Cyclization *vs.* Elimination Reactions of 5-Aryl-5-hydroxy 1,3-Diones: One-Pot Synthesis of 2-Aryl-2,3-dihydro-4*H*-pyran-4-ones

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2-Aryl-2,3-dihydro-4*H*-pyran-4-ones were prepared in one step by cyclocondensation of 1,3-diketone dianions with aldehydes. The use of HCl (10%) for the aqueous workup proved to be very important to avoid elimination reactions of the 5-aryl-5-hydroxy 1,3-diones formed as intermediates. The $TiCl_4$-mediated cyclization of a 2-aryl-2,3-dihydro-4*H*-pyran-4-one with 1,3-silyloxybuta-1,3-diene resulted in cleavage of the pyranone moiety and formation of a highly functionalized benzene derivative.

Introduction. – 2,3-Dihydro-4*H*-pyran-4-ones are present in a variety of natural products, such as curcumin (*Fig. 1*), and are of considerable pharmacological relevance [1]. 2,3-Dihydro-4*H*-pyran-4-ones have been prepared by hetero-*Diels–Alder* reaction of aldehydes with *Danishefsky*'s diene [2] or related dienes [3][4]. A catalytic approach to enantiomerically pure 2,3-dihydro-4*H*-pyran-4-ones has been reported [5]. It is based on the condensation of 1,3-bis(silyloxy)buta-1,3-dienes[1]) with aldehydes. These methods are limited by the fact that the synthesis of the (unstable) dienes requires two to three steps and needs a special handling. In addition, they cannot be stored for a long period of time, some of them not even at $-20°$. 2,3-Dihydro-4*H*-pyran-4-ones have also been prepared by Pd^{II}-catalyzed oxidative cyclizations of β-hydroxy enones [7], by reactions of β-ethoxy-α,β-unsaturated lactones [8], by $(i\text{-}Pr)_2NLi$ (LDA)-mediated reactions of 3-methoxy 2-en-1-ones with aldehydes and subsequent acid-mediated cyclization [9], and by reactions of lithiated dithianes with epoxides and subsequent deprotection, oxidation, and cyclization [10].

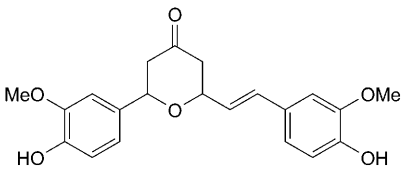
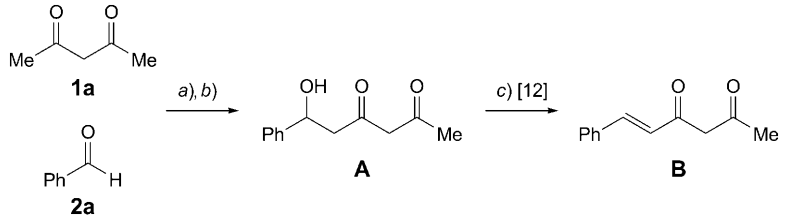


Fig. 1. *Structure of curcumin*

[1]) For a review of 1,3-bis(trimethylsilyloxy) 1,3-dienes, see [6].

Results and Discussion. – The reaction of 1,3-dicarbonyl dianions with aldehydes has been reported to give 5-hydroxy 1,3-dicarbonyl compounds, which undergo HCl/MeOH-mediated dehydration or transformation into 2,3-dihydro-4*H*-pyran-4-ones [11][2]). The natural product stegobinone has been prepared by this methodology [13]. 5-Hydroxy 1,3-diketones were transformed into 2-alkyl-2,3-dihydro-4*H*-pyran-4-ones by using TsOH (CH_2Cl_2, 24 h, reflux, *Dean–Stark* trap, 3-Å molecular sieves) [14]. However, this method is limited to the mentioned pyran-4-ones. Dehydration (elimination of H_2O) was observed in case of aromatic substrates. For example, the reaction of TsOH with 6-hydroxy-6-phenylhexane-2,4-dione (**A**), prepared by condensation of the dianion of acetylacetone (**1a**) with benzaldehyde (**2a**), gave 6-phenylhex-5-ene-2,4-dione (**B**) rather than the desired pyran-4-one **3a** (*Scheme 1* and *Table*) [14]. The facile formation of **B** is a result of the conjugation of the C=C bond with the aryl group. *Denmark* and *Heemstra* reported the TFA-mediated transformation of **A** into **3a** (0.001 equiv. of TFA in CH_2Cl_2, 0°) [5]. Recently, we have reported preliminary results related to the synthesis of 2-aryl-2,3-dihydro-4*H*-pyran-4-ones [15]. Here, we report full details, a significant extension of the scope, and an application of our methodology.

Scheme 1. *Synthesis and Dehydration of* **A**

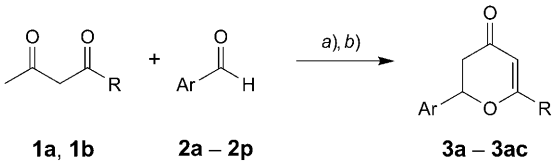


a) 1. NaH, THF, 0°, 15 min, 2. BuLi, 20 min, 0°, 3. **2a**, 15 min, 0°. *b*) NH_4Cl (sat.). *c*) TsOH, CH_2Cl_2, 24 h, reflux, *Dean–Stark* trap, 3-Å molecular sieves.

We have found that a variety of 2-aryl-2,3-dihydro-4*H*-pyran-4-ones can be successfully prepared in good yields and in only one step by reaction of 1,3-diketone dianions with aromatic aldehydes and subsequent aqueous workup using HCl (10%). 5-hydroxy-5-phenylhexane-2,4-dione (**A**) was prepared by LDA-mediated condensation of acetylacetone (**1a**) with PhCHO (**2a**) according to the procedure of *Miller* and coworkers [14]. An aqueous solution of NH_4Cl was used for the aqueous workup which did not result in elimination or cyclization of **A**. The reaction of a $MeNO_2$ solution of **A** with catalytic amounts of $FeCl_3 \cdot 6\,H_2O$ (10 mol-%) afforded the desired product in high yield (*Scheme 2* and *Table*). The same result was obtained by employment of HCl (10%). Finally, we have developed a one-pot protocol: the reaction of the dianion of acetylacetone (**1a**) (generated by means of 2.5 equiv. of LDA) with PhCHO (**2a**; $-78 \rightarrow 20°$, 12 h), addition of HCl (10%) and, after 15 min, extraction of the mixture with AcOEt afforded the desired pyran-4-one **3a** in 87% yield (*Scheme 2*). The formation of **3a** (rather than **B**) can be explained by acid-mediated attack of the OH group onto the CO group and subsequent elimination of H_2O. While an elimination was

[2]) For a review of cyclization reactions of dianions, see [12].

Scheme 2. *Synthesis of* **3a**–**3ac**



1a, **1b** **2a** – **2p** **3a** – **3ac**

a) 1. $(i\text{-}Pr)_2NLi$ (LDA; 2.5 equiv), THF, 0°, 1 h; 2. −78°, **1a**, **1b**, 1 h; 3. **2a**–**2p**, −78° → 20°, 12 h. *b*) addition of HCl (10%), 15 min, 20°, then extraction (AcOEt).

Table. *Synthesis of* **3a**–**3ac**

Compound **1**	Compound **2**	Product **3**	R	Ar	Yield [%][a])
a	**a**	**a**	Me	Ph	87
a	**b**	**b**	Me	2-Cl−C_6H_4	65
a	**c**	**c**	Me	3-Cl−C_6H_4	70
a	**d**	**d**	Me	4-Cl−C_6H_4	76
a	**e**	**e**	Me	3-Br−C_6H_4	69
a	**f**	**f**	Me	3-Me−C_6H_4	76
a	**g**	**g**	Me	4-Me−C_6H_4	89
a	**h**	**h**	Me	4-Et−C_6H_4	90
a	**i**	**i**	Me	4-MeO−C_6H_4	64
a	**j**	**j**	Me	2,3-$(MeO)_2C_6H_4$	73
a	**k**	**k**	Me	2,4-$(MeO)_2C_6H_4$	70
a	**l**	**l**	Me	3-HO−C_6H_4	67
a	**m**	**m**	Me	4-HO−C_6H_4	69
a	**n**	**n**	Me	3-NO_2−C_6H_4	57
a	**o**	**o**	Me	4-NO_2−C_6H_4	60
a	**p**	**p**	Me	4-Ph−C_6H_4	86
a	**q**	**q**	Me	Furan-2-yl	87
a	**r**	**r**	Me	Thiophen-2-yl	82
b	**a**	**s**	Ph	Ph	78
b	**b**	**t**	Ph	2-Cl−C_6H_4	62
b	**d**	**u**	Ph	4-Cl−C_6H_4	66
b	**e**	**v**	Ph	3-Br−C_6H_4	71
b	**g**	**w**	Ph	4-Me−C_6H_4	79
b	**i**	**x**	Ph	4-MeO−C_6H_4	72
b	**k**	**y**	Ph	2,4-$(MeO)_2C_6H_4$	61
b	**m**	**z**	Ph	4-HO−C_6H_4	73
b	**n**	**aa**	Ph	3-NO_2−C_6H_4	68
b	**o**	**ab**	Ph	4-NO_2−C_6H_4	67
b	**p**	**ac**	Ph	4-Ph−C_6H_4	83

[a]) Yields of isolated products.

observed with TsOH, a cyclization was induced by using an aqueous solution of HCl (10%, 20°). Therefore, the presence of water might play a role in the reaction. While the reaction with TsOH was carried out under reflux conditions, the reaction with CF_3COOH (TFA), as reported by *Denmark* and *Heemstra* [5], was carried out at 0°

(16 h). Therefore, the temperature seems to play an important role whether an elimination or cyclization reaction occurs. The silica-gel chromatography of the products may also play a role to induce a complete transformation of **A** into **3a**.

The reaction of the dianions of acetylacetone (**1a**) and benzoylacetone (**1b**) with aldehydes **2a**–**2r** afforded the 2-aryl-2,3-dihydro-4*H*-pyran-4-ones **3a**–**3ac** in very good yields (*Scheme 2* and *Table*). The structures of all products were established by spectroscopic methods. The structures of **3p** and **3v** were additionally confirmed by X-ray crystal structure analysis (*Figs. 2* and *3*)[3]).

In conclusion, a variety of 2-aryl-2,3-dihydro-4*H*-pyran-4-ones were prepared in one step by cyclocondensation of 1,3-diketone dianions with aldehydes and subsequent workup using HCl (10%).

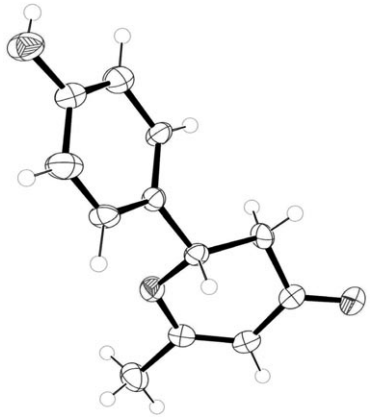


Fig. 2. *ORTEP Plot of* **3p** (50% probability level)

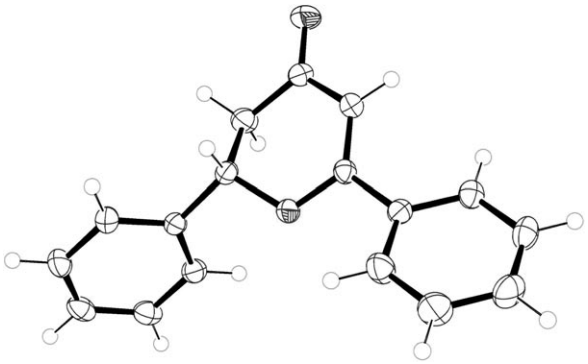


Fig. 3. *ORTEP Plot of* **3v** (50% probability level)

[3]) CCDC-769126 and 769127 contain all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: *Cambridge Crystallographic Data Centre*, 12 Union Road, GB-Cambridge CB21EZ; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Experimental Part

General Comments. All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. Prep.-scale chromatography: silica gel (SiO_2, 60–200 mesh; *Merck*). M.p.: Microheating table *HMK 67/1825 Kuestner* (*Büchi* apparatus); uncorrected. IR Spectra: *Nicolet 380* FT-IR spectrameter; in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AVANCE 300 III and Bruker AVANCE 250 II spectrometer*. EI-MS and ESI-MS: *Finnigan MAT 95-XP* instrument; in *m/z*.

*General Procedure for the Synthesis of 2,3-Dihydro-4*H*-pyran-4-ones* **3a**–**3ac**. A THF soln. of LDA (12.5 mmol) was prepared by addition of BuLi (5 ml, 12.5 mmol; 2.5M soln. in hexanes) to a THF soln. (15 ml) of $(i\text{-}Pr)_2NH$ (1.26 g, 12.5 mmol) at 0°. After stiring for 1 h, the soln. was cooled to −78°, and pentane-2,4-dione (0.50 g, 5.0 mmol) was added. After stirring for 1 h at −78°, aldehyde (5.0 mmol) was added, and the soln. was allowed to warm to 20° within 24 h. HCl (10%, 15 ml) was added, and the mixture was allowed to stand for 15 min. AcOEt (25 ml) was added. The org. and aq. layers were separated, and the latter was extracted with AcOEt (3 × 50 ml). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (SiO_2; heptane/AcOEt 2:1) to give **3a**–**3ac**.

*2,3-Dihydro-6-methyl-2-phenyl-4*H*-pyran-4-one* (**3a**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2a** (0.53 g, 5.0 mmol) in THF (15 ml): **3a** (0.82 g, 87%). Colorless crystalline solid. M.p. 45–48°. IR (KBr): 3062*w*, 3033*w*, 2962*w*, 2918*w*, 1661*s*, 1603*s*, 1392*s*, 1327*s*, 1237*m*, 1179*m*, 1023*m*, 999*s*, 950*m*, 808*m*, 755*s*, 696*s*. ^1H-NMR (300 MHz, $CDCl_3$): 1.98 (*s*, Me); 2.51 (*dd*, *J* = 3.3, 16.8, 1 H, CH_2); 2.76 (*dd*, *J* = 14.0, 1 H, CH_2); 5.31 (*dd*, *J* = 3.6, 14.0, CH); 5.36 (*s*, 1 olefin. H); 7.28–7.33 (*m*, 5 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.1 (Me); 42.4 (CH_2); 80.8 (CH); 105.2 (olefin. CH); 126.1, 128.8, 133.0 (arom. CH); 138.1 (arom. C); 174.3 (olefin. C); 192.3 (CO). GC/EI-MS (70 eV): 188 (2, M^+), 170 (8), 155 (6), 145 (36), 104 (100), 91 (2), 78 (16), 77 (12). HR-ESI-TOF-MS: 189.0908 ($[M+H]^+$, $C_{12}H_{13}O_2^+$; calc. 189.0910). Anal. calc. for $C_{12}H_{13}O_2$: C 76.57, H 6.43; found: C 76.43, H 6.40.

*2-(2-Chlorophenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3b**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2b** (0.70 g, 5.0 mmol) in THF (15 ml): **3b** (0.72 g, 65%). Colorless viscous oil. IR (KBr): 3411*w*, 3066*w*, 2918*w*, 1706*w*, 1604*s*, 1575*s*, 1471*m*, 1437*m*, 1398*m*, 1358*m*, 1287*m*, 1232*m*, 1032*s*, 752*s*. ^1H-NMR (300 MHz, $CDCl_3$): 2.07 (*s*, Me); 2.58 (*dd*, *J* = 13.7, 1 H, CH_2); 2.71 (*dd*, *J* = 4.0, 16.8, 1 H, CH_2); 5.44 (*s*, 1 olefin. H); 5.76 (*dd*, *J* = 4.0, 13.7, CH); 7.28 (*t*, *J* = 7.4, 1 arom. H); 7.32 (*d*, *J* = 8.6, 1 arom. H); 7.36 (*t*, *J* = 7.5, 1 arom. H); 7.59 (*d*, *J* = 7.5, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (Me); 41.1 (CH_2); 77.7 (CH); 105.3 (olefin. CH); 127.2, 127.3, 127.6, 127.8 (arom. CH); 131.7, 136.1 (arom. C); 174.2 (olefin. C); 191.7 (CO). GC/EI-MS (70 eV): 222 (3, M^+), 187 (20), 181 (10), 179 (26), 140 (33), 139 (11), 138 (100), 103 (38), 102 (10), 77 (13). HR-EI-MS: 222.0442 (M^+, $C_{12}H_{11}ClO_2^+$; calc. 222.0442).

*2-(3-Chlorophenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3c**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2c** (0.70 g, 5.0 mmol) in THF (15 ml): **3c** (0.78 g, 70%). Solid. M.p. 54–55°. IR (KBr): 3399*w*, 3066*w*, 2958*w*, 2921*w*, 2853*w*, 1714*w*, 1663*s*, 1607*s*, 1573*m*, 1431*m*, 1391*s*, 1325*s*, 1237*m*, 1159*m*, 1064*m*, 1002*m*, 879*m*, 783*m*, 690*m*, 582*m*. ^1H-NMR (300 MHz, $CDCl_3$): 2.02 (*s*, Me); 2.52 (*dd*, *J* = 3.5, 16.8, 1 H, CH_2); 2.74 (*dd*, *J* = 13.9, 1 H, CH_2); 5.28 (*dd*, *J* = 3.6, 13.9, CH); 5.37 (*s*, 1 olefin. H); 7.27 (*t*, *J* = 6.7, 1 arom. H); 7.29 (*d*, *J* = 8.7, 1 arom. H); 7.32 (*d*, *J* = 8.4, 1 arom. H); 7. 35 (*s*, 1 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.0 (Me); 42.3 (CH_2); 79.9 (CH); 105.4 (olefin. CH); 124.1, 126.3, 128.9, 130.1 (arom. CH); 134.7, 140.2 (arom. C); 174.0 (olefin. C); 191.7 (CO). GC/EI-MS (70 eV): 222 (7, M^+), 204 (10), 179 (24), 140 (32), 139 (10), 138 (100), 103 (33), 77 (13). HR-EI-MS: 222.0439 (M^+, $C_{12}H_{11}ClO_2^+$; calc. 222.0442).

*2-(4-Chlorophenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3d**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2d** (0.70 g, 5.0 mmol) in THF (15 ml): **3d** (0.84 g, 76%). Colorless crystalline solid. M.p. 81–82°. IR (KBr): 3037*w*, 2965*w*, 2808*w*, 2889*w*, 1714*w*, 1600*s*, 1489*m*, 1392*m*, 1245*m*, 1087*m*, 1001*m*, 822*s*, 652*m*, 547*m*. ^1H-NMR (300 MHz, $CDCl_3$): 2.09 (*s*, Me); 2.59 (*dd*, *J* = 3.7, 16.7, 1 H, CH_2); 2.77 (*dd*, *J* = 14.0, 1 H, CH_2); 5.37 (*dd*, *J* = 3.8, 14.0, CH); 5.45 (*s*, 1 olefin. H); 7.33–7.37 (*m*, 2 arom. H); 7.39–7.42 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (Me); 42.3 (CH_2); 80.0 (CH); 105.3 (olefin. CH); 127.5, 129.0 (arom. CH); 134.6, 137.7 (arom. C); 174.0 (olefin. C); 191.8 (CO).

GC/EI-MS (70 eV): 222 (3, M^+), 204 (11), 179 (24), 140 (33), 139 (10), 138 (100), 103 (23), 77 (10). HR-EI-MS: 222.0443 (M^+, $C_{12}H_{11}ClO_2^+$; calc. 222.0442).

*2-(3-Bromophenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3e**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2e** (0.92 g, 5.0 mmol) in THF (15 ml): **3e** (0.92 g, 69%). Colorless crystalline solid. M.p. 59–60°. IR (KBr): 3073*w*, 2968*w*, 2879*w*, 1655*s*, 1604*s*, 1472*m*, 1428*m*, 1388*s*, 1323*s*, 1256*s*, 1002*s*, 881*m*, 866*m*, 854*m*, 778*s*, 694*s*, 681*s*, 621*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.01 (*s*, Me); 2.51 (*dd*, *J* = 4.0, 16.7, 1 H, CH_2); 2.67 (*dd*, *J* = 14.0, 1 H, CH_2); 5.30 (*dd*, *J* = 3.5, 14.0, CH); 5.37 (*s*, 1 olefin. H); 7.21 (*t*, *J* = 6.2, 1 arom. H); 7.22 (*d*, *J* = 6.7, 1 arom. H); 7.43 (*d*, *J* = 6.7, 1 arom. H); 7.51 (*s*, 1 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.0 (Me); 42.3 (CH_2); 79.9 (CH); 105.4 (olefin. CH); 122 (arom. C); 124.6, 129.2, 130.3, 131.8 (arom. CH); 140.4 (arom. C); 174.0 (olefin. C); 191.6 (CO). GC/EI-MS (70 eV): 266 (7, M^+), 250 (11), 248 (11), 184 (98), 182 (100), 144 (30). HR-ESI-MS: 265.9935 (M^+, $C_{12}H_{11}{}^{79}BrO_2^+$; calc. 265.9937), 267.9917 (M^+, $C_{12}H_{11}{}^{81}BrO_2^+$; calc. 267.9917).

*2,3-Dihydro-6-methyl-2-(3-methylphenyl)-4*H*-pyran-4-one* (**3f**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2f** (0.60 g, 5 mmol) in THF (15 ml): **3f** (0.77 g, 76%). Colorless oil. IR (KBr): 3317*w*, 3028*w*, 2918*w*, 2734*w*, 2610*w*, 1664*s*, 1604*s*, 1490*w*, 1435*w*, 1359*m*, 1256*m*, 1183*m*, 1095*w*, 1025*m*, 951*m*, 886*m*, 808*m*, 759*m*, 699*m*, 660*w*, 618*w*, 551*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.08 (*s*, Me); 2.38 (*s*, Me of Ar), 2.53 (*dd*, *J* = 3.5, 16.8, 1 H, CH_2); 2.78 (*dd*, *J* = 14.1, 1 H, CH_2); 5.33 (*dd*, *J* = 3.5, 14.1, CH); 5.42 (*s*, 1 olefin. H); 7.17 (*d*, *J* = 7.8, 1 arom. H); 7.20 (*d*, *J* = 7.2, 1 arom. H); 7.22 (*s*, 1 arom. H); 7.29 (*t*, *J* = 7.5, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1 (Me); 21.4 (Me of Ar); 42.3 (CH_2); 80.9 (CH); 105.1 (olefin. CH); 123.2, 126.9, 128.7, 129.5 (arom. CH); 138.1, 138.5 (arom. C); 174.2 (olefin. C); 192.2 (CO). GC/EI-MS (70 eV): 202 (3, M^+), 184 (14), 160 (15), 159 (41), 119 (10), 118 (100), 117 (60), 115 (17), 91 (17). HR-EI-MS: 202.0989 (M^+, $C_{13}H_{14}O_2^+$; calc. 202.0988). Anal. calc. for $C_{13}H_{14}O_2$: C 77.20, H 6.98; found: C 77.01, H 6.794.

*2,3-Dihydro-6-methyl-2-(4-methylphenyl)-4*H*-pyran-4-one* (**3g**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2g** (0.60 g, 5 mmol) in THF (15 ml): **3g** (0.90 g, 89%). Colorless crystalline solid. M.p. 44–45°. IR (KBr): 3278*w*, 2998*w*, 2920*w*, 2865*w*, 1661*s*, 1600*s*, 1513*m*, 1339*m*, 1244*m*, 1183*m*, 1019*s*, 811*m*, 539*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.98 (*s*, Me); 2.29 (*s*, Me of Ar); 2.48 (*dd*, *J* = 3.5, 16.7, 1 H, CH_2); 2.73 (*dd*, *J* = 14.1, 1 H, CH_2); 5.26 (*dd*, *J* = 3.4, 14.1, CH); 5.34 (*s*, 1 olefin. H); 7.12–7.16 (*m*, 2 arom. H); 7.19–7.24 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1 (Me); 21.2 (Me of Ar); 42.2 (CH_2); 80.8 (CH); 105.1 (olefin. CH); 126.2, 129.4 (arom. CH); 137.2, 138.8 (arom. C); 174.4 (olefin. C); 192.5 (CO). EI-MS (70 eV): 202 (2, M^+), 184 (11), 160 (22), 159 (30), 119 (10), 118 (100), 117 (60), 115 (16), 91 (17). HR-EI-MS: 202.0989 (M^+, $C_{13}H_{14}O_2^+$; calc. 202.0988). Anal. calc. for $C_{13}H_{14}O_2$: C 77.20, H 6.98; found: C 77.21, H 6.95.

*2-(4-Ethylphenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3h**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2h** (0.67 g, 5.0 mmol) in THF (15 ml): **3h** (0.97 g, 90%). Colorless crystalline solid. M.p. 72–73°. IR (KBr): 3308*w*, 3058*w*, 2963*w*, 2933*w*, 2871*w*, 2608*w*, 1806*w*, 1714*w*, 1658*s*, 1602*s*, 1546*m*, 1435*m*, 1390*s*, 1326*m*, 1230*m*, 1178*m*, 998*s*, 815*m*, 791*m*, 659*m*, 539*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.27 (*t*, *J* = 7.5, *Me*CH_2); 2.08 (*s*, Me); 2.54 (*dd*, *J* = 3.5, 16.8, 1 H, CH_2); 2.69 (*q*, *J* = 7.5, MeCH_2); 2.84 (*dd*, *J* = 14.1, 1 H, CH_2); 5.26 (*dd*, *J* = 3.5, 14.1, CH); 5.45 (*s*, 1 olefin. H); 7.26–7.28 (*m*, 2 arom. H); 7.34–7.36 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.5 (*Me*CH_2); 21.5 (Me); 28.6 (Me*C*H_2); 42.2 (CH_2); 80.8 (CH); 105.1 (olefin. CH); 126.3, 128.3 (arom. CH); 135.4, 145.1 (arom. C); 174.3 (olefin. C); 192.5 (CO). EI-MS (70 eV): 216 (2, M^+), 198 (13), 174 (29), 173 (30), 133 (10), 132 (77), 118 (10), 117 (100), 115 (18), 91 (14). HR-EI-MS: 216.1145 (M^+, $C_{14}H_{16}O_2^+$; calc. 216.1145).

*2,3-Dihydro-2-(4-methoxyphenyl)-6-methyl-4*H*-pyran-4-one* (**3i**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2i** (0.68 g, 5.0 mmol) in THF (15 ml): **3i** (0.70 g, 64%). Colorless solid. M.p. 64–65°. IR (KBr): 2998*w*, 2934*w*, 2836*w*, 1712*m*, 1608*s*, 1511*s*, 1461*m*, 1396*m*, 1242*s*, 1173*s*, 1149*s*, 1028*s*, 1006*m*, 957*m*, 930*m*, 869*m*, 828*s*, 818*s*, 798*m*, 658*m*, 545*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.98 (*s*, Me); 2.47 (*dd*, *J* = 3.4, 16.8, 1 H, CH_2); 2.74 (*dd*, *J* = 14.1, 1 H, CH_2); 3.75 (*s*, MeO); 5.25 (*dd*, *J* = 3.4, 14.1, CH); 5.34 (*s*, CH); 6.85–6.88 (*m*, 2 arom. H); 7.25–7.28 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1 (Me); 42.1 (CH_2); 55.3 (MeO); 80.6 (CH); 105.1 (olefin. CH); 114.1, 127.8 (arom. CH); 130.1, 160.0 (arom. C); 174.4 (olefin. C); 192.6 (CO). GC/EI-MS (70 eV): 218 (7, M^+), 200 (8), 175 (13), 160 (22), 134 (100), 119 (21), 91 (14), 77 (5). HR-EI-MS: 218.0938 (M^+, $C_{13}H_{14}O_3^+$; calc. 218.0938).

*2-(2,3-Dimethoxyphenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3j**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2j** (0.83 g, 5.0 mmol) in THF (15 ml): **3j** (0.91 g, 73%). Solid. M.p. 86–87°. IR (KBr): 2962*w*, 2937*w*, 2835*w*, 1721*w*, 1664*w*, 1602*m*, 1586*m*, 1478*m*, 1429*m*, 1395*m*, 1302*m*, 1273*m*, 1219*m*, 1082*m*, 999*s*, 927*m*, 856*m*, 785*m*, 747*m*, 629*m*, 558*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.99 (*s*, Me); 2.49 (*dd*, *J* = 3.5, 16.8, 1 H, CH_2); 2.66 (*dd*, *J* = 14.3, 1 H, CH_2); 3.79 (*s*, MeO); 3.81 (*s*, MeO); 5.45 (*s*, 1 olefin. H); 5.65 (*dd*, *J* = 3.5, 14.3, CH); 6.77 (*d*, *J* = 7.7, 1 arom. H); 7.01 (*t*, *J* = 7.4, 1 arom. H); 7.8 (*d*, *J* = 7.8, 1 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.1 (Me); 41.7 (CH_2); 55.8, 60.0 (2 MeO); 76.1 (CH); 105.0 (olefin. CH); 111.6, 118.3, 124.3 (arom. CH); 132.0, 146.2, 152.3 (arom. C); 174.5 (olefin. C); 192.7 (CO). EI-MS (70 eV): 248 (M^+, 37), 230 (19), 217 (30), 206 (47), 205 (51), 175 (21), 174 (20), 164 (78), 150 (10), 149 (100), 121 (75), 91 (29), 78 (20), 77 (21). HR-ESI-TOF-MS: 249.1118 ($[M+H]^+$, $C_{14}H_{16}O_4^+$; calc. 249.1121). Anal. calc. for $C_{14}H_{16}O_4$: C 67.73, H 6.50; found: C 67.70, H 7.19.

*2-(2,4-Dimethoxyphenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one* (**3k**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2k** (0.83 g, 5.0 mmol) in THF (15 ml): **3k** (0.86 g, 70%). Solid. M.p. 108–110°. IR (KBr): 3073*w*, 2971*w*, 2837*w*, 1655*s*, 1603*s*, 1583*s*, 1508*m*, 1461*m*, 1439*m*, 1158*s*, 1031*m*, 1020*m*, 991*s*, 827*s*, 804*s*, 547*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.99 (*s*, Me); 2.49 (*dd*, *J* = 3.7, 16.7, 1 H, CH_2); 2.56 (*dd*, *J* = 14.0, 1 H, CH_2); 3.73 (*s*, MeO); 3.75 (*s*, MeO); 5.33 (*s*, 1 olefin. H); 5.61 (*dd*, *J* = 3.7, 14.0, CH); 6.41 (*s*, 1 arom. H); 6.46 (*d*, *J* = 8.4, 1 arom. H); 7.30 (*d*, *J* = 8.4, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1 (Me); 41.4 (CH_2); 55.3, 55.4 (2 MeO); 75.9 (CH); 98.4 (arom. CH); 104.9 (olefin. CH); 105.3 (arom. CH); 119.2 (arom. C); 127.4 (arom. CH); 157.3, 161.0 (arom. C); 174.8 (olefin. C); 193.3 (CO). GC/EI-MS (70 eV): 248 (27, M^+), 205 (21), 164 (100), 149 (83), 121 (45), 91 (13), 77 (12). HR-EI-MS: 248.1041 (M^+, $C_{14}H_{16}O_4^+$; calc. 248.1043). Anal. calc. for $C_{14}H_{16}O_4$: C 67.73, H 6.50; found: C 67.64, H 6.57.

*2,3-Dihydro-2-(3-hydroxyphenyl)-6-methyl-4*H*-pyran-4-one* (**3l**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2l** (0.61 g, 5.0 mmol) in THF (15 ml): **3l** (0.68 g, 67%). Solid. M.p. 140–142°. IR (KBr): 3052*m*, 2957*m*, 2829*w*, 2600*w*, 1633*m*, 1596*m*, 1580*s*, 1574*s*, 1484*m*, 1397*m*, 1360*m*, 1220*s*, 1175*m*, 1025*m*, 1004*m*, 939*m*, 786*m*, 697*m*, 529*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.10 (*s*, Me); 2.55 (*dd*, *J* = 3.7, 16.9, 1 H, CH_2); 2.81 (*dd*, *J* = 13.8, 1 H, CH_2); 5.40 (*dd*, *J* = 3.6, 13.8, CH); 5.46 (*s*, 1 olefin. H); 6.78 (*t*, *J* = 7.4, 1 arom. H); 6.89 (*d*, *J* = 7.8, 1 arom. H); 6.91 (*d*, *J* = 7.3, 1 arom. H); 7.24 (*s*, 1 arom. H); 9.46 (br. *s*, OH). ^{13}C-NMR (75 MHz, (D_6)DMSO): 21.1 (Me); 42.9 (CH_2); 82.1 (CH); 105.3 (olefin. CH); 114.1, 116.6, 118.3, 130.8 (arom. CH); 141.2, 158.9 (arom. C); 177.5 (olefin. C); 195.4 (CO). GC/EI-MS (70 eV): 204 (12, M^+), 186 (13), 161 (24), 120 (100), 91 (21). HR-EI-MS: 204.0784 ($C_{12}H_{12}O_3^+$; calc. 204.0781).

*2,3-Dihydro-2-(4-hydroxyphenyl)-6-methyl-4*H*-pyran-4-one* (**3m**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2m** (0.61 g, 5.0 mmol) in THF (15 ml): **3m** (0.70 g, 69%). Colorless crystalline solid. M.p. 160–161°. IR (KBr): 3151*w*, 3069*w*, 2974*w*, 2900*w*, 1630*m*, 1615*m*, 1576*m*, 1515*m*, 1463*m*, 1393*m*, 1251*m*, 1234*s*, 1224*m*, 1188*m*, 1066*m*, 1017*m*, 997*m*, 818*s*, 792*m*, 744*m*, 666*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.96 (*s*, Me); 2.37 (*dd*, *J* = 3.5, 16.9, 1 H, CH_2); 2.77 (*dd*, *J* = 14.1, 1 H, CH_2); 5.25 (*dd*, *J* = 3.5, 14.1, CH); 5.32 (*s*, 1 olefin. H); 6.68–6.73 (*m*, 2 arom. H); 7.15–7.20 (*m*, 2 arom. H); 9.52 (br. *s*, OH). ^{13}C-NMR (75 MHz, (D_6)DMSO): 21.1 (Me); 42.7 (CH_2); 82.3 (CH); 105.1 (olefin. CH); 116.3, 129.1 (arom. CH); 130.4, 159.2 (arom. C); 177.8 (olefin. C); 195.9 (CO). GC/EI-MS (70 eV): 204 (51, M^+), 186 (43), 171 (28), 161 (79), 147 (100), 119 (29), 91 (21), 77 (8). HR-EI-MS: 204.0782 (M^+, $C_{12}H_{12}O_3^+$; calc. 204.0781).

*2,3-Dihydro-6-methyl-2-(3-nitrophenyl)-4*H*-pyran-4-one* (**3n**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2n** (0.75 g, 5.0 mmol) in THF (15 ml): **3n** (0.66 g, 57%). Solid. M.p. 108–109°. IR (KBr): 3089*w*, 2915*w*, 1721*m*, 1611*m*, 1524*s*, 1479*m*, 1413*m*, 1346*s*, 1308*m*, 1231*m*, 1055*m*, 928*m*, 804*m*, 735*s*, 684*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.05 (*s*, Me); 2.59 (*dd*, *J* = 4.0, 16.6, 1 H, CH_2); 2.71 (*dd*, *J* = 13.6, 1 H, CH_2); 5.40 (*s*, CH); 5.44 (*dd*, *J* = 4.0, 13.6, CH); 7.55 (*t*, *J* = 7.9, 1 arom. H); 7.67 (*d*, *J* = 7.7, 1 arom. H); 8.18 (*d*, *J* = 8.1, 1 arom. H); 8.26 (*s*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (Me); 42.3 (CH_2); 79.3 (CH); 105.6 (olefin. CH); 121.1, 123.6, 129.9, 131.9 (arom. CH); 140.4, 148.5 (arom. C); 173.7 (olefin. C); 190.9 (CO). EI-MS (70 eV): 233 (6, M^+), 176 (11), 174 (6), 152 (25), 150 (22), 100 (58), 91 (8), 85 (100), 105 (21), 100 (58), 77 (29), 43 (68). HR-EI-MS: 233.0679 (M^+, $C_{12}H_{11}NO_4^+$; calc. 233.0683).

*2,3-Dihydro-6-methyl-2-(4-nitrophenyl)-4*H-*pyran-4-one* (**3o**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2o** (0.75 g, 5.0 mmol) in THF (15 ml): **3o** (0.70 g, 60%). Colorless crystalline solid. M.p. 128–130°. IR (KBr): 3074*w*, 2905*w*, 2847*w*, 1721*m*, 1651*s*, 1598*s*, 1512*s*, 1494*m*, 1436*m*, 1396*m*, 1342*s*, 1330*s*, 1296*m*, 1234*m*, 1184*m*, 1161*m*, 1104*m*, 1071*m*, 1030*m*, 1009*m*, 950*m*, 899*m*, 850*s*, 833*s*, 747*m*, 697*m*, 682*m*, 648*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.05 (*s*, Me); 2.58 (*dd*, *J* = 4.4, 16.7, 1 H, CH_2); 2.67 (*dd*, *J* = 13.1, 1 H, CH_2); 5.62 (*s*, 1 olefin. H); 5.45 (*dd*, *J* = 4.5, 13.1, CH); 7.51–7.54 (*m*, 2 arom. H); 8.20–8.23 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (Me); 42.3 (CH_2); 79.4 (CH); 105.7 (olefin. CH); 124.1, 126.7 (arom. CH); 145.2, 148.0 (arom. C); 173.7 (olefin. C); 190.9 (CO). GC/EI-MS (70 eV): 233 (10, M^+), 200 (11), 191 (23), 174 (15), 149 (100), 119 (41), 103 (32), 102 (14), 91 (28), 77 (42), 69 (10), 51 (11), 43 (19). HR-EI-MS: 233.0678 (M^+, $C_{12}H_{11}NO_4^+$; calc. 233.0683).

*2-(1,1′-Biphenyl-4-yl)-2,3-dihydro-6-methyl-4*H-*pyran-4-one* (**3p**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2p** (0.91 g, 5.0 mmol) in THF (15 ml): **3p** (1.13 g, 86%). Colorless crystalline solid. M.p. 76–77°. IR (KBr): 3056*w*, 3027*w*, 2990*w*, 2836*w*, 1712*w*, 1660*m*, 1601*s*, 1485*m*, 1432*m*, 1394*m*, 1331*m*, 1235*m*, 1000*s*, 951*m*, 899*m*, 872*m*, 763*m*, 730*m*, 701*s*, 657*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.01 (*s*, Me); 2.55 (*dd*, *J* = 3.0, 16.8, 1 H, CH_2); 2.78 (*dd*, *J* = 14.1, 1 H, CH_2); 5.36 (*dd*, *J* = 3.4, 14.1, CH); 5.45 (*s*, 1 olefin. H); 7.26–7.57 (*m*, 9 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.1 (Me); 42.2 (CH_2); 80.6 (CH); 105.2 (olefin. CH); 126.6, 127.1, 127.4, 127.6, 128.8 (arom. CH); 137.0, 140.4, 141.8 (arom. C); 174.3 (olefin. C); 192.3 (CO). EI-MS (70 eV): 264 (6, M^+), 222 (18), 221 (19), 180 (100), 165 (10), 152 (9). HR-EI-MS: 264.1144 (M^+, $C_{18}H_{16}O_2^+$; calc. 264.1145).

*2-(Furan-2-yl)-2,3-dihydro-6-methyl-4*H-*pyran-4-one* (**3q**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2q** (0.48 g, 5.0 mmol) in THF (15 ml): **3q** (0.77 g, 87%). Colorless crystalline solid. M.p. 57–58°. IR (KBr): 3076*w*, 2962*w*, 2917*w*, 1660*s*, 1603*s*, 1434*m*, 1390*s*, 1315*s*, 1235*s*, 1196*m*, 1167*m*, 1155*m*, 1034*m*, 992*s*, 944*m*, 850*m*, 810*m*, 701*s*, 630*m*, 595*m*. ^{1}H-NMR 300 MHz, $CDCl_3$): 1.96 (*s*, Me); 2.56 (*dd*, *J* = 3.8, 16.3, 1 H, CH_2); 2.92 (*dd*, *J* = 13.0, 1 H, CH_2); 5.36 (*dd*, *J* = 3.8, 13.0, CH); 5.33 (*s*, CH); 6.33 (*t*, *J* = 3.3, 1 furyl H); 6.37 (*d*, *J* = 3.2, 1 furyl H); 7.40 (*d*, *J* = 1.7, 1 furyl H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.0 (Me); 38.5 (CH_2); 73.3, 105.2 (CH); 109.4, 110.5, 143.4 (furyl CH); 150.3 (furyl C); 173.6 (olefin. C); 191.5 (CO). GC/EI-MS (70 eV): 178 (14, M^+), 160 (5), 94 (100), 66 (17), 65 (12), 39 (11). HR-EI-MS: 178.0623 (M^+, $C_{10}H_{10}O_3^+$; calc. 178.0625).

*2,3-Dihydro-6-methyl-2-(thiophen-2-yl)-4*H-*pyran-4-one* (**3r**). With a THF soln. of LDA (12.5 mmol), **1a** (0.50 g, 5.0 mmol), and **2r** (0.56 g, 5.0 mmol) in THF (15 ml): **3r** (0.80 g, 82%). Redish viscous oil. IR (KBr): 3139*w*, 3127*w*, 3078*w*, 2914*w*, 1657*m*, 1604*s*, 1503*m*, 1439*m*, 1387*s*, 1322*s*, 1183*s*, 1147*s*, 1000*s*, 900*m*, 864*m*, 841*m*, 820*m*, 741*s*, 683*m*, 597*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.07 (*s*, Me); 2.77 (*dd*, *J* = 4.0, 16.7, 1 H, CH_2); 2.93 (*dd*, *J* = 12.6, 1 H, CH_2); 5.44 (*s*, CH); 5.64 (*dd*, *J* = 4.0, 12.6, CH); 7.04 (*d*, *J* = 3.5, 1 thienyl H); 7.12 (*t*, *J* = 3.5, 1 thienyl H); 7.39 (*d*, *J* = 5.0, 1 thienyl H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1, (Me); 42.1 (CH_2); 76.2 (CH); 105.4 (CH); 126.1, 126.6, 126.9 (thienyl CH); 140.8 (thienyl C); 173.7 (olefin. C); 191.5 (CO). EI-MS (70 eV): 194 (7, M^+), 176 (16), 161 (10), 151 (12), 110 (100), 109 (13). HR-EI-MS: 194.0399 (M^+, $C_{10}H_{10}O_2S^+$; calc. 194.0396).

*2,3-Dihydro-2,6-diphenyl-4*H-*pyran-4-one* (**3s**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2a** (0.53 g, 5.0 mmol) in THF (15 ml): **3s** (0.97 g, 78%). Colorless crystalline solid. M.p. 93–94°. IR (KBr): 3292*w*, 3064*w*, 3029*w*, 2896*w*, 1710*s*, 1650*s*, 1592*m*, 1570*m*, 1490*m*, 1382*m*, 1315*m*, 1245*m*, 1178*m*, 1046*m*, 937*m*, 854*m*, 762*s*, 692*s*, 664*m*, 614*m*, 569*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.69 (*dd*, *J* = 3.4, 16.6, 1 H, CH_2); 3.02 (*dd*, *J* = 13.6, 1 H, CH_2); 5.75 (*dd*, *J* = 3.4, 13.6, CH); 6.21 (*s*, 1 olefin. H); 7.40–7.88 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 41.8 (CH_2); 80.1 (CH); 101.9 (olefin. CH); 126.4, 126.5, 128.54, 128.59, 128.8, 131.7 (arom. CH); 132.2, 138.5 (arom. C); 168.7 (olefin. C); 192.0 (CO). EI-MS (70 eV): 250 (6, M^+), 232 (11), 145 (25), 144 (17), 105 (40), 104 (100), 103 (18), 78 (16), 77 (23). HR-EI-MS: 250.0991 ($C_{17}H_{14}O_2^+$; calc. 250.0988). Anal. calc. for $C_{17}H_{14}O_2$: C 81.58, H 5.64; found: C 81.56, H 5.72.

*2-(2-Chlorophenyl)-2,3-dihydro-6-phenyl-4*H-*pyran-4-one* (**3t**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2b** (0.70 g, 5.0 mmol) in THF (15 ml): **3t** (0.88 g, 62%). Colorless crystalline solid. M.p. 96–98°. IR (KBr): 3282*w*, 3063*w*, 3035*w*, 2968*w*, 2916*w*, 1651*s*, 1595*s*, 1570*m*, 1450*m*, 1378*s*, 1327*s*, 1293*m*, 1233*m*, 1131*m*, 1071*m*, 993*m*, 941*m*, 856*m*, 805*m*, 772*m*, 754*s*, 685*s*, 669*s*, 616*m*, 567*m*, 540*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.68 (*dd*, *J* = 3.3, 16.7, 1 H, CH_2); 3.07 (*dd*, *J* = 14.0, 1 H, CH_2); 5.95 (*dd*, *J* = 3.2, 14.0, CH), 6.25 (*s*, 1 olefin. H); 7.47–7.89 (*m*, 9 arom. H). ^{13}C-NMR

(62 MHz, (D_6)DMSO): 40.2 (CH_2); 77.2 (CH); 101.9 (olefin. CH); 126.4, 127.7, 128.1, 128.8, 129.7, 130.4, 131.8 (arom. CH); 131.9, 132.0, 135.3 (arom. C); 168.8 (olefin. C); 191.6 (CO). GC/EI-MS (70 eV): 284 (9, M^+), 249 (22), 179 (10), 178 (10), 140 (34), 139 (10), 138 (100), 105 (48), 103 (35), 102 (11), 77 (29). HR-EI-MS: 284.0599 ($C_{17}H_{13}ClO_2^+$; calc. 284.0599). Anal. calc. $C_{17}H_{13}ClO_2$: C 71.71, H 4.60; found: C 71.74, H 4.62.

*2-(4-Chlorophenyl)-2,3-dihydro-6-phenyl-4*H*-pyran-4-one* (**3u**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2d** (0.70 g, 5.0 mmol) in THF (15 ml): **3u** (0.94 g, 82%). Colorless crystalline solid. M.p. 90–92°. IR (KBr): 3281*w*, 3089*w*, 3058*w*, 2965*w*, 2895*w*, 1651*s*, 1595*s*, 1568*s*, 1492*s*, 1449*m*, 1376*m*, 1328*m*, 1293*m*, 1215*m*, 1160*m*, 1089*m*, 993*m*, 855*m*, 835*m*, 804*m*, 768*s*, 681*s*, 664*s*, 615*m*, 566*m*, 540*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.72 (*dd*, *J* = 3.4, 16.6, 1 H, CH_2); 3.05 (*dd*, *J* = 13.6, 1 H, CH_2); 5.78 (*dd*, *J* = 3.4, 13.6, CH); 6.21 (*s*, 1 olefin. H); 7.35–7.56 (*m*, 5 arom. H); 7.62–7.65 (*m*, 2 arom. H); 7.84–7.88 (*m*, 2 arom. H). ^{13}C-NMR (62 MHz, (D_6)DMSO): 41.6 (CH_2); 79.3 (CH); 101.9 (olefin. CH); 126.4, 128.4, 128.5, 128.8, 131.7 (arom. CH); 132.1, 133.1, 137.5 (arom. C); 168.6 (olefin. C); 191.8 (CO). GC/EI-MS (70 eV): 284 (6, M^+), 179 (13), 178 (10), 140 (32), 139 (10), 138 (100), 105 (44), 103 (25), 102 (10), 77 (24). HR-ESI-TOF-MS: 284.0603 ($C_{17}H_{13}ClO_2^+$; 284.0599). Anal. calc. $C_{17}H_{13}ClO_2$: C 71.71, H 4.60; found: C 71.65, H 4.95.

*2-(3-Bromophenyl)-2,3-dihydro-6-phenyl-4*H*-pyran-4-one* (**3v**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2e** (0.92 g, 5.0 mmol) in THF (15 ml): **3v** (1.16 g, 72%). Colorless crystalline solid. M.p. 103–104°. IR (KBr): 3291*w*, 3057*w*, 2976*w*, 2910*w*, 1722*w*, 1651*s*, 1593*s*, 1567*m*, 1492*m*, 1448*m*, 1366*m*, 1292*m*, 1241*m*, 1174*m*, 1073*m*, 991*m*, 946*m*, 880*m*, 830*m*, 783*m*, 767*s*, 684*s*, 661*m*, 612*m*, 586*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.70 (*dd*, *J* = 3.4, 16.7, 1 H, CH_2); 3.04 (*dd*, *J* = 13.7, 1 H, CH_2); 5.80 (*dd*, *J* = 3.3, 13.7, CH); 6.21 (*s*, 1 olefin. H); 7.41–7.64 (*m*, 6 arom. H), 7.81–7.88 (*m*, 3 arom. H). ^{13}C-NMR (62 MHz, (D_6)DMSO): 41.2 (CH_2); 79.3 (CH); 102.0 (olefin. CH); 121.8 (arom. C); 125.6, 126.4, 128.8, 129.3, 130.8, 131.4, 131.7 (arom. CH); 132.1, 141.2 (arom. C); 168.6 (olefin. C); 191.8 (CO). GC/EI-MS (70 eV): 328 (5, M^+), 312 (13), 310 (12), 224 (12), 222 (11), 184 (85), 183 (10), 182 (88), 144 (14), 106 (10), 105 (100), 103 (46), 102 (21), 77 (55), 51 (13). HR-MS: 328.0089 (M^+, $C_{17}H_{13}{}^{79}BrO_2^+$; calc. 328.0093), 330.0073 (M^+, $C_{17}H_{13}{}^{81}BrO_2^+$; calc. 330.0073). Anal. calc. for $C_{17}H_{13}BrO_2$: C 62.03, H 3.98; found: C 62.01, H 3.97.

*2,3-Dihydro-2-(4-methylphenyl)-6-phenyl-4*H*-pyran-4-one* (**3w**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2g** (0.60 g, 5.0 mmol) in THF (15 ml): **3w** (1.04 g, 79%). Colorless crystalline solid. M.p. 72–73°. IR (KBr): 3065*w*, 2918*w*, 1713*w*, 1648*s*, 1590*s*, 1566*s*, 1489*m*, 1411*m*, 1377*s*, 1329*s*, 1248*m*, 1047*m*, 936, 828*m*, 809*s*, 771*s*, 687*s*, 558*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.2 (*s*, Me); 2.67 (*dd*, *J* = 4.0, 16.5, 1 H, CH_2); 2.88 (*dd*, *J* = 13.3, 1 H, CH_2); 5.57 (*dd*, *J* = 3.9, 13.4, CH); 6.04 (*s*, 1 olefin. H); 7.20–7.41 (*m*, 9 arom. H). ^{13}C-NMR (62 MHz, $CDCl_3$): 21.2 (Me); 42.9 (CH_2); 81.0 (CH); 102.3 (olefin. CH); 126.2, 126.6, 127.6, 129.7, 131.7 (arom. CH); 132.6, 135.2, 138.8 (arom. C); 170.4 (olefin. C); 193.2 (C). EI-MS (70 eV): 264 (4, M^+), 246 (13), 159 (34), 158 (13), 118 (100), 117 (51), 91 (16), 77 (15). HR-EI-MS: 264.1144 ($C_{18}H_{16}O_2^+$; calc. 264.1145).

*2,3-Dihydro-2-(4-methoxyphenyl)-6-phenyl-4*H*-pyran-4-one* (**3x**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2i** (0.68 g, 5.0 mmol) in THF (15 ml): **3x** (1.0 g, 72%). Colorless crystalline solid. M.p. 94–95°. IR (KBr): 3271*w*, 3082*w*, 3014*w*, 2933*w*, 2837*w*, 1712*w*, 1650*m*, 1588*m*, 1507*s*, 1494*m*, 1453*m*, 1375*m*, 1325*m*, 1288*m*, 1209*m*, 1158*m*, 1124*m*, 1029*s*, 954*m*, 835*m*, 733*s*, 695*s*, 674*m*, 617*m*, 573*m*, 527*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.61 (*dd*, *J* = 3.3, 16.7, 1 H, CH_2); 3.05 (*dd*, *J* = 13.7, 1 H, CH_2); 3.79 (*s*, MeO); 5.68 (*dd*, *J* = 3.3, 13.7, CH); 6.18 (*s*, 1 olefin. H); 7.00–7.03 (*m*, 2 arom. H), 7.46–7.55 (*m*, 5 arom. H); 7.81–7.85 (*m*, 2 arom. H). ^{13}C-NMR (62 MHz, (D_6)DMSO): 41.6 (CH_2); 55.1 (Me); 80.0 (CH); 101.7 (olefin. CH); 113.9, 126.3, 128.2, 128.7 (arom. CH); 130.3 (arom. C); 131.6 (arom. CH); 132.3, 159.4 (arom. C); 168.8 (olefin. C); 192.3 (CO). GC/EI-MS (70 eV): 280 (4, M^+), 262 (13) 175 (30), 134 (100), 119 (20), 105 (15), 91 (16), 77 (14). HR-EI-MS: 280.1097 ($C_{18}H_{16}O_3^+$; calc. 280.1094). Anal. calc. for $C_{18}H_{16}O_3$: C 77.12, H 5.75; found: C 77.27, H 5.70.

*2,3-Dihydro-2-(2,4-dimethoxyphenyl)-6-phenyl-4*H*-pyran-4-one* (**3y**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2k** (0.83 g, 5.0 mmol) in THF (15 ml): **3y** (0.96 g, 73%). Colorless crystalline solid. M.p. 101–102°. IR (KBr): 3271*w*, 3082*w*, 2966*w*, 2933*w*, 2837*w*, 1650*m*, 1613*m*, 1566*m*, 1453*m*, 1375*m*, 1288*m*, 1209*m*, 1158*m*, 1029*m*, 954*m*, 835*m*, 773*s*, 695*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.67 (*dd*, *J* = 4.0, 16.8, 1 H, CH_2); 2.78 (*dd*, *J* = 13.5, 1 H, CH_2); 3.77 (*s*, 2 Me); 5.80 (*dd*, *J* = 4.0, 13.5, CH);

6.03 (*s*, 1 olefin. H); 6.45 (*s*, 1 arom. H); 6.50 (*d*, *J* = 8.4, 1 arom. H); 7.34 – 7.42 (*m*, 4 arom. H); 7.71 (*d*, *J* = 8.1, 1 arom. H). ^{13}C-NMR (75 MHz, (D$_6$)DMSO): 41.9 (CH$_2$); 55.4 (2 MeO); 76.2 (CH); 98.5 (arom. CH); 102.1 (arom. CH); 104.4 (olefin. CH); 117.4, 124.7 (arom. C); 126.6, 127.4, 128.6, 131.5 (arom. CH); 155.5, 159.1 (arom. C); 168.9 (olefin. C); 192.0 (CO). EI-MS (70 eV): 310 (20, M^+), 205 (67), 165 (13.4), 164 (100), 149 (73), 121 (39.1), 105 (24.8), 91 (11), 77 (20). HR-MS: 311.1275 ([M + H]$^+$, $C_{19}H_{19}O_4^+$; calc. 311.1278).

*2,3-Dihydro-2-(4-hydroxyphenyl)-6-phenyl-4*H-*pyran-4-one* (**3z**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2m** (0.61 g, 5 mmol) in THF (15 ml): **3z** (0.97 g, 73%). Colorless crystalline solid. M.p. 181 – 182°. IR (KBr): 3075*m*, 2963*m*, 2818*m*, 2753*w*, 2691*w*, 2613*w*, 1614*m*, 1565*m*, 1490*m*, 1367*m*, 1298*w*, 1236*m*, 1171*m*, 1072*m*, 991*m*, 934*m*, 865*m*, 821*s*, 770*s*, 687*s*, 639*m*, 583*m*. ^{1}H-NMR (300 MHz, (D$_6$)DMSO): 2.57 (*dd*, *J* = 3.3, 16.6, 1 H, CH$_2$); 3.01 (*dd*, *J* = 13.8, 1 H, CH$_2$); 5.60 (*dd*, *J* = 3.3, 13.8, CH); 6.15 (*s*, 1 olefin. H); 6.81 – 6.84 (*m*, 2 arom. H); 7.38 – 7.51 (*m*, 5 arom. H); 7.79 – 7.82 (*m*, 2 arom. H); 9.61 (br. *s*, OH). ^{13}C-NMR (75 MHz, (D$_6$)DMSO): 41.6 (CH$_2$); 80.2 (CH); 101.7 (olefin. CH); 115.9 (arom. CH); 125.7 (arom. C); 126.3 (arom. CH); 127.0 (arom. C); 128.3 (arom. CH); 128.6 (arom. C); 128.7 (arom. CH); 130.2 (arom. C); 131.6 (arom. CH); 132.3, 157.7 (arom. C); 168.9 (olefin. C); 192.4 (CO). GC/EI-MS (70 eV): 266 (21, M^+), 248 (53), 161 (88), 160 (35), 147 (31), 121 (31), 120 (100), 119 (32), 106 (20), 105 (76), 91 (55), 84 (10), 77 (37), 69 (20), 51 (10), 44 (19), 43 (11). HR-EI-MS: 266.093631 (M^+, $C_{17}H_{14}O_3^+$; calc. 266.0938). Anal. calc. for $C_{17}H_{14}O_3$: C 77.12, H 5.75; found: C 75.93, H 6.40.

*2,3-Dihydro-2-(3-nitrophenyl)-6-phenyl-4*H-*pyran-4-one* (**3aa**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2n** (0.75 g, 5.0 mmol) in THF (15 ml): **3aa** (1.0 g, 68%). Colorless crystalline solid. M.p. 104 – 105°. IR (KBr): 3107*w*, 3088*w*, 3068*w*, 2930*w*, 2894*w*, 1613*s*, 1573*s*, 1519*m*, 1494*m*, 1458*m*, 1393*m*, 1345*s*, 1285*m*, 1237*m*, 1185*m*, 1147*m*, 1060*m*, 1019*m*, 898*m*, 874*m*, 818*m*, 764*s*, 684*s*, 616*m*, 541*m*. ^{1}H-NMR (300 MHz, (D$_6$)DMSO): 2.77 (*dd*, *J* = 3.4, 16.5, 1 H, CH$_2$); 3.07 (*dd*, *J* = 13.8, 1 H, CH$_2$); 5.93 (*dd*, *J* = 3.4, 13.7, CH); 6.24 (*s*, 1 olefin. H); 7.46 – 8.28 (*m*, 8 arom. H), 8.46 (*s*, 1 arom. H). ^{13}C-NMR (62 MHz, (D$_6$)DMSO): 41.7 (CH$_2$); 79.0 (CH); 102.1 (olefin. CH); 121.2, 123.3, 126.4, 128.8, 130.2, 131.7, 133.0 (arom. CH); 140.7, 147.8 (arom. C); 168.5 (olefin. C); 191.5 (CO). GC/EI-MS (70 eV): 295 (2, M^+), 162 (34), 161 (27), 151 (37), 150 (34), 147 (28), 120 (11), 105 (100), 104 (7), 78 (12), 77 (85), 76 (10), 69 (47), 51 (37), 50 (13), 43 (18). HR-EI-MS: 295.0840 ($C_{17}H_{13}NO_4^+$; calc. 295.0839).

*2,3-Dihydro-2-(4-nitrophenyl)-6-phenyl-4*H-*pyran-4-one* (**3ab**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2o** (0.75 g, 5.0 mmol) in THF (15 ml): **3ab** (0.98 g, 67%). Solid. M.p. 118 – 119°. IR (KBr): 3108*w*, 3089*w*, 3068*w*, 2931*w*, 2895*w*, 1611*s*, 1573*s*, 1519*m*, 1495*m*, 1457*m*, 1394*m*, 1346*s*, 1286*m*, 1238*m*, 1185*m*, 1147*m*, 1060*m*, 1019*m*, 898*m*, 874*m*, 818*m*, 764*s*, 684*s*, 616*m*, 541*m*. ^{1}H-NMR (300 MHz, (D$_6$)DMSO): 2.73 (*dd*, *J* = 4.2, 16.8, 1 H, CH$_2$); 2.82 (*dd*, *J* = 13.2, 1 H, CH$_2$); 5.64 (*dd*, *J* = 4.1, 13.2, CH); 6.09 (*s*, 1 olefin. H); 7.37 – 8.27 (*m*, 9 arom. H). ^{13}C-NMR (75 MHz, (D$_6$)DMSO): 42.9 (CH$_2$); 79.7 (CH); 102.6 (olefin. CH); 124.2, 126.6, 126.8, 128.8, 132.1 (arom. CH); 135.4, 145.2 (arom. C); 169.8 (olefin. C); 191.4 (CO). GC/EI-MS (70 eV): 295 (48, M^+), 294 (14), 176 (19), 173 (26), 144 (14), 115 (14), 106 (12), 105 (100), 102 (15), 77 (36), 69 (22), 51 (11). HR-EI-MS: 295.0842 ($C_{17}H_{13}NO_4^+$; calc. 295.0839).

*2-(1,1′-Biphenyl-4-yl)-2,3-dihydro-6-phenyl-4*H-*pyran-4-one* (**3ac**). With a THF soln. of LDA (12.5 mmol), **1b** (0.81 g, 5.0 mmol), and **2p** (0.91 g, 5.0 mmol) in THF (15 ml): **3ac** was isolated as a colorless crystalline solid (1.35 g, 83%). M.p. 110 – 111°. IR (KBr): 3368*w*, 3029*w*, 2964*w*, 1650*s*, 1593*s*, 1568*s*, 1487*m*, 1448*m*, 1378*m*, 1365*m*, 1229*m*, 1046*m*, 930*m*, 839*m*, 760*s*, 728*s*, 689*s*, 665*m*, 621*m*, 614*m*, 579*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 2.71 (*dd*, *J* = 3.8, 16.7, CH); 2.89 (*dd*, *J* = 13.2, 1 H, CH$_2$); 5.56 (*dd*, *J* = 3.7, 13.2, CH); 6.08 (*s*, 1 olefin. H); 7.26 – 7.50 (*m*, 14 arom. C). ^{13}C-NMR (75 MHz, CDCl$_3$): 42.9 (CH$_2$); 80.8 (CH); 102.3 (olefin. CH); 126.7, 127.1, 127.3, 127.6, 128.7, 128.8, 131.8, 132.5 (arom. CH); 127.0, 137.1, 140.4, 141.8 (arom. C); 170.3 (olefin. C); 192.8 (CO). GC/EI-MS (70 eV): 326 (5, M^+), 308 (9), 221 (27), 180 (100), 165 (10), 105 (29), 91 (2), 77 (9). HR-EI-MS: 326.1300 (M^+, $C_{23}H_{18}O_2^+$; calc. 326.1301). Anal. calc. for $C_{23}H_{18}O_2$ C 84.64, H 5.56; found: C 84.63, H 5.54.

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