3,4-Dihydroisocoumarins from α-Bromo-*o*-tolunitrile and Ketones or Aldehydes

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o-Cyanobenzyllithium (**3**) was efficiently generated by lithium–tellurium exchange of the corresponding benzylic telluride **2** prepared in situ from lithium butanetellurolate and α-bromo-*o*-tolunitrile (**1**). Reaction of ketones or aldehydes with **3** afforded substituted 2-hydroxyethylbenzonitriles **4** in high yields. The subsequent acid-catalyzed lactonization gave 3-substituted 3,4-dihydroisocoumarins **5** in good yields. All these successive reactions could be performed in the same reaction flask without isolation of intermediates.

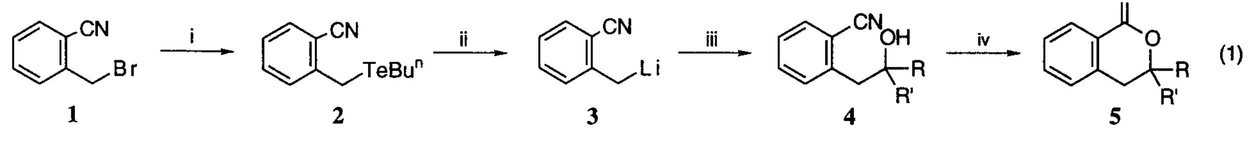
3,4-Dihydroisocoumarins **5** are an important class of lactones which occur in a number of plants.[1] Recently, Bestmann and co-workers have described that 3,4-dihydro-8-hydroxyisocoumarins are a new class of ant trail pheromones.[2] To date many efforts have been devoted to the preparation of **5**.[1-3] We have recently revealed that benzyl butyl tellurides react with butyllithium to give benzyllithiums via lithium–tellurium exchange.[4] As a synthetic application of this reaction, we report here a convenient one-pot method for the synthesis of 3,4-dihydroisocoumarins **5** from α-bromo-*o*-tolunitrile (**1**) and ketones or aldehydes (Scheme).

Since butyl *o*-cyanobenzyl telluride (**2**) produced from α-bromo-*o*-tolunitrile (**1**) and lithium butanetellurolate is somewhat unstable toward oxygen and/or light, it was used without isolation.[4] Although the telluride **2** has a cyano group which can act as an electrophilic reaction site, butyllithium exclusively attacks the tellurium atom of **2** to give *o*-cyanobenzyllithium (**3**) under the conditions examined. At − 70 °C, though, the generation of **3** was affected by competitive Wurtz-type coupling. Examination of the reaction conditions revealed that the reaction was very clean at − 105 °C and, was complete within 15 min. The generated **3** was trapped with aldehydes or ketones to afford the corresponding alcohols **4** in good yields.[5] This is in large contrast to a report that a direct exchange reaction of **1** with butyllithium under the same conditions gives the corresponding coupling product predominantly.[6]

Heating **4** in the presence of an appropriate acid gave 3,4-dihydroisocoumarins **5** in good yields. It was possible to obtain 3,4-dihydroisocoumarins **5** without isolation of **4** by successive acid treatment in the same reaction flask. The results of the syntheses of several 3,4-dihydroisocoumarins **5** from **1** performed by stepwise and one-pot procedures are summarized in the Table. Usually lactonization is completed in refluxing tetrahydrofuran but in the cases of alcohols having a vinyl or an aryl substituent at the 3-position (**5c, d, h**), higher temperatures (for example refluxing 1,2-dimethoxyethane) appears essential. Besides sulfuric acid, trifluoromethanesulfonic acid and *p*-toluenesulfonic acid were suitable for lactonization. As for **5d** a better yield was obtained with *p*-toluenesulfonic acid. When norbornanone was employed (run 17), product **5g** was obtained as a single stereoisomer although its configuration has not been determined yet. This method can be applied successfully to the synthesis of **5i** which has biological activities (diuretic and hypotensive-antihypertensive activities).[7]

The present method is a useful addition to hitherto known methods of 3,4-dihydroisocoumarin synthesis, since it provides a variety of 3,4-dihydroisocoumarins from readily available materials by easy operation.

All reactions were carried out under Ar atmosphere. Melting points were measured with a Yanagimoto micro melting apparatus (uncorrected). Boiling points represented refer to the temperature of Kugelrohr distillation apparatus. IR spectra were recorded on a Perkin-Elmer model 1610 FT-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL JNM270-GSX FT-NMR spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP2000 or -QP1000 instrument. HRMS and elemental analyses were performed by Analysis Center at Osaka University. All

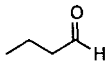
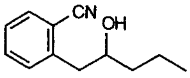
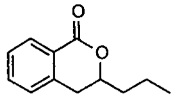
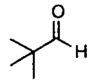
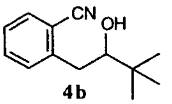
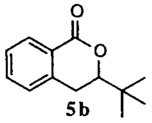
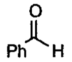
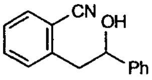
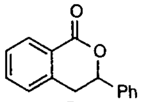
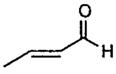
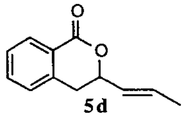
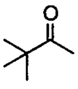
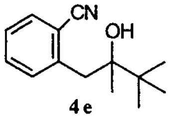
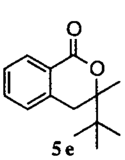
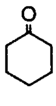
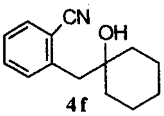
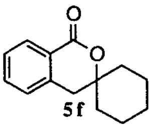
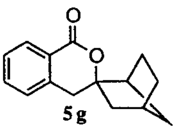
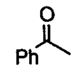
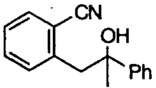
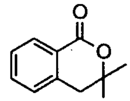
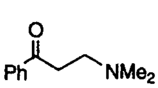
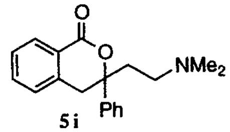


(i) *n*-BuTeLi (1 eq), THF, 0 °C, 30 min.
(ii) *n*-BuLi (1 eq), THF/Et_2O (1:1), −105 °C, 15 min.
(iii) RCOR' (1eq), −105 to 20 °C, 1 h.
(iv) H_2SO_4 or *p*-TsOH (2 eq)/H_2O (0.2 mL), 66 or 85 °C, 6 or 24 h.

4, 5	R	R'
a	*n*-Pr	H
b	*t*-Bu	H
c	Ph	H
d	(*E*)-CH_3-CH=CH_2	H
e	*t*-Bu	Me
f	–$(CH_2)_5$–	
g	2-norbornyl	
h	Ph	Me
i	Ph	$CH_2CH_2NMe_2$

Scheme

Table. Synthesis of *o*-Cyanophenethyl Alcohols and 3,4-Dihydroisocoumarins[a]

Run	RCOR′	Product **4**	Yield (%)[b]	Acid	Solvent	Product **5**	Yield (%)[b]
1		 **4a**	95	CF_3SO_3H	THF	 **5a**	93^{c}
2				H_2SO_4	THF		96, 100^{d}
3				H_2SO_4	DME		95^{c}
4				H_2SO_4	dioxane		90^{c}
5				*p*-TsOH	THF		$99^{c,e}$
6		 **4b**	88	H_2SO_4	THF	 **5b**	80^{c}
7				H_2SO_4	DME		93
8		 **4c**	89	H_2SO_4	THF	 **5c**	$10^{c,d}$
9				H_2SO_4	DME		63^{c}
10				H_2SO_4	DME		81
11				H_2SO_4	DME	 **5d**	$5^{c,d}$
12				*p*-TsOH	DME		47^{c}
13		 **4e**	85	H_2SO_4	THF	 **5e**	88^{e}
14				H_2SO_4	DME		88^{e}
15		 **4f**	91	H_2SO_4	DME	 **5f**	69^{d}
16				*p*-TsOH	DME		$85^{c,d}$
17				*p*-TsOH	DME	 **5g**	$69^{c,f}$
18		 **4h**	86	H_2SO_4	THF	 **5h**	$5^{c,d}$
19				H_2SO_4	DME		81^{e}
20				*p*-TsOH	THF	 **5i**	57^{c}

[a] Reaction conditions: **1** (2.1 mmol), BuTeLi (2.1 mmol), THF (5 mL), 0°C, 30 min; BuLi (2.1 mol), THF/Et_2O (1 : 1, 10 mL), −105°C, 15 min; RCOR′ (2.1 mmol), −105 to 20°C, 1 h; acid (4.2 mmol), H_2O (0.2 mL), reflux, 6 or 12 h.

[b] Isolated yield.

[c] Without isolation of the alcohols **4**.

[d] GC yield.

[e] Reaction time of acid catalyzed cyclization was 24 h.

[f] A single isomer, the relative configuration has not been determined yet.

new compounds **4a–c, e, f** and **5a, b, e–h** gave satisfactory microanalyses (C ± 0.28, H ± 0.25, N ± 0.16). Et_2O, THF and DME were purchased from Nacalai Tesque, Inc. and were purified by published methods.[8] BuLi (1.6 M hexane solution) was purchased from Kanto Chem. Co., Inc. and used after titration.[9]

Butyl *o*-Cyanobenzyl Telluride (2):

To a THF solution of BuTeLi [2.12 mmol, freshly prepared from BuLi (1.59 M, 1.33 mL, 2.12 mmol) and Te powder (0.272 g, 2.12 mmol) at 0°C in THF (5 mL)], was added 2-$NCC_6H_4CH_2Br$ (**1**; 0.415 g, 2.12 mmol) at the same temperature and the mixture was stirred for 0.5 h. This solution can be used for subsequent reactions without purification while the formation of **2** has been confirmed in the following way. The solvent was removed in vacuo, and hexane (5 mL) was added. Filtration of the precipitated LiBr using a sintered glass filter (G4 grade) followed by evaporation afforded an essentially pure **2**, whose NMR spectra were identical with those given in the literature.[4]

1-(2-Cyanophenyl)pentan-2-ol (4a); Typical Procedure:

To a solution of **2** (2.12 mmol) prepared as above, was added Et_2O (5 mL). The mixture was cooled to − 105 °C, and a hexane solution of BuLi (1.59 M, 1.33 mL, 2.12 mmol) was added. After stirring for 15 min PrCHO (0.152 g, 2.12 mmol) was added. The mixture was stirred for another 1 h allowing the temperature to rise to 20 °C. Water (10 mL) was added the products were extracted with Et_2O (20 mL × 3), the combined Et_2O layers were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography [40 mm × 80 mm] of the reddish orange residue on silica gel gave 0.357 g (89 %) of **4a** [eluent: Et_2O (80 mL)] along with 0.487 g (95 %) of Bu_2Te [eluent: hexane (150 mL)].

2-(2-Hydroxypentyl)benzonitrile (**4a**): light yellow oil; bp 200 °C/5 Torr.

IR (neat): $\nu = 3441$ (OH), 2225 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 0.94$ (t, $J = 7.1$ Hz, 3 H, CH_3), 1.35–1.65 (m, 4 H, $C\underline{H}_2C\underline{H}_2CH_3$), 1.87 (br, 1 H, OH), 2.86 (dd, $J = 13.8, 8.4$ Hz, 1 $H_{benzylic}$), 3.06 (dd, $J = 13.8, 4.0$ Hz, 1 $H_{benzylic}$), 3.83–3.96 (m, 1 H, CH), 7.32 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.39 (d, $J =$ 7.6 Hz, 1 H_{arom}), 7.53 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.62 (d, $J = 7.6$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 13.9$, 18.8, 39.4, 42.5, 71.8, 113.0, 118.2, 126.8, 130.8, 132.6, 132.8, 143.1.

MS (EI, relative intensity, %): $m/z = 189$ (M^+, 1.5), 172 (0.4), 156 (0.2), 146 (6), 128 (1), 117 (100), 90 (10), 55 (7), 43 (4).

2-(2-Hydroxy-3,3-dimethylbutyl)benzonitrile (**4b**): light yellow oil; bp 180 °C/5 Torr.

IR (neat): $\nu = 3499$ (OH), 2225 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 1.03$ (s, 9 H, CH_3), 1.04 (s, 1 H, OH), 2.68 (dd, $J = 13.7, 10.7$, 1 $H_{benzylic}$), 3.15 (dd, $J = 13.7, 1.7$ Hz, 1 $H_{benzylic}$), 3.48 (dd, $J = 10.7, 1.7$ Hz, 1 H, CH), 7.31 (d, $J = 7.6$ Hz, 1 H_{arom}), 7.41 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.53 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.62 (d, $J = 7.6$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 25.6$, 35.3, 37.0, 80.1, 112.9, 118.2, 126.7, 131.0, 132.5, 132.8, 144.4.

MS (EI, relative intensity, %): $m/z = 203$ (M^+, 1), 188 (3), 186 (0.8), 170 (2), 146 (23), 130 (10), 117 (100), 87 (19), 69 (9), 57 (19), 41 (9).

2-(2-Hydroxy-2-phenylethyl)benzonitrile (**4c**): light yellow oil; bp 220 °C/5 Torr.

IR (neat): $\nu = 3456$ (OH), 2225 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 2.28$ (br, 1 H, OH), 3.16 (dd, $J = 13.5, 8.0$ Hz, 1 $H_{benzylic}$), 3.24 (dd, $J = 13.5, 5.0$ Hz, 1 $H_{benzylic}$), 4.98 (dd, $J = 8.0, 5.0$ Hz, 1 H, CH), 7.24–7.35 (m, 7 H_{arom}), 7.47 (t, $J = 8.3$ Hz, 1 H_{arom}), 7.60 (d, $J = 8.3$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 44.4$, 74.4, 113.0, 118.2, 125.7, 127.0, 127.8, 128.5, 131.0, 132.5, 132.7, 142.3, 143.3.

MS (EI, relative intensity, %): $m/z = 223$ (M^+, 7), 205 (4), 190 (1), 178 (2), 165 (1), 146 (2), 117 (57), 107 (100), 79 (32).

2-(2-Hydroxy-2,3,3-trimethylbutyl)benzonitrile (**4e**): light yellow oil; bp 220 °C/5 Torr.

IR (neat): $\nu = 3442$ (OH), 2225 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 0.98$ (s, 3 H, CH_3), 1.05 (s, 9 H, CH_3), 1.19 (br, 1 H, OH), 2.70 (d, $J = 13.2$ Hz, 1 $H_{benzylic}$), 3.01 (d, $J = 13.2$ Hz, 1 $H_{benzylic}$), 7.37 (d, $J = 7.6$ Hz, 1 H_{arom}), 7.49 (t, $J =$ 7.6 Hz, 1 H_{arom}), 7.51 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.64 (d, $J = 7.6$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 21.9$, 25.7, 38.3, 41.0, 77.3, 111.1, 119.2, 127.7, 129.9, 132.8, 134.2, 143.3.

MS (EI, relative intensity, %): $m/z = 217$ (M^+, 1), 202 (2), 101 (100).

2-[(1-Hydroxycyclohexyl)methyl]benzonitrile (**4f**): light yellow oil; bp 170 °C/ 5 Torr.

IR (neat): $\nu = 3492$ (OH), 2226 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 1.23$ (br, 1 H, OH), 1.45–1.60 [m, 10 H, $(CH_2)_5$], 2.98 (d, $J = 13.9$ Hz, 1 $H_{benzylic}$), 3.41 (d, $J = 13.9$ Hz, 1 $H_{benzylic}$), 7.32 (d, $J = 7.6$ Hz, 1 H_{arom}), 7.42 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.51 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.62 (d, $J =$ 7.6 Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 21.8$, 25.5, 37.2 47.4, 71.9, 114.1, 119.1, 126.7, 131.7, 132.0, 132.6, 141.5.

MS (EI, relative intensity, %): $m/z = 215$ (M^+, 3), 198 (2), 197 (1), 186 (0.5), 172 (5), 144 (2), 135 (1), 130 (3), 117 (25), 99 (100), 81 (46), 55 (10), 43 (7).

2-(2-Hydroxy-2-phenylpropyl)benzonitrile (**4h**): light yellow oil; bp 200 °C/5 Torr.

IR (neat): $\nu = 3480$ (OH), 2226 cm^{-1} (CN).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 1.62$ (s, 3 H, CH_3), 1.92 (br, 1 H, OH), 3.24 (d, $J = 13.7$ Hz, 1 $H_{benzylic}$), 3.35 (d, $J = 13.7$ Hz, 1 $H_{benzylic}$), 7.14 (d, $J = 7.8$ Hz, 1 H_{arom}), 7.25–7.43 (m, 7 H_{arom}), 7.58 (d, $J = 7.8$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 29.2$, 48.4, 75.0, 114.4, 118.9, 124.9, 127.0, 127.1, 128.2, 131.7, 131.9, 132.0, 141.2, 146.8.

MS (EI, relative intensity, %): $m/z = 237$ (M^+, 1), 222 (4), 204 (1), 160 (2), 121 (100), 116 (10), 77 (10), 43 (85).

3,4-Dihydro-3-propylisocoumarin (5a); Typical Procedure (Table, run 2):

Water (0.2 mL) and conc. H_2SO_4 (0.22 mL, 4.2 mmol) were added to a solution of **4a** (0.21 g, 1.10 mmol) in THF (10 mL) and the mixture was refluxed for 6 h. After washing with aq sat. solution of $NaHCO_3$ (10 mL), the mixture was dried ($MgSO_4$) and concentrated. Bulb-to-bulb distillation (bath temp. 155 °C) of the resulting residue gave 0.200 g (96 %) of **5a** as a colorless oil.

3,4-Dihydro-3-propylisocoumarin (5a); Typical One-Pot Procedure (Table, run 1):

A pale yellow transparent solution of BuTeLi (2.12 mmol) was prepared by the addition of BuLi (1.59 M, 1.34 mL, 2.12 mmol) to a suspension of Te powder (0.272 g, 2.12 mmol) in THF (5 mL) at 0 °C. To this solution was added $2\text{-}NCC_6H_4CH_2Br$ (**1**; 0.415 g, 2.12 mmol) and the mixture was stirred for 30 min. After addition of Et_2O (5 mL), the mixture was cooled to − 105 °C and a hexane solution of BuLi (1.59 M, 1.34 mL, 2.12 mmol) was added using a syringe. After stirring for 15 min, butyraldehyde (0.152 mg, 2.11 mmol) was added at the same temperature. The mixture was warmed up to 20 °C with stirring for 1 h, then H_2SO_4 (36 N, 0.22 mL, 4.2 mmol), DME (20 mL) and water (0.2 mL) were added. The flask was dipped in an oil bath maintained at bath temperature of 110 °C for 6 h with stirring. After cooling to 20 °C, Et_2O (30 mL) was added. Filtration using a sintered glass filter (G4), washing with a sat. aq solution of $NaHCO_3$ (5 mL) and water (3 × 5 mL), followed by drying ($MgSO_4$) and removal of the solvent in vacuo afforded a crude product. Bulb-to-bulb distillation (bath temp. 155 °C) gave 0.383 g (95 %) of **5a** as a colorless oil.

3,4-Dihydro-3-propyl-1H-2-benzopyran-1-one (3,4-Dihydro-3-propylisocoumarin) (**5a**): colorless oil; bp 155 °C/5 Torr.

IR (neat): $\nu = 1724$ cm^{-1} (C=O).

^1H NMR ($CDCl_3$, 270 MHz): $\delta = 0.98$ (t, $J = 7.2$ Hz, 3 H, CH_3), 1.43–1.76 (m, 2 H, CH_2), 1.81–1.94 (m, 2 H, CH_2), 2.90 (dd, $J = 16.2, 4.5$ Hz, 1 $H_{benzylic}$), 2.97 (dd, $J = 16.2, 10.1$ Hz, 1 $H_{benzylic}$), 4.53 (dtd, $J = 10.1$, 7.2, 4.5 Hz, 1 H, CH), 7.24 (d, $J = 7.6$ Hz, 1 H_{arom}), 7.37 (t, $J = 7.6$ Hz, 1 H_{arom}), 7.52 (t, $J = 7.6$ Hz, 1 H_{arom}), 8.08 (d, $J = 7.6$ Hz, 1 H_{arom}).

^{13}C NMR ($CDCl_3$, 68 MHz): $\delta = 13.8$, 18.1, 33.1, 36.9, 78.4, 125.2, 127.3, 127.5, 130.1, 133.6, 139.2, 165.6.

MS (EI, relative intensity, %): $m/z = 190$ (M^+, 10), 147 (48), 119 (68), 118 (100), 91 (25), 90 (29), 89 (12).

3,4-Dihydro-3-(1,1-dimethylethyl)-1H-2-benzopyran-1-one (**5b**): colorless oil; bp 165 °C/5 Torr.

IR (neat): $\nu = 1720$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.08$ (s, 9 H, CH$_3$), 2.84 (dd, $J = 16.1, 2.9$ Hz, 1 H$_{\text{benzylic}}$), 3.00 (dd, $J = 16.1, 12.7$ Hz, 1 H$_{\text{benzylic}}$), 4.15 (dd, $J = 12.7, 2.9$ Hz, 1 H, CH), 7.26 (d, $J = 7.8$ Hz, 1 H$_{\text{arom}}$), 7.37 (t, $J = 7.8$ Hz, 1 H$_{\text{arom}}$), 7.52 (t, $J = 7.8$ Hz, 1 H$_{\text{arom}}$), 8.08 (d, $J = 7.8$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz): $\delta = 25.6, 28.4, 34.0, 86.1, 125.2, 127.4, 127.5, 130.1, 133.5, 139.7, 165.9$.

MS (EI, relative intensity, %): $m/z = 204$ (M$^+$, 8), 189 (3), 147 (94), 119 (100), 91 (31), 65 (6), 57 (9), 41 (9).

3,4-Dihydro-3-phenyl-1H-2-benzopyran-1-one (**5c**): colorless needles; mp 89–91 °C (Lit.[10] mp 90–91 °C).

IR (KBr): $\nu = 1728$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 3.11$ (dd, $J = 16.4, 3.3$ Hz, 1 H$_{\text{benzylic}}$), 3.31 (dd, $J = 16.4, 11.9$ Hz, 1 H$_{\text{benzylic}}$), 5.52 (dd, $J = 11.9, 3.3$ Hz, 1 H, CH), 7.27 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 7.36–7.48 (m, 6 H$_{\text{arom}}$), 7.55 (t, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 8.13 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz, only 12 peaks were found): $\delta = 35.5, 79.9, 125.1, 126.1, 127.3, 127.8, 128.6, 130.3, 133.9, 138.5, 138.9, 165.2$.

MS (EI, relative intensity, %): $m/z = 224$ (M$^+$, 10), 167 (19), 118 (100), 77 (65).

3,4-Dihydro-3-[(E)-prop-1-enyl]-1H-2-benzopyran-1-one (**5d**):[11] colorless oil; bp 180 °C/5 Torr.

IR (neat): $\nu = 1726$ (C=O), 1610 cm^{-1} (C=C).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.75$ (dd, $J = 6.7, 1.7$ Hz, 3 H, CH$_3$), 2.99 (dd, $J = 16.5, 4.4$, 1 H$_{\text{benzylic}}$), 3.08 (dd, $J = 16.5, 10.0$ Hz, 1 H$_{\text{benzylic}}$), 4.97 (dddd, $J = 10.0, 6.7, 4.4, 0.85$ Hz, 1 H, CH$_2$C$\underline{\text{H}}$), 5.67 (ddq, $J = 15.1, 6.7, 1.7$ Hz, 1 H, CH$_3$CH=C$\underline{\text{H}}$), 5.91 (dqd, $J = 15.1, 6.7, 0.85$ Hz, 1 H, CH$_3$C$\underline{\text{H}}$=CH), 7.25 (d, $J = 7.7$ Hz, 1 H$_{\text{arom}}$), 7.38 (t, $J = 7.7$ Hz, 1 H$_{\text{arom}}$), 7.54 (t, $J = 7.7$ Hz, 1 H$_{\text{arom}}$), 8.09 (d, $J = 7.7$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz, only 11 peaks were found): $\delta = 17.7, 33.6, 78.9, 125.2, 127.4, 128.2, 130.2, 130.7, 133.7, 138.9, 165.2$.

MS (EI, relative intensity, %): $m/z = 188$ (M$^+$, 9), 160 (13), 145 (5), 118 (100), 90 (33).

3,4-Dihydro-3-(1,1-dimethylethyl)-3-methyl-1H-2-benzopyran-1-one (**5e**): colorless crystals; mp 83.5–84.0 °C; bp 165–170 °C/5 Torr.

IR (KBr): $\nu = 1720$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.11$ (s, 9 H, CH$_3$), 1.28 (s, 3 H, CH$_3$), 2.72 (d, $J = 16.3$ Hz, 1 H$_{\text{benzylic}}$), 3.40 (d, $J = 16.3$ Hz, 1 H$_{\text{benzylic}}$), 7.23 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 7.36 (t, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 7.50 (t, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 8.09 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz): $\delta = 19.5, 25.1, 33.0, 37.7, 87.0, 124.8, 127.2, 128.3, 129.9, 133.6, 138.6, 165.1$.

MS (EI, relative intensity, %): $m/z = 218$ (M$^+$, 0.2), 203 (0.4), 161 (100), 147 (6), 133 (40), 118 (21), 105 (6), 90 (12), 57 (7), 43 (8).

3,4-Dihydro-3,3-pentamethylene-1H-2-benzopyran-1-one (**5f**): colorless oil; bp 175 °C/4 Torr.

IR (neat): $\nu = 1715$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.22$–1.88 (m, 10 H, CH$_2$, cyclohexyl), 3.02 (d, $J = 14.2$ Hz, 1 H, 1 H$_{\text{benzylic}}$), 3.39 (d, $J = 14.2$ Hz, 1 H$_{\text{benzylic}}$), 7.21 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 7.36 (t, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 7.52 (t, $J = 7.6$ Hz, 1 H$_{\text{arom}}$), 8.08 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz, only 12 peaks were found): $\delta = 21.6, 25.3, 36.1, 38.2, 81.8, 125.2, 127.3, 128.0, 129.9, 133.7, 137.7, 165.0$.

MS (EI, relative intensity, %): $m/z = 216$ (M$^+$, 19), 173 (16), 160 (23), 145 (6), 131 (2), 118 (100), 90 (18), 77 (2), 63 (2), 55 (2), 41 (5).

3,4-Dihydro-3(2-norbornylidene)-1H-2-benzopyran-1-one (**5g**): colorless needles; mp 110.5–111.0 °C. The relative configuration has not been determined yet.

IR (KBr): $\nu = 1719$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.34$–1.71 (m, 7 H$_{\text{norbornyl}}$), 2.58–2.62 (m, 1 H$_{\text{norbornyl}}$), 2.23–2.33 (m, 2 H$_{\text{norbornyl}}$), 3.00 (d, $J = 15.2$ Hz, 1 H$_{\text{benzylic}}$), 3.09 (d, $J = 15.2$ Hz, 1 H$_{\text{benzylic}}$), 7.23 (d, $J = 7.3$ Hz, 1 H$_{\text{arom}}$), 7.36 (t, $J = 7.3$ Hz, 1 H$_{\text{arom}}$), 7.52 (t, $J = 7.3$ Hz, 1 H$_{\text{arom}}$), 8.07 (d, $J = 7.3$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz): $\delta = 22.0, 27.9, 36.4, 38.4, 38.7, 44.6, 45.2, 88.4, 125.6, 127.4, 127.9, 130.0, 133.6, 138.7, 165.8$.

MS (EI, relative intensity, %): $m/z = 228$ (M$^+$, 76), 173 (13), 160 (100), 145 (5), 131 (5), 118 (69), 90 (26), 67 (10), 41 (10).

3,4-Dihydro-3-methyl-3-phenyl-1H-2-benzopyran-1-one (**5h**): colorless oil; bp 200–210 °C/3 Torr.

IR (neat): $\nu = 1716$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.74$ (s, 3 H, CH$_3$), 3.38 (d, $J = 16.2$ Hz, 1 H$_{\text{benzylic}}$), 3.52 (d, $J = 16.2$ Hz, 1 H$_{\text{benzylic}}$), 7.17–7.47 (m, 8 H$_{\text{arom}}$), 8.00 (d, $J = 7.6$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz, only 13 peaks were found): $\delta = 30.0, 39.0, 83.5, 124.6, 127.3, 127.4, 127.6, 128.4, 129.8, 133.8, 137.8, 143.5, 165.1$.

MS (EI, relative intensity, %): $m/z = 238$ (M$^+$, 6), 223 (6), 195 (7), 178 (2), 165 (1), 118 (100), 90 (20), 77 (7), 51 (2).

3,4-Dihydro-3-[2-(N,N-dimethylamino)ethyl]-3-phenyl-1H-2-benzopyran-1-one (**5i**): colorless crystals; mp 94.0–94.5 °C (Lit.[7] mp 90.0–95.5 °C), bp 210 °C/3 Torr.

IR (KBr): $\nu = 1723$ cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$, 270 MHz): $\delta = 1.99$ (t, $J = 7.4$ Hz, 2 H, Me$_2$NCH$_2$C$\underline{\text{H}}_2$), 2.10 (s, 6 H, CH$_3$N),2.27 (t, $J = 7.4$ Hz, 2 H, C$\underline{\text{H}}_2$NMe$_2$), 3.18 (d, $J = 13.6$ Hz, 1 H$_{\text{benzylic}}$), 3.43 (d, $J = 13.6$ Hz, 1 H$_{\text{benzylic}}$), 7.20–7.55 (m, 8 H$_{\text{arom}}$), 8.00 (d, $J = 7.7$ Hz, 1 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$, 68 MHz, only 15 peaks were found): $\delta = 38.7, 45.3, 55.9, 85.3, 125.7, 126.4, 127.4, 127.6, 127.9, 128.4, 129.9, 133.8, 137.7, 141.8, 165.0$.

MS (EI, relative intensity, %): $m/z = 295$ (M$^+$, 0.5), 237 (4), 218 (34), 147 (56), 118 (100), 90 (20), 77 (12).

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