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Tetrahedron
Tetrahedron 64 (2008) 983–987

# Facile synthesis of 1,8-naphthalimides in palladium-catalysed aminocarbonylation of 1,8-diiodo-naphthalene

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Received 14 September 2007; revised 2 October 2007; accepted 4 October 2007
Available online 7 October 2007

Dedicated to Professor Csaba Szántay on the occasion of his 80th birthday

**Abstract**—1,8-Diiodo-naphthalene was aminocarbonylated with various primary and secondary amines in the presence of palladium(0) complexes formed in situ from palladium(II) acetate and triphenylphosphine. In the case of primary amines, depending on the amine to substrate ratio, two types of products have been obtained in highly chemoselective reaction: dicarboxamides and *N*-substituted imides have been formed at high and low amine to substrate ratio, respectively. The reaction tolerates the ester functionality, so that amino acid esters could serve as *N*-nucleophiles and in this way, naphthalimides possessing stereogenic centre in the *N*-substituent could be synthesised.


## 1. Introduction

The carbonylation of iodoaromatics and their synthetic analogues in homogeneous catalytic reactions is well-known for the wide audience of chemists.[1,2] By using various amines and alcohols as *N*- and *O*-nucleophiles, carboxamides/ketocarboxamides and esters/ketoesters can be synthesised in aminocarbonylation and alkoxycarbonylation, respectively.[3] There are several applications concerning the synthesis of simple building blocks and the functionalisation of biologically important skeletons as well.[4]

The palladium-catalysed homogeneous catalytic reaction might be especially efficient in those cases where the target carboxamides are hardly available via the conventional carboxylic acid—carboxylic halide—carboxamide pathway (e.g., with bulky substituents at the amide nitrogen). We extended this methodology to the application of various amino acid esters as *N*-nucleophiles. It has to be noted that although the N-acylation of amino acids is widely used in synthetic chemistry, the sporadic results have been published for the use of amino acid derivatives for the introduction of a carboxamide moiety.[5,6]

Among the iodoaromatics, 1,8-diiodo-naphthalene was also used as a substrate in some homogeneous catalytic reactions. It was reacted with an appropriate ferrocenyl substituted boroxin derivative in Suzuki coupling with the aim of investigating parallel and perpendicular stacking of ferrocene rings attached to a sterically desired backbone.[7] The same homogeneous catalytic reaction was used for the coupling of 1,8-diiodo-naphthalene with ruthenocenyl-dioxaborolane, resulting in ruthenoceno[*a*]acenaphthylene of peculiar redox behaviours.[8]

One type of the title compounds, *N*-alkyl-1,8-naphthalimide derivatives, has been known as fluorosensors and their spectral-luminescent characteristics have been studied in detail. Several derivatives functionalised at the 4 and 5 positions have been synthesised by conventional synthetic procedures[9–11] and palladium-catalysed Sonogashira[12] and Stille coupling reactions.[13] *N*-Phenyl- and *N*-benzyl-1,8-naphthalimide have been synthesised by the conventional reaction of 1,8-naphthalene-dicarboxylic anhydride and aniline[14,15] and benzylamine,[14] respectively. *N*-Phenyl-imide can also be obtained by the phenylation of 1,8-naphthalimide by phenyl-boronates[16] or by the phenylation of *N*-Br-1,8-naphthalimide.[17]

Encouraged by the increasing importance of various *N*-substituted imides serving as intermediates for the synthesis of substituted heterocycles,[18] especially those possessing protected amino acid derivatives, we decided to investigate the possibility of extending the scope of the aminocarbonylation methodology to novel type of 'double acylation' of the amino functionality of amino acid esters by highly reactive palladium-acyl intermediates. Accordingly, two types of aminocarbonylation of 1,8-diiodo-naphthalene leading to *N*-substituted carboxamides and imides are published in the present paper.

*Keywords*: Iodoaromatics; Aminocarbonylation; Carbon monoxide; Palladium; Amine; Carbonylation.
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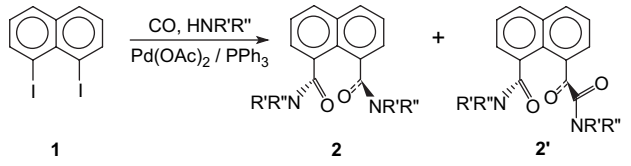
doi:10.1016/j.tet.2007.10.026

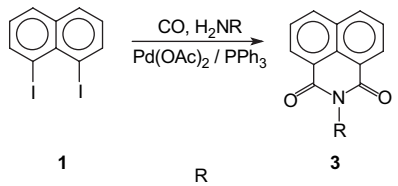
## 2. Results and discussion

1,8-Diiodo-naphthalene (**1**), synthesised from 1,8-diamino-naphthalene,[19] was reacted with carbon monoxide and various amines such as *tert*-butylamine (**a**), aniline (**b**), piperidine (**d**) and morpholine (**e**) (Scheme 1). Carrying out the reaction in an amine excess (amine to **1** ratio of up to 3/1), 1,8-dicarboxamides (**2d**, **2e**) of expected structure were obtained as major products. Furthermore, as previously observed with aryl iodides,[20] the reaction is accompanied by the formation of compounds possessing both carboxamide and ketocarboxamide functionalities (**2′d**, **2′e**) due to partial double carbon monoxide insertion (Table 1). By using 1,8-diiodo-napthalene as a substrate, the chemoselectivity is strongly dependant on the carbon monoxide pressure. Unlike the simple iodoarenes, ketocarboxamides have been formed in traces only under atmospheric carbon monoxide pressure, i.e., the corresponding dicarboxamides could be isolated in excellent yields. However, the unsymmetrically substituted naphthalenes possessing both carboxamide and glyoxylamide functionalities have been observed in comparable amount to dicarboxamides (**2d**, **2e**) under 40 bar carbon monoxide pressure. The lack of the selective formation of bis(ketocarboxamides), i.e., the double insertion of carbon monoxide into both iodoarene moieties of the starting material can be explained by the steric reasons. The use of the primary amines, *tert*-butylamine (**a**), aniline (**b**) and benzylamine (**c**) resulted in the corresponding carboxamides (**2a**–**2c**) in traces only. The ring-closure products **3a**–**3c** have been obtained in these cases (vide infra) (Scheme 2). Only **3b** and **3c** could be isolated in acceptable yield. The *tert*-butyl analogue **3a** underwent decomposition during isolation and work-up, resulting in a rather complicated mixture containing the corresponding anhydride, acid and amide derivatives.




| | R' | R" |
|---|---|---|
| **a** | H | *t*-Bu |
| **b** | H | Ph |
| **d** | -(CH$_2$)$_5$- | |
| **e** | -(CH$_2$)$_2$O(CH$_2$)$_2$- | |

**Scheme 1**. Synthesis of 1,8-naphthalene-dicarboxamides in palladium-catalysed aminocarbonylation of **1**.




| R | |
|---|---|
| **a** | *t*-Bu |
| **b** | Ph |
| **c** | $CH_2Ph$ |
| **f** | $CH_2COOCH_3$ |
| **g** | $CH(CH_3)COOCH_3$ |
| **h** | $CH(CH(CH_3)_2)COOCH_3$ |

**Scheme 2**. Synthesis of *N*-substituted 1,8-naphthalimides in palladium-catalysed aminocarbonylation of **1**.

Reducing the amine to **1** ratio to nearly 1/1, various *N*-substituted 1,8-naphthalimides with unfunctionalised amines (**3b**, **3c**) and those with the ester functionality (**3f**–**3h**) were obtained in highly chemoselective reaction in the presence of simple primary amines (**b**, **c**) and amino acid methylesters with $NH_2$ termini (**f**–**h**), respectively (Scheme 2). To the best of our knowledge, no imide formation has been observed in aminocarbonylation reaction by using either diiodoaromatics, bis(iodoalkenes), with sterically appropriate structure or their corresponding triflate analogues. In order to achieve yields of synthetic interest, the reaction had to be conducted under 40 bar carbon monoxide pressure in elevated reaction times (Table 2).

A side reaction leading to naphthalene-1,8-dicarboxylic anhydride was observed when amines of low reactivity were used in the aminocarbonylation reaction. In the presence of traces of water in the solvent (and even the adsorbed water on the wall of the glass flask), the palladium-acyl

**Table 2**. Synthesis of 1,8-naphthalimides in palladium-catalysed aminocarbonylation of **1**[a]

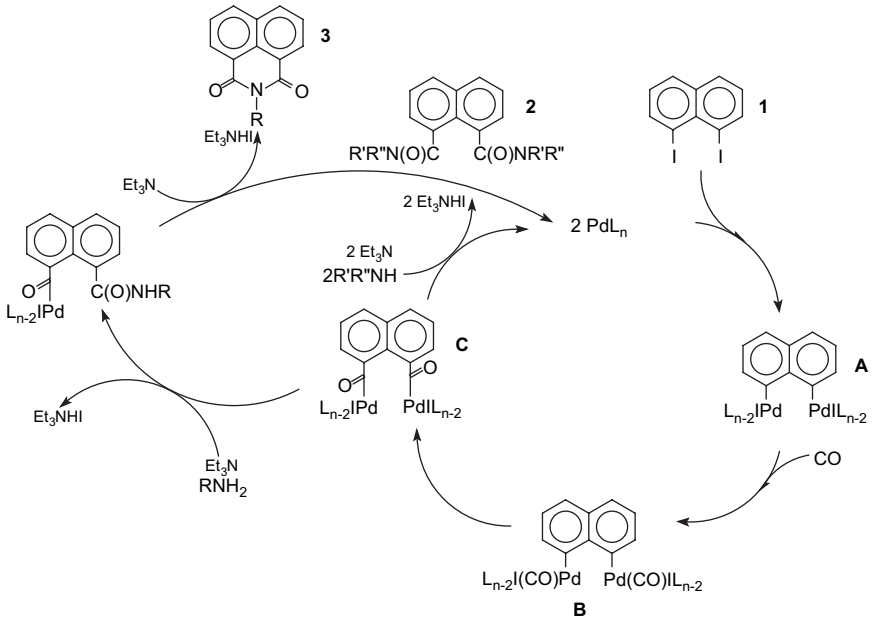
| Amine | Reaction time [h] | Isolated yield[b] (imide) [%] |
|---|---|---|
| $^t$BuNH$_2$ (**a**) | 42 | 0 (**3a**) |
| PhNH$_2$ (**b**) | 42 | 80 (**3b**) |
| PhCH$_2$NH$_2$ (**c**) | 42 | 82 (**3c**) |
| GlyOMe (**f**) | 90 | 77 (**3f**) |
| AlaOMe (**g**) | 90 | 78 (**3g**) |
| ValOMe (**h**) | 90 | 69 (**3h**) |

[a] Reaction conditions: 0.025 mmol Pd(OAc)$_2$, 0.05 mmol PPh$_3$, 0.5 mmol 1,8-diiodo-naphthalene (**1**), 0.55 mmol amine (**b**, **c**, **f**–**h**), 10 ml DMF, 40 bar CO.
[b] Practically, complete conversion (>98%) has been obtained in all cases.

**Table 1**. Synthesis of dicarboxamides in palladium-catalysed aminocarbonylation of **1**[a]

| Amine | Reaction time [h] | *p*(CO) [bar] | Yield/isolated yield[b] (1,8-diamide) [%] | Yield/isolated yield[b] (1-amide-8-ketoamide) [%] |
|---|---|---|---|---|
| $^t$BuNH$_2$ (**a**) | 22 | 40 | 20/0 (**3a**)[c] | 0 (**2′a**) |
| Aniline (**b**) | 22 | 1 | >98/75 (**3b**)[d] | 0 (**2′b**) |
| Aniline (**b**) | 22 | 40 | >98/72 (**3b**)[d] | 0 (**2′b**) |
| Piperidine (**d**) | 24 | 1 | >99/85 (**2d**) | <1 (**2′d**) |
| Piperidine (**d**) | 24 | 40 | 78/70 (**2d**) | 22/15 (**2′d**) |
| Morpholine (**e**) | 66 | 1 | >99/87 (**2e**) | <1 (**2′e**) |
| Morpholine (**e**) | 66 | 40 | 63/50 (**2e**) | 37/25 (**2′e**) |

[a] Reaction conditions: 0.025 mmol Pd(OAc)$_2$, 0.05 mmol PPh$_3$, 0.5 mmol 1,8-diiodo-naphthalene (**1**), 3.0 mmol **a** (2 mmol **b**, 1.5 mmol **d**, **e**), 10 ml DMF.
[b] Practically, complete conversion (>98%) has been obtained in all cases.
[c] Naphthalene-1,8-dicarboxylic anhydride was isolated.
[d] The corresponding ring-closure products (*N*-substituted naphthalimides) have been formed exclusively.




**Scheme 3**. The formation of **2** and **3** rationalised by a simplified reaction mechanism.

intermediate (**C**, vide infra, Scheme 3) undergoes hydrolysis leading to the corresponding anhydride. The amount of anhydride can be substantially decreased by using flame-dried apparatus. It has to be noted that similar side reaction providing carboxylic acid and anhydride has been observed with 17-iodo-androst-16-ene derivatives as well.[21]

The formation of the above products can be rationalised on the basis of the following simplified reaction mechanism (Scheme 3). The oxidative addition of the iodoaryl bond of **1** to palladium(0) complexes ($PdL_n$, where L stands for triphenylphosphine and solvent donor ligands), formed in situ from palladium(II) acetate and triphenylphosphine, resulted in the corresponding bis(palladium-aryl) catalytic intermediate (**A**). It is followed by carbon monoxide activation yielding a complex with terminal carbonyl ligand (**B**) and its insertion into palladium–aryl bond results in the corresponding bis(palladium-acyl) complex (**C**). This catalytic intermediate could react with a primary amine in two ways: (i) by using the amine in 3-fold (or larger) excess, the two acyl moieties react independently resulting in dicarboxamides (**2**) (or **2′** by double carbon monoxide insertion) and (ii) by using the substrate and amine in equimolar amount, both acyl moieties react with the same *N*-nucleophile yielding imides (**3**).

## 3. Conclusions

The palladium-catalysed aminocarbonylation of 1,8-diiodonaphthalene can be carried out in high isolated yields. While the application of secondary amines resulted in the formation of 1,8-dicarboxamides as major products and 1-amide-8-ketoamide derivatives as minor ones that of the primary amines provided the corresponding *N*-substituted 1,8-naphthalimides. The highly selective formation of the latter products in a novel type of aminocarbonylation reaction can be explained by the reaction of both palladium-acyl moieties, situated in sterically highly favoured positions, with the same amino group. The high chemoselectivity, the easy work-up of the reaction mixtures, as well as the high functional group tolerance of aminocarbonylation, regarding functional groups both at the *N*-alkyl substituent and at the aryl moieties, make these reactions of synthetic importance.

## 4. Experimental

### 4.1. General procedures

$^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 and 100.62 MHz, respectively. Chemical shifts $\delta$ are reported in parts per million relative to $CHCl_3$ (7.26 and 77.00 ppm for $^1H$ and $^{13}C$, respectively). Elemental analyses were carried out on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

1,8-Diiodo-naphthalene was synthesised as described previously.[19] The amines were purchased from Aldrich and were used without any further purification. Solvents were dried and purified by generally used procedures.

### 4.2. Aminocarbonylation experiments towards 1,8-naphthalene-dicarboxamides at normal pressure

In a typical experiment a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), $PPh_3$ (13.1 mg, 0.05 mmol), 1,8-diiodo-naphthalene (**1**, 0.5 mmol) and primary or secondary amine (**a**–**e**, 1.5–3.0 mmol) (see Table 1) was dissolved in 10 ml DMF under argon. Triethylamine (1.0 ml) was added to the homogeneous yellow solution and the atmosphere was changed to carbon monoxide. The colour changed to dark red. The reaction was conducted for up to 66 h at 50 °C. Some metallic palladium was formed at the end of the reaction, which

was filtered. (A sample of this solution was immediately analysed by GC–MS.) The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 ml) and washed with water (20 ml). The organic phase was thoroughly washed twice with 5% HCl (20 ml), saturated $NaHCO_3$ (20 ml), brine (20 ml), dried over $Na_2SO_4$ and concentrated to a yellow waxy material or a thick oil. Chromatography (silica, EtOAc/$CHCl_3$=1/9 or silica, EtOAc/$CHCl_3$=1/1) yielded the desired dicarboxamides (**2d**, **2e**) or carboxamide–ketocarboxamides (**2′d**, **2′e**), respectively.

### 4.3. Aminocarbonylation experiments towards 1,8-naphthalene-dicarboxamides at high pressure

The DMF solution of the catalyst precursor and reactants (amounts given in Section 4.2) was transferred under argon into a 100 ml stainless steel autoclave. The reaction vessel was pressurised to 40 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for 24 h. The work-up procedure is identical with that given above.

### 4.4. Aminocarbonylation experiments towards 1,8-naphthalimides at high pressure

In a typical experiment a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), $PPh_3$ (13.1 mg, 0.05 mmol), 1,8-diiodo-naphthalene (**1**, 0.5 mmol), unfunctionalised primary amine (**a**–**c**, 0.55 mmol) (or amino acid methylester hydrochlorides possessing primary amine functionality (**f**–**h**)) and triethylamine (1.0 ml) was dissolved in 10 ml DMF under argon into a 100 ml stainless steel autoclave. The reaction vessel was pressurised to 40 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for up to 90 h.

Some metallic palladium was formed at the end of the reaction, which was filtered. (A sample of this solution was immediately analysed by GC–MS.) The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 ml) and washed with water (20 ml). The organic phase was thoroughly washed twice with 5% HCl (20 ml), saturated $NaHCO_3$ (20 ml), brine (20 ml), dried over $Na_2SO_4$ and concentrated to a yellow waxy material. Chromatography (silica, EtOAc/$CHCl_3$=1/9, then chloroform/ethanol=1/1) yielded the desired naphthalimides (**3b**, **3c**, **3f**–**3h**) as solids.

### 4.5. Characterization of the products

**4.5.1. 1,8-Bis(*N*,*N*-penta-1′,5′-diyl-carboxamido)-naphthalene (2d).** $^1$H NMR ($CDCl_3$) $\delta$: 7.82 (d, 8.1 Hz, 2H, Naph), 7.42 (t, 7.0, 8.1 Hz, 2H, Naph), 7.36 (d, 7.0 Hz, 2H, Naph), 4.12 (d, 2H, 12 Hz, 2N(C$H_a$H$_b$)), 3.18–3.40 (m, 6H, $(CH_2)_2$+2N($CH_aH_b$)), 1.4–1.8 (m, 12H, 2×$(CH_2)_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 169.7, 134.9, 134.4, 129.7, 126.9, 125.7, 125.2, 48.4, 42.2, 25.7, 25.3, 24.6. IR (KBr, $cm^{-1}$): 1625 (CON). MS *m*/*z* (rel int. %): 350 (9), 265 (80), 238 (36), 180 (42), 127 (28), 84 (100). Anal. Calcd for $C_{22}H_{26}N_2O_2$ (350.46): C, 75.40; H, 7.48; N, 7.99. Found: C, 75.20; H, 7.65; N, 7.72. $R_f$ (10% EtOAc/$CHCl_3$) 0.48; off-white solid, mp 190 °C.

**4.5.2. 1-[*N*,*N*-(Penta-1′,5′-diyl)-carboxamido]-8-[*N*,*N*-(penta-1″,5″-diyl)-glyoxylamido]-naphthalene (2′d).** $^1$H NMR ($CDCl_3$) $\delta$: 8.04–8.09 (m, 2H, Naph), 7.90 (dd, 7.0, 8.1 Hz, 1H, Naph), 7.50–7.56 (m, 3H, Naph), 3.30–4.02 (m, 8H, 4×N($CH_2$)), 1.45–1.85 (m, 12H, 6×$CH_2$). $^{13}$C NMR ($CDCl_3$) $\delta$: 193.6, 170.9, 165.2, 135.5, 135.4, 134.8, 133.5, 130.9, 130.2, 128.4, 126.5, 125.9, 124.7, 49.3, 46.6, 42.5, 42.4, 26.2, 25.5, 25.4, 25.3, 24.7, 24.5. IR (KBr, $cm^{-1}$): 1678 (CO), 1637 (br, 2×CON). MS *m*/*z* (rel int. %): 378 (2), 295 (6), 266 (100), 210 (18), 180 (15), 126 (11). Anal. Calcd for $C_{22}H_{26}N_2O_3$ (378.47): C, 72.99; H, 6.92; N, 7.40. Found: C, 72.88; H, 6.75; N, 7.22. $R_f$ (30% EtOAc/$CHCl_3$) 0.49; off-white solid, mp 136 °C.

**4.5.3. 1,8-Bis[*N*,*N*-(3′-oxa-penta-1′,5′-diyl)-carboxamido]-naphthalene (2e).** $^1$H NMR ($CDCl_3$) $\delta$: 7.92 (d, 8.1 Hz, 2H, Naph), 7.46 (t, 7.0, 8.1 Hz, 2H, Naph), 7.38 (d, 7.0 Hz, 2H, Naph), 3.9 (m, 4H, 2N$CH_2$), 3.85 (br s, 8H, 4×$CH_2$), 3.4–3.6 (m, 4H, 2×$CH_2$). $^{13}$C NMR ($CDCl_3$) $\delta$: 170.3, 135.2, 133.0, 130.4, 127.5, 126.2, 125.2, 66.4, 66.3, 48.0, 42.0. IR (KBr, $cm^{-1}$): 1632 (CON). MS *m*/*z* (rel int. %): 354 (3), 268 (100), 224 (16), 180 (37), 127 (24). Anal. Calcd for $C_{20}H_{22}N_2O_4$ (354.41): C, 67.78; H, 6.26; N, 7.90. Found: C, 67.59; H, 6.45; N, 7.76. $R_f$ (10% EtOAc/$CHCl_3$) 0.18; off-white solid, mp 77 °C.

**4.5.4. 1-[*N*,*N*-(3′-Oxa-penta-1′,5′-diyl)-carboxamido]-8-[*N*,*N*-(3″-oxa-penta-1″,5″-diyl)-glyoxylamido]-naphthalene (2′e).** $^1$H NMR ($CDCl_3$) $\delta$: 8.08 (m, 2H, Naph), 7.95 (d, 8.0 Hz, 1H, Naph), 7.52–7.58 (m, 3H, Naph), 3.55–3.95 (m, 16H, 8×$CH_2$). $^{13}$C NMR ($CDCl_3$) $\delta$: 192.9, 171.1, 165.2, 135.9, 135.4, 133.6, 133.3, 130.9, 130.6, 130.4, 128.8, 126.2, 125.2, 67.0, 66.6, 66.3, 66.0, 48.7, 45.9, 42.1, 42.0. IR (KBr, $cm^{-1}$): 1673 (CO), 1643 (br, 2×CON). MS *m*/*z* (rel int. %): 382 (3), 297 (6), 268 (100), 224 (11), 180 (30), 126 (13). Anal. Calcd for $C_{21}H_{22}N_2O_5$ (382.42): C, 65.96; H, 5.80; N, 7.33. Found: C, 65.79; H, 5.85; N, 7.16. $R_f$ (50% EtOAc/$CHCl_3$) 0.27; off-white solid, mp 77 °C.

**4.5.5. *N*-(*tert*-Butyl)-1,8-naphthalimide (3a).** MS *m*/*z* (rel int. %): 253 (5), 238 (100), 180 (73), 153 (30), 126 (25).

**4.5.6. *N*-Phenyl-1,8-naphthalimide (3b).**[14] $^1$H NMR ($CDCl_3$) $\delta$: 8.64 (d, 7.6 Hz, 2H, Naph), 8.26 (d, 8.2 Hz, 2H, Naph), 7.92 (t, 7.6, 8.2 Hz, 2H, Naph), 7.55 (t, 7.2 Hz, 2H, Ph), 7.47 (t, 7.2 Hz, 1H, Ph), 7.32 (d, 7.2 Hz, 2H, Ph). $^{13}$C NMR ($CDCl_3$) $\delta$: 164.3, 135.2, 134.2, 133.3, 129.3, 128.6, 128.5, 127.4, 126.9, 122.8. IR (KBr, $cm^{-1}$): 1662 (CON). MS *m*/*z* (rel int. %): 273 (81), 272 (100), 228 (38), 180 (30), 126 (26). Anal. Calcd for $C_{18}H_{11}NO_2$ (273.29): C, 79.11; H, 4.06; N, 5.13. Found: C, 79.02; H, 4.25; N, 5.02. $R_f$ (10% EtOAc/$CHCl_3$) 0.76; yellow solid, mp 182 °C. The spectral data were in accordance with the literature data.

**4.5.7. *N*-Benzyl-1,8-naphthalimide (3c).**[15] $^1$H NMR ($CDCl_3$) $\delta$: 8.59 (d, 7.6 Hz, 2H, Naph), 8.18 (d, 8.2 Hz, 2H, Naph), 7.72 (t, 7.6, 8.2 Hz, 2H, Naph), 7.52 (d, 7.2 Hz, 2H, Ph), 7.20–7.31 (m, 3H, Ph), 5.39 (s, 2H, $CH_2$). $^{13}$C NMR ($CDCl_3$) $\delta$: 164.1, 137.3, 133.9, 131.5, 131.3, 128.9, 128.4, 127.4, 126.9, 122.6, 43.5. IR (KBr, $cm^{-1}$): 1655 (CON). MS *m*/*z* (rel int. %): 287 (100), 207 (14), 181 (46), 153 (56), 127 (34). Anal. Calcd for $C_{19}H_{13}NO_2$ (287.32): C, 79.43; H, 4.56; N, 4.87. Found: C, 79.32; H, 4.72; N, 4.67.

$R_f$ (10% EtOAc/$CHCl_3$) 0.84; off-white solid, mp 192 °C. The spectral data were in accordance with the literature data.

**4.5.8. *N*-(Methoxycarbonyl-methyl)-1,8-naphthalimide (3f).** $^1$H NMR ($CDCl_3$) $\delta$: 8.58 (d, 7.6 Hz, 2H, Naph), 8.20 (d, 8.2 Hz, 2H, Naph), 7.72 (t, 7.6, 8.2 Hz, 2H, Naph), 4.95 (s, 2H, $CH_2$), 3.76 (s, 3H, $OCH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 168.5, 163.8, 135.2, 134.3, 133.3, 127.4, 126.9, 122.1, 52.4, 41.2. IR (KBr, $cm^{-1}$): 1753 (COO), 1661 (CON). MS *m*/*z* (rel int. %): 269 (31), 237 (21), 210 (100), 180 (30), 126 (24). Anal. Calcd for $C_{15}H_{11}NO_4$ (269.26): C, 66.91; H, 4.12; N, 5.20. Found: C, 66.70; H, 4.25; N, 5.01. $R_f$ (10% EtOAc/$CHCl_3$) 0.67; white solid, mp 167 °C.

**4.5.9. *N*-(1′-Methoxycarbonyl-ethyl)-1,8-naphthalimide (3g).** $^1$H NMR ($CDCl_3$) $\delta$: 8.58 (d, 7.6 Hz, 2H, Naph), 8.20 (d, 8.2 Hz, 2H, Naph), 7.72 (t, 7.6, 8.2 Hz, 2H, Naph), 5.75 (q, 7 Hz, 1H, C*H*$CH_3$), 3.70 (s, 3H, $OCH_3$), 1.67 (d, 7 Hz, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 170.9, 163.5, 135.3, 134.2, 133.3, 127.4, 126.9, 122.4, 52.3, 49.0, 14.7. IR (KBr, $cm^{-1}$): 1738 (COO), 1660 (CON). MS *m*/*z* (rel int. %): 283 (34), 251 (21), 224 (100), 180 (46), 126 (27). Anal. Calcd for $C_{16}H_{13}NO_4$ (283.28): C, 67.84; H, 4.63; N, 4.94. Found: C, 67.61; H, 4.75; N, 4.76. $R_f$ (10% EtOAc/$CHCl_3$) 0.70; yellow solid, mp 143 °C.

**4.5.10. *N*-(1′-Methoxycarbonyl-2′-methyl-propyl)-1,8-naphthalimide (3h).** $^1$H NMR ($CDCl_3$) $\delta$: 8.60 (d, 7.6 Hz, 2H, Naph), 8.22 (d, 8.2 Hz, 2H, Naph), 7.78 (t, 7.6, 8.2 Hz, 2H, Naph), 5.37 (d, 7.4 Hz, 1H, NCH), 3.66 (s, 3H, $OCH_3$), 2.80–2.88 (m, 1H, C*H*$(CH_3)_2$), 1.31 (d, 7.1 Hz, 3H, CHC*H*$_3$), 0.8 (d, 7.1 Hz, 3H, CHC*H*$_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 170.3, 163.9, 135.2, 134.2, 133.4, 126.9, 122.2, 58.4, 52.0, 27.6, 22.0, 19.0. IR (KBr, $cm^{-1}$): 1736 (COO), 1663 (CON). MS *m*/*z* (rel int. %): 311 (40), 237 (18), 198 (100), 180 (52), 126 (28). Anal. Calcd for $C_{18}H_{17}NO_4$ (311.34): C, 69.44; H, 5.50; N, 4.50. Found: C, 69.22; H, 5.57; N, 4.38. $R_f$ (10% EtOAc/$CHCl_3$) 0.77; pale yellow solid, mp 158 °C.

## Acknowledgements

The authors thank the Hungarian Research Fund (OTKA NI61591) and the Joint Project of the European Union—Hungarian National Development Program (GVOP-3.2.1-2004-04-0168/3) for the financial support and Johnson Matthey for the generous gift of palladium(II) acetate.

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