Tetrahedron 72 (2016) 1533–1540

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of bridged biarylbisquinones and effects of biaryl dihedral angles on photo- and electro-chemical properties

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 23 January 2016
Accepted 1 February 2016
Available online 2 February 2016

Keywords:
Auxochrome
Biarylbisquinone
Biaryl conformation
Diels–Alder reaction
Energy band gap

ABSTRACT

A series of bridged biarylbisquinones, QBINOLs **1**–**4**, and their corresponding monomers, QNaphs **5**–**6**, were designed to demonstrate the influence of biaryl conformation on the photo- and electro-chemical properties of the molecules. All target compounds were synthesized from the Diels–Alder reaction between silyl enol ethers of the corresponding naphthyl or binaphthyl derivatives and *p*-benzoquinone. Addition of an OMe auxochrome or formation of the dimeric structures affect the absorption spectra and the energy band gap (Eg), but not the reduction potentials of the molecules. Narrowing the dihedral angles of the QBINOLs by shortening methylene bridges limited the contribution of bridging OR auxochromes and therefore resulted in lower HOMO levels and larger Eg.

1. Introduction

The specific conformation of a biaryl axis greatly influences not only the molecular structure but also the electronic and optical properties of biaryl molecules.[1] Conformational studies of binaphthyl derivatives are therefore of great interest. The ability to control the biaryl conformation could lead to applications in the design of asymmetric catalysts with improved enantioselectivity,[2] specific molecular recognition,[3] and helical twisting of liquid crystals.[4] The conformation of biaryls, as described in terms of the dihedral angle, can be controlled by varying the length of a linking group between each aryl ring.[1b,5] A specific conformation would then possess a unique set of molecular properties due to the difference in the degree of π-orbital overlap between the two monomer subunits. Thus, by simply changing the length of the bridge which is synthetically straightforward, the optical and electrochemical properties of the materials can potentially be manipulated.

Quinones with extended π-conjugation attached with electron donating and/or electron withdrawing functional groups have widely been used in designing novel organic materials, e.g., helical columnar liquid crystals and self-assembling helical aggregation,[6] nonlinear optical (NLO) materials,[7] or as a chiral catalytic system in asymmetric reactions.[8] In this work, a series of dimeric quinone-conjugated biaryl structures (Fig. 1) were designed to investigate the effect of changing the conformation along the biaryl axis on the

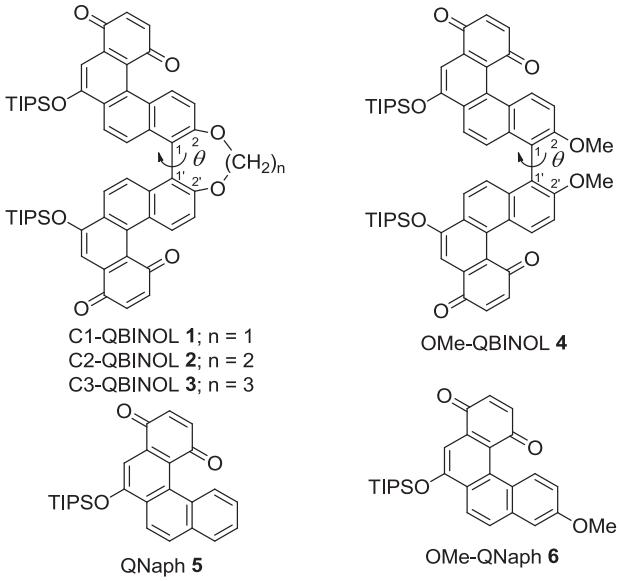

Fig. 1. Chemical structures of QBINOLs **1**–**4**, QNaph **5** and OMe-QNaph **6**, as well as the assigned dihedral angle (θ).

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http://dx.doi.org/10.1016/j.tet.2016.02.001
0040-4020/

photo- and electronic properties of the system. The structure consists of two parts, i.e., i) a biaryl with an alkyl linker which has different chain lengths to control the molecular conformation of the biaryl system, and ii) a quinone which is a key component used for the study of photo- and electronic properties.

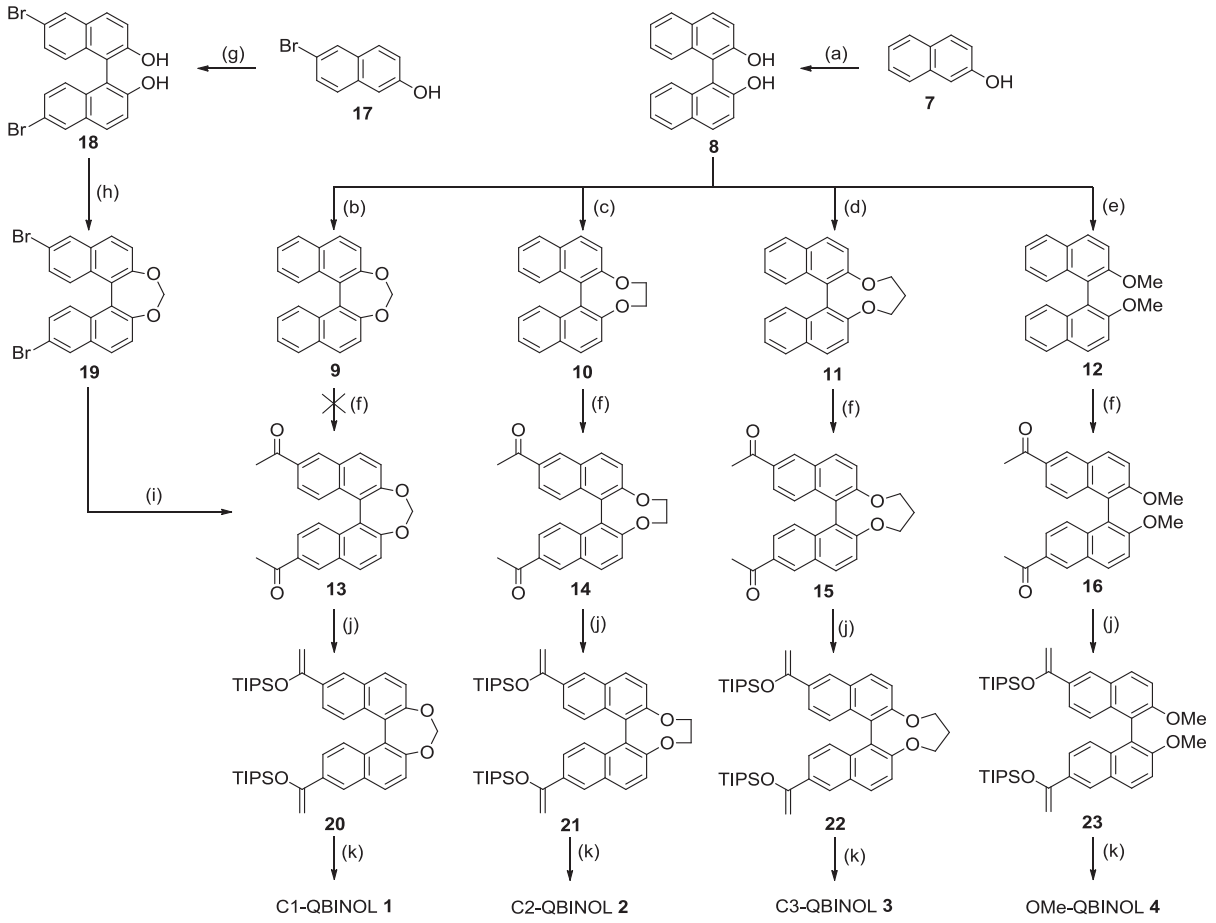
2. Results and discussion

The synthesis of biarylbisquinone derivatives, assigned as QBINOLs **1**–**4**, as well as their corresponding monomeric quinone–naphthyl derivatives, QNaphs **5**–**6**, is illustrated in Schemes 1 and 2. Oxidative coupling of commercially available 2-naphthol (**7**) was carried out by using $FeCl_3$ in boiling H_2O to yield BINOL (**8**) in 91% yield.[9] Then BINOL (**8**) was alkylated with CH_2I_2, $Br(CH_2)_2Br$, $Br(CH_2)_3Br$, and CH_3I to provide compounds **9**–**12** in 85, 21, 77, and 89% yield, respectively.[5c,d,10]

BINOLs **9**–**12** were then treated with acetyl chloride (AcCl) in the presence of a suspension of aluminium chloride ($AlCl_3$) in 1,2-dichloroethane under a N_2 atmosphere at 0 °C for 4 h to achieve the compounds **14**–**16** in 90, 97 and 95% yield, respectively.[11] However, under these conditions, compound **9** failed to give the diacetylated product due to the cleavage of the acetal linker. Thus, an alternative route towards compound **13** was needed. Oxidative coupling reaction of a commercially available 6-bromo-2-naphthol (**17**) with a stoichiometric amount of $CuCl_2{\cdot}2H_2O$ in degassed MeOH under N_2 atmosphere at room temperature for 12 h provided compound **18** in 87% yield.[12] Compound **18** was then alkylated with CH_2I_2 in the presence of K_2CO_3 in refluxing acetone to provide compound **19** in 64% yield. Bis-lithiation of 6,6′-dibromo-2,2′-binaphthol **19** with *n*-BuLi at −78 °C followed by trapping of the dianion intermediate with *N*,*N*-dimethyl-acetamide yielded compound **13** in 34% yield.[13]

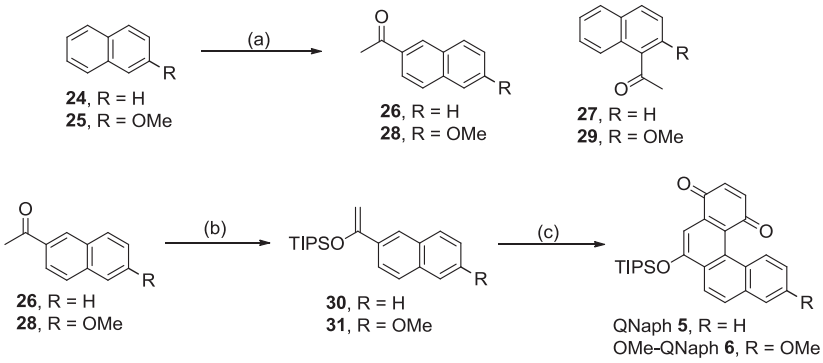
Subsequently, diacetyl binaphthols **13**–**16** were treated with triisopropylsilyl triflate (TIPSOTf) in the presence of triethylamine (Et_3N) to give silyl enol ethers **20**–**23**, respectively. Without further purification, the silyl enol ethers were then subjected to the Diels–Alder reaction[14] with excess *p*-benzo-quinone in refluxing toluene to afford the target QBINOLs **1**–**4** in low to moderate yields. The high regioselectivity of the Diels–Alder reaction was precedent and could be rationalized in terms of the preservation of the naphthalene B ring's aromaticity upon addition to the α-position.[14c]

The synthetic steps towards QNaph **5** and OMe-QNaph **6** are



Scheme 1. Synthesis of QBINOLs **1**–**4**. Conditions: (a) $FeCl_3$, boiling H_2O, 3 h, **8** (91%); (b) CH_2I_2, K_2CO_3, acetone, reflux, 2 days, **9** (85%); (c) $Br(CH_2)_2Br$, K_2CO_3, acetone, reflux, 2 days, **10** (21%); (d) $Br(CH_2)_3Br$, K_2CO_3, acetone, reflux, 6 h, **11** (77%); (e) CH_3I, K_2CO_3, acetone, reflux, 3 h, (89%); (f) AcCl, $AlCl_3$, 1,2-dichloroethane, N_2, 0 °C, 4 h, **13** (not observed), **14** (90%), **15** (97%), and **16** (95%); (g) $CuCl_2{\cdot}2H_2O$, degassed MeOH, N_2, rt, 12 h, (87%); (h) CH_2I_2, K_2CO_3, acetone, reflux, 2 days, (64%); (i) 1) *n*-BuLi, THF, N_2, −78 °C, 2 h, 2) *N*,*N*-dimethylacetamide, −78 °C, 4 h, (34%); (j) TIPSOTf, Et_3N, CH_2Cl_2, N_2, 0 °C to rt, 4 h; (k) *p*-benzoquinone, toluene, reflux, 2 days, **1** (31%), **2** (13%), **3** (23%), and **4** (49%).

summarized in Scheme 2. Friedel–Crafts acetylation of naphthalene (**24**) and 2-methoxynaphthalene (**25**) with AcCl in the presence of $AlCl_3$ in 1,2-dichloroethane at 0 °C for 4 h gave 2-acetyl naphthalene (**26**) in 19% yield and 6-methoxy-2-acetyl naphthalene (**28**) in 51% yield, respectively, along with the undesired, more electronically favoured regioisomers,[15] 1-acetyl naphthalene (**27**) and 2-methoxy-1-acetyl naphthalene (**29**) in 73% and 46% yield, respectively. Compounds **26** and **28** were then treated with TIPSOTf in the presence of Et_3N to afford silyl enol ethers **30** and **31**, which were, without purification, then subjected to Diels–Alder reaction



Scheme 2. Synthesis of QNaph **5** and OMe-QNaph **6**. Conditions: (a) AcCl, $AlCl_3$, 1,2-dichloroethane, N_2, 0 °C, 4 h, **26** (19%), **27** (73%), **28** (51%), and **29** (46%); (b) TIPSOTf, Et_3N, CH_2Cl_2, N_2, 0 °C to rt, 4 h; (c) *p*-benzoquinone, toluene, reflux, 2 days, **5** (8%), and **6** (67%).

with excess *p*-benzoquinone in refluxing toluene to provide the desired adducts **5** and **6** in 8% and 67% yields, respectively, in two steps.

The absorption spectra of compounds **1**–**6** were measured in $CHCl_3$ solution (1×10^{-5} M) as shown in Fig. 2 and the data were summarized in Table 1. In Fig. 2, considering the absorption spectra of the quinone moiety in the region of 375–580 nm, assigned as n-π* transition,[16] it was found that the band for OMe-QNaph **6** was bathochromically shifted to 442 nm, when compared with that of QNaph **5** at 424 nm. The observed red shift is the expected outcome from the addition of an auxochrome OMe group to QNaph.[17] In comparison between the monomeric OMe-QNaph **6** and the dimeric OMe-QBINOL **4**, both absorption spectra are similar in shape but red shift was observed in the case of dimeric structure OMe-QBINOL **4**. The shift implied the π-electron contribution of two phenanthryl units through the coplanar resonance structure in the excited state as suggested by Friedel.[18]

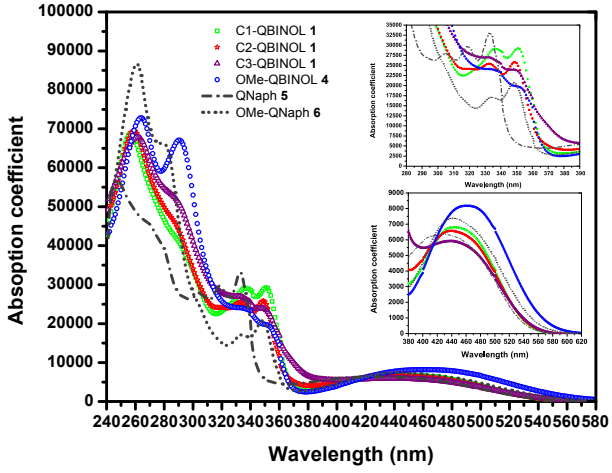


Fig. 2. UV–vis absorption spectra of compounds **1**–**6** in $CHCl_3$ solution (1.0×10^{-5} M).

Interestingly, when the dihedral angles (θ, defined as C_2–C_1–$C_{1'}$–$C_{2'}$ in Fig. 1) of the dimeric biaryl frameworks were decreased from non-bridged OMe-QBINOL **4** to bridged QBINOLs **1**–**3** by consecutively shortening the methylene linkage, the blue shifts were observed. This observation is closely related to the previous findings reported by Tebby et al.[5a] who studied the UV absorption of biphenyl systems. The observed blue shift could be explained in terms of the rigidity of the bridged binaphthyl structures which are locked by the linker. The linking groups constrain the orientation of the oxygen lone pair electron orbitals leading to the diminishing in the contribution of lone pair electrons of oxygen atoms on the bridges to the π-system of the aromatic ring.

Table 1
Photophysical properties of compounds **1**–**6**

Compound	λ_{abs}[a]/nm (ε)
C1-QBINOL **1**	257 (68,749), 337 (29,001), 351 (29,247), 442 (6710)
C2-QINOL **2**	259 (69,322), 333 (25,286), 349 (25,641), 441 (6601)
C3-QBINOL **3**	261 (67,820), 283 (53,587), 332 (26,871), 348 (23,838), 437 (5836)
OMe-QBINOL **4**	264 (72,710), 291 (67,055), 336 (23,838), 351 (19,686), 461 (8103)
QNaph **5**	247 (56,456), 267 (46,621), 305 (27,745), 319 (29,630), 333 (32,908), 424 (6332)
OMe-QNaph **6**	261 (86,341), 279 (66,317), 334 (16,872), 348 (20,642), 442 (7311)

[a] Absorption wavelengths in dilute chloroform solution (1×10^{-5} M).

The absorption in the region of 240–360 nm represents the characteristic patterns of the phenanthrene π–π* transition.[19] Similar to the quinone region, the maximum absorption of the OMe-QNaph **6**, observed at 277 nm and 349 nm, was red shifted when compared with the related absorptions of QNaph **5** at 268 nm and 333 nm, indicating the effect of the electron donating OMe group. The absorption peaks of the dimeric OMe-QBINOL **4** showed a bathochromic shift at both 291 nm and 351 nm when compared to the monomeric OMe-QNaph **6**. Interestingly, changing the lengths of the methylene linkages in QBINOLs **1**–**4** affected only the absorptivity, but not their λ_{max}. In the region of 265–295 nm, the absorption intensity at around 290 nm decreased upon shortening the linking bridge while the absorption at about 350 nm increased. These experimental data support the effect of dihedral angle on the electronic spectra of the binaphyl derivatives although it is inconclusive whether the effect of orbital overlap between the auxochrome and π-conjugate system or the extended conjugation between the two binaphthyls is a major contributor.

In order to evaluate the electrochemical properties of compounds **1**–**6**, cyclic voltammetry (CV) was studied in MeCN with 0.1 M of nBu$_4$NPF$_6$ as supporting electrolyte. CV curves of all compounds (Fig. 3), showed two reversible reduction peaks. Since the two quinone moieties in all biarylbisquinones are further apart, the first reduction peak corresponds to the one-electron reduction of each quinone (Q), leading to the bis-semiquinone radical anion ($Q^{\bullet-}$). The second peak corresponds to the successive second one-electron reduction, representing the formation of bis-quinone dianion (Q^{2-}).[20] The onset reduction potentials of compounds **1**–**6** were −1.13, −1.14, −1.13, −1.13, −1.13, and −1.14 V, respectively. These values were almost identical suggesting that neither addition of the OMe group, formation of dimeric structures nor the conformation of the binaphthyls has a direct effect on the reduction process.

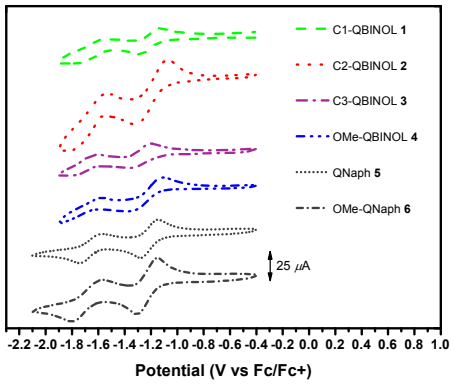


Fig. 3. Cyclic voltammogram for compounds **1**–**6** in 0.1 M nBu$_4$NPF$_6$ of MeCN solution. Scan rate is 50 mV/s.

The energy band gap (E_g) between HOMO and LUMO of each compound could then be calculated from the combination of the CV and UV data (Fig. 4).[21] The differences in the energy band gap was mainly from the differences in HOMO levels since the LUMO levels, as derived from the reduction potentials, are almost identical. Accordingly, E_g of OMe-QNaph **6** is smaller than that of QNaph **5** as a result of the electron donating OMe group on the phenanthrene ring which raises the E_{HOMO} and consequently reduces the E_g.[22] For the biarylbisquinones, their E_g values are related with the dihedral angle and the observed tendency of E_g is C1-**1**>C2-**2**>C3-**3**>OMe-**4**. With respect to the effect of the electron donor on the E_g, the difference in E_g of QBINOLs **1**–**4** could thus be influenced by the dihedral angle which affects the electron donating ability of the bridging OR auxochromes. The shorter the length of the bridge, the smaller the dihedral angle of the binaphthyl core, and therefore the E_{HOMO} becomes lower in the order of C1-**1**<C2-**2**<C3-**3**<OMe-**4**. This result then suggests that the orientation of lone pair electrons of O atoms on the linking group is constrained with smaller dihedral angles, leading to a decrease in the electron-donating ability of the O atom to the aromatic system, and consequently, ability to raise HOMO levels.

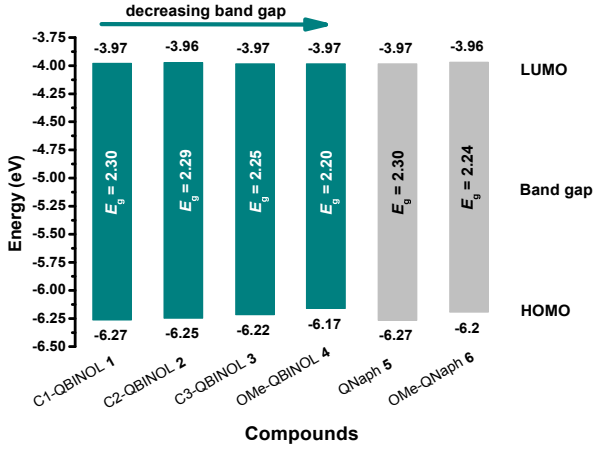


Fig. 4. Energy diagram of compounds **1**–**6**.

3. Conclusion

In summary, QBINOLs **1**–**4**, QNaph **5** and OMe-QNaph **6**, were successfully synthesized by using Diels–Alder reaction between silyl enol ether derivatives and *p*-benzoquinone as the key step. CV data showed that the reduction potentials of all compounds were related to the reduction of the quinone moiety and were almost identical. UV data showed a bathochromic shift as a result of the addition of an electron donating auxochrome. Dimeric structures of QBINOLs also affected the electronic properties through extended conjugation especially in the aromatic region in the UV spectra. However, when the dihedral angles of the dimeric QBINOLs were decreased by shortening the bridges, the absorption edge in the quinone region was slightly blue shifted. This observation suggests that, despite a possible greater degree of extended conjugation between the two aryl substructures, the degree of electronic contribution from the OR group which was a key contributor to the energy band gap, is limited due to the constrained orbital structure of oxygen at the bridge, resulting in the lower HOMO level and the larger Eg.

4. Experimental section

4.1. General method

All materials, unless otherwise noted, were obtained from commercial suppliers and used as provided. Solvents and reagents were distilled before used. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under nitrogen to obtain dry and oxygen free solvent. In addition, DMF, CH_2Cl_2, and *N*,*N*-dimethylacetamide (DMA) were distilled from CaH_2. Degassed MeOH was obtained by N_2 gas bubbling under ultrasonication. Reactions were typically monitored by thin layer chromatography (TLC) unless otherwise noted. Melting points were determined by a Buchi M-565 automated digital melting point apparatus and were reported as observed. ^{1}H and ^{13}C spectra were recorded on Bruker Avance DRX 300, 400 or 500 FT-NMR spectrometer. Mass spectra were recorded on Bruker Data Analysis Esquire-LC spectrometer. UV–visible absorption spectra were measured using Jasco V-530 UV–vis spectrophotometer. The spectrograde chloroform was used to dissolve test compounds for UV–Visible spectroscopy. CV experiments were determined using Autolab PGSTAT12.

4.2. 1,1′-Binaphthalene-2,2′-diol or BINOL (8)[9]

To a suspension of 2-naphthol (**7**) (3.00 g, 20.81 mmol) in H_2O (100 mL) was added anhydrous $FeCl_3$ (5.00 g, 30.83 mmol) and the mixture was then refluxed for 3 h. Subsequently, the crude product was extracted from reaction mixture with ethyl acetate. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. Finally, column chromatography (Silica gel; 8:2 hexane/ethyl acetate as an eluent) was followed to provide 1,1′-binaphthalene-2,2′-diol (**8**) (2.71 g, 91%) as a white solid, mp 210–212 °C (lit. mp 216–218 °C);[9b] ν_{max}(neat) 3484, 3399, 1617, 1595, 1509, 1470, 1461, 1380, 1321, 1209, 1168, 1141, 1124, 825, 814, 750, 664 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.16 (2H, d, *J* 8.4 Hz, Ar), 7.30–7.33 (2H, m, Ar), 7.36–7.39 (4H, m, Ar), 7.89 (2H, d, *J* 8.1 Hz, Ar), 7.97 (2H, d, *J* 9.0 Hz, Ar); δ_C (125 MHz, $CDCl_3$) 110.9, 117.8, 124.0, 124.2, 127.5, 128.4, 129.5, 131.4, 133.4, 152.7; HRMS (ESI): MNa^+, found: 309.0887. $C_{20}H_{14}O_2Na$ requires 309.0886.

4.3. 6,6′-Dibromo-[1,1′-binaphthalene]-2,2′-diol (18)[12]

A solution of 6-bromonaphthalen-2-ol (**17**) (10.00 g, 44.83 mmol) and $CuCl_2 \cdot 2H_2O$ (16.00 g, 93.85 mmol) in degassed methanol (150 mL) was stirred under nitrogen for 15 min. A solution of *tert*-butylamine (20.00 mL, 190.32 mmol) in methanol (100 mL) was added over a period of 30 min. The resulting solution was stirred at room temperature for 5 h. Then, the reaction mixture was cooled down to 0 °C and then 6 M of HCl was carefully added. Methanol was evaporated under reduced pressure and the residue

was diluted with ethyl acetate (100 mL) and washed with brine (2×50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to yield a crude product, which was then purified by column chromatography (Silica gel; 8:2 hexane/ethyl acetate as an eluent) to finally give 6,6′-dibromo-[1,1′-binaphthalene]-2,2′-diol (**18**) (8.66 g, 87%) as a pale brown solid, mp 203–204 °C (lit. mp 200–202 °C);[23] ν_{max}(neat) 3481, 1612, 1585, 1493, 1465, 1379, 1345, 1309, 1264, 1211, 1143, 1067, 927, 875, 811, 735, 669 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.96 (2H, d, *J* 9.0 Hz, Ar), 7.37 (2H, dd, *J* 8.9 2.0 Hz, Ar), 7.40 (2H, d, *J* 8.9 Hz, Ar), 7.89 (2H, d, *J* 9.0 Hz, Ar), 8.05 (2H, d, *J* 2.0 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 110.7, 118.0, 119.0, 125.9, 130.5, 130.6, 130.7, 130.9, 131.9, 153.0; HRMS (ESI): MNa^+, found 464.9092. $C_{20}H_{12}Br_2O_2Na$ requires 464.9096.

4.4. General procedure A: synthesis of compounds 9–12 and 19

To a mixture of BINOL (**8**) or dibromobinaphthol **18** (1.75 mmol) and alkyldihalide (1.75 mmol) or methyliodide (17.5 mmol) in acetone (50 mL) was added K_2CO_3 (17.5 mmol). The reaction was then refluxed until BINOL was completely consumed (monitored by TLC). After that the reaction mixture was filtered by reduced pressure, the filtrate was evaporated to dryness to yield the crude product which was then purified by column chromatography (Silica gel; 19:1 hexane/ethyl acetate as an eluent) to provide BINOL derivatives.

*4.4.1. Dinaphtho[2,1-d:1′,2′-f][1,3]dioxepine (**9**).*[10] White solid; mp 173–175 °C (lit. mp 83–84 °C);[24] 85% yield; ν_{max}(neat) 2958, 2920, 2897, 2851, 1587, 1505, 1460, 1326, 1266, 1238, 1138, 1078, 969, 925, 816, 747, 662 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.61 (2H, s, OCH_2O), 7.22 (2H, m, Ar), 7.34–7.45 (6H, m, Ar), 7.86 (2H, d, *J* 8.2 Hz, Ar), 7.90 (2H, d, *J* 8.7 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 103.1, 120.9, 125.0, 126.0, 126.1, 126.9, 128.4, 130.3, 131.8, 132.1, 151.2; HRMS (ESI): MNa^+, found: 321.0889. $C_{21}H_{14}O_2Na$ requires 321.0886.

*4.4.2. 4,5-Dihydrodinaphtho[2,1-e:1′,2′-g][1,4]dioxocine (**10**).*[10] White solid; mp 219–222 °C (lit. mp 214–215 °C);[25] 21% yield; ν_{max}(neat) 2959, 2926, 2855, 1587, 1504, 1465, 1326, 1277, 1222, 1200, 1076, 1051, 937, 886, 814, 754 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.16–4.27 (2H, m, $OCH_aH_bCH_aH_bO$), 4.38–4.49 (2H, m, $OCH_aH_bCH_aH_bO$), 7.23–7.28 (4H, m, Ar), 7.40–7.45 (2H, m, Ar), 7.48 (2H, d, *J* 8.8 Hz, Ar), 7.92 (2H, d, *J* 8.1 Hz, Ar), 8.01 (2H, d, *J* 8.8 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 73.0, 122.4, 124.2, 124.7, 126.2, 127.1, 128.0, 130.7, 131.0, 133.0, 156.5; HRMS (ESI): MNa^+, found 335.1041. $C_{22}H_{16}O_2Na$ requires 335.1043.

*4.4.3. 5,6-Dihydro-4H-dinaphtho[2,1-f:1′,2′-h][1,5]dioxonine (**11**).*[10] White solid; mp 266–268 °C (lit. mp 165–166 °C);[25] 77% yield; ν_{max}(neat) 2968, 2945, 2874, 1587, 1504, 1467, 1327, 1269, 1243, 1209, 1078, 1035, 1017, 818, 758, 700 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.97–2.00 (2H, m, $OCH_2CH_2CH_2O$), 4.32–4.45 (4H, m, $OCH_2CH_2CH_2O$), 7.24–7.29 (4H, m, Ar), 7.38–7.42 (2H, m, Ar), 7.49 (2H, d, *J* 8.9 Hz, Ar), 7.92 (2H, d, *J* 8.1 Hz, Ar), 7.99 (2H, d, *J* 8.9 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 30.7, 71.9, 119.2, 123.9, 124.2, 126.2, 126.3, 128.1, 129.6, 130.4, 133.4, 154.7; HRMS (ESI): MNa^+, found 349.1215. $C_{23}H_{18}O_2Na$ requires 349.1199.

*4.4.4. 2,2′-Dimethoxy-1,1′-binaphthalene (**12**).*[10] White solid; mp 196–198 °C (lit. mp 224–225 °C);[26] 89% yield; ν_{max}(neat) 2955, 2918, 2837, 1618, 1589, 1504, 1460, 1263, 1248, 1147, 1089, 1062, 1049, 1018, 895, 809, 745, 678 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.80 (6H, s, 2× *Me*O), 7.14 (2H, d, *J* 8.5 Hz, Ar), 7.22–7.27 (2H, m, Ar), 7.32–7.37 (2H, m, Ar), 7.49 (2H, d, *J* 9.0 Hz, Ar), 7.90 (2H, d, *J* 8.2 Hz, Ar), 8.01 (2H, d, *J* 9.0 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 55.2, 105.7, 118.7, 123.6, 126.3, 126.7, 127.6, 128.9, 129.4, 134.5, 157.6; HRMS (ESI): MNa^+, found 337.1204. $C_{22}H_{18}O_2Na$ requires 337.1199.

*4.4.5. 9,14-Dibromodinaphtho[2,1-d:1′,2′-f][1,3]dioxepine (**19**).*[10] White solid; mp 209–212 °C (lit. mp 204–205 °C);[27] 64% yield; ν_{max}(neat) 2964, 2901, 2856, 1582, 1326, 1239, 1070, 1032, 976, 871, 809, 655, 559 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.61 (2H, s, OCH_2O), 7.23 (2H, d, *J* 9.1 Hz, Ar), 7.31 (2H, dd, *J* 9.1 1.9 Hz, Ar), 7.42 (2H, d, *J* 8.8 Hz, Ar), 7.82 (2H, d, *J* 8.8 Hz, Ar), 8.02 (2H, d, *J* 1.9 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 103.2, 119.2, 122.2, 125.9, 128.3, 129.6, 130.4, 130.5, 132.9, 151.6; HRMS (APCI): MH^+, found 454.9285. $C_{21}H_{13}Br_2O_2$ requires 454.9277.

4.5. 1,1′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepine-9,14-diyl) diethanone (13)[13]

To a solution of 9,14-dibromodinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepine (**19**) (224 mg, 0.49 mmol) in dry THF (15 mL) at −78 °C under nitrogen, *n*-butyllithium (*n*-BuLi) (1.14 M solution in hexane, 1.08 mL, 1.23 mmol) was added dropwise. The mixture was kept stirring at −78 °C for an additional 2 h, then anhydrous *N*,*N*-dimethylacetamide (0.18 mL, 1.94 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 2 h. The reaction mixture was later quenched by saturated ammonium chloride (NH_4Cl) aqueous solution and extracted with EtOAc (3×25 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was chromatographed (Silica gel; 8:2 hexane/ethyl acetate as eluent) to provide 1,1′-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepine-9,14-diyl)-diethanone (**13**) (64 mg, 34%) as a white solid, mp 160–163 °C; ν_{max}(neat) 3060, 2959, 2907, 1675, 1617, 1586, 1464, 1358, 1242, 1187, 1073, 1032, 1001, 937, 823, 733, 686 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.73 (6H, s, 2× *Me*C═O), 5.74 (2H, s, OCH_2O), 7.47 (2H, d, *J* 8.9 Hz, Ar), 7.56 (2H, d, *J* 8.7 Hz, Ar), 7.85 (2H, dd, *J* 8.9 and 1.6 Hz, Ar), 8.14 (2H, d, *J* 8.7 Hz, Ar), 8.58 (2H, d, *J* 1.6 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 26.7, 103.3, 122.0, 124.4, 125.8, 127.0, 130.6, 130.9, 132.3, 133.8, 134.3, 153.4, 197.7; HRMS (ESI): MNa^+, found 405.1098. $C_{25}H_{18}O_4Na$ requires 405.1097.

4.6. General procedure B: synthesis of compounds 14, 15, 16, 26, and 28

To a suspension of aluminium (III) chloride ($AlCl_3$) (8.62 mmol) in 1,2-dichloroethane (20 mL), was added acetyl chloride (AcCl) (8.58 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 45 min. Dimeric BINOLs **14**–**16** (4.13 mmol) or naphthalene **24** and 2-methoxynapthalene **25** (8.27 mmol) was then added and stirred at 0 °C for 4 h. Then, the reaction mixture was quenched with H_2O (30 mL), extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated to dryness. The crude product was purified by column chromatography with 2% CH_2Cl_2 in hexane as eluent to obtain the desired acetyl adducts.

*4.6.1. 1,1′-(4,5-Dihydrodinaphtho[2,1-e:1′,2′-g][1,4] dioxo-cine-10,15-diyl)diethanone (**14**).*[11] White solid; mp 219–221 °C; 90% yield; ν_{max}(neat) 3058, 2953, 2926, 2865, 1673, 1615, 1588, 1468, 1439, 1356, 1258, 1225, 1185, 1070, 937, 895, 821, 734, 697 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.70 (6H, s, 2× *Me*C═O), 4.16–4.26 (2H, m, $OCH_aH_bCH_aH_bO$), 4.42–4.52 (2H, m, $OCH_aH_bCH_aH_bO$), 7.25 (2H, d, *J* 8.9 Hz, Ar), 7.53 (2H, d, *J* 8.8 Hz, Ar), 7.79 (2H, dd, *J* 8.9 1.6 Hz, Ar), 8.14 (2H, d, *J* 8.8 Hz, Ar), 8.55 (2H, d, *J* 1.6 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 26.6, 72.7, 123.5, 123.8, 124.5, 127.1, 130.0, 130.2, 132.6, 133.5, 135.1,

158.5, 197.7; HRMS (ESI): MNa^+, found 419.1248. $C_{26}H_{20}O_4Na$ requires 419.1254.

*4.6.2. 1,1′-(5,6-Dihydro-4H-dinaphtho[2,1-f:1′,2′-h][1,5] diox-onine-11,16-diyl) diethanone (**15**).*[11] White solid; mp 295–298 °C; 97% yield; ν_{max}(neat) 3060, 2948, 2887, 1676, 1616, 1473, 1424, 1358, 1271, 1218, 1189, 1072, 1033, 951, 897, 819, 736, 700 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.99–2.05 (2H, m, $OCH_2CH_2CH_2O$), 2.72 (6H, s, 2× *Me*C=O), 4.36–4.51 (4H, m, $OCH_2CH_2CH_2O$), 7.28 (2H, d, *J* 8.9 Hz, Ar), 7.56 (2H, d, *J* 8.9 Hz, Ar), 7.82 (2H, dd, *J* 8.9 1.6 Hz, Ar), 8.13 (2H, d, *J* 8.9 Hz, Ar), 8.56 (2H, d, *J* 1.6 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 26.6, 30.5, 72.0, 120.0, 123.5, 124.7, 126.2, 129.4, 130.5, 131.7, 133.1, 135.6, 157.1, 197.9; HRMS (ESI): MH^+, found 411.1583. $C_{27}H_{23}O_4$ requires 411.1591.

*4.6.3. 1,1′-(2,2′-Dimethoxy-[1,1′-binaphthalene]-6,6′-diyl) diethanone (**16**).*[11] Yellow solid; mp 250–252 °C (lit. mp 184–186 °C);[11] 95% yield; ν_{max}(KBr) 3007, 2946, 2842, 1669, 1620, 1588, 1355, 1247, 1174, 834, 796 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.71 (6H, s, 2× *Me*C=O), 3.83 (6H, s, 2× *Me*OAr), 7.13 (2H, d, *J* 8.9 Hz, Ar), 7.55 (2H, d, *J* 9.1 Hz, Ar), 7.80 (2H, dd, *J* 8.9 1.6 Hz, Ar), 8.15 (2H, d, *J* 9.1 Hz, Ar), 8.54 (2H, d, *J* 1.6 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 26.5, 56.5, 114.3, 118.7, 124.6, 125.3, 127.9, 130.6, 131.6, 132.5, 136.2, 157.0, 197.8; HRMS (APCI): MH^+, found 399.1596. $C_{26}H_{23}O_4$ requires 399.1591.

*4.6.4. 1-(Naphthalen-2-yl)ethanone (**26**).*[11] Pale yellow liquid; 19% yield; ν_{max}(neat) 3058, 3004, 2923, 2853, 1675, 1627, 1465, 1430, 1362, 1275, 1226, 1191, 1129, 944, 861, 819, 747 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.73 (3H, s, *Me*C=O), 7.52–7.63 (2H, m, Ar), 7.86–7.90 (2H, m, Ar), 7.96 (1H, d, *J* 8.4 Hz, Ar), 8.03 (1H, dd, *J* 8.6 1.7 Hz, Ar), 8.50 (1H, s, Ar); δ_C (75 MHz, $CDCl_3$) 26.7, 123.9, 126.7, 127.7, 128.4, 129.5, 130.2, 132.5, 134.4, 135.5, 198.1; HRMS (ESI): MH^+, found 171.0803. $C_{12}H_{11}O$ requires 171.0804.

*4.6.5. 1-(Naphthalen-1-yl)ethanone (**27**).*[11] Pale yellow liquid; 73% yield; ν_{max}(neat) 3050, 3004, 2923, 2852, 1673, 1572, 1506, 1429, 1352, 1276, 1237, 1189, 1126, 1014, 940 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.73 (3H, s, *Me*C=O), 7.45–7.64 (3H, m, Ar), 7.85–7.99 (3H, m, Ar), 8.78 (1H, d, *J* 8.4 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 29.8, 124.2, 125.9, 126.3, 127.9, 128.3, 128.6, 130.0, 132.9, 133.8, 135.2, 201.7; HRMS (ESI) MNa^+, found 193.0626. $C_{12}H_{10}ONa$ requires 193.0624.

*4.6.6. 1-(6-Methoxynaphthalen-2-yl)ethanone (**28**).*[11] White solid; mp 99–101 °C (lit. mp 98–100 °C);[28] 51% yield; ν_{max}(KBr) 3063, 3002, 2966, 2935, 1675, 1602, 1479, 1440, 1359, 1275, 821, 742 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.72 (3H, s, *Me*C=O), 3.97 (3H, s, *Me*OAr), 7.17 (1H, d, *J* 2.4 Hz, Ar), 7.22 (1H, dd, *J* 8.9 2.4 Hz, Ar), 7.78 (1H, d, *J* 8.6 Hz, Ar), 7.87 (1H, d, *J* 8.9 Hz, Ar), 8.03 (1H, dd, *J* 8.6 1.7 Hz, Ar), 8.41 (1H, d, *J* 1.7 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 26.5, 55.4, 105.7, 119.7, 124.6, 127.1, 127.8, 130.0, 131.1, 132.6, 137.2, 159.7, 197.8; HRMS (APCI): MH^+, found 201.0942. $C_{13}H_{13}O_2$ requires 201.0910.

*4.6.7. 1-(2-Methoxynaphthalen-1-yl)ethanone (**29**).*[11] White solid; mp 53–55 °C (lit. mp 59 °C);[29] 46% yield; δ_H (300 MHz, $CDCl_3$) 2.53 (3H, s, *Me*C=O), 3.81 (3H, s, *Me*OAr), 7.12 (1H, d, *J* 9.1 Hz, Ar), 7.17–7.26 (1H, m, Ar), 7.30–7.37 (1H, m, Ar), 7.61–7.67 (2H, m, Ar), 7.72 (1H, d, *J* 9.1 Hz, Ar); δ_C (75 MHz, $CDCl_3$) δ 32.6, 56.2, 112.7, 123.5, 123.9, 124.9, 127.5, 128.0, 128.7, 130.2, 131.4, 153.9, 205.0; HRMS (ESI): MNa^+, found 223.0735. $C_{13}H_{13}NaO_2$ requires 223.0730.

4.7. General procedure C: synthesis of silyl enol ethers 20–23, 30, and 31

To a solution of acetyl naphthalene derivatives or diacetyl binaphthyl derivatives (0.20 g, 1.18 mmol) in dry CH_2Cl_2 (5 mL), triethylamine (Et_3N) (0.5 mL for acetyl naphthalene derivatives) or (1.0 mL for diacetyl binaphthyl derivatives) was added at 0 °C under nitrogen. The reaction mixture was stirred for 10 min, followed by addition of triisopropylsilyl triflate (TIPSOTf) (1.24 mmol for acetyl naphthalene derivatives) or (2.48 mmol for diacetyl binaphthyl derivatives). The reaction mixture was warmed up to room temperature and stirred for 4 h. Then, the reaction mixture was quenched with 10% NaOH. The reaction mixture was then washed with saturated $NaHCO_3$ (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and dried under vacuum to afford the desired silyl enol ether. The product would be used in the next step without further purification.

*4.7.1. 9,14-Bis(1-((triisopropylsilyl)oxy)vinyl)dinaphtho[2,1-d:1′,2′-f][1,3]dioxepine (**20**).* Brown oil; ν_{max}(neat) 2940, 2864, 1679, 1613, 1583, 1463, 1295, 1190, 1079, 1006, 882, 809, 674 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.17 (36H, d, *J* 7.2 Hz, 2× $(Me_2CH)_3SiO$), 1.31–1.37 (6H, sep, *J* 7.2 Hz, 2× $(Me_2CH)_3SiO$), 4.53 (2H, d, *J* 1.6 Hz, $2CH_aH_b$=), 4.99 (2H, d, *J* 1.6 Hz, $2CH_aH_b$=), 5.70 (2H, s, OCH_2O), 7.46–7.48 (4H, m, Ar), 7.58 (2H, dd, *J* 9.0 1.6 Hz, Ar), 7.99 (2H, d, *J* 8.7 Hz, Ar), 8.24 (2H, d, *J* 1.6 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 12.8, 18.1, 90.7, 103.1, 121.1, 123.8, 124.7, 126.0, 126.6, 130.9, 131.5, 131.9, 134.3, 151.4, 155.7; HRMS (ESI) MH^+, found 695.3941. $C_{43}H_{59}O_4Si_2$ requires 695.3946.

*4.7.2. 10,15-Bis(1-((triisopropylsilyl)oxy)vinyl)-4,5-dihydrodi-naphtho[2,1-e:1′,2′-g][1,4]dioxocine (**21**).* Brown oil; ν_{max}(neat) 2940, 2864, 1611, 1586, 1465, 1332, 1294, 1191, 1076, 1011, 881, 805, 673 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.13 (36H, d, *J* 7.0 Hz, 2× $(Me_2CH)_3SiO$), 1.27–1.35 (6H, sep, *J* 7.0 Hz, 2× $Me_2CH)_3SiO$), 4.12–4.18 (2H, m, $OCH_aH_bCH_aH_bO$), 4.34–4.41 (2H, m, OCH_aH_b-CH_aH_bO), 4.46 (2H, d, *J* 1.6 Hz, $2CH_aH_b$=), 4.91 (2H, d, *J* 1.6 Hz, $2CH_aH_b$=), 7.17 (2H, d, *J* 9.0 Hz, Ar), 7.40 (2H, d, *J* 8.8 Hz, Ar), 7.47 (2H, dd, *J* 9.0 1.6 Hz, Ar), 7.95 (2H, d, *J* 8.8 Hz, Ar), 8.17 (2H, d, *J* 1.6 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 12.9, 17.9, 73.2, 109.3, 120.4, 120.7, 124.5, 125.2, 126.5, 128.7, 129.4, 132.2, 133.3, 134.6, 134.8, 135.5, 140.7, 157.3, 158.4, 185.4, 187.0; HRMS (ESI): MH^+, found 709.4108. $C_{44}H_{61}O_4Si_2$ requires 709.4103.

*4.7.3. 11,16-Bis(1-((triisopropylsilyl)oxy)vinyl)-5,6-dihydro-4H-dinaphtho[2,1-f:1′,2′-h][1,5]dioxonine (**22**).* Brown oil; ν_{max}(neat) 2938, 2864, 1613, 1587, 1464, 1381, 1296, 1251, 1078, 1043, 1010, 882, 802, 672 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.13 (36H, d, *J* 7.2 Hz, 2× $(Me_2CH)_3SiO$), 1.26–1.36 (6H, sep, *J* 7.2 Hz, 2× $Me_2CH)_3SiO$), 1.93–1.95 (2H, m, $OCH_2CH_2CH_2O$), 4.31–4.39 (4H, m, OCH_2CH_2-CH_2O), 4.44 (2H, d, *J* 1.4 Hz, $2CH_aH_b$=), 4.90 (2H, d, *J* 1.4 Hz, $2CH_aH_b$=), 7.18 (2H, d, *J* 8.9 Hz, Ar), 7.42 (2H, d, *J* 8.8 Hz, Ar), 7.49 (2H, dd, *J* 8.9 1.6 Hz, Ar), 7.93 (2H, d, *J* 8.8 Hz, Ar), 8.16 (2H, d, *J* 1.6 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 12.8, 18.1, 30.6, 71.9, 90.0, 119.3, 123.7, 124.0, 124.5, 125.9, 130.1, 130.2, 133.2, 133.6, 154.9, 156.0; HRMS (ESI): MH^+, found 723.4255. $C_{45}H_{63}O_4Si_2$ requires 723.4259.

*4.7.4. 6,6′-Bis[1-(triisopropylsiloxy)-ethenyl]-2,2′-dimethoxy-1,1′-binaphthalene) (**23**).* Pale brown solid; ν_{max}(KBr) 3071, 2944, 2866, 1638, 1624, 1585, 1460, 1384, 1269, 1176, 1146, 808, 737 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.19 (36H, d, *J* 7.0 Hz, 2× $(Me_2CH)_3SiO$), 1.32–1.39 (6H, sep, *J* 7.0 Hz, 2× $Me_2CH)_3SiO$), 3.79 (6H, s, 2× *Me*OAr), 4.47 (2H, d, *J* 1.8 Hz, $2CH_aH_b$=), 4.92 (2H, d, *J* 1.8 Hz, $2CH_aH_b$=), 7.08 (2H, d, *J* 9.0 Hz, Ar), 7.47 (2H, d, *J* 9.0 Hz, Ar), 7.51 (2 h, dd, *J* 9.0 1.8 Hz, Ar), 8.00 (2H, d, *J* 9.0 Hz, Ar), 8.20 (2H, d, *J* 1.8 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 12.8, 18.1, 56.8, 89.7, 114.3, 119.4, 124.0, 124.4, 125.0, 128.8, 130.0, 132.9, 133.8, 155.3, 156.1; HRMS (ESI): MH^+, found 711.4261. $C_{44}H_{63}O_4Si_2$ requires 711.4259.

*4.7.5. Triisopropyl((1-(naphthalen-2-yl)vinyl)oxy)silane (**30**).* Pale brown solid; ν_{max}(neat) 2942, 2893, 2866, 2726, 1612, 1505, 1464, 1309, 1250, 1015, 882, 804, 677 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.06

(18H, d, *J* 7.4 Hz, (Me_2CH)$_3$SiO), 1.18–1.25 (3H, sep, *J* 7.4 Hz, (Me$_2$C*H*)$_3$SiO), 4.43 (1H, d, *J* 1.8 Hz, C*H*$_a$H$_b$=), 4.90 (1H, d, *J* 1.8 Hz, CH$_a$*H*$_b$=), 7.32–7.36 (2H, m, Ar), 7.64–7.75 (4H, m, Ar), 8.05 (1H, s, 1H); δ_C (100 MHz, $CDCl_3$) 12.8, 18.1, 90.8, 123.5, 124.3, 126.0, 127.5, 128.5, 133.2, 135.1, 156.0; HRMS (ESI): MH^+, found 349.1955. $C_{21}H_{30}NaOSi$ requires 349.1958.

*4.7.6. Triisopropyl((1-(6-methoxynaphthalen-2-yl)vinyl)oxy) silane (**31**).* Brown oil; ν_{max}(neat) 3062, 2944, 2866, 1632, 1598, 1463, 1388, 1260, 1164, 804, 737 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.06 (18H, d, *J* 7.0 Hz, (Me_2CH)$_3$SiO), 1.16–1.29 (3H, sep, *J* 7.0 Hz, (Me$_2$C*H*)$_3$SiO), 3.78 (3H, s, *Me*OAr), 4.38 (1H, d, *J* 1.8 Hz, C*H*$_a$H$_b$=), 4.85 (1H, d, *J* 1.8 Hz, CH$_a$*H*$_b$=), 6.98–7.04 (2H, m, Ar), 7.53–7.64 (3H, m, Ar), 7.97 (1H, s, Ar); δ_C (75 MHz, $CDCl_3$) 12.8, 18.1, 55.2, 89.9, 105.6, 118.8, 124.0, 124.2, 126.4, 128.6, 130.0, 133.1, 134.4, 156.1, 157.9; HRMS (ESI): MH^+, found 379.2066. $C_{22}H_{32}NaO_2Si$ requires 379.2064.

4.8. General procedure D: synthesis of QBINOLs 1–4 and QNaphs 5–6

A solution of silyl enol ethers (0.83 mmol) and *p*-benzoquinone (9.92 mmol for naphthyl silyl enol ethers) or (19.84 mmol for binaphthyl silyl enol ethers) in toluene (20 mL) was refluxed for 48 h. The reaction mixture was then cooled down to room temperature. The remaining *p*-benzoquinone was filtered and washed with hexane. The solution was collected and the solvent was evaporated to dryness. The crude product was purified by column chromatography (Silica gel; 8:2 hexane/ethyl acetate as an eluent) to provide quinone-naphthyl derivatives or quinone-binaphthyl derivatives.

*4.8.1. 11,16-Bis((triisopropylsilyl)oxy)benzo[5,6]phenanthro [2,1-d] benzo[5,6]phenanthro[1,2-f][1,3]dioxepine-6,9,18,21-tetraone or C1-QBINOL **1**.* Red solid; mp 290–294 °C; 31% yield; ν_{max}(neat) 2944, 2865, 1660, 1611, 1574, 1509, 1416, 1383, 1341, 1295, 1244, 1062, 1006, 926, 883, 833, 798, 731 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.11–1.14 (36H, m, 2× (Me_2CH)$_3$SiO), 1.41–1.48 (6H, m, 2× Me$_2$C*H*)$_3$SiO), 5.74 (2H, s, OC*H*$_2$O), 6.97 (2H, d, *J* 10.2 Hz, 2C*H*$_a$=CH$_b$), 7.11 (2H, d, *J* 10.2 Hz, 2CH$_a$=C*H*$_b$), 7.45 (2H, d, *J* 9.1 Hz, Ar), 7.58 (2H, s, Ar), 7.78 (2H, d, *J* 9.3 Hz, Ar), 8.04 (2H, d, *J* 9.3 Hz, Ar), 8.48 (2H, d, *J* 9.1 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 12.9, 17.9, 103.5, 109.6, 119.3, 120.6, 125.2, 126.2, 127.6, 128.4, 129.4, 132.4, 133.1, 134.0, 134.8, 135.6, 140.7, 152.9, 157.3, 185.4, 186.9; HRMS (ESI): MNa^+, found 925.3564. $C_{55}H_{58}O_8Si_2Na$ requires 925.3562.

*4.8.2. 12,17-Bis((triisopropylsilyl)oxy)-2,3-dihydrobenzo [5,6]phenanthro[2,1-e]benzo[5,6]phenanthro[1,2-g][1,4]dioxo-cine-7,10,19,22-tetraone or C2-QBINOL **2**.* Red solid; 13% yield; ν_{max}(neat) 2941, 2866, 1660, 1611, 1573, 1507, 1463, 1416, 1383, 1295, 1238, 1062, 999, 882, 832, 796, 732, 684 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.00–1.05 (36H, m, 2× (Me_2CH)$_3$SiO), 1.27–1.40 (6H, m, 2×Me$_2$C*H*)$_3$SiO), 4.10–4.19 (2H, m, OC*H*$_a$H$_b$C*H*$_a$H$_b$O), 4.33–4.42 (2H, m, OCH$_a$*H*$_b$CH$_a$*H*$_b$O), 6.87 (2H, d, *J* 10.2 Hz, 2C*H*$_a$=CH$_b$), 7.02 (2H, d, *J* 10.2 Hz, 2CH$_a$=C*H*$_b$), 7.33 (2H, d, *J* 9.2 Hz, Ar), 7.46 (2H, s, Ar), 7.48 (2H, d, *J* 9.4 Hz, Ar), 7.92 (2H, d, *J* 9.4 Hz, Ar), 8.41 (2H, d, *J* 9.2 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 12.9, 17.9, 73.2, 109.3, 120.4, 120.7, 124.5, 125.2, 126.6, 128.7, 129.4, 132.2, 133.3, 134.6, 134.8, 135.5, 140.7, 157.3, 158.4, 185.4, 187.0; HRMS (ESI): MH^+, found 917.3902. $C_{56}H_{61}O_8Si_2$ requires 917.3899.

*4.8.3. 13,18-Bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-benzo[5,6] phenanthro[2,1-f]benzo[5,6]phenanthro[1,2-h][1,5] dioxonine-8,11,20,23-tetraone or C3-QBINOL **3**.* Red solid; mp 100–103 °C; 23% yield; ν_{max}(neat) 2925, 2865, 1662, 1611, 1574, 1512, 1462, 1416, 1380, 1298, 1242, 1059, 1003, 930, 883, 833, 793, 687 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.07–1.13 (36H, m, 2× (Me_2CH)$_3$SiO), 1.39–1.45 (6H, m, 2× Me$_2$C*H*)$_3$SiO), 1.99–2.01 (2H, m, OCH$_2$C*H*$_2$CH$_2$O), 4.35–4.40 (2H, m, OC*H*$_a$H$_b$CH$_2$ C*H*$_a$H$_b$O), 4.44–4.49 (2H, m, OCH$_a$*H*$_b$CH$_2$CH$_a$*H*$_b$O), 6.94 (2H, d, *J* 10.1 Hz, 2C*H*$_a$=CH$_b$), 7.09 (2H, d, *J* 10.1 Hz, 2CH$_a$=C*H*$_b$), 7.39 (2H, d, *J* 9.2 Hz, Ar), 7.52 (2H, s, Ar), 7.58 (2H, d, *J* 9.3 Hz, Ar), 8.02 (2H, d, *J* 9.3 Hz, Ar), 8.47 (2H, d, *J* 9.2 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 12.9, 18.0, 30.1, 71.7, 109.1, 116.4, 120.7, 124.1, 125.0, 125.6, 128.1, 129.3, 132.2, 132.5, 134.7, 134.8, 135.5, 140.8, 156.8, 157.3, 185.5, 187.0; HRMS (ESI): MH^+, found 931.4058. $C_{57}H_{63}O_8Si_2$ requires 931.4056.

*4.8.4. 3,3′-Dimethoxy-7,7′-bis((triisopropylsilyl)oxy)[4,4′-bibenzo[c] phenanthrene]-9,9′,12,12′-tetraone or OMe-QBINOL **4**.* Red solid; mp 282–284 °C; 49% yield; ν_{max}(KBr) 2945, 2867, 1667, 1613, 1573, 1463, 1386, 1244, 1169, 828, 737 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.15 (36H, d, *J* 7.5 Hz, 2× (Me_2CH)$_3$SiO), 1.41–1.51 (6H, sep, *J* 7.5 Hz, 2× Me$_2$C*H*)$_3$SiO), 3.86 (6H, s, 2× *Me*OAr), 6.96 (2H, d, *J* 10.1 Hz, 2C*H*$_a$=CH$_b$), 7.12 (2H, d, *J* 10.1 Hz, 2CH$_a$=C*H*$_b$), 7.32–7.39 (4H, m, Ar), 7.53 (2H, s, Ar), 7.99 (2H, d, *J* 9.4 Hz, Ar), 8.54 (2H, d, *J* 9.4 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 13.0, 18.0, 56.3, 108.9, 110.8, 119.4, 120.4, 123.7, 125.0, 127.7, 128.9, 132.1, 132.8, 134.7, 135.1, 135.4, 140.9, 157.1, 157.3, 185.6, 187.1; HRMS (APCI): MH^+, found 919.4043. $C_{56}H_{63}O_8Si_2$ requires 919.4056.

*4.8.5. 6-((Triisopropylsilyl)oxy)benzo[c]phenanthrene-1,4-dione or QNaph **5**.* Red solid; 8% yield; ν_{max}(neat) 2947, 2867, 1663, 1613, 1567, 1526, 1383, 1301, 1253, 1217, 1088, 1064, 881, 848, 781, 753, 686 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.19 (18H, d, *J* 7.5 Hz, (Me_2CH)$_3$SiO), 1.49–1.53 (3H, sep, *J* 7.5 Hz, (Me$_2$C*H*)$_3$SiO), 6.92 (1H, d, *J* 10.1 Hz, C*H*$_a$=CH$_b$), 7.06 (1H, d, *J* 10.1 Hz, CH$_a$=C*H*$_b$), 7.44–7.48 (1H, m, Ar), 7.56 (1H, s, Ar), 7.59–7.62 (1H, m, Ar), 7.87–7.89 (2H, m, Ar), 8.20 (1H, d, *J* 9.0 Hz, Ar), 8.34 (1H, d, *J* 8.4 Hz, Ar); δ_C (100 MHz, $CDCl_3$) 13.0, 18.0, 109.4, 119.7, 124.9, 125.6, 127.9, 128.1, 128.4, 129.2, 130.1, 130.2, 132.0, 134.0, 134.5, 135.4, 140.7, 157.2, 185.4, 186.9; HRMS (ESI): MH^+, found 431.2032. $C_{27}H_{31}O_3Si$ requires 431.2037.

*4.8.6. 10-Methoxy-6-((triisopropylsilyl)oxy)benzo[c]phenan-threne-1,4-dione or OMe-Qnaph **6**.* Red viscous liquid; 67% yield; ν_{max}(KBr) 3061, 2944, 2866, 1666, 1618, 1573, 1462, 1384, 1246, 1162, 825, 737 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.22 (18H, d, *J* 7.4 Hz, (Me_2CH)$_3$SiO), 1.48–1.56 (3H, sep, *J* 7.4 Hz, (Me$_2$C*H*)$_3$SiO), 3.98 (3H, s, *Me*OAr), 6.91 (1H, d, *J* 10.1 Hz, C*H*$_a$=CH$_b$), 7.05 (1H, d, *J* 10.1 Hz, CH$_a$=C*H*$_b$), 7.11 (1H, dd, *J* 9.3, 2.7 Hz, Ar), 7.21 (1H, d, *J* 2.7 Hz, Ar), 7.53 (1H, s, Ar), 7.80 (1H, d, *J* 8.9 Hz, Ar), 8.20 (1H, d, *J* 8.9 Hz, Ar), 8.27 (1H, d, *J* 9.3 Hz, Ar); δ_C (75 MHz, $CDCl_3$) 13.0, 18.0, 55.4, 107.5, 108.7, 115.6, 120.3, 123.5, 124.8, 128.9, 129.5, 131.8, 132.1, 134.6, 135.3, 135.8, 140.7, 157.2, 159.2, 185.5, 186.8; HRMS (APCI): MH^+, found 461.2145. $C_{28}H_{33}O_4Si$ requires 461.2143.

Acknowledgements

This research was supported by Mahidol University. Scholarship supports from the Development and Promotion of Science and Technology Talents Program (DPST) for K.W. and from the Center for Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry (PERCH-CIC) for N.B. are gratefully acknowledged.

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