Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Skeletal Photoinduced Rearrangement of Diarylethenes: Ethene Bridge Effects.

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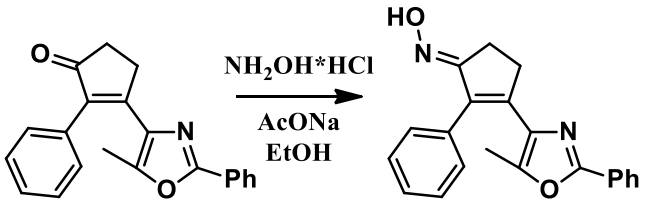
I. Synthesis and characterization of starting diarylethenes

I.1. Synthesis of Monooxime 1c.

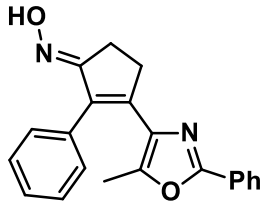


1a **1c**

Scheme S1.

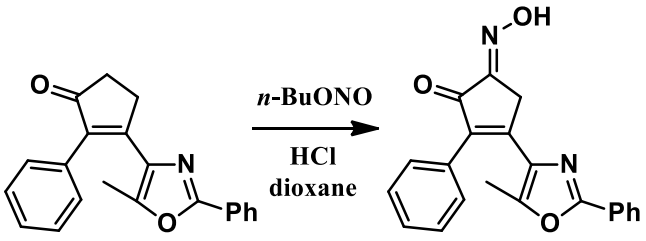
The mixture of diarylcyclopentenone (DCP) **1a** (2.0 mmol), hydroxylamine hydrochloride (6.0 mmol) and anhydrous sodium acetate (6.0 mmol) in ethanol (7 mL) was refluxed for 3 h and poured into crushed ice (70 mL). The residue was filtered off, washed with water (2×30 mL) and recrystallized from cold ethanol.

(*E*)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone oxime (1c)



Beige powder, yield 64% (0.42 g); m.p. 223-225°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.71 (s, 3H, CH_3), 2.79-2.81 (m, 2H, CH_2), 2.94-2.95 (m, 2H, CH_2), 7.28-7.36 (m, 5H, H^{arom}), 7.49-7.50 (m, 3H, H^{arom}), 7.86-7.87 (m, 2H, H^{arom}), 10.69 (s, 1H, NOH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 11.4, 25.9, 32.4, 126.0 (2C), 127.1, 127.6, 128.3 (2C), 129.5 (2C), 129.9 (2C), 130.8, 133.2, 134.6, 137.2, 142.8, 146.2, 159.2, 165.9; HRMS (ESI-TOF) m/z [M + H]+ calc. for $C_{21}H_{18}N_2O_2$ 331.1441, found 331.1441; MS (EI) m/z 330 (21%) [M], 105 (33%), 77 (35%), 43 (100%).

I.2. Synthesis of Ketoximes 1d.



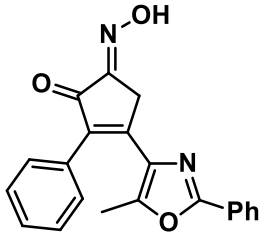
1a **1d**

Scheme S2.

To cooled (12 °C) solution of DCP **1a** (3.0 mmol) and fresh-prepared n-butyl nitrite (3.6 mmol) in dioxane (15 mL) conc. hydrochloric acid (0.36 mL) was added dropwise and solution was stirred at room temperature for 2 h. The reaction mixture was poured into cold water (100 mL) and extracted with ethyl acetate (3×30 mL), combined organic phases were washed with water (50

mL), dried with magnesium sulfate and evaporated in vacuum. The residue was purified by column chromatography eluting by petrol. ester / ethyl acetate 3:1.

(*E*)-5-(hydroxyimino)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone (1d)



Yellow powder, yield 18% (0.19 g); m.p. 211-213°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.97 (s, 3H, CH_3), 3.74 (s, 2H, CH_2), 7.31-7.34 (m, 2H, H^{arom}), 7.37-7.43 (m, 3H, H^{arom}), 7.52-7.53 (m, 3H, H^{arom}), 7.85-7.87 (m, 2H, H^{arom}), 12.51 (s, 1H, NOH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 12.4, 31.1, 126.3 (2C), 126.6, 128.3, 128.5 (2C), 129.6 (2C), 129.8 (2C), 131.3, 132.3,132.6, 140.9, 150.8, 151.9, 152.7, 159.6, 190.2; HRMS (ESI-TOF) m/z [M + H]+ calc. for $C_{21}H_{16}N_2O_3$ 345.1234, found 345.1233; MS (EI) m/z 344 (30%) [M], 196 (19%), 154 (38%), 105 (48%), 77 (46%), 43 (100%).

II. ^{1}H NMR monitoring of photoreaction 1d.

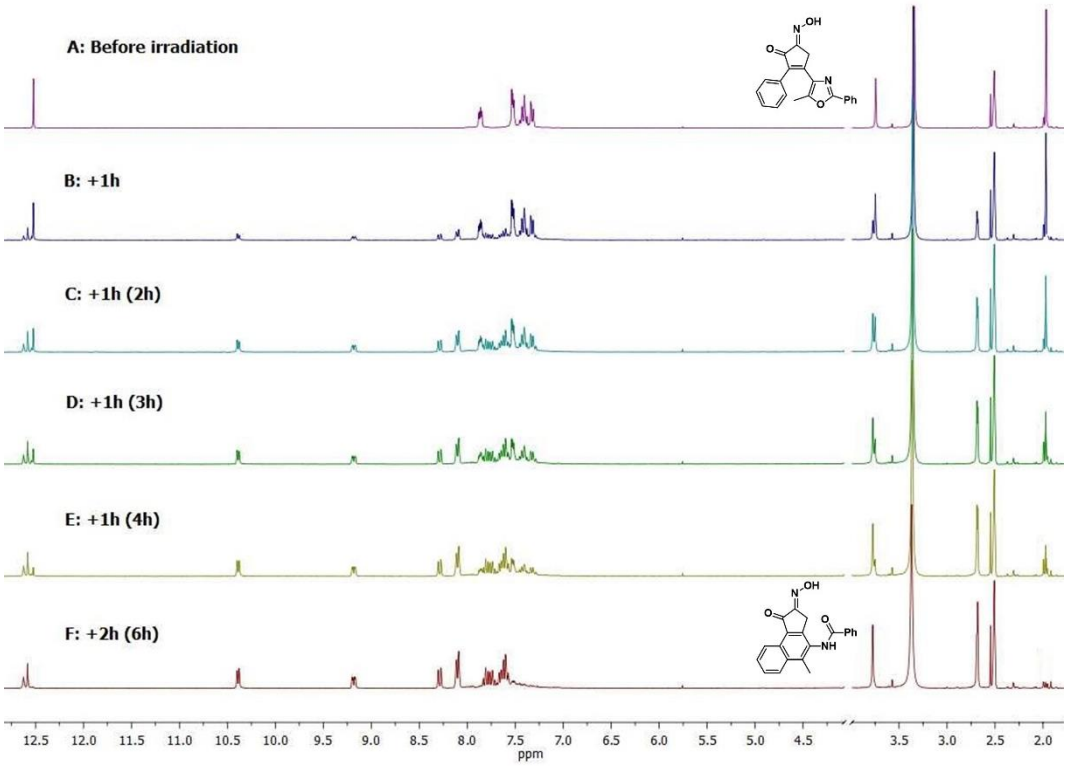


Fig. S1. ^{1}H NMR monitoring of photoreaction of **1d** in DMSO-d_6 induced by UV light (365 nm).

III. DFT calculations

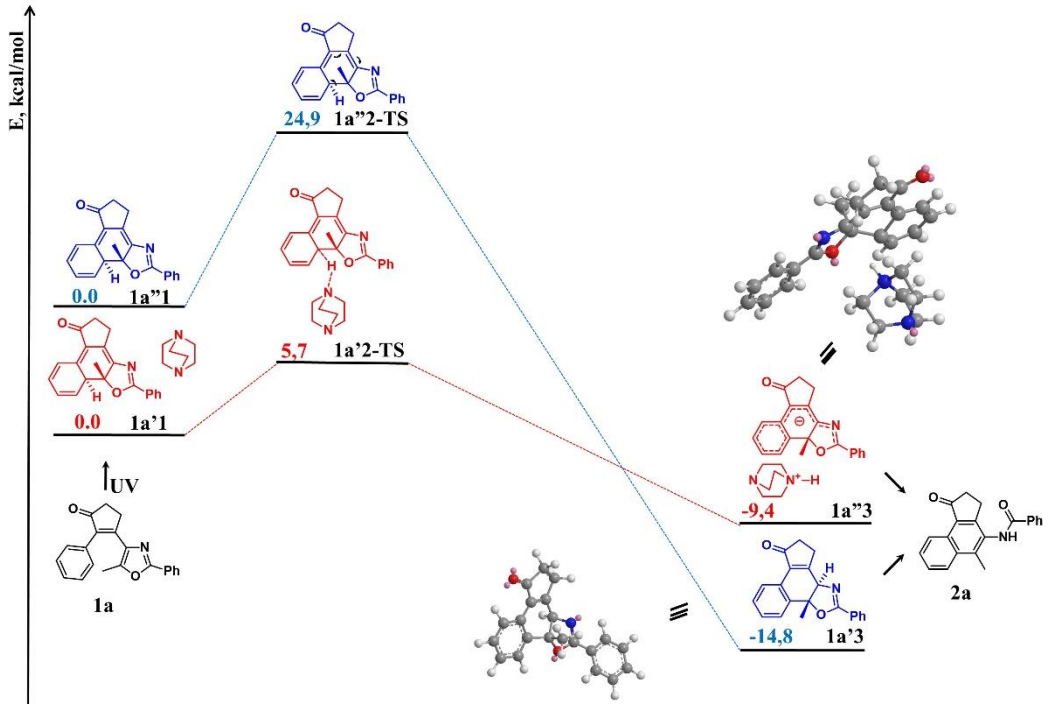


Fig. S2. Energy profile of the [1,5]-shift and proton elimination of a **1a**.

Cartesian coordinate columns of the optimized structure of compound **1f"1** (B3LYP/6-31g(d,p)

PCM=toluene

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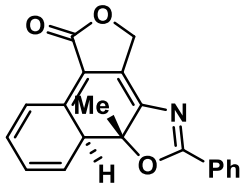
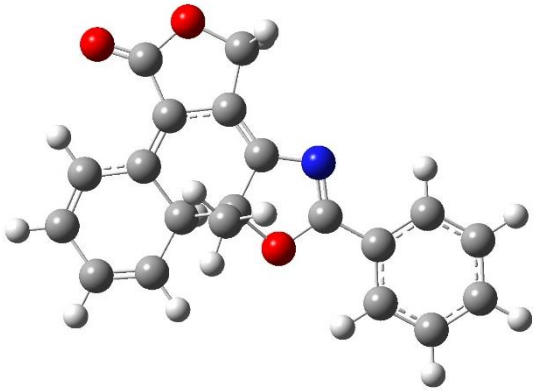
EE + Thermal Enthalpy Correction = -1051.265438

EE + Thermal Free Energy Correction = -1051.331207





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38	H	0.1469780	1.9789300	2.2139890
39	H	-0.4692440	0.3542680	2.5859960

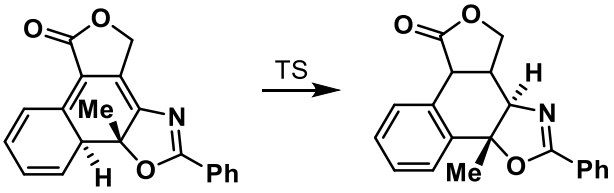
Transition state of [1,5]-shift of compound **1f"2** (B3LYP/6-31g(d,p), Berny algorithm)

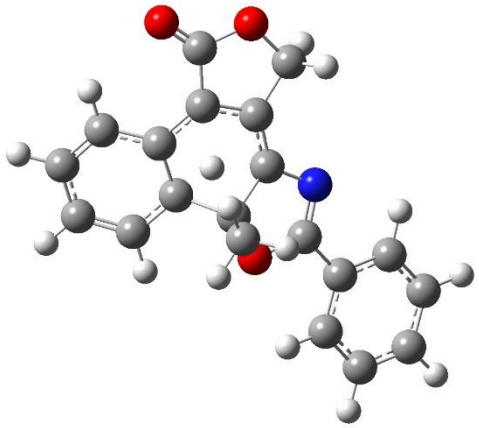
PCM=toluene

Imaginary Freq = 1

EE + Thermal Enthalpy Correction = -1051.225175

EE + Thermal Free Energy Correction = -1051.290168





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35	H	-5.9701220	1.9144340	0.3927900
36	H	-3.4990980	1.8504250	0.6259210
37	H	1.2542180	0.2176730	2.5795600
38	H	0.1102410	1.5716450	2.6591020
39	H	-0.4866100	-0.0998130	2.7364920

Cartesian coordinate columns of the optimized structure of compound **1f"3** (B3LYP/6-31g(d,p)

PCM=toluene

Imaginary Freq = 0

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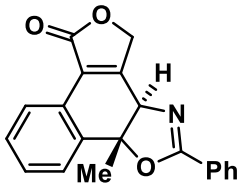
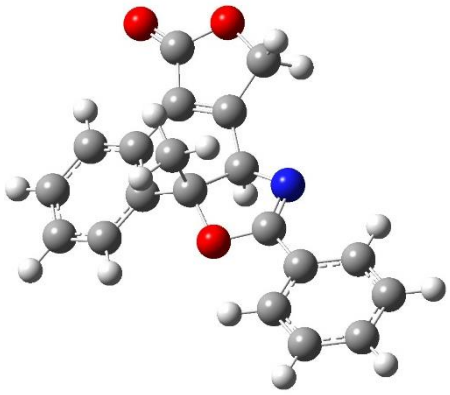
EE + Thermal Free Energy Correction = -1051.352311





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39	H	1.1219380	-0.0844040	2.2828290

Cartesian coordinate columns of the optimized structure of compound **1f'1** (B3LYP/6-31g(d,p)

PCM=toluene

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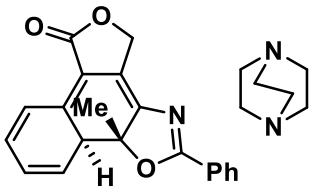

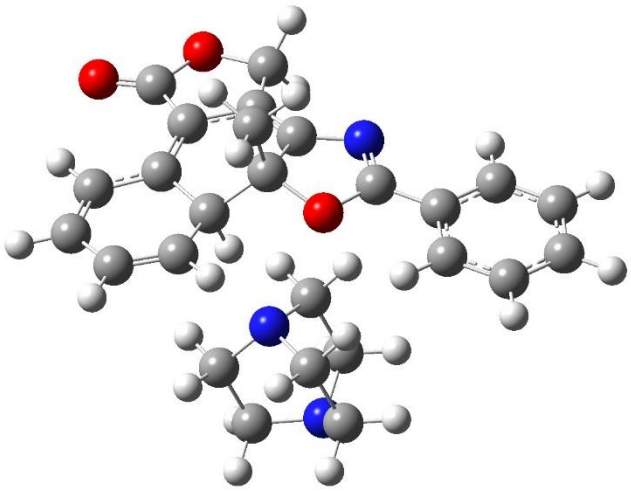

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Transition state of [1,5]-shift of compound **1f'2** (B3LYP/6-31g(d,p), Berny algorithm)

PCM=toluene

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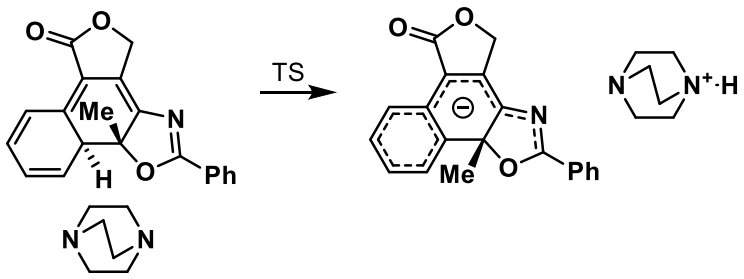
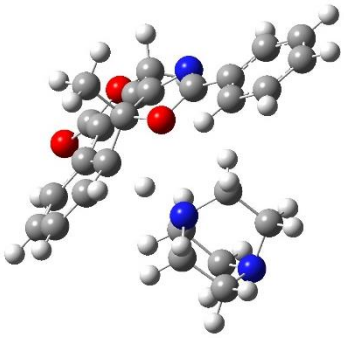
EE + Thermal Enthalpy Correction = -1396.421476

EE + Thermal Free Energy Correction = -1396.505854





1	C	2.3657480	-1.6045860	-0.4157780
2	C	1.1233120	-1.9891160	-1.0225840
3	C	1.4426220	-2.5040010	-2.4010780
4	O	2.8819430	-2.4517270	-2.4963420
5	C	3.4389790	-1.9003850	-1.3514390
6	C	2.4084170	-0.8433220	0.7571080
7	C	1.1239910	-0.4475520	1.3865850
8	C	-0.0205070	-1.4068470	1.1055310
9	C	-0.0438580	-1.7999070	-0.3639360
10	C	3.6149920	-0.3295250	1.3298370
11	C	3.5943700	0.3813310	2.5031010
12	C	2.3756320	0.6315480	3.2130690
13	C	1.1949260	0.1750710	2.7020490
14	O	-1.3425740	-0.7580370	1.2142050
15	C	-2.0446740	-1.2072770	0.1193510
16	N	-1.3614700	-1.8121970	-0.8075520
17	O	4.6441290	-1.7355250	-1.2767750
18	C	-3.4719380	-0.9045460	0.0752640
19	C	-4.2251510	-1.2501090	-1.0619380
20	C	-5.5849570	-0.9645120	-1.1118000
21	C	-6.2126820	-0.3301250	-0.0338080

22	C	-5.4705110	0.0145310	1.0975050
23	C	-4.1075080	-0.2711060	1.1571320
24	C	-0.0433360	-2.6299120	2.0366880
25	C	-0.7545930	3.9100910	-0.1863490
26	N	0.1489730	4.0373600	-1.3414320
27	C	-0.5246830	2.5509210	0.5452850
28	C	-0.0738210	2.9005660	-2.2499080
29	C	1.8203490	2.6880010	-0.0702700
30	N	0.6005140	1.8348020	-0.1142850
31	C	1.5418430	4.0029210	-0.8664630
32	C	0.2501090	1.5511770	-1.5341290
33	H	1.1209000	-3.5398120	-2.5541290
34	H	1.0148680	-1.8925280	-3.2047990
35	H	0.8521400	0.6421230	0.6247550
36	H	4.5488510	-0.5567300	0.8278320
37	H	4.5304530	0.7404850	2.9225560
38	H	2.4053950	1.1487790	4.1671190
39	H	0.2640360	0.3245230	3.2436520
40	H	-3.7259490	-1.7401810	-1.8906470
41	H	-6.1598670	-1.2355890	-1.9922400
42	H	-7.2750150	-0.1091950	-0.0762020
43	H	-5.9549510	0.5024660	1.9380660
44	H	-3.5296290	-0.0170820	2.0384970
45	H	0.9070640	-3.1656500	1.9613120
46	H	-0.1880530	-2.3225790	3.0765880
47	H	-0.8497070	-3.3128050	1.7540020
48	H	-0.5710910	4.7524730	0.4876710
49	H	-1.7865140	3.9890180	-0.5416160
50	H	-0.2568780	2.6864230	1.5972020
51	H	-1.3993630	1.8977580	0.5064520
52	H	-1.1159620	2.9259250	-2.5826700
53	H	0.5586270	3.0318990	-3.1331030

54	H	2.0471420	2.8800340	0.9809830
55	H	2.6475260	2.1114750	-0.4913170
56	H	2.2030480	4.0808760	-1.7346750
57	H	1.7171730	4.8809460	-0.2373760
58	H	-0.5949290	0.8596090	-1.5435950
59	H	1.1041530	1.0399180	-1.9842860

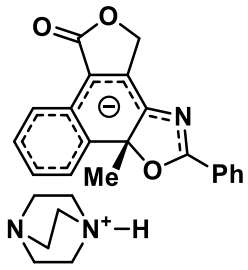
Cartesian coordinate columns of the optimized structure of compound **1f'3** (B3LYP/6-31g(d,p)

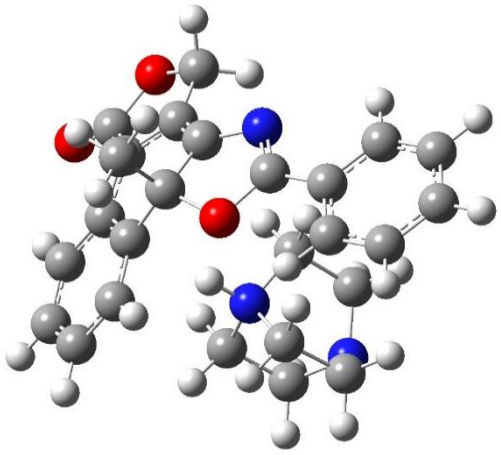
PCM=toluene

Imaginary Freq = 0

EE + Thermal Enthalpy Correction = -1396.442785

EE + Thermal Free Energy Correction = -1396.529484





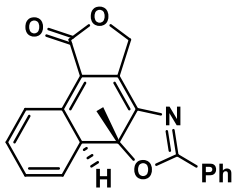
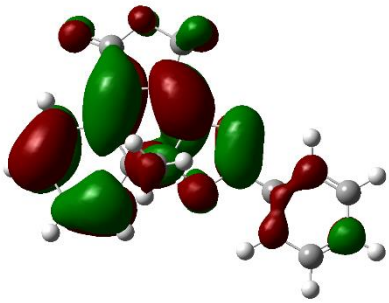
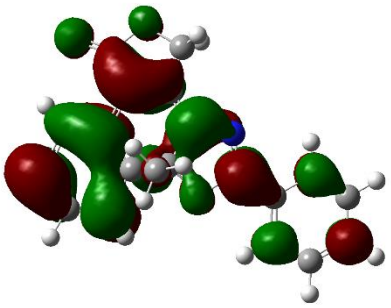
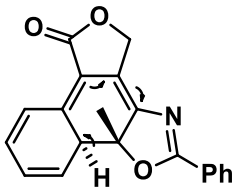
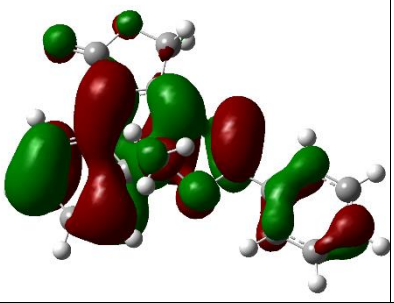
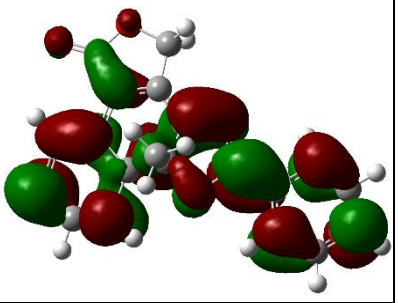
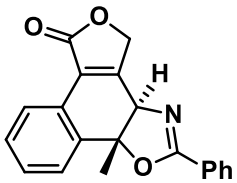
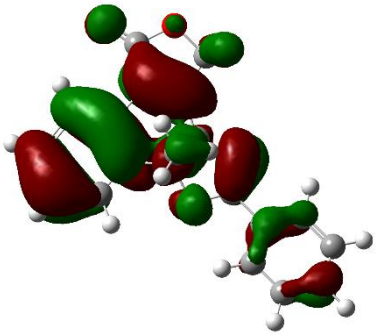
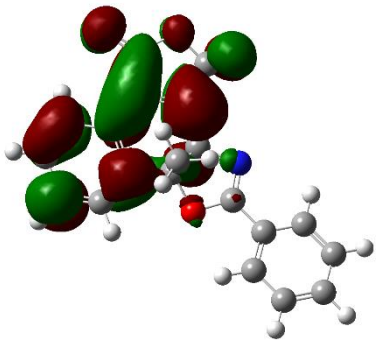
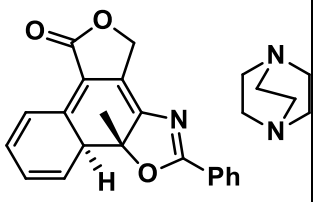
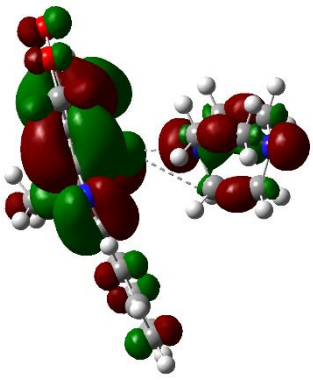
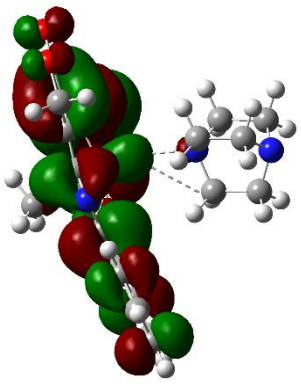
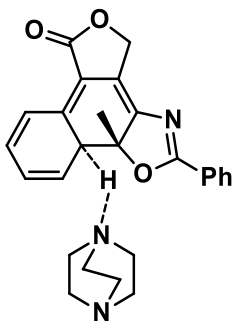
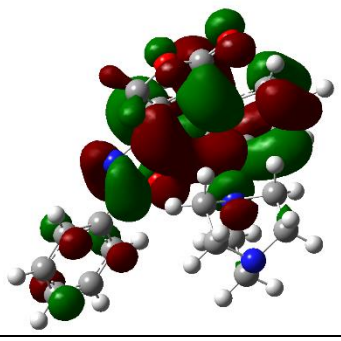
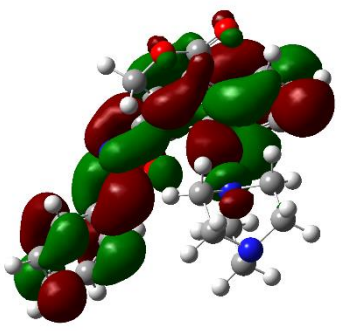
1	C	2.4621410	-1.4628010	-0.5348830
2	C	1.2590540	-1.7965040	-1.2090020
3	C	1.6044740	-1.9982690	-2.6619690
4	O	3.0160840	-1.7399330	-2.7551890
5	C	3.5279570	-1.3936680	-1.4975490
6	C	2.4282360	-0.9198000	0.7957920
7	C	1.1884620	-0.9391550	1.5221560
8	C	0.0457860	-1.7678050	0.9689120
9	C	0.0653580	-1.8154200	-0.5472770
10	C	3.5352650	-0.2698830	1.4028410
11	C	3.4180000	0.3388420	2.6438970
12	C	2.1946950	0.3389150	3.3373780
13	C	1.0984100	-0.3125400	2.7757060
14	O	-1.2735950	-1.1394850	1.1894240
15	C	-1.9520340	-1.3126710	-0.0078680
16	N	-1.2333040	-1.6957350	-1.0229970
17	O	4.7072580	-1.0824680	-1.3962210
18	C	-3.3618560	-0.9519880	-0.0300840
19	C	-4.0932600	-1.0306790	-1.2326390
20	C	-5.4380460	-0.6812960	-1.2603720

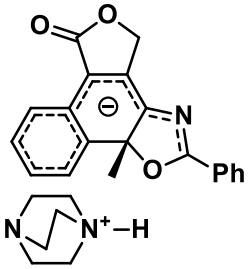
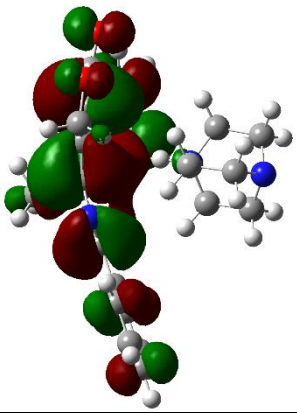
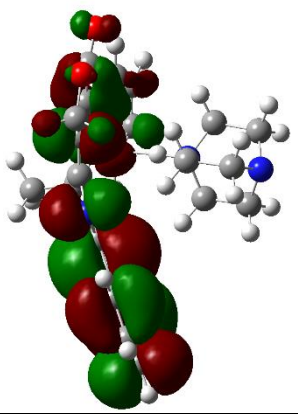
21	C	-6.0817780	-0.2444170	-0.0958700
22	C	-5.3650410	-0.1661580	1.0996470
23	C	-4.0169040	-0.5194730	1.1388220
24	C	-0.0088420	-3.1660560	1.6093630
25	C	-1.0535430	3.6619630	0.0945530
26	N	-0.0906970	4.0212760	-0.9561220
27	C	-0.6876890	2.2934090	0.7396910
28	C	-0.1225500	3.0053450	-2.0182940
29	C	1.6909350	2.7187780	0.2090360
30	N	0.5307260	1.7722180	0.0162220
31	C	1.2608780	4.0939140	-0.3834120
32	C	0.2404420	1.5997800	-1.4567950
33	H	1.4090570	-3.0241570	-2.9962290
34	H	1.0699950	-1.3197890	-3.3392100
35	H	0.7802070	0.8517100	0.4271900
36	H	4.4735240	-0.2563930	0.8588480
37	H	4.2858110	0.8250880	3.0823950
38	H	2.1132390	0.8081780	4.3131550
39	H	0.1536890	-0.3523350	3.3118400
40	H	-3.5872520	-1.3711560	-2.1296230
41	H	-5.9910890	-0.7493160	-2.1928120
42	H	-7.1330840	0.0260950	-0.1218320
43	H	-5.8592570	0.1639590	2.0089880
44	H	-3.4642890	-0.4765900	2.0706600
45	H	0.9412390	-3.6812660	1.4410820
46	H	-0.1766910	-3.0882310	2.6884620
47	H	-0.8112430	-3.7614850	1.1630310
48	H	-1.0579600	4.4506820	0.8511310
49	H	-2.0516930	3.6187930	-0.3482030
50	H	-0.4142450	2.3702230	1.7933670
51	H	-1.4676830	1.5377870	0.6423800
52	H	-1.1225620	2.9917020	-2.4587700
53	H	0.5820800	3.2971360	-2.8009770
54	H	1.9013500	2.7482740	1.2789840
55	H	2.5497970	2.2763960	-0.2972080

56	H	1.9571990	4.4038100	-1.1665510
57	H	1.2692090	4.8630480	0.3931450
58	H	-0.5655250	0.8697960	-1.5436960
59	H	1.1398120	1.1746430	-1.9040580

IV. Molecular orbitals

Molecular orbitals of **1f** and **2f** according to B3LYP/6-31g(d,p) level of theory.

№/ №	Compound	HOMO	LUMO
1			
2			
3			
4			
5			

6			

V. UV-vis spectra of obtained compounds

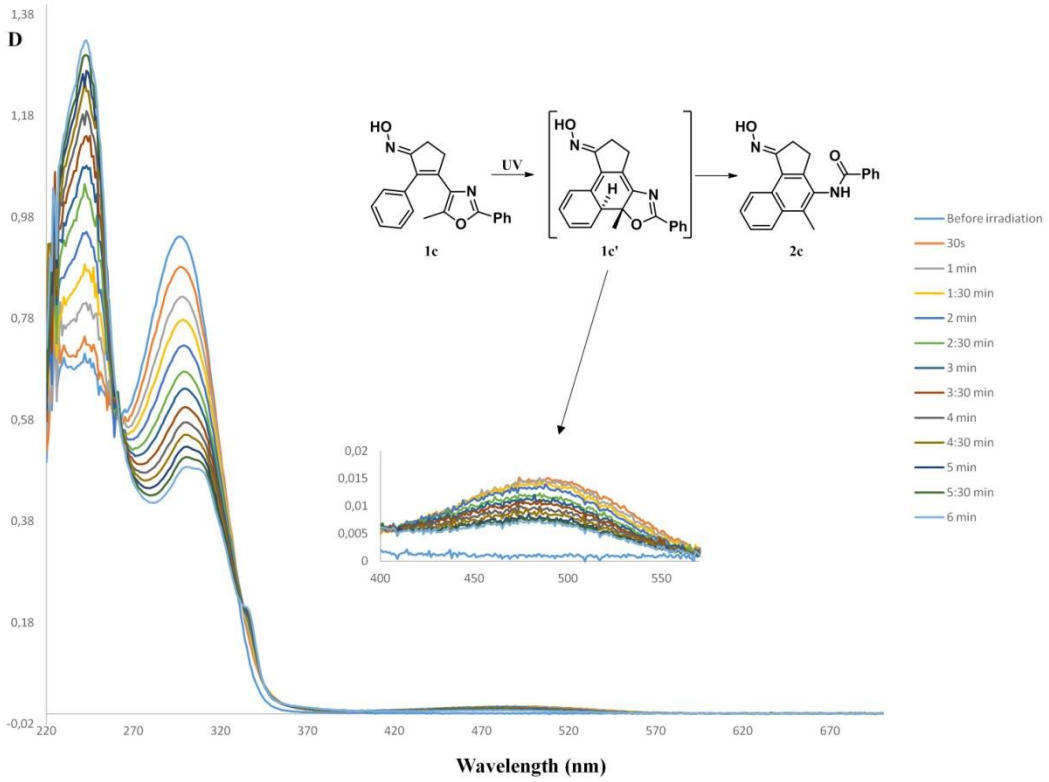


Fig. S3. Absorption spectra of an acetonitrile solution of **1c** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

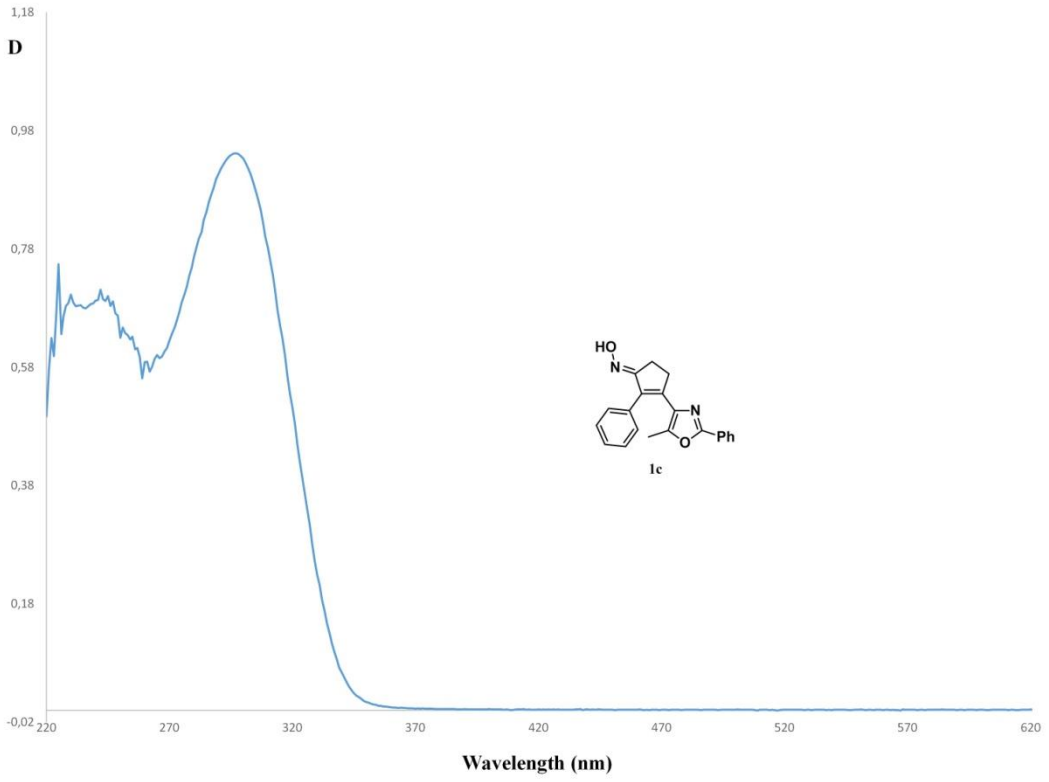


Fig. S4. UV absorption spectrum of diarylethene **1c** in acetonitrile solution (C = 3.0×10^{-5} M, T = 298°K).

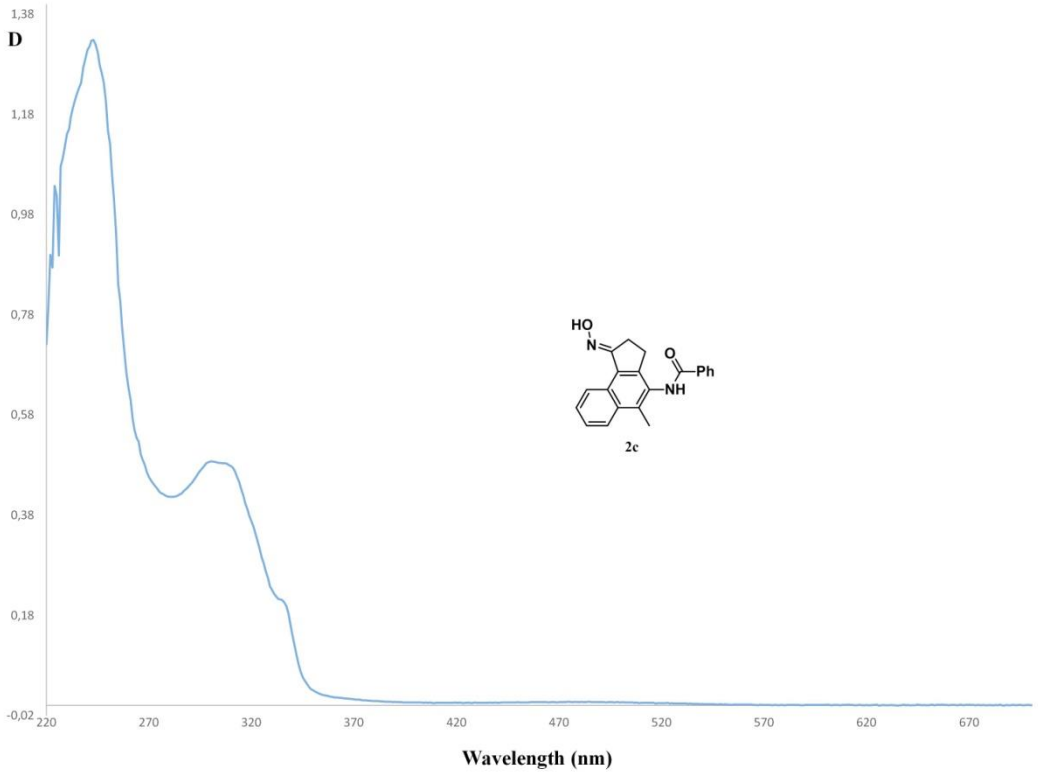


Fig. S5. UV absorption spectrum of photoproduct **2c** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

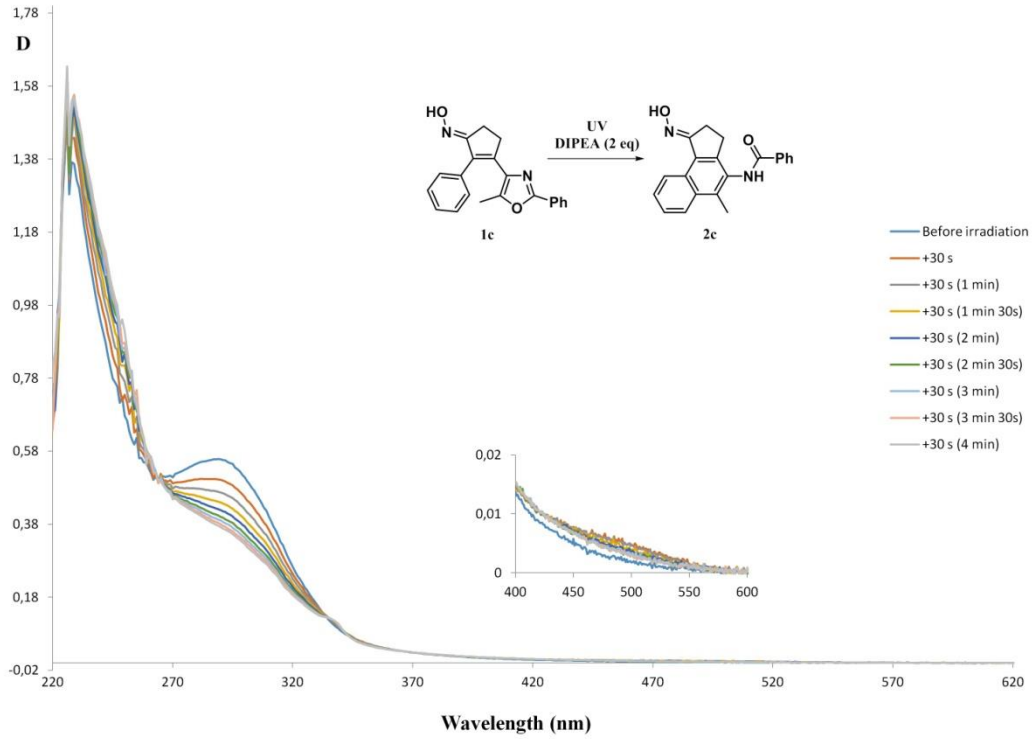


Fig. S6. Absorption spectra of an acetonitrile solution of **1c** with 2 eq DIPEA obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

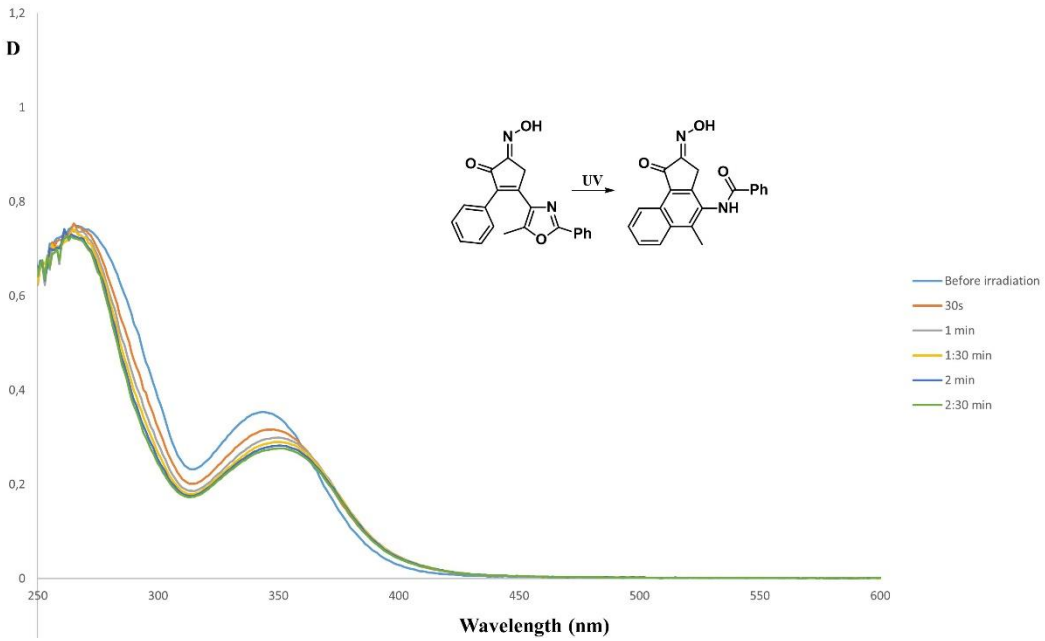


Fig. S7. Absorption spectra of an acetonitrile solution of **1d** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

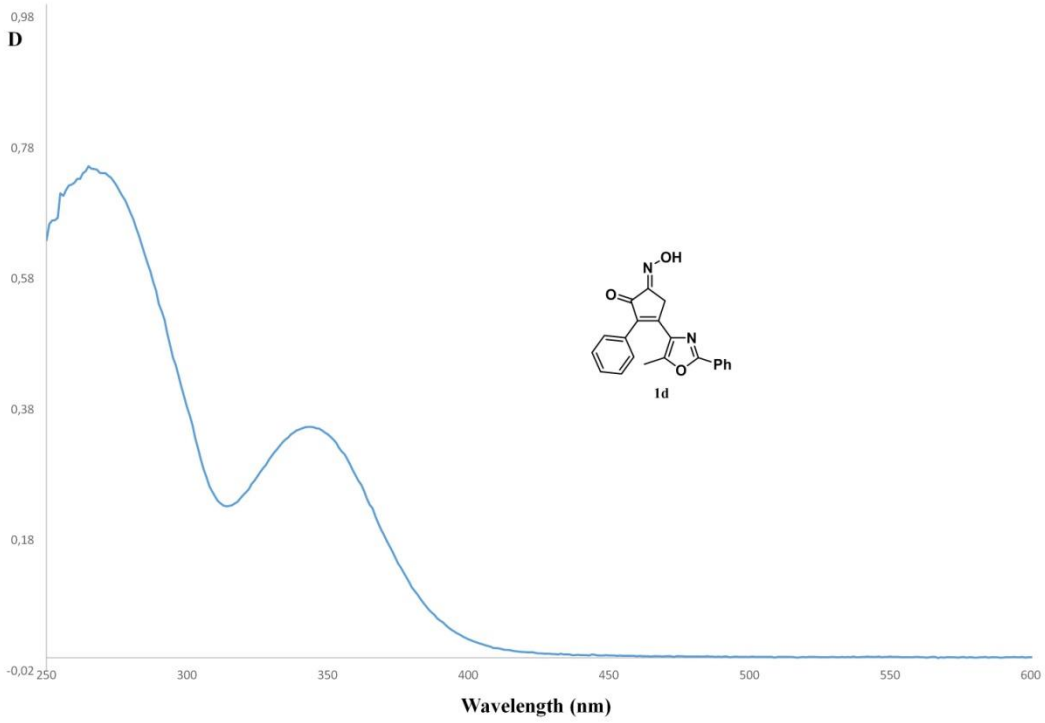


Fig. S8. UV absorption spectrum of diarylethene **1d** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

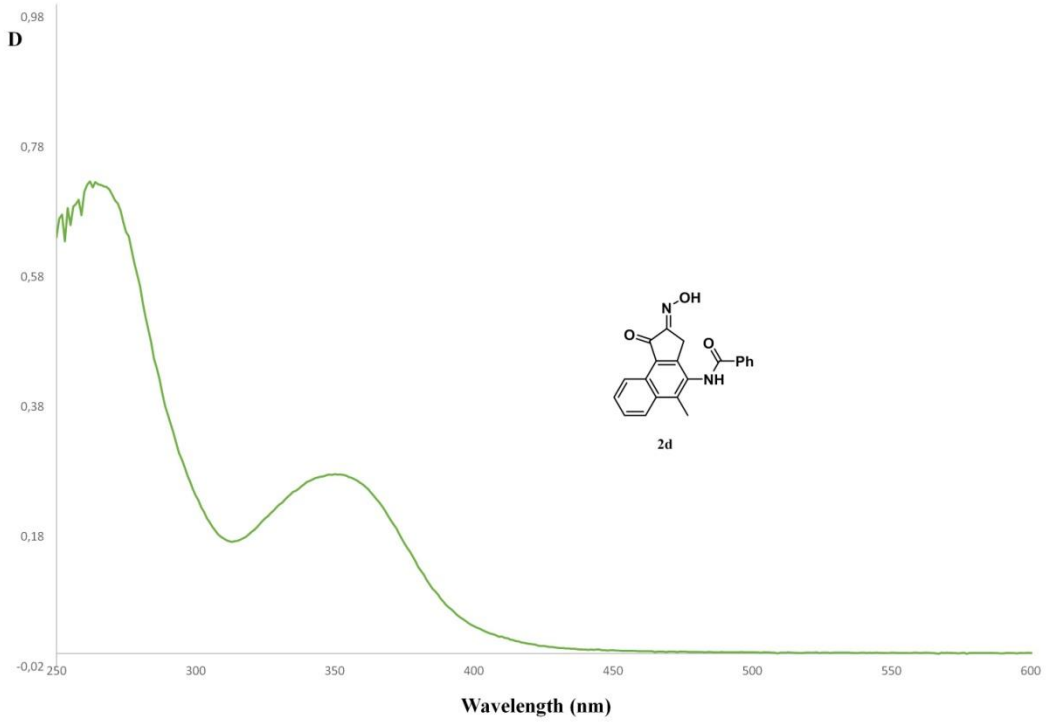


Fig. S9. UV absorption spectrum of photoproduct 2**d** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

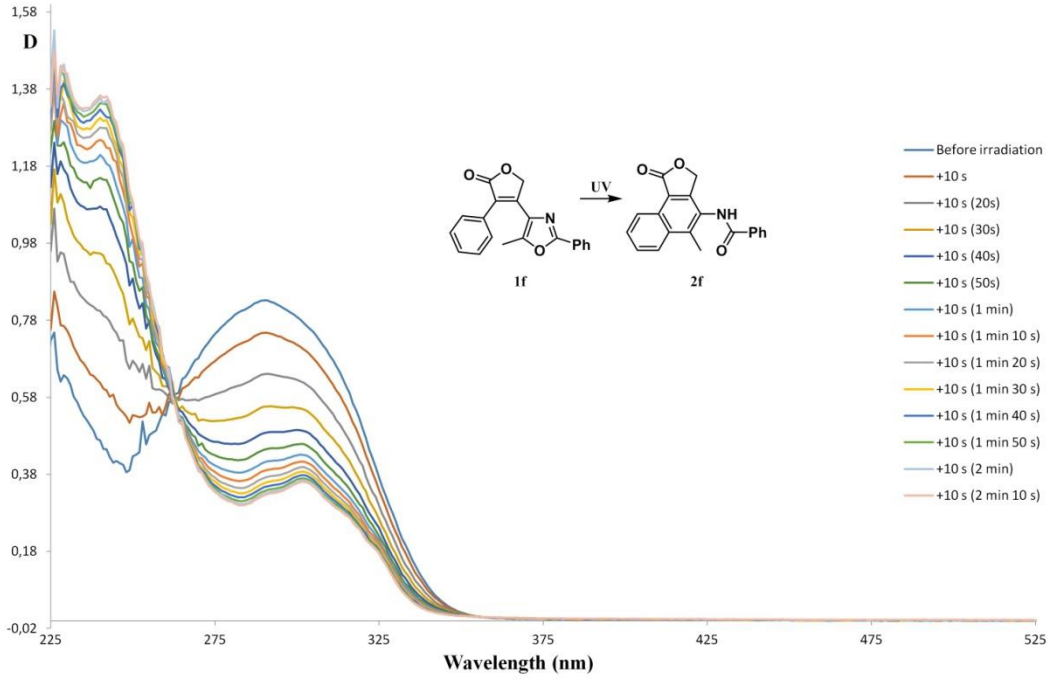


Fig. S10. Absorption spectra of an acetonitrile solution of **1f** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

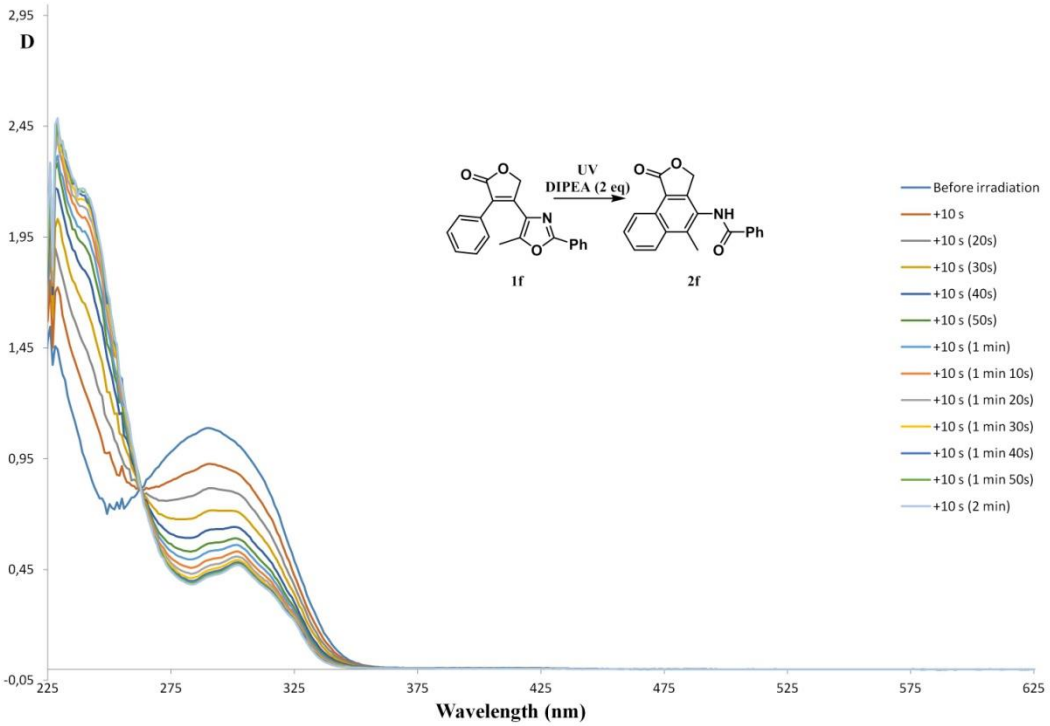


Fig. S11. Absorption spectra of an acetonitrile solution of **1f** with 2 eq DIPEA obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298ºK.

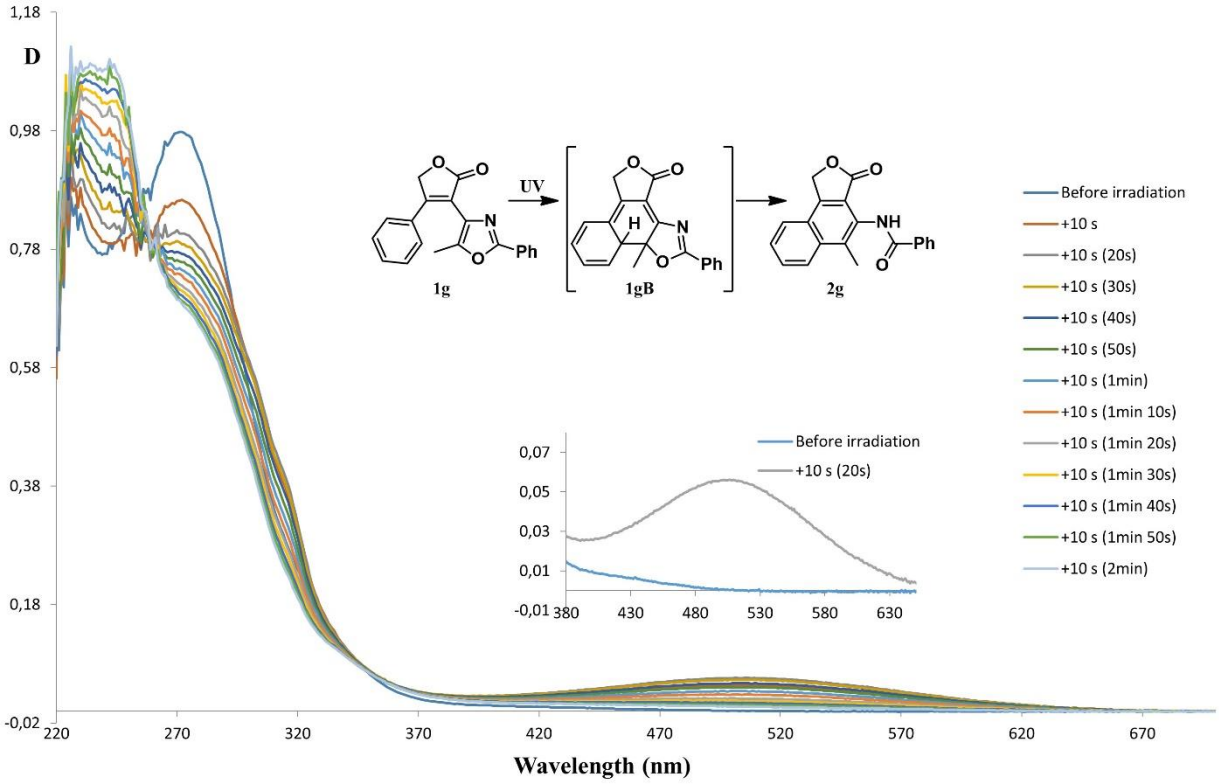


Fig. S12. Absorption spectra of an acetonitrile solution of **1g** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298ºK and colored intermediate **1gB** observed at 525 nm (on inset).

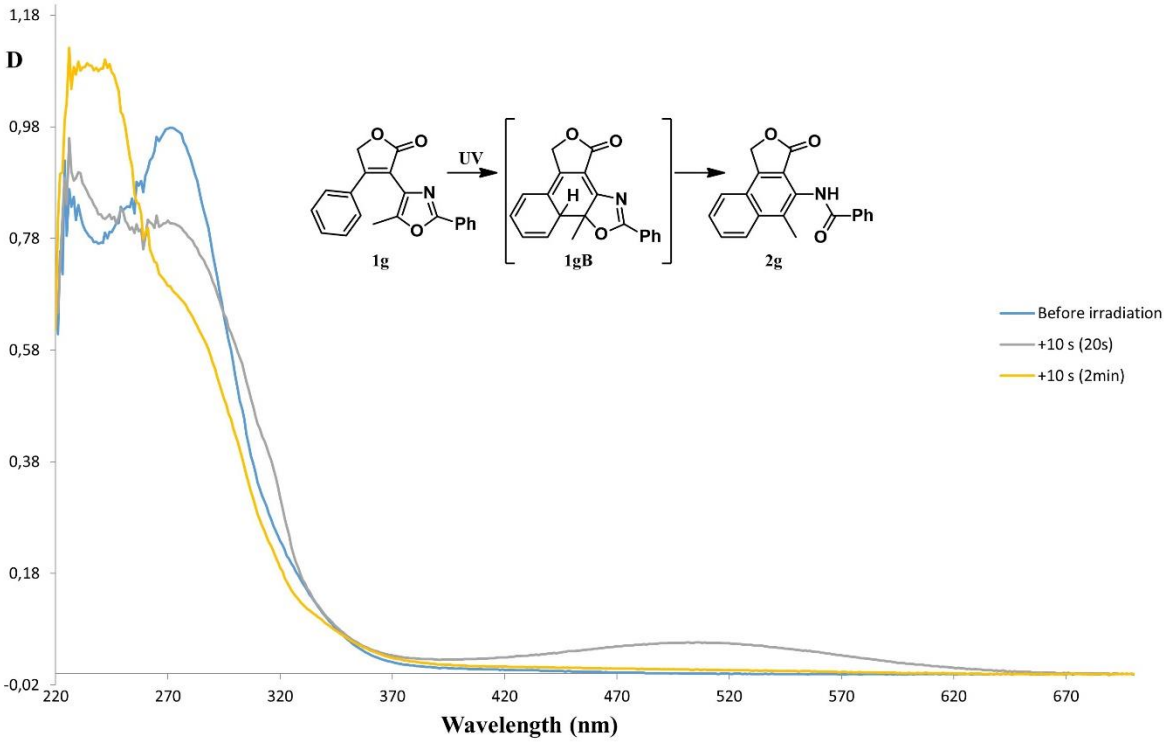


Fig. S13. Absorption spectra of **1g**, **1gB** and **2g** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

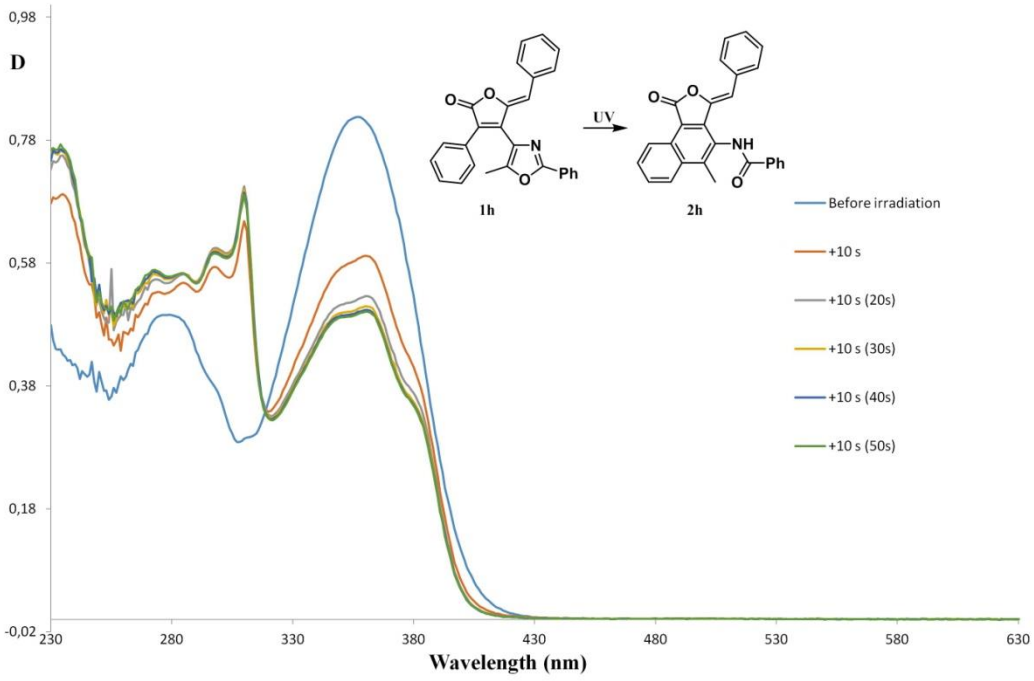


Fig. S14. Absorption spectra of an acetonitrile solution of **1h** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

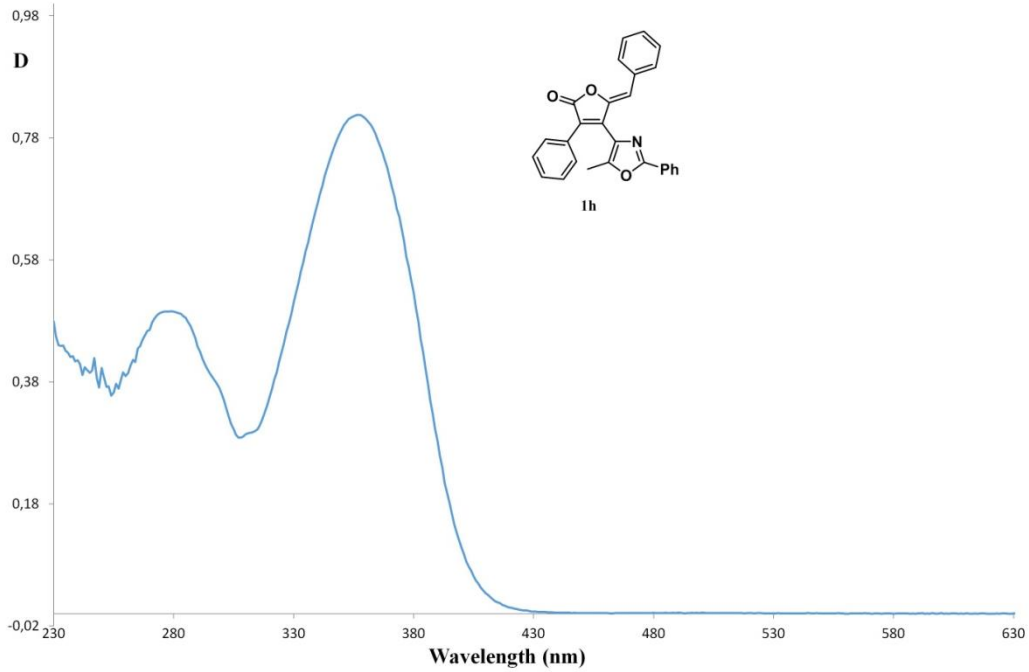


Fig. S15. UV absorption spectrum of diarylethene **1h** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

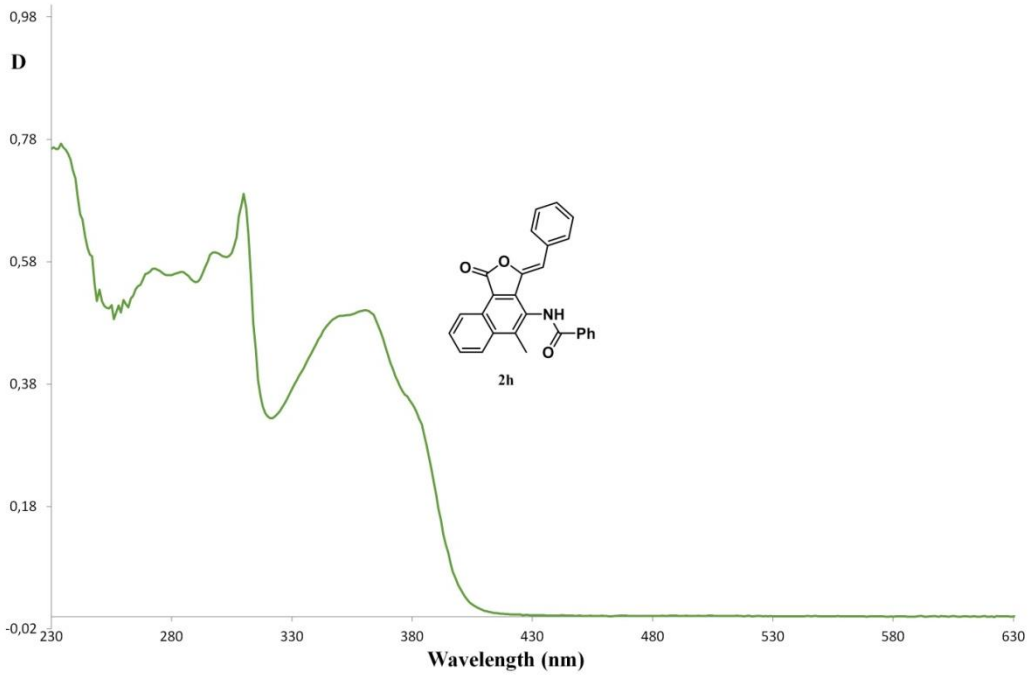


Fig. S16. UV absorption spectrum of photoproduct 2**h** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

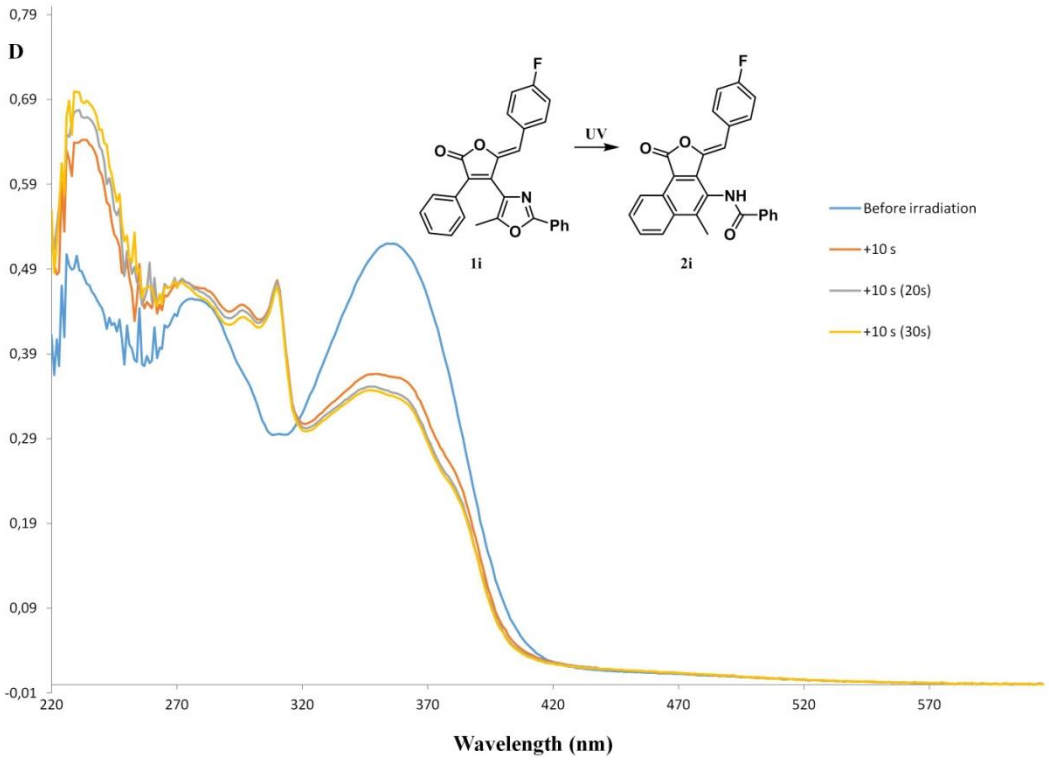


Fig. S17. Absorption spectra of an acetonitrile solution of **1i** obtained under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

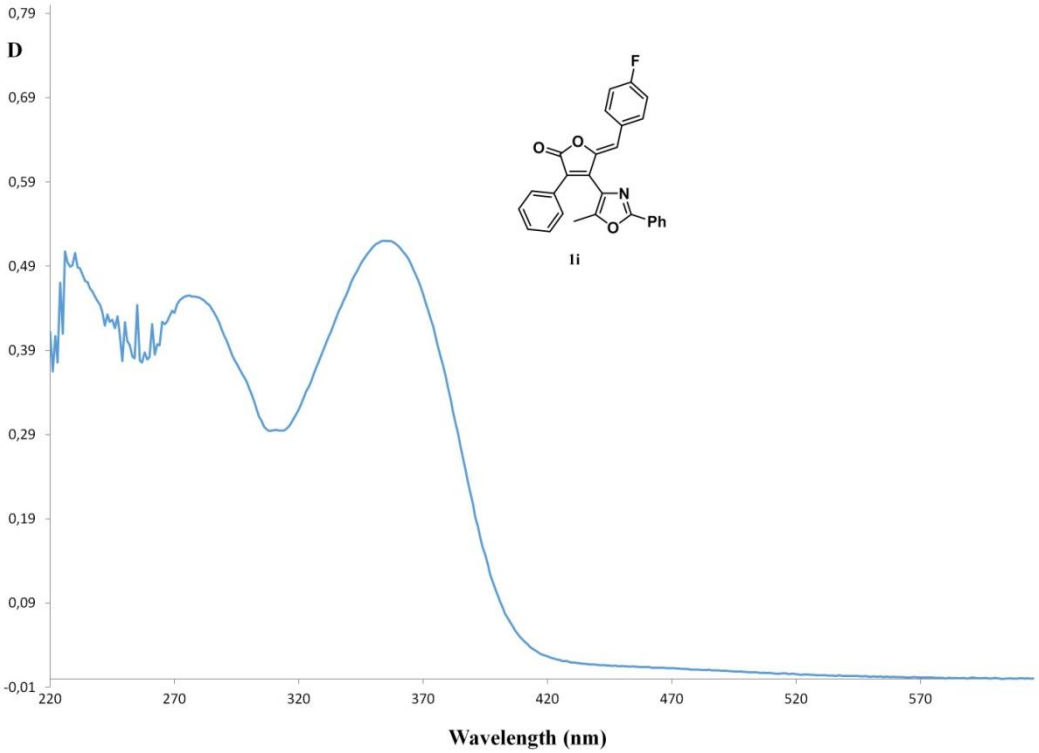


Fig. S18. UV absorption spectrum of diarylethene **1i** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

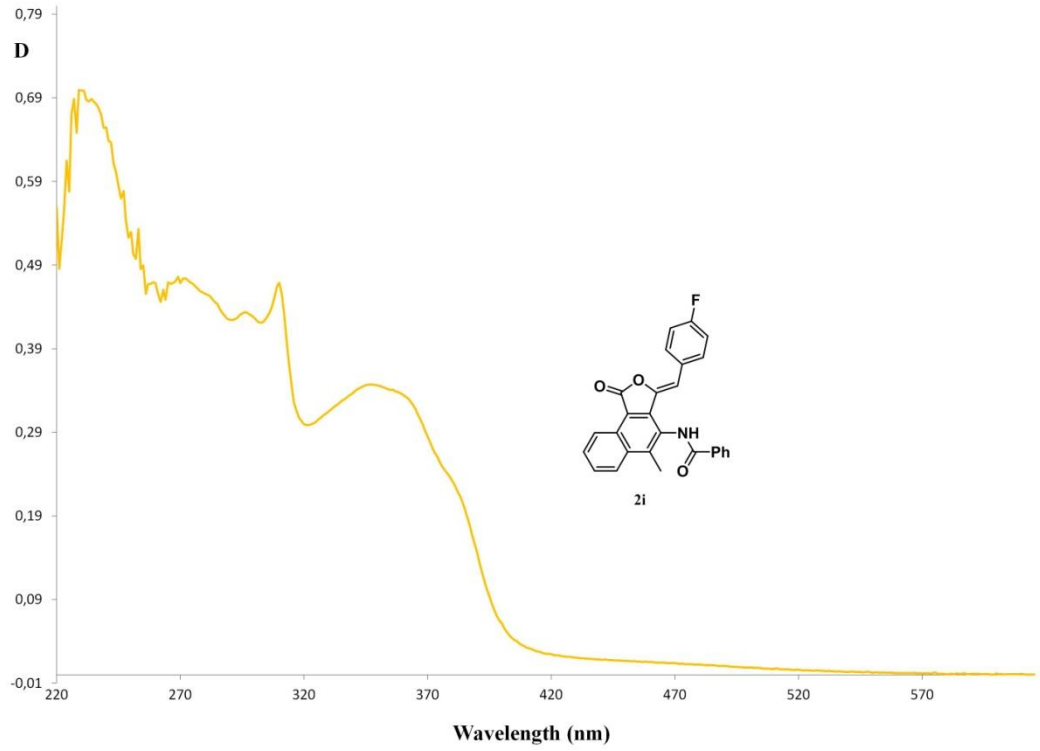


Fig. S19. UV absorption spectrum of photoproduct 2**i** in acetonitrile solution (C = 3.0×10^{-5} M), T = 298°K.

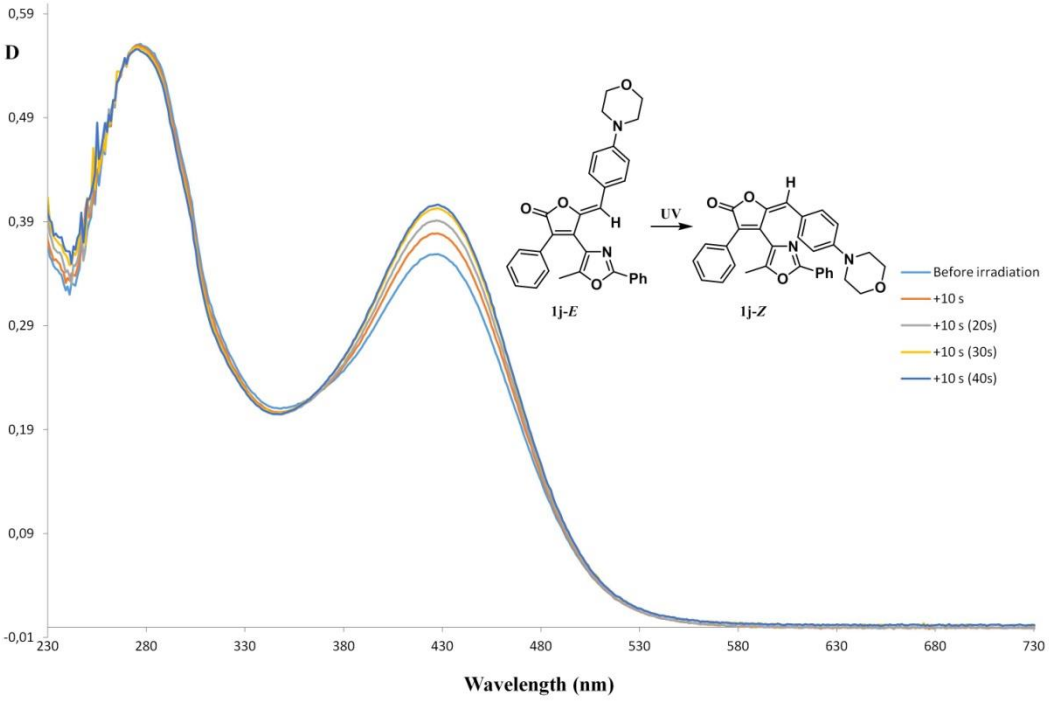


Fig. S20. Changes in the absorption spectrum of diarylethene **1j-*E*** under irradiation with UV light (λ = 365 nm); C = 3.0×10^{-5} M, T = 298°K.

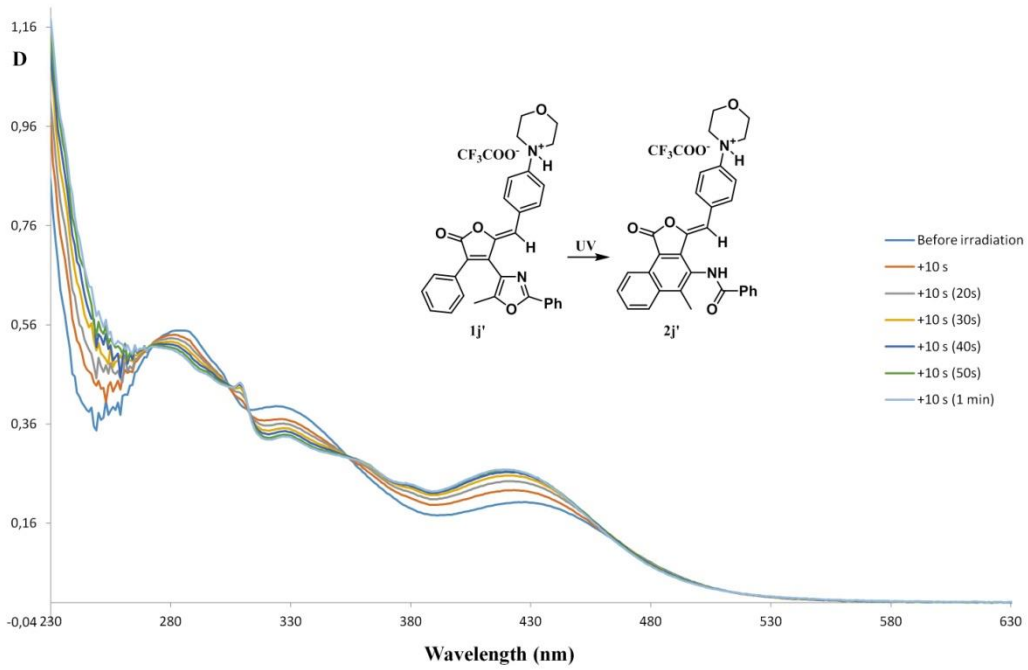
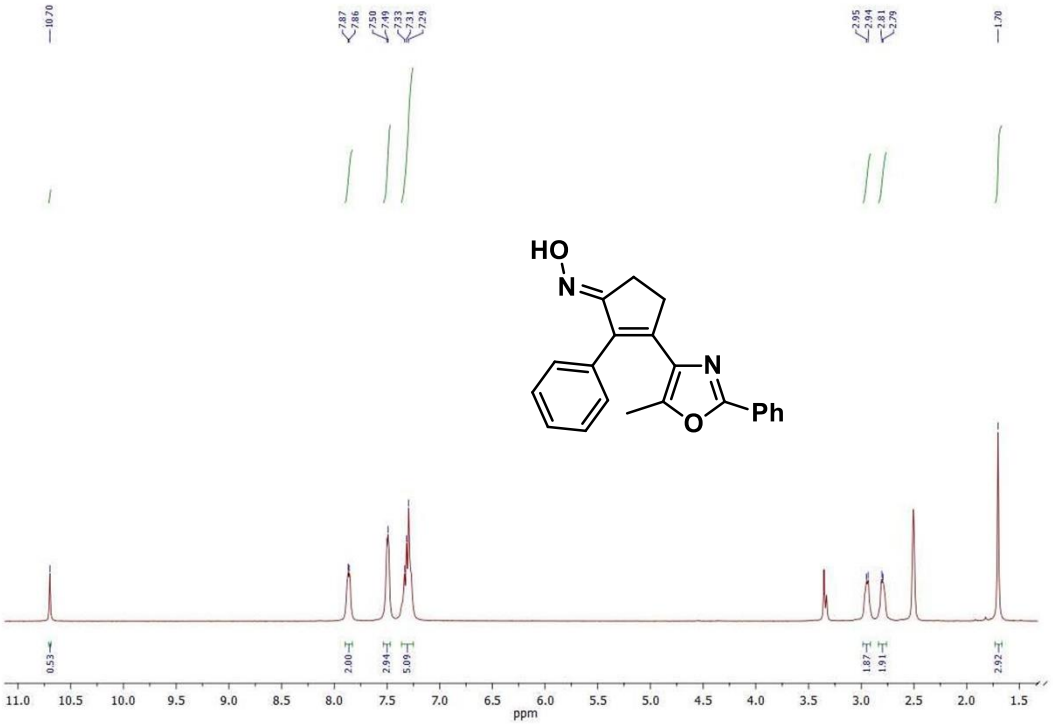
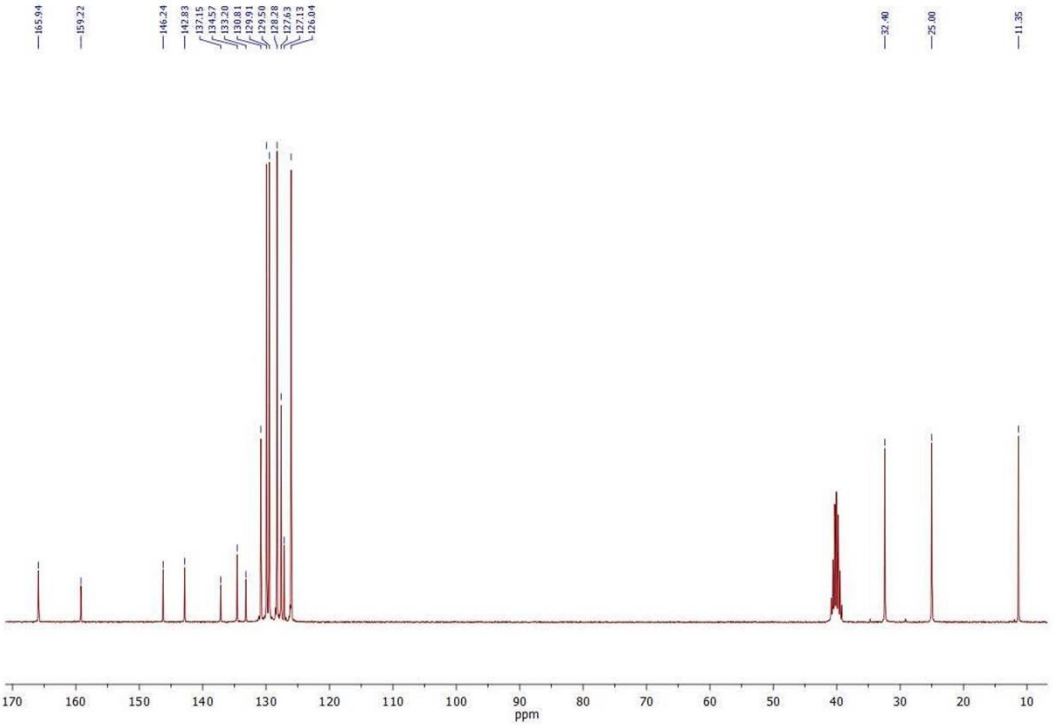


Fig. S21. Changes in the absorption spectrum of diarylethene **1j'** under irradiation with UV light (365 nm) in acetonitrile solution in the presence of 10 eq CF_3COOH ($C = 3.0\times10^{-5}$ M), T = 298°K.

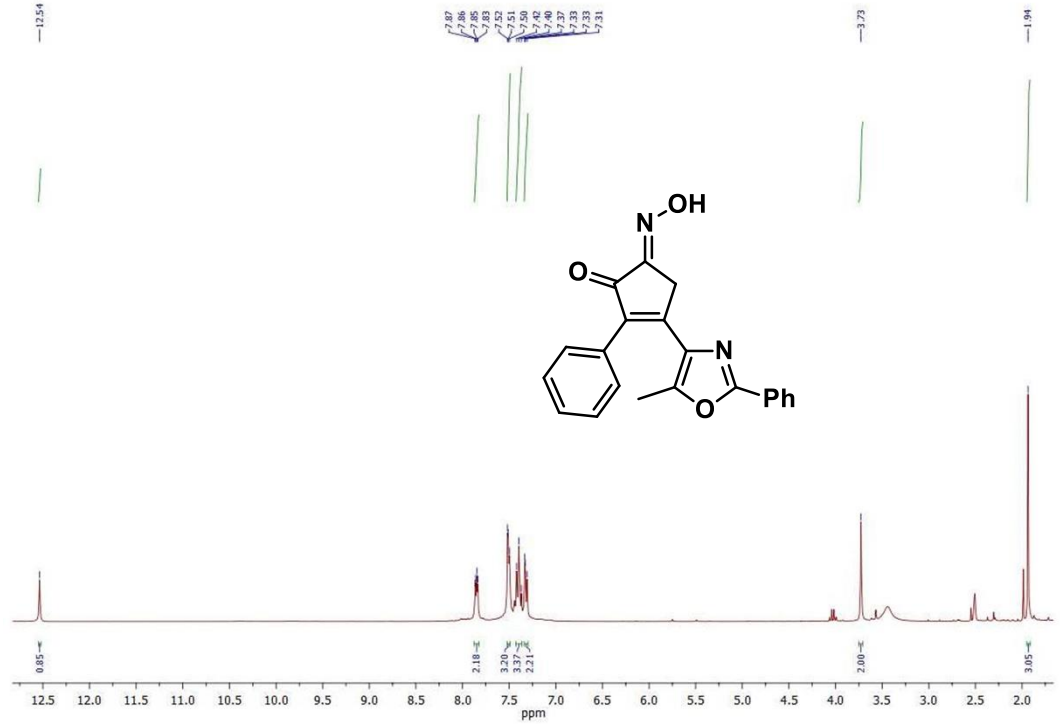
VI. Copies of ^{1}H and ^{13}C NMR spectra

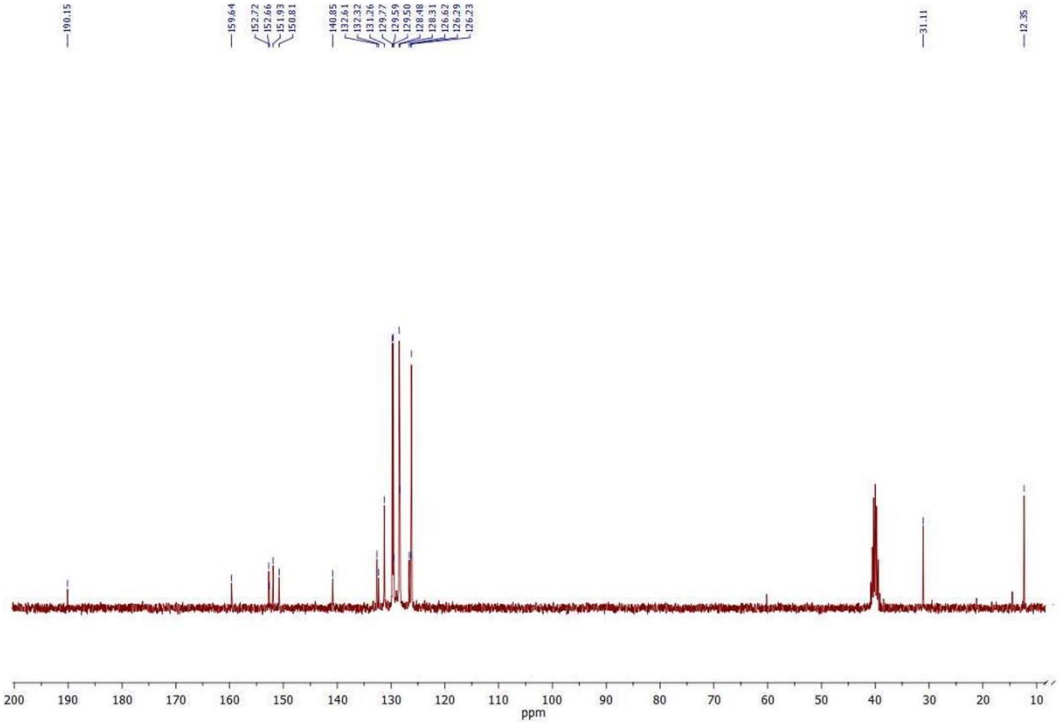
(*E*)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone oxime (1c)





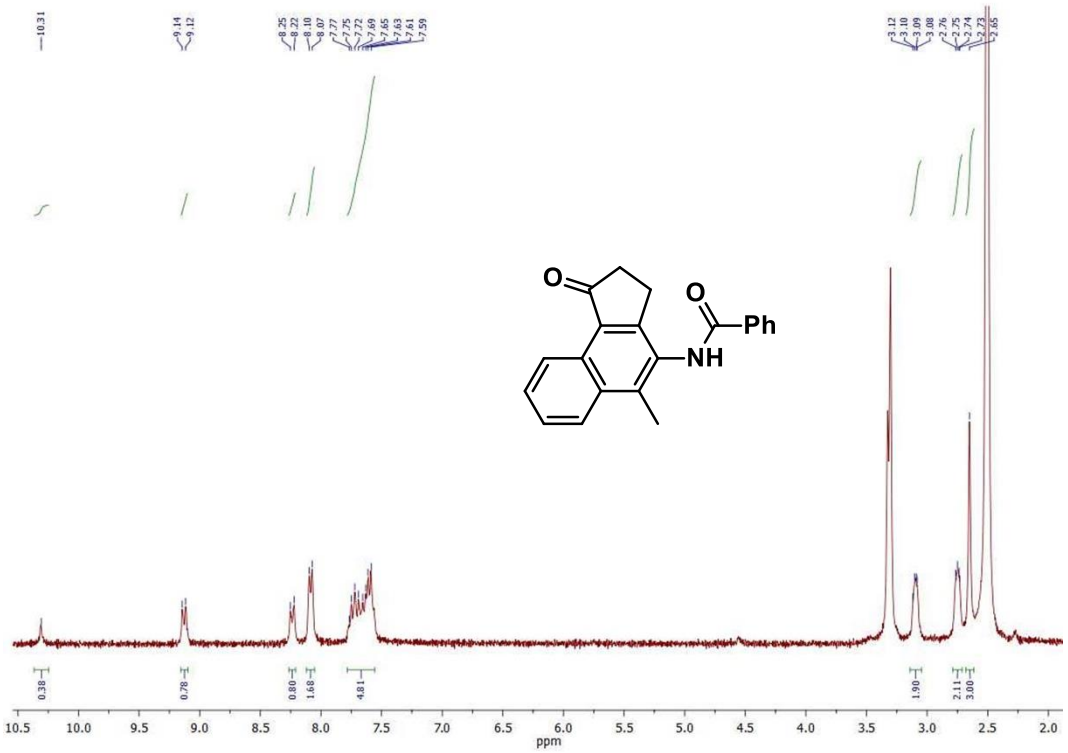
(*E*)-5-(hydroxyimino)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone (1d)



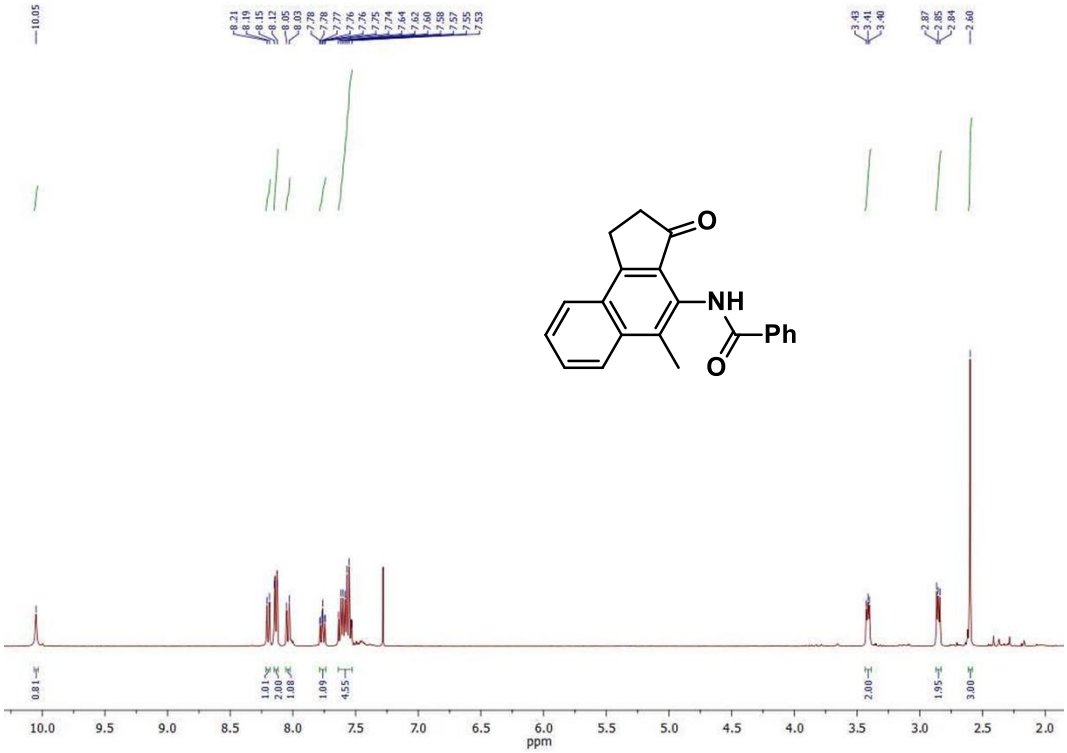


VII. Copies of ^{1}H and ^{13}C NMR spectra of photoproducts

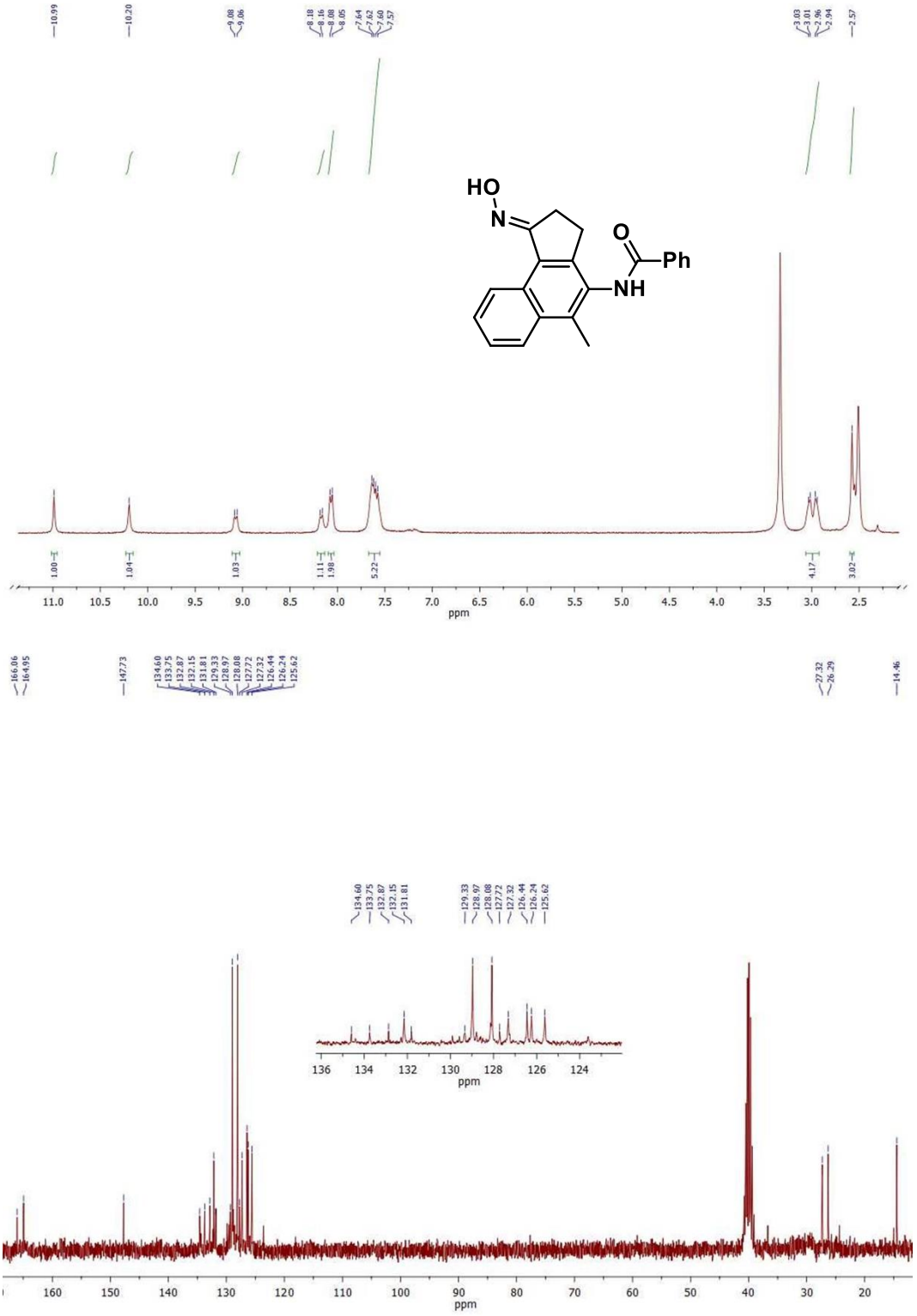
_N_-(5-methyl-1-oxo-2,3-dihydro-1_H_-cyclopenta[_a_]naphthalen-4-yl)benzamide (2a)



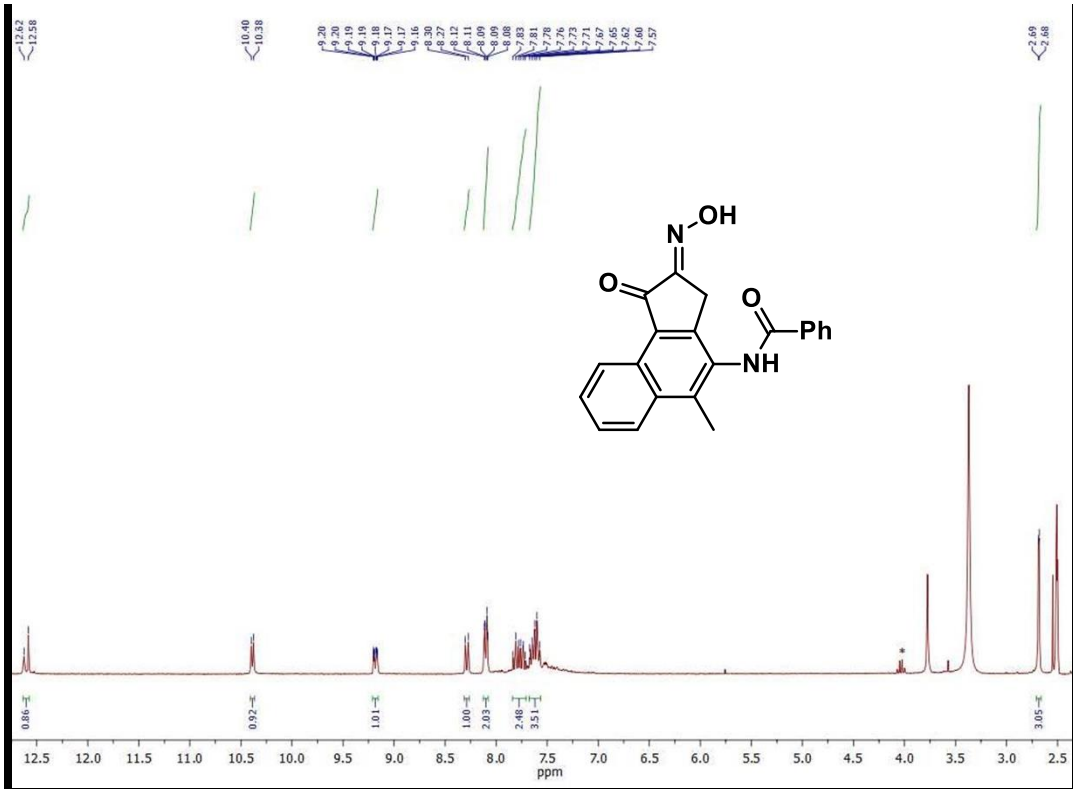
***N*-(5-methyl-3-oxo-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2b)**

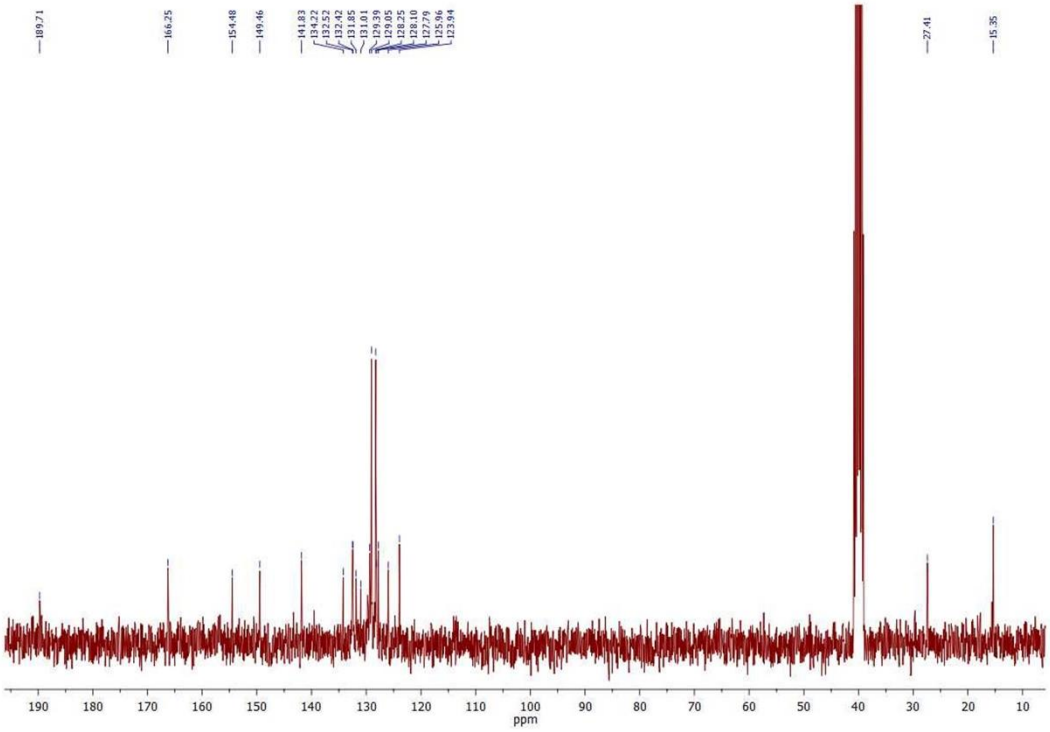


(*E*)-*N*-(1-(hydroxyimino)-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2c)

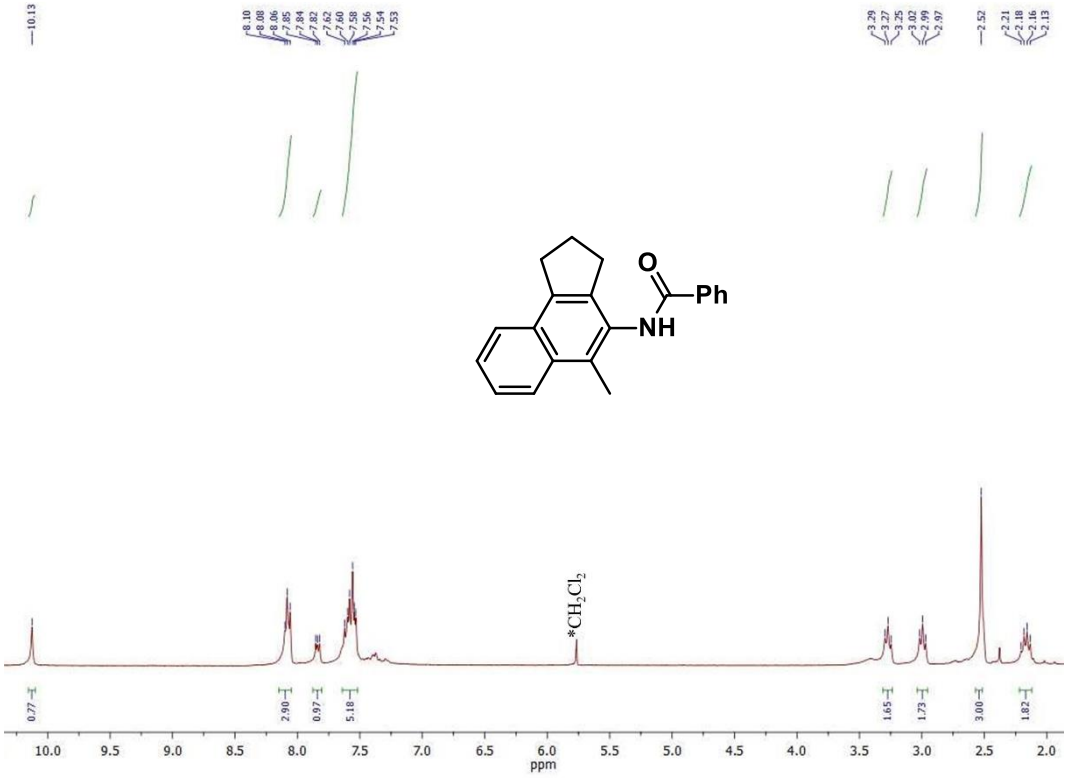


(*E*)-*N*-(2-(hydroxyimino)-5-methyl-1-oxo-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2d)

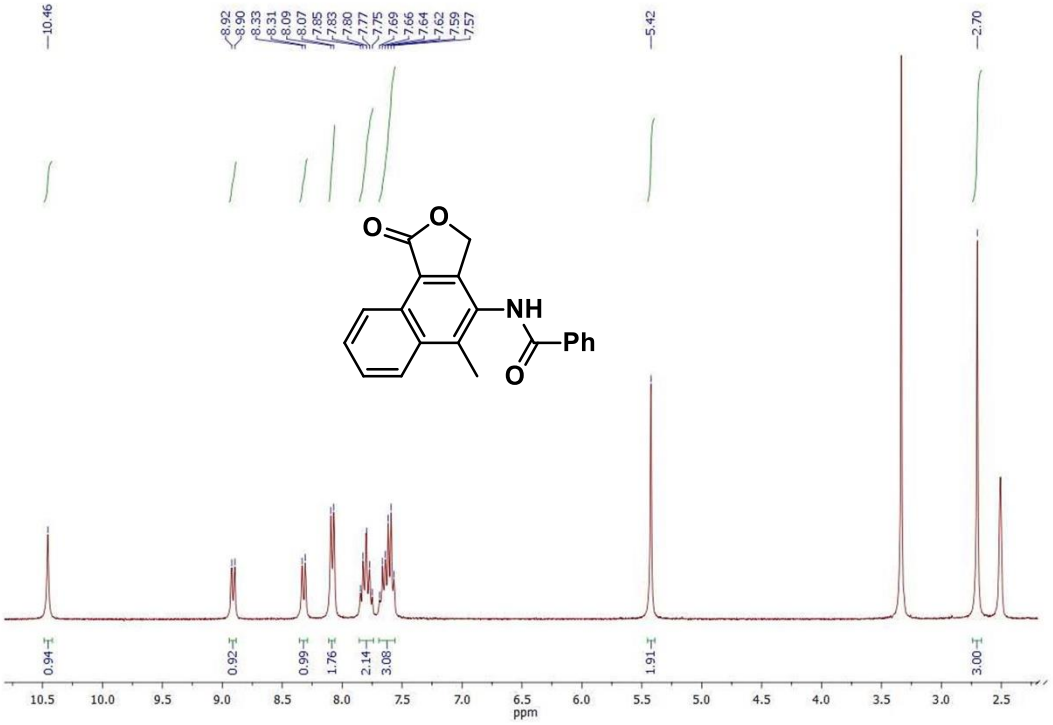




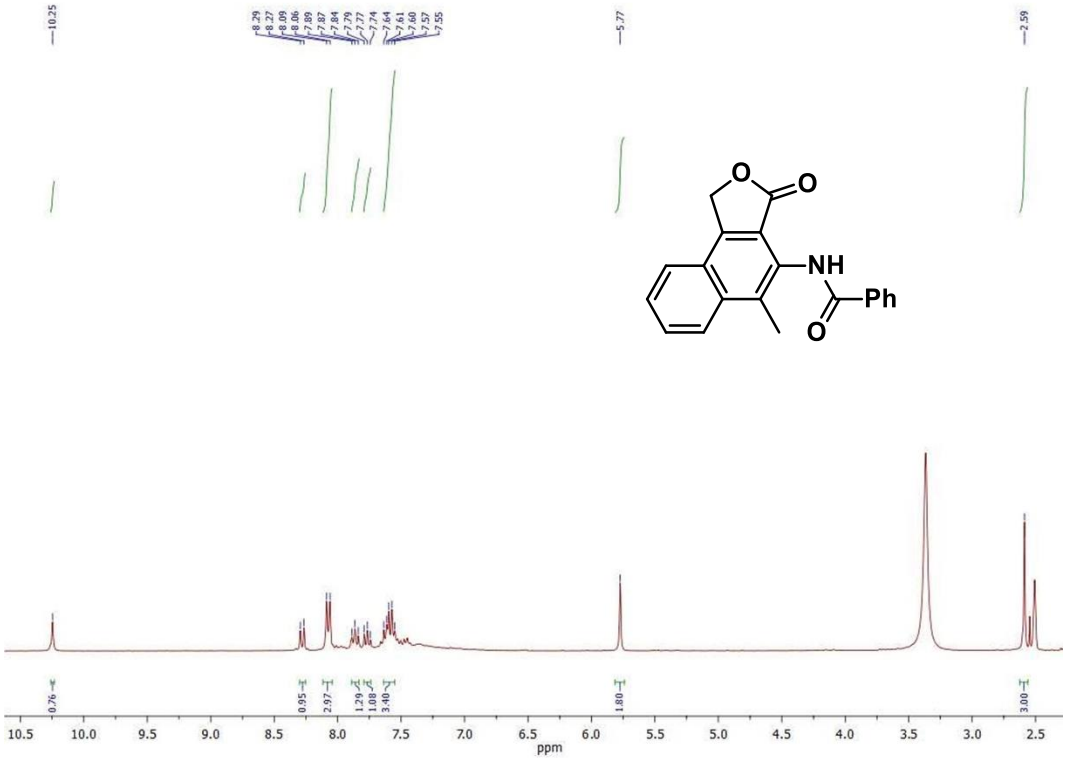
***N*-(5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2e)**

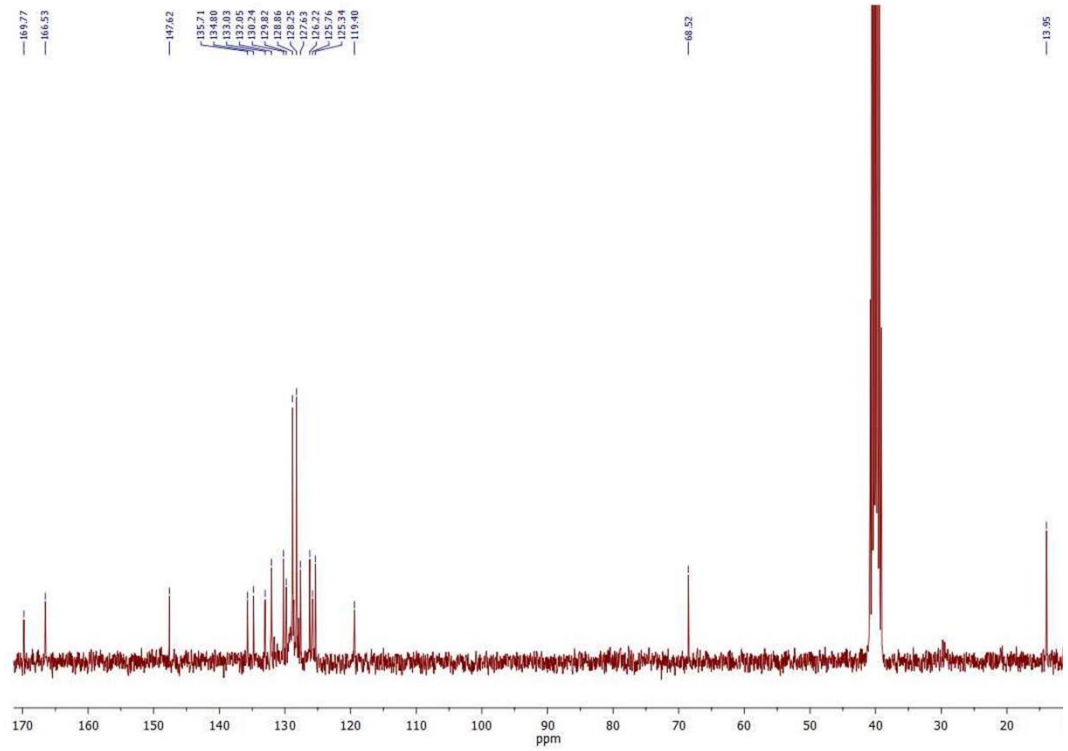


***N*-(5-methyl-1-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4-yl)benzamide (2f)**



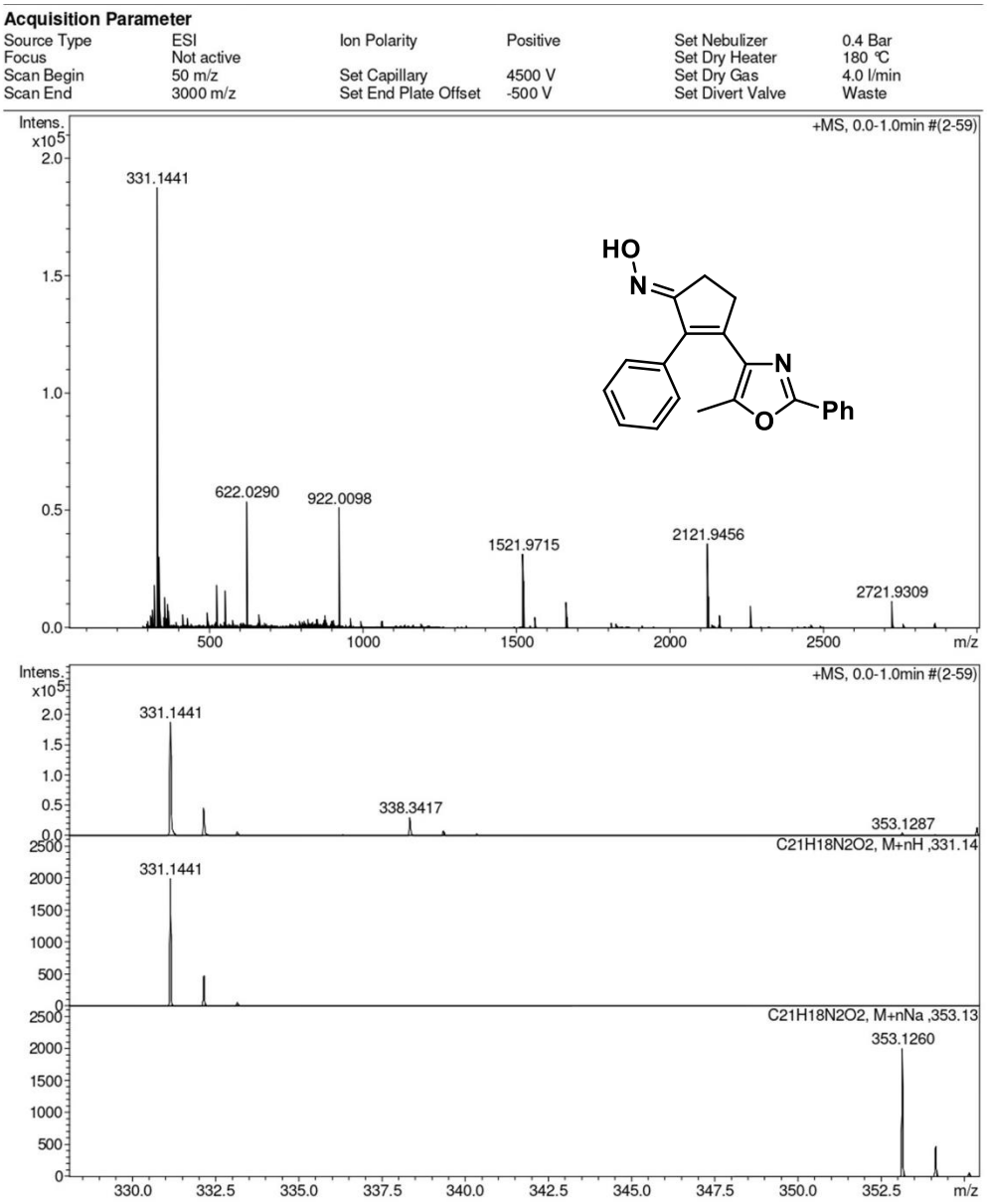
***N*-(5-methyl-3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4-yl)benzamide (2g)**



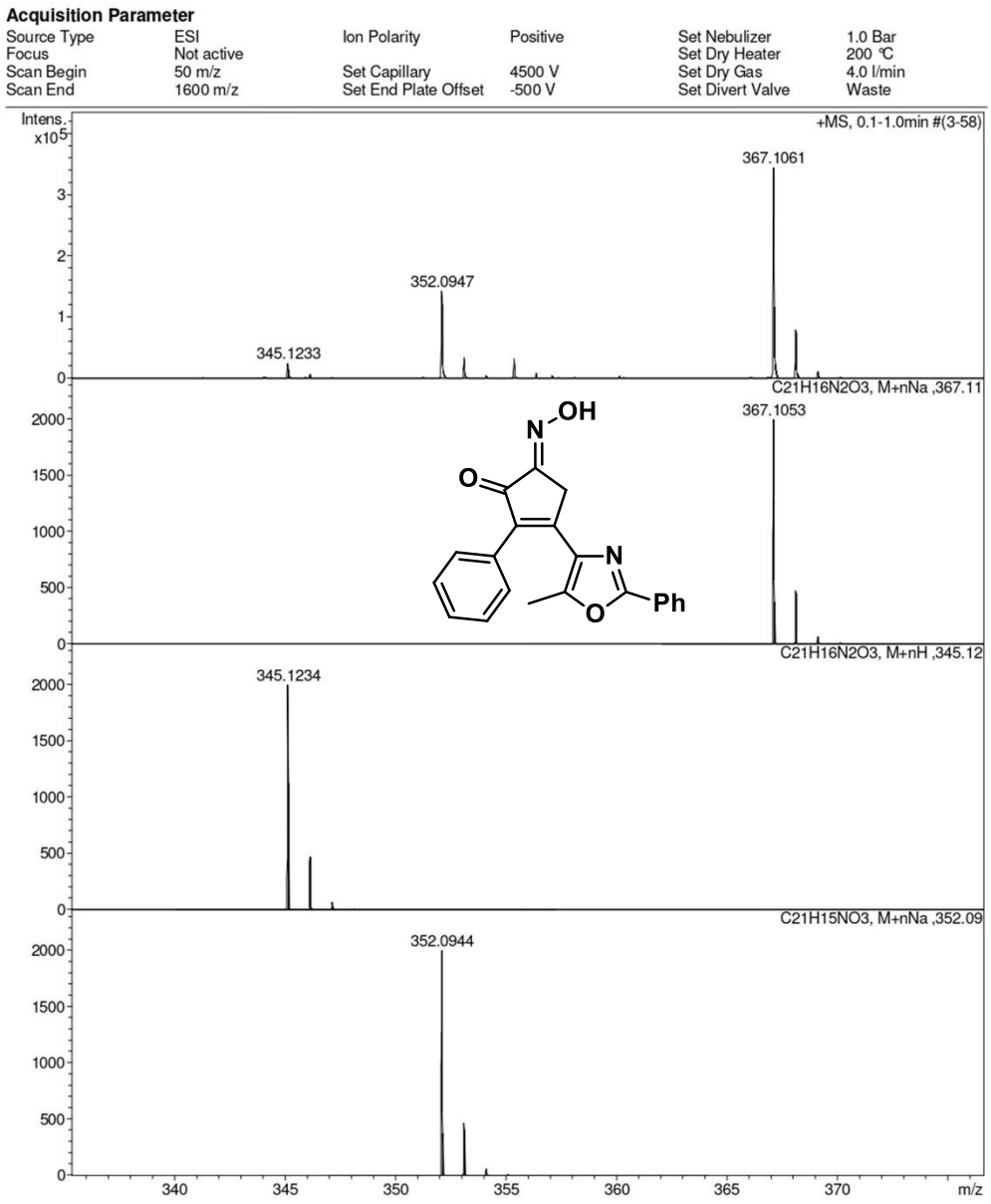


VIII. Copies of HRMS spectra

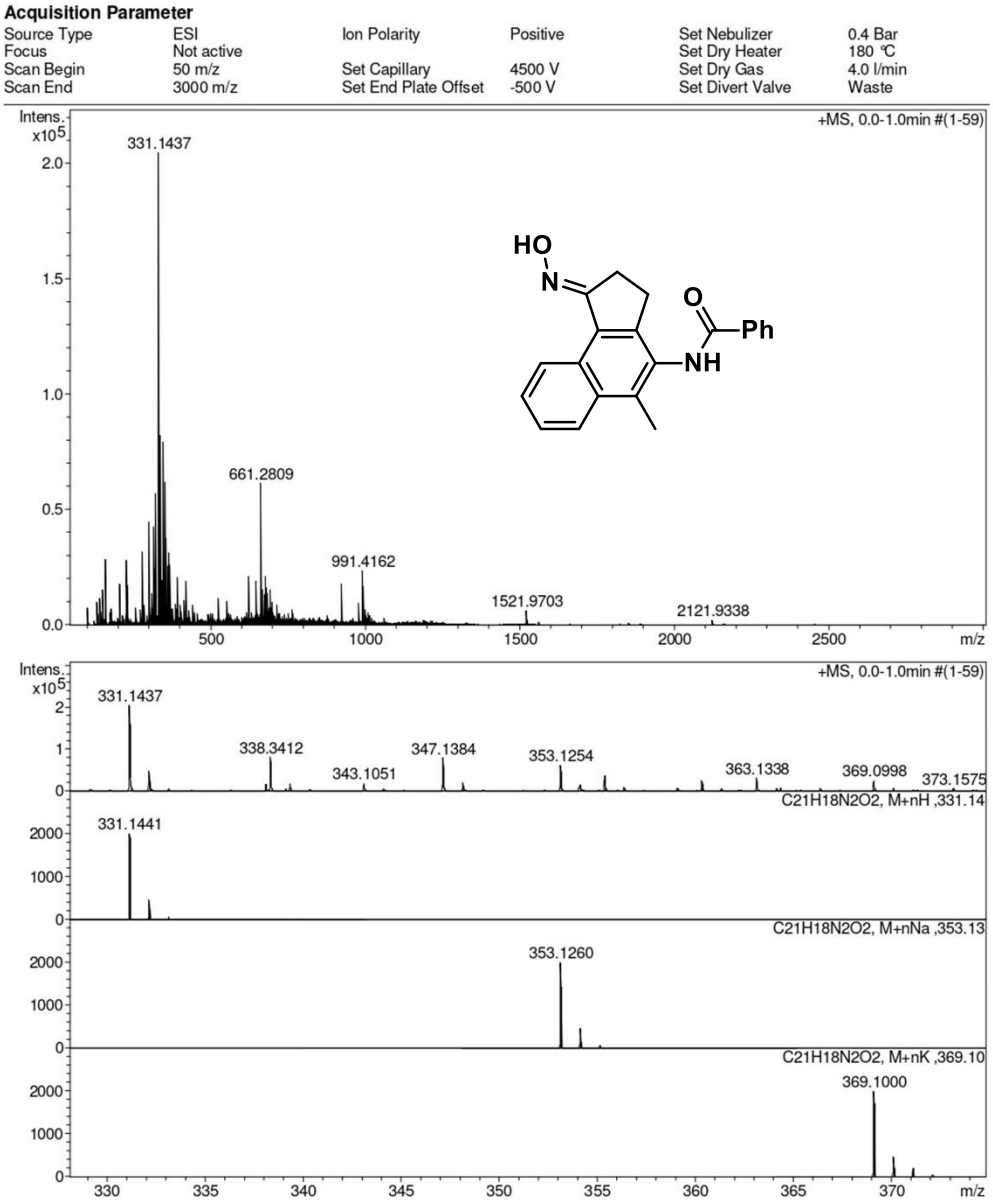
(*E*)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone oxime (1c)



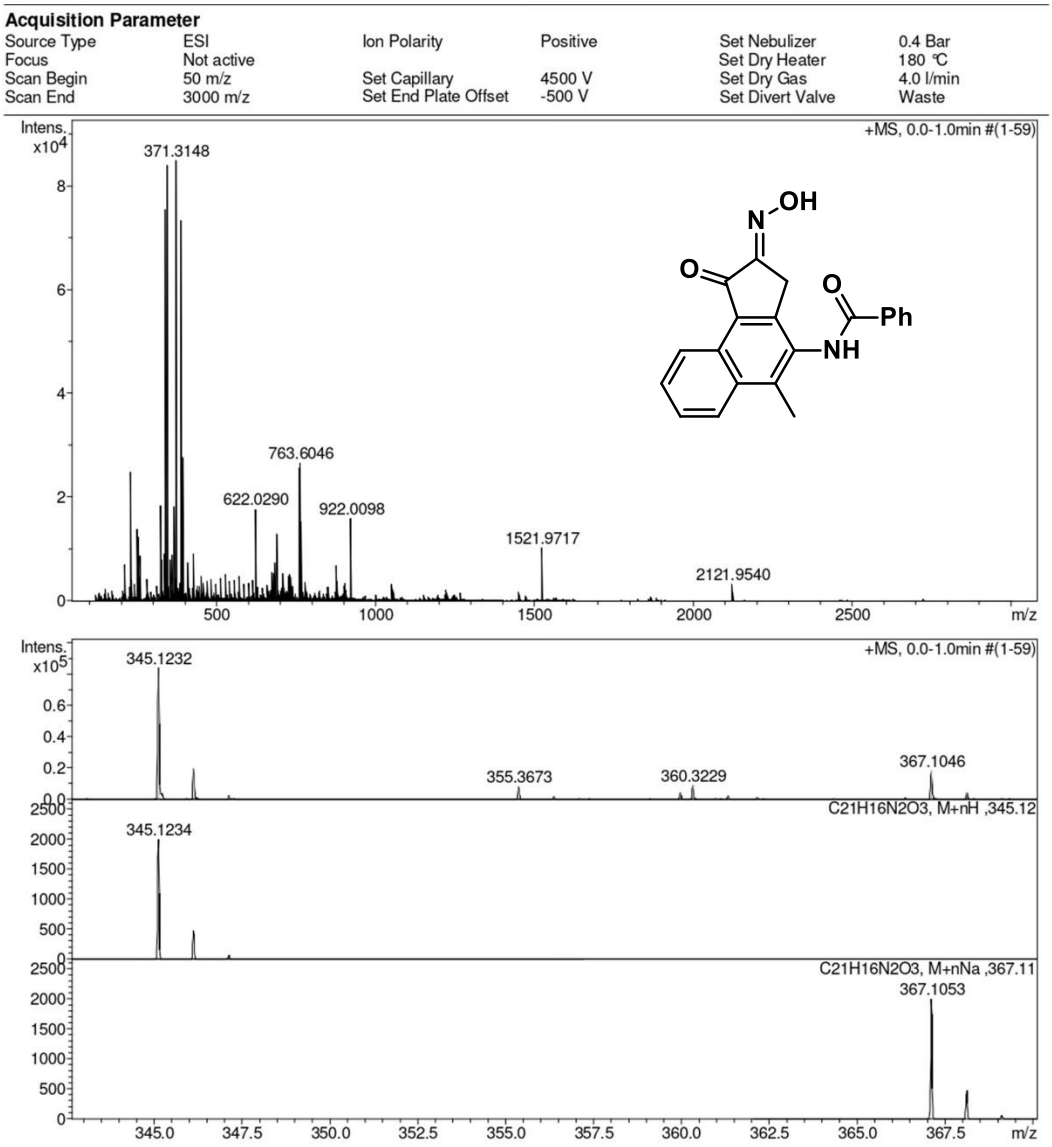
(*E*)-5-(hydroxyimino)-3-(5-methyl-2-phenyloxazol-4-yl)-2-phenylcyclopent-2-enone (1d)



(*E*)-*N*-(1-(hydroxyimino)-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2c)



(*E*)-*N*-(2-(hydroxyimino)-5-methyl-1-oxo-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl)benzamide (2d)



N-(5-methyl-3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4-yl)benzamide (2g)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste