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Palladium(II) and bidentate phosphine-catalyzed selective synthesis of *N*-aryl-2-pyrrolidinones via cyclocarbonylative coupling of 2-aminophenol and 2-aminothiophenol†

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The inter- and intra-molecular regioselective cyclocarbonylative coupling of 2-aminophenol (1a) and 2-aminothiophenol (1b) with various allylhalides was achieved in the presence of a catalytic amount of palladium acetate and 1,4-bis(diphenylphosphino)butane to afford *N*-aryl-2-pyrrolidinones (3, 4) in 47–65% yields. Other aminophenol derivatives have also been used and gave good yields of the corresponding *N*-aryl-2-pyrrolidinones. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: intermolecular; cyclocarbonylation; coupling; palladium; pyrrolidinones

INTRODUCTION

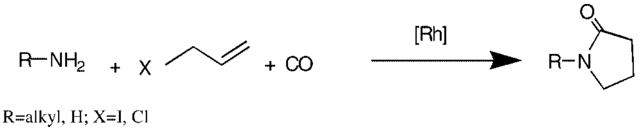
Heterocyclic compounds count among many natural products, such as vitamins, hormones, and antibiotics. In addition, they are found in pharmaceuticals and herbicides, the 2-pyrrolidinone skeleton is one of the most important nitrogen heterocycles for pharmaceutical applications.[1–3] Cyclocarbonylation reactions catalyzed by homogeneous systems provide new approaches to the synthesis of five-, six-, and seven-membered ring heterocycles.[4–8] Whereas various methodologies have been used for the catalytic synthesis of *N*-alkyl-2-pyrrolidinones, *N*-allyl-2-pyrrolidinones or *N*-benzyl-2-pyrrolidinones,[9–14] to our knowledge, there are no examples of the catalytic synthesis of *N*-aryl-2-pyrrolidinones. In the literature, limited data are available for the non-catalytic synthesis of *N*-aryl pyrrolidinones involving traditional reactions of aniline, or its derivatives, with butyrolactone under drastic reaction conditions.[15]

For an example, the rhodium-catalyzed synthesis of *N*-alkyl-2-pyrrolidinones from allylic halides, CO, and primary alkylamines (Scheme 1) has been described, where the reactions required drastic conditions of temperature and gas pressure.[9]

In this context, we report important results obtained on the regioselective cyclocarbonylative coupling reaction of 2-aminophenol derivatives **1a,c–e** or 2-aminothiophenol (**1b**) with allyl halides, catalyzed by palladium acetate [Pd(OAc)$_2$] and 1,4-bis(diphenylphosphino)butane (dppb) to give *N*-aryl-2-pyrrolidinones in relatively good yields.

RESULTS AND DISCUSSION

When 2-aminophenol (**1a**) was allowed to react with one equivalent of allylbromide and one equivalent of triethylamine in the presence of a catalytic amount of Pd(OAc)$_2$ and dppb in toluene under 600 psi of a mixture of CO and H$_2$ (1:1) at 100 °C for 48 h, *N*-(2-hydroxyphenyl)-2-pyrro-



Scheme 1.

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Table 1. Cyclocarbonylation reaction of 2-aminophenol (**1a**) and 2-aminothiophenol (**1b**) with allylbromide[a]

								Product distribution		
Run	RNH_2	P_{CO} (psi)	P_{H_2} (psi)	T (°C)	Time (h)	Phosphine	Conversion (%)	**3a** (**3b**)	**4a** (**4**)	**5a**
1	**1a**	300	300	120	48	dppb	90	56	24	20
2	**1a**	500	100	120	48	dppb	87	54	36	10
3	**1a**	100	500	120	48	dppb	85	41	38	21
4	**1a**	100	100	120	48	dppb	76	54	30	16
5	**1a**	300	300	100	48	dppb	85	65	20	15
6	**1a**	100	500	120	24	dppb	72	54	25	21
7	**1a**	100	200	120	48	dppb	74	60	18	22
8	**1a**	100	100	120	24	dppb	73	70	5	25
9	**1a**	100	100	120	18	dppb	80	85	traces	15
10	**1a**	100	500	120	48	dppe	<5	–	–	–
11	**1a**	100	500	120	48	dppp	<5	–	–	–
12	**1b**	100	200	120	24	dppb	50	–	–	
13	**1b**	300	300	120	24	dppb	85	80	20	–
14	**1b**	300	300	100	48	dppb	90	80	20	–

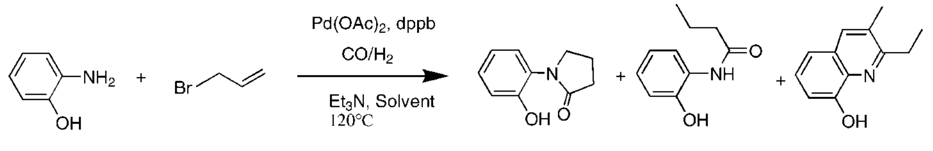
[a] Reaction conditions: catalyst (0.13 mmol); dppb (0.15 mmol); $R-NH_2$ (2 mmol); allyl bromide (2 mmol). Solvent: toluene (10 ml); triethylamine (2 mmol).

lidinone (**3a**) was isolated in 65% yield (Table 1, entry 5), together with *N*-(2-hydroxyphenyl)-butyramide (**4a**) and 8-hydroxy-2-ethyl-3-methyl quinoline (**5a**) (see Scheme 2).

Various reaction conditions were explored, such as the CO/H_2 ratio, ligand, and the time of the reaction, in order to optimize the yields toward the pyrrolidinone **3a** (Table 1).

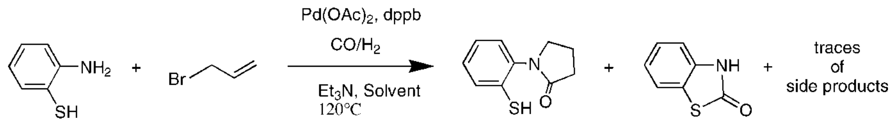
We observed that the best yields for the pyrrolidinone derivative **3a** were achieved using $Pd(OAc)_2$ and dppb as the catalytic system (Table 1). The use of 1,3-bis(diphenylphosphino)propane (dppp) or 1,2-bis(diphenylphosphino)ethane (dppe) as ligand, instead of dppb, led to a mixture of other products, such as mono- and bis-allylation products obtained as minor products in the case of dppe as ligand. Consistent quantities of unknown compounds and traces of cyclocarbonylation product formed in the case of dppp (Table 1, entries 10 and 11). In addition, the replacement of dppb with other monodentate phosphine ligands, such as PPh_3 and PCy_3, gave only traces of **3a**. The structure of **3a** was confirmed by X-ray analysis (see Experimental Details section).

It is important to note that the presence of hydrogen gas was crucial for the catalytic process; in fact, a blank run carried out in absence of H_2 gave poor yields of cyclocarbonylation product besides the consistent quantities of mono- and bis-allylation products and traces of other unknown compounds. From Table 1 it is possible to observe that the



1a **3a** **4a** **5a**

Scheme 2.



1b **3b** **4**

Scheme 3.

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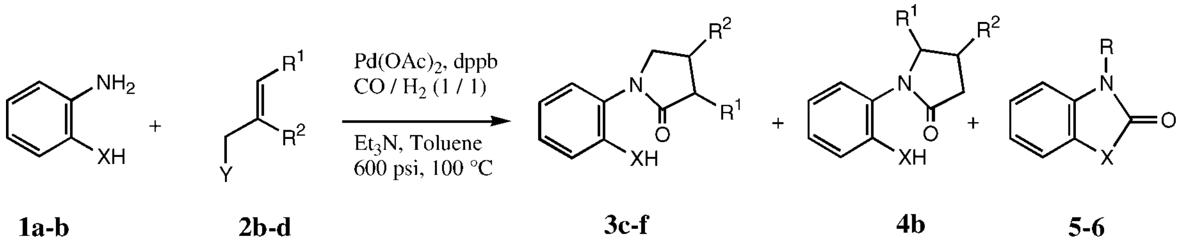


1a (X=O)
1b (X=S)

2b (R^1=CH_3, R^2=H, Y=Br)
2c (R^1=H, R^2=CH_3, Y=Cl)
2d (R^1=Ph, R^2=H, Y=Cl)

3c (R^1=CH_3, R^2=H, X=O)
3d (R^1=H, R^2=CH_3, X=O)
3e (R^1=Ph, R^2=H, X=O)
3f (R^1=H, R^2=CH_3, X=S)

4b (R^1= CH_3, R^2= H, X=O)

5(R=CH_2CH=CH-Ph, X=O)
6 (R = n-C_4H_9, X=S)

Scheme 4.

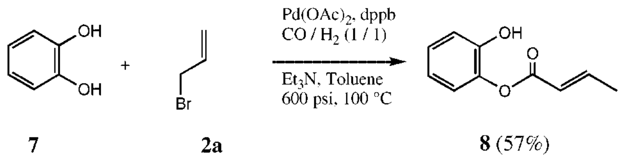
yield of **3a** increases with a decrease of the reaction time (Table 1, entries 8 and 9).

2-Aminothiophenol (**1b**) undergoes a similar cyclocarbonylative coupling reaction leading to *N*-2-thiophenyl-pyrrolidinone (**3b**) in acceptable yield (55%) after 48 h, together with minor amounts of (3*H*-benzothiazol-2-one) (**4**) and traces of unknown side products (Scheme 3).

To our knowledge, these results are the first examples of the catalytic synthesis of *N*-aryl-2-pyrrolidinones occurring with good yields and regioselectivity under relatively mild conditions. Other allylhalides (**2b–d**) were also carbonylated in the presence of 2-aminophenol and 2-aminothiophenol to produce the corresponding pyrrolidinone derivatives **3c–f** and **4b** according to Scheme 4.

The results in Table 2 show the dependence of the yields of the products on the R_1 and R_2 groups. In fact, the cyclocarbonylation reaction of **1a** with crotylbromide (**2b**) affords the two *N*-aryl-2-pyrrolidinone derivatives **3c** and **4b** in 60% total yield (**3c/4b** = 47/53) (Table 2, entry 1); but the cyclocarbonylation of **1a** in the presence of 3-chloro-2-methyl-1-propene (**2c**) gave exclusively *N*-2-hydroxyphenyl-3-methyl-2-pyrrolidinone (**3d**) in 62% isolated yield (Table 2, entry 2). However, **1a** with cinnamyl bromide (**2d**) gave a mixture of *N*-(2-hydroxyphenyl)-3-phenyl-2-pyrrolidinone (**3e**) and the five-membered ring **5** in 65% total yield (**3e/5** = 42/58) (Table 2, entry 3). Interestingly, only the five-membered ring heterocycle **6** was isolated from the reaction of the cyclocarbonylation of **1b** with **2b** (Table 2, entry 4); a low yield (10%) of *N*-arylpyrrolidinone **3f** was obtained in the reaction of **1b** with **2c** (Table 2, entry 5). Competition between the reactions of coupling and carbonylation via the insertion of CO on nitrogen or sulfur clearly showed the total control of carbonylation, with almost no coupling occurring. This can be simply explained by the acidity of the hydrogen atom attached to sulfur, which can be easily removed by triethylamine as a base.

No catalytic cyclocarbonylation was obtained from the



Scheme 5.

Table 2. Intramolecular cyclocarbonylation of **1a** and **1b** with allylhalogenides **2b–d** catalyzed by $Pd(OAc)_2$–dppb–CO–H_2[a]

				Product distribution[c] (%)			
Entry	Substrate **1**	Allylhalogenide **2**	Isolated yield[b] (%)	**3c-f**	**4b**	**5**	**6**
1	**1a**	**2b**	60	47	53		
2	**1a**	**2c**	62	100			
3	**1a**	**2d**	65	42		58	
4	**1b**	**2b**	50				100
5	**1b**	**2c**	10	100			

[a] Reaction conditions: $Pd(OAc)_2$ (0.13 mmol), dppb (0.15 mmol), substrate (2.0 mmol), allylhalogenide (2.0 mmol), triethylamine (2.0 mmol), toluene (10 ml), CO (300 psi), H_2 (300 psi), 120 °C, 48 h.
[b] Isolated yield.
[c] Determined by gas chromatography and ^1H NMR spectroscopy.

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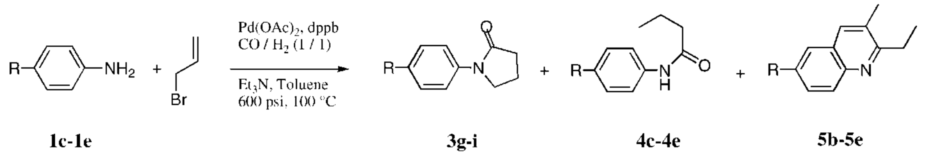

1c: R=-C_6H_5; **1d**: R=-CH_3; **1e**: R=-OCH_3.

Scheme 6.

reaction of catechol (**7**) with allylbromide; only the carbonylative coupling product **8** was identified (Scheme 5).

The carbonylation of 4-aminobiphenyl (**1c**), *p*-toluidine (**1d**), and *p*-anisidine (**1e**) (2 mmol) with allylbromide in toluene under 600 psi of CO/H_2 was performed. The pyrrolidinones **3g–i** were isolated in acceptable selectivity (40–70%), together with the amide derivatives **4b–e** (30–50%) and the quinoline derivatives **5b–d** (0–20%) (Scheme 6). The results are summarized in Table 3.

Although detailed mechanistic studies to identify the organometallic intermediates are currently in progress, we believe that this one-pot reaction could proceed in two steps. The first step involves palladium-assisted coupling reaction between the amine group of the 2-aminophenol and the allyl bromide to form the intermediate $\mathbf{2{-}OH{-}C_6H_4{-}NH{-}CH_2CH{=}CH_2}$. This later undergoes cyclocarbonylation, also in the presence of palladium as catalyst, producing the pyrrolidinone as the final product.

We have not been able to confirm experimentally the hypothesis for the possible **step-by-step** pathway for these reactions, owing to the instability of *N*-allylation products; in fact, we could not isolate them as pure compounds due to their easy oxidation, and decomposition after their synthesis was observed during the work-up of the reactions.

This represents one of the main reasons for which the **one-pot** synthesis of *N*-**aryl**-pyrrolidinones using $Pd(OAc)_2$–dppb as a homogeneous catalytic system represents a very useful and convenient alternative to the stoichiometric methods reported in literature.

In summary, the cyclocarbonylative coupling of 2-aminophenol and 2-aminothiophenol catalyzed by the $Pd(OAc)_2$–dppb–CO–H_2 system showed good activity in producing important pyrrolidinone derivatives in high yields. The carbonylation reaction was sensitive to the type of halide and to the experimental conditions.

EXPERIMENTAL DETAILS

Materials and measurements

$Pd(OAc)_2$, dppb, and all the starting materials were purchased from Aldrich. Melting points were obtained on an electrothermal apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer at room temperature and chemical shifts are reported relative to Me_4Si. IR and mass spectrometry (MS) were performed, respectively, on Perkin–Elmer 683 and Hewlett-Packard GC/Mass MSD 5971 instruments.

General experimental procedure

In a typical experiment, **1a** (2 mmol) was reacted with allylbromide (2 mmol) and triethylamine (2 mmol) in toluene as the solvent (10 ml) using $Pd(OAc)_2$ (0.13 mmol) and dppb (0.15 mmol) as the catalytic system in the presence of CO and H_2.

The reaction mixture was heated with stirring for 18–48 h at 100–120 °C (oil bath temperature). The reaction mixture was cooled to room temperature, the solution was concentrated, and the residue was extracted with ether. The pyrrolidinone derivative **3a** was isolated in 65% yield (Table 1, entry 5) from the *N*-(2-hydroxyphenyl)-butyramide (**4a**), and the 8-hydroxy-2-ethyl-3-methyl quinoline (**5a**) after separation by column chromatography using petroleum

Table 3. Intramolecular cyclocarbonylation of **1c**, **1d** and **1e** with allylbromides catalyzed by $Pd(OAc)_2$–dppb–CO–H_2[a]

Run	Substrate	Solvent	P_{CO} (psi)	P_{H_2} (psi)	Conversion (%)	Product distribution (%)		
1	**1c**	Toluene	300	300	80	**3g** (40)	**4c** (40)	**5b** (20)
2	**1c**	CH_2Cl_2	300	300	90	**3g** (50)	**4c** (50)	**5b** (–)
3	**1c**	Toluene	300	300	80	**3g** (50)	**4c** (30)	**5b** (20)
4	**1c**	Toluene	300	–	70	**3g** (70)	**4c** (–)	**5b** (30)
5	**1d**	Toluene	300	300	70	**3h** (50)	**4d** (35)	**5c** (15)
6	**1e**	Toluene	300	300	85	**3i** (54)	**4c** (34)	**5d** (12)

[a] Reaction conditions: catalyst (0.13 mmol); dppb (0.15 mmol); $R{-}NH_2$ (2 mmol); Allyl bromide (2 mmol); solvent (10 ml); triethylamine (2 mmol); temperature 120 °C.

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ether and diethyl ether 1/1 (v/v) as eluant and then characterized.

Analogous work-ups were used for the other pyrrolidinone derivatives.

Selected data for the isolated compounds

Compound **3a**

N-(2-Hydroxyphenyl)-2-pyrrolidinone; m.p. 129–130 °C. IR (neat): 1660 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 2.30 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.71 (t, J = 8 Hz, 2H, $\mathrm{COC}\mathit{H}_2\mathrm{CH_2}$), 3.98 (t, J = 7 Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2}$), 6.93–7.19 (m, 4H, Ph), 8.55 (br, s, 1H, O*H*).

^{13}C NMR (CDCl$_3$), δ (ppm): 19.55, 32.26, 50.91, 120.53, 120.84, 121.11, 123.20, 127.72, 150.11, 176.17.

MS, *m/z* (%): 177 (44), 122 (100), 120 (20), 95 (9), 77 (7), 65 (9), 52 (8).

X-ray analysis results. Formula: $C_{10}H_{11}NO_2$; formula weight: 177.20; crystal system: triclinic; space group: *P*1; Unit cell dimension: a = 8.269(2) Å, b = 9.978(2) Å, c = 11.361(2) Å; α = 77.496(3) °, β = 79.602(3) °, γ = 76.888(3) °; volume: 882.8(3) Å^3; Z = 4; radiation (Mo Kα) 0.710 73 Å. T = 293 K; calculated density: 1.333 g cm^{-3}; crystal size: 0.4 × 0.2 × 0.05 mm^3.

Compound **3b**

N-(2-Thiophenyl)-2-pyrrolidinone; m.p. 170–171 °C. IR (neat): 1660 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 2.0–2.4 (m, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CO}$), 2.6–3.2 (m, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2}$), 7.24–7.80 (m, 4H, Ph), 8.38 (br, s, 1H, S*H*).

^{13}C NMR (CDCl$_3$), δ (ppm): 27.50, 32.45, 36.98, 125.82, 128.16, 130.41, 133.26, 138.04, 141.74, 176.63.

MS, *m/z* (%): 193 (100), 165 (14), 151 (26), 136 (51), 125 (85), 109 (14), 94 (39), 69 (55), 65 (10).

Compound **3c**

N-(2-Hydroxyphenyl)-3-methyl-2-pyrrolidinone; oil. IR (neat): 1660 cm^{-1};

^{1}H NMR (CDCl$_3$), δ (ppm): 1.19 (d, J = 6.3 Hz, 3H, CH$_3$), 2.60 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 2.69 (m, 2H, $\mathrm{COC}\mathit{H}_2\mathrm{CH}$), 4.48 (m, 1H, $\mathrm{NC}\mathit{H}\mathrm{CH_3}$), 6.80–7.30 (m, 4H, Ph), 8.90 (br, s, 1H).

^{13}C NMR (CDCl$_3$), δ (ppm): 16.13, 28.42, 38.04, 48.71, 120.46, 120.79, 120.99, 125.05, 127.60, 150.12, 178.68.

MS, *m/z* (%): 191 (63), 176 (4), 149 (7), 135 (17), 122 (100), 120 (36), 86 (14), 84 (22), 65 (7).

Compound **3d**

N-(2-Hydroxyphenyl)-4-methyl-2-pyrrolidinone; m.p. 54–56 °C. IR (neat): 1660 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 1.24 (d, J = 6.5 Hz, 3H, $\mathrm{C}\mathit{H}_3$), 2.35 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 2.62–2.89 (m, 2H), 3.61 (dd, J = 6.5 Hz, J = 9.7 Hz, 1H), 4.00 (dd, J = 7.5 Hz, J = 9.7 Hz, 1H), 6.92–7.10 (m, 4H, Ph), 8.56 (br, s, 1H, O*H*).

^{13}C NMR (CDCl$_3$), δ (ppm): 19.19, 28.08, 40.29, 57.85, 120.47, 120.76, 121.07, 127.66, 150.07, 175.72.

MS, *m/z* (%): 191 (45), 122 (100), 120 (17), 95 (7), 77 (4), 65 (4).

Compound **3e**

N-(2-Hydroxyphenyl)-3-phenyl-2-pyrrolidinone; oil. IR (neat): 1660 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 2.42 (dd, J = 9.5 Hz, J = 8.4 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{Ph}$), 2.64–3.0 (m, 2H), 3.88–4.20 (m, 2H), 6.92–7.50 (m, 9H), 8.50 (br, s, 1H, O*H*).

^{13}C NMR (CDCl$_3$), δ (ppm): 29.42, 48.85, 49.37, 120.64, 120.99, 121.14, 127.60, 127.88, 127.96, 128.39, 128.94, 138.26, 150.21, 176.22.

MS, *m/z* (%): 253 (100), 149 (38), 135 (21), 122 (58), 120 (60), 118 (37), 117 (52), 91 (16), 65 (8).

Compound **4b**

N-(2-Hydroxyphenyl)-5-methyl-2-pyrrolidinone; oil. IR (neat): 1660 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 1.19 (d, J = 6.2 Hz, 3H), 1.79–2.07 (m, 1H), 2.27–2.60 (m, 1H), 2.69 (m, 2H), 4.48 (m, 1H), 6.90–7.25 (m, 4H, Ph), 8.90 (br, s, 1H, SH).

^{13}C NMR (CDCl$_3$), δ (ppm): 20.13, 27.42, 31.18, 56.86, 120.75, 120.83, 122.88, 124.02, 128.00, 151.53, 176.02.

MS, *m/z* (%): 191 (79), 176 (60), 148 (12), 130 (5), 115 (4).

Compound **4a**

N-(2-Hydroxyphenyl)-butyramide; oil. IR (neat): (OH) 3284 (C=O) 1757 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 0.99 (t, J = 7.4 Hz 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2}$), 1.75 (six signals, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 2.41 (t, J = 7.4 Hz, 2H, $\mathrm{COCH_2C}\mathit{H}_2\mathrm{CH_2}$), 6.79–7.22 (m, 4H), 8.10 (s, br, 1H), 9.0 (s, br, 1H).

^{13}C NMR (CDCl$_3$), δ (ppm): 13.55, 19.21, 38.78, 120.42, 122.11, 124.06, 125.73, 126.82, 148.36, 173.71.

MS, *m/z* (%): 179 (19), 109 (100), 80 (9), 43 (4).

Compound **5a**

8-Hydroxy-2-ethyl-3-methyl quinoline; oil. IR (neat): (OH) 3392, 2925, 1725, 1575, 1494, 1457, 1233, 750 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 1.41 (t, J = 7.4 Hz, 3H, $\mathrm{CH_2C}\mathit{H}_3$), 2.46 (d, J = 0.6 Hz, 3H, $\mathrm{C}\mathit{H}_3$), 2.63 (quartet, J = 7.4 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 7.40–7.00 (m, 4H), 7.72–7.65 (m, 2H), 7.90–7.84 (m, 3H), 7.81 (s, 1H).

^{13}C NMR (CDCl$_3$), δ (ppm): 11.85, 19.01, 28.59, 108.59, 116.75, 126.64, 130.50, 135.45, 151.68.

MS, *m/z* (%): 187 (72), 186 (100), 159 (21), 91 (15), 77 (5), 51 (8).

Compound **5**

3-(3-Phenyl-allyl)-2,3-dihydro-benzooxazole; oil. IR (neat): 1775 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 4.62 (dd, J = 1.3 Hz, J = 6.2 Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH{=}CH}$), 6.24 (dt, J_d = 15.9 Hz, J_t = 6.2 Hz, 1H, $\mathrm{NCH_2C}\mathit{H}\mathrm{{=}CH}$), 6.69 (d, J = 15.9 Hz, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{Ph}$), 7.00–7.43 (m, 9H).

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^{13}C NMR (CDCl$_3$), δ (ppm): 44.36, 108.91, 110.08, 121.63, 122.55, 123.88, 126.56, 128.25, 128.65, 128.70, 134.16, 135.67, 142.65, 171.02.

MS, *m/z* (%): 251 (11), 117 (100), 115 (36), 91 (15), 77 (5), 51 (8).

Compound **6**

3-Butyl-2,3-dihydro-benzothiazole; m.p. 125–127 °C. IR (neat): 1775 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 0.97 (t, J = 7.5 Hz, 3H, CH_3CH$_2$), 1.47 (m, 3H, CH_2CH$_3$), 1.86 (m, 2H, CH_2CH$_2$CH$_3$), 3.12 (t, J = 7.5 Hz, 2H, NCH_2CH$_2$), 7.34–7.97 (m, 4H, Ph).

^{13}C NMR (CDCl$_3$), δ (ppm): 13.76, 22.29, 31.76, 34.04, 121.44, 122.45, 124.57, 125.82, 135.10, 153.20, 172.41.

MS, *m/z* (%): 207 (<1), 191 (4), 176 (4), 162 (27), 149 (100), 108 (9), 83 (6), 68 (7).

Compound **8**

But-2-enoic acid 2-hydroxy-phenyl ester; oil. IR (neat): (OH) 3400 (C=O) 1775 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 1.99 (dd, J = 1.6 Hz, J = 6.9 Hz, 3H CH_3CH=CH), 5.64 (br, s, 1H, OH), 6.09 (m, 1H, CH$_3$CH=CH), 6.80–7.15 (m, 4H, Ph), 7.25 (d, J = 15.5 Hz, 1H, CH=CHCO).

^{13}C NMR (CDCl$_3$), δ (ppm): 18.31, 115.34, 117.89, 120.93, 121.30, 122.38, 126.92, 147.15, 148.49, 164.71.

MS, *m/z* (%): 178 (19), 110 (12), 69 (100), 41 (8).

Compound **3g**

1-Biphenyl-4-yl-pyrrolidin-2-one; m.p. 184–185 °C. IR (neat): (CO) 1679 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 2.09–2.25 (m, CH$_2$CH_2CH$_2$), 2.63 (t, J = 7.7 Hz, 2H, COCH_2CH$_2$), 3.89 (t, J = 7.0 Hz, 2H, NCH_2CH$_2$), 7.72–7.25 (m, 9H, Biph).

^{13}C NMR (CDCl$_3$), δ (ppm): 17.97, 32.72, 48.73, 120.12, 126.83, 127.11, 127.37, 128.74, 137.19, 138.60, 140.42, 174.26.

MS, *m/z* (%): 237 (69), 182 (100), 152 (26), 127 (3), 115 (3), 77 (3), 76 (4), 55 (2).

Compound **5b**

2-Ethyl-3-methyl-6-phenyl-quinoline; m.p. 68–69 °C. IR (neat): 3057, 3029, 2968, 2927, 2870, 1659, 1598, 1484, 909, 838, 761, 699 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ (ppm): 1.37 (t, J = 7.5 Hz, 3H, CH$_2$CH_3), 2.48 (d, J = 0.8 Hz, 3H, CH_3), 2.63 (quartet, J = 7.5 Hz, 2H, CH_2CH$_3$), 7.52–7.36 (m, 3H), 7.72–7.65 (m, 2H), 7.90–7.84 (m, 3H), 8.09 (d, J = 9.3 Hz, 1H).

^{13}C NMR (CDCl$_3$), δ (ppm): 12.86, 19.12, 29.46, 124.42, 127.32, 127.40, 127.45, 127.98, 128.83, 128.86, 129.81, 135.96, 138.29, 140.67, 145.99, 163.36.

MS, *m/z* (%): 247 (100), 246 (100), 219 (26), 203 (7), 189 (10), 165 (6), 115 (4), 77 (2), 76 (4), 55 (2).

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