

SUPPORTING INFORMATION

A New Cross-Coupling Based Synthesis of Carpanone

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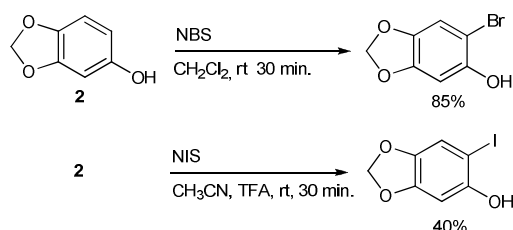
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General experimental procedures: All reactions were carried out under a N₂ atmosphere, unless otherwise stated. NMR spectra were recorded (BRUKER 400 MHz, ¹H, and 100 MHz, ¹³C) in CDCl₃ (which also provided the lock signal at $\delta = 7.26$ for ¹H and $\delta = 77.16$ ppm and ¹³C). IR spectra were recorded on a Brüker Tensor 27 (pike) instrument and only the strongest or structurally most important peaks were listed. Silica gel (40-63 μ m) was used for column chromatography. TLC plates were visualized under UV light and sprayed with KMnO₄ (5% in water). Dichloromethane and THF were purified by passing through an alumina column. High resolution mass spectra were recorded with a Nermag R30-10 apparatus. Melting points were measured with a Stuart Scientific SMP3 melting point apparatus and are uncorrected.

Regioselective halogenation of sesamol

Sesamol was reacted with either NBS or NIS to yield the corresponding expected compound regioselectively (Scheme 1).¹ The iodo compound was very sensitive and partly decomposed during chromatography, even when protected from light.

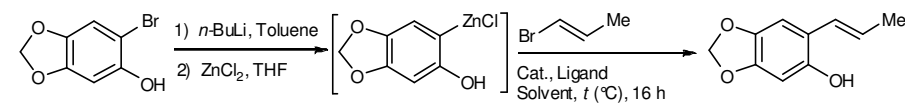


Scheme 1. Regioselective halogenation of sesamol.

Cross-coupling reactions involving halogenated sesamol

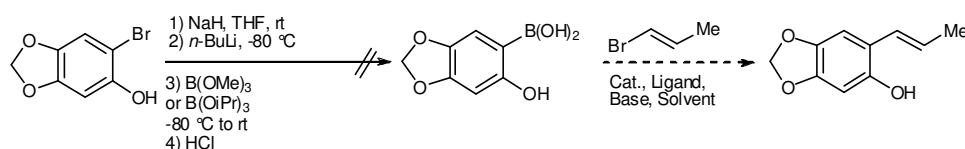
As 6-iodos sesamol was extremely sensitive, we used its brominated analogue for cross-coupling reactions. We first tried Negishi cross-coupling. All attempts failed (Table 1). Only unidentified degradation products were obtained.

¹ Carreno, M. C.; Garcia Ruano, J. L.; Sanz, G.; Toledo, M. A.; Urbano, A. *J. Org. Chem.* **1995**, 60, 5328.

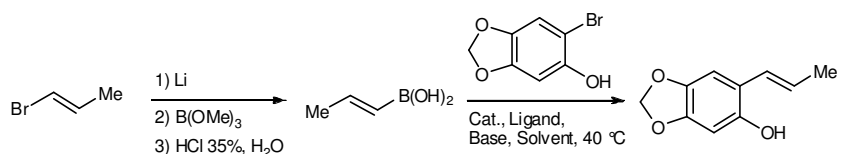
Table 1: Failed Negishi cross-coupling.


Entry	Catalyst	Ligand	Solvent	Temperature (°C)	Yield (%)
1	PdCl ₂ (PPh ₃) ₂	--	THF	60	0
2	Pd(dba) ₂	tfp	THF	60	0
3	PdCl ₂ (dppf)	--	THF	60	0
4	Pd(dba) ₂	P(<i>t</i> Bu) ₃	DMF	rt	0

We then focused on the Suzuki-Miyaura cross-coupling. Borylation of bromosesamol failed (Scheme 2).

**Scheme 2 :** Failed borylation of unprotected 6-bromosesamol

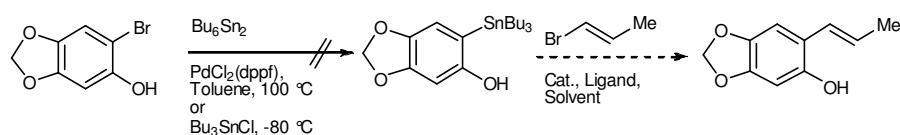
We also tried the “Umpeled” Suzuki-Miyaura cross-coupling. The reaction between 6-bromosesamol and propenyl boronic acid failed whatever the conditions (Table 2).

Table 2 : Failed Suzuki-Miyaura cross-coupling with bromosesamol.


Entry	Catalyst	Ligand	Base	Solvent	Yield (%)
1	Pd(OAc) ₂	--	K ₂ CO ₃ , <i>n</i> -Bu ₄ NBr	DMF/H ₂ O	0
2	Pd(OAc) ₂	--	NaF	THF	0
3	Pd(dba) ₂	PPh ₃	K ₂ CO ₃	Toluene	0
4 ^a	Pd(OAc) ₂	X-Phos	NaF	THF	0
5	Pd(dba) ₂	P(<i>o</i> -tol) ₃	NaF	THF	0

^a/ Reaction carried out at 60 °C.

We finally studied Stille cross-coupling. Stannylation of bromosamol failed (Scheme 3).



Scheme 3 : Failed stannylation of bromosamol.

We then envisaged the cross-coupling reaction between bromosamol and tributylpropenylstannane. This strategy also led to a failure (Table 3).

Table 3: Failed Stille cross-coupling with bromosamol.

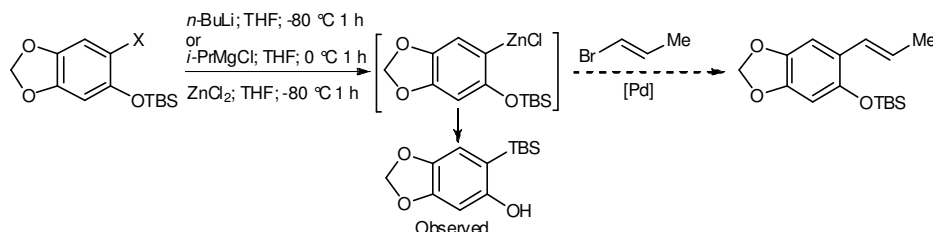
Entry	Catalyst	Ligand	Solvent	Yield (%)
1	PdCl ₂ (AsPh ₃) ₂ /CuCl	--	DMSO	0
2	PdCl ₂ (AsPh ₃) ₂ /CuI	--	DMSO	0
3	PdCl ₂ (MeCN) ₂ /CuCl	--	DMSO	0
4	PdCl ₂ (MeCN) ₂ /CuI	--	DMSO	0
5	PdCl ₂ (PPh ₃) ₂ /CuCl	--	DMSO	0
6	PdCl ₂ (PPh ₃) ₂ /CuI	--	DMSO	0
7	Pd(dba) ₂ /CuI	P(<i>t</i> Bu) ₃	DMSO	0
8	Pd(dba) ₂ /CuCl	P(<i>t</i> Bu) ₃	DMSO	0
9	Pd(dba) ₂	P(<i>t</i> Bu) ₃	Toluene	0
10	Pd(dba) ₂ /CsF	P(<i>t</i> Bu) ₃	DMF	0
11 ^a	Pd(dba) ₂ /CsF	P(<i>t</i> Bu) ₃	Toluene	0
12	Pd(dba) ₂ /CsF	P(<i>t</i> Bu) ₃	Toluene	0
13 ^a	Pd(dba) ₂	P(<i>t</i> Bu) ₃	DMF	0
14 ^a	Pd(dba) ₂ /CuCl	P(<i>t</i> Bu) ₃	DMF	0

^a/ Reaction carried out at 40 °C.

Therefore, we decided to protect sesamol as a TBS ether.

Cross-coupling reactions with TBS protected sesamol

We tried to prepare the zincated sesamol *via* metal/halogen exchange with *n*-BuLi or *i*-PrMgCl and transmetalation with ZnCl₂. Unfortunately, we observed only retro-Brook rearrangement and no zincated sesamol was observed (Scheme 4).



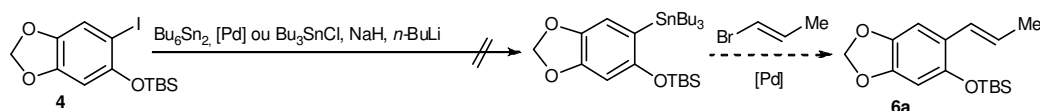
Scheme 4 : Attempted Negishi cross-coupling with TBS-protected zincated sesamol.

The “Umpeled” reaction between propenylzinc chloride and protected iodosesamol led to the formation of some desired product (Table 4). The best result was obtained with tri(*tert*-butylphosphine) as ligand (entry 6). However, yields remained modest and the experimental conditions were too drastic in view to design a diversity-oriented synthesis.

Table 4 : Negishi coupling with protected 6-iodosesamol

Entry	Catalyst	Ligand	Solvent	Temperature (°C)	Yield (%)
1	PdCl ₂ (dppf)	--	THF	50	0
2	PdCl ₂ (PPh ₃) ₂	--	THF	50	7
3	Pd(dba) ₂	tfp	THF	50	7
4	Pd(dba) ₂	P(<i>t</i> Bu) ₃	THF	50	18
5	Pd(dba) ₂	X-Phos	THF	50	0
6	Pd(dba) ₂	P(<i>t</i> Bu) ₃	DMF	80	46

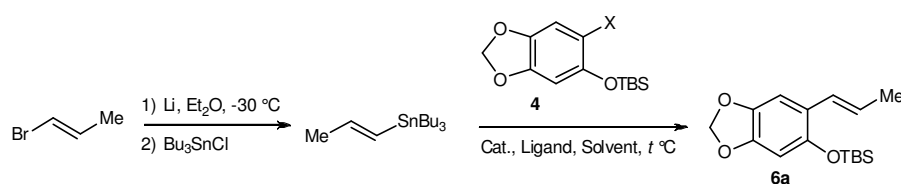
We then focused on the Stille cross-coupling. We first tried to stannylate the protected iodosesamol. This strategy remained unsuccessful (Scheme 5).



Scheme 5 : Attempted stannylation of TBS-protected 6-iodosamosol.

The “Umpeled” cross-coupling between propenyltributylstannane and protected iodosomesol with $\text{PdCl}_2(\text{AsPh}_3)_2$ as a catalyst led to the expected compound. The yield remained modest and operating conditions were not suitable for a diversity-oriented synthesis. (Table 5).

Table 5 : Stille cross-coupling between propenyltributylstannane and protected halosomesol.



Entry	X	Catalyst	Ligand	Solvent	Temperature (°C)	Yield (%)
1	Br	$\text{Pd}(\text{dba})_2$	PPh_3	HMPA	100	0
2	I	$\text{Pd}(\text{dba})_2$	PPh_3	DMSO	80	13
3	I	$\text{PdCl}_2(\text{AsPh}_3)_2$	--	DMSO	80	24
4	I	$\text{PdCl}_2(\text{AsPh}_3)_2/\text{CuCl}$	--	THF	80 ^a	34

^a/ Reaction carried out in a sealed tube.

We then studied in detail the Suzuki-Miyaura cross-coupling between bromopropene and borylated, protected sesamol. See the Letter for details.

Carpanization with $\text{PhI}(\text{OAc})_2$

Although Lindsley reported that $\text{PhI}(\text{OAc})_2$ was effective only to produce carpanone analogs deriving from precursors less electron rich than 2-propenylsesamol,² the mechanism associated to this reagent proposed by Shair³ deals with carpanization of 2-propenylsesamol itself. In our hands reaction of deprotected **6a** with $\text{PhI}(\text{OAc})_2$ did lead to carpanone, although in a moderate yield.

² a) Daniels, R. N.; Fadeyi, O. O.; Lindsley, C. W. *Org. Lett.* **2008**, *10*, 4097-4100; b) Fadeyi, O. O.; Daniels, R. N.; DeGuire, S. M.; Lindsley, C. W. *Tetrahedron Lett.* **2009**, *50*, 3084-3087.

³ Goess, B. C.; Hannoush, R. N.; Chan, L. K.; Kirchhausen, T.; Shair, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 5391-5403.

Treatment of 2-allylsesamol **7** with 1.0 equiv. of $\text{PhI}(\text{OAc})_2$ afforded acetate **8** in 32% yield. When 0.5 equiv. of $\text{PhI}(\text{OAc})_2$ was used, the yield of isolated **8** dropped to 13%.

Enantioselective attempts toward carpanone

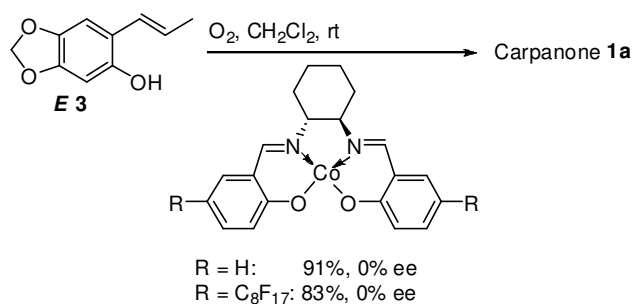
An enantioselective approach to carpanone was attempted from propenyl sesamol **E 3** using either chiral non racemic bisoxazoline ligands (Table 6) or $\text{Co}(\text{salen})$ catalysts (Scheme 6)⁴. Both approaches led to racemic mixtures.

Table 6: Attempted enantioselective access to carpanone using bisoxazoline ligands.

E 3 $\xrightarrow[\text{chiral ligand}]{\text{PdCl}_2 (10 \text{ mol } \%), \text{O}_2, \text{MeOH}/\text{H}_2\text{O}, 35^\circ\text{C}}$ Carpanone **1a**

Entry	Chiral ligand	Ee (%) ^a	Yield (%)
1		0	70
2		0	97

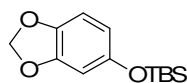
^a/ Determined by ^1H -NMR spectroscopy using (+)- $\text{Eu}(\text{hfc})_3$ as the chiral shift reagent.



Scheme 6: Attempted enantioselective access to carpanone using chiral $\text{Co}(\text{salen})$ catalysts.

⁴ Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1981**, 22, 4437-4440.

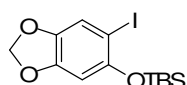
***tert*-Butyl(6-iodobenzo[*d*][1,3]dioxol-5-yloxy)dimethylsilane (4)**



Benzo[*d*][1,3]dioxol-5-yloxy)(*tert*-butyl)dimethylsilane (TBS-2)

A flame-dried flask was charged with sesamol (2.79 g, 20.2 mmol, 1 equiv.), imidazole (2.08 g, 30.6 mmol, 1.51 equiv.) and DMF (20 mL). *tert*-Butyldimethylchlorosilane (3.25 g, 21.6 mmol, 1.07 equiv.) in DMF (15 mL) was added. The reaction mixture was stirred at rt for 1 h, then hydrolyzed (50 mL) and extracted with Et₂O (3x30 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/AcOEt 85/15), affording the expected product (5.01 g, 98%) as a colorless viscous oil.

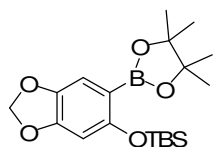
¹H NMR (400 MHz, CDCl₃) δ_H: 6.65 (d, *J* = 8.3 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 6.28 (dd, *J* = 2.4, 8.3 Hz, 1H), 5.90 (s, 2H), 0.99 (s, 9H), 0.18 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ_C: 150.6, 148.1, 142.0, 111.7, 108.0, 102.6, 101.2, 25.8, 18.3, -4.4; IR (film): 2926, 2856, 1484, 1252, 1186 cm⁻¹; HRMS for C₁₃H₂₁O₃Si calcd 253.12545, found 253.12493.



***tert*-Butyl(6-iodobenzo[*d*][1,3]dioxol-5-yloxy)dimethylsilane (4)**

A flame-dried flask was charged with the protected sesamol (2.53 g, 10.0 mmol, 1 equiv.) and acetonitrile (20 mL). The solution was protected from light and *N*-iodosuccinimide (2.475 g, 11.0 mmol, 1.10 equiv.) dissolved in acetonitrile (20 mL) was added. Trifluoroacetic acid (112 μL, 1.508 mmol, 0.15 equiv.) was added and the reaction mixture was heated to 50 °C for 90 minutes. After cooling to rt, the reaction was hydrolyzed with aqueous Na₂S₂O₃ (20 mL) and extracted with AcOEt (3x10 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/ CH₂Cl₂, 90/10), affording the title compound (3.54 g, 94%) as a yellow solid.

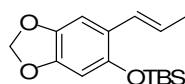
m.p.: 36 °C; ¹H NMR (400 MHz, CDCl₃) δ_H: 7.14 (s, 1H), 6.44 (s, 1H), 5.93 (s, 2H), 1.05 (s, 9H), 0.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ_C: 150.1, 148.8, 142.8, 117.5, 101.8, 100.9, 77.4, 26.1, 18.5, -3.8; IR (solid): 2928, 2856, 1503, 1180, 1080, 1037, 932, 865, 778; HRMS for C₁₃H₁₉IO₃Si calcd 378.01427, found 378.01414.



***tert*-Butyldimethyl(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d][1,3]dioxo-5-yloxy)silane (5)**

A flame-dried flask was charged with iodide **4** (1.47 g, 3.88 mmol, 1 equiv.) and PdCl₂dppf (293 mg, 0.4 mmol, 0.10 equiv.), toluene (18 mL), pinacol borane (952 μ L, 6.56 mmol, 1.69 equiv.) and Et₃N (4.4 mL, 31.5 mmol, 8.12 equiv.). The flask was sealed and heated to 110 °C for 20 h. After cooling to rt, the reaction mixture was hydrolyzed with aqueous saturated NH₄Cl (50 mL) and extracted with AcOEt (3x15 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/CH₂Cl₂, 80/20), affording the expected compound (1.25 g, 85%) as an orange solid.

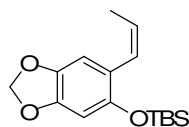
m.p.: 80-81 °C; ¹H NMR (400 MHz, CDCl₃) δ _H: 7.09 (s, 1H), 6.35 (s, 1H), 5.90 (s, 2H), 1.30 (s, 12H), 1.02 (s, 9H), 0.21 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ _C: 156.9, 150.9, 141.7, 114.4, 102.0, 101.3, 83.2, 26.1, 25.1, 18.5, -4.1; IR (solid): 2977, 2930, 2856, 1618, 1143, 1112, 880, 834, 777; HRMS for C₁₉H₃₁BO₅NaSi calcd 401.19260, found 401.19289.



***(E)*-tert-butyl dimethyl(6-(prop-1-enyl)benzo[d][1,3]dioxol-5-yloxy)silane (6a)**

A flame-dried flask was charged with boronate **5** (180 mg, 0.5 mmol, 1 equiv.), PdCl₂(PPh₃)₂ (35 mg, 0.05 mmol, 0.10 equiv.), potassium *tert*butylate (168.3 mg, 1.5 mmol, 3 equiv.), toluene (1.5 mL) and *trans*-bromopropene (73 μ L, 0.85 mmol, 1.70 equiv.). The reaction mixture was stirred at rt for 2 h, hydrolyzed (30 mL) and extracted with AcOEt (3x15 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/CH₂Cl₂, 80/20), affording the expected compound (75 mg, 60%) as a slightly yellow oil.

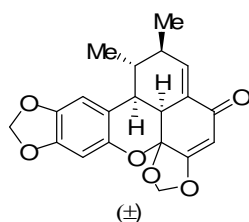
¹H NMR (400 MHz, CDCl₃) δ _H: 6.87 (s, 1H), 6.61 (dq, *J* = 1.5, 15.8 Hz, 1H), 6.34 (s, 1H), 5.94 (dq, *J* = 6.5, 15.7 Hz, 1H), 5.88 (s, 2H), 1.85 (dd, *J* = 1.7, 6.6 Hz, 3H), 1.02 (s, 9H), 0.17 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ _C: 147.0, 146.8, 142.3, 126.2, 123.4, 111.8, 104.8, 101.8, 101.1, 25.9, 18.8, 18.4, -4.2; IR (film): 2928, 2857, 1502, 1253, 1175, 1072, 939, 836, 778; HRMS for C₁₆H₂₅O₃Si calcd 293.15675, found 293.15636.



(Z)-tert-butyl dimethyl(6-(prop-1-enyl)benzo[d][1,3]dioxol-5-yl)oxy silane (6b)

A flame-dried flask was charged with boronate **5** (1.05 g, 2.778 mmol, 1 equiv.), $\text{PdCl}_2(\text{PPh}_3)_2$ (187.0 mg, 0.266 mmol, 0.09 equiv.), 1*N* aqueous potassium hydroxide (9 mL, 9 mmol, 3.24 equiv.), toluene (8 mL) and *cis*-bromopropene (350 μL , 4.117 mmol, 1.48 equiv.). The reaction mixture was stirred at rt for 24 h, hydrolyzed (50 mL) and extracted with AcOEt (3x30 mL). The combined organic layers were dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/ CH_2Cl_2 , 90/10), affording the expected compound (690 mg, 85%) as a slightly yellow oil.

^1H NMR (400 MHz, CDCl_3) δ_{H} : 6.75 (s, 1H), 6.41 (dq, $J = 1.5, 11.4$ Hz, 1H), 6.39 (s, 1H), 5.91 (s, 2H), 5.68 (dq, $J = 7.0, 11.6$ Hz, 1H), 1.81 (dd, $J = 1.9, 7.2$ Hz, 3H), 0.98 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} : 148.2, 146.7, 141.4, 126.4, 125.3, 121.4, 109.3, 101.9, 101.1, 25.9, 18.4, 14.7, -4.2; IR (film): 2929, 2857, 1503, 1176, 1039, 835, 778; HRMS for $\text{C}_{16}\text{H}_{25}\text{O}_3\text{Si}$ calcd 293.15675, found 293.15666.



Carpanone (1a)

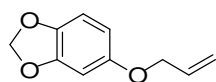
A flame-dried flask was charged with alkene **6a** (83 mg, 0.284 mmol, 1 equiv.), THF (0.5 mL) and TBAF (364 μL , 0.364 mmol, 1.28 equiv.). After 30 minutes, CuCl_2 (6.9 mg, 0.05 mmol, 0.17 equiv.), NaOAc (60 mg, 0.44 mmol, 1.55 equiv.), MeOH (0.3 mL) and water (0.3 mL) were added. The flask was purged with O_2 and heated to 50 $^\circ\text{C}$ for 4 h. After cooling to rt, the reaction mixture was hydrolyzed (10 mL) and extracted with AcOEt (3x10 mL). The combined organic layers were dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/ AcOEt, 90:10), affording the target (39 mg, 73%) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ_{H} : 7.01 (ddd, $J = 2.3, 0.9, 5.0$ Hz, 1H), 6.80 (s, 1H), 6.33 (s, 1H), 5.90 (d, $J = 1.5$ Hz, 1H), 5.87 (d, $J = 1.5$ Hz, 1H), 5.70 (s, 1H), 5.67 (s, 1H), 5.64 (s, 1H), 3.28 (dd, $J = 7.4, 2.1$ Hz), 3.17 (ddd, $J = 7.4, 2.3, 2.3$ Hz), 2.52 (m, 1H), 2.23 (m, 1H), 1.14 (d, $J = 7.2$ Hz), 0.71 (d, $J = 7.6$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} : 187.1, 168.5, 146.8,

145.3, 143.3, 142.8, 126.4, 115.4, 107.2, 101.3, 100.5, 99.4, 98.9, 36.3, 35.6, 35.3, 33.6, 21.6, 21.3

These spectral data are in good agreement with those from the literature.⁵

6-Allylbenzo[1,3]dioxol-5-ol (7)

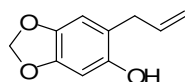


5-allyloxybenzo[1,3]dioxole

A flame-dried flask was charged with sesamol (1.38 g, 10 mmol, 1 equiv.), K₂CO₃ (2.76 g (20 mmol, 2 equiv.) and acetone (10 mL). Allylbromide (1.45 g, 12 mmol, 1.2 equiv.) was added. The reaction mixture was heated at 50 °C for 3 h. After cooling to rt, the salts were filtered off. The mother liquor was concentrated *in vacuo*. It afforded 1.70 g (95%) of the expected product as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ_H: 6.69 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.34 (dd, *J* = 2.5, 8.4 Hz, 1H), 6.03 (m, 1H), 5.91 (s, 2H), 5.38 (dq, *J* = 0.9, 18.7 Hz, 1H), 5.27 (dq, *J* = 0.6, 9.6 Hz, 1H), 4.46 (m, 2H).

These data are in good agreement with those from the literature.²



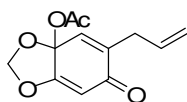
6-Allylbenzo[1,3]dioxol-5-ol (7)

A Schlenk tube was charged with 5-allyloxybenzo[1,3]dioxole (335.5 mg, 1.885 mmol, 1 equiv.) and DMF (2 mL). The tube was sealed and placed into a preheated oil bath (190 °C). The reaction mixture was stirred at this temperature for 3 h. After cooling to rt, the reaction mixture was hydrolyzed and extracted with AcOEt. The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/ AcOEt, 9/1). It yielded 280 mg (83%) of the expected compound as a white solid.

¹H NMR (400 MHz, CDCl₃) δ_H: 6.58 (s, 1H), 6.43 (s, 1H), 6.01-5.91 (m, 1H), 5.88 (s, 2H), 5.15 (m, 2H), 4.67 (br.s., 1H), 3.30 (d, *J* = 6.2 Hz, 2H).

These data are in good agreement with those from the literature.²

⁵ Baxendale, R.; Lee, A. L.; Ley, S. V. *J. Chem. Soc., Perkin Trans. I* **2002**, 1850.



Methyl 5-allyl-6-oxo-3a, 6-dihydrobenzo[d][1,3]dioxole-3a-carboxylate (8)

A flame-dried flask was charged with 6-allylbenzo[1,3]dioxol-5-ol **7** (88.4 mg, 0.497 mmol, 1 equiv.) and CH₂Cl₂ (1 mL). The solution was cooled to 0 °C and iodobenzene diacetate (169.7 mg, 0.527 mmol, 1.06 equiv.) dissolved in CH₂Cl₂ (1 mL) was added dropwise. After 15 minutes, the solution was warmed to rt and stirred for 1 h. The reaction mixture was hydrolyzed (20 mL) and extracted with AcOEt (3x10 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (cyclohexane/AcOEt, 80/20 to 70/30), affording the expected compound (38 mg, 32%) as a brown oil.

¹H NMR (400 MHz, CDCl₃) δ_H: 5.84 (s, 1H), 5.83 (s, 1H), 5.73 (s, 1H), 5.70-5.66 (m, 1H), 5.42 (s, 1H), 5.14 (s, 1H), 5.10 (m, 1H), 2.57 (ddt, *J* = 1.1, 6.6, 13.4 Hz, 1H), 2.48 (dd, *J* = 7.9, 12.5 Hz, 1H), 2.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ_C: 195.8, 169.4, 162.9, 146.2, 130.0, 120.5, 103.9, 102.1, 99.0, 79.6, 44.4, 20.9; IR (film): 2930, 1743, 1640, 1385, 1223; HRMS for C₁₂H₁₂O₅Na calcd 259.05769, found 259.05800.

