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Studies on the synthesis and spectral properties of novel 4-benzofuranyl-1,8-naphthalimide derivatives

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Abstract

A new series of 4-benzofuranyl-*N*-alkyl-1,8-naphthalimides was prepared from 4-ethynyl-*N*-alkyl-1,8-naphthalimides and substituted *o*-iodophenols catalyzed by a $Pd(PPh_3)_2Cl_2/CuI$ system under mild conditions. The starting materials, 4-ethynyl-*N*-alkyl-1,8-naphthalimides, were synthesized with trimethylsilylacetylene by Sonogashira coupling reaction. The absorption and fluorescence spectra of these benzofuran-1,8-naphthalimides were recorded and the quantum yields were measured using quinine sulfate as the standard. The UV/vis absorption spectra were in the range of 380–400 nm and the emission spectra were in the range of 500–520 nm.

Keywords: 1,8-Naphthalimide; Benzofuran; Synthesis; Absorption; Fluorescence quantum yield; Palladium catalysts

1. Introduction

Derivatives of 1,8-naphthalimide usually exhibit strong fluorescence. They have been widely used in many fields [1–4]. In general, the excellent fluorescent properties of commercial 1,8-naphthalimide compounds depend largely on the presence of strong electron-donating groups, typically such groups as alkoxy and alkylamine, at the C-4 position. For example, 4-alkoxy-1,8-naphthalimides have been used as fluorescent brightening agents [5–8] and 4-alkylamine-1,8-naphthalimides have been used as fluorescent dyes [9–10]. Recently, a series of furanphthalimides, furo[2,3-*b*][1]naphtha[4*a*,7*a*-*e*,*f*]pyrida-5,7-diones, have been designed as new potential DNA intercalators [11] and chemilinescent probes for singlet oxygen [12].

Because of these excellent fluorescent properties and broad application, we have designed a new type of 1,8-naphthalimides with a larger π-conjugated group at the C-4 position of the naphthalene moiety. In this paper, a new series of *N*-alkyl-1,8-naphthalimides with a benzofuranyl at the C-4 position were prepared by palladium(0) coupling reaction. The UV/vis absorption and fluorescence emission spectral properties were studied in DMF and quantum yields were determined using quinine sulfate as the emission standard.

2. Results and discussion

2.1. Synthesis of N-alkyl-4-benzofuranyl-1,8-naphthalimides

N-Alkyl-4-benzofuranyl-1,8-naphthalimides **3** were synthesized by palladium(0)-catalyzed Sonogashira coupling cyclizations [13–18] with 4-ethynyl-1,8-naphthalimides **2**

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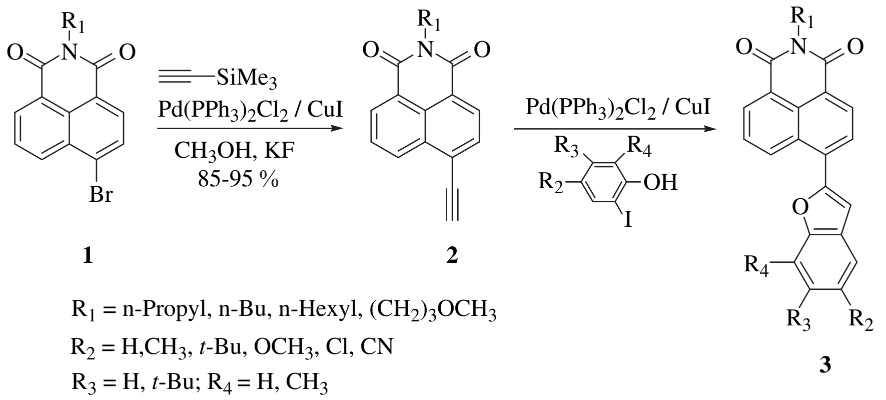


Scheme 1. Synthesis of *N*-alkyl-4-benzofuran-1,8-naphthalimides.

and substituted *o*-iodophenols as starting materials, as shown in Scheme 1.

4-Bromo-1,8-naphthalimides **1** were reacted first with a slight excess of trimethylsilylacetylene in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ by Sonogashira coupling reaction [19] in triethylamine solution and then the silyl group was removed by treatment with anhydrous potassium fluoride in methanol at room temperature to provide 4-ethynyl-1,8-naphthalimides **2** in excellent yields (Scheme 1).

4-Benzofuranyl-1,8-naphthalimides **3** were prepared by the coupling of **2** with *o*-iodophenol catalyzed by palladium. The effect of several Pd(II) catalysts including $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd_2(dba)_3$ and Pd/C on the reactions was investigated. The most effective catalyst was $Pd(PPh_3)_2Cl_2$, which uses CuI as co-catalyst in 1,4-dioxane (DOX) with tetramethylguanidine (TMG) as base. The isolated yields and melting point of products **3** are shown in Table 1.

In the preparation of 4-benzofuranyl-1,8-naphthalimides **3**, several N-substituted 4-ethynyl-1,8-naphthalimide and *o*-iodophenols were investigated. The yields, with a 1:1 mole ratio of **2** and *o*-iodophenols, were moderate to good in Pd(0)-catalyzed coupling reactions. In each case, the conversion of the starting materials exceeded 98% (HPLC) and the yields of isolated **3** ranged from 55 to 70%. It can be seen that changing substituents has little influence on yields.

2.2. UV/vis and fluorescence spectra

The UV/vis absorption and fluorescence spectra of compounds **3** were measured in DMF solution; the data are presented in Table 2.

Among compounds **3a**, **3c**, **3i** and **3n** (entries 1, 3, 9 and 14), with no substituents in the benzofuran ring, the maximum absorption ($\lambda_{max,uv}$) was in the range of 392–396 nm. But for compounds **3d** and **3j** (entries 4 and 10), with one methyl at the 5-position (R_2) of the benzofuran ring, the $\lambda_{max,uv}$ was in the range of 397–398.5 nm. Furthermore, for compounds **3b**, **3g** and **3k** (entries 2, 7 and 11), which have two methyls in

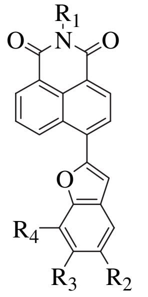
Table 1
Synthesis of 4-benzofuranyl-1,8-naphthalimides via palladium-catalyzed coupling of substituted *o*-iodophenols with 4-ethynyl-1,8-naphthalimides[a]

Entry	Compounds	R_1	R_2	R_3	R_4	Yield (%)[b]	mp (°C)
1	**3a**	*n*-Propyl	H	H	H	55	186.0–187.0
2	**3b**	*n*-Propyl	CH_3	H	CH_3	57	174.0–176.0
3	**3c**	*n*-Bu	H	H	H	70	130.0–132.0
4	**3d**	*n*-Bu	CH_3	H	H	64	140.0–141.0
5	**3e**	*n*-Bu	*t*-Bu	H	H	58	170.0–171.5
6	**3f**	*n*-Bu	H	*t*-Bu	H	62	183.0–184.0
7	**3g**	*n*-Bu	CH_3	H	CH_3	64	124.5–125.5
8	**3h**	*n*-Bu	Cl	H	H	68	174.5–176.0
9	**3i**	*n*-Hexyl	H	H	H	68	124.5–126.0
10	**3j**	*n*-Hexyl	CH_3	H	H	57	148.5–149.5
11	**3k**	*n*-Hexyl	CH_3	H	CH_3	60	132.5–134.0
12	**3l**	*n*-Hexyl	Cl	H	H	64	139.5–141.0
13	**3m**	*n*-Hexyl	CN	H	H	61	213.0–214.0
14	**3n**	$(CH_2)_3OCH_3$	H	H	H	56	136.0–137.5

[a] Reactions were carried out with **2** (0.40 mmol), *o*-iodophenol (0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 5% mol), CuI (0.02 mmol, 5% mol), 1,4-dioxane (4 ml) and TMG (0.25 ml) under nitrogen at 70–80 °C for 4 h.

[b] Isolated yields.

Table 2
The UV/vis absorption and fluorescence emission spectra of compounds **3**



3a R_1 = *n*-Propyl, R_2 = H, R_3 = H, R_4 = H; **3b** R_1 = *n*-Propyl, R_2 = CH_3, R_3 = H, R_4 = CH_3;
3c R_1 = *n*-Bu, R_2 = H, R_3 = H, R_4 = H; **3d** R_1 = *n*-Bu, R_2 = CH_3, R_3 = H, R_4 = H;
3e R_1 = *n*-Bu, R_2 = *t*-Bu, R_3 = H, R_4 = H; **3f** R_1 = *n*-Bu, R_2 = H, R_3 = *t*-Bu, R_4 = H;
3g R_1 = *n*-Bu, R_2 = CH_3, R_3 = H, R_4 = CH_3; **3h** R_1 = *n*-Bu, R_2 = Cl, R_3 = H, R_4 = H;
3i R_1 = *n*-Hexyl, R_2 = H, R_3 = H, R_4 = H; **3j** R_1 = *n*-Hexyl, R_2 = CH_3, R_3 = H, R_4 = H;
3k R_1 = *n*-Hexyl, R_2 = CH_3, R_3 = H, R_4 = CH_3; **3l** R_1 = *n*-Hexyl, R_2 = Cl, R_3 = H, R_4 = H;
3m R_1 = *n*-Hexyl, R_2 = CN, R_3 = H, R_4 = H; **3n** R_1 = $(CH_2)_3OCH_3$, R_2 = H, R_3 = H, R_4 = H

Entry	Compounds	$\lambda_{max,uv}$ (nm)[a]	ϵ ($\times 10^4$)	$\lambda_{max,fl}$ (nm)[a]	λ (nm)	ϕ_F[b]
1	**3a**	393.0	2.072	504.0	111.0	0.62
2	**3b**	400.5	2.013	512.5	112.0	0.67
3	**3c**	396.0	2.149	503.0	107.0	0.74
4	**3d**	398.5	2.214	508.0	109.5	0.59
5	**3e**	397.0	2.221	508.5	111.5	0.72
6	**3f**	404.0	2.205	519.0	115.0	0.52
7	**3g**	400.0	2.056	512.5	112.5	0.61
8	**3h**	386.5	2.226	493.0	106.5	0.75
9	**3i**	392.0	2.140	504.0	112.0	0.61
10	**3j**	397.0	2.197	508.5	111.5	0.56
11	**3k**	400.0	2.112	512.5	112.5	0.52
12	**3l**	386.5	2.276	493.0	106.5	0.71
13	**3m**	378.5	2.259	470.0	91.5	0.73
14	**3n**	393.0	2.116	504.0	111.0	0.54

[a] Selected excitation wavelength of the standard and the tested samples was 350 nm.
[b] ϕ was determined by using 1×10^{-6} mol/l quinine sulfate in 0.5 mol/l H_2SO_4 ($\phi=0.55$) as the standard.

the benzofuran ring, the $\lambda_{max,\ uv}$ was in the range of 400–400.5 nm. It is interesting that the largest bathochromic shift in the UV/vis absorption occurred when a *t*-butyl was on the 6-position (R_3) of the benzofuran ring (**3f**, entry 6). In addition, when a chlorine (Cl, entries 8 and 12) was at the benzofuran ring, the $\lambda_{max,uv}$ was at 386.5 nm, and when there was a cyano group (CN, entry 13) at the benzofuran ring, the $\lambda_{max,uv}$ was at 378.5 nm.

Compounds **3a**–**3g** (entries 1–7), **3I**–**3k** (entries 9–11) and **3n** (entry 14) had a strong yellow-green fluorescence, with maximum emission ($\lambda_{max,fl}$) between 503 and 519 nm and a Stoke's shift of 107–115 nm, among which the $\lambda_{max,fl}$ of compound **3f** (entry 6) showed the greatest red shift (519 nm) and greatest Stoke's shift (115 nm). A chlorine on the benzofuran ring (Compounds **3h** and **3l**, entries 8 and 12) produces an intense green fluorescence, $\lambda_{max,fl}$ of 493 nm and a smaller Stoke's shift (106.5). Compound **3m** (entry 13), with a cyano group at the benzofuran ring, had a blue fluorescence with the maximum at 470 nm and the smallest Stoke's shift (91.5 nm). Thus it can be seen that increasing the charge density of the substituents apparently causes the bathothromic shift in the emission spectra. When comparing **3c**, **3d** and **3g** (entries 3, 4 and 7), it is interesting to note that with each additional methyl added to the benzofuran ring, the fluorescence emission maximum is increased about 4 nm.

The fluorescence quantum yield ϕ was determined from the absorption and fluorescence spectra of compounds **3** in DMF at a concentration of 1×10^{-6} mol/l. Quinine sulfate (quantum yield 0.55) was used as the standard [20,21]. The tabulated data (Table 2) show that the studied compounds have moderate quantum yields of $\phi = 0.52 - 0.75$. It is notable, when comparing **3d** with **3h** (entries 4 and 8) or **3j** with **3m** (entries 10 and 13), that the quantum yields of **3h** and **3m** (entries 8 and 13), which have a chlorine or electron-acceptor cyano (CN) substituent on the naphthalimide molecule, are higher than those compounds which have electron-donating substituents (**3d**, **3j**).

3. Conclusions

N-Alkyl-4-benzofuranyl-1,8-naphthalimides were synthesized by Pd-promoted heteroannulation of ethynyl-1,8-naphthalimides and *o*-iodophenols. Fluorescence quantum yields were found to range from 0.52 to 0.75 and Stoke's shifts were between 91.5 and 115.0 nm. Compounds with an electron-donating group produced a bathochromic effect, while electron-withdrawing groups (CN) or a chlorine group (Cl) had a hypsochromic effect on the spectra. Experiments on further applications are currently underway in our laboratory.

4. Experimental

4.1. Materials and equipment

The spectra of ^1H NMR and ^{13}C NMR were recorded on a Mercury Vx 300 (Varian) with TMS as the internal standard. A Nicolet Impact 400 was used to determine the IR spectra. The mass spectra were obtained on an APEXII-FTMS. UV/vis absorption spectra were taken on a Shimadzu UV-2100 spectrometer. Fluorescence spectra were recorded using a Perkin Elmer LS-50B fluorescence spectrophotometer. Silica gel (100–140 mesh) was used for column chromatography. DOX was dried over 4A sieves, and triethylamine was dried with natrium slip, then distilled. Elemental analyses were recorded on an Elementar Varioel apparatus.

4.2. General procedure for the preparation of substituted 4-benzofuranyl-1,8-naphthalimide

A 25-ml round-bottomed, two-necked flask was charged with 0.20 mmol of 4-ethynyl-1,8-naphthalimide, 0.20 mmol of substituted *o*-iodophenol, 0.01 mmol of $Pd(PPh_3)_2Cl_2$ (7 mg, 5% mol), and 0.02 mmol of CuI (4 mg). A rubber serum cap was placed over one neck of the flask and a stopcock adapter in the other. The flask was evacuated and filled with nitrogen several times. Dry 1,4-dioxane (4 ml) and tetramethyl-guanidine (0.25 ml) were added via syringe through the serum cap. The reaction mixture was then placed in an oil bath at 70–80 °C and stirred magnetically for 4 h.

After completion of the reaction, the mixture was neutralized with diluted hydrochloric acid, then extracted with 20 ml dichloromethane, washed first with 20 ml saturated brine and then distilled water two or three times, and dried over $MgSO_4$. After removal of the solvents, products were separated by flash column chromatography on silica gel eluting with a 90:10 hexane: ethyl acetate mixture.

4.2.1. N-n-Propyl-4-(2-benzofuranyl)-1,8-naphthalimide (**3a**)

Mp 186–187 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J=7.2 Hz, 3H, CH_3), 1.79 (m, J=7.5 Hz, 2H, CH_2), 4.17 (m, J=7.5 Hz, 2H, CH_2), 7.27 (d, J=1.8 Hz, 1H, ArH), 7.33 (td, J=7.8 Hz, 1.2 Hz, 1H, ArH), 7.41 (td, J=7.8 Hz, 1.2 Hz, 1H, ArH), 7.63 (dd, J=7.8 Hz, 0.9 Hz, 1H, ArH), 7.71 (dd, J=7.8 Hz, 1.2 Hz, 1H, ArH), 7.83 (dd, J=8.4 Hz, 7.2 Hz, 1H, ArH), 8.14 (d, J=7.5 Hz, 1H, ArH), 8.64 (d, J=7.5 Hz, 1H, ArH), 8.66 (dd, J=7.5 Hz, 1.2 Hz, 1H, ArH), 8.93 (dd, J=8.7 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 11.5, 21.4, 42.0, 108.5, 111.5, 121.6, 122.6, 123.1, 123.5, 125.6, 127.1, 127.5, 128.5, 128.7, 128.9, 130.6 131.4 132.0, 133.9, 153.5, 155.4, 193.8, 164.1; δ IR (KBr) ν 3080, 3020, 2960, 2940, 2860, 1690, 1660, 1580, 1510, 1450, 1390, 1360, 1240, 1080, 790, 760 cm^{-1}; Anal. Calcd for $C_{23}H_{17}NO_3$: C, 77.73; H 4.82; N, 3.94. Found: C, 77.70; H, 4.98; N, 3.79.

4.2.2. N-n-Propyl-4-[2-(5,7-dimethylbenzofuranyl)]-1,8-naphthalimide (**3b**)

Mp 174–176 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J=7.5 Hz, 3H, CH_3), 1.77 (m, J=7.2 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 4.12 (m, J=7.5 Hz, 2H, CH_2), 6.96 (s, 1H, ArH), 7.09 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.75 (dd, J=8.4 Hz, 7.2 Hz, 1H, ArH), 8.05 (d, J=7.8 Hz, 1H, ArH), 8.54 (d, J=7.8 Hz, 1H, ArH), 8.58 (dd, J=7.5 Hz, 1.2 Hz, 1H, ArH), 8.86 (dd, J=8.4 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 11.6, 15.2, 21.4, 21.5, 42.0, 108.6, 118.6, 121.0, 122.4, 123.1, 126.7, 127.3, 128.0, 128.1, 128.5, 128.9, 130.5, 131.2, 131.9, 133.0, 134.0, 153.0, 153.1, 163.5, 163.8; δ IR (KBr) ν 3120, 3020, 2960, 2940, 2860, 1690, 1660, 1580, 1440, 1390, 1360, 1240, 1210, 1080, 860, 780, 750 cm^{-1}; HRMS (M^+): Calcd for $C_{25}H_{21}NO_3$ 383.1521, Found 383.1517.

4.2.3. N-n-Butyl-4-(2-benzofuranyl)-1,8-naphthalimide (**3c**)

Yellow solid, Mp 130–132 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J=7.2 Hz, 3H, CH_3), 1.40 (m, J=7.2 Hz, 2H, CH_2), 1.64 (m, J=7.5 Hz, 2H, CH_2), 4.06 (m, J=7.5 Hz, 2H, CH_2), 7.09 (d, J=0.6 Hz, 1H, ArH), 7.20 (td, J=7.8 Hz, 0.9 Hz, 1H, ArH), 7.29 (td, J=7.5 Hz, 1.2 Hz, 1H, ArH), 7.47 (dd, J=7.8 Hz, 0.9 Hz, 1H, ArH), 7.56 (dd, J=7.8 Hz, 0.6 Hz, 1H, ArH), 7.65 (dd, J=8.4 Hz, 7.2 Hz, 1H, ArH), 7.95 (d, J=7.8 Hz, 1H, ArH), 8.45 (d, J=7.8 Hz, 1H, ArH), 8.49 (dd, J=7.2 Hz, 0.9 Hz, 1H, ArH), 8.74 (dd, J=8.4 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.8, 20.4, 30.1, 40.2, 108.4, 111.4, 121.5, 122.5, 123.0, 123.5, 125.6, 126.9, 127.3, 128.4, 128.7, 130.4, 131.2, 131.8, 133.6, 153.4, 155.3, 163.6, 163.9; δ IR (KBr) ν 3060, 3020, 2940, 2920, 2860, 1690, 1660, 1580, 1510, 1390, 1360, 1240, 1080, 790, 760 cm^{-1}; Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H 5.18; N, 3.79. Found: C, 78.08; H, 5.16; N, 3.54.

4.2.4. N-n-Butyl-4-[2-(5-methylbenzofuranyl)]-1,8-naphthalimide (**3d**)

Yellow solid, mp 140–141 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.5 Hz, 3H, CH_3), 1.47 (m, J=7.8 Hz, 2H, CH_2), 1.74 (m, J=7.5 Hz, 2H, CH_2), 2.50 (s, 3H, CH_3), 4.20 (m, J=7.5 Hz, 2H, CH_2), 7.20 (d, J=0.6 Hz, 1H, ArH), 7.22 (dd, J=8.4 Hz, 1.5 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.51 (d, J=8.1 Hz, 1H, ArH), 7.83 (dd, J=8.4 Hz, 7.2 Hz, 1H, ArH), 8.13 (d, J=7.5 Hz, 1H, ArH), 8.64 (d, J=7.5 Hz, 1H, ArH), 8.66 (dd, J=7.5 Hz, 0.9 Hz, 1H, ArH), 8.93 (dd, J=8.4 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.8, 20.4, 21.3, 30.2, 40.3, 108.3, 111.0, 121.2, 122.4, 123.0, 126.9, 127.0, 127.4, 128.6, 128.6, 128.8, 130.5, 130.7, 131.3, 132.1, 134.0, 153.6, 153.9, 163.8, 164.1; δ IR (KBr) ν 3140, 3040, 2960, 2940, 2860, 1700, 1660, 1580, 1550, 1460, 1440, 1390, 1350, 1240, 1200, 1100, 780, 760 cm^{-1}; Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H 5.52; N, 3.65. Found: C, 78.33; H, 5.46; N, 3.46.

*4.2.5. N-n-Butyl-4-[2-(5-t-butylbenzofuranyl)]-1,8-naphthalimide (**3e**)*

Light yellow solid, mp 170–171.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.5 Hz, 3H, CH_3), 1.43 (s, 9H, *t*-Bu), 1.45 (m, J=7.5 Hz, 2H, CH_2), 1.74 (m, J=7.5 Hz, 2H, CH_2), 4.19 (t, J=7.5 Hz, 2H, CH_2), 7.24 (s, 1H, ArH), 7.49 (dd, J=9.0 Hz, 1.8 Hz, 1H, ArH), 7.56 (d, J=9.0 Hz, 1H, ArH), 7.71 (d, J=1.5 Hz, 1H, ArH) 7.80 (td, J=8.7 Hz, 1.2 Hz, 1H, ArH), 8.11 (dd, J=7.5 Hz, 1.2 Hz, 1H, ArH), 8.62 (dd, J=8.1 Hz, 1.5 Hz, 1H, ArH), 8.65 (dd, J=7.2 Hz, 1.5 Hz, 1H, ArH), 8.92 (dd, J=8.4 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.8, 20.4, 30.2, 31.8, 34.8, 40.3, 108.8, 110.8, 117.6, 122.4, 123.0, 123.7, 126.9, 127.3, 128.2, 128.5, 128.8, 130.5, 131.2, 132.0, 134.0, 146.7, 153.6, 153.7, 163.7, 164.0; IR (KBr) ν 3140, 3040, 2960, 2940, 2860, 1700, 1660, 1590, 1510, 1460, 1440, 1390, 1360, 1270, 1230, 1190, 1160, 1100, 1080, 870, 780, 750 cm^{-1}; Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H 6.40; N, 3.29. Found: C, 79.11; H, 6.52; N, 3.12.

*4.2.6. N-n-Butyl-4-[2-(6-t-butylbenzofuranyl)]-1,8-naphthalimide (**3f**)*

Mp 183.0–184.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.5 Hz, 3H, CH_3), 1.44 (s, 9H, *t*-Bu), 1.46 (m, J=7.8 Hz, 2H, CH_2), 1.72 (m, J=7.5 Hz, 2H, CH_2), 4.21 (t, J=7.5 Hz, 2H, CH_2), 7.24 (s, 1H, ArH), 7.42 (dd, J=8.1 Hz, 1.8 Hz, 1H, ArH), 7.64 (d, J=8.1 Hz, 1H, ArH), 7.67 (s, 1H, ArH) 7.83 (dd, J=8.4 Hz, 7.8 Hz, 1H, ArH), 8.14 (d, J=7.8 Hz, 1H, ArH), 8.65 (d, J=7.5 Hz, 1H, ArH), 8.68 (d, J=7.2 Hz, 1H, ArH), 8.97 (d, J=8.4 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.9, 20.4, 30.2, 31.6, 35.2, 40.3, 108.1, 108.4, 120.9, 121.5, 122.3, 123.1, 126.0, 127.4, 128.6, 128.9, 130.6, 131.3, 132.2, 134.2, 149.9, 153.4, 155.9, 163.8, 164.1; IR (KBr) ν 3100, 3080, 2960, 2940, 2860, 1700, 1660, 1590, 1390, 1360, 1270, 1230, 1080, 850, 780 cm^{-1}; Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H 6.40; N, 3.29. Found: C, 79.14; H, 6.50; N, 3.16.

*4.2.7. N-n-Butyl-4-[2-(5,7-dimethylbenzofuranyl)]-1,8-naphthalimide (**3g**)*

Mp 124.5–125.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.2 Hz, 3H, CH_3), 1.47 (m, J=7.5 Hz, 2H, CH_2), 1.73 (m, J=7.8 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 4.20 (m, J=7.5 Hz, 2H, CH_2), 7.02 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.29 (s, 1H, ArH), 7.81 (dd, J=8.4 Hz, 7.2 Hz, 1H, ArH), 8.13 (d, J=7.8 Hz, 1H, ArH), 8.63 (d, J=7.8 Hz, 1H, ArH), 8.65 (dd, J=7.5 Hz, 0.9 Hz, 1H, ArH), 8.94 (dd, J=8.4 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR δ 13.8, 15.1, 20.4, 21.3, 30.2, 40.3, 108.7, 118.6, 121.2, 122.3, 123.1, 126.8, 127.4, 128.0, 128.1, 128.6, 128.9, 130.6, 131.3, 132.1, 133.1, 134.3, 153.1, 153.2, 163.8, 164.1; δ IR (KBr) ν 3120, 3010, 2960, 2940, 2860, 1690, 1660, 1580, 1550, 1460, 1440, 1390, 1360, 1240, 1220, 1080, 860, 790, 760 cm^{-1}; Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H 5.83; N, 3.52. Found: C, 78.28; H, 5.93; N, 3.30.

*4.2.8. N-n-Butyl-4-[2-(5-chlorobenzofuranyl)]-1,8-naphthalimide (**3h**)*

Mp 174.5–175.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.2 Hz, 3H, CH_3), 1.47 (m, J=7.2 Hz, 2H, CH_2), 1.73 (m, J=7.5 Hz, 2H, CH_2), 4.19 (m, J=7.5 Hz, 2H, CH_2), 7.19 (s, 1H, ArH), 7.35 (dd, J=9.0 Hz, 1.8 Hz, 1H, ArH), 7.54 (d, J=9.0 Hz, 1H, ArH), 7.65 (d, J=2.4 Hz, 1H, ArH), 7.83 (dd, J=8.4 Hz, 7.5 Hz, 1H, ArH), 8.11 (d, J=7.8 Hz, 1H, ArH), 8.63 (d, J=7.8 Hz, 1H, ArH), 8.63 (dd, J=7.8 Hz, 1.2 Hz, 1H, ArH), 8.85 (dd, J=8.4 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.8, 20.4, 30.2, 40.3, 107.8, 112.5, 121.0, 123.0, 123.1, 125.8, 127.3, 127.6, 128.6, 128.8, 129.1, 129.8, 130.4, 131.4, 131.7, 133.2, 153.7, 155.0, 163.7, 164.0; δ IR (KBr) ν 3140, 3040, 2960, 2940, 2860, 1690, 1660, 1580, 1510, 1450, 1390, 1360, 1270, 1230, 1190, 1080, 860, 780, cm^{-1}; Anal. Calcd for $C_{24}H_{18}ClNO_3$: C, 71.38; H 4.49; N, 3.47. Found: C, 71.38; H, 4.45; N, 3.24.

*4.2.9. N-n-Hexyl-4-(2-benzofuranyl)-1,8-naphthalimide (**3i**)*

Mp 124.5–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7.5 Hz, 3H, CH_3), 1.38 (m, J=7.5 Hz, 6H, 3CH_2), 1.72 (m, J=7.8 Hz, 2H, CH_2), 4.12 (m, J=7.5 Hz, 2H, CH_2), 7.16 (d, J=0.9 Hz, 1H, ArH), 7.28 (td, J=7.8 Hz, 1.2 Hz, 1H, ArH), 7.37 (td, J=7.8 Hz, 1.2 Hz, 1H, ArH), 7.56 (dd, J=7.8 Hz, 0.9 Hz, 1H, ArH), 7.64 (dd, J=7.5 Hz, 1.2 Hz, 1H, ArH), 7.72 (dd, J=8.4 Hz, 7.5 Hz, 1H, ArH), 8.01 (d, J=7.5 Hz, 1H, ArH), 8.51 (d, J=7.5 Hz, 1H, ArH), 8.56 (dd, J=7.2 Hz, 1.2 Hz, 1H, ArH), 8.80 (dd, J=8.7 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 22.5, 26.7, 27.9, 31.4, 40.4, 108.4, 111.4, 121.4, 122.4, 122.9, 123.4, 125.5, 126.8, 127.2, 128.3, 128.4, 128.6, 130.3, 131.1, 131.7, 133.5, 153.3, 155.2, 163.5, 163.8; δ IR (KBr) ν 3140, 3060, 3040, 2960, 2940, 2860, 1700, 1660, 1580, 1550, 1480, 1460, 1300, 1240, 1220, 1100, 1080, 860, 820, 780, 740 cm^{-1}; Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H 5.83; N, 3.52. Found: C, 78.53; H, 5.81; N, 3.34.

*4.2.10. N-n-Hexyl-4-[2-(5-methylbenzofuranyl)]-1,8-naphthalimide (**3j**)*

Mp 148.5–149.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=7.8 Hz, 3H, CH_3), 1.38 (m, 6H, 3CH_2), 1.74 (m, J=7.5 Hz, 2H, CH_2), 2.50 (s, 3H, CH_3), 4.19

(t, J = 7.5 Hz, 2H, CH_2), 7.20 (s, 1H, ArH), 7.22 (dd, J = 8.4 Hz, 1.5 Hz, 1H, ArH), 7.49 (s, 1H, ArH), 7.51 (d, J = 8.4, 1H, ArH), 7.83 (dd, J = 8.4 Hz, 7.5 Hz, 1H, ArH), 8.14 (d, J = 7.8 Hz, 1H, ArH), 8.65 (d, J = 7.5 Hz, 1H, ArH), 8.67 (dd, J = 7.5 Hz, 1.2 Hz, 1H, ArH), 8.94 (dd, J = 8.4 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 21.4, 22.6, 26.8, 28.1, 31.6, 40.6, 108.3, 111.0, 121.2, 122.5, 123.1, 127.0, 127.4, 128.7, 128.9, 130.6, 131.3, 132.1, 133.1, 134.1, 153.7, 154.0, 163.8, 164.1; IR (KBr) ν 3100, 3040, 2960, 2940, 2860, 1700, 1660, 1580, 1510, 1460, 1440, 1390, 1360, 1240, 1200, 1080, 790 cm^{-1}; Anal. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H 6.12; N, 3.40. Found: C, 78.73; H, 6.23; N, 3.25.

4.2.11. *N-n-Hexyl-4-[2-(5,7-dimethylbenzofuranyl)]-1,8-naphthalimide (**3k**)*

Mp 132.5–134 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.38 (m, 6H, $3CH_2$), 1.74 (m, J = 7.5 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 4.19 (m, J = 7.5 Hz, 2H, CH_2), 7.03 (s, 1H, ArH), 7.12 (s, 1H, ArH), 7.30 (s, 1H, ArH), 7.82 (dd, J = 8.7 Hz, 7.2 Hz, 1H, ArH), 8.14 (d, J = 8.1 Hz, 1H, ArH), 8.64 (d, J = 7.8 Hz, 1H, ArH), 8.66 (dd, J = 7.5 Hz, 1.2 Hz, 1H, ArH), 8.94 (dd, J = 8.4 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 15.1, 21.3, 22.6, 26.8, 28.1, 31.5, 40.6, 108.7, 118.6, 121.2, 122.4, 123.1, 126.9, 127.4, 128.0, 128.2, 128.7, 129.0, 130.6, 131.3, 132.1, 133.1, 134.3, 153.1, 153.3, 163.8, 164.1; IR (KBr) ν 3140, 3060, 3040, 2960, 2940, 2860, 1700, 1660, 1580, 1550, 1480, 1460, 1380, 1350, 1240, 1210, 1100, 1080, 850, 780, 750 cm^{-1}; Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H 6.40; N, 3.29. Found: C, 78.93; H, 6.45; N, 3.02.

4.2.12. *N-n-Hexyl-4-[2-(5-chlorobenzofuranyl)]-1,8-naphthalimide (**3l**)*

Mp 139.5–141.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H, CH_3), 1.42 (m, 6H, $3CH_2$), 1.75 (m, J = 7.8 Hz, 2H, CH_2), 4.18 (m, J = 7.5 Hz, 2H, CH_2), 7.20 (s, 1H, ArH), 7.36 (dd, J = 8.4 Hz, 2.1 Hz, 1H, ArH), 7.55 (d, J = 8.7 Hz, 1H, ArH), 7.66 (d, J = 2.1 Hz, 1H, ArH), 7.83 (dd, J = 8.7 Hz, 7.5 Hz, 1H, ArH), 8.12 (d, J = 8.1 Hz, 1H, ArH), 8.65 (d, J = 7.5 Hz, 1H, ArH), 8.67 (dd, J = 7.8 Hz, 0.9 Hz, 1H, ArH), 8.86 (dd, J = 8.4 Hz, 0.9 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 22.6, 26.8, 28.0, 31.5, 40.6, 107.8, 112.5, 121.0, 123.0, 123.2, 125.8, 127.4, 127.6, 128.6, 128.8, 129.1, 129.8, 130.5, 131.4, 131.7, 133.3, 153.8, 155.0, 163.7, 164.0; IR (KBr) ν 3140, 3060, 2960, 2940, 2850, 1700, 1660, 1580, 1450, 1360, 1250, 1200, 1080, 860, 780, cm^{-1}; Anal. Calcd for $C_{26}H_{22}ClNO_3$: C, 72.30; H 5.13; N, 3.24. Found: C, 72.38; H, 5.25; N, 3.10.

4.2.13. *N-n-Hexyl-4-[2-(5-cyanobenzofuranyl)]-1,8-naphthalimide (**3m**)*

Mp 213–214 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.40 (m, 6H, $3CH_2$), 1.74 (m, J = 7.5 Hz, 2H, CH_2), 4.18 (t, J = 7.8 Hz, 2H, CH_2), 7.32 (s, 1H, ArH), 7.68 (dd, J = 8.7 Hz, 1.5 Hz, 1H, ArH), 7.74 (d, J = 8.7, 1H, ArH), 7.86 (dd, J = 8.7 Hz, 7.2 Hz, 1H, ArH), 8.07 (d, J = 0.9 Hz, 1H, ArH), 8.16 (d, J = 7.8 Hz, 1H, ArH), 8.67 (dd, J = 7.8 Hz, 1H, ArH), 8.69 (dd, J = 7.5 Hz, 1.2 Hz, 1H, ArH), 8.82 (dd, J = 8.4 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.57, 22.1, 26.3, 27.6, 31.1, 40.2, 107.2, 107.3, 112.3, 118.6, 122.9, 123.1, 126.1, 127.3, 127.5, 128.3, 128.4, 128.5, 128.8, 130.0, 130.9, 131.1, 132.1, 155.6, 156.4, 163.1, 163.4; IR (KBr) ν 3150, 3060, 3040, 2960, 2940, 2860, 2210, 1700, 1660, 1580, 1480, 1460, 1390, 1360, 1280, 1240, 1080, 900, 860, 790 cm^{-1}; HRMS (M^+): Calcd for $C_{27}H_{22}N_2O_3$: 422.1630, Found 422.1629.

4.2.14. *N-(3-Methoxypropyl)-4-(2-benzofuranyl)-1,8-naphthalimide (**3n**)*

Mp 136–137.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (m, 2H, CH_2), 3.34 (s, 3H, CH_3), 3.54 (t, J = 6.6 Hz, 2H, CH_2), 4.30 (t, J = 7.5 Hz, 2H, CH_2), 7.27 (s, 1H, ArH), 7.35 (td, J = 7.8 Hz, 1.2 Hz, 1H, ArH), 7.41 (td, J = 7.5 Hz, 1.2 Hz, 1H, ArH), 7.63 (dd, J = 7.8 Hz, 0.9 Hz, 1H, ArH), 7.71 (m, J = 7.8 Hz, 1H, ArH), 7.82 (dd, J = 8.4 Hz, 7.2 Hz, 1H, ArH), 8.14 (d, J = 7.5 Hz, 1H, ArH), 8.64 (d, J = 7.5 Hz, 1H, ArH), 8.66 (dd, J = 6.9 Hz, 1.2 Hz, 1H, ArH), 8.93 (dd, 9.0 Hz, 1.2 Hz, 1H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.2, 38.0, 58.5, 70.6, 108.5, 111.5, 121.6, 122.6, 123.1, 123.5, 125.6, 127.1, 127.5, 128.6, 128.7, 128.9, 130.6, 131.4, 132.1, 133.9, 153.6, 155.5, 163.8, 164.1; IR (KBr) ν 3120, 3060, 3020, 2960, 2940, 2860, 1700, 1660, 1580, 1480, 1450, 1390, 1360, 1260, 1240, 1110, 1080, 900, 860, 790, 750m^{-1}; HRMS (M^+): Calcd for $C_{24}H_{19}NO_4$: 385.1314. Found 385.1310.

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