Synthesis of Bicyclic Salicylates by [3+3] Cyclization of 1,3-Bis(Silyl Enol Ethers) with Cyclic 3-(Silyloxy)alk-2-en-1-ones

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Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

Bicyclic salicylates were prepared by [3+3] cyclization of 1,3-bis(silyl enol ethers) with cyclic 3-(silyloxy)alk-2-en-1-ones.

Key words: Arenes, Cyclizations, Silyl Enol Ethers

Introduction

1,3-Bis(silyl enol ethers) represent versatile synthetic building blocks [1]. In 1980, Chan and coworkers developed an elegant approach to salicylates based on formal [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 3-(silyloxy)alk-2-en-1-ones [2]. These cyclizations proceed by conjugated addition of the terminal carbon atom of the 1,3-bis(silyl enol ether) onto the 3-(silyloxy)alk-2-en-1-one and subsequent cyclization by intramolecular Mukaiyama aldol reaction. In recent years, we have reported the application of this method to the synthesis of a variety of functionalized arenes [3]. In their early work, Chan and coworkers also reported the synthesis of 5,6,7,8-tetrahydronaphthalenes by cyclization of 1,3-bis(silyl enol ethers) with 3-(silyloxy)alk-2-en-1-ones prepared from cyclohexanone and tetralone. Herein, we report a systematic study of the [3+3] cyclization of 1,3-bis(silyl enol ethers) with various cyclic 3-(silyloxy)alk-2-en-1-ones.

Results and Discussion

The reaction of cycloalkanones **1a** – **g** with ethyl formate and KO*t*Bu in THF afforded, according to a known procedure [5], the *Z*-2-(hydroxymethylidene)-cycloalkanones **2a** – **g** (Scheme 1, Table 1). Derivative **2b** was formed with very good regioselectivity. Treatment of an ether solution of **2a** – **g** with triethylamine (NEt_3) and chlorotrimethylsilane (Me_3SiCl) gave the cyclic 3-(silyloxy)alk-2-en-1-ones **3a** – **g** as mixtures of regioisomers. The regioselectivity could not be improved by employment of LDA instead of NEt_3. The $TiCl_4$-mediated cyclization of **3a** – **g** with 1,3-bis(silyl enol ether) **4a**, prepared from methyl acetoacetate, afforded the bicyclic salicylates **5a** – **g**. The synthesis of **5a** was previously reported by Chan and coworkers [2]. The formation of 5,6,7,8-tetrahydronaphthalenes **5a** – **d** proceeded with very good regioselectivity. Whereas the 3-(silyloxy)alk-2-en-1-ones **3a** and **3b** were regioisomerically pure, **3c** and **3d** remained as mixtures of regioisomers. For **5c** and **5d**, the regioselectivity of the cyclization can be explained, as previously discussed by Chan for the cyclization of **4a** with 1-phenyl-1-(trimethylsilyloxy)but-1-en-3-one [2], by a $TiCl_4$-mediated isomerization of the 3-(silyloxy)alk-2-en-1-one. In contrast, the cyclization of **4a** with regioisomerically pure **3e**, prepared from cycloheptanone, afforded an unseparable mixture of regioisomers **5e-A** and **5e-B**. This result can again be explained by $TiCl_4$-mediated isomerization of the 3-(silyloxy)alk-2-en-1-one. The cyclization of **4a** with **3f** and **3g**, prepared from cyclooctanone and cyclododecanone, afforded the corresponding 5,8- and 5,12-bicyclic products **5f** and **5g**, respectively, as mixtures of regioisomers. The regioisomeric ratios of the products again do not reflect the regioisomeric ratios of the respective 3-(silyloxy)alk-2-en-1-ones. Attempted cyclization of **3e** with the 1,3-bis(silyl enol ether) derived from acetylacetone was not successful.

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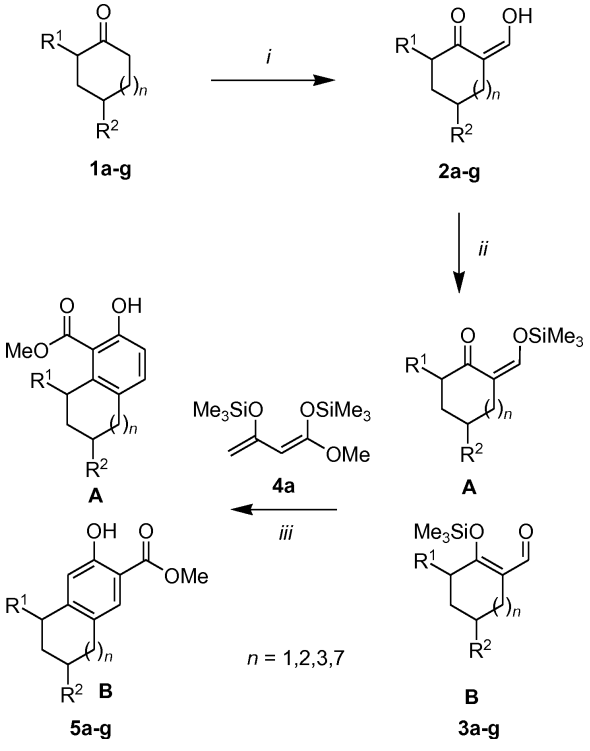
Table 1. Products and yields.

	n	R^1	R^2	% (**2**)[a]	% (**3**)[a]	A/B[b]	% (**5**)[a]	A/B[b]
a	1	H	H	75[c]	88[c]	> 98 : 2	75[c]	> 98 : 2
b	1	Me	H	66	89	9 : 2	22	> 98 : 2
c	1	H	Me	75	90	4 : 1	26	24 : 1
d	1	H	Ph	90	95	> 98 : 2	30	24 : 1
e	2	H	H	97	89	> 98 : 2	56	3 : 2
f	3	H	H	75	80	6 : 1	38	11 : 1
g	7	H	H	98	74	9 : 1	23	5 : 2

[a] Yields of isolated products; [b] by ^{1}H NMR; [c] ref. [2].

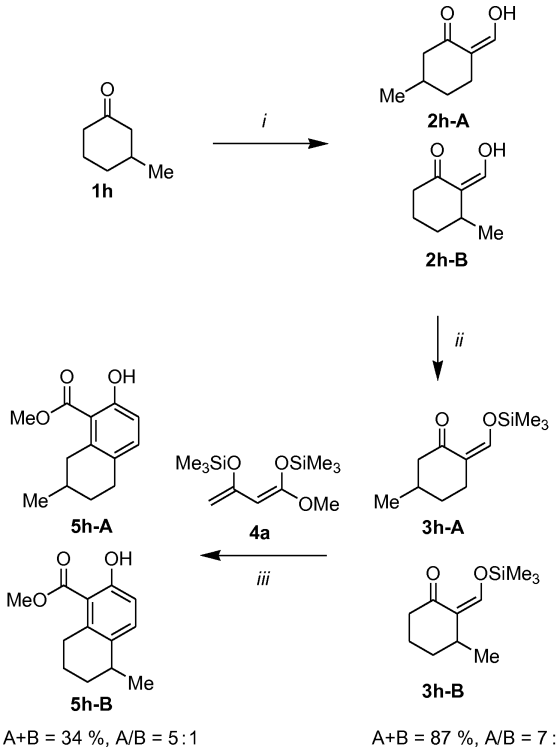
5	R	%[a]	A/B[b]
i	OMe	34	1 : 1
j	Me	12	> 98 : 2

Table 2. Products and yields.
[a] Yields of isolated products;
[b] by ^{1}H NMR.

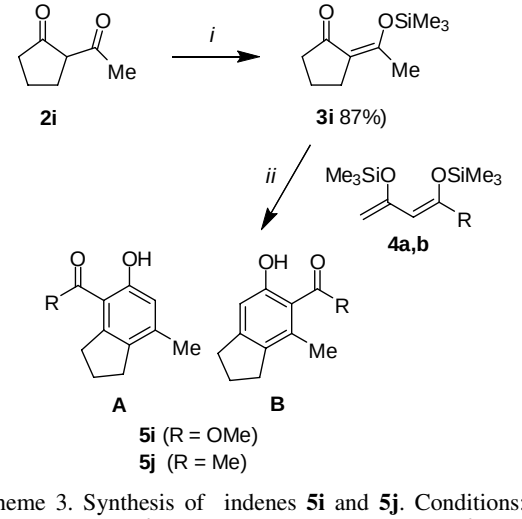


Scheme 1. Synthesis of **5a-g**. Conditions: *i*, KO*t*Bu, HCO_2Et, THF, 0 °C, 3 h, 20 °C, 48 h; *ii*, 1) NEt_3, Et_2O, 20 °C, 30 min, 2) Me_3SiCl, Et_2O, 20 °C, 48 h; *iii*, $TiCl_4$, −78 °C, 30 min, −78 → 20 °C, 14 h.

The formylation of 3-methylcyclohexanone (**1h**) afforded an unseparable regioisomeric mixture of 2-(hydroxymethylidene)-5-(methyl)cyclohexan-1-one (**2h-A**) and of 2-(hydroxymethylidene)-3-(methyl) cyclohexan-1-one (**2h-B**) which were transformed into 3-(silyloxy)alk-2-en-1-ones **3h-A** and **3h-B** (Scheme 2). The $TiCl_4$-mediated cyclization of the regioisomeric mixture of **3h-A** and **3h-B** (A/B = 7 : 2) with **4a** afforded **3h-A** and **3h-B**, respectively, as a mixture of regioisomers (A/B = 5 : 1).



Scheme 2. Synthesis of **5h**. Conditions: *i*, KO*t*Bu, HCO_2Et, THF, 0 °C, 3 h, 20 °C, 48 h; *ii*, 1) NEt_3, Et_2O, 20 °C, 30 min, 2) Me_3SiCl, Et_2O, 20 °C, 48 h; *iii*, $TiCl_4$, −78 °C, 30 min, −78 → 20 °C, 14 h.



Scheme 3. Synthesis of indenes **5i** and **5j**. Conditions: *i*, 1) NEt_3, Et_2O, 20 °C, 30 min, 2) Me_3SiCl, Et_2O, 20 °C, 48 h; *ii*, $TiCl_4$, −78 °C, 30 min, −78 → 20 °C, 14 h.

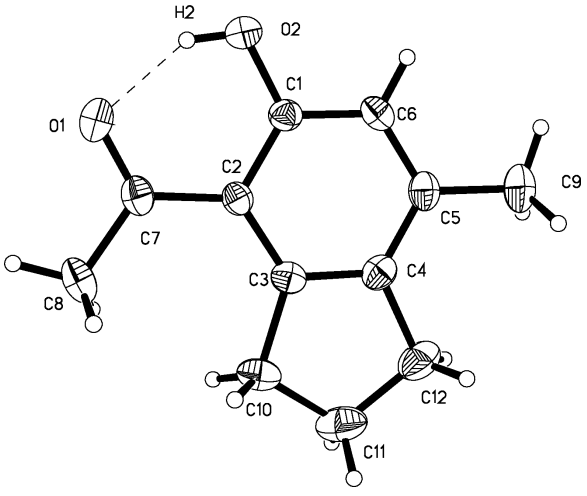


Fig. 1. Molecular structure of **5j** in the solid state (ORTEP; displacement ellipsoids at the 50 % probability level).

The reaction of **4a** with 2-(trimethylsilyloxymethylidene)cyclopentanone resulted in the formation of a complex mixture. The silylation of 2-acetylcyclopentan-1-one (**2i**) afforded the 3-(silyloxy)alk-2-en-1-one **3i**. The $TiCl_4$-mediated cyclization of **3i** with **4a** yielded the indene **5i** as a mixture of regioisomers (Scheme 3, Table 2). The cyclization of **3i** with 1,3-bis(silyl enol ether) **4b**, prepared from acetylacetone, gave the indene **5j**, albeit, in low yield. The structure of **5j** was independently confirmed by crystal structure analysis (Fig. 1) [4].

Experimental Section

General procedure for the synthesis of 2-formylcycloalkanones

To a THF solution of KO*t*Bu was added ethyl formate dropwise at 0 °C. After completion of the evolution of gas, a mixture of cycloalkanone, and ethyl formate was slowly added at 0 °C. After stirring of the mixture for 3 h at 0 °C, the temperature of the solution was allowed to slowly rise to 20 °C within 48 h. Subsequently, an aqueous solution of hydrochloric acid (50 mL, 1 M) and ethyl acetate (50 mL) were added. The organic and the aqueous layer were separated, and the latter was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with an aquoeus solution of NaOH (3 × 100 mL, 1 M). To the aqueous layer was added hydrochloric acid (200 mL, 10 %), and the solution was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent removed from the filtrate *in vacuo* to leave the product **2**.

*2-(Hydroxymethylidene)-6-methylcyclohexanone (**2b**)* [6]

Starting with 2-methylcyclohexanone (9.535 g, 85.00 mmol), a 1.0 M solution of KO*t*Bu (10.492 g, 93.50 mmol) in THF (93.5 mL) and ethyl formate (84.378 g, 1.24 mol), **2b** was isolated as an orange oil (7.881 g, 66 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (d, ^3J = 7.0 Hz, 3H, CH_3), 1.29 – 1.41 (m, 1H, CH_2), 1.46 – 1.61 (m, 1H, CH_2), 1.67 – 1.85 (m, 2H, CH_2), 2.27 – 2.33 (m, 2H, CH_2), 2.35 – 2.48 (m, 1H, CH), 8.56 (s, 1H, CH), 14.52 (br, s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4 (CH_3), 20.9, 23.7, 29.9 (CH_2), 35.8 (CH), 108.2 (COH), 187.0 (CH), 188.5 (C=O). – IR (neat, cm^{-1}): ν = 3411 (br, w), 3291 (br, w), 3222 (br, w), 2963 (s), 2935 (s), 2862 (s), 1711 (s), 1637 (s), 1587 (s), 1452 (s). – MS (EI, 70 eV): *m/z* (%) = 140 (100) $[M]^+$, 112 (31), 97 (93), 85 (33), 79 (35). – HRMS (EI, 70 eV): *m/z* = 140.0830 (calcd. 140.0832 for $C_8H_{12}O_2$, $[M]^+$).

*2-(Hydroxymethylidene)-4-methylcyclohexanone (**2c**)* [7]

Starting with 4-methylcyclohexanone (10.085 g, 90.00 mmol), a 1.0 M solution of KO*t*Bu (11.109 g, 99.0 mmol) in THF (99 mL) and ethyl formate (89.338 g, 1.21 mol), **2c** was isolated as an orange oil (9.461 g, 75 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98 (d, ^3J = 6.0 Hz, 3H, CH_3), 1.22 – 1.35 (m, 1H, CH_2), 1.58 – 1.75 (m, 2H, CH_2), 1.85 – 1.96 (m, 1H, CH_2), 2.30 – 2.41 (m, 3H, CH, CH_2), 8.56 (s, 1H, CH), 14.33 (br, s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.0 (CH_3), 28.8 (CH), 29.1, 30.9, 31.4 (CH_2), 108.3 (COH), 184.8 (C=O), 187.2 (*C*=CH). – IR (neat, cm^{-1}): ν = 3389 (br, w), 3365 (br, w), 3261 (br, w), 3192 (br, w), 2954 (s), 2929 (s), 2871 (s), 1711 (s), 1644 (s), 1590 (s), 1458 (s), 1415 (s). – MS (EI, 70 eV): *m/z* (%) = 140 (100) $[M]^+$, 125 (42), 111 (28), 98 (77), 70 (80). – HRMS (EI, 70 eV): *m/z* = 140.083545 (calcd. 140.083181 for $C_8H_{12}O_2$, $[M]^+$).

*2-Hydroxymethylidene-4-phenylcyclohexanone (**2d**)* [8]

Starting with 4-phenylcyclohexanone (9.932 g, 57.0 mmol), a 1.0 M solution of KO*t*Bu (7.036 g, 63.00 mmol) in THF (63 mL) and ethyl formate (56.582 g, 764.0 mmol), **2d** was isolated as an orange solid (10.367 g, 90 %). M. p. 58 – 60 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.79 – 2.10 (m, 2H, CH_2), 2.43 – 2.68 (m, 4H, CH_2), 2.78 – 2.92 (m, 1H, CH), 7.21 – 7.39 (m, 5H, CH), 8.69 (s, 1H, C=CH), 14.44 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.2, 31.2, 31.5 (CH_2), 40.2 (CH), 108.5 (C), 126.6, 126.7, 128.6 (CH), 145.0 (C), 184.1 (COH), 187.7 (C=O). – IR (Nujol, cm^{-1}): ν = 1634 (m), 1596 (m), 1576 (m), 1491 (w), 1304 (m), 1249 (w), 1174 (m), 886 (w), 769 (w), 731 (w). – MS (70 eV): *m/z* (%) = 202 (38) $[M]^+$, 174 (3), 104 (100), 81 (13), 78 (13). – Anal. for $C_{13}H_{14}O_2$ (202.10): calcd. C 77.20, H 6.98; found C 77.28, H 7.06.

*2-(Hydroxymethylidene)cycloheptanone (**2e**)* [5]

Starting with cycloheptanone (10.095 g, 90.0 mmol), a 1.0 M solution of KO*t*Bu (11.109 g, 99.0 mmol) in THF (99 mL) and ethyl formate (89.338 g, 1.21 mol), **2e** was isolated as an orange oil (11.272 g, 97 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.47 – 1.73 (m, 6H, CH_2), 2.13 – 2.21 (m, 2H, CH_2), 2.41 – 2.49 (m, 2H, CH_2), 7.64 (d, ^3J = 8.6 Hz, 1H, CH), 14.69 (d, ^3J = 8.6 Hz, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.5, 28.5, 29.7, 31.6, 41.9 (CH_2), 114.5 (C), 170.7 (COH), 204.2 (C=O). – IR (Nujol, cm^{-1}): ν = 3428 (br, w), 2160 (br, w), 3087 (w), 2926 (s), 2854 (s), 1733 (m), 1708 (m), 1634 (s), 1584 (s), 1451 (s), 1434 (s), 1407 (s). – MS (EI, 70 eV): *m/z* (%) = 140 (100) $[M]^+$, 125 (24), 111 (51), 83 (41), 79 (29). – HRMS (EI, 70 eV): *m/z* = 140.08300 (calcd. 140.08318 for $C_8H_{12}O_2$, $[M]^+$).

*2-(Hydroxymethylidene)cyclooctanone (**2f**)* [9]

Starting with cyclooctanone (10.096 g, 80.0 mmol), a 1.0 M solution of KO*t*Bu (9.875 g, 88.00 mmol) in THF (88 mL) and ethyl formate (79.411 g, 1.07 mol), **2f** was isolated as a yellow oil (9.251 g, 75 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 – 1.52 (m, 6H, CH_2), 1.62 – 1.70 (m, 2H, CH_2), 2.21 – 2.26 (m, 2H, CH_2), 2.36 – 2.41 (m, 2H, CH_2), 8.09 (s, 1H, CH), 14.90 (br, s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3, 25.6, 25.9, 28.1, 32.3, 35.1 (CH_2), 112.6 (C), 180.0 (COH), 195.7 (C=O). – IR (neat, cm^{-1}): ν = 3428 (br, w), 3307.5 (w), 3299 (w), 2930 (s), 2858 (s), 1704 (s), 1629 (s), 1465 (s), 1448 (s), 1400 (m). – MS (EI, 70 eV): *m/z* (%) = 154 (74) $[M]^+$, 126 (34), 111 (68), 98 (47), 86 (100). – HRMS (EI, 70 eV): *m/z* = 154.09903 (calcd. 154.09883 for $C_9H_{14}O_2$, $[M]^+$).

*2-(Hydroxymethylidene)cyclododecanone (**2g**)* [10]

Starting with cyclododecanone (10.938 g, 60.00 mmol), a 1.0 M solution of KO*t*Bu (7.416 g, 132.0 mmol) in THF (60 mL) and ethyl formate (59.561 g, 804.0 mmol), **2g** was isolated as a yellow solid (12.698 g, 98 %), m. p. 59 – 60 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 – 1.45 (m, 14H, CH_2), 1.47 – 1.58 (m, 2H, CH_2), 1.72 – 1.80 (m, 2H, CH_2), 2.22 – 2.36 (m, 2H, CH_2), 8.56 (s, 1H, CH), 15.23 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.6, 23.6, 24.0, 24.2, 24.3, 24.4, 25.0, 26.0, 29.7, 31.3 (CH_2), 64.0 (C), 187.1 (COH), 198.9 (C=O). – IR (Nujol, cm^{-1}): ν = 2615 (br, m), 2574 (br, m), 2429 (w), 1711 (w), 1656 (m), 1566 (s), 1318 (m), 1285 (w), 1240 (s), 1220 (s). – MS (EI, 70 eV): *m/z* (%) = 210 (30) $[M]^+$, 182 (21), 149 (24), 125 (36), 111 (67), 98 (100). – HRMS (EI, 70 eV): *m/z* = 210.1612 (calcd. 210.1614 for $C_{13}H_{22}O_2$, $[M]^+$).

*2-(Hydroxymethylidene)-5-methylcyclohexanone (**2h-A**) and 2-(hydroxymethylidene)-3-methylcyclohexanone (**2h-B**)* [11]

Starting with 3-methylcyclohexanone (10.095 g, 90.00 mmol), a 1.0 M solution of KO*t*Bu (11.109 g, 99.00 mmol) in THF (99 mL) and ethyl formate (89.338 g, 1206.00 mmol), **2h-A** and **2h-B** were isolated as mixture of regioisomers (A/B = 9 : 1) as an orange oil (9.150 g, 73 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.99 (d, ^3J = 6.5 Hz, 3H, CH_3), 1.16 – 1.29 (m, 1H, CH_2), 1.66 – 1.86 (m, 2H, CH_2), 1.91 – 2.03 (m, 1H, CH_2), 2.23 – 2.46 (m, 3H, CH_2), 8.65 (s, 1H, C=CH), 14.35 (br, s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 22.5 (CH_2), 27.7 (CH), 30.7, 39.3 (CH_2), 108.2 (C), 184.3 (COH), 187.8 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11 (d, ^3J = 7.0, 3H, CH_3), 1.16 – 1.29 (m, 1H, CH_2), 1.66 – 1.86 (m, 2H, CH_2), 1.91 – 2.03 (m, 1H, CH_2), 2.23 – 2.46 (m, 3H, CH_2), 8.71 (s, 1H, C=CH), 14.65 (br, s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (CH_3), 22.3 (CH_2), 30.4 (C), 31.5, 41.0 (CH_2), 114.2 (C), 185.5 (COH), 187.7 (C=O). – IR (Nujol, cm^{-1}): ν = 3400 (br, w), 3272 (br, w), 3235 (br, w), 3209 (br, w), 2955 (s), 2929 (s), 2871 (s), 1712 (s), 1640 (s), 1411 (m). – MS (EI, 70 eV): *m/z* (%) = 140 (90) $[M]^+$, 125 (28), 111 (39), 97 (38), 70 (100). – HRMS (EI, 70 eV): *m/z* = 140.083055 (calcd. 140.083181 for $C_8H_{12}O_2$, $[M]^+$).

*General procedure for the synthesis of 3-(silyloxy)alk-2-en-1-ones **3***

Triethylamine was added to a diethyl ether solution of the 2-formylcycloalkanone **2**. After stirring for 30 min at 20 °C, chlorotrimethylsilane was added. After stirring the mixture for 2 d at 20 °C, it was filtered under argon atmosphere, the filter cake was washed with diethyl ether (2×), and the solvent was removed *in vacuo* (bath temperature 40 °C). The products were used without further purification. Due to their unstable nature, compounds **3e** – **g** were used directly after their preparation.

*6-Methyl-2-(trimethylsilyloxymethylidene)cyclohexanone (**3b-A**) and 2-formyl-6-methyl-1-(trimethylsilyloxy)cyclohexene (**3b-B**)*

Starting with **2b** (4.000 g, 28.5 mmol), triethylamine (3.461 g, 34.20 mmol) and chlorotrimethylsilane (4.025 g, 37.10 mmol) in diethyl ether (90 mL), **3b** was isolated as a mixture of regioisomers (A/B = 9 : 2) as a yellow oil (5.349 g, 89 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.19 (s, 9H, CH_3), 1.07 (d, ^3J = 7.1 Hz, 3H, CH_3), 1.30 – 1.61 (m, 2H, CH_2), 1.71 – 1.97 (m, 2H, CH_2), 2.13 – 2.30 (m, 2H, CH_2), 2.51 – 2.63 (m, 1H, CH), 7.34 (dd, ^4J = 2.0 Hz, ^4J = 2.0 Hz, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.9 ($SiMe_3$), 16.1 (CH_3), 21.3, 23.1, 31.3 (CH_2), 42.9 (CH), 119.0 (C), 148.9 (C=CH), 203.0 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.19 (s, 9H, CH_3), 1.14 (d, ^3J = 7.1 Hz,

3H, CH_3), 1.30 – 1.61 (m, 3H, CH_2, CH), 1.71 – 1.97 (m, 2H, CH_2), 2.13 – 2.30 (m, 2H, CH_2), 8.53 (s, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.7 ($SiMe_3$), 17.0 (CH_3), 20.6, 23.3, 29.7 (CH_2), 45.4 (CH), 107.9, 173.3 (C), 190.1 (C=O).

*4-Methyl-2-(trimethylsilyloxymethylidene)cyclohexanone (**3c-A**) and 2-formyl-4-methyl-1-(trimethylsilyloxy)cyclohexene (**3c-B**)*

Starting with **2c** (4.000 g, 28.50 mmol), triethylamine (3.461 g, 34.20 mmol) and chlorotrimethylsilane (4.025 g, 37.10 mmol) in diethyl ether (90 mL), **3c** was isolated as a mixture of regioisomers (A/B = 4 : 1) as a yellow oil (5.465 g, 90 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.22 (s, 9H, CH_3), 1.00 (d, ^3J = 6.0 Hz, 3H, CH_3), 1.53 – 1.87 (m, 4H, CH_2), 2.18 – 2.46 (m, 2H, CH_2), 2.64 – 2.71 (m, 1H, CH), 7.40 (dd, ^4J = 1.5 Hz ^4J = 2.4 Hz, 1H, C=CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.5 ($SiMe_3$), 21.6 (CH_3), 29.0 (CH), 31.1, 31.4, 38.9 (CH_2), 118.9 (C), 150.0 (C=CH), 201.1 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.23 (s, 9H, CH_3), 0.95 (d, ^3J = 6.3 Hz, 3H, CH_3), 1.16 – 1.48 (m, 4H, CH_2), 1.53 – 1.87 (m, 1H, CH), 2.18 – 2.46 (m, 2H, CH_2), 10.02 (s, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.4 ($SiMe_3$), 21.0 (CH_3), 28.3 (CH), 27.7, 28.9, 30.2 (CH_2), 104.7 (C), 168.5 (CH), 190.3 (C=O).

*4-Phenyl-2-(trimethylsilyloxymethylidene)cyclohexanone (**3d-A**) and 2-formyl-4-phenyl-1-(trimethylsilyloxy)cyclohexene (**3d-B**)*

Starting with **2d** (3.000 g, 14.9 mmol), triethylamine (1.801 g, 17.80 mmol) and chlorotrimethylsilane (2.097 g, 19.3 mmol) in diethyl ether (90 mL), **3d** was isolated as a mixture of regioisomers (A/B > 95 : 5) as a yellow oil (5.233 g, 87 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.24 (s, 9H, CH_3), 1.96 – 2.15 (m, 2H, CH_2), 2.30 – 2.63 (m, 3H, CH, CH_2), 2.83 – 3.11 (m, 2H, CH_2), 7.22 – 7.36 (m, 5H, Ph), 7.52 (dd, ^4J = 1.5 Hz, ^4J = 1.6 Hz, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.4 ($SiMe_3$), 30.1, 31.2, 39.3 (CH_2), 40.4 (CH), 118.8 (C), 126.4, 126.7, 128.5 (CH_{Ph}), 145.8 (C), 150.8 (CH), 200.4 (C=O). – **B**: ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.4 ($SiMe_3$), 31.5, 31.9, 38.8 (CH_2), 40.2 (CH), 118.8 (C), 126.3, 126.7, 128.4 (CH), 148.2 (C), 187.7 (C), 190.2 (C=O).

*5-Methyl-2-(trimethylsilyloxymethylidene)cyclohexanone (**3h-A**) and 2-formyl-3-methyl-1-(trimethylsilyloxy)cyclohexene (**3h-B**)*

Starting with **2h** (4.000 g, 28.5 mmol), triethylamine (3.461 g, 34.2 mmol) and chlorotrimethylsilane (4.025 g, 37.1 mmol) in diethyl ether (90 mL), **3h** was isolated as a mixture of regioisomers (A/B = 7 : 2) as a yellow oil (5.233 g, 87 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 9H, CH_3), 0.95 (d, ^3J = 7.1 Hz, 3H, CH_3), 1.18 – 1.49 (m, 2H, CH_2), 1.55 – 1.85 (m, 2H, CH_2), 2.00 – 2.18 (m, 2H, CH_2), 2.39 – 2.51 (m, 1H, CH), 7.22 (dd, ^4J = 2.0 Hz, ^4J = 2.0 Hz, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.6 ($SiMe_3$), 21.6 (CH_3), 29.6, 30.8, 39.8 (CH_2), 47.9 (CH), 118.7 (C), 149.8 (CH), 201.0 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.09 (s, 9H, CH_3), 1.01 (d, ^3J = 7.1 Hz, 3H, CH_3), 1.18 – 1.49 (m, 3H, CH_2, CH), 1.55 – 1.85 (m, 2H, CH_2), 2.00 – 2.18 (m, 2H, CH_2), 8.40 (s, 1H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.7 ($SiMe_3$), 22.0 (CH_3), 27.4, 28.6, 39.6 (CH_2), 45.7 (CH), 112.1, 168.0 (C), 190.1 (C=O).

*General procedure for the synthesis of bicyclic salicylates **5***

To a CH_2Cl_2 solution of **3** and of 1,3-bis(silyl enol ether) **4a**,**b** was slowly added $TiCl_4$ at −78 °C. After stirring the solution for 30 min at −78 °C, the temperature of the solution was allowed to rise to 20 °C within 14 h. To the solution were added hydrochloric acid (20 mL, 10 %) and CH_2Cl_2 (30 mL). The organic and the aqueous layer were separated, and the latter was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (silica gel, EtOAc/heptane = 1 : 50).

*Methyl-7-hydroxy-1-methyl-1,2,3,4-tetrahydronaphthalene-8-carboxylate (**5b**)*

Starting with **3b** (1.000 g, 4.70 mmol), **4a** (1.228 g, 4.70 mmol), CH_2Cl_2 (6.0 mL), and $TiCl_4$ (0.894 g, 4.70 mmol), **5b** was isolated as a yellow oil (0.223 g, 22 %). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12 (d, ^3J = 7.0 Hz, 3H, CH_3), 1.60 – 1.88 (m, 4H, CH_2), 2.67 – 2.73 (m, 2H, CH_2), 3.79 – 3.85 (m, 1H, CH), 3.95 (s, 3H, OCH_3), 6.76 (d, ^3J = 8.5 Hz, 1H, Ar), 7.09 (d, ^3J = 8.5 Hz, 1H, Ar), 10.50 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.8 (CH_2), 23.5 (CH_3), 29.5 (CH_2), 30.1 (CH), 30.4 (CH_2), 52.2 (OCH_3), 112.2 (C), 115.3 (CH_{Ar}), 128.1 (C), 136.0 (CH_{Ar}), 144.3 (C), 144.3 (COH), 160.0 C=O). – IR (neat, cm^{-1}): ν = 3396 (br, w), 3390 (br, w), 2950 (s), 2934 (s), 2870 (m), 1732 (s), 1660 (s), 1595 (s), 1465 (s), 1439 (s). – MS (EI, 70 eV): *m/z* (%) = 220 (22) $[M]^+$, 188 (100), 173 (19), 145 (21), 115 (18). – HRMS (EI, 70 eV): *m/z* = 220.10995 (calcd. 220.10940 for $C_{13}H_{16}O_3$, $[M]^+$).

*Methyl 6-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalene-5-carboxylate (**5c-A**) and methyl 6-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalene-7-carboxylate (**5c-B**)*

Starting with **3c** (1.000 g, 4.70 mmol), **4a** (1.228 g, 4.70 mmol), CH_2Cl_2 (6.0 mL), and $TiCl_4$ (0.894 g, 4.70 mmol), **5c** was isolated as a mixture of regioisomers (A/B = 24 : 1) as a yellow solid (0.285 g, 28 %). M. p. 44 – 45 °C. – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 (d, ^3J = 6.4 Hz, 3H, CH_3), 1.21 – 1.36 (m, 1H, CH_2), 1.66 – 1.94 (m, 2H, CH_2), 2.24 – 2.41 (m, 1H, CH), 2.68 – 2.82 (m, 1H, CH_2), 2.84 – 3.02 (m, 1H, CH_2), 3.03 – 3.17 (m, 1H, CH_2), 3.94 (s,

3H, OCH_3), 6.77 (d, ^3J = 8.6 Hz, 1H, Ar), 7.10 (d, ^3J = 8.6 Hz, 1H, Ar), 10.90 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6 (CH-*C*H_3), 28.2 (*C*H-CH_3), 29.5, 31.6, 38.5 (CH_2), 52.0 (OCH_3), 98.7 (C), 115.2 (CH_{Ar}), 128.7 (C), 136.0 (CH_{Ar}), 138.8 (C), 160.5 (COH), 172.3 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 5.5 Hz, 3H, CH_3), 1.21 – 1.36 (m, 1H, CH_2), 1.66 – 1.94 (m, 2H, CH_2), 2.24 – 2.41 (m, 1H, CH), 2.68 – 2.82 (m, 1H, CH_2), 2.84 – 3.02 (m, 1H, CH_2), 3.03 – 3.17 (m, 1H, CH_2), 3.19 (s, 3H, OCH_3), 6.69 (s, 1H, Ar), 7.50 (s, 1H, Ar), 10.42 (s, 1H, OH). – IR (Nujol, cm^{-1}): ν = 1665 (s), 1595 (m), 1347 (m), 1271 (w), 1216 (s), 1204 (s), 1175 (s), 1131 (s), 1078 (w), 1010 (w). – MS (EI, 70 eV): *m/z* (%) = 220 (19) $[M]^+$, 188 (100), 146 (56), 115 (16), 91 (11). – HRMS (EI, 70 eV): *m/z* = 220.10919 (calcd. 220.10940 for $C_{13}H_{16}O_3$, $[M]^+$). – Anal. for $C_{13}H_{16}O_3$ (220.11): calcd. C 70.89, H 7.32; found C 70.93, H 7.46.

*Methyl 6-hydroxy-2-phenyl-1,2,3,4-tetrahydronaphthalene-5-carboxylate (**5d-A**) and methyl 6-hydroxy-2-phenyl-1,2,3,4-tetrahydronaphthalene-7-carboxylate (**5d-B**)*

Starting with **3d** (1.000 g, 3.61 mmol), **4a** (0.940 g, 3.61 mmol), CH_2Cl_2 (4.5 mL), and $TiCl_4$ (0.685 g, 3.61 mmol), **5d** was isolated as mixture of regioisomers (A/B = 24 : 1) as a colorless solid (0.300 g, 30 %). M. p. 104 – 105 °C. – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71 – 1.92 (m, 1H, CH_2), 2.09 – 2.23 (m, 1H, CH_2), 2.78 – 3.04 (m, 3H, CH_2, CH), 3.05 – 3.31 (m, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.82 (d, ^3J = 8.5 Hz, 1H, Ar), 7.15 (d, ^3J = 8.5 Hz, 1H, Ar), 7.19 – 7.38 (m, 5H, Ph), 11.00 (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.1, 30.4, 38.0, (CH_2), 39.6 (CH), 52.1 (OCH_3), 112.1 (C), 115.6 (CH_{Ar}), 126.3, 126.8 (CH_{Ph}), 128.4 (C), 128.5 (CH_{Ph}), 135.9 (CH_{Ar}), 138.5, 146.3 (C), 160.3 (COH), 172.2 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71 – 1.92 (m, 1H, CH_2), 2.09 – 2.23 (m, 1H, CH_2), 2.78 – 3.04 (m, 3H, CH_2, CH), 3.05 – 3.31 (m, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.75 (s, 1H, Ar), 7.56 (s, 1H, Ar), 7.19 – 7.38 (m, 5H, Ph), 10.48 (s, 1H, OH). – IR (Nujol, cm^{-1}): ν = 1716 (w), 1645 (m), 1600 (m), 1319 (m), 1257 (w), 1217 (s), 1189 (m), 1131 (m), 1059 (w), 1004 (w). – MS (EI, 70 eV): *m/z* (%) = 282 (72) $[M]^+$, 250 (100), 222 (11), 178 (16), 146 (98). – HRMS (EI, 70 eV): *m/z* = 282.12470 (calcd. 282.12505 for $C_{18}H_{18}O_3$, $[M]^+$).

*Methyl 7-(hydroxy)benzocycloheptane-6-carboxylate (**5e-A**) and methyl 6-(hydroxyl)benzocycloheptane-7-carboxylate (**5e-B**)*

Starting with **3e** (1.000 g, 4.70 mmol), **4a** (1.228 g, 4.70 mmol), CH_2Cl_2 (6.0 mL), and $TiCl_4$ (0.894 g, 4.70 mmol), **5e** was isolated as a mixture of regioisomers (A/B = 3 : 2) as a yellow oil (0.583 g, 56 %). – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 – 1.70 (m, 4H, CH_2), 1.76 – 1.84 (m, 2H, CH_2), 2.95 – 2.99 (m, 4H, CH_2), 3.93 (s, 3H, OCH_3), 6.70 (d, ^3J = 8.2 Hz, 1H, Ar), 7.12 (d, ^3J = 8.2 Hz, 1H, Ar), 9.76 (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8, 28.0, 31.7, 32.2, 35.4 (CH_2), 52.2 (CH_3), 114.1 (C), 117.7 (CH_{Ar}), 134.7 (C), 136.0 (CH_{Ar}), 145.0 (C), 158.2 (COH), 171.7 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 – 1.70 (m, 4H, CH_2), 1.76 – 1.84 (m, 2H, CH_2), 2.69 – 2.76 (m, 4H, CH_2), 3.91 (s, 3H, OCH_3), 6.73 (s, 1H, Ar), 7.52 (s, 1H, Ar), 10.53 (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1, 28.7, 32.4, 35.6, 36.9 (CH_2), 52.0 (CH_3), 109.4 (C), 117.7, 129.3 (CH_{Ar}), 134.5, 152.6 (C), 159.9 (COH), 170.6 (C=O). – IR (Nujol, cm^{-1}): ν = 3420 (br, w), 3380 (br, w), 3199 (br, w), 3010 (w), 2923 (s), 2851 (s), 1732 (s), 1672 (s), 1622 (m), 1599 (s). – MS (EI, 70 eV): *m/z* (%) = 220 (19) $[M]^+$, 188 (100), 159 (10), 145 (10), 131 (10). – HRMS (EI, 70 eV): *m/z* = 220.10918 (calcd. 220.10940 for $C_{13}H_{16}O_3$, $[M]^+$).

*Methyl 8-(hydroxy)benzocyclooctane-7-carboxylate (**5f-A**) and methyl 7-(hydroxy)benzocyclooctane-8-carboxylate (**5f-B**)*

Starting with **3f** (1.000 g, 4.42 mmol), **4a** (1.168 g, 4.42 mmol), CH_2Cl_2 (8.8 mL), and $TiCl_4$ (0.838 g, 4.42 mmol), **5f** was isolated as a mixture of regioisomers (A/B = 11 : 1) as a colorless oil (0.387g, 38 %). – **A**: ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 1.23 (m, 2H, H-4), 1.39 (m, 2H, H-3), 1.60 (m, 2H, H-2), 1.71 (m, 2H, H-5), 2.69 (m, 2H, H-1), 3.02 (m, 2H, H-6), 3.91 (s, 3H, OMe), 6.76 (d, ^3J = 8.5 Hz, 1H, H-9), 7.13 (d, ^3J = 8.5 Hz, 1H, H-10), 10.63 (s, 1H, OH). – ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.6 (C-4), 26.6 (C-3), 29.0 (C-6), 30.9 (C-5), 32.2 (C-2), 32.9 (C-1), 51.9 (OMe), 112.5 (C-7), 115.3 (C-9), 133.8 (C-10a), 135.5 (C-10), 142.4 (C-6a), 160.2 (C-8), 171.9 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 – 1.45 (m, 4H, CH_2), 1.58 – 1.77 (m, 4H, CH_2), 2.72 (t, ^3J = 6.3 Hz, 2H, CH_2), 3.05 (t, ^3J = 6.3 Hz, 2H, CH_2), 3.94 (s, 3H, CH_3), 6.79 (d, ^3J = 8.5 Hz, H, Ar), 7.16 (d, ^3J = 8.5 Hz, 1H, Ar), 10.68 (s, 1H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7, 25.8, 26.4, 31.2, 31.7, 32.3 (CH_2), 52.0 (CH_3), 110.1 (C), 117.2, 129.5 (CH_{Ar}), 133.8 (C), 150.5 (C), 159.7 (COH), 170.4 (C=O). – IR (Nujol, cm^{-1}): ν = 3420 (br, w), 3411 (br, w), 3245 (w), 2925 (s), 2854 (m), 1732 (m), 1708 (m), 1661 (s), 1596 (s), 1466 (s), 1439 (s). – MS (EI, 70 eV): *m/z* (%) = 234 (40) $[M]^+$, 202 (100), 174 (10), 159 (27), 146 (14). – HRMS (EI, 70 eV): *m/z* = 234.1247 (calcd. 234.1250 for $C_{14}H_{18}O_3$, $[M]^+$).

*Methyl 13-(hydroxy)benzocyclododecane-12-carboxylate (**5g-A**) and methyl 8-hydroxy-benzocyclododecane-12-carboxylate (**5g-B**)*

Starting with **3g** (1.000 g, 3.54 mmol), **4a** (0.936 g, 3.54 mmol), CH_2Cl_2 (7.0 mL), and $TiCl_4$ (0.671 g,

3.54 mmol), **5g** was isolated as a mixture of regioisomers (A/B = 24 : 1) as a yellow solid (0.215 g, 21 %). M. p. 52 – 53 °C. – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 – 1.72 (m, 16H, CH_2), 2.54 – 2.64 (m, 2H, CH_2), 2.94 – 3.00 (m, 2H, CH_2), 3.94 (s, 3H, CH_3), 6.80 (d, ^3J = 8.5 Hz, 1H, Ar), 7.25 (d, ^3J = 8.5 Hz, 1H, Ar), 10.34 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.7, 22.8, 26.3, 26.6, 27.1, 27.7, 28.5, 29.5, 30.3, 30.5 (CH_2), 52.2 (CH_3), 113.3 (C), 115.3 (CH_{Ar}), 133.2 (C), 136.2 (CH_{Ar}), 142.7 (C), 159.6 (COH), 172.0 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 – 1.72 (m, 16H, CH_2), 2.23 – 2.37 (m, 2H, CH_2), 2.42 – 2.48 (m, 2H, CH_2), 3.91 (s, 3H, CH_3), 6.77 (s, 1H, Ar), 7.62 (s, 1H, Ar), 10.42 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.3, 22.9, 25.3, 25.7, 26.0, 26.4, 28.6, 29.2, 30.1, 40.4 (CH_2), 52.0 (CH_3), 113.3 (C), 117.7, 130.5, (CH_{Ar}), 132.7, 136.2 (C), 159.6 (COH), 172.0 (C=O). – IR (Nujol, cm^{-1}): ν = 3221 (br, w), 1712 (w), 1680 (s), 1661 (s), 1590 (w), 1342 (m), 1295 (m), 1270 (m), 1214 (s), 1127 (m). – MS (EI, 70 eV): *m/z* (%) = 290 (44) $[M]^+$, 258 (100), 187 (8), 161 (9), 147 (11). – HRMS (EI, 70 eV): *m/z* = 290.1873 (calcd. 290.1876 for $C_{18}H_{26}O_3$, $[M]^+$).

*Methyl 7-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalene-8-carboxylate (**5h-A**) and methyl 6-hydroxy-1-methyl-1,2,3,4-tetrahydronaphthalene-5-carboxylate (**5h-B**)*

Starting with **3h** (1.000 g, 4.70 mmol), **4a** (1.228 g, 4.70 mmol), CH_2Cl_2 (6.0 mL), and $TiCl_4$ (0.894 g, 4.70 mmol), **5h** was isolated as a mixture of regioisomers (A/B = 5 : 1) as a yellow solid (0.346 g, 34 %). M. p. 43 – 44 °C. – **A**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (d, ^3J = 6.4 Hz, 3H, CH-CH_3), 1.26 – 1.38 (m, 1H, CH_2), 1.58 – 1.74 (m, 1H, CH_2), 1.74 – 1.88 (m, 1H, CH_2), 2.43 – 2.58 (m, 1H, CH_2), 2.69 – 2.79 (m, 2H, CH_2), 3.03 – 3.15 (m, 1H, CH), 3.94 (s, 3H, OCH_3), 6.71 (d, ^3J = 8.6 Hz, 1H, Ar), 7.12 (d, ^3J = 8.6 Hz, 1H, Ar), 10.83 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.2 (CH-*C*H_3), 29.3 (CH), 29.6, 30.5, 38.1 (CH_2), 52.0 (OCH_3), 112.2 (C), 115.1 (CH_{Ar}), 128.4 (C), 135.7 (CH_{Ar}), 138.9 (C), 160.3 (COH), 172.1 (C=O). – **B**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.7 Hz, 3H, CH-CH_3), 1.26 – 1.38 (m, 1H, CH_2), 1.58 – 1.74 (m, 1H, CH_2), 1.74 – 1.88 (m, 2H, CH_2), 2.69 – 2.79 (m, 2H, CH_2), 3.03 – 3.15 (m, 1H, CH), 3.91 (s, 3H, OCH_3), 6.82 (s, ^3J = 8.4 Hz, 1H, Ar), 7.26 (d, ^3J = 8.4 Hz, 1H, Ar), 10.42 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.4 (CH-*C*H_3), 30.0, 30.3 (CH_2), 32.5 (CH), 38.1 (CH_2), 52.0 (OCH_3), 115.1 (CH_{Ar}), 116.8 (C), 133.9, 135.2 (C), 138.9 (CH_{Ar}), 160.3 (COH), 172.1 (C=O). – IR (neat, cm^{-1}): ν = 1734 (w), 1712 (w), 1664 (s), 1597 (s), 1336 (s), 1321 (s), 1263 (s), 1220 (s), 1192 (s), 1174 (m). – MS (EI, 70 eV): *m/z* (%) = 220 (17) $[M]^+$, 188 (100), 173 (6), 146 (24), 118 (23). – HRMS (EI, 70 eV): *m/z* = 220.10938 (calcd. 220.10940 for $C_{13}H_{16}O_3$, $[M]^+$).

*4-Methoxycarbonyl-7-methyl-2,3-dihydroinden-5-ol (**5i-A**) and 5-methoxycarbonyl-4-methyl-2,3-dihydroinden-6-ol (**5i-B**)*

Starting with **3i** (1.000 g, 5.04 mmol), **4a** (1.313 g, 5.04 mmol), CH_2Cl_2 (10 mL), and $TiCl_4$ (0.956 g, 5.04 mmol), **5i** was isolated as a mixture of regioisomers (A/B = 1 : 1) as a colorless solid (0.352 g, 34 %). M. p. 64 – 65 °C. – **A**: ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 2.03 (m, 2H, H-2), 2.21 (s, 3H, CH_3), 2.73 (t, $^3J_{1,2}$ = 7.5 Hz, 2H, H-1), 3.17 (t, $^3J_{2,3}$ = 7.5 Hz, 2H, H-3), 3.91 (s, 3H, OMe), 6.62 (s, 1H, H-6), 10.00 (s, 1H, OH). – ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 19.9 (CH_3), 24.3 (C-2), 30.5 (C-1), 35.6 (C-3), 51.7 (OMe), 107.4 (C-4), 115.9 (C-6), 134.8 (C-7a), 141.8 (C-7), 145.9 (C-3a), 161.3 (C-5), 171.8 (C=O). – **B**: ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 2.03 (m, 2H, H-2), 2.42 (s, 3H, CH_3), 2.80 (t, $^3J_{2,3}$ = 7.5 Hz, 2H, H-3), 2.88 (t, $^3J_{1,2}$ = 7.5 Hz, 2H, H-1), 3.93 (s, 3H, OMe), 6.71 (s, 1H, H-7), 11.12 (s, 1H, OH). – ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 19.7 (CH_3), 24.3 (C-2), 31.6 (C-3), 33.8 (C-1), 51.8 (OMe), 110.9 (C-7), 110.2 (C-5), 135.3 (C-3a), 135.8 (C-4), 151.3 (C-7a), 161.9 (C-6), 172.5 (C=O). – IR (Nujol, cm^{-1}): ν = 3123 (br, w), 3102 (br, w), 3100 (br, w), 1667 (s), 1615 (m), 1581 (w), 1581 (w), 1333 (s), 1203 (s), 1145 (m). – MS (EI, 70 eV): *m/z* (%) = 206 (19) $[M]^+$, 174 (100), 146 (17), 131 (7), 115 (31). – HRMS (EI, 70 eV): *m/z* = 206.0941 (calcd. 206.0937 for $C_{12}H_{14}O_3$, $[M]^+$).

*4-Acetyl-7-methyl-2,3-dihydroinden-5-ol (**5j**)*

Starting with **3i** (1.000 g, 5.04 mmol), **4b** (1.230 g, 5.04 mmol), CH_2Cl_2 (10 mL), and $TiCl_4$ (0.956 g, 5.04 mmol), **5j** was isolated as a yellow solid (0.116 g, 12 %). M. p. 115 – 116 °C. – ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 2.11 („quint", 2H, H-2), 2.22 (s, 3H, CH_3), 2.59 (s, 3H, OMe), 2.76 (t, $^3J_{1,2}$ = 7.6 Hz, 2H, H-1), 3.19 (t, $^3J_{2,3}$ = 7.6 Hz, 2H, H-3), 6.63 (s, 1H, H-6), 12.79 (s, 1H, OH). – ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.1 (CH_3), 24.7 (C-2), 30.3 (C-1), 31.9 (OMe), 36.7 (C-3), 116.4 (C-4), 117.0 (C-6), 134.9 (C-7a), 143.0 (C-7), 144.7 (C-3a), 162.7 (C-5), 204.7 (C=O). – IR (Nujol, cm^{-1}): ν = 1622 (m), 1595 (m), 1569 (w), 1354 (s), 1298 (w), 1234 (m), 1205 (w), 1139 (w), 1034 (w), 1139 (w). – MS (EI, 70 eV): *m/z* (%) = 190 (39) $[M]^+$, 175 (100), 128 (9), 115 (12), 91 (16). – HRMS (EI, 70 eV): *m/z* = 190.0985 (calcd. 190.0988 for $C_{12}H_{14}O_2$, $[M]^+$).

*X-Ray structure determination of **5j***

Crystal size: 0.33 × 0.33 × 0.07 mm^3, monoclinic crystal system, space group $C2/c$, a = 10.1094(3), b = 10.8657(3), c = 17.8120(5) Å, β = 96.471(1)°, V = 1944.11(10) Å^3, Z = 8, T = 173 K, μ(MoK_α) = 0.87 cm^{-1}, θ range for data collection 2.76 – 27.50°, index ranges (h, k, l): ±13, −14/ + 13, ±22, 13881 measured reflections, 2206 independent reflec-

tions, R_{int} = 0.0232, GOF (F^2) = 1.034, $R1/wR2$ [$I \geq 2\sigma(I)$] = 0.0425/0.1151, $R1/wR2$ (all data) = 0.0505/0.1256, $\Delta\rho_{fin}$ (max/min) = 0.303/−0.181 e Å^{-3}. Remarks: Data collection was performed using an X8Apex diffractometer system with MoK_α radiation and CCD area detector. The structure was solved with Direct Methods and refined against F^2 (software used: Bruker SHELXTL). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated at idealized positions and refined using the riding model [4].

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