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Naphthoquinone Diels–Alder Reactions: Approaches to the ABC Ring System of Beticolin

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The syntheses of highly substituted anthraquinones through Diels–Alder reaction by using naphthoquinones are described. As an application, the first synthesis of the ABC tricycle of beticolin 0 (**1**) is reported. By using substituted naphthoquinone monoketal dienophiles, the congested quaternary center, the alkenyl methyl group and the oxo-substituent on the C ring could be established in the desired 1,3-relationship. By switching to a 1,4-naphthoquinone dienophile, cycloaddition reaction of sensitive substrates succeed with nearly quantitative yield at moderate temperatures.

Introduction

Beticolin 0 (**1**; Figure 1), is a naturally occurring xanthone produced by the fungal phytopathogen *Cercospora beticola*[1,2] Infection of sugar beet plants with this fungus causes leaf spot disease (cercosporiosis), making it the most destructive foliar pathogen of sugar beet worldwide.[3] The structure of **1** was determined in 1996, four years after the structural elucidation of the first member of the beticolin family. Beticolin 0 shares the same polycyclic skeleton with 19 congeners that incorporate chlorinated tetrahydroxanthone and anthraquinone subunits, which combine to form a unique bicyclo[3.2.2]nonane framework. A similar motif is found in the structurally related acremoxanthones A–D,[4] acremonidins A–C,[5] xanthoquinodins A_1–A_6, B_1–B_5,[6] and xanthoquinodin-like molecules JBIR-97, -98, and -99.[7]

Biological studies have revealed a broad cytotoxic profile for all beticolins. The compounds interact with multiple cellular targets and can even dimerize to form nonspecific ion channels.[8] The above notwithstanding, and despite the fact that many naturally occurring xanthones have attracted significant interest from the synthetic community,[9] little synthetic work has been recorded in the beticolin domain. Studies on the assembly of the bicyclo[3.2.2]nonane system of the natural products by radical cyclization chemistry have been reported; however, beticolins have yet to yield to total synthesis.

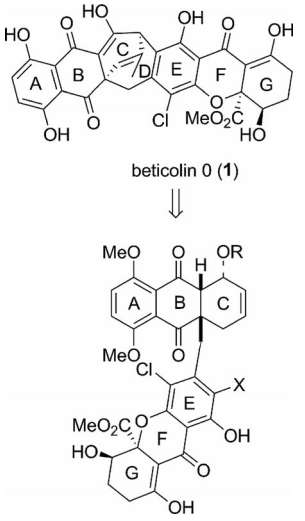

Figure 1. Structure of beticolin 0 (**1**) and our retrosynthetic analysis.

In 1992, the first structure of a beticolin was assigned by X-ray analysis and NMR spectroscopic studies,[10] followed by the isolation and structure elucidation of beticolin 0 (**1**) in 1996.[2] Although biological effects and structures have been known for decades, no total or partial syntheses were published.[11] In this study we focused our investigations towards the synthesis of the anthraquinone-subunit bearing the quaternary center. Moreover preliminary model studies towards bicyclo[3.2.2]nonane systems were conducted by Duffault by using radical cyclization.[12]

Our strategy for the formation of the ABC tricycle **2** involved a Diels–Alder reaction of a naphthoquinone monoacetal building block **3** with diene **4** (Scheme 1). In this way, the quaternary center, the alkenyl methyl group and the oxo-substituent should be established in a 1,3-relationship to each other. Our synthesis commenced with a

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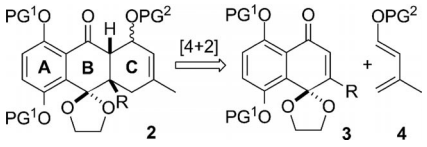
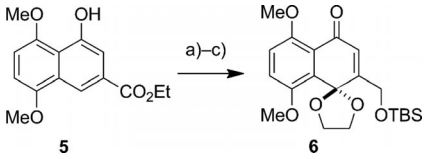
three-step preparation of naphthol **5** (Scheme 2).[13] Previously reported reduction[14] and silylation[13a] of **5** afforded the naphthol derivative (84% over two steps). Oxidative ketalization by using phenyliodine bis(trifluoroacetate) (PIFA) and ethylene glycol[15] gave ketal **6** in low yield (36%).



Scheme 1. Retrosynthetic analysis of ABC tricycle **2**.



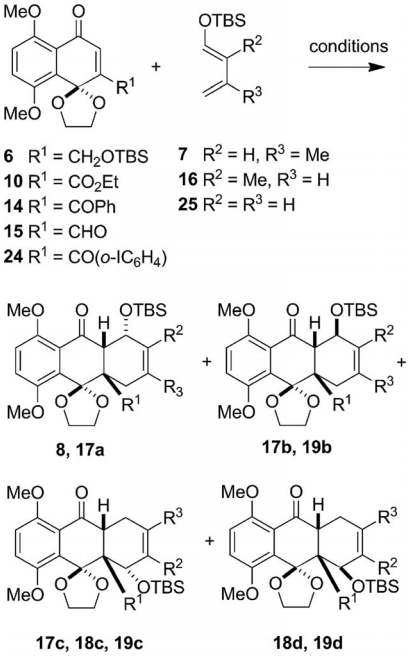
Scheme 2. Reagents and conditions: (a) $LiAlH_4$, THF, room temp., 86%; (b) *tert*-butyldimethylsilyl (TBSCl), imidazole, dimethylformamide (DMF), room temp., 98%; (c) PIFA, ethylene glycol, MeCN, 0 °C, 36%.

With dienophile **6** in hand we explored conditions for the naphthoquinone monoketal Diels–Alder reaction. The desired tricycle **8** was obtained as a single diastereomer by stirring **6** with diene **7** under harsh microwave conditions in 64% yield [quant. based on recovered starting material (brsm) yield; Table 1, Entry 1]. Next we aspired to generate a tricycle with a substituent at the quaternary center chemically orthogonal to the OTBS-group at the C ring. It was thought that an ester group should enhance the reactivity of dienophile **10** (Scheme 3). Therefore, **5** was oxidized with PIFA in ethylene glycol. The reaction stopped after oxidation to hydroquinone **9** although PIFA was added in excess. Additional treatment of purified **9** with PIFA gave ester-substituted dienophile **10** in 41% yield over two steps.

The reaction of dienophile **10** with diene **7** under microwave conditions resulted in a mixture of regioisomers **17a/b** (69%, *dr* 3:1) and **17c** (16%; Table 1, Entry 3).[16] The formation of **17c** was quite surprising because the quinoid keto group should dictate the regioselectivity of the Diels–Alder reaction towards product **17a/b**. This result became clear because the quinoid keto group is conjugated with the aromatic methoxy group and therefore more basic. When thermal conditions were applied to the reactions, yields for both reactions could be improved by prolonged reaction times; thereby, tricycle **8** could be obtained in 91% yield (Table 1, Entry 2) and the ratio of **17a/b** and **17c** could be increased in favor for desired cycloadduct **17a/b** (Table 1, Entry 4).

More activated dienophile **14** (Scheme 3) was successfully converted into tricycle **18c/d**, even though the yield was lower than before (32–43% yield; Table 1, Entries 6 and 7). Although both carbonyl groups in **14** were in benzylic positions and should show similar carbonyl activity, only undesired isomer **18c/d** was observed.

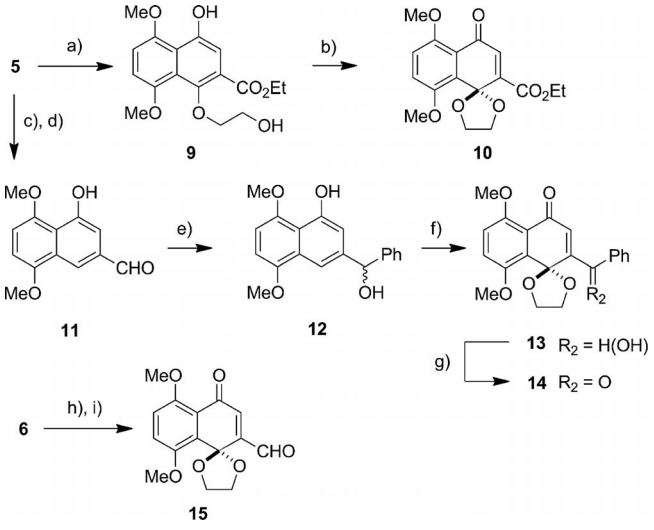
Table 1. Scope and observed regioselectivities of the Diels–Alder reaction.



Entry	R^1		R^2	R^3	Product (yield [%], *dr*)
1	**6** CH_2OTBS	**7**	H	Me	**8** (64%, quant. brsm)[a]
2	**6** CH_2OTBS	**7**	H	Me	**8** (91%)[b]
3	**10** CO_2Et	**7**	H	Me	**17a/b** (69%, *dr* 3:1), **17c** (16%)[a]
4	**10** CO_2Et	**7**	H	Me	**17a/b** (81%, *dr* 4:1), **17c** (16%)[b]
5	**13** CH(OH)Ph	**7**	H	Me	n.r.[c]
6	**14** COPh	**7**	H	Me	**18c/d** (32%, *dr* 2.5:1)[a]
7	**14** COPh	**7**	H	Me	**18c/d** (43%, *dr* 2:1)[b]
8	**15** CHO	**16**	Me	H	**19b/c** (60%, *dr* 1:1.1)[a]
9	**22**[d]	**7**	H	Me	degradation[a]
10	**24** CO(*o*-IC_6H_4)	**25**	H	H	degradation[a][b]

[a] μW, 300 W, 0.5 h, 170 °C. [b] 120–170 °C, 1.5 h. [c] μW, 300 W, 8 h, 170 °C; n.r.: no reaction. [d] Conversion to corresponding ketal directly before cycloaddition. μW = microwave irradiation.

However, deactivation by the ketal group resulted in higher basicity of the cyclic carbonyl group.[17] In summary, the electronic rather than the steric nature of substituent R^1 (Table 1) had the greatest influence on the regioselective outcome. To take advantage of this feature, it was planned to let aldehyde **15** (Scheme 3) react with siloxy diene **16** (prepared from TMS-protected diene[18]; Table 1). Based on the computational analysis of the combination of orbital coefficients, the reactions should undergo the cycloaddition in a predictable way to give tricycle **19c/d** with the desired 1,3-relationship of quaternary center and alkenyl methyl group. Therefore, **6** (Scheme 3) was desilylated (93% yield) and subsequently oxidized to give **15** in good yield (91%). Cycloaddition of aldehyde **15** with diene **16** gave an unexpected mixture of regioisomers **19b/c** (60%, *dr* 1:1.1; Table 1, Entry 8). Fortunately, tricycle **19c** could be separated by HPLC and crystallized. X-ray analysis confirmed the structure of desired structure **19c** (Figure 2). This out-



Scheme 3. Reagents and conditions: (a) PIFA, ethylene glycol, MeCN, room temp., 54%; (b) PIFA, MeCN, 0 °C, 75%; (c) $LiAlH_4$, THF, r.t., 86%; (d) $Py*SO_3$, NEt_3, dimethyl sulfoxide (DMSO), 50 °C, quant.; (e) PhMgCl, THF, –78 °C, 91%; (f) PIFA, ethylene glycol, MeCN, 0 °C, 76%; (g) Dess–Martin periodinane (DMP), CH_2Cl_2, r.t., 81%; h) tetra-*n*-butylammonium fluoride (TBAF), THF, 0 °C, 93%; i) DMP, CH_2Cl_2, r.t., 91%.

come can be rationalized through steric repulsion between the alkenyl methyl group and the OTBS group of siloxy diene **16** with the ethylene ketal function of dienophile **15**. The alignment of orbital coefficients should accomplish generation of regioisomer **19c** or **19d**, whereas the steric repulsion during the transition state gave rise to tricycle **19b**.[19]

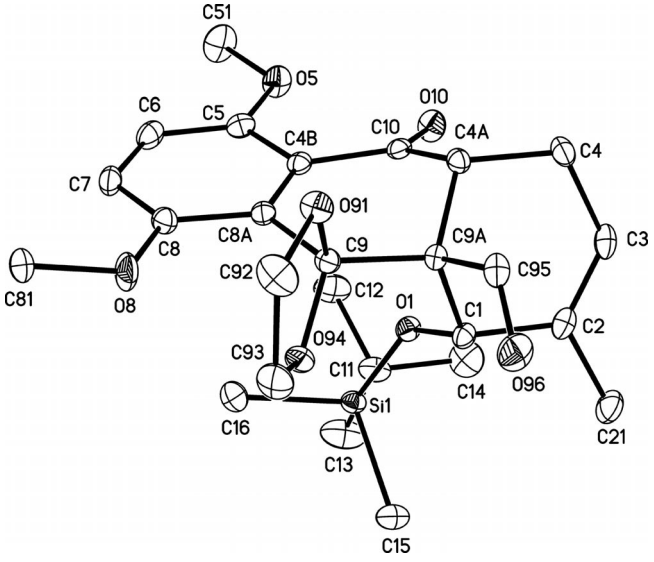
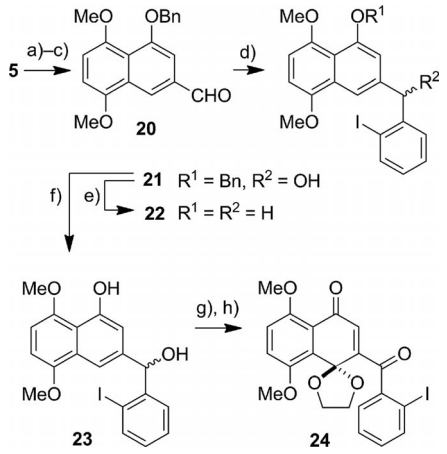


Figure 2. Molecular structure of **19c** representing the ABC ring of beticolin 0 (**1**) (H atoms omitted for clarity, displacement parameters are drawn at 50% probability level).[20]

Next we envisaged the installation of a halogenated aromatic ring for the planned Heck reaction to install the last ring. Therefore, naphthol **5** was benzylated[13a] and a subsequent reduction-oxidation sequence yielded **20** (86% yield over three steps; Scheme 4). Aldehyde **20** was subjected to addition of 2-iodophenyl Grignard reagent based on Togni's protocol.[21]



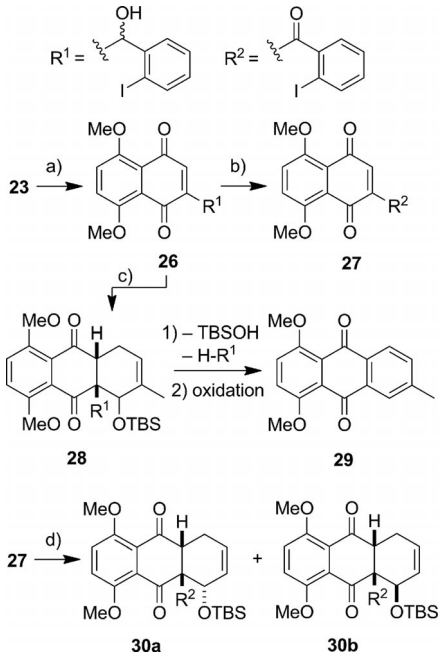
Scheme 4. Reagents and conditions: (a) BnBr, Cs_2CO_3, DMF, room temp., 91%; (b) $LiAlH_4$, THF, 0 °C, quant.; (c) $Py*SO_3$, NEt_3, DMSO, 50 °C, 94%; (d) 1,2-$C_6H_4I_2$, *i*PrMgCl, THF, –25 °C to 10 °C, 86%; (e) $AlCl_3$, CH_2Cl_2, r.t., 72%; (f) BBr_3, CH_2Cl_2, –78 °C, 56%; (g) PIFA, ethylene glycol, MeCN, 0 °C, 78%; (h) DMP, CH_2Cl_2, r.t., 69%.

Deprotection of **21** turned out to be difficult. Surprisingly, addition of $AlCl_3$[22] to **21** in CH_2Cl_2 led to deprotection as well as to benzylic reduction to furnish **22** in 72% yield. Naphthol derivative **22** was oxidized and directly subjected to a cycloaddition reaction with diene **7** (Scheme 4; Table 1, Entry 9). Heating of the corresponding ketal resulted in decomposition through de-iodination. Because dienophile **14** reacted smoothly (Table 1, Entries 6 and 7), we aimed for the synthesis of iodo analogue **24** (Scheme 4). One equivalent of boron tribromide selectively cleaved the benzyl group of **21** in presence of methoxyethers in reasonable yield (56%) to give **23**. Subsequent ketalization and oxidation afforded desired building block **24** (54% yield over two steps). Even with the use of sterically less demanding diene **25** (Table 1, prepared from TMS-protected diene),[23] dienophile **24** underwent thermal de-iodination (Table 1, Entry 10).

It is known that 1,4-naphthoquinones exhibit higher reactivity relative to their monoketal analogs because of electronic and steric reasons. However, cycloadducts of 1,4-naphthoquinones are prone to aromatization.[17] In addition, only a small number of publications have been reported regarding the substituents on the quinone part for intermolecular cycloaddition reactions (mostly small substituents like boronic acids,[24] alkyl,[25] and carbonyl substituents[26]). In reactions with demanding aromatic residues on the quinoid position, substituted 1,4-naphthoquinones did not react with a clear regioselectivity owing to secondary orbital effects.[27]

Thus, **23** was subjected to oxidation to give **26** in 83% yield (Scheme 5). Independent of scale, cycloaddition of **26** with diene **16** yielded only small quantities of product **28**. As a result of a retro-aldol reaction, aromatic compound

29 appeared during the cycloaddition reaction and during purification. To suppress the retro-aldol reaction, tricarbonyl **27** was synthesized from **26** in 79% yield. To our delight, dienophile **27** reacted smoothly at just 50 °C to stable products **30a** and **30b** in 98% yield for both isomers (*dr* 3:1), which could be separated by HPLC.



Scheme 5. Reagents and conditions: (a) PIFA, MeCN/H_2O, 0 °C to room temp. 83%; (b) DMP, CH_2Cl_2, r.t., 79%; (c) neat **16**, 62 °C; (d) neat **25**, 50 °C, **30a** (74%), **30b** (24%).

Because **30a** revealed, through NOESY experiments, a *trans*-relationship of the silyl ether group and the iodophenyl ketone residue, we concluded that **30b** is the *cis*-isomer. By using 2D COSY experiments, we can exclude other regioisomers in which the proton would be in an α-position relative to the carbonyl group adjacent to the proton right on the silyl ether.

In conclusion, the first synthesis of the ABC tricycle of beticolin 0 (**1**) (Figure 1) is described. By using substituted naphthoquinone monoketals as dienophiles, the congested quaternary center and the substituted C ring could be synthesized. An X-ray structure of tricycle **19c** could be obtained. By switching to 1,4-naphthoquinone **27** as dienophile, the cycloaddition reaction succeeded with nearly quantitative yield at mild temperatures. Studies towards the ring closure of **30a/b** to the bicyclo[3.2.2]nonane system are currently ongoing.

Experimental Section

General: NMR spectra were recorded with a Bruker Avance 300, a Bruker AM 400, a Bruker DRX 500 spectrometer or with a 600 MHz Bruker Avance III spectrometer as solutions. Chemical shifts are reported as signals downfield from tetramethylsilane (TMS) and are referenced to residual solvent peaks. The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and combinations thereof (e.g. dt = doublet of triplets). Some samples were measured by using Bruker BioSpin GmbH under the following conditions: These samples were dissolved in 600 microliter $CDCl_3$ with 0.03% tetramethylsilane (TMS, Deutero GmbH, 99.8% deuterated). NMR experiments were acquired with a Bruker AV-III 400 MHz NMR spectrometer equipped with a Broadband-Fluorine Observe (BBFO) probe, with resonance frequencies of 400.13 MHz for ^1H and 100.61 for ^{13}C. The temperature was set to 300.0 K by using a BSCU-05 temperature control unit. The chemical shift scale was internally referenced to the TMS signal (δ = 0.00 ppm) for ^1H, and to the $CDCl_3$ signal (δ =77.0 ppm) for ^{13}C. For each sample the following experiments were performed: ^1H, ^1H-decoupled ^{13}C-jmod (multiplicity modulated ^{13}C). MS (EI) (electron impact mass spectrometry) was performed by using a *Finnigan* MAT 90 (70 eV). In cases for which no MS (EI) spectra could be measured, owing to high volatility of the compound, the GC–MS spectra was used for characterization. IR (infrared spectroscopy) was recorded on a FT-IR Bruker alpha. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Analytical thin layer chromatography (TLC) was carried out on Merck silica-gel-coated aluminum plates (silica gel 60, F254), detected under UV-light at 254 nm. Solvent mixtures are expressed as volume/volume. Solvents, reagents and chemicals were purchased from Acros, ABCR, Alfa Aesar or Sigma Aldrich. Dry CH_2Cl_2 was distilled from calcium hydride prior to use. Dry tetrahydrofuran (THF) was distilled from sodium with benzophenone as indicator. Other dry reagents or solvents (e.g. dry ethylene glycol or dry acetonitrile) were commercially available. All other solvents, reagents and chemicals were used as received. All reactions involving moisture sensitive reactants were executed under an argon atmosphere with oven-dried and/or flame-dried glassware. All reactions under microwave conditions were performed in a Discover® microwave reactor from CEM. The power was down-regulated automatically when the maximum temperature was reached. All reactions were performed in a vessel and the temperature was measured by an infrared temperature control.

2′-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-5′,8′-dimethoxy-4′*H*-spiro-[[1,3]dioxolane-2,1′-naphthalen]-4′-one (6): A solution of 3-{[(*tert*-butyldimethylsilyl)oxy]methyl}-5,8-dimethoxynaphthalen-1-ol (see ref.[13,14]) (0.285 g, 0.818 mmol) was dissolved in dry acetonitrile (2.70 mL). This solution was added at 0 °C dropwise to a mixture of PIFA (0.978 g, 2.27 mmol) in dry ethylene glycol (6.34 mL) and dry acetonitrile (1.80 mL). After the addition was completed the yellow solution was stirred at 0 °C for 8 h, then satd. aq. $NaHCO_3$ solution was added to the reaction mixture. The product was extracted with EtOAc, the extract was washed with brine, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification by using column chromatography (silica gel, EtOAc/*c*-hexane, 1:2) afforded 2′-{[(*tert*-butyldimethylsilyl)oxy]-methyl}-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**6**; 120.4 mg, 0.296 mmol, 36% yield) as light yellow crystals. R_f = 0.44 (EtOAc/*c*-hexane, 1:1), m.p. 130.3–132.5 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.13 (d, J = 9.2 Hz, 1 H), 7.00 (d, J = 9.2 Hz, 1 H), 6.44 (t, J = 1.9 Hz, 1 H), 4.49–4.37 (m, 4 H), 4.25–4.17 (m, 2 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 0.94 (s, 9 H), 0.11 (s, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.3, 157.4, 154.3, 151.6, 131.5, 125.6, 121.3, 118.5, 114.7, 103.8, 68.9, 59.3, 57.0, 56.9, 26.1, 18.6, 1.2, –5.3 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1647, 1468, 1250, 1217, 1146, 1101, 1050, 995, 813 cm^{-1}. MS (EI): *m*/*z* (%) = 406 (9) [M^+], 349 (22) [(M – *t*Bu)$^+$], 305 (32), 291 (6) [(M – TBS)$^+$], 260 (100). HRMS (EI): calcd. for $C_{21}H_{30}O_6Si$ 406.1812; found 406.1814. X-ray analysis confirmed the proposed structure (CCDC-943150).

Ethyl 4-Hydroxy-1-(2-hydroxyethoxy)-5,8-dimethoxy-2-naphthoate (9): Ethyl 4-hydroxy-5,8-dimethoxy-2-naphthoate (**5**) (see ref.[13]) (1.00 g, 3.62 mmol) was dissolved in dry acetonitrile (12.0 mL). The solution was added slowly over 15 min at 0 °C to a mixture of PIFA (3.42 g, 7.96 mmol) in dry ethylene glycol (28.0 mL) and dry acetonitrile (8.00 mL). After the addition was completed the bright yellow solution was stirred at 0 °C for 15 min. Then satd. aq. $NaHCO_3$ solution was added to the reaction mixture. The product was extracted with EtOAc, and the extract was washed with brine, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by using column chromatography (silica gel, EtOAc/*c*-hexane, 1:1 to 2:1 to pure EtOAc) to yield ethyl 4-hydroxy-1-(2-hydroxyethoxy)-5,8-dimethoxy-2-naphthoate (**9**; 653 mg, 1.94 mmol, 54% yield) as yellow crystals. R_f = 0.25 (EtOAc/*c*-hexane, 2:1), m.p. 107.8–111.5 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 7.23 (s, 1 H), 6.87–6.77 (m, 2 H), 4.38 (q, J = 7.1 Hz, 2 H), 4.13–4.05 (m, 2 H), 4.03 (s, 3 H), 3.93–3.85 (m, 5 H), 3.78 (br. s, 1 H), 1.39 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4, 152.0, 150.6, 150.3, 148.8, 123.0, 122.8, 119.5, 111.5, 107.8, 106.9, 78.0, 62.1, 61.5, 57.3, 56.8, 14.4 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1698, 1424, 1197, 1136, 1026, 809 cm^{-1}. MS (EI): *m*/*z* (%) = 336 (100) [M$^+$], 246 (61) [$C_{13}H_{10}O_5^+$], 245 (35) [$C_{13}H_9O_5^+$], 203 (27) [$C_{12}H_{11}O_3^+$]. HRMS (EI): calcd. for $C_{17}H_{20}O_7$ 336.1208; found 336.1209. X-ray analysis confirmed the proposed structure (CCDC-943141).

Ethyl 5′,8′-Dimethoxy-4′-oxo-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-2′-carboxylate (10): Ethyl 4-hydroxy-1-(2-hydroxyethoxy)-5,8-dimethoxy-2-naphthoate (**9**; 295 mg, 0.877 mmol) was dissolved in dry acetonitrile (8.80 mL). The solution was added dropwise over 1 h to a solution of PIFA (1.05 mg, 2.44 mmol) in dry acetonitrile (8.80 mL) at 0 °C. The solution was warmed up to room temp. overnight. Then satd. aq. $NaHCO_3$ solution was added to the reaction mixture. The product was extracted with EtOAc, the extract was dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product with column chromatography (silica gel, EtOAc/*c*-hexane, 1:2 to 1:1) afforded ethyl 5′,8′-dimethoxy-4′-oxo-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-2′-carboxylate (**10**; 219 mg, 0.654 mmol, 75% yield) as bright yellow crystals. R_f = 0.27 (EtOAc/*c*-hexane, 1:1), m.p. 128.5–131.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 9.3 Hz, 1 H), 7.00 (d, J = 9.2 Hz, 1 H), 6.95 (s, 1 H), 4.52–4.47 (m, 2 H), 4.43–4.37 (m, 2 H), 4.29 (q, J = 7.1 Hz, 2 H), 3.89 (s, 6 H), 1.36 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.5, 164.4, 154.2, 151.6, 142.9, 135.0, 132.1, 120.3, 119.4, 114.1, 103.4, 70.4, 61.6, 56.8, 56.8, 14.2 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1732, 1664, 1479, 1108, 1061, 949, 826 cm^{-1}. MS (EI): *m*/*z* = 334 [M$^+$], 306 [(M – CO)$^+$], 279, 252, 233. HRMS (EI): calcd. for $C_{17}H_{18}O_7$ 334.1054; found 334.1053; calcd. C 61.07, H 5.43; found C 61.11, H 5.52. X-ray analysis confirmed the proposed structure (CCDC-943152).

3-[Hydroxy(phenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (12): In a flask 4-hydroxy-5,8-dimethoxy-2-naphthaldehyde (**11**[16]; 1.37 g, 5.91 mmol) was dissolved in dry THF (120 mL) and cooled to –78 °C. Then phenylmagnesium chloride (2.0 M in THF; 8.87 mL, 17.7 mmol) was added dropwise to the orange solution. The mixture was warmed up to room temp. overnight. Then the reaction was carefully quenched with water. Extraction with EtOAc, drying with sodium sulfate, filtration and evaporation of the solvents afforded the crude product. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 3:7 to 1:2) afforded 3-[hydroxy(phenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (**12**; 1.66 g, 5.35 mmol, 91% yield) as pale yellow crystals. R_f = 0.27 (EtOAc/*c*-hexane, 1:2), m.p. 142.0–143.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (s, 1 H), 7.84–7.81 (m, 1 H), 7.45–7.41 (m, 2 H), 7.35–7.28 (m, 2 H), 7.25–7.22 (m, 1 H), 6.88 (d, J = 1.6 Hz, 1 H), 6.65 (s, 2 H), 5.92 (s, 1 H), 3.99 (s, 3 H), 3.94 (s, 3 H), 2.31 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8, 150.5, 150.1, 143.8, 143.3, 128.6, 128.4, 127.7, 126.8, 115.3, 110.5, 109.8, 103.7, 103.5, 76.6, 56.5, 55.8 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3360, 1450, 1376, 1260, 1087, 970, 803, 721, 698, 628 cm^{-1}. MS (EI): *m*/*z* (%) = 311 (25) [[M + H]$^+$], 310 (4) [M$^+$], 294 (40) [(M – OH)$^+$], 282 (24) [(M – CO)$^+$], 268 (23), 136 (52), 120 (62), 108 (100) [(C_4H_8O)$^+$]. HRMS (EI): calcd. for $C_{19}H_{18}O_4$ 310.1201; found 310.1205 and calcd. for $C_{19}H_{18}O_4$ [M + H]$^+$ 311.1281; found 311.1283. X-ray analysis confirmed the proposed structure (CCDC-943153).

2′-[Hydroxy(phenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (13): 3-[Hydroxy(phenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (**12**; 250 mg, 0.806 mmol) was dissolved in dry acetonitrile (7.50 mL). Then the solution was added dropwise at 0 °C to a mixture of PIFA (762 mg, 1.77 mmol) in dry ethylene glycol (6.24 mL, 112 mmol) and dry acetonitrile (1.90 mL). The mixture was stirred for 6 h and allowed to warm to room temp. Then the reaction was quenched with satd. aq. $NaHCO_3$ solution and extracted with EtOAc. Drying with sodium sulfate, filtration and evaporation of the solvents afforded the crude material. Purification by column chromatography (silica gel, CH_2Cl_2/MeOH, 97.5:2.5) afforded 2′-[hydroxy(phenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**12**; 226 mg, 0.612 mmol, 76% yield) as a deep orange oil (note: a small quantity of this compound could be crystallized as orange crystals). R_f = 0.34 (CH_2Cl_2/MeOH, 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.2 Hz, 2 H), 7.37–7.25 (ddd, J = 10.3, 8.6, 5.0 Hz, 3 H), 7.13 (d, J = 9.2 Hz, 1 H), 6.98 (d, J = 9.2 Hz, 1 H), 6.23 (s, 1 H), 5.52 (s, 1 H), 4.50–4.40 (m, 1 H), 4.34 (dq, J = 11.5, 5.9 Hz, 2 H), 4.11–4.05 (m, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 2.92 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.5, 157.2, 154.2, 151.2, 140.5, 131.3, 129.5, 128.5, 128.0, 126.9, 120.8, 118.8, 114.6, 104.6, 70.8, 69.2, 69.1, 56.9, 56.9 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1640, 1579, 1476, 1253, 1142, 1055, 954, 700 cm^{-1}. MS (EI): *m*/*z* (%) = 368 (2) [M$^+$], 84 (100). HRMS (EI): calcd. for $C_{21}H_{20}O_6$ 368.1258; found 368.1260. X-ray analysis confirmed the proposed structure (CCDC-943154).

2′-Benzoyl-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (14): In a flask 2′-[hydroxy(phenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**13**; 156 mg, 0.424 mmol) was dissolved in dry CH_2Cl_2 (4.20 mL). The solution was treated at 0 °C with Dess–Martin periodinane (15 wt.-% in CH_2Cl_2; 1.32 mL, 0.635 mmol). The resulting orange mixture was stirred at room temp. for 2 h. Afterwards the solvents were removed in vacuo. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:1) afforded 2′-benzoyl-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**14**; 126 mg, 0.343 mmol, 81% yield) as a yellow oil. R_f = 0.25 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.6 Hz, 2 H), 7.61 (t, J = 7.3 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 7.22 (d, J = 9.3 Hz, 1 H), 7.05 (d, J = 9.3 Hz, 1 H), 6.22 (s, 1 H), 4.32 (t, J = 6.1 Hz, 2 H), 4.09 (t, J = 6.1 Hz, 2 H), 3.91 (s, 3 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1, 183.5, 154.3, 151.6, 150.7, 136.7, 134.0, 130.9, 130.6, 130.2, 128.7, 120.4, 119.8, 114.6, 103.6, 68.7, 57.0, 56.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1665, 1477, 1253, 1059, 729 cm^{-1}. MS (EI): *m*/*z* (%) = 366 (100) [M$^+$], 294 (35), 279 (24), 261 (13) [(M – PhCO)$^+$], 233 (87). HRMS (EI): calcd. for $C_{21}H_{18}O_6$ 366.1104; found 366.1103.

5′,8′-Dimethoxy-4′-oxo-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-2′-carbaldehyde (15): A solution of 2′-{[(*tert*-butyldimethyl-

silyl)oxy]methyl}-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**6**; 90.6 mg, 0.223 mmol) in dry THF (3.00 mL) was cooled to 0 °C. Then TBAF (1.0 M in THF; 0.245 mL, 0.245 mmol) was added and the resulting solution was stirred for 5 h at this temperature. The reaction was quenched with brine and diluted with EtOAc. The aqueous phase was extracted with EtOAc. Drying with sodium sulfate, filtration and evaporation of the solvents afforded the crude material. Purification by column chromatography (silica gel, CH_2Cl_2/MeOH, 30:1) gave 2′-(hydroxymethyl)-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (60.5 mg, 0.207 mmol, 93% yield) a pale yellow solid. R_f = 0.28 (CH_2Cl_2/MeOH, 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 9.2 Hz, 1 H), 7.00 (d, J = 9.2 Hz, 1 H), 6.40 (t, J = 1.6 Hz, 1 H), 4.48–4.42 (m, 2 H), 4.39 (d, J = 1.6 Hz, 2 H), 4.28–4.22 (m, 2 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 2.05 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.2, 156.7, 154.3, 151.5, 131.3, 126.4, 120.9, 118.8, 114.6, 103.9, 69.0, 59.9, 56.9, 57.0 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1641, 1277, 1144, 1051, 955, 814 cm^{-1}. MS (EI): *m*/*z* (%) = 292 (100) [M$^+$], 233 (66), 189 (24). HRMS (EI): calcd. for $C_{15}H_{16}O_6$ 292.0949; found 292.0947.

In a flask 2′-(hydroxymethyl)-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (109 mg, 0.374 mmol) was dissolved in dry CH_2Cl_2 (7.05 mL). The yellow solution was cooled to 0 °C and Dess–Martin periodinane (15 wt.-% in CH_2Cl_2) (1.17 mL, 0.560 mmol) was added dropwise. The mixture was stirred for 1 h at room temp. The solvent was evaporated and the crude product was subjected to column chromatography [silica gel, EtOAc/*c*-hexane (1:2) stepwise to pure EtOAc] to afford 5′,8′-dimethoxy-4′-oxo-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-2′-carbaldehyde (**15**; 98.7 mg, 0.340 mmol, 91% yield) as deep red crystals. R_f = 0.27 (EtOAc/*c*-hexane, 1:1), m.p. 209–212 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1 H), 7.22 (d, J = 9.3 Hz, 1 H), 7.03 (d, J = 9.3 Hz, 1 H), 6.72 (s, 1 H), 4.50–4.45 (m, 2 H), 4.45–4.39 (m, 2 H), 3.90 (s, 3 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.3, 184.7, 154.4, 151.9, 147.7, 140.3, 131.2, 120.5, 120.0, 114.3, 102.5, 70.1, 56.8, 56.8 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1706, 1579, 1467, 1258, 1039, 894, 802, 493 cm^{-1}. MS (EI): *m*/*z* (%) = 290 (100) [M$^+$], 247 (19) [(M – C_2H_3O)$^+$], 233 (49), 217 (16). HRMS (EI): calcd. for $C_{15}H_{14}O_6$ 290.0794; found 290.0790. X-ray analysis confirmed the proposed structure (CCDC-943155).

4-(Benzyloxy)-5,8-dimethoxy-2-naphthaldehyde (20): Ethyl 4-(benzyloxy)-5,8-dimethoxy-2-naphthoate (4.23 g, 11.6 mmol; see ref.[13a]) was dissolved in dry THF (58.0 mL). The solution was added dropwise at 0 °C to a stirred suspension of $LiAlH_4$ (1.07 g, 28.1 mmol) in dry THF (40.0 mL). The solution was stirred for 35 min at 0 °C. The mixture was then carefully worked up by adding water under external ice cooling, followed by an excess of diluted hydrochloric acid (2.0 M). The crude product was isolated by extraction with EtOAc and the extract was washed in turn with water, satd. aq. $NaHCO_3$, and finally with brine. Drying with sodium sulfate, filtration and evaporation of solvents afforded [4-(benzyloxy)-5,8-dimethoxynaphthalen-2-yl]methanol (3.74 g, 11.5 mmol, quant. yield) as a white or light yellow powder. ^{1}H-NMR and TLC of the crude product showed high purity. Otherwise further purification could be performed by column chromatography (silica gel, EtOAc/*c*-hexane, 3:7 to 1:1). R_f = 0.23 (EtOAc/*c*-hexane, 3:7), m.p. 145.5–147.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.81 (m, 1 H), 7.61 (dd, J = 7.8, 0.8 Hz, 2 H), 7.42 (dd, J = 10.2, 4.7 Hz, 2 H), 7.36–7.30 (m, 1 H), 7.01 (d, J = 1.4 Hz, 1 H), 6.78 (d, J = 8.5 Hz, 1 H), 6.75 (d, J = 8.5 Hz, 1 H), 5.20 (s, 2 H), 4.79 (s, 2 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 1.76 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.4, 151.2, 149.7, 138.8, 137.6, 128.8, 128.5, 127.7, 127.2, 118.5, 112.8, 108.3, 107.0, 104.8, 71.6, 65.8, 57.3, 55.9 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1606, 1466, 1362, 1276, 1146, 1082, 805, 728, 693 cm^{-1}. MS (EI): *m*/*z* (%) = 324 (100) [M$^+$], 233 (15) [(M – Bn)$^+$], 91 (3) [(C_7H_8)$^+$]. HRMS (EI): calcd. for $C_{20}H_{20}O_4$ 324.1358; found 324.1362; calcd. C 74.06, H 6.21; found C 73.78, H 6.23. X-ray analysis confirmed the proposed structure (CCDC-943156).

In a flask pyridine–sulfur trioxide (6.05 g, 38.0 mmol) was dissolved in dry dimethyl sulfoxide (DMSO; 13.6 mL) and stirred for 10 min. Afterwards the solution was added dropwise to a mixture of [4-(benzyloxy)-5,8-dimethoxynaphthalen-2-yl]methanol (3.74 g, 11.5 mmol) in dry DMSO (57.6 mL) containing dry triethylamine (20.9 mL, 150 mmol). The mixture was stirred at 50 °C for 8 h. The ochre mixture was worked up by adding an excess of water (note: the more water was added the less DMSO was in the crude product which facilitated the purification). The aqueous phase was extracted with EtOAc and dried with sodium sulfate. Filtration and evaporation of solvents afforded the crude product. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:9 to 2:8) afforded 4-(benzyloxy)-5,8-dimethoxy-2-naphthaldehyde (**20**; 3.50 g, 10.9 mmol, 94% yield) as bright yellow crystals. R_f = 0.29 (EtOAc/*c*-hexane, 1:4), m.p. 133.7–136.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1 H), 8.40 (d, J = 1.5 Hz, 1 H), 7.65–7.60 (m, 2 H), 7.46–7.39 (m, 3 H), 7.37–7.31 (m, 1 H), 6.99 (d, J = 8.6 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 1 H), 5.28 (s, 2 H), 4.00 (s, 3 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.5, 157.0, 151.2, 150.7, 137.1, 134.2, 128.6, 128.1, 127.8, 127.1, 123.6, 121.8, 111.4, 105.9, 102.8, 71.2, 57.6, 56.0 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1682, 1597, 1514, 1460, 1354, 1271, 1067, 799, 742 cm^{-1}. MS (EI): *m*/*z* (%) = 322 (100) [M$^+$], 279 (11), 231 (34) [(M – Bn)$^+$], 149 (27), 91 (93) [(C_7H_7)$^+$]. HRMS (EI): calcd. for $C_{20}H_{18}O_4$ 322.1207; found 322.1205; calcd. C 74.52, H 5.63; found C 74.14, H 5.60.

[4-(Benzyloxy)-5,8-dimethoxynaphthalen-2-yl](2-iodophenyl)methanol (21): The Grignard reagent was prepared freshly before use. In a flask 1,2-diiodobenzene (65.0 μL, 0.500 mmol) was dissolved in dry THF (1.50 mL) under argon. After cooling to –30 °C, isopropylmagnesium chloride (0.250 mL, 0.500 mmol; 2.0 M solution in THF) was added dropwise. The resulting mixture was warmed over a period of 20 min to –20 °C. At this temperature a solution of 4-(benzyloxy)-5,8-dimethoxy-2-naphthaldehyde (**20**; 161 mg, 0.499 mmol) in dry THF (4.00 mL) was added to the Grignard reagent. The mixture was warmed up to 10 °C over 4 h. The reaction was diluted with diethyl ether (5 mL) and afterwards quenched with aq. satd. NH_4Cl solution (5 mL) under ice bath cooling. Then the layers were separated and the aqueous phase was extracted with diethyl ether. The combined organic layers were dried with brine and then with sodium sulfate. After filtration the solvents were evaporated in vacuo. The crude product obtained was purified by column chromatography (silica gel, EtOAc/*c*-hexane, 0.5:9.5 to 1:9) to afford [4-(benzyloxy)-5,8-dimethoxynaphthalen-2-yl](2-iodophenyl)methanol (**21**; 227 mg, 0.431 mmol, 86% yield) as a white powder along with some unreacted starting material. R_f = 0.37 (EtOAc/*c*-hexane, 3:7), m.p. 157–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.84 (dd, J = 7.9, 1.1 Hz, 1 H), 7.57–7.52 (m, 2 H), 7.43 (dd, J = 7.8, 1.7 Hz, 1 H), 7.40–7.34 (m, 2 H), 7.31 (td, J = 7.2, 3.1 Hz, 2 H), 7.01–6.94 (m, 2 H), 6.76 (q, J = 8.5 Hz, 2 H), 6.17 (s, 1 H), 5.15 (s, 2 H), 3.93 (s, 3 H), 3.88 (s, 3 H), 2.51 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.1, 151.2, 149.9, 145.5, 140.1, 139.7, 137.6, 129.6, 128.8, 128.7, 128.5, 127.6, 127.3, 118.7, 113.3, 108.7, 107.4, 104.9, 99.2, 79.4, 71.6, 57.5, 56.0 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1601, 1359, 1268, 1065, 811, 750 cm^{-1}. MS (EI): *m*/*z* (%) = 527/526 (28/100) [M$^+$], 436/435 (14/49) [(M – Bn)$^+$], 400 (29), 364 (41), 308 (44) [($C_{20}H_{20}O_3$)$^+$], 91 (70) [(C_7H_7)$^+$]. HRMS (EI): calcd. for $C_{26}H_{23}IO_4$ 526.0643; found

526.0641. X-ray analysis confirmed the proposed structure (CCDC-943157).

3-(2-Iodobenzyl)-5,8-dimethoxynaphthalen-1-ol (22): In a small flask [4-(benzyloxy)-5,8-dimethoxynaphthalen-2-yl](2-iodophenyl)-methanol (**21**; 7.00 mg, 0.013 mmol) was stirred together with aluminum chloride (12.0 μmol, 2.10 mg) in dry CH_2Cl_2 (500 μL) at room temp. The mixture turned brown. After 3 h all starting material was gone as indicated by TLC. The mixture was filtered through Celite then water was added followed by extraction with ethyl acetate. The combined organic layers were dried with brine and then with sodium sulfate. After filtration the solvents were evaporated in vacuo. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 0.5:9.5 to 1:4) afforded 3-(2-iodobenzyl)-5,8-dimethoxynaphthalen-1-ol (**22**; 4.00 mg, 9.52 μmol, 72% yield) as an orange oil. Note: the product was very sensitive to oxidation. Right after purification by HPLC [Jasco HPLC, column: Vydac Protein & Peptide C18, method: from 40% to 95% acetonitrile within 20 min (mixture acetonitrile/water + 0.1% TFA), 19.6 min for **22**, at 25 °C] a satisfyingly ^{1}H NMR spectrum was recorded, but shortly thereafter ^{1}H and ^{13}C NMR spectra showed increasing impurities again. We also synthesized the de-iodo-analogue of **22** with nearly identical R_f value and a similar ^{1}H NMR spectra relative to **22**. R_f = 0.27 (EtOAc/*c*-hexane, 1:9). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.33 (s, 1 H), 7.78 (d, J = 7.9 Hz, 1 H), 7.50 (s, 1 H), 7.15 (d, J = 7.4 Hz, 1 H), 7.05 (d, J = 7.6 Hz, 1 H), 6.83 (td, J = 7.8, 1.4 Hz, 1 H), 6.67 (d, J = 1.2 Hz, 1 H), 6.56 (s, 2 H), 4.11 (s, 2 H), 3.93 (s, 3 H), 3.85 (s, 3 H) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1637, 1384, 1247, 1088, 1051, 1010, 724 cm^{-1}. MS (EI): *m*/*z* (%) = 421/420 (9/53) [M$^+$], 390 (37), 263 (100). HRMS (EI): calcd. for $C_{19}H_{17}IO_3$ 420.0224; found 420.0222.

3-[Hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (23): In a flask [4-(benzyloxy)-5,8-dimethoxynaphthalen-2-yl](2-iodophenyl)methanol (**21**; 512 mg, 0.973 mmol) was stirred in dry CH_2Cl_2 (24.3 mL) at –78 °C. Then a solution of boron tribromide (1.0 M in CH_2Cl_2; 1.07 mL, 1.07 mmol) was added dropwise at this temperature. The solution turned deep red. After 30 min the reaction was quenched by adding brine at –78 °C. The aqueous phase was extracted with CH_2Cl_2 and then with EtOAc. Drying with brine, sodium sulfate, filtration and evaporation of solvents gave the crude product. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:4 to 3:7) afforded 3-[hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (**23**; 239 mg, 0.547 mmol, 56% yield) as a light yellow crystalline foam. R_f = 0.28 (EtOAc/*c*-hexane, 3:7), m.p. 74.0–76.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (s, 1 H), 7.87 (d, J = 1.1 Hz, 1 H), 7.82 (dd, J = 7.9, 0.8 Hz, 1 H), 7.51 (dd, J = 7.8, 1.6 Hz, 1 H), 7.33 (dd, J = 11.1, 4.0 Hz, 1 H), 6.96 (td, J = 7.7, 1.7 Hz, 1 H), 6.87 (d, J = 1.6 Hz, 1 H), 6.67–6.60 (m, 2 H), 6.15 (s, 1 H), 3.98 (s, 3 H), 3.92 (s, 3 H), 2.45 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.7, 150.6, 150.1, 145.3, 141.7, 139.7, 129.6, 128.8, 128.7, 128.3, 115.3, 111.5, 110.2, 103.8, 103.6, 99.1, 79.3, 56.5, 55.9 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3370, 1613, 1514, 1451, 1380, 1245, 1087, 1045, 798, 744 cm^{-1}. MS (FAB): *m*/*z* = 436 [M$^+$], 419 [(M – OH)$^+$], 292. HRMS (FAB): calcd. for $C_{19}H_{17}IO_4$ 436.0174; found 436.0172; calcd. C 52.31, H 3.93; found C 52.64, H 4.02.

2′-(2-Iodobenzoyl)-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (24): In a flask 3-[hydroxy(2-iodophenyl)-methyl]-5,8-dimethoxynaphthalen-1-ol (**23**; 70.0 mg, 0.160 mmol) was dissolved in acetonitrile (1.00 mL). The solution was added at 0 °C to a mixture of PIFA (221 mg, 0.513 mmol) in dry ethylene glycol (1.24 mL, 22.3 mmol) and acetonitrile (0.370 mL). The mixture was allowed to come room temp. and stirred at this temperature for 10 h. The reaction was quenched with satd. aq. $NaHCO_3$ solution and the aqueous phase was extracted with EtOAc. Drying with sodium sulfate, filtration and evaporation of the solvents afforded the crude material. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:1 to 1.25:1) afforded 2′-[hydroxy(2-iodophenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (62.3 mg, 0.126 mmol, 78% yield) as a yellow amorphous solid (note: the compound could be co-crystallized one time on small quantity with $CDCl_3$ to afford yellow crystals). R_f = 0.21 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, J = 7.9, 0.9 Hz, 1 H), 7.62 (dd, J = 7.8, 1.6 Hz, 1 H), 7.41 (dd, J = 11.0, 4.1 Hz, 1 H), 7.17 (d, J = 9.2 Hz, 1 H), 7.04 (td, J = 7.6, 1.7 Hz, 1 H), 7.02 (d, J = 9.2 Hz, 1 H), 6.04 (s, 1 H), 5.70 (s, 1 H), 4.57–4.46 (m, 2 H), 4.41 (dt, J = 8.2, 6.1 Hz, 1 H), 4.25 (dd, J = 14.5, 6.7 Hz, 1 H), 3.88 (s, 6 H), 3.20 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.3, 154.9, 154.4, 151.4, 142.0, 139.8, 131.3, 130.1, 129.7, 129.2, 128.7, 121.0, 118.8, 114.7, 104.9, 98.9, 74.9, 69.2, 69.2, 57.0, 56.9 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1649, 1275, 1064, 964, 764 cm^{-1}. MS (EI): *m*/*z* (%) = 495/494 (22/100) [M$^+$], 448 (9), 368 (8) [(M – I)$^+$], 323 (5), 261 (25) [($C_{14}H_{13}O_5$)$^+$]. HRMS (EI): calcd. for $C_{21}H_{19}IO_6$ 494.0228; found 494.0226. X-ray analysis confirmed the proposed structure (CCDC-943158).

In a small flask 2′-[hydroxy(2-iodophenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (22.1 mg, 0.045 mmol) was dissolved in CH_2Cl_2 (1.00 mL). At 0 °C the mixture was treated with Dess–Martin periodinane (15 wt.-% in CH_2Cl_2; 186 μL, 0.089 mmol). The mixture was stirred overnight and then the mixture was allowed to warm to room temp. The solvent was evaporated and the residue was subjected to purification by column chromatography. Purification with (silica gel, EtOAc/*c*-hexane, 4:6) afforded 2′-(2-iodobenzoyl)-5′,8′-dimethoxy-4′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-4′-one (**24**; 15.2 mg, 0.031 mmol, 69% yield) as red amorphous solid. R_f = 0.33 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 7.9 Hz, 1 H), 7.45–7.37 (m, 2 H), 7.23 (d, J = 9.3 Hz, 1 H), 7.20–7.12 (m, 1 H), 7.03 (d, J = 9.3 Hz, 1 H), 6.31 (s, 1 H), 4.53–4.47 (m, 2 H), 4.47–4.40 (m, 2 H), 3.92 (s, 3 H), 3.89 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.0, 184.4, 154.3, 151.7, 147.9, 143.4, 140.5, 136.9, 132.1, 131.8, 129.9, 128.1, 120.4, 119.8, 114.2, 103.6, 92.4, 70.7, 56.9, 56.8 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1634, 1577, 1478, 1255, 1059, 984, 803 cm^{-1}. MS (EI): *m*/*z* (%) = 493/492 (20/90) [M$^+$], 365 (25) [(M – I)$^+$], 261 (19) {[M – (I-C_6H_4-CO)]$^+$}, 233 (100). HRMS (EI): calcd. for $C_{21}H_{17}IO_6$ 492.0072; found 492.0070.

2-[Hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalene-1,4-dione (26): 3-[Hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalen-1-ol (**23**; 40.0 mg, 0.092 mmol) was dissolved in a 2:1 mixture of acetonitrile (2.90 mL) and water (1.45 mL). The solution was cooled with an ice bad to 0 °C, followed by the addition of PIFA (138 mg, 0.321 mmol). The reaction mixture turned deep red. The ice bath was removed and the mixture was stirred at for 6 h at room temp. (note: shorter reaction times or lower temperatures resulted in a mixture of quinone and hydroquinone). The reaction was quenched with satd. aq. $NaHCO_3$, followed by extraction with EtOAc. The organic layer was washed with brine and dried with sodium sulfate. After filtration the solvents were evaporated in vacuo to yield the crude product. Purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:1 to 1.25:1) yielded 2-[hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalene-1,4-dione (**26**; 34.4 mg, 0.076 mmol, 83% yield) as deep red amorphous solid. R_f = 0.25 (EtOAc/*c*-hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 1 H), 7.56 (dd, J = 7.8, 1.5 Hz, 1 H), 7.41 (t, J = 7.5 Hz, 1 H), 7.33 (s, 2 H), 7.04 (td, J = 7.7, 1.6 Hz, 1 H), 6.32 (d, J = 0.6 Hz, 1 H), 6.11 (s, 1 H), 3.97 (s, 3 H), 3.95 (s,

3 H), 3.41 (br. s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.6, 184.8, 154.2, 153.7, 148.5, 141.6, 139.6, 135.2, 129.9, 128.7, 128.3, 120.9, 120.2, 98.7, 74.3, 56.9, 56.8 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1645, 1561, 1432, 1204, 1046, 966 cm^{-1}. MS (EI): *m*/*z* (%) = 450 (50) [M$^+$], 435 (24), 323 (100) [(M – I)$^+$], 305 (40), 231 (35) [($C_{13}H_{11}O_4$)$^+$]. HRMS (EI): calcd. for $C_{19}H_{15}IO_5$ 449.9962; found 449.9964.

2-(2-Iodobenzoyl)-5,8-dimethoxynaphthalene-1,4-dione (27): In a flask 2-[hydroxy(2-iodophenyl)methyl]-5,8-dimethoxynaphthalene-1,4-dione (**26**; 111 mg, 0.247 mmol) was dissolved in dry CH_2Cl_2 (6.16 mL). At 0 °C the mixture was treated with Dess–Martin periodinane (15 wt.-% in CH_2Cl_2) (1.03 mL, 0.493 mmol). The red mixture was stirred overnight thereby the reaction was allowed to come to room temp. The solvent was evaporated and the residue was subjected to purification by column chromatography. Purification with (silica gel, EtOAc/*c*-hexane, 1:1 to 1.25:1) to yield 2-(2-iodobenzoyl)-5,8-dimethoxynaphthalene-1,4-dione (**27**; 87.2 mg, 0.195 mmol, 79% yield) as deep red amorphous solid. R_f = 0.29 (EtOAc/*c*-hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 7.9, 0.9 Hz, 1 H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.44 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.36 (s, 2 H), 7.19 (td, *J* = 7.7, 1.7 Hz, 1 H), 6.99 (s, 1 H), 3.98 (s, 3 H), 3.92 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.9, 184.6, 182.3, 154.1, 153.8, 144.7, 141.9, 140.9, 137.5, 133.1, 131.2, 128.4, 121.2, 121.1, 120.5, 93.0, 57.1, 57.0 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1649, 1562, 1252, 1201, 823, 753 cm^{-1}. MS (EI): *m*/*z* (%) = 451/450 (3/14) [(M + 2 H)$^+$], 449/448 (3/12) [M$^+$], 321 (100) [(M – I)$^+$]. HRMS (EI): calcd. for $C_{19}H_{13}IO_5$: 447.9806; found 447.9808.

General Procedure for Naphthoquinone Monoketal Diels–Alder Reactions

Procedure A: The dienophile was placed with a stirring bar in a closed vial and covered with approx. 200 µL diene. The flask was placed into the microwave reactor and treated for 30 min at 170 °C by 300 W (power was down-regulated automatically when the maximum temperature was reached). By irradiation the suspension turned into a clear solution.

Procedure B: The dienophile was placed with a stirring bar in a suitable flask and covered with approx. 200 µL diene. The flask was stirred at 170 °C for 90 min. After cooling down, the solution was directly subjected to column chromatography.

Alternatively, unreacted diene could also be recovered by Kugelrohr distillation before column chromatography. The relative stereochemistry of the products was confirmed by NOESY as well as TOCSY experiments on a 600 MHz Bruker Avance III spectrometer.

Diels–Alder Reaction to Tricycle 8

Procedure A: Dienophile **6** (8.70 mg, 0.021 mmol), diene **7**, purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:9 to 2:8), 8.20 mg of 8 (0.014 mmol, 64% yield) along with unreacted starting material (quant. brsm yield).

Procedure B: Dienophile **6** (59.1 mg, 0.145 mmol), diene **7**, purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:9 to 2:8), 80.1 mg of **8** (0.132 mmol, 91% yield).

{(4*R*,4a*R*,9a*R*)-4,9a-Bis[(*tert*-butyldimethylsilyl)oxy]-5,8-dimethoxy-2-methyl-4,4a-dihydro-1*H*-spiro(anthracene-9,2′-[1,3]dioxolan)-10(9a*H*)-one} (8): Colorless oil. R_f = 0.49 (EtOAc/*c*-hexane, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (d, *J* = 9.1 Hz, 1 H), 6.83 (d, *J* = 9.1 Hz, 1 H), 5.07 (s, 1 H), 4.62–4.55 (m, 1 H), 4.13 (dd, *J* = 12.4, 6.7 Hz, 1 H), 3.95 (dd, *J* = 13.4, 6.6 Hz, 1 H), 3.92–3.87 (m, 1 H), 3.87 (d, *J* = 9.3 Hz, 1 H), 3.80 (s, 3 H), 3.83–3.77 (m, 1 H), 3.74 (s, 3 H), 3.68 (d, *J* = 9.3 Hz, 1 H), 3.16 (d, *J* = 6.6 Hz, 1 H), 2.19 (d, *J* = 16.7 Hz, 1 H), 2.07 (d, *J* = 16.7 Hz, 1 H), 1.29 (s, 3 H), 0.86 (s, 9 H), 0.85 (s, 9 H), 0.08 (s, 3 H), 0.02 (d, *J* = 1.0 Hz, 6 H), –0.01 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.1, 150.6, 150.4, 134.9, 130.2, 130.1, 125.1, 116.1, 114.2, 110.3, 68.7, 67.1, 66.4, 65.0, 57.8, 57.2, 57.0, 47.6, 32.0, 26.1, 25.8, 22.7, 18.5, 18.1, –4.4, –4.7, –5.2, –5.4 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2928, 1705, 1471, 1254, 1057, 833, 772 cm^{-1}. MS (EI): *m*/*z* (%) = 604 (30) [M$^+$], 547 (57) [(M – *t*Bu)$^+$], 415 (100) [($C_{22}H_{27}O_6Si$)$^+$]. HRMS (EI): calcd. for $C_{32}H_{52}O_7Si_2$ 604.3253; found 604.3252.

Diels–Alder Reaction to Tricycles 17a, 17b, 17c

Procedure A: Dienophile **10** (34.4 mg, 0.103 mmol), diene **7**, purification by column chromatography (silica gel, EtOAc/*c*-hexane, 2:8 to 3:7), 37.8 mg (0.071 mmol, 69% yield) of **17a/b** (*dr* 3:1); 8.50 mg (0.016 mmol, 16% yield) of **17c**.

Procedure B: Dienophile **10** (91.0 mg, 0.272 mmol), diene **7** (500 µL), purification by column chromatography (silica gel, EtOAc/*c*-hexane, 1:4 to 3:7), 118 mg (0.222 mmol, 81% yield) of **17a/b** (*dr* 4:1); 22.5 mg (0.042 mmol, 16% yield) of **17c**.

The mixture of **17a/b** could not be separated by column chromatography or HPLC.

Ethyl (4*R*,4a*S*,9a*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]-5,8-dimethoxy-2-methyl-10-oxo-4,4a,9a,10-tetrahydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolane]-9a-carboxylate (17a): Major isomer, extracted signals from mixture with **17b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 9.1 Hz, 1 H), 6.87 (d, *J* = 9.1 Hz, 1 H), 5.44 (s, 1 H), 4.60 (s, 1 H), 4.27–4.08 (m, 5 H), 3.98–3.88 (m, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.68 (d, *J* = 5.1 Hz, 1 H), 2.76 (d, *J* = 17.5 Hz, 1 H), 2.14 (d, *J* = 17.8 Hz, 1 H), 1.58 (s, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 0.78 (s, 9 H), 0.02 (s, 3 H), 0.00 (s, 3 H) ppm.

Ethyl (4*S*,4a*S*,9a*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]-5,8-dimethoxy-2-methyl-10-oxo-4,4a,9a,10-tetrahydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolane]-9a-carboxylate (17b): Most signals are covered by **17a**. See spectra for details. **Mixture 17a/b:** colorless oil. R_f = 0.48 (EtOAc/*c*-hexane, 1:1). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.2, 193.5, 171.9, 171.6, 153.5, 151.7, 151.2, 149.7, 138.4, 135.4, 133.4, 131.4, 129.9, 125.9, 125.2, 124.0, 122.5, 121.2, 120.1, 119.4, 117.7, 115.0, 114.6, 113.9, 110.3, 109.7, 108.3, 67.9, 67.5, 67.2, 66.0, 65.4, 61.6, 60.8, 59.3, 58.3, 57.9, 57.3, 57.1, 57.0, 52.8, 43.2, 33.2, 32.5, 26.1, 26.0, 25.8, 23.3, 23.2, 18.3, 18.0, 14.2, 13.5, –3.4, –4.4, –4.7 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1710, 1477, 1269, 1208, 1002, 959, 920, 836, 805, 776, 723 cm^{-1}. MS (EI): *m*/*z* (%) = 532 (19) [M$^+$], 475 (100) [(M – *t*Bu)$^+$], 402 (45) [($C_{22}H_{26}O_7$)$^+$]. HRMS (EI): calcd. for $C_{28}H_{40}O_8Si$ 532.2491; found 532.2493.

Ethyl (1*S*,4a*R*,9a*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5,8-dimethoxy-3-methyl-10-oxo-4,4a,9a,10-tetrahydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolane]-9a-carboxylate (17c): Colorless oil. R_f = 0.64 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 9.1 Hz, 1 H), 6.89 (d, *J* = 9.1 Hz, 1 H), 5.47–5.35 (m, 1 H), 4.91 (d, *J* = 5.6 Hz, 1 H), 4.39–4.25 (m, 3 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.96–3.86 (m, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.58 (d, *J* = 6.8 Hz, 1 H), 3.06 (d, *J* = 18.5 Hz, 1 H), 2.23 (dd, *J* = 18.0, 6.6 Hz, 1 H), 1.69 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 0.52 (s, 9 H), –0.09 (s, 3 H), –0.37 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.0, 171.0, 152.4, 151.6, 137.4, 133.2, 125.0, 122.2, 118.2, 114.2, 110.0, 68.8, 68.3, 67.4, 62.6, 61.1, 57.2, 57.2, 44.6, 27.5, 25.5, 23.4, 17.9, 14.2, –4.9, –5.2 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1720, 1693, 1471, 1262, 1072, 1009, 958, 879, 833, 778, 715, 547 cm^{-1}. MS (EI): *m*/*z* (%) = 532 (1) [M$^+$], 475 (100) [(M – *t*Bu)$^+$]. HRMS (EI): calcd. for $C_{28}H_{40}O_8Si$ 532.2495; found 532.2492.

Diels–Alder Reaction to Tricycles 18c, 18d

Procedure A: Dienophile **14** (8.70 mg, 0.024 mmol), diene **7**, purification by column chromatography (silica gel, EtOAc/*c*-hexane, 3:7 to 2:3), 4.3 mg (7.61 μmol, 32% yield) of **18c/d** (*dr* 2.5:1).

Procedure B: Dienophile **14** (130 mg, 0.354 mmol), diene **7** (300 μL), purification by column chromatography (silica gel, EtOAc/*c*-hexane, 3:7 to 2:3), 85.8 mg (0.152 mmol, 43% yield) of **18c/d** (*dr* 2:1). The mixture of **18c/d** could not be separated by column chromatography or HPLC.

(1*S*,4a*R*,9a*R*)-9a-Benzoyl-1-[(*tert*-butyldimethylsilyl)oxy]-5,8-dimethoxy-3-methyl-4,4a-dihydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolan]-10(9a*H*)-one (18c): Major isomer, extracted signals from mixture with **18d**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.33–7.29 (m, 1 H), 7.21 (dd, *J* = 8.0, 7.5 Hz, 2 H), 6.98 (d, *J* = 9.1 Hz, 1 H), 6.91 (d, *J* = 9.1 Hz, 1 H), 5.66–5.63 (m, 1 H), 5.24 (d, *J* = 4.7 Hz, 1 H), 4.19 (dd, *J* = 13.4, 6.9 Hz, 1 H), 4.14–4.04 (m, 2 H), 3.92–3.88 (m, 1 H), 3.82 (s, 3 H), 3.74 (dd, *J* = 9.9, 8.0 Hz, 1 H), 3.54 (s, 3 H), 2.60 (dd, *J* = 17.7, 8.0 Hz, 1 H), 2.45 (dd, *J* = 17.8, 9.9 Hz, 1 H), 1.75 (s, 3 H), 0.60 (s, 9 H), 0.00 (s, 3 H), –0.06 (s, 3 H) ppm.

(1*R*,4a*R*,9a*R*)-9a-Benzoyl-1-[(*tert*-butyldimethylsilyl)oxy]-5,8-dimethoxy-3-methyl-4,4a-dihydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolan]-10(9a*H*)-one (18d): Most signals are covered by **18c**. See spectra for details. **Mixture 18c/d:** pale yellow amorphous solid. R_f = 0.48 (EtOAc/*c*-hexane, 2:8). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.8, 202.3, 198.2, 192.6, 154.1, 151.6, 151.4, 150.4, 140.7, 140.1, 138.1, 133.5, 132.0, 131.4, 130.6, 129.6, 129.4, 128.8, 128.5, 128.4, 128.0, 127.9, 127.4, 127.2, 126.4, 125.0, 123.4, 122.4, 121.4, 117.6, 115.4, 114.9, 110.5, 108.8, 68.1, 67.1, 66.9, 66.6, 65.6, 65.3, 62.5, 58.2, 57.5, 57.1, 57.1, 54.1, 45.1, 33.4, 33.1, 26.1, 26.0, 25.9, 25.8, 23.3, 23.2, 18.2, 18.1, –3.0, –3.7, –4.6, –5.1 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 1676, 1470, 1269, 1047, 827, 771, 699 cm^{-1}. MS (EI): *m*/*z* (%) = 564 (16) [M$^+$], 507 (70) [(M – *t*Bu)$^+$], 459 (28) [(M – PhCO)$^+$], 209 (60), 149 (100), 105 (76) [(C_7H_6O)$^+$]. HRMS (EI): calcd. for $C_{32}H_{40}O_7Si$ 564.2545; found 564.2543.

Diels–Alder Reaction to Tricycles 19b, 19c

Procedure A: Dienophile **15** (72.6 mg, 0.250 mmol), diene **16** (350 μL), purification by column chromatography (silica gel, EtOAc/*c*-hexane, 0.5:9.5 to 3:7), 73.2 mg (0.150 mmol, 60% yield) of **19b/c** (*dr* 1.1:1). Compound **19c** was separated by HPLC [Jasco HPLC, column: Vydac Protein & Peptide C18, method: from 40% to 95% acetonitrile within 20 min (mixture acetonitrile/water), 18.750 min for **19c**, 19.308 min for **19b**, at 25 °C].

(4*R*,4a*S*,9a*S*)-4-[(*tert*-Butyldimethylsilyl)oxy]-5,8-dimethoxy-3-methyl-10-oxo-4,4a,9a,10-tetrahydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolane]-9a-carbaldehyde (19b): Colorless oil. Compound **19b** was enriched by HPLC. Extracted signals from a mixture with **19c.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.77 (s, 1 H), 7.03 (d, *J* = 9.2 Hz, 1 H), 6.90 (d, *J* = 9.2 Hz, 1 H), 5.16 (s, 1 H), 4.38–4.33 (m, 1 H), 4.22–4.15 (m, 1 H), 4.14–4.04 (m, 1 H), 4.04–3.95 (m, 2 H), 3.81 (s, 3 H), 3.77 (s, 3 H), 3.62 (d, *J* = 4.5 Hz, 1 H), 2.52 (d, *J* = 13.4 Hz, 1 H), 2.33 (d, *J* = 16.9 Hz, 1 H), 1.67 (s, 3 H), 0.89 (s, 9 H), 0.12 (s, 3 H), 0.08 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.9, 192.9, 151.9, 150.5, 139.0, 129.5, 126.1, 118.5, 118.3, 114.4, 109.7, 68.8, 66.9, 66.6, 58.1, 57.5, 56.8, 52.4, 25.9, 24.7, 19.5, 18.4, –4.4, –4.8 ppm.

(1*S*,4a*R*,9a*R*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5,8-dimethoxy-2-methyl-10-oxo-4,4a,9a,10-tetrahydro-1*H*-spiro[anthracene-9,2′-[1,3]dioxolane]-9a-carbaldehyde (19c): Colorless oil/prisms. R_f = 0.29 (EtOAc/*c*-hexane, 3:7). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.66 (s, 1 H), 7.06 (d, *J* = 9.2 Hz, 1 H), 6.94 (d, *J* = 9.1 Hz, 1 H), 5.41 (s, 1 H), 4.64 (s, 1 H), 4.46–4.33 (m, 1 H), 4.24 (ddd, *J* = 23.3, 12.9, 7.0 Hz, 2 H), 3.93 (dd, *J* = 9.2, 4.5 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 3.61 (d, *J* = 7.1 Hz, 1 H), 3.22 (d, *J* = 18.4 Hz, 1 H), 2.19–1.97 (m, 1 H), 1.72 (s, 3 H), 0.60 (s, 9 H), 0.06 (d, *J* = 4.3 Hz, 3 H), –0.67 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.9, 193.2, 152.5, 151.6, 134.2, 131.8, 124.5, 124.0, 117.7, 114.2, 110.8, 69.4, 69.1, 67.7, 63.7, 57.0, 56.7, 42.8, 25.7, 22.9, 21.0, 18.5, –4.7, –5.3 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2927, 1706, 1473, 1268, 1065, 830, 776 cm^{-1}. MS (EI): *m*/*z* (%) = 488 (not listed) [M$^+$], 431 (100) [(M – *t*Bu)$^+$], 403 (20) [($C_{21}H_{27}O_6Si$)$^+$], 358 (67) [($C_{20}H_{22}O_6$)$^+$]. HRMS (EI): calcd. for $C_{26}H_{36}SiO_7$ 488.2232; found 488.2230. X-ray analysis confirmed the proposed structure (CCDC-928347).

Diels–Alder Reaction to Tricycles 30a, 30b: In a flask 2-(2-iodobenzoyl)-5,8-dimethoxynaphthalene-1,4-dione (**27**; 18.1 mg, 0.040 mmol) was stirred with (*E*)-(buta-1,3-dien-1-yloxy)(*tert*-butyl)dimethylsilane (**25**; 150 μL). After 1 h at 50 °C the deep red suspension became a clear yellow solution, which was directly purified by column chromatography (silica gel, EtOAc/*c*-hexane, 1:9 to 2:3) to afford **30a** (18.7 mg, 0.030 mmol, 74%) as a yellow oil as well as compound **30b**. The latter compound showed impurities in the ^{1}H NMR spectra and was purified again by HPLC [Jasco HPLC, column: Vydac Protein & Peptide C18, 5% water/95% acetonitrile (both solvents with 0.1% TFA), 26.925 min at 25 °C] to give **30b** (6.0 mg, 9.49 μmol, 24%) as an orange oil.

(1*S*,4a*R*,9a*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]-9a-(2-iodobenzoyl)-5,8-dimethoxy-1,4,4a,9a-tetrahydroanthracene-9,10-dione (30a): R_f = 0.48 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.9 Hz, 1 H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.34–7.27 (m, 2 H), 7.23 (d, *J* = 9.3 Hz, 1 H), 7.06 (td, *J* = 7.7, 1.6 Hz, 1 H), 5.96–5.84 (m, 1 H), 5.77–5.64 (m, 1 H), 5.05 (d, *J* = 5.1 Hz, 1 H), 3.94 (s, 3 H), 3.89 (s, 3 H), 3.83 (d, *J* = 6.5 Hz, 1 H), 2.98 (d, *J* = 18.7 Hz, 1 H), 2.17–2.07 (m, 1 H), 0.52 (s, 9 H), –0.08 (s, 3 H), –0.22 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.6, 193.4, 193.2, 154.4, 151.5, 141.8, 141.3, 131.6, 129.7, 127.6, 127.4, 126.4, 124.7, 121.7, 118.5, 94.7, 70.0, 69.1, 58.1, 57.2, 47.3, 29.8, 25.4, 21.6, 17.8, –4.3, –5.5 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2926, 1703, 1461, 1260, 1196, 1012, 899, 836, 776, 670 cm^{-1}. MS (EI): *m*/*z* (%) = 632 (not listed) [M$^+$], 617 (not listed) [(M – Me)$^+$], 604 (not listed) [($C_{27}H_{29}IO_6Si$)$^+$], 575 (39) [(M – *t*Bu)$^+$], 401 (3) [($C_{22}H_{29}O_5Si$)$^+$], 312 (56), 231 (100) [(C_7H_4IO)$^+$]. HRMS (EI): calcd. for $C_{29}H_{33}IO_6Si$ 632.1089; found 632.1091.

(1*R*,4a*R*,9a*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]-9a-(2-iodobenzoyl)-5,8-dimethoxy-1,4,4a,9a-tetrahydroanthracene-9,10-dione (30b): R_f = 0.30 (EtOAc/*c*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.86 (d, *J* = 7.2 Hz, 1 H), 7.39 (dd, *J* = 11.0, 4.2 Hz, 1 H), 7.21 (d, *J* = 9.3 Hz, 1 H), 7.13 (d, *J* = 9.3 Hz, 1 H), 7.05 (td, *J* = 7.7, 1.5 Hz, 1 H), 6.05–5.92 (m, 1 H), 5.80 (ddd, *J* = 10.0, 5.1, 2.1 Hz, 1 H), 5.30 (d, *J* = 4.8 Hz, 1 H), 3.87 (s, 3 H), 3.78 (dd, *J* = 12.4, 6.5 Hz, 1 H), 3.75 (s, 3 H), 2.60–2.50 (m, 1 H), 2.07–1.96 (m, 1 H), 0.77 (s, 9 H), 0.09 (s, 3 H), –0.18 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1, 192.1, 154.7, 152.3, 142.2, 140.0, 132.3, 129.3, 128.2, 127.5, 126.0, 125.7, 122.3, 120.9, 120.3, 95.6, 72.8, 67.0, 57.6, 57.2, 47.1, 29.9, 27.9, 26.1, 25.8, 18.3, –3.6, –4.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2928, 1681, 1472, 1261, 1197, 1032, 962, 838 cm^{-1}. MS (EI): *m*/*z* (%) = 633/632 (1/3) [M$^+$], 617 (1) [(M – Me)$^+$], 575 (69) [($C_{25}H_{24}IO_6Si$)$^+$], 506 (1) [(M – I)$^+$], 448 (38) [($C_{25}H_{24}O_6Si$)$^+$], 401 (50) [(M – (I-C_6H_4-CO))$^+$], 231 (100) [C_7H_4IO]. HRMS (EI): calcd. for $C_{29}H_{33}IO_6Si$ 632.1089; found 632.1091.

CCDC-943150 (for **6**), -943151 (for **9**), -943152 (for **10**), -943153 (for **12**), -943154 (for **13**), -943155 (for **15**), -928347 (for **19c**),

-943156 (for **20**), -943157 (for **21**), and -943158 {for 2′-[hydroxy(2-iodophenyl)methyl]-5′,8′-dimethoxy-4′*H*-spiro([1,3]dioxolane-2,1′-naphthalen)-4′-one} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic data; copies of the ^{1}H NMR and ^{13}C NMR spectra of all key intermediates and final products are available online.

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