Research Article

Regioselective 5-*exo*-Trig Heterocyclization of 2-Allyl-1-naphthols under the Influence of *N*-Iodosuccinimide or Molecular Iodine in Aqueous Micelle

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Regioselective iodocyclization of a series of allylhydroxy naphthalene precursors involving *N*-iodosuccinimide and environment friendly green approach associated with surfactant-promoted molecular-iodine-mediated 5-*exo*-trig cyclization strategies has been explored.

1. Introduction

Heterocyclic compounds, the vital building blocks in organic synthesis, are omnipresent in various natural products and bioactive compounds [1–4]. In general, heterocyclic compounds containing naphthalene moiety are well known for their antimicrobial activities, HIV-1 integrase inhibitory effect, anti-inflammatory activity, inhibition of protein tyrosine kinases, and inactivation of enveloped viruses [5–15]. Over the years, organic chemists are actively involved in the syntheses of oxygen, nitrogen, and sulphur containing benzofuran and benzopyran heterocycles [16–20], with different reagents such as *N*-iodosuccinimide [21–24], pyridine hydrotribromide [25–27], hexamethylenetetramine hydrotribromide [28], and mercuric acetate [29, 30] and, subsequently, several new methodologies have been revealed.

In recent years, there has been a flurry of reports for the synthesis of a large number of biologically active heterocycles [31–35] via molecular-iodine-mediated iodocyclization reactions as iodine is inexpensive, easily available, and nontoxic in nature, and additionally iodonium-annulated heteroannulations are extremely effective because they offer an alternative pathway and as a result of which the synthesis of complex molecules, which are not always accessible by the use of common organometallic reagents, becomes easier.

Previously, Majumdar *et al.* explored the $\text{SnCl}_4\text{-I}_2$ mediated regioselective 6-*endo* and 5-*exo* cyclization of a number of *ortho*-allylenols [36], *ortho*-cyclohexenyl phenol, and *ortho*-cyclohexenyl enol systems [37] involving temperature-dependent ring closure, and they also synthesized benzoxepine derivatives [38] using highly regioselective, tandem iodocyclization procedure. Molecular-iodine-mediated cyclization has recently been demonstrated for the synthesis of 3,4-dihydro-2*H*-1,4-benzoxazine derivatives [39].

It is very obvious that most of the organic compounds are insoluble or partially soluble in water and therefore it is a big problem to carry out any reaction in aqueous media without using any catalysts or additives or surfactants. Indeed, there are only few attempts, by using additives [40, 41] to achieve iodine-annulated heterocyclization in water media, and the iodocyclization of 2-allyl-1-hydroxy naphthalene was achieved [42] in 42% yield under heating at 50°C. Iodocyclization of 2-allyl-1-hydroxy naphthalene was carried out in presence of iodine and sodium bicarbonate using organic solvents such as dichloromethane [43]. The pioneering work of Majumdar and coworkers recently explored [44] surfactant promoted synthesis of angularly fused furano-pyrone/coumarin and quinolone derivatives in aqueous media. Recent literature also revealed [45–50] the surfactant promoted synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one in aqueous medium.

Ortho-Allyl naphthols are important intermediates for our current study, and the [3,3] sigmatropic shift (Claisen rearrangement) of allyl aryl ethers is a convenient route to achieve *ortho*-allyl naphthols.

Our recent research activity in the reagents *N*-iodosuccinimide and surfactant catalyzed iodine annulated heterocyclization in aqueous media prompted us to undertake such studies leading to benzofuran ring systems involving 5-*exo*-trig pathway. In this paper, we will explore the reaction of several substituted allylhydroxy naphthalene precursors with *N*-iodosuccinimide in acetonitrile and also using surfactant-promoted iodine-annulated heterocyclization in aqueous media.

2. Results and Discussion

The requisite precursors **3(a-d)** for this strategy were prepared according to the standard published procedures in the literature [45–47], and another precursor (**3e**) was also prepared using same methodology from the corresponding α -naphthol (**1**) by allylation with cinnamyl bromide followed by Claisen rearrangement in a traditional manner.

We initially attempted the iodocyclization of allylhydroxy naphthalene precursor (**3a**) by using the reagent *N*-iodosuccinimide [21–24] in acetonitrile solvent at 0–5°C under nitrogen atmosphere. It is quite obvious that such iodocyclization may take place either by 5-*exo*-trig or 6-*endo*-trig mode. In case of our present study, we obtained 2-(iodomethyl)-2,3-dihydronaphtho [1,2-*b*]furanderivative (**4a**) involving 5-*exo*-trig mode and the benzofuran ring structure was established unambiguously by spectroscopic data of (**4a**).

The formation of benzofuran moiety in the iodocyclization is further evident from the dehydroiodination of **4a** with alcoholic KOH or DBU in toluene under reflux. From the study of ¹H NMR spectra of the dehydroiodinated product of **4a**, the appearance of a singlet at δ 2.56 for the methyl protons and a singlet at δ 6.48 for the =CH proton obviously proved the presence of benzofuran moiety and supported its structure as **5a**. If the 6-*endo*-trig mode was in operation, the heterocyclization would furnish **4a'** in lieu of **4a** and dehydroiodination would generate **5a'**. The formation of benzofuran ring structure through 5-*exo*-trig heterocyclization was further supported from the experiment that the cyclized product **4b** obtained from **3b** did not undergo any dehydroiodination reaction upon treatment with refluxing alcoholic KOH or DBU in toluene under reflux, as there is no hydrogen in the favourable position so as to undergo dehydroiodination. On the other hand, 6-*endo*-trig cyclization would afford **4b'** which on subsequent dehydroiodination reaction would easily generate **5b'**. Due to the same reason, cyclized product **4c** could not participate in dehydroiodination and **4d** underwent such reaction.

Similar iodocyclization reaction with *N*-iodosuccinimide was also performed with rest of the precursors **3(b-e)** to produce **4(b-e)** involving 5-*exo*-trig pathway.

We then directed our attention towards the reaction of allylhydroxy naphthalene precursors **3(a-e)** with surfactant-promoted molecular-iodine-annulated heterocyclization in

TABLE 1: Optimized reaction conditions for molecular iodine annulated 5-*exo*-trig cyclization of a series of allylhydroxy naphthalene precursors in aqueous micelles using CTAB as surfactant.

Entry	Substrate (3a) mmol	Surfactant (CTAB) mmol	Iodine equiv.	Water mL.	Time (h)	Yield (%) of product (4a)
1	0.5	0.10	0.5	10	3	28
2	0.5	0.10	1.0	10	3	48
3	0.5	0.15	1.0	10	4	51
4	0.5	0.20	1.0	10	5	54
5	0.5	0.25	1.2	10	6	59
6	0.5	0.30	1.4	10	8	86
7	0.5	0.40	1.4	10	10	84
8	0.5	0.40	1.5	10	12	82

TABLE 2: Summarized results of the cyclization strategy in two methods

Entry	Substrate	Product	Yield (%) (Condition A) ^a	Yield (%) (Condition B) ^a
1	3a	4a	76	88
2	3b	4b	70	84
3	3c	4c	73	82
4	3d	4d	71	83
5	3e	4e	74	80

Condition A: substrates **3(a-e)** (0.5 mmol), NIS (0.5 mmol), MeCN, 0°C-r.t., 2 h; Condition B: substrates **3(a-e)** (0.5 mmol), I₂ (1.4 equiv.), CTAB (0.30 mmol), H₂O (10 mL), r.t., 8 h.

^aIsolated yields are reported. (All reactions were performed under the optimized reaction conditions).

aqueous media as it is well established that the reactivity of organic reactions in aqueous medium is greatly increased by the presence of surfactant like hexadecyltrimethylammonium bromide (CTAB) [44].

So we started our reaction by using equimolecular amount of the precursor **3a** (0.5 mmol) and molecular I₂ (0.5 mmol) with CTAB (0.10 mmol), but the yield of the product **4a** was very poor (entry 1, Table 1). We decided to increase the concentration of I₂ keeping CTAB concentration intact and the yield of the product **4a** was increased to 48% when the concentration of the molecular I₂ (1.0 mmol) is doubled (entry 2, Table 1). Then we thought it wise to increase the concentration of CTAB as well to see whether it can increase the yield of **4a** anymore. The best result was obtained by using CTAB (0.30 mmol) and molecular iodine (1.4 equivalent) in water (10 mL) for 8 hours at room temperature (Scheme 1; optimized condition, entry 6, Table 1).

The cyclized products **4(a-e)** obtained in both these methodologies gave the same spot (R_f = 0.45 in petroleum ether-ethyl acetate = 9 : 1) in TLC and are therefore identical. The comparative studies in both methods are summarized in Table 2.

The mechanism for the *N*-iodosuccinimide-mediated cyclization and molecular-iodine-annulated cyclization in water in presence of CTAB as surfactant is described in

SCHEME 1: Iodocyclization of different 2-allylnaphthalene derivatives. *Reagents and conditions:* (i) $R^1R^2C=CR^3-CH_2X$ ($X = Br, Cl$), Me_2CO , K_2CO_3 , NaI , reflux, 6–8 h; (ii) *o*-DCB, reflux, 8–10 h; (iii) *Condition A*: substrates **3(a–e)** (0.5 mmol), NIS (0.5 mmol), $MeCN$ (15 mL), $0^\circ C$ -r.t., 3 h; *Condition B*: substrates **3(a–e)** (0.5 mmol), I_2 (1.4 equiv.), CTAB (0.30 mmol), H_2O (10 mL), r.t., 8 h; (iv) KOH (1.0 mmol), $EtOH$ (5 mL), reflux, 2 h.

Scheme 2 is supposed to follow the electrophilic cyclization pathway. Initially the allylnaphthoxy precursor **3a** may generate the iodonium intermediate **3a'**, which undergoes 5-*exo*-trig cyclization to produce the cyclized product **4a**. On the other hand, the alternative 6-*endo*-trig pathway to produce **4a'** is disfavoured and thus ruled out. The same mechanism is followed throughout the entire series of precursors.

In conclusion, it may be said that two effective methodologies involving *N*-iodosuccinimide and surfactant-promoted molecular-iodine-annulated 5-*exo*-trig heterocyclization have been explored for the regioselective synthesis of 2-(iodomethyl)-2,3-dihydronaphtho [1,2-*b*]furan derivatives, and the benzofuran ring structure for iodocyclization was unambiguously established by the dehydroiodination reaction. The comparative study between these two methods revealed the superior nature of the environment friendly surfactant catalyzed method in aqueous medium as well as from the point of view of its high reaction yields.

3. Experimental

All the reagents were obtained from commercial sources and used as received. Except methanol (which was HPLC-grade), the remaining solvents were dried and distilled before use. Elemental analyses and Mass spectra (ESI+) were performed at the Indian Institute of Chemical Biology, Kolkata. IR spectra were recorded on KBr discs on a Perkin Elmer L 120-000A apparatus ν_{max} (in cm^{-1}). Routine 1H NMR (300, 400 and 500 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker DPX-300, Bruker DPX-400, and Bruker DPX-500 instruments at 298 K. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. In all cases the solvent for the NMR experiments was $CDCl_3$ (99.9%) and the references were $SiMe_4$ [for 1H and $^{13}C\{^1H\}$ NMR experiments]. Silica gel [(100–200, 230–400 mesh), SRL, India] was used for chromatographic separation. Silica gel G [E-Marck (India)] and Silica gel 60F 254 [E-Marck

(Germany)] were used for TLC. Petroleum ether refers to the fraction boiling between 60 and $80^\circ C$.

3.1. Typical Procedure for the Preparation of 1-allyloxy Naphthalene Derivatives 2(a–e). A mixture of α -naphthol **1** (1 mmol), corresponding allyl halide (1.2 mmol) and anhydrous K_2CO_3 (3 g), and NaI (80 mg) were refluxed in anhydrous acetone (50 mL) under nitrogen atmosphere for 6–8 h. The mixture was cooled, filtered, and the solvent was evaporated. The residual mass was extracted with CH_2Cl_2 (2×25 mL), washed with water (2×25 mL), and dried ($MgSO_4$). The solvent (CH_2Cl_2) was removed using rotary evaporator and the residual gummy mass was purified by SiO_2 column chromatography over silica gel (100–200 mesh) using petroleum ether-ethyl acetate (9 : 1) as eluent to furnish the desired 1-allyloxy naphthalene derivatives **2(a–e)**.

3.2. Typical Procedure for the Preparation of Precursors: 2-allyl-naphthalen-1-ol 3(a–e). Compounds **3(a–d)** were prepared according to the literature procedure [45–50]. 1-(Cinnamyloxy)naphthalene (**2e**) (1 mmol) was refluxed in *o*-dichlorobenzene (4 mL) for about 6 h. The mixture was cooled and directly subjected to SiO_2 column chromatography. The desired product 2-(1-phenylallyl)naphthalen-1-ol (**3e**) was obtained in pure form after usual column chromatographic separation using petroleum ether-ethyl acetate (8 : 2) as eluent and compound (**3e**) has identical spectral data as reported previously [51].

3.3. Method (a): General Procedure for the *N*-iodosuccinimide-Mediated Heterocyclization of 3(a–e): Synthesis of 2-(iodomethyl)-2,3-dihydronaphtho[1,2-*b*]furan Derivatives 4(a–e). *N*-Iodosuccinimide (0.113 g, 0.5 mmol) was added to a dry and freshly distilled acetonitrile (15 mL) solution of the compounds **3(a–e)** (0.5 mmol) at $0-5^\circ C$ under argon atmosphere. The reaction mixture was then magnetically stirred for 2 h 30 minutes at $0-5^\circ C$ and then at room

SCHEME 2: Probable mechanistic route for the formation of **4a**.

temperature for further 30 minutes. When all the starting material was consumed (as detected by TLC), acetonitrile was removed from the reaction mixture under reduced pressure. The residual mass was then extracted with EtOAc and was washed with 10% NaHSO₃ solution (3 × 25 mL) and water (3 × 25 mL) and dried (MgSO₄). The final residual mass after removal of the solvent (EtOAc) was subjected to SiO₂ column chromatography using petroleum ether-ethyl acetate (9:1) as eluent to give 5-*exo*-trig cyclized products **4(a–e)**.

To scale up the procedure, the substrate **3a** (1 g, 5.43 mmol) was dissolved in dry and freshly distilled acetonitrile (30 mL) solution, and *N*-Iodosuccinimide (1.23 g, 5.43 mmol) was added at 0–5°C under argon atmosphere. The same procedure as utilized before and the usual column chromatography furnished **4a** (1.28 g) in 76% yield.

3.4. Method (b): General Procedure for the Surfactant Catalyzed Molecular-iodine-mediated Cyclization of 3(a–e) in Aqueous Medium. A reaction mixture containing 2-allylnaphthalene-1-ol (**3a–e**) (0.5 mmol), surfactant CTAB (0.30 mmol), and water (10 mL) was stirred magnetically at room temperature for 1 h. Molecular iodine (1.4 equivalent) was added, and the reaction mixture was stirred at this temperature for an additional period of 7 h (optimized reaction condition, Table 1). After the reaction was over (as detected by TLC), the reaction mixture was extracted with EtOAc (3 × 15 mL), washed with 10% NaHSO₃ solution (2 × 10 mL), and then by brine (2 × 10 mL), dried over anhydrous magnesium sulfate. The crude mass was purified by SiO₂ column chromatography using petroleum ether-ethyl acetate (9:1) as eluent to give the pure products **4(a–e)**.

From the comparison of identical TLC, m. p, mixed m. p. and super imposable IR and also from NMR data; the cyclized products **4(a–e)** obtained in both methods (method a & method b) were found to be identical and thus they are same products.

3.5. 2-(Iodomethyl)-2,3-dihydronaphtho [1,2-*b*]furan (4a**).** White solid, mp 72–74°C; IR (KBr) ($\nu_{\max}$ /cm^{−1}): 3056, 2955, 1593, 1439, 1390, 1258, 1166, 1062, 1001, 921, 801, 735, 647, 562; ¹H NMR (300 MHz, CDCl₃): δ_{H} (ppm) 3.21 (dd, *J* = 15.9, 6.6 Hz, 1H), 3.40 (dd, *J* = 10.2, 7.8 Hz, 1H), 3.49–3.58 (m, 2H), 5.02–5.12 (m, 1H), 7.29–7.33 (m, 1H, ArH),

7.37–7.45 (m, 3H, ArH), 7.77–7.80 (m, 1H, ArH), 7.92–7.94 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ_{C} (ppm) 9.2, 36.8, 82.2, 118.6, 120.3, 120.5, 121.3, 122.6, 125.4, 125.7, 127.8, 133.9, 154.3; LRMS (70 eV, EI) *m/z*: 309 [M⁺]; [Found: C, 50.22; H, 3.47. Calcd. for C₁₃H₁₁IO: C, 50.35; H, 3.58%].

3.6. 2-(Iodomethyl)-2-methyl-2,3-dihydronaphtho [1,2-*b*]furan (4b**).** Brown solid, mp 64–66°C; IR (KBr) ($\nu_{\max}$ /cm^{−1}): 2974, 2927, 1596, 1576, 1441, 1394, 1378, 1296, 1169, 1062, 880, 802, 752, 654; ¹H NMR (500 MHz, CDCl₃): δ_{H} (ppm) 1.78 (s, 3H, CH₃), 3.26 (d, *J* = 15.5 Hz, 1H), 3.52 (d, *J* = 15.5 Hz, 1H), 3.54 (s, 2H), 7.31 (d, *J* = 8.5 Hz, 1H, ArH), 7.36–7.48 (m, 3H, ArH), 7.80–7.82 (m, 1H, ArH), 7.83 (d, *J* = 7.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ_{C} (ppm) 15.8, 26.4, 42.3, 87.4, 118.9, 120.5, 121.6, 123.0, 125.4, 125.8, 127.9, 134.1, 153.9; HRMS: 324.0016 [M]⁺; 346.9911 [M+Na]⁺; Anal. calcd. for C₁₄H₁₃IO: C, 51.87; H, 4.04%. Found: C, 51.98; H, 4.16%.

3.7. 2-(Iodomethyl)-3,3-dimethyl-2,3-dihydronaphtho [1,2-*b*]furan (4c**).** Orange yellow gummy mass; IR (KBr) ($\nu_{\max}$ /cm^{−1}): 2972, 1570, 1380, 1251, 1150, 980, 790, 706; ¹H NMR (300 MHz, CDCl₃): δ_{H} (ppm) 1.46 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 3.22–3.29 (m, 2H), 5.28–5.43 (m, 1H, >CH–), 7.44–7.59 (m, 2H, ArH), 7.62–7.81 (m, 2H, ArH), 7.99 (d, *J* = 8.4 Hz, 1H, ArH), 8.14–8.21 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ_{C} (ppm) 8.7, 21.8, 45.5, 92.8, 120.1, 120.8, 122.7, 125.4, 125.8, 126.2, 127.8, 134.9, 162.8; LRMS (70 eV, EI) *m/z*: 338 [M⁺]; [Found: C, 53.40; H, 4.62. Calcd. for C₁₅H₁₅IO: C, 53.27; H, 4.47%].

3.8. 2-(Iodomethyl)-3-methyl-2,3-dihydronaphtho [1,2-*b*]furan (4d**).** Gummy yellowish green mass; IR (KBr) ($\nu_{\max}$ /cm^{−1}): 2963, 2926, 1596, 1576, 1464, 1440, 1399, 1377, 1276, 1168, 1075, 937, 805, 753, 667; ¹H NMR (300 MHz, CDCl₃): δ_{H} (ppm) 1.29 (d, *J* = 7.2 Hz, 3H, CH₃), 3.34–3.59 (m, 2H), 3.59–3.70 (m, 1H), 5.11–5.14 (m, 1H, >CH–), 7.23–7.28 (m, 1H, ArH), 7.39–7.46 (m, 1H, ArH), 7.77–7.94 (m, 2H, ArH), 7.95–7.97 (m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ_{C} (ppm) 8.4, 14.3, 43.8, 86.4, 118.1, 120.4, 121.9, 124.4, 125.6, 125.7, 127.8, 129.9, 134.0, 153.5; LRMS (70 eV, EI) *m/z*: 324 [M⁺]; [Found: C, 51.98; H, 4.20. Calcd. for C₁₄H₁₃IO: C, 51.87; H, 4.04%].

3.9. 2-(Iodomethyl)-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan (4e). Yellowish brown solid, mp 134–135°C; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3059, 1639, 1595, 1575, 1494, 1396, 1264, 1167, 1069, 997, 865, 803, 752, 699; ^1H NMR (400 MHz, CDCl_3): δ_{H} (ppm) 3.24 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.42 (dd, $J = 10.8, 8.2$ Hz, 1H), 5.23–5.36 (m, 1H), 5.40 (d, $J = 8.0$ Hz, 1H), 7.04–7.50 (m, 6H, ArH), 7.76–7.83 (m, 4H, ArH), 8.03–8.14 (m, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) 8.6, 55.5, 87.2, 115.5, 119.6, 122.8, 123.8, 125.2, 125.6, 126.2, 126.5, 127.4, 128.3, 129.4, 134.4, 142.5, 155.3; LRMS (70 eV, EI): m/z : 387 $[\text{M}+\text{H}]^+$; [Found: C, 59.18; H, 4.04. Calcd. for $\text{C}_{19}\text{H}_{15}\text{IO}$: C, 59.09; H, 3.91%].

3.10. Typical Procedure for the Dehydriodination of Compounds 4a, 4d, and 4e. Compound 4a (1 mmol) was dissolved in rectified spirit (5 mL), and potassium hydroxide (0.56 g, 1 mmol) was added and the reaction mixture was refluxed for 2 h. After the reaction was over (as detected by TLC), rectified spirit was removed and the residue was extracted with dichloromethane and washed with water (2×25 mL) and dried (Na_2SO_4). The residual mass after removal of the solvent was subjected to column chromatography over silica gel using petroleum ether-ethyl-acetate (8 : 1) as eluent to give product 5a (80%). By using similar procedure, we got compounds 5d (76%) and 5e (82%).

3.11. 2-Methylnaphtho[1,2-*b*]furan (5a). White solid, mp 78–80°C; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3062, 2918, 2852, 1603, 1574, 1437, 1384, 1315, 1173, 1082, 938, 815, 744, 686; ^1H NMR (300 MHz, CDCl_3): δ_{H} (ppm) 2.56 (s, 3H, CH_3), 6.48 (s, 1H), 7.41–7.62 (m, 4H, ArH), 7.91 (d, $J = 8.4$ Hz, 1H, ArH), 8.27 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) 14.1, 103.6, 119.2, 119.6, 121.1, 122.9, 124.3, 124.5, 126.0, 128.3, 130.7, 149.8, 154.5; HRMS: $[\text{M}+\text{H}]^+$ 183.0815; [Found: C, 85.52; H, 5.69. Calcd. for $\text{C}_{13}\text{H}_{10}\text{O}$: C, 85.69; H, 5.53%].

3.12. 2,3-Dimethylnaphtho[1,2-*b*]furan (5d). Orange yellow gummy mass; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3071, 2922, 1642, 1569, 1441, 1380, 1252, 1175, 1042, 981, 729, 670; ^1H NMR (300 MHz, CDCl_3): δ_{H} (ppm) 2.48 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.49 (q, $J = 7.4$ Hz, 1H, ArH), 7.58 (q, $J = 7.4$ Hz, 1H, ArH), 7.69–7.78 (m, 2H, ArH), 7.99 (d, $J = 8.8$ Hz, 1H, ArH), 8.57 (d, $J = 8.8$ Hz, 1H, ArH); LRMS (70 eV, EI): m/z : 196 $[\text{M}]^+$; [Found: C, 85.79; H, 6.04. Calcd. for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.16%].

3.13. 2-Methyl-3-phenylnaphtho[1,2-*b*]furan (5e). Light yellow solid, mp 62–64°C; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3062, 2922, 1634, 1570, 1490, 1385, 1270, 1217, 968, 741; ^1H NMR (400 MHz, CDCl_3): δ_{H} (ppm) 2.46 (s, 3H, CH_3), 7.37–7.48 (m, 1H, ArH), 7.52–7.69 (m, 2H, ArH), 7.59 (q, $J = 8.8$ Hz, 2H, ArH), 7.88 (q, $J = 8.8$ Hz, 4H, ArH), 7.99 (d, $J = 8.2$ Hz, 1H, ArH), 8.09 (d, $J = 8.2$ Hz, 1H, ArH); LRMS (70 eV, EI): m/z : 258 $[\text{M}]^+$; [Found: C, 88.22; H, 5.34. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}$: C, 88.34; H, 5.46%].

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