Supporting Information

Continuous-flow Fe-Zeolite catalyzed temperature directed synthesis of bioactive tetraketones and xanthenes using epoxides and cyclic-1,3-diketones via Meinwald rearrangement

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1. General information and data collection:

All the chemicals were purchased from Sigma-Aldrich and Thermofischer Scientific and used without further modification. All solvents were purchased from Rankem and Finar Chemicals. Deuterated solvents were used as received. Column chromatographic separations were performed over 100−200 mesh silica-gel. Visualization was accomplished with UV light. The ^{1}H and $^{13}C\{1H\}$ NMR spectra were recorded on 400 and 100 MHz, respectively, using Bruker or JEOL spectrometers. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet. HRMS spectra were obtained with Waters-synapt G2 using electrospray ionization (ESI-TOF). Infrared (ATIR) spectra were obtained with a Bruker Alpha-E infrared spectrometer. Single-crystal diffraction analysis data were collected at 100K with a BRUKER KAPPA APEX III CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Mo Kα radiation and Cu-Kα radiation.

2. Preparation of the Fe@Zeolite Catalyst[1]: 5 g of zeolite was suspended in 20 mL of deionized water. A 10% $FeCl_3.6H_2O$ solution was prepared in deionized water. This suspension was stirred for 6 h in rotary evaporator for uniform dispersion. Water was removed under vacuum, and the metal loaded samples were dried at 120 °C for 2 h. The dried samples were calcined at 500 °C for 8 h. The % of Fe on Zeolite support was analysed by Microwave Plasma Atomic Emission Spectroscopy (MP-AES) analysis which showed that catalyst contains 2.63% of Fe.

3. Experimental procedure:

A. Procedure for starting material preparation: Substrates (2-(p-tolyl)oxirane and 2-methyl-2-phenyloxirane) prepared according to reported literature procedure.[2, 3]

B. Experimental procedure for the synthesis of tetraketone (3) from epoxide and cyclic-1,3-dione in batch: Cyclic-1,3-diketone **1** (2 equivalent), epoxide **2** (1 equivalent), and 30 mg of 2.63% Fe-zeolite were mixed in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and heated at 160 °C for 8 h. After completion of the reaction, the solvent was evaporated in rotary evaporator and the crude reaction mixture was directly purified by 100-200 mesh silica-gel column chromatography (EtOAc: n-hexane= 5:95 to 10:90) to afford the tetraketone **3**.

C. General procedure for the synthesis of xanthene (4) via cyclisation reaction of tetra ketones: To an oven dried 10 mL sealed tube 50 mg tetraketone **3** and 30 mg of 2.63% Fe-zeolite were added and then 2 mL toluene was added. Next the reactor was placed in a preheated oil bath and heated at 180 °C in Carousel hot plate for 8 h. After completion of the reaction, the solvent was removed using rotary evaporator and the crude reaction mixture was directly purified by 100-200 mesh silica-gel column chromatography (EtOAc: n-hexane= 10:90 to 20:80) to afford the xanthene **4**.

D. General procedure for synthesis of tetraketone from epoxide and cyclic-1,3-diketone under continuous-flow: In a typical procedure, the 10 mL 0.1M solution of epoxide and 10 mL 0.2 M cyclic-1,3-diketone in 1,4-dioxane were premixed and flown through Omnifit® (6.6 x 150 mm) packed bed column packed with 2.63% Fe-Zeolite up to 6 cm (1.0 g) at 2-3 bar pressure at 140 °C with 0.1 mL/min flow rate and residence time t_R = 20 min. After reaction completion, the catalyst bed was washed with 1,4-dioxane. The solvent was evaporated under vacuum. The residue was further purified by 100-200 mesh silica gel chromatography (EtOAc : hexane= 5:95 to 10:90) to afford the pure product **3**.

E. General procedure for synthesis of tetraketone from aldehyde and cyclic-1,3-diketone in continuous-flow: In a typical procedure, the 5 mL 0.1M solution of aldehyde and 5 mL 0.2 M cyclic-1,3-diketone in 1,4-dioxane were premixed and flown through Omnifit® (6.6 x 150 mm) packed bed column packed with 2.63% Fe-Zeolite up to 6 cm (1.0 g) of bed at room temperature at 2-3 bar pressure at 140 °C with 0.1 mL/min flow rate and residence time t_R = 20 min. After reaction completion, the catalyst bed was washed with 1,4-dioxane. The solvent was evaporated using a rotary evaporator. The residue was directly purified by silica gel chromatography (EtOAc : hexane= 5:95 to 20:80).

F. General procedure for the synthesis of xanthene (6) via cyclisation reaction of tetra ketones: To an oven dried 10 mL sealed tube 50 mg tetraketone **6** and 30 mg of 2.63% Fe-zeolite were added and then 2 mL toluene was added. Next the reactor was placed in a preheated oil bath and heated at 180 °C in Carousel hot plate for 8 h. After completion of the reaction, the solvent was removed using rotary evaporator and the crude reaction mixture was directly purified by 100-200 mesh silica-gel column chromatography (EtOAc: n-hexane= 10:90 to 20 :80) to afford the xanthene **7**.

G. Experimental procedure for the gram scale synthesis of tetraketone (3a) from styrene oxide and 5,5-dimethyl cyclohexane-1,3-dione in batch: 5,5-dimethylcyclohexane-1,3-dione **1a** (2.3 gm, 16.66 mmol), styrene oxide **2a** (1 gm, 8.33 mmol), and 600 mg of 2.63% Fe-zeolite were mixed in an oven dried sealed tube and 2 mL toluene was added. Then the reaction mixture was heated at 160 °C for 8 h. After completion of the reaction, the solvent was evaporated in rotary evaporator and the crude reaction mixture was directly purified by 100-200 mesh silica-gel column chromatography (EtOAc: n-hexane= 5:95) to afford 2,2'-(2-phenylethane-1,1-diyl) bis (3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3a** (2.31 g, 72.39 %) as White Crystal.

H. Experimental procedure for the gram scale synthesis of tetraketone (3a) from styrene oxide and 5,5-dimethylcyclohexane-1,3-dione in flow: 60 mL 0.1M solution of styrene oxide (720 mg, 6 mmol) and 60 mL 0.2 M 5,5-dimethylcyclohexane-1,3-diketone (1680 mg, 12 mmol) in 1,4-dioxane were premixed and flown through Omnifit® (6.6 x 150 mm) packed bed column packed with 2.63% Fe-Zeolite up to 6 cm (1g) at 2-3 bar pressure at 140 ^{o}C with 0.1 mL/min flow rate and residence time t_R = 20 min. After reaction completion, the catalyst bed was washed with 1,4-dioxane. The solvent was evaporated under vacuum. The residue was further purified by 100-200 mesh silica gel chromatography (EtOAc : hexane= 5 to 90) to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3a** (1.03 g mg, 62.5% yield)as the pure product .

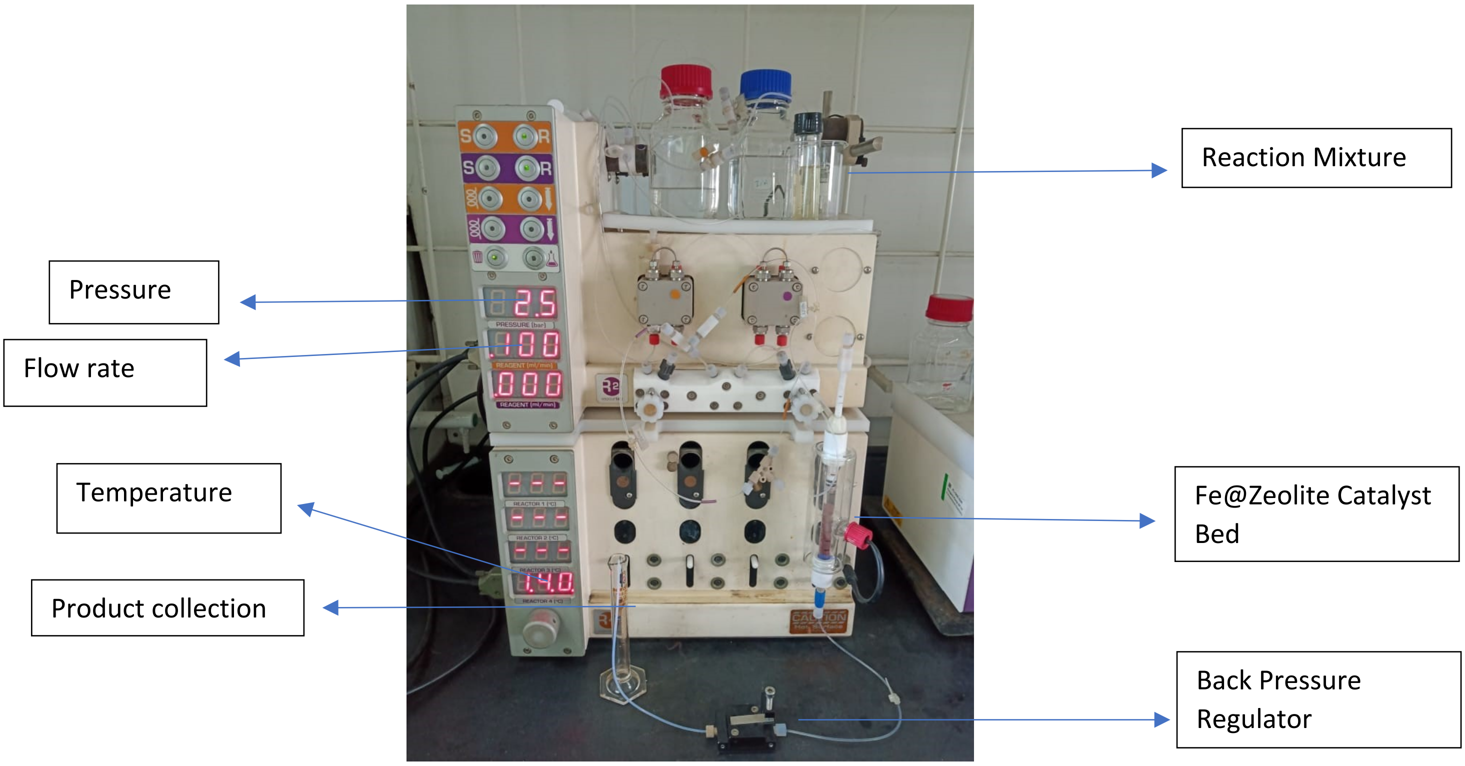


Figure 1: Set up for reaction in continuous flow

4. Experimental procedure for recyclability:

(a) First run of the catalyst: 5,5-dimethylcyclohexane-1,3-dione **1a** (350 mg, 2.5 mmol), styrene oxide **2a** (150 mg, 1.25 mmol), and 90 mg of Fe-zeolite were introduced in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and the reaction was conducted for 8h under vigorous stirring. The catalyst was separated by filtration and the catalyst thus separated was washed twice with toluene and subjected to drying in oven for 2 h. The solvent of the filtrate solution was evaporated under rotary evaporator and directly by 100-200 mesh silica gel column chromatography to afford **3a** (397mg, 84%). The weight of the dried catalyst was 72 mg after cooling.

(b) Second run of the catalyst: 5,5-dimethylcyclohexane-1,3-dione **1a** (279 mg, 1.99 mmol), styrene oxide **2a** (119 mg, 0.99 mmol), and 72 mg of Fe-zeolite were introduced in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and the reaction was conducted for 8h under vigorous stirring. The catalyst was separated by filtration and the catalyst thus separated was washed twice with toluene and subjected to drying in oven for 2 h. The solvent of the filtrate solution was evaporated under rotary evaporator and directly by 100-200 mesh silica gel column chromatography to afford **3a** (285 mg, 76%). The weight of the dried catalyst was 72 mg after cooling.

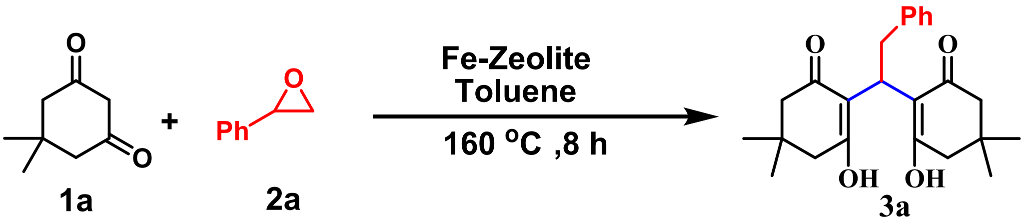
(c) Third run of the catalyst: 5,5-dimethylcyclohexane-1,3-dione **1a** (232 mg, 1.99 mmol), styrene oxide **2a** (100 mg, 0.83 mmol), and 60 mg of Fe-zeolite were introduced in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and the reaction was conducted for 8h under vigorous stirring. The catalyst was separated by filtration and the catalyst thus separated was washed twice with toluene and subjected to drying in oven for 2 h. The solvent of the filtrate solution was evaporated under rotary evaporator and directly by 100-200 mesh silica gel column chromatography to afford **3a** (238 mg, 75%). The weight of the dried catalyst was 46 mg after cooling.

(d) Fourth run of the catalyst: 5,5-dimethylcyclohexane-1,3-dione **1a** (178 mg, 1.276 mmol), styrene oxide **2a** (76 mg, 0.638 mmol), and 46 mg of Fe-zeolite were introduced in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and the reaction was conducted for 8 h under vigorous stirring. The catalyst was separated by filtration and the catalyst thus separated was washed twice with toluene and subjected to drying in oven for 2 h. The solvent of the filtrate solution was evaporated under rotary evaporator and directly by 100-200 mesh silica gel column chromatography to afford **3a** (173mg, 75%). The weight of the dried catalyst was 28 mg after cooling.

(e) Fifth run of the catalyst: 5,5-dimethylcyclohexane-1,3-dione **1a** (106 mg, 0.75 mmol), styrene oxide **2a** (46 mg, 0.38 mmol), and 28 mg of Fe-zeolite were introduced in an oven dried sealed tube and 2 mL toluene was added. Then the reactor was placed in a preheated oil bath and the reaction was conducted for 8 h under vigorous stirring. The catalyst was separated by filtration and the catalyst thus separated was washed twice with toluene and subjected to drying in oven for 2 h. The solvent of the filtrate solution was evaporated under rotary evaporator and directly by 100-200 mesh silica gel column chromatography to afford **3a** (94 mg, 65%). The weight of the dried catalyst was 11 mg after cooling.

5. Calculation of E-factor and atom economy of compound 3a

We have calculated the green chemistry matrix for model reaction with the help of literature report.[4]



MW	140.18	120.15	382.5
mmol	0.832	0.416	0.347
amount	116	50	133

E-factor:

The ideal value of E-factor is zero.

E-factor = [total mass of raw materials - the total mass of product]/ mass of product.

E-factor of 3a = [(116 + 50)-133]/133

= 0.25

Process mass intensity (PMI):

PMI= ∑ (mass of stoichiometric reactants)/[mass of product]

= (116+50)/ 133

= 1.25

Reaction mass efficiency (RME):

RME = [mass of product /∑ (mass of stoichiometric reactants)] × 100

= [133 / (116+50)] × 100

= 80.12%

Carbon Efficiency (CE):

CE denotes the percentage of carbon in the reactants that remains in the product.

CE= [Amount of carbon in product/ Total carbon present in reactants] x 100

= [no. of moles of product x no. of carbons in product / (moles of 1a x carbons in 1a + moles of 2a x carbons in 2)] x 100

= [0.347 x 24 / (0.416 x 8 + 0.832 x 8)] x 100

= [8.345 / (3.328 + 6.656)] x 100

= 83.6%

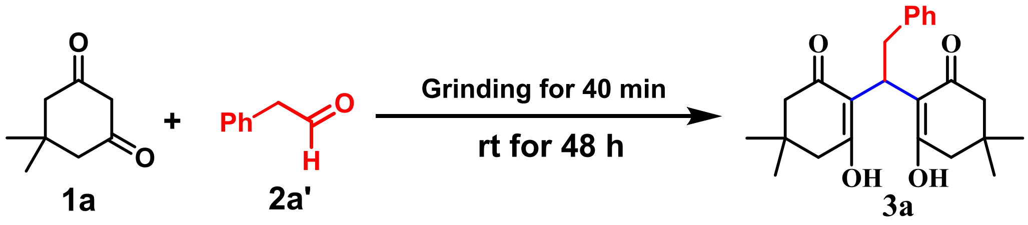
Turnover Number (TON):

TON = (mmol of product / mmol of active catalyst)

= (0.347/0.00016)

= 2168.7

Calculation of E-factor and atom economy of compound 3a from reported procedure[5,6]



MW	140.18	120.15	382.5
mmol	4	2	1.3
amount	560	240	497

E-factor:

The ideal value of E-factor is zero.

E-factor = [total mass of raw materials - the total mass of product]/ mass of product.

E-factor of 3a = [(560 + 240)-497]/497

= 0.60

Process mass intensity (PMI):

PMI= ∑ (mass of stoichiometric reactants)/[mass of product]

= (560+240)/ 497

= 1.61

Reaction mass efficiency (RME):

RME = [mass of product /∑ (mass of stoichiometric reactants)] × 100

= [497 / (560+240)] × 100

= 62.125 %

Carbon Efficiency (CE):

CE denotes the percentage of carbon in the reactants that remains in the product.

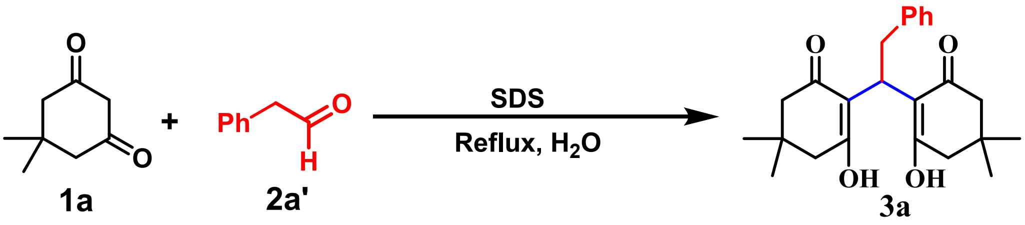
CE= [Amount of carbon in product/ Total carbon present in reactants] x 100

= [no. of moles of product x no. of carbons in product / (moles of 1a x carbons in 1a + moles of 2a x carbons in 2)] x 100

= [1.3 x 24 / (4 x 8 + 2 x 8)] x 100

= [31.2 / (32 + 16)] x 100

= 65 %



MW	140.18	120.15	382.5
mmol	2	2	0.83
amount	280	240	318

We have considered 2a as limiting reagent. Normally, 2 mmol cyclic-1,3-diketone should react with 1 mmol of aldehyde. Therefore, evidently 2a will be excess and only 1 mmol of it will react with dimedone.

E-factor:

The ideal value of E-factor is zero.

E-factor = [total mass of raw materials - the total mass of product]/ mass of product.

E-factor of 3a = [(280 + 120)-318]/318

= 0.26

Process mass intensity (PMI):

PMI= ∑ (mass of stoichiometric reactants)/[mass of product]

= (280+120)/ 318

= 1.26

Reaction mass efficiency (RME):

RME = [mass of product /∑ (mass of stoichiometric reactants)] × 100

= [318 / (280+120)] × 100

= 79.5 %

Carbon Efficiency (CE):

CE denotes the percentage of carbon in the reactants that remains in the product.

CE= [Amount of carbon in product/ Total carbon present in reactants] x 100

= [no. of moles of product x no. of carbons in product / (moles of 1a x carbons in 1a + moles of 2a x carbons in 2)] x 100

= [0.83 x 24 / (2 x 8 + 1 x 8)] x 100

= [19.92 / (16 + 8)] x 100

= 83 %

6. Analytical data for the product:

2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(3a)*****:**

Batch condition: Prepared according to general procedure (**A**), using styrene oxide (50 mg, 0.416 mmol) and 5,5-dimethylcyclohexane-1,3-dione (116 mg, 0.816 mmol) to 2,2'-(2-phenylethane-1,1-diyl) bis (3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **1a** (133 mg, 84%) as a White Crystal.

Flow condition: Prepared according to general procedure **(C)**, a solution of 0.2 M 5,5-dimethylcyclohexane-1,3-dione (280 mg, 2 mmol) and 0.1 M styrene oxide (120 mg, 1 mmol) in 20 mL dioxane were flown through the packed bed of Fe-Zeolite (bed height 6.0 cm) with 2.2 bar at 0.1 mL/min to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3a** (173 mg, 79.7% yield). Melting point: 158-160 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ [ppm] = 12.79 (s, 2H), 7.19 (m, 4H), 7.11 (m, 1H), 4.37 (t, J = 8 Hz, 1H), 3.32 (d, J = 8 Hz, 2H), 2.23 (s, 4H), 2.19 (d, J = 2.9 Hz, 4H), 1.00 (s, 6H), 0.69 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 190.3, 190.0, 140.0, 128.8, 128.5, 126.3, 116.1, 46.9, 46.1, 34.7, 31.3, 30.9, 30.1, 25.9. IR (neat): 3003.95, 1709.95 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{30}O_4$: 383.2222; found: 383.2215. Crystal preparation: The crystal is grown by simple recrystallization method. The pure compound isolated after column chromatography is dissolved in dichloromethane and layered with hexane and kept at room temperature for 2 days to get pure crystal.

2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(3b):***

Batch condition: Prepared according to general procedure **(A)**, using 5,5-dimethylcyclohexane-1,3-dione (104 mg, 0.74 mmol) and 2-(p-tolyl)oxirane (50 mg, 0.373 mmol) to afford 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3b** (60 mg, 41%) as a yellow solid.

Flow condition: Prepared according to general procedure **(C)**, a solution of 0.1 M 5,5-dimethylcyclohexane-1,3-dione (140 mg, 1 mmol) and 0.05 M 2-(p-tolyl)oxirane (67 mg, 0.5 mmol) in 20 mL 1,4-dioxane were flown through the packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar at 0.1 mL/min to afford 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3b** (118 mg, 40% yield). Melting point: 165-167 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.77 (s, 2H), 7.05 (d, J = 4 Hz, 2H), 7.00 (d, J = 8Hz, 2H), 4.33 (t, J =

8 Hz, 1H), 3.27 (d, *J* = 8 Hz, 2H), 2.24 (d, *J* = 4 Hz, 8H), 2.19 (s, 3H), 1.00 (s, 6H), 0.71 (s, 6H). 13C{1H} NMR (100 MHz, $CDCl_3$) δ [ppm] = δ 190.2, 189.9, 137.1, 135.7, 129.0, 128.6, 116.1, 46.9, 46.1, 34.2, 31.3, 30.9, 29.9, 25.9, 20.9. IR (neat): 3361, 1589 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{32}O_4$ 397.2379; found 397.2374.

2,2'-(2-(4-bromophenyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(3c)*****:** Prepared according to general procedure (**A**), using 5,5-dimethylcyclohexane-1,3-dione (70 mg, 0.50 mmol) and 2-(4-bromophenyl)oxirane (50 mg, 0.25 mmol) to afford 2,2'-(2-(4-bromophenyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3c** (80 mg, 67 %) as white solid. Melting point: 131-133 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 4.31 (t, *J* = 8 Hz, 1H), 3.27 (d, *J* = 8 Hz, 2H), 2.23 (s, 4H), 2.20 (s, 4H), 1.00 (s, 6H), 0.73 (s, 6H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.4, 190.03, 139.1, 131.5, 130.6, 120.1, 115.8, 46.9, 46.1, 34.11, 31.2, 30.9, 30.0, 25.9. IR (neat): 3407, 1712 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{29}BrO_4$ 461.1327; found 461.1325.

2,2'-(2-phenylpropane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***)(3d):*** Prepared according to general procedure **(A)**, using 5,5-dimethylcyclohexane-1,3-dione (104 mg, 0.74 mmol) and 2-methyl-2-phenyloxirane (50 mg, 0.373 mmol) to afford 2,2'-(2-phenylpropane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3d** (81 mg, 58%) as a yellow solid. Melting point: 156-158 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.71 (s, 2H), 7.18 (m, 1H), 7.08 (m, 1H), 4.16 (d, *J* = 12 Hz, 1H), 4.10 (m, 1H), 2.36 (m, 4H),1.99 (m, 4H), 1.15 (m, 12H), 0.87 (s, 3H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.6, 189.4, 128.6, 126.9, 126.4, 116.6, 115.6, 47.2, 45.9, 37.4, 31.1, 30.3, 30.2, 26.8, 24.9, 22.4. IR (neat): 3402, 1708 cm-1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{30}O_4$: 397.2379; found: 397.2377.

2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) ***(3e):***

Batch condition: Prepared according to general procedure **(A)**, using styrene oxide (50 mg, 0.416 mmol) and 4,4-dimethylcyclohexane-1,3-dione (116 mg, 0.832 mmol) to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) **3e** (110 mg, 70%) as a white solid.

Flow condition: Prepared according to general procedure **(C)**, a solution of 0.2 M 4,4-dimethylcyclohexane-1,3-dione (280 mg, 2 mmol) and 0.1 M styrene oxide (120mg, 1 mmol) in 20 mL dioxane was flown through the packed bed of Fe-zeolite (bed height 6.0 cm) with 2.2 bar pressure at 0.1 mL/min to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) **3e** (143 mg, 54% yield). Melting point: 138-140 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.19 (s, 2H), 7.15 (m, 5H), 4.20 (t, *J* = 32 Hz , 1H), 3.21 (d, *J* = 8 Hz, 2H), 2.37 (m, 4H), 1.56 (m, 4H), 1.05 (m, 12H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ [ppm] = 204.1, 203.7, 182.9, 182.2, 140.6, 129.2, 128.5, 126.3, 115.6, 39.7, 34.9, 34.2, 32.1, 28.4, 27.8. IR (neat): 2927, 1718 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for for $C_{24}H_{30}O_4$ 383.2222 ; found 383.2221.

2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) ***(3f)*****:** Prepared according to general procedure **(A)**, using 2-(p-tolyl)oxirane (50 mg, 0.373 mmol) and 4,4-dimethylcyclohexane-1,3-dione (104.44 mg, 0.746 mmol) to afford 2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) **3f** (70 mg, 48%) as a white solid. Melting point: 142-144 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 2H), 6.98 (m, 4H), 4.15 (t, *J* = 8 Hz, 1H), 3.19 (d, *J* = 8Hz, 2H), 2.41 (m, 4H), 2.27 (s, 3H), 1.6 (m, 4H), 1.08 (s,3H), 1.06 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ [ppm] = 204.1, 203.8, 182.9, 182.1, 137.3, 135.5, 128.8,128.7, 115.4, 39.7, 38.9, 34.6, 34.2, 28.4,, 26.2, 26.0, 24.3.

IR (neat): 3434, 1741 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{25}H_{32}O_4$ 397.2379; found 397.2369.

2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5-methylcyclohex-2-en-1-one) ***(3g):***

Batch condition: Prepared according to general procedure (**A**), using styrene oxide (50 mg, 0.416 mmol) and 5-methylcyclohexane-1,3-dione (128mg, 0.832 mmol) to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5-methylcyclohex-2-en-1-one) **3g** (117 mg, 80%) as a White solid.

Flow condition: - Prepared according to general procedure **(C)**, a solution of 0.2 M 5-methylcyclohexane-1,3-dione (256 mg, 2 mmol) and 0.1 M styrene oxide (120mg, 1 mmol) in 20 mL dioxane was flown through the packed bed of Fe-zeolite (bed height 6.0 cm) with 2.2 bar at 0.1 mL/min to afford 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3g** (148 mg, 61% yield). Melting point: 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 13.13 (s, 2H), 7.13 (m, 5H), 4.18 (t, J = 8 Hz, 1H), 3.38 (dd, J = 13.7, 9.2 Hz, 1H), 3.27 (d, J = 8 Hz, 2H), 3.18 (dd, J = 13.7, 7.9 Hz, 1H), 2.42 (m, 8H), 1.00 (d, J = 4 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 191.6, 191.1, 128.6, 128.3, 128.1, 126.1, 116.8, 41.7, 40.9, 34.8, 32.1, 27.4, 20.5. IR (neat): 2954, 1726 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{22}H_{26}O_4$: 355.1909; found: 355.1918.

2'-(2-phenylethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **(3h):**

Batch condition: Prepared according to general procedure (**A**), using styrene oxide (50 mg, 0.416 mmol) and cyclohexane-1,3-dione (112mg, 0.832 mmol) to afford 2'-(2-phenylethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3h** (84 mg, 62%) as a yellow solid.

Flow condition: - Prepared according to general procedure (**C**), a solution of 0.2 M cyclohexane-1,3-dione (224 mg, 2 mmol) and 0.1 M styrene oxide (120 mg, 1 mmol) in 20 mL dioxane was flown through the packed bed of Fe-zeolite (bed height 6.0 cm) with 2.2 bar at 0.1

mL/min to afford 2'-(2-phenylethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3h** (110 mg, 61% yield). Melting point: 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 13.11 (s, 2H), 7.07 (m, 5H), 4.12 (t, J = 8 Hz, 1H), 3.19 (d, J = 8 Hz, 2H), 2.23 (m, 12 H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ [ppm] = 191.8, 191.4, 140.5, 128.7, 128.2, 126.2, 117.4, 34.9, 33.5, 32.7, 32.2, 19.9. IR (neat): 2945, 1716 cm-1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{22}O_4$: 327.1596; found: 327.1599.

2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) ***(3i)*****:** Prepared according to general procedure **(A)**, using 2-(p-tolyl)oxirane (50 mg, 0.373 mmol) and cyclohexane-1,3-dione (84 mg, 0.746 mmol) to afford 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3i** (79 mg, 62%) as a yellow solid. Melting point: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.17 (s, 2H), 7.00 (m, 4H), 4.17 (t, *J* = 8 Hz, 1H), 3.23 (d, *J* = 8 Hz, 2H), 2.44 (m, 3H), 2.33 (m, 4H), 2.28 (s, 3H), 2.25 (m, 1H), 1.84 (m, 2H), 1.61 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] = 191.7, 191.2, 137.1, 135.3, 129.0, 125.5, 117.1, 34.5, 33.5, 32.7, 32.2, 21.0, 19.8. IR (neat): 2938, 1730 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}O_4$ 341.1753; found 341.1749.

2,2'-(propane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **(3j):** Prepared according to general procedure (**A**), using 2-methyloxirane (50 mg, 0.86 mmol) and 5,5-dimethylcyclohexane-1,3-dione (240 mg, 1.72 mmol) to afford 2,2'-(propane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3j** (60 mg, 22%) as a white solid. Melting point: 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (s, 2H), 3.81 (t, *J* = 8 Hz, 1H), 2.28 (m, 8H), 2.05 (m, 2H), 1.07 (s, 6H), 1.05 (s, 6H), 0.83 (t, *J* = 8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.2, 189.6, 116.5, 47.1, 46.3, 31.7, 31.2, 29.9, 26.6, 22.4, 13.6. IR (neat): 2961, 1724 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{28}O_4$ 321.2066; found 321.2065.

2,2'-(hexane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(3k)*****:** Prepared according to general procedure (**A**), using 2-butyloxirane (50 mg, 0.499 mmol) and 5,5-dimethylcyclohexane-1,3-dione (139 mg, 0.998 mmol) to afford 2,2'-(hexane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one **3k** (49 mg, 27%) as a white solid. Melting point: 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.49 (s, 2H), 3.91(t, *J* = 8 Hz, 1H), 2.28 (m, 8H), 1.24 (m, 6 H), 1.06 (s, 6H), 1.06 (s, 6H), 0.88 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.0, 189.7, 116.7, 47.1, 46.3, 31.8, 31.2, 29.9, 29.7, 29.7, 29.5, 29.3, 29.3, 29.2, 29.1, 26.6, 22.7, 14.2. IR (neat): 2948, 2867, 1717 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{34}O_4$ 363.2535; found 363.2542.

2,2'-(octane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(3l)*****:** Prepared according to general procedure (**A**), using 2-hexyloxirane (50 mg, 0.390 mmol) and 5,5-dimethylcyclohexane-1,3-dione (109 mg, 0.780 mmol) to afford 2,2'-(octane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3l** (47 mg, 31%) as a white solid. Melting point: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ12.49 (s, 2H), 3.90 (t, *J* = 8 Hz, 1H), 2.27 (m, 8H), 1.45 (m, 12 H), 1.06 (s, 6H), 1.05 (s, 6H), 0.85 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.0, 189.7, 116.7, 47.1, 46.3, 31.8, 31.2, 29.9, 29.6, 29.3, 29.3, 29.2, 29.1, 26.6, 22.7, 14.2. IR (neat): 2927, 2864, 1723 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{38}O_4$ 391.2848; found 391.2860.

*2,2'-(cyclopentylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one)****(3m):*** Prepared according to general procedure **(A)**, using 7-oxabicyclo[4.1.0]heptane (50 mg, 0.51 mmol) and 5,5-dimethylcyclohexane-1,3-dione (142 mg, 1.018 mmol) at 160 °C in toluene to afford 2,2'-(cyclopentylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3m** (80 mg, 44%) as a white solid. Melting point: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 2H), 3.58 (d, J = 24 Hz, 1H), 3.15 (m, 1H), 2.28 (m, 4H), 2.27 (m, 4H), 1.60 (m, 8H), 1.07 (s, 6H), 1.06 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.2, 189.6, 117.0, 47.0, 46.2, 38.3, 36.6, 32.9, 31.1, 30.2, 26.5, 25.4. IR (neat): 2952, 2868, 1717 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{32}O_4$ 361.2379; found 361.2374.

9-benzyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4a)*****:** Prepared according to general procedure **(B)**, using 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3a** (50 mg, 0.131 mmol) at 180 °C in toluene to afford 9-benzyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4a** (40 mg, 85%) as a yellow solid. Melting point: 120-122 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 3H), 6.86 (m, 2H), 4.06 (t, J = 4 Hz, 1H), 2.91 (d, J = 4 Hz, 2H), 2.28 (s, 4H), 2.14 (m, 4H), 1.05 (s, 6H), 1.04 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 197.3, 164.2, 138.9, 130.1, 127.7, 126.2, 113.9, 51.2, 40.8, 38.2, 32.1, 28.6, 27.5. IR (neat):1660 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{28}O_3$ 365.2116; found 365.2115.

3,3,6,6-tetramethyl-9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4b):*** Prepared according to general procedure **(B)**, using 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3b** (50 mg, 0.133 mmol) in toluene at 180 °C to afford 3,3,6,6-tetramethyl-9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4b** (39 mg, 83%) as a light yellow solid . Melting point: 126-128 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 4Hz, 2H), 6.74 (d, J = 4 Hz, 2H), 4.03 (t, J = 4 Hz, 1H), 2.88 (d, J = 4Hz, 2H), 2.28 (S, 4H), 2.27 (s, 4H), 2.17 (d, J = 8 Hz, 3H), 1.06 (s, 6H), 1.05 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 197.2, 135.6, 135.5, 129.9, 128.4, 113.9, 51.1, 40.8, 37.7, 32.0, 28.6, 28.5, 27.5, 21.1. IR (neat): 1665 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{30}O_3$ 379.2273; found 379.2264.

9-(4-bromobenzyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4c)****:* Prepared according to general procedure **(B)**, using 2,2'-(2-(4-bromophenyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **3c** (40 mg, 0.087 mmol) in toluene at

180 °C to afford 9-(4-bromobenzyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4c** (18 mg, 17%) as yellow solid. Melting point: 122-124 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, *J* = 8 Hz, 2H), 6.75 (d, *J* = 8 Hz, 2H), 4.04 (t, *J* = 4 Hz, 1H), 2.90 (d, *J* = 4 Hz, 2H), 2.28 (s, 4H), 2.21 (d, J = 4 Hz, 4H), 1.55 (s, 6H), 1.06 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 207.1, 197.2, 164.3, 138.0, 131.6, 120.1, 113.5, 51.1, 40.8, 37.6, 32.0, 31.0, 28.6. IR (neat): 1742 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{27}BrO_3$ 443.1222; found 443.1219.

9-benzyl-3,6-dimethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4d):*** Prepared according to general procedure **(B)**, using 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3g** in toluene at 180 °C to afford 9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4d** (29 mg, 61%) as yellow solid. Melting point: 118-120 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (m, 3H), 6.77 (m, 2H), 4.06 (t, *J* = 4 Hz, 1H), 2.82 (m, 2H), 2.53 (d, *J* = 12 Hz, 2H), 2.21 (m, 4H), 2.04 (m, 4H), 1.08 (d, *J* = 4 Hz, 3H), 1.06 (d, *J* = 2.76 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 197.2, 165.2, 138.4, 130.3, 127.7, 126.7, 113.3, 45.5, 37.8, 35.1, 28.7, 28.0, 21.0. IR (neat): 1721.38 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{22}H_{24}O_3$ 337.1803; found 337.1804

9-benzyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4e):*** Prepared according to general procedure **(B)**, using 2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3h** (50 mg, 0.153 mmol) in toluene at 180 °C to afford 9-benzyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4e** (31 mg, 65%) as a light yellow solid. Melting point: 124-126 °C $^{.1}$H NMR (400 MHz, CDCl$_3$) δ 7.17 (m, 3H), 6.81 (m, 2H), 4.09 (t, *J* = 4Hz, 1H), 2.82 (d, *J* =4 Hz, 2H), 2.49 (m, 2H), 2.38 (m, 2H), 2.23 (m, 4H), 1.98 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 197.3, 165.8, 138.5, 130.2, 127.4, 126.2, 114.6, 38.2, 37.2, 27.1, 26.9, 20.5.

IR (neat): 1718 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{20}O_3$ 309.1490; found 309.1489.

9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(4f)*****:** Prepared according to general procedure **(B)**, using 2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) **3i** in toluene at 180 °C to afford 9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4f** (36.0 mg, 76%) as yellow solid. Melting point: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8 Hz, 2H), 6.69 (d, *J* = 8 Hz, 2H), 4.07 (t, *J* = 4 Hz, 1H), 2.78 (d, *J* = 4 Hz, 2H), 2.49 (m, 2H), 2.38 (m, 2H), 2.29 (s, 3H), 2.22 (m, 4H), 1.98 (m, 4H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 197.3, 165.7, 135.6, 135.3, 130.1, 128.1, 114.7, 37.7, 37.2, 27.1, 26.9, 21.2, 20.5. IR (neat): 1739 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{22}O_3$ 323.1647; found: 323.1645.

4-(bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)benzonitrile ***(6a):*** Prepared according to general procedure (**D**), a solution of 0.1 M 4-formylbenzonitrile (65 mg, 0.50 mmol) in 5 mL 1,4-dioxane and 5,5-dimethylcyclohexane-1,3-dione (140 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford 4-(bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)benzonitrile **6a** (119 mg, 87% from 7 mL collected reaction mixture) as white solid. Melting point: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 11.79 (s, 2H), 7.56 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 5.51 (s, 1H), 2.45 (m, 4H), 2.35 (m, 4H), 1.22 (s, 6H), 1.11 (s, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.9, 189.5, 144.3, 132.1, 127.6, 118.9, 114.8, 109.8, 47.0, 46.4, 33.3, 31.5, 29.6, 27.5. IR (neat): 2952, 1717 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{27}NO_4$: 394.2018; found: 394.2014.

2,2'-((4-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(6b):*** Prepared according to general procedure (**D**), a solution of 0.1 M 4-nitrobenzaldehyde (75 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M dimedone (140 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 4.8 bar pressure at 0.1 mL/min to afford 2,2'-((4-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6b** (127mg, 90% from 6.9 mL collected reaction mixture) as white solid. Melting point: 187-189 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ [ppm] = 11.80 (s, 2H), 8.15 (m, 1H), 8.13 (m, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 5.55 (s, 1H), 2.46 (m, 4H), 2.36 (m, 4H), 1.24 (s, 6H), 1.11 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 190.9, 189.6, 146.5, 146.2, 127.7, 123.5, 114.9, 47.0, 46.4, 33.3, 31.5, 29.5, 27.5. IR (neat): 3362, 1710 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{23}H_{27}NO_6$: 414.1916; found: 414.1919.

*2,2'-((3,5-dimethoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one)**(6c)***:

Prepared according to general procedure (**D**), a solution of 0.1 M 3,5-dimethoxybenzaldehyde (83 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M 5,5-dimethylcyclohexane-1,3-dione (140 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford 2,2'-((3,5-dimethoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6c** (108 mg, 70% from 7 mL collected reaction mixture) as white solid. Melting point: 184-186 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ [ppm] = 11.97 (s, 2H), 6.78 (d, J = 8 Hz, 1H), 6.62 (m, 2H), 5.51 (s, 1H), 3.84 (s, 1H), 3.77 (s, 3H), 2.43 (m, 4H), 2.33 (m, 4H), 1.24 (s, 6H), 1.11 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ [ppm] = 190.4, 189.4, 148.7, 147.0, 130.4, 118.9, 115.8, 110.5, 55.8, 55.7, 47.1, 46.4, 32.3, 31.2, 29.9, 27.1. IR (neat): 2954, 1710 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{25}H_{32}O_6$: 429.2277; found: 429.2280.

*2,2'-((4-(benzyloxy)phenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one)**(6d):***

Prepared according to general procedure (**D**), a solution of 0.1 M 4-(benzyloxy)benzaldehyde (106 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M dimedone (140 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford 2,2'-((4-(benzyloxy)phenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6d** (66 mg, 59% from 5 mL collected reaction mixture) as yellow solid. Melting point: 222-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 11.91 (s, 2H), 7.40 (m, 4H), 7.32 (m, 1H), 7.00 (m, 2H), 6.88 (m, 2H), 5.48 (s, 1H), 5.03 (s, 2H), 2.43 (m, 4H), 2.33 (m, 4H), 1.22 (s, 6H), 1.10 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.4, 189.4, 156.9, 137.2, 130.2, 128.6, 127.9, 127.8, 127.5, 115.8, 114.6, 70.0, 47.1, 46.5, 32.1, 31.4, 29.7, 27.4. Melting point: 195-197 °C. IR (neat): 2924, 1739 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{34}O_5$: 475.2484; found: 475.2482.

2,2'-((4-fluorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) ***(6e)*****:** Prepared according to general procedure (**D**), a solution of 0.1 M 4-fluorobenzaldehyde (62 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M dimedone (140 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford 2,2'-((4-fluorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6e** (63 mg, 65% from 5 mL collected reaction mixture) as white solid. Melting point: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 11.88 (s, 2H), 7.03 (m, 2H), 6.95 (m, 2H), 5.48 (s. 1H), 2.39 (m, 8H), 1.22 (s, 6H), 1.10 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 190.6, 189.4, 128.3, 128.2, 115.6, 115.1, 114.9, 47.0, 46.4, 32.2, 31., 29.6, 27.41. IR (neat): 2956, 1716 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{27}FO_4$: 387.1970; found: 387.1970.

2,2'-(p-tolylmethylene)bis(3-hydroxycyclohex-2-en-1-one) ***(6f):*** Prepared according to general procedure (**D**),), a solution of 0.1 M 4-methylbenzaldehyde (60 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M cyclohexa-1,3-dione (112 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford 2,2'-(p-tolylmethylene)bis(3-hydroxycyclohex-2-en-1-one) **6f** (84 mg, 74% from 7 mL collected reaction mixture) as white solid. Melting point: 190-192 °C. ^{1}H NMR (400 MHz,

$CDCl_3$) δ [ppm] = 12.35 (s, 2H), 7.06 (d, *J* = 8 Hz, 2H), 6.98 (d, *J* = 8 Hz, 2H), 5.43 (s, 1H), 2.60 (m, 4H), 2.41 (m, 4H), 2.30 (s, 3H), 2.03 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 192.0, 190.9, 135.3, 134.7, 128.9, 126.4, 116.6, 33.5, 33.0, 32.6, 20.9, 20.1. IR (neat): 3449, 1740 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{22}O_4$: 327.1596; found: 327.1595.

2,2'-(phenylmethylene)bis(3-hydroxycyclohex-2-en-1-one) ***(6g):*** Prepared according to general procedure (**D**), a solution of 0.1 M benzaldehyde (53 mg, 0.5 mmol) in 5 mL 1,4-dioxane and 0.2 M 1,3-cyclohexadione (112 mg, 1 mmol) in 5 mL 1,4-dioxane were flown through a packed bed of Fe-zeolite (bed height 6.0 cm) with 2-3 bar pressure at 0.1 mL/min to afford **6g** 2,2'-(phenylmethylene)bis(3-hydroxycyclohex-2-en-1-one) (119 mg, 64% from 6 mL collected reaction mixture) as white solid. Melting point: 216-218 °C. ^1H NMR (400 MHz, $CDCl_3$) δ [ppm] = 12.35 (s, 2H), 7.28 (m, 1H), 7.24 (m, 1H), 7.16 (m, 2H), 5.47 (s, 1H), 2.61 (m, 4H), 2.44 (m, 4H), 2.03 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 192.1, 190.9, 137.9, 128.2, 126.5, 125.9, 116.4, 33.5, 32.9, 20.1, 18.9. IR (neat): 3494, 1708 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{20}O_4$: 313.1440; found: 313.1446.

4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile ***(7a):*** Prepared according to general procedure (**E**), To an oven dried 10 mL sealed tube, 4-(bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)benzonitrile **6a** (50 mg, 0.127 mmol), 0.03% iron zeolite and 2 mL toluene were added and heated at 180 °C for 8 h affording 4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile **7a** (44 mg, 93%) as white solid. Melting point: 220-222 °C. ^1H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.52 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 4.76 (s, 1H), 2.48 (s, 4H), 2.20 (m, 4H), 1.11 (s, 6H), 0.98 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 196.3, 162.9, 149.4, 132.0, 129.3, 119.0, 114.6, 110.2, 67.1, 50.6, 40.8, 32.2, 29.2, 27.3. IR (neat): 1740 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{25}NO_3$: 376.1916; found: 376.1912.

3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(7b):*** Prepared according to general procedure (**E**), To an oven dried 10 mL sealed tube 2,2'-((4-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one (30 mg, 0.0726 mmol), 0.03% Fe-zeolite and 2 mL toluene were added and heated at 180 °C for 8 h affording 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **7b** (24 mg, 85%) as white solid. Melting point: 222-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.09 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H), 4.62 (s, 1H), 2.4 (s, 4H), 2.21 (m, 4H), 1.11 (s, 6H), 0.99 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 196.3, 162.9, 151.5, 146.5, 129.4, 123.5, 114.6, 50.6, 40.9, 32.7, 32.2, 29.3, 27.3. IR (neat): 1710 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{25}NO_5$: 396.1811; found: 396.1811.

9-(3,5-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(7c)*****:** Prepared according to general procedure (**E**), To an oven dried 10 mL sealed tube 2,2'-((3,5-dimethoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6c** (50 mg, 0.117 mmol), 0.03% Fe-zeolite and 2 mL toluene were added and heated at 180 °Cfor 8 h affording 9-(3,5-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **7c** (38 mg, 81%) as white solid. Melting point: 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 6.90 (d, *J* = 4 Hz, 1H), 6.74 (m, 2H), 4.70 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.45 (s, 4H), 2.21 (m, 4H), 1.10 (s, 6H), 1.00 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 196.5, 162.1, 148.5, 147.5, 136.9, 120.1, 115.8, 112.3, 110.9, 55.9, 55.8, 50.8, 40.9, 32.2, 31.2, 29.3, 27.3. IR (neat): 1710 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{30}O_5$: 410.2093; found: 410.2090.

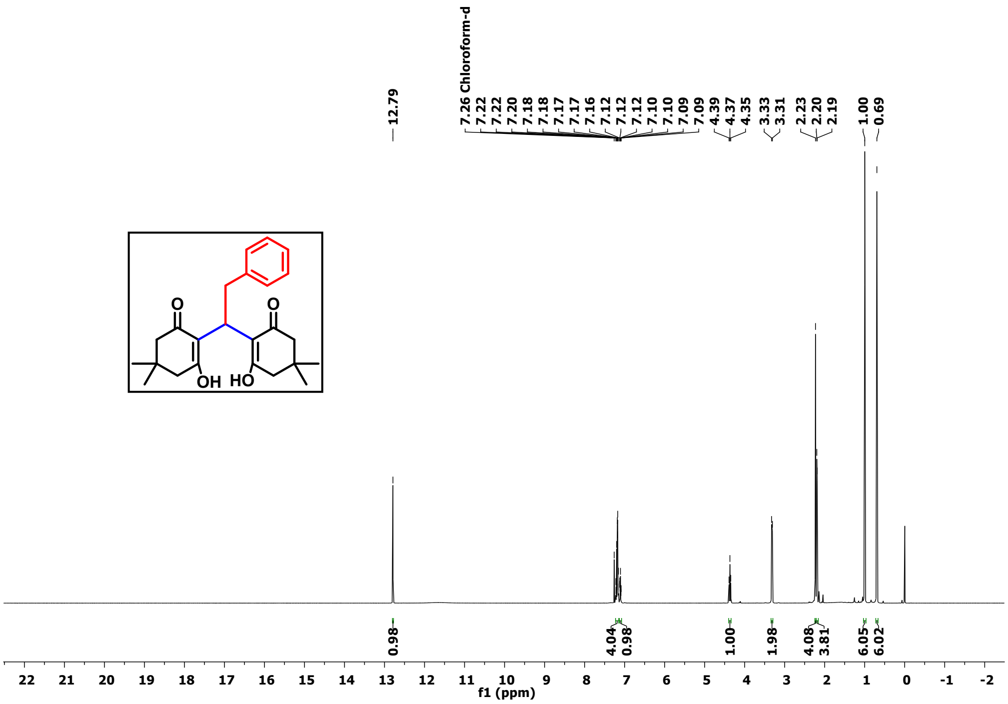
9-(4-(benzyloxy)phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***7(d):*** Prepared according to general procedure (**E**), To an oven dried 10 mL sealed tube 2,2'-((4-(benzyloxy)phenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) **6d** (30 mg, 0.063 mmol), 0.03% Fe-zeolite and 2 mL toluene were added and heated at 180 °Cfor

8 h affording 9-(4-(benzyloxy)phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **7d** (22 mg, 77%) as white solid. Melting point: 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.38 (m, 4H), 7.30 (m,1H), 7.21 (s, 1H), 7.19 (s, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 4.97 (s, 2H), 4.70 (s, 1H), 2.45 (s, 4H), 2.19 (m, 4H), 1.11 (s, 6H), 0.99 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 196.5, 162.1, 157.4, 137.2, 136.8, 129.4, 128.5, 127.6, 115.8, 114.4, 69.9, 50.78, 40.9, 32.2, 30.9, 29.3, 27.4. IR (neat): 2956, 1709 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{32}O_4$: 457.2379; found: 457.2380.

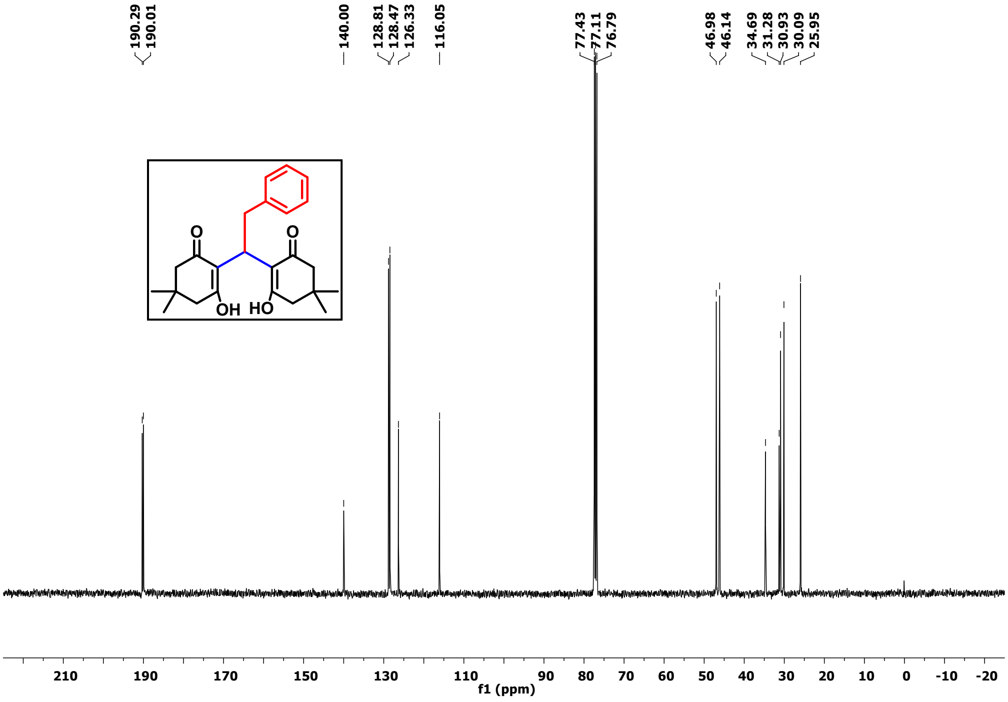
9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione ***(7e):*** Prepared according to general procedure (**E**), To an oven dried 10 mL sealed tube 2,2'-(p-tolylmethylene)bis(3-hydroxycyclohex-2-en-1-one) **6b** (30 mg, 0.0919 mmol), 0.03% Fe-zeolite and 2 mL toluene were added and heated at 180 °Cfor 8 h affording 9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **7e** (20 mg, 72%) as white solid. Melting point: 216-218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.18 (d, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 4.77 (s, 1H), 2.61 (m, 4H), 2.33 (m, 4H), 2.25 (s, 3H), 2.00 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ [ppm] = 196.6, 163.8, 141.5, 135.9, 128.9, 128.3, 117.0, 36.9, 31.2, 27.2, 21.1, 20.3. IR (neat): 1741 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{20}O_3$: 331.1309; found: 331.1309.

7. Copies of NMR and HRMS spectra

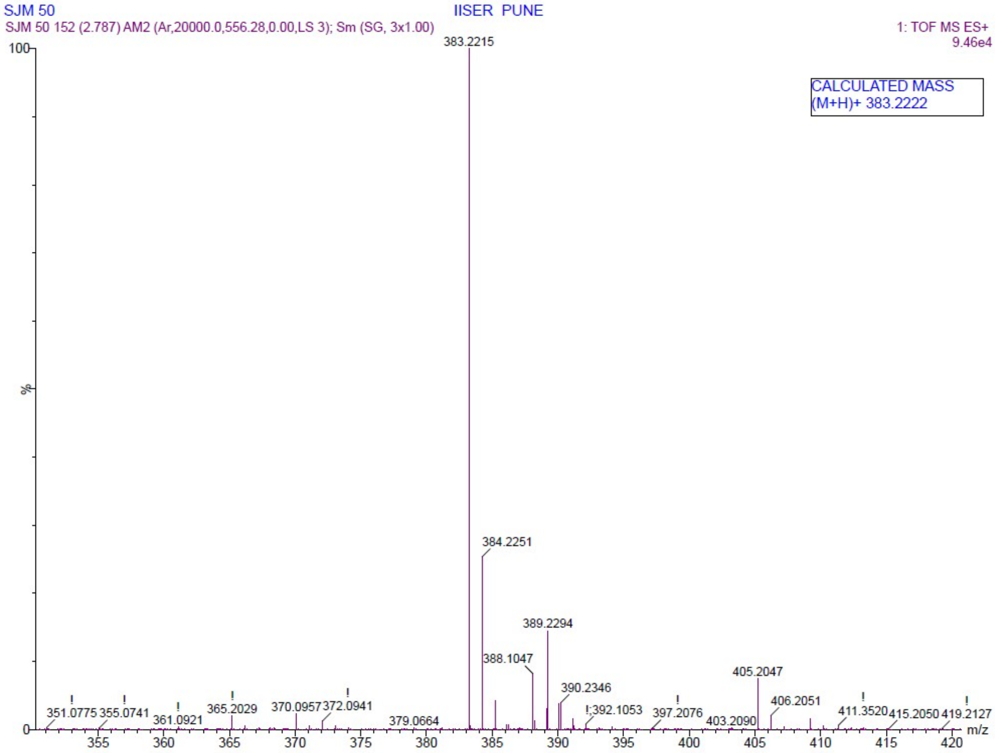
2,2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one



^{1}H NMR of **3a**, 400 MHz, $CDCl_3$

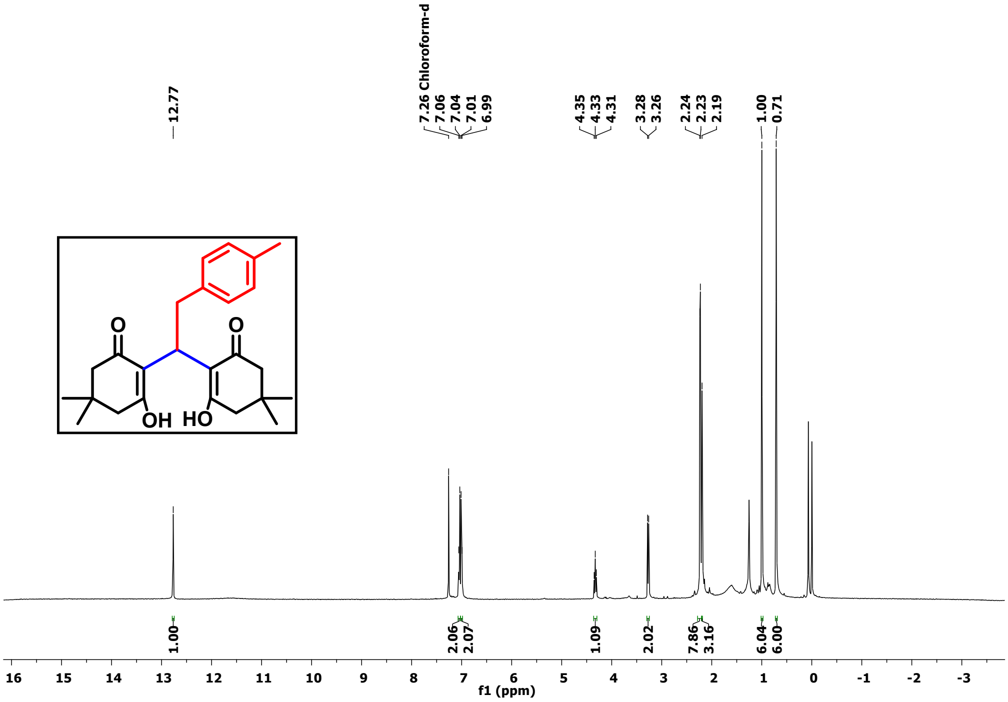


^{13}C {^{1}H} NMR of **3a**, 100 MHz, $CDCl_3$

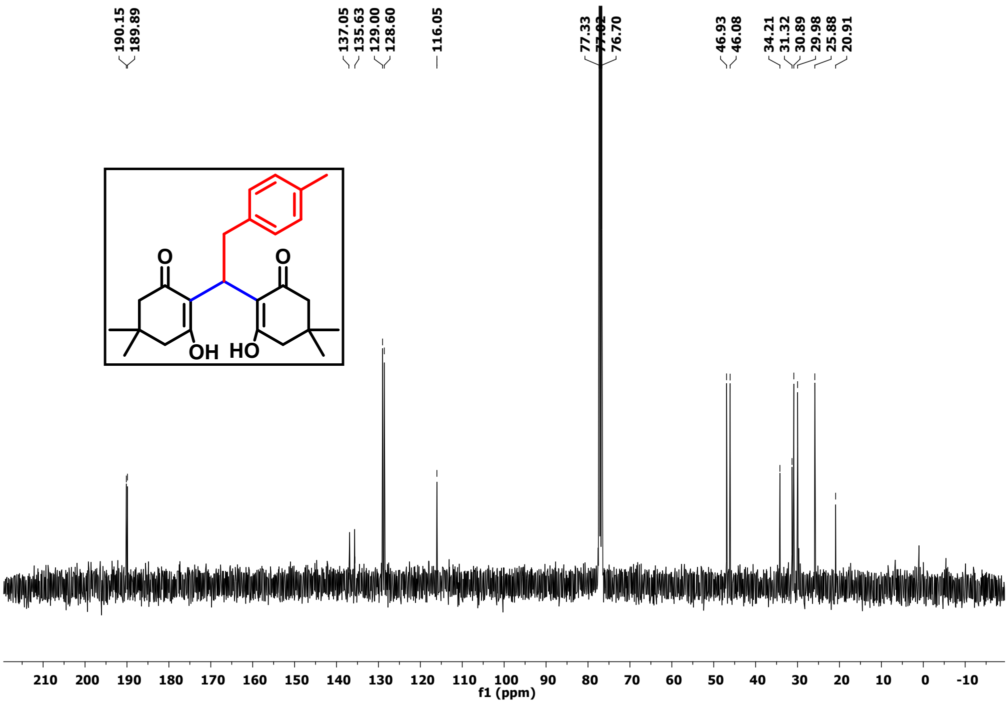


HRMS (ESI-TOF) of 3a

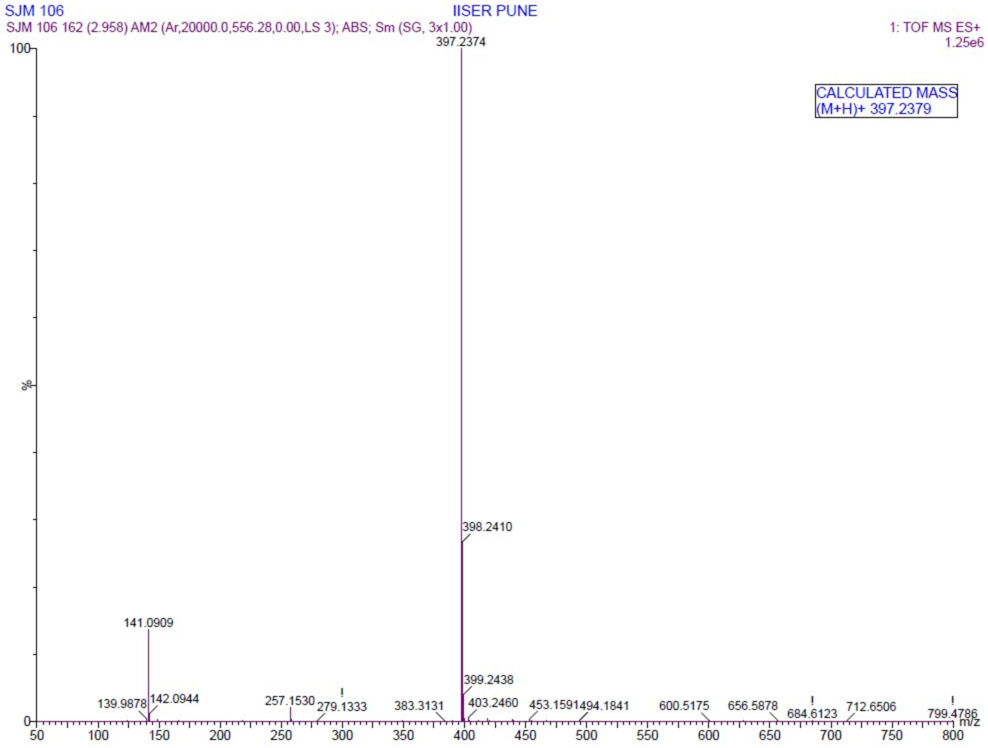
2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3b)



^{1}H NMR of **3b**, 400 MHz, CDCl$_3$

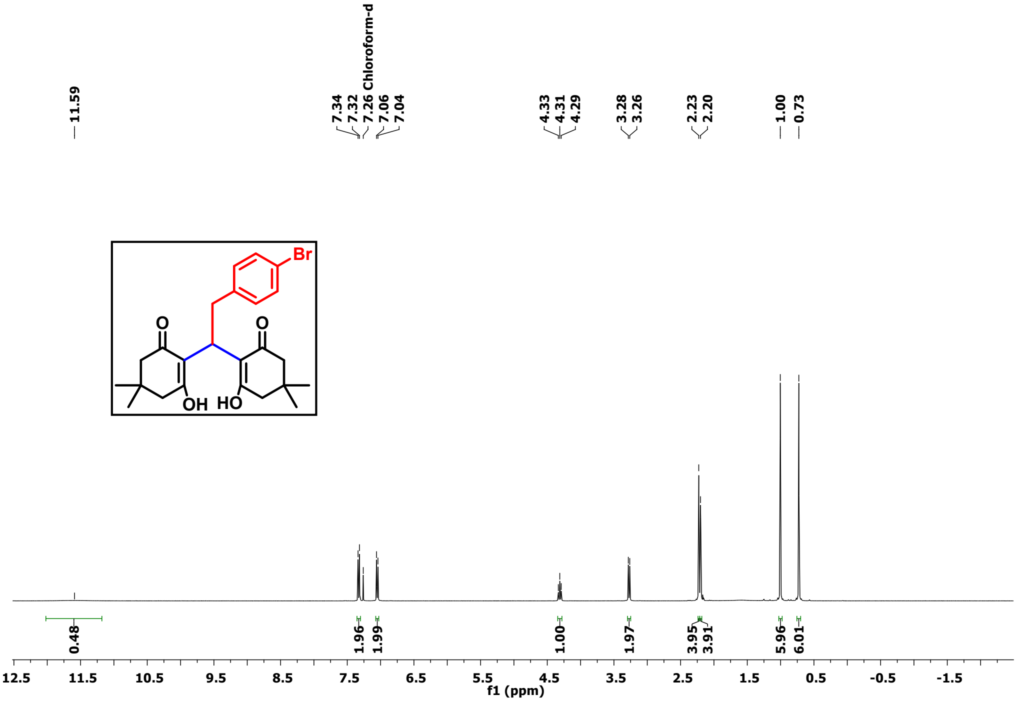


$^{13}C\ \{^1H\}$ NMR of **3b**, 100 MHz, $CDCl_3$

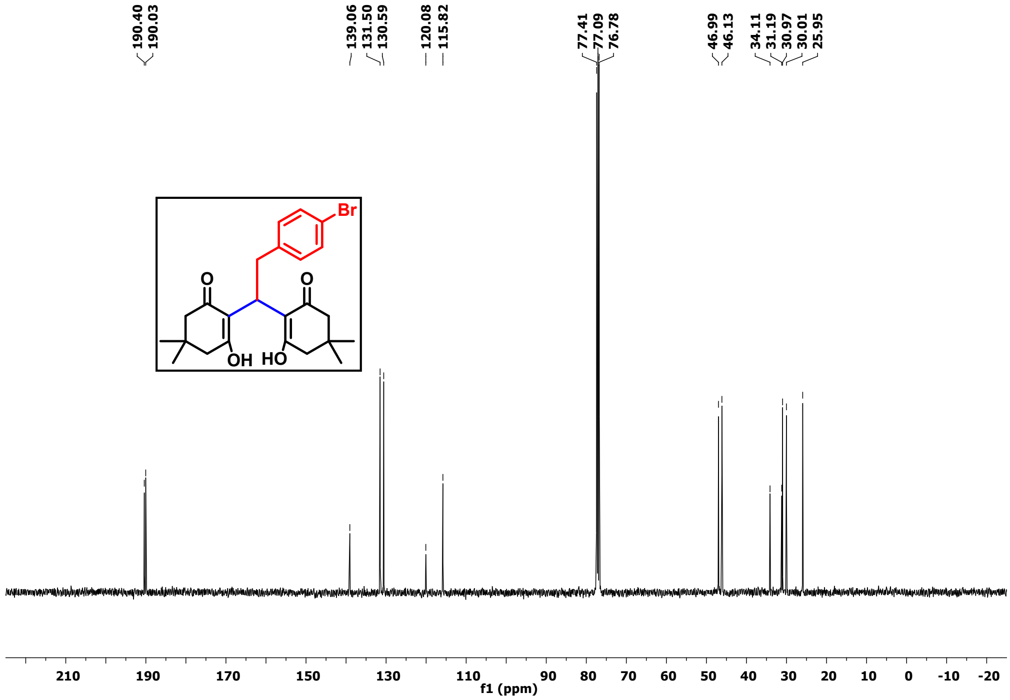


HRMS (ESI-TOF) of 3b

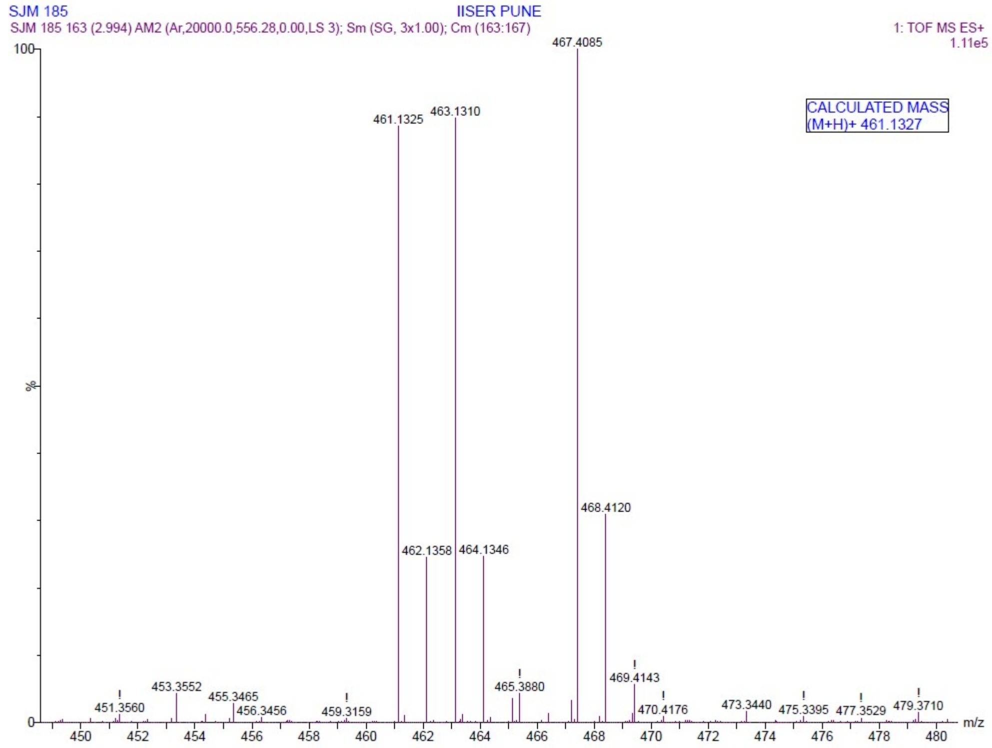
2,2'-(2-(4-bromophenyl)ethane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3c)



^{1}H NMR of **1c**, 400 MHz, CDCl$_3$

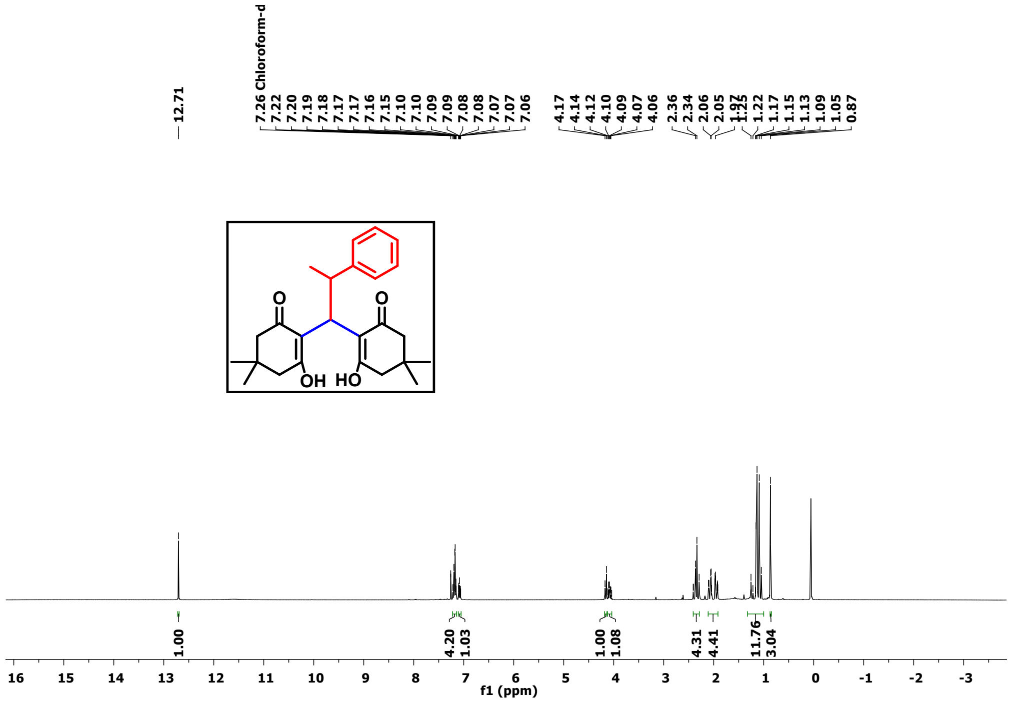


^{13}C {^{1}H} NMR of **3c**, 100 MHz, CDCl$_3$

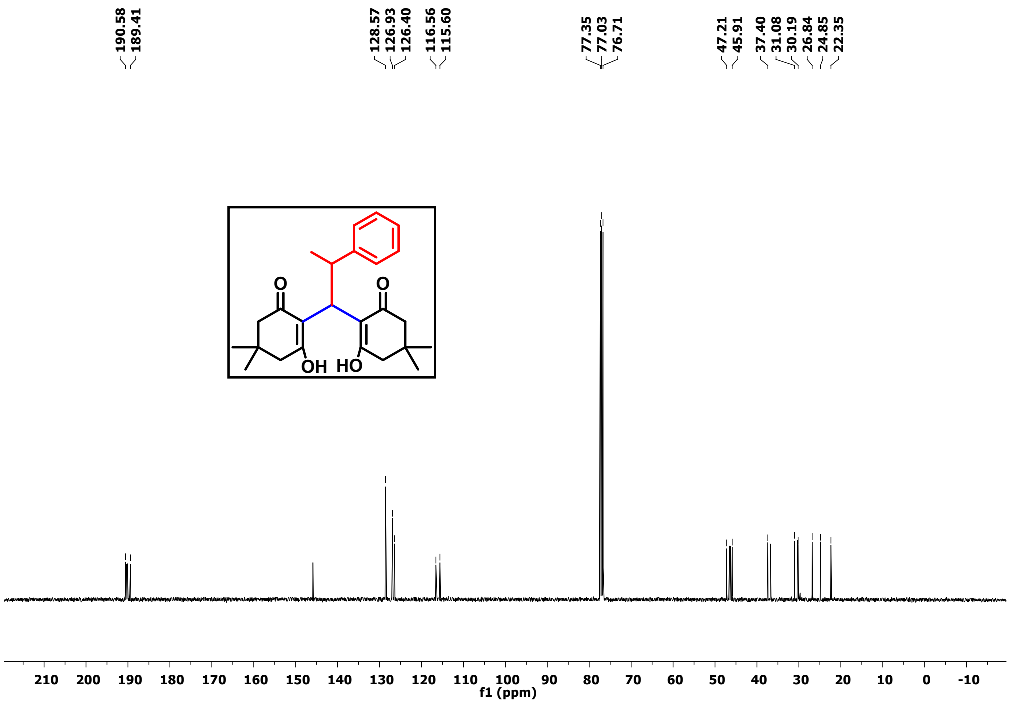


HRMS (ESI-TOF) of 3c

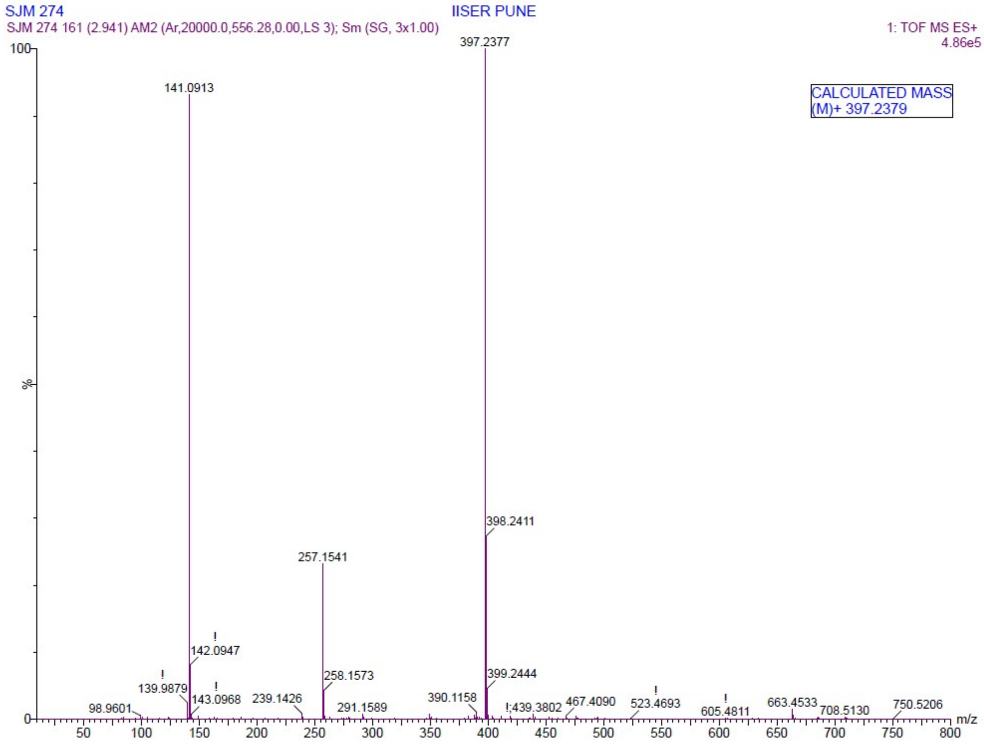
2,2'-(2-phenylpropane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3d)



^{1}H NMR of **3d**, 400 MHz, CDCl$_3$

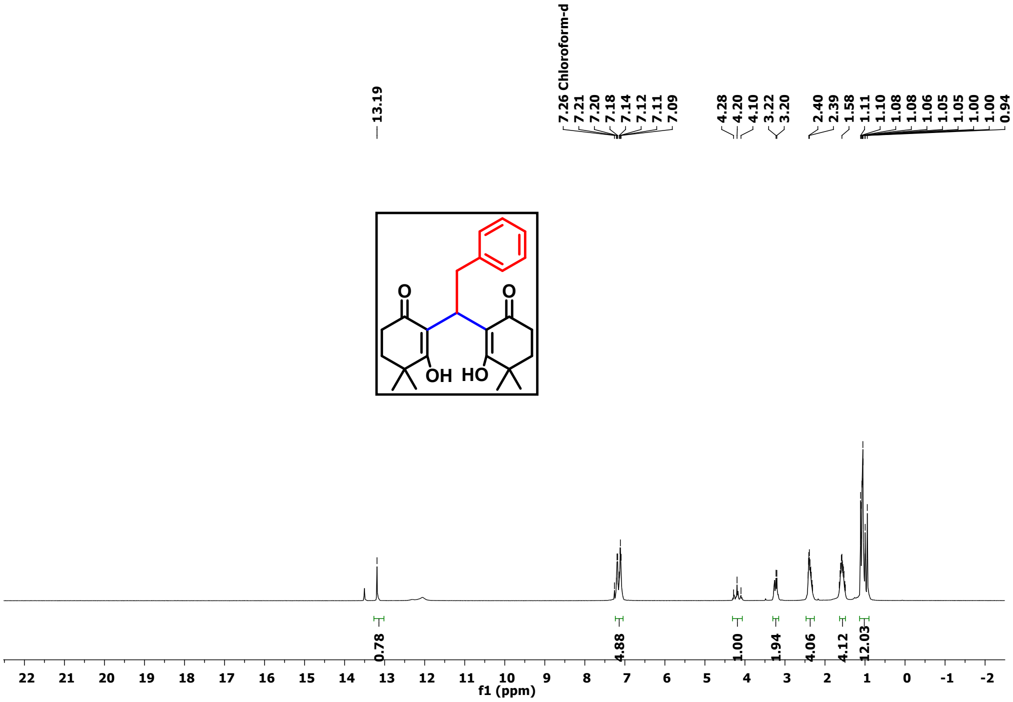


^{13}C {^{1}H} NMR of **3d**, 100 MHz, CDCl$_{3}$

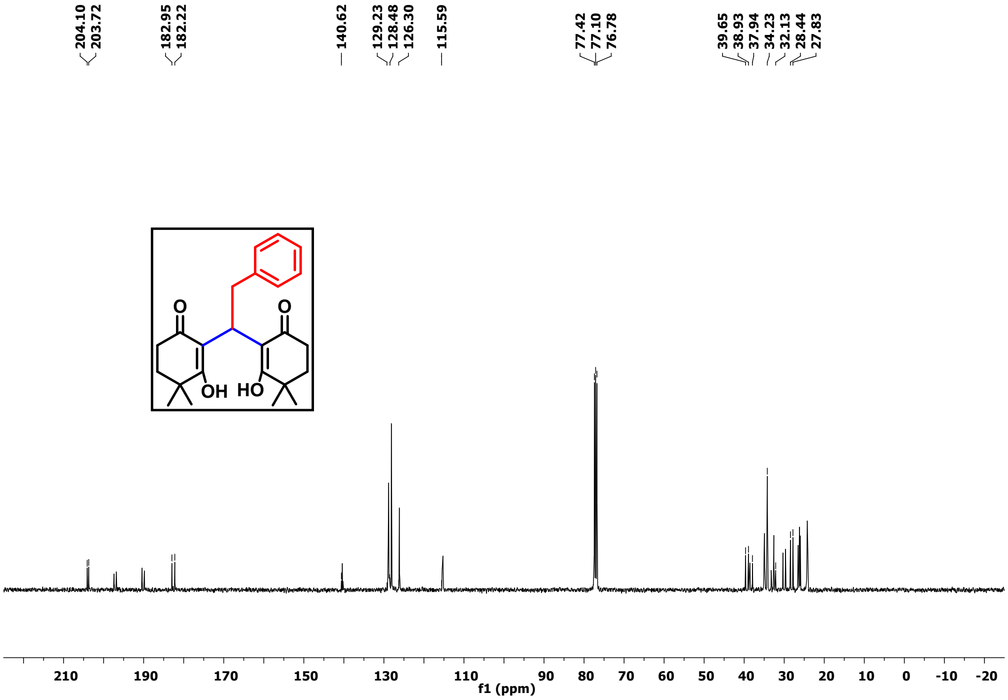


HRMS (ESI-TOF) of 3d

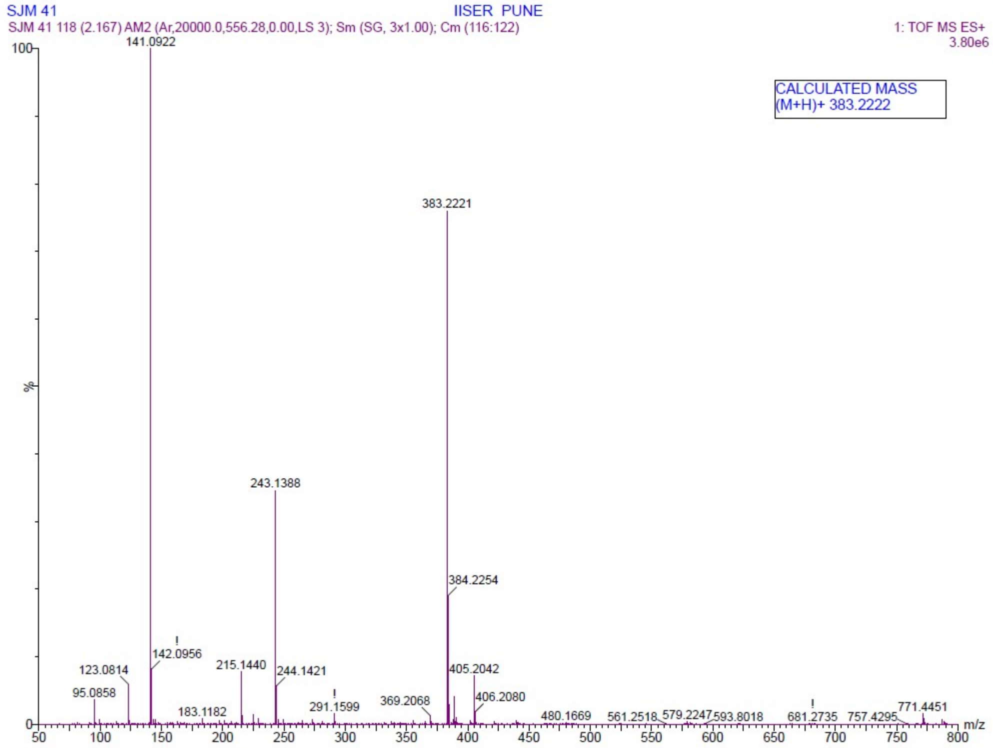
2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) (3e)



^{1}H NMR of **3e**, 400 MHz, CDCl$_3$

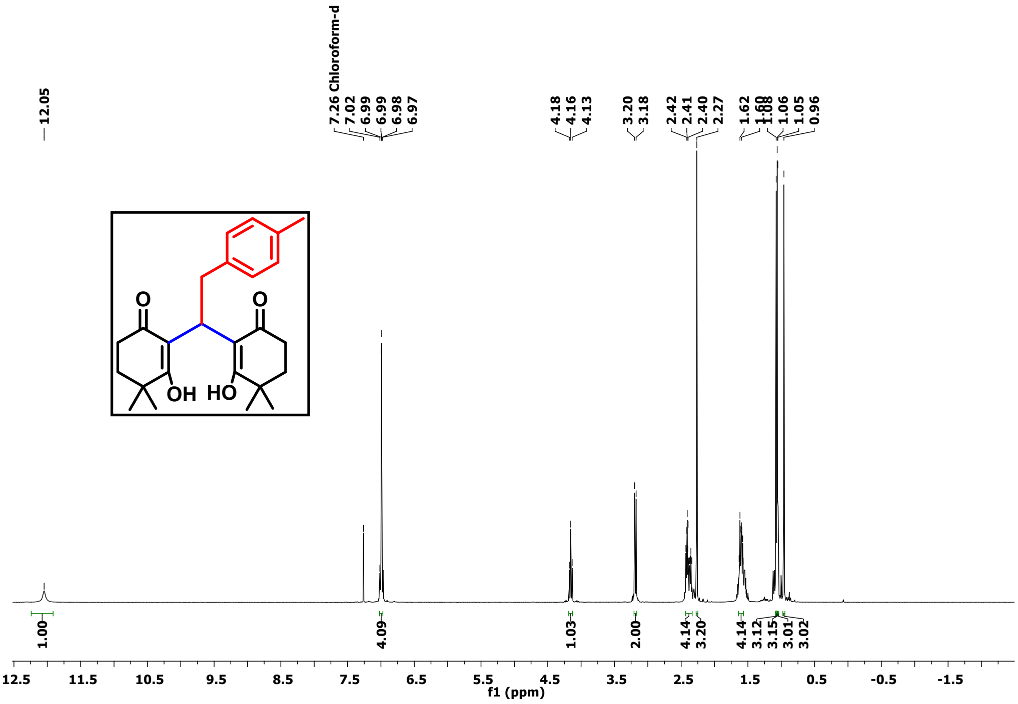


^{13}C {^{1}H} NMR of **3e**, 100 MHz, CDCl$_3$

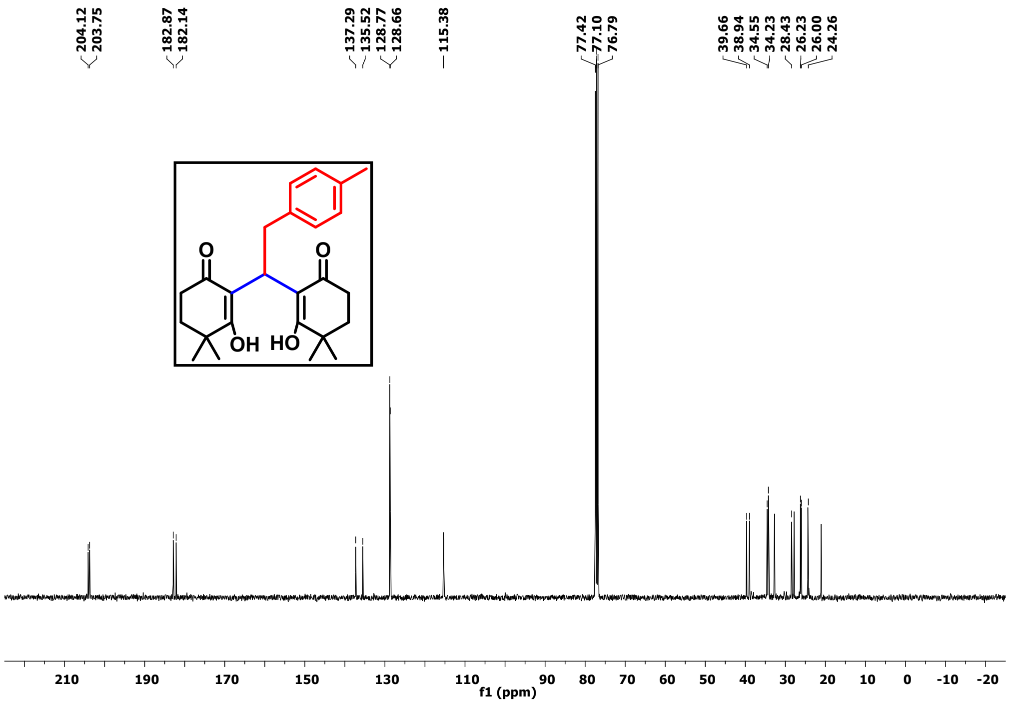


HRMS (ESI-TOF) of 3e

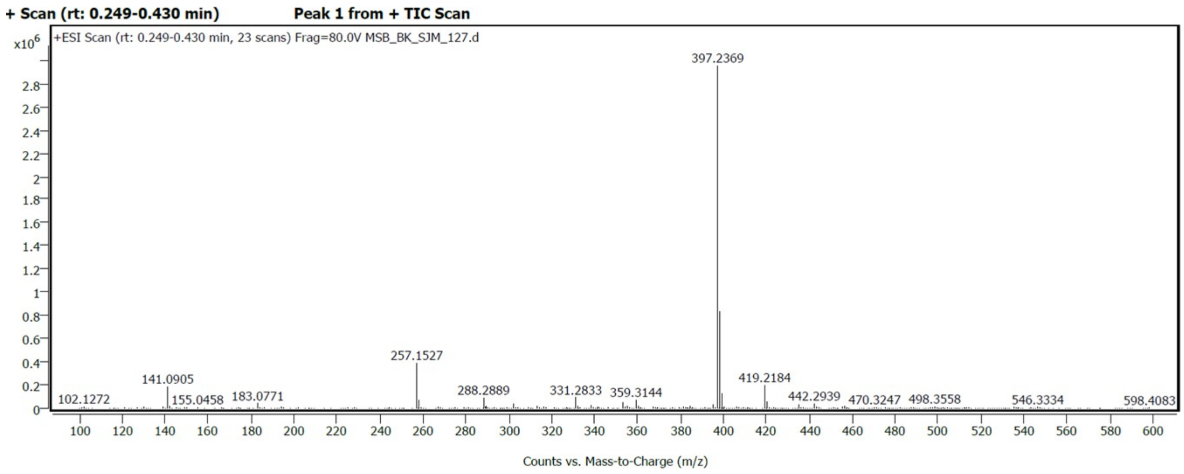
2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxy-4,4-dimethylcyclohex-2-en-1-one) (3f)



^{1}H NMR of **3f**, 400 MHz, $CDCl_3$

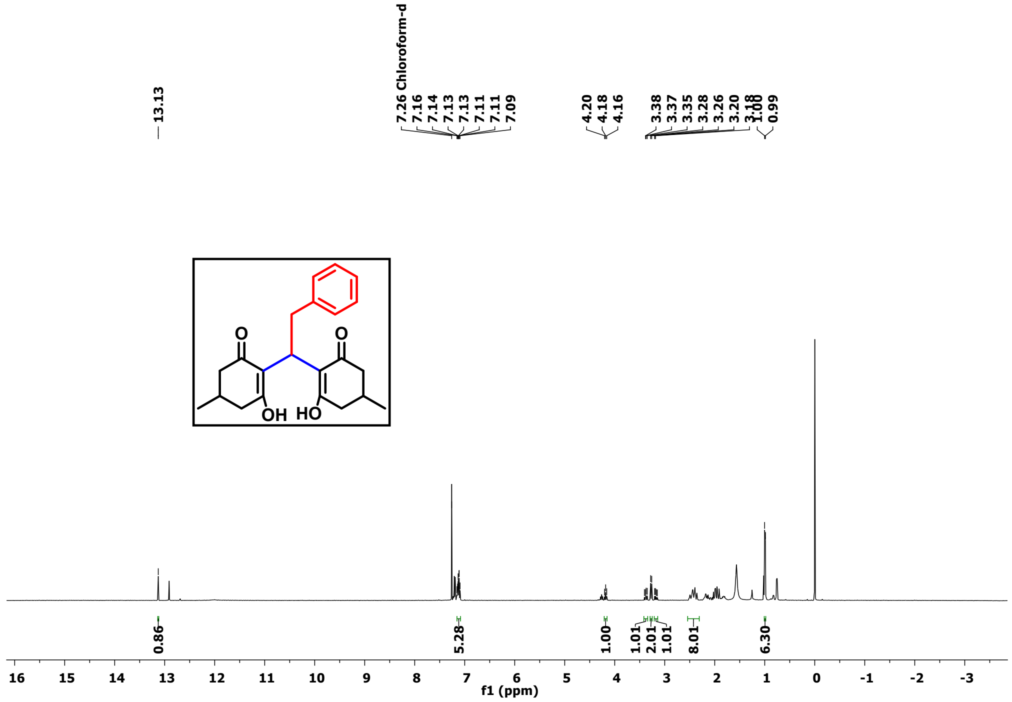


^{13}C {^{1}H} NMR of **3f**, 100 MHz, CDCl$_3$

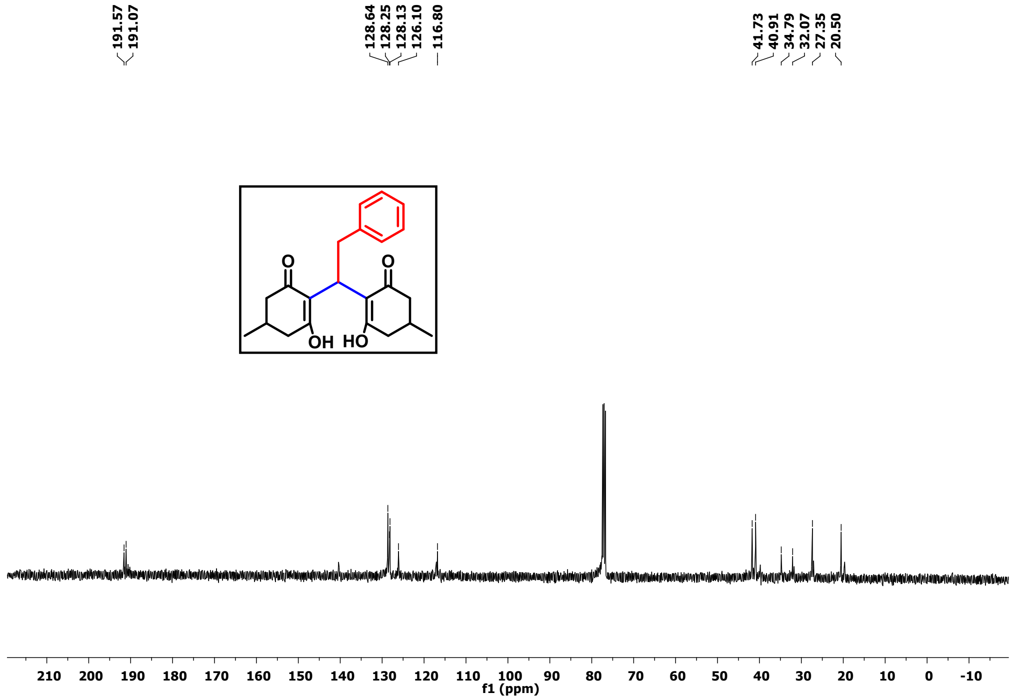


HRMS (ESI-TOF) of 3f

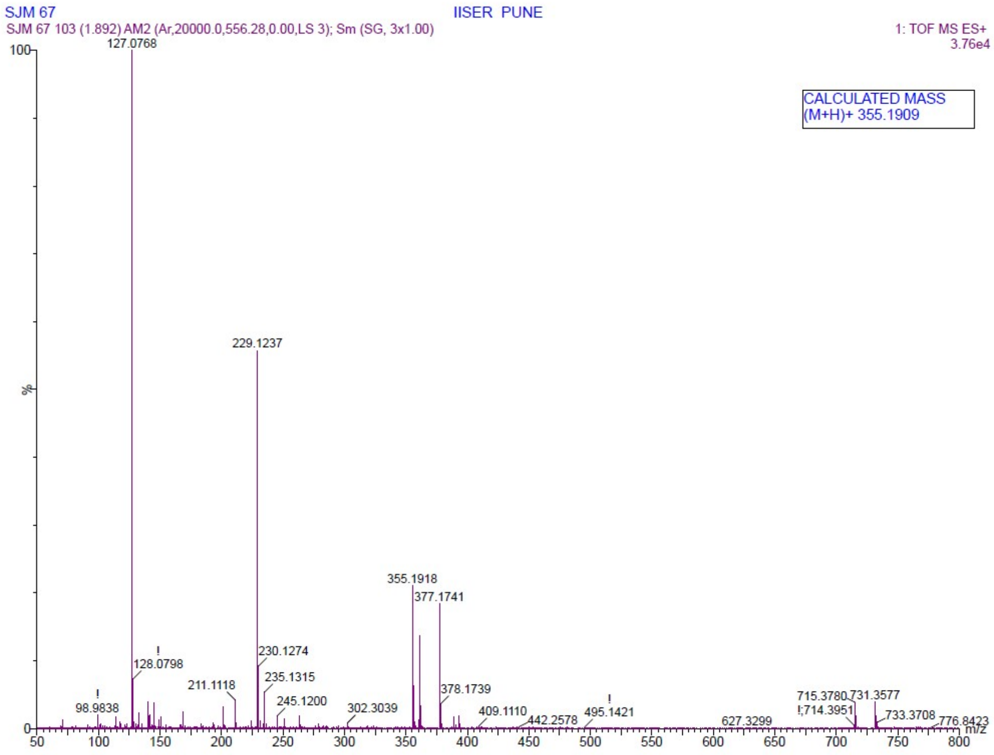
2'-(2-phenylethane-1,1-diyl)bis(3-hydroxy-5-methylcyclohex-2-en-1-one) (3g)



^{1}H NMR of **3g**, 400 MHz, CDCl$_3$

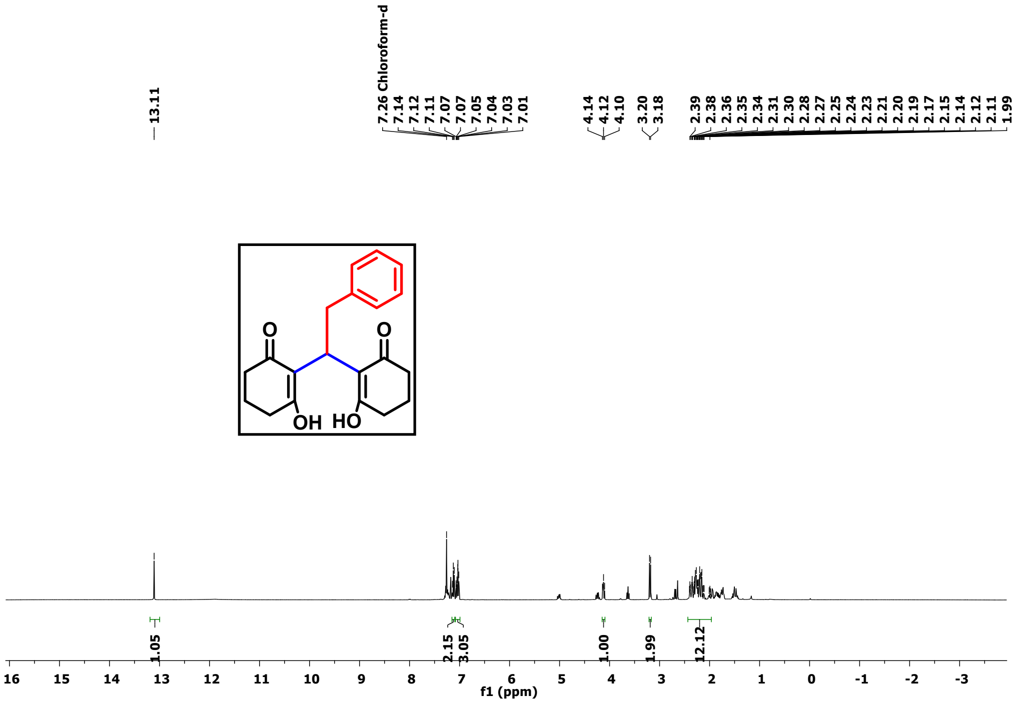


^{13}C {^{1}H} NMR of **3g**, 100 MHz, CDCl$_3$

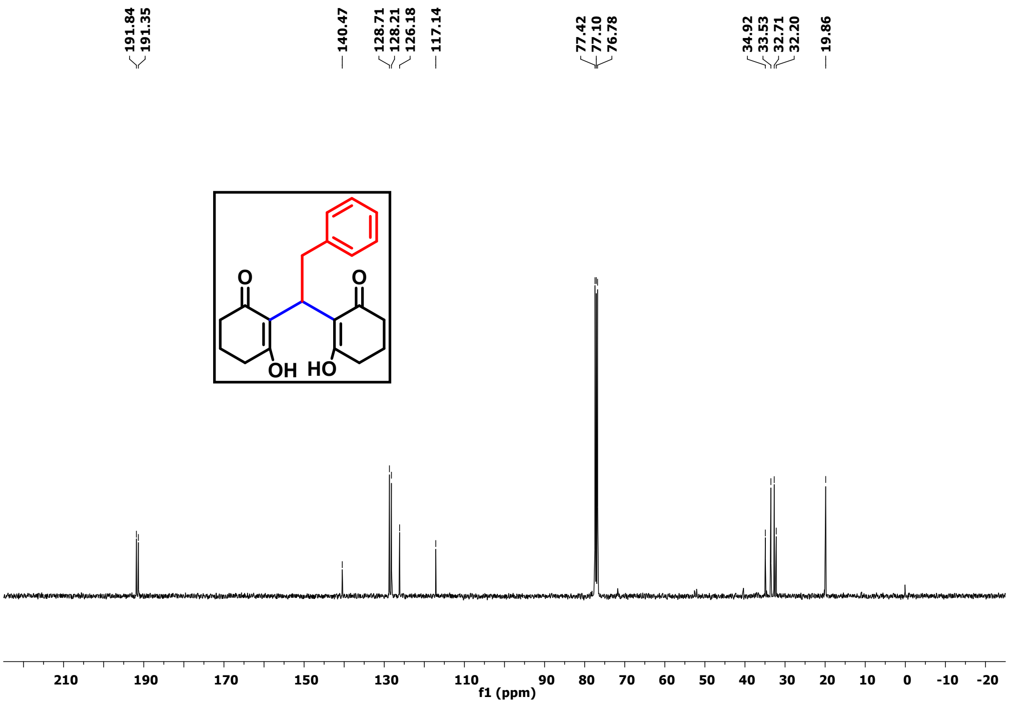


HRMS (ESI-TOF) of 3g

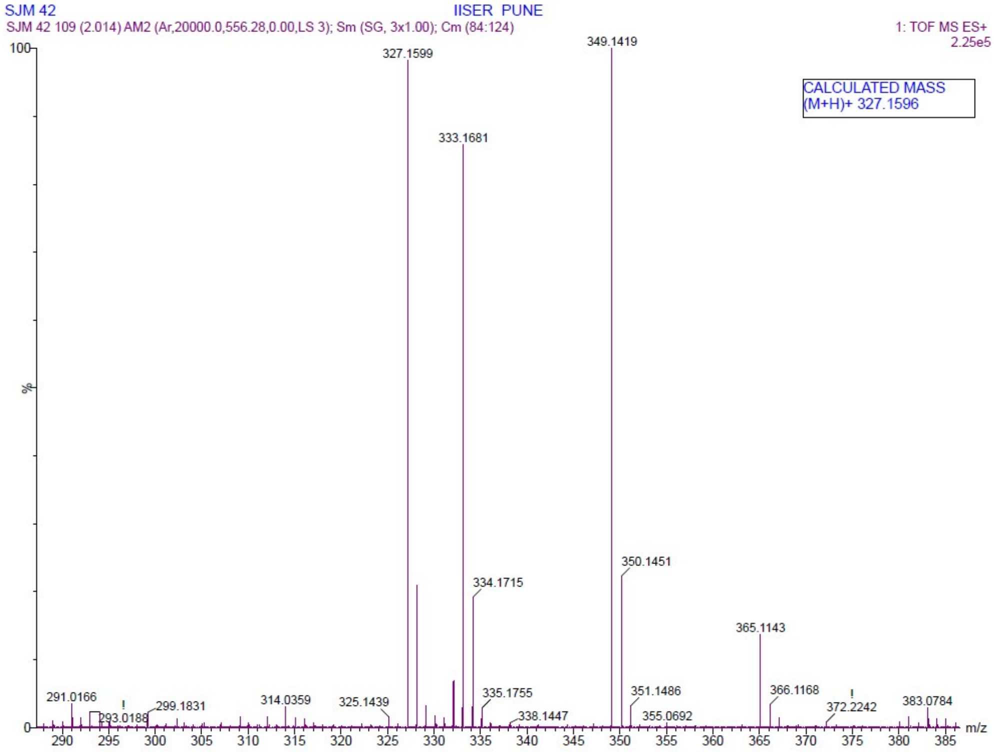
2'-(2-phenylethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) (3h)



^{1}H NMR of **3h**, 400 MHz, CDCl$_3$

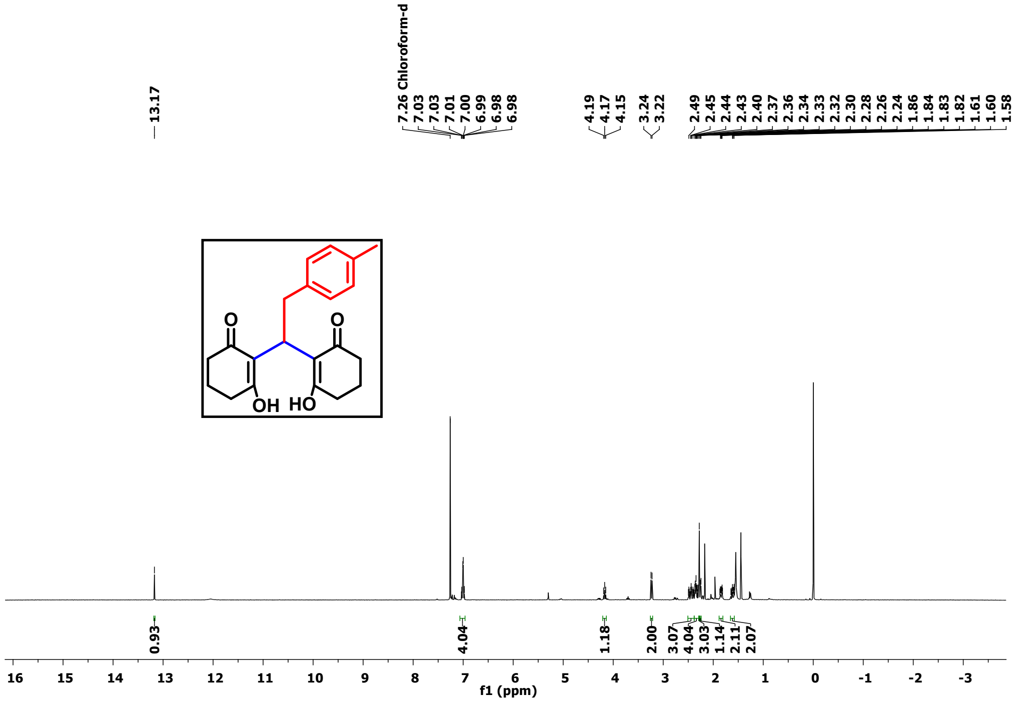


$^{13}C\ \{^1H\}$ NMR of **3h**, 100 MHz, $CDCl_3$

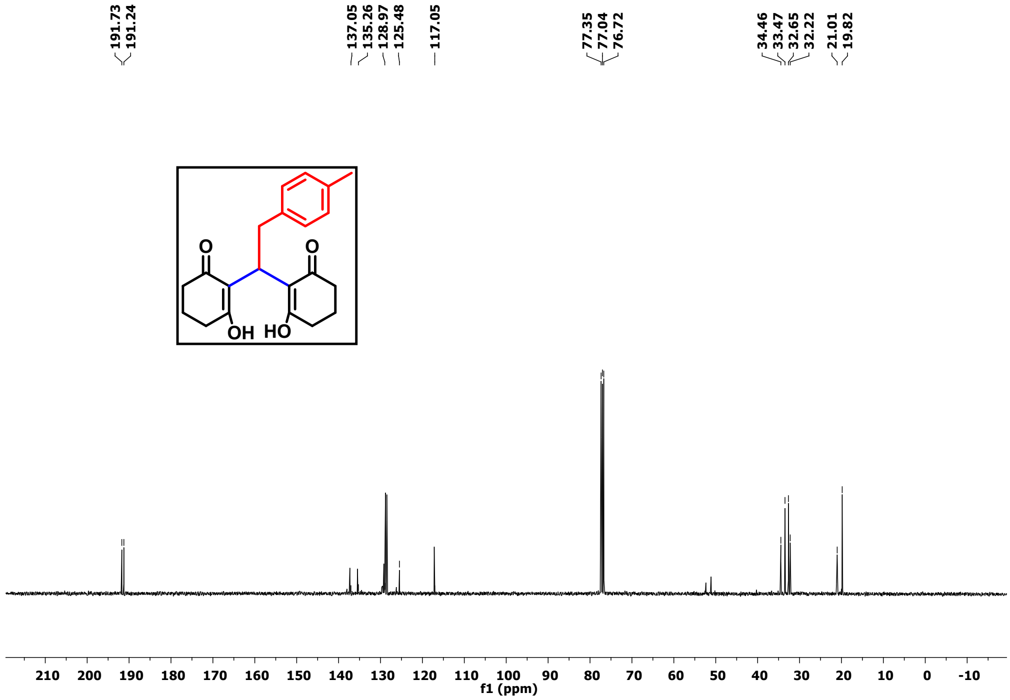


HRMS (ESI-TOF) of 3h

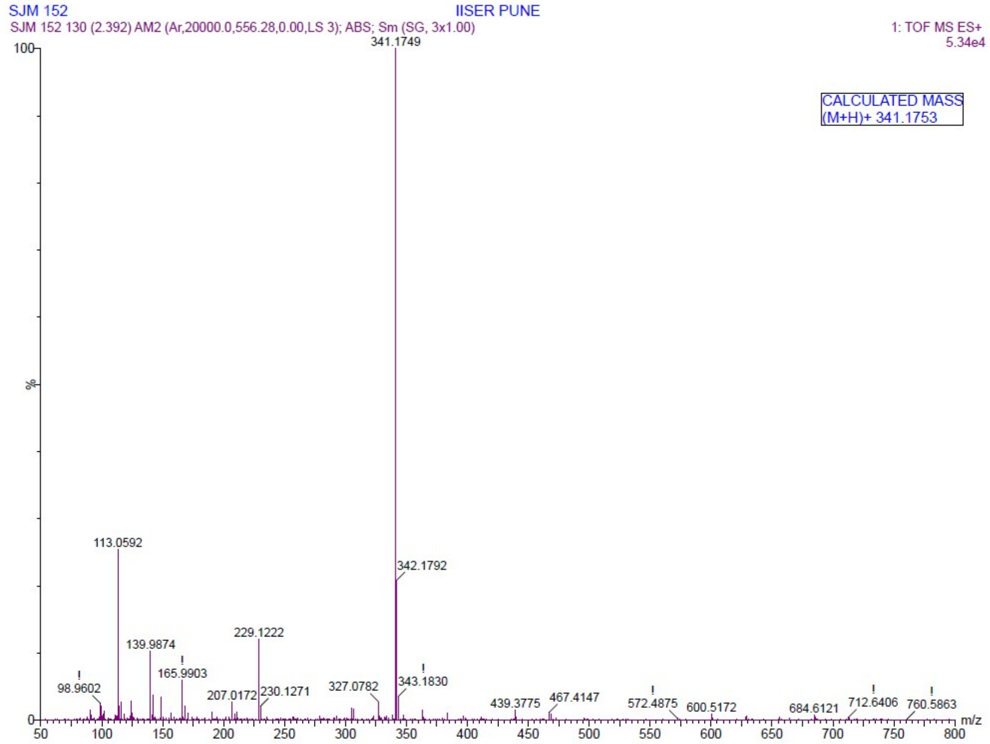
2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(3-hydroxycyclohex-2-en-1-one) (3i)



^{1}H NMR of **3i**, 400 MHz, $CDCl_3$

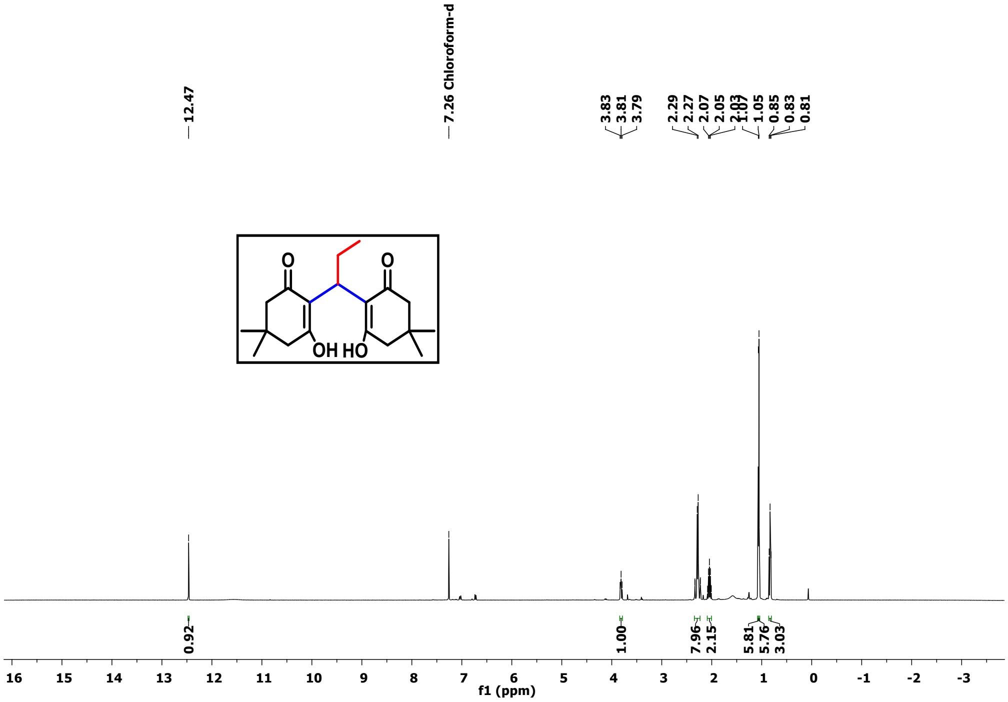


^{13}C {^{1}H} NMR of **3i**, 100 MHz, $CDCl_3$

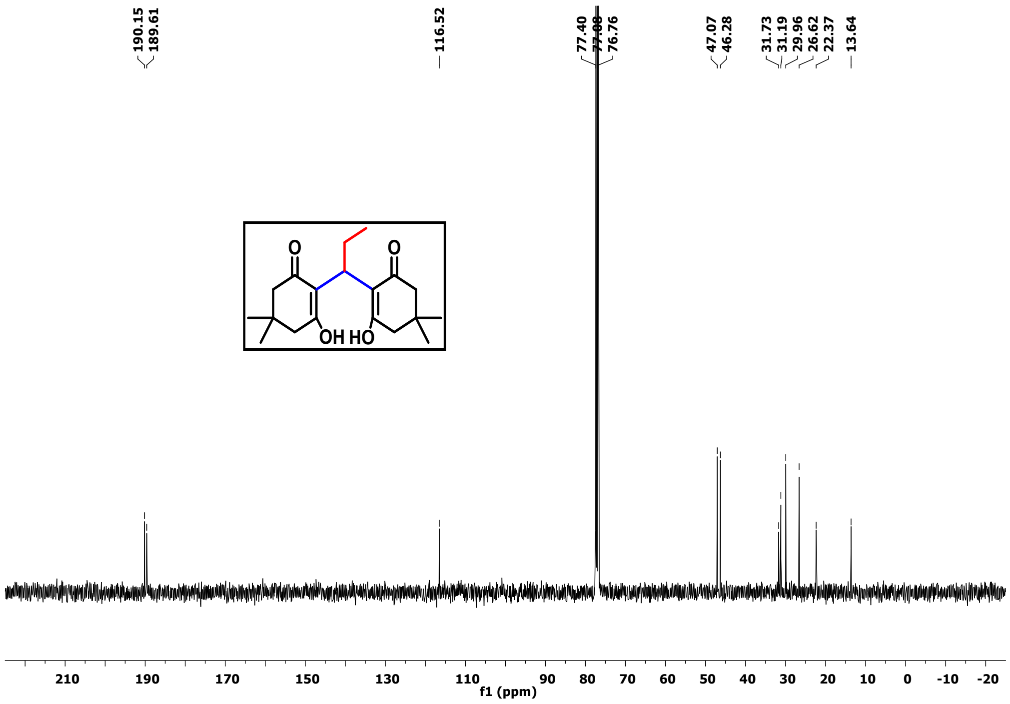


HRMS (ESI-TOF) of 3i

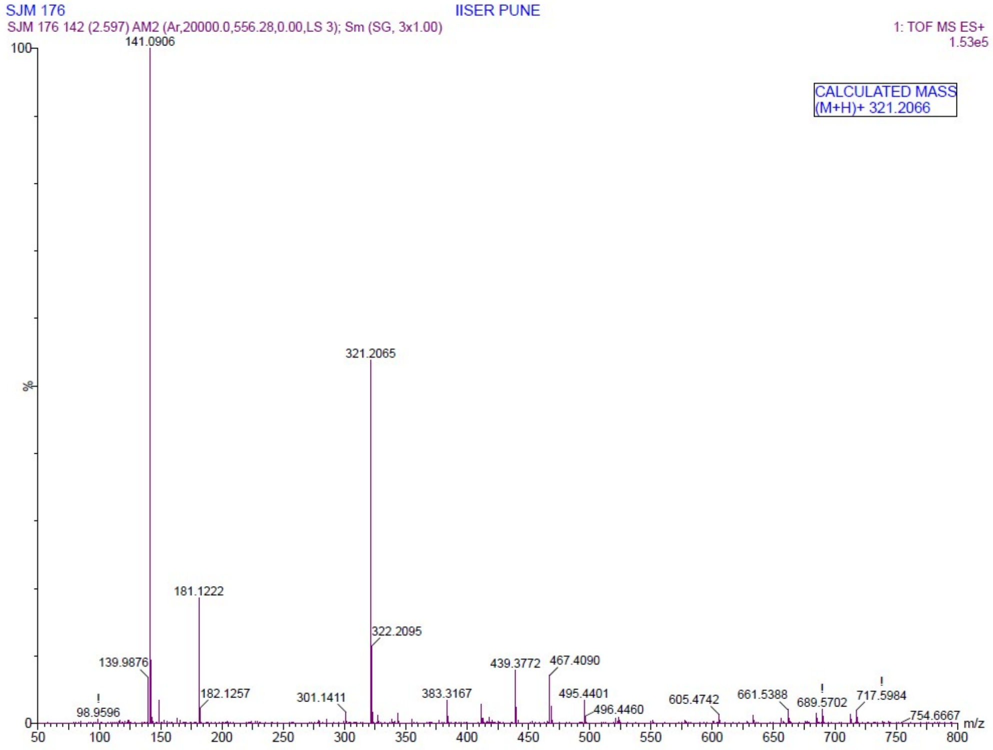
2,2'-(propane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3j)



^{1}H NMR of **3j**, 400 MHz, $CDCl_3$

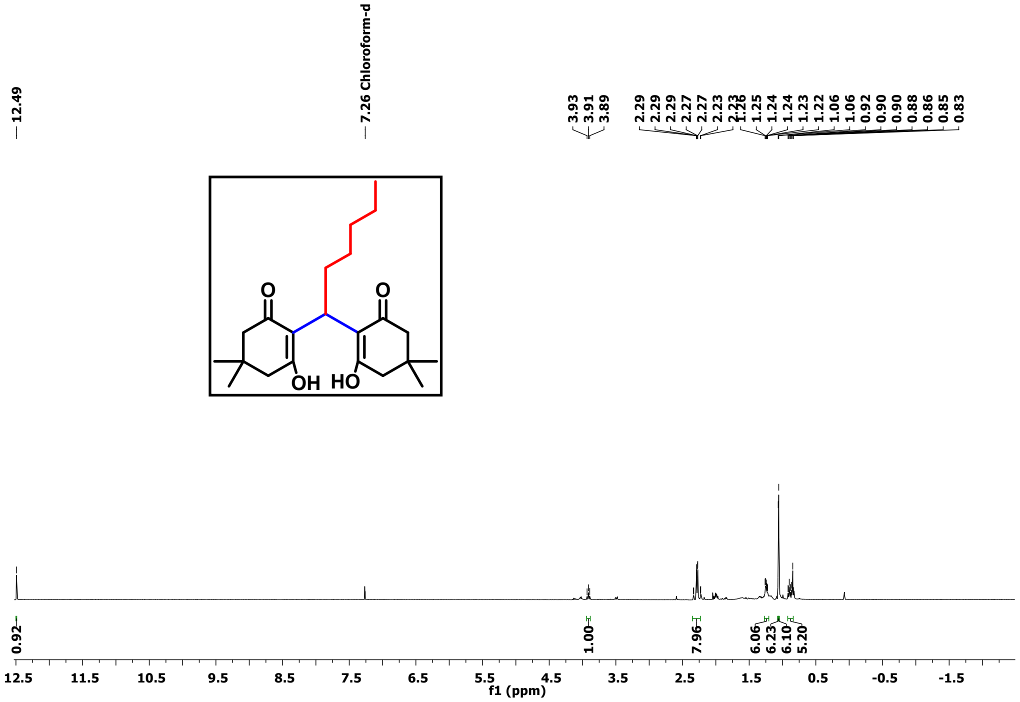


^{13}C {^{1}H} NMR of **3j**, 100 MHz, $CDCl_3$

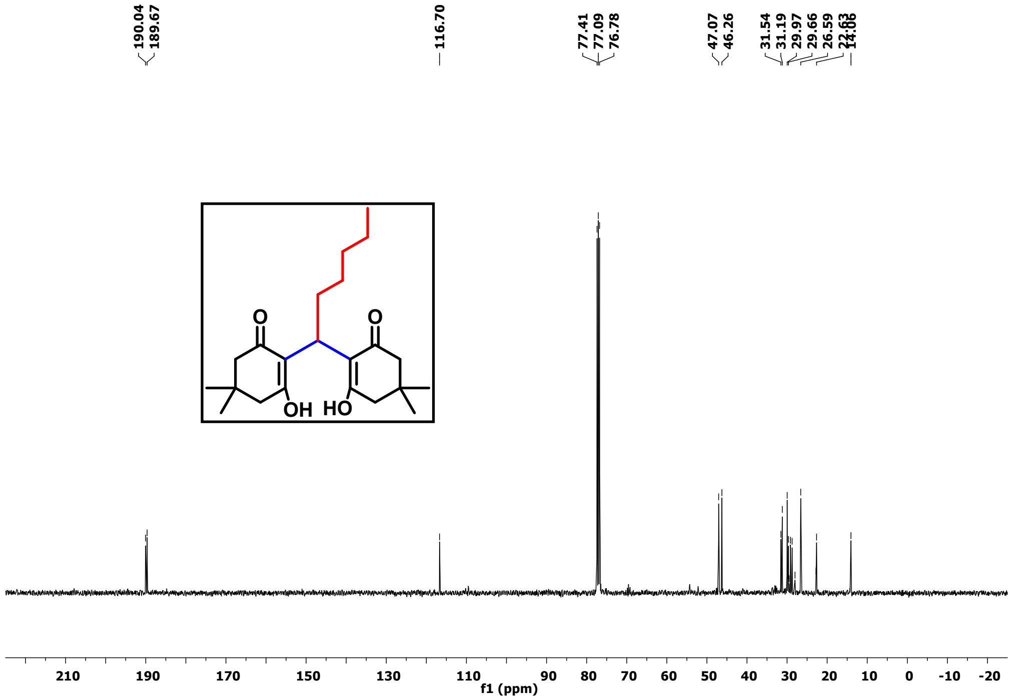


HRMS (ESI-TOF) of 3j

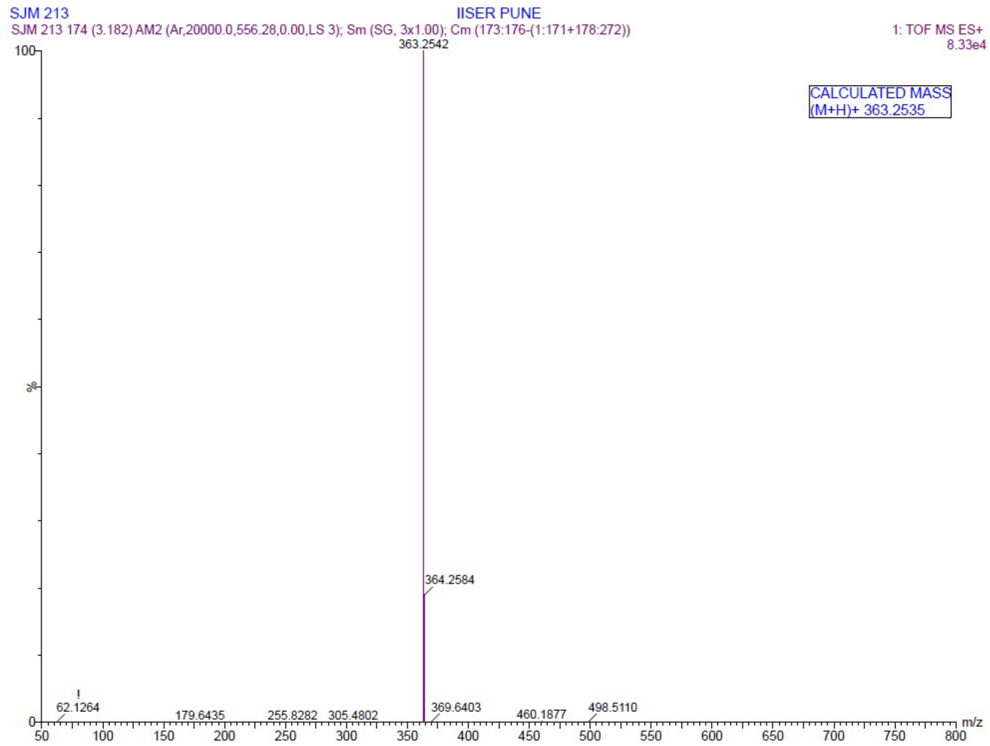
2,2'-(hexane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3k)



^{1}H NMR of **3k**, 400 MHz, CDCl$_3$

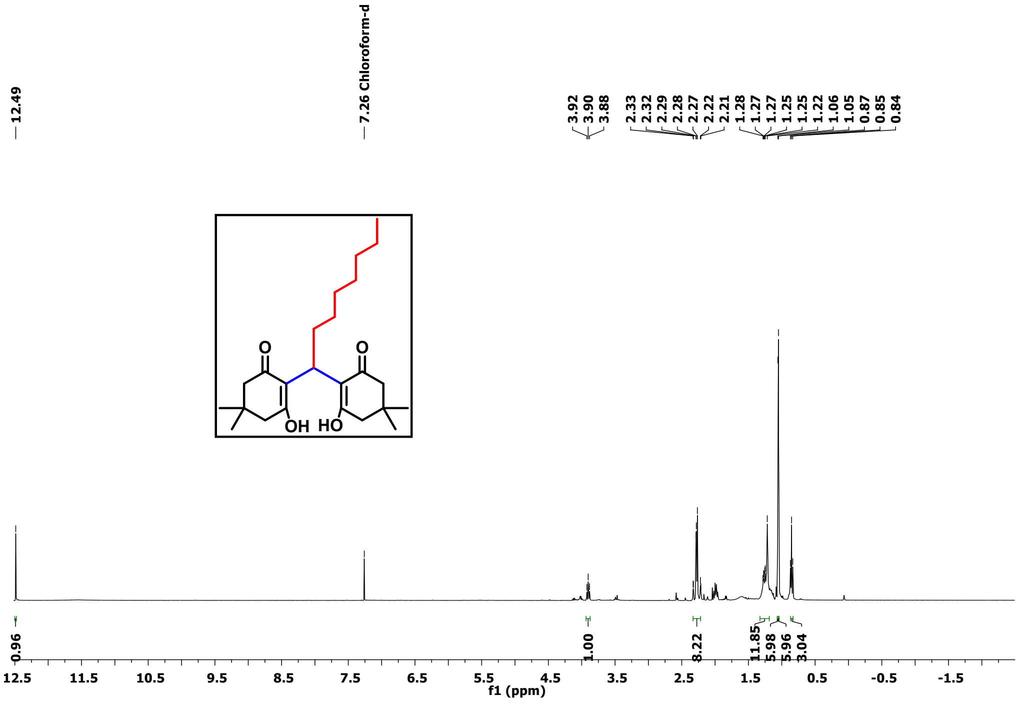


^{13}C {^{1}H} NMR of **3k**, 100 MHz, CDCl$_3$

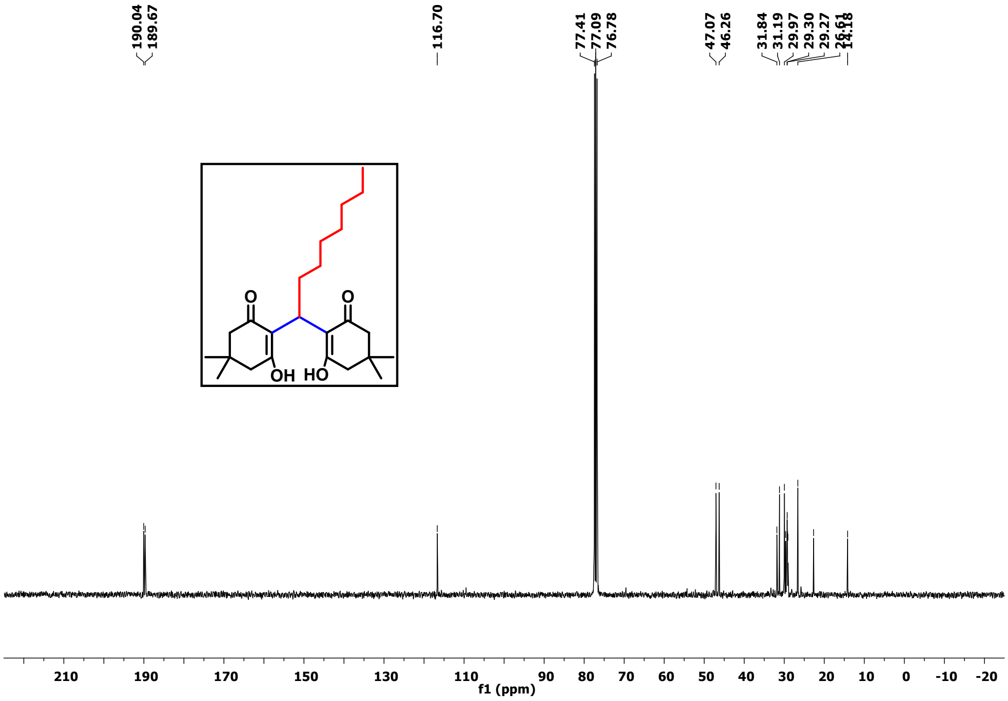


HRMS (ESI-TOF) of 3k

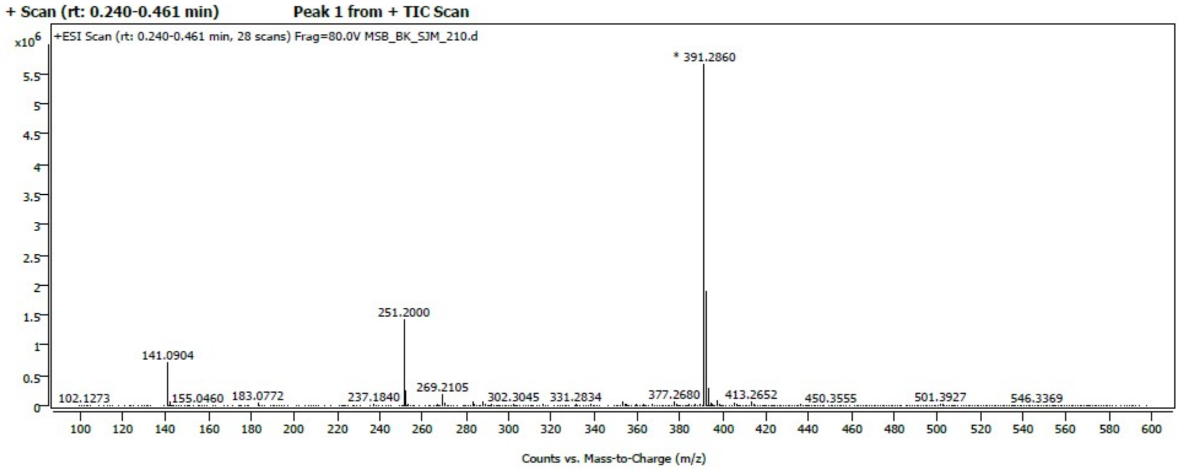
2,2'-(octane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (3l)



^{1}H NMR of **3l**, 400 MHz, $CDCl_3$

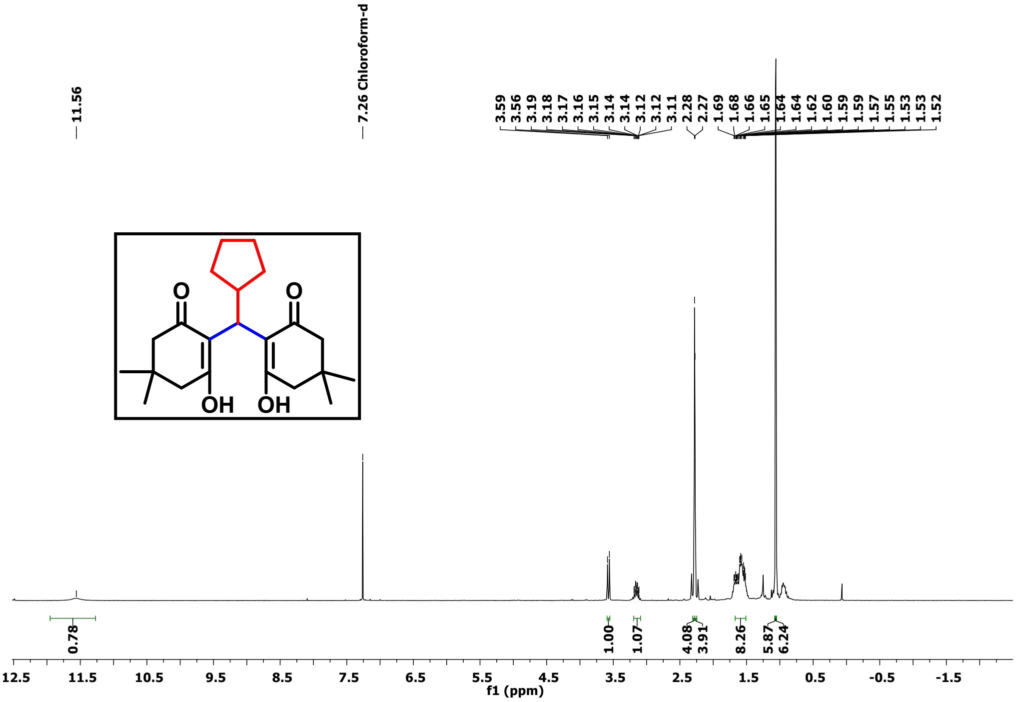


^{13}C {^{1}H} NMR of **3l**, 100 MHz, CDCl$_3$

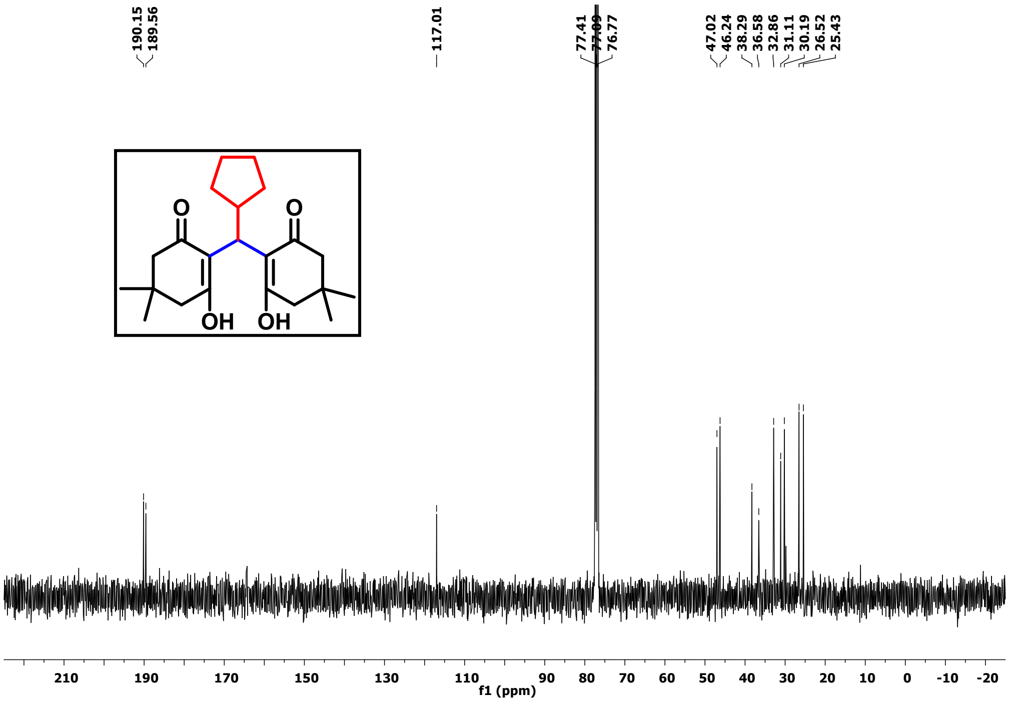


HRMS (ESI-TOF) of 3l

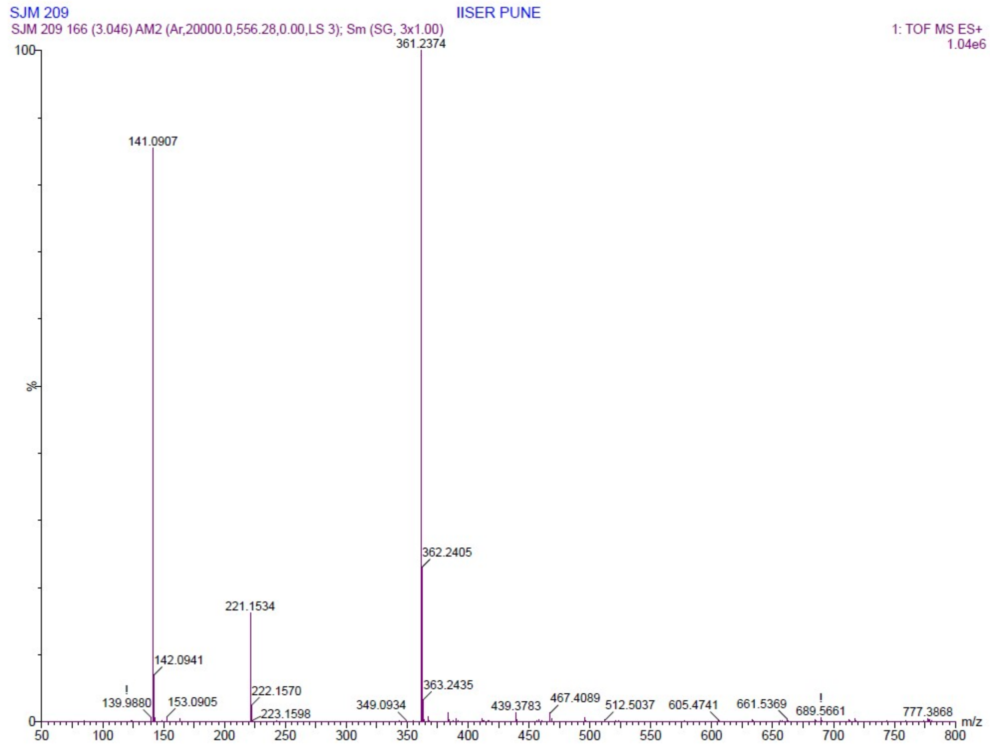
2,2'-(cyclopentylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one)*(3m):*



^{1}H NMR of **3m**, 400 MHz, CDCl$_3$

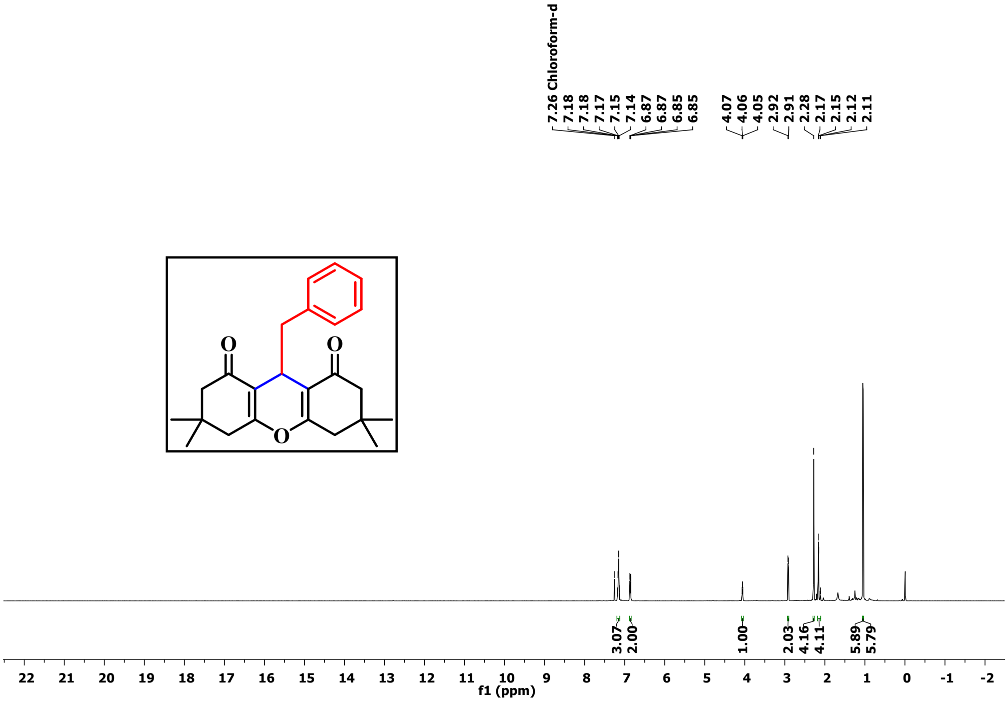


^{13}C {^{1}H} NMR of **3m**, 100 MHz, CDCl$_3$

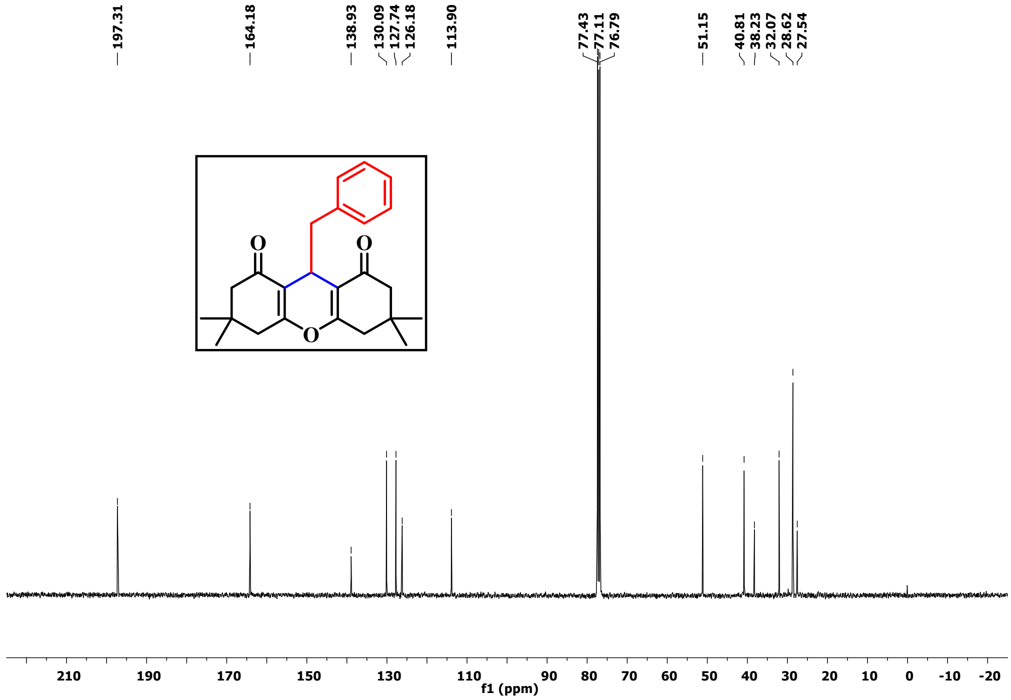


HRMS (ESI-TOF) of 3m

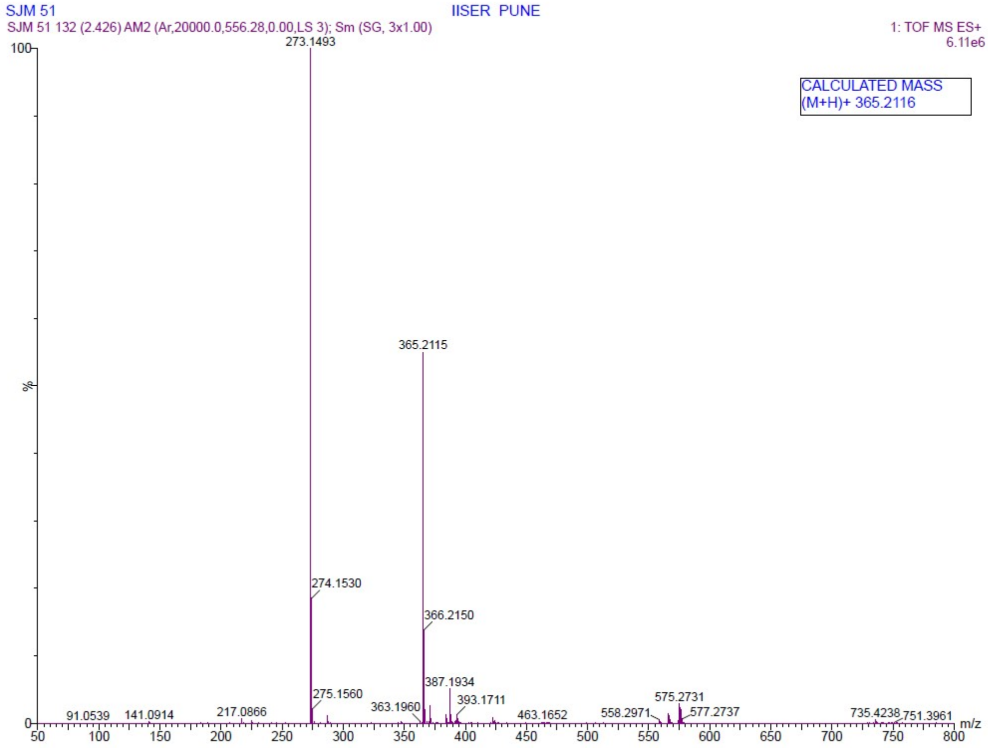
9-benzyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4a)



^{1}H NMR of **4a**, 400 MHz, CDCl$_3$

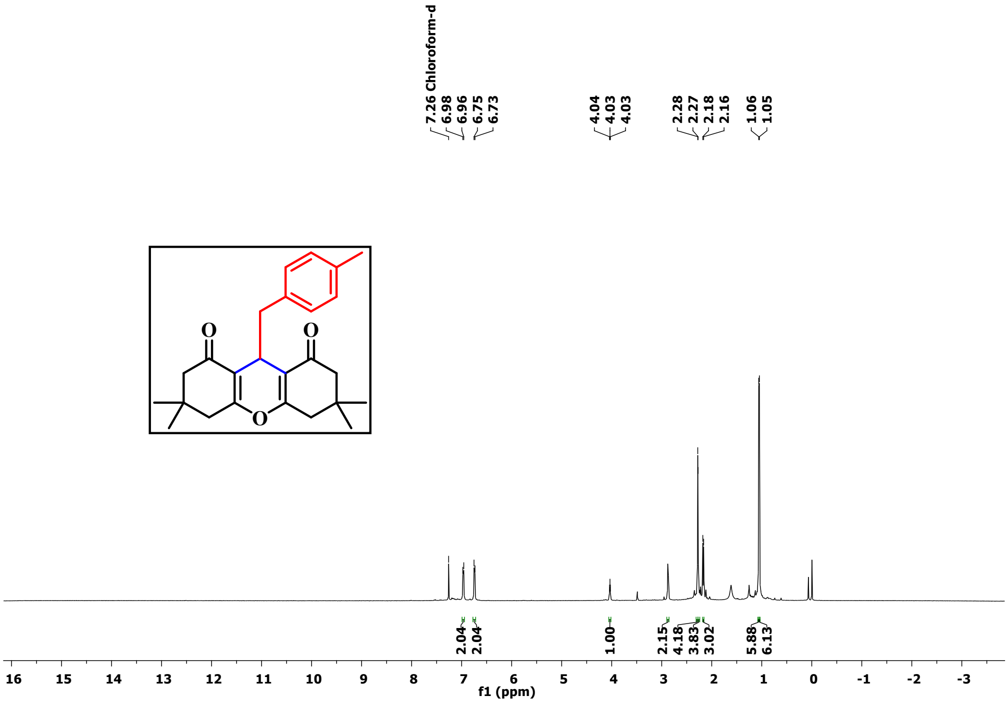


^{13}C {^{1}H} NMR of **4a**, 100 MHz, $CDCl_3$

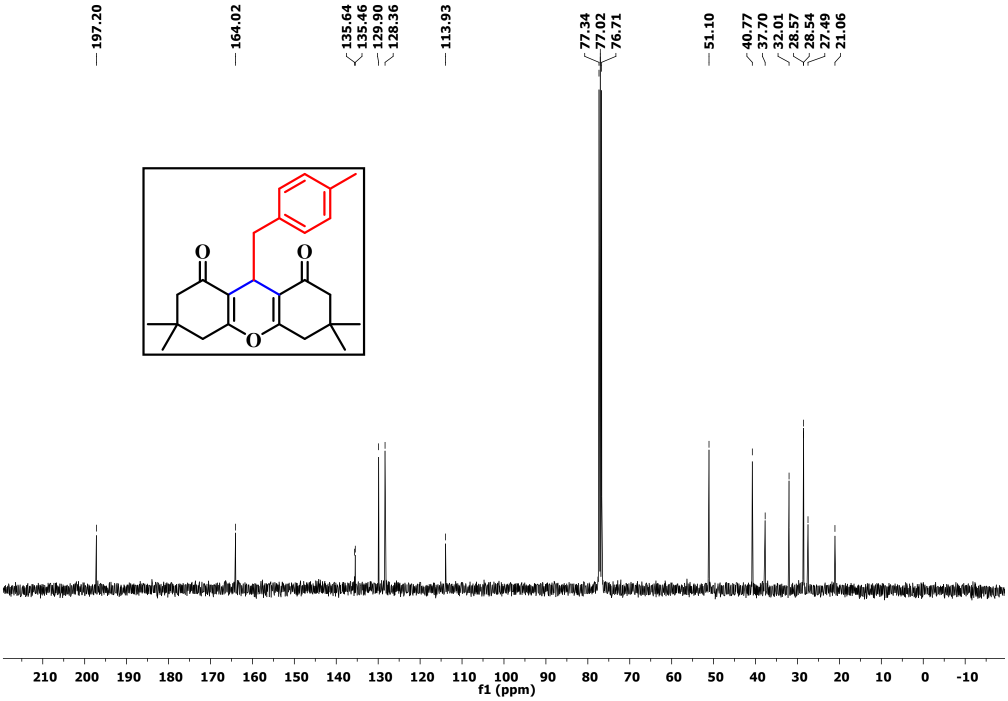


HRMS (ESI-TOF) of 4a

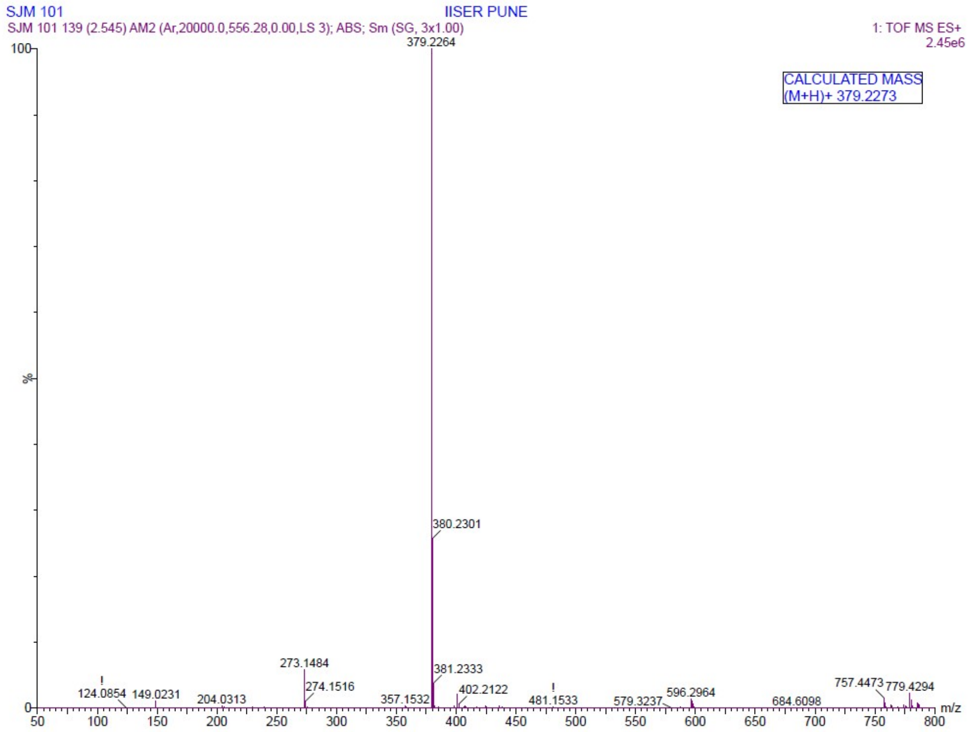
3,3,6,6-tetramethyl-9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4b)



^{1}H NMR of **4b**, 400 MHz, CDCl$_3$

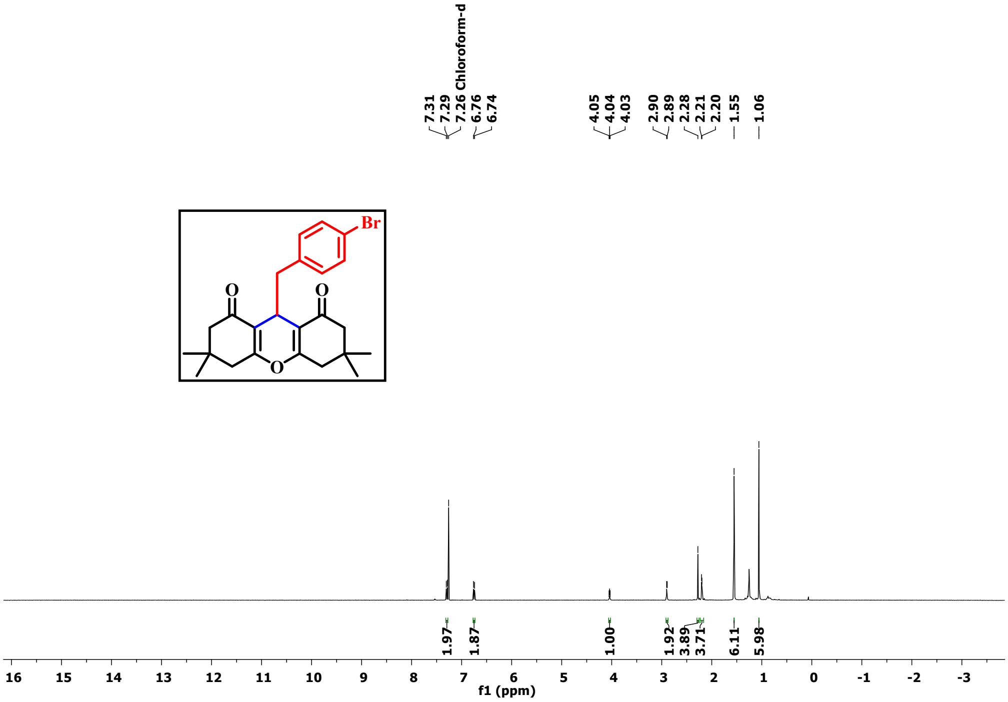


^{13}C {^{1}H} NMR of **4b**, 100 MHz, CDCl$_3$

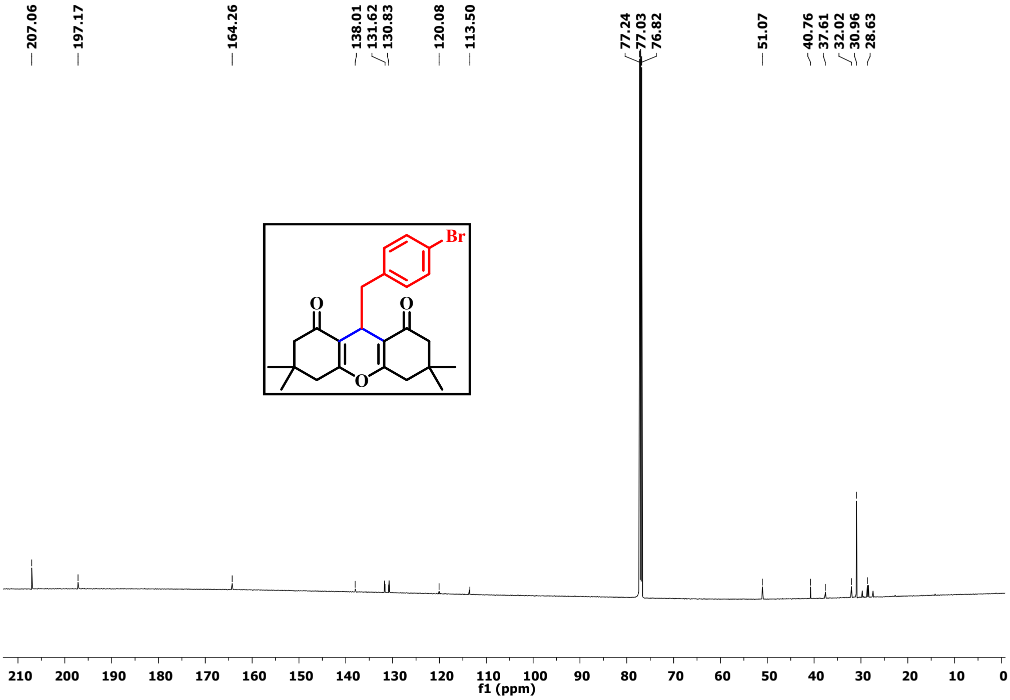


HRMS (ESI-TOF) of 4b

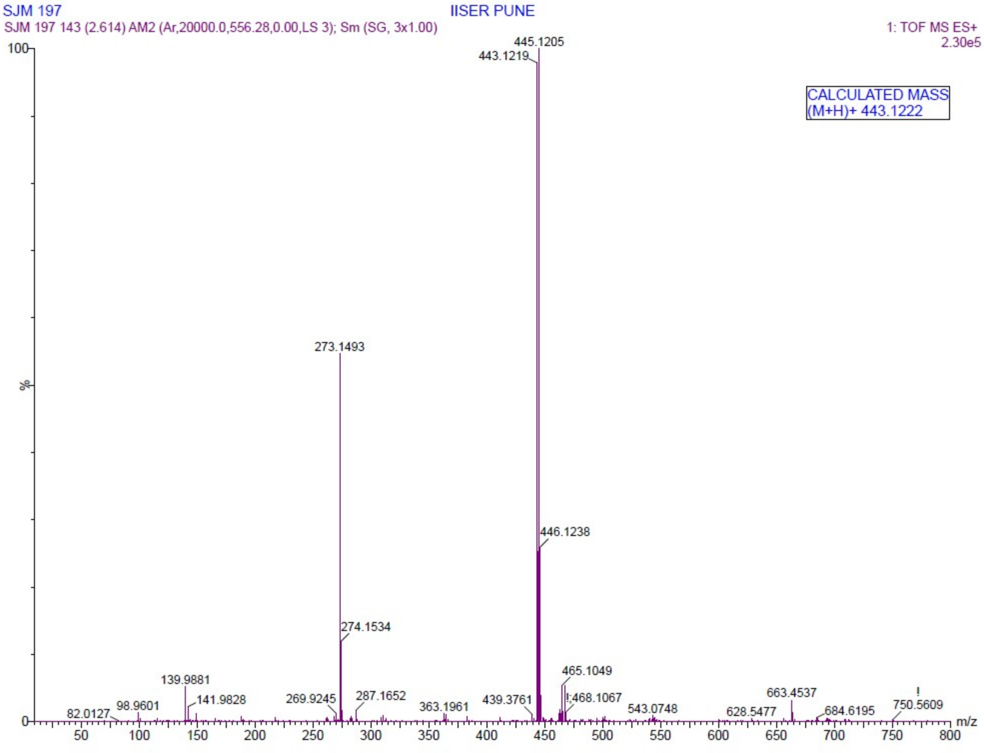
9-(4-bromobenzyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4c)



^{1}H NMR of **4c**, 400 MHz, $CDCl_3$

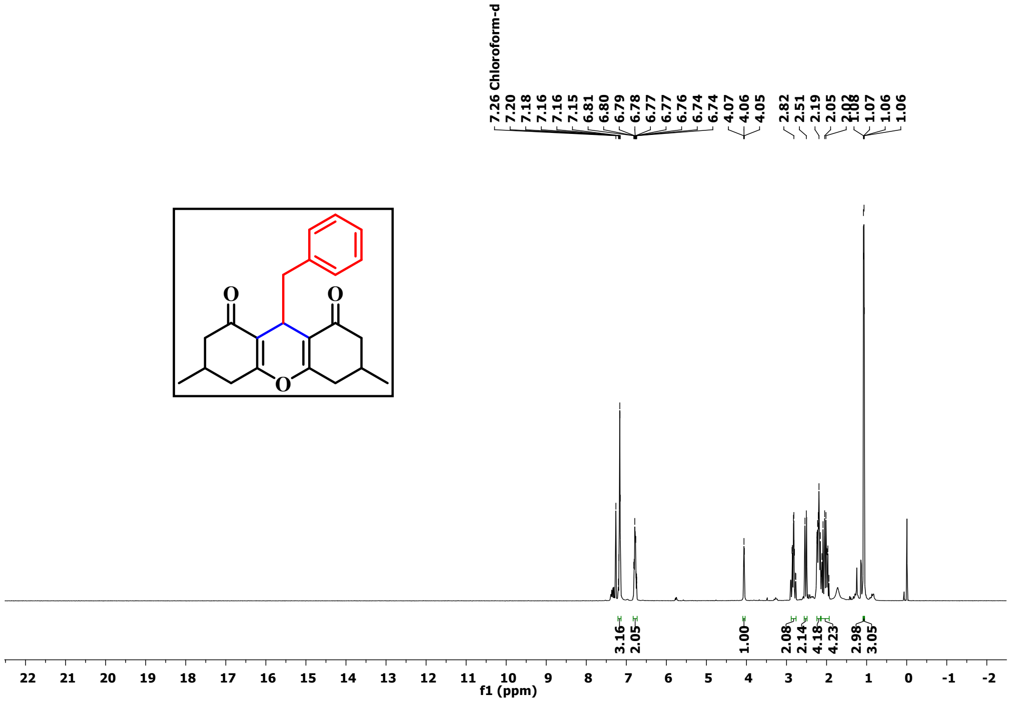


^{13}C {^{1}H} NMR of **4c**, 100 MHz, CDCl$_3$

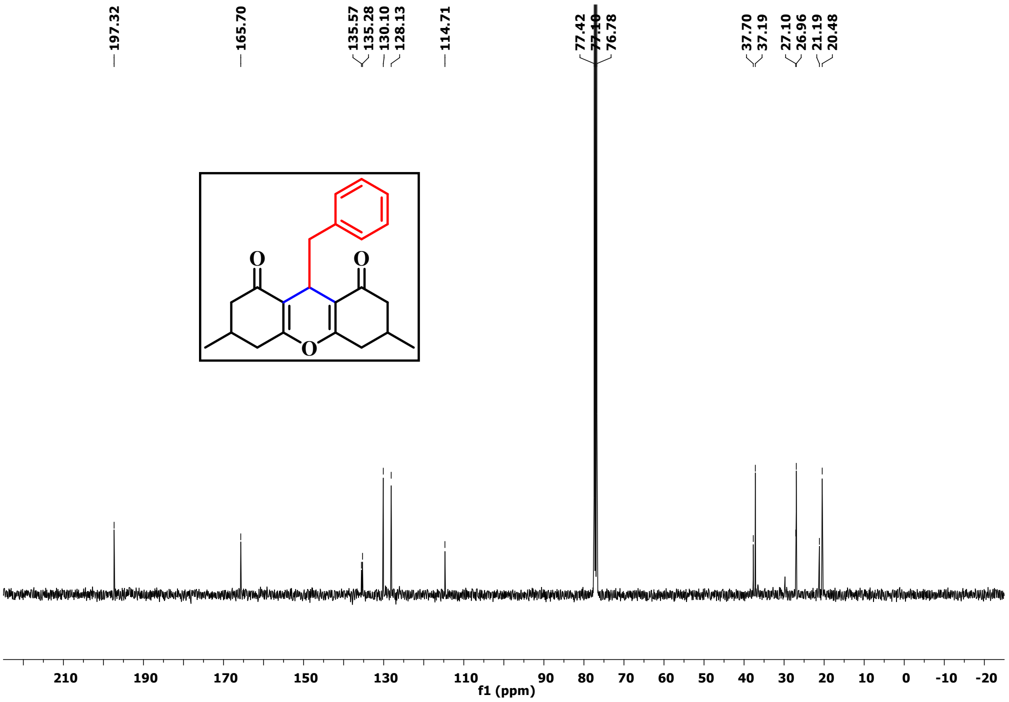


HRMS (ESI-TOF) of 4c

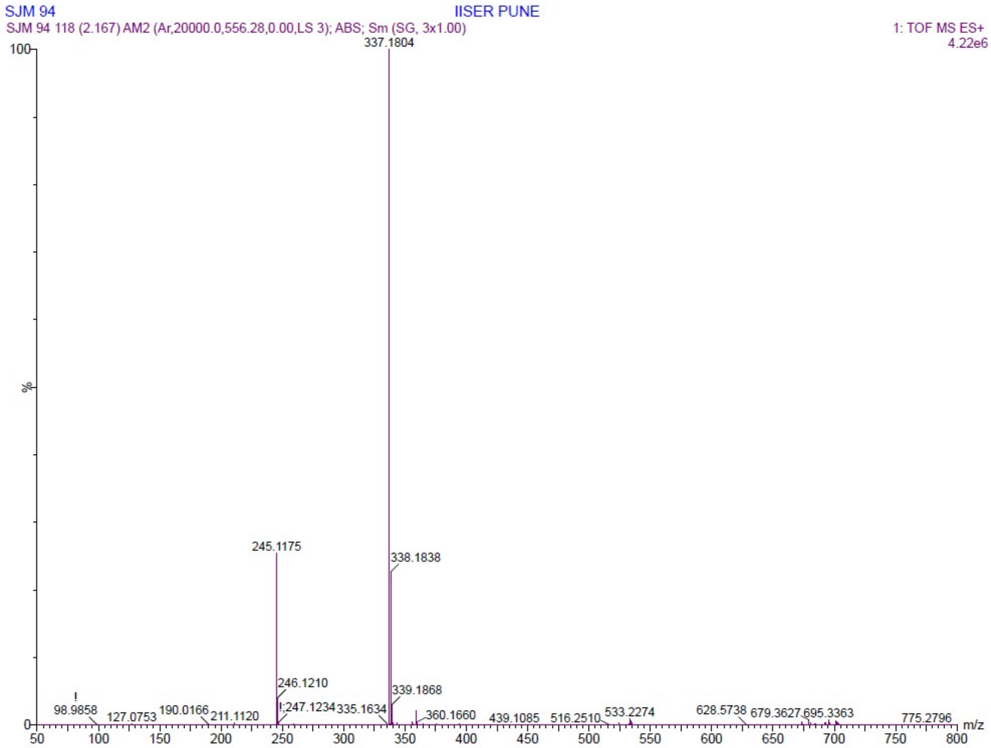
3,6-dimethyl-9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4d)



^{1}H NMR of **4d**, 400 MHz, CDCl$_3$

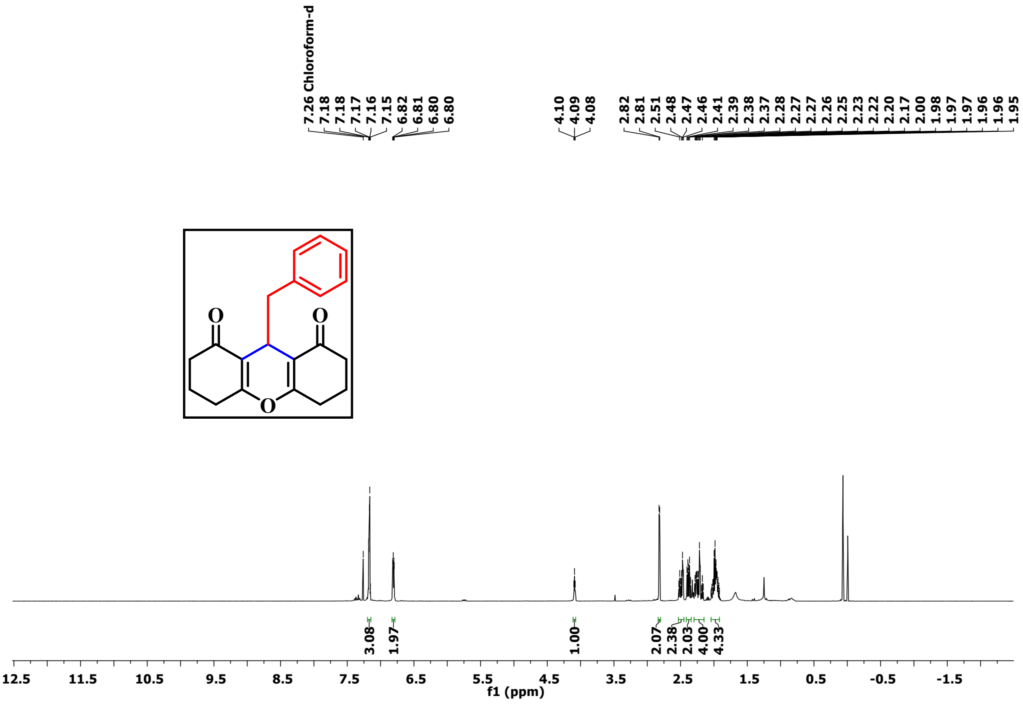


^{13}C {^{1}H} NMR of **4d**, 100 MHz, CDCl$_3$

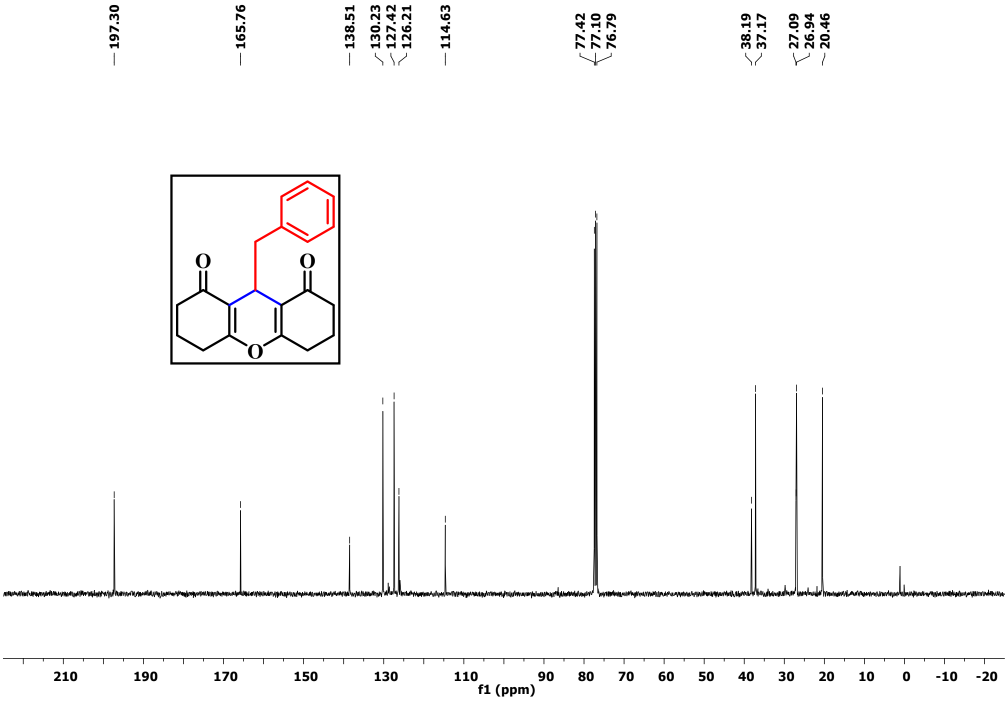


HRMS (ESI-TOF) of 4d

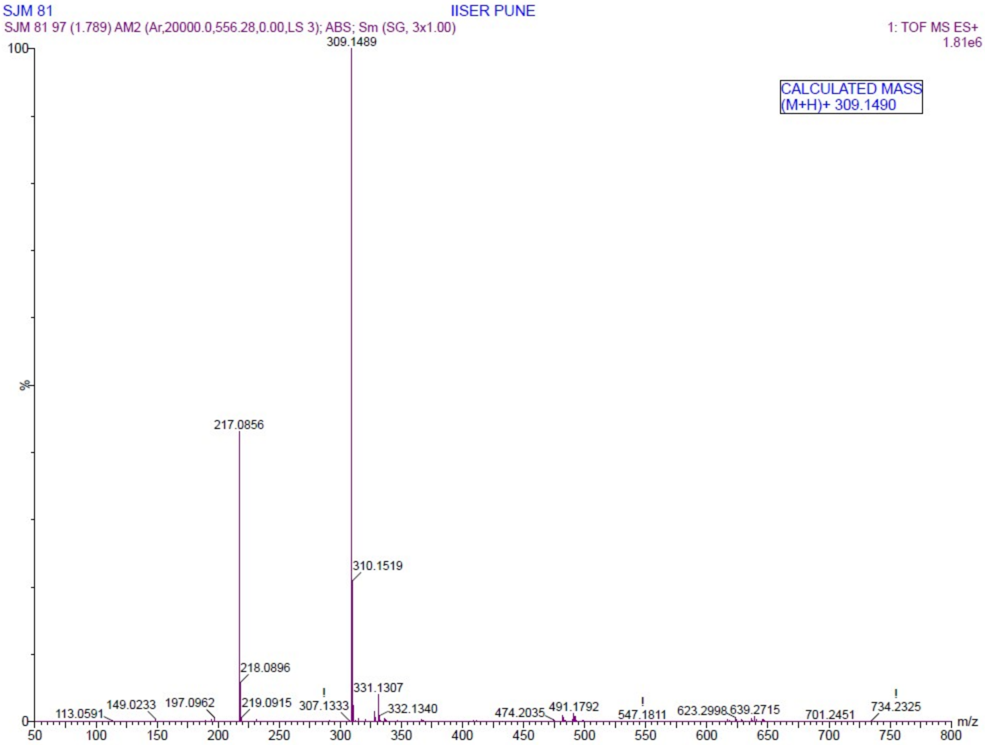
9-benzyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4e)



^{1}H NMR of **4e**, 400 MHz, CDCl$_3$

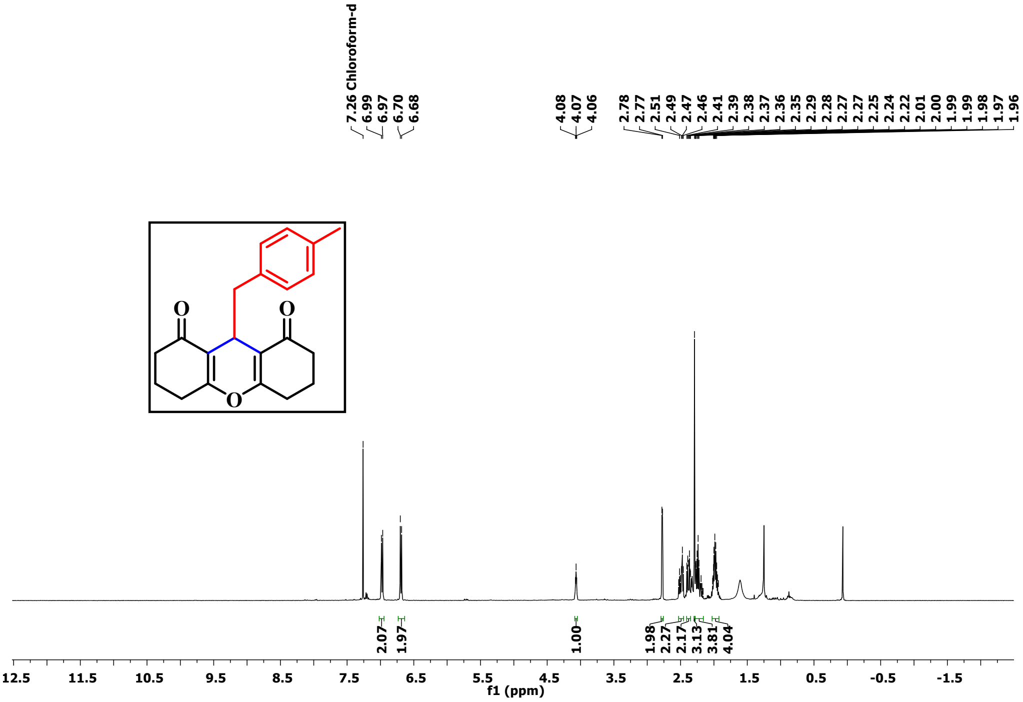


^{13}C {^{1}H} NMR of **4e**, 100 MHz, $CDCl_3$

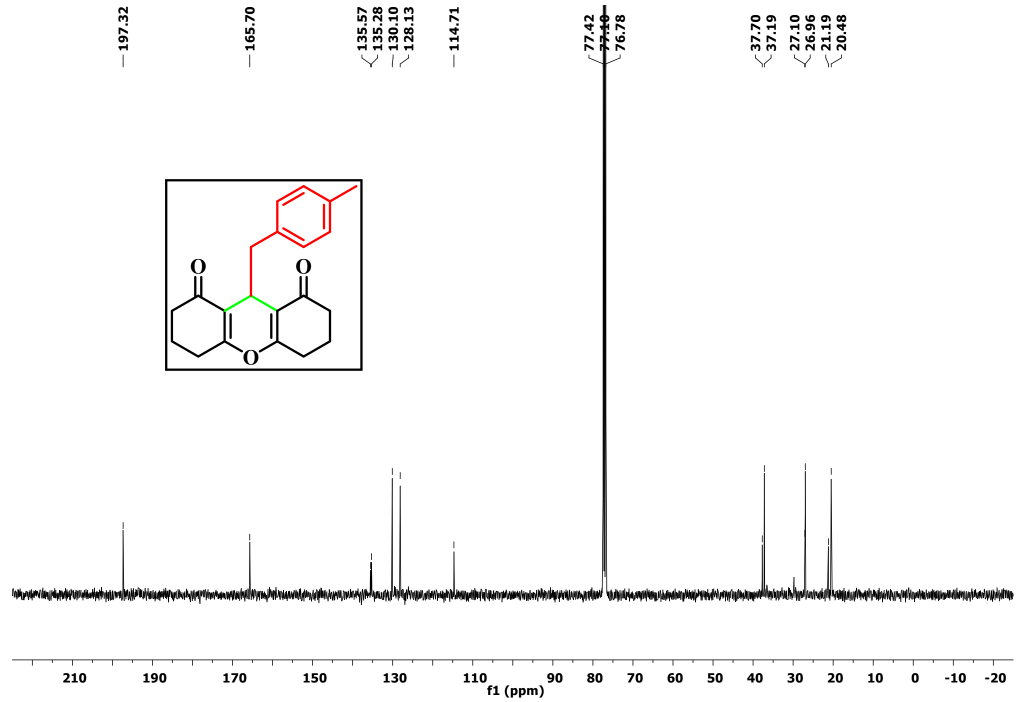


HRMS (ESI-TOF) of 4e

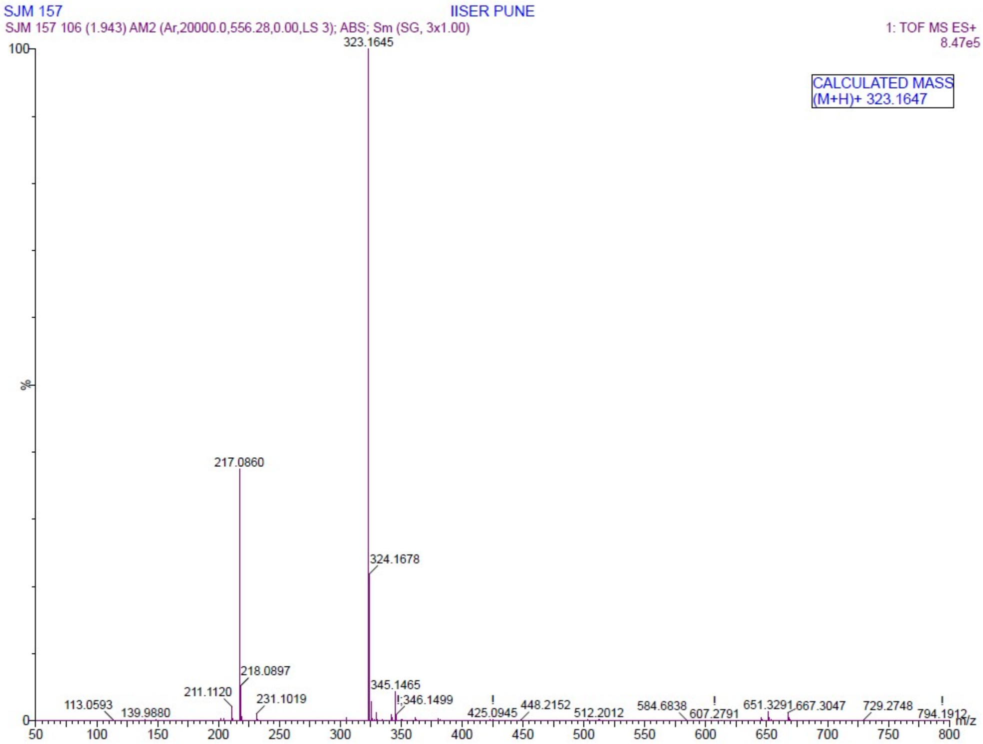
9-(4-methylbenzyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4f)



^{1}H NMR of **4f**, 400 MHz, CDCl$_3$

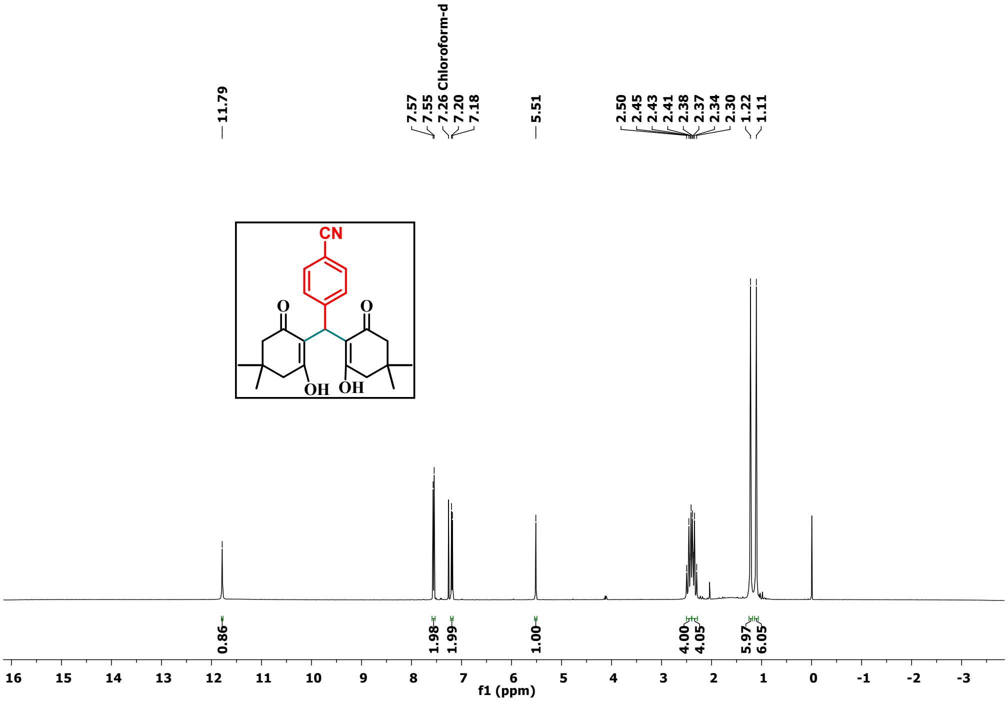


^{13}C {^{1}H} NMR of **4f**, 100 MHz, CDCl$_3$

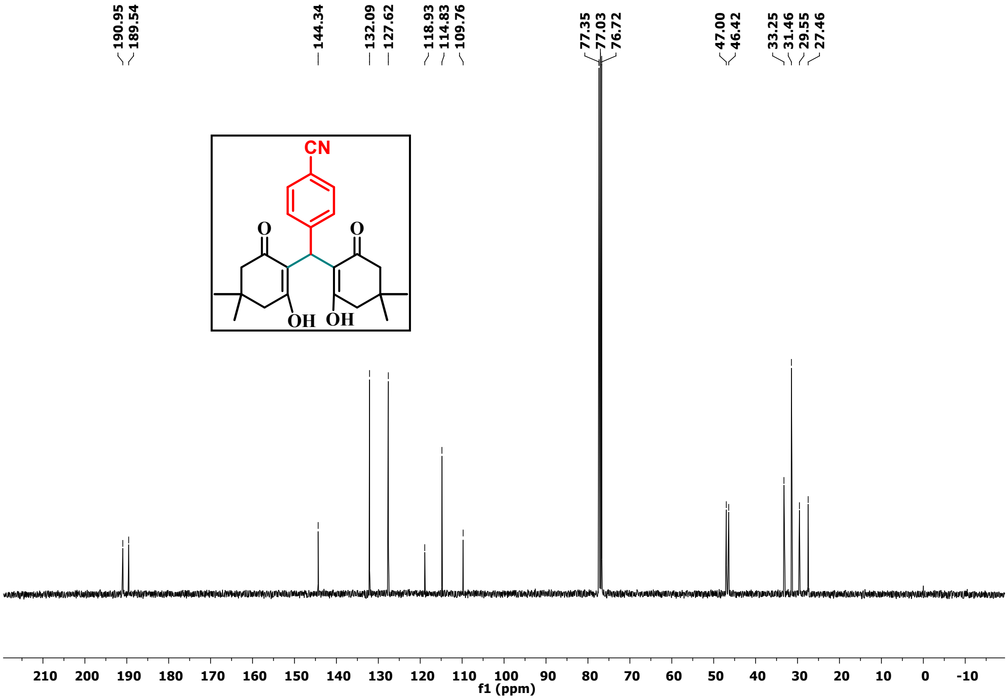


HRMS (ESI-TOF) of 4f

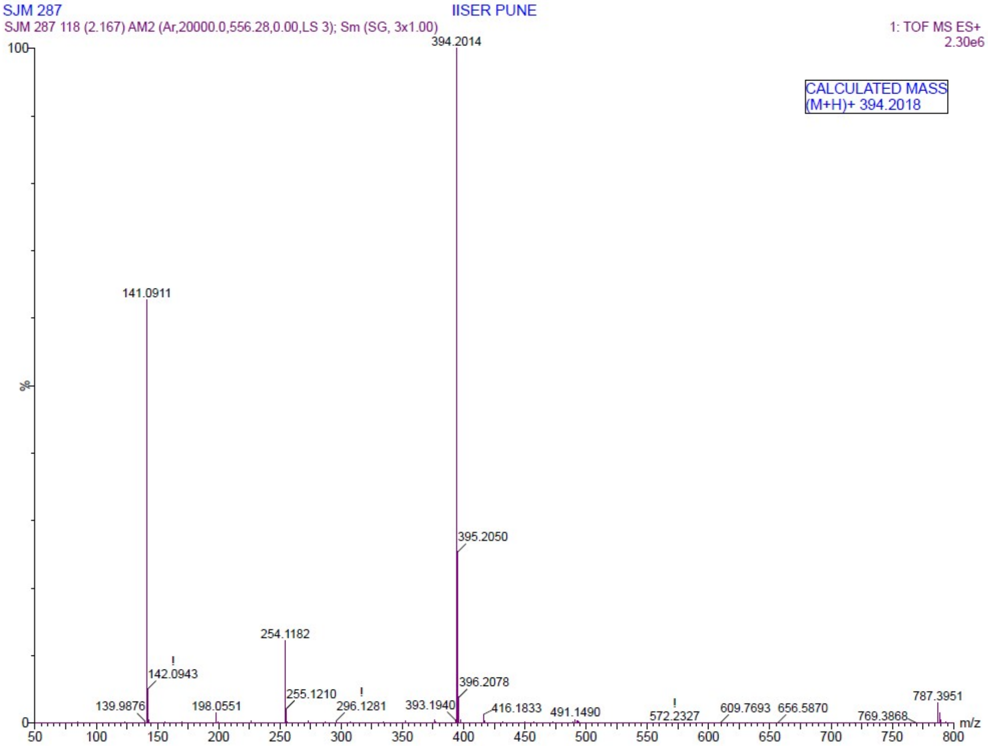
4-(bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)benzonitrile (6a)



^{1}H NMR of **6a**, 400 MHz, $CDCl_3$

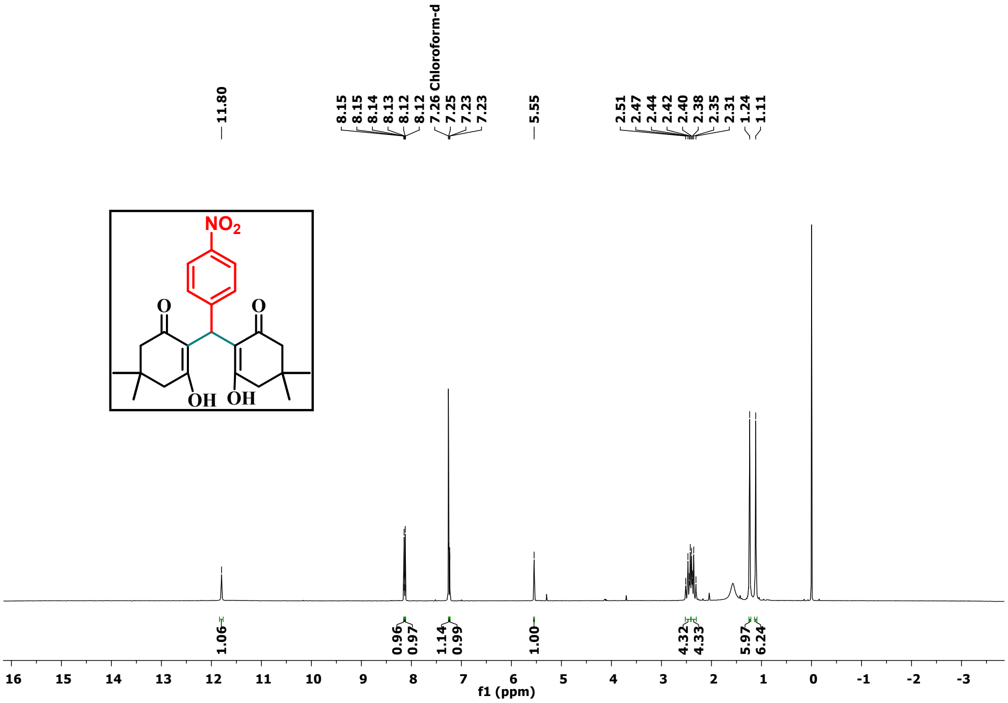


^{13}C {^{1}H} NMR of **6a**, 100 MHz, CDCl$_3$

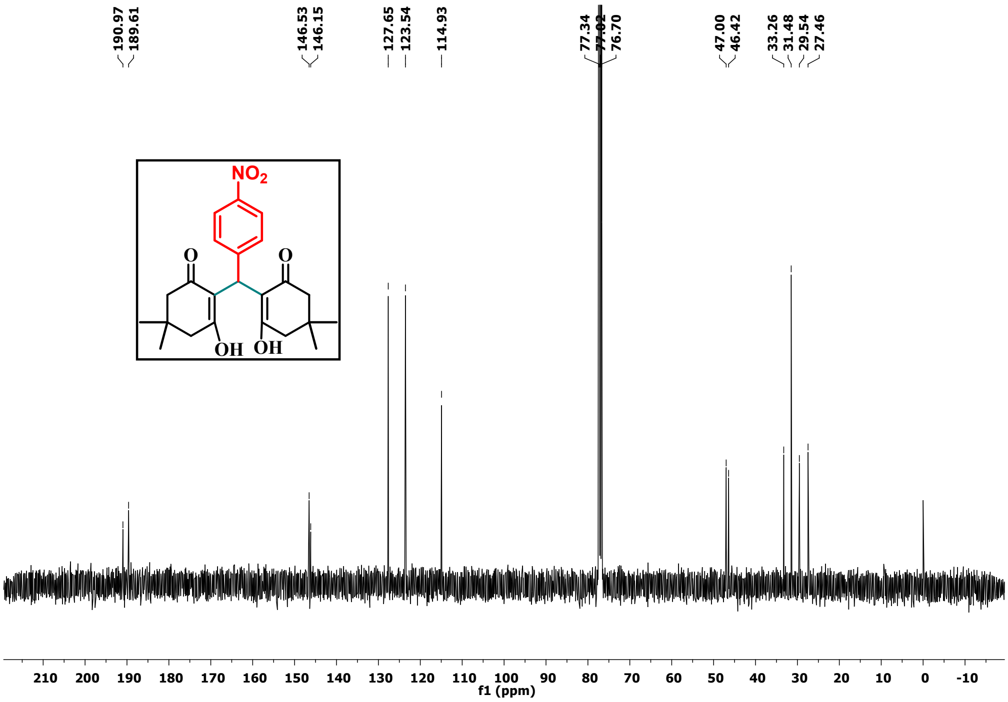


HRMS (ESI-TOF) of 6a

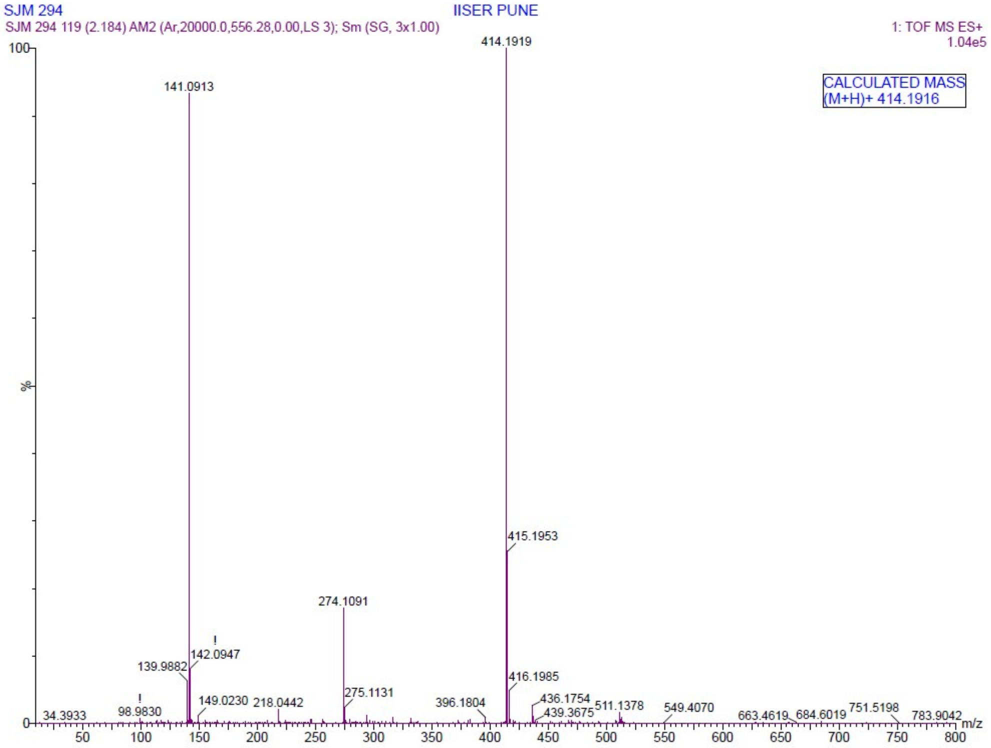
2,2'-((4-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (6b)



^{1}H NMR of **6b**, 400 MHz, $CDCl_3$

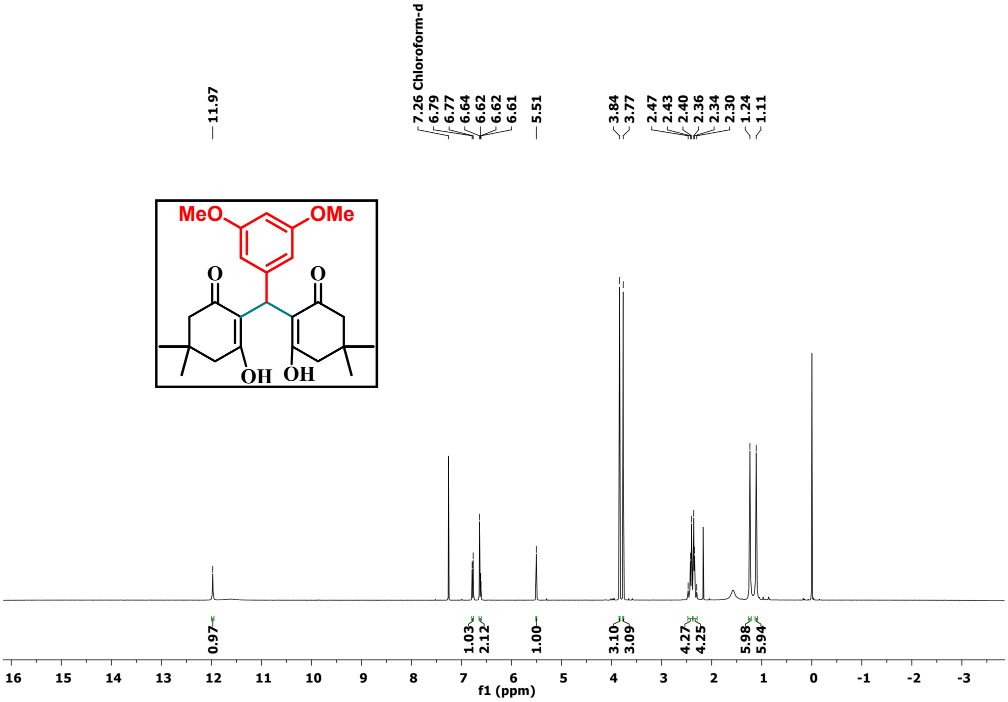


^{13}C {^{1}H} NMR of **6b**, 100 MHz, $CDCl_3$

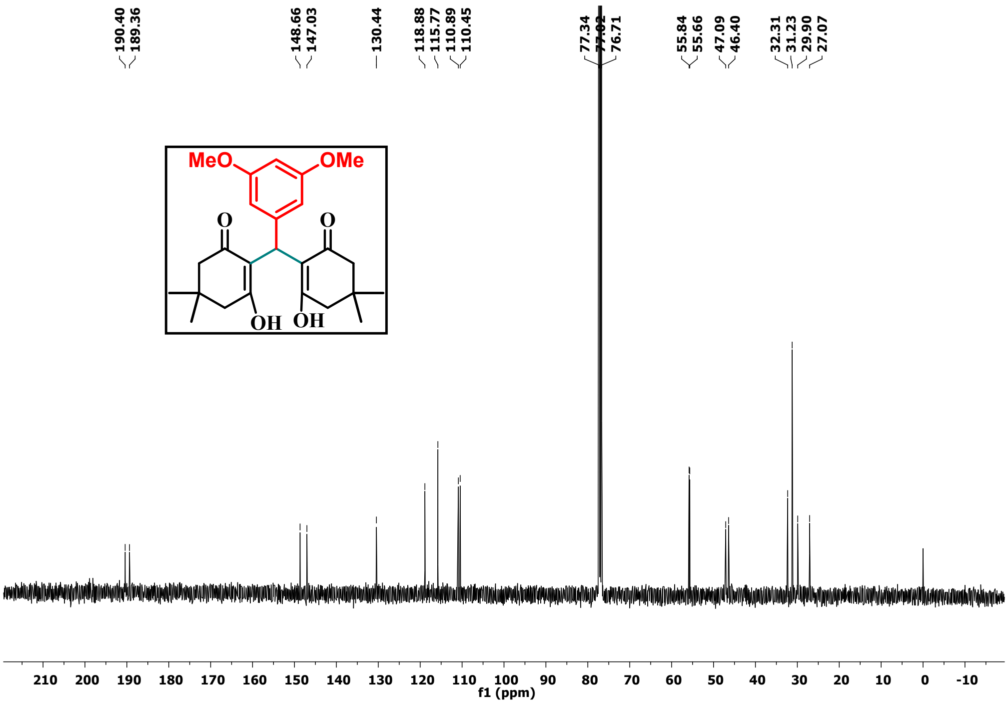


HRMS (ESI-TOF) of 6b

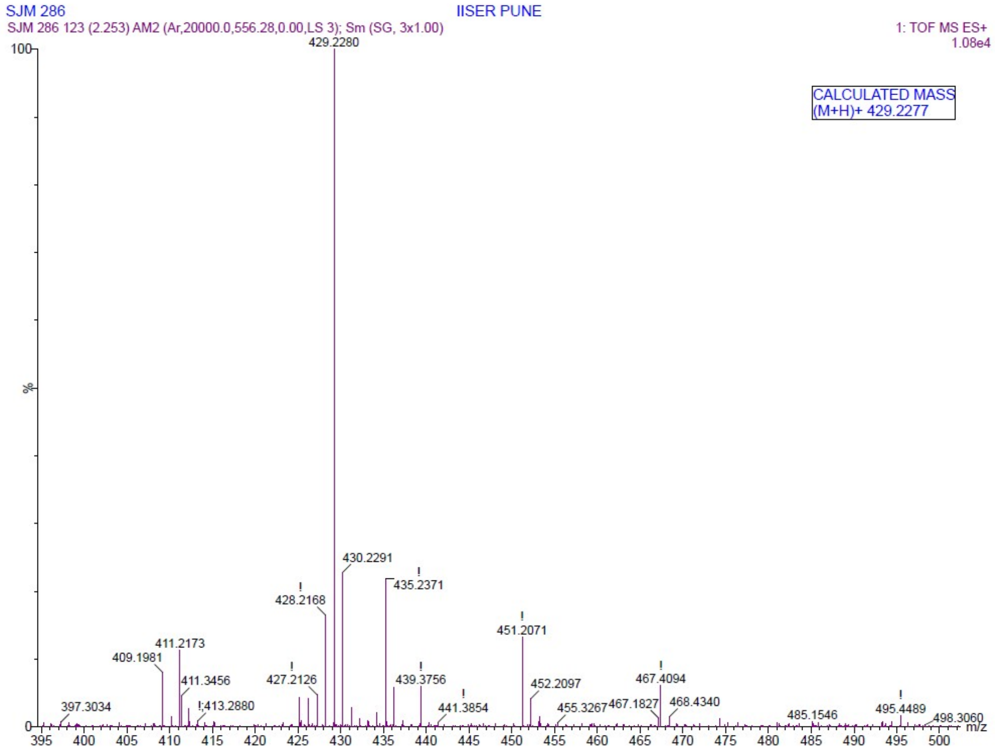
2,2'-((3,5-dimethoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (6c)



^{1}H NMR of **6c**, 400 MHz, $CDCl_3$

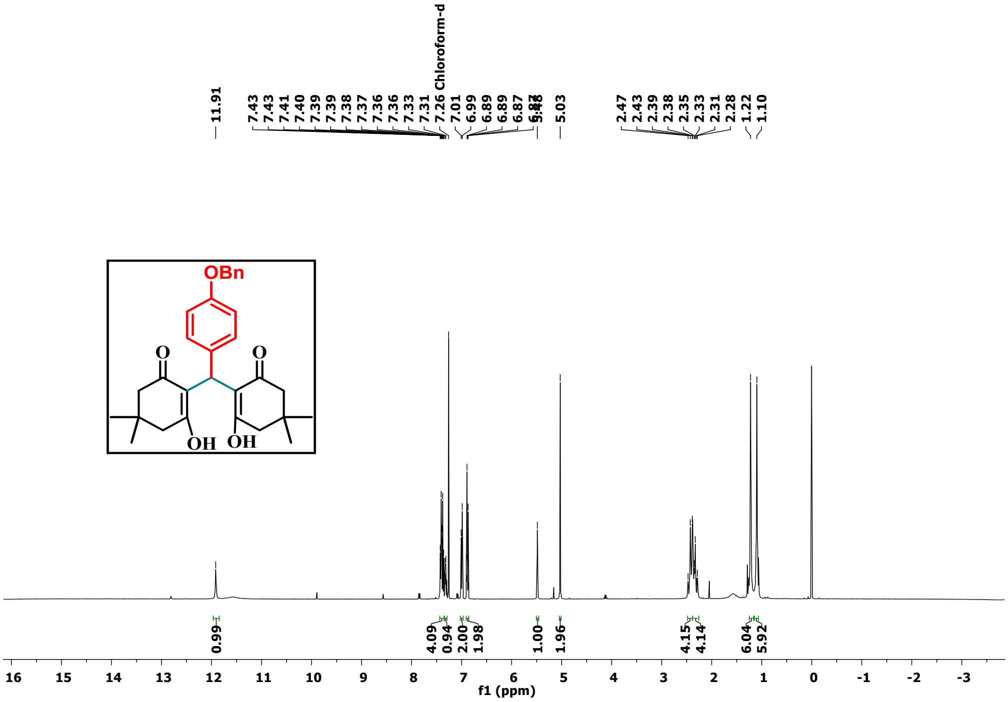


^{13}C {^{1}H} NMR of **6c**, 100 MHz, CDCl$_3$

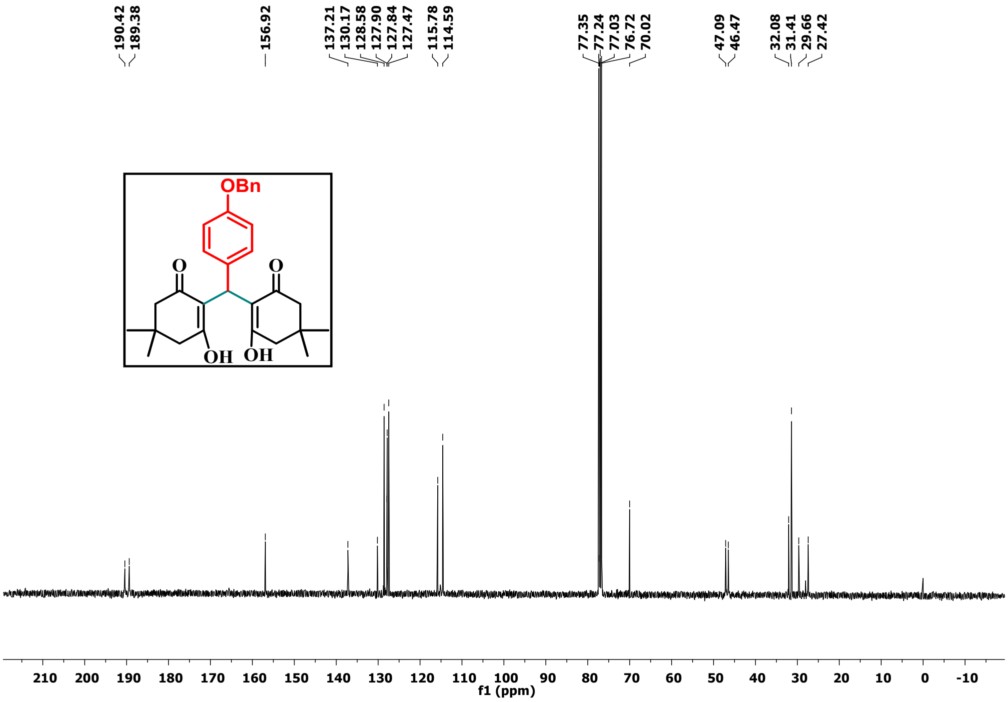


HRMS (ESI-TOF) of 6c

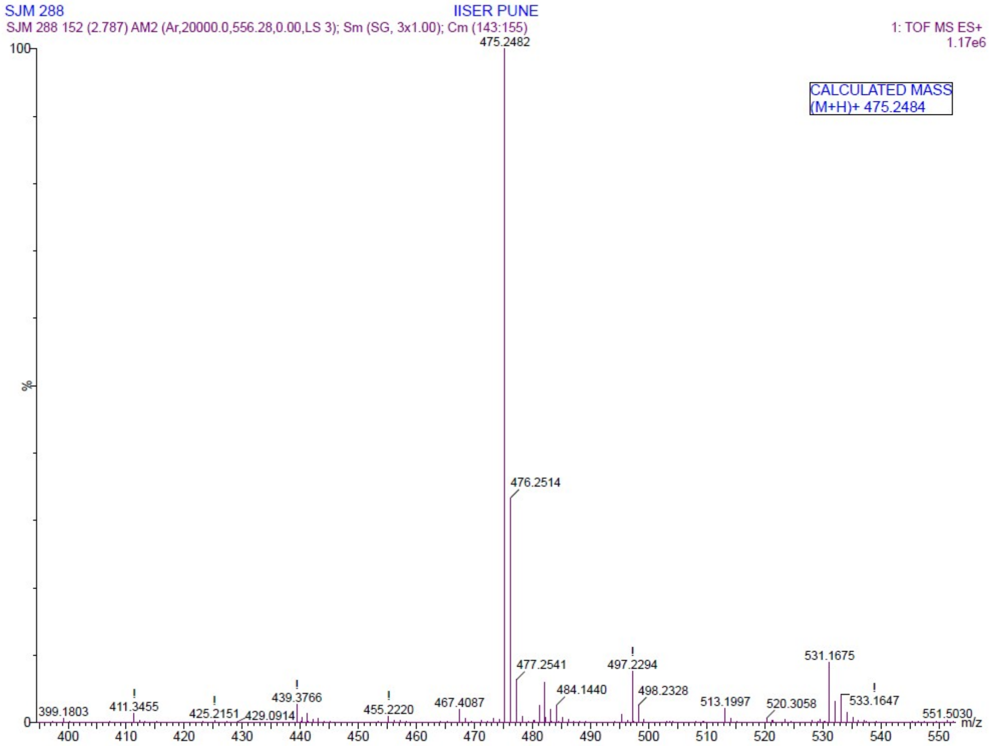
2,2'-((4-(benzyloxy)phenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (6d)



^{1}H NMR of **6d**, 400 MHz, $CDCl_3$

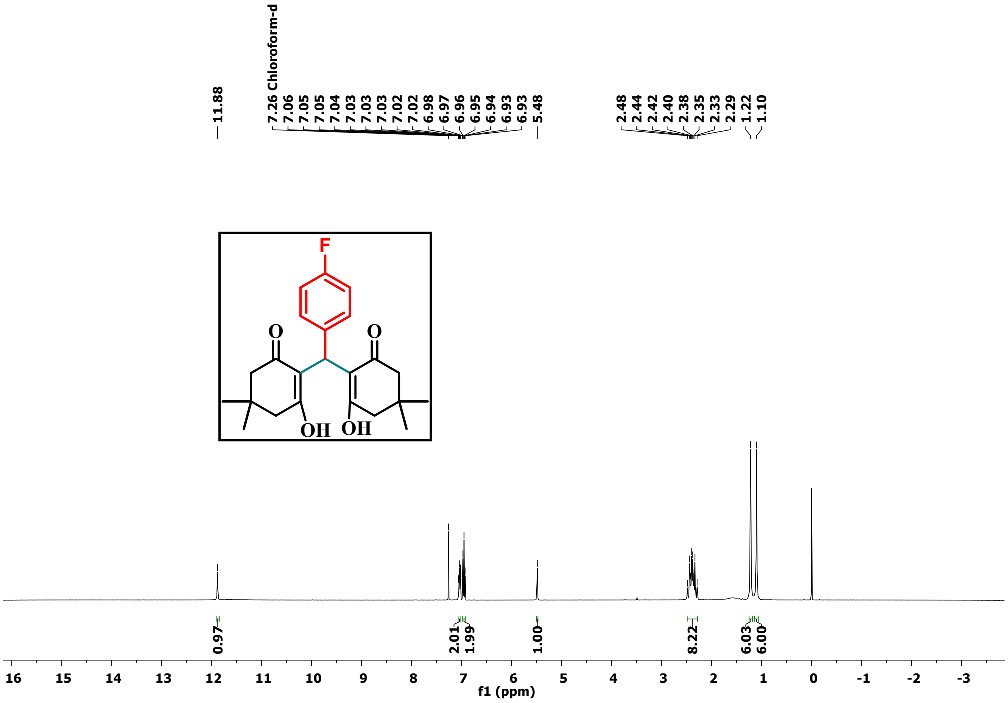


^{13}C {^{1}H} NMR of **6d**, 100 MHz, $CDCl_3$

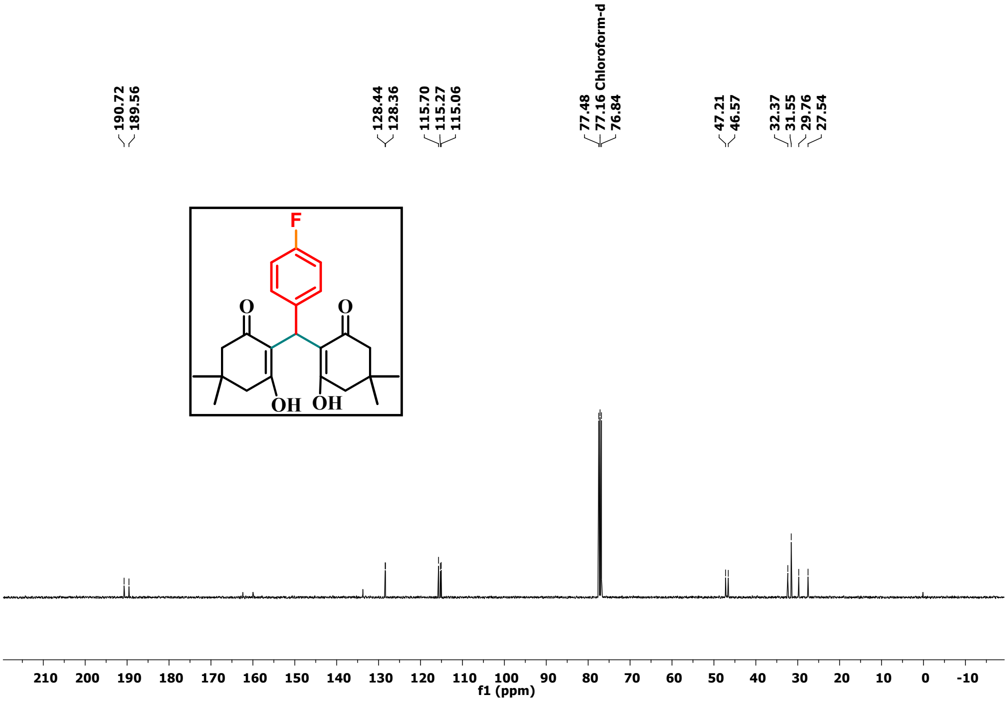


HRMS (ESI-TOF) of 6d

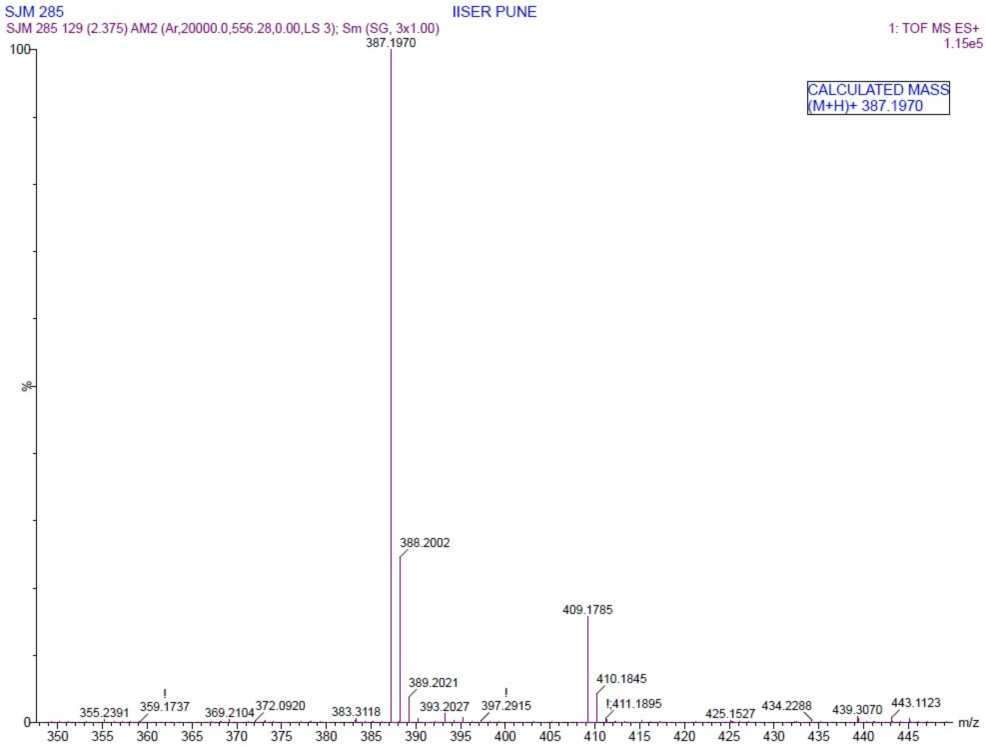
2,2'-((4-fluorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (6e)



^{1}H NMR of **6e**, 400 MHz, CDCl$_3$

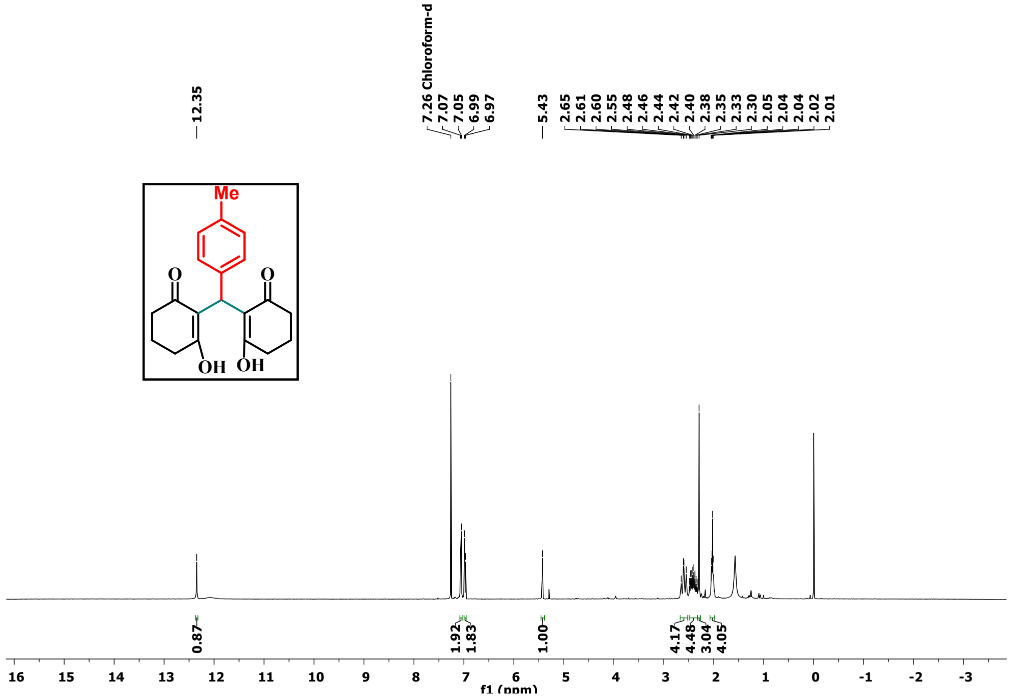


^{13}C {^{1}H} NMR of **6e**, 100 MHz, CDCl$_3$

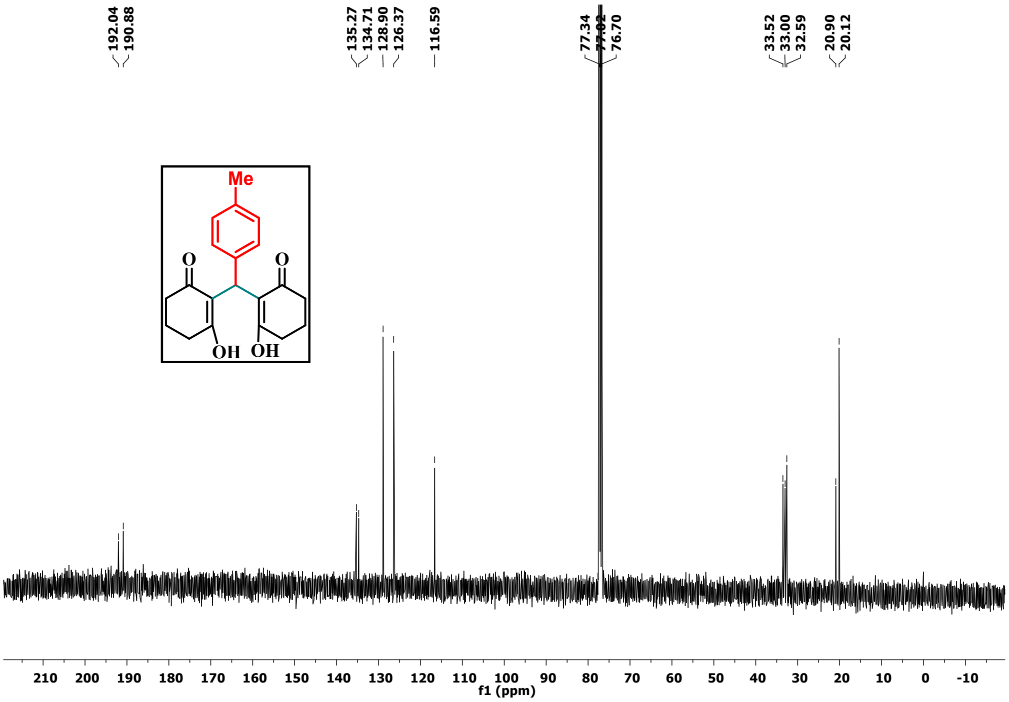


HRMS (ESI-TOF) of 6e

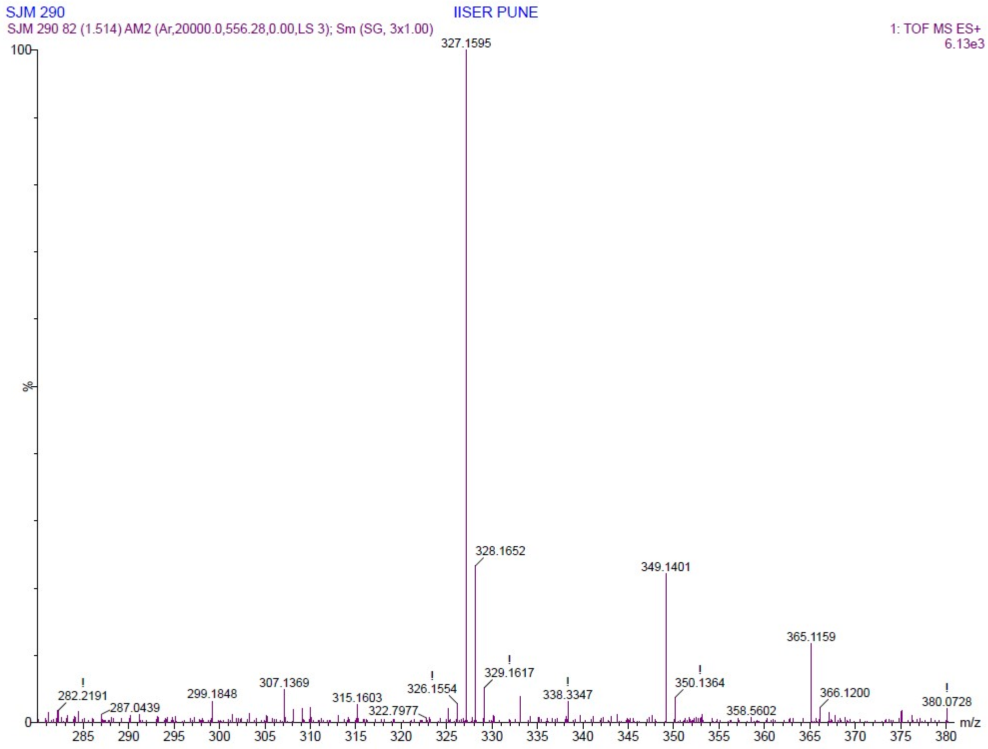
2,2'-(p-tolylmethylene)bis(3-hydroxycyclohex-2-en-1-one) (6f)



^{1}H NMR of **6f**, 400 MHz, $CDCl_3$

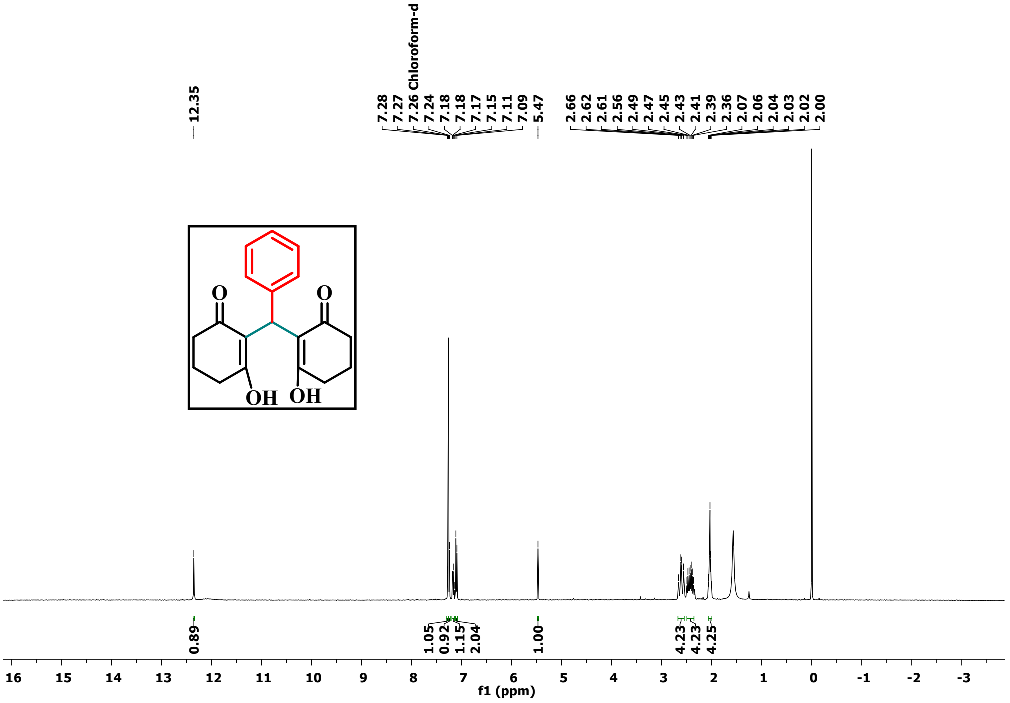


$^{13}C\ \{^{1}H\}$ NMR of **6f**, 100 MHz, $CDCl_3$

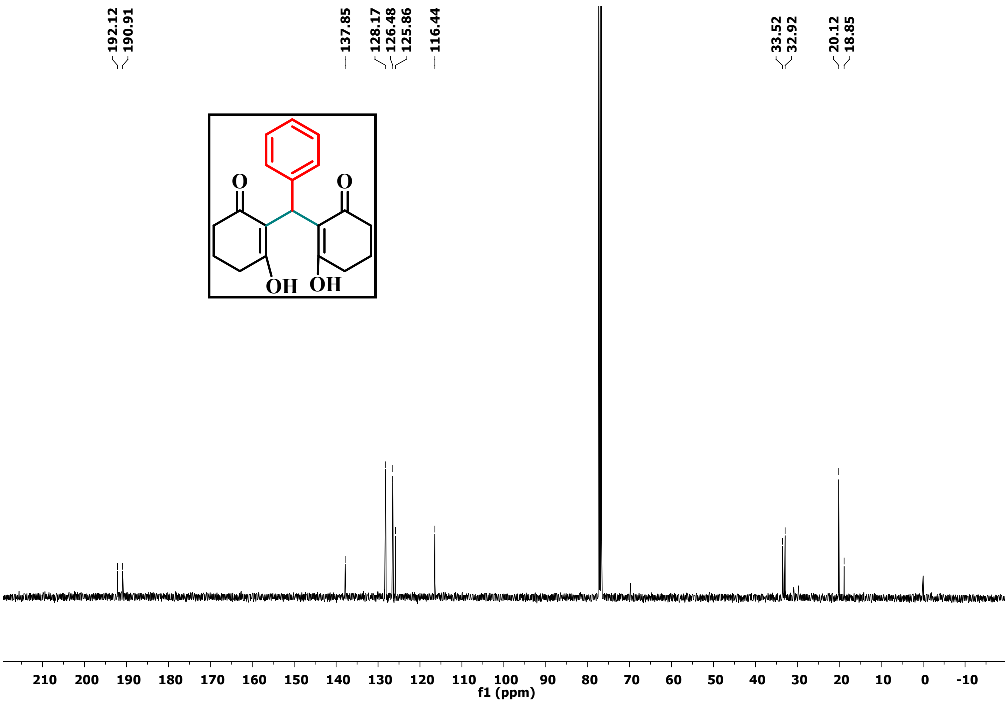


HRMS (ESI-TOF) of 6f

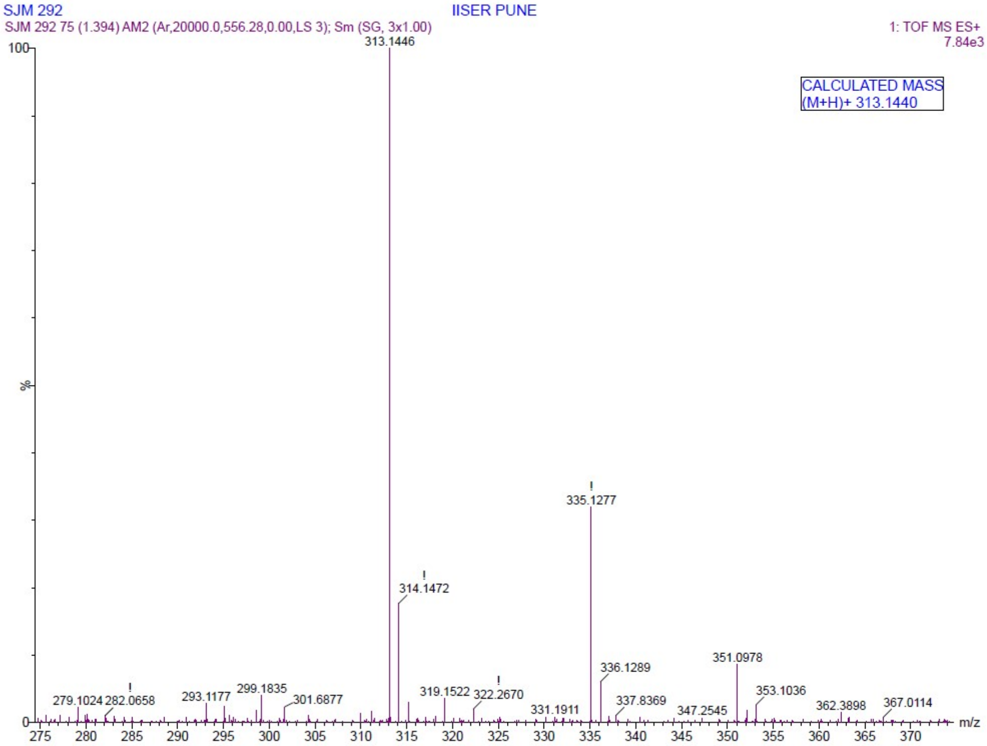
2,2'-(phenylmethylene)bis(3-hydroxycyclohex-2-en-1-one) (6g)



^{1}H NMR of **6g**, 400 MHz, CDCl$_3$

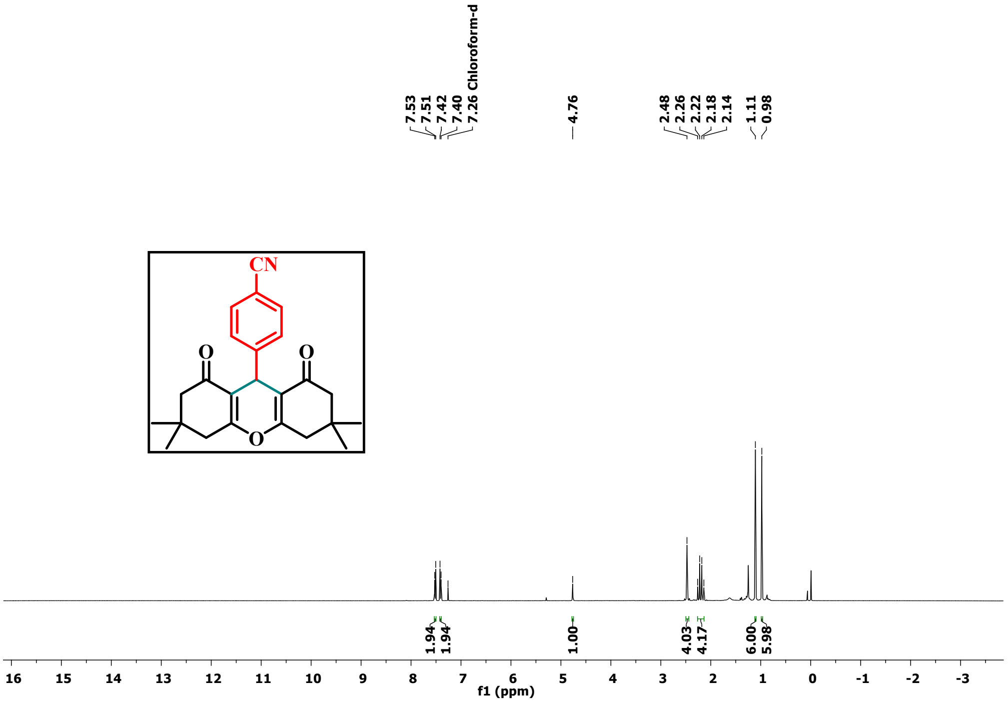


^{13}C {^{1}H} NMR of **6g**, 100 MHz, $CDCl_3$

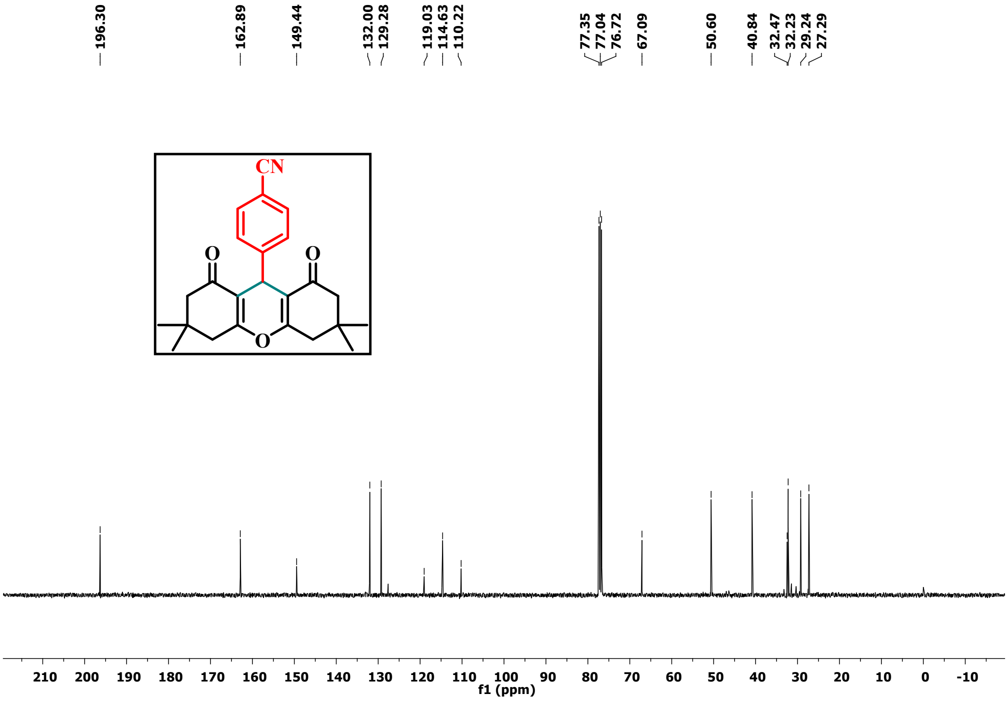


HRMS (ESI-TOF) of 6g

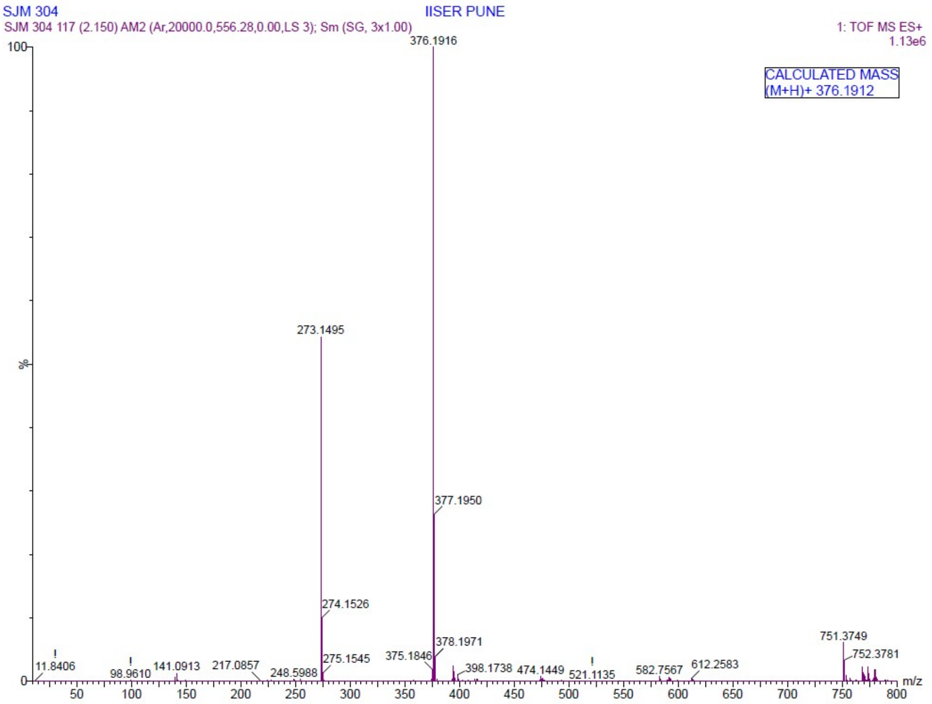
4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile (7a)



^{1}H NMR of **7a**, 400 MHz, $CDCl_3$

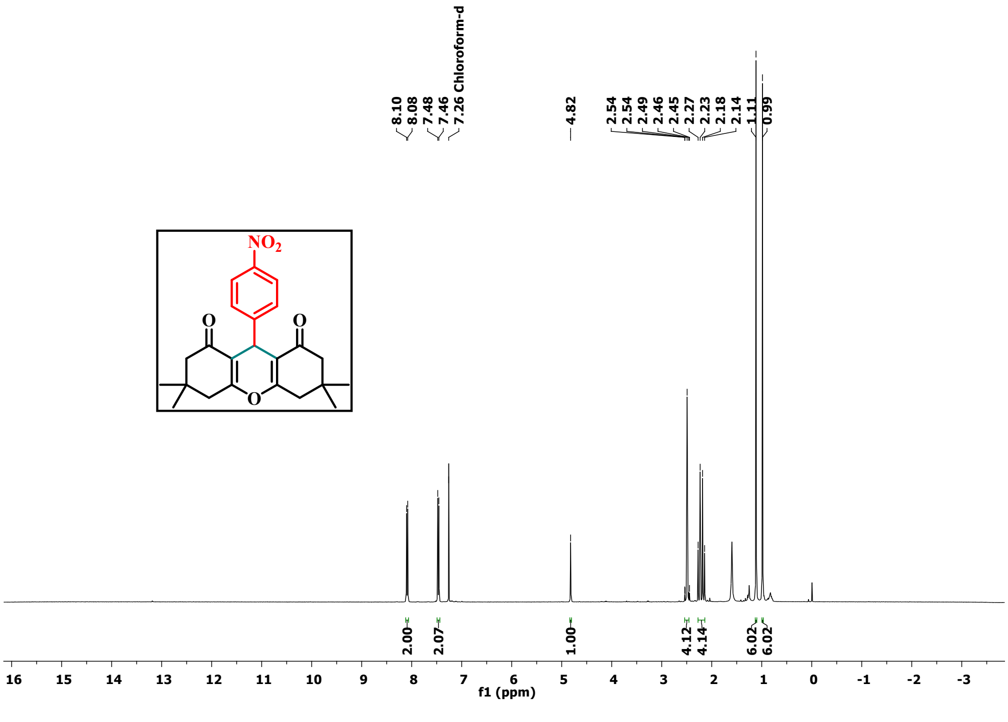


^{13}C {^{1}H} NMR of **7a**, 100 MHz, $CDCl_3$

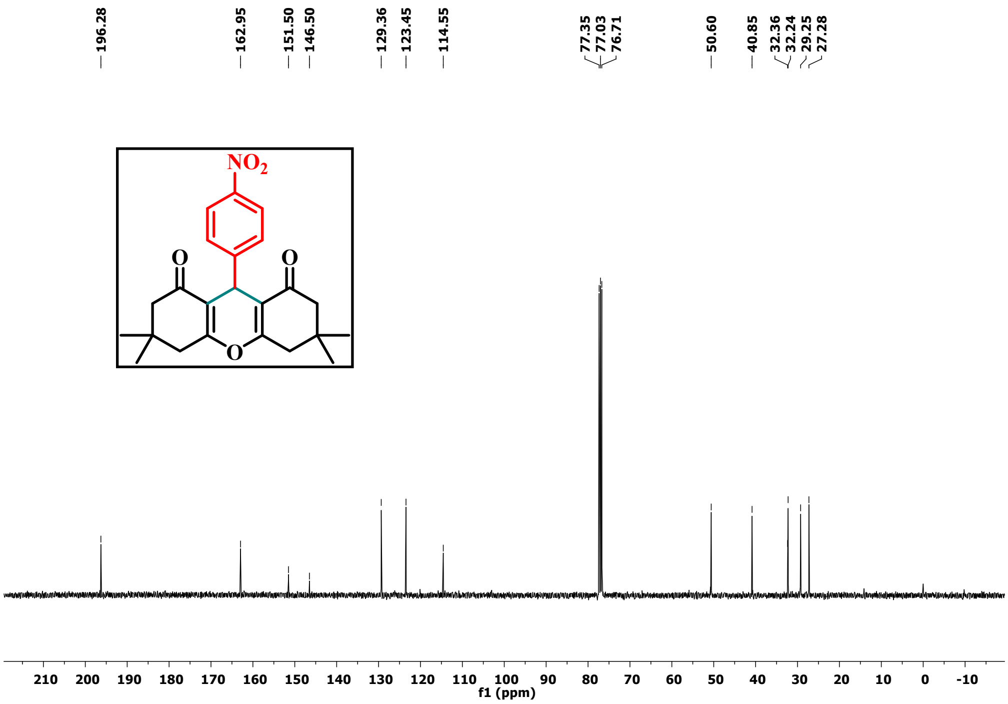


HRMS (ESI-TOF) of 7a

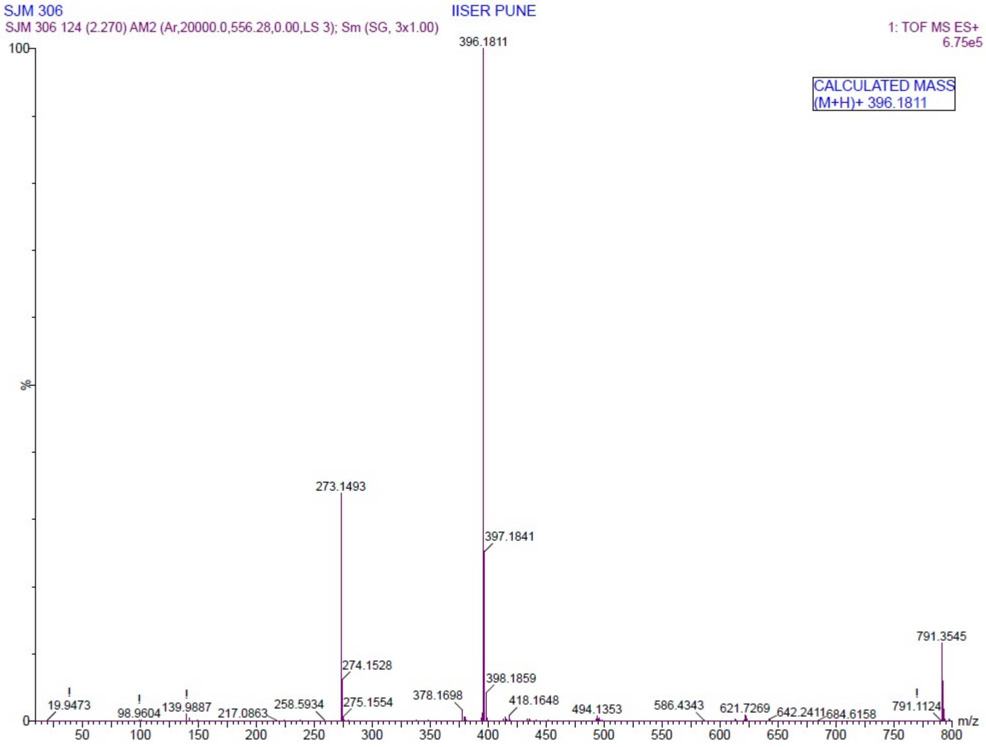
3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7b)



^{1}H NMR of **7b**, 400 MHz, $CDCl_3$

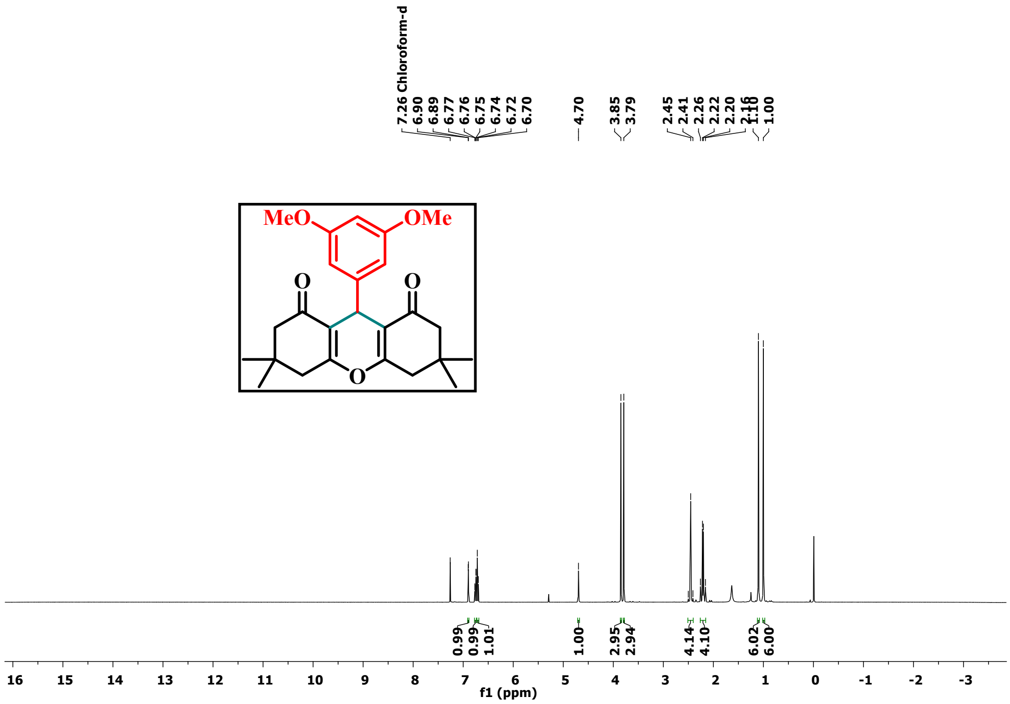


$^{13}C\ \{^{1}H\}$ NMR of **7b**, 100 MHz, $CDCl_3$

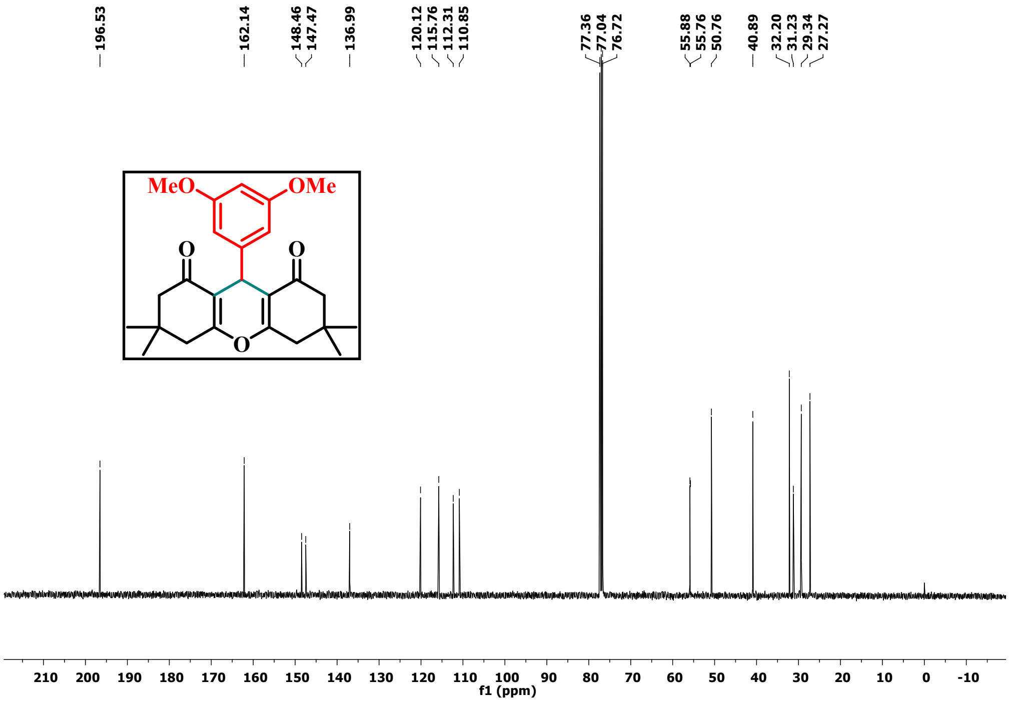


HRMS (ESI-TOF) of 7b

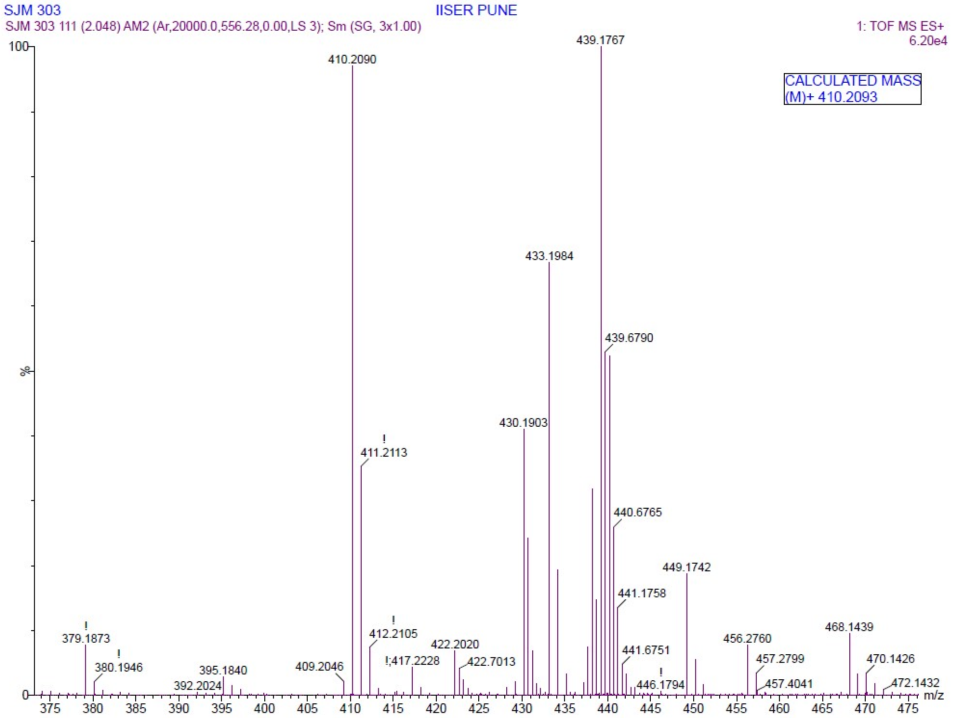
9-(3,5-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7c)



^{1}H NMR of **7c**, 400 MHz, $CDCl_3$

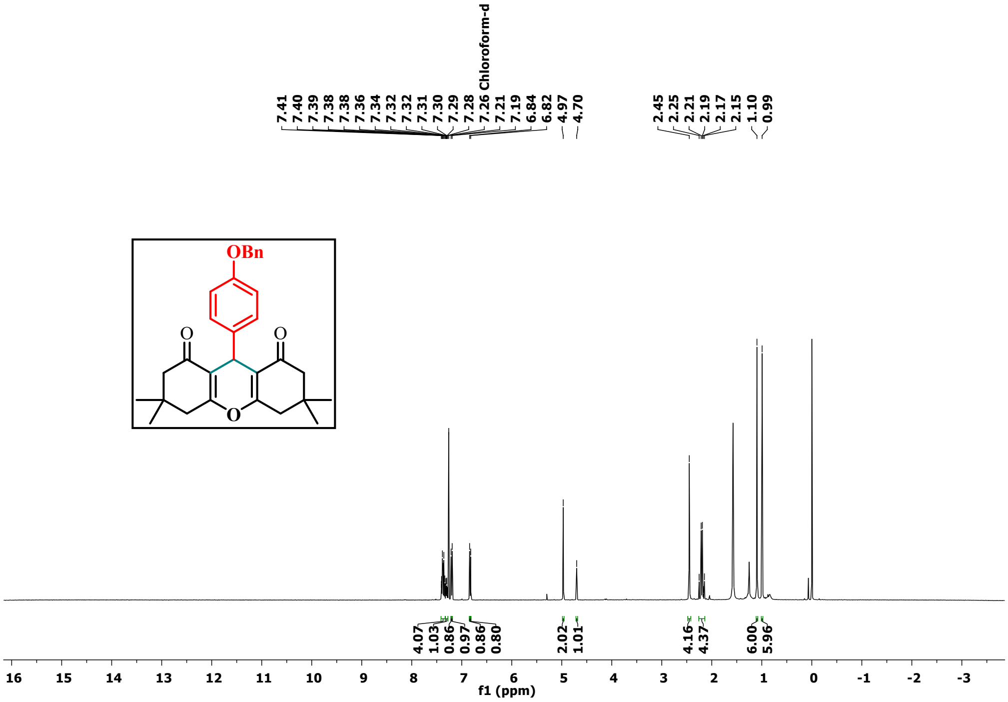


^{13}C {^{1}H} NMR of **7c**, 100 MHz, $CDCl_3$

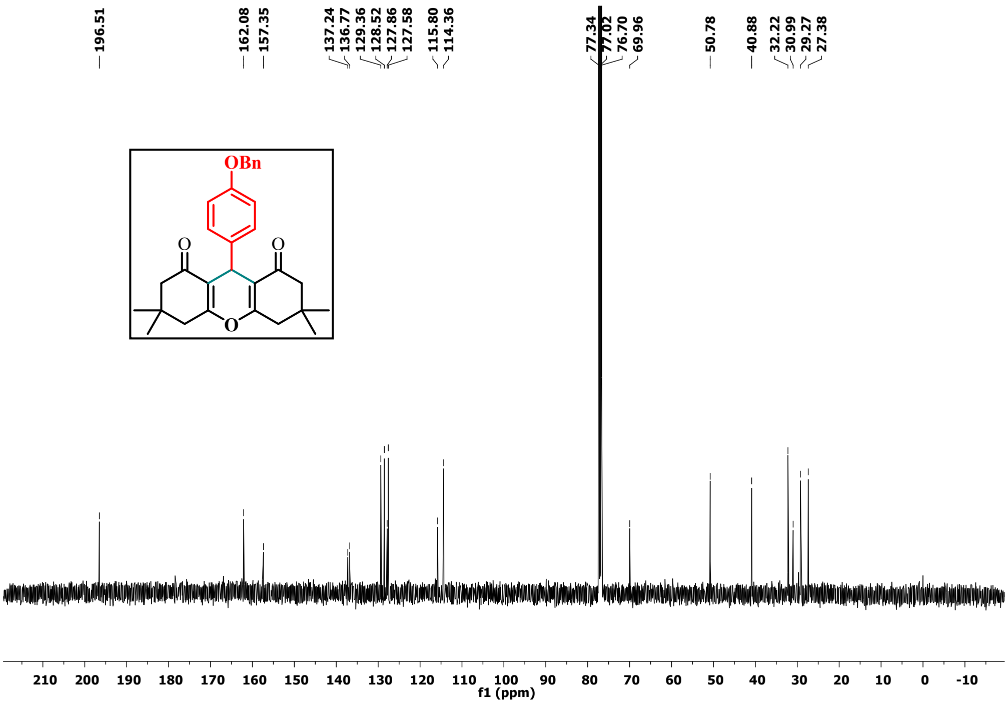


HRMS (ESI-TOF) of 7c

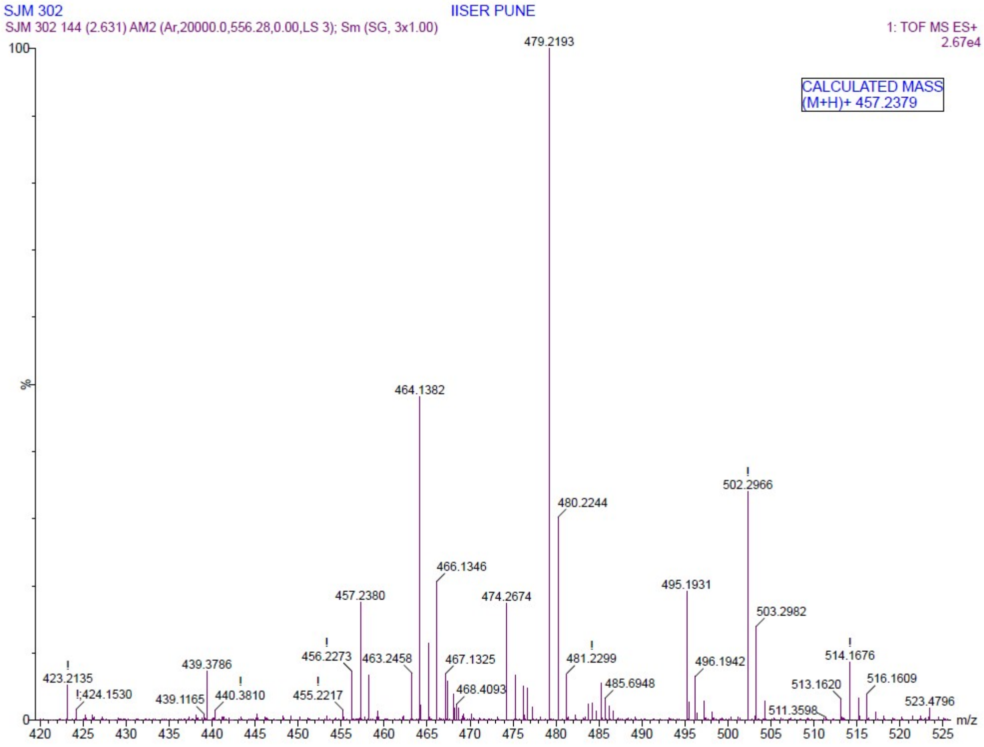
9-(4-(benzyloxy)phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7d)



^{1}H NMR of **7d**, 400 MHz, CDCl$_3$

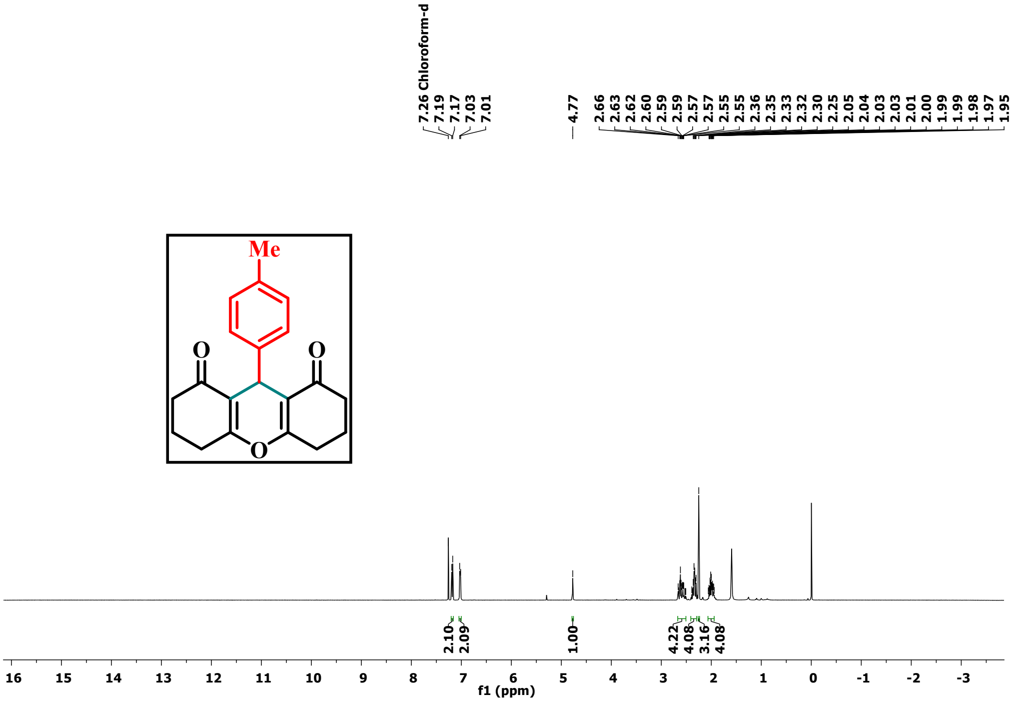


$^{13}C\ \{^{1}H\}$ NMR of **7d**, 100 MHz, $CDCl_3$

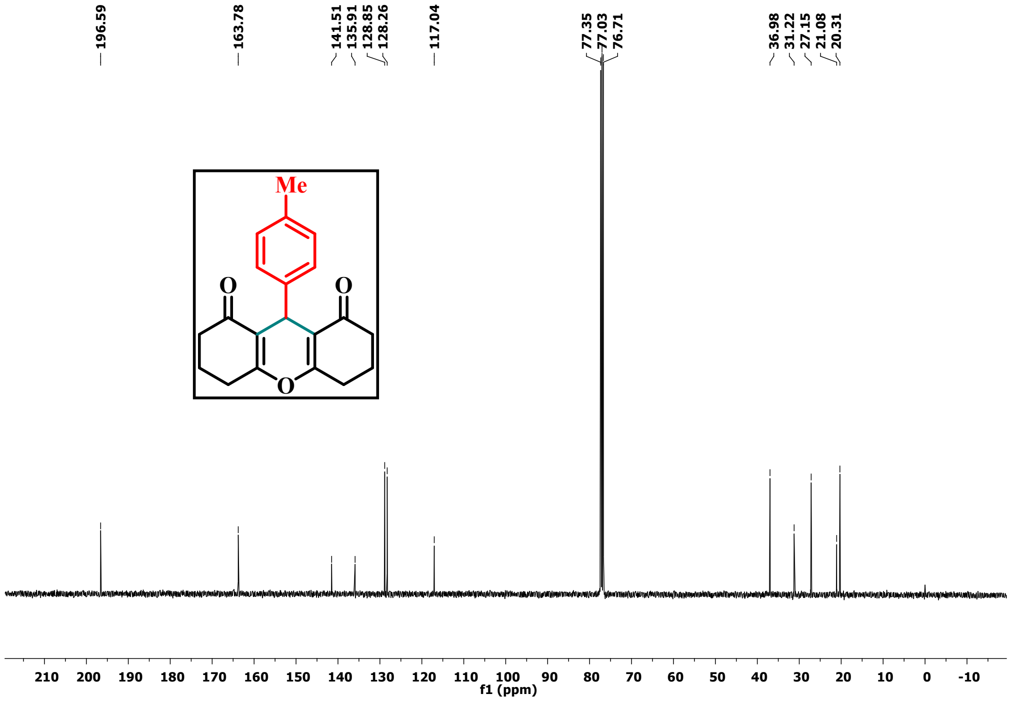


HRMS (ESI-TOF) of 7d

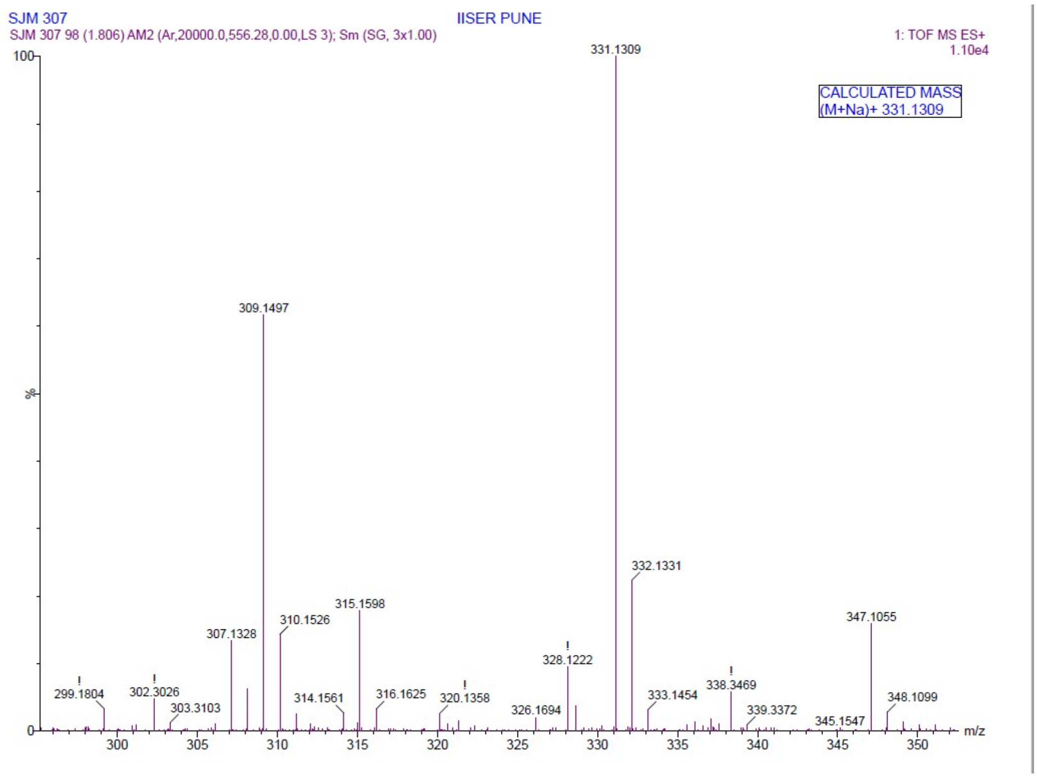
9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7e)



^{1}H NMR of **7e**, 400 MHz, CDCl$_3$

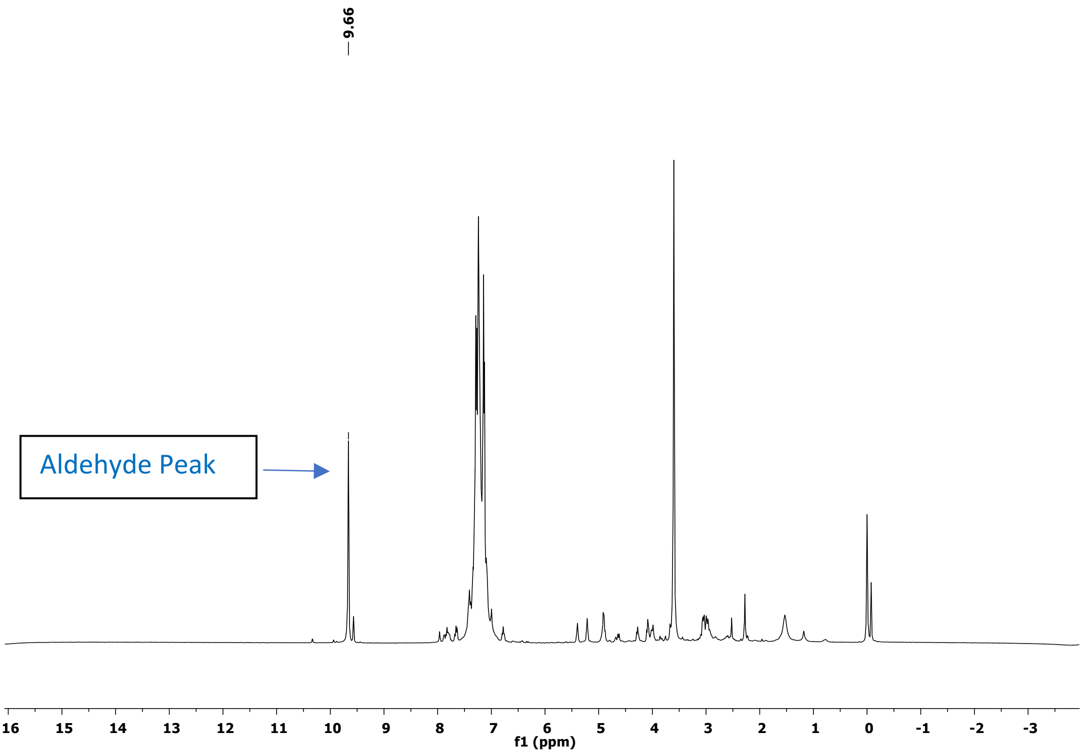


^{13}C {^{1}H} NMR of **7e**, 100 MHz, CDCl$_3$



HRMS (ESI-TOF) of 7e

^{1}H NMR of crude reaction mixture of styrene oxide heated at 160 ^{o}C



^{1}H NMR of crude reaction mixture of styrene oxide, 400 MHz, $CDCl_3$

8. GCMS analysis of the Control Experiment:

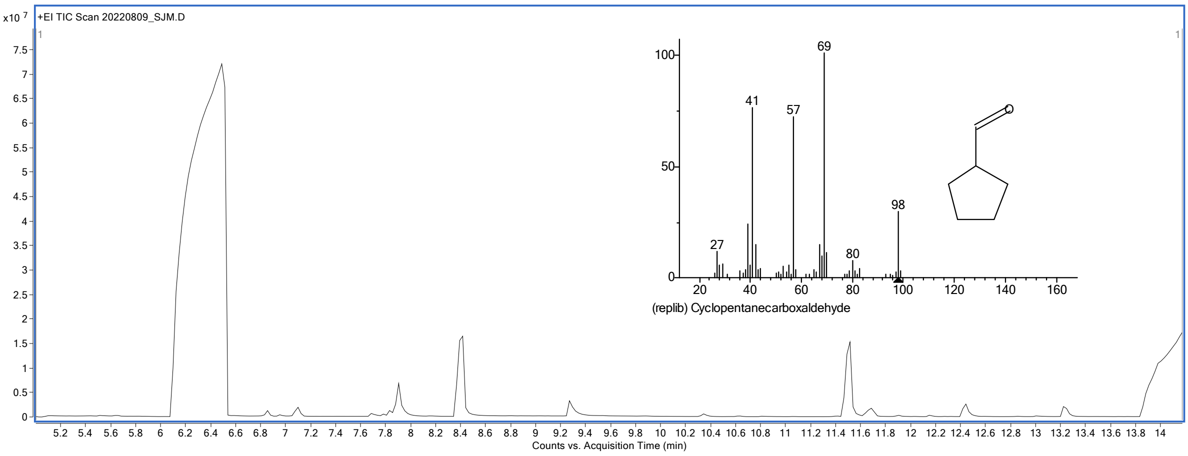


Fig-S1: GCMS spectrum for the reaction of epoxy cyclohexane with Fe-Zeolite

9. ORTEP drawings of 3a showing thermal ellipsoids at the 50% probability level

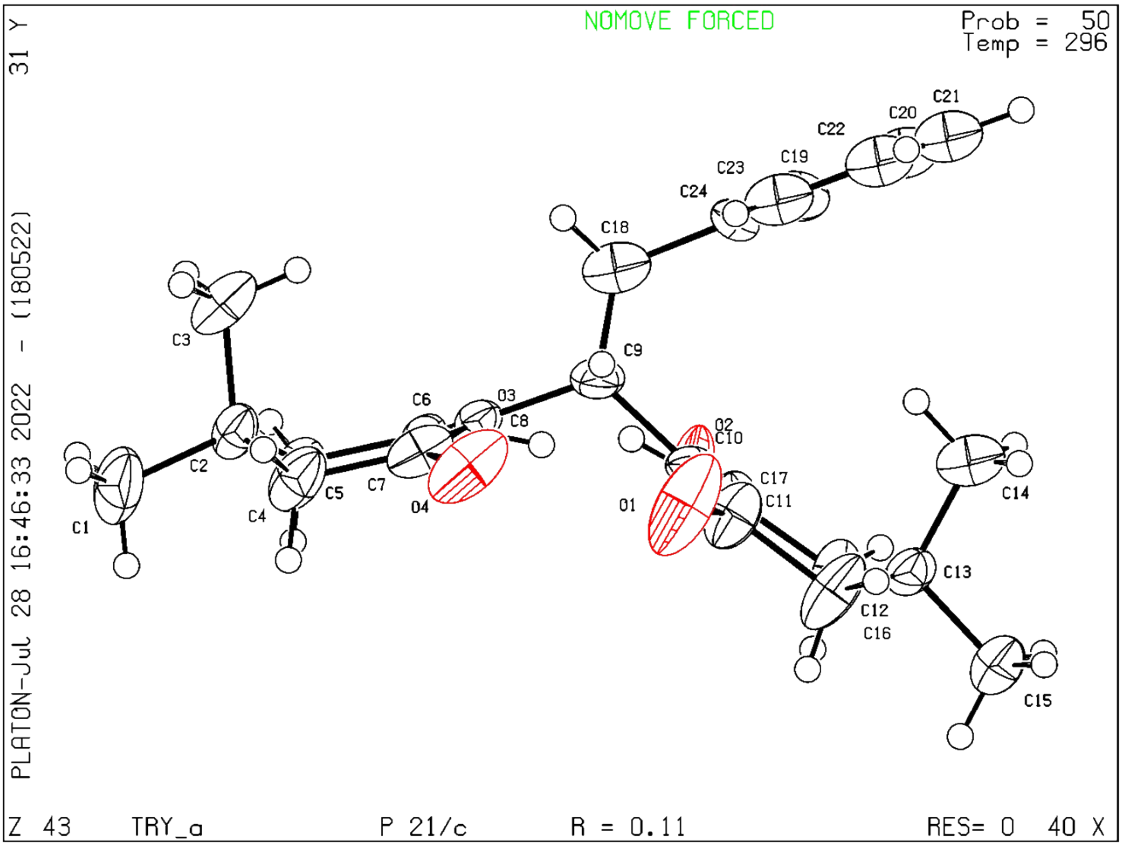


Figure S2: ORTEP drawing of 3a showing thermal ellipsoids at the 50% probability level3

Table S1: Crystallographic parameters table for 3a

Parameters	**3a**
Emperical formula	$C_{24}H_{30}O_4$
Formula Mass/g mol^{-1}	382.5
Experimental crystal description	Needle
Colour	White
Dcalcd/g cm^{-3}	1.230
Crystal system	Monoclinic
Space group	P 21/c
a/ Å	8.702(3)
b/ Å	20.224(7)
c/ Å	11.877(4)
α/ deg	90
β/ deg	98.716(9)
√/ deg	90
V/Å^3	2066.2(12)
Z	4
T / K	296(2)
Diffraction Source	MoK\a
Diffraction radiation wavelength/ Å	0.71073
Diffraction reflection theta full	19.924
Reflection number total	1903
Reflection number gt	1729
μ/mm-1	0.082
F(000)	824
R1,wR2 [I>2σ(I)]	0.1078, 0.2679
R1,wR2(all data)	0.1147, 0.2744
GoF	1.006

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