Metathetic Approach Towards Macrocyclic *bis*-Ethers and in Sequence use of Barbier Reaction and RCM for Spirocyclic Ethers

Sulagna Brahma, Susama Maity and Jayanta K. Ray*

Department of Chemistry, Indian Institute of Technology Kharagpur 721302, India:
jkray@chem.iitkgp.ernet.in

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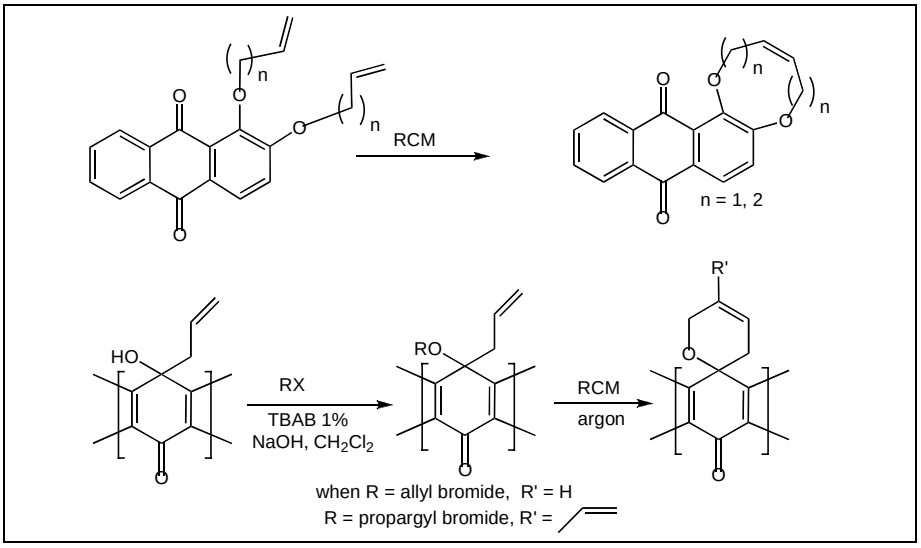

An efficient method for the synthesis of novel macrocyclic *bis*-ethers from alizarin and also some new spiro ethers from various substituted ketones by the use of Barbier and ring-closing metathesis (RCM) reactions has been developed.

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INTRODUCTION

Macrocyclic *bis*-ethers [1] and spirocyclic ethers [2] are important from biological and medicinal point of view [3,4]. Inspired by these beneficial effects of *bis*-ethers and spirocyclic compounds, we became interested to synthesize some macrocycles and spiro cyclic ethers.

The key steps of our syntheses are indium-mediated Barbier reactions [5] and ring-closing metathesis (RCM) reactions by Grubbs' 1st generation catalyst. The Barbier reaction is important for introducing both hydroxyl group and a carbon-carbon double bond simultaneously in a molecule. Indium-mediated allylation of carbonyl compounds [6] has attracted much interest among organic chemists due to the unusual reactivity of indium particularly in aqueous media [7-11]. Ring-closing metathesis reaction [12-18] is now widely popular due to its operational simplicity, as it requires no additional reagents except negligible amounts of catalyst and the other product is in most cases a volatile ethylene molecule. The catalyst used for this purpose is popularly known as Grubbs' 1st generation catalyst, [19] benzyl-idene-*bis*-(tricyclohexylphosphine)ruthenium dichloride. We aimed to synthesize some *bis*-ethers of well-defined stereochemistry and spiro compounds by the combinations of these two important reactions. Although some spiro compounds and macrocyclic *bis*-ethers have already been reported [20-27], our methodology adds another direction over the reported procedure.

Benzoannulated quinones, *e.g.*, anthracycline antibiotics such as doxorubicin, idarubicin and daunorubicins have been widely used as antitumor agents. Various naphthacenediones have also been used as antibiotics.

Benzoannulation of quinones using a double Claisen rearrangement followed by RCM and DDQ oxidation has already developed [23,28].

RESULTS AND DISCUSSION

We took alizarin as a starting material. Alizarin was *bis*-alkylated by using allyl bromide and butenyl bromide respectively in presence of anhydrous potassium carbonate in refluxing acetone, which produced the double allylated products in impressive yields [29]. Then the *bis*-alkylated products (**1a**) and (**2a**) were subjected to ring closing metathesis (RCM) reaction to give (**1b**) and (**2b**) (Entries No. **1** & **2**, Table 1).

The product **1b** was isolated as yellow solid, in excellent yield (91%) and ^{1}H NMR spectra revealed *cis*-(*Z*) stereochemistry of the newly formed double bond.

Encouraged by this pleasing outcome, we have extended our works for several quinones and some other ketones like anthrone, fluorenone *etc*. as starting materials. At first, they were subjected to allylation by indium-allyl bromide in presence of sodium iodide in dry DMF to get the homoallylic alcohol [29]. Then further allylation was carried out by using phase transfer catalyst (TBAB) and allyl bromide in distilled dichloromethane in the presence of 1% sodium hydroxide solution to give double allylated product (**3a**-**8a**). Finally RCM reaction of double allylated product by Grubbs' catalyst in dry and degassed dichloromethane furnished the spiro compounds (**3b**-**8b**) in excellent yields. After getting sound results from the allyl-allyl system, we extended our work with the allyl-propargyl system and we obtained the same type of 6-membered spiro ether derivatives as shown in Table 1 (Table 1, Entries No. **9** & **10**).

Table 1

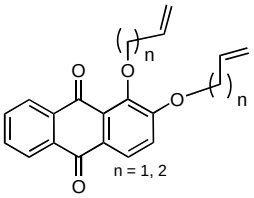
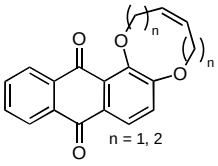
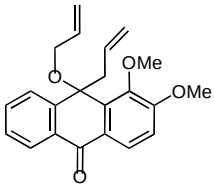
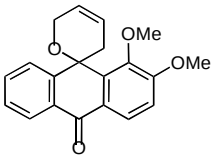
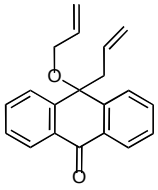
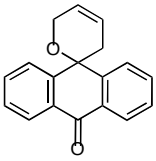
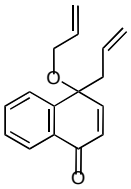
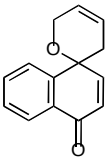
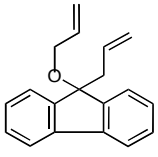
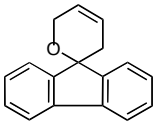
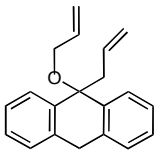
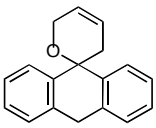
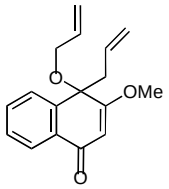
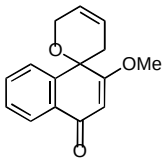
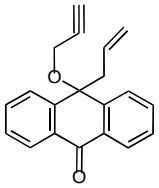
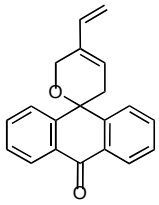
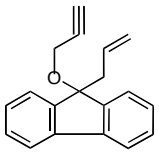
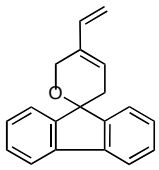
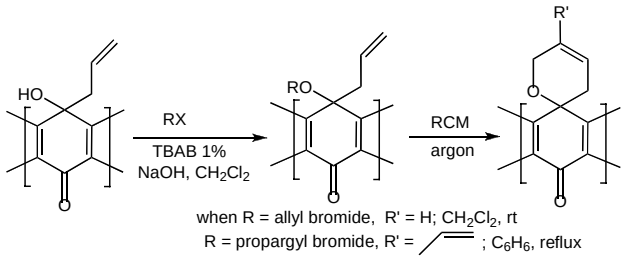
Entry	Substrates	Products	Time (h)	Yield (%)
1. and 2.	 **1a & 2a**	 **1b & 2b**	2, 5	91, 40
3.	 **3a**	 **3b**	4	89
4.	 **4a**	 **4b**	2	90
5.	 **5a**	 **5b**	4	78
6.	 **6a**	 **6b**	2	93
7.	 **7a**	 **7b**	4	85

Table 1 (continued)

Entry	Substrates	Products	Time (h)	Yield (%)
8.	 **8a**	 **8b**	4	75
9.	 **9a**	 **9b**	12	67
10.	 **10a**	 **10b**	12	65

Scheme 1



The general procedure for obtaining the starting material used in the final step, *i.e.,* the metathesis reaction is shown in Scheme 1. The stereochemistry of the newly formed double bond in all the synthesized compounds is *cis*.

In conclusion, we have developed a new route that converts the keto compounds to spiro-ethers. Furthermore, the compounds obtained from propargyl bromide (**9b**, **10b**) can be used as dienes for various Diels-Alder reaction for the preparation of polycyclic compounds.

EXPERIMENTAL

All reagents and solvents were reagent grade. Further purification and drying by standard methods were employed in each step. All organic solvents were evaporated under pressure with a rotary evaporator. The plates used for thin-layer chromatography (TLC) were E. Merck silicagel $60F_{254}$ (0.25 mm thickness) precoated on aluminium plates, and they were visualized under 254 nm UV light. Column chromatography was performed using silica gel; (60-120 mesh and 230-400 mesh for flash column chromatography, SRL). NMR spectra were recorded on a Bruker spectrometer (200 MHz and 300 MHz for ^{1}H). All NMR measurements were carried out at 300 K in deuterated chloroform solution (dried with 4 A molecular sieves) unless otherwise stated. Chemical shifts were reported as parts per million (ppm) in δ unit in the scale relative to the resonance of $CDCl_3$ (7.26 ppm in the ^{1}H, 77.00 ppm for the central line of the triplet in the ^{13}C modes, respectively). Coupling constant (*J*) were reported in Hz. Splitting patterns were described by using the following abbreviation: s, singlet: d, doublet; t, triplet; q, quartet; m, multiplate; brs, broad singlet; brd, broad doublet. ^{1}H NMR data are reported in this order: chemical shift; multiplicity, number of protons, coupling constant (s). IR spectra were recorded on a Parkin-Elmer 830 machine. Mass spectra were obtained from IICB, Kolkata and determined at an ionization voltage of 70 eV. Relevant data were tabulated as m/z. Elemental analyses were performed at IIT, Kharagpur.

General Procedure for the Synthesis of Homoallylic Alcohol (Barbier Reaction). To a stirred suspension of In-metal (1.05 mmol) and sodium iodide (1.55 mmol), in dry DMF (2-3 mL) at room temperature, allyl bromide was added dropwise. The stirring was continued at room temperature until all the indium metal dissolved. To this solution, ketones (1 mmol) in DMF (1-2 mL) was added dropwise and stirred further for 3-5 h (completion of the reaction was checked by TLC). The reaction mixture was quenched with a few drops of dil HCl and diluted with water. It was then extracted with ethyl acetate and the

organic layer was thoroughly washed with water and dried. Removal of the solvent under reduced pressure followed by purification of the residue obtained furnished homoallylic alcohol.

Procedure for the Preparation of Double Allylated Compounds (1a and 2a). To a stirred solution of alizarin (1 mmol) and K_2CO_3 (2.5 m mol) in dry acetone, allyl bromide/butenyl bromide (2.5 mmol) was added drop wise at room temperature. It was then refluxed for at least 4-5 h (completion of the reaction was checked by TLC). Reaction mixture was filtered and the volume of the filtrate was reduced to half then quenched with water. The organic layer was extracted with ether. Removal of the solvent under reduced pressure followed by purification furnished double allylated product as yellow solid.

The General Phase Transfer Catalyst Procedure for the Preparation of Double Allylated Compounds (3a-8a). 9-Allyl-9*H*-fluoren-9-ol (222 mg, 1 mmol), and allyl bromide (0.18 ml, 3 mmol) in distilled dichloromethane (8.3 mL) was added to a solution of tetrabutylammoniumbromide (13.3 mg, 0.04 mmol) in 1% NaOH solution (8.3 mL). The mixture was refluxed for 12 h (completion of the reaction was checked by TLC). It was cooled; the organic layer was separated and washed with water (8 ml) and then with brine solution (8 ml). Removal of the solvent gave the product, which was purified by column chromatography (silica gel) using 2% ethyl acetate in petroleum ether as eluent. The product 9-allyl-9-vinyloxy fluorenone (**6a**) was obtained as colorless liquid. Compound **3a**, **4a**, **5a**, **7a** and **8a** can also be prepared by following similar procedure.

Experimental Procedure for the Preparation of 9a and 10a. NaH (2.5 mmol), taken in a two neck round bottom flask, was thoroughly washed with petroleum ether (2-3 times) and then dried under vacuum after which dry THF was added. The monoallylated product (1 mmol) was dissolved in THF and slowly added into the NaH solution in ice-cold condition. Formation of anion was indicated by color change. After the formation of anion, propargyl bromide was added and stirring was continued at rt (monitored by TLC). Reaction mixture was quenched in water and extracted with ether. Solvent was removed under reduced pressure and then the product was purified by column chromatography (flash silica gel, 10:1 petroleum ether/ ethyl) acetate as eluent.

Experimental RCM Procedure for the Preparation of Compounds 1b-8b. To a stirred solution of 1,2-*bis*-vinyloxy anthraquinone (**1a**) (1 mmol) in dry and degassed dichloromethane, Grubbs' catalyst (10 mmol %) was added under an argon atmosphere. The reaction mixture was stirred for 2 h at rt 25 °C under an argon atmosphere (monitored by TLC). Solvent was removed under reduced pressure and then the product was purified by column chromatography (flash silica gel) using 2% ethyl acetate in petroleum ether as eluent. The product (**1b**) was obtained as yellow crystals. Similar procedure can be used for the preparation of compound **2b**-**8b**.

Experimental RCM Procedure for (9a and 10a). To a stirred solution of 10-allyl-10-ethynyloxy-10*H*-anthracene-9-one (**9a**) (32 mg, 0.11 mmol) in dry and degassed benzene (20 mL), Grubbs' catalyst (10 mmol%) was added under an argon atmosphere. The reaction mixture was refluxed for 12 h under an argon atmosphere (completion of the reaction was checked by TLC). Solvent was removed under reduced pressure and then the product was purified by column chromatography (flash silica gel) using 2% ethyl acetate in petroleum ether as eluent. The product 5-Vinyl-3,6-dihydro-2*H*-pyranyl-10*H*-anthracene-9-one (**9b**) was obtained as yellow liquid.

Spectral Data. Precursors of compound 4a/10a [30], 5a [29-31], 6a/9a [32], 8a [31,33] are reported in the literature. Precursor of Compound (3a). Red solid, mp 102-105 °C (chloroform); IR (KBr) ν_{max}: 3304, 1680 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.66 (d, 2H, *J* = 7.2 Hz), 3.96 (s, 3H), 3.97 (s, 3H), 4.52-4.60 (m, 2H), 4.75-4.80 (m, 2H), 4.98-5.16 (m, 1H), 7.17-7.48 (m, 1H), 7.55-7.67 (m, 1H), 7.86 (d, 1H, *J* = 7.8 Hz), 8.12 (d, 1H, J = 7.7 Hz). *Anal*. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85 Found: C, 73.69; H, 5.98.

Precursor of Compound (7a). Yellow solid, mp 83-85 °C; IR (KBr) ν_{max}: 3350, 1270 cm^{-1}; (chloroform); ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.67-2.73 (m, 2H), 4.36-4.41 (m, 2H), 4.55-4.66 (m, 1H), 4.74-4.79 (m, 1H), 5.16-5.33 (m, 1H), 7.40-7.78 (m, 6H), 8.25-8.38 (m, 2H). *Anal*. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.82 Found: C, 86.32; H, 6.89.

1,2-*bis*-Allyloxyanthraquinone (1a). Yellow solid, mp 172 °C (chloroform); IR (KBr) ν_{max}: 1673, 1576, 1332, 1273 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): *δ* 4.65-4.73 (m, 4H), 5.25-5.52 (m, 4H), 6.01-6.29 (m, 2H), 7.24 (d, 1H, *J* = 8.6 Hz), 7.72-7.79 (m, 2H), 8.13 (d, 1H, *J* = 8.5 Hz), 8.21-8.28 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 182.57, 182.33, 158.16, 148.55, 135,12, 134.05, 133.41, 132.91, 131.99, 127.49, 127.40, 127.14, 126.58,125.02, 118.35, 118.18, 117.48, 74.68, 69.74. *Anal*. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03 Found: C, 74.79; H, 5.20.

1,2-*bis*-But-3-enyloxyanthraquinone (2a). Yellow solid, mp 189 °C (chloroform); IR (KBr) ν_{max}: 1678, 1576, 1350, 1270 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.66-2.72 (m, 4H), 4.87-5.50 (m, 4H), 5.16-5.51 (m, 4H), 6.04-6.21 (m, 2H), 6.99-7.06 (m, 2H), 7.29-7.60 (m, 2H), 8.03 (d, 1H, *J* = 6.5 Hz), 8.23 (d, 1H, *J* = 7.2 Hz). *Anal*. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79 Found: C, 75.76; H, 5.85.

10-Allyl-10-allyloxy-3,4-dimethoxy-10*H*-anthracene-9-one (3a). Yellow solid, mp 210 °C (chloroform); IR (KBr) ν_{max}: 1668, 1580, 1340, 1290 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.39-2.79 (m, 4H), 3.97 (s, 3H), 3.98 (s, 3H), 4.45-4.79 (m, 4H), 5.02-5.11 (m, 1H), 5.39-5.48 (m, 1H), 7.23-7.42 (m, 2H), 7.54-7.65 (m, 1H), 7.90 (d, 1H, *J* = 7.9 Hz), 8.22-8.40 (m, 2H). *Anal*. Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33 Found: C, 75.45; H, 6.38.

10-Allyl-10-allyloxy-10*H*-anthracene-9-one (4a). Yellow crystalline solid, mp 120 °C (chloroform); ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.84 (d, 2H, *J* = 7.2 Hz), 3.56 (d, 2H, *J* = 5.2 Hz), 4.40-4.49 (m, 2H), 4.65 (d, 1H, *J* = 9.9 Hz), 4.91-5.04 (m, 1H), 5.09-5.33 (m, 1H), 5.81-5.95 (m, 1H), 7.42- 7.53 (m, 2H), 7.66-7.73 (m, 2H), 7.80-7.84 (m, 2H), 8.29 (d, 2H, *J* = 7.8 Hz); EI-MS: 290 (M^+, 100%). *Anal*. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25 Found: C, 82.78; H, 6.31.

4-Allyl-4-allyloxy-3-methoxy-4*H*-naphthalen-1-one (5a). Yellow viscous liquid; IR (KBr) ν_{max}: 1725, 1597, 1372, 1327, 1291, 617 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.24-2.34 (m, 2H), 2.60-2.71 (m, 2H), 4.49 (d, 2H, *J* = 5.1 Hz), 4.50-4.87 (m, 2H), 5.28-5.63 (m, 2H), 7.35-7.43 (m, 2H), 7.57-7.65 (m, 2H), 7.80 (d, 1H, *J* = 7.8 Hz), 8.02 (d, 1H, *J* = 7.8 Hz). *Anal*. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71 Found: C, 79.78; H, 6.95.

9-Allyl-9-allyloxy-9*H*-fluorene (6a). Yellow viscous liquid; ^1H NMR (200 MHz, $CDCl_3$): *δ* 2.86 (d, 2H, *J* = 7.2 Hz), 3.34 (d, 2H, *J* = 5.4 Hz), 4.79-4.88 (m, 1H), 5.00-5.19 (m, 1H), 5.42-5.55 (m, 2H), 5.68-5.82 (m, 2H), 7.27-7.41 (m, 4H), 7.48 (d, 2H, *J* = 6.6 Hz), 7.63 (d, 2H, *J* = 7.5 Hz). *Anal*. Calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92 Found: C, 86.91; H, 6.95.

9-Allyl-9-allyloxy-9,10-dihydro-anthracene (7a). Pale yellow solid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.68 (d, 2H, J = 7.34 Hz), 4.53-4.62 (m, 2H), 4.76 (d, 2H, J = 1.9 Hz), 4.81 (d, 2H, J = 1.8 Hz), 5.04-5.13 (m, 2H), 7.40-7.48 (m, 4H), 7.60-7.68 (m, 2H), 7.87-7.90 (m, 2H), 8.15-8.17 (m, 2H). *Anal*. Calcd. for $C_{20}H_{20}O$: C, 86.92; H, 7.29 Found: C, 86.89; H, 7.32.

4-Allyl-4-allyloxy-3-methoxy-4*H*-naphthalen-1-one (8a). Pale yellow viscous compound; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.41 (d, 2H, J = 6.1 Hz), 3.43-3.51 (m, 2H), 4.80-5.05 (m, 2H), 5.08-5.13 (m, 2H), 5.72-5.84 (m, 2H), 7.64-7.74 (m, 3H), 8.01-8.11 (m, 2H). *Anal*. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71 Found: C, 75.61; H, 6.65.

10-Allyl-10-prop-2-ynyloxy-10*H*-anthracene-9-one (9a). Yellow viscous liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.24-2.34 (m, 1H), 2.60-2.71 (m, 2H), 4.49 (d, 2H, J = 5.0 Hz), 4.73-4.98 (m, 2H), 5.28-5.63 (m, 1H), 7.26-7.43 (m, 2H), 7.57-7.65 (m, 2H), 7.78-7.82 (m, 2H), 7.99-8.04 (m, 2H). *Anal*. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59 Found: C, 83.53; H, 6.02.

9-Allyl-9-propa-1,2-dienyloxy-9*H*-fluorene (10a). Yellow viscous liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.22-2.30 (m, 1H), 2.89 (d, 2H, J = 6.4 Hz), 3.49 (d, 2H, J = 2.4 Hz), 4.78-4.85 (m, 2H), 5.39-5.43 (m, 1H), 7.27-7.38 (m, 4H), 7.50-7.53 (m, 2H), 7.62 (d, 2H, J = 5.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 182.75, 142.62, 133.95, 133.74, 133.32, 132.41, 130.23, 128.34, 127.07, 126.07, 119.72, 79.62, 79.09, 73.91, 52.63, 52.36. *Anal*. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19 Found: C, 87.57; H, 6.95.

2,5-Dihydro-9.10-anthraquino[1,2-*b*]dioxocene (1b). Yellow solid, mp 168 °C (from chloroform); IR (KBr) λ_{max} 1736 and 1656 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.02 (d, 2H, J = 1.9 Hz), 5.18 (dd, 2H, J = 2.1 & 1.9 Hz), 5.94-6.00 (m, 2H), 7.28 (d, 1H, J = 8.5 Hz), 7.70-7.80 (m, 2H), 8.07 (d, 1H, J = 8.7 Hz), 8.20-8.27 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 67.19, 73.99, 125.14, 125.30, 126.46, 126.55, 127.03, 127.65, 129.13, 132.56, 133.43, 133.74, 134.08, 134.82, 147.39, 155.70, 182.25 and 182.73; EI-MS: 292 (M$^+$, 64%), 251, 210, 182, 154, 126 (100%) and 75. *Anal*. Calcd. for $C_{18}H_{12}O_4$: C, 74.11; H, 4.14 Found: C, 74.20; H, 4.36.

7,10-Dihydro-6*H*-5,11-dioxa-9.10-anthraquino[1,2-*b*]cyclononene (2b). Yellow solid, mp 175 °C (from chloroform); IR (KBr) λ_{max} 1740 and 1664 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.35- 2.46 (m, 2H), 4.25-4.35 (m, 2H), 4.36-4.49 (m, 2H), 5.94-6.01 (m, 2H), 7.28 (d, 2H, J = 10.5 Hz), 7.72-7.80 (m, 2H), 8.07 (d, 2H, J = 8.4 Hz), 8.22-8.28 (m, 2H). *Anal*. Calcd. for $C_{20}H_{16}O_4$: C, 75.05; H, 5.03 Found: C, 75.28; H, 5.12.

3,6-Dihydro-2*H*-pyranyl-3,4-dimethoxy-10*H*-anthracene-9-one (3b). White solid, mp 132-134 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.83-2.89 (m, 1H), 3.38-3.44 (m, 1H), 3.99 (s, 6H), 4.79-4.85 (m, 2H), 5.40-5.49 (m, 2H), 7.09 (d, 1H, J = 8.7 Hz, *o*-proton of OMe containing ring), 7.48 (t, 1H, J = 7.0 Hz), 7.72 (t, 1H, J = 6.7 Hz), 8.16 (d, 1H, J = 8.7 Hz, *o*-proton of OMe containing ring), 8.22 (d, 1H, J = 1.2 Hz), 8.25 (d, 1H, J = 1.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 182.70, 159.05, 149.60, 145.82, 137.94, 135.04, 133.80, 132.49, 131.61, 127.66, 126.93, 125.85, 124.98, 119.22, 119.05, 111.92, 61.40, 56.25, 52.63, 29.63. *Anal*. Calcd. for $C_{20}H_{18}O_4$: C, 74.54; H, 5.63 Found: C, 74.79; H, 5.84.

3,6-Dihydro-2*H*-pyranyl-10*H*-anthracene-9-one (4b). White solid, mp 250-252 °C (from chloroform); IR (KBr) λ_{max} 1730 and 1651 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.68-2.71 (m, 2H), 4.47-4.51 (m, 2H), 6.02-6.10 (m, 1H), 6.17-6.24 (m, 1H), 7.42-7.51 (m, 2H), 7.56-7.64 (m, 2H), 7.76-7.82 (m, 2H), 8.20-8.24 (m, 1H), 8.29-8.34 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.47, 63.43, 71.49, 124.35, 126.23, 127.20, 127.94, 128.39, 130.74, 132.91, 133.41, 134.03, 147.21 and 184.37. EI-MS (m/z): 262 (M$^+$, 16%), 208, 180 (100%), 152, 126 and 75. *Anal*. Calcd. for $C_{18}H_{14}O_2$: C, 82.40; H, 5.38 Found: C, 82.89; H, 5.52.

3,6-Dihydro-2*H*-pyranyl-4*H*-naphthalene-1-one (5b). Yellow viscous compound; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.22-2.56 (m, 1H), 2.58-2.80 (m, 1H), 4.75-4.51 (m, 2H), 5.27-5.74 (m, 2H), 7.57-7.63 (m, 2H), 7.68-7.73 (m, 2H), 8.04-8.09 (m, 2H). *Anal*. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70 Found: C, 79.34; H, 5.81.

3,6-Dihydro-2*H*-pyranyl-9*H*-fluorene (6b). Pale yellow viscous compound; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56-2.59 (m, 2H), 4.48-4.53 (m, 2H), 6.06-6.14 (m, 2H), 7.25-7.30 (m, 2H), 7.34-7.40 (m, 2H), 7.58 (d, 2H, J = 7.4 Hz), 7.65 (d, 2H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.07, 139.84, 128.99, 127.75, 126.41, 124.36, 123.80, 119.93, 63.51, 32.27, 29.66; EI-MS: 234 (M$^+$, 100%), 221, 202, 189, 180 (100%), 165, 152 (100%). *Anal*. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02 Found: C, 86.99; H, 6.21.

3,6-Dihydro-2*H*-pyranyl-9,10-dihydroanthracene (7b). Yellow semisolid compound; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.68 (d, 2H, J = 7.3 Hz), 2.61 (d, 2H, J = 8.8 Hz), 4.50 (d, 2H, J = 2.2 Hz), 6.03-6.02 (m, 1H), 6.27-5.98 (m, 1H), 7.48-7.40 (m, 2H), 7.68-7.60 (m, 2H), 7.88 (d, 2H, J = 7.8 Hz), 8.15 (d, 2H, J = 1.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 35.33, 53.80, 63.65, 120.03, 123.40, 123.79, 126.39, 127.69, 129.01, 137.65 and 146.83. *Anal*. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49 Found: C, 87.17; H, 6.71.

3,6-Dihydro-2*H*-pyranyl-3-methoxy-4*H*-naphthalene-1-one (8b). Brown viscous compound; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.25-2.61 (m, 1H), 2.59-2.89 (m, 1H), 3.35 (s, 3H), 4.75-4.51 (m, 2H), 5.27-5.74 (m, 2H) 7.57-7.63 (m, 2H), 7.68-8.10 (m, 3H); ESI-MS (m/z): 243 (M$^+$+1). *Anal*. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82 Found: C, 74.29; H, 5.75.

5-Vinyl-3,6-dihydro-2*H*-pyranyl-10*H*-anthracene-9-one (9b). White solid, mp 185 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.80-2.88 (m, 2H), 3.70 (d, 1H, J = 2.4 Hz), 4.65 (s, 2H), 5.09-5.19 (m, 1H), 6.00-6.20 (m, 1H), 6.39 (m, 1H), 7.43-7.85 (m, 6H), 8.20-8.31 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.36, 52.63, 73.91, 79.09, 79.62, 119.72, 126.06, 127.07, 128.34, 130.23, 132.41, 133.74, 142.62 and 182.75; ESI-MS (m/z): 289 (M$^+$+1). *Anal*. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59 Found: C, 83.29; H, 5.61.

5-Vinyl-3,6-dihydro-2*H*-pyranyl-10*H*-fluorene (10b). Pale yellow viscous liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.90 (d, 2H, J = 7.2 Hz), 3.49-3.57 (m, 2H), 4.78-4.85 (m, 2H), 5.35-5.44 (m, 2H), 7.25-7.42 (m, 4H), 7.46-7.54 (m, 2H), 7.61-7.68 (m, 2H); ESI-MS (m/z): 261 (M$^+$+1); ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.09, 140.57, 132.26, 129.26, 127.77, 124.55, 119.91, 118.36, 87.65, 73.32, 44.18. *Anal*. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19 Found: C, 87.70; H, 6.23.

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