Chloranil as an Efficient Oxidant of the Cyclohexadiene Intermediates Formed by a Cycloaddition of Substituted 2*H*-Pyran-2-ones and Styrenes En Route to the Boscalid Derivatives

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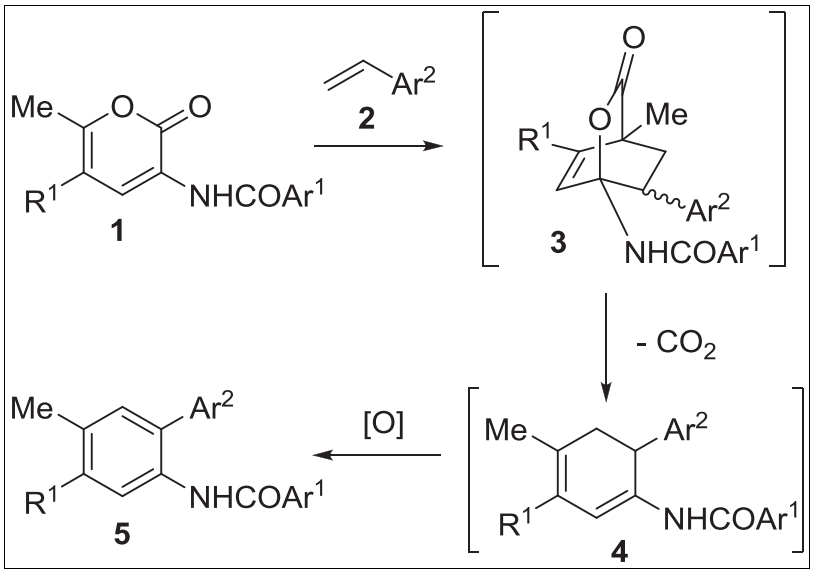
Received October 21, 2015
DOI 10.1002/jhet.2603
Published online 00 Month 2016 in Wiley Online Library (wileyonlinelibrary.com).



We describe a three-step one-pot metal-free domino procedure yielding a set of boscalid derivatives, parent compound being a highly important agrochemical agent. The first step of the process consists of the Diels–Alder reaction between a substituted *2H*-pyran-2-one and styrene derivatives, followed by the elimination of CO_2 and aromatization (oxidation). The last step was found to be efficiently promoted by the application of chloranil as the oxidant. Alternatively, activated carbon Darco KB could also act as the dehydrogenation catalyst necessitating a larger excess of the styrene to act as the hydrogen acceptor.

J. Heterocyclic Chem., **00,** 00 (2016).

INTRODUCTION

The quest for the preparation of novel plant-protecting compounds is an ongoing task, as the resistance of plant pathogens to the established treatments is often evolving rather rapidly. The case of boscalid [1–6], a well-known fungicide widely applied against various ascomycete pathogens damaging commercially grown fruit and vegetable plants is no exception in this regard, spurring the recent introduction of its novel derivatives Xemium and Bixafen, by BASF and Bayer, respectively. In this connection, we would like to report our recent results from the field of synthesis of various biphenyl–benzamide systems, including such that closely resemble the parent boscalid compound.

2*H*-Pyran-2-ones represent an easily accessible and versatile heterocyclic system that is a convenient starting point for the preparation of plethora of important and useful compounds [7,8]. Previously [9–12], we have reported the application of substituted 3-acylamino-2*H*-pyran-2-ones as dienes for the Diels–Alder reaction with phenylacetylene, 4-chlorophenylacetylene, and some other analogues (such as vinyl ethers acting as masked acetylenes) [13,14] as means for the preparation of various biphenyl systems additionally containing acylamino group. This strategy was applicable also for the preparation of a methyl derivative of boscalid, as well as for some other derivatives. However, substituted acetylenes being rather expensive and many of them commercially not available, we decided to explore the other possible pathway: instead of acetylenes to use styrenes as dienophiles (acting as synthetic substitutes). Of course, such an approach needs an additional synthetic step; the primary intermediate formed upon the cycloaddition of 2*H*-pyran-2-one derivatives and styrenes (i.e., oxabicyclo[2.2.2]octenes), followed by the elimination of a molecule of CO_2 (via a retro-hetero-Diels–Alder reaction) is of a cyclohexadiene structure, therefore, necessitating an oxidation step that leads to the final aromatic product. It is obvious that this last step is not

needed when acetylene derivative acts as the dienophile, because in such case after the elimination of CO_2, aromatic system is formed directly.

For this oxidation step, we (and others) have already successfully employed active charcoal Darco KB [9,15–17] as a heterogeneous dehydrogenation catalyst (in such case, the excess of the styrene was acting as the oxidant, possibly in conjunction with the acceptorless pathway of the dehydrogenation taking place) [18–21]. Alternatively, this dehydrogenation could also be achieved by the application of chloranil (tetrachloro-1,4-benzoquinone) as proved previously [9]. Herein, we report on the application of chloranil for the preparation of an extended set of boscalid derivatives via cycloaddition of styrenes as dienophiles and a wider set of 3-aroylamino-2*H*-pyran-2-ones as dienes in acetonitrile under microwave irradiation. Our main emphasis was on the investigation of 2*H*-pyran-2-one derivatives being unsubstituted at position 5 or, alternatively, containing an electron donating substituent at this position.

RESULTS AND DISCUSSION

Besides the previously applied dienophiles, styrene (**2a**), and 4-chlorostyrene (**2b**), here we additionally investigated 4-methylstyrene (**2c**) as the dienophile for the Diels–Alder reaction with substituted 6-methyl-2*H*-pyran-2-ones **1** possessing at the position 5 electron-donating groups (i.e., 4-MeO-C_6H_4- (**1a**) or 3,4-$(MeO)_2C_6H_3$- (**1b**)), and for comparison, we investigated also the reactivity of a derivative possessing an electron-withdrawing group ($-CO_2Et$) (**1c**) at the position 5 or, alternatively, having a hydrogen (**1d–h**) at this position. Additionally, all 2*H*-pyran-2-ones **1** were substituted by various 3-aroylamino groups, with aryl moieties including phenyl (**1a**,**b**,**h**), 3,4,5-trimethoxyphenyl (**1c**), various chloropyridyl groups (**1d**,**e**), 4-nitrophenyl (**1f**) or 4-dimethylaminophenyl group (**1 g**). For the oxidation step (i.e., **4** → **5**), we applied either active charcoal Darco KB (as the heterogeneous dehydrogenation catalyst with the styrenes **2** acting as the sink for hydrogen) or chloranil. In addition, we also investigated the possibility of the use of some other co-oxidants (e.g., $KBrO_3$, V_2O_5, or SeO_2) in conjunction with chloranil. All reactions have been carried out under microwave irradiation in closed vessels. In the case of heterogeneous catalysis, we have conducted the reactions in closed thick-walled ACE glass tubes with the application of conventional heating (oil bath).

Application of Darco KB as the dehydrogenation catalyst. One of our aims was to investigate the reactivity of electron-rich starting 2*H*-pyran-2-ones **1a**,**b** (i.e., those possessing a 3-(4-methoxyphenyl)- or 3-(3,4-dimethoxyphenyl)- groups) for the cycloaddition of styrenes **2** with the active charcoal Darco KB as the dehydrogenation catalyst. In this regard, we first conducted a set of reactions between 4-methoxyphenyl derivative **1a** (0.5 mmol) and styrene (**2a**) (2.4 mmol) in toluene (4 mL) with the addition of Darco KB (75 mg). The reactions were conducted in closed ACE glass tubes with heating on an oil bath for 2 h at various temperatures (160°C, 180°C, and 200°C) (Table 1, Entries 1–3). With the increase of temperature, it was evident from the ^{1}H NMR spectra of crude reaction mixtures that the conversion toward **5a** [11] increases as well, and that at the highest temperature it reaches 100% (Table 1, Entry 3). On the other hand, when the amount of the dienophile **2a** was decreased from 2.4 to 1.8 mmol under otherwise identical conditions as in Entry 3 (Table 1), the reaction was again not complete (**1a**:**5a** = 0.2:1) (Table 1, Entry 4). For easier isolation of the products, in these experiments toluene was used instead of the decalin as applied previously [9].

Similar to the results with styrene were also those obtained for the cycloaddition of 4-chlorostyrene (**2b**); when heating **1a** (0.5 mmol) with **2b** (2.4 mmol) in toluene with the addition of Darco KB (75 mg) in closed ACE glass tube at 200°C for 2 h, the conversion toward **5b** also reached

Table 1

Effect of different reaction conditions on the formation of **5** from **1** (0.5 mmol) and **2** (2.4 mmol) in closed ACE glass tubes with Darco KB (75 mg) as the dehydrogenation catalyst in toluene (4 mL).

	Starting 2*H*-pyran-2-ones **1**			Dienophiles **2**					
Entry	R^1	Ar^1		Ar^2		Temp. (°C)	Time (h)	Ratio **1**: **5**[a]	Product (isolated yield, %)
1	4-$MeOC_6H_4$	Ph	**1a**	Ph	**2a**	160	2	2.3: 1	**5a**
2	4-$MeOC_6H_4$	Ph	**1a**	Ph	**2a**	180	2	0.4: 1	**5a**
3	4-$MeOC_6H_4$	Ph	**1a**	Ph	**2a**	200	2	0: 1	**5a** (62)
4	4-$MeOC_6H_4$	Ph	**1a**	Ph	**2a**[b]	200	2	0.2: 1	**5a**
5	4-$MeOC_6H_4$	Ph	**1a**	4-Cl-C_6H_4	**2b**	200	2	0: 1	**5b** (70)
6	3,4-$(MeO)_2C_6H_3$	Ph	**1b**	Ph	**2a**	200	2	0: 1	**5d** (53)

[a]Data estimated from methyl signals in ^{1}H NMR spectra of the crude reaction mixture.
[b]With 1.8 mmol of **2a**.

100% (Table 1, Entry 5). Analogous were the results in the case of starting **1b** (0.5 mmol) and styrene (**2a**) (2.4 mmol) as the dienophile, where 2 h of heating at 200°C (with the addition of Darco KB (75 mg)) was necessary for the synthesis of **5d** to be complete (Table 1, Entry 6). In this way, we prepared three boscalid derivatives **5a**,**b**,**d** with satisfactory isolated yields (53–70%). However, to shorten the reaction times and to increase the conversions, a large excess of the dienophiles **2** was needed (4.8 eq.). This is understandable, as one has to take into account that styrenes **2** act not only as dienophiles but also as the sacrificial hydrogen acceptors after the dehydrogenation of **4** takes place by the assistance of the heterogeneous catalyst Darco KB. However, one has to keep in mind that at least a part of the hydrogen liberated during this dehydrogenation might take place via the acceptor-less mechanism and therefore does not need the spare styrenes **2**. It is also important to stress that efficient isolation of the products from the reaction mixtures containing Darco KB as the catalyst is only possible by continuous extraction (with the Soxhlet apparatus), otherwise there are substantial losses of the product due to its adsorption on the surface of the active carbon.

Application of chloranil as the oxidant. The other option for the dehydrogenation of **4** to yield the final boscalid-like products **5** is an application of a suitable oxidant. Previously, we have shown that chloranil is one of the possible choices; therefore, we decided to re-examine the reactions between **1a** and 4-chlorostyrene (**2b**). In a closed vessel, a mixture of the starting **1a** (0.5 mmol), 4-chlorostyrene (**2b**) (0.6 mmol), chloranil (0.5 mmol), and acetonitrile (1.5 mL) was irradiated in a focused microwave reactor at 140°C for 2 h. ^{1}H NMR analysis of the crude reaction mixture showed that some of the starting **1a** remained unreacted (**1a**:**5b** = 0.25:1) (Table 2, Entry 1). When the reaction was repeated with a longer reaction time (3 h) (Table 2, Entry 2) and other reaction parameters being identical as previously mentioned, the conversion was increased, but the reaction was still not completed (**1a**:**5b** = 0.2:1). The complete conversion toward **5b** was achieved only after 3 h of microwave irradiation and with the amount of styrene **2b** being increased to 1.2 mmol (for 0.5 mmol **1a** and with all other parameters being the same as previously mentioned) (Table 2, Entry 3). In this way, it was possible to prepare the product **5b** in good isolated yield (78%); here the result was better as that obtained with Darco KB (70% yield of **5b**) (Table 1, Entry 5).

Similar were also results with the starting 2*H*-pyran-2-one **1b** (0.5 mmol) upon the cycloaddition of styrene (**2a**) (0.6 mmol or 1.2 mmol, Table 2) conducted under microwave irradiation in a closed vessel with chloranil (0.5 mmol) as the oxidant and acetonitrile (1.5 mL) as the solvent. After 2 h of irradiation at 140°C with 0.6 mmol of **2a** being applied, the conversion toward **5d** was only around 50% (**1b**:**5d** = 1:1) (Table 2, Entry 4). Upon the increase of the reaction time to 3 h and increase of the amount of **2a** to 1.2 mmol, the reaction could be completed (Table 2, Entry 5) and not a trace of the starting **1b** could be detected by ^{1}H NMR spectrum of the crude reaction mixture. In this case, the isolated yield of **5d** reached by the application of chloranil was also higher than the yield obtained with Darco KB (74% vs 53%).

In both of the examples described earlier (i.e., the preparation of **5b**,**d**), it is of interest to note that in the case of chloranil acting as the oxidant the amount of dienophiles **2** necessary for the complete conversion of **1** to **5** could be halved (from 4.8 eq. to 2.4 eq. of **2**), the reaction temperature could be decreased (from 200°C oil bath to the microwave irradiation at the temperature set to 140°C), albeit with an increase of reaction time (from 2 to 3 h) (Table 1, Entries 5 and 6 vs Table 2, Entries 3 and 5). All these changes of reaction conditions are presumably a direct consequence of the change in the dehydrogenation step (**4** → **5**); in the cases of the chloranil acting as the oxidant, the dehydrogenation takes places under milder conditions than is the case of Darco KB, which is acting merely as the dehydrogenation catalyst, whereas the actual oxidant is represented by the excess of the dienophiles (styrenes **2**) (Scheme 1).

To the reaction mixtures, a small amount of BHT (2,6-di-*tert*-butyl-4-methylphenol) (1.8 mol%) was also added [9], acting as a radical scavanger to diminish the extent

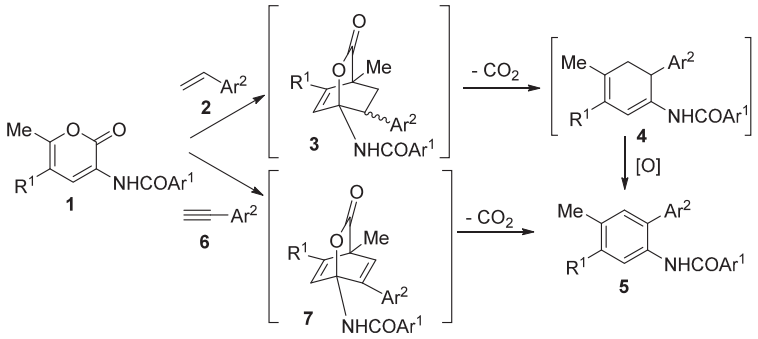
Table 2

Effect of different reaction conditions on the formation of **5** from **1** (0.5 mmol) and **2** in closed vessels under microwave irradiation at 140°C with chloranil (0.5 mmol) as the oxidant, BHT (1.8 mol%) and in acetonitrile (1.5 mL) as the solvent.

	Starting 2*H*-pyran-2-ones **1**			Dienophiles **2**						
Entry	R^1	Ar^1		Ar^2		Amount of **2** (mmol)	Oxidant	Time (h)	Ratio **1**: **5**[a]	Product (isolated yield, %)
1	4-$MeOC_6H_4$	Ph	**1a**	4-Cl-C_6H_4	**2b**	0.6	chloranil	2	0.25: 1	**5b**
2	4-$MeOC_6H_4$	Ph	**1a**	4-Cl-C_6H_4	**2b**	0.6	chloranil	3	0.2: 1	**5b**
3	4-$MeOC_6H_4$	Ph	**1a**	4-Cl-C_6H_4	**2b**	1.2	chloranil	3	0: 1	**5b** (78)
4	3,4-$(MeO)_2C_6H_3$	Ph	**1b**	Ph	**2a**	0.6	chloranil	2	1: 1	**5d**
5	3,4-$(MeO)_2C_6H_3$	Ph	**1b**	Ph	**2a**	1.2	chloranil	3	0: 1	**5d** (74)

[a]Data estimated from methyl signals in ^{1}H NMR spectra of the crude reaction mixture.

Scheme 1. Reaction sequence for the preparation of boscalid derivatives **5** starting from 2*H*-pyran-2-ones **1** and either styrenes **2** or acetylenes **6** acting as the dienophiles.



of unwanted radical-initiated polymerizations of styrenes **2**.

In all cases described herein, the cycloaddition step is regiospecific yielding after the complete domino reaction only the products **5** having the 1,4-arrangement of the hydrogen atoms 3-H and 6-H on the aromatic ring. None of the other regioisomers, that is, structures with 1,3-arrangement of these two hydrogen atoms, have been observed. This is clearly evident from the ^{1}H NMR spectra of products **5a–g** showing singlet signals for 3-H and 6-H, consistent with the smallest coupling constants existing between the 1,4 arranged protons on the benzene rings ($J = 0$–1 Hz) [11], whereas in the other case two doublets should appear. Furthermore, these findings are also in agreement with our previous results [10,11,22,23] that cycloadditions of unsymmetrically substituted dienophiles with a hydrogen substituent on one side of the multiple bond generally proceed in a regioselective manner, whereas dienophiles containing substituents on both sides of the multiple bond (such as *N*,*N*-diethylpropynamine and ethyl but-2-ynoat) yield both regioisomers. In some cases, the regioselectivity was also corroborated by HMBC NMR studies showing the correlation between 5-Me and 6-H groups (that would not appear if the regioselectivity was reversed) [11].

When the reaction mixture is heated by the microwave irradiation, it is also important to note that its actual temperature could be higher than the measured one, as the measurement is conducted on the outer wall of the reaction vessel, whereas the reaction sample is heated in situ by the direct interaction of the microwave irradiation and polar and/or ionic species [24].

Besides the products **5b**,**d**, prepared as described earlier (Table 2, Entries 3 and 5), the conditions elucidated earlier have been found to be appropriate for successful preparation of further cycloadducts **5c**,**e–h**,**j–o**. For comparison, the product **5i** was prepared under neat microwave conditions (with the liquid additive *n*-BuOH) [25] by the

Table 3

Reaction conditions and yields for the synthesis of **5**[a].

	Starting 2*H*-pyran-2-ones **1**			Dienophiles **2** (or **6**)				
Entry	R^1	Ar^1		Ar^2		Product **5**	Time (h)	Isolated yield (%)[b]
1	4-$MeOC_6H_4$	Ph	**1a**	4-Me-C_6H_4	**2c**	**5c**	3	75
2	3,4-$(MeO)_2C_6H_3$	Ph	**1b**	4-Cl-C_6H_4	**2b**	**5e**	3	71
3	3,4-$(MeO)_2C_6H_3$	Ph	**1b**	4-Me-C_6H_4	**2c**	**5f**	3	72
4	CO_2Et	Ph	**1c**	4-Me-C_6H_4	**2c**	**5 g**	3	82
5	H	3,4,5-$(MeO)_3C_6H_2$	**1d**	4-Cl-C_6H_4	**2b**	**5 h**	3	60
6	H	2-Cl-nicotinoyl	**1e**	Ph	**6a**	**5i**	1[c]	90
7	H	6-Cl-nicotinoyl	**1f**	Ph	**2a**	**5j**	3	75
8	H	6-Cl-nicotinoyl	**1f**	4-Cl-C_6H_4	**2b**	**5 k**	3	68
9	H	4-$O_2NC_6H_4$	**1 g**	Ph	**2a**	**5 l**	3	74
10	H	4-$O_2NC_6H_4$	**1 g**	4-Cl-C_6H_4	**2b**	**5 m**	3	76
11	H	4-$(NMe_2)C_6H_4$	**1 h**	Ph	**2a**	**5n**	3	70
12	H	4-$(NMe_2)C_6H_4$	**1 h**	4-Cl-C_6H_4	**2b**	**5o**	3	76

[a]Reaction conditions: 2*H*-pyran-2-ones **1** (1 mmol), dienophiles **2** (2.4 mmol) in acetonitrile (1.5 mL) with the addition of chloranil (1 mmol) and BHT (1.8 mol%) under microwave irradiation at 140°C (140 W).
[b]Isolated yield.
[c]Dienophile **6a** (1.2 mmol) and *n*-BuOH (100 mg) as the additive under microwave irradiation at 180°C (150 W).

cycloaddition of phenylacetylene (**6a**) instead of styrene (**2a**), therefore eliminating the need of applying chloranil. All of the products **5b–o** thus prepared represent novel derivatives of boscalid and were isolated in good yields (60–90%) (Table 3).

The application of other mixed oxidation systems, where an appropriate co-oxidant would decrease the amount of the necessary chloranil was unfortunately not successful. We investigated the cycloaddition between the starting 2*H*-pyran-2-one **1a** (1 mmol) and styrene (**2**) (2.4 mmol) in acetonitrile solvent (1.5 mL) with the addition of chloranil (0.1 mmol) and a suitable co-oxidant ($KBrO_3$, V_2O_5 or SeO_2) (0.9 mmol). The reaction mixtures were heated under reflux condition for 3 h, and thereafter, the crude reaction mixtures were analyzed by ^{1}H NMR analysis. In all three cases, no conversion toward **5a** was found, in the complex reaction mixture only the starting **1a** was detected (together with the compounds stemming from oxidative degradation and/or polymerization side reactions).

CONCLUSION

The application of suitable styrenes **2** (economically more viable than their corresponding substituted phenylacetylenes **6**) acting as dienophiles for the Diels–Alder reaction with easily obtainable substituted 2*H*-pyran-2-ones **1** was found to be the most appropriate way to prepare derivatives of boscalid, that is, a set of compounds **5a–o**, obtained in good yields (60–90%) via a three-step one-pot metal-free domino procedure. When the substituted aromatic products **5** are desired, the importance of the last reaction step is crucial; the boscalid derivatives can only be obtained after the oxidation (dehydrogenation) of the intermediary-formed cyclohexadienes **4**. The most efficient reagent for this transformation was found to be chloranil, closely followed by Darco KB as a heterogeneous dehydrogenation catalyst (with the excessive amount of the styrenes acting as the actual hydrogen scavengers). Other oxidative systems (chloranil together with an inorganic co-oxidant) were not found to be appropriate under the applied conditions.

EXPERIMENTAL

Melting points were determined on a micro hot stage apparatus. ^{1}H NMR spectra were recorded at 29°C with a Bruker (Rheinstein, Germany) Avance DPX 300 spectrometer at 300 MHz or Bruker Avance III spectrometer at 500 MHz instruments using TMS as an internal standard. ^{13}C NMR spectra were recorded at 29°C with the Bruker Avance DPX 300 spectrometer at 75.5 MHz or Bruker Avance III spectrometer at 125.5 MHz and were referenced against the central line of the solvent signal ($CDCl_3$ triplet at 77.0 ppm or DMSO-d_6 septet at 39.5 ppm). The coupling constants (*J*) are given in Hertz. IR spectra were obtained with a BioRad (Hercules, CA, USA) FTS 3000MX spectrometer as KBr pellets or with a Bruker (Ettlingen, Germany) Alpha Platinum ATR spectrometer on a solid support. MS spectra were recorded with a VG Analytical (Wythenshawe, UK) AutoSpec Q and Waters-Micromass (Milford, MA, USA) Q-TOF Premier spectrometers. Elemental analyses (C, H, N) were conducted using a Perkin–Elmer (Waltham, MA, USA) 2400 series II CHNS/O analyzer. The starting compounds **1a–h** were prepared according to the published procedures: the synthesis of **1a–c** starts from appropriate compounds containing activated CH_2 groups (i.e., 4-methoxyphenylacetone, 3,4-dimethoxyphenylacetone or ethyl acetoacetate), C_1-synthon (DMFDMA) and hippuric acid as described previously [26–28]. Starting **1d–h** are obtained from the parent 3-benzoylamino compounds (prepared as described earlier), followed by the removal of the benzoyl group and re-protecting the amine functionality with another aroyl group, as described [29,30]. All other reagents and solvents were used as received from commercial suppliers.

Microwave reactions were conducted in air using a focused microwave unit (Discover by CEM Corporation, Matthews, NC). The machine consists of a continuous, focused microwave power-delivery system with an operator-selectable power output from 0 to 300 W. Reactions were performed in darkness in glass vessels (capacity 10 mL) sealed with the septum. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature controller mounted under the reaction vessel and measuring the temperature of the outer surface of the reaction vessel. The mixtures were stirred with a Teflon-coated magnetic stirring bar in the vessel. Temperature, pressure, and power profiles were recorded using commercially available software provided by the manufacturer of the microwave unit.

General procedure for the synthesis of 5a–o with the application of chloranil as the oxidant. A mixture of the starting 2*H*-pyran-2-one **1a–h** (1 mmol), the corresponding substituted styrene **2a–c** (2.4 mmol), chloranil (tetrachloro-1,4-benzoquinone) (1 mmol, 246 mg), and BHT (4 mg, 1.8 mol%) in acetonitrile (1.5 mL) was irradiated in the focused monomode microwave equipment for 3 h (Table 2, Entries 3 and 5 and Table 3). The power was set to 140 W, the final temperature to 140°C, and ramp time to 5 min. Thereafter, the reaction mixture was cooled, diluted with CH_2Cl_2 (100 mL), and washed with 5% NaOH solution (2 × 30 mL). The organic phase was dried over Na_2SO_4, and the volatile components were removed in vacuo yielding crude products **5a–o**. Products **5a**,**h–o** were crystallized from the appropriate solvents, whereas **5b–g** were purified by column

chromatography (SiO_2, elution with petroleum ether/EtOAc, 3:1). Fractions containing products were combined and evaporated under vacuo; the residue was treated with a mixture of petroleum ether and EtOAc (3:1) (0.5 mL), and the remaining solid was collected by filtration under reduced pressure to yield pure products **5b–g**. For the analysis, all of the products were crystallized from the appropriate solvent.

N-(4''-Methoxy-5'-methyl-[1,1':4',1''-terphenyl]-2'-yl)benzamide (5a) [11]. Off-white solid, yield 62%, 122 mg, recrystallization from EtOH, mp 129–130°C (EtOH), lit. [11] mp 129–130°C (EtOH); ir: 1671, 1609, 1579, 1561, 1525, 1504, 1490 cm^{-1}.

N-(4-Chloro-4''-methoxy-5'-methyl-[1,1':4',1''-terphenyl]-2'-yl) benzamide (5b). Pale yellow solid, yield 78%, 166 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 198–201°C; ir: 3438, 1666, 1607, 1579, 1569, 1273 cm^{-1}; ^1H nmr (300 MHz, $CDCl_3$): δ 2.31 (s, 3H, Me), 3.87 (s, 3H, MeO), 6.97 and 7.35 (AA'XX', J = 8.5 Hz, 2H each, C_6H_4), 7.17 (s, 1H, 6-H), 7.43 (m, 4H, C_6H_4), 7.49 (m, 3H, Ph), 7.63 (m, 2H, Ph), 7.79 (br s, 1H, NH), 8.29 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 20.3, 55.5, 113.7, 123.9, 126.9, 129.0, 129.5, 130.49, 130.55, 130.8, 131.9, 132.0, 132.3, 132.4, 133.6, 134.2, 134.8, 136.7, 142.2, 158.9, 165.2 ppm; ms (ESI+, TOF): m/z 428 ($[M+H]^+$). *Anal*. Calcd for $C_{27}H_{22}ClNO_2 \times 0.5\ H_2O$: C, 74.22; H, 5.31; N, 3.21. Found: C, 74.35; H, 5.26; N, 3.10.

N-(4''-Methoxy-4,5'-dimethyl-[1,1':4',1''-terphenyl]-2'-yl) benzamide (5c). Pale yellow solid, yield 75%, 306 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 147–150°C; ir: 3436, 1668, 1608, 1561, 1526, 1274 cm^{-1}; ^1H nmr (500 MHz, $CDCl_3$): δ 2.31 (s, 3H, Me), 2.44 (s, 3H, Me), 3.86 (s, 3H, MeO), 6.96 (m, 2H, Ar), 7.19 (s, 1H, 6-H), 7.32 (m, 2H, Ar), 7.38 (m, 6H, Ar), 7.47 (m, 1H, Ar), 7.63 (m, 2H, Ar), 8.00 (br s, 1H, NH), 8.40 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 20.3, 21.4, 55.4, 113.6, 123.0, 127.0, 128.8, 129.3, 130.0, 130.5, 131.2, 131.70, 131.73, 132.1, 132.7, 133.9, 135.0, 135.1, 138.0, 141.6, 158.8, 165.0 ppm; ms (ESI+, TOF): m/z 408 ($[M+H]^+$). *Anal*. Calcd for $C_{28}H_{25}NO_2 \times 0.6\ H_2O$: C, 80.39; H, 6.31; N, 3.35. Found: C, 80.44; H, 6.02; N, 3.29.

N-(3'',4''-Dimethoxy-5'-methyl-[1,1':4',1''-terphenyl]-2'-yl) benzamide (5d). White solid, yield 74%, 156 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 218–221°C; ir: 3217, 1635, 1601, 1577, 1551, 1290 cm^{-1}; ^1H nmr (300 MHz, $CDCl_3$): δ 2.32 (s, 3H, Me), 3.92 (s, 3H, MeO), 3.94 (s, 3H, MeO), 6.96 (m, 3H, Ar), 7.21 (s, 1H, 6-H), 7.38 (m, 2H, Ar), 7.50 (m, 6H, Ar), 7.60 (m, 2H, Ar), 7.94 (br s, 1H, NH), 8.42 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 20.3, 56.09, 56.10, 111.0, 112.8, 121.7, 122.9, 126.9, 128.2, 128.9, 129.3, 129.5, 131.5, 131.8, 132.0, 132.6, 134.2, 134.9, 138.1, 142.0, 148.2, 148.6, 165.1 ppm (1 signal hidden); ms (ESI+, TOF): m/z 424 ($[M+H]^+$). *Anal*. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.15; H, 6.05; N, 3.20.

N-(4-Chloro-3'',4''-dimethoxy-5'-methyl-[1,1':4',1''-terphenyl]-2'-yl)benzamide (5e). Pale yellow solid, yield 71%, 325 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 214–217°C; ir: 3228, 1735, 1634, 1554, 1509, 1452 cm^{-1}; ^1H nmr (500 MHz, $CDCl_3$): δ 2.32 (s, 3H, Me), 3.92 (s, 3H, MeO), 3.94 (s, 3H, MeO), 6.95 (m, 3H, Ar), 7.18 (s, 1H, 6-H), 7.42 (m, 4H, Ar), 7.50 (m, 3H, Ar), 7.64 (m, 2H, Ar), 7.80 (br s, 1H, NH), 8.30 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 20.3, 56.10, 56.11, 111.0, 112.7, 121.7, 123.8, 126.9, 129.0, 129.5, 130.7, 130.8, 131.97, 132.01, 132.3, 132.4, 134.0, 134.3, 134.8, 136.6, 142.4, 148.3, 148.6, 165.3 ppm; ms (ESI+, TOF): m/z 458 ($[M+H]^+$). *Anal*. Calcd for $C_{28}H_{24}ClNO_3 \times 0.25\ H_2O$: C, 72.72; H, 5.34; N, 3.03. Found: C, 72.81; H, 5.06; N, 2.95.

N-(3'',4''-Dimethoxy-4,5'-dimethyl-[1,1':4',1''-terphenyl]-2'-yl) benzamide (5f). White solid, yield 72%, 315 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 146–149°C; ir: 3228, 1634, 1603, 1572, 1554, 1243 cm^{-1}; ^1H nmr (500 MHz, $CDCl_3$): δ 2.32 (s, 3H, Me), 2.44 (s, 3H, Me), 3.92 (s, 3H, MeO), 3.94 (s, 3H, MeO), 6.96 (m, 3H, Ar), 7.20 (s, 1H, 6-H), 7.32 (m, 2H, Ar), 7.39 (m, 4H, Ar), 7.48 (m, 1H, Ar), 7.63 (m, 2H, Ar), 8.00 (br s, 1H, NH), 8.42 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 20.3, 21.4, 56.1, 111.0, 112.8, 121.7, 122.8, 127.0, 128.9, 129.3, 130.0, 131.4, 131.7, 131.8, 132.1, 132.7, 134.3, 135.0, 138.1, 141.8, 148.2, 148.6, 165.1 ppm (2 signals hidden); ms (ESI+, TOF): m/z 438 ($[M+H]^+$). *Anal*. Calcd for $C_{29}H_{27}NO_3 \times 0.33\ H_2O$: C, 78.54; H, 6.29; N, 3.16. Found: C, 78.44; H, 6.03; N, 3.09.

Ethyl 2-benzamido-4',5-dimethyl-[1,1'-biphenyl]-4-carboxylate (5g). White solid, yield 82%, 305 mg, purification by column chromatography (elution with petroleum ether: EtOAc 3:1), mp 175–178°C; ir: 3220, 1666, 1643, 1567, 1540, 1220 cm^{-1}; ^1H nmr (500 MHz, $CDCl_3$): δ 1.43 (t, J = 7.0 Hz, 3H, CH_3CH_2), 2.43 (s, 3H, Me), 2.61 (s, 3H, Me), 4.39 (q, J = 7.0 Hz, 2H, CH_3CH_2), 7.17 (s, 1H, 6-H), 7.32 (m, 4H, Ar), 7.41 (m, 2H, Ar), 7.50 (m, 1H, Ar), 7.64 (m, 2H, Ar), 7.97 (br s, 1H, NH), 9.01 (s, 1H, 3-H) ppm; ^{13}C nmr (125 MHz, $CDCl_3$): δ 14.5, 21.3, 21.4, 61.0, 123.5, 127.0, 128.9, 129.0, 129.7, 130.1, 131.9, 132.8, 133.4, 134.3, 134.8, 136.0, 136.2, 138.6, 165.2, 167.4 ppm; ms (ESI+, TOF): m/z 374 ($[M+H]^+$). *Anal*. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.25; H, 6.10; N, 3.71.

N-(4'-Chloro-5-methyl-[1,1'-biphenyl]-2-yl)-3,4,5-trimethoxybenzamide (5h). White solid, yield 60%, 248 mg, recrystallization from *i*-Pr_2O, mp 148.5–151°C; ir: 3252, 1639, 1585, 1526, 1504, 1493 cm^{-1}; ^1H nmr (300 MHz,

$CDCl_3$): δ 2.38 (s, 3H, Me), 3.80 (s, 6H, 3-MeO, 5-MeO), 3.86 (s, 3H, 4-MeO), 6.77 (s, 2H, C_6H_2), 7.08 (d, J = 2.1 Hz, 1H, 6-H), 7.26 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H, 4-H), 7.39 and 7.48 (AA'XX', J = 8.6 Hz, 2H each, C_6H_4), 7.68 (br s, 1H, NH), 8.33 (s, 1H, 3-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.8, 56.0, 60.8, 103.9, 121.5, 129.2, 129.4, 129.9, 130.1, 130.8, 131.4, 132.3, 134.0, 134.2, 136.9, 140.9, 153.1, 164.3 ppm; ms (ESI–, TOF): m/z 410 ($[M–H]^-$). *Anal*. Calcd for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N, 3.40. Found: C, 67.06; H, 5.27; N, 3.46.

2-Chloro-N-(5-methyl-[1,1'-biphenyl]-2-yl)nicotinamide (5i). Prepared from **1e** (1 mmol) and **6a** (1.2 mmol), with *n*-BuOH (100 mg), under microwave irradiation at 180°C (150 W), without chloranil. Pale yellow solid, yield 90%, 290 mg, recrystallization from *i*-Pr_2O, mp 117–120°C; ir: 3242, 1672, 1656, 1587, 1580 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 7.12 (d, J = 1.4 Hz, 1H, 6-H), 7.25 (dd, J_1 = 8.4 Hz, J_2 = 1.4 Hz, 1H, 4-H), 7.32 (dd, J_1 = 7.7 Hz, J_2 = 4.7 Hz, 1H, 5'-H), 7.40 (m, 5H, Ar), 8.13 (dd, J_1 = 7.7 Hz, J_2 = 2.0 Hz, 1H, 4'-H or 6'-H), 8.15 (br s, 1H, NH), 8.32 (d, J = 8.4 Hz, 1H, 3-H), 8.42 (dd, J_1 = 4.7 Hz, J_2 = 2.0 Hz, 1H, 4'-H or 6'-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.9, 121.8, 122.7, 128.05, 128.95, 129.3, 130.7, 131.3, 131.8, 133.4, 134.8, 138.0, 139.9, 146.7, 151.0, 162.3 ppm (1 signal hidden); ms (ESI+, TOF): m/z 323 ($[M+H]^+$). *Anal*. Calcd for $C_{19}H_{15}ClN_2O$: C, 70.70; H, 4.68; N, 8.68. Found: C, 70.92; H, 4.60; N, 8.57.

6-Chloro-N-(5-methyl-[1,1'-biphenyl]-2-yl)nicotinamide (5j). Pink-brown solid, yield 75%, 240 mg, recrystallization from *i*-Pr_2O, mp 119–122°C; ir: 3275, 1643, 1589, 1524 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 7.13 (d, J = 2.0 Hz, 1H, 6-H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, 4-H), 7.45 (m, 6H, Ph, 5'-H), 7.82 (br s, 1H, NH), 7.98 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, 4'-H), 8.31 (d, J = 8.4 Hz, 1H, 3-H), 8.46 (d, J = 2.4 Hz, 1H, 2'-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.9, 121.7, 124.4, 128.2, 129.04, 129.06, 129.15, 129.4, 130.6, 131.5, 133.1, 134.9, 137.84, 137.88, 147.5, 154.2, 162.0 ppm; ms (ESI+, TOF): m/z 323 ($[M+H]^+$). *Anal*. Calcd for $C_{19}H_{15}ClN_2O$: C, 70.70; H, 4.68; N, 8.68. Found: C, 70.85; H, 4.94; N, 8.39.

6-Chloro-N-(4'-chloro-5-methyl-[1,1'-biphenyl]-2-yl) nicotinamide (5k). Off-white solid, yield 68%, 242 mg, recrystallization from *i*-Pr_2O/aceton, mp 86–89°C; ir: 3294, 1646, 1617, 1586, 1556, 1522 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 7.10 (d, J = 2.1 Hz, 1H, 6-H), 7.26 (m, 1H, 4-H), 7.35 and 7.46 (AA'XX', J = 8.4 Hz, 2H each, C_6H_4), 7.41 (dd, J_1 = 8.4 Hz, J_2 = 0.6 Hz, 1H, 5'-H), 7.67 (br s, 1H, NH), 8.00 (dd, J_1 = 8.4 Hz, J_2 = 2.5 Hz, 1H, 4'-H), 8.21 (d, J = 8.4 Hz, 1H, 3-H), 8.53 (d, J = 2.5 Hz, 1H, 2'-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.9, 122.4, 124.5, 129.3, 129.4, 129.5, 130.4, 130.7, 131.3, 132.2, 134.4, 135.3, 136.4, 137.9, 147.6, 154.5, 162.3 ppm; ms (ESI+, TOF): m/z 357 ($[M+H]^+$). *Anal*. Calcd for $C_{19}H_{14}Cl_2N_2O$: C, 63.88; H, 3.95; N, 7.84. Found: C, 64.06; H, 4.18; N, 7.69.

N-(5-Methyl-[1,1'-biphenyl]-2-yl)-4-nitrobenzamide (5l). Pale brown solid, yield 74%, 245 mg, recrystallization from EtOH, mp 149–152 °C; ir: 3252, 1647, 1601, 1528, 1487 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, Me), 7.14 (d, J = 2.1 Hz, 1H, 6-H), 7.26 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H, 4-H), 7.40 – 7.54 (m, 5H, Ar), 7.74 and 8.23 (AA'XX', J = 8.7 Hz, 2H each, C_6H_4), 7.90 (br s, 1H, NH), 8.32 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.9, 121.7, 123.8, 127.9, 128.2, 129.08, 129.13, 130.62, 131.6, 133.1, 135.0, 137.9, 140.3, 149.5, 162.8 ppm (1 signal hidden); ms (ESI–, TOF): m/z 331 ($[M–H]^-$). hrms calcd for $C_{20}H_{15}N_2O_3$ (M–H) 331.1083. Found 331.1088.

N-(4'-Chloro-5-methyl-[1,1'-biphenyl]-2-yl)-4-nitrobenzamide (5m). Pale brown solid, yield 76%, 279 mg, recrystallization from EtOH, mp 194–197 °C; ir: 3233, 1639, 1599, 1523, 1485 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 7.10 (d, J = 2.0 Hz, 1H, 6-H), 7.26 (dd, J_1 = 8.1 Hz, J_2 = 2.0 Hz, 1H, 4-H), 7.35 and 7.47 (AA'XX', J = 8.7 Hz, 2H each, C_6H_4), 7.76 (br s, 1H, NH), 7.77 and 8.26 (AA'XX', J = 8.7 Hz, 2H each, C_6H_4), 8.20 (d, J = 8.1 Hz, 1H, 3-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.9, 122.5, 124.0, 128.0, 129.4, 129.5, 130.5, 130.7, 131.4, 132.2, 134.4, 135.4, 136.5, 140.1, 149.7, 163.2 ppm; ms (ESI–, TOF): m/z 365 ($[M–H]^-$). *Anal*. Calcd for $C_{20}H_{15}ClN_2O_3$: C, 65.49; H, 4.12; N, 7.64. Found: C, 65.75; H, 4.11; N, 7.37.

4-Dimethylamino-N-(5-methyl-[1,1'-biphenyl]-2-yl)benzamide (5n). Pale orange solid, yield 70%, 230 mg, recrystallization from *i*-Pr_2O, mp 118–120 °C; ir: 3427, 3317, 1665, 1636, 1607, 1511 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, Me), 2.99 (s, 6H, NMe_2), 6.60 (m, 2H, Ar), 7.09 (d, J = 2.0 Hz, 1H, 6-H), 7.21 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, 4-H), 7.46 (m, 7H, Ar), 7.81 (br s, 1H, NH), 8.40 (d, J = 8.4 Hz, 1H, 3-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.8, 39.9, 111.0, 121.1, 121.3, 127.8, 128.3, 128.9, 129.0, 129.3, 130.3, 131.9, 132.9, 133.1, 138.4, 152.4, 164.8 ppm; ms (ESI+, TOF): m/z 331 ($[M+H]^+$). *Anal*. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 80.17; H, 6.78; N, 8.18.

N-(4'-Chloro-5-methyl-[1,1'-biphenyl]-2-yl)-4-(dimethylamino) benzamide (5o). Off-white solid, yield 76%, 275 mg, recrystallization from *i*-Pr_2O, mp 133–136 °C; ir: 3426, 3229, 1634, 1609, 1515 cm^{-1}; ^{1}H nmr (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, Me), 3.01 (s, 6H, NMe_2), 6.63 and 7.51 (AA'XX', J = 9.0 Hz, 2H each, C_6H_4), 7.05 (d, J = 1.8 Hz, 1H, 6-H), 7.22 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H, 4-H), 7.37 and 7.45 (AA'XX', J = 8.7 Hz, 2H each, C_6H_4), 7.66 (br s, 1H, NH), 8.31 (d, J = 8.4 Hz, 1H, 3-H) ppm; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 20.8, 40.0, 111.1,

121.1, 122.0, 128.3, 129.1, 129.3, 130.3, 130.6, 131.2, 132.7, 133.6, 133.8, 137.0, 152.5, 165.0 ppm; ms (ESI+, TOF): m/z 365 ($[M+H]^+$). *Anal*. Calcd for $C_{22}H_{21}ClN_2O \times 0.2\ H_2O$: C, 71.71; H, 5.85; N, 7.60. Found: C, 71.75; H, 5.59; N, 7.35.

Acknowledgments. We gratefully acknowledge the Ministry of Higher Education, Science and Technology of the Republic of Slovenia and the Slovenian Research Agency for financial support P1-0230-0103 (and young researcher grant for AJ) as well as Basileus IV Erasmus Mundus Project (grant for JS). Dr. B. Kralj and Dr. D. Žigon (Centre for Mass Spectroscopy, "Jožef Stefan" Institute, Ljubljana, Slovenia) are gratefully acknowledged for the mass measurements. This work was also partially supported with infrastructure of EN → FIST Centre of Excellence, Ljubljana.

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