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Diversity-Oriented Approach to Biologically Relevant Molecular Frameworks Starting with β-Naphthol and Using the Claisen Rearrangement and Olefin Metathesis as Key Steps

Sambasivarao Kotha,* Kalyaneswar Mandal, Arti Tiwari, and Shaikh M. Mobin[a]

Abstract: A diversity-oriented approach for the synthesis of various structurally different molecular frameworks from readily accessible and common precursors is described. A Claisen rearrangement followed by ring-closing metathesis or ethylene-promoted ring-closing enyne metathesis has been utilized as the key synthetic transformation to generate naphthoxepine derivatives. The ring-closing metathesis approach has also been used to generate spirocyclic compounds and the pleiadene framework.

Keywords: Claisen rearrangement · diversity-oriented synthesis · metathesis · naphthoxepines · spiro compounds

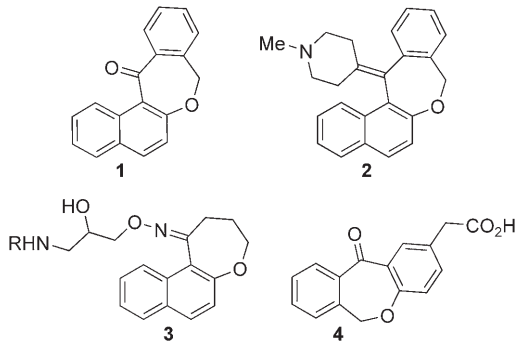
Introduction

Recently there has been increasing interest, both in academia and in industry, in the synthesis of diverse collection of "drug-like" molecules and their screening for lead identification with optimized properties useful for medicinal chemistry—this is the goal of diversity-oriented synthesis (DOS).[1] DOS involves three key elements: building blocks, stereochemistry, and molecular skeleton.

Generation of high levels of stereochemical and/or skeletal diversity is considered highly challenging. Divergent reaction pathways are efficient means of generating structural diversity, particularly through the creation of diverse molecular frameworks and functional groups. Skeletal diversity is generated by the use of different sets of reagents or reaction conditions to transform common substrates into collections of products with varied molecular skeletons.[2]

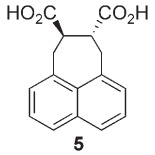
Here we report a diversity-oriented approach for the synthesis of skeletally different molecular frameworks from one or more readily available starting material(s) through the application of simple reactions such as the Claisen rearrangement and olefin metathesis as key steps (Scheme 1).

The skeletons (**A**–**D**) shown in Scheme 1 are the core structural motifs for various biologically active natural or unnatural products. Oxepine **A**, for example, is an important structural element present in numerous biologically active molecules. In addition, naphthoxepine derivatives **1** and **2** are used as antipsychotic drugs.[3] Similarly, naphthoxepine oxime ether **3** was found to be useful as a potential hypotensive agent,[4] whilst the dibenzoxepine derivative isoxepac (**4**) is used as an antiinflammatory drug.[5]

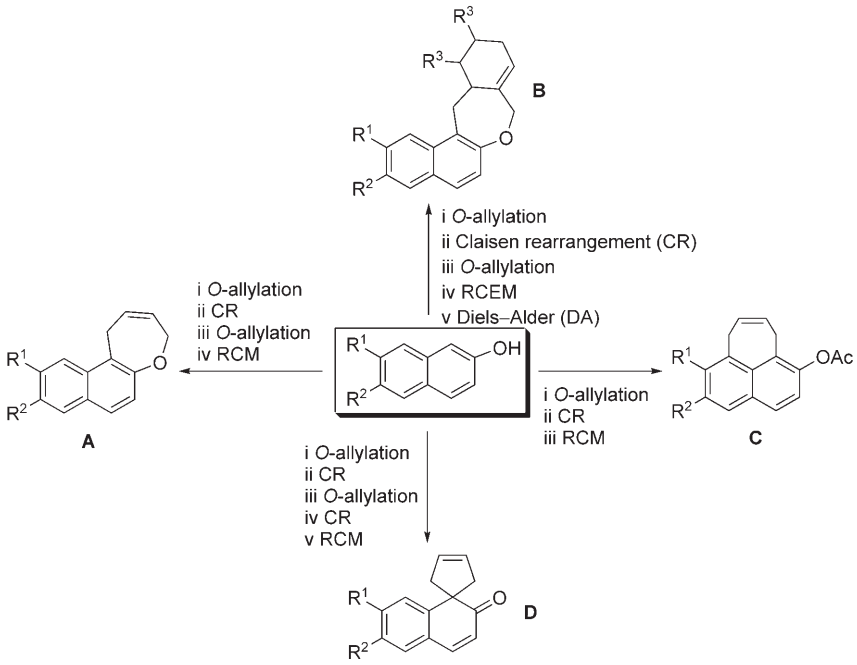


Interestingly, *trans*-2,3-pleiadanedicarboxylic acid (**5**) has been identified as a promising inhibitor of prephenate dehydrogenase (PDH) in the *E. coli* T-protein responsible for the biosynthesis of tyrosine.[6]

In connection with molecular framework **D** (Scheme 1), it has been found that a similar spirocyclic cyclopentanoid core is present in a variety of pharmacologically active terpenoids such as stemaranes[7] and scopadulanes. A broad pharmacological profile has been observed for scopadulan diter-

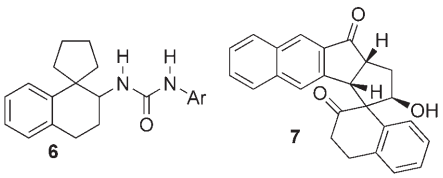


[a] Prof. Dr. S. Kotha, K. Mandal, A. Tiwari, S. M. Mobin
Department of Chemistry
Indian Institute of Technology, Bombay
Powai, Mumbai-400 076 (India)
Fax: (+91) 22-2572-3480
E-mail: srk@chem.iitb.ac.in



Scheme 1. Synthesis of a diverse range of molecular frameworks from β-naphthol derivatives.

penes.[8] Scopadulcic acid B, and scopadulciol are powerful inhibitors of H^+ and K^+ adenosine triphosphate. Conformationally constrained analogues of *N*-phenyl-*N'*-aralkylurea **6** act as potential ACAT inhibitors,[9] whereas the spirocyclic model compound **7** binds with remarkable efficiency to bulged DNA oligonucleotides, offering potential for the design of therapeutic agents.[10]

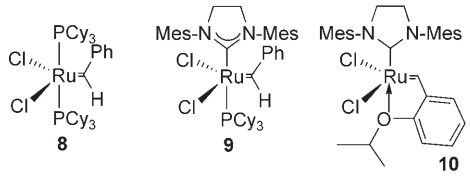


Although various synthetic approaches to these ring skeletons are available, there is a need to develop a unified approach in which such a diverse range of molecular frameworks can be assembled from a readily accessible common precursor in a short synthetic sequence. Motivated by these considerations, we have conceived a diversity-oriented approach for the generation of skeletally different molecular frameworks from the readily available β-naphthol by use of microwave-assisted silica gel-supported Claisen rearrangements[11] and Grubbs catalyst-induced ring-closing metatheses (RCMs) or ring-closing enyne metatheses (RCEMs) as key steps. The preliminary results of this research were published during 2004.[12]

With the development of the commercially available and well defined metal carbene complexes **8**,[13a] **9**,[13b] and **10**,[13c] olefin metathesis has attracted much attention from synthetic organic chemists, and numerous strategies based on metathesis as a key step have been developed.[14] Although RCM has gained popularity, enyne metathesis is less well explored.[15] Intramolecular enyne metathesis is particularly attractive as the double bond of the enyne is cleaved and the alkylidene part of the alkene migrates to the alkyne carbon, giving a cyclized compound containing a 1,3-diene moiety, a useful synthon for various cycloaddition strategies.[16]

Results and Discussion

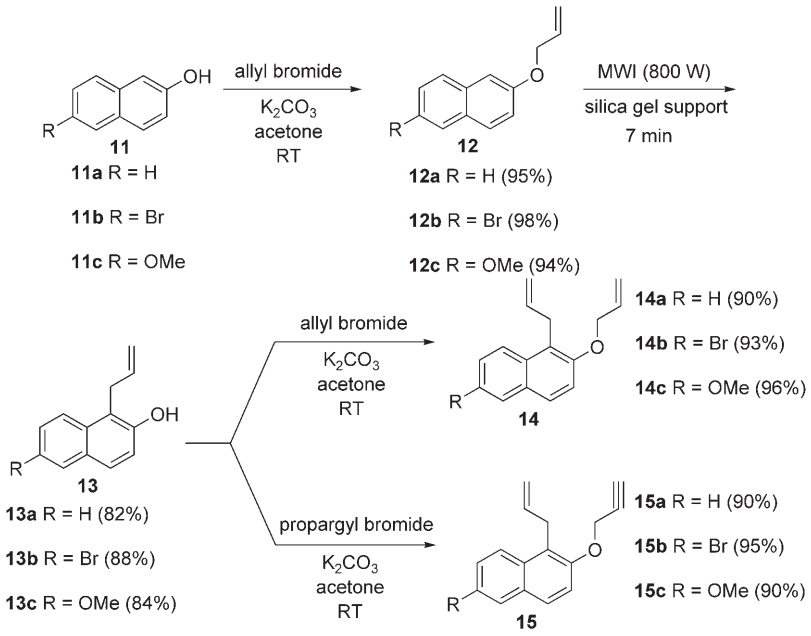
For the synthesis of oxepine molecular frameworks **A** and **B** (Scheme 1), *O*-allylation of β-naphthol derivatives **11a–c** was carried with allyl bromide



and potassium carbonate by stirring in acetone at room temperature. Claisen rearrangements of compounds **12a–c** were then achieved with the aid of microwave irradiation (MWI) on a silica gel support in the absence of solvent, and the products **13a–c** were obtained within 7 min (Scheme 2). MWI has become a useful tool in organic synthesis, thanks to the rate enhancement, higher yields, and improved selectivity often observed with respect to more conventional reaction conditions.[17] We found that the Claisen rearrangements of **12a–c** under MWI conditions on a silica gel support had advantages over the conventional conditions in several respects.[18] Some of these include: i) quick and economically advantageous, and ii) better safety, due to the absence of solvent during the reaction. In addition, the end products are usually separable from the silica gel by simple chromatography.

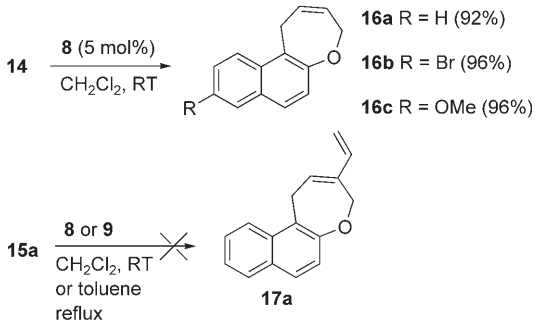
The desired building blocks **14a–c** for the RCM reactions were prepared by *O*-allylation of the β-naphthol derivatives **13a–c** by the conventional allylation procedure reported previously.[12] Repetition of the same reaction sequence with propargyl bromide in place of allyl bromide resulted in the generation of enyne building blocks **15a–c** in good yields (Scheme 2).

With the diene and enyne building blocks to hand, the metathesis reaction to provide the desired oxepine skeletons



Scheme 2. Preparation of RCM and RCEM precursors.

was attempted (Scheme 3). Treatment of the dienes **14a–c** with the catalyst **8** (5 mol%) at room temperature in dichloromethane (DCM) as solvent furnished the desired

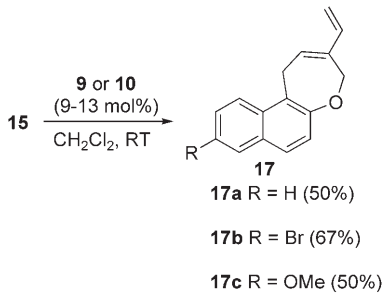


Scheme 3. RCM of **14** and attempted RCEM of **15a**.

naphthoxepine derivatives **16a–c** in good yields.[19] However, attempted RCEM of compound **15a** to deliver **17a** in the presence either of Grubbs first-generation catalyst (**8**) or of the more reactive second-generation catalysts (**9** and **10**) with stirring in DCM at room temperature was unsuccessful. Even under forcing reaction conditions (toluene at reflux) no detectable amount of metathesis product formation was observed, the unreacted starting material being recovered.

In view of the beneficial role of ethylene in RCEM, we decided to conduct the RCEM under ethylene.[20] Attempts to achieve metathesis of compound **15a** under ethylene in DCM in the presence of Grubbs first-generation catalyst (**8**) were unsuccessful, but the more reactive second-generation catalysts **9** and **10** gave the desired RCEM product in the presence of ethylene in good yield (Scheme 4).[21]

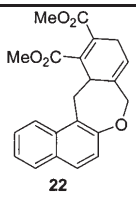
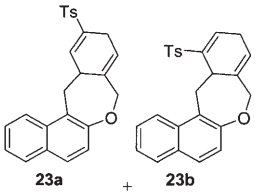
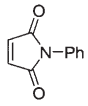
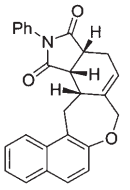
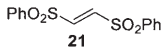
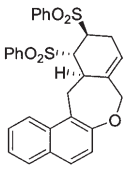
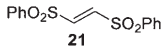
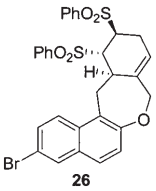
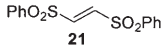
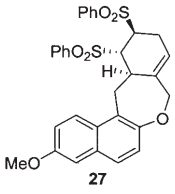
Since some of these dienes were found to be highly sensitive substrates, they were immediately used for Diels–Alder (DA) reactions. Hence, to obtain skeletally diverse naphthoxepine derivatives, dienes **17a–c** were treated with various reactive dienophiles (**18**–**21**), and the results of the highly stereoselective DA reactions are summarized in Table 1. Heating of diene **17a** with dimethyl acetylenedicarboxylate (DMAD, **18**) afforded the desired DA adduct **22** in a moderate isolated yield (entry 1, Table 1), while the DA reaction between the diene **17a** and *p*-toluenesulfonylacetylene (**19**) furnished a 9:1 mixture of regioisomers



Scheme 4. RCEM of **15**.

23a and **23b** in 61% combined yield (entry 2, Table 1).[22] Several attempts to isolate the minor isomer (**23b**) in its pure form by silica gel column chromatography were unsuccessful. The cycloaddition between compound **17a** and *N*-phenylmaleimide (**20**) afforded the single diastereomer **28** in a moderate yield (38%; entry 3, Table 1). Along similar lines, treatment of diene **17a** with *trans*-1,2-bis(phenylsulfonyl)ethylene (**21**) in toluene proceeded smoothly, delivering the DA adduct **29** (entry 4, Table 1) as a single diastereomer in 42% yield, whereas similarly, the DA reactions between dienes **17b** or **17c** and **21** under reaction conditions identical to those described for diene **17a** provided the corresponding cycloadducts **30** and **31** in moderate and good yields, respectively (entries 5 and 6, Table 1). The low to moderate yields of some of the cycloadducts could be attributed to the propensity of these sensitive dienes to polymerize. In a separate experiment, the cycloaddition between compound **17c** and **21** was therefore conducted without isolation of the diene, in order to avoid diene decomposition during workup and purification.[23] Although a slight improvement in the yield (33% over two steps) was observed, this one-pot operation

Table 1. Diels–Alder reactions between compounds **17a–c** and dienophiles **18–21**.

Entry	Diene	Dienophile	Diels–Alder adduct[a]	Yield [%][b]
1	**17a**	 **18**	 **22**	49
2	**17a**	 **19**	 **23a** + **23b**	61
			23a : **23b** = 9 : 1	
3	**17a**	 **20**	 **24**	38
4	**17a**	 **21**	 **25**	42
5	**17b**	 **21**	 **26**	74
6	**17c**	 **21**	 **27**	54

[a] All the reactions were carried out in toluene at 90 °C or reflux temperature. [b] Yield of isolated product.

was not taken further because of the increasingly complex nature of the product mixture (by TLC).

The stereochemistries of all the cycloadducts were determined with the aid of ^{1}H, ^{13}C, NOE, and COSY NMR spectral analysis. The regiochemistry of the major isomer **23a** was established from the observed NOE between H_a and H_b in the NOE difference spectrum (Figure 1). In compound **24**, the observed coupling constants for H_b in the ^{1}H NMR spectrum were found to be 9.2 Hz and 6.5 Hz, reflecting the *cis* relationship between H_a, H_b, and H_c (Figure 1), while in compound **26** the stereochemical assignment of H_a and H_b

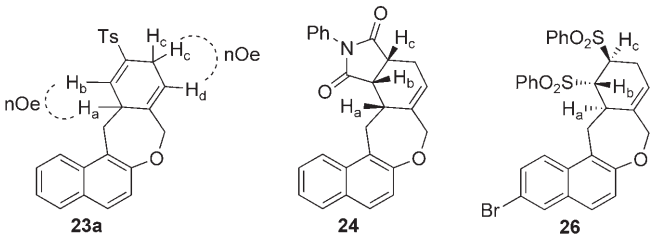


Figure 1. Stereochemistries assigned for **23a**, **24**, and **26**.

was unequivocally established by single-crystal X-ray analysis, as shown in Figure 2. Unambiguous assignments of the other analogues **25** and **27** were achieved by ^{1}H NMR analysis, through comparison of their coupling constants with those observed for cycloadduct **26**.

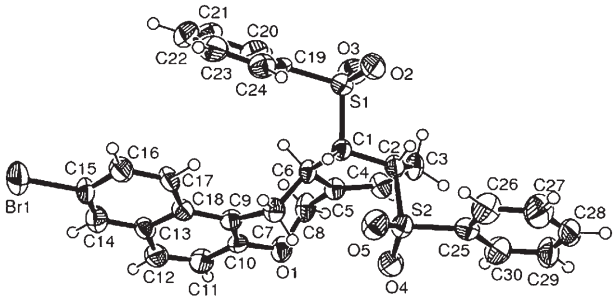


Figure 2. ORTEP diagram of compound **26**.

In addition to the expected three-bond coupling in H,H-COSY, $H_{d/d'}$ of compound **26** shows cross-peaks with H_a (Figure 3A) and $H_{f/f'}$ (Figure 3B), corresponding to long-range homoallylic coupling over five bonds. Similar weak homoallylic coupling was also observed in the H,H-COSY spectra of other analogues of **26**.

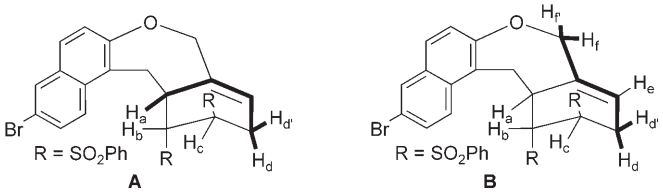
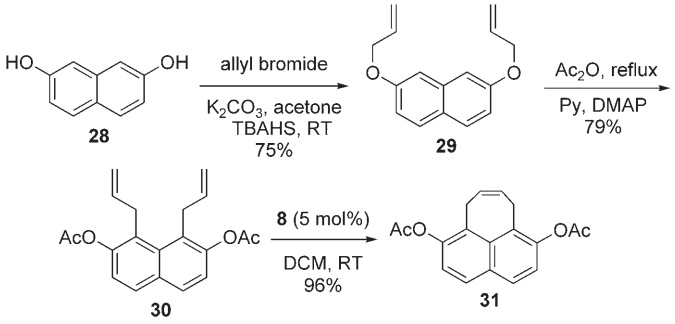


Figure 3. Homoallylic coupling (^5J) observed from H,H-COSY of **26**.

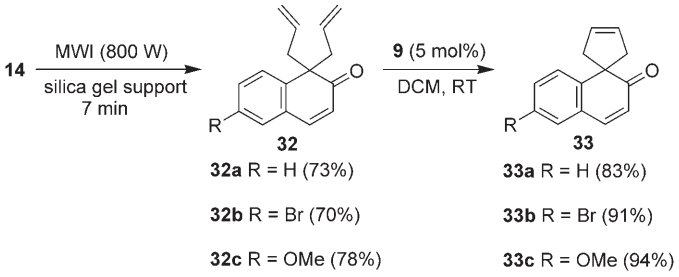
It appeared that naphthalene-2,7-diol might also be a suitable starting material for assembling a 7,10-dihydropleiadene framework (**C**, Scheme 1). To begin with, *O*-allylation of naphthalene-2,7-diol (**28**) was carried out under conventional allylation conditions with allyl bromide and potassium carbonate in the presence of catalytic amounts of tetrabutylammonium hydrogensulfate (TBAHS), with stirring in acetone at room temperature (Scheme 5). Attempted Claisen rearrangements of **29** either by conventional heating or under MWI conditions produced complex mixtures of prod-



Scheme 5. Synthesis of a 7,10-dihydropleiadene derivative from **28**.

ucts as indicated by TLC, but a one-pot Claisen rearrangement and acetyl protection procedure exclusively delivered the desired rearranged product **30** (79%). RCM of the diene **30** in the presence of Grubbs first-generation catalyst (**8**) in DCM at room temperature gave the pleiadene derivative **31** in 96% yield.

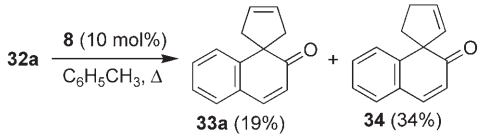
In an attempt to produce the cyclopentanoid spiro skeleton **D** (Scheme 1), the desired diolefinic precursor was prepared by Claisen rearrangement of compound **14** on a silica gel support under MWI conditions (Scheme 6), but only in-



Scheme 6. Synthesis of cyclopentanoid spirocyclics from β-naphthol.

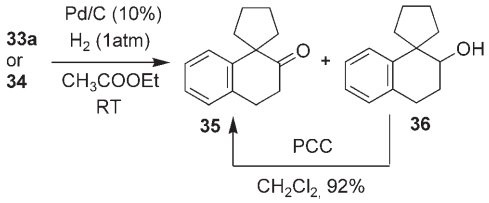
complete conversion of the starting material was observed, with the ratio of the starting material and the product remaining constant after 7 min (optimized time) of exposure to MWI conditions. Even after prolonged exposure (>20 min) of the reaction mixture to MWI conditions the starting material and product ratio remained the same.

Treatment of olefin **32** with the more reactive second-generation catalyst **9** in DCM at room temperature gave the expected metathesis product **33** in good yield (Scheme 6),[12] though RCM of compound **32a** in the presence of Grubbs first-generation catalyst was found to be very slow. Products **33a** and **34** were obtained when compound **32a** was heated at reflux in toluene in the presence of the Grubbs catalyst **8** for seven days.[24] Both of these products exhibited characteristic dienone absorption bands at 1663 and 1664 cm^{-1}, respectively, in their IR spectra and showed molecular ion peaks at *m*/*z* 196 in their mass spectra. The ^1H NMR spectral data for compound **34** included two different multiplets, corresponding to the two nonequivalent olefinic protons, and the presence of 14 lines in the proton-decoupled ^{13}C NMR spectral data indicated that **34** was an isomer of **33a** (Scheme 7).[12]



Scheme 7. RCM of **32a** in the presence of Grubbs first-generation catalyst.

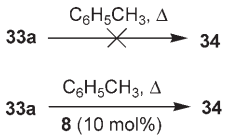
Palladium/carbon-catalyzed hydrogenations of the two isomers **33a** and **34** both gave the same reduced products **35** and **36** in 1:1 ratios, which further confirmed that compound **34** seems to be the double bond isomer of **33a** (Scheme 8).[12]



Scheme 8. Pd/C-catalyzed hydrogenations of **33a** and **34**.

Alcohol **36** appears to be the product of complete reduction of either compound **33a** or **34**, and its structure was confirmed by its reoxidation to the corresponding ketone **35** (Scheme 8). Later on, the ketone **35** was converted into the corresponding known hydrazone derivative and its identity was established by melting point comparison.[25]

At this juncture we were suspecting that prolonged heating might be responsible for the isomerization of **33a** to **34**, and to examine this possibility, compound **33a** was heated at reflux in toluene in the absence of Grubbs catalyst for seven days. No isomerized product **34** was observed, however, which clearly indicates that thermal isomerization of **33a** to **34** in the absence of Grubbs catalyst was not viable, but in the presence of Grubbs catalyst **8** (10 mol%) under the above conditions, compound **33a** gave the isomerized product **34** in 66% yield (Scheme 9).[12]

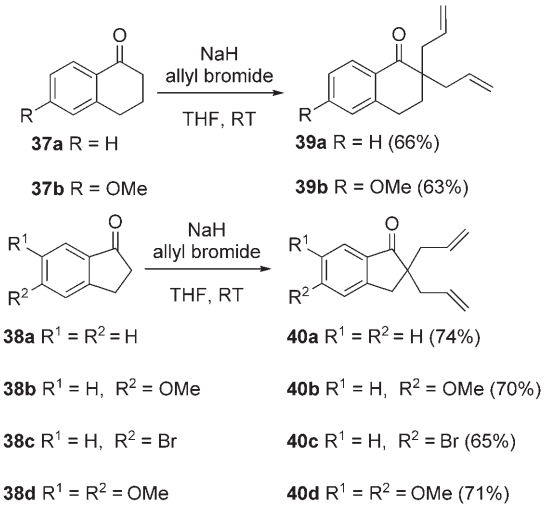


Scheme 9. Grubbs catalyst-induced isomerization of **33a**.

Recent literature reports dealing with olefin isomerization in the presence of Grubbs catalyst are limited to substrates containing oxygen or nitrogen substituents in their allylic or homoallylic positions.[26] We have observed that isomerization of the double bond is also feasible in the presence of Grubbs catalyst under thermal conditions in the absence of alcohol, ether, or amide functional groups in the allylic or homoallylic positions. A possible mechanism for the isomer-

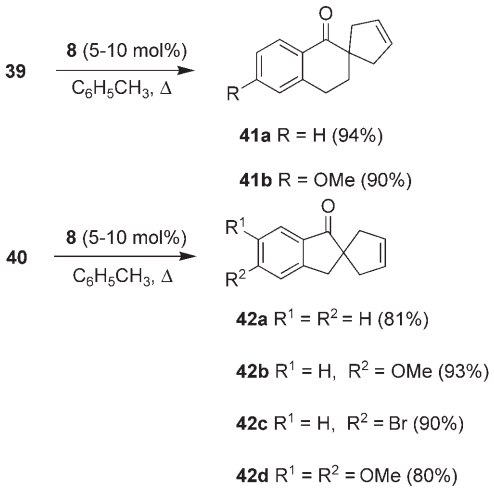
ization reaction, involving a 16-electron Ru complex, may involve intramolecular hydrogen transfer followed by β-elimination.[12] However, it is believed that the ruthenium hydride species generated in situ by catalyst decomposition is responsible for the isomerization.[27]

A structurally similar but strategically different approach to spiro systems starting from tetralone and indanone derivatives such as **37** and **38** has been conceived. In order to demonstrate the spiroannulation strategy, the desired diallyl precursor materials (**39** and **40**) were prepared by allylation of the tetralone or indanone derivatives (**37** and **38**, respectively) by treatment with allyl bromide in the presence of sodium hydride with stirring in THF at room temperature (Scheme 10).



Scheme 10. Preparation of RCM precursors.

With various diallylated products now to hand, the next task was to demonstrate the key RCM reactions for the preparation of spirocyclic tetralone and indanone derivatives. Exposure of olefins **39a–b** and **40a–d** to catalyst **8** in toluene at reflux thus furnished the desired spiro cyclopentanoid derivatives **41a–b** and **42a–d**, respectively, in good yields (Scheme 11).

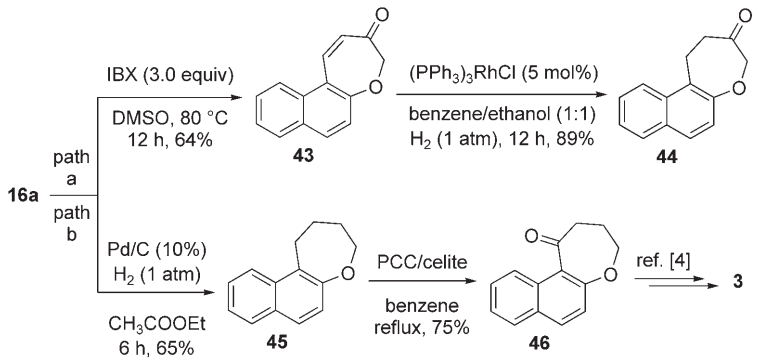


Scheme 11. RCM of **39** and **40** in the presence of Grubbs first-generation catalyst.

To demonstrate the utility of this approach we would like to disclose a formal total synthesis of naphthoxepine oxime ether **3**, a potential hypotensive agent. Two synthetic routes from oxepine **16a** to the desired key intermediate ketone **46** can be envisaged. Initially, a sequence consisting of 2-iodoxybenzoic acid(IBX)-mediated benzylic oxidation followed by Wilkinson's catalyst-induced hydrogenation did not furnish the desired ketone **46** but instead produced a rearranged product **44** (Path a, Scheme 12). A different sequence based on palladium/carbon-catalyzed hydrogenation, followed by pyridinium chlorochromate(PCC)-mediated benzylic oxidation,[28] however, furnished the desired intermediate **46** (Path b, Scheme 12), which has previously been converted to compound **3** in a couple of steps.[4]

Conclusion

This approach to DOS clearly demonstrates our capability to deliver a diverse set of biologically relevant cyclic structures from bench-top chemicals through the use of microwave-assisted silica gel-supported Claisen rearrangements and Grubbs catalyst-induced metatheses as key steps. Non-metathetic behavior of Grubbs catalyst was observed in addition to the metathesis reaction. Because of the presence of reactive functionality in the end product we anticipate that our method should also be extendable to the construction of appendage-diverse small-molecule libraries. In view of the importance of the molecular frameworks described here and



Scheme 12. Formal synthesis of compound **3**.

the simplicity of the procedure, our methodology is likely to find useful application in the design of small "drug-like" molecules.

Experimental Section

General remarks: All reactions were monitored by thin layer chromatography (TLC) carried out on glass plates coated with Acme's silica gel GF 254 (containing 13% calcium sulfate as a binder). Visualization of the spots on TLC plates was achieved by exposure either to iodine vapor or to UV light. Flash chromatography was performed on Acme's silica gel (100–200 mesh). Petroleum ether refers to the fraction of boiling point 60–80 °C. Metathesis catalysts were purchased from Sigma–Aldrich Chemical Co., Milwaukee, USA. All the commercial grade reagents were used without further purification. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer in KBr/$CHCl_3$/CCl_4. ^{1}H NMR (300, 400 MHz) and ^{13}C NMR (75.4, 100.6 MHz) spectra were determined at room temperature on a Varian VXR 300 or AX 400 Mercury Plus in $CDCl_3$ solutions. In some cases (to save $CDCl_3$) we have used $CDCl_3$ and CCl_4 systems to record NMR spectral data. Coupling constants (J values) are given in hertz (Hz). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane as internal reference. High-resolution mass spectra were determined on a Micromass Q-Tof spectrometer. Elemental analysis was performed on a Carlo–Erba MOD 1106 CHN analyzer.

General procedure for Claisen rearrangements: Preactivated silica gel (100–200 mesh, 5–10 times the weight of the starting substrate; preactivation of the silica gel was achieved by MWI (Ken Star, OM-992E) for 5 min) was added to a dichloromethane solution of starting material in a beaker and the solvent was then evaporated. The resulting homogeneous mixture of the substrate and silica gel was then irradiated in a microwave oven (power 800 W) for 7 min (optimized time). The crude reaction mixture was purified by flash chromatography. Elution of the column with an appropriate mixture of ethyl acetate and petroleum ether gave the required product.

1-Allyl-2-naphthol (13a):[29] Compound **12a** (1.16 g, 6.3 mmol) was mixed with silica gel (5 g) and the system was then irradiated in a microwave oven as described in the general procedure for 7 min. The crude reaction mixture was then directly loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **13a** as a brown, crystalline solid (958 mg, 82%). M.p. 57 °C (lit.: 56 °C).[29b]

1-Allyl-6-bromo-2-naphthol (13b):[30] Compound **12b** (218 mg, 0.8 mmol) was mixed with silica gel (2 g), and the system was then irradiated in a microwave oven for 7 min as described in the general procedure. The crude reaction mixture was then directly loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **13b** as a white, crystalline solid (184 mg, 84%). M.p. 90 °C (lit.: 86–87 °C).[30]

1-Allyl-6-methoxy-2-naphthol (13c):[31] Compound **12c** (201 mg, 0.9 mmol) was mixed with silica gel (2 g), and the system was then irradiated in a microwave oven for 7 min as described in the general procedure. The crude reaction mixture was then directly loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2.5%) gave compound **13c** as a white, crystalline solid (176 mg, 88%). M.p. 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.79 (d, J = 5.6 Hz, 2H; CH_2CH=CH_2), 3.89 (s, 3H; OCH_3), 5.01–5.10 (m, 3H; CH_2CH=CH_2 and OH), 6.0–6.10 (m, 1H; CH_2CH=CH_2), 7.06 (d, J = 8.8 Hz, 1H; ArH), 7.10 (d, J = 2.4 Hz, 1H; ArH), 7.16 (dd, J = 9, 2.6 Hz, 1H; ArH), 7.55 (d, J = 8.8 Hz, 1H; ArH), 7.80 ppm (d, J = 9.2 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C, TMS): δ = 29.5, 55.4, 106.9, 116.0, 117.4, 118.5, 119.0, 124.7, 127.0, 128.6, 130.4, 135.9, 149.7, 155.7 ppm.

1,1-Diallylnaphthalen-2(1*H*)-one (32a):[32] Compound **14a** (30 mg, 0.134 mmol) was mixed with silica gel (346 mg), and the system was then irradiated in a microwave oven for 7 min as described in the general procedure. The crude reaction mixture was then subjected to flash chromatographic purification (silica gel, EtOAc in petroleum ether, 0.5 → 2.0%) to afford compound **32a** as a colorless liquid (22 mg, 73%) along with unreacted starting material **14a** (7 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.59 (dd, J = 13.4, 7.2 Hz, 2H; 2×CHHCH=CH_2), 2.90 (dd, J = 13.6, 7.2 Hz, 2H; 2×CHHCH=CH_2), 4.77–4.87 (m, 4H; 2×CH_2CH=CH_2), 5.21–5.32 (m, 2H; 2×CH_2CH=CH_2), 6.16 (d, J = 10 Hz, 1H; C(O)CH=CH), 7.20–7.32 (m, 2H; ArH), 7.39 (d, J = 10 Hz, 1H; C(O)CH=CH), 7.43–7.46 ppm (m, 2H; ArH); ^{1}H NMR chemical shift values were matched with literature values.[32b]

1,1-Diallyl-6-bromonaphthalen-2(1*H*)-one (32b): Compound **14b** (76 mg, 0.25 mmol) was mixed with silica gel (710 mg), and the system was then irradiated in a microwave oven for 7 min as described in the general procedure. The crude reaction mixture was then subjected to flash chromatographic purification (silica gel, EtOAc in petroleum ether, 0.5 → 2.5%) to afford compound **32b** as a colorless liquid (53 mg, 70%) along with unreacted starting material **14b** (20 mg, 26%). R_f = 0.25 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.54 (dd, J = 13.6, 7.2 Hz, 2H; 2×CHHCH=CH_2), 2.89 (dd, J = 13.6, 7.2 Hz, 2H; 2×CHHCH=CH_2), 4.79–4.86 (m, 4H; 2×CH_2CH=CH_2), 5.2–5.3 (m, 2H; 2×CH_2CH=CH_2), 6.19 (d, J = 10.4 Hz, 1H; C(O)CH=CH), 7.30 (d, J = 7.6 Hz, 1H; ArH), 7.31 (d, J = 10.0 Hz, 1H; C(O)CH=CH), 7.45 (d, J = 2.4 Hz, 1H; ArH), 7.55 ppm (dd, J = 8, 2.2 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C, TMS): δ = 46.1, 55.8, 118.5, 120.5, 127.2, 128.7, 131.9, 132.1, 132.5, 132.8, 142.5, 143.6, 202.4 ppm; IR (neat): $\tilde{\nu}$ = 1658 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 302 nm (5122 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{16}OBr$ [M+H]: 303.0385; found: 303.0400.

1,1-Diallyl-6-methoxynaphthalen-2(1*H*)-one (32c): Compound **14c** (81 mg, 0.32 mmol) was mixed with silica gel (750 mg), and the system was then irradiated in a microwave oven for 7 min as described in the general procedure. The crude reaction mixture was then subjected to flash chromatographic purification (silica gel, EtOAc in petroleum ether, 0.5 → 3%) to afford compound **32c** as a colorless liquid (63 mg, 78%) along with unreacted starting material **14c** (15 mg, 19%). R_f = 0.1 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.55 (dd, J = 13.4, 7.0 Hz, 2H; 2×CHHCH=CH_2), 2.87 (dd, J = 13.4, 7.4 Hz, 2H; 2×CHHCH=CH_2), 3.85 (s, 3H; OCH_3), 4.77–4.87 (m, 4H; 2×CH_2CH=CH_2), 5.22–5.32 (m, 2H; 2×CH_2CH=CH_2), 6.16 (d, J = 9.6 Hz, 1H; C(O)CH=CH), 6.82 (d, J = 2.8 Hz, 1H; ArH), 7.0 (dd, J = 8, 2.8 Hz, 1H; ArH), 7.34 ppm (d, J = 9.2 Hz, 2H; ArH and C(O)CH=CH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C, TMS): δ = 46.3, 55.29, 55.33, 113.8, 115.9, 118.0, 126.5, 128.1, 131.8, 132.7, 135.5, 145.1, 158.0, 203.4 ppm; IR (neat): $\tilde{\nu}$ = 1651 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 308 nm (5091 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{19}O_2$ [M+H]: 255.1385; found: 255.1381.

1-Allyl-2-(allyloxy)naphthalene (14a):[33] Potassium carbonate (200 mg, 1.4 mmol) and allyl bromide (140 mg, 1.2 mmol) were added to a solution of compound **13a** (133 mg, 0.7 mmol) in dry acetone and the reaction mixture was then allowed to stir at room temperature. After completion of the reaction (4 h, TLC monitoring) the crude reaction mixture was filtered through a celite pad. The residue was washed with dichloromethane (3×10 mL), and evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with petroleum ether gave compound **14a** as a colorless liquid (145 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.89 (dt, J = 6.0, 2.0 Hz, 2H; $ArCH_2$), 4.67 (dt, J = 4.8, 1.6 Hz, 2H; OCH_2), 4.98–5.03 (m, 2H; $ArCH_2CH$=CH_2), 5.28 (d, J = 10.4 Hz, 1H; OCH_2CH=CHH), 5.44 (d, J = 17.2 Hz, 1H; OCH_2CH=CHH), 6.0–6.14 (m, 2H; 2×CH_2CH=CH_2), 7.25 (d, J = 8.2 Hz, 1H; ArH), 7.34 (ddd, J = 8.0, 7.0, 0.8 Hz, 1H; ArH), 7.47 (ddd, J = 8.3, 6.6, 1.2 Hz, 1H; ArH), 7.72 (d, J = 8.8 Hz, 1H; ArH), 7.78 (d, J = 8.0 Hz, 1H; ArH), 7.95 ppm (d, J = 8.8 Hz, 1H; ArH); ^{1}H NMR chemical shift values were matched with literature values.[33]

1-Allyl-2-(allyloxy)-6-bromonaphthalene (14b): Potassium carbonate (194 mg, 1.4 mmol) and allyl bromide (127 mg, 1.0 mmol) were added to a solution of compound **13b** (185 mg, 0.703 mmol) in dry acetone. The reaction mixture was then allowed to stir at room temperature for 4 h and was then filtered through a celite pad. The residue was washed with DCM (3×10 mL). Evaporation of the solvent gave the crude product,

which was loaded onto a silica gel column, and elution of the column with petroleum ether gave compound **14b** as a colorless liquid (199 mg, 93%). R_f = 0.6 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 3.85 (dt, J = 6, 1.6 Hz, 2H; $ArCH_2$), 4.66 (dt, J = 5.2, 1.6 Hz, 2H; OCH_2), 4.93–5.02 (m, 2H; $ArCH_2CH{=}CH_2$), 5.28 (dd, J = 10.6, 1.6 Hz, 1H; $OCH_2CH{=}CHH$), 5.43 (dd, J = 17, 1.6 Hz, 1H; $OCH_2CH{=}CHH$), 5.96–6.12 (m, 2H; 2× $CH_2CH{=}CH_2$), 7.25 (d, J = 8.8 Hz, 1H; ArH), 7.51 (dd, J = 9.2, 2.4 Hz, 1H; ArH), 7.62 (d, J = 9.2 Hz, 1H; ArH), 7.79 (d, J = 9.2 Hz, 1H; ArH), 7.92 ppm (d, J = 2.0 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 29.3, 70.2, 115.3, 116.0, 117.2, 117.4, 121.9, 125.6, 127.0, 129.6, 130.3, 130.5, 131.8, 133.6, 136.4, 153.8 ppm; UV ($CHCl_3$): λ_{max} (ε) = 252 nm (7952 $mol^{-1}dm^3cm^{-1}$).

1-Allyl-2-(allyloxy)-6-methoxynaphthalene (14c): Potassium carbonate (198 mg, 1.4 mmol) and allyl bromide (129 mg, 1.0 mmol) were added to a solution of compound **13c** (153 mg, 0.715 mmol) in dry acetone. The reaction mixture was then allowed to stir at room temperature for 4 h and filtered through a celite pad, and the residue was washed with DCM (3× 10 mL). Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, and elution of the column with petroleum ether gave compound **14c** as a colorless liquid (174 mg, 96%). R_f = 0.36 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.86 (dt, J = 6, 1.6 Hz, 2H; $ArCH_2$), 3.89 (s, 3H; OCH_3), 4.63 (dt, J = 5.2, 1.6 Hz, 2H; OCH_2), 4.95–5.0 (m, 2H; $ArCH_2CH{=}CH_2$), 5.26 (dd, J = 10.4, 1.6 Hz, 1H; $OCH_2CH{=}CHH$), 5.43 (dd, J = 18, 1.6 Hz, 1H; $OCH_2CH{=}CHH$), 5.98–6.13 (m, 2H; 2× $CH_2CH{=}CH_2$), 7.09 (d, J = 2.4 Hz, 1H; ArH), 7.15 (dd, J = 9.2, 2.8 Hz, 1H; ArH), 7.22 (d, J = 9.2 Hz, 1H; ArH), 7.61 (d, J = 9.2 Hz, 1H; ArH), 7.85 ppm (d, J = 9.2 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 29.4, 55.3, 70.6, 106.3, 115.0, 116.0, 117.0, 119.0, 122.2, 125.3, 126.5, 128.5, 130.4, 134.0, 136.8, 152.1, 155.9 ppm; UV ($CHCl_3$): λ_{max} (ε) = 276 nm (5740 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{19}O_2$ [M+H]: 255.1385; found: 255.1396.

1,4-Dihydronaphtho[2,1-*b*]oxepine (16a): Grubbs catalyst **9** (5 mg, 0.006 mmol, 5 mol%) was added to a solution of diene **14a** (30 mg, 0.13 mmol) in dry, degassed DCM (3 mL), and the reaction mixture was allowed to stir at room temperature. After completion of the reaction (4 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel, EtOAc in petroleum ether, 1.5%) to give compound **16a** as a white, crystalline solid (24 mg, 92%). R_f = 0.35 (silica gel, EtOAc/petroleum ether 1:49); m.p. 84°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.91 (d, J = 3 Hz, 2H; $ArCH_2$), 4.60–4.63 (m, 2H; OCH_2), 5.5 (d, J = 11.4 Hz, 1H; $ArCH_2CH$), 5.96 (dt, J = 11.4, 5.2 Hz, 1H; OCH_2CH), 7.23 (d, J = 8.4 Hz, 1H; ArH), 7.35 (dd, J = 7.8, 6.9 Hz, 1H; ArH), 7.45 (dd, J = 7.2, 8.4 Hz, 1H; ArH), 7.67 (d, J = 8.7 Hz, 1H; ArH), 7.77 (d, J = 8 Hz, 1H; ArH), 7.98 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$ + CCl_4, 25°C, TMS): δ = 24.7, 70.6, 121.8, 123.1, 124.3, 126, 126.1, 128.1 (2C), 128.7, 130.5, 131.2, 131.8, 156.2 ppm; UV ($CHCl_3$): λ_{max} (ε) = 283 nm (3888 $mol^{-1}dm^3cm^{-1}$); MS: m/z: 196 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{12}O$: C 85.68, H 6.16; found: C 85.28, H 6.51.

9-Bromo-1,4-dihydronaphtho[2,1-*b*]oxepine (16b): Grubbs catalyst **9** (3 mg, 0.004 mmol, 5 mol%) was added to a solution of diene **14b** (23 mg, 0.076 mmol) in dry, degassed DCM (3 mL), and the reaction mixture was allowed to stir at room temperature. After completion of the reaction (1 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel, EtOAc in petroleum ether, 1.5%) to give compound **16b** as a white, crystalline solid (20 mg, 96%). R_f = 0.54 (silica gel, EtOAc/petroleum ether 1:49); m.p. 110°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.88–3.90 (m, 2H; $ArCH_2$), 4.64–4.67 (m, 2H; OCH_2), 5.51–5.57 (m, 1H; $ArCH_2CH$), 5.93–6.01 (m, 1H; OCH_2CH), 7.29 (d, J = 8.7 Hz, 1H; ArH), 7.55 (dd, J = 9.1, 2.1 Hz, 1H; ArH), 7.61 (d, J = 8.4 Hz, 1H; ArH), 7.89 (d, J = 9 Hz, 1H; ArH), 7.97 ppm (d, J = 2.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 24.7, 70.7, 118.4, 123.1, 125.0, 125.6, 127.3, 128.1, 129.4, 130.2, 130.6, 131.0, 132.3, 156.4 ppm; UV ($CHCl_3$): λ_{max} (ε) = 252 nm (6328 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{12}OBr$ [M+H]: 275.0072; found: 275.0085.

9-Methoxy-1,4-dihydronaphtho[2,1-*b*]oxepine (16c): Grubbs catalyst **9** (6 mg, 0.007 mmol, 5 mol%) was added to a solution of diene **14c** (35 mg, 0.137 mmol) in dry, degassed DCM (3 mL), and the reaction mixture was allowed to stir at room temperature. After completion of the reaction (1 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel, EtOAc in petroleum ether, 2%) to give compound **16c** as a white, crystalline solid (30 mg, 96%). R_f = 0.3 (silica gel, EtOAc/petroleum ether 1:49); m.p. 82°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.87–3.96 (m, 5H; $ArCH_2$ and OCH_3), 4.60–4.69 (m, 2H; OCH_2), 5.52 (d, J = 8.1 Hz, 1H; $ArCH_2CH$), 5.94–6.0 (m, 1H; OCH_2CH), 7.13 (d, J = 2.4 Hz, 1H; ArH), 7.17 (dd, J = 8.8, 2.4 Hz, 1H; ArH), 7.25 (d, J = 8.4 Hz, 1H; ArH), 7.60 (d, J = 8.4 Hz, 1H; ArH), 7.94 ppm (d, J = 9.6 Hz, 1H; ArH); HRMS (Q-Tof ES+): m/z calcd for $C_{15}H_{15}O_2$ [M+H]: 227.1072; found: 227.1082.

1-Allyl-2-(prop-2-yn-1-yloxy)naphthalene (15a): Anhydrous powdered potassium carbonate (414 mg, 3 mmol) and propargyl bromide (250 mg, 2.1 mmol) were added to a solution of compound **13a** (259 mg, 1.4 mmol) in dry acetone (10 mL). The reaction mixture was then allowed to stir at room temperature for 6 h and was then filtered through a celite pad. The residue was washed with dichloromethane (3×10 mL), the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1%) to provide compound **15a** as a white, crystalline solid (280 mg, 90%). R_f = 0.4 (silica gel, EtOAc/petroleum ether 1:49); m.p. 38°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.49 (t, J = 2.5 Hz, 1H; $CH_2C{\equiv}CH$), 3.89 (d, J = 5.8 Hz, 2H; $CH_2CH{=}CH_2$), 4.81 (d, J = 2.5 Hz, 2H; $CH_2C{\equiv}CH$), 4.96–5.03 (m, 2H; $CH_2CH{=}CH_2$), 5.98–6.11 (m, 1H; $CH_2CH{=}CH_2$), 7.34–7.39 (m, 2H; ArH), 7.48 (ddd, J = 8.5, 6.9, 1.1 Hz, 1H; ArH), 7.76 (d, J = 9.2 Hz, 1H; ArH), 7.80 (d, J = 8.1 Hz, 1H; ArH), 7.95 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 29.4, 57.6, 75.4, 79.2, 115.2, 115.4, 122.7, 123.8, 123.9, 126.4, 128.1, 128.5, 130.0, 133.2, 136.7, 152.7 ppm; IR (neat): $\tilde{\nu}$ = 3293 cm^{-1} (≡C–H st), 2121 cm^{-1} (C≡C st); UV ($CHCl_3$): λ_{max} (ε) = 283 nm (4387 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{15}O$ [M+H]: 223.1123; found: 223.1130.

1-Allyl-6-bromo-2-(prop-2-yn-1-yloxy)naphthalene (15b): Anhydrous powdered potassium carbonate (220 mg, 1.6 mmol) and propargyl bromide (142 mg, 1.2 mmol) were added to a solution of compound **13b** (212 mg, 0.8 mmol) in dry acetone (7 mL). The reaction mixture was then allowed to stir at room temperature for 4 h and was then filtered through a celite pad. The residue was washed with dichloromethane (3×10 mL), the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1%) to provide compound **15b** as a white, crystalline solid (230 mg, 95%). R_f = 0.6 (silica gel, EtOAc/petroleum ether 1:49); m.p. 64°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.50 (t, J = 2.4 Hz, 1H; $CH_2C{\equiv}CH$), 3.85 (dt, J = 5.7, 1.5 Hz, 2H; $CH_2CH{=}CH_2$), 4.82 (d, J = 2.1 Hz, 2H; $CH_2C{\equiv}CH$), 4.91–5.03 (m, 2H; $CH_2CH{=}CH_2$), 5.95–6.08 (m, 1H; $CH_2CH{=}CH_2$), 7.38 (d, J = 9 Hz, 1H; ArH), 7.52 (dd, J = 9.1, 2.4 Hz, 1H; ArH), 7.66 (d, J = 9 Hz, 1H; ArH), 7.81 (d, J = 9.3 Hz, 1H; ArH), 7.94 ppm (d, J = 2.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 29.3, 57.5, 75.7, 78.9, 115.5, 116.3, 117.7, 122.9, 125.8, 127.2, 129.7, 130.4, 131.0, 131.8, 136.4, 152.9 ppm; IR (neat): $\tilde{\nu}$ = 3296 cm^{-1} (≡C–H st), 2121 cm^{-1} (C≡C st); UV ($CHCl_3$): λ_{max} (ε) = 284 nm (5522 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{14}O$ ([M+H−Br]: 222.1045; found: 222.1039.

1-Allyl-6-methoxy-2-(prop-2-yn-1-yloxy)naphthalene (15c): Anhydrous powdered potassium carbonate (246 mg, 1.78 mmol) and propargyl bromide (159 mg, 1.3 mmol) were added to a solution of compound **13c** (191 mg, 0.89 mmol) in dry acetone (7 mL). The reaction mixture was then allowed to stir at room temperature for 6 h and filtered through a celite pad. The residue was washed with dichloromethane (3×10 mL), the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1.5%) to provide compound **15c** as a colorless liquid

(280 mg, 90%). R_f = 0.36 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.48 (t, J = 2.4 Hz, 1H; $CH_2C{\equiv}CH$), 3.86 (dt, J = 4.5, 1.5 Hz, 2H; $CH_2CH{=}CH_2$), 3.90 (s, 3H; OCH_3), 4.78 (d, J = 2.1 Hz, 2H; $CH_2C{\equiv}CH$), 4.94–5.03 (m, 2H; $CH_2CH{=}CH_2$), 5.97–6.10 (m, 1H; $CH_2CH{=}CH_2$), 7.10 (d, J = 2.7 Hz, 1H; ArH), 7.16 (dd, J = 9.3, 2.4 Hz, 1H; ArH), 7.33 (d, J = 9 Hz, 1H; ArH), 7.64 (d, J = 8.7 Hz, 1H; ArH), 7.86 ppm (d, J = 9 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 29.5, 55.4, 58.0, 75.3, 79.4, 106.5, 115.3, 116.4, 119.2, 123.3, 125.6, 126.7, 128.6, 131.1, 136.8, 151.4, 156.3 ppm; IR (neat): $\tilde{\nu}$ = 3292 cm^{-1} (≡C–H st), 2121 cm^{-1}; (C≡C st); UV ($CHCl_3$): λ_{max} (ε) = 275 nm (5128 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{17}O_2$ [M+H]: 253.1229; found: 253.1238.

General experimental procedure for the ring-closing enyne metathesis of 15a–c: The enyne compound (1 equiv) in dry DCM was degassed with nitrogen for 15 min and then with ethylene gas for 10 min. Grubbs catalyst **9** or **10** (9–13 mol%, portionwise addition at different time intervals) was then added, and finally the vessel was kept under 1 atm ethylene pressure (balloon pressure). The reaction mixture was then stirred at room temperature. After completion of the reaction (TLC monitoring), the pressure was released, the resulting brown solution was concentrated under reduced pressure, and the crude product was purified by silica gel flash chromatography. Elution of the column with an appropriate mixture of ethyl acetate and petroleum ether gave the required compound.

RCEM of 15a with Hoveyda catalyst 10: Catalyst **10** (6 mg, 0.009 mmol, 10 mol%, in two portions at 1.5 h interval) was added to a solution of enyne **15a** (20 mg, 0.09 mmol) in dry, degassed DCM (4 mL) as described in the general procedure and the reaction mixture was then stirred at room temperature in the presence of ethylene (1 atm). After completion of the reaction (3 h, TLC monitoring) the resulting brown solution was concentrated under reduced pressure and the crude product was then purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1%) to afford 3-vinyl-1,4-dihydronaphtho[2,1-*b*]oxepine (**17a**) as a colorless liquid (10 mg, 50%). R_f = 0.42 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.99 (d, J = 6.3 Hz, 2H; $ArCH_2$), 4.85 (d, J = 1.8 Hz, 2H; OCH_2), 4.90 (d, J = 18.3 Hz, 1H; CH=CH*H*), 4.91 (d, J = 11.4 Hz, 1H; CH=CH*H*), 6.07 (t, J = 6.3 Hz, 1H; CH_2CH), 6.23 (dd, J = 18.0, 10.8 Hz, 1H; $CH{=}CH_2$), 7.31 (d, J = 8.7 Hz, 1H; ArH), 7.40 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H; ArH), 7.51 (ddd, J = 7.7, 7.7, 1.2 Hz, 1H; ArH), 7.73 (d, J = 8.7 Hz, 1H; ArH), 7.83 (d, J = 8.5 Hz, 1H; ArH), 8.03 ppm (d, J = 8.4 Hz, 1H; ArH); HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{15}O$ [M+H]: 223.1123; found: 223.1114.

RCEM of 15a with Grubbs catalyst 9: Grubbs catalyst **9** (9 mg, 0.01 mmol, 10 mol%, in two portions at 1.5 h interval) was added to a solution of enyne **15a** (20 mg, 0.09 mmol) in dry, degassed DCM (3 mL) as described in the general procedure and the reaction mixture was then stirred at room temperature in the presence of ethylene (1 atm). After completion of the reaction (3 h, TLC monitoring) the resulting brown solution was concentrated under reduced pressure and the crude product was then purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1%) to afford the diene 3-vinyl-1,4-dihydronaphtho[2,1-*b*]oxepine (**17a**) as a colorless liquid (9 mg, 45%).

9-Bromo-3-vinyl-1,4-dihydronaphtho[2,1-*b*]oxepine (17b): Catalyst **9** (11 mg, 0.013 mmol, 9 mol%, in two portions at 2 h interval) was added to a solution of enyne **15b** (45 mg, 0.149 mmol) in dry, degassed DCM (10 mL) as described in the general procedure and the reaction mixture was then stirred at room temperature in the presence of ethylene (1 atm). After completion of the reaction (4 h, TLC monitoring) the resulting brown solution was concentrated under reduced pressure and the crude product was then purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1.5%) to afford diene **17b** as a white, crystalline solid (30 mg, 67%). R_f = 0.62 (silica gel, EtOAc/petroleum ether 1:49); m.p. 122°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.95 (d, J = 5.7 Hz, 2H; $ArCH_2$), 4.85 (d, J = 1.5 Hz, 2H; OCH_2), 4.91 (d, J = 17.4 Hz, 1H; CH=CH*H*), 4.92 (d, J = 12.0 Hz, 1H; CH=CH*H*), 6.05 (t, J = 5.7 Hz, 1H; CH_2CH), 6.22 (dd, J = 18.2, 11.4 Hz, 1H; $CH{=}CH_2$), 7.32 (d, J = 9 Hz, 1H; ArH), 7.55 (dd, J = 9.2, 2.4 Hz, 1H; ArH), 7.62 (d, J = 9 Hz, 1H; ArH), 7.88 (d, J = 9 Hz, 1H; ArH), 7.97 ppm (d, J = 2.1 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 24.5, 70.4, 111.1, 118.4, 122.8, 124.8, 127.4, 127.9, 129.5, 130.11, 130.13, 130.6, 132.3, 136.7, 137.5, 156.2 ppm; HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{14}OBr$ [M+H]: 301.0228; found: 301.0231.

9-Methoxy-3-vinyl-1,4-dihydronaphtho[2,1-*b*]oxepine (17c): Catalyst **9** (13 mg, 0.015 mmol, 13 mol%, in two portions at 2 h interval) was added to a solution of enyne **15c** (30 mg, 0.119 mmol) in dry, degassed DCM (10 mL) as described in the general procedure and the reaction mixture was then stirred at room temperature in the presence of ethylene (1 atm). After completion of the reaction (4 h, TLC monitoring) the resulting brown solution was concentrated under reduced pressure and the crude product was then purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1.5%) to afford diene **17c** as a colorless liquid (15 mg, 50%). R_f = 0.38 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 3.90–3.96 (m, 5H; $ArCH_2$ and OCH_3), 4.83 (d, J = 1.8 Hz, 2H; OCH_2), 4.89 (d, J = 17.4 Hz, 1H; CH=CH*H*), 4.90 (d, J = 12.3 Hz, 1H; CH=CH*H*), 6.05 (t, J = 6.0 Hz, 1H; CH_2CH), 6.22 (dd, J = 18.0, 11.4 Hz, 1H; $CH{=}CH_2$), 7.12–7.19 (m, 2H; ArH), 7.27 (d, J = 9.9 Hz, 1H; ArH), 7.61 (d, J = 8.4 Hz, 1H; ArH), 7.92 ppm (d, J = 9 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 24.6, 55.4, 70.6, 106.8, 110.8, 118.9, 122.0, 124.5, 126.8-(2C), 128.2, 130.2, 132.4, 136.7, 137.8, 154.4, 156.6 ppm; HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{17}O_2$ [M+H]: 253.1229; found: 253.1232.

General procedure for the Diels–Alder reactions of 17a–c: Dienophile (1.5 equiv) was added to a solution of the diene **17** (1 equiv) in dry toluene and the mixture was heated in toluene. After completion of the reaction (TLC monitoring), the solution was concentrated under reduced pressure and the crude product was purified by silica gel flash chromatography. Elution of the column with an ethyl acetate and petroleum ether mixture gave the desired DA adduct.

Diels–Alder reaction between 17a and DMAD: Dienophile **18** (19 mg, 0.134 mmol) was added to a solution of the diene **17a** (25 mg, 0.112 mmol) in toluene (12 mL) and the mixture was heated (90°C, 24 h). The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 15%) to afford DA adduct **22** as a colorless, thick liquid (20 mg, 49%). R_f = 0.33 (silica gel, EtOAc/petroleum ether 1:4); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.97 (dd, J = 14.4, 10.4 Hz, 1H; ArC*H*H), 3.06–3.09 (m, 1H; C=CHC*H*H), 3.19 (dd, J = 6.6, 2.6 Hz, 1H; C=CHCH*H*), 3.39–3.45 (m, 1H; $ArCH_2CH$), 3.77 (dd, J = 14.6, 1.8 Hz, 1H; ArCH*H*), 3.83 (s, 3H; OCH_3), 3.92 (s, 3H; OCH_3), 4.25 (d, J = 12.4 Hz, 1H; OC*H*H), 4.71 (d, J = 12.8 Hz, 1H; OCH*H*), 5.78 (t, J = 3.2 Hz, 1H; C=C*H*CH_2), 7.24 (d, J = 8.8 Hz, 1H; ArH), 7.40–7.44 (m, 1H; ArH), 7.50–7.55 (m, 1H; ArH), 7.70 (d, J = 8.8 Hz, 1H; ArH), 7.83 (d, J = 8.4 Hz, 1H; ArH), 7.99 ppm (d, J = 8.8 Hz, 1H; ArH); IR (neat): $\tilde{\nu}$ = 1727 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 240 nm (30800 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{22}H_{20}O_5Na$ [M+Na]: 387.1208; found: 387.1198.

Diels–Alder reaction between 17a and 19: Dienophile **19** (21 mg, 0.117 mmol) was added to a solution of the diene **17a** (20 mg, 0.09 mmol) in toluene (7 mL) and the mixture was heated (90°C, 24 h). The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 15%) to afford DA adduct **23** as a mixture of two regioisomers (22 mg, **23a**/**23b** = 9:1) in 61% combined yield. The data given below are only for the major isomer **23a**. R_f = 0.20 (silica gel, EtOAc/petroleum ether 1:4); m.p. 170°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.43 (s, 3H; CH_3), 2.84–2.87 (m, 2H; C=CHCH_2), 3.10 (dd, J = 15.0, 10.5 Hz, 1H; ArC*H*H), 3.37–3.44 (m, 1H; $ArCH_2CH$), 3.65 (dd, J = 15.0, 2.7 Hz, 1H; ArCH*H*), 4.41 (d, J = 12.9 Hz, 1H; OC*H*H), 4.66 (d, J = 12.6 Hz, 1H; OCH*H*), 5.69 (br s, 1H; $OCH_2C{=}CH$), 7.15–7.17 (m, 1H; $ArCH_2CHC{=}CH$), 7.19 (d, J = 8.7 Hz, 1H; ArH), 7.29 (d, J = 8.1 Hz, 2H; ArH), 7.41–7.47 (m, 1H; ArH), 7.54–7.60 (m, 1H; ArH), 7.66–7.72 (m, 3H; ArH), 7.83 (d, J = 8.4 Hz, 1H; ArH), 8.05 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 21.7, 24.7, 32.8, 37.8, 77.3, 120.6, 121.7, 123.0, 124.4, 124.6, 126.7, 128.2, 128.4, 128.8, 129.9, 130.9, 132.8, 135.4, 135.7, 137.9, 138.4, 144.5, 157.4 ppm; IR (neat): $\tilde{\nu}$ = 1309 cm^{-1} (SO_2, *asym.* st), 1148 cm^{-1} (SO_2,

sym. st); UV ($CHCl_3$): λ_{max} (ε) = 244 nm (12462 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{25}H_{23}O_3S$ [*M*+H]: 403.1368; found: 403.1377.

Diels–Alder reaction between 17a and *N*-phenylmaleimide: Dienophile **19** (28 mg, 0.16 mmol) was added to a solution of the diene **17a** (18 mg, 0.08 mmol) in toluene (10 mL) and the mixture was heated in toluene (90 °C, 12 h). The solution was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 20 %) to afford DA adduct **24** as a white solid (12 mg, 38 %). R_f = 0.38 (silica gel, EtOAc/petroleum ether 3:7); m.p. 140 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.34–2.41 (m, 1H; C=CHC*H*H), 2.87 (ddd, *J* = 15.6, 6.6, 2.1 Hz, 1H; C=CHCH*H*), 3.10–3.39 (m, 1H; $ArCH_2CH$), 3.35–3.44 (m, 1H; NC(O)C*H*CH_2), 3.50 (dd, *J* = 9.2, 6.5 Hz, 1H; NC(O)C*H*CH), 3.78 (dd, *J* = 16.0, 3.0 Hz, 1H; ArC*H*H), 4.04 (dd, *J* = 16.0, 13.2 Hz, 1H; ArCH*H*), 4.51 (d, *J* = 12.9 Hz, 1H; OC*H*H), 5.16 (d, *J* = 12.9 Hz, 1H; OCH*H*), 6.06 (t, *J* = 3.3 Hz, 1H; C=C*H*CH_2), 7.05 (d, *J* = 9.3 Hz, 1H; ArH), 7.24–7.54 (m, 7H; ArH), 7.62 (d, *J* = 9 Hz, 1H; ArH), 7.77 (d, *J* = 7.5 Hz, 1H; ArH), 8.08 ppm (d, *J* = 8.7 Hz, 1H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.6, 27.2, 38.0, 40.3, 44.9, 71.7, 118.1, 121.4, 122.7, 123.7, 125.1, 126.6, 126.7, 128.5, 128.7, 128.9, 129.4, 130.0, 131.9, 133.8, 140.4, 154.8, 177.1, 178.7 ppm; IR (neat): $\tilde{\nu}$ = 1708 cm^{-1} (C=O st); UV (CH_2Cl_2): λ_{max} (ε) = 244 nm (4334 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{26}H_{22}NO_3$ [*M*+H]: 396.1600; found: 396.1602.

(±)-11,12-Bis-(benzenesulfonyl)-8,10,11,12,12a,13-hexahydro-7-oxabenzo[5,6]cyclohepta[1,2-*a*]naphthalene (25): Dienophile **21** (17 mg, 0.055 mmol) was added to a solution of the diene **17a** (8 mg, 0.036 mmol) in toluene (12 mL) and the mixture was heated (90 °C, 24 h). The solution was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 35 %) to afford DA adduct **25** as a white solid (8 mg, 42 %). R_f = 0.18 (silica gel, EtOAc/petroleum ether 3:7); m.p. 204–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.60 (brs, 2H; C=CHCH_2), 3.01 (dd, *J* = 15.3, 2.1 Hz, 1H; ArC*H*H), 3.27 (d, *J* = 12.3 Hz, 1H; $ArCH_2CH$), 3.69 (dd, *J* = 15, 12 Hz, 1H; ArCH*H*), 4.18–4.21 (m, 1H; CH_2CHSO_2Ph), 4.24 (brs, 1H; CHC*H*SO_2Ph), 4.47 (d, *J* = 13.2 Hz, 1H; OC*H*H), 4.74 (d, *J* = 13.5 Hz, 1H; OCH*H*), 5.80 (brs, 1H; C=C*H*CH_2), 7.16 (d, *J* = 9 Hz, 1H; ArH), 7.29–7.79 (m, 13H; ArH), 7.84–7.87 ppm (m, 2H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.6, 32.9, 34.4, 55.5, 63.3, 77.3, 119.3, 121.7, 122.9, 123.2, 124.2, 126.4, 128.4, 128.6, 129.0 (2C), 129.8 (2C), 130.6, 133.1, 134.4, 134.5, 136.4, 137.1, 137.7, 157.6 ppm; IR (neat): $\tilde{\nu}$ = 1309 cm^{-1} (SO_2, *asym*. st), 1147 cm^{-1} (SO_2, *sym*. st); UV ($CHCl_3$): λ_{max} (ε) = 248 nm (6760 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{30}H_{27}O_5S_2$ [*M*+H]: 531.1300; found: 531.1307.

(±)-11,12-Bis-(benzenesulfonyl)-3-bromo-8,10,11,12,12a,13-hexahydro-7-oxa-benzo[5,6]cyclohepta[1,2-*a*]naphthalene (26): Dienophile **21** (25 mg, 0.08 mmol) was added to a solution of the diene **17b** (17 mg, 0.056 mmol) in toluene (10 mL) and the mixture was heated at reflux. After the completion of the reaction (48 h, TLC monitoring), the solution was concentrated under reduced pressure and the crude product was purified by flash chromatography (silica gel, EtOAc in petroleum ether, 30 %) to afford DA adduct **26** as a white solid (25 mg, 74 %). R_f = 0.2 (silica gel, EtOAc/petroleum ether 3:7); m.p. 222 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.59 (brs, 2H; C=CHCH_2), 2.95 (dd, *J* = 15.3, 2.6 Hz, 1H; ArCH*H*), 3.25 (d, *J* = 12 Hz, 1H; $ArCH_2CH$), 3.68 (dd, *J* = 15.3, 12 Hz, 1H; ArC*H*H), 4.16–4.19 (m, 1H; CH_2CHSO_2Ph), 4.22 (brs, 1H; CHC*H*SO_2Ph), 4.48 (d, *J* = 13.2 Hz, 1H; OC*H*H), 4.74 (d, *J* = 12.9 Hz, 1H; OCH*H*), 5.81 (brs, 1H; C=C*H*CH_2), 7.17 (d, *J* = 8.7 Hz, 1H; ArH), 7.32 (d, *J* = 9.0 Hz, 1H; ArH), 7.39–7.62 (m, 7H; ArH), 7.72 (t, *J* = 7.1 Hz, 1H; ArH), 7.82–7.91 ppm (m, 5H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.6, 32.9, 34.3, 55.5, 63.2, 77.3, 118.0, 119.6, 123.0, 123.4, 124.7, 127.5, 128.9, 129.0, 129.6, 129.8 (2C), 130.5, 131.7, 131.8, 134.5, 134.6, 136.1, 137.1, 137.6, 157.8 ppm; IR (neat): $\tilde{\nu}$ = 1308 cm^{-1} (SO_2, *asym*. st), 1146 cm^{-1} (SO_2, *sym*. st); UV ($CHCl_3$): λ_{max} (ε) = 250 nm (9676 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{30}H_{26}O_5S_2Br$ [*M*+H]: 609.0405; found: 609.0380.

(±)-11,12-Bis-(benzenesulfonyl)-3-methoxy-8,10,11,12,12a,13-hexahydro-7-oxa-benzo[5,6]cyclohepta[1,2-*a*]naphthalene (27): Dienophile **21** (30 mg, 0.097 mmol) was added to a solution of the diene **17c** (15 mg, 0.059 mmol) in toluene (15 mL) and the mixture was heated at reflux in toluene. After the completion of the reaction (39 h, TLC monitoring) the solution was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 30 %) to afford DA adduct **27** as a white solid (18 mg, 54 %). R_f = 0.17 (silica gel, EtOAc/petroleum ether 3:7); m.p. 205 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.59 (brs, 2H; C=CHCH_2), 2.96 (dd, *J* = 15.2, 2.4 Hz, 1H; ArC*H*H), 3.20 (d, *J* = 12 Hz, 1H; $ArCH_2CH$), 3.67 (dd, *J* = 15.2, 12 Hz, 1H; ArCH*H*), 3.91 (s, 3H; OCH_3), 4.21–4.23 (m, 1H; CH_2CHSO_2Ph), 4.25 (brs, 1H; CHC*H*SO_2Ph), 4.41 (d, *J* = 13.2 Hz, 1H; OC*H*H), 4.70 (d, *J* = 13.2 Hz, 1H; OCH*H*), 5.79 (brs, 1H; C=C*H*CH_2), 7.00 (dd, *J* = 7.1, 2.1 Hz, 1H; ArH), 7.08 (d, *J* = 2.1 Hz, 1H; ArH), 7.13 (d, *J* = 6.6 Hz, 1H; ArH), 7.30 (d, *J* = 6.9 Hz, 1H; ArH), 7.46–7.53 (m, 3H; ArH), 7.58–7.63 (m, 3H; ArH), 7.72 (t, *J* = 5.6 Hz, 1H; ArH), 7.86–7.88 ppm (m, 4H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.4, 32.9, 34.4, 55.3, 55.4, 63.1, 77.3, 106.6, 118.8, 119.3, 122.1, 123.9, 124.4, 126.9, 128.1, 128.8, 128.9, 129.6, 129.7, 131.7, 134.3, 134.5, 136.3, 137.1, 137.6, 156.0, 156.3 ppm; IR (neat): $\tilde{\nu}$ = 1308 cm^{-1} (SO_2, *asym*. st), 1146 cm^{-1} (SO_2, *sym*. st); UV ($CHCl_3$): λ_{max} (ε) = 250 nm (10706 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{31}H_{29}O_6S_2$ [*M*+H]: 561.1406; found: 561.1423.

2,7-Bis(allyloxy)naphthalene (29):[34] Anhydrous powdered potassium carbonate (6.9 g, 0.05 mol), allyl bromide (2.5 mL, 31.0 mmol), and a catalytic amount of tetrabutylammonium hydrogensulfate were added to a solution of naphthalene-2,7-diol (2 g, 12.5 mmol) in dry acetone (50 mL). The reaction mixture was then allowed to stir at room temperature for 30 min and was then filtered through a celite pad. The residue was washed with dichloromethane (3×30 mL), the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 1.5 %) to afford compound **29** as a white, crystalline solid (2.24 g, 75 %). M.p. 64 °C (lit.: 62.5–63 °C).[34]

1,8-Diallylnaphthalene-2,7-diyl diacetate (30):[34] Pyridine (173 mg, 2.19 mmol) and catalytic amount of 4-(dimethylamino)pyridine were added to a solution of **29** (210 mg, 0.88 mmol) in acetic anhydride (1 mL). The reaction mixture was then heated at reflux. After the completion of the reaction (18 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 3 %) to afford compound **30** as a white, crystalline solid (225 mg, 79 %). R_f = 0.53 (silica gel, EtOAc/petroleum ether 1:19); m.p. 105 °C (lit.: 103–103.5 °C).[34]

Ring-closing metathesis of 30: Grubbs catalyst **8** (4 mg, 0.005 mmol, 5 mol %) was added to a solution of diene **30** (31 mg, 0.096 mmol) in dry, degassed DCM (4 mL), and the reaction mixture was allowed to stir at room temperature. After the completion of the reaction (7 h, TLC monitoring), the solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, EtOAc in petroleum ether, 3 %) to give 7,10-dihydrocyclohepta[*de*]naphthalene-1,6-diyl diacetate (**31**) as a white, crystalline solid (27 mg, 96 %). R_f = 0.43 (silica gel, EtOAc/petroleum ether 1:19); m.p. 202–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.39 (s, 6H; 2×$COCH_3$), 3.77 (d, *J* = 6.0 Hz, 4H; 2×$ArCH_2$), 6.15 (t, *J* = 4.2 Hz, 2H; 2×$ArCH_2CH$), 7.08 (d, *J* = 9.3 Hz, 2H; ArH), 7.63 ppm (d, *J* = 9 Hz, 2H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.0, 25.9, 120.9, 125.9, 128.5, 130.7, 132.2, 134.2, 145.8, 169.7 ppm; IR (neat): $\tilde{\nu}$ = 1748 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 288 nm (6059 $mol^{-1}dm^3cm^{-1}$); HRMS (Q-Tof ES+): *m/z* calcd for $C_{18}H_{16}O_4Na$ [*M*+Na]: 319.0946; found: 319.0956.

RCM of 32a with Grubbs second-generation catalyst 9: Grubbs catalyst **9** (7 mg, 0.008 mmol, 6 mol %) was added to a solution of compound **32a** (32 mg, 0.14 mmol) in dry, degassed DCM (5 mL) and the reaction mixture was then allowed to stir at room temperature. After completion of the reaction (6 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 2 %) to afford 2′*H*-spi-

ro[cyclopent-3-ene-1,1′-naphthalen]-2′-one (**33a**) as a colorless liquid (23 mg, 83%). R_f = 0.15 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.62 (d, J = 13.8 Hz, 2H; 2×C*H*HCH), 3.17 (d, J = 13.8 Hz, 2H; 2×CH*H*CH), 5.78 (s, 2H; 2×CHHC*H*), 6.19 (d, J = 9.9 Hz, 1H; C(O)C*H*=CH), 7.26–7.30 (m, 2H; ArH), 7.36–7.39 (m, 2H; ArH), 7.43 ppm (d, J = 9.6 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$ + CCl_4, 25°C, TMS): δ = 49.3, 55.9, 125.1, 125.8, 126.8, 128.1, 128.7, 129, 130.5, 144.9, 149.6, 203.7 ppm; IR (neat): $\tilde{\nu}$ = 1663 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 308 nm (4624 mol^{-1}dm^{3}cm^{-1}); HRMS (EI): m/z calcd for $C_{14}H_{12}O$ [M+H]: 196.0888; found: 196.0874.

RCM of 32b with Grubbs second-generation catalyst 9: Grubbs catalyst **9** (1.5 mg, 0.002 mmol, 2.5 mol%) was added to a solution of compound **32b** (22 mg, 0.072 mmol) in dry, degassed DCM (3 mL) and the reaction mixture was then allowed to stir at room temperature. After completion of the reaction (2 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether, 2%) to afford 6′-bromo-2′*H*-spiro[cyclopent-3-ene-1,1′-naphthalen]-2′-one (**33b**) as a colorless liquid (18 mg, 91%). R_f = 0.2 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.60 (d, J = 13.8 Hz, 2H; 2×C*H*HCH), 3.16 (d, J = 13.5 Hz, 2H; 2×CH*H*CH), 5.79 (s, 2H; 2×CH_2C*H*), 6.25 (d, J = 9.9 Hz, 1H; C(O)C*H*=CH), 7.26 (d, J = 7.8 Hz, 1H; ArH), 7.38 (d, J = 9.9 Hz, 1H; C(O)CH=C*H*), 7.45–7.49 ppm (m, 2H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 49.1, 55.7, 120.3, 126.0, 127.4, 128.5, 129.8, 131.4, 133.1, 143.6, 148.1, 203.6 ppm; IR (neat): $\tilde{\nu}$ = 1662 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 303 nm (6683 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{12}$OBr [M+H]: 275.0072; found: 275.0071.

RCM of 32c with Grubbs second-generation catalyst 9: Grubbs catalyst **9** (1.5 mg, 0.002 mmol, 1.8 mol%) was added to a solution of compound **32c** (24 mg, 0.094 mmol) in dry, degassed DCM (2 mL) and the reaction mixture was then allowed to stir at room temperature. After completion of the reaction (2 h, TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc in petroleum ether 2.5%) to afford 6′-methoxy-2′*H*-spiro[cyclopent-3-ene-1,1′-naphthalen]-2′-one (**33c**) as a colorless liquid (20 mg, 94%). R_f = 0.05 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 2.60 (d, J = 13.5 Hz, 2H; 2×C*H*HCH), 3.15 (d, J = 13.8 Hz, 2H; 2×CH*H*CH), 3.83 (s, 3H; OCH_3), 5.79 (s, 2H; 2×CH_2C*H*), 6.22 (d, J = 9.9 Hz, 1H; C(O)C*H*=CH), 6.81 (d, J = 2.7 Hz, 1H; ArH), 6.92 (dd, J = 8.5, 2.9 Hz, 1H; ArH), 7.29 (d, J = 8.4 Hz, 1H; ArH), 7.41 ppm (d, J = 9.9 Hz, 1H; C(O)CH=C*H*); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 49.3, 55.4 (2C), 113.4, 116.4, 125.3, 126.8, 128.6, 128.8, 141.6, 145.1, 158.1, 204.0 ppm; IR (neat): $\tilde{\nu}$ = 1661 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 258 nm (9189 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{15}H_{15}O_2$ [M+H]: 227.1072; found: 227.1083.

RCM of 32a with Grubbs first-generation catalyst: Grubbs catalyst **8** (55 mg, 0.07 mmol, 10 mol%, added portionwise at different time intervals) was added to a solution of compound **32a** (150 mg, 0.7 mmol) in dry, degassed toluene (15 mL). The reaction mixture was then heated at reflux for 7 days, the solvent was then removed under reduced pressure, and the crude product was purified by silica gel column chromatography. Elution of the column with EtOAc/petroleum ether (2%) gave starting material (11 mg) and **33a** (23 mg, 19%, based on starting material recovered) showing the same spectral data as compound **33a** obtained by RCM of **32a** with second-generation Grubbs catalyst **9**. Further elution of the column with EtOAc/petroleum ether (2%) gave 2′*H*-spiro[cyclopent-2-ene-1,1′-naphthalen]-2′-one (**34**) as a colorless liquid (41 mg, 34%, based on starting material recovered). R_f = 0.1 (silica gel, EtOAc/petroleum ether 1:49); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4, 25°C, TMS): δ = 2.01–2.09 (m, 1H; C*H*HCH$_2$CH=CH), 2.53–2.78 (m, 3H; CH*H*C*H*$_2$CH=CH), 5.54 (dt, J = 5.4, 2.1 Hz, 1H; CH_2C*H*=CH), 6.20 (d, J = 9.5 Hz, 1H; C(O)C*H*=CH), 6.23 (dt, J = 5.4, 2.2 Hz, 1H; CH_2CH=C*H*), 7.20–7.36 (m, 4H; ArH), 7.46 ppm (d, J = 9.8 Hz, 1H; C(O)CH=C*H*); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 32.8, 40.2, 65.9, 125.3, 127.2, 127.4, 129.1, 129.5, 130.4, 133.4, 135.6, 145.4, 146.4, 203.6 ppm; IR (neat): $\tilde{\nu}$ = 1664 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 307 nm (5246 mol^{-1}dm^{3}cm^{-1}); HRMS (EI): m/z calcd for $C_{14}H_{12}O$ [M]$^+$: 196.0888; found: 196.0889.

Isomerization of 33a to 34 in the presence of Grubbs first-generation catalyst: Grubbs catalyst **8** (9 mg, 0.01 mmol, 10 mol%, added portionwise at different time intervals) was added to a solution of compound **33a** (20 mg, 0.1 mmol) in dry, degassed toluene (5 mL) and the reaction mixture was then heated at reflux. After completion of the reaction (48 h, TLC monitoring) the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with EtOAc/petroleum ether (2%) gave 2′*H*-spiro[cyclopent-2-ene-1,1′-naphthalen]-2′-one (**34**) as a colorless liquid (13 mg, 66%) showing the same spectral data as compound **34** obtained by RCM of **32a**.

Palladium/carbon-catalyzed hydrogenation of 33a: Pd (10% on carbon, 13 mg) and freshly distilled ethyl acetate (15 mL) were placed in a three-necked flask (25 mL). The solvent was saturated with hydrogen (atmospheric pressure) for 30 min, followed by addition of **33a** (24 mg, 0.12 mmol) in ethyl acetate (1 mL). After completion of the reaction (1 h, TLC monitoring), the catalyst was removed by filtration, the filtrate was concentrated, and the crude product was then purified by silica gel flash column chromatography. Elution of the column with EtOAc/petroleum ether (2%) gave 3′,4′-dihydro-2′*H*-spiro[cyclopentane-1,1′-naphthalen]-2′-one (**35**) as a colorless liquid (12 mg, 48%). R_f = 0.4 (silica gel, EtOAc/petroleum ether 1:19); m.p. (2,4-dinitrophenylhydrazone derivative of **35**) 118–119°C (lit.: 122–123°C);[25] Continued elution of the column with the same solvent system gave (±)-3′,4′-dihydro-2′*H*-spiro[cyclopentane-1,1′-naphthalen]-2′-ol (**36**) as a white, crystalline solid (11 mg, 45%). R_f = 0.1 (silica gel, EtOAc/petroleum ether 1:19); m.p. 70°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.55 (brs, 1H; OH), 1.75–2.17 (m, 10H; (CH_2)$_4$ and CH(OH)CH_2), 2.8 (td, J = 17.2, 6 Hz, 1H; ArC*H*H), 3.15 (td, J = 16.6, 8.1 Hz, 1H; ArCH*H*), 3.80 (d, J = 4 Hz, 1H; C*H*OH), 7.04–7.27 ppm (m, 4H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 25.7, 26.7, 27.3, 27.6, 37.1, 41.9, 51.3, 74.5, 125.5, 126.3, 127.5, 128.6, 134.7, 145.0 ppm; IR (neat): $\tilde{\nu}$ = 3377 cm^{-1} (br, O–H st); UV ($CHCl_3$): λ_{max} (ε) = 266 nm (574 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{14}H_{18}O$: C 83.11, H 8.97; found: C 82.78, H 8.97.

Palladium/carbon-catalyzed hydrogenation of compound 34: Pd (10% on carbon, 14 mg) and freshly distilled ethyl acetate (15 mL) were placed in a three-necked flask (25 mL). The solvent was saturated with hydrogen (atmospheric pressure) for 30 min, followed by addition of **34** (26 mg, 0.13 mmol) in ethyl acetate (1 mL). After completion of the reaction (1 h, TLC monitoring), the catalyst was removed by filtration, the filtrate was concentrated, and the crude product was then purified by silica gel flash column chromatography. Elution of the column with EtOAc/petroleum ether (2%) gave compound **35** (13 mg, 49%) and **36** (11 mg, 42%). The ^{1}H spectral data for these compounds were found to be identical with those for the earlier reported compounds.

Oxidation of compound 36: Compound **36** (10 mg, 0.05 mmol) in anhydrous DCM (3 mL) was added in one portion to a vigorously stirred suspension of PCC (15 mg, 0.07 mmol) in anhydrous DCM (10 mL), and stirring was continued at room temperature for 2 h. Anhydrous ether (50 mL) was added and decanted off, and the black residue was washed with ether (3×20 mL). The combined ether extracts were concentrated and the crude product was purified by flash column chromatography. Elution of the column (silica gel) with EtOAc/petroleum ether (10%) gave compound **35** (9 mg, 92%) as a colorless liquid showing the same spectral data as compound **35** obtained by Pd/carbon-catalyzed reduction of compounds **33a** or **34**.

General procedure for the diallylation: A solution of tetralone (1 equiv) in dry THF (5 mL) was added dropwise with stirring under nitrogen to a solution of sodium hydride (2.5 equiv) in dry THF (7 mL) in a flame-dried flask. The allyl bromide (2.5 equiv) was then added and the reaction mixture was stirred at room temperature. After completion (TLC monitoring), the reaction mixture was quenched with ethyl acetate, diluted with water, and extracted with diethyl ether (50×3 mL). The organic layer was washed with water and brine and dried over sodium sulfate,

the crude product was purified by silica gel column chromatography, and elution of the column with EtOAc/petroleum ether gave the desired diallylated product.

2,2-Diallyl-3,4-dihydronaphthalen-1(2*H*)-one (39a):[35] Compound **37a** (500 mg, 3.56 mmol) and allyl bromide (0.81 mL, 8.9 mmol) were added to a solution of sodium hydride (356 mg, 8.9 mmol) in dry THF (7 mL). The reaction mixture was allowed to stir at room temperature for 4 h, and the reaction was then worked up with ether (3×50 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **39a** (515 mg, 66%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.02 (t, J = 6.4 Hz, 2H; ArCH_2CH_2), 2.30 (d$^1/_2$ABq, J = 8.4, 8.0 Hz, 2H; 2× CHHCH=CH_2), 2.5 (d$^1/_2$ABq, J = 10.8, 7 Hz, 2H; 2×CHHCH=CH_2), 2.98 (t, J = 6.4 Hz, 2H; ArCH_2), 5.03–5.16 (m, 4H; CH_2CH=CH_2), 5.72–5.83 (m, 2H; CH_2CH=CH_2), 7.21 (d, J = 7.6 Hz, 1H; ArH), 7.28 (td, J = 7.6, 0.8 Hz, 1H; ArH), 7.45 (td, 1H; J = 7.4, 1.4 Hz, ArH), 8.04 (dd, J = 7.8, 1.2 Hz, 1H; ArH).

2,2-Diallyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (39b): 6-Methoxytetralone (**37b**, 200 mg, 1.37 mmol) and allyl bromide (0.37 mL, 3.43 mmol) were added to a solution of sodium hydride (137 mg, 3.43 mmol) in dry THF (7 mL), the reaction mixture was allowed to stir at room temperature for 8 h, and the reaction was then worked up with ether (3×50 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, and elution of the column with EtOAc/petroleum ether (4%) gave compound **39b** (182 mg, 63%) as a yellow, oily liquid. R_f = 0.6 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.00 (t, J = 6.8 Hz, 2H; ArCH_2CH_2), 2.30 (d$^1/_2$ABq, J = 14, 7.6 Hz, 2H; 2×CHHCH=CH_2), 2.50 (d$^1/_2$ABq, J = 13.6, 6.8 Hz, 2H; 2×CHHCH=CH_2), 2.90 (t, 2H; J = 6.4 Hz, ArCH_2), 3.84 (s, 3H; OCH_3), 5.04–5.08 (m, 4H; 2×CH_2CH=CH_2), 5.72–5.84 (m, 2H; 2×CH_2CH=CH_2), 6.60 (d, J = 2 Hz, 1H; ArH), 6.80 (dd, J = 8.8, 2 Hz, 1H; ArH), 8.00 ppm (d, J = 8.8 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 25.6, 30.7, 39.5 (2C), 47.6, 55.5, 112.4, 113.4 (2C), 118.2 (2C), 125.6, 130.5, 134.2, 145.8, 163.5, 199.8 ppm; IR (neat): $\tilde{\nu}$ = 1671 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{21}O_2$ [M+H]: 229.1228; found: 229.1238.

2,2-Diallyl-2,3-dihydroinden-1-one (40a):[36] Indan-1-one (**38a**, 500 mg, 3.78 mmol) and allyl bromide (0.805 mL, 9.46 mmol) were added to a solution of sodium hydride (378 mg, 9.46 mmol) in dry THF (7 mL), the reaction mixture was then allowed to stir at room temperature for 4 h, and the reaction was then worked up with ether (3×100 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **40a** as a yellow, oily liquid (593 mg, 74%). R_f = 0.7 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.31 (d$^1/_2$ABq, J = 13.6, 8.4 Hz, 2H; 2×CHHCH=CH_2), 2.45 (d$^1/_2$ABq, J = 13.8, 6.8 Hz, 2H; 2× CHHCH=CH_2), 3.03 (s, 2H; ArCH_2), 4.96–5.09 (m, 4H; 2×CH_2CH= CH_2), 5.54–5.64 (m, 2H; 2×CH_2CH=CH_2), 7.35 (t, J = 7.4 Hz, 1H; ArH), 7.43 (d, J = 8 Hz, 1H; ArH), 7.58 (td, J = 7.4 Hz, 1.2 Hz, 1H; ArH), 7.73 ppm (d, J = 7.6 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): 36.0, 41.6 (2C), 52.1, 118.4 (2C), 123.7 (2C), 126.1, 127.3, 133.3, 134.8, 136.6, 152.8, 209.6 ppm; IR (neat): $\tilde{\nu}$ = 1711 cm^{-1} (C=O st).

2,2-Diallyl-5-methoxy-2,3-dihydroinden-1-one (40b): 5-Methoxyindanone (**38b**, 200 mg, 1.23 mmol) and allyl bromide (0.3 mL, 3.08 mmol) were added to a solution of sodium hydride (123.5 mg, 3.08 mmol) in dry THF (7 mL). The reaction mixture was allowed to stir at room temperature for 6 h and the reaction was then worked up with ether (3×50 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **40b** (208 mg, 70%) as a yellow, viscous liquid. R_f = 0.5 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.29 (d$^1/_2$ABq, J = 13.4, 8 Hz, 2H; 2×CHHCH=CH_2), 2.44 (d$^1/_2$ABq, J = 13, 6.4 Hz, 2H; 2×CHHCH=CH_2), 2.97 (s, 2H; ArCH_2), 3.87 (s, 3H; OCH_3), 4.96–5.09 (m, 4H; 2×CH_2CH=CH_2), 5.54–5.64 (m, 2H; 2×CH_2CH=CH_2), 6.84 (d, J = 2 Hz, 1H; ArH), 6.89 (dd, J = 8.6, 2 Hz, 1H; ArH), 7.66 ppm (d, 1H; J = 8.4 Hz, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 36.0, 41.8 (2C), 52.3, 55.6, 109.4, 109.5, 115.5, 118.3, 125.4 (2C), 129.9, 133.5, 155.9, 165.6, 207.9 ppm; IR (neat): $\tilde{\nu}$ = 1654 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{16}H_{18}O_2$ [M+H]: 265.1204; found: 265.1211.

2,2-Diallyl-5-bromo-2,3-dihydroinden-1-one (40c): 5-Bromoindanone (**38c**, 100 mg, 0.48 mmol) and allyl bromide (0.1 mL, 1.18 mmol) were added to a solution of sodium hydride (47.5 mg, 1.18 mmol) in dry THF (5 mL). The reaction mixture was allowed to stir at room temperature for 3 h and the reaction was then worked up with ether (3×50 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (1%) gave compound **40c** (90 mg, 65%) as a pale yellow liquid. R_f = 0.9 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.30 (d$^1/_2$ABq, J = 13.4, 8 Hz, 2H; 2×CHHCH=CH_2), 2.44 (d$^1/_2$ABq, J = 13.8, 6.4 Hz, 2H; 2×CHHCH=CH_2), 3.0 (s, 2H; ArCH_2), 4.97–5.09 (m, 4H; 2× CH_2CH=CH_2), 5.51–5.61 (m, 2H; 2×CH_2CH=CH_2), 7.49 (dt, J = 8.0, 0.8 Hz, 1H; ArH), 7.59 ppm (d, J = 9.2 Hz, 2H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 35.8, 41.8 (2C), 52.5, 118.8 (2C), 125.1 (2C), 129.8, 130.3, 131.1, 133.1, 135.7, 154.7, 208.7 ppm; IR (neat): $\tilde{\nu}$ = 1639 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{15}H_{16}OBr$ [M+H]: 291.0385; found: 291.0379.

2,2-Diallyl-5,6-dimethoxy-2,3-dihydroinden-1-one (40d): 5,6-Dimethoxyindanone (**38d**, 500 mg, 6.5 mmol) and allyl bromide (0.55 mL, 6.5 mmol) were added to a solution of sodium hydride (260 mg, 6.5 mmol) in dry THF (7 mL). The reaction mixture was allowed to stir at room temperature for 8 h and the reaction was then worked up with ether (3×100 mL) as described in the general procedure. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (5%) gave compound **40d** (505 mg, 71%) as a white, crystalline solid. R_f = 0.25 (silica gel, EtOAc/petroleum ether 1:10); m.p. 77°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.16 (d$^1/_2$ABq, J = 13.6, 8.4 Hz, 2H; 2× CHHCH=CH_2), 2.31 (d$^1/_2$ABq, J = 13.6, 6.4 Hz, 2H; 2×CH_2CH=CH_2), 2.81 (s, 2H; ArCH_2), 3.77 (s, 3H; OCH_3), 3.83 (s, 3H; OCH_3), 4.82–4.95 (m, 4H; 2×CH_2CH=CH_2), 5.41–5.51 (m, 2H; 2×CH_2CH=CH_2), 6.73 (s, 1H; ArH), 7.02 ppm (s, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 35.6, 41.7 (2C), 52.3, 55.9, 56.0, 104.1, 107.2, 107.3, 118.2, 129.3, 133.5 (2C), 148.1, 149.4, 155.7, 208.2 ppm; IR (neat): $\tilde{\nu}$ = 1694 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{17}H_{21}O_3$ [M+H]: 273.1491; found: 273.1499.

General procedure for the RCM: Grubbs first-generation catalyst (10–15 mol%) was added to a solution of a diallylated derivative of a substrate in dry toluene. The reaction mixture was degassed with nitrogen for 20 min and then heated at reflux under nitrogen for 48 h. The solvent was then removed on a rotary evaporator and the resulting crude product was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether gave the RCM product.

RCM of 2,2-diallyl-3,4-dihydronaphthalen-1(2*H*)-one (39a): Grubbs first-generation catalyst (21.8 mg, 12 mol%) was added to a solution of diallylated 1-tetralone **39a** (50 mg, 0.23 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (3%) gave compound **41a** as a yellow, oily liquid (41 mg, 94%). R_f = 0.7 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.07 (t, J = 6.4 Hz, 2H; ArCH_2CH_2), 2.29 (dd, J = 17.6, 2.4 Hz, 2H; 2×CH= CHCHH), 2.79 (dd, J = 19.2, 2.4 Hz, 2H; 2×CH=CHCHH), 2.94 (t, J = 6.4 Hz, 2H; ArCH_2), 5.56 (s, 2H; CH=CH), 7.13 (d, J = 8 Hz, 1H; ArH), 7.21 (t, J = 7.6 Hz, 1H; ArH), 7.36 (td, J = 7.2, 1.2 Hz, 1H; ArH), 7.98 ppm (d, J = 8 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 26.2, 35.0, 41.9 (2C), 52.1, 126.8, 128.2, 128.4 (2C), 128.8, 131.8, 133.3, 143.6, 201.4 ppm; IR (neat): $\tilde{\nu}$ = 1682 cm^{-1} (C=O st), HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{14}O$ [M+H]: 199.1123; found: 199.1131.

RCM of 2,2-diallyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (39b): Grubbs first-generation catalyst (17.6 mg, 11 mol%) was added to a solution of diallylated 6-methoxytetralone **39b** (50 mg, 0.24 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h under nitrogen atmosphere. The solvent was then removed in a rotary evaporator and the resulting crude product was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave the RCM product **41b** (40 mg, 90%) as a yellowish liquid. R_f = 0.4 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.12 (t, J = 6.8 Hz, 2H; $ArCH_2CH_2$), 2.36 (d, J = 14.8 Hz, 2H; 2×CH=CHCHH), 2.87 (d, J = 14.8 Hz, 2H; 2×CH=CHCHH), 2.98 (t, 2H; J = 6.4 Hz, $ArCH_2$), 3.85 (s, 3H; OCH_3), 5.63 (s, 2H; CH=CH), 6.67 (d, J = 1.6 Hz, 1H; ArH), 6.83 (dd, J = 8.8, 2.4 Hz, 1H; ArH), 8.03 ppm (d, J = 8 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 26.5, 35.1, 42.1 (2C), 51.6, 55.5, 112.4, 113.3, 125.2, 128.2 (2C), 130.7, 146.1, 163.5, 200.4 ppm; IR (neat): $\tilde{\nu}$ = 1671 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{15}H_{17}O_2$ [M+H]: 229.1272; found: 229.1268.

RCM of 2,2-diallyl-2,3-dihydroinden-1-one (40a): Grubbs first-generation catalyst (19.36 mg, 10 mol%) was added to a solution of diallylated indan-1-one **40a** (50 mg, 0.24 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **42a** (32 mg, 81%) as a reddish brown, viscous liquid. R_f = 0.6 (silica gel, EtOAc/petroleum ether 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.33 (d, J = 16 Hz, 2H; 2×CH=CHCHH), 2.91 (d, J = 16 Hz, 2H; 2×CH=CHCHH), 3.18 (s, 2H; $ArCH_2$), 5.73 (s, 2H; CH=CH), 7.40 (td, J = 8.4, 0.4 Hz, 1H; ArH), 7.6 (td, J = 8, 0.8 Hz, 1H; ArH), 7.79 (dd, J = 8, 0.8 Hz, 1H; ArH), 7.73 ppm (d, J = 8 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 45.5, 45.6, 55.6, 62.3, 110.1, 124.4, 126.6, 127.6, 128.9, 134.9, 136.4, 152.9, 210.6 ppm; IR (neat): $\tilde{\nu}$ = 1710 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{13}H_{12}ONa$ [M+Na]: 207.0786; found: 207.0788.

RCM of 2,2-diallyl-5-methoxy-2,3-dihydroinden-1-one (40b): Grubbs first-generation catalyst (23.6 mg, 14 mol%) was added to a solution of bis-allylated 5-methoxyindanone **40b** (50 mg, 0.21 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (4%) gave compound **42b** (40 mg, 93%) as an off-white solid. R_f = 0.4 (silica gel, EtOAc/petroleum ether 1:10); m.p. 112°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.32 (d, J = 15.2 Hz, 2H; 2×CH=CHCHH), 2.89 (d, J = 15.2 Hz, 2H; 2×CH=CHCHH), 3.12 (s, 2H; $ArCH_2$), 3.88 (s, 3H; OCH_3), 5.72 (s, 2H; CH=CH), 6.87 (d, J = 2 Hz, 1H; ArH), 6.92 (dd, J = 8.6, 2.0 Hz, 1H; ArH), 7.71 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 45.7 (2C), 45.8, 55.8 (2C), 109.8, 115.5, 126.1, 128.91, 128.93, 129.6, 155.8, 165.6, 209.6 ppm; IR (neat): $\tilde{\nu}$ = 1703 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{15}O_2$ [M+H]: 215.1072; found: 215.1070.

RCM of 2,2-diallyl-5-bromo-2,3-dihydroinden-1-one (40c): Grubbs first-generation catalyst (16.9 mg, 15 mol%) was added to a solution of diallylated 5-bromoindanone **40c** (40 mg, 0.13 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (2%) gave compound **42c** (33 mg, 90%) as a light yellow solid. R_f = 0.8 (silica gel, EtOAc/petroleum ether 1:10); m.p. 83°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.34 (d, J = 14.8 Hz, 2H; 2×CH=CHCHH), 2.88 (d, J = 15.2 Hz, 2H; 2×CH=CHCHH), 3.15 (s, 2H; $ArCH_2$), 5.72 (s, 2H; CH=CH), 7.52 (dd, J = 8, 0.8 Hz, 1H; ArH), 7.62–7.65 ppm (m, 2H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 45.1, 45.5 (2C), 55.8, 125.5 (2C), 128.7, 129.8, 130.2, 131.2, 135.2, 154.5, 209.1 ppm; IR (neat): $\tilde{\nu}$ = 1706 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{13}H_{12}OBr$ [M+H]: 263.0072; found: 263.0067.

RCM of 2,2-diallyl-5,6-dimethoxy-2,3-dihydroinden-1-one (40d): Grubbs first-generation catalyst (15.1 mg, 10 mol%) was added to a solution of diallylated 5,6-dimethoxyindanone **40d** (50 mg, 0.18 mmol) in dry toluene (5 mL) and the system was heated at reflux for 48 h. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (6%) gave compound **42d** (36 mg, 80%) as a white, crystalline solid. R_f = 0.2 (silica gel, EtOAc/petroleum ether 1:10); m.p. 153°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.33 (d, J = 14.8 Hz, 2H; 2×CH=CHCHH), 2.89 (d, J = 14.4 Hz, 2H; 2×CH=CHCHH), 3.09 (s, 2H; $ArCH_2$), 3.92 (s, 3H; OCH_3), 3.97 (s, 3H; OCH_3), 5.73 (s, 2H; CH=CH), 6.86 (s, 1H; ArH), 7.26 ppm (s, 1H; ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C, TMS): δ = 45.6 (2C), 55.8, 56.22, 56.24, 56.3, 104.8 (2C), 107.5, 128.9 (2C), 148.1, 149.7, 155.7, 209.2 ppm; IR (neat): $\tilde{\nu}$ = 1694 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{15}H_{17}O_3$ [M+H]: 245.1178; found: 245.1185.

Naphtho[2,1-*b*]oxepin-3(4*H*)-one (43): IBX (107 mg, 0.382 mmol) was added to a solution of compound **16a** (25 mg, 0.127 mmol) in DMSO (3 mL) and the mixture was heated to 80°C for 8 h. The reaction mixture was then cooled to room temperature, diluted with Et_2O and washed with $NaHCO_3$ (5%, 2×10 mL), water (2×10 mL), and brine (10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the crude product, which was loaded onto a silica gel column, elution of which with EtOAc/petroleum ether (5%) gave compound **43** (17 mg, 64%) as a thick, yellow liquid. R_f = 0.2 (silica gel, EtOAc/petroleum ether 1:19); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 4.65 (s, 2H; OCH_2), 6.61 (d, J = 12.0 Hz, 1H; COCH=CH), 7.33 (d, J = 8.8 Hz, 1H; ArH), 7.49–7.53 (m, 1H; ArH), 7.61–7.65 (m, 1H; ArH), 7.86–7.89 (m, 2H; ArH), 8.00 (d, J = 12.8 Hz, 1H; COCH=CH), 7.11 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C, TMS): δ = 79.3, 120.7, 121.0, 123.1, 125.5, 128.1, 129.1, 129.8, 130.9, 133.0, 133.4, 137.3, 159.1, 197.5 ppm; IR (neat): $\tilde{\nu}$ = 1668 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 238 nm (6006 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{11}O_2$ [M+H]: 211.0759; found: 211.0751.

1,2-Dihydronaphtho[2,1-*b*]oxepin-3(4*H*)-one (44): Compound **43** (10 mg, 0.047 mmol) in dry benzene and ethanol (14 mL, 1:1) in a sealed tube was degassed with nitrogen for 10 mins. Wilkinson's catalyst (2 mg, 0.002 mmol, 5 mol%) was added and hydrogen gas was bubbled for 10 mins. Finally, the reaction vessel was kept under 1 atm hydrogen pressure and stoppered tightly, and the reaction mixture was then heated at 80°C. After completion of the reaction (12 h, TLC monitoring) the pressure was released, the resulting brown solution was concentrated under reduced pressure, and the crude product was purified by silica gel flash chromatography. Elution of the column with 5% EtOAc/petroleum ether gave compound **44** (9 mg, 89%) as a thick, colorless liquid. R_f = 0.2 (silica gel, EtOAc/petroleum ether 1:19); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 3.26 (t, J = 6.8 Hz, 2H; $ArCH_2$), 3.48 (t, J = 6.6 Hz, 2H; $ArCH_2CH_2$), 4.58 (s, 2H; OCH_2), 7.22 (d, J = 8.8 Hz, 1H; ArH), 7.27–7.48 (m, 1H; ArH), 7.52–7.57 (m, 1H; ArH), 7.70 (d, J = 8.8 Hz, 1H; ArH), 7.82–7.84 (m, 1H; ArH), 7.90 ppm (dd, J = 8.4, 0.8 Hz, 1H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C, TMS): δ = 24.8, 39.5, 79.3, 122.19, 122.22, 123.0, 125.0, 127.0, 128.8 (2C), 131.0, 133.3, 156.2, 212.1 ppm; IR (neat) : $\tilde{\nu}$ = 1727 cm^{-1} (C=O st); UV ($CHCl_3$): λ_{max} (ε) = 238 nm (7377 mol^{-1}dm^{3}cm^{-1}); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{13}O_2$ [M+H]: 213.0916; found: 213.0907.

1,2,3,4-Tetrahydronaphtho[2,1-*b*]oxepine (45):[37] Pd (10% on carbon, 14 mg) and freshly distilled ethyl acetate (10 mL) were placed in a three-necked flask (25 mL). The solvent was saturated with hydrogen (atmospheric pressure) for 30 min, followed by addition of **16a** (80 mg, 0.408 mmol) in ethyl acetate (1 mL). After completion of the reaction (6 h, monitored by ^{1}H NMR), the catalyst was removed by filtration, the filtrate was concentrated, and the crude product was then purified by silica gel flash column chromatography. Elution of the column with EtOAc/petroleum ether (1.5%) gave compound **45** as a white solid (65 mg, 81%). R_f = 0.35 (silica gel, EtOAc/petroleum ether 1:49); m.p. 60°C (lit.: 59°C);[37] ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.82–1.88 (m, 2H; $ArCH_2CH_2$), 1.99–2.08 (m, 2H; OCH_2CH_2), 3.26 (t, J = 5.8 Hz, 2H; $ArCH_2$), 4.12 (t, J = 5.8 Hz, 2H; OCH_2), 7.20 (d, J = 8.8 Hz, 1H; ArH), 7.36–7.40 (m, 1H; ArH), 7.46–7.51 (m, 1H; ArH), 7.64 (d, J = 8.8 Hz, 1H; ArH), 7.79–7.81 (m, 1H; ArH), 8.05 ppm (d, J = 8.4 Hz, 1H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C, TMS): δ = 25.0, 26.6, 32.1, 73.4, 122.2, 123.4, 124.1, 126.2, 127.6, 128.4, 128.7, 131.0, 133.1, 158.4; MS (Q-Tof ES+): m/z = [M+H]: 199.

3,4-Dihydronaphtho[2,1-*b*]oxepin-1(2*H*)-one (46):[38] A finely powdered and homogenized mixture of pyridinium chlorochromate (161 mg, 0.75 mmol) and celite (2 g) was added to a solution of compound **45** (15 mg, 0.075 mmol) in dry benzene (7 mL) and the reaction mixture was then stirred and heated at reflux. After completion of the reaction (7 h, TLC monitoring) the reaction mixture was diluted with diethyl ether (10 mL) and filtered through a short pad of celite and anhydrous magnesium sulfate. The residue was then washed with diethyl ether (2×10 mL), the combined ether extracts were concentrated, and the crude product was purified by silica gel flash column chromatography. Elution of the column with EtOAc/petroleum ether (5%) gave compound **46** (12 mg, 75%) as a white solid. M.p. 135°C (lit.: 138°C).[38a] ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.30 (tt, J = 6.4, 6.8 Hz, 2H; OCH_2CH_2), 2.98 (t, J = 6.8 Hz, 2H; $COCH_2$), 4.34 (t, J = 6.4 Hz, 2H; OCH_2), 7.21 (d, J = 8.8 Hz, 1H; ArH), 7.40–7.45 (m, 1H; ArH), 7.53–7.56 (m, 1H; ArH), 7.79 (d, J = 7.2 Hz, 1H; ArH), 7.86 (d, J = 8.8 Hz, 1H; ArH), 8.60 ppm (d, J = 8.8 Hz, 1H; ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C, TMS): δ = 27.9, 42.5, 73.0, 121.1, 124.9, 125.0, 128.3, 128.5, 130.3, 131.1, 133.8, 161.2, 204.3 ppm; IR (neat): $\tilde{\nu}$ = 1678 cm^{-1} (C=O st); HRMS (Q-Tof ES+): m/z calcd for $C_{14}H_{13}O_2$ [M+H]: 213.0916; found: 213.0913.

X-ray crystallographic data for compound 26: $C_{30}H_{25}BrO_5S_2$, M = 609.53, monoclinic, space group, $P2_1$, a = 12.0280(12), b = 7.7420(8), c = 15.197(3) Å, β = 109.823(11)°, V = 1331.3(4) Å^3, T = 293(2) K, Z = 2, μ(Mo-K$_\alpha$) = 1.741 mm^{-1}, 2830 reflections measured, 2711 unique (R_{int} = 0.0423), observed with $I > 2\sigma(I)$, which were used in all refinements. R_1 = 0.0444, wR_2 = 0.0851 for the observed data.

CCDC-603947 contains 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.

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