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Synthesis of some polymerisable fluorescent dyes

L.G.F. Patrick, A. Whiting*

Department of Chemistry, University Science Laboratories, University of Durham, South Road, Durham, DH1 3LE, UK

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Abstract

The preparation of some fluorescent polymerisable dyes and brighteners derived from 4-subsituted *N*-alkyl-1,8-naphthalimide are presented. Each of the dyes were copolymerised with styrene giving coloured fluorescent polymers that were stable to solvent extraction.

Keywords: Naphthalimide; Dye; Fluorescence; Polymerisation; Monomer; Heck; Fluorophore

1. Introduction

Derivatives of *N*-substituted-1,8-naphthalimides have found application in a number of areas including fluorescent dyes [1], light emitting diodes [2–4], liquid crystal displays [5] and ion probes [6]. Polymerisable dyes can be used for the bulk coloration of a polymer or to produce a macromolecular (or polymeric) dye that can be added to a non-coloured polymer prior to processing [7]. The advantage of using polymerisable dyes over conventional dyes is that the dye becomes chemically bonded to the polymer. The dye, therefore, cannot be extracted from the polymer. The solvent-fastness of a polymer coloured with a polymerisable dye is, as a consequence, much greater than a polymer coloured with conventional dyes [7].

The use of 1,8-naphthalimide derivatives in electronic devices has become increasingly popular due to the good light stability and high quantum yield of suitably substituted derivatives [2–4]. Fluorescent polymers prepared from polymerisable dyes can be used to prepare electronic devices using spin coating techniques rather than by vapour phase deposition, allowing the economical fabrication of large films of material [2]. Additionally, the chemical bonding of the dye to a polymer prevents the dye from recrystallising within the electronic device [2].

In this paper we present the preparation of a number of unsaturated fluorescent dyes and brighteners derived from 1,8-naphthalimide (Table 1) and give a brief report of their polymerisation with styrene.

2. Results and discussion

2.1. Synthesis

The bisalkenic moiety **2** was readily prepared by reaction of allylamine with 4-sulfo-1,8-naphthalic

* Corresponding author. Tel.: +44-191-374-7491.
E-mail address: andy.whiting@durham.ac.uk (A. Whiting).

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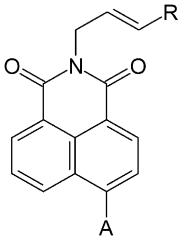
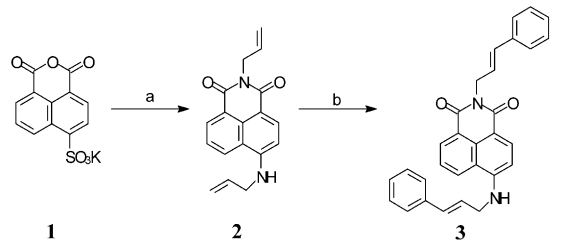
Table 1

	Dye	A	R
	**2**	$NHCH_2CH=CH_2$	H
	3	$NHCH_2CH=CHC_6H_5$	C_6H_5
	6	NHC_4H_9	H
	7	NHC_4H_9	C_6H_5
	8	NHC_4H_9	$C_6H_4(CO)CH_3$
	9	NHC_4H_9	$C_6H_4CO_2C_2H_5$
	12	SC_4H_9	H
	13	SC_4H_9	C_6H_5
	14	SC_4H_9	$C_6H_4CO_2C_2H_5$
	15	SC_4H_9	$C_6H_4CH_2O(CO)CH_3$
	20	NHAc	H
	21	NHAc	C_6H_5



Scheme 1. (a) Allylamine; (b) PhI, KOAc, TBAI, $Pd(OAc)_2$, DMF, yield 14–51%.

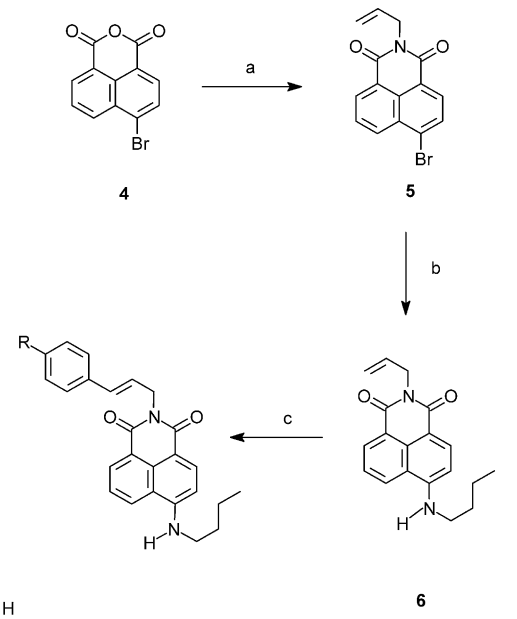
anhydride potassium salt **1** in aqueous solution at 130 °C (Scheme 1) in reasonable yield (70%). Successful preparation of the bisstyryl derivative of **2** was achieved by the use of the Heck reaction [8,9]. Coupling of **2** with iodobenzene in the presence of palladium(II) acetate, triethylamine and triphenylphosphine in acetonitrile resulted in the formation of complex mixture of fluorescent compounds, which included a small amount of the desired compound **3**. The remaining compounds were not identified. Modification of the coupling procedure to that used by Satake et al. [10], which employs potassium acetate as the base in the presence of a phase transfer catalyst, resulted in the formation of **3** in low yields (14%). A significant quantity of the dye was found to self polymerise during purification by column chromatography and recrystallisation. Modification of the purification procedure to use a short dry silica column for initial clean-up and the inclusion of 4-*tert*-butylcatechol as a radical inhibitor in the solvents used, resulted in a significant increase in yield (51%). The modified work-up procedure was used in all subsequent coupling reactions.

N-substituted-4-butylamino-1,8-naphthalimide dyes containing a single polymerisable functional group were prepared by condensation 4-bromo-1,8-naphthalic anhydride **4** and allylamine, followed by substitution of the bromide with butylamine and subsequent derivatisation using the Heck reaction as appropriate.

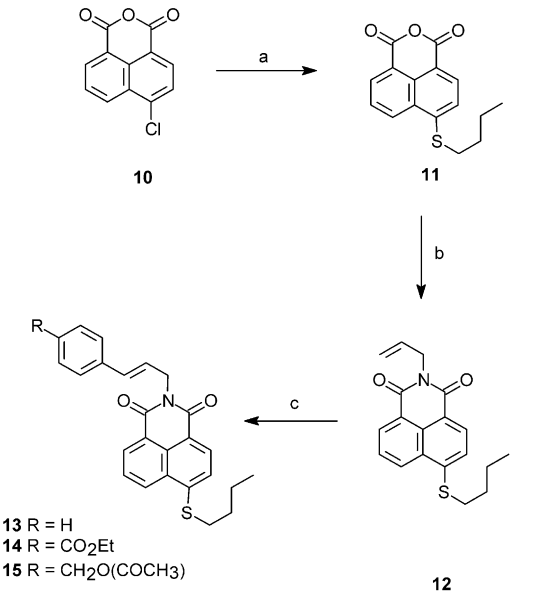
Thus, excess allylamine and 4-bromo-1,8-naphthalic anhydride **4** were gently refluxed in methanol to produce *N*-allyl-4-bromo-1,8-naphthalimide **5** in good yield (68%) (Scheme 2). Subsequent reaction of **5** with butylamine in DMSO at 80 °C afforded **6** in quantitative yields. Implementation of the Heck reaction, based on the conditions used by Shimizu et al. [10] and the modified work-up procedure described earlier, allowed coupling of iodobenzene with **6** to form **7** in 71% yield. Coupling of **6** with ethyl 4-bromobenzoate and 4-iodoacetophenone was similarly achieved, forming **8** and **9** in 74 and 19% yield respectively.

The dyes described in this discussion so far are yellow in colour with green fluorescence. Alteration of the group occupying the 4-position of *N*-alkyl-4-alkylamino-1,8-naphthalimides to an acylamino or sulfanyl group hypsochromically shifts the absorption and emission bands of the fluorophore, such that the fluorophore emits blue light [11,12]. Such compounds find application as brighteners or can be used for the construction of blue LEDs [2,3].

4-Butylsulfanyl-1,8-naphthalimide derivatives were prepared by the route illustrated in Scheme 3.



Scheme 2. (a) $CH_2=CHCH_2NH_2$, MeOH, reflux, 68% yield; (b) $CH_3(CH_2)_3NH_2$, DMSO, 97% yield; (c) ArI or ArBr, KOAc, TBAI, $Pd(OAc)_2$, DMF, **7** 71%, **8** 74%, **9** 19% yield.



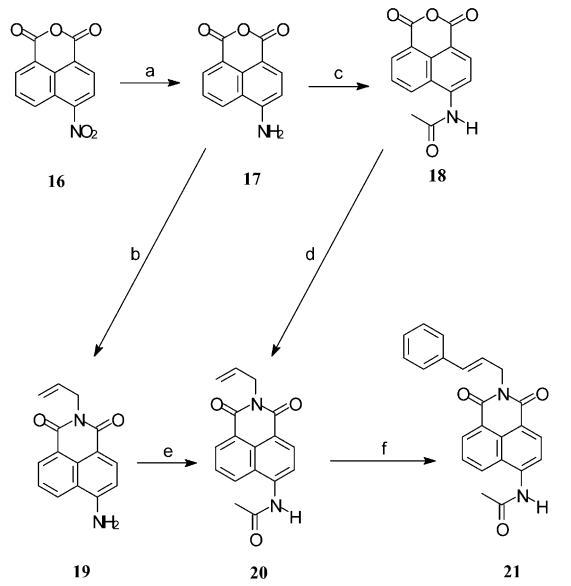
Scheme 3. (a) $CH_3(CH_2)_3SH$, KOH (aq), DMF, R.T.; (b) $CH_2=CHCH_2NH_2$, EtOH, reflux, 36% yield from **11**; (c) ArI or ArBr, KOAc, TBAI, $Pd(OAc)_2$, DMF, yield **13** 19%, **14** 28%, **15** 7% from **12**.

Treatment of 4-chloro-1,8-naphthalimide **10** with butanethiol in the presence of KOH yielded 4-butylsulfanyl-1,8-naphthalic anhydride **11**, which was subsequently reacted with allylamine in refluxing ethanol to give *N*-allyl-4-butylsulfanyl-1,8-naphthalimide **12** in 36% yield (from **10**).

Compound **12** was found to be a pale yellow compound with intense blue fluorescence. Coupling of iodobenzene with **12** required long reaction times and furnished **13** in 19% yield. In all of the coupling reactions of **12** investigated, the coupling was initially found to occur at the expected rate. As the reaction progressed, however, the rate of reaction appeared to decrease with time. This was probably due to the sulfur binding the palladium catalyst, preventing further formation of coupled products. This was supported by the fact that significant quantities of unreacted alkene were present upon termination of the reaction. Low yields of coupled products were also obtained when coupling **12** with ethyl 4-bromobenzoate and 4-bromobenzyl bromide, which produced **14** and **15** in 28 and 7% yields respectively. Interestingly, acetate anion was found to displace the bromine of 4-bromobenzyl bromide under the conditions used.

As illustrated in Scheme 4, 4-acetylamino-*N*-allyl-1,8-naphthalimide **20** was prepared by two synthetic pathways. In the first sequence, hydrogenation of 4-nitro-1,8-naphthalic anhydride **16**, in the presence of palladium on carbon catalyst, gave the desired 4-amino-1,8-naphthalic anhydride **17**. This was subsequently treated with allylamine to yield *N*-allyl-4-amino-1,8-naphthalimide **19** in 54% yield. Acetylation of **19** was achieved by refluxing in acetic acid/acetic anhydride to furnish the desired acetylamino derivative **20** in 31% yield from **16**. In the second synthetic sequence **16** was reduced as before and was subsequently acetylated. The product from this reaction was then treated with allylamine to yield the desired compound **20** in increased yield (58% from **16**).

Coupling of **20** with iodobenzene by the Heck reaction gave the desired styryl derivative **21** in a moderate yield (59%).



Scheme 4. (a) H_2, DMF, Pd/C, R.T., yield 73%; (b) $CH_2=CHCH_2NH_2$, DMF, EtOH, 80 °C, yield 75% from 124; (c) CH_3COOH, $(CH_3CO)_2$, 85 °C; (d) $CH_2=CHCH_2NH_2$, EtOH, reflux, yield 58% from **16**; (e) CH_3COOH, $(CH_3CO)_2$, reflux, yield 31% from **16**; (f) PhI, KOAc, TBAI, $Pd(OAc)_2$, DMF, yield 59% from **20**.

2.2. Polymerisation

Styrene was bulk polymerised in the presence of each of the allyl dyes (**2**, **6**, **12**, **20**) and their styryl derivatives (**3**, **7**–**9**, **13**–**15**, **21**) using a radical initiator. All of the dyes dissolved in the warm monomeric mixture apart from **21**, which was found to be only partially soluble and formed an opaque monomeric solution. Subsequently, all of the polymers, except those prepared in the presence of **21**, were transparent and fluorescent upon completion of the polymerisation. The polymers prepared in the presence of **21** were opaque and fluorescent. After repeated cycles of solvation and precipitation, using suitable solvents, the polymers remained fluorescent. The process of solvation and precipitation removes any unreacted dye and low molecular weight polymers produced. The consistent fluorescence of the polymers after repeated solvation-precipitation cycles indicates that the dyes were covalently bonded to the polymer. The colour of the polymers produced and the fluorescence of each was the same as the dye used to prepare the polymer. This indicates that the nature of the fluorophores do not change during the polymerisation process.

The degree of polymerisation in each case was reflected by the viscosity of the polymers produced. Dyes **3**, **6**, **12**–**15**, **20**, **21** all produced a solid mass of polymer, which suggest the formation of high molecular weight polymers. Interestingly, dyes that contained a monostyryl group and a butylamino function in the 4-position of the naphthyl ring (**7**–**9**) were found to produce viscous but mobile polymeric mixtures upon polymerisation, suggesting the formation of low molecular weight polymers. The remaining dye, the bisallyl derivative **2**, produced polymeric mixtures that were very mobile, and after a number of solvation and precipitation cycles, little polymeric material was recovered. An increase of the concentration of **2** in the monomeric mixture (from ca. 0.2 to 10% w/v) resulted in the quenching of the polymerisation process suggesting that **2** inhibits radical polymerisation.

The variation in the reactivity of polymerisable 4-substituted-*N*-alkyl-1,8-naphthalimide dyes containing different groups in the 4-position of the naphthyl ring has also been observed in the literature [13], though no thorough investigations of the phenomenon were undertaken. With the exception of **6**, these results verify the testimonies found in the literature, which suggest that the presence of a secondary amine in the 4-position of naphthalimide reduces the reactivity of unsaturated naphthalimide dyes toward radical polymerisation.

Comparison of the polymers obtained using dyes **2**, **3**, **6** and **7** indicates that the modification of the allyl group to a styryl group has unpredictable effects on the polymerisation of styrene.

As indicated earlier, **2** was found to inhibit polymerisation. Conversion of the allyl groups to styryl groups in this case appeared to increase the reactivity of the dye. Conversely, conversion of the allyl group of **6** to the styryl group in **7** appeared to decrease the reactivity of the dye. The above findings seem to suggest that the rate of polymerisation is affected by the combined nature of the groups attached to the 4-position and the imide nitrogen, and is not solely dictated by specific groups in either position. Further investigation into rates of polymerisation and determination of the average

molecular weight of the polymers obtained, using a more extensive range of polymerisable naphthalimide dyes, needs to be undertaken before any conclusive evidence can be presented as to the effects of structure on the polymerisation rate.

2.3. Summary

The synthesis of a range of polymerisable dyes and brighteners has been presented. Such compounds are potentially useful as low migration fluorescent dyes or brighteners for polymers; specialist coatings for plastics or paper; and are convenient monomers for the preparation of fluorescent polymers for use in electronic devices.

3. Experimental

4-Sulfo-1,8-naphthalic anhydride potassium salt was obtained as a 'paste' from Hollidays Dyes and Chemicals, Huddersfield, UK and was dried over P_2O_5 under reduced pressure (ca. 2 mm Hg). All other reagents were obtained from Aldrich, Acros, BDH, or Lancaster and were used without any further purification. Evaporations were carried out using a Buchi rotary evaporator followed by evaporation under high vacuum (typically ca. 2.0 mmHg).

All products were dried over P_2O_5 under reduced pressure (ca. 2 mmHg) before analysis. Melting points were determined with a heated block and mercury in glass thermometer and are uncorrected. Combustion analyses were performed on Perkin-Elmer 240C or Carlo-Erba 1 106 elemental analysers. UV spectra were recorded on Perkin-Elmer Lambda 15 spectrometer. IR spectra were recorded using a Perkin-Elmer 783 spectrometer. ^{1}H NMR spectra were recorded at 200, 300 or 400 MHz on Bruker AC200, AC300 or A90 spectrometers, respectively, using residual incompletely deuterated solvent as internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 or 100 MHz on a Bruker AC300 or A90 spectrometers, respectively, using deuterated solvent as internal standard. Fast atom bombardment (FAB) mass spectra were obtained from a Kratos MS50 spectrometer, using a 2-nitrophenol matrix. Electron impact (EI) (70 eV) and chemical ionisation (CI) (using ammonia gas) mass spectra were obtained from Finnigan MAT 8430 or Kratos MS25 spectrometers. High resolution mass spectrometry was carried out using a Kratos Concept IS spectrometer.

3.1. N-Allyl-4-allylamino-1,8-naphthalimide **2**

4-Sulfo-1,8-naphthalic anhydride potassium salt (10.0 g, 32 mmol) and allylamine (8.2 g, 144 mmol) were dissolved in water (300 ml) and stirred at 130 °C in an autoclave for 36 h. The reaction was then allowed to cool, precipitating **2** as a yellow solid (6.4 g, 70%); m.p. 189–190 °C (lit. [11] 181–182 °C); (found C, 73.8; H, 5.6; N, 9 6; $C_{18}H_{16}O_2N_2$ requires C, 74.0; H, 5.5; N, 9.6%); λ_{max}(EtOH)/nm 204.1 (ε/dm^3 mol^{-1} cm^{-1} 39,750), 258.0 (18170), 282.5 (18,850), 324.0 (1560), 339.2 (790), 439.6 (15570); ν_{max}(nujol)/cm^{-1} inter alia 3400 (N–H), 1685, 1680, 1635 (C=O); δ_H(300 MHz, $CDCl_3$) 4.09 (2H, d, J 5.4, $NHC\underline{H}_2CH=CH_2$), 4.79 (2H, br d, J 5.6, $CH_2C\underline{H}_2N[CO]_2$), 5.15–5.43 (5H, m, integral reduces to 4H upon addition of D_2O $NCH_2CH=C\underline{H}_2$ and N–H), 5.90–6.14 (2H, m, $2\times NCH_2C\underline{H}=CH_2$), 6.73 (1H, d, J 8.4, 3-H), 7.63 (1H, br t, J 7.9, 6-H), 8.12 (1H, dd, J 1.1 and 8.4, 7-H), 8.47 (1H, d, J 8.5, 2-H), 8.59 (1H, dd, J 1.1 and 7.4, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 41.4 (t, $CH_2\underline{C}H_2N[CO]_2$), 45.1 (t, $HN\underline{C}H_2$), 104.5 (d, C-3), 107.9 (s), 116.1 (t, $CH=\underline{C}H_2$), 116.2 (t, $CH=\underline{C}H_2$), 120.3 (s), 121.9 (s), 124.4 (d, C-6), 128.6 (d, C-5), 129.5 (s), 130.8 (d, C-7), 133.4 (d, $\underline{C}H=CH_2$), 134.1 (d, $\underline{C}H=CH_2$), 134.3 (d, C-2), 150.6 (s, C-4), 162.7 (s, C-11), 163.5 (s, C-12); m/z (FAB) inter alia 293 ($M^+ + H$, 100%).

3.2. N-Allyl-4-bromo-1,8-naphthalimide **5**

Allylamine (0.27 ml, 3.6 mmol) and 4-bromo-1,8-naphthalic anhydride (1.0 g, 3.6 mmol) were dissolved in methanol (30 ml) and stirred under reflux for 4 h. Cooling of the reaction solution precipitated **5** as a white solid (1.14 g, 68%); m.p. 139–140 °C (lit. [14] 129–130 °C); (found C, 56.9; H, 2.9; N, 4.4; Br 25.5; $C_{16}H_{10}NO_2Br$ requires C, 57.0;

H, 3.2; N, 4.4; Br, 25.3%); λ_{max}(EtOH)/nm 201.5 (ε/dm^3 mol^{-1} cm^{-1} 18,680), 212.1 (18410), 236.8 (40150), 342.3 (15,900), 354.8 (13,450); ν_{max}(nujol)/cm^{-1} inter alia 1690, 1625 (C=O); δ_H(300 MHz, $CDCl_3$) 4.8l (2H, d, *J* 5.8, N$\underline{C}H_2CH=CH_2$), 5.20–5.38 (2H, m, $CH_2CH=C\underline{H}_2$), 5.91–6.08 (1H, m, $CH_2C\underline{H}=CH_2$), 7.86 (1 H, br t, *J* 8.0, 6-H), 8.06 (1H, *J* 7.8, 2-H), 8.44 (1 H, d, *J* 7.8, 3-H), 8.59 (1H, dd, *J* 1.3 and 8.5, 7-H), 8.68 (1H, dd, *J* 1.0 and 7.5, 5-H); δ_C(75 MHz, $CDCl_3$); 42.4 (t, N$\underline{C}H_2CH=CH_2$), 121.9 (s), 122.8 (s), 127.9 (d), 128.7 (s), 130.2 (s), 130.4 (s), 130.9 (d), 131.1 (d), 131.9 (2×d), 133.1 (d), 163.0 (s, C-11 and C-12); *m*/*z* (FAB) inter alia 316 ($M^{+\bullet}$, ^{79}Br 100%).

3.3. N-Allyl-4-butylamino-1,8-naphthalimide **6**

15 (2.0 g, 6.3 mmol) and butylamine (6.2 ml, 63.0 mmol) were dissolved in dimethylsulfoxide (17 ml) and stirred at 80°C overnight. The resulting solution was then poured into ice (ca. 50 g) and ca. 5 g of sodium chloride was to precipitate the title compound as a yellow solid (1.9 g, 97%); m.p. 140–141 °C; (Found C, 73.8; H, 6.6; N, 9.1; $C_{19}H_{20}N_2O_2$ requires C, 74. 0; H, 6.5; N, 9.1%); λ_{max}(EtOH)/nm 208.3 (ε/dm mol^{-1} cm^{-1} 43,630), 229.7 (23,390), 259.0 (27,060), 283.9 (28,820), 324.8 (2570), 340.3 (1420), 444 (23,940); ν_{max}(nujol)/cm^{-1} inter alia 3370 (N–H), 1680, 1640 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.95 (3H, t, *J* 7.4, $C\underline{H}_3CH_2$), 1.43 (2H, sextet, *J* 7.4, $CH_3C\underline{H}_2CH_2$), 1.68 (2H, quintet, *J* 7.3, $CH_2C\underline{H}_2CH_2$), 3.35 (2H, q, *J* 6.6, collapses to a triplet upon deuteration, $NHC\underline{H}_2CH_2$), 4.61 (2H, dt, *J* 5.2 and 1.6, $[CO]_2NC\underline{H}_2CH=CH_2$), 5.06–5.12 (2H, m, $CH_2CH=C\underline{H}_2$), 5.88–5.97 (1H, m, $CH_2C\underline{H}=CH_2$), 6.71 (1H, d, *J* 8.5, 3-H), 7.64 (1H, dd, *J* 8.4 and 7.4, 6-H), 7.73 (1H, t, *J* 5.4, disappears upon addition of D_2O, N–H), 8.22 (1H, d, *J* 8.5, 2-H), 8.39 (1H, dd, *J* 7.3 and 1.0, 7-H), 8.68 (1H, dd, *J* 8.7 and 1.2, 5-H); δ_C(100 MHz), $[CD_3]_2SO$) 13.9 (q, $\underline{C}H_3CH_2$), 20.0 (t, $\underline{C}H_2CH_3$), 30.1 (t, $CH_2\underline{C}H_2CH_2$), 41.4 (t, $\underline{C}H_2CH=CH_2$), 42.7 (t, $CH_2\underline{C}H_2NH$), 103.7 (d, C-3), 107.4 (s), 116.1 (t, $\underline{C}H_2=CH$), 120.2 (s), 121.8 (s), 124.1 (d, C-6), 128.7 (d, C-5), 129.5 (s), 130.7 (d, C-7), 133.5 (d, $CH_2=\underline{C}H$), 134.3 (d, C-2), 150.8 (s, C-4), 162.6 (s, C-11), 163.5 (s, C-12); *m*/*z* (FAB) inter alia 309(M^+ + H, 100%).

3.4. General procedure for the preparation of N-[(E)-3-arylallyl)]-4-butylamino-1,8-naphthalimides

N-Allyl-4-butylamino-1,8-naphthalimide **6** (1.39 g, 4.5 mmol), palladium(II) acetate (0.05 g, 0.25 mmol), potassium acetate (1.33 g, 13.6 mmol), tetrabutylammonium chloride (1.50 g, 5.4 mmol) and the appropriate iodo/bromobenzene (13.6 mmol) were suspended in *N*,*N*-dimethylformamide (30 ml) and stirred at ca. 75–85 °C for 24 h. The reaction was then allowed to cool to room temperature, before pouring in to water (75 ml) and extracting with ethyl acetate (3×25 ml). A small quantity of 4-*tert*-butylcatechol was added to the combined extracts, which were washed with water (3×25 ml), dried (Na_2SO_4) and evaporated affording a viscous brown oil that was purified silica gel chromatography (9:2:1 DCM:40–60 petroleum ether:ethyl acetate containing a small amount of 4-*tert*-butylcatechol as eluant).

3.5. 4-Butylamino-N-[(E)-3-phenylallyl]-1,8-naphthalimide 7

Using iodobenzene (1.38 g, 6.75 mmol) a sticky yellow solid was obtained, trituration (MeOH: water 1:1) yielded title compound **7** as a yellow solid (1.2 g, 71%); m.p. 129–133 °C dec.; (found C, 78.1; H, 6.1; N, 7.4; $C_{25}H_{24}N_2O_2$ requires: C, 78.1; H, 6.3; N, 7.3%); λ_{max}(EtOH)/nm 204.9 (ε/dm^3 mol^{-1} cm^{-1} 52,720), 230.8 (21,360), 256.9 (28,840), 284.1 (20,190), 445.6 (15,340); ν_{max}(nujol)/cm^{-1} inter alia 3375 (N–H), 1680, 1640, 1580 (C=O); δ_H(400 MHz,$[CD_3]_2SO$) 0.96 (3H, t, *J* 7.3, $C\underline{H}_3CH_2$), 1.45 (2H, sextet, *J* 7.4, $CH_3C\underline{H}_2CH_2$), 1.71 (2H, quintet, *J* 7.3, $CH_2C\underline{H}_2CH_2$), 3.39 (2H, q, *J* 5.5, collapses to triplet upon addition of D_2O, $CH_2\underline{C}H_2N$–H), 4.80 (2H, d, *J* 5.5, N$\underline{C}H_2CH=CH_2$), 6.30–6.61 (2H, m, $NCH_2C\underline{H}=C\underline{H}$), 6.79 (1H, d, *J* 9.0, 3-H), 7.12–7.47 (5H, m, phenyl-H), 7.69 (1H, t, *J* 8.0, 6-H), 7.80 (1H, t, *J* 5.3, disappears upon addition of D_2O, N-H), 8.29 (1H, d, *J* 8.5, 2-H), 8.46 (1H, d, *J* 7.0, 7-H), 8.73 (1H, d, *J* 8.5, 5-H); δ_C(100 MHz, $[CD_3]_2SO$); 13.9 (q, $\underline{C}H_3CH_2$), 20.0 (t, $CH_3\underline{C}H_2CH_2$), 30.1 (t, $CH_2\underline{C}H_2CH_2$), 41.1 (t, N$\underline{C}H_2CH$), 42.7 (t, $\underline{C}H_2NH$), 103.7 (d, C-3), 107.5 (s), 120.2 (s), 121.9 (s), 124.1 (d, C-6), 125.1 (d, $\underline{C}$-H phenyl), 126.3 (d, $\underline{C}$–H phenyl), 127.6 (d,

$CH_2\underline{C}H=CH$), 128.6 (d, C-5 and $\underline{C}$-H phenyl), 129.6 (s), 130.7 (d, C-7), 131.5 (d, $CH_2CH=\underline{C}H$), 134.3 (d, C-2), 136.5 (s, quaternary phenyl), 150.8 (s, C-4), 162.8 (s, C-11), 163.7 (s, C-12); *m*/z (FAB) inter alia 385 ($M^+ + H$, 100%), 293 (83), 281 (82).

3.6. 4-Butylamino-N-[(E)-3-(4-ethoxycarbonyl) phenylallyl]-1,8-naphthalimide **8**

Using ethyl 4-bromo-benzoate (3.1 g, 13.5 mmol) the title compound **8** was afforded as a yellow solid (1.5 g, 74%); m.p. 180–181 °C; λ_{max}(EtOH)/nm 279.0 (ε/dm^3 mol^{-1} cm^{-1} 63,360), 445.5 (29,320); ν_{max}(nujol)/cm^{-1} inter alia 3400 (N–H), 1700, 1680, 1640, 1580 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.97 (3H, t, *J* 7.0, $C\underline{H}_3CH_2CH_2$), 1.32 (3H, t, *J* 7.0, $C\underline{H}_3CH_2O$), 1.45 (2H, sextet, *J* 7.0, $CH_3C\underline{H}_2CH_2$), 1.71 (2H. quintet, *J* 6.9, $CH_2C\underline{H}_2CH_2$), 3.40 (2H, br s, $CH_2C\underline{H}_2NH$), 4.30 (2H, q, *J* 6.9, $CH_3C\underline{H}_2O$), 4.83 (2H, br s, 13-H), 6.51–6.66 (2H, m, $NC\underline{H}_2C\underline{H}=C\underline{H}$), 6.80 (1H, d, *J* .5, 3-H), 7.56 (2H, d, *J* 8.0, phenyl-H), 7.70 (1H, t, *J* 7.8, 6-H), 7.81 (1H, br s, disappears upon addition of D_2O, N–H), 7.87 (2H, d, *J* 8.0, phenyl-H), 8.30 (1H, d, *J* 8.5, 2-H), 8.47 (1H, d, *J* 7.0, 7-H), 8.75 (1H, d, *J* 8.0, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 13.9 (q, $\underline{C}H_3[CH_2]_3N$), 14.3 (q, $OCH_2\underline{C}H_3$), 20.0 (t, $CH_2\underline{C}H_2CH_3$), 30.1 (t, $CH_2\underline{C}H_2CH_2$), 41.1 (t, C-13), 42.7 (t, $CH_2\underline{C}H_2NH$), 60.8 (t, $O\underline{C}H_2CH_3$), 104. 0 (d, C-3), 107.5 (s), 120.3 (s), 122.0 (s), 124.4 (d, C-6), 126.5 (C-H), 128.5 (d), 128.9 (d), 129.6 (d), 129.8 (s), 130.1 (d), 130.9 (d, C-7), 134.6 (d, C-2), 141.2 (s), 151.0 (s, C-4), 162.8 (s, C-11), 163.9 (s, C-12), 165.6 (s, $\underline{C}O_2CH_2CH_3$); *m*/*z* (EI) 456.2051 (M^+, $C_{28}H_{28}N_2O_4$ requires 456.2049); (FAB) inter alia 457 ($M^+ + H$, 100%), 293 (42), 281 (36).

3.7. N-[(E)-3-(4-Acetyl-phenyl)allyl]-4-butylamino-1,8-naphthalimide **9**

Using 4-iodoacetophenone (3.3 g, 13.6 mmol) the title compound was afforded as a yellow solid (0.36 g, 19%); m.p. 210 °C; λ_{max}(EtOH)/nm 283.5 (61,070), 449.5 (29,320); ν_{max}(nujol)/cm^{-1} inter alia 3390 (N–H), 1670, 1640, 1580 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.97 (3H, t, *J* 7.3, $C\underline{H}_3CH_2CH_2$), 1.45 (2H, sextet, *J* 7.4, $CH_3C\underline{H}_2CH_2$), 1.71 (2H, quintet, *J* 7 3, $CH_2C\underline{H}_2CH_2$), 3.40 (2H, q, *J* 6.5, collapses to triplet upon addition of D_2O, $CH_2C\underline{H}_2N$–H), 4.83 (2H, d, *J* 4.0, $NC\underline{H}_2CH=CH$), 6.51–6.66 (2H, m, $NCH_2C\underline{H}=C\underline{H}$), 6.81 (1H, d, *J* 8.5, 3-H), 7.57 (2H, d, *J* 8 5, phenyl-H), 7.71 (1H, t, *J* 7.8, 6-H), 7.82 (1H, t, *J* 5.3, disappears upon addition of D_2O, N-H), 7.88 (2H, d, *J* 8.5, phenyl-H), 8.30 (1H, d, *J* 8.5, 2-H), 8.47 (1H, d, *J* 7.0, 7-H), 8.75 (1H, d, *J* 8.5, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 13.9 (q, $CH_2CH_2\underline{C}H_3$), 20.0 (t, $CH_2\underline{C}H_2CH_3$), 26.8 (q, $\underline{C}H_3CO$), 30.1 (t, $CH_2\underline{C}H_2CH_2$), 41.1 (t, C-13), 42.7 (t, $CH_2\underline{C}H_2NH$), 103.9 (d, C-3), 107.5 (s), 120.3 (s), 121.9 (s), 124.3 (d, C-6), 126.5 (d), 128.5 (d), 128.7 (d), 128.9 (d), 129.7 (s), 130.1 (d), 130.9 (d, C-7), 134.5 (d, C-2), 135.7 (s), 141.1 (s), 150.9 (s, C-4), 162.8 (s, C-11), 163.7 (s, C-12), 197.4 (s, $CH_3\underline{C}O$); *m*/*z* (EI) 426.1941 (M^+, $C_{27}H_{26}N_2O_3$ requires 426.1943); (FAB) inter alia 427 ($M^+ + H$, 29%), 293 (100), 281 (73).

3.8. N-Allyl-4-butylsulfanyl-1,8-naphthalimide **12**

An aqueous solution of potassium hydroxide (1.2 g, 20 mmol in 5 ml) was added dropwise to a mixture of 4-chloro-1,8-naphthalic anhydride (5.0 g, 21 mmol), butanethiol (2.1 ml, 20 mmol) and *N,N*-dimethylformamide (75 ml) at room temperature. After stirring for 1 hr the mixture was poured onto crushed ice (ca. 200 g). The resulting precipitate, was filtered, washed with water and air dried before redissolving in ethanol (100 ml). Allylamine (4.5 ml, 60 mmol) was then added and the solution was refluxed for 6 h. The reaction liquor was cooled and the precipitate collected by filtration. Recrystallisation of the precipitate from ethyl acetate/40–60 petroleum ether gave the title compound as yellow needles (2.5 g, 36%); m.p. 84 °C λ_{max}(EtOH)/nm 254.3 (ε/dm^3 mol^{-1} cm^{-1} 31,760), 392.5 (25,030); ν_{max}(nujol)/cm^{-1} inter alia 1690, 1650 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.95 (3H, t, *J* 7.3, $C\underline{H}_3CH_2CH_2$), 1.52 (2H, sextet, *J* 7.3, $CH_3C\underline{H}_2CH_2$), 1.73 (2H, quintet, *J* 7.4, $CH_2C\underline{H}_2CH_2$), 3.26 (2H, t, *J* 7.3, $CH_2C\underline{H}_2S$), 4.65 (2H, d, *J* 5.5, $NC\underline{H}_2CH=CH_2$), 5.10–5.19 (2H, m, $NCH_2CH=C\underline{H}_2$), 5.88–6.01 (1H, m, $NCH_2C\underline{H}=CH_2$), 7.73 (1 H, d, *J* 8.0, 3-H), 7.87 (1 H, t, *J* 7.8, 6-H), 8.35 (1H, d, *J* 8.0, 2-H), 8.48–8.54

(2H, m, 5-H and 7-H); δ_C(100 MHz, $[CD_3]_2SO$) 13.7 (q, $\underline{C}H_3CH_2$), 21.7 (t, $CH_3\underline{C}H_2CH_2$), 30.0 (t, $CH_2\underline{C}H_2CH_2$), 30.8 (t, $CH_2\underline{C}H_2S$), 41.8 (t, $N\underline{C}H_2CH=CH_2$), 116.5 (t, $NCH_2CH=\underline{C}H_2$), 118.2 (s), 122.6 (s), 122.9 (d), 127.3 (d), 127.7 (s), 128.7 (s), 129.8 (d), 130.7 (d), 131.2 (d), 133.0 (d), 145.1 (s, C-4), 163.0 (2×s, C-11 and C-12); *m/z* (EI) 325.1133 (M^+, $C_{19}H_{19}NO_2S$ requires 325.1136); (FAB) inter alia 326 ($M^+ + H$, 100%).

3.9. General procedure for the preparation of 4-butylsulfanyl-N-[(E)-3-phenyl-allyl]-1,8-naphthalimides

N-Allyl-4-butylsulfanyl-1,8-naphthalimide **12** (0.80 g, 2.5 mmol), palladium(II) acetate (0.05 g, 0.25 mmol), potassium acetate (1.33 g, 13.6 mmol), tetrabutylammonium chloride (1.50 g, 5.4 mmol) and the appropriate halobenzene (6.8 mmol) were suspended in *N,N*-dimethylformamide (30 ml) and stirred at ca. 70–80 °C for 2 days. The reaction was then allowed to cool before adding ethyl acetate (50 ml) and water (50 ml) and stirring for a further hour. The resulting solution was extracted with ethyl acetate (3×30 ml), a small quantity of 4-*tert*-butylcatechol was added to the combined extracts, which were washed with water (3×30 ml), dried ($MgSO_4$) and evaporated to produce a viscous brown oil. Purification by silica gel chromatography (40–60 petroleum ether:EtOAc 3:1 to neat EtOAc gradient) and crystallisation (DCM:MeOH) gave the required products.

3.10. 4-Butylsulfanyl-N-[(E)-3-phenylallyl]-1,8-naphthalimide ***13***

Using iodobenzene (1.38 g, 6.76 mmol) the title compound **13** was afforded as a yellow solid (0.35 g, 19%); m.p. 100–101 °C; (found C, 74.5; H, 6.1; N, 3.5; S, 7.7; $C_{25}H_{23}NO_2S$ requires C, 74.8; H, 5.8; N, 3.5; S, 8.0%); λ_{max}(EtOH)/nm 253.5 (ε/dm^3 mol^{-1} cm^{-1} 38,530), 347.5 (8410),395.0 (19,710); ν_{max}(nujol)/cm^{-1} inter alia 1680, 1650 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.93 (3H, t, *J* 7.3, $C\underline{H}_3CH_2CH_2$), 1.49 (2H, sextet, *J* 7.4, $CH_3C\underline{H}_2CH_2$), 1.68 (2H, quintet, *J* 7.4, $CH_2C\underline{H}_2CH_2$), 3.15 (2H, t, *J* 7.3, $CH_2C\underline{H}_2S$), 4.76 (2H, d, *J* 5.3, $NC\underline{H}_2CH=CH$), 6.38 (1H, dt, *J* 16.1 and 5.9, $NCH_2C\underline{H}=CH$), 6.60 (1H, d, *J* 16.1, $NCH_2CH=C\underline{H}$), 7.21 (1H, m, phenyl-H), 7.28 (2H, br t, *J* 7.5, phenyl-H), 7.40 (2H, br d, *J* 7.3, phenyl-H), 7.53 (1H, d, *J* 8.0, 3-H), 7.73 (1H, t, *J* 7.9, 6-H), 8.21 (1H, d, *J* 7.8, 2-H), 8.32 (1H, d, *J* 8.3, 7-H), 8.38 (1H, d, *J* 7.3, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 13.6 (q, $\underline{C}H_3CH_2$), 21.7 (t, $CH_3\underline{C}H_2CH_2$), 30.0 (t), 30.8 (t), 41.5 (t, $NC\underline{H}_2CH=CH$), 118.1 (s), 122.5 (d), 122.6 (s), 124.5 (d), 126.4 (d), 127.0 (d), 127.5 (s), 127.7 (d), 128.4 (s), 128.7 (d), 129.5 (d), 130.4 (d), 131.0 (d), 131.9 (d), 136.4 (s, phenyl quaternary), 145.0 (s, C-4), 162.9 (s, C-11), 163.0 (s, C-12); *m/z* (FAB) inter alia 401 ($M^{+\bullet}$, 100%), 310 (53).

3.11. 4-Butylsulfanyl-N-[(E)-3-(4-ethoxycarbonyl) phenylallyl]-1,8-naphthalimide ***14***

Using ethyl 4-bromobenzoate (1.55 g, 6.76 mmol) the title compound was obtained as a yellow solid (0.91 g, 28%); m.p. 120 °C (found C, 71.1; H, 5.9; N, 3.0; S, 6.5; $C_{28}H_{27}NO_4S$ requires C, 71.0; H, 5.8; N, 3.0; S, 6.8%); λ_{max}(EtOH)/nm 274.0 (ε/dm^3 mol^{-1} cm^{-1} 51,760), 394.5 (26,050); ν_{max}(nujol)/cm^{-1} inter alia 1700, 1690, 1650 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.96 (3H, t, *J* 7.3, $C\underline{H}_3(CH_2)_3S$), 1.32 (3H, t, *J* 7.1, $C\underline{H}_3CH_2O$), 1.52 (2H, sextet, *J* 7.4, $CH_3C\underline{H}_2CH_2$), 1.75 (2H, quintet, *J* 7.3, $CH_2C\underline{H}_2CH_2$), 3.29(2H, t, *J* 7.4, CH_2S), 4.30 (2H, q, *J* 7.1, $CH_3C\underline{H}_2O$), 4.86 (2H, d, *J* 4.7, $NC\underline{H}_2CH=CH$), 6.52–6.73 (2H, m, $NCH_2C\underline{H}=C\underline{H}$), 7.57 (2H, d, *J* 8.4, phenyl-H), 7.80 (1H, d, *J* 8.1, 3-H), 7.84–7.96 (3H, m, 6-H and phenyl-H), 8.43 (1H, d, *J* 7.9, 2-H), 8.56–8.60 (2H, m, 5-H and 7-H); δ_C(100 MHz, $[CD_3]_2SO$); 13.6 (q, $\underline{C}H_3CH_2CH_2$), 14.3 (q, $\underline{C}H_3CH_2$), 21.7 (t, $CH_3\underline{C}H_2CH_2$), 30.0 (t, $CH_2\underline{C}H_2CH_2$), 30.8 (t, $CH_2\underline{C}H_2S$), 41.4 (t, $NC\underline{H}_2CH=CH$), 60.7 (t, $\underline{C}H_2O$), 118.2 (s), 122.7 (d), 126.5 (d), 127.1 (d), 127.6 (s), 127.8 (d), 128.6 (s), 128.7 (s), 129.5 (d), 129.6 (d), 130.4 (d), 130.5 (d), 131.1 (d), 141.1 (s), 145.1 (s), 163.0 (s, C-11), 163.1 (s, C-12), 165.5 (s, $\underline{C}O_2C_2H_5$); *m/z* (FAB) inter alia 474 ($M^+ + H$, 100%), 428 (38), 310 (98), 298 (92).

3.12. N-[(E)-3-(4-Acetoxymethylphenyl)allyl]-4-butylsulfanyl-1,8-naphthalimide ***15***

Using 4-bromobenzyl bromide (1.69 g, 6.76 mmol) the title compound **15** as an orange solid

(0.14 g, 7%); m.p.°C; λ_{max}(EtOH)/nm 255.5 (ε/dm^3 mol^{-1} cm^{-1} 46,270), 391.5 (20,760); ν_{max}(nujol)/cm^{-1} (nujol) inter alia 1720, 1680, l630 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 0.93 (3H, t, *J* 7.4, C<u>H</u>$_3$CH$_2$), 1.48 (2H, sextet, *J* 7.4, CH$_3$C<u>H</u>$_2$CH$_2$), 1.68 (2H, quintet, *J* 7.4, CH$_2$C<u>H</u>$_2$CH$_2$), 2.04 (3H, s, C<u>H</u>$_3$C=O), 3.15 (2H, t, *J* 7.3, CH$_2$C<u>H</u>$_2$S), 4.75 (2H, br d, *J* 5.8, NC<u>H</u>$_2$CH=CH), 5.00 (2H, s, C<u>H</u>$_2$O(-CO)CH$_3$), 6.39 (1H, dt, *J* 16.1 and 5.9, NCH$_2$C<u>H</u>=CH), 6.59 (1H, d, *J* 15.8, NCH$_2$CH=C<u>H</u>), 7.26 (2H, d, *J* 8.3, phenyl-H), 7.41 (2H, d, *J* 8.3, phenyl-H), 7.53 (1H, d, *J* 8.0, 3-H), 7.72 (1H, t, *J* 7.9, 6-H), 8.20 (1H, d, *J* 8.0, 2-H), 8.31 (1H, d, *J* 8.3, 7-H), 8.38 (1H, d, *J* 7.0, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 13.6 (q, <u>C</u>H$_3$CH$_2$), 20.8 (q, CH$_3$CO), 21.7 (t, CH$_3$<u>C</u>H$_2$CH$_2$), 30.0 (t, CH$_2$<u>C</u>H$_2$CH$_2$), 30.8 (t), 41.4 (t, <u>C</u>H$_2$N), 65.3 (t, <u>C</u>H$_2$O), 118.1 (s), 122.4 (d), 122.5 (s), 124.8 (d), 126.4 (d), 127.0 (d), 127.5 (s), 128.4 (d), 129.5 (d), 130.4 (d), 131.0 (d), 131.3 (d), 135.5 (s), 136.2 (s), 145.0 (s, C-4), 162.9 (s, C-13), 163.0 (s, C-12), 170.3 (s, CH$_3$<u>C</u>O$_2$); *m*/*z* (CI) inter alia 474.1739 (M$^+$+H, $C_{28}H_{28}O4NS$ requires 474.1737); (FAB) inter alia 474 (M$^+$+H, 36%), 414 (100), 310 (35), 298 (42).

3.13. N-Allyl-4-amino-1,8-naphthalimide **19**

4-Nitro-1,8-naphthalic anhydride **16** (3 g, 12.3 mmol) was dissolved in 50 ml of *N*,*N*-dimethylformamide and saturated with hydrogen in the presence of 10% w/w Pd/C (0.67 g, 5 mol%). After 24 h, the resulting thick solution was warmed slightly and filtered to remove the catalyst. Brine (ca. 500 ml) was then added to the filtrate, to precipitate 4-amino-1,8-naphthalic anhydride **17** as a yellow solid. Filtration, washing with water and drying gave **17** (1.9 g, 73%). **17** (0.5 g, 2.4 mmol) and allylamine (0.54 ml, 7 mmol) were then dissolved in *N,N*-dimethylformamide/ethanol (2 ml/5 ml) and heated to 80 °C for 6 h. The resulting solution was then allowed to cool to room temperature and ethanol (5 ml) was added to precipitate the title compound **21** as orange needles (0.44 g 75% from **17**); m.p. 225–226 °C dec.; λ_{max}(EtOH)/nm 202.4 (ε/dm^3 mol^{-1} 35,060), 227.9 (12,500), 256.7 (20,850), 275.3 (16,930), 323.2 (1680), 339.2 (860), 435.0 (12,670); ν_{max}(nujol)/cm^{-1} inter alia 3450, 3320, 3215 (N-H); 1660,1630, (C=O); δ_H(300 MHz, $[CD_3]_2SO$) 4.63 (2H, br d, *J* 5.2, C<u>H</u>$_2$N), 5.04–5.14 (2H, m, CH$_2$CH=C<u>H</u>$_2$), 5.87–5.99 (1H, m, CH$_2$C<u>H</u>=CH$_2$), 6.87 (1H, d, *J* 8.4, 3-H), 7.49 (2H, br s, disappears upon addition of D_2O, NH$_2$), 7.67 (1H, br t, *J* 7.8, 6-H), 8.21 (1H, d, *J* 8.4, 2-H), 8.44 (1H, dd, *J* 7.3 and 1.0, 7-H), 8. 64 (1H, dd, *J* 8.4 and 0.8, 5-H); δ_C(75 MHz, $[CD_3]_2SO$); 41.5 (t, <u>C</u>H$_2$N), 107.6 (s), 108.3 (d, C-3), 116.1 (t, <u>C</u>H$_2$=CHCH$_2$), 119.5 (s), 121.8 (s), 124.0 (d, C-6), 129.5 (d, C-5), 129.9 (s), 131.1 (d, C-7), 133.6 (d, CH$_2$=<u>C</u>HCH$_2$), 134.1 (d, C-2), 152.9 (s, C-4), 162.7 (s, C-11), 163.6 (s, C-12);*m*/*z* (EI) inter alia 253.0893 (M$^+$, $C_{15}H_{12}N_2O_2$ requires 252.08987); (CI) inter alia 253 (M$^+$+H, 100%).

3.14. 4-Acetylamino-N-allyl-1,8-naphthalimide **20**

3.14.1. Procedure 1

N-Allyl-4-amino-1,8-naphthalimide **19** (200 mg, 0.79 mmol) was suspended in acetic acid (3.3 ml) and acetic anhydride (1.2 ml). The suspension was refluxed for 1 h. After cooling to room temperature, the desired product **20** was precipitated. Recrystallisation from ethanol afforded the title compound **20** as a grey solid (136 mg, 58%).

3.14.2. Procedure 2

4-Nitro-1,8-naphthalic anhydride (3.0 g, 12.4 mmol) was dissolved in *N,N*-dimethylformamide (45 ml). The resulting solution was saturated with hydrogen in the presence of 10% w/w Pd/C (0.6 g, 5 mol%,) for 2 days. The resulting viscous solution was warmed slightly, filtered to remove the catalyst, and then poured into saturated brine (ca. 500 ml) to precipitate 4-amino-1,8-naphthalic anhydride as a yellow solid. The amine was removed by filtration, suspended in acetic acid (50 ml) and acetic anhydride (18 ml), and stirred for 12 h at ca. 85 °C. The suspension was then allowed to cool to room temperature and the resulting acetamide was removed by filtration and suspended in ethanol (25 ml). Allylamine (1.4 g, 25 mmol) was then added and the resulting mixture was gently refluxed for 48 h. After cooling to room temperature, the title compound **20** precipitated as a grey solid (2.1 g, 58%); m.p. 254–255 °C dec.; (found C, 69.3; H, 4.8; N, 9.5; $C_{17}H_{14}N_2O_3$ requires C, 69.4; H, 4.8; N, 9.5%); λ_{max}(EtOH)/nm 207.7 (ε/dm^3 mol^{-1}

cm^{-1} 10,810), 240.1 (11,890), 365.3 (5290); ν_{max}(nujol)/cm^{-1} 3270 (N-H), 1660, 1640 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 2.3 (3H, s, CH_3), 4.67 (2H, d, *J* 5.4, $NC\underline{H}_2CH=CH_2$), 5.11–5.19 (2H, m, $NCH_2CH=C\underline{H}_2$), 5.89–6.02 (1H, m, $NCH_2C\underline{H}=CH_2$), 7.91 (1 H, dd, *J* 7.3 and 8.5, 6-H), 8.42 (2H, ABq, *J* 8.3 and δ 49.6, 3-H and 2-H), 8.55 (1 H, dd, *J* 7.2 and 1.0, 7-H), 8.74 (1H, dd, *J* 8.5 and 1.1, 5-H), 10.44 (1H, s, disappears upon addition of D_2O, N-H); δ_C(100 MHz, $[CD_3]_2SO$) 24.3 (q, $\underline{C}H_3CO$), 41.7 (t, $N\underline{C}H_2$), 116.5 (t, $NCH_2CH=\underline{C}H_2$), 117.1 (s), 119.0 (d, C-3), 122.1 (s), 123.8 (s), 126.3 (d, C-6). 128.3 (s), 129.2 (d, C-5), 130.9 (d, C-7), 131.7 (d, 2-H), 133.0 (d, $NCH_2\underline{C}H=CH_2$), 140.5 (s), 162.6 (C-11), 163.2 (C-12), 169.7 ($CH_3\underline{C}O$); *m*/*z* (FAB) inter alia 295 ($M^+ + H$, 100%).

3.15. 4-Acetylamino-N-[(E)-3-phenylallyl]-1,8-naphthalimide **21**

N-Allyl-4-acetylamino-1,8-naphthalimide (0.50 g, 1.7 mmol), palladium(II) acetate (0.02 g, 0.1 mmol), potassium acetate (0.50 g, 5.1 mmol), tetrabutylammonium chloride (0.56 g, 2.0 mmol) and iodobenzene (0.29 ml, 2.6 mmol) were suspended in *N,N*-dimethylformamide (15 ml) and stirred at ca. 70–80 °C for 24 h. The reaction mixture was then allowed to cool before pouring into water (50 ml) and extracting with ethyl acetate (3×20 ml). A small quantity of 4-*tert*-butylcatechol was added to the combined extracts, which were washed with water (3×20 ml), dried (Na_2SO_4) and evaporated to yield a brown oil. The oil was dissolved in dichloromethane and passed through a short silica gel column. The solvent was evaporated and the resulting solid was recrystallised from dichloromethane/ethyl acetate/butanol to yield the title compound as a yellow/green solid (0.37 g, 59%); m.p. 204–242 °C; (found C, 74.4; H, 4.7; N, 7.5; $C_{23}H_{18}N_2O_3$ requires C, 74.6; H, 4.9; N, 7.6%); λ_{max}(EtOH)/nm 240.5 (ε/dm^3 mol^{-1} cm^{-1} 60,460), 292.5 (8100), 365.0 (19,500); ν_{max}(nujol)/cm^{-1} inter alia 3270 (N-H), 1690, 1650, 1585 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 2.30 (3H, s, $CH_3C=O$), 4.82 (2H, d, *J* 5.6, $NC\underline{H}_2CH$), 6.54–7.46 (2H, m, $NCH_2C\underline{H}=C\underline{H}$), 7.85–7.94 (5H, m, phenyl-H), 7.90 (1H, t, *J* 7.9, 6-H), 8.41 (2H, ABq, *J* 8.1 and δ 49.4, 2-H and 3-H), 8.55 (1H, d, *J* 7.1, 7-H), 8.73 (1H, d, *J* 8.7, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 24.3 (q, CH_3), 41.4 (t, $\underline{C}H_2N$), 117.4 (s), 119.2 (d, C-3), 122.3 (s), 124.0 (s), 124.6 (d, C-4), 126.4 (d), 127.7 (d), 128.5 (s), 128.7 (d), 129.3 (d, C-5), 131.0 (d, C-7), 131.7 (d, $NCH_2CH=\underline{C}H$), 131.8 (d, C-2), 136.4 (s), 140.5 (s), 162.8 (s, C-11), 163.4 (s, C-12), 169.7 (s, $CH_3\underline{C}=O$); *m*/*z* (FAB) inter alia 371 ($M^+ + H$, 4%), 307 (5), 242 (100).

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