Rh-Catalyzed Sequential Hydroarylation/Hydrovinylation–Heterocyclization of β-(2-Aminophenyl)-α,β-ynones with Organoboron Derivatives: A New Approach to Functionalized Quinolines

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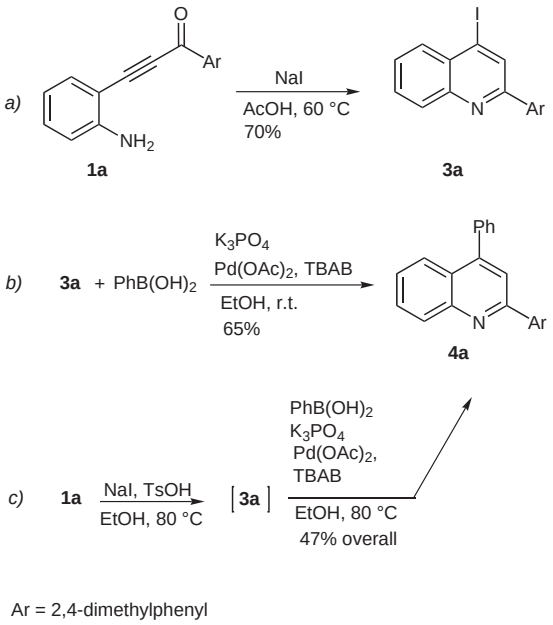
Abstract: 4-Aryl and 4-vinyl quinolines were prepared via a sequential procedure involving regioselective Rh(acac)(C_2H_2)/dppf-catalyzed hydroarylation/hydrovinylation of β-(2-aminophenyl)-α,β-ynones with arylboronic acids or potassium aryl and vinyl trifluoroborates, followed by nucleophilic attack of the amino group onto the carbonyl.

Key words: quinolines, hydroarylation, rhodium, alkynones, arylboronic acids

The quinoline scaffold is found in a variety of biologically active compounds, and quinoline-containing drugs are widely used in treatment of *Plasmodium falciparum* malaria.[1] Pharmacological studies on new quinoline derivatives appears frequently in current literature dealing with HIV-1 replication inhibition,[2] antimicrobial activity,[3] antihelmintic properties,[4] antimalarial activity[5] and inhibition of VEGF receptors;[6] in particular, 4-arylquinolines have been evaluated for their activity against West Nile Virus,[7] and have found application as ligands of peripheral benzodiazepine receptor.[8] Moreover, conjugated polymers incorporating a 2,4-diarylquinoline subunit are useful chemosensors for fluoride ion,[9] and 1,8-di(4-quinolyl)naphtalene derivatives are selective fluorescent sensors for metal ions in aqueous solution.[10] Consequently, there is a great current synthetic interest in assembling quinoline ring system from acyclic precursors.[11]

As a part of our ongoing efforts[12] to discover new routes to heterocycles starting from functionalized alkynes bearing proximate nucleophilic centers, we focused on β-(2-aminophenyl)-α,β-ynones **1** as useful building blocks for the synthesis of quinolines through sequential processes involving conjugate-addition-type[13] or cycloaddition[14] reactions followed by cyclization through nucleophilic attack of the amino group onto the carbonyl (cycloamination). In this context, we showed that the reaction of **1** with NaI in acetic acid affords 4-iodoquinolines **3**. The potential of **3** as precursors for increasing molecular complexity via palladium-catalyzed reactions has been considered;[13] therefore, the combined addition of NaI to **1**/palladium-catalyzed Suzuki–Miyaura cross-coupling reaction[15] could represent a general entry into 4-aryl and 4-vinylquinolines. Indeed, the reaction of **1a** with NaI in acetic acid gave the 4-iodoquinoline **3a** (Scheme 1, *a*); subsequent cross-coupling with phenylboronic acid at room temperature[16] resulted in the formation of **4aa** in good yield (Scheme 1, *b*).



Scheme 1

Nevertheless, the one-pot synthesis of 4-aryl and 4-vinylquinolines **4** starting from **1** represents a more interesting challenge.[17] In order to achieve this goal, we investigated the development of a one-pot/two-step synthetic protocol. NaI (2 equiv) was added to **1a** in ethanol at 80 °C in the presence of 1 equivalent of TsOH; after the complete conversion of **1a** to **3a** (3 h), $PhB(OH)_2$ (1.3 equiv), K_3PO_4 (3 equiv), $Pd(OAc)_2$ (0.03 equiv) and TBAB (0.08 equiv) were added to the reaction mixture allowing the formation of **4a** in 47% overall yield after 6 hours at 80 °C (Scheme 1, *c*). Probably there is room for optimization; however, the main drawback of this procedure is constituted by the acidic conditions required in the first step,[18] while the Suzuki–Miyaura cross-coupling

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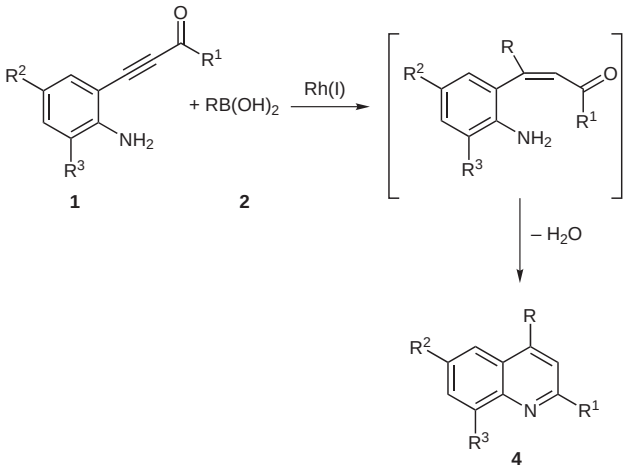
requires the presence of a base.[15] This hampers the possibility of a multicomponent process. Considering that sequential processes that allows the direct conversion of starting materials into products are more environmentally benign than traditional multistep procedures,[17] we turned to a completely different methodology.

The Pd-catalyzed hydroarylayion/hydrovinylation reaction of disubstituted alkynes with aryl halides or vinyl triflates represents a useful tool in heterocyclic synthesis, since the *syn*-stereochemistry of the addition allows cyclization reactions to occur when the two substituents on the triple bond posses suitable nucleophilic/electrophilic centers.[19] The palladium-catalyzed sequential hydroarylation of α,β-ynones **1** with aryl iodides/cycloamination has been previously investigated.[20] Disappointingly, the reaction proceeded with low regioselectivity, affording a mixture of 4-aryl- and 3-arylquinolines.

On the other hand, the rhodium-catalyzed hydroarylation of alkynes with arylboronic acids has recently received much attention.[21] The reaction shows the same stereochemical outcome of the above-mentioned palladium-catalyzed process, but electronic factors seems to play a more important role in determining the regioselectivity.[21e] In particular, methyl trimethylsilylpropynoate was selectively arylated at the β-position with respect to the carbonyl, despite the presence of a bulky $SiMe_3$ group on that position.[21a]

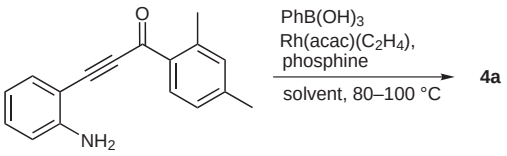
Then, we envisaged that α,β-ynones **1** could be regioselectively converted into **4** in a sequential manner employing this methodology (Scheme 2).



Scheme 2

Although several examples of rhodium-catalyzed tandem addition–cyclization reactions have been described,[22] to the best of our knowledge, the sequential rhodium-catalyzed addition of an organoboron species to alkynones/cycloamination reaction has not been yet studied. Herein, we report the results of our investigation.

The reaction of phenylboronic acid with **1a** was chosen as a model system (Scheme 3), and some of the results obtained under different reaction conditions are reported in Table 1. By using Rh(acac)(C_2H_2)/dppf as catalyst, **4a** was isolated in good to high yield with almost complete regioselectivity (NMR and GC-MS analysis showed that its regioisomeric purity is higher than 96%).



1a

Scheme 3

According to a reported procedure,[21a] an excess of **2a** is necessary to obtain the best result (entry 1); however, the quantity of boronic acid could be reduced with still-acceptable results (entry 3–5). The use of a 2:1 Rh/dppf ratio seems preferable to a 1:1 ratio (entries 1, 2). The replacement of dioxane with a greener solvent such as aqueous ethanol is also possible, although in our hands the former gave better yields (entries 7–9). The dppp was slightly less effective than dppf in dioxane–water (compare entries 1 and 6), and in ethanol the two ligands gave similar yields.

We next extended the methodology to different α,β-ynones/boron derivatives.[23,24] Our results are summarized in Table 2. Quinolines **4** were isolated in moderate to high yields; reaction conditions are not fully optimized, and five equivalents of arylboronic acid **2** were generally used, although the use of a lower excess is also possible (entries 3, 4). The process tolerates electron-withdrawing as well as electron-donating substituents on the α,β-ynone and arylboronic acid moieties. Substituents on the benzenic ring of quinoline can also be introduced (entry 12), and heteroarylboronic acids can be used as well (entries 8–11). Moreover, the use of aryl- and vinyltrifluoroborate salts **5** is allowed (entries 5, 6, 14); the reactions of **1** with **5** were not optimized, and were carried out in the same manner as arylboronic acids.[23] Organotrifluoroborate salts have emerged as promising new compounds that can overcome some limitations of other organoboron derivatives;[25] however, to the best of our knowledge, these salts have not been used in the rhodium-catalyzed hydroarylation of alkynes. Finally, starting from the vinyl-substituted α,β-ynone **1g**, 2-vinyl-4-arylquinolines or 2,4-divinylquinolines can be obtained (entries 13, 14). It is also worth nothing that addition of the organorhodium intermediates onto the ketone moiety of **1** was never observed under the present reaction conditions. This process (that is a useful tool for the conversion of aldehydes to alcohols[26a] and ketones[26b]) has been reported starting from cyclobutanones and $ArB(OH)_2$ in the presence of Rh(acac)(C_2H_4)$_2$/*t*-Bu_3P and Cs_2CO_3 in dioxane at 100 °C[27a] or, intramolecularly, starting from 5-yn-1-ones at room temperature.[27b]

Table 1 Rhodium-Catalyzed Sequential Hydroarylation–Cyclization of **1a** with Phenylboronic Acid **2a**[a]

Entry	Solvent	Temp (°C)	Time (h)	Equiv of **2a**	Yield of **4a** (%)[b]
1	10:1 dioxane–H_2O	100	4	5	80
2	10:1 dioxane–H_2O	100	6	5	65[c]
3	10:1 dioxane–H_2O	100	5.5	2	55
4	10:1 dioxane–H_2O	100	5.5	3	67
5	10:1 dioxane–H_2O	100	5.5	4	70
6	10:1 dioxane–H_2O	100	4	5	75[d]
7	95:% EtOH–H_2O	80	4	5	67
8	95:% EtOH–H_2O	100	4	5	66
9	95:% EtOH–H_2O	100	4	5	67[d]

[a] Reactions were carried out on a 0.4 mmol scale in 1 mL of solvent under nitrogen atmosphere using the following molar ratios: **1a**:Rh(acac)(C_2H_2):dppf = 1:0.033:0.066.
[b] Yields are based on **1a**, refer to single runs and are given for isolated product.
[c] Using 0.033 equiv of dppf.
[d] Using dppp as ligand.

Table 2 Synthesis of 4-Aryl/Vinylquinolines **4**[a,b]

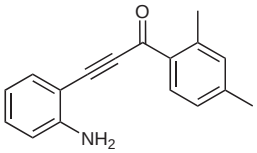
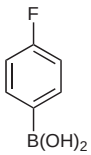
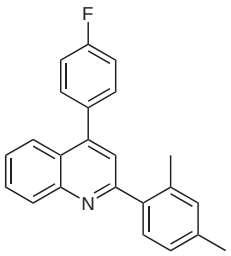
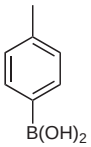
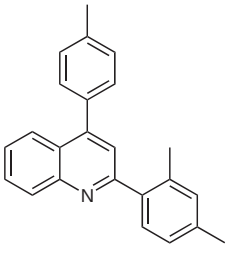
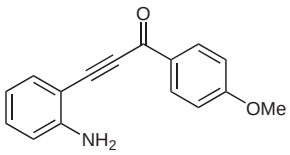
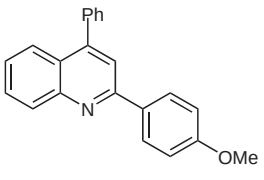
Entry	α,β-Ynone **1**	Organoboron compound **2**	Reaction time (h)	Quinoline **4**	Yield (%)
1	 **1a**	 **2b**	5	 **4b**	55
2	**1a**	 **2c**	5	 **4c**	70
3	 **1b**	**2a**	5	 **4d**	82
4	**1b**	**2a**	6.5	**4d**	75[c]

Table 2 Synthesis of 4-Aryl/Vinylquinolines **4**[a,b] (continued)

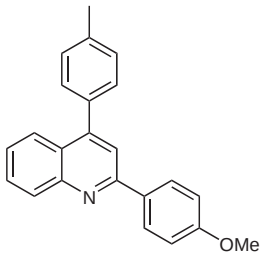
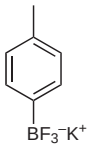
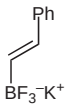
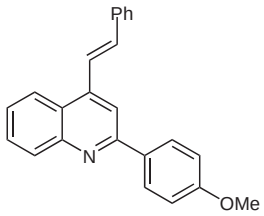
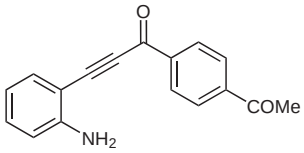
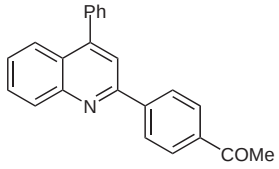
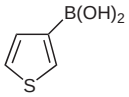
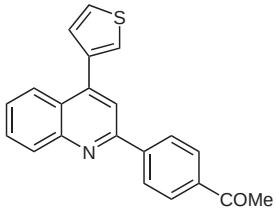
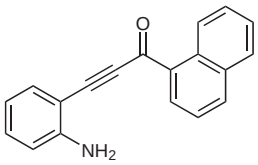
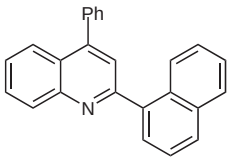
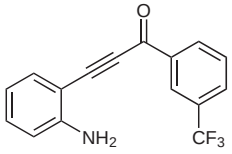
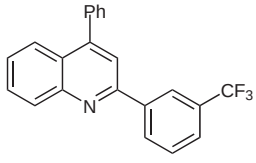
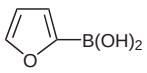
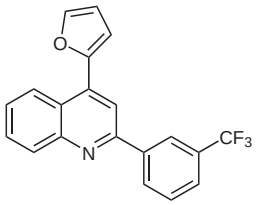
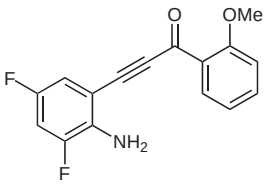
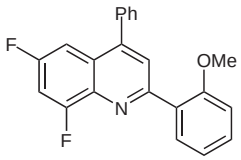
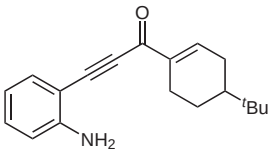
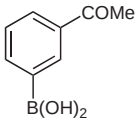
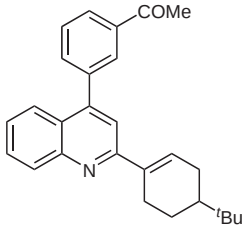
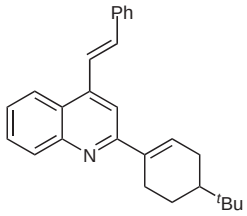
Entry	α,β-Ynone **1**	Organoboron compound **2**	Reaction time (h)	Quinoline **4**	Yield (%)
4	**1b**	**2c**	8	 **4e**	60
5	**1b**	 **5c**	8	**4e**	50
6	**1b**	 **5d**	6	 **4f**	61
7	 **1c**	**2a**	4.5	 **4g**	82
8	**1c**	 **2e**	16	 **4h**	68
9	 **1d**	**2a**	7	 **4i**	50
10	 **1e**	**2a**	5	 **4j**	59

Table 2 Synthesis of 4-Aryl/Vinylquinolines **4**[a,b] (continued)

Entry	α,β-Ynone **1**	Organoboron compound **2**	Reaction time (h)	Quinoline **4**	Yield (%)
11	**1e**	 **2f**	5	 **4k**	80
12	 **1f**	**2a**	20	 **4l**	60[d]
13	 **1g**	 **2g**	7	 **4m**	75
14	**1g**	**5d**	7	 **4n**	60

[a] Reactions were carried out at 100 °C on a 0.4 mmol scale in 1 mL of dioxane and 0.1 mL of H_2O, under N_2 atmosphere, using the following molar ratio: **1**:**2**:Rh(acac)$(C_2H_4)_2$:dppf = 1:5:0.033:0.066 or **1**:**5**:Rh(acac)$(C_2H_4)_2$:dppf = 1:5:0.033:0.066.
[b] Yields refer to single runs and are given for pure isolated product.
[c] Using 3 equiv of **2a**.
[d] Using 0.06 equiv of Rh(acac)$(C_2H_4)_2$ and 0.12 equiv of dppf.

In conclusion, we have developed an efficient and experimentally simple procedure for the conversion of β-(2-aminophenyl)-α,β-ynones **1** into 4-aryl and 4-vinylquinolines **4** through an unprecedented sequential process involving a regioselective rhodium-catalyzed hydroarylation–cycloamination reaction.

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(23) **Typical Procedure:** To a mixture of **1c** (0.106 g, 0.40 mmol), phenylboronic acid (0.244 g, 2 mmol), $Rh(acac)(C_2H_4)_2$ (0.0035 g, 0.014 mmol) and dppf (0.015 g, 0.027 mmol) in a screw-capped Pyrex tube were added dioxane (1 mL) and H_2O (0.1 mL). The tube was purged with N_2, closed and the mixture was stirred at 100 °C for 4.5 h. After cooling, the mixture was purified by column chromatography (silica gel; hexane–EtOAc, 97:3) to give **4g** (0.106 g, 82% yield); mp 116–117 °C. IR (KBr): 1690, 1610, 1600 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.29 (d, *J* = 8.5 Hz, 2 H), 8.26–8.22 (m, 1 H), 8.09 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.83 (s, 1 H, C3–H), 7.78–7.70 (m, 1 H), 7.54–7.45 (m, 6 H), 2.65 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 197.8, 155.4, 149.5, 148.8, 143.8, 138.2, 137.4, 130.2, 129.8, 129.5, 128.8, 128.6, 128.5, 127.7, 126.9, 126.0, 125.7, 119.2, 26.8. MS (EI): *m/z* (%) = 323 (100) [M^+], 309 (8), 281 (20).

(24) **Characterization of other quinoline derivatives.**
Compound **4a**: oil. IR (neat): 1610, 1590, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.22 (d, *J* = 8.3 Hz, 1 H), 7.95 (d, *J* = 7.9 Hz, 1 H), 7.76–7.68 (m, 1 H), 7.55–7.44 (m, 8 H), 7.14 (s, 1 H), 7.17–7.10 (m, 1 H), 2.45 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 159.8, 148.4, 148.3, 138.3, 138.2, 137.8, 135.9, 131.7, 130.0, 129.8, 129.6, 129.4, 128.6, 128.3, 126.7, 126.3, 125.6, 125.1, 122.6, 21.2, 20.4. MS (EI): *m/z* (%) = 309 (100) [M^+].
Compound **4b**: oil. IR (neat): 1610, 1590, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.22 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 8.3 Hz, 1 H), 7.76–7.68 (m, 1 H), 7.54–7.42 (m, 5 H), 7.24–7.09 (m, 3 H), 7.13 (s, 1 H), 2.44 (s, 3 H), 2.37 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 162.9 (d, *J* = 248.0 Hz, C–F), 159.9, 148.5, 147.2, 138.4, 137.7, 135.9, 134.2 (d, *J* = 3.2 Hz), 131.7, 131.4, 131.2, 130.1, 129.8, 129.5, 126.8, 126.5, 125.3, 122.7, 115.7 (d, *J* = 21.5 Hz), 21.2, 20.4. MS (EI): *m/z* (%) = 327 (100) [M^+].
Compound **4c**: oil. IR (neat): 1600, 1590, 1550 cm^{-1}.^1H NMR ($CDCl_3$): δ = 8.24 (d, *J* = 8.3 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.74–7.66 (m, 1 H), 7.48–7.42 (m, 5 H), 7.30 (d, *J* = 7.9 Hz, 2 H), 7.13 (s, 1 H), 7.17–7.09 (s, 1 H), 2.45 (s, 3 H), 2.43 (s, 3 H), 2.37 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 159.8, 148.4, 148.3, 138.2, 137.8, 135.8, 135.2, 131.6, 129.9, 129.8, 129.5, 129.3, 128.7, 126.7, 126.2, 125.6, 125.3, 122.6, 21.3, 21.2, 20.4. MS (EI): *m/z* (%) = 323 (100) [M^+].
Compound **4d**: oil. IR (neat): 1610, 1600, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.20 (d, *J* = 8.5 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 2 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 7.74 (s, 1 H), 7.71–7.63 (m, 1 H), 7.53–7.50 (m, 5 H), 7.43–7.35 (m, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 160.8, 156.4, 148.9, 148.8, 138.5, 132.1, 129.9, 129.5, 129.4, 128.9, 128.5, 128.3, 125.9, 125.6, 125.5, 118.8, 114.2, 55.3. MS (EI): *m/z* (%) = 311 (100) [M^+].
Compound **4e**: mp 118–120 °C. IR (KBr): 1600, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.21–8.10 (m, 1 H), 8.15 (d, *J* = 8.8 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.74 (s, 1 H), 7.72–7.65 (m, 1 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.44–7.35 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 1 H), 2.45 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 160.9, 156.5, 149.1, 148.9, 138.2, 135.7, 132.4, 129.9, 129.5, 129.34, 129.27, 128.9, 127.4, 125.8, 125.7, 118.8, 114.2, 55.4, 21.3. MS (EI): *m/z* (%) = 325 (100) [M^+].
Compound **4f**: mp 120–121 °C. IR (KBr): 1620, 1600, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.17–8.10 (m, 4 H), 7.97 (s, 1 H), 7.79 (d, *J* = 16.1 Hz, 1 H), 7.72–7.59 (m, 3 H), 7.52–7.30 (m, 5 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 160.7, 156.8, 148.8, 143.5, 136.8, 134.8, 132.5, 130.2, 129.4, 128.9, 128.7, 127.1, 125.9, 123.7, 123.3, 114.7, 114.2, 55.4. MS (EI): *m/z* (%) = 337 (100) [M^+].
Compound **4h**: mp 89–90 °C. IR (KBr): 1680, 1610, 1590 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.25–8.23 (m, 1 H), 8.27 (d, *J* = 8.5 Hz, 2 H), 8.08 (d, *J* = 8.5 Hz, 2 H), 8.10–8.05 (m, 1 H), 7.87 (s, 1 H), 7.94–7.17 (m, 1 H), 7.60–7.50 (m, 3 H), 7.40–7.35 (m, 1 H), 2.65 (s, 3 H). ^{13}C NMR ($CDCl_3$):

δ = 197.8, 155.5, 148.5, 144.5, 143.4, 138.5, 137.4, 130.2, 129.9, 128.9, 127.7, 127.0, 126.5, 125.6, 125.1, 119.1, 26.7. MS (EI): *m/z* (%) = 329 (71) [M^+], 314 (100), 286 (41).
Compound **4i**: mp 112–113 °C. IR (KBr): 1600, 1560 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.30 (d, *J* = 8.6 Hz, 1 H), 8.26–8.20 (m, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.96–7.90 (m, 2 H), 7.81–7.72 (m, 2 H), 7.67 (s, 1 H), 7.61–7.47 (m, 9 H). ^{13}C NMR ($CDCl_3$): δ = 159.0, 148.7, 138.7, 138.1, 134.0, 131.3, 130.1, 129.6, 129.1, 128.6, 128.5, 128.4, 127.8, 126.6, 125.9, 125.7, 125.5, 125.4, 123.4. MS (EI): *m/z* (%) = 331 (100) [M^+], 255 (40).
Compound **4j**: mp 82–83 °C. IR (KBr): 1600, 1560 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.49 (s, 1 H), 8.37 (d, *J* = 7.5 Hz, 1 H), 8.25 (d, *J* = 8.6 Hz, 1 H), 7.91 (d, *J* = 8.5 Hz, 1 H), 7.80 (s, 1 H), 7.80–7.60 (m, 3 H), 7.55–7.44 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ = 155.1, 149.7, 148.9, 140.4, 138.2, 130.8, 130.3, 129.8, 129.6, 129.3, 128.7, 128.6, 126.8, 125.9 (q, *J* = 3.6 Hz), 125.7, 124.4 (q, *J* = 3.7 Hz), 118.9, 29.7. MS (EI): *m/z* (%) = 349 (100) [M^+].
Compound **4k**: mp 75–77 °C. IR (KBr): 1600, 1570, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.48–8.33 (m, 3 H), 8.19 (d, *J* = 8.4 Hz, 1 H), 8.06 (s, 1 H), 7.76–7.55 (m, 5 H), 7.01 (d, *J* = 3.3 Hz, 1 H), 6.63 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 155.2, 151.0, 149.2, 144.1, 140.2, 136.9, 130.7, 130.5, 129.8, 129.3, 127.2, 125.9 (q, *J* = 3.6 Hz), 125.2, 124.4 (q, *J* = 3.7 Hz), 123.7, 116.1, 112.4, 112.1. MS (EI): *m/z* (%) = 339 (100) [M^+].
Compound **4l**: mp 125–127 °C. IR (KBr): 1610, 1590, 1570 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.96 (s, 1 H), 7.97–7.91 (m, 1 H), 7.56–7.49 (m, 5 H), 7.46–7.10 (m, 4 H), 7.01 (d, *J* = 8.2 Hz, 1 H), 3.85 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 159.6 (dd, J_1 = 247.1 Hz, J_2 = 12.0 Hz), 158.8 (dd, J_1 = 259.9 Hz, J_2 = 13.4 Hz), 157.3, 156.1, 146.8 (dd, J_1 = 3.2 Hz, J_2 = 5.4 Hz), 137.8, 131.8, 130.7, 129.4, 129.0, 128.8, 128.6, 125.4, 121.4, 111.3, 105.2–104.2 (two overlapping multiplets), 55.7. MS (EI): *m/z* (%) = 347 (100) [M^+], 316 (51).
Compound **4m**: mp 88–90 °C. IR (KBr): 1790, 1590, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.15–8.06 (m, 3 H), 7.74–7.60 (m, 4 H), 7.52 (s, 1 H), 7.46–7.42 (m, 1 H), 6.81 (t, *J* = 2.6 Hz, 1 H), 3.05–2.95 (m, 1 H), 2.66 (s, 3 H), 2.60–2.25 (m, 2 H), 2.10–1.90 (m, 2 H), 1.45–1.35 (m, 2 H), 0.94 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ = 197.5, 158.4, 148.4, 147.0, 139.2, 137.6, 134.0, 133.0, 130.9, 130.1, 129.3, 128.8, 128.5, 128.3, 128.1, 126.0, 125.0, 118.3, 43.9, 32.2, 27.9, 27.5, 27.2, 26.7, 24.3. MS (EI): *m/z* (%) = 384 (100) [M^+], 327 (40).
Compound **4n**: mp 117–119 °C. IR (KBr): 1590, 1550, 1510 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.13–8.06 (m, 2 H), 7.78 (d, *J* = 15.9 Hz, 1 H), 7.74 (s, 1 H), 7.70–7.56 (m, 3 H), 7.51–7.26 (m, 4 H), 7.30 (d, *J* = 15.9 Hz, 1 H), 6.81 (t, *J* = 2.6 Hz, 1 H), 3.05–2.92 (m, 1 H), 2.65–2.30 (m, 2 H), 2.20–2.00 (m, 2 H), 1.50–1.35 (m, 2 H), 0.94 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ = 158.9, 148.4, 142.7, 137.8, 136.9, 134.5, 130.4, 130.2, 129.1, 128.9, 128.6, 127.1, 125.7, 125.4, 123.9, 123.2, 114.2, 44.0, 32.3, 27.9, 27.7, 27.3, 23.3. MS (EI): *m/z* (%) = 368 (50) [M^+], 353 (15), 311 (100).

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