Supplementary Information

Metal-Free Oxidative C(sp^2)-H Arylation of Cyclopentene-1,3-diones with *β*-Naphthols

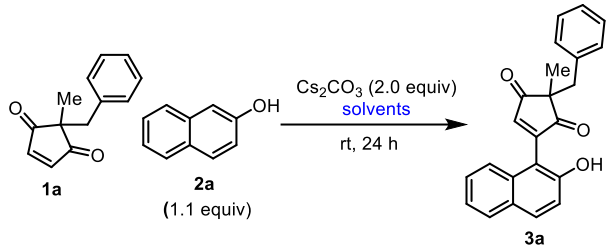
Sundaram Maurya[a,b], Sandip B. Jadhav[a,b], Rambabu Chegondi,*[a,b]

[a]Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India. [b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India.

E-mail: rchegondi@iict.res.in; cramhcu@gmail.com

1. Additional Screening and Optimization Data:

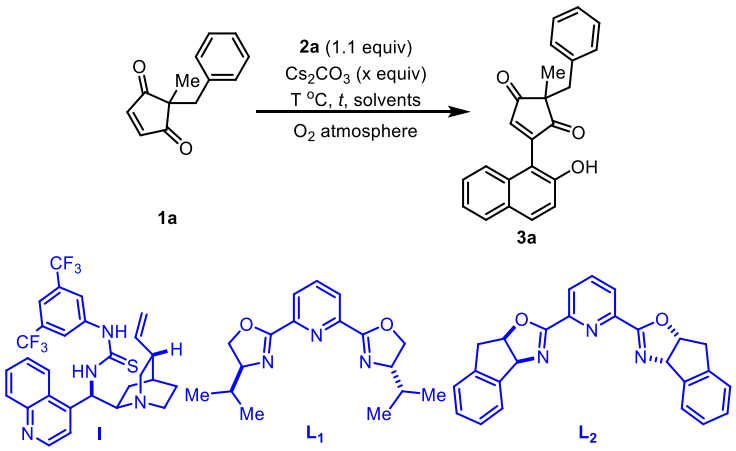
Table S_1: Solvent screening in inert conditions[a,b]



entry	atmosphere	solvent	yield(%)
1.	Ar	$CHCl_3$	0
2.	Ar	CH_2Cl_2	0
3.	Ar	THF	0
4.	Ar	MeCN	0

[a]Reaction conditions: **1a** (40.0 mg, 0.20 mmol), **2a** (31.6 mg, 0.22 mmol), Cs_2CO_3 (130.2 mg, 2.0 equiv). [b]Only Michael addition intermediate **3a'** was observed in traces in case of MeCN solvent after 24 h reaction time.

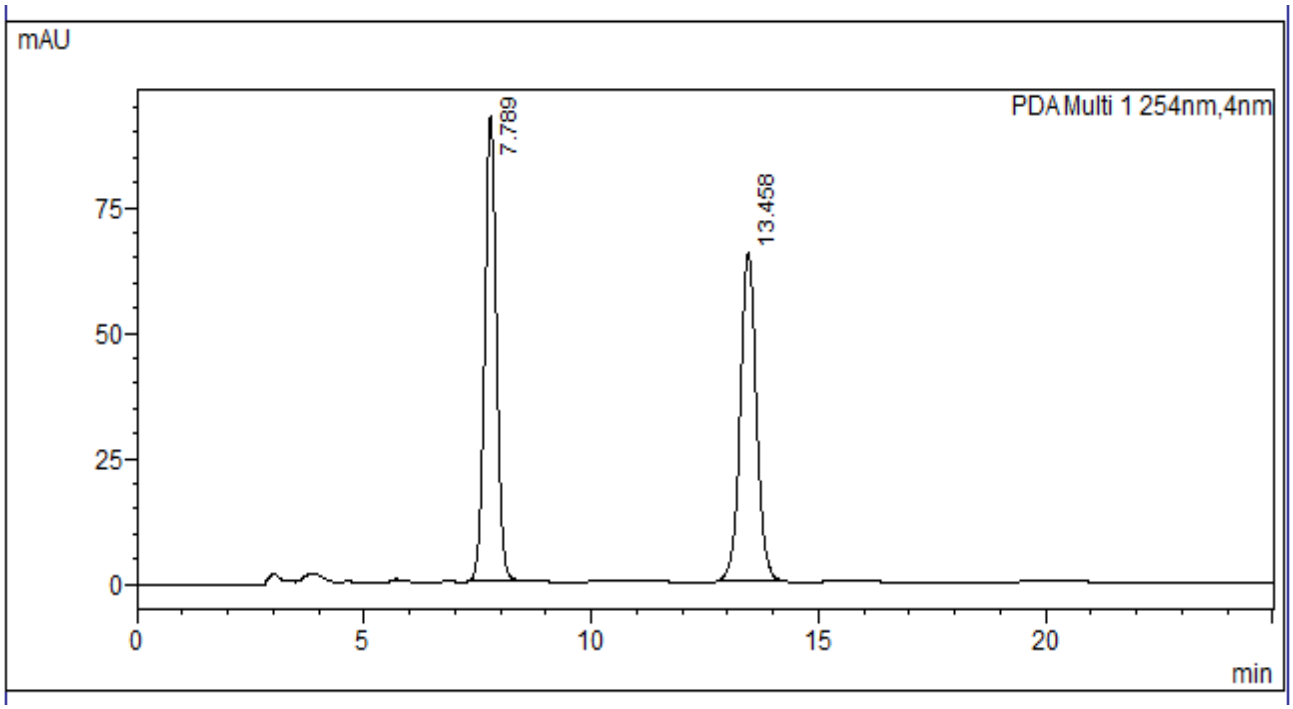
Table S2: Enantioselective C(sp^2)-H arylation[a]



entry	catalyst	ligand	Cs_2CO_3 equiv	solvent	temp (°C)	yield (%)[b]	ee[d]
1.	**I** (20 mol%)	-	10 mol%	MeCN	rt	<15	0
2.	**I** (30 mol%)	-	-	MeCN	rt	0	0
3.	**I** (30 mol%)	-	2.0	MeCN	rt	84	10
4.	**I** (20 mol%)	-	2.0	MeCN	rt	82	9
5.	$Sc(OTf)_3$ (5 mol%)[c]	-	-	$CHCl_3$	0	-	0
6.	$Sc(OTf)_3$ (5 mol%)[c]	L_1 (10 mol%)	2.0	$CHCl_3$	-40	53	6
7.	$Sc(OTf)_3$ (5 mol%)[c]	L_2 (10 mol%)	2.0	$CHCl_3$	-40	28	0

[a]Reaction conditions:[1,2] **1a** (40.0 mg, 0.20 mmol), **2a** (31.6 mg, 0.22 mmol) in O_2 atmosphere. [b]Isolated yields of products after column chromatography. [c]$Sc(OTf)_3$ reactions include LiBr as an additive and 4 Å molecular sieves, and reaction time being 60 h. [d]Enantiomeric excess (*ee*) was determined by HPLC analysis using a chiral stationary phase.

Chiral HPLC analysis of the product **3a**: Daicel Chiralpak IA 250X4.6 mm 5µ column; hexane/2-propanol = 85/15, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 7.789 min (major), 13.458 min (minor).

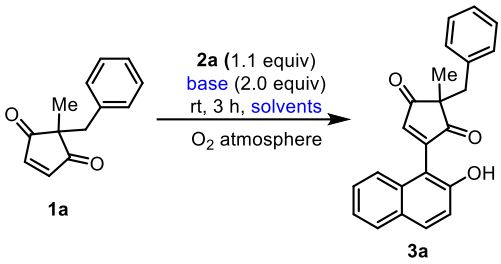


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.789	1647064	92310	50.531	58.511
2	13.458	1612462	65456	49.469	41.489
Total		3259527	157766	100.000	100.000

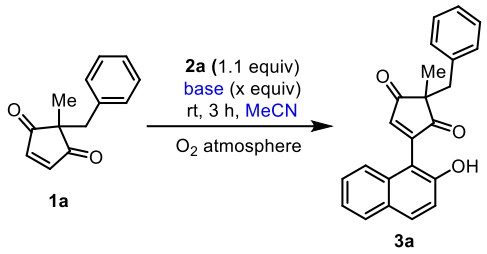
Table S3: Base & Solvents Screening[a]



entry	base	solvent	Yield (%)[b]
1	Cs_2CO_3	MeOH	<5
2	Cs_2CO_3	DCM	28
3	Cs_2CO_3	$CHCl_3$	70
4	Cs_2CO_3	1,2-DCE	<10
5	Cs_2CO_3	1,4 Dioxane	NR
6	Cs_2CO_3	*t*-BuOH	NR
7	Cs_2CO_3	Toluene	NR
8	Cs_2CO_3	DMSO	<5
9	Cs_2CO_3	THF	61
10	CsOAc	MeCN	31
11	K_2CO_3	MeCN	51
12	NaOMe	MeCN	<10
13	NaH	MeCN	<5
14	NaOAc	MeCN	NR
15	Et_3N	MeCN	NR
16	DBU	MeCN	<10
17	*t*-BuOK	MeCN	NR
18	DABCO	MeCN	NR

[a]Reaction conditions: **1a** (40.0 mg, 0.20 mmol), **2a** (31.6 mg, 0.22 mmol). [b]Isolated yields of products after column chromatography.

Table S4: Base Equivalence & Reaction Time Screening[a]



entry	base (equiv)	time(h)	atmosphere	yield (%)[b]
1	Cs_2CO_3 (2.0)	3	Air	63
2	Cs_2CO_3 (2.0)	3	O_2	86
3	Cs_2CO_3 (2.0 at 0 °C)	3	O_2	32
4	Cs_2CO_3 (2.0 at 65 °C)	3	O_2	78
5	Cs_2CO_3 (0.1)	3	O_2	20
6	Cs_2CO_3 (0.3)	3	O_2	36
7	Cs_2CO_3 (0.5)	3	O_2	45
8	Cs_2CO_3 (1.0)	3	O_2	56
9	Cs_2CO_3 (1.5)	3	O_2	67
10	Cs_2CO_3 (3.0)	3	O_2	77
11	Cs_2CO_3 (2.0)	12	O_2	83
12	Cs_2CO_3 (2.0)	24	O_2	81
13	Cs_2CO_3 (2.0)	48	O_2	67

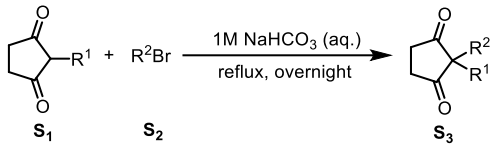
[a]Reaction conditions: **1a** (40.0 mg, 0.20 mmol), **2a** (31.6 mg, 0.22 mmol). [b]Isolated yields of products after column chromatography.

2. General details:

General Information: Unless otherwise noted, all reagents were used as received from commercial suppliers. Cesium Carbonate and substituted *β*-naphthols were purchased from Sigma Aldrich and Prince Scientific, respectively and used without further purification. All reactions were performed under oxygen atmosphere and in oven-dried glassware equipped with magnetic stirring bar. All solvents were dried before use following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), using *p*-anisaldehyde stain or *β*-naphthol stain. Column chromatography was carried out using silica gel (60-120 mesh) packed in glass columns. NMR spectra were recorded at 400, and 500 MHz (H), at 100, and 125 MHz (C), and at 376, and 377 MHz (F), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm), or CD_3OD (H: δ = 4.870 ppm and 3.310 ppm and C: δ = 49.00 ppm), or Acetone-d_6 (H: δ = 2.050 ppm and 2.840 ppm and C: δ = 206.260 ppm and 29.840 ppm), or DMSO-d_6 (H: δ = 2.500 ppm and 3.330 ppm and C: δ = 39.520 ppm) as internal standards, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques. HPLC analysis was performed on Shimadzu LC-20AD with UV detector.

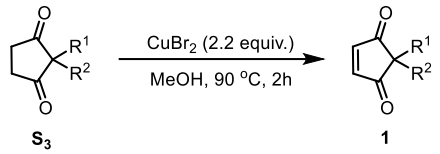
3. Experimental procedures and analytical data:

3a. Preparation of 2,2-disubstituted cyclopentane-1,3-dione (S_3):[2]



2-Alkyl cyclopentane-1,3-dione **S_1** (4.46 mmol, 1.0 equiv) was added to 5.0 mL of 1.0 M aq. $NaHCO_3$ solution (375 mg, 4.46 mmol, 1.0 equiv) in lots and the suspension was stirred at rt until a clear pale coloured solution was obtained. To this mixture was added the alkyl bromide **S_2** (8.93 mmol, 2.0 equiv) and the resulting biphasic solution was stirred vigorously at 80 ^oC overnight. The reaction mixture was cooled and then diluted with 20 mL of EtOAc, organic phase was separated and the aqueous phase was extracted with EtOAc (2 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (9-10% EtOAc in Hexanes) to obtain a colourless crystalline solid **S_3**.

3b. Preparation of 2,2-disubstituted cyclopentene-1,3-dione 1:[2]



To a solution of 2,2-disubstituted cyclopent-4-ene-1,3-dione **S_3** (0.99 mmol) in 20 mL of MeOH was added copper (II) bromide (2.2 mmol) and the resulting brown solution was stirred at 90 °C under nitrogen atmosphere. After 2 h, the reaction mixture was cooled to rt, quenched with 10 mL of distilled water followed by 10 mL of 1.0 M aq. HCl solution, 20 mL of CH_2Cl_2 was added and the organic phase was separated from aqueous phase. Aqueous phase was washed with additional CH_2Cl_2 (2 × 20 mL), combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (2-5% EtOAc in hexanes) to obtain a yellow crystalline solid **1**.

2,2-Dialkyl cyclopentene-1,3-diones **1a**, **1p**, **1j**, **1f**, **1d, 1k** and **1t** were prepared according to a previously reported procedure.[2a]

Compounds **1i**, **1q**, **1o** and **1b** were prepared according to a previously reported procedure.[3]

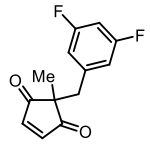
Compounds **1u**, **1v**, **1c** and **1g** were prepared according to a previously reported procedure.[4]

Compounds **1e** were prepared according to a previously reported procedure.[5]

Compound **1w** was prepared according to a previously reported procedure.[6]

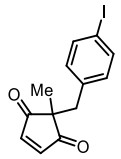
Compound **1x** and **1y** were prepared according to a previously reported procedure.[2b]

2-(3,5-Difluorobenzyl)-2-methylcyclopent-4-ene-1,3-dione (1h):



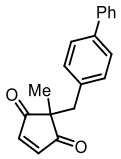
The compound was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.6) to afford an pale yellow solid in 78% yield (155 mg): mp = 80–82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 2H), 6.58 (tt, J = 9.0, 2.3 Hz, 1H), 6.52 – 6.30 (m, 2H), 2.94 (s, 2H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 162.8 (dd, J_{CF} = 249.2, 12.8 Hz), 148.9, 139.4 (t, J_{CF} = 9.1 Hz), 112.9 (dd, J_{CF} = 18.3, 6.7 Hz), 102.8 (t, J_{CF} = 25.2 Hz), 52.2, 40.0, 19.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4 (s, 2F); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}F_2O_2$+, 237.0727; found: 237.0727.

2-(4-Iodobenzyl)-2-methylcyclopent-4-ene-1,3-dione (1l):



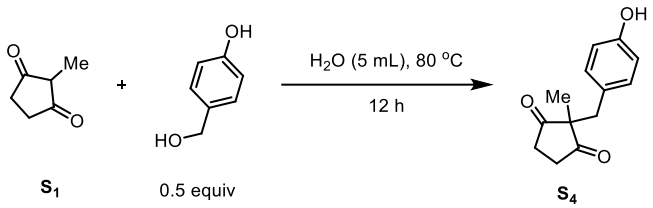
The compound was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.6) to afford a pale yellow solid in 85% yield (169 mg): mp = 104–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.02 (s, 2H), 6.67 (d, J = 8.3 Hz, 2H), 2.92 (s, 2H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 148.9, 137.6, 135.3, 131.8, 92.9, 52.4, 40.1, 19.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}IO_2^+$, 326.9882; found: 326.9900.

2-([1,1'-Biphenyl]-4-ylmethyl)-2-methylcyclopent-4-ene-1,3-dione (1m):



The compound was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.6) to afford an pale yellow solid in 67% yield (133 mg): mp = 78–80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.40 (ddd, J = 7.9, 4.4, 2.2 Hz, 4H), 7.33 – 7.29 (m, 1H), 7.03 – 6.98 (m, 4H), 3.03 (s, 2H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 148.9, 140.5, 139.8, 134.7, 130.2, 128.9, 127.4, 127.1, 127.0, 52.6, 40.5, 19.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_3^+$, 277.1229; found: 277.1233.

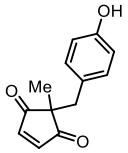
3c. Preparation of 2-(4-hydroxybenzyl)-2-methylcyclopent-4-ene-1,3-dione S_4:[7]



To a suspension of 2-methyl-1,3-cyclopentanedione (500 mg, 4.46 mmol, 1.0 equiv) in water (5 mL) was added *p*-hydroxybenzyl alcohol (277 mg, 2.23 mmol, 0.5 equiv), and the solution was stirred at 80 °C for 12 h. The reaction mixture was extracted with EtOAc (2 x 20 mL) and combined organic solvent was dried over anhydrous Na_2SO_4 and purified via column chromatography (1:1 EtOAc/hexanes as the solvent system) to give 95% of 2-(4-hydroxybenzyl)-2-methyl-1,3-cyclo-pentanedione **S_4**.

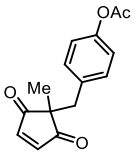
Further, olefination of **S_4** to obtain **1r** was performed via procedure in Section 2b.

2-(4-Hydroxybenzyl)-2-methylcyclopent-4-ene-1,3-dione (1r):



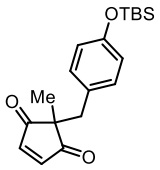
The compound purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an pale yellow solid in 70% yield (138 mg): mp = 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.83 – 6.72 (m, 2H), 6.67 – 6.55 (m, 2H), 5.72 (s, 1H), 2.92 (s, 2H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 154.8, 149.0, 130.9, 127.5, 115.3, 52.8, 40.1, 19.2; HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{13}H_{11}O_3^-$, 215.0703; found: 215.0702.

4-((1-Methyl-2,5-dioxocyclopent-3-en-1-yl)methyl)phenyl acetate (1n):[8]



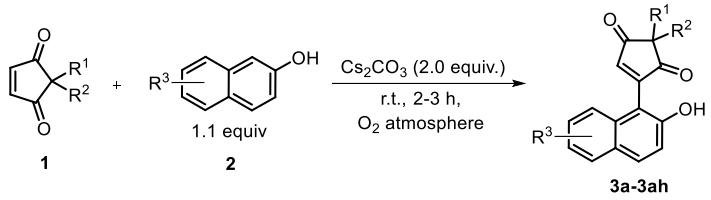
The compound was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.7) to afford an yellow solid in 91% yield (180 mg): mp = 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.95 – 6.65 (m, 4H), 2.96 (s, 2H), 2.23 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 169.3, 149.7, 148.9, 133.2, 130.8, 121.5, 52.5, 40.1, 21.2, 19.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}O_4^+$, 259.0970; found: 259.0978.

2-(4-((*tert*-Butyldimethylsilyl)oxy)benzyl)-2-methylcyclopent-4-ene-1,3-dione (1s):[9]



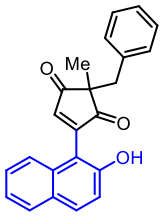
The compound was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.8) to afford an off-white solid in 79% yield (156 mg): mp = 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 2.92 (s, 2H), 1.22 (s, 3H), 0.92 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 154.8, 148.9, 130.8, 128.5, 120.1, 52.9, 40.5, 25.8, 19.2, 18.3, -4.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{27}O_3Si^+$, 331.1730; found: 331.1740.

3d. General Procedure for the Metal-Free formal C(sp^2)-H Arylation 3:



To an oven-dried 10 mL round-bottomed flask changed with 2,2-disubstituted cyclopent-4-ene-1,3-dione **1** (0.40 mmol, 1.0 equiv) and substituted *β*-naphthol **2** (0.44 mmol, 1.1 equiv) in 2.0 mL of dry MeCN (0.2 M) was added Cs_2CO_3 base (260 mg, 0.8 mmol, 2.0 equiv) and the reaction mixture was stirred for 2-3 h at room temperature under oxygen atmosphere. After judging by TLC, the reaction was quenched/diluted with 5 mL of distilled water. The aqueous phase was then washed with 10 mL EtOAc, and 5 mL brine and was washed with additional EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (12-16% EtOAc/Hexanes) to obtain the desired arylation product **3**.

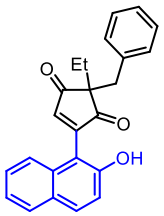
2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3a):



The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 86% yield (118 mg): mp = 164–166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.16 (m, 4H), 7.13 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.51

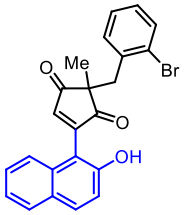
(d, J = 8.2 Hz, 1H), 3.17 (dd, J = 29.7, 13.1 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 205.0, 158.0, 152.3, 149.2, 135.9, 133.0, 132.2, 130.0, 129.3, 128.9, 128.4, 127.6, 127.5, 124.1, 123.7, 119.3, 110.4, 54.2, 42.0, 19.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}O_3^+$, 343.1334; found: 343.1336.

2-Benzyl-2-ethyl-4-(2-hydroxynaphthalen-1-yl)cyclopent-4-ene-1,3-dione (3b):



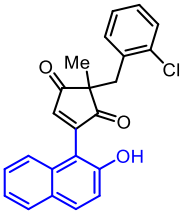
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 91% yield (133 mg): mp = 146–148°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.29 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.22 – 7.16 (m, 5H), 7.07 (d, J = 8.9 Hz, 1H), 7.02 (dt, J = 3.7, 2.3 Hz, 2H), 6.89 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 3.14 (dd, J = 33.8, 13.0 Hz, 2H), 2.07 – 2.00 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 205.6, 159.8, 152.1, 150.7, 135.8, 132.7, 132.2, 130.0, 129.2, 128.9, 128.3, 127.4, 124.0, 123.7, 119.0, 110.5, 59.2, 41.3, 28.0, 9.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_3^+$, 357.1491; found: 357.1482.

2-(2-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3c):



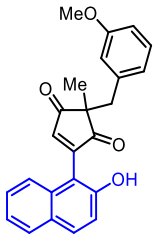
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 83% yield (140 mg): mp = 166–168°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 12.5, 5.1 Hz, 2H), 7.66 (s, 1H), 7.51 – 7.47 (m, 1H), 7.36 – 7.24 (m, 3H), 7.21 – 7.13 (m, 2H), 7.11 – 7.04 (m, 2H), 6.92 (d, J = 8.4 Hz, 1H), 3.40 (dd, J = 35.1, 7.8 Hz, 2H), 1.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.0, 203.8, 157.6, 152.5, 148.3, 135.3, 133.5, 132.8, 132.1, 131.7, 129.0, 128.9, 128.3, 127.4, 127.3, 125.2, 123.8, 123.3, 119.2, 110.2, 53.0, 40.6, 19.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrO_3^+$, 421.0439; found: 421.0441.

2-(2-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3d):



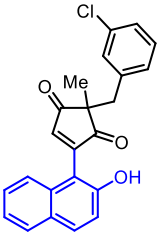
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a red solid in 76% yield (115 mg): mp = 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.63 (s, 1H), 7.37 – 7.27 (m, 3H), 7.26 (s, 1H), 7.19 – 7.12 (m, 3H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 3.37 (dd, *J* = 25.3, 13.6 Hz, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 204.1, 157.8, 152.7, 148.6, 134.7, 133.7, 133.06, 132.27, 132.2, 130.4, 129.2, 128.9, 128.6, 127.5, 127.1, 124.1, 123.5, 119.4, 110.4, 53.3, 38.5, 19.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClO_3^+$, 377.0945; found: 377.0943.

4-(2-Hydroxynaphthalen-1-yl)-2-(3-methoxybenzyl)-2-methylcyclopent-4-ene-1,3-dione (3e):



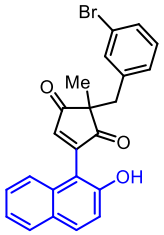
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a red solid in 81% yield (121 mg): mp = 168–170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 15.7, 8.4 Hz, 2H), 7.30 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.23 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.16 (s, 1H), 7.13 – 7.08 (m, 2H), 6.76 – 6.71 (m, 1H), 6.62 – 6.57 (m, 2H), 6.57 – 6.52 (m, 1H), 3.60 (s, 3H), 3.14 (dd, *J* = 26.6, 13.0 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 204.9, 159.9, 157.9, 152.4, 149.2, 137.4, 133.0, 132.3, 130.0, 129.3, 128.4, 127.5, 124.1, 123.7, 122.2, 119.4, 115.2, 113.4, 110.4, 55.2, 54.1, 42.2, 19.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_4^+$, 373.1440; found: 373.1430.

2-(3-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3f):



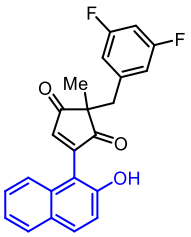
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 77% yield (116 mg): mp = 146–148°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 8.7, 3.3 Hz, 1H), 7.36 – 7.16 (m, 5H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 6.99 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 1H), 3.12 (dd, *J* = 32.1, 13.2 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 205.1, 158.3, 152.1, 148.8, 137.9, 134.6, 132.7, 132.0, 131.0, 129.9, 129.0, 128.4, 128.2, 127.7, 127.6, 124.1, 123.2, 118.7, 110.1, 53.6, 41.0, 20.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClO_3^+$, 377.0945; found: 377.0941.

2-(3-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3g):



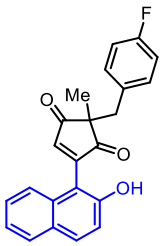
The compound purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 75% yield (126 mg): mp = 174–176°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.36 – 7.27 (m, 3H), 7.22 (t, *J* = 1.8 Hz, 1H), 7.20 (s, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.67 (d, *J* = 7.8 Hz, 1H), 3.12 (dd, *J* = 25.9, 13.1 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 204.7, 158.1, 152.3, 148.9, 138.2, 133.0, 132.7, 132.2, 130.7, 130.4, 129.2, 128.7, 128.5, 127.7, 124.2, 123.4, 122.9, 119.1, 110.3, 53.8, 41.1, 19.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrO_3^+$, 421.0439; found: 421.0433.

2-(3,5-Difluorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3h):



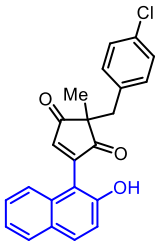
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a red solid in 89% yield (134 mg): mp = 172–174°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 (s, 1H), 7.08 – 7.00 (m, 1H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.69 – 6.56 (m, 3H), 3.12 (dd, *J* = 23.4, 13.2 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.3, 204.7, 163.0 (dd, J_{CF} = 249.7, 12.8 Hz), 158.2, 152.1, 148.6, 139.6 (t, J_{CF} = 9.0 Hz), 132.9, 132.1, 129.2, 128.6, 127.6, 124.2, 123.1, 118.6, 113.1 (dd, J_{CF}= 19.3, 5.9 Hz), 110.1, 103.0 (t, J_{CF} = 25.1 Hz), 53.4, 40.7, 20.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.97 (s, 2F); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}F_2O_3^+$, 379.1146; found: 379.1139.

2-(4-Fluorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3i):



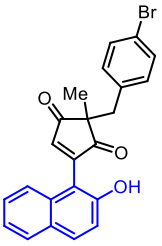
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 85% yield (123 mg): mp = 164–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.28 – 7.22 (m, 1H), 7.15 (s, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.91 – 6.83 (m, 2H), 6.52 (d, *J* = 8.3 Hz, 1H), 3.13 (dd, *J* = 25.4, 13.3 Hz, 2H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 205.0, 162.3 (d, J_{CF} = 246.1 Hz), 158.3, 152.2, 149.0, 132.9, 132.1, 131.7 (d, J_{CF} = 2.8 Hz), 131.5 (d, J_{CF} = 7.9 Hz), 129.2, 128.5, 127.5, 124.2, 123.3, 119.1, 115.7 (d, J_{CF} = 21.3 Hz), 110.3, 53.9, 40.8, 19.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.02 (s, 1F); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}FO_3^+$, 361.1240; found: 361.1242.

2-(4-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3j):



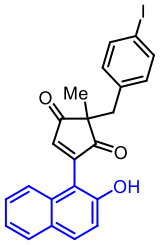
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 81% yield (122 mg): mp = 154–156°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.35 – 7.28 (m, 2H), 7.18 – 7.13 (m, 3H), 7.10 (s, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.47 (d, *J* = 7.6 Hz, 1H), 3.12 (dd, *J* = 26.5, 13.2 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 205.0, 158.3, 152.2, 149.0, 134.4, 133.5, 132.9, 132.1, 131.2, 129.2, 129.1, 128.5, 127.7, 124.2, 123.2, 119.0, 110.3, 53.9, 41.0, 19.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClO_3^+$, 377.0945; found: 377.0942.

2-(4-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3k):



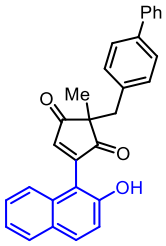
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 77% yield (130 mg): mp = 183–185°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.37 – 7.28 (m, 4H), 7.15 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.04 (s, 1H), 6.92 – 6.87 (m, 2H), 6.53 – 6.46 (m, 1H), 3.11 (dd, *J* = 21.0, 13.1 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 204.8, 158.3, 152.2, 149.1, 134.9, 133.0, 132.0, 132.0, 131.6, 129.3, 128.5, 127.8, 124.3, 123.2, 121.7, 119.1, 110.4, 53.8, 41.1, 19.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrO_3^+$, 421.0439; found: 421.0430.

4-(2-Hydroxynaphthalen-1-yl)-2-(4-iodobenzyl)-2-methylcyclopent-4-ene-1,3-dione (3l):



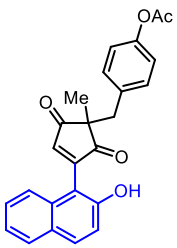
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 92% yield (172 mg): mp = 180–182°C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.10 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.14 (m, 5H), 6.85 (d, *J* = 8.3 Hz, 2H), 3.03 (dd, *J* = 38.4, 13.2 Hz, 2H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 206.6, 205.3, 159.5, 153.1, 148.6, 138.2, 137.9, 137.0, 133.1, 132.0, 129.0, 128.9, 127.7, 124.2, 123.9, 118.4, 110.9, 92.9, 52.9, 40.6, 20.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}IO_3^+$, 469.0301; found: 469.0299.

2-([1,1'-Biphenyl]-4-ylmethyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3m):



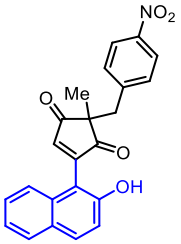
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 86% yield (144 mg): mp = 176–178°C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.99 (s, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.10 (dd, *J* = 12.3, 7.9 Hz, 4H), 6.93 (s, 1H), 3.08 (dd, *J* = 40.1, 13.1 Hz, 2H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 206.6, 205.6, 159.6, 153.2, 148.8, 141.3, 140.4, 136.5, 133.0, 132.1, 131.5, 129.7, 129.1, 128.9, 128.2, 127.6, 127.5, 124.4, 123.9, 118.5, 111.2, 53.2, 41.1, 20.5 HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}O_3^+$, 419.1647; found: 419.1646.

4-((3-(2-Hydroxynaphthalen-1-yl)-1-methyl-2,5-dioxocyclopent-3-en-1-yl)methyl)phenyl acetate (3n):



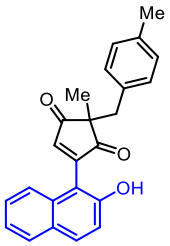
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford an orange solid in 78% yield (125 mg): mp = 166–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.38 – 7.28 (m, 2H), 7.16 (s, 1H), 6.99 (dd, *J* = 8.6, 5.5 Hz, 4H), 6.94 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.11 (dd, *J* = 72.6, 13.0 Hz, 2H), 2.32 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 206.2, 171.6, 158.4, 151.9, 149.8, 149.1, 134.2, 132.1, 131.2, 128.7, 128.4, 127.2, 124.1, 123.8, 121.8, 118.4, 110.7, 53.6, 41.4, 21.4, 19.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}O_5^+$, 401.1389; found: 401.1378.

4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(4-nitrobenzyl)cyclopent-4-ene-1,3-dione (3o):



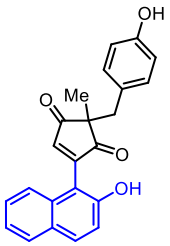
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.2) to afford an orange solid in 93% yield (144 mg): mp = 173–175°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.72 (dd, *J* = 8.4, 4.1 Hz, 2H), 7.30 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.25 – 7.13 (m, 4H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.88 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 3.24 (dd, *J* = 21.8, 13.0 Hz, 2H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 205.0, 158.7, 152.4, 148.7, 147.7, 143.8, 133.1, 132.2, 131.4, 129.3, 129.0, 127.7, 124.5, 124.2, 123.1, 118.9, 110.2, 53.7, 41.0, 20.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}NO_5^+$, 388.1185; found: 388.1174.

4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(4-methylbenzyl)cyclopent-4-ene-1,3-dione (3q):



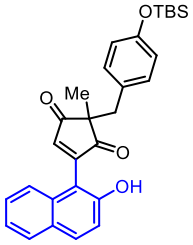
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 73% yield (104 mg): mp = 172–174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.30 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 7.25 (s, 1H), 7.18 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.13 (s, 1H), 7.10 (dd, *J* = 8.9, 1.4 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 1H), 3.13 (dd, *J* = 27.1, 13.1 Hz, 2H), 2.25 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 205.1, 158.0, 152.5, 149.3, 137.2, 133.0, 132.8, 132.3, 129.6, 129.3, 128.4, 127.2, 124.1, 123.7, 119.4, 110.5, 54.3, 41.8, 21.2, 19.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_3^+$, 357.1491; found: 357.1472.

2-(4-Hydroxybenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3r):



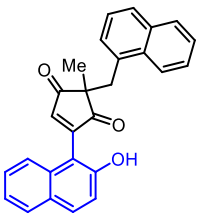
The compound was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.5) to afford a yellow solid in 83% yield (119 mg): mp = 210–212 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.78 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.30 – 7.08 (m, 5H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.20 (s, 1H), 3.01 (dd, *J* = 52.6, 13.3 Hz, 2H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 208.3, 207.4, 157.8, 149.6, 133.3, 132.3, 132.2, 129.4, 128.9, 128.2, 127.8, 124.8, 124.2, 118.3, 116.3, 111.1, 79.4, 54.1, 41.4, 20.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}O_4^+$, 359.1283; found: 359.1272.

2-(4-((*tert*-Butyldimethylsilyl)oxy)benzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3s):



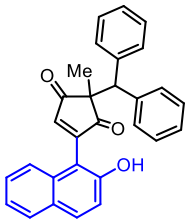
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford an orange solid in 52% yield (98 mg): mp = 138–140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.33 – 7.27 (m, 2H), 7.17 (s, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 7.02 (s, 1H), 6.89 – 6.84 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.66 – 6.61 (m, 2H), 3.10 (dd, *J* = 25.7, 13.2 Hz, 2H), 1.44 (s, 3H), 0.94 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 205.1, 158.0, 155.2, 152.5, 149.4, 133.1, 132.3, 130.8, 129.4, 128.4, 127.7, 124.15, 123.7, 120.4, 119.8, 110.6, 54.3, 41.4, 25.7, 19.5, 18.2, -4.4, -4.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{33}O_4Si^+$, 473.2148; found: 473.2141.

4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(naphthalen-1-ylmethyl)cyclopent-4-ene-1,3-dione (3t):



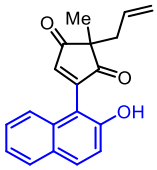
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a red solid in 72% yield (113 mg): mp = 156–158°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.76 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.67 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.45 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.25 – 7.17 (m, 3H), 7.00 – 6.94 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 5.99 (d, *J* = 8.5 Hz, 1H), 3.71 (dd, *J* = 40.9, 13.8 Hz, 2H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 205.0, 157.9, 152.3, 149.1, 134.3, 132.8, 132.3, 132.0, 131.7, 129.0, 128.8, 128.4, 128.2, 127.2, 126.5, 126.0, 125.4, 124.8, 123.9, 123.3, 119.2, 110.1, 54.4, 38.3, 19.8 HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}O_3^+$, 393.1491; found: 393.1476.

2-Benzhydryl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3u):



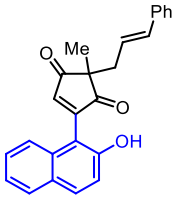
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 84% yield (141 mg): mp = 164–166°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 16.1, 8.4 Hz, 2H), 7.50 (dd, *J* = 20.6, 7.8 Hz, 4H), 7.34 – 7.18 (m, 8H), 7.18 (s, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 7.04 (s, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 4.52 (s, 1H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 205.2, 157.7, 152.4, 149.2, 139.7, 133.0, 132.3, 129.8, 129.7, 128.9, 128.4, 127.5, 127.4, 124.2, 123.8, 119.3, 110.4, 58.2, 56.6, 19.4 HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}O_3^+$, 419.1647; found: 419.1623.

2-Allyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3v):



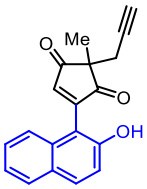
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a brown semi-solid in 72% yield (84 mg): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.45 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.41 (s, 1H), 7.40 – 7.35 (m, 2H), 7.10 (d, *J* = 8.9 Hz, 1H), 5.69 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.16 – 5.08 (m, 2H), 2.61 – 2.53 (m, 2H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 205.2, 157.4, 152.5, 148.0, 132.8, 132.3, 131.8, 129.2, 128.7, 127.6, 124.1, 123.4, 120.0, 119.0, 110.4, 51.9, 39.4, 19.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}O_3^+$, 293.1178; found: 293.1177.

2-Cinnamyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3w):



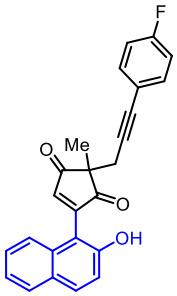
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a yellow solid in 80% yield (104 mg): mp = 150–152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.38 (s, 1H), 7.32 – 7.17 (m, 6H), 7.14 – 7.07 (m, 2H), 7.03 (s, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.6, 7.7 Hz, 1H), 2.73 (d, *J* = 7.7 Hz, 2H), 1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 205.3, 157.7, 152.4, 148.4, 136.6, 135.0, 132.9, 132.3, 129.3, 128.7, 127.8, 127.7, 126.5, 124.2, 123.6, 123.0, 119.1, 110.6, 52.5, 39.0, 19.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{20}O_3^+$, 369.1491; found: 369.1482.

4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(prop-2-yn-1-yl)cyclopent-4-ene-1,3-dione (3x):



The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a yellow semi-solid in 79% yield (135 mg): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.72 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.53 (s, 1H), 7.50 – 7.42 (m, 1H), 7.42 – 7.34 (m, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.03 (s, 1H), 2.77 – 2.64 (m, 2H), 2.06 (t, *J* = 2.7 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 203.6, 157.5, 152.5, 148.6, 133.0, 132.3, 129.3, 128.7, 127.6, 124.2, 123.7, 119.1, 110.3, 79.0, 72.4, 50.7, 24.1, 18.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{14}O_3^+$, 291.1021; found: 291.1018.

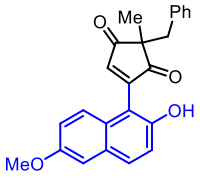
2-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3y):



The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a yellow solid in 85% yield (108 mg): mp = 166–168°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.59 (d, *J* = 8.5 Hz,

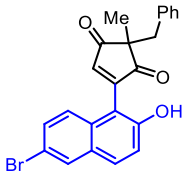
1H), 7.51 (s, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.18 – 7.00 (m, 3H), 6.96 – 6.80 (m, 2H), 2.92 (dd, *J* = 36.6, 16.4 Hz, 2H),1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.1, 204.0, 162.4 (d, *J* = 249.4 Hz), 157.7, 152.4, 148.5, 133.7 (d, *J* = 8.4 Hz), 133.0, 132.2, 129.2, 128.6, 127.5, 124.1, 123.6, 119.0, 115.4 (d, *J* = 22.0 Hz), 110.4, 83.9, 83.2, 51.0, 25.1, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.92 (s, 1F); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{17}FO_3^+$, 385.1240; found: 385.1236.

2-Benzyl-4-(2-hydroxy-6-methoxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3aa):



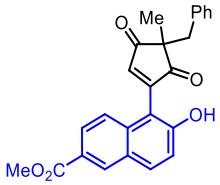
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 78% yield (116 mg): mp = 148–150°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.9 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.10 (s, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 7.05 – 6.97 (m, 3H), 6.85 (dd, *J* = 9.3, 2.5 Hz, 2H), 6.34 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 3H), 3.15 (dd, *J* = 30.5, 13.1 Hz, 2H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 204.9, 158.1, 156.2, 150.5, 148.9, 135.8, 131.5, 130.3, 129.7, 128.8, 127.4, 127.2, 125.2, 119.7, 119.6, 110.8, 106.6, 55.4, 54.0, 41.9, 19.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_4^+$, 373.1439; found: 373.1428.

2-Benzyl-4-(6-bromo-2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3ab):



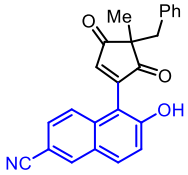
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 72% yield (121 mg): mp = 170–172°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.10 (d, *J* = 8.9 Hz, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 7.01 (dt, *J* = 3.6, 2.1 Hz, 2H), 6.24 (d, *J* = 8.8 Hz, 1H), 3.16 (dd, *J* = 34.8, 13.1 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 204.8, 157.5, 152.5, 149.3, 135.9, 131.8, 130.8, 130.6, 130.4, 130.3, 129.8, 129.0, 127.6, 125.5, 120.5, 117.9, 110.7, 54.2, 42.1, 19.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrO_3^+$, 421.0439; found: 421.0441.

Methyl 5-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-6-hydroxy-2-naphthoate (3ac):



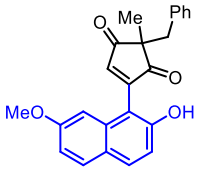
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford an orange solid in 86% yield (138 mg): mp = 176–178°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.7 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.74 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.34 (s, 1H), 7.24 – 7.17 (m, 3H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.12 (s, 1H), 7.01 (dd, *J* = 8.0, 1.4 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 1H), 3.96 (s, 3H), 3.17 (dd, *J* = 29.5, 13.0 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 205.1, 167.4, 157.8, 154.6, 149.7, 136.2, 135.1, 134.5, 131.6, 130.1, 129.3, 128.0, 128.0, 127.2, 126.0, 124.3, 120.5, 110.9, 54.6, 52.7, 42.4, 19.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}O_5^+$, 401.1389; found: 401.1385.

5-(4-Benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-6-hydroxy-2-naphthonitrile (3ad):



The compound purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a yellow solid in 61% yield (90 mg): mp = 166–168°C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.31 (s, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.44 – 7.23 (m, 7H), 7.07 – 7.02 (m, 2H), 3.09 (dd, *J* = 50.7, 13.1 Hz, 2H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 206.4, 205.3, 158.2, 155.9, 149.2, 137.09, 134.9, 134.5, 132.7, 130.8, 129.3, 128.0, 127.9, 127.8, 125.9, 120.2, 119.6, 111.5, 107.1, 53.2, 41.4, 20.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}NO_3^+$, 368.1287; found: 368.1285.

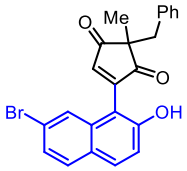
2-Benzyl-4-(2-hydroxy-7-methoxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3ae):



The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 75% yield (112 mg): mp = 154–156°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.20 – 7.13 (m, 3H), 7.07 – 7.01 (m, 2H), 6.97 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.28 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 3H), 3.24 – 3.08 (m, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 205.1, 159.2, 158.2, 153.2,

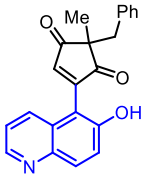
148.3, 135.9, 133.8, 132.9, 130.2, 129.9, 128.8, 127.5, 124.7, 116.8, 115.7, 109.5, 103.7, 55.5, 53.8, 41.4, 20.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_4^+$, 373.1440; found: 373.1429.

2-Benzyl-4-(7-bromo-2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3af):



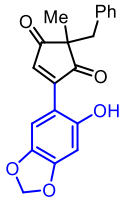
The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid in 67% yield (113 mg): mp = 173–175°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.60 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.28 – 7.18 (m, 2H), 7.13 (s, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.69 (s, 1H), 3.17 (dd, *J* = 31.2, 13.1 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 204.3, 157.1, 153.2, 148.9, 135.2, 133.2, 132.7, 129.7, 129.2, 128.8, 127.9, 127.5, 127.4, 125.1, 122.1, 119.7, 109.4, 54.0, 41.9, 19.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrO_3^+$, 421.0439; found: 421.0440.

2-Benzyl-4-(6-hydroxyquinolin-5-yl)-2-methylcyclopent-4-ene-1,3-dione (3ag):



The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid in 52% yield (71 mg): mp = 180–182°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.3, 1.5 Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.23 – 7.09 (m, 6H), 7.04 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 1H), 3.14 (dd, *J* = 49.4, 13.1 Hz, 2H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.6, 206.0, 157.5, 154.3, 148.6, 146.2, 141.9, 136.3, 133.5, 131.3, 130.2, 128.8, 128.0, 127.2, 122.9, 121.7, 110.2, 53.5, 41.5, 19.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO_3^+$, 344.1287; found: 344.1280.

2-Benzyl-4-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-methylcyclopent-4-ene-1,3-dione (3ai):

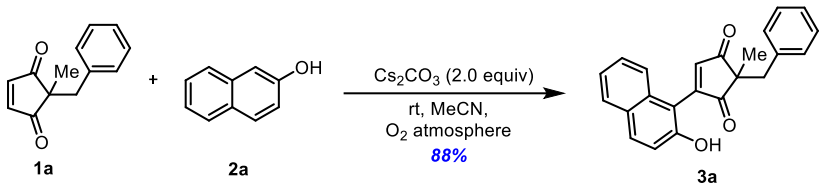


The compound was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown semi-solid in 65% yield (87 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.17 – 7.07 (m, 3H), 6.99 –

6.88 (m, 3H), 6.57 (s, 1H), 6.43 (s, 1H), 5.95 (s, 2H), 3.07 (dd, *J* = 29.18, 13.25 Hz, 2H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 203.2, 158.4, 154.4, 153.4, 142.6, 141.3, 135.4, 129.68, 128.6, 127.4, 107.7, 106.9, 102.3, 100.5, 54.99, 41.9, 19.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}O_5^+$, 337.1076; found: 337.1074.

3e. Gram-scale Synthesis and Synthetic utility :

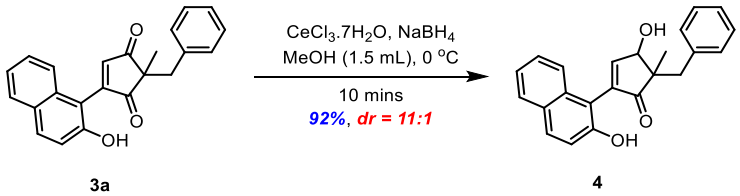
Gram-scale Synthesis of 3a



An oven-dried 10 mL round-bottomed flask charged with 2-benzyl-2-methyl cyclopent-4-enedione **1a** (1.00 g, 4.99 mmol, 1.0 equiv) and *β*-Naphthol **2a** (0.79 g, 5.49 mmol, 1.1 equiv) in 20 mL of dry MeCN was added Cs_2CO_3 base (3.25 g, 9.98 mmol, 2.0 equiv) and the reaction mixture was stirred for 3 h at room temperature under oxygen atmosphere. The reaction was then quenched/diluted with 15 mL of distilled water. The aqueous phase was then washed with 20 mL EtOAc, and 10 mL brine and was washed with additional EtOAc (2 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (12% EtOAc/Hexanes as the solvent system) to obtain a yellow crystalline solid **3a** in 88% yield (1.50 g).

Regioselective Luche Reduction:[4]

5-Benzyl-4-hydroxy-2-(2-hydroxynaphthalen-1-yl)-5-methylcyclopent-2-en-1-one (4):

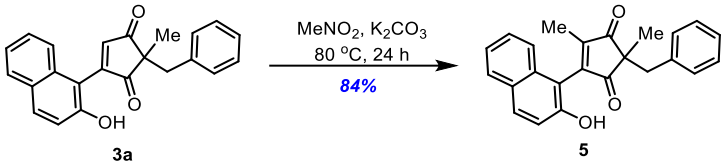


In an oven dried 10 mL round-bottom flask, **3a** (51 mg, 0.15 mmol, 1.0 equiv.) and $CeCl_3.7H_2O$ (112 mg, 0.30 mmol, 2.0 equiv.) was taken in 2.0 mL of absolute methanol under argon and the resulting solution was cooled to 0 °C. To this was added $NaBH_4$ (5.7 mg, 0.15 mmol, 1.0 equiv.) at once and the resulting mixture was stirred at 0 °C. After 10 min, reaction mixture was quenched with 2 mL of sat. NH_4Cl solution and diluted with 5 mL CH_2Cl_2 and extracted with additional CH_2Cl_2 (2 × 5 mL). Combined organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture (with *dr* = 11:1, as obtained from ^{1}H-NMR) was purified by

silica-gel flash column chromatography (20% EtOAc/hexanes; R_f = 0.2) to obtain the major diastereomer as an orange semi-solid **4** in 92% yield (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.16 – 7.07 (m, 6H), 7.04 (d, *J* = 8.9 Hz, 1H), 4.70 (d, *J* = 2.3 Hz, 1H), 3.03 (s, 2H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.6, 162.8, 152.5, 141.3, 137.4, 132.8, 131.1, 130.7, 129.5, 128.6, 128.4, 127.0, 126.9, 123.8, 123.7, 120.0, 111.7, 78.8, 56.4, 41.1, 22.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}O_3^+$, 345.1491; found: 345.1479.

Formal C(sp^2)-H Alkylation:[2b]

2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2,5-dimethylcyclopent-4-ene-1,3-dione (5):

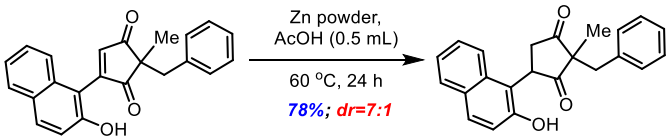


3a **5**

To a clean pressure tube charged with **3a** (21 mg, 0.06 mmol, 1.0 equiv) and K_2CO_3 (17 mg, 0.12 mmol, 2.0 equiv) was added 1.0 mL of CH_3NO_2. The tube was flushed with argon and stirred at 80 °C in a pre-heated oil bath for 24 h. The pressure tube was cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by silica-gel column chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford **5** in 84% yield (72 mg) to afford a yellow solid; mp = 200–202°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.9 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.13 – 7.04 (m, 2H), 7.03 – 6.97 (m, 2H), 3.14 (dd, *J* = 40.1, 13.0 Hz, 2H), 1.64 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 208.4, 206.4, 159.8, 155.9, 153.5, 137.8, 133.0, 132.0, 131.1, 129.65, 129.1, 128.3, 127.8, 124.8, 124.1, 118.4, 110.5, 79.5, 53.4, 42.1, 20.6, 10.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_3^+$, 357.1491; found: 357.1492.

Conjugate Bond Reduction:[4]

2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopentane-1,3-dione (3a′):



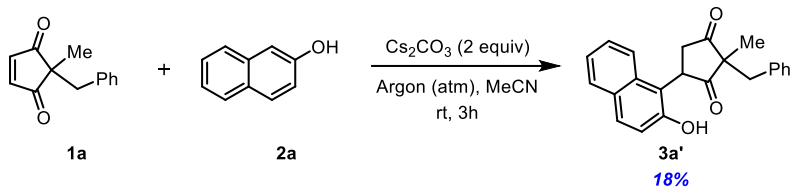
3a **3a'**

In an oven dried reaction vial, arylated compound **3a** (17.1 mg, 0.05 mmol) was added followed by Zn powder (19.6 mg, 0.3 mmol). Then, contents were dissolved in 1 mL of acetic acid and the reaction mixture was stirred at 60 °C in a pre-heated oil bath for 24 h in argon atmosphere. After complete consumption of **3a**, the reaction mixture was filtered, washed with EtOAc, and concentrated *in vacuo*. The crude product obtained was purified with flash silica-gel column chromatography (20% EtOAc in Hexanes; R_f = 0.5) to obtain **3a′** (as mixture of inseparable

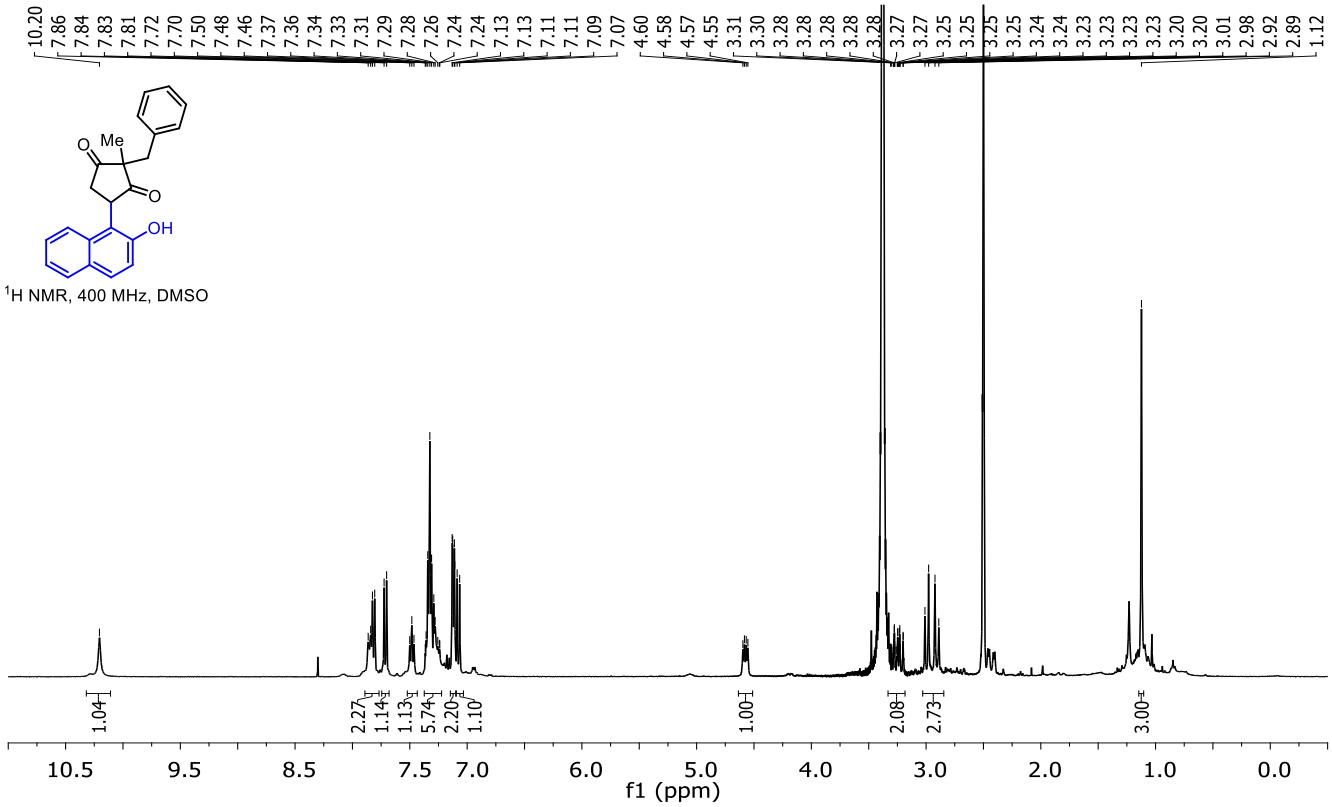
isomers with *dr* = 7:1 as determined by ^{1}H NMR spectroscopy) in 78% yield (13.4 mg) as colorless semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 5.6, 2.4 Hz, 5H), 7.54 – 7.47 (m, 2H), 7.43 – 7.37 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.26 (q, *J* = 12.6 Hz, 2H), 2.84 (qd, *J* = 19.4, 9.5 Hz, 2H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD) δ 219.4, 219.2, 150.4, 135.3, 132.9, 130.1, 129.3, 128.6, 128.3, 128.2, 127.2, 126.3, 122.3, 120.7, 118.8, 116.8, 59.0, 45.0, 44.8, 43.1, 18.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}O_3^+$, 345.1491; found: 345.1489.

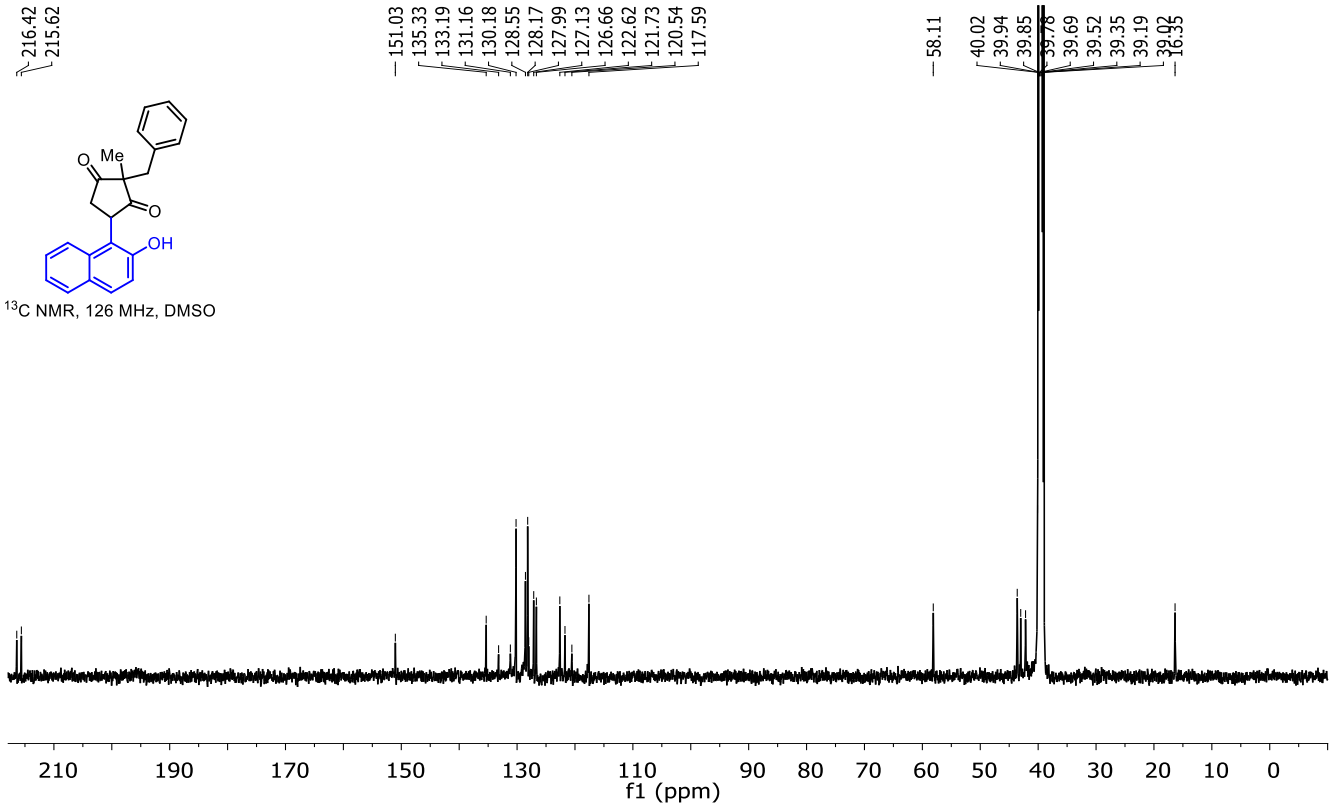
4. Mechanistic studies:

4a. Isolation of Michael Addition Intermediate 3a':

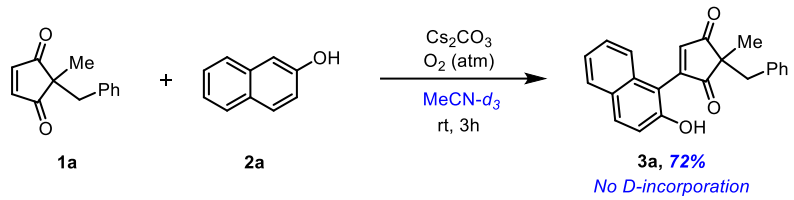


To an oven-dried 10 mL round-bottomed flask charged with 2,2-disubstituted cyclopent-4-ene-1,3-dione **1** (80.0 mg, 0.40 mmol, 1.0 equiv) and substituted *β*-naphthol **2** (63.4 mg, 0.44 mmol, 1.1 equiv) in 2.0 mL of dry MeCN (0.2 M). To this was added Cs_2CO_3 base (260 mg, 0.8 mmol, 2.0 equiv) and the reaction mixture was stirred for 3 h at room temperature under argon atmosphere. The reaction was then quenched/diluted with 5 mL of distilled water. The aqueous phase was then washed with 10 mL EtOAc, and 5 mL brine and was washed with additional EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (12% EtOAc/Hexanes) to obtain the desired Michael addition intermediate product **3a'** in 18% yield (25 mg) as colourless semi-solid; ^{1}H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.83 (dd, *J* = 14.5, 8.3 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.22 (m, 5H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 4.58 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.33 – 3.18 (m, 2H), 2.95 (dd, *J* = 35.3, 13.1 Hz, 2H), 1.12 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 216.4, 215.6, 151.0, 135.3, 133.2, 131.2, 130.2, 128.6, 128.2, 128.0, 127.1, 126.7, 122.6, 121.7, 120.5, 117.6, 58.1, 43.6, 43.0, 42.2, 16.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}O_3^+$, 345.1491; found: 345.1489.

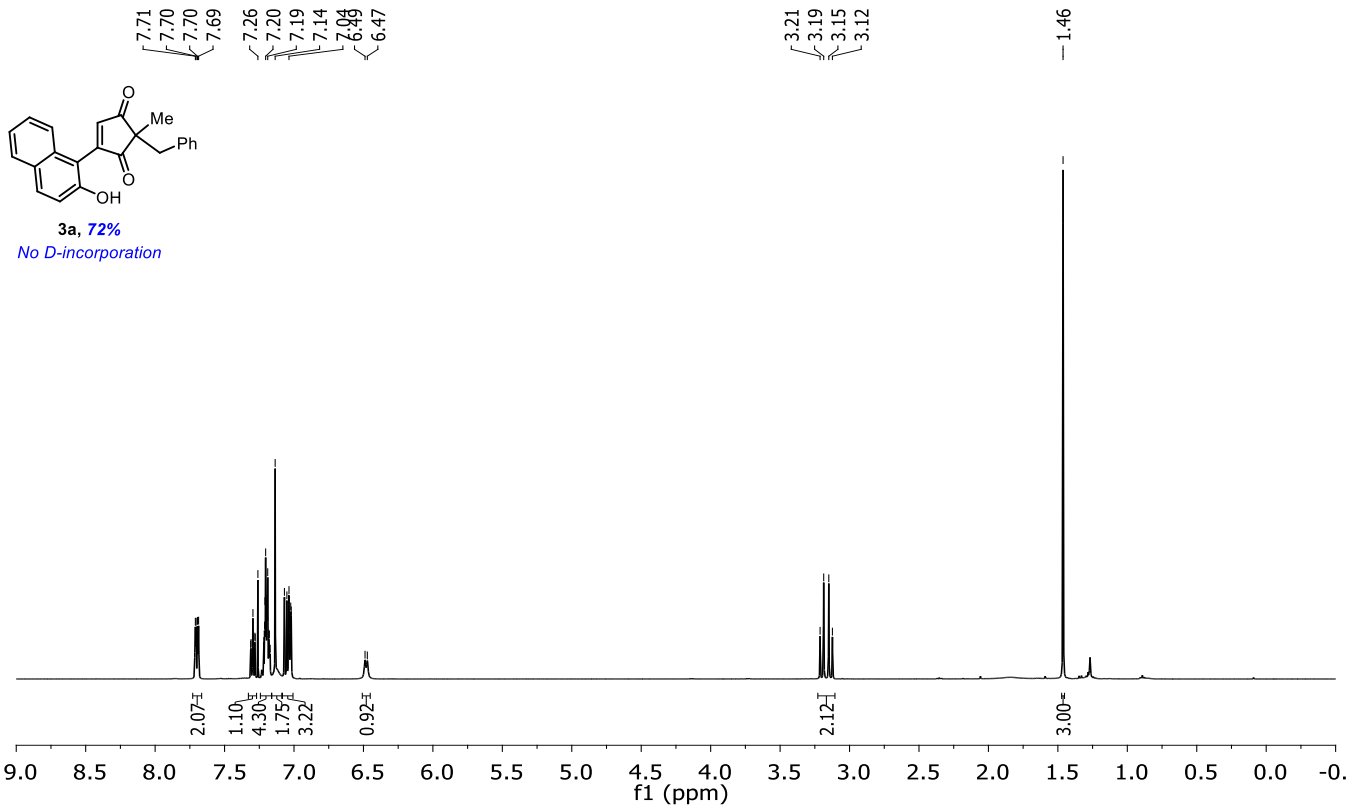

Me
O
O
OH
1H NMR, 400 MHz, DMSO
f1 (ppm)


Me
O
O
OH
13C NMR, 126 MHz, DMSO
f1 (ppm)

4b. Reaction in MeCN-d_3:

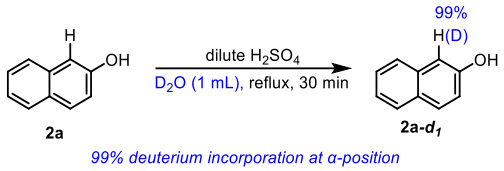


An oven-dried 10 mL round-bottomed flask charged with 2-benzyl-2-methyl cyclopent-4-enedione **1a** (30 mg, 0.15 mmol, 1.0 equiv) and *β*-Naphthol **2a** (24 mg, 0.17 mmol, 1.1 equiv) in 2 mL of dry MeCN-d_3 was added Cs_2CO_3 base (98 mg, 0.3 mmol, 2.0 equiv) and the reaction mixture was stirred for 3 h at room temperature under oxygen atmosphere. The reaction was then quenched/diluted with 5 mL of distilled water. The aqueous phase was then washed with 10 mL EtOAc, and 5 mL brine and was washed with additional EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (12% EtOAc/Hexanes as the solvent system) to obtain a yellow crystalline solid **3a** in 72% yield with 0% deuterium incorporation, as estimated ^{1}H NMR spectroscopy.

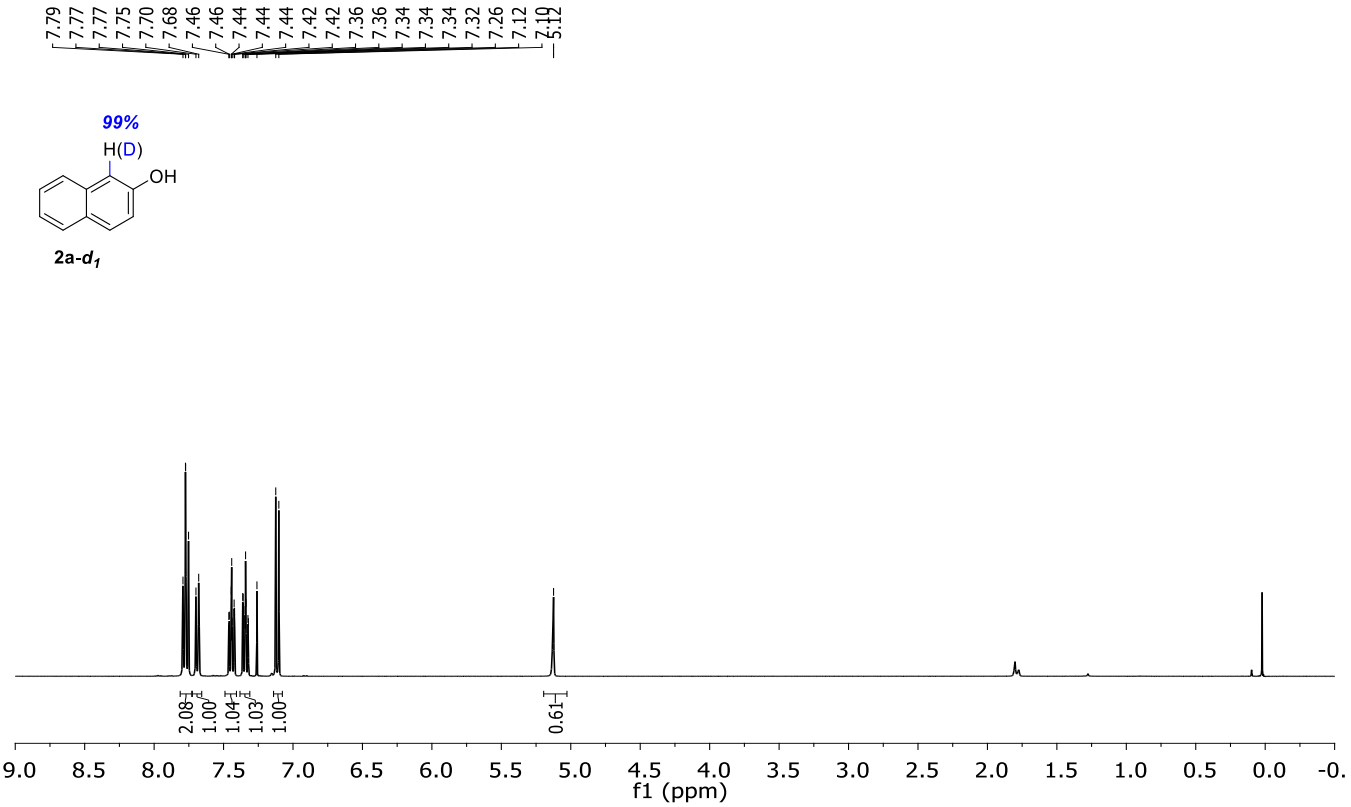


4c. Reaction with 2a-d_1:

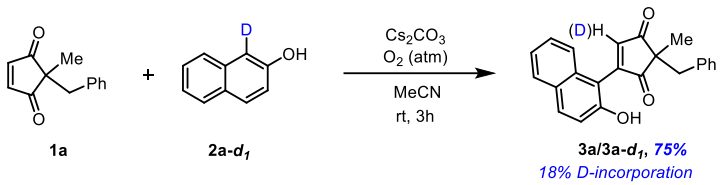
Preparation of 2a-d_1:[10]



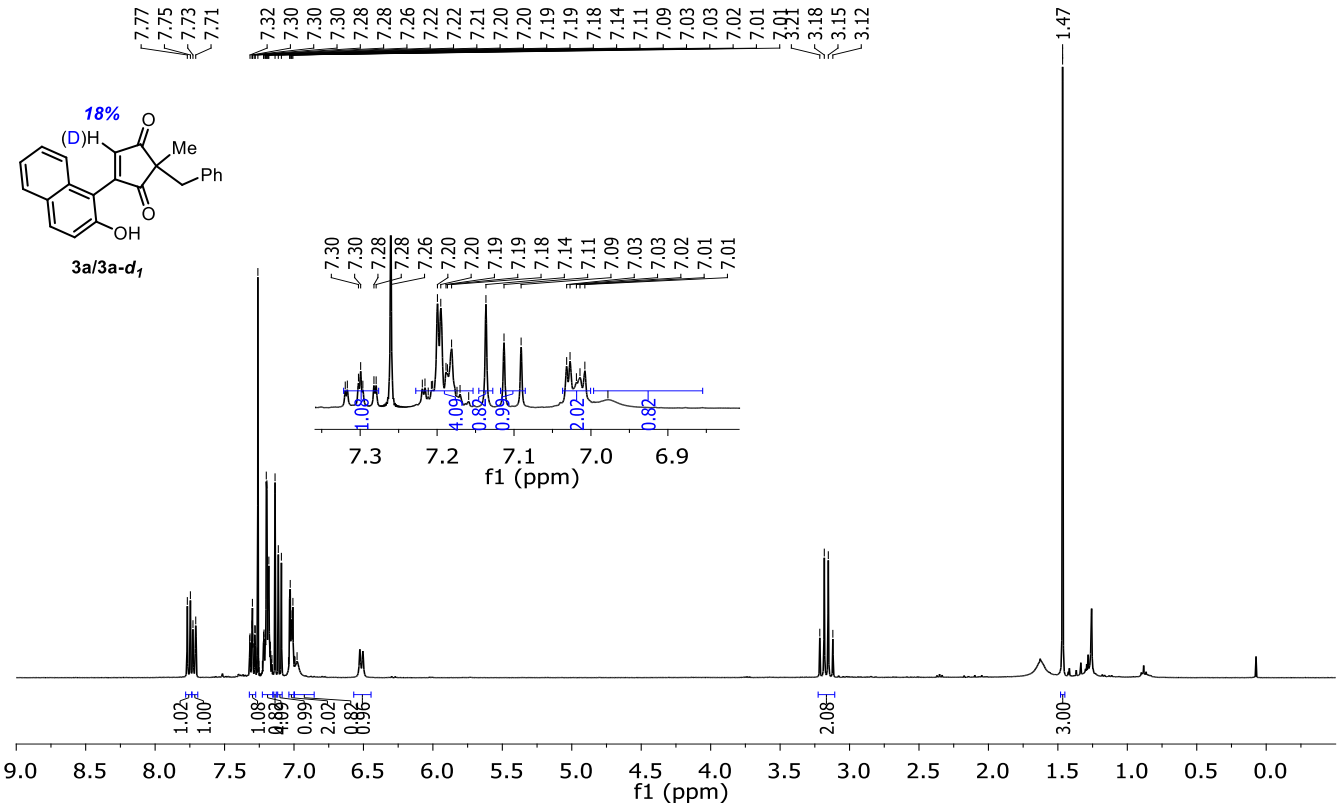
A solution of β-Naphthol **2a** (60 mg, 0.42 mmol) in D_2O (1 mL) containing H_2SO_4 (20 µL) was refluxed for 30 min and then cooled to room temperature. The reaction mixture was diluted with 3 mL of CH_2Cl_2 and organic layer was separated and dried over anhydrous Na_2SO_4 and solvent was removed *in vacuo*. The obtained sample was analyzed with ^{1}H NMR and deuterium incorporation was observed to be 99% at α-position.



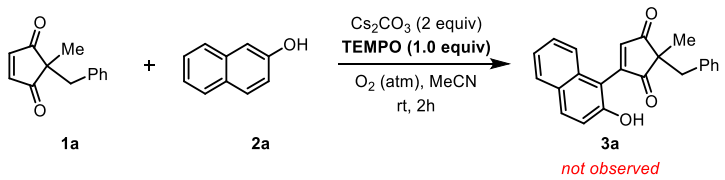
Reaction with 2a-*d*$_1$:



An oven-dried 10 mL round-bottomed flask charged with 2-benzyl-2-methyl cyclopent-4-enedione **1a** (30 mg, 0.15 mmol, 1.0 equiv) and *β*-Naphthol **2a-*d*$_1$** (24 mg, 0.17 mmol, 1.1 equiv) in 2 mL of dry MeCN was added Cs_2CO_3 base (98 mg, 0.3 mmol, 2.0 equiv) and the reaction mixture was stirred for 3 h at room temperature under oxygen atmosphere. The reaction was then quenched/diluted with 5 mL of distilled water. The aqueous phase was then washed with 10 mL EtOAc, and 5 mL brine and was washed with additional EtOAc (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated uder reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (12% EtOAc/Hexanes as the solvent system) to obtain a yellow crystalline solid **3a/3a-*d*$_1$** in 75% yield with 18% deuterium incorporation, as estimated ^{1}H NMR spectroscopy.



4d. Reaction in the presence of TEMPO:



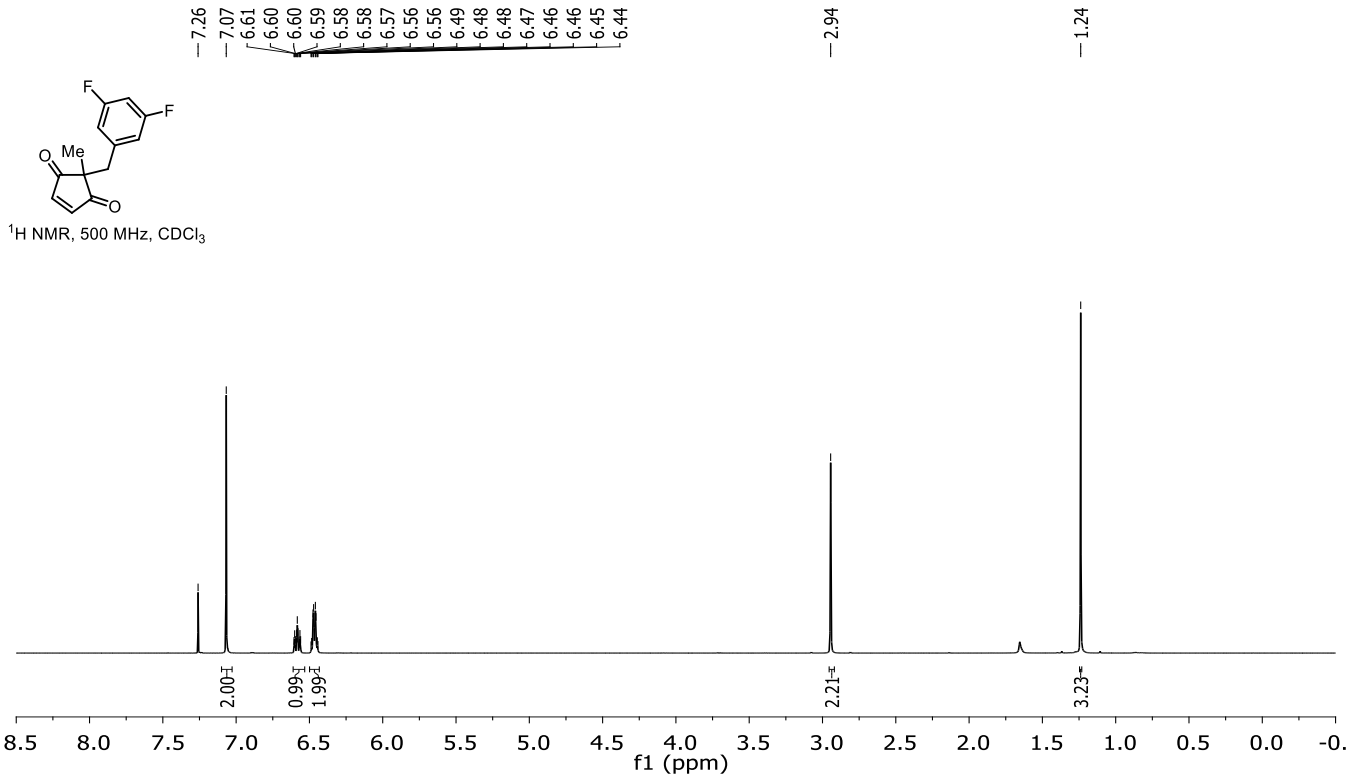
An oven-dried 10 mL round-bottomed flask charged wtih 2-benzyl-2-methyl cyclopent-4-ene-1,3-dione **1a** (30.0 mg, 1.0 equiv, 0.15 mmol) and *β*-Naphthol **2a** (23.7 mg, 1.1 equiv, 0.17 mmol) in 2 mL of dry MeCN was added TEMPO (23.4 mg, 1.0 equiv, 0.15 mmol), and Cs_2CO_3 (98 mg, 2.0 equiv, 0.30 mmol) and the reaction mixture was stirred at room temperature under oxygen atmosphere for 3 h. After judging by TLC, the product **3a** was not observed and the starting materials **1a** and **2a** were recovered.

5. References:

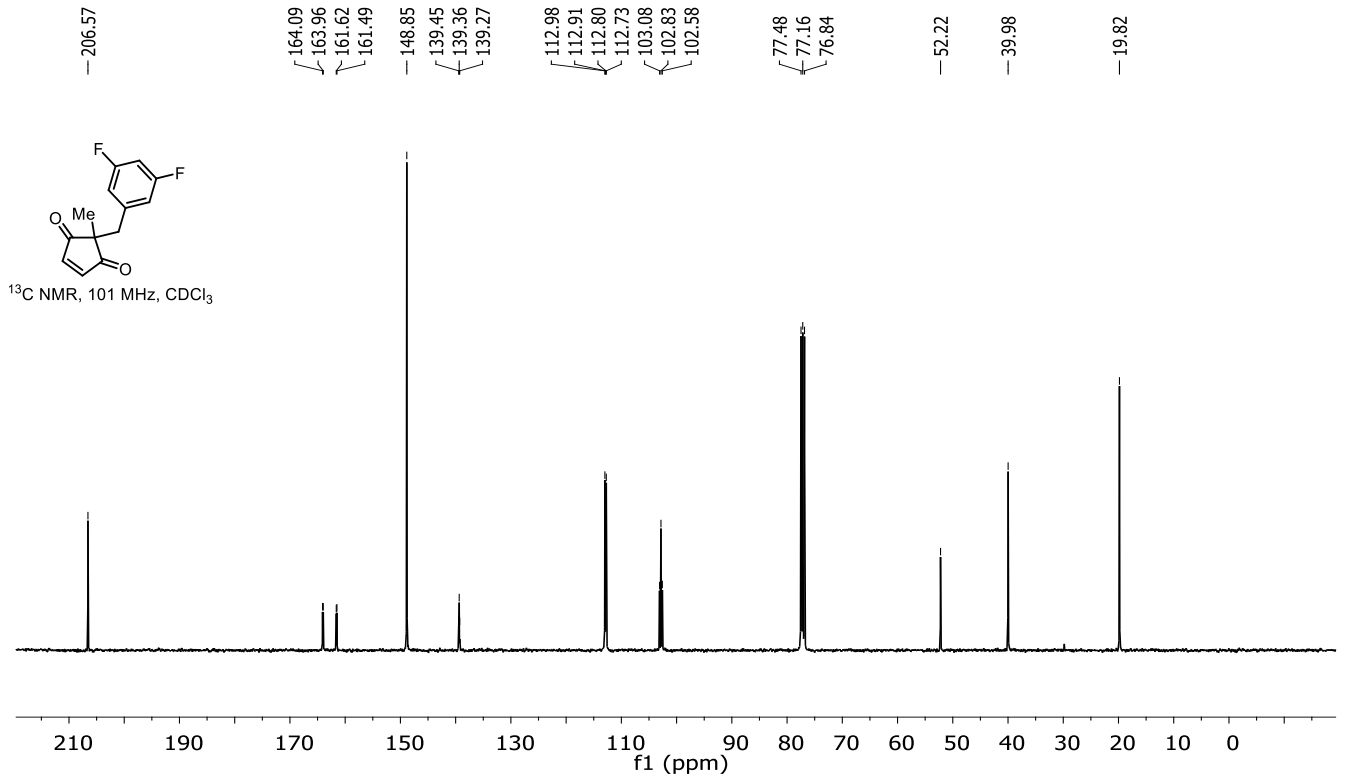
1. Y. Ge, C. Qin, L. Bai, J. Hao, J. Liu and X. Luan, *Angew. Chem. Int. Ed.*, 2020, ***59***, 18985–18989.
2. a) M. S. Manna and S. Mukherjee, *J. Am. Chem. Soc.*, 2015, ***137***, 130–133; b) A. Donthoju, L. R. Magham, N. Singh, N. Manjula and R. Chegondi, *J. Org. Chem.*, 2019, ***84***, 15735–15744.
3. S. Zhuo, T. Zhu, L. Zhou, C. Mou, H. Chai, Y. Lu, L. Pan, Z. Jin and Y. R. Chi, *Angew. Chem. Int. Ed.*, 2019, ***58***, 1784–1788.
4. H. Liang, X. Zhou, L. Zheng and J. Wang, *J. Org. Chem.*, 2019, ***84***, 11306–11315.
5. T. Das, P. Saha and V. K. Singh, *Org. Lett.*, 2015, ***17***, 5088–5091.
6. J. George, H. Y. Kim and K. Oh, *Org. Lett.*, 2018, ***20***, 2249–2252.
7. V. B. Patil, J. B. Nanubolu and R. Chegondi, *Chem. Commun*., 2021, ***57***, 5574–5577.
8. R. Gava, M. Á. Fuentes, M. Besora, T. R. Belderrain, K. Jacob, F. Maseras, M. Etienne, A. Caballero and P. J. Pérez, *ChemCatChe.*, 2014, ***6***, 2206–2210.
9. A. Bartoszewicz, M. Kalek, J. Nilsson, R. Hiresova and J. Stawinski, *Synlett*., 2008, ***1***, 37–40.
10. R. Giles, I. Kim, W. E. Chao, J. Moore and K. W. Jung, *J. Chem. Educ.*, 2014, ***91***, 1220–1223.

6. NMR Spectra:

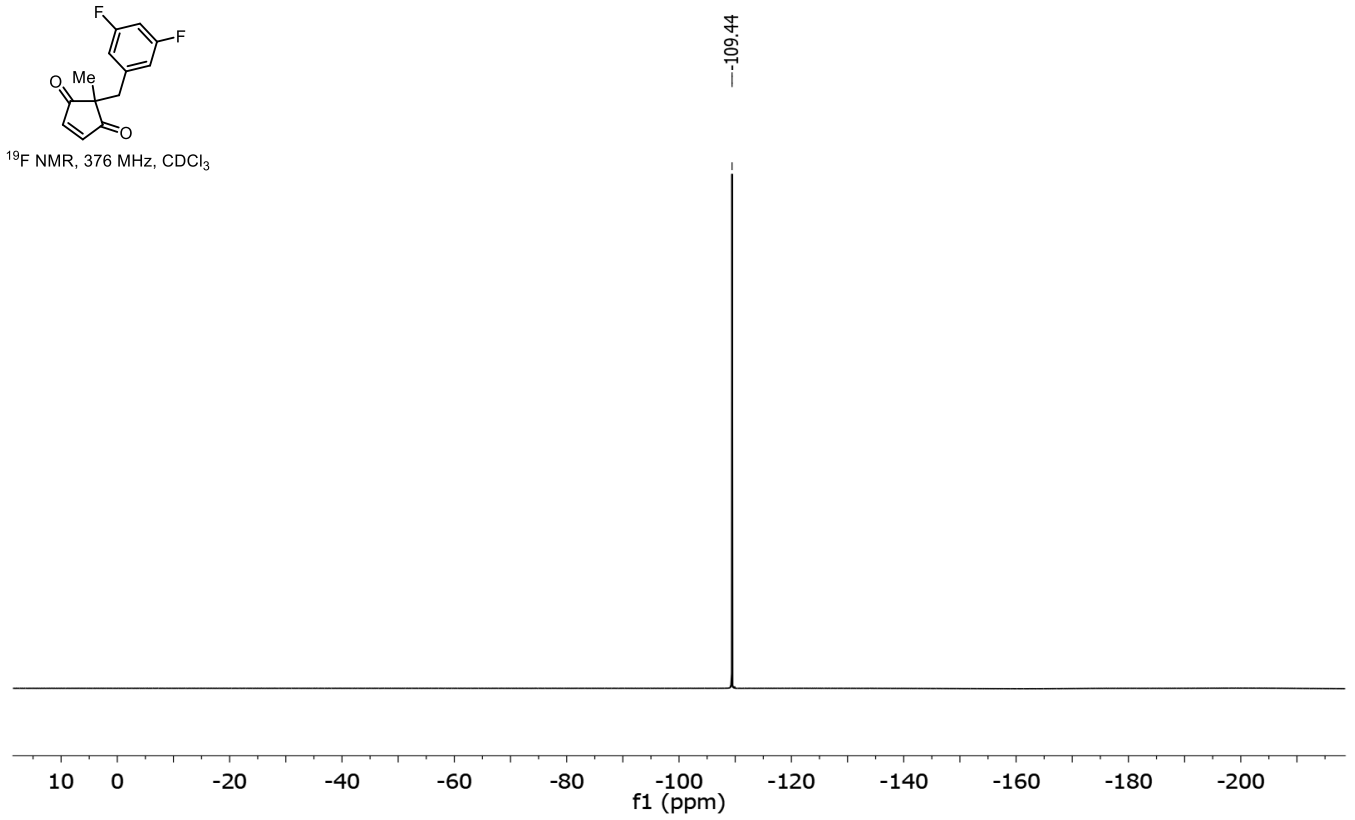
2-(3,5-Difluorobenzyl)-2-methylcyclopent-4-ene-1,3-dione (1h):



^{1}H NMR, 500 MHz, $CDCl_3$

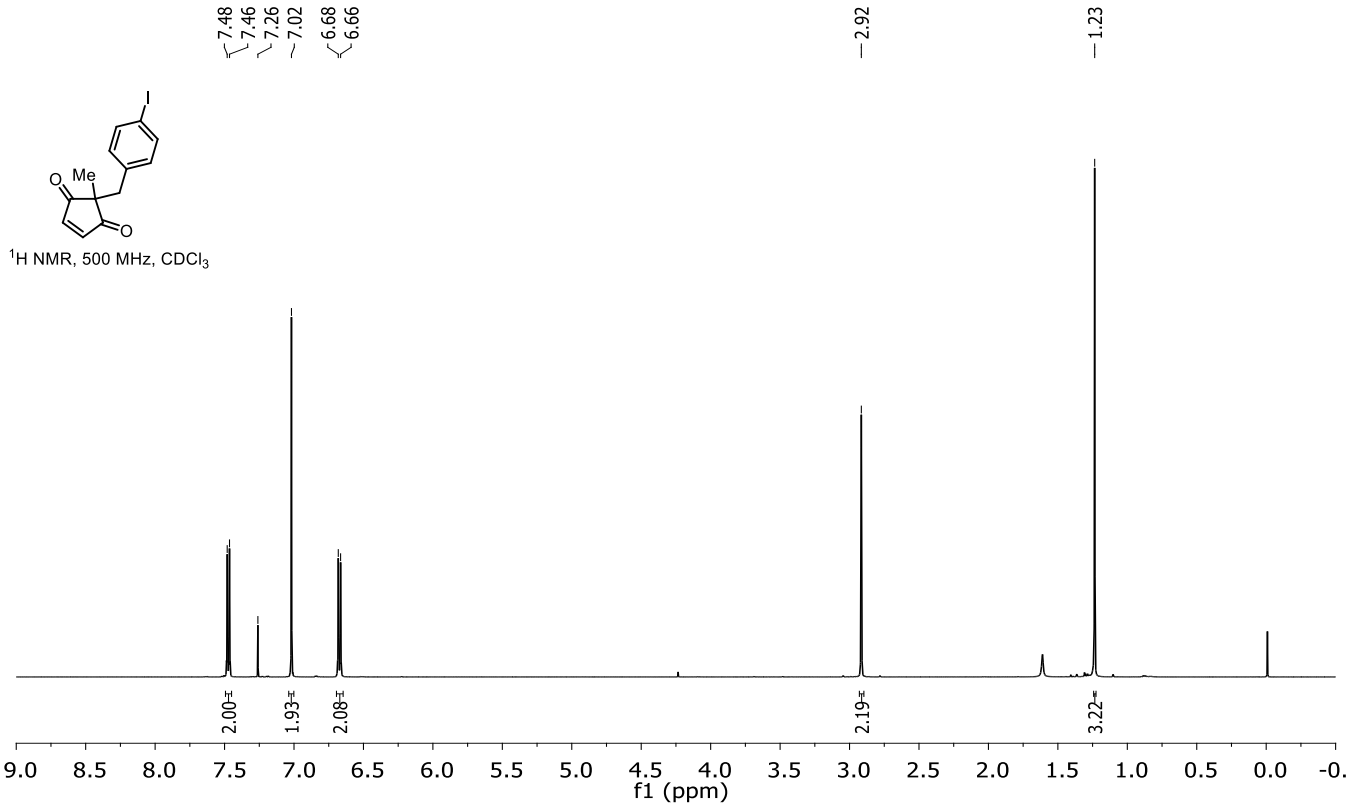


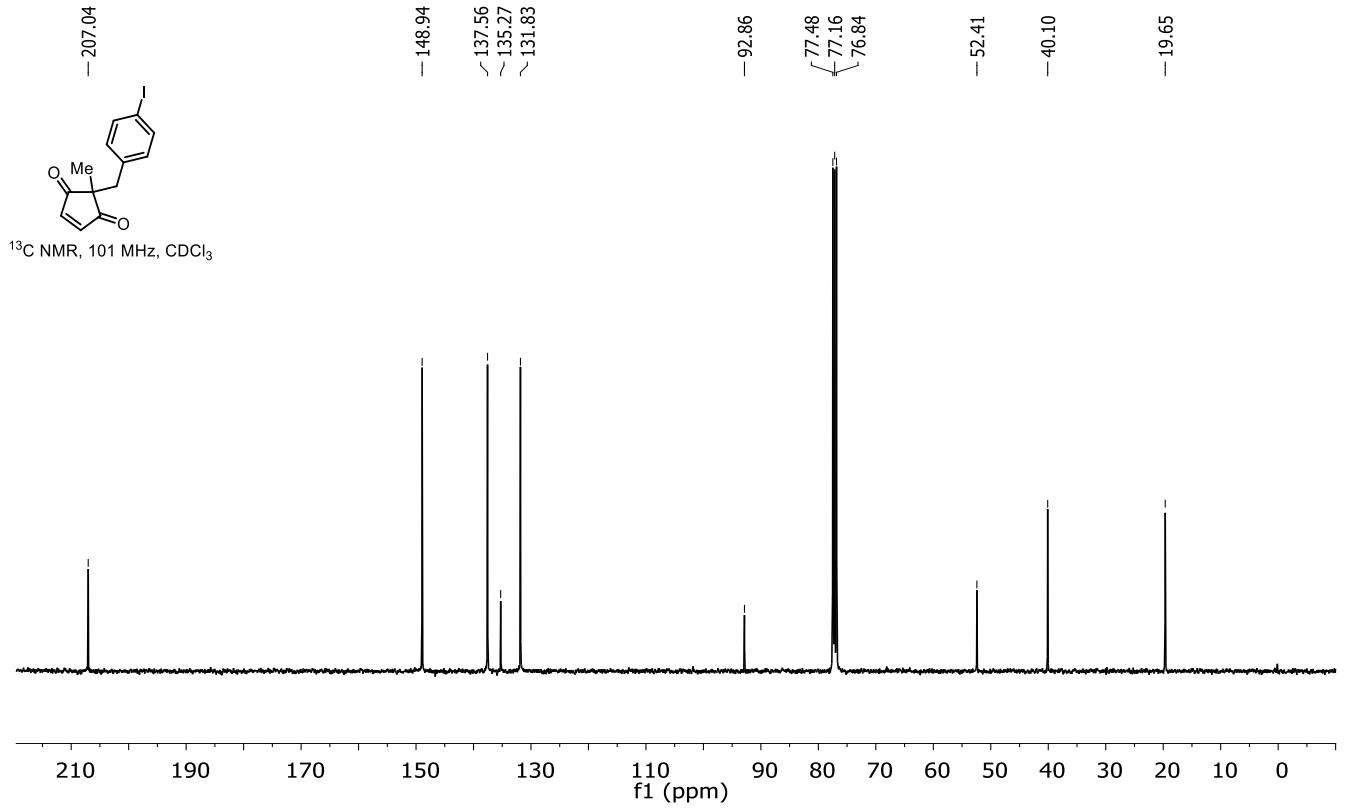
^{13}C NMR, 101 MHz, $CDCl_3$



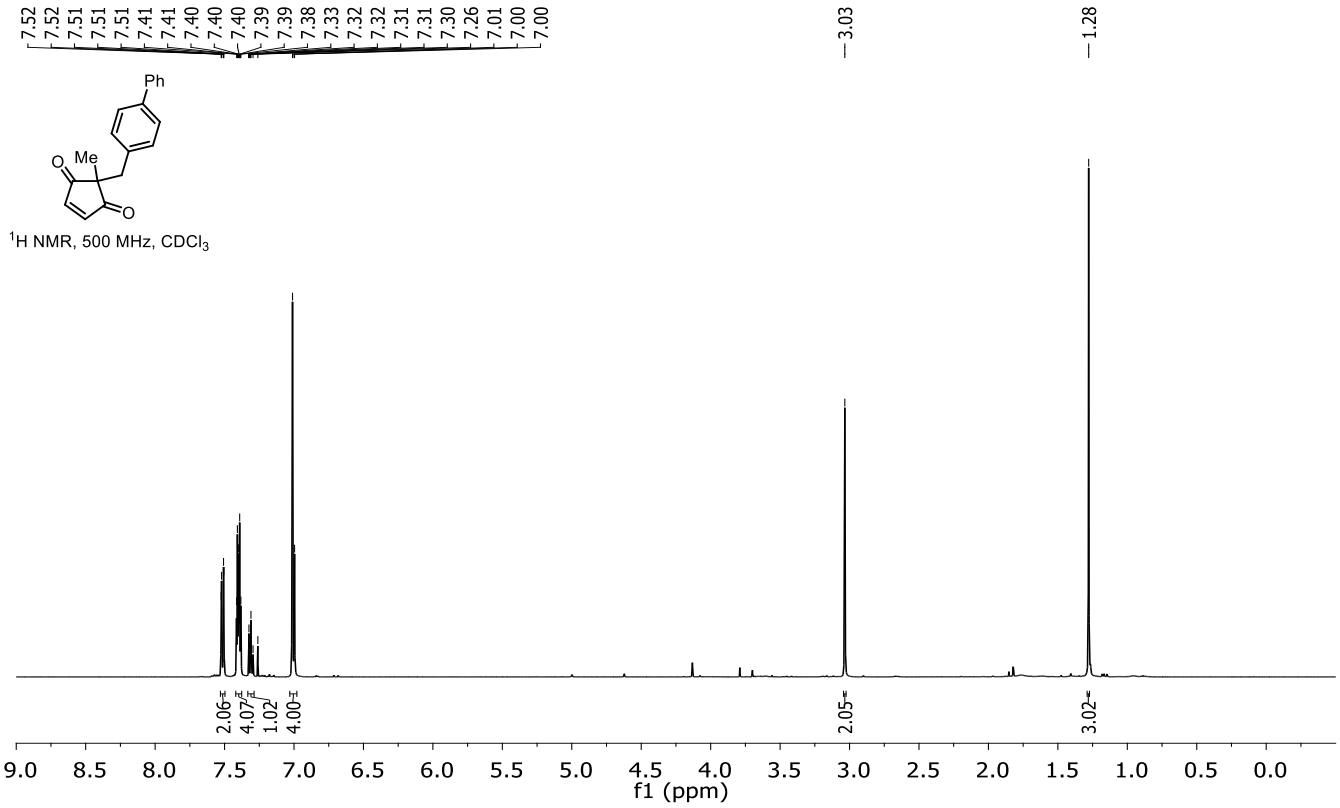
^{19}F NMR, 376 MHz, $CDCl_3$

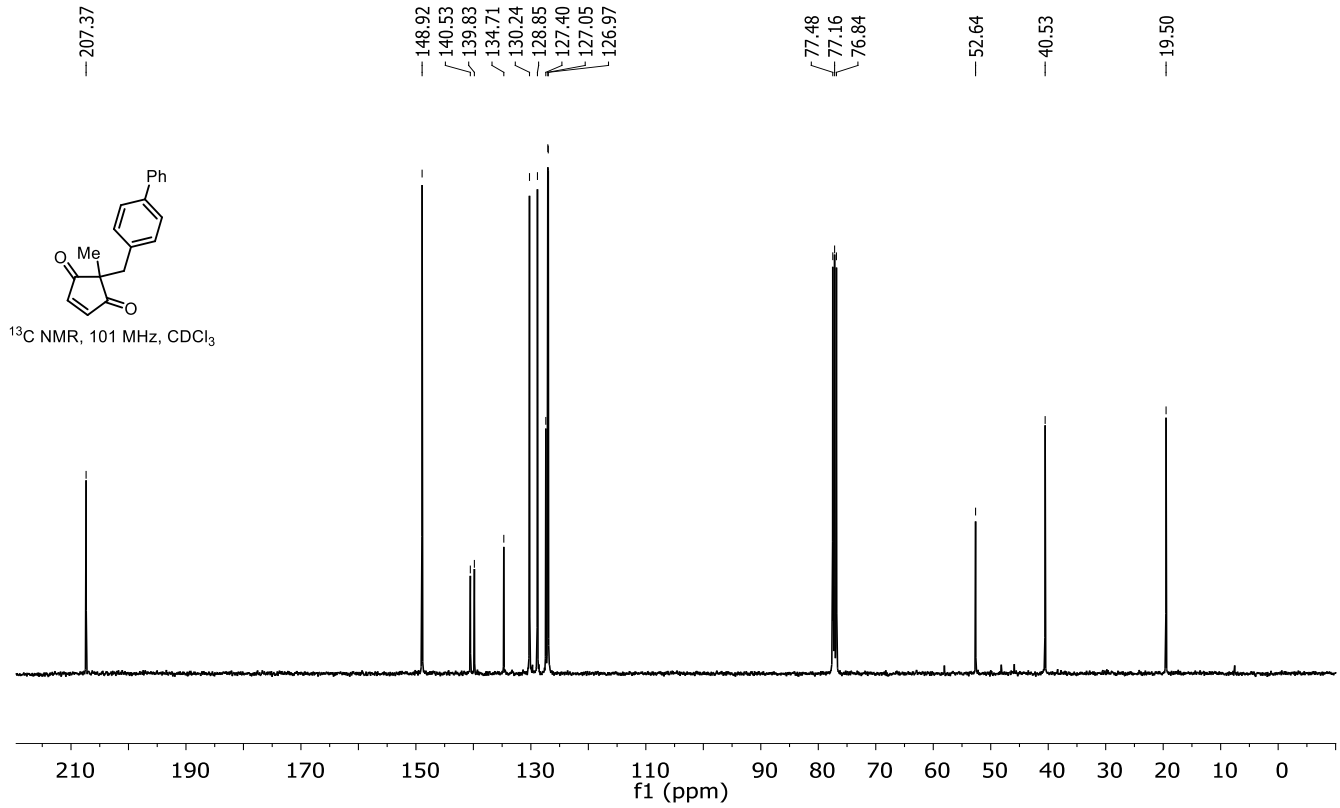
2-(4-Iodobenzyl)-2-methylcyclopent-4-ene-1,3-dione (1l):



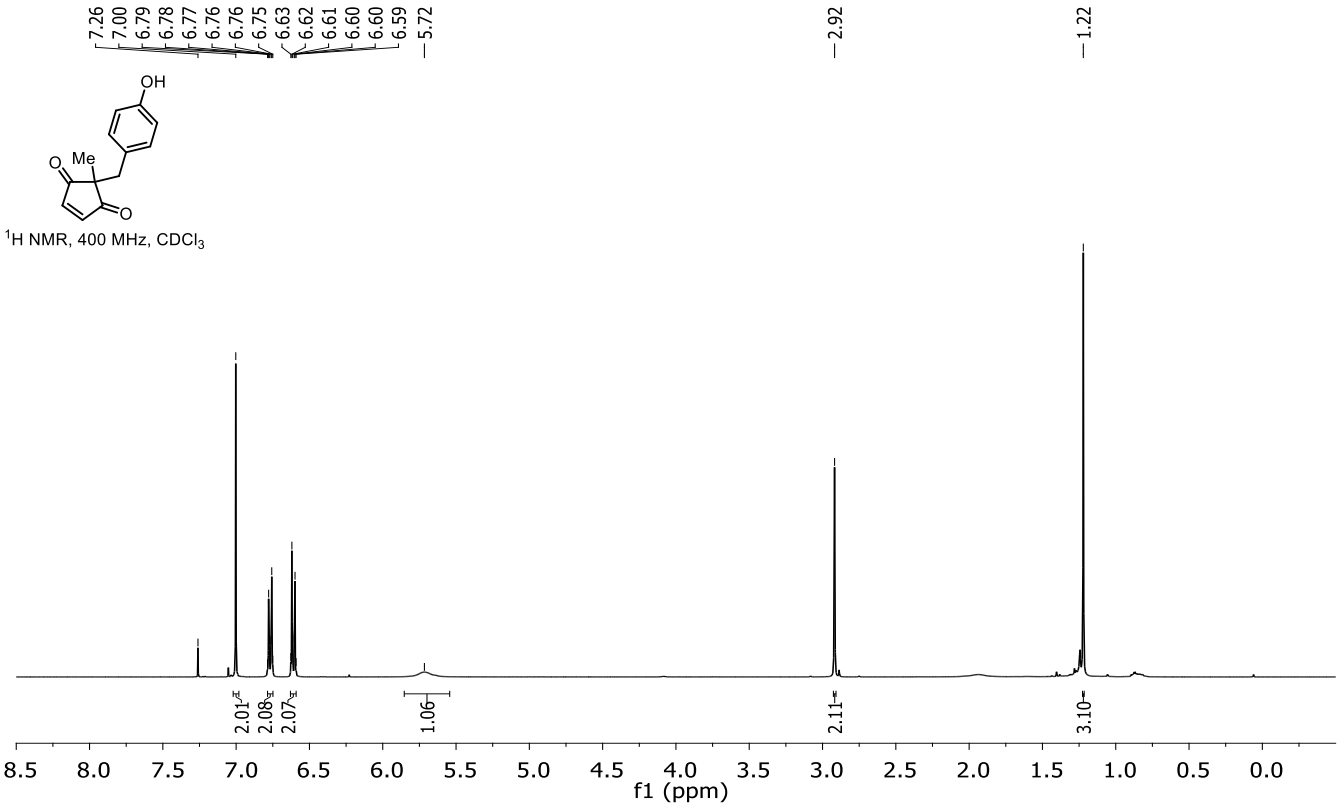


2-([1,1'-Biphenyl]-4-ylmethyl)-2-methylcyclopent-4-ene-1,3-dione (1m):

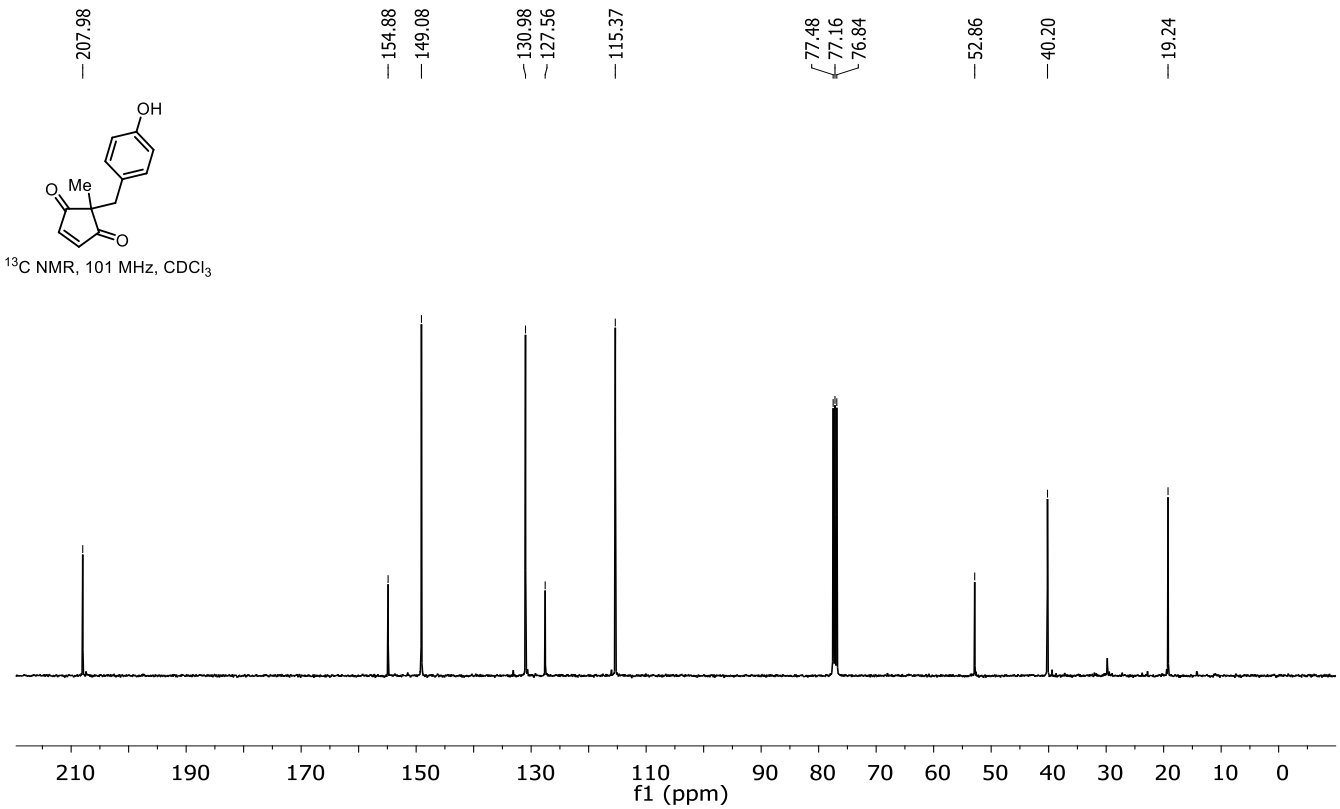




2-(4-Hydroxybenzyl)-2-methylcyclopent-4-ene-1,3-dione (1r):

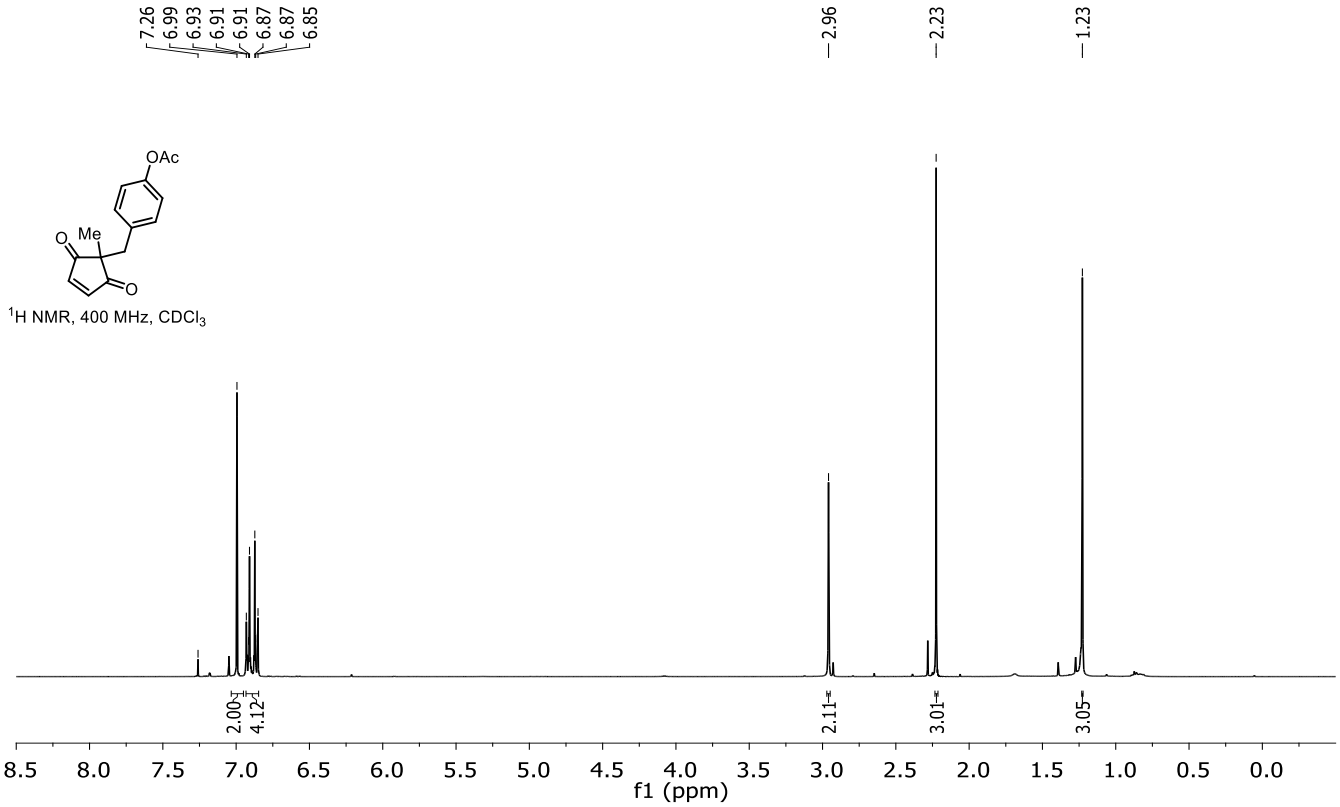


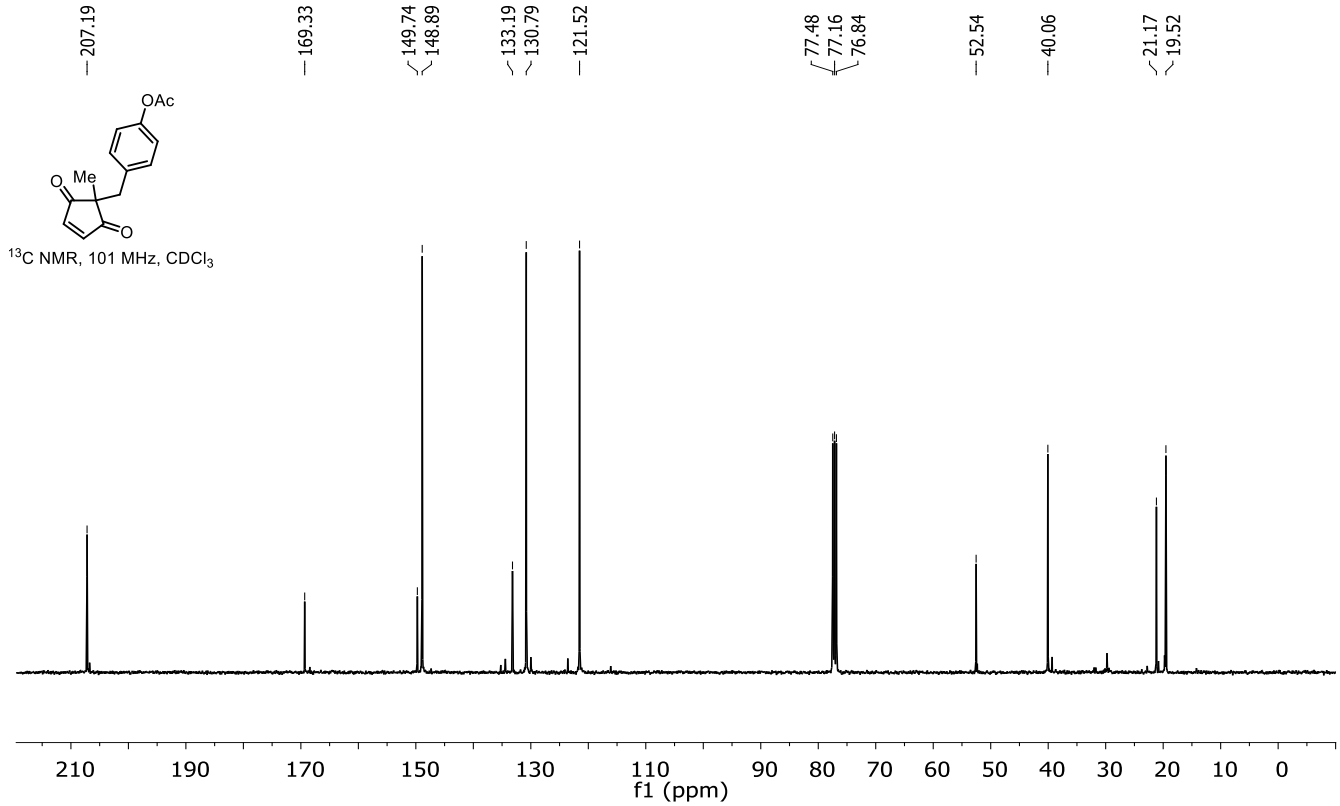
^{1}H NMR, 400 MHz, $CDCl_3$



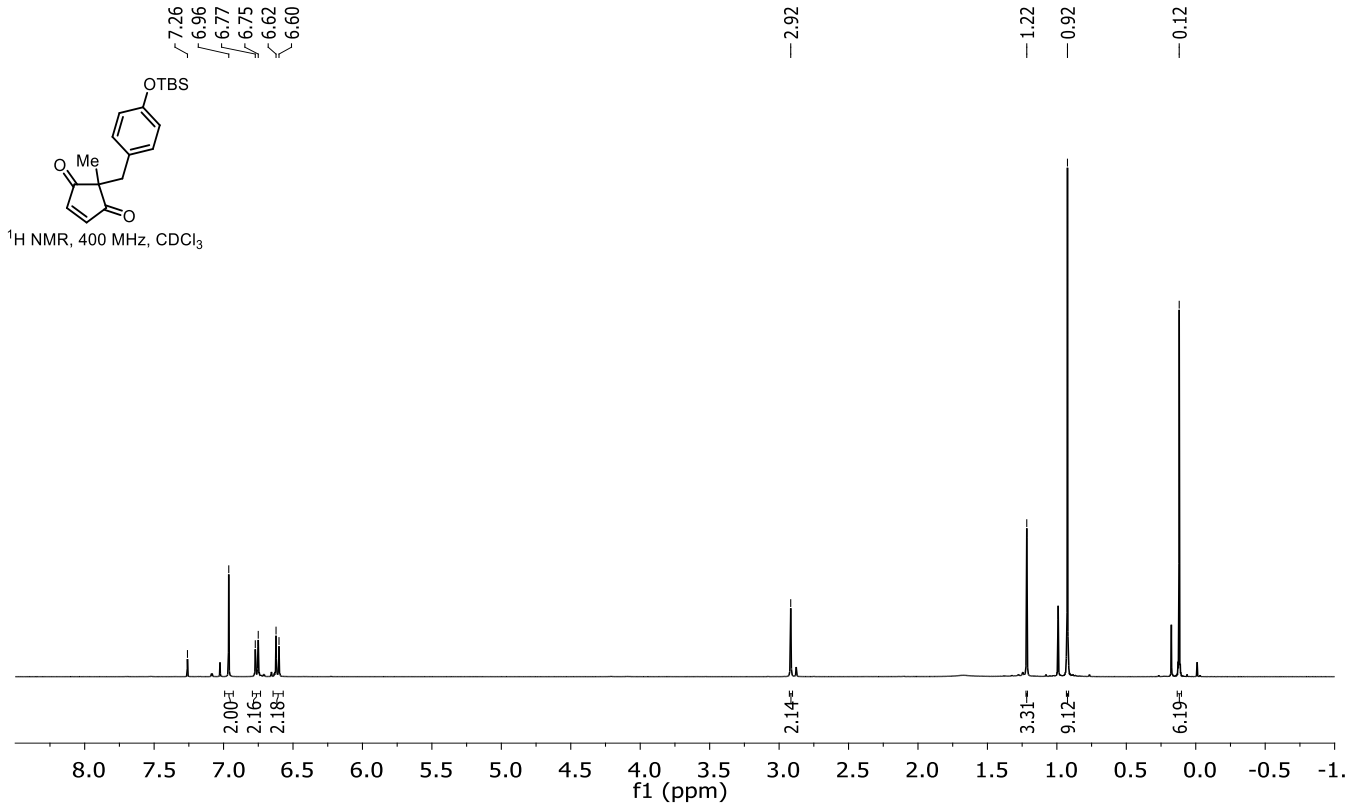
^{13}C NMR, 101 MHz, $CDCl_3$

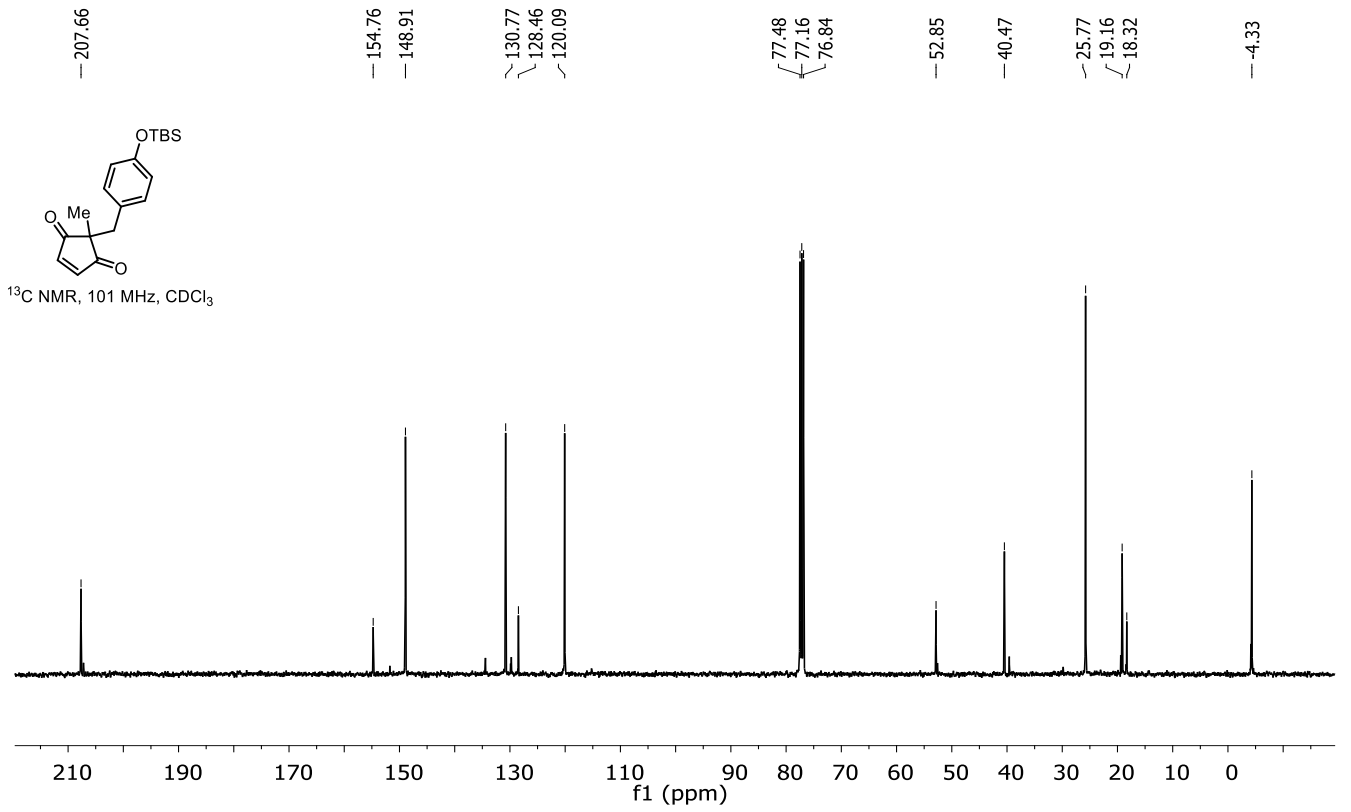
4-((1-Methyl-2,5-dioxocyclopent-3-en-1-yl)methyl)phenyl acetate (1n):



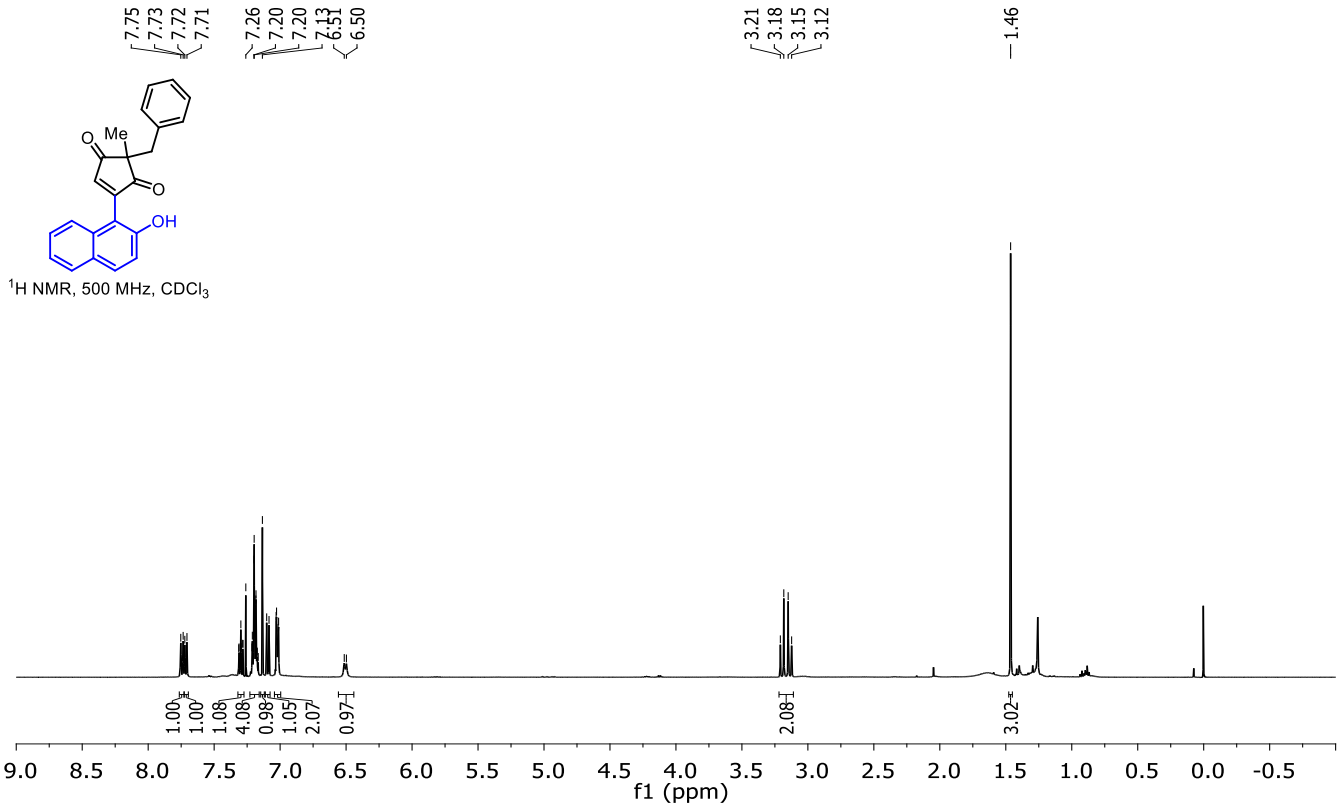


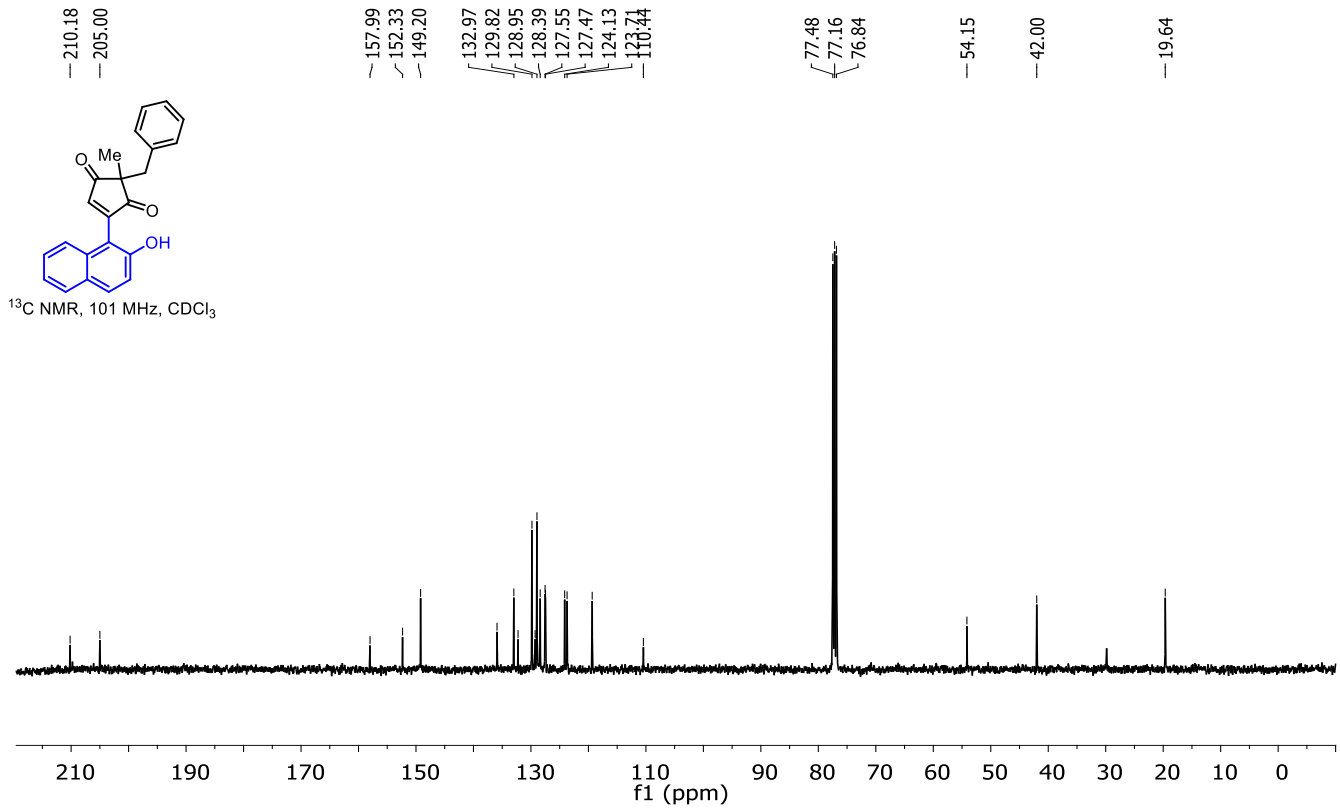
2-(4-((*tert*-Butyldimethylsilyl)oxy)benzyl)-2-methylcyclopent-4-ene-1,3-dione (1s):



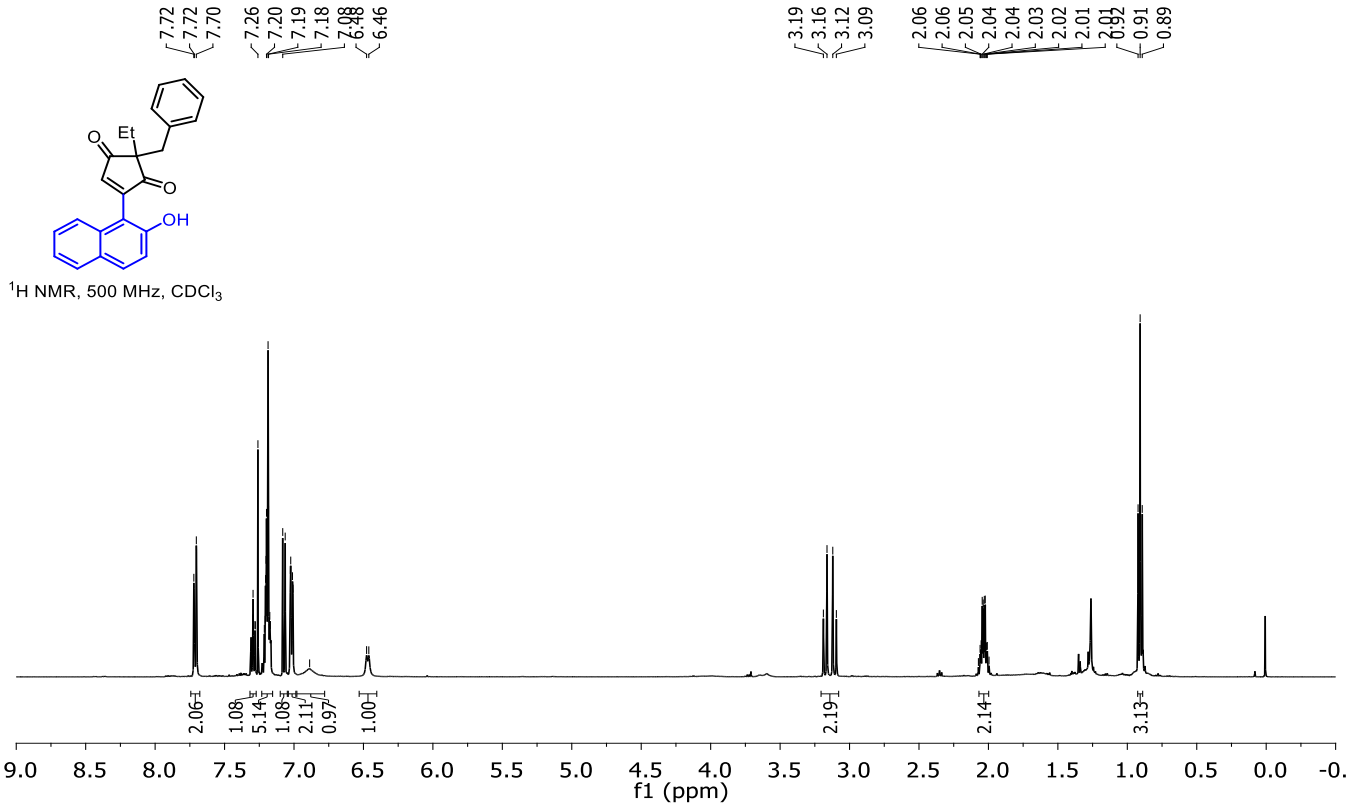


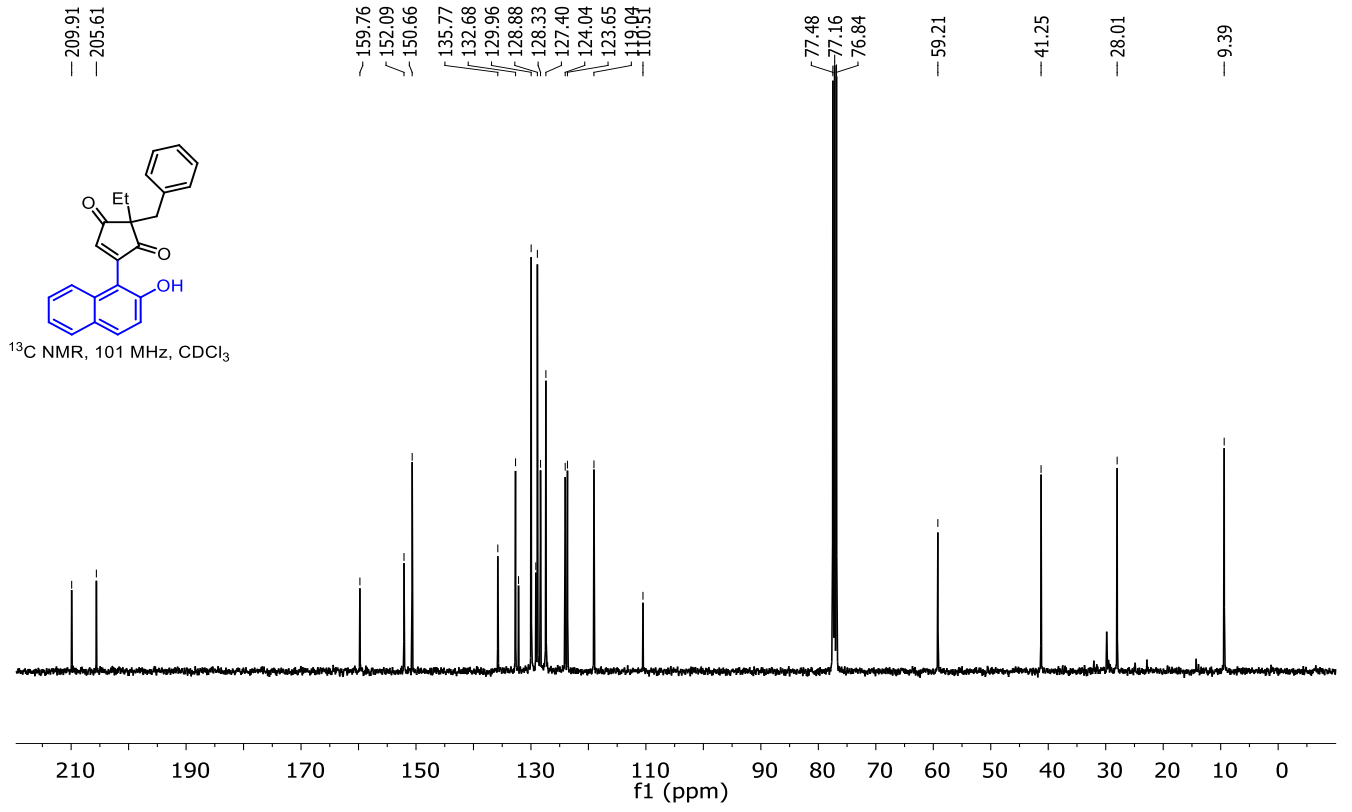
2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3a):



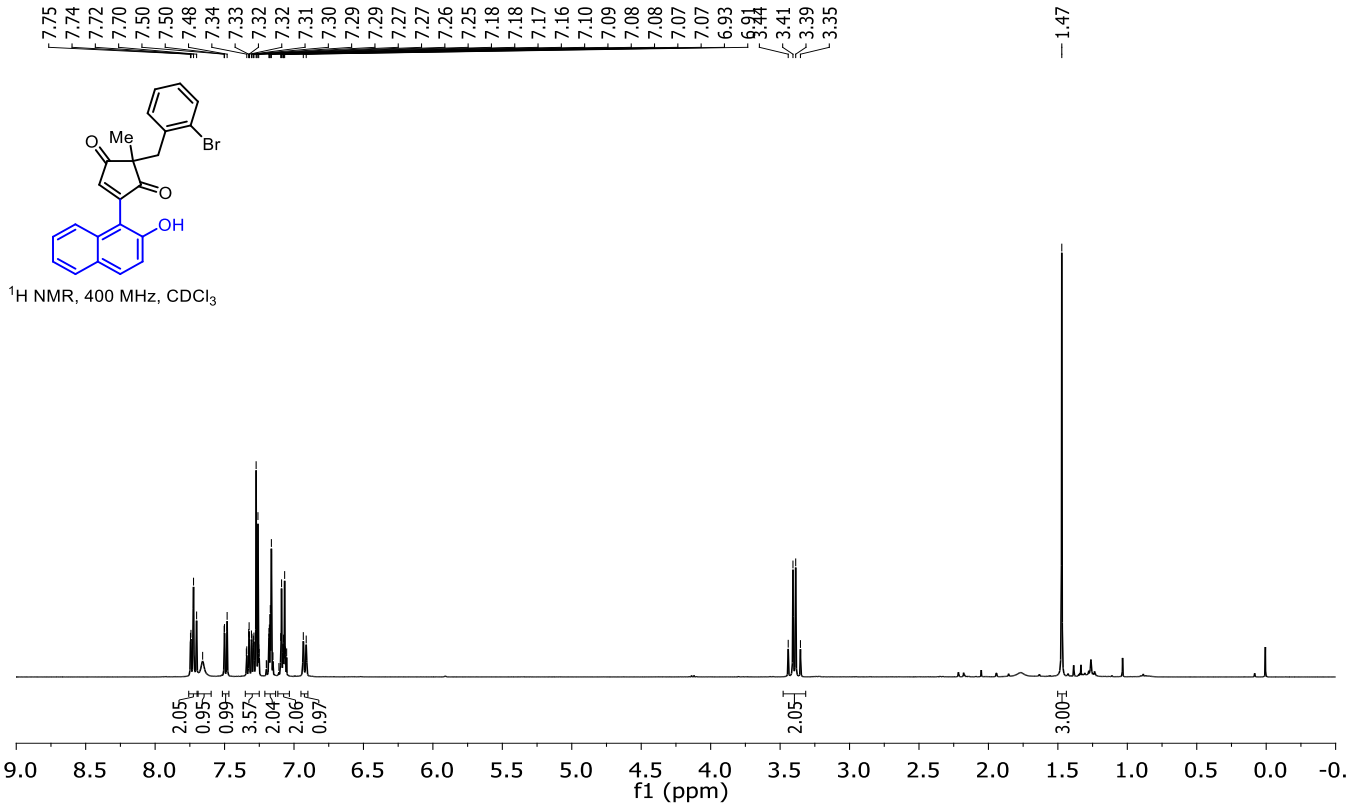


2-Benzyl-2-ethyl-4-(2-hydroxynaphthalen-1-yl)cyclopent-4-ene-1,3-dione (3b):

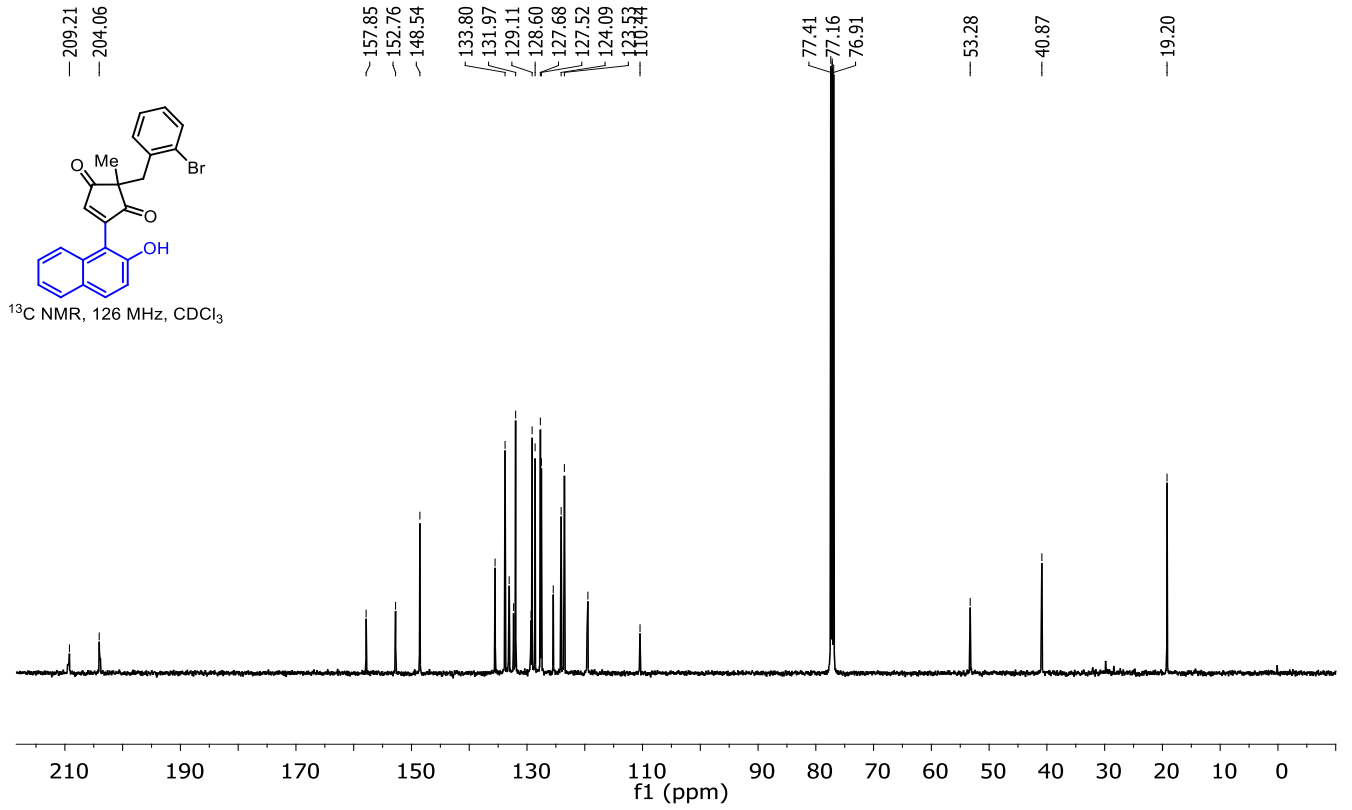




2-(2-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3c):

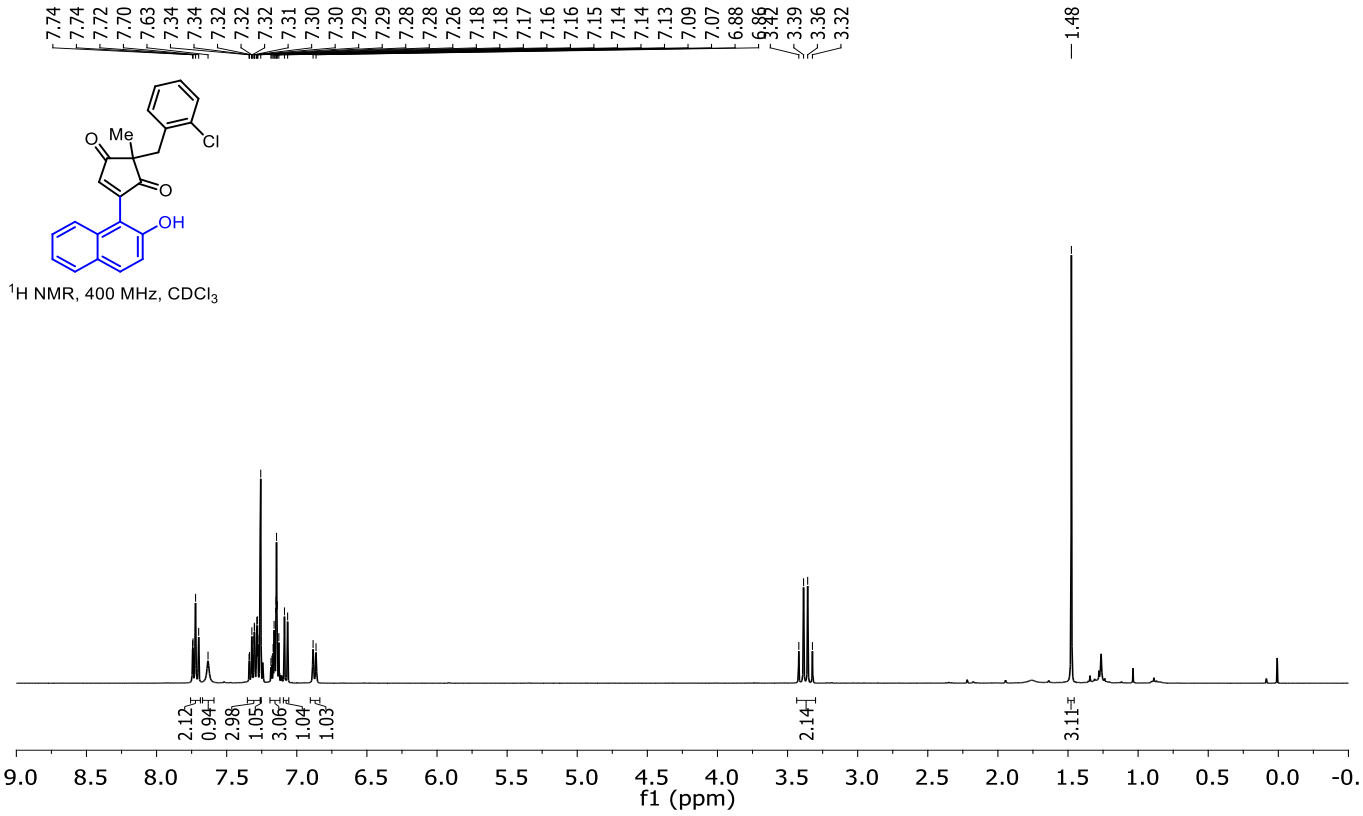


^{1}H NMR, 400 MHz, $CDCl_3$

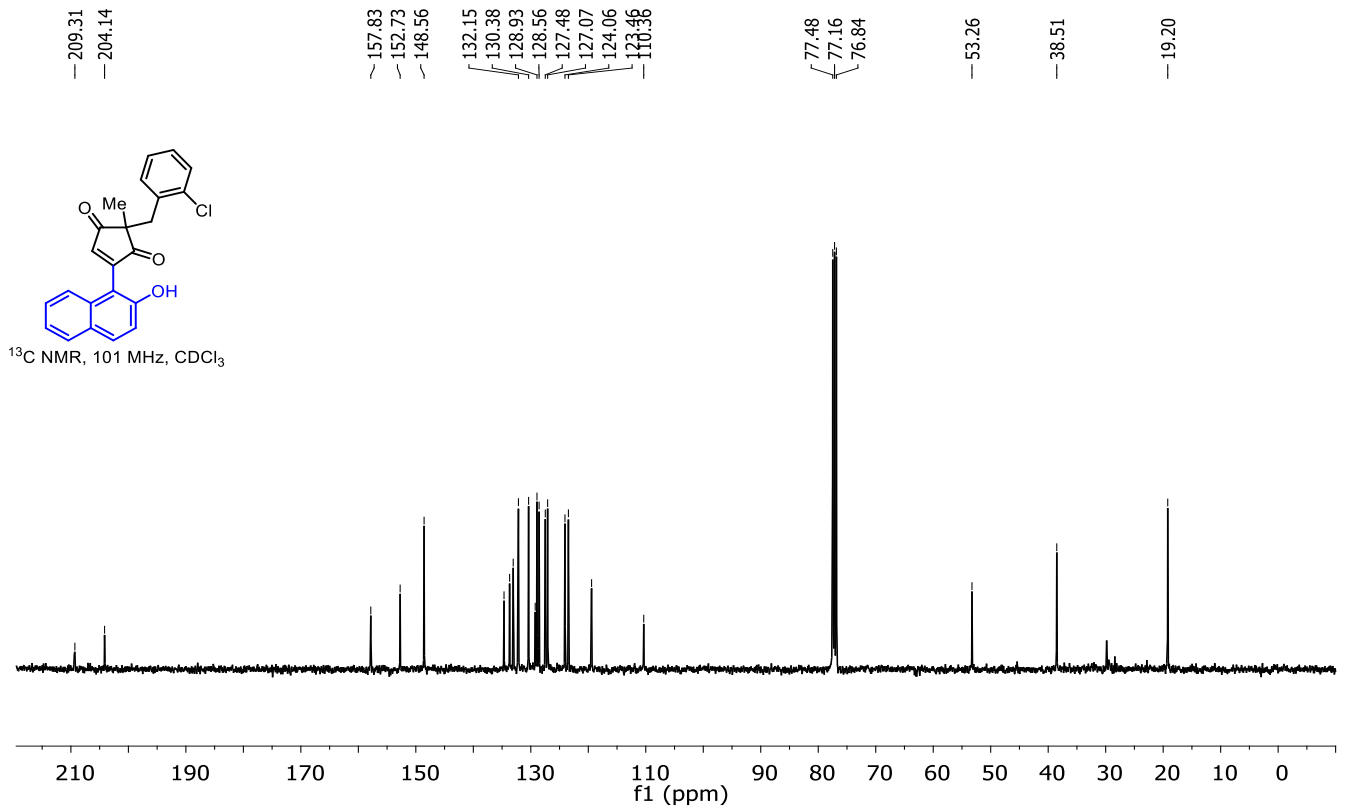


^{13}C NMR, 126 MHz, $CDCl_3$

2-(2-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3d):

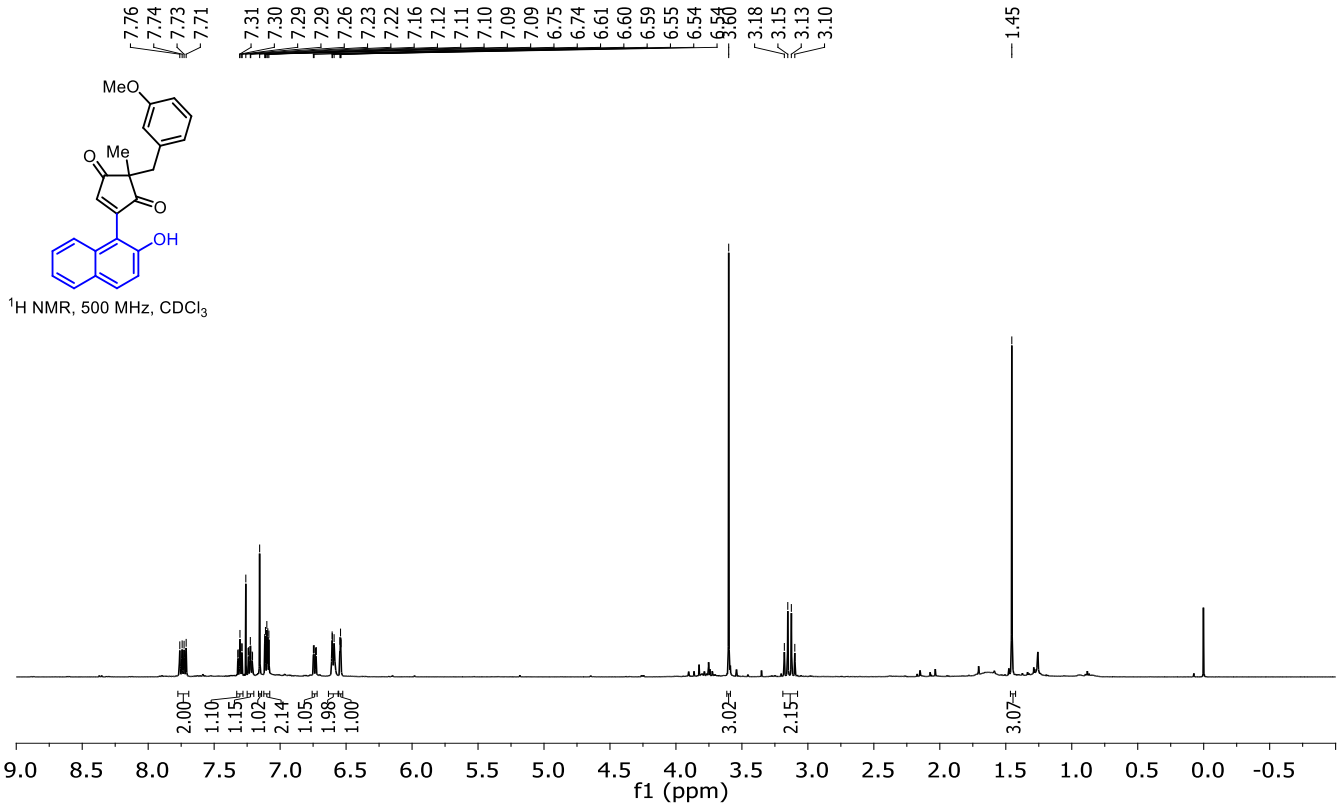


^{1}H NMR, 400 MHz, $CDCl_3$

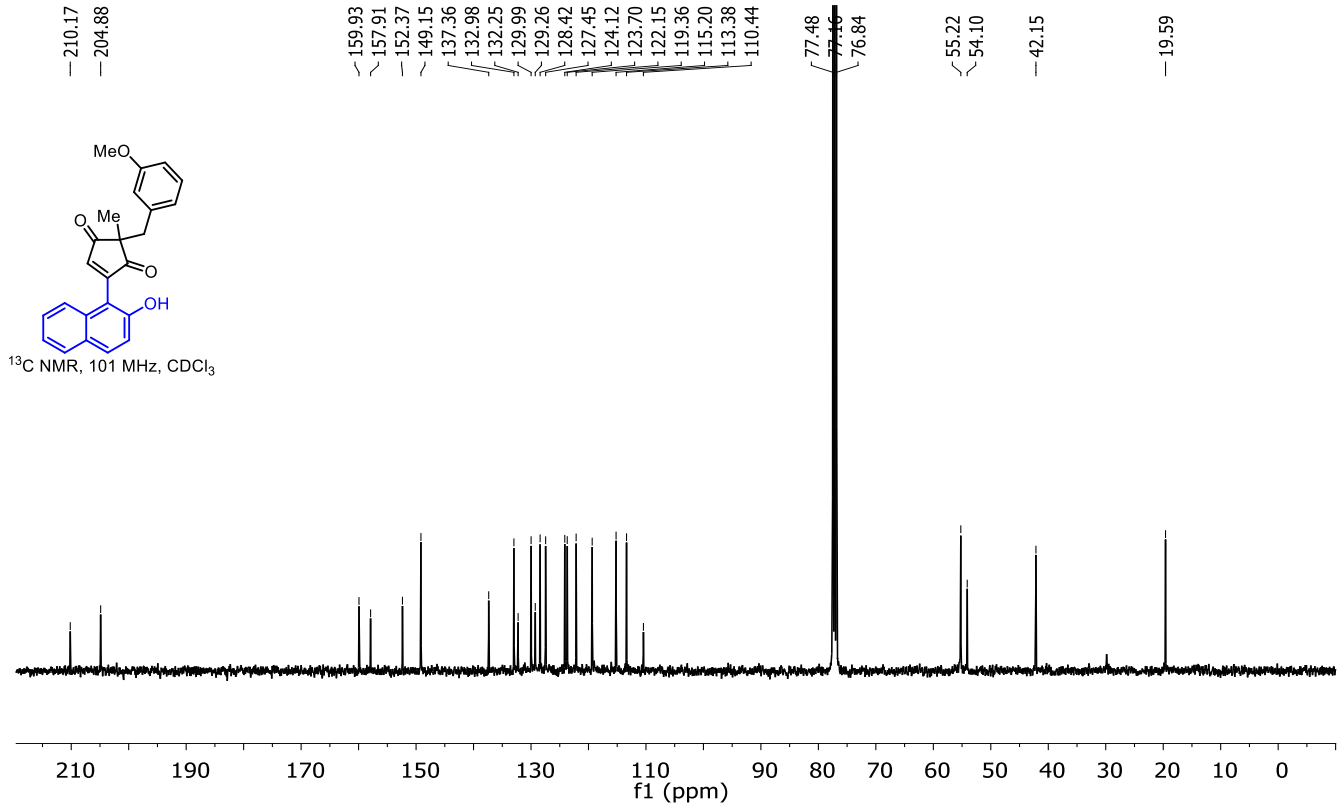


^{13}C NMR, 101 MHz, $CDCl_3$

4-(2-Hydroxynaphthalen-1-yl)-2-(3-methoxybenzyl)-2-methylcyclopent-4-ene-1,3-dione (3e):

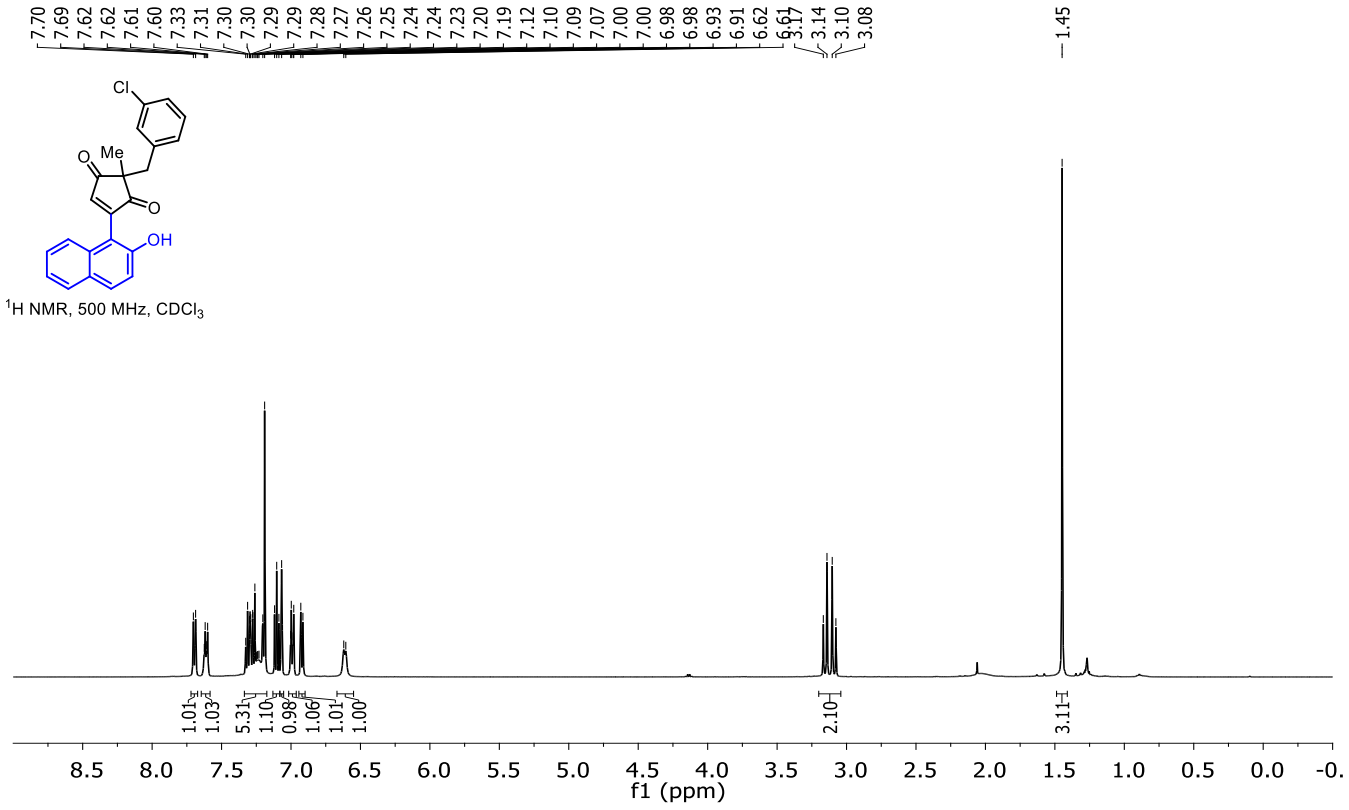


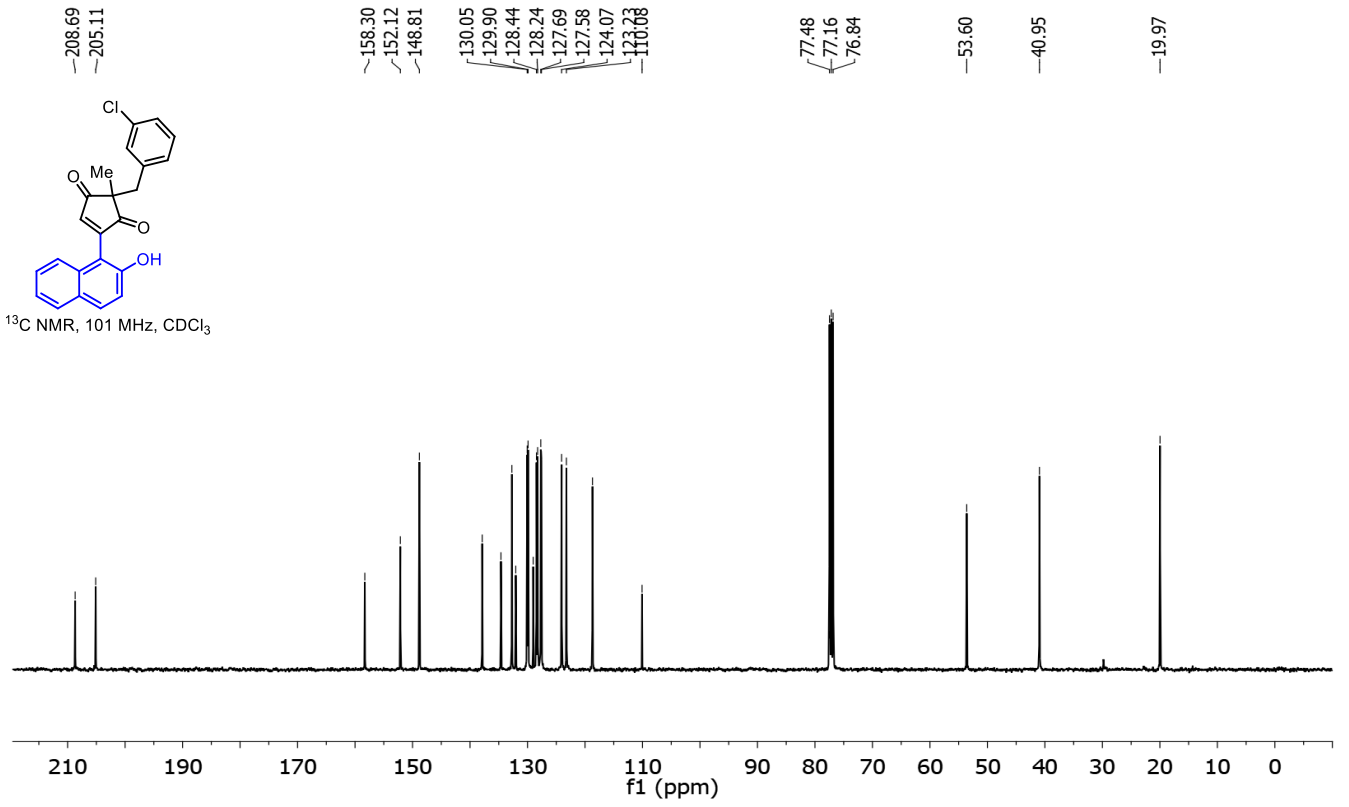
^{1}H NMR, 500 MHz, $CDCl_3$



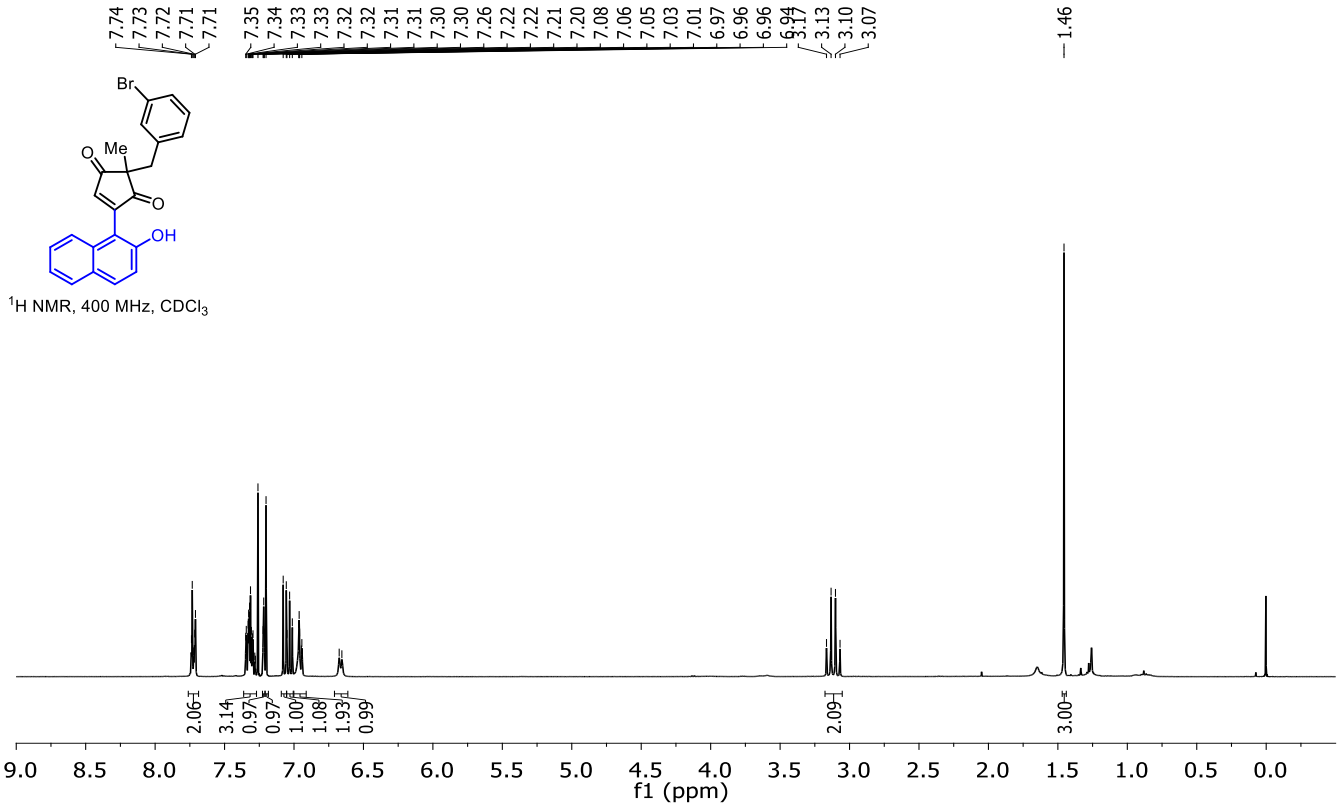
^{13}C NMR, 101 MHz, $CDCl_3$

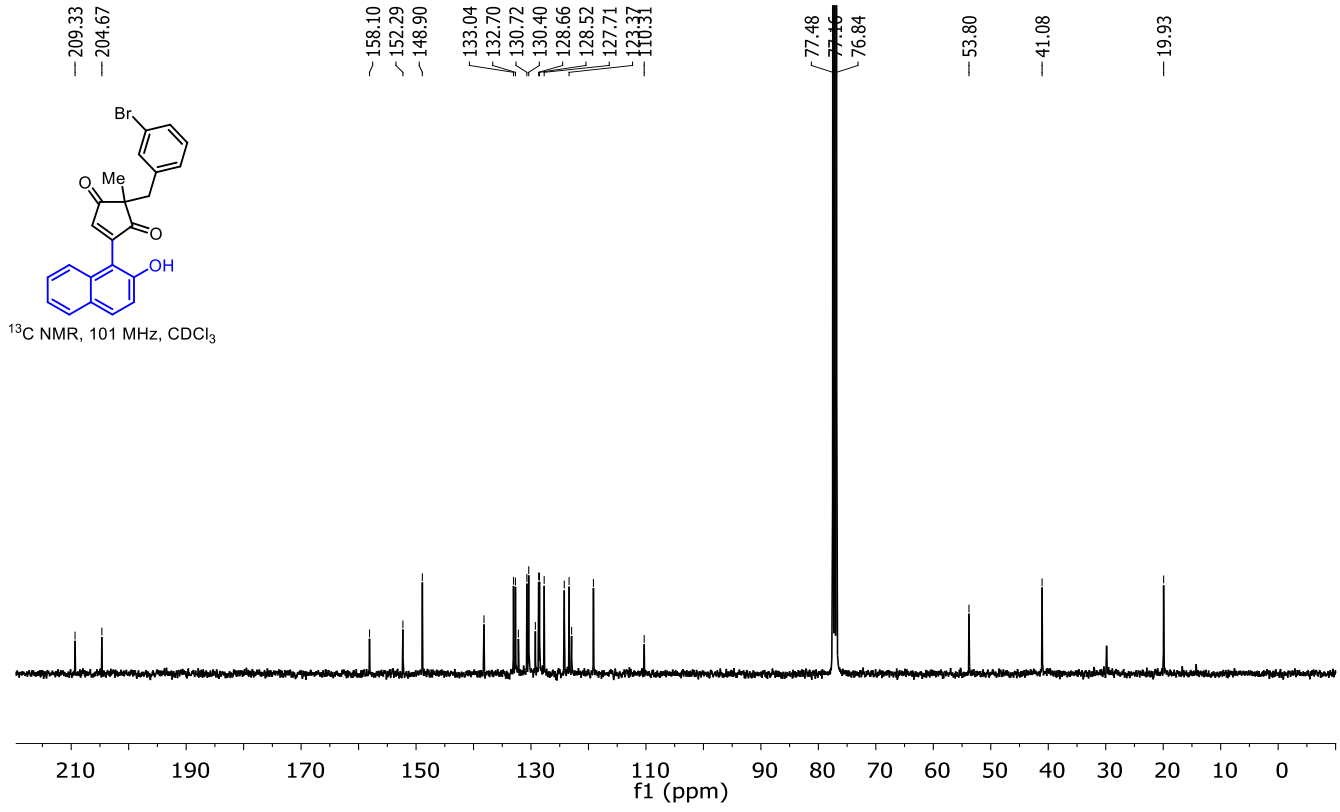
2-(3-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3f):



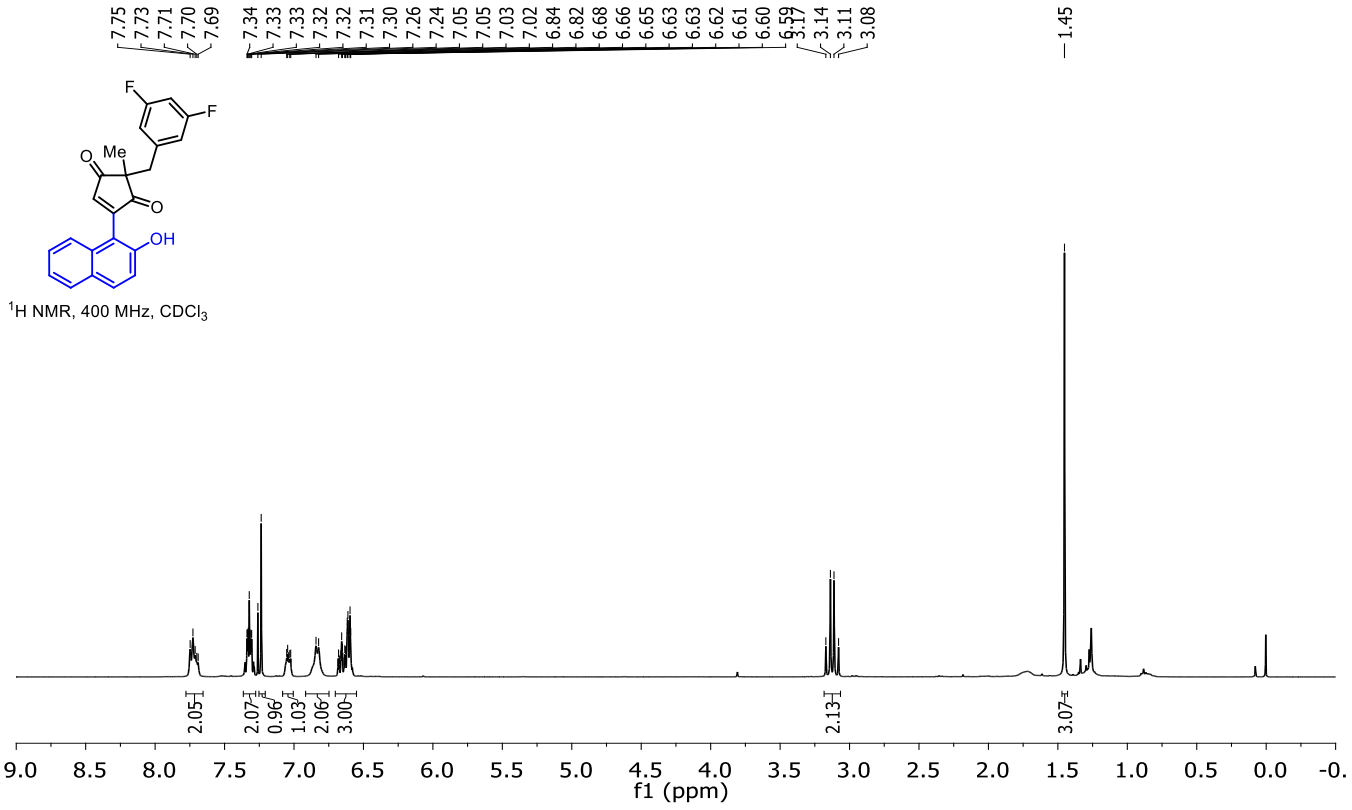


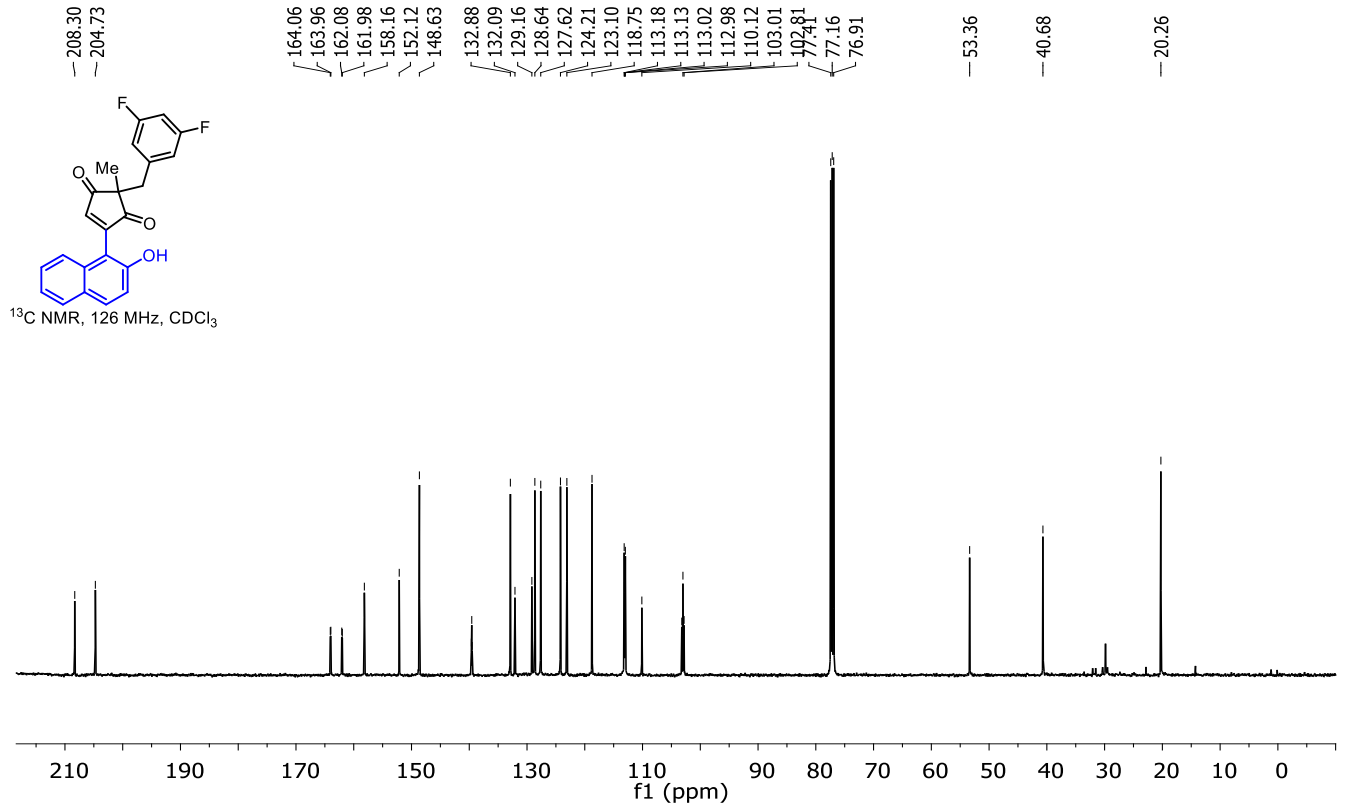
2-(3-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3g):

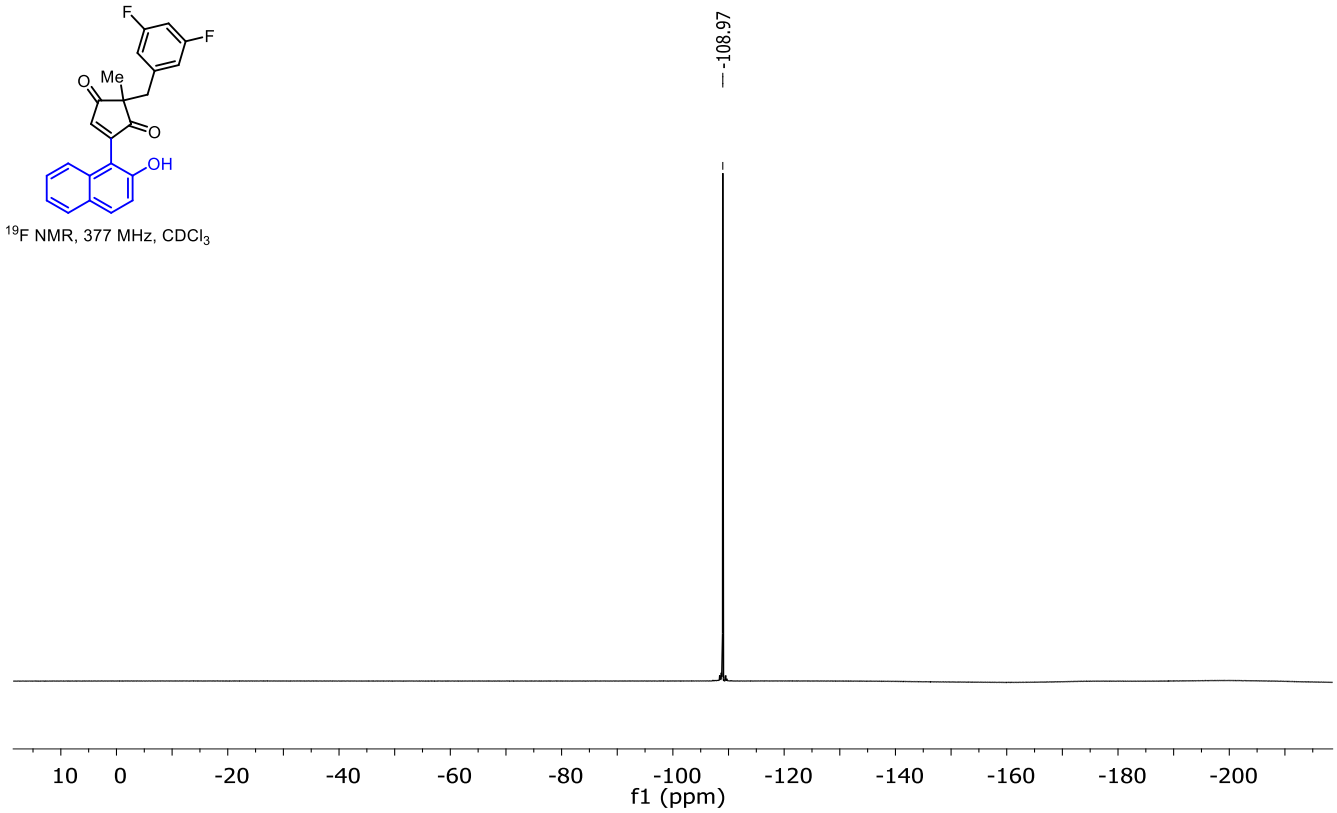




2-(3,5-Difluorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3h):

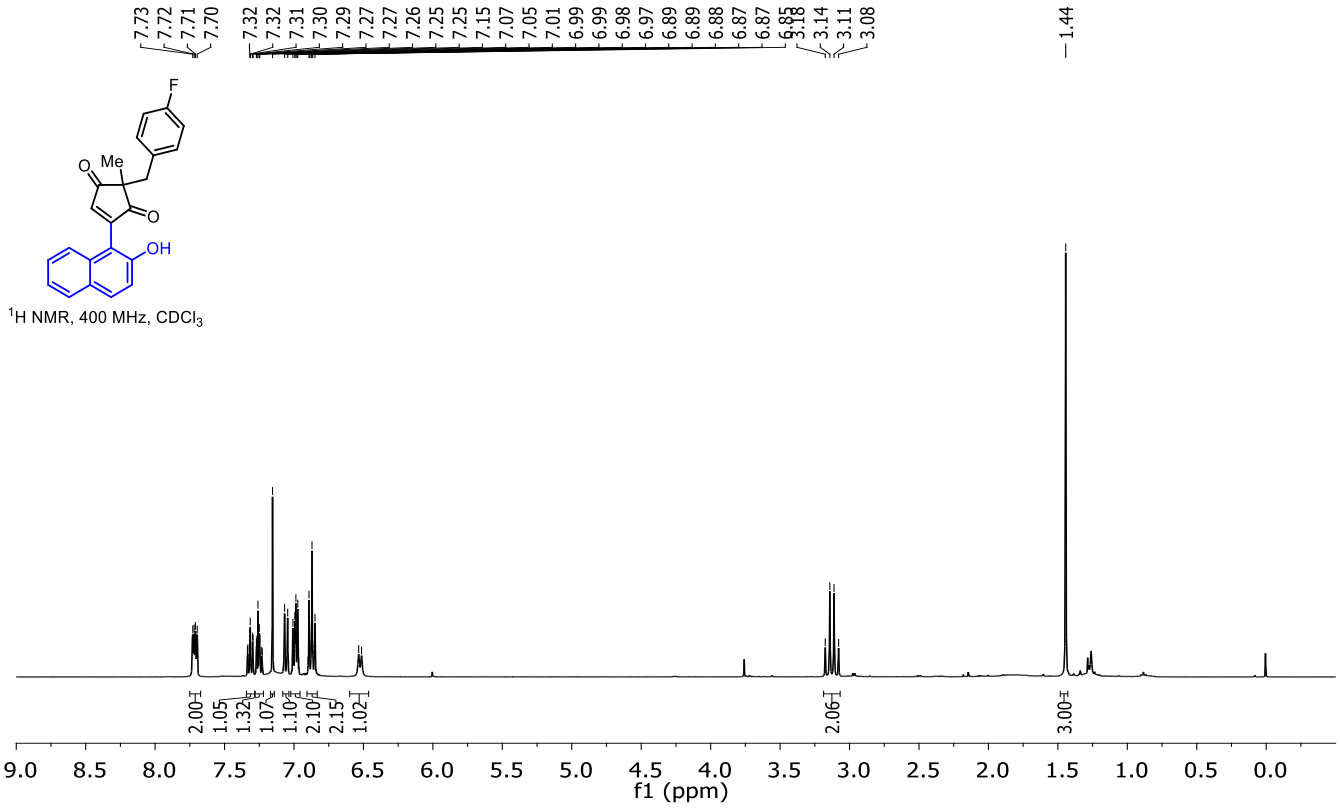


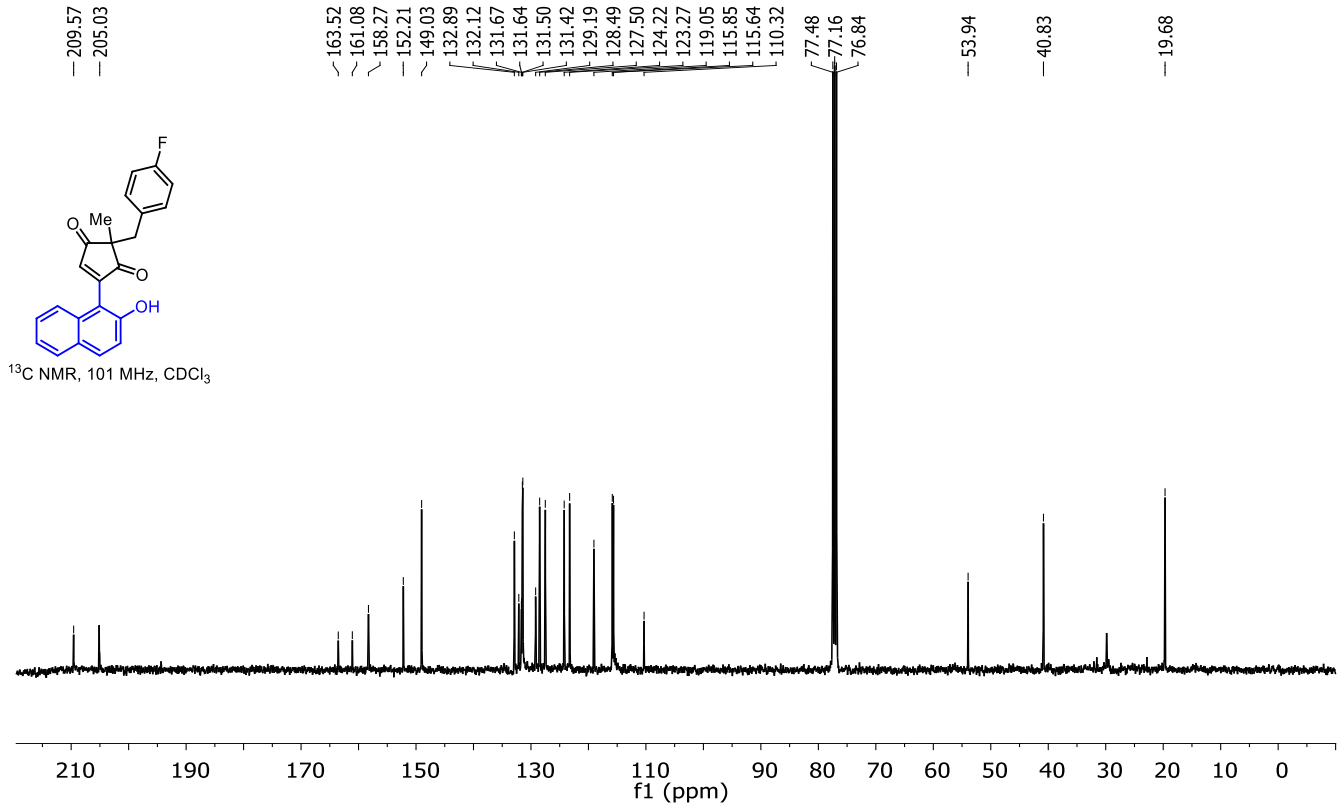


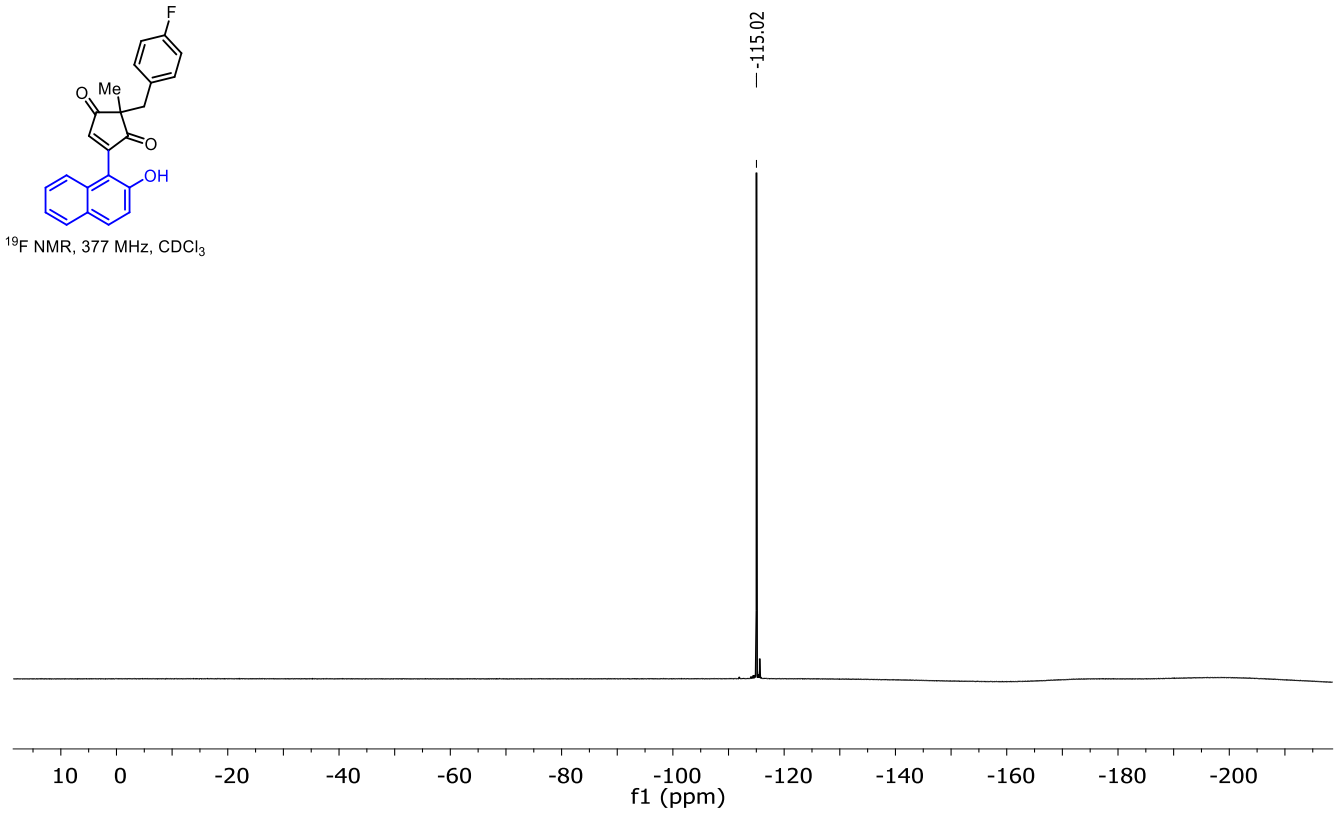


^{19}F NMR, 377 MHz, $CDCl_3$

2-(4-Fluorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3i):

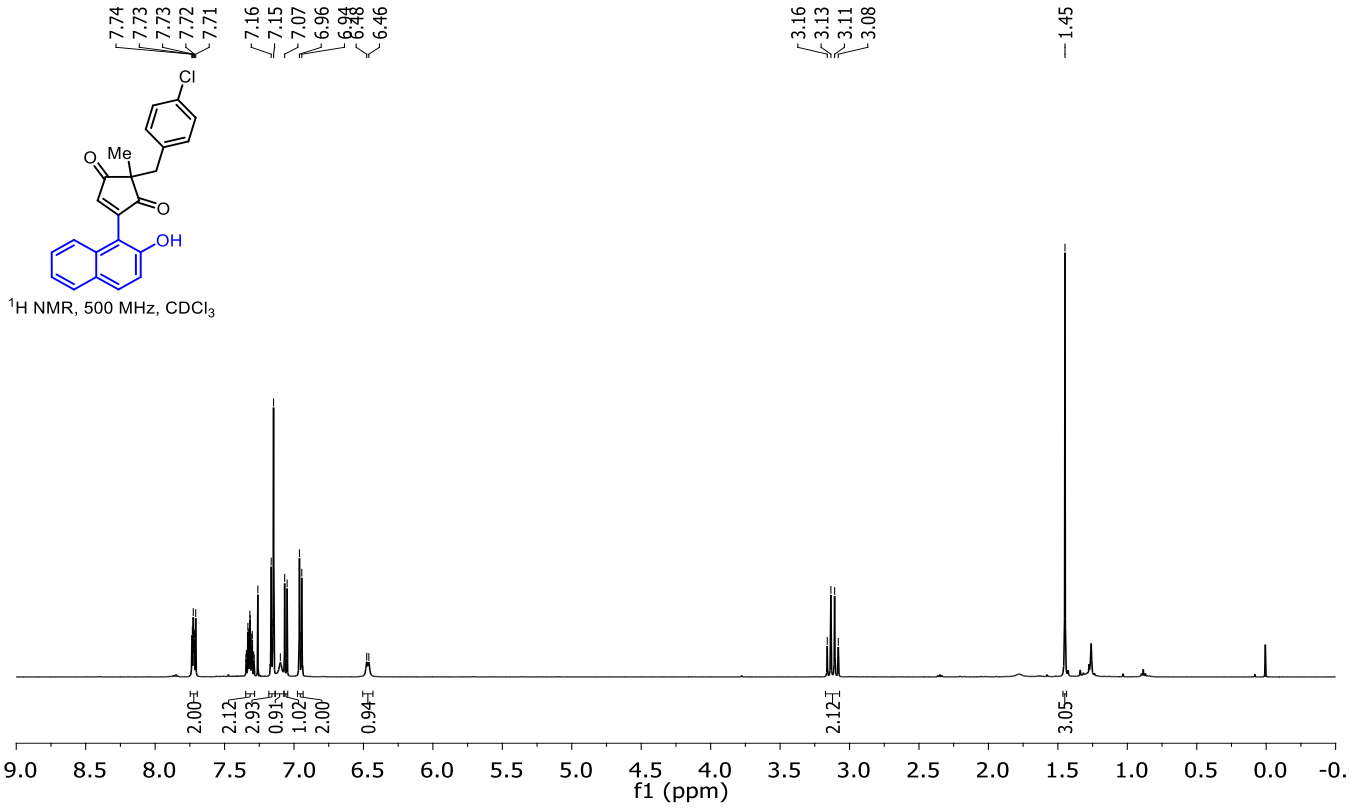


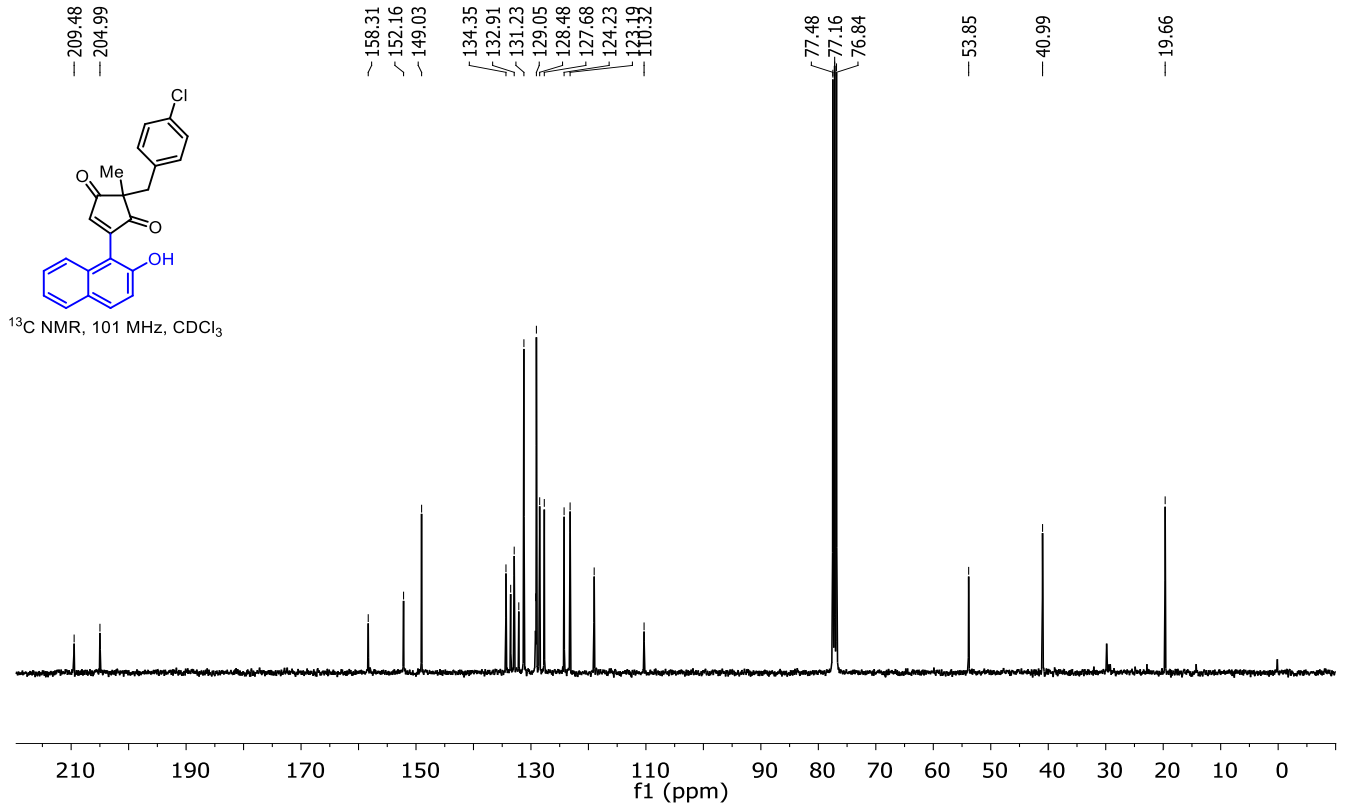




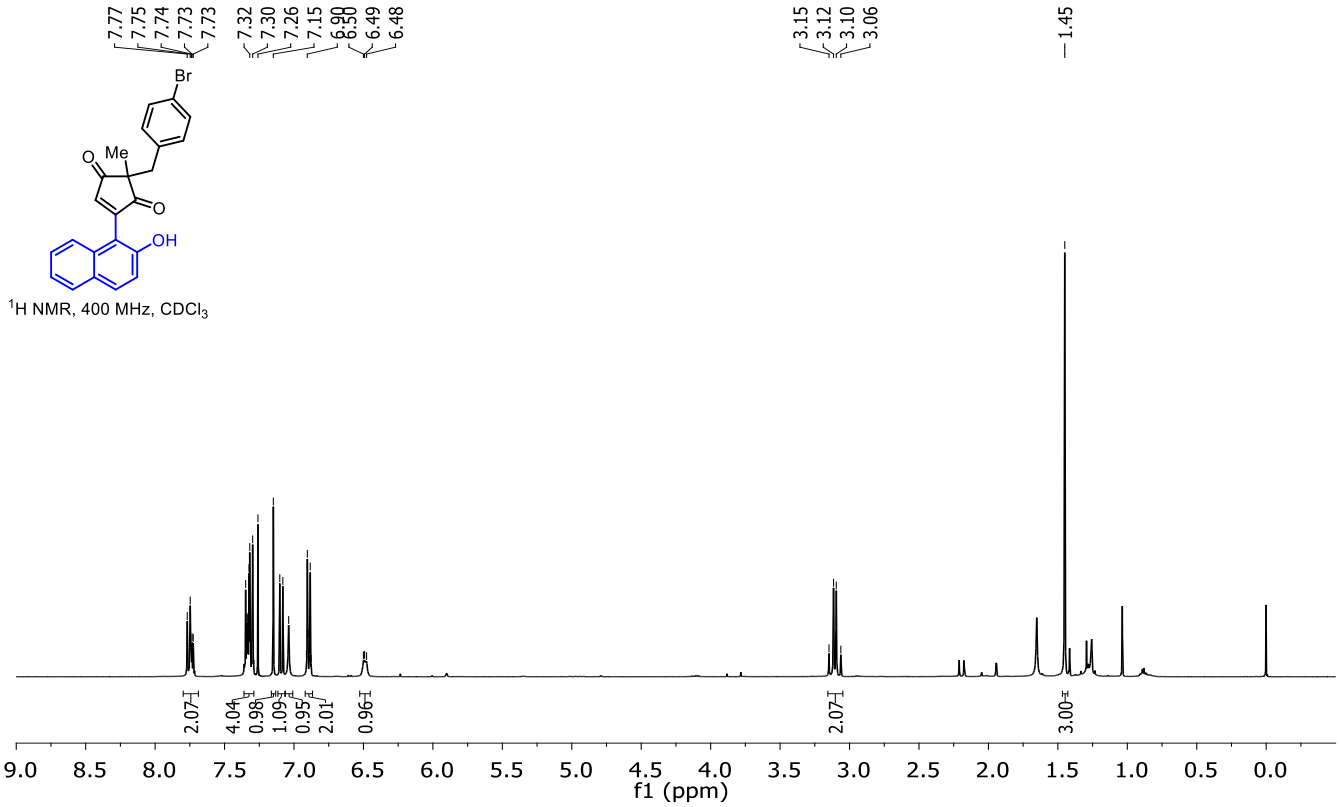
^{19}F NMR, 377 MHz, $CDCl_3$

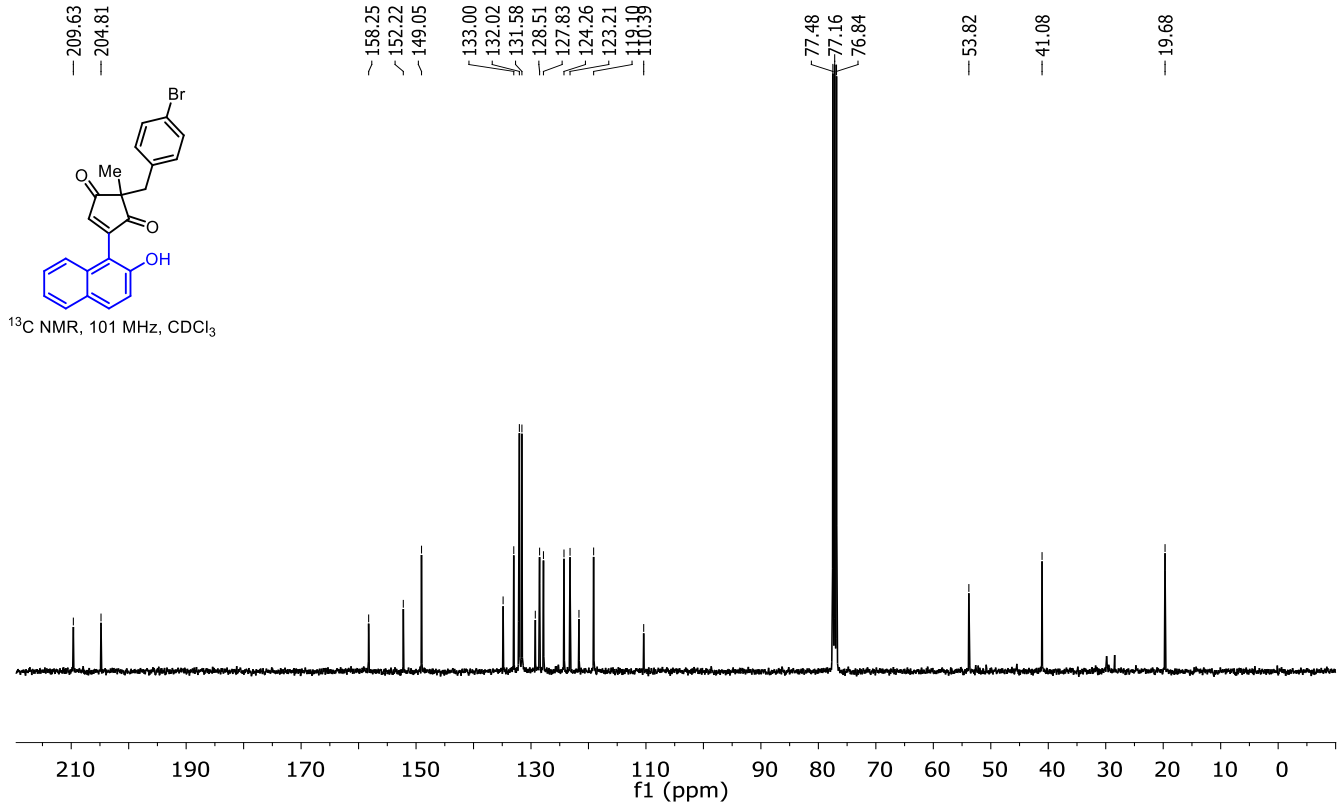
2-(4-Chlorobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3j):



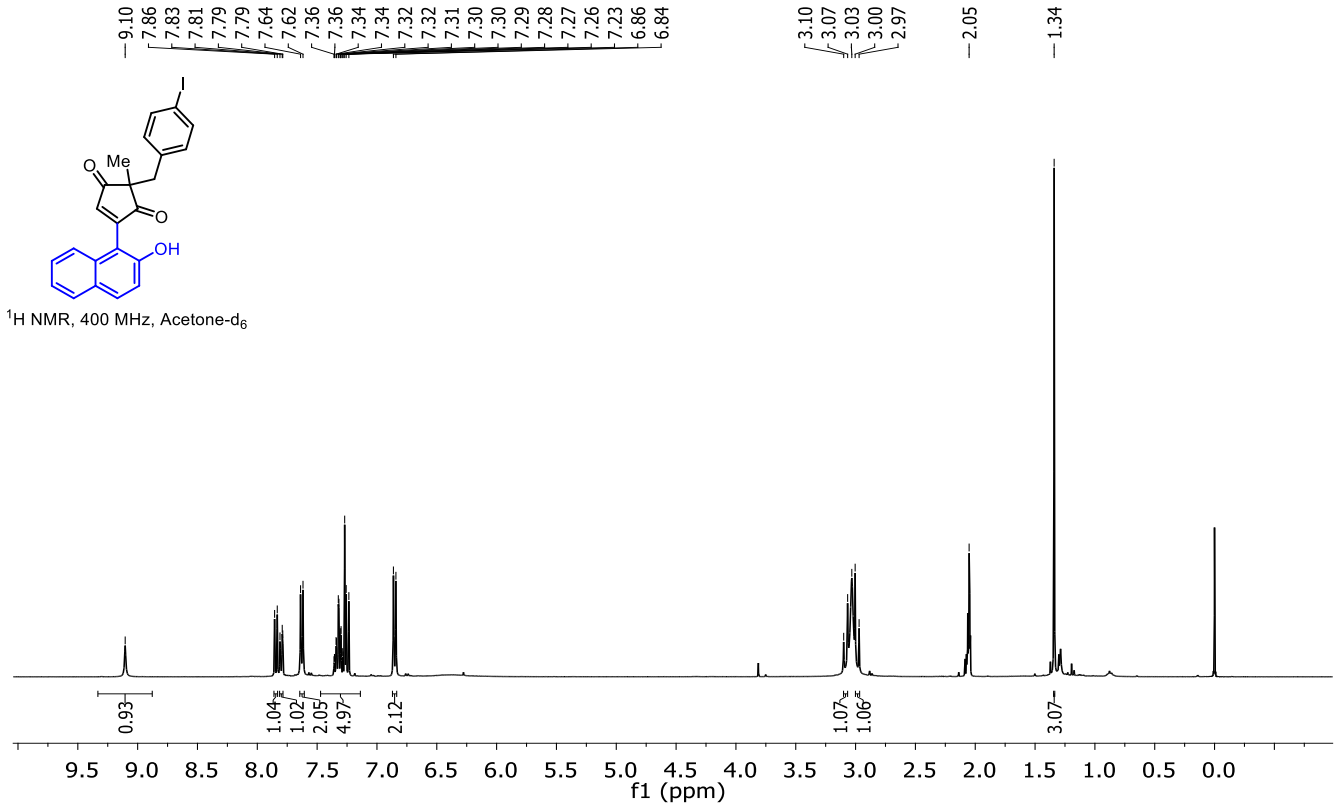


2-(4-Bromobenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3k):

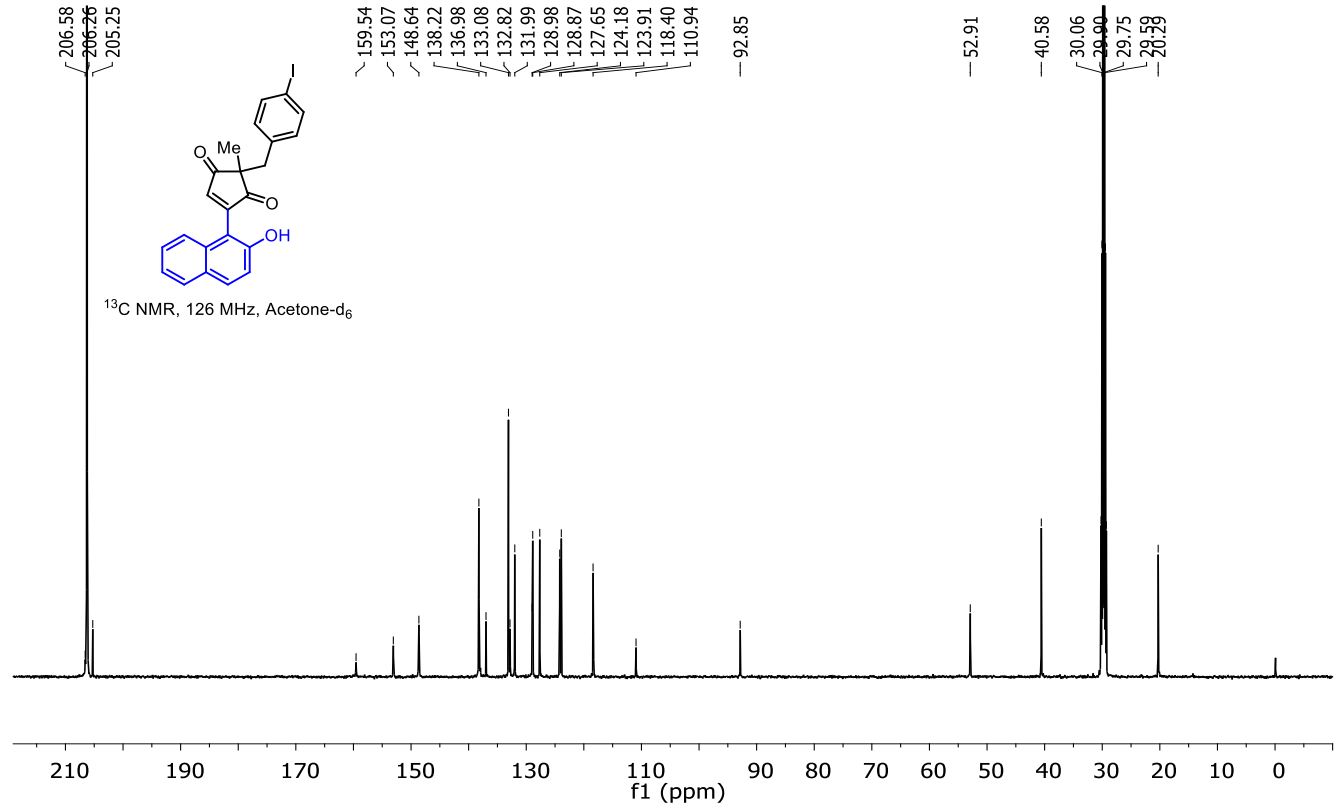




4-(2-Hydroxynaphthalen-1-yl)-2-(4-iodobenzyl)-2-methylcyclopent-4-ene-1,3-dione (3l):

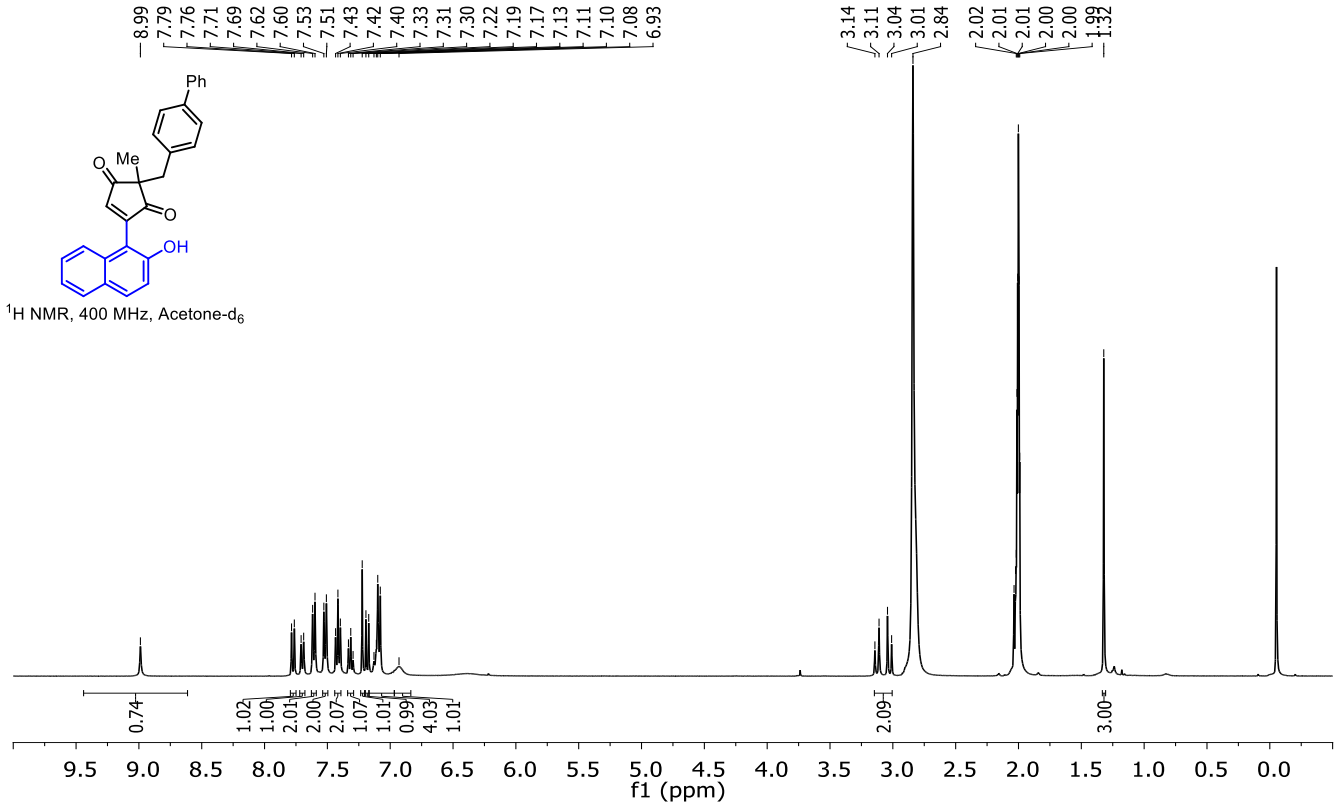


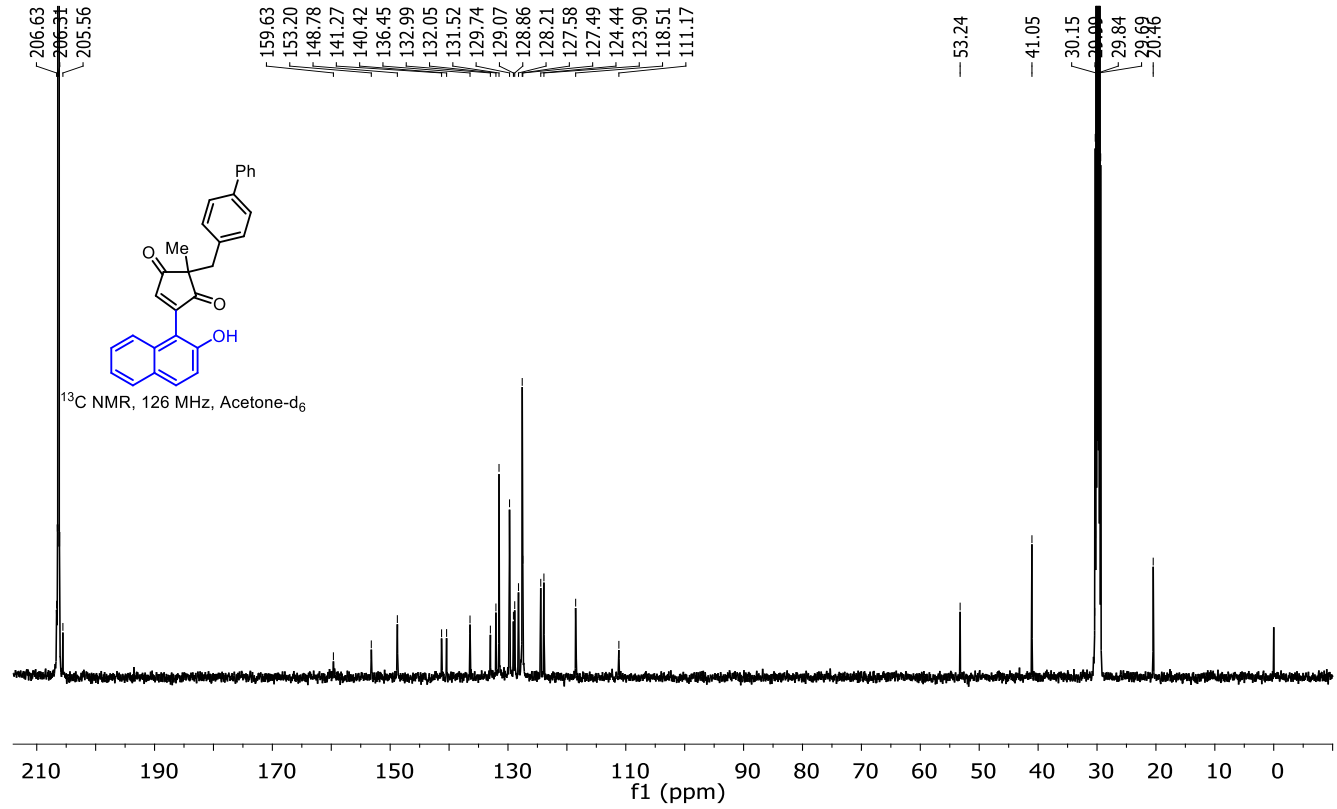
^{1}H NMR, 400 MHz, Acetone-d_6



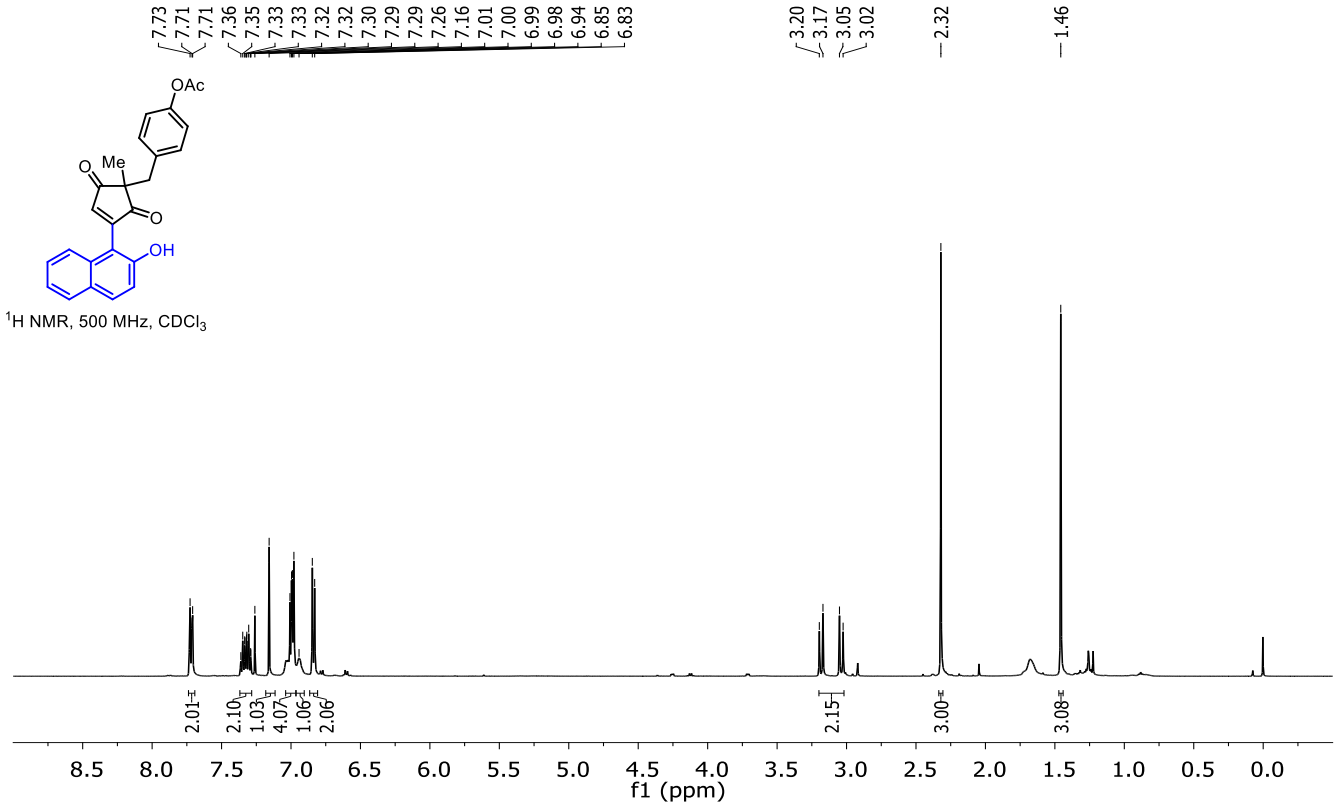
^{13}C NMR, 126 MHz, Acetone-d_6

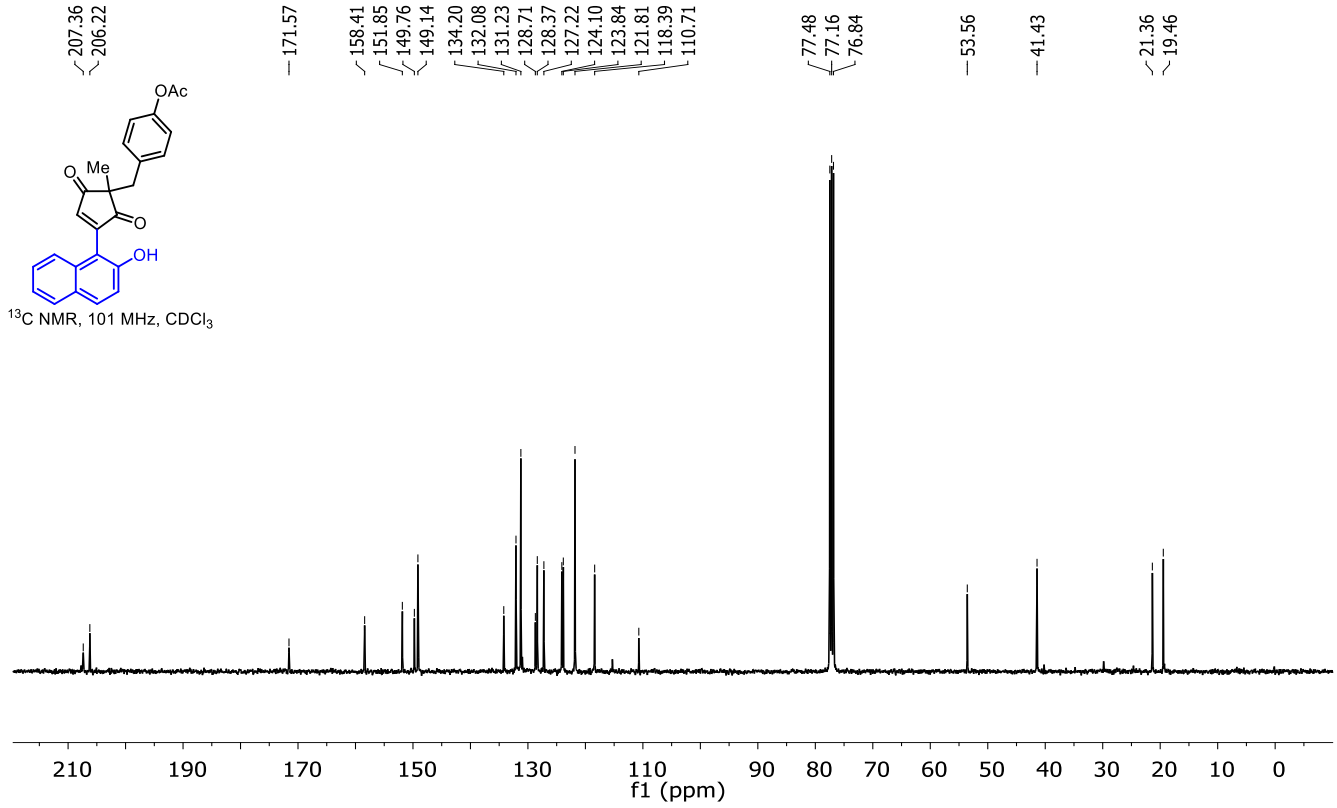
2-([1,1'-Biphenyl]-4-ylmethyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3m):



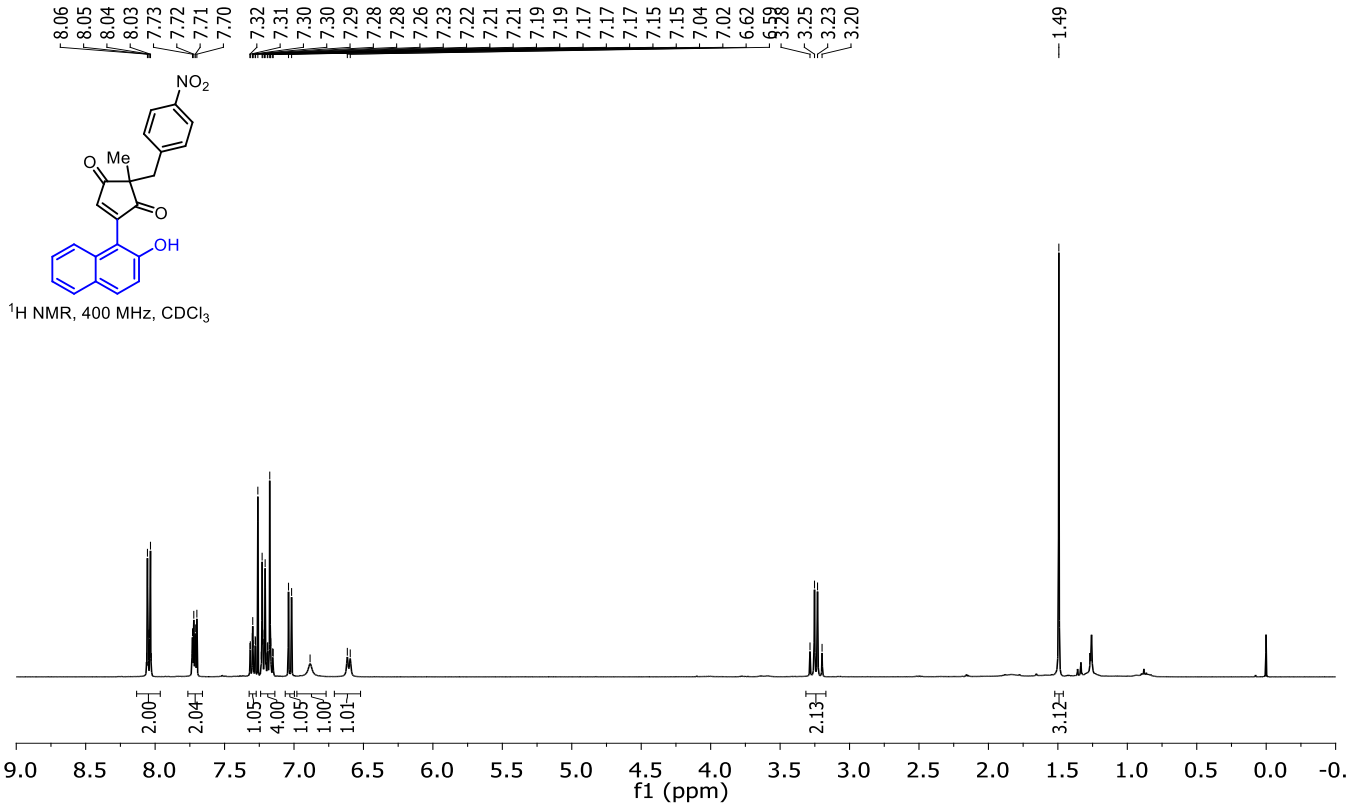


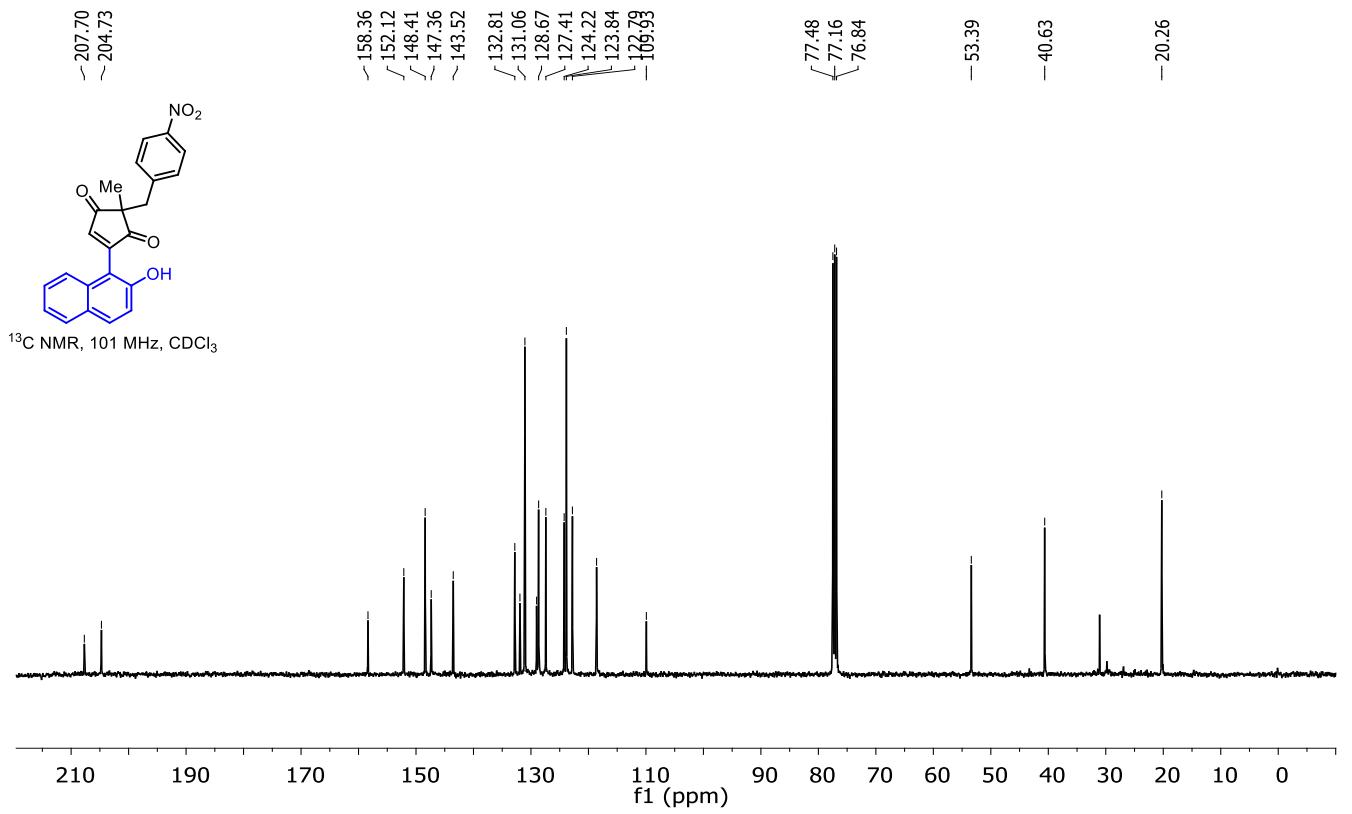
4-((3-(2-Hydroxynaphthalen-1-yl)-1-methyl-2,5-dioxocyclopent-3-en-1-yl)methyl)phenyl acetate (3n):



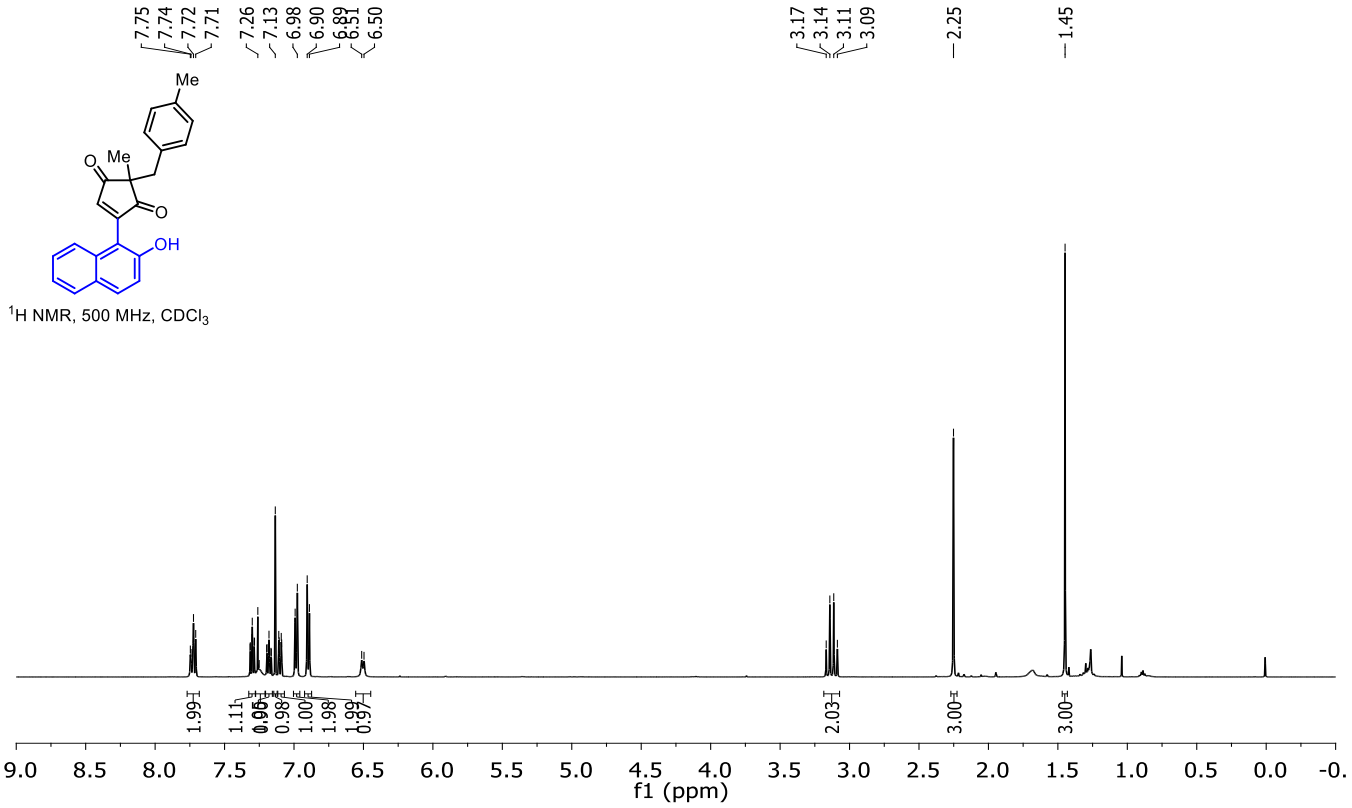


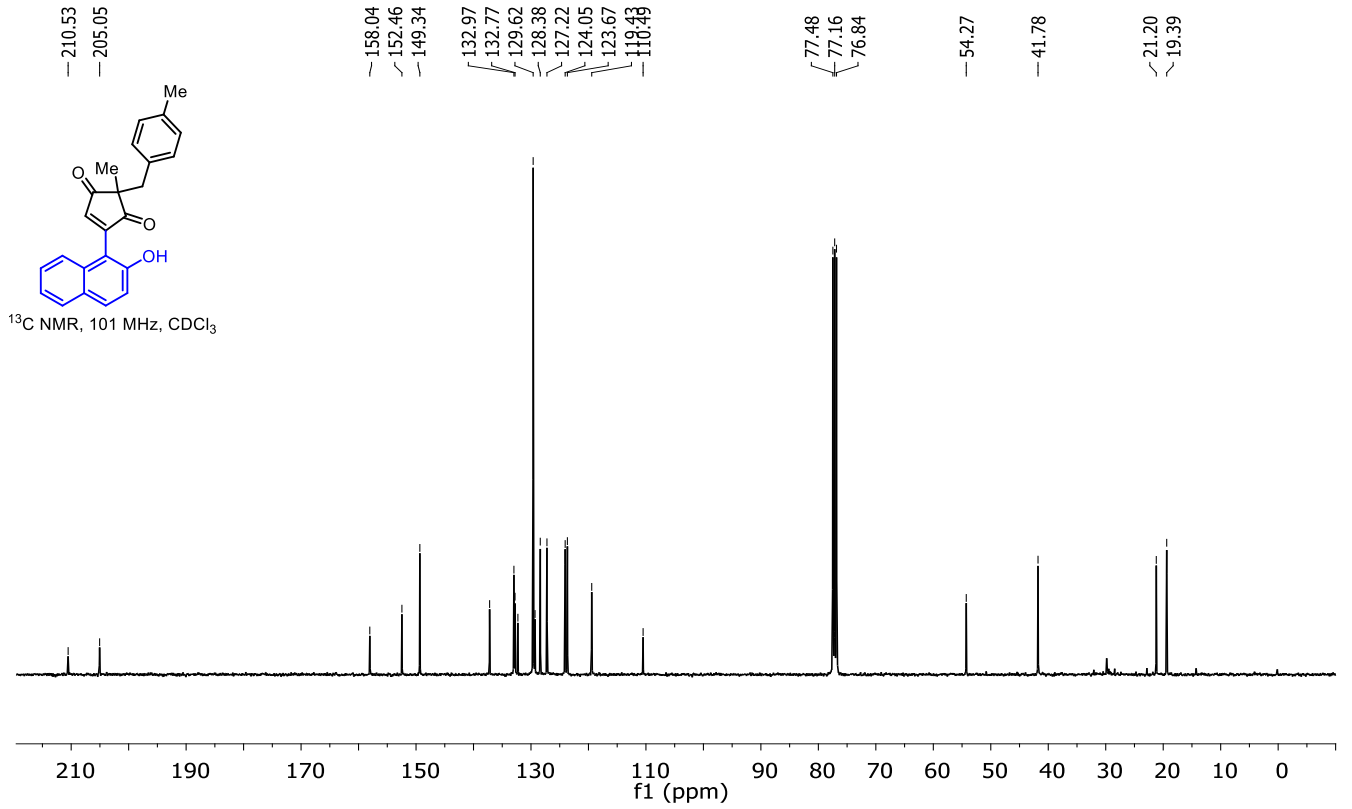
4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(4-nitrobenzyl)cyclopent-4-ene-1,3-dione (3o):



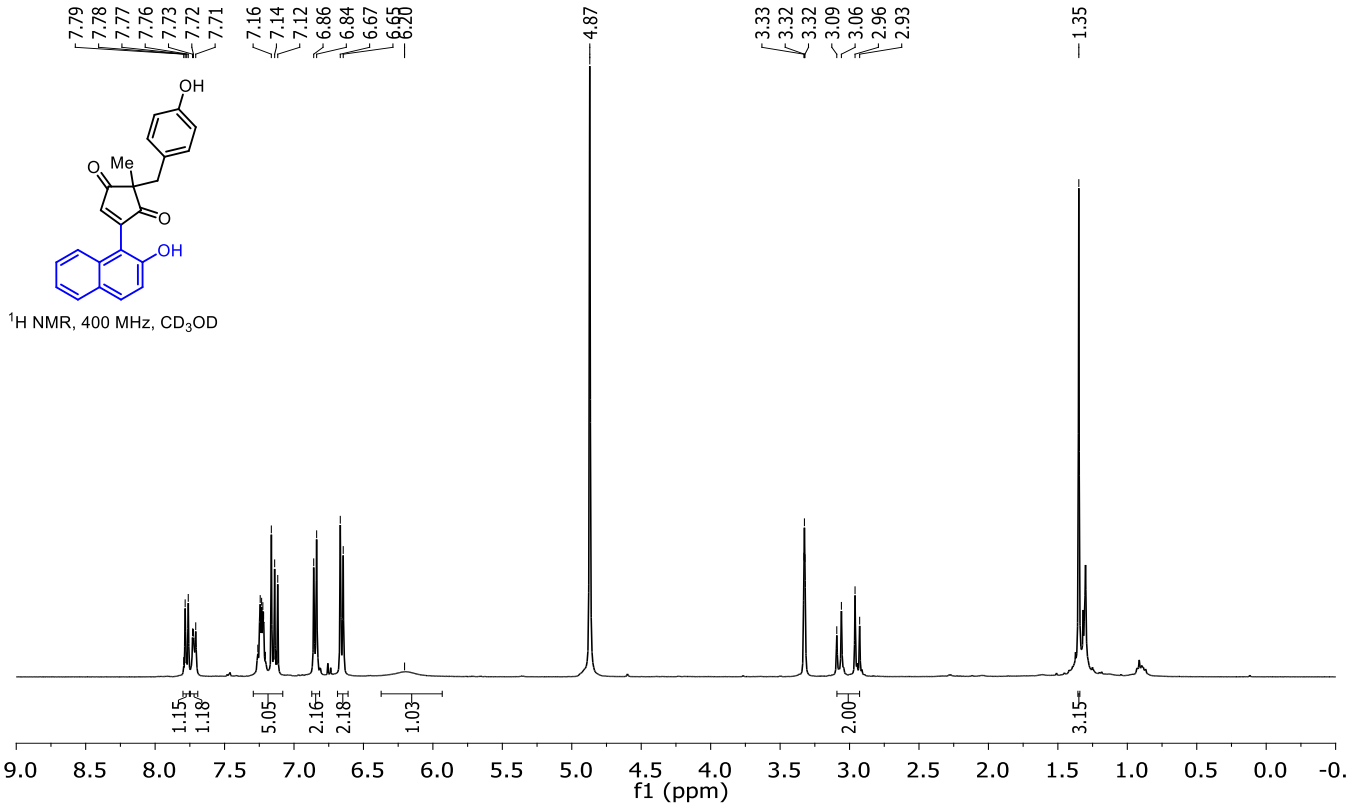


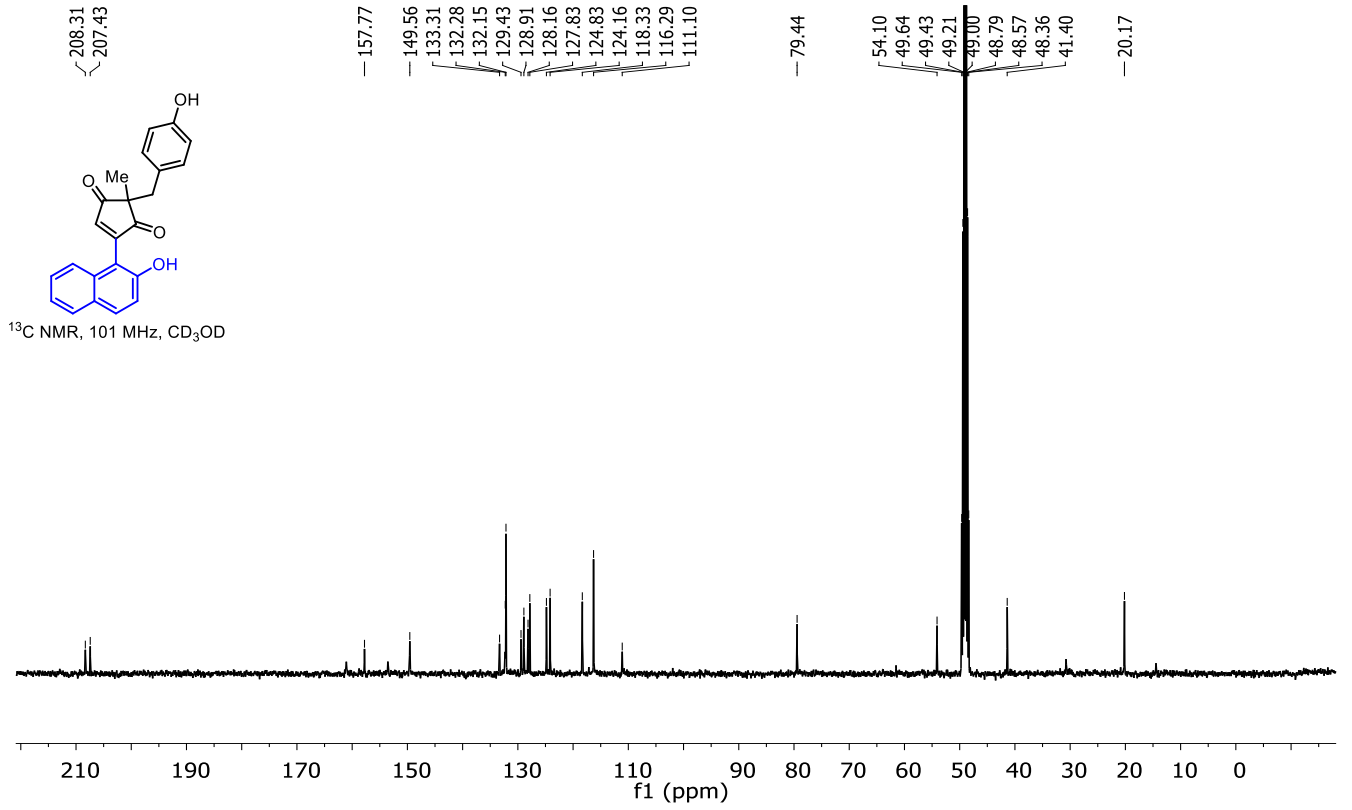
4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(4-methylbenzyl)cyclopent-4-ene-1,3-dione (3q):



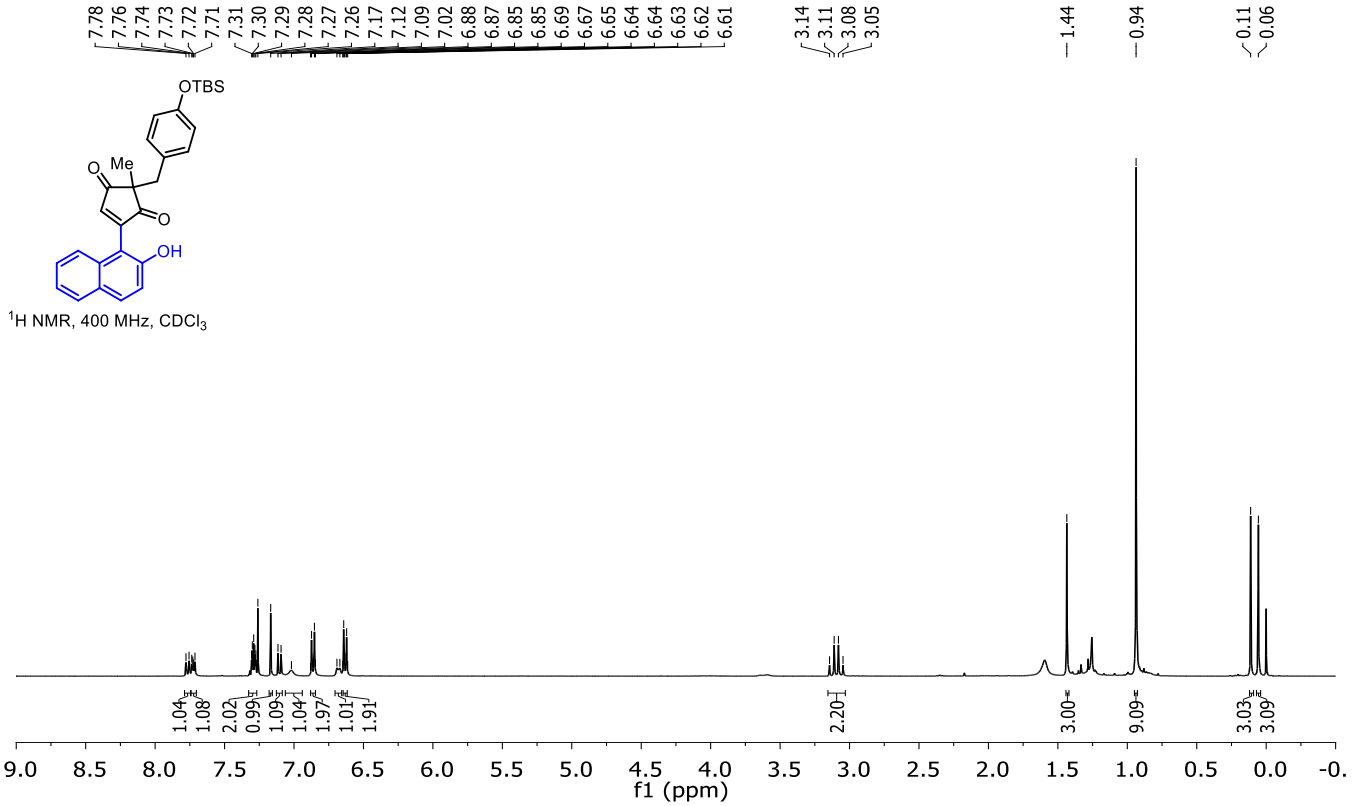


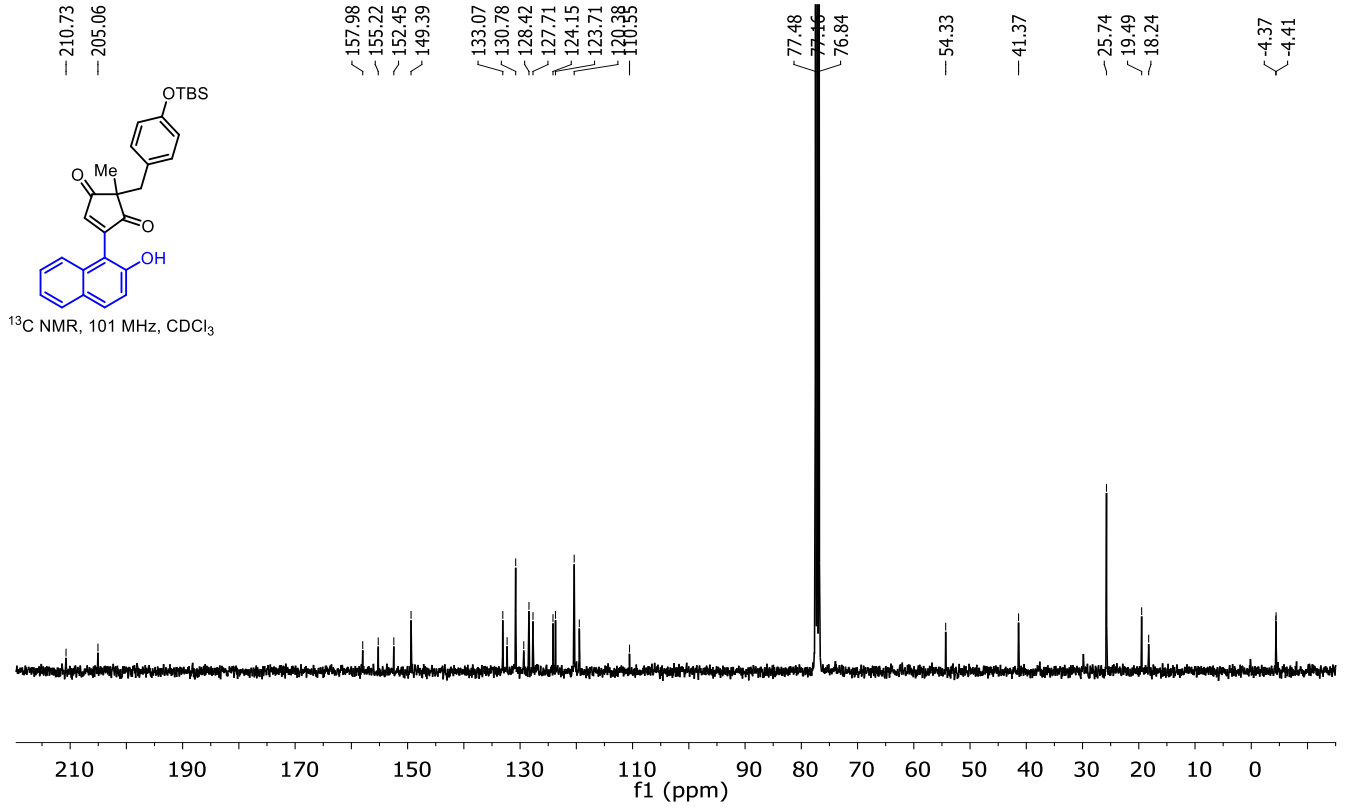
2-(4-Hydroxybenzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3r):



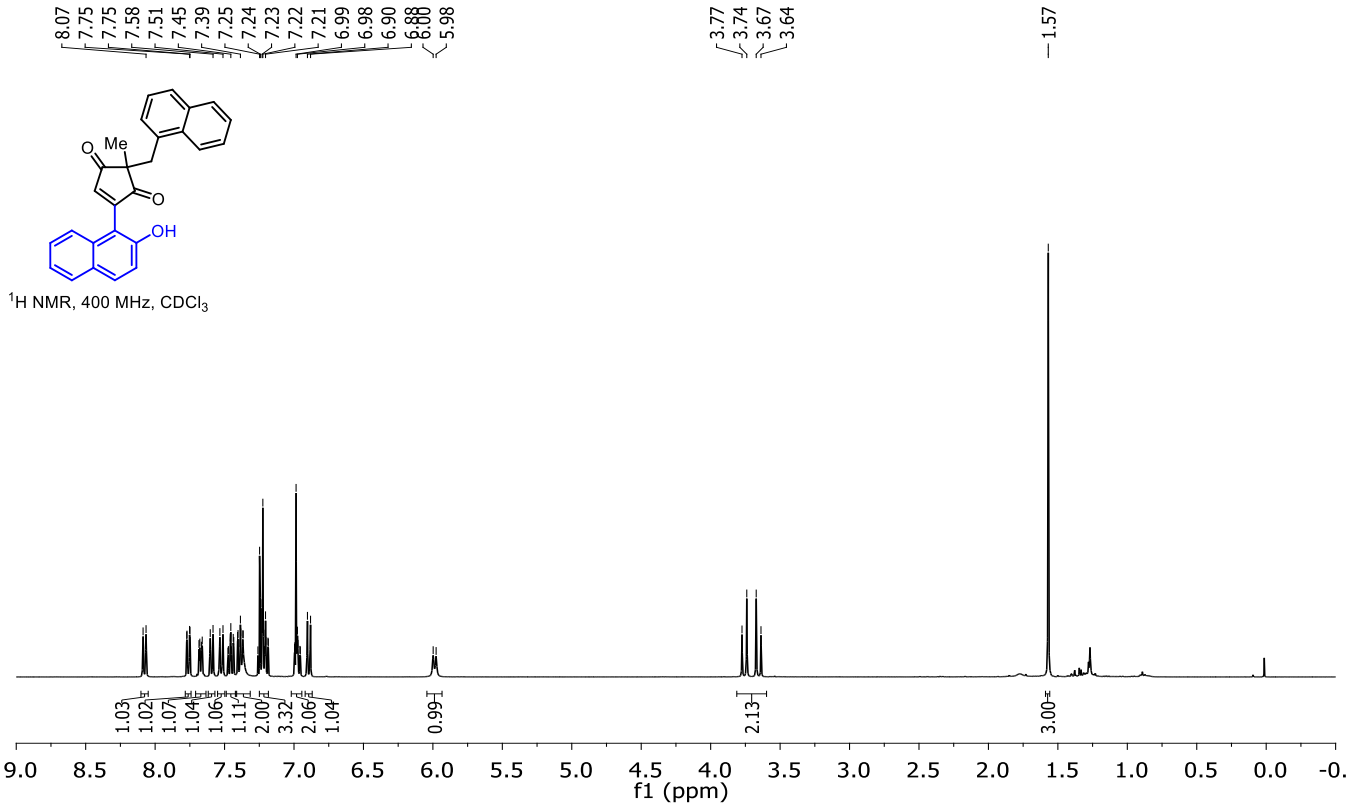


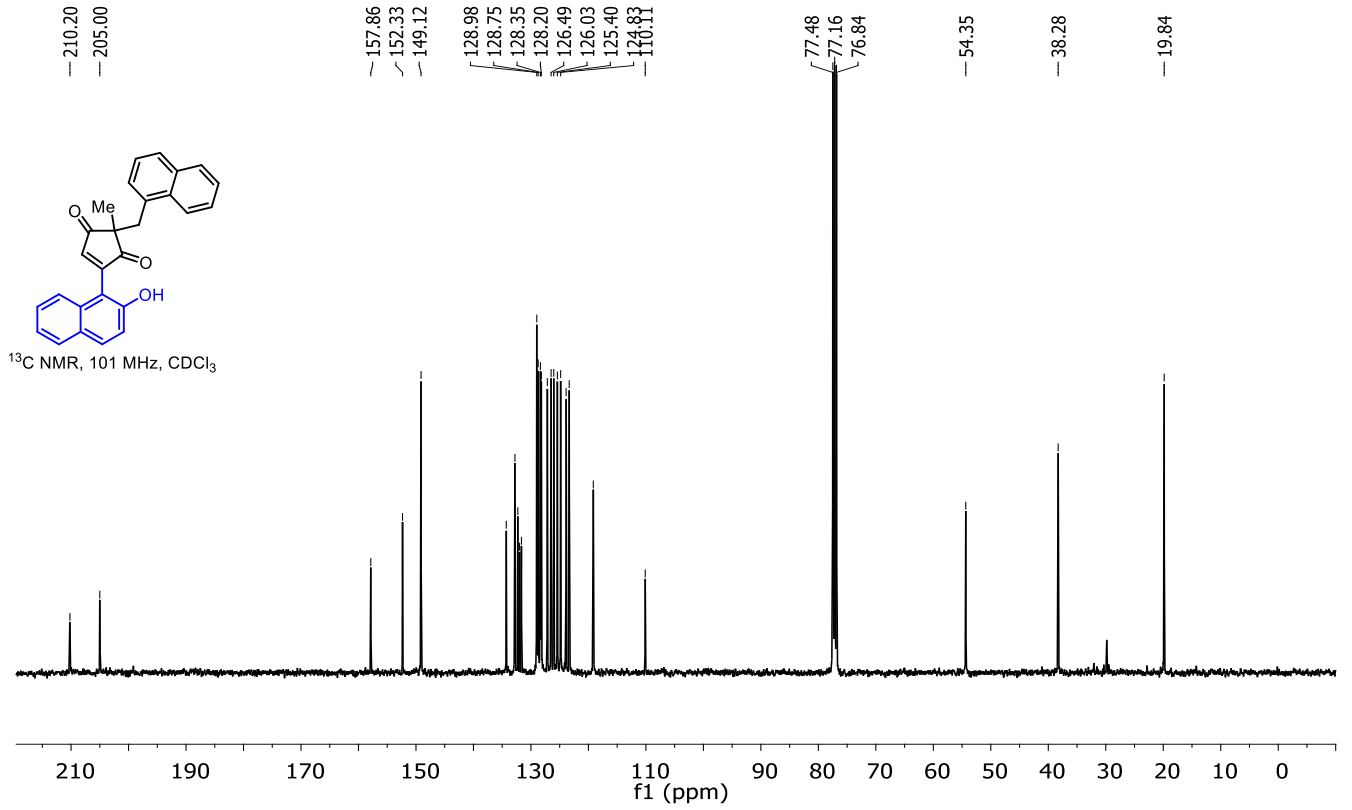
2-(4-((*tert*-Butyldimethylsilyl)oxy)benzyl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3s):



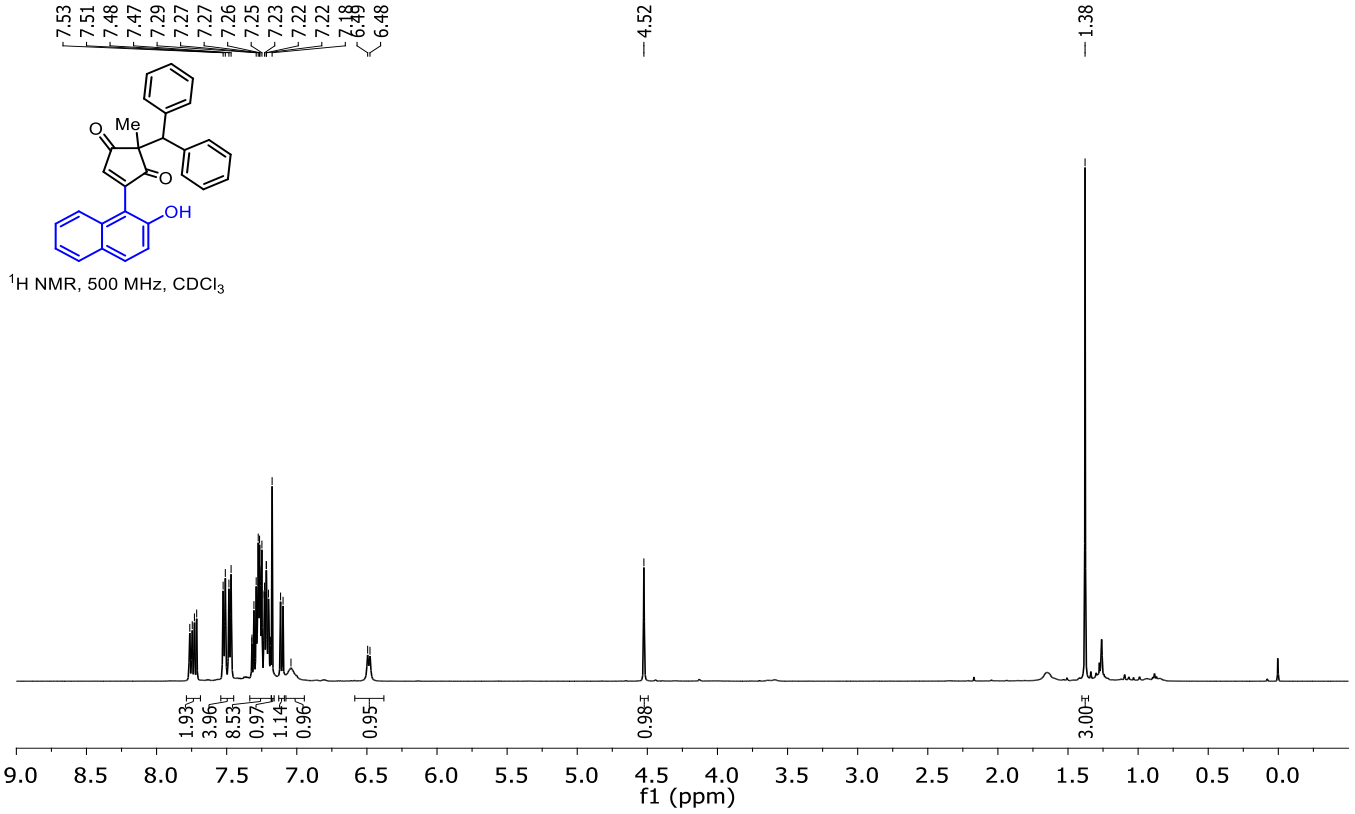


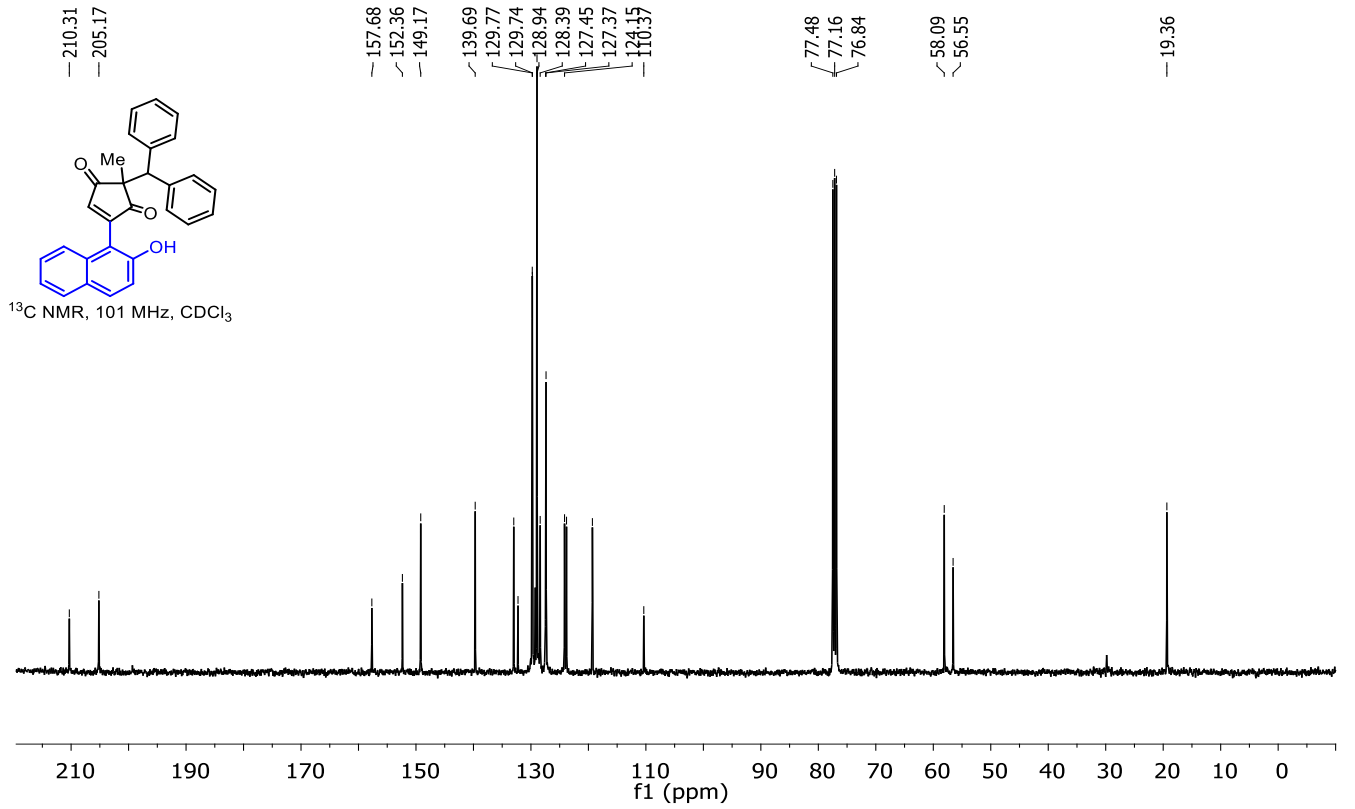
4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(naphthalen-1-ylmethyl)cyclopent-4-ene-1,3-dione (3t):



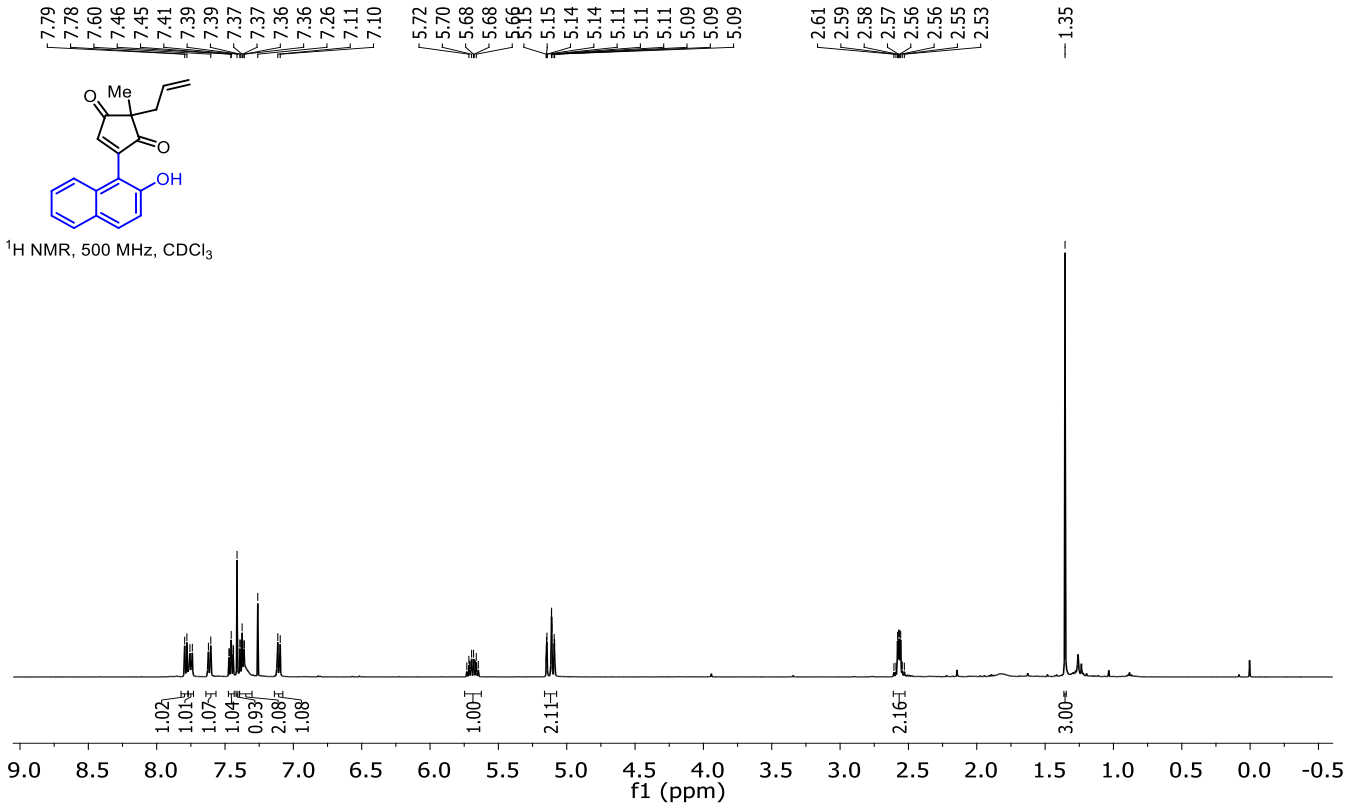


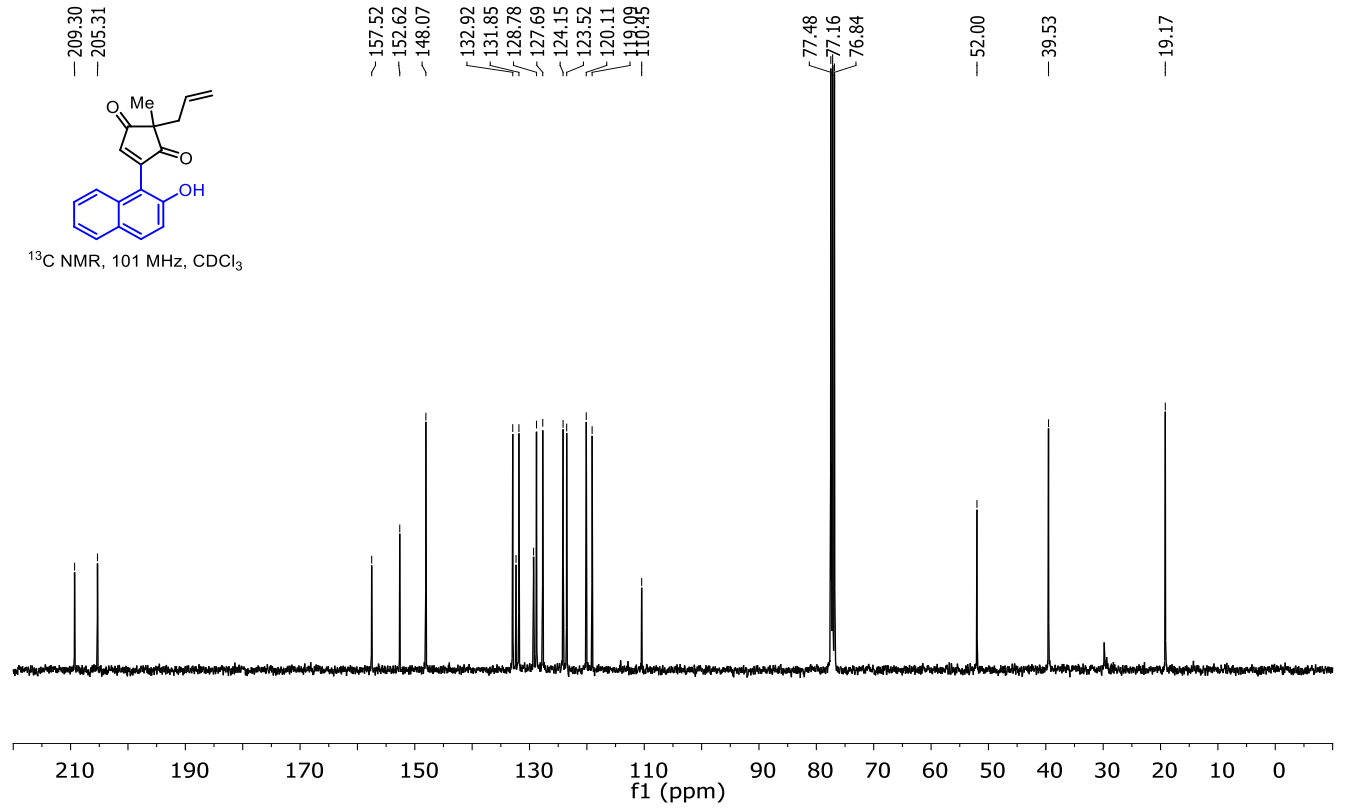
2-Benzhydryl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3u):



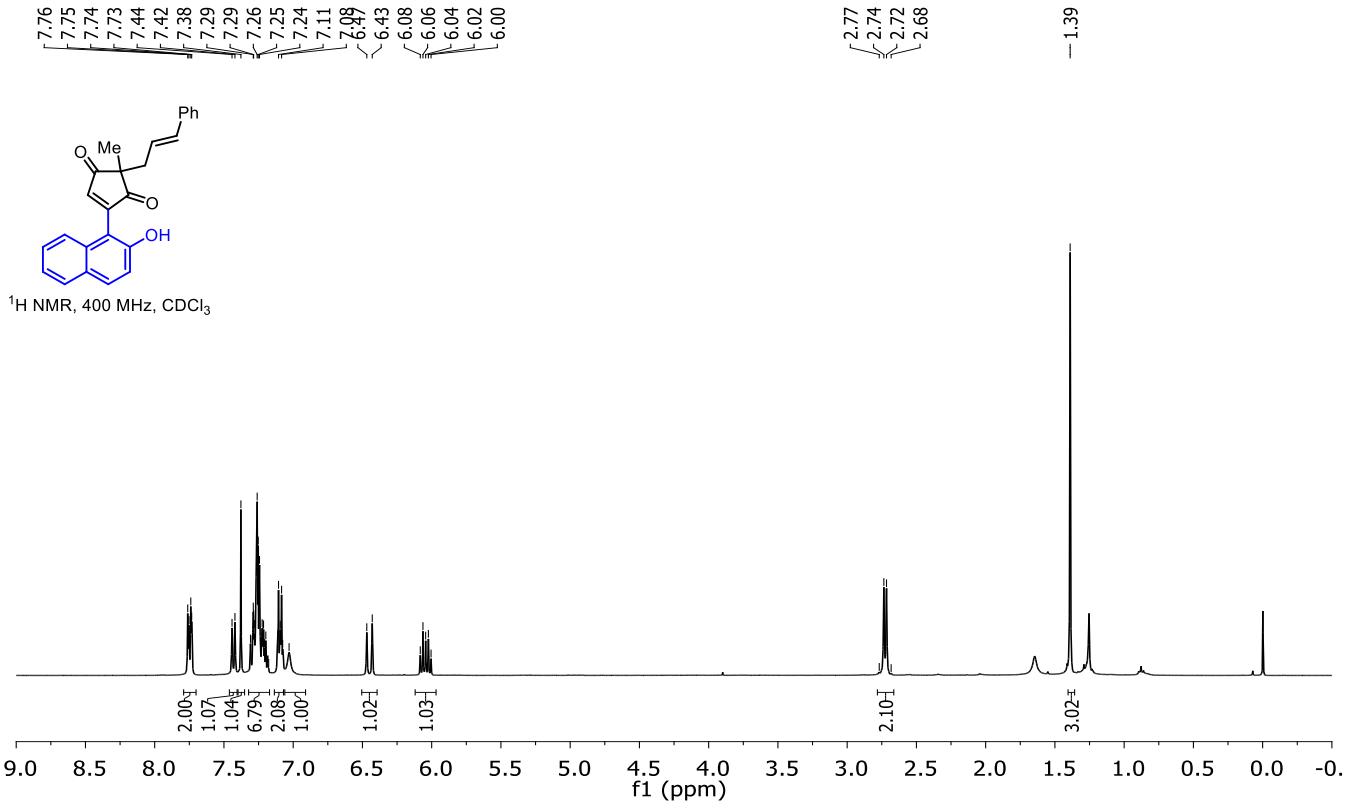


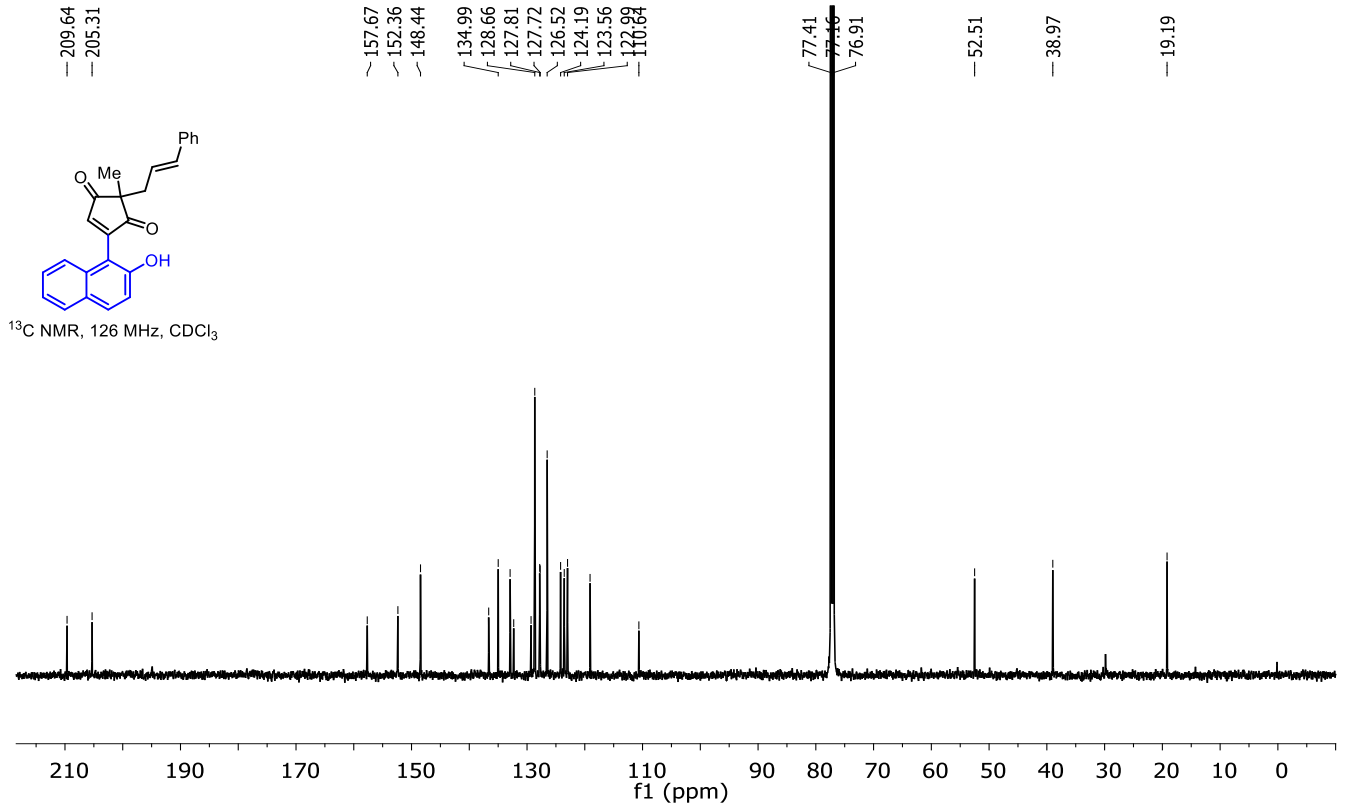
2-Allyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3v):



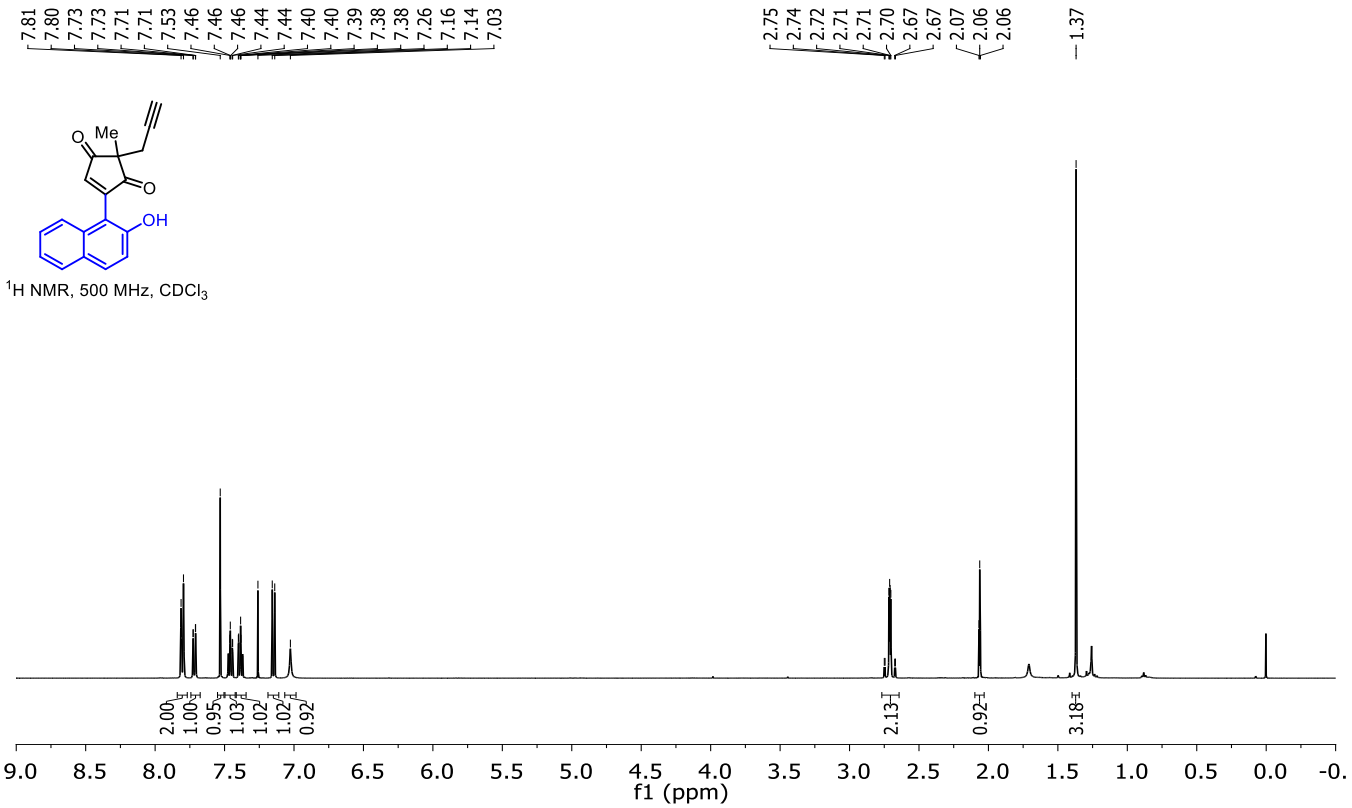


2-Cinnamyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3w):

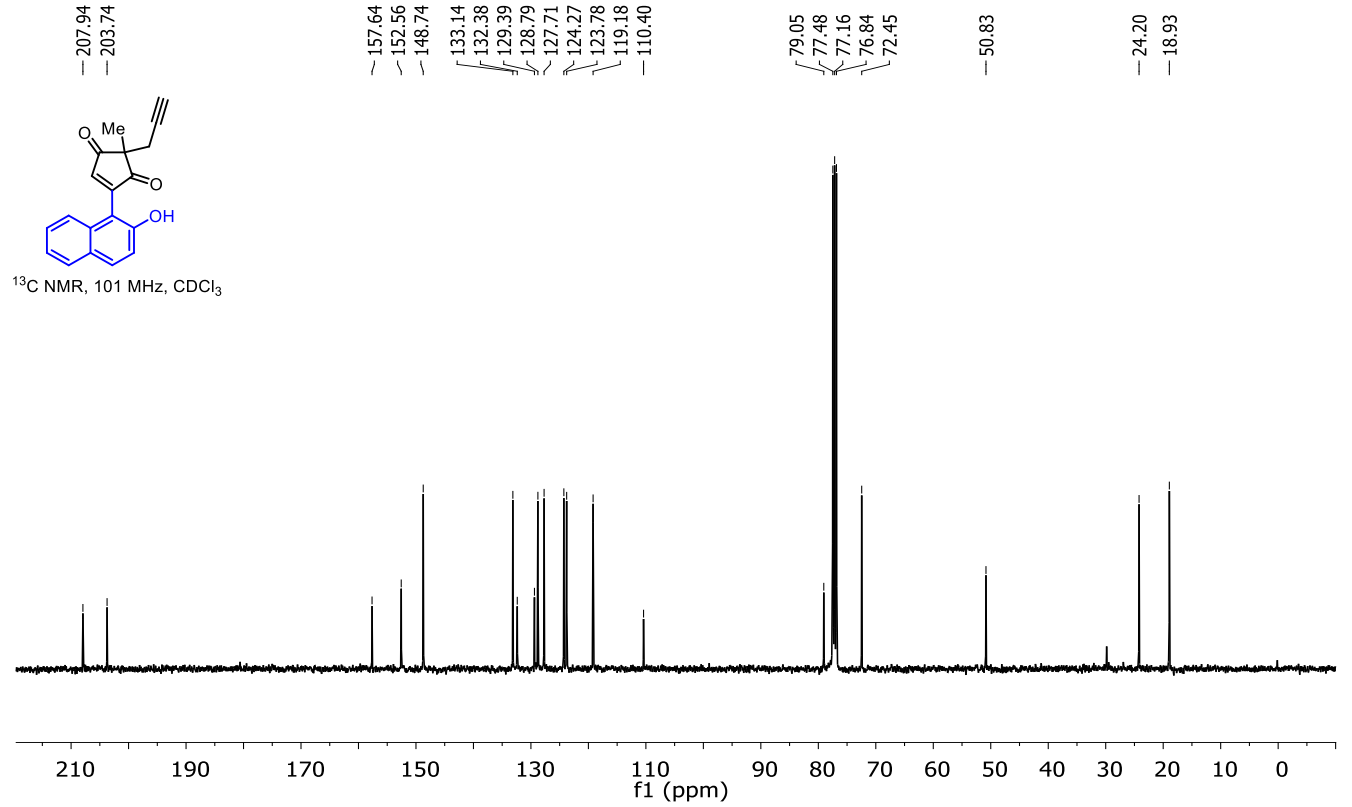




4-(2-Hydroxynaphthalen-1-yl)-2-methyl-2-(prop-2-yn-1-yl)cyclopent-4-ene-1,3-dione (3x):

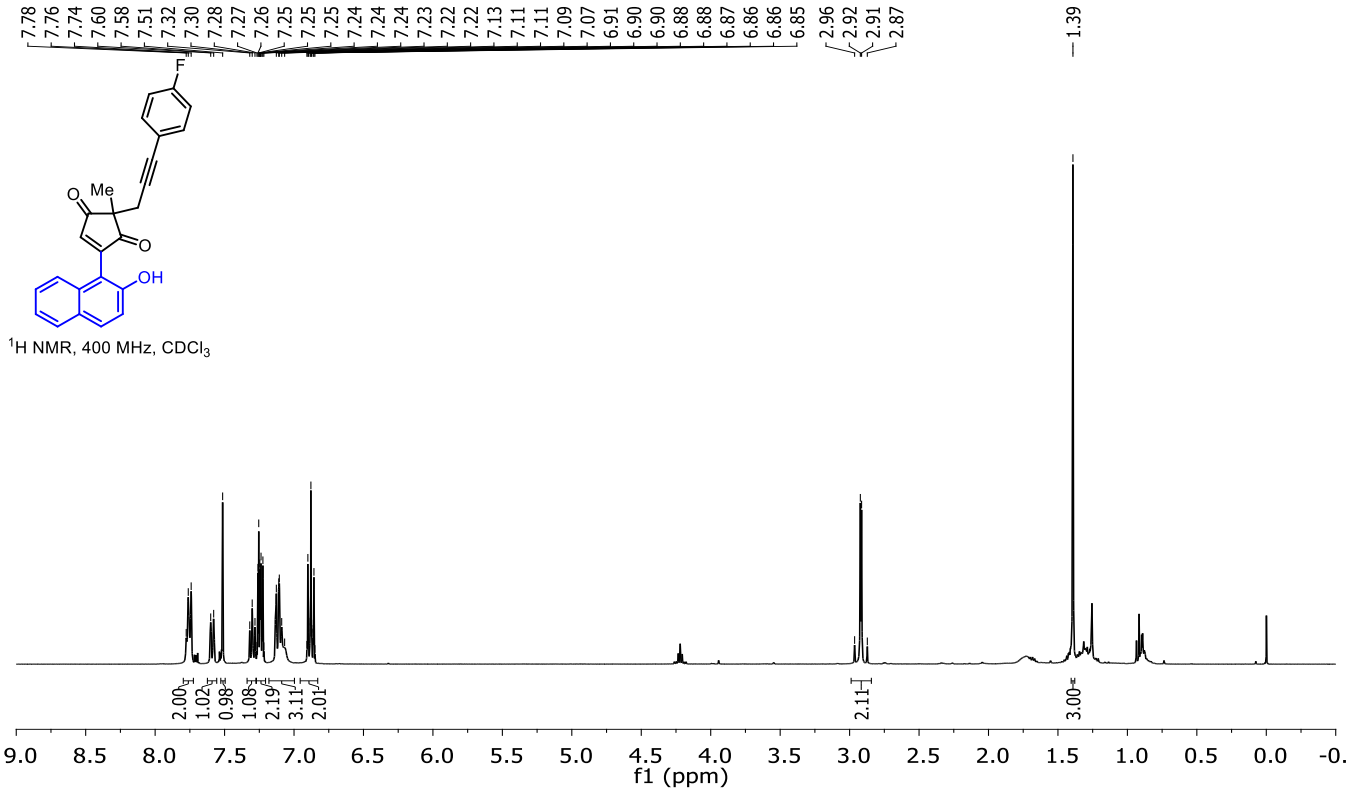


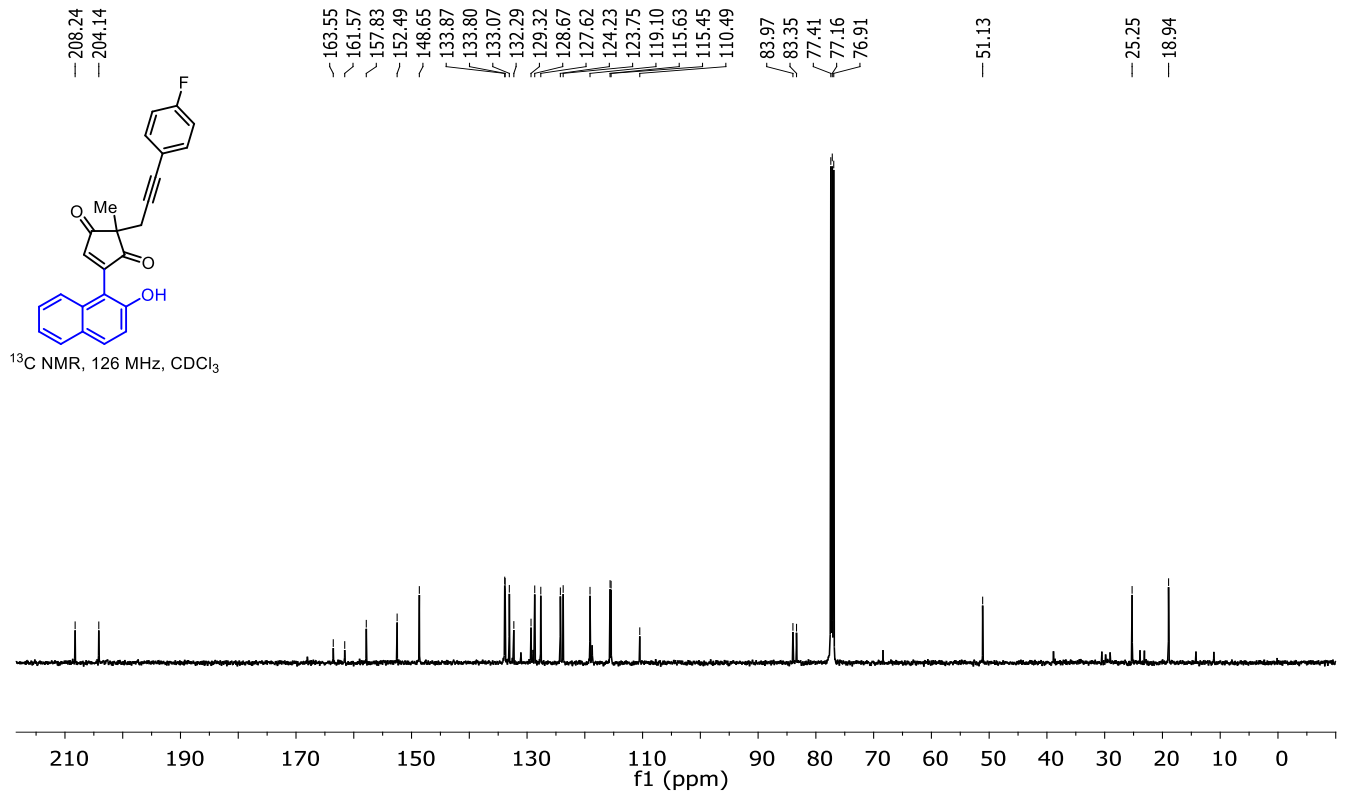
^{1}H NMR, 500 MHz, $CDCl_3$

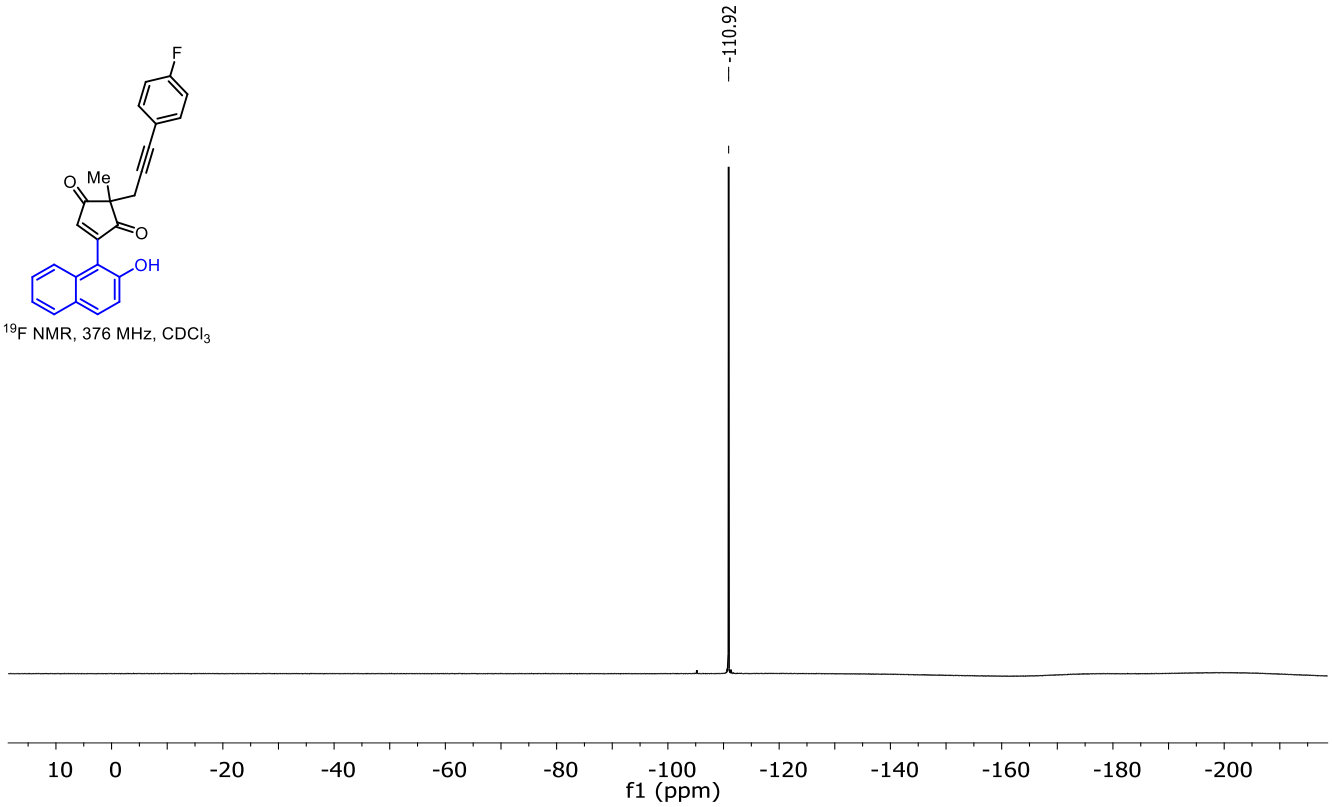


^{13}C NMR, 101 MHz, $CDCl_3$

2-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3y):

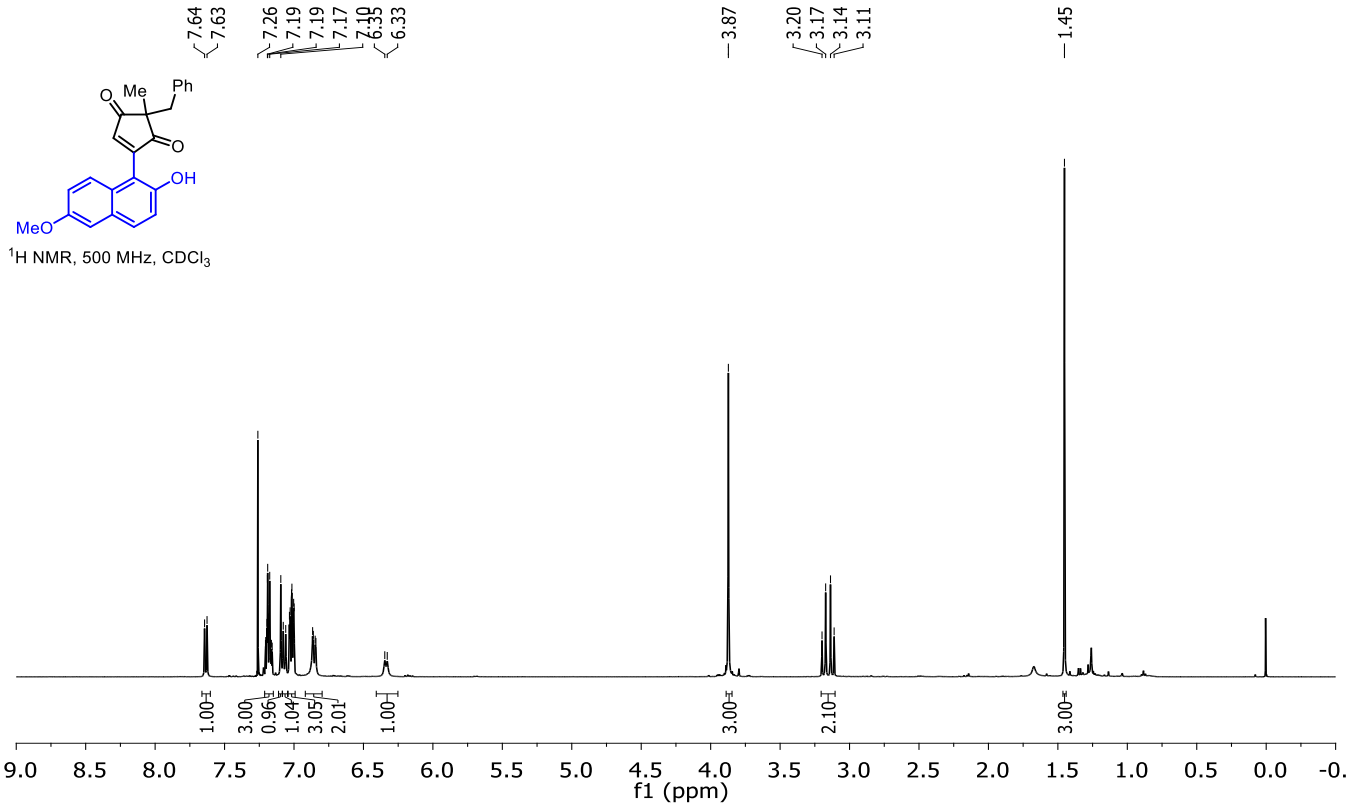


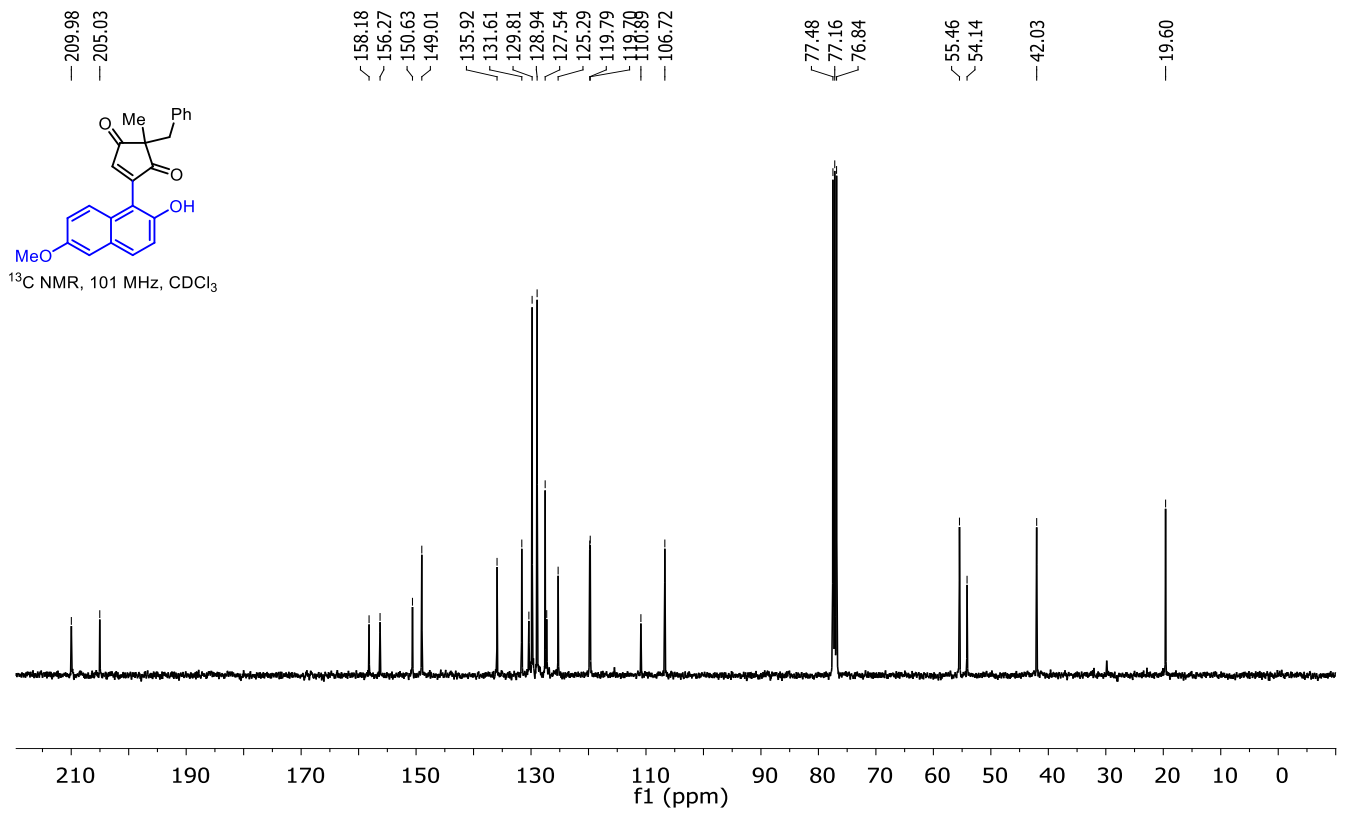




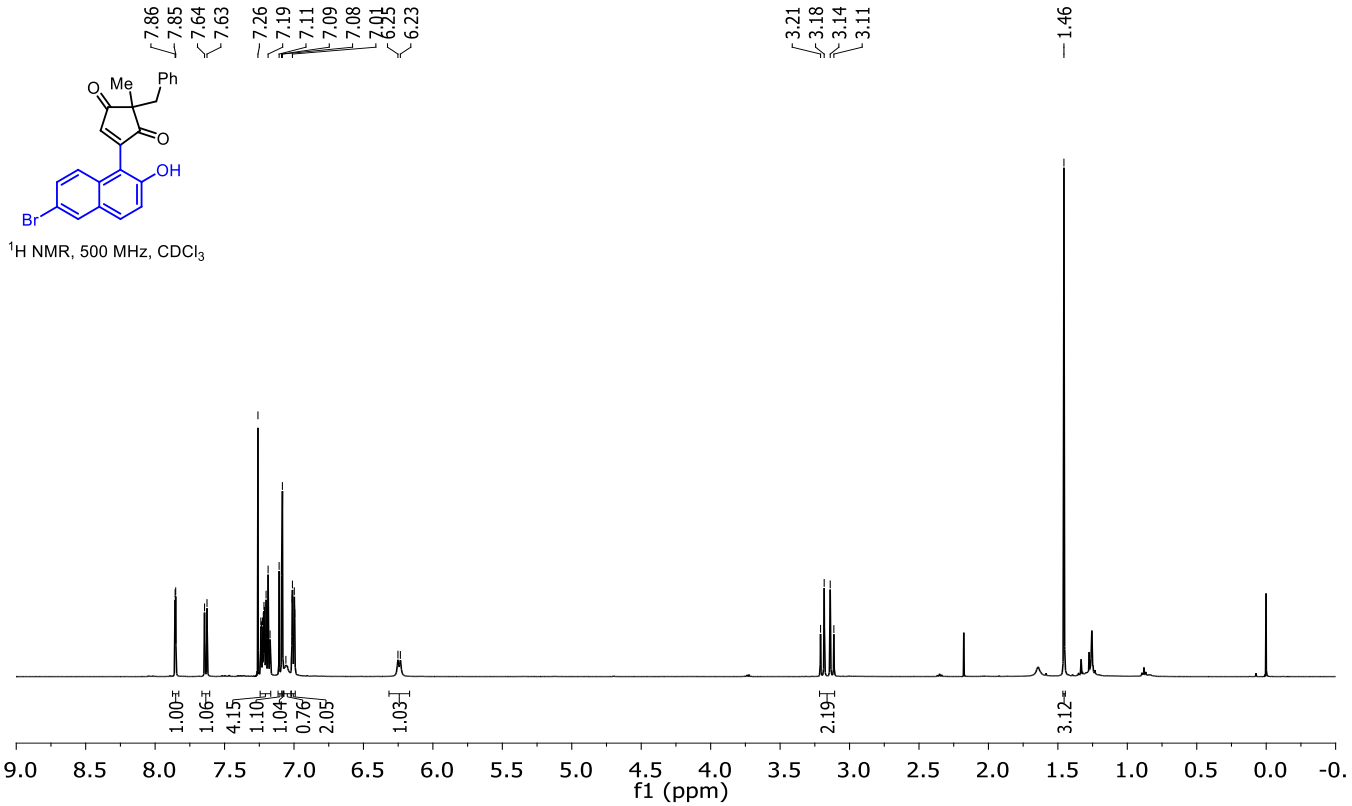
^{19}F NMR, 376 MHz, $CDCl_3$

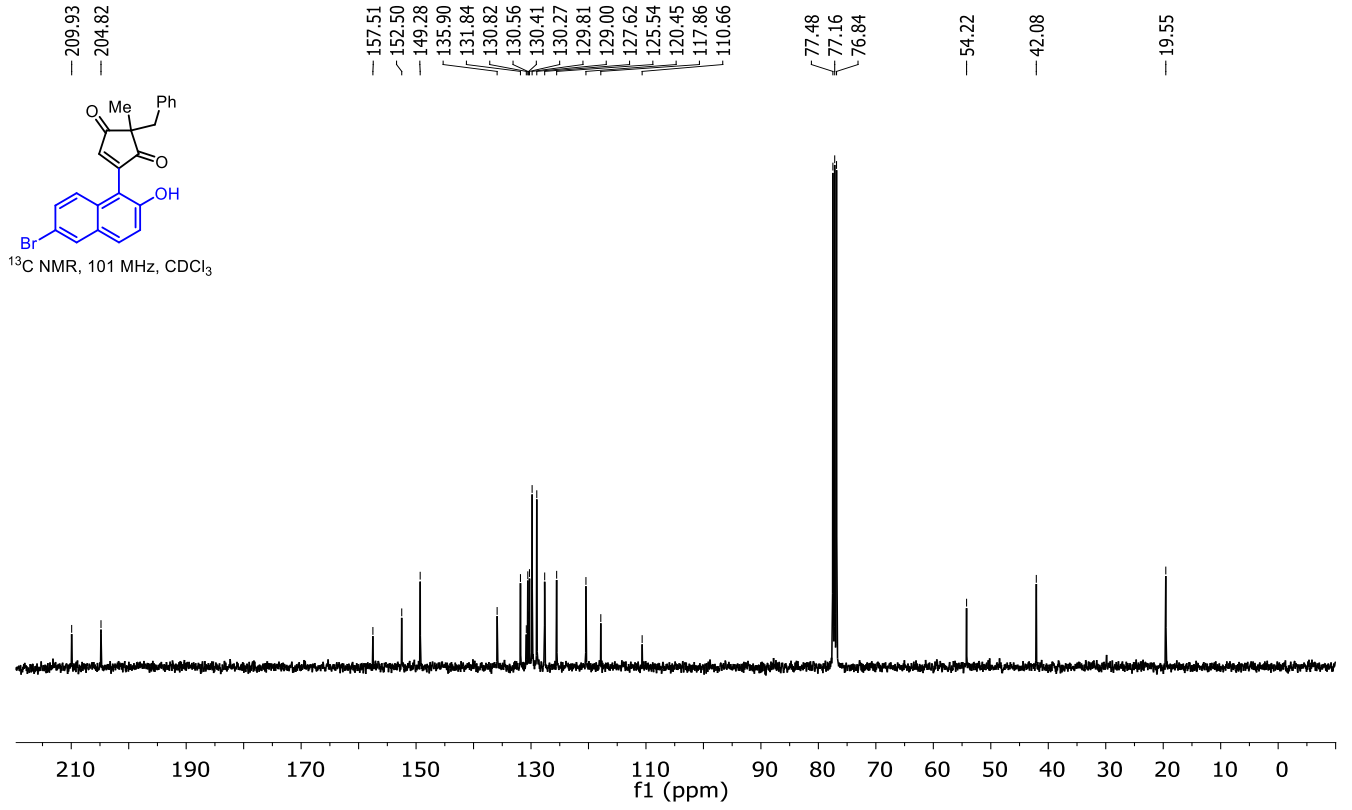
2-Benzyl-4-(2-hydroxy-6-methoxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3aa):



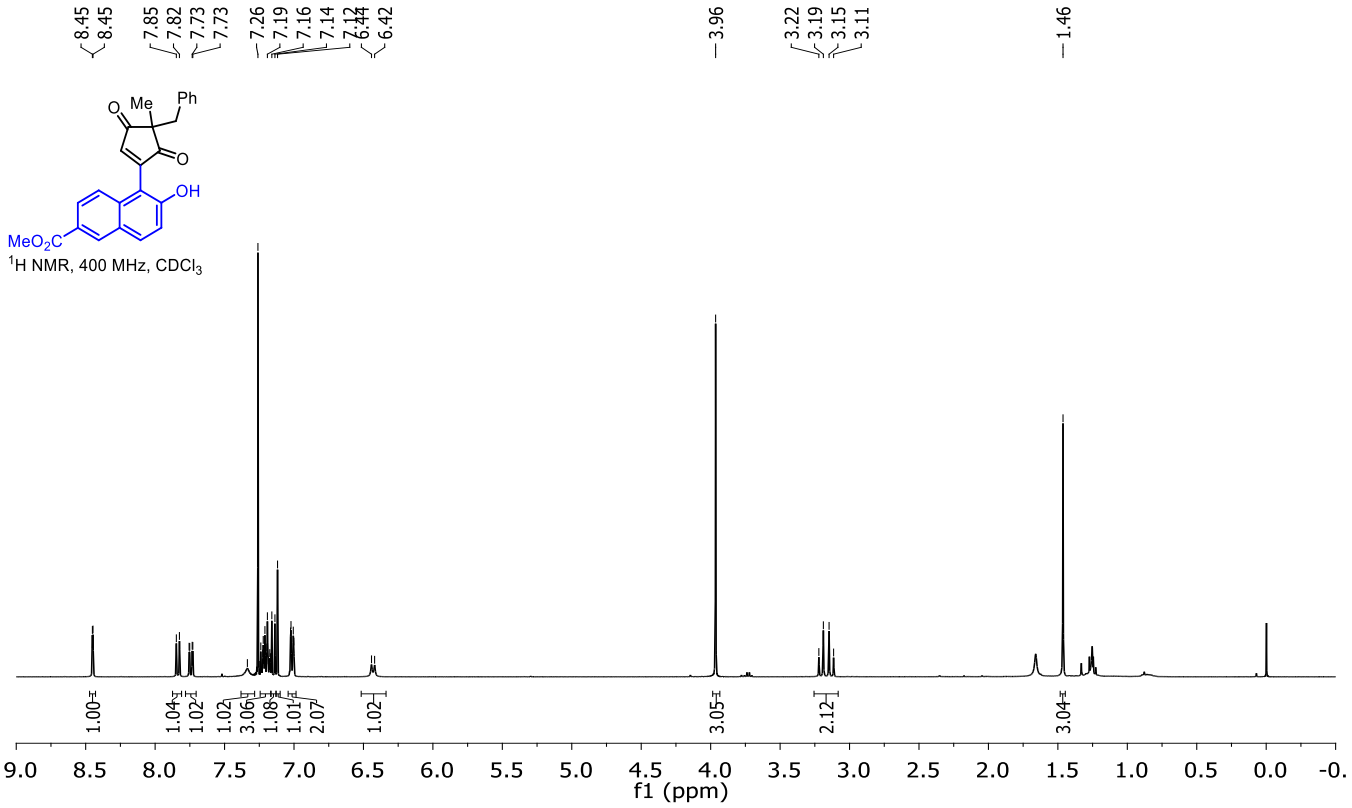


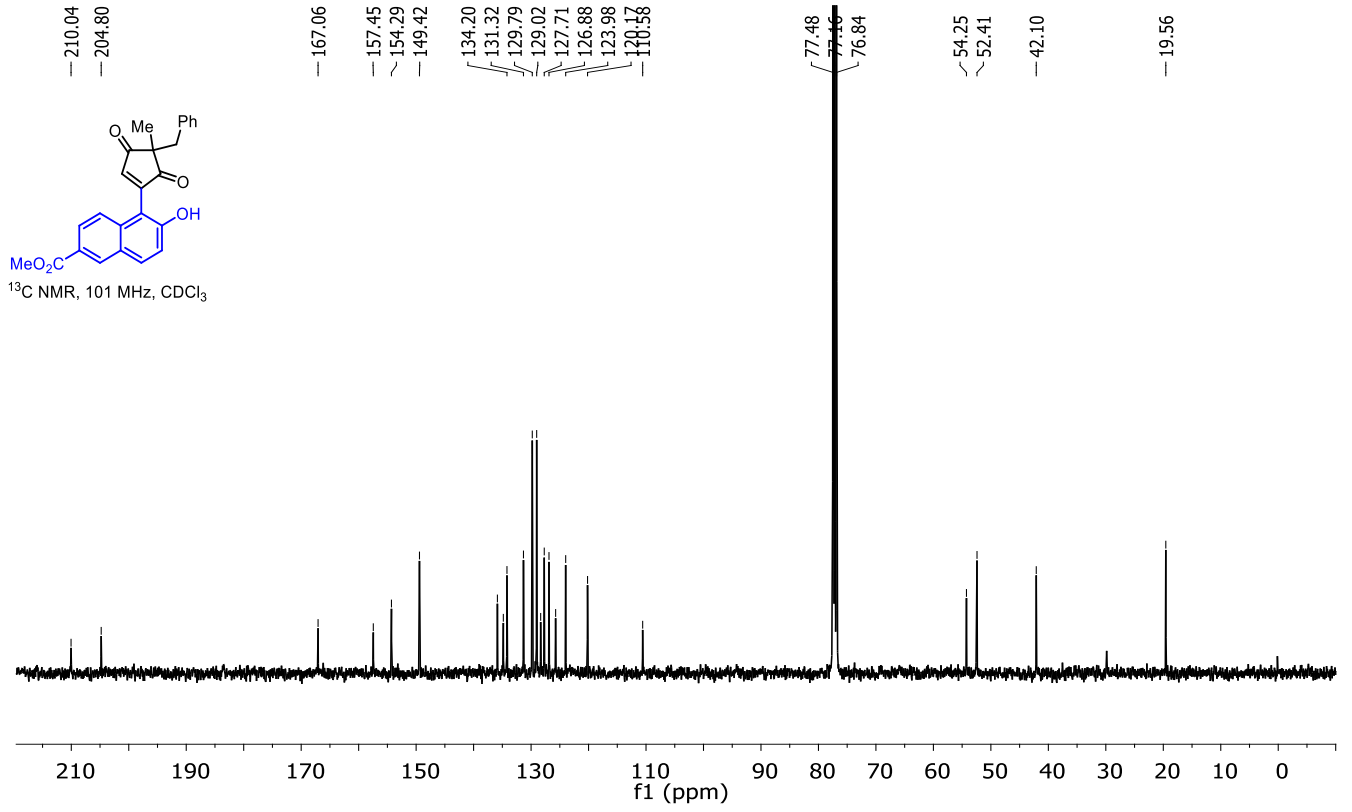
2-Benzyl-4-(6-bromo-2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3ab):



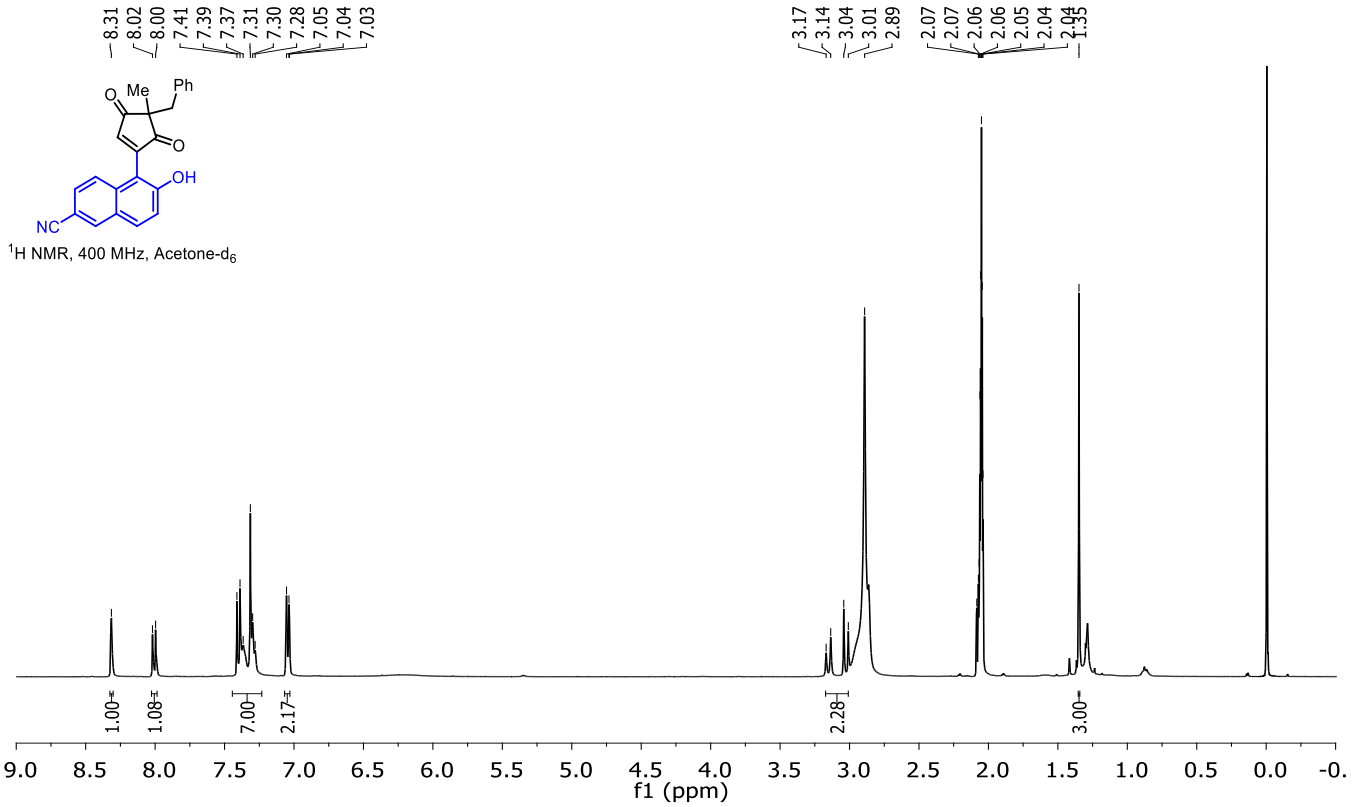


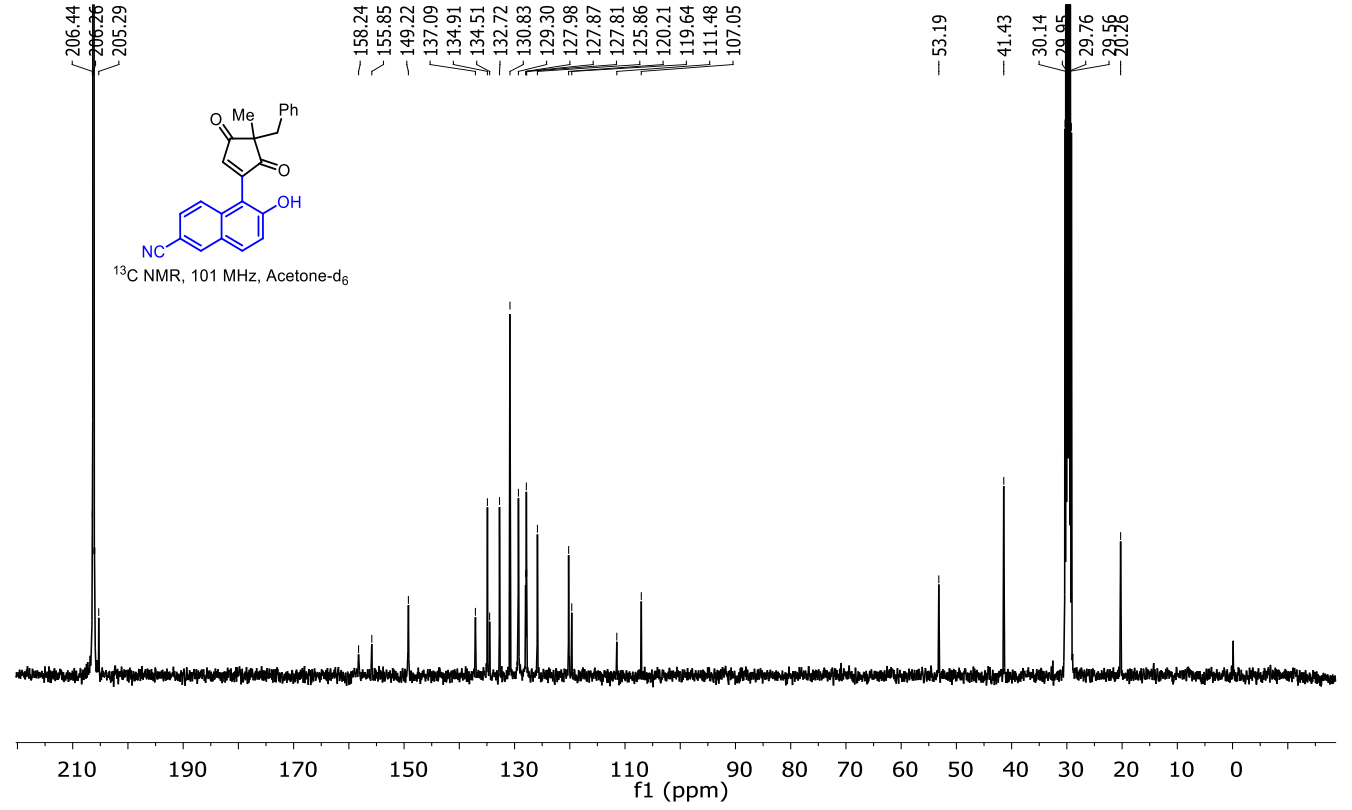
Methyl 5-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-6-hydroxy-2-naphthoate (3ac):



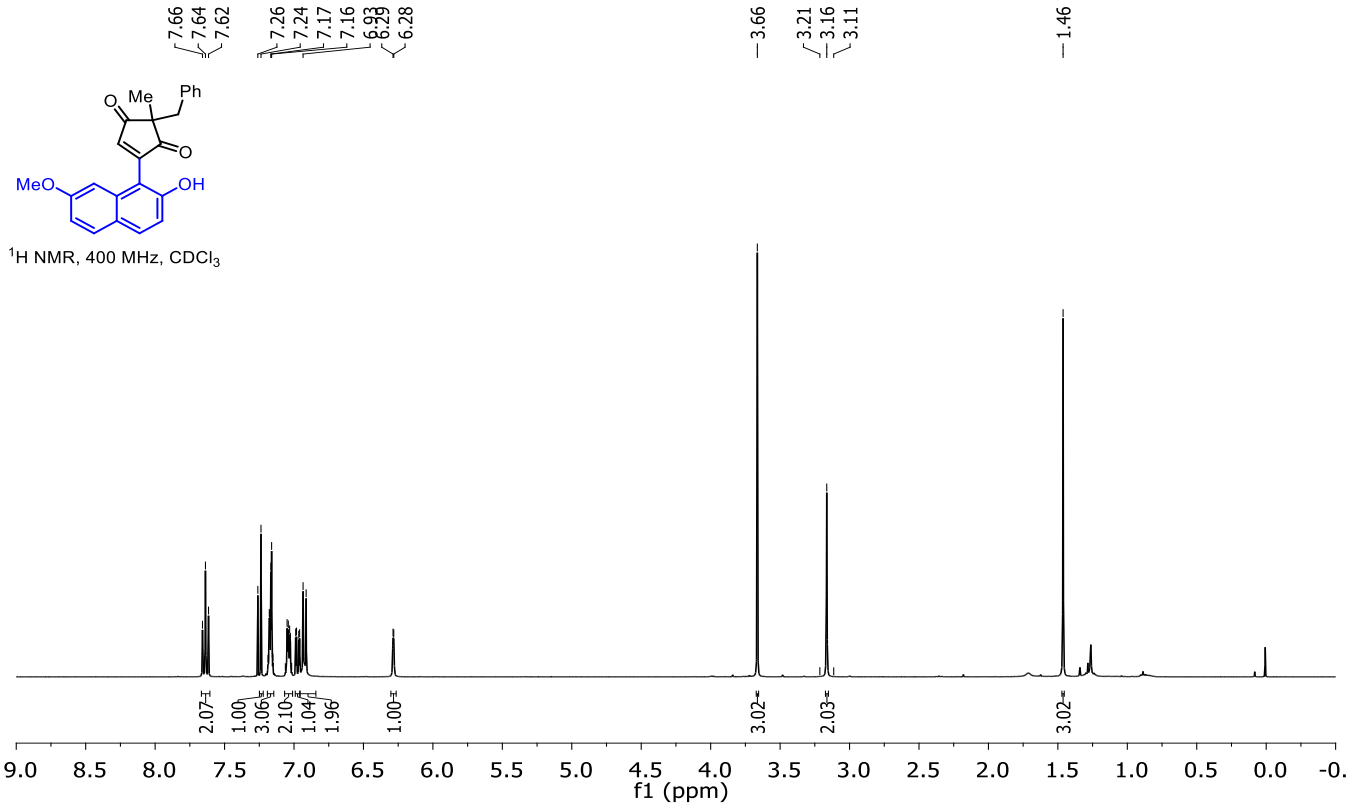


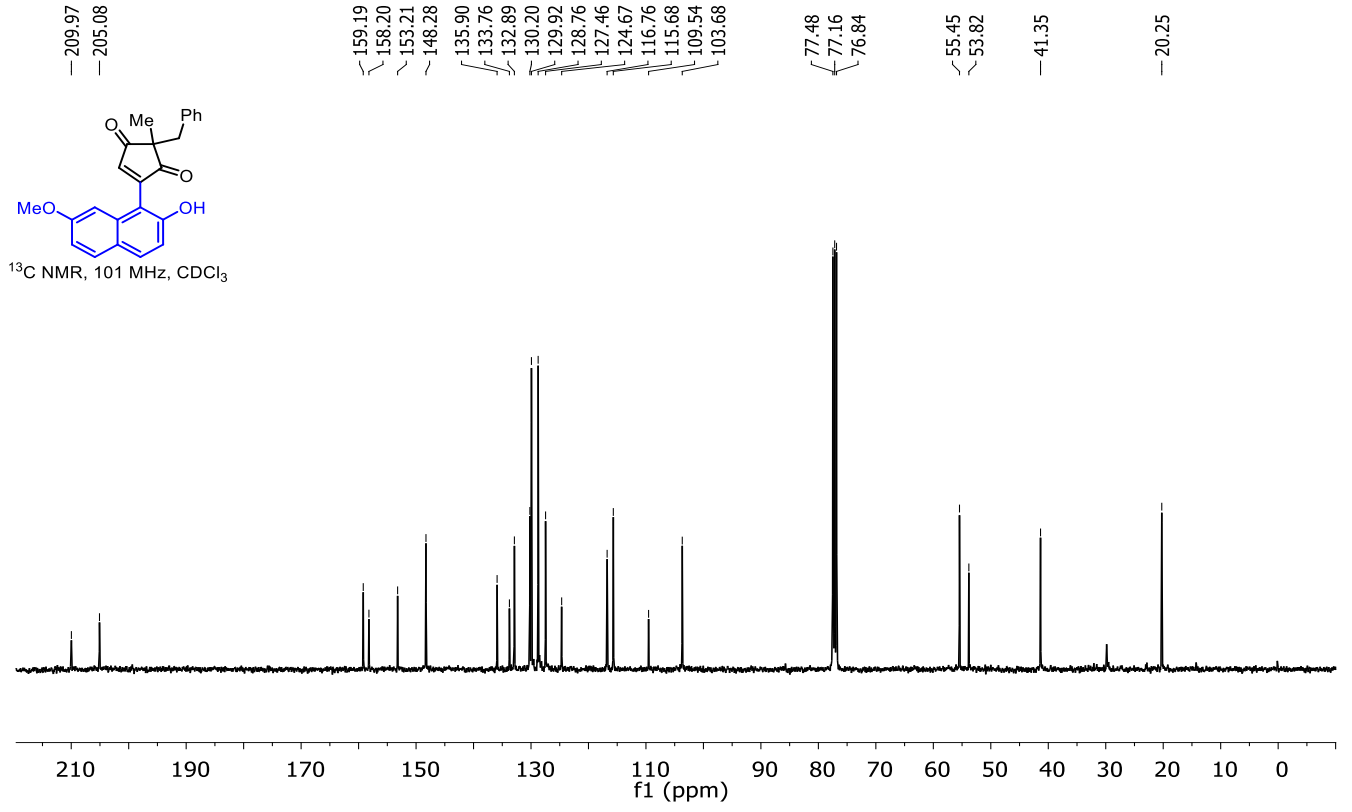
5-(4-Benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-6-hydroxy-2-naphthonitrile (3ad):



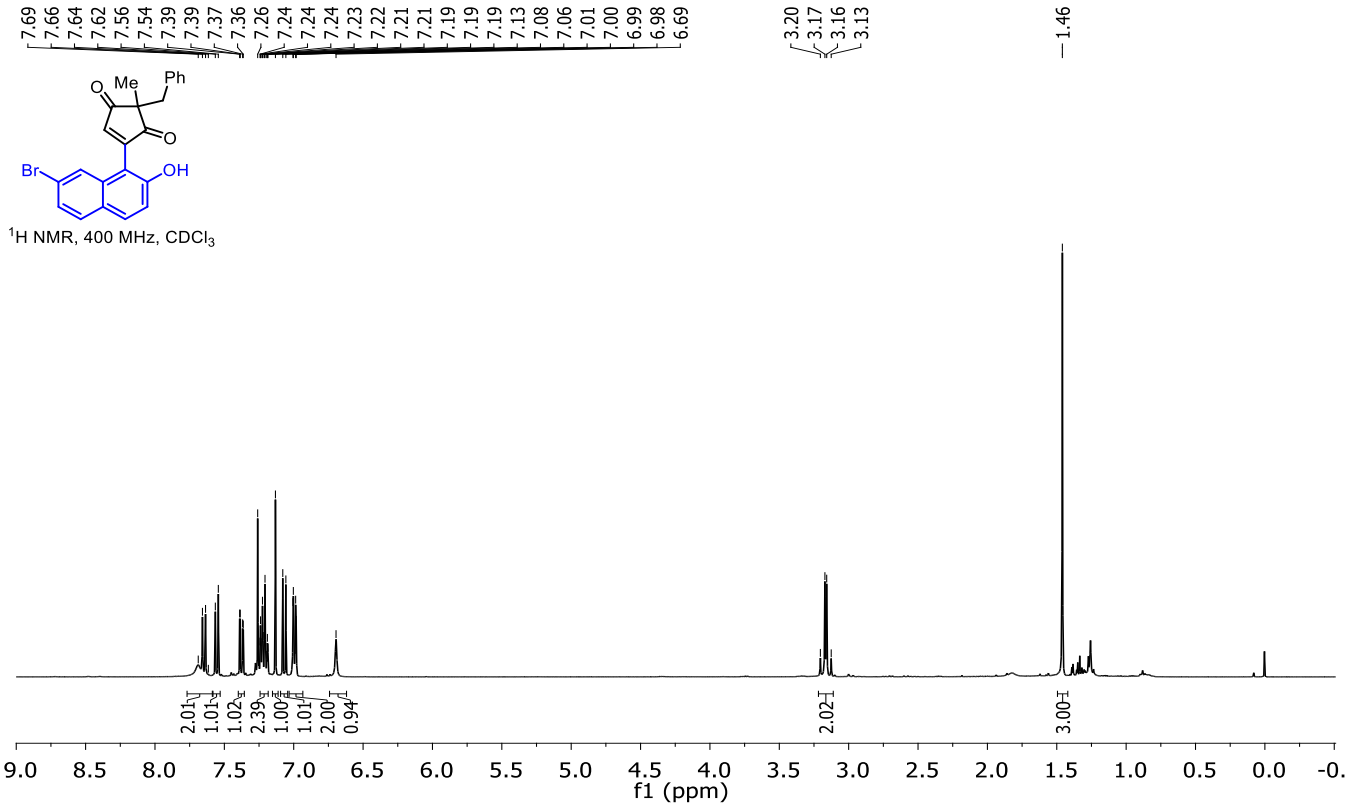


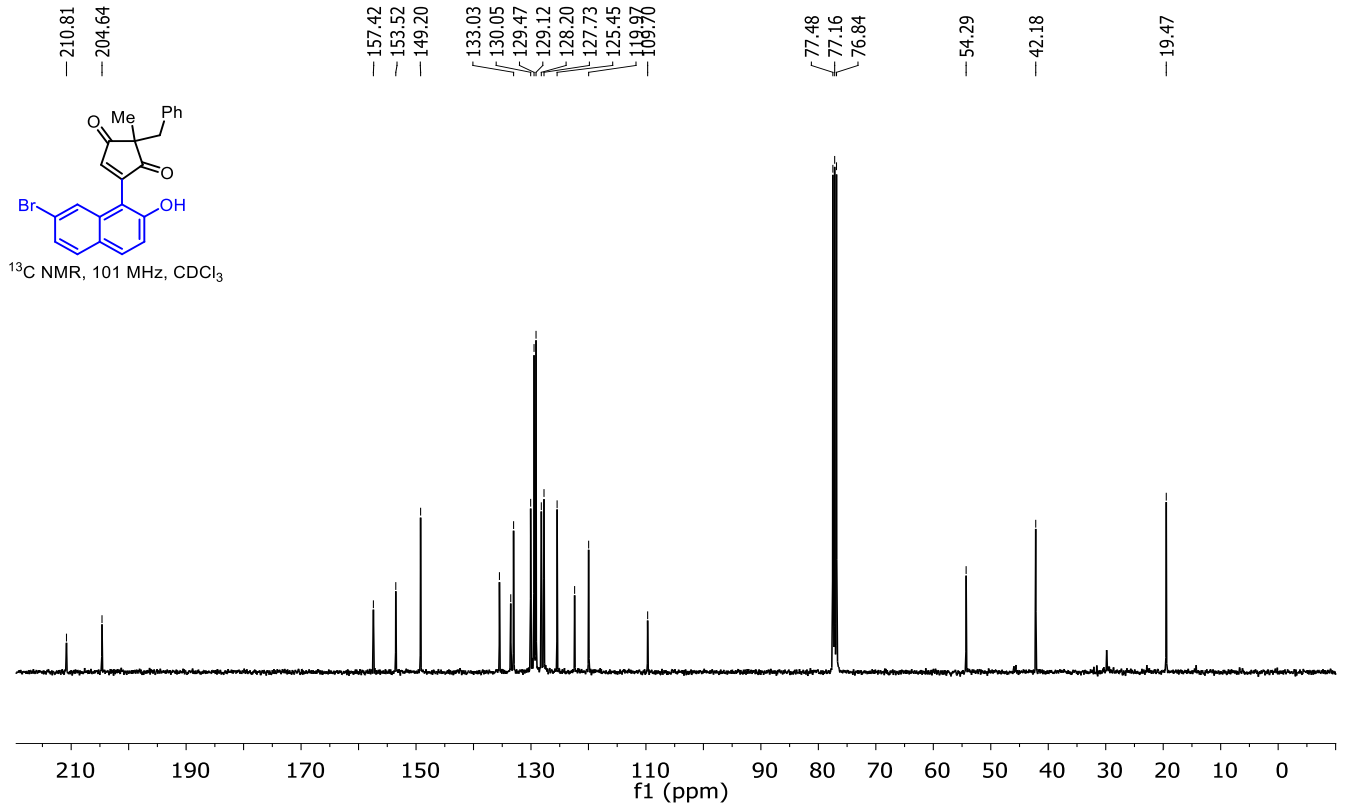
2-Benzyl-4-(2-hydroxy-7-methoxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3ae):



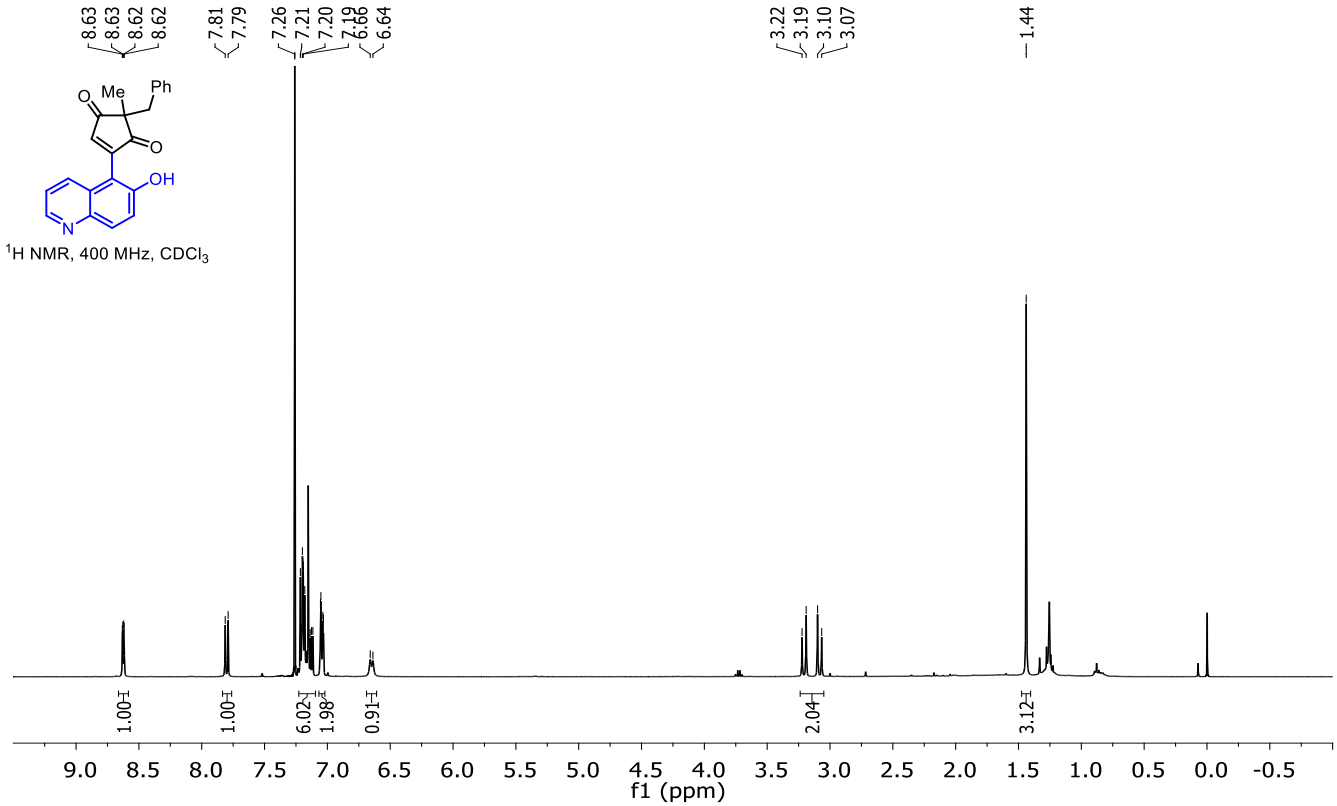


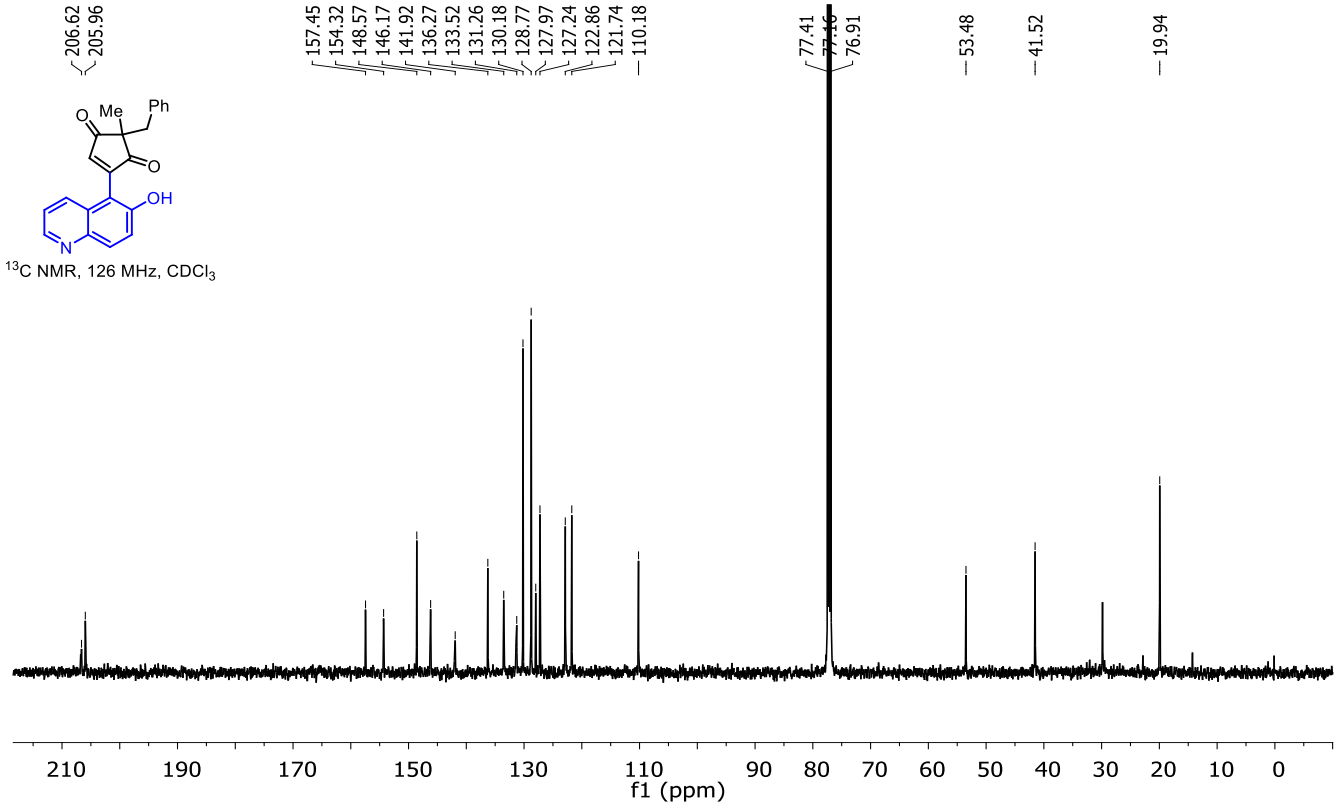
2-Benzyl-4-(7-bromo-2-hydroxynaphthalen-1-yl)-2-methylcyclopent-4-ene-1,3-dione (3af):



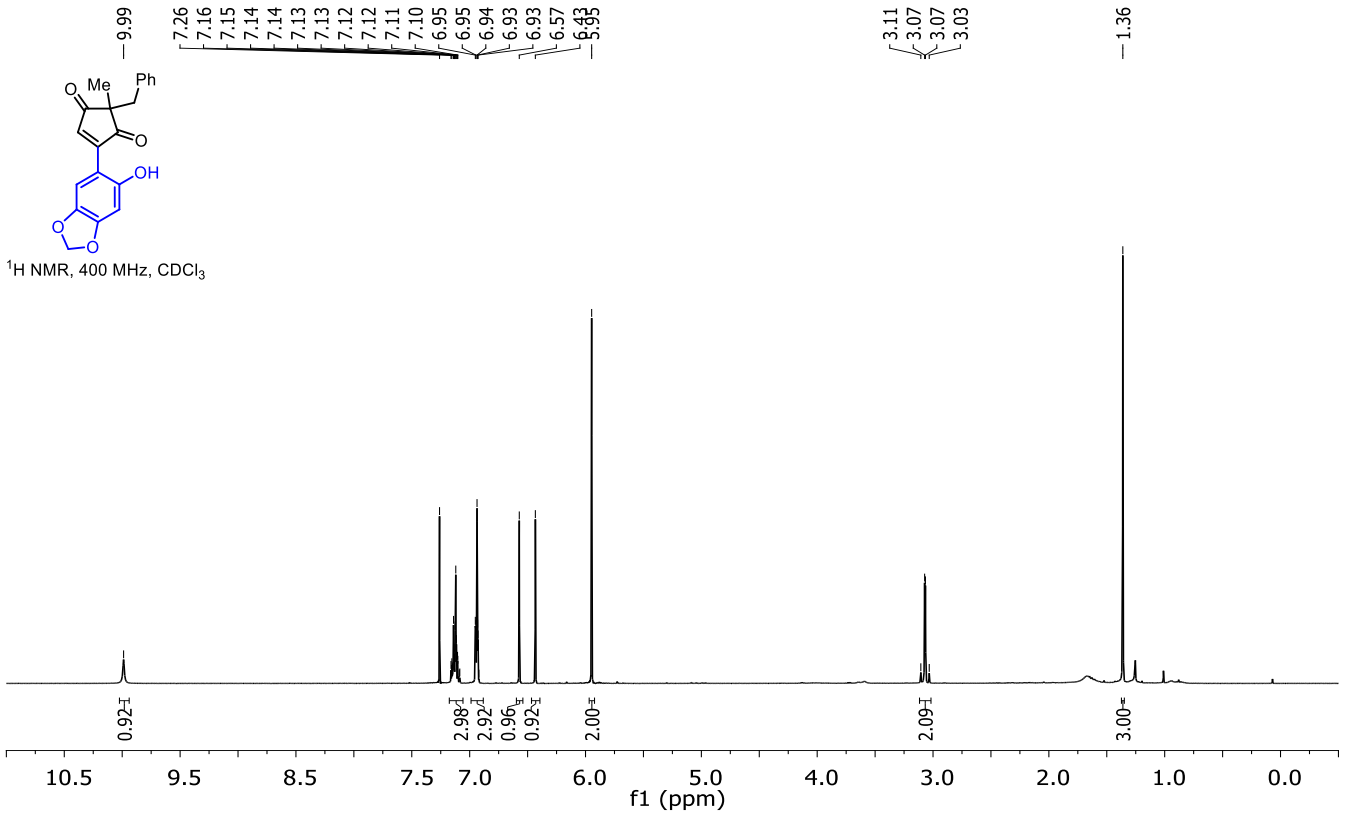


2-Benzyl-4-(6-hydroxyquinolin-5-yl)-2-methylcyclopent-4-ene-1,3-dione (3ag):

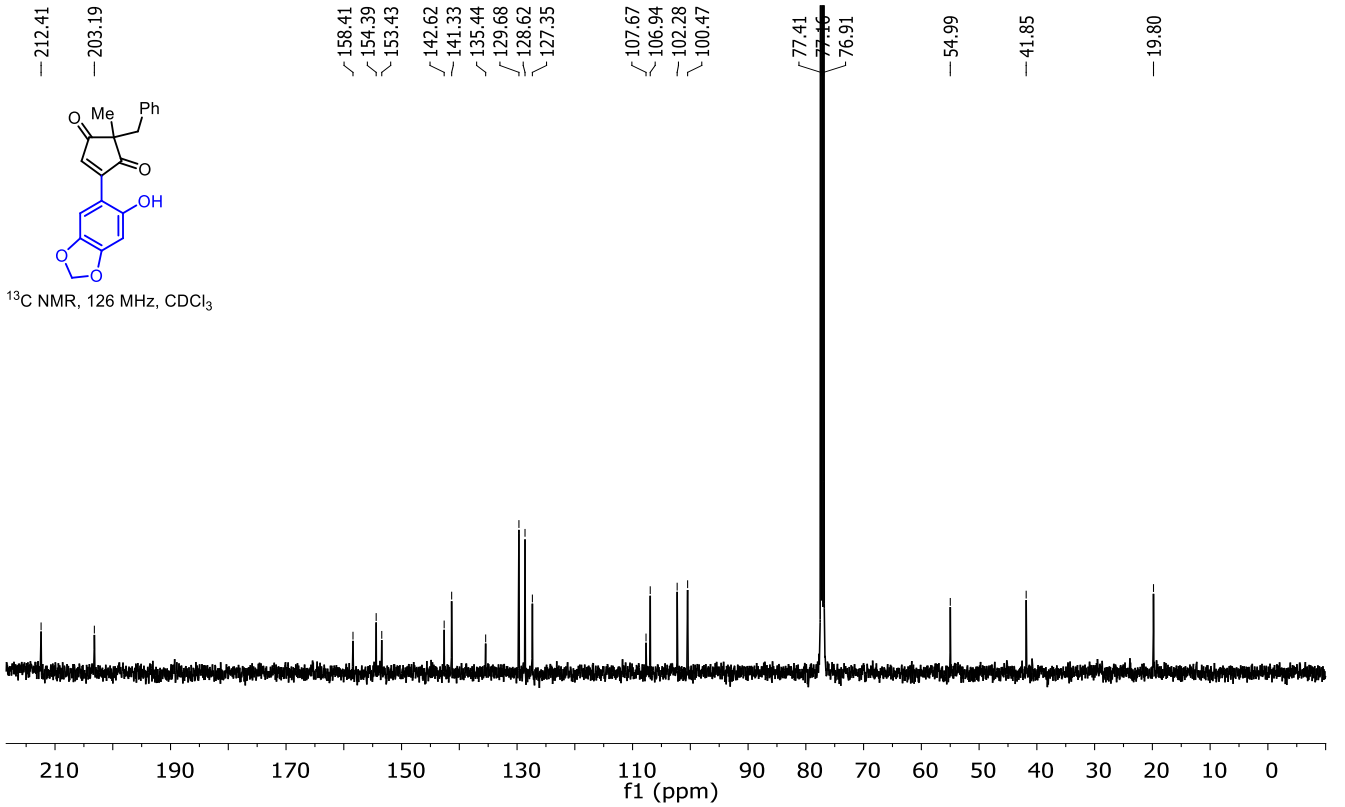




2-Benzyl-4-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-methylcyclopent-4-ene-1,3-dione (3ai):

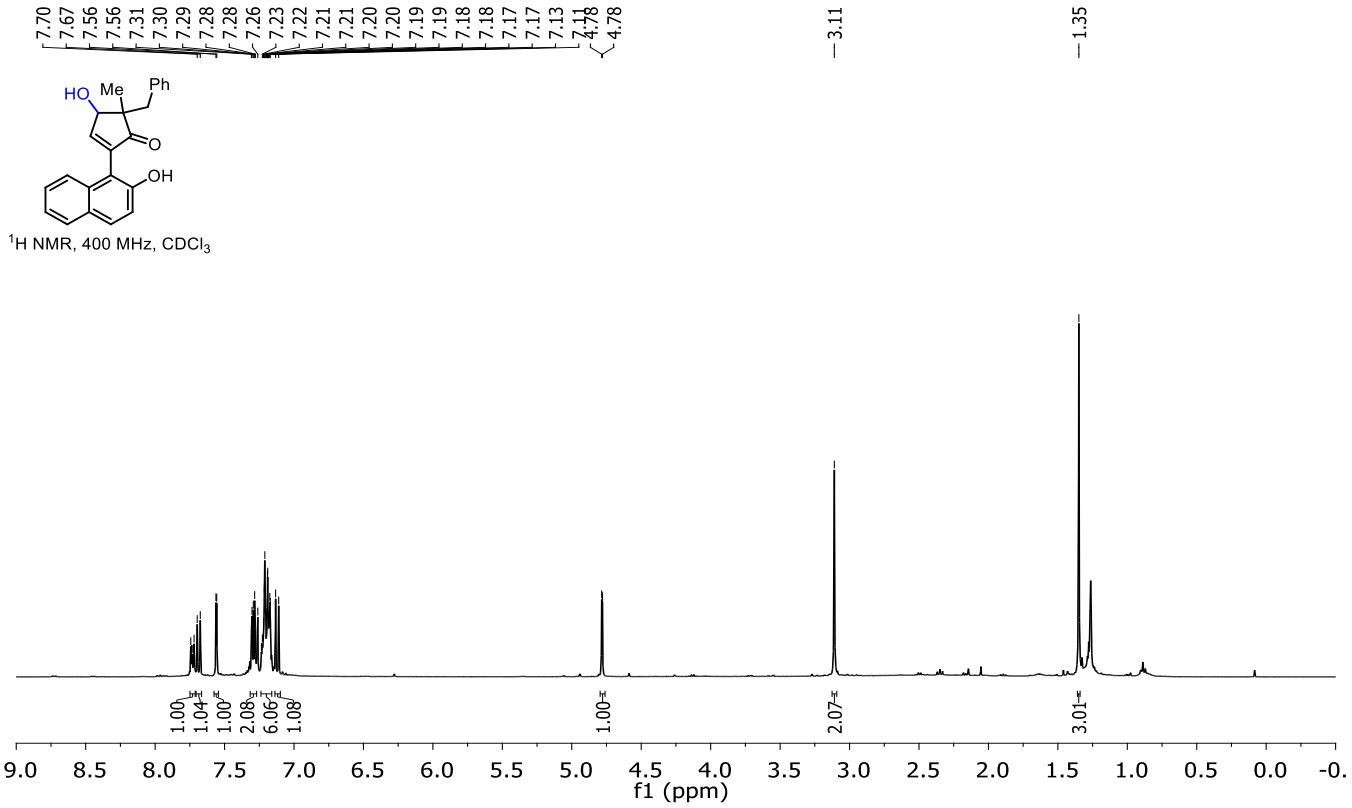


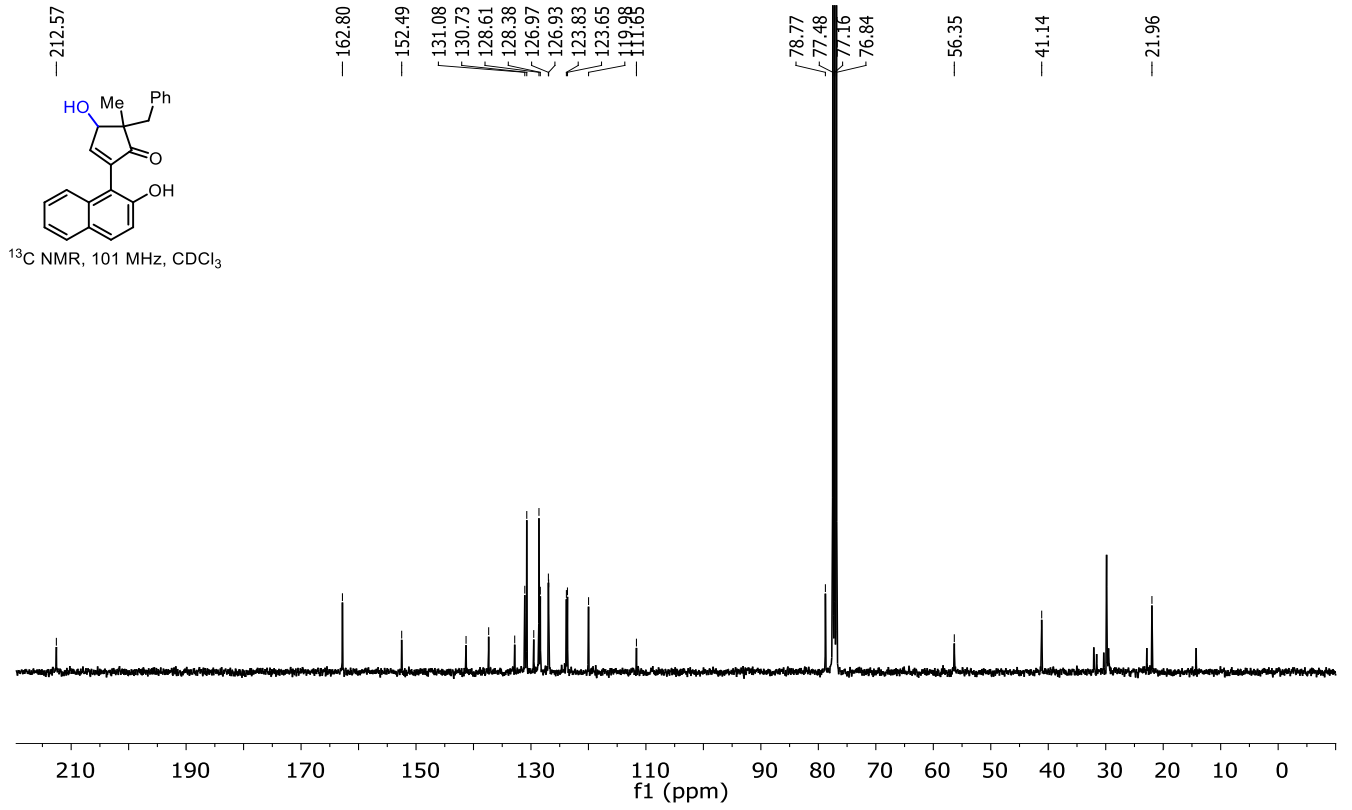
^{1}H NMR, 400 MHz, $CDCl_3$



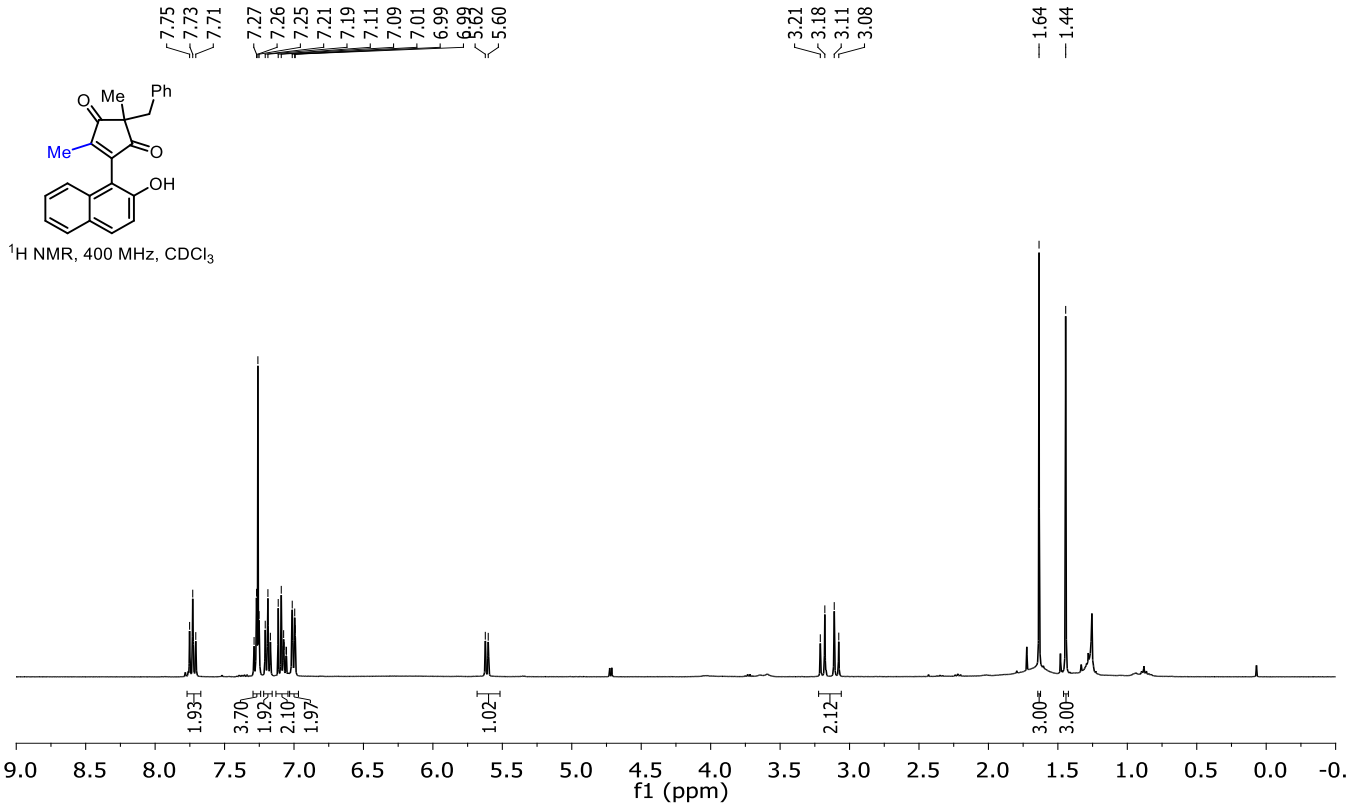
^{13}C NMR, 126 MHz, $CDCl_3$

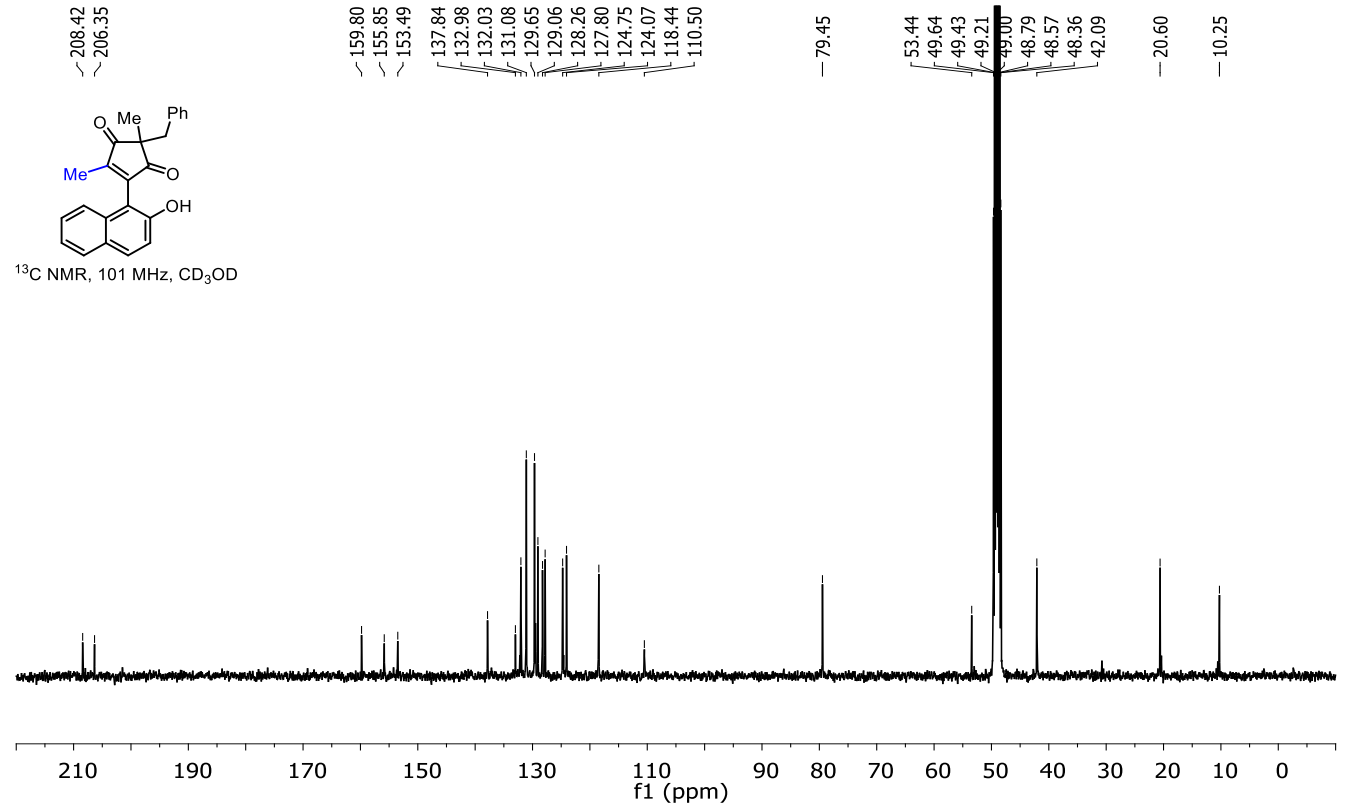
5-Benzyl-4-hydroxy-2-(2-hydroxynaphthalen-1-yl)-5-methylcyclopent-2-en-1-one (4):





2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2,5-dimethylcyclopent-4-ene-1,3-dione (5):





2-Benzyl-4-(2-hydroxynaphthalen-1-yl)-2-methylcyclopentane-1,3-dione (3a'):