Supporting Information

Pd(0) Catalyzed intramolecular Heck reaction: A general route for fused oxepine derivatives

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General Remarks:

¹H NMR (200 MHz), ¹H NMR (400 MHz) spectra were recorded on a BRUKER-AC 200MHz and 400MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet), coupling constant (Hz). ¹³C NMR (50 MHz), ¹³C NMR (100MHz) spectra were recorded on a BRUKER-AC 200 MHz and 400MHz Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: 77.0 ppm). EIMS (70 ev) spectra were taken using a VG Autospec mass spectrometer. Chromatographic purification was done with either 60-120 or 100-200 mesh silica gel (SRL). For reaction monitoring, precoated silica gel 60 F254 TLC sheets (Merck) were used. Petroleum ether refers to the fraction boiling in the range 60-80 °C. DMF was dried, distilled and stored over molecular sieves (4 Å).

Experimental details

General procedure for the synthesis of bromoaldehydes (1):¹

A mechanically stirred solution of dimethylformamide (3 mmol) in anhydrous chloroform was cooled in ice bath while phosphorous tribromide (2.7 mmol) was added drop-wise over a period of 15 min. The resulting white suspension was warmed to rt and stirred for additional 20 min. A solution of starting ketomethylene compound (1 mmol) in chloroform was added drop-wise over 10 min. Stirring was continued for 8 h at rt. The reaction mixture was then poured in ice water. Solid sodium bicarbonate was carefully added to neutralize the acids and the mixture was extracted several times with dichloromethane. The organic part was then washed with cold water thoroughly, dried with sodium sulphate and evaporated. Purification of the residue was done by silica gel (60-120 mesh) column chromatography.

General procedure for the synthesis of Aromatic bromoaldehydes (2):²

β -Bromovinyl aldehyde (1 mmol) and DDQ (dichlorodicyano benzoquinone) (6 mmol) were kept in round bottom flask. Then dry benzene (6 mL) was added to the reaction vessel. After that, the total reaction mixture was heated for 16 h then the crude reaction mixture was filtered by dichloromethane (20 mL). The filtrate was dried and the crude product was purified by column chromatography.

General procedure for the synthesis of bromoalcohols (3)^{1,2}

Bromoaldehydes **1** (1 mmol) or aromatic bromoaldehydes **2** (1 mmol) and sodium borohydride (2 equiv.) were kept in two naked flask. Then acetonitrile solvent (5-6 mL) was added and stirred at room temperature for 2-3 h. After completion of the reaction, the reaction mixture was diluted with water and extracted with ethyl acetate (20 mL $\times$ 3) and dried over anhydrous Na₂SO₄. The solvent was evaporated and the crude product was purified by preparative thin layer chromatography (petroleum ether: ethyl acetate 20:1).

(1-Bromo-3,4-dihydro-naphthalen-2-yl)-methanol (3a)

Yellow liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.63 (t, 2H, $J=7.4$ Hz), 2.92 (t, 2H, $J=7.4$ Hz), 4.57 (s, 2H), 7.16-7.32(m, 3H), 7.67(m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 27.3, 27.9, 66.2, 119.4, 126.4, 126.7, 127.0, 128.1, 136.2, 138.7, 139.6. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 3342, 2988, 2834, 1620. Anal. Calcd for C₁₁H₁₁BrO: C, 55.25; H, 4.64. Found: C, 55.21; H, 4.62.

(1-Bromo-5-methoxy-3,4-dihydro-naphthalen-2-yl)-methanol (3b)

Liquid, ^1H NMR (CDCl_3 , 400 MHz) δ : 2.52 (t, 2H, $J = 7.6\text{Hz}$), 2.87 (t, 2H, $J = 7.6\text{Hz}$), 3.85 (s, 3H), 4.44 (s, 2H), 6.85 (d, 1H, $J = 8\text{Hz}$), 7.17-7.44 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 20.2, 27.3, 55.3, 67.2, 111.1, 114.1, 119.2, 126.6, 127.5, 135.8, 138.9, 155.4.

IR ν_{max} (CHCl_3 , cm^{-1}) 3325, 2969, 2838, 1622. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$: C, 53.55; H, 4.87. Found: C, 53.50; H, 4.95.

(1-Bromo-6-methoxy-3,4-dihydro-naphthalen-2-yl)-methanol(3c)

Liquid, ^1H NMR (CDCl_3 , 400 MHz) δ : 2.54(t, 2H, $J=7.6\text{Hz}$), 2.82(t, 2H, $J = 7.6\text{Hz}$), 3.81(s, 3H), 4.48(s, 2H), 6.67(d, 1H, $J=2.4\text{Hz}$), 6.75(dd, 1H, $J=2.4\text{Hz}$, $J= 8.8\text{Hz}$), 7.54(d, 1H, $J= 8.8\text{Hz}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 27.2, 28.3, 55.3, 66.2, 111.1, 113.1, 119, 126.6, 128.5, 135.8, 137.9, 157.4. IR ν_{max} (CHCl_3 , cm^{-1}) 3330, 2972, 2830, 1627. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$: C, 53.55; H, 4.87. Found: C, 53.59; H, 4.89.

(1-Bromo-7-methoxy-3,4-dihydro-naphthalen-2-yl)-methanol(3d)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.52 (t, 2H, $J = 7.2\text{Hz}$), 2.75 (t, 2H, $J = 7.2\text{Hz}$), 3.81 (s, 3H), 4.48 (s, 2H), 6.73 (dd, 1H, $J = 2.4\text{Hz}$, $J = 8\text{Hz}$), 7.00 (d, 1H, $J = 8\text{Hz}$), 7.21 (d, 1H, $J = 2.4\text{Hz}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 27.0, 27.7, 55.5, 66.3, 113.1, 113.3, 119.2, 127.8, 128.45, 134.7, 139, 158.4. IR ν_{max} (CHCl_3 , cm^{-1}) 3367, 2945, 2833, 1620. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BrO}_2$: C, 53.55; H, 4.87. Found: C, 53.61; H, 4.93.

(1-Bromo-4-methyl-3,4-dihydro-naphthalen-2-yl)-methanol (3e)

Liquid, ^1H NMR(CDCl_3 , 400 MHz) δ : 1.23 (d, 3H, $J = 6.8\text{Hz}$), 2.39 (dd, 1H, $J = 7.6\text{Hz}$, $J = 16\text{Hz}$), 2.70 (dd, 1H, $J = 6.4\text{Hz}$, $J = 16\text{Hz}$), 2.99 (m, 1H), 4.50 (m, 2H), 7.15 (m, 1H), 7.23 (m, 2H), 7.65 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 20.3, 27.34, 55.32, 37.23, 111.08, 114.02, 119.20, 126.63, 127.52, 135.83, 138.94, 155.39. IR ν_{max} (CHCl_3 , cm^{-1}) 3360, 2952, 2830, 1620. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BrO}$: C, 56.94; H, 5.18. Found: C, 56.93; H, 5.24.

(2-Bromo-3,4-dihydro-naphthalen-1-yl)-methanol (3f)

Yellow liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.80-2.93 (m, 4H), 4.74 (s, 2H), 7.10-7.28 (m, 3H), 7.51 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 23.0, 28.0, 63.9, 122.8, 126.6, 127.0, 127.2, 128.0, 133.2, 136.1, 136.5. IR ν_{max} (CHCl_3 , cm^{-1}) 3367, 2957, 2838, 1623. Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}$: C, 55.25; H, 4.64. Found: C, 55.27; H, 4.73.

(1-Bromo-naphthalen-2-yl)-methanol (3g)

White solid, mp 79-80 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 200 MHz) δ : 4.96 (s, 2H), 7.45-7.63 (m, 3H), 7.76 (t, 2H, $J = 7.4\text{Hz}$), 8.26 (d, 1H, $J = 8.2\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 65.7, 122.3, 125.8, 126.5, 126.9, 127.5, 127.9, 128.2, 132.1, 134.0, 137.8. IR ν_{max} (CHCl_3 , cm^{-1}) 3338, 2962, 2831, 1627. Anal. Calcd for $\text{C}_{11}\text{H}_9\text{OBr}$: C, 55.72; H, 3.83. Found: C, 55.80; H, 3.90.

(1-Bromo-7-methoxy-naphthalen-2-yl)-methanol (3h)

White solid, mp 77-80 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 200 MHz) δ : 3.95 (s, 3H), 4.92 (s, 2H), 7.11-7.17 (dd, 1H, $J_1 = 9.0\text{Hz}$, $J_2 = 2.4\text{Hz}$), 7.43 (d, 1H, $J = 8.2\text{Hz}$), 7.53 (d, 1H, $J = 2.2\text{Hz}$), 7.66-7.72 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 55.4, 66.0, 105.3, 119.4, 121.0, 123.6, 127.6, 129.7, 129.8, 133.5, 138.3, 159.1. IR ν_{max} (CHCl_3 , cm^{-1}) 3344, 2957, 2849, 1633. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{BrO}_2$: C, 53.96; H, 4.15. Found: C, 54.90; H, 4.17.

(1-Bromo-4-methyl-naphthalen-2-yl)-methanol (3i)

White solid, mp 78-79 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ : 2.58 (s, 3H), 4.86 (s, 2H), 7.39 (s, 1H), 7.46-7.59 (m, 2H), 7.86-7.92 (m, 1H), 8.24-8.30 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 19.3, 65.8, 120.3, 124.4, 126.4, 126.8, 127.1, 127.5, 132.0, 133, 134.5, 137.2. IR ν_{max} (CHCl_3 , cm^{-1}) 3334, 2966, 2834, 1620. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{OBr}$: C, 57.39; H, 4.42. Found: C, 57.45; H, 4.49.

(2-Bromo-naphthalen-1-yl)-methanol (3j)

White solid, mp 80-82 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.31 (s, 2H), 7.51-7.69 (m, 4H), 7.84 (d, 1H, $J = 8.0\text{Hz}$), 8.25 (d, 1H, $J = 8.00\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 61.8, 123.1, 124.2, 126.2, 127.5, 128.6, 130.0, 130.1, 132.9, 133.1, 134.6. IR ν_{max} (CHCl_3 , cm^{-1}) 3322, 2941, 2838, 1609. Anal. Calcd for $\text{C}_{11}\text{H}_9\text{OBr}$: C, 55.72; H, 3.83. Found: C, 55.85; H, 3.93.

(1-Bromo-6-methoxy-naphthalen-2-yl)-methanol (3k)

White solid, mp 85–87 °C; ¹H NMR (CDCl₃, 200 MHz) δ: 3.94 (s, 3H), 5.30 (s, 2H), 7.12 (s, 1H), 7.23-7.26 (m, 1H), 7.56 (d, 1H, *J* = 7.6Hz), 7.67-7.73 (m, 1H), 8.21 (d, 1H, *J* = 9.2Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 55.4, 61.52, 119.9, 120.0, 125.8, 126.6, 127.5, 128.2, 128.6, 135.2, 135.7, 157.9. IR ν_{max} (CHCl₃, cm⁻¹) 3325, 2942, 2847, 1623. Anal. Calcd for C₁₂H₁₁BrO₂: C, 53.96; H, 4.15. Found: C, 54.03; H, 4.22.

(4,6-dibromo-1,2-dihydronaphthalen-3-yl)methanol (3l)

Yellow liquid, ¹H NMR (CDCl₃, 500 MHz) δ: 2.53 (t, 2H, *J* = 7.0Hz), 2.85 (t, 2H, *J* = 7.0Hz), 4.46 (s, 2H), 7.09 (d, 1H, *J* = 8.0Hz), 7.40 (d, 1H, *J* = 8.0Hz), 7.80 (d, 1H, *J* = 1.5Hz). ¹³C NMR (CDCl₃, 125 MHz) δ: 27.3, 28.4, 36.4, 120.5, 121.1, 128.6, 130.5, 131.3, 134.7, 135.3, 136.7. IR ν_{max} (CHCl₃, cm⁻¹) 3330, 2953, 2842, 1621. Anal. Calcd for C₁₁H₁₀Br₂O: C, 41.55; H, 3.17. Found: C, 41.53; H, 3.21.

General procedure for the synthesis of bromomethylvinylbromides (4)²

The alcohols **3** (1 mmol) and carbon tetrachloride solvent (5-6 mL) were placed in a two-necked flask. Then phosphorustribromide (0.25 mmol) was added under heating condition at 60 °C. After that stirring was continued at room temperature for 30 minutes then the reaction mixture was washed with sodium bicarbonate solution and the combined organics were extracted by dichloromethane solvent. The solution was dried over anhydrous Na₂SO₄ and after evaporation of solvent we got bromomethylvinyl bromide derivatives **4**.

4-Bromo-3-bromomethyl-1,2-dihydro-naphthalene (4a)

Yellow liquid, ¹H NMR (CDCl₃, 200 MHz) δ: 2.71 (t, 2H, *J* = 7.8Hz), 3.01 (t, 2H, *J* = 7.8Hz), 4.53 (s, 2H), 7.24-7.27 (m, 1H), 7.33-7.45 (m, 2H), 7.81 (d, 1H, *J* = 7.0Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 28.0, 28.7, 37.3, 123.0, 127.0, 127.2, 127.7, 129.0, 133.4, 135.3, 136.0. IR ν_{max} (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₁H₁₀Br₂: C, 43.75; H, 3.34. Found: C, 43.79; H, 3.41.

4-Bromo-3-bromomethyl-8-methoxy-1,2-dihydro-naphthalene (4b)

Yellow liquid, ¹H NMR (CDCl₃, 200 MHz) δ: 2.53 (t, 2H, *J* = 7.4Hz), 2.87 (t, 2H, *J* = 7.4Hz), 3.84 (s, 3H), 4.38 (s, 2H), 7.08-7.36 (m, 2H), 8.85 (d, 1H, *J* = 7.8Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 20.1, 27.5, 37.3, 55.6, 111.5, 113.9, 120.2, 126.6, 127.4, 136.2, 139.0, 155.8.

IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₂Br₂O: C, 43.41; H, 3.64. Found: C, 43.48; H, 3.70.

4-Bromo-3-bromomethyl-7-methoxy-1,2-dihydro-naphthalene (4c)

Yellow liquid, ¹H NMR(CDCl₃, 200 MHz) δ : 2.53 (t, 2H, J = 7.2Hz), 2.83 (t, 2H, J = 7.2Hz), 3.73 (s, 3H), 4.39 (s, 2H), 6.67-6.71 (m, 2H), 7.56 (d, 1H, J = 8.6Hz). ¹³CNMR (CDCl₃, 50MHz) δ : 28.3, 28.8, 37.7, 55.3, 111.4, 113.2, 122.7, 126.5, 129.3, 132.4, 137.8, 160.0. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₂Br₂O: C, 43.41; H, 3.64. Found: C, 43.47; H, 3.72.

4-Bromo-3-bromomethyl-6-methoxy-1,2-dihydro-naphthalene (4d)

Yellow liquid, ¹H NMR(CDCl₃, 200 MHz) δ : 2.52 (t, 2H, J = 8.2Hz), 2.80 (t, 2H, J = 8.2Hz), 3.82 (s, 3H), 4.37 (s, 2H), 6.72-6.77 (dd, 1H, J_1 = 8.2Hz, J_2 = 2.2Hz), 7.02 (d, 1H, J = 8.0Hz), 7.23 (d, 1H, J = 2.2Hz). ¹³CNMR (CDCl₃, 50MHz) δ : 27.06, 29.11, 37.19, 55.49, 113.79, 113.85, 122.81, 127.99, 128.16, 134.43, 134.90, 158.55. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₂Br₂O: C, 43.41; H, 3.64. Found: C, 43.45; H, 3.70.

4-Bromo-3-bromomethyl-1-methyl-1,2-dihydro-naphthalene (4e)

White semisolid ¹H NMR(CDCl₃, 200 MHz) δ : 1.25 (d, 3H, J = 7.0Hz), 2.21-2.36 (dd, 1H, J_1 = 16Hz, J_2 = 6.6Hz), 2.66-2.78 (dd, 1H, J_1 = 16.0Hz, J_2 = 6.4Hz), 2.88-3.08 (m, 1H), 4.19 (d, 1H, J = 10Hz), 4.30 (d, 1H, J = 10.0Hz), 7.07-7.37 (m, 3H), 7.54-7.70 (m, 1H). ¹³CNMR (CDCl₃, 50 MHz) δ : 20.1 (CH₃), 31.9, 36.0, 37.5, 122.1, 125.9, 126.8, 127.9, 129.0, 132.5, 133.2, 141.0. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₂Br₂: C, 45.61; H, 3.83. Found: C, 45.59; H, 3.91.

3-Bromo-4-bromomethyl-1,2-dihydro-naphthalene (4f)

Yellow liquid, ¹H NMR(CDCl₃, 200 MHz) δ : 2.67-2.90 (m, 4H), 4.52 (s, 2H), 7.02-7.29 (m, 3H), 7.36-7.46 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 29.2, 31.1, 35.8, 123.5, 127.2, 127.9, 128.9, 132.0, 132.4, 134.6, 136.7. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₁H₁₀Br₂: C, 43.75; H, 3.34. Found: C, 43.83; H, 3.40.

1-Bromo-2-bromomethyl-naphthalene (4g)

Yellow liquid, ¹H NMR(CDCl₃, 200 MHz) δ : 4.85 (s, 2H), 7.12-7.26 (m, 3H), 7.67-7.81 (m, 2H), 8.32 (d, 1H, J = 8.2Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 34.9, 125.01, 127.3, 127.7,

127.8, 127.9, 128.2, 128.4, 132.5, 134.2, 135.0. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₁H₈Br₂: C, 44.04; H, 2.69. Found: C, 44.13; H, 2.75.

1-Bromo-2-bromomethyl-7-methoxy-naphthalene (4h)

White solid, mp 80-82 °C, ¹H NMR(CDCl₃, 400 MHz) δ : 4.00 (s, 3H), 4.87 (s, 2H), 7.19-7.24 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.40 (d, 1H, $J = 8.4$ Hz), 7.71 (s, 1H), 7.78 (d, 2H, $J = 9.8$ Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 35.16, 55.64, 106.29, 120.17, 123.73, 125.53, 128.12, 129.7, 129.95, 134.07, 135.56, 159.50. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₀Br₂O: C, 43.67; H, 3.05. Found: C, 43.72; H, 3.10.

1-Bromo-2-bromomethyl-4-methyl-naphthalene (4i)

White solid, mp 109-110 °C, ¹H NMR(CDCl₃, 200 MHz) δ : 2.65 (s, 3H), 4.82 (s, 2H), 7.36 (s, 1H), 7.56-7.62 (m, 2H), 7.93-7.98 (m, 1H), 8.34-8.39 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 19.38, 35.06, 122.90, 124.59, 127.21, 127.63, 128.48, 132.53, 133.66, 134.59, 135.01, 137.8. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₀Br₂: C, 45.90; H, 3.21. Found: C, 45.97; H, 3.28.

2-Bromo-1-bromomethyl-naphthalene (4j)

White solid, mp 85-86 °C, ¹H NMR(CDCl₃, 200 MHz) δ : 5.01 (s, 2H), 7.47-7.67 (m, 4H), 7.81 (d, 1H, $J = 8.0$ Hz), 8.08 (d, 1H, $J = 8.4$ Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 30.4, 122.6, 123.9, 126.6, 127.8, 128.9, 130.4, 130.7, 132.2, 132.5, 132.9. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₁H₈Br₂: C, 44.04; H, 2.69. Found: C, 44.02; H, 2.76.

1-Bromo-2-bromomethyl-6-methoxy-naphthalene (4k)

White solid, mp 58-60 °C, ¹H NMR(CDCl₃, 200 MHz) δ : 3.83 (s, 3H), 4.84 (s, 2H), 7.09 (d, 1H, $J = 2.4$ Hz), 7.21-7.27 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 2.4$ Hz), 7.41 (d, 1H, $J = 9.0$ Hz), 7.55 (d, 1H, $J = 9.0$ Hz), 8.22 (d, 1H, $J = 8.4$ Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 35.2, 55.5, 106.1, 120.4, 124.9, 126.6, 127.1, 127.9, 128.2, 129.5, 132.5, 135.6. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2952, 2830, 1620, 1530. Anal. Calcd for C₁₂H₁₀Br₂O: C, 43.67; H, 3.05. Found: C, 43.74; H, 3.12.

4,6-dibromo-3-(bromomethyl)-1,2-dihydronaphthalene (4l)

Yellow liquid, ^1H NMR (CDCl_3 , 500 MHz) δ : 2.62 (t, 2H, $J=7.0\text{Hz}$), 2.95 (t, 2H, $J=7.0\text{Hz}$), 4.51 (s, 2H), 7.12 (d, 1H, $J=8.5\text{Hz}$), 7.45 (d, 1H, $J=8.5\text{Hz}$), 7.84 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 27.3, 28.7, 36.8, 120.8, 121.1, 128.6, 130.5, 131.3, 134.9, 135.3, 137.0. IR ν_{max} (CHCl_3 , cm^{-1}) 3332, 2960, 2845. Anal. Calcd for $\text{C}_{11}\text{H}_9\text{Br}_3$: C, 34.69; H, 2.38. Found: C, 34.72; H, 2.45.

Experimental details

General procedure for the synthesis of *O*-homoallylated derivatives (5)

NaH (2.5 mmol), taken in a two neck flask, was thoroughly washed with benzene (2-3 times). It was then dried under vacuum and dry THF (5 mL) was added in it. But-3-en-1-ol was added into the NaH solution in ice-cold condition. The resulting mixture was stirred continuously for 30 minute at 0 °C then bromomethylvinyl bromide derivative **4** was added in it. After completion of the reaction, the reaction mixture was quenched in ice-water mixture and extracted with ether. Solvent was removed under reduced pressure and then the product was purified by column chromatography.

4-Bromo-3-but-3-enyloxymethyl-8-methoxy-1,2-dihydro-naphthalene (5b)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.32-2.45 (m, 4H), 2.83 (t, 2H, $J=8.0\text{Hz}$), 3.56 (t, 2H, $J=6.6\text{Hz}$), 3.84 (s, 3H), 4.39 (s, 2H), 5.03-5.15 (m, 2H), 5.77-5.91 (m, 1H), 6.84 (d, 1H, $J=8.0\text{Hz}$), 7.24-7.35 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 19.7, 26.5, 34.3, 55.7, 69.5, 73.3, 110.7, 115.9, 116.5, 120.0, 124.7, 126.6, 134.8, 135.3, 137.3, 156.0. IR ν_{max} (CHCl_3 , cm^{-1}) 2965, 2843, 1627, 1538. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_2$: C, 59.45, H, 5.92. Found: C, 59.49, H, 5.93.

4-Bromo-3-but-3-enyloxymethyl-7-methoxy-1,2-dihydro-naphthalene (5c)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.38 (t, 2H, $J=6.4\text{Hz}$), 2.49 (t, 2H, $J=8.4\text{Hz}$), 2.83 (t, 2H, $J=8.4\text{Hz}$), 3.49 (t, 2H, $J=6.4\text{Hz}$), 3.84 (s, 3H), 4.44 (s, 2H), 5.05-5.18 (m, 2H), 5.80-5.94 (m, 1H), 6.70-6.81 (m, 2H), 7.58 (d, 1H, $J=8.4\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 26.9, 28.3, 34.3, 55.3, 69.3, 73.2, 111.2, 113.2, 116.4, 119.7, 126.9, 128.6, 134.2, 135.3, 138.2, 159.5. IR ν_{max} (CHCl_3 , cm^{-1}) 2967, 2835, 1631, 1543. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_2$: C, 59.45, H, 5.92. Found: C, 59.47, H, 5.94.

4-Bromo-3-but-3-enyloxymethyl-6-methoxy-1,2-dihydro-naphthalene (5d)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.27-2.52 (m, 4H), 2.76 (t, 2H, $J = 7.2\text{Hz}$), 3.50-3.64 (m, 2H), 3.82 (s, 3H), 4.39 (s, 2H), 5.05 (d, 1H, $J = 9.2\text{Hz}$), 5.17 (d, 1H, $J = 7.0\text{Hz}$), 5.75-5.95 (m, 1H), 6.71-6.76 (dd, 1H, $J_1 = 8.2\text{Hz}$, $J_2 = 2.4\text{Hz}$), 7.03 (d, 1H, $J = 8.2\text{Hz}$), 7.24 (d, 1H, $J = 2.4\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 26.9, 27.4, 34.3, 55.4, 69.5, 73.4, 113.1, 113.4, 116.5, 116.6, 127.8, 128.6, 135.1, 135.3, 137.8, 158.5. IR ν_{max} (CHCl_3 , cm^{-1}) 2941, 2838, 1624, 1532. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_2$: C, 59.45, H, 5.92. Found: C, 59.48, H, 5.95.

4-Bromo-3-but-3-enyloxymethyl-1-methyl-1,2-dihydro-naphthalene (5e)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 1.25 (d, 3H, $J = 7.0\text{Hz}$), 2.27-2.24 (m, 2H), 2.55-2.67 (m, 1H), 2.92-2.99 (m, 2H), 3.52 (t, 2H, $J = 6.6\text{Hz}$), 4.38 (s, 2H), 5.02-5.16 (m, 2H), 5.77-5.88 (m, 1H), 7.13-7.17 (m, 1H), 7.19-7.26 (m, 2H), 7.64-7.68 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 19.8, 31.9, 34.3, 34.6, 69.4, 73.4, 116.5, 119.4, 125.6, 126.6, 127.3, 128.4, 132.8, 135.3, 135.6, 141.3. IR ν_{max} (CHCl_3 , cm^{-1}) 2936, 2835, 1619, 1523. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}$: C, 62.55, H, 6.23. Found: C, 62.58, H, 6.25.

3-Bromo-4-but-3-enyloxymethyl-1,2-dihydro-naphthalene (5f)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.34-2.39 (m, 2H), 2.84-2.89 (m, 2H), 3.54-3.63 (m, 4H), 4.62 (s, 2H), 4.62-5.19 (m, 2H), 5.79-5.85 (m, 1H), 7.09-7.22 (m, 1H), 7.49-7.52 (m, 1H), 7.81 (d, 1H, $J = 7.6\text{Hz}$), 8.04 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 23.8, 30.3, 38.8, 69.3, 71.5, 116.3, 123.3, 124.4, 126.4, 127.3, 128.3, 128.8, 130.1, 130.9, 132.5. IR ν_{max} (CHCl_3 , cm^{-1}) 2962, 2843, 1628, 1534. Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{BrO}$: C, 61.45, H, 5.84. Found: C, 61.49, H, 5.83.

1-Bromo-2-but-3-enyloxymethyl-naphthalene (5g)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.37-2.55 (m, 2H), 3.70 (t, 2H, $J = 6.8\text{Hz}$), 4.89 (s, 2H), 5.60-5.24 (m, 2H), 5.88-5.93 (m, 1H), 7.51-7.70 (m, 3H), 7.87 (d, 2H, $J = 8.0\text{Hz}$), 8.37 (d, 1H, $J = 8.2\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 34.3, 70.2, 72.9, 116.5, 122.4, 126.0, 126.4, 127.0, 127.4, 127.7, 128.1, 132.2, 134.0, 135.2, 136.1. IR ν_{max} (CHCl_3 , cm^{-1}): 2958, 2827, 1623, 1536. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{BrO}$: C, 61.87, H, 5.19. Found: C, 61.90, H, 5.25.

1-Bromo-2-but-3-enyloxymethyl-7-methoxy-naphthalene (5h)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.38-2.48 (m, 2H), 3.63 (t, 2H, $J = 6.8\text{Hz}$), 3.95 (s, 3H), 4.80 (s, 2H), 5.03-5.16 (m, 2H), 5.60-6.0 (m, 1H), 7.22-7.28 (dd, 1H, $J = 8.0\text{Hz}$), 7.45 (d, 1H, $J = 8.0\text{Hz}$), 7.85 (s, 1H), 7.91 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 34.3, 55.4, 71.6, 72.2, 105.3, 117.3, 119.2, 121.0, 123.6, 127.3, 129.3, 129.7, 133.4, 134.5, 136.3, 158.9. IR ν_{max} (CHCl_3 , cm^{-1}) 2953, 2845, 1629, 1540. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{BrO}_2$: C, 59.83, H, 5.33. Found: C, 59.82, H, 5.30.

1-Bromo-2-but-3-enyloxymethyl-4-methyl-naphthalene (5i)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.33-2.55 (m, 2H), 2.65 (s, 3H), 3.63 (t, 2H, $J = 6.6\text{Hz}$), 4.78 (s, 2H), 5.06 (d, 1H, $J = 9.4\text{Hz}$), 5.23 (d, 1H, $J = 18.0\text{Hz}$), 5.78-5.98 (m, 1H), 7.45 (s, 1H), 7.51-7.60 (m, 2H), 7.94 (d, 1H, $J = 7.0\text{Hz}$), 8.33 (d, 1H, $J = 8.6\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 19.4, 34.3, 70.2, 72.9, 116.5, 120.41, 124.4, 126.3, 126.8, 127.0, 127.6, 132.1, 133.3, 134.1, 135.2, 135.5. IR ν_{max} (CHCl_3 , cm^{-1}): 2960, 2827, 1615, 1534. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{BrO}$: C, 62.96, H, 5.61. Found: C, 63.00, H, 5.59.

2-Bromo-1-but-3-enyloxymethyl-naphthalene (5j),

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.32-2.43 (m, 2H), 3.64 (t, 2H, $J = 6.8\text{Hz}$), 4.97-5.14 (m, 2H), 5.17 (s, 2H), 5.78-5.88 (m, 1H), 7.43-7.64 (m, 4H), 7.78-7.83 (m, 1H), 8.22 (d, 1H, $J = 7.8\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 34.2, 69.4, 69.5, 116.4, 123.9, 124.9, 126.1, 127.2, 128.4, 130.1, 130.1, 132.4, 132.8, 133.7, 135.2. IR ν_{max} (CHCl_3 , cm^{-1}) 2945, 2842, 1613, 1522. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{BrO}$: C, 61.87, H, 5.19. Found: C, 61.85, H, 5.23.

1-Bromo-2-but-3-enyloxymethyl-6-methoxy-naphthalene (5k)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.35-2.45 (m, 2H), 3.56 (t, 2H, $J = 6.6\text{Hz}$), 3.84 (s, 3H), 4.39 (s, 2H), 5.03-5.15 (m, 2H), 5.77-5.91 (m, 1H), 6.83 (d, 1H, $J = 8.0\text{Hz}$), 7.16-7.35 (m, 2H), 7.59 (d, 1H, $J = 8.2\text{Hz}$), 8.19 (d, 1H, $J = 9.2\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 34.3, 55.4, 70.0, 72.8, 105.9, 116.5, 119.9, 122.6, 126.1, 126.5, 126.7, 127.6, 128.7, 133.5, 132.2, 158.0. IR ν_{max} (CHCl_3 , cm^{-1}) 2936, 2841, 1619, 1524. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{BrO}_2$: C, 59.83, H, 5.33. Found: C, 59.85, H, 5.29.

4,6-dibromo-3-((but-3-enyloxy)methyl)-1,2-dihydronaphthalene (5l)

Liquid, ^1H NMR (CDCl_3 , 500 MHz) δ : 2.45-2.50 (m, 2H), 2.59-2.62 (t, 2H, $J = 7.5$ Hz), 2.86-2.89 (t, 2H, $J = 7.5$ Hz), 3.62-3.64 (t, 2H, $J = 7.0$ Hz), 4.48 (s, 2H), 5.15-5.24 (m, 2H), 5.91-5.97 (m, 1H), 7.09 (d, 1H, $J = 8.0$ Hz), 7.40-7.42 (d, 1H, $J = 8.0$ Hz), 7.87 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 26.7, 27.2, 34.2, 69.5, 73.1, 116.5, 118.3, 120.3, 128.5, 129.9, 130.7, 133.1, 135.2, 135.6, 138.7. IR ν_{max} (CHCl_3 , cm^{-1}) 2941, 2847, 1624. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{Br}_2\text{O}$: C, 48.42, H, 4.33. Found: C, 48.45, H, 4.34.

2-(3-methylbut-3-enyloxy)methyl-1-bromo-3,4-dihydronaphthalene (6)

Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 1.81 (s, 3H), 2.39-2.45 (t, 2H, $J = 7.0$ Hz), 2.42-2.55 (t, 2H, $J = 7.8$ Hz), 2.71-2.79 (t, 2H, $J = 7.8$ Hz), 3.52 (t, 2H, $J = 7.0$ Hz), 4.42 (s, 2H), 4.92 (s, 1H), 5.07 (s, 1H), 7.08-7.61 (m, 3H), 7.63 (d, 1H, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 19.2, 26.9, 27.9, 35.1, 70.2, 74.1, 117.3, 119.1, 126.7, 127.0, 127.2, 128.1, 133.7, 136.1, 137.5, 138.2. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}$: C, 62.55, H, 6.23. Found: C, 62.53, H, 6.22.

Typical experimental procedure for Heck reaction (7)

Compounds (7, 1equiv.), $\text{Pd}(\text{OAc})_2$ (10 mol%), PPh_3 (0.25 equiv.), Cs_2CO_3 (1.2 equiv.), DMF (6 mL) were placed in a two neck round bottom flask. After degassing with N_2 , the mixture was heated to 80-85°C for 4-5h. After cooling the reaction mixture was diluted with cold water and extracted with ether (20 mL x 3) and dried (Na_2SO_4). The solvent was evaporated and the crude product was purified by preparative thin layer chromatography.

4-Methoxy-11-methylene-5,6,7,9,10,11-hexahydro-8-oxa-cyclohepta[a]naphthalene (7b)

White solid, mp 52-53 °C, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.17 (t, 2H, $J = 8.4$ Hz), 2.61 (t, 2H, $J = 6.0$ Hz), 2.76 (t, 2H, $J = 8.4$ Hz), 3.84 (s, 3H), 3.89 (t, 2H, $J = 6.0$ Hz), 4.30 (s, 2H), 4.94 (s, 1H), 5.32 (s, 1H), 6.77 (d, 1H, $J = 8.00$ Hz), 7.00 (d, 1H, $J = 7.8$ Hz), 7.12 (t, 1H, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 20.2, 27.5, 29.9, 39.7, 55.8, 71.7, 74.7, 109.5, 117.1, 118.6, 124.1, 126.3, 134.7, 137.1, 144.9, 156.0. IR ν_{max} (CHCl_3 , cm^{-1}) 2988, 2954, 1615, 1532. HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ [$\text{M}^+ + \text{H}$]: 243.1387, found: 243.1390.

3-Methoxy-11-methylene-5,6,7,9,10,11-hexahydro-8-oxa-cyclohepta[a]naphthalene (7c)

Colourless Liquid, ^1H NMR (CDCl_3 , 200 MHz) δ : 2.20 (t, 2H, $J = 7.8$ Hz), 2.59 (t, 2H, $J = 5.8$ Hz), 2.73 (t, 2H, $J = 8.0$ Hz), 3.80 (s, 3H), 3.83 (t, 2H, $J = 6.6$ Hz), 4.28 (s, 2H), 4.97 (s, 1H), 5.33 (s, 1H), 6.70 (m, 2H), 7.30 (d, 1H, $J = 7.8$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 27.9,

28.8, 39.4, 55.3, 71.7, 74.5, 110.8, 113.3, 116.7, 126.6, 128.7, 131.7, 135.2, 137.8, 144.8, 158.3. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2994, 2847, 1620, 1535. HRMS calcd for C₁₆H₁₈O₂ [M⁺+H]: 243.1387, found: 243.1385.

2-Methoxy-11-methylene-5,6,7,9,10,11-hexahydro-8-oxa-cyclohepta[a]naphthalene(7d)

White solid, mp 79-80 °C, ¹H NMR (CDCl₃, 200 MHz) δ : 2.19 (t, 2H, J = 8.0 Hz), 2.58-2.73 (m, 4H), 3.77 (s, 3H), 3.92 (t, 2H, J = 6.0 Hz), 4.29 (s, 2H), 5.00 (s, 1H), 5.34 (s, 1H), 6.65-6.70 (dd, 1H, J_1 = 7.8 Hz, J_2 = 2.6 Hz), 6.95 (d, 1H, J = 2.6 Hz), 7.04 (d, 1H, J = 8.0 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ : 27.3, 28.1, 39.3, 55.3, 71.5, 74.4, 111.0, 111.9, 117.0, 127.7, 128.1, 135.0, 135.3, 136.7, 144.2, 158.0. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2982, 283, 1633, 1542. HRMS calcd for C₁₆H₁₈O₂ [M⁺+H]: 243.1387, found: 243.1390.

5-Methyl-11-methylene-5,6,7,9,10,11-hexahydro-8-oxa-cyclohepta[a]naphthalene(7e)

Colourless Liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 1.31 (d, 3H, J = 7.2 Hz), 1.95-2.05 (m, 1H), 2.33-2.44 (m, 1H), 2.62 (t, 2H, J = 6.2 Hz), 2.84-2.95 (m, 1H), 3.90 (t, 2H, J = 6.2 Hz), 4.28 (s, 2H), 4.99 (s, 1H), 5.34 (s, 1H), 7.13-7.18 (m, 3H), 7.35-7.41 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 19.6, 32.2, 35.7, 39.6, 71.5, 74.8, 116.8, 125.7, 126.1, 126.8, 126.9, 132.6, 134.8, 135.0, 140.9, 144.6. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2998, 2848, 1635, 1534. HRMS calcd for C₁₆H₁₈O [M⁺+H]: 227.1438, found: 227.1440.

7-Methylene-5,6,7,8,9,11-hexahydro-10-oxa-cyclohepta[a]naphthalene (7f)

White semisolid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.46 (t, 2H, J = 6.6 Hz), 2.61-2.95 (m, 4H), 3.93 (t, 2H, J = 6.4 Hz), 4.73 (s, 2H), 5.19 (s, 1H), 5.32 (s, 1H), 7.04 (m, 1H), 7.12-7.16 (m, 2H), 7.46-7.54 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 21.8, 29.1, 39.4, 66.4, 69.8, 106.8, 121.7, 126.5, 127.3, 127.6, 129.0, 129.9, 132.8, 135.9, 139.8. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2996, 2842, 1623, 1545. HRMS calcd for C₁₅H₁₆O [M⁺+H]: 213.1281, found: 213.1283.

11-Methylene-7,9,10,11-tetrahydro-8-oxa-cyclohepta[a]naphthalene (7g)

Colourless Liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.59 (t, 2H, J = 5.2 Hz), 4.14 (t, 2H, J = 5.2 Hz), 4.78 (s, 2H), 5.13 (s, 1H), 5.69 (s, 1H), 7.26 (d, 1H, J = 7.8 Hz), 7.42-7.53 (m, 2H), 7.74 (d, 1H, J = 8.2 Hz), 7.79-7.86 (m, 1H), 8.21-8.29 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 39.4, 75.1, 75.2, 116.8, 118.2, 125.5, 125.8, 125.9, 126.3, 127.1, 128.4, 130.9, 133.6, 140.8,

145.3. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2991, 2836, 1626, 1549. HRMS calcd for C₁₅H₁₄O[M⁺+H]: 211.1125, found: 211.1127.

2-Methoxy-11-methylene-7,9,10,11-tetrahydro-8-oxa-cyclohepta[a]naphthalene (7h)

Colourless Liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.58 (t, 2H, J = 5.4Hz), 3.90 (s, 3H), 4.23 (t, 2H, J = 5.4Hz), 4.75 (s, 2H), 5.19 (s, 1H), 5.67 (s, 1H), 7.11-7.27 (m, 1H), 7.43 (s, 1H), 7.59-7.79 (m, 3H). ¹³C NMR (CDCl₃, 50 MHz) δ : 39.5, 55.3, 75.3, 75.8, 117.5, 118.1, 124.3, 124.4, 126.8, 129.0, 129.2, 129.3, 129.6, 129.8, 132.5, 134.9. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2984, 2845, 1629, 1528. HRMS calcd for C₁₆H₁₆O₂[M⁺+H]: 241.1230, found: 241.1232.

5-Methyl-11-methylene-7,9,10,11-tetrahydro-8-oxa-cyclohepta[a]naphthalene (7i)

White solid, mp 104-105 °C, ¹H NMR (CDCl₃, 200 MHz) δ : 2.56 (t, 2H, J = 5.4Hz), 2.67 (s, 3H), 4.09-4.16 (m, 2H), 4.74 (s, 2H), 5.02 (s, 1H), 5.66 (s, 1H), 7.14 (s, 1H), 7.35-7.53 (m, 2H), 7.89-8.02 (m, 1H), 8.24-8.29 (m, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 19.4, 39.6, 75.2, 76.2, 118.2, 124.2, 125.4, 125.6, 126.6, 127.4, 131.1, 132.5, 133.2, 139.1, 145.5, 145.5. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2987, 2848, 1631, 1547. HRMS calcd for C₁₆H₁₆O[M⁺+H]: 225.1281, found: 225.1279.

7-Methyl-5,6,9,11-tetrahydro-10-oxa-cyclohepta[a]naphthalene (7j)

Colourless Liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.31 (s, 3H), 3.77 (d, 2H, J = 6.6Hz), 4.87 (s, 2H), 6.21 (t, 1H, J = 6.8Hz), 7.35-7.61 (m, 4H), 7.96 (d, 1H, J = 8.2Hz), 8.27 (d, 1H, J = 8.2Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 22.0, 61.4, 62.8, 123.4, 124.0, 125.3, 125.9, 126.9, 127.2, 128.4, 128.6, 130.1, 133.0, 140.3, 143.4. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2980, 2834, 1616, 1533. Anal. Calcd for C₁₅H₁₄O: C, 85.68, H, 6.71. Found: C, 85.65, H, 6.78.

3-Methoxy-11-methylene-7,9,10,11-tetrahydro-8-oxa-cyclohepta[a]naphthalene (7k)

Colourless Liquid, ¹H NMR (CDCl₃, 200 MHz) δ : 2.54 (t, 2H, J = 5.2Hz), 3.89 (s, 3H), 4.07 (t, 2H, J = 5.2Hz), 4.72 (s, 2H), 5.08 (s, 1H), 5.63 (s, 1H), 7.08-7.13 (m, 2H), 7.27 (d, 1H, J = 8.2Hz), 7.57 (d, 1H, J = 8.2Hz), 8.16 (d, 1H, J = 9.2Hz). ¹³C NMR (CDCl₃, 50 MHz) δ : 39.5, 55.3, 75.2, 75.3, 105.8, 118.1, 118.8, 125.6, 126.4, 127.1, 127.7, 131.4, 134.9, 141.0, 145.6, 149.2, 157.4. IR $\nu_{\max}$ (CHCl₃, cm⁻¹) 2985, 2852, 1618, 1531. HRMS calcd for C₁₆H₁₆O₂[M⁺+H]: 241.1230, found: 241.1233.

10-bromo-1,2,3,5,6,7-hexahydro-1-methylenenaphtho[2,1-c]oxepine (7l)

Yellow Liquid, ^1H NMR (CDCl_3 , 500 MHz) δ : 2.70-2.81 (m, 2H), 2.80-2.85 (t, 2H, $J = 7.5\text{Hz}$), 2.90-2.98 (t, 2H, $J = 7.5\text{Hz}$), 3.99-4.01 (t, 2H, $J = 6.0\text{ Hz}$), 4.40 (s, 2H), 5.03 (s, 1H) 5.40 (s, 1H), 7.18 (d, 1H, $J = 8.0\text{Hz}$), 7.40 (d, 1H, $J = 8.0\text{Hz}$), 7.59 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 27.7, 30.2, 39.4, 71.5, 74.3, 114.1, 115.9, 117.5, 123.5, 124.1, 128.2, 128.7, 129.7, 135.9, 139.2. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{BrO}$: C, 61.87; H, 5.19. Found: C, 61.90; H, 5.21.

References

1. a) . Jana, R.;Samanta, S.*Tetrahedron Lett.***2008**, 49, 851.
b)Jana,R.; Chatterjee,I.;Samanta,S.;Ray,J. K. *Org. lett.***2008**, 10, 4795.
c) Jana,R.; Biswas,A.; Samanta,S.; Ray, J. K. *Synthesis*, **2010**, 12, 2092.
2. Nandi, S.; Ray, J. K. *Tetrahedron Lett.***2009**, 50, 6993.