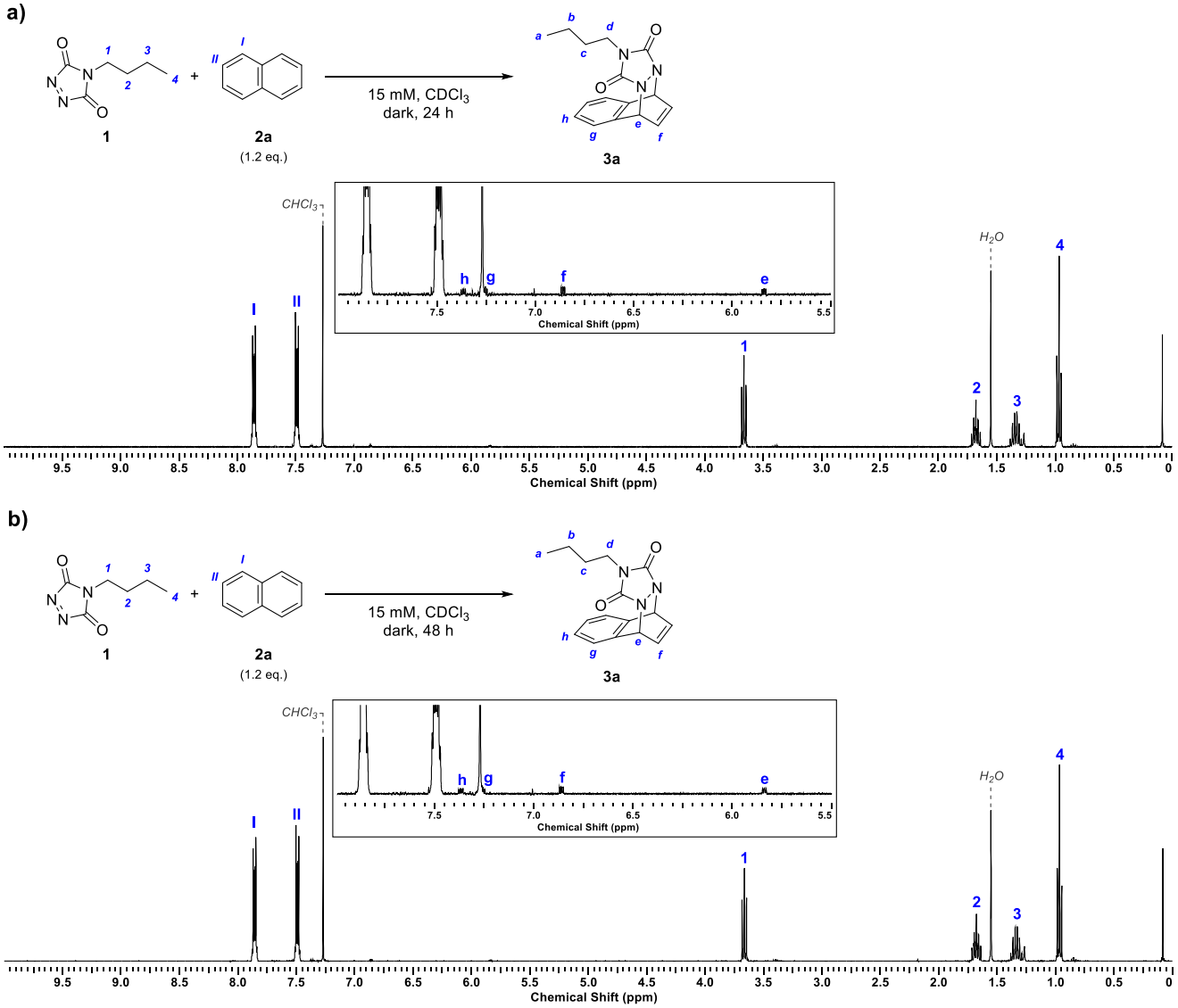


Figure S3. ^{1}H-NMR spectra obtained upon mixing 4-*n*-butyl-TAD **1** with plain naphthalene **2a** (1.2 eq.) in deuterated chloroform ($CDCl_3$, 15 mM), kept in the dark. a) An equilibrium concentration is reached after 24 hours, whereby ca. 2 % of the corresponding cycloadduct **3a** is formed. b) No change in concentration of **3a** was observed over the course of 48 hours (bottom).

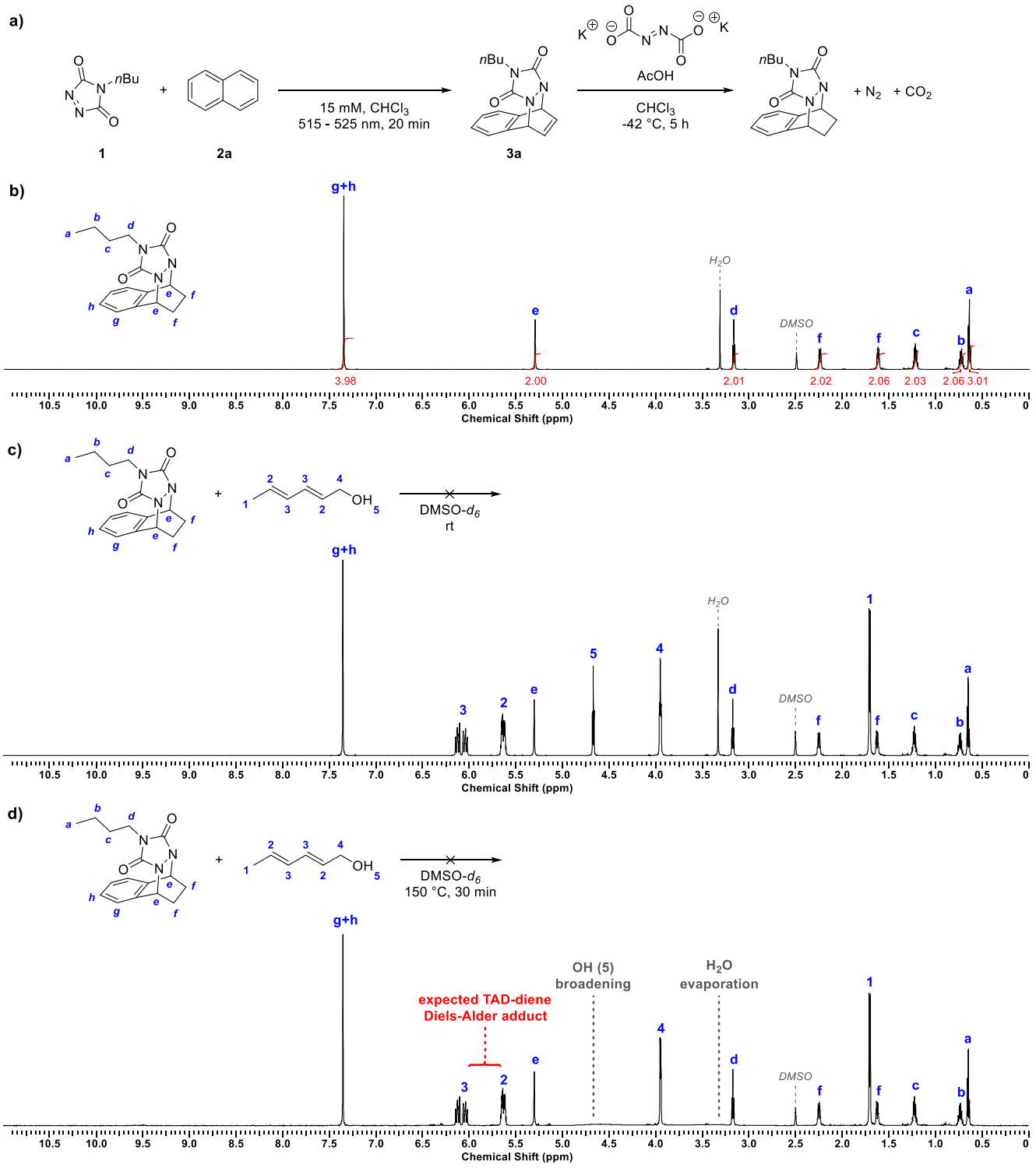


Figure S4. Assessment of the driving force for the spontaneous cycloreversion of **3a**. a) Visible light-induced formation of cycloadduct **3a** and subsequent diimide-mediated reduction of the isolated double bond. b) ^{1}H-NMR spectrum (DMSO-d_6) of the reduced cycloadduct. c) ^{1}H-NMR spectrum after addition of a conjugated diene that acts as an irreversible TAD-trap, indicating the room temperature stability of the reduced TAD-naphthalene cycloadduct. d) No change in the ^{1}H-NMR spectrum is observed upon heating for 30 minutes at 150 °C, which confirms the irreversible nature of the TAD-naphthalene adduct and therefore removal of the cycloreversion driving force when the isolated double bond in **3a** is removed.

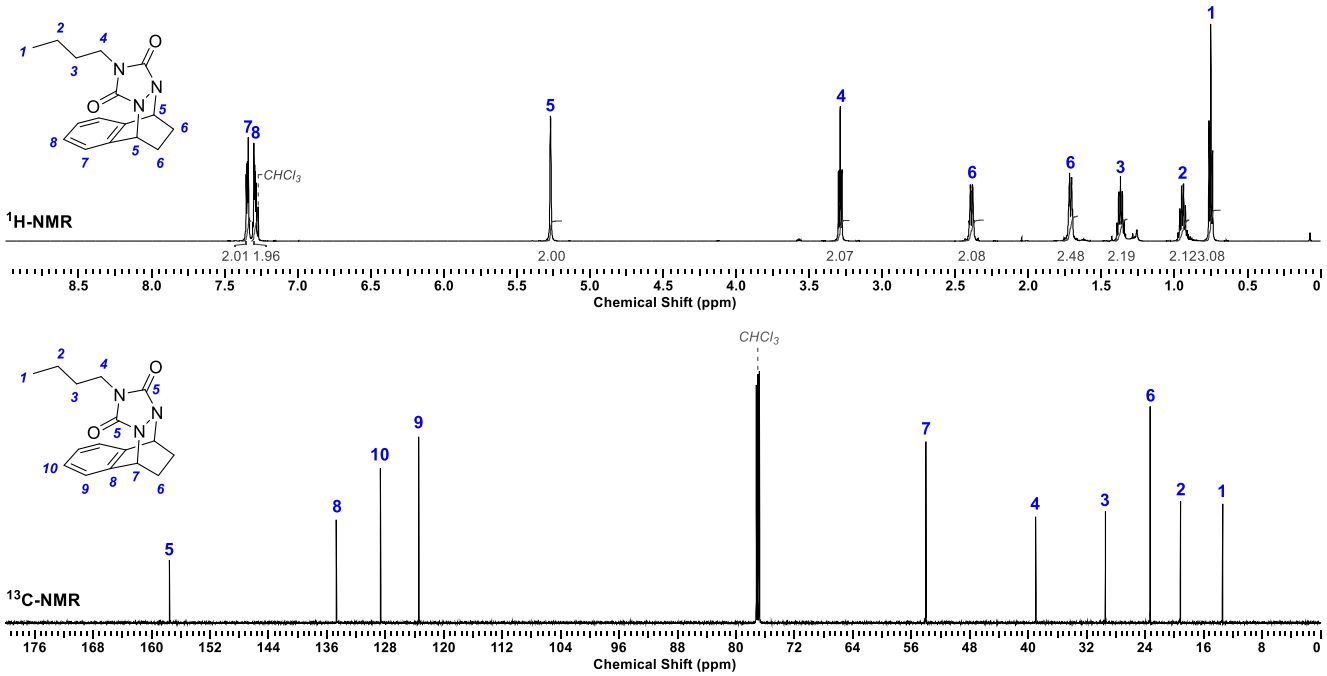


Figure S5. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of the TAD-naphthalene cycloadduct obtained after reduction of **3a**.

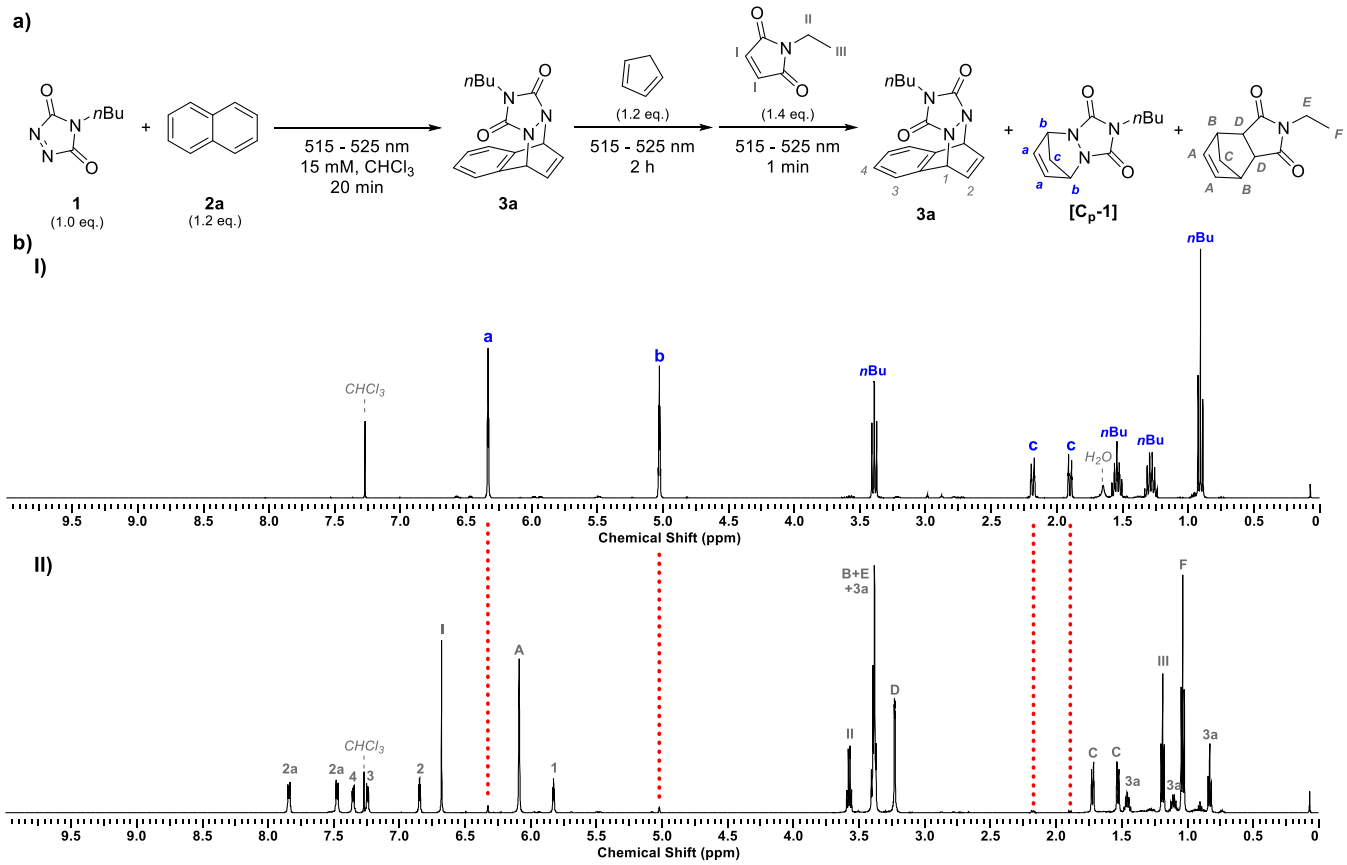


Figure S6. Light-stabilisation of the covalent TAD-naphthalene cycloadduct. a) Trapping experiment consisting of the sequential addition of cyclopentadiene and N-ethylmaleimide, designed to detect the amount of TAD that is released from cycloadduct **3a** under continuous green light irradiation (2 h, λ = 515 – 525 nm, 3 x 3 W LEDs). b) Offline ^{1}H-NMR analysis ($CDCl_3$) of the trapping experiment carried out under dark conditions (spectrum I) and after irradiation (spectrum II) highlights the still dynamic behaviour of **3a** upon irradiation, which is evidenced by trace amounts (i.e. less than 5 %) of the newly formed TAD-cyclopentadiene adduct [**C_p-1**]. Nonetheless, the closed covalently bound cycloadduct **3a** remains predominantly formed (i.e. > 95 %) over the course of 2 h visible light impact.

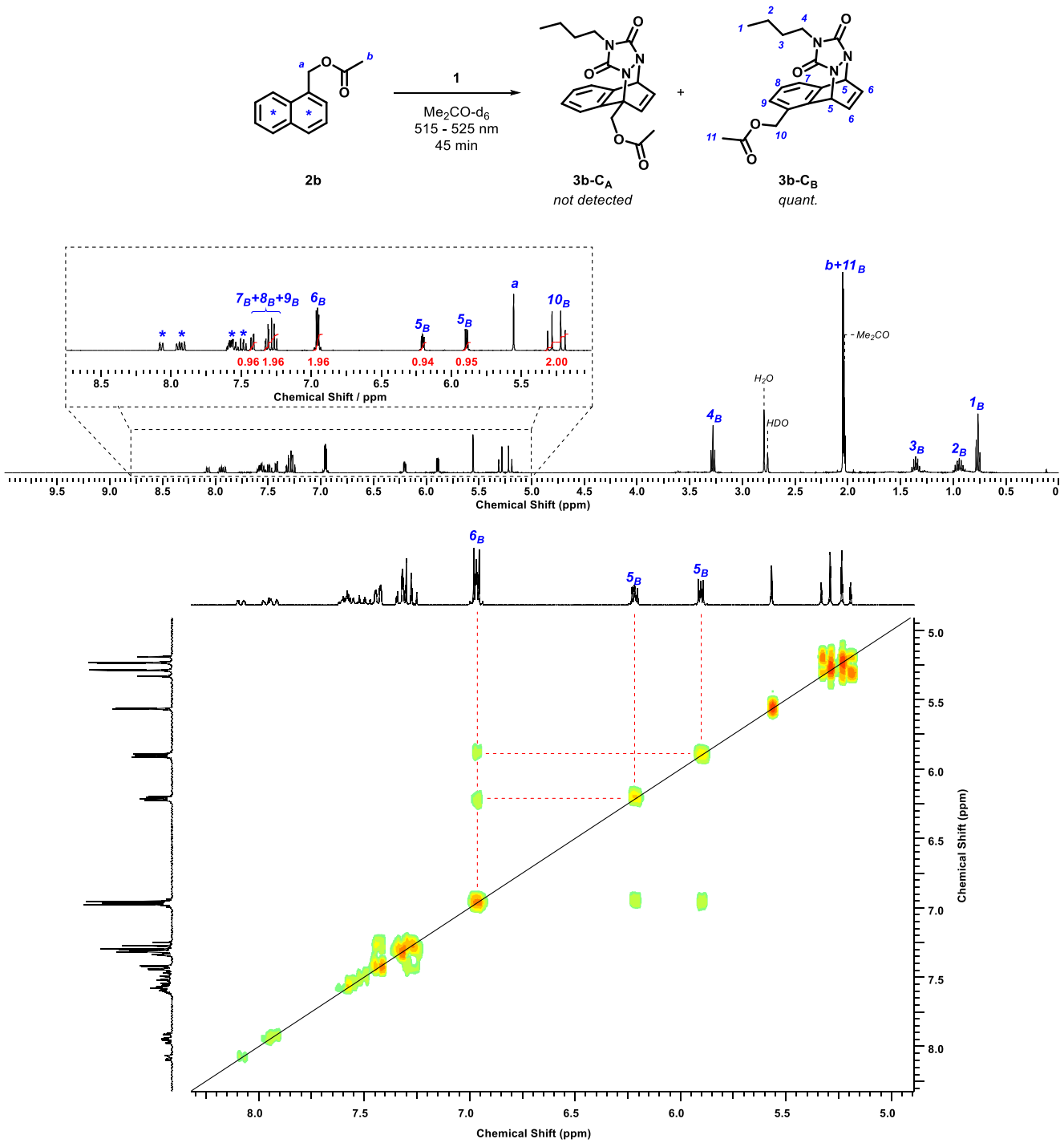


Figure S7. Structure elucidation of cycloadducts **3b**, formed by 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO- d_6) in the presence of naphthalen-1-ylmethyl acetate **2b** (1.2 eq.). Only regioisomer **3b-C$_B$**, i.e. the cycloadduct formed onto the non-substituted ring, is detected. Peaks were assigned in accordance to 2D COSY-NMR from which the exclusive regioselectivity was confirmed (bottom).

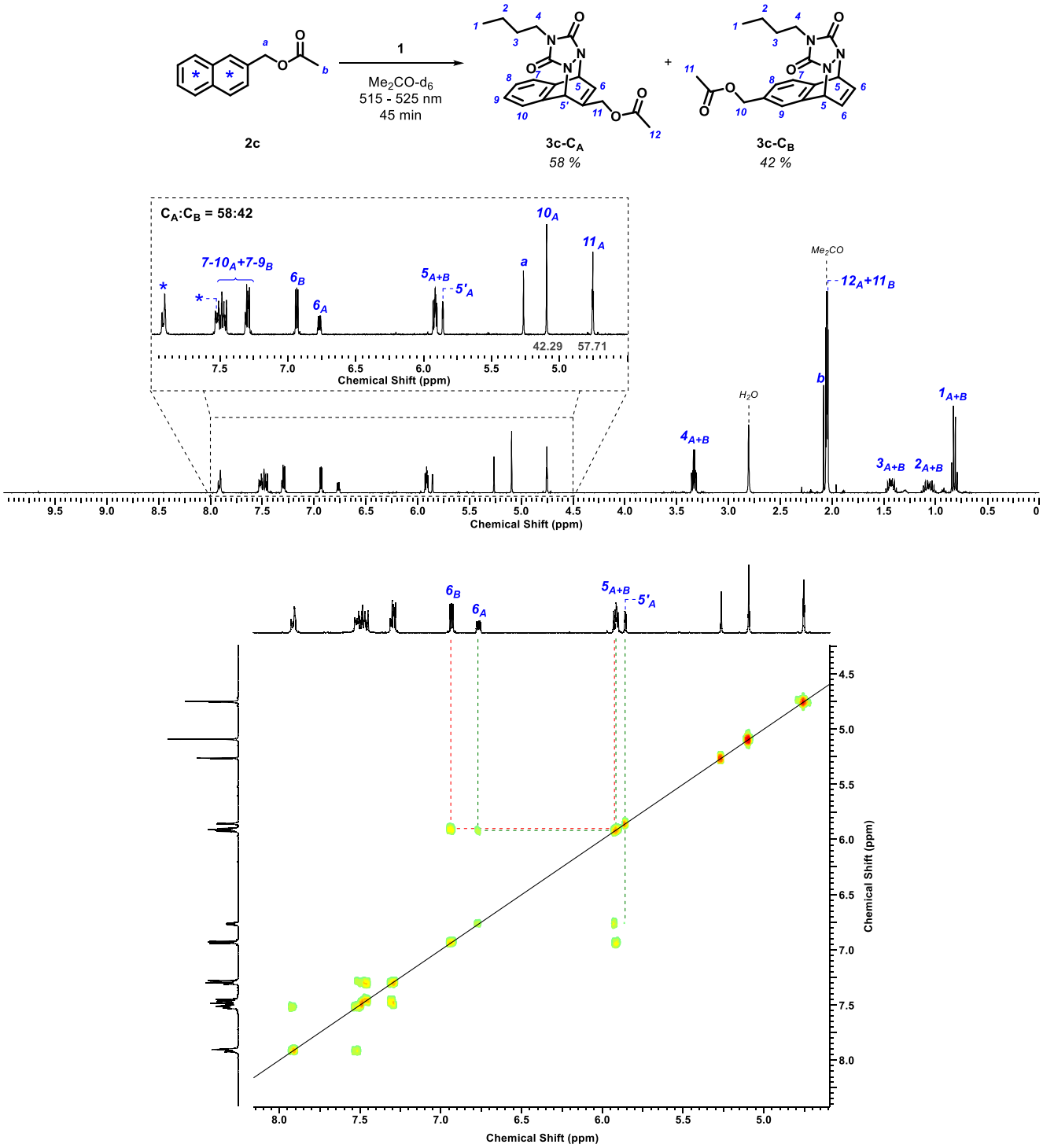


Figure S8. Structure elucidation of cycloadducts **3c**, formed by 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO- d_6) in the presence of naphthalen-2-ylmethyl acetate **2c** (1.2 eq.). Both regioisomers **3c-C$_A$** and **3c-C$_B$**, i.e. the cycloadduct formed onto the substituted and non-substituted ring, respectively are detected. Peaks were assigned in accordance to 2D COSY-NMR from which the regioisomers were identified (bottom). The regioisomeric excess was determined based on proton integration of well resolved signals (inset ^{1}H-NMR spectrum).

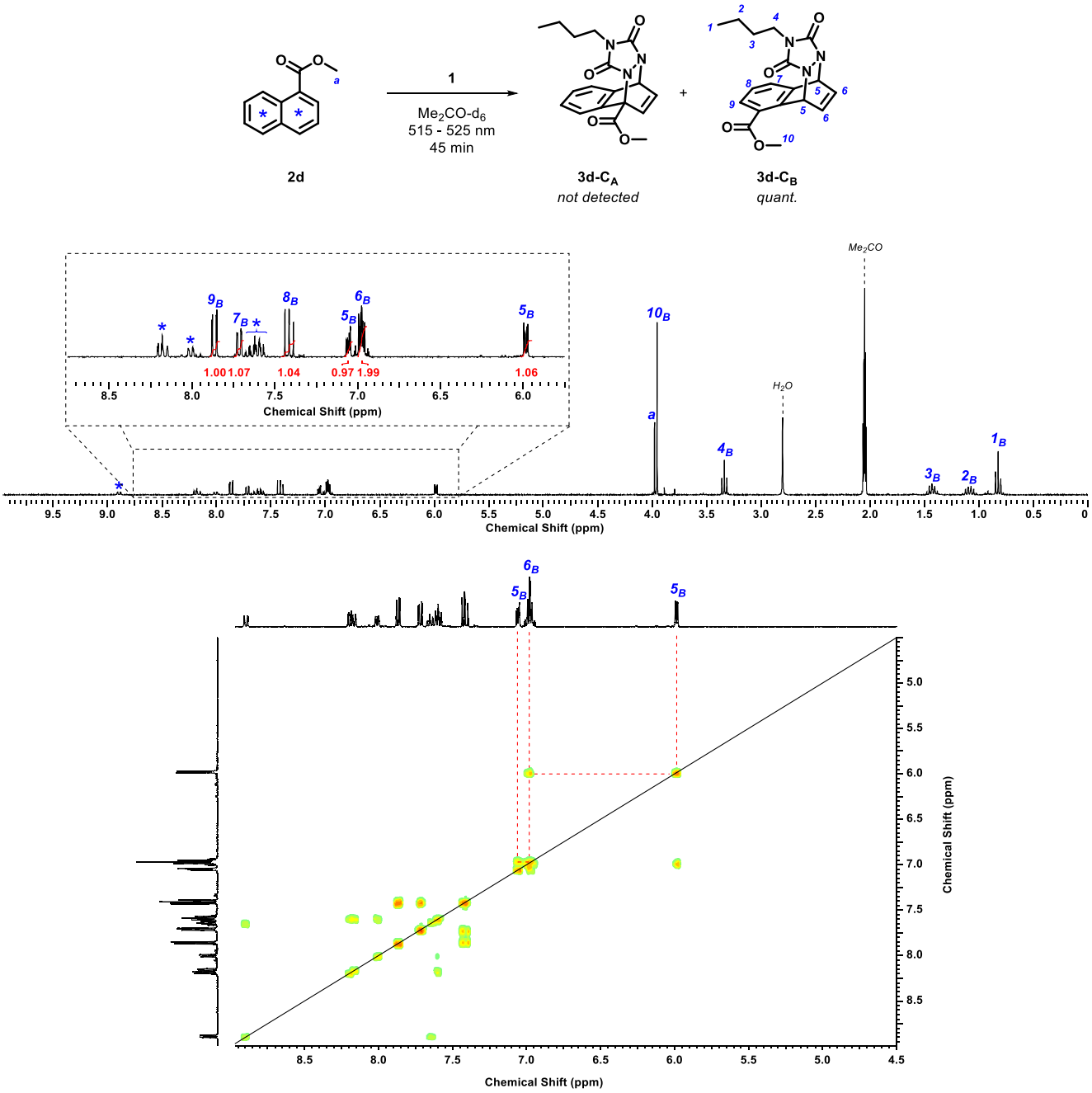


Figure S9. Structure elucidation of cycloadducts **3d**, formed by 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of methyl 1-naphthoate **2d** (1.2 eq.). Only regioisomer **3d-C$_B$**, i.e. the cycloadduct formed onto the non-substituted ring, is detected. Peaks were assigned in accordance to 2D COSY-NMR from which the exclusive regioselectivity was confirmed (bottom).

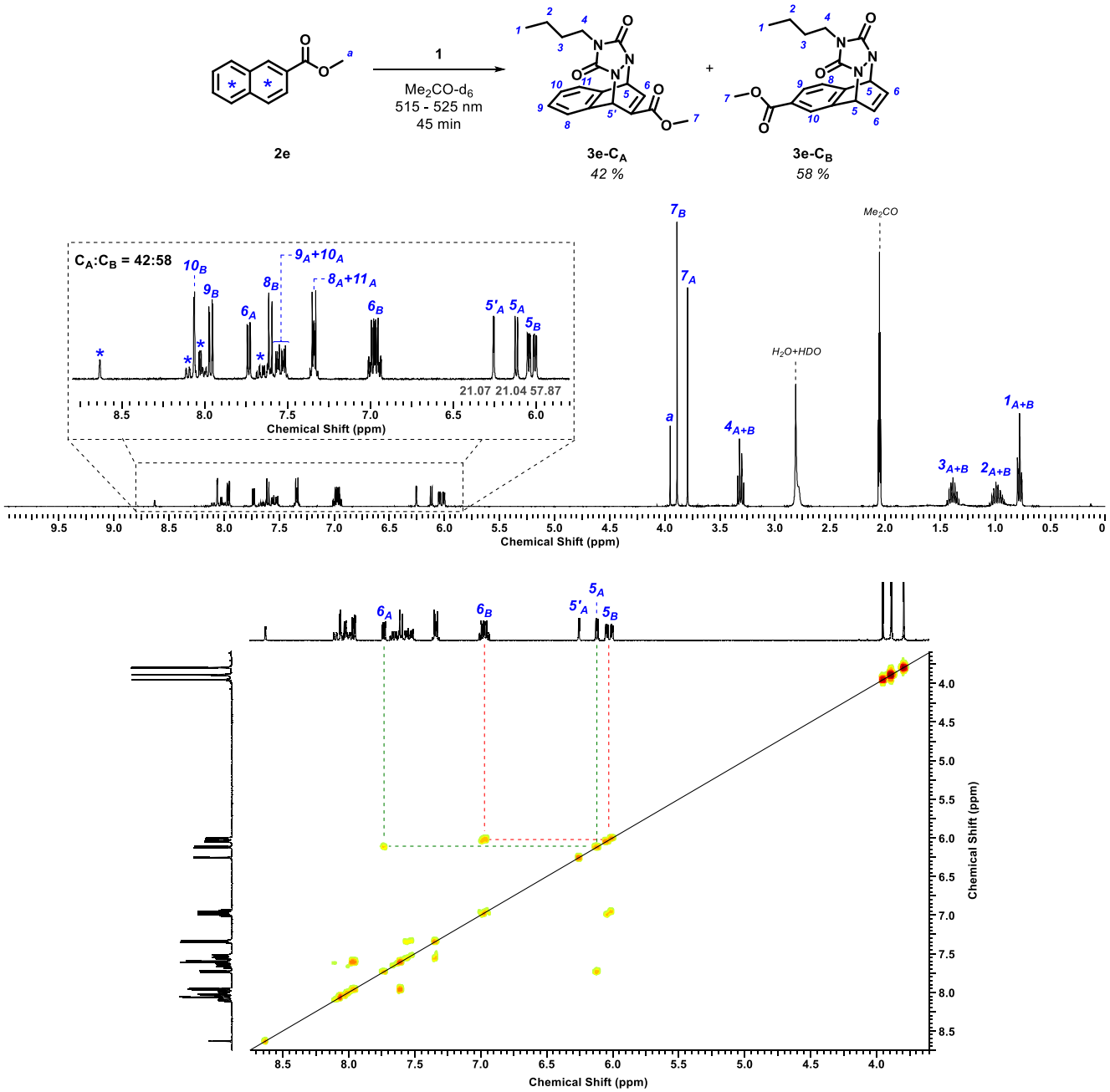


Figure S10. Structure elucidation of cycloadducts **3e**, formed by 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of methyl 2-naphthoate **2e** (1.2 eq.). Both regioisomers **3e-C$_A$** and **3e-C$_B$**, i.e. the cycloadduct formed onto the substituted and non-substituted ring, respectively are detected. Peaks were assigned in accordance to 2D COSY-NMR from which the regioisomers were identified (bottom). The regioisomeric excess was determined based on proton integration of well resolved signals (inset ^{1}H-NMR spectrum).

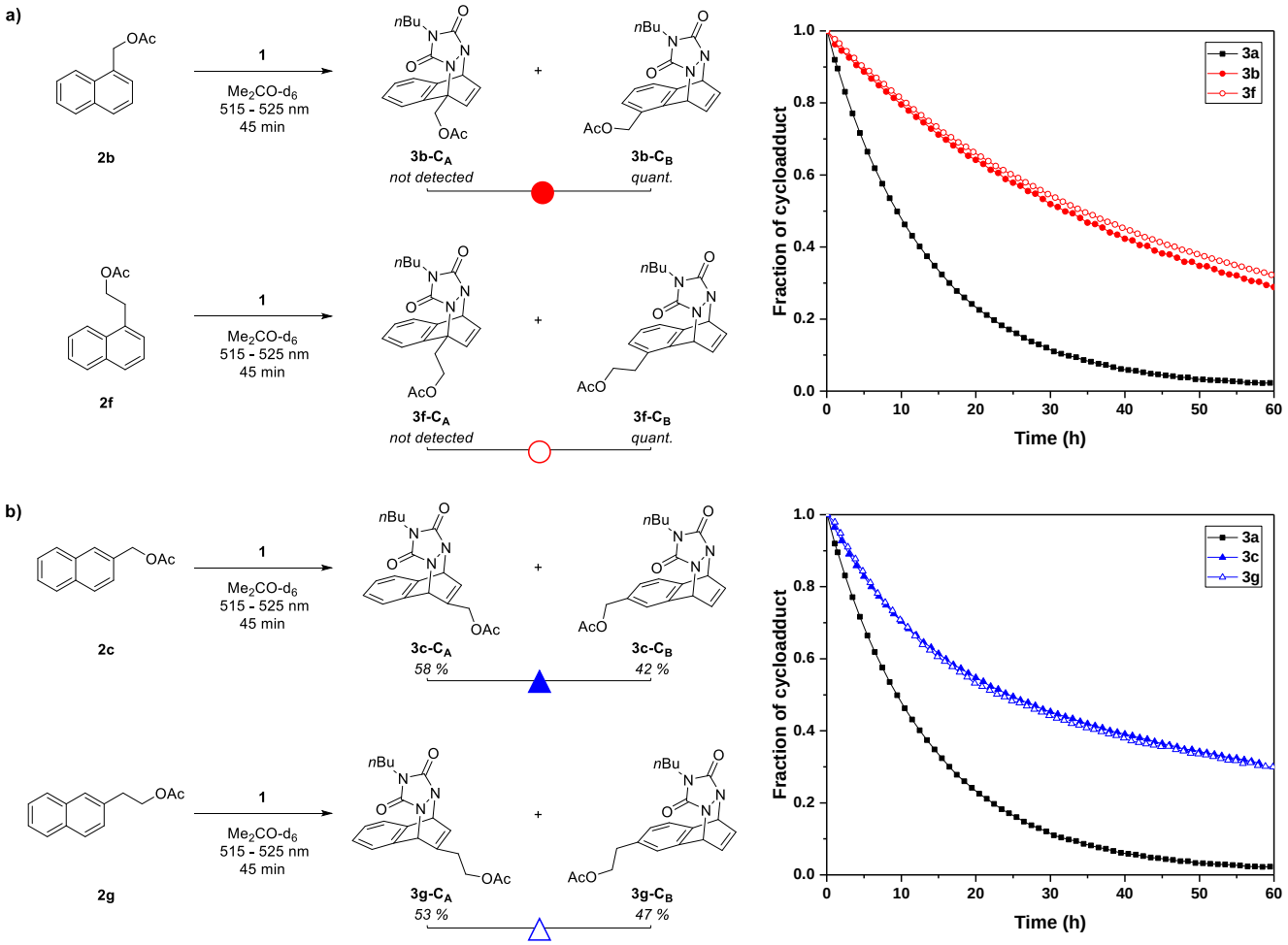
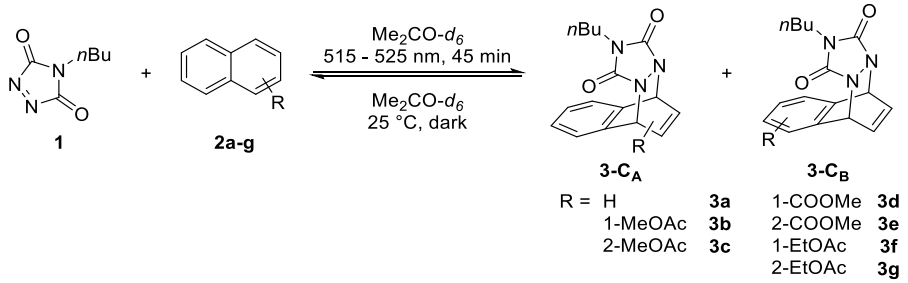


Figure S11. Effect of increasing the alkyl-spacer length on the naphthalene scaffold with regard to its light-driven TAD-cycloaddition and subsequent thermal cycloreversion. a) 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of methyl and ethyl acetate 1-substituted naphthalene, i.e. **2b** and **2f**, respectively (1.2 eq.) in the presence of **1** (15 mM, Me_2CO-d_6) exclusively affords cycloaddition onto the non-substituted ring C_B. Subsequent kinetic monitoring of the retro-reaction upon standing in the dark (25 °C, Me_2CO-d_6) gave similar cycloreversion profiles. b) Also for the 2-substituted naphthalene derivatives, no significant difference in both TAD-based cycloaddition and cycloreversion was observed upon increasing the alkyl-spacer between the naphthalene scaffold and the acetate group, as was evidenced by the similar regioisomer composition and cycloreversion profiles obtained for the monomer mimics **2c** and **2g**.

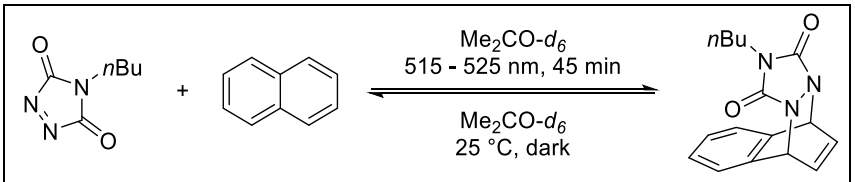
Table S1. Naphthalene compounds studied in the visible light-induced cycloaddition reaction with **1** (15 mM, Me_2CO-d_6, room temperature, λ = 515 – 525 nm) with their corresponding regioisomer composition reached after 45 min of irradiation and their subsequent cycloreversion rates upon standing in the dark at 25 °C (Me_2CO-d_6).



	R	Cycloaddition		Cycloreversion	
		C_A (%)	C_B (%)	$k_{obs}^{25\,°C}(C_A)$ (10^{-5} s^{-1})	$k_{obs}^{25\,°C}(C_B)$ (10^{-5} s^{-1})
3a	H	100 %[a], with $C_A = C_B$		2.03[a]	2.03[a]
3b	1-MeOAc	0	100	-	0.63
3c	2-MeOAc	58	42	0.31	2.23
3d	1-COOMe	0	100	-	0.41
3e	2-COOMe	42	58	1.07	1.53
3f	1-EtOAc	0	100	-	0.58
3g	2-EtOAc	53	47	0.33	1.94

[a]Addition of **1** to plain naphthalene **2a** does not give a mixture of regioisomers due to its symmetry.

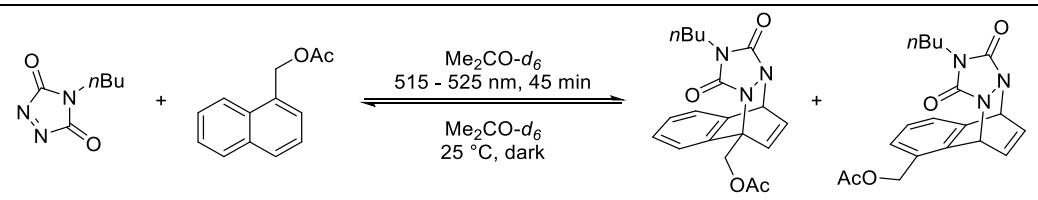
Table S2. Fraction of cycloadduct **3a** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2a** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2a** **3a**

Time (h)	Fraction **3a**	Time (h)	Fraction **3a**
0.05	> 0.99	30.47	0.110
1.10	0.920	31.47	0.104
1.47	0.895	32.47	0.098
2.47	0.831	33.47	0.094
3.47	0.771	34.47	0.086
4.47	0.717	35.47	0.081
5.47	0.664	36.47	0.076
6.47	0.618	37.47	0.072
7.47	0.576	38.47	0.066
8.47	0.536	39.47	0.061
9.47	0.499	40.47	0.059
10.47	0.462	41.47	0.056
11.47	0.431	42.47	0.052
12.47	0.401	43.47	0.048
13.47	0.374	44.47	0.047
14.47	0.348	45.47	0.044
15.47	0.324	46.47	0.041
16.47	0.300	47.47	0.038
17.47	0.278	48.47	0.038
18.47	0.260	49.47	0.033
19.47	0.242	50.47	0.032
20.47	0.225	51.47	0.031
21.47	0.211	52.47	0.029
22.47	0.197	53.47	0.029
23.47	0.182	54.47	0.027
24.47	0.171	55.47	0.026
25.47	0.160	56.47	0.023
26.47	0.148	57.47	0.023
27.47	0.138	58.47	0.022
28.47	0.129	59.47	0.022
29.47	0.121		

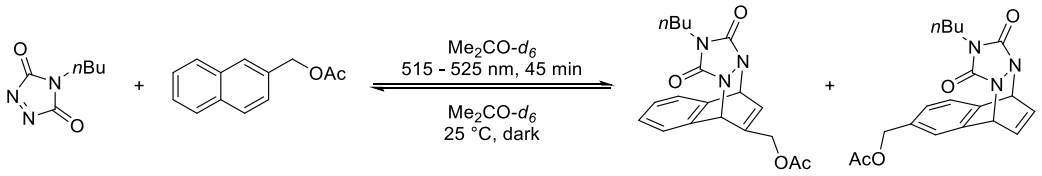
Table S3. Fraction of cycloadduct **3b** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2b** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2b** **3b-C_A** **3b-C_B**

Time (h)	Fraction **3b**	C_A:C_B	Time (h)	Fraction **3b**	C_A:C_B
0.05	> 0,99	< 0.01	31.00	0.511	< 0.01
1.12	0.963	< 0.01	32.00	0.499	< 0.01
2.00	0.945	< 0.01	33.00	0.493	< 0.01
3.00	0.926	< 0.01	34.00	0.480	< 0.01
4.00	0.905	< 0.01	35.00	0.467	< 0.01
5.00	0.887	< 0.01	36.00	0.463	< 0.01
6.00	0.867	< 0.01	37.00	0.454	< 0.01
7.00	0.849	< 0.01	38.00	0.440	< 0.01
8.00	0.831	< 0.01	39.00	0.434	< 0.01
9.00	0.814	< 0.01	40.00	0.423	< 0.01
10.00	0.796	< 0.01	41.00	0.418	< 0.01
11.00	0.779	< 0.01	42.00	0.405	< 0.01
12.00	0.761	< 0.01	43.00	0.403	< 0.01
13.00	0.746	< 0.01	44.00	0.390	< 0.01
14.00	0.728	< 0.01	45.00	0.382	< 0.01
15.00	0.712	< 0.01	46.00	0.379	< 0.01
16.00	0.698	< 0.01	47.00	0.370	< 0.01
17.00	0.682	< 0.01	48.00	0.359	< 0.01
18.00	0.668	< 0.01	49.00	0.359	< 0.01
19.00	0.653	< 0.01	50.00	0.348	< 0.01
20.00	0.642	< 0.01	51.00	0.346	< 0.01
21.00	0.631	< 0.01	52.00	0.339	< 0.01
22.00	0.614	< 0.01	53.00	0.329	< 0.01
23.00	0.606	< 0.01	54.00	0.324	< 0.01
24.00	0.589	< 0.01	55.00	0.321	< 0.01
25.00	0.579	< 0.01	56.00	0.312	< 0.01
26.00	0.570	< 0.01	57.00	0.306	< 0.01
27.00	0.555	< 0.01	58.00	0.303	< 0.01
28.00	0.548	< 0.01	59.00	0.294	< 0.01
29.00	0.533	< 0.01	60.00	0.289	< 0.01
30.00	0.519	< 0.01			

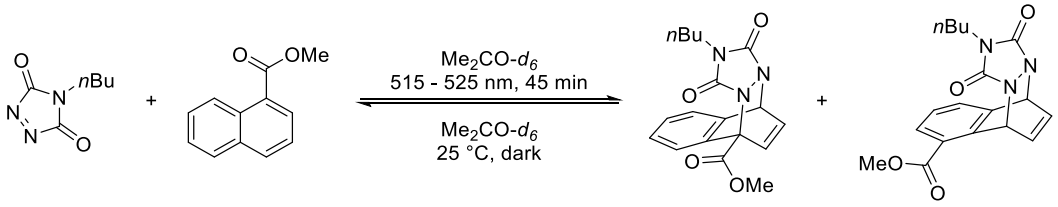
Table S4. Fraction of cycloadduct **3c** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2c** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2c** **3c-C_A** **3c-C_B**

Time (h)	Fraction **3c**	C_A:C_B	Time (h)	Fraction **3c**	C_A:C_B
0.12	> 0.99	57.6 : 42.4	30.00	0.453	90.3 : 9,7
1.00	0.964	59.2 : 40.8	31.00	0.446	90.7 : 9.3
2.00	0.927	60.8 : 39.2	32.00	0.439	90.9 : 9.1
3.00	0.890	62.6 : 37.4	33.00	0.434	91.0 : 9.0
4.00	0.858	64.2 : 35.8	34.00	0.425	91.8 : 8.2
5.00	0.828	65.8 : 34.2	35.00	0.419	91.8 : 8.2
6.00	0.800	67.5 : 32.5	36.00	0.413	92.1 : 7.9
7.00	0.773	68.8 : 31.2	37.00	0.407	92.4 : 7.6
8.00	0.749	70.4 : 29.6	38.00	0.400	92.9 : 7.1
9.00	0.724	71.8 : 28.2	39.00	0.395	93.0 : 7.0
10,00	0.704	73.3 : 26.7	40.00	0.391	93.2 : 6.8
11.00	0.683	74.7 : 25.3	41.00	0.386	93.2 : 6.8
12.00	0.665	75.8 : 24.2	42.00	0.380	93.3 : 6.7
13.00	0.646	77.3 : 22.7	43.00	0.376	93.5 : 6.5
14.00	0.631	78.2 : 21.8	44.00	0.370	93.8 : 6.2
15.00	0.614	79.3 : 20.7	45.00	0.364	94.0 : 6.0
16.00	0.599	80.3 : 19.7	46.00	0.360	94.2 : 5.8
17.00	0.584	81.5 : 18.5	47.00	0.355	94.1 : 5.9
18.00	0.573	82.3 : 17.7	48.00	0.349	94.3 : 5.7
19.00	0.560	83.2 : 16.8	49.00	0.347	94.1 : 5.9
20.00	0.547	84.1 : 15.9	50.00	0.342	94.3 : 5.7
21.00	0.537	84.9 : 15.1	51.00	0.339	94.3 : 5.7
22.00	0.523	85.8 : 14.2	52.00	0.335	94.3 : 5.7
23.00	0.515	86.3 : 13.7	53.00	0.331	94.5 : 5.5
24.00	0.503	87.1 : 12.9	54.00	0.325	94.7 : 5.3
25.00	0.495	87.6 : 12.4	55.00	0.324	94.5 : 5.5
26.00	0.485	88.5 : 11.5	56.00	0.319	94.5 : 5.5
27.00	0.478	88.7 : 11.3	57.00	0.315	94.7 : 5.3
28.00	0.470	89.2 : 10.8	58.00	0.310	94.8 : 5.2
29.00	0.459	90.1 : 9.9			

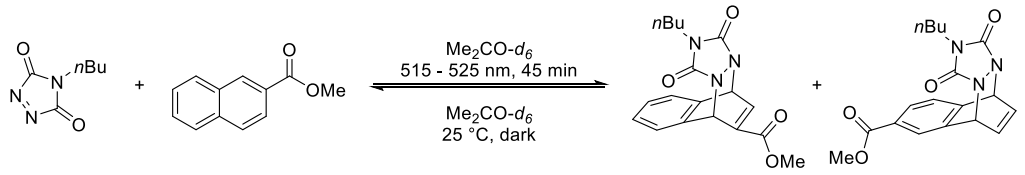
Table S5. Fraction of cycloadduct **3d** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2d** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2d** **3d-C_A** **3d-C_B**

Time (h)	Fraction **3d**	C_A:C_B	Time (h)	Fraction **3d**	C_A:C_B
0.05	> 0.99	< 0.01	30.62	0.645	< 0.01
1.10	0.977	< 0.01	31.62	0.634	< 0.01
1.62	0.969	< 0.01	32.62	0.624	< 0.01
2.62	0.954	< 0.01	33.62	0.616	< 0.01
3.62	0.940	< 0.01	34.62	0.610	< 0.01
4.62	0.927	< 0.01	35.62	0.599	< 0.01
5.62	0.914	< 0.01	36.62	0.590	< 0.01
6.62	0.901	< 0.01	37.62	0.583	< 0.01
7.62	0.888	< 0.01	38.62	0.574	< 0.01
8.62	0.877	< 0.01	39.62	0.568	< 0.01
9.62	0.866	< 0.01	40.62	0.561	< 0.01
10.62	0.852	< 0.01	41.62	0.551	< 0.01
11.62	0.839	< 0.01	42.62	0.545	< 0.01
12.62	0.830	< 0.01	43.62	0.537	< 0.01
13.62	0.818	< 0.01	44.62	0.531	< 0.01
14.62	0.806	< 0.01	45.62	0.522	< 0.01
15.62	0.795	< 0.01	46.62	0.516	< 0.01
16.62	0.783	< 0.01	47.62	0.509	< 0.01
17.62	0.774	< 0.01	48.62	0.500	< 0.01
18.62	0.763	< 0.01	49.62	0.492	< 0.01
19.62	0.751	< 0.01	50.62	0.488	< 0.01
20.62	0.741	< 0.01	51.62	0.479	< 0.01
21.62	0.730	< 0.01	52.62	0.474	< 0.01
22.62	0.722	< 0.01	53.62	0.469	< 0.01
23.62	0.711	< 0.01	54.62	0.463	< 0.01
24.62	0.700	< 0.01	55.62	0.455	< 0.01
25.62	0.691	< 0.01	56.62	0.449	< 0.01
26.62	0.684	< 0.01	57.62	0.443	< 0.01
27.62	0.672	< 0.01	58.62	0.435	< 0.01
28.62	0.663	< 0.01	59.62	0.428	< 0.01
29.62	0.651	< 0.01			

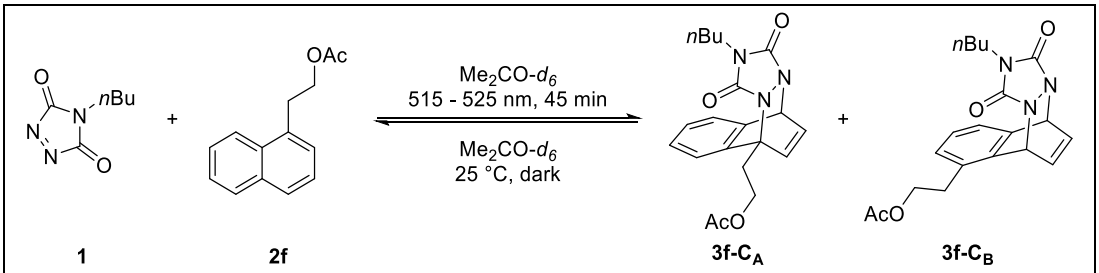
Table S6. Fraction of cycloadduct **3e** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2e** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2e** **3e-C_A** **3e-C_B**

Time (h)	Fraction **3e**	C_A:C_B	Time (h)	Fraction **3e**	C_A:C_B
0.05	> 0.99	41.8 : 58.2	30.77	0.235	53.4 : 46.6
1.10	0.952	42.8 : 57.2	31.77	0.223	53.8 : 46.2
1,77	0.921	43.1 : 56.9	32.77	0.213	54.0 : 46.0
2.77	0.879	43.6 : 56.4	33.77	0.206	54.3 : 45.7
3.77	0.837	43.6 : 56.4	34.77	0.196	54.5 : 45.5
4.77	0.796	44.3 : 55.7	35.77	0.183	55.2 : 44.8
5.77	0.757	44.6 : 55.4	36.77	0.178	55.1 : 44.9
6.77	0.723	45.1 : 54.9	37.77	0.168	55.4 : 44.6
7.77	0.691	45.6 : 54.4	38.77	0.163	55.6 : 44.4
8.77	0.657	45.6 : 54.4	39.77	0.154	55.7 : 44.3
9.77	0.626	46.1 : 53.9	40.77	0.149	56.5 : 43.5
10.77	0.601	46.3 : 53.7	41.77	0.143	56.4 : 43.6
11.77	0.572	46.6 : 53.4	42.77	0.137	56.6 : 43.4
12.77	0.545	47.1 : 52.9	43.77	0.129	57.0 : 43.0
13.77	0.520	47.4 : 52.6	44.77	0.123	57.6 : 42.4
14.77	0.494	47.8 : 52.2	45.77	0.119	57.4 : 42.6
15.77	0.471	48.2 : 51.8	46.77	0.111	58.1 : 41.9
16.77	0.450	48.7 : 51.3	47.77	0.106	57.3 : 42.7
17.77	0.431	48.8 : 51.2	48.77	0.105	57.4 : 42.6
18.77	0.410	49.0 : 51.0	49.77	0.099	58.7 : 41.3
19.77	0.391	49.4 : 50.6	50.77	0.094	57.4 : 42.6
20.77	0.373	49.7 : 50.3	51.77	0.092	59.6 : 40.4
21.77	0.356	50.2 : 49.8	52.77	0.089	59.3 : 40.7
22.77	0.340	50.6 : 49.4	53.77	0.083	60.2 : 39.8
23.77	0.326	51.2 : 48.8	54.77	0.080	60.0 : 40.0
24.77	0.309	51.4 : 48.6	55.77	0.075	58.5 : 41.5
25.77	0.296	51.7 : 48.3	56.77	0.073	58.6 : 41.4
26.77	0.281	52.1 : 47.9	57.77	0.069	58.5 : 41.5
27.77	0.270	52.3 : 47.7	58.77	0.065	60.3 : 39.7
28.77	0.258	52.7 : 47.3	59.77	0.065	60.3 : 39.7
29.77	0.248	53.0 : 47.0			

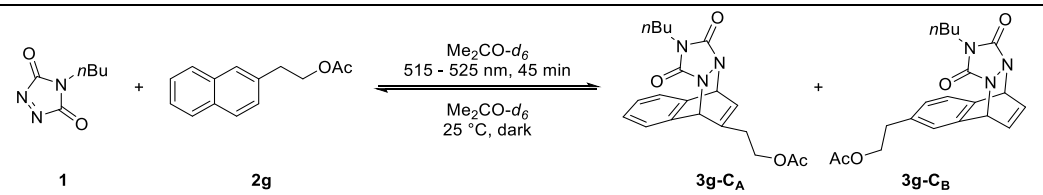
Table S7. Fraction of cycloadduct **3f** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2f** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



1 **2f** **3f-C_A** **3f-C_B**

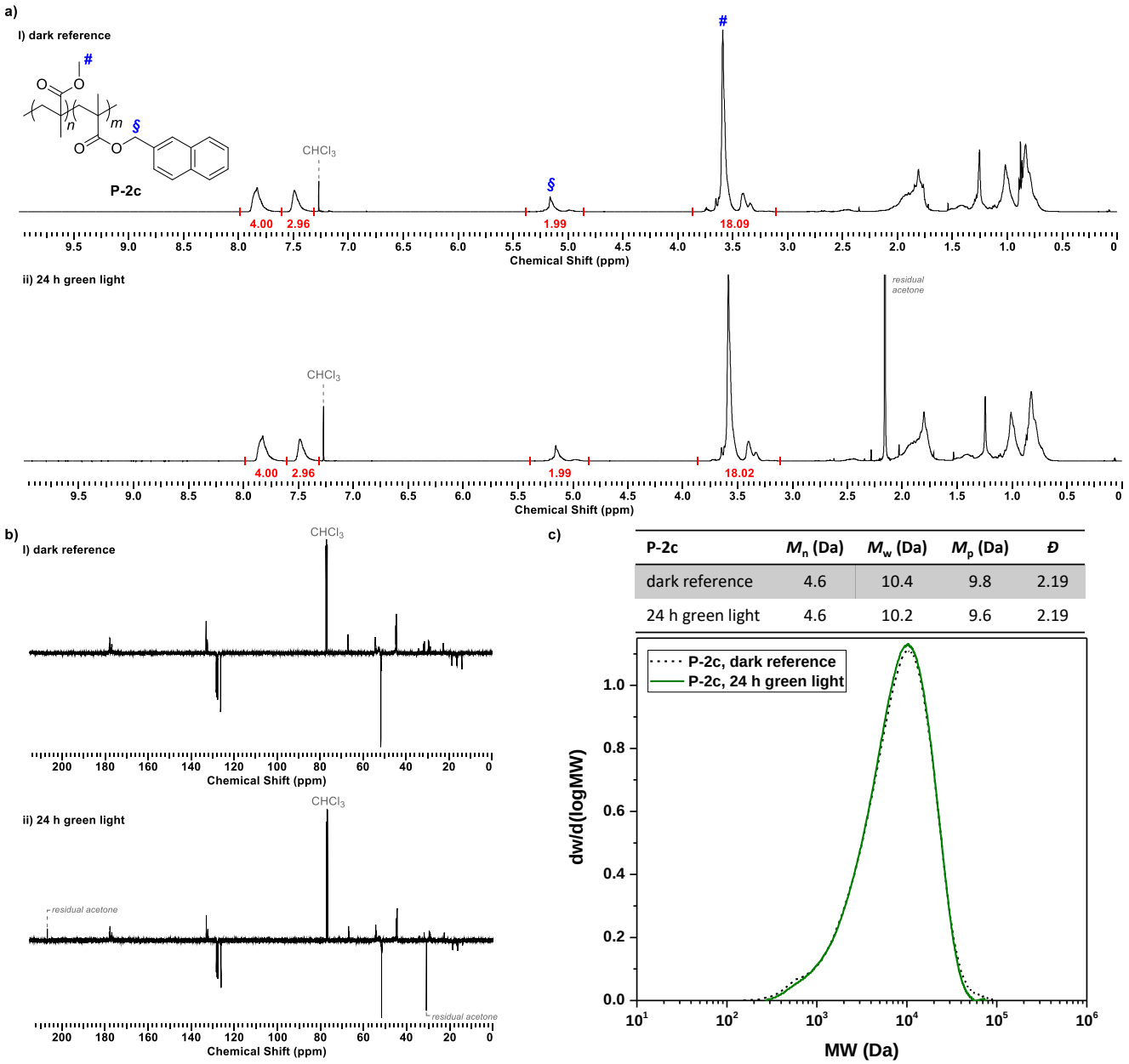
Time (h)	Fraction **3f**	C_A:C_B	Time (h)	Fraction **3f**	C_A:C_B
0.05	> 0.99	< 0.01	30.68	0.537	< 0.01
1.08	0.977	< 0.01	31.68	0.526	< 0.01
1.68	0.965	< 0.01	32.68	0.515	< 0.01
2.68	0.943	< 0.01	33.68	0.506	< 0.01
3.68	0.925	< 0.01	34.68	0.496	< 0.01
4.68	0.904	< 0.01	35.68	0.489	< 0.01
5.68	0.888	< 0.01	36.68	0.478	< 0.01
6.68	0.869	< 0.01	37.68	0.470	< 0.01
7.68	0.852	< 0.01	38.68	0.462	< 0.01
8.68	0.834	< 0.01	39.68	0.453	< 0.01
9.68	0.817	< 0.01	40.68	0.446	< 0.01
10.68	0.800	< 0.01	41.68	0.437	< 0.01
11.68	0.782	< 0.01	42.68	0.428	< 0.01
12.68	0.766	< 0.01	43.68	0.421	< 0.01
13.68	0.750	< 0.01	44.68	0.414	< 0.01
14.68	0.735	< 0.01	45.68	0.406	< 0.01
15.68	0.718	< 0.01	46.68	0.401	< 0.01
16.68	0.704	< 0.01	47.68	0.392	< 0.01
17.68	0.691	< 0.01	48.68	0.387	< 0.01
18.68	0.678	< 0.01	49.68	0.380	< 0.01
19.68	0.664	< 0.01	50.68	0.374	< 0.01
20.68	0.651	< 0.01	51.68	0.368	< 0.01
21.68	0.638	< 0.01	52.68	0.362	< 0.01
22.68	0.625	< 0.01	53.68	0.356	< 0.01
23.68	0.614	< 0.01	54.68	0.351	< 0.01
24.68	0.602	< 0.01	55.68	0.345	< 0.01
25.68	0.591	< 0.01	56.68	0.339	< 0.01
26.68	0.580	< 0.01	57.68	0.334	< 0.01
27.68	0.569	< 0.01	58.68	0.329	< 0.01
28.68	0.558	< 0.01	59.68	0.322	< 0.01
29.68	0.547	< 0.01			

Table S8. Fraction of cycloadduct **3g** in Me_2CO-d_6 when kept in the dark at 25 °C, after being formed by 45-min irradiation of **1** (1.0 eq., 15 mM, Me_2CO-d_6) in the presence of **2g** (1.2 eq.) at λ = 515-525 nm (3 x 3W green LEDs).



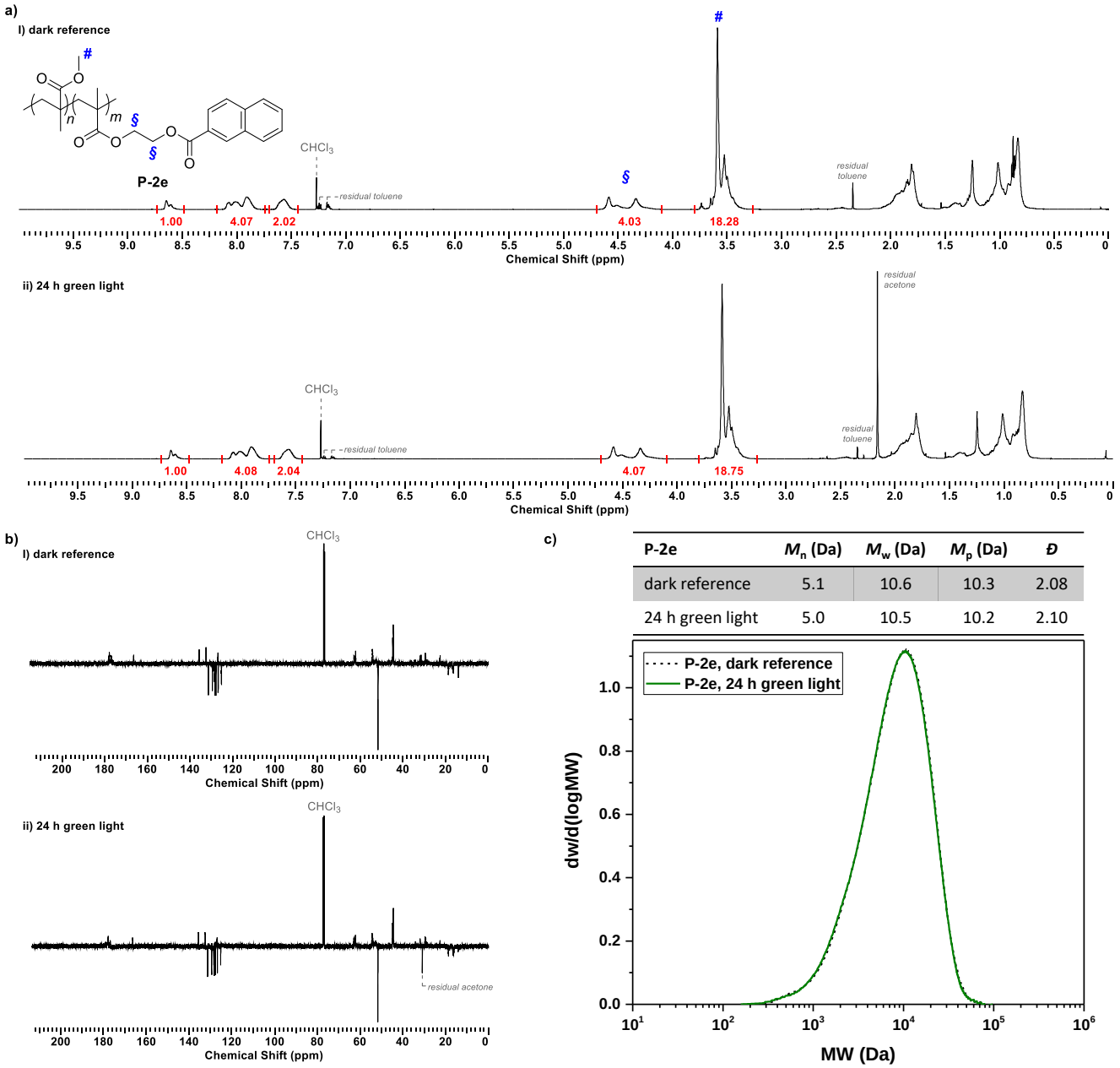
1 **2g** **3g-C_A** **3g-C_B**

Time / h	Fraction **3g**	C_A:C_B	Time / h	Fraction **3g**	C_A:C_B
0.05	> 0.99	52.9 : 47.1	30.85	0.435	83.7 : 16.3
1.08	0,979	53.6 : 46.4	31.85	0.429	83.6 : 16.4
1.85	0.948	55.0 : 45.0	32.85	0.420	84.3 : 15.7
2.85	0.910	56.5 : 43.5	33.85	0.415	84.3 : 15.7
3.85	0.877	58.1 : 41.9	34.85	0.408	84.7 : 15.3
4.85	0.844	59.6 : 40.4	35.85	0.404	84.8 : 15.2
5.85	0.811	61.2 : 38.8	36.85	0.397	85.2 : 14.8
6.85	0.781	62.8 : 37.2	37.85	0.391	85.5 : 14.5
7.85	0.756	64.2 : 35.8	38.85	0.387	85.4 : 14.6
8.85	0.734	65.5 : 34.5	39.85	0.380	85.4 : 14.6
9.85	0.708	67.0 : 33.0	40.85	0.372	85.9 : 14.1
10.85	0.687	68.0 : 32.0	41.85	0.367	85.9 : 14.1
11.85	0.663	69.4 : 30.6	42.85	0.364	85.8 : 14.2
12.85	0.639	70.8 : 29.2	43.85	0.360	85.7 : 14.3
13.85	0.624	71.7 : 28.3	44.85	0.356	85.7 : 14.3
14.85	0.605	73.0 : 27.0	45.85	0.357	84.2 : 15.8
15.85	0.592	74.1 : 25.9	46.85	0.347	85.9 : 14.1
16.85	0.578	74.8 : 25.2	47.85	0.343	85.9 : 14.1
17.85	0.563	75.8 : 24.2	48.85	0.338	85.8 : 14.2
18.85	0.549	77.0 : 23.0	49.85	0.336	85.6 : 14.4
19.85	0.532	77.5 : 22.5	50.85	0.333	85.6 : 14.4
20.85	0.523	78.3 : 21.7	51.85	0.328	85.5 : 14.5
21.85	0.512	79.3 : 20.7	52.85	0.322	85.8 : 14.2
22.85	0.502	80.0 : 20.0	53.85	0.318	85.6 : 14.4
23.85	0.494	80.5 : 19.5	54.85	0.317	85.1 : 14.9
24.85	0.483	80.8 : 19.2	55.85	0.309	85.7 : 14.3
25.85	0.477	81.2 : 18.8	56.85	0.311	85.2 : 14.8
26.85	0.469	81.9 : 18.1	57.85	0.303	85.8 : 14.2
27.85	0.460	82.0 : 18.0	58.85	0.301	85.4 : 14.6
28.85	0.451	82.6 : 17.4	59.85	0.299	84.0 : 16.0
29.85	0.442	83.5 : 16.5			



P-2c	M_n (Da)	M_w (Da)	M_p (Da)	$Đ$
dark reference	4.6	10.4	9.8	2.19
24 h green light	4.6	10.2	9.6	2.19

Figure S12. Photostability of naphthalene-containing polymer **P-2c** under visible light impact (200 mg mL^{-1} in Me_2CO, λ = 515 – 525 nm, 3 x 3 W LEDs, 24 h) assessed by comparing a) ^{1}H-NMR spectra ($CDCl_3$), b) ^{13}C-NMR spectra ($CDCl_3$), and c) SEC elugrams ($CHCl_3$, calibrated on PMMA standards) before and after irradiation.



P-2e	M_n (Da)	M_w (Da)	M_p (Da)	$Đ$
dark reference	5.1	10.6	10.3	2.08
24 h green light	5.0	10.5	10.2	2.10

Figure S13. Photostability of naphthalene-containing polymer **P-2e** under visible light impact (200 mg mL^{-1} in Me_2CO, λ = 515 – 525 nm, 3 x 3 W LEDs, 24 h) assessed by comparing a) ^{1}H-NMR spectra ($CDCl_3$), b) ^{13}C-NMR spectra ($CDCl_3$), and c) SEC elugrams ($CHCl_3$, calibrated on PMMA standards) before (dashed, black line) and after irradiation (full, green line).

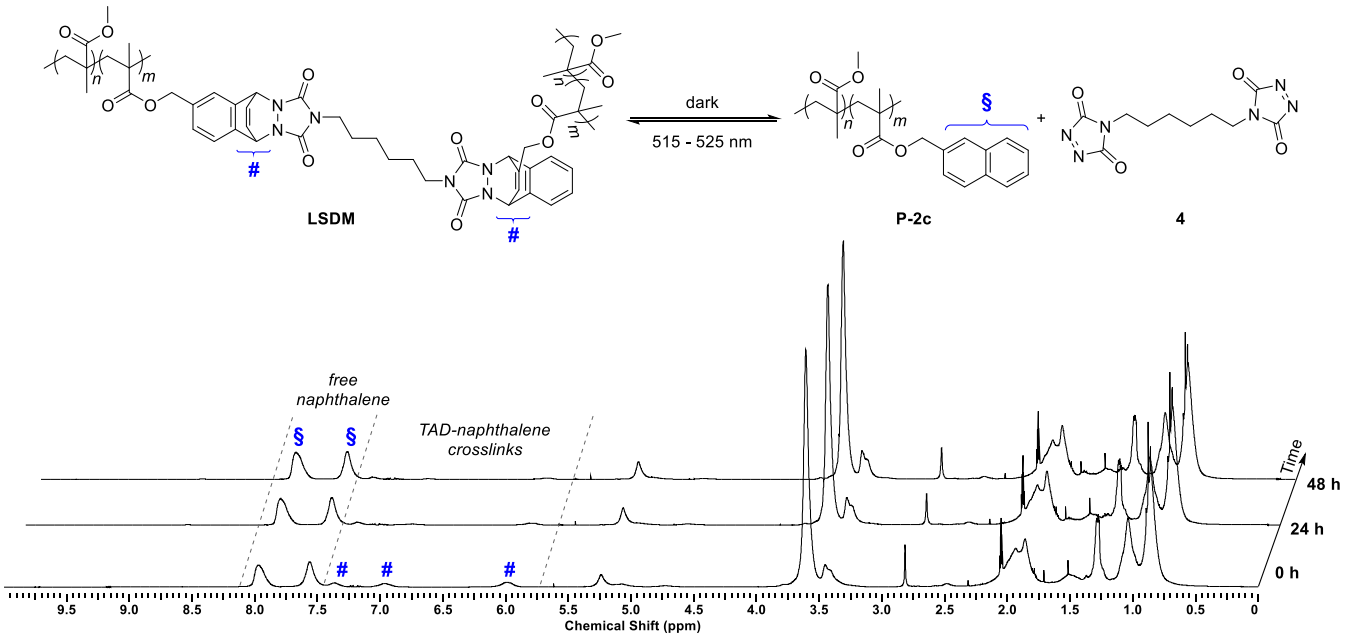


Figure S14. ^{1}H-NMR spectra (Me_2CO-d_6) of a solution of naphthalene-containing polymer **P-2c** (75 mg mL^{-1} in Me_2CO-d_6) in the presence of bisTAD crosslinker **4** (0.5 equimolar amount of TAD to naphthalene), recorded immediately after visible light-induced crosslinking (λ = 515 – 525 nm, 3 x 3 W LEDs, 1 h) and after decrosslinking upon standing in the dark for 24 h and 48 h at room temperature, thereby indicating the disappearance of the TAD-naphthalene cycloadduct crosslinking junctions over time.

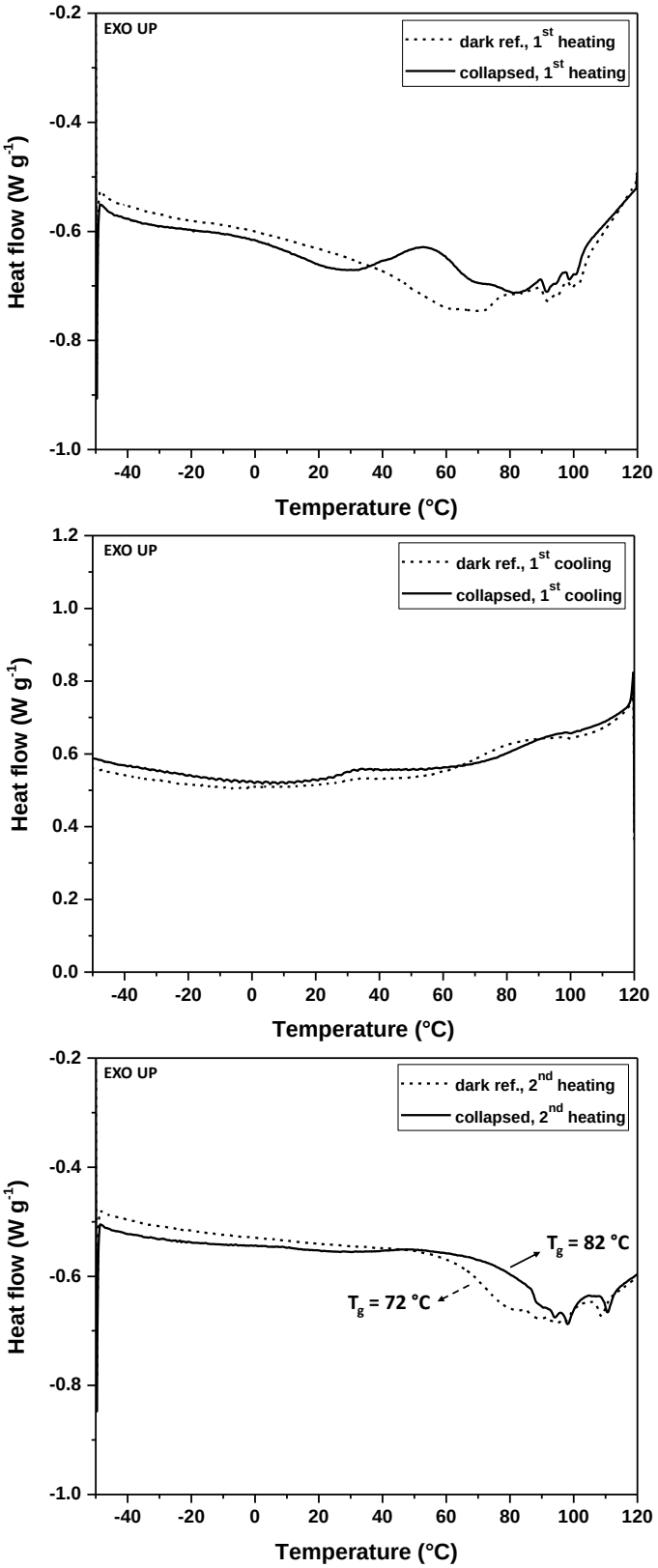


Figure S15. DSC thermograms (5 °C min^{-1}) of the naphthalene/TAD formulation **P-2e**/**4** recorded before crosslinking (i.e. a dark reference) and after decrosslinking of a cured sample (λ = 515 – 525 nm, 3 x 3 W LEDs, 1.5 h) by standing in the dark for 2 days at room temperature. The formulations were prepared in anhydrous acetone (210 mg mL^{-1} **P-2e** with equimolar ratios of naphthalene to TAD crosslinker **4**) and the solvent was removed *in vacuo* at room temperature prior to analysis.

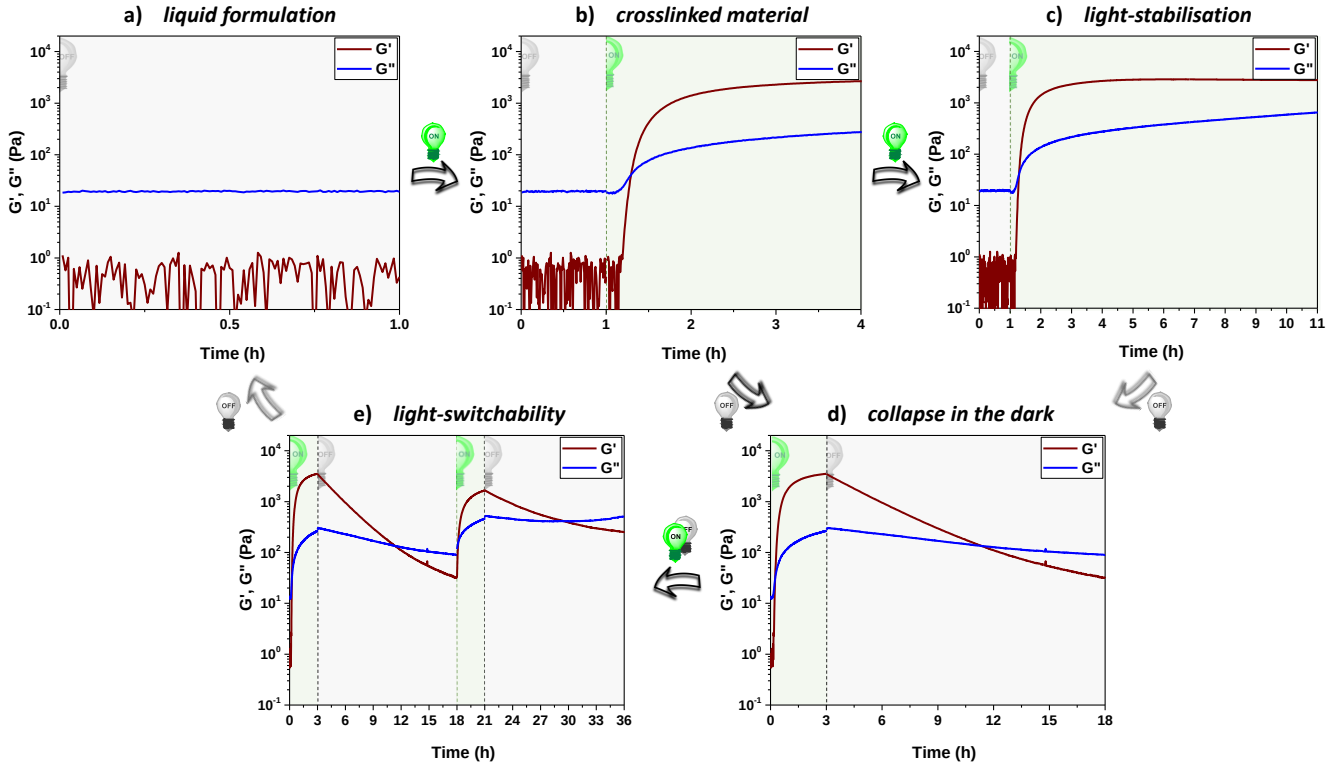


Figure S16. Rheological evaluation of light-stabilised dynamic material **P-2c/4**. a) Whereas the initial liquid formulation of naphthalene-containing polymer **P-2c** (0.20 g mL^{-1} in propylene carbonate) and TAD crosslinker **4** (equimolar amount of TAD to naphthalene) was shown to be non-reactive when kept in the dark for 1 h, b) a crosslinked material was effectively obtained after 3 h of irradiation (λ = 400 – 500 nm) as indicated by the response in viscoelastic behaviour. c) Keeping the light switched on for an additional 7 h did not affect the network integrity, evidencing the light-stabilisation of the thus formed covalent polymer network. d) In the dark (at 25 °C), a steep decline of the material's stiffness is monitored over time, which illustrates the dissociation of the crosslinking points through the spontaneous cycloreversion. e) Finally, the bonding/debonding process can be re-initiated by consecutive periods of visible light (3 h) and darkness (15 h).

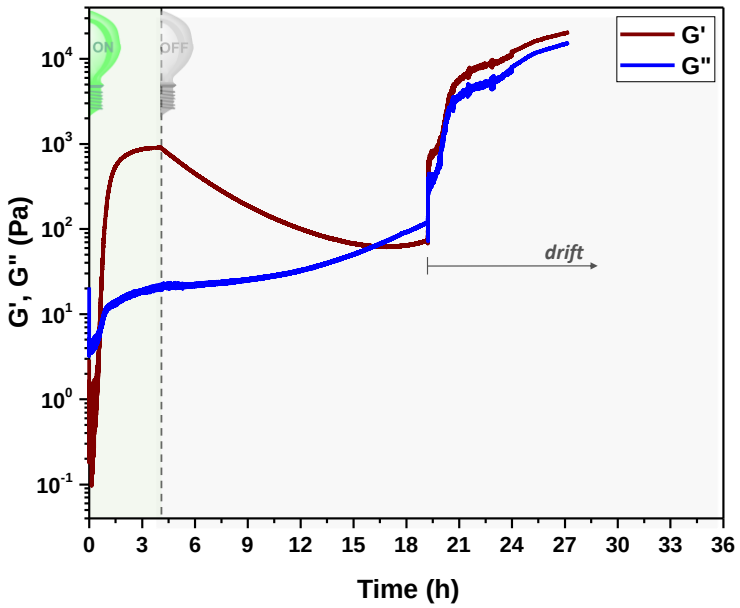


Figure S17. Rheological evaluation of light-stabilised dynamic material **P-2c/4**, formed after 4 h of visible light irradiation (λ = 400 – 500 nm) of naphthalene-containing polymer **P-2c** (0.20 g mL^{-1} propylene carbonate) and TAD crosslinker **4** (equimolar amount of TAD to naphthalene), without controlling the normal force during the period of darkness results in erroneous values in the storage and loss moduli whilst monitoring the collapse of the material.

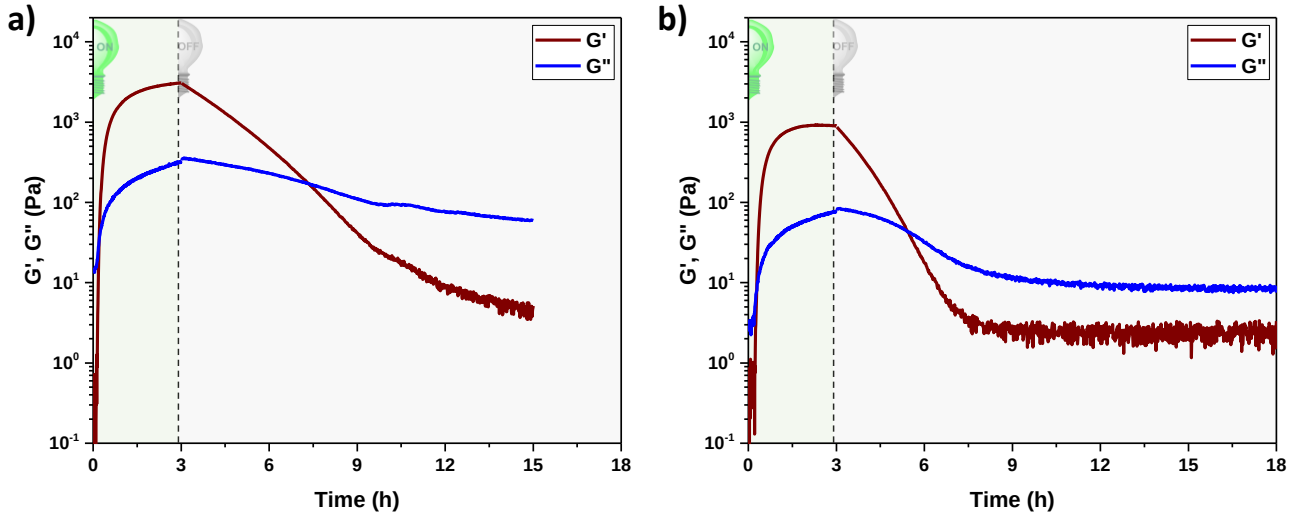


Figure S18. Effect of the amount of TAD crosslinker **4** during the rheological evaluation of light-stabilised dynamic material **P-2e/4**. a) Viscoelastic response upon photocuring (3 h, λ = 400 – 500 nm) of the initial liquid formulation of naphthalene-containing polymer **P-2e** (0.21 g mL^{-1} in propylene carbonate) in the presence of TAD crosslinker **4** (with equimolar ratios of naphthalene to TAD) and subsequent decrosslinking when the thus formed material is kept in the dark (25 °C). b) A similar viscoelastic behaviour is observed when lowering the amount of TAD crosslinker **4** (i.e. [TAD]:[naphthalene] = 0.5:1.0), although a lower storage and loss modulus is reached after complete photocuring whilst the weaker gel was found to disintegrate faster upon standing in darkness.

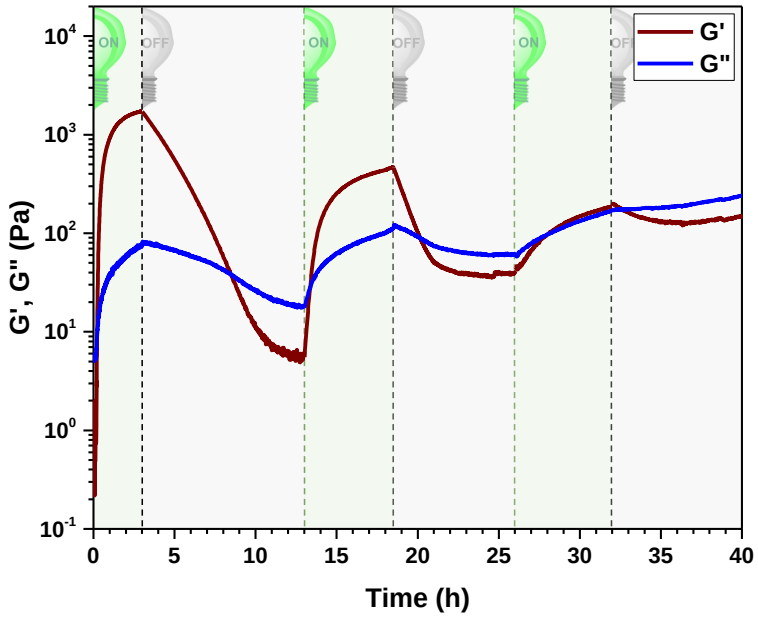


Figure S19. Effect of cyclability during the rheological evaluation of light-stabilised dynamic material **P-2e/4**. Vscoelastic response during cycles of photocuring (λ = 400 – 500 nm) of the initial liquid formulation of naphthalene-containing polymer **P-2e** (0.21 g mL^{-1} in propylene carbonate) in the presence of TAD crosslinker **4** (with equimolar ratios of naphthalene to TAD) followed by decrosslinking of the thus formed material in the dark (25 °C), indicating a deviation in material properties. Although consecutive sol-gel transitions are still observed repeatably up to three cycles, the gels weaken during irradiation whereas the solutions get higher in viscosity over time.

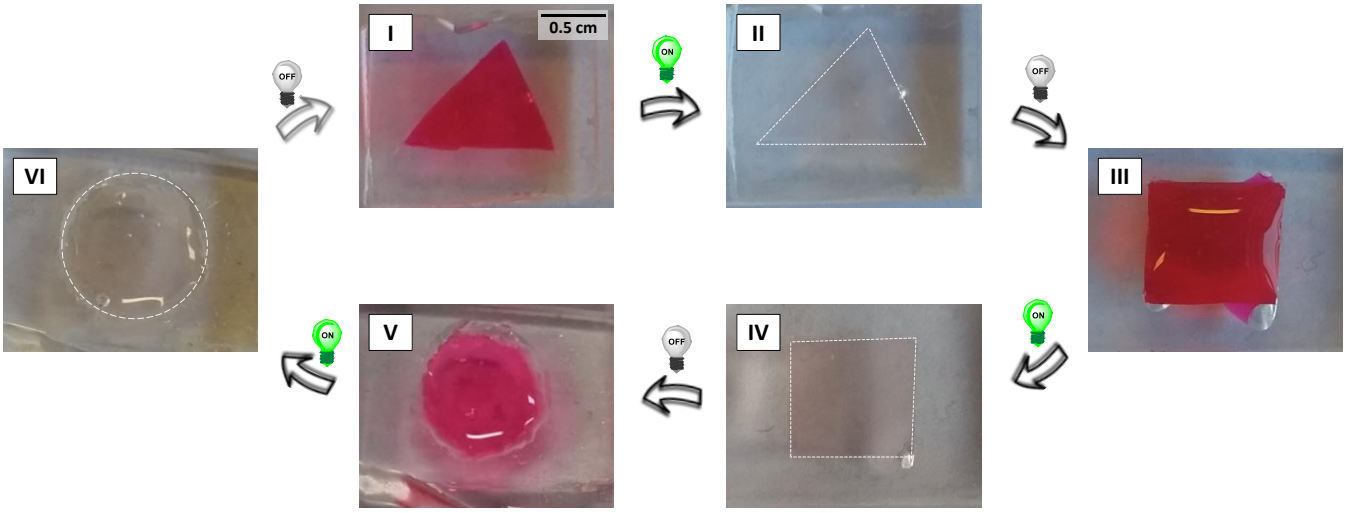


Figure S20. Macroscopic light-switchable sol-gel transitions, illustrated by a series of shape transformations. A triangular **P-2e**/**4**-based LSDM was obtained after crosslinking a solution of **P-2e** (0.42 g mL^{-1} in propylene carbonate) and bisTAD **4** (equimolar ratio of TAD to naphthalene) with green light (3 h, λ = 515 – 525 nm, 3 x 3 W LEDs, I -> II). The resulting colourless triangle network was next placed in a rectangular mould and kept overnight at room temperature in the dark, thereby evidencing the decrosslinking process by flowing across the newly shaped mould (II -> III). The crosslinking (IV) and subsequent collapse (V) of the network was eventually repeated in a circular shape to give a cylindrical LSDM (VI).

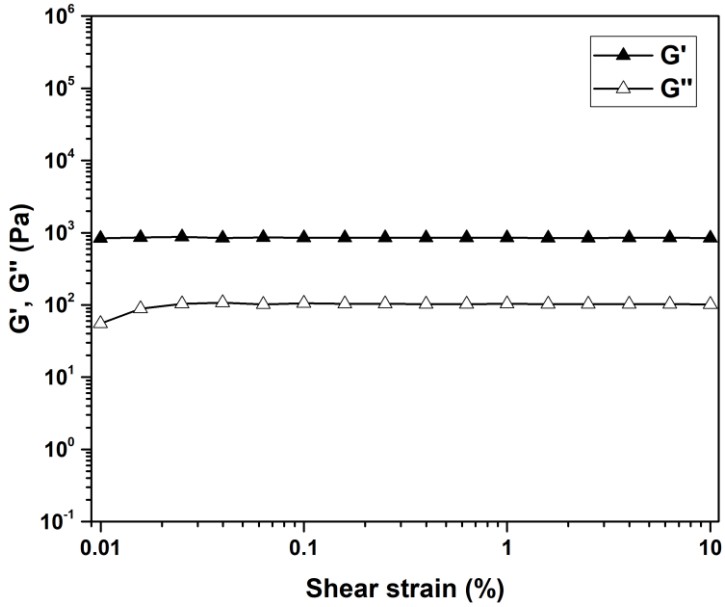


Figure S21. Strain sweep at 25 °C recorded under continued irradiation of the material obtained after visible light-induced crosslinking (3 h at λ = 400 – 500 nm) of naphthalene-containing polymer **P-2e** (0.21 g mL^{-1} in propylene carbonate) in the presence of TAD-crosslinker **4** (equimolar amount of naphthalene to TAD), indicating that the rheology measurements conducted at 1 % shear strain are carried out in the linear viscoelastic regime.

Supplementary Methods

Instrumentation

Differential scanning calorimetry (DSC). Differential Scanning Calorimetry (DSC) measurements were carried out with a Mettler Toledo 1/700 calorimeter, equipped with Full Range Sensor (FRS5) containing 56 thermocouples, a liquid nitrogen cooling system that enables a temperature range of -150 °C to 700 °C and an automatic sample robot. All measurements were carried out under a nitrogen atmosphere in standard 40 µL aluminium crucibles containing 3 to 10 mg of the polymeric material, which are hermetically sealed although the crucible lit is purged with a needle. A consecutive heating-cooling-heating run was performed over a broad temperature range of -150 °C to 150 °C at a rate of 10 °C min^{-1} or -50 °C to 120 °C at a rate of 5 °C min^{-1} for the synthesised copolymers or LSDM formulations before and after decrosslinking, respectively. The resulting thermograms were analysed with the STARe Excellence Software and the glass transition temperature (T_g) that is reported was taken as the midpoint from the second heating run, which is defined as the intercept of the DSC curve and the bisector of the angle formed by extrapolation of the baselines before and after the transition.

Electrospray ionisation mass spectrometry (ESI-MS). Mass spectra were recorded on a LTQ Orbitrap XL Q Exactive mass spectrometer (ThermoFischer Scientific), equipped with a HESI II probe and calibrated by means of premixed calibration standards containing caffeine, Met-Arg-Ph-Ala acetate and a mixture of fluorinated phosphazenes in the mass range m/z = 74 - 1822. Samples were dissolved in THF:MeOH (3:2 v/v) that is doped with 100 µmol sodium trifluoroacetate, and manually injected with a flow rate of 5 µL min^{-1} at a constant spray voltage of 4.6 kV, capillary temperature of 320 °C and S-lens RF level set to 62.0.

Hyphenated liquid chromatography-mass spectrometry (LC-MS). LC-MS measurements were carried out on an 1100 series LC/MSD system (Agilent Technologies) containing a diode array detector and single quad MS. Analytical reversed phase HPLC was performed on a Phenomex Luna C18 (2) column (dimensions 5 µm x 250 mm x 4.6 mm) in a solvent mixture of acetonitrile and water (gradient of 0 to 100 % in 15 minutes) and the eluted compounds were detected by UV-absorbance at 214 nm. High resolution mass spectrometry (HRMS) was carried out with an Agilent 6220 accurate-mass time-of-flight (TOF) analyser containing a multimode ionisation (MMI) source. The ACD/Labs Spectrus software package was used to analyse the elugram and mass spectra.

Light-emitting diodes (LEDs). 3 x 3 W light emitting high power LEDs were purchased from Avonec, glued onto an anodised aluminium cooling element (50 x 25 mm) and connected in a series circuit to a constant-current transformer (700 mA). Spectral details of the LEDs are available from the supplier on https://avonec.de/images/515nm-525nm.jpg.

The luminous flux per unit area of the green LEDs (λ = 515 – 525 nm) was measured using a Mavolux 5032C and the conversion to radiometric units, i.e. the irradiance in W m^{-2}, was performed by determining the luminous efficacy of radiation based on the emission spectrum of the light source, collected by a fibre coupled QE65000 spectrometer (Ocean Optics). The peak wavelength was found to be 518 nm, with a full width at half maximum of 30 nm. The irradiance was determined for both experimental setups used, which are depicted in Figure S22. On the one hand, small molecule studies were carried out by placing the recipient in the middle of 3 x 3 W LEDs at a distance of 3 cm, resulting in an emission power of 16 mW cm^{-2} for each LED (Setup A, Figure S22). Crosslinking experiments on the other hand were conducted by irradiating the recipient from the bottom or the top with the LEDs positioned at a distance of 10 cm (3 mW cm^{-2}, Setup B in Figure S22b).

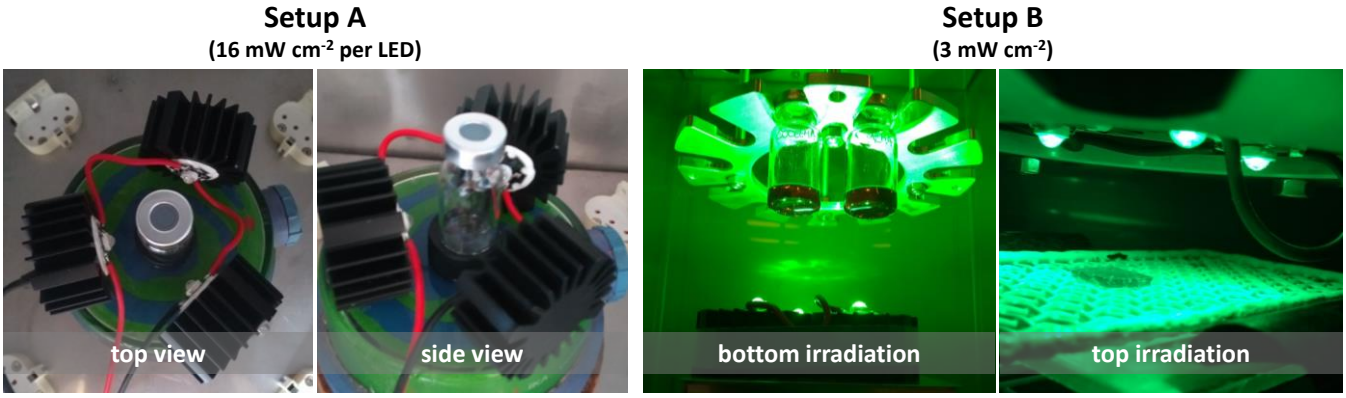


Figure S22. Setups used for LED irradiation during model studies (A) and crosslinking experiments (B).

Nuclear magnetic resonance (NMR) spectroscopy. NMR spectra were recorded on a Bruker Avance 300 (300 MHz), Bruker Ascend 400 (400 MHz) or Bruker Avance II (500 MHz) FT-NMR spectrometer at 25 °C in the solvent as indicated. Chemical shifts (δ) are expressed in parts per million (ppm) whereby the residual solvent peaks serve as an internal standard. The resonance multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), sext (sextuplet) or m (multiplet). Standard parameters in terms of number of scans, pulse delay, acquisition time, tilt angle and pulse time:

^{1}H spectra (300 MHz: ns = 16, D1 = 1.0 s, AQ = 2.65 s, 30°, P1 = 7.25 µs; 400 MHz: ns = 16, D1 = 1.0 s, AQ = 4.10 s, 30°, P1 = 7.75 µs; 500 MHz: ns = 16, D1 = 1.0 s, AQ = 3.28 s, 30°, P1 = 13.83 µs);

^{13}C spectra (300 MHz: ns = 3072, D1 = 2.0 s, AQ =1.82 s, 30°, P1 = 7.50 µs; 400 MHz: ns = 3072, D1 = 2.0 s, AQ = 1.36 s, 30°, P1 = 7.50 µs; 500 MHz: ns = 3072, D1 = 2.0 s, AQ = 1.10 s, 30°, P1 = 7.50 µs).

Rheology. Rheology experiments were conducted with a Modular Compact Rheometer (MCR) 302 (Anton Paar) containing an air-bearing-supported synchronous Electrically Commutated (EC) motor, integrated normal force sensor, TruRate^{TM} sample-adaptive controller, TruStrain^{TM} real-time position control and a Convection Temperature Device 180 (CTD 180) heating unit. The lower detection limit, defined by the generated torque in the specific deformation applied, is specified at 0.5 nN m. Measurements were designed and analysed using of the RheoCompass^{TM} software.

Photocuring experiments were conducted under isothermal conditions (25 °C) in a closed oven (keeping away external light) using a glass parallel plate (33 mm diameter), with a viscoelastic moving profile in oscillatory mode with a pre-set shear gap (typically between 0.2 mm and 0.1 mm), 0.1 % shear strain and 1 Hz angular frequency, whilst keeping the normal force constant (e.g. set at 0 N, or 0.2 N). Measurements were performed with the OmniCure S2000 containing a high pressure 200 W mercury vapor short arc broad emitting UV-lamp equipped with a 400 – 500 nm bandpass filter to select visible light emission. The incident light is guided by an optical fibre to the bottom of the glass plate to irradiate the sample (62 mW cm^{-2}, measured at the position where the sample is applied).

To prevent the low viscous sample to flow from underneath the moving profile prior to curing and during decrosslinking, mineral oil (non-miscible with the propylene carbonate solutions) was applied around the edges. Amplitude sweeps with a logarithmic increase in shear strain (oscillating) from 0.01 % to 10 % at a constant frequency of 1 Hz were carried out on each crosslinked sample in order to ensure the experiments were conducted within the linear viscoelastic regime (cf. Figure S21).

Size-exclusion chromatography (SEC). Size-exclusion chromatography (SEC) was carried out in $CHCl_3$ at 35 °C with a solvent flow rate of 1 mL min^{-1} on a Waters instrument equipped with Styragel

HR3-5 serial columns 5 µm (Waters) and 2410 Waters Refractive Index detector. The system was calibrated on poly(methyl methacrylate) standards and analysis was performed with the Breeze Millennium software.

Inolas wavelength-tunable laser system. Wavelength-tunable visible laser light was generated by a Splitlight 600 OPO Nd:YAG Tunable Laser System, supplied by Innolas, making use of an Optical Parametric Oscillator (OPO) to produce a tunable laser output between 410 and 670 nm or, with a second modular unit, between 270 and 410 nm. The OPO is operated by a diode pumped Nd:YAG laser at a 100 Hz repetition rate and the output energy was regulated by a variable attenuator (polariser) coupled to a Coherent Energy Max PC power meter to measure the energy of the incident laser pulses. The generated laser light was guided through a prism and directed to the bottom of the sample, placed in a home-made cylindrical sample holder with 0.8 cm diameter. Experiments were carried out in a temperature-regulated laser room at 18 °C with a predefined pulse energy of 2 mJ. Irradiance is estimated to be around 120 mW cm^{-2}, based on an estimated full width at half maximum of 5 nm derived from the emission spectrum.

UV/vis spectrometry. UV/vis spectra were recorded on a Varian Cary 300 Bio spectrometer at 25 °C.

Materials

Acetic acid (> 99.5 %, Sigma-Aldrich); acetyl chloride (> 99 %, Acros); aluminium chloride (> 99.9 %, Alfa Aesar); aluminium oxide, activated basic, Brockmann I (Sigma); 2,2'-azobis(2-methylpropionitrile) (AIBN, 98 %, Janssen Chimica); azodicarboxamide (97 %, Sigma); 2-(bromomethyl)naphthalene (96 %, Alfa); chloroform-*d* ($CDCl_3$, 99.8 %, Euriso-top); concentrated aqueous hydrochloric acid (36 %, Chem-Lab); concentrated sulfuric acid (99 %, Sigma-Aldric); deuterated acetone-d_6 (Me_2CO-d_6, 99.9 %, Euriso-top); deuterated dimethyl sulfoxide-d_6 (DMSO-d_6, 99.8 %, Euriso-top); dicyclopentadiene (95 %, Acros); 1-dodecanethiol (DDT, > 98 %, Sigma); *N*-ethylmaleimide (crystalline, ≥ 98 %, Sigma); 2-hydroxyethyl methacrylate (98 %, Sigma); magnesium sulfate monohydrate (≥ 99 %, Roth); methacrylic acid (99 %, Sigma); 4-methoxyphenol (99 %, Acros); methyl methacrylate (99 %, Sigma); mineral oil, light oil (Bio-Reagent for molecular biology, Sigma); naphthalene (**2a**, 99 %, Acros); 1-naphthalenemethanol (98 %, Alfa); 2-(naphthalen-1-yl)ethan-1-ol (> 95 %, TCI); 2-(naphthalen-2-yl)ethan-1-ol (2-naphthaleneethanol, > 95 %, TCI); 1-naphthoic acid (98 %, Alfa); 2-naphthoic acid (98 %, Sigma); 2-naphthoyl chloride (98 %, TCI); potassium carbonate (≥ 99 %, Roth); potassium hydroxide (99 %, Roth); silica (60 Å, ≥ 99.5 %, ROCC); sodium bicarbonate (99 %, Roth); *trans*,*trans*-2,4-hexadien-1-ol (HDEO; > 97 %, Sigma Aldrich) and triethylamine (99 %, Sigma-Aldrich) were used as received from the supplier.

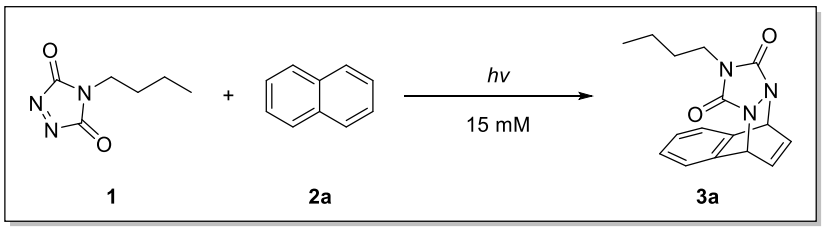
All solvents and products were used without any pre-treatment or purification, unless specified here bellow or in the experimental or synthesis procedure.

Cyclopentadiene (C_p) was obtained as a colourless liquid by thermal cracking of dicyclopentadiene at 180 °C, stored at -18 °C and used within 3 days.

2,2'-azobis(2-methylpropionitrile) (AIBN) was recrystalised twice from methanol prior to use and stored at 4 °C in the absence of ambient light.

Experimental procedures

Visible light-induced formation of cycloadduct 3a



A solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 4.65 mg, 3.0 10^{-5} mol, 1.0 eq.) and naphthalene (**2a**, 3.94 mg, 3.0 10^{-5} mol, 1.0 eq.) in 2 mL carbon tetrachloride was transferred into a crimped neck glass vial and placed in the sample holder of a wavelength tunable laser. Irradiation with green laser light at λ = 544 nm (2.0 mJ, 100 Hz) gave a clear colourless solution within 5 minutes. After complete photobleaching was observed, 0.05 mL of the reaction mixture was diluted to 0.033 mM upon addition of carbon tetrachloride and subjected to UV/vis analysis (refer to Figure S1). Comparison with a reference sample kept in the dark (wrapped in aluminium foil) indicated the complete consumption of **1** after irradiation. Upon standing in the dark in the UV/vis spectrophotometer, however, **1** was rapidly regenerated.

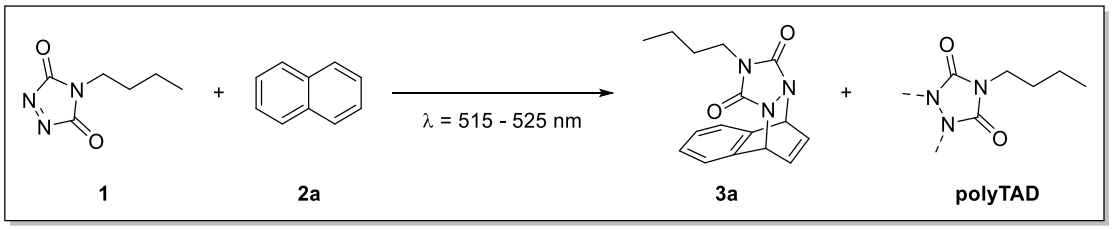
In a similar experiment, the photoreaction was carried out with LED irradiation sources (3 x 3 W). Both with UV-A (λ = 370 – 380 nm) and green light (λ = 515 – 525 nm), photobleaching was observed within 30 and 20 minutes, respectively. Changing the solvent to acetonitrile also resulted in photobleaching when **1** + **2a** was subjected to green light (λ = 515 – 525 nm, 3 x 3 W LEDs), albeit after prolonged irradiation times (i.e. 1 hour).

More quantitative insights into the photobleaching process were obtained by affecting the photoreaction in a deuterated solvent, thereby enabling ^{1}H-NMR-analysis. Thus, solutions of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 4.65 mg, 3.0 10^{-5} mol, 1.0 eq.) and naphthalene (**2a**, 3.94 mg, 3.0 10^{-5} mol, 1.0 eq.) in 2 mL deuterated chloroform and deuterated acetone-d_6 (15 mM) were subjected to green LED light (λ = 515 – 525 nm, 3 x 3 W) for 20 and 45 minutes, respectively, until photobleaching was observed. The resulting mixture was then transferred into an NMR-tube and immediately subjected to ^{1}H-NMR analysis, with the corresponding spectra depicted in Figure 2b (Me_2CO-d_6) and Figure S2c ($CDCl_3$).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.84 (t, 3H, C*H*$_3$, *J* = 7.3 Hz), 1.12 (m, 2H, CH_3-C*H*$_2$), 1.47 (m, 2H, N-CH_2-C*H*$_2$), 3.40 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz), 5.84 (t, 2H, Ar-C*H*-N *J* = 3.7 Hz), 6.86 (t, 2H, Ar-CH-C*H*=CH, *J* = 4.0 Hz), 7.25 (m, 2H, Ar*H*), 7.36 (m, 2H, Ar*H*).

^{1}H-NMR (400 MHz, Me_2CO-d_6): δ (ppm) = 0.81 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 1.05 (m, 2H, CH_3-C*H*$_2$), 1.41 (m, 2H, N-CH_2-C*H*$_2$), 3.32 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz), 5.89 (dd, 2H, Ar-C*H*-N *J* = 4.0, 3.2 Hz), 6.93 (dd, 2H, Ar-CH-C*H*=CH, *J* = 4.2, 3.1 Hz), 7.27 (m, 2H, Ar*H*), 7.45 (m, 2H, Ar*H*).

Visible light-induced cycloaddition versus photopolymerisation



In order to address the competition that might occur between the visible light-induced cycloaddition reaction of **1** with **2a** and the exclusive homopolymerisation of **1**, irradiation experiments were carried out in deuterated chloroform to enable ^{1}H-NMR analysis of the reaction outcome.

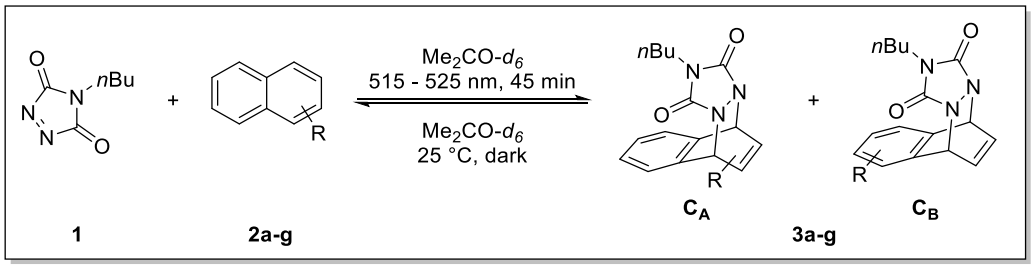
As a reference experiment, a plain solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 4.65 mg, 3.0 10^{-5} mol, 1.0 eq.) in 2 mL deuterated chloroform (15 mM) was subjected to green light at λ = 515 – 525 nm (3 x 3 W LEDs). After 20 minutes, a clear colourless solution was obtained, which was immediately submitted for ^{1}H-NMR analysis. As expected, the resulting mixture exclusively contained the TAD-photopolymer (refer to Figure S2a).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.95 (broad m, 3H, CH_3), 1.40 (broad m, 3H, CH_3-CH_2), 1.68 (broad m, 3H, N-CH_2-CH_2), 3.31 + 3.60 (t + broad m, 2H, N-CH_2).

Next, a solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 4.65 mg, 3.0 10^{-5} mol, 1.0 eq.) in the presence of naphthalene (**2a**, 3.94 mg, 3.0 10^{-5} mol, 1.0 eq.) in 2 mL deuterated chloroform-*d* (15 mM) was irradiated with green light at (λ = 515 – 525 nm, 3 x 3 W LEDs). Again, photobleaching was observed within 20 minutes and the colourless mixture was analysed via ^{1}H-NMR. The TAD-naphthalene cycloadduct **3a** was shown to be predominantly formed, with only minor traces (i.e. < 2 %) of the photopolymer detected (refer to Figure S2c). In contrast, less than 1 % of cycloadduct **3a** was detected in a reference sample that was kept in the dark for 20 minutes (wrapped in aluminium foil), indicating the true light-induced nature of the TAD-naphthalene cycloaddition reaction (refer to Figure S2b).

Finally, a solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 4.65 mg, 3.0 10^{-5} mol, 1.0 eq.) and naphthalene (**2a**, 3.94 mg, 3.0 10^{-5} mol, 1.0 eq.) in 2 mL deuterated acetone-d_6 (15 mM) was irradiated with green light (λ = 515 – 525 nm, 3 x 3 W LEDs). In contrast to the similar experiment in chloroform, no trace of the TAD-polymer was detected in the resulting ^{1}H-NMR spectrum. Thus, the cycloaddition reaction was found to be the exclusive pathway when irradiating a 15 mM acetone solution of **1** and **2a**.

Kinetic measurements of the cycloreversion process



General procedure to determine the cycloreversion kinetics of TAD-naphthalene adducts **3a**-**g**.

A solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione **1** (3.53 mg, 0.023 mmol, 1.0 eq.) and naphthalene **2a-g** (0.027 mmol, 1.2 eq.) in 1.5 mL deuterated acetone-d_6 (15 mM) was divided over two NMR-tubes.

A first NMR tube was irradiated with green LEDs (λ = 515 – 525 nm, 3 x 3 W) for 45 min. Complete photobleaching was observed and the resulting mixture was immediately submitted for ^{1}H-NMR analysis (see below for NMR assignment of cycloadducts **3a-g** and refer to Figures S23-S29 for the corresponding spectra). From then onwards, the NMR sample remained in the autosampler of the NMR spectrometer at 25 °C and shielded from ambient light, whereby several spectra were recorded over the course of 60 h in 1-h intervals. Integration of well-resolved signals in the ^{1}H-NMR spectra allowed to determine the concentration of the TAD-naphthalene (regioisomeric) cycloadducts at distinct times (refer to Tables S2-S8), from which cycloreversion profiles at 25 °C in the dark were derived (refer to Figure 3 and Figure S11). Peaks in the ^{1}H-NMR spectra were assigned based on 2D COSY NMR correlations (cf. Figures S7-S10). Clean first order kinetics were observed over several half-life time intervals and the respective cycloreversion rate coefficients $k_{obs}^{25°C}$ were determined from the logarithmic relationship of the decrease in cycloadduct concentration over time (Table S1).

The second NMR tube was kept in the dark (25 °C, wrapped in aluminium foil) throughout the cycloreversion study and served as a reference to determine the thermal equilibrium concentration of the cycloadduct.

Cycloadduct 3a.

The two possibly formed regioisomers are identical (i.e. **3a-C$_A$** = **3a-C$_B$**). **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3a:** δ (ppm) = 0.81 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 1.05 (m, 2H, CH$_3$-C*H*$_2$), 1.41 (m, 2H, N-CH$_2$-C*H*$_2$), 3.32 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz), 5.89 (dd, 2H, Ar-C*H*-N *J* = 4.0, 3.2 Hz), 6.93 (dd, 2H, Ar-CH-C*H*=CH, *J* = 4.2, 3.1 Hz), 7.27 (m, 2H, Ar*H*), 7.45 (m, 2H, Ar*H*).

Cycloadduct 3b.

3b-C$_A$:3b-C$_B$ = 0:100. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3b-C$_B$**: δ (ppm) = 0.77 (t, 3H, C*H*$_3$, *J* = 7.3 Hz), 0.95 (m, 2H, CH$_3$-C*H*$_2$), 1.36 (m, 2H, N-CH$_2$-C*H*$_2$), 2.06 (s, 3H, C(O)C*H*$_3$), 3.29 (t, 2H, N-C*H*$_2$, *J* = 6.8 Hz), 5.26 (dd, 2H, C(O)-O-C*H*$_2$, *J* = 37.2, 12.5 Hz), 5.90 (m, 1H, Ar-C*H*-N), 6.21 (m, 1H, Ar-C*H*-N), 6.96 (m, 2H, Ar-CH-C*H*=CH), 7.24-7.35 (m, 2H, Ar*H*), 7.43 (dd, 1H, Ar*H*, *J* = 7.1, 1.2 Hz).

Cycloadduct 3c.

3c-C$_A$:3c-C$_B$ = 58:42. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3c-C$_A$**: δ (ppm) = 0.83 (t, 3H, C*H*$_3$, *J* = 7.3 Hz), 1.08 (m, 2H, CH$_3$-C*H*$_2$), 1.43 (m, 2H, N-CH$_2$-C*H*$_2$), 2.05 (s, 3H, C(O)C*H*$_3$), 3.34 (t, 2H, N-C*H*$_2$, *J* = 6.9 Hz), 4.75 (m, 2H, Ar-C*H*$_2$), 5.86 (d, 1H, Ar-C*H*-N; *J* = 1.8 Hz), 5.92 (m, 1H, Ar-C*H*-N), 7.43-7.56 (m, 4H, Ar*H*). **3c-C$_B$**: some resolved resonances, δ (ppm) = 5.09 (s, 2H, Ar-C*H*$_2$), 5.92 (m, 2H, Ar-C*H*-N), 6.93 (m, 2H, Ar-CH-C*H*=CH).

Cycloadduct 3d.

3d-C$_A$:3d-C$_B$ = 0:100. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3d-C$_B$**: δ (ppm) = 0.82 (t, 3H, C*H*$_3$, *J* = 7.4 Hz), 1.09 (m, 2H, CH$_3$-C*H*$_2$), 1.43 (m, 2H, N-CH$_2$-C*H*$_2$), 3.34 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz), 3.95 (s, 3H,

OC*H*$_3$), 5.98 (dd, 1H, Ar-C*H*-N, *J* = 5.1, 2.3 Hz), 6.92-7.03 (m, 2H, Ar-CH-C*H*=CH), 7.41 (dd, 1H, Ar*H*, *J* = 8.0, 7.4 Hz), 7.72 (dd, 1H, Ar*H*, *J* = 7.3, 0.8 Hz), 7.87 (dd, 1H, Ar*H*, *J* = 8.0, 1.2 Hz).

Cycloadduct 3e.

3e-C$_A$:3e-C$_B$ = 42:58. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3e-C$_A$**: δ (ppm) = 0.78 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 0.98 (m, 2H, CH$_3$-C*H*$_2$), 1.39 (m, 2H, N-CH$_2$-C*H*$_2$), 3.32 (t, 2H, N-C*H*$_2$, *J* = 6.8 Hz), 3.79 (s, 3H, OC*H*$_3$), 6.12 (d, 1H, Ar-C*H*-N, *J* = 6.4 Hz), 6.26 (d, 1H, Ar-C*H*-N, *J* = 1.5 Hz), 7.34 (m, 2H, Ar*H*), 7.49-7.59 (m, 2H, Ar*H*), 7.73 (dd, 1H, Ar-CH-C*H*=C, *J* = 6.1, 1.8 Hz). **3e-C$_B$**: some resolved resonances, δ (ppm) = 3.89 (s, 3H, OC*H*$_3$), 6.01 (dd, 1H, Ar-C*H*-N, *J* = 5.2, 1.6 Hz), 6.04 (dd, 1H, Ar-C*H*-N, *J* = 5.3, 1.9 Hz), 6.97 (m, 2H, Ar-CH-C*H*=CH), 7.62 (m, 1H, Ar*H*), 7.96 (m, 1H, Ar*H*), 8.06 (m, 1H, Ar*H*).

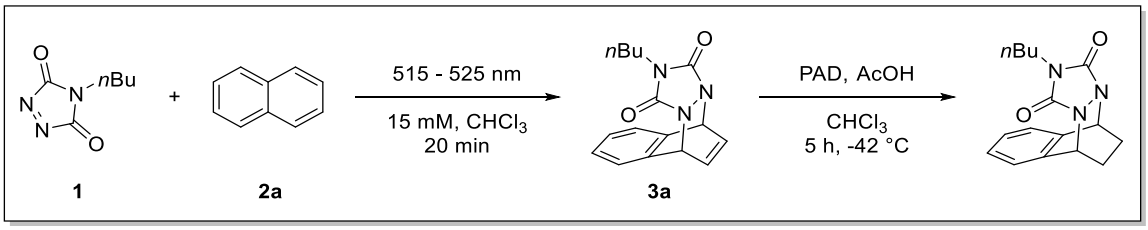
Cycloadduct 3f.

3f-C$_A$:3f-C$_B$ = 0:100. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3f-C$_B$**: δ (ppm) = 0.78 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 0.96 (m, 2H, CH$_3$-C*H*$_2$), 1.38 (m, 2H, N-CH$_2$-C*H*$_2$), 1.99 (s, 3H, C(O)C*H*$_3$), 3.13 (m, 2H, Ar-C*H*$_2$), 3.30 (t, 2H, N-C*H*$_2$, *J* = 6.8 Hz), 4.24 (m, 2H, C(O)-O-C*H*$_2$), 5.86 (dd, 1H, Ar-C*H*-N, *J* = 5.0, 2.4 Hz), 6.20 (dd, 1H, Ar-C*H*-N, *J* = 4.9, 2.2 Hz), 6.96 (m, 2H, Ar-CH-C*H*=CH), 7.18-7.25 (m, 2H, Ar*H*), 7.30-7.35 (m, 1H, Ar*H*).

Cycloadduct 3g.

3g-C$_A$:3g-C$_B$ = 53:47. **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$): 3g-C$_A$:** δ (ppm) = 0.82 (t, 3H, C*H*$_3$, *J* = 7.1 Hz), 1.06 (m, 2H, CH$_3$-C*H*$_2$), 1.42 (m, 2H, N-CH$_2$-C*H*$_2$), 1.92 (s, 3H, C(O)C*H*$_3$), 2.64 (m, 1H, Ar-C*H*$_2$), 3.33 (t, 2H, N-C*H*$_2$, *J* = 6.9 Hz), 4.09 + 4.23 (m, 2H, O-C*H*$_2$), 5.81 (d, 2H, Ar-C*H*-N, *J* = 1.9 Hz), 5.85 (d, 2H, Ar-C*H*-N, *J* = 6.1 Hz), 6.58 (m, 1H, Ar-CH-C*H*=CH), 7.36-7.53 (m, 4H, Ar*H*). **3g-C$_B$**: some resolved resonances, δ (ppm) = 2.94 (t, 1H, Ar-C*H*$_2$, *J* = 7 Hz), 4.23 (s, 2H, O-C*H*$_2$), 5.86 (m, 2H, Ar-C*H*-N), 6.92 (m, 2H, Ar-CH-C*H*=CH).

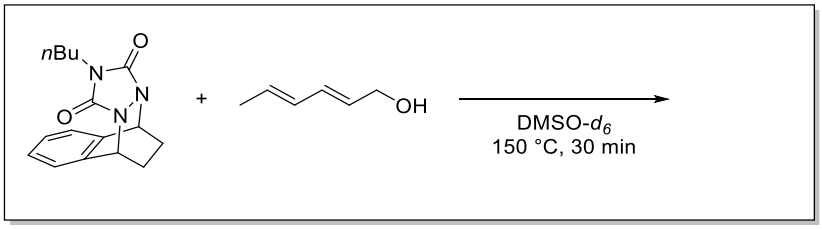
Reduction of cycloadduct 3a



A solution of 4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**, 46.5 mg, 0.3 mmol, 1.0 eq.) and naphthalene (**2a**, 39.4 mg, 0.3 mmol, 1.0 eq.) in 20 mL anhydrous chloroform (beforehand deoxygenated by flushing with nitrogen gas for 20 min) was placed in a photoreactor and irradiated at λ = 515 – 525 nm for 20 minutes with 3 x 3 W green LEDs. After photobleaching was observed, the reaction mixture was transferred into a flask and cooled at -42 °C in a liquid nitrogen-acetonitrile bath. To this, potassium azodicarboxylate (PAD, 0.58 g, 3.0 mmol, 10 eq.) was added at -42 °C, followed by the addition of acetic acid (0.86 mL, 15.0 mmol, 50 eq.) to the cloudy yellow suspension. The resulting mixture was stirred at -42 °C, during which the suspension slowly turned into a solution. After 2 hours, the mixture was slowly warmed in an ice water bath to 0 °C. After 5 hours, the obtained faint yellow cloudy suspension was allowed to warm to room temperature and 10 mL water was added. The mixture was washed with 20 mL aqueous saturated sodium bicarbonate solution and phase separated. The aqueous phase was washed with 20 mL chloroform and the combined organic phases were washed with 20 mL brine. Drying over magnesium sulfate, followed by solvent removal *in vacuo* gave a dark yellow oil, which was purified by means of preparative thin layer chromatography (silica, ethyl acetate:hexane 1:1, R_F = 0.91). The resulting yellow oil was subjected a second time to preparative thin layer chromatography (silica, ethyl acetate:hexane 1:4, R_F = 0.75) to remove traces of unreacted naphthalene, leaving a pure fraction of reduced cycloadduct as a yellow oil (25 mg – 29 %).

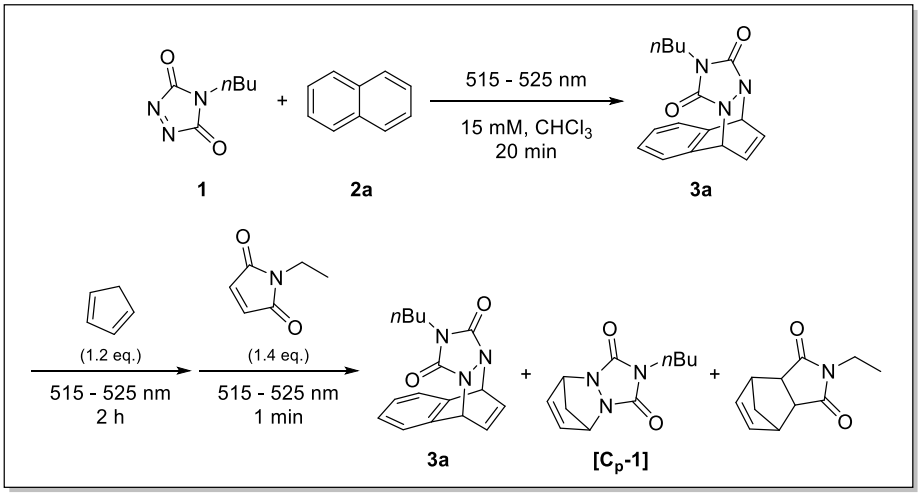
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.75 (t, 3H, C*H*$_3$, *J* = 7.3 Hz), 0.94 (m, 2H, C*H*$_2$-CH$_3$), 1.37 (m, 2H, N-CH$_2$-C*H*$_2$), 1.71 (m, 2H, Ar-CH-C*H*$_2$), 2.39 (m, 2H, Ar-CH-C*H*$_2$), 3.29 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz), 5.27 (s, 2H, N-C*H*-Ar), 7.29 (m, 2H, Ar*H*), 7.34 (m, 2H, Ar*H*). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 13.41 (CH_3), 19.17 (CH_2), 23.30 (CH_2), 29.44 (CH_2), 38.97 (CH_2), 54.01 (CH), 123.42 (CH), 128.65 (CH), 134.70 (C), 157.54 (C)**. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$):** δ (ppm) = 0.65 (t, 3H, C*H*$_3$, *J* = 7.0 Hz), 0.74 (m, 2H, C*H*$_2$-CH$_3$), 1.22 (m, 2H, N-CH$_2$-C*H*$_2$), 1.62 (m, 2H, Ar-CH-C*H*$_2$), 2.26 (m, 2H, Ar-CH-C*H*$_2$), 3.17 (t, 2H, N-C*H*$_2$, *J* = 6.6 Hz), 5.30 (s, 2H, N-C*H*-Ar), 7.35 (s, 4H, Ar*H*) (refer to Figure S4b and Figure S5a-b as well as Figure S30).

Thermal cycloreversion test of the reduced cycloadduct



A solution of cycloadduct **3a** after reduction (25 mg, 0.09 mmol, 1.0 eq.) and *trans*,*trans*-2,4-hexadien-1-ol (HDEO, 12 mg, 0.12 mmol, 1.4 eq.) in 0.7 mL deuterated DMSO-d_6 was transferred into an NMR tube and placed in a preheated oil bath at 150 °C for 30 minutes. After cooling to room temperature, the resulting mixture was submitted for ^{1}H-NMR analysis. The lack of thermal reversibility of the reduced TAD-naphthalene cycloadduct was evidenced by the absence of a newly formed TAD-HDEO cycloadduct (cf. Figure S4). Thus, no thermal cycloreversion occurred upon removal of the isolated endocyclic double bond.

Light-stabilised cycloadduct formation

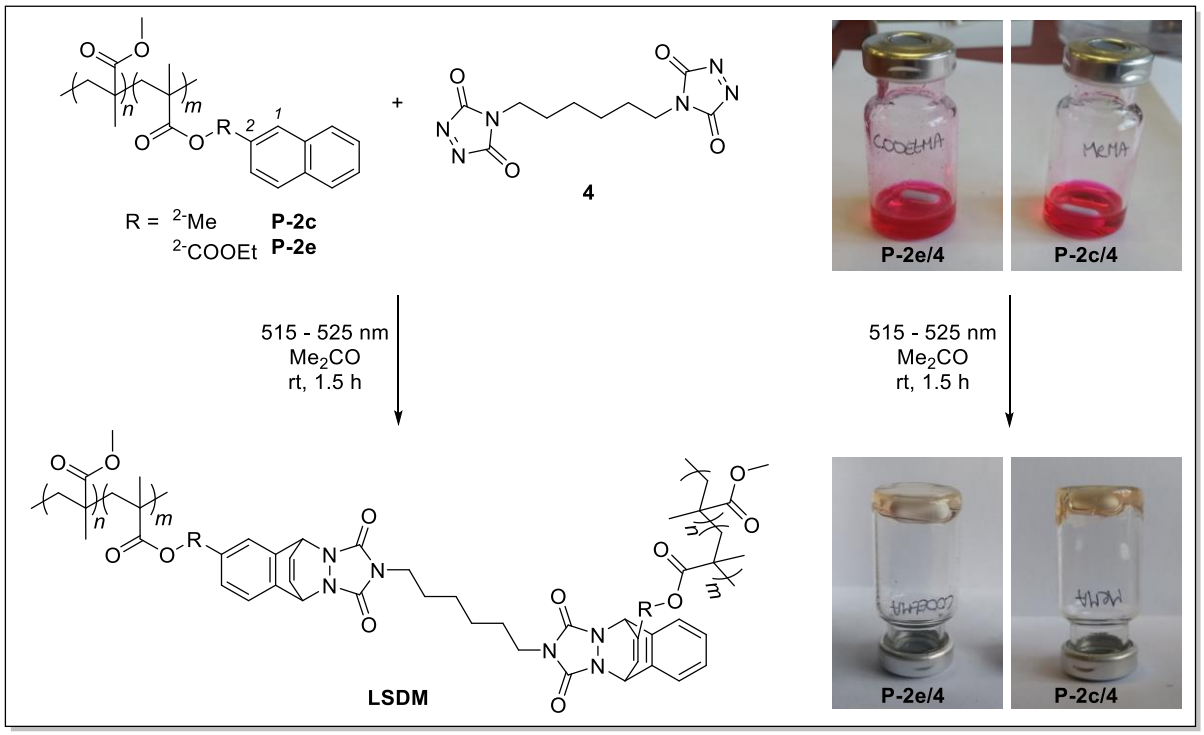


A previously described trapping experiment[1] was devised to detect the amount of liberated TAD moieties under continuous irradiation through the sequential addition of cyclopentadiene and *N*-ethylmaleimide. Applying the same trapping experiment here allowed us to determine the amount of covalent TAD/naphthalene bonds that are at least opened once under prolonged irradiation times. Specifically, cyclopentadiene (1.2 eq.) was added to a preformed solution of the cycloadduct **3a** (15 mM in $CDCl_3$, 20 min at λ = 515 – 525 nm), while the green light was kept switched on, and the resulting mixture was continued to be irradiated for an additional 2 h to allow for any released **1** to be irreversibly trapped by the diene (cf. Figure S6a). The residual non-reacted cyclopentadiene was eventually quenched under irradiation upon addition of *N*-ethylmaleimide (1.4 eq.), after which the light was switched off. Offline inspection of the resulting ^{1}H-NMR spectrum allowed to determine the amount of trapped TAD into the Diels-Alder adduct $\mathbf{C_p}$**-1** to be less than 5 %, which in turn gives the fraction of cycloadduct that remained stabilised throughout the irradiation period (refer to Figure S6b). It should be noted that the here observed fraction of cycloreversion is determined in the presence of an irreversible TAD-quencher and therefore considerably overestimates the degree of cycloreversion with respect to an autonomous TAD/naphthalene system where no kinetic trap is present. Nonetheless, the photochemical equilibrium remains near-quantitatively populated by covalently bound **3a** under prolonged visible light impact.

Photostability assessment of naphthalene-containing polymers P-2c and P-2e

A solution of naphthalene-containing polymer **P-2c** (100 mg, 0.12 mmol) or **P-2e** (105 mg, 0.12 mmol) in 0.5 mL anhydrous acetone was irradiated for 24 h with 3 x 3 W green LEDs at λ = 515 -525 nm. The resulting colourless solutions were evaporated to give a white residue, which was subjected to ^{1}H- and ^{13}C-NMR as well as SEC analysis. Comparison with a non-irradiated reference sample allowed to verify the photostability of the naphthalene-containing polymers under visible light impact (refer to Figures S12-S13).

Preparation of LSDMs through triazolinedione-naphthalene photoinduced crosslinking



Crosslinking in solution

A solution of naphthalene-containing polymer **P-2c** (200 mg, 0.24 mmol naphthalene, 1.0 eq.) or **P-2e** (210 mg, 0.24 mmol naphthalene, 1.0 eq.) and bisfunctional TAD **4** (34 mg, 0.12 mmol, 0.5 eq.) in 1 mL anhydrous acetone was irradiated with 3 x 3 W green LEDs at λ = 515 – 525 nm. Within 1.5 hours, photobleaching was observed and a crosslinked gel was formed. No visual change in the network integrity was observed when irradiation was continued for 5 hours.

Crosslinking in solution for ^{1}H-NMR analysis

A solution of naphthalene-containing polymer **P-2c** (75 mg, 0.09 mmol naphthalene, 1.0 eq.) and bisfunctional TAD **4** (5 mg, 0.02 mmol, 0.25 eq.) in 0.75 mL deuterated acetone-d_6 was transferred into an NMR tube and irradiated with 3 x 3 W green LEDs at λ = 515 – 525 nm. Within 1 hour, photobleaching was observed and a crosslinked gel was formed, verified by an inversion test of the NMR tube. Immediately after the light was switched off, the gel was submitted to ^{1}H-NMR analysis (cf. Figure S14). The subsequent decrosslinking was monitored after 24 h and 48 h by placing the NMR tube in the dark (wrapped in aluminium foil).

Crosslinking in solution for rheology

A polymer formulation of naphthalene-containing polymer **P-2c** (200 mg, 0.24 mmol naphthalene, 1.0 eq.) or **P-2e** (210 mg, 0.24 mmol naphthalene, 1.0 eq.) and bisfunctional TAD **4** (34 mg, 0.12 mmol, 0.5 eq.) in 0.25 mL anhydrous acetone was prepared to assess the rheological behaviour of the TAD-naphthalene system. 8 drops of the formulation were deposited on the lower parallel glass plate (33 mm diameter) of the rheometer (refer to instrumentation section), thereby avoiding the formation of air bubbles. The upper part of the moving profile (PP25) was lowered (0.10 to 0.20 mm gap) and the excess amount of the formulation was trimmed at the edges of the moving profile. The samples were measured in oscillatory mode under isothermal conditions (i.e. at 25 °C) in a closed oven so to prevent interference of ambient light. After a certain time in the dark, photocuring was affected by switching on a broad emitting UV-lamp equipped with a filter in the visible range, i.e. $\lambda = 400 – 500$ nm. After curing, a normal force of 0.2 N was applied whilst the sample was kept irradiated. Afterwards, the light was switched off and the collapse of the material was monitored in the dark. At the end of the dark time, the normal force was reinstated to 0 N and a second photocuring was carried out, if desired. The rheology profiles, showing G' and G" as a function of time are depicted in Figure 4 and Figures S16-S19.

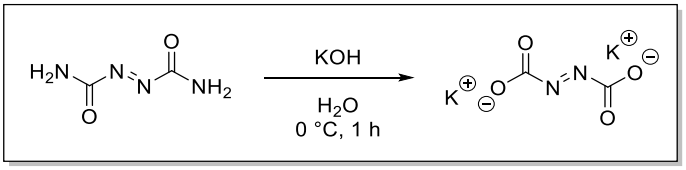
Synthetic procedures

Synthesis of 4-*n*-butyl-triazoline-3,5-dione (4-*n*-butyl-TAD, 1)

4-*n*-butyl-1,2,4-triazoline-3,5-dione (4-*n*-butyl-TAD, **1**) was synthesised according to a literature procedure,[2] followed by sublimation under reduced pressure (0.1 mbar) at 40 °C to give **1** as carmine red crystals. The reactive compound was stored in the dark at -18 °C and typically used within several weeks. Purity was regularly checked via ^{1}H-NMR prior to use.

^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ (ppm) = 0.88 (t, 3H, C*H*$_3$, *J* = 7.3 Hz), 1.30 (sext, 2H, C*H*$_2$-CH$_3$, *J* = 7.3 Hz), 1.56 (quint, 2H, N-CH$_2$-C*H*$_2$, *J* = 7.3 Hz), 3.47 (t, 2H, N-C*H*$_2$, *J* = 7.0 Hz). **^{13}C-NMR (100 MHz, DMSO-*d*$_6$):** δ (ppm) = 13.32 (CH$_3$), 19.11 (CH$_2$), 28.72 (CH$_2$), 40.34 (CH$_2$), 160.15 (C)**.**

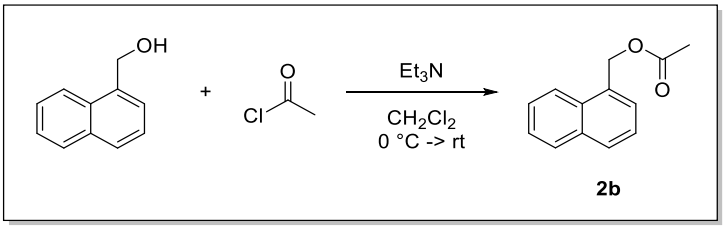
Synthesis of potassium azodicarboxylate (PAD)



A solution of potassium hydroxide (6.2 g, 0.110 mol, 40 wt %) in 15.5 mL water was cooled in an ice water bath at 0 °C. To this, azodicarboxamide (2.5 g, 0.021 mol, 1.0 eq.) was added in small portions, maintaining the temperature below 5 °C. The yellow suspension was stirred at 0 – 5 °C for 1 hour, filtered and dried to the air overnight at room temperature to give potassium azodicarboxylate (PAD) as a yellow powder (2.52 g – 62 %).

Synthesis of naphthalene model compounds

Synthesis of naphthalen-1-ylmethyl acetate (2b)

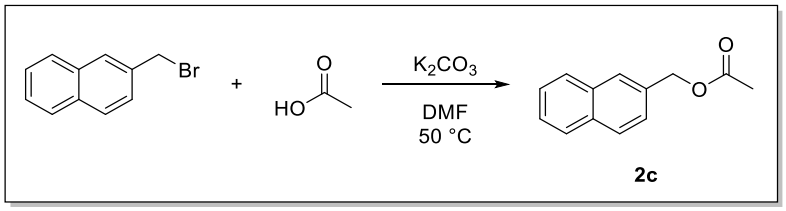


A solution of 1-naphthalenemethanol (1.00 g, 6.32 mmol, 1.0 eq.) in 20 mL dichloromethane was placed under inert atmosphere and cooled at 0 °C in an ice water bath. Triethylamine (1.06 mL, 7.59 mmol, 1.2 eq.) was added at 0 °C, followed by the dropwise addition of acetyl chloride (0.54 mL, 7.59 mmol, 1.2 eq.). The resulting mixture was stirred overnight at room temperature, diluted with 20 mL dichloromethane and quenched with 40 mL 1 M aqueous hydrochloric acid. The organic phase was separated and the aqueous phase was washed with dichloromethane (2 x 40 mL), after which the combined organic phases were washed with brine (2 x 20 mL) and eventually dried over magnesium sulfate. Solvent removal *in vacuo,* followed by overnight drying in a vacuum oven at 40 °C, gave naphthalen-1-ylmethyl acetate **2b** as a dark yellow oil (1.20 g – 95 %).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 2.13 (s, 3H, C*H*$_3$), 5.59 (s, 2H, C*H*$_2$), 7.45-7.50 (m, 1H, Ar*H*), 7.51-7.62 (m, 3H, Ar*H*), 7.84-7.94 (m, 2H, Ar*H*), 8.04 (d, 1H, Ar*H*, *J* = 8.4 Hz). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ (ppm) = 21.00 (CH$_3$), 64.55 (CH$_2$), 123.51 (CH), 125.25 (CH), 125.93 (CH), 126.55 (CH), 127.48 (CH), 128.70 (CH), 129.29 (CH), 131.41 (C), 131.60 (C), 133.71 (C), 170.95 (C). **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$):** δ (ppm) = 2.06 (s, 3H, C*H*$_3$), 5.57 (s, 2H, C*H*$_2$), 7.49 (dd, 1H, Ar*H*, *J* = 8.2, 7.0 Hz),

7.62-7.62 (m, 3H, Ar*H*), 7.89-7.99 (m, 2H, Ar*H*), 8.08 (m, 1H, Ar*H*). **^{13}C-NMR (100 MHz, Me$_2$CO-*d*$_6$):** δ (ppm) = 20.88 (CH_3), 64.82 (CH_2), 124.59 (CH), 126.25 (CH), 126.88 (CH), 127.43 (CH), 128.16 (CH), 129.56 (CH), 129.96 (CH), 132.61 (C), 133.03 (C), 134.81 (C), 170.96 (C). **LC-MS (m/z):** 218.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc*.: 218.1176, *found*: 218.1180 $[M+NH_4]^+$.

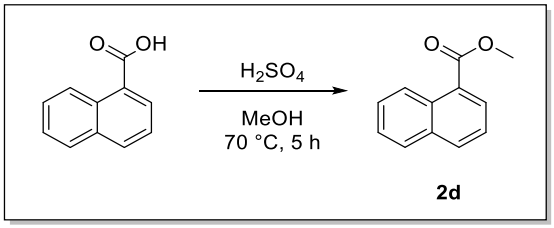
Synthesis of naphthalen-2-ylmethyl acetate (2c)



A mixture of 2-(bromomethyl)naphthalene (1.00 g, 4.74 mmol, 1.0 eq.) and potassium carbonate (0.98 g, 7.11 mmol, 1.5 eq.) in 20 mL anhydrous DMF was placed under inert atmosphere. Acetic acid (0.40 mL, 7.11 mmol, 1.5 eq.) was added and the resulting mixture was heated at 50 °C for 16 hours. After cooling to room temperature, 40 mL ethyl acetate was added and the mixture was washed with water (1 x 40 mL) and brine (2 x 40 mL). The organic phase was dried over magnesium sulfate, followed by solvent removal *in vacuo* and the residue was dried overnight in a vacuum oven at 40 °C. Naphthalen-2-ylmethyl acetate **2c** was obtained as an off-white powder (0.85 g – 90 %).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 2.15 (s, 3H, C*H*$_3$), 5.29 (s, 2H, C*H*$_2$), 7.45-7.55 (m, 3H, Ar*H*), 7.82-7.89 (m, 4H, Ar*H*). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ (ppm) = 21.02 (CH_3), 66.42 (CH_2), 125.87 (CH), 126.25 (CH), 126.28 (CH), 127.35 (CH), 127.67 (CH), 127.94 (CH), 128.35 (CH), 133.08 (C), 133.16 (C), 133.32 (C), 170.90 (C). **^{1}H-NMR (400 MHz, Me$_2$CO-*d*$_6$):** δ (ppm) = 2.08 (s, 3H, C*H*$_3$), 5.26 (s, 2H, C*H*$_2$), 7.49-7.55 (m, 3H, Ar*H*), 7.89-7.93 (m, 4H, Ar*H*). **^{13}C-NMR (100 MHz, Me$_2$CO-*d*$_6$):** δ (ppm) = 20.92 (CH_3), 66.62 (CH_2), 126.86 (CH), 127.13 (CH), 127.24 (CH), 127.89 (CH), 128.61 (CH), 128.84 (CH), 129.12 (CH), 134.12 (C), 134.31 (C), 135.18 (C), 170.98 (C). **LC-MS (m/z):** 218.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc*.: 218.1176, *found*: 218.1175 $[M+NH_4]^+$.

Synthesis of methyl 1-naphthoate (2d)

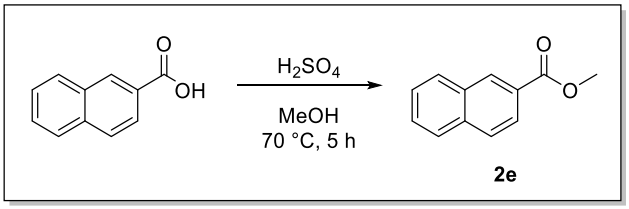


A mixture of 1-naphthoic acid (1.00 g, 5.81 mmol, 1.0 eq.) and concentrated sulfuric acid (0.31 g, 5.81 mmol, 1.0 eq.) in 5 mL anhydrous methanol was placed under inert atmosphere and refluxed at 70 °C. After 5 hours, the clear solution was cooled to ambient temperature and evaporated *in vacuo* to dryness. The residue was dissolved in 20 mL dichloromethane and washed with 20 mL water. The aqueous phase was extracted with dichloromethane (2 x 20 mL) and the combined organic phases washed with water (1 x 20 mL), saturated aqueous sodium bicarbonate solution (2 x 20 mL) and brine (1 x 20 mL). The clear organic phase was dried over magnesium sulfate followed by solvent removal *in vacuo* and overnight drying in a vacuum oven at 40 °C. Methyl 1-naphthoate **2d** was obtained as a faint yellow oil (0.92 g – 85 %).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 4.02 (s, 3H, C*H*$_3$), 7.47-7.58 (m, 2H, Ar*H*), 7.64 (ddd, 1H, Ar*H*, *J* = 8.6, 6.9, 1.3 Hz), 7.90 (dt, 1H, Ar*H*, *J* = 8.1, 0.6 Hz), 8.03 (d, 1H, Ar*H*, *J* = 8.2 Hz), 8.21 (dd, 1H,

Ar*H*, *J* = 7.3, 1.3 Hz), 8.95 (dd, 1H, Ar*H*, *J* = 8.7, 0.9 Hz). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 52.07 (CH_3), 124.42 (CH), 125.76 (CH), 126.14 (CH), 127.01 (C), 127.69 (CH), 128.48 (CH), 130.16 (CH), 131.28 (C), 133.30 (CH), 133.78 (C), 169.96 (C). **^{1}H-NMR (400 MHz, Me_2CO-d_6):** δ (ppm) = 3.98 (s, 3H, CH_3), 7.55-7.62 (m, 2H, Ar*H*), 7.65 (m, 1H, Ar*H*), 8.00 (dt, 1H, Ar*H*, *J* = 8.1, 0.8 Hz), 8.15 (d, 1H, Ar*H*, *J* = 8.2 Hz), 8.19 (dd, 1H, Ar*H*, *J* = 7.3, 1.3 Hz), 8.90 (m, 1H, Ar*H*). **^{13}C-NMR (100 MHz, Me_2CO-d_6):** δ (ppm) = 52.44 (CH_3), 125.59 (CH), 126.51 (CH), 127.16 (CH), 128.11 (C), 128.54 (CH), 129.54 (CH), 130.91 (CH), 132.11 (C), 134.17 (CH), 134.90 (C), 168.28 (C). **LC-MS (m/z):** 187.1 $[M+H]^+$.

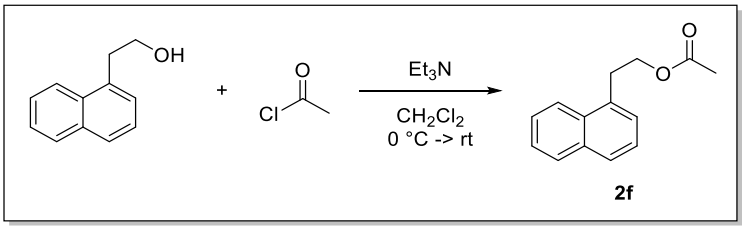
Synthesis of methyl 2-naphthoate (2e)



A mixture of 2-naphthoic acid (1.00 g, 5.81 mmol, 1.0 eq.) and concentrated sulfuric acid (0.31 g, 5.81 mmol, 1.0 eq.) in 5 mL anhydrous methanol was placed under inert atmosphere and refluxed at 70 °C. After 5 hours, the clear solution was cooled to ambient temperature and evaporated *in vacuo* to dryness. The residue was dissolved in 20 mL dichloromethane and washed with 20 mL water. The aqueous phase was extracted with dichloromethane (2 x 20 mL) and the combined organic phases washed with water (1 x 20 mL), saturated aqueous sodium bicarbonate solution (2 x 20 mL) and brine (1 x 20 mL). The clear organic phase was dried over magnesium sulfate, followed by solvent removal *in vacuo* and overnight drying in a vacuum oven at 40 °C, to give methyl 2-naphthoate **2e** as a white powder (0.94 g – 87 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.00 (s, 3H, CH_3), 7.54-7.64 (m, 2H, Ar*H*), 7.90 (d, 2H, Ar*H*, *J* = 8.7 Hz), 7.97 (dd, 1H, Ar*H*, *J* = 7.9, 0.6 Hz), 8.08 (dd, 1H, Ar*H*, *J* = 8.5, 1.7 Hz), 8.63 (s, 1H, Ar*H*). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 52.22 (CH_3), 125.22 (CH), 126.62 (CH), 127.40 (C), 127.75 (CH), 128.14 (CH), 128.22 (CH), 129.34 (CH), 131.06 (CH), 132.49 (C), 135.51 (C), 167.27 (C). **^{1}H-NMR (400 MHz, Me_2CO-d_6):** δ (ppm) = 3.95 (s, 3H, CH_3), 7.58-7.70 (m, 2H, Ar*H*), 7.96-8.07 (d, 2H, Ar*H*), 8.09 (d, 1H, Ar*H*, *J* = 8.1 Hz), 8.63 (s, 1H, Ar*H*). **^{13}C-NMR (100 MHz, Me_2CO-d_6):** δ (ppm) = 52.53 (CH_3), 125.94 (CH), 127.83 (CH), 128.56 (C), 128.73 (CH), 129.24 (CH), 129.37 (CH), 130.28 (CH), 131.61 (CH), 133.59 (C), 136.54 (C), 167.41 (C). **LC-MS (m/z):** 187.1 $[M+H]^+$.

Synthesis of 2-(naphthalen-1-yl)ethyl acetate (2f)

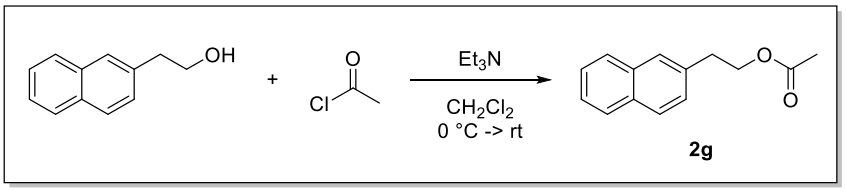


A solution of 2-(naphthalen-1-yl)ethan-1-ol (1.00 g, 5.81 mmol, 1.0 eq.) in 20 mL dichloromethane was placed under inert atmosphere and cooled at 0 °C. Triethylamine (0.97 mL, 6.97 mmol, 1.2 eq.) was added at 0 °C, followed by the dropwise addition of acetyl chloride (0.50 mL, 6.97 mmol, 1.2 eq.). The resulting mixture was stirred overnight at room temperature, diluted with 20 mL dichloromethane and quenched with 40 mL 1 M aqueous hydrochloric acid. The organic phase was separated and the aqueous phase was washed with dichloromethane (2 x 40 mL). The combined organic phases were washed with brine (2 x

20 mL) and dried over magnesium sulfate. Solvent removal *in vacuo* followed by overnight drying in a vacuum oven at 40 °C gave 2-(naphthalen-1-yl)ethyl acetate **2f** as a dark yellow oil (1.18 g – 95 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.08 (s, 3H, C*H*$_3$), 3.45 (t, 2H, Ar-C*H*$_2$, *J* = 7.4 Hz), 4.45 (t, 2H, O-C*H*$_2$, *J* = 7.4 Hz), 7.38-7.48 (m, 2H, Ar*H*), 7.49-7.61 (m, 2H, Ar*H*), 7.79 (d, 1H, Ar*H*, *J* = 8.1 Hz), 7.89 (d, 1H, Ar*H*, *J* = 8.8 Hz), 8.13 (d, 1H, Ar*H*, *J* = 8.5 Hz). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 20.93 (CH_3), 32.13 (CH_2), 64.39 (CH_2), 123.50 (CH), 125.41 (CH), 125.59 (CH), 126.10 (CH), 126.88 (CH), 127.38 (CH), 128.75 (CH), 131.99 (C), 133.63 (C), 133.79 (C), 171.00 (C). **^{1}H-NMR (400 MHz, Me_2CO-*d_6*):** δ (ppm) = 1.98 (s, 3H, C*H*$_3$), 3.42 (t, 2H, Ar-C*H*$_2$, *J* = 7.3 Hz), 4.37 (t, 2H, O-C*H*$_2$, *J* = 7.2 Hz), 7.41-7.48 (m, 2H, Ar*H*), 7.49-7.60 (m, 2H, Ar*H*), 7.78-7.83 (m, 1H, Ar*H*), 7.92 (dt, 1H, Ar*H*, *J* = 8.1, 0.7 Hz), 8.18 (m, 1H, Ar*H*). **^{13}C-NMR (100 MHz, Me_2CO-*d_6*):** δ (ppm) 20.91 (CH_3), 32.85 (CH_2), 64.94 (CH_2), 124.62 (CH), 126.50 (CH), 126.57 (CH), 127.03 (CH), 128.02 (CH), 128.23 (CH), 129.67 (CH), 133.11 (C), 135.02 (C), 135.08 (C), 171.09 (C). **LC-MS (m/z):** 232.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc*.: 232.1332, *found*: 232.1337 $[M+NH_4]^+$.

Synthesis of 2-(naphthalen-2-yl)ethyl acetate (2g)

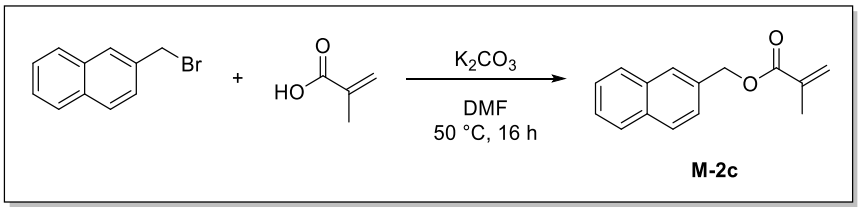


A solution of 2-(naphthalen-2-yl)ethan-1-ol (1.00 g, 5.81 mmol, 1.0 eq.) in 20 mL dichloromethane was placed under inert atmosphere and cooled at 0 °C. Triethylamine (0.97 mL, 6.97 mmol, 1.2 eq.) was added at 0 °C, followed by the dropwise addition of acetyl chloride (0.50 mL, 6.97 mmol, 1.2 eq.). The resulting mixture was stirred overnight at room temperature, diluted with 20 mL dichloromethane and quenched with 40 mL 1 M aqueous hydrochloric acid. The organic phase was separated and the aqueous phase was washed with dichloromethane (2 x 40 mL). The combined organic phases were washed with brine (2 x 20 mL) and dried over magnesium sulfate. Solvent removal *in vacuo* followed by overnight drying in a vacuum oven at 40 °C gave 2-(naphthalen-2-yl)ethyl acetate **2g** as a yellow oil (1.15 g – 93 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.07 (s, 3H, C*H*$_3$), 3.13 (t, 2H, Ar-C*H*$_2$, *J* = 7.0 Hz), 4.41 (t, 2H, O-C*H*$_2$, *J* = 7.1 Hz), 7.39 (dd, 1H, Ar*H*, *J* = 8.4, 1.6 Hz), 7.44-7.54 (m, 2H, Ar*H*), 7.70 (s, 1H, Ar*H*), 7.78-7.88 (m, 3H, Ar*H*). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 20.90 (CH_3), 35.15 (CH_2), 64.76 (CH_2), 125.45 (CH), 126.00 (CH), 127.21 (CH), 127.22 (CH), 127.44 (CH), 127.58 (CH), 128.04 (CH), 132.22 (C), 133.48 (C), 135.24 (C), 170.97 (C). **^{1}H-NMR (400 MHz, Me_2CO-*d_6*):** δ (ppm) = 1.97 (s, 3H, C*H*$_3$), 3.10 (t, 2H, Ar-C*H*$_2$, *J* = 7.0 Hz), 4.34 (t, 2H, O-C*H*$_2$, *J* = 7.0 Hz), 7.41-7.51 (m, 3H, Ar*H*), 7.76 (s, 1H, Ar*H*), 7.82-7.90 (m, 3H, Ar*H*). **^{13}C-NMR (100 MHz, Me_2CO-*d_6*):** δ (ppm) = 20.87 (CH_3), 35.89 (CH_2), 65.33 (CH_2), 126.38 (CH), 126.95 (CH), 128.18 (CH), 128.39 (CH), 128.43 (CH), 128.51 (CH), 128.91 (CH), 133.38 (C), 134.70 (C), 136.88 (C), 171.00 (C). **LC-MS (m/z):** 232.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc*.: 232.1332, *found*: 232.1342 $[M+NH_4]^+$.

Synthesis of naphthalene-containing methacrylate monomers

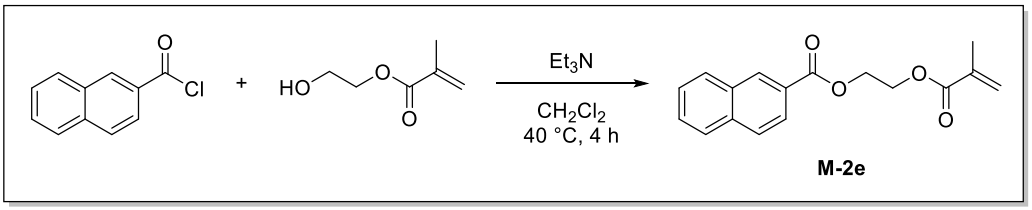
Synthesis of naphthalen-2-ylmethyl methacrylate (M-2c)



A mixture of methacrylic acid (3.37 mL, 39.6 mmol, 1.0 eq.) and potassium carbonate (6.1 g, 43.6 mmol, 1.1 eq.) in 200 mL anhydrous DMF was placed under inert atmosphere. 2-(Bromomethyl)naphthalene (9.2 g, 43.6 mmol, 1.1 eq.) was added dropwise and the resulting mixture was heated at 50 °C for 16 hours. After cooling to room temperature, 400 mL ethyl acetate was added and the organic phase was washed with brine (3 x 400 mL) and dried over magnesium sulfate. Solvent evaporation *in vacuo* gave a clear yellow oil that solidified upon standing at room temperature. The crude residue was dissolved in a minimal amount of ethyl acetate and purified by means of column chromatography (silica, ethyl acetate:hexanes 1:5, R_F = 0.45). 4-Methoxyphenol was added as an inhibitor prior to solvent evaporation *in vacuo* to give naphthalen-2-ylmethyl methacrylate **M-2c** as an off-white residue (7.70 g – 86 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.00 (dd, 3H, C*H*$_3$, *J* = 1.32 (x2) Hz), 5.37 (s, 2H, C*H*$_2$), 5.61 (m, 1H, C=C*H*), 6.20 (m, 1H, C=C*H*), 7.45-7.56 (m, 3H, Ar*H*), 7.81-7.91 (m, 4H, Ar*H*). **^{13}C-NMR (75 MHz, $CDCl_3$):** δ (ppm) = 18.36 (CH_3), 66.56 (CH_2), 125.80 (CH), 125.87 (CH_2), 126.22 (CH), 126.27 (CH), 127.18 (CH), 127.70 (CH), 127.97 (CH), 128.35 (CH), 133.08 (C),133.18 (C), 133.52 (C), 136.24 (C), 167.28 (C). **LC-MS (m/z):** 244.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc*.: 244.1332, *found*: 244.1340 $[M+NH_4]^+$.

Synthesis of 2-(methacryloyloxy)ethyl 2-naphthanoate (M-2e)



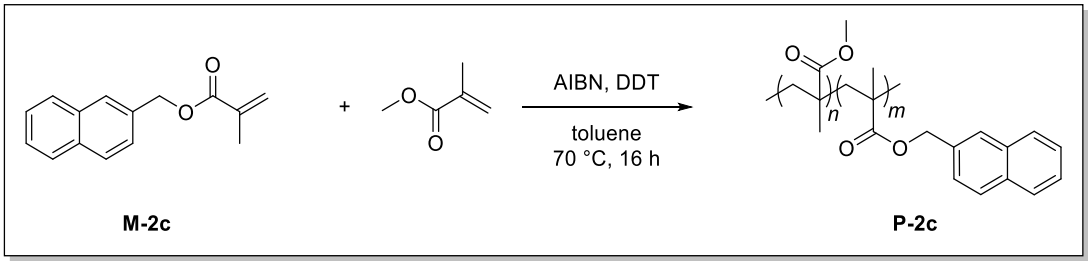
A solution of 2-naphthoyl chloride (5.00 g, 26.2 mmol, 1.0 eq.) was placed under inert atmosphere and cooled at 0 °C. Triethylamine (4.02 mL, 28.9 mmol, 1.1 eq.) was added at 0 °C, followed by the dropwise addition of 2-hydroxyethyl methacrylate (3.50 mL, 28.9 mmol, 1.1 eq.). The resulting mixture was heated to mild reflux at 40 °C for 4 hours. The resulting cloudy mixture was cooled to room temperature and diluted with 20 mL dichloromethane and quenched with 20 mL aqueous saturated ammonium chloride solution. The clear suspension was phase separated and the aqueous phase was washed with dichloromethane (1 x 20 mL). The combined organic phases were washed with brine (1 x 20 mL), dried over magnesium sulfate and the solvent was removed *in vacuo*. The crude colorless oil was dissolved in a minimal amount of ethyl acetate and purified by means of column chromatography (silica, ethyl acetate:hexanes 1:9, R_F = 0.25). 4-Methoxyphenol was added as an inhibitor prior to solvent evaporation *in vacuo* to eventually give 2-(methacryloyloxy)ethyl 2-naphthanoate **M-2e** as a clear and colorless oil that solidified to a white powder upon standing at room temperature (6.81 g – 91 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.98 (dd, 3H, C*H*$_3$, *J* = 0.5 (x2) Hz), 4.55 (m, 2H, Ar-CO-O-C*H*$_2$), 4.65 (m, 2H, Ar-CO-O-CH$_2$-C*H*$_2$), 5.61 (quin, 1H, C=C*H*, *J* = 1.6 Hz), 6.20 (dq, 1H, C=C*H*, *J* = 1.7, 0.9 Hz), 7.52-7.65 (m, 2H, Ar*H*), 7.90 (m, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 8.07 (dd, 1H, Ar*H*, *J* = 8.5, 1.7 Hz), 8.63 (s, 1H, Ar*H*). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ (ppm) = 18.28 (CH_3), 62.44 (CH_2), 62.74 (CH_2), 125.17 (CH), 126.11 (CH_2), 126.68 (CH), 127.05 (C), 127.75 (CH), 128.20 (CH),

128.34 (CH), 129.37 (CH), 131.25 (CH), 132.44 (C), 135.59 (C), 135.94 (C), 166.47 (C), 167.18 (C). **LC-MS (m/z):** 302.2 $[M+NH_4]^+$. **HRMS (m/z):** *calc.*: 302.1387, *found*: 302.1396 $[M+H]^+$.

Synthesis of naphthalene-containing polymers

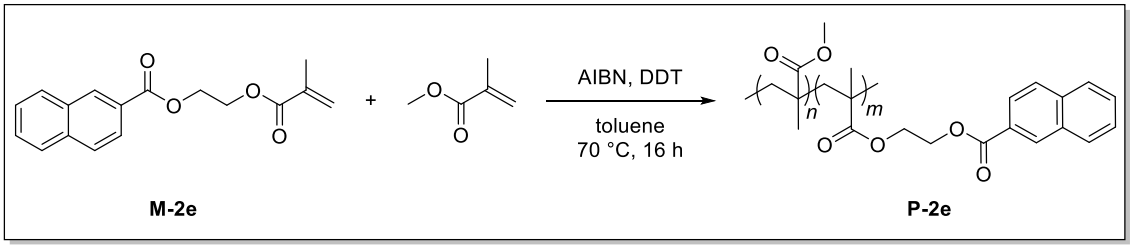
Synthesis of naphthalen-2-ylmethyl methacrylate-containing polymer (P-2c)



Naphthalen-2-ylmethyl methacrylate (**M-2c**, 2.04 g, 9.0 mmol, 15 eq.) was dissolved in 4 mL of toluene and passed over a column of basic aluminium oxide to remove the inhibitor. The column was flushed with another 2 mL of toluene. Methyl methacrylate (MMA, 5.46 mL, 51.0 mmol, 85 eq.) was next added to the toluene solution, after the inhibitor was removed by passing over a column of basic aluminium oxide. The combined monomer solution was added to an airtight crimped headspace vial containing 2,2'-azo-bis(2-methylpropionitrile) (AIBN, 98.5 mg, 0.60 mmol, 1.0 eq.) and a stirring bar, which was placed under inert atmosphere prior to monomer addition. Another 6 mL of toluene was added and the resulting mixture was flushed for 20 minutes by bubbling with nitrogen gas. Subsequently, 1-dodecanethiol (DDT, 0.29 mL, 1.20 mmol, 2.0 eq.), which was deoxygenated by bubbling with nitrogen gas for 20 minutes, was added and the mixture was placed in a preheated oil bath at 70 °C. After 16 hours, the polymer mixture was opened to the air and cooled in liquid nitrogen after which 6 mL of tetrahydrofuran was added. The polymer solution was precipitated in 300 mL of ice cold methanol and the white precipitate was collected through filtration. The residue was dissolved in a minimal amount of tetrahydrofuran and precipitated a second time in a 10-fold excess of ice cold *n*-hexane. Drying of the obtained residue in a vacuum oven at 40 °C overnight gave the naphthalene-containing polymer **P-2c** as a white powder (6.09 g – ca. 85 %). Fraction of naphthalene, determined via ^{1}H-NMR: 14.2 mol % or 27.2 wt % (cf. Figure S12a).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.44-2.25 (C*H*$_3$ + C*H*$_2$ polymer backbone), 3.24-3.70 (O-C*H*$_3$), 4.84-5.33 (2H, ArC*H*$_2$), 7.33-7.62 (3H, Ar*H*), 7.66-8.01 (4H, Ar*H*). **SEC ($CHCl_3$, PMMA standards):** M_n = 4.6 kDa, M_w = 10.4 kDa, M_p = 9.8 kDa, $Đ$ = 2.19. **DSC:** T_g = 87 °C. **TGA:** $T_{d,\,5\,\%}$ = 263 °C.

Synthesis of 2-(methacryloyloxy)ethyl 2-naphthanoate-containing into polymer (P-2e)



2-(Methacryloyloxy)ethyl 2-naphthanoate (**M-2e**, 2.56 g, 9.0 mmol, 15 eq.) was dissolved in 4 mL of toluene and passed over a column of basic aluminium oxide to remove the inhibitor. The column was flushed with another 2 mL of toluene. Methyl methacrylate (MMA, 5.46 mL, 51.0 mmol, 85 eq.) was next added to the toluene solution, after the inhibitor was removed by passing over a column of basic aluminium oxide. The combined monomer solution was added to an airtight crimped headspace vial containing

2,2'-azobis(2-methylpropionitrile) (AIBN, 98.5 mg, 0.60 mmol, 1.0 eq.) and a stirring bar, which was placed under inert atmosphere prior to monomer addition. Another 6 mL of toluene was added and the resulting mixture was flushed for 20 minutes by bubbling with nitrogen gas. Subsequently, 1-dodecanethiol (DDT, 0.29 mL, 1.20 mmol, 2.0 eq.), which was deoxygenated by bubbling with nitrogen gas for 20 minutes, was added and the mixture was placed in a preheated oil bath at 70 °C. After 16 hours, the polymer mixture was opened to the air and cooled in liquid nitrogen after which 6 mL of tetrahydrofuran was added. The polymer solution was precipitated in 300 mL of ice cold methanol and the white precipitate was collected through filtration. The residue was dissolved in a minimal amount of tetrahydrofuran and precipitated a second time in a 10-fold excess of ice cold *n*-hexane. Drying of the obtained residue in a vacuum oven at 40 °C overnight gave the naphthalene-containing polymer **P-2e** as a white powder (5.87 g – ca. 81 %). Fraction of naphthalene, determined via ^{1}H-NMR: 14.1 mol % or 31.8 wt % (cf. Figure S13a).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.66-2.13 (C*H*$_3$ + C*H*$_2$ polymer backbone), 3.30-3.69 (O-C*H*$_3$), 4.06-4.71 (4H, C(O)O-C*H*$_2$), 7.40-7.68 (2H, Ar*H*), 7.77-8.17 (4H, Ar*H*), 8.48-8.74 (1H, Ar*H*). **SEC ($CHCl_3$, PMMA standards):** M_n = 5.1 kDa, M_w = 10.6 kDa, M_p = 10.3 kDa, $Đ$ = 2.08. **DSC:** T_g = 82 °C. **TGA:** $T_{d,\,5\,\%}$ = 267 °C.

Synthesis of bisfunctional triazolinedione crosslinker 4

The bisfunctional 1,2,4-triazoline-3,5-dione crosslinker **4** (bisTAD) was synthesised according to a literature procedure[3] and obtained as a carmine red powder. The reactive crosslinker was stored in the dark at -18 °C and typically used within several weeks. Purity was regularly checked via ^{1}H-NMR prior to use.

^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) = 1.29 (m, 4H, N-CH_2-CH_2-C*H*$_2$), 1.55 (m, 4H, N-CH_2-C*H*$_2$), 3.45 (m, 4H, N-C*H*$_2$). **^{13}C-NMR (75 MHz, DMSO-d_6):** δ (ppm) = 25.24 (CH_2), 26.46 (CH_2), 40.51 (CH_2), 160.13 (C)**.**

Supplementary NMR spectra

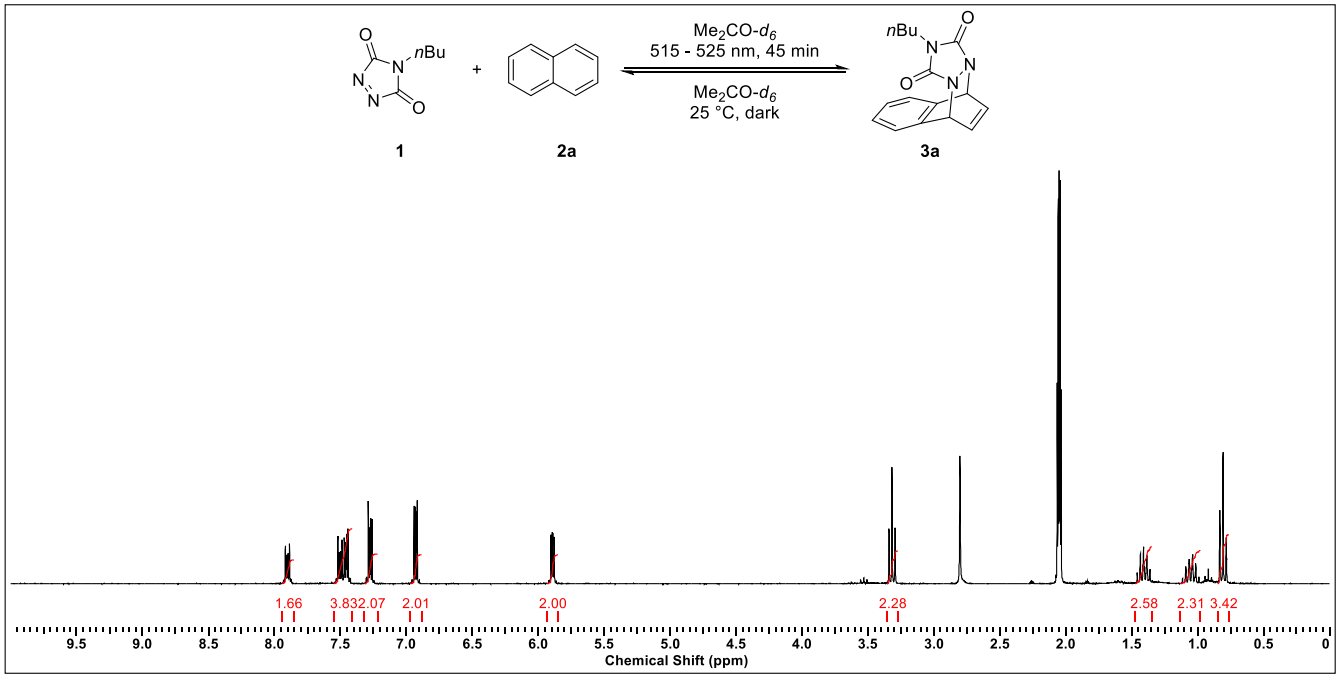


Figure S23. ^{1}H-NMR spectrum (Me_2CO-d_6) of cycloadduct **3a**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of plain naphthalene **2a** (1.2 eq.).

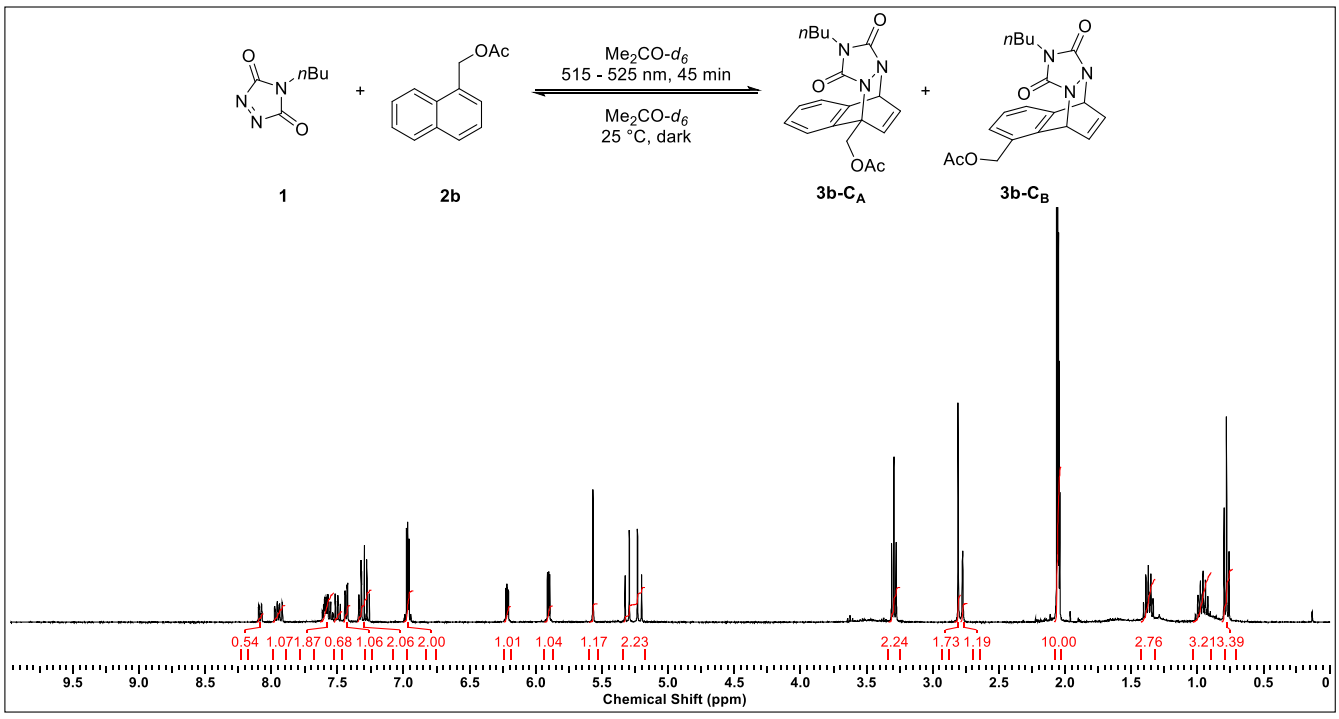


Figure S24. ^{1}H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3b**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of naphthalen-1-ylmethyl acetate **2b** (1.2 eq.).

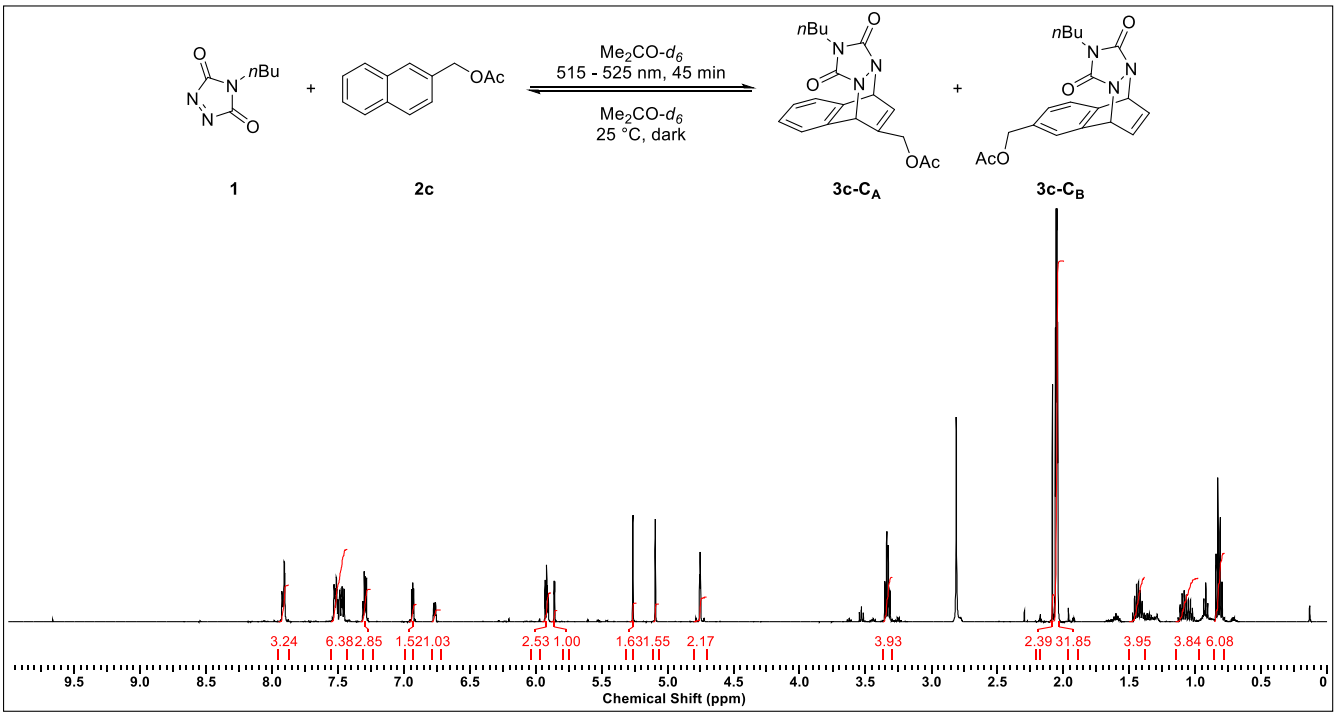


Figure S25. ^{1}H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3c**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of naphthalen-2-ylmethyl acetate **2c** (1.2 eq.).

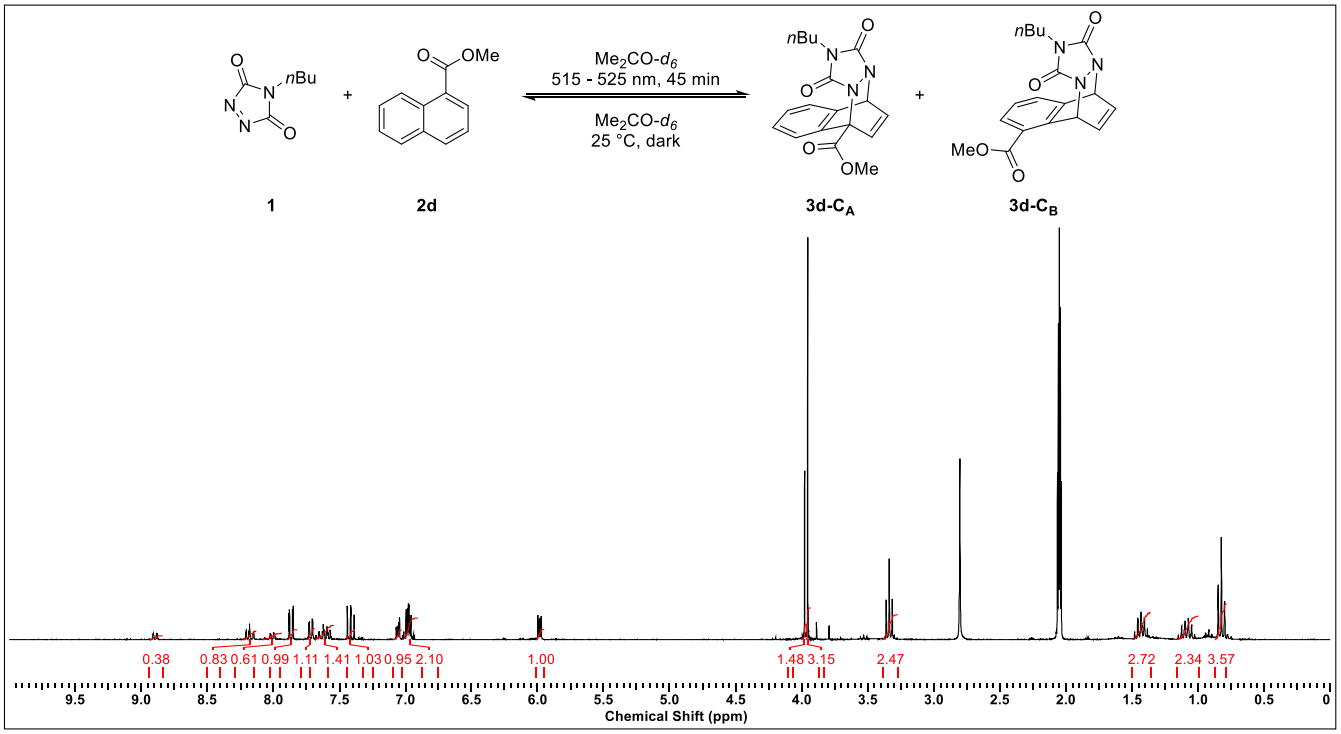


Figure S26. ^{1}H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3d**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of methyl 1-naphthoate **2d** (1.2 eq.).

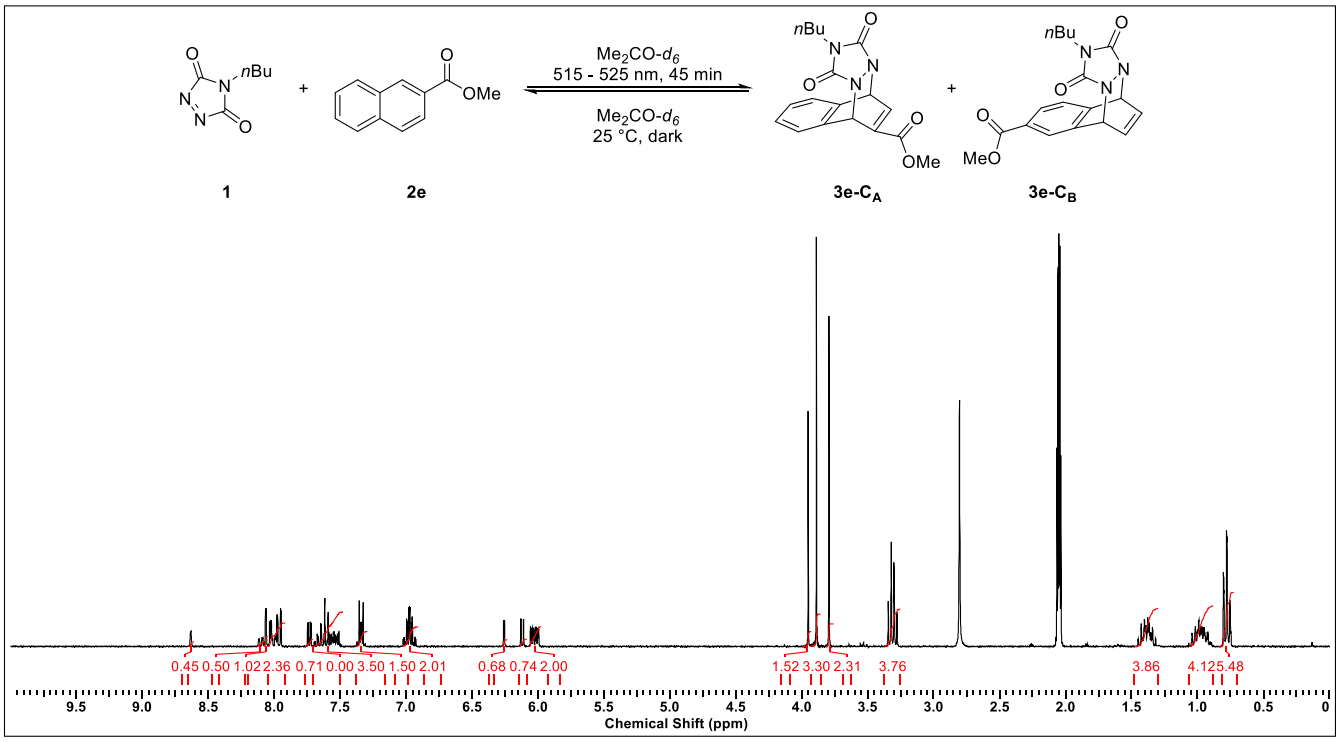


Figure S27. [1]H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3e**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of methyl 2-naphthoate **2e** (1.2 eq.).

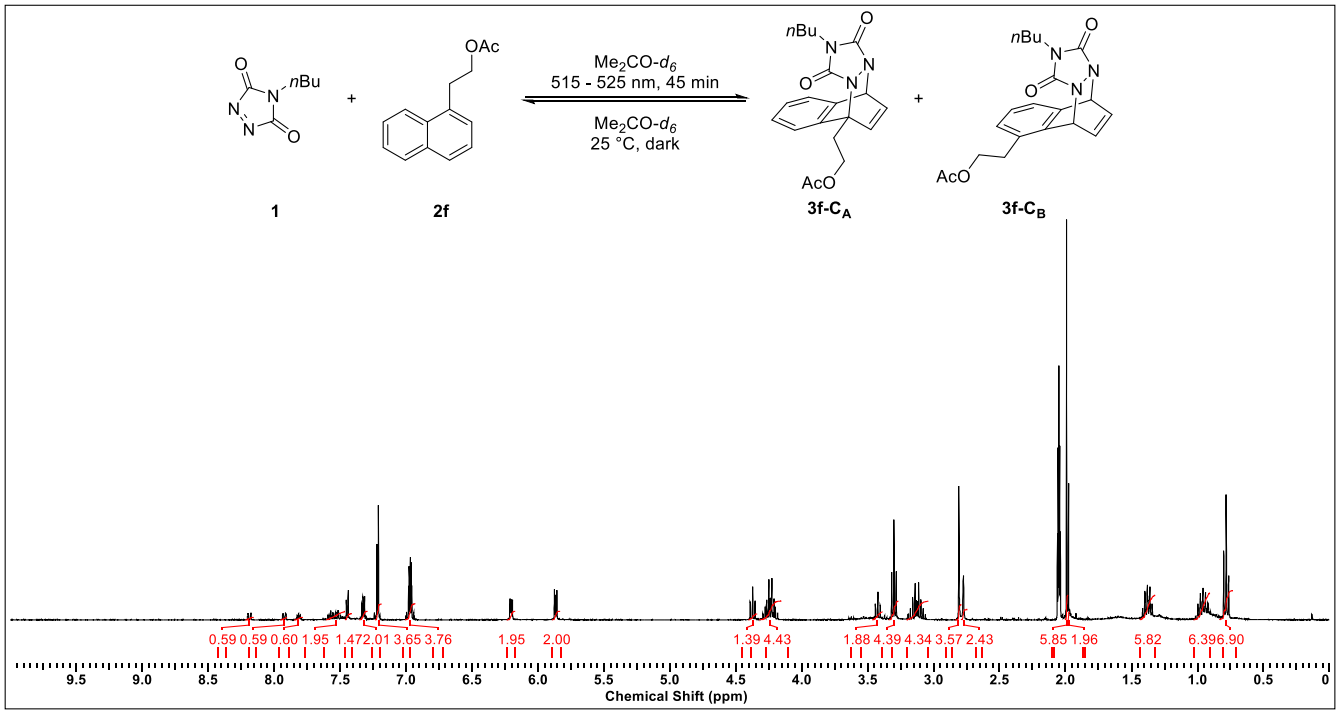


Figure S28. [1]H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3f**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of 2-(naphthalen-1-yl)ethyl acetate **2f** (1.2 eq.).

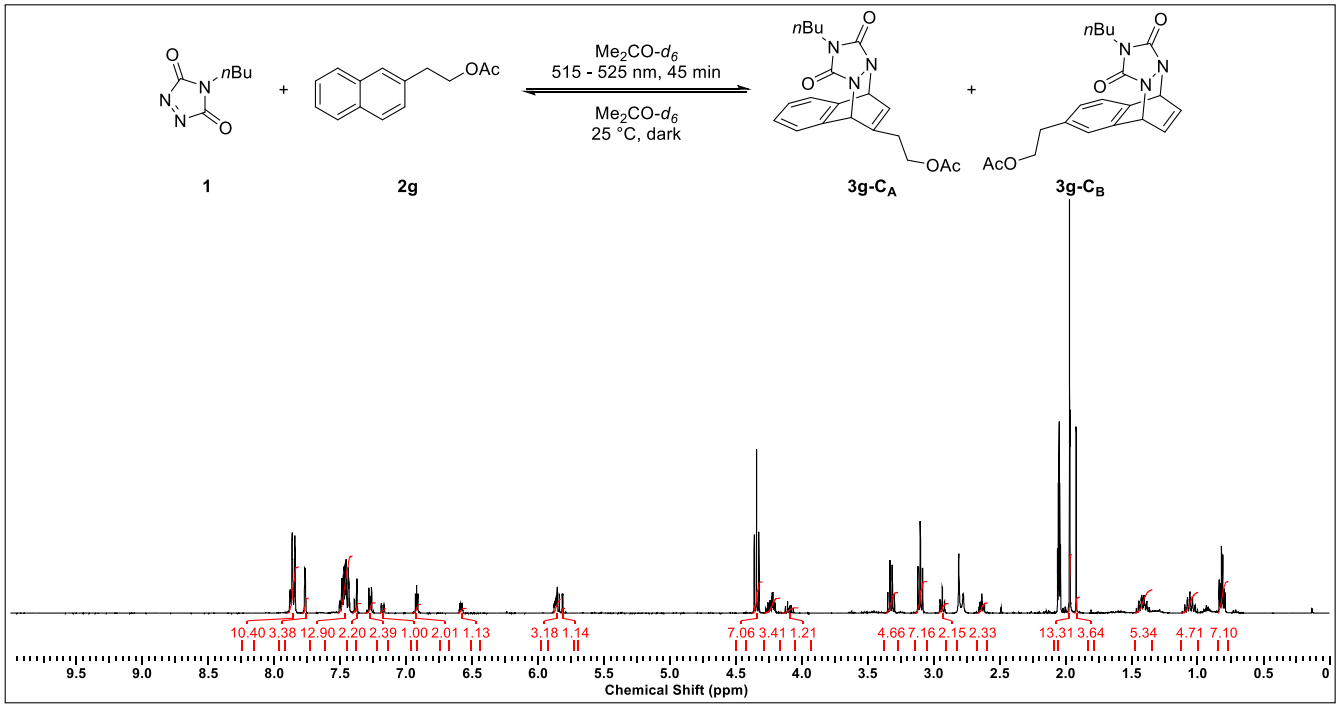


Figure S29. ^{1}H-NMR spectrum (Me_2CO-d_6) of cycloadducts **3g**, recorded after 45-min green light irradiation (λ = 515 – 525 nm, 3 x 3 W LEDs) of 4-*n*-butyl-TAD **1** (15 mM, Me_2CO-d_6) in the presence of 2-(naphthalen-2-yl)ethyl acetate **2g** (1.2 eq.).

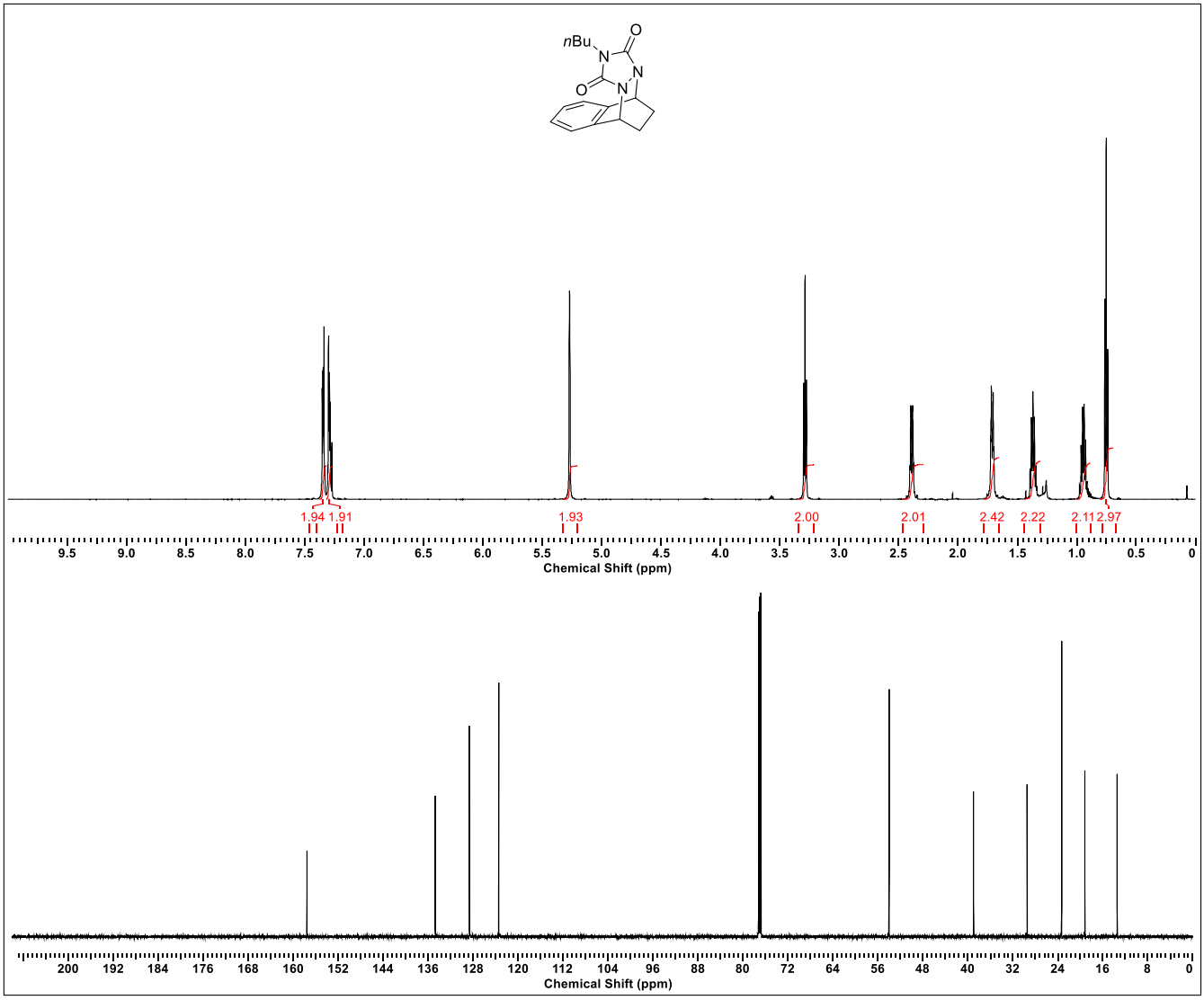


Figure S30. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of the TAD-naphthalene cycloadduct obtained after reduction of **3a**.

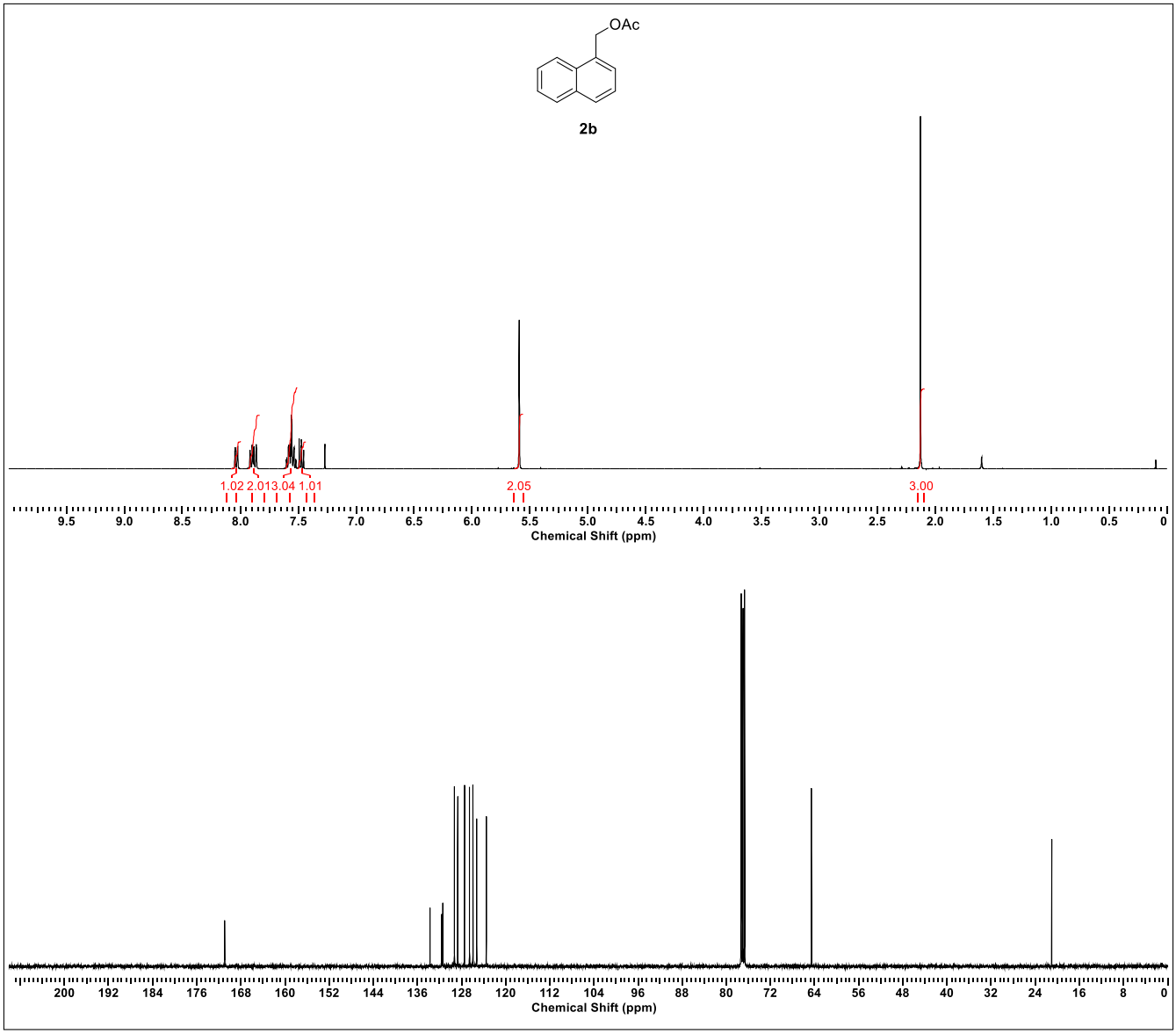


Figure S31. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of naphthalen-1-ylmethyl acetate **2b**.

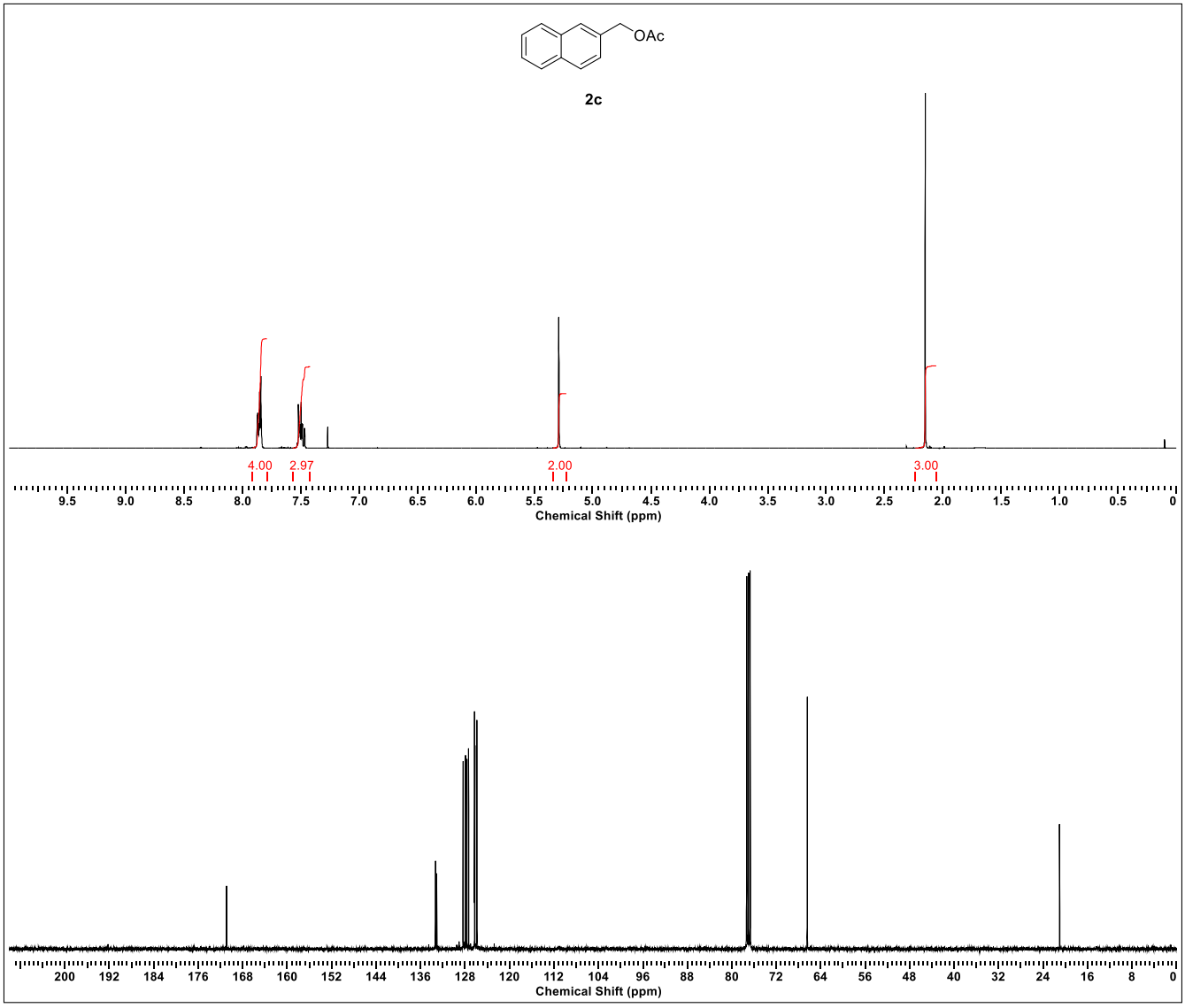


Figure S32. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of naphthalen-2-ylmethyl acetate **2c**.

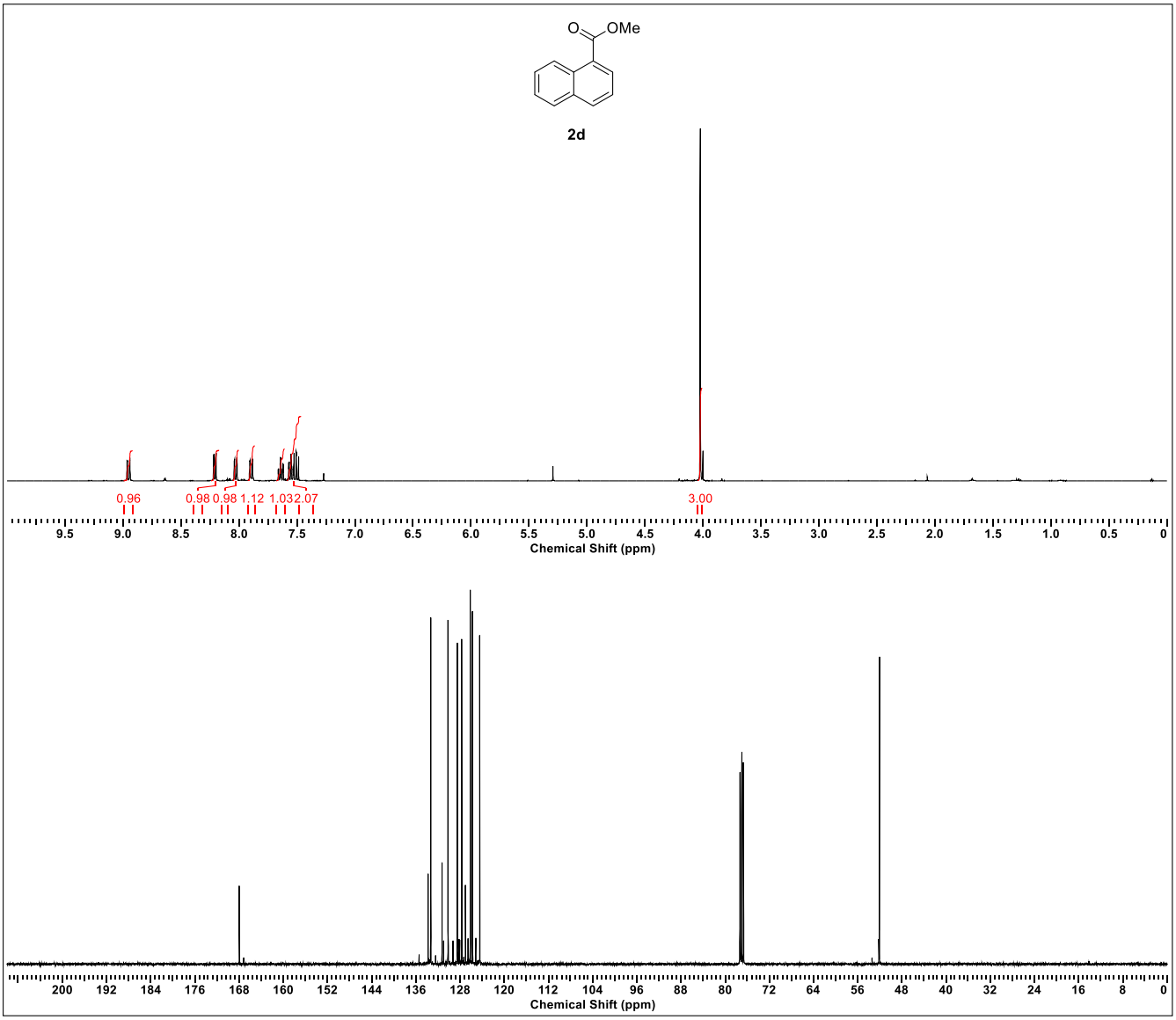


Figure S33. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of methyl 1-naphthoate **2d**.

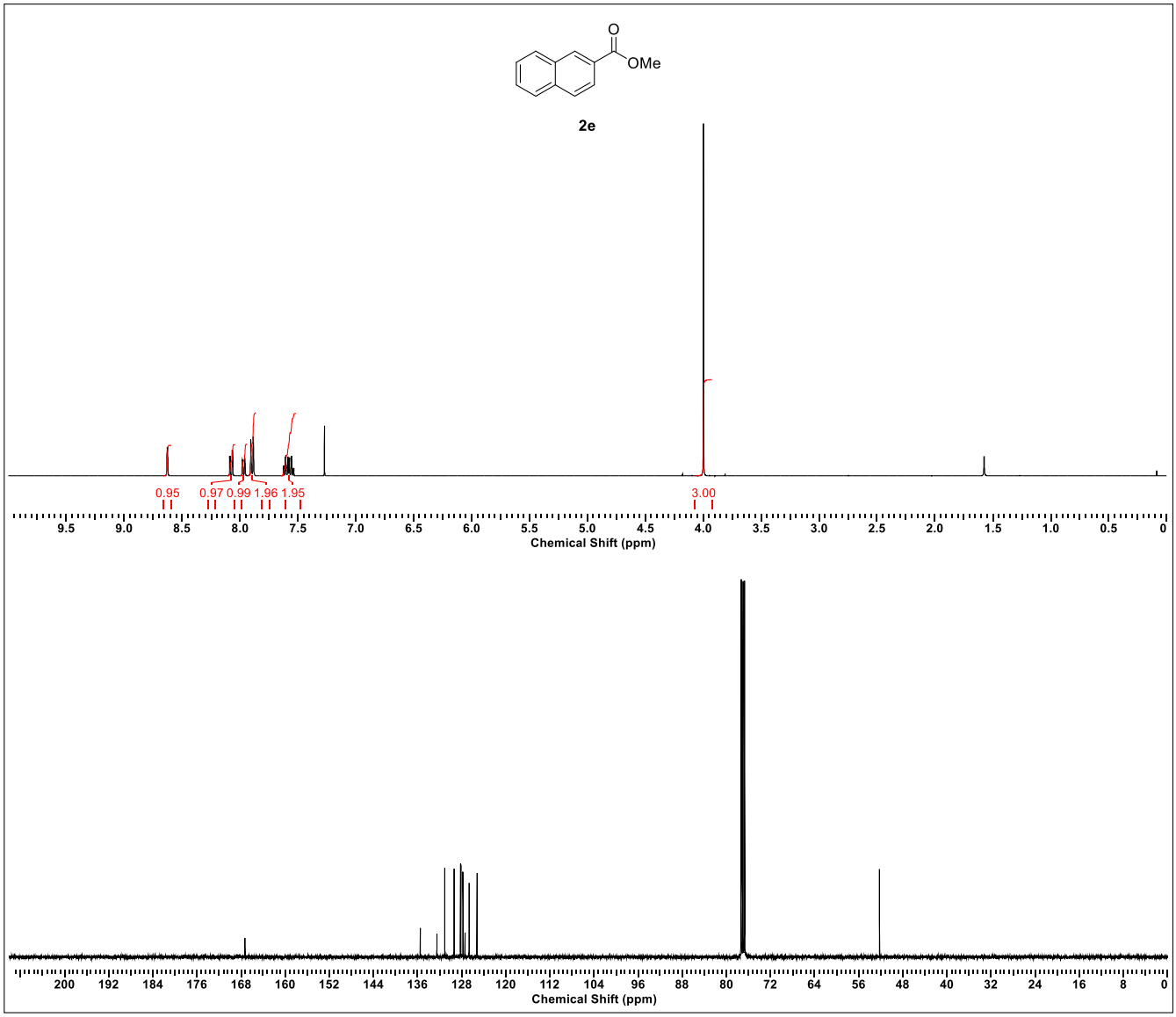


Figure S34. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of methyl 2-naphthoate **2e**.

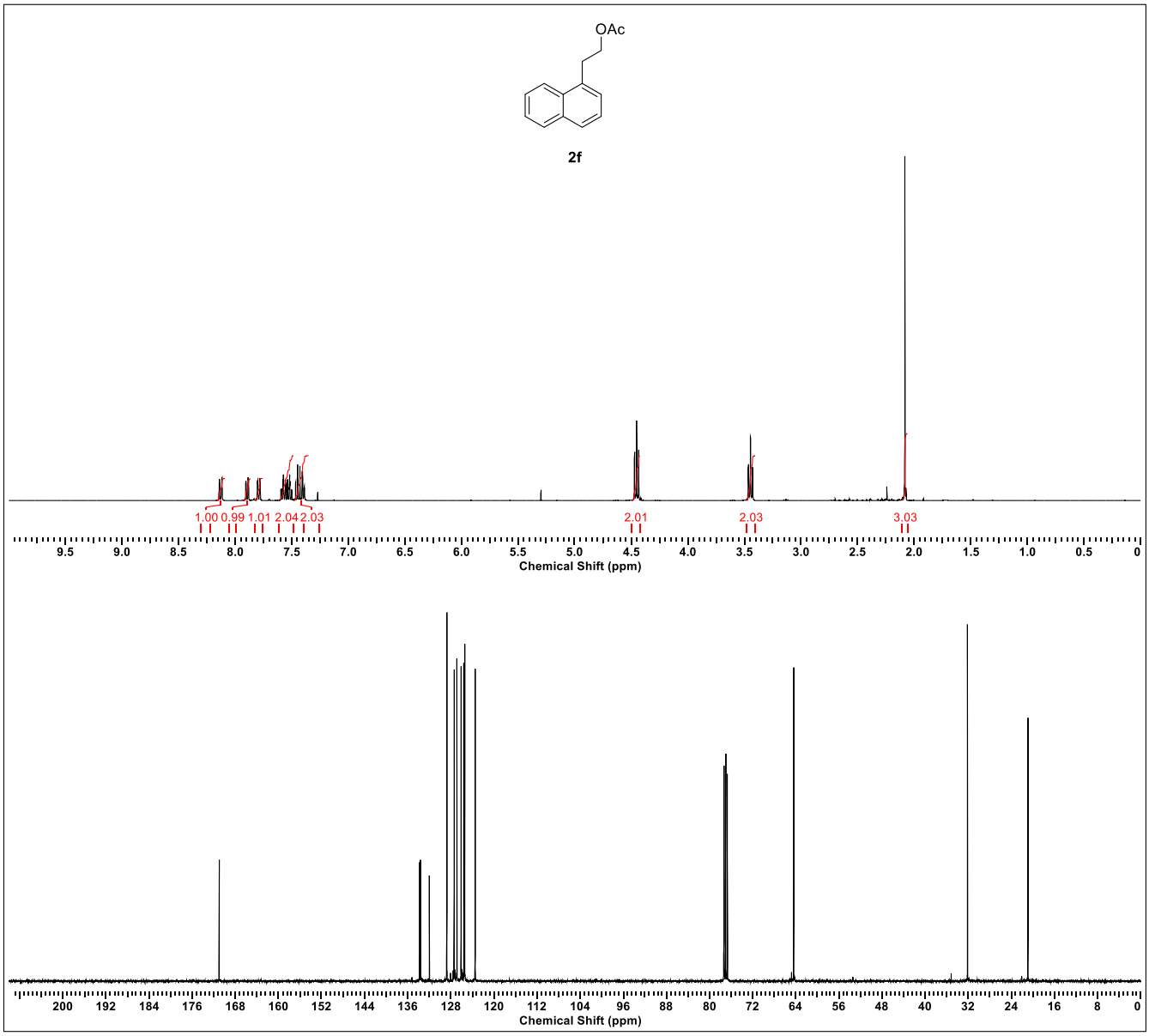


Figure S35. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of 2-(naphthalen-1-yl)ethyl acetate **2f**.

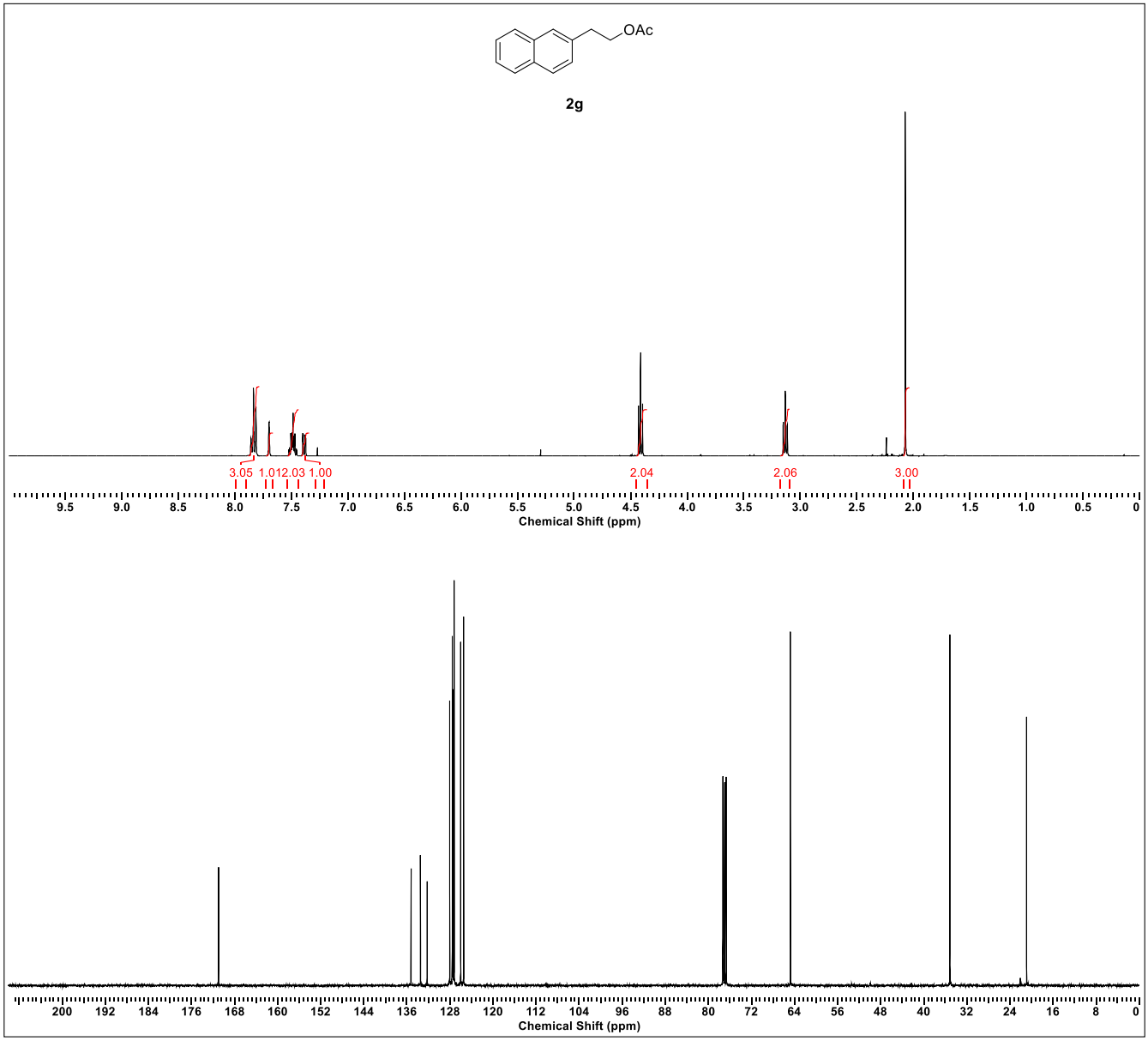


Figure S36. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of 2-(naphthalen-2-yl)ethyl acetate **2g**.

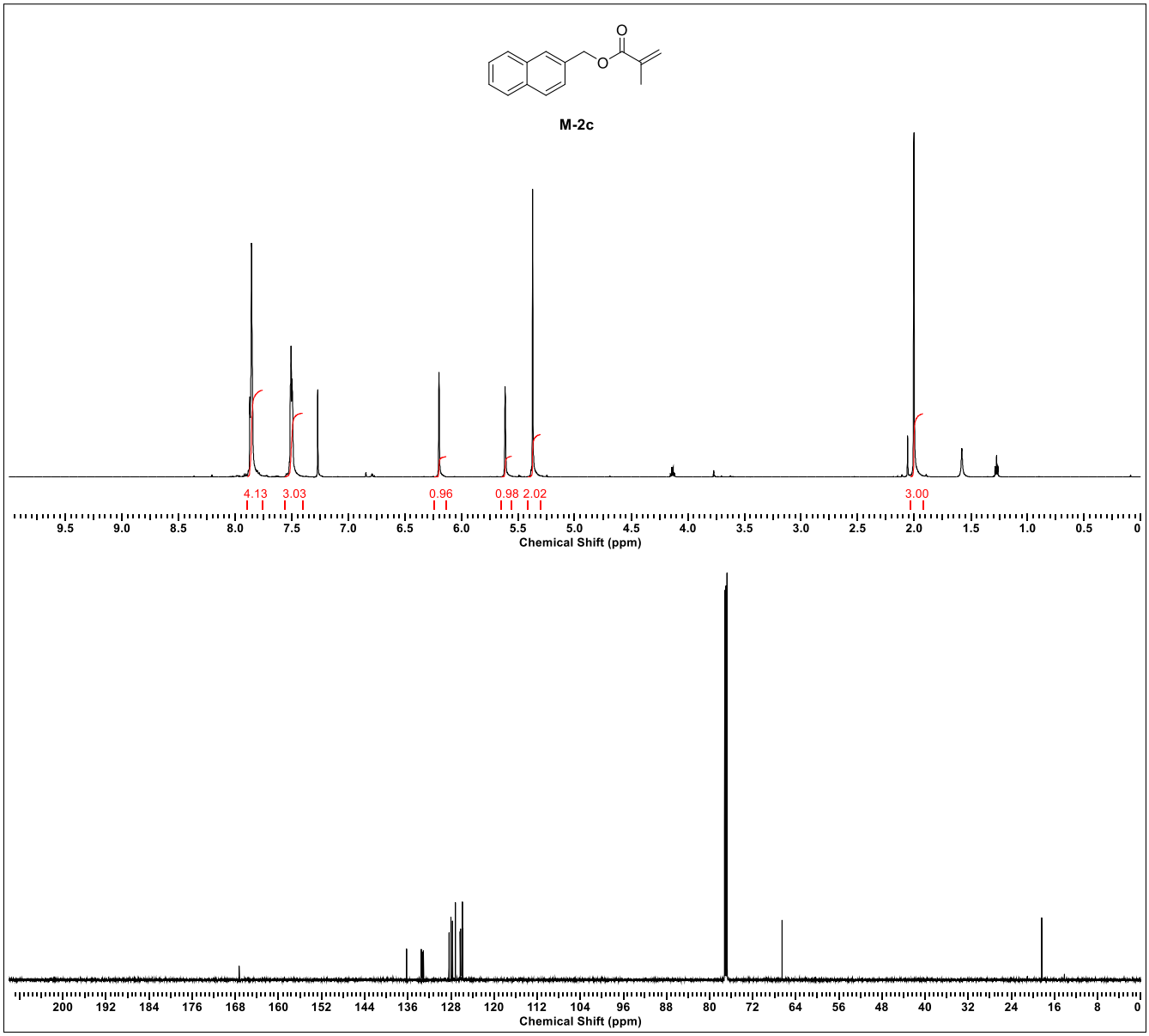


Figure S37. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of naphthalen-2-ylmethyl methacrylate **M-2c**.

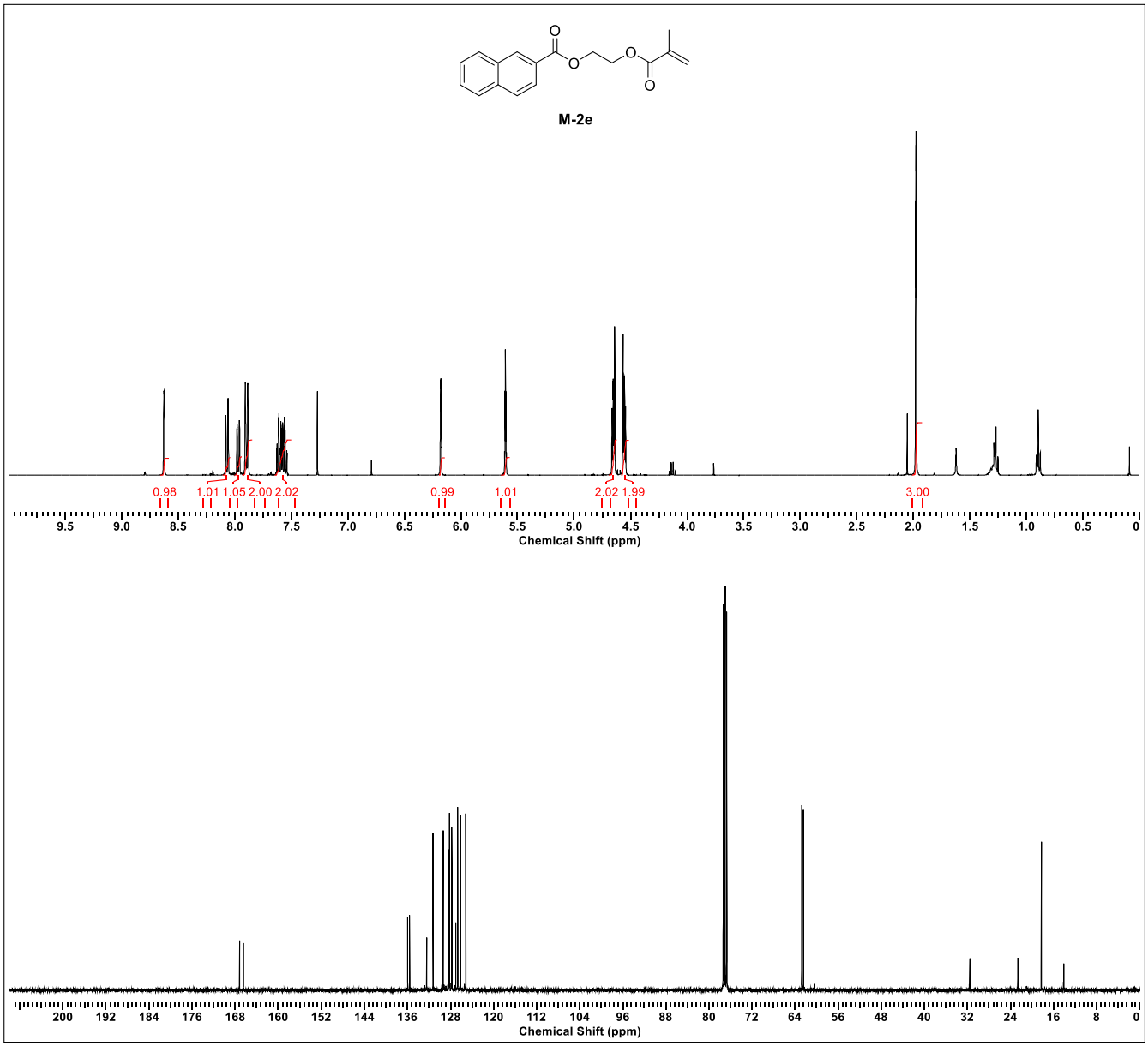


Figure S38. ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of 2-(methacryloyloxy)ethyl 2-naphthoate **M-2e**.

Supplementary references

1. Houck, H. A.; Du Prez, F. E.; Barner-Kowollik, C., Controlling thermal reactivity with different colors of light. *Nat. Commun.* **2017,** *8* (1), 1869.
2. Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J. M.; Du Prez, F. E., Triazolinediones enable ultrafast and reversible click chemistry for the design of dynamic polymer systems. *Nat. Chem.* **2014,** *6* (9), 815-821.
3. Houck, H. A.; De Bruycker, K.; Barner-Kowollik, C.; Winne, J. M.; Du Prez, F. E., Tunable Blocking Agents for Temperature-Controlled Triazolinedione-Based Cross-Linking Reactions. *Macromolecules* **2018,** *51* (8), 3156-3164.