Synthesis of Phenanthrene and Alkyl Phenanthrenes by Palladium(0)-Catalyzed Pericyclic Reactions

Rathin Jana, Anup Biswas, Shubhankar Samanta, Jayanta K. Ray*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India
Fax +91(3222)282252; E-mail: jkray@chem.iitkgp.ernet.in

Received 27 February 2010; revised 5 March 2010

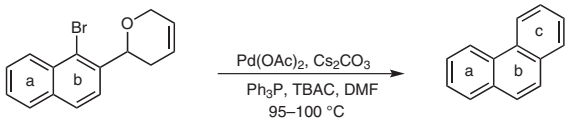
Abstract: Palladium-catalyzed pericyclic reactions have been developed for the synthesis of phenanthrenes. This method is also useful for the synthesis of monoalkyl and dialkyl phenanthrene derivatives.

Key words: pericyclic reaction, Pd catalyst, polycyclic aromatic hydrocarbon, alkyl phenanthrene

Methyl phenanthrene belongs to an important group of alkyl–aromatic hydrocarbons that are present in natural environments[1] and arises through the combustion of wood and coal. There are a great variety of methods available for the synthesis of phenanthrene and its derivatives,[2] but perhaps the most extensive method is the classical Haworth synthesis. This method might be employed for the convenient introduction of alkyl groups into the desired position on the phenanthrene moiety.[3] Li et al. reported palladium-catalyzed cyclotrimerization of allene with arynes for the selective synthesis of phenanthrenes in moderate to good yields.[4] Furstner et.al reported a method starting from readily available biphenyl derivatives containing an alkyne unit at one of the *ortho* positions and converted them into substituted phenanthrenes in the presence of catalytic amounts of $PtCl_2$, AuCl and $AuCl_3$ in toluene.[5]

Recently, we have synthesized 9,10-dihydrophenanthrenes by palladium-catalyzed electrocyclic reactions starting from vinyl bromoaldehydes.[6] We have also applied our methodology starting from aromatic bromoaldehydes, and have obtained phenanthrene and alkyl phenanthrenes in good yields.

Importantly, this methodology allows the introduction of an alkyl group to one or two positions of the newly formed benzene ring (ring **c**) of the phenanthrene (Scheme 1).



Scheme 1

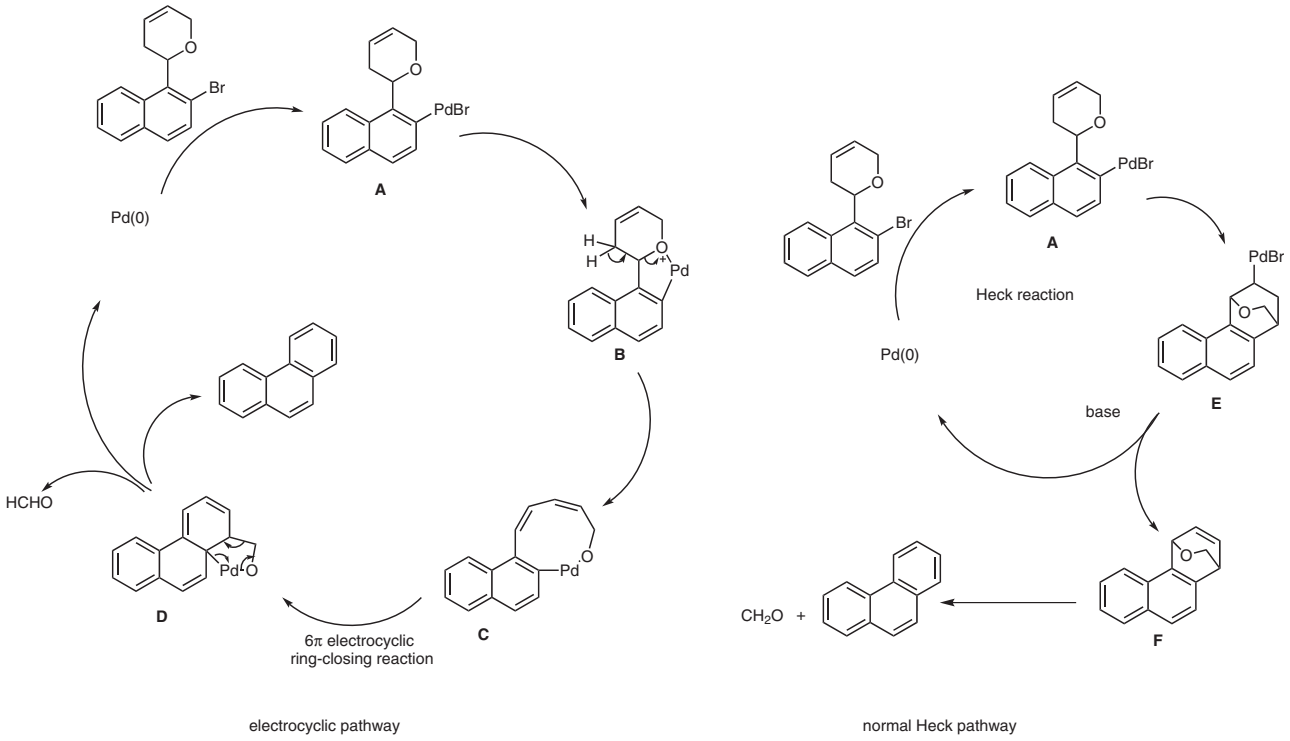
The catalytic cycle (Scheme 2) involves an initial oxidation of Pd(0) to generate an alkenyl palladium(II) intermediate (**A**) via oxidative addition of the Pd(0) to the substrate, which then co-ordinates with oxygen to generate the intermediate (**B**). This undergoes proton abstraction followed by rearrangement to afford the nine-membered cyclic Pd–O complex (**C**). This complex undergoes a 6 electrocyclic ring-closure reaction forming complex (**D**), which is followed by formaldehyde elimination to afford phenanthrene. Recently Lan et al. proposed an alternative mechanism for the formation of 9,10-dihydrophenanthrenes that proceeds through an intramolecular Heck reaction. Using theoretical calculations, they investigated both mechanisms and found that the intramolecular Heck mechanism[7] is lower in energy than the electrocyclic pathway (Scheme 2); this is also expected to be same for aromatic systems.

First, aromatic bromoaldehydes **1a** or **1b** were treated with allyl bromide and sodium iodide in the presence of indium metal to provide the corresponding alcohols **2a** and **2b**. These alcohols were allylated in the presence of sodium hydride in tetrahydrofuran at 0 °C, leading to the diallylated compounds **3a** and **3b**, which were subjected to a metathesis reaction using 2nd generation Grubbs catalyst to obtain the desired cyclic precursors **4a** and **4b**, respectively. These cyclic precursors were finally treated with palladium(II) acetate, triphenylphosphine, cesium carbonate in *N*,*N*-dimethylformamide at 85–90 °C to afford phenanthrene (**5a**) and 2-methoxyphenanthrene (**5b**) in good yields (Scheme 3).

To introduce an alkyl group to the phenanthrene ring, aromatic bromoaldehydes **1a**, **1b**, and **1c** were treated with allyl bromide and sodium iodide in the presence of indium metal, leading to the corresponding alcohols **2a**, **2b**, and **2c**. These alcohols were methallylated with methallyl bromide in the presence of sodium hydride in tetrahydrofuran at 0 °C, to furnish the diallylated compounds **3c**, **3d**, and **3e**, which were then subjected to a metathesis reaction using 2nd generation Grubbs catalyst to provide the cyclic precursors **4c**, **4d**, and **4e**, respectively. These cyclic precursors were finally treated with palladium(II) acetate, triphenylphosphine, and cesium carbonate in *N*,*N*-dimethylformamide at 85–90 °C to afford the alkyl phenanthrenes **5c**, **5d**, and **5e**, respectively, as shown in Scheme 4.

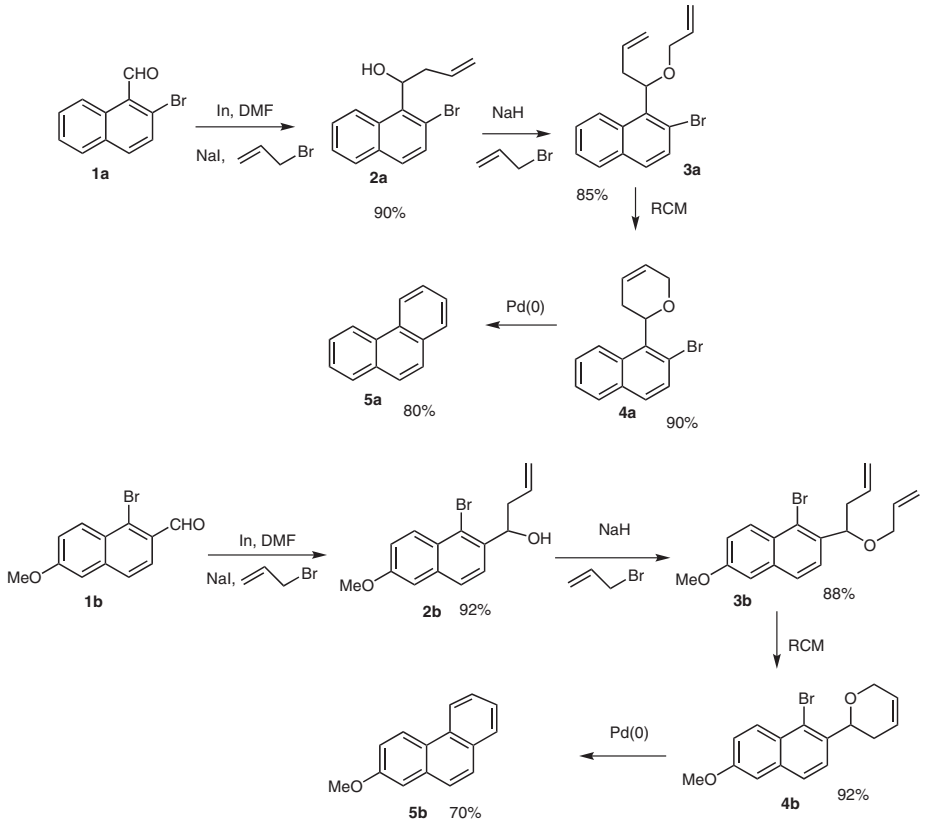
To introduce a methyl group to other positions of the phenanthrene moiety, the aromatic bromoaldehydes **1a**,

SYNTHESIS 2010, No. 12, pp 2092–2100
Advanced online publication: 12.04.2010
DOI: 10.1055/s-0029-1218726; Art ID: Z05010SS



Scheme 2

1b, and **1c** were treated with methallyl bromide and sodium iodide in presence of indium metal to obtain compounds **2d**, **2e**, and **2f**, respectively. These alcohols were then allylated in the presence of sodium hydride in tetrahydrofuran at 0 °C, leading to the diallylated compounds **3f**, **3g**, and **3h**, which were subjected to a metathesis reaction using 2nd generation Grubbs catalyst to obtain the desired cyclic precursors **4f**, **4g**, and **4h**, re-



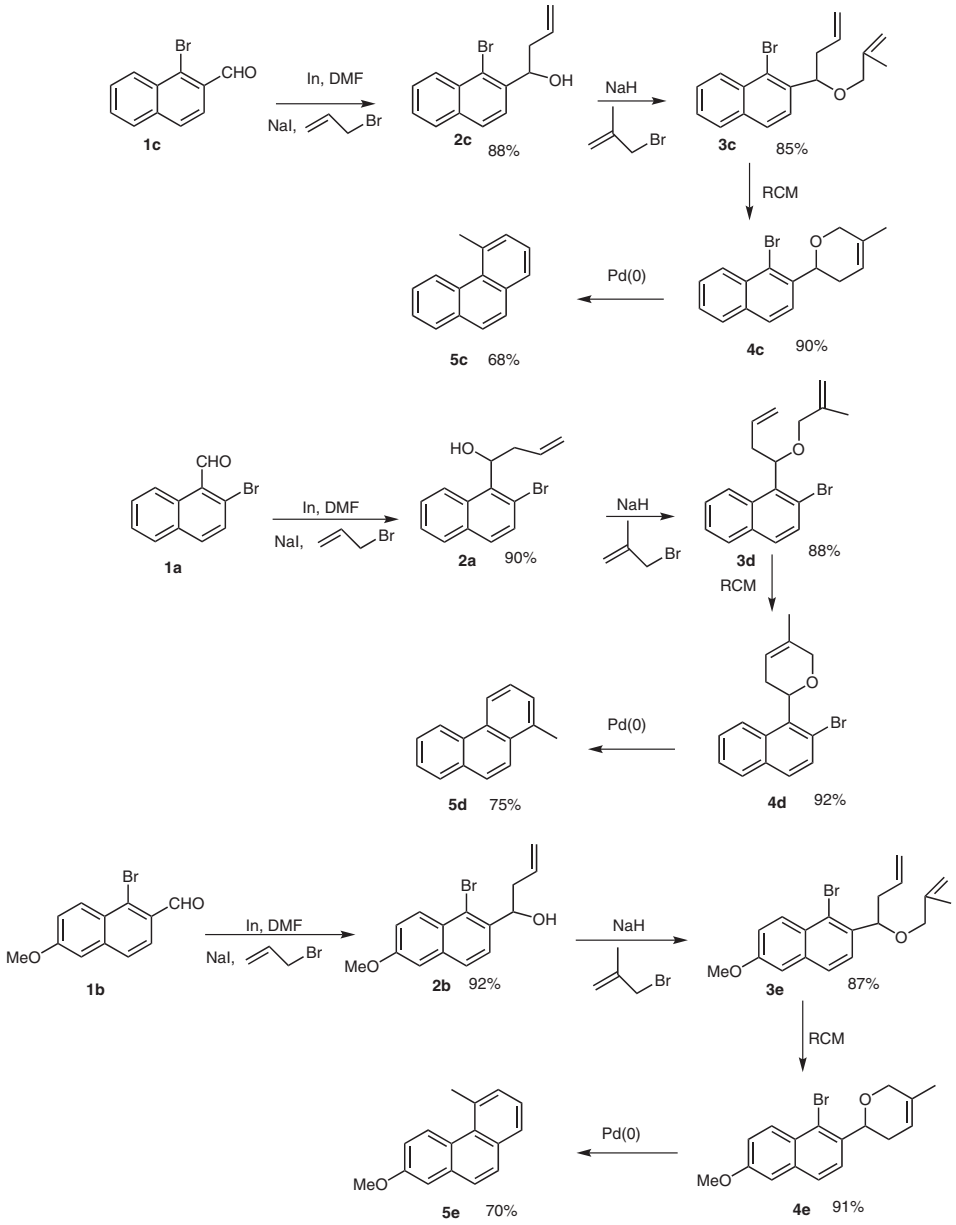
Scheme 3

spectively. These cyclic precursors were finally treated with palladium(II) acetate, triphenylphosphine, and cesium carbonate in *N*,*N*-dimethylformamide at 85–90 °C to afford alkyl phenanthrenes **5f**, **5g**, and **5h**, respectively (Scheme 5).

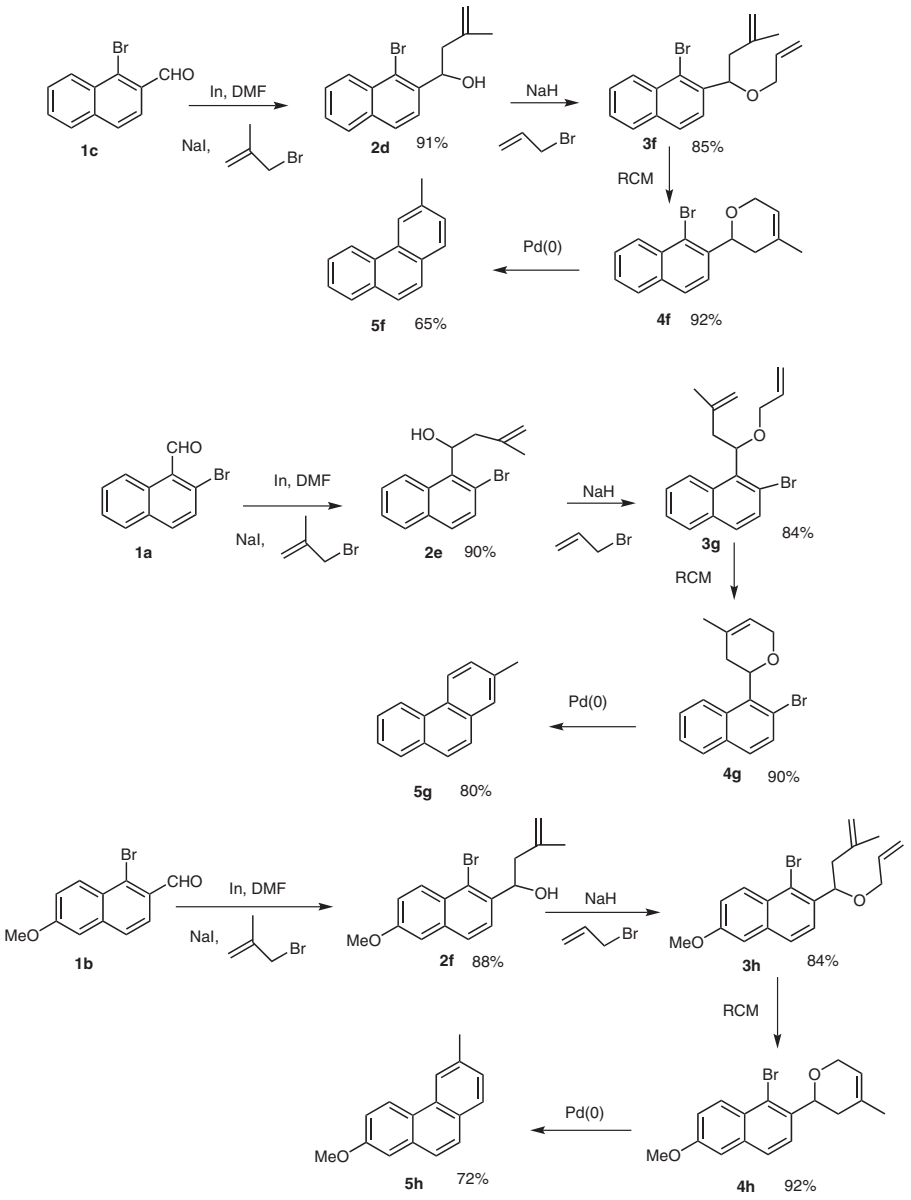
It was also possible to introduce two alkyl groups at the **c**-ring of the phenanthrene system using our newly developed method. Although there are a few methods known for the introduction of two alkyl groups. First, aromatic bromoaldehydes **1a** or **1c** were treated with methallyl bromide and sodium iodide in presence of indium metal to obtained the corresponding alcohols **2d** and **2e**. These alcohols were methallylated in the presence of sodium hydride in tetrahydrofuran at 0 °C, leading to the diallylated compounds **3i** and **3j**, which were then subjected to a metathesis reaction using 2nd generation Grubbs catalyst to obtain the desired cyclic precursors **4i** and **4j**, respectively. These cyclic precursors were finally treated with palladium(II) acetate, triphenylphosphine, and cesium carbonate in *N*,*N*-dimethylformamide at 85–90 °C to obtain the dialkyl phenanthrenes **5i** and **5j** in good yields (Scheme 6).

In conclusion, we have developed a new method for the synthesis of mono and dialkylated phenanthrene derivatives. This method will also be useful for the synthesis of higher homologous of polynuclear aromatic hydrocarbons.

^{1}H NMR (200 MHz or 400 MHz) spectra were recorded with a Bruker AC 200 MHz or 400 MHz spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br s = broad singlet, m = multiplet, dd = double doublet), coupling



Scheme 4



Scheme 5

constant (Hz), and proton integral. ^{13}C NMR (50 MHz or 100 MHz) spectra were recorded with a Bruker AC 200 MHz and 400 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: δ = 77.0 ppm). MS (EI, 70 eV) spectra were taken using a VG Autospec mass spectrometer. Elemental analyses were carried out in Perkin–Elmer 2400 instrument. Melting points were measured in open capillaries and are uncorrected. Chromatographic purification was performed with silica gel 60–120 mesh (SRL). Precoated silica gel 60 F254 TLC sheets (Merck) were used to monitor the reactions. Petroleum ether (PE) refers to the fraction boiling in the range 60–80 °C.

Synthesis of Homoallyl Alcohols; General Procedure

A mixture of 1-bromo-2-propene (0.363 g, 3 mmol) or 1-bromo-2-methyl-2-propene (0.405 g, 3 mmol), indium metal (0.138 g, 1.2 mmol) and NaI (0.450 g, 3 mmol) in DMF (3–4 mL) was stirred at r.t. until the complex was completely formed. A solution of bromoaldehyde **1a–c** (1 mmol) in DMF was then added to the reaction mixture. The reaction was monitored by TLC and, after 5–6 h, the reaction mixture was quenched with a few drops of 1 M HCl solution. It was then extracted with CH_2Cl_2, which was thoroughly washed with sodium thiosulphate and then brine. Evaporation of the solvent followed by purification by silica gel (60–120 mesh) column chromatography provided the pure product.

1-(2-Bromonaphthalen-1-yl)but-3-en-1-ol (2a)

Liquid.

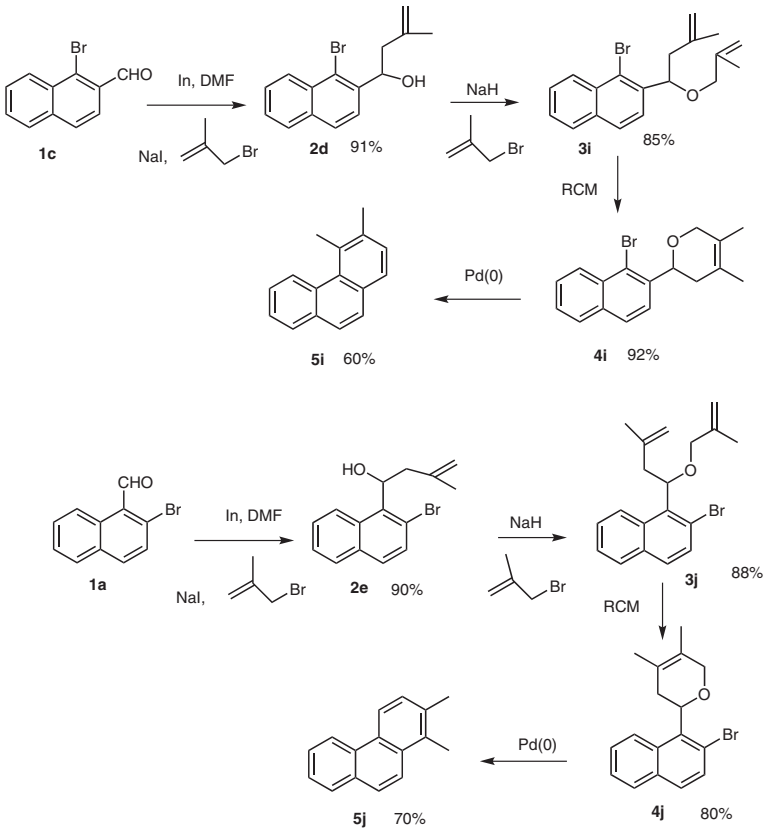
^1H NMR (200 MHz, $CDCl_3$): δ = 2.64–2.77 (m, 1 H), 2.90–3.05 (m, 1 H), 5.13–5.25 (m, 2 H), 5.80–6.03 (m, 2 H), 7.46–7.58 (m, 4 H), 7.81 (m, 1 H), 8.81 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.04, 74.94, 118.16, 121.27, 125.93, 126.02, 126.29, 128.81, 129.52, 130.28, 132.28, 133.73, 134.66, 136.75.

Anal. Calcd for $C_{14}H_{13}OBr$: C, 60.67; H, 4.73. Found: C, 60.80; H, 4.85.

1-(1-Bromo-6-methoxynaphthalen-2-yl)but-3-en-1-ol (2b)

Liquid.



Scheme 6

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.38–2.53 (m, 1 H), 2.64–2.75 (m, 1 H), 3.93 (s, 3 H), 5.16–5.25 (m, 2 H), 5.42 (dd, *J* = 4, 8.4 Hz, 1 H), 5.82–5.98 (m, 1 H), 7.12 (s, 1 H), 7.22 (m, 1 H), 7.61–7.75 (m, 2 H), 8.22 (d, *J* = 9.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.23, 55.43, 72.59, 106.04, 118.54, 119.92, 121.51, 124.84, 126.82, 127.43, 128.99, 134.36, 135.24, 138.30, 158.03.

Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92. Found: C, 58.78; H, 4.85.

1-(1-Bromonaphthalen-2-yl)but-3-en-1-ol (2c)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.17 (br s, 1 H), 2.42–2.53 (m, 1 H), 2.63–2.68 (m, 1 H), 5.17–5.26 (m, 2 H), 5.43 (dd, *J* = 4, 8.2 Hz, 1 H), 5.82–5.99 (m, 1 H), 7.47–7.70 (m, 3 H), 7.83 (m, 2 H), 8.34 (dd, *J* = 1, 8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.18, 72.71, 118.70, 121.56, 124.36, 126.51, 127.36, 127.46, 128.03, 128.07, 132.11, 134.10, 134.28, 140.75.

Anal. Calcd for $C_{14}H_{13}OBr$: C, 60.67; H, 4.73. Found: C, 60.77; H, 4.65.

1-(1-Bromonaphthalen-2-yl)-3-methylbut-3-en-1-ol (2d)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.93 (s, 3 H), 2.24–2.36 (m, 2 H), 2.59–2.66 (m, 1 H), 4.94 (s, 1 H), 4.98 (s, 1 H), 5.50 (dd, *J* = 2.4, 10 Hz, 1 H), 7.47–7.63 (m, 2 H), 7.72–7.85 (m, 3 H), 8.33 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.14, 46.65, 71.05, 114.34, 121.34, 124.24, 126.45, 127.26, 127.43, 128.13, 128.19, 132.12, 134.10, 140.99, 142.52.

Anal. Calcd for $C_{15}H_{15}BrO$: C, 61.87; H, 5.19. Found: C, 61.75; H, 5.28.

1-(2-Bromonaphthalen-1-yl)-3-methylbut-3-en-1-ol (2e)
Liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H), 2.52 (m, 2 H), 2.93 (m, 1 H), 4.96 (s, 1 H), 4.99 (s, 1 H), 5.90 (dd, *J* = 3.6, 10.4 Hz, 1 H), 7.41–7.56 (m, 2 H), 7.58 (s, 2 H), 7.80 (dd, *J* = 6.4, 8 Hz, 1 H), 8.83 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.29, 44.75, 73.35, 114.027, 121.11, 125.90 (2C), 126.16, 128.70, 129.48, 130.16, 132.25, 133.67, 136.81, 142.38.

Anal. Calcd for $C_{15}H_{15}BrO$: C, 61.87; H, 5.19. Found: C, 61.95; H, 5.13.

1-(1-Bromo-6-methoxynaphthalen-2-yl)but-3-en-1-ol (2f)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 3 H), 1.98 (br s, 1 H), 2.21–2.32 (m, 1 H), 2.53–2.6 (m, 1 H), 3.91 (s, 3 H), 4.90 (m, 1 H), 5.40 (d, *J* = 3 Hz, 1 H), 5.45 (d, *J* = 3 Hz, 1 H), 7.07 (d, *J* = 2.4 Hz, 1 H), 7.17–7.23 (m, 1 H), 7.66 (m, 2 H), 8.20 (d, *J* = 9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.10, 46.73, 55.42, 70.89, 106.05, 114.20, 119.91, 121.5, 124.72, 126.91, 127, 128.90, 135.24, 138.51, 142.57, 158.01.

Anal. Calcd for $C_{16}H_{17}BrO_2$: C, 59.83; H, 5.33. Found: C, 59.95; H, 5.21.

Allylation of Homoallyl Alcohols: General Procedure
NaH (0.060 g, 2.5 mmol) was placed in a two-necked flask and thoroughly washed with benzene (2–3 times), then dried under vacuum and anhydrous THF (5 mL) was added. The mono-homoally-

lated product **2a–f** (1 mmol) was dissolved in THF (3 mL) and slowly added into the ice-cold NaH solution. Formation of the anion was indicated by color change. After the formation of the anion, allyl bromide was added and stirring was continued at r.t.. The reaction mixture was quenched with ice-water and extracted with Et_2O (2 × 20 mL). Solvent was removed under reduced pressure and the product was purified by column chromatography.

1-(1-Allyloxybut-3-enyl)-2-bromonaphthalene (3a)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.65–2.75 (m, 1 H), 2.91–3.02 (m, 1 H), 3.82–3.87 (m, 2 H), 5.00–5.27 (m, 4 H), 5.52 (dd, *J* = 6.2, 8.4 Hz, 1 H), 5.80–5.98 (m, 2 H), 7.47–7.59 (m, 4 H), 7.81 (m, 1 H), 8.88 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.35, 69.91, 82.19, 117.05, 117.14, 123.03, 125.72, 126.13, 126.42, 128.75, 129.72, 130.25, 132.46, 133.63, 134.70, 134.79, 135.05.

Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.49; H, 5.28.

2-(1-Allyloxybut-3-enyl)-1-bromo-6-methoxynaphthalene (3b)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.51–2.58 (m, 2 H), 3.78–3.93 (m, 2 H), 3.94 (s, 3 H), 5.01–5.30 (m, 5 H), 5.84 (m, 2 H), 7.13 (m, 1 H), 7.23 (dd, *J* = 2.6, 9.2 Hz, 1 H), 7.57 (m, 1 H), 7.72 (m, 1 H), 8.23 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.23, 55.47, 69.88, 80.03, 106.23, 116.95, 117.00, 119.80, 122.95, 125.36, 126.90, 127.54, 129.07, 134.56, 134.75, 135.39, 136.89, 158.19.

Anal. Calcd for $C_{18}H_{19}BrO_2$: C, 62.26; H, 5.52. Found: C, 62.20; H, 5.65.

1-Bromo-2-[1-(2-methylallyloxy)but-3-enyl]naphthalene (3c)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3 H), 2.57 (t, *J* = 6.4 Hz, 2 H), 3.73 (d, *J* = 12.6 Hz, 1 H), 3.84 (d, *J* = 12.6 Hz, 1 H), 4.91–5.18 (m, 5 H), 5.85–6.02 (m, 1 H), 7.49–7.65 (m, 3 H), 7.84 (d, *J* = 8 Hz, 2 H), 8.34 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.76, 41.23, 72.89, 79.98, 112.44, 117.18, 123.02, 124.81, 126.54, 127.47, 128.09, 128.17, 132.19, 134.20, 134.61, 139.40, 142.09.

Anal. Calcd for $C_{18}H_{19}BrO$: C, 65.27; H, 5.78. Found: C, 65.36; H, 5.65.

2-Bromo-1-[1-(2-methylallyloxy)but-3-enyl]naphthalene (3d)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 2.61–2.74 (m, 1 H), 2.93–3.07 (m, 1 H), 3.74 (m, 2 H), 4.82 (s, 1 H), 4.87 (s, 1 H), 5.06 (m, 2 H), 5.5 (m, 1 H), 5.83–6.04 (m, 1 H), 7.40–7.55 (m, 4 H), 7.80 (m, 1 H), 8.88 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.81, 29.78, 40.36, 72.85, 82.12, 112.54, 117.04, 125.79, 125.94, 126.11, 126.38, 128.71, 129.67, 125.94, 126.11, 126.38, 128.71, 129.67, 130.23, 132.40, 133.61, 134.89, 135.09, 142.15.

Anal. Calcd for $C_{18}H_{19}BrO$: C, 65.27; H, 5.78. Found: C, 65.40; H, 5.60.

1-Bromo-6-methoxy-2-[1-(2-methylallyloxy)but-3-enyl]naphthalene (3e)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (s, 3 H), 2.52–2.59 (m, 2 H), 3.64–3.86 (m, 2 H), 3.93 (s, 3 H), 4.9–5.14 (m, 5 H), 5.86–6.01 (m, 1 H), 7.12 (d, *J* = 2.4 Hz, 1 H), 7.22–7.28 (m, 1 H), 7.59 (d, *J* = 8.6 Hz, 1 H), 7.73 (d, *J* = 8.6 Hz, 1 H), 8.25 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.92, 41.51, 55.65, 72.95, 80.05, 106.35, 112.51, 117.24, 120.00, 123.12, 125.54, 127.10, 127.70, 129.24, 134.87, 135.55, 137.10, 142.33, 158.33.

Anal. Calcd for $C_{19}H_{21}BrO_2$: C, 63.17; H, 5.86. Found: C, 63.31; H, 5.77.

2-(1-Allyloxy-3-methylbut-3-enyl)-1-bromonaphthalene (3f)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.89 (s, 3 H), 2.47 (d, *J* = 7 Hz, 2 H), 3.80–3.85 (m, 1 H), 3.89–3.93 (m, 1 H), 4.82 (m, 2 H), 5.15–5.30 (m, 3 H), 5.84–6.30 (m, 1 H), 7.52–7.67 (m, 3 H), 7.82 (m, 2 H), 8.37 (dd, *J* = 8, 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.86, 45.12, 70.03, 79.23, 112.90, 117.15, 122.91, 124.72, 126.51, 127.36, 127.41, 128.17 (2C), 132.19, 134.64, 139.86, 142.36.

Anal. Calcd for $C_{18}H_{19}BrO$: C, 65.27; H, 5.78. Found: C, 65.17; H, 5.88.

1-(1-Allyloxy-3-methylbut-3-enyl)-2-bromonaphthalene (3g)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.91 (s, 3 H), 2.58 (m, 1 H), 2.99 (m, 1 H), 3.85–3.99 (m, 2 H), 4.82 (s, 1 H), 4.88 (s, 1 H), 5.15–5.31 (m, 1 H), 5.69 (dd, *J* = 4.8, 9.2 Hz, 1 H), 5.82 (m, 1 H), 7.53–7.60 (m, 2 H), 7.65 (s, 2 H), 7.83–7.83 (m, 1 H), 8.99 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.80, 43.96, 69.88, 81.08, 112.96, 117.20, 122.83, 125.79, 125.92, 126.09, 128.69, 129.50, 130.18, 132.47, 133.62, 134.72, 135.58, 142.54.

Anal. Calcd for $C_{18}H_{19}BrO$: C, 65.27; H, 5.78. Found: C, 65.43; H, 5.70.

2-(1-Allyloxy-3-methylbut-3-enyl)-1-bromo-6-methoxynaphthalene (3h)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 2.46 (m, 2 H), 3.73–3.91 (m, 2 H), 3.94 (s, 3 H), 4.79 (m, 1 H), 5.13–5.29 (m, 3 H), 5.81–5.95 (m, 1 H), 7.12 (d, *J* = 2.4 Hz, 1 H), 7.25 (dd, *J* = 2.4, 9 Hz, 1 H), 7.58 (dd, *J* = 2.2, 8.4 Hz, 1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 8.24 (d, *J* = 9 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.01, 45.36, 55.56, 70.04, 79.24, 106.30, 112.98, 117.19, 119.97, 123.00, 125.39, 127.15, 127.65, 129.15, 134.86, 135.50, 137.49, 142.54, 158.28.

Anal. Calcd for $C_{19}H_{21}BrO_2$: C, 63.17; H, 5.86. Found: C, 63.30; H, 5.71.

1-Bromo-2-[3-methyl-1-(2-methylallyloxy)but-3-enyl]naphthalene (3i)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (s, 3 H), 1.90 (s, 3 H), 2.49 (m, 2 H), 3.68 (d, *J* = 12.4 Hz, 1 H), 3.83 (d, *J* = 12.4 Hz, 1 H), 4.83–4.99 (m, 4 H), 5.25 (dd, *J* = 5.4, 7.6 Hz, 1 H), 7.49–7.68 (m, 3 H), 7.84 (dd, *J* = 2.4, 8.6 Hz, 2 H), 8.36 (dd, *J* = 8.2, 0.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.88, 23.07, 45.41, 73.22, 79.57, 112.50, 113.21, 123.07, 124.93, 126.66, 127.55 (2C), 128.32 (2C), 132.41, 134.39, 140.14, 142.36, 142.58.

Anal. Calcd for $C_{19}H_{21}BrO$: C, 66.09; H, 6.13. Found: C, 65.95; H, 6.25.

2-Bromo-1-[3-methyl-1-(2-methylallyloxy)but-3-enyl]naphthalene (3j)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.67 (s, 3 H), 1.88 (s, 3 H), 2.54 (m, 1 H), 2.94 (m, 1 H), 3.73 (m, 2 H), 4.85 (m, 4 H), 5.56 (dd, *J* = 4.6, 9.2 Hz, 1 H), 7.47–7.59 (m, 4 H), 7.81 (m, 1 H), 8.92 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.77, 22.82, 44.07, 72.91, 81.25, 112.44, 113.05, 122.81, 125.84, 126.07, 126.65, 129.56, 130.17, 133.60, 132.5, 135.66, 142.21, 142.61.

Anal. Calcd for $C_{19}H_{21}BrO$: C, 66.09; H, 6.13. Found: C, 66.25; H, 6.27.

RCM; General Procedure

To a stirred solution of double allylated compound **3** (1 mmol) in anhydrous and degassed CH_2Cl_2 (10 mL), Grubbs catalyst[8] ($C_{46}H_{65}Cl_2N_2PRu$; 0.084 g, 10 mmol%) was added in an argon atmosphere. The reaction mixture was stirred for 3–5 h at r.t. under an argon atmosphere. The solvent was removed under reduced pressure and the product was purified by column chromatography.

2-(2-Bromonaphthalen-1-yl)-3,6-dihydro-2*H*-pyran (4a)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.23–2.33 (m, 1 H), 2.78–2.92 (m, 1 H), 4.45 (m, 2 H), 5.60 (dd, *J* = 4, 10.8 Hz, 1 H), 5.90–6.00 (m, 2 H), 7.44–7.52 (m, 2 H), 7.59 (s, 2 H), 7.77–7.82 (m, 1 H), 8.78 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.69, 66.64, 78.04, 121.24, 124.43, 125.94, 126.25, 126.30, 126.74, 128.59, 129.66, 129.94, 132.22, 133.65, 135.73.

Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53. Found: C, 62.51; H, 4.36.

2-(1-Bromo-6-methoxynaphthalen-2-yl)-3,6-dihydro-2*H*-pyran (4b)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15–2.29 (m, 1 H), 2.43–2.54 (m, 1 H), 3.93 (s, 3 H), 4.45 (m, 2 H), 5.17 (dd, *J* = 3.4, 8.2 Hz, 1 H), 5.87–5.95 (2 H), 7.11 (d, *J* = 2.6 Hz, 1 H), 7.25 (dd, *J* = 2.6, 9.4 Hz, 1 H), 7.63–7.76 (m, 2 H), 8.22 (d, *J* = 9.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.73, 55.60, 66.95, 75.84, 106.26, 120.07, 121.42, 124.79, 125.07, 126.50, 127.30, 127.57, 129.30, 135.40, 137.85, 158.24.

Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.47; H, 4.56.

2-(1-Bromonaphthalen-2-yl)-5-methyl-3,6-dihydro-2*H*-pyran (4c)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70 (s, 3 H), 2.04–2.22 (m, 1 H), 2.42–2.55 (m, 1 H), 4.19–4.40 (m, 2 H), 5.15 (dd, *J* = 3.4, 10.4 Hz, 1 H), 5.64 (m, 1 H), 7.46–7.63 (m, 2 H), 7.71 (m, 1 H), 7.79–7.87 (m, 2 H), 8.32 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.67, 31.86, 69.99, 75.91, 118.94, 121.36, 124.36, 126.44, 127.41, 127.45, 128.18, 128.29, 132.07, 133.10, 134.06, 140.10.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.47; H, 5.13.

2-(2-Bromonaphthalen-1-yl)-5-methyl-3,6-dihydro-2*H*-pyran (4d)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 2.25–2.33 (m, 1 H), 2.79–2.93 (m, 1 H), 4.35 (m, 2 H), 5.60 (dd, *J* = 3.4, 11 Hz, 1 H), 5.73 (m, 1 H), 7.43–7.68 (m, 4 H), 7.82 (m, 1 H), 8.84 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.95, 29.71, 69.97, 78.16, 118.85, 121.42, 126.00, 126.25, 126.51, 128.64, 129.68, 130.06, 132.36, 133.61, 133.75, 135.88.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.52; H, 5.10.

2-(1-Bromo-6-methoxynaphthalen-2-yl)-5-methyl-3,6-dihydro-2*H*-pyran (4e)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70 (s, 3 H), 2.10–2.23 (m, 1 H), 2.41–2.50 (m, 1 H), 3.92 (s, 3 H), 4.19–4.40 (m, 2 H), 5.12 (dd, *J* = 3.4, 10.4 Hz, 1 H), 5.64 (m, 1 H), 7.11 (s, 1 H), 7.23 (dd, *J* = 2.2, 9 Hz, 1 H), 7.62–7.75 (m, 2 H), 8.23 (d, *J* = 9 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.77, 31.63, 55.59, 70.18, 75.95, 106.28, 119.12, 120.04, 121.52, 125.03, 127.04, 127.61, 129.28, 133.24, 135.39, 137.83, 158.22.

Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.41; H, 5.02.

2-(1-Bromonaphthalen-2-yl)-4-methyl-3,6-dihydro-2*H*-pyran (4f)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78 (s, 3 H), 2.07–2.21 (m, 1 H), 2.32–2.41 (m, 1 H), 4.41 (t, *J* = 1.8 Hz, 1 H), 5.19 (dd, *J* = 3.4, 10 Hz, 1 H), 5.55 (d, *J* = 1 Hz, 1 H). 7.47–7.64 (m, 2 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.83 (m, 2 H), 8.34 (dd, *J* = 1, 8.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.09, 36.25, 66.77, 76.09, 119.89, 121.39, 124.52, 126.59, 127.55, 127.61, 128.32, 128.48, 132.19, 132.39, 134.19, 140.29.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.49; H, 5.15.

2-(2-Bromonaphthalen-1-yl)-4-methyl-3,6-dihydro-2*H*-pyran (4g)

liquid,

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 2.07–2.16 (m, 1 H), 2.7–2.83 (m, 1 H), 4.40 (m, 2 H), 5.53–5.62 (m, 2 H), 7.43–7.58 (m, 2 H), 7.59 (s, 2 H), 7.77–7.82 (m, 1 H), 8.77 (dd, *J* = 5, 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.92, 34.38, 66.57, 78.17, 120.25, 121.25, 125.99, 126.30, 126.50, 128.66, 129.69, 130.05, 132.01, 132.27, 133.69, 135.81.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.25; H, 5.09.

2-(1-Bromo-6-methoxynaphthalen-2-yl)-4-methyl-3,6-dihydro-2*H*-pyran (4h)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.77 (s, 3 H), 2.16–2.38 (m, 2 H), 3.94 (s, 3 H), 4.39 (m, 2 H), 5.11–5.19 (m, 1 H), 5.54 (m, 1 H), 7.12 (d, *J* = 2.6 Hz, 1 H), 7.25 (m, 1 H), 7.63–7.76 (m, 2 H), 8.23 (dd, *J* = 3, 9.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.08, 36.42, 55.61, 66.81, 76.01, 106.30, 119.92, 120.06, 121.44, 125.09, 127.32, 127.61, 129.31, 132.45, 135.41, 137.92, 158.24.

Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.39; H, 5.25.

2-(1-Bromonaphthalen-2-yl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (4i)

Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.66 (s, 3 H), 1.77 (s, 3 H), 2.10 (m, 2 H), 4.13–4.38 (m, 2 H), 5.23 (dd, *J* = 3.6, 10.2 Hz, 1 H), 7.47–7.64 (m, 2 H), 7.70–7.89 (m, 3 H), 8.35 (dd, *J* = 0.8, 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.03, 18.46, 36.95, 70.50, 76.52, 121.35, 124.12, 124.49, 124.61, 126.48, 127.45, 127.53, 128.25, 128.37, 132.16, 134.14, 140.28.

Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.52; H, 5.25.

2-(2-Bromonaphthalen-1-yl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (4j)
Liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.67 (s, 3 H), 1.76 (s, 3 H), 2.09 (m, 1 H), 2.79 (m, 1 H), 4.16 (m, 2 H), 5.6 (dd, *J* = 3.8, 8 Hz, 1 H), 7.44–7.55 (m, 2 H), 7.64 (s, 2 H), 7.75–7.82 (m, 1 H), 8.77 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.15, 18.38, 35.18, 70.46, 78.76, 121.36, 123.92, 125.09, 125.96, 126.21, 126.54, 128.62, 129.63, 130.05, 132.40, 133.77, 135.92.

Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.21; H, 5.53.

Palladium-Catalyzed Oxidative Cyclization: General Procedure
The appropriate pyran derivative **4a**–**j** (1 mmol), $Pd(OAc)_2$ (0.0224 g, 10 mmol%), PPh_3 (0.131 g, 0.5 mmol), TBAC (0.277 g, 1 mmol), and Cs_2CO_3 (0.652 g, 2 mmol) was flushed with argon, and DMF (5–6 mL) was added. After degasifying with argon, the mixture was heated to 85–90 °C for 1.5–2 h. The reaction mixture was cooled, diluted with ice water and extracted with Et_2O (2 × 20 mL). The solvent was evaporated after drying (Na_2SO_4) and the product was purified by silica gel (60–120 mesh) column chromatography.

Phenanthrene (5a)[9]
Solid; mp 97–99 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58–7.68 (m, 4 H), 7.74 (s, 2 H), 7.79 (d, *J* = 8 Hz, 2 H), 8.70 (d, *J* = 8 Hz, 2 H).

2-Methoxyphenanthrene (5b)[10]
Solid; mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (s, 3 H), 7.27 (m, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.60–7.68 (m, 2 H), 7.73 (d, *J* = 9.2 Hz, 1 H), 7.86 (d, *J* = 8 Hz, 1 H), 8.59 (d, *J* = 8 Hz, 2 H).

4-Methylphenanthrene (5c)[10]
Solid; mp 52–54 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.17 (s, 3 H), 7.50 (m, 2 H), 7.59–7.67 (m, 2 H), 7.71 (s, 2 H), 7.79 (m, 1 H), 7.94 (dd, *J* = 2, 8.4 Hz, 1 H), 8.94 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.37, 125.52, 125.74, 125.83, 127.04, 127.41, 127.47, 127.96, 128.66, 130.03, 131.18, 131.62, 133.44, 133.69, 135.49.

1-Methylphenanthrene (5d)[11]
Solid; mp 121–123 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.76 (s, 3 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.53–7.63 (m, 3 H), 7.79 (d, *J* = 9.2 Hz, 1 H), 7.90 (d, *J* = 8 Hz, 1 H), 7.96 (d, *J* = 7.2 Hz, 1 H), 8.59 (d, *J* = 8.4 Hz, 1 H), 8.71 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.96, 120.89, 122.88, 122.97, 126.17, 126.43, 126.56, 126.71, 127.79, 128.49, 130.38, 130.70, 130.84, 131.70, 134.89.

2-Methoxy-5-methylphenanthrene (5e)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (s, 3 H), 3.98 (s, 3 H), 7.25 (m, 1 H), 7.31 (d, *J* = 2.8 Hz, 1 H), 7.40–7.48 (m, 2 H), 7.64 (d, *J* = 8.8 Hz, 1 H), 7.70–7.75 (m, 2 H), 8.84 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.32, 55.27, 109.06, 115.38, 124.92, 125.94, 126.59, 127.49, 128.56, 128.89, 130.15, 131.20, 132.68, 134.60, 135.09, 157.20.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.57; H, 6.49.

3-Methylphenanthrene (5f)[12]
Solid; mp 63–65 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3 H), 7.43 (d, *J* = 8 Hz, 1 H), 7.56–7.72 (m, 4 H), 7.79 (d, *J* = 8 Hz, 1 H), 7.87 (d, *J* = 8 Hz, 1 H), 8.48 (s, 1 H), 8.68 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.07, 122.34, 122.55, 125.89, 126.25, 126.66, 128.23, 128.33, 128.45, 129.68, 129.95, 130.25, 132.12, 136.22.

2-Methylphenanthrene (5g)[11]
Solid; mp 57–59 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H), 7.45–7.52 (m, 1 H), 7.55–7.72 (m, 5 H), 7.89 (d, *J* = 8 Hz, 1 H), 8.60 (d, *J* = 8.4 Hz, 1 H), 8.67 (d, *J* = 8 Hz, 1 H).

2-Methoxy-6-methylphenanthrene (5h)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3 H), 3.96 (s, 3 H), 7.27 (m, 2 H), 7.36 (d, *J* = 8 Hz, 1 H), 7.60 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 8 Hz, 1 H), 8.37 (s, 1 H), 8.57 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.08, 55.32, 108.44, 116.77, 121.82, 124.6, 124.31, 125.42, 127.27 (2C), 128.32, 128.92, 130.5, 133.52, 136.31, 158.10.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.57; H, 6.49.

3,4-Dimethylphenanthrene (5i)[13]
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.57 (s, 3 H), 2.96 (s, 3 H), 7.42 (d, *J* = 8 Hz, 1 H), 7.54–7.59 (m, 2 H), 7.61–7.65 (m, 3 H), 7.88 (m, 1 H), 8.72 (m, 1 H).

1,2-Dimethylphenanthrene (5j)[11]
Solid; mp 141–143 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 2.66 (s, 3 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.54–7.64 (m, 2 H), 7.76 (d, *J* = 9.2 Hz, 1 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 8.02 (d, *J* = 9.2 Hz, 1 H), 8.49 (d, *J* = 8.4 Hz, 1 H), 8.67 (d, *J* = 8 Hz, 1 H).

Acknowledgment

Financial support from DST (New Delhi) and CSIR (New Delhi) for fellowships to R.J. and S.S. is gratefully acknowledged. Financial support from CSIR is also gratefully acknowledged. D.S.T. is thanked for providing funds for the project and creating the 400 MHz NMR facility under the IRPHA programme.

References

(1) (a) Watson, M. D.; Fethtenkotter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267. (b) Harvey, R. G. *Curr. Org. Chem.* **2004**, *8*, 303.
(2) (a) Floyd, A. J.; Dyke, S. F.; Ward, A. S. E. *Chem. Rev.* **1976**, *76*, 509. (b) Mallory, F. B.; Mallory, C. W. *Org.*

React. (N.Y.) **1984**, *30*, 1. (c) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769. (d) Hamaza, K.; Abu-Reziq, R.; Avnir, D.; Blum, J. *Org. lett.* **2004**, *6*, 925. (e) Levy, L. A.; Sashikumar, V. P. *J. Org. Chem.* **1985**, *50*, 1760. (f) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (g) Plater, M. J. *Tetrahedron Lett.* **1995**, *35*, 801. (h) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325. (i) Sonoda, M.; Itahashi, K.; Tobe, Y. *Tetrahedron Lett.* **2002**, *43*, 5269. (j) Bonifacio, M. C.; Robertson, C. R.; Jung, J. Y.; King, B. T. *J. Org. Chem.* **2005**, *70*, 8522. (k) Ichikawa, J.; Yokota, M.; Kudo, T.; Umezaki, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4870. (l) Pena, D.; Perez, D.; Guitian, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (m) Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A. Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035.

(3) Jackson, A. H.; Shannon, P. V. R.; Taylor, P. W. *J. Chem. Soc., Perkin Trans. 2* **1981**, 286.

(4) Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Huang, X.-C.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 3199.

(5) Mamane, V.; Hannen, P.; Furstner, A. *Chem. Eur. J.* **2004**, *10*, 4556.

(6) Jana, R.; Chatterjee, I.; Samanta, S.; Ray, J. K. *Org. Lett* **2008**, *10*, 4795.

(7) Lan, Y.; Wang, C.; Sowa, J. R.; Wu, Y.-D. *J. Org. Chem.* **2010**, *75*, 951.

(8) (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (b) Kulkarni, A. A.; Diver, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 8110.

(9) Bardhan, J. C.; Sengupta, S. C. *J. Chem. Soc.* **1932**, *2520*, 2798.

(10) Mallory, F. B.; Rudolph, M. J.; Oh, S. M. *J. Org. Chem.* **1989**, *54*, 4619.

(11) Krasodomski, W.; Luczynski, M. K.; Wilamowski, J.; Sepiol, J. J. *Tetrahedron* **2003**, *59*, 5677.

(12) de Meijere, A.; Song, Z. Z.; Lansky, A.; Hyuda, S.; Rauch, K.; Noltemeyer, M.; Konig, B.; Knieriem, B. *Eur. J. Org. Chem.* **1998**, 2289.

(13) Jung, K.-Y.; Koreeda, M. *J. Org. Chem.* **1989**, *54*, 5667.