Synthesis of substituted 2,5-dihydro-1-naphthoxepines from 1-naphthol via ring-closing metathesis

Jui-Chi Tsai,[a] Sie-Rong Li,[a] Liang-Yeu Chen,[a] Po-Yuan Chen,[b] Sodio Chih-Neng Hsu,[b] Chun-Nan Lin,[a] and Eng-Chi Wang[b]*

[a]*Institute of Pharmaceutical Sciences, Kaohsiung Medical University, Kaohsiung City, Taiwan 807*

[b]*Faculty of Medicinal & Applied Chemistry, Kaohsiung Medical University, Kaohsiung City, Taiwan 807*

E-mail: enchwa@kmu.edu.tw

Abstract

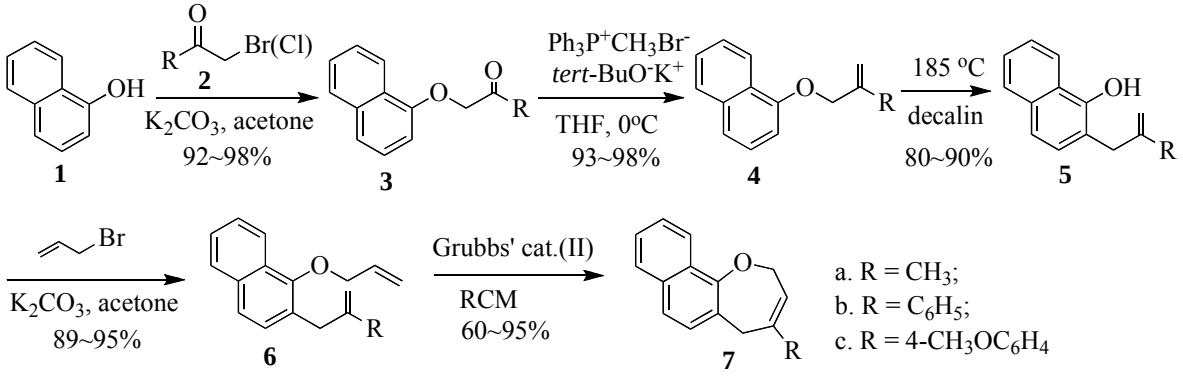
The syntheses of 4-substituted and 5-substituted 2,5-dihydro-1-naphthoxepines are described. 1-Naphthol, starting material, was subjected to sequential reactions of *O*-alkylation, the Wittig reaction, the Claisen reaction, *O*-allylation, and ring-closing metathesis to provide 4-substituted 2,5-dihydro-1-naphthoxepines. Similarly, 5-substituted 2,5-dihydro-1-naphthoxepines were produced in good yields.

Keywords: Ring-closing metathesis, Claisen rearrangement, 1-naphthol, 4-substituted 2,5-dihydro-1-naphthoxepines, 5-substituted 2,5-dihydro-1-naphthoxepines.

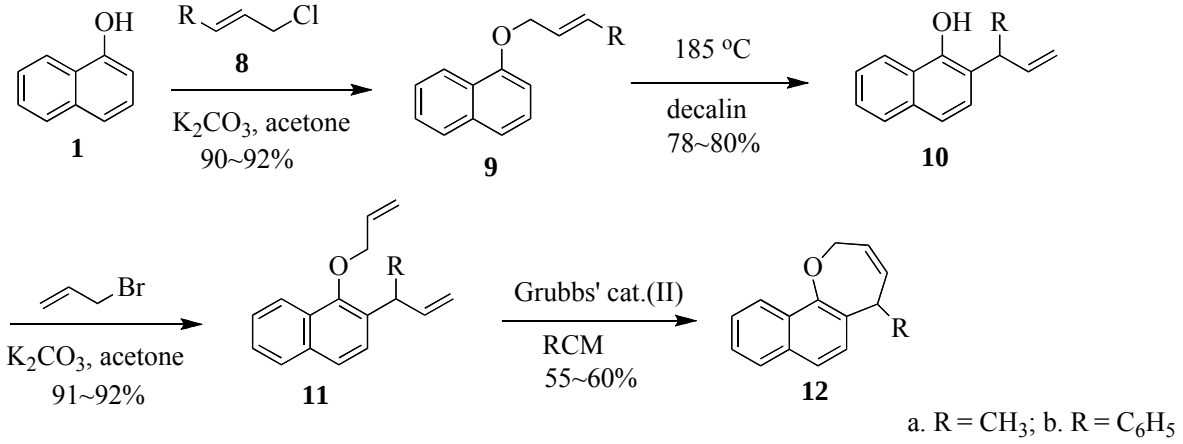
Introduction

In the last decade, considerale efforts have been made in our laboratory to utilize the Claisen rearrangement and ring-closing metathesis as key steps to prepare benzocarbocyclic and benzoheterocyclic compounds.[1] Recently Kotha, *et al*.,[2] using the same strategy but developing a new approach to biologically relevant 2-naphthoxepines prompted us to search for some related compounds. From a literature survey, it was clear that naphthoxepines have been paid little attention[3] and the synthesis of substituted 2,5-dihydro-1-naphthoxepines (2,5-dihydronaphth[1,2-*b*]oxepines) have not been described. Herein, we disclose an alternative method for the synthesis of 4-substituted and 5-substituted 2,5-dihydro-1-naphthoxepines. The synthesis started from 1-naphthol and was based on the Claisen rearrangement and ring-closing metathesis as key steps as shown in Schemes 1, and 2.

Scheme 1. Synthesis of 4-substituted 2,5-dihydro-1-naphthoxepines(**7a-c**)



Scheme 2. Synthesis of 5-substituted 2,5-dihydro-1-naphthoxepines(**12a-b**)

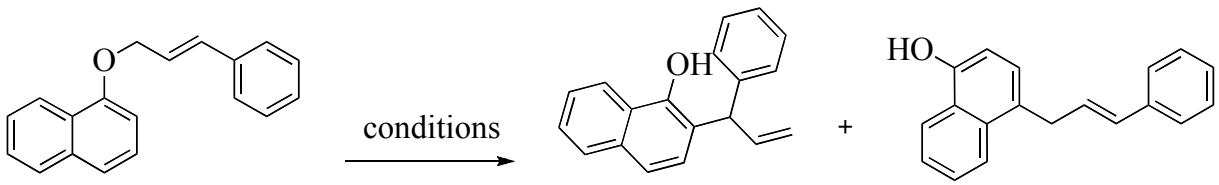


Results and Discussion

As shown in Scheme 1, the reaction of 1-naphthol (**1**) with chloroacetone (**2a**), bromoacetophenone (**2b**), and 2-bromo-1-(4-methoxyphenyl)ethanone (**2c**) in the presence of dry potassium carbonate in refluxing acetone for 3-4 h, gave 1-(substituted)-2-(1-naphthalenyloxy)ethanones (**3a-c**) in 92 - 98% yields. Reaction of **3a-c** with methylenetriphenylphosphorane generated from the reaction of methyltriphenylphosphonium bromide and potassium *tert*-butoxide at 0°C *in situ* afforded 1-[2-(substituted)-allyloxy]naphthalenes (**4a-c**) in yields of 93 - 98%. Subsequently, compounds **4a-c** were heated to 185 °C to bring about Claisen rearrangement to lead 2-(2-substituted allyl)-1-naphthols (**5a-c**) which have satisfactory spectral data, in yields of 80 - 90%. The *O*-allylation of **5a-c** was easily achieved by the general procedure to give 1-allyloxy-2-[2-(substituted)allyl]naphthalenes (**6a-c**)

in yields of 89 - 95%. Finally by treatment of **6a-c** with Grubbs' catalyst (II) the desired 4-(substituted)-2,5-dihydro-1-naphthoxepines (**7a-c**) were produced in yields of 60 - 95%, respectively. Furthermore, as shown in Scheme 2, 1-allyloxynaphthalenes (**9a-b**) prepared from 1-naphthol (**1**) with crotyl chloride (**8a**), and cinnamyl chloride (**8b**) were heated to 185 – 190 ^{o}C in decalin for 0.75 - 2.5 h to give, *via* Claisen rearrangement, 2-allyl-1-naphthols (**10a-b**) in 78 - 80% yields. In the reaction producing **9b**, besides the *ortho*-product **10b**, its isomeric *para*-product **10c** was also obtained. In a search for the optimal conditions for yielding **10b**, various conditions were investigated and the results were depicted as Table 1.

Table 1. Conditions and percentage yields of the Claisen rearrangement of **9b**



9b **10b** **10c**

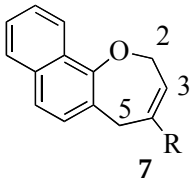
Compound	Conditions (^{o}C/solvent)	Reaction time (hr)	Products (% yields)*	
9b	185/Decalin	0.5	**10b** (51)	**10c** (7)
		0.75	**10b** (78)	**10c** (12)
		1.0	**10b** (65)	**10c** (17)
		1.5	**10b** (46)	**10c** (26)
		3.0	**10b** (15)	**10c** (68)
9b	217/Diethylaniline	0.5	**10b** (18)	**10c** (48)
		0.75	**10b** (12)	**10c** (63)
		1.0	**10b** (5)	**10c** (82)

*The isolated yield was indicated.

As shown in Table 1, a bulky allyl group, as in **9b**, favors *ortho*-product **10b** at shorter reaction times of 0.75 h in decalin. On the other hand, at the longer 1 h reaction time in diethylaniline, the *para*-product **10c** predominates. This means that **10c** is thermodynamically more stable than **10b** because of conjugated character of **10c**. The isomeric **10b** and **10c** can be easily distinguished by ^{1}H-NMR measurements. Following the general procedure, **10a-b** were reacted with allyl bromide to afford 2-allyl-1-allyloxynaphthalenes (**11a-b**) in 91- 92% yields, respectively. Treatment of **11a-b** with Grubbs' catalyst (II) produced 5-substituted 2,5-dihydro-1-naphthoxepines (**12a-b**) in yields of 55 - 60%. The compounds in Scheme 2 are all new and gave satisfactory spectral data. A comparison of selected protons for compounds **7** and **12** in ^{1}H-NMR spectra is compiled at Table 2.

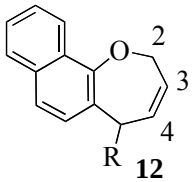
Thus, we have established a new route to prepare 4-substituted-2,5-dihydro-1-naphthoxepines (**7a-c**) and 5-substituted 2,5-dihydro-1-naphthoxepines (**12a-b**), from 1-naphthol.

Table 2. A comprasion of selected protons of compound **7** and **12** in ^{1}H-NMR



7

a. R = CH_3
b. R = C_6H_5
c. R = 4'-$CH_3OC_6H_4$



12

a. R = CH_3
b. R = C_6H_5

Compound	H-2	H-3	H-4	H-5	Yield (%)
7a	4.63 (dd)	5.30 (tq)	-	3.55 (s)	95
7b	4.93 (dd)	5.79 (t)	-	4.13 (s)	60
7c	4.88 (dd)	5.71 (t)	-	4.06 (s)	60
12a	4.54-4.76 (m)	5.48-5.52 (m)	5.84-5.90 (m)	-	60
12b	4.86-4.92 (m)	5.77-5.82 (m)	6.10-6.16 (m)	-	55

Experimental Section

General Procedures. Melting points (Yanaco micro melting-point apparatus) are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Varian Gemini-200 or Varian Unity plus 400 Spectrometer. Chemical shifts are indicated in parts per million with respect to TMS. Elemental analyses were recorded on a Heraeus CHN-O Rapid analyzer. Mass spectra were recorded on a Chem/hp/middle spectrometer connected to a Hewlett Packard series II model gas-liquid chromatograph. HRMS spectra were performed on a JEOL JMS SX/SX 102A instrument. Silica gel (230-400 mesh) for column chromatography and precoated silica gel plates (60 F-254) for TLC was purchased from E. Merck Co. UV light (254 nm) was used to detect spots on TLC plates after development.

General procedure for the preparation of 1-(substituted)-2-(1-naphthalenyloxy)etha- nones (**3a-c**)

Under the protection of nitrogen, to a solution of 1-naphthol (7.21 g, 50.0 mmol) dissolved in dry acetone (150 mL) was added K_2CO_3 (9.67 g, 70.0 mmol) and substituted 2-bromoacetophenone (**2a-c**) (60.0 mmol) in sequence. The reaction mixture obtained was heated to reflux for 3-4 h, monitored by TLC. After cooling to room temperature, the resulting reaction mixture was filtered to remove the solid. The filtrate was was concentrated *in vacuo* to remove the solvent.

The resulting residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 10) to provide pure **3a-c**, respectively.

1-(1-Naphthalenyloxy)propan-2-one (**3a**).[4] (9.40 g, 94%) was obtained as colorless liquid, R_f = 0.54 (ethyl acetate: *n*-hexane = 1: 7), [1] H-NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H, CH_3), 4.56 (s, 2H, $OC\underline{H}_2COCH_3$), 6.57 (d, *J* = 7.2 Hz, 1H, ArH), 7.28 (t, *J* = 8.4 Hz, 1H, ArH), 7.43 (d, *J* = 8.4 Hz, 1H, ArH), 7.45-7.50 (m, 2H, ArH), 7.75-7.79 (m, 1H, ArH), 8.28-8.32 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 26.6, 72.9, 104.7, 121.2, 121.7, 125.2, 125.4, 125.5, 126.5, 127.4, 134.4, 153.2, 205.6 ; IR (neat) cm^{-1}: 1110.2, 1272.5, 1398.1, 1579.2, 1721.5, 2902.3, 3054.5; EI-MS (70eV) *m/z* (rel. intensity, %) 200 (M^+, 100), 201 (28), 183 (15), 157 (35), 143 (16), 129 (35), 128 (18), 127 (29), 126 (13), 115 (35); HRMS (EI, *m*/z): Calcd. for $C_{13}H_{12}O_2$: 200.0837. Found: 200.0838.

2-(1-Naphthalenyloxy)-1-phenylethanone (3b).[5] (12.84 g, 98%) was obtained as colorless crystals, mp 70-71 °C, R_f = 0.63 (ethyl acetate: *n*-hexane = 1: 7), [1] H-NMR ($CDCl_3$, 200 MHz) δ 5.41 (s, 2H, $ArOC\underline{H}_2CC_6H_5$), 6.78 (d, *J* = 7.6 Hz, 1H, ArH), 7.35 (t, *J* = 8.2 Hz, 1H, ArH), 7.47-7.56 (m, 2H, $ArOCH_2CC_6\underline{H}_5$), 7.58-7.66 (m, 4H, ArH, $ArOCH_2C$- $C_6\underline{H}_5$), 7.80-7.85 (m, 1H, ArH), 8.04-8.09 (m, 2H, $ArOCH_2CC_6\underline{H}_5$), 8.37-8.42 (m, 1H, ArH) ; ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 71.2, 105.3, 121.3, 122.2, 125.5, 125.6, 126.6, 127.4, 128.3, 128.8, 133.8, 134.6, 153.8, 154.9, 194.5 ; IR (KBr) cm^{-1}:1122.2, 1217.9, 1395.4, 1579.3, 1704.6, 2902.9, 3059.7 ; EI-MS (70eV) *m/z* (rel. intensity,%) 262 (M^+, 35), 128 (10), 127 (24), 126(10), 115(27), 106 (8), 105 (100), 91 (14), 77 (52), 51 (16); HRMS (EI, *m*/z): Calcd. for $C_{18}H_{14}O_2$: 262.0994. Found: 262.0993.

1-(4-Methoxyphenyl)-2-(1-naphthalenyloxy)ethanone (**3c**).[6] (13.49 g, 92%) was obtained as colorless crystals, mp 77-78 °C, R_f = 0.47 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.86 (s, 3H, OCH_3), 5.34 (s, 2H, $ArOCH_2CO$), 6.77 (d, *J* = 7.6 Hz, 1H, ArH), 6.95 (dt, *J* =9.6, 2.8 Hz, 2H, ArH), 7.33 (t, *J* = 8.0 Hz, 1H, ArH), 7.44-7.52 (m, 3H, ArH), 7.79 (dt, *J* = 6.8, 2.4 Hz, 1H, ArH), 8.05 (dt, *J* = 9.6, 2.8 Hz, 2H, ArH), 8.34-8.36 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 55.5, 71.2, 105.2, 114.0, 121.2, 122.1, 125.4, 125.6, 126.5, 127.4, 127.7, 130.7, 134.5, 153.8, 164.0, 193.2; IR (KBr) cm^{-1}:1121.9, 1178.7, 1228.4, 1395.2, 1598.0, 1687.5, 2913.2, 3052.2 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 292 (M^+,68), 149 (7), 136 (24), 135 (100), 121(14), 115 (8), 77 (17), HRMS (EI, *m*/z): Calcd. for $C_{19}H_{16}O_3$: 292.1099. Found: 292.1120.

General procedure for the preparation of 1-[2-(substituted)allyloxy]naphthalene (4a-c)

Under dry nitrogen, methyltriphenylphosphonium bromide (10.72 g, 30.0 mmol) suspended in dry THF (100 mL) was cooled to 0 °C. To this cooled suspension, *t*-BuO^-K^+ (3.64 g, 32.5 mmol) was added in portions and the mixture was stirred at 0 °C for 30 min. After which time, 1-substituted-2-(1-naphthalenyloxy)ethanone (**3a-c**) (25.0 mmol) in anhydrous THF (50 mL) was added, and the mixture was left stirring for 3 h at 0 °C. Then, the resulting mixture was quenched with saturated NH_4Cl solution and extracted with dichloromethane (50 mL x 3). The organic layers were combined, washed with brine, and then dried with anhydrous magnesium sulfate. After filtration, the filtrate was concentrated *in vacuo* to remove the solvent. The

resulting residue was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 1: 10) to give pure **4a-e**, respectively.

1-(2-Methyallyloxy)naphthalene (4a).[7] (4.85 g, 98%) was obtained as colorless liquid, R_f= 0.89 (ethyl acetate: *n*-hexane = 1: 7); [1] H-NMR ($CDCl_3$, 400 MHz) δ 1.88 (s, 3H, CH_3), 4.55 (s, 2H, $OC\underline{H}_2COCH_3$), 5.02 (d, *J* =1.2 Hz, 1H, $OCH_2C=C\underline{H}_aH_b$), 5.19 (d, *J* =1.2 Hz, 1H, $OCH_2C=CH_a\underline{H}_b$), 6.75 (d, *J* = 7.6 Hz, 1H, ArH), 7.31 (t, *J* = 8.0 Hz, 1H, ArH), 7.39 (d, *J* = 8.4 Hz, 1H, ArH), 7.43-7.47 (m, 2H, ArH), 7.74-7.81 (m, 1H, ArH), 8.30-8.33 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 19.6, 71.8, 105.0, 112.6, 120.3, 122.1, 125.2, 125.8, 125.8, 126.4, 127.5, 134.5, 140.9, 154.4; EI-MS (70eV) *m/z* (rel. intensity, %) 198 (M^+, 100), 199 (18), 183(59), 165 (16), 157 (9), 156 (11), 155 (32), 153 (15), 129 (14), 128 (22); HRMS (EI, *m*/z): Calcd. for $C_{14}H_{14}O$: 198.1045. Found: 198.1048.

1-(2-Phenylallyloxy)naphthalene (4b).[8] (6.32 g, 98%) was obtained as colorless liquid, R_f = 0.83 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.91 (s, 2H, $ArOC\underline{H}_2CC_6H_5$), 5.50 (d, *J* = 0.8 Hz, 1H, $ArOCH_2C=C\underline{H}_aH_b$), 5.58 (d, *J* = 0.8 Hz, 1H, $ArOCH_2C=CH_a\underline{H}_b$), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 7.20-7.45 (m, 9H, ArH, $ArOCH_2C$- $C_6\underline{H}_5$), 7.70-7.72 (m, 1H, ArH), 8.23-8.25 (m, 1H, ArH) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 69.8, 105.1, 114.6, 120.5, 122.1, 125.2, 125.7, 126.0, 126.4, 127.4, 127.9, 128.4, 134.5, 138.3, 142.9, 154.2 ; EI-MS (70eV) *m/z* (rel. intensity,%) 260 (M^+, 100), 261 (21), 259 (27), 246 (11), 245 (47), 217 (27), 215 (12), 129 (22), 128 (29), 77 (14); HRMS (EI, *m*/z): Calcd. for $C_{19}H_{16}O$: 260.1201. Found: 260.1205.

1-[2-(4-Methoxyphenyl)allyloxy]naphthalene (**4c**) (6.79 g, 93%) was obtained as colorless liquid, R_f = 0.72 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.71 (s, 3H, OCH_3), 4.96 (s, 2H, $ArOC\underline{H}_2$), 5.45 (d, *J* = 1.2 Hz, 1H, $R_1R_2C=C\underline{H}_aH_b$), 5.96, (d, *J* = 1.2 Hz, 1H, $R_1R_2C=CH_a\underline{H}_b$), 6.78-6.86 (m, 3H, ArH), 7.28-7.46 (m, 6H, ArH), 7.73-7.77 (m, 1H, ArH), 8.21-8.26 (m, 1H, ArH), ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 55.1, 70.0, 105.1, 113.0, 113.7, 120.4, 122.1, 125.2, 125.7, 126.3, 127.1, 127.3, 130.7, 134.5, 142.2, 154.3, 159.4; EI-MS (70 eV) *m/z* (rel. intensity, %): 290 (M^+, 100), 276 (12), 275 (6), 274 (15), 247 (5), 246 (7), HRMS (EI, *m*/z): Calcd. for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1285.

General procedure for the preparation of 2-(2-substituted allyl)-1-naphthol (5a-c)

Under the protection of dry nitrogen, 1-(2-substituted allyloxy)naphthalene (**4a-c**) (23.0 mmol) in decalin (30 mL) was heated to 185-190 ^{o}C for 2.5 h. The reaction mixture was distilled off the solvent by Kugehror apparatus at 4 mm Hg. The resulting residue was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 1: 10) to give pure **5a-c**, respectively.

2-(2-Methylallyl)-1-naphthol (5a).[7](3.97 g, 87%) was obtained as colorless liquid, R_f = 0.58 (ethyl acetate: *n*-hexane = 1: 7), [1] H-NMR ($CDCl_3$, 400 MHz) δ 1.75 (s, 3H, CH_3), 3.53 (s, 2H, $ArC\underline{H}_2C=CH_2$), 4.98 (d, *J* = 1.2 Hz, 1H, $ArCH_2C=C\underline{H}_aH_b$), 4.99 (d, *J* = 1.2 Hz, 1H, $ArCH_2C=CH_a\underline{H}_b$), 5.77 (s, 1H, OH), 7.20 (d, *J* = 8.8 Hz, 1H, ArH), 7.39 (d, *J* = 8.4 Hz, 1H, ArH), 7.42-7.48 (m, 2H, ArH), 7.76-7.78 (m, 1H, ArH), 8.17-8.20 (m, 1H, ArH) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 22.0, 40.7, 112.8, 117.6, 120.1, 121.5, 124.9, 125.2, 125.8, 127.4, 129.0, 133.8, 144.7,

150.1 ; EI-MS (70eV) *m/z* (rel. intensity,%) 198 (M^+, 100), 199 (16), 183 (77), 165 (26), 156 (16), 155 (50), 153 (25), 152 (13), 129 (23), 128 (44); HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{14}O$: 198.1045. Found: 198.1043.

2-(2-Phenylallyl)-1-naphthol (5b). (5.38 g, 90%) was obtained as colorless crystals, mp 114-115 °C, R_f = 0.66 (ethyl acetate: *n*-hexane = 1: 7); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.95 (s, 2H, $ArC\underline{H}_2C=CH_2$), 5.08 (s, 1H, ArOH), 5.53 (d, *J* = 0.8 Hz, 1H, $ArCH_2C=C\underline{H}_aH_b$), 5.57 (d, *J* = 0.8 Hz, 1H, $ArCH_2C=CH_a\underline{H}_b$), 7.23 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.31 (m, 3H, ArH, $ArCH_2CC_6\underline{H}_5$), 7.37 (d, *J* = 8.4 Hz, 1H, ArH), 7.39-7.48 (m, 4H, ArH, $ArCH_2CC_6\underline{H}_5$), 7.73-7.75 (m, 1H, ArH), 8.13-8.16 (m, 1H, ArH) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 37.0, 114.3, 117.9, 120.4, 121.3, 124.8, 125.2, 125.8, 126.0, 127.5, 127.9, 128.4, 128.8, 133.7, 140.1, 145.8, 149.5 ; EI-MS (70eV) *m/z* (rel. intensity,%) 260 (M^+,100), 261 (21), 259 (28), 245 (51), 217 (34), 215 (17), 129 (34), 128 (54), 127 (19), 77 (20); HRMS (EI, *m*/*z*): Calcd. for $C_{19}H_{16}O$: 260.1201, Found: 260.1204.

2-[2-(4-Methoxyphenyl)allyl]-1-naphthol (5c). (5.34 g, 80%) was obtained as colorless crystals, mp 123-124 °C, R_f = 0.53 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.75 (s, 3H, OCH_3), 3.95 (s, 2H, $ArC\underline{H}_2C(Ar_1)=CH_2$), 5.06 (d, *J* = 0.8 Hz, 1H, $ArCH_2C(Ar_1)=C\underline{H}_aH_b$), 5.48 (d, *J* = 0.8 Hz, 1H, $ArCH_2C(Ar_1)=CH_a\underline{H}_b$), 5.65 (s, 1H, ArOH), 6.82 (dt, *J* = 9.6, 2.8 Hz, 2H, ArH), 7.22 (d, *J* = 8.0 Hz, 1H, ArH), 7.38 (d, *J* = 8.0 Hz, 1H, ArH), 7.39-7.46 (m, 4H, ArH), 7.74-7.76 (m, 1H, ArH), 8.14-8.16 (m, 1H, ArH), ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 37.3, 55.2, 112.7, 113.7, 117.9, 120.3, 121.4, 124.8, 125.2, 125.7, 127.2, 127.5, 128.9, 132.3, 133.7, 145.2, 149.7, 159.4; EI-MS (70 eV) *m/z* (rel. intensity, %): 290 (M^+,100), 276 (11), 275 (52), 247 (23), 215 (10), 202 (10), 181(14), 128 (13); HRMS (EI, *m*/*z*): Calcd. for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1285.

General procedure for the preparation of 1-allyloxy-2-[2-(substituted)allyl]naphtha- lene (6a-c)

Under the protection of dry nitrogen, to 2-[2-(substituted)allyl]-1-naphthol 20.0 mmol (**5a-c**) dissolved in dry acetone (120 mL) was added K_2CO_3 (3.87 g, 28.0 mmol) and allyl bromide (2.90 g, 24.0 mmol). The reaction mixture was heated at reflux for 4 h. After cooling to room temperature, the reaction mixture was filtered to remove the solid. The filtrate which was obtained was concentrated *in vacuo* to remove the solvent. The residue which was obtained was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 10) to give pure **6a-c**, respectively.

1-Allyloxy-2-(2-methylallyl)naphthalene (6a). (3.40 g, 95%) was obtained as a colorless liquid, R_f = 0.90 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.74 (s, 3H, CH_3), 3.53 (s, 2H, $ArC\underline{H}_2C=CH_2$), 4.47 (dt, *J* = 5.2, 1.6 Hz, 2H, $ArOC\underline{H}_2CHCH_2$), 4.68 (d, *J* = 1.2 Hz, 1H, $ArCH_2C=C\underline{H}_aH_b$), 4.84 (d, *J* = 1.2 Hz, 1H, $ArCH_2C=CH_a\underline{H}_b$), 5.29 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 1H, $ArOCH_2CH=C\underline{H}_aH_b$), 5.50 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, $ArOCH_2CH=CH_a\underline{H}_b$), 6.18 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $ArOCH_2C\underline{H}=CH_2$), 7.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.39-7.48 (m, 2H, ArH), 7.54 (d, *J* = 8.4 Hz, 1H, ArH), 7.77-7.79 (m, 1H, ArH), 8.08-8.10 (m, 1H, ArH); ^{13}C-NMR

($CDCl_3$, 100 MHz) δ 22.6, 37.9, 75.2, 112.0, 117.1, 122.1, 123.8, 125.5, 125.8, 127.9, 128.0, 128.3, 128.4, 133.9, 134.0, 144.9, 152.6; EI-MS (70eV) *m/z* (rel. intensity, %) 238 (M^+, 100), 239 (21), 223(21), 195(32), 182(41), 181(60), 165(50), 153(38), 152(26), 141(23); HRMS (EI, *m*/*z*): Calcd. for $C_{17}H_{18}O$: 238.1358. Found: 238.1356.

1-Allyloxy-2-(2-phenylallyl)naphthalene (6b). (5.42 g, 95%) was obtained as a colorless liquid, R_f = 0.86 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.03 (s, 2H, $ArC\underline{H}_2C{=}CH_2$), 4.50 (dt, *J* = 5.2, 1.6 Hz, 2H, $ArOC\underline{H}_2CH{=}CH_2$), 4.94 (d, *J* = 1.2 Hz, 1H, $ArCH_2C{=}C\underline{H}_aH_b$), 5.27 (ddt, *J* = 10.4, 1.6, 1.6, Hz, 1H, $ArOCH_2CH{=}C\underline{H}_aH_b$), 5.48 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H, $ArOCH_2CH{=}CH_a\underline{H}_b$), 5.49 (d, *J* = 1.2 Hz, 1H, $ArCH_2C{=}CH_a\underline{H}_b$), 6.17 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, $ArOCH_2C\underline{H}{=}CH_aH_b$), 7.16-7.28 (m, 3H, ArH, $ArCH_2CC_6\underline{H}_5$), 7.31 (d, *J* = 8.8 Hz, 1H, ArH), 7.38-7.52 (m, 5H, ArH, $ArCH_2CC_6\underline{H}_5$), 7.74-7.77 (m, 1H, ArH), 8.09-8.11 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 35.1, 75.2, 114.4, 117.3, 122.2, 123.9, 125.6, 125.8, 126.0, 127.5, 127.8, 127.9, 128.2, 128.3, 128.4, 133.9, 133.9, 140.9, 147.0, 152.5 ; EI-MS (70eV) *m/z* (rel.intensity,%) 300 (M^+, 100), 301 (24), 285 (15), 244 (16), 182 (13), 181 (26), 165 (22), 153 (17), 152 (19), 115(14); HRMS (EI, *m*/*z*): Calcd. for $C_{22}H_{20}O$: 300.1514, Found: 300.1516.

1-Allyloxy-2-[2-(4-methoxyphenyl)allyl]naphthalene (6c). (5.87 g, 89%) was obtained as a colorless liquid, R_f = 0.75 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H, CH_3), 3.99 (s, 2H, CH_2), 4.50 (dt, *J* = 5.2, 1.6 Hz, 2H, $ArOC\underline{H}_2CH{=}CH_2$), 4.88 (d, *J* = 1.2 Hz, 1H, $R_1R_2C{=}C\underline{H}_aH_b$), 5.25-5.29 (m, 1H, $ArOCH_2CH{=}C\underline{H}_aH_b$), 5.43 (d, *J* = 1.2 Hz, 1H, $R_1R_2C{=}CH_a\underline{H}_b$), 5.46-5.51 (m, 1H, $ArOCH_2CH{=}CH_a\underline{H}_b$), 6.12-6.22 (m, 1H, $ArOCH_2C\underline{H}{=}CH_2$), 6.77 (dt, *J* = 6.8, 2.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.8 Hz, 1H, ArH), 7.36-7.46 (m, 4H, ArH) 7.49 (d, *J* = 8.4 Hz, 1H, ArH), 7.74 (d, *J* = 8.0 Hz, 1H, ArH), 8.10 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 35.1, 55.0, 75.1, 112.7, 113.5, 117.3, 122.1, 123.9, 125.5, 125.8, 127.0, 127.8, 127.9, 128.2, 128.3, 133.1, 133.8, 133.9, 146.0, 152.4 159.0; EI-MS (70 eV) *m/z* (rel. intensity, %): 330 (M^+,100), 329 (6), 316 (8), 315 (31), 289 (14), 287 (5), 274 (16), 181(8); HRMS (EI, *m*/*z*): Calcd. for $C_{23}H_{22}O_2$: 330.1620. Found: 330.1632.

General procedure for the preparation of 4-substituted-2,5-dihydro-1-naphthoxepine (7a-c)

1-Allyloxy-2-[2-(substituted)allyl]naphthalene (**6a-c**) (2.0 mmol) dissolved in dichloro- methane (200 mL) was stirred and Grubbs' catalyst (II) (0.085 g, 5% mol) added under the protection of dry nitrogen. The reaction mixture was continually stirred at room temperature **(7a)** for 10 min., **(7b)** and **(7c)** for 24 h until the consumption of starting material as monitored by TLC. After filtration, the filtrate was concentrated in *vacuo* to remove the solvent. The resulting residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 50) to give pure **7a-c**, respectively.

4-Methyl-2,5-dihydro-1-naphthoxepine (7a). (0.40 g, 95%) was obtained as a colorless liquid, R_f = 0.90 (ethyl acetate: *n*-hexane = 1: 7); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.85 (d, *J* = 1.6 Hz, 3H, $ArOCH_2CH{=}CRC\underline{H}_3$), 3.55 (s, 2H, $ArOCH_2CH{=}C(CH_3)C\underline{H}_2$), 4.63 (each 1 H, dd, *J* = 3.6, 3.6 Hz, 2H, $ArOC\underline{H}_a\underline{H}_bCH{=}CR$), 5.30 (tq, *J* = 3.6, 1.6 Hz, 1H, $ArOCH_2C\underline{H}{=}CR$), 7.15 (d, *J* = 8.4

Hz, 1H, ArH), 7.37-7.47 (m, 3H, ArH), 7.76 (dd, *J* = 8.4, 1.2 Hz, 1H, ArH), 8.17 (dd, *J* = 7.6, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 26.1, 37.4, 69.4, 121.3, 121.5, 122.8, 125.5, 125.7, 127.5, 127.6, 127.7, 128.7, 133.7, 134.5, 153.3; EI-MS (70 eV) *m/z* (rel. intensity, %): 210 (M^+,62), 209 (30), 196 (15), 195 (100), 194 (14), 165 (15), 128 (11); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{14}O$: 210.1045. Found: 210.1049.

4-Phenyl-2,5-dihydro-1-naphthoxepine (7b). (0.33 g, 60%) was obtained as colorless crystals, R_f = 0.85 (ethyl acetate: *n*-hexane = 1: 7); mp 95-96 ^oC, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.13 (s, 2H, $ArOCH_2CH=CRC\underline{H}_2$), 4.93 (each 1 H, dd, *J* = 3.6, 3.6 Hz, 2H, $ArOC\underline{H}_a\underline{H}_bCH=CR$), 5.79 (t, *J* = 3.6 Hz, 1H, $ArOCH_2C\underline{H}CR$), 7.27 (d, *J* = 10.8 Hz, 1H, ArH), 7.26-7.32 (m, 1H, $ArOCH_2CH=CRAr\underline{H}$), 7.35-7.47 (m, 4H, $ArOCH_2CH=CRAr\underline{H}$), 7.48-7.56 (m, 3H, ArH), 7.84 (d, *J* = 8.0 Hz, 1H, ArH), 8.24 (dd, *J* =8.4, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 35.9, 69.6, 121.5, 123.1, 124.9, 125.7, 125.9, 126.0, 127.1, 127.5, 127.6, 127.7, 128.4, 129.2, 133.9, 138.6, 143.9, 153.2 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 272 (M^+, 55), 271 (49), 258 (21), 57 (100), 253 (15), 228 (17), 195 (26); HRMS (EI, *m*/*z*): Calcd. for $C_{20}H_{16}O$: 272.1201. Found: 272.1209.

4-(4-Methoxyphenyl)-2,5-dihydro-1-naphthoxepine (7c). (0.36 g, 60%) was obtained as a colorless liquid, R_f =0.72 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.79 (s, 3H, $ArOCH_3$), 4.06 (s, 2H, $ArOCH_2CH=CRC\underline{H}_2$), 4.88 (each 1 H, dd, *J* = 3.6, 3.6 Hz, 2H, $ArOC\underline{H}_a\underline{H}_bCH=CR$), 5.71 (t, *J* = 3.6 Hz, 1H, $ArOCH_2C\underline{H}=CR$), 6.87 (dd, *J* = 6.8, 2.0 Hz, 2H, ArH), 7.25 (d, *J* = 8.4 Hz, 1H, ArH), 7.33 (dd, *J* = 6.8, 2.0 Hz, 2H, ArH), 7.41-7.51 (m, 3H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H ,ArH), 8.21 (dd, *J* = 8.4, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 36.0 ,55.3, 69.4, 113.7, 121.5, 122.9, 123.3, 125.6, 125.8, 127.1, 127.5, 127.6, 127.7, 128.7, 133.8, 136.3, 138.4, 153.1, 158.8 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 302 (M^+, 38), 301(14), 288 (22), 287 (100), 272 (8), 244 (12); HRMS (EI, *m*/*z*): Calcd. for $C_{21}H_{18}O_2$: 302.1307. Found: 302.1300.

General procedure for the preparation of 1-allyloxynaphthalenes (9a-b)

Under the protection of nitrogen, to a solution of 1-naphthol (**1**) (7.21 g, 50.0 mmol) dissolved in dry acetone (150 mL) was added K_2CO_3 (9.67 g, 70.0 mmol) followed by crotyl chloride (**8a**) or cinnamyl chloride (**8b**) (60.0 mmol), respectively. The reaction mixture was heated at reflux for 3-4 h, monitored by TLC. After cooling to room temperature, the reaction mixture was filtered to remove the solid. The filtrate which was obtained was concentrated *in vacuo* to remove the solvent. The resulting residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 10) to provide pure **9a-b**, respectively.

1-(2*E*-Butenyloxy)naphthalene (9a).[9] (9.14 g, 92%) was obtained as a colorless liquid, R_f = 0.75 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.72 (dd, *J* = 3.6, 1.2 Hz, 3H, $ArOCH_2CH=CHC\underline{H}_3$), 4.52 (dd, *J* = 5.6, 1.2 Hz, 2H, $ArOC\underline{H}_2CH=CHCH_3$), 5.73-5.89 (m, 2H, $ArOCH_2C\underline{H}= C\underline{H}CH_3$), 6.70 (d, *J* = 7.2 Hz, 1H, ArH), 7.27-7.49 (m, 4H, ArH), 7.73 (dt, *J* = 9.6, 2.8 Hz, 1H, ArH), 8.28-8.32 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.8, 68.7, 104.9, 120.1, 122.1, 125.0, 125.8, 126.1, 126.3, 126.3, 127.3, 129.8, 134.5, 154.4 ; EI-MS (70

eV) *m/z* (rel. intensity, %): 198 (M^+,100), 183 (95), 157 (58), 145 (50), 144 (94), 116 (52), 115 (52); HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{14}O$: 198.1045. Found: 198.1046.

1-(*3E*-Phenylallyloxy)naphthalene (9b).[10] (11.64 g, 90%) was obtained as a colorless liquid, R_f = 0.71 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.89 (dd, *J* = 5.6, 1.6 Hz, 2H, ArOC$\underline{H}_2$CH=CHC$_6$H$_5$), 6.54 (dt, *J* = 16.0, 5.6 Hz, 1H, ArOCH$_2$C$\underline{H}$=CHC$_6$H$_5$), 6.81-6.87 (m, 1H, ArOCH$_2$CH=C$\underline{H}$C$_6$H$_5$), 6.89 (d, *J* = 7.2 Hz, 1H, ArH), 7.25-7.52 (m, 9H, ArH), 7.79-7.82 (m, 1H, ArH), 8.33-8.36 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 68.9, 105.2, 120.4, 122.1, 124.6, 125.2, 125.8, 126.4, 126.6, 127.5, 127.9, 128.6, 132.8, 134.6, 136.5, 154.4 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 260(M^+,100), 259(50), 245(54), 217(29), 215(24), 181(22), 153(17), 128(18); HRMS (EI, *m*/*z*): Calcd. for $C_{19}H_{16}O$: 260.1201, Found: 260.1200.

General procedure for the preparation of 2-allyl-1-naphthols (10a-b)

Under the protection of dry nitrogen, 1- allyloxynaphthalenes (**9a-b**) (23.0 mmol) in decalin (30 mL) was heated to 185-190^{o}C for 2.5 hr for **10a**, and 0.75 hr for **10b**, respectively. The reaction mixture which was obtained was distilled off the solvent by Kugehror apparatus at 4 mmHg. The resulting residue was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 1: 10) to give pure **10a-b**, respectively.

2-(1-Methylallyl)-1-naphthol (10a).[9] (6.34 g, 80%) was obtained as a colorless liquid, R_f = 0.39 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.43 (d, *J* = 6.8 Hz, 3H, ArCH(C$\underline{H}_3$)CH=CH$_2$), 3.68-3.75 (m, 1H, ArC$\underline{H}$(CH$_3$)CH=CH$_2$), 5.21-5.27 (m, 2H, ArCH-(CH$_3$)CH=C$\underline{H}_2$), 5.77 (s, 1H, ArOH), 6.12 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H, ArCH-(CH$_3$)C$\underline{H}$=CH$_2$), 7.22 (d, *J* = 8.4 Hz, 1H, ArH), 7.38-7.44 (m, 3H, ArH), 7.72-7.75 (m, 1H, ArH), 8.15-8.17 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 18.5, 38.5, 114.9, 120.4, 121.4, 122.8, 125.0, 125.2, 125.7, 126.1, 127.4, 133.4, 142.1, 148.9 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 198 (M^+,100), 184 (73), 183 (100), 165 (28), 155 (47), 154 (17), 153 (30), 151 (21); HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{14}O$: 198.1045. Found: 198.1047.

2-(1-Phenylallyl)-1-naphthol (10b).[9] (8.11 g, 78%) was obtained as a colorless liquid, R_f = 0.67 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.09 (br d, *J* = 6.8 Hz, 1H, ArC$\underline{H}$(C$_6$H$_5$)CH=CH$_2$), 5.13 (ddd, *J* = 16.8, 1.6, 1.6 Hz, 1H, ArCH(C$_6$H$_5$)CH=C$\underline{H}_a$H$_b$), 5.40 (ddd, *J* = 10.4, 1.6, 1.6 Hz, 1H, ArCH(C$_6$H$_5$)CH=CH$_a\underline{H}_b$), 5.53 (s, 1H, ArOH), 6.46 (ddd, *J* = 16.8, 10.0, 6.4 Hz, 1H, ArCH(C$_6$H$_5$)C$\underline{H}$=CH$_2$), 7.21 (d, *J* = 8.4 Hz, 1H, ArH), 7.26-7.39 (m, 5H, ArCH(C$_6\underline{H}_5$)CH=CH$_2$), 7.43-7.51 (m, 3H, ArH), 7.80-7.82 (m, 1H, ArH), 8.16-8.19 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 50.1, 117.6, 120.4, 121.5, 121.8, 125.1, 125.3, 126.0, 127.1, 127.4, 127.5, 128.6, 128.9, 133.7, 139.1, 141.0, 149.0 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 260 (M^+,100), 259 (44), 245 (56), 231(23), 217 (37), 215 (25), 202 (25), 181 (20); HRMS (EI, *m*/*z*): Calcd. for $C_{19}H_{16}O$: 260.1201. Found: 260.1203.

4-(3-Phenylallyl)-1-naphthol (10c). (1.25 g, 12%) was obtained as a yellowish brown liquid, R_f = 0.33 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.91 (d, *J* = 5.2 Hz, 2H, ArC$\underline{H}_2$CH=CH), 5.25 (s, 1H, ArOH), 6.43 (d, *J* = 16.0 Hz, 1H, ArCH$_2$CH =C$\underline{H}$), 6.49 (dt, *J* = 16.0, 5.2 Hz, 1H, ArCH$_2$C$\underline{H}$=CH), 6.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.15-7.37 (m, 6H,

$ArCH_2CH=CHC_6\underline{H}_5$, ArH), 7.48-7.55 (m, 2H, ArH), 8.01-8.04 (m, 1H, ArH), 8.22-8.25 (m, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 36.0, 108.2, 122.2, 124.1, 124.8, 125.0, 126.1, 126.2, 126.5, 127.0, 128.5, 128.7, 129.3, 131.0, 133.0, 137.5, 150.4 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 260 (M^+, 100), 182 (24), 181 (32), 170 (27), 169 (66), 141 (24), 128 (24), 115 (35). HRMS (EI, *m*/*z*): Calcd. for $C_{19}H_{16}O$: 260.1201. Found: 260.1200.

General procedure for the preparation of 2-Allyl-1-allyloxy-naphthalenes (11a-b)

Under the protection of nitrogen, to a solution of 2-allyl-1-naphthol (**10a-b**) (5.52 g, 30.0 mmol) dissolved in dry acetone (120 mL) was added K_2CO_3 (5.80 g, 42.0 mmol) followed by addng allyl bromide (4.35 g, 36.0 mmol). The reaction mixture was heated to reflux for 3-4 h and monitored by TLC. After cooling to room temperature, the reaction mixture was filtered to remove the solid. The filtrate which was obtained was concentrated *in vacuo* to remove the solvent. The resulting residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 10) to provide pure **11a-b**, respectively.

1-Allyloxy-2-(1-methylallyl)naphthalene (11a).[9] (6.18 g, 92%) was obtained as a colorless liquid, R_f = 0.76, (ethyl acetate: *n*- hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.48 (d, *J* = 4.8 Hz, 3H, $ArCH(C\underline{H}_3)CH=CH_2$), 4.27-4.30 (m, 1H, $ArC\underline{H}(CH_3)CH=CH_2$), 4.59 (ddd, *J* = 5.6, 2.8, 1.2 Hz, 2H, $ArOC\underline{H}_2CH=CH_2$), 5.13-5.19 (m, 2H, $ArCH(CH_3)$ $CH=C\underline{H}_2$), 5.41 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H, $ArOCH_2CH=C\underline{H}_aH_b$) 5.61 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H, $ArOCH_2CH=CH_a\underline{H}_b$), 6.13-6.21 (m, 1H, $ArOCH_2C\underline{H}=CH_2$), 6.25-6.34 (m, 1H, $ArCH(CH_3)C\underline{H}=CH_2$), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H, ArH), 7.48-7.58 (m, 2H, ArH), 7.68 (d, *J* = 8.8 Hz, 1H, ArH), 7.87 (dt, *J* = 8.4, 0.8 Hz, 1H, ArH), 8.18 (dt, *J* = 8.4, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 20.5, 35.3, 75.6, 113.4, 117.3, 122.2, 124.3, 125.6, 125.6, 125.9, 127.9, 128.2, 133.6, 133.7, 133.9, 143.0, 151.3; EI-MS (70 eV) *m/z* (rel. intensity, %): 238 (M^+,100), 223 (22), 196 (16), 194 (12), 182 (18), 181 (31), 179 (15), 165 (11); HRMS (EI, *m*/*z*): Calcd. for $C_{17}H_{18}O$: 238.1358, Found: 238.1356.

1-Allyloxy-2-(1-phenylallyl)naphthalene (11b). (8.19 g, 91%), was obtained as a colorless liquid, R_f = 0.73 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.44-4.59 (m, 2H, $ArOC\underline{H}_2CH=CH_2$), 5.08-5.16 (m, 1H, $ArC\underline{H}$ $(C_6H_5)CH=CH_2$), 5.34-5.41 (m, 2H, $ArCH(C_6H_5)CH=C\underline{H}_2$), 5.57 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 1H, $ArOCH_2CH=C\underline{H}_aH_b$), 5.60 (ddt, *J* = 16.0, 1.6, 1.6 Hz, 1H, $ArOCH_2CH=CH_a\underline{H}_b$), 6.21-6.32 (m, 1H, $ArOCH_2C\underline{H}=CH_2$), 6.41-6.50 (m, 1H, $ArCH(C_6H_5)C\underline{H}=CH_2$), 7.25-7.29 (m, 1H, ArH), 7.35-7.38 (m, 5H, $ArCH(C_6\underline{H}_5)$ $CH=CH_2$), 7.50-7.59 (m, 2H, ArH), 7.66 (d, *J* = 8.8 Hz, 1H, ArH), 7.88 (d, *J* = 8.0 Hz, 1H, ArH), 8.20 (d, *J* = 8.0 Hz, 1H, ArH), ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 47.1, 75.4, 116.8, 117.2, 122.3, 124.2, 125.8, 125.9, 126.2, 127.2, 127.9, 128.3, 128.5, 131.5, 133.8, 133.8, 140.5, 143.2, 152.1 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 300 (M^+, 100), 298 (25), 259 (63), 209 (59), 207 (20), 182 (20), 181 (51), 165 (24); HRMS (ESI, *m*/*z*): Calcd. for $C_{22}H_{20}ONa$: 323.1412, Found: 323.1415.

General procedure for the preparation of 5-substituted 2,5-dihydro-1-naphthoxepines (12a-b)

Under the protection of dry nitrogen, 2-allyl-1-allyloxy-naphthalenes (**11a-c**) (2.0 mmol) dissolved in dichloromethane (200 mL) was stirred and added Grubbs' catalyst (II) (0.085 g, 5% mol. The reaction mixture was continually stirred at room temperature for 24 h until the consumption of starting material which was monitored by TLC. After filtration, the filtrate was concentrated in *vacuo* to remove the solvent. The resulting residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1: 50) to give pure **12a-c**, respectively.

5-Methyl-2,5-dihydro-1-naphthoxepine (12a). (0.38 g, 60%) was obtained as a colorless liquid, R_f = 0.74 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.52 (d, *J* = 7.2 Hz, 3H, ArCH ($C\underline{H}_3$)CH=CH), 3.68-3.72 (m, 1H, ArC$\underline{H}$(CH_3)CH=CH), 4.54-4.76 (m, 2H, ArOC$\underline{H}_2$CH= CH), 5.48-5.52 (m, 1H, ArOCH_2C$\underline{H}$=CH), 5.84-5.90 (m, 1H, OCH=C$\underline{H}$CH(CH_3)Ar), 7.24 (d, *J* = 8.4 Hz, 1H, ArH), 7.41-7.50 (m, 2H, ArH), 7.53 (d. *J* = 8.0 Hz, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 8.20 (dd, *J* = 8.4, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.6, 38.1, 69.7, 121.5, 123.6, 125.6, 125.9, 126.2, 126.3, 127.6, 128.1, 132.2, 133.7, 135.6, 152.7 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 210(M^+,100), 197(13), 196(46), 195.7(59), 195(33), 165(17); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{14}O$: 210.1045. Found: 210.1048.

5-Phenyl-2,5-dihydro-1-naphthoxepine (12b). (0.45 g, 55%) was obtained as a colorless liquid, R_f = 0.68 (ethyl acetate: *n*-hexane = 1: 7), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.62-4.69 (m, 1H, CH=CHC$\underline{H}$(C_6H_5)Ar), 4.86-4.92 (m, 2H, ArOC$\underline{H}_2$CH=CHCH), 5.77-5.82 (m, 1H, ArOCH_2C$\underline{H}$=CHCH), 6.10-6.16 (m, 1H, CH=CHC$\underline{H}$(C_6H_5)Ar), 7.18-7.32 (m, 5H, CH=CHCH-($C_6\underline{H}_5$)Ar), 7.43-7.52 (m, 3H, ArH), 7.54 (d, *J* = 8.8 Hz, 1H, ArH), 7.80 (dd, *J* = 8.8, 1.2 Hz, 1H, ArH), 8.22 (dd, *J* = 8.8, 0.8 Hz, 1H, ArH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 50.1, 69.7, 121.8, 123.7, 125.9, 126.0, 126.4, 127.5, 127.6, 127.9, 128.1, 128.2, 128.5, 129.4, 133.5, 133.9, 143.0, 152.7 ; EI-MS (70 eV) *m/z* (rel. intensity, %): 272 (M^+, 100), 271 (61), 257 (96), 228 (29), 215 (23), 195 (58), 181 (48), 165 (33); HRMS (ESI, *m*/*z*): Calcd. for $C_{20}H_{16}ONa$: 295.1099, Found: 295.1101.

Acknowledgements

Financial support (Grant no., NSC-96-2113-M-037-006) from NSC, Taiwan is grateful.

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