Supporting Information-I

Conformation-controlled Catalytic Asymmetric Synthesis of Swaminathan Ketones

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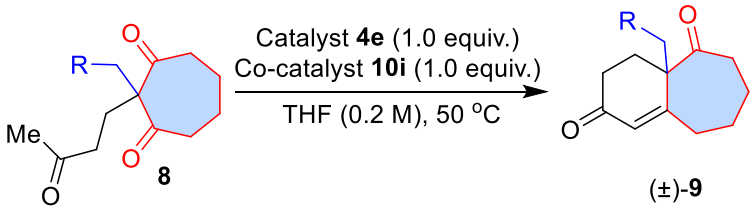
General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 500 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received.

Table S1. Racemic substrate scope with respect to various functionalized triketones **8** to furnish racemic S. ketone and analogues (±)-**9**.[a]



Entry	R	*t* [h]	Yield [%][b]
1[c]	C_6H_5 (±)-**9a**	16	90
2	4-FC_6H_4 (±)-**9d**	7	85
3	4-BrC_6H_4 (±)-**9f**	7	81
4	4-$OMeC_6H_4$ (±)-**9k**	7	87
5	4-$CF_3C_6H_4$ (±)-**9p**	7	84
6	2-furfuryl (±)-**9r**	7	84
7	2-thiophenyl (±)-**9s**	7	80
8	4-pyridinyl (±)-**9u**	7	83
9	2-napthyl (±)-**9x**	10	78
10	H (±)-**9oo**	5	90
11	CH_3 (±)-**9y**	7	80
12[c]	$CH_2CH_2CH_3$ (±)-**9aa**	16	85
13[c]	$CH(CH_3)_2$ (±)-**9dd**	16	84
14[c]	CH_2OCH_2Ph (±)-**9gg**	16	81
15[c]	$CH_2CH_2OCH_2Ph$ (±)-**9hh**	15	80

[a] Reactions were carried out in THF (0.2 M) at 50 °C with 1.0 equiv of **4e** and 1.0 equiv. of AcOH relative to the compound **8** (0.1 mmol). [b] yield refers to the coloum purified product. [c] Reactions were carried out at rt using Et_2O (0.2 M) as solvent

The reaction of benzyl substituted triketone **8a** in the presence of 1.0 equiv. of pyrrolidine **4e** and 1.0 equiv. of acetic acid **10i** in diethylether (0.2 M) at room temperature afforded the desired racemic S. ketone analogue (±)-**9a** with 90% yield in 16 h (Table S1, entry 1). Interestingly, all the aromatic, heteroaromatic substituted triketones **8d**, **8f**, **8k**, **8p**, **8r**, **8s**, **8u** and **8x** proceeded smoothly in THF (0.2 M) at 50 °C because of the solubility issues affording the racemic S. ketones (±)-**9d**, (±)-**9f**, (±)-**9k**, (±)-**9p**, (±)-**9r**, (±)-**9s**, (±)-**9u** and (±)-**9x** in 7-10 h with 78-90% yields (Table S1, entries 2-9). Whereas, aliphatic substituted triketones **8oo**, **8y**, **8aa**, **8dd**, **8gg**

and **8hh** performed well in dietheylether (0.2 M) furnishing the corresponding racemic S. ketones (±)-**9oo**, (±)-**9y**, (±)-**9aa**, (±)-**9dd**, (±)-**9gg** and (±)-**9hh** in 5-16 h with 80-90% yield (Table S1, entries 10-15).

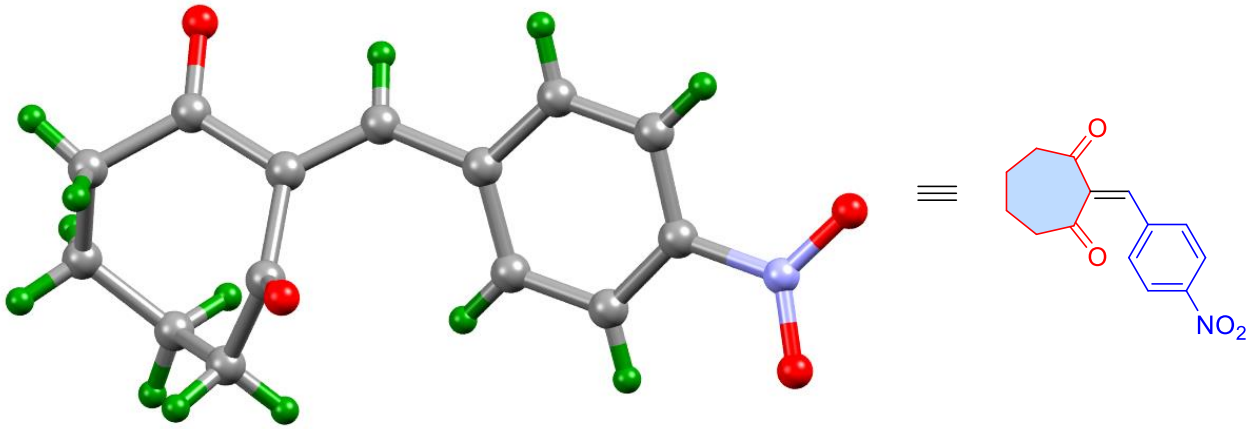


***Figure S1*:** Crystal structure of 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (**5n**).

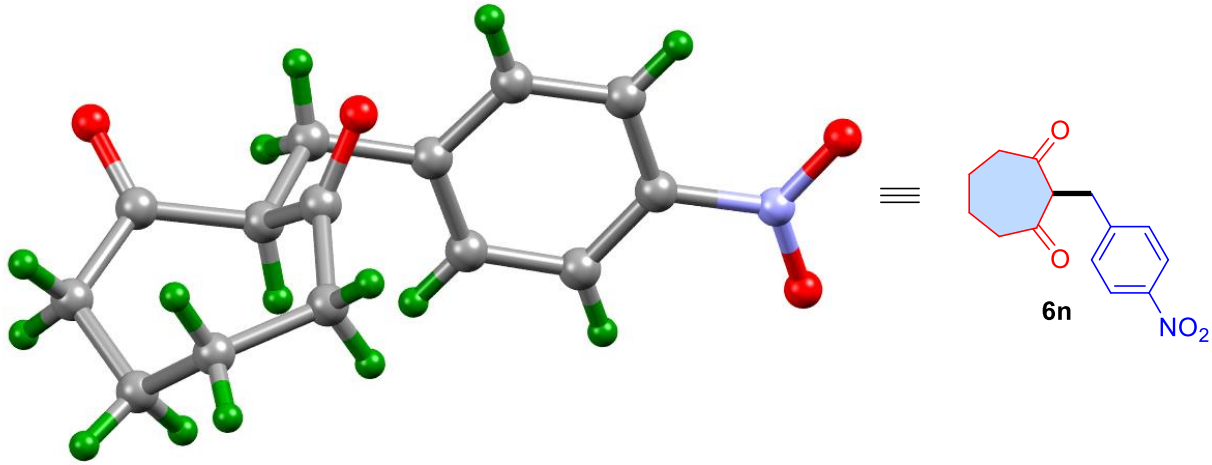


***Figure S2*:** Crystal structure of 2-(4-nitrobenzyl)cycloheptane-1,3-dione (**6n**).

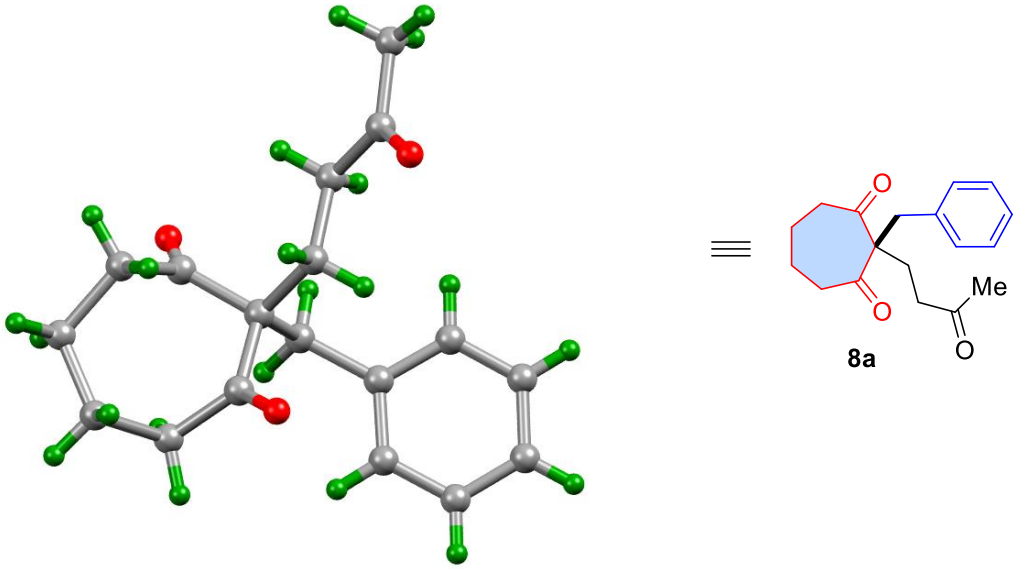


***Figure S3*:** Crystal structure of 2-benzyl-2-(3-oxobutyl)cycloheptane-1,3-dione (**8a**).

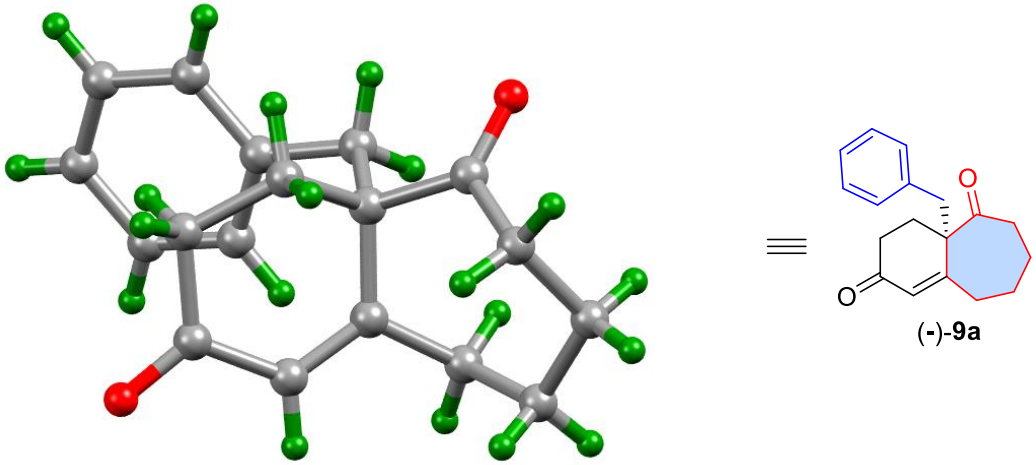


***Figure S4*:** Crystal structure of (*S*)-4a-benzyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione (-)-**9a**.

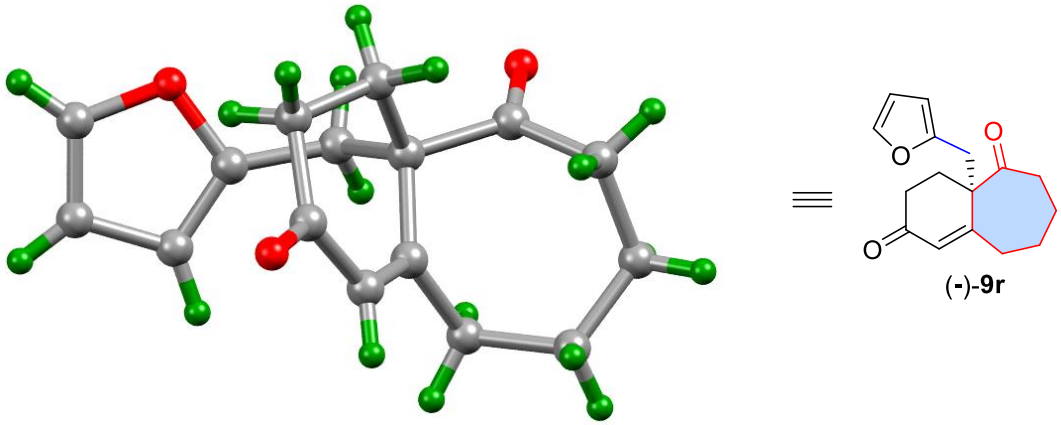


***Figure S5*:** Crystal structure of (*S*)-4a-(furan-2-ylmethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione (-)-**9r**.

DFT Calculations for the HOMO-LUMO Energy Gap:

The molecules (**B1**), (**B2**), (**B3**), and (**B4**) were optimized using CAM-B3LYP[1a-b] method with 6-311++g*[2] basis set in the Gaussian 09 suite of program.[3] Using the obtained orbital energies from the current calculations, a pictorial representation is shown below. The picture of energy difference between the HOMO **3** (Hantzsch ester) and LUMO of (**B1**), (**B2**), (**B3**) and (**B4**) shows a visible trend of increase in the HOMO-LUMO energy gap which benefits in explaining the experimental studies.

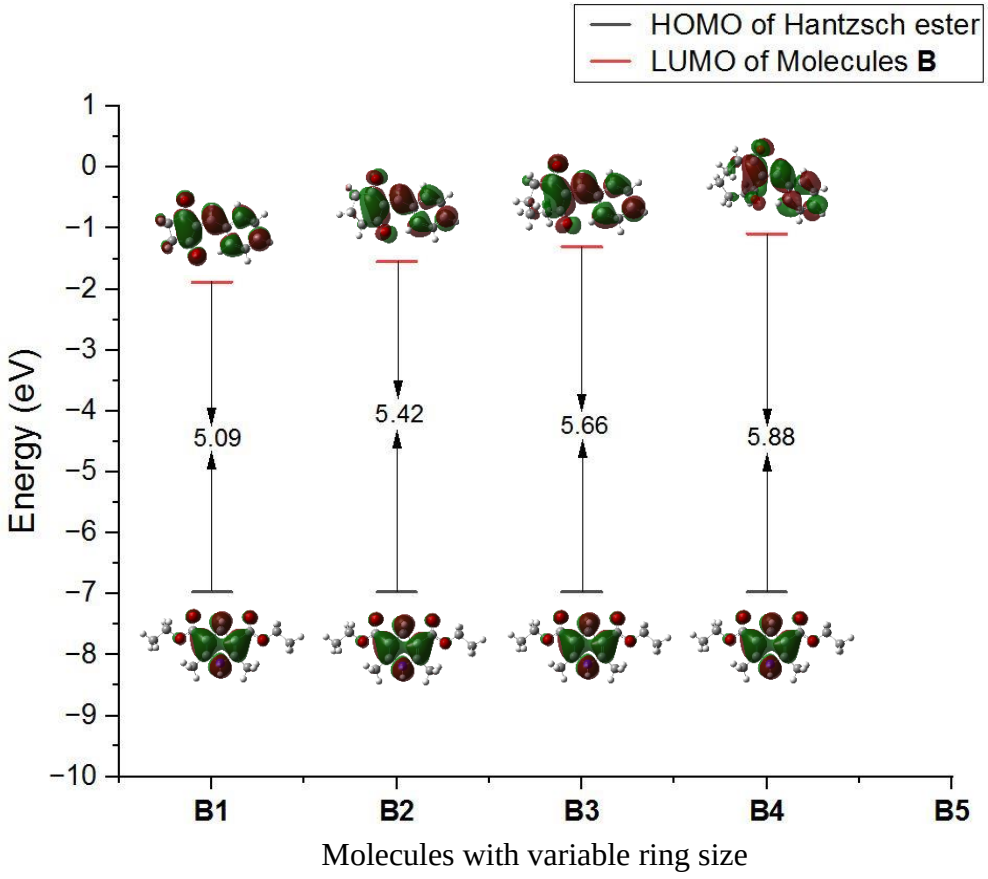


Figure S6. Graph showing the trends in $HOMO_{(Hantzsch\ ester)}$-$LUMO_{(olefins\ with\ variable\ ring\ size)}$ gap.

The cartesian coordinates of the optimized geometries of molecules (**B1**), (**B2**), (**B3**), (**B4**) and Hantzsch ester **3** are shown below, respectively.

2-benzylidenecyclopentane-1,3-dione (**B1**):

Input orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1.196409	0.144380	0.356637
6	0.579403	0.052949	1.244326
6	-0.995975	-0.177024	3.508976
6	0.308766	-1.199561	1.763741
6	0.068959	1.214880	1.846860
6	-0.727926	1.080077	2.993724
6	-0.481957	-1.315829	2.900499
1	0.712039	-2.084450	1.284911
1	-1.128239	1.964703	3.468005
1	-0.697950	-2.295633	3.312340
1	-1.613138	-0.268953	4.395554
6	0.418032	2.473246	1.216717
1	1.041471	2.354343	0.329870
6	0.154450	3.777136	1.468168
6	0.723225	4.795393	0.543699
6	0.300376	6.183309	0.996496
6	-0.517112	5.982683	2.272728
6	-0.612957	4.479971	2.515752
1	1.193824	6.793864	1.139048
1	-0.268334	6.649485	0.189051
1	-1.529711	6.385504	2.211910
1	-0.057186	6.435976	3.153515
8	-1.233556	4.005812	3.441051
8	1.412176	4.567808	-0.421552

2-benzylidenecyclohexane-1,3-dione (**B2**):

Input orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1.512888	2.943233	4.599033
6	0.842960	2.183937	4.209595
6	-0.883746	0.262675	3.231832
6	0.371865	1.196229	5.054781
6	0.480411	2.223190	2.851446
6	-0.406542	1.245272	2.378701
6	-0.495787	0.228427	4.564514
1	0.673689	1.184985	6.095925
1	-0.723687	1.273052	1.348901
1	-0.876216	-0.544933	5.222936
1	-1.572590	-0.482386	2.849624
6	1.074199	3.314259	2.086901
1	1.535278	4.054243	2.737594
6	1.270591	3.629338	0.781761
6	1.615220	3.071704	-1.691173
6	2.650614	5.162362	-0.804018
6	1.853347	4.555002	-1.948145
6	2.066601	4.892461	0.566792
6	0.847320	2.843740	-0.406987
1	2.579200	2.554140	-1.605849
1	3.661767	4.735136	-0.793589
1	0.893353	5.070376	-2.054906
1	1.057005	2.592045	-2.494876
1	2.772376	6.241627	-0.900481
1	2.384824	4.693609	-2.891959
8	2.269041	5.673240	1.470743
8	-0.078308	2.058982	-0.388526

2-benzylidenecycloheptane-1,3-dione (**B3**):

Input orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.291001	3.259725	3.075981
1	-2.096429	3.874189	2.679740
6	-0.262289	4.060107	3.737695
6	1.604881	5.822210	4.863388
6	-0.271212	5.429115	3.423209
6	0.689906	3.599812	4.656241
6	1.609428	4.478005	5.209589
6	0.657848	6.298552	3.965437
1	-1.016886	5.807548	2.731806
1	0.694455	2.559360	4.939527
1	2.335291	4.105363	5.923783
1	0.637552	7.348632	3.696516
1	2.329668	6.500153	5.300833
6	-1.455382	1.955747	2.758158
6	-0.406036	-0.221159	1.936268
6	-1.355760	-1.363985	2.325321
6	-2.716953	1.654053	1.979369
6	-0.467511	0.866108	2.988466
1	-0.674616	0.179431	0.955461
1	0.622605	-0.578365	1.882116
1	-0.896387	-1.961392	3.115953
1	-1.485442	-2.024360	1.462995
6	-3.291237	0.242199	1.894455
1	-4.357966	0.373998	2.089229
1	-3.231244	-0.058173	0.842030
6	-2.712631	-0.842496	2.797908
1	-3.421331	-1.672386	2.852469
1	-2.628511	-0.460978	3.820900
8	0.256002	0.808172	3.960240
8	-3.338988	2.545089	1.442963

2-benzylidenecyclooctane-1,3-dione (**B4**):

Input orientation:

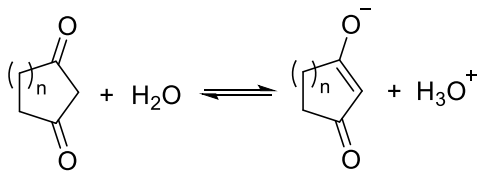
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.759601	0.814172	0.287568
6	-1.911968	0.567326	1.752297
6	-2.763046	0.201831	-0.676075
1	-3.236221	1.056998	-1.168255
1	-3.554766	-0.335861	-0.151798
6	-0.945851	-2.063631	0.136609
1	-0.358608	-2.980782	0.211405
6	-1.910526	-2.036086	1.346157
1	-1.736528	-2.896369	1.991721
1	-2.944270	-2.136825	0.998077
6	-1.879250	-0.843047	2.285222
1	-0.210137	-1.255964	0.196787
6	-2.075260	-0.669246	-1.733186
1	-2.744789	-0.795758	-2.587910
1	-1.209292	-0.113138	-2.101064
6	-1.637694	-2.047134	-1.232229
1	-0.966327	-2.481128	-1.978744
1	-2.503887	-2.717464	-1.188965
8	-0.868593	1.509957	-0.147766
8	-1.849332	-1.037603	3.480508
6	-2.140819	1.534418	2.658653
1	-2.301752	1.151812	3.664047
6	-2.309054	2.986633	2.541445
6	-2.769716	5.748829	2.493124
6	-3.178666	3.590804	3.459569
6	-1.647021	3.802612	1.617359
6	-1.879607	5.170132	1.598951
6	-3.419947	4.953508	3.428208
1	-3.677109	2.974718	4.200902
1	-0.933343	3.367447	0.933638
1	-1.351033	5.789603	0.882898
1	-4.106365	5.397440	4.140512
1	-2.945859	6.818694	2.471611

Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantzsch ester) (**3**):

Input orientation:

	Atomic Number	Coordinates (Angstroms) X	Y	Z
N	7	-1.241526	-0.009127	3.859133
C	6	-0.402479	-1.277878	2.062037
C	6	-0.390002	1.242884	2.056126
C	6	-1.021436	1.214860	3.246591
C	6	-1.033711	-1.238077	3.252282
H	1	-1.746001	-0.004526	4.728424
C	6	-0.136634	-2.498998	1.292245
O	8	-0.675389	-3.631773	1.796802
C	6	-0.112144	2.457725	1.280658
O	8	-0.641250	3.597826	1.778900
O	8	0.537389	2.451486	0.261008
O	8	0.511744	-2.503716	0.271848
C	6	0.146076	-0.021668	1.422186
H	1	1.242336	-0.027005	1.458282
H	1	-0.081395	-0.023065	0.355408
C	6	-0.372808	4.791587	1.027683
H	1	0.707536	4.930351	0.960314
H	1	-0.748264	4.659880	0.011689
C	6	-1.048694	5.940279	1.736474
H	1	-0.662746	6.061496	2.750329
H	1	-2.127685	5.786679	1.796066
H	1	-0.868858	6.870361	1.193173
C	6	-0.418855	-4.831637	1.051178
H	1	0.660089	-4.980504	0.982973
H	1	-0.794600	-4.701628	0.035068
C	6	-1.104076	-5.970597	1.766685
H	1	-0.717758	-6.090209	2.780588
H	1	-0.933469	-6.904982	1.227813
H	1	-2.181541	-5.806914	1.827042
C	6	-1.576918	-2.391283	4.048603
H	1	-0.839633	-3.181192	4.163140
H	1	-2.441938	-2.835403	3.556056
H	1	-1.883148	-2.060556	5.043517
C	6	-1.553050	2.377056	4.037633
H	1	-0.809095	3.161558	4.145665
H	1	-1.859339	2.054528	5.035224
H	1	-2.415777	2.825343	3.544757

Theory behind the determination of pK_a using potentiometry:



A **A**$^-$ (n = 1 to 4)

The dissociation constant of the acid K_a is given by the following equation:

$$K_a = \frac{[H_3O^+]\,[\bar{A}\,]}{[A]}$$

$$[H_3O^+] = \frac{K_a\,[A]}{[A^-]}$$

Taking -log on both sides

$$-\log[H_3O^+] = -\log K_a + \log \frac{[A^-]}{[A]}$$

$$pH = pK_a + \log \frac{[A^-]}{[A]}$$

When the weak acid **A** is titrated against NaOH solution, pH of the titrant solution increases since the concentration of $\mathbf{A}^-$ increases and the concentration of **A** decreases

When A is exactly half titrated, $[A^-] = [A]$

Thus, pK_a = pH at the half equivalance point.

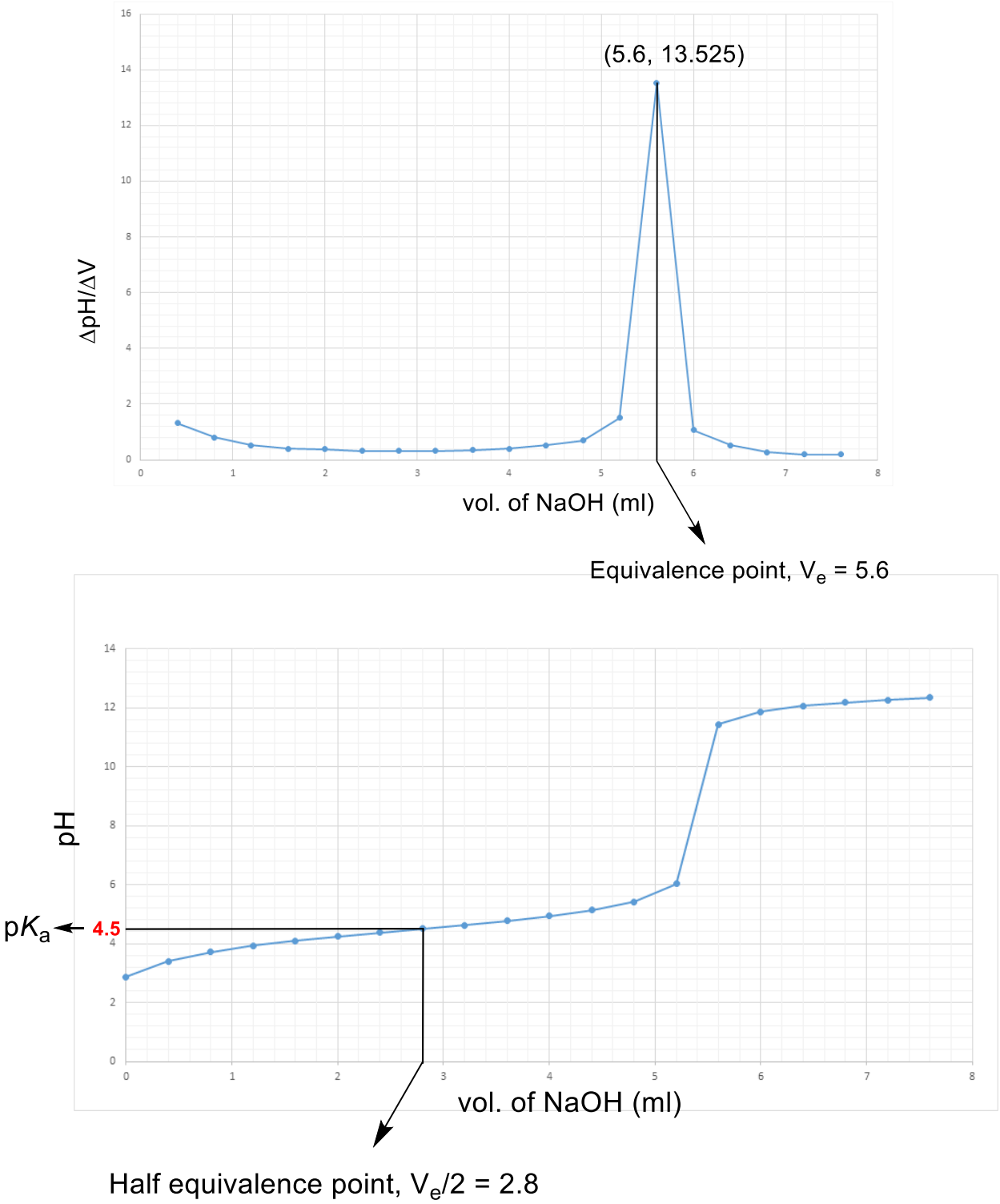


Figure S7: Graphs for the determination of pK_a of cyclopentane-1,3-dione.

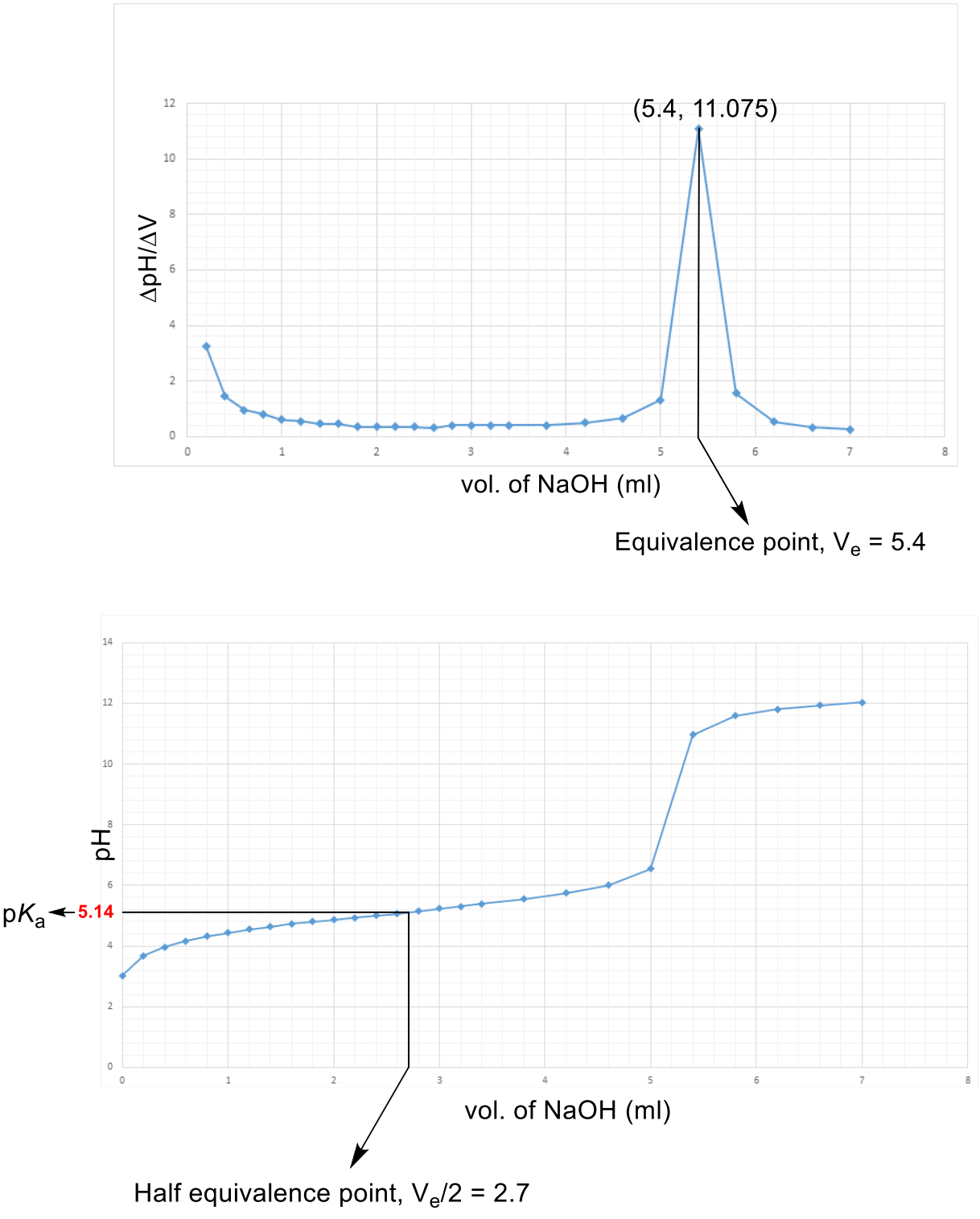


Figure S8: Graphs for the determination of pK_a of cyclohexane-1,3-dione.

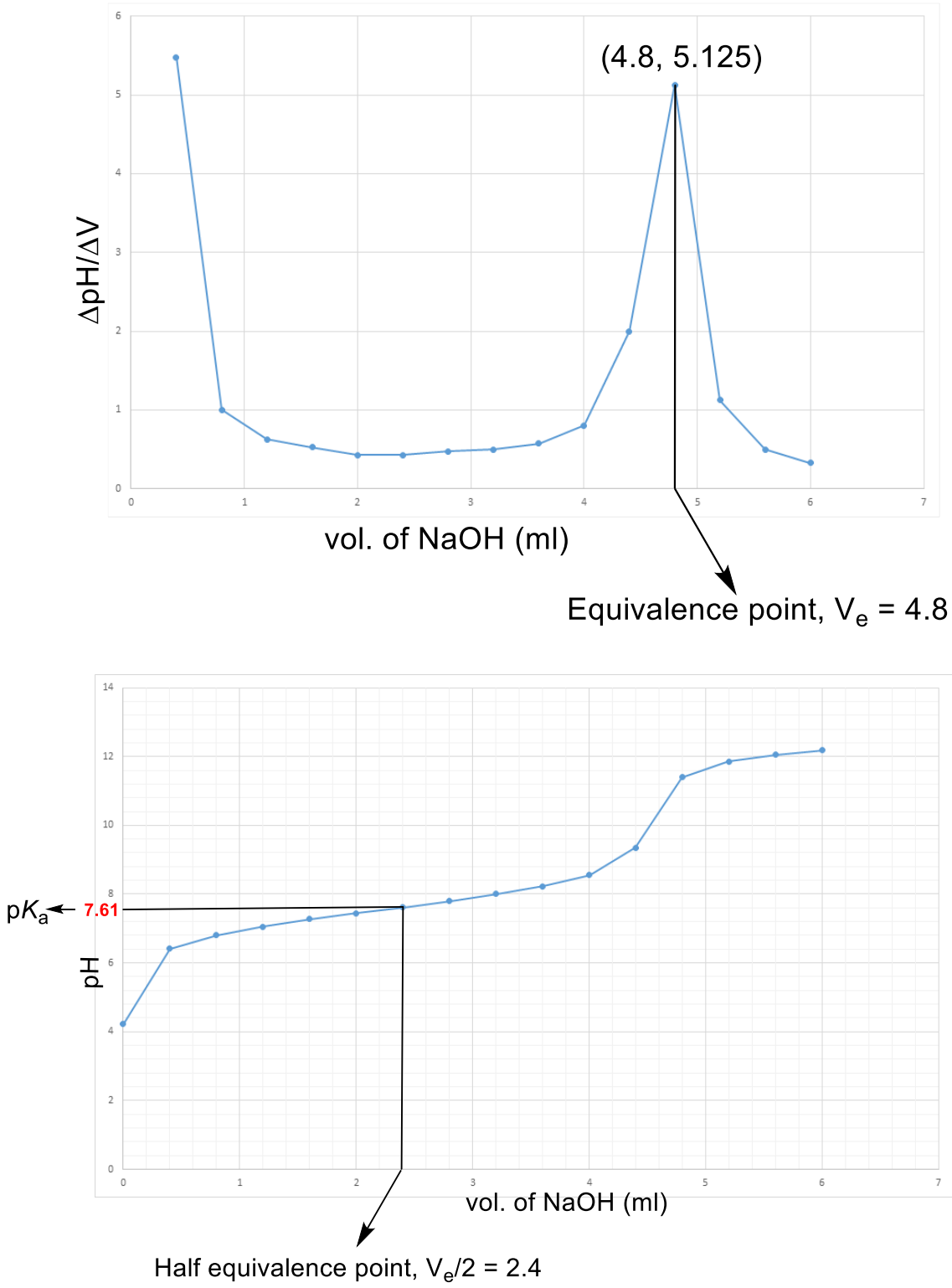


Figure S9: Graphs for the determination of pK_a of cycloheptane-1,3-dione.

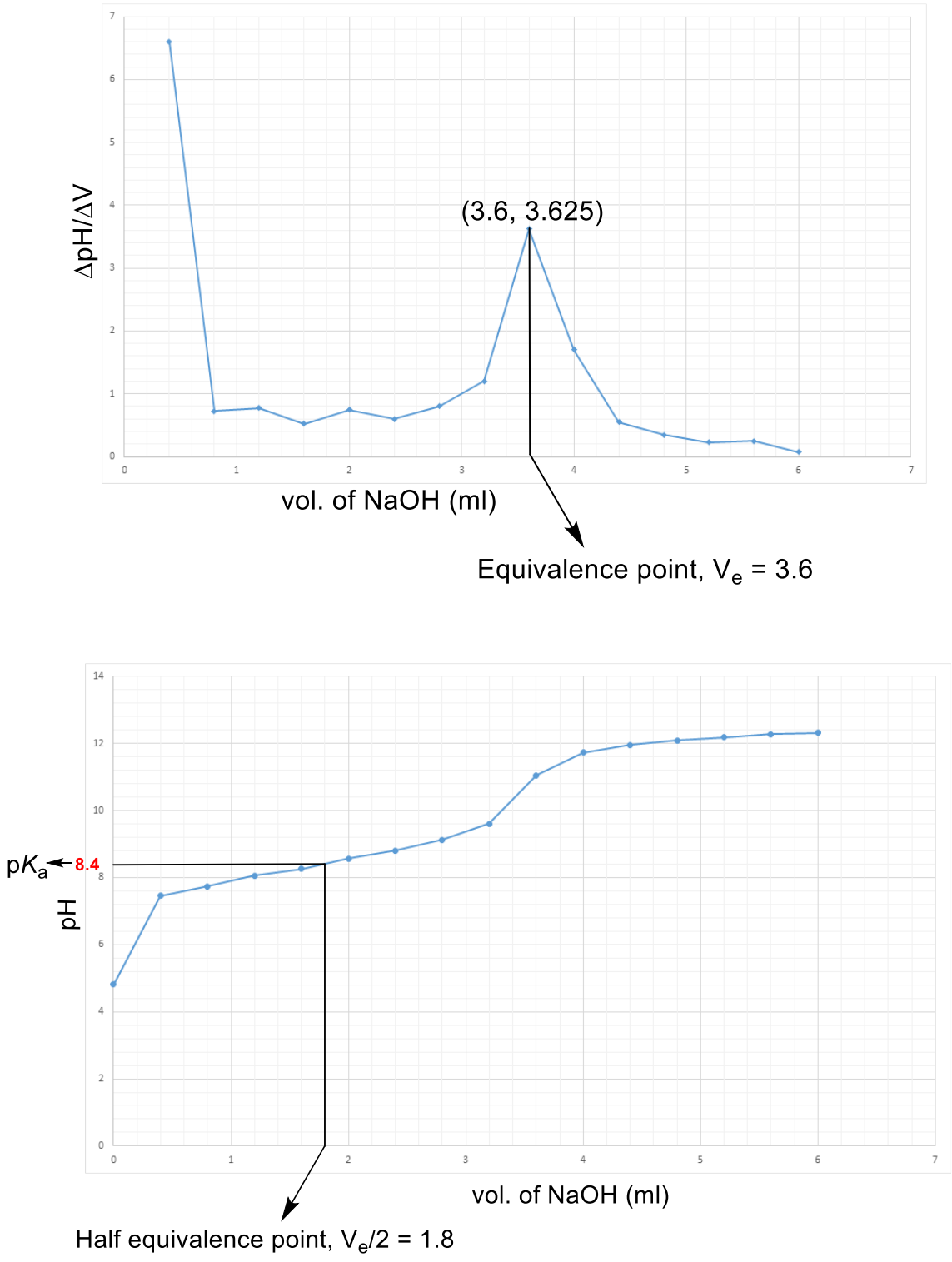


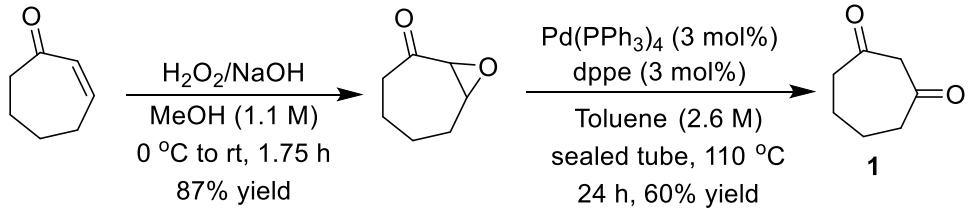
Figure S10: Graphs for the determination of pK_a of cyclooctane-1,3-dione.

General Experimental Procedures

Procedure A: **General Procedure for Determination of pK_a using Potentiometry**:

In order to determine the pK_a of the cyclic-1,3-diones **A** (with ring size varing fron five to eight), the cyclic-1,3-diones were titrated against aqueous NaOH. For this, 0.1 M solution of **A** in H_2O was prepared and was taken in a beaker which is fitted with pH meter having glass-calomel electrode. Apart from this, 0.1 M solution of aqueous NaOH was prepared and used for titration. Initially, the pH of the solution **A** was recorded before the addition of NaOH. Then, the pH readings were continuously recorded with the consecutive addition of 0.4 ml of NaOH using burette. Make sure that the solution is mixed well after the addition of each 0.4 ml of NaOH before recording the pH. Collect the values until a sudden rise in pH is observed. Continue to collect another 4-5 readings after that. Now, the equivalence point $\mathbf{V_e}$ can be easily determined by plotting ΔpH/ΔV against the volume of NaOH as shown in the above Figures S7-S10. Then, another graph was made by plotting pH against volume of NaOH. From these two graphs, we can easily determine the pK_a of the cyclic-1,3-diones **A** since the pK_a will become equal to pH at the half-equivalence point $\mathbf{V_e}$/2.

Procedure B: **Modified Procedure for the Synthesis of Cycloheptane-1,3-dione 1:**[4]



Step-1: To a solution of cyclohept-2-enone (2.0 g, 18.16 mmol, 1.0 equiv.) in methanol (13.5 mL) was added 30% H_2O_2 (4.53 mL, 2.6 equiv.) at -4 °C, followed by 10% aq. NaOH (2.3 mL). The resulting mixture was stirred at 0 °C for 40 min followed by 1.0 h at room temperature. Then, the reaction mixture was diluted with brine solution (100 mL) and extracted with DCM, dried with Na_2SO_4 and evapourated under vacuum to afford pure epoxide (colourless oil) which can be directly used in the next step without further purification. Yield: 87% (2.0 g); IR (Neat): ν_{max} 2931, 2859, 1699, 1448, 1355, 1252, 1180, 933, 839 and 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500

MHz) δ 3.39-3.35 (2H, m), 2.65-2.60 (1H, m), 2.46-2.42 (1H, m), 2.31-2.28 (1H, m), 1.83-1.65 (4H, m), 1.03-0.95 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz) δ 210.3 (C, *C*=O), 59.3 (CH), 55.0 (CH), 40.4 (CH_2), 27.3 (CH_2), 23.4 (CH_2), 22.9 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_7H_{10}O_2Na$ 149.0578; Found 149.0579.

Step-2: To the above obtained epoxide (2.0 g, 15.85 mmol, 1.0 equiv.) in dry toluene (6.0 mL) was added $Pd(PPh_3)_4$ (550 mg, 0.47 mmol, 3 mol%) and 1,2-bis(diphenylphosphino)ethane (189.5 mg, 0.47 mmol, 3 mol%). The reaction was bubbled with N_2 for 10 min, sealed in a 15 mL pressure tube and heated at 110 ^oC for 24 h. The reaction was cooled to room temperature and the solid was filtered off. The filterate was collected, concentrated and purified by coloumn chromatography using ethyl acetate:hexanes (12:88) to afford pure cyclohept-1,3-dione **1**. Yield: 60% (1.2 g); IR (Neat): ν_{max} 2936, 1715, 1691, 1452, 1327, 1204, 1132 and 922 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.59 (2H, s), 2.59-2.56 (4H, m), 1.99-1.96 (4H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz) δ 204.9 (2 x C, 2 x *C*=O), 59.7 (CH_2), 44.0 (2 x CH_2), 25.0 (2 x CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_7H_{10}O_2Na$ 149.0578; Found 149.0578.

Procedure C: **General Procedure for Organocatalytic Three-Component Reductive Coupling**: In an oven dried reaction vial equipped with a magnetic stirring bar at rt was taken cycloheptane-1,3-dione **1 (**0.3 mmol, 1.0 equiv.), to which catalyst **4a**/**c** (0.06 mmol, 20 mol%), Hantzsch ester **3** (0.36 mmol, 1.2 equiv.) and 1.0 mL of 1-butanol was added and stirred for 20 seconds followed by the addition of aldehyde **2** (0.6 mmol, 2.0 equiv.) and allowed to stir for respective reaction times. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure 2-alkyl-cycloheptane-1,3-diones **6**.

Procedure D: **General Procedure for the Michael addition of MVK to 6**: In an oven dried reaction vial equipped with a magnetic stirring bar at rt was taken *C*-alkylated cycloheptane-1,3-dione **6** (0.2 mmol, 1.0 equiv.) and methyl vinyl ketone **7** (0.6 mmol, 3.0 equiv.) to which catalyst Et_3N **4f** (0.2 mmol, 1.0 equiv.) was added and stirred at room temperature for respective reaction times. After the completion of reaction, the reaction mixture was concentrated under

reduced pressure and purified by column chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure Michael adducts **8**.

Procedure E: **General Procedure for the Preparation of Racemic S. Ketones** (±)-**9**: In an oven dried glass vial was taken Michael adduct **8** (0.1 mmol, 1.0 equiv.) to which catalyst pyrrolidine **4e** (0.1 mmol, 1.0 equiv.) and co-catalyst acetic acid **10i** (0.1 mmol, 1.0 equiv.) were added in THF (0.5 mL, 0.2 M) and allowed to stir at room temperature for respective reaction times. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure racemic Swaminathan ketones (±)-**9**.

Procedure F: **General Procedure for the Preparation of Chiral S. Ketones** (-)-**9**: In an oven dried glass vial was taken Michael adduct **8** (0.1 mmol, 1.0 equiv.) to which catalyst dihydroquinine-NH_2 **4i** (0.02 mmol, 20 mol%) and co-catalyst benzoic acid **10g** (0.03 mmol, 30 mol%) were added in C_6F_6 (0.5 mL, 0.2 M) and allowed to stir for respective reaction times at 60 ^oC on a hot plate. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure chiral S. ketones (-)-**9**.

Procedure G: **General Procedure for the Synthesis of Michael Adduct 6pp**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken methyl vinyl ketone **7** (0.4 mmol, 1.0 equiv.) and diisopropylethylamine (0.8 mmol, 2.0 equiv.) in EtOH (2.0 ml) and stirred at room temperature for 5 minutes. To this, the solution of cycloheptane-1,3-dione (0.4 mmol, 1.0 equiv.) in EtOH (2.0 ml) was added dropwise. Allowed the reaction mixture to stir at room temperature for 2.5 hours. Then, the reaction mixture was concentrated under vacuum and purified by coloumn chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure compound **6pp**.

Procedure H: **General Procedure for the Synthesis of Alkylation Product 8pp**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken compound **6pp** (0.2

mmol, 1.0 equiv.) in dry THF (1.0 ml). To this, *t*BuOK (0.2 mmol, 1.0 equiv.) was added under inert atmosphere and allowed to stir for 5 minutes. Then, corresponding alkyl bromide, (bromomethyl)(4-chlorophenyl)sulfane (1.0 mmol, 5.0 equiv.) was added and allowed to stir at room temperature for 6 h. Then, the reaction mixture was concentrated under vacuum and purified by coloumn chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure alkylation compound **8pp**.

Procedure I: **General Procedure for the Desulfurization of** (-)-**9pp to S. Ketone** (-)-**9oo**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken compound (-)-**9pp** (0.2 mmol, 1.0 equiv.) and dissolved in EtOH (2.0 mL). To this one small full table spoon of Raney nickel (200 mg) was added and allowed to stir at room temperature for 1.0 hour. After the completion of reaction, the reaction mixture was carefully filtered through a pack of celiete and washed with ethanol thrice. The collected filterate was concentrated under vacuum and purified using coloumn chromatography to afford pure S. ketone product (-)-**9oo**.

Procedure J: **General Procedure for the Regioselective Reduction of** (-)-**9a**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken chiral S. ketone (-)-**9a** (0.1 mmol, 1.0 equiv.) in 0.5 mL EtOH (0.2 M) and stirred at 0 °C for 5 min after which half portion of $NaBH_4$ (0.035 mmol, 0.35 equiv.) was added and allowed to stir at same temperature for 3.0 h. Then, added another half portion of $NaBH_4$ (0.035 mmol, 0.35 equiv.) to the reaction mixture and allowed to stir for another 3 h at the same temperature. After completion of reaction, the crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Pure chiral product (-)-**11a** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure K: **General Procedure for the Olefin Reduction of** (-)-**9a**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken chiral S. ketone (-)-**9a** (0.1 mmol, 1.0 equiv.) in 0.5 mL 3-picoline (0.2 M) and 10% Pd/C (10 mol%) was added and stirred at room temperature for 30 h under hydrogen atmosphere (hydrogen bladder). After the

completion of reaction, the reaction mixture was diluted with EtOAc (5.0 mL) and washed five times with 4% aq. HCl (5 mL) inorder to remove 3-picoline from the reaction mixture, and the organic layer was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to afford pure reduced product (+)-**12a**.

Procedure L: **General Procedure for the Simmons-Smith Reaction of** (-)-**11a**: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken compound (-)-**11a** (0.1 mmol, 1.0 equiv.) in 1.0 mL anhydrous DCM (0.1 M) and stirred at -10 ^{o}C for 5 min. To this, diethyl zinc (1.5 M in toluene, 0.5 mmol, 5.0 equiv.) was added dropwise followed by diiodomethane (0.5 mmol, 5.0 equiv.). The cooling bath was allowed to warm to room temperature in over 3.0 h and the reaction was stirred for an additional 1.0 h, after which the TLC showed complete consumption of (-)-**11a**. To the reaction mixture, a saturated NH_4Cl (5 mL) was added and was diluted with EtOAc (10 mL) and 10% aq. HCl (5 mL). The layers were separated and the organic layer was then successively washed with saturated aq. Na_2SO_3 (5 mL), saturated aq. $NaHCO_3$ (5 mL) and saturated NaCl (5 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give crude product, and purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to afford pure chiral tricyclic compound (-)-**13a**.

Procedure M: **General Procedure for the Epoxidation of** (-)-**11a**: In an oven dried round bottomed flask, *m*-CPBA (0.12 mmol, 1.2 equiv.) was added to a stirred solution of allylic alcohol (-)-**11a** (0.1 mmol, 1.0 equiv.) in 0.5 mL anhydrous DCM (0.2 M) at 0 ^{o}C and allowed to warm to room temperature and stirred for 1.5 h. After the completion of reaction, the reaction mixture was diluted with DCM, washed with 10% aq. K_2CO_3 (5 mL), brine solution (5 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give crude product, and purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to afford pure chiral epoxide (-)-**14a**.

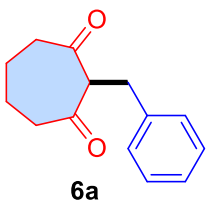
Procedure N: **General Procedure for the Regioselective Wittig Reaction of** (+)**-12a**:

Step-1: Preparation of 1.0 M methylenetriphenylphosphorane solution: In an oven dried round bottomed flask equipped with a magnetic stirring bar was taken methyltriphenylphosphonium bromide (1.0 mmol, 1.0 equiv.) in 1.0 mL dry THF (1.0 M) and cooled to 0 °C. To this *n*-BuLi (1.0 mmol, 1.0 equiv.) was added drop wise at the same temperature. Then, the ice bath was removed and the reaction mixture was allowed to stir at room temperature for 30 min. during which dark yellow colour develops and sustains upon the formation of ylide. This is the 1.0 M ylide stock solution.

Step-2: In a seperate oven dried round bottomed flask equipped with a magnetic stirring bar was taken compound (+)-**12a** (0.1 mmol, 1.0 equiv.) in 0.5 mL dry THF (0.2 M) and cooled to 0 °C. To this, 0.2 mL of freshly prepared 1.0 M ylide solution (0.2 mmol, 2.0 equiv.) was added dropwise allowed to stir for 35 min. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to afford pure compound (+)-**15a**.

Procedure O: **General Procedure for the Preparation of 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (5n)**: In an oven dried reaction vial equipped with a magnetic stirring bar at rt was taken cycloheptane-1,3-dione **1** (0.3 mmol, 1.0 equiv.), to which catalyst **4a** (0.06 mmol, 20 mol%), and 1.0 mL of 1-butanol was added and stirred for 20 seconds followed by the addition of *p*-nitrobenzaldehyde **2n** (0.6 mmol, 2.0 equiv.) and allowed to stir for 2.0 h. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to afford pure 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (**5n**).

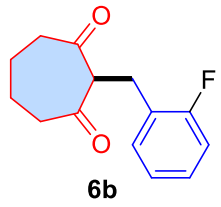
2-Benzylcycloheptane-1,3-dione (6a): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (3:97) and isolated as light yellow solid. Yield: 90% (58 mg); Mp.: 48-50 °C; IR (Neat): ν_{max} 3305, 1703, 1453, 1275, 1261, 1075, 750 and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.25-7.22 (2H, m), 7.18-7.13 (3H, m), 4.21 (1H, t, *J* = 7.0 Hz), 3.15 (2H, d, *J* = 6.5 Hz), 2.55 (2H, ddd, *J* = 13.7, 8.7, 4.5 Hz), 2.46 (2H, ddd, *J* = 13.7, 9.5, 3.5 Hz), 2.12-2.05



6a

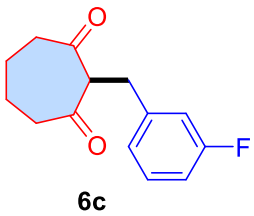
(2H, m), 1.88-1.82 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.5 (2 x C, 2 x *C*=O), 139.1 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 68.4 (CH), 44.3 (2 x CH_2), 31.9 (CH_2), 25.1 (2 x CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1229; Found 217.1231.

2-(2-Fluorobenzyl)cycloheptane-1,3-dione (6b): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 80% (56 mg). IR (Neat): ν_{max} 2924, 2853, 1721, 1695, 1583, 1491, 1453, 1321, 1228, 1113, 1093, 910, 797 and 756 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 7.21-7.14 (2H, m), 7.03-6.95 (2H, m), 4.29 (1H, t, *J* = 7.0 Hz), 3.16 (2H, d, *J* = 7.0 Hz), 2.58 (2H, ddd, *J* = 14.1, 8.7, 4.5 Hz), 2.50 (2H, ddd, *J* = 14.5, 8.5, 4.0 Hz), 2.15-2.07 (2H, m), 1.89-1.84 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): *δ* 205.1 (2 x C, 2 x *C*=O), 161.1 (C, d, *J* = 243.7 Hz, *C*-F), 131.9 (CH, d, *J* = 5.0 Hz), 128.2 (CH, d, *J* = 7.5 Hz), 125.7 (C, d, *J* = 16.2 Hz), 124.0 (CH, d, *J* = 3.7 Hz), 115.1 (CH, d, *J* = 22.5 Hz), 66.6 (CH), 44.2 (2 x CH_2), 25.78 (CH_2), 25.77 (2 x CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): *δ* -117.7; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{16}FO_2$ 235.1134; Found 235.1128.



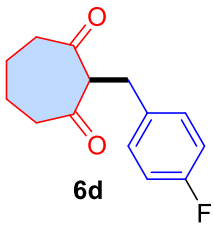
6b

2-(3-Fluorobenzyl)cycloheptane-1,3-dione (6c): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as light yellow solid. Mp.: 108-110 °C. Yield: 84% (59 mg). IR (Neat): ν_{max} 3013, 2968, 1738, 1431, 1396, 1228, 1215, 1040, 922 and 718 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 7.21-7.17 (1H, m), 6.91 (1H, d, *J* = 7.5 Hz), 6.88-6.84 (2H, m), 4.21 (1H, t, *J* = 7.0 Hz), 3.13 (2H, d, *J* = 7.0 Hz), 2.57 (2H, ddd, *J* = 14.2, 8.5, 4.0 Hz), 2.47 (2H, ddd, *J* = 14.5, 8.7, 4.0 Hz), 2.14-2.06 (2H, m), 1.89-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): *δ* 205.0 (2 x C, 2 x *C*=O), 162.7 (C, d, *J* = 243.7 Hz, *C*-F), 141.6 (C, d, *J* = 7.5 Hz), 129.8 (CH, d, *J* = 8.7 Hz), 124.6 (CH, d, *J* = 2.5 Hz), 115.8 (CH, d, *J* = 21.2 Hz), 113.2 (CH, d, *J* = 21.2 Hz), 68.0 (CH), 44.4 (2 x CH_2), 31.5 (CH_2, d, *J* = 2.5 Hz), 24.9 (2 x CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): *δ* -113.3; HRMS (ESI-TOF) *m*/*z*: $[M + K]^+$ Calcd for $C_{14}H_{15}FO_2K$ 273.0693; Found 273.0696.

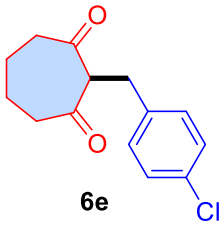


6c

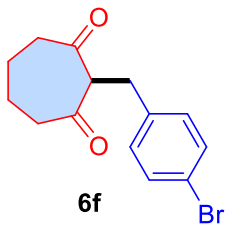
2-(4-Fluorobenzyl)cycloheptane-1,3-dione (6d): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow solid. Mp.: 62-64 °C. Yield: 85% (60 mg). IR (Neat): ν_{max} 2937, 1720, 1694, 1601, 1508, 1452, 1347, 1275, 1260, 1158, 1135, 750 and 544 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12-7.10 (2H, m), 6.95-6.90 (2H, m), 4.16 (1H, t, J = 7.0 Hz), 3.11 (2H, d, J = 6.5 Hz), 2.55 (2H, ddd, J = 14.4, 9.7, 3.5 Hz), 2.46 (2H, ddd, J = 14.2, 8.5, 4.0 Hz), 2.13-2.05 (2H, m), 1.89-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.3 (2 x C, 2 x *C*=O), 161.5 (C, d, J = 244 Hz, *C*-F), 134.7 (C), 130.4 (2 x CH, d, J = 7.0 Hz), 115.2 (2 x CH, d, J = 22.0 Hz), 68.4 (CH), 44.3 (2 x CH_2), 31.0 (CH_2), 25.0 (2 x CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -116.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}FO_2$ 235.1134; Found 235.1129.



2-(4-Chlorobenzyl)cycloheptane-1,3-dione (6e): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as light yellow solid. Mp.: 95-97 °C. Yield: 80% (60 mg). IR (Neat): ν_{max} 2943, 1719, 1693, 1490, 1450, 1407, 1317, 1264, 1219, 1128, 1091, 1049 and 1013 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19 (2H, td, J = 8.0, 4.0 Hz), 7.07 (2H, br d, J = 8.5 Hz), 4.16 (1H, t, J = 6.5 Hz), 3.09 (2H, d, J = 6.5 Hz), 2.54 (2H, ddd, J = 14.0, 8.7, 4.0 Hz), 2.45 (2H, ddd, J = 14.0, 9.5, 4.0 Hz), 2.12-2.05 (2H, m), 1.87-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.1 (2 x C, 2 x *C*=O), 137.6 (C), 132.1 (C), 130.4 (2 x CH), 128.5 (2 x CH), 68.2 (CH), 44.3 (2 x CH_2), 31.1 (CH_2), 24.9 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{16}{}^{35}ClO_2$ 251.0839; Found 251.0842; *m/z*: $[M + 2 + H]^+$ Calcd for $C_{14}H_{16}{}^{37}ClO_2$ 253.0809; Found 253.0814.

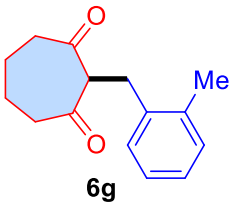


2-(4-Bromobenzyl)cycloheptane-1,3-dione (6f): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as white solid. Mp.: 69-71 °C. Yield: 82% (73 mg). IR (Neat): ν_{max} 2937, 2860, 1718, 1693, 1487, 1456, 1401, 1315, 1209, 1070, 1054, 915 and 814 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (2H, td, J = 8.5, 2.5 Hz), 7.02 (2H, br d, J = 8.5 Hz), 4.16 (1H, t, J = 6.5 Hz), 3.08 (2H, d, J = 6.5 Hz), 2.55 (2H, ddd, J = 14.2, 8.7, 4.5 Hz), 2.46 (2H, ddd, J = 13.8, 9.5, 3.5 Hz), 2.12-2.05 (2H,



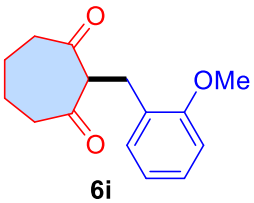
m) 1.88-1.82 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.1 (2 x C, 2 x *C*=O), 138.1 (C), 130.8 (2 x CH), 131.5 (2 x CH), 120.2 (C), 68.1 (CH), 44.4 (2 x CH_2), 31.2 (CH_2), 25.0 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{16}O_2{}^{79}Br$ 295.0334; Found 295.0330; *m/z*: $[M + 2 + H]^+$ Calcd for $C_{14}H_{16}O_2{}^{81}Br$ 297.0313; Found 297.0309.

2-(2-Methylbenzyl)cycloheptane-1,3-dione (6g): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 90% (62 mg). IR (Neat): ν_{max} 2935, 1721, 1694, 1452, 1321, 1208, 1120, 1097, 910 and 741 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.13-7.09 (2H, m), 7.08-7.02 (2H, m), 4.15 (1H, t, *J* = 6.5 Hz), 3.16 (2H, d, *J* = 7.0 Hz), 2.58 (2H, ddd, *J* = 14.1, 8.5, 4.0 Hz), 2.51 (2H, ddd, *J* = 14.1, 8.5, 4.0 Hz), 2.30 (3H, s, Ar-C*H*$_3$), 2.13-2.06 (2H, m), 1.91-1.83 (2H. m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.7 (2 x C, 2 x *C*=O), 137.2 (C), 136.2 (C), 130.4 (CH), 129.2 (CH), 126.5 (CH), 125.9 (CH), 67.0 (CH), 44.2 (2 x CH_2), 28.9 (CH_2), 25.3 (2 x CH_2), 19.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_2Na$ 253.1204; Found : 253.1209.



6g

2-(4-Methylbenzyl)cycloheptane-1,3-dione (6h): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 94% (65 mg). IR (Neat): ν_{max} 2928, 2154, 1720, 1694, 1514, 1450, 1321, 1218, 1186, 909, 809, 730 and 544 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.06-7.02 (4H, m), 4.16 (1H, t, *J* = 7.0 Hz), 3.11 (2H, d, *J* = 6.5 Hz), 2.55 (2H, ddd, *J* = 13.8, 8.7, 3.5 Hz), 2.46 (2H, ddd, *J* = 14.1, 8.7, 3.5 Hz), 2.29 (3H, s, Ar-C*H*$_3$), 2.12-2.04 (2H, m), 1.88-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.7 (2 x C, 2 x *C*=O), 135.9 (C), 135.8 (C), 129.1 (2 x CH), 128.8 (2 x CH), 68.5 (CH), 44.3 (2 x CH_2), 31.4 (CH_2), 25.1 (2 x CH_2), 21.0 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_2Na$ 253.1204; Found 253.1208.



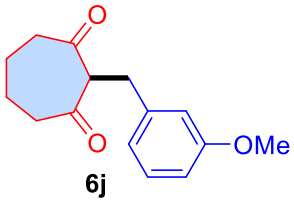
6h

6i

2-(2-Methoxybenzyl)cycloheptane-1,3-dione (6i): Prepared by following the procedure **C** and purified by column chromatography using

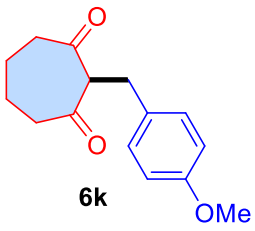
EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 86% (63 mg). IR (Neat): ν_{max} 2921, 2851, 2359, 1721, 1695, 1600, 1493, 1460, 1322, 1243, 1119, 1290, 1259, 1211, 1153, 1046, 909, 780 and 693 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.17 (1H, dt, J = 8.0, 1.5 Hz), 7.12 (1H, dd, J = 7.5, 1.5 Hz), 6.84 (1H, dt, J = 7.5, 1.0 Hz), 6.80 (1H, br d, J = 8.5 Hz), 4.15 (1H, t, J = 6.5 Hz), 3.78 (3H, s, OCH_3), 3.14 (2H, d, J = 6.5 Hz), 2.57-2.47 (4H, m), 2.08-2.02 (2H, m), 1.88-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 206.4 (2 x C, 2 x C=O), 157.3 (C), 131.1 (CH), 127.7 (CH), 127.1 (C), 120.5 (CH), 110.1 (CH), 66.8 (CH), 55.0 (CH_3, OCH_3), 43.9 (2 x CH_2), 27.4 (CH_2), 25.6 (2 x CH_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O_3$ 247.1334; Found 247.1339.

2-(3-Methoxybenzyl)cycloheptane-1,3-dione (6j): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 90% (66 mg). IR (Neat): ν_{max} 2937, 2031, 1721, 1694, 1599, 1583, 1488, 1452, 1316, 1290, 1259, 1211, 1153, 1046, 909, 780 and 693 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.15 (1H, t, J = 7.5 Hz), 6.73-6.69 (3H, m), 4.21 (1H, t, J = 6.5 Hz), 3.77 (3H, s, OCH_3), 3.13 (2H, d, J = 6.5 Hz), 2.56 (2H, ddd, J = 14.0, 8.5, 4.0 Hz), 2.47 (2H, ddd, J = 14.0, 9.7, 3.5 Hz), 2.11-2.06 (2H, m) 1.87-1.82 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.4 (2 x C, 2 x C=O), 159.6 (C), 140.7 (C), 129.4 (CH), 121.2 (CH), 114.7 (CH), 111.7 (CH), 68.3 (CH), 55.1 (CH_3, OCH_3), 44.3 (2 x CH_2), 31.8 (CH_2), 25.0 (2 x CH_2). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_3Na$ 269.1154; Found 269.1154.



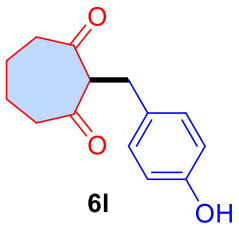
6j

2-(4-Methoxybenzyl)cycloheptane-1,3-dione (6k): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 93% (69 mg). IR (Neat): ν_{max} 2934, 1986, 1720, 1694, 1610, 1610, 1582, 1511, 1453, 1299, 1245, 1178, 1114, and 1033 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.06 (2H, d, J = 8.5 Hz), 6.78 (2H, d, J = 8.0 Hz), 4.12 (1H, t, J = 7.0 Hz), 3.76 (3H, s, OCH_3), 3.09 (2H, d, J = 6.5 Hz), 2.53 (2H, ddd, J = 13.8, 8.7, 4.0 Hz), 2.45 (2H, ddd, J = 13.5, 9.5, 3.5 Hz), 2.08-2.03 (2H, m) 1.87-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.8 (2 x C, 2 x C=O), 158.1 (C), 131.0 (C), 129.9 (2 x CH), 113.8 (2 x CH), 68.7 (CH), 55.2 (CH_3,



6k

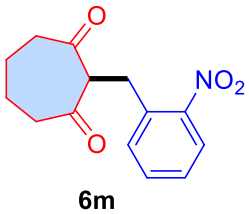
OCH_3), 44.3 (2 x CH_2), 31.0 (CH_2), 25.2 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}O_3$ 247.1334; Found 247.1335.



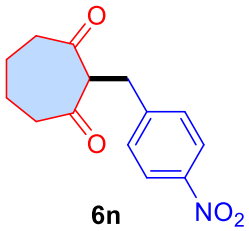
6l

2-(4-Hydroxybenzyl)cycloheptane-1,3-dione (6l): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as light yellow solid. Mp.: 83-85 °C. Yield: 85% (59 mg). IR (Neat): ν_{max} 3335, 2929, 2857, 1711, 1678, 1614, 1596, 1394, 1263, 1094, 973 and 739 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.00 (2H, td, *J* = 8.5, 3.0 Hz), 6.89 (2H, td, *J* = 8.5, 3.0 Hz), 5.20 (1H, br s, O*H*), 4.12 (1H, t, *J* = 7.0 Hz), 3.07 (2H, d, *J* = 6.5 Hz), 2.54 (2H, ddd, *J* = 13.8, 8.5, 4.5 Hz), 2.46 (2H, ddd, *J* = 13.7, 9.5, 3.5 Hz), 2.11-2.03 (2H, m), 1.88-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 206.2 (2 x C, 2 x *C*=O), 154.2 (C), 130.9 (C), 130.2 (2 x CH), 115.3 (2 x CH), 68.7 (CH), 44.3 (2 x CH_2), 31.1 (CH_2), 25.2 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_3Na$ 255.0997; Found 255.0998.

2-(2-Nitrobenzyl)cycloheptane-1,3-dione (6m): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as white solid. Mp.: 67-69 °C. Yield: 95% (74 mg). IR (Neat): ν_{max} 2952, 2863, 1710, 1688, 1608, 1574, 1519, 1449, 1231, 1357, 1313, 1265, 1051, 1033, 959 and 738 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.95 (1H, dd, *J* = 8.2, 1.5 Hz), 7.49 (1H, dt, *J* = 7.5, 1.5 Hz), 7.43 (1H, dd, *J* = 7.5, 1.5 Hz), 7.36 (1H, dt, *J* = 7.0, 1.5 Hz), 4.52 (1H, t, *J* = 6.5 Hz), 3.40 (2H, d, *J* = 6.0 Hz), 2.64 (2H, ddd, *J* = 14.8, 8.7, 4.0 Hz), 2.52 (2H, ddd, *J* = 14.8, 8.7, 4.0 Hz), 2.17-2.09 (2H, m), 1.89-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.3 (2 x C, 2 x *C*=O), 149.1 (C), 134.7 (C), 133.9 (CH), 133.2 (CH), 127.8 (CH), 125.0 (CH), 67.2 (CH), 44.4 (2 x CH_2), 29.4 (CH_2), 24.7 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}NO_4Na$ 284.0899; Found 284.0897.



6m

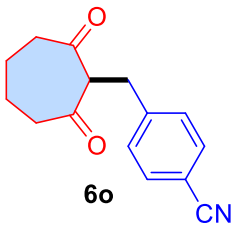


6n

2-(4-Nitrobenzyl)cycloheptane-1,3-dione (6n): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as white solid. Mp.: 115-117 °C. Yield: 93% (73 mg). IR (Neat): ν_{max} 2929, 2874, 1716, 1691, 1594, 1507, 1456, 1433, 1342, 1210, 1111, 910, 856 and 751 cm^{-1}. ^1H NMR ($CDCl_3$, 500

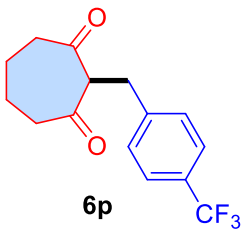
MHz): δ 8.09 (2H, m), 7.32 (2H, d, J = 8.5 Hz), 4.26 (1H, t, J = 7.0 Hz), 3.22 (2H, d, J = 7.0 Hz), 5.16 (2H, ddd, J = 14.2, 8.7, 4.5 Hz), 4.98 (2H, ddd, J = 14.0, 9.7, 3.5 Hz), 2.15-2.08 (2H, m), 1.90-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.4 (2 x C, 2 x *C*=O), 147.1 (C), 146.6 (C), 129.9 (2 x CH), 123.6 (2 x CH), 67.7 (CH), 44.4 (2 x CH_2), 31.6 (CH_2), 24.8 (2 x CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{16}NO_4$ 262.1079; Found 262.1077.

2-(4-Cyanobenzyl)cycloheptane-1,3-dione (6o): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as white solid. Mp.: 69-71 °C. Yield: 97% (70 mg). IR (Neat): ν_{max} 2935, 1714, 1689, 1433, 1215, 1113 and 825 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (2H, br d, J = 8.0 Hz), 7.27 (2H, br d, J = 7.5 Hz), 4.20 (1H, t, J =7.0 Hz), 3.19 (2H, d, J = 7.0 Hz), 2.58 (2H, ddd, J = 14.3, 8.5, 4.0 Hz), 2.49 (2H, ddd, J = 14.0, 9.7, 4.0 Hz), 2.15-2.01 (2H, m), 1.91-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.5 (2 x C, 2 x C=O), 144.9 (C), 132.1 (2 x CH), 129.8 (2 x CH), 118.8 (C), 110.3 (C), 67.6 (CH), 44.3 (2 x CH_2), 31.8 (CH_2), 24.8 (2 x CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{15}H_{15}NNaO_2$ 264.1000; Found 264.1010.



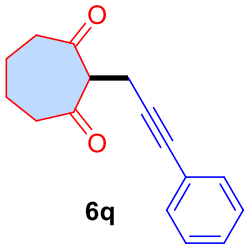
6o

2-(4-(Trifluoromethyl)cycloheptane-1,3-dione (6p): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as white solid. Mp.: 67-69 °C. Yield: 89% (76 mg). IR (Neat): ν_{max} 2922, 2054, 1716, 1689, 1617, 1453, 1371, 1286, 1157, 1102, 1049, 969 and 748 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50 (2H, d, J = 8.0 Hz), 7.28 (2H, d, J = 8.0 Hz), 4.23 (1H, t, J = 7.0 Hz), 3.19 (2H, d, J = 6.5 Hz), 2.58 (2H, ddd, J = 14.5, 8.5, 4.0 Hz), 2.49 (2H, ddd, J = 14.6, 8.7, 3.5 Hz), 2.15-2.07 (2H, m), 1.90-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.8 (2 x C, 2 x *C*=O), 143.3 (C), 129.4 (2 x CH), 128.7 (C, q, J = 32.5 Hz), 125.3 (2 x CH, q, J = 3.75 Hz), 124.2 (C, q, J = 270 Hz, *C*F_3), 68.0 (CH), 44.4 (2 x CH_2), 31.6 (CH_2), 24.9 (2 x CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -62.5; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{16}F_3O_2$ 285.1102; Found 285.1101.



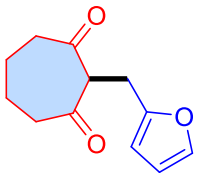
6p

2-(3-Phenylprop-2-yn-1-yl)cycloheptane-1,3-dione (6q): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 0.7:9.3) and isolated as yellow oil. Yield: 83% (60 mg). IR (Neat): ν_{max} 2927, 2631, 2334, 1722, 1697, 1597, 1490, 1442, 1416, 1316, 1245, 1193, 1129 and 1070 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.33 (2H, m), 7.26-7.25 (3H, m), 4.24 (1H, t, J = 6.5 Hz), 2.91 (2H, d, J = 6.5 Hz), 2.69 (2H, ddd, J = 14.6, 8.5, 3.5 Hz), 2.56 (2H, ddd, J = 14.6, 8.5, 3.5 Hz), 2.18-2.11 (2H, m), 1.91-1.87 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 204.0 (2 x C, 2 x *C*=O), 131.5 (2 x CH), 128.1 (2 x CH), 127.8 (CH), 123.3 (C), 86.7 (C), 81.5 (C), 65.4 (CH), 44.2 (2 x CH_2), 24.7 (2 x CH_2), 16.4 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_2Na$ 263.1048; Found 263.1053.



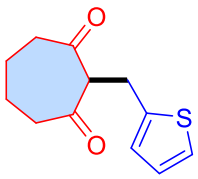
6q

2-(Furan-2-ylmethyl)cycloheptane-1,3-dione (6r): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 94% (58 mg). IR (Neat): ν_{max} 2935, 1721, 1694, 1595, 1506, 1452, 1354, 1215, 1163, 1072, 1010, 910, 805, 733 and 595 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24 (1H, t, J = 2.0 Hz), 6.23 (1H, t, J = 2.0 Hz), 5.99 (1H, d, J = 3.5 Hz), 4.36 (1H, t, J = 6.5 Hz), 3.17 (2H, d, J = 6.5 Hz), 2.64 (2H, ddd, J = 14.6, 9.0, 4.0 Hz), 2.49 (2H, ddd, J = 14.5, 9.0, 4.0 Hz), 2.17-2.10 (2H, m), 1.88-1.85 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.5 (2 x C, 2 x *C*=O), 152.6 (C), 141.2 (CH), 110.3 (CH), 106.4 (CH), 65.0 (CH), 44.2 (2 x CH_2), 24.8 (2 x CH_2), 24.4 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{14}O_3Na$ 229.0841; Found 229.0839.



6r

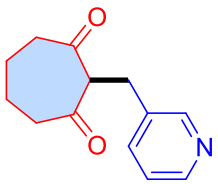
2-(Thiophen-2-ylmethyl)cycloheptane-1,3-dione (6s): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as brown oil. Yield: 95% (63 mg). IR (Neat): ν_{max} 2929, 1719, 1693, 1430, 1209, 909 and 696 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.09 (1H, dd, J = 5.25, 1.5 Hz), 6.87 (1H, dd, J = 5.25, 3.5 Hz), 6.77 (1H, dd, J = 3.5, 1.0 Hz), 4.30 (1H, t, J = 6.5 Hz), 3.37 (2H, d, J = 7.0 Hz), 2.62 (2H, ddd, J = 14.5, 8.7, 4.5 Hz), 2.49 (2H, ddd, J = 14.6, 8.7, 3.5 Hz), 2.17-2.09 (2H, m), 1.89-1.82 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.6 (2 x C, 2 x *C*=O), 141.2 (C), 126.8 (CH),



6s

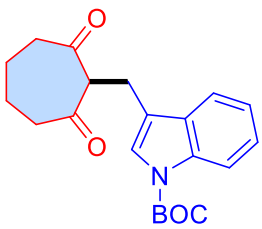
125.9 (CH), 123.8 (CH), 68.4 (CH), 44.5 (2 x CH_2), 26.1 (CH_2), 24.7 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}O_2S$ 223.0793; Found 223.0790.

2-(Pyridin-3-ylmethyl)cycloheptane-1,3-dione (6t): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (3.0:7.0 to 3.2:6.8) and isolated as yellow oil. Yield: 81% (53 mg). IR (Neat): ν_{max} 2931, 2865, 1718, 1696, 1596, 1479, 1425, 1373, 1320, 1185, 1129, 1048, 912 and 866 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.41 (2H, br s), 7.50 (1H, d, J = 8.0 Hz), 7.17 (1H, t, J = 6.5 Hz), 4.22 (1H, t, J = 7.0 Hz), 3.12 (2H, d, J = 7.0 Hz), 2.59-2.54 (2H, m), 2.49-2.45 (2H, m), 2.10-2.06 (2H, m), 1.88-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 204.6 (2 x C, 2 x *C*=O), 150.0 (CH), 147.6 (CH), 136.9 (CH), 134.7 (C), 123.3 (CH), 67.8 (CH), 44.4 (2 x CH_2), 29.0 (CH_2), 24.8 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{16}NO_2$ 218.1181; Found 218.1178.



6t

2-(Pyridin-4-ylmethyl)cycloheptane-1,3-dione (6u): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (3.0:7.0 to 3.2:6.8) and isolated as yellow oil. Yield: 89% (58 mg). IR (Neat): ν_{max} 3033, 2928, 2863, 1720, 1696, 1602, 1558, 1416, 1373, 1252, 1216, 1134, 1068 and 1042 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.46 (2H, dd, J = 4.5, 1.5 Hz), 7.09 (2H, dd, J = 4.5, 1.5 Hz), 4.24 (1H, t, J = 7.0 Hz), 3.13 (2H, d, J = 7.0 Hz), 2.59 (2H, ddd, J = 14.5, 8.7, 4.5 Hz), 2.49 (2H, ddd, J = 14.6, 9.0, 2.0 Hz), 2.16-2.08 (2H, m), 1.94-1.86 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 204.4 (2 x C, 2 x *C*=O), 149.7 (2 x CH), 148.4 (C), 124.4 (2 x CH), 67.2 (CH), 44.4 (2 x CH_2), 31.1 (CH_2), 24.8 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{16}NO_2$ 218.1181; Found 218.1180.

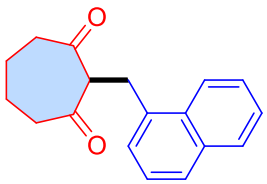


6v

***tert*-Butyl-3-((2,7-dioxocycloheptyl)methyl)-1*H*-indole-1-carboxylate (6v):** Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as orange solid. Mp.: 110-112 °C. Yield: 70% (75 mg). IR (Neat): ν_{max} 2921, 2851, 1963, 1724, 1608, 1452, 1370, 1308, 1254, 1222, 1156, 1082, 1017, 909, 765, 747 and 589 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (1H, br

s), 7.50 (1H, d, *J* = 7.5 Hz), 7.33-7.28 (2H, m), 7.25-7.22 (1H, m), 4.31 (1H, t, *J* = 7.0 Hz), 3.24 (2H, dd, *J* = 6.0, 1.0 Hz), 2.60 (2H, ddd, *J* = 13.8, 9.0, 4.0 Hz), 2.51 (2H, ddd, *J* = 14.0, 9.5, 4.0 Hz), 2.14-2.06 (2H, m), 1.90-1.82 (2H, m), 1.65 (9H, s). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.4 (2 x C, 2 x *C*=O), 149.6 (C, O-*C*=O), 135.4 (C), 130.2 (C), 124.3 (CH), 123.6 (CH), 122.4 (CH), 118.8 (CH), 117.6 (C), 115.2 (CH), 83.5 (C), 66.4 (CH), 44.3 (2 x CH_2), 28.2 (3 x CH_3), 25.0 (2 x CH_2), 21.2 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ Calcd for $C_{21}H_{29}N_2O_4$ 373.2127; Found 373.2129.

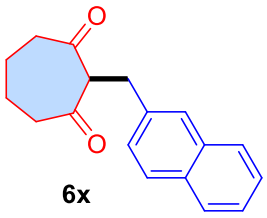
2-(Naphthalen-1-ylmethyl)cycloheptane-1,3-dione (6w): Prepared by following the procedure



6w

C and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.8:9.2) and isolated as yellow oil. Yield: 83% (66 mg). IR (Neat): ν_{max} 3045, 2935, 1720, 1694, 1596, 1509, 1540, 1344, 1323, 1263, 1206, 1134, 1018, 909 and 778 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (1H, d, *J* = 8.5 Hz), 7.85 (1H, d, *J* = 8.0 Hz), 7.71 (1H, d, *J* = 7.5 Hz), 7.52 (1H, br dt, *J* = 8.0, 1.5 Hz), 7.47 (1H, br dt, *J* = 8.0, 1.5 Hz), 7.35 (1H, t, *J* = 7.5 Hz), 7.32 (1H, d, *J* = 7.5 Hz), 4.32 (1H, t, *J* = 6.5 Hz), 3.65 (2H, d, *J* = 6.5 Hz), 2.56-2.52 (4H, m), 2.09-2.01 (2H, m), 1.90-1.83 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.7 (2 x C, 2 x *C*=O), 135.0 (C), 133.9 (C), 131.5 (C), 129.0 (CH), 127.4 (CH), 127.2 (CH), 126.2 (CH), 125.5 (CH), 125.4 (CH), 123.2 (CH), 67.3 (CH), 44.2 (2 x CH_2), 28.7 (CH_2), 25.1 (2 x CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ Calcd for $C_{18}H_{22}NO_2$ 284.1651; Found 284.1651.

2-(Naphthalen-2-ylmethyl)cycloheptane-1,3-dione (6x): Prepared by following the procedure

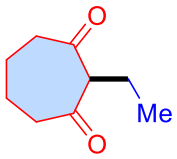


6x

C and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.8:9.2) and isolated as white solid. Mp.: 69-71 °C. Yield: 91% (73 mg). IR (Neat): ν_{max} 2923, 2853, 1719, 1693, 1631, 1599, 1507, 345, 1207, 1168, 1126, 1106, 1038, 961, 816 and 748 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79-7.73 (3H, m), 7.61 (1H, br s), 7.43 (2H, m), 7.29 (1H, dd, *J* = 8.5, 1.5 Hz), 4.32 (1H, t, *J* = 7.0 Hz), 3.32 (2H, d, *J* = 7.0 Hz), 2.56 (2H, ddd, *J* = 14.0, 8.5, 4.0 Hz), 2.47 (2H, ddd, *J* = 13.8, 9.5, 3.5 Hz), 2.13-2.05 (2H, m), 1.88-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 205.4 (2 x C, 2 x *C*=O), 136.6 (C), 133.4 (C), 132.1 (C), 128.0 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 127.4 (CH), 126.0 (CH), 125.4 (CH), 68.4

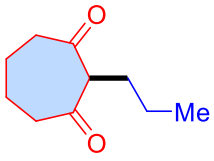
(CH), 44.4 (2 x CH_2), 32.0 (CH_2), 25.0 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}O_2$ 267.1385; Found 267.1386.

2-Ethylcycloheptane-1,3-dione (6y): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 80% (37 mg). IR (Neat): ν_{max} 2918, 1687, 1406, 1273, 1189, 921, 734 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.56 (1H, t, J = 7.0 Hz), 2.57-2.45 (4H, m), 2.08-2.00 (2H, m), 1.90-1.80 (4H, m), 0.85 (3H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.6 (2 x C, 2 x *C*=O), 68.4 (CH), 43.7 (2 x CH_2), 25.8 (2 x CH_2), 19.7 (CH_2), 11.6 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{15}O_2$ 155.1072; Found 155.1076.



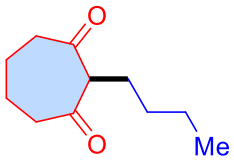
6y

2-Propylcycloheptane-1,3-dione (6z): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 86% (43 mg). IR (Neat): ν_{max} 2931, 2359, 1694, 1454, 1209 and 911 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.63 (1H, t, J = 7.0 Hz), 2.56-2.45 (4H, m), 2.06-1.99 (2H, m), 1.89-1.81 (2H, m), 1.79-1.74 (2H, m), 1.26-1.19 (2H, m), 0.88 (3H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.7 (2 x C, 2 x *C*=O), 66.6 (CH), 43.6 (2 x CH_2), 28.4 (CH_2), 25.9 (2 x CH_2), 20.3 (CH_2), 13.8 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{16}O_2Na$ 191.1048; Found 191.1041.



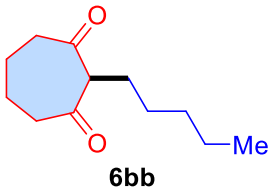
6z

2-Butylcycloheptane-1,3-dione (6aa): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 94% (51 mg). IR (Neat): ν_{max} 2930, 2867, 1721, 1696, 1453, 1204, 1142, 757 and 576 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.64 (1H, t, J = 7.0 Hz), 2.58-2.47 (4H, m), 2.09-2.01 (2H, m), 1.91-1.83 (2H, m), 1.82-1.78 (2H, m), 1.34-1.25 (2H, m), 1.22-1.16 (2H, m) 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.7 (2 x C, 2 x *C*=O), 66.9 (CH), 43.7 (2 x CH_2), 29.3 (CH_2), 26.1 (CH_2), 25.9 (2 x CH_2), 22.6 (CH_2) 13.8 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{19}O_2$ 183.1385; Found 183.1381.



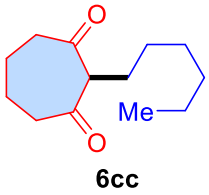
6aa

2-Pentylcycloheptane-1,3-dione (6bb): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 92% (54 mg). IR (Neat): ν_{max} 2924, 2855, 2361, 2339, 1723, 1694, 1454, 1217, 1125, 670 and 587 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.63 (1H, t, J = 7.0 Hz), 2.58-2.47 (4H, m), 2.09-2.00 (2H, m), 1.92-1.84 (2H, m), 1.82-1.77 (2H, m), 1.32-1.17 (6H, m), 0.87 (3H, t, J =7.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.7 (2 x C, 2 x *C*=O), 66.9 (CH), 43.7 (2 x CH_2), 31.6 (CH_2), 26.8 (CH_2), 26.3 (CH_2), 25.9 (2 x CH_2), 22.3 (CH_2), 13.9 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{21}O_2$ 197.1542; Found 197.1547.



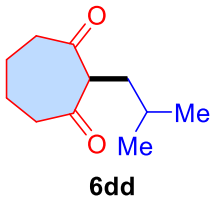
6bb

2-Hexylcycloheptane-1,3-dione (6cc): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 83% (52 mg). IR (Neat): ν_{max} 2927, 2858, 1702, 1454, 1173, 1142, 734 and 600 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.63 (1H, t, J = 7.0 Hz), 2.58-2.47 (4H, m), 2.09- 2.01 (2H, m), 1.91-1.84 (2H, m), 1.82-1.78 (2H, m), 1.30-1.17 (8H, m), 0.87 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.7 (2 x C, 2 x *C*=O), 66.9 (CH), 43.7 (2 x CH_2), 31.5 (CH_2), 29.1 (CH_2), 27.0 (CH_2), 26.3 (CH_2), 25.9 (2 x CH_2), 22.5 (CH_2), 14.0 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{23}O_2$ 211.1698; Found 211.1693.



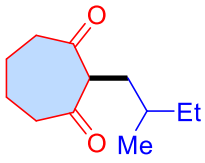
6cc

2-Isobutylcycloheptane-1,3-dione (6dd): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 70% (38 mg). IR (Neat): ν_{max} 2953, 2868, 1722, 1695, 1454, 1211, 1175, 683 and 576 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.73 (1H, t, J = 7.0 Hz), 2.58-2.46 (4H, m), 2.08-2.01 (2H, m), 1.90-1.82 (2H, m), 1.70 (2H, t, J = 7.0 Hz), 1.53-1.42 (1H, m), 0.86 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.8 (2 x C, 2 x *C*=O), 65.0 (CH), 43.6 (2 x CH_2), 35.0 (CH_2), 26.0 (2 x CH_2), 25.8 (CH), 22.4 (2 x CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{18}O_2Na$ 205.1204; Found 205.1205.



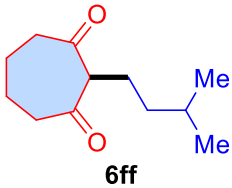
6dd

2-(2-Methylbutyl)cycloheptane-1,3-dione (6ee): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 85% (50 mg). IR (Neat): ν_{max} 2957, 2929, 1694, 1456, 1202, 1141, 909 and 549 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.75 (1H, t, J = 6.5 Hz), 2.60-2.49 (4H, m), 2.09-2.01 (2H, m), 1.91-1.83 (3H, m), 1.64-1.58 (1H, m), 1.37-1.21 (2H, m), 1.17-1.09 (1H, m), 0.87-0.82 (6H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 207.9 (C, *C*=O), 207.8 (C, *C*=O), 64.9 (CH), 43.7 (CH_2), 43.5 (CH_2), 33.0 (CH_2), 32.0 (CH), 29.4 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 18.9 (CH_3), 11.1 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{21}O_2$ 197. 1542; Found 197. 1546.



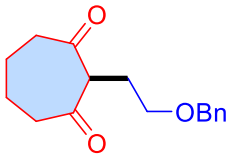
6ee

2-Isopentylcycloheptane-1,3-dione (6ff): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as colourless oil. Yield: 90% (53 mg). IR (Neat): ν_{max} 2953, 2359, 1723, 1695, 1454, 1205, 1125, 685 and 575 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.60 (1H, t, J = 7.0 Hz), 2.56-2.47 (4H, m), 2.07-2.00 (2H, m), 1.90-1.83 (2H, m), 1.81-1.76 (2H, m), 1.53-1.47 (1H, m), 1.09-1.04 (2H, m), 0.85 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.6 (2 x C, 2 x *C*=O), 67.1 (CH), 43.7 (2 x CH_2), 36.2 (CH_2), 28.0 (CH), 25.8 (2 x CH_2), 24.3 (CH_2), 22.3 (2 x CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{20}O_2Na$ 219.1361; Found 219.1359.



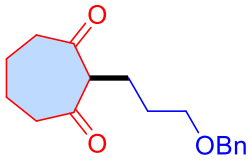
6ff

2-(2-(Benzyloxy)ethyl)cycloheptane-1,3-dione (6gg): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.8:9.2) and isolated as colourless oil. Yield: 75% (59 mg). IR (Neat): ν_{max} 2939, 1720, 1365, 1216, 1070, 909 and 715 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.32 (2H, m), 7.29-7.26 (3H, m), 4.42 (2H, s), 4.09 (1H, t, J = 7.0 Hz), 3.45 (2H, t, J = 6.0 Hz), 2.60-2.55 (2H, m), 2.49-2.44 (2H, m), 2.14 (2H, q, J = 7.0 Hz), 2.11-2.05 (2H, m), 1.87-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 206.2 (2 x C, 2 x *C*=O), 138.2 (C), 128.3 (2 x CH), 127.7 (2 x CH), 127.6 (CH), 72.8 (CH_2), 67.4 (CH_2), 63.4 (CH), 44.1 (2 x CH_2), 26.3 (CH_2), 25.2 (2 x CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{21}O_3$ 261.1491; Found 261.1493.



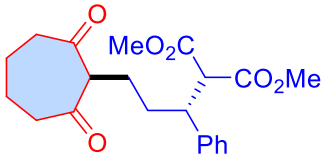
6gg

2-(3-(Benzyloxy)propyl)cycloheptane-1,3-dione (6hh): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.8:9.2) and isolated as colourless oil. Yield: 78% (64 mg). IR (Neat): ν_{max} 3012, 2969, 1738, 1367, 1232, 1216 and 718 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36-7.31 (4H, m), 7.29-7.26 (1H, m), 4.46 (2H, s), 3.82 (1H, t, J = 7.0 Hz), 3.46 (2H, t, J = 6 Hz), 2.56-2.51 (2H, m), 2.49-2.43 (2H, m), 2.06-2.00 (2H, m), 1.93-1.89 (2H, m), 1.87-1.79 (2H, m), 1.58-1.53 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.0 (2 x C, 2 x *C*=O), 138.4 (C), 128.3 (2 x CH), 127.7 (2 x CH), 127.5 (CH), 72.9 (CH_2), 70.1 (CH_2), 66.3 (CH), 43.9 (2 x CH_2), 27.1 (CH_2), 25.5 (2 x CH_2), 23.3 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{26}NO_3$ 292.1913; Found 292.1916.



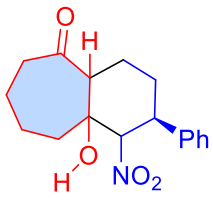
6hh

Dimethyl (*R*)-2-(3-(2,7-dioxocycloheptyl)-1-phenylpropyl)malonate [(+)-6ii]: Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.9:8.9) and isolated as yellow oil. Yield: 96% (108 mg). $[\alpha]_D^{25}$ = +10.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2923, 2853, 1725, 1694, 1434, 1249, 1155 and 702 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.30-7.27 (2H, m), 7.21 (1H, tt, J = 7.5, 1.0 Hz), 7.18-7.16 (2H, m), 3.75 (3H, s, OC*H*$_3$), 3.64-3.61 (2H, m), 3.41 (3H, s, OC*H*$_3$), 3.34-3.29 (1H, m), 2.53-2.44 (2H, m), 2.42-2.36 (2H, m), 2.03-1.96 (2H, m), 1.84-1.76 (2H, m), 1.68-1.57 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.0 (C, *C*=O), 206.7 (C, *C*=O), 168.7 (C, O-*C*=O), 168.0 (C, O-*C*=O), 140.0 (C), 128.5 (2 x CH), 128.2 (2 x CH), 127.2 (CH), 66.1 (CH), 58.4 (CH), 52.6 (CH_3, O*C*H_3), 52.2 (CH_3, O*C*H_3), 45.5 (CH), 43.73 (CH_2), 43.71 (CH_2), 30.9 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 23.9 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_6$ 397.1627; Found 397.1633.



(+)-**6ii**

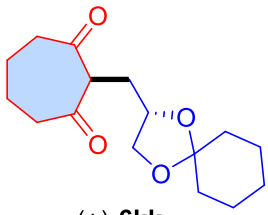
(2*S*)-9a-Hydroxy-1-nitro-2-phenyldecahydro-5*H*-benzo[7]annulen-5-one [(-)-6'jj]: Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as white solid. Mp.: 141-143 °C. Yield: 92% (84 mg). $[\alpha]_D^{25}$ = -127.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 3523, 2941, 1693, 1542, 1334, 1249, 698 and 544 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, single isomer): δ 7.32-7.30 (2H, m), 7.26-7.23 (1H, m), 7.20-7.18 (2H,



(-)-**6'jj**

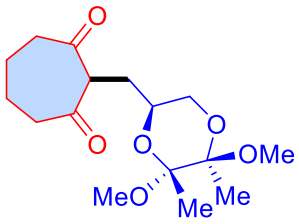
m), 4.63 (1H, d, J = 12.0 Hz), 3.58 (1H, dt, J = 12.7, 4.0 Hz), 3.18 (1H, br d, J = 1.5 Hz), 2.81-2.75 (1H, m), 2.65 (1H, br dd, J = 12.6, 1.8 Hz), 2.59-2.55 (1H, m), 2.28 (1H, dq, J = 13.0, 4.1 Hz), 2.08-1.99 (1H, m), 2.03-1.98 (1H, m), 1.89-1.85 (1H, m), 1.81-1.76 (1H, m), 1.75-1.71 (1H, m), 1.70-1.67 (1H, m), 1.66-1.62 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz, single isomer): δ 210.8 (C, *C*=O), 139.2 (C), 128.9 (2 x CH), 127.8 (CH), 127.2 (2 x CH), 98.5 (CH), 71.5 (C), 55.9 (CH), 43.7 (CH), 43.6 (CH_2), 40.2 (CH_2), 31.5 (CH_2), 23.9 (CH_2), 23.4 (CH_2), 22.2 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{25}N_2O_4$ 321.1814; Found 321.1813.

(*S*)-2-((1,4-Dioxaspiro[4.5]decan-2-yl)methyl)cycloheptane-1,3-dione (+)-(6kk): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 77% (65 mg). $[\alpha]_D^{25}$ = +14.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2932, 2859, 1722, 1695, 1445, 1203, 1099, 1039, 928 and 910 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.14 (1H, dd, J = 10.0, 5.0 Hz), 4.01-3.98 (2H, m), 3.50-3.46 (1H, m), 2.68-2.62 (2H, m), 2.52-2.44 (2H, m), 2.17 (1H, dq, J = 6.0, 3.5 Hz), 2.15-2.07 (2H, m), 1.89-1.81 (3H, m), 1.53-1.49 (10H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.9 (C, *C*=O), 205.8 (C, *C*=O), 109.5 (C), 73.0 (CH), 69.0 (CH_2), 63.1 (CH), 44.4 (CH_2), 44.0 (CH_2), 36.5 (CH_2), 35.0 (CH_2), 30.2 (CH_2), 25.1 (CH_2), 25. (CH_2), 25.01 (CH_2), 24.0 (CH_2), 23.8 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{24}O_4Na$ 303.1572; Found 303.1570.



(+)-**6kk**

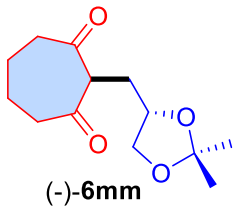
2-(((2*S*,5*R*,6*R*)-5,6-Dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)methyl)cycloheptane-1,3-dione (-)-(6ll): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 72% (68 mg). $[\alpha]_D^{25}$ = -135.5° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2932, 1725, 1695, 1449, 1361, 1117, 1036, and 956 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.25 (1H, dd, J = 9.5, 4.5 Hz), 3.80 (1H, tt, J = 10.5, 3.0 Hz), 3.47 (1H, t, J = 11.0 Hz), 3.40-3.37 (1H, m), 3.22 (3H, s, OCH_3), 3.16 (3H, s, OCH_3), 2.64-2.58 (2H, m), 2.52-2.44 (2H, m), 2.13-2.01 (3H, m), 1.88-1.77 (2H, m), 1.73-1.68 (1H, m), 1.23 (3H, s, CH_3), 1.22 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.6 (C, *C*=O), 205.5 (C, *C*=O), 99.0 (C), 97.9 (C), 64.5 (CH), 63.4 (CH_2), 61.9 (CH),



(-)-**6ll**

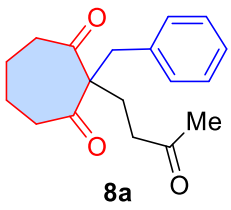
47.95 (CH_3, OCH_3), 47.92 (CH_3, OCH_3), 44.4 (CH_2), 43.8 (CH_2), 27.3 (CH_2), 25.2 (CH_2), 24.9 (CH_2), 17.8 (CH_3), 17.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{16}H_{30}NO_6$ 332.2073; Found 332.2079.

(*S*)-2-((2,2-Dimethyl-1,3-dioxolan-4-yl)methyl)cycloheptane-1,3-dione [(-)-6mm]: Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 76% (55 mg). $[\alpha]_D^{25}$ = -21.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2932, 1721, 1694, 1453, 1370, 1211, 1155, 1061, 972, 910, 840 and 470 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 4.17 (1H, dd, *J* = 9.0, 4.0 Hz), 4.03-3.99 (2H, m), 3.52-3.49 (1H, m), 2.70-2.60 (2H, m), 2.54-2.45 (2H, m), 2.21 (1H, m), 2.16-2.06 (2H, m), 1.90-1.80 (3H, m), 1.35 (3H, s, C*H*$_3$), 1.28 (3H, s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 205.9 (C, *C*=O), 205.7 (C, *C*=O), 109.0 (C), 73.4 (CH), 69.3 (CH_2), 63.0 (CH), 44.4 (CH_2), 44.0 (CH_2), 30.2 (CH_2), 26.8 (CH_3), 25.5 (CH_3), 25.1 (CH_2), 24.9 (CH_2). HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1262.



(-)-**6mm**

(*S*)-2-(3,7-Dimethyloct-6-en-1-yl)cycloheptane-1,3-dione [(+)-6nn]: Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 0.5:9.5) and isolated as yellow oil. Yield: 82% (65 mg). $[\alpha]_D^{25}$ = +8.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2922, 2854, 1722, 1697, 1455, 1378, 1180 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.06 (1H, tt, *J* = 7.0, 3.5 Hz), 5.60 (1H, t, *J* = 7.0 Hz), 2.56-2.48 (4H, m), 2.06-2.00 (2H, m), 1.97-1.72 (6H, m), 1.66 (3H, s, C*H*$_3$), 1.58 (3H, s, C*H*$_3$), 1.41-1.27 (2H, m), 1.24-0.98 (3H, m), 0.85 (3H, d, *J* = 7.0 Hz, C*H*$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 207.68 (C, *C*=O), 207.66 (C, *C*=O), 131.1 (C), 124.7 (CH), 67.2 (CH), 43.7 (2 x CH_2), 36.7 (CH_2), 34.2 (CH_2), 32.4 (CH), 25.9 (CH_2), 25.8 (CH_2), 25.7 (CH_3), 25.4 (CH_2), 23.9 (CH_2), 19.3 (CH_3), 17.6 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{29}O_2$ 265.2168; Found 265.2166.



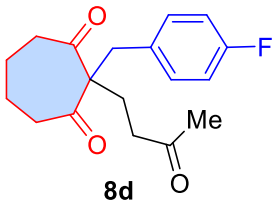
(+)-**6nn**

8a

2-Benzyl-2-(3-oxobutyl)cycloheptane-1,3-dione (8a): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 95-97

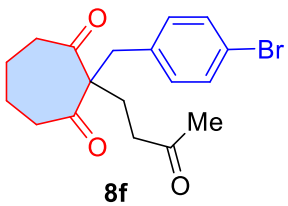
°C. Yield: 93% (53 mg). IR (Neat): ν_{max} 2951, 2867, 1707, 1689, 1448, 1356, 1170, 1130, 1083 and 750 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.23-7.17 (3H, m), 6.97 (2H, br d, J = 7.0 Hz), 3.09 (2H, s), 2.44-2.41 (2H, m), 2.36-2.30 (4H, m), 2.10 (3H, s, CH_3), 2.03 (2H, t, J = 7.5 Hz), 1.86-1.77 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.6 (2 x C, 2 x C=O), 206.7 (C, C=O), 135.8 (C), 129.9 (2 x CH), 128.4 (2 x CH), 126.9 (CH), 68.8 (C), 42.5 (2 x CH_2), 37.4 (CH_2), 36.9 (CH_2), 30.0 (CH_3), 27.8 (2 x CH_2), 24.8 (CH_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_3$ 287.1647; Found 287.1649.

2-(4-Fluorobenzyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8d): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 100-102 °C. Yield: 94% (57 mg). IR (Neat): ν_{max} 2937, 2867, 1705, 1689, 1601, 1509, 1448, 1359, 1265, 1133, 1094, 974, 851 and 784 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.97-6.89 (4H, m), 3.05 (2H, s), 2.44-2.40 (2H, m), 2.35-2.27 (4H, m), 2.11 (3H, s, CH_3), 2.04 (2H, t, J = 7.5 Hz), 1.86-1.80 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.6 (2 x C, 2 x C=O), 206.6 (C, C=O), 161.9 (C, d, J = 248.7 Hz, C-F), 131.5 (C, d, J = 2.5 Hz), 131.4 (2 x CH, d, J = 7.5 Hz), 115.3 (2 x CH, d, J = 21.2 Hz), 68.7 (C), 42.6 (2 x CH_2), 37.4 (CH_2), 36.3 (CH_2), 30.0 (CH_3), 27.7 (2 x CH_2), 25.0 (CH_2); ^{19}F NMR ($CDCl_3$, 375 MHz): δ -115.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{21}FO_3Na$ 327.1372; Found 327.1376.



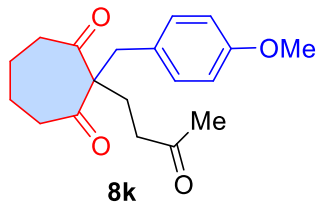
8d

2-(4-Bromobenzyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8f): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 107-109 °C. Yield: 93% (68 mg). IR (Neat): ν_{max} 2935, 1714, 1688, 1695, 1477, 1458, 1327, 1178, 1127, 1067, 1016, 800 and 727 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.37 (2H, td, J = 8.5, 3.0 Hz), 6.89 (2H, br d, J = 8.5 Hz), 3.05 (2H, s), 2.47-2.42 (2H, m), 2.37-2.32 (4H, m), 2.13 (3H, s, CH_3), 2.06 (2H, t, J = 8.0 Hz), 1.91-1.80 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.5 (2 x C, 2 x C=O), 206.6 (C, C=O), 134.9 (C), 131.65 (2 x CH), 131.56 (2 x CH), 121.1 (C), 68.6 (C), 42.6 (2 x CH_2), 37.3 (CH_2), 36.5 (CH_2), 30.1 (CH_3), 27.8 (2 x CH_2), 25.0 (CH_2). HRMS (ESI-TOF) m/z:



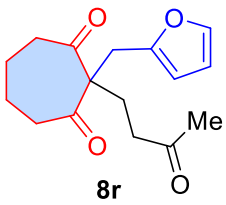
8f

[M + Na]$^+$ Calcd for $C_{18}H_{21}{}^{79}BrO_3Na$ 387.0572; Found 387.0573; *m/z*: [M + 2 + Na]$^+$ Calcd for $C_{18}H_{21}{}^{81}BrO_3Na$ 389.0551; Found 389.0555.



2-(4-Methoxybenzyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8k): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 105-107 °C. Yield: 94% (59 mg). IR (Neat): ν_{max} 2936, 2202, 2008, 1715, 1686, 1610, 1511, 1439, 1371, 1318, 1250, 1174, 1033, 813, 779 and 712 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.88 (2H, td, J = 9.0, 2.0 Hz), 6.75 (2H, td, J = 8.5, 2.0 Hz), 3.75 (3H, s, OCH_3), 3.03 (2H, s), 2.44-2.39 (2H, m), 2.35-2.29 (4H, m), 2.10 (3H, s, CH_3), 2.03 (2H, t, J = 4.0 Hz), 1.87-1.76 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.9 (2 x C, 2 x *C*=O), 206.9 (C, *C*=O), 158.5 (C), 130.9 (2 x CH), 127.6 (C), 113.8 (2 x CH), 68.9 (C), 55.2 (CH_3, OCH_3), 42.6 (2 x CH_2), 37.5 (CH_2), 36.2 (CH_2), 30.0 (CH_3), 27.8 (2 x CH_2), 24.9 (CH_2). HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{24}O_4Na$ 339.1572; Found 339.1572.

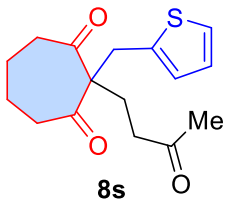
2-(4-(Trifluoromethyl)benzyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8p): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 85-87 °C. Yield: 91% (64 mg). IR (Neat): ν_{max} 2922, 1721, 1688, 1623, 1464, 1426, 1322, 1161,1109, 1067, 1032, and 857 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50 (2H, d. J = 8 Hz), 7.13 (2H, d, J = 8 Hz), 3.15 (2H, s), 2.49-2.44 (2H, m), 2.39-2.31 (4H, m), 2.14 (3H, s, CH_3), 2.07 (2H, t, J = 7.5 Hz), 1.91-1.81 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.3 (2 x C, 2 x *C*=O), 206.5 (C, *C*=O), 140.1 (C), 130.3 (2 x CH), 129.4 (C, q, J = 32.5 Hz), 125.3 (2 x CH, q, J = 3.75 Hz), 124.0 (C, q, J = 275.0 Hz, *C*F_3), 68.7 (C), 42.6 (2 x CH_2), 37.4 (CH_2), 36.8 (CH_2), 30.1 (CH_3), 27.8 (2 x CH_2), 25.0 (CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -62.6. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{19}H_{22}F_3O_3$ 355.1521; Found 355.1514.



2-(Furan-2-ylmethyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8r): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as

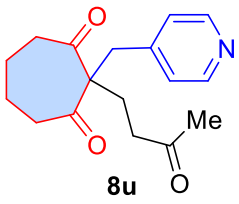
white solid. Mp.: 78-80 °C. Yield: 92% (51 mg). IR (Neat): ν_{max} 2937, 2359, 2160, 1709, 1696, 1501, 1439, 1324, 1124, 1170, 1012, 925, 738, 530 and 477 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24-7.23 (1H, m), 6.24-6.23 (1H, m), 5.99 (1H, d, J = 3.0 Hz), 3.13 (2H, s), 2.51-2.47 (2H, m), 2.43-2.38 (2H, m), 2.34 (2H, t, J = 7.5 Hz), 2.10 (3H, s, CH_3), 2.04 (2H, t, J = 4.0 Hz), 1.88-1.83 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.2 (2 x C, 2 x C=O), 207.0 (C, C=O), 149.9 (C), 141.9 (CH), 110.4 (CH), 108.4 (CH), 67.2 (C), 41.7 (2 x CH_2), 37.4 (CH_2), 30.0 (CH_3), 29.4 (CH_2), 28.0 (2 x CH_2), 24.2 (CH_2). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_4Na$ 299.1259; Found 299.1261.

2-(3-oxobutyl)-2-(thiophen-2-ylmethyl)cycloheptane-1,3-dione (8s): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as off-white solid. Mp.: 77-79 °C. Yield: 75% (44 mg). IR (Neat): ν_{max} 2969, 1738, 1367, 1216, 1119, 896, 722 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.13 (1H, dd, J = 5.2, 1.5 Hz), 6.88 (1H, dd, J = 5.2, 3.0 Hz), 6.66 (1H, br d, J = 3.5 Hz), 3.31 (2H, s), 2.49-2.45 (2H, m), 2.38-2.33 (4H, m), 2.12 (2H, t, J = 8.5 Hz), 2.12 (3H, s, CH_3), 1.91-1.82 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.4 (2 x C, 2 x C=O), 206.7 (C, C=O), 137.1 (C), 127.3 (CH), 127.0 (CH), 124.8 (CH), 68.5 (C), 42.3 (2 x CH_2), 37.4 (CH_2), 31.3 (CH_2), 30.0 (CH_3), 27.8 (2 x CH_2), 24.7 (CH_2). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_3SNa$ 315.1031; Found 315.1033.



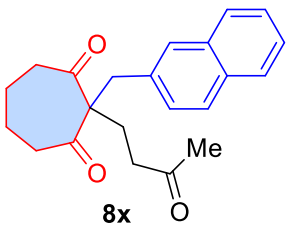
8s

2-(3-Oxobutyl)-2-(pyridin-4-ylmethyl)cycloheptane-1,3-dione (8u): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 83-85 °C. Yield: 91% (52 mg). IR (Neat): ν_{max} 2928, 2857, 1713, 1691, 1600, 1448, 1325, 1168, 1130, 1070, and 518 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.47 (2H, s), 6.94 (2H, d, J = 5.0 Hz), 3.05 (2H, s), 2.47-2.43 (2H, m), 2.35-2.28 (4H, m), 2.11 (3H, s, CH_3), 2.06 (2H, t, J = 7.5 Hz), 1.89-1.77 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 210.6 (2 x C, 2 x C=O), 205.9 (C, C=O), 149.9 (2 x CH), 145.2 (C), 125.3 (2 x CH), 69.0 (C), 42.6 (2 x CH_2), 37.4 (CH_2), 36.8 (CH_2), 29.8 (CH_3), 27.5 (2 x CH_2), 25.7 (CH_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{22}NO_3$ 288.1600; Found 288.1597.

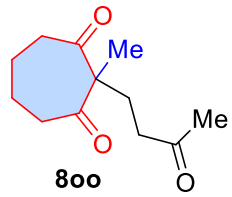


8u

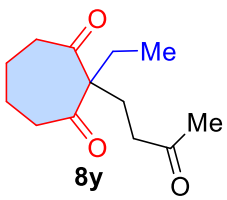
2-(Naphthalen-2-ylmethyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8x): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 79-81 °C. Yield: 85% (57 mg). IR (Neat): ν_{max} 2948, 1713, 1688, 1695, 1454, 1330, 1372, 1264, 1175, 1130, 1070, 956, 895, and 734 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78-7.76 (1H, m), 7.74 (1H, dd, J = 6.2, 3.0 Hz), 7.70 (1H, d, J = 8.5 Hz), 7.48 (1H, br s), 7.45-7.42 (2H, m), 7.10 (1H, dd, J = 7.5, 2.0 Hz), 3.26 (2H, s), 2.46-2.40 (4H, m), 2.34-2.30 (2H, m), 2.13 (3H, s, CH_3), 2.11-2.08 (2H, m), 1.90-1.75 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.8 (2 x C, 2 x C=O), 206.9 (C, C=O), 133.4 (C), 133.3 (C), 132.3 (C), 128.8 (CH), 128.04 (CH), 128.03 (CH), 127.63 (CH), 127.60 (CH), 126.2 (CH), 125.8 (CH), 69.0 (C), 42.7 (2 x CH_2), 37.5 (CH_2), 37.2 (CH_2), 30.0 (CH_3), 28.0 (2 x CH_2), 25.2 (CH_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_3$ 337.1804; Found 337.1805.



2-Methyl-2-(3-oxobutyl)cycloheptane-1,3-dione (8oo): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 95% (40 mg). IR (Neat): ν_{max} 2937, 2864, 1714, 1690, 1446, 1369, 1324, 1165, 1088, 1054, 950 and 898 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.48-2.39 (4H, m), 2.31 (2H, t, J = 7.5 Hz), 2.09 (3H, s, CH_3), 2.04 (2H, t, J = 7.5 Hz), 1.85 (4H, t, J = 2.5 Hz), 1.15 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 212.3 (2 x C, 2 x C=O), 207.1 (C, C=O), 63.5 (C), 41.3 (2 x CH_2), 37.6 (CH_2), 29.9 (CH_3), 27.9 (2 x CH_2), 26.7 (CH_2), 17.7 (CH_3). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1337.

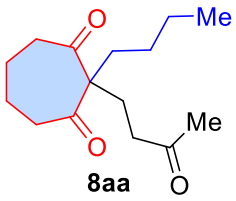


2-Ethyl-2-(3-oxobutyl)cycloheptane-1,3-dione (8y): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 80% (36 mg). IR (Neat): ν_{max} 2969, 1738, 1366, 1216, 1093 and 898 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.46-2.42 (4H, m), 2.22 (2H, t, J = 8.0 Hz), 2.10 (3H, s, CH_3), 2.09-2.05 (2H, m), 1.88-1.85 (4H, m), 1.83-1.79 (2H, m), 0.68 (3H, t, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 212.3 (2 x C, 2 x C=O), 207.1 (C, C=O), 67.5 (C), 41.7 (2 x CH_2), 37.2 (CH_2),



30.0 (CH_3), 28.1 (2 x CH_2), 22.7 (CH_2), 22.5 (CH_2), 7.7 (CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_3Na$ 247.1310; Found 247.1311.

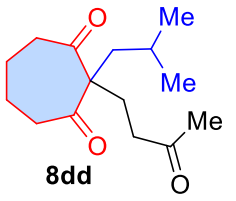
2-Butyl-2-(3-oxobutyl)cycloheptane-1,3-dione (8aa): Prepared by following the procedure **D**



8aa

and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 90% (45 mg). IR (Neat): ν_{max} 2934, 1689, 1446, 1326, 1171, 963 and 727 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.44-2.41 (4H, m), 2.21 (2H, t, *J* = 7.0 Hz), 2.08 (3H, s, C*H*$_3$), 2.06 (2H, br t, *J* = 8.5 Hz), 1.87-1.83 (4H, m), 1.75-1.71 (2H, m), 1.30-1.22 (2H, m), 0.95-0.90 (2H, m), 0.85 (3H, t, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.4 (2 x C, 2 x *C*=O), 207.1 (C, *C*=O), 67.2 (C), 41.7 (2 x CH_2), 37.3 (CH_2), 30.0 (CH_3), 29.7 (CH_2), 28.1 (2 x CH_2), 25.4 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 12.8 (CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{25}O_3$ 253.1804; Found 253.1803.

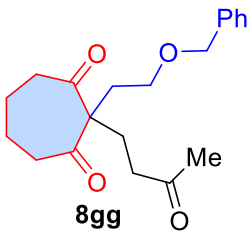
2-Isobutyl-2-(3-oxobutyl)cycloheptane-1,3-dione (8dd): Prepared by following the procedure



8dd

D and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 91% (46 mg). IR (Neat): ν_{max} 2942, 1689, 1446, 1322, 1171, 1103, 898 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.46-2.43 (4H, m), 2.23-2.19 (2H, m), 2.15-2.13 (2H, m), 2.10 (3H, s, C*H*$_3$), 1.91-1.83 (4H, m), 1.77 (2H, d, *J* = 6.2 Hz), 1.50-1.40 (1H, m), 0.82 (6H, d, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 212.4 (2 x C, 2 x *C*=O), 206.6 (C, *C*=O), 67.4 (C), 41.8 (2 x CH_2), 39.3 (CH_2), 37.7 (CH_2), 29.8 (CH_3), 28.2 (2 x CH_2), 24.2 (2 x CH_3), 23.8 (CH), 23.5 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{25}O_3$ 253.1804; Found 253.1804.

2-(2-(Benzyloxy)ethyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8gg): Prepared by following

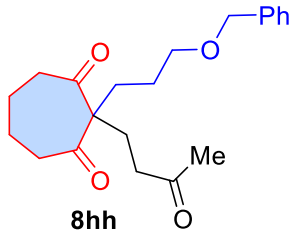


8gg

the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as colourless oil. Yield: 90% (59 mg). IR (Neat): ν_{max} 2929, 2860, 2359, 2340, 1715, 1690, 1448, 1364, 1325, 1265, 1089, 1027 and 773 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31-7.24 (5H, m), 4.32 (2H, s), 3.35 (2H, t, *J* = 6.0 Hz), 2.41 (4H, t, *J* = 6.0 Hz), 2.22-2.18 (2H, m), 2.11 (4H, m), 2.05 (3H, s, C*H*$_3$), 1.87-1.78 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.9 (2 x C, 2 x *C*=O), 207.0 (C, *C*=O), 137.8 (C), 128.3 (2 x

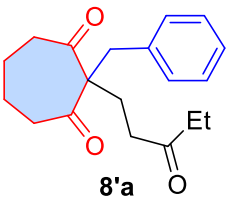
CH), 127.7 (2 x CH), 127.6 (CH), 73.1 (CH_2), 65.7 (C), 65.3 (CH_2), 41.7 (2 x CH_2), 37.5 (CH_2), 30.8 (CH_2), 29.9 (CH_3), 28.1 (2 x CH_2), 23.5 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_4Na$ 353.1729; Found 353.1731.

2-(3-(Benzyloxy)propyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8hh): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as colourless oil. Yield: 90% (62 mg). IR (Neat): ν_{max} 2936, 2861, 2355, 2169, 1714, 1688, 1452, 1362, 1326, 1094, 898, 738 and 699 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34-7.27 (5H, m), 4.46 (2H, s), 3.42 (2H, t, *J* = 6.0 Hz), 2.44 (4H, m), 2.23 (2H, t, *J* = 8.0 Hz), 2.08 (2H, t, *J* = 8.0 Hz), 2.06 (3H, s, C*H*$_3$), 1.89-1.85 (6H, m), 1.32-1.26 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.1 (2 x C, 2 x *C*=O), 207.1 (C, *C*=O), 138.3 (C), 128.3 (2 x CH), 127.5 (3 x CH), 72.9 (CH_2), 69.8 (CH_2), 66.8 (C), 41.6 (2 x CH_2), 37.2 (CH_2), 30.0 (CH_3), 28.0 (2 x CH_2), 26.5 (CH_2), 23.6 (CH_2), 22.9 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{21}H_{32}NO_4$ 362.2331; Found 362.2336.



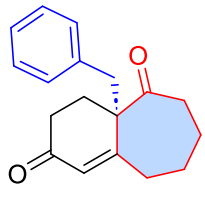
8hh

2-Benzyl-2-(3-oxopentyl)cycloheptane-1,3-dione (8'a): Prepared by following the procedure **D** by taking ethyl vinyl ketone **7'** instead of methyl vinyl ketone **7** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as a white solid. Mp.: 89-91 °C. Yield: 93% (56 mg). IR (Neat): ν_{max} 2935, 1705, 1684, 1454, 1331, 1111 and 742 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.23-7.18 (3H, m), 6.97 (2H, br d, *J* = 7.0 Hz), 3.09 (2H, s), 2.45-2.40 (2H, m), 2.39-2.31 (6H, m), 2.04 (2H, t, *J* = 7.8 Hz), 1.86-1.78 (4H, m), 1.01 (3H, t, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.7 (2 x C, 2 x *C*=O), 209.6 (C, *C*=O), 135.8 (C), 129.9 (2 x CH), 128.4 (2 x CH), 126.9 (CH), 68.9 (C), 42.5 (2 x CH_2), 36.9 (CH_2), 36.2 (CH_2), 36.0 (CH_2), 27.8 (2 x CH_2), 24.9 (CH_2), 7.7 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_3Na$ 323.1623; Found 323.1622.



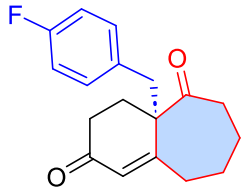
8'a

(*S*)-4a-Benzyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-**9a**]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 96-98 °C. Yield: 93% (25 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 15.65 min (major), t_R = 13.41 min (minor); $[\alpha]_D^{25}$ = -178.0° [*c* = 0.1, $CHCl_3$, >99.9% *ee*]; IR (Neat): ν_{max} 2929, 2859, 1703, 1664, 1616, 1493, 1450, 1333, 1242, 1115, 1080, 867, 730 and 701 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.21-7.19 (3H, m), 7.15-7.13 (2H, m), 6.13 (1H, s, olefinic-*H*), 3.29 (1H, d, *J* = 13.5 Hz), 3.17 (1H, d, *J* = 13.5 Hz), 2.70-2.65 (1H, m), 2.40-2.33 (2H, m), 2.23-2.14 (2H, m), 2.06-1.99 (1H, m), 1.96-1.91 (3H, m), 1.53-1.38 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.2 (C, *C*=O), 197.6 (C, *C*=O), 165.1 (C), 137.3 (C), 130.6 (CH), 130.3 (2 x CH), 128.3 (2 x CH), 126.8 (CH), 57.5 (C), 40.5 (CH_2), 39.0 (CH_2), 36.5 (CH_2), 32.5 (CH_2), 31.5 (CH_2), 31.2 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_2$ 269.1542; Found 269.1542.



(-)-**9a**

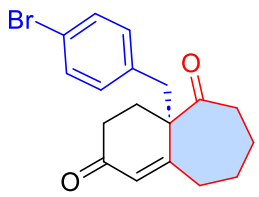
(*S*)-4a-(4-Fluorobenzyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-**9d**]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 75-77 °C. Yield: 91% (26 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.89 min (major), t_R = 13.91 min (minor); $[\alpha]_D^{25}$ = -170.0° [*c* = 0.1, $CHCl_3$, 92% *ee*]; IR (Neat): ν_{max} 2934, 2861, 1706, 1668, 1616, 1508, 1451, 1358, 1220, 1156, 1120, 1097 and 838 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.16-7.13 (2H, m), 6.96-6.92 (2H, m), 6.17 (1H, s, olefinic-*H*), 3.33 (1H, d, *J* = 13.5 Hz), 3.13 (1H, d, *J* = 13.5 Hz), 2.72-2.66 (1H, m), 2.43-2.39 (1H, m), 2.36-2.32 (2H, m), 2.23-2.13 (2H, m), 1.98-1.92 (3H, m), 1.47 (2H, br t, *J* = 3.0 Hz), 1.30 (1H, dt, *J* = 12.7, 2.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.1 (C, *C*=O), 197.4 (C, *C*=O), 165.2 (C), 161.9 (C, d, *J* = 243.7 Hz, *C*-F), 133.1 (C, d, *J* = 3.7 Hz), 131.8 (2 x CH, d, *J* = 7.5 Hz), 130.6 (CH), 115.2 (2 x CH, d, *J* = 21.2 Hz), 57.5 (C), 40.6 (CH_2),



(-)-**9d**

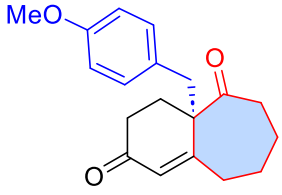
38.1 (CH_2), 36.8 (CH_2), 32.5 (CH_2), 31.5 (CH_2), 31.3 (CH_2), 27.1 (CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -115.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}FO_2$ 287.1447; Found 287.1446.

(*S*)-4a-(4-Bromobenzyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9f]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 103-105 °C. Yield: 92% (32 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.93 min (major), t_R = 15.78 min (minor); $[\alpha]_D^{25}$ = -150.0° [*c* = 0.1, $CHCl_3$, 91% *ee*]; IR (Neat): ν_{max} 2933, 1706, 1666, 1616, 1487, 1072, and 842 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34 (2H, td, *J* = 8.0, 1.5 Hz), 7.05 (2H, br d, *J* = 8.0 Hz), 6.14 (1H, s, olefinic-*H*), 3.30 (1H, d, *J* = 13.5 Hz), 3.07 (1H, d, *J* = 13.5 Hz), 2.69-2.64 (1H, m), 2.41-2.27 (3H, m), 2.24-2.18 (2H, m), 1.94-1.90 (3H, m), 1.47-1.43 (2H, m), 1.25 (1H, dt, *J* = 12.5, 2.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.0 (C, *C*=O), 197.3 (C, *C*=O), 165.0 (C), 136.4 (C), 132.1 (2 x CH), 131.4 (2 x CH), 130.6 (CH), 120.9 (C), 57.5 (C), 40.5 (CH_2), 38.3 (CH_2), 36.9 (CH_2), 32.5 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}{}^{79}BrO_2$ 347.0647; Found 347.0646; *m/z*: $[M + 2 + H]^+$ Calcd for $C_{18}H_{20}{}^{81}BrO_2$ 349.0626; Found 349.0627.



(-)-**9f**

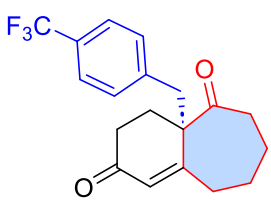
(*S*)-4a-(4-Methoxybenzyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9k]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 112-114 °C. Yield: 90% (27 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 41.99 min (major), t_R = 35.45 min (minor); $[\alpha]_D^{25}$ = -159.0° [*c* = 0.1, $CHCl_3$, 93% *ee*]; IR (Neat): ν_{max} 2926, 2857, 1704, 1665, 1610, 1510, 1449, 1247, 1177, 1032 and 832 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.05 (2H, td, *J* = 8.5, 2.0 Hz), 6.75 (2H, td, *J* = 9.0, 2.0 Hz), 6.13 (1H, s, olefinic-*H*), 3.76 (3H, s, OCH_3), 3.24 (1H, d, *J* = 14.0 Hz), 3.12 (1H, d, *J* =



(-)-**9k**

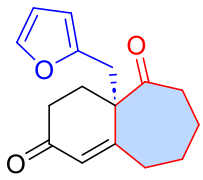
14.0 Hz), 2.69-2.64 (1H, m), 2.38-2.31 (2H, m), 2.28-2.23 (1H, m), 2.19-2.04 (2H, m), 1.96-1.89 (3H, m), 1.49-1.39 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.0 (C, *C*=O), 198.3 (C, *C*=O), 166.1 (C), 159.1 (C), 131.8 (2 x CH), 131.1 (CH), 129.8 (C), 114.3 (2 x CH), 58.1 (C), 55.7 (CH_3, O*C*H_3), 41.2 (CH_2), 38.8 (CH_2), 37.2 (CH_2), 33.1 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 27.7 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_3$ 299.1647; Found: 299.1644.

(*S*)-4a-(4-(Trifluoromethyl)benzyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9p]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 84-86 °C. Yield: 90% (30 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 17.45 min (major), t_R = 21.64 min (minor); $[\alpha]_D^{25}$ = -154.0° [*c* = 0.1, $CHCl_3$, 96% *ee*]; IR (Neat): ν_{max} 2933, 2863, 1708, 1671, 1617, 1452, 1324, 1162, 1113, 1067 and 860 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (2H, d, *J* = 8.0 Hz), 7.30 (2H, d, *J* = 8.0 Hz), 6.15 (1H, s, olefinic-*H*), 3.41 (1H, d, *J* = 13.5 Hz), 3.15 (1H, d, *J* = 13.5 Hz), 2.70-2.65 (1H, m), 2.42-2.38 (2H, m), 2.28-2.20 (3H, m), 1.95-1.92 (3H, m), 1.48-1.43 (2H, m), 1.18 (1H, dt, *J* = 12.5, 2.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 210.9 (C, *C*=O), 197.1 (C, *C*=O), 164.8 (C), 141.6 (C), 130.8 (2 x CH), 130.7 (CH), 129.2 (C, q, *J* = 33.0 Hz), 125.2 (2 x CH, q, *J* = 3.0 Hz), 124.1 (C, q, *J* = 270.0 Hz, *C*F_3), 57.6 (C), 40.5 (CH_2), 38.7 (CH_2), 36.9 (CH_2), 32.5 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 27.1 (CH_2). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -62.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{20}F_3O_2$ 337.1415; Found 337.1417.



(-)-**9p**

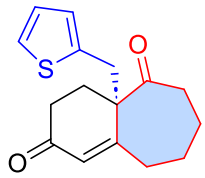
(*S*)-4a-(Furan-2-ylmethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9r]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 68-70 °C. Yield: 91% (23 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 25.17 min (major), t_R = 30.75 min (minor); $[\alpha]_D^{25}$ = -109.0° [*c* = 0.1, $CHCl_3$, 95% *ee*]; IR (Neat): ν_{max} 2933, 1705, 1668, 1260, 1150, 1009 and 741 cm^{-1}. ^{1}H NMR ($CDCl_3$,



(-)-**9r**

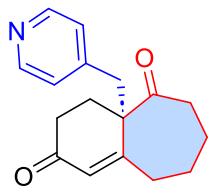
500 MHz): δ 7.25 (1H, dd, J = 2.0, 1.0 Hz), 6.26 (1H, dd, J = 3.0, 1.5 Hz), 6.11 (1H, s, olefinic-*H*), 6.08 (1H, d, J = 3.0 Hz), 3.27 (1H, d, J = 15.0 Hz), 3.18 (1H, d, J = 15.0 Hz), 2.69-2.64 (1H, m), 2.48-2.45 (1H, m), 2.40-2.37 (1H, m), 2.33-2.29 (1H, m), 2.20-2.08 (2H, m), 2.07-1.90 (4H, m), 1.58-1.55 (1H, m), 1.51-1.48 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.1 (C, *C*=O), 197.6 (C, *C*=O), 164.6 (C), 151.3 (C), 141.4 (CH), 130.3 (CH), 110.8 (CH), 108.9 (CH), 56.4 (C), 40.6 (CH_2), 35.5 (CH_2), 32.2 (CH_2), 31.8 (CH_2), 31.5 (CH_2), 31.0 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{19}O_3$ 259.1334; Found 259.1336.

(*S*)-4a-(Thiophene-2-ylmethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9s]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 79-81 °C. Yield: 88% (24 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 25.72 min (major), t_R = 33.03 min (minor); $[\alpha]_D^{25}$ = -171.0° [c = 0.1, $CHCl_3$, 92% *ee*]; IR (Neat): ν_{max} 2925, 2856, 1704, 1664, 1616, 1448, 1537, 1232, 1119, 1079, 867, 707 and 551 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14 (1H, dd, J = 5.5, 1.5 Hz), 6.88 (1H, dd, J = 5.0, 3.5 Hz), 6.80 (1H, br d, J = 3.5 Hz), 6.14 (1H, s, olefinic-*H*), 3.42 (2H, br s), 2.70-2.64 (1H, m), 2.44-2.33 (3H, m), 2.31-2.17 (2H, m), 2.00-1.91 (3H, m), 1.56-1.46 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.4 (C, *C*=O), 197.5 (C, *C*=O), 165.2 (C), 139.1 (C), 130.5 (CH), 127.6 (CH), 126.7 (CH), 125.2 (CH), 57.4 (C), 40.7 (CH_2), 36.3 (CH_2), 33.9 (CH_2), 32.6 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 27.0 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_2SNa$ 297.0925; Found 297.0925.



(-)-**9s**

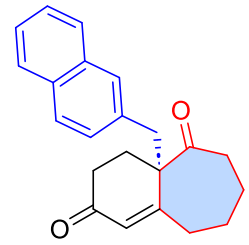
(*S*)-4a-(Pyridin-4-ylmethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9u]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as yellow oil. Yield: 92% (25 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 39.09 min (major), t_R = 35.75 min (minor); $[\alpha]_D^{25}$ = -137.0° [c = 0.1, $CHCl_3$, 93% *ee*]; IR

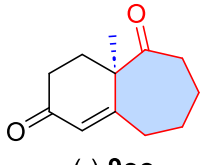


(-)-**9u**

(Neat): ν_{max} 2931, 2860, 1705, 1664, 1600, 1416, 1360, 1224, 1122, and 826 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.46 (2H, d, J = 6.0 Hz), 7.14 (2H, d, J = 6.0 Hz), 6.15 (1H, s, olefinic-*H*), 3.35 (1H, d, J =13.5 Hz), 3.05 (1H, d, J = 13.5 Hz), 2.69-2.64 (1H, m), 2.42-2.38 (2H, m), 2.30-2.25 (3H, m), 1.94-1.90 (3H, m), 1.47-1.42 (2H, m), 1.20-1.15 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 210.7 (C, *C*=O), 196.9 (C, *C*=O), 164.4 (C), 149.7 (2 x CH), 146.7 (C), 130.7 (CH), 125.8 (2 x CH), 57.5 (C), 40.4 (CH_2), 38.3 (CH_2), 37.0 (CH_2), 32.5 (CH_2), 31.53 (CH_2), 31.50 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_2$ 270.1494; Found 270.1493.

(*S*)-4a-(Naphthalen-2-ylmethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9x]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as white solid. Mp.: 125-127 °C. Yield: 92% (29 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 17.00 min (major), t_R = 18.26 min (minor); $[\alpha]_D^{25}$ = -288.0° [*c* = 0.1, $CHCl_3$, 91% *ee*]; IR (Neat): ν_{max} 2924, 2854, 1705, 1668, 1617, 1450, 1151, 1120, and 754 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.79-7.74 (2H, m), 7.70 (1H, d, J = 8.5 Hz), 7.64 (1H, s), 7.47-7.41 (2H, m), 7.29 (1H, dd, J = 6.5, 2.0 Hz), 6.16 (1H, s, olefinic-*H*), 3.53 (1H, d, J = 13.5 Hz), 3.30 (1H, d, J = 13.5 Hz), 2.71-2.66 (1H, m), 2.43-2.39 (1H, m), 2.33-2.18 (4H, m), 2.02-1.99 (1H, m), 1.93-1.87 (2H, m), 1.51-1.39 (2H, m), 1.30 (1H, td, J = 10.0, 2.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.3 (C, *C*=O), 197.6 (C, *C*=O), 165.6 (C), 135.0 (C), 133.3 (C), 132.2 (C), 130.6 (CH), 129.0 (CH), 128.6 (CH), 127.82 (CH), 127.62 (CH), 127.58 (CH), 126.1 (CH), 125.7 (CH), 57.8 (C), 40.6 (CH_2), 39.1 (CH_2), 36.8 (CH_2), 32.6 (CH_2), 31.5 (CH_2), 31.5 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}O_2$ 319.1698; Found 319.1694.

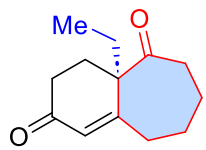

(-)-**9x**


(-)-**9oo**

(*R*)-4a-Methyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9oo]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 90% (17 mg). The enantiomeric excess (*ee*) was

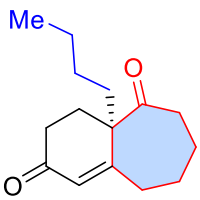
determined by chiral stationary phase HPLC using a Daicel chiralpak ID column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 12.78 min (major), t_R = 14.48 min (minor); $[\alpha]_D^{25}$ = -3.4° [*c* = 0.1, $CHCl_3$, 59% *ee*]; IR (Neat): ν_{max} 2931, 1706, 1668, 1448, 1333, 1234, 1155 and 865 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.02 (1H, s, olefinic-*H*), 2.70-2.64 (1H, m), 2.57-2.43 (3H, m), 2.37-2.33 (1H, m), 2.20 (1H, dt, *J* = 13.5, 5.5 Hz), 2.10-2.03 (1H, m), 2.00-1.89 (2H, m), 1.75 (1H, qd, *J* = 13.2, 3.0 Hz), 1.60-1.52 (2H, m), 1.35 (3H, s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.8 (C, *C*=O), 197.7 (C, *C*=O), 167.1 (C), 128.6 (CH), 52.7 (C), 40.3 (CH_2), 35.2 (CH_2), 32.7 (CH_2), 32.3 (CH_2), 31.2 (CH_2), 27.4 (CH_2), 18.9 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{17}O_2$ 193.1229; Found 193.1230.

(*R*)-4a-Ethyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9y]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 90% (19 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 24.10 min (major), t_R = 29.61 min (minor); $[\alpha]_D^{25}$ = -42.0° [*c* = 0.1, $CHCl_3$, 88% *ee*]; IR (Neat): ν_{max} 2928, 1738, 1671, 1365, 1216 and 864 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.09 (1H, s, olefinic-*H*), 2.63 (1H, dt, *J* = 12.5, 2.5 Hz), 2.56-2.52 (1H, m), 2.51-2.46 (1H, m), 2.43-2.37 (2H, m), 2.26-2.20 (1H, m), 2.12-2.04 (2H, m), 1.98-1.92 (3H, m), 1.85-1.79 (1H, m), 1.64-1.53 (2H, m), 0.98 (3H, t, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.5 (C, *C*=O), 198.0 (C, *C*=O), 166.7 (C), 129.6 (CH), 55.9 (C), 41.6 (CH_2), 36.0 (CH_2), 33.4 (CH_2), 31.6 (CH_2), 30.5 (CH_2), 27.8 (CH_2), 26.8 (CH_2), 10.1 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}O_2$ 207.1385; Found 207.1385.



(-)-**9y**

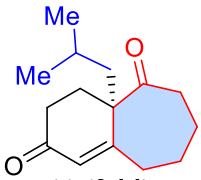
(*R*)-4a-Butyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9aa]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 90% (21 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 19.45 min (major), t_R = 23.45 min (minor); $[\alpha]_D^{25}$ = -63.0° [*c* = 0.1, $CHCl_3$,



(-)-(**9aa**)

86% *ee*]; IR (Neat): ν_{max} 2931, 2861, 1667, 1450, 1616, 1333, 1152, 864 and 729 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.07 (1H, s, olefinic-*H*), 2.62 (1H, dt, *J* = 12.5, 2.5 Hz), 2.54-2.46 (2H, m), 2.42-2.35 (2H, m), 2.25-2.18 (1H, m), 2.11-2.02 (2H, m), 1.96-1.83 (3H, m), 1.75-1.69 (1H, m), 1.64-1.51 (2H, m), 1.41-1.19 (4H, m), 0.89 (3H, t, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.5 (C, *C*=O), 198.0 (C, *C*=O), 166.9 (C), 129.4 (CH), 55.8 (C), 41.5 (CH_2), 36.0 (CH_2), 34.8 (CH_2), 33.4 (CH_2), 31.6 (CH_2), 30.9 (CH_2), 27.7 (CH_2), 26.8 (CH_2), 23.5 (CH_2), 13.9 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{23}O_2$ 235.1698; Found 235.1693.

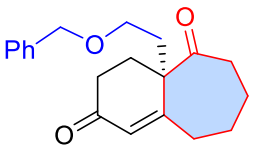
(*S*)-4a-Isobutyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9dd]:



(-)-(**9dd**)

Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 90% (21 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IC-3 column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 17.63 min (major), t_R = 22.27 min (minor); $[\alpha]_D^{25}$ = -49.0° [*c* = 0.1, $CHCl_3$, 71% *ee*]; IR (Neat): ν_{max} 2931, 2864, 1668, 1614, 1449, 1334, 1257, 1152, 1081, 916 and 867 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.09 (1H, s, olefinic-*H*), 2.63 (1H, dt, *J* = 12.2, 2.5 Hz), 2.57-2.50 (2H, m), 2.44-2.35 (2H, m), 2.25-2.18 (1H, m), 2.12-2.07 (2H, m), 1.96-1.88 (2H, m), 1.81-1.71 (3H, m), 1.63-1.51 (2H, m), 0.92 (3H, d, *J* = 6.0 Hz), 0.91 (3H, d, *J* = 6.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 212.2 (C, *C*=O), 198.0 (C, *C*=O), 167.0 (C), 129.8 (CH), 56.2 (C), 43.3 (CH_2), 41.2 (CH_2), 36.4 (CH_2), 33.4 (CH_2), 31.6 (CH_2), 31.3 (CH_2), 26.7 (CH_2), 25.0 (CH), 24.9 (CH_3), 24.6 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{23}O_2$ 235.1698; Found 235.1696.

(*S*)-4a-(2-(Benzyloxy)ethyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9gg]:

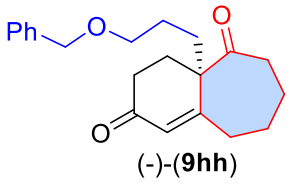


(-)-(**9gg**)

Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as colourless oil. Yield: 85% (27 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 93:7, flow rate 0.7 mL/min, λ = 254 nm), t_R = 44.28 min (major), t_R = 47.55 min (minor); $[\alpha]_D^{25}$ = -72.0° [*c* = 0.1, $CHCl_3$, 87% *ee*]; IR (Neat): ν_{max} 3024, 2930, 2859, 1738, 1668, 1365, 1216, 1093 and 739 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32-

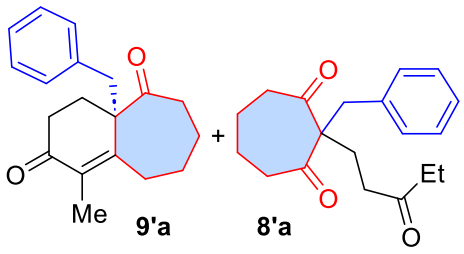
7.29 (2H, m), 7.25-7.24 (3H, m), 6.04 (1H, s, olefinic-*H*), 4.43 (2H, ABq, *J* = 12.0 Hz, OC*H*$_2$Ph), 3.65-3.57 (2H, m), 2.66-2.60 (2H, m), 2.50-2.47 (1H, m), 2.42-2.32 (2H, m), 2.24-2.15 (2H, m), 2.07-2.02 (2H, m), 1.96-1.89 (3H, m), 1.62-1.45 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.4 (C, *C*=O), 197.9 (C, *C*=O), 166.1 (C), 138.0 (C), 129.5 (CH), 128.3 (2 x CH), 127.6 (CH), 127.5 (2 x CH), 73.0 (CH_2), 67.1 (CH_2), 54.9 (C), 40.8 (CH_2), 35.9 (CH_2), 34.0 (CH_2), 33.1 (CH_2), 31.5 (CH_2), 30.6 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{24}O_3Na$ 335.1623; Found 335.1618.

(*R*)-4a-(3-(Benzyloxy)propyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione



(-)-(**9hh**)

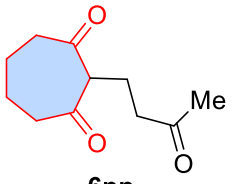
[(-)-9hh]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as colourless oil. Yield: 86% (28 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 93:7, flow rate 0.7 mL/min, λ = 254 nm), t_R = 42.77 min (major), t_R = 41.32 min (minor); $[\alpha]_D^{25}$ = -56.0^o [*c* = 0.1, $CHCl_3$, 82% *ee*]; IR (Neat): ν_{max} 2935, 2858, 1738, 1450, 1667, 1364, 1228, 1098 739 and 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.30 (4H, m), 7.29-7.27 (1H, m), 6.07 (1H, s, olefinic-*H*), 4.50 (2H, s, OC*H*$_2$Ph), 3.49-3.46 (2H, m), 2.63 (1H, dt, *J* = 12.0, 2.5 Hz), 2.53-2.47 (2H, m), 2.43-2.37 (2H, m), 2.27-2.21 (1H, m), 2.10-2.02 (2H, m), 1.97-1.91 (3H, m), 1.83 (1H, dt, *J* = 13.2, 3.5 Hz), 1.79-1.73 (1H, m), 1.67-1.51 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.4 (C, *C*=O), 197.9 (C, *C*=O), 166.5 (C), 138.3 (C), 129.6 (CH), 128.3 (2 x CH), 127.6 (2 x CH), 127.5 (CH), 72.9 (CH_2), 70.4 (CH_2), 55.4 (C), 41.4 (CH_2), 36.0 (CH_2), 33.3 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 30.7 (CH_2), 26.8 (CH_2), 25.9 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{27}O_3$ 327.1960; Found 327.1965.



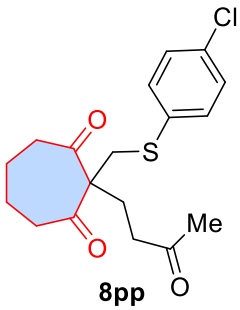
(*S*)-4a-Benzyl-1-methyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione (9'a): Prepared by following the procedure **F** using reflux temperature (85 ^{o}C) for 48 h and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as inseparable 1:1.88 mixture of product **9'a** and starting material **8'a** as white solid because of

their equal affinity towards silica gel. Mp.: 97-99 °C. Yield: 25% (7 mg) of **9'a** + 47% (14 mg) of **8'a**. The enantiomeric excess (*ee*) of **9'a** was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 15.79 min (major), t_R = 10.94 min (minor); 19% *ee*; For cyclized product **9'a** data: IR (Neat): ν_{max} 2929, 1691, 1663, 1452, 1259, 1081, 1019, 798 and 728 cm^{-1}. For cyclized product **9'a** data: ^1H NMR ($CDCl_3$, 500 MHz): δ 7.42-7.19 (3H, m), 7.10-7.09 (2H, m), 3.22 (2H, q, J = 13.5 Hz), 2.74-2.69 (1H, m), 2.55 (1H, dd, J = 13.2, 5.5 Hz), 2.30-2.25 (1H, m), 2.19-2.13 (1H, m), 2.09-2.03 (2H, m), 1.84 (3H, s), 1.57-1.46 (3H, m), 1.34-1.23 (3H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 212.3 (C, *C*=O), 197.1 (C, *C*=O), 156.9 (C), 137.9 (C), 135.1 (C), 130.3 (2 x CH), 128.2 (2 x CH), 126.7 (CH), 58.2 (C), 40.4 (CH_2), 39.1 (CH_2), 33.7 (CH_2), 32.6 (CH_2), 30.2 (CH_2), 28.35 (CH_2), 28.3 (CH_2), 10.7 (CH_3). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_2$ 283.1698; Found 283.1699.

2-(3-Oxobutyl)cycloheptane-1,3-dione (6pp): Prepared by following the procedure **G** and purified by column chromatography using EtOAc/hexane (2.5:7.5 to 2.8:7.2) and isolated as colourless oil. Yield: 45% (35 mg); IR (Neat): ν_{max} 2937, 2176, 1711, 1691, 1443, 1164 and 909 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.81 (1H, t, J = 7.0 Hz), 2.59-2.54 (2H, m), 2.51-2.46 (2H, m), 2.44 (2H, t, J =7.0 Hz), 2.11 (3H, s, C*H*$_3$), 2.06-2.02 (4H, m), 1.89-1.81 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 208.2 (C, *C*=O), 206.9 (2 x C, 2 x *C*=O), 65.3 (CH), 43.9 (2 x CH_2), 40.2 (CH_2), 29.9 (CH_3), 25.5 (2 x CH_2), 20.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1173.



6pp

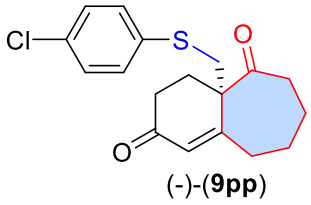


8pp

2-(((4-Chlorophenyl)thio)methyl)-2-(3-oxobutyl)cycloheptane-1,3-dione (8pp): Prepared by following the procedure **H** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as yellow oil. Yield: 82% (58 mg); IR (Neat): ν_{max} 2929, 2147, 1715, 1692, 1475, 1446, 1092, 1010, 817 and 739 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.28-7.26 (2H, m), 7.26-7.24 (2H, m), 3.33 (2H, s), 2.40-2.36 (4H, m), 2.24 (4H, s), 2.08 (3H, s, C*H*$_3$), 1.89-1.80 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 210.4 (2 x C, 2 x *C*=O), 206.6 (C, *C*=O), 133.9 (C), 133.1 (C), 132.1 (2 x CH), 129.1 (2 x CH), 67.1 (C), 41.6 (2 x CH_2), 37.1 (CH_2), 36.1 (CH_2), 29.9 (CH_3), 28.1 (2 x CH_2), 23.6 (CH_2). HRMS

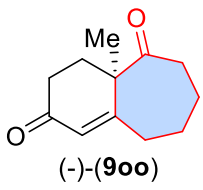
(ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{22}{}^{35}ClO_3S$ 353.0978; Found 353.0981; *m/z*: $[M + 2 + H]^+$ Calcd for $C_{18}H_{22}{}^{37}ClO_3S$ 355.0949; Found 355.0950.

(*S*)-4a-(((4-Chlorophenyl)thio)methyl)-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9pp]: Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.8:8.2) and isolated as yellow oil. Yield: 91% (35 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak IG column (hexane/2-propanol = 93:7, flow rate 0.7 mL/min, λ = 254 nm), t_R = 51.79 min (major), t_R = 57.50 min (minor); $[\alpha]_D^{25}$ = -142.0° [*c* = 0.1, $CHCl_3$, 93% *ee*]; IR (Neat): ν_{max} 2928, 2856, 2358, 1706, 1668, 1475, 1449, 1274, 1260, 1151, 1094, 817 and 750 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.28 (2H, m), 7.23 (2H, m), 6.11 (1H, s, olefinic-*H*), 3.49 (1H, d, *J* =13.5 Hz), 3.22 (1H, d, *J* = 13.5 Hz), 2.66 (1H, dt, *J* = 12.2, 2.5 Hz), 2.60-2.52 (1H, m), 2.45-2.36 (3H, m), 2.28-2.24 (2H, m), 2.09-2.06 (1H, m), 2.03-1.96 (2H, m), 1.65-1.48 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 211.3 (C, *C*=O), 197.2 (C, *C*=O), 163.4 (C), 135.5 (C), 132.8 (C), 131.5 (2 x CH), 130.9 (CH), 129.2 (2 x CH), 56.4 (C), 40.7 (CH_2), 40.2 (CH_2), 35.7 (CH_2), 33.2 (CH_2), 31.5 (CH_2), 30.7 (CH_2), 27.2 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}{}^{35}ClO_2S$ 335.0873; Found 335.0874; *m/z*: $[M + 2 + H]^+$ Calcd for $C_{18}H_{20}{}^{37}ClO_2S$ 337.0843; Found 337.0840.



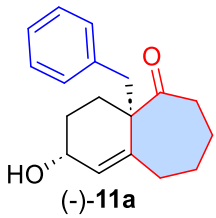
(-)-(**9pp**)

(*R*)-4a-methyl-4,4a,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,5(3*H*)-dione [(-)-9oo]: Prepared by following the procedure **I** and purified by column chromatography using EtOAc/hexane (1.5:8.5 to 1.6:8.4) and isolated as colourless oil. Yield: 80% (31 mg). The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak ID column (hexane/2-propanol = 90:10, flow rate 0.7 mL/min, λ = 254 nm), t_R = 14.36 min (major), t_R = 16.43 min (minor); $[\alpha]_D^{25}$ = -30.0° [*c* = 0.1, $CHCl_3$, 92% *ee*].



(-)-(**9oo**)

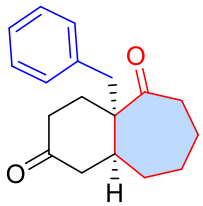
(2*R*,4a*S*)-4a-Benzyl-2-hydroxy-2,3,4,4a,6,7,8,9-octahydro-5*H*-benzo[7]annulen-5-one [(-)-11a]: Prepared by following the procedure **J** and purified by column chromatography using EtOAc/hexane (1.7:8.3 to 2.0:8.0) and isolated as colourless oil. Yield: 80% (22 mg); $[\alpha]_D^{25}$ = -67.0° [*c* = 0.1, $CHCl_3$,



(-)-**11a**

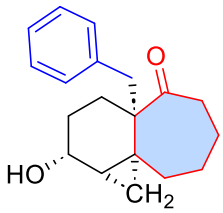
>99% *ee*, >20:1 *dr*]; IR (Neat): ν_{max} 3360, 2930, 1703, 1695, 1616, 1448, 1450, 1009, 729 and 701 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24-7.22 (2H, m), 7.20-7.19 (1H, m), 7.17-7.15 (2H, m), 5.84 (1H, d, J = 2.5 Hz, olefinic-*H*), 4.14-4.11 (1H, m), 3.15 (1H, d, J = 13.5 Hz), 3.08 (1H, d, J = 14.0 Hz), 2.70-2.64 (1H, m), 2.31-2.23 (2H, m), 1.91-1.88 (2H, m), 1.78-1.73 (1H, m), 1.68-1.61 (2H, m), 1.53-1.40 (4H, m), 1.01-0.94 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 214.3 (C, *C*=O), 141.4 (C), 138.6 (C), 132.1 (CH), 130.6 (2 x CH), 127.9 (2 x CH), 126.4 (CH), 66.7 (CH), 56.2 (C), 40.7 (CH_2), 40.1 (CH_2), 34.8 (CH_2), 32.5 (CH_2), 30.0 (CH_2), 27.7 (CH_2), 26.8 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{23}O_2$ 271.1696; Found 271.1698.

(4a*S*,9a*S*)-4a-Benzyloctahydro-1*H*-benzo[7]annulene-2,5-dione [(+)-12a]: Prepared by following the procedure **K** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 0.6:9.4) and isolated as colourless oil. Yield: 75% (20 mg); $[\alpha]_D^{25}$ = +42.0° [*c* = 0.1, $CHCl_3$, >99% *ee* and >30:1 *dr*]; IR (Neat): ν_{max} 2924, 2855, 1699, 1451, 1318, 1175, 1071, 961, 770, 731, 701 and 541 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.30-7.23 (3H, m), 7.06-7.04 (2H, m), 3.24 (1H, d, J = 14.0 Hz), 3.07 (1H, d, J = 14.0 Hz), 2.96 (1H, dd, J = 14.5, 6.0 Hz), 2.55-2.44 (3H, m), 2.34-2.29 (1H, m), 2.27-2.23 (2H, m), 2.10-2.04 (1H, m), 2.00-1.93 (1H, m), 1.86-1.83 (1H, m), 1.83-1.77 (1H, m), 1.72-1.68 (1H, m), 1.44-1.38 (2H, m) 1.35-1.25 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 215.5 (C, *C*=O), 211.0 (C, *C*=O), 136.1 (C), 129.6 (2 x CH), 128.4 (2 x CH), 127.1 (CH), 55.9 (C), 45.6 (CH_2), 42.03 (CH_2), 41.99 (CH), 41.7 (CH_2), 37.1 (CH_2), 33.0 (CH_2), 29.3 (CH_2), 28.5 (CH_2), 27.1 (CH_2). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{23}O_2$ 271.1698; Found 271.1694.



(+)-**12a**

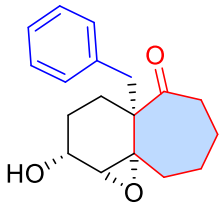
(1a*S*,2*R*,4a*S*,9a*R*)-4a-Benzyl-2-hydroxydecahydro-5*H*-cyclopropa[1,6]benzo[1,2][7]annulen-5-one [(-)-13a]: Prepared by following the procedure **L** and purified by column chromatography using EtOAc/hexane (1.7:8.3 to 2.0:8.0) and isolated as colourless oil. Yield: 60% (17 mg); $[\alpha]_D^{25}$ = -59.0° [*c* = 0.1, $CHCl_3$, >99% *ee* and >30:1 *dr*]; IR (Neat): ν_{max} 3432, 2925, 1697, 1452, 1026, 701 and 586 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.38 (2H, d, J = 7.5 Hz), 7.24-7.17 (3H, m), 4.33-4.29 (1H, m), 3.32 (1H, d, J = 13.0



(-)-**13a**

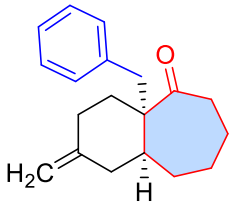
Hz), 2.71-2.65 (2H, m), 2.50-2.47 (1H, m), 1.85-1.80 (1H, m), 1.71-1.63 (1H, m), 1.62 (1H, br s), 1.51-1.45 (2H, m), 1.40-1.33 (3H, m), 1.31-1.28 (2H, m), 1.22-1.16 (1H, m), 0.93 (1H, t, J = 5.0 Hz), 0.60-0.56 (1H, m), 0.39 (1H, dd, J = 8.7, 5.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 214.7 (C, *C*=O), 139.0 (C), 131.5 (2 x CH), 127.7 (2 x CH), 126.0 (CH), 66.6 (CH), 53.8 (C), 42.5 (CH_2), 41.1 (CH_2), 39.3 (CH_2), 31.7 (CH_2), 28.0 (CH_2), 26.5 (CH_2), 26.48 (C), 26.1 (CH_2), 24.5 (CH), 18.0 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{24}NaO_2$ 307.1674; Found 307.1671.

(1a*R*,2*R*,4a*S*,9a*S*)-4a-Benzyl-2-hydroxyoctahydrocyclohepta[1,6]benzo[1,2-b]oxiren-5(1a*H*)-one [(-)-**14a**]**:** Prepared by following the procedure **M** and purified by column chromatography using EtOAc/hexane (1.6:8.4 to 1.7:8.3) and isolated as colourless oil. Yield: 72% (21 mg); $[\alpha]_D^{25}$ = -7.9° [*c* = 0.1, $CHCl_3$, >99% *ee* and >30:1 *dr*]; IR (Neat): ν_{max} 3385, 2932, 1702, 1450, 1616, 1012, 873, 702 and 571 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (2H, br d, J = 7.0 Hz), 7.25-7.22 (2H, m), 7.19-7.17 (1H, m), 4.13 (1H, dd, J = 10.0, 5.5 Hz), 3.27 (1H, d, J = 13.0 Hz), 3.17 (1H, s), 2.89 (1H, d, J = 13.5 Hz), 2.61-2.56 (1H, m), 2.48-2.46 (1H, m), 1.86-1.84 (1H, m), 1.77-1.60 (4H, m), 1.51 (1H, dt, J = 13.5, 3.5 Hz), 1.39-1.30 (3H, m), 0.96-0.91 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 211.4 (C, *C*=O), 138.4 (C), 131.7 (2 x CH), 127.8 (2 x CH), 126.2 (CH), 68.8 (CH), 66.1 (C), 61.5 (CH), 55.7 (C), 42.0 (CH_2), 38.3 (CH_2), 37.9 (CH_2), 32.2 (CH_2), 28.2 (CH_2), 26.8 (CH_2), 25.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{23}O_3$ 287.1647; Found 287.1648.



(-)-(**14a**)

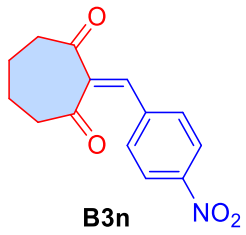
(4a*S*,9a*S*)-4a-Benzyl-2-methylenedecahydro-5*H*-benzo[7]annulen-5-one [(+)-**15a**]**:** Prepared by following the procedure **N** and purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.2:8.8) and isolated as colourless oil. Yield: 85% (23 mg); $[\alpha]_D^{25}$ = +5.9° [*c* = 0.1, $CHCl_3$, >99% *ee* and >30:1 *dr*]; IR (Neat): ν_{max} 2925, 2360, 1695, 1450, 1132, 884, 726, 699 and 564 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27-7.20 (3H, m), 7.02-7.01 (2H, m), 4.68 (1H, br d, J = 1.5 Hz, olefinic-*H*), 4.62 (1H, d, J = 2.0 Hz, olefinic-*H*), 3.06 (1H, d, J = 13.5 Hz), 3.00 (1H, d, J = 13.5 Hz), 2.80 (1H, br td, J = 13.5, 2.0 Hz), 2.42-2.37 (1H, m), 2.33-2.26 (1H, m), 2.24-2.19 (1H, m), 2.16-2.10 (2H, m), 2.06 (1H, td, J = 13.5, 2.0 Hz), 1.85-1.74 (3H, m), 1.55-1.49



(+)-**15a**

(2H, m), 1.40-1.33 (2H, m), 1.28-1.22 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 217.5 (C, *C*=O), 145.3 (C), 137.1 (C), 129.8 (2 x CH), 128.2 (2 x CH), 126.6 (CH), 108.3 (CH_2), 54.3 (C), 41.3 (CH_2), 41.2 (CH_2), 40.6 (CH), 39.3 (CH_2), 33.0 (CH_2), 30.4 (CH_2), 29.8 (CH_2), 28.6 (CH_2), 27.9 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{25}O$ 269.1905; Found 269.1896.

2-(4-nitrobenzylidene)cycloheptane-1,3-dione (5n): The title compound was prepared following the procedure **O** and purified by column chromatography using EtOAc/hexane (0.6 : 9.4 to 1.2 : 8.8), and isolated as a white solid. Mp.: 125-127 ^{o}C. Yield: 82% (63.7 mg). IR (Neat): ν_{max} 2958, 1700, 1677, 1512, 1340, 1258, 1103, 1009, 797, 695 and 501 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (2H, td, *J* = 8.5, 2.5 Hz), 7.62 (1H, s, olefinic-*H*), 7.59 (2H, td, *J* = 8.5, 2.5 Hz), 2.80-2.77 (2H, m), 2.68-2.65 (2H, m), 2.08-2.00 (4H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 207.8 (C, *C*=O), 195.7 (C, *C*=O), 148.4 (C), 143.4 (C), 139.4 (C), 137.7 (CH), 130.9 (2 x CH), 123.8 (2 x CH), 43.9 (CH_2), 41.7 (CH_2), 24.8 (CH_2), 24.5 (CH_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}NO_4$ 260.0923; Found 260.0921.



B3n

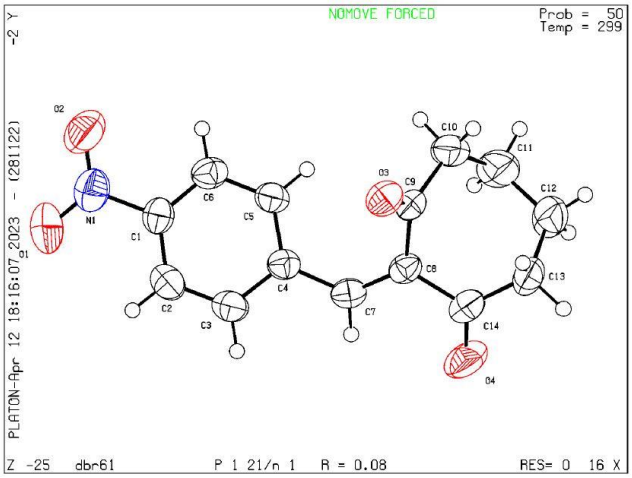
X-Ray Single Crystal Data for 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (5n). The Ellipsoid Contour % Probability Levels are 50%

Crystallized from Hexane-Ethyl acetate; $C_{14}H_{13}NO_4$; Mr = 259.25; monoclinic; space group = *P 21/n*; A metallic yellowish yellow crystal of 0.21x0.2x0.14 mm^3 was used.

Table S2. Crystal data and structure refinement for 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (CCDC-2258238)

```
Bond precision:   C-C = 0.0043 A          Wavelength=0.71073

Cell:             a=11.3019(4)     b=6.9207(3)          c=16.2735(6)
                  alpha=90         beta=101.713(4)      gamma=90
Temperature:      299 K

                 Calculated                Reported
Volume           1246.36(9)                1246.36(9)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C14 H13 N O4              C14 H13 N O4
Sum formula      C14 H13 N O4              C14 H13 N O4
Mr               259.25                    259.25
Dx,g cm-3        1.382                     1.382
Z                4                         4
Mu (mm-1)        0.102                     0.102
F000             544.0                     544.0
F000'            544.30
h,k,lmax         14,8,20                   14,8,20
Nref             2682                      2593
Tmin,Tmax        0.979,0.986               0.604,1.000
Tmin'            0.979

Correction method= # Reported T Limits: Tmin=0.604 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.967           Theta(max)= 26.849

R(reflections)= 0.0765( 1982)                wR2(reflections)=
                                             0.2262( 2593)
S = 1.076                Npar= 172
```

Ellipsoid plot for 2-(4-nitrobenzylidene)cycloheptane-1,3-dione (**5n**):



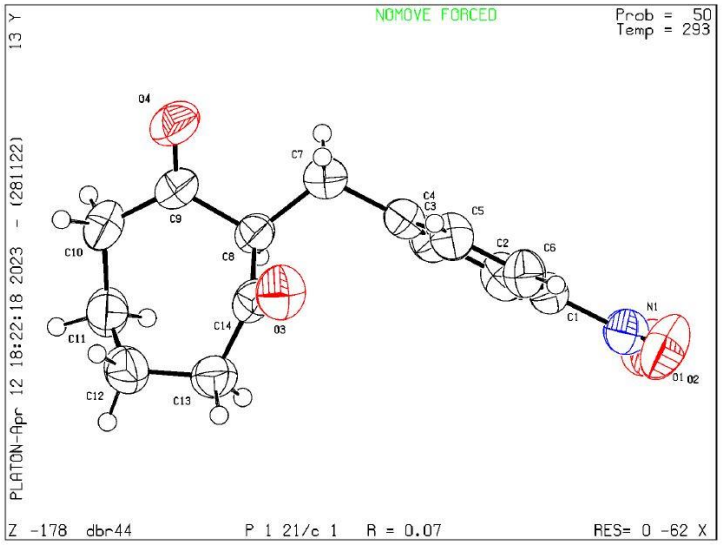
X-Ray Single Crystal Data for 6n. The Ellipsoid Contour % Probability Levels are 50%

Crystallized from Hexane-Ethyl acetate; $C_{14}H_{15}NO_4$; Mr = 261.27; monoclinic; space group = *P 21/c*; A clear whiteish crystal of 0.5x0.3x0.2 mm^3 was used.

Table S3. Crystal data and structure refinement for **6n** (CCDC-2258239)

```
Bond precision:   C-C = 0.0036 A          Wavelength=0.71073

Cell:             a=16.4952(7)     b=5.8210(3)          c=14.2222(7)
                  alpha=90         beta=112.011(5)      gamma=90
Temperature:      293 K

                  Calculated                Reported
Volume            1266.06(11)               1266.06(11)
Space group       P 21/c                    P 1 21/c 1
Hall group        -P 2ybc                   -P 2ybc
Moiety formula    C14 H15 N O4              C14 H15 N O4
Sum formula       C14 H15 N O4              C14 H15 N O4
Mr                261.27                    261.27
Dx,g cm-3         1.371                     1.371
Z                 4                         4
Mu (mm-1)         0.101                     0.101
F000              552.0                     552.0
F000'             552.30
h,k,lmax          21,7,18                   20,7,17
Nref              2745                      2646
Tmin,Tmax         0.964,0.980               0.726,1.000
Tmin'             0.951

Correction method= # Reported T Limits: Tmin=0.726 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.964            Theta(max)= 26.903

R(reflections)= 0.0692( 1651)                    wR2(reflections)=
                                                 0.2185( 2646)
S = 1.060                  Npar= 172
```

Ellipsoid plot for **6n**:



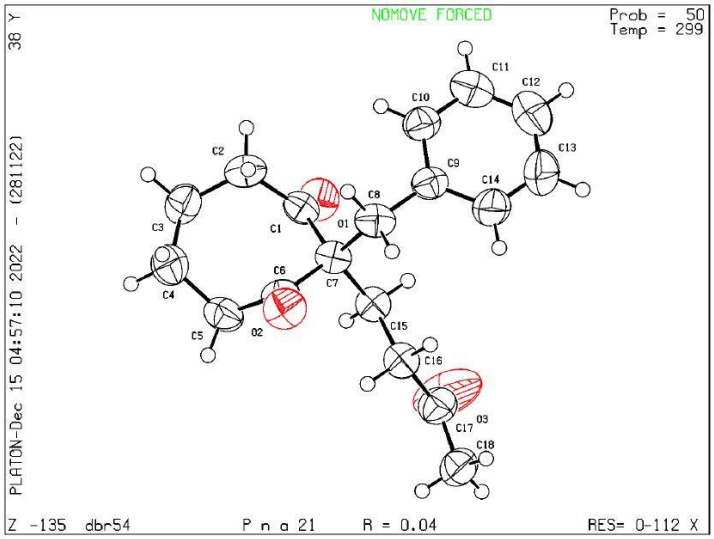
X-Ray Single Crystal Data for 8a. The Ellipsoid Contour % Probability Levels are 50%

Crystallized from Hexane-Ethyl acetate; $C_{18}H_{22}O_3$; Mr = 286.36; orthorhombic; space group = *P n a 21*; A clear whiteish crystal of 0.21x0.2x0.16 mm^3 was used.

Table S4. Crystal data and structure refinement for **8a** (CCDC-2258240)

```
Bond precision:   C-C = 0.0051 A          Wavelength=0.71073

Cell:             a=8.6941(4)     b=17.9069(10)     c=10.1924(5)
                  alpha=90        beta=90           gamma=90
Temperature:      299 K

                  Calculated                  Reported
Volume            1586.80(14)                 1586.80(14)
Space group       P n a 21                    P n a 21
Hall group        P 2c -2n                    P 2c -2n
Moiety formula    C18 H22 O3                  C18 H22 O3
Sum formula       C18 H22 O3                  C18 H22 O3
Mr                286.36                      286.35
Dx,g cm-3         1.199                       1.199
Z                 4                           4
Mu (mm-1)         0.080                       0.080
F000              616.0                       616.0
F000'             616.30
h,k,lmax          10,21,12                    10,21,12
Nref              2803[ 1488]                 2473
Tmin,Tmax         0.983,0.987                 0.709,1.000
Tmin'             0.983

Correction method= # Reported T Limits: Tmin=0.709 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.66/0.88        Theta(max)= 25.027

R(reflections)= 0.0434( 1948)                 wR2(reflections)=
                                              0.1091( 2473)
S = 1.040                  Npar= 191
```

Ellipsoid plot for **8a**:



X-Ray Single Crystal Data for (-)-9a. The Ellipsoid Contour % Probability Levels are 50%

Crystallized from Ethyl acetate; $C_{18}H_{20}O_2$; Mr = 268.34; orthorhombic; space group = *P 21 21 21*; A clear whiteish crystal of 0.23x0.2x0.14 mm^3 was used.

Table S5. Crystal data and structure refinement for (-)-**9a** (CCDC-2258241)

Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=7.3138(4) b=12.6070(6) c=15.9123(10)
alpha=90 beta=90 gamma=90

Temperature: 299 K

	Calculated	Reported
Volume	1467.20(14)	1467.19(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C18 H20 O2	C18 H20 O2
Sum formula	C18 H20 O2	C18 H20 O2
Mr	268.34	268.34
Dx,g cm-3	1.215	1.215
Z	4	4
Mu (mm-1)	0.078	0.078
F000	576.0	576.0
F000'	576.26	
h,k,lmax	9,16,20	9,15,20
Nref	3188[1844]	3074
Tmin,Tmax	0.982,0.989	0.637,1.000
Tmin'	0.982	

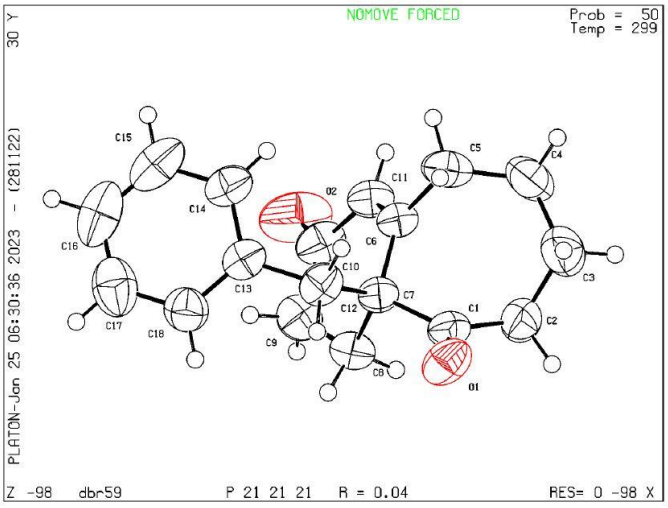
Correction method= # Reported T Limits: Tmin=0.637 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.67/0.96 Theta(max)= 26.924

R(reflections)= 0.0381(2378) wR2(reflections)= 0.1021(3074)

S = 1.044 Npar= 182

Ellipsoid plot for **(-)-9a**:



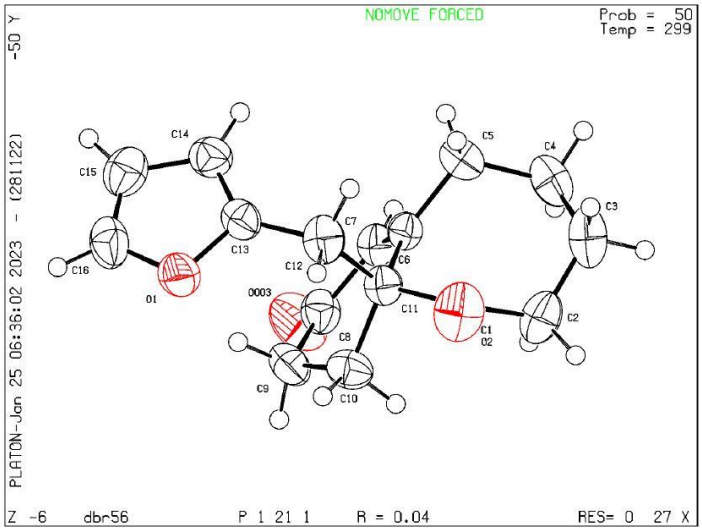
X-Ray Single Crystal Data for (-)-9r. The Ellipsoid Contour % Probability Levels are 50%

Crystallized from Ethyl acetate; $C_{16}H_{18}O_3$; Mr = 258.30; monoclinic; space group = *P 21*; A clear whiteish crystal of 0.2x0.15x0.1 mm^3 was used.

Table S6. Crystal data and structure refinement for (-)-**9r** (CCDC-2258242)

```
Bond precision:   C-C = 0.0045 A          Wavelength=0.71073

Cell:             a=7.9700(5)     b=11.1812(6)         c=7.9888(4)
                  alpha=90        beta=110.788(7)      gamma=90
Temperature:      299 K

                 Calculated                Reported
Volume           665.57(7)                 665.57(7)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C16 H18 O3                C16 H18 O3
Sum formula      C16 H18 O3                C16 H18 O3
Mr               258.30                    258.30
Dx,g cm-3        1.289                     1.289
Z                2                         2
Mu (mm-1)        0.088                     0.088
F000             276.0                     276.0
F000'            276.14
h,k,lmax         10,14,10                  9,14,10
Nref             2911[ 1533]               2639
Tmin,Tmax        0.984,0.991               0.502,1.000
Tmin'            0.983

Correction method= # Reported T Limits: Tmin=0.502 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.91        Theta(max)= 27.009

R(reflections)= 0.0433( 2006)                wR2(reflections)=
                                             0.0974( 2639)
S = 0.978                  Npar= 172
```

Ellipsoid plot for **(-)-9r**:



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